Late-Stage Peptide Functionalization by Transition Metal-free and Palladium-Catalyzed C–H Arylations

Dissertation

for the award of the degree

“Doctor rerum naturalium” (Dr.rer.nat.)

of the Georg-August-Universität Göttingen

within the doctoral program chemistry

of the Georg-August-University School of Science (GAUSS)

submitted by

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Göttingen, 2022

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Date of the oral examination: March 8th, 2022

Danksagung

Es ist nun an der Zeit den vielen Menschen zu danken, ohne die diese Dissertation so nicht zustande gekommen wäre. Der größte Dank gilt meinem Doktorvater Prof. Dr. Lutz Ackermann für die Möglichkeit die vorliegende Arbeit in seinem Arbeitskreis anzufertigen und die großartige Betreuung in dieser Zeit. Die zahlreichen Ratschläge und neuen Impulse erlaubten es mir das gestellte Thema mit Leben zu füllen und auftauchende Hürden zu meistern. Des weiteren bin ich dankbar, dass ich Chemie im internationalen Umfeld auf mehreren Tagungungen erleben durfte.

Prof. Dr. Dietmar Stalke danke ich für Übernahme des Zweitgutachtens. Mein weiterer Dank gilt Prof. Dr. Manuel Alcarazo, Prof. Dr. Sven Schneider, Jun.-Prof. Dr. Johannes Walker und Dr. Michael John für die Mühe des Lesens dieser Arbeit und die Teilnahme an der Prüfungskommission.

Vielen Dank Gabi und Bianca für die Unterstützung in bürokratischen Fragen. Außerdem geht mein Dank an Karsten und Stefan, auf deren Expertise und Einsatz in technischen Fragen immer zu zählen war.

Der Zentralen Analytik unter Leitung von Dr. Holm Frauendorf und der NMR-Abteilung unter Leitung von Dr. Michael John danke ich für die schnelle und zuverlässige Messung aller Proben.

Von essentieller Bedeutung für das Gelingen dieser Arbeit waren Dr. Torben Rogge und Dr. João Oliveira. Ohne euch wären die DFT Berechnung nicht zustande gekommen. Vielen Dank für eure Hilfe.

Ein herzliches Dankeschön an Torben, Joao, Ralf, Isaac, Nikolaos, Leonardo, Johanna, Maximilian, Isaac, Shou-Kun, Uttam, Long und Svenja für gewissenhaftes Korrekturlesen.

Das Arbeiten hätte nicht halb so viel Spaß gemacht und zu den wertvollen Resulaten geführt, wären da nicht Dr. Yingjun Zhu, Dr. Wei Wang und Chuan Dong gewesen. Mit euch in den verschiedenen Projekten zu arbeiten war mir eine Freude. Nicht vergessen und bedanken möchte ich mich bei allen Laborkollegen, Alexandra, Yingjun, Chuan, Janson, Gandeepan, Qingqing, Lada, Eloisa, Korni, Jie und Wei für die Hilfsbereitschaft und gute Stimmung besonders in Zeiten in denen die Chemie nicht stimmte. Dem ganzen Arbeitskreis gebührt Dank für die überaus lehrreiche und unterhaltsame Zeit im Labor und bei diversen Unternehmungen außerhalb.

Zu guter Letzt gebührt meiner Familie größter Dank für ihre Liebe, ihr Verständnis und ihren Rückhalt. Danke Michael, dass du diesen Weg mit mir gehst. Danke Robin und Ylvie, dass ihr so süße, fröhliche, schnell wachsende und Chaos stiftende Monster seid.

List of Abbrevations

AA	amino acid
Ac	acetyl
Ala	alanine
AMLA	ambiphilic metal ligand activation
AQ	8-aminoquinoline
Ar	aryl
Asp	aspartic acid
ATR	attenuated total reflectance
BDE	bond dissociation energy
BHAS	base-promoted homolytic aromatic substitution
BIES	base-assisted internal electrophilic substitution
Bn	benzyl
Boc	*tert*-butyloxycarbonyl
br	broad
Bz	benzoyl
calcd.	calculated
CAN	cerium ammonium nitrate
cat	catalytic
Cbz	benzyloxycarbonyl group
CDC	cross-dehydrogenative coupling
CMD	concerted metalation deprotonation
δ	chemical shift
DCE	1,2-dichloroethane
DCIB	1,2-dichloro-2-methylpropane
DFT	density functional theory
DG	directing group
DMA	*N*,*N*-dimethylacetamide
DMEDA	*N*,*N*'-dimethylethylendiamine
DMF	*N*,*N*-dimethylformamide
DMPU	*N*,*N*-dimethylpropyleneurea/1,3-dimethyl-1,3-diazinan-2-one

DNA	deoxyribose nulceic acid
dppbz	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphanyl)ethane
dppm	1,1-bis(diphenylphosphino)methane
dtbpy	2,6-di-*tert*-butyl-pyridine
ee	enantiomeric excess
EI	electron ionization
equiv	equivalents
ESI	electrospray ionization
Et	ethyl
eV	electron volt
FDA	Food and Drug Administration
FG	functional group
Fmoc	9-fluorenylmethyloxycarbonyl
Glu	glutamine
Gly	glycine
GVL	γ-valerolactone
h	hours
HASPO	heteroatom-substituted secondary phosphine oxide
Het	heteroatom
HOAc	acetic acid
HPLC	High performance liquid chromatography
HPMV	heteropolymolybdovanadic acid ($H_4PMo_{11}VO_{40}$)
HFIP	1,1,1,3,3,3-Hexafluoro-2-propanol
Hz	Hertz
IDCA	internal dehydrogenative C–H amination
Ile	isoleucine
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene
*i*Pr	*iso*-propyl
IR	infrared spectroscopy
J	coupling constant

L	ligand
Leu	leucine
Li-Quinoline	3,4-Dihydro-2,5-dimethyl-2*H*-pyrano[2,3-b]quinoline
m	*meta*
Me	methyl
Mes	mesityl
mg	milligram
MIA	2-methoxyiminoacetyl
mL	milliliter
m. p.	melting point
MQ	5-methoxyl-8-aminoquinoline
MS	mass spectrometry
m/z	mass/charge
NCA	*N*-carboxyanhydride
NCL	native chemical ligation
NFSI	*N*-fluorodibenzenesulfonimide
NHC	*N*-heterocyclic carbene
NMP	*N*-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
NOESY	Nuclear Overhauser Effect Spectroscopy
o	*ortho*
OAc	acetoxy group
*o*PBA	*ortho* phenyl benzoic acid
p	*para*
PA	2-picolinic acid/picolinamide
PBS	phosphate buffered saline
PCy_3	Tricyclohexylphosphine
PG	protecting group
PIP	2-(2-pyridyl)-2-*iso*-propyl
Piv	pivaloyl/2,2-dimethylacetyl
Ph	phenyl

Phe	phenylalanine
Phth	phthaloyl
R	rest
SCM	side chain modified
S_EAr	electrophilic aromatic substitution
Selectfluor	1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)
SEM	2-(trimethylsilyl)ethoxymethyl
Ser	serine
SPhos	2-dicyclohexylphosphino-2’,6’-dimethoxybiphenyl
SPPS	solid-phase peptide synthesis
T	temperature
TAA	*N*-aryl-1,2,3-triazole-4-carboxylic acid
TADDOL	α,α,α’,α’-tetraaryl-2,2-disubstituted 1,3-dioxolane-4,5-dimethanol
TAM	triazolyldimethylmethyl/1,2,3-triazolyldimethylmethyl
*t*AmOH	*tert*-Amyl alcohol/2-methylbutan-2-ol
TA-Py	1,2,3-triazole-2-pyridine amide
*t*Bu	*tert*-butyl
*t*BuOH	*tert*-Butanol/2-methyl-2-propanol
*t*BuOOBz	*tert*-butyl benzoyl peroxide
TCE	1,1,2,2-tetrachloroethane
TFA	trifluoroacetic acid
Tfa	trifluoroacetyl
Thr	threonine
TLC	thin layer chromatography
TM	transition metal
TMEDA	*N,N,N‘,N‘*-tetramethylethylenediamine
TMP	2,2,6,6-tetramethylpiperidides
Tol	tolyl
Trp	tryptophan
Ts	toluenesulfonyl
TS	transition state

Tyr	tyrosine
UAA	unnatural amino acid
XPhos	2-dicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl
Xantphos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene
2-NO_2BzOH	*ortho*-nitrobenzoic acid
2-picoline	2-methylpyridine
2,6-lutidine	2,6-dimethylpyridine

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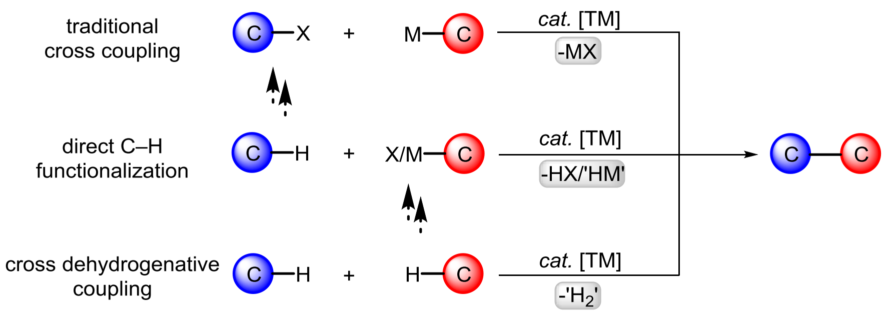
1. Introduction

The development of mild and selective procedures for (C–C) and (C–Het) bond formation represents a critical challenge in molecular chemistry. Since the publication of the 12 principles of Green Chemistry in 1998 by *Anastas* and *Warner*, chemists in academia and industry have made countless contributions to the field of Green Chemistry by designing more sustainable, safe, environmentally-benign and cost-efficient processes.[1] Catalysis allows for energy- and resource-efficient chemical transformations with reduced waste formation, improved atom- and step-economy and increased reactivities and selectivities. Thus, it is considered a key technology in Green Chemistry and has found its way into the production of fine chemicals and pharmaceuticals.[2]

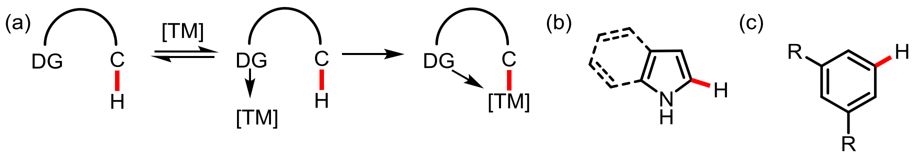
1.1 Transition metal-catalyzed C–H functionalization

Traditional transition metal-catalyzed cross-coupling chemistry is one of the most common synthetic techniques. Consequently, *Heck*, *Negishi* and *Suzuki* have been awarded the Nobel Prize in Chemistry in 2010 for their contributions to the development of palladium-cataylzed cross-couplings.[3] Starting from the first research in the mid 1960s, chemists developed numerous new efficient methods employing milder and more versatile catalytic systems with transition metals, such as palladium, nickel, copper, zinc, cobalt, rhodium, ruthenium, and molybdenum.[4] Palladium is often the metal of choice due to the high catalytic efficiency enabling reactions with a) high functional group tolerance b) at lower temperatures and c) high turnover numbers (TONs), which is especially important for applications to large-scale synthesis.[5] Cross-coupling reactions offer the great advantage that they proceed with excellent regioselectivity, which is determined by the leaving groups on both substrates (Scheme 1). The prize for the selectivity is the necessary prefunctionalization of the substrates and the formation of stoichiometric amounts of chemical waste (MX). With respect to step- and atom-economy, direct C–H functionalizations have emerged as attractive alternatives, reducing expensive prefunctionalization steps and minimizing waste production.[6] Usually the nucleophilic organometallic reagent C–M is replaced by the C–H bond, which is subsequently coupled with the electrophilic (pseudo)halide, although direct C–H couplings with organometallic reagents are also known.[6r, 6ac] The oxidative coupling between two C–H bonds represents an ideal straightforward transformation, as it does not require any prefunctionalization and (formally) generates hydrogen as the byproduct (Scheme 1). Theoretically, one C–H bond is activated by the catalyst, thereby generating a carbon nucleophile, and is then coupled with the carbon electrophile, which has been formed *in situ* by oxidation.[6w, 7]



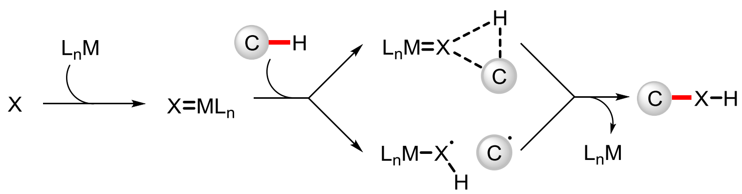
Scheme 1: Strategies for transition metal-catalyzed C–H functionalizations.

The main challenges in direct C–H functionalizations are the inherently low reactivity of C–H bonds and the control of the selectivity in molecules, that posses many electronically and sterically similar C–H bonds. Several strategies have been established to achieve reactions with excellent levels of selectivity. The introduction of a Lewis basic directing group (DG) is one of the most common ways.[8] The coordination to the DG brings the metal into proximity of the desired C–H bond and lowers the energy barrier for the cleavage of the bond through formation of a cyclic transition state. Another strategy is the utilization of electronically activated C–H bonds. Additionally, installation of sterical bulk within the substrate allows for site-selective transformations by blocking adjacent C–H bonds. These approaches are considered as substrate-based strategies in contrast to the catalyst-based control strategy, in which modification of the catalyst structure or the reaction conditions exerts control over site-selectivity (Scheme 2).[9]



Scheme 2: Strategies for site-selectivity in C–H functionalizations *via* (a) directing group (b) electronically activated substrates and (c) steric control.

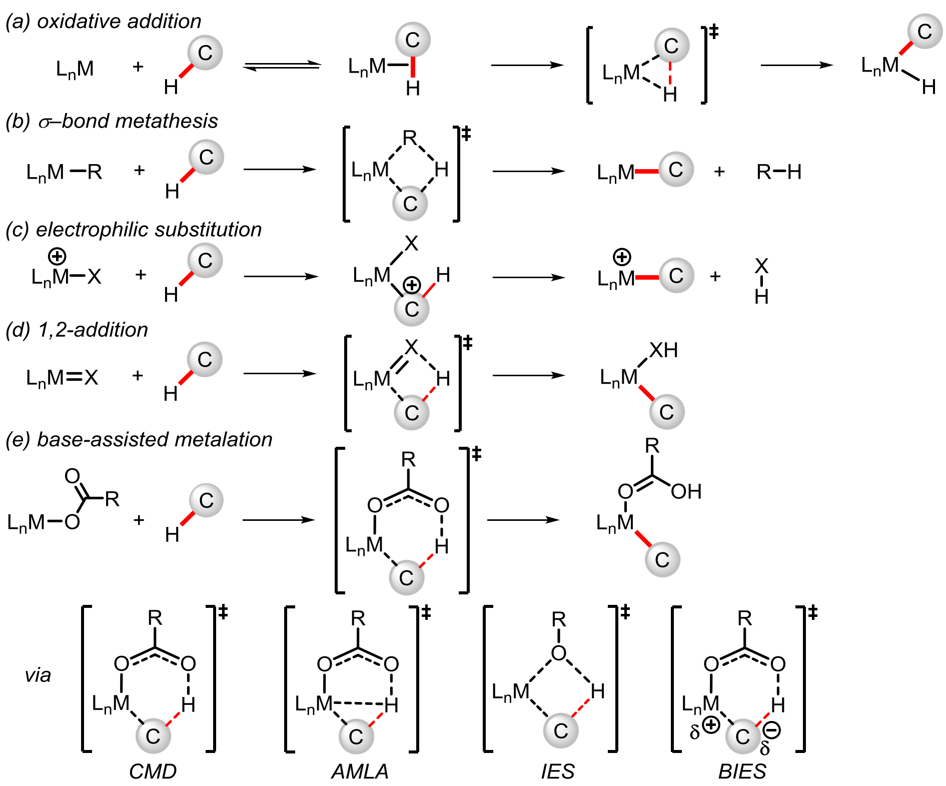
C–H functionalizations can be categorized into two different classes with respect to the involved mechanisms: 1) outer-sphere mechanisms (C–H insertions[10], C–H oxidations, homolytic cleavage) without the formation of a carbon–metal bond intermediate (Scheme 3) and 2) inner-sphere mechanisms, involving an organometallic species, which is generated by the cleavage of a C–H bond.[11] This direct C–H metalation by the active metal catalyst is commonly termed C–H activation.[12]



Scheme 3: C–H functionalization through outer-sphere mechanisms.

For the elementary C–H metalation step, five mechanistic pathways are generaly accepted (Scheme 4). Oxidative addition usually occurs with low-valent electron-rich late transition metal complexes, whereas σ-bond metathesis is typical for early transition metals and lanthanides with a d^0 electron configuration, which are not capable of oxidative processes. The electrophilic substitution is a feasible pathway for late transition metals in higher oxidation states. Alkylidene or amido complexes of transition metals of groups III to V might metalate the C–H bond *via* a 1,2-addition resembling a σ-bond metathesis, but without release of XH.[11a, 13] Base-assisted metalations require a bidentate base, which enables the formation of a six-membered transition state and has been termed concerted metalation-deprotonation (CMD, *Fagnou*)[14] or ambiphilic metal-ligand activation (AMLA, *Davies* and *Macgregor*),[13c] whereas an alternative four-membered transition state has been proposed for an internal electrophilic substitution

(IES, *Goddard*)[15] with monodentate alkoxyl or hydroxyl ligands at iridium. While C–H bonds with kinetic acidity react preferentially in CMD and AMLA C–H activation mechanisms, the base-assisted internal electrophilic substitution (BIES, *Ackermann*)[16] *via* a six-membered transition state was introduced to rationalize the preferred activation of electron-rich substrates with electrophilic transition metal catalysts.



Scheme 4: Plausible mechanisms for transition metal-catalyzed C–H activations.

Regarding the C–H activation of different C–H bonds, C(sp^3)–H bonds are especially challenging due to their low acidity, high bond dissociation energies and lack of reactive orbitals to interact with the orbitals of the transition metal catalyst.[6l, 11c, 17] Although C(sp^3)–H bonds have lower bond dissociation energies than C(sp^2)–H bonds (Figure 1), the bond strength of the formed M–C bond must also be considered. The activation of a C(sp^2)–H bond generates a M–C(sp^2) species, which is more stable than the corresponding M–C(sp^3) species.[18] It has been observed in palladium-catalyzed C–H functionalizations, that primary C(sp^3)–H bonds are selectively transformed over secondary or tertiary bonds in contrast to the known reactivity in radical or electrophilic mechanisms.[6l, 9b, 19]

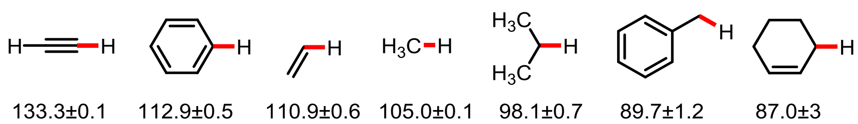
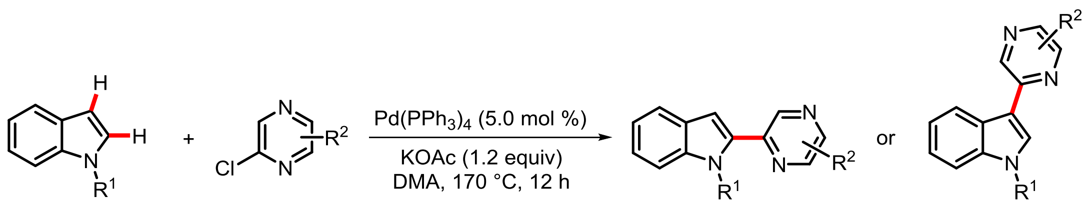


Figure 1: Bond Dissociation Energies of typical C–H bonds. Values are given in kcal/mol.[20]

In addition to the selective and efficient formation of the desired C–C or C–Het bond, the control of the stereochemical outcome of a reaction is of utmost importance in modern synthetic chemistry. The field of stereoselective, especially diastereoselective and enantioselective, transition metal-catalyzed C–H activations has been studied extensively in the past decades, but further research is needed with respect to new catalysts, substrate scope, versatility and efficacy.[21] Diastereomers and enantiomers of a compound often exhibit different physical and biological properties, whose accurate analysis is nowadays an integral part in the regulatory processes and thus in drug research and development. The need for novel asymmetric synthetic procedures brought forth numerous pioneering developments in catalysis such as the homogenous asymmetric hydrogenation independently developed by *Knowles* and *Noyori* in 1968. Together with *Sharpless*, who developed asymmetric oxidation reactions in the 1970s and 1980s, they were awarded with the Nobel Prize in Chemistry in 2001.[22] Nowadays, asymmetric catalytic procedures employing chiral transition metal catalysts with various ligands, chiral organocatalysts, chiral auxiliaries or various enzymes are established for a number of stereolselective transformations.[6e, 6f, 21, 23]

1.1.1 Palladium-catalyzed C–H arylation of indoles

The nitrogen-containing heterocycle indole is ubiquitously present in natural products[24] and is also considered a privileged structure in medicinal chemistry, which is capable of binding to multiple receptors with high affinity.[25] Indole is present in a number of marketed drugs[26] and an outstanding heterocyclic compund in drug discovery[24b, 27]. 2-Arylindoles exhibit a wide range of pharmacological activites, such as anticancer, antibacterial, antiviral, antiinflammtory, antitubercular or antidiabetic activity.[27c] The structural variety paired with the biological activity of indole derivatives made the development of versatile and sustainable synthetic protocols an attractive goal for organic chemists. Functionalized indoles can be prepared by two synthetic strategies. In the first approach, the indole ring is constructed from non-heterocyclic precursors through condensation or metal-catalyzed reactions. Besides the well-known named reactions, such as the *Fischer*[28] *Larock*[29] or *Bartoli*[30] indole synthesis, numerous transition metal-catalyzed cyclizations have been developed.[31] The second strategy comprises the functionalization of the indole nucleus either through traditional cross-coupling reactions with suitable prefunctionalized substrates or through direct C–H activation. In the 1980s, *Ohta* observed that a protecting group on the indole nitrogen had a major impact on the site-selectivity in palladium-catalyzed arylations of indoles **1** with chloropyrazines **2**. A tosyl group enabled the formation of the C3-arylated products, whereas *NH* free and *N*-alkylated indoles were arylated at C2 (Scheme 5).[32] Prior to the studies by *Ohta*, C-2 arylations of *N*-acetylindoles employing stoichiometric amounts of palladium acetate were performed by *Itahara* in the 1980s.[33]



R^1 = H **(1a)**
R^1 = Tos **(1b)**

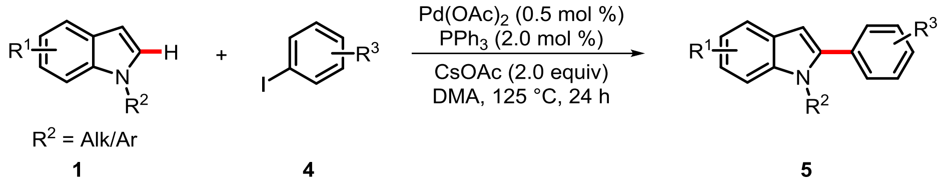
2

3a
(for R^1 = H)

3b
(for R^1 = Tos)

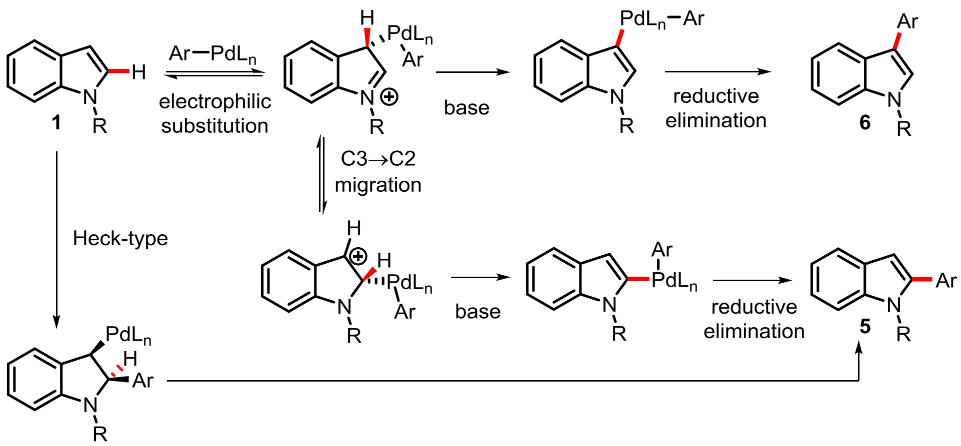
Scheme 5: Palladium-catalyzed direct C–H arylation of indoles **1** with 2-chloropyrazines **2**.

Two decades later, the *Sames* group developed protocols for C-2 arylations of *N*-substituted and *NH*-free indoles.[34] *N*-substituted indoles **1** were successfully coupled with aryliodides **4**, employing $Pd(OAc)_2$ and PPh_3 as the catalyst and CsOAc as the base (Scheme 6).



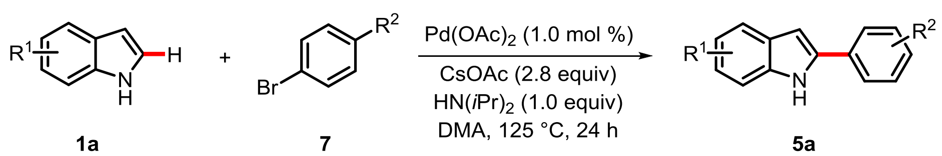
Scheme 6: C2-selective C–H arylation of *N*-substituted indoles **1**.

Concerning the regioselectivity, mechanistic studies indicated that the reaction proceeds *via* electrophilic substitution at the C3-position followed by C3→C2 migration, deprotonation and reductive elimination, whereas a direct metalation at C2 (through σ-bond metathesis) or a *Heck*-type reaction was not supported by mechanistic studies (Scheme 7).[35]



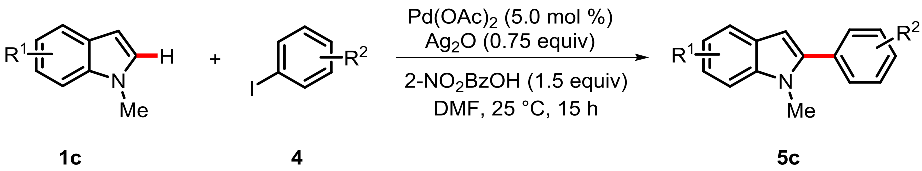
Scheme 7: Possible mechanistic pathways for the arylation of indoles **1**.

Subsequently, the arylation of SEM-protected indoles employing a robust Pd-NHC complex[36] and the arylation of *N*H-free indoles employing a palladium catalyst without a phosphine ligand were reported (Scheme 8).[37]



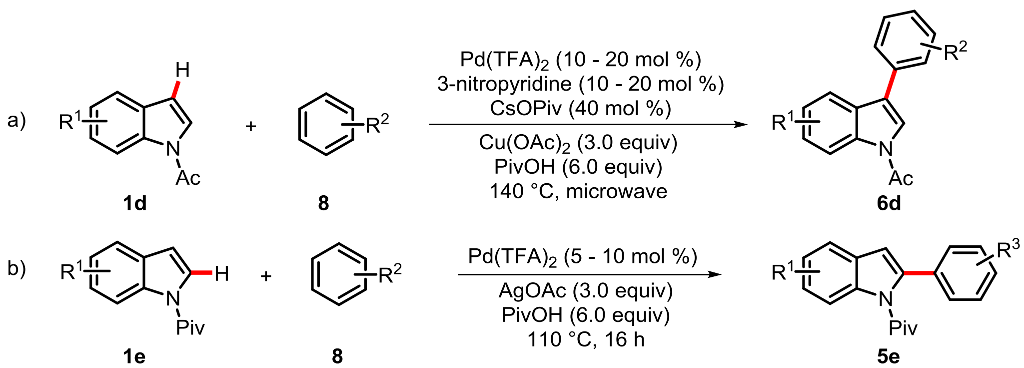
Scheme 8: Phosphine-free C2-arylation of *N*H-free indoles **1**.

In 2008, *Larossa* and *Lebrasseur* published the palladium-catalyzed C2 arylation of *N*-methylindoles at room temperature, which afforded the products **5** in high yields (Scheme 9).[38] A set of functional groups at both the indole and the aryl iodide was well tolerated. A palladium(0)/palladium(II) catalytic pathway was assumed. After oxidative addition of the aryl iodide, iodine-carboxylate ligand exchange forms a highly reactive cationic palladium species, which then undergoes carboxylate-assisted electrophilic palladation.



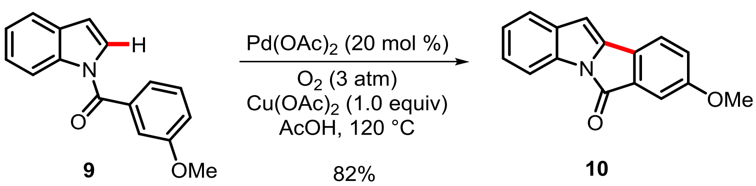
Scheme 9: Palladium-catalyzed C2-arylation of indoles **1c** by *Larossa.*

Fagnou and co-workers disclosed methods that permitted dual C–H activation for the synthesis of arylated indoles *via* palladium-catalyzed oxidative cross-coupling reactions of indoles **1** and arenes **8**.[39] Most notably, the C3:C2 selectivity of the reaction was highly dependent on the choice of the terminal oxidant (Scheme 10). $Cu(OAc)_2$ enabled the arylation at the C2 position, while AgOAc predominantly delivered C3-arylated indoles. The oxidative approach avoided prefunctionalizations of the substrates, however the lack of selectivity limited the scope of the reaction.



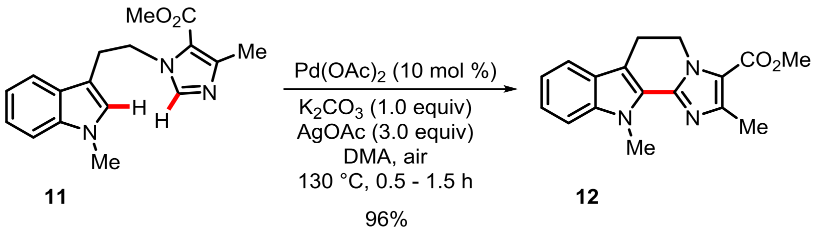
Scheme 10: Oxidative C–C coupling of indoles **1** and arenes **8**.

In 2007, the group of *DeBoef* reported on the inter- and intramolecular oxidative coupling of benzofuranes and indoles with arenes.[40] The intramolecular cyclization of indole **9** containing an electron-donating methoxy group at the arene delivered the product **10** in high yield (Scheme 11).



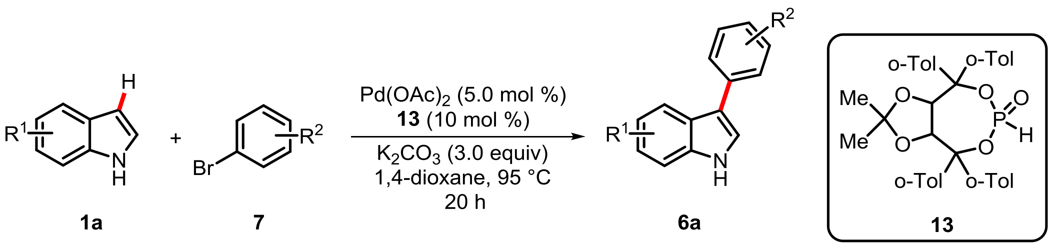
Scheme 11: Intramolecular C–C coupling of indole **9**.

Another oxidative approach was developed by *Shi* in 2008. The C2-selective palladium-cataylzed coupling of electron-rich indoles with aryl boronic acids under an atmosphere of oxygen proceeded under mild reaction conditions with a good functional group tolerance.[41] The group of *Greaney* reported on the intramolecular oxidative C–H coupling for the efficient synthesis of seven-, eight- and nine-membered ring compounds.[42] The system was limited to indoles bearing an electron-withdrawing group at the C3 position. Furthermore, *Favi* developed an intramolecular palladium-catalyzed oxidative coupling procedure with an alkyl linker between the C3 atom of the indole and a nitrogen atom of the heterocyclic coupling partner, thus enabling the synthesis of indole-imidazoles, indole-pyrroles and indole-triazoles (Scheme 12).[43]



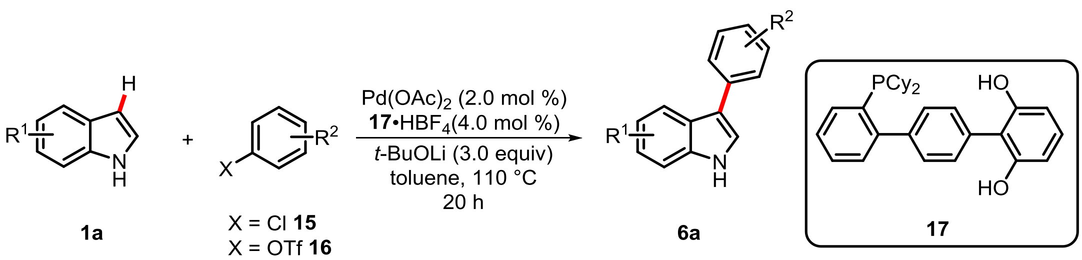
Scheme 12: Intramolecular oxidative coupling of indole **11**.

A protocol for arylations of the more electrophilic C3 position of indoles was reported by the group of *Zhang* employing arylbromides **7**.[44] In 2009, the group of *Ackermann* reported on the palladium-catalyzed C3-selective arylation of *N*H-free indoles **1a** with arylbromides **7** employing the air-stable heteroatom-substituted secondary phosphine oxide (HASPO) preligand **13** (Scheme 13).[45]



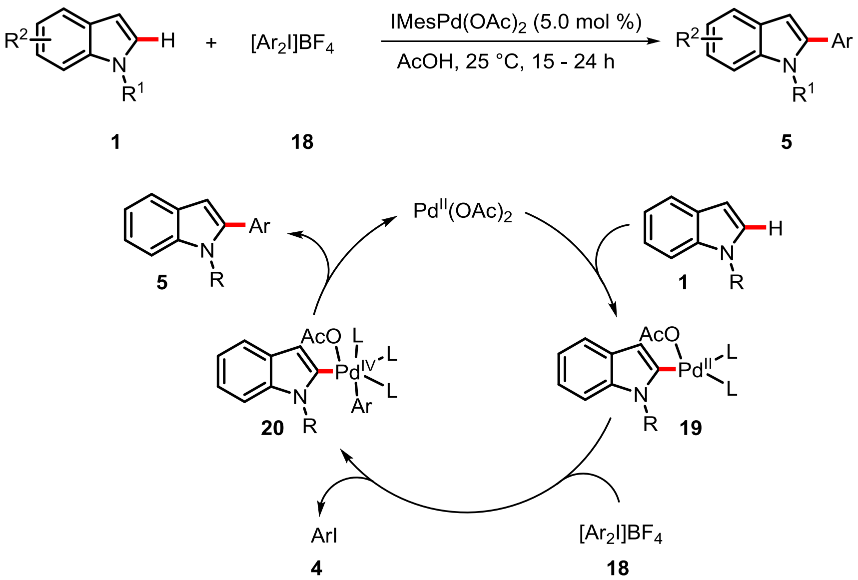
Scheme 13: C3-selective arylation of indoles **1a** employing HASPO preligand **13**.

More recently, aryl chlorides **15** and triflates **16**, which are less reactive compared to aryl iodides and bromides, have been successfully employed in C3-selective arylations of *N*-unsubstituted indoles using the palladium-dihydroxyterphenylphosphine catalyst **17**, occuring without undesired *N*-arylations[46] (Scheme 14).[47] Interestingly, other prominent phosphine ligands including Xantphos, SPhos and XPhos were ineffective.



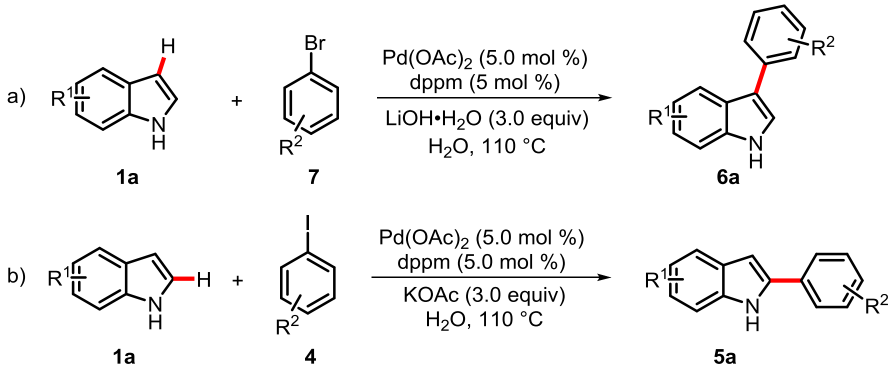
Scheme 14: C3-selective arylation of indoles **1a** with aryl chlorides **15** and aryl triflates **16**.

Besides aryl halides or triflates, more reactive arylating reagents, such as hypervalent iodine reagents or diazonium salts[48] have been applied in palladium-catalyzed direct C–H arylations. Diaryliodonium salts or diaryl-λ3-iodanes are iodine(III) compounds known for more than 120 years, which have been used as electrophiles in direct arylations and in transition metal-catalyzed cross coupling reactions due to their high reactivity, availability, stability and low toxicity.[49] In 2006, the group of *Sanford* reported on the direct arylation of indoles **1** using [Ar-I-Ar]BF_4 **18** at room temperature (Scheme 15).[50] This protocol enabled the arylation of a range of indoles with differently substituted arenes with a high selectivity for arylation at the C2 position. Based on previous work on C–H activation/C–C coupling reactions,[51] the reaction was proposed to proceed *via* a palladium(II)/palladium(IV) catalytic cycle, initiated by electrophilic palladation of the indole. Regarding the mechanism, initial attack at C3 followed by migration to C2, or a direct attack at C2 are plausible. Subsequent oxidative addition of the formed σ-indole palladium complex **19** with [Ar_2I]BF_4 forms a palladium(IV) species **20**, which undergoes reductive elimination to release the product **5** and regenerate the catalyst.



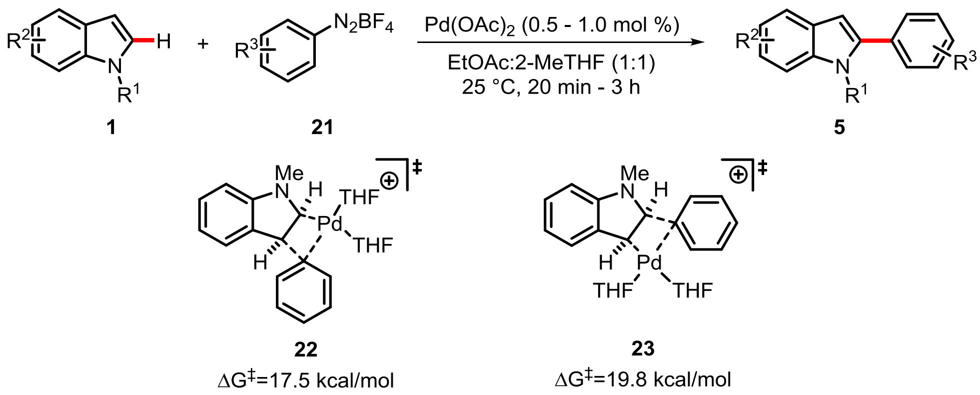
Scheme 15: C2 arylation of indoles **1** with [Ar_2I]BF_4 **18** and proposed catalytic cycle.

The group of *Djakovitch* described a palladium-catalyzed arylation of *N*H-free indoles **1a** with aryl halides **7** on water displaying a base/halide-controlled regioselectivity, which allowed for the preparation of C2-arylindoles **5a** or C3-arylindoles **6a** (Scheme 16).[52] Two plausible mechanistic pathways explained the site-selectivity of the reaction. The C2-arylindoles were formed *via* a concerted metalation-deprotonation mechanism at the C2 position or an electrophilic palladation at the C3 position, followed by C3→C2 migration and subsequent rearomatization in the presence of a weak acetate base, whereas strong bases and bromide anions promoted the rearomatization at the C3 position.



Scheme 16: Site-selective arylation of indoles **1a** on water.

Mechanistic studies by *Shi* in 2012 on novel tetranuclear palladacycles containing *N*-phenyl- and *N*-methylindole indicated that the regioselectivity of the palladation depends on the substituent at the indole nitrogen atom and the pH value of the reaction medium. Acidic conditions favored a palladation at the C2 position, while basic conditions favored the C3 position.[53] Besides aryliodonium salts, palladium-catalyzed C2-selective arylations of indoles and benzofurans with aryldiazonium salts at ambient temperatures in an open-flask procedure have been reported more recently (Scheme 17).[54] DFT calculations and mechanistic studies suggested a palladium(0)/palladium(II) *Heck*-*Matsuda*-type reaction, starting with oxidative addition of the aryldiazonium salt to palladium(0) followed by carbopalladation favoring C2-arylation (**22**) over C3-arylation (**23**). Instead of the conventional *syn*-*β*-hydride elimination, which is not possible due to the rigid ring system, a BF_4^- anion assisted *anti*-*β*-deprotonation-rearomatization could be involved.[54a]

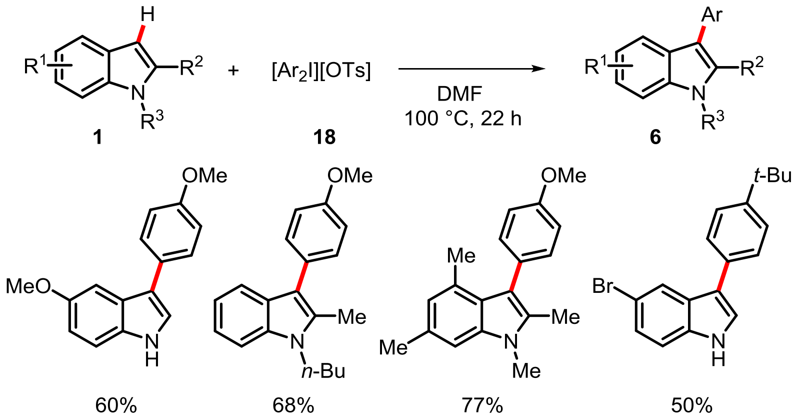


Scheme 17: C2-selective arylation of indoles **1** with aryldiazonium salts **21** and calculated transition states **22** and **23** of the *Heck*-type palladation.

In recent years, further developments on heterogenous reusable catalysts[55] and the utilization of greener media[54a] including “on water” procedures[56] for the site-selective arylation of indoles have been described. Besides the broad range of C–H functionalizations under palladium catalysis, such as alkylations,[57] alkenylations,[58] allylation[59] or alkynylation,[60] various C–H functionalizations have been disclosed employing ruthenium,[61] rhodium,[62] iridium[63] or gold[64] based catalysts.[65] The substitution of precious 4d and 5d transition metal catalysts by inexpensive, earth-abundant and less toxic 3d metals has drawn much attention in the last decades and new catalytic methodologies for regioselective C–H functionalizations of indoles under nickel,[66] mangan,[67] cobalt,[68] iron[69] or copper[70] catalysis have been described along the years.[71] Moreover, the site-selective C–H functionalization at the C4 to C7 position of indoles has been explored.[71-72]

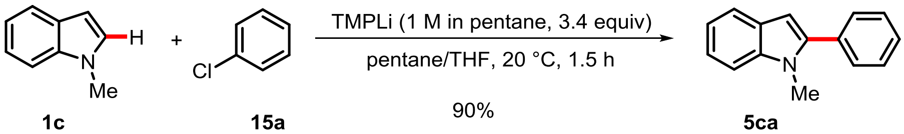
1.1.2 Transition metal-free arylation of indoles

Despite the development of transition metal-catalyzed cross-couplings and direct C–H functionalizations for the synthesis of pharmaceuticals and agrochemicals, one major concern is the analysis, removal and recovery of the expensive and toxic metal species. Palladium is classified as a class 2B metal (ICH Q3D(R1)Guideline – European Medicines Agency),[73] meaning that elemental impurities must be evaluated in the final drug with respect to the Permitted Daily Exposure (PDE) when palladium is used as a catalyst in the synthetic process. The PDEs for palladium are 100, 10 and 1 µg/day (oral, parenteral and inhalation exposure). To meet the criteria regarding the content of residual palladium in the final product, different techniques have been developed including various scavengers,[74] functionalized silica gel,[75] fixed bed adsorption processes,[76] binary systems containing a chelating agent in combination with a solid absorbent,[77] aqueous solutions with chelating agent[78] in addition to the classic methods such as distillation, crystallization or extraction with metal chelating agents.[79] The success of each purification method depends on the organic compound, the present palladium species and the applied conditions, leading to necessary optimization studies to reveal an efficient and cost-effective method. In addition, heterogeneous catalysis can be very effective for reducing the palladium contamination. On the contrary, transition metal-free coupling reactions for C–C bond or C–Het bond formations are highly desirable for more sustainable synthetic processes and purification procedures.[80] A major issue with metal-free reactions and their reproducibility is the reaction set-up, as well as the detection and quantification of metal contaminations, since even trace amounts of Palladium (50 ppb) have been proven active in coupling reactions.[81] One viable alternative to transition metal-catalyzed cross coupling reactions is the synthesis of (hetero)biaryls *via* aryne intermediates.[82] In the last decade, the base-promoted homolytic aromatic substitution (BHAS)[83] has emerged as a useful strategy for the formation of (hetero)biaryls since *Itami* reported on the *tert*-butoxide-promoted coupling of arylhalides with electron-deficient nitrogenheterocycles in 2008. Furthermore, transition metal-free arylations of indoles have been accomplished through the utilization of diazonium salts,[84] hypervalent iodine reagents,[85] or electrochemistry.[86] In 2011, the group of *Ackermann* reported on metal-free arylations of indoles **1** and pyrroles employing diaryliodonium salts **18** as arylating reagents (Scheme 18).[85b] The direct arylation of indoles afforded *N*-substituted and *NH*-free arylated indoles in good yields and with excellent site-selectivities for the C3-arylated products. Two distinct trends were observed with unsymmetrically substituted diaryliodonium salts. First, the transfer of the less sterically hindered arene was favored, and second, the less electron-rich arene was transferred preferentially.



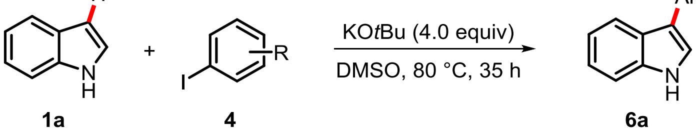
Scheme 18: Metal-free arylation of indoles **1** with diaryliodonium tosylates **18**.

Daugulis and *Truong* disclosed base-promoted arylations of 5- and 6-membered heterocycles with aryl chlorides **15** in 2011 (Scheme 19).[87] It was proposed that the aryl anion generated through deprotonation of the heterocycle attacks the benzyne formed from the aryl chlorides **15a**. Subsequently protonation generates the biaryl product. It is important to note that the most acidic C–H bond of the heterocycle is functionalized selectively.



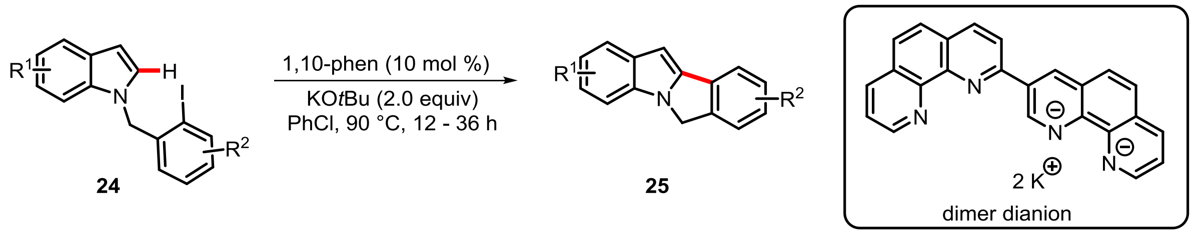
Scheme 19: Base-promoted arylation of *N*-methylindole **1c**.

The group of *Wu* reported on the transition metal-free coupling of *N*H-free indoles **1a** and pyrroles with aryl halides **4** (Scheme 20).[88] Potassium *tert*-butoxide promoted the reaction in degassed solvent. The reaction proceeded with good selectivity for the C3-arylated product, albeit delivering the *N*-arylated indole as an undesired side-product. Mechanistic studies including EPR measurements, isotopic labelling, experiments with radical scavengers and electron transfer inhibitors indicated that an aryne species, radicals and/or electron transfer processes were involved. However, a precise mechanism was not proposed.



Scheme 20: KO*t*Bu-promoted C3-arylation of *NH*-free indoles **1a**.

The intramolecular radical C–H arylation of *N*-(2-iodobenzyl)indoles using 1,10-phenanthroline and potassium *tert*-butoxide was disclosed in 2018 (Scheme 21).[89] Based on previous reports,[90] a plausible mechanism was proposed, starting with the reaction of 1,10-phenanthroline and KO*t*Bu which generates a dimer dianion[90b] as the reactive electron donor.



Scheme 21: Phenanthroline/KO*t*Bu-promoted intramolecular radical C–H arylation of indole **24**.

1.2 C–H functionalization of *α*-amino acids, peptides and proteins

Peptides and proteins perform various vital functions within living organisms including catalyzing reactions, transporting molecules and replicating DNA.[91] They are macromolecules build from at least one long chain of amino acids connected *via* peptide bonds and are usually folded into a specific three-dimensional structure after the biosynthesis (translation). Peptides and proteins are of key importance for pharmaceutical research and over 80 peptide drugs are on the market for the treatment of various diseases such as diabetes, cancer, chronic pain or HIV infection.[92] In nature peptides and proteins are usually modified after translation (post-translational modifications, PTMs), thereby increasing the functional and structural diversity and regulating the biological activity.[93] PTMs include phosphorylation, acylation, *N*-methylation,[94] lipidation[95] and glycosylation, among others, and can occur at the peptide backbone, at amino acid side chains, the *N*- or *C*-termini of the peptide and protein. Since the 1940s chemists and biochemists studied the synthesis, structures, modifications and biological activities of polypeptides and proteins leading to thousands of publications. There are two general routes to synthesize (sidechain) modified polypeptides chemically: (1) synthesis of the peptide chain employing already modified amino acid building blocks or (2) through site-selective modifications at reactive sidechains of the polypeptide.[93, 96] The second approach has also been named "tag-and-modify" strategy by *Davis.*[97] A chemical "tag", which is a functional group of a natural or unnatural amino acid (UAA) (Figure 2), is coupled with a reagent bearing the chosen modification in a chemoselective reaction. Thus, the efficient synthesis of amino acid building blocks and their incorporation in polypeptides and proteins is required.

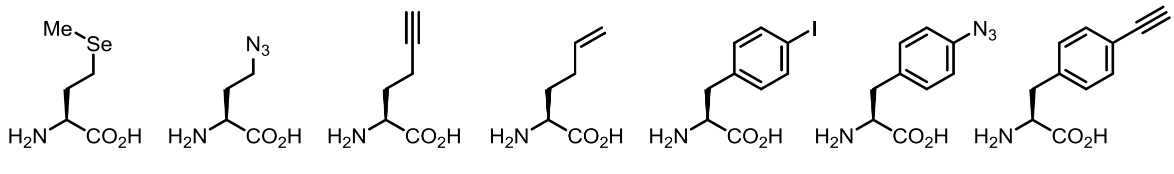
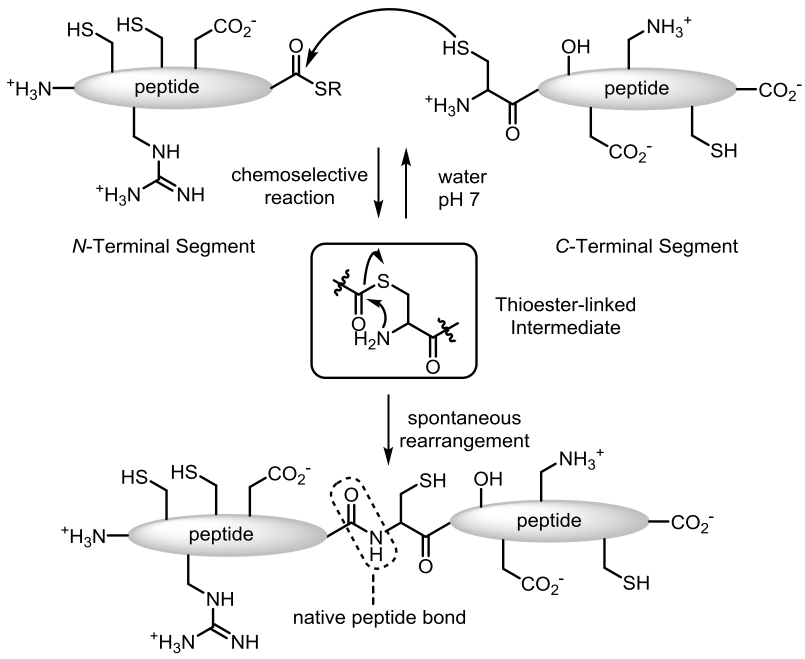


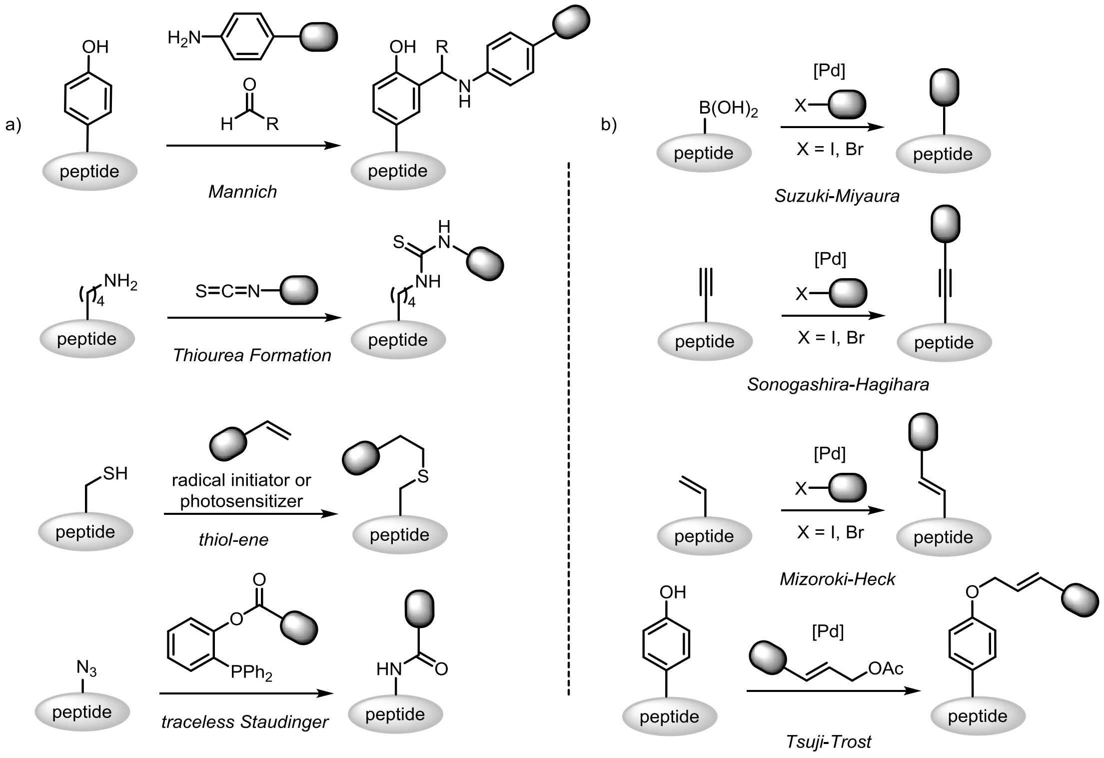
Figure 2: Examples of unnatural *α*-amino acids: Selenomethionine (Se-Met), Azidohomoalanine (Aha), Homopropargylglycine (Hpg), Homoallylglycine (Hag), *p*-Iodophenylalanine (*p*-IF), *p*-Azidophenylalanine (*p*-AzF), and *p*-Ethynylphenylalanine (*p*-EtF).[98]

The development of the solid-phase peptide synthesis (SPPS) by *Merrifield* enabled the efficient and selective synthesis of peptides through sequential coupling of amino acid derivatives on an insoluble porous support (resin).[99] It allowed the standardized synthesis of peptides containing more than 30 amino acid residues, thus overcoming the limitations of classic organic synthesis in solution including the poor solubility, time-consuming coupling reactions and purification. In 1984, *Merrifield* was awarded the Nobel Prize in Chemistry for his pioneering work. Even the incorporation of unnatural amino acids is possible, but the synthesis of longer polypeptide chains (>50 amino acid residues) remains challenging.[100] The native chemical ligation (NCL) employing two unprotected peptide segments, a *C*-terminal peptide thioester and a *N*-terminal cysteinyl peptide was reported by *Kent* in 1994 and enabled the synthesis of large peptides in a chemoselective manner (Scheme 22).[101]



Scheme 22: Peptide synthesis *via* native chemical ligation.

Until now the NCL method together with its various additions, that have been developed over the last two decades provided access to hundred of protein targets bearing even unnatural amino acids and PTMs. NCL inspired further ligation techniques and found widespread synthetic application in material science, medicinal chemistry and chemical biology.[100c, 102] Chemical modification and labeling techniques based on reactions with reactive amino acid side chains are even possible *in vivo*, because nowadays unnatural amino acids can be incorporated in proteins in a site-specific or residue-specific fashion using the cellular biosynthetic machinery.[96c, 98, 103] In general, efficient modification methods for peptides and proteins are also bioorthogonal reactions between two functional groups, which are not present in natural biomolecules. Ideally, the reaction takes place under physiological conditions with fast rates, tolerates all functional groups present within living cells and does not interfere with biological processes. Transition-metal free and transition-metal mediated modifications at AAS, such as cysteine and lysine, or at UAAs have been developed in recent years including palladium-catalyzed cross-coupling reactions (*Suzuki-Miyaura* by *Davies*[97b, 104]), ruthenium-catalyzed olefin metathesis (*Grubbs,*[105] *Verdine*[106]) and copper-catalyzed azide-alkyne cycloadditions (CuAAC by *Schultz,*[107] *Tirrell*[108]) (Scheme 23).[96d, 109]

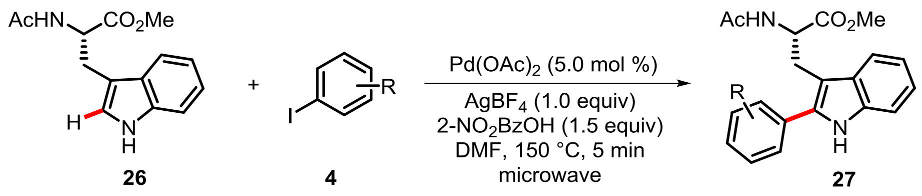


Scheme 23: Examples of a) transition metal-free and b) palladium-mediated peptide modifications.

In recent years, various transition metal-catalyzed direct C–H functionalizations have been developed as a more atom- and step-economic alternative for the (late-stage) modification of *α*-amino acids and peptides.[110] In addition to the required selectivities of such C–H functionalizations, racemization-free reaction conditions and efficient kinetics are necessary for a synthetically useful procedure.

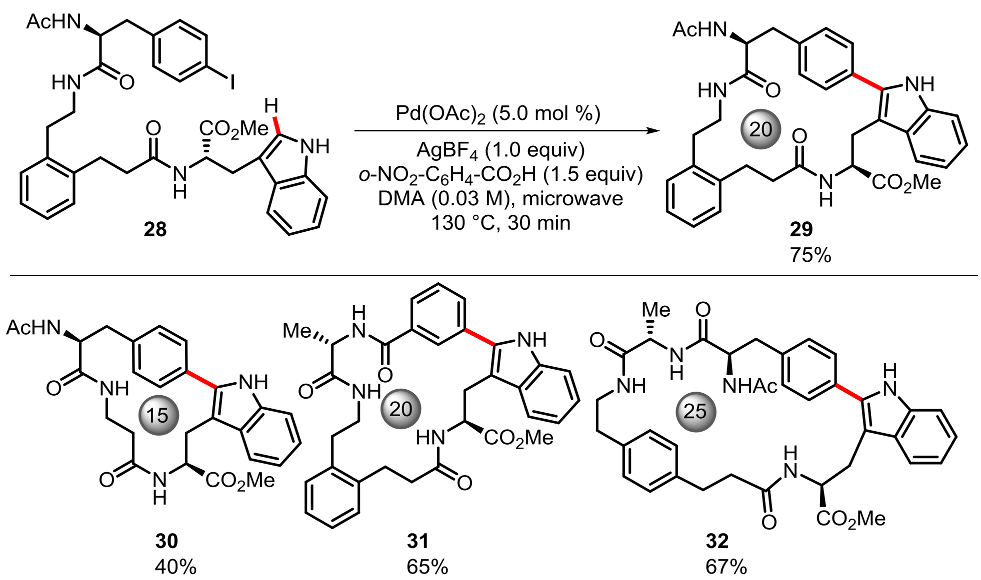
1.2.1 Palladium-catalyzed C–H arylations of tryptophan

Among the canonical *α*-amino acids, phenylalanine, tyrosine, tryptophan and histidine hold a special place due to their aromatic side chains and their importance for the biological activity of peptides and proteins. Thus, these amino acids have been employed as substrates for metal-catalyzed C(sp^2)–H functionalizations in recent years.[110f, 111] Tryptophan featuring the indole moiety is often found crucial for the biological activity of proteins or peptides and has a relatively low natural abundance.[112] Furthermore, it is a fluorescent marker[113] with a higher brightness ($\varepsilon\Phi_F$)[113c] than phenylalanine or tyrosine. Properties like fluorescence intensity, wavelength maximum (λ_{max}), band shape or fluorescence lifetimes are sensitive to the local enviroment, thus they are important for protein quantifications and studies on folding/unfolding of proteins, substrate binding and protein-protein interactions.[114] Thus, tryptophan has become an attractive substrate for site-selective C–H functionalizations. Inspired by the work of *Larossa,*[38] *Albericio* and *Lavilla* disclosed palladium-catalyzed C2-arylations of tryptophan **26** and tryptophan-containing peptides in 2010 (Scheme 24).[115] The arylation of peptides with *N*-acetyl and free carboxylic acids proceeded under mild conditions in an aqueous medium. Aromatic, acidic and basic amino acids did not affect the efficiency of the arylation, but sulphur-containing amino acids were not suitable.



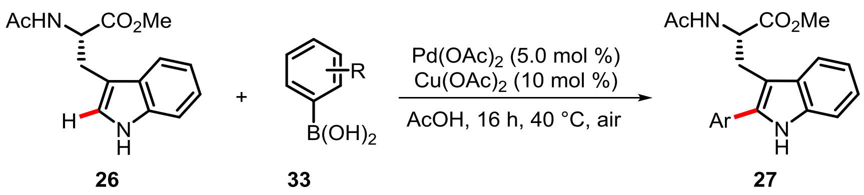
Scheme 24: C2-arylation of tryptophan **26**.

In 2013, the same group developed a palladium-catalyzed arylation of tryptophan that was not restricted to *N*-acetyl protected substrates, but could be applied to free amines, Fmoc- or Trifluoroacetyl (Tfa)-protected substrates.[116] In recent decades, cyclic and especially stapled peptides have emerged as important biologically active compounds, recieving considerable attention in the area of drug discovery.[117] The cyclization can lead to an improved cell permeability,[118] a resistance to peptide proteases,[119] helix stabilization[120] and higher binding to the target compared to the parental peptides. Naturally occurring cyclic scaffolds display different connectivites, such as head-to-tail, disulfide bonds, lactam brigdes or cyclophane units. Macrocyclization can be categorized into four types: head-to-tail, head-to-side chain, side chain-to-tail and side chain-to-side chain cyclization and can be achieved either *via* direct cyclization of the present functional groups or through introduction of a linker. Throughout the years chemists have developed a variety of methods for macrocyclizations.[121] Stapling is the introduction of a synthetic brace —staple— between the side chains of two amino acids separated along the sequence.[117c, 117d, 122] Originally, *Verdine* and coworkers —based on the work of *Grubbs* and *Blackwell*[105]— coined the term peptide stapling for the synthesis of brigded *α*-helical peptides by ring-closing metathesis (RCM) in the late 1990s.[106b] *James* disclosed palladium-catalyzed indole C2-arylations for the macrocyclization of peptidomimetics.[123] The cyclization between sidechains of nearby amino acids has the advantage that potential interactions between *N*- or *C*-termini and target receptors are not hindered. 15- to 25-membered macrocycles were successfully synthesized in good to excellent yields and linkers containing aryl groups with *o*-, *m*- or *p*-substitution pattern, alkyl chains or alanine were well tolerated (Scheme 25).



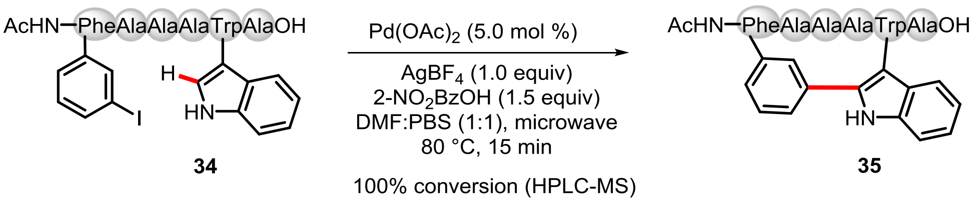
Scheme 25: Macrocyclization through 2-aryl-indole coupling.

Subsequently, *Fairlamb* and coworkers developed palladium-catalyzed protocols for the arylation of tryptophan and tryptophan-containing peptides.[124] In 2014, a set of highly fluorescent arylated tryptophans was synthesized by treatment of *N*-acetyl tryptophanester **26** with aryl boronic acids **33** (Scheme 26).[124c]



Scheme 26: C2-arylation of tryptophan **26** with aryl boronic acids **33**.

Based on mechanistic studies palladium nanoparticles were postulated as the active species, but subsequent studies indicated that the reaction proceeded in a homogenous fashion, although palladium nanoparticles are formed during catalyst turnover. Furthermore, the arylation of tryptophans employing aryldiazonium salts as arylating reagents has been accomplished.[124a] The procedure had significantly improved green reaction metrics as determined by CHEM21[125] green metrics toolkit due to the increased yields, lower reaction temperature, changed catalytic system, simple purification and the greener solvent[126] ethyl acetate. In 2015, *Albericio* and *Lavilla* reported on a palladium-catalyzed stapling method between tryptophan and iodophenylalanine or iodotyrosine (Scheme 27).[127] The macrocyclization was accomplished in solution as well as on resin. Besides glycine, alanine, valine and isoleucine, which contain containing only short aliphatic sidechains, serine, prolin, asparagine, arginine and aspartic acid, especially in the tumor-homing signalling sequences Asn-Gly-Arg (NGR) and Arg-Gly-Asp (RGD)[128] were suitable subtrates.



Scheme 27: Stapling between Trp and *m*-I-Phe.

1.2.2 Bidentate directing groups in *α*-amino acid and peptide C(sp^3)–H arylations

Bidentate directing groups have emerged as efficient auxiliaries for C–H functionalizations of inert C(sp^2)–H and more challenging C(sp^3)–H bonds, which have not been realized with conventional monodentate directing groups.[6d, 6h, 6o, 6u, 129] Figure 3 shows a set of *N*,*N*- and *N*,*S*-bidentate directing groups that have been successfully employed in transition metal-catalyzed C–H functionalizations.

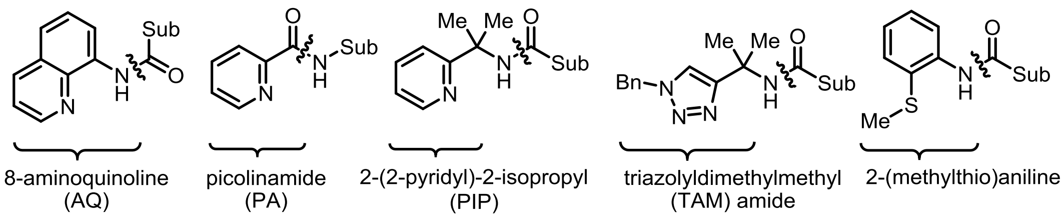
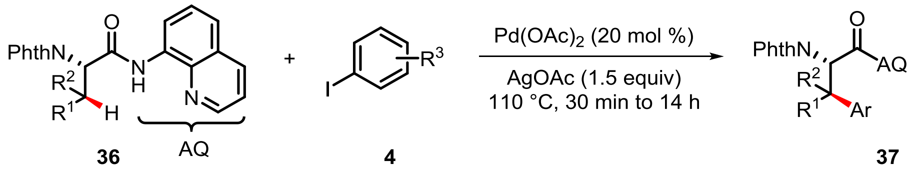


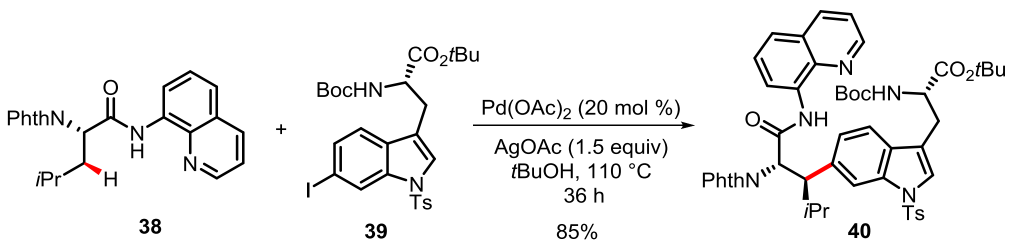
Figure 3: Examples of *N*,*N*- and *N*,*S*-bidentate directing groups. Sub = substrate

Based on the earlier work from *Daugulis* in 2005,[51b] the group of *Corey* reported on the 8-Aminoquinoline (AQ)-directed *β*-acetoxylation and -arylation of *N*-phthaloyl-protected *α*-amino acids **36** (Scheme 28).[130] Leucine and phenylalanine were selectively monoarylated, whereas alanine delivered the geminal diarylated product. Isoleucine and valine were transformed into the *γ*-arylated products. Notably, the 2*S*,3*S*-configuration of the product **37** was confirmed by single-crystal X-Ray diffraction analysis.



Scheme 28: Palladium-catalyzed *β*-arylation of amino acids.

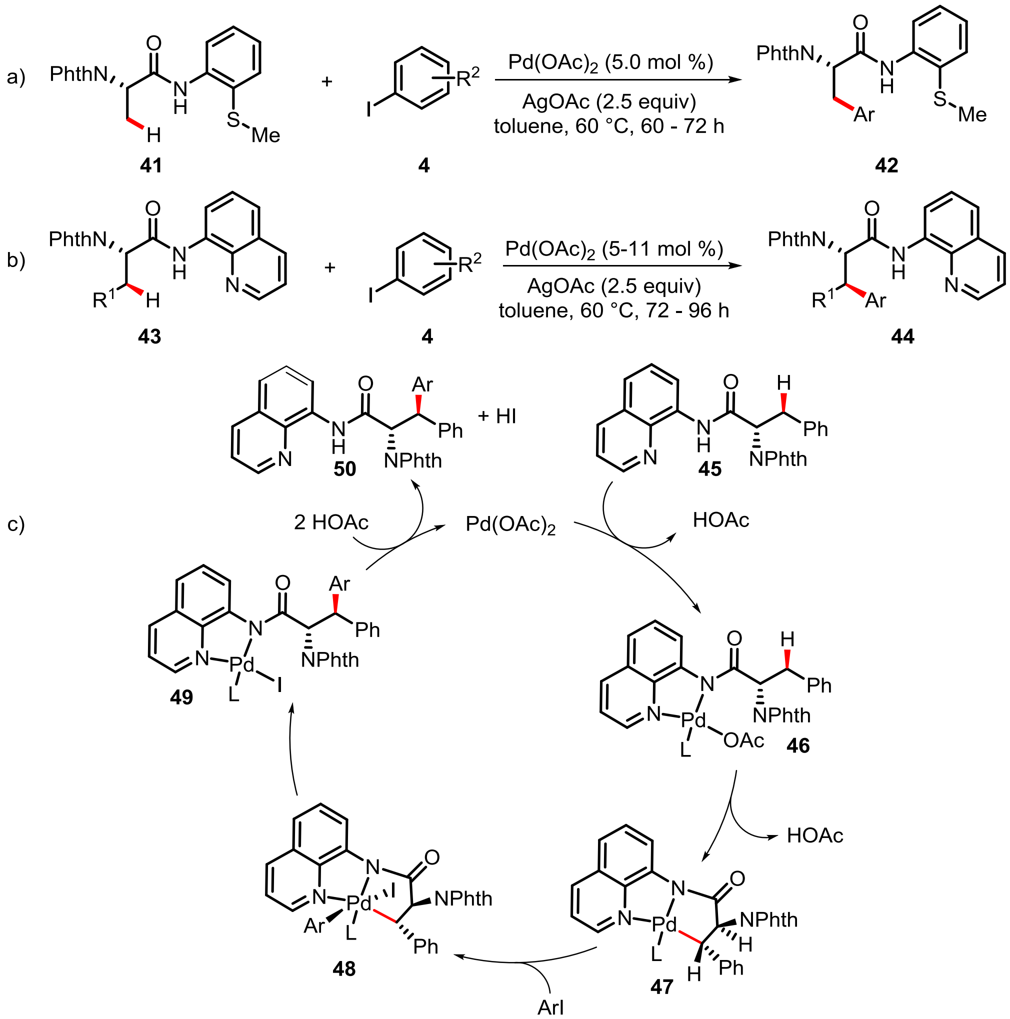
Chen and coworkers applied this AQ-directed C(sp^3)–H arylation approach to the coupling of leucine (C*β*) to tryptophan (Iodo at C6) in the totalsynthesis of Celogentin C,[131] a bicyclic nonribosomal peptide, which has been isolated from the seed of *Celosia argentea* (Scheme 29).[132]



Scheme 29: C(sp^3)–H arylation in the totalsynthesis of Celogentin C.

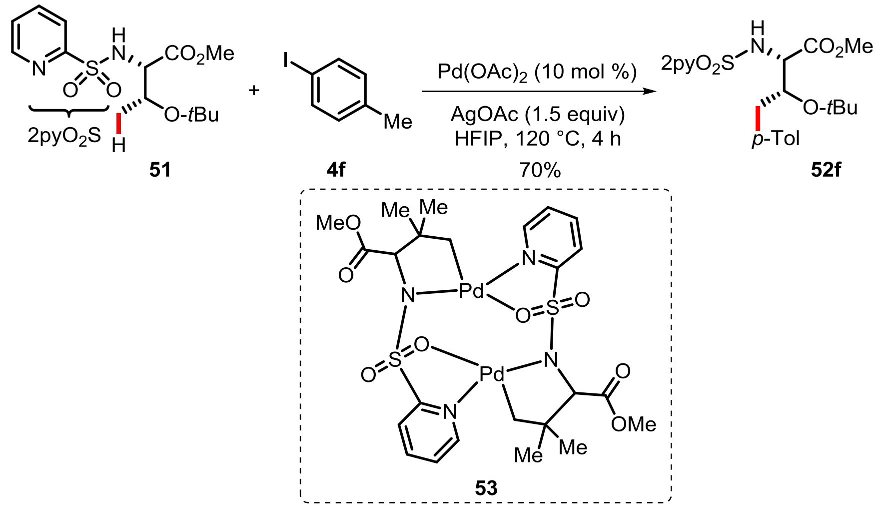
In 2012, *Daugulis* demonstrated the 2-(methylthio)aniline auxiliary-enabled monoarylation of methyl groups, whereas 8-Aminoquinoline enabled the diarylation of methyl groups and the diastereoselective monoarylation of methylene groups (Scheme 30a and b).[133] *N*-Phthaloyl-protected alanine, phenylalanine, leucine and lysine were successfully coupled with (hetero)aryl iodides **4**. A palladium(II)/palladium/(IV) pathway was proposed for the direct C(sp^3)–H arylation. H/D exchange experiments indicated that the diastereoselectivity was established at the C–H palladation step due to the favored *trans* arrangement of the phenyl and the phthaloyl groups in intermediate **47** in the five-membered palladacycle (Scheme 30c). Then, oxidative addition of aryl iodide generates palladium(IV)-

intermediate **48**, which undergoes reductive elimination. Both steps proceed under retention of the configuration. Finally, ligand exchange yields product **50**.



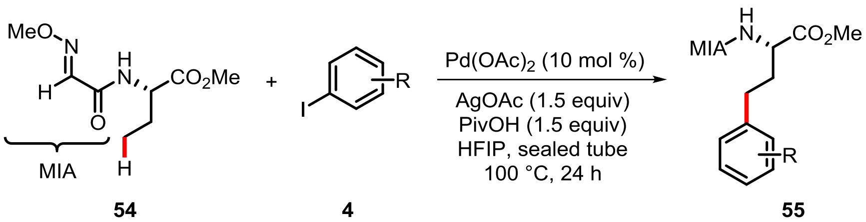
Scheme 30: *β*-Arylation of a) methyl C(sp^3)–H bonds b) methylene C(sp^3)–H bonds and c) plausible palladium(II)/palladium(IV) catalytic cycle.

A palladium-catalyzed *γ*-arylation of amino acids was described in 2013 by *Carretero* and *Fernández-Ibáñez*.[134] The *N*-2-(pyridyl)sulfonyl directing group enabled C(sp^3)–H arylations with aryl iodides (Scheme 31). Previously the *N*-2-(pyridyl)sulfonyl group had been used in C(sp^2)–H alkenylations and olefinations.[58a, 135] The arylation procedure was limited to primary *γ*-C(sp^3)–H bonds of proteinogenic and non-proteinogenic amino acids such as valine, isoleucine, allo-isoleucine, threonine or homoalanine, providing the corresponding arylated products in moderate to excellent yields. The stoichiometric reaction of *tert*-leucine with Pd(OAc)$_2$ yielded the bimetallic intermediate **53** with a *N*,*O*-bidentate coordination of the directing group to palladium and the metalation at the *γ*-methyl group. The reductive removal of the sulfonyl moiety delivered the coresponding *N*H-free amino acid ester in good yield and with less than 2% racemization as determined by HPLC.



Scheme 31: *N*-2-(pyridyl)sulfonyl directed palladium-catalyzed *γ*-arylation of amino acid derivatives **51** and bimetallic palladacycle complex **53**.

Ma reported on the *γ*-arylation of primary C–H bonds of 2-aminobutanoic acid **54** and other amino acids (Scheme 32).[136] The arylation of aminobutanoic acids generates substituted homophenylalanines, a moity used in peptidomimetics and in marketed drugs, such as enalapril[137] and quinapril[138]. 2-Methoxyiminoacetyl (MIA) was introduced as a *N*-terminal directing group, which is easily removed by hydrolysis with KOH (1N) in dioxane at room temperature or transformed into a Boc-protected glycine through hydrogenation and subsequent protection.



Scheme 32: MIA-directed primary *γ* C(sp^3)–H arylation of 2-aminobutanoic acid **54**.

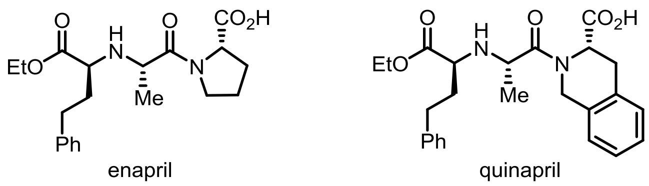
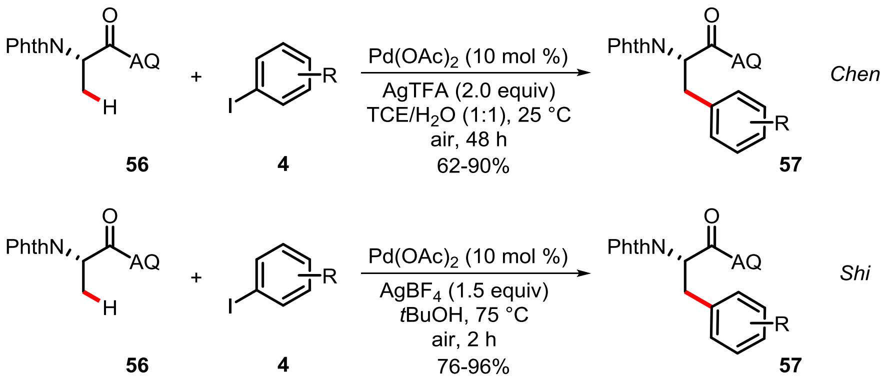


Figure 4: ACE-Inhibitors enapril and quinapril.

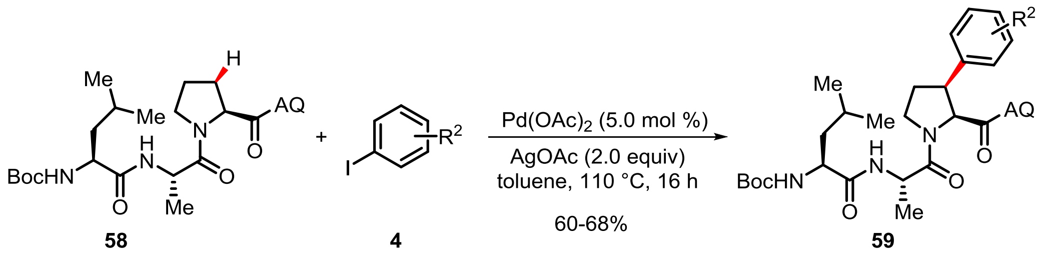
The selective methyl C(sp^3)–H monoarylation of alanine employing 2-(pyridin-2-yl)isopropylamine (PIP) as a *C*-terminal directing group was developed by *Shi* and coworkers.[139] *α*-Amino-*β*-lactams were obtained through palladium-catalyzed sequential monoarylation/amidation. In accordance with the already mentioned arylations, the *trans*-orientation of the phthaloyl group and the phenyl ring was favored and the alternative diastereomer was not observed. Despite the progress with AQ-directed procedures, the first AQ-directed *β*-monoarylation of methyl C–H bonds of alanine **56** with aryliodides **4** was reported in 2014 by the group of *Chen* (Scheme 32).[140] Besides 8-aminoquinoline, the 5-methoxyl-

8-aminoquinoline (MQ) auxiliary also facilitated the arylation, having the advantage of an easier and milder cleavage procedure compared to AQ. Later in the same year, another monoarylation was described by *Shi et al*. (Scheme 33).[141] Both groups demonstrated sequential C–H functionalizations affording various *β*-disubstituted alanine derivatives in a diastereoselective fashion.



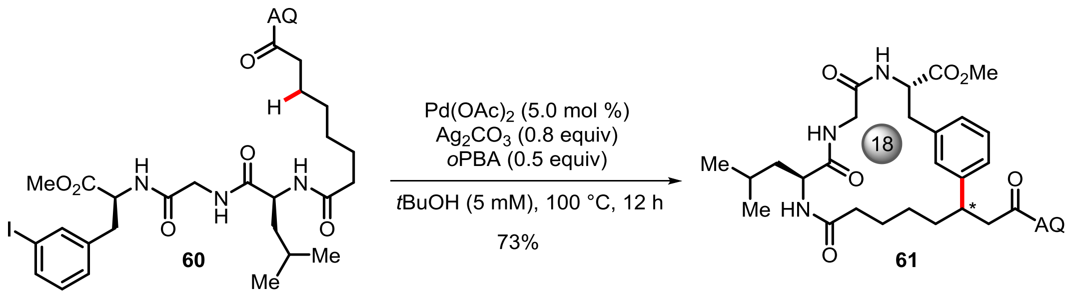
Scheme 33: AQ-directed monoarylation of alanine derivative **56**.

Kazmaier utilized 8-aminoquinoline as the directing group in *β*-arylations of Boc-protected phenylalanine-, proline- and picolinic acid-containing peptides with aryl iodides **4**.[142] Besides single amino acids, the arylation of di- and tripeptides could be accomplished without epimerization of the stereogenic centers in the peptide chain (Scheme 34). However, the removal of AQ through complete Boc-protection and saponification using LiOH/H_2O_2 resulted in a racemic mixture, which reduces the synthetic utility of the procedure.



Scheme 34: *β*-arylation of proline-containing tripeptide **58**.

Naturally occurring cyclophanes are rigid three-dimensional structures with often extraordinary physical and chemical properties. Thus, the synthesis of such moieties has received much attention in recent years.[143] *Chen et al*. published on 8-aminoquinoline-directed palladium-catalyzed intramolecular C(sp^3)–H arylation for the synthesis of cyclophane braced peptide macrocycles (Scheme 35).[144] Different types of linear peptide precursors were utilized, containing iodinated aromatic amino acids (Phe, Tyr or Trp) or modified lysine, glutamine or serine bearing various iodoaryl groups in the synthesis of 11-membered up to 26-membered macrocyclic compounds. 3 compounds showed significant activities against Myc (myelocytomatosis viral oncogene homologue)-related cancer cell lines.

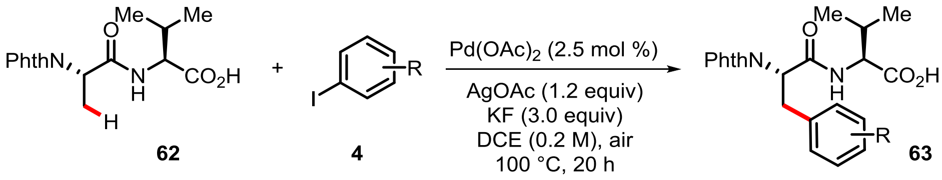


Scheme 35: AQ-directed macrocyclization *via* C(sp[3])–H arylation with *m*-I-Phe.

Despite the considerable progress in the field of C–H activation, a major drawback of covalently bond directing groups are the two additional reaction steps required for the installation of the directing groups on the substrate and the removal after the C–H functionalization reaction. These two steps need to proceed with excellent yield under reaction conditions mild enough to prevent epimerization at the stereogenic centers of the peptide chain. In recent years, transient directing groups that reversibly and temporarily bind to the substrate, enable the C–H functionalization and dissociate from the product have been employed in transition metal-catalyzed C–H activation reactions.[6e, 6j, 145]

1.2.3 Backbone-assisted and ligand-controlled C(sp³)–H arylation of *α*-amino acids and peptides

Since the 1960s, metal complexes of amino acids and peptides of almost all metals ions have been studied, thus illuminating their kinetic, thermodynamic and structural properties. In the case of amino acids and peptides, the formation of a 5-membered chelate by coordination of the terminal amino group and the amide oxygen is the most common motif for metal ions such as copper(II) or nickel(II). In addition, metal ions can promote the amide deprotonation by coordination, although the amide itself is only a weak acid (p*K*a~15).[146] In metalloproteins the main binding sites are usually donor atoms in the side chains such as the nitrogen atom of histidin, the sulfur atom of cystein or the oxygen atom of glutamin.[147] In 2014, *Yu et al.* disclosed the external directing group-free C(sp[3])–H arylation and acetoxylation at the *N*-terminal amino acid sidechain of various peptides (Scheme 36).[148] The methyl C–H bond in alanine, the benzylic C–H bond in phenylalanine and the secondary C–H bonds in 1-aminocyclopropanecarboxylic acid and 1-aminocyclobutanecarboxylic acids were suitable substrates for a reaction with aryliodides containing electron-withdrawing or electron-donating substituents at the *ortho*-, *meta-* or *para*-position. Dipeptide esters proved unreactive under the reaction conditions, indicating that the carboxylic acid group is involved in the coordination of the palladium center.



Scheme 36: Backbone-assisted arylation of dipeptide **62**.

Intrigued by previous findings on mono-*N*-protected amino acids (MPAA) ligands in palladium(II)-catalyzed functionalizations,[149] a similar *N*,*O*- and *N*,*N*-bidentate coordination of the peptide backbone to palladium was postulated to promote the C–H functionalization at the sidechain of the peptide (Figure 5).

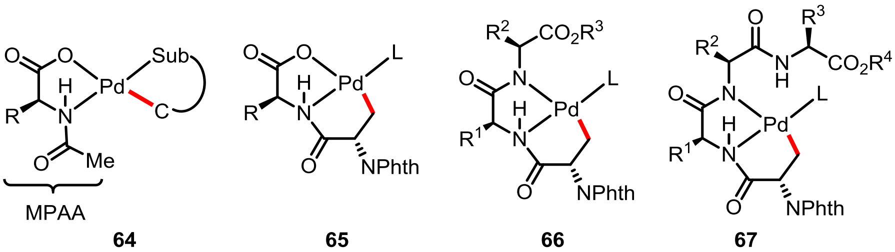
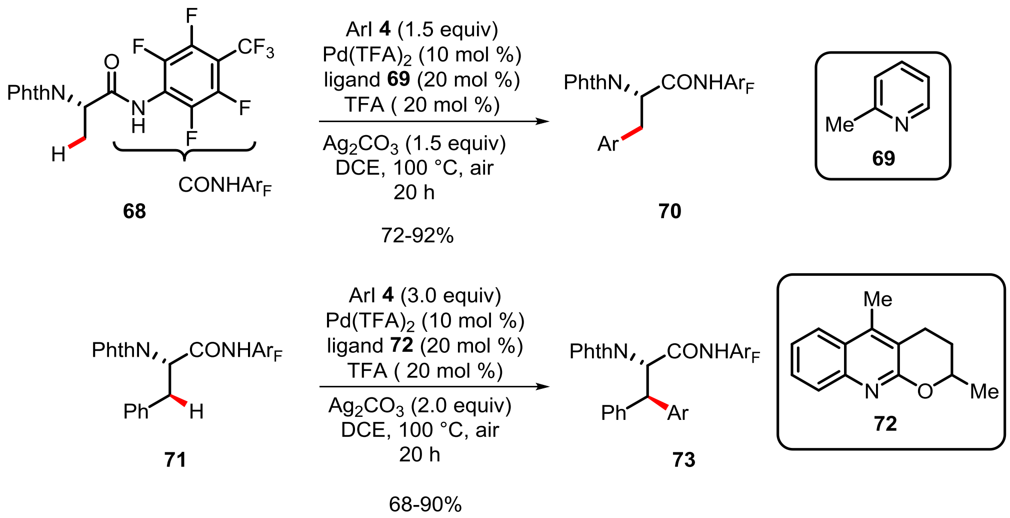


Figure 5: Palladacycles with MPAA ligands compared to palladacycles of di-, tri- and tetrapeptides. Sub = substrate, L = ligand.

Furthermore, *Yu* reported on a ligand controlled procedure to achieve the synthesis of *β*-Ar(1)-*β*-Ar(2)-*α*-amino acids using their amide auxiliary ($CONHAr_F$, Ar_F = *p*-$CF_3C_6F_4$) which has previously enabled functionalizations of $C(sp^2)$–H and $C(sp^3)$–H bonds.[150] This catalyst-controlled approach enabled arylations with a set of differently substituted (hetero)aryliodides. An evaluation of various ligands showed that 2-picoline (**69**) and the Li-Quinoline **72** were the most efficient ligands (Scheme 37). A palladium(II)/palladium(IV) catalytic cycle was proposed to commence with redox-neutral C–H activation, then oxidative addition of aryl iodide generates a palladium(IV) intermediate and finally, reductive elimination yields the product and regenerates the palladium(II) catalyst. Intramolecular deuterium kinetic isotop effect (KIE) k_H/k_D measurements indicated that the ligand is involved in the C–H activation step, while the characterization of two synthesized palladacycles of the primary and secondary C–H activation confirmed that palladium is bound to two ligands by the nitrogen atoms and to the amino acid derivative in a five-membered palladacycle by the carbon and the nitrogen atom of the deprotonated amide (Figure 6).



Scheme 37: Ligand-promoted arylation of alanine derivatives **68** and phenylalanine derivatives **71**.

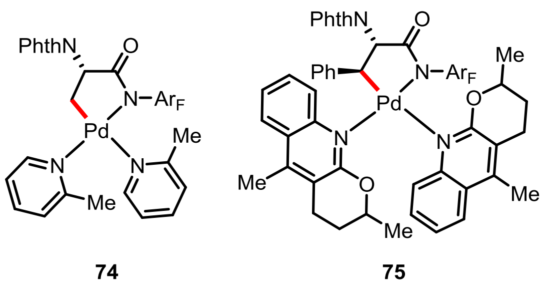
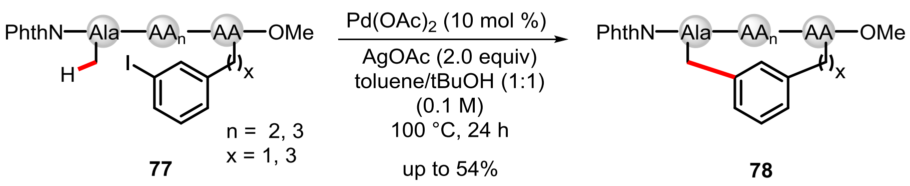


Figure 6: Primary and secondary C(sp^3)–H activation intermediates **74** and **75**.

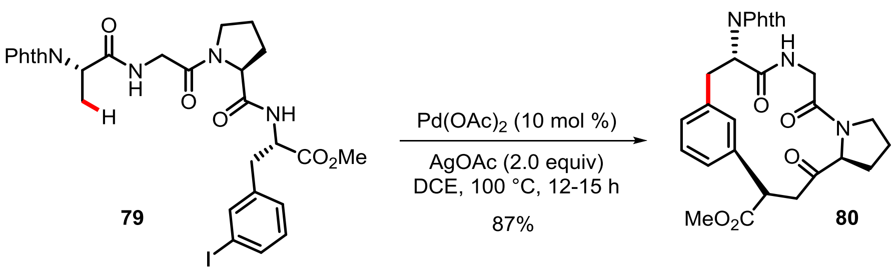
Later, *Yu* and coworkers found that a simple *N*-methoxyamide group was a viable and inexpensive alternative to CONHAr$_F$.[151] 2-picoline (**69**) and 2,6-lutidine (**76**) efficiently promoted arylations of methyl and methylene bonds with (hetero)aryliodides. Moreover, an external directing group-free procedure for palladium-catalyzed C(sp^3)–H arylations of α-amino acids with pyridine-type ligands was reported in 2017.[152] Palladium coordination by the free carboxylic acid of the amino acids enabled the β-arylation with iodoarenes.

Noisier and *Albericio* employed *Yu*´s backbone-assisted C(sp^3)–H activation[148] as a starting point for the development of a C(sp^3)–C(sp^2) peptide macrocyclization between alanine and iodophenylalanine residues.[153] The *N*-terminal *β*-carbon atom of alanine or 2-aminoisobutyric acid (Aib) of tetra- and pentapeptides PhthAla-AA$_n$-3-I-PheOMe **77** was interamolecularly coupled with 3-Iodophenylalanine or 3-Iodophenylpropylglycine (Scheme 38). However, the secondary C(sp^3)–H bond of phenylalanine was not suitable. Peptides containing proline, cysteine, methionine, histidine and tryptophan delivered only low yields of the desired cyclic products. A solid-phase/on-resin procedure was also developed.



Scheme 38: Late-stage C(sp^3)–H stapling between alanine and 3-iodophenylalanine.

At the same time, the group of *Wang* reported a similar stapling procedure (Scheme 38), which proceeded in solution and in solid-phase peptide synthesis.[154] The secondary C(sp^3)–H arylation at phenylalanine proceeded with excellent diastereoselectivity but in general with only low conversion. Moreover, the procedure was applied for the synthesis of ring A of the natural product celogentin C (Figure 7). The biological properties of all cyclized peptides were evaluated and compared to their parental noncyclic precursors. The cyclization led to an improved stability against proteolytic degradation and enhanced the integrin binding in the case of a cyclic RGD peptide.



Scheme 39: Late-stage C(sp^3)–H arylation for stapled peptides **80**.

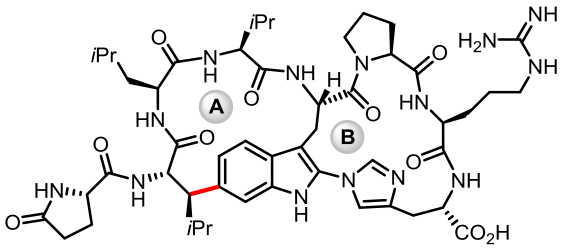
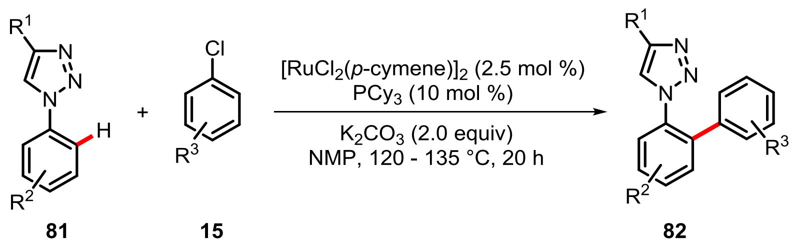


Figure 7: Celogentin C with Cβ–Ar linkage.

The group of *Ackermann* recently employed internal asparagine as directing group in the palladium-catalyzed *β*-C(sp^3)–H arylation of *N*-terminal alanine in a representative set of peptides with aryl iodides.[155] Due to the importance of chemical modifications of peptides and proteins for chemical biology, medicinal chemistry and drug development,[92e, 92f, 156] a broad range of transition metal-catalyzed C–H functionalizations has been developed in recent years. Among them, C(sp^2)–H functionalizations at the C2 position of tryptophan have been reported under rhodium,[157] ruthenium,[158] iridium,[159] and gold[160] catalysis.[161] Site-selective modifications at the C4 to C7 position of tryptophan have been disclosed lately, such as C7-amidation,[162] C4-acetoxylation[162] and C4-olefination[163]. Moreover, inexpensive, earth-abundant and less toxic 3d metals such as manganese[164] and cobalt[165] have been successfully employed for C(sp^2)–H functionalizations of peptides in recent years.[161] However, palladium-catalyzed C(sp^3)–H functionalizations of peptides have been greatly expanded in the last decade, including alkynylations,[166] silylation,[167] alkylation,[168] glycosylation,[169] chalcogenation[170] and the already mentioned arylations.[110g, 171]

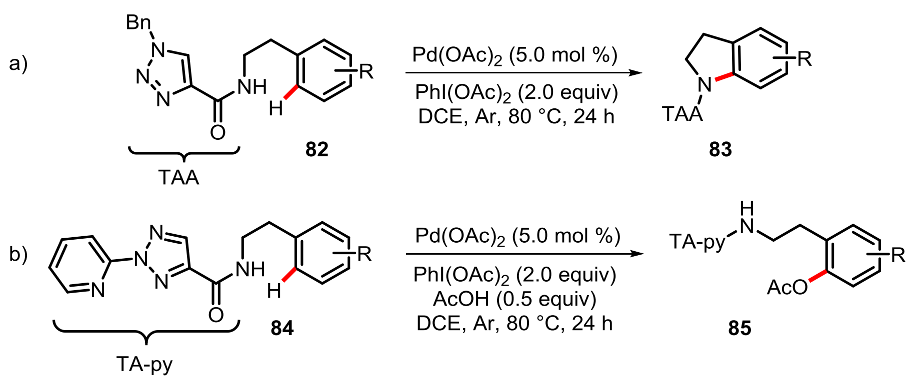
1.3 Triazoles as bidentate directing groups

The straightforward copper-catalyzed *Huisgen* cycloaddition of alkyl/aryl azides and terminal alkynes to form 1,4-disubstituted 1,2,3-triazoles[172] and their applications in peptidomimetics,[173] material sciences,[174] as ligands in catalysis, in medicinal chemistry[175] and drug development[176] and other research fields made them an attractive alternative to known bidentate directing groups. Concerning the reactivity of triazoles itself, the acidic C–H bond at position 5 of 1,4-disubstituted 1,2,3-triazoles has been successfully arylated in the presence of palladium[177] or copper catalysts.[178] *Ackermann et al.* developed a procedure for ruthenium-catalyzed C(sp^2)–H arylations of *N*-aryl-1,2,3-triazoles **81** with aryl bromides[179] and chlorides[180] employing for the first time a triazole as the directing group (Scheme 40).



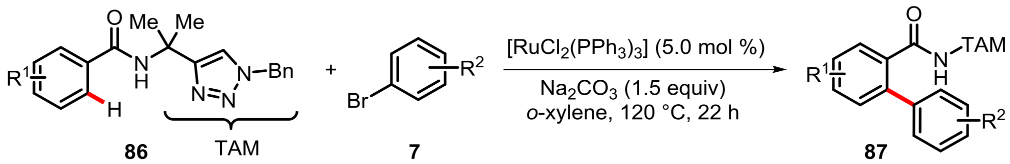
Scheme 40: Triazole-directed ruthenium-catalyzed C(sp^2)–H arylation.

In 2013, *Shi* and coworkers reported on palladium-catalyzed C–H functionalizations employing 1,2,3-triazole-4-carboxylic acids as directing groups.[181] The choice of the substitution pattern of the triazole determined the predominant outcome of the functionalization. A 1,4-disubstituted triazole gave rise to the cyclized products **85** (Scheme 41 a), whereas a 2,4-disubstituted triazole promoted the acetoxylation (Scheme 41 b).



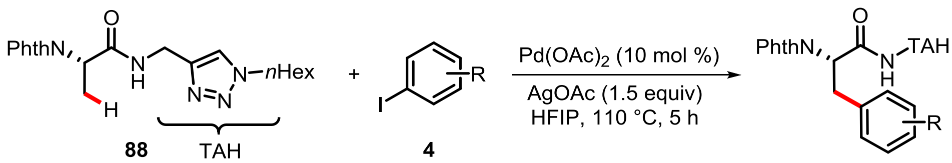
Scheme 41: Palladium-catalyzed triazole-directed a) cyclization and b) acetoxylation.

The group of *Ackermann* developed methods for iron-catalyzed[182] and ruthenium-catalyzed[183] direct arylations of sp^2- and sp^3-hybridized C–H bonds employing bidentate triazolyldimethylmethyl (TAM) amide as the directing group (Scheme 42).



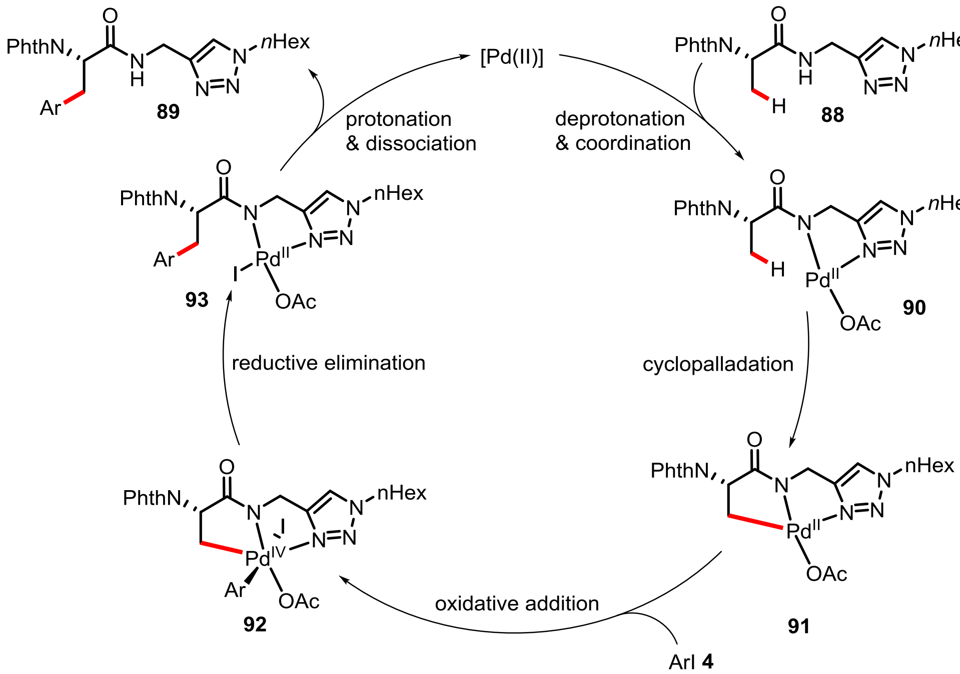
Scheme 42: Ruthenium-catalyzed TAM-assisted direct arylations with aryl bromides.

The palladium-catalyzed olefination with 1,2,3-triazoles as a removable directing group and oxygen as the terminal oxidant was disclosed by *Shi*.[184] A 4,5-disubstituted 1,2,3-triazole enabled the desired C(sp^2)–H olefination with alkenes, whereas a free C–H bond at the C5 position of the triazole was otherwise prone to olefination under the reaction conditions. In 2015, the group of *Ding* reported on the 1,2,3-triazole amide-directed palladium-cataylzed arylation of amino acid derivatives (Scheme 43).[185] Methyl C–H bonds of *N*-phthaloyl-protected alanine **88** and derivatives, such as 3-aminoisobutyric acid or 2-amino-2-propanoic acid, were successfully arylated with aryliodides **4**. However, the procedure was not applicable to secondary C–H bonds such as the benzylic C–H bond in phenylalanine.



Scheme 43: TAH-assisted palladium-catalyzed arylation of alanine **88** with aryliodides **4**.

In accordance with previously reported bidentate-directed palladium-catalyzed arylations, the reaction was proposed to proceed through reversible C–H palladation to generate the five-membered palladium(II) intermediate **91**, subsequent oxidative addition of the aryliodide to form palladium(IV) intermediate **92** and finally, reductive elimination and protodemetalation to generate the palladium(II) catalyst and release the desired product **89** (Scheme 44).



Scheme 44: Proposed mechanism of TAH-directed alanine arylation.

In recent years, *Ackermann* reported on triazole-enabled iron-catalyzed C–H activations allowing C–H arylation, alkylation, allylation, alkenylation and C–H/N–H annulation.[186] Mechanistic studies by *Neidig* isolated and identified low-spin iron(II) complexes as key cyclometalated iron intermediates in triazole-directed C–H arylations and allylations.[187] *Shi* reported on olefinations and alkynylations under palladium catalysis with 1,2,3-triazole amine directing groups.[188] Moreover, triazole-assisted peptide modifications under palladium catalysis enabled late-stage BODIPY-labeling[189] and glycosilation[169] by chemo-, site- and diastereo-selective C(sp^3)–H activation.

1.4 Computational studies on palladium-catalyzed C–H activations

In the following section an overview of computational studies on palladium-catalyzed C–H activations and functionalizations is presented. In the past two decades, computational methods such as density functional theory (DFT) calculations enabled a deeper insight into organometallic reaction mechanisms.[190] The calculation of various short-lived intermediates and transition states in combination with experimental data elucidated key steps concerning the observed reactivities and selectivities, thus inspiring further improvements and new developments. Computational studies have made a strong contribution to the understanding of C–H activation mechanisms.[13b, 13c, 14, 16e, 191] Pioneering computational studies by *Sakai* on the heteroatom-assisted intermolecular C–H activation of benzene and methane by palladium or platinum formate complexes M(κ^2-O_2CH)$_2$ indicated that the C–H activation of benzene proceeds in a two-step process.[192] κ^2-κ^1 coordination change of the formate ligand and the formation of a σ-complex, is followed by C–H cleavage *via* a six-membered transition state. In 2005, *Davies*, *Macgregor* and coworkers reported on the intramolecular cyclometallation of dimethylbenzylamine with palladiumacetate.[193] Their DFT studies supported that the formation of agostic intermediate **95** and subsequent deprotonation through a six-membered transition state **TS 95** is involved rather than the Wheland intermediate **97**, which had been proposed by *Ryabov et al.* (Figure

8).[194] A four-membered transition state **TS 98** as well as an alternative oxidative addition **TS 99** was found to have significantly higher activation barriers.

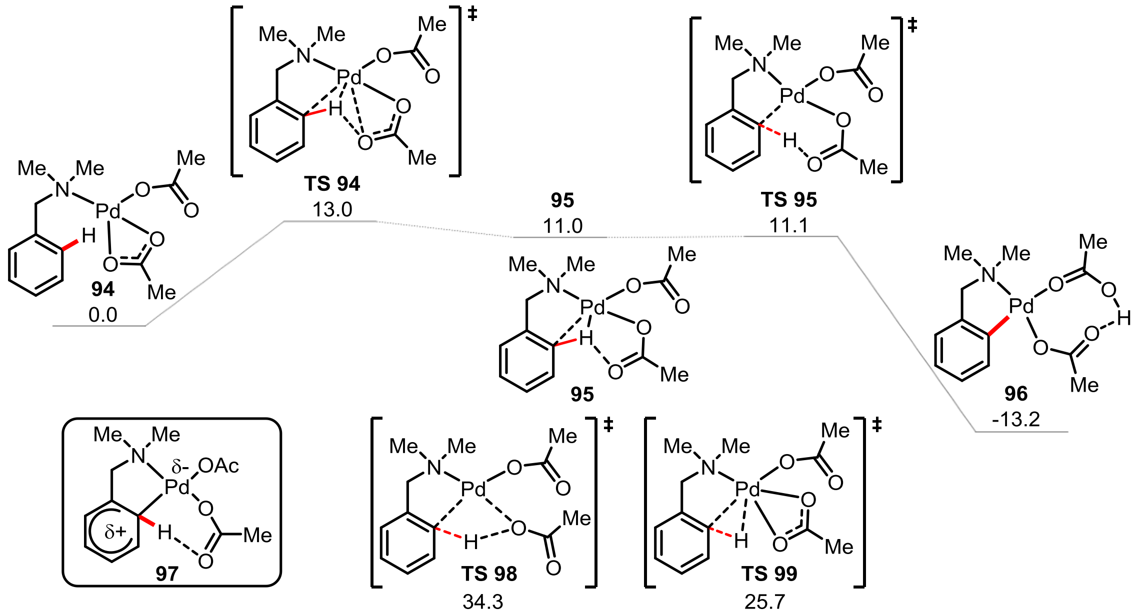


Figure 8: Calculated cyclometalation pathway, 4-membered and oxidative addition transition states with Gibbs free energies (ΔG‡ in kcal/mol) vs Wheland intermediate.

The term ambiphilic metal-ligand activation (AMLA)[13c] was subsequently introduced for such activation processes, emphasizing the role of the electron-deficient metal centre and the ligand acting as an intramolecular base.

Since the introduction of the term "agostic" for interactions of a transition metal and *σ*-C–H bond in close proximity to the metal center,[195] the topic has gained considerable attention in organometallic chemistry and catalysis.[196] In catalysis, agostic intermediates have been proposed and calculated as key structures promoting the cleavage of C(sp^2)–H and C(sp^3)–H bonds. In general, agostic interactions can be characterized as three-center-two-electron bonds between a metal center and a CH group of a ligand (C–H•••M) with certain geometric parameters and spectroscopic properties. The simple Dewar-Chatt-Duncanson[197] model can be used to describe the agostic interaction in an orbital picture: charge donation from the occupied *σ*-C–H bonding orbital to empty orbitals of the metal (TM←C–H *σ*) and *π* back-donation from the metal to the anti-bonding C–H orbital (TM→C–H *π*). Furthermore, recent studies revealed the importance of short-range London dispersion,[198] structural constraints[199] and hyperconjugation[200] for agostic interactions, which are still not fully understood.

Echavarren/*Maseras* studied intramolecular C(sp^2)–H activations on bromobenzyldiaryl-methanes. In computational studies the proton-abstraction *via* three distinct mechanisms was modelled since the observed reactivites and selectivities were inconsistent with an aromatic electrophilic substitution. Intramolecular and intermolecular proton abstraction with bicarbonate were both accessible (**TS 101** and **TS 102**), whereas proton abstraction with bromine (**TS 100**) was substantially higher in energy (Figure 9).[201]

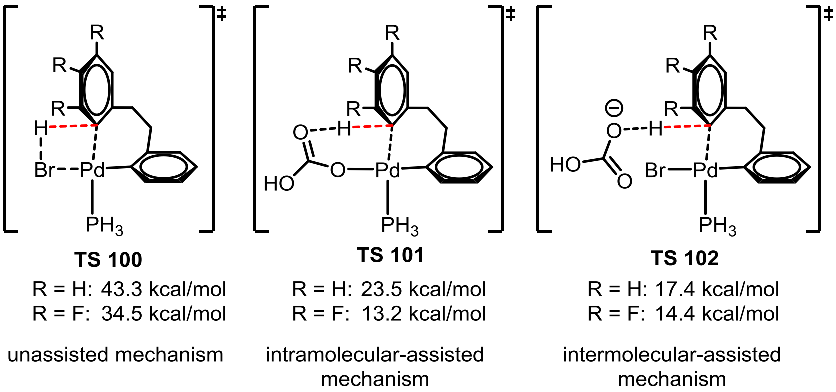


Figure 9: Transition states of the three proposed proton-abstraction mechanisms and Gibbs free energies.

In the case of intermolecular arylations of perfluorobenzenes with arylbromides, a DFT study by *Fagnou* and coworkers showed that a concerted metalation-deprotonation (CMD) pathway with a coordinated bicarbonate ligand (**TS 103**) was the most favorable mechanism, albeit the mechanism with a bromine ligand (**TS 104**) could not be excluded. The mechanism with both bromine and carbonate coordinated to palladium (**TS 105**) delivered selectivities that did not correlate to the experimental results (Figure 10).[202] Attempts to locate pathways for other mechanisms, namely oxidative addition and an electrophilic aromatic substitution failed.

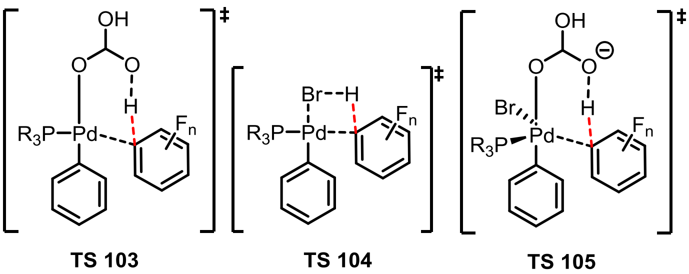


Figure 10: Concerted metalation-deprotonation transition states.

Furthermore, C(sp^3)–H activation has also been studied computationally in recent years. In 2007, *Fagnou* and coworkers reported on the intramolecular alkane arylation in the presence of catalytic amounts of palladium to accomplish the synthesis of 2,2-dialkyldihydrobenzofurans **107** (Figure 11 a).[203] The reaction showed a preference for methyl C–H bonds over secondary C–H bonds. DFT studies and kinetic isotope effect experiments indicated the C–H activation to proceed via a concerted inner-sphere palladation-deprotonation, which was enabled by agostic interactions between the *σ*-C–H bond and palladium(II) in the transition state. A set of transition states for the C–H activation at the different positions of the substrates **106** was modelled. The C–H activation of a methyl C–H bond (**TS 106.1**) was energetically favorable compared to a secondary C–H bond (**TS 106.2**) or a methyl C–H bond through a seven-membered palladacycle (**TS 106.3**) (Figure 11 b). A palladium(IV) pathway involving an oxidative addition of the C(sp^3)–H bond was ruled out due to the high energy of the palladium(IV)-alkyl intermediate (ΔG_{298K} = 47.7 kcal/mol).

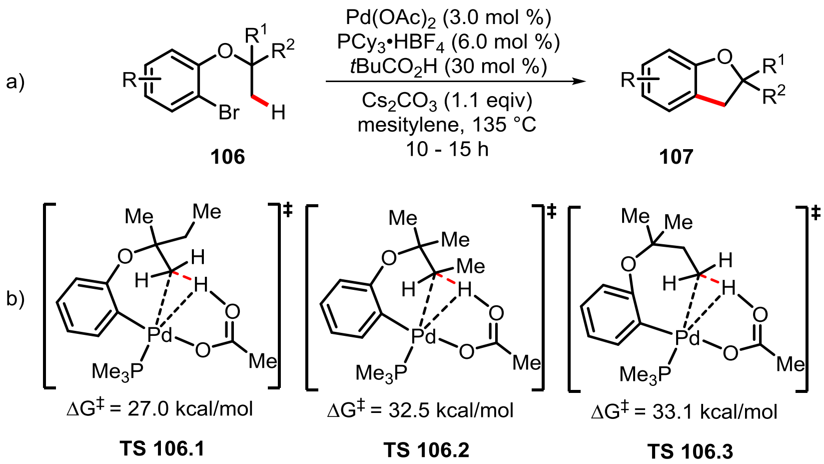


Figure 11: a) Intramolecular alkane arylation and b) transition states **TS 106.1** - **106.3** for C(sp^3)–H activation with Gibbs free energies relative to Pd(Ar)(OAc)(PMe_3).

Clot performed DFT calculations on the synthesis of benzocyclobutanes (Figure 12 a) to elucidate the role of the base in the C–H cleavage process.[204] Experimentally, carbonate was more efficient compared to bicarbonate and acetate. Starting point of the modelled C–H activation step was the Pd(II) complex **108.1** formed by oxidative addition of the substrate 2-bromo-*tert*-butylbenzene with a tri-*tert*-butyl-phosphine ligand, and bromine located *trans* to the vacant site (Figure 12 b with carbonate shown). Ligand exchange of bromine with carbonate (and respectively bicarbonate or acetate) delivered intermediate **108.2** featuring an agostic interaction. The computed activation barriers for the C–H cleavage step **TS 108.2** confirmed the highest activity with a carbonate base and identified the C–H cleavage as the rate-limiting step, which was in good agreement with the experimentally observed KIE.

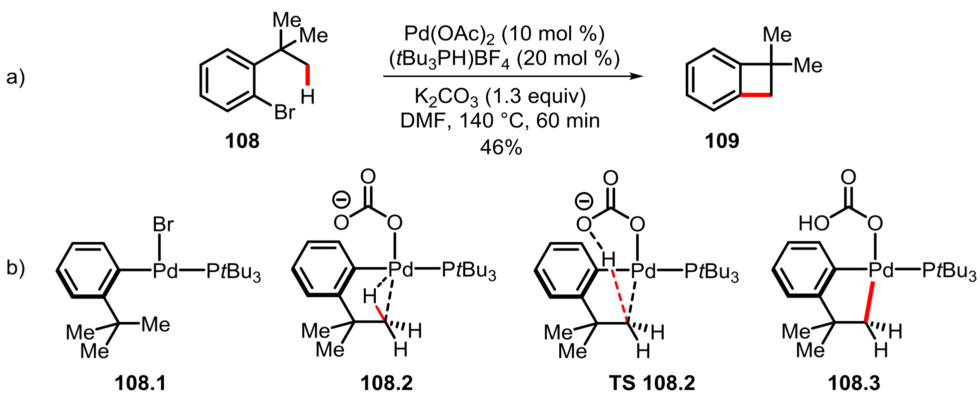


Figure 12: a) Palladium-catalyzed synthesis of benzocyclobutane. b) Ligand exchange and C–H cleavage.

Stereochemistry and stereoselective synthesis is of utmost importance in modern chemistry, in particular in pharamceutical- and agrochemistry, since enantiomers and diastereomers of molecules often differ widely in their biological activities. The stereoselective functionalization of prochiral C(sp^3)–

H bonds represents a major challenge that has been addressed by synthetic chemists in the past decades with remarkable progress.[21d, 21e, 205] As already mentioned, the Nobel Prize in Chemistry in 2001 was awarded to *Knowles*, *Noyori* and *Sharpless* for their pioneering work on asymmetric hydrogenations and oxidations. The discovery and design of enantioselective transformations remains challenging due to the fact that high enantioselectivites can arise from small energy differences of only a few kcal/mol between the crucial transition states, thus small deviations from an optimal catalytic system can cause poor results.[206] Developments in organic synthesis together with improvements in processor speed and memory capacity stimulated the application of computational chemistry to catalyst design. Quantitative computational analysis of a catalytic system is usually performed after the optimization, in which the important properties for the stereoinduction of a given catalyst have already been identified. In the last 20 years, numerous computational methods[207] have been developed for the predictive rational catalyst design as an alternative to expensive and time-consuming labwork, but a reliable method has proven elusive.[206]

The groups of *Yu* and *Houk* reported their experimental and computational investigations on oxazoline-directed palladium-catalyzed diastereoselective C(sp^3)–H iodination and acetoxylation reactions[208] based on the proposed formation of a bicyclic transition state with minimal steric repulsion (Figure 13).[209] Despite the favorable transition states, a smaller *iso*-propyl substituent led to stable catalyst resting states before the C–H cleavage step, which increased the overall energy barriers, thus resulting in a low reactivity. The diastereoselectivity was rationalized by the energy difference of 2.3 kcal/mol between the transition states **TS 110.1** and **TS 110.2** leading to the major (*S*,*S*)-product and the minor (*S*,*R*)-product, respectively. Moreover, trinuclear palladacycles were ruled out as the active species in the C–H cleavage step due to high energies of the transition states.

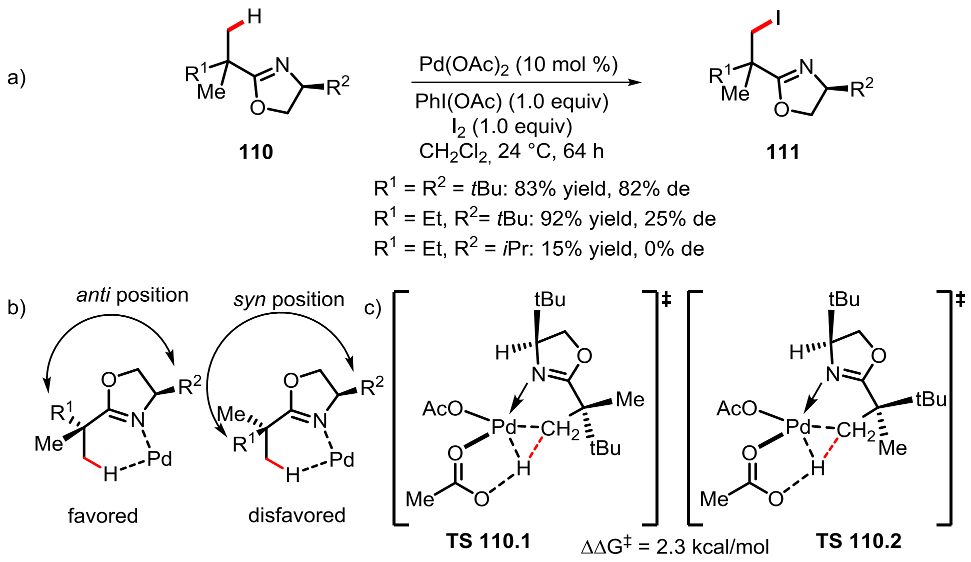


Figure 13: a) Palladium-catalyzed C(sp^3)–H iodination. b) proposed model for the stereoinduction. c) calculated transition states.

In addition to carboxylates, the amidate oxygen of monoprotected amino acid (MPAA) ligands can also act as an intramolecular base in a CMD-type mechanism, which was revealed in combined experimental and computational studies.[149a, 210] Furthermore, in 2016, *Yu*, *Houk* and coworkers introduced chiral acetyl-protected aminoethyl quinoline (APAQ) ligands for the palladium-catalyzed enantioselective arylation of *β*-methylene C–H bonds of aliphatic amides and presented DFT calculations on the origin of the enantioselectivity in the C–H activation step (Figure 13).[211] The *N*,*N*-bidentate APAQ ligand **113** promoted the C–H cleavage as an internal base, and, at the same time, induced the enantioselectivity through the favored orientation of the bulky aryl substituent and the substrate methyl group on opposite sites (**TS 112.1**).

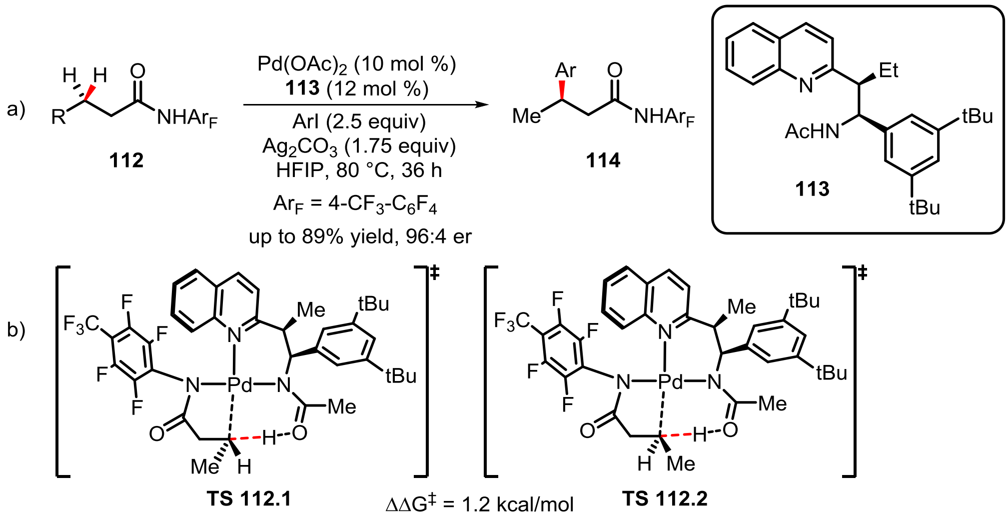
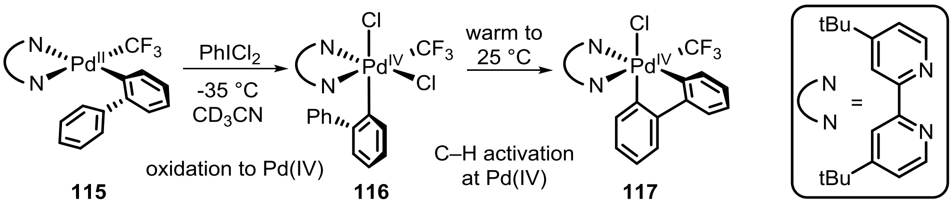


Figure 14: a) Palladium-catalyzed *β*-methylene C–H arylation. b) Favored transition states of the C–H activation.

The examples of C–H activations mentioned above involved a palladium(II) center without change of the oxidation state, but palladium(II)/palladium(IV) catalytic cycles and C–H activations at high-valent palladium(IV) have also been proposed and investigated recently.[212] Most notably, C–H activations at palladium(IV) proceeded with different siteselectivities compared to analogous C–H activations at palladium(II). *Wang*/*Wang* reported detailed DFT calculations on C(sp^3)–H arylations of an alanine derivative developed by the *Yu* group,[150d] elucidating a palladium(II)/palladium(IV) catalytic cycle.[213] After bicarbonate-assisted C–H activation, oxidative addition of iodobenzene forms the palladium(IV) intermediate and subsequent reductive elimination affords the product. The calculated results correlated well with the experiments, such as the measured KIE and isolated intermediates. The first detailed studies of octahedral palladium(IV) complexes were performed by *Canty*.[51c] *Sanford et al.* described C–H activations at palladium(IV) complexes with bidentate 4,4'-di-*tert*-butylbipyridine (dtbpy)[214] (Scheme 45) and tridentate tris(2-pyridyl)-methane (Py_3CH)[215] ligands.



Scheme 45: C–H activation at palladium(IV) by experiment.

Fang and coworkers performed DFT studies on the formation of the palladium(IV) complex **116** and the subsequent C–H activation mechanism with the 2,2'-bis(4-tert-butylbipyridine) ligand.[216] They revealed that the palladium(IV) intermediate **116.1** is most probably formed through an one-step oxidative addition of $PhICl_2$ via **TS 115**, which is the rate-determining step, while the C–H activation *via* **TS 116.2** is facilitated by an outer-shell chloride ion acting as the base without any severe structural distortion (<C···H···Cl ≈ 180°) (Figure 15).

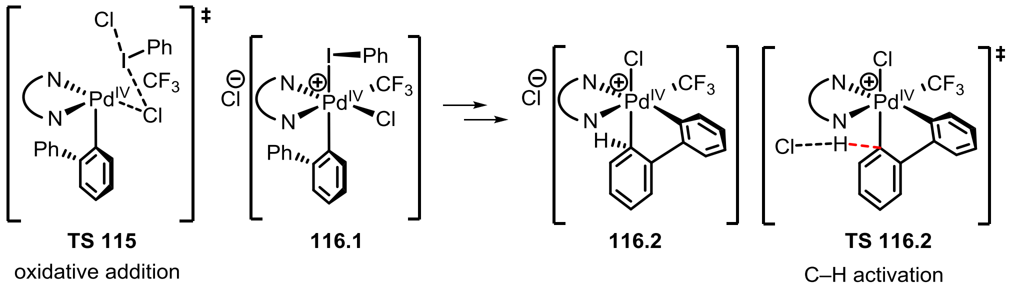
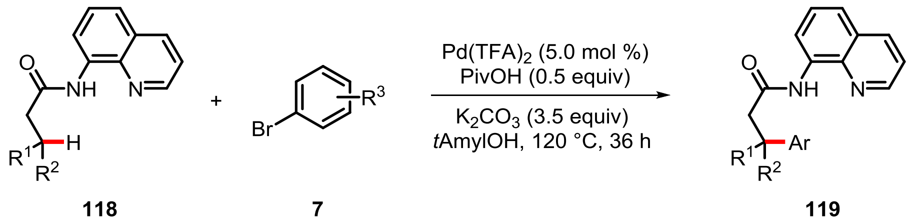


Figure 15: Palladium(II) → palladium(IV) oxidation and chloride-promoted C–H cleavage.

The groups of *Wu* and *Zeng* developed a palladium(II)-catalyzed intermolecular arylation for the regiospecific coupling of unactivated C(sp³)–H bonds with aryl bromides by assistance of 8-aminoquinoline as directing group (Scheme 46).[217]



Scheme 46: Intermolecular arylation with aryl bromides.

Computational DFT-studies were performed to distinguish two feasible palladium(II)/palladium(IV) pathways. The oxidative addition of aryl bromide/C–H activation at palladium(IV) (pathway A) was compared to the C–H activation at palladium(II)/oxidative addition of aryl bromide (pathway B). Pathway A is very unlikely due to high energy barriers for the oxidative addition (**TS 118.1-A**) and the CMD mechanism at palladium(IV) (**TS 118.2-A**) (Figure 16).

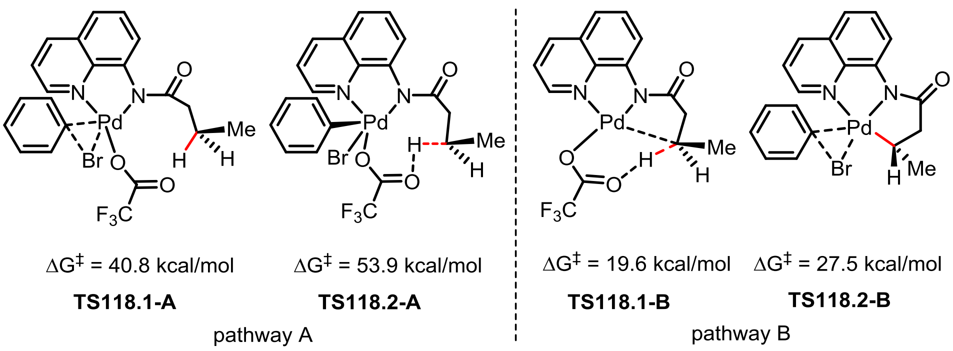
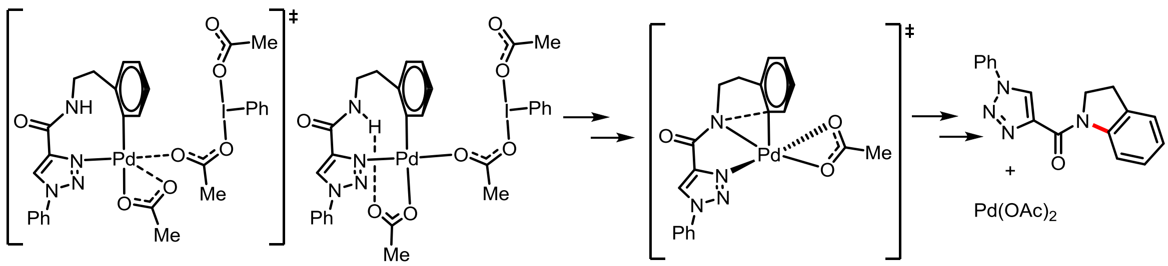


Figure 16: Selected transition states of pathway A and B with energy barriers.

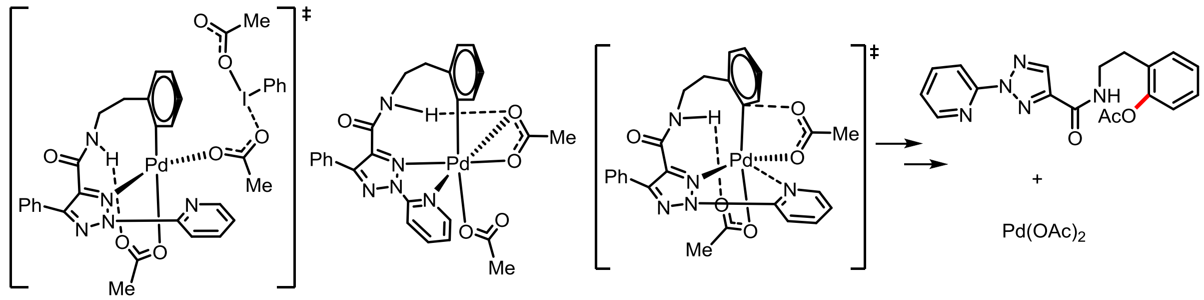
Concerning palladium(III) intermediates, in particular binuclear palladium(III) complexes have been proposed and studied (computational) by the groups of *Ritter*[218] and *Yates*.[219] DFT calculations on the triazole-directed C(sp^2)–H activation reported by *Shi*[181] have been performed to investigate the origin of the observed chemoselectivity and elucidate wether palladium(III) species are involved in the mechanism.[220] The calculations indicated that palladium(III) intermediates are actually involved in the pathways with the two triazole directing groups leading to the cyclization and the substitution product. The favorable pathway for the cyclization starts with C–H activation via CMD, followed by oxidation via **TS 82.1** of the palladium(II) intermediate with PhI(OAc)$_2$ to form the corresponding palladium(III)aryl intermediate **82.2**. The alternative formation of a palladium(IV) intermediate is kinetically disfavored. Subsequent deprotonation of the amide nitrogen with palladium(III) and release of acetic acid generates the palladium intermediate **82.3** (not shown in Figure 17), which finally undergoes reductive elimination via **TS 82.3**.



	TS 82.1	**82.2**	**TS 82.3**	
ox. state:	II → III	III	III → I	
ΔG:	-5.9	-18.4	-0.5	-51.1

Figure 17: Selected intermediates and transition states with Gibbs free energies (ΔG in kcal/mol) of the cyclization pathway.

The favorable pathway for substitution starts with C–H activation via CMD, followed by oxidation via **TS 84.1** to form palladium(III) intermediate **84.2** and reductive C–O bond formation via **TS 84.2** (Figure 18). Similar to the cyclization pathway, oxidation to palladium(IV) was excluded due to the high energy barrier. Oxidation of palladium(I) to palladium(II) with PhI(OAc)$_2$ regenerates the catalyst in both pathways. The corresponding cyclization and substitution pathways were calculated, but the results clearly showed that this pathways are kinetically disfavored.



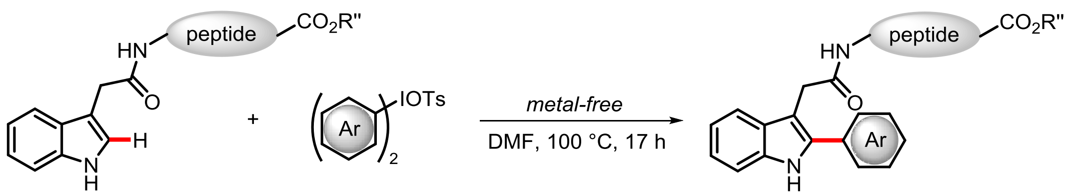
	TS 84.1	84.2	TS 84.2	
ox. state:	II → III	III	III → I	
ΔG:	-13.0	-18.7	-7.5	-52.3

Figure 18: Selected intermediates and transition states with Gibbs free energies (ΔG in kcal/mol) of the substitution pathway.

2. Objectives

During the last years, transition metal-catalyzed C–H activations have been explored as a powerful and sustainable approach for selective C–C and C–Het bond formations. The development of a plethora of methods for the chemo- and site-selective funtionalization of various substrate classes has significantly expanded the toolbox for synthetic organic chemists. Besides, transition metal-free C–H transformations have been investigated as greener alternative synthetic strategies which could avoid the use of inexpensive and potentially toxic transition metal, thus, the costly removal of these metals. Ongoing researches by the group of *Ackermann* and others showed remarkable progress in the late-stage diversification of valuable organic molecules, such as *N*-heterocycles or peptides. The development of efficient C–H functionalizations of peptides is challenging due to the need for i) mild racemization-free reaction conditions with high functional group tolerance, ii) highyl selective transformations which proceed in the presence of many different C–H bonds and iii) fast kinetics to deliver synthetically useful yields. Additionally, methods for the *in vitro* or *in vivo* diversifications of peptides or other biomolecules require robust catalytic systems operating in the presence of water and air.

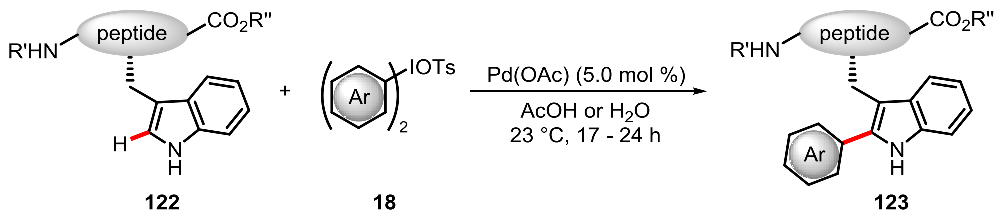
Based on the reported metal-free direct arylation of indoles at the C3 position with diaryliodonium salts **18** by *Ackermann*,[85b] *Dr. Yingjun Zhu* developed a novel direct C2-arylation of indoles bearing an acetamide functionality at the C3 position. Furthermore, this metal-free transformation enabled the arylation of peptide-containing indolylacetamides **120**. At the outset of this thesis, the substrate scope of this C–H arylation should be explored with respect to both substrates (Scheme 47). Moreover, studies with enantiomeric-pure peptides should be carried out to exclude a potential racemization during the reaction.



120 **18** **121**

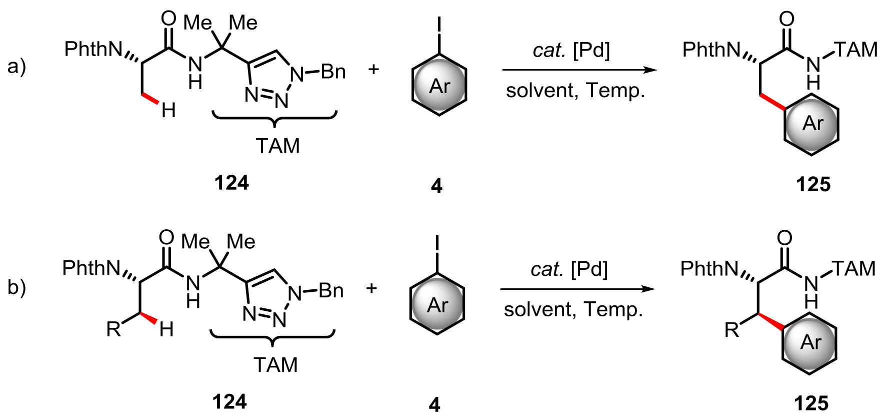
Scheme 47: Transition metal-free C(sp^2)–H arylation of peptide-containing indolylacetamides **120**.

The chemical modification of the amino acid tryptophan, which is rarely present in proteins together with its spectroscopic properties and role for biological activity, should next be studied. Palladium-catalyzed direct C2-arylations of tryptophan and tryptophan-containing peptides using aryl iodides and arylboronic acids were developed by *Lavilla*[115-116] and *Fairlamb*.[124b, 124c] In order to accomplish a more efficient and milder arylations, *Dr. Yingjun Zhu* identified diaryliodonium salts **18** as suitable arylating reagents for the palladium-catalyzed arylation at ambient temperature (Scheme 48). Notably, the arylation was also operating in water. Based on these findings the viable robustness should be investigated.



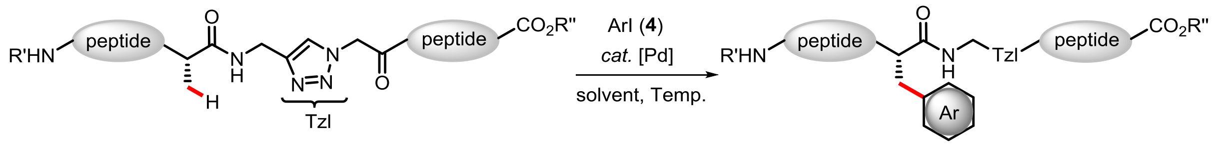
Scheme 48: Palladium-catalyzed direct C(sp^2)–H arylation of tryptophan-containing peptides **122**.

Recently, 1,4-substituted 1,2,3-triazoles have been employed as amide bond mimics[173] and versatile modifyable directing group in transition metal-catalyzed transformations. *Ackermann* and coworkers had reported on triazole-directed C–H functionalizations of C(sp^2)–H and C(sp^3)–H bonds under ruthenium, iron and palladium catalysis.[182-183, 186f, 221] However, triazole-directed C–H functionalizations of amino acids and peptides were unprecedented. With regard to the importance of modified peptides for biological and chemical science, we were interested in developing a novel triazole-directed palladium-catalyzed C(sp^3)–H functionalization of peptides, which allowed for the synthesis of highly decorated peptides in a racemization-free manner. Therefore, the C(sp^3)–H arylation of alanine derivative **124** bearing the TAM directing group with aryliodides **4** was probed (Scheme 49 a)). Moreover, a major part of this thesis was devoted to the development of the C–H functionalization of secondary C(sp^3)–H bonds in phenylalanine derivatives **124** (Scheme 49 b)). Importantly, the strategy should exert high levels of chemo-, site- and stereo-selectivity. Moreover, the C–H functionalization and the removal of the triazole moiety should proceed without racemization of all stereogenic centers. Furthermore, we were interested in the application of our approach to peptide labeling and C–H ligation.



Scheme 49: Palladium-catalyzed triazole-directed C(sp^3)–H arylation of amino acids.

Due to the fact that 1,2,3-triazoles have been employed in various peptidomimetic studies, the question arose whether a palladium-based catalytic system could enable the unprecedented positional-selective arylation of triazole-containing peptidomimetics **137** (Scheme 50). Such a methodology would set the stage for highly desirable post-synthetic sidechain diversifications of peptides at an internal position by peptidomimetics for the first time.



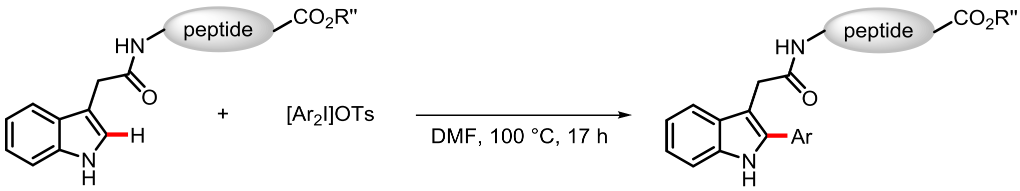
Scheme 50: Palladium-catalyzed direct arylation of triazole-containing peptidomimetics **137**.

A detailed understanding of reaction mechanisms is of utmost importance for the identification of efficient catalysts and the development of new transformations. Thus, computational investigations by means of DFT should be conducted on the palladium-catalyzed functionalizations under triazole-assistance to gain insight into the catalytic pathway, especially the key elementary steps, which determine the site- and stereo-selectivities.

3. Results and Discussion

3.1 Transition metal-free C–H arylation of indolylacetamides

Indole is an important moiety in naturally occuring and synthetic compounds with various biological activities.[25a, 25c, 25d] The group of *Ackermann* has developed several transition-metal catalyzed methods for the indolesynthesis *via* direct C–H bond functionalization or through intermolecular annulation.[45, 222] In addition, an efficient metal-free C3-selective arylation of indoles with highly reactive diaryliodonium salts has been reported.[85b] On the basis of these studies, *Dr*. *Yingjun Zhu* developed metal-free direct C–H arylations of indolylacetamides **120** with diaryliodonium tosylates **18** (Scheme 51). An indolylacetyl group as an unnatural tag at the *N*-terminal end of the peptide enabled the chemo- and site-selective late-stage modification of peptides in the absence of toxic metals.



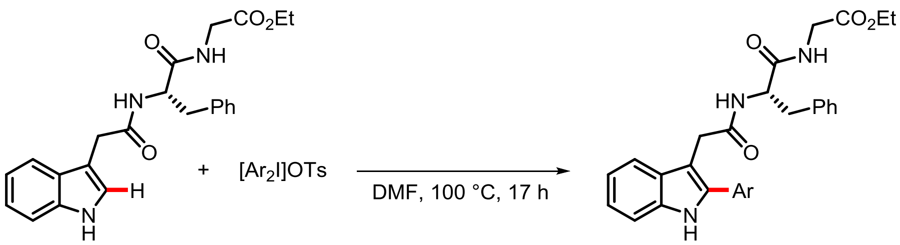
120 **18** **121**

Scheme 51: Metal-free arylations of peptide-containig indolylacetamides **120**.

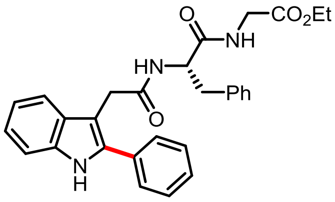
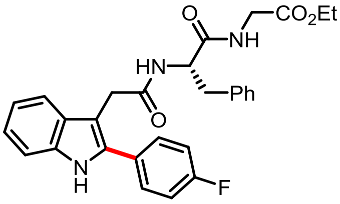
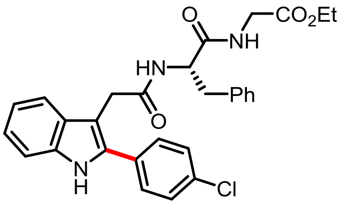
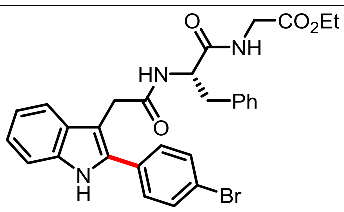
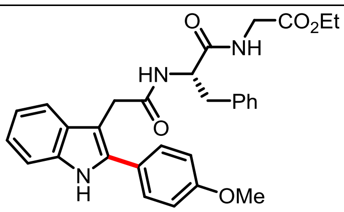
3.1.1 Scope of metal-free arylations of peptide-containing indolylacetamides

In the course of this thesis, the scope of the C–H arylation was examined. Initially, the dipeptide **120a** was treated with a representative set of diaryliodonium tosylates **18** bearing both electron-poor or electron-rich substituents at the *para*-position of the arenes under the otherwise optimized reaction conditions (Table 1). Generally, the products **121aa-121ae** were obtained in good to excellent yields. The results indicated, that the electron density on the arene did not significantly affect the formation of the desired products, as the electron-withdrawing fluoro substituent furnished almost the same isolated yield (entry 2, **121ab)** as the electron-donating methoxy substituent (entry 5, **121ae**). Fortunately, the halogen-containing motifs were well-tolerated (entries 2-4), which with allow for further diversification of the products **121**.

Table 1: Metal-free C–H arylations of dipeptide **120a** with diaryliodonium tosylates **18**.[a]



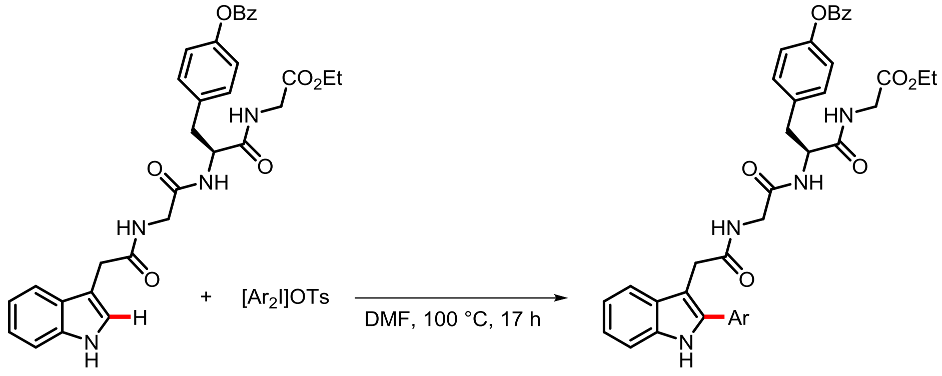
120a **18** **121**

Entry	Ar	Product	Isolated Yield (%)
1	Ph **18a**	 **121aa**	95
2	4-FC$_6$H$_4$ **18b**	 **121ab**	71
3	4-ClC$_6$H$_4$ **18c**	 **121ac**	63
4	4-BrC$_6$H$_4$ **18d**	 **121ad**	65
5	4-MeOC$_6$H$_4$ **18e**	 **121ae**	75

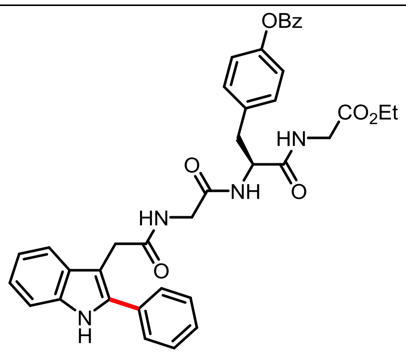
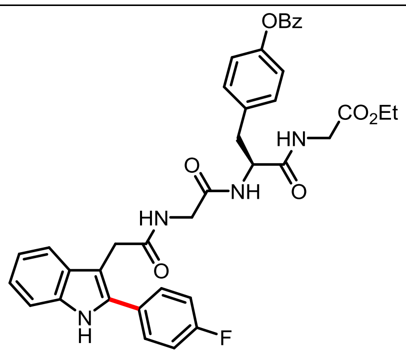
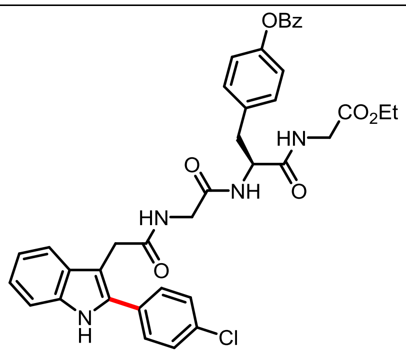
[a] General reaction conditions: **120** (0.250 mmol), **18** (0.375 mmol), DMF (2.0 mL), 100 °C, 17 h, under N_2.

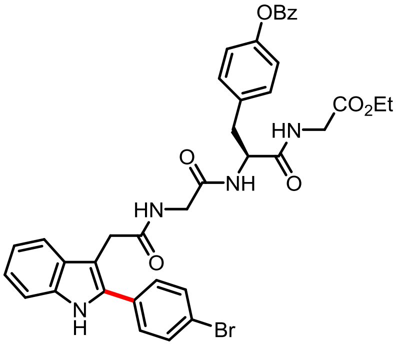
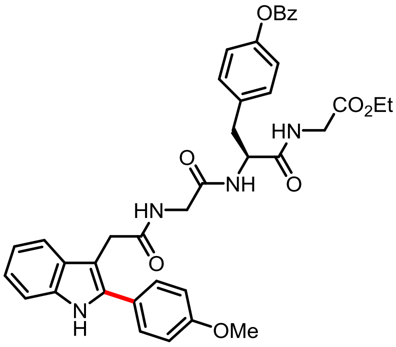
Further elongation of the peptide chain did not diminish the efficancy, as shown in Table 2, when tripeptide **120b** was directly functionalized. The isolated yields were comparable to the ones with dipeptide **120a**. Again, the halogen substituents were well tolerated and the products **121bb-121bd** were isolated in moderate to excellent yields (Table 2, entries 2-4). Electron-rich aryliodonium tosylate **18e** afforded the arylated product **121be** also in excellent yield (entry 5).

Table 2: Metal-free C–H arylations of tripeptide **120b** with diaryliodonium tosylates **18**.[a]



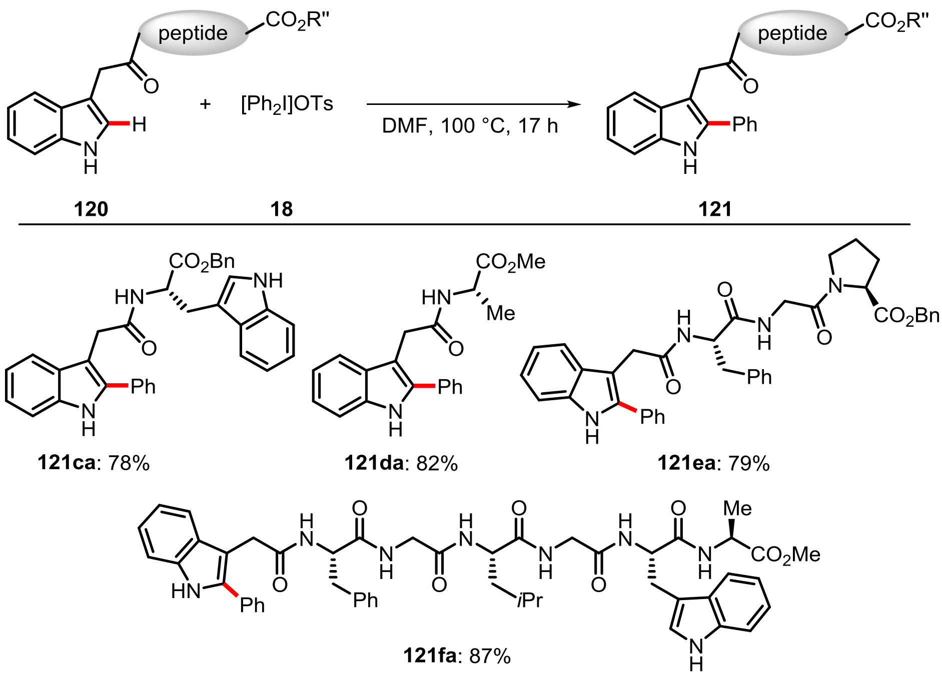
120b **18** **121**

Entry	Ar	Product	Isolated yield (%)
1	Ph **18a**	 **121ba**	62
2	4-FC$_6$H$_4$ **18b**	 **121bb**	82
3	4-ClC$_6$H$_4$ **18c**	 **121bc**	56

Entry	Ar	Product	Isolated yield (%)
4	4-BrC_6H_4 **18d**	 **121bd**	69
5	4-$MeOC_6H_4$ **18e**	 **121be**	81

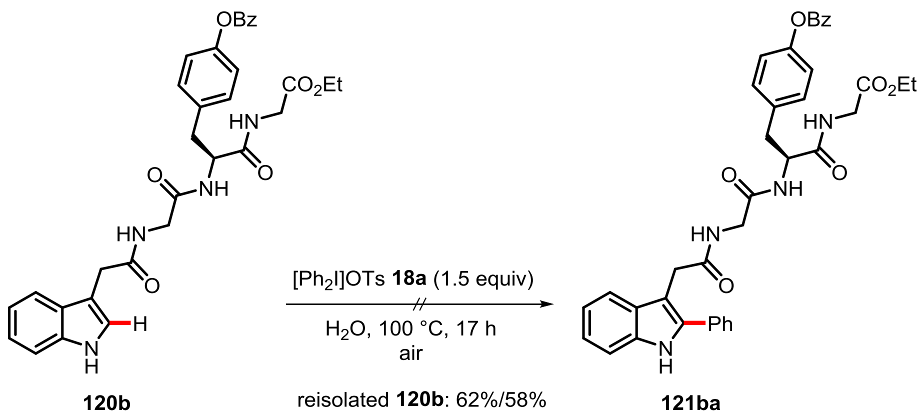
[a] General reaction conditions: **120b** (0.250 mmol), **18** (0.375 mmol), DMF (2.0 mL), 100 °C, 17 h, under N_2.

Moreover, several peptides were arylated at the *N*-terminal indole-3-acetamide moiety in moderate to good yields by *Dr. Yingjun Zhu* (Scheme 52) and *Jasper Ploog*.[223] Most notably, various functionalized amino acids were well tolerated. Tryptophan-containing peptides were exclusively functionalized at the artificial indole-3-acetamide moiety, while the tryptophan indole moiety was retained, displaying the excellent selectivity of the transition metal-free arylation for the indole-3-acetamide. Even a hexapeptide was arylated without any decrease in reactivity. Importantly, a racemization was not observed in the arylation of the peptides.



Scheme 52: Metal-free arylation of peptides **120** performed by *Dr. Yingjun Zhu*.

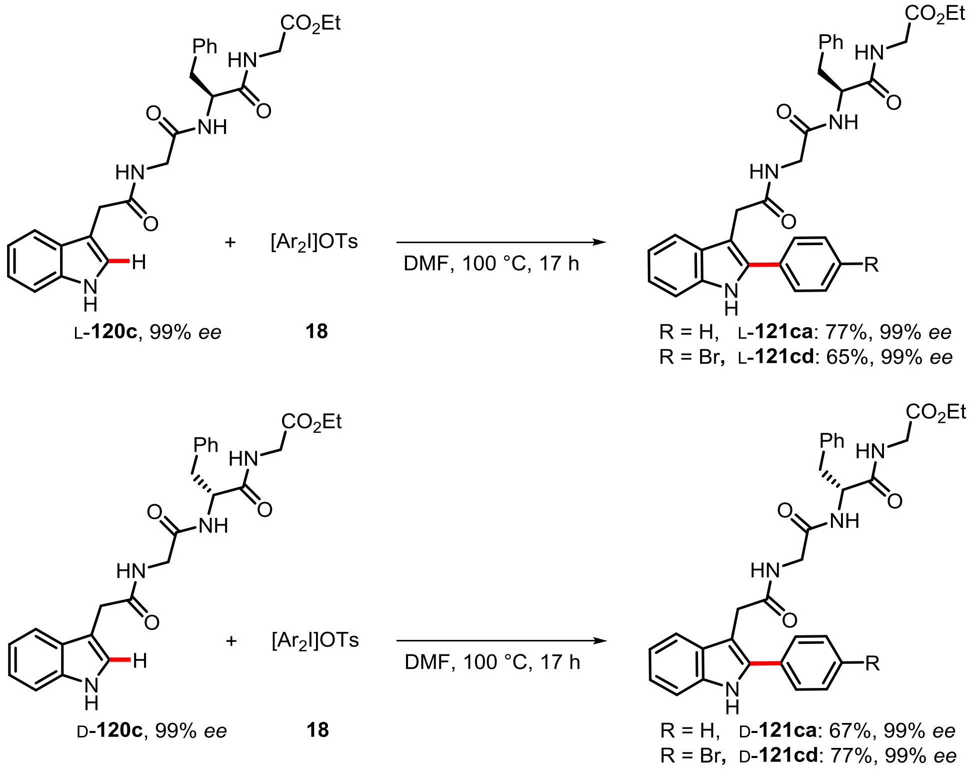
Next, the arylation of peptide **120b** was tested in water (Scheme 53), since methods for late-stage *in vitro* or *in vivo* diversifications of peptides and other biopolymers would arguably ideally proceed in an aqueous environment and under air. Unfortunately, no product was obtained in water under air. This test reaction was repeated twice and both of the times around 60% of substrate **120b** were reisolated.



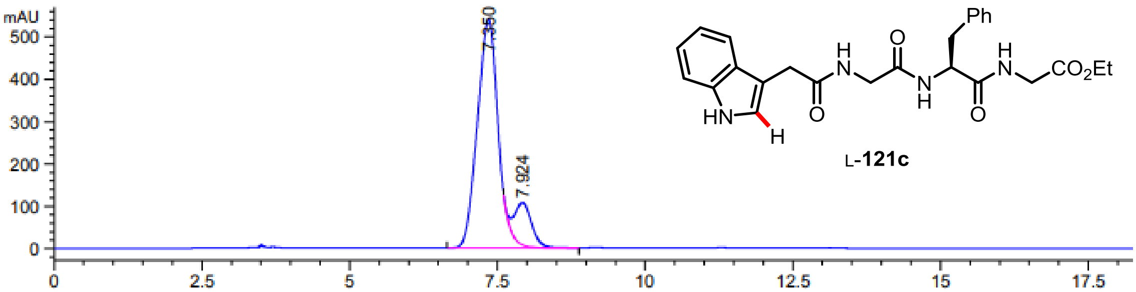
Scheme 53: Attempted metal-free direct arylation in water.

3.1.2 Studies on the potential racemization of enantiomerically pure substrates

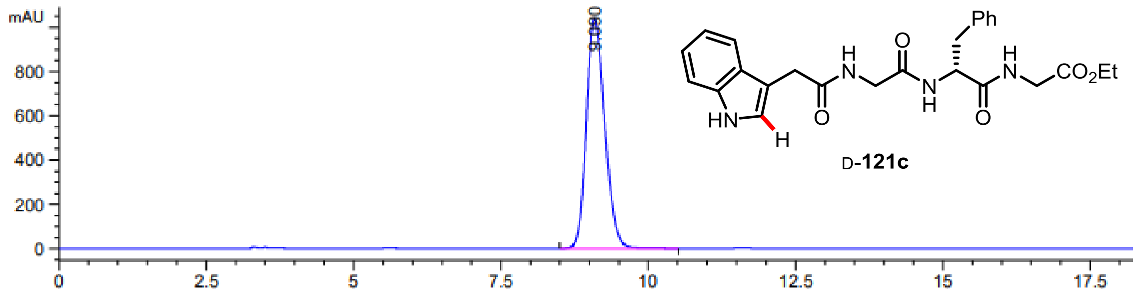
The stereochemical integrity of peptides is of crucial importance in efficient functionalizations, thus, a selective modification should proceed with high stereo-, site- and chemo-selectivity without racemization of the stereogenic centers in the peptide. In addition to the racemization-free formation of the desired products observed by *Jasper Ploog* and *Dr. Yingjun Zhu*, the enantiomerically pure tripeptides L-**120c** and D-**120c** were prepared from the commercially available L- and D-phenylalanine and reacted under the optimized reaction conditions. The products **121c** were obtained in good yields. The enantiomeric excess of all compounds was determined by HPLC analysis on chiral stationary phase showing no decrease of the enantiomeric excess (Scheme 54).



Scheme 54: Probing racemization for transition metal-free arylation of enantiopure indole-3-acetamides **120c**.

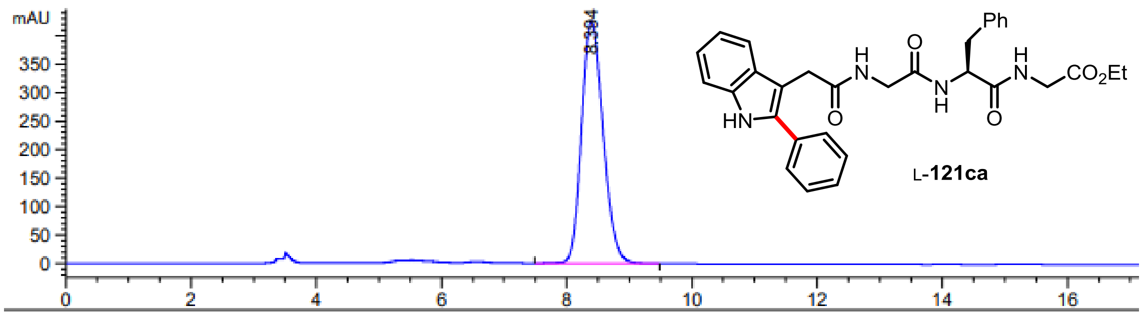


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.350	BV R	0.3724	1.32228e4	542.43018	86.7647
2	7.924	VB E	0.3038	2017.03430	99.81395	13.2353

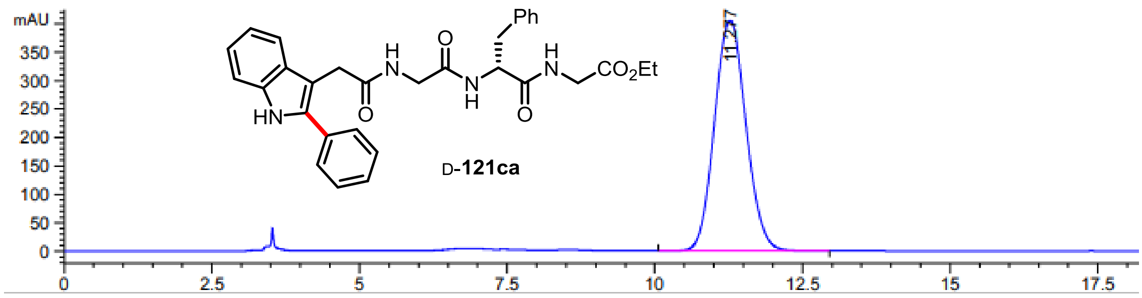


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.090	BB	0.3360	2.25517e4	1040.04321	100.0000

Figure 19: HPLC-Chromatograms of the enantiopure substrates L-**121c** [t_R = 7.350 min] (t_R = 7.924 min impurity), and D-**121c** [t_R = 9.090 min]. IC-3 *n*-hexane/ethyl acetate 20/80, flow rate: 1.0 mL/mn, detection at 274 nm.

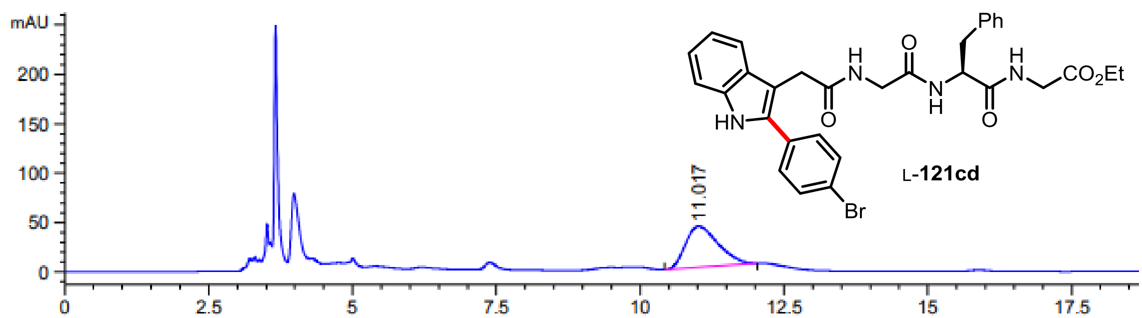


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.394	BB	0.3738	1.01740e4	425.80359	100.0000

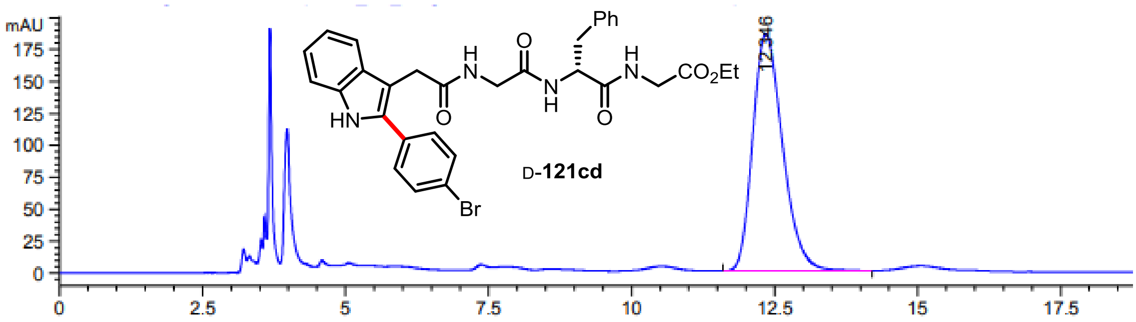


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.277	BB	0.5756	1.50304e4	404.37469	100.0000

Figure 20: HPLC-Chromatograms of the enantiopure compounds L-**121ca** [t_R = 8.394 min] and D-**121ca** [t_R = 11.277 min]. IC-3 *n*-hexane/ethyl acetate 30/70, flow rate: 1.0 mL/mn, detection at 274 nm.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.017	BB	0.5618	1626.77100	41.36956	100.0000

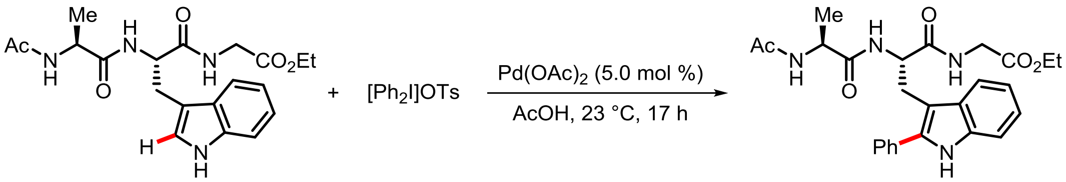


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.346	BB	0.5604	6728.41943	185.41110	100.0000

Figure 21: HPLC-Chromatograms of the enantiopure compounds L-**121cd** [t_R = 11.017 min] and D-**121cd** [t_R = 12.346 min]. IC-3 *n*-hexane/ethyl acetate 40/60, flow rate: 1.0 mL/mn, detection at 274 nm.

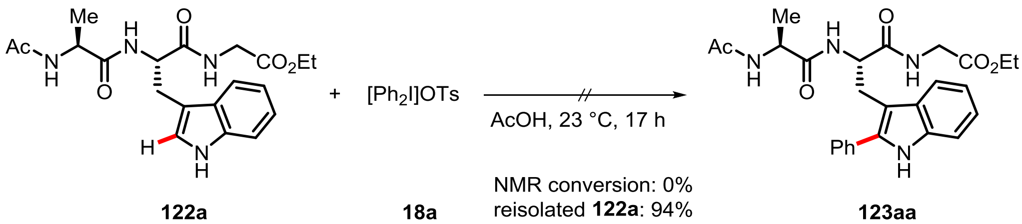
3.2 Palladium-catalyzed C–H arylation of tryptophan

With the transition metal-free peptide arylation in hand, the idea for a tryptophan-selective arylation arose, thereby avoiding the prefunctionalization with an indolylacetyl group as an unnatural tag at the *N*-terminal end of the peptide. *Lavilla*[115-116] and *Fairlamb*[124b, 124c] had previously reported on palladium-catalyzed methods accomplishing the arylation of tryptophan in moderate to good yields. However, these reactions suffered from a relatively high catalyst loading, high amounts of arylating reagent, and/or oxidants as well as elevated reaction temperatures. The optimization of the reaction conditions by *Dr. Yingjun Zhu* revealed a combination of $Pd(OAc)_2$ as catalyst and diaryliodonium tosylates **18** as arylating reagent at 23 °C in acetic acid to be most efficient (Scheme 55). Furthermore, it turned out that water could be employed as reaction medium, albeit with a slight decrease in the obtained yield.



Scheme 55: Optimized reaction conditions for the palladium-catalyzed C–H arylation of tryptophan **122a**.

Furthermore, a palladium-free control experiment was performed in order to confirm that palladium is required for the arylation of tryptophan (Scheme 56). As expected, the attempted palladium-free transformation furnished no product. The hypervalent iodine(III) compound **18** is not reactive enough to arylate tryptophan even at elevated temperatures (see section 3.1.1 or *Zhu*[224]).

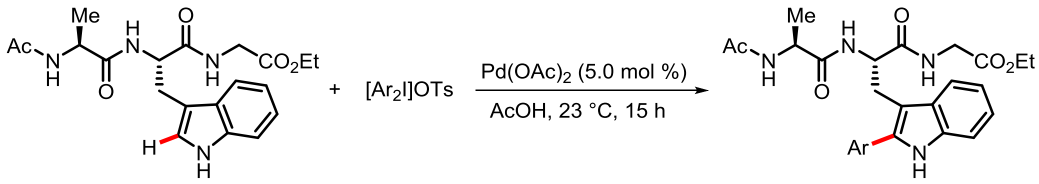


Scheme 56: Attempted transition metal-free C–H arylation of tripeptide **122a**.

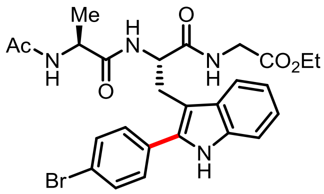
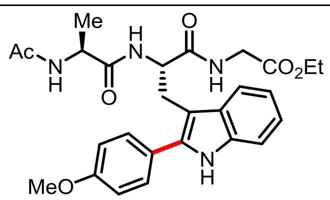
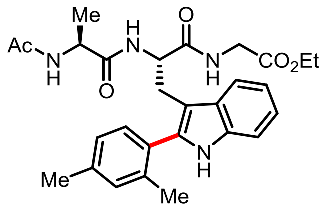
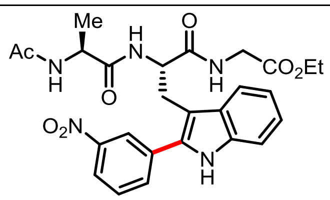
3.2.1 Scope of diaryliodonium tosylates and peptides

With the optimized reaction conditions in hand, the versatility of the palladium-catalyzed arylation was next tested. Initially, the scope of the direct arylation was explored starting with differently substituted diaryliodonium tosylates **18**. The results for the tryptophan-containing tripeptide **122a** are summarized in Table 3. The reaction proceeded smoothly with the substrates **18d** and **18e** bearing bromo- and methoxy-substituents in the *para*-position (entries 1-2) and delivered the desired products **123ad** and **123ae** in high yields. However the reaction with **18g**, bearing a methyl group in the sterically demanding *ortho*-position of the arene, demonstrated reduced efficiency (entry 3). In the case of substrate **18h** bearing a nitro group, ^1H NMR analysis of the reaction mixture indicated the formation of product **123ah**, but the reaction proceeded only with low conversion and isolation of a pure sample of **123ah** was not accomplished (entry 4).

Table 3: Palladium-catalyzed arylations of tripeptide **122a** with diaryliodonium tosylates **18**.[a]



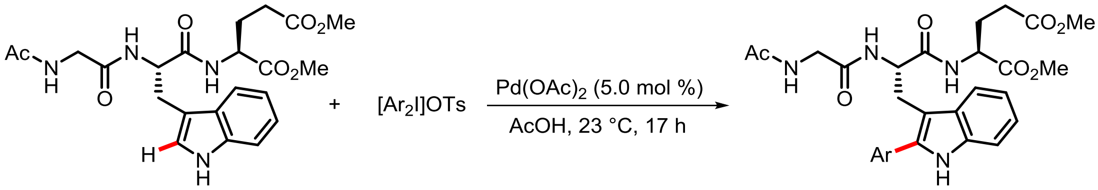
122a **18** **123**

Entry	Ar	Product	Isolated yield (%)
1	4-BrC_6H_4 **18d**	 **123ad**	81
2	4-MeOC_6H_4 **18e**	 **123ae**	85
3	2,4-$Me_2C_6H_3$ **18g**	 **123ag**	51
4	3-$NO_2C_6H_4$ **18h**	 **123ah**	-

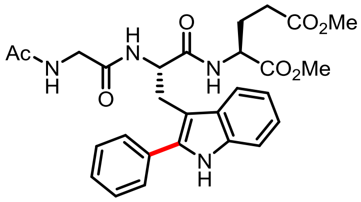
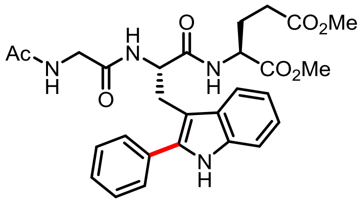
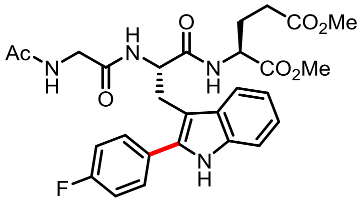
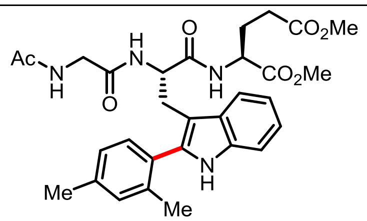
[a] General reaction conditions: **123a** (0.20 mmol), **18** (0.30 mmol), $Pd(OAc)_2$ (5.0 mol %), AcOH (2.0 mL), 23 °C, 15 h, under N_2.

The results of the palladium-catalyzed direct arylations of tripeptide **122b** with a small set of diaryliodonium tosylates **18** are shown in Table 4. The unsubstituted diphenyliodonium tosylate **18a** and the 4-fluorophenyliodonium tosylate **18b** furnished high yields of the desired arylated tryptophans **123ba** and **123bb** (Table 4, entries 1 and 3). The catalytic efficiency was still good, when the loading of the catalyst was reduced to 1.0 mol % $Pd(OAc)_2$ and the product **123ba** was obtained in 56% isolated yield (entry 2). The catalytic system proved again rather ineffective for sterically more demanding substituents in the *ortho*-position of the arene (entry 4).

Table 4: Palladium-catalyzed arylations of tripeptide **122b** with diaryliodonium tosylates **18**.[a]



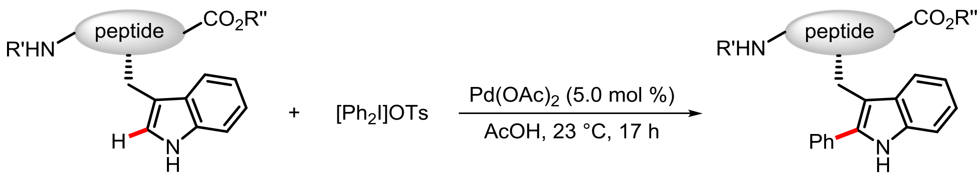
122b **18** **123**

Entry	Ar	Product	Isolated yield (%)
1	Ph **18a**	 **123ba**	78
2	Ph **18a**	 **123ba**	56[b]
3	$4\text{-}FC_6H_4$ **18b**	 **123bb**	81
4	$2,4\text{-}Me_2C_6H_3$ **18g**	 **123bg**	33

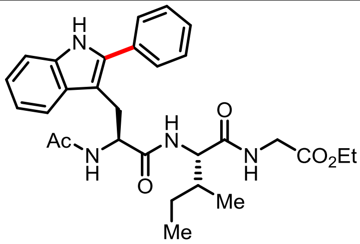
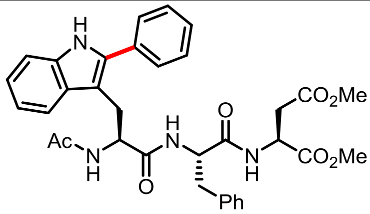
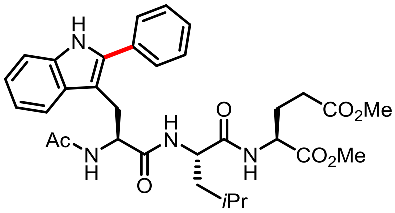
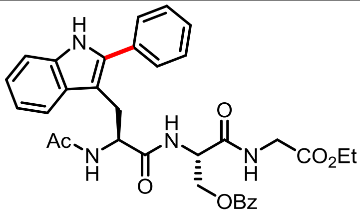
[a] General reaction conditions: **122b** (0.20 mmol), **18** (0.30 mmol), $Pd(OAc)_2$ (5.0 mol %), AcOH (3.0 mL), 23 °C, 17 h, under N_2. [b] $Pd(OAc)_2$ (1.0 mol %).

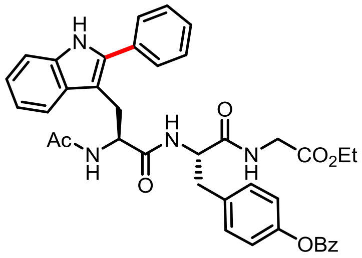
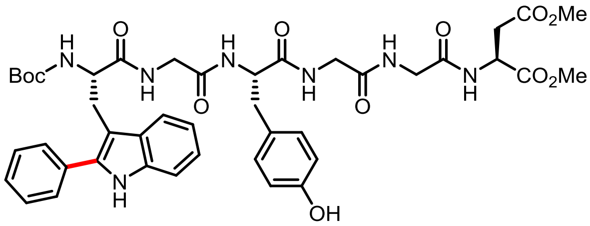
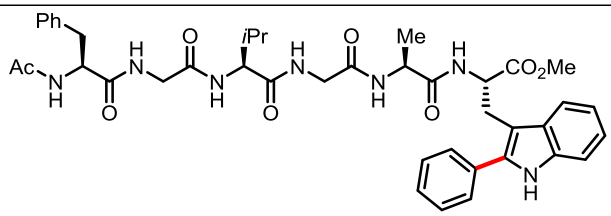
Thereafter, the scope of the direct arylation was explored by testing several peptides **122** (Table 5). Generally, the palladium-catalyzed $C(sp^2)$–H functionalization proceeded with excellent chemo- and site-selectivity delivering the arylated peptides in yields up to 93%. The position of the tryptophan residue within the peptide sequence had no significant influence on the efficacy of the catalysis. In the tested peptides the yields for a tryptophan in the *N*-terminal position (Table 5, entries 1-5) were as good as when it was at an internal position (Table 4, entry 1) or at the *C*-terminal position (Table 5, entry 6). It turned out that in the adjacent amino acid side chains bulkier groups such as the protected tyrosine **122g** (entry 5) were well tolerated, but for leucin-containing peptide **122e** the yield decreased significantly (entry 3). Importantly, hexapeptide **122h** with alkyl and aromatic groups in the side chain proved to be a suitable substrate (entry 7), while boc-protected hexapeptide **122i** with a free phenolic OH group delivered 20% isolated yield of the desired product **123ia** (entry 6).

Table 5: Palladium-catalyzed arylations of peptides **122** with diphenyliodonium tosylate **18a**.[a]



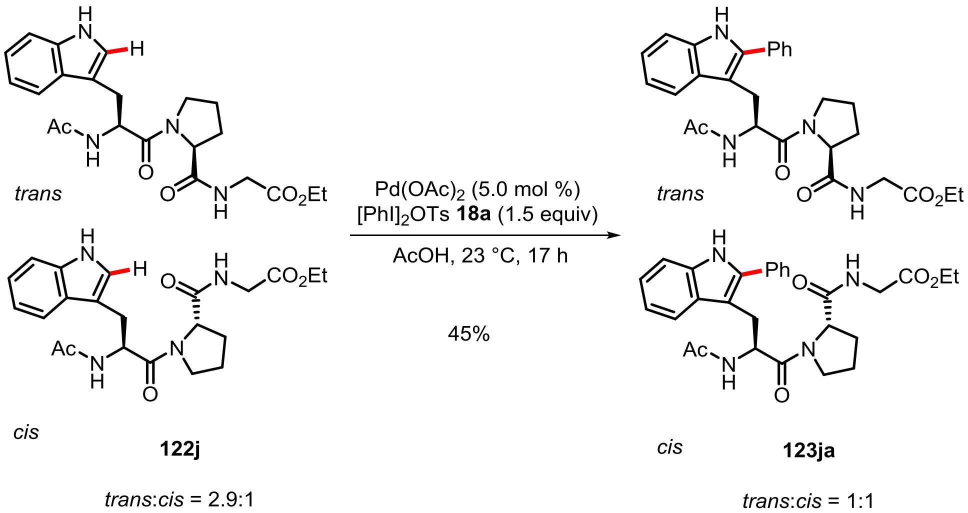
122 **18a** **123**

Entry	Substrate	Product	Isolated yield (%)
1	Ac-Trp-Ile-Gly-OEt **122c**	 **123ca**	93
2	Ac-Trp-Phe-Asp-(OMe)2 **122d**	 **123da**	84
3	Ac-Trp-Leu-Glu-(OMe)2 **122e**	 **123ea**	59
4	Ac-Trp-Ser(OBz)-Gly-OEt		73

Entry	Substrate	Product	Isolated yield (%)
	122f	**123fa**	
5	Ac-Trp-Tyr(OBz)-Gly-OEt		82
	122g	**123ga**	
6	Boc-Trp-Gly-Tyr-Gly-Gly-Asp-(OMe)2		20
	122i	**123ia**	
7[b]	Ac-Phe-Gly-Val-Gly-Ala-Trp-OMe		83[c]
	122h	**123ha**	

[a] General reaction conditions: **122** (0.20 mmol), **18a** (0.30 mmol), $Pd(OAc)_2$ (5.0 mol %), AcOH (3.0 mL), 23 °C, 17 h, under N_2. [b] $Pd(OAc)_2$ (7.5 mol %), under air. [c] Conversion determined by HPLC analysis.

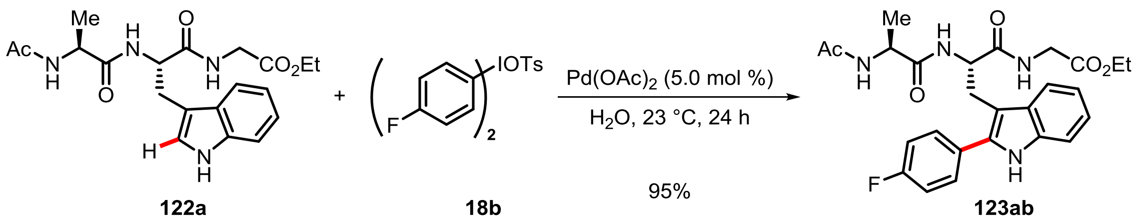
Furthermore, the proline-containing dipeptide **122j** was tested (Scheme 57). Proline holds a special place among the canonical amino acids as it is the only secondary amine with a cyclic structure and constituent of many proteins.[91a] Proline affects the secondary structure of proteins and is often found at the end of *α* helix or in turns or loops.[225] In studies on model peptides it was found that in peptide bonds to proline (AA-pro) both *trans* and *cis* isomers are populated with different *cis* isomer content depending on the exact amino acid sequence and the ionization state of terminal groups.[226] In the vast majority of to date studied peptide bonds the *trans* form is found.[227] *Cis*/*trans* isomerization is considered as a slow process and of key importance for folding/unfolding of proteins.[228] The *cis*:*trans* ratio of the Trp-Pro peptide bond of the substrate was estimated to be 1:2.9 by ^{1}H-NMR analysis in DMSO-d_6. The desired product **123ja** was isolated in 45% yield with a *cis*:*trans* ratio of 1:1 in DMSO-d_6 indicating that the procedure was in principle applicable to proline-containing peptides, albeit with *cis*/*trans* isomerization of the Trp-Pro peptide bond.



Scheme 57: Direct C–H arylation of proline-containing peptide **122j**.

3.2.2 Water as reaction medium

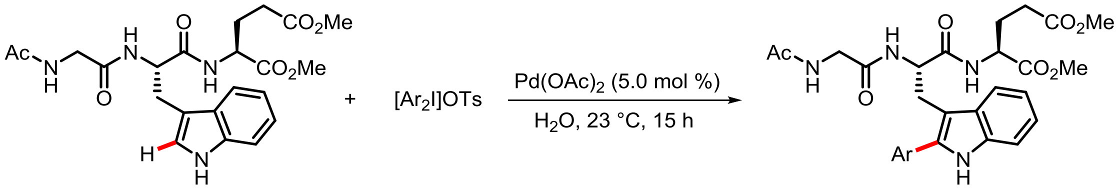
As discussed previously, methods for the site-selective chemical modification of peptides and proteins or other biological macromolecules should ideally be operative with water as the reaction medium at a neutral pH and ambient temperature. Thus, *Dr. Yingjun Zhu* found that water was well tolerated and the arylation of the tripeptide Ac-Ala-Trp-Gly-OEt (**122a**) with differently substituted symmetrical diaryliodonium tosylates **18** furnished the desired products in good to excellent yields (Scheme 58).



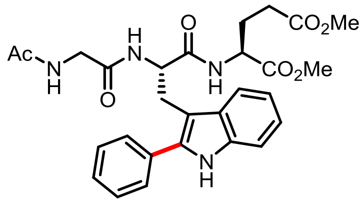
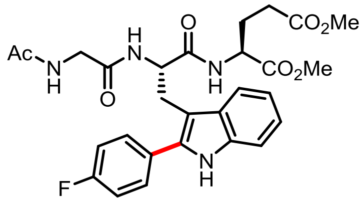
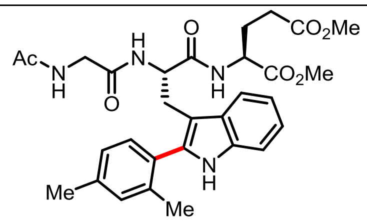
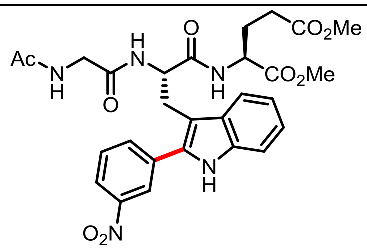
Scheme 58: Palladium-catalyzed direct C–H arylations of tripeptide **122a** in water.

Subsequently, the transformation in water was examined with other substrates. *Dr. Yingjun Zhu* showed that the conversion was strongly substrate-dependant. Ac-Ala-Trp-Ala-OMe and Ac-Gly-Trp-Glu-(OMe)$_2$ provided significantly lower yields compared to Ac-Ala-Trp-Gly-OEt. First, Ac-Gly-Trp-Glu-(OMe)$_2$ (**122b**) was reacted with a representative set of diaryliodonium tosylates **18**. Unfortunately, the conversion with this tripeptide was rather low. Thus the isolated yields were only moderate (Table 6). The C–H arylation with the sterically demanding bis(2,4-dimethylphenyl)-iodonium tosylate (**18g**) afforded the arylated product **123bg** in 44% yield (entry 3), which was only slightly higher than the yields for diphenyliodonium tosylate (**18a**) (entry 1) and bis(4-fluorophenyl)-iodonium tosylate (**18b**) (entry 2). In the case of the electron-deficient aryl group in bis(3-nitro-phenyl)iodonium tosylate (**18h**) the reactivity dropped significantly and only 12% yield of the product **123bh** were isolated (entry 4).

Table 6: Palladium-catalyzed arylations of Ac-Gly-Trp-Glu-(OMe)$_2$ (**122b**) in H_2O.[a]



122b **18** **123**

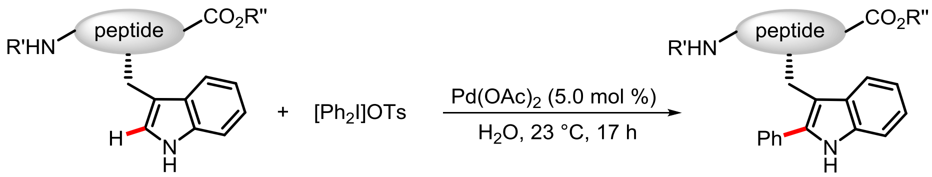
Entry	Ar	Prduct	Isolated yield (%)
1	Ph **18a**	 **123ba**	42
2[b]	4-FC$_6$H$_4$ **18b**	 **123bb**	34
3	2,4-Me$_2$C$_6$H$_3$ **18g**	 **123bg**	44
4	3-NO$_2$C$_6$H$_4$ **18h**	 **123bh**	12

[a] General reaction conditions: **122b** (0.25 mmol), **18** (0.375 mmol), Pd(OAc)$_2$ (5.0 mol %), H_2O (2.0 mL), 23 °C, 15 h, under N_2.[b] **122b** (0.20 mmol), **18** (0.30 mmol), Pd(OAc)$_2$ (5.0 mol %), H_2O (2.0 mL), 23 °C, 15 h, under N_2.

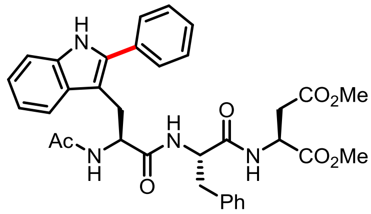
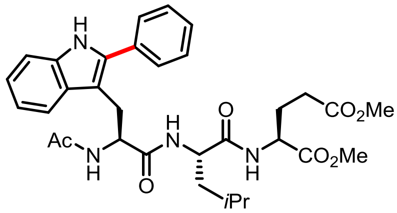
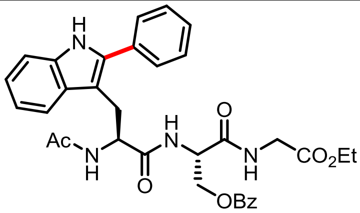
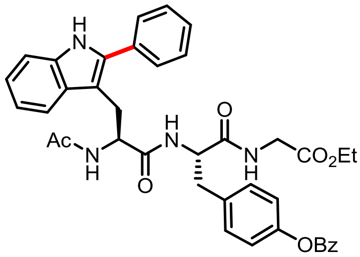
In addition to the scope in acetic acid as solvent, the tripeptides **122** were also tested in water as reaction medium (Table 7). Unfortunately, low conversion was observed and the isolated yields were unsatisfactory. Ac-Trp-Phe-Asp-(OMe)$_2$ (**122d**) gave the highest yield of 32% (entry 1), whereas Ac-Trp-Ser(OBz)-Gly-OEt (**122f**) afforded no desired product (entry 3). The arylation of Ac-Trp-Leu-Glu-(OMe)$_2$ (**122e**) and Ac-Trp-Tyr(OBz)-Gly-OEt (**122g**) afforded the arylated products **123ea** and **123ga** in 16%

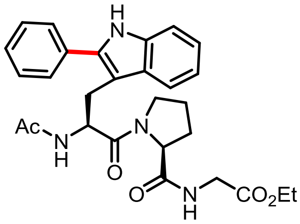
and 19% yield, respectively (entries 2, 4). The proline-containig peptide Ac-Trp-Pro-Gly-OEt (**122j**) furnished a high yield of 55% (entry 5), but *cis*/*trans* isomerization was again observed (compare the desired product **123ja** in Scheme 57). In general the efficacy of the arylation in water highly depended on the peptide **122** and the diaryliodonium tosylate **18**, which could be due to the observed low solubility of the compounds in water.

Table 7: Palladium-catalyzed arylations of peptides **122** with $[Ph_2I]OTs$ **18a** in H_2O.[a]



122 **18a** **123**

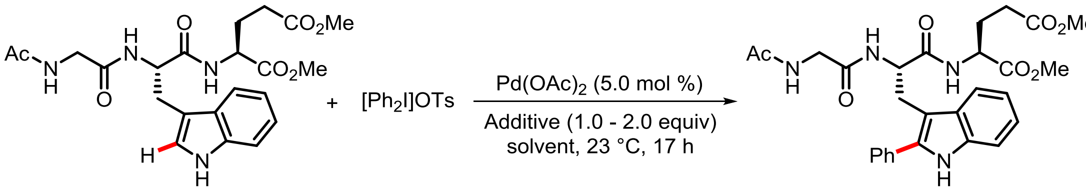
Entry	Substrate	Product	Isolated yield (%)
1	Ac-Trp-Phe-Asp-OMe₂ **122d**	 **123da**	32[b]
2	Ac-Trp-Leu-Glu-(OMe)₂ **122e**	 **123ea**	16
3	Ac-Trp-Ser(OBz)-Gly-OEt **122f**	 **122fa**	-
4	Ac-Trp-Tyr(OBz)-Gly-OEt **122g**	 **122ga**	19

Entry	Substrate	Product	Isolated yield (%)
5	Ac-Trp-Pro-Gly-OEt **122j**	 **123ja**	55[c][d]

[a] General reaction conditions: **122** (0.20 mmol), **18a** (0.30 mmol), $Pd(OAc)_2$ (5.0 mol %), H_2O (2.0 mL), 23 °C, 17 h, under N_2. [b] 57% of **122d** reisolated [c] 24 h. [d] *trans*-product **123ja** shown, *cis*:*trans* ratio = 1:1.

With the aim to accomplish high conversions, an optimization of additives and buffer solutions was performed with substrate Ac-Gly-Trp-Glu-$(OMe)_2$ (**122b**). Table 8 shows the attempted reaction conditions. Addition of bases, such as carbonate or acetate (entries 1-3) shut down the reaction completely, whereas an buffer solution with a *pH*-value of 5 afforded the arylated product in 11% yield (entry 4). The addition of acetic acid led to increased conversion and yields (entries 6 and 7). Water is in principle applicable, but the efficacy of the arylation highly depends on the peptide and its solubility.

Table 8: Optimization study for the arylation of Ac-Gly-Trp-Glu-$(OMe)_2$ (**122b**) in water.[a]



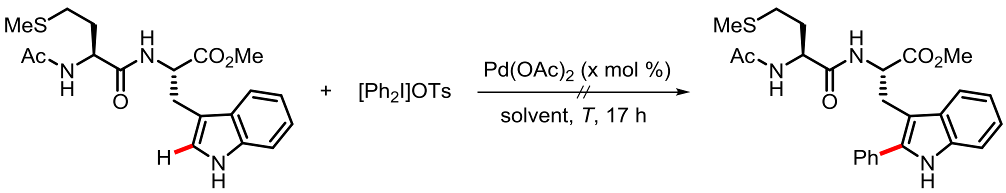
122b **18a** **123ba**

Entry	Additive	Solvent	Isolated yield (%)
1	K_2CO_3 (1.0 equiv)	H_2O	-
2	NaOAc (1.0 equiv)	H_2O	-
3	KOAc (1.0 equiv)	H_2O	-
4	-	Buffer solution *pH* = 5[b]	11
5	-	Buffer solution *pH* = 8[c]	traces
6	AcOH (1.0 equiv)	H_2O	27
7	AcOH (2.0 equiv)	H_2O	38

[a] General reaction conditions: **122b** (0.20 mmol), **18a** (0.30 mmol), $Pd(OAc)_2$ (5.0 mol %), solvent (3.0 mL), 23 °C, 17 h, under N_2. [b] APPLICHEM (Citric acid/NaOH). [c] APPLICHEM ($B(OH)_3$/HCl/NaOH).

So far, hydroxy groups in the side chain of the peptides were protected (benzoyl) as well as the *N*- and the *C*-termini (*N*-acetyl, ethyl or methylester). A robustness screen performed by *Dr. Yingjun Zhu* showed that *N*-Acetyl *α*-amino acids bearing free hydroxyl, carboxyamide or carboxylic acid groups were well tolerated under aqueous conditions, whereas peptides containing methionine or trityl-protected cysteine delivered no desired arylation product in acetic acid.[229] Studies regarding the metal binding affinity and selectivity of peptides have shown that the thioether moiety can be the main metal binding site in complexes of palladium(II), platinum(II) and silver(I).[147a] Moreover the formation of thioether palladium(II) complexes proceeds with faster reaction rates than the formation of complexes with *N*-donor ligands, although complexes with *N*-donor ligands are usually thermodynamically more stable.[230] In addition to *Dr. Yingjun Zhu's* findings, dipeptide Ac-Met-Trp-OMe (**122n**) was probed as sulfur-containing substrate. Table 9 shows the results of the attempted palladium-catalyzed arylations. Unfortunately, the desired product was not formed under the tested reaction conditions. First, the transformation was attempted in acetic acid and in water, but ^{1}H NMR and LC-MS analysis showed no arylated species and no conversion of substrate **122n** (entries 1-2). Increasing the reaction temperature to 80 °C and higher loading of the catalyst to 30 mol % did not deliver the product (entries 3-4). Next the addition of a second metal species with a high binding affinity towards sulfur was probed. This metal species should outcompete the binding of palladium to the thioether, thus keeping enough palladium free to accomplish the C–H arylation. According to studies regarding the affinity of metals to thioethers, zinc appears to have a strong affinity for sulfur.[231] Neither addition of zinc acetate in a water/acetic acid mixture at ambient temperature, nor addition of elemental zinc in acetic acid at 80 °C furnished the arylated product (entries 5-6). Reisolation of the dipeptide in almost quantitative yield showed that side reactions such as palladium-catalyzed hydrolysis[232] or sulfonium salt formation[233] were not occurring under the tested reaction conditions (entry 5).Hence, it was assumed that the coordination of palladium to the thioether generates an inactive palladium species and impedes the desired C–H arylation.

Table 9: Attempted arylations of Ac-Met-Trp-OMe (**122n**) with diphenyliodonium tosylate **18a**.[a]



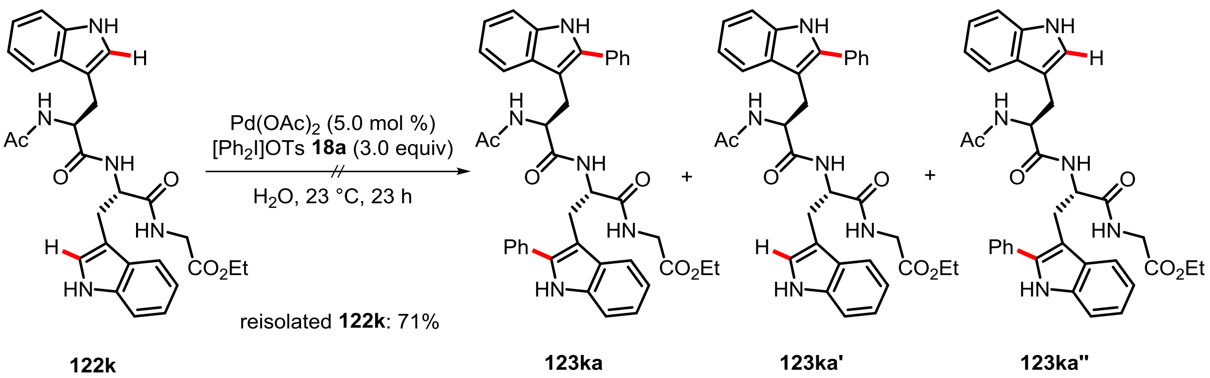
122n **18a** **122na**

Entry	$Pd(OAc)_2$ (mol %)	Additive	Solvent	*T* (°C)	Isolated yield (%)
1	5.0		AcOH	23	-[b]
2	5.0		H_2O	23	-[b]
3	5.0		AcOH	80	-[b]
4	30		AcOH	80	-[b]
5	5.0	$Zn(OAc)_2$	AcOH/H_2O	23	-[b] [c]
6	30	Zn	AcOH	80	-[b]

[a] General reaction conditions: **122n** (0.20 mmol), **18a** (0.30 mmol), $Pd(OAc)_2$, solvent (2.0 mL), *T*, 17 h, under N_2. [b] LC-MS analysis: unreacted **122n**. [c] 93% of **122n** reisolated.

3.2.3 Tripeptides containing two tryptophans

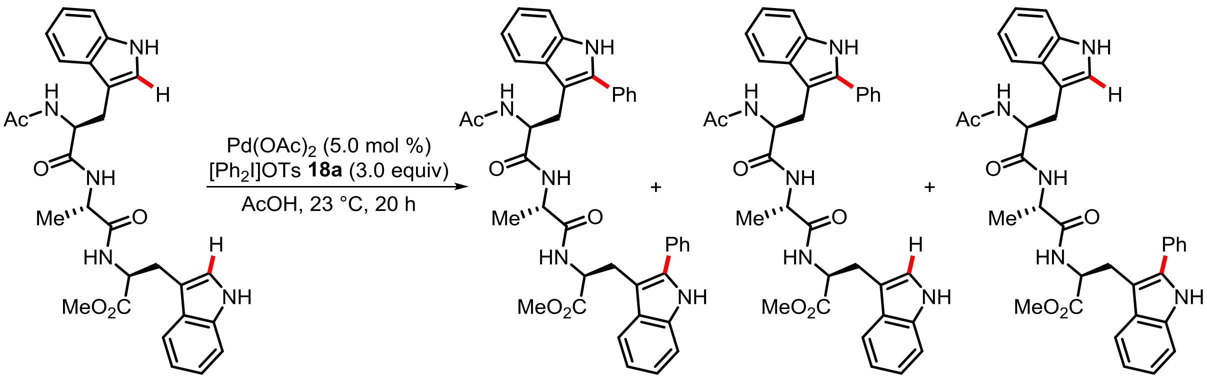
Since the position of the tryptophan residue in small peptides showed no negative effect on the outcome of the palladium-catalyzed direct arylation, the applicability of the palladium catalyst on substrates containing two tryptophans was tested. Hence Ac-Trp-Trp-Gly-OEt (**122k**) and Ac-Trp-Ala-Trp-OMe (**122l**) were synthezised and treated with diphenyliodonium tosylate **18a** under palladium catalysis. In the case of Ac-Trp-Trp-Gly-OEt (**122k**) water was chosen as solvent (Scheme 59). ^{1}H NMR analysis indicated the formation of arylated species by typical lowfield-shifted NH signals (>11 ppm), but the efficacy of the catalytic system was unsufficient and 71% of substrate **122k** were reisolated. Besides the poor conversion, the separation of the desired products was difficult and it was not possible to isolate even analytical amounts of pure compounds.



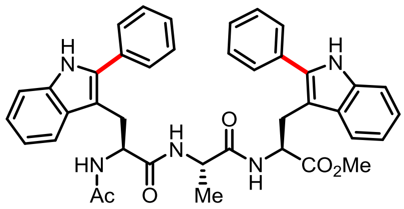
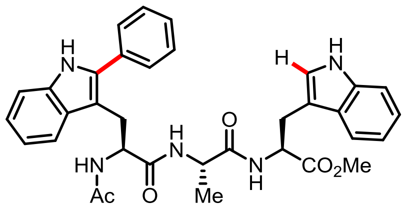
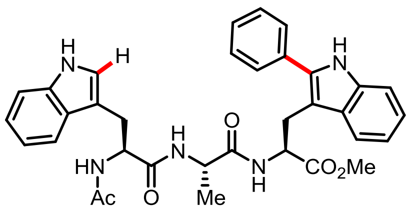
Scheme 59: Attempted palladium-catalyzed arylation of Ac-Trp-Trp-Gly-OEt (**122k**).

Incomplete conversion was also observed with substrate Ac-Trp-Ala-Trp-OMe (**122l**) in acetic acid and in water (Table 10). The choice of solvent was found to effect the reactivity and selectivity of the transformation. The bisarylated peptide **122la** was the main product in acetic acid and the isolated yield was 36%. The monoarylation product **123al'** at the *N*-terminal tryptophan was isolated in 27% yield and the arylation at the *C*-terminal tryptophan was only observed in traces. In the aqueous system almost a 1:1:1 mixture of the three products was obtained. Further screening of the reaction conditions, such as increasing the catalyst loading, increasing the reaction time or the amount of diphenyliodonium tosylate **18a**, did not improve the yields. It seemed that the steric bulk of the two indole moieties impedes the formation of the intermediate palladacycle and thus decreasing the reaction rate.

Table 10: Palladium-catalyzed arylations of tripeptide Ac-Trp-Ala-Trp-OMe (**122l**).[a]



122l **123la** **123la'** **123la"**

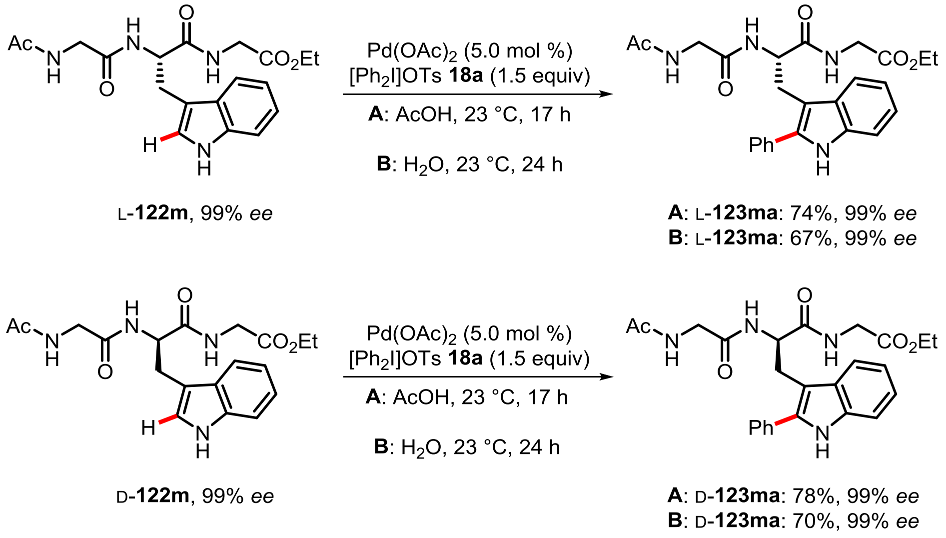
entry	product	Isolated yield (%)
1	 **123la**	36 15[b] 33[c] 30[d] -[e]
2	 **123la'**	27 14[b] 28[c] 10[d] -[e]
3	 **123la''**	5 13[b] 10[c] 12[d] -[e]

[a] General reaction conditions: **122l** (0.20 mmol), **18a** (0.60 mmol), $Pd(OAc)_2$ (5.0 mol %), AcOH (4.0 mL), 23 °C, 20 h, under N_2. [b] H_2O (6.0 mL), 24 h. [c] AcOH (3.0 mL), 17 h. [d] $Pd(OAc)_2$ (7.5 mol %), AcOH (3.0 mL), 49 h. [e] **18a** (1.2 mmol), AcOH (6.0 mL), 17 h, conversion <30% by HPLC-MS, not isolated.

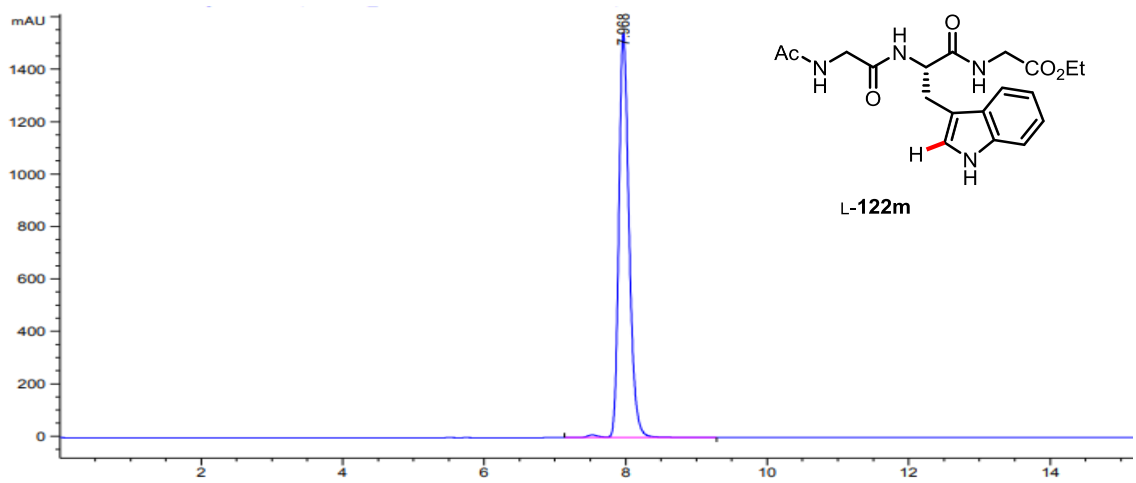
3.2.4 Studies on the potential racemization of enantiomerically pure substrates

The newly developed palladium-catalyzed direct C–H arylation proceeded at ambient temperature without addition of base and importantly, no racemization at the stereogenic centers was observed *via*

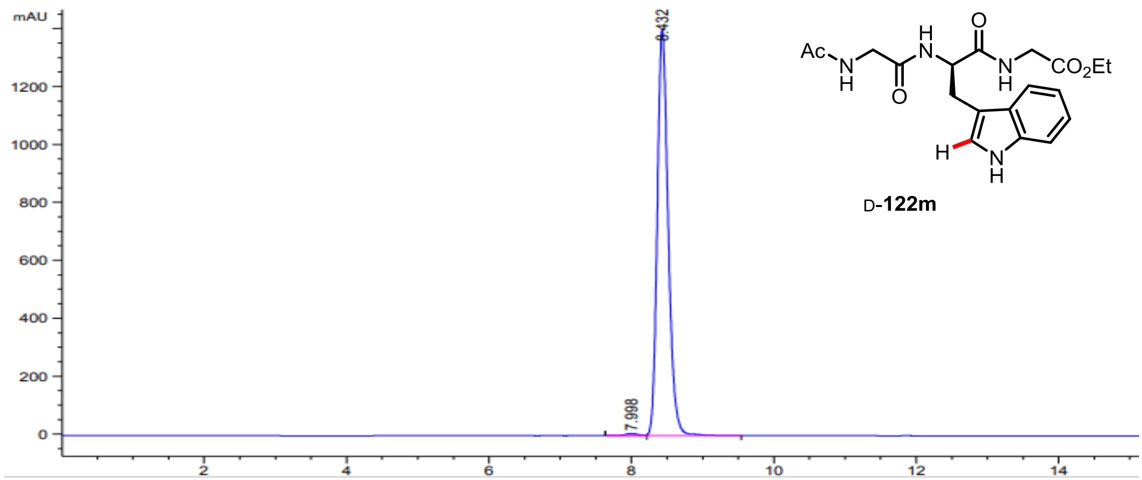
NMR analysis. Since transition-metal-catalysts, for example rhodium[234] and palladium[235], have been used for the racemization of *N*-Acyl α-amino acids, our method was carefully investigated for a potential racemization at the stereogenic center of the amino acid by HPLC analysis on chiral stationary phase. Thus, both enantiomers of tripeptide Ac-Gly-Trp-Gly-OEt (**122m**) were synthezised starting from the commercially available enantiomerically pure D- and L-tryptophan and treated with diphenyliodonium tosylate **18a** under the optimized reaction conditions. As shown in Scheme 60, the isolated yields of L- and D-**123ma** were good for both solvents. Pleasingly, the excellent *ee* of 99% of both enantiomers of the substrates and products verified that no loss of stereoinformation has happended during the C(sp^2)–H arylation.



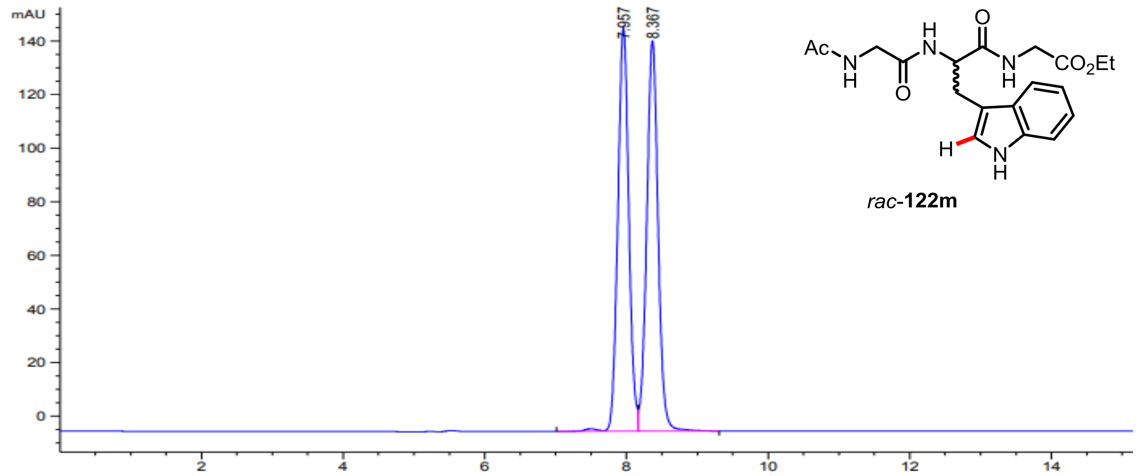
Scheme 60: Probing racemization for C–H arylation of enantiopure tripeptide **122m**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.968	VB R	0.1541	1.55734e4	1539.32532	100.0000

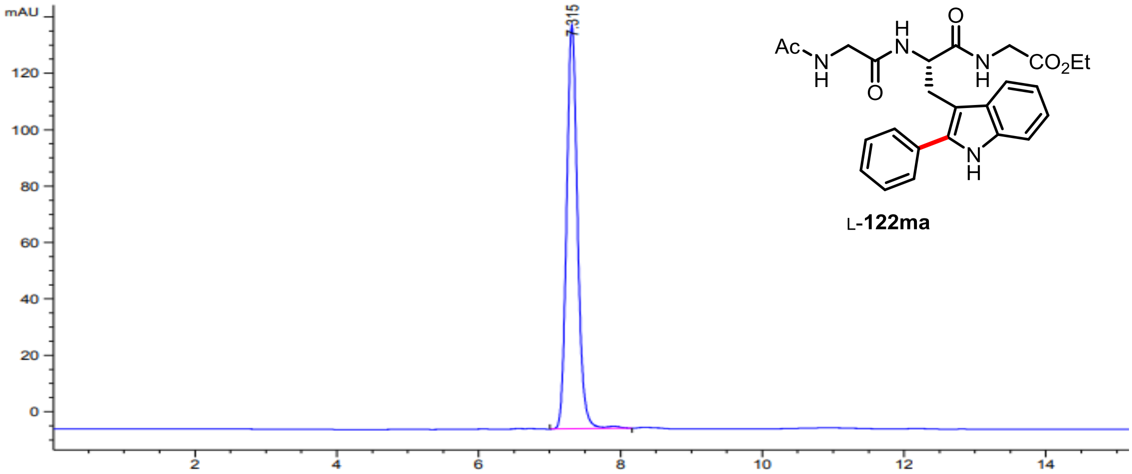


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.998	BV E	0.1869	93.12580	7.76437	0.6210
2	8.432	VB R	0.1631	1.49037e4	1401.44763	99.3790



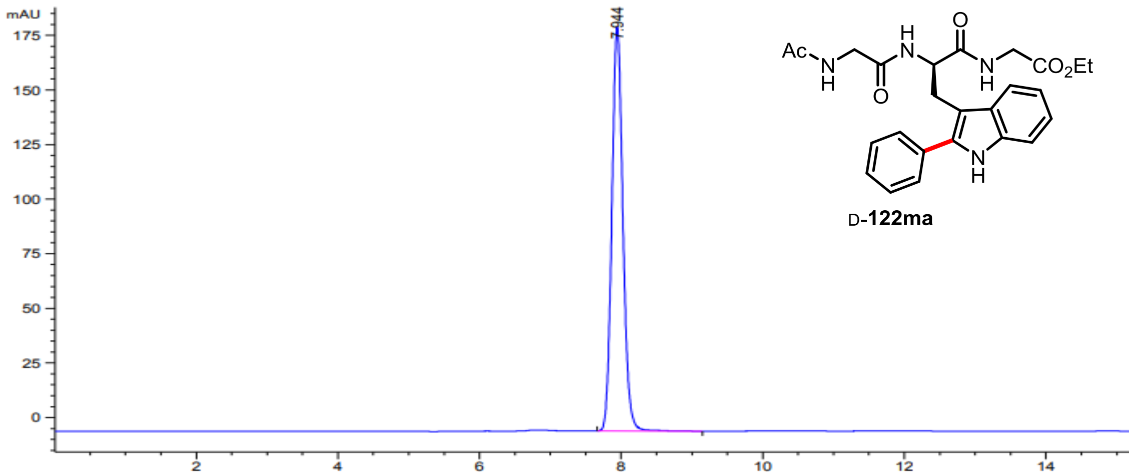
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.957	VV R	0.1657	1623.99866	150.68242	49.9797
2	8.367	VB	0.1723	1625.32019	145.51639	50.0203

Figure 22: HPLC-Chromatograms of the enantiopure compounds L-**122m** [t_R = 7.968 min], D-**122m** [t_R = 8.432 min] and the racemic mixture *rac*-**122m**. IC-3 acetonitril/methanol 96.5/3.5 gradient to 94.5/5.5, flow rate: 0.65 mL/min, detection at 273 nm.



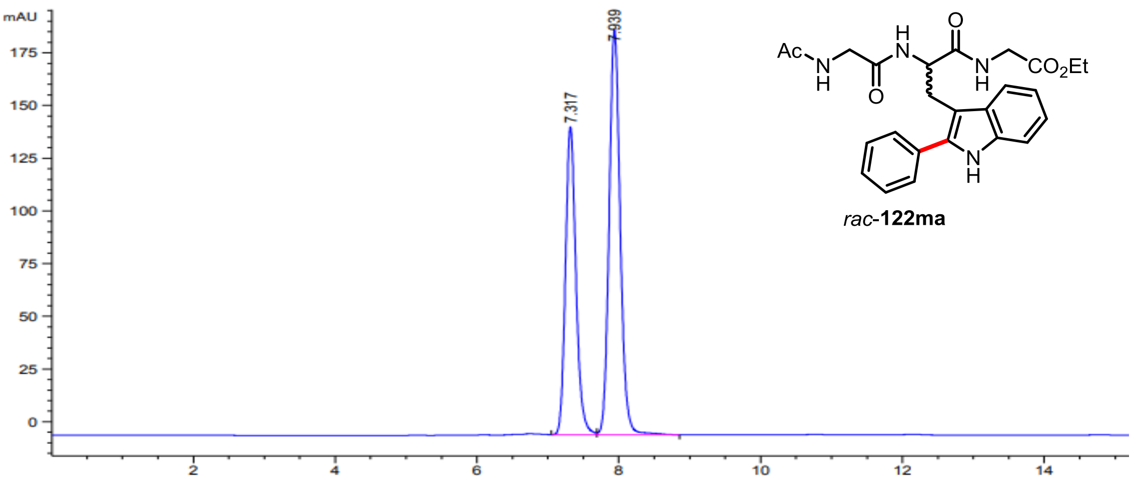
L-**122ma**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.315	BV R	0.1651	1534.83093	143.18916	100.0000



D-**122ma**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.944	BB	0.1678	2008.67114	184.79094	100.0000



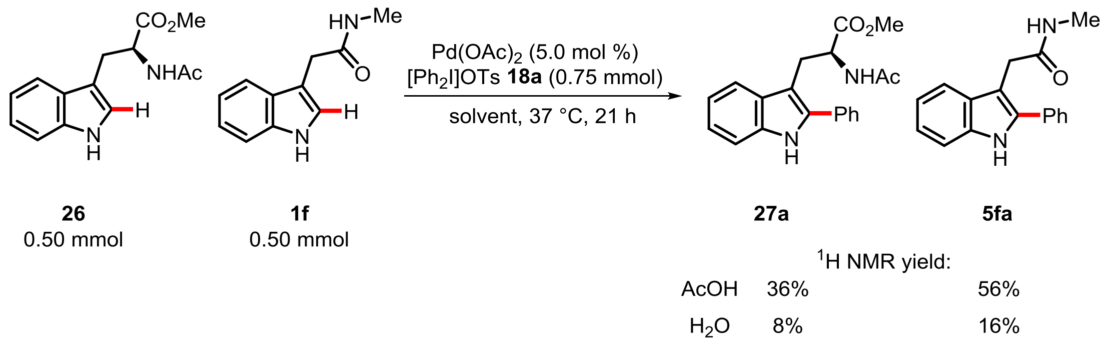
rac-**122ma**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.317	BV	0.1565	1497.21057	146.17003	41.8469
2	7.939	VB	0.1664	2080.62280	192.05064	58.1531

Figure 23: HPLC-Chromatograms of the enantiopure compounds L-**122ma** [t_R = 7.944 min] and D-**122ma** [t_R = 7.315 min] and the racemic mixture *rac*-**122ma**. IC-3 acetonitril/methanol 96.5/3.5 gradient to 94.5/5.5, flow rate: 0.65 mL/min, detection at 273 nm.

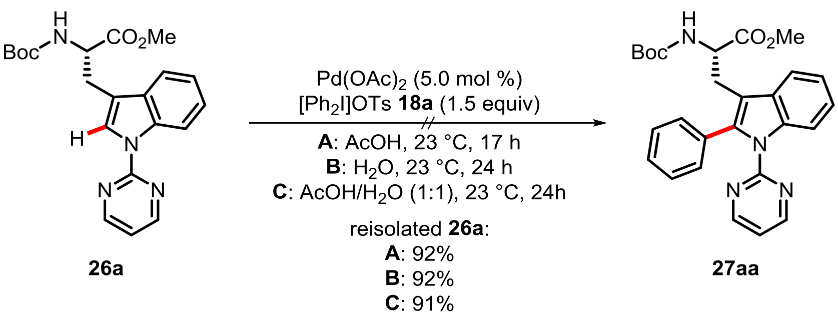
3.2.5 Chemoselectivity of the C–H arylation

Given the excellent chemo-selectivity and site-selectivity of the metal-free procedure for the indolyl-3-acetamide C2–H bond over the tryptophan-indol C2–H bond, a competition experiment between indolylacetamide **1f** and tryptophan **26** under palladium-catalysis was performed. Interestingly, the intermolecular competition experiment indicated the preferential conversion of indolylacetamide **1f** over tryptophan **26** (Scheme 61).



Scheme 61: Intermolecular competition experiment between indolylacetamide **1f** and tryptophan **26**.

Regarding transition metal-catalyzed C–H arylations of tryptophan, the group of *Ackermann* has reported the ruthenium-catalyzed arylation of a 2-pyrimidyl decorated tryptophan with aryl bromides in 2011.[236] Therefore, an additional arylation of pyrimidyl tryptophan **26a** under palladium catalysis was examined. As it turned out the pyrimidyl group was not tolerated, no product was obtained and compound **26a** could be reisolated in high yields (Scheme 62).

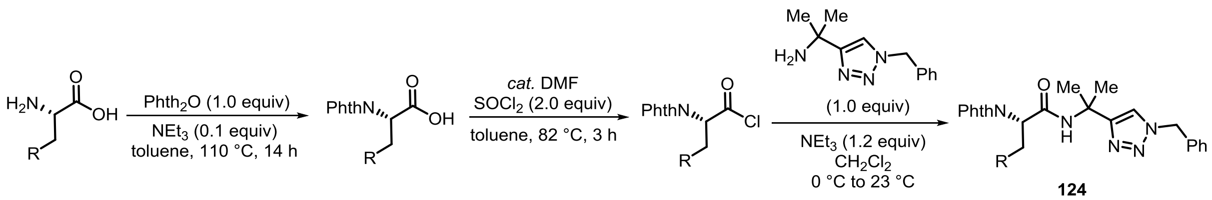


Scheme 62: Attempted palladium-catalyzed arylation of *N*-2-pyrimidyl tryptophan **26a**.

3.3 Palladium-catalyzed arylation of C(sp3)–H bonds in amino acids using triazole-assistance

During recent years, peptides have found major applications in pharmaceutical industry and asymmetric catalysis,[2] due to their various bioactivities and their structural diversity.[92a-d, 237] Unnatural or non-canonical amino acids have gained more and more attention, because they could expand the chemical complexity of peptides allowing to modify their structure, functions and stabilities.[96b, 103c, 238] Transition metal-catalyzed direct C–H functionalizations employing readily available natural chiral amino acids have been developed as alternative methods to elaborate asymmetric synthesis or enzymatic resolution of the corresponding racemate.[110a-c] Among others, *Daugulis*[133] and *Shi*[141, 239] developed palladium(II)-catalyzed C(sp3)–H bond functionalizations of amino acid derivatives using bidentate directing groups.

Since the *Ackermann* group has previously studied 1,2,3-triazoles as bidentate directing groups[6ac] for palladium-,[221a] ruthenium-[183] and iron-catalyzed[182, 186f, 221b] C–H functionalizations, the palladium(II)-catalyzed triazole-assisted direct arylation of amino acids seemed to be an attractive objective. Thus, the amino acids derivatives **124** were synthesized, starting with the protection of the amine and subsequent formation of the acide chloride by treatment with thionyl chloride. Reaction of the acid chloride with the triazole amine afforded the desired amino acid derivatives 124 (Scheme 63). The triazole amine was synthesized according to a previously reported procedure.[182]

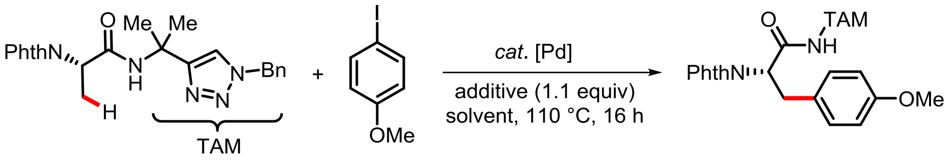


Scheme 63: Synthesis of the starting material **124**.

3.3.1 Optimization studies for the primary C–H arylation of alanine

The following optimization was performed in collaboration with *Ms*. *Chuan Dong* and reactions she performed are labelled accordingly. At the outset of the optimization studies, *N*-phthaloylalanine TAM amide **124a** and 4-iodoanisole (**4e**) were selected as substrates of choice with 5.0 mol % of $Pd(OAc)_2$ as palladium source and stoichiometric amounts of AgOAc as additive (Table 11). First, the excess of aryliodide **4e** was reduced to 1.5 equivalents without loss of catalytic efficacy (entries 1-4). Unfortunately, a 1:1 ratio of substrate **124a** to aryliodide **4e** led to incomplete conversion (entries 5-6). In the absence of a palladium(II) precatalyst even at 110 °C reaction temperature, product formation was not observed, and the *N*-phthaloylalanine TAM amide **124a** could be reisolated in almost quantitative yield (entry 7). Among a set of representative solvents, toluene was identified as optimal (entries 8-11). While $Pd(OAc)_2$, $PdCl_2$, and $Pd_2(dba)_3$ provided satisfactory results, $Pd(TFA)_2$ led to an almost quantitative formation of the desired product (entries 4, 11-13). Increasing the catalyst loading to 10 mol % did not provide a significant improvement (entries 14-15). Furthermore, the choice of silver salt turned out to be crucial. While AgF and Ag_2CO_3 gave good yields, when $AgNO_3$ was used the yield decreased as low as 23% and $AgSbF_6$ shut down the reaction completely (entries 16-19). Based on findings by *Larossa,*[240] a combination of Me_4NCl and KOAc as inexpensive substitute for AgOAc was also tested, which did not afford the desired product in competitive yield (entries 20-21). Gratifyingly, the best conditions consisting of substrate **124a**, 1.5 equivalents of aryliodide (**4e**) in the presence of 5.0 mol % $Pd(TFA)_2$ and 1.1 equivalents of AgOAc at 110 °C in toluene led to the desired product **125ae** in 73% yield (entry 12).

Table 11: Optimization of palladium(II)-catalyzed primary C(sp^3)–H arylation of alanine **124a**.[a]



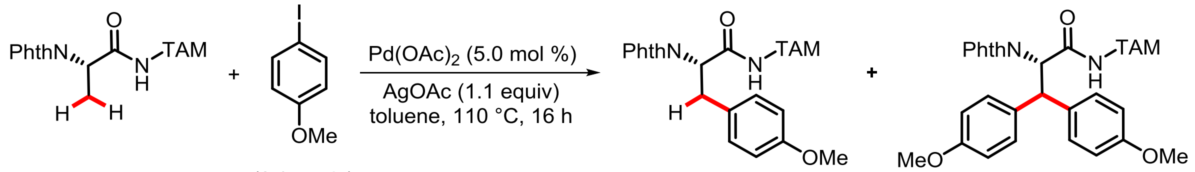
Entry	**4e** [equiv.]	[Pd]	Additive	Solvent	Isolated yield
1	4.0	$Pd(OAc)_2$	AgOAc	toluene	(71)
2	3.0	$Pd(OAc)_2$	AgOAc	toluene	53[b]
3	2.0	$Pd(OAc)_2$	AgOAc	toluene	77[d]
4	1.5	$Pd(OAc)_2$	AgOAc	toluene	(72) 53[b]
5	1.1	$Pd(OAc)_2$	AgOAc	toluene	33 (48)[b]
6	1.0	$Pd(OAc)_2$	AgOAc	toluene	(42)[b]
7	1.0	-	AgOAc	toluene	-
8	1.5	$Pd(OAc)_2$	AgOAc	*o*-xylene	(69)
9	1.5	$Pd(OAc)_2$	AgOAc	AcOH	(65)
10	1.5	$Pd(OAc)_2$	AgOAc	*t*AmOH	(61)[b]
11	1.5	$PdCl_2$	AgOAc	toluene	(75)[b]
12	**1.5**	**$Pd(TFA)_2$**	**AgOAc**	**toluene**	**73 (91)[b]**
13	1.5	$Pd_2(dba)_3$	AgOAc	toluene	(72)[b]
14	1.5	$Pd(OAc)_2$[c]	AgOAc	toluene	(49)[b]
15	1.5	$Pd(TFA)_2$[c]	AgOAc	toluene	(72)[b]
16	1.5	$Pd(TFA)_2$	AgF	toluene	(75)[b]
17	1.5	$Pd(TFA)_2$	Ag_2CO_3	toluene	(66)[b]
18	1.5	$Pd(TFA)_2$	$AgNO_3$	toluene	(23)[b]
19	1.5	$Pd(TFA)_2$	$AgSbF_6$	toluene	- [b]
20	1.5	$Pd(OAc)_2$	Me_4NCl (2.1 equiv.) KOAc (2.8 equiv.)	toluene	31
21	1.5	$Pd(TFA)_2$	Me_4NCl (2.1 equiv.) KOAc (2.8 equiv.)	toluene	(35)

[a] General reaction conditions: **124a** (0.20 mmol), **4e** (0.80 mmol), Additive (0.22 mmol), [Pd] (5.0 mol %), solvent (2.0 mL), 110 °C, 16 h, under N_2; yields in parenthesis refer to ^{1}H NMR yields

Entry	**4e** [equiv.]	[Pd]	Additive	Solvent	Isolated yield

using 1,3,5-trimethoxybenzene as internal standard. [b] Performed by *Ms Chuan Dong*. [c] [Pd] (10.0 mol %). [d] 10% of **125aee** isolated.

It should be noted that the diarylation of substrate **124a** was also observed (Scheme 64 and Table 11, entry 3) and the diarylated product **125aee** was isolated in 10% yield. The formation of this sideproduct illustrated the potential of the developed method to arylate secondary C(sp^3)–H bond of phenylalanine and other amino acids.



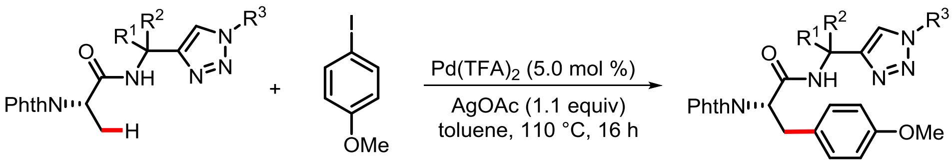
124a **4e** **125ae**: 77% **125aee**: 10%

Scheme 64: Direct C(sp^3)–H arylation and diarylation of alanine **124a**.

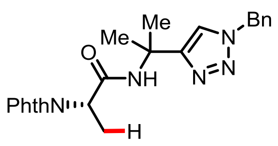
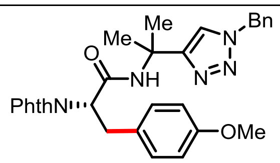
3.3.2 Influence of the triazole moiety

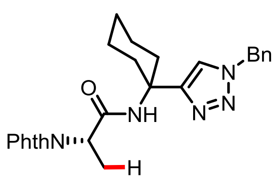
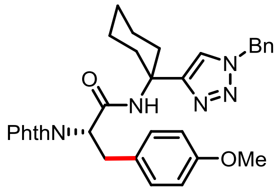
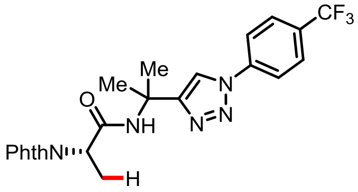
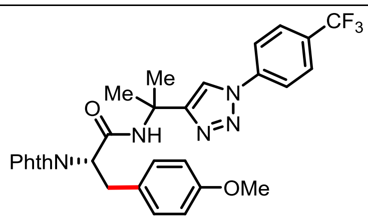
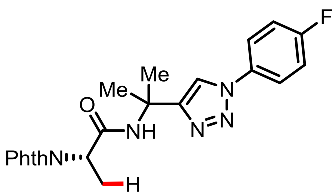
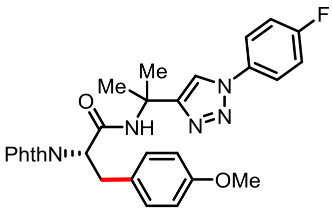
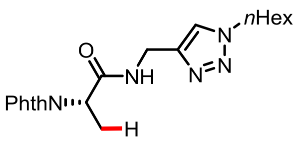
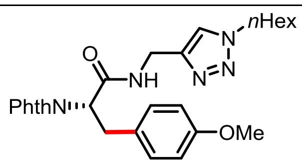
With the optimized reaction conditions in hand, the influence of different substitution patterns on the triazole moiety on the catalytic system was probed (Table 12). Electron-donating alkyl-substituents on the amide backbone were found to be beneficial (entries 1-4), which is in accordance with the proposed bidentate coordination to the transition metal-catalyst over the N3-nitrogen atom of the triazole and the nitrogen atom of the amide. Moreover, the electronic nature of *N*-substituents on the 1,2,3-triazole had almost no effect on the catalytic efficacy as the less electron-donating *N*-aryl-substituents (entries 3-4) were efficiently converted into the desired products. Moreover, the triazole directing group used by *Ding* delivered only moderate yields under the optimized reaction conditions (entry 5).

Table 12: Tested substitution pattern on the triazole amide.[a]



124 **4e** **125**

Entry	Substrate **124**	Product **125**	Isolated yield (%)
1	 **124a**	 **125ae**	73

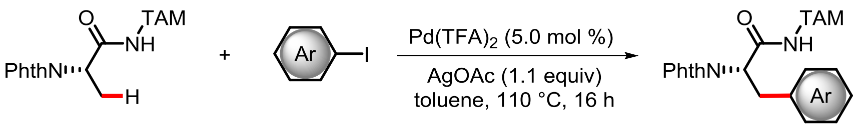
Entry	Substrate **124**	Product **125**	Isolated yield (%)
2	 **124b**	 **125be**	93
3	 **124c**	 **125ce**	68
4	 **124d**	 **125de**	78
5	 **124a'**	 **125a'e**	52[b]

[a] General reaction conditions: **124** (0.20 mmol), **4e** (0.30 mmol), AgOAc (0.22 mmol), $Pd(TFA)_2$ (5.0 mol %), toluene (2.0 mL), 110 °C, 16 h, under N_2. [b] Performed by *Ms Chuan Dong*.

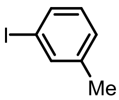
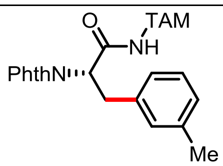
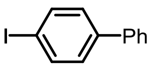
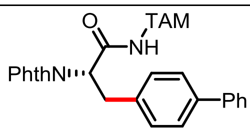
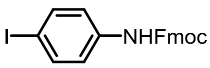
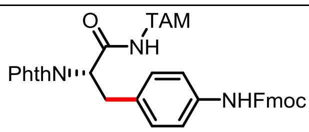
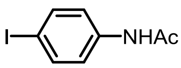
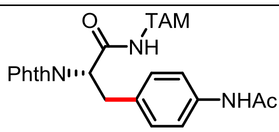
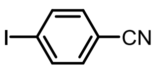
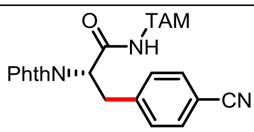
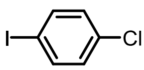
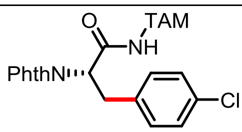
3.3.3 Scope and limitations

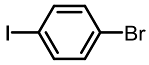
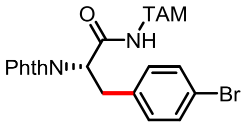
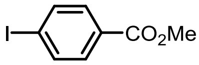
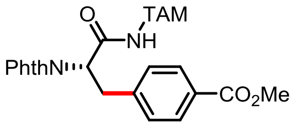
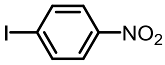
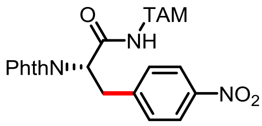
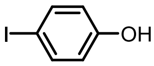
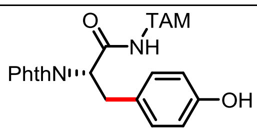
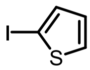
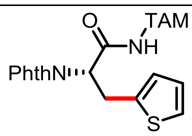
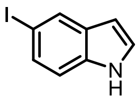
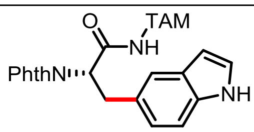
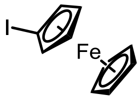
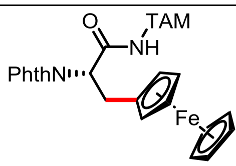
Subsequently, the scope of the C(sp^3)–H arylation was explored with a representative set of electron-rich and electron-deficient arenes. The results are summarized in Table 13. Generally, the desired amino acid derivatives were obtained in good to excellent yields, although sterically more demanding arenes furnished lower yields or even proved unreactive (**4s** and **4u** Figure 24). A methyl group in the 3-position did not reduce the catalytic efficacy (entry 1). It should be noted that arenes with various functional groups in the 4-position were found as suitable substrates. The arylation with aryl iodides featuring a phenyl **4i**, protected amines **4j**, **4k**, and the ester **4m** could be accomplished in good yields without the formation of any side product (entries 2-4 and 8). Chloro-, bromo- and hydroxyl-substituents on the arene moiety resulted in moderate yields, but remarkably displayed high chemoselectivity as no side reaction was observed (entries 6-7 and 10). Moreover, satisfactory results were obtained in the arylation of alanine derivative **124a** with electron-deficient arenes **4l** and **4n** bearing a nitrile and a nitro group (entries 5, 9). Importantly, the catalytic system proved effective for the arylation employing various heteroarenes. The arylation with indole **4q** and thiophene **4p** provided 64% of **125aq** and 81% of **125ap**, respectively (entries 11-12). However, in the case of iodoferrocene **4r** the arylation proceeded with low conversion, furnishing 34% of the desired product **125ar** (entry 13). Further examples were performed by *Ms Chuan Dong*, including valuable functional groups on the arene, such as ketones and halogenes in 3-position.[241]

Table 13: Scope of aryliodides **4** in the direct C(sp^3)–H arylations of alanine **124a**.[a]



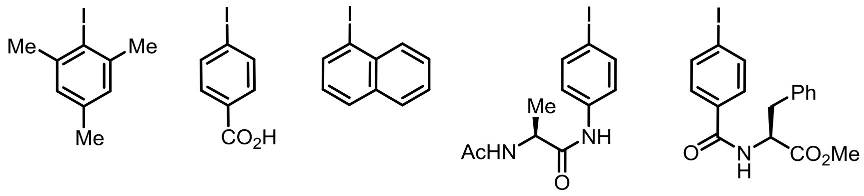
124a **4** **125**

Entry	ArI	Product	Isolated yield (%)
1	 **4h**	 **125ah**	67[b]
2	 **4i**	 **125ai**	75
3	 **4j**	 **125aj**	78
4	 **4k**	 **125ak**	68
5	 **4l**	 **125al**	53
6	 **4c**	 **125ac**	50[b]

Entry	ArI	Product	Isolated yield (%)
7	 **4d**	 **125ad**	45
8	 **4m**	 **125am**	81
9	 **4n**	 **125an**	48
10	 **4o**	 **125ao**	49
11	 **4p**	 **125ap**	81
12	 **4q**	 **125aq**	64
13	 **4r**	 **125ar**	34

[a] General reaction conditions: **124a** (0.20 mmol), **4** (0.30 mmol), AgOAc (0.22 mmol), $Pd(TFA)_2$ (5.0 mol %), toluene (2.0 mL), 110 °C, 16 h, under N_2. [b] $Pd(OAc)_2$ (5.0 mol %)

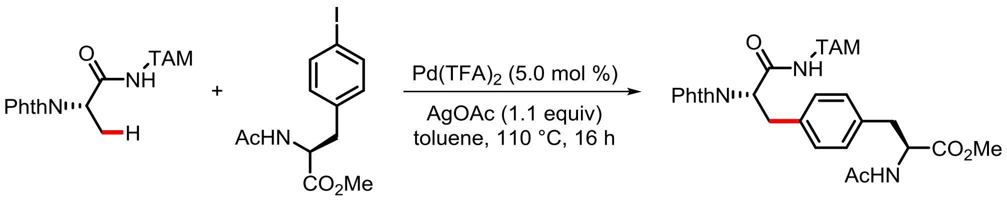
Our method proved unsuitable for the aryliodides summarized in Figure 24. In these cases, no product formation or only traces of the desired products were observed. In the case of 2,4,6-trimethyl-iodobenzene (**4s**) and 1-iodonapthalene (**4u**) the two sterically demanding *ortho*-substituents probably prevented the key oxidative addition to occur. The free benzoic acid **4t** was not tolerated, while the ester gave excellent results (Table 13, entry 8). The amino acid derivatives **4v** and **4w** did not deliver the desired products.



4s **4t** **4u** **4v** **4w**

Figure 24: Unreactive aryliodides in the palladium-catalyzed direct C(sp^3)–H arylation of alanine **124a**.

However, *N*-acetyl-4-iodo-L-phenylalaninemethylester (L-**4x**) delivered the product L-**125ax** in a good yield of 57% (Scheme 65). This result illustrated the potential of the developed method for chemical ligation. Importantly, in the arylation with the enantiomerically pure L-iodophenylalanine L-**4x** only the desired product L-**125ax** was isolated and the stereochemical information of both substrates (L-**4x**, L-**125ax**) was fully retained.

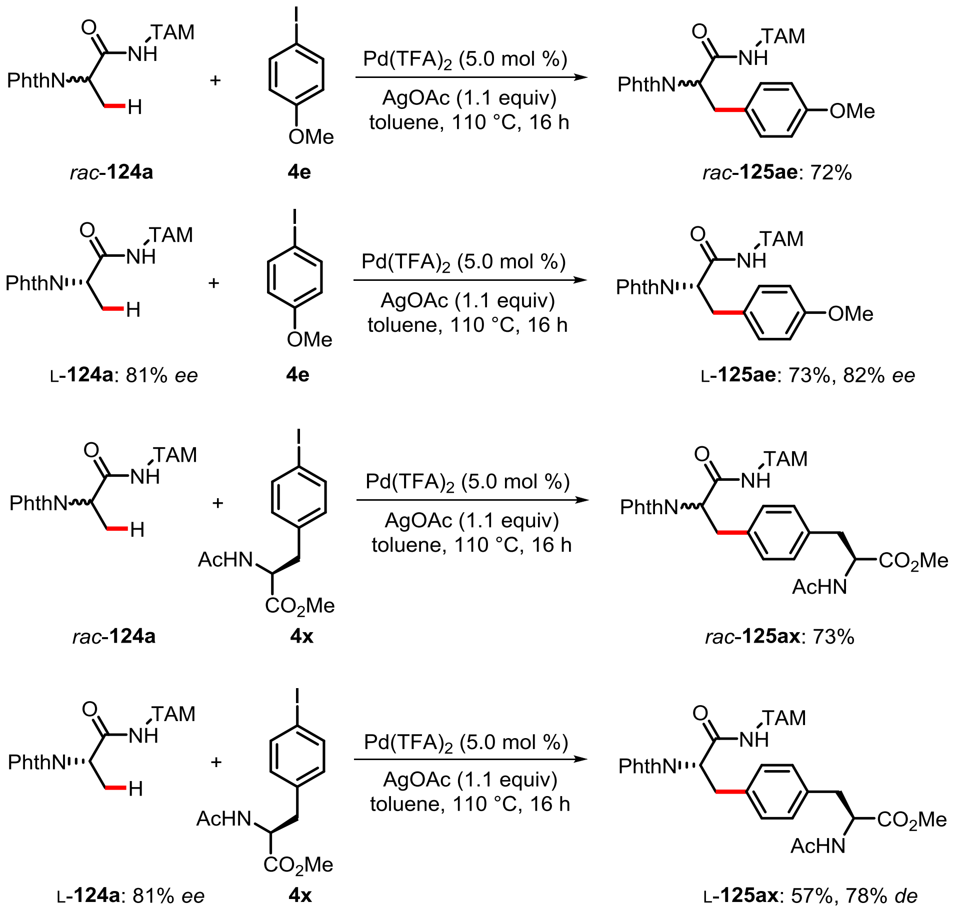


L-**124a** L-**4x** L-**125ax**: 57%

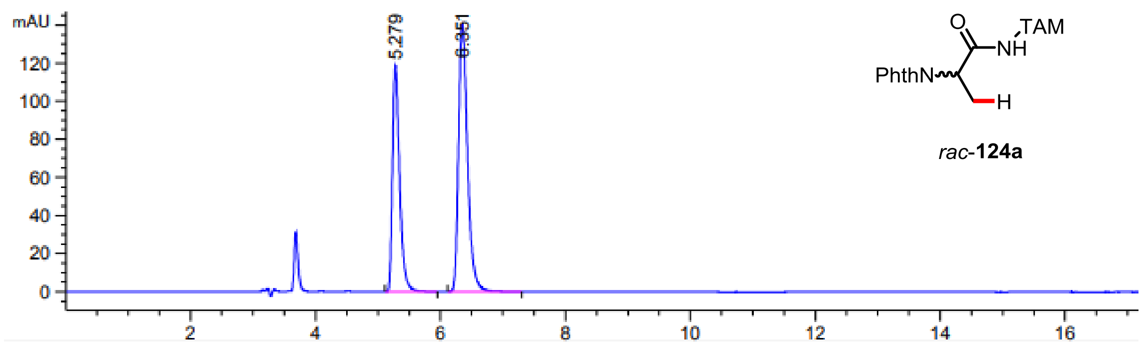
Scheme 65: Chemical ligation with *N*-acetyl-4-L-iodophenylalaninemethylester (L-**4x**).

3.3.4 Studies on the potential racemization of enantiomerically pure compounds

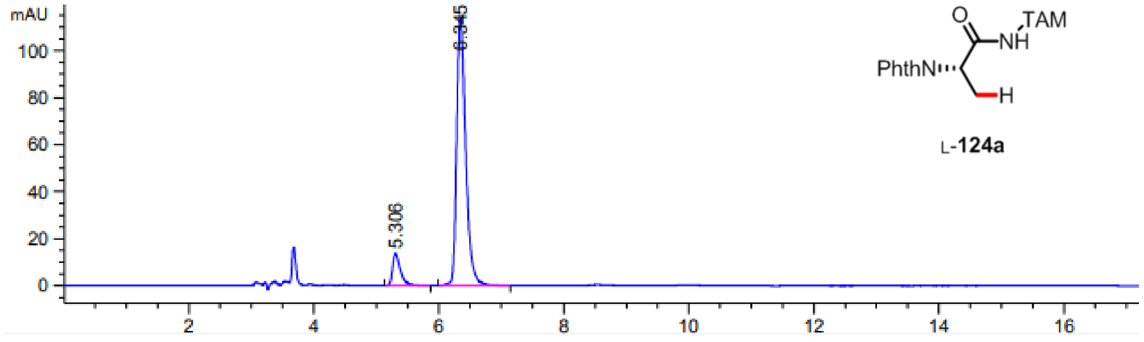
In order to verify that the palladium-catalyzed arylation proceeded without racemization, HPLC analysis on chiral stationary phase was conducted. Therefore the racemic alanine derivative *rac*-**124a** was synthesized and arylated with 4-methoxyiodobenzene (**4e**) and L-iodophenylalanine L-**4x**. The products *rac*-**125ae** and *rac*-**125ax** were isolated in good yields of 72% and 73%, respectively. HPLC analysis of the racemic compounds and L-**124a**, L-**125ae** and L-**125ax** confirmed that racemization did not occurr (Scheme 66).



Scheme 66: Racemization study for palladium-catalyzed C(sp^3)–H arylation of alanine **124a**.

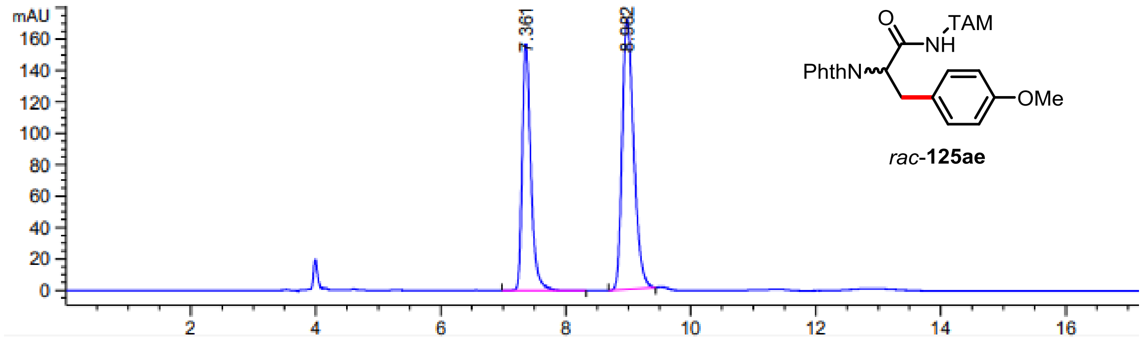


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.279	BB	0.1223	950.50531	118.84903	40.5206
2	6.351	BB	0.1522	1395.22546	140.12001	59.4794

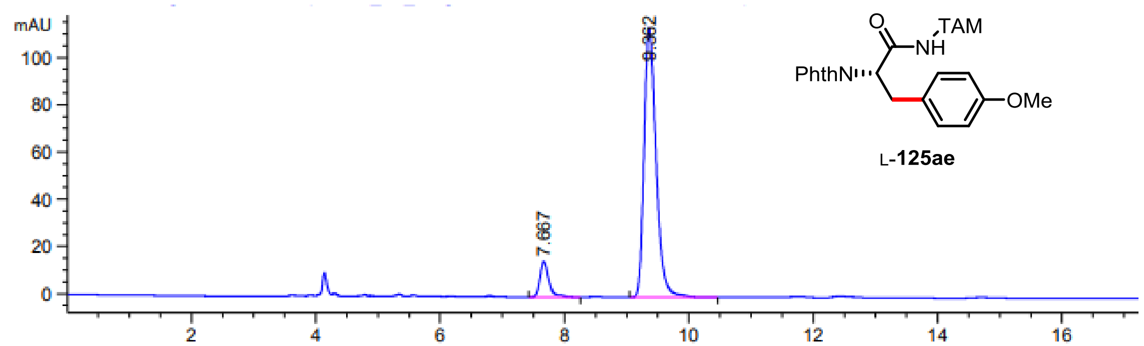


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.306	BB	0.1324	120.19539	13.55730	9.4999
2	6.345	BB	0.1531	1145.03271	114.04834	90.5001

Figure 25: HPLC-Chromatograms of compounds *rac*-**124a** and L-**124a** [t_R = 6.345 min]. IC-3 *n*-hexane/ethyl acetate 30/70, flow rate: 1.0 mL/min, detection at 274 nm.

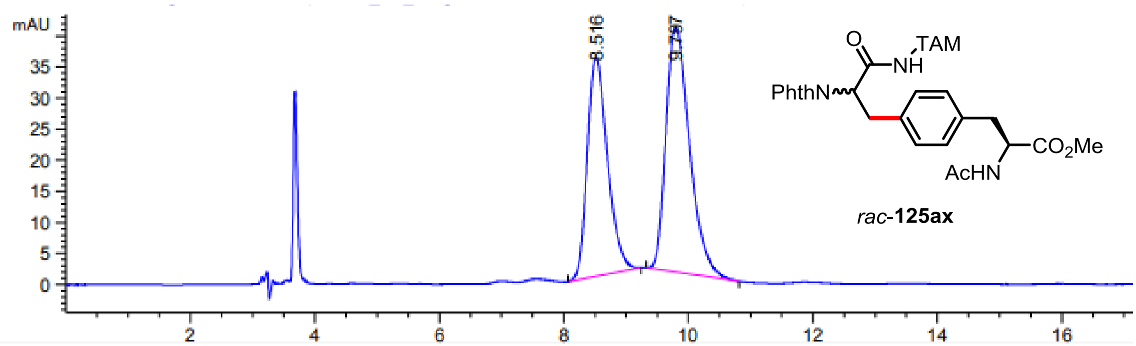


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.361	BB	0.1507	1337.28259	133.74455	41.5330
2	8.982	BB	0.1965	1882.52527	145.89459	58.4670

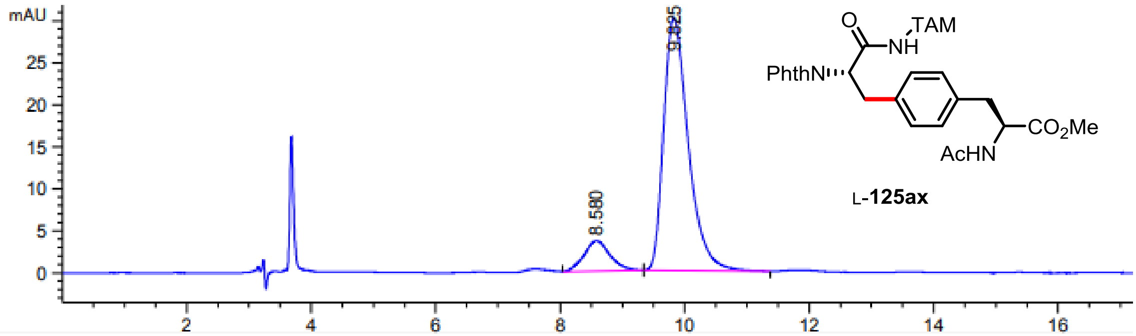


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.667	BB	0.1531	154.66618	15.15038	9.1945
2	9.362	BB	0.2054	1527.49207	113.92889	90.8055

Figure 26: HPLC-Chromatograms of compounds *rac*-**125ae** and L-**125ae** [t_R = 9.362 min]. ID-3 *n*-hexane/ethyl acetate 30/70, flow rate: 1.0 mL/min, detection at 274 nm.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.516	BB	0.3428	795.62469	35.18633	43.2980
2	9.797	BB	0.4064	1041.92932	39.29398	56.7020



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.580	BB	0.3431	104.05569	3.62256	11.2101
2	9.825	BB	0.4125	824.17548	30.00430	88.7899

Figure 27: HPLC-Chromatograms of compounds *rac*-**125ax** and L-**125ax** [t_R = 9.825 min]. IC-3 *n*-hexane/ethyl acetate 30/70, flow rate: 1.0 mL/min, detection at 274 nm.

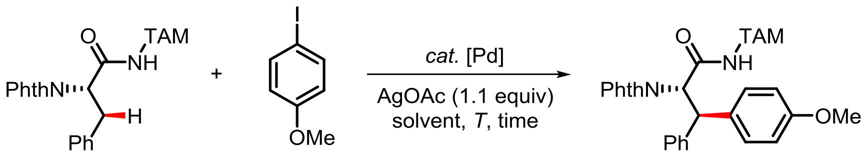
3.3.5 Triazole-directed C(sp^3)–H arylation of phenylalanine derivatives

The new triazole-guided palladium-catalyzed direct C(sp^3)–H arylation allowed the site-selective modification of alanine derivatives. The installation of various functional groups was accomplished without loss of stereochemical information. Remarkably, chemical ligation was in principle feasible, albeit only shown on single amino acids so far. Since the formation of diarylated side product **125aee** had shown that the protocol was in principle compatible with the secondary C(sp^3)–H bonds, the more challenging arylation of phenylalanine and other amino acids was examined.

3.3.6 Optimization studies

Based on the successful diarylation of alanine, the C(sp^3)–H arylation of phenylalanine was subsequently optimized (Table 14). Some of the reactions were performed by *Ms Chuan Dong* and are labelled accordingly. At the outset, the envisioned reaction for *N*-phthaloylphenylalanineTAMamide **124e** and 4-methoxyiodobenzene (**4e**) was tested under the optimized conditions for the primary C(sp^3)–H arylation. This first reaction already furnished a high isolated yield of 60% (entry 1). Higher loading of the catalyst and raising the temperature to 130 °C proved beneficial (entries 2-3). Adding 2.0 equivalents of the aryliodide **4e** led to higher conversion, whereas 3.0 equivalents delivered a slightly reduced yield (entries 4, 6-7). An increased amount of 2.0 equivalents of AgOAc furnished a slightly reduced yield (entry 5). Changing the solvent from toluene to *o*-xylene and prolonging the reaction time to 20 hours gave the best isolated yield of 89% (entry 8). Compared to Pd(TFA)$_2$, Pd(OAc)$_2$ gave a slightly reduced yield, and in the absence of the palladium catalyst product formation was not observed (entries 9-10).

Table 14: Optimization studies for the palladium-catalyzed secondary C(sp^3)–H arylation of phenylalanine **124e**.[a]



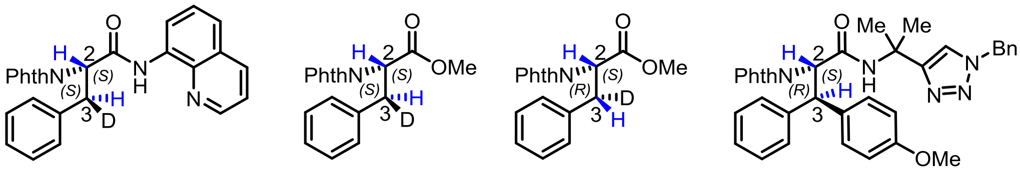
124e **4e** **125ee**

Entry	**4e** (equiv)	[Pd] (mol %)	Solvent	*T* (°C)	time (h)	Isolated yield (%)
1	1.5	Pd(TFA)$_2$ (5.0)	toluene	110	16	60
2	1.5	Pd(TFA)$_2$ (10)	toluene	110	16	(77)[b]
3	1.5	Pd(TFA)$_2$ (10)	toluene	130	16	(84)[b]
4	2.0	Pd(TFA)$_2$ (10)	toluene	130	16	(88)[b]
5	2.0	Pd(TFA)$_2$ (10)	toluene	130	16	(80)[c]
6	3.0	Pd(TFA)$_2$ (10)	toluene	130	16	71 (78)
7	3.0	Pd(TFA)$_2$ (10)	*o*-xylene	130	16	71 (76)
8	**2.0**	**Pd(TFA)$_2$ (10)**	***o*-xylene**	**130**	**20**	**89**
9	2.0	Pd(OAc)$_2$ (10)	*o*-xylene	130	20	81
10	2.0	-	*o*-xylene	130	20	-

[a] General reaction conditions: **124e** (0.20 mmol), **4e** (0.30 mmol), AgOAc (0.22 mmol), solvent (2.0 mL), *T*, time, under N$_2$; yields in parenthesis refer to ^{1}H NMR yields using 1,3,5-trimethoxy-benzene as internal standard. [b] Performed by *Ms Chuan Dong*. [c] AgOAc (0.40 mmol).

The *trans*-configuration of the *N*-phthaloyl group and of the new arene substituent was established based on the coupling constant $J_{H2\text{-}H3}$ = 12.6 Hz of the *trans*-configured protons in product **125ee**, which was comparable to the reported coupling constants in deuterated phenylalanine derivatives **36a** and

126a (Figure 28).[133, 242] In phenylalanine **126b** the (*R*)-configuration at C3 leads to a significantly smaller coupling constant ($J_{H2\text{-}H3}$ = 4.8 Hz).[242]



(2*S*,3*S*)-**36a** $J_{H2\text{-}H3}$ = 11.5 Hz *Daugulis*

(2*S*,3*S*)-**126a** $J_{H2\text{-}H3}$ = 11.7 Hz

(2*S*,3*R*)-**126b** $J_{H2\text{-}H3}$ = 4.8 Hz *Easton*

(2*S*,3*R*)-**125ee** $J_{H2\text{-}H3}$ = 12.6 Hz

Figure 28: Comparison of phenylalanine derivatives and the corresponding $J_{H2\text{-}H3}$ coupling constants.

Furthermore, the structure was verified through NOE experiments. The 2D-NOESY spectrum of product **125ee** (Figure 29) clearly showed interactions between the amide group and the *p*-methoxyphenyl group (marked with 1) and between the methyl groups and the *p*-methoxyphenyl group (marked with 2). The origin of the diastereoselectivity of the reaction is rationalized within the mechanistic proposal and the computational studies (see section 3.4.1).

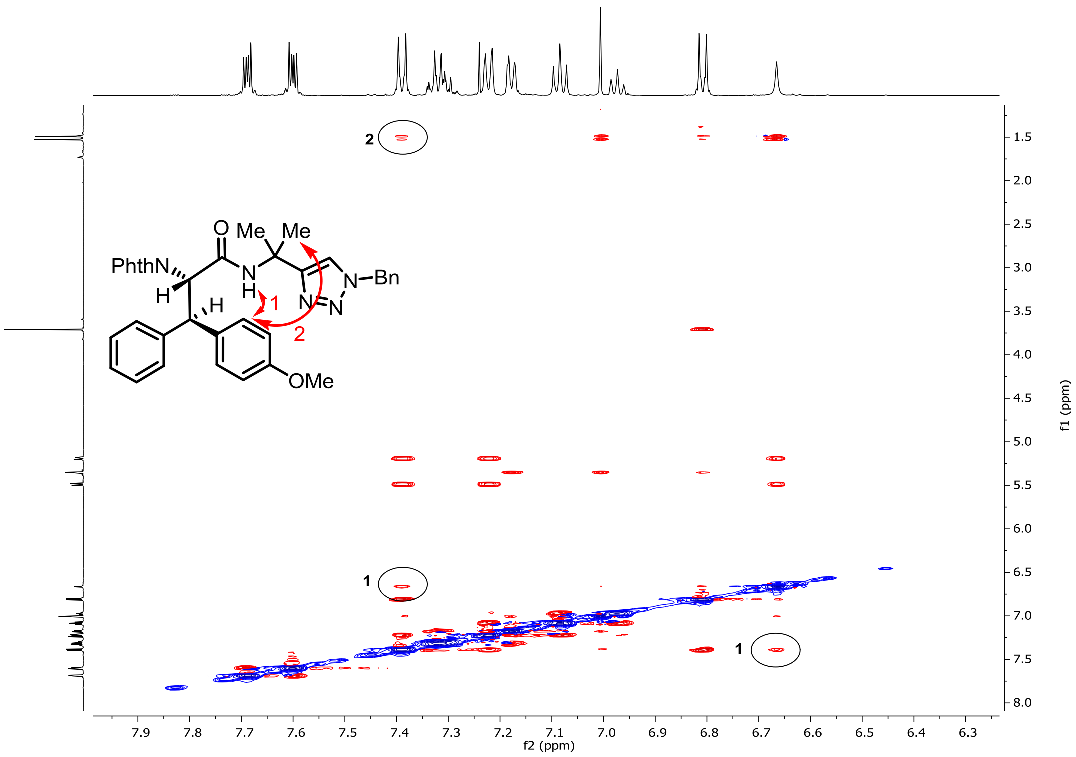
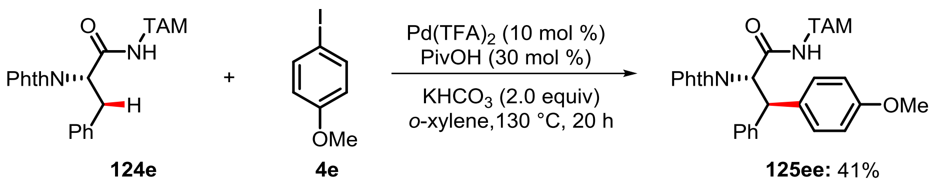


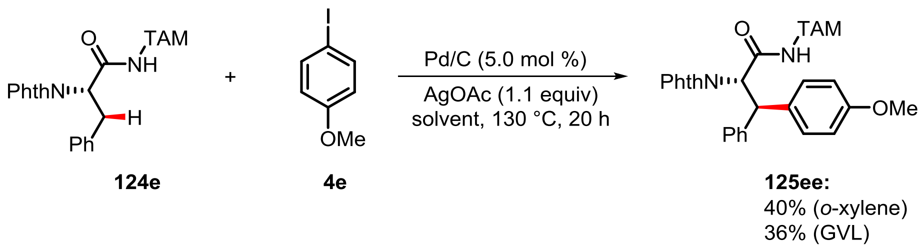
Figure 29: 2D-NOESY spectrum of **125ee** with marked interactions.

Next, it was tested, whether silver-free reactions conditions could give access to the arylated products. Substitutition of the expensive silver additives with inexpensive and convenient mild bases and organic salts is attractive from an economical and environmental perspective, by reducing the overall cost of a process and avoiding the formation of stoichiometric amounts of undesired metallic waste. In previously reported palladium-catalyzed triazole-assisted C–H arylations of benzamides by *Ackermann*, $KHCO_3$ as mild base in combination with 1-adamantenecarboxylic acid or pivalic acid gave optimal results.[221a] However, applying a combination of $KHCO_3$ and pivalic acid for the arylation of the amino acid substrate **124e** delivered only a moderate yield of 41% (Scheme 67). In principle the C–H arylation proceeded under silver-free conditions, but further optimization would be necessary to accomplish synthetically useful results.



Scheme 67: Direct C–H arylation of phenylalanine **124e** under silver-free reaction conditions.

Additionally, the applicability of heterogeneous catalysts was investigated (Scheme 68). The groups of *Ackermann* and *Vaccaro* had previously developed C–H arylations of 1,2,3-triazoles with a reusable heterogeneous palladium catalyst employing the biomass-derived *γ*-valerolactone (GVL) as the solvent.[177a] Hence, palladium on charcoal was probed as catalyst in the reaction of phenylalanine **124e** with 4-methoxyiodobenzene (**4e**) in *o*-xylene or GVL. However, both reactions afforded moderate yields of the arylated product **125ee**.

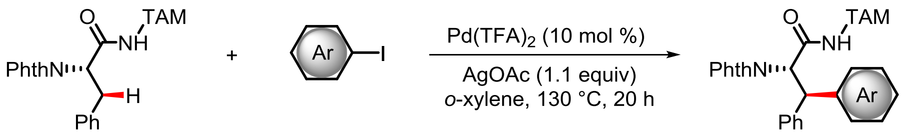


Scheme 68: Direct secondary C–H arylation of phenylalanine **124e** with a palladium heterogeneous-based catalyst.

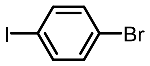
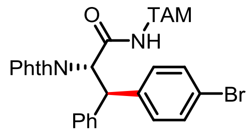
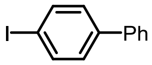
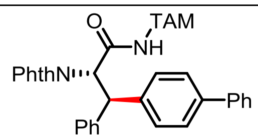
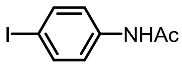
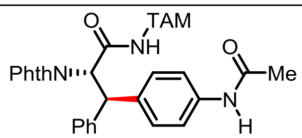
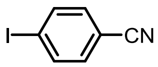
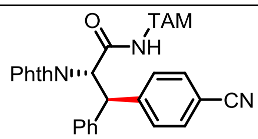
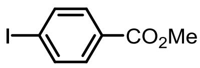
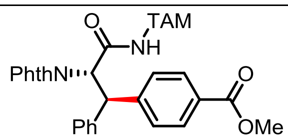
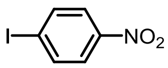
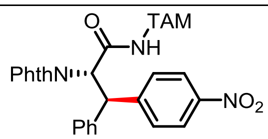
3.3.7 Scope and limitations

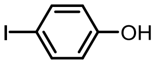
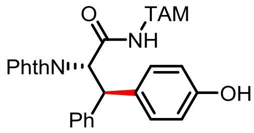
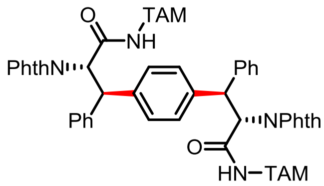
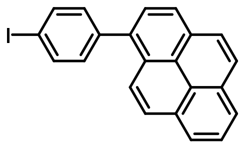
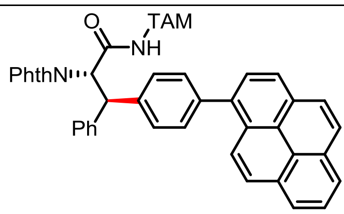
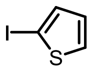
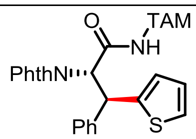
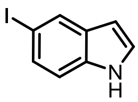
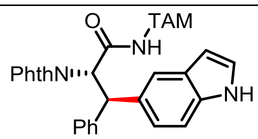
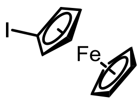
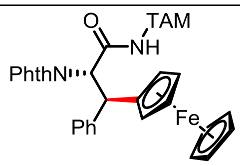
With the optimized conditions in hand, the versatility of our catalytic system for the regioselective C–H arylation of phenylalanine derivative **124e** was probed. Electron-deficient and electron-rich arenes served as viable substrates, delivering the arylated products **125** in moderate to good yields with excellent diastereoselectivity (Table 15). Remarkably, 1-bromo-4-iodobenzene (**4d**) was efficiently converted into the corresponding product **125ed**, which provides a synthetic handle for further diversifications through traditional cross coupling chemistry (entry 1). Protected amine and phenyl substituents **4k** and **4i** were well tolerated (entries 2, 3). Fortunately, electron-withdrawing nitrile and nitro substituents furnished **125el** and **125en** in excellent 91% and 69% isolated yield, respectively (entries 4, 6), whereas an ester functionality and a free phenolic hydroxyl group gave rise to the desired products **125em** and **125eo** in only moderate yields (entries 5, 7). The arylation with 1,4-diiodobenzene **4y** afforded **125ey** in synthetically useful yield, allowing chemical ligation (entry 8). Likewise, **4z** bearing 1-pyrene in the *para*-position led to **125ez** in a good yield of 85% (entry 9), which exhibited an increased fluorescence (see section 5.3.3.1). However, the direct arylation with the hetereoarenes 2-iodothiophene (**4p**) or 5-iodoindole (**4q**) proceeded with lower conversions and the isolation of an analytical amount of pure product was not accomplished (entries 10-11). In the case of iodoferrocene (**4r**) 18% of the desired product **125er** were obtained (entry 12).

Table 15: Scope of aryliodides **4** in the palladium-catalyzed direct C(sp^3)–H arylations of phenylalanine **124e**.[a]



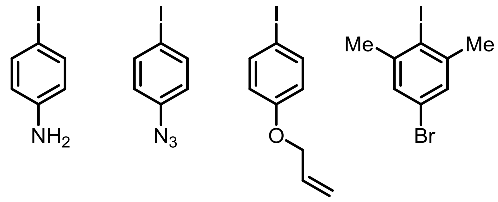
124e **4** **125**

Entry	Ar	Product	Isolated Yield (%)
1	 **4d**	 **125ed**	74
2	 **4i**	 **125ei**	50
3	 **4k**	 **125ek**	62
4	 **4l**	 **125el**	91
5	 **4m**	 **125em**	36
6	 **4n**	 **125en**	69

Entry	Ar	Product	Isolated Yield (%)
7	 **4o**	 **125eo**	20
8	 **4y**	 **125ey**	52
9	 **4z**	 **125ez**	85
10	 **4p**	 **125ep**	-[b]
11	 **4q**	 **125eq**	-[b]
12	 **4r**	 **125er**	18

[a] General reaction conditions: **124e** (0.20 mmol), **4** (0.40 mmol), AgOAc (0.22 mmol), $Pd(TFA)_2$ (10 mol %), *o*-xylene (2.0 mL), 130 °C, 20 h, under N_2. [b] Conversion <10% determined by LC-MS and ^1H NMR analysis.

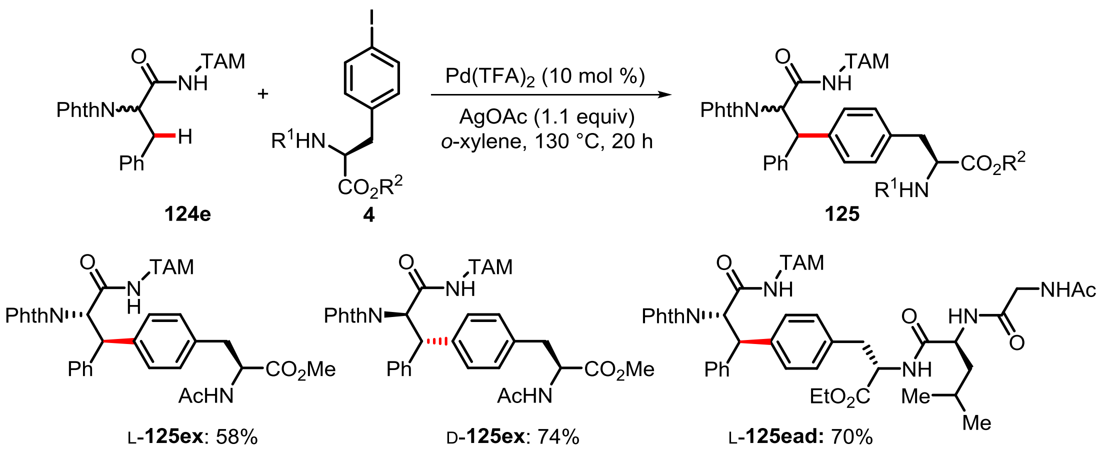
The substrates shown in Figure 30 were not suitable for the reaction and formation of the desired products was not observed. Free amine **4aa** showed no reactivity. Azide-containing arene **4ab** was also not tolerated. The arylation with **4ac** bearing an alkene did not provide the desired product. As already observed in the arylation of alanine, the catalytic system proved sensitive towards steric hinderance, thus the sterically encumbered arene **4s** showed no conversion.



4aa **4ab** **4ac** **4s**

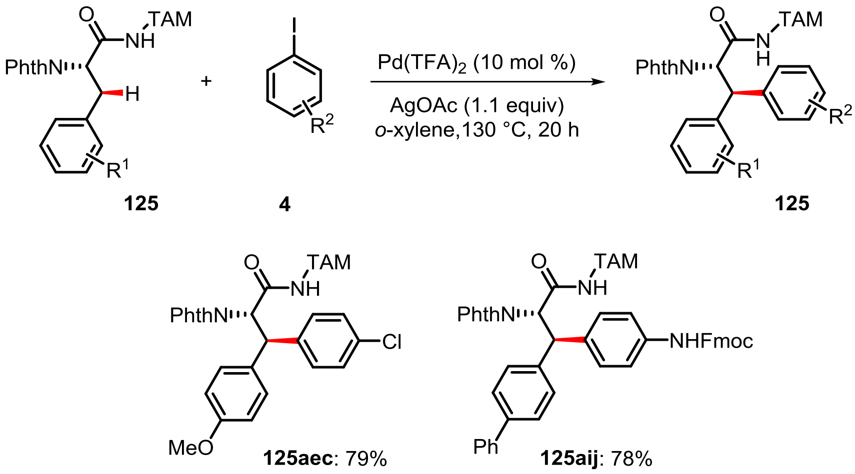
Figure 30: Unreactive aryliodides in the direct C–H arylation of phenylalanine **124e**.

In order to explore to which extend the direct arylation was applicable for chemical ligation, enantiomerically pure substrates L/D-**124e** were tested with a small set of enantiopure coupling partners under the optimized reaction conditions. The arylation of L- and D-phenylalanineTAM–**124e** with L-4-iodophenylalanine (L-**4x**), furnished the corresponding unnatural dipeptides L-**125ex** and D-**125ex** in good yields of 58% and 74%, respectively (Scheme 69). As expected, the stereochemical information was retained, hence L-**125ex** and D-**125x** were diastereomers, which was confirmed by distinct resonances in the ^{1}H NMR and ^{13}C NMR. Moreover, the direct C–H arylation of L-**124e** with tripeptide **4ad** gave rise to L-**125ead** in 70% isolated yield.



Scheme 69: Chemical ligation of phenylalanine under the optimized reaction conditions.

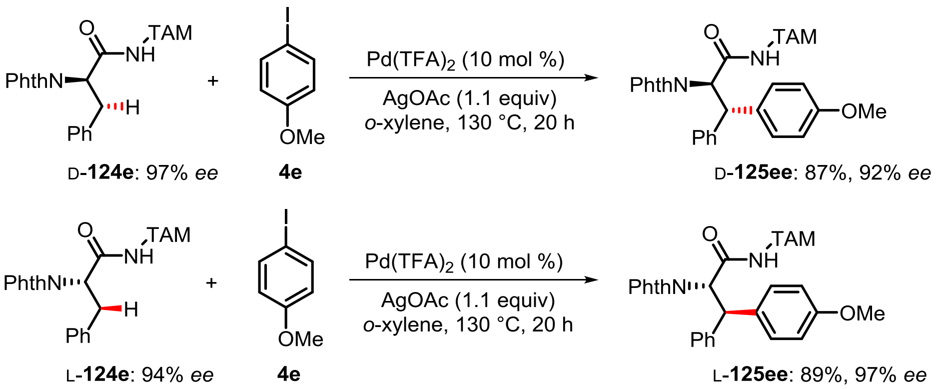
Since our strategy had such an ample scope and excellent functional group tolerance, a sequential diarylation was examined. As representative examples, the two products of the arylation of alanine **125ae** and **125ai**, bearing a methoxy and a phenyl substitutent were chosen and treated with 1-chloro-4-iodobenzene (**4c**) and (9*H*-fluoren-9-yl)methyl (4-iodophenyl)carbamate (**4j**), respectively (Scheme 70). The desired products **125aec** and **125aij** were smoothly isolated in stereo-, site- and chemoselective fashion. Changing the sequence of the arylation with D-alanine should allow the synthesis of all four possible stereoisomers.



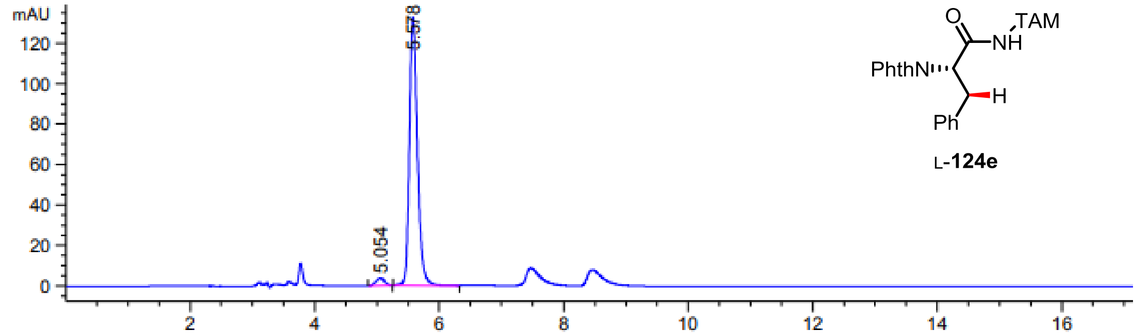
Scheme 70: Sequential diarylation for the synthesis of highly decorated phenylalanine.

3.3.8 Studies on the potential racemization of enantiomerically pure compounds

As the next important step, the developed protocol was checked for racemization to ensure that the elevated temperature and increased loading of palladium catalyst did not lead to undesired loss of stereochemical information. The enantiomerically pure L- and D-phenylalaninetriazole amide **124e** were synthesized starting from the commercially available L- and D-phenylalanine and arylated with 4-iodoanisole (**4e**) under the optimized reaction conditions (Scheme 71). HPLC analysis on chiral stationary phase confirmed that the catalytic system had no impact on the enantiomeric excess of the arylated amino acid derivatives.

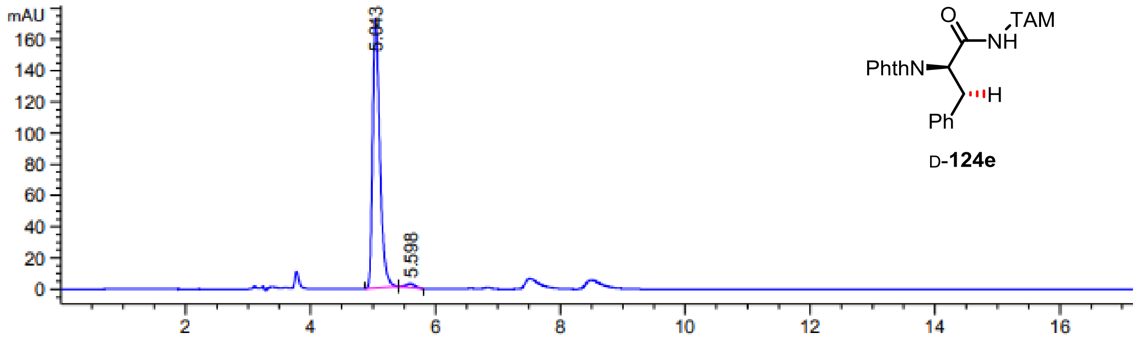


Scheme 71: Probing racemization for palladium-catalyzed arylation of enantiopure phenylalanine **124e**.



L-**124e**

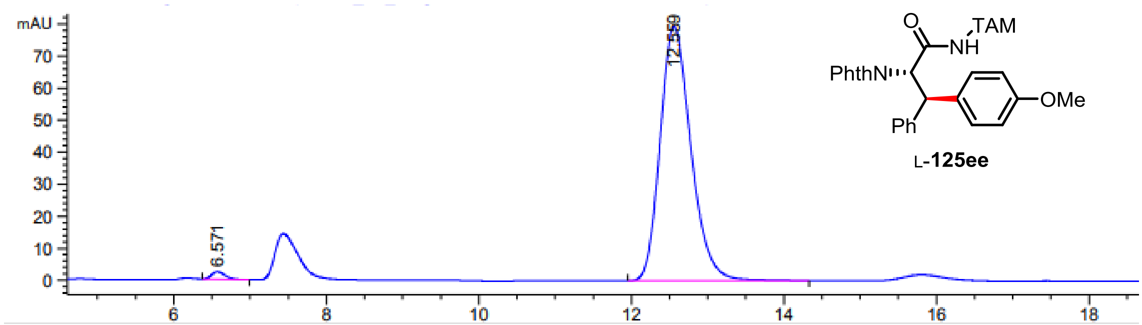
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.054	BB	0.1423	36.10215	3.78500	2.9460
2	5.578	BB	0.1367	1189.36377	132.57529	97.0540



D-**124e**

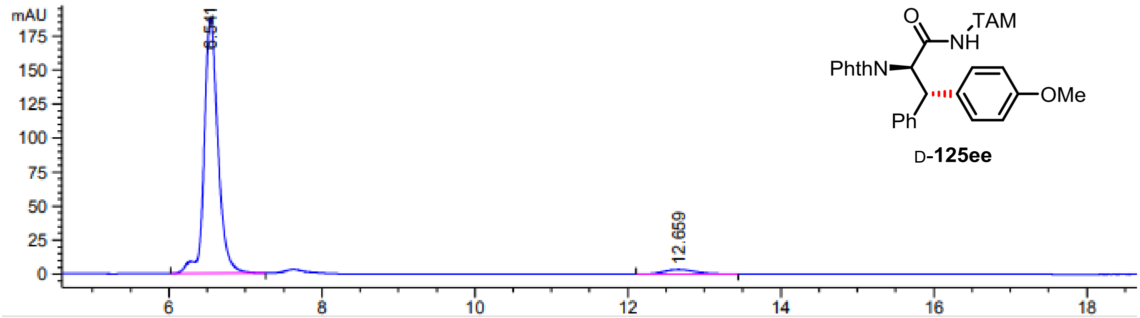
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.043	BB	0.1210	1375.03857	172.49893	98.2894
2	5.598	BB	0.1401	23.93136	2.51397	1.7106

Figure 31: HPLC-Chromatograms of the enantiopure compounds L-**124e** [t_R = 5.578 min] and D-**124e** [t_R = 5.043 min]. IC-3 *n*-hexane/ethyl acetate 40/60, flow rate: 1.0 mL/min, detection at 274 nm.



L-**125ee**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.116	BV	0.0669	46.90473	9.45426	1.9628
2	3.263	VB	0.0625	11.91203	2.92870	0.4985
3	3.929	BV R	0.0760	67.79385	13.39906	2.8369
4	6.571	BB	0.1859	29.16574	2.34865	1.2205
5	12.559	BB	0.4281	2233.95801	79.44205	93.4814



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.105	BV R	0.0363	312.05728	128.47353	10.9886
2	3.260	VB E	0.0647	11.03720	2.59328	0.3887
3	3.347	BB	0.0804	7.70622	1.33464	0.2714
4	3.930	BV R	0.0719	57.57761	12.22842	2.0275
5	4.325	BB	0.0706	8.13408	1.73767	0.2864
6	6.541	VB R	0.1850	2344.68018	187.68784	82.5644
7	12.659	BB	0.3538	98.62569	3.46820	3.4730

Figure 32: HPCL-Chromatograms of the enantiopure compounds L-**125ee** [t_R = 12.559 min] and D-**125ee** [t_R = 6.541 min]. IC-3 *n*-hexane/ethyl acetate 50/50, flow rate: 1.0 mL/min, detection at 274 nm.

3.3.9 Fluorescence studies of the arylated phenylalanines

The fluorescence properties for the selected arylated phenylalanines **125ee**, **125ei**, **125ej**, **125en**, and **125ez** are presented in Figure 33 and Table 16. The fluorescence intensity of three compounds was negligible (**125ee**, **125ei**, **125en**) and only two showed significant fluorescence, **125ej** bearing a Fmoc-protected amine and **125ez** bearing a pyrene substituent in the *para*-position of the phenyl group. In the case of the simple arenes, the electron-deficient arene in **125en** showed the lowest intensity. The Stokes shift ranged from 2 to 137 nm. **125ej** exhibited a rather sharp fluorescence with high intensity and a small Stokes shift of 37 nm, while the pyrene chromophore of **125ez** exhibited a broad fluorescence and a Stokes shift of 123 nm.

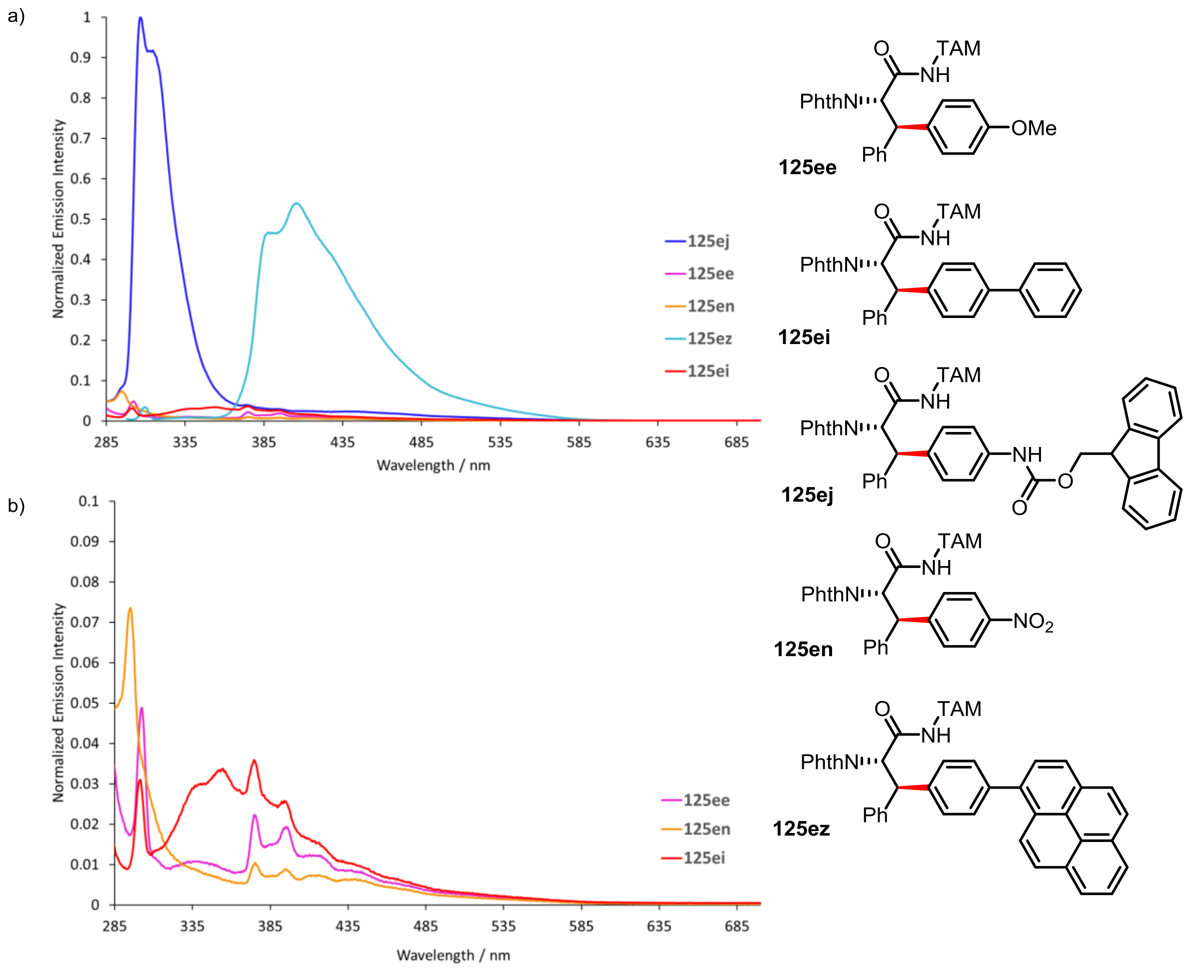


Figure 33: a) Fluorescence spectra for arylated phenylalanines **125**. b) Emission of compounds **125ee**, **125ei** and **125en**. Excitation at the wavelengths (absorption λ_{max}) given in **Table 16**. All compounds were measured in DMSO.

Table 16: Fluorescence data of compounds **125ee**, **125ei**, **125ej**, **125en**, and **125ez**.

Entry	Compound	Absorption λ_{max}/nm	Emission λ_{max}/nm	Stokes shift/nm
1	**125ee**	276	278	(2)[a]
2	**125en**	270	272	(2)[a]
3	**125ei**	275	375	100[b]
4	**125ez**	282	405	123
5	**125ej**	270	307	37

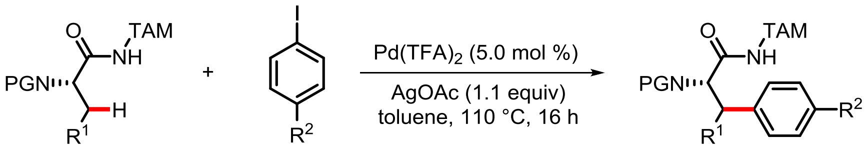
[a] Fluorescence intensity and Stokes shift negligible. [b] Fluorescence intensity negligible.

3.3.10 C(sp^3)–H functionalization of amino acids possesing an β-C–H bond

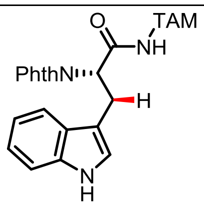
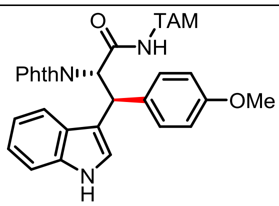
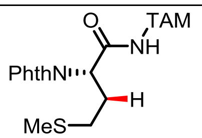
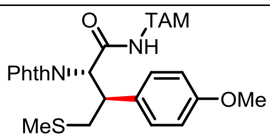
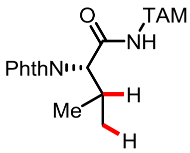
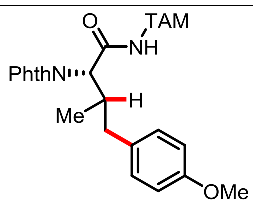
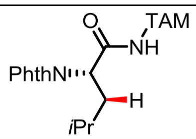
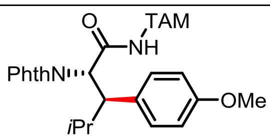
The triazole-guided palladium-catalyzed direct C(sp^3)–H arylation had successfully been applied to alanine and phenylalanine with ample scope regarding differently substituted aryliodides. Next, a series of amino acids was tested under the established reaction conditions (Table 17). Of particular interest were the functional group tolerance and the regioselectivity of the catalytic system. Thus, tryptophan

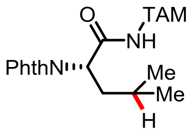
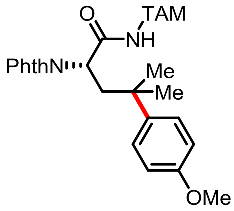
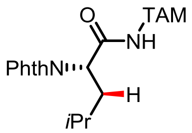
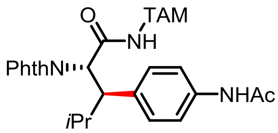
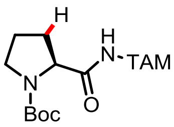
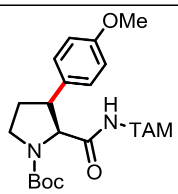
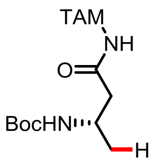
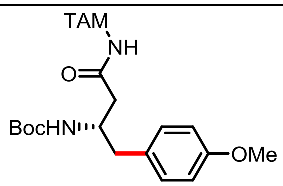
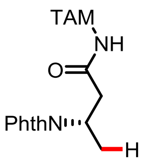
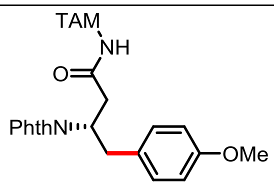
127a and methionine **127b** were unsuitable substrates (entries 1-2). The arylation of valine delivered only traces of product **128ce**, albeit the isolation of a pure sample could not be accomplished (entry 3). The arylation took place at a primary C–H bond of a methyl group according to ^{1}H NMR analysis of the crude product, which would indicate that a C–H activation of a primary C–H bond *via* a seven-membered transition state is more favorable than a C–H activation of a tertiary C–H bond *via* a six-membered transition state (see section 3.4.1). In the reaction of leucine **127d** with 4-iodoanisole (**4e**) product **127de** was isolated in low yield, whereas the isolation of the product of the tertiary C–H arylation **127de'** was not accomplished (entries 4-5). Regarding the stereochemistry of the *β*-carbon atom, the $J_{H2\text{-}H3}$ coupling constant indicated the formation of the (2*S*,3*R*)-isomer comparable to the *β*-phenylleucine derivative synthesized by *Corey* and coworkers.[130] The arylation of leucine **127d** with *N*-(4-iodophenyl)-acetamide (**4k**) delivered the product **128dk** in 24% yield (entry 6). In the case of proline, LC-MS analysis indicated trace formation of the desired product (entry 7), while in the arylation of L-*β*-homoalanine no product was detected (entries 8, 9).

Table 17: Attempted triazole assisted C–H arylation of different amino acids.[a]



127 **4** **128**

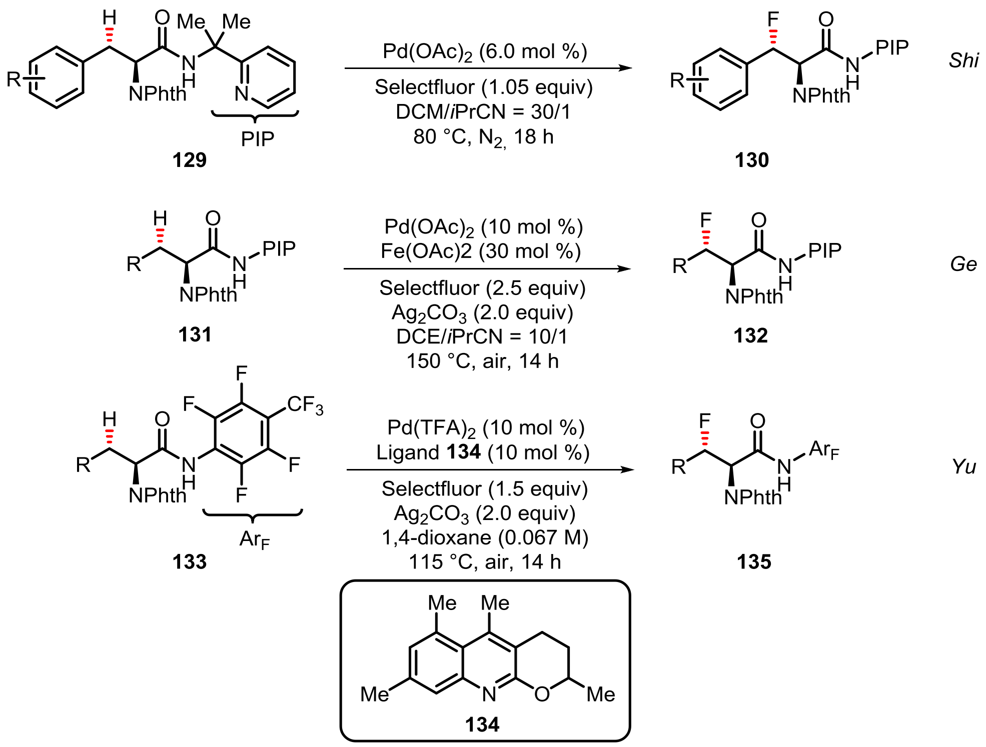
Entry	Substrate	Product	Isolated yield [%]
1	 **127a**	 **128ae**	- -[b]
2	 **127b**	 **128be**	-
3	 **127c**	 **128ce**	traces
4	 **127d**	 **128de**	15[c]

Entry	Substrate	Product	Isolated yield [%]
5	 **127d**	 **128de'**	-
6	 **127d**	 **128dk**	24
7	 **127e**	 **128ee**	traces
8	 **127f**	 **128fe**	-
9	 **127g**	 **128ge**	-

[a] General reaction conditions: **127** (0.20 mmol), **4** (0.30 mmol), $Pd(TFA)_2$ (5.0 mol %), AgOAc (0.22 mmol), toluene (2.0 mL), 110 °C, 16 h, under N_2. [b] **4** (0.4 mmol), $Pd(TFA)_2$ (10 mol%), *o*-xylene (2.0 mL), 130 °C, 20 h, under N_2. [c] 79% of substrate **127d** reisolated.

3.3.11 Attempted triazole-directed C(sp^3)–H fluorination

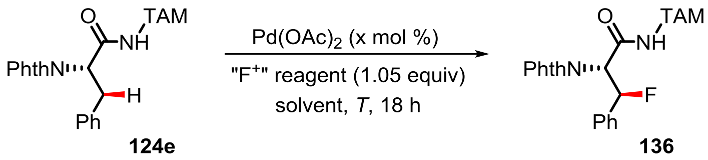
With the successful triazole-directed arylation of phenylalanine in hand, the palladium-catalyzed direct C–H fluorination was tested as the next important step. Fluorination is of major importance in medicinal chemistry[243] and drug design as can be seen with nearly 150 fluorinated drugs reaching the market since 1955 and estimations from 2010 showed that at least 20% of the administered drugs contained fluorine atoms or fluoroalkylgroups.[244] There are only few tropical and sub-tropical plants and microorganisms known that are capable of organofluorine biosynthesis with fluoroacetate being the most abundant fluorinated compound.[245] Fluorinated amino acids (FAA) are important in peptide and protein engineering, because they alter properties such as hydrophobicity, polarity, protease stability, protein folding, protein-protein interactions and among others enzyme activity.[245-246] Since fluorinated compounds are rare in nature, the need for reliable synthetic transformations led to different fluorination strategies for the generation of enantio- or diastereo-pure *α*-amino acids.[247] Despite the progress on direct C(sp^2)–H fluorination reactions, there are only few examples on the challenging transition metal-catalyzed direct aliphatic or benzylic C(sp^3)–H fluorination. In 2015, three reports on the palladium-catalyzed fluorination in the *β*-C(sp^3)-position of *α*-amino acids were reported independently by the groups of *Yu*,[248] *Shi*,[249] and *Ge*.[250] *Yu* revealed that a quinoline-based ligand gave optimal results in the stereoselective fluorination of *α*-amino acids. *Shi* and *He* independently developed diastereoselective methylene C(sp^3)–fluorinations employing the 2-(pyridine-2-yl)isopropyl amine (PIP amine) as directing group. In all three methodologies Selectfluor® proved to be the best fluorinating agent.



Scheme 72: Stereoselective *β*-C(sp^3)–H fluorination of amino acid derivatives.

Table 18 shows the performed attempts for the triazole-directed C(sp^3)–H fluorination. First, model substrate **124e** was reacted with Selectfluor in toluene employing Pd(OAc)$_2$ as palladium source (Table 18, entry 1). Unfortunately, no fluorinated product was formed and 90% of substrate **124e** was reisolated. Changing the solvent to acetonitrile, *N*,*N*-dimethylformamide, dichloro-methane, tetrahydrofuran or a mixture of dichloromethane/isopropylnitrile did not result in product formation (entries 2-9). The use of NFSI also did not lead to a successful fluorination (entries 10-12). All reaction mixtures were carefully analyzed by LC-MS and ^{19}F NMR and the desired fluorination was not observed in any case. Thus, no further optimization was conducted.

Table 18: Attempted benzylic C–H fluorination of phenylalanine **124e**.



Entry	“F⁺” reagent	Pd(OAc)$_2$ (x mol %)	Solvent	T (°C)	Isolated Yield (%)	RSM (%)[b]
1	Selectfluor	5.0	toluene	110	-	90
2	Selectfluor	5.0	MeCN	80	-	44
3	Sleectfluor	5.0	DMF	80	-	86
4	Selectfluor	5.0	CH_2Cl_2	50	-	87
5	Selectfluor	5.0	CH_2Cl_2/*i*PrCN (30/1)	50	-	87
6	Selectfluor	5.0	THF	50	-	83
7	Selectfluor	5.0	THF/*i*PrCN (30/1)	50	-	86
8	Selectfluor	6.0	CH_2Cl_2/*i*PrCN (30/1)	80	-	81
9	Selectfluor	6.0	toluene	23	-	88
10	NFSI	6.0	toluene	23	-	86
11	NFSI	6.0	CH_2Cl_2/*i*PrCN (30/1)	23	-	87
12	NFSI	6.0	CH_2Cl_2/*i*PrCN (30/1)	80	-	55

Selectfluor® NFSI

[a] General reaction conditions: **124e** (0.30 mmol), “F⁺” reagent (0.315 mmol), Pd(OAc)$_2$ (5.0-6.0 mol %), solvent (2.0 mL), *T*, 18 h, under N_2. [b] Recovered starting material **124e**.

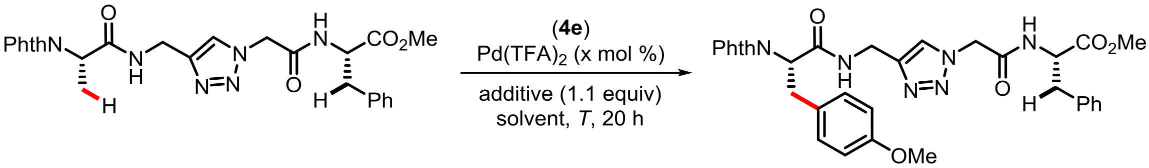
3.3.12 Direct C–H arylation of internal triazole containing peptides

Thus, the TAM directing group had been installed at the carboxy termini of amino acids and the cleavage of the TAM group had been successfully performed by *Dr. Wei Wang* and *Dr. Melanie Lorion*.[241b] Considering 1,2,3-triazoles are known as peptide bond surrogates, the C–H arylation of internal triazole containing peptides was investigated next. As a model substrate the pseudotetrapeptide Phth*N*-Ala-Gly-Tzl-Gly-Phe-OMe **137a** was chosen, featuring the 1,4-disubstituted triazole moiety. It should be noted that the reaction proceeded with excellent positional selectivity, delivering only **138ae** as the sole product, although substrate **137a** has two viable sites for C(sp^3)–H arylation (Table 19).

3.3.13 Optimization studies for primary C–H arylation of internal triazole peptides

Initially, Phth*N*-Ala-Gly-Tzl-Gly-Phe-OMe **137a** was treated with 4-iodoanisole (**4e**) under the previously established conditions, furnishing only 12% of the desired product **138ae** (Table 19, entry 1). Several solvents were tested, *N*,*N*-dimethylformamide and acetic acid gave similar isolated yields, 1,2-dichloroethane and toluene showed higher conversions, whereas dichloro-methane proved to be unsuitable (entries 2-6). Increased loading of the palladium catalyst and prolonged heating led to satisfactory conversion in toluene (entry 7) and synthetically useful isolated yield of 57% in 1,2-dichloroethane (entry 8). It turned out that heating the reaction mixture to 130 °C gave rise to a excellent yield of 80% (entry 9). Replacement of the silver salt with inexpensive bases was also examined. However, substitution of the silver additive with KTFA or NaTFA led to significantly decreased conversions (entries 13-14), while NH_4OAc and NaOAc shut down the reaction completely (entries 10, 12). Only KOAc furnished a moderate conversion (entry 11), proving that substitution of silver additives is in principle feasible, but further optimizations would be necessary to achieve good yields.

Table 19: Optimization of the primary C–H arylation of peptide **137a** with aryliodide **4e**.[a]



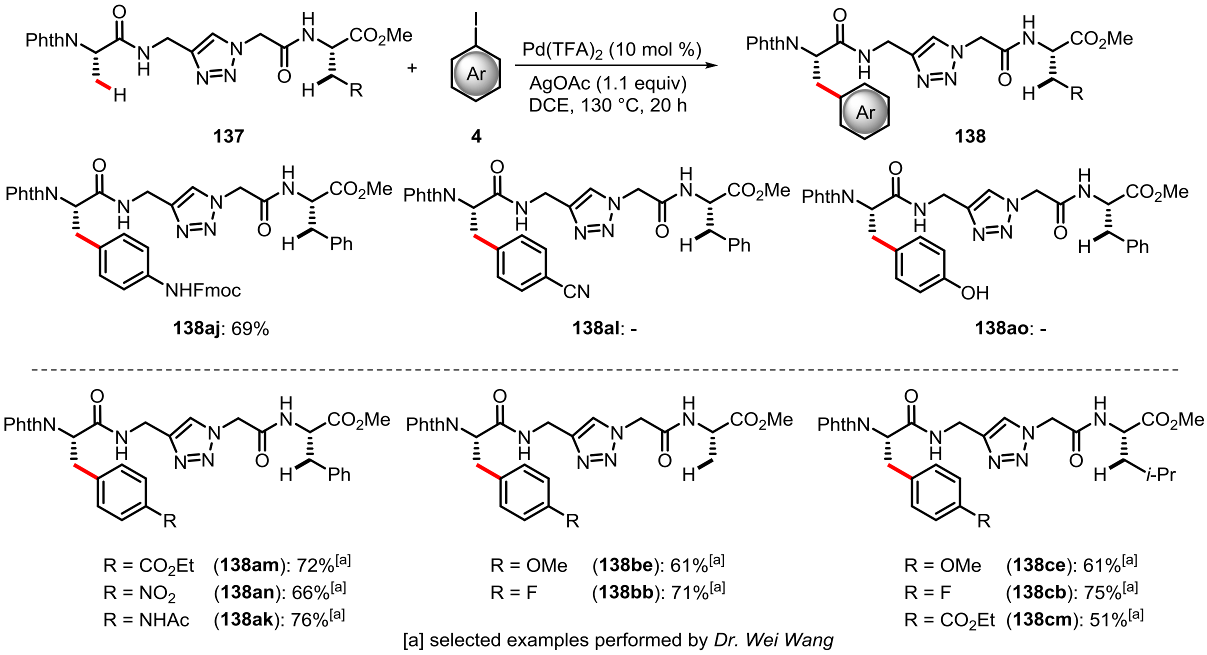
137a **138ae**

Entry	$Pd(TFA)_2$ (x mol %)	Additive	Solvent	*T* (°C)	Isolated yield (%)
1	5.0	AgOAc	*o*-xylene	130	12[b]
2	5.0	AgOAc	DMF	100	-[b]
3	5.0	AgOAc	AcOH	100	10[b]
4	5.0	AgOAc	CH_2Cl_2	23	-[b]
5	5.0	AgOAc	DCE	80	25[b][c]
6	5.0	AgOAc	toluene	110	30[b][c]
7	10	AgOAc	toluene	110	60[c] [d]
8	10	AgOAc	DCE	80	57[d]
9	**10**	**AgOAc**	**DCE**	**130**	**80**
10	10	NH_4OAc[e]	DCE	130	-
11	10	KOAc[e]	DCE	130	38[c]
12	10	NaOAc[e]	DCE	130	-
13	10	KTFA[e]	DCE	130	<10[c]
14	10	NaTFA[e]	DCE	130	<10[c]

[a] General reaction conditions: **137a** (0.20 mmol), **4e** (0.40 mmol), $Pd(TFA)_2$ (5.0-10 mol %), additive (0.22 mmol), solvent (2.0 mL), *T*, 20 h, under N_2. [b] **4e** (0.30 mmol). [c] Conversion determined by LC-MS analysis. [d] 72 h. [e] additive (0.40 mmol).

3.3.14 Scope of internal triazole peptide C(sp^3)–H arylation

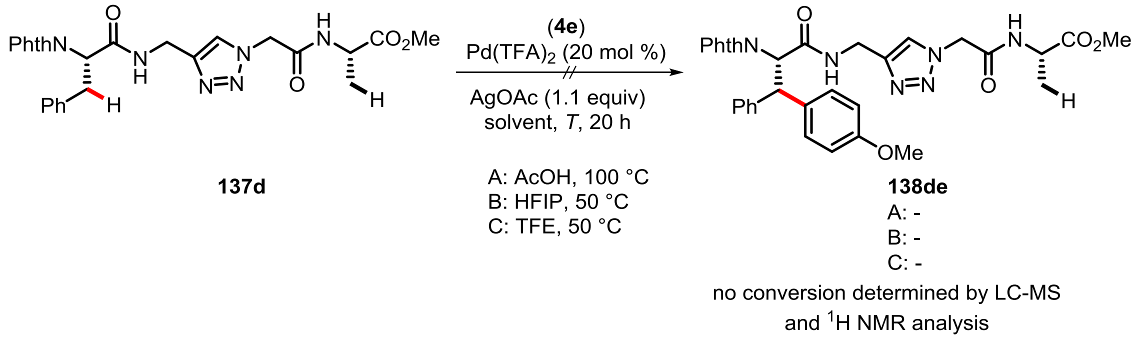
With the optimized conditions in hand, the versatility of the direct C–H arylation was examined with a representative set of iodoarenes **4** (Scheme 73). The reaction with the Fmoc-protected amine **4j** proceeded smoothly and delivered product **138aj** in 69% isolated yield. In the case of a nitrile substituent, the conversion dropped significantly and it was not possible to isolate product **138al** in pure form. The reaction conditions seemed too harsh for 4-iodophenol (**4o**), since no product **138ao** was observed and reisolation of the iodoarene failed, while **137a** could be reisolated in almost quantitative yield. Further arylations were performed by *Dr. Wei Wang* and *Dr. Mélanie M. Lorion*.[241b] They could show that a set of pseudopeptides Phth*N*-Ala-Gly-Tzl-Gly-$AA_{(n)}$-OMe **137** was efficiently arylated with differently substituted iodoarenes **4**.



Scheme 73: Internal triazole-assisted primary C–H arylation of peptides.

3.3.15 Attempted C(sp^3)–H arylation of phenylalanine- and valine-containing peptides

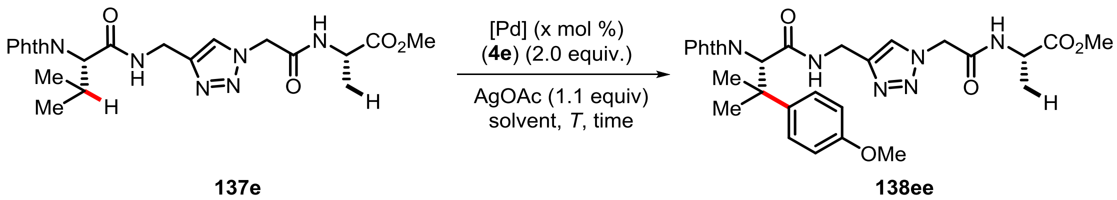
After screening the reaction conditions for the regioselective direct C–H arylation of Phth*N*-Ala-Gly-Tzl-Gly-Phe-OMe **137a**, substrates Phth*N*-Phe-Gly-Tzl-Gly-Ala-OMe **137d** and Phth*N*-Val-Gly-Tzl-Gly-Ala-OMe **137e** were also tested (Table 20). Regarding Phth*N*-Phe-Gly-Tzl-Gly-Ala-OMe **137d** only a small set of solvents was tested. Reacting **137d** with 4-iodoanisole (**4e**), silver acetate and a relatively high catalyst loading of 20 mol % of $Pd(TFA)_2$ at 100 °C in acetic acid delivered no product **138de**. Switching the solvent to hexafluoroisopropanol or trifluoroethanol afforded no conversion (Scheme 74).



Scheme 74: Attempted internal triazole-assisted secondary C–H arylation of peptide **137d**.

Concerning the direct arylation of valine, initially, substrate Phth*N*-Val-Gly-Tzl-Gly-Ala-OMe **137e** was probed with 4-iodoanisole (**4e**), 5.0 mol % of Pd(TFA)$_2$ and 1.1 equivalents of AgOAc in 1,2-dichloroethane at 80 °C. No conversion was observed in this case (Table 20, entry 1). Dichloromethane and toluene proved also unsuitable for the direct arylation (entries 2-3). Increased loading of the palladium catalyst and prolonged reaction time, furnished traces of a molecule, which showed the expected mass by LC-MS analysis, but attemps to isolate this compound were not successful (entries 4, 5). Applying the previously established optimal conditions for the arylation of Phth*N*-Ala-Gly-Tzl-Gly-Phe-OMe **137a** led to trace formation of product **138ee**, which could not be isolated (entry 6).

Table 20: Attempted tertiary C–H arylation of valin containing peptide **137e**.[a]



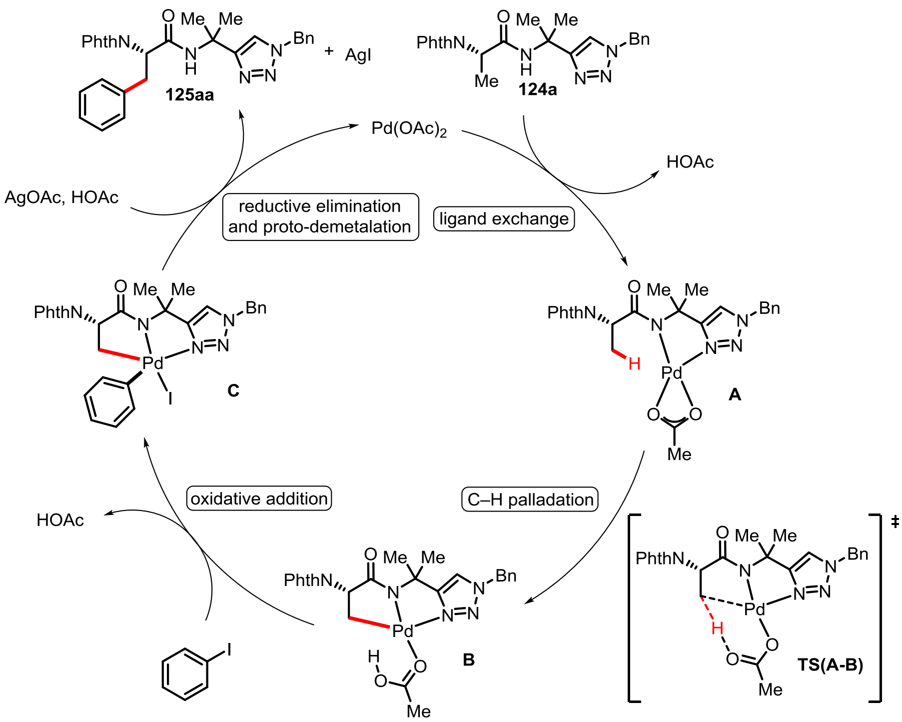
Entry	[Pd] (x mol %)	Solvent	*T* (°C)	Time (h)	Conversion (%)
1	Pd(TFA)$_2$ 5.0	DCE	80	24	-
2	Pd(TFA)$_2$ 5.0	CH_2Cl_2	23	24	-
3	Pd(TFA)$_2$ 5.0	toluene	110	24	-
4	Pd(OAc)$_2$ 10	toluene[b]	110	72	traces[c]
5	Pd(OAc)$_2$ 10	DCE[b]	80	72	traces[c]
6[d]	Pd(TFA)$_2$ 10	DCE	130	20	traces[c]

[a] General reaction conditions: **137e** (0.10 mmol), **4e** (0.20 mmol), [Pd], AgOAc (0.11 mmol), solvent (1.0 mL), *T*, time, under N_2. [b] Solvent (2.0 mL). [c] LC-MS: traces of a molecule with the expected mass. [d] **137e** (0.20 mmol), **4e** (0.40 mmol), Pd(TFA)$_2$ (10 mol %), AgOAc (0.22 mmol), solvent (2.0 mL), 130 °C, 20 h, under N_2.

3.4 Computational studies on the palladium-catalyzed triazole-directed C(sp^3)–H arylations

3.4.1 Computational studies on the palladium-catalyzed triazole-directed C(sp^3)–H arylation of phenylalanine

In the following chapter, the performed computational studies on the triazole-directed C(sp^3)–H arylations of phenylalanine (**124e**), leucine (**127d**) and pseudotetrapeptide (**137a**) will be discussed. Intrigued by the observed selectivities (vide supra) the complete catalytic cycles were investigated, possible intermediates, transition states and the corresponding energy barriers were calculated in order to identify the selectivity-determining step. Geometry optimizations were performed at the TPSS-D3(BJ)/def2-TZVP level of theory, while single-point calculations were performed at the B3LYP-D3(BJ)/def2-TZVP+SMD (*o*-xylene or DCE) (for full details see 6.1). Based on previous findings[133, 183, 185, 220] a plausible mechanism was proposed for alanine (**124a**), which is shown in Scheme 75. Initially, ligand exchange on palladium(II) acetate leads to the formation of palladium(II) complex **A**, which undergoes C–H bond metalation *via* a carboxylate-assisted deprotonation transition state **TS(A-B)** that affords **C**. Oxidative addition of iodobenzene to generate palladium(IV) intermediate **D** is followed by a reductive elimination forming the C–C bond. Proto-demetalation affords the desired product. Silver acetate is proposed to act as halide scavenger, regenerating the active palladium(II) acetate species.[240] It has been shown that the enantio- and diastereo-selectivity is determined in the C–H activation step[21d, 251] or, less likely, in the reductive elimination step,[252] thus, the regioisomeric transition states for these steps were studied to better understand the observed selectivity.



Scheme 75: Proposed catalytic cycle for palladium-catalyzed C–H arylation of TAM-alanine **124a**.

The free energy profile for the C–H activation of *N*-phthaloylphenylalanineTAMamide (**124e**) is shown in Figure 34. Starting from the $Pd_3(OAc)_6$ trimer and substrate **124e** the formation of **1.1** is endergonic by 7.2 kcal/mol. Then, deprotonation of the N–H bond, coordination to the Pd(II) center and release of acetic acid leads to the stable complex **1.2** with one acetate group still coordinated to palladium in a κ^2-fashion. Regarding the diastereoselectivity, the C–H activation of the two viable protons was investigated and the energy barriers for the generation of the new chiral center compared. The pathway leading to the (2*S*,3*S*)-diastereomer (red line) is less favorable compared to the pathway to the (2*S*,3*R*)-diastereomer (black line). Acetate changes from a bidentate (**1.2**) to a monodentate ligand in agostic intermediates **1.3**/**1.3'**, provides a vacant coordination site for the C–H bond. The distances between palladium and hydrogen were relatively short and angles between palladium, hydrogen and carbon were small (Table 24 section 0.6.1.06.1.1.2), which is in good agreement with the known structural properties of agostic interactions.[196b] **1.3'** is 6.5 kcal/mol less stable than **1.3**. It is noteworthy, that the *α*, *β*-hydrogen atoms are almost in a *gauche*-confirmation (dihedral angle ψ(H*α*–C–C–H*β*) 42.5°) in **1.3'**, while **1.3** represents the *anti*-confirmation (dihedral angle ψ(H*α*–C–C–H*β*) -169.6°), which was also observed in the coupling constants $J_{H2\text{-}H3}$ of the isolated products. Both transition states **TS1.(3-4)** and **TS1.(3-4)'** involve simultaneous cleavage of the C–H bond and formation of the palladium–carbon and the oxygen–hydrogen bonds**.** The energy barriers for the C–H activation are 18.1 kcal/mol (**1.2** → **TS1.(3-4)**) and 21.6 kcal/mol (**1.2** → **TS1.(3-4)'**), respectively, thus the C–H activation of the pro-*R* hydrogen atom is more favorable than the C–H activation of the pro-*S* hydrogen atom by 3.5 kcal/mol. The dihedral angles ψ(H–C–C–H) are 44.1° (**TS1.(3-4)'**) and -171.7° (**TS1.(3-4)**). The small dihedral angle in **TS1.(3-4)'** leads to an increased steric hinderance compared to **TS1.(3-4)**. In **TS1.(3-4)'** relatively short H–H distances between the *β*-hydrogen atom and an *α*-hydrogen atom (d(H–H: 2.250 Å)), a hydrogen atom of the phenyl group (d(H–H: 2.216 Å)) and the activated hydrogen atom (d(H–H: 1.553 Å)) have been determined (Figure 35). Furthermore, the C–H distance between the *β*-hydrogen atom and a carbon atom of the phenyl ring is 2.498 Å, which is smaller than the sum of the van-der-Waals-radii[253] C–H: 2.600 Å (C 1.500 Å, H 1.100 Å). The large dihedral angle in **TS1.(3-4)** prevents the close contact between the benzylic hydrogen atoms. The shortest H–H distance found between the *α*-hydrogen atom and a hydrogen atom of the phenyl group is 2.296 Å The transition state structures show only minor differences regarding the C–H activation itself. The H–Pd distance is larger in **TS1.(3-4)** by 0.003 Å, whereas the H–O and the Pd–C distances are larger in **TS1.(3-4)'** by 0.051 Å (H–O) and 0.014 Å (Pd–C). The bond angles α(Pd–H–C) are 81.9° (**TS.(3-4)**) and 83.9° (**TS1.(3-4)'**) (Table 25 section 0.6.1.06.1.1.2). The C–H activation affords the five-membered metallacycle intermediates **1.4** and **1.4'**. The (2*S*,3*R*)-diastereomer **1.4** is 4.4 kcal/mol more stable than the (2*S*,3*S*)-diastereomer **1.4'**. The oxidation state of palladium(II) was retained in this CMD/AMLA type mechanism.

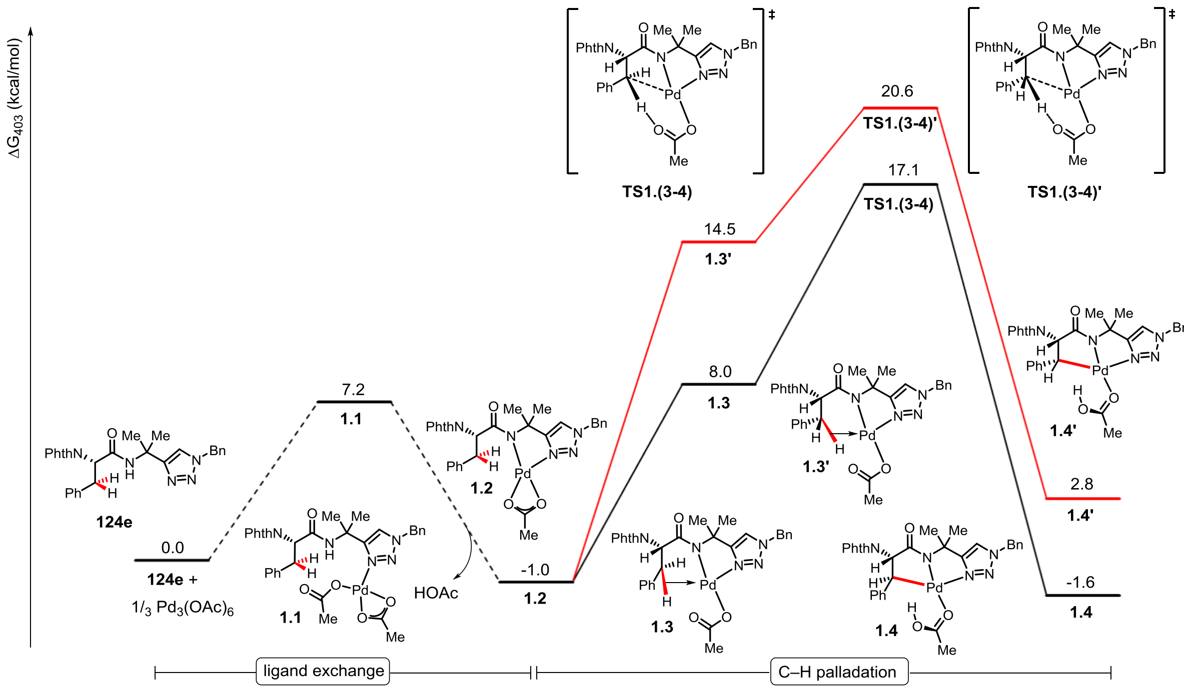


Figure 34: Relative Gibbs free energy diagram for the active palladium catalyst formation and cyclometalation-deprotonation step. Pathway leading to the (2*S*,3*S*)-diastereomer (red), pathway leading to the (2*S*,3*R*)-diastereomer (black).

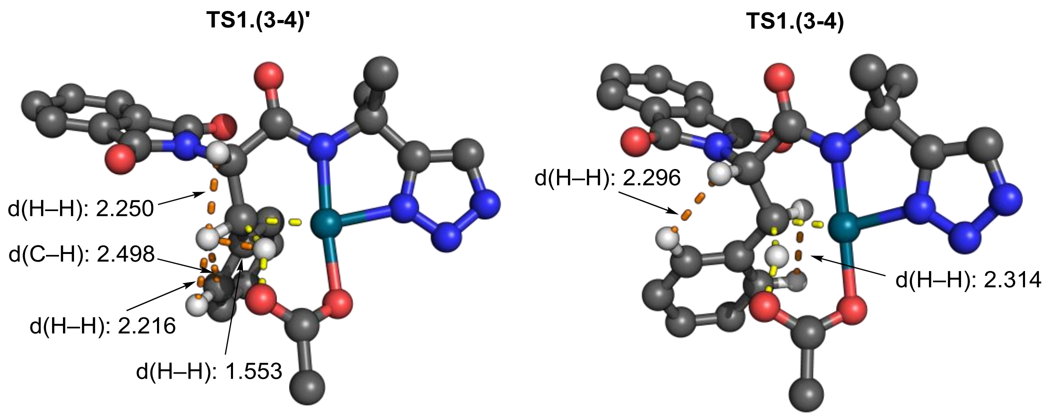


Figure 35: Optimized geometries of transition states **TS1.(3-4)'** (left) and **TS1.(3-4)** (right). Distances are given in Å and non-participating hydrogen atoms have been omitted for clarity.

A Mayer bond order analysis of the agostic intermediates and transition states of the C–H cleavage, indicated the C–H activation within a CMD regime with a dominant C–H cleavage (Table 21). For the C–H bond, the bond order decreases from 0.92 in intermediate **1.2** over 0.65 in intermediate **1.3** to a value of 0.23 in **TS1.(3-4)**. The values for the diastereomeric structures **1.3'** and **TS1.(3-4)'** are 0.63 and 0.29, respectively. The values for the bond orders are in line with the observed C–H distances. Here, the C–H distance was found to increase from 1.097 Å in **1.2**, over 1.151 Å (**1.3**) and 1.178 Å (**1.3'**) to 1.477 Å (**TS1.(3-4)**) and 1.431 Å (**TS1.(3-4)'**). The bond order of the O–H bond increases from <0.1 in **1.2** over 0.13 (**1.3/1.3'**) and to 0.36 in **TS1.(3-4)** and 0.31 in **TS1.(3-4)'**, while at the same time the bond order of the Pd–C bond increases from a neglectable value of <0.1 in **1.2** over 0.31 (**1.3/1.3'**) to 0.48

(**TS1.(3-4)**) and 0.42 (**TS1.(3-4)’**). Here, the O–H distance was found to decrease from 2.657 Å in palladacycle **1.2** over 2.150 Å (**1.3**) and 2.083 Å to 1.397 Å (**TS1.(3-4)**) and 1.448 Å (**TS1.(3-4)’**).

Table 21: Mayer bond order analysis for the C–H palladation step.

Bond	**1.2**	**1.3**	**1.3’**	**TS1.(3-4)**	**TS1.(3-4)’**
C–H	0.9208	0.6454	0.6302	0.2302	0.2880
Pd–C	<0.1	0.3062	0.3073	0.4766	0.4227
O–H	<0.1	0.1316	0.1285	0.3647	0.3126

Consequently, the calculations were also performed with a trifluoroacetate ligand instead of acetate in order to elucidate the origin of the higher reactivity which had been observed with $Pd(TFA)_2$ compared to $Pd(OAc)_2$. Figure 36 shows the free energy profile for the reaction starting from trimeric $Pd_3(TFA)_6$ and substrate **124e**. The formation of the (2*S*,3*R*)-diastereomer (black line) is energetically more favorable then the formation of the (2*S*,3*S*)-diastereomer (red line), which is in good agreement with the experimental results. Coordination of the triazole nitrogen atom to palladium is endergonic by 3.5 kcal/mol generating intermediate **1.1a**. Subsequent deprotonation of the amide, coordination to palladium(II) and release of acetic acid leads to complex **1.2a**, which is 0.4 kcal/mol more stable than $Pd_3(TFA)_6$. Relaxed surface scans of the Pd–H distance led to intermediates **1.3a**/**1.3a’** and transition states **TS1.(3-4)a**/**TS1.(3-4)a’**. NBO analysis of intermediates **1.3a** and **1.3a’** confirmed agostic interactions comparable to **1.3**/**1.3’** (Table 24 section 6.1.1.2) The energy differences between diastereomeric intermediates **1.3a**, **1.3a’** and transition states **TS1.(3-4)a**, **TS1.(3-4)a’** are 4.7 kcal/mol and 2.2 kcal/mol, respectively. The *trans*-arragement of the *α*,*β*-hydrogen atoms in **TS1.(3-4)a** results in significantly longer distances (d(H–H) and d(C–H)) compared to **TS1.(3-4)a’** (Figure 37), diminishing the steric repulsion, thus explaining the lower energy barrier for the C–H cleavage step. The energy barriers for the C–H activation are 15.8 kcal/mol (**1.2a** → **TS1.(3-4)a**) and 18.0 kcal/mol (**1.2a** → **TS1.(3-4)a’**), which is lower than that for the reaction with an acetate ligand in which the energy barriers are 18.1 kcal/mol (**1.2** → **TS1.(3-4)**) and 21.6 kcal/mol (**1.2** → **TS1.(3-4)’**). Trifluoroacetate stabilizes the agostic intermediate prior to the C–H activation, the transition states and lowers the energy barrier. Cyclometalated intermediate **1.4a’** is 6.5 kcal/mol less favorable than **1.4a**.

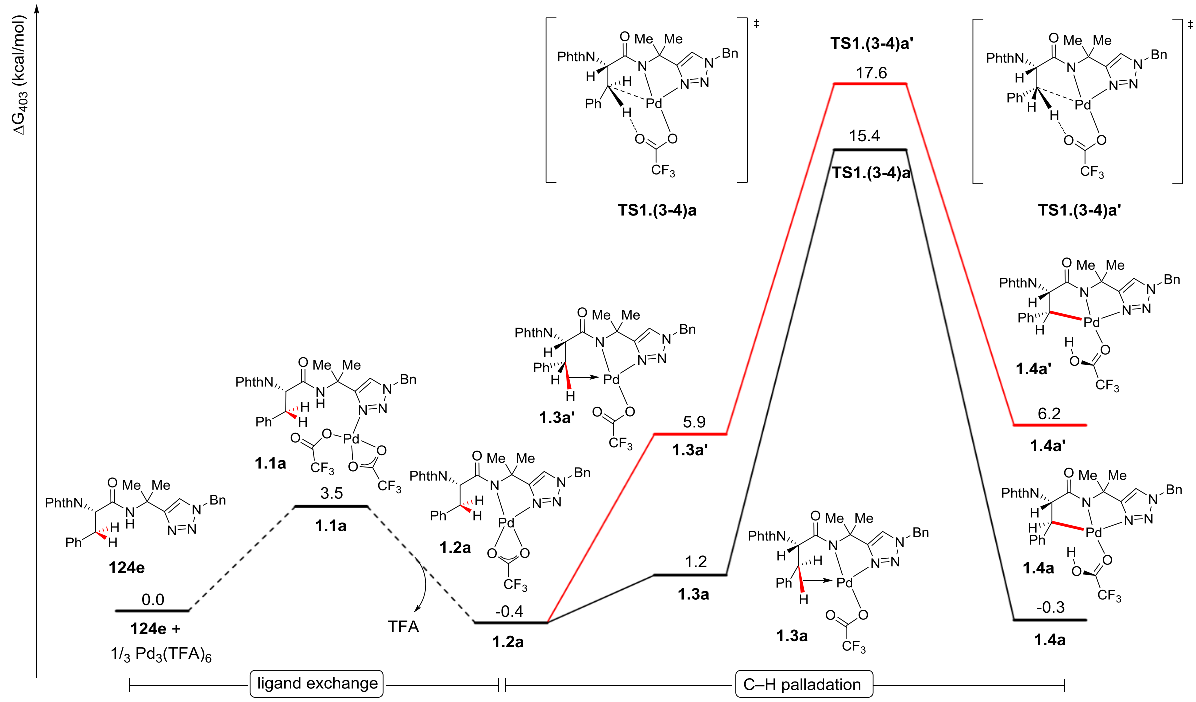


Figure 36: Relative Gibbs free energy diagram for the active palladium catalyst formation and cyclometallation-deprotonation step. Pathway leading to the (2*S*,3*S*)-diastereomer (red), pathway leading to the (2*S*,3*R*)-diastereomer (black).

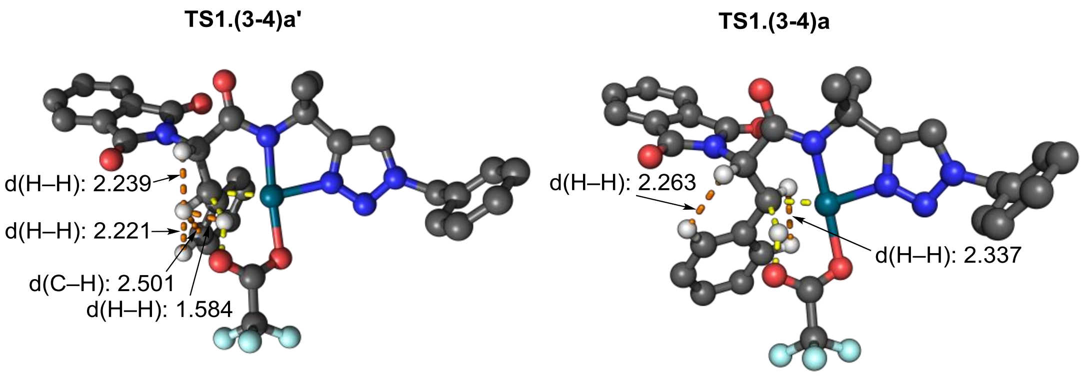


Figure 37: Optimized geometries of transition states **TS1.(3-4)a'** (left) and **TS1.(3-4)a** (right). Distances are given given in Å and non-participating hydrogen atoms have been omitted for clarity.

In a Mayer bond order analysis for the C–H palladation the bond order of the C–H bond was found to decrease from 0.92 in complex **1.2a** over 0.16 and 0.23 in the transition states **TS1.(3-4)a/TS1.(3-4)a'** to neglectable value of <0.1 in the palladacycles **1.4a** and **1.4a'** (**Table 22**. At the same time, the bond order of the Pd–C bond increases from <0.1 in **1.2a** over 0.50 (**TS1.(3-4)a**) and 0.44 (**TS1.(3-4a)a'**) to 0.59 in and 0.71 in the palladacycle **1.4a** and **1.4a'**. The observed distances are in line with the calculated bond orders. Here, the C–H distance was found to increase from 1.097 Å in **1.2a** over 1.592 Å (**TS1.(3-4)a**) and 1.538 Å (**TS1.(3-4)a'**) to 3.048 Å (**1.4a**) and 2.667 Å (**1.4a'**), while the Pd–C distance decreased from 3.384 Å (**1.2a**) over 2.164 (**TS1.(3-4)a**) and 2.175 Å (**TS1.(3-4)a'**) to 2.060 Å and 2.051. Å in the palladacycles **1.4a** and **1.4a'**, respectively. Additionally, the O–H bond order increases from <0.1 (**1.2a**) over 0.37 (**TS1.(3-4)a**) and 0.35 (**TS1.(3-4)a'**) to final values of 0.72 (**1.4a**) and 0.71 (**1.4a'**), while the observed O–H distance decreases from 2.661 Å (**1.2a**) over 1.378 Å (**TS1.(3-4a)**) and 1.377 Å (**TS1.(3-4)a'**) to final values of 1.023 Å (**1.4a**) and 1.028 Å (**1.4a'**).

Table 22: Mayer bond order analysis for the C–H palladation step.

Bond	**1.2a**	**1.3a**	**1.3a'**	**TS1.(3-4)a**	**TS1.(3-4)a'**	**1.4a**	**1.4a'**
C–H	0.9224	0.6397	0.5392	0.1605	0.2295	<0.1	<0.1
Pd–C	<0.1	0.1848	0.1985	0.4989	0.4386	0.5898	0.7127
O–H	<0.1	<0.1	<0.1	0.3661	0.3498	0.7192	0.7104

With the results for the six-membered concerted metalation-deprotonation mechanism in hand, other mechanisms, namely the oxidative addition leading to a palladium(IV)-hydride species and ambiphilic metal-ligand activation *via* a four-membered transition state (AMLA-4) were studied. The results for the AMLA-4 mechanism are shown in Figure 38. The pathway leading to the (2*S*,3*R*)-product **1.4-4** (black line) is also favored by this mechanism. Starting from complex **1.2** the initial formation of agostic complexes **1.3-4** and **1.3'-4** is endergonic and the values of 9.6 kcal/mol and 13.8 kcal/mol are comparable to **1.3**/**1.3'** (Figure 34). The subsequent concerted C–H bond cleavage and Pd–C bond formation would occur via transition states **TS1.(3-4)-4** and **TS1.(3-4)'-4** to afford intermediates **1.4-4**/**1.4'-4**. It is noteworthy, that the energy barriers for the C–H cleavage via a four-membered transition state are 31.8 kcal/mol (**1.3** → **TS1.(3-4)-4**) and 37.1 kcal/mol (**1.3** → **TS1.(3-4)'-4**), respectively. Compared to the energy barriers for the six-membered concerted metalation-deprotonation mechanism the AMLA-4-type is less favorable by 13.7 kcal/mol and 15.5 kcal/mol, which indicates that the C–H activation proceeding via a four-membered transition state is very unlikely. A comparison of the structures shows that the four-membered transition states have significantly longer Pd–O bonds while the Pd–C bonds are comparable (Table 26 section 6.1.1.2).

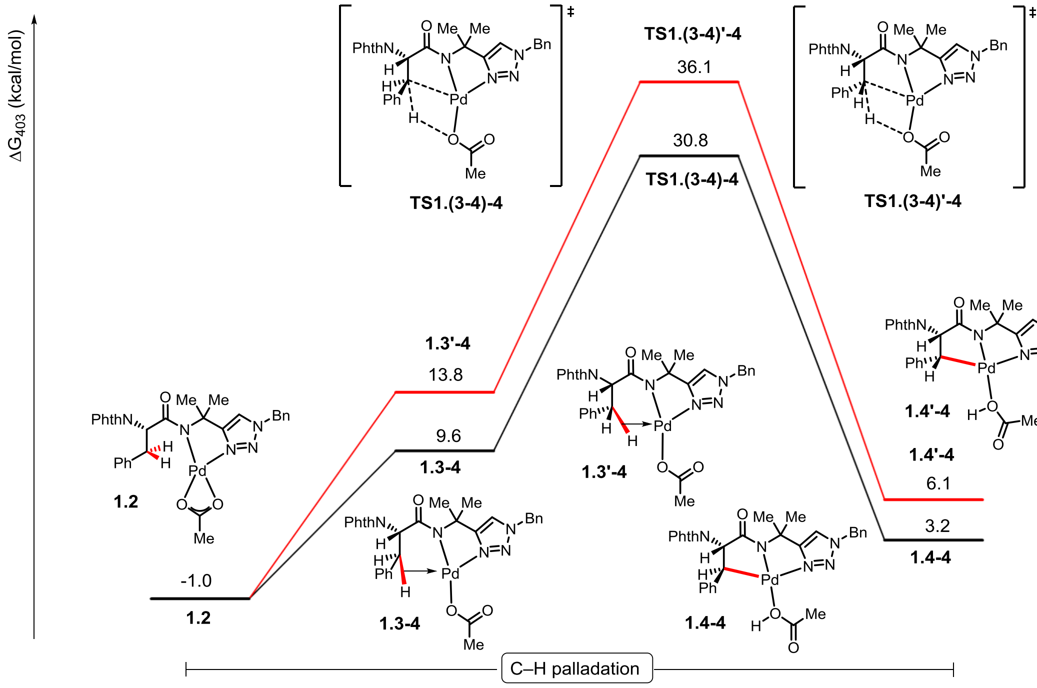


Figure 38: Relative Gibbs free energy diagram for the C–H activation *via* an AMLA-4 mechanism. Pathway leading to the (2*S*,3*S*)-diastereomer (red), pathway leading to the (2*S*,3*R*)-diastereomer (black).

The oxidative addition of the benzylic C–H bond leading to the formation of a Pd(IV)-alkyl-hydride intermediate could not be located successfully. Starting from palladium complex **1.2** relaxed surface scans computed at the TPSS-D3(BJ)/def2-SVP level of theory and subsequent optimizations led to palladium(IV) complexes **1.4-OA**/**1.4'-OA** and the already known agostic complexes **1.3**/**1.3'**, but failed for the transition states. Figure 39 shows the Pd(IV)-alkyl-hydride intermediates in comparison to the Pd(II) species **1.4**/**1.4'**. **1.4-OA**/**1.4'-OA** have a relative Gibbs free energy of 21.9 kcal/mol and 25.9 kcal/mol, which are the highest values for intermediates in all calculations performed on phenylalanine in this thesis and even higher than many of the transition states, indicating that this pathway *via* oxidative addition is highly unfavorable.

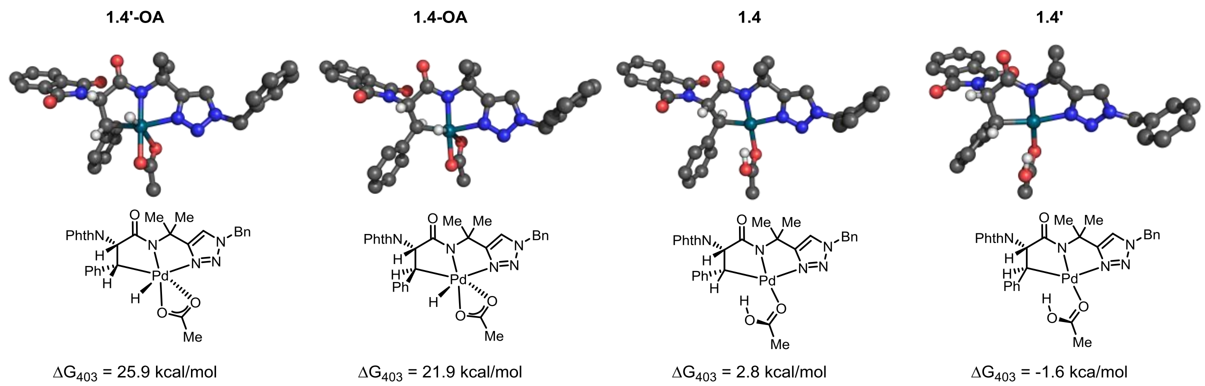


Figure 39: Comparison of palladium(IV) complexes **1.4'-OA**/**1.4-OA** and palladium(II) complexes **1.4**/**1.4'**. Gibbs free energies (ΔG_{403}) are with respect to $Pd_3(OAc)_6$ and separate substrate. Non-participating hydrogen atoms have been omitted for clarity.

Next, the oxidative addition of 4-fluoroiodobenzene (**4b**) and the subsequent reductive elimination forming the C–C bond was investigated. It is noteworthy, that the arene has two possible sites to attack the palladium centre: from the front (pathway A) and the backside (pathway B) of the palladium-triazole plane. The results for pathway A are shown in Figure 40.

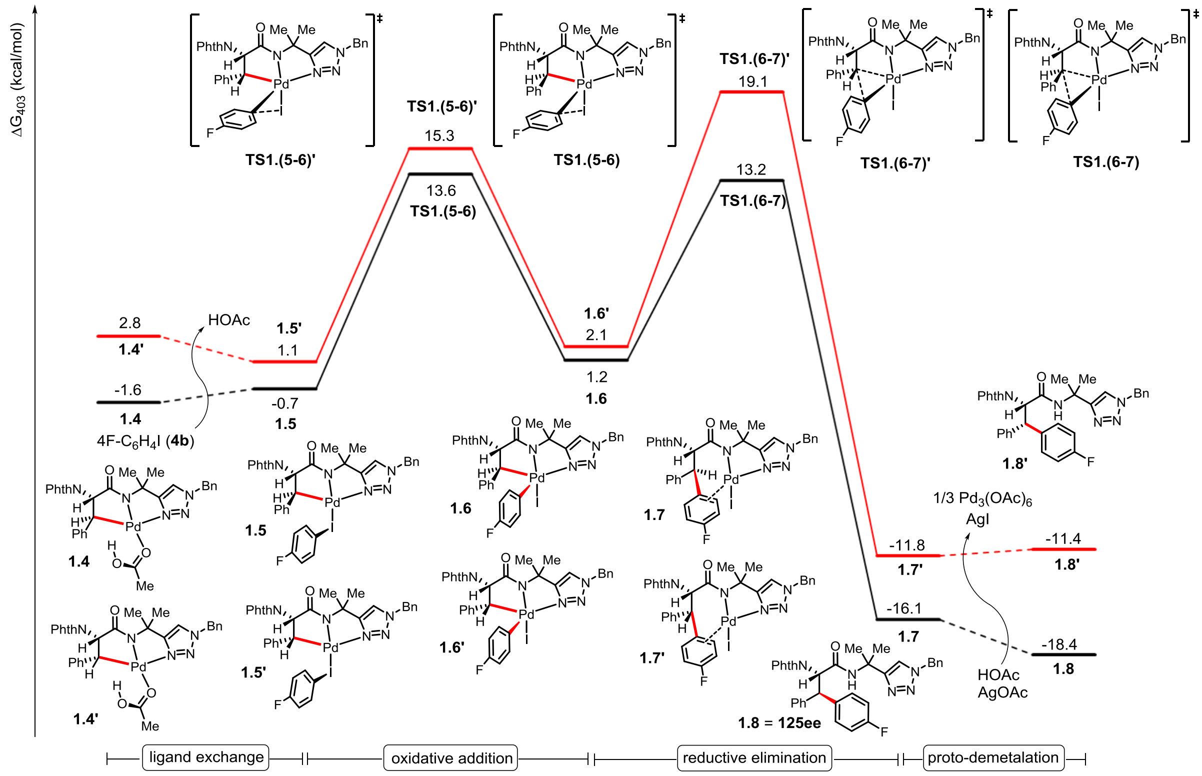


Figure 40: Relative Gibbs free energy diagram for the oxidative addition and reductive elimination pathway A. Pathway leading to the (2*S*,3*S*)-diastereomer (red), pathway leading to the (2*S*,3*R*)-diastereomer (black).

In general, the *cis*-configuration (red line) of the *α*,*β*-protons [(2*S*,2*S*)-diastereomer] is energetically less favorable than the *trans*-configuration (black line) [(2*S*,3*R*)-diastereomer]. Moreover, the transition states of the oxidative addition and reductive elimination are lower in energy (relative Gibbs free energy and energy barrier) than the transition states of the C–H cleavage. Ligand exchange of acetic acid with 4-fluoroiodobenzene (**4b**) leads to formation of intermediates **1.5** and **1.5'.** The energy difference between **1.5** and **1.5'** is 1.8 kcal/mol. The transition states **TS1.(5-6)** and **TS1.(5-6)'** of the oxidative addition have an energy barrier of 15.2 kcal/mol and 16.3 kcal/mol, respectively. From intermediates **1.5**/**1.5'** to the transition states **TS1.(5-6)**/**TS1.(5-6)'** the 4-fluorophenylring itself rotates, so that the dihedral angle ψ(Pd–I–C–C) changes significantly from 149.0° (**1.5**) to 103.7° (**TS1.(5-6)**) and from -157.1° (**1.5'**) to -99.5° (**TS1.(5-6)'**) (Atoms marked with blue circles in Figure 41).

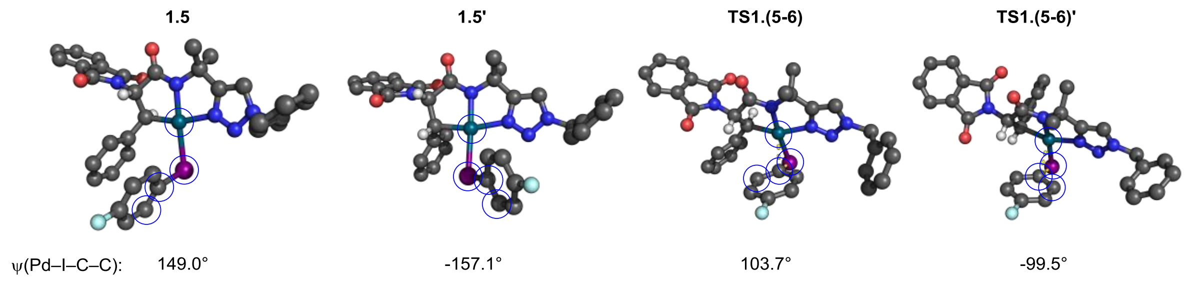


Figure 41: Optimized geometries of intermediates **1.5**/**1.5'** and transition states **TS1.(5-6)**/**TS1.(5-6)'** with dihedral angle ψ(Pd–I–C–C). Non-participating hydrogen atoms have been omitted for clarity.

With formation of the palladium(IV) complexes the 4-fluorophenyl group rotates once more and the dihedral angles ψ(N–Pd–C–C) are now 144.6° (**1.6**) and -76.9° (**1.6'**). Palladium(IV) complex **1.6** is slightly (0.9 kcal/mol) more stable than **1.6'**. The reductive elimination delivering **1.7** *via* transition state **TS1.(6-7)** is favored under this mechanism with an energy barrier of 14.8 kcal/mol (**1.4** → **TS1.(6-7)**), while transition state **TS1.(6-7)'** has an energy barrier of 20.1 kcal/mol (**1.2** → **TS1.(6-7)'**). The 4-fluorophenylring has rotated further and the dihedral anlges ψ(N–Pd–C–C) are 171.9° (**TS1.(6-7)**) and -43.5° (**TS1.(6-7)'**) (Atoms marked with blue circles in Figure 42). In **TS1.(6-7)'** the 4-fluorophenyl group is closer to the *β*-hydrogen atom (d(C–H): 2.157 Å and 2.444 Å), while in **TS1.(6-7)** the shortest C–H distance between the phenyl group and the 4-fluorophenyl group is 0.419 Å longer (d(C–H): 2.567 Å)

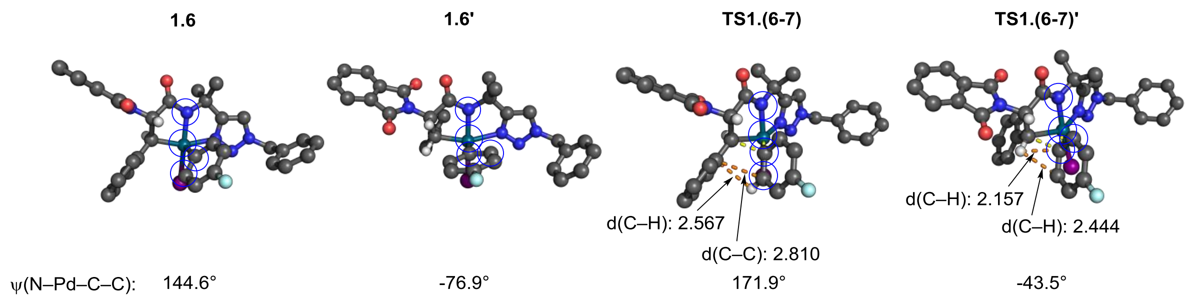


Figure 42: Optimized geometries of intermediates **1.6**/**1.6'** and transition states **TS1.(6-7)**/**TS1.(6-7)'** with selected distances and dihedral angle ψ(N–Pd–C–C). Distances are given in Å. Non-participating hydrogen atoms have been omitted for clarity.

The C–H activation *via* a CMD mechanism has a higher energy barrier of 18.1 kcal/mol and 21.6 kcal/mol (Figure 34), which indicates that the C–H activation is the rate-determining step. Palladium coordinates to the 4-fluorophenylring in a η^2-fashion in both intermediates **1.7**/**1.7'**, before proto-demetalation with silveracetate and acetic acid generates products **1.8 (125ee)**/**1.8'**. (2*S*,3*R*)-**1.8** is 7.0 kcal/mol more stable than (2*S*,3*S*)-**1.8'**. The C–H activation step was found to be the diastereoselectivity-determining step, because an inversion of the generated stereocenter was not occurring during the oxidative addition or reductive elimination. The Boltzmann distribution of the transition state isomers **TS1.(3-4)**/**TS1.(3-4)'** and **TS1.(3-4)a**/**TS1.(3-4)a'** for the CMD mechanisms with acetate and trifluoroacetate ligands coordinated to palladium (OAc: $\Delta\Delta G^{‡}$ = 3.5 kcal/mol; TFA: $\Delta\Delta G^{‡}$ = 2.2 kcal/mol) at 403 K indicates a (2*S*,3*R*):(2*S*,3*S*) product ratio of 98.8:1.2 (OAc) and 94.0:6.0 (TFA), which is in very good agreement with the selectivity observed in the experiment. Besides pathway A, another possible pathway B was explored, where the 4-fluoroidobenzene is located at the back of the palladium-triazole plane (Figure 43). The (2*S*,3*R*)-diastereomer (black line) was found to be energetically more favorable than the corresponding (2*S*,3*S*)-diastereomer (red line).

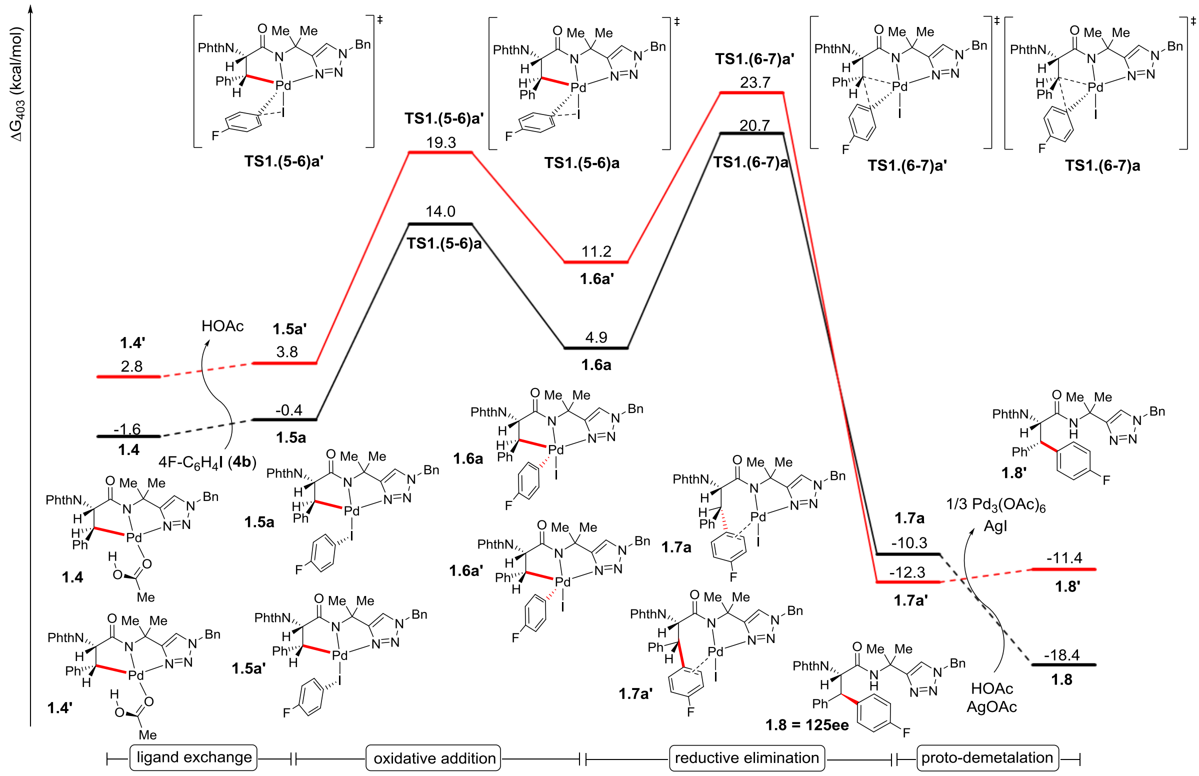


Figure 43: Relative Gibbs free energy diagram for the oxidative addition and reductive elimination pathway B. Pathway leading to the (2*S*,3*S*)-diastereomer (red), pathway leading to the (2*S*,3*R*)-diastereomer (black).

The first step is the exergonic ligand exchange to form palladium(II) complexes **1.5a** and **1.5a'**. The oxidative addition requires an energy barrier of 15.6 kcal/mol (**1.4** → **TS1.(5-6)a**) and 20.3 kcal/mol (**1.2** → **TS1.(5-6)a'**), respectively. The energy barriers of the CMD mechanism are higher in energy by 2.5 kcal/mol ((2*S*,3*R*)-diastereomer) and 1.3 kcal/mol ((2*S*,3*S*)-diastereomer). As in pathway A the 4-fluorophenyl group rotates and the dihedral angles ψ(Pd–I–C–C) change from -150.7° (**1.5a**) to -107.6° (**TS1.(5-6)a**) and from -165.4° (**1.5a'**) to -112.0° (**TS1.(5-6)a'**) (Figure 44). The *cis*-configuration of the α,β-hydrogen atoms brings the phenyl and the phthaloyl group closer together, thus significantly shorter N–C distances were found in these palladium complexes (d(N–C): 2.889 Å in **TS1.(5-6)a'** vs 3.033 Å in **TS1.(5-6)a**). The distance between the nitrogen atom N2 of the triazole and the hydrogen atom at the *ortho*-position of the 4-fluoroiodobenzene is d(N–H): 2.233 Å in **TS1.(5-6)a'** and 2.399 Å in **TS1.(5-6)a**. Compared to the sums of the van-der-Waals-radii[253] N–C: 3.250 Å (C 1.700 Å, N 1.550 Å) and N–H: 2.550 Å (N 1.550 Å, H 1.100 Å) the short distances cause steric repulsion and higher relative Gibbs free energies in the case of the *cis*-configuration. Another difference is the bond angle α(N–Pd–I), which is 162.3° in **TS1.(5-6)a** and 146.7° in **TS1.(5-6)a'**, so that the iodine atom is now located in front of the palladium-triazole plane.

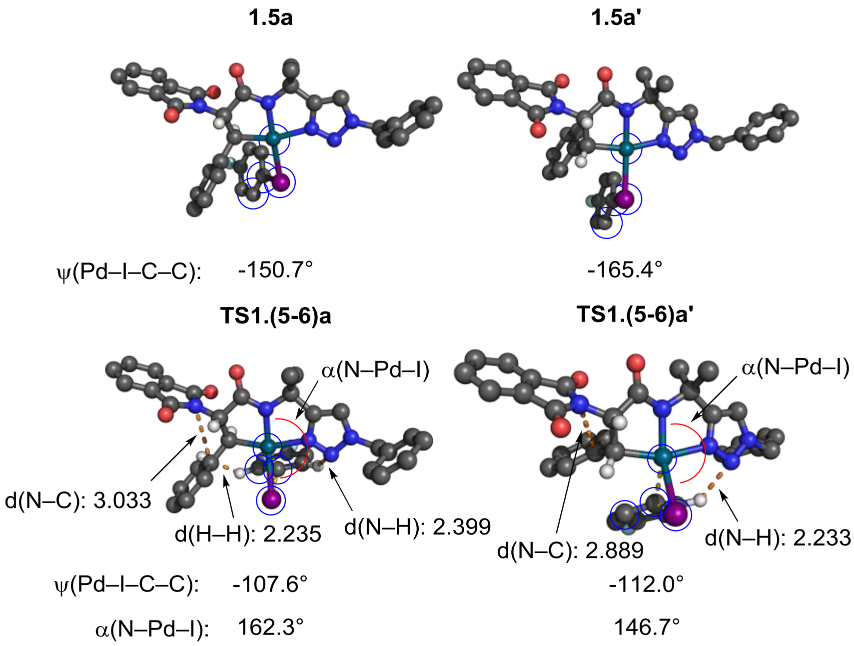


Figure 44: Optimized geometries of intermediates **1.5a**/**1.5a'** and transition states **TS1.(5-6)a/TS1.(5-6)a'** with selected distances, bond angles α(N–Pd–I) and dihedral angles ψ(Pd–I–C–C). Distances are given in Å. Non-participating hydrogen atoms have been omitted for clarity.

Palladium(IV) complex **1.6a** is 6.3 kcal/mol more stable than **1.6a'**. Transition state **TS1.(6-7)a'** is 3.0 kcal/mol less stable than the corresponding transition state **TS1.(6-7)a**. The overall energy barriers for the reductive elimination were determined to be 24.7 kcal/mol (**1.2** → **TS1.(6-7)a'**) and 22.3 kcal/mol (**1.4** → **TS1.(6-7)a**), respectively. The dihedral angle ψ(N–Pd–C–C) changes from -48.6° (**1.6a**) and -161.4° (**1.6a'**) to 33.3° (**TS1.(6-7)a**) and -176.9° (**TS1.(6-7)a'**) (Figure 45). The *cis*-configuration of the *α,β*-hydrogen atoms results in more steric hinderance in the transition state **TS1.(6-7)s'** compared to the *trans*-configuration in **TS1.(6-7)a**. The shortest distance between the *β*-hydrogen atom and a carbon atom of the phenyl group is d(H–C): 2.454 Å in **TS1.(6-7)a'**. The N–C distance between the phthaloyl-protected nitrogen atom and the C1 carbon atom of the phenyl group is d(N–C): 2.908 Å. The shortest H–H distances between the *α*- and the *β*-hydrogen atoms are d(H–H): 2.160 Å, and between the *β*-hydrogen atom and the *ortho* hydrogen atom of the phenyl group is d(H–H): 2.156 Å. In **TS1.(6-7)a** the distance between the *β*-hydrogen atom and a carbon atom of the phenyl group is d(H–C): 2.549 Å. The N–C distance between the phthaloyl-protected nitrogen and the C1 atom of the phenyl group is d(N–C): 3.342 Å (not marked in Figure 45), which 0.434 Å longer compared to the N–C distance in **TS1.(6-7)a'**. The H–H distance between the *α*-hydrogen atom and an *ortho*-hydrogen atom of the phenyl group is d(H–H): 2.119 Å . Compared to the energy barriers of the C–H cleavage step the energy barriers of the reductive elimination of both diastereomeric transition states are higher in energy by 4.2 kcal/mol ((2*S*,3*R*)-diastereomer) and 3.1 kcal/mol ((2*S*,3*S*)-diastereomer), which indicates that the reductive elimination is the rate-determining step. The formation of the C–C bond affords the stable intermediates **1.7a** and **1.7a'**, in which the 4-fluorophenyl groups are coordinated in an η^2-coordination to palladium.

The last step is the proto-demetalation with acetic acid and AgOAc, releasing the products **1.8 (125ee)**/**1.8’**, silveriodide and palladium acetate.

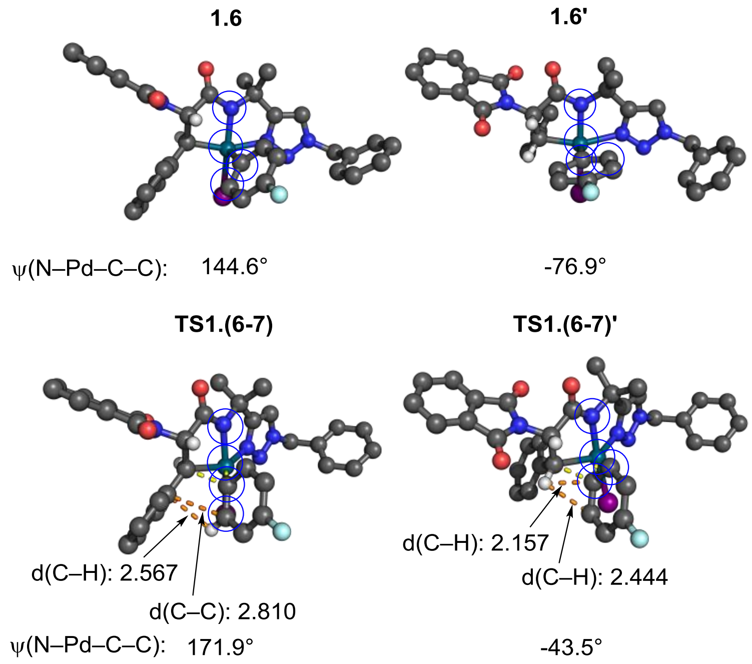


Figure 45: Optimized geometries of intermediates **1.6a**/**1.6a’** and transition states **TS1.(6-7)a**/**TS1.(6-7)a’** with selected distances and dihedral angles ψ(N–Pd–C–C). Distances are given in Å. Non-participating hydrogen atoms have been omitted for clarity.

In pathway A and B, it was suggested that iodine abstraction and regeneration of palladium acetate occurs after the formation of the C–C bond. In spite of the fact that the calculated intermediates, transition states and Gibbs free energies were reasonable and supported the proposed catalytic cycle, additional pathways C and D involving a halogen-acetate ligand exchange directly after the oxidative addition were investigated. Pathway C shows the alternative mechanism leading to the (2*S*,3*R*)-diastereomer (Figure 46), while in pathway D the (2*S*,3*S*)-diastereomer is formed. Starting with the product of the oxidative addition palladium(IV) intermediates **1.6**/**1.6a**, addition of AgOAc generates AgI and intermediates **1.7b**/**1.7c**, which differ in energy by 0.7 kcal/mol. Transition state **TS1.(7-8)c** is 9.9 kcal/mol less stable than **TS1.(7-8)b** and the overall energy barriers of the reductive elimination are 24.6 kcal/mol (**1.4** → **TS1.(7-8)b**) and 34.5 kcal/mol (**1.4** → **TS1.(7-8)c**), which is 6.5 kcal/mol (*trans*-configuration of *α,β*-hydrogen atoms) and 12.9 kcal/mol (*cis*-configuration of *α,β*-hydrogen atoms) higher in energy compared to the C–H activation via a CMD mechanism. In palladium complex **TS1.(7-8)c** the *β*-hydrogen atom is on the same site of the palladium-triazole plane as the 4-fluorophenyl group. The shortest C–H distance between the *β*-hydrogen atom and a carbon atom of the 4-fluorophenyl group is 2.069 Å (Figure 47), which is smaller than the sum of van-der-Waals-radii[253] of C (1.700 Å) and H (1.100 Å). This steric repulsion destabilizes **TS1.(7-8)c**. There is no comparable close contact in **TS1.(7-8)b**. It was found that the acetate coordination shifts from κ^2 to κ^1 (transition state) and finally palladium coordinates η^2 to the 4-fluorophenylgroup. Dissociation of the arene and κ^2-coordination of palladium to acetate leads to intermediates **1.9b** and **1.9c**. **1.9c** is 11.6 kcal/mol more stable than **1.9b**, but both complexes are more stable than 1/3 $Pd_3(OAc)_6$ and the separate substrate. The last step is the proto-demetalation with acetic acid, releasing product **1.8 (125ee)** and regenerating palladium acetate.

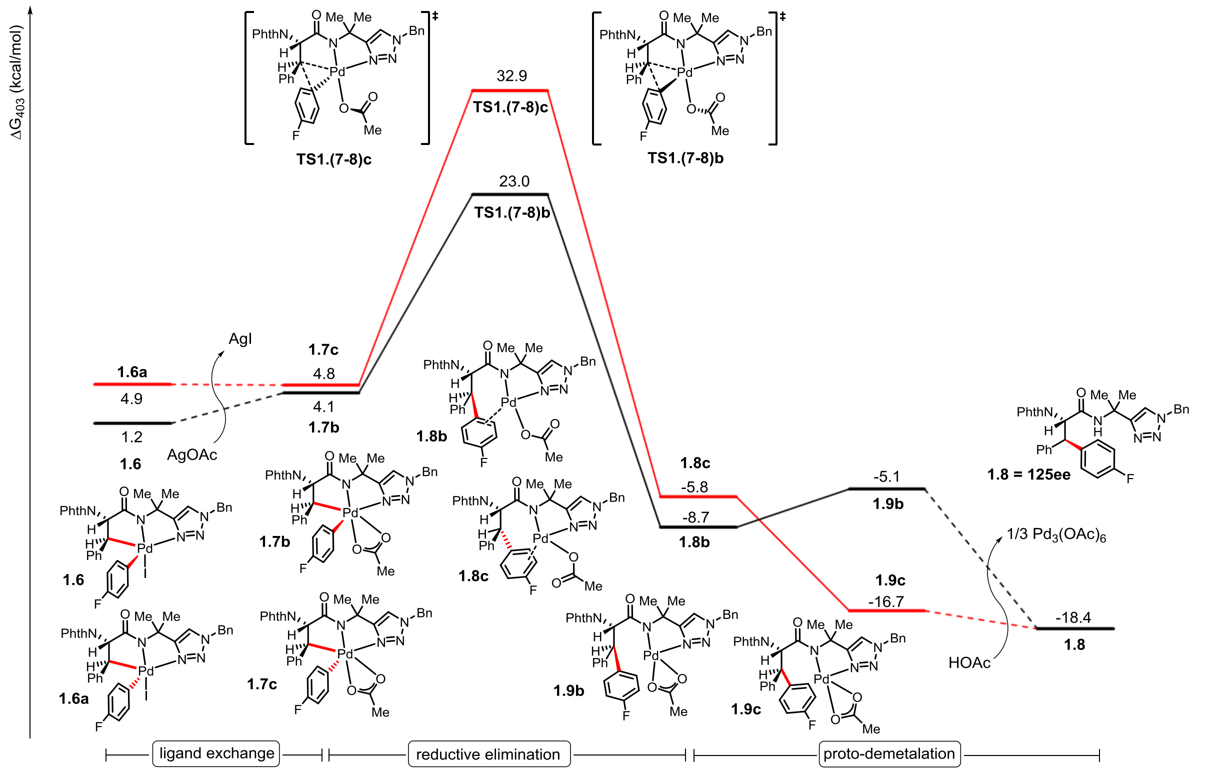


Figure 46: Relative Gibbs free energy diagram for the reductive elimination pathway C. Arene moiety located in front (black), arene moiety at the back (red) of the palladium-triazole plane.

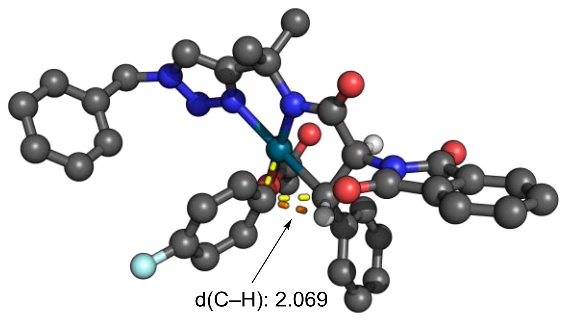


Figure 47: Optimized geometry of transition state **TS1.(7-8)c** with selected distance given in Å.

The energy profile for the alternative C–C bond formation leading to the (*S*,*S*)-diastereomer is shown in Figure 48. Starting from intermediates **1.6'** and **1.6a'** iodine-acetate ligand exchange delivers intermediates **1.7b'** and **1.7c'**. Transition state **TS1.(7-8)b'** is 2.1 kcal/mol less favorable than **TS1.(7-8)c'** and the overall energy barriers of the reductive elimination are 33.2 kcal/mol (**1.2** → **TS1.(7-8)b'**) and 31.1 kcal/mol (**1.2** → **TS1.(7-8)c'**), respectively. The acetate changes from a bidentate to a monodentate ligand. Palladium coordinates to a C–C bond from the phenyl group in intermediate **1.8b'**, whereas in **1.8c'** it is a C–C bond from the 4-fluorophenylgroup. Dissociation of the arene and

κ^2-coordination of palladium to acetate affords intermediates **1.9b'/1.9c'**. Finally, protonation with acetic acid affords product **1.8'**. The energy barriers of the reductive elimination with an acetate coordinated to palladium (pathway C and D) are higher in energy than the energy barriers with an iodine ligand coordinated to palladium (pathway A and B).

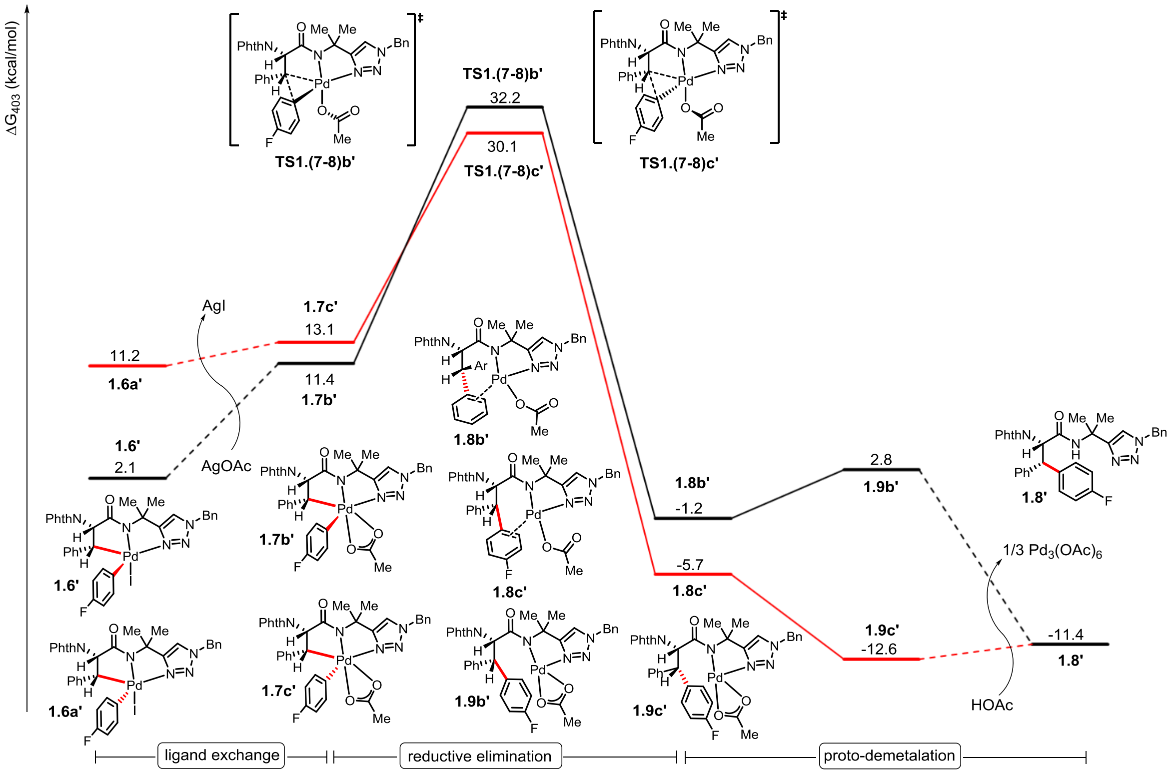


Figure 48: Relative Gibbs free energy diagram for the reductive elimination pathway D. Arene moiety located in front (black), arene moiety at the back (red) of the palladium-triazole plane.

It is noteworthy, that in all four studied pathways A, B, C and D the oxidative addition and reductive elimination steps occur with retention of the stereocenter formed in the C–H cleavage step. The C–H activation is therefore the diastereoselectivity-determining step. Based on the energy barriers it be can assumed that the (*S*,*R*)-diastereomeric palladacycle with the *trans*-configuration of the *α*,*β*-hydrogen atoms is the major product of the C–H activation, that undergoes subsequent oxidative addition and reductive elimination to form the observed (*S*,*R*)-diastereomeric arylated product. Reductive elimination step has the highest energy barrier is thus the rate-determining step.

3.4.2 Computational studies on the palladium-catalyzed triazole-direct C(sp^3)–H arylation of leucine

The palladium-catalyzed triazole-directed C(sp^3)–H arylation was successfully employed on alanine and phenylalanine generating the products in good yields with ample scope. Unfortunately, tryptophan was not a suitable substrate and leucine gave rather low yields. In the case of leucine, the reaction has not only to be diastereo- but also position-selective, due to the two secondary C(sp^3)–H bonds and one remote tertiary C(sp^3)–H bond, which could be functionalized. Computational studies were performed in order to elucidate the mechanism and identify the selectivity-determining step. The energy profile for the C–H activation of the secondary C–H bonds is shown in Figure 49. After coordination of the nitrogen atom N3 of the triazole to palladium, deprotonation of the amide N–H and release of acetic acid, the C–H activation proceeds *via* one out of three stereoisomers. The first step is the formation of the intermediates **2.3**, **2.3a** and **2.3'** with the agostic interaction between the C(sp^3)–H bond and palladium. In **2.3** the *α*,*β*-hydrogen atoms are in an *anti*-arrangement (dihedral angle ψ(H*α*–C–C–H*β*): -170.4°), while in **2.3a** (dihedral angle ψ(H*α*–C–C–H*β*): 83.5°) and **2.3'** (dihedral angle H*α*–C–C–H*β*: 52.3°) the hydrogen atoms are in a *gauche*-arrangement. The transition states **TS2.(3-4)'**, **TS2.(3-4)** and **TS2.(3-4)a** have nearly the same relative Gibbs free energy and the crucial bond lengths and angles are almost identical (Table 28, Table 29 and Table 30 section 6.1.2.2). The small energy differences indicate, that the different orientations of the isopropryl group and hence differences in sterical hinderance does not contribute much to the overall energy of the transition state. **TS2.(3-4)'** is 1.0 kcal/mol more stable than **TS2.(3-4)a** and only 0.2 kcal/mol more stable than **TS2.(3-4)**. **TS2.(3-4)** and **TS2.(3-4)a** lead to the (2*S*,3*S*)-diastereomer, whereas **TS2.(3-4)'** leads to the (2*S*,3*R*)-diastereomer. The cyclometalated products **2.4** and **2.4a** have almost the same structure, but the acetic acid is located on opposite sites of the palladium-triazole plane.

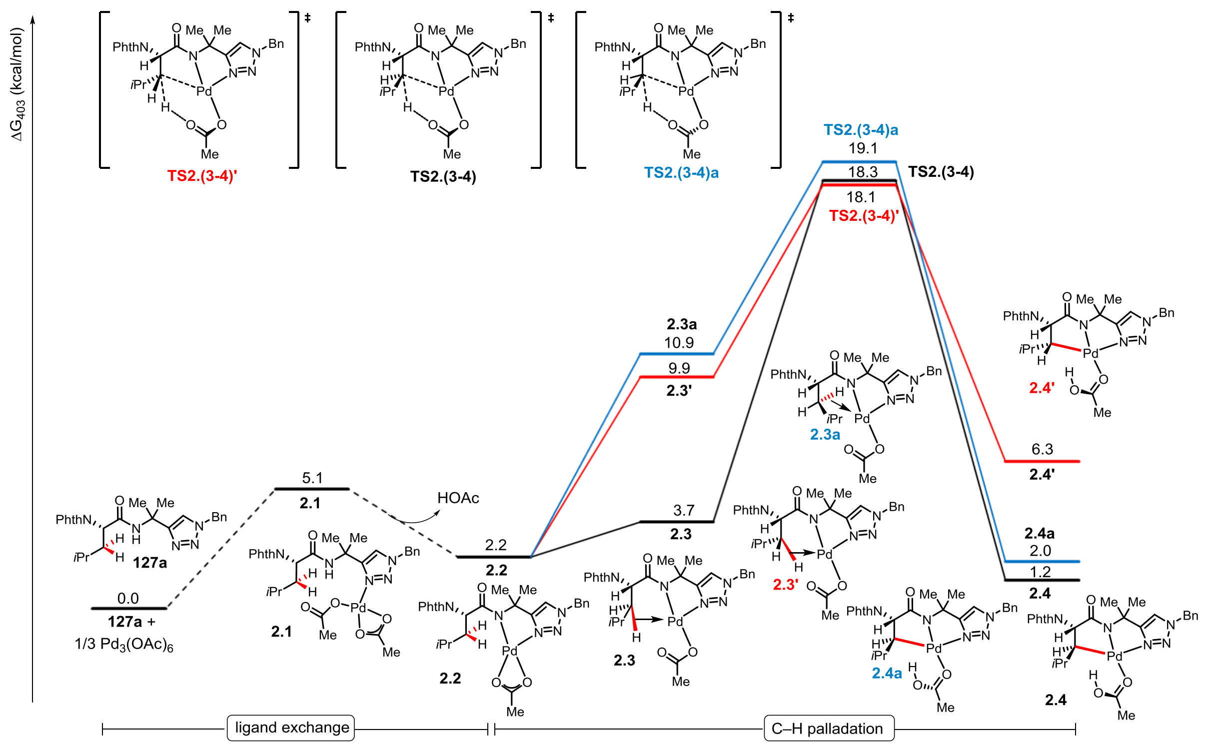


Figure 49: Relative Gibbs free energy diagram for the C(sp³)–H activation of secondary C(sp³)–H bonds of TAM-leucine **127a**. Pathways leading to the (2*S*,3*R*)-diastereomer (red), the (2*S*,3*S*)-diastereomer attack from the back (blue) and the front (black) of the palladium-triazole plane.

Figure 50 shows the energy profile for the C(sp³)–H activation of the tertiary C–H bond of leucine. After formation of palladium intermediate **2.2** the agostic complexes **2.3b** and **2.3c** are formed, which have almost the same Gibbs free energy of 12.5 kcal/mol and 12.6 kcal/mol, but they are less favorable than the agostic complexes of the secondary C–H activation (Figure 49). The κ^2-acetate coordination changes to κ^1-coordination to palladium, leaving a vacant coordination site on palladium for the agostic interaction and the subsequent C–H activation. The C–H activation proceeds *via* a CMD mechanism. The new C–Pd bond is formed, while the acetate ligand acts as a base to deprotonate the alkyl side chain (**TS2.(3-4)b/TS2.(3-4)c**). The transition states are 14.4 kcal/mol (**TS2.(3-4)c**) and 12.0 kcal/mol (**TS2.(3-4)b**) less stable than **TS2.(3-4)'**, which is the transition state of the secondary C–H activation with the lowest energy barrier, indicating that the formation of the six-membered palladacycle is much less favorable than the corresponding five-membered palladacycle.

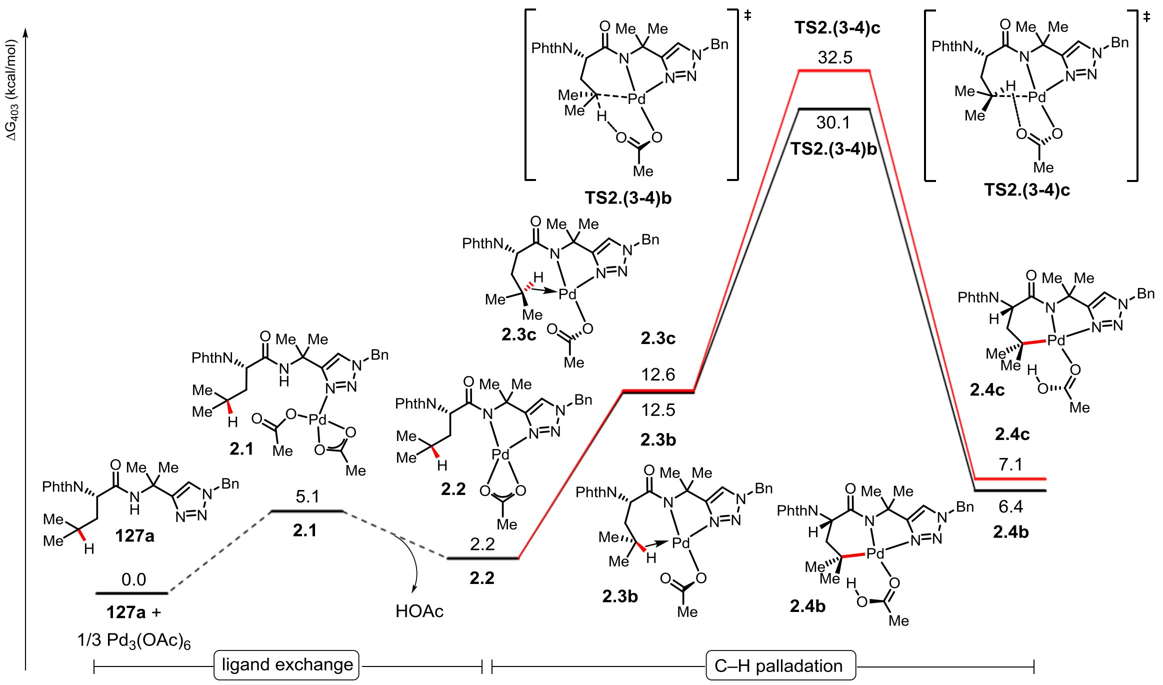


Figure 50: Relative Gibbs free energy profile for the C(sp^3)–H activation of the tertiary C(sp^3)–H bond of TAM-leucine **127a**. Attack from the back (red), the front (black) of the palladium-triazole plane.

A comparison of the five optimized geometries of the C–H activation transition states elucidates the causes of the high energy barrier in the case of the six-membered palladacycle (Table 28, Table 29 and Table 30 section 6.1.2.2 and Figure 51) C–H activation forces the molecules into a certain geometry to achieve the necessary orbital overlap, while at the same time maintaining minimal ring strain in the palladacycle. As one could expect, the Pd–C distance (around 2.20 Å) and the Pd–O distance (around 2.07 Å) are almost the same in each structure, because a stable Pd–C bond is formed while the acetate ligand acts as a base. The bidentate coordination of the triazole amide to palladium generates relatively constant bond angles and bond lengths in this five-membered palladacycle in all isomers, but the increased ring size in **TS2.(3-4)b**/**TS2.(3-4)c** causes larger bond angles and dihedral angles compared to the five-membered isomers **TS2.(3-4)**/**TS2.(3-4)a**/**TS2.(3-4)’** (Table 28, Table 29 and Table 30 section 6.1.2.2). The isomers **TS2.(3-4)’** and **TS2.(3-4)a** have comparable structures regarding the relative position of the β-hydrogen atoms and the methyl groups of the amino acid sidechain (Figure 51). The β-hydrogen atoms are close to the proton (d($H\beta$–H_{act}): 1.540 Å and 1.528 Å), which gets transferred and the oxygen atom of the acetate ligand which acts as base (d($H\beta$–$O_{Acetate}$): 2.374 Å and 2.379 Å). The distances are considerably shorter than the sums of the van-der-Waals-radii[253] of the atoms (H 1.100 Å, O 1.520 Å). One methyl group is in close proximity to the oxygen atom, which coordinates to palladium (d(H–O)≈ 2.650 Å), while the other methyl group is near to the palladium centre. The Pd–C and Pd–H distances are d(Pd–C_{Me})≈ 3.2 Å and d(Pd–H_{Me})≈ 2.7 Å. Opposed to **TS2.(3-4)’**/**TS2.(3-4)a** both methyl groups in **TS2.(3-4)** are close to the acetate ligand, whereas the Pd–C distances of d(Pd–C_{Me}): 3.866 Å and 4.435 Å are significantly longer than in **TS2.(3-4)’**/**TS2.(3-4)a**. The shortest H–O, C–O and H–C distances are d(H_{Me}–O): 2.272 Å, d(C_{Me}–O): 2.988 Å and d(H_{Me}–$C_{Acetate}$): 2.592 Å. **TS2.(3-4)a** is slightly higher in energy than **TS2.(3-4)/TS2.(3-4)'**, but the fact that the three stereoisomers differ by only around 1 kcal/mol, indicates that the sterics add only a minor contribution to the overall Gibbs free energy.

Regarding the C–H activation on the tertiary C(sp^3)–H bond, transition states **TS2.(3-4)b** and **TS2.(3-4)c** share two structural characteristics, first the *α*-hydrogen atom is in close proximity to a methyl group, second one of the two methyl groups is in close proximity to the acetate ligand. **TS2.(3-4)b** has shorter H–C and H–O distances, but longer C–O distances than **TS2.(3-4)c**. In **TS2.(3-4)b/TS2.(3-4)c** one methyl group lies in the palladium-triazole plane, while the major difference between **TS2.(3-4)b** and **TS2.(3-4)c** is the position of the second methyl group, which sticks out of the palladium-triazole plane. In **TS2.(3-4)c** the C–H activation occurs at the back side of the palladium-triazole plane and the methyl group comes close to the palladium centre, hence the short Pd–H and Pd–C distances of d(Pd–H): 2.724 Å, d(Pd–H): 2.865 Å and d(Pd–C): 2.711 Å. **TS2.(3-4)c** has the highest energy barrier of all five transition states.

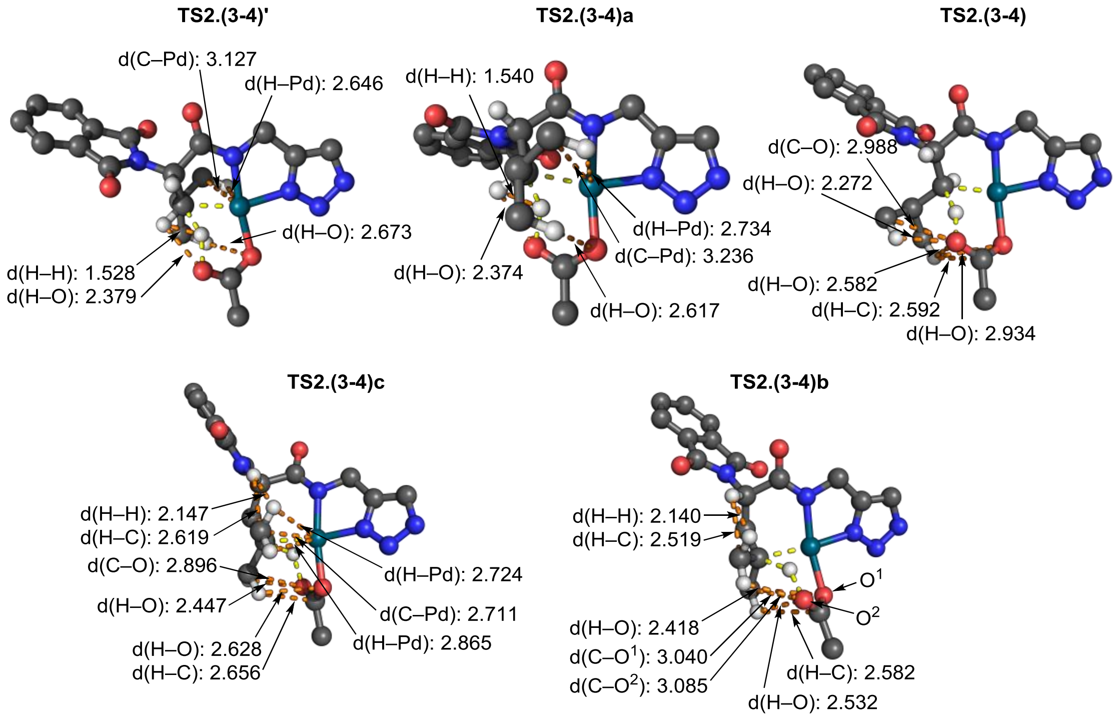


Figure 51: Optimized geometries of the five isomeric C(sp^3)–H activation transition states of leucine with selected distances. Benzyl groups, methyl groups and non-participating hydrogens atoms have been omitted for clarity. Distances are given in Å.

As the next important step, the oxidative addition of iodobenzene (**4a**) and the subsequent reductive elimination were calculated for all isomers. Figure 52 shows the energy profile for the isomers with a *trans*-configuration of the *α*,*β*-hydrogen atoms. Starting with the cyclometalated intermediates **2.4**/**2.4a** ligand exchange of acetic acid with iodobenzene (**4a**) generates **2.5** and **2.5a**. Due to the coordination of iodobenzene (**4a**) to palladium *via* the iodine atom, the phenyl residue has two feasible orientations with respect to the palladium-triazole plane (front side and back side). For the isomers with the phenyl and the isopropyl residues on opposite sites of the palladium-triazole plane (red line) the energy barriers for the oxidative addition and reductive elimination are lower by 0.9 kcal/mol (**TS2.(5-6)a**: 19.1 kcal/mol,

TS2.(5-6): 18.2 kcal/mol) and 1.3 kca/mol (**TS2.(6-7)a**: 27.2 kcal/mol, **TS2.(6-7)**: 25.9 kcal/mol). The dihedral angle ψ(Pd–I–C–C) between the palladium-triazole plane and the aromatic ring in **2.5** is 25.6° and in **2.5a** 21.1°. From **2.5**/**2.5a** to the transition states of the oxidative addition the phenyl ring rotates and the dihedral angle ψ(Pd–I–C–C) (four atoms marked with blue circles in Figure 53) increases to 100.3° (**TS2.(5-6)**) and 99.3° (**TS2.(5-6)a**). The energy difference between palladium(IV) complexes **2.6** and **2.6a** is 1.1 kcal/mol. The transition states and the energy barriers of the reductive elimination are higher in energy than the corresponding oxidative addition and the C–H cleavage. This indicates that the reductive elimination is the rate-determining step of the reaction. The phenyl ring rotates from intermediates **2.6**/**2.6a** to the transition states of the reductive elimination **TS2.(6-7)**/**TS2.(6-7)a** (dihedral angle ψ(N–Pd–C–C), marked with blue circles in Figure 54). The reductive elimination leads to intermediates **2.7**/**2.7a**. In **2.7**/**2.7a** the phenyl group is coordinated to palladium in an η^2-coordination. Proto-demetalation with acetic acid and AgOAc affords product **2.8** and regenerates the palladium catalyst.

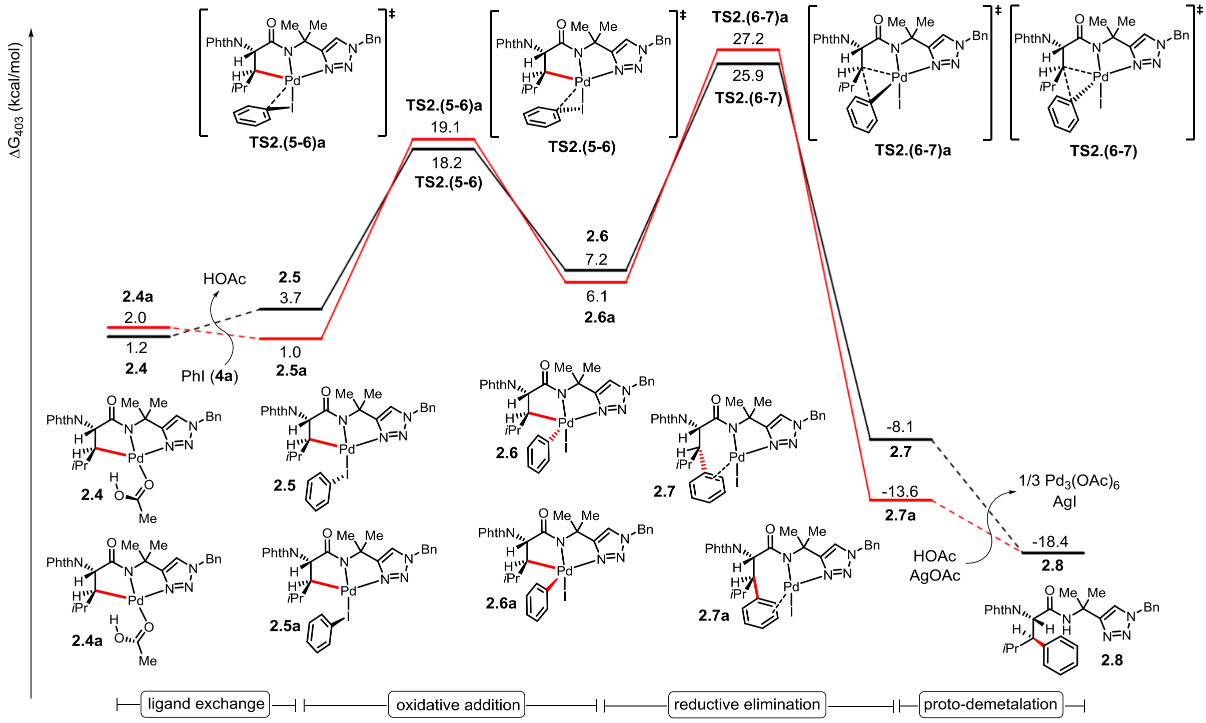


Figure 52: Relative Gibbs free energy profile for the oxidative addition and reductive elimination of leucine isomers with *trans*-configuration of the *α*,*β*-hydrogen atoms. Arene moiety located in front (red), arene moiety at the back (black) of the palladium-triazole plane

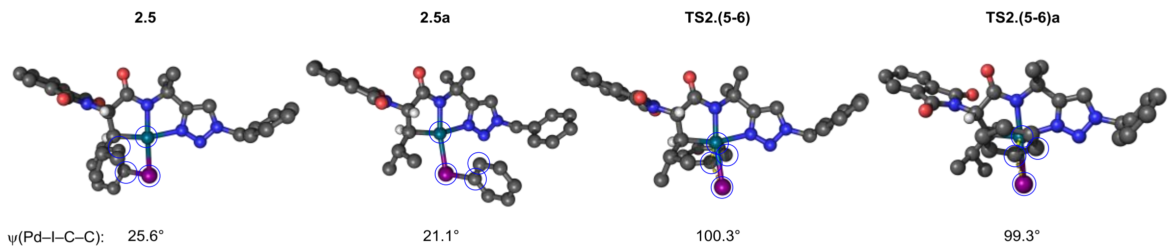


Figure 53: Optimized geometries of intermediates **2.5/2.5a** and transition states **TS2.(5-6)/TS2.(5-6)a** with selected dihedral angles ψ(Pd–I–C–C). Non-participating hydrogen atoms have been omitted for clarity.

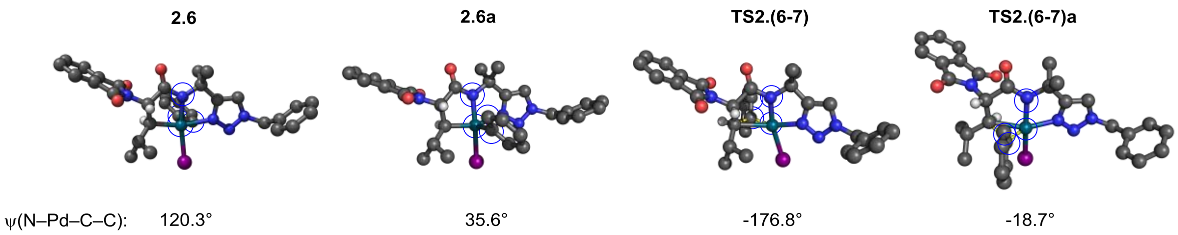


Figure 54: Optimized geometries of intermediates **2.6/2.6a** and transition states **TS2.(6-7)/TS2.(6-7)a** with selected dihedral angles ψ(N–Pd–C–C). Non-participating hydrogen atoms have been omitted for clarity.

Figure 55 shows the energy profile for the oxidative addition and reductive elimination of leucine isomers with *cis*-configuration of the *α*,*β*-hydrogen atoms. The energy difference between transition states of the two isomers is larger than between the corresponding isomers with *trans*-configuration. Starting from palladium complex **2.4'** ligand exchange of acetic acid with iodobenzene affords intermediates **2.5'**/**2.5a'**, which are 4.6 kcal/mol (**2.5'**) and 6.2 kcal/mol (**2.5a'**) less stable than 1/3 $Pd_3(OAc)_6$ and separate substrate. The energy difference of the isomers increases to 16.5 kcal/mol for the transition states of the oxidative addition **TS2.(5-6)'** and **TS2.(5-6)a'**. The energy barriers were determined to be 14.9 kcal/mol (**TS2.(5-6)'**) and 31.4 kcal/mol (**TS2.(5-6)a'**), respectively. A closer analysis of the structures indicates that steric repulsion is the main cause for the higher energy barrier of **TS2.(5-6)a'**. From **2.5'**/**2.5a'** to **TS2.(5-6)'**/**TS2.(5-6)a'** the phenyl ring itself rotates and the dihedral angle ψ(Pd–I–C–C) changes significantly from 24.4° to 101.7° (**2.5'** → **TS2.(5-6)'**) and from 174.9° to 107.6° (**2.5a'** → **TS2.(5-6)a'**) (four atoms marked with blue circles in Figure 56). In the case of **TS2.(5-6)a'** a hydrogen atom at the *ortho*-position of the phenyl group is in close proximity to a hydrogen atom of a methyl group from the isopropyl residue (d(H–H): 1.842 Å). The shortest distance in **TS2.(5-6)'** between a *ortho*-hydrogen of the phenyl group and the *β*-hydrogen atom was determined to be d(H–H): 2.114 Å. Palladium(IV) complex **2.6'** is 7.6 kcal/mol more favorable than **2.6a'**. Rotation of the phenyl group results in the dihedral angle ψ(N–Pd–C–C) of 131.2° (**2.6a'**) and 104.9° (**2.6'**). The energy difference between the two isomers remains almost constant for the reductive elimination step. Transition state **TS2.(6-7)'** has an energy barrier of 24.2 kcal/mol which is 7.7 kcal/mol lower in energy than **TS2.(6-7)a'** (31.9 kcal/mol). Compared to the C–H activation and the oxidative addition, the reductive elimination has the highest activation barriers. In **TS2.(6-7)a'** a close contact (d(C–H): 2.387 Å) between a hydrogen atom of a methyl group from the isopropyl residue and a carbon atom (*ortho*-position) of the phenyl group was determined as marked with dashed orange lines in Figure 56. The distance between a hydrogen atom at the *ortho*-position of the phenyl group and the amide carbon atom is d(C–H): 2.245 Å, while the distance between the iodine atom and a hydrogen (*ortho*-position) of the phenyl group is 2.736 Å (d(I–H)). In **TS2.(6-7)'** the distance between the *β*-hydrogen atom and the carbon atom (*ortho*-position) of the phenyl group is 2.134 Å (d(C–H)), because the aromatic ring is approaching the *β*-carbon atom from the front of the palladium-triazole-plane, but there is no close contact between the isopropyl and the phenyl group. The distance between the *α*-hydrogen atom and a carbon atom (*ortho*-position) of the phenyl group is 2.429 Å (d(C–H)) and the distance between the amide carbon atom and a hydrogen atom (*ortho*-position) of the phenyl group is 2.555 Å (d(C–H)). Compared to the sum of the van-der-Waals-radii of C (1.700 Å), H (1.100 Å) and I (1.980 Å) the relatively short C–H and I–H distances in **TS2.(6-7)a'** cause steric repulsion, which seems to be the main reason for the higher energy barrier. Starting from **2.6'**/**2.6a'** the phenyl group rotates and the dihedral angle ψ(N–Pd–C–C) is 166.9° (**TS2.(6-7)'**) and 154.3° (**TS2.(6-7)a'**), respectively. Palladium(II) complexes **2.7'**/**2.7a'** are more favorable than $Pd_3(OAc)_6$ and separate substrate by 8.8 kcal/mol (**2.7'**) and 11.7 kcal/mol (**2.7a'**). The last step is the proto-demetalation and regeneration of the catalyst. Product (2*S*,2*S*)-**2.8'** is 11.8 kcal/mol more stable than $Pd_3(OAc)_6$ and **127d**, but 6.6 kcal/mol less stable than the diastereomeric product (2*S*,3*R*)-**2.8**.

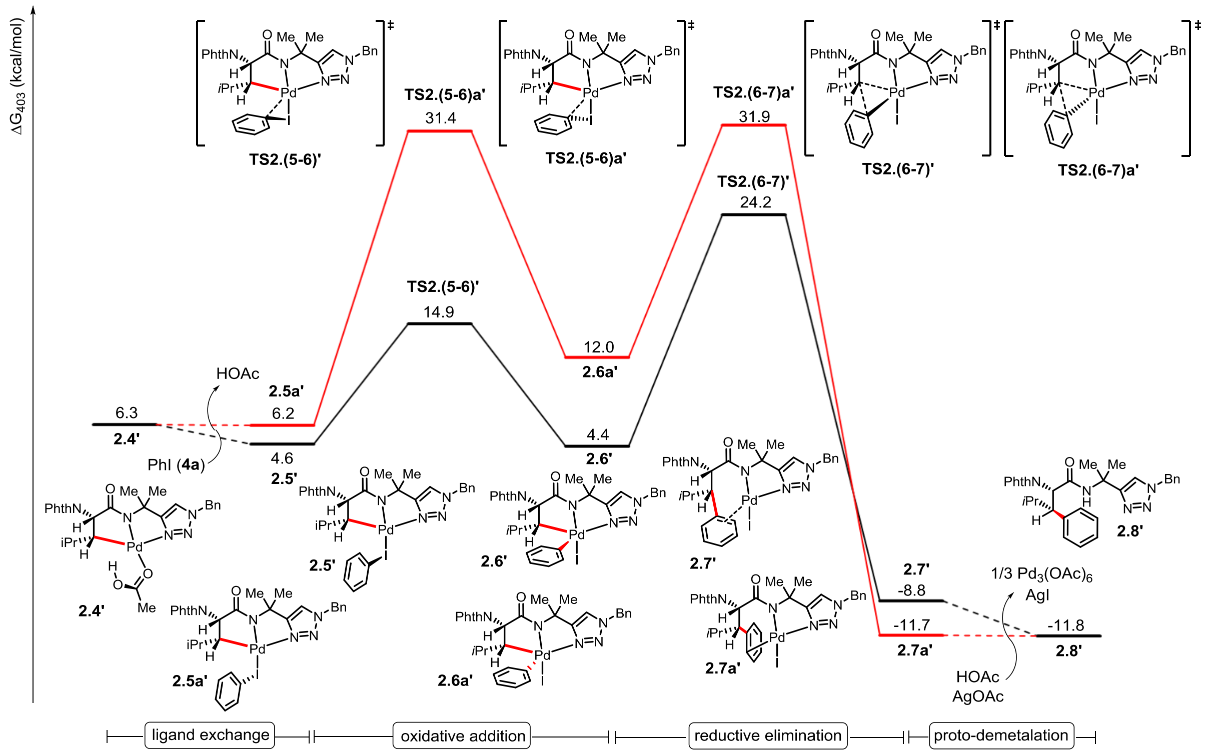


Figure 55: Relative Gibbs free energy profile for the oxidative addition and reductive elimination of leucine with *cis*-configuration of the *α*,*β*-hydrogen atoms. Arene moiety located in front (black), arene moiety at the back (red) of the palladium-triazole plane

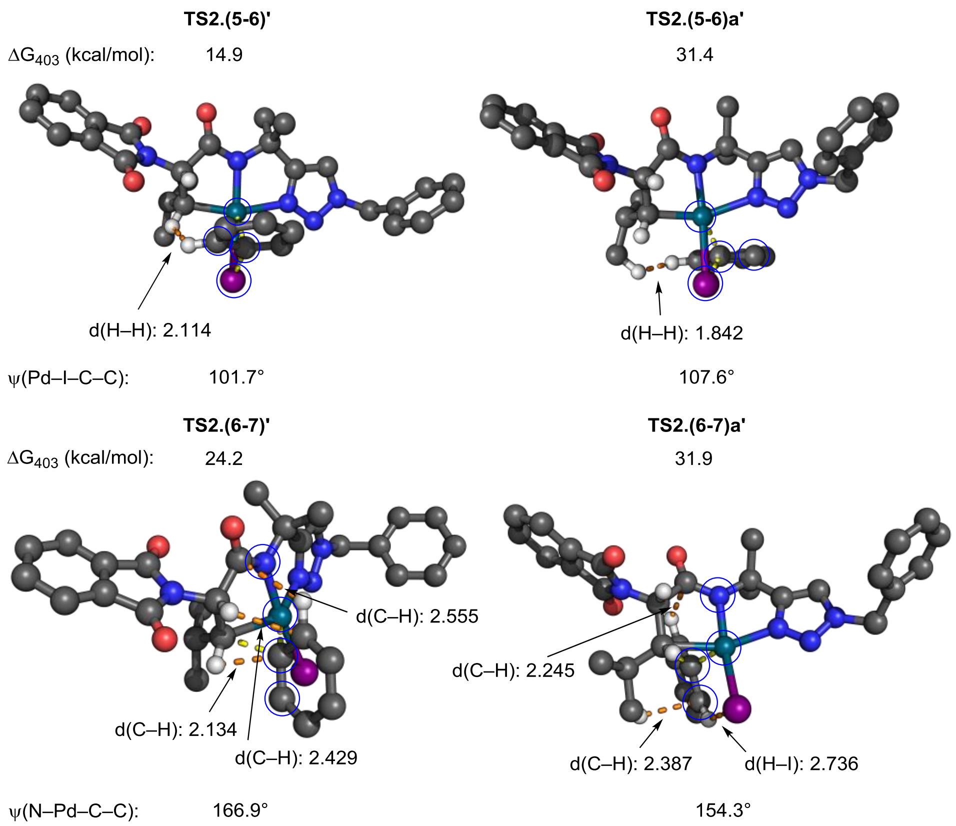


Figure 56: Optimized geometries of transition states **TS2.(5-6)'**/**TS2.(5-6)a'** and **TS2.(6-7)'**/**TS2.(6-7)a'** with selected distances and dihedral angles ψ(Pd–I–C–C) and ψ(N–Pd–C–C). Non-participating hydrogen atoms have been omitted for clarity. Distances are given in Å.

Finally, the energy profile for the oxidative addition and reductive elimination at the tertiary carbon atom was studied (Figure 57). Compared to the C–H cleavage and the reductive elimination, the oxidative addition is the step with the smallest energy barrier. Upon acetic acid-iodobenzene ligand exchange intermediates **2.5b**/**2.5c** are formed which differ in the orientation of the iodobenzene relative to the palladium-triazole plane. In **2.5b** the aromatic ring is located on the back side of the palladium-triazole plane, in **2.5c** at the front. The computed energy barriers for the oxidative addition are 23.6 kcal/mol (**2.5c** → **TS2.(5-6)c**) and 24.6 kcal/mol (**2.5b** → **TS2.(5-6)c**), both significantly lower than for the C–H activation (>30 kcal/mol, Figure 50). The phenyl group rotates and the dihedral angle ψ(Pd–I–C–C) changes from -17.9° (**2.5b**) and 21.2° (**2.5c**) to -102.6° (**TS2.(5-6)b**) and 101.9° (**TS2.(5-6)c**) (marked with blue circles in Figure 58). Intermediate **2.6b** is 1.6 kcal/mol lower in energy than **2.6c**. The phenyl ring rotates from **2.6b**/**2.6c** to transition states of the reductive elimination **TS2.(6-7)b**/**TS2.(6-7)c** leading to the dihedral angles ψ(N–Pd–C–C) of 18.7° and -176.5° (four atoms marked with blue circles in Figure 59). Transition state **TS2.(6-7)c** has an Gibbs free energy of 40.3 kcal/mol, which is 7.6 kcal/mol higher in energy than **TS2.(6-7)b** (32.8 kcal/mol). The distances and angles regarding the formation of the C–C bond are almost identical (Table 31 section 6.1.2.2) but in transition state **TS2.(6-7)c** the phenyl group is closer to the leucin backbone, so that in addition to the close contact between hydrogen and carbon (d(C–H): 2.491 Å, 2.467 Å and 2.458 Å) two short H–H distances of d(H–H): 1.868 Å and 2.064 Å are found. In **TS2.(6-7)b** the H–H distances are longer, whereas the C–H distances are shorter compared to **TS2.(6-7)c** (Figure 59). Proto-demetalation of intermediates **2.7b** and **2.7c** generates the product

2.8b. The transition states of the reductive elimination have by far the highest energy barriers compared to the C–H cleavage and the oxidative addition, indicating that the formation of the C–C bond is the rate-determining step.

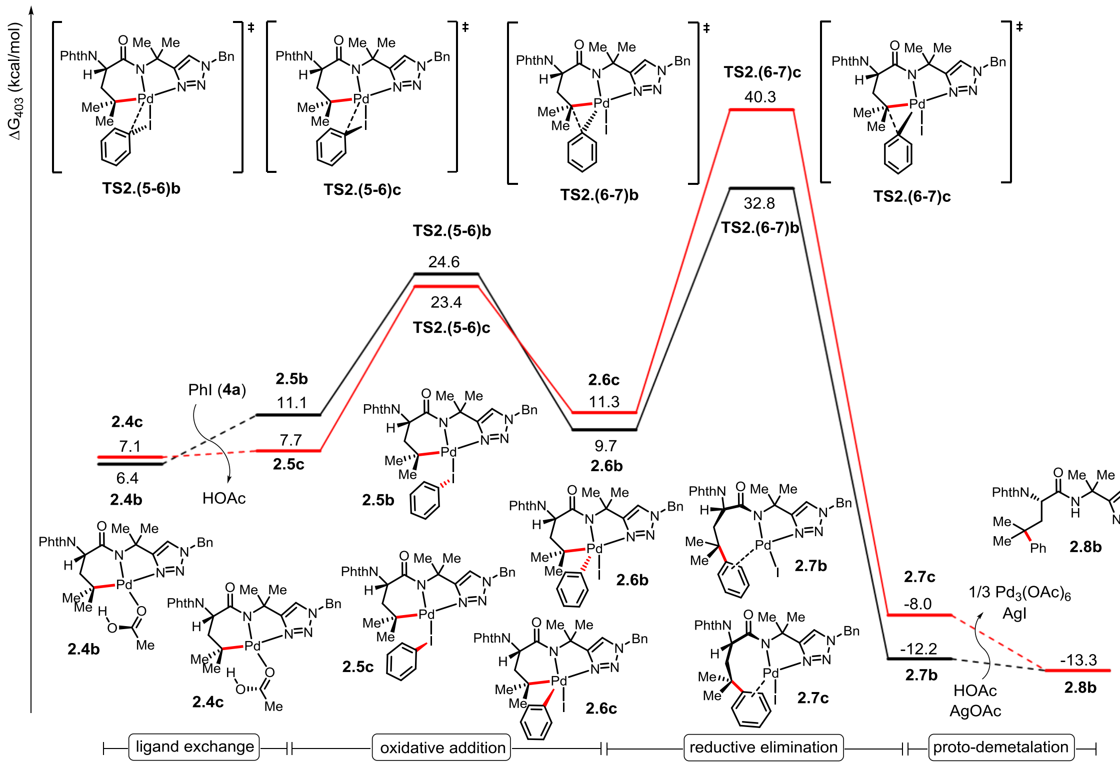


Figure 57: Relative Gibbs free energy profile for the oxidative addition and reductive elimination at the tertiary carbon atom of leucine. Arene moiety located in front (black), arene moiety at the back (red) of the palladium-triazole plane

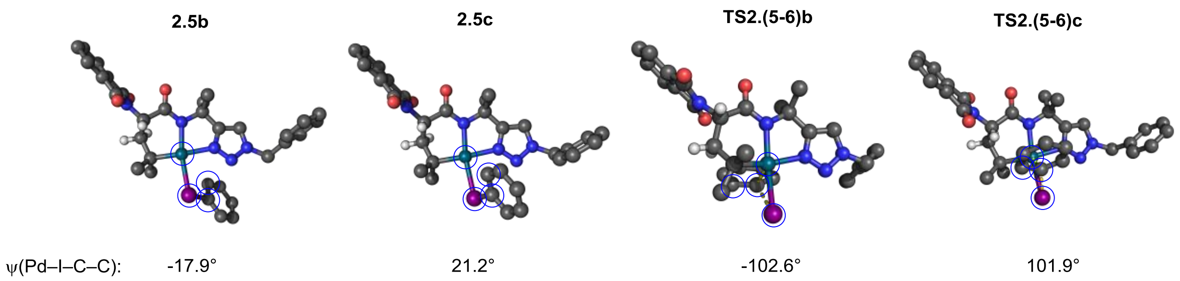


Figure 58: Optimized geometries of intermediates **2.5b**/**2.5c** and transition states **TS2.(5-6)b**/**TS2.(5-6)c** with selected dihedral angles ψ(Pd–I–C–C). Non-participating hydrogen atoms have been omitted for clarity.

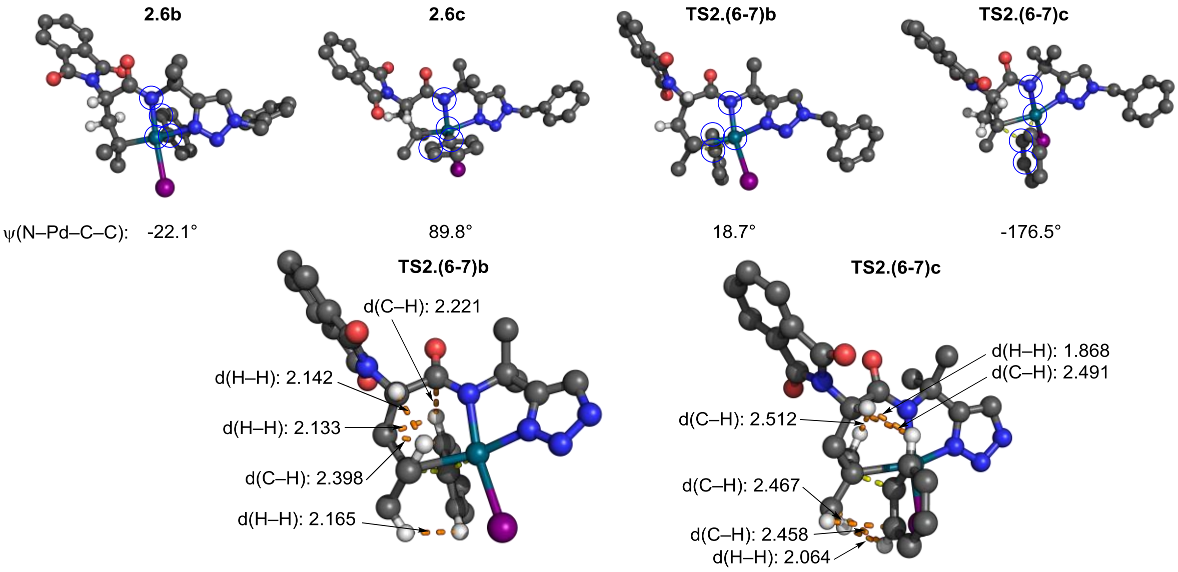


Figure 59: Optimized geometries of intermediates **2.6b**/**2.6c** and transition states **TS2.(6-7)b**/**TS2.(6-7)c** with selected distances and dihedral angles ψ(N–Pd–C–C). Non-participating hydrogen atoms and benzyl groups have been omitted for clarity. Distances are given in Å.

The found energy activation barriers suggest that in the C(sp^3)–H functionalization of leucine/the secondary C–H bond the C–H cleavage is the stereo-determining step, while the reductive elimination forming the C–C bond is the rate-determing step. In comparison to the arylation of phenylalanine (see section 3.4.1) the activation barriers of the C–H cleavage of the diastereomeric hydrogen atoms are much closer in energy, they differ only by $\Delta\Delta G^{\ddagger}$ = 0.2 kcal/mol. The (2*S*,3*R*)-product has the lowest energy barrier (**2.4’** $\Delta G^{\ddagger}$= 18.1 kcal/mol), but the (2*S*,3*S*)-product (**2.8**) is overall thermodynamically favored by 6.6 kcal/mol. The results indicate that the C(sp^3)–H functionalization of the tertiary C–H bond is highly unfavourable due to the found activation barriers of the C–H cleavage ($\Delta G^{\ddagger}$> 30 kcal/mol) and the reductive elimination ($\Delta G^{\ddagger}$> 32 kcal/mol).

3.4.3 Computational studies on the palladium-catalyzed triazole-directed arylation of peptide 137a

After the triazole directed arylation of phenylalanine and leucine, the utilization of a 1,2,3-triazole as an internal directing group in a peptide was investigated next. The developed palladium-catalyzed functionalization enabled the C(sp^3)–H arylation of a broad range of peptides with excellent position-selectivity.[241b] To further investigate the origin of the chemo- and position-selectivity DFT studies were performed on the model substrate Phth*N*-Ala-Gly-Tzl-Gly-Phe-OMe **137a** which has two viable sites for C–H functionalization. First, the C–H functionalization on the alanine site was studied leading to the isolated product **138aa** and second the functionalization of the benzylic C–H bond on the phenylalanine site, which was not observed in the experiments. Coordination of the metal center by the electron-rich N3 nitrogen atom of the 1,2,3-triazole has been termed regular[254] and for monodentate ligands it is the commonly observed binding mode, whereas coordination to the N2 nitrogen atom has been termed inverse[255] and is now studied for a range of 1,2,3-triazoles and metal ions.[256] It has been shown that the favored coordination and stability of bidentate complexes with 1,4-disubstituted 1,2,3-triazoles is highly depending on the second coordinating group.[254a, 254b, 254d, 255a, 255c, 255e, 257] The energy profile for the C–H activation on the primary C(sp³)–H bond is shown in Figure 60.

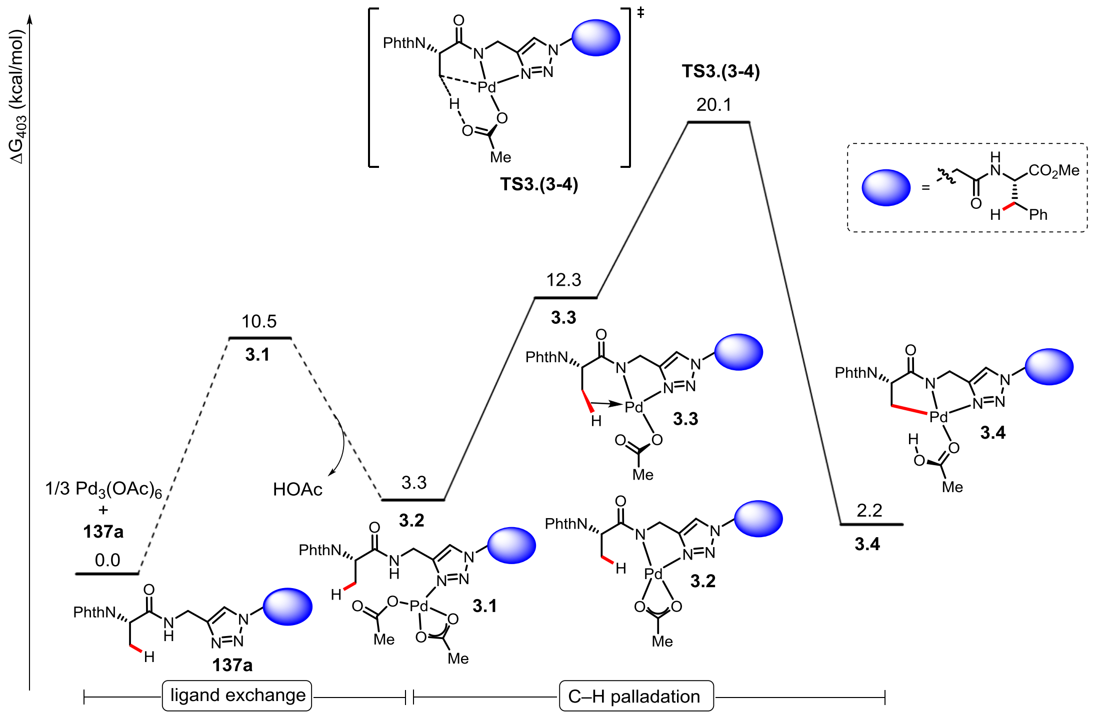


Figure 60: Relative Gibbs free energy profile for C–H activation on the primary C(sp³)–H of substrate **137a**.

The first step is the endergonic coordination of palladium acetate by the nitrogen atom N3 of the triazole. Subsequent deprotonation of the amide nitrogen, coordination to palladium and release of acetic acid affords intermediate **3.2**. The distance between palladium and the methyl carbon atom is d(Pd–C): 3.468 Å. The five-membered chelate with palladium(II) is planar and the dihedral angle ψ(N–Pd–N–C) is -18.7° (Table 33 section 6.1.3.2). Decreasing the distance between carbon and palladium leads to intermediate **3.3**, which is 12.3 kcal/mol less stable than 1/3 $Pd_3(OAc)_6$. A stabilizing agostic interaction was confirmed *via* NBO analysis of **3.3.** The acetate ligand changed from a bidentate to a monodentate coordination, leaving a vacant coordination site for the carbon atom. The Pd–C distance in **3.3** is d(Pd–C): 2.383 Å, the Pd–H distance is d(Pd–H): 1.879 Å with a bond angle of α(Pd–H–C): 100.6° (Figure 61). In transition state **TS3.(3-4)** the Pd–C bond and the O–H bond are formed in a concerted fashion, while the C–H bond is cleaved. The energy barrier of 20.1 kcal/mol is comparable to the energy barriers in the case of phenylalanine and reasonable for a reaction at 130 °C. As expected, the Pd–C distance has decreased (d(C–Pd): 2.180 Å) along with the O–H distance (d(O–H): 1.381 Å) and the bond angle α(Pd–H–C) is now 80.3°. Intermediate **3.4** with the five-membered palladacycle is only 2.2 kcal/mol higher in energy than 1/3 $Pd_3(OAc)_6$ and separate substrate **137a**.

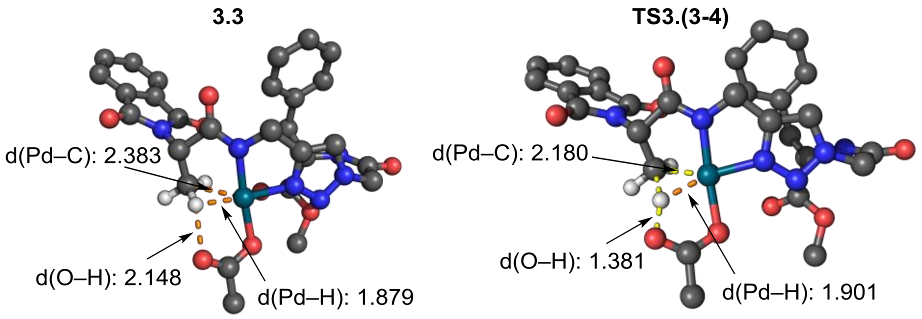


Figure 61: Optimized geometries of intermediate **3.3** and transition state **TS3.(3-4)**. Non-participating hydrogen atoms have been omitted for clarity. Distances are given in Å.

Starting from the product of the C–H activation **3.4**, the subsequent oxidative addition and reductive elimination was studied. Two pathways were identified (Figure 62). In the first pathway, iodobenzene-acetic acid ligand exchange takes place and acetic acid is released (red line), while in the second pathway the acetic acids remains coordinated to the substrate through the amide nitrogen atom (blue line), which is higher in terms of Gibbs free energy and therefore less likely. Coordination of iodobenzene to palladium affords palladium(II) complexes **3.5**/**3.5a**. The transition state of the oxidative addition has a Gibbs free energy of 12.5 kcal/mol (**TS3.(5-6)**) and 24.4 kcal/mol (**TS3.(5-6)a**), respectively. The energy barrier for the reductive elimination is 15.4 kcal/mol (**3.6** → **TS3.(6-7)**), which is 4.7 kcal/mol lower in energy than the energy barrier for the C–H cleavage.

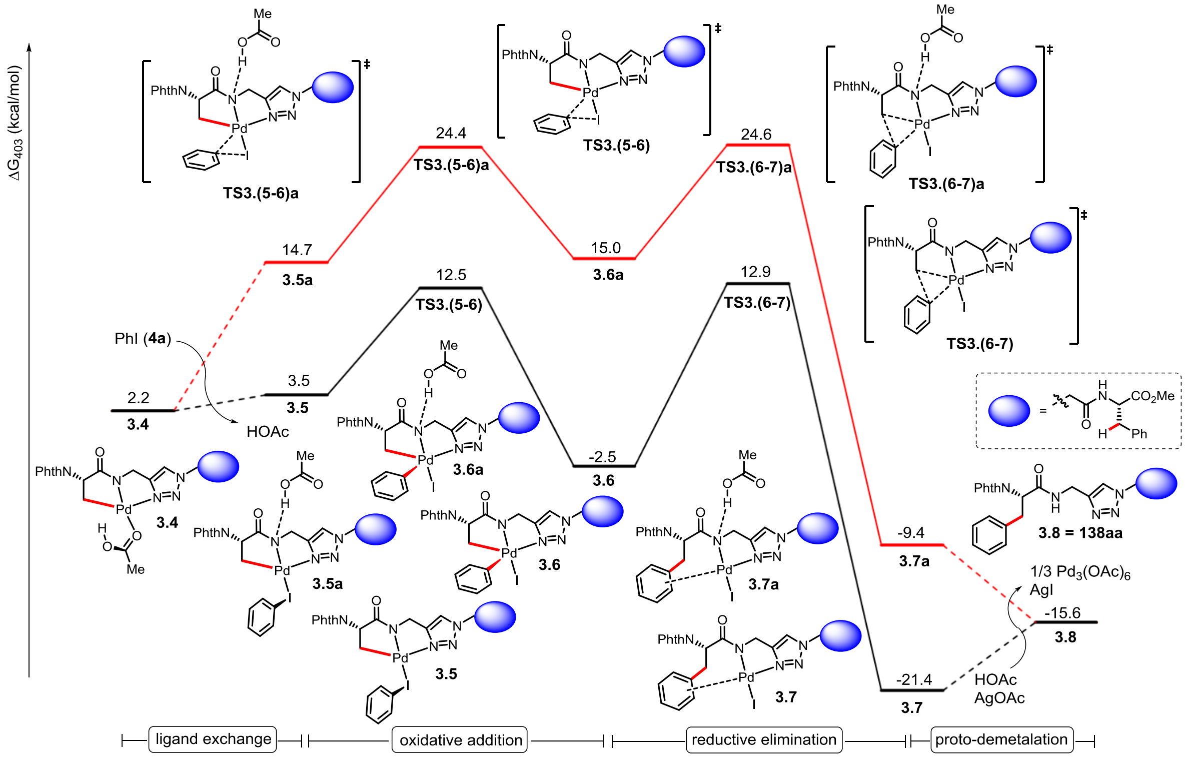


Figure 62: Relative Gibbs free energy profile for the oxidative addition and reductive elimination of **137a** (alanine residue) with HOAc (red) and without HOAc (black).

The C–H activation of only one of the two prochiral benzylic hydrogen atoms was investigated next. The energy profile for the C–H activation at the benzylic position of substrate **137a** is shown in Figure 63. The first step is the coordination of palladium by the nitrogen atom N2 of the 1,2,3-triazole moiety, which is endergonic by 6.6 kcal/mol. Subsequent coordination by the amide nitrogen and release of acetic acid affords palladium complex **3.2’**. The distance between the benzyl carbon atom and palladium is d(C–Pd): 3.913 Å. The six-membered chelate with palladium(II) adopts a boat confirmation and the dihedral angle ψ(N–Pd–N–C) (four atoms marked with blue circles in Figure 64) is -44.5°. Compared to **3.2’** the five-membered chelate **3.2** has a smaller dihedral angle ψ(N–Pd–N–C) of -18.7° and the distance between palladium and the methyl carbon atom is d(C–Pd): 3.468 Å. **3.2’** is 1.6 kcal/mol less stable than **3.2**. Atomic charge analysis using Mulliken population analysis and natural population analysis (Table 34 section 6.1.3.3) showed lower electron-densities at N2 compared to N3. This difference has already been accounted for the preferred coordination of palladium to N3 in the literature.[254a, 254b, 254d]

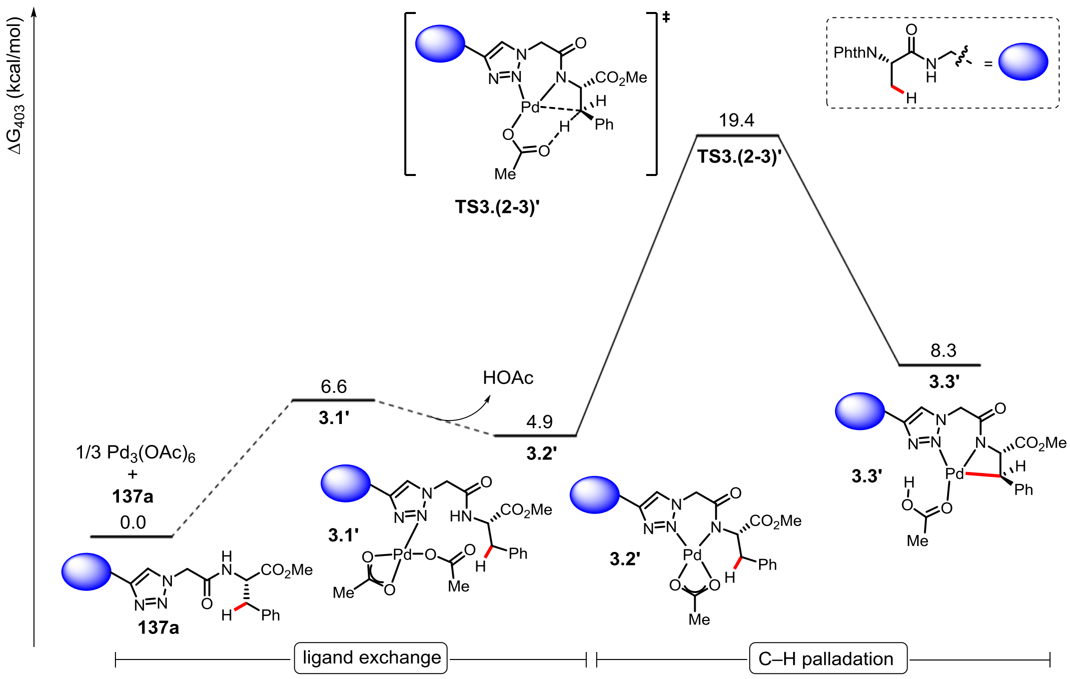


Figure 63: Relative Gibbs free energy profile for C–H activation at the benzylic position of substrate **137a**.

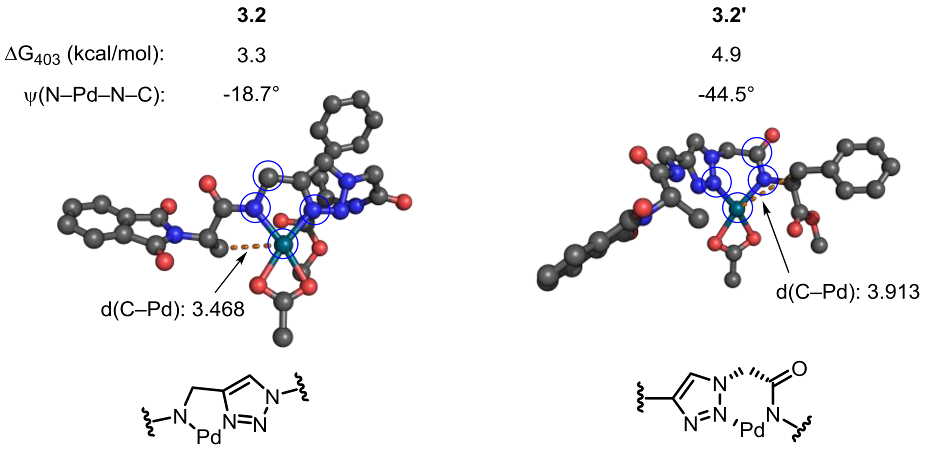
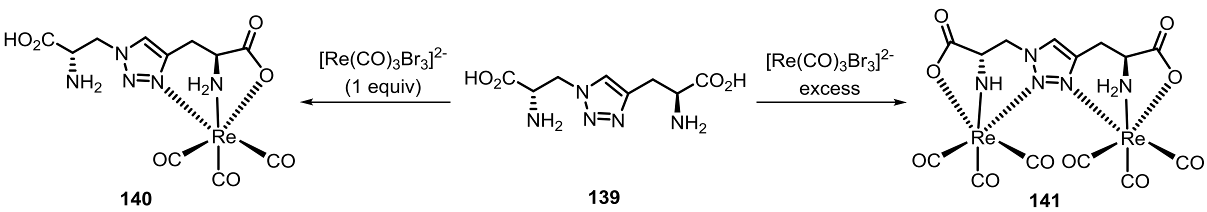


Figure 64: Comparison of different chelation modes with selected distances (d(C–Pd)) and dihedral angles ψ(N–Pd–N–C). Distances are given in Å. Relative Gibbs free energies are with respect to 1/3 $Pd_3(OAc)_6$ and separate substrate **137a**. Hydrogen atoms have been omitted for clarity.

Compared to the regular chelation of palladium (Figure 60) a relaxed surface scan led directly to transition state **TS3.(2-3)'**, but no agostic intermediate was found. The C–H cleavage step proceeds *via* a CMD mechanism, which has an energy barrier of 19.4 kcal/mol. Although the energy barrier of the C–H clevage is 0.7 kcal/mol lower in energy than the regular chelation (20.1 kcal/mol **TS3.(3-4)**), the product of this C–H cleavage was not observed in the direct arylation. The methylester and the phenyl group are one different sites of the C–C bond. The product of the C–H activation **3.3'** is 8.3 kcal/mol higher in energy than 1/3 $Pd_3(OAc)_6$ and separate substrate and 6.1 kcal/mol higher in energy than **3.4**. Compared to **3.4** the intermediate of the regular chelation with two five-membered palladacycles, **3.3'** consists of a six-membered palladacycle and a four-membered palladacycle. Five- or six-membered metallacycle are the classic intermediates involved in C–H bond functionalizations,[6y, 13a, 258] whereas four-membered palladacycles are rare,[259] because the formation of the strained four-membered ring is usually kinetically and thermodynamically disfavored. Furthermore, *Schibli* and *Mindt* revealed for the 1,2,3-triazole ligand **139** with two *N*,*N*,*O*-tridentate chelating systems that the reaction with one equivalent of a rhenium species exclusively formed the product **140**, in which the metal is coordinated to N3, whereas the possible N2 coordination was not observed. A bimetallic species **141**, in which both tridentate chelating systems are coordinated by rhenium, is formed when an excess of the metal species is used (Scheme 76).[254a, 260] Hence, the calculated pathway with the coordination of palladium to N2 and the subsequent C–H activation at the C-terminal amino acid seems feasible regarding the energy barriers, but the higher electron density at N3 propably favors the coordination of palladium through N3 and the C–H activation at the *N*-terminal amino acid.



Scheme 76: Monodentate or bidentate coordination of triazole-containig ligand **139**.

The energy profile for the oxidative addition and reductive elimination pathway at the benzylic position is shown in Figure 65. Starting from the product of the C–H activation **3.3'**, upon acetic acid dissociation and iodobenzene coordination, the palladium(II) complex **3.4'** is formed. The subsequent oxidative addition has a barrier of 16.6 kcal/mol and leads to the high-valent Pd(IV) intermediate **3.5'**. The formation of the C–C bond *via* reductive elimination transition state **TS3.(5-6)'** has a Gibbs free energy of 16.5 kcal/mol, which is 2.9 kcal/mol lower than the energy barrier for the C–H activation step (**TS3.(2-3)'**, Figure 63). Proto-demetalation with acetic acids affords the final C(sp^3)–H arylation product **3.7'** and regenerates the catalyst.

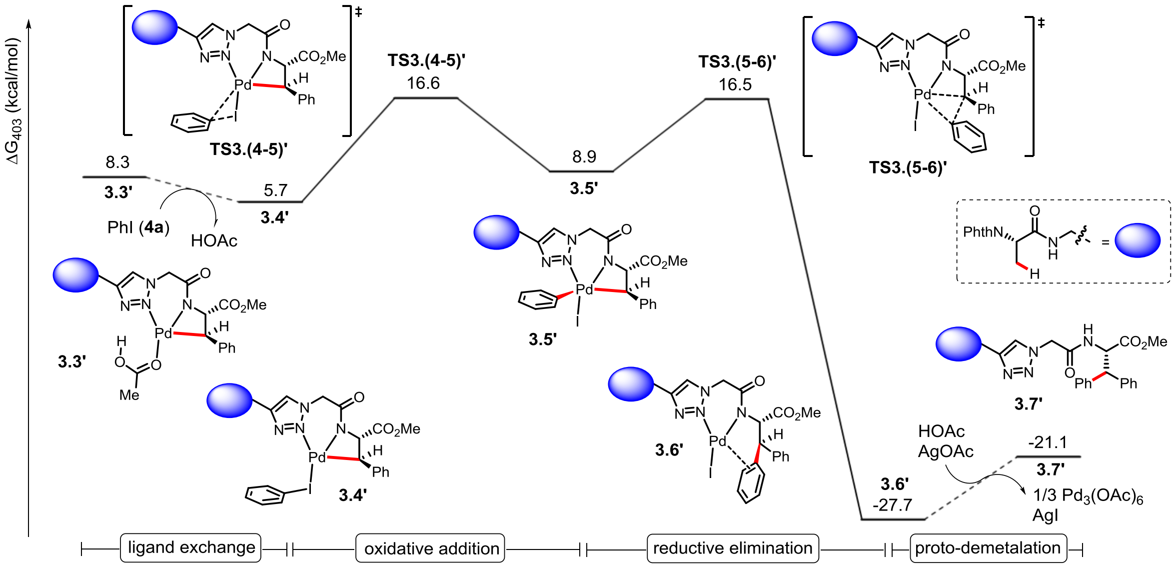


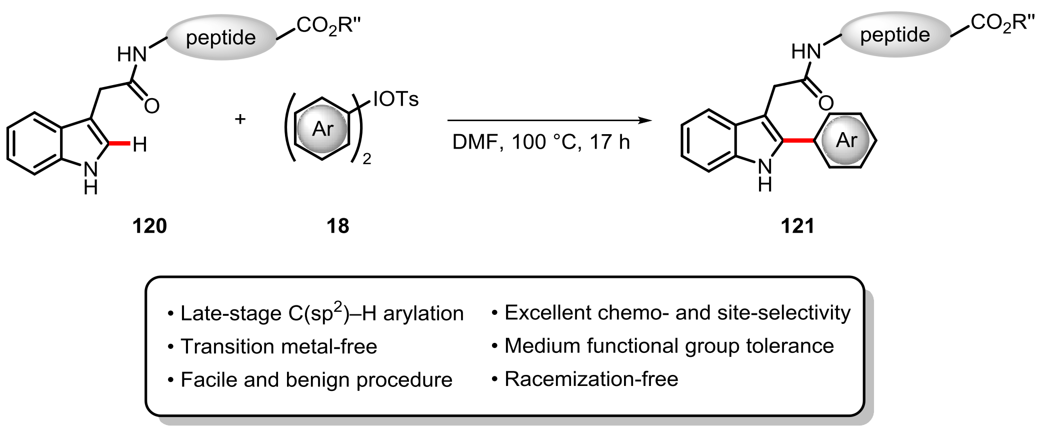
Figure 65: Relative Gibbs free energy diagram for the oxidative addition and reductive elimination at the benzylic position of **137a.**

In the case of the primary C(sp^3)–H functionalization the DFT calculations indicate that the C–H cleavage is the rate-determinig step, while the facile oxidative addition of the aryl iodide and reductive elimination forming the C–C bond have lower activation energy barriers. The higher electron density at N3 of the 1,2,3-triazole compared to the electron density at N2 favors the coordination of palladium and is the origin of the excellent position-selectivity of the C–H arylation.

4. Summary and Outlook

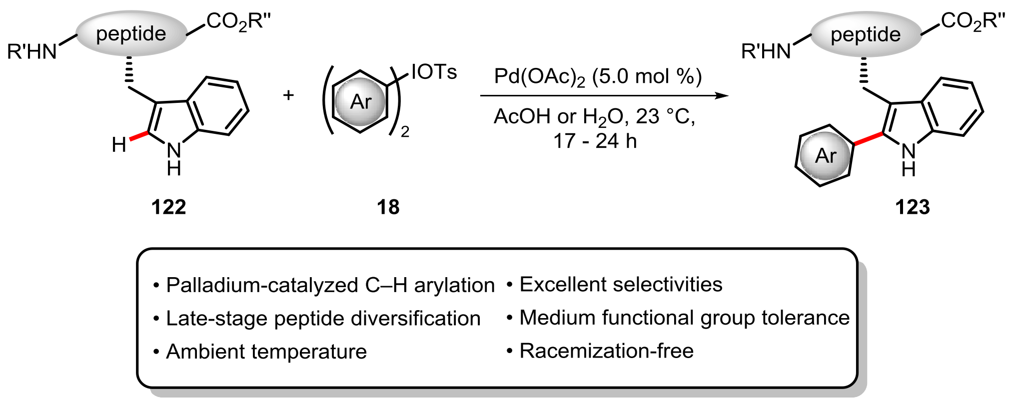
Peptide modifications are of great importance for biological probe design, medicinal chemistry and drug development.[96c, 109a-c] In contrast to the conventional time- and resource-consuming peptide synthesis, late-stage C–H functionalization has emerged as an alternative step- and atom-economic strategy for postsynthetic peptide modifications.[110a-c] Transition metal-free transformations rely upon nucleophilic natural amino acids, particularly cysteine and lysine, and a plethora of methods for *in vitro* and *in vivo* protein modification were developed in the last decades. Moreover, the development of chemical, enzymatic and genetic methods for the incorporation of unnatural amino acids into proteins enabled subsequent bioorthogonal metal-free and metal-mediated chemical modifications.[96d, 98, 109a, 109b, 261] Palladium surfaced as a key player for covalent peptide modifications through established C–C and C–Het bond forming reactions and direct C–H functionalizations.[110g, 171] Despite the progress in biocompatible peptide modifications in recent years, the chemo- and site-selective functionalization of a specific C–H bond in the presence of various reactive functional groups within the amino acid chain or the cellular environment remains a challenging task. To meet the ever-growing demand for novel and sustainable peptide functionalizations, the aim of this work was the development of late-stage peptide modifications through transition metal-free and palladium-catalyzed C–H functionalizations.

In the first project, the substrate scope for the transition metal-free direct C–H-arylation of peptides bearing the indol-3-acetamide motif as *N*-terminal tag was explored. Diaryliodonium tosylates **18** as arylating reagents enabled the arylation of di-, tri- and even hexapeptides with high levels of chemo- and siteselectivity in a user-friendly and benign procedure.[223] Importantly, our method proceeded without racemization and proved tolerant to valuable functional groups, in particular, the installation of halogen-containing arenes as synthetic handles illustrated the potential of this approach for further diversifications through cross-coupling reactions. To our delight, the direct C–H arylation of tryptophan containing peptides took exclusively place at the *N*-terminal indolyl-3-acetamide moiety, while the tryptophan indole moiety was retained. Mechanistic studies conducted by *Dr. Yingjun Zhu* provided strong experimental evidence for an underlying S_EAr type mechanism.



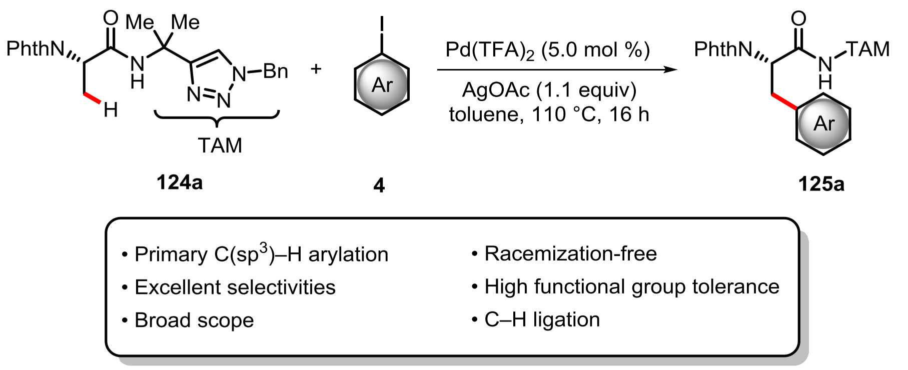
Scheme 77: Transition metal-free C2-arylation of peptide-containing indolyl-3-acetamides **120**.

Subsequently, the C–H arylation of tryptophan-containing peptides **122** with diaryliodonium salts **18** under palladium catalysis was accomplished in the second project.[229] The reaction procedeed at ambient temperature with a medium functional group tolerance and enabled the arylation of various peptides witch high levels of chemo- and site-selectivity. The use of water as solvent was possible, albeit with a decreased performance of the catalytic system. Importantly, investigations with enantiomerically pure and racemic peptides confirmed that our methodology was racemization-free.



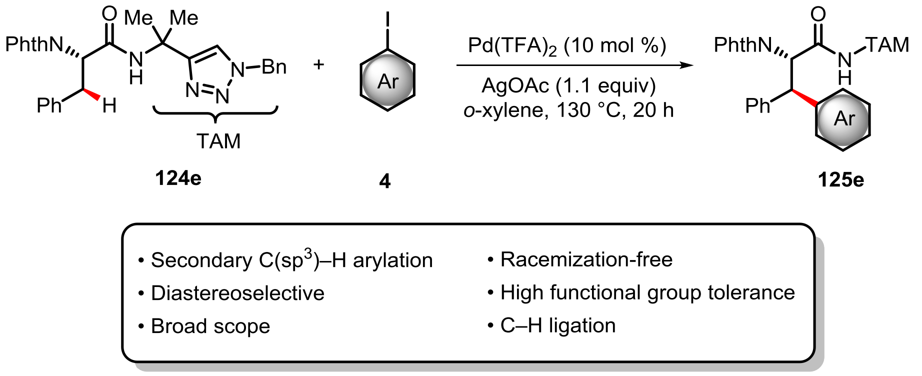
Scheme 78: Palladium-catalyzed arylations of tryptophan containing peptides **122**.

In the third project, the palladium-catalyzed C(sp^3)–H arylation of amino acids and peptides using triazole-assistance was realized.[241b] 1,2,3-Triazoles are a class of heterocycles which are easily prepared by copper- and ruthenium-catalyzed *Huisgen* cycloaddition, closely resemble amide-bonds featuring enhanced stability against enzymatic degradation. Due to these properties triazoles found numerous applications in peptidomimetic chemistry for backbone- and sidechain modifications such as cyclization or labeling.[173] In recent years, triazoles were employed as removable directing groups in transition metal C–H functionalizations under palladium-, ruthenium or iron-catalysis.[182-183, 186f, 221a] Based on these works, we developed a robust catalytic method for the triazole-directed *β*-C(sp^3)–H arylation of alanine derivative **124a** with aryliodides **4** (Scheme 79). Our protocol was compatible with a broad array of (hetero)aryliodides featuring versatile functional groups such as halides, nitriles and amides. The corresponding products were delivered in good yields with excellent chemo- and site-selectivity. Furthermore, chemical ligation with L-iodophenylalanine was also accomplished. Gratifingly, studies with racemic and enatiomerically pure substrates showed that no racemization happened during the reaction.



Scheme 79: Triazole-directed primary C(sp^3)–H arylation of alanine derivative **124a**.

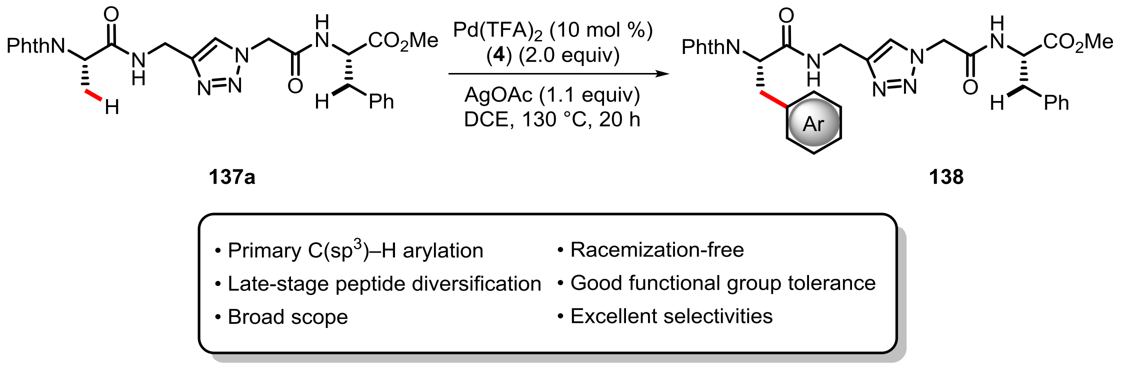
Subsequently, we explored the more challenging *β*-C(sp^3)–H arylation of phenylalanine derivative **124e** using triazole assistance (Scheme 80). The functionalization featured high levels of chemo-, site- and diastereo-selectivity. Gratifyingly, the versatile arylation proceeded without racemization, valuable functional groups such as amides, halogens or ketones were tolerated and the desired products were delivered in good to excellent yields. Moreover, the synthetic utility of our approach was reflected by efficient late-stage ligation with iodophenylalanine containing peptides as well as labeling with fluorescent probes. Computational DFT studies provided strong support for a palladium(II/IV) catalytic pathway commencing with the diastereo-determining C–H palladation *via* a six-membered carboxylate-assisted transition state. Mayer bond order analysis indicated the C–H palladation within a CMD regime with a dominant C–H cleavage.



Scheme 80: Triazole-directed secondary C(sp^3)–H arylation of phenylalanine derivative **124e**.

Furthermore, it was probed whether the developed protocol was applicable to other amino acids containing *β*-C(sp^3)–H bonds. The moderate yields of the desired products showed that the arylation was in principle possible, but optimizations would be needed for the extension of the substrate scope towards other unnatural and canonical amino acids. Additionally, DFT studies on the arylation of leucine indicated that the arylation of the *γ*-C–H bond is very unlikely due to the found activation energy barrier of the C–H cleavage *via* a seven-membered transition state.

Finally, the unprecedented internal triazole-directed C–H arylation of peptides under palladium catalysis was accomplished. The peptide bond isosteric 1,4-disubstituted triazole enabled the functionalization in a chemo- and position-selective fashion. Mild reaction conditions ensured the late-stage racemization-free C(sp^3)–H arylation with ample substrate scope. In addition, DFT studies on the reaction mechanism suggested a palladium(II/IV) manifold and indicated that the found higher electron density at N3 compared to N2 is the cause for the preferred coordination by palladium and the subsequent C–H palladation, which is consistent with the excellent positionselectivity observed in the experiments.



Scheme 81: Palladium-catalyzed internal triazole-directed C(sp^3)–H arylation of peptides **137a**.

5. Experimental Section

5.1 General Remarks

Unless otherwise stated, all reactions were carried out under a N_2 atmosphere using standard Schlenk techniques. Syringes for handling of dry solvents or liquid reagents were flushed with nitrogen threefold prior to use. New glassware and new stirring bars were used for all metal-free reactions.

Vacuum

The following pressures were measured on the used vacuum pump and are uncorrected: membrane pump vacuum (MPV): 5.0 mbar, oil pump vacuum (OPV): 0.1 mbar.

Melting Points

Melting points were measured using a *Stuart® Melting Point Apparatus SMP3* from BARLOWORLD SCIENTIFIC or BÜCHI *540 Melting Point Apparatus*. The reported values are not corrected.

Solvents

Solvents for column chromatography were distilled under reduced pressure prior to use. All anhydrous solvents for reactions involving moisture-sensitive reagents were dried, distilled and stored under inert atmosphere (Ar or N_2) according to the following standard procedures:
Acetic Acid was degassed before its use applying repeated Freeze-Pump-Thaw degassing procedure.
Water was ultra-sonicated for 4 h under an atmosphere of N_2.
***tert*-Amyl alcohol** was stirred over sodium chips for 5 h at 120 °C and distilled under ambient pressure.
1,2-Dichloroethane or ***N*,*N*-dimethylformamide** were stirred with CaH_2 for 8 h, degassed and distilled under reduced pressure.
Dichloromethane was purified using a M. BRAUN *SPS-800* solvent purification system and was stored over molecular sieves.
Dimethyl sulfoxide was stirred with CaH_2 for 4 h, degassed and distilled under reduced pressure.
Methanol was stirred over MgOMe for 3 h at 65 °C prior to distillation.
Toluene was pre-dried over KH and distilled over sodium/benzophenone.
***o*-Xylene** was stirred at 160 °C over sodium/benzophenone and distilled under ambient pressure.

Chromatography

Analytical thin layer chromatography (TLC) was performed 0.25 mm silica gel *60F plates* (MACHEREY-NAGEL) with 254 nm fluorescent indicator from MERCK. Plates were either visualized under ultraviolet light or developed by treatment with Iodine on silica gel, a $KMnO_4$ solution, acidic Cer(IV)-solution or Ninhydrin solution followed by careful warming with a heat gun. Chromatographic purification of products was accomplished by flash column chromatography on MERCK silica gel, *grade 60* (0.040–0.063 mm and 0.063–0.200 mm, 70–230 mesh ASTM).

Gel Permeation Chromatography (GPC)

Preparative separations were performed on a *LC 9110 II Next* from JAI equipped with a *JAIGEL-2HH* or a *JAIGEL-2.5HR* column with a 3 mL sample loop using Chloroform of HPLC-grade (stab. with EtOH) as solvent and a flow rate of 3.5 mL/min. The instrument was equipped with the *UV-Vis 4ch NEXT* detector and the *RI-700 NEXT* detector. All samples were filtrated through Polytetrafluorethylen-(PTFE)-Filter (0.2 µm) from Roth or VWR prior to separation.

HPLC and LC-MS

High Performance Liquid Chromatography (HPLC): Analytical separations were performed on an *Infinity 1290* from AGILENT with columns from DAICEL: CHIRALPAK® IA-3, IC-3, ID-3 or IF-3 (4.6 mm x 250 mm, 3 µm) and a flow rate of 0.65 mL/min or 1mL/min. The absorption was measured at 250 nm, 273, 274 nm or 290 nm. LC-MS Chromatograms were recorded on *6100s Series* Single Quad from AGILENT with a Zorbax SB-C18 (4.6 x 150 mm, 5 µm) column. The flow rate was set to 0.5 mL/min with detection at 270 nm and 290 nm. The following methods were used:

Measuring time	t/min	MeCN (0.1% TFA)	H_2O (0.1% TFA)
15	0	60%	40%
	5	100%	0%
	13	100%	0%
	15	60%	40%
22	0	60%	40%
	5	100%	0%
	20	100%	0%
	22	60%	40%

Infrared Spectroscopy (IR)

Infrared spectra were recorded using a BRUKER *Alpha-P ATR* spectrometer. Liquid samples were measured as thin film and solid samples neat. Analysis of the spectral data was performed using the *OPUS 6* software from BRUKER. Absorption is given in wavenumbers (cm^{-1}). Spectra were recorded in the range from 4000 to 400 cm^{-1}.

Fluorescence-Spectroscopy

Fluorescence excitation and emission data in solution were recorded on a JASCO *FP-8500* spectroscope. The widths of excitation and emission slits were held constant at 2.5 and 5 nm, respectively. The scan speed was adjusted to 200 nm/min. Analysis of the recorded spectra was carried out using *Origin Pro 8.5G*. HPLC-grade/p.A. grade DMSO was used and the samples diluted to a concentration of 1 mg/L.

Mass Spectrometry

EI- and EI-HRMS spectra were measured on a JOEL *AccuTOF* or a FINNIGAN *MAT 95* mass spectrometer. ESI- and ESI-HRMS spectra were recorded on a BRUKER micrOTOF, *maXis*, *APEX IV 7T*

FTICR, FINNIGAN *LCQ* or a THERMO SCIENTIFIC *LTQ Orbitrap XL* mass spectrometer. The ratios of mass to charge are indicated, intensities relative to the base peak (I = 100) are written in parentheses.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (NMR) spectra were recorded at 300, 400, 500 or 600 MHz (^{1}H NMR), 75, 100 or 125 MHz (^{13}C NMR and APT) and 282 MHz (^{19}F NMR) on VARIAN *Mercury VX-300*, *Inova 500*, *Inova 600*, BRUKER *Avance 300*, *Avance 400*, *Avance III HD 400* and *Avance III HD 500* instruments. Chemical shifts are reported as δ-values in ppm relative to the residual proton peak or the carbon peak of the deuterated solvent.

	^{1}H NMR	^{13}C NMR
$CDCl_3$	7.26 ppm	77.16 ppm
DMSO-d_6	2.50 ppm	39.52 ppm
$MeOD_4$	4.87/3.31 ppm	49.00 ppm

For characterization of the observed resonance multiplicities the following abbreviations were applied: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *dd* (doublet of doublet), *dt* (doublet of triplet), or analogue representations. The coupling constants *J* are reported in Hertz (Hz). Analyses of the recorded spectra were carried out using *MestReNova 10* software.

Reagents

Chemicals obtained from commercial sources (purity >95%) were used without further purification. 3-Chloroperoxybenzoic acid (mCPBA) was purchased with a purity of 70-75% (containing 3-Chlorobenzoic acid and water) from ACROS. It was used after drying under vacuum at ambient temperature for 1h (calculated 81% wt). The following compounds were synthezised according to previously reported literature procedures:

Diaryl iodonium salts **18a**-**h**,[262] protected amino acids and peptides,[263] homologated alanine **127f**,[264] *N*-pyrimidyl-tryptophan **26**,[265] triazole amides and triazole amino acids.[182-183, 185]

The following compounds were kindly provided by the persons named below:

Dr. Yingjun Zhu: **120a** (partly), **1f**, **4v**, **4w**, **4x, 5fa, 26**.

Dr. Alexandra Schischko: **4z**

5.2 General Procedures

General procedure A: Metal-free C(sp^2)–H arylations of peptide-containing indolylacetamides with symmetrical diaryliodonium salts in DMF

A mixture of peptide **120** (0.250 mmol, 1.00 equiv.), diaryliodonium tosylate **18** (0.375 mmol, 1.50 equiv.) in DMF (2.00 mL) was stirred at 100 °C for 17 h. At ambient temperature, the crude reaction mixture was directly purified by column chromatography on silica gel to yield the desired product **121**.

General procedure B1: Palladium-catalyzed C(sp^2)–H arylations of tryptophan-containing peptides with symmetrical diaryliodonium salts in AcOH

A mixture of tryptophan-containing peptide **122** (0.20 mmol, 1.00 equiv.), diaryliodonium tosylate **18** (0.30 mmol, 1.50 equiv.) and $Pd(OAc)_2$ (5.0 mol %) in AcOH (3.00 mL) was stirred at 23 °C for 17 h. At ambient temperature, H_2O (5.00 mL) was added, and the aqueous layer was extracted with EtOAc (3 x 20 mL). The organic layers were combined, and the solvents were removed *in vacuo*. The crude product was purified by column chromatography on silica gel to yield the desired product **123**.

General procedure B2: Palladium-catalyzed C(sp^2)–H arylations of tryptophan-containing peptides with symmetrical diaryliodonium salts in water

A mixture of tryptophan-containing peptide **122** (0.20 mmol, 1.00 equiv.), diaryliodonium tosylate **18** (0.30 mmol, 1.50 equiv.) and $Pd(OAc)_2$ (5.0 mol %) with water (3.00 mL) was stirred at 23 °C for 24 h. After the indicated reaction time, MeOH (5.00 mL) was added, and the solvents were removed *in vacuo*. The residue was purified by column chromatography on silica gel to yield the desired product **123**.

General procedure C1: Palladium-catalyzed primary C(sp^3)–H arylations of Phth*N*-Ala-NHTAM with aryl iodides in toluene

A mixture of Phth*N*-Ala-NHTAM **124a** (0.20 mmol, 1.00 equiv.), iodoarene **4** (0.30 mmol, 1.50 equiv.), $Pd(TFA)_2$ (5.0 mol %) and AgOAc (0.22 mmol, 1.10 equiv.) in toluene (2.00 mL) was stirred at 110 °C for 16 h. After cooling to ambient temperature, the reaction was diluted with EtOAc (15 mL) and then filtered through a pad of Celite and washed with EtOAc (50 mL). The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel or gel permeation chromatography to yield the desired product **125**.

General procedure C2: Palladium-catalyzed secondary C(sp^3)–H arylations of Phth*N*-Phe-NHTAM with aryl iodides in *o*-xylene

A mixture of Phth*N*-Phe-NHTAM **124e** (0.20 mmol, 1.00 equiv.), iodoarene **4** (0.40 mmol, 2.00 equiv.), $Pd(TFA)_2$ (10 mol %) and AgOAc (0.22 mmol, 1.00 equiv.) in *o*-xylene (2.00 mL) was stirred at 130 °C for 20 h. After cooling to ambient temperature, the reaction was diluted with EtOAc (15 mL) and then filtered through a pad of Celite and washed with EtOAc (50 mL). The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel or gel permeation chromatography to yield the desired product **125**.

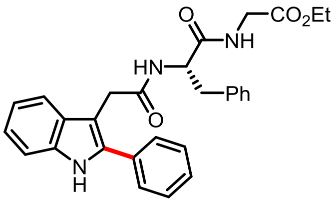
General procedure C3: Palladium-catalyzed primary C(sp3)–H arylations of triazole-containing peptides with aryl iodides in DCE

A mixture of Phth*N*-Ala-Gly-Tzl-Gly-Phe-OMe **130a** (0.20 mmol, 1.00 equiv.), iodoarene **4** (0.40 mmol, 2.00 equiv.), $Pd(TFA)_2$ (10 mol %) and AgOAc (0.22 mmol, 1.10 equiv.) in DCE (2.00 mL) was stirred at 130 °C for 20 h in a pressure tube. After cooling to ambient temperature, the reaction was diluted with EtOAc (15 mL) and then filtered through a pad of Celite and washed with EtOAc (50 mL). The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel or gel permeation chromatography to yield the desired product **131**.

5.3 Experimental Procedures and Analytical Data

5.3.1 Analytical Data for Arylated Peptide-Containing Indolylacetamides

Synthesis of Ethyl [2-(2-phenyl-1*H*-indol-3-yl)acetyl]-*L*-phenylalanyl-glycinate (121aa)



The general procedure A was followed using ethyl [2-(1*H*-indol-3-yl)acetyl]-*L*-phenylalanyl-glycinate (**120a**) (61.1 mg, 0.15 mmol) and diphenyliodonium tosylate (**18a**) (101.8 mg, 0.225 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 1/1) yielded **121aa** (71 mg, 95%) as a pale white solid (m. p. = 220–221 °C).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 11.18 (s, 1H), 8.47 (t, J = 5.8 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 7.7 Hz, 2H), 7.48 (dd, J = 7.7, 7.7 Hz, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.32 (dd, J =7.8, 7.8 Hz, 2H), 7.27 (d, J = 6.9 Hz, 2H), 7.24 (dd, J = 7.4, 7.2 Hz, 2H), 7.22–7.18 (m, 1H), 7.10 (ddd, J = 8.0, 7.0, 1.2 Hz, 1H), 6.94 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 4.61 (ddd, J = 9.9, 8.4, 4.1 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.92 (dd, J = 17.5, 5.8 Hz, 1H), 3.84 (dd, J = 17.5, 5.8 Hz, 1H), 3.66 (d, J = 15.8 Hz, 1H), 3.60 (d, J = 15.8 Hz, 1H), 3.07 (dd, J = 13.9, 4.1 Hz, 1H), 2.83 (dd, J = 13.9, 9.9 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H).

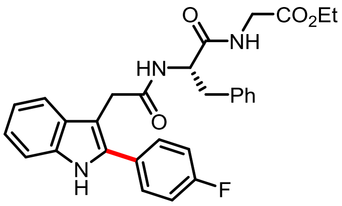
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.8 (C$_q$), 170.6 (C$_q$), 169.6 (C$_q$), 137.7 (C$_q$), 135.8 (C$_q$), 135.8 (C$_q$), 132.4 (C$_q$), 129.1 (CH), 128.7 (C$_q$), 128.5 (CH), 128.0 (CH), 128.0 (CH), 127.4 (CH), 126.2 (CH), 121.4 (CH), 119.0 (CH), 118.6 (CH), 110.8 (CH), 105.7 (C$_q$), 60.4 (CH$_2$), 54.8 (CH$_2$), 53.8 (CH), 37.6 (CH$_2$), 31.5 (CH$_2$), 14.0 (CH$_3$).

IR (ATR): 3375, 3283, 1735, 1642, 1528, 1335, 1026, 772, 745, 699 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 506 (100) [M+Na]$^+$, 484 (95) [M+H]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{29}H_{30}N_3O_4$ [M+H]$^+$: 484.2231; found: 484.2236.

Synthesis of Ethyl {2-[2-(4-fluorophenyl)-1H-indol-3-yl]acetyl}-L-phenylalanyl-glycinate (121ab)



The general procedure A was followed using Ethyl [2-(1*H*-indol-3-yl)acetyl]-*L*-phenylalanyl-glycinate (**120a**) (101.9 mg, 0.25 mmol) and bis(4-fluorophenyl)iodonium tosylate (**18b**) (183.1 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 3/2) yielded **121ab** (89 mg, 71%) as a light brown solid (m. p. = 218–220 °C).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 11.21 (s, 1H), 8.50 (t, J = 5.8 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 7.78 (ddd, J = 8.5, 5.3, 2.5 Hz, 2H), 7.50–7.17 (m, 9H), 7.11 (ddd, J = 8.0, 7.0, 1.2 Hz, 1H), 6.96 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 4.65 (ddd, J = 9.8, 8.4, 4.1 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.93 (dd, J = 17.4, 5.8 Hz, 1H), 3.87 (dd, J = 17.4, 5.8 Hz, 1H), 3.65 (d, J = 15.8 Hz, 1H), 3.59 (d, J = 15.8 Hz, 1H), 3.11 (dd, J = 13.9, 4.1 Hz, 1H), 2.87 (dd, J = 13.9, 9.8 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.6 (C$_q$), 170.4 (C$_q$), 169.4 (C$_q$), 161.4 (d, $J_{C\text{-}F}$ = 244.9 Hz, C$_q$), 137.6 (C$_q$), 135.6 (C$_q$), 134.7 (C$_q$), 129.8 (d, $J_{C\text{-}F}$ = 8.0 Hz, CH), 129.0 (CH), 128.8 (d, $J_{C\text{-}F}$ = 3.0 Hz, C$_q$), 128.5 (C$_q$), 127.8 (CH), 126.0 (CH), 121.3 (CH), 118.9 (CH), 118.6 (CH), 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz, CH), 110.7 (CH), 105.7 (C$_q$), 60.3 (CH$_2$), 53.8 (CH$_2$), 40.7 (CH$_2$), 37.6 (CH$_2$), 31.4 (CH$_2$), 14.0 (CH$_3$).

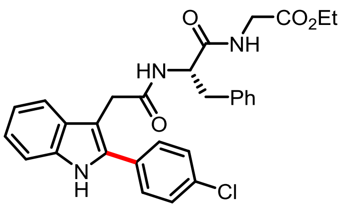
^{19}F NMR (283 MHz, DMSO-d$_6$): δ = –109.8 (tp, J = 9.2, 4.9 Hz).

IR (ATR): 3394, 3271, 3066, 1744, 1646, 1502, 1199, 1045, 841, 744, 698 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1025 (15) [2M+Na]$^+$, 752 (12), 524 (30) [M+Na]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{29}H_{29}FN_3O_4$ [M+H]$^+$: 502.2137; found: 502.2144.

Synthesis of Ethyl {2-[2-(4-chlorophenyl)-1*H*-indol-3-yl]acetyl}-*L*-phenylalanyl-glycinate (121ac)



The general procedure A was followed using Ethyl (2-(1*H*-indol-3-yl)acetyl]-*L*-phenylalanyl-glycinate (**120a**) (101.9 mg, 0.25 mmol) and bis(4-chlorophenyl)iodonium tosylate (**18c**) (196.5 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 2/1 → 1/1) yielded **121ac** (81 mg, 63%) as a light brown solid (m. p. = 240–242 °C).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 11.23 (s, 1H), 8.48 (t, J = 5.9 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 7.77–7.70 (m, 2H), 7.54–7.47 (m, 2H), 7.36 (dd, J = 14.1, 8.0 Hz, 2H), 7.31–7.17 (m, 5H), 7.10 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H), 6.94 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 4.62 (ddd, J = 10.0, 8.7, 4.2 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.91 (dd, J = 17.3, 5.9 Hz, 1H), 3.85 (dd, J = 17.3, 5.8 Hz, 1H), 3.65 (d, J = 15.6 Hz, 1H), 3.58 (d, J = 15.6 Hz, 1H), 3.08 (dd, J = 13.8, 4.1 Hz, 1H), 2.85 (dd, J = 13.8, 10.1 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H).

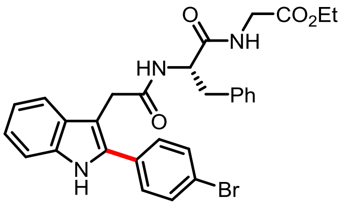
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.6 (C_q), 170.3 (C_q), 169.4 (C_q), 137.6 (C_q), 135.7 (C_q), 134.3 (C_q), 131.9 (C_q), 131.1 (C_q), 129.4 (CH), 129.0 (CH), 128.6 (C_q), 128.4 (CH), 127.8 (CH), 126.0 (CH), 121.6 (CH), 119.0 (CH), 118.6 (CH), 110.8 (CH), 106.3 (C_q), 60.3 (CH_2), 53.8 (CH), 40.7 (CH_2), 37.6 (CH_2), 31.4 (CH_2), 14.0 (CH_3).

IR (ATR): 3401, 3260, 3263, 1746, 1645, 1515, 1197, 1092, 1012, 834, 627 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1576 (14), 1057 (84) [2M+Na]$^+$, 540 (100) [M+Na]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{29}H_{29}ClN_3O_4$ [M+H]$^+$: 518.1847; found: 518.1860.

Synthesis of Ethyl {2-[2-(4-bromoophenyl)-1*H*-indol-3-yl]acetyl}-*L*-phenylalanyl-glycinate (121ad)



The general procedure A was followed using Ethyl [2-(1*H*-indol-3-yl)acetyl]-*L*-phenylalanyl-glycinate (120**a**) (101.9 mg, 0.25 mmol) and bis(4-bromophenyl)iodonium tosylate (**18d**) (224.5 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 3/2) yielded 121**ad** (86 mg, 61%) as a light brown solid (m. p. = 244–247 °C).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 11.23 (s, 1H), 8.46 (t, J = 5.9 Hz, 1H), 8.30 (d, J = 8.5 Hz, 1H), 7.66 (dd, J = 8.8 Hz, 2H), 7.63 (dd, J = 9.0 Hz, 2H), 7.35 (dd, J = 13.1, 8.0 Hz, 2H), 7.30–7.17 (m, 5H), 7.10 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 6.93 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 4.61 (ddd, J = 10.0, 8.6, 4.2 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.90 (dd, J = 17.3, 5.9 Hz, 1H), 3.84 (dd, J = 17.3, 5.8 Hz, 1H), 3.63 (d, J = 15.6 Hz, 1H), 3.57 (d, J = 15.6 Hz, 1H), 3.07 (dd, J = 13.8, 4.1 Hz, 1H), 2.83 (dd, J = 13.8, 10.1 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H).

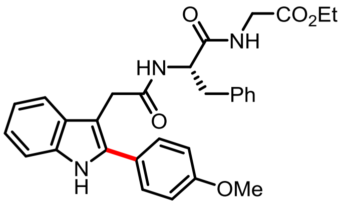
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.6 (C$_q$), 170.3 (C$_q$), 169.4 (C$_q$), 137.6 (C$_q$), 135.7 (C$_q$), 134.3 (C$_q$), 131.5 (C$_q$), 131.3 (CH), 129.7 (CH), 128.9 (CH), 128.6 (C$_q$), 127.8 (CH), 126.0 (CH), 121.6 (CH), 120.5 (C$_q$), 119.0 (CH), 118.6 (CH), 110.8 (CH), 106.3 (C$_q$), 60.3 (CH$_2$), 53.8 (CH), 40.7 (CH$_2$), 37.6 (CH$_2$), 31.4 (CH$_2$), 14.0 (CH$_3$).

IR (ATR): 3310, 3060, 1741, 1646, 1527, 1203, 1007, 829, 735 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1147 (44) [2M+Na]$^+$ (^{81}Br), 1145 (22) [2M+Na]$^+$ (^{79}Br), 586 (100) [M+Na]$^+$ (^{81}Br), 584 (100) [M+Na]$^+$ (^{79}Br).

HR-MS (ESI): *m/z* calcd for $C_{29}H_{29}BrN_3O_4$ [M+H]$^+$ (^{79}Br): 562.1336; found: 562.1331.

Synthesis of Ethyl {2-[2-(4-methoxyphenyl)-1*H*-indol-3-yl]acetyl}-*L*-phenylalanyl-glycinate (121ae)



The general procedure A was followed using Ethyl [2-(1*H*-indol-3-yl)acetyl]-*L*-phenylalanyl-glycinate (**120a**) (101.9 mg, 0.25 mmol) and bis(4-methoxyphenyl)iodonium tosylate (**18e**) (194.5 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 1/1) yielded **121ae** (96 mg, 75%) as a light brown solid (m. p. = 199–202 °C).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 11.06 (s, 1H), 8.46 (t, *J* = 5.9 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.35–7.14 (m, 7H), 7.05 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.91 (dd, *J* = 7.9, 7.0 Hz, 1H), 4.62 (ddd, *J* = 9.4, 8.4, 4.1 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.90 (dd, *J* = 17.4, 5.9 Hz, 1H), 3.86 (d, *J* = 17.4, 5.9 Hz, 1H), 3.81 (s, 3H), 3.60 (d, *J* = 15.8 Hz, 1H), 3.54 (d, *J* = 15.8 Hz, 1H), 3.07 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.83 (dd, *J* = 13.8, 9.4 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H).

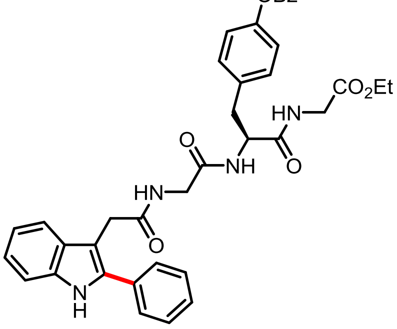
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.6 (C$_q$), 170.5 (C$_q$), 169.4 (C$_q$), 158.6 (C$_q$), 137.6 (C$_q$), 135.7 (C$_q$), 135.4 (C$_q$), 129.1 (CH), 129.0 (CH), 128.7 (C$_q$), 127.8 (CH), 126.0 (CH), 124.8 (C$_q$), 120.9 (CH), 118.6 (CH), 118.4 (CH), 113.9 (CH), 110.5 (CH), 104.7 (C$_q$), 60.3 (CH$_2$), 55.1 (CH$_3$), 53.8 (CH), 40.7 (CH$_2$), 37.6 (CH$_2$), 31.6 (CH$_2$), 14.0 (CH$_3$).

IR (ATR): 3397, 3263, 3061, 1751, 1644, 1504, 1248, 1177, 1027, 835, 727, 697 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1049 (10) [2M+Na]$^+$, 686 (2), 536 (100) [M+Na]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{30}H_{32}N_3O_5$ [M+H]$^+$: 514.2336; found: 514.2322.

Synthesis of Ethyl 2-(2-Phenyl-1*H*-indol-3yl)acetyl-glycyl-*L*-tyrosyl(benzoyloxy)-glycinate (121ba)



The general procedure A was followed using Ethyl 2-(1*H*-indol-3yl)acetyl-glycyl-*L*-tyrosyl(benzoyloxy)-glycinate (**121b**) (146.1 mg, 0.25 mmol) and diphenyliodonium tosylate (**18a**) (169.6 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 1/3 → 1/6) yielded **121ba** (103 mg, 62%) as a light brown solid (m. p. = 188–191 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.24 (s, 1H), 8.49 (t, *J* = 5.9 Hz, 1H), 8.14 (t, *J* = 5.4 Hz, 1H), 8.13 (d, *J* = 8.6 Hz, 2H), 8.12 (d, *J* =

8.2 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.73 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.62 (dd, *J* = 8.6, 7.5 Hz, 2H), 7.59 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.48 (dd, *J* = 7.9, 7.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.10 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 6.94 (ddd, *J* = 7.9, 7.0, 1.2 Hz, 1H), 4.60 (ddd, *J* = 9.6, 8.2, 4.4 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.84 (d, *J* = 5.9 Hz, 2H), 3.82 (dd, *J* = 16.6, 5.4 Hz, 1H), 3.68 (s, 2H), 3.65 (dd, *J* = 16.6, 5.4 Hz, 1H), 3.09 (dd, *J* = 13.9, 4.4 Hz, 1H), 2.80 (dd, *J* = 13.9, 9.6 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H).

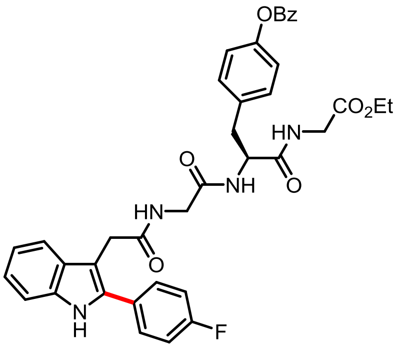
^{13}C NMR (126 MHz, DMSO-d$_6$): *δ* = 171.2 (C$_q$), 170.9 (C$_q$), 169.3 (C$_q$), 168.5 (C$_q$), 164.3 (C$_q$), 148.9 (C$_q$), 135.8 (C$_q$), 135.7 (C$_q$), 135.3 (C$_q$), 133.8 (CH), 132.3 (C$_q$), 130.0 (CH), 129.5 (CH), 128.8 (C$_q$), 128.7 (CH), 128.6 (C$_q$), 128.4 (CH), 127.9 (CH), 127.3 (CH), 121.3 (CH), 121.2 (CH), 118.7 (CH), 118.6 (CH), 110.9 (CH), 105.6 (C$_q$), 60.3 (CH$_2$), 53.6 (CH), 42.1 (CH$_2$), 40.7 (CH$_2$), 37.0 (CH$_2$), 31.7 (CH$_2$), 14.0 (CH$_3$).

IR (ATR): 3284, 1733, 1629, 1508, 1264, 1197, 1167, 1062, 707 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 2004 (8), 1674 (6), 1343 (62) [2M+Na]$^+$, 683 (100) [M+Na]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{38}H_{37}N_4O_7$ [M+H]$^+$: 661.2657; found: 661.2649.

Synthesis of Ethyl 2-[2-(4-Fluorophenyl)-1*H*-indol-3yl]acetyl-glycyl-*L*-tyrosyl(benzoyloxy)-glycinate (121bb)



The general procedure A was followed using Ethyl 2-(1*H*-indol-3yl)acetyl-glycyl-*L*-tyrosyl(benzoyloxy)-glycinate (**120b**) (146.1 mg, 0.25 mmol) and bis(4-fluorophenyl)iodonium tosylate (**18b**) (183.1 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 1/3) yielded **121bb** (136 mg, 82%) as a light brown solid (m. p. = 205–208 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): *δ* = 11.24 (s, 1H), 8.49 (t, *J* = 5.8 Hz, 1H), 8.20 (t, *J* = 5.6 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 8.12 (d, *J* = 8.6 Hz, 2H), 7.89 (dd, *J* = 7.5, 6.8 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 6.8 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.10 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.00 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 4.60 (ddd, *J* = 9.7, 8.8, 4.3 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.84 (d, *J* = 5.8 Hz, 2H), 3.82 (dd, *J* = 16.6, 5.6 Hz, 1H), 3.67 (dd, *J* = 16.6, 5.6 Hz, 1H), 3.65 (s, 2H), 3.09 (dd, *J* = 13.8, 4.3 Hz, 1H), 2.80 (dd, *J* = 13.8, 9.7 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d$_6$): *δ* = 171.2 (C$_q$), 170.9 (C$_q$), 169.3 (C$_q$), 168.5 (C$_q$), 164.3 (C$_q$), 161.5 (d, J_{C-F} = 244.6 Hz, C$_q$), 148.9 (C$_q$), 135.7 (C$_q$), 135.3 (C$_q$), 134.8 (C$_q$), 133.8 (CH), 130.0 (CH), 129.9 (d, J_{C-F} = 8.1 Hz, CH), 129.5 (CH), 128.9 (C$_q$), 128.8 (d, J_{C-F} = 21.3 Hz, C$_q$), 128.7 (CH), 128.6 (C$_q$), 121.4 (CH), 121.2 (CH), 118.8 (CH), 118.7 (CH), 115.3 (d, J_{C-F} = 21.3 Hz, CH), 110.9 (CH), 105.7 (C$_q$), 60.3 (CH$_2$), 53.6 (CH), 42.1 (CH$_2$), 40.7 (CH$_2$), 37.0 (CH$_2$), 31.5 (CH$_2$), 14.0 (CH$_3$).

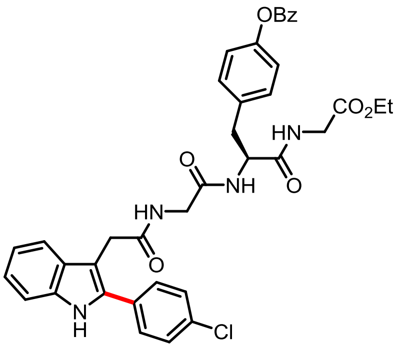
^{19}F NMR (283 MHz, DMSO-*d*$_6$): *δ* = -114.5 (ttd, *J* = 8.7, 5.5 2.8 Hz).

IR (ATR): 3291, 2963, 1734, 1627, 1506, 1259, 1197, 1013, 793, 705 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 2058 (8), 1716 (5), 1379 (53) [2M+Na]$^+$, 701 (100) [M+Na]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{38}H_{36}FN_4O_7$ $[M+H]^+$: 679.2563; found: 679.2562

Synthesis of Ethyl 2-[2-(4-Chlorophenyl)-1*H*-indol-3yl]acetyl-glycyl-L-tyrosyl(benzoyloxy)-glycinate (121bc)



The general procedure A was followed using ethyl 2-(1*H*-indol-3yl)acetyl-glycyl-L-tyrosyl(benzoyloxy)-glycinate (**120b**) (146.1 mg, 0.25 mmol) and bis(4-chlorophenyl)iodonium tosylate (**18c**) (195.5 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 1/3) yielded **121bc** (97 mg, 56%) as a light brown solid (m. p. = 192–195 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.29 (s, 1H), 8.48 (t, *J* = 5.9 Hz, 1H), 8.23 (t, *J* = 5.6 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.74 (ddd, *J* = 7.9, 1.0, 0.9 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.60 (dd, *J* = 8.6, 7.9 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.11 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 7.00 (ddd, *J* = 7.9, 7.0, 1.2 Hz, 1H), 4.60 (ddd, *J* = 9.2, 8.6, 4.4 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.84 (d, *J* = 5.9 Hz, 2H), 3.82 (dd, *J* = 16.2, 5.6 Hz, 1H), 3.66 (s, 2H), 3.64 (dd, *J* = 16.2, 5.6 Hz, 1H), 3.09 (dd, *J* = 13.8, 4.4 Hz, 1H), 2.80 (dd, *J* = 13.8, 9.2 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H).

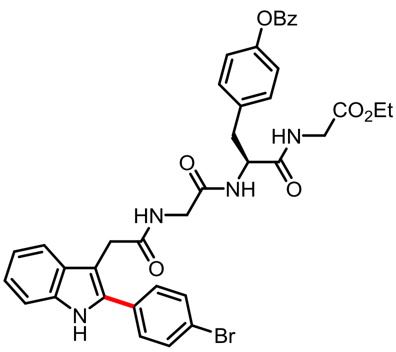
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.2 (C$_q$), 170.9 (C$_q$), 169.3 (C$_q$), 168.5 (C$_q$), 164.3 (C$_q$), 148.9 (C$_q$), 135.8 (C$_q$), 135.3 (C$_q$), 134.4 (C$_q$), 133.7 (CH), 132.0 (C$_q$), 131.1 (C$_q$), 130.0 (CH), 129.5 (CH), 129.5 (CH), 128.8 (C$_q$), 128.7 (CH), 128.6 (C$_q$), 128.4 (CH), 121.6 (CH), 121.2 (CH), 118.9 (CH), 118.7 (CH), 110.9 (CH), 106.3 (C$_q$), 60.3 (CH_2), 53.6 (CH), 42.1 (CH_2), 40.7 (CH_2), 37.0 (CH_2) 31.5 (CH_2), 14.0 (CH_3).

IR (ATR): 3292, 1735, 1645, 1628, 1508, 1264, 1199, 1064, 951, 705 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 2107 (8), 1760 (4), 1411 (42) $[M+Na]^+$.

HR-MS (ESI): *m/z* calcd for $C_{38}H_{36}ClN_4O_7$ $[M+H]^+$: 695.2273; found: 695.2255.

Synthesis of Ethyl 2-[2-(4-Bromophenyl)-1*H*-indol-3yl]acetyl-glycyl-L-tyrosyl(benzoyloxy)-glycinate (121bd)



The general procedure A was followed using Ethyl 2-(1*H*-indol-3yl)acetyl-glycyl-L-tyrosyl(benzoyloxy)-glycinate (**120b**) (142.9 mg, 0.25 mmol) and bis(4-bromophenyl)iodonium tosylate (**18d**) (224.8 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 1/3) yielded **121bd** (125 mg, 69%) as an orange solid (m. p. = 177–180 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.29 (s, 1H), 8.48 (t, *J* = 5.9 Hz, 1H), 8.23 (t, *J* = 5.5 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.60 (dd, *J* = 8.6, 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.12 (ddd, *J* = 8.2, 7.0, 1.0 Hz, 1H), 7.00 (ddd, *J* = 7.9, 7.0, 1.2 Hz, 1H), 4.60 (ddd, *J* = 9.1, 8.6, 4.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.84 (d, J = 5.9 Hz, 2H), 3.81 (dd, J = 16.2, 5.5 Hz, 1H), 3.67 (s, 2H), 3.65 (dd, J = 16.2, 5.5 Hz, 1H), 3.09 (dd, J = 13.8, 4.8 Hz, 1H), 2.80 (dd, J = 13.8, 9.1 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H).

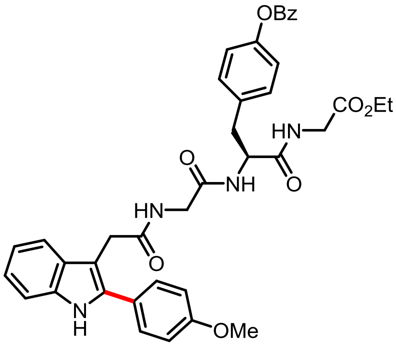
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.2 (C$_q$), 170.8 (C$_q$), 169.3 (C$_q$), 168.5 (C$_q$), 164.3 (C$_q$), 148.9 (C$_q$), 135.8 (C$_q$), 135.3 (C$_q$), 134.5 (C$_q$), 133.8 (CH), 131.5 (C$_q$), 131.3 (CH), 130.0 (CH), 129.8 (CH), 129.5 (CH), 128.8 (C$_q$), 128.8 (CH), 128.7 (C$_q$), 121.7 (CH), 121.2 (CH), 120.6 (C$_q$), 118.9 (CH), 118.8 (CH), 110.9 (CH), 106.3 (C$_q$), 60.4 (CH$_2$), 53.6 (CH), 42.1 (CH$_2$), 40.7 (CH$_2$), 37.0 (CH$_2$), 31.5 (CH$_2$), 14.0 (CH$_3$).

IR (ATR): 3293, 1736, 1627, 1508, 1263, 1199, 1010, 704 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 763 (2) [M+Na]$^+$ (^{81}Br), 233 (2).

HR-MS (ESI): *m/z* calcd for $C_{38}H_{35}BrN_4NaO_7$ [M+Na]$^+$ (^{79}Br): 761.1581; found: 761.1579.

Synthesis of Ethyl 2-[2-(4-Methoxyphenyl)-1*H*-indol-3yl]acetyl-glycyl-*L*-tyrosyl(benzoyloxy)-glycinate (121be)



The general procedure A was followed using Ethyl 2-(1*H*-indol-3yl)acetyl-glycyl-*L*-tyrosyl(benzoyloxy)-glycinate (**120b**) (146.1 mg, 0.25 mmol) and bis(4-methoxyphenyl)iodonium tosylate (**18e**) (192.1 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 1/3) yielded **121be** (139 mg, 81%) as a light brown solid (m. p. = 164–167 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.13 (s, 1H), 8.47 (t, J = 5.8 Hz, 1H), 8.16–8.10 (m, 4H), 7.74 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.60 (dd, J = 8.6, 7.8 Hz, 2H), 7.57 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.31 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 7.07 (dd, J = 8.2, 7.1 Hz, 1H), 7.05 (d, J = 8.5 Hz, 2H), 6.98 (dd, J = 7.9, 7.1 Hz, 1H), 4.60 (ddd, J = 9.1, 8.4, 4.5 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.84 (d, J = 5.8 Hz, 2H), 3.82 (dd, J = 16.2, 5.5 Hz, 1H), 3.80 (s, 3H), 3.67 (dd, J = 16.2, 5.5 Hz, 1H), 3.65 (s, 2H), 3.09 (dd, J = 14.2, 4.5 Hz, 1H), 2.80 (dd, J = 14.2, 9.1 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H).

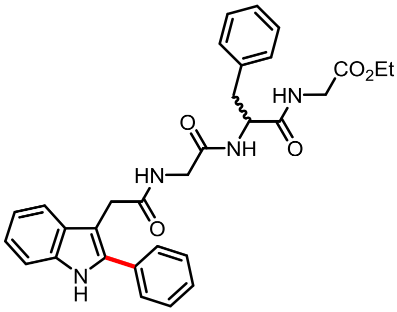
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.2 (C$_q$), 171.1 (C$_q$), 169.3 (C$_q$), 168.5 (C$_q$), 164.3 (C$_q$), 158.6 (C$_q$), 148.9 (C$_q$), 135.8 (C$_q$), 135.5 (C$_q$), 135.3 (C$_q$), 133.7 (CH), 130.0 (CH), 129.5 (CH), 129.2 (CH), 128.9 (C$_q$), 128.8 (C$_q$), 128.7 (CH), 124.8 (C$_q$), 121.2 (CH), 121.0 (CH), 118.5 (CH), 118.4 (CH), 113.9 (CH), 110.7 (CH), 104.6 (C$_q$), 60.3 (CH$_2$), 55.1 (CH), 53.6 (CH$_3$), 42.1 (CH$_2$), 40.7 (CH$_2$), 37.0 (CH$_2$), 31.7 (CH$_2$), 14.0 (CH$_3$).

IR (ATR): 3289, 1744, 1623, 1518, 1216, 739, 697 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 2094 (5), 1746 (6), 1509 (9), 1403 (41) [2M+Na]$^+$, 1055 (7) , 797 (17), 713 (100) [M+Na]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{39}H_{39}N_4O_8$ [M+H]$^+$: 691.2762; found: 691.2761.

Synthesis of Ethyl 2-(2-phenyl-1*H*-indol-3yl)acetyl-glycyl-*L*-phenylalanyl-glycinate (*L*-121ca) or Ethyl 2-(2-phenyl-1*H*-indol-3yl)acetyl-glycyl-*D*-phenylalanyl-glycinate (*D*-121ca)



The general procedure A was followed using Etyl 2-(1*H*-indol-3yl)acetyl-glycyl-*L*-phenylalanyl-glycinate (L-**120c**) or Ethyl 2-(1*H*-indol-3yl)acetyl-glycyl-*D*-phenylalanyl-glycinate (*D*-**120c** (116 mg, 0.25 mmol) and diphenyliodonium tosylate (**18a**) (169.6 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc 1/2) yielded *L*-**121ca** (105 mg, 77%) *D*-**121ca** (89.6 mg, 67%) as a light brown solid (m. p. = 188–190 °C).

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.22 (s, 1H), 8.42 (t, *J* = 5.8 Hz, 1H), 8.14–8.02 (m, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.49 (dd, J = 7.8, 7.2 Hz, 2H), 7.43–7.33 (m, 2H), 7.25–7.16 (m, 5H), 7.10 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 6.99 (dd, J = 7.8, 7.0 Hz, 1H), 4.55 (ddd, *J* = 9.3, 4.5, 4.0 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.81 (d, *J* = 5.8 Hz, 2H), 3.76 (d, *J* = 5.5 Hz, 1H), 3.69–3.55 (m, 3H), 3.04 (dd, *J* = 13.9, 4.3 Hz, 1H), 2.74 (dd, *J* = 13.9, 9.6 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

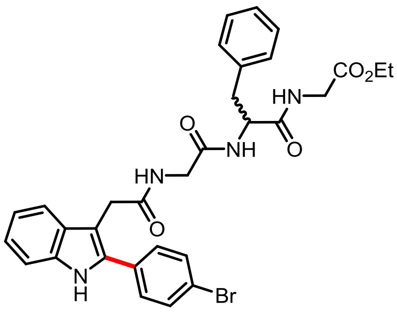
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.3 (C$_q$), 170.9 (C$_q$), 169.3 (C$_q$), 168.4 (C$_q$), 137.5 (C$_q$), 135.7 (C$_q$), 135.7 (C$_q$), 132.3 (C$_q$), 128.9 (CH), 128.7 (C$_q$), 128.4 (CH), 127.9 (CH), 127.8 (CH), 127.3 (CH), 126.1 (CH), 121.3 (CH), 118.7 (CH), 118.6 (CH), 110.9 (CH), 105.6 (C$_q$), 60.3 (CH$_2$), 53.6 (CH), 42.1 (CH$_2$), 40.7 (CH$_2$), 37.6 (CH$_2$), 31.7 (CH$_2$), 14.0 (CH$_3$).

IR (ATR): 3271, 1746, 1667, 1630, 1565, 1521, 1455, 1434, 1194, 742 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1081 (10) [2M+H]$^+$, 563 (30) [M+Na]$^+$, 541 (50) [M+H]$^+$, 340 (24), 191 (45), 154 (100).

HR-MS (ESI): *m/z* calcd for $C_{31}H_{33}N_4O_5$ [M+H]$^+$: 541.2445; found: 541.2445.

Synthesis of Ethyl 2-[2-(4-bromophenyl)-1*H*-indol-3yl]acetyl-glycyl-*L*-phenylalanyl-glycinate (*L*-121cd) or Ethyl 2-[2-(4-bromophenyl)-1*H*-indol-3yl]acetyl-glycyl-*D*-phenylalanyl-glycinate (*D*-121cd)



The general procedure A was followed using Ethyl 2-(1*H*-indol-3yl)acetyl-glycyl-*L*-phenylalanyl-glycinate (*L*-**120c**) or Ethyl 2-(1*H*-indol-3yl)acetyl-glycyl-*D*-phenylalanyl-glycinate (*D*-**120c**) (118.1 mg, 0.25 mmol) and bis(4-bromophenyl)iodonium tosylate (**18d**) (229.1 mg, 0.375 mmol). After 17 h, purification by column chromatography (*n* hexane/EtOAc 1/2) yielded *L*-**121cd** (102.9 mg, 65%) or *D*-**121cd** (120.5 mg, 77%) as a light brown solid (m. p. = 166–169 °C).

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.28 (s, 1H), 8.43 (t, *J* = 5.8 Hz, 1H), 8.17 (t, *J* = 5.5 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.77–7.71 (m, 2H), 7.70–7.63 (m, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.40–7.33 (m, 1H), 7.31–7.15 (m, 5H), 7.12 (ddd, *J* = 8.1, 7.1,1.1 Hz, 1H), 6.99 (dd, *J* = 7.5, 7.1, 1.0 Hz, 1H), 4.55 (ddd, *J* = 9.6, 4.5, 3.8 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.82 (t, *J* = 5.5 Hz, 2H), 3.76 (d, *J* = 5.7 Hz, 1H), 3.63 (d, *J* = 4.1 Hz, 2H), 3.59 (d, *J* = 5.6 Hz,1H), 3.04 (dd, *J* = 13.9, 4.4 Hz, 1H), 2.81–2.67 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.3 (C_q), 170.8 (C_q), 169.3 (C_q), 168.4 (C_q), 137.5 (C_q), 135.8 (C_q), 134.4 (C_q), 131.5 (C_q), 131.3 (CH), 129.8 (CH), 128.9 (CH), 128.6 (C_q), 127.8 (CH), 126.1 (CH), 121.7 (CH), 120.6 (C_q), 118.8 (CH), 118.7 (CH), 110.9 (CH), 106.3 (C_q), 60.3 (CH_2), 53.6 (CH), 42.0 (CH_2), 40.7 (CH_2), 37.6 (CH_2), 31.5 (CH_2), 14.0 (CH_3).

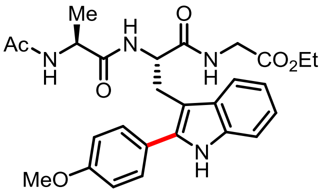
IR (ATR): 3280, 1740, 1644, 1517, 1487, 1455, 1442, 1198, 1009, 742 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 733 (25), 682 (26), 655 (30), 633 (45), 619 (100) $[M-H]^-$ (^{81}Br), 516 (70), 502 (65), 414 (60), 388 (55), 362 (51), 300 (95).

HR-MS (ESI): *m/z* calcd for $C_{31}H_{30}BrN_4O_5$ $[M-H]^-$ (^{81}Br): 619.1387; found: 619.1363.

5.3.2 Analytical Data for Arylated Tryptophan-Containing Peptides

Synthesis of Ethyl Acetyl-*L*-alanyl-*L*-(4-methoxyphenyl)tryptophyl-glycinate (123ae)



The general procedure B1 was followed using Ethyl acetyl-*L*-alanyl-*L*-tryptophyl-glycinate (**122a**) (80.5 mg, 0.20 mmol) and bis(4-methoxyphenyl)iodonium tosylate (**18e**) (153.7 mg, 0.30 mmol). After 15 h, purification by column chromatography (EtOAc/MeOH 40/1) yielded **123ae** (86 mg, 85%) as a pale white solid (m. p. = 230–232 °C).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 11.03 (s, 1H), 8.09 (t, *J* = 5.7 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.07 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.98 (dd, *J* = 8.2, 7.0 Hz, 1H), 4.64 (ddd, *J* = 8.3, 7.0, 7.0 Hz, 1H), 4.20 (dq, *J* = 7.2, 7.2 Hz, 1H), 4.04 (dq, *J* = 7.1, 1.7 Hz, 2H), 3.82 (s, 3H), 3.71 (dd, *J* = 17.3, 5.7 Hz, 1H), 3.60 (dd, *J* = 17.3, 5.7 Hz, 1H), 3.27 (dd, *J* = 14.4, 7.0 Hz, 1H), 3.06 (dd, *J* = 14.4, 7.0 Hz, 1H), 1.79 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 7.2 Hz, 3H).

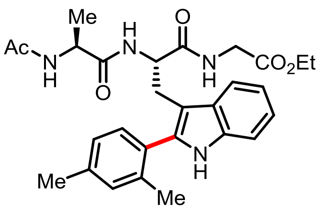
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.6 (C$_q$), 171.3 (C$_q$), 169.0 (C$_q$), 169.0 (C$_q$), 158.4 (C$_q$), 135.5 (C$_q$), 135.2 (C$_q$), 129.2 (CH), 128.8 (C$_q$), 125.0 (C$_q$), 120.8 (CH), 118.7 (CH), 118.3 (CH), 113.8 (CH), 110.6 (CH), 106.4 (C$_q$), 60.2 (CH$_2$), 55.1 (CH$_3$), 53.7 (CH), 48.3 (CH), 40.8 (CH$_2$), 27.9 (CH$_2$), 22.4 (CH$_3$), 17.7 (CH$_3$), 14.0 (CH$_3$).

IR (ATR): 3279, 1733, 1632, 1539, 1246, 1181, 1033, 775, 744 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1039 (63) [2M+Na]$^+$, 531 (94) [M+Na]$^+$, 509 (100) [M+H]$^+$, 396 (9), 265 (13).

HR-MS (ESI): *m/z* calcd for $C_{27}H_{33}N_4O_6$ [M+H]$^+$: 509.2395; found: 509.2400.

Synthesis of Ethyl Acetyl-*L*-alanyl-*L*-(2,4-dimethylphenyl)tryptophyl-glycinate (123ag)



The general procedure B1 was followed using Ethyl acetyl-*L*-alanyl-*L*-tryptophyl-glycinate (**122a**) (62.8 mg, 0.156 mmol) and bis(2,4-dimethylphenyl)iodonium tosylate (**18g**) (115.0 mg, 0.226 mmol). After 15 h, purification by column chromatography (EtOAc/MeOH 50/1) yielded **123ag** (40.7 mg, 51%) as a pale white solid (m. p. = 144–146 °C).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 10.87 (s, 1H), 7.97 (t, *J* = 5.7 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 8.2, 7.5 Hz, 1H), 6.99 (dd, *J* = 7.8, 7.5 Hz, 1H), 4.52 (ddd, *J* = 8.3, 7.8, 7.8 Hz, 1H), 4.16 (dq, *J* = 7.3, 7.3 Hz, 1H), 4.04 (dq, *J* = 7.1, 1.7 Hz, 2H), 3.69 (dd, *J* = 17.4, 5.7 Hz, 1H), 3.62 (dd, *J* = 17.4, 5.7 Hz, 1H), 3.06 (dd, *J* = 14.3, 7.8 Hz, 1H), 2.82 (dd, *J* = 14.3, 7.8 Hz, 1H), 2.35 (s, 3H), 2.12 (s, 3H), 1.77 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 7.3 Hz, 3H).

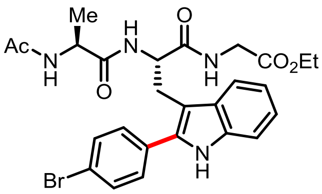
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.5 (C$_q$), 171.3 (C$_q$), 169.1 (C$_q$), 168.8 (C$_q$), 137.1 (C$_q$), 136.8 (C$_q$), 135.8 (C$_q$), 135.5 (C$_q$), 130.7 (CH), 130.4 (CH), 129.4 (C$_q$), 127.8 (C$_q$), 125.9 (CH), 120.5 (CH), 118.6 (CH), 118.1 (CH), 110.6 (CH), 107.2 (C$_q$), 60.2 (CH$_2$), 53.5 (CH), 48.2 (CH), 40.7 (CH$_2$), 27.5 (CH$_2$), 22.4 (CH$_3$), 20.8 (CH$_3$), 19.6 (CH$_3$), 17.8 (CH$_3$), 13.9 (CH$_3$).

IR (ATR): 3279, 2982, 1626, 1523, 1458, 1371, 1194, 744 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1035 (59) $[2M+Na]^+$, 529 (91) $[M+Na]^+$, 507 (100) $[M+H]^+$, 394 (13), 263 (14).

HR-MS (ESI): *m/z* calcd for $C_{28}H_{35}N_4O_5$ $[M+H]^+$: 507.2602; found: 507.2607.

Synthesis of Ethyl Acetyl-*L*-alanyl-*L*-(4-bromophenyl)tryptophyl-glycinate (123ad)



The general procedure B1 was followed using Ethyl acetyl-*L*-alanyl-*L*-tryptophyl-glycinate (**122a**) (80.5 mg, 0.20 mmol) and bis(4-bromophenyl)iodonium tosylate (**18d**) (183.0 mg, 0.30 mmol). After 15 h, purification by column chromatography (EtOAc/MeOH 50/1) yielded **123ad** (93 mg, 81%) as a pale white solid (m. p. = 239–241 °C).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 11.19 (s, 1H), 8.14 (t, J = 5.8 Hz, 1H), 7.92 (d, J = 7.2 Hz, 1H), 7.91 (d, J = 8.3 Hz, 2H), 7.69–7.62 (m, 4H), 7.34 (d, J = 8.1 Hz, 1H), 7.10 (dd, J = 8.1, 7.0 Hz, 1H), 7.00 (ddd, J = 7.9, 7.0 Hz, 1H), 4.65 (ddd, J = 8.3, 7.1, 7.1 Hz, 1H), 4.20 (dq, J = 7.2, 7.2 Hz, 1H), 4.04 (dq, J = 7.1, 1.7 Hz, 2H), 3.70 (dd, J = 17.7, 5.8 Hz, 1H), 3.59 (dd, J = 17.7, 5.8 Hz, 1H), 3.28 (dd, J = 14.4, 7.1 Hz, 1H), 3.08 (dd, J = 14.4, 7.1 Hz, 1H), 1.79 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H), 1.08 (d, J = 7.2 Hz, 3H).

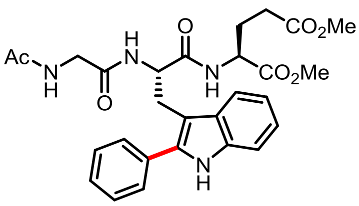
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.7 (C_q), 171.2 (C_q), 169.0 (C_q), 169.0 (C_q), 135.8 (C_q), 133.9 (C_q), 131.7 (C_q), 131.2 (CH), 129.9 (CH), 128.7 (C_q), 121.5 (CH), 120.3 (C_q), 119.0 (CH), 118.6 (CH), 110.9 (CH), 107.9 (C_q), 60.3 (CH_2), 53.6 (CH), 48.3 (CH), 40.8 (CH_2), 27.9 (CH_2), 22.4 (CH_3), 17.7 (CH_3), 13.9 (CH_3).

IR (ATR): 3273, 1737, 1631, 1538, 1192, 827, 738, 698 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1139 (15) $[2M+Na]^+$ (^{81}Br), 1137 (30) $[2M+Na]^+$ (^{81}Br/^{79}Br), 1135 (15) $[2M+Na]^+$ (^{79}Br), 581 (100) $[M+Na]^+$ (^{81}Br), 579 (100) $[M+Na]^+$ (^{79}Br), 559 (63) $[M+H]^+$ (^{81}Br), 557 (63) $[M+H]^+$ (^{79}Br), 446 (14), 444 (14), 315 (13), 313 (13).

HR-MS (ESI): *m/z* calcd for $C_{26}H_{30}BrN_4O_5$ $[M+H]^+$ (^{79}Br): 557.1394; found: 557.1400.

Synthesis of Dimethyl Acetyl-glycyl-*L*-phenyltryptophyl-*L*-glutamate (123ba)



The general procedure B1 was followed using dimethyl acetyl-*L*-glycyl-*L*-tryptophyl-*L*-glutamate (**122b**) (115.4 mg, 0.25 mmol) and diphenyliodonium tosylate (**18a**) (169.6 mg, 0.375 mmol). After 15 h, purification by column chromatography (EtOAc/MeOH 60/1 → 40/1) yielded **123ba** (83.7 mg, 78%) as a pale white solid (m. p. = 172–174 °C). A reduced catalyst loading of 1.0 mol % $Pd(OAc)_2$ yielded (75.1 mg, 56%) of **123ba**.

The general procedure B2 was followed using dimethyl acetyl-*L*-glycyl-*L*-tryptophyl-*L*-glutamate **(122b)** (115.1 mg, 0.25 mmol) and diphenyliodonium tosylate (**18a**) (169.6 mg, 0.375 mmol). After 15 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.2) yielded **123ba** (56.4 mg, 42%) as a pale white solid (m. p. = 172–174 °C).

^{1}H NMR (500 MHz, DMSO-d$_6$): *δ* = 11.12 (s, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.98 (t, *J* = 5.5 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 2H), 7.48 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.37 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.08 (ddd, *J* = 8.0, 7.1, 1.2 Hz, 1H), 6.98 (dd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 4.68 (ddd, *J* = 8.4, 7.8, 7.8 Hz, 1H), 4.24 (dt, *J* = 7.7, 5.5 Hz, 1H), 3.64 (dd, *J* = 16.5, 5.7 Hz, 1H), 3.57 (s, 3H), 3.48 (s, 3H), 3.45 (dd, *J* = 16.5, 5.7 Hz, 1H), 3.31 (dd, *J* = 14.4, 7.8 Hz, 1H), 3.07 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.28 (t, *J* = 7.7 Hz, 2H), 1.94 (dt, *J* = 7.7, 5.5 Hz, 1H), 1.82 (dt, *J* = 7.7, 5.5 Hz, 1H), 1.80 (s, 3H).

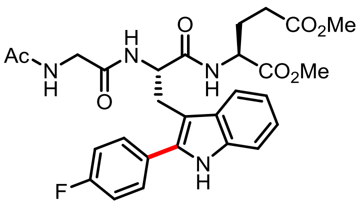
^{13}C NMR (126 MHz, DMSO-d$_6$): *δ* = 172.3 (C$_q$), 171.2 (C$_q$), 171.0 (C$_q$), 169.4 (C$_q$), 168.3 (C$_q$), 135.7 (C$_q$), 135.1 (C$_q$), 132.5 (C$_q$), 128.7 (C$_q$), 128.3 (CH), 127.9 (CH), 127.0 (CH), 121.1 (CH), 118.9 (CH), 118.4 (CH), 110.8 (CH), 107.3 (C$_q$), 53.7 (CH), 51.6 (CH), 51.2 (CH$_3$), 51.0 (CH$_3$), 42.1 (CH$_2$), 29.4 (CH$_2$), 27.8 (CH$_2$), 26.0 (CH$_2$), 22.3 (CH$_3$).

IR (ATR): 3272, 1733, 1635, 1521, 1436, 1204, 742, 698 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1095 (29) [2M+Na]$^+$, 559 (100) [M+Na]$^+$, 537 (67) [M+H]$^+$, 438 (4), 362 (4).

HR-MS (ESI): *m/z* calcd for $C_{28}H_{33}N_4O_7$ [M+H]$^+$: 537.2344; found: 537.2349.

Synthesis of Dimethyl Acetyl-glycyl-*L*-(4-fluorophenyl)tryptophyl-*L*-glutamate (123bb)



The general procedure B1 was followed using dimethyl acetyl-*L*-glycyl-*L*-tryptophyl-*L*-glutamate (**122b**) (92.1 mg, 0.20 mmol) and bis(4-fluorophenyl)iodonium tosylate (**18b**) (146.5 mg, 0.30 mmol). After 15 h, purification by column chromatography (EtOAc/MeOH 60/1 → 30/1) yielded **123bb** (89.7 mg, 81%) as a pale white solid (m. p. = 168–170 °C).

The general procedure B2 was followed using dimethyl acetyl-*L*-glycyl-*L*-tryptophyl-*L*-glutamate (**122b**) (92.1 mg, 0.20 mmol) and bis(4-fluorophenyl)iodonium tosylate (**18b**) (146.5 mg, 0.30 mmol). After 15 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.2) yielded **123bb** (37.2 mg, 34%) as a pale white solid (m. p. = 168–170 °C).

^{1}H NMR (300 MHz, DMSO-d$_6$): *δ* = 11.13 (s, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 8.01–7.91 (m, 2H), 7.76–7.64 (m, 3H), 7.36–7.26 (m, 3H), 7.09 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.99 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 4.67 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.31–4.17 (m, 1H), 3.65 (dd, *J* = 16.6, 5.9 Hz, 1H), 3.57 (s, 3H), 3.49 (s, 3H), 3.46 (dd, *J* = 16.5, 5.9 Hz, 1H), 3.34–3.19 (m, 1H), 3.03 (dd, *J* = 14.4, 7.7 Hz, 1H), 2.28 (t, *J* = 7.6 Hz, 2H), 2.03–1.70 (m, 2H), 1.81 (s, 3H).

^{19}F NMR (282 MHz, DMSO-d$_6$): *δ* = -114.77 (tt, *J* = 8.9, 5.5 Hz).

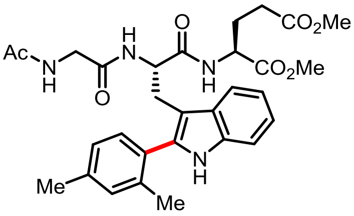
^{13}C NMR (126 MHz, DMSO-d$_6$): *δ* = 172.3 (C$_q$), 171.2 (C$_q$), 170.4 (d, $J_{C\text{-}F}$ = 224.7 Hz, C$_q$), 168.3 (C$_q$), 162.2 (C$_q$), 160.3 (C$_q$),161.2 (d, $J_{C\text{-}F}$ = 244.5 Hz, C$_q$), 135.7 (C$_q$), 134.2 (C$_q$), 130.0 (d, $J_{C\text{-}F}$ = 8.1 Hz, CH), 129.1 (d, $J_{C\text{-}F}$ = 3.1 Hz, C$_q$), 128.6 (C$_q$), 121.2 (CH), 118.9 (CH), 118.5 (CH), 115.2 (d, $J_{C\text{-}F}$ = 21.3 Hz, CH), 110.8 (CH), 107.3 (C$_q$), 53.6 (CH), 51.7 (CH$_3$), 51.2 (CH$_3$), 51.0 (CH), 42.1 (CH$_2$), 29.4 (CH$_2$), 27.7 (CH$_2$), 26.0 (CH$_2$), 22.3 (CH$_3$).

IR (ATR): 3273, 1735, 1661, 1632, 1540, 1439, 1258, 1220, 1199, 1173, 740 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1131 (5) $[2M+Na]^+$, 577 (15) $[M+Na]^+$, 191 (10), 107 (100).

HR-MS (ESI): *m/z* calcd for $C_{28}H_{31}FNaN_4O_7$ $[M+Na]^+$: 577.2069; found: 577.2065.

Synthesis of Dimethyl Acetyl-glycyl-*L*-(2,4-dimethylphenyl)tryptophyl-*L*-glutamate (123bg)



The general procedure B1 was followed using dimethyl acetyl-*L*-glycyl-*L*-tryptophyl-*L*-glutamate (**122b**) (115.1 mg, 0.25 mmol) and bis(2,4-dimethylphenyl)iodonium tosylate (**18g**) (190.7 mg, 0.375 mmol). After 15 h, purification by column chromatography (EtOAc/MeOH 60/1 → 40/1) yielded **123bg** (45.9 mg, 33%) as a pale white solid (m. p. = 153–155 °C).

The general procedure B2 was followed using dimethyl acetyl-*L*-glycyl-*L*-tryptophyl-*L*-glutamate (**122b**) (115.1 mg, 0.25 mmol) and bis(2,4-dimethylphenyl)iodonium tosylate (**18g**) (190.7 mg, 0.375 mmol). After 15 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.2) yielded **123bg** (61.4 mg, 44%) as a pale white solid (m. p. = 153–155 °C).

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 10.87 (s, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.93 (t, *J* = 5.6 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.15 (s, 1H), 7.03 (ddd, *J* = 22.0, 13.6, 6.9 Hz, 3H), 4.53 (ddd, *J* = 8.6, 8.6, 5.4 Hz, 1H), 4.21 (ddd, *J* = 8.6, 7.7, 5.1 Hz, 1H), 3.64–3.57 (m, 1H), 3.58 (s, 3H), 3.54 (s, 3H), 3.41 (dd, *J* = 16.4, 5.4 Hz, 1H), 3.07 (dd, *J* = 14.4, 5.4 Hz, 1H), 2.77 (dd, *J* = 14.5, 8.9 Hz, 1H), 2.35 (s, 3H), 2.30 (t, *J* = 7.7 Hz, 2H), 2.12 (s, 3H), 2.00–1.89 (m, 1H) 1.88–1.77 (m, 1H), 1.79 (s, 3H).

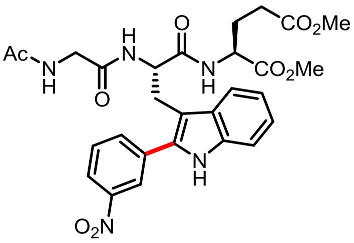
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 172.3 (C_q), 171.4 (C_q), 171.1 (C_q), 169.4 (C_q), 168.2 (C_q), 137.2 (C_q), 136.9 (C_q), 135.8 (C_q), 135.5 (C_q), 130.6 (CH), 130.4 (CH), 129.4 (C_q), 127.8 (C_q), 125.9 (CH), 120.5 (CH), 118.7 (CH), 118.1 (CH), 110.6 (CH), 107.3 (C_q), 53.5 (CH), 51.7 (CH_3), 51.2 (CH_3), 51.1 (CH), 42.1 (CH_2), 29.5 (CH_2), 27.2 (CH_2), 26.0 (CH_2), 22.3 (CH_3), 20.8 (CH_3), 19.6 (CH_3).

IR (ATR): 3271, 1742, 1658, 1600, 1545, 1258, 1277, 1112, 769 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1151 (5) $[2M+Na]^+$, 587 (20) $[M+Na]^+$, 191 (12), 107 (100).

HR-MS (ESI): *m/z* calcd for $C_{30}H_{36}NaN_4O_7$ $[M+Na]^+$: 587.2476; found: 587.2476.

Synthesis of Dimethyl Acetyl-glycyl-*L*-(3-nitrophenyl)tryptophyl-*L*-glutamate (123bh)



The general procedure B2 was followed using dimethyl acetyl-*L*-glycyl-*L*-tryptophyl-*L*-glutamate (**122b**) (115.1 mg, 0.25 mmol) and bis(3-nitrophenyl)iodonium tosylate (**18h**) (203.4 mg, 0.375 mmol). After 15h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.2) yielded **123bh** (18 mg, 12%) as a pale white solid (m. p. = 195–197 °C).

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.42 (s, 1H), 8.45 (t, *J* = 1.8 Hz, 1H), 8.21 (dd, *J* = 8.3, 2.2 Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.94 (t, *J* = 5.7 Hz, 1H), 7.83–7.70 (m, 2H), 7.38 (d, *J*

= 7.9 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 4.67 (dd, J = 7.3, 7.3 Hz, 1H), 4.28–4.14 (m, 1H), 3.63 (dd, J = 16.5, 5.8 Hz, 1H), 3.57 (s, 3H), 3.52–3.42 (m, 1H), 3.49 (s, 3H), 3.41–3.30 (m, 1H), 3.12 (dd, J = 14.5, 7.4 Hz, 1H), 2.26 (t, J = 7.7 Hz, 2H), 2.04–1.80 (m, 2H), 1.80 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 172.3 (C$_q$), 171.1 (C$_q$), 170.8 (C$_q$), 169.4 (C$_q$), 168.4 (C$_q$), 147.9 (C$_q$), 136.1 (C$_q$), 134.2 (CH), 132.7 (C$_q$), 129.9 (CH), 128.6 (C$_q$), 122.1 (CH), 122.0 (CH), 121.6 (CH), 119.3 (CH), 118.8 (CH), 111.1 (CH), 109.1 (C$_q$), 53.4 (CH), 51.7 (CH$_3$), 51.2 (CH$_3$), 51.0 (CH), 42.1 (CH$_2$), 29.4 (CH$_2$), 27.6 (CH$_2$), 26.0 (CH$_2$), 22.3 (CH$_3$).

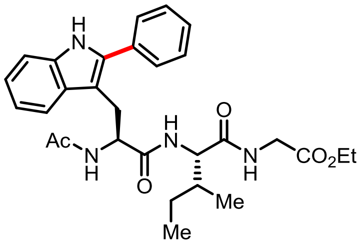
Due to overlap, one resonance is missing.

IR (ATR): 3270, 1735, 1632, 1528, 1439, 1266, 1201, 1096, 742 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1185 (24) [2M+Na]$^+$, 604 (100) [M+Na]$^+$, 582 (30) [M+H]$^+$, 107 (38).

HR-MS (ESI): *m/z* calcd for $C_{28}H_{31}NaN_5O_9$ [M+Na]$^+$: 604.2014; found: 604.2009.

Synthesis of Ethyl Acetyl-*L*-(phenyl)tryptophyl-*L*-isoleucyl-glycinate (123ca)



The general procedure B1 was followed using Ethyl acetyl-*L*-tryptophyl-*L*-isoleucyl-glycinate (**122c**) (111.1 mg, 0.25 mmol) and diphenyliodonium tosylate (**18a**) (169.6 mg, 0.375 mmol). After 15 h, purification by column chromatography (CH_2Cl_2/MeOH 40/1 → 30/1) yielded **123ca** (121.7 mg, 93%) as a light brown solid (m. p. = 195–198 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.13 (s, 1H), 8.15 (t, J = 6.0 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.72–7.67 (m, 3H), 7.58 (d, J = 8.9 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.11–7.05 (m, 1H), 7.01–6.94 (m, 1H), 4.68 (td, J = 8.2, 6.2 Hz, 1H), 4.20 (dd, J = 8.9, 7.1 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.79–3.62 (m, 2H), 3.37 (q, J = 7.3 Hz, 1H), 3.34–3.21 (m, 1H), 3.11–3.01 (m, 2H), 1.68 (s, 3H), 1.42 (ddt, J = 14.7, 7.2, 3.6 Hz, 1H), 1.24 (t, J = 7.3 Hz, 1H), 1.21–1.14 (m, 3H), 1.04 (ddd, J = 13.6, 9.3, 7.3 Hz, 1H), 0.85–0.78 (m, 6H).

^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.0 (C$_q$), 170.9 (C$_q$), 169.4 (C$_q$), 168.9 (C$_q$), 135.8 (C$_q$), 135.1 (C$_q$), 132.8 (C$_q$), 128.9 (C$_q$), 128.5 (CH), 128.0 (CH), 127.2 (CH), 121.2 (CH), 119.8 (CH), 118.5 (CH), 110.9 (CH), 107.8 (C$_q$), 60.3 (CH$_2$), 56.5 (CH), 54.0 (CH), 40.6 (CH$_2$), 27.6 (CH$_2$), 24.1 (CH$_2$), 22.4 (CH$_3$), 15.0 (CH$_3$), 13.9 (CH$_3$), 11.1 (CH$_3$), 7.1 (CH).

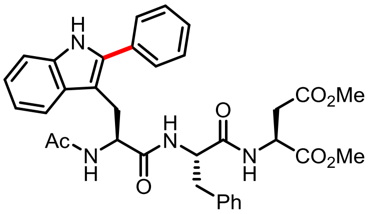
IR (ATR): 3416, 3269, 1719, 1628, 1539, 1299, 1240, 742 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1064 (55) [2M+Na]$^+$, 543 (100) [M+Na]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{29}H_{37}N_4O_5$ [M+H]$^+$: 521.2758; found: 521.2747.

Synthesis of Dimethyl Acetyl-*L*-(phenyl)tryptophyl-*L*-phenylalanyl-aspartate (123da)

The general procedure B1 was followed using Dimethyl acetyl-*L*-tryptophyl-*L*-phenylalanyl-aspartate (**122d**) (134.1 mg, 0.25 mmol) and diphenyliodonium tosylate (**18a**) (169.6 mg, 0.375 mmol). After 15 h,



purification by column chromatography (CH_2Cl_2/MeOH 20/1) yielded **123da** (129 mg, 84%) as a pale white solid (m. p. = 235–237 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.13 (s, 1H), 8.40 (d, J = 7.9 Hz, 1H), 7.82 (dd, J = 11.8, 8.6 Hz, 2H), 7.70–7.65 (m, 3H), 7.50 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.20 (tt, J = 14.9, 7.4 Hz, 5H), 7.11–7.06 (m, 1H), 7.02–6.97 (m, 1H), 4.65–4.57 (m, 2H), 4.53 (p, J = 8.2, 7.2 Hz, 1H), 3.60 (s, 6H), 3.18 (dd, J = 14.6, 5.2 Hz, 1H), 3.01 (d, J = 14.3 Hz, 1H), 3.01 (t, J = 14.1 Hz, 1H), 2.90–2.72 (m, 2H), 2.66 (dd, J = 16.6, 6.6 Hz, 1H), 1.63 (d, J = 0.9 Hz, 3H).

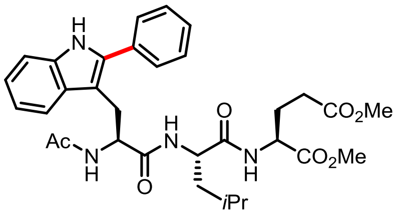
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.0 (C$_q$), 170.8 (C$_q$), 170.4 (C$_q$), 170.3 (C$_q$), 168.9 (C$_q$), 137.3 (C$_q$), 135.9 (C$_q$), 135.2 (C$_q$), 132.8 (C$_q$), 129.3 (CH), 128.9 (C$_q$), 128.6 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 126.2 (CH), 121.3 (CH), 119.1 (CH), 118.5 (CH), 110.9 (CH), 107.8 (C$_q$), 54.1 (CH), 53.4 (CH), 52.1 (CH_3), 51.6 (CH_3), 48.4 (CH), 37.5 (CH_2), 35.5 (CH_2), 27.4 (CH_2), 22.4 (CH_3).

IR (ATR): 3274, 1736, 1637, 1537, 1435, 1200, 1170, 743 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1248 (25) [2M+Na]$^+$, 635 (100) [M+Na]$^+$, 613 (20) [M+H]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{34}H_{36}NaN_4O_7$ [M+Na]$^+$: 635.2476; found: 635.2455.

Synthesis of Dimethyl Acetyl-*L*-(phenyl)tryptophyl-*L*-leucyl-glutamate (123ea)



The general procedure B1 was followed using dimethyl acetyl-*L*-tryptophyl-*L*-leucyl-glutamate (**122e**) (103.3 mg, 0.20 mmol) and diphenyliodonium tosylate (**18a**) (135.7 mg, 0.30 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.1) yielded **123ea** (70 mg, 59%) as a pale white solid (m. p. = 110–113 °C).

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.11 (s, 1H), 8.13 (d, J = 7.4 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.7 Hz, 3H), 7.49 (t, J = 7.5 Hz, 2H), 7.39 (d, J = 7.3 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 7.0 Hz, 1H), 6.99 (t, J = 7.1 Hz, 1H), 4.72–4.58 (m, 1H), 4.37–4.17 (m, 2H), 3.58 (d, J = 3.0 Hz, 6H), 3.30 (dd, J = 14.4, 5.6 Hz, 1H), 3.09 (dd, J = 14.4, 8.3 Hz, 1H), 2.36 (t, J = 7.6 Hz, 2H), 2.03–1.94 (m, 1H), 1.88–1.77 (m, 1H), 1.66 (s, 3H), 1.61–1.32 (m, 3H), 0.86 (d, J = 9.1 Hz, 3H), 0.84 (d, J = 9.1 Hz, 3H).

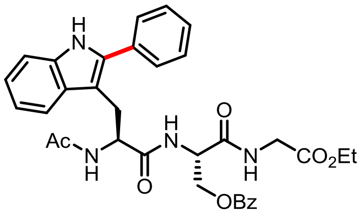
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 172.5 (C$_q$), 171.8 (C$_q$), 171.7 (C$_q$), 171.1 (C$_q$), 169.0 (C$_q$), 135.9 (C$_q$), 135.2 (C$_q$), 132.9 (C$_q$), 128.9 (C$_q$), 128.5 (CH), 128.1 (CH), 127.2 (CH), 121.3 (CH), 119.2 (CH), 118.5 (CH), 110.9 (CH), 107.7 (C$_q$), 54.0 (CH), 51.7 (CH_3), 51.3 (CH_3), 51.1 (CH), 50.9 (CH), 40.9 (CH_2), 29.5 (CH_2), 27.5 (CH_2), 25.8 (CH_2), 23.9 (CH), 22.9 (CH_3), 22.4 (CH_3), 21.9 (CH_3).

IR (ATR): 3281, 2953, 1736, 1639, 1520, 1436, 1203, 767 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1224 (30) [2M+K]$^+$, 687 (25), 631 (100) [M+K]$^+$, 418 (5), 289 (6).

HR-MS (ESI): *m/z* calcd for $C_{32}H_{40}KN_4O_7$ [M+K]$^+$: 631.2529; found: 631.2522.

Synthesis of Ethyl Acetyl-*L*-(phenyl)tryptophyl-*L*-seryl(benzoyloxy)-glycinate (123fa)



The general procedure B1 was followed using ethyl acetyl-*L*-tryptophyl-*L*-seryl(benzoyloxy)-glycinate (**122f**) (78.4 mg, 0.15 mmol) and diphenyliodonium tosylate (**18a**) (101.8 mg, 0.225 mmol). After 15 h, purification by column chromatography (EtOAc/MeOH 400/1) yielded **123fa** (65.3 mg, 73%) as a pale white solid (m. p. = 230–232 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.15 (s, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 8.12 (t, *J* = 5.9 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.96 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.69 (dd, *J* = 8.2, 1.0 Hz, 3H), 7.64 (tt, *J* = 7.9, 1.3 Hz, 1H), 7.49 (td, *J* = 8.0, 6.1 Hz, 4H), 7.40–7.34 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.08 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.99 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1H), 4.78–4.69 (m, 2H), 4.44 (dd, *J* = 11.0, 4.9 Hz, 1H), 4.32 (dd, *J* = 11.0, 6.7 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.80 (dd, *J* = 17.3, 5.9 Hz, 1H), 3.74 (dd, *J* = 17.4, 5.9 Hz, 1H), 3.33 (dd, *J* = 14.5, 6.3 Hz, 1H), 3.10 (dd, *J* = 14.5, 7.9 Hz, 1H), 1.65 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

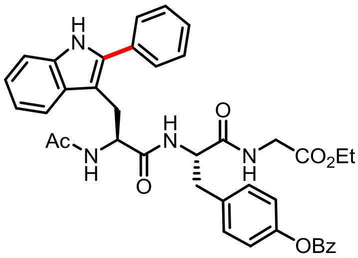
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.4 (C$_q$), 168.9 (C$_q$), 168.7 (C$_q$), 168.4 (C$_q$), 165.2 (C$_q$), 135.8 (C$_q$), 135.3 (C$_q$), 133.3 (CH), 132.8 (C$_q$), 129.4 (C$_q$), 129.3 (CH), 128.8 (C$_q$), 128.5 (CH), 128.5 (CH), 128.0 (CH), 127.2 (CH), 121.3 (CH), 119.0 (CH), 118.6 (CH), 110.9 (CH), 107.5 (C$_q$), 64.1 (CH$_2$), 60.3 (CH$_2$), 53.9 (CH), 51.3 (CH), 40.8 (CH$_2$), 27.6 (CH$_2$), 22.4 (CH$_3$), 13.9 (CH$_3$).

IR (ATR): 3275, 1726, 1633, 1542, 1273, 1213, 1129, 734 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 711 (35), 660 (40), 633 (42), 597 (100) [M-H]$^-$, 475 (10).

HR-MS (ESI): *m/z* calcd for $C_{33}H_{34}N_4O_7$ [M-H]$^-$: 597.2355; found: 597.2351.

Synthesis of Ethyl Acetyl-*L*-(phenyl)tryptophyl-*L*-tyrosyl(benzoyloxy)-glycinate (123ga)



The general procedure B1 was followed using ethyl acetyl-*L*-tryptophyl-*L*-tyrosyl(benzoyloxy)-glycinate (**122g**) (119.7 mg, 0.20 mmol) and diphenyliodonium tosylate (**18a**) (135.7 mg, 0.30 mmol). After 15 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.1) yielded **123ga** (110.9 mg, 82%) as a pale white solid (m. p. = 236–238 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.14 (s, 1H), 8.16 (t, *J* = 5.9 Hz, 1H), 8.11 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.73 (ddt, *J* = 8.8, 7.2, 1.3 Hz, 1H), 7.72–7.67 (m, 3H), 7.62–7.56 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.37 (td, *J* = 7.3, 1.3 Hz, 1H), 7.34 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.31–7.28 (m, 2H), 7.15–7.11 (m, 2H), 7.07 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.00 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 4.69–4.62 (m, 1H), 4.62–4.55 (m, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.84–3.70 (m, 2H), 3.27–3.14 (m, 1H), 3.12–2.95 (m, 2H), 2.82 (dd, *J* = 13.9, 8.3 Hz, 1H), 1.65 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

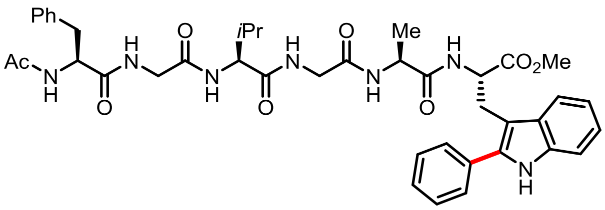
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 170.9 (C$_q$), 170.7 (C$_q$), 169.2 (C$_q$), 168.6 (C$_q$), 164.2 (C$_q$), 148.9 (C$_q$), 135.7 (C$_q$), 135.0 (2 C$_q$), 133.7 (CH), 132.6 (C$_q$), 130.1 (CH), 129.5 (CH), 128.8 (C$_q$), 128.7 (C$_q$), 128.7 (CH), 128.4 (CH), 127.9 (CH), 127.0 (CH), 121.1 (CH), 121.1 (CH), 119.0 (CH), 118.4 (CH), 110.8 (CH), 107.6 (C$_q$), 60.3 (CH$_2$), 53.9 (CH), 53.4 (CH), 40.7 (CH$_2$), 36.9 (CH$_2$), 27.5 (CH$_2$), 22.4 (CH$_3$), 14.0 (CH$_3$).

IR (ATR): 3274, 1732, 1636, 1540, 1264, 1196, 1081, 703 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 787 (25), 719 (30), 673 (100) $[M-H]^-$, 471 (30), 417 (35).

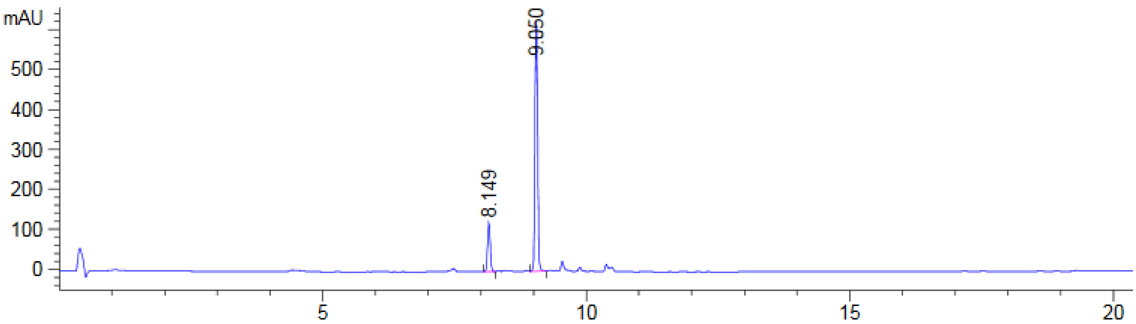
HR-MS (ESI): *m/z* calcd for $C_{39}H_{37}N_4O_7$ $[M-H]^-$: 673.2668; found: 673.2660.

Synthesis of Methyl Acetyl *L*-phenylalanyl-glycinyl-*L*-valinyl-glycinyl-*L*-alanyl-*L*-(phenyl)tryptophanate (123ha)



The general procedure B1 was followed using methyl acetyl *L*-phenylalanyl-glycyl-*L*-valyl-glycyl-*L*-alanyl-*L*-tryptophanate (**122h**) (138.4 mg, 0.20 mmol) and diphenyliodonium tosylate (**18a**) (135.7 mg, 0.30 mmol). After 21 h, the reaction mixture was analyzed by HPLC, which showed a conversion of 83%. An analytically pure sample **123ha** (23.8 mg, 15%) was obtained by column chromatography (CH_2Cl_2/EtOAc/MeOH 1/4/0.65) as a pale white solid. (m. p. = 244–246 °C).

Chromatogram of the reaction mixture, **122h** t_R = 8.149 min, **123ha** t_R = 9.050 min, column: Zorbax SB-C18, solvent: water/acetonitrile 90/10 gradient to acetonitrile 100, flow rate: 0.65 mL/min, detection at 290 nm.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.149	BB	0.0561	433.07706	119.94444	16.6678
2	9.050	BB	0.0542	2165.21509	628.44543	83.3322

^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.22 (s, 1H), 8.37 (d, J = 7.4 Hz, 1H), 8.27 (t, J = 5.7 Hz, 1H), 8.21 (t, J = 5.7 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.62 (dd, J = 8.2, 1.1 Hz, 2H), 7.56 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.41–7.34 (m, 2H), 7.26–7.24 (m, 4H), 7.20–7.16 (m, 1H), 7.14–7.07 (m, 1H), 7.06–6.98 (m, 1H), 4.56–4.44 (m, 2H), 4.32 (p, J = 7.1 Hz, 1H), 4.16 (dt, J = 8.4, 5.9 Hz, 1H), 3.83–3.65 (m, 4H), 3.36 (dd, J = 14.5, 8.9 Hz, 1H), 3.28 (s, 3H), 3.23 (dd, J = 14.5, 6.1 Hz, 1H), 3.03 (dd, J = 13.9, 4.5 Hz, 1H), 2.77 (dd, J = 13.9, 10.0 Hz, 1H), 2.05–1.98 (m, 1H), 1.76 (s, 3H), 1.15 (d, J = 7.0 Hz, 3H), 0.86 (dd, J = 12.8, 6.8 Hz, 6H).

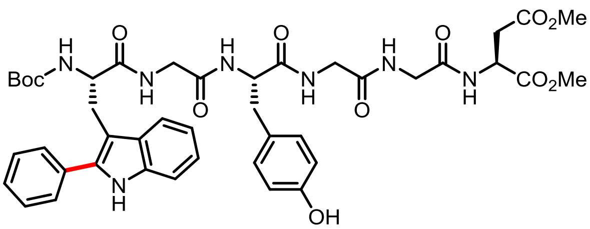
^{13}C NMR (126 MHz, DMSO-d_6): δ = 172.0 (C_q), 171.8 (C_q), 171.7 (C_q), 171.1 (C_q), 169.3 (C_q), 168.8 (C_q), 168.1 (C_q), 138.0 (C_q), 135.9 (C_q), 135.4 (C_q), 132.6 (C_q), 129.0 (CH), 128.6 (CH), 128.6 (C_q),128.0 (CH), 127.9 (CH), 127.4 (CH), 126.1 (CH), 121.5 (CH), 118.9 (CH), 118.5 (CH), 111.1 (CH), 106.5 (C_q), 57.9 (CH), 54.2 (CH), 53.2 (CH), 51.5 (CH_3), 47.7 (CH), 42.1 (CH_2), 41.9 (CH_2), 37.3 (CH_2), 30.2 (CH), 27.1 (CH_2), 22.4 (CH_3), 19.1 (CH_3), 18.4 (CH_3), 18.0 (CH_3).

IR (ATR): 3290, 2960, 1630, 1513, 1437, 1367, 1217, 741 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1559 (7) $[2M+Na]^+$, 926 (5), 846 (10) $[M+2K]^+$, 790 (100) $[M+Na]^+$, 768 (50) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{41}H_{49}NaN_7O_8$ $[M+Na]^+$: 790.3535; found: 790.3531.

Synthesis of Dimethyl *tert*-butoxycarbonyl *L*-(phenyl)tryptophyl-glycyl-*L*-tyrosyl-glycyl-glycyl-*L*-aspartate (123ia)



The general procedure B1 was followed using dimethyl *tert*-butoxycarbonyl *L*-tryptophyl-glycyl-*L*-tyrosyl-glycyl-glycyl-*L*-aspartate (**122i**) (156.4 mg, 0.20 mmol) and diphenyliodonium tosylate (**18a**) (135.7 mg, 0.30 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/5/0.6) yielded **123ia** (44.5 mg, 20 %) as a pale white solid (m. p. = 149–150 °C decomposition).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.13 (s, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 8.24 (t, *J* = 5.6 Hz, 1H), 8.01–7.93 (m, 2H), 7.89 (dd, *J* = 5.5 Hz, 1H), 7.70–7.64 (m, 3H), 7.48 (dd, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.09 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 2H), 4.68 (dd, *J* = 7.4, 6.8 Hz, 1H), 4.46–4.39 (m, 1H), 4.33–4.26 (m, 1H), 3.79–3.71 (m, 4H), 3.63 (s, 3H), 3.61 (s, 3H), 3.47–3.41 (m, 1H), 3.33 (dd, *J* = 14.6, 4.9 Hz, 1H), 3.09 (dd, *J* = 14.5, 8.4 Hz, 1H), 2.95 (dd, *J* = 14.0, 4.7 Hz, 1H), 2.82 (dd, *J* = 16.5, 6.2 Hz, 1H), 2.76–2.66 (m, 3H), 1.21 (s, 9H).

^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.9 (C_q), 171.7 (C_q), 171.1 (C_q), 170.5 (C_q), 169.1 (C_q), 168.9 (C_q), 168.8 (C_q), 155.9 (C_q), 155.0 (C_q), 136.0 (C_q), 135.2 (C_q), 133.0 (C_q), 130.1 (CH), 129.3 (C_q), 128.7 (CH), 128.1 (CH), 128.0 (C_q), 127.4 (CH), 121.5 (CH), 119.2 (CH), 118.7 (CH), 115.0 (CH), 111.0 (CH), 108.0 (C_q), 78.2 (C_q), 55.8 (CH), 54.6 (CH), 52.2 (CH_3), 51.7 (CH_3), 48.5 (CH), 42.1 (2 CH_2), 41.7 (CH_2), 36.6 (CH_2), 35.6 (CH_2), 27.9 (CH_3), 27.4 (CH_2).

IR (ATR): 3281, 2961, 1733, 1637, 1533, 1422, 1237, 1169, 769, 741 cm^{-1}.

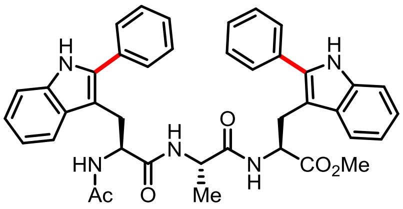
MS (ESI) *m/z* (relative intensity) 1738 (12) $[2M+Na]^+$, 880 (100) $[M+Na]^+$, 758 (18).

HR-MS (ESI): *m/z* calcd for $C_{43}H_{51}NaN_7O_{12}$ $[M+Na]^+$: 880.3488; found: 880.3495.

Synthesis of Methyl Acetyl *L*-(phenyl)tryptophyl-*L*-alanyl-*L*-(phenyl)tryptophanate (123la), Methyl Acetyl *L*-(phenyl)tryptophyl-*L*-alanyl-*L*-tryptophanate (123la') and Methyl Acetyl *L*-tryptophyl-*L*-alanyl-*L*-(phenyl)tryptophanate (123la'')

The general procedure B1 was followed using methyl acetyl *L*-tryptophyl-*L*-alanyl-*L*-tryptophanate (**122l**) (103.5 mg, 0.20 mmol) and diphenyliodonium tosylate (**18a**) (271.4 mg, 0.60 mmol) in acetic acid (4.00 mL). After 20 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.1) yielded **123la** (48.5 mg, 36%) , **123la'** (32.3 mg, 27%) and **123la''** (6.5 mg, 5%) as pale white solids (**123la** m. p. = 178–181 °C, **123la'** m. p. = 164–166 °C, **123la'** m. p. = 169–171 °C).

123la:



^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.21 (s, 1H), 11.13 (s, 1H), 8.26 (d, *J* = 7.2 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.72–7.66 (m, 3H), 7.61 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.50–7.46 (m, 4H), 7.39–7.34 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.10 (ddd, *J* = 7.0, 6.9, 1.0 Hz, 1H), 7.07 (ddd, *J* = 7.0, 6.9, 1.0 Hz, 1H), 7.02 (ddd, *J* = 7.1, 7.0, 0.9 Hz, 1H), 6.97 (ddd, J = 7.0, 6.9, 0.9 Hz, 1H), 4.62 (td, *J* = 8.2, 5.9 Hz, 1H), 4.49–4.42 (m, 1H), 4.24 (dq, *J* = 7.0, 7.0 Hz, 1H), 3.36–3.27 (m, 2H), 3.24 (s, 3H), 3.21 (dd, *J* = 14.5, 5.8 Hz, 1H), 3.09 (dd, *J* = 14.5, 8.0 Hz, 1H), 1.65 (s, 3H), 1.11 (d, *J* = 7.0 Hz, 3H).

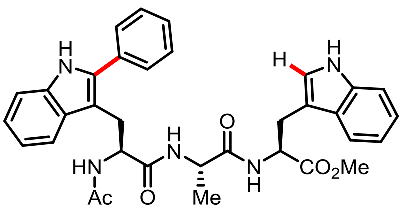
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.7 (C$_q$), 171.7 (C$_q$), 170.8 (C$_q$), 168.9 (C$_q$), 135.8 (2 C$_q$), 135.4 (C$_q$), 135.2 (C$_q$), 132.9 (C$_q$), 132.6 (C$_q$), 128.9 (C$_q$), 128.6 (CH), 128.5 (C$_q$), 128.5 (CH), 128.1 (CH), 127.9 (CH), 127.4 (CH), 127.2 (CH), 121.5 (CH), 121.2 (CH), 119.1 (CH), 118.8 (CH), 118.5 (CH), 118.4 (CH), 111.1 (CH), 110.9 (CH), 107.7 (C$_q$), 106.4 (C$_q$), 54.0 (CH), 53.2 (CH), 51.4 (CH_3), 47.8 (CH), 27.6 (CH_2), 27.0 (CH_2), 22.5 (CH_3), 18.2 (CH_3).

IR (ATR): 3276, 3063, 1749, 1661, 1628, 1542, 1457, 1449, 1432, 1208, 741 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1377 (12) [2M+K]$^+$, 708 (100) [M+K]$^+$, 107 (15).

HR-MS (ESI): *m/z* calcd for $C_{40}H_{39}KN_5O_5$ [M+K]$^+$: 708.2583; found: 708.2583.

123la’:



^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.11 (s, 1H), 10.82 (s, 1H), 8.17 (d, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.72–7.64 (m, 3H), 7.52–7.43 (m, 3H), 7.38–7.30 (m, 3H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.10–7.03 (m, 2H), 6.99 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 6.95 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1H), 4.62 (td, *J* = 8.2, 5.9 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 1H), 4.28 (dq, *J* = 7.0, 7.0 Hz, 1H), 3.51 (s, 3H), 3.35–3.27 (m, 1H), 3.16–3.02 (m, 3H), 1.65 (s, 3H), 1.14 (d, *J* = 7.0 Hz, 3H).

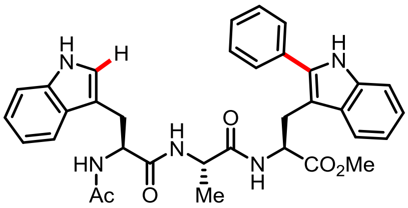
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 172.0 (C$_q$), 171.9 (C$_q$), 170.8 (C$_q$), 168.9 (C$_q$), 136.0 (C$_q$), 135.8 (C$_q$), 135.3 (C$_q$), 132.9 (C$_q$), 128.9 (C$_q$), 128.5 (CH), 128.1 (CH), 127.2 (CH), 127.0 (C$_q$), 123.6 (CH), 121.3 (CH), 120.9 (CH), 119.1 (CH), 118.5 (CH), 118.3 (CH), 117.9 (CH), 111.4 (CH), 110.9 (CH), 109.1 (C$_q$), 107.6 (C$_q$), 53.9 (CH), 53.2 (CH), 51.6 (CH_3), 47.8 (CH), 27.6 (CH_2), 26.9 (CH_2), 22.5 (CH_3), 18.3 (CH_3).

IR (ATR): 3274, 3061, 1728, 1636, 1540, 1508, 1456, 1223, 1207, 740 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1225 (21) [2M+K]+, 632 (100) [M+K]+, 107 (18).

HR-MS (ESI): *m/z* calcd for $C_{34}H_{35}KN_5O_5$ [M+K]$^+$: 632.2270; found: 632.2277.

123la’’:



^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.20 (s, 1H), 10.74 (s, 1H), 8.26 (d, *J* = 7.3 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.68–7.43 (m, 5H), 7.43–7.27 (m, 4H), 7.17–6.90 (m, 5H), 4.59–4.45 (m, 2H), 4.30 (dq, *J* = 7.2, 7.2 Hz, 1H), 3.36 (dd, *J* = 14.5, 9.1 Hz, 1H), 3.28 (s, 3H), 3.26–3.15 (m, 1H), 3.14–3.04 (m, 1H), 2.90 (dd, *J* = 15.0, 9.2 Hz, 1H), 1.77 (s, 3H), 1.17 (d, *J* = 7.2 Hz, 3H).

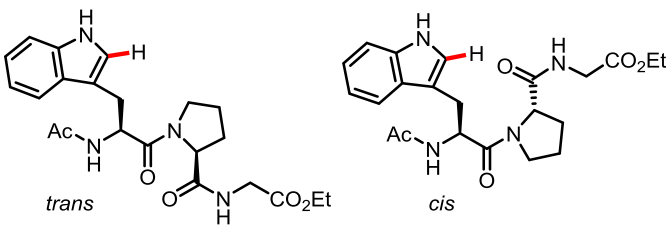
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 172.0 (C$_q$), 171.8 (C$_q$), 171.3 (C$_q$), 169.1 (C$_q$), 136.0 (C$_q$), 135.8 (C$_q$), 135.4 (C$_q$), 132.6 (C$_q$), 128.6 (CH), 128.6 (C$_q$), 127.9 (CH), 127.4 (CH), 127.3 (C$_q$), 123.4 (CH), 121.5 (CH), 120.7 (CH), 118.8 (CH), 118.4 (CH), 118.4 (CH), 118.0 (CH), 111.1 (CH), 111.1 (CH), 110.2 (C$_q$), 106.5 (C$_q$), 53.3 (CH), 53.2 (CH), 51.5 (CH$_3$), 47.9 (CH), 27.6 (CH$_2$), 27.2 (CH$_2$), 22.5 (CH$_3$), 18.0 (CH$_3$).

IR (ATR): 3273, 3058, 1733, 1661, 1540, 1458, 1252, 1201, 741 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1225 (11) [2M+K]$^+$, 632 (100) [M+K]$^+$, 616 (22) [M+Na]$^+$, 594 (15) [M+H]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{34}H_{35}KN_5O_5$ [M+K]$^+$: 632.2270; found: 632.2269.

Synthesis of Ethyl Acetyl-*L*-(phenyl)tryptophyl-*L*-prolyl-glycinate (123ja)



The general procedure B1 was followed using ethyl acetyl-*L*-tryptophyl-*L*-prolyl-glycinate (**122j**) (85.7 mg, 0.20 mmol) and diphenyliodonium tosylate (**18a**) (135.7 mg, 0.30 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.25) yielded **123ja** (45.8 mg, 45%) as a pale white solid (m. p. = 145–147 °C).

The general procedure B2 was followed using Ethyl Acetyl-*L*-tryptophyl-*L*-prolyl-glycinate (**122j**) (85.7 mg, 0.20 mmol) and diphenyliodonium tosylate (**18a**) (135.7 mg, 0.30 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.3) yielded **123ja** (55.6 mg, 55%) as a pale white solid (m. p. = 145–147 °C).

Ratio of *trans*- and *cis* product: 1:1 according to ^{1}H NMR analysis. Assignment of all resonances was not possible due to their overlapping.

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.33 (s, 1H), 11.18 (s, 1H), 8.46 (t, *J* = 6.0 Hz, 1H), 8.28 (d, *J* = 6.0 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.71–7.65 (m, 4H), 7.50 (dd, *J* = 7.5 Hz, 4H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.42–7.37 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.13 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.10 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.03 (dd, *J* = 6.9, 1.0 Hz, 1H), 7.01 (dd, *J* = 7.0, 0.9 Hz, 1H), 5.00 (q, *J* = 8.2 Hz, 1H), 4.59–4.52 (m, 1H), 4.33 (dd, *J* = 8.5, 3.3 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 4.05–3.96 (m, 2H), 3.70 (dd, *J* = 6.0, 3.5 Hz, 2H), 3.66 (dd, *J* = 17.4, 6.2 Hz, 1H), 3.55 (dd, *J* = 17.4, 5.9 Hz, 1H), 3.53–3.48 (m, 1H), 3.34–3.29 (m, 3H), 3.28–3.19 (m, 2H), 3.17–3.11 (m, 2H), 3.06 (dd, *J* = 14.6, 8.2 Hz, 1H), 2.99 (ddd, J = 11.4, 10.1, 7.6 Hz, 1H), 1.97–1.88 (m, 2H), 1.86 (s, 3H), 1.85–1.77

(m, 1H), 1.73 (ddd, J = 12.7, 7.5, 4.9 Hz, 2H), 1.67 (s, 3H), 1.61–1.51 (m, 1H), 1.33 (ddt, J = 13.5, 7.0, 4.1 Hz, 1H), 1.21 (ddt, J = 9.0, 5.1, 2.4 Hz, 1H), 1.17 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H), 0.42 (tt, J = 12.0, 7.7 Hz, 1H).

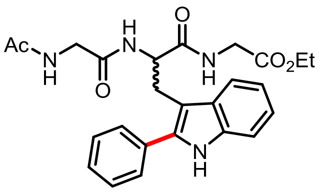
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.5 (C$_q$), 171.0 (C$_q$), 170.6 (C$_q$), 170.6 (C$_q$), 169.5 (C$_q$), 169.4 (C$_q$), 169.2 (C$_q$), 168.7 (C$_q$), 135.8 (C$_q$), 135.7 (C$_q$), 135.6 (C$_q$), 135.4 (C$_q$), 132.8 (C$_q$), 132.3 (C$_q$), 128.7 (C$_q$), 128.7 (CH), 128.5 (CH), 128.4 (C$_q$), 128.3 (CH), 127.9 (CH), 127.6 (CH), 127.4 (CH), 121.8 (CH), 121.3 (CH), 119.0 (CH), 118.8 (CH), 118.7 (CH), 118.7 (CH), 111.0 (CH), 107.3 (CH), 106.0 (CH), 60.4 (CH$_2$), 60.3 (CH$_2$), 59.5 (CH), 59.3 (CH), 52.4 (CH), 50.8 (CH), 46.7 (CH$_2$), 46.1 (CH$_2$), 41.0 (CH$_2$), 40.5 (CH$_2$), 29.6 (CH$_2$), 28.8 (CH$_2$), 28.0 (CH$_2$), 27.2 (CH$_2$), 23.9 (CH$_2$), 22.2 (CH$_3$), 22.1 (CH$_3$), 21.2 (CH$_2$), 13.9 (CH$_3$), 13.9 (CH$_3$).

IR (ATR): 3273, 3060, 1735, 1659, 1560, 1433, 1380, 1289, 1240, 1096, 743 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1047 (20), 543 (100) [M+K]$^+$, 527 (10) [M+Na]$^+$, 505 (24) [M+H]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{28}H_{33}N_4O_5$ [M+H]$^+$: 505.2451; found: 505.2445.

Synthesis of Ethyl Acetyl-glycyl-*L*-(phenyl)tryptophyl-glycinate (*L*-123ma) and Acetyl-glycyl-*D*-(phenyl)tryptophyl-glycinate (*D*-123ma)



The general procedure B1 was followed using ethyl acetyl-glycyl-*L*-tryptophyl-glycinate (*L*-**122m**) or ethyl acetyl-glycyl-*D*-tryptophyl-glycinate (*D*-**122m**) (77.7 mg, 0.20 mmol) and diphenyliodonium tosylate (**18a**) (135.7 mg, 0.30 mmol). After 17 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.4) yielded *L*-**123ma** (69.1 mg, 74%) or *D*-**123m** (72.4 mg, 78%) as a pale white solid (m. p. = 200–203 °C).

The general procedure B2 was followed using ethyl acetyl-glycyl-*L*-tryptophyl-glycinate (*L*-**123m**) or ethyl acetyl-glycyl-*D*-tryptophyl-glycinate (*D*-**123m**) (77.7 mg, 0.20 mmol) and diphenyliodonium tosylate (**18a**) (135.7 mg, 0.30 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc/MeOH 1/4/0.4) yielded *L*-**123ma** (61.6 mg, 67%) or *D*-**123ma** (65.2 mg, 70%) as a pale white solid (m. p. = 200–203 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.14 (s, 1H), 8.27 (t, J = 5.8 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.92 (t, J = 5.7 Hz, 1H), 7.73–7.67 (m, 3H), 7.52–7.47 (m, 2H), 7.38 (tt, J = 7.1, 1.2 Hz, 1H), 7.36–7.32 (m, 1H), 7.10 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.01 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 4.73 (q, J = 7.5 Hz, 1H), 4.05 (qd, J = 7.1, 1.5 Hz, 2H), 3.77–3.68 (m, 2H), 3.67–3.56 (m, 1H), 3.48 (dd, J = 16.6, 5.5 Hz, 1H), 3.36–3.30 (m, 1H), 3.09 (dd, J = 14.5, 7.5 Hz, 1H), 1.81 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H).

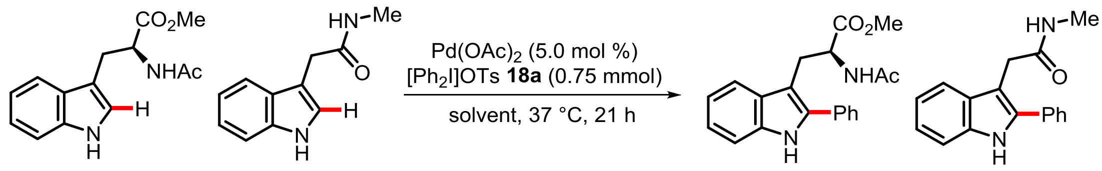
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 171.5 (C$_q$), 169.5 (C$_q$), 169.3 (C$_q$), 168.5 (C$_q$), 135.9 (C$_q$), 135.4 (C$_q$), 132.8 (C$_q$), 129.0 (C$_q$), 128.5 (CH), 128.1 (CH), 127.2 (CH), 121.3 (CH), 119.1 (CH), 118.6 (CH), 111.0 (CH), 107.4 (C$_q$), 60.3 (CH$_2$), 53.6 (CH), 42.0 (CH$_2$), 40.8 (CH$_2$), 28.1 (CH$_2$), 22.3 (CH$_3$), 14.0 (CH$_3$).

IR (ATR): 3278, 3061, 1738, 1645, 1517, 1448, 1373, 1199, 743 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 967 (21) [2M+K]$^+$, 503 (100) [M+K]$^+$, 487 (38) [M+Na]$^+$, 465 (16) [M+H]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{25}H_{28}N_4O_5K$ $[M+K]^+$: 503.1691; found: 503.1694.

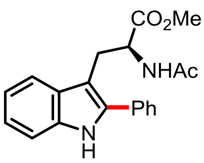
6.1.3.2 Intermolecular competition experiment



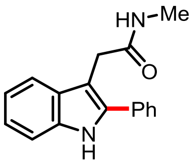
26 0.50 mmol; **1f** 0.50 mmol; **27a**; **5fa**

^{1}H NMR yield:	27a	5fa
AcOH	36%	56%
H_2O	8%	16%

Synthesis of Methyl (*S*)-2-acetamido-3-(2-phenyl-1*H*-indol-3-yl)propanoate/Methyl Acetyl L-(phenyl)tryptophanate (27a) and *N*-Methyl-2-(2-phenyl-1*H*-indol-3-yl)acetamide (5fa)



27a



5fa

A) A mixture of methyl acetyl L-tryptophanate (**26**) (130.1 mg, 0.50 mmol), 2-(1*H*-indol-3-yl)-*N*-methylacetamide (**1f**) (94.1 mg, 0.50 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5.0 mol %) and diphenyliodonium tosylate (**18a**) (339.2 mg, 0.75 mmol) in acetic acid (2.00 mL) was stirred at 37 °C for 21 h. After cooling to roomtemperature, the mixture was diluted with H_2O (5 mL), and the aqueous layer was extracted with EtOAc (3 x 20 mL). The organic layers were combined, and the solvents were removed *in vacuo*. The crude product was purified by column chromatography (*n*-hexane/EtOAc/MeOH 2.5/3.5/0.1) to yield the desired products **27a** and **5fa** as an inseperable mixture (135.4 mg, ratio by ^{1}H NMR: **5fa**:**27a** = 55:45, **5fa**: 74.5 mg, 56%, **27a**: 60.9 mg, 36%).

B) A mixture of methyl acetyl L-tryptophanate (**26**) (130.1 mg, 0.50 mmol), 2-(1*H*-indol-3-yl)-*N*-methylacetamide (**1f**) (94.1 mg, 0.50 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5.0 mol %) and diphenyliodonium tosylate (**18a**) (339.2 mg, 0.75 mmol) in water (2.00 mL) was stirred at 37 °C for 21 h. After cooling to roomtemperature, MeOH (5 mL) was added and the solvents were removed *in vacuo*. The crude product was purified by column chromatography (*n*-hexane/EtOAc/MeOH 2.5/3.5/0.1) to yield the desired products **27a** and **5fa** as an inseperable mixture (35.3 mg, ratio by ^{1}H NMR: **5fa**:**27a** = 60:40, **5fa**: 21 mg, 16%, **27a**: 14 mg, 8%).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 11.23 (s, 1H), 11.21 (s, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.88 (q, *J* = 4.6 Hz, 1H), 7.84–7.77 (m, 2H), 7.67–7.61 (m, 2H), 7.61–7.57 (m, 3H), 7.54–7.46 (m, 3H), 7.42–7.34 (m, 4H), 7.16–7.08 (m, 2H), 7.06–6.98 (m, 2H), 4.54 (dd, *J* = 7.8, 7.8 Hz, 1H), 3.61 (s, 2H), 3.36 (s, 3H), 3.38–3.27 (m, 1H), 3.24–3.17 (m, 1H), 2.62 (d, *J* = 4.6 Hz, 3H), 1.75 (s, 3H).

Assignment of the resonances was not possible due to their overlapping.

^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 172.1 (C_q), 171.1 (C_q), 169.1 (C_q), 135.9 (C_q), 135.8 (C_q), 135.8 (C_q), 135.4 (C_q), 132.7 (C_q), 132.5 (C_q), 128.8 (C_q), 128.7 (C_q), 128.6 (CH), 128.5 (CH), 128.0 (CH), 127.9 (CH), 127.4 (CH), 127.4 (CH), 121.5 (CH), 121.4 (CH), 118.7 (CH), 118.7 (CH), 118.5 (CH), 111.1

(CH), 111.0 (CH), 106.8 (C_q), 106.0 (C_q), 53.1 (CH), 51.5 (CH_3), 31.8 (CH_2), 27.0 (CH_2), 25.7 (CH_3), 22.2 (CH_3).

Due to overlap, one resonance is missing.

IR (ATR): 3280, 3012, 2959, 1735, 1650, 1523, 1434, 1260, 1095, 1012, 740 cm^{-1}.

5fa: **MS** (EI) *m/z* (relative intensity) 336 (10) $[M]^+$, 264 (23) $[M]^+$, 206 (100).

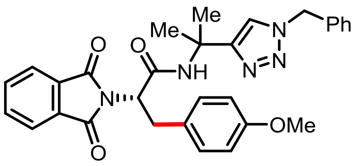
HR-MS (ESI): *m/z* calcd for $C_{20}H_{21}N_2O_3$ $[M+H]^+$: 337.1547; found: 337.1544.

7a: **MS** (ESI) *m/z* (relative intensity) 375 (100) $[M+K]^+$, 337 (40) $[M+H]^+$, 303 (84) $[M+K]^+$, 287 (50) $[M+Na]^+$, 265 (95) $[M+H]^+$, 206 (74).

HR-MS (ESI): *m/z* calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$: 265.1335; found: 265.1332.

5.3.3 Analytical Data for Arylated Triazole-containing amino acids and peptides

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-Dioxoisoindolin-2-yl)-3-(4-methoxyphenyl)propanamide (125ae)



The general procedure C1 was followed using Pd(OAc)$_2$ (2.2 mg, 5.0 mol %), Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 4-iodanisole (**4e**) (97.2 mg, 0.40 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 7/4) and gel permeation chromatography yielded **125ae** (80.3 mg, 77%) as a white solid (m. p. = 186–188 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.66 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.41 (s, 1H), 7.38–7.31 (m, 3H), 7.26–7.22 (m, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.74 (br s, 1H), 6.69 (d, *J* = 8.7 Hz, 2H), 5.47 (s, 2H), 4.98 (dd, *J* = 9.5, 7.4 Hz, 1H), 3.69 (s, 3H), 3.47–3.41 (m, 2H), 1.70 (s, 3H), 1.69 (s, 3H).

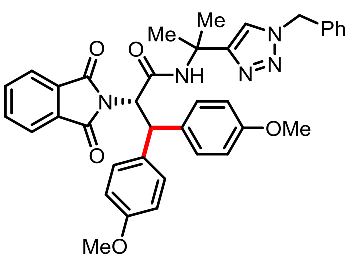
^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.0 (C_q), 168.0 (C_q'), 167.4 (C_q), 158.4 (C_q), 153.3 (C_q), 134.7 (C_q), 134.1 (CH), 131.5 (C_q), 130.0 (CH), 129.0 (CH), 128.6 (CH), 128.0 (CH), 123.4 (CH), 120.5 (CH), 114.0 (CH), 56.3 (CH), 55.1 (CH_3), 54.1 (CH_2), 51.9 (C_q), 34.1 (CH_2), 27.9 (CH_3), 27.3 (CH_3).

IR (ATR): 3254, 3144, 3044, 2983, 2936, 1709, 1669, 1511, 1382, 1242, 717 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1069 (27) $[2M+Na]^+$, 546 (65) $[M+Na]^+$, 524 (100) $[M+H]^+$, 472 (15), 450 (11), 200 (9).

HR-MS (ESI): *m/z* calcd for $C_{30}H_{30}N_5O_4$ $[M+H]^+$: 524.2292; found: 524.2293.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3,3-bis(4-methoxyphenyl)propanamide (125aee)



The general procedure C1 was followed using Pd(OAc)$_2$ (2.2 mg, 5.0 mol %), Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 4-iodanisole (**4e**) (97.2 mg, 0.40 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 7/4) and gel permeation chromatography yielded **125aee** (12.6 mg, 10%) as a white solid (m. p. = 200–202 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.62 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.41–7.37 (m, 2H), 7.36–7.28 (m, 3H), 7.19 (dd, *J* = 7.9, 1.0 Hz, 2H), 7.17–7.12 (m, 2H), 7.01 (s, 1H), 6.85–6.79 (m, 2H), 6.70 (s, 1H), 6.67–6.61 (m, 2H), 5.46 (d, *J* = 12.6 Hz, 1H), 5.36 (d, *J* = 2.7 Hz, 2H), 5.15 (d, *J* = 12.6 Hz, 1H), 3.72 (s, 3H), 3.60 (s, 3H), 1.54 (s, 3H), 1.50 (s, 3H).

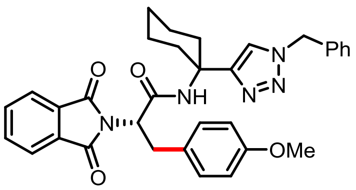
^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.2 (C_q), 166.5 (C_q), 158.9 (C_q), 158.4 (C_q), 152.8 (C_q), 135.1 (C_q), 134.2 (CH), 133.1 (C_q), 133.0 (C_q), 131.4 (C_q), 129.3 (CH), 129.1 (CH), 128.5 (CH), 128.5 (CH), 127.9 (CH), 123.6 (CH), 120.9 (CH), 114.6 (CH), 114.2 (CH), 59.5 (CH), 55.4 (CH_3), 55.2 (CH_3), 53.9 (CH_2), 51.8 (C_q), 49.3 (CH), 28.1 (CH_3), 27.6 (CH_3).

IR (ATR): 3351, 3011, 1712, 1624, 1492, 1377, 1320, 1265, 1170, 1101 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1313 (45), 689 (50), 662 (80), 630 (100) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{37}H_{36}N_5O_3$ $[M+H]^+$: 630.2711; found: 630.2713.

Synthesis of (*S*)-*N*-[1-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)cyclohexyl]-2-(1,3-dioxoisoindolin-2-yl)-3-(4-methoxyphenyl)propanamide (125be)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM^{cy} (**124b**) (91.5 mg, 0.20 mmol) and 4-iodoanisole (**4e**) (70.2 mg, 0.30 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 1/1/1) yielded **125be** (104.3 mg, 93%) as a white solid (m. p. = 167–169 °C).

^{1}**H NMR** (600 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.68 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.48 (s, 1H), 7.37–7.29 (m, 3H), 7.25–7.21 (m, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.42 (br s, 1H), 5.46 (s, 2H), 4.98 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.69 (s, 3H), 3.45 (d, *J* = 8.4 Hz, 2H), 2.41 (d, *J* = 13.4 Hz, 1H), 2.31 (d, *J* = 13.6 Hz, 1H), 2.00–1.93 (m, 2H), 1.60–1.45 (m, 4H), 1.44–1.36 (m, 1H), 1.34–1.26 (m, 1H).

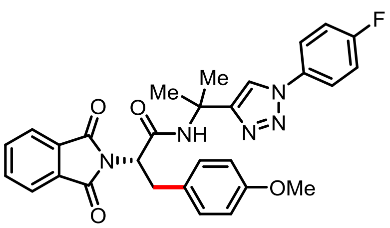
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 168.0 (C_q), 167.5 (C_q), 158.5 (C_q), 152.4 (C_q), 135.0 (C_q), 134.2 (CH), 131.5 (C_q), 129.9 (CH), 129.0 (CH), 128.6 (C_q), 128.5 (CH), 128.0 (CH), 123.6 (CH), 121.7 (CH), 114.2 (CH), 56.7 (CH), 55.3 (CH_3), 54.4 (C_q), 54.1 (CH_2), 35.4 (CH_2), 35.1 (CH_2), 34.4 (CH_2), 25.5 (CH_2), 21.9 (CH_2), 21.9 (CH_2).

IR (ATR): 2937, 1712, 1670, 1550, 1513, 1452, 1384, 1249, 1118, 1036 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 586 (100) $[M+Na]^+$, 564 (63) $[M+H]^+$, 301 (50).

HR-MS (ESI): *m/z* calcd for $C_{33}H_{34}N_5O_4$ $[M+H]^+$: 564.2605; found: 564.2605.

Synthesis of (*S*)-2-(1,3-dioxoisoindolin-2-yl)-*N*-{2-[1-(4-fluorophenyl)-1*H*-1,2,3-triazol-4-yl]propan-2-yl}-3-(4-methoxyphenyl)propanamide (125ce)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM^F (**124c**) (84.3 mg, 0.20 mmol) and 4-iodoanisole (**4e**) (70.2 mg, 0.30 mmol). After 16 h, purification by gel permeation chromatography yielded **125ce** (79.7 mg, 76%) as a white solid (m. p. = 182–185 °C).

^{1}**H NMR** (600 MHz, $CDCl_3$): δ = 7.96 (s, 1H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.68 (dd, *J* = 9.0, 4.6 Hz, 2H), 7.65 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.20–7.12 (m, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.78 (br s, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 5.03 (dd, *J* = 10.2, 6.5 Hz, 1H), 3.66 (s, 3H), 3.50 (dd, *J* = 14.2, 6.5 Hz, 1H), 3.43 (dd, *J* = 14.2, 10.3 Hz, 1H), 1.78 (s, 3H), 1.75 (s, 3H).

^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 168.0 (C_q), 167.6 (C_q), 162.2 (d, $^1J_{C-F}$ = 248.4 Hz, C_q), 158.5 (C_q), 153.3 (C_q), 134.2 (CH), 133.4 (d, $^4J_{C-F}$ = 3.1 Hz, C_q), 131.5 (C_q), 130.0 (CH), 128.5 (C_q), 123.5 (CH), 122.4 (d, $^3J_{C-F}$ = 8.6 Hz, CH), 119.4 (CH), 116.6 (d, $^2J_{C-F}$ = 23.1 Hz, CH), 114.1 (CH), 56.4 (CH), 55.2 (CH_3), 52.0

(C_q), 34.4 (CH_2), 28.4 (CH_3), 28.1 (CH_3).

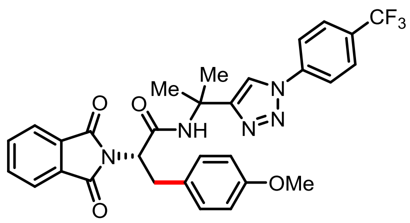
^{19}F NMR (282 MHz, $CDCl_3$): δ = -112.6 (tt, J = 8.0, 4.7 Hz).

IR (ATR): 3138, 2931, 1716, 1677, 1657, 1512, 1382, 1248, 1235, 1177, 1056 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1077 (86) $[2M+Na]^+$, 810 (20), 550 (100) $[M+Na]^+$, 528 (65) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{29}H_{26}N_5O_4FNa$ $[M+Na]^+$: 550.1860; found: 550.1860.

Synthesis of (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-methoxyphenyl)-*N*-(2-{1-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazol-4-yl}propan-2-yl)propanamide (125de)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM^{CF3} (**124d**) (94.3 mg, 0.20 mmol) and 4-iodoanisole (**4e**) (70.2 mg, 0.30 mmol). After 16 h, purification by gel permeation chromatography yielded **125de** (77.6 mg, 67%) as a white solid (m. p. = 191–194 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.89 (d, J = 8.6 Hz, 2H), 7.80–7.71 (m, 4H), 7.67 (dd, J = 5.4, 3.0 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 6.72 (d, J = 8.6 Hz, 2H), 6.68 (m, 1H), 5.03 (dd, J = 10.1, 6.6 Hz, 1H), 3.67 (s, 3H), 3.50 (dd, J = 14.2, 6.6 Hz, 1H), 3.42 (dd, J = 14.2, 10.1 Hz, 1H), 1.79 (s, 3H), 1.76 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.0 (C_q), 167.7 (C_q), 158.6 (C_q), 153.7 (C_q), 139.6 (C_q), 134.3 (CH), 131.5 (C_q), 130.4 (d, $^2J_{C-F}$ = 33.1 Hz, C_q), 130.0 (CH), 128.5 (C_q), 127.0 (q, $^3J_{C-F}$ = 3.6 Hz, CH), 123.6 (CH), 123.7 (d, $^1J_{C-F}$ = 271.8 Hz, C_q), 120.3 (CH), 119.1 (CH), 114.2 (CH), 56.4 (CH), 55.3 (CH_3), 52.1 (C_q), 34.5 (CH), 28.4 (CH_3), 28.2 (CH_3).

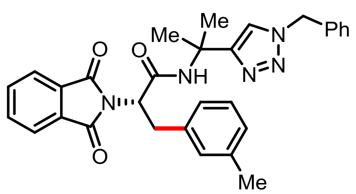
^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.6.

IR (ATR): 2957, 23926, 1715, 1683, 1616, 1512, 1385, 1321, 1251, 1166, 1122, 1069 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1177 (89) $[2M+Na]^+$, 1155 (19) $[2M+H]^+$, 600 (100) $[M+Na]^+$, 578 (50) $[M+H]^+$, 317 (20).

HR-MS (ESI): *m/z* calcd for $C_{30}H_{27}N_5O_4F_3$ $[M+H]^+$: 578.2010; found: 578.2007.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(*m*-tolyl)propanamide (125ah)



The general procedure C1 was followed using $Pd(OAc)_2$ (2.2 mg, 5.0 mol %), Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 1-iodo-3-methylbenzene (**4h**) (65.4 mg, 40 µL, 0.30 mmol). After 16 h, purification by gel permeation chromatography yielded **125ah** (68.2 mg, 67%) as a white solid (m. p. = 172–175 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76 (dd, J = 5.5, 3.0 Hz, 2H), 7.68 (dd, J = 5.5, 3.1 Hz, 2H), 7.42 (s, 1H), 7.39–7.28 (m, 3H), 7.27–7.24 (m, 2H), 7.05 (dd, J = 7.5, 7.5 Hz, 1H), 6.98–6.91 (m, 3H), 6.70 (br s, 1H), 5.47 (s, 2H), 5.01 (dd, J = 10.1, 6.5 Hz, 1H), 3.49 (dd, J = 14.1, 6.5 Hz, 1H), 3.44 (dd, J = 14.1, 10.1 Hz, 1H), 2.17 (s, 3H), 1.70 (s, 3H), 1.68 (s, 3H).

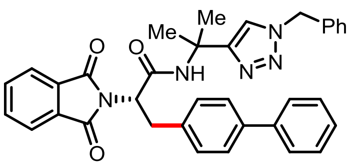
^{13}C NMR (126 MHz, $CDCl_3$): *δ* = 168.1 (C_q), 167.5 (C_q), 153.4 (C_q), 138.3 (C_q), 136.8 (C_q), 134.8 (C_q), 134.2 (CH), 131.7 (C_q), 129.9 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.8 (CH), 126.0 (CH), 123.5 (CH), 120.6 (CH), 56.3 (CH), 54.2 (CH_2), 52.0 (C_q), 35.0 (CH_2), 28.1 (CH_3), 27.9 (CH_3), 21.3 (CH_3).

IR (ATR): 3245, 1708, 1669, 1553, 1440, 1380, 1333, 1292,1261, 1223, 1170, 1106 1058, 774 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1037 (100) $[2M+Na]^+$, 1015 (10) $[2M+H]^+$, 781 (15), 530 (85) $[M+Na]^+$, 508 (50) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{30}H_{30}N_5O_3$ $[M+H]^+$: 508.2343; found: 508.2343.

Synthesis of (*S*)-3-[(1,1'-Biphenyl)-4-yl]-*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)propanamide (125ai)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 4-iodo-1,1′-biphenyl (**4i**) (84.0 mg, 0.30 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1/1) yielded **125ai** (85.4 mg, 75%) as a pale white solid (m. p. = 157–159 °C).

^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.65 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.47 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.44 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.38–7.31 (m, 5H) 7.30–7.27 (m, 1H), 7.24 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.87 (br s, 1H), 5.44 (s, 2H), 5.10 (dd, *J* = 8.9, 7.9 Hz, 1H), 3.58 (d, *J* = 8.5 Hz, 2H), 1.73 (s, 3H), 1.71 (s, 3H).

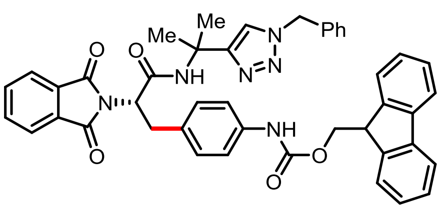
^{13}C NMR (126 MHz, $CDCl_3$): *δ* = 168.0 (C_q), 167.3 (C_q), 153.2 (C_q), 140.5 (C_q), 139.5 (C_q), 135.8 (C_q),134.6 (C_q), 134.1 (CH), 131.4 (C_q), 129.3 (CH), 129.0 (CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.2 (CH), 127.1 (CH), 126.8 (CH), 123.5 (CH), 120.4 (CH), 56.1 (CH), 54.0 (CH_2), 51.9 (C_q), 34.5 (CH_2), 27.9 (CH_3), 27.7 (CH_3).

IR (ATR): 3261, 3143, 3034, 2979, 2912, 1711, 1674, 1383, 875, 761 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1139 (15) $[2M+H]^+$, 570 (100) $[M+H]^+$, 418 (39).

HR-MS (ESI): *m/z* calcd for $C_{35}H_{32}N_5O_3$ $[M+H]^+$: 570.2500; found: 570.2491.

Synthesis of (*S*)-(9*H*-Fluoren-9-yl)methyl {4-[3-({2-[1-benzyl-1*H*-1,2,3-triazol-4-yl]propan-2-yl}amino)-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]phenyl}carbamate (125aj)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and (9*H*-fluoren-9-yl)methyl (4-iodophenyl)carbamate (**4j**) (132.4 mg, 0.30 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 1/1/1) and gel permeation chromatography yielded **125aj** (113.2 mg, 78%) as a white solid (m. p. = 200–201 °C).

^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.74 (d, *J* = 7.6 Hz, 2H), 7.73–7.69 (m, 2H), 7.62 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.44 (s, 1H), 7.37 (dd, J = 7.4, 7.4 Hz, 2H), 7.32 (dd, J = 7.2, 7.2 Hz, 3H), 7.28–7.24 (m, 3H), 7.24–7.20 (m, 2H), 7.16 (dd, J = 14.0, 7.0 Hz, 1H), 7.03 (d, J = 7.7 Hz, 2H), 6.95 (s, 1H), 6.89 (br s, 1H), 5.43 (s, 2H), 5.07–5.02 (m, 1H), 4.42 (d, J = 6.4 Hz, 2H), 4.18 (dd, J = 6.7, 6.7 Hz, 1H), 3.53–3.40 (m, 2H), 1.72 (s, 3H), 1.70 (s, 3H).

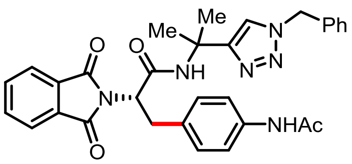
^{13}C NMR (76 MHz, $CDCl_3$): δ = 168.1 (C_q), 167.5 (C_q), 153.3 (C_q), 143.8 (Cq), 143.7 (C_q), 141.3 (C_q), 136.7 (C_q), 134.7 (C_q), 134.2 (CH), 131.7 (C_q), 131.5 (C_q), 129.5 (CH), 129.1 (CH), 128.7 (CH), 128.1 (CH), 127.8 (CH), 127.1 (CH), 125.0 (CH), 123.6 (CH), 120.7 (CH), 120.0 (CH), 118.9 (CH), 66.9 (CH_2), 56.3 (CH), 54.1 (CH_2), 52.0 (C_q), 47.1 (CH), 34.3 (CH_2), 28.1 (CH_3), 27.9 (CH_3).

IR (ATR): 3313, 2924, 1709, 1600, 1524, 1450, 1416, 1383, 1316, 1082, 1050, 759 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1484 (20) [2M+Na]$^+$, 785 (25), 753 (100) [M+Na]$^+$, 731 (75) [M+H]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{44}H_{39}N_6O_5$ [M+H]$^+$: 731.2976; found 731.2970.

Synthesis of (*S*)-3-(4-acetamidophenyl)-*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)propanamide (125ak)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and *N*-(4-iodophenyl) acetamide (**4k**) (78.3 mg, 0.30 mmol). After 16 h, purification by column chromatography (EtOAc/CH_2Cl_2 4/1) yielded **125ak** (74.6 mg, 68%) as a pale white solid (m. p. = 148–150 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (br s, 1H), 7.68 (dd, J = 5.5, 3.1 Hz, 2H), 7.61 (dd, J = 5.5, 3.1 Hz, 2H), 7.39 (s, 1H), 7.34–7.27 (m, 3H), 7.37–7.22 (m, 2H), 7.19 (d, J = 7.0 Hz, 2H), 6.99 (d, J = 7.0 Hz, 2H), 6.84 (br s, 1H), 5.40 (s, 2H), 4.96 (dd, J = 10.4, 6.3 Hz, 1H), 3.48–3.36 (m, 2H), 2.00 (s, 3H), 1.66 (s, 3H), 1.64 (s, 3H).

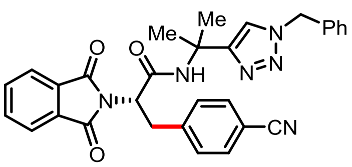
^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.6 (C_q), 167.9 (C_q), 167.5 (C_q), 153.2 (C_q), 137.1 (C_q), 134.6 (C_q), 134.1 (CH), 132.1 (C_q), 131.3 (C_q), 129.2 (CH), 129.0 (CH), 128.6 (CH), 128.0 (CH), 123.4 (CH), 120.7 (CH), 119.8 (CH), 56.3 (CH), 54.1 (CH_2), 52.0 (C_q), 34.5 (CH_2), 28.1 (CH_3), 27.9 (CH_3), 24.4 (CH_3).

IR (ATR): 3309, 3063, 2927, 1710, 1665, 1514, 1411, 1382, 1316, 1260, 1087, 809 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1123 (20) [2M+Na]$^+$, 573 (100) [M+Na]$^+$, 551 (30) [M+H]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{31}H_{31}N_6O_4$ [M+H]$^+$: 551.2401; found 551.2400.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-(4-cyanophenyl)-2-(1,3-dioxoisoindolin-2-yl)propanamide (125al)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 4-iodobenzonitrile (**4l**) (68.7 mg, 0.30 mmol). After 16 h, purification by gel permeation chromatography yielded **125al** (54.2 mg, 53%) as a pale white solid (m. p. = 208–211 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (dd, J = 5.5, 3.0 Hz, 2H), 7.69 (dd, J = 5.5, 3.0 Hz, 2H), 7.42 (s, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.37–7.30 (m, 3H), 7.25–7.22 (m, 4H), 6.99 (br s, 1H), 5.46 (s, 2H), 5.04 (dd, J = 10.2, 6.5 Hz, 1H), 3.64–3.53 (m, 2H), 1.72 (s, 3H), 1.71 (s, 3H).

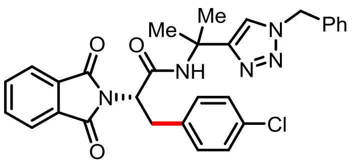
^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.7 (C_q), 166.7 (C_q), 153.2 (C_q), 142.6 (C_q), 134.5 (C_q), 134.4 (CH), 132.3 (CH), 131.2 (C_q), 129.7 (CH), 129.1 (CH), 128.7 (CH), 128.0 (CH), 123.6 (CH), 120.3 (CH), 118.6 (C_q), 110.8 (C_q), 55.3 (CH), 54.1 (CH_2), 52.0 (C_q), 34.8 (CH_2), 27.9 (CH_3), 27.7 (CH_3).

IR (ATR): 3258, 3140, 3045, 2928, 2227, 1710, 1689, 1382, 711 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1059 (17) $[2M+Na]^+$, 541 (40) $[M+Na]^+$, 519 (100) $[M+H]^+$, 240 (33).

HR-MS (ESI): *m/z* calcd for $C_{30}H_{27}N_6O_3$ $[M+H]^+$: 519.2139; found: 519.2141.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl)-3-(4-chloro-phenyl)-2-(1,3-dioxoisoindolin-2-yl)propanamide (125ac)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 1-chloro-4-iodo benzene (**4c**) (71.5 mg, 0.30 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 1/1/1) yielded (**125ac**) (52.7 mg, 50%) as a white solid (m. p. = 213–215 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (dd, J = 5.5, 3.0 Hz, 2H), 7.70 (dd, J = 5.5, 3.0 Hz, 2H), 7.39 (s, 1H), 7.38–7.31 (m, 3H), 7.29–7.22 (m, 2H), 7.12 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 6.82 (br s, 1H), 5.47 (s, 2H), 5.00 (dd, J = 10.3, 6.5 Hz, 1H), 3.55–3.43 (m, 2H), 1.72 (s, 3H), 1.71 (s, 3H).

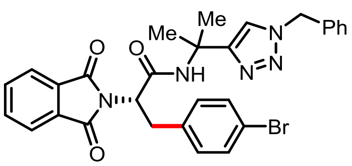
^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.9 (C_q), 167.1 (C_q), 153.3 (C_q), 135.2 (C_q), 134.6 (C_q), 134.3 (CH), 132.7 (C_q), 131.3 (C_q), 130.2 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 123.6 (CH), 120.3 (CH), 55.9 (CH), 54.1 (CH_2), 52.0 (C_q), 34.2 (CH_2), 27.9 (CH_3), 27.8 (CH_3).

IR (ATR): 3265, 3143, 3047, 2983, 2935, 1709, 1684, 1383, 1363, 720 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 550 (24) $[M+Na]^+$, 528 (100) $[M+H]^+$, 200 (13).

HR-MS (ESI): *m/z* calcd for $C_{29}H_{27}ClN_5O_3$ $[M+H]^+$: 528.1797; found: 528.1781.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-(4-bromophenyl)-2-(1,3-dioxoisoindolin-2-yl)propanamide (125ad)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 1-bromo-4-iodo benzene (**4d**) (84.8 mg, 0.30 mmol). After 16 h, purification by gel permeation chromatography yielded **125ad** (51.9 mg, 45%) as a pale white solid (m. p. = 195–197 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77 (dd, J = 5.5, 3.0 Hz, 2H), 7.70 (dd, J = 5.5, 3.0 Hz, 2H), 7.40–7.31 (m, 3H), 7.27 (dd, J = 11.9, 8.1 Hz, 5H), 7.02 (d, J = 8.3 Hz, 2H), 6.83 (s, 1H), 5.47 (s, 2H), 5.00 (dd, J = 10.2, 6.1 Hz, 1H), 3.51–3.43 (m, 2H), 1.72 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.9 (C_q), 167.1 (C_q), 135.8 (C_q), 134.7 (C_q), 134.4 (CH), 131.8 (CH), 131.5 (C_q), 130.7 (CH), 129.2 (CH), 128.7 (CH), 128.1 (CH), 123.7 (CH), 120.9 (C_q), 56.1 (CH), 54.4 (CH_2), 34.5 (CH_2), 28.2 (CH_3), 28.0 (CH_3).

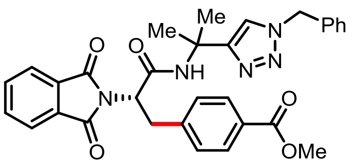
Due to overlap, two resonances are missing.

IR (ATR): 2984, 1709, 1685, 1530, 1489, 1384, 1363, 1216, 1054, 875 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1013 (20), 596 (80) [M+Na]$^+$ (^{81}Br), 572 (70) [M+H]$^+$ (^{81}Br), 440 (100).

HR-MS (ESI): *m/z* calcd for $C_{29}H_{27}N_5O_3Br$ [M+H]$^+$: 572.1292; found: 572.1280.

Synthesis of (*S*)-4-(3-{[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl]propan-2-yl}amino)-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl)benzoate (125am)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and methyl-4-iodo benzoate (**4m**) (78.6 mg, 0.30 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1/1) yielded **125am** (88.9 mg, 81%) as a pale white solid (m. p. = 182–185 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.3 Hz, 2H), 7.75 (dd, *J* =5.5, 3.1 Hz, 2H), 7.68 (dd, *J* =5.5, 3.1 Hz, 2H), 7.40 (s, 1H), 7.39–7.33 (m, 3H), 7.28–7.24 (m, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.82 (s, 1H), 5.49 (s, 2H), 5.05 (dd, *J* = 10.7, 6.1 Hz, 1H), 3.86 (s, 3H), 3.65–3.50 (m, 2H), 1.72 (s, 3H), 1.71 (s, 3H).

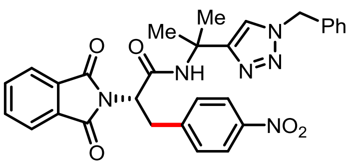
^{13}C NMR (126 MHz, $CDCl_3$): δ =167.8 (C_q), 167.0 (C_q), 166.8 (C_q), 153.3 (C_q), 142.2 (C_q), 134.6 (C_q), 134.3 (CH), 131.3 (C_q), 129.9 (CH), 129.1 (CH), 129.0 (CH), 128.8 (C_q), 128.7 (CH), 128.1 (CH), 123.6 (CH), 120.3 (CH), 55.7 (CH), 54.1 (CH_2), 52.0 (C_q), 50.9 (CH_3), 34.8 (CH_2), 27.9 (CH_3), 27.8 (CH_3).

IR (ATR): 3227, 3043, 2925, 2854, 1774, 1708, 1682, 1383, 1278, 1106, 718 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1125 (17) [2M+Na]$^+$, 574 (28) [M+Na]$^+$, 552 (100) [M+H]$^+$, 172 (9).

HR-MS (ESI): *m/z* calcd for $C_{31}H_{30}N_5O_5$ [M+H]$^+$: 552.2241; found: 552.2244.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(4-nitrophenyl)propanamide (125an)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 1-iodo-4-nitrobenzene (**4n**) (74.7 mg, 0.30 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc/acetone 3/1/1) yielded **125an** (51.1 mg 48%) as a pale white solid (m. p. =191 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.7 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.40 (s, 1H), 7.38–7.34 (m, 3H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 7.8, 1.7 Hz, 2H), 6.95 (br s, 1H), 5.46 (s, 2H), 5.06 (dd, *J* = 10.6, 6.1 Hz, 1H), 3.70–3.55 (m, 2H), 1.73 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9 (C_q), 167.9 (C_q), 166.8 (C_q), 153.4 (C_q), 147.1 (C_q), 144.9 (C_q), 134.6 (CH), 131.3 (C_q), 130.0 (CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 123.9 (CH), 123.9 (CH), 120.4

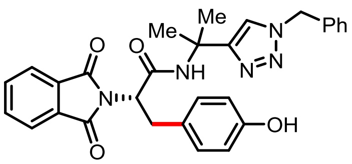
(CH), 55.5 (CH), 54.3 (CH_2), 52.2 (C_q), 34.8 (CH_2), 28.0 (CH_3), 27.9 (CH_3).

IR (ATR): 3207, 3028, 2942, 1711, 1682, 1538, 1347, 712, 684 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1099 (46) $[2M+Na]^+$, 561 (100) $[M+Na]^+$, 539 (93) $[M+H]^+$, 300 (14), 240 (32), 214 (14).

HR-MS (ESI): *m/z* calcd for $C_{29}H_{26}N_6O_5Na$ $[M+Na]^+$: 561.1857; found: 561.1855.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(4-hydroxyphenyl)propanamide (125ao)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 4-iodophenol (**4o**) (66.0 mg, 0.30 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 1/1/1) yielded **125ao** (49.3 mg, 49%) as a pale white solid (m. p. = 161–163 °C).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.08 (s, 1H), 8.15 (s, 1H), 7.91 (s, 1H), 7.82–7.76 (m, 4H), 7.37–7.33 (m, 2H), 7.33–7.27 (m, 3H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 5.55 (s, 2H), 4.91 (t, *J* = 8.3 Hz, 1H), 3.35–3.31 (m, 2H), 1.62 (s, 3H), 1.61 (s, 3H).

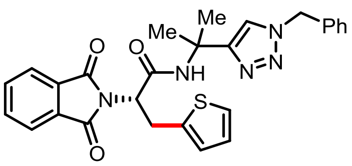
^{13}C NMR (126 MHz, DMSO-d_6): δ = 167.4 (C_q), 166.8 (C_q), 155.5 (C_q), 152.8 (C_q), 135.9 (C_q), 134.2 (CH), 131.1 (C_q), 129.4 (CH), 128.5 (CH), 127.8 (CH), 127.6 (CH), 127.5 (C_q), 122.8 (CH), 121.3 (CH), 114.9 (CH), 55.4 (CH), 52.6 (CH_2), 51.0 (C_q), 33.3 (CH_2), 28.1 (CH_3), 28.0 (CH_3).

IR (ATR): 3490, 3228, 3135, 3036, 1701, 1677, 1515, 1385, 1264, 1220, 1116, 1059, 874, 718 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1041 (10) $[2M+Na]^+$, 532 (100) $[M+Na]^+$, 510 (15) $[M+H]^+$, 440 (8).

HR-MS (ESI): *m/z* calcd for $C_{29}H_{27}N_5O_4Na$ $[M+Na]^+$: 532.1955; found: 532.1953.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(thiophen-2-yl)propanamide (125ap)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 2-iodothiophen (**4p**) (63.1 mg, 35 µL, 0.30 mmol). After 16 h, purification by gel permeation chromatography yielded **125ap** (80.9 mg, 81%) as a pale white solid (m. p. = 174–177 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.42 (s, 1H), 7.37–7.30 (m, 3H), 7.25–7.22 (m, 2H), 7.02 (dd, *J* = 4.8, 1.5 Hz, 1H), 6.81 (br s, 1H), 6.79–6.74 (m, 2H), 5.45 (s, 2H), 5.00 (dd, *J* = 10.5, 5.8 Hz, 1H), 3.78 (dd, *J* = 15.1, 10.5 Hz, 1H), 3.71 (dd, *J* = 15.1, 5.8 Hz, 1H), 1.71 (s, 3H), 1.69 (s, 3H).

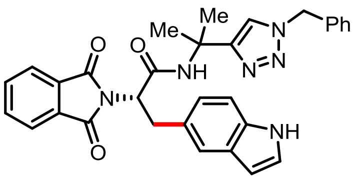
^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.8 (C_q), 166.8 (C_q), 153.2 (C_q), 138.9 (C_q), 134.7 (CH), 134.2 (C_q), 131.6 (C_q), 129.1 (CH), 128.6 (CH), 128.0 (CH), 126.9 (CH), 126.4 (CH), 124.7 (CH), 123.6 (CH), 120.5 (CH), 56.5 (CH), 54.2 (CH_2), 52.2 (C_q), 29.3 (CH_2), 28.1 (CH_3), 28.0 (CH_3).

IR (ATR): 3158, 3035, 1710, 1674, 1558, 1382, 1361, 1173, 1092, 1062, 871, 724 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1085 (40), 554 (100), 532 (30), 522 (18) [M+Na]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{27}H_{25}N_5NaO_3S$ [M+Na]$^+$: 522.1570; found: 522.1561.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(1*H*-indol-5-yl)propanamide (125aq)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 5-iodo-1*H*-indol (**4q**) (72.9 mg, 0.30 mmol). After 16 h, purification by gel permeation chromatography yielded **125aq** (68.7 mg, 64 %) as a dark grey solid (m. p. = 150–152 °C).

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 10.86 (s, 1H), 8.20 (s, 1H), 7.92 (s, 1H), 7.79–7.72 (m, 4H), 7.38–7.32 (m, 2H), 7.32–7.26 (m, 4H) 7.21–7.19 (m, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 6.91 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.23 (dd, *J* = 2.0, 2.0 Hz, 1H), 5.55 (s, 2H), 5.02 (dd, *J* = 10.5, 6.2 Hz, 1H), 3.57–3.47 (m, 2H), 1.63 (s, 3H), 1.63 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 167.4 (C_q), 166.8 (C_q), 155.5 (C_q), 152.8 (C_q), 135.9 (C_q), 134.2 (CH), 131.1 (C_q), 129.4 (CH), 128.5 (CH), 128.5 (CH), 127.8 (CH), 127.6 (CH), 127.6 (CH), 127.5 (C_q), 122.8 (CH), 121.3 (CH), 114.9 (CH), 55.4 (CH), 52.6 (CH_2), 51.0 (C_q), 33.3 (CH_2), 28.1 (CH_3), 28.0 (CH_3)

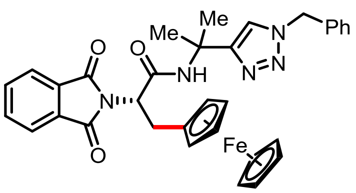
Due to overlap, two resonances are missing.

IR (ATR): 3379, 3130, 3047, 1705, 1682, 1554, 1386, 1315, 1221, 1171, 1110, 1059, 767 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1087 (50) [2M+Na]$^+$, 555 (100) [M+Na]$^+$, 533 (55) [M+H]$^+$.

HR-MS (ESI): *m/z* calcd for $C_{31}H_{28}N_6O_3Na$ [M+Na]$^+$: 555.2115; found: 555.2104.

Synthesis of (*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(ferrocenyl)propanamide (125ar)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and Iodferrocene (**4r**) (93.6 mg, 0.30 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 1/1/1) yielded **125ar** (41 mg, 34%) as a yellow solid (m. p. = 155–157 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.42 (s, 1H), 7.40–7.34 (m, 3H), 7.26 (d, *J* = 6.4 Hz, 2H), 6.60 (br s, 1H), 5.47 (s, 2H), 4.72 (dd, *J* = 9.5, 6.6 Hz, 1H), 4.13 (s, 1H), 4.10 (s, 5H), 4.01 (s, 1H), 3.91 (s, 1H), 3.86 (s, 1H), 3.26–3.19 (m, 2H), 1.70 (s, 3H), 1.69 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.9 (C_q), 167.4 (C_q), 153.3 (C_q), 134.8 (C_q), 134.2 (CH), 131.7 (C_q), 129.1 (CH), 128.7 (CH), 128.1 (CH), 123.6 (CH), 120.6 (CH), 69.0 (CH), 68.9 (CH), 68.8 (CH), 68.4 (CH), 68.3 (CH), 56.9 (CH), 54.3 (CH_2), 52.1 (C_q), 29.9 (CH_2), 28.2 (CH_3), 28.1 (CH_3).

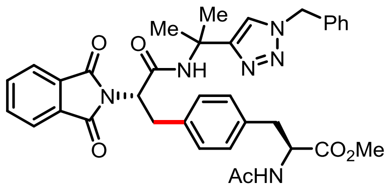
Due to overlap, one resonance is missing.

IR (ATR): 3242, 3153, 3043, 1710, 1672, 1554, 1381, 1296, 1091, 872, 830, 806, 721 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1225 (26) $[2M+Na]^+$, 624 (100) $[M+Na]^+$, 602 (24) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $[C_{33}H_{31}N_5O_3FeNa]^+$: 624.1669; found: 624.1676.

Synthesis of (*S*)-Methyl 2-acetamido-3-(4-{(1*R*,2*S*)-3-[(2-{1-benzyl-1*H*-1,2,3-triazol-4-yl}propan-2-yl)amino]-2-(1,3-dioxoisoindolin-2-yl)-3-oxo-1-phenylpropyl}phenyl)propanoate (124ax)



The general procedure C1 was followed using Phth*N*-Ala-NHTAM (**124a**) (83.5 mg, 0.20 mmol) and 4-iodo-*L*-phenyl alanine (**4x**) (104.1 mg, 0.30 mmol). After 16 h, purification by gel permeation chromatography yielded **125ax** (72.9 mg, 57%) as a pale white solid (m. p. = 212–214 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.66 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.42 (s, 1H), 7.37–7.28 (m, 3H), 7.25–7.21 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.80 (s, 1H), 5.97 (d, *J* = 7.7 Hz, 1H), 5.45 (s, 2H), 4.98 (dd, *J* = 10.3, 6.4 Hz, 1H), 4.74 (ddd, *J* = 7.7, 5.9, 5.9 Hz, 1H), 3.60 (s, 3H), 3.48 (dd, *J* = 14.2, 6.4 Hz, 1H), 3.43 (dd, *J* = 14.2, 10.3 Hz, 1H), 2.99 (dd, *J* = 14.0, 5.9 Hz, 1H), 2.92 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.87 (s, 3H), 1.68 (s, 3H), 1.67 (s, 3H).

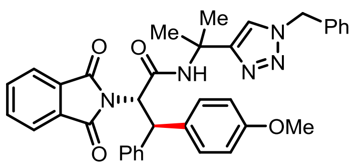
^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.9 (C_q), 169.5 (C_q), 167.8 (C_q), 167.2 (C_q), 153.3 (C_q), 135.7 (C_q), 134.7 (C_q), 134.6 (C_q), 134.2 (CH), 131.5 (C_q), 129.5 (CH), 129.1 (CH), 129.1 (CH), 128.6 (CH), 128.0 (CH), 123.5 (CH), 120.5 (CH), 56.2 (CH), 54.2 (CH_2), 53.1 (CH), 52.3 (CH_3), 52.1 (C_q), 37.5 (CH_2), 34.7 (CH_2), 28.1 (CH_3), 28.0 (CH_3), 23.1 (CH_3).

IR (ATR): 1743, 1711, 1656, 1516, 1456, 1436, 1381, 1214, 1173, 718 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1359 (10), 1327 (20), 1295 (18) $[2M+Na]^+$, 1273 (10) $[2M+H]^+$, 691 (50), 669 (96) $[M+Na]^+$, 637 (100) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{35}H_{37}N_6O_6$ $[M+H]^+$: 637.2769; found: 637.2767.

Synthesis of (2*S*,3*R*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(4-methoxyphenyl)-3-phenylpropanamide (125ee)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and 4-iodoanisol (**4e**) (93.6 mg, 0.40 mmol). After 20 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 1/1/1) and gel permeation chromatography yielded **125ee** (106.7 mg, 89%) as a pale yellow solid (m. p. = 188–190 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.62 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.36–7.30 (m, 3H), 7.27–7.16 (m, 4H), 7.11 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.03 (s, 1H), 7.02–6.98 (m, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.68 (br s, 1H), 5.51 (d, *J* = 12.6 Hz, 1H), 5.37 (s, 2H), 5.21 (d, *J* = 12.6 Hz, 1H), 3.73 (s, 3H), 1.55 (s, 3H), 1.51 (s, 3H).

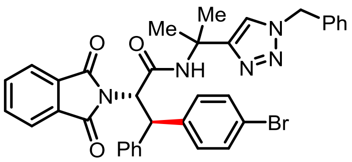
^{13}C NMR (100 MHz, $CDCl_3$): δ =167.9 (C_q), 166.2 (C_q), 158.7 (C_q), 152.6 (C_q), 140.7 (C_q), 134.8 (C_q), 133.9 (CH), 132.4 (C_q), 131.2 (C_q), 129.2 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 127.7 (CH), 127.3 (CH), 126.8 (CH), 123.3 (CH), 120.7 (CH), 114.5 (CH), 59.3 (CH), 55.3 (CH_3), 53.8 (CH_2), 51.8 (C_q), 50.1 (CH), 28.0 (CH_3), 27.6 (CH_3).

IR (ATR): 3375, 3141, 2971, 1698, 1609, 1514, 1381, 1028, 715, 698 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1221 (43) $[2M+Na]^+$, 622 (75) $[M+Na]^+$, 600 (100) $[M+H]^+$, 381 (5).

HR-MS (ESI): *m/z* calcd for $C_{36}H_{34}N_5O_4$ $[M+H]^+$: 600.2605; found: 600.2603.

Synthesis of (2*S*,3*R*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl]propan-2-yl)-3-(4-bromophenyl)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanamide (125ed)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and 1-bromo-4-iodo benzene (**4d**) (112.8 mg, 0.40 mmol). After 20 h, purification by gel permeation chromatography yielded **125ed** (95.9 mg, 74%) as a pale yellow solid (m. p. = 199–200 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.64 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.40–7.30 (m, 7H), 7.25–7.22 (m, 4H), 7.11 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.05 (s, 1H), 7.02 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.96 (br s, 1H), 5.47 (d, *J* = 12.5 Hz, 1H), 5.45 (d, *J* = 15.0 Hz, 1H), 5.41 (d, *J* = 15.0 Hz, 1H), 5.25 (d, *J* = 12.6 Hz, 1H), 1.57 (s, 3H), 1.55 (s, 3H).

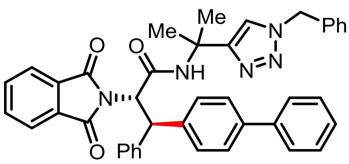
^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.0 (C_q), 166.1 (C_q), 152.7 (C_q), 139.8 (C_q), 139.5 (C_q), 134.9 (C_q), 134.2 (CH), 132.0 (CH), 131.2 (C_q), 130.1 (CH), 129.1 (CH), 128.8 (CH), 128.6 (CH), 128.0 (CH), 127.6 (CH), 127.3 (CH), 123.6 (CH), 121.2 (C_q), 120.7 (CH), 59.4 (CH), 54.2 (CH_2), 52.0 (C_q), 50.3 (CH), 28.1 (CH_3), 27.7 (CH_3).

IR (ATR): 1777, 1714, 1689, 1547, 1455, 1377, 1330, 1220, 1114, 1074, 1012 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 672 (100) $[M+Na]^+$ (^{81}Br), 670 (99) $[M+Na]^+$ (^{79}Br), 650 (75) $[M+H]^+$ (^{81}Br), 648 (73) $[M+H]^+$ (^{79}Br).

HR-MS (ESI): *m/z* calcd for $C_{35}H_{31}BrN_5O_3$ $[M+H]^+$: 648.1605; found: 648.1587.

Synthesis of (2*S*,3*R*)-3-[(1,1'-Biphenyl)-4-yl]-*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanamide (125ei)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and 4-iodo-1,1′-biphenyl (**4i**) (112.0 mg, 0.40 mmol). After 20 h, purification by gel permeation chromatography yielded **125ei** (64.8 mg, 50%) as a pale yellow solid (m. p. = 152–155 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.62 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.57–7.50 (m, 6H), 7.43 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.36–7.31 (m, 3H), 7.30–7.27 (m, 3H), 7.14 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.06–7.01 (m, 4H), 6.72 (br s, 1H), 5.61 (d, *J* = 12.5 Hz, 1H), 5.35 (d, *J* = 12.6 Hz, 1H), 5.23 (s, 2H), 1.56 (s, 3H), 1.51 (s, 3H).

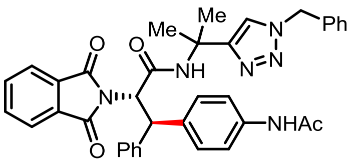
^{13}C NMR (76 MHz, $CDCl_3$): δ = 168.1 (C_q), 166.3 (C_q), 152.8 (C_q), 140.4 (C_q), 140.3 (C_q), 140.2 (C_q), 139.6 (C_q), 138.0 (CH), 134.9 (C_q), 134.2 (CH), 131.3 (C_q), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 123.5 (CH), 120.7 (CH), 59.2 (CH), 53.8 (CH_2), 51.9 (C_q), 50.5 (CH), 28.0 (CH_3), 27.6 (CH_3).

IR (ATR): 3286, 3029, 1717, 1550, 1377, 1334, 1221, 1176, 1122, 1100, 1055, 760 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 668 (100) $[M+Na]^+$, 365 (25), 203 (35).

HR-MS (ESI): *m/z* calcd for $C_{41}H_{35}N_5O_3Na$ $[M+Na]^+$: 668.2632; found: 668.2611.

Synthesis of (2*S*,3*R*)-3-(4-Acetamidophenyl)-*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanamide (125ek)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and *N*-(4-iodophenyl) acetamide (**4k**) (104.4 mg, 0.40 mmol). After 20 h, purification by column chromatography (EtOAc/CH_2Cl_2 4.5/1) yielded **125ek** (77.3 mg, 62%) as a pale yellow solid (m. p. = 157–159 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.60 (m, 5H), 7.41–7.28 (m, 7H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.17–7.13 (m, 2H), 7.11–7.05 (m, 3H), 7.02–6.98 (m, 1H), 6.84 (br s, 1H), 5.51 (d, *J* = 12.6 Hz, 1H), 5.35 (s, 2H), 5.23 (d, *J* = 12.6 Hz, 1H), 2.09 (s, 3H), 1.55 (s, 3H), 1.51 (s, 3H).

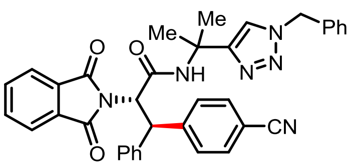
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.6 (C_q), 168.2 (C_q), 166.6 (C_q), 152.8 (C_q), 140.4 (C_q), 137.6 (C_q) 136.0 (C_q), 135.1 (C_q), 134.2 (CH), 131.3 (C_q), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.6 (CH), 127.9 (CH), 127.6 (CH), 127.1 (CH), 123.6 (CH), 121.0 (CH), 120.4 (CH), 59.3 (CH), 53.9 (CH_2), 51.9 (C_q), 50.3 (CH), 28.1 (CH_3), 27.7 (CH_3), 24.7 (CH_3).

IR (ATR): 3336, 3031, 1710, 1601, 1530, 1496, 1371, 1319, 1263, 1218, 1049, 717 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1275 (30) $[2M+Na]^+$, 649 (100) $[M+Na]^+$, 627 (55) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{37}H_{34}N_6O_4Na$ $[M+Na]^+$: 649.2534; found: 649.2523.

Synthesis of (2*S*,3*R*)-*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-ylpropan-2-yl]-3-(4-cyanophenyl)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanamide (125el)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and 4-iodobenzonitrile (**4l**) (91.6 mg, 0.40 mmol). After 20 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 1/1/1) and by gel permeation chromatography yielded **125el** (108.4 mg, 91%) as a white solid (m. p. = 178–181 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.61 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.38–7.28 (m, 3H), 7.25–7.15 (m, 5H), 7.13–7.09 (m, 3H), 7.01 (dd, *J* = 7.4, 7.4 Hz, 1H), 5.51 (d, *J* = 12.5 Hz, 1H), 5.43–5.36 (m, 3H), 1.55 (s, 3H), 1.53 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$): δ =167.9 (C_q), 165.9 (C_q), 152.7 (C_q), 145.9 (C_q), 138.9 (C_q), 134.7 (C_q), 134.3 (CH), 132.5 (CH), 131.0 (C_q), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 127.9 (CH), 127.7

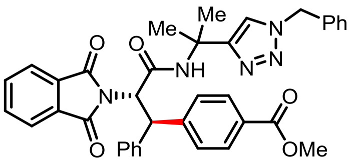
(CH), 127.5 (CH), 123.6 (CH), 120.4 (CH), 118.7 (C_q), 110.7 (C_q), 58.8 (CH), 54.0 (CH_2), 51.7 (C_q), 50.4 (CH), 27.6 (CH_3), 27.5 (CH_3).

IR (ATR): 3365, 1705, 1687, 1494, 1352, 1218, 1175, 1101, 1048, 725 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1275 (50), 1243 (45), 649 (100), 627 (55), 617 (25) $[M+Na]^+$, 595 (15) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{36}H_{30}N_6O_3Na$ $[M+Na]^+$: 617.2272; found: 617.2248.

Synthesis of Methyl 4-[(1*R*,2*S*)-3-{[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]amino}-2-(1,3-dioxoisoindolin-2-yl)-3-oxo-1-phenylpropyl]benzoate (125em)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and methyl-4-iodo benzoate (**4m**) (104.8 mg, 0.40 mmol). After 20 h, purification by gel permeation chromatography yielded **125em** (45.3 mg, 36%) as a white solid (m. p. = 178–180 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.63 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.37–7.29 (m, 3H), 7.27–7.21 (m, 3H), 7.20–7.15 (m, 2H), 7.11 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.09–7.07 (m, 1H), 7.03–6.99 (m, 1H), 6.91 (br s, 1H), 5.54 (d, *J* = 12.5 Hz, 1H), 5.41–5.32 (m, 3H), 3.87 (s, 3H), 1.54 (s, 3H), 1.51 (s, 3H).

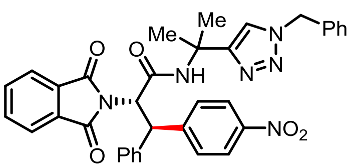
^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.9 (C_q), 166.6 (C_q), 166.0 (C_q), 152.7 (C_q), 145.6 (C_q), 139.5 (C_q), 134.8 (C_q), 134.2 (CH), 131.2 (C_q), 130.2 (CH), 129.2 (C_q), 129.0 (CH), 128.8 (CH), 128.6 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 123.6 (CH), 120.6 (CH), 59.2 (CH), 54.1 (CH_2), 52.2 (CH_3), 52.0 (C_q), 50.7 (CH), 27.9 (CH_3), 27.7 (CH_3).

IR (ATR): 3332, 3132, 2944, 1713, 1687, 1377, 1278, 1177, 1109, 1055, 1015, 765 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1277 (50) $[2M+Na]^+$, 682 (45), 650 (100) $[M+Na]^+$, 628 (85) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{37}H_{34}N_5O_5$ $[M+H]^+$: 628.2554; found: 628.2537.

Synthesis of (2*S*,3*R*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindo lin-2-yl)-3-(4-nitrophenyl)-3-phenylpropanamide (125en)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and 1-iodo-4-nitrobenzene (**4n**) (99.6 mg, 0.40 mmol). After 20 h, purification by gel permeation chromatography yielded **125en** (84.8 mg, 69%) as a white solid (m. p. = 174–176 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.8 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.65 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.40–7.29 (m, 3H), 7.23–7.21 (m, 2H), 7.20–7.17 (m, 3H), 7.17–7.11 (m, 3H), 7.06–7.02 (m, 1H), 5.52 (d, *J* = 12.4 Hz, 1H), 5.44 (d, *J* = 12.4 Hz, 1H), 5.42 (d, *J* = 15.5 Hz, 1H), 5.37 (d, *J* = 15.5 Hz, 1H), 1.56 (s, 3H), 1.55 (s, 3H).

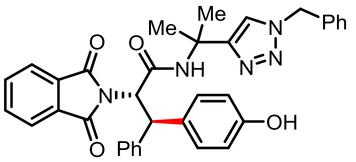
^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.9 (C_q), 165.9 (C_q), 152.7 (C_q), 147.9 (C_q), 146.9 (C_q), 138.7 (C_q), 134.6 (C_q), 134.4 (CH), 131.1 (C_q), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.7 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 123.9 (CH), 123.7 (CH), 120.4 (CH), 59.1 (CH), 54.2 (CH_2), 51.9 (C_q), 50.4 (CH), 27.8 (CH_3), 27.6 (CH_3).

IR (ATR): 3260, 3067, 1715, 1685, 1377, 1364, 1344, 1220, 1178, 1060, 716 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1251 (75) $[2M+Na]^+$, 637 (100) $[M+Na]^+$, 615 (70) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{35}H_{31}N_6O_5$ $[M+H]^+$: 615.2350; found: 615.2348.

Synthesis of (2*S*,3*R*)-*N*-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-hydroxyphenyl)-3-phenylpropanamide (125eo)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and 4-Iodophenol (**4o**) (88.0 mg, 0.40 mmol). After 20 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 3/4/3) yielded **124eo** (23 mg, 20%) as a pale white solid (m. p. = 169–170 °C).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.33 (s, 1H), 7.80–7.71 (m, 4H), 7.35 (d, J = 8.6 Hz, 2H), 7.33–7.28 (m, 4H), 7.25 (s, 1H), 7.24–7.20 (m, 4H), 7.11 (dd, *J* = 7.7, 7.7 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 2H), 5.59 (d, *J* = 12.2 Hz, 1H), 5.43 (s, 2H), 5.30 (d, *J* = 12.2 Hz, 1H), 1.38 (s, 3H), 1.37 (s, 3H).

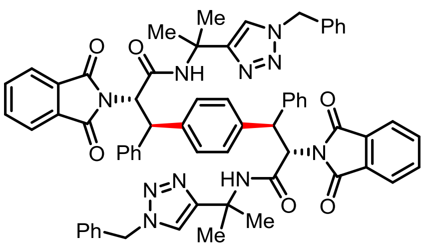
^{13}C NMR (126 MHz, DMSO-d_6): δ = 167.0 (C_q), 165.7 (C_q), 156.0 (C_q), 152.5 (C_q), 141.7 (C_q), 135.7 (C_q), 134.4 (CH), 131.2 (C_q), 130.4 (C_q), 129.3 (CH), 128.4 (CH), 128.0 (CH), 127.7 (CH), 127.5 (CH), 127.2 (CH), 126.2 (CH), 122.9 (CH), 120.8 (CH), 115.1 (CH), 57.7 (CH), 52.6 (CH_2), 50.9 (C_q), 48.7 (CH), 27.7 (CH_3), 27.5 (CH_3).

IR (ATR): 3490, 3228, 3135, 3036, 1701, 1677, 1515, 1385, 1264, 1220, 1116, 1059, 874, 718 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1101 (24), 1009 (56), 608 (20) $[M+Na]^+$, 516 (100).

HR-MS (ESI): *m/z* calcd for $C_{35}H_{32}N_5O_4$ $[M+H]^+$: 586.2449; found: 586.2438.

Synthesis of (2*S*,2'*S*,3*R*,3'*R*)-3,3'-(1,4-Phenylene)bis{*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanamide} (125ey)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and 1,4-diiodo benzene (**4y**) (33 mg, 0.10 mmol). After 20 h, purification by gel permeation chromatography yielded **125ey** (54.9 mg, 52%) as a pale yellow solid (m. p. = 177–180 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (dd, *J* = 5.5, 3.0 Hz, 4H), 7.61 (dd, *J* = 5.5, 3.0 Hz, 4H), 7.37–7.30 (m, 10H), 7.22–7.19 (m, 4H), 7.18–7.16 (m, 6H), 7.04 (dd, *J* = 7.7, 7.7 Hz, 4H), 6.94 (dd, *J* = 7.4, 7.4 Hz, 2H), 6.53 (br s, 2H), 5.47 (d, *J* = 12.4 Hz, 2H), 5.34 (s, 4H), 5.24 (d, *J* = 12.4 Hz, 2H), 1.37 (s, 6H), 1.30 (s, 6H).

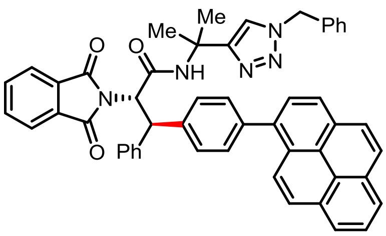
^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.9 (C_q), 166.1 (C_q), 152.8 (C_q), 140.3 (C_q), 140.0 (C_q), 135.1 (C_q), 134.1 (CH), 131.3 (C_q), 129.0 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 128.0 (CH), 127.7 (CH), 127.0 (CH), 123.5 (CH), 120.8 (CH), 58.9 (CH), 54.0 (CH_2), 51.9 (C_q), 50.4 (CH), 27.8 (CH_3), 27.6 (CH_3).

IR (ATR): 1774, 1704, 1497, 1468, 1454, 1378, 1363, 1333, 1216, 1048 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1083 (100) $[M+Na]^+$, 550 (80).

HR-MS (ESI): *m/z* calcd for $C_{64}H_{56}N_{10}O_6Na$ $[M+Na]^+$: 1083.4277; found: 1083.4279.

Synthesis of (2*S*,3*R*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-phenyl-3-[4-(pyren-1-yl)phenyl]propanamide (125ez)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and 1-(4-iodophenyl)pyrene (**4z**) (161.7 mg, 0.40 mmol). After 20 h, purification by gel permeation chromatography yielded **125ez** (131 mg, 85%) as a yellow solid (m. p. = 218–220 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20 (dd, *J* = 7.8, 1.5 Hz, 2H), 8.16 (d, *J* = 7.6 Hz, 1H), 8.12–8.08 (m, 3H), 8.04–7.97 (m, 2H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.75 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.63 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.43–7.40 (m, 2H), 7.28–7.23 (m, 1H), 7.23–7.15 (m, 5H), 7.12–7.06 (m, 1H), 7.03 (dd, *J* = 7.8, 1.5 Hz, 2H), 6.78 (br s, 1H), 5.69 (d, *J* = 12.6 Hz, 1H), 5.47 (d, *J* = 12.6 Hz, 1H), 5.30 (d, *J* = 3.2 Hz, 2H), 1.64 (s, 3H), 1.60 (s, 3H).

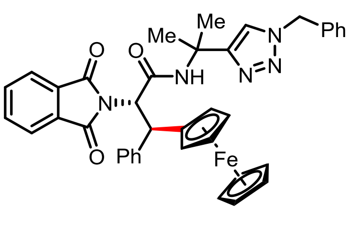
^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.0 (C_q), 166.4 (C_q), 152.9 (C_q), 140.5 (C_q), 140.4 (C_q), 139.6 (C_q), 136.9 (C_q), 134.7 (C_q), 134.1 (CH), 131.5 (C_q), 131.4 (C_q), 131.4 (CH), 131.0 (C_q), 130.7 (C_q), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.4 (CH), 127.8 (CH), 127.8 (CH), 127.6 (CH), 127.6 (CH), 127.6 (CH), 127.4 (CH), 127.2 (CH), 126.1 (CH), 125.2 (CH), 125.1 (CH), 125.0 (C_q), 124.9 (CH), 124.9 (C_q), 124.7 (CH), 123.5 (CH), 120.7 (CH), 59.3 (CH), 54.1 (CH_2), 52.1 (C_q), 50.8 (CH), 28.1 (CH_3), 27.8 (CH_3).

IR (ATR): 3365, 2967, 1710, 1517, 1454, 1380, 1262, 1086, 1047, 1014, 716 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1562 (80) $[2M+Na]^+$, 792 (100) $[M+Na]^+$, 770 (95) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{51}H_{40}N_5O_3$ $[M+H]^+$: 770.3126; found: 770.3118.

Synthesis of (2*S*,3*R*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-(ferrocenyl)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanamide (125er)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**124e**) (98.7 mg, 0.20 mmol) and iodoferrocene (**4r**) (124.8 mg, 0.40 mmol). After 20 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 1/1/1) yielded **125er** (24 mg, 18%) as a yellow (m. p. = 170–172 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.58 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.38–7.29 (m, 6H), 7.25–7.18 (m, 4H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.35 (br s, 1H), 5.45 (d, *J* = 15.0 Hz, 1H), 5.41 (d, *J* = 15.0 Hz, 1H), 4.97 (d, *J* = 12.1 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.19 (s, 1H), 4.13 (s, 2H), 3.95 (s, 1H), 3.69 (s, 5H), 1.61 (s, 3H), 1.59 (s, 3H).

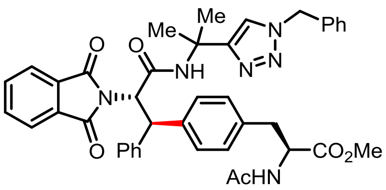
^{13}C NMR (126 MHz, $CDCl_3$): *δ* = 167.8 (C_q), 166.4 (C_q), 152.7 (C_q), 141.3 (C_q), 134.9 (C_q), 133.9 (CH), 131.3 (C_q), 129.0 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 127.0 (CH), 123.3 (CH), 121.2 (CH), 89.4 (C_q), 71.3 (CH), 69.1 (CH), 68.9 (CH), 67.2 (CH), 66.2 (CH), 61.5 (CH), 54.1 (CH_2), 51.8 (C_q), 45.0 (CH), 28.0 (CH_3), 27.7 (CH_3).

IR (ATR): 3031, 2979, 2932, 1706, 1524, 1454, 1379, 1332, 1105, 1050 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1355 (30) $[2M+H]^+$, 710 (10), 700 (35) $[M+Na]^+$, 678 (100) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{39}H_{36}N_5O_3Fe$ $[M+H]^+$: 678.2163; found: 678.2157.

Synthesis of (*S*)-Methyl 2-acetamido-3-{4-[(1*R*,2*S*)-3-({2-[1-benzyl-1*H*-1,2,3-triazol-4-yl]propan-2-yl}amino)-2-(1,3-dioxoisoindolin-2-yl)-3-oxo-1-phenylpropyl]phenyl}propanoate (*L*-125ex)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (*L*-**124e**) (98.7 mg, 0.20 mmol) and (*S*)-Methyl 2-acetamido-3-(4-iodophenyl)propanoate (**4x**) (138.9 mg, 0.40 mmol). After 20 h, purification by gel permeation chromatography yielded *L*-**125ex** (82.6 mg, 58%) as a pale white solid (m. p. = 166–169 °C).

^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.68 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.59 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.36–7.30 (m, 4H), 7.25–7.19 (m, 4H), 7.09 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.98–6.95 (m, 1H), 6.65 (br s, 1H), 6.44 (d, *J* = 7.5 Hz, 1H), 5.50 (d, *J* = 12.5 Hz, 1H), 5.43–5.38 (m, 2H), 5.27 (d, *J* = 12.5 Hz, 1H), 4.80 (ddd, *J* = 7.3, 5.8, 5.8 Hz, 1H), 3.66 (s, 3H), 3.06–3.02 (m, 2H), 1.97 (s, 3H), 1.52 (s, 3H), 1.46 (s, 3H).

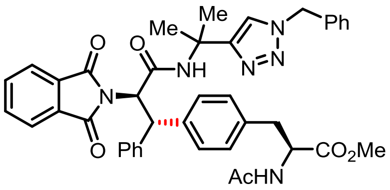
^{13}C NMR (126 MHz, $CDCl_3$): *δ* = 171.8 (C_q), 170.0 (C_q), 167.9 (C_q), 166.3 (C_q), 152.7 (C_q), 140.4 (C_q), 139.3 (C_q), 135.3 (C_q), 134.7 (C_q), 134.0 (CH), 131.3 (C_q), 130.1 (CH), 129.0 (CH), 128.6 (CH), 128.6 (CH), 128.3 (CH), 128.0 (CH), 127.5 (CH), 126.9 (CH), 123.4 (CH), 120.7 (CH), 58.9 (CH), 54.1 (CH_2), 53.1 (CH), 52.3 (CH_3), 51.8 (C_q), 50.4 (CH), 37.0 (CH_2), 27.7 (CH_3), 27.5 (CH_3), 23.1 (CH_3).

IR (ATR): 3324, 3029, 1710, 1667, 1515, 1376, 1271, 1214, 1125, 1012, 716 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1447 (30) $[2M+Na]^+$, 735 (100) $[M+Na]^+$, 713 (35) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{41}H_{41}N_6O_6$ $[M+H]^+$: 713.3082; found: 713.3079.

Synthesis of (*S*)-Methyl 2-acetamido-3-{4-[(1*S*,2*R*)-3-({2-[1-benzyl-1*H*-1,2,3-triazol-4-yl]propan-2-yl}amino)-2-(1,3-dioxoisoindolin-2-yl)-3-oxo-1-phenylpropyl]phenyl}propanoate (D-125ex)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (*D*-**125e**) (98.7 mg, 0.20 mmol) and (*S*)-Methyl 2-acetamido-3-(4-iodophenyl)propanoate (**4x**) (138.9 mg, 0.40 mmol). After 20 h, purification by gel permeation chromatography yielded *D*-**125ex** (104.8 mg, 74%) as a pale white solid (m. p. = 175–177 °C).

^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.68 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.60 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.38–7.30 (m, 4H), 7.29–7.25 (m, 2H), 7.24–7.19 (m, 4H), 7.09 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.00–6.95 (m, 3H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.42 (br s, 1H), 5.48–5.40 (m, 3H), 5.24 (d, *J* = 12.5 Hz, 1H), 4.85 (ddd, *J* = 7.8, 5.5, 5.5 Hz, 1H), 3.69 (s, 3H), 3.08 (dd, *J* = 14.1, 5.5 Hz, 2H), 3.04 (dd, *J* = 14.1, 5.5 Hz, 2H), 1.95 (s, 3H), 1.51 (s, 3H), 1.50 (s, 3H).

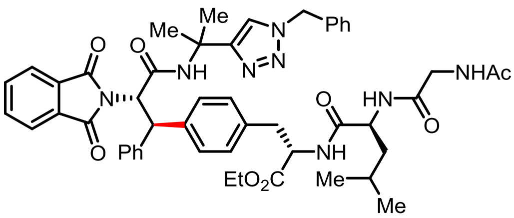
^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.8 (C_q), 170.1 (C_q), 167.9 (C_q), 166.4 (C_q), 152.3 (C_q), 140.4 (C_q), 139.2 (C_q), 135.3 (C_q), 134.8 (C_q), 134.0 (CH), 131.3 (C_q), 130.2 (CH), 129.0 (CH), 128.6 (CH), 128.6 (CH), 128.3 (CH), 128.0 (CH), 127.5 (CH), 126.9 (CH), 123.4 (CH), 121.2 (CH), 59.0 (CH), 54.1 (CH_2), 53.2 (CH), 52.3 (CH_3), 51.6 (C_q), 50.3 (CH), 37.1 (CH_2), 27.6 (CH_3), 27.5 (CH_3), 23.1 (CH_3).

IR (ATR): 3293, 3028, 1711, 1661, 1454, 1375, 1272, 1215, 1125, 716 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1447 (30) $[2M+Na]^+$, 735 (100) $[M+Na]^+$, 713 (35) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{41}H_{41}N_6O_6$ $[M+H]^+$: 713.3082; found: 713.3079.

Synthesis of (*S*)-Ethyl 2-[(*S*)-2-(2-acetamidoacetamido)-4-methylpentanamido]-3-{4-[(1*R*,2*S*)-3-({2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl}amino)-2-(1,3-dioxoisoindolin-2-yl)-3-oxo-1-phenylpropyl]phenyl}propanoate (125ead)



The general procedure C2 was followed using Phth*N*-Phe-NHTAM (**125e**) (98.7 mg, 0.20 mmol) and (*S*)-ethyl 2-[(*S*)-2-(2-acetamidoacetamido)-4-methylpentanamido]-3-(4-iodophenyl)propanoate (**4ad**) (159.4 mg, 0.30 mmol). After 20 h, purification by gel permeation chromatography yielded **125ead** (126.2 mg, 70%) as a pale white solid (m. p. = 188–190 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.60 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.38–7.36 (m, 1H), 7.35–7.30 (m, 3H), 7.29–7.24 (m, 3H), 7.22 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.19 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.10–7.03 (m, 4H), 6.98–6.91 (m, 4H), 5.44 (d, *J* = 12.4 Hz, 1H), 5.43 (s, 2H), 5.25 (d, *J* = 12.4 Hz, 1H), 4.74 (dd, *J* = 6.5, 5.7 Hz, 1H), 4.54–4.49 (m, 1H), 4.13 (ddd, *J* = 7.1, 7.1, 7.1 Hz, 2H), 3.93 (dd, *J* = 16.9, 5.1 Hz, 1H), 3.85 (dd, *J* = 16.9, 5.1 Hz, 1H), 3.13 (dd, *J* = 14.2, 5.7 Hz, 1H), 3.00 (dd, *J* = 14.2, 6.5 Hz, 1H), 1.97 (s, 3H), 1.70–1.65 (m, 2H), 1.55–1.53 (m, 4H), 1.47 (s, 3H), 1.17 (dd, *J* = 7.1, 7.1 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H).

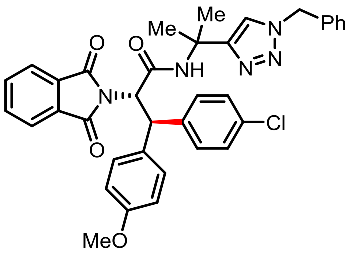
^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.8 (C_q), 171.1 (C_q), 170.8 (C_q), 169.2 (C_q), 167.9 (C_q), 166.5 (C_q), 152.3 (C_q), 140.2 (C_q), 138.9 (C_q), 135.2 (C_q), 134.7 (C_q), 134.1 (CH), 131.2 (C_q), 129.9 (CH), 129.0 (CH), 128.6 (CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 127.0 (CH), 123.4 (CH), 121.5 (CH), 61.6 (CH_2), 58.9 (CH), 54.1 (CH_2), 53.0 (CH), 52.1 (CH), 51.3 (C_q), 50.1 (CH), 43.3 (CH_2), 40.9 (CH_2), 36.6 (CH_2), 27.7 (CH_3), 27.5 (CH_3), 24.9 (CH), 23.1 (CH_3), 23.0 (CH_3), 22.1 (CH_3), 14.3 (CH_3).

IR (ATR): 2958, 1714, 1649, 1523, 1378, 1269, 1203, 718, 699, 530 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 919 (100) $[M+Na]^+$, 468 (20).

HR-MS (ESI): *m/z* calcd for $C_{50}H_{56}N_8O_8Na$ $[M+Na]^+$: 919.4113; found: 919.4118.

Synthesis of (2*S*,3*R*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-(4-chlorophenyl)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-methoxyphenyl)propanamide (125aec)



The general procedure C2 was followed using (**125ae**) (104.7 mg, 0.20 mmol) and 1-chloro-4-iodobenzene (**4c**) (95.4 mg, 0.40 mmol). After 20 h, purification by gel permeation chromatography yielded **125aec** (100.2 mg, 79%) as a white solid (m. p. = 199–200 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.64 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.37 (dm, *J* = 8.5 Hz, 2H), 7.34–7.28 (m, 3H), 7.22–7.18 (m, 4H), 7.13 (d, *J* = 8.7 Hz, 2H), 7.04 (s, 1H), 6.97 (br s, 1H), 6.64 (d, *J* = 8.7 Hz, 2H), 5.43 (d, *J* = 12.6 Hz, 1H), 5.41 (d, *J* = 15.0 Hz, 1H), 5.37 (d, *J* = 15.0 Hz, 1H), 5.22 (d, *J* = 12.6 Hz, 1H), 3.60 (s, 3H), 1.56 (s, 3H), 1.54 (s, 3H).

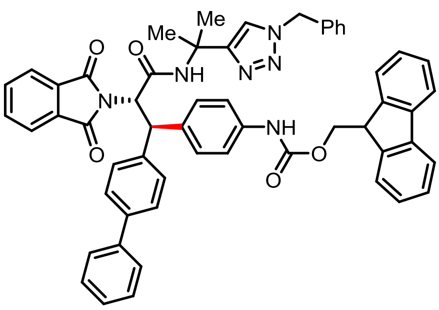
^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.0 (C_q), 166.2 (C_q), 158.5 (C_q), 152.7 (C_q), 139.3 (C_q), 134.9 (C_q), 134.2 (CH), 132.9 (C_q), 131.9 (C_q), 131.2 (C_q), 129.6 (CH), 129.0 (CH), 129.0 (CH), 128.5 (CH), 128.5 (CH), 127.9 (CH), 123.6 (CH), 120.6 (CH), 114.2 (CH), 59.6 (CH), 55.2 (CH_3), 54.1 (CH_2), 51.9 (C_q), 49.4 (CH), 28.0 (CH_3), 27.6 (CH_3).

IR (ATR): 3286, 2936, 1714, 1511, 1491, 1372, 1121, 1091, 1014, 715 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1280 (20) $[2M+Na]^+$, 656 (100) $[M+Na]^+$.

HR-MS (ESI): *m/z* calcd for $C_{36}H_{32}ClN_5O_4Na$ $[M+Na]^+$: 656.2035; found: 656.2029.

Synthesis of (9*H*-Fluoren-9-yl)methyl {4-[(1*R*,2*S*)-1-[(1,1'-biphenyl)-4-yl]-3-{[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]amino}-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]phenyl}carbamate (125aij)



The general procedure C2 was followed using (**125ai**) (112 mg, 0.20 mmol) and (9*H*-fluoren-9-yl)methyl(4-iodophenyl)carbamate (**4j**) (173.9 mg, 0.40 mmol). After 20 h, purification by gel permeation chromatography yielded **125aij** (135.4 mg, 78% (5% impurity)) as a white solid (m. p. = 191–193 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.6 Hz, 2H), 7.69–7.66 (m, 2H), 7.60–7.55 (m, 4H), 7.42–7.40 (m, 2H), 7.38–7.20 (m, 19H), 7.11–7.08 (m, 2H), 7.02 (s, 1H), 6.85–6.81 (m, 1H), 5.55 (d, *J* = 12.6 Hz, 1H), 5.36–5.27 (m, 3H), 4.51 (d, *J* = 6.4 Hz, 2H), 4.22 (dd, *J* = 6.4, 6.4 Hz, 1H), 1.57 (s, 3H), 1.53 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.0 (C_q), 166.3 (C_q), 153.3 (C_q), 152.7 (C_q), 143.7 (C_q), 141.6 (C_q), 140.3 (C_q), 139.6 (C_q), 139.5 (C_q), 137.2 (C_q), 135.4 (C_q), 135.0 (C_q), 134.1 (CH), 131.3 (C_q), 129.0 (CH), 128.9 (CH), 128.7 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.3 (CH), 127.2 (CH), 127.2 (CH), 126.8 (CH), 124.9 (CH), 123.5 (CH), 120.8 (CH), 120.1 (CH), 66.9 (CH_2), 59.4 (CH), 53.9 (CH_2), 52.0 (C_q), 50.0 (CH), 47.3 (CH), 28.2 (CH_3), 27.7 (CH_3)

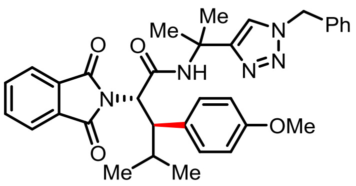
Due to overlap, two resonances are missing.

IR (ATR): 3293, 3030, 1703, 1603, 1531, 1450, 1386, 1321, 1050, 713 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1788 (5) $[2M+Na]^+$, 905 (100) $[M+Na]^+$, 461 (35).

HR-MS (ESI): *m/z* calcd for $C_{56}H_{46}N_6O_5Na$ [M+Na]$^+$: 905.3422; found: 905.3416.

Synthesis of (2*S*,3*R*)-*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(4-methoxyphenyl)-4-methylpentanamide (128de)



The general procedure C2 was followed using Phth*N*-Leu-NHTAM (**127d**) (98.7 mg, 0.20 mmol) and 4-Iodanisol (**4e**) (70.2 mg, 0.30 mmol). After 20 h, purification by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2 3/4/3) yielded **128de** (16.8 mg, 15%) as a white solid (m. p. = 183–185 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.38–7.29 (m, 3H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.18 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 1H), 6.52 (br s, 1H), 5.36 (d, *J* = 15.0 Hz, 1H), 5.31 (d, *J* = 15.0 Hz, 1H), 5.19 (d, *J* = 12.6 Hz, 1H), 3.83 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.77 (s, 3H), 1.82–1.71 (m, 1H),1.43 (s, 3H), 1.40 (s, 3H), 0.75 (d, *J* = 6.8 Hz, 3H), 0.70 (d, *J* = 6.8 Hz, 3H).

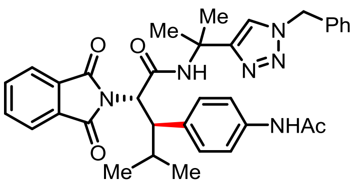
^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.7 (C_q), 167.0 (C_q), 159.0 (C_q), 152.8 (C_q), 135.1 (C_q), 134.4 (CH), 131.8 (C_q), 129.0 (CH), 128.6 (C_q), 128.5 (CH), 128.2 (CH), 127.9 (CH), 123.8 (CH), 120.9 (CH), 113.9 (CH), 58.2 (CH), 55.4 (CH_3), 53.8 (CH_2), 51.7 (C_q), 48.5 (CH), 28.9 (CH), 28.1 (CH_3), 27.7 (CH_3), 21.6 (CH_3), 16.2 (CH_3).

IR (ATR): 3233, 3114, 3047, 2981, 2932, 1710, 1668, 1512, 1385, 1259, 1123, 1012, 716 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1169 (67), 1153 (45), 604 (73) [M+K]$^+$, 588 (100) [M+Na]$^+$, 566 (25) [M+H]$^+$.

HR-MS (ESI): *m/z* calcd for [$C_{33}H_{35}N_5O_4Na$]$^+$: 588.2581; found: 588.2576.

Synthesis of (2*S*,3*R*)-3-(4-Acetamidophenyl)-*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-4-methylpentanamide (128dk)



The general procedure C2 was followed using Phth*N*-Leu-NHTAM (**127d**) (51.7 mg, 0.113 mmol) and *N*-(4-iodophenyl)acetamide (**4k**) (44.1 mg, 0.169 mmol). After 20 h, purification by column chromatography *(*EtOAc/CH_2Cl_2 4/1) yielded **128dk** (16.0 mg, 24%) as a pale white solid (m. p. = 161–163 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.55 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.37–7.29 (m, 3H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 6.6 Hz, 2H), :6.89 (s, 1H), 6.64 (br s, 1H), 5.36 (s, 2H), 5.20 (d, *J* = 12.6 Hz, 1H), 3.88 (dd, *J* = 12.6, 3.2 Hz, 1H), 2.11 (s, 3H), 1.79 (qd, *J* = 6.8, 3.3 Hz, 1H), 1.44 (s, 3H), 1.40 (s, 3H), 0.75 (d, *J* = 6.8 Hz, 3H), 0.70 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.5 (C_q), 168.4 (C_q), 166.8 (C_q), 152.7 (C_q), 137.5 (C_q), 135.1 (C_q), 134.4 (CH), 132.3 (C_q), 132.2 (C_q), 131.7 (C_q), 130.7 (CH), 129.0 (CH), 128.5 (CH), 127.7 (CH), 123.8

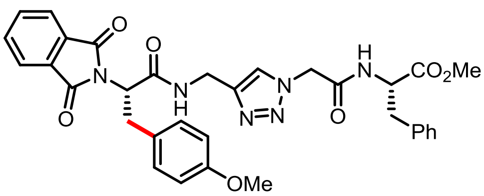
(CH), 120.8 (CH), 119.5 (CH), 58.3 (CH), 53.9 (CH_2), 51.8 (C_q), 48.8 (CH), 29.0 (CH), 28.1 (CH_3), 27.8 (CH_3), 24.8 (CH_3), 21.7 (CH_3), 16.4 (CH_3).

IR (ATR): 3233, 3114, 3047, 2981, 2932, 1710, 1668, 1512, 1385, 1259, 1123, 1012, 716 cm^{-1}.

MS (ESI) *m/z* (relative intensity) 1223 (20), 1207 (23), 631 (55) $[M+K]^+$, 615 (100) $[M+Na]^+$, 593 (14) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $[C_{34}H_{36}N_6O_4Na]^+$: 615.2690; found: 615.2686.

Synthesis of (*S*)-Methyl 2-[2-(4-{[(*S*)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-methoxyphenyl)propanamido]methyl}-1*H*-1,2,3-triazol-1-yl)acetyl]-*L*-phenylalaninate (138ae)



The general procedure C3 was followed using Phth*N*-Ala-Gly-Tzl-Gly-Phe-OMe (**137a**) (103.7 mg, 0.20 mmol) and 4-iodoanisole (**4e**) (93.6 mg, 0.40 mmol). After 20 h, purification by column chromatography (EtOAc/*n*-hexane 8/1 → EtOAc/*n*-hexane 10/1) yielded **138ae** (100 mg, 80%) as a white solid (m. p. = 150–152 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.65–7.50 (m, 3H), 7.51 (br s, 1H), 7.25–7.15 (m, 4H), 7.08–7.04 (m, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 5.03 (dd, *J* = 11.2, 5.5 Hz, 1H), 4.98 (d, *J* = 16.4 Hz, 1H), 4.85 (d, *J* = 16.4 Hz, 1H), 4.82–4.77 (m, 1H), 4.43–4.32 (m, 2H), 3.64 (s, 3H), 3.63 (s, 3H), 3.49 (dd, *J* = 14.3, 5.5 Hz, 1H), 3.41 (dd, *J* = 14.3, 11.2 Hz, 1H), 3.08 (dd, *J* = 13.9, 5.5 Hz, 1H), 2.97 (dd, *J* = 13.9, 7.2 Hz, 1H).

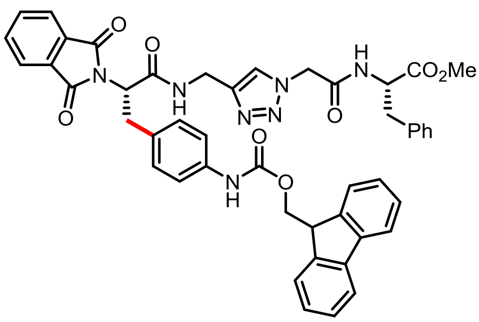
^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.5 (C_q), 168.7 (C_q), 167.8 (C_q), 164.9 (C_q), 158.3 (C_q), 144.9 (C_q), 135.6 (C_q), 134.1 (CH), 131.5 (C_q), 129.9 (CH), 129.2 (CH), 128.7 (C_q), 128.6 (CH), 127.2 (CH), 124.2 (CH), 123.4 (CH), 114.0 (CH), 55.5 (CH), 55.2 (CH_3), 53.7 (CH), 52.6 (CH_3) 52.5 (CH_2), 37.8 (CH_2), 35.2 (CH_2), 33.9 (CH_2).

IR (ATR): 2956, 1774, 1711, 1673, 1612, 1531, 1382, 1246, 1217, 1029 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1271 (45) $[2M+Na]^+$, 647 (100) $[M+Na]^+$, 625 (37) $[M+H]^+$.

HR-MS (ESI) *m/z* calcd for $C_{33}H_{33}N_6O_7$ $[M+H]^+$: 625.2405; found: 625.2403.

Synthesis of (*S*)-Methyl [2-(4-{[(S)-3-[4-({[(9*H*-fluoren-9-yl)methoxy]carbonyl}amino)-phenyl]-2-(1,3-dioxoiso indolin-2-yl)propanamido]methyl}-1*H*-1,2,3-triazol-1-yl)acetyl]-*L*-phenylalaninate (138aj)



The general procedure C3 was followed using Phth*N*-Ala-Gly-Tzl-Gly-Phe-OMe (**137a**) (103.7 mg, 0.20 mmol) and (9*H*-fluoren-9-yl)methyl(4-iodo-phenyl)carbamate (**4j**) (176.5 mg, 0.40 mmol). After 20 h, purification by column chromatography (EtOAc/*n*-hexane 8/1 → EtOAc/*n*-hexane 12/1) yielded **138aj** (114.7 mg, 69%) as a white solid (m. p. = 144–147 °C).

^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.70 (d, *J* = 7.6 Hz, 2H), 7.67–7.55 (m, 6H), 7.54–7.50 (m, 2H), 7.37–7.33 (m, 2H), 7.25–7.08 (m, 9H), 7.04–6.99 (m, 2H), 6.98–6.96 (m, 2H), 5.04 (dd, *J* = 10.9, 5.7 Hz, 1H), 4.95 (d, *J* = 16.3 Hz, 1H), 4.84 (d, *J* = 16.3 Hz, 1H), 4.82–4.75 (m, 1H), 4.43–4.30 (m, 4H), 4.14 (dd, *J* = 6.7, 6.7 Hz, 1H), 3.60 (s, 3H), 3.50 (dd, *J* = 14.1, 5.6 Hz, 1H), 3.40 (dd, *J* = 14.1, 11.3 Hz, 1H), 3.05 (dd, *J* = 13.9, 5.5 Hz, 1H), 2.95 (dd, *J* = 13.9, 7.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): *δ* = 171.6 (C_q), 171.1 (C_q), 168.6 (C_q), 167.9 (C_q), 165.0 (C_q), 144.9 (C_q), 143.7 (C_q), 141.3 (C_q), 135.6 (C_q), 134.2 (CH), 131.4 (C_q), 129.5 (CH), 129.2 (CH), 128.6 (CH), 127.7 (CH), 127.6 (CH), 127.2 (CH), 127.1 (CH), 125.0 (CH), 124.2 (CH), 123.5 (CH), 120.0 (CH), 66.9 (CH_2), 60.5 (CH_2), 55.5 (CH), 53.7 (CH), 52.6 (CH_3), 52.5 (C_q), 47.2 (CH), 37.8 (CH_2), 35.2 (CH_2), 34.2 (CH_2).

Due to overlap, two resonances are missing.

IR (ATR): 3284, 1710, 1667, 1526, 1383, 1350, 1223, 1051 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1685 (5) $[2M+Na]^+$, 1267 (15), 854 (100) $[M+Na]^+$, 541 (35), 435 (45).

HR-MS (ESI) *m/z* calcd for $C_{47}H_{41}N_7O_8Na$ $[M+Na]^+$: 854.2909; found: 854.2895.

6.1.3.2 Fluorescence Data of arylated TAM-containing phenylalanines

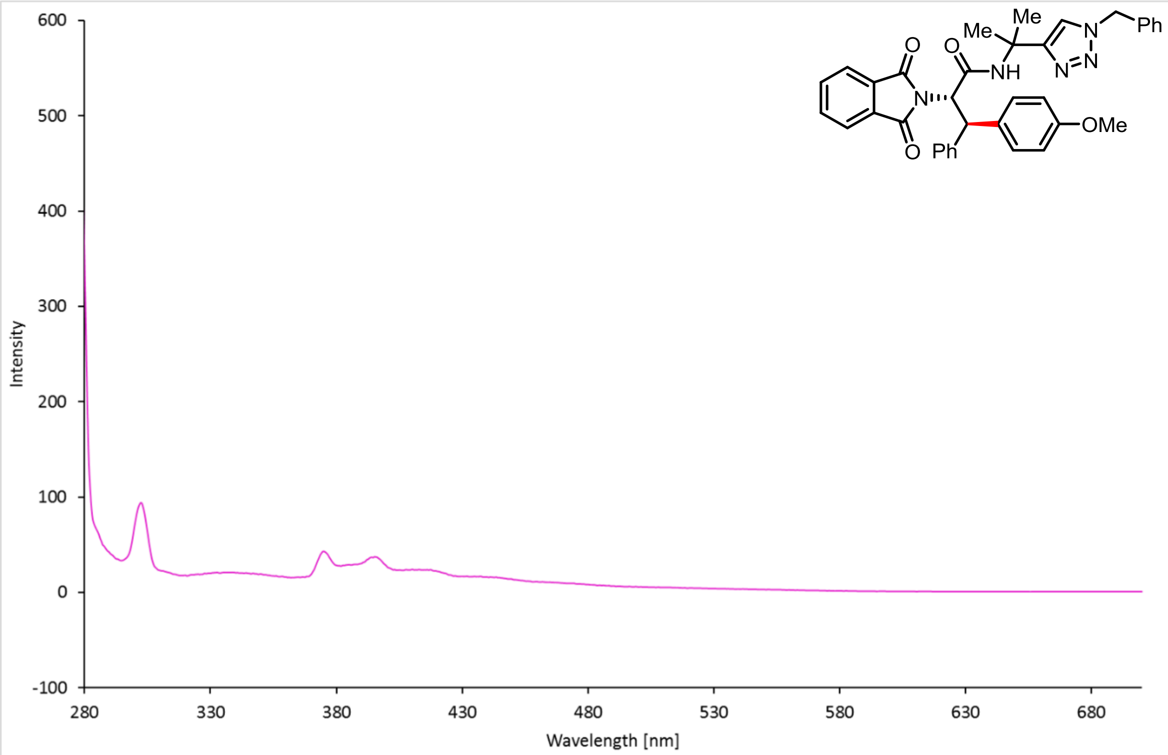


Figure 66: Fluorescence emission spectra of **125ee** in DMSO (2.2·10^{-4} mol/L, excitation at 276 nm).

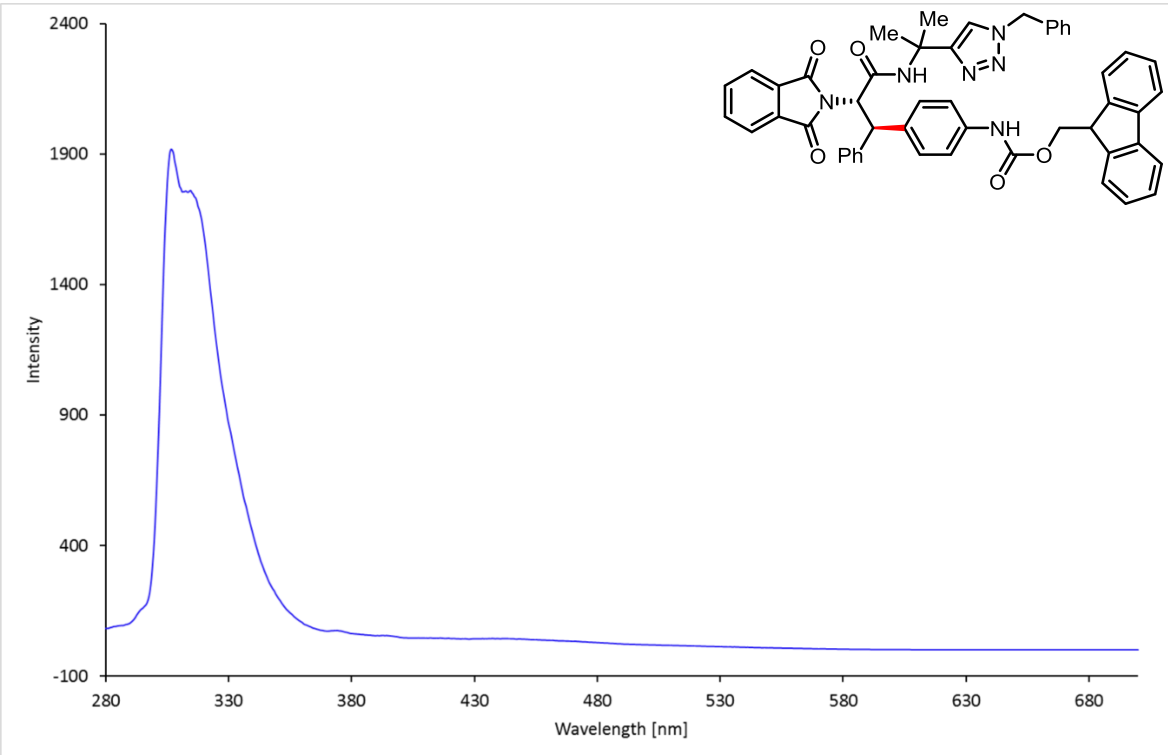


Figure 67: Fluorescence emission spectra of **125ej** in DMSO (1.9·10^{-4} mol/L, excitation at 270 nm).

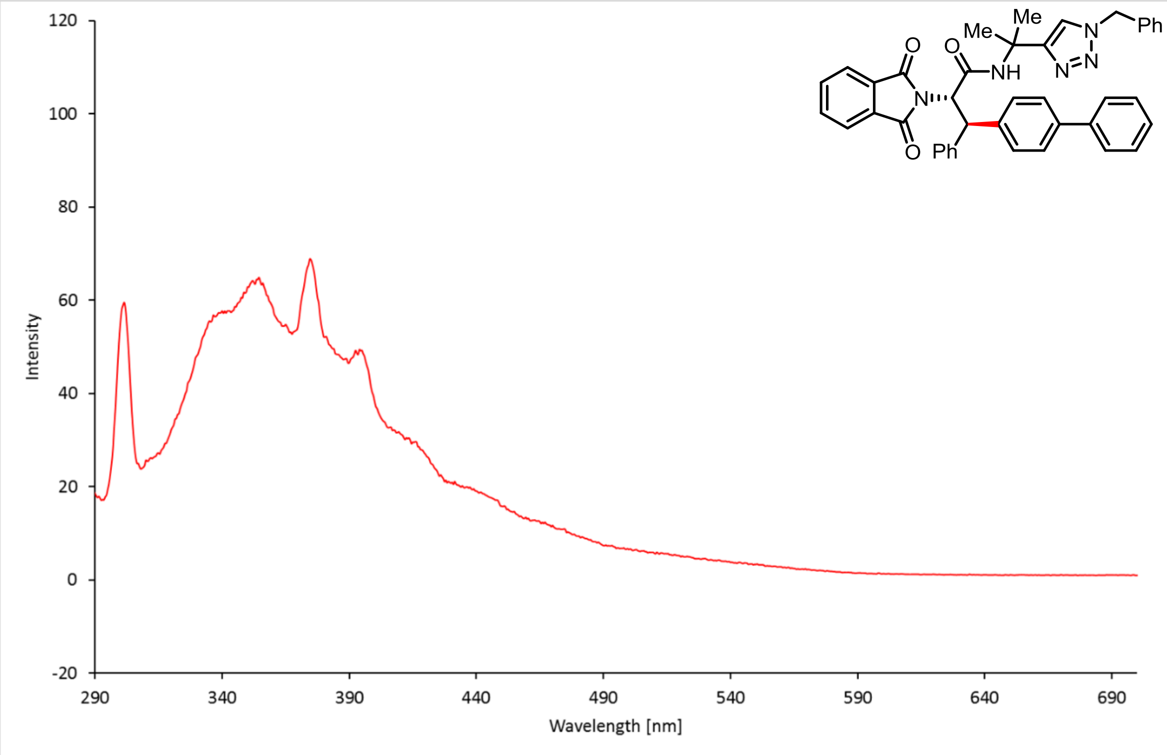


Figure 68: Fluorescence emission spectra of **125ei** in DMSO (2.3·10^{-4} mol/L, excitation at 275 nm).

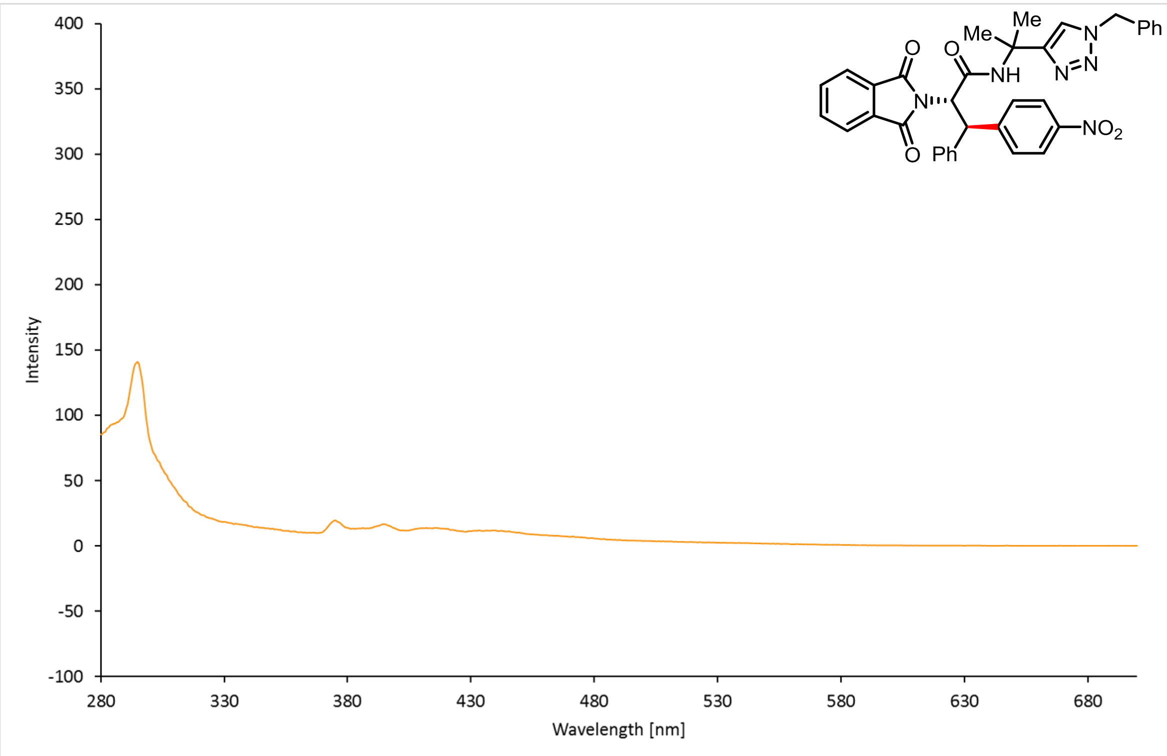


Figure 69: Fluorescence emission spectra of **125en** in DMSO (1.8·10^{-4} mol/L, excitation at 270 nm).

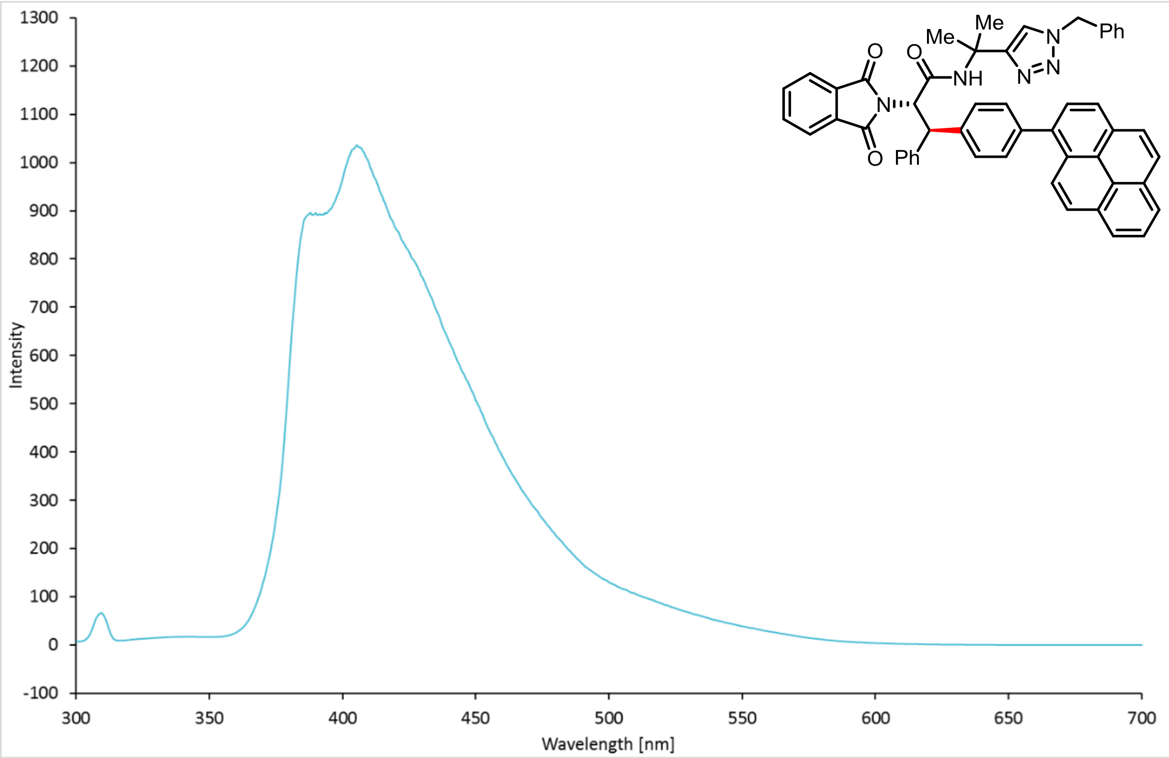


Figure 70: Fluorescence emission spectra of **125ez** in DMSO (1.9·10^{-4} mol/L, excitation at 282 nm).

6. Computational Details

6.1 General Remarks

All structures were optimized at the TPSS[266] level in combination with D3 dispersion corrections with Becke-Johnson damping scheme (D3(BJ)).[267] Frequency calculations were carried out at the same level of theory in order to identify all stationary points as either intermediates (no imaginary frequencies) or as transition states (one imaginary frequency) and to provide thermal and non-thermal corrections to the free energy in gas-phase at 403.15 K. Palladium was described with the def2-TZVP basis set in combination with Stuttgart-Dresden effective core potentials, while on all other atoms the def2-TZVP basis set was used.[268] Transition states were located by performing relaxed surface scans through one variable, while the others were allowed to relax. The electronic energy was then refined through B3LYP[269] single-point calculations on the optimized geometries in combination with RIJCOSX approximations and dispersion corrections (D3(BJ)), with def2-TZVP basis set.

Solvent effects were included in the single-point calculations through the use of the Conductor-like Screening Model (COSMO)[270] with a dielectric constant of $\varepsilon = 2.5454$ (1,2-Xylene) or $\varepsilon = 10.3600$ (1,2-Dichloroethane). Energies reported are unless otherwise stated Gibbs free energies in kcal/mol, which were calculated by addition of the entropy contribution at 403 K and 1 atm (S(403)) and gas-phase thermal and non-thermal correction at 403 K and 1 atm (ΔH(403)) to the single-point energies (E(solvent)). All calculations were performed using the ORCA program package version 3.0.3.[271] In all calculations the keywords GRID4, TightSCF, SlowConv and in the geometry optimizations TightOPT was used. NBO calculations were carried out at the TPSS-D3(BJ)/def2-TZVP level of theory using NBO version 5.9.[272] Computed structures were illustrated using PyMOL version 1.8.x. Bond orders correspond to Mayer bond orders at the TPSS-D3(BJ)/def2-TZVP level of theory as implemented in ORCA.

6.1.1 Phenylalanine

6.1.1.1 Electronic energies and correction values

Table 23: Electronic energies and correction values in Hartree for calculations at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Structure	E(1,2-Xylene)	ΔΔH(403)	S(403)	Dispersion
124e	-1620.616270	0.553926	0.137496	-0.160531
1.1	-2205.537096	0.679801	0.188013	-0.214733
1.2	-1976.438840	0.606083	0.163408	-0.181112
1.3	-1976.424923	0.603687	0.160619	-0.184009
TS1.(3-4)	-1976.406493	0.599718	0.160619	-0.186545
1.4	-1976.442968	0.604149	0.158292	-0.185877
1.3‘	-1976.415195	0.603007	0.159344	-0.188385
TS1.(3-4)‘	-1976.403021	0.598428	0.157177	-0.188006
1.4‘	-1976.433147	0.605032	0.162117	-0.191051
1.1a	-2801.046744	0.636163	0.215849	-0.216935
1.2a	-2274.188854	0.583626	0.163312	-0.182444
1.3a	-2274.187206	0.581324	0.160189	-0.185147
TS1.(3-4)a	-2274.159327	0.576867	0.160874	-0.188248

Structure	E(1,2-Xylene)	ΔΔH(403)	S(403)	Dispersion
1.4a	-2274.187618	0.582158	0.163041	-0.187292
1.3a‘	-2274.177952	0.582067	0.162723	-0.190161
TS1.(3-4)a‘	-2274.156173	0.577003	0.160794	-0.189040
1.4a‘	-2274.177288	0.581912	0.162627	-0.191791
1.3-4	-1976.421709	0.606499	0.164157	-0.184317
TS1.(3-4)-4	-1976.382960	0.600007	0.162547	-0.185779
1.4-4	-1976.433422	0.604003	0.160093	-0.185745
1.3‘-4	-1976.411942	0.605840	0.166499	-0.188968
TS1.(3-4)‘-4	-1976.375303	0.597874	0.159759	-0.186221
1.4‘-4	-1976.427555	0.605511	0.162914	-0.190618
1.4-OA	-1976.401458	0.601234	0.159488	-0.185687
1.4‘-OA	-1976.395224	0.602817	0.160922	-0.190359
1.5	-2375.926516	0.627157	0.167966	-0.217159
TS1.(5-6)	-2375.903482	0.627085	0.168141	-0.221064
1.6	-2375.920829	0.630067	0.173511	-0.227393
TS1.(6-7)	-2375.902486	0.627434	0.170026	-0.224074
1.7	-2375.954116	0.630289	0.167902	-0.223602
1.5‘	-2375.921246	0.628462	0.171599	-0.216899
TS1.(5-6)‘	-2375.901363	0.625425	0.165846	-0.220018
1.6‘	-2375.921501	0.628904	0.170181	-0.227741
TS1.(6-7)‘	-2375.893748	0.629101	0.171121	-0.226537
1.7‘	-2375.947944	0.630256	0.167201	-0.226994
1.5a	-2375.925655	0.627152	0.168284	-0.214533
TS1.(5-6)a	-2375.902693	0.627425	0.168491	-0.218248
1.6a	-2375.918118	0.629485	0.169671	-0.222377
TS1.(6-7)a	-2375.892203	0.627434	0.168412	-0.223423
1.7a	-2375.945576	0.630108	0.167137	-0.226683
1.5a‘	-2375.921482	0.628462	0.167089	-0.219358
TS1.(5-6)a‘	-2375.896217	0.627730	0.166978	-0.225985
1.6a‘	-2375.906826	0.628730	0.170133	-0.228976
TS1.(6-7)a‘	-2375.888541	0.627434	0.167280	-0.226763
1.7a‘	-2375.948658	0.630238	0.167264	-0.224428
1.7b	-2306.672852	0.684543	0.181161	-0.233344
TS1.(7-8)b	-2306.641839	0.682926	0.180459	-0.228149
1.8b	-2306.695897	0.685632	0.179742	-0.228208
1.9b	-2306.688651	0.687220	0.182706	-0.231829
1.7c	-2306.671011	0.686039	0.183519	-0.228392
TS1.(7-8)c	-2306.627372	0.682879	0.179137	-0.231732
1.8c	-2306.688973	0.686693	0.182993	-0.233219
1.9c	-2306.707105	0.687978	0.183503	-0.229235
1.7b‘	-2306.662433	0.684405	0.179934	-0.234138
TS1.(7-8)b‘	-2306.629381	0.683103	0.178483	-0.231532
1.8b‘	-2306.688148	0.684384	0.174276	-0.233720
1.9b‘	-2306.675961	0.687095	0.182690	-0.231779
1.7c‘	-2306.659951	0.684605	0.179918	-0.232529
TS1.(7-8)c‘	-2306.629243	0.684151	0.183089	-0.231656
1.8c‘	-2306.690361	0.686864	0.181686	-0.230720
1.9c‘	-2306.700273	0.687424	0.183280	-0.229110
1.8 (125ee)	-1950.883458	0.637961	0.165177	-0.196679
1.8‘	-1950.875954	0.636660	0.160109	-0.202636
HOAc	-229.083228	0.069153	0.048111	-0.006999
TFA	-526.834127	0.047856	0.053338	-0.008165
C_6H_5I	-529.316279	0.100019	0.056876	-0.024885
4F-C_6H_4I	-628.566570	0.093212	0.061210	-0.025199
AgOAc	-751.011602	0.121125	0.079122	-0.030760
AgI	-444.739213	0.005797	0.041450	-0.003638
$Pd_3(OAc)_6$	-1754.784039	0.358830	0.145735	-0.113710
$Pd_3(TFA)_6$	-3541.288855	0.231438	0.165719	-0.121035

6.1.1.2 Selected geometrical properties

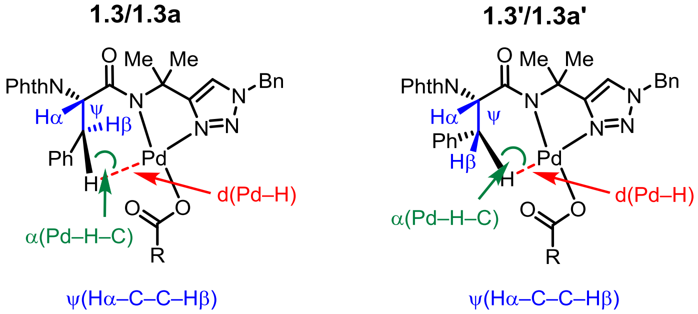


Figure 71: Selected bond distances (d(Pd–H)), bond angles (α(Pd–H–C)) and dihedral angles (ψ(Hα–C–C–Hβ)) of intermediates with agostic interactions. Distances are marked in red, angles are marked in green and dihedral angles are marked in blue.

Table 24: Selected bond distances (d), angles (α) and dihedral angles (ψ) of intermediates with agostic interactions. Distances are given in Ångströms (Å), angles are given in degree (°). Figure 71 shows the distances, angles and dihedral angles.

Structure	d(Pd–H) / Å	α(Pd–H–C) / °	ψ(H*α*–C–C–H*β*) / °
1.3	1.833	102.7	-169.6
1.3'	1.784	104.7	42.5
1.3a	1.824	102.0	170.6
1.3a'	1.780	104.9	40.3

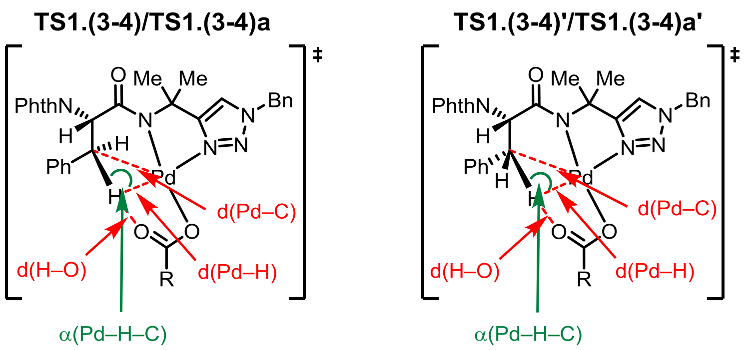


Figure 72: Selected bond distances (d(Pd–H), d(Pd–C), d(H–O)) and bond angles (α(Pd–H–C)) of transition states of the C–H cleavage of phenylalanine. Distances are marked in red, angles are marked in green.

Table 25: Selected bond distances (d) and angles (α) of transition states of the C–H cleavage of phenylalanine. Distances are given in Ångströms (Å), angles are given in degree (°). Figure 72 shows the distances, angles and dihedral angles.

Structure	d(Pd–H) / Å	d(Pd–C) / Å	d(H–O) / Å	α(Pd–H–C) / °
TS1.(3-4)	1.840	2.191	1.397	81.9
TS1.(3-4)'	1.837	2.205	1.448	83.9
TS1.(3-4)a	1.796	2.164	1.378	79.1
TS1.(3-4)a'	1.841	2.175	1.377	79.5

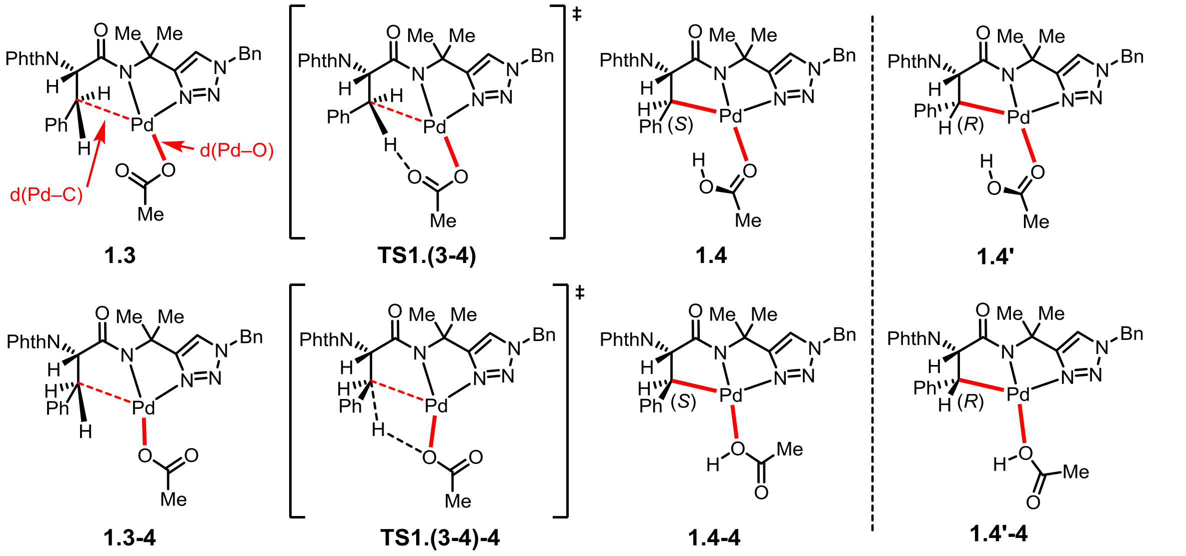


Figure 73: Selected bond distances (d(Pd–C), d(Pd–O)) of the acetate-assisted C–H cleavage of phenylalanine. Distances are marked in red. For simplicity, only **1.4’** and **1.4’-4** with (*R*)-configuration are shown.

Table 26: Selected bond distances (d(Pd–O), d(Pd–C)), relative Gibbs free energies and energy barriers of the 6-membered and the 4-membered C–H activation pathway. Distances are given in Ångströms (Å), relative Gibbs free energies and barriers are given in kcal/mol.

Structure	d(Pd–O) / Å	d(Pd–C) / Å	ΔG‡ / kcal/mol	ΔΔG‡ / kcal/mol
1.3	2.027	2.367	8.0	
TS1.(3-4)	2.070	2.191	17.1	18.1
1.4	2.121	2.061	-1.6	
1.3’	2.024	2.375	14.5	
TS1.(3-4)’	2.064	2.205	20.6	21.6
1.4’	2.115	2.053	2.8	
1.3-4	2.019	2.348	9.6	
TS1.(3-4)-4	2.150	2.176	30.8	31.8
1.4-4	2.184	2.060	3.2	
1.3’-4	2.021	2.406	13.8	
TS1.(3-4)’-4	2.164	2.157	36.1	37.1
1.4’-4	2.180	2.045	6.1	

6.1.2 Leucin

6.1.2.1 Electronic energies and correction values

Table 27: Electronic energies and correction values in Hartree for calculations at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Structure	E(1,2-Xylene)	ΔΔH(403)	S(403)	Dispersion
127a	-1507.512124	0.556423	0.136777	-0.143275
2.1	-2092.440114	0.679796	0.180937	-0.196289
2.2	-1863.334415	0.607393	0.156699	-0.172589
2.3	-1863.328122	0.607764	0.161097	-0.174934
TS2.(3-4)	-1863.300890	0.603686	0.160986	-0.176908
2.4	-1863.332221	0.607367	0.160476	-0.174604
2.3a	-1863.318725	0.605825	0.157033	-0.178408
TS2.(3-4)a	-1863.301444	0.602163	0.157543	-0.179735
2.4a	-1863.332839	0.605977	0.157161	-0.174149
2.3‘	-1863.318426	0.607193	0.160237	-0.177231
TS2.(3-4)‘	-1863.301739	0.603545	0.160300	-0.178946
2.4‘	-1863.328150	0.606242	0.155344	-0.175864
2.3b	-1863.316572	0.606186	0.156922	-0.175233
TS2.(3-4)b	-1863.285593	0.602260	0.155982	-0.178345
2.4b	-1863.325179	0.607351	0.159201	-0.175534
2.3c	-1863.315250	0.606135	0.158006	-0.174706
TS2.(3-4)c	-1863.280850	0.602551	0.157161	-0.177576
2.4c	-1863.324282	0.607069	0.158802	-0.176106
2.5	-2163.564156	0.637606	0.165814	-0.203791
TS2.(5-6)	-2163.542757	0.636134	0.162643	-0.209182
2.6	-2163.558941	0.639444	0.167248	-0.212662
TS2.(6-7)	-2163.533313	0.636945	0.160603	-0.213688
2.7	-2163.588429	0.641172	0.163838	-0.216482
2.8	-1738.531717	0.647460	0.158436	-0.186642
2.5a	-2163.565872	0.638781	0.169575	-0.206038
TS2.(5-6)a	-2163.539316	0.637285	0.165766	-0.212608
2.6a	-2163.560441	0.639181	0.167217	-0.216296
TS2.(6-7)a	-2163.527988	0.638413	0.165256	-0.213601
2.7a	-2163.595613	0.640774	0.164986	-0.215358
2.5‘	-2163.563513	0.637433	0.164874	-0.206182
TS2.(5-6)‘	-2163.545569	0.637111	0.165974	-0.212095
2.6‘	-2163.562537	0.639009	0.167742	-0.215373
TS2.(6-7)‘	-2163.534128	0.638251	0.163727	-0.215281
2.7‘	-2163.589944	0.641204	0.163567	-0.216052
2.8‘	-1738.519025	0.648596	0.161735	-0.186814
2.5a‘	-2163.560462	0.637421	0.165256	-0.203232
TS2.(5-6)a‘	-2163.522636	0.636438	0.161942	-0.210468
2.6a‘	-2163.553583	0.639932	0.165495	-0.215214
TS2.(6-7)a‘	-2163.521365	0.638293	0.164380	-0.214300
2.7a‘	-2163.592416	0.641109	0.165495	-0.212061
2.5b	-2163.555085	0.635818	0.161336	-0.204189
TS2.(5-6)b	-2163.531576	0.636999	0.164523	-0.213593
2.6b	-2163.556641	0.639260	0.165416	-0.220203
TS2.(6-7)b	-2163.523626	0.638940	0.161256	-0.215862
2.7b	-2163.594029	0.640566	0.164221	-0.215188
2.5c	-2163.558830	0.637225	0.164332	-0.207329
TS2.(5-6)c	-2163.532790	0.636935	0.165129	-0.212815
2.6c	-2163.551577	0.638602	0.167217	-0.213925
TS2.(6-7)c	-2163.510872	0.638646	0.161751	-0.214276
2.7c	-2163.584756	0.641745	0.167997	-0.222222
2.8b	-1738.523294	0.647076	0.158404	-0.181133
HOAc	-229.083228	0.069153	0.048111	-0.006999

Structure	E(1,2-Xylene)	ΔΔH(403)	S(403)	Dispersion
C_6H_5I	-529.316279	0.100019	0.056876	-0.024882
AgOAc	-751.011602	0.121125	0.079122	-0.030760
AgI	-444.739213	0.005797	0.041450	-0.003638
$Pd_3(OAc)_6$	-1754.784039	0.358830	0.145735	-0.113710

6.1.2.2 Selected geometrical properties

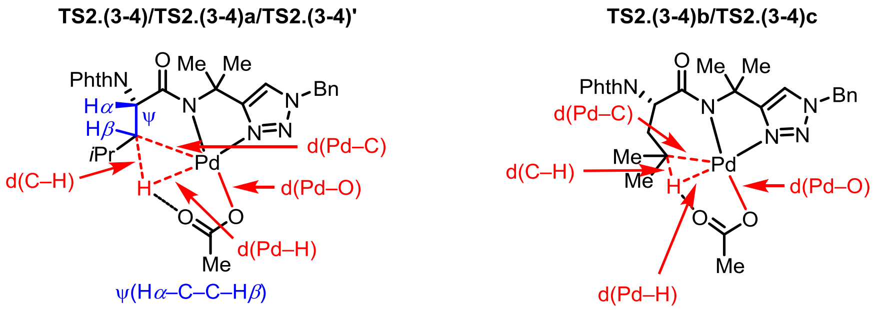


Figure 74: Selected bond distances (d(C–H), d(Pd–C), d(Pd–O), d(Pd–H)) and dihedral angles (ψ(H*α*–C–C–H*β*) of the C–H cleavage. Distances are marked in red, dihedral angle is marked in blue.

Table 28: Selected bond distances (d) and dihedral angles (ψ) of the transition states of the C–H cleavage. Distances are given in Ångströms (Å) and angles are given in degree (°). Figure 74 shows the bond distances and dihedral angles.

Structure	d(Pd–C) / Å	d(Pd–O) / Å	d(Pd–H) / Å	d(C–H) / Å	ψ(H*α*–C–C–H*β*) / °
TS2.(3-4)	2.188	2.077	1.914	1.558	170.4
TS2.(3-4)'	2.220	2.067	1.866	1.450	52.3
TS2.(3-4)a	2.210	2.069	1.839	1.459	83.5
TS2.(3-4)b	2.227	2.072	1.755	1.543	-
TS2.(3-4)c	2.169	2.052	1.607	1.654	-

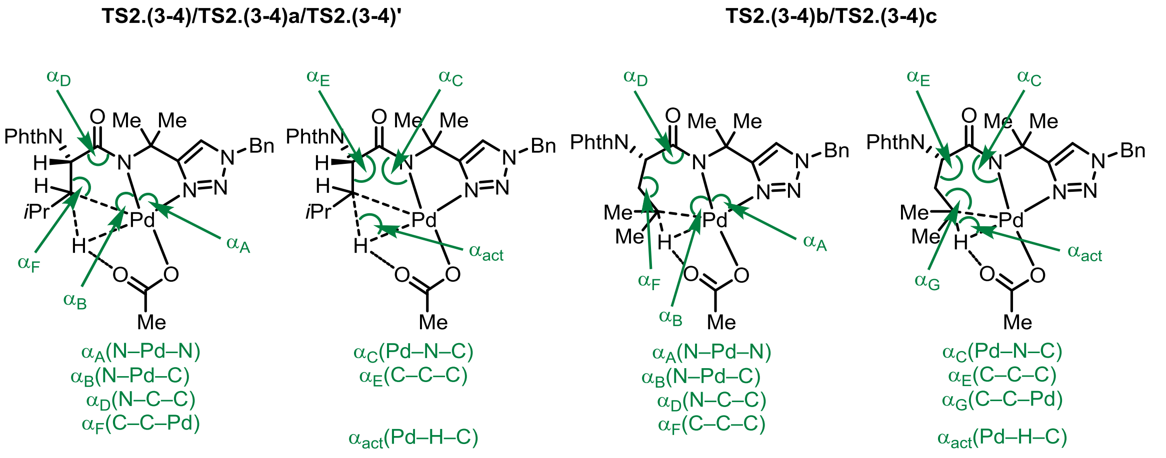


Figure 75: Selected bond angles (α_{act}(Pd–H–C), α_A(N–Pd–N), α_B(N–Pd–C), α_C(Pd–N–C), α_D(N–C–C), α_E(C–C–C), α_F(C–C–Pd/N), α_G(C–C–C)) of the transition states of the C–H cleavage. Bond angles are marked in green.

Table 29: Selected bond angles (α_{act}, α_A – α_G) of the transition states of the C–H cleavage. Angles are given in degree (°). Figure 75 shows the selected bond angles.

Structure	α_{act}(Pd–H–C) / °	α_A(N–Pd–N) / °	α_B(N–Pd–C) / °	α_C(Pd–N–C) / °
TS2.(3-4)	77.4	80.8	81.7	119.9
TS2.(3-4)'	83.0	80.4	82.4	120.0
TS2.(3-4)a	83.5	80.8	82.0	120.0
TS2.(3-4)b	84.7	80.0	94.3	128.0
TS2.(3-4)c	83.4	80.5	94.5	128.3
Structure	α_D(N–C–C) / °	α_E(C–C–C) / °	α_F(C–C–Pd/C) / °	α_G(C–C–Pd) / °
TS2.(3-4)	112.5	112.6	102.7	-
TS2.(3-4)'	110.7	116.4	99.4	-
TS2.(3-4)a	113.0	116.4	103.3	-
TS2.(3-4)b	117.6	117.9	114.8	94.3
TS2.(3-4)c	117.8	119.2	115.4	112.1

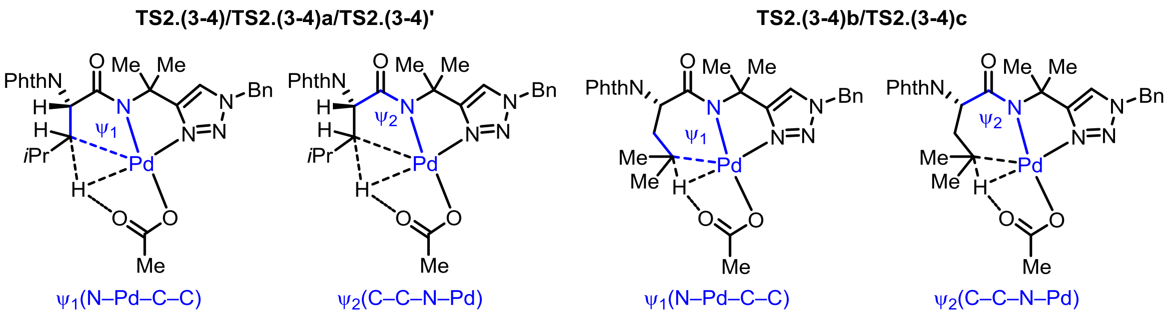


Figure 76: Selected dihedral angles (ψ_1(N–Pd–C–C) and ψ_2(C–C–N–Pd)) of the transition states of the C–H cleavage. Dihedral angles are marked in blue.

Table 30: Selected dihedral angles (ψ_1 and ψ_2) and relative Gibbs free energies of the transition states of the C–H cleavage. Dihedral angles are given in degree (°), relative Gibbs free energies are given in kcal/mol. Figure 76 shows the selected dihedral angles ψ_1 and ψ_2.

Structure	ψ_1(N–Pd–C–C) / °	ψ_2(C–C–N–Pd) / °	$\Delta G^{\ddagger}$ / kcal/mol
TS2.(3-4)	-24.4	4.3	18.3
TS2.(3-4)'	-25.7	2.3	18.1
TS2.(3-4)a	19.2	10.4	19.1
TS2.(3-4)b	42.1	-22.2	30.1
TS2.(3-4)c	30.1	27.2	32.5

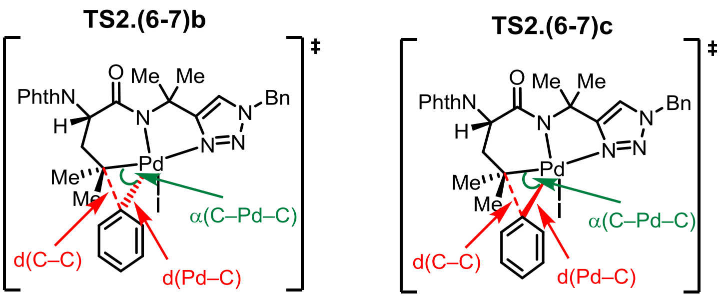


Figure 77: Selected bond distances (d(C–C), d(Pd–C)) and bond angles (α(C–Pd–C) of the C–C bond formation. Distances are marked in red, bond angles are marked in green.

Table 31: Selected bond distances (d) and bond angles (α) of the transition states of the C–C bond formation. Distances are given in Ångströms (Å) and angles are given in degree (°). Figure 77 shows the bond distances and dihedral angles.

Structure	d(Pd–C) / Å	d(C–C) / Å	α(C–Pd–C) / °
TS2.(6-7)b	2.132	2.032	52.4
TS2.(6-7)c	2.119	1.995	51.7

6.1.3 Internal Triazole

6.1.3.1 Electronic Energies and Correction Values

Table 32: Electronic energies and correction values in Hartree for calculations at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Structure	E(1,2-Dichloroethane)	ΔΔH(403)	S(403)	Dispersion
137a	-1786.185584	0.550512	0.153161	-0.156264
3.1	-2371.110923	0.671444	0.192411	-0.201479
3.2	-2142.004363	0.598212	0.170499	-0.180936
3.3	-2141.989328	0.598324	0.171376	-0.189350
TS3.(3-4)	-2141.973659	0.593276	0.169607	-0.186930
3.4	-2142.006775	0.597091	0.168746	-0.185066
3.5	-2442.235731	0.628690	0.177687	-0.209297
TS3.(5-6)	-2442.220466	0.628806	0.178754	-0.215291
3.6	-2442.244582	0.630516	0.180188	-0.224527
TS3.(6-7)	-2442.223717	0.628047	0.174133	-0.219541
3.7	-2442.281101	0.631040	0.174467	-0.222917
3.5a	-2671.336561	0.699066	0.196188	-0.233121
TS3.(5-6)a	-2671.319137	0.698698	0.197734	-0.238413
3.6a	-2671.333820	0.702750	0.202100	-0.240069
TS3.(6-7)a	-2671.321812	0.699594	0.195630	-0.236985
3.7a	-2671.376116	0.704205	0.199599	-0.242084
3.8 (131aa)	-2017.200526	0.636255	0.163918	-0.189011
3.1‘	-2371.117337	0.672151	0.193017	-0.202142
3.2‘	-2142.002471	0.598202	0.169942	-0.168558
TS3.(2-3)‘	-2141.971202	0.595875	0.175679	-0.193026
3.3‘	-2141.995326	0.598940	0.172380	-0.192743
3.4‘	-2442.230324	0.629972	0.180906	-0.222294
TS3.(4-5)‘	-2442.210500	0.631136	0.184603	-0.227884
3.5‘	-2442.224952	0.631565	0.182802	-0.228198
TS3.(5-6)‘	-2442.214922	0.630987	0.180061	-0.222637
3.6‘	-2442.286754	0.633363	0.181049	-0.219782
3.7‘	-2017.205614	0.637010	0.168284	-0.187268
HOAc	-229.087730	0.069153	0.048111	-0.006999
C_6H_5I	-529.318224	0.100019	0.056876	-0.024881
AgOAc	-751.016002	0.121125	0.079122	-0.030760
AgI	-444.744692	0.005797	0.041450	-0.003638
$Pd_3(OAc)_6$	-1754.794320	0.358830	0.145735	-0.113710

6.1.3.2 Selected geometrical properties

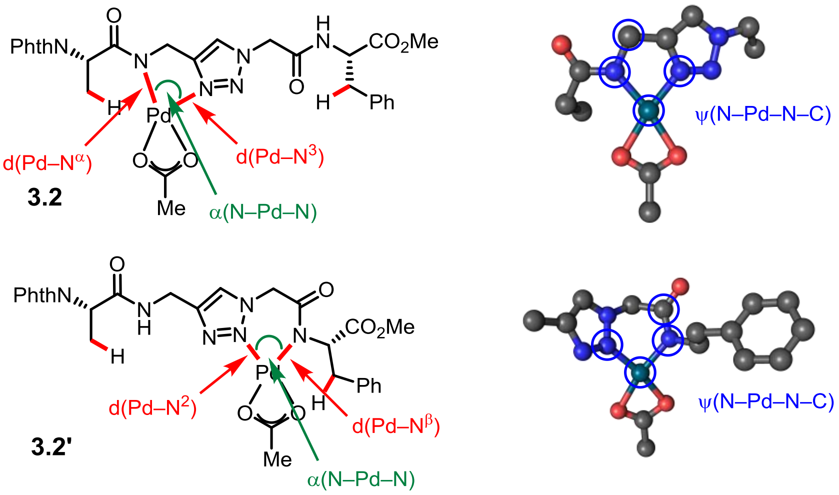


Figure 78: Selected bond distances (d(Pd–N)), bond angles (α(N–Pd–N)) and dihedral anlges ψ(N–Pd–N–C) of palladium complexes **3.2** and **3.2'**. Distances are marked in red, bond angles are marked in green and dihedral angles are marked in blue.

Table 33: Selected bond distances, bond angles and dihedral angles of palladium complexes **3.2** and **3.2'**. Distances are given in Ångströms (Å) and angles are given in degree (°). Figure 78 shows the selected distances, angles and dihedral angles.

Structure	d(Pd–C) / Å	d(Pd–N$^{\alpha/\beta}$) / Å	d(Pd–N$^{2/3}$) / Å	α(N–Pd–N) / °	ψ(N–Pd–N–C) / °
3.2	3.468	2.012	1.977	79.6	-18.7
3.2'	3.913	2.013	1.986	86.1	-44.5

6.1.3.3 Atomic charge analysis

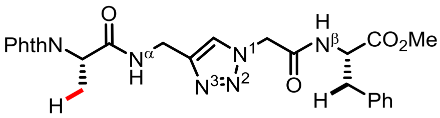


Figure 79: Atom numbering scheme for **137a**.

Table 34: Mulliken population analysis (MPA) and natural population analysis (NPA) on the atoms at the TPSS-D3(BJ)/def2-TZVP level of theory. Numbering of the atoms is shown in Figure 79.

Structure	Atom	MPA	NPA
137a	N^{1}	0.100691	-0.15699
	N^{2}	-0.160409	-0.06932
	N^{3}	-0.119194	-0.23224
	N$^{\alpha}$	-0.276327	-0.55758
	N$^{\beta}$	-0.255490	-0.56962
3.1	N^{1}	0.126246	-0.12837
	N^{2}	-0.128965	-0.04128
	N^{3}	-0.039260	-0.23259
	N$^{\alpha}$	-0.289972	-0.57537
	N$^{\beta}$	-0.254320	-0.56291
	Pd	0.454296	0.87846
3.2	N^{1}	0.130215	-0.12851
	N^{2}	-0.203968	-0.03782
	N^{3}	-0.007571	-0.23334

Structure	Atom	MPA	NPA
	N^{α}	-0.315761	-0.56530
	N^{β}	-0.239729	-0.56051
	Pd	0.303421	0.79364
3.1'	N^{1}	0.153335	-0.10944
	N^{2}	0.011077	-0.07466
	N^{3}	-0.144410	-0.19148
	N^{α}	-0.262400	-0.57333
	N^{β}	-0.264014	-0.56963
	Pd	0.354813	0.85651
3.2'	N^{1}	0.088282	-0.10511
	N^{2}	0.013390	-0.05546
	N^{3}	-0.223992	-0.21478
	N^{α}	-0.254153	-0.56701
	N^{β}	-0.311530	-0.53919
	Pd	0.293115	0.81091

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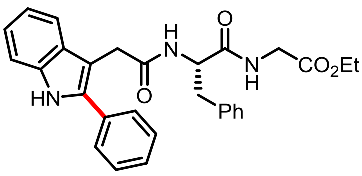
8. NMR Spectra



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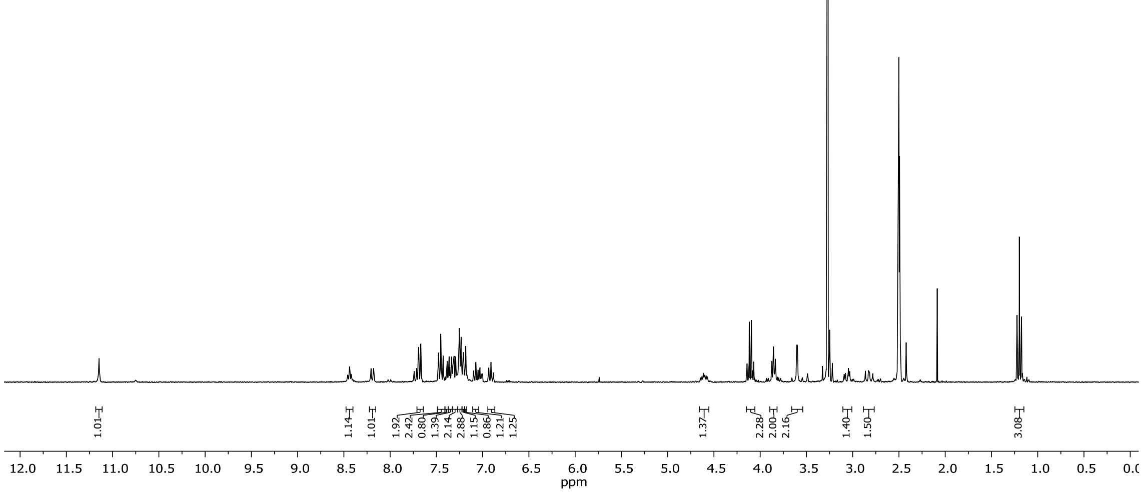

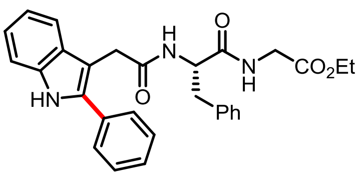

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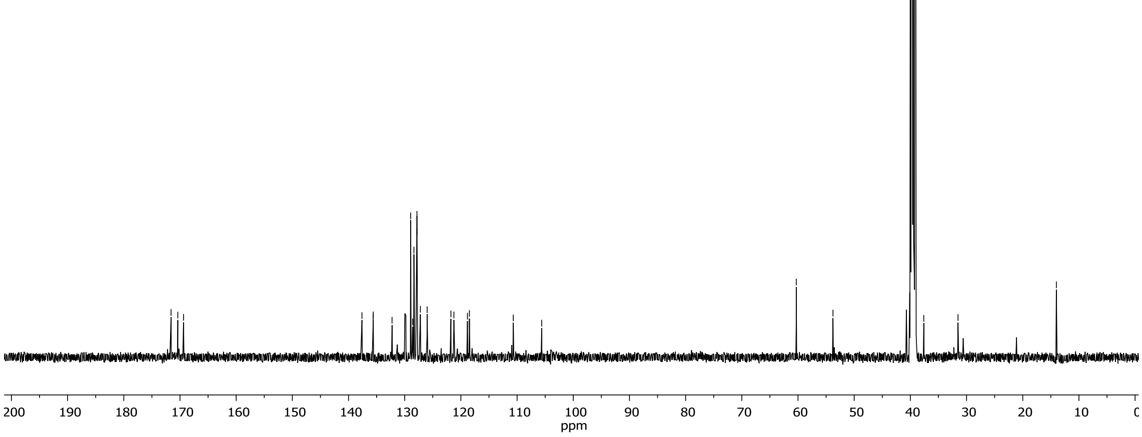
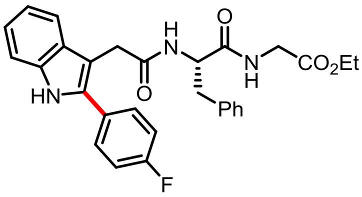
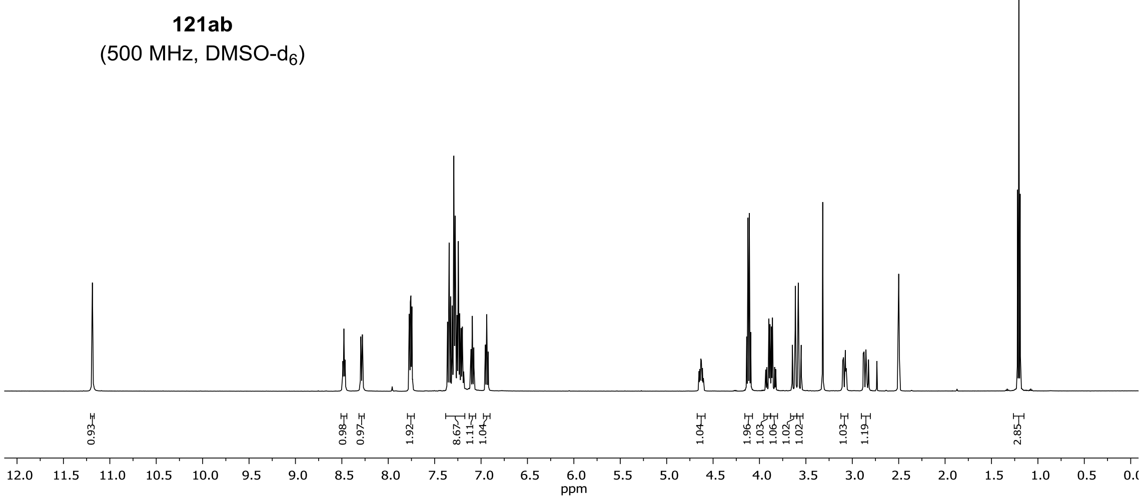
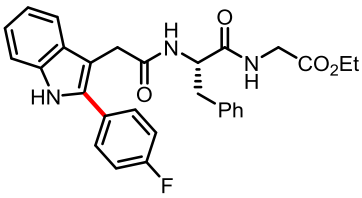


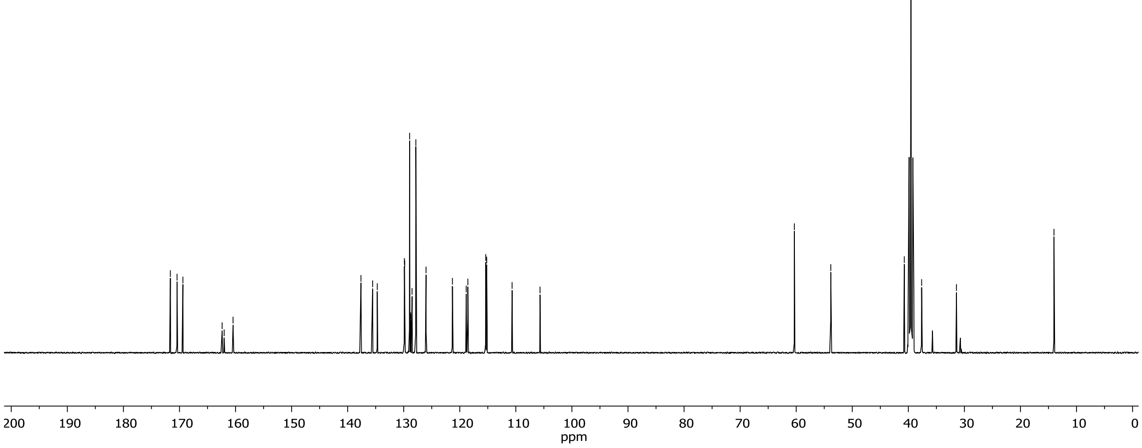


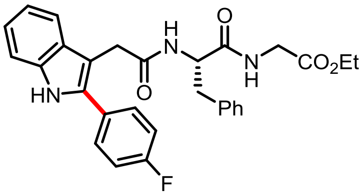
121ab
(500 MHz, DMSO-d_6)



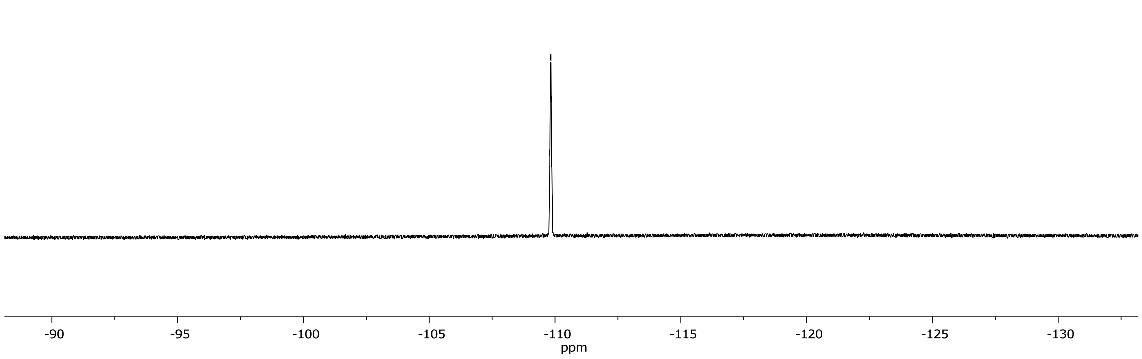


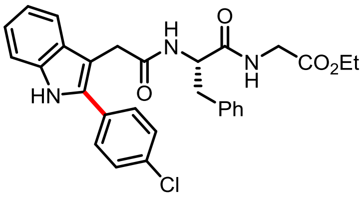
121ab
(126 MHz, DMSO-d_6)



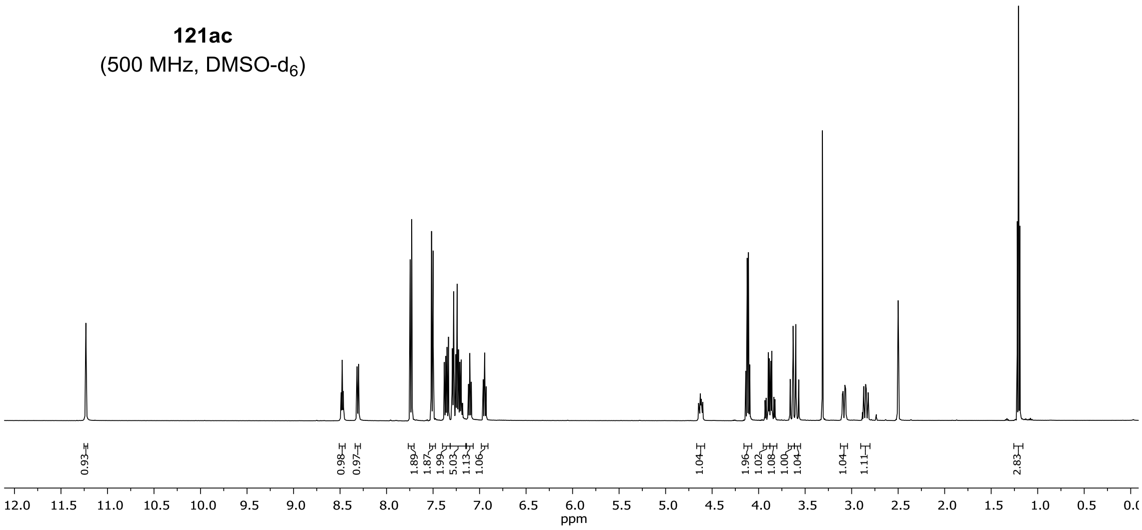


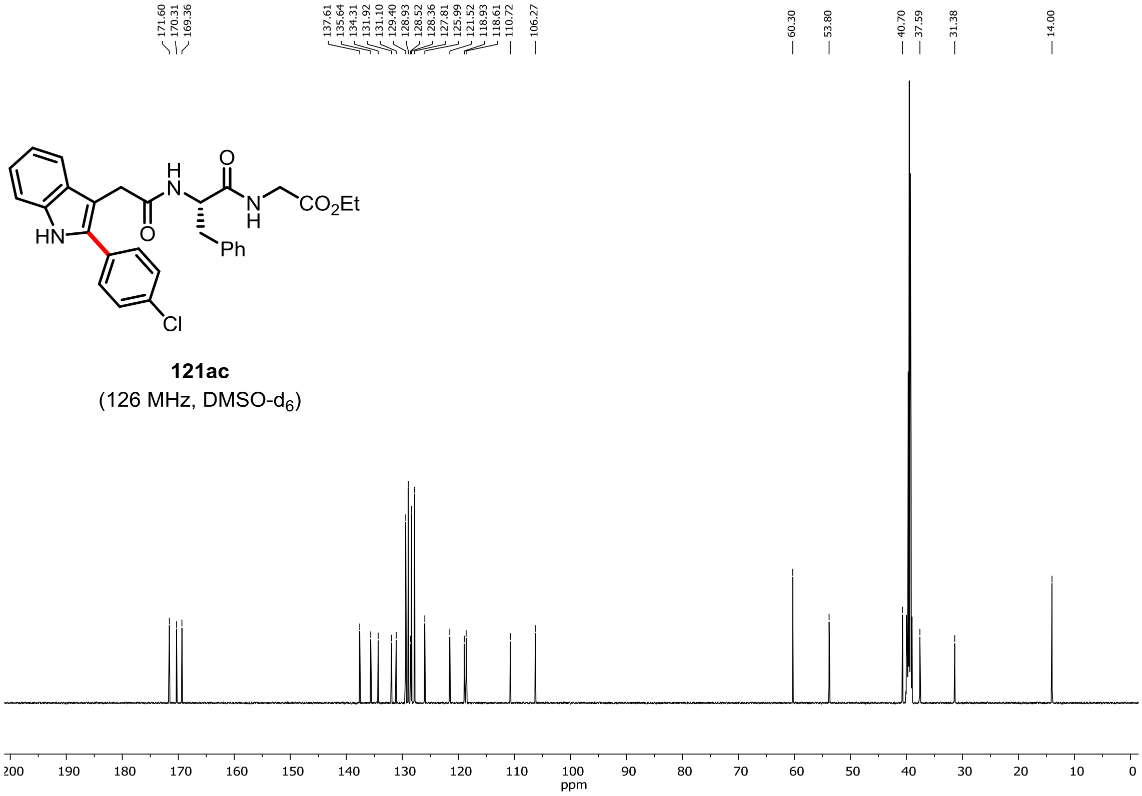
121ab
(283 MHz, DMSO-d_6)



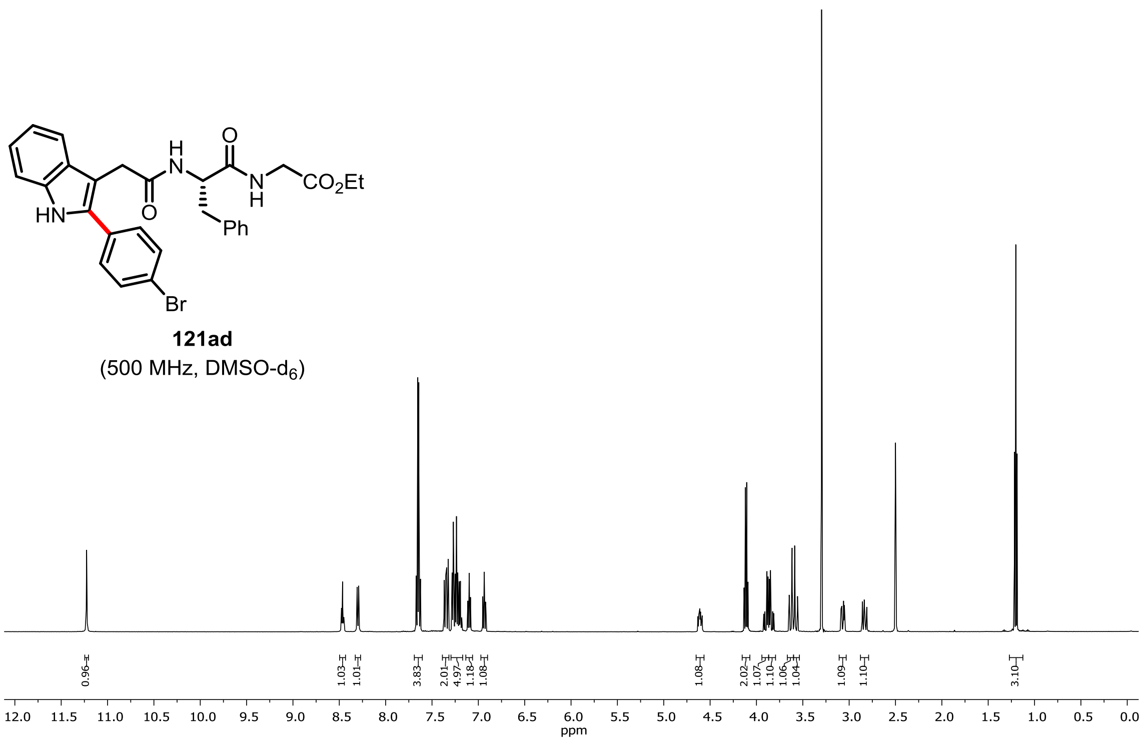


121ac
(500 MHz, DMSO-d_6)

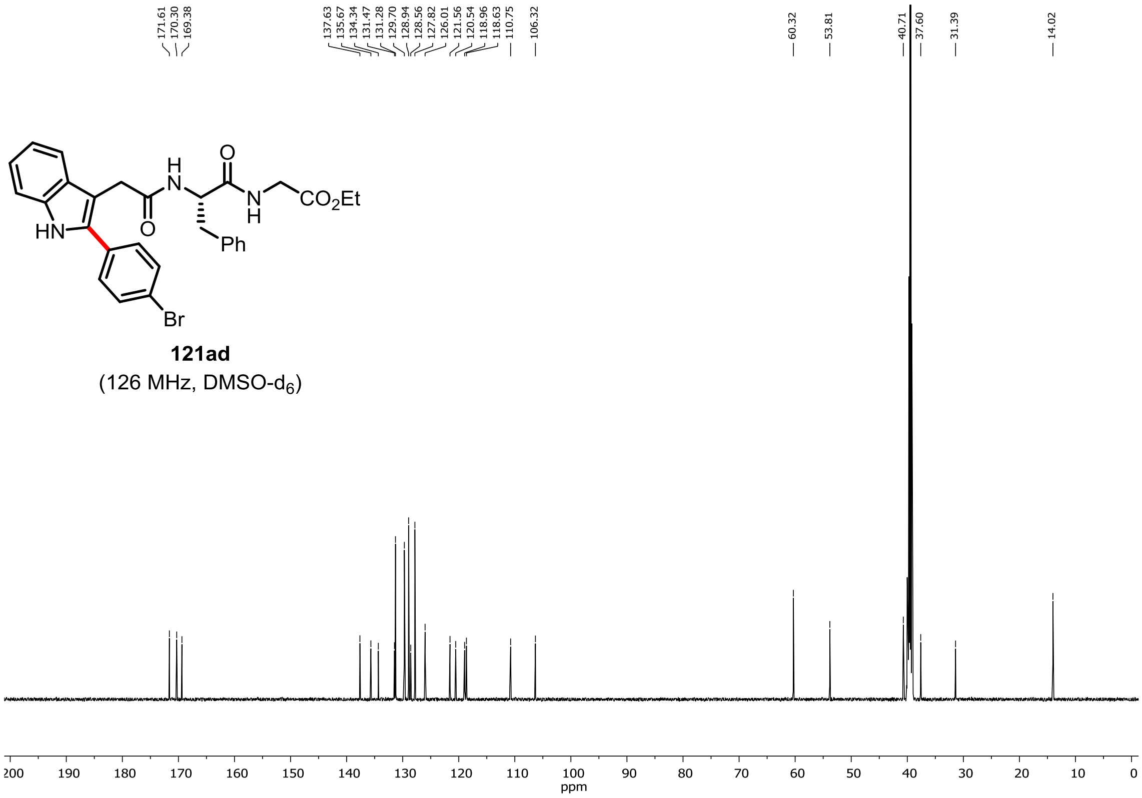




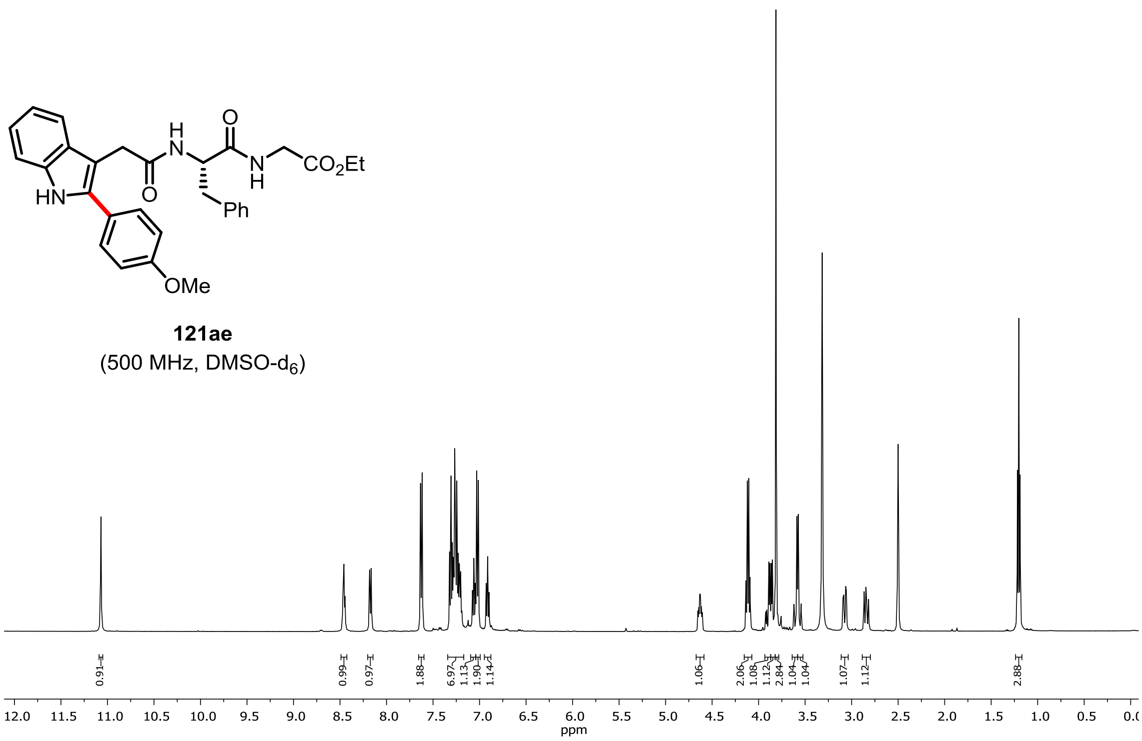
121ac
(126 MHz, DMSO-d_6)



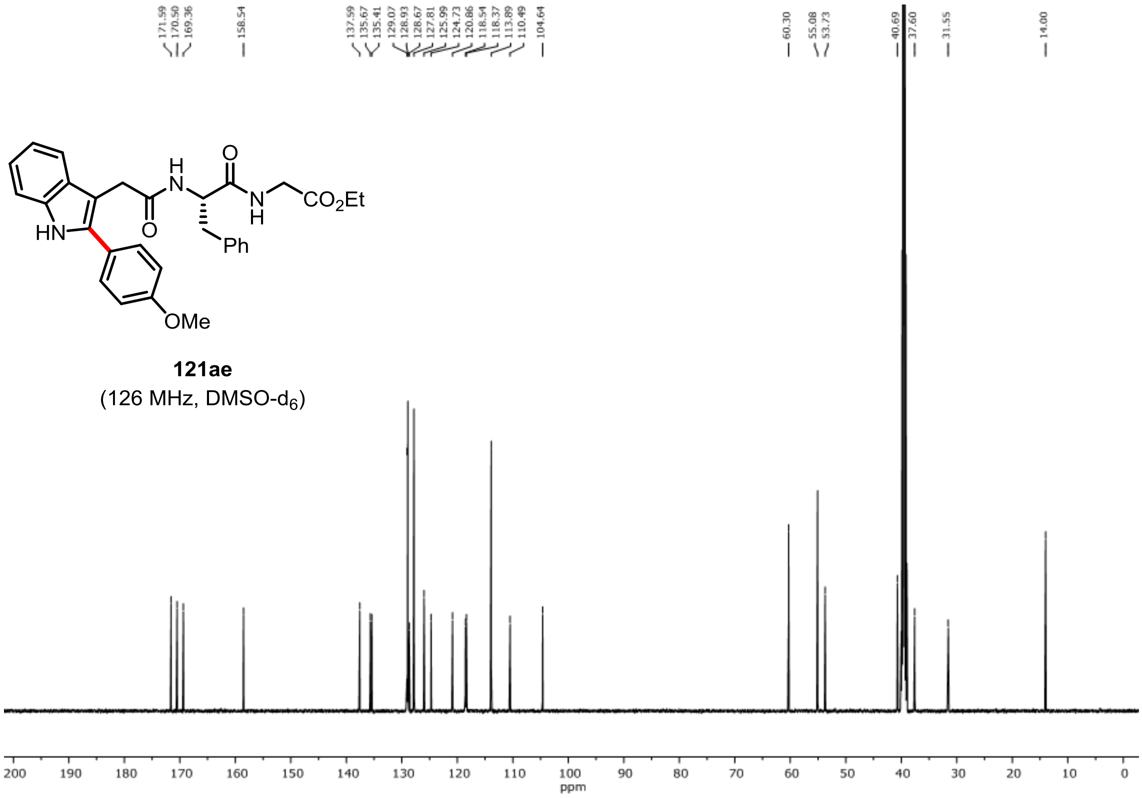
121ad
(500 MHz, DMSO-d_6)



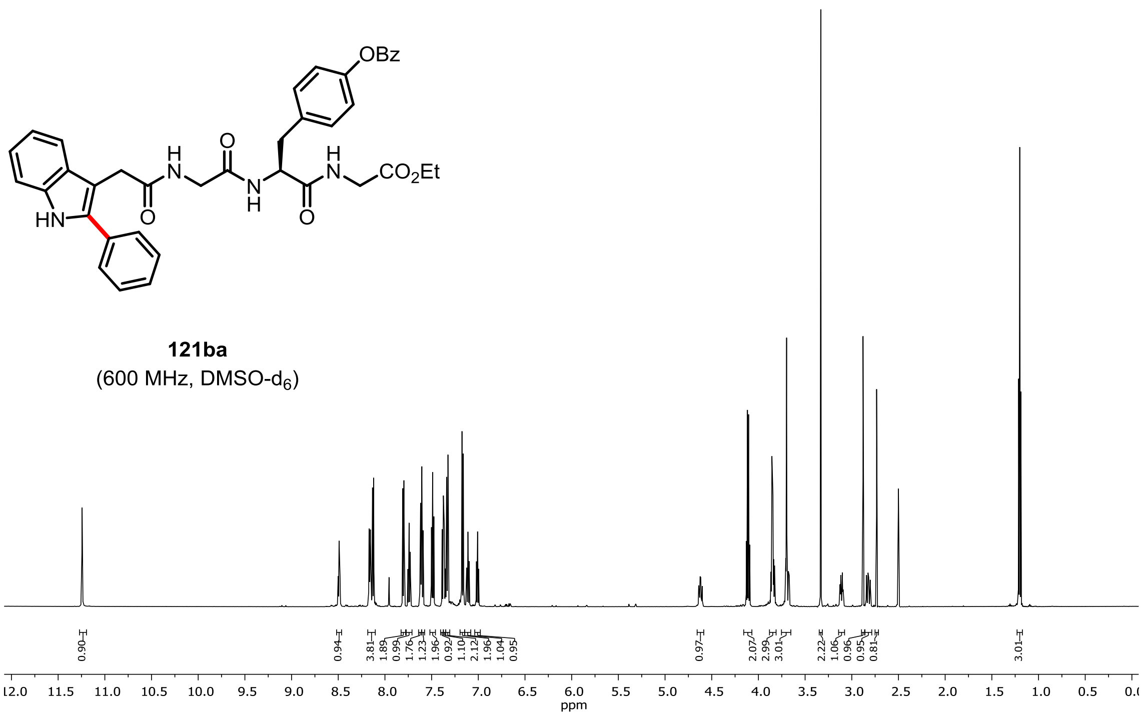
121ad
(126 MHz, DMSO-d_6)



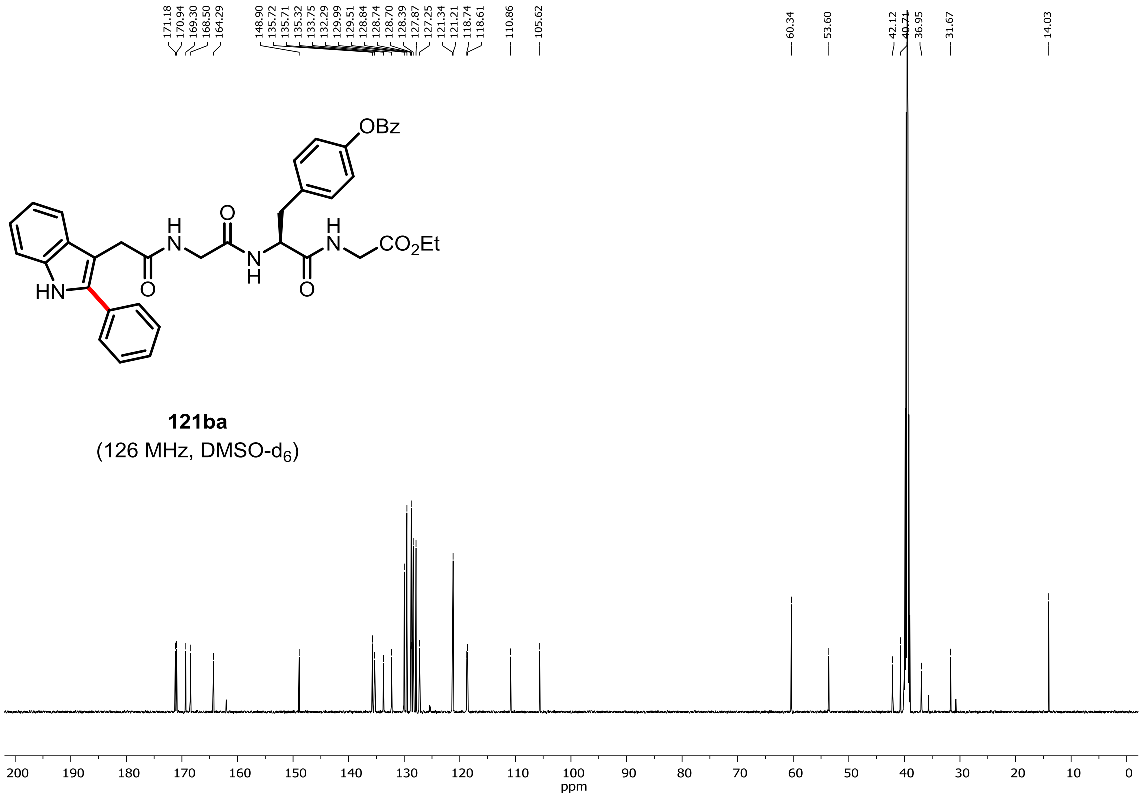
121ae
(500 MHz, DMSO-d_6)



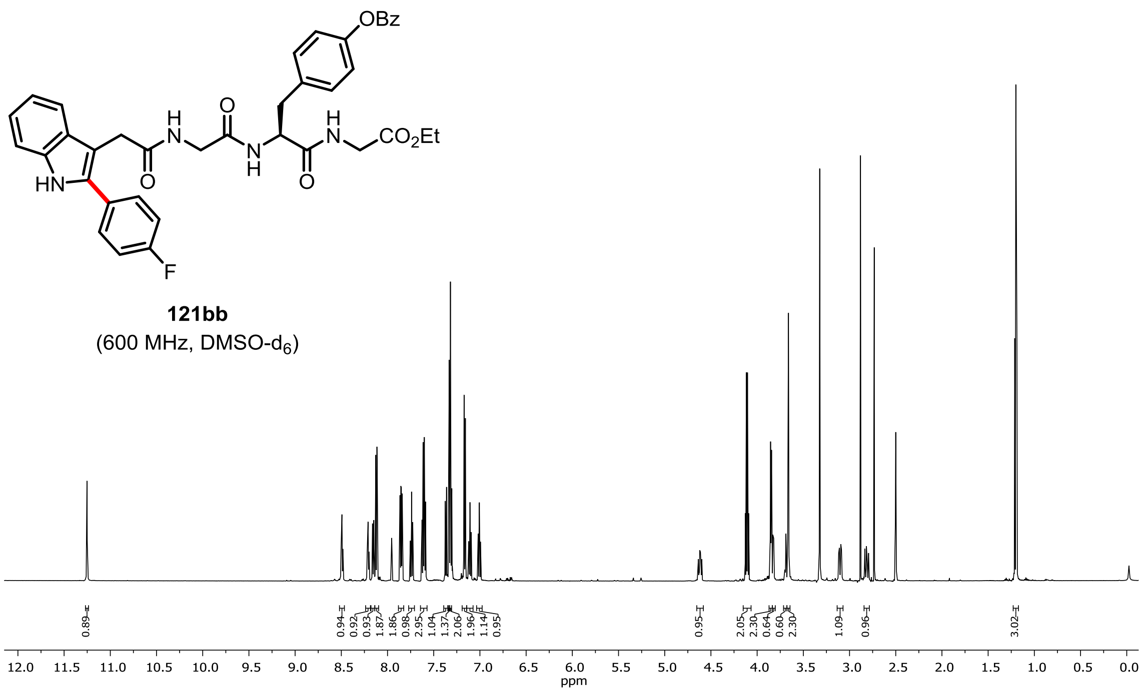
121ae
(126 MHz, DMSO-d_6)



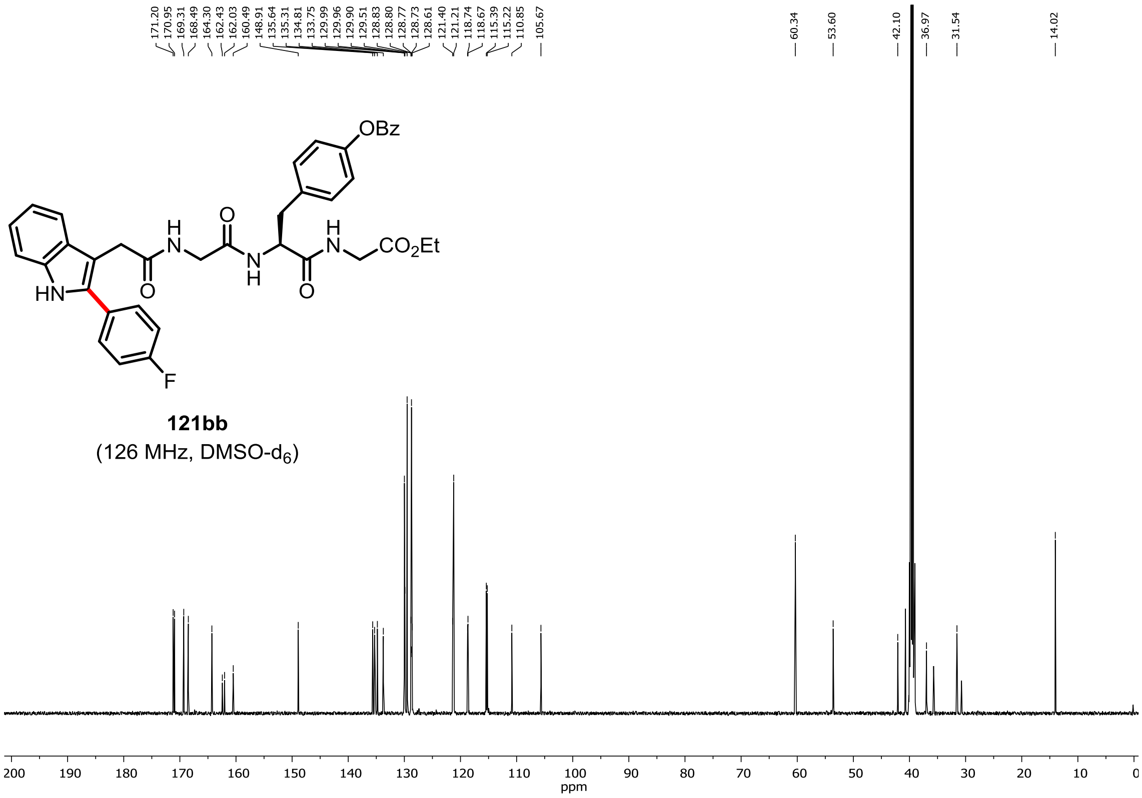
121ba
(600 MHz, DMSO-d_6)



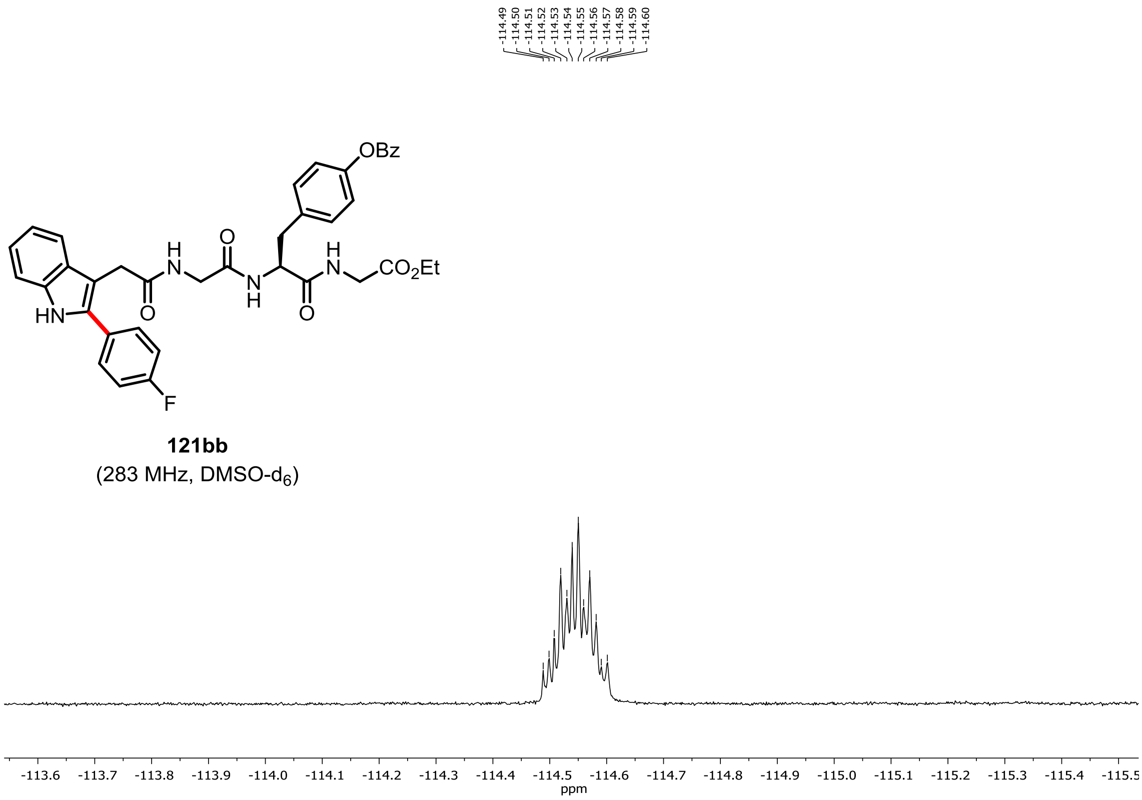
121ba
(126 MHz, DMSO-d_6)



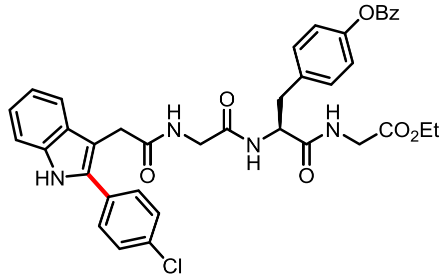
121bb
(600 MHz, DMSO-d_6)



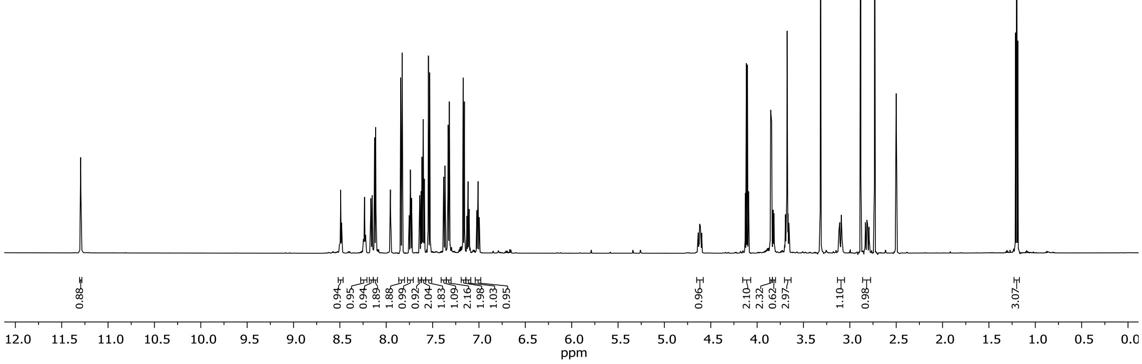
121bb
(126 MHz, DMSO-d$_6$)

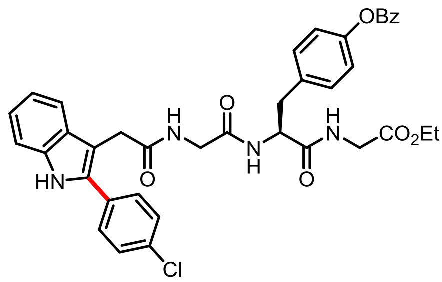


121bb
(283 MHz, DMSO-d$_6$)

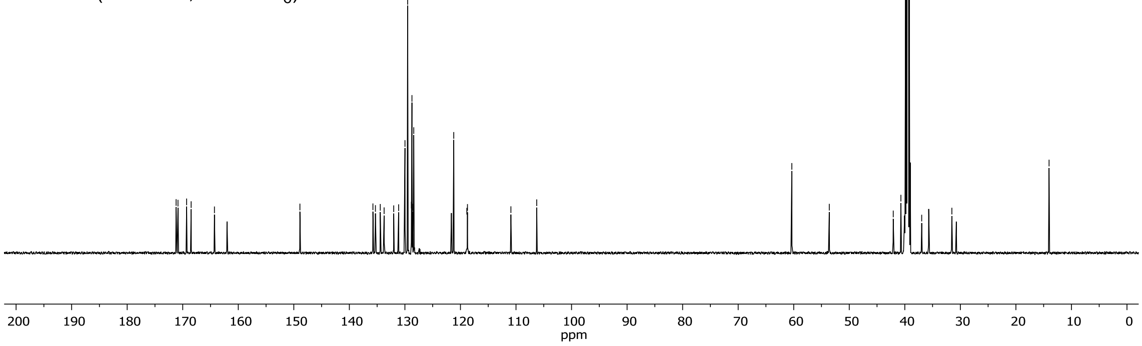


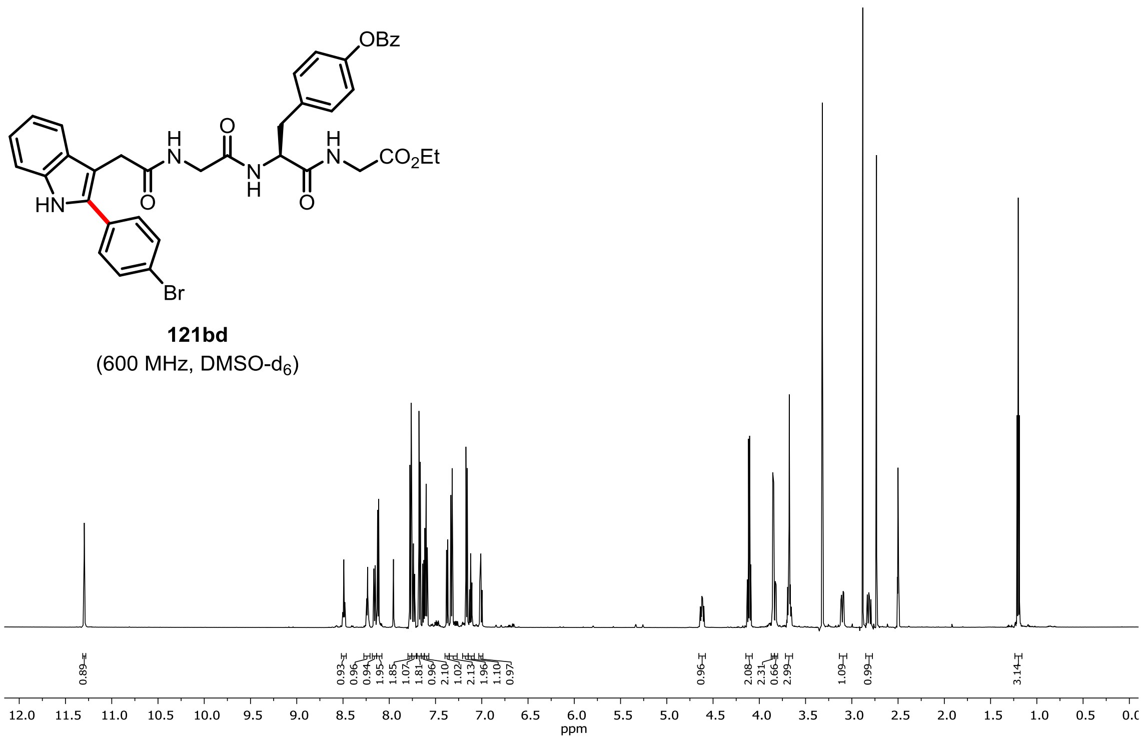
121bc
(600 MHz, DMSO-d_6)

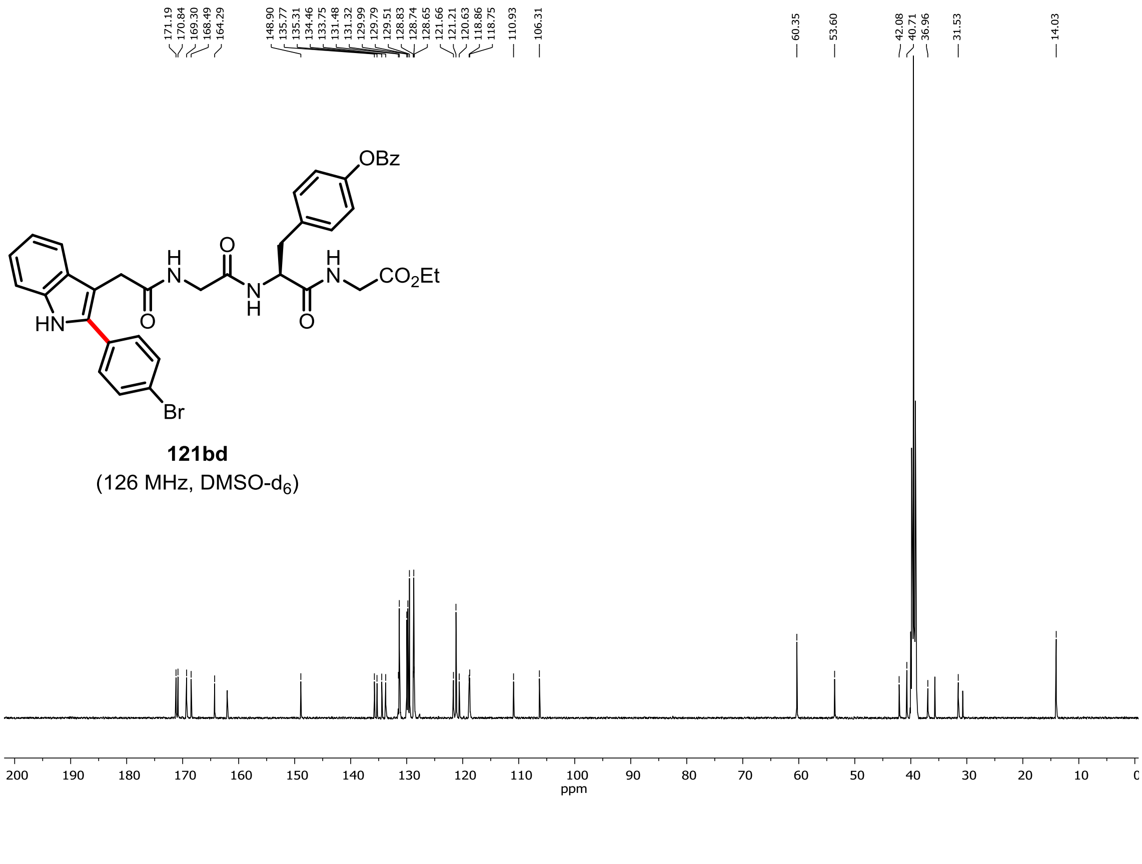


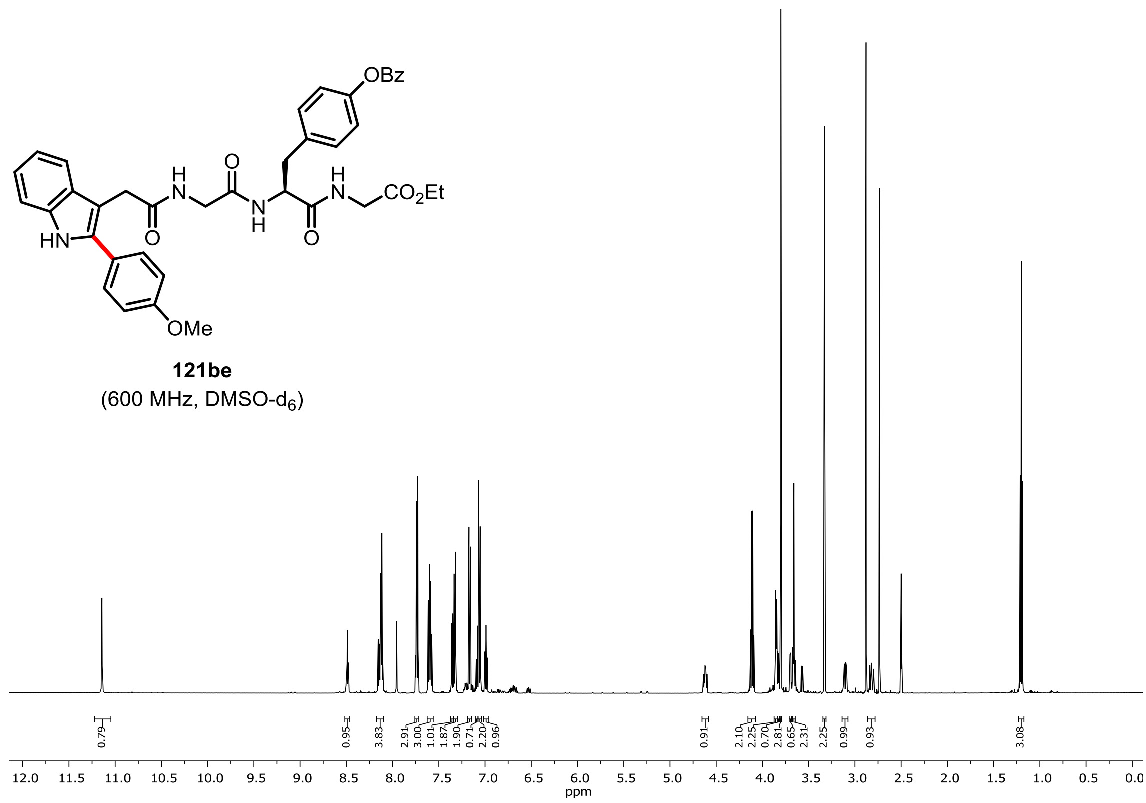


121bc
(126 MHz, DMSO-d_6)

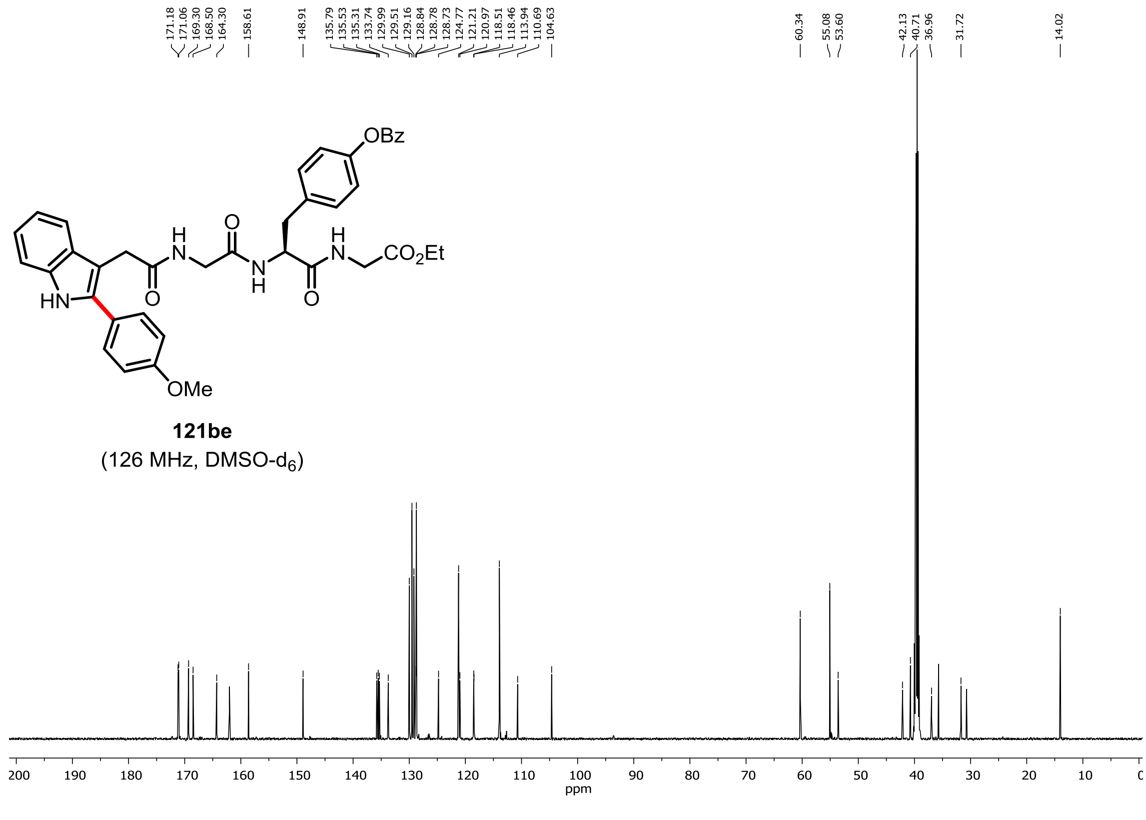



OBz
HN
Br
CO2Et
121bd
(600 MHz, DMSO-d6)
ppm

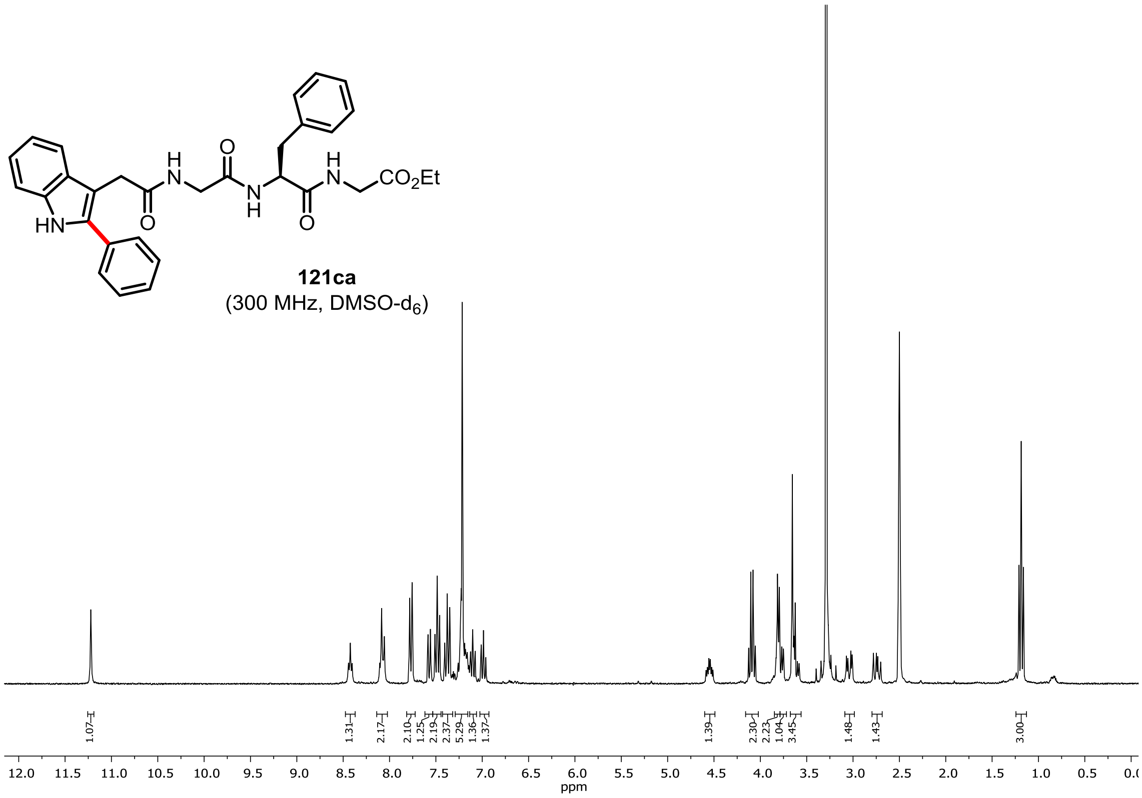

171.19
170.84
169.30
168.49
164.29
148.90
135.77
135.31
134.46
133.75
131.48
131.32
129.99
129.79
129.51
128.83
128.74
128.65
121.66
121.21
120.63
118.86
118.75
110.93
106.31
60.35
53.60
42.08
40.71
36.96
31.53
14.03
121bd
(126 MHz, DMSO-d6)
ppm



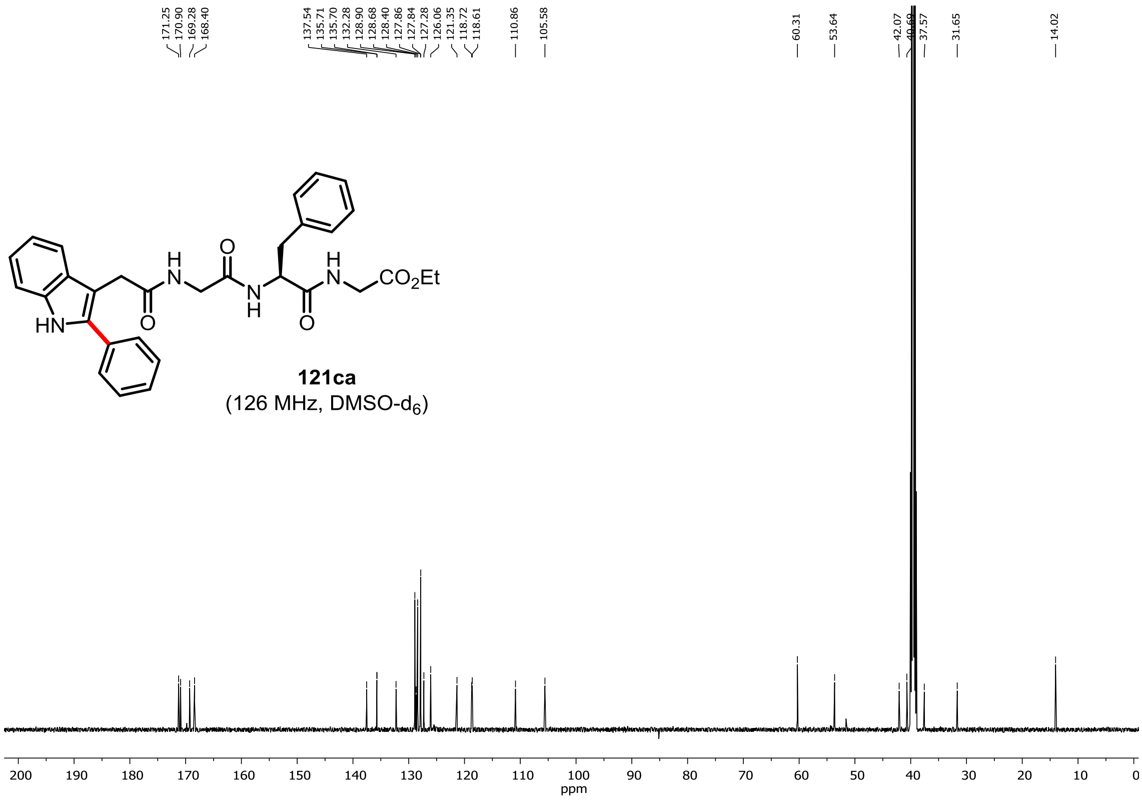
121be
(600 MHz, DMSO-d_6)



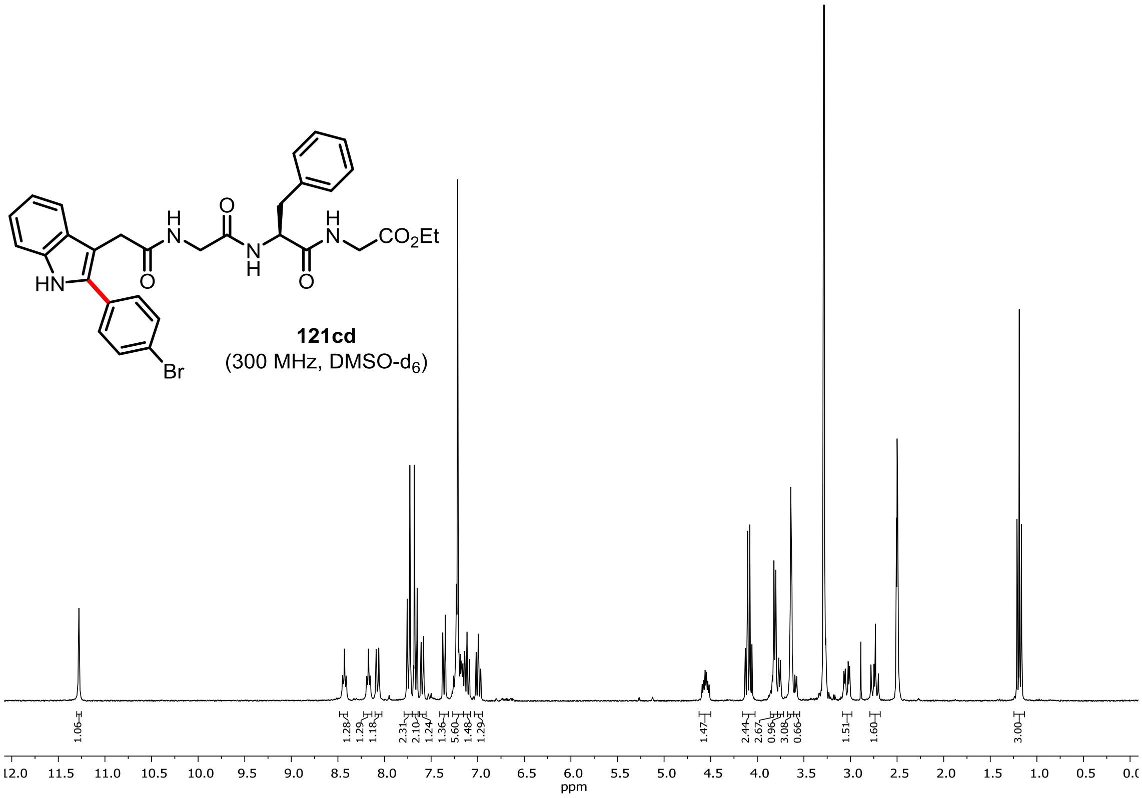
121be
(126 MHz, DMSO-d_6)



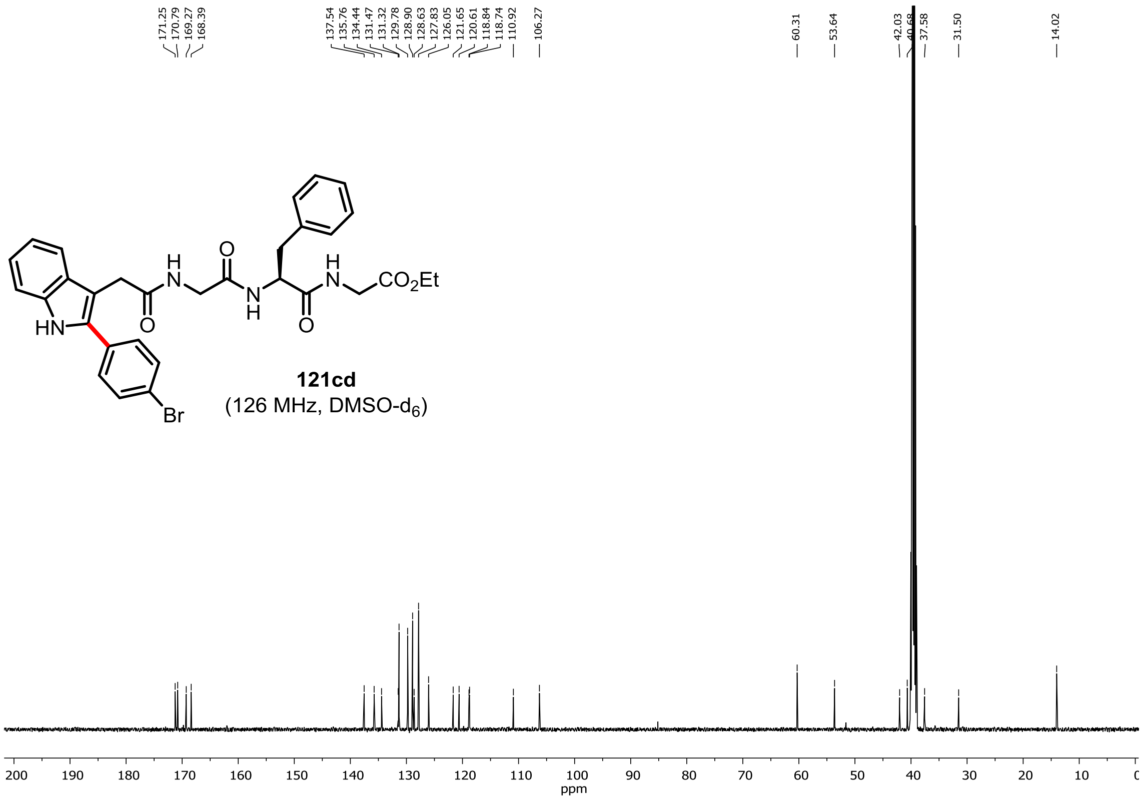
121ca
(300 MHz, DMSO-d_6)



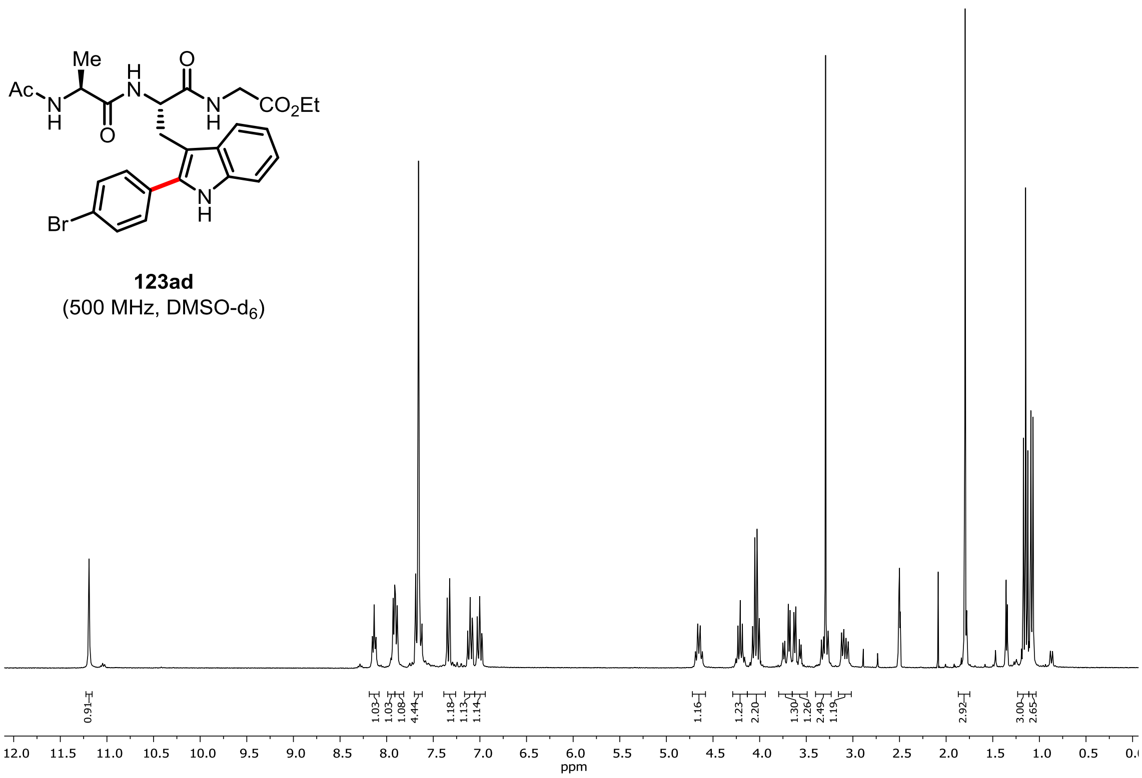
121ca
(126 MHz, DMSO-d_6)



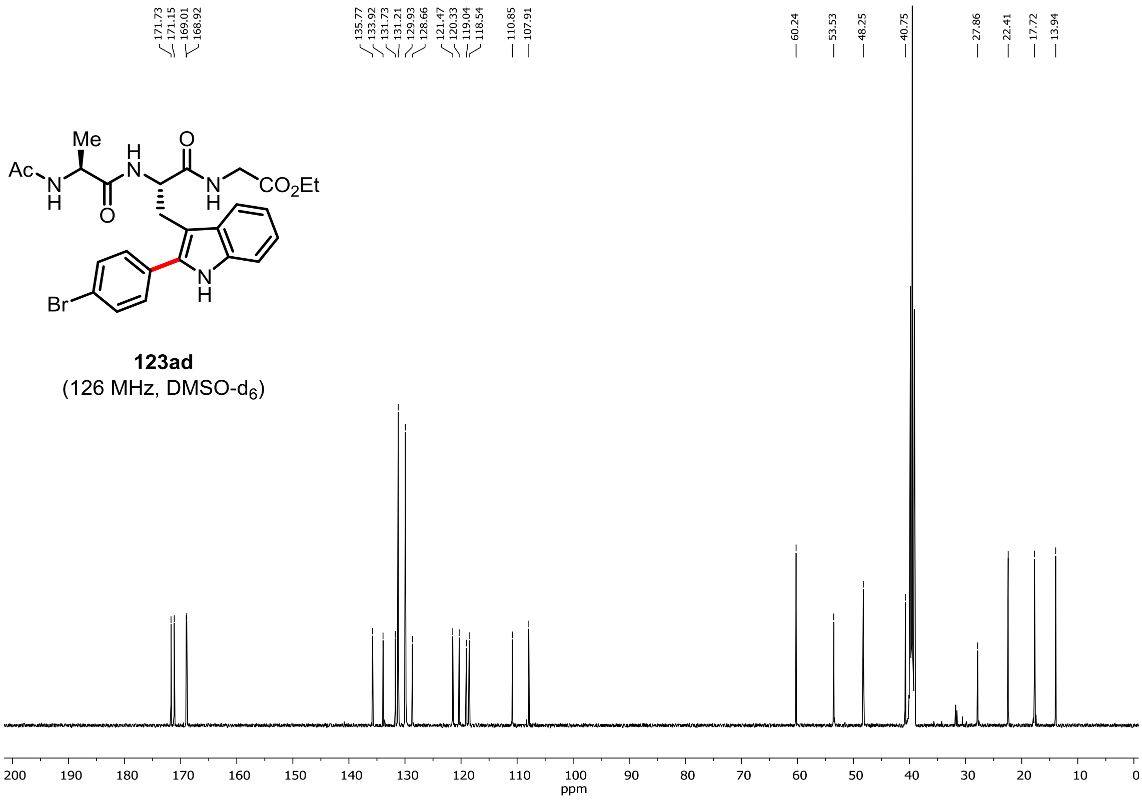
121cd
(300 MHz, DMSO-d$_6$)



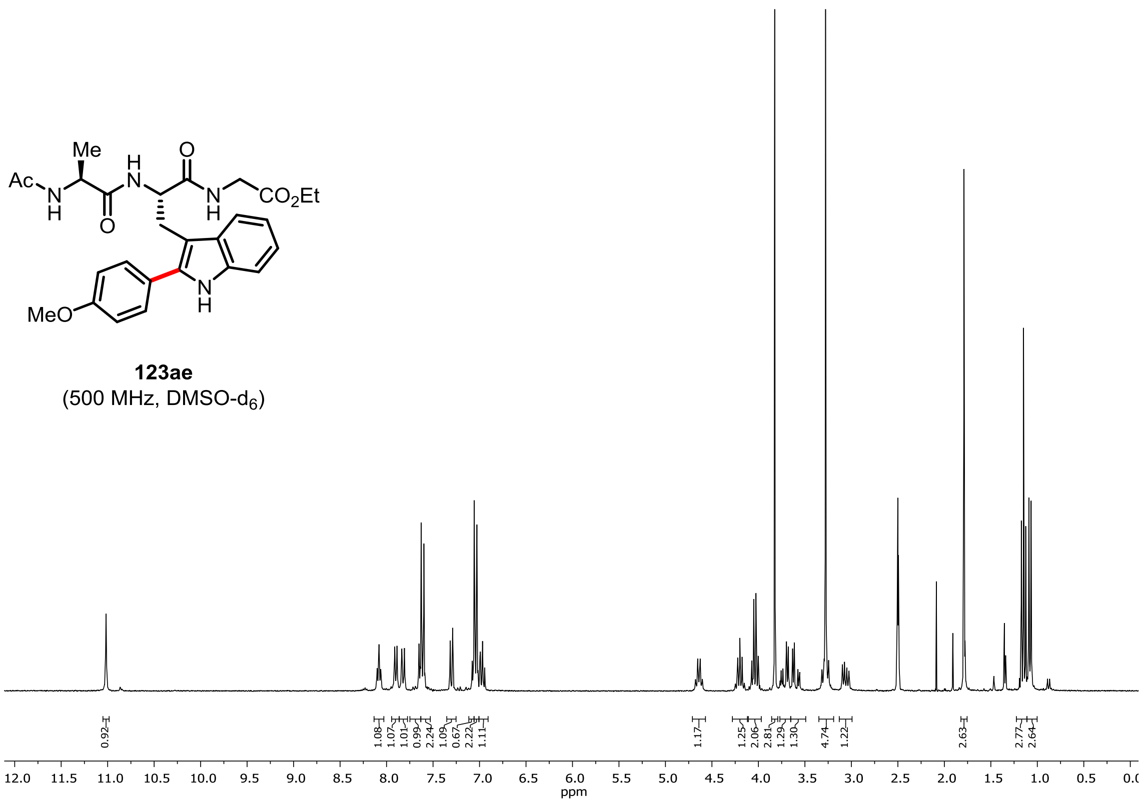
121cd
(126 MHz, DMSO-d$_6$)



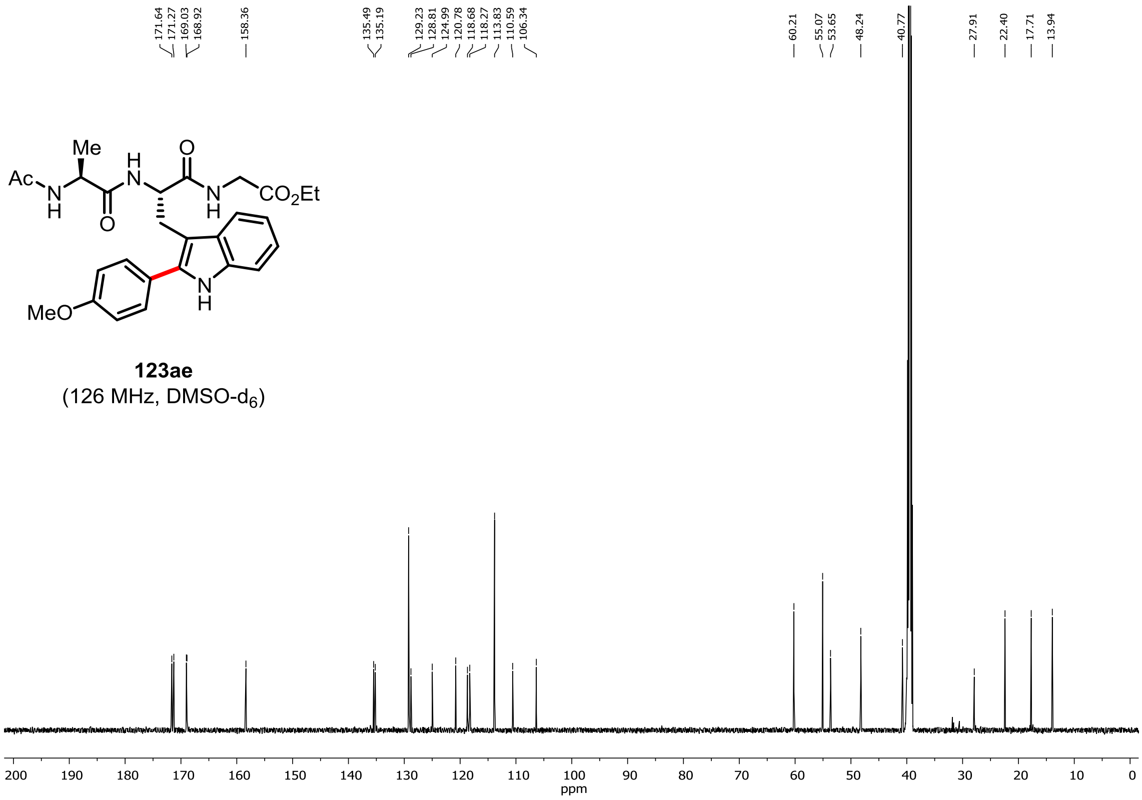
123ad
(500 MHz, DMSO-d_6)



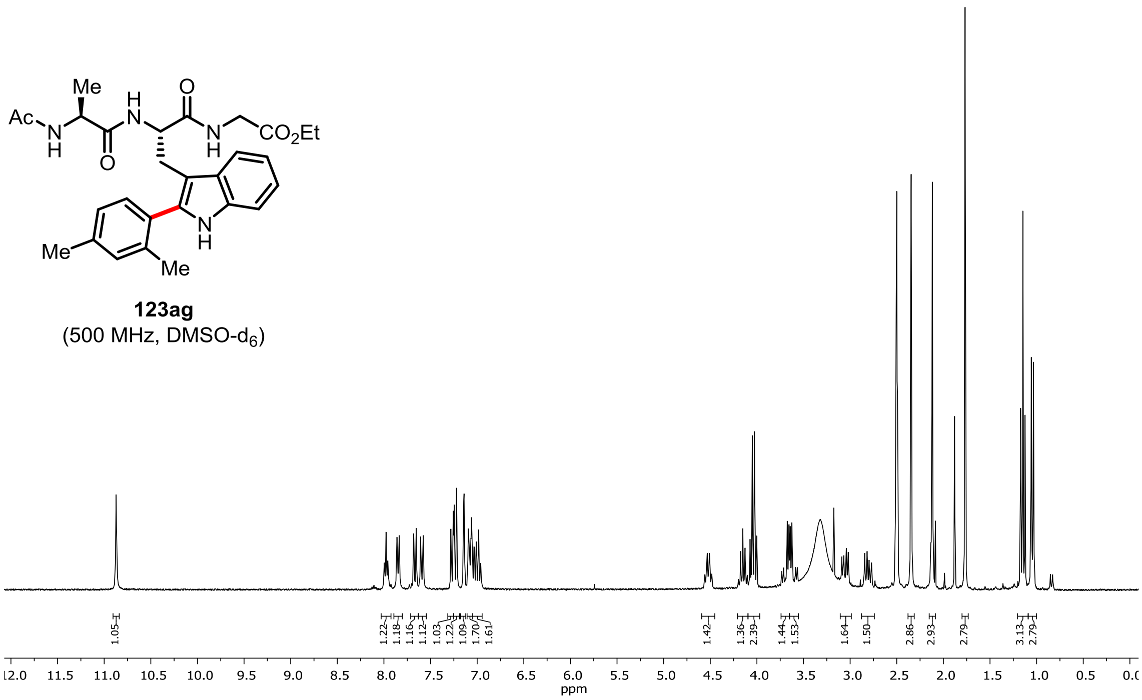
123ad
(126 MHz, DMSO-d_6)



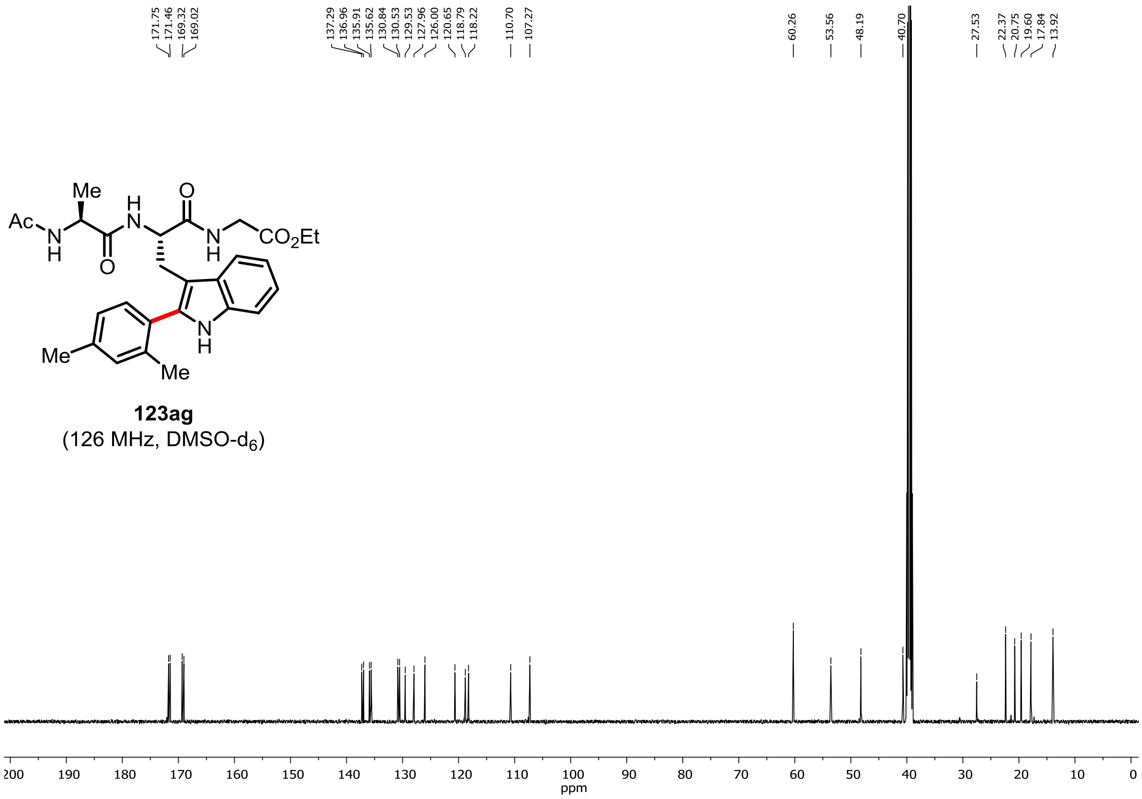
123ae
(500 MHz, DMSO-d_6)



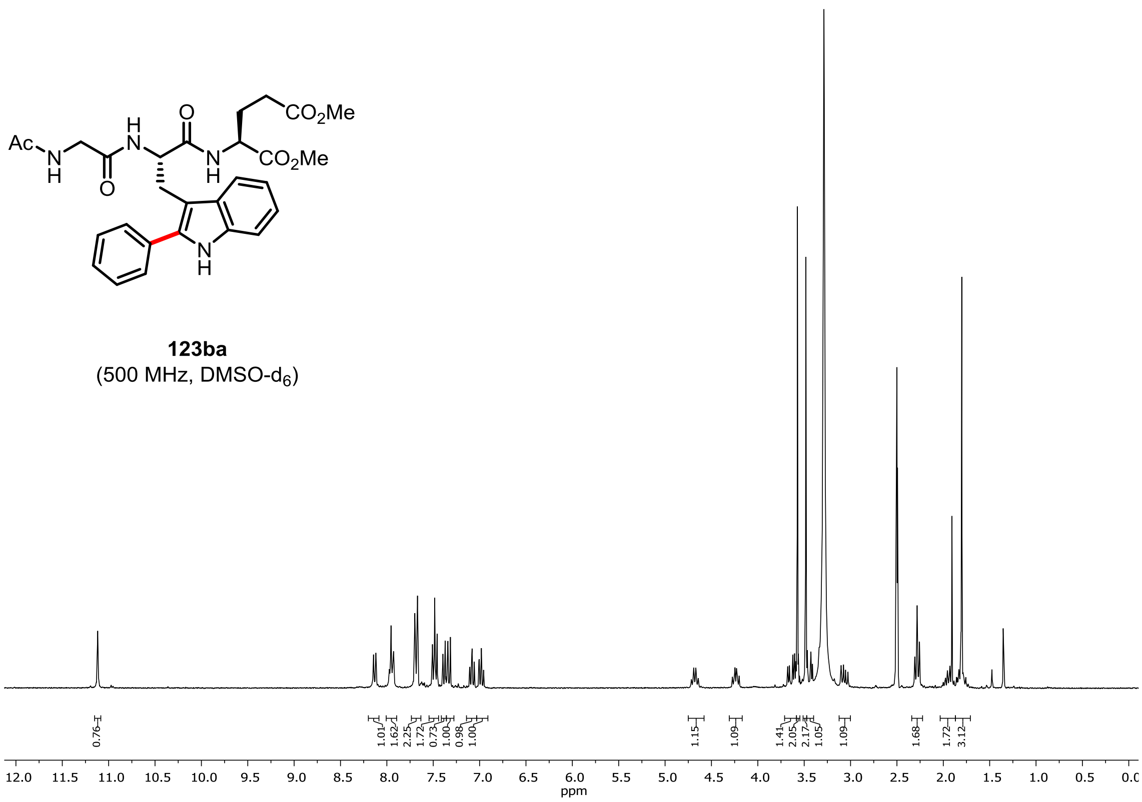
123ae
(126 MHz, DMSO-d_6)



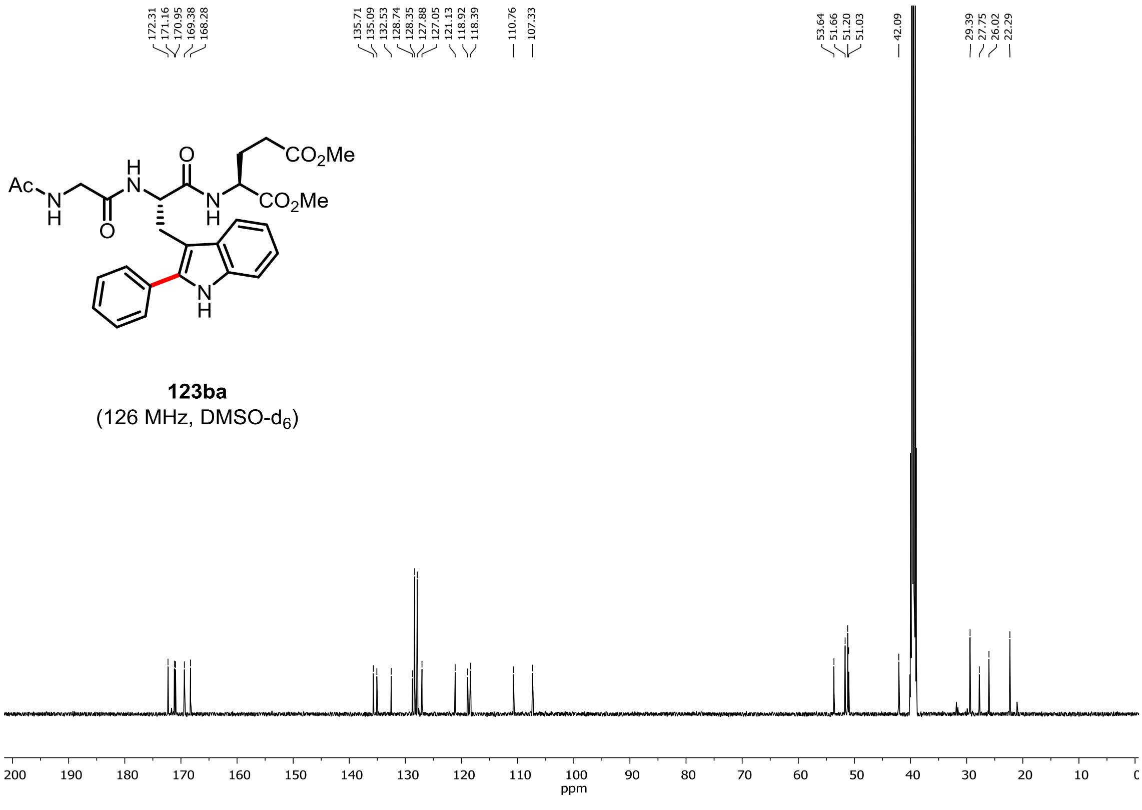
123ag
(500 MHz, DMSO-d$_6$)



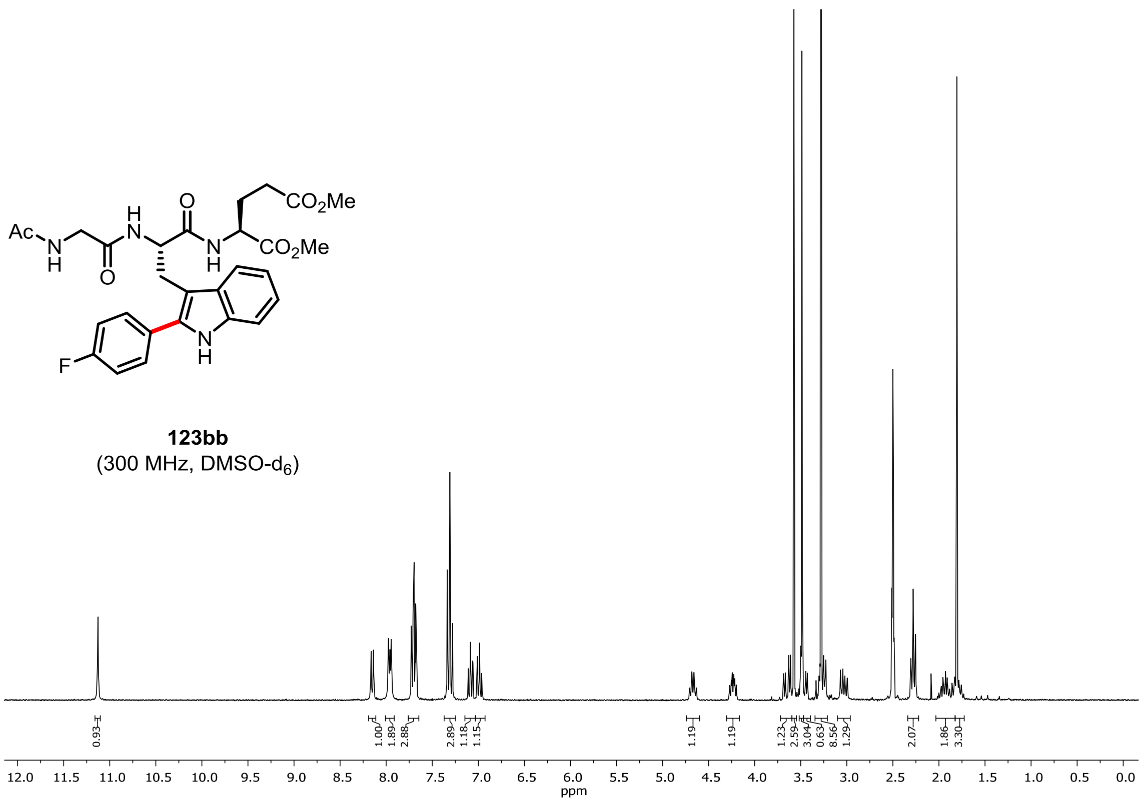
123ag
(126 MHz, DMSO-d$_6$)



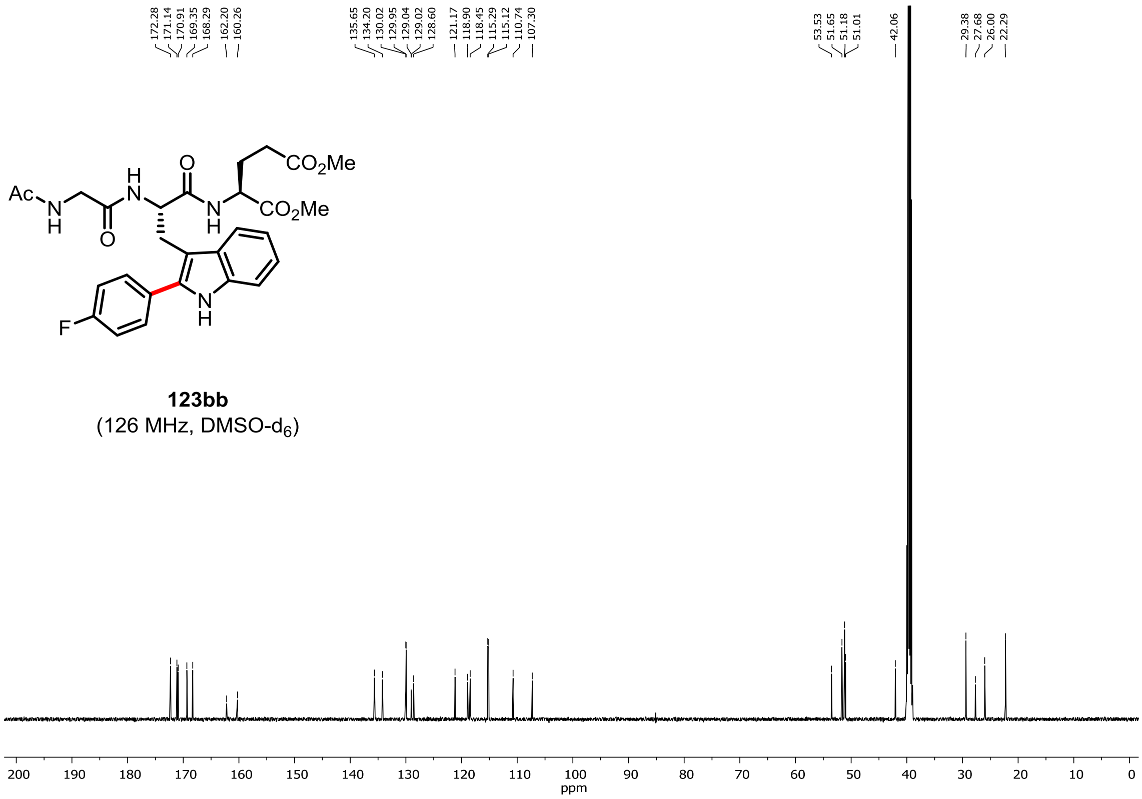
123ba
(500 MHz, DMSO-d_6)



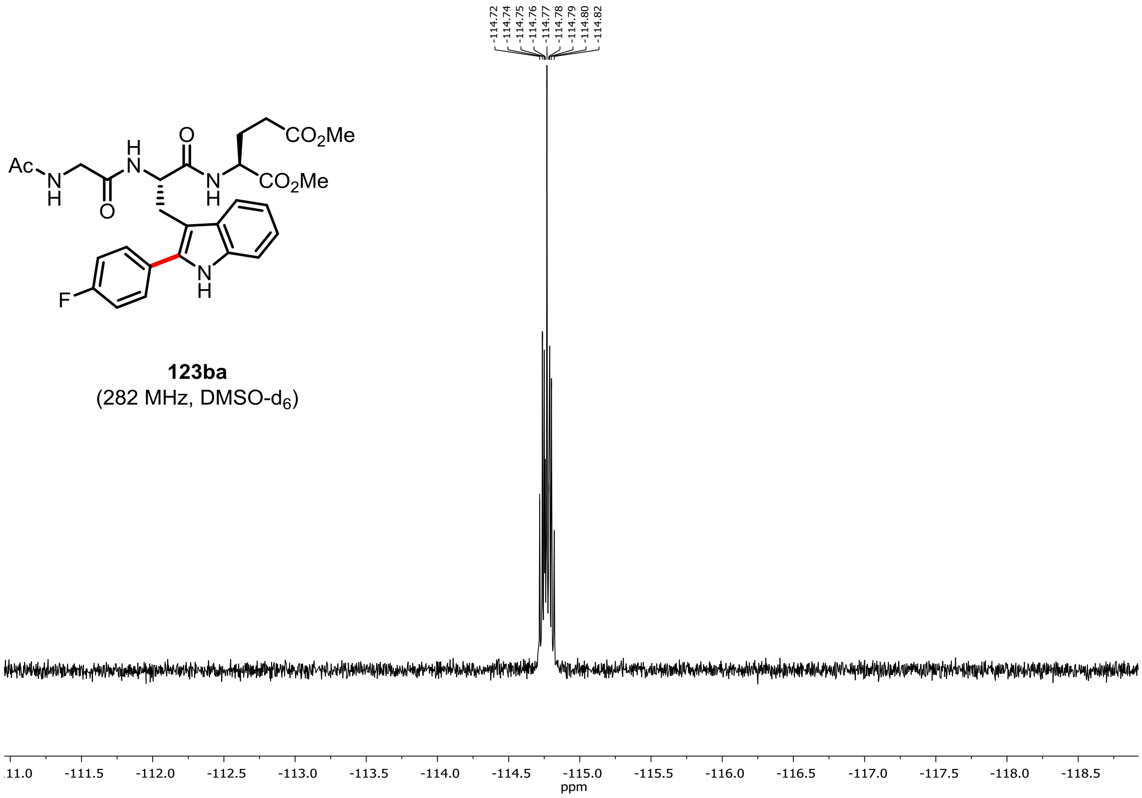
123ba
(126 MHz, DMSO-d_6)



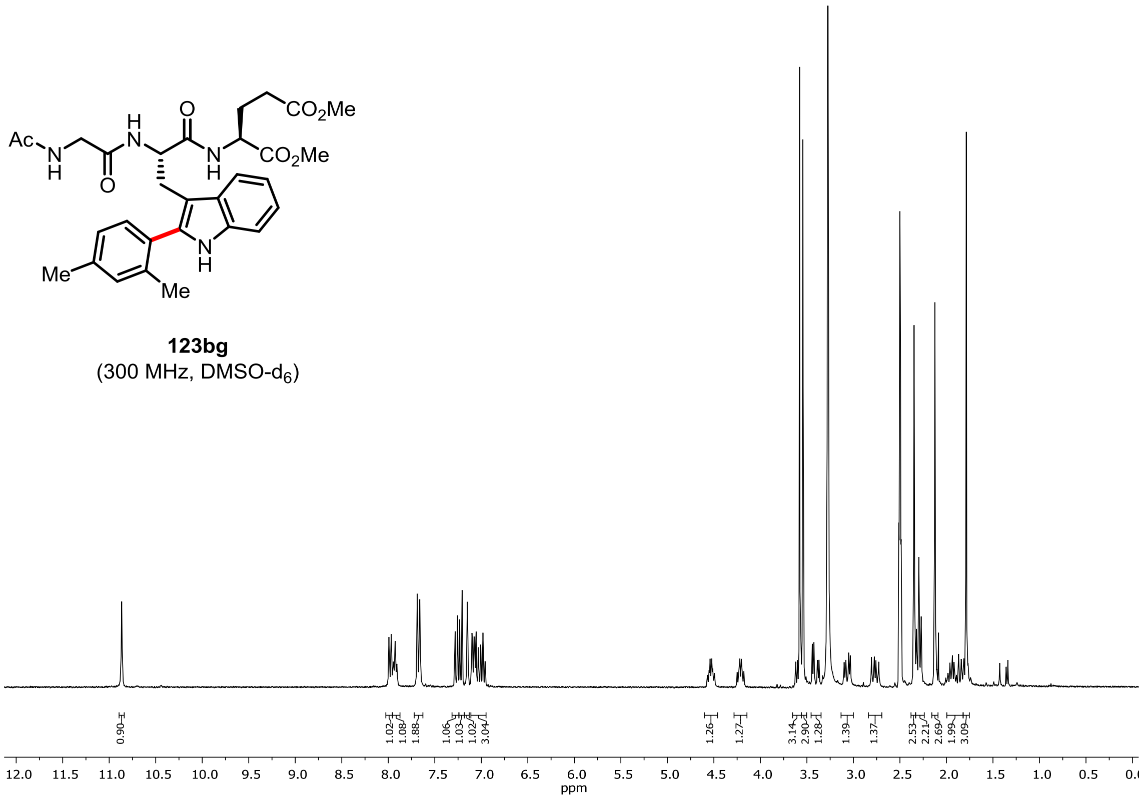
123bb
(300 MHz, DMSO-d_6)



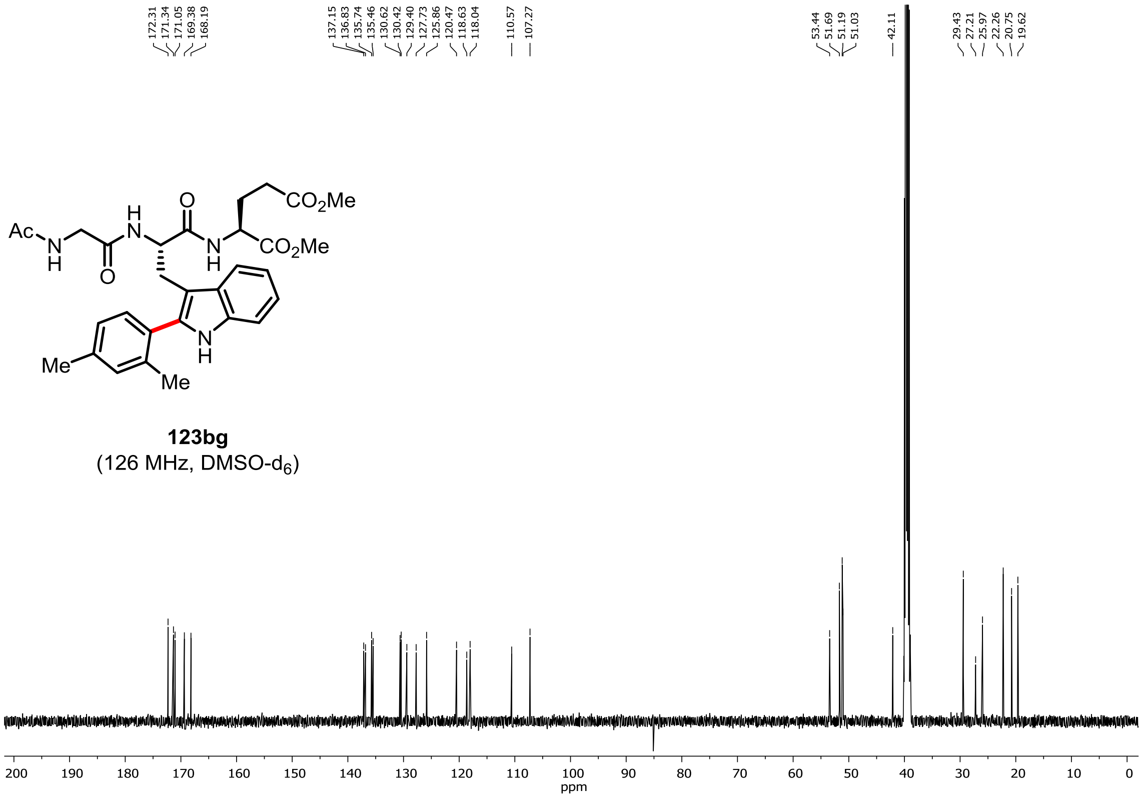
123bb
(126 MHz, DMSO-d_6)



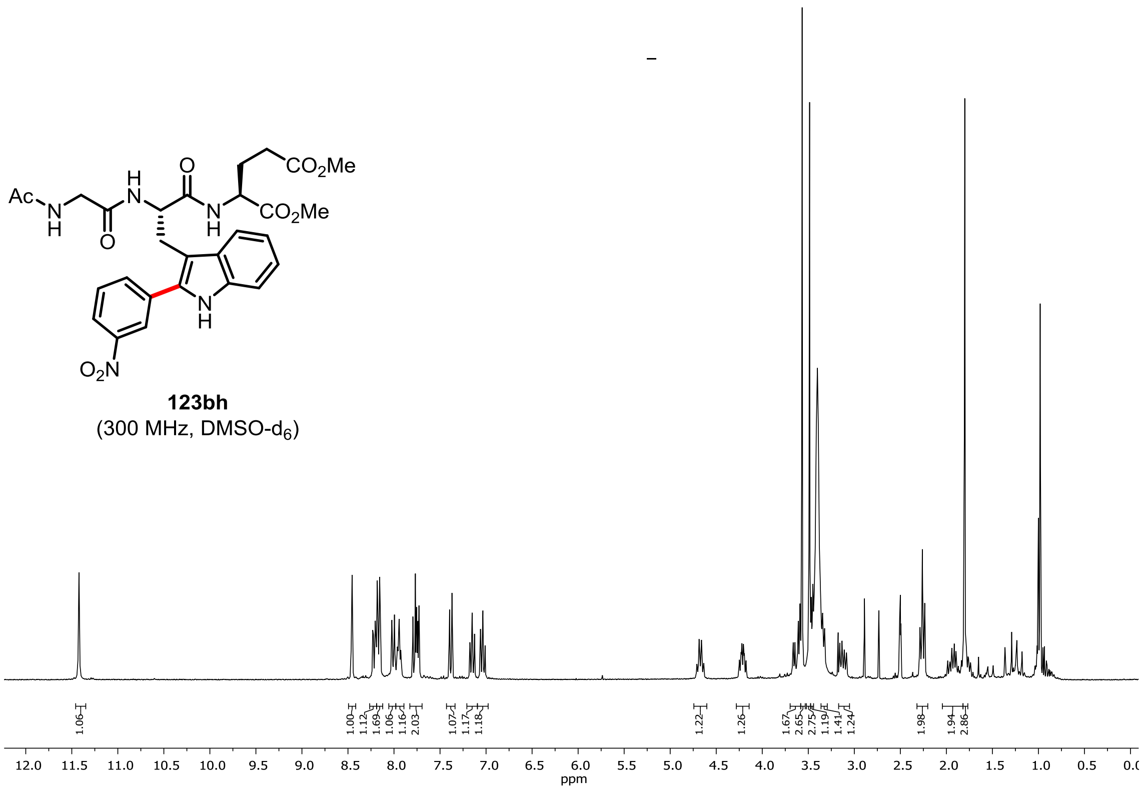
123ba
(282 MHz, DMSO-d_6)



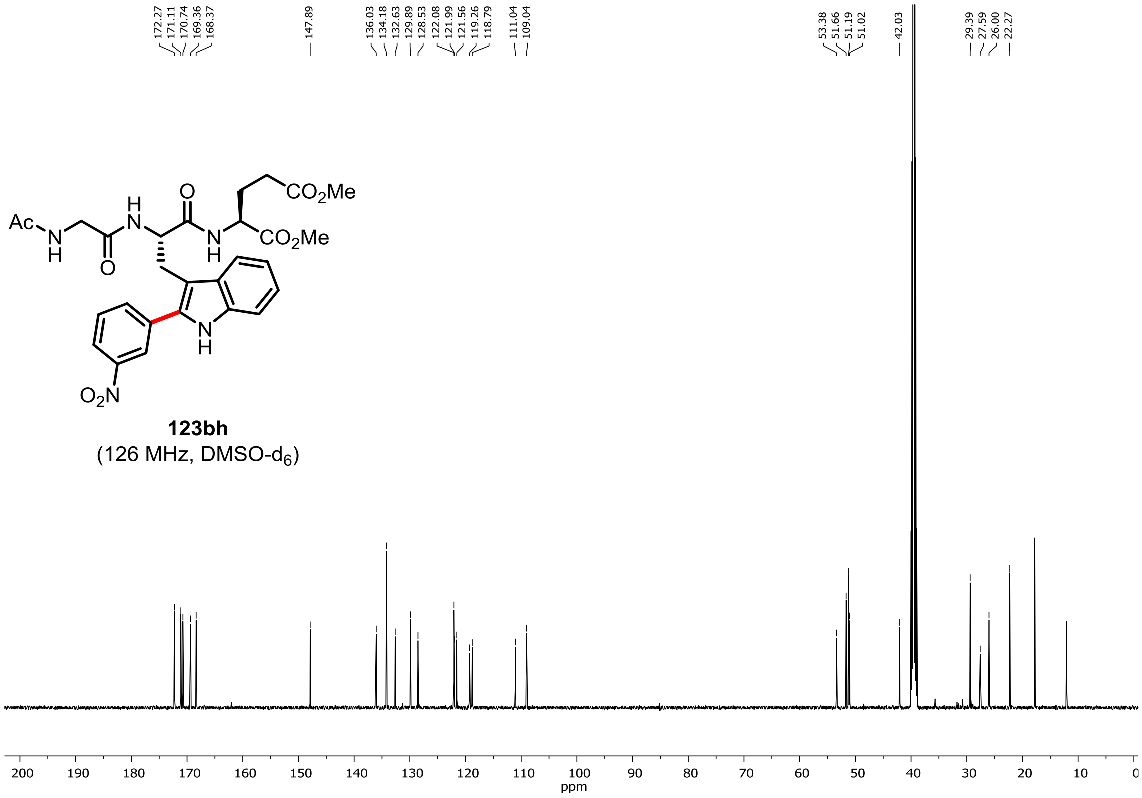
123bg
(300 MHz, DMSO-d_6)



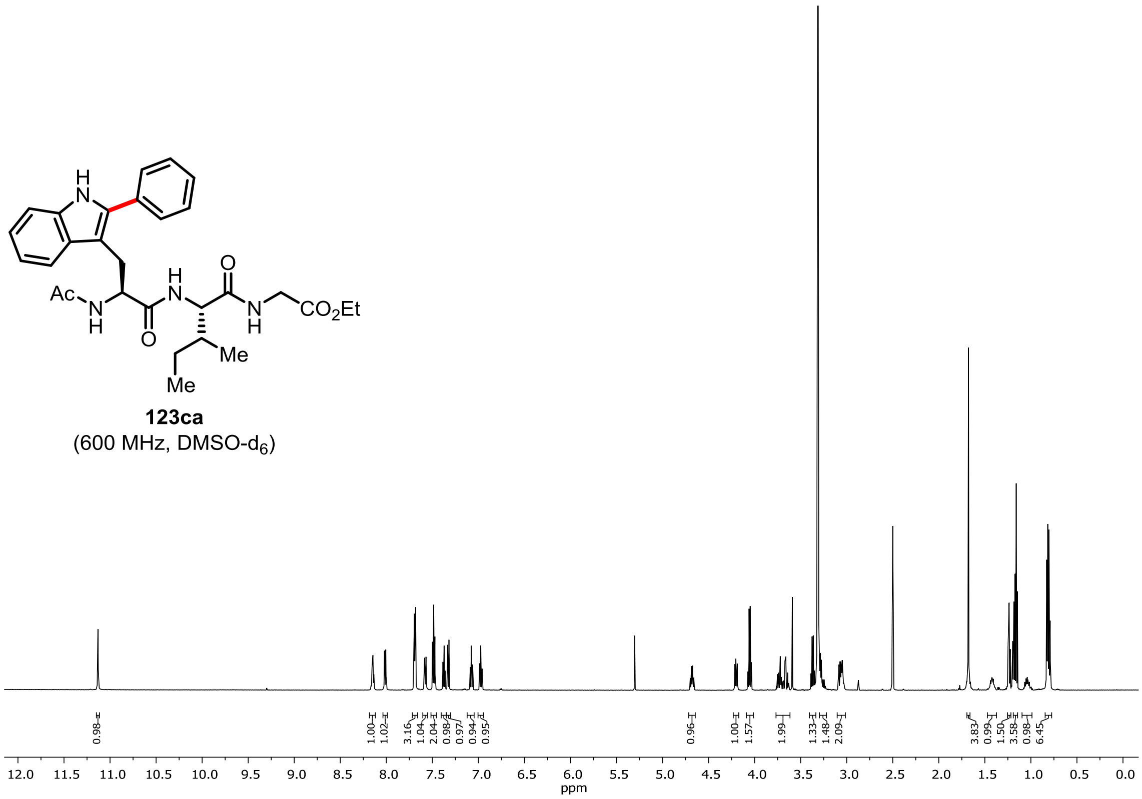
123bg
(126 MHz, DMSO-d_6)



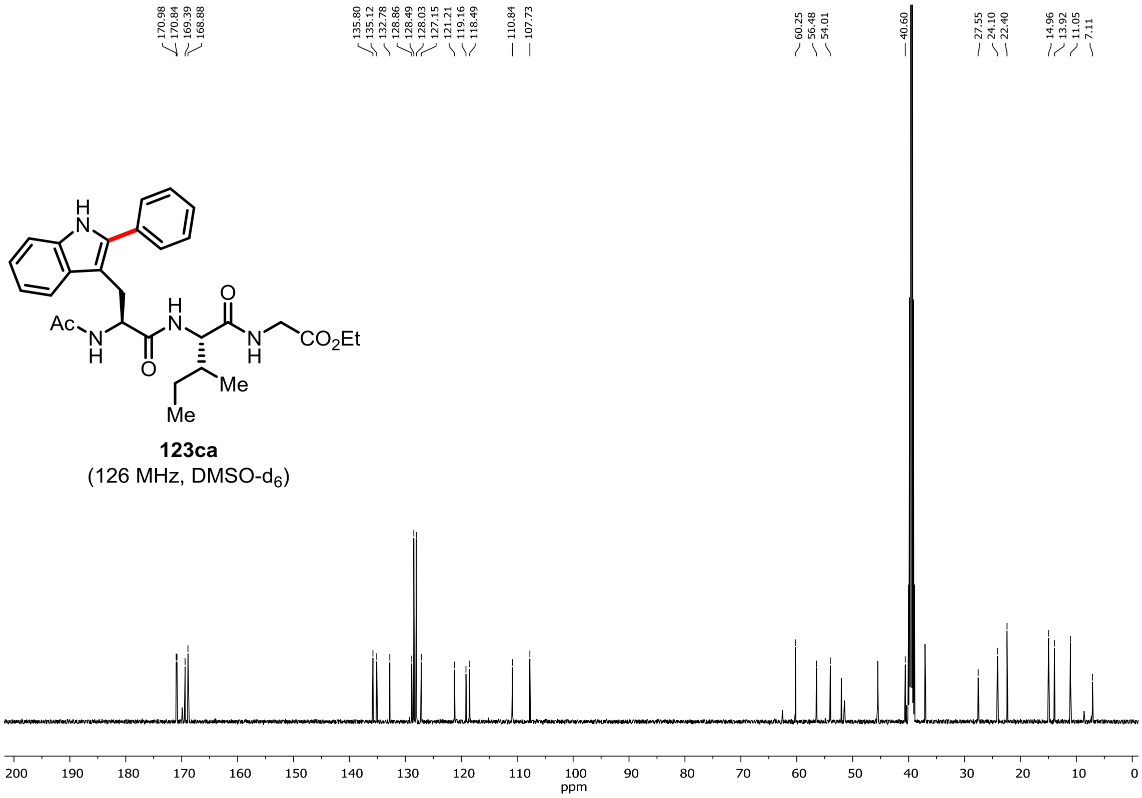
123bh
(300 MHz, DMSO-d_6)



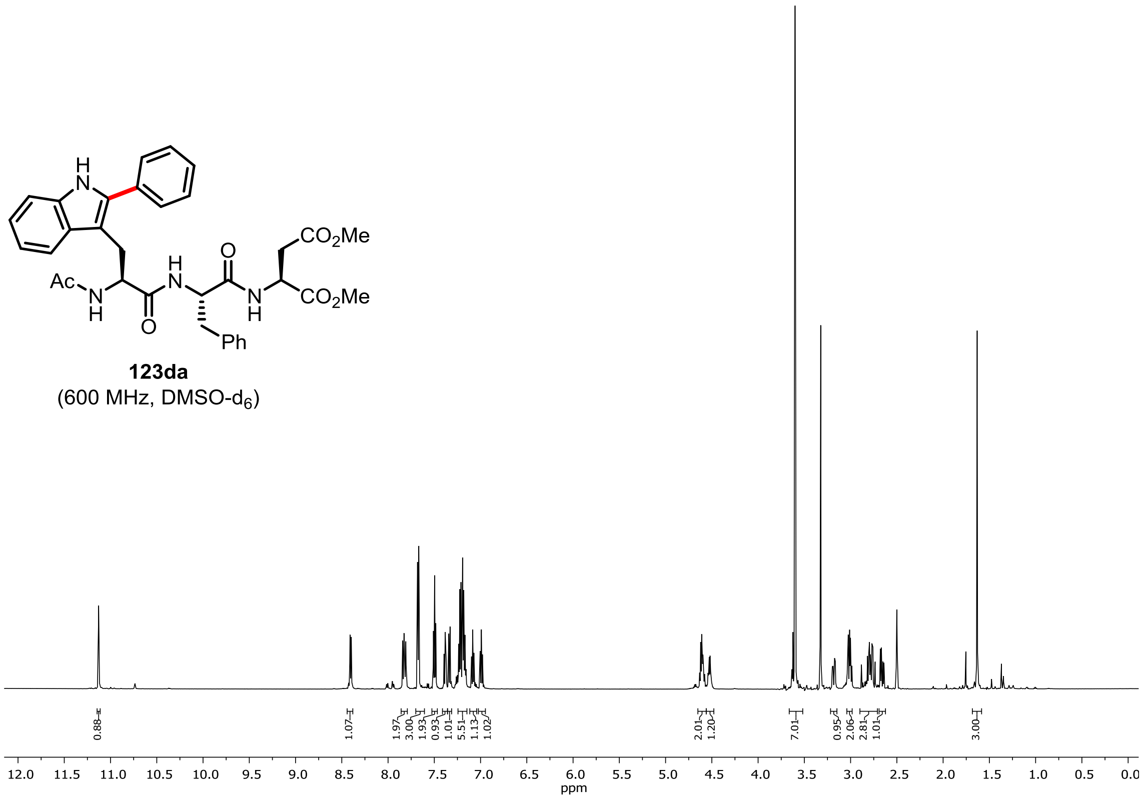
123bh
(126 MHz, DMSO-d_6)



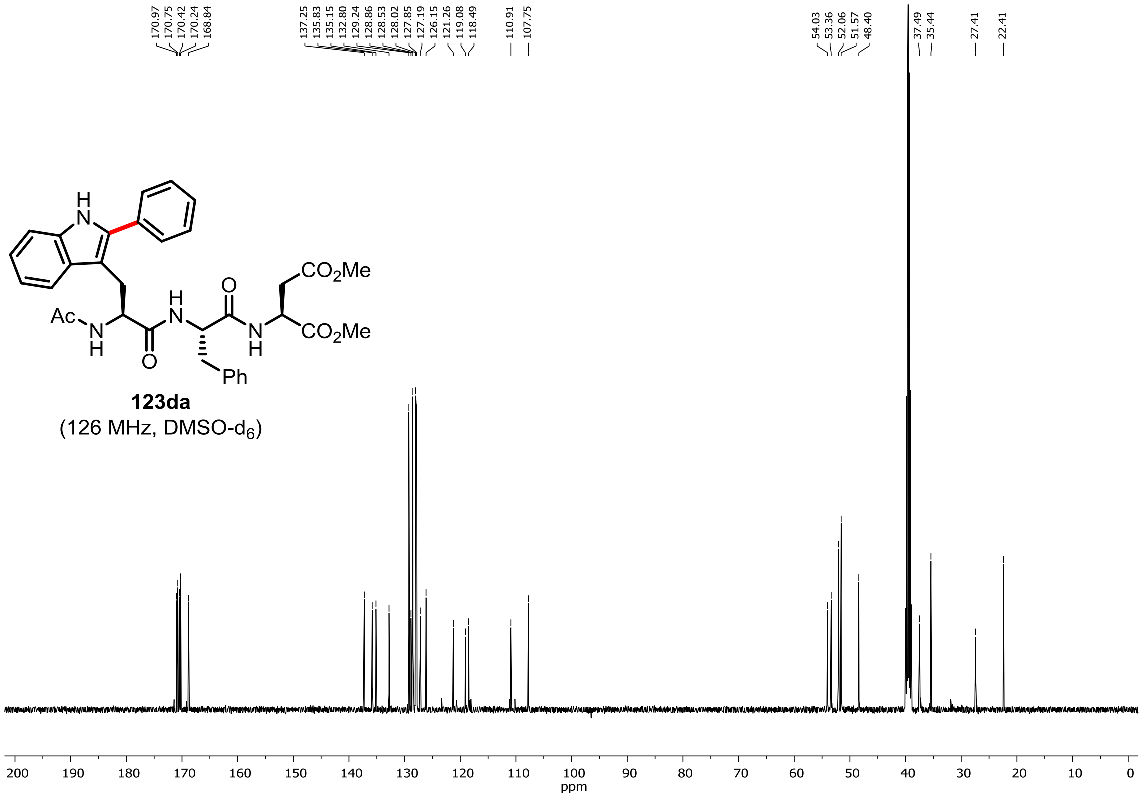
123ca
(600 MHz, DMSO-d_6)

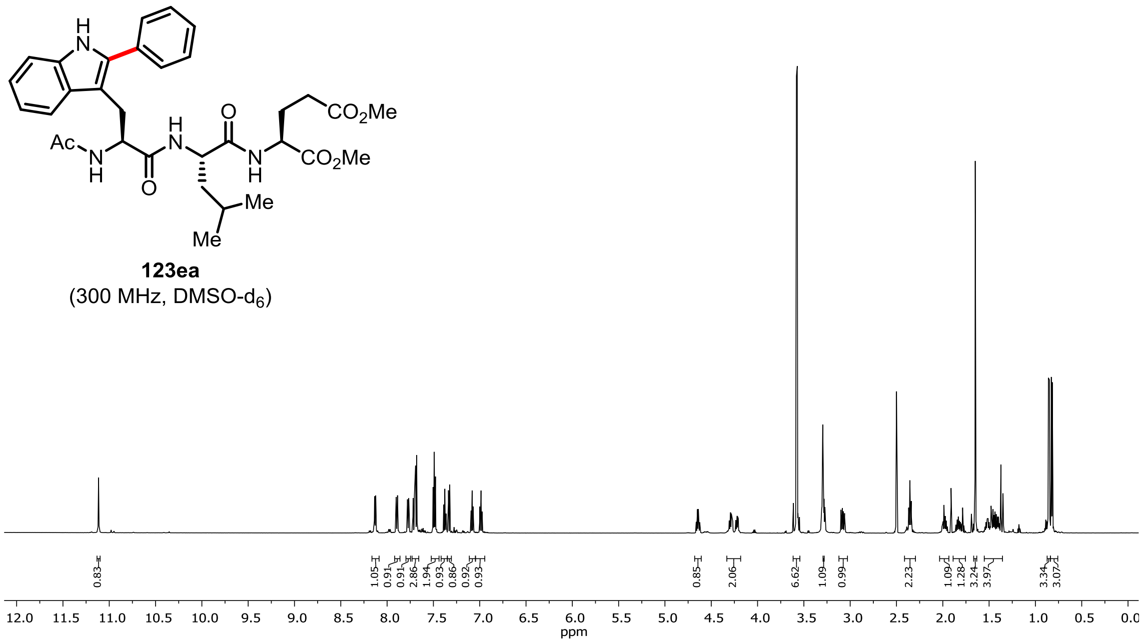


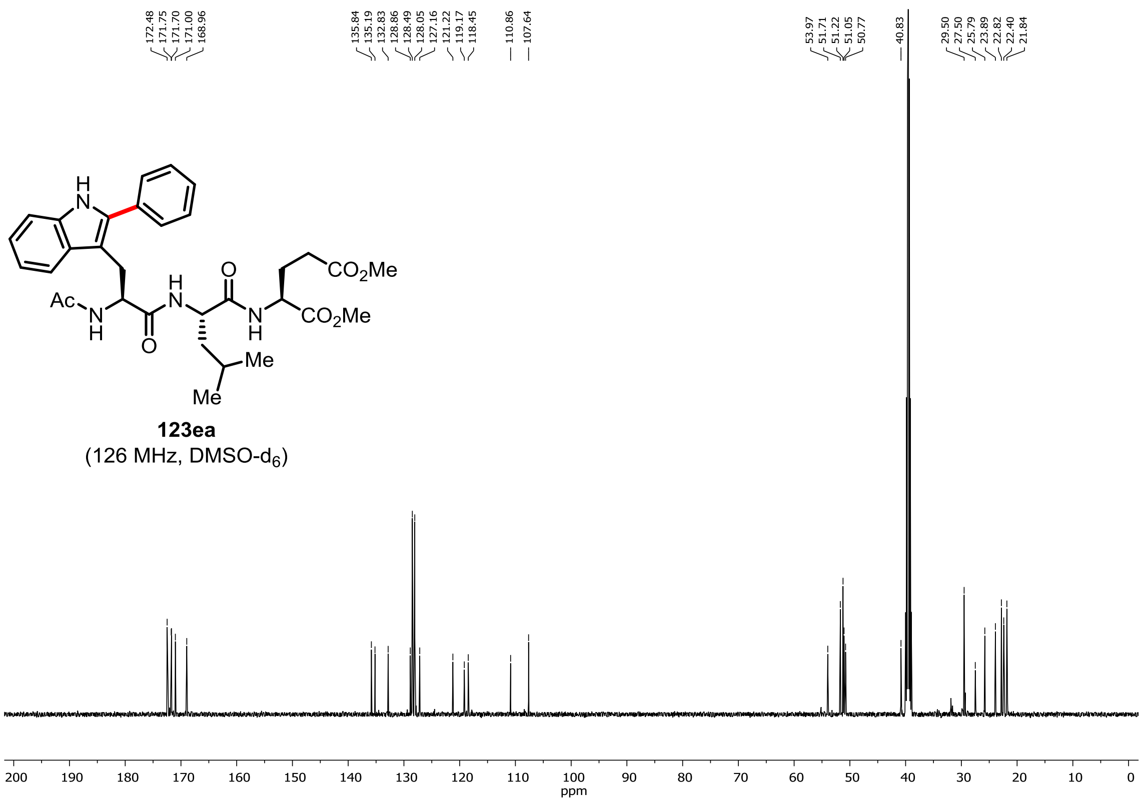
123ca
(126 MHz, DMSO-d_6)



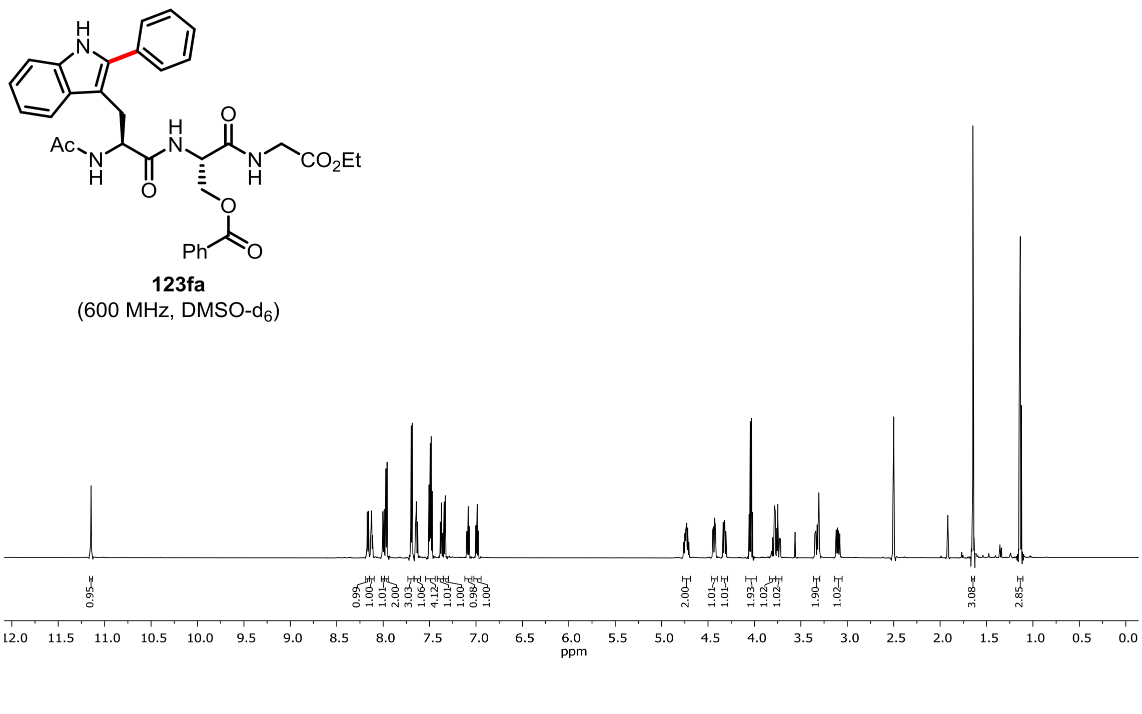
123da
(600 MHz, DMSO-d_6)


123da
(126 MHz, DMSO-d6)
ppm


123ea
(300 MHz, DMSO-d6)
ppm

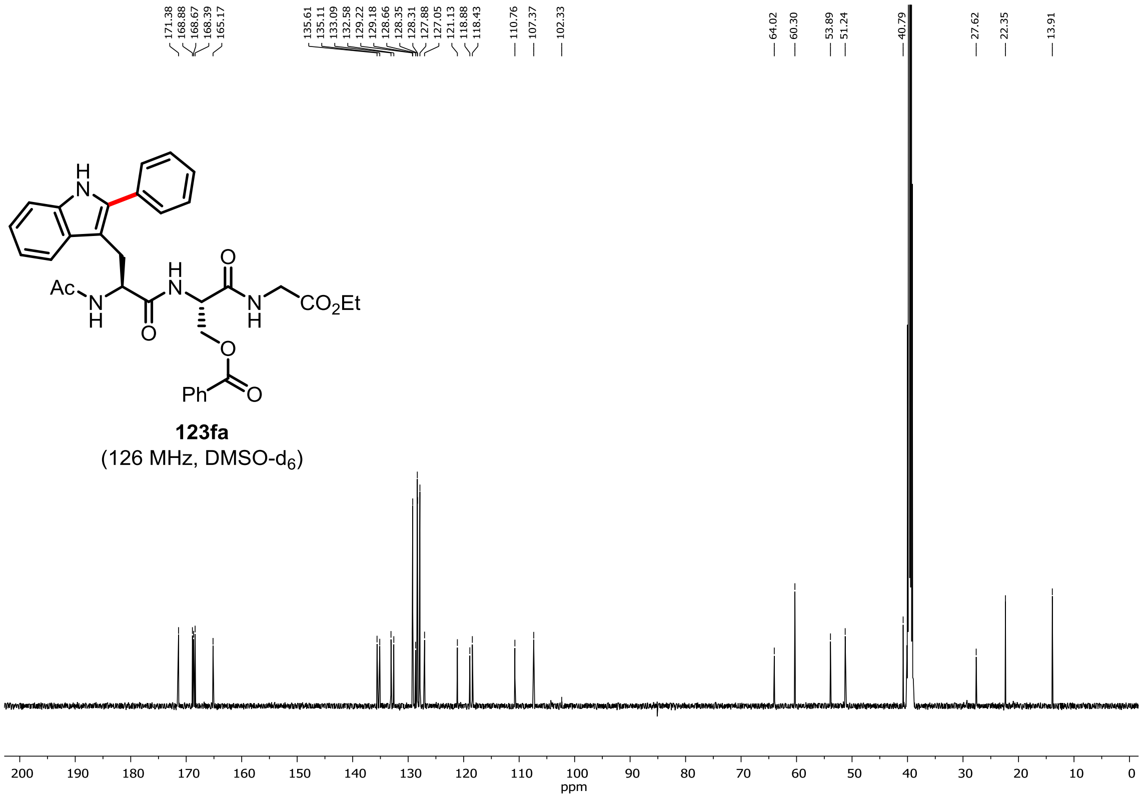


123ea
(126 MHz, DMSO-d_6)

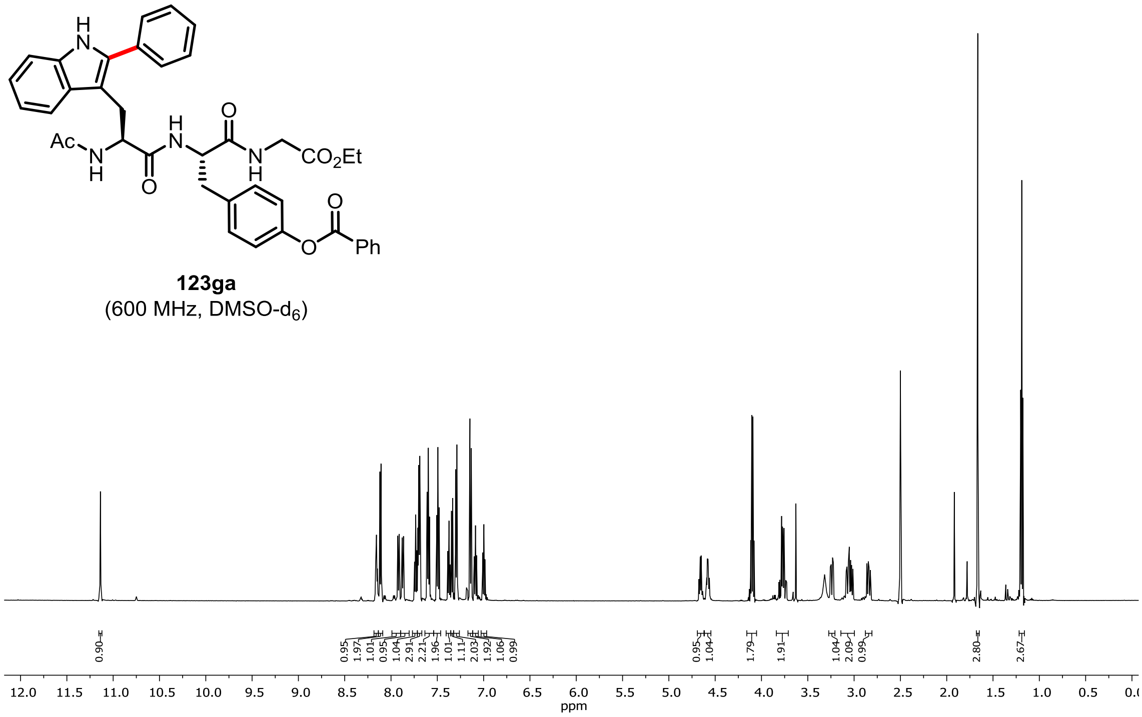


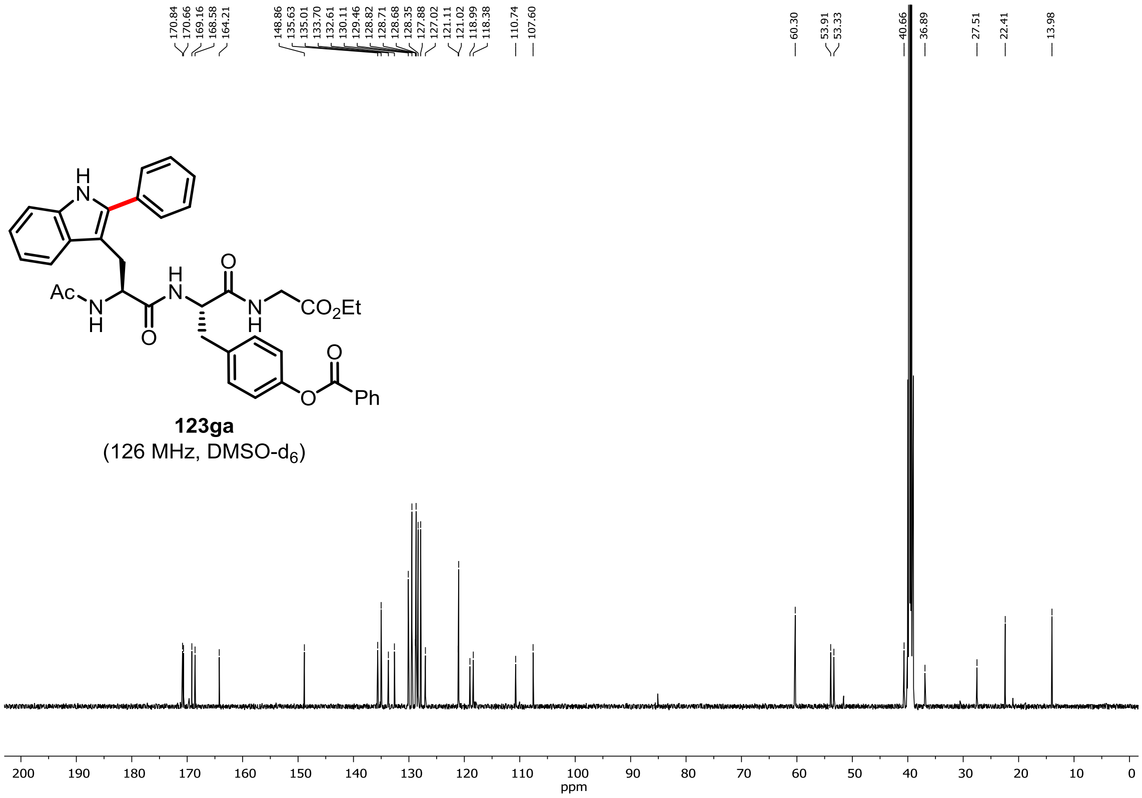
123fa
(600 MHz, DMSO-d_6)

123fa
(126 MHz, DMSO-d$_6$)

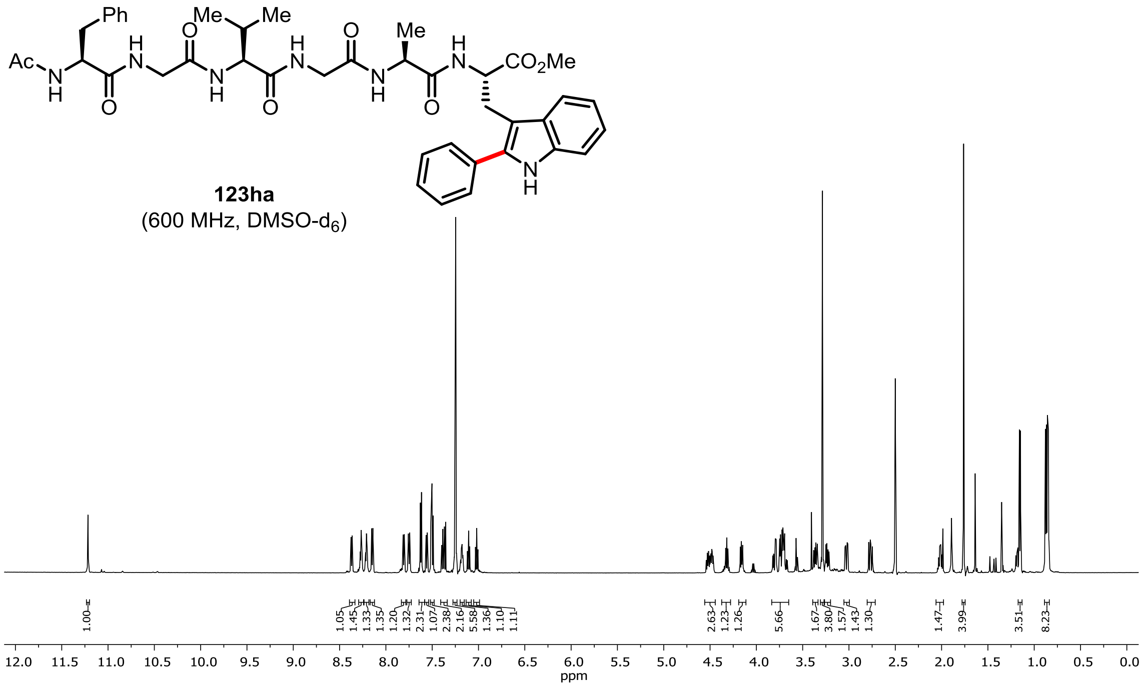


123ga
(600 MHz, DMSO-d$_6$)

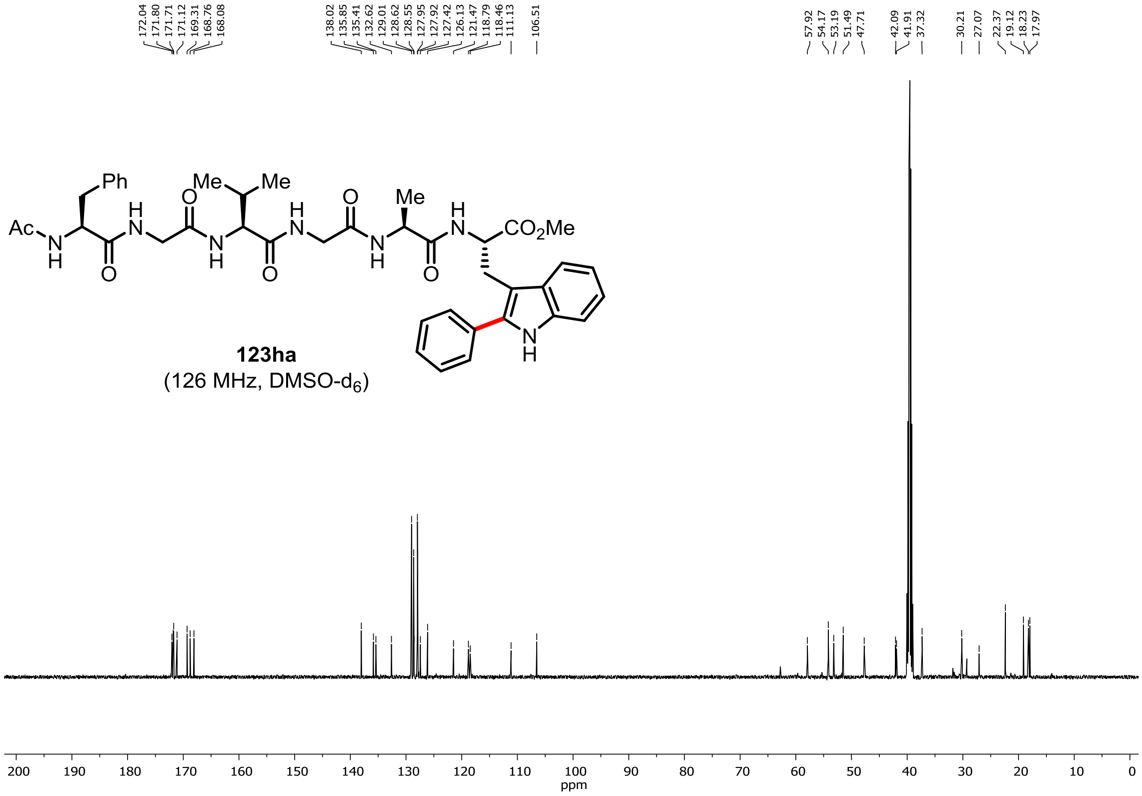




123ga
(126 MHz, DMSO-d$_6$)



123ha
(600 MHz, DMSO-d$_6$)


172.04
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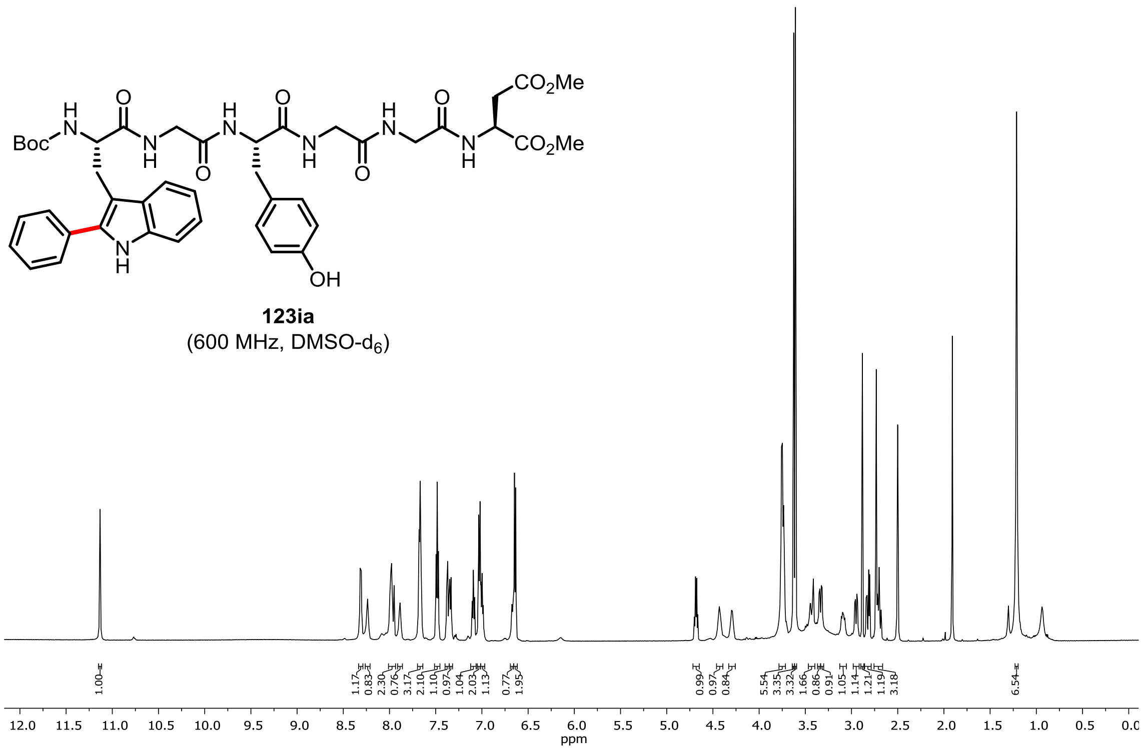
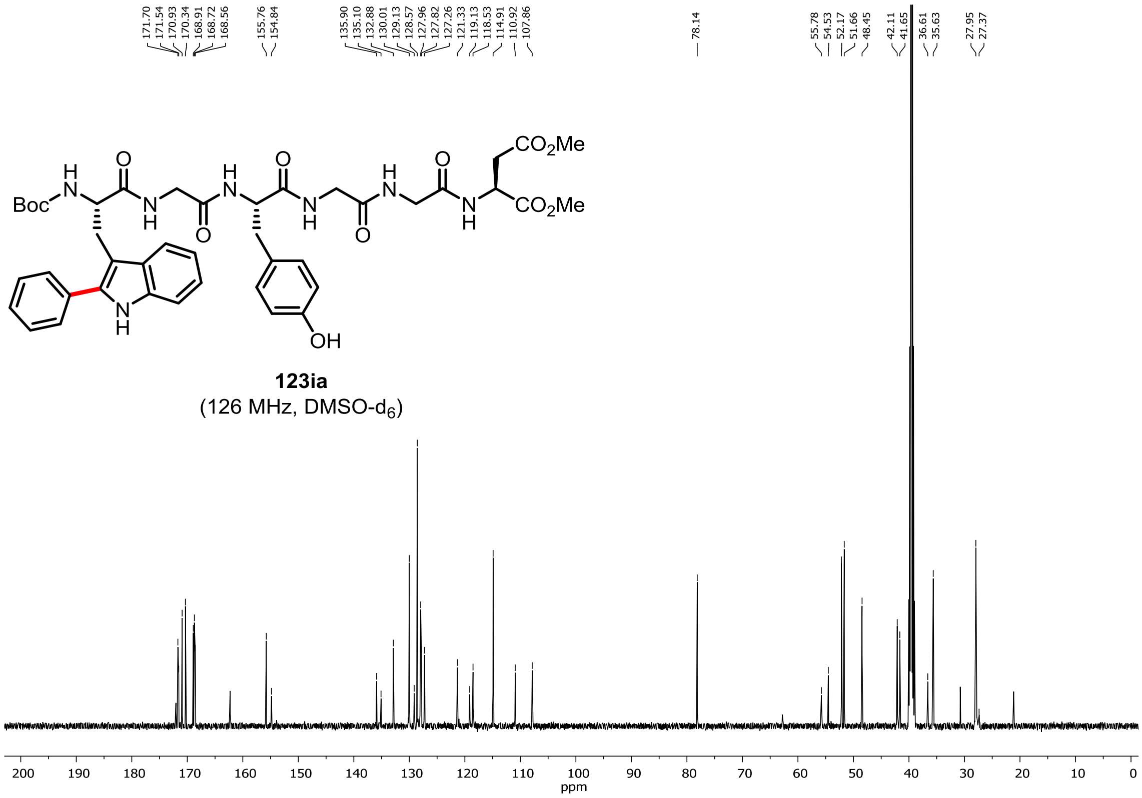
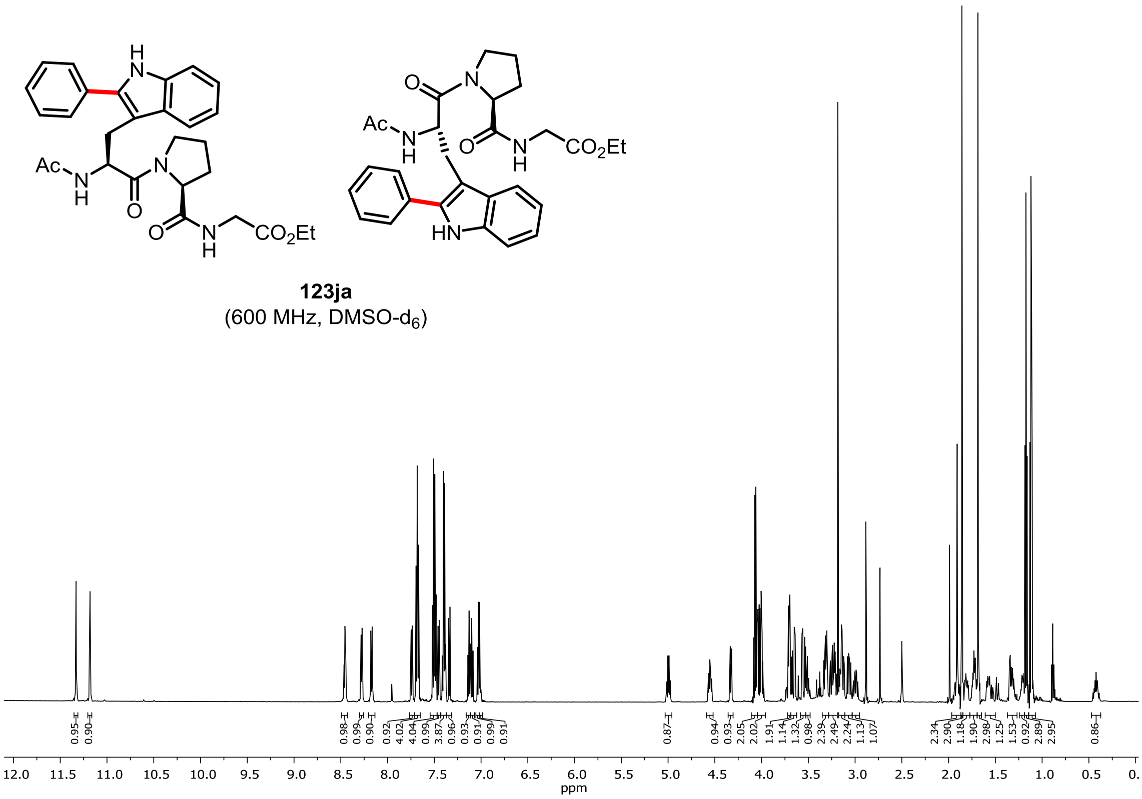
171.71
171.12
169.31
168.76
168.08
138.02
135.85
135.41
132.62
129.01
128.62
128.55
127.95
127.92
127.42
126.13
121.47
118.79
118.46
111.13
106.51
57.92
54.17
53.19
51.49
47.71
42.09
41.91
37.32
30.21
27.07
22.37
19.12
18.23
17.97
Ph
Me
Me
Ac
H
N
O
CO2Me
123ha
(126 MHz, DMSO-d6)
ppm

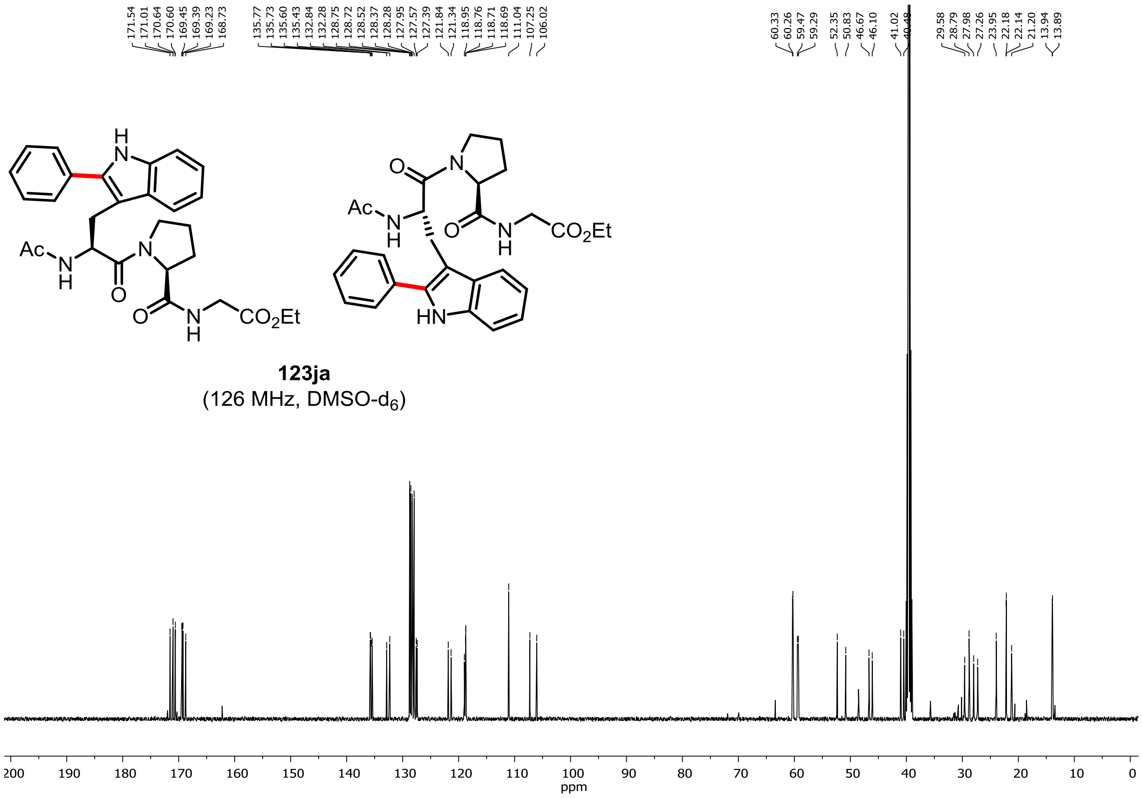

CO2Me
Boc
H
N
O
OH
123ia
(600 MHz, DMSO-d6)
ppm



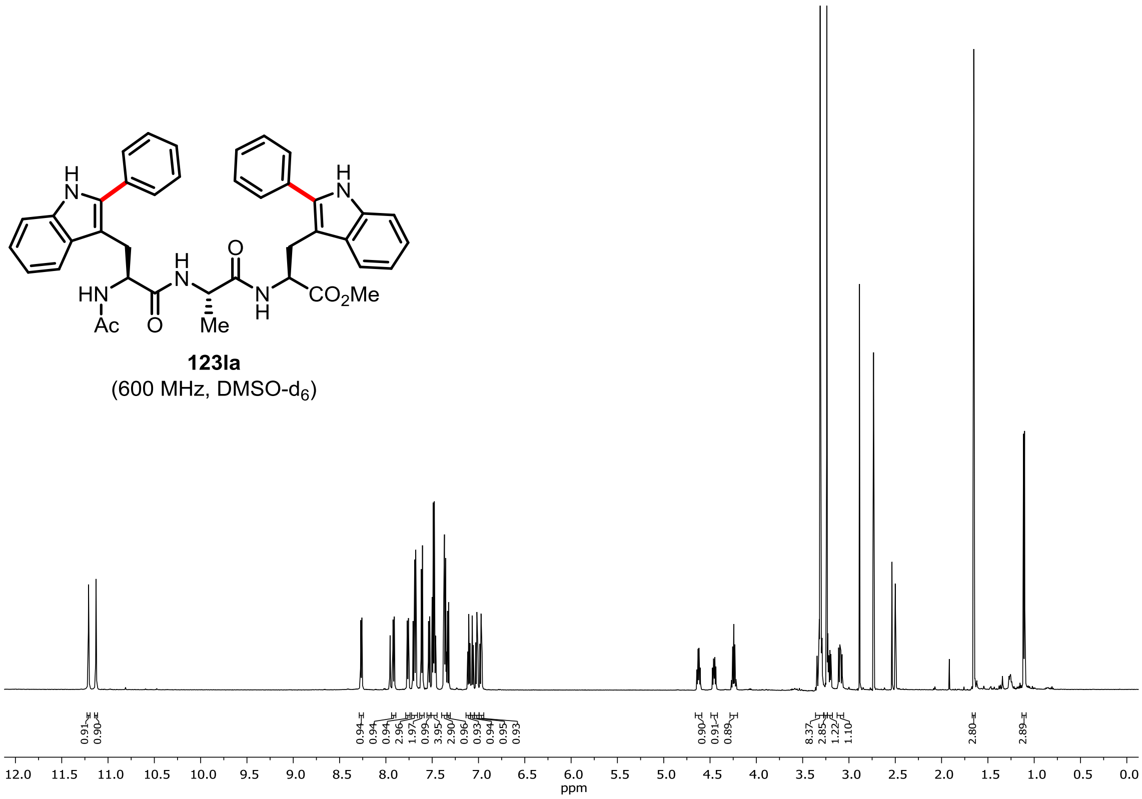
123ia
(126 MHz, DMSO-d_6)



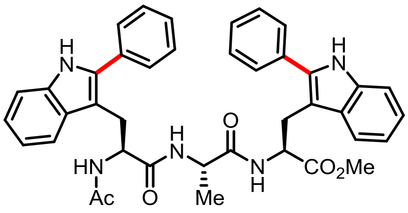
123ja
(600 MHz, DMSO-d_6)



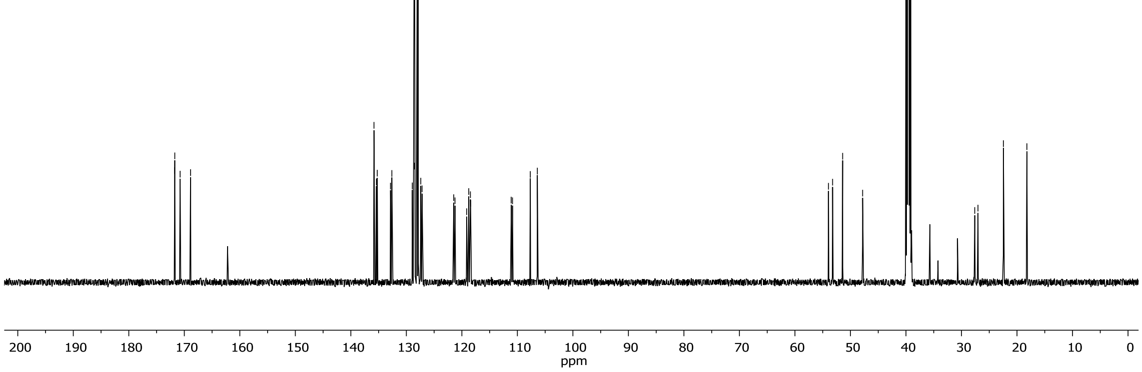
123ja
(126 MHz, DMSO-d_6)

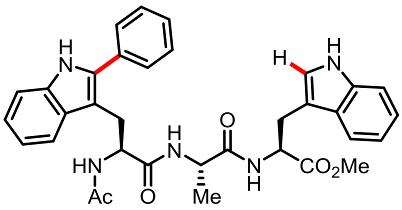


123la
(600 MHz, DMSO-d_6)

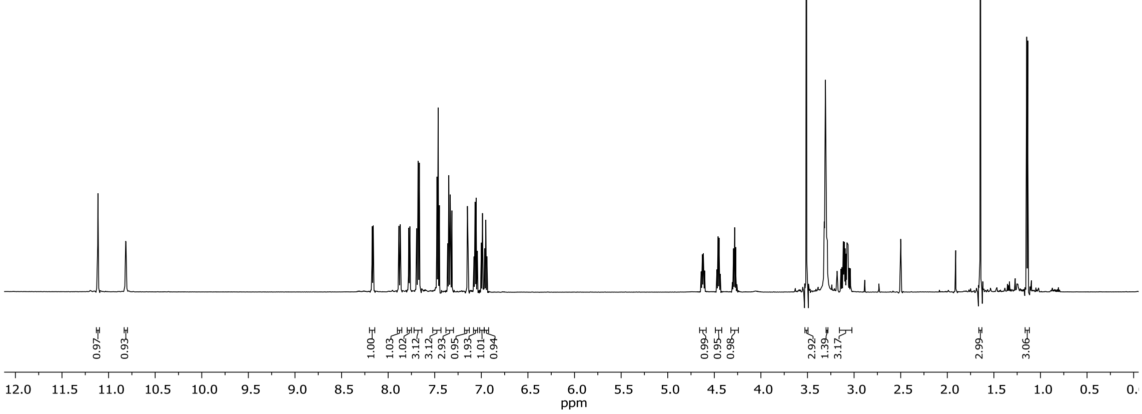


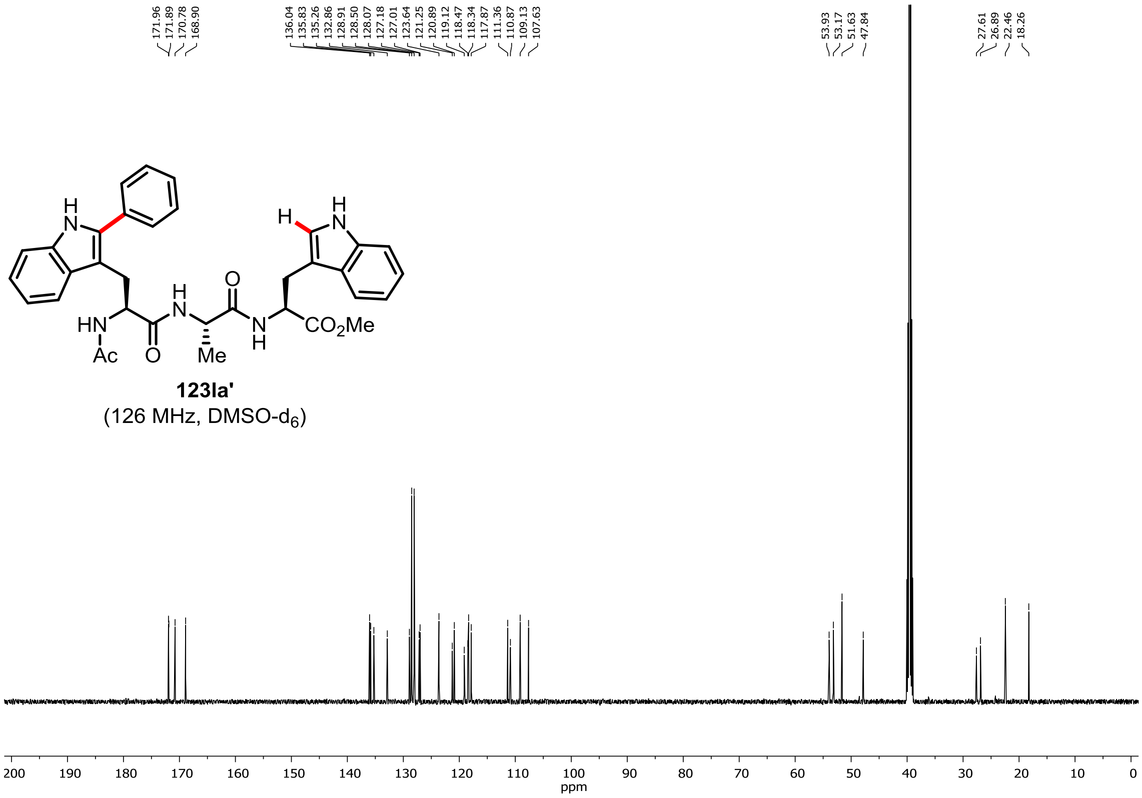
123la
(126 MHz, DMSO-d$_6$)



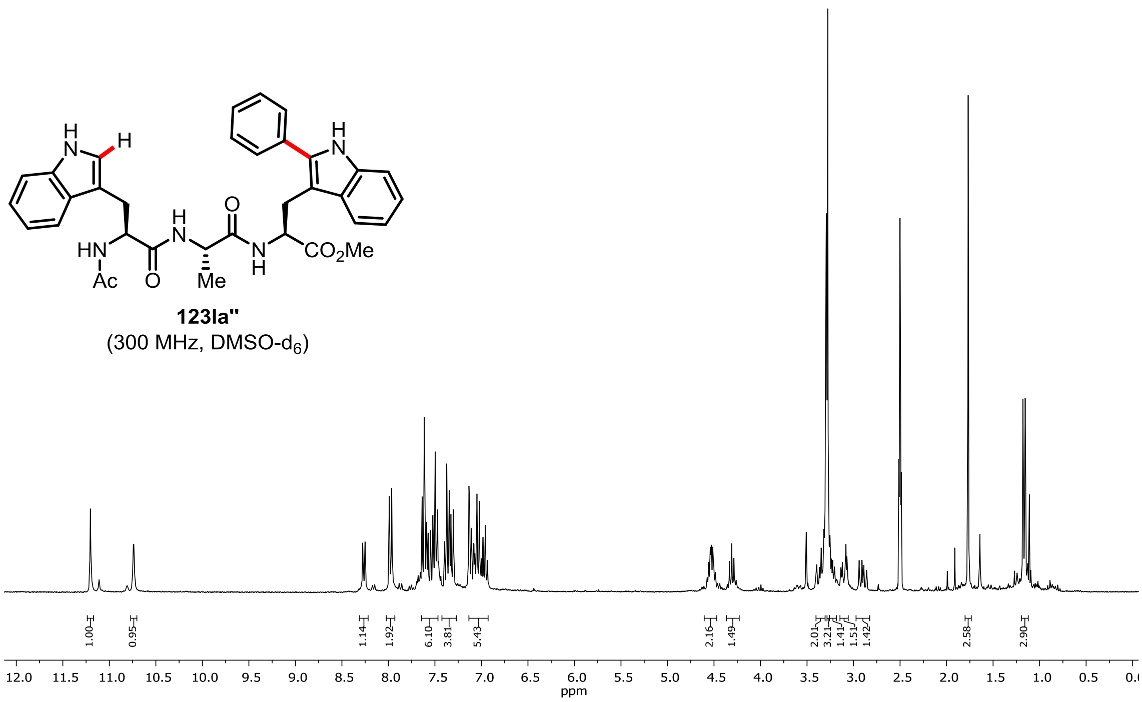


123la'
(600 MHz, DMSO-d$_6$)

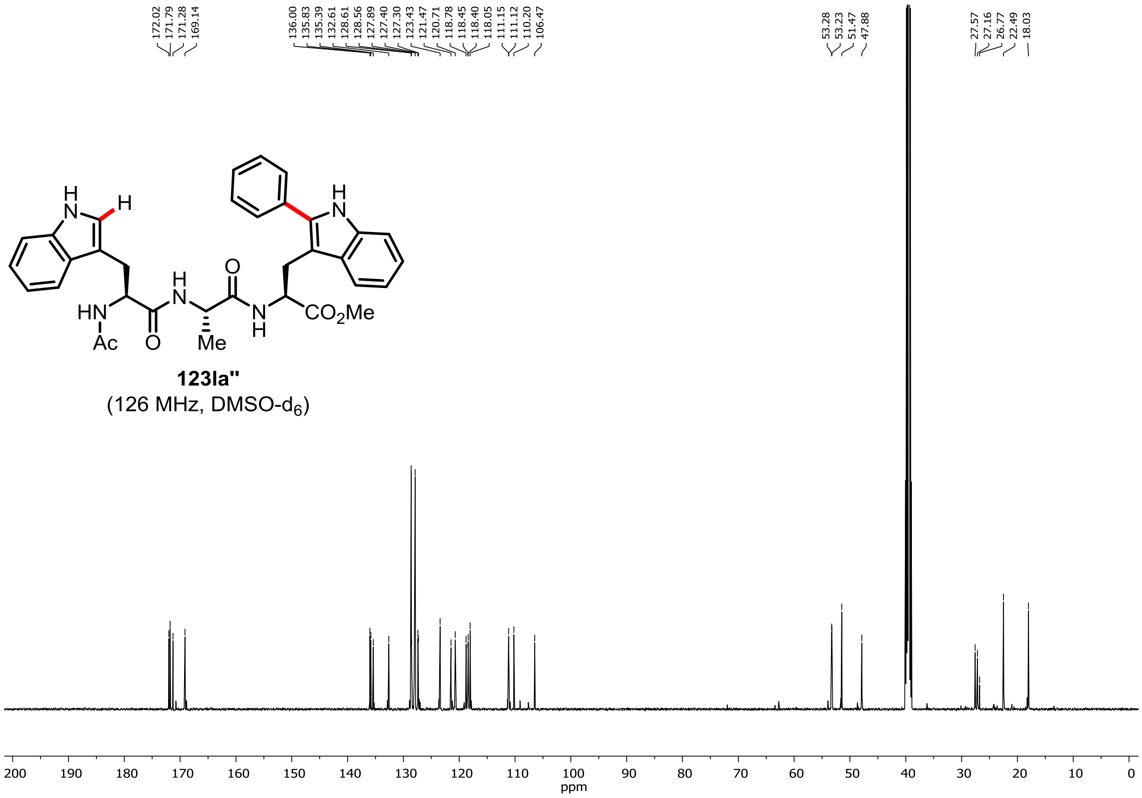




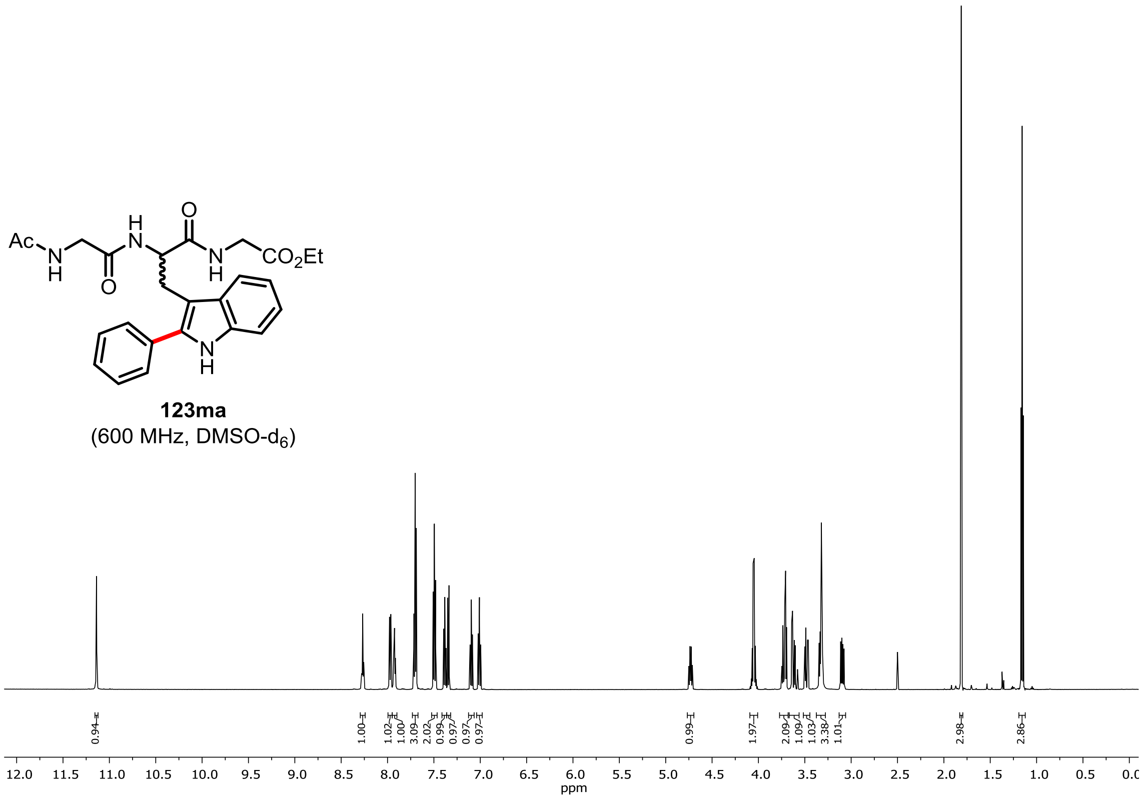
123la'
(126 MHz, DMSO-d$_6$)



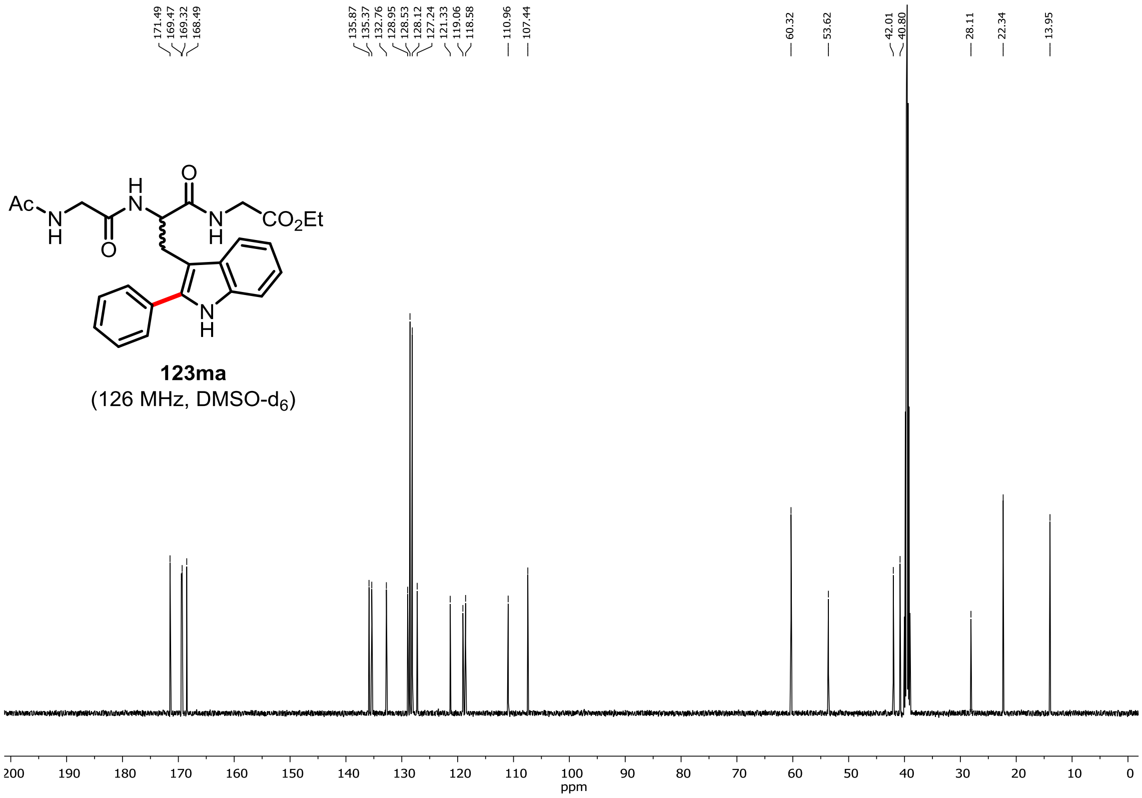
123la''
(300 MHz, DMSO-d$_6$)

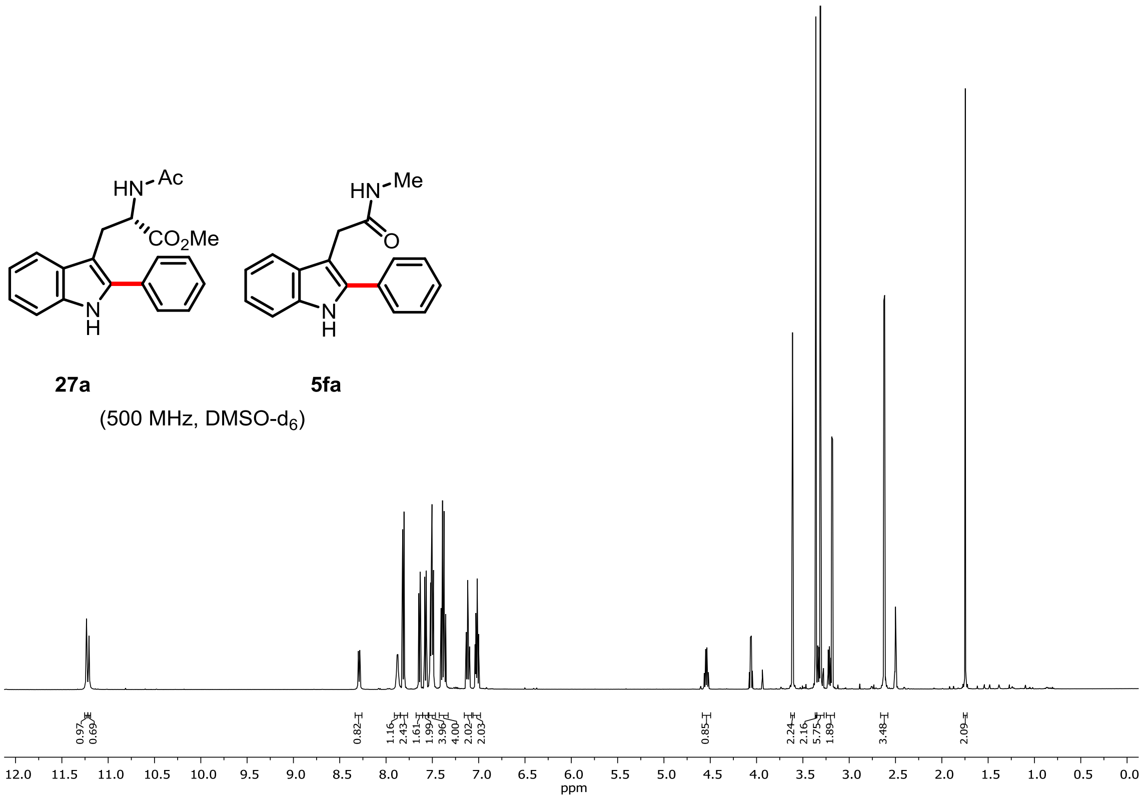


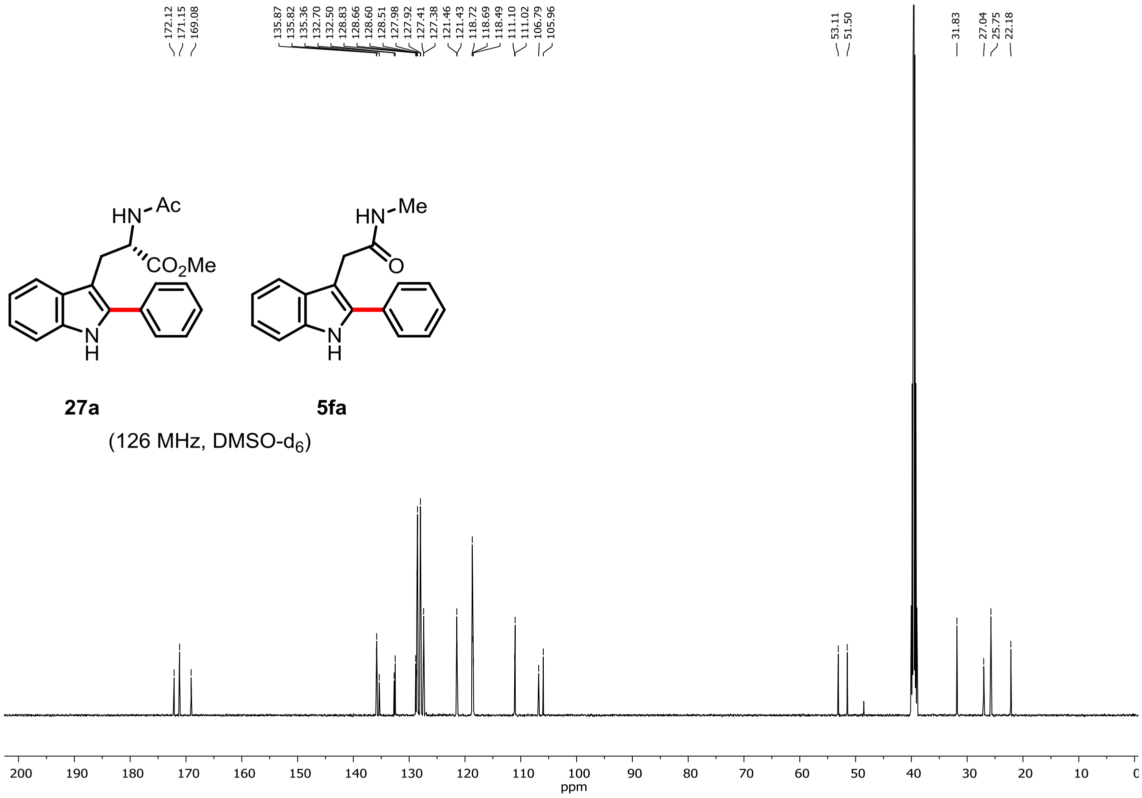
123la''
(126 MHz, DMSO-d_6)



123ma
(600 MHz, DMSO-d_6)

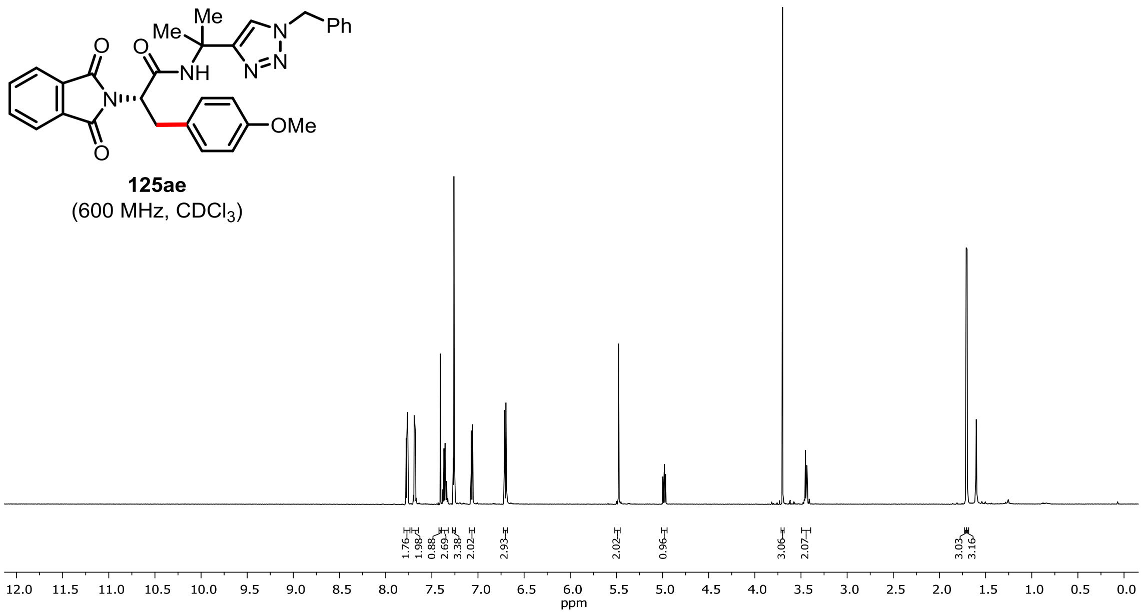

123ma
(126 MHz, DMSO-d6)
ppm


27a
5fa
(500 MHz, DMSO-d6)
ppm



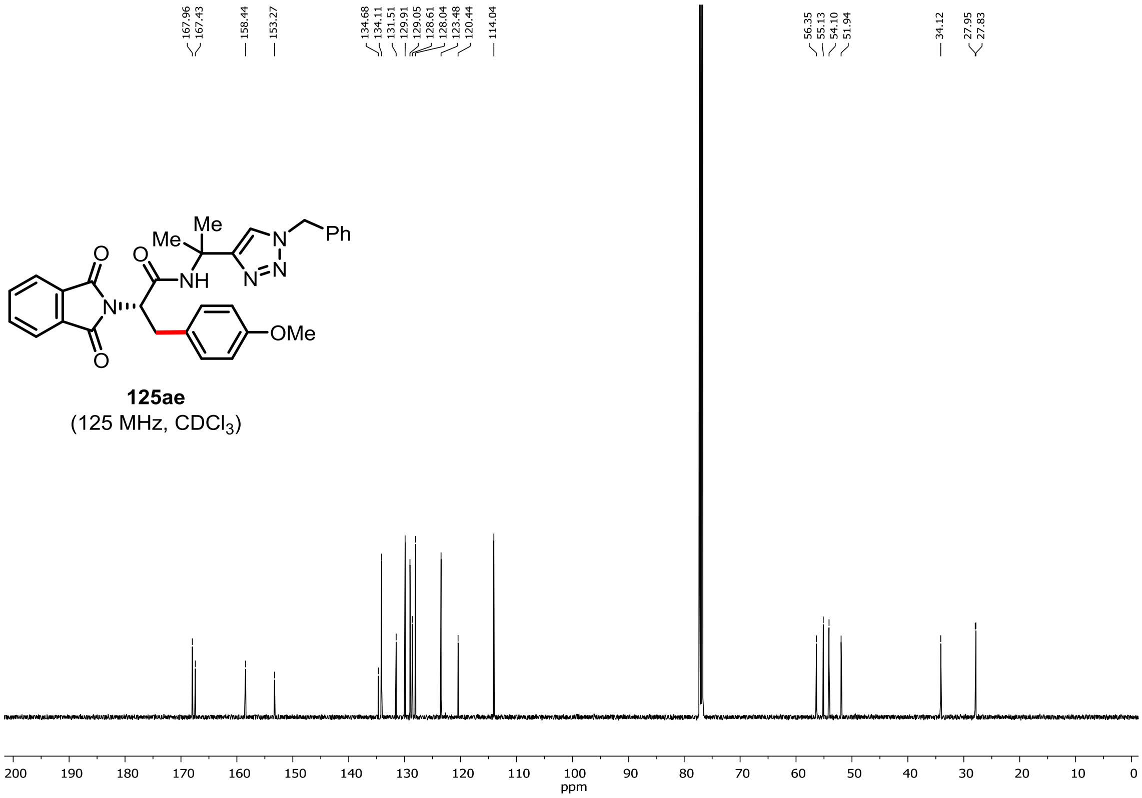
27a **5fa**

(126 MHz, DMSO-d_6)

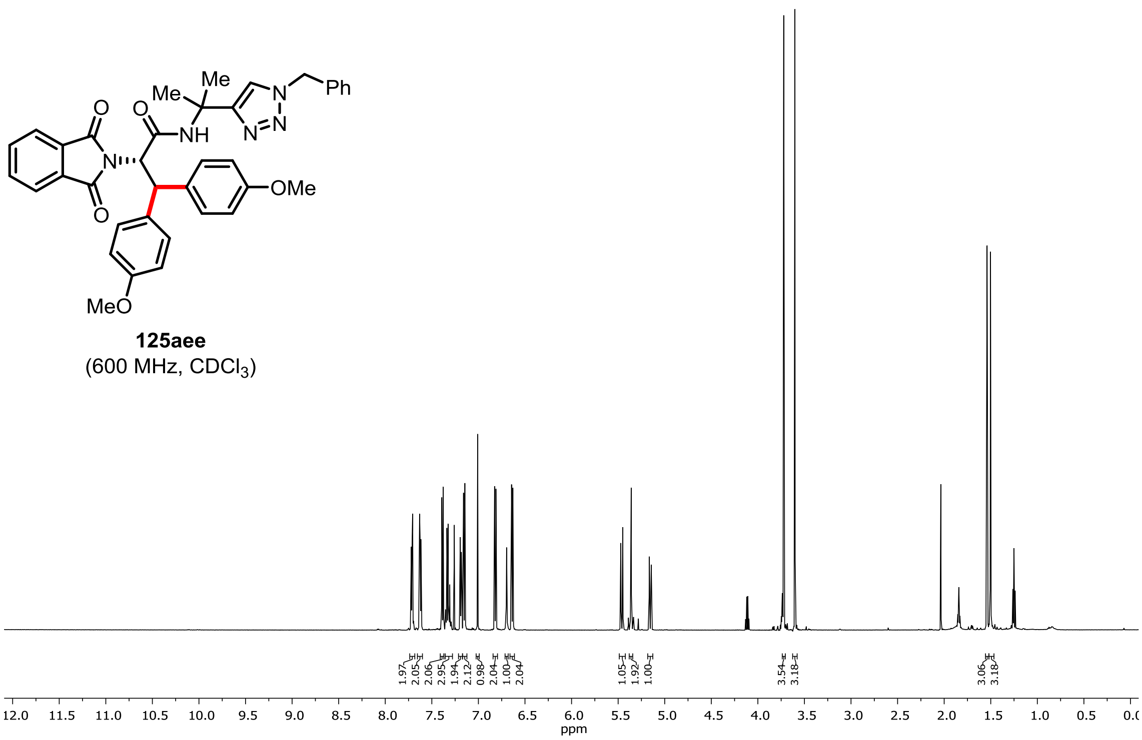


125ae

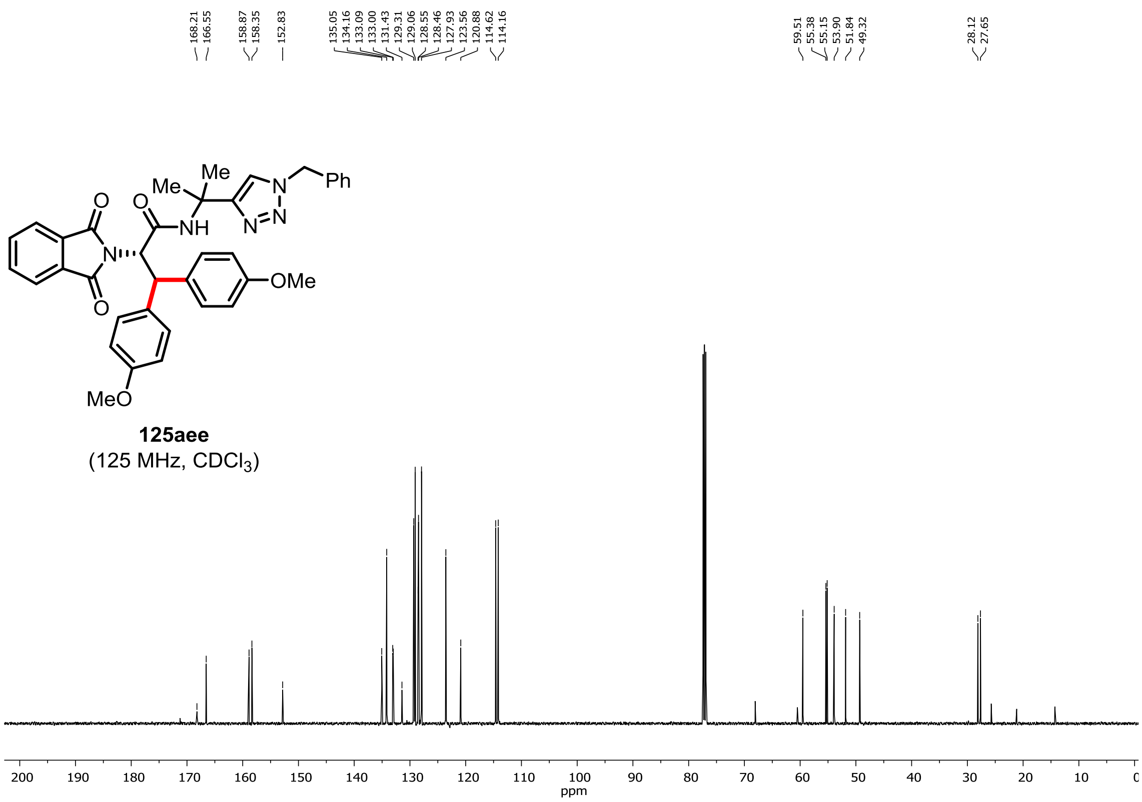
(600 MHz, $CDCl_3$)



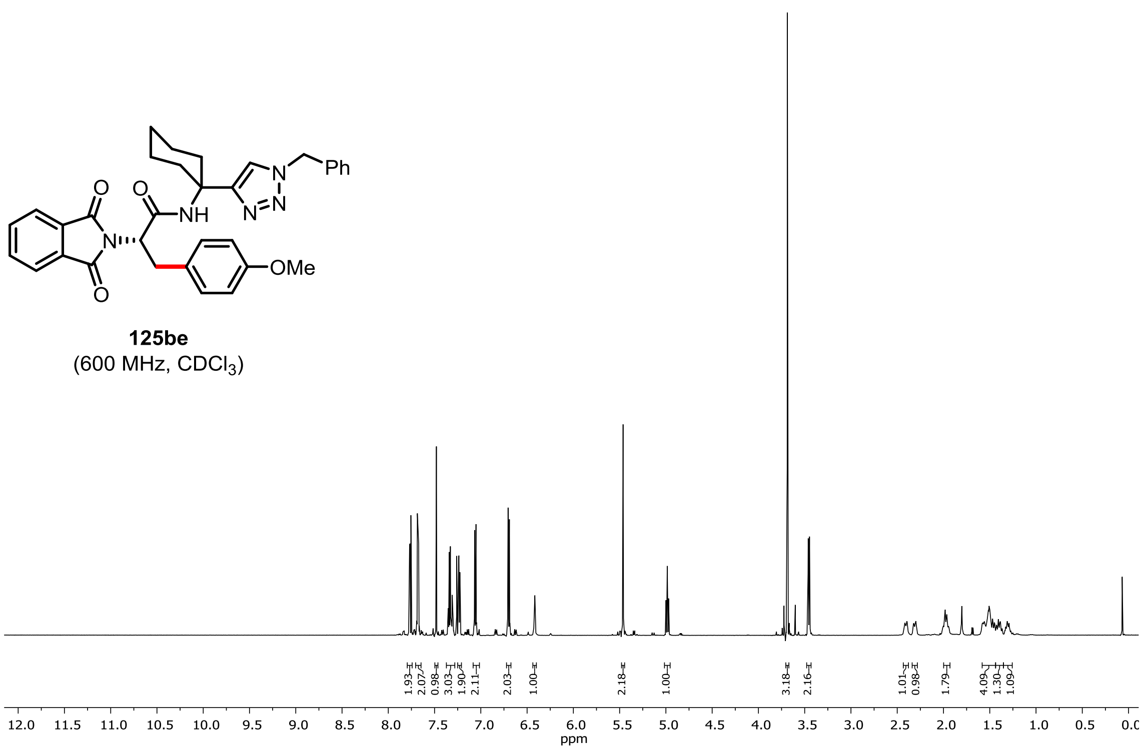
125ae
(125 MHz, $CDCl_3$)



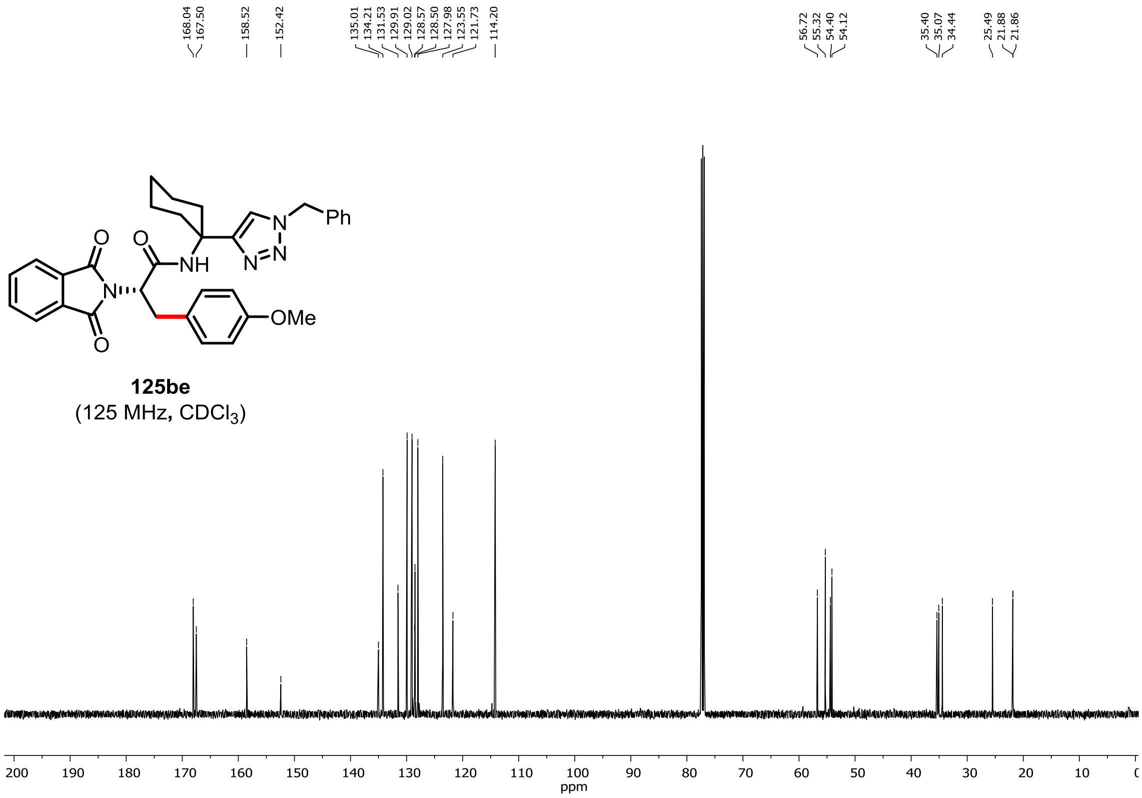
125aee
(600 MHz, $CDCl_3$)

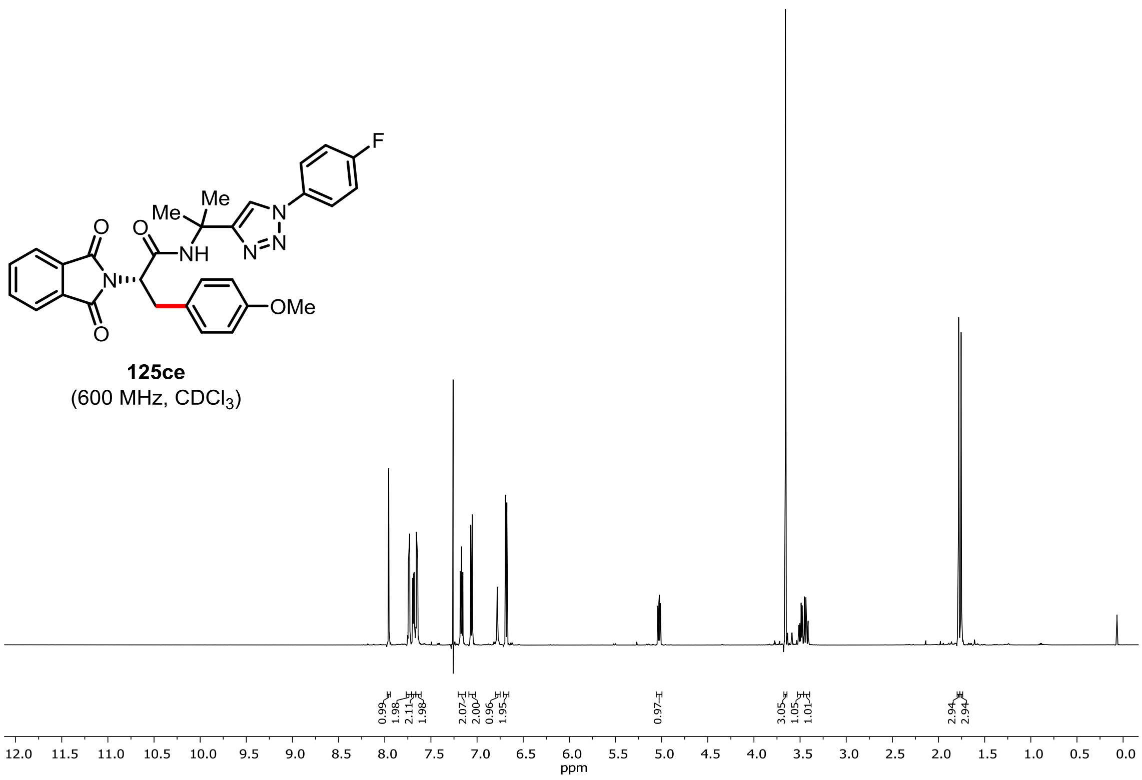


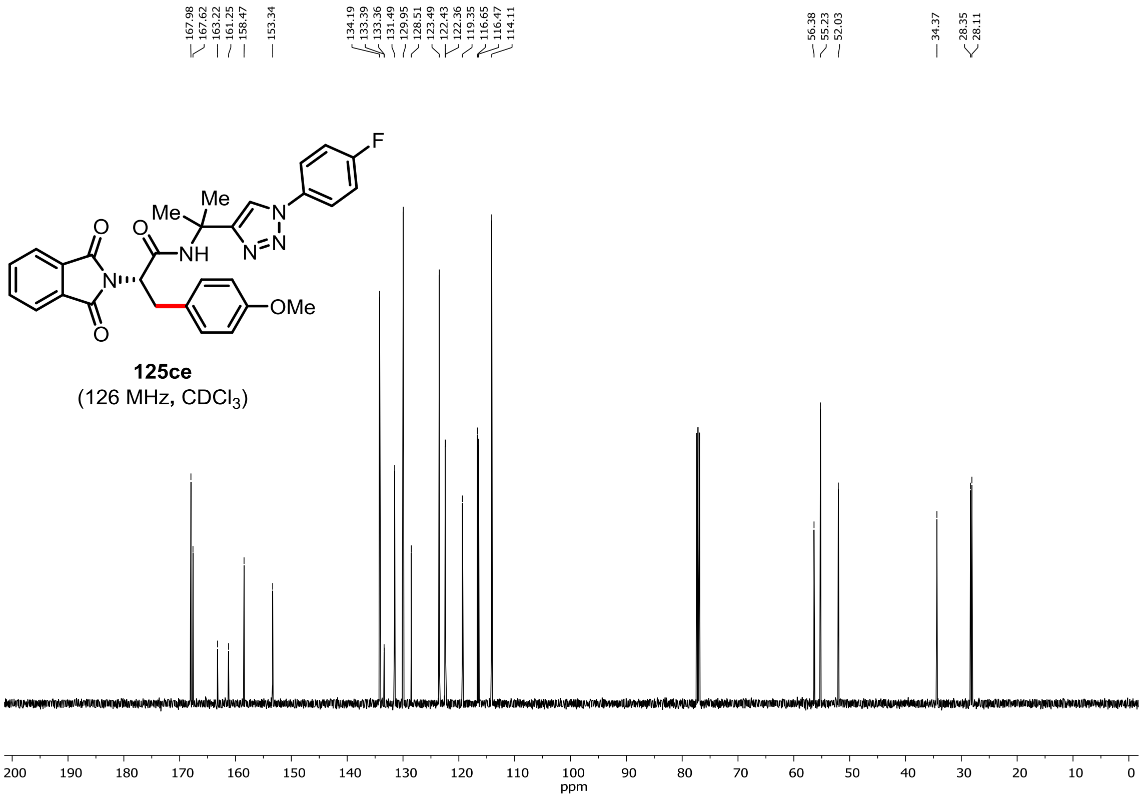
125aee
(125 MHz, $CDCl_3$)



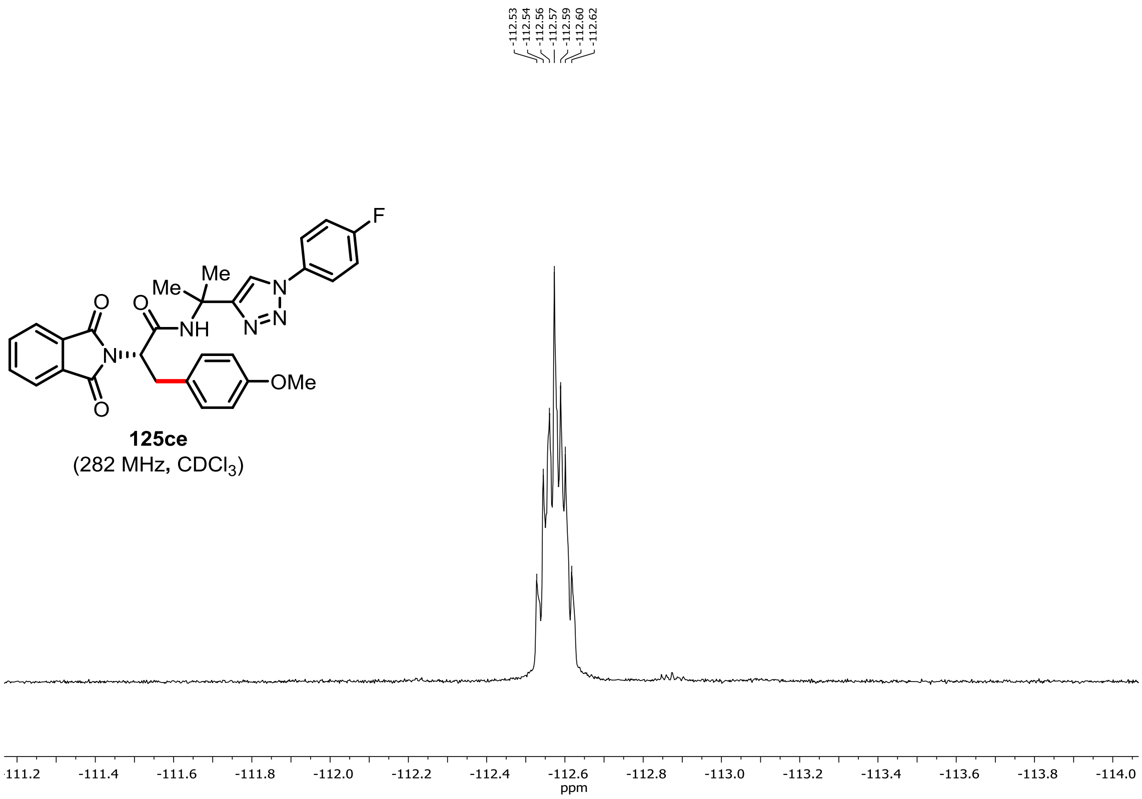
125be
(600 MHz, $CDCl_3$)


168.04
167.50
158.52
152.42
135.01
134.21
131.53
129.91
129.02
128.57
128.50
127.98
123.55
121.73
114.20
56.72
55.32
54.40
54.12
35.40
35.07
34.44
25.49
21.88
21.86
O
O
O
NH
N
N
N
N
Ph
OMe
125be
(125 MHz, CDCl$_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

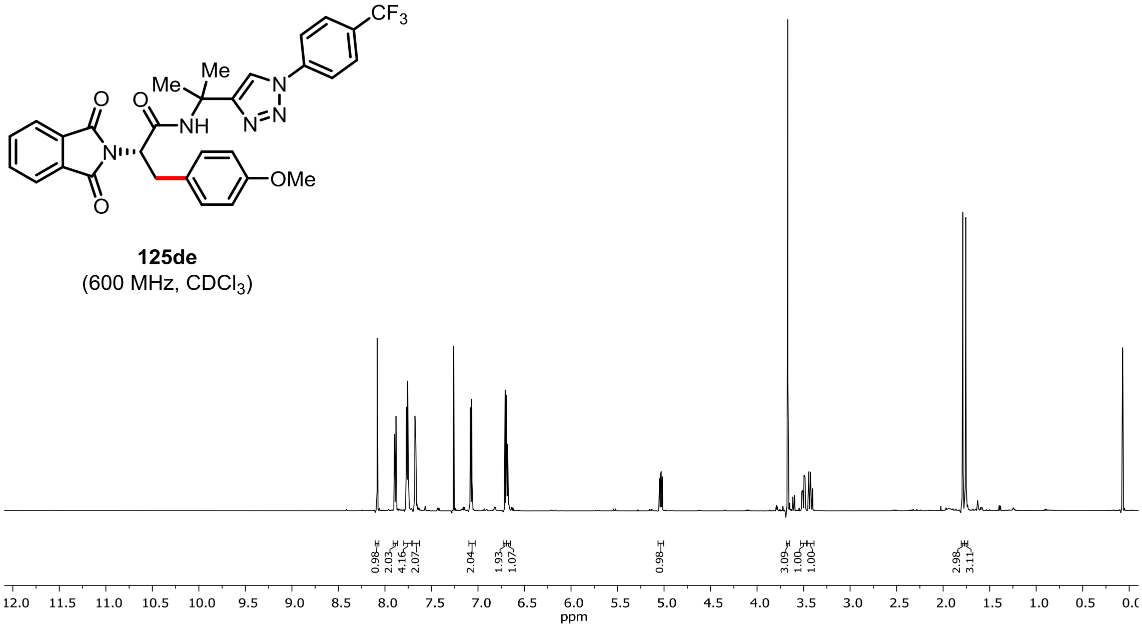

F
Me
Me
O
O
O
NH
N
N
N
N
OMe
125ce
(600 MHz, CDCl$_3$)
0.99
1.98
2.11
1.98
2.07
2.00
0.96
1.95
0.97
3.05
1.05
1.01
2.94
2.94
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



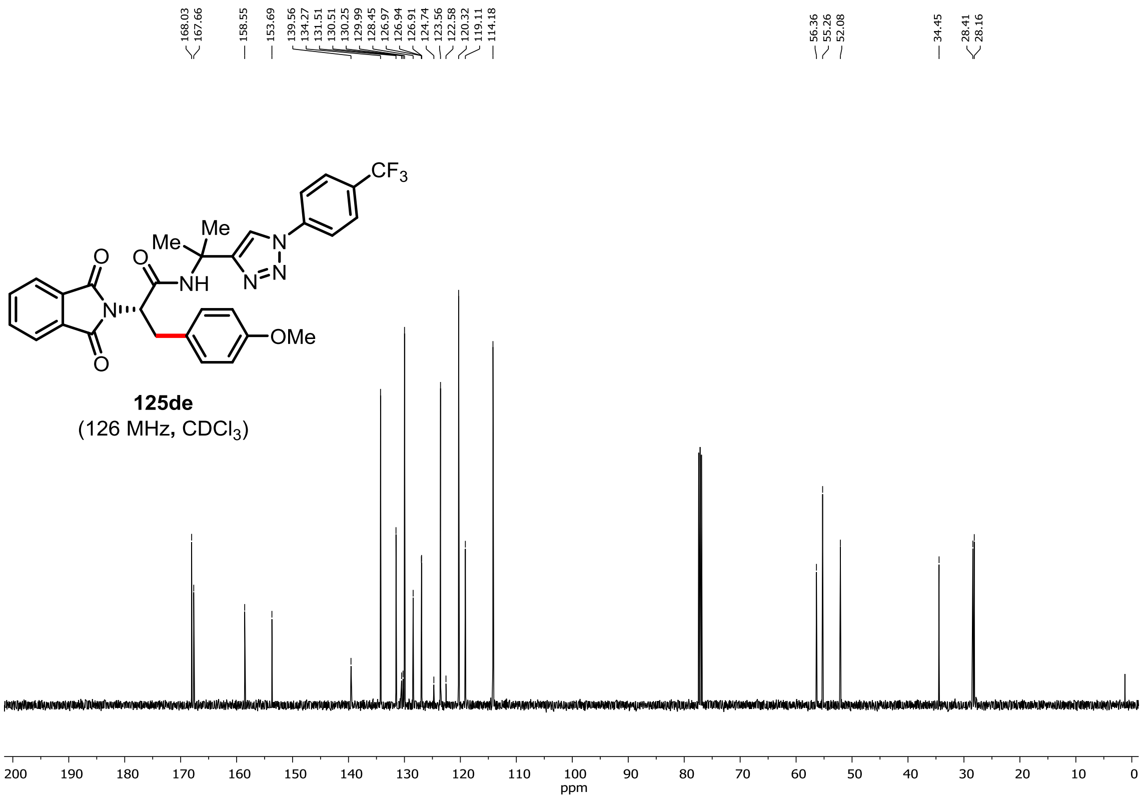
125ce
(126 MHz, $CDCl_3$)



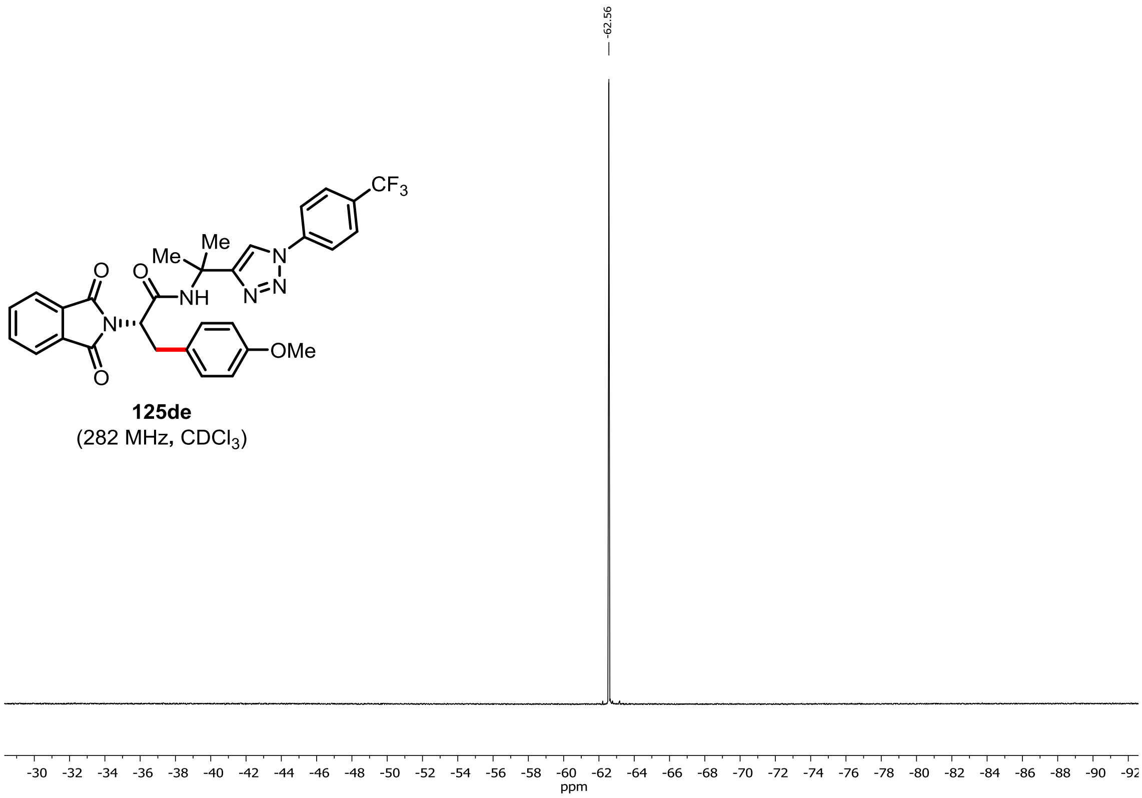
125ce
(282 MHz, $CDCl_3$)



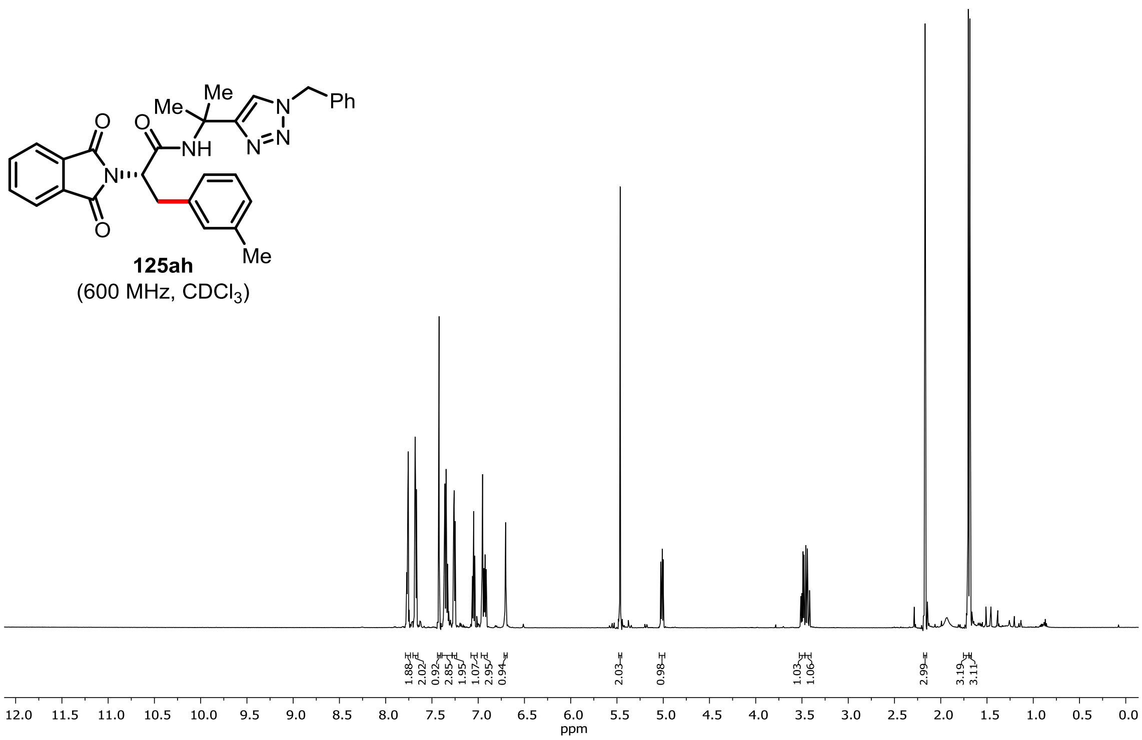
125de
(600 MHz, $CDCl_3$)



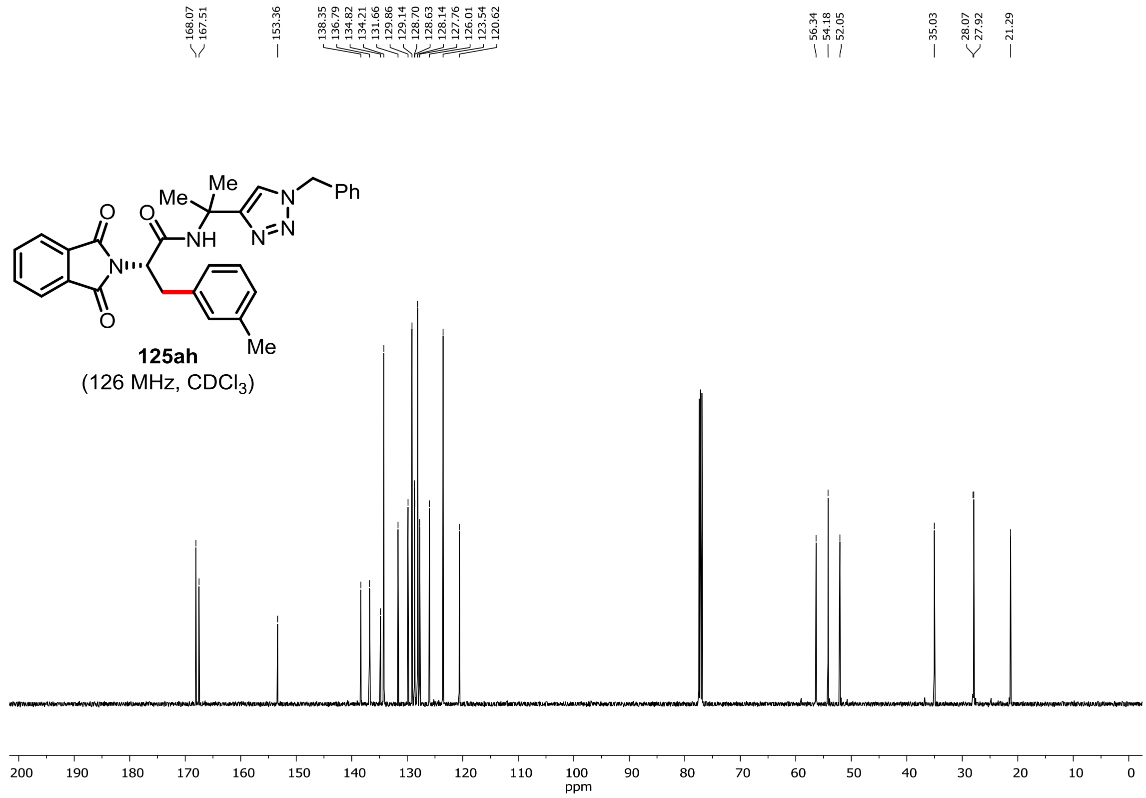
125de
(126 MHz, $CDCl_3$)

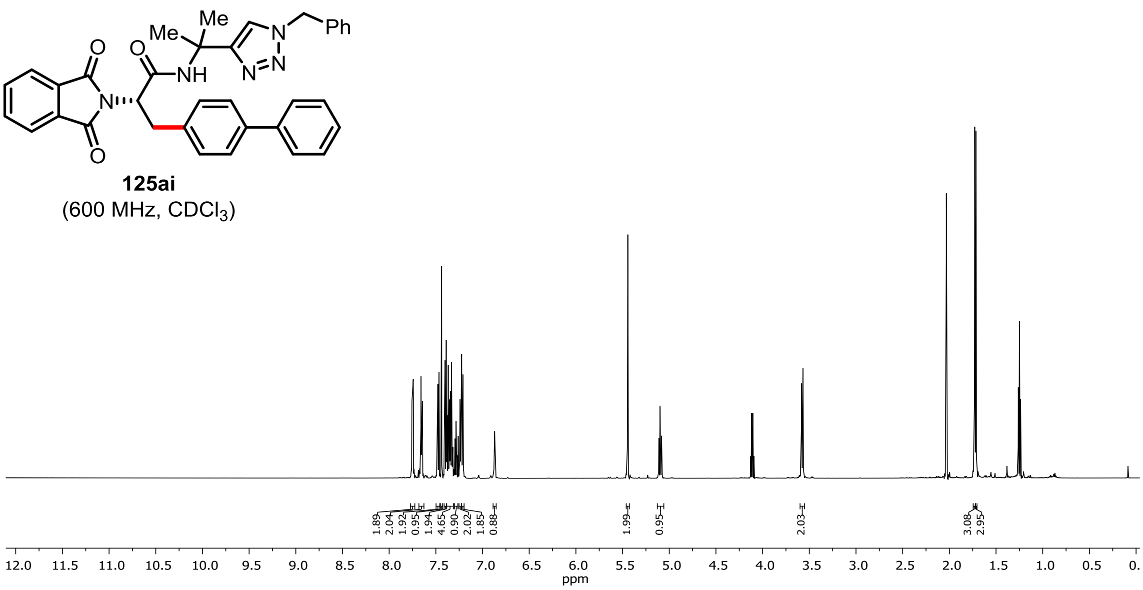


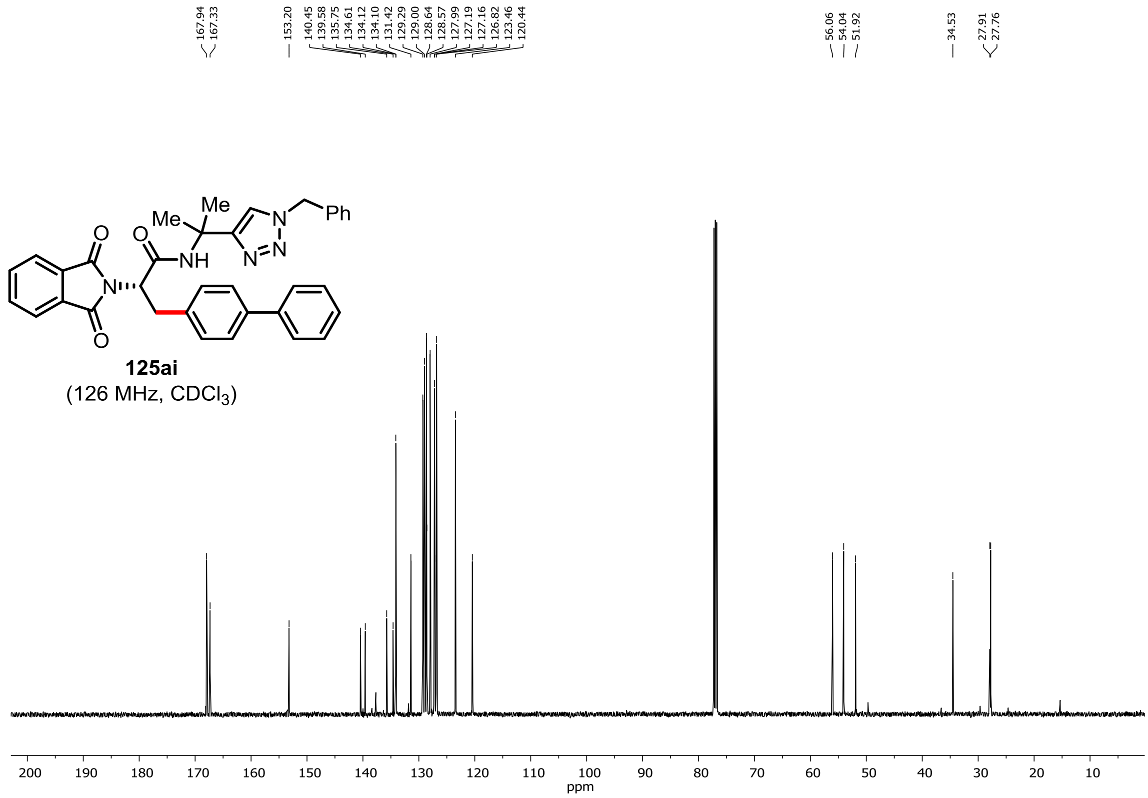
125de
(282 MHz, $CDCl_3$)



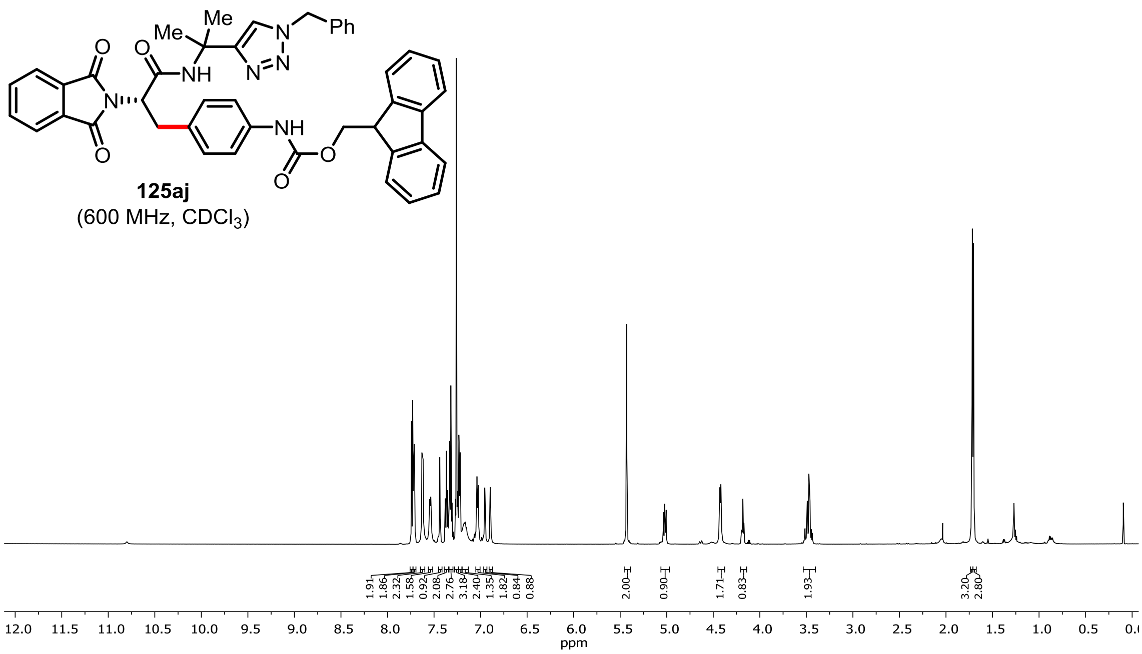
125ah
(600 MHz, $CDCl_3$)


168.07
167.51
153.36
138.35
136.79
134.82
134.21
131.66
129.86
129.14
128.70
128.63
128.14
127.76
126.01
123.54
120.62
56.34
54.18
52.05
35.03
28.07
27.92
21.29
Me
Me
Ph
O
O
NH
N
N
N
N
O
Me
125ah
(126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

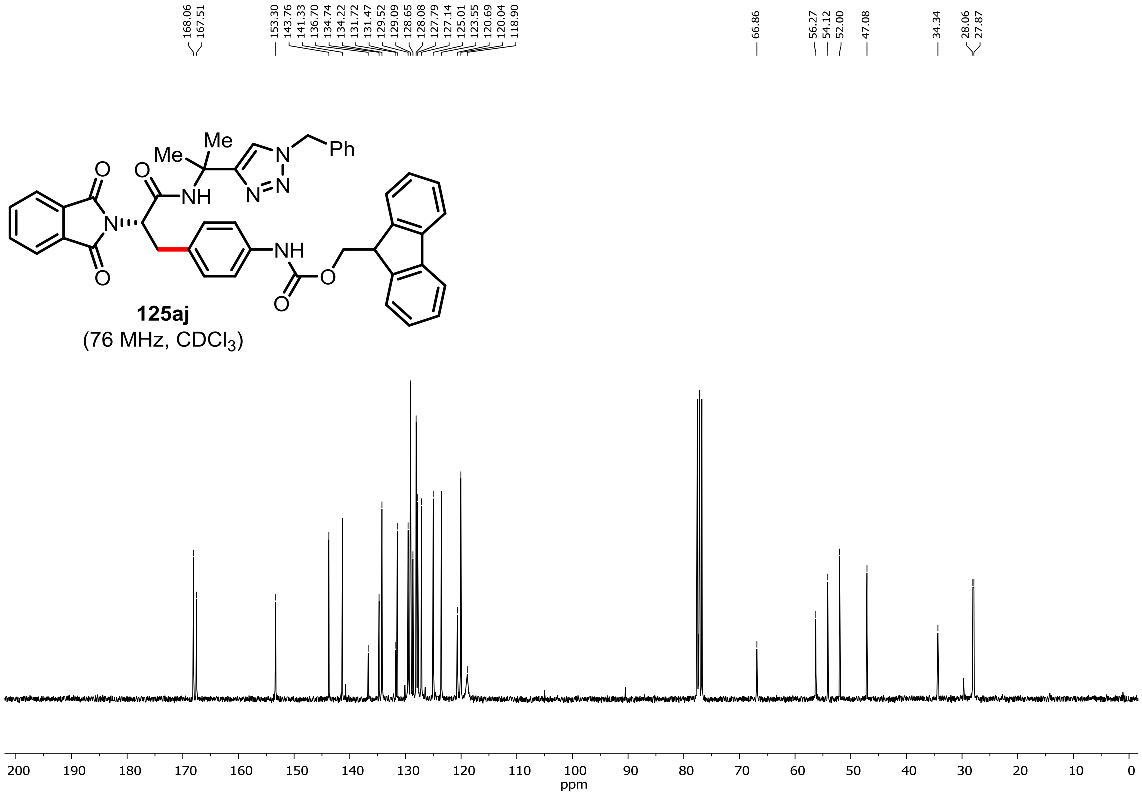

Me
Me
Ph
O
O
NH
N
N
N
N
O
125ai
(600 MHz, CDCl3)
1.89
2.04
1.92
0.95
1.94
4.65
0.90
2.02
1.85
0.88
1.99
0.95
2.03
3.08
2.95
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
ppm



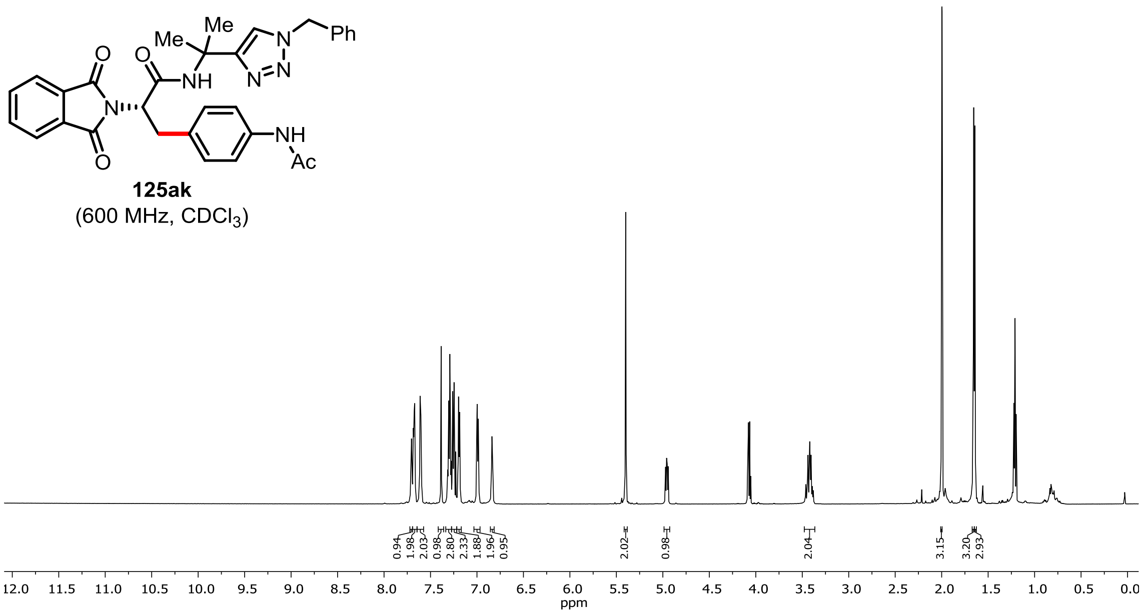
167.94
167.33
153.20
140.45
139.58
135.75
134.61
134.12
134.10
131.42
129.29
129.00
128.64
128.57
127.99
127.19
127.16
126.82
123.46
120.44
56.06
54.04
51.92
34.53
27.91
27.76
Me
Me
O
O
NH
N
N
N
N
Ph
O
125ai
(126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm



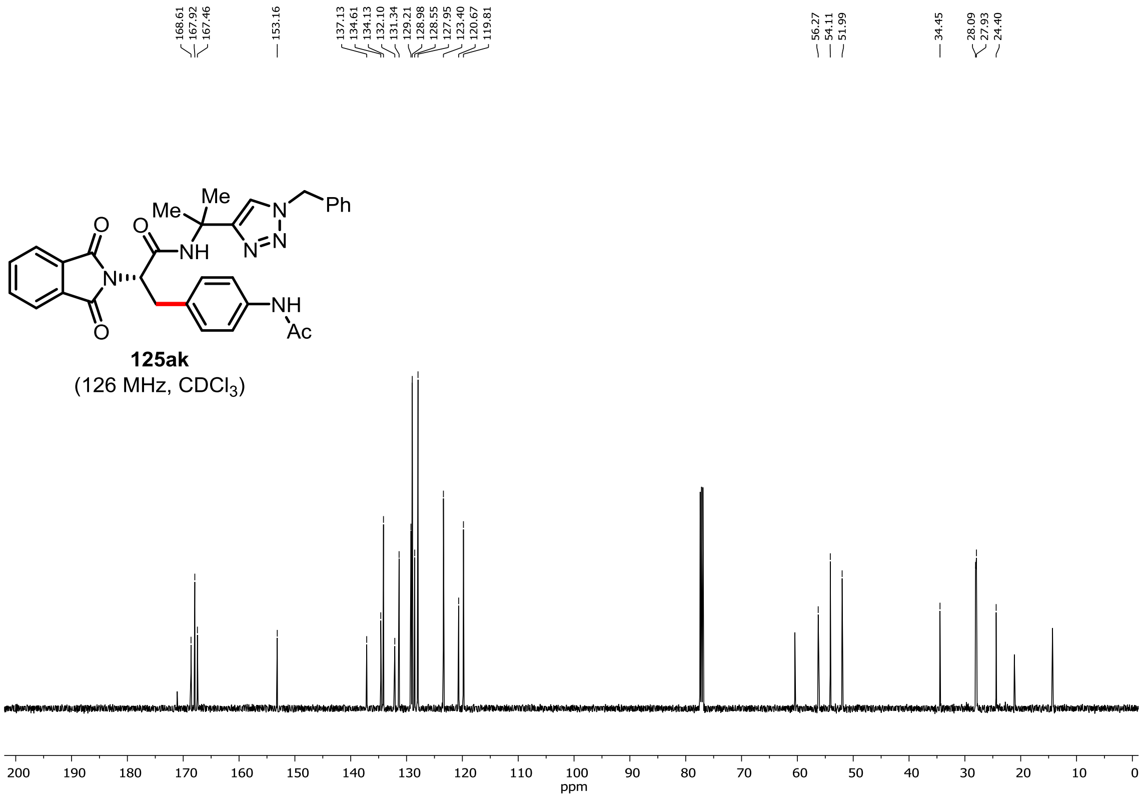
Me
Me
O
O
NH
N
N
N
N
Ph
O
NH
O
O
125aj
(600 MHz, CDCl3)
1.91
1.86
2.32
1.58
0.92
2.08
2.76
3.18
2.40
1.35
1.82
0.84
0.88
2.00
0.90
1.71
0.83
1.93
3.20
2.80
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm



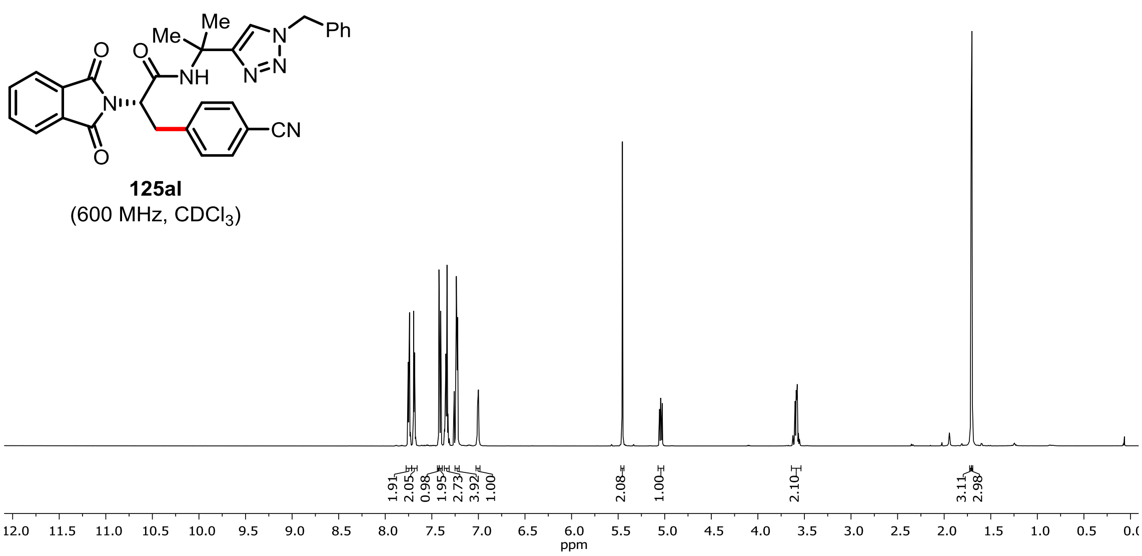
125aj
(76 MHz, $CDCl_3$)



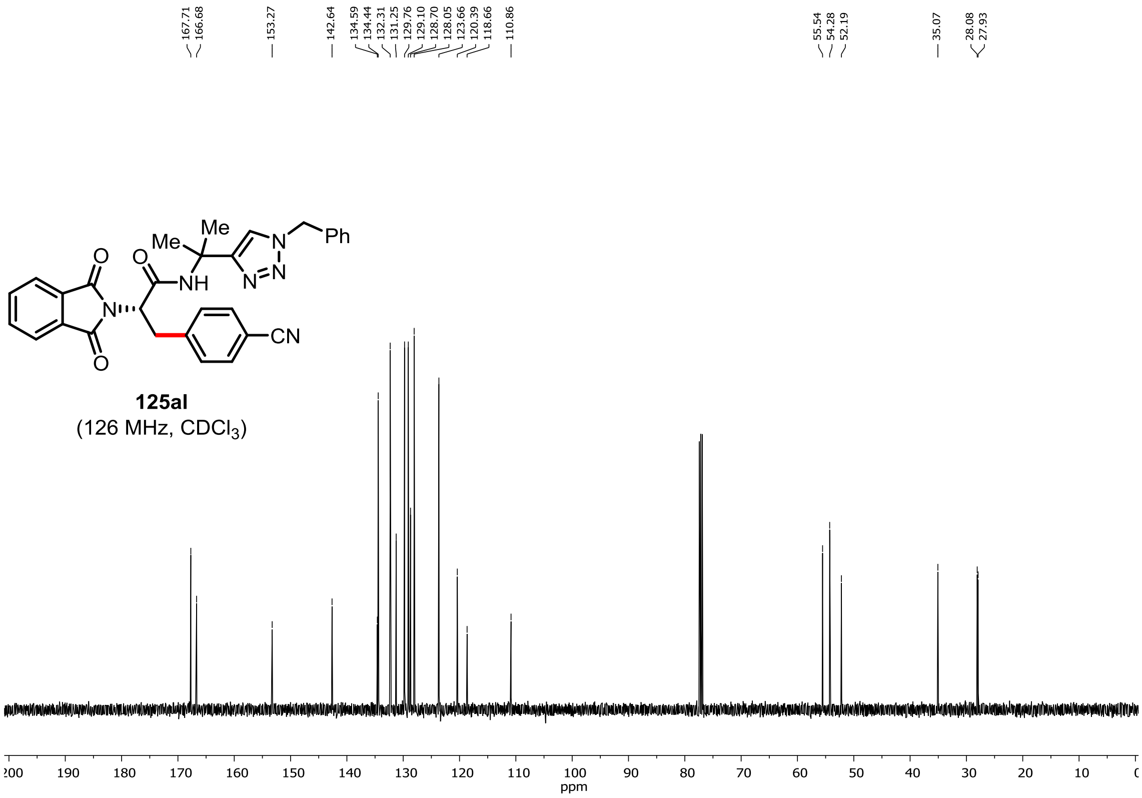
125ak
(600 MHz, $CDCl_3$)



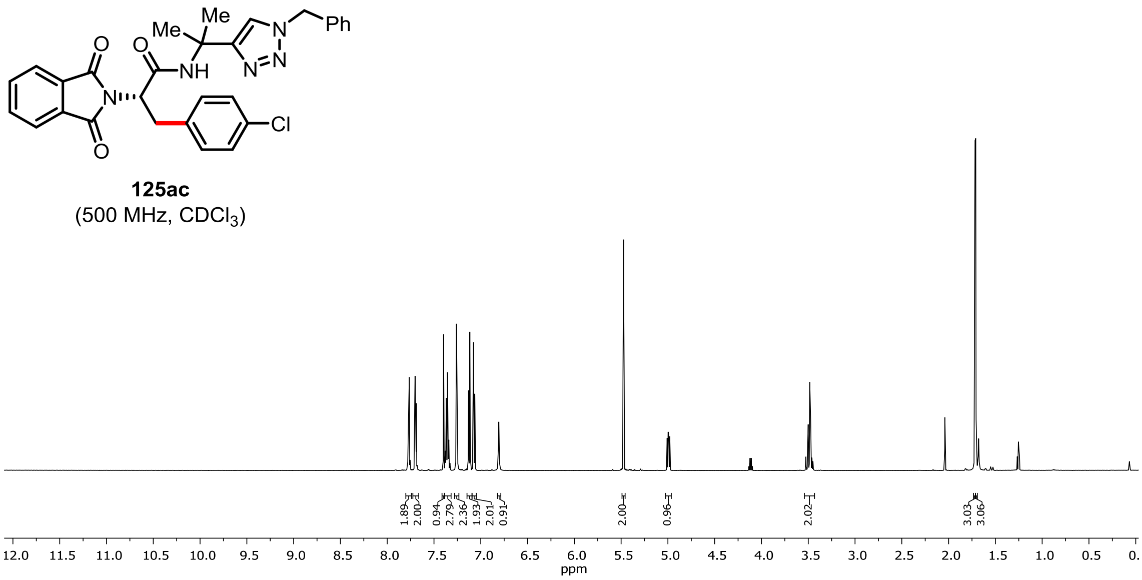
125ak
(126 MHz, $CDCl_3$)



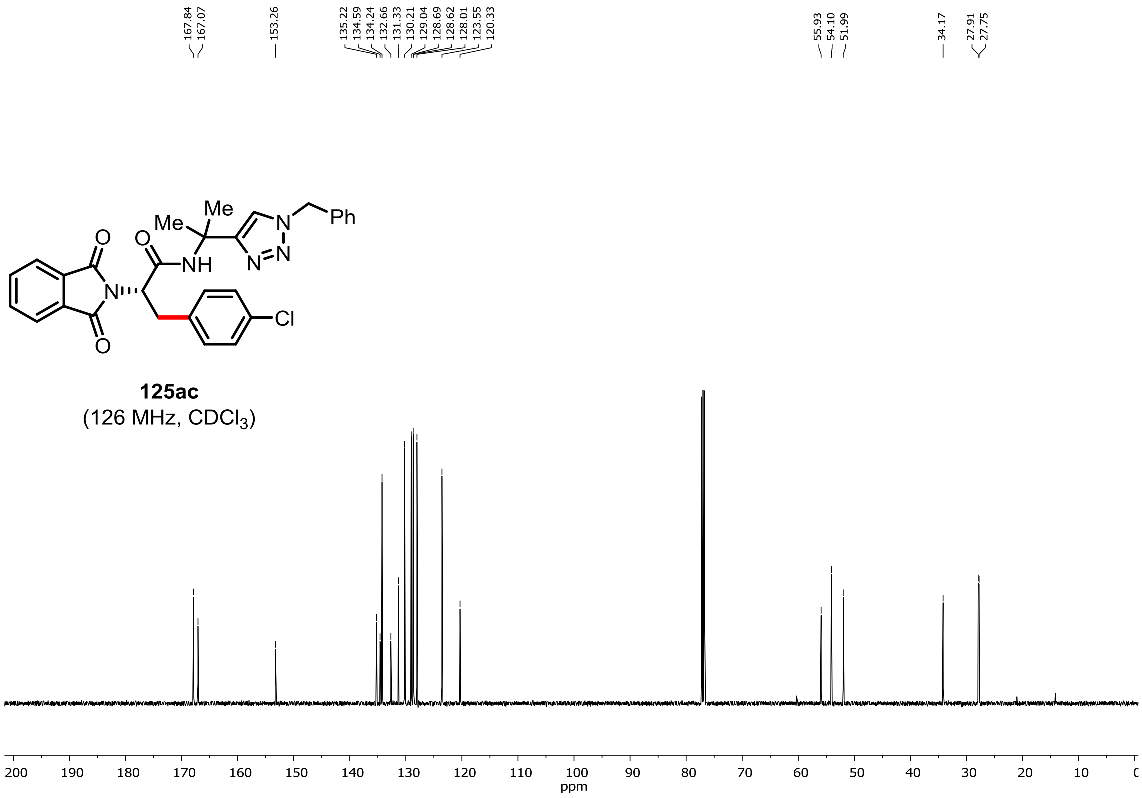
125al
(600 MHz, $CDCl_3$)



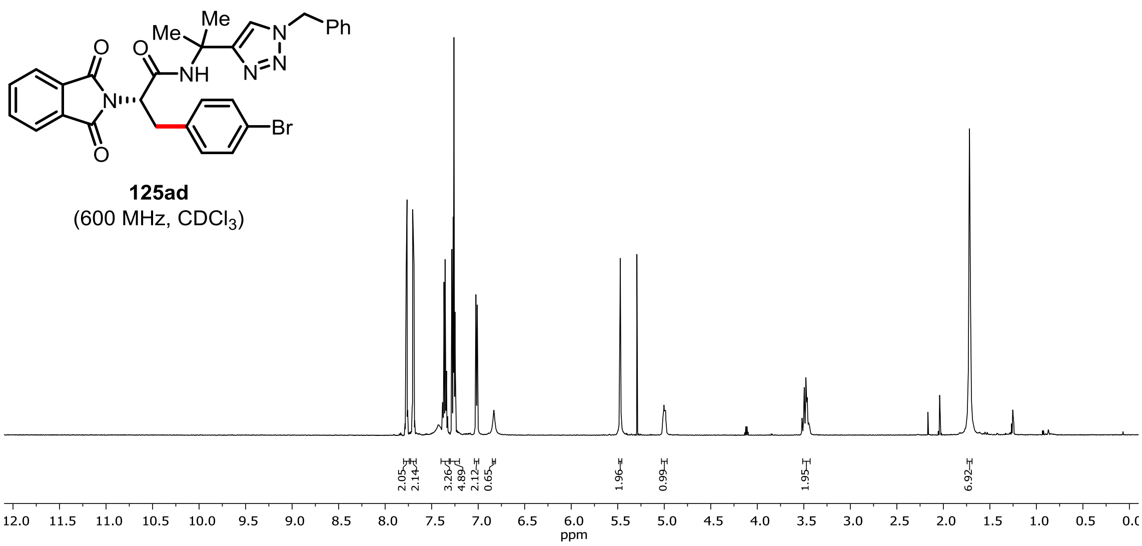
125al
(126 MHz, $CDCl_3$)



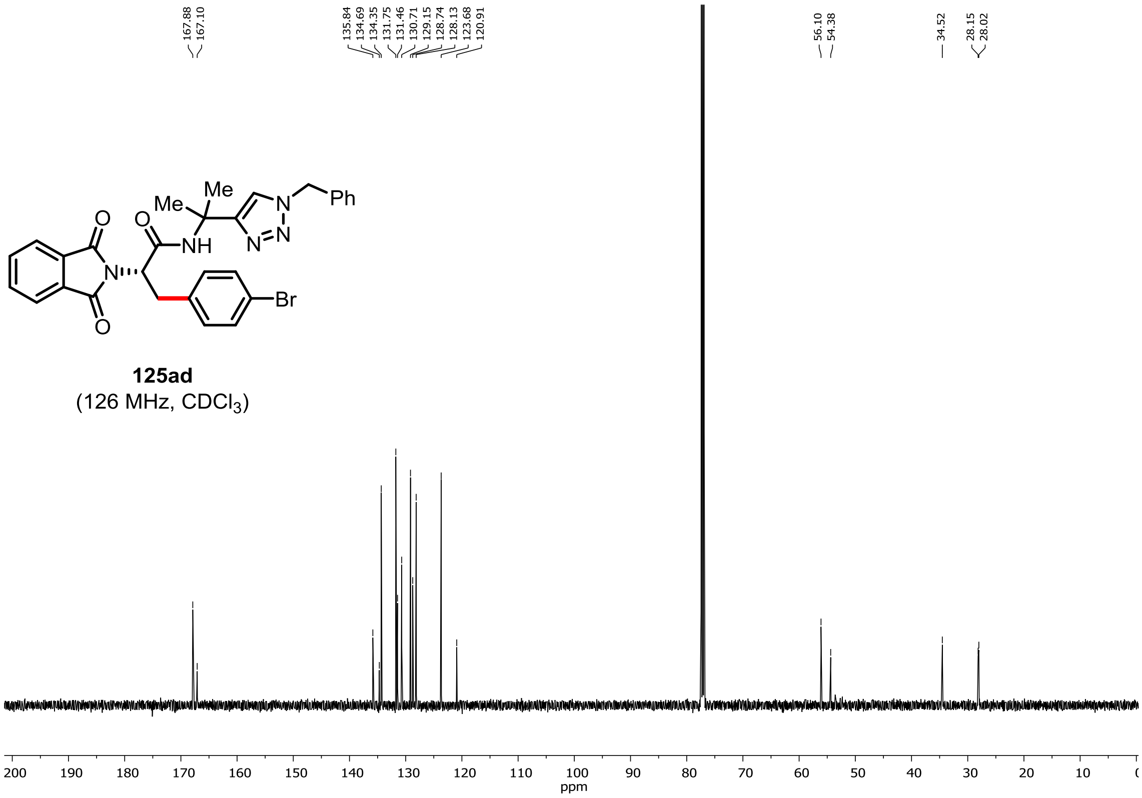
125ac
(500 MHz, $CDCl_3$)



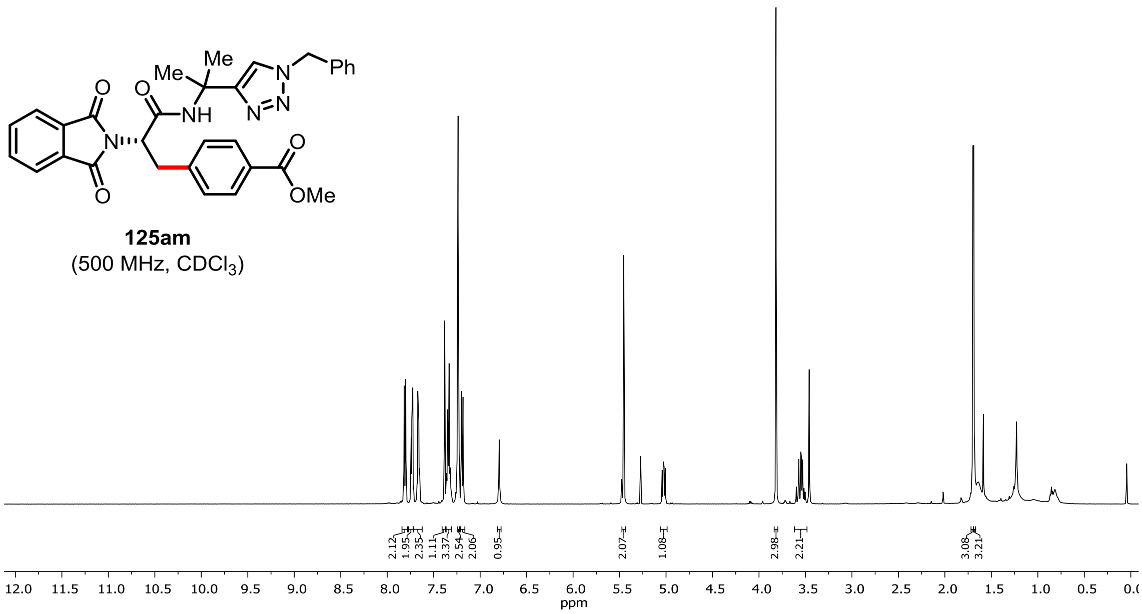
125ac
(126 MHz, $CDCl_3$)



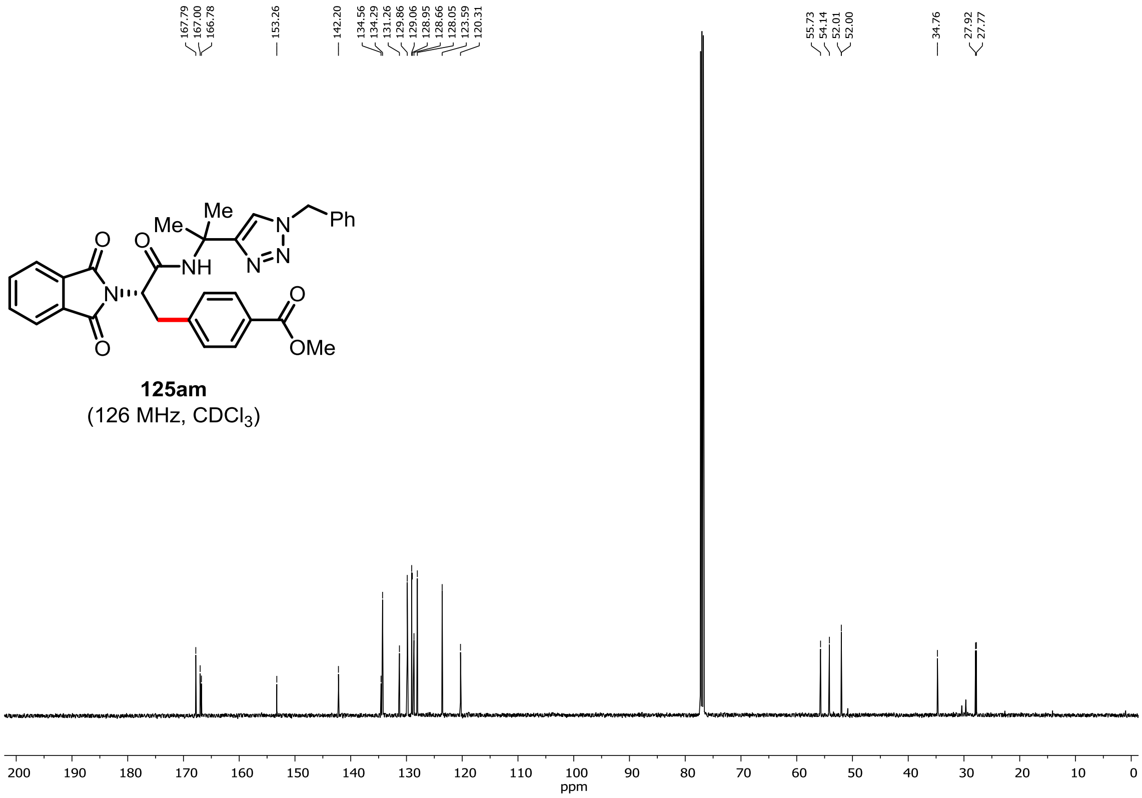
125ad
(600 MHz, $CDCl_3$)



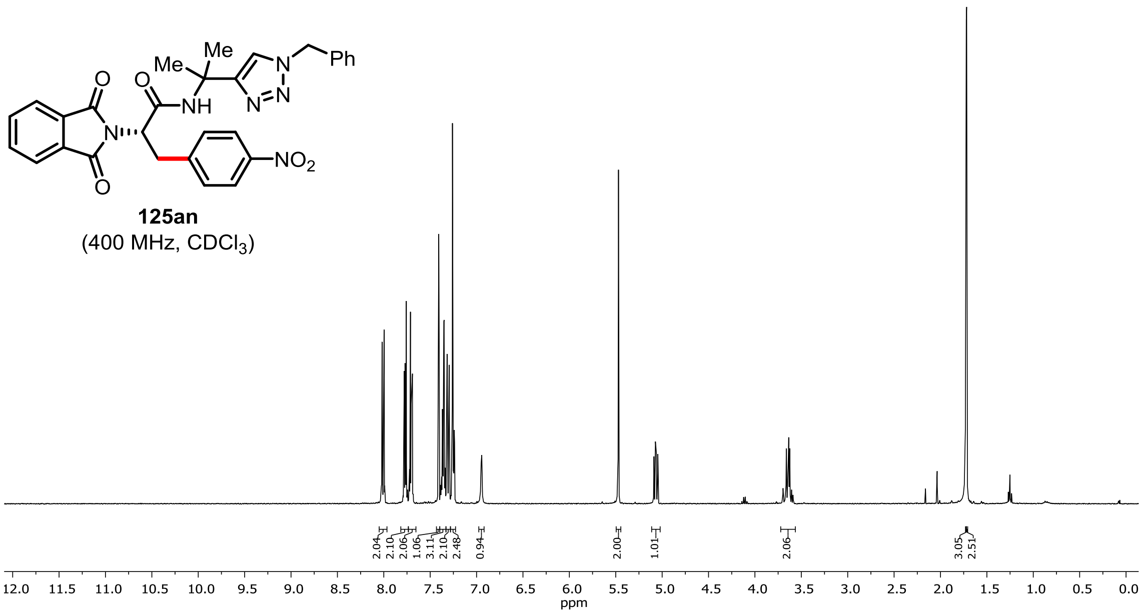
125ad
(126 MHz, $CDCl_3$)



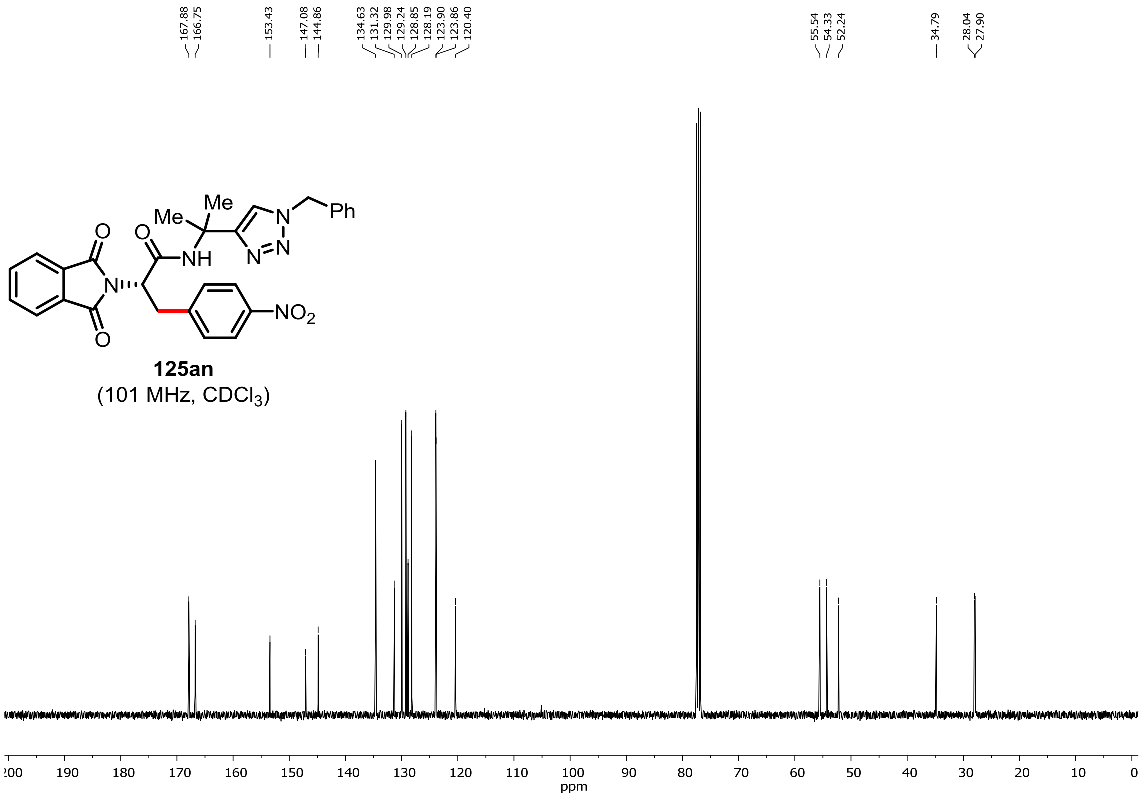
125am
(500 MHz, $CDCl_3$)



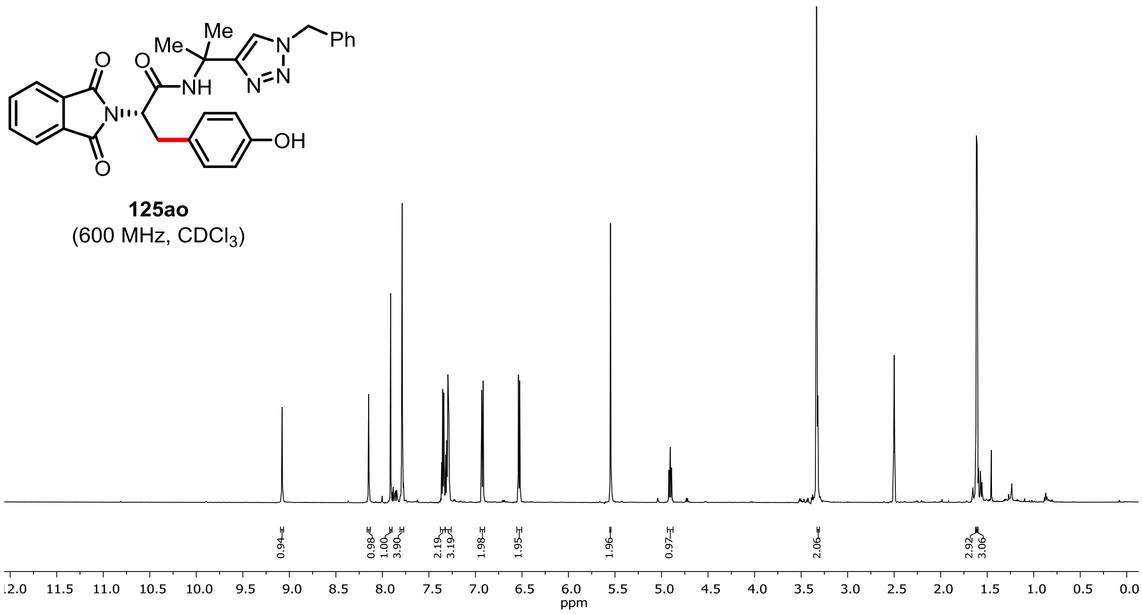
125am
(126 MHz, $CDCl_3$)



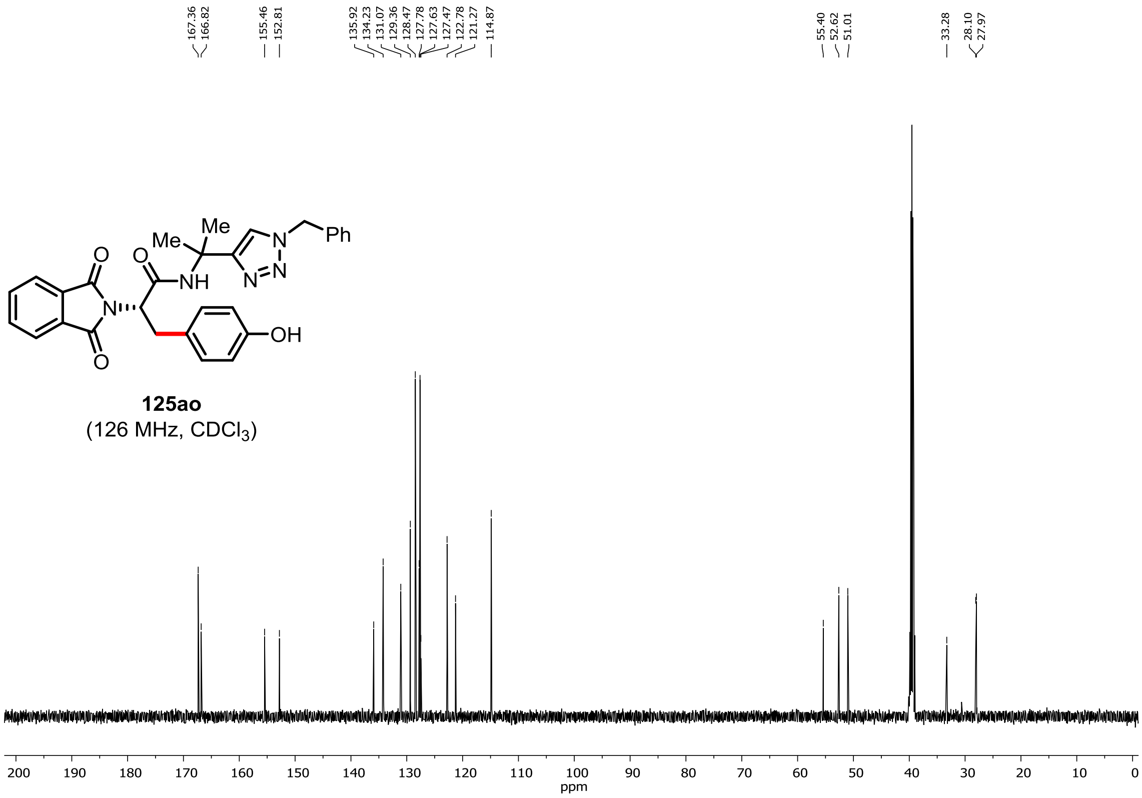
125an
(400 MHz, $CDCl_3$)



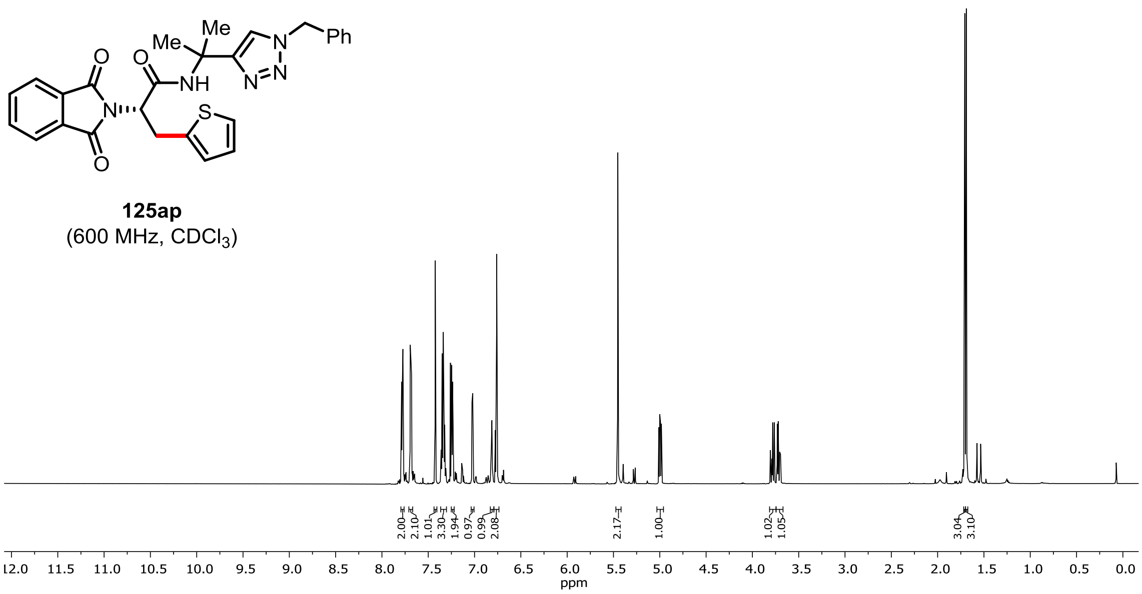
125an
(101 MHz, $CDCl_3$)



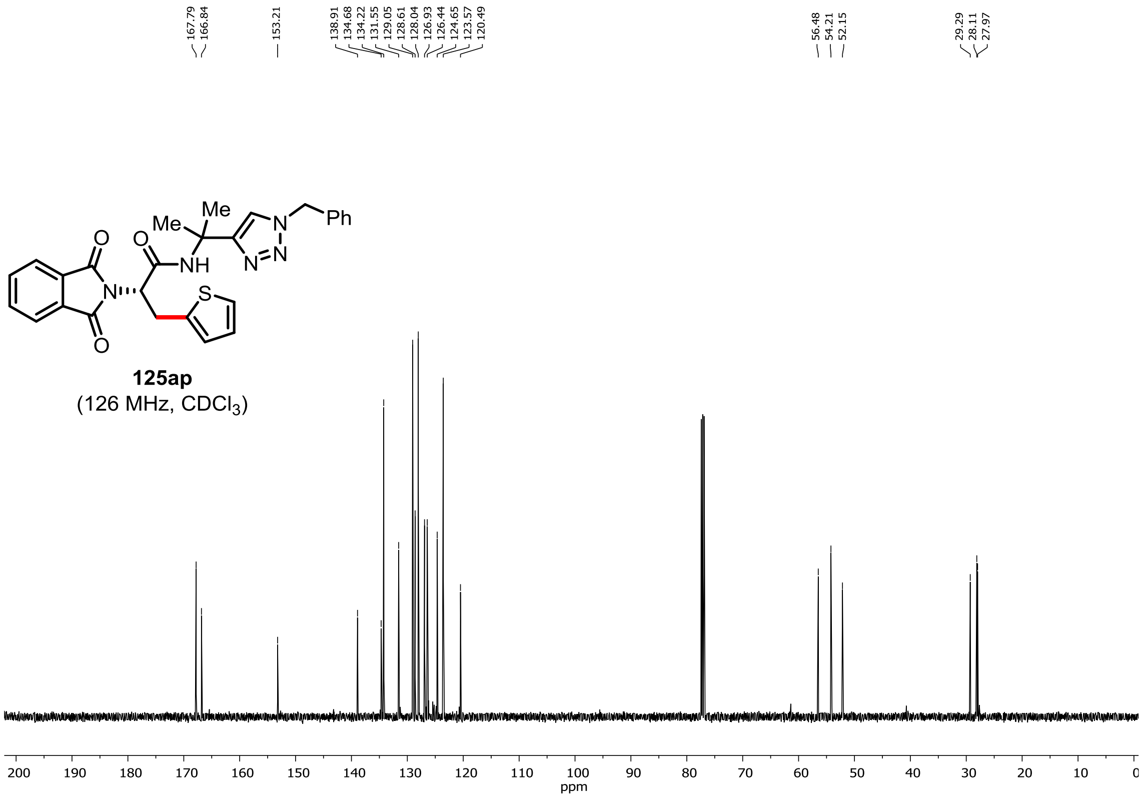
125ao
(600 MHz, $CDCl_3$)



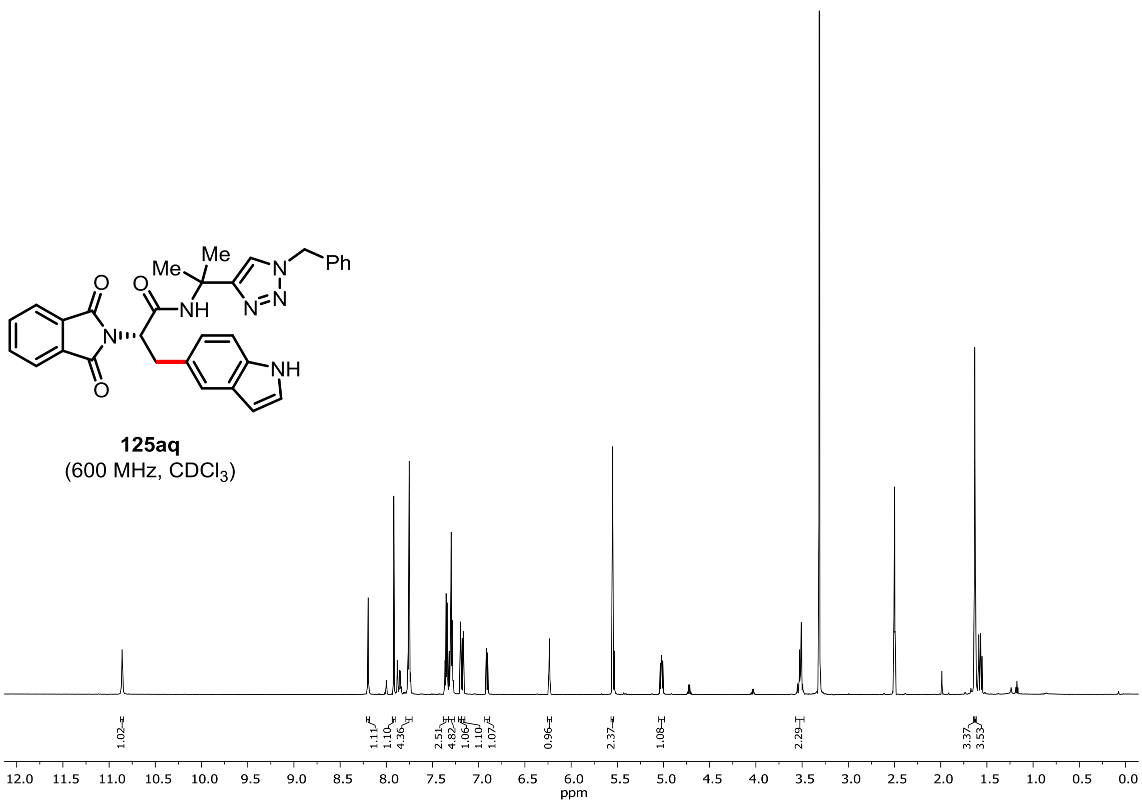
125ao
(126 MHz, $CDCl_3$)



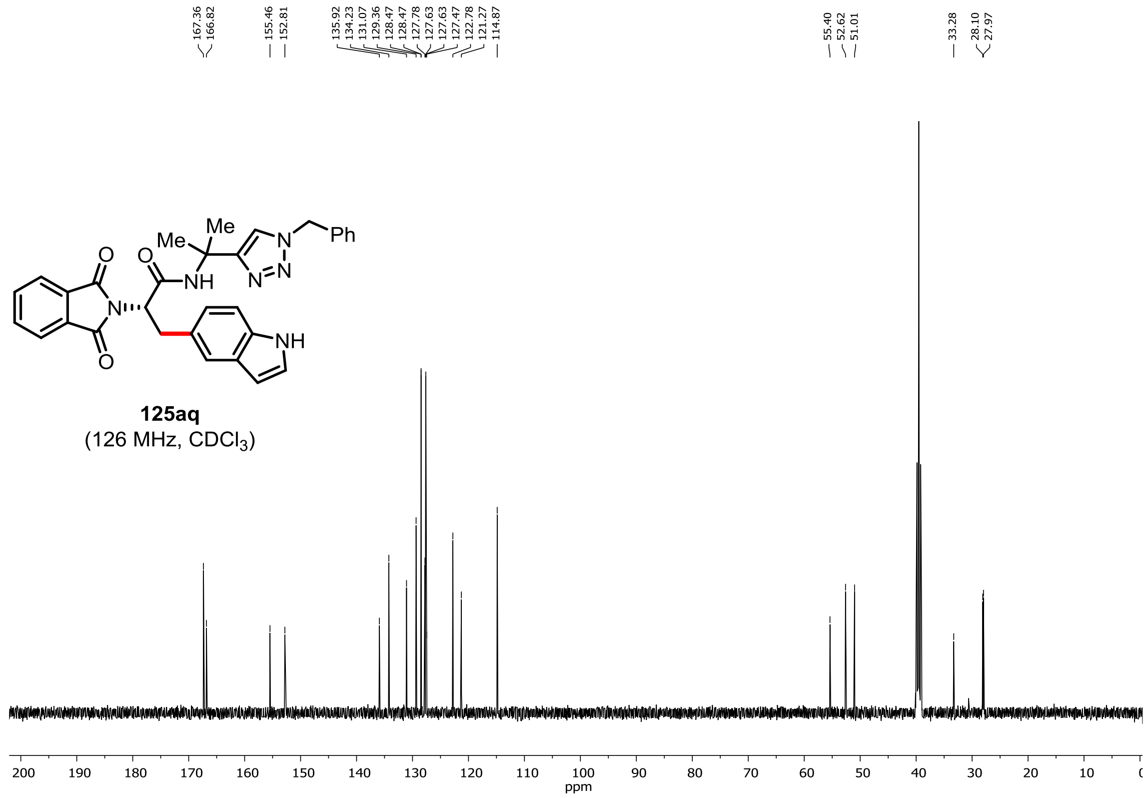
125ap
(600 MHz, $CDCl_3$)



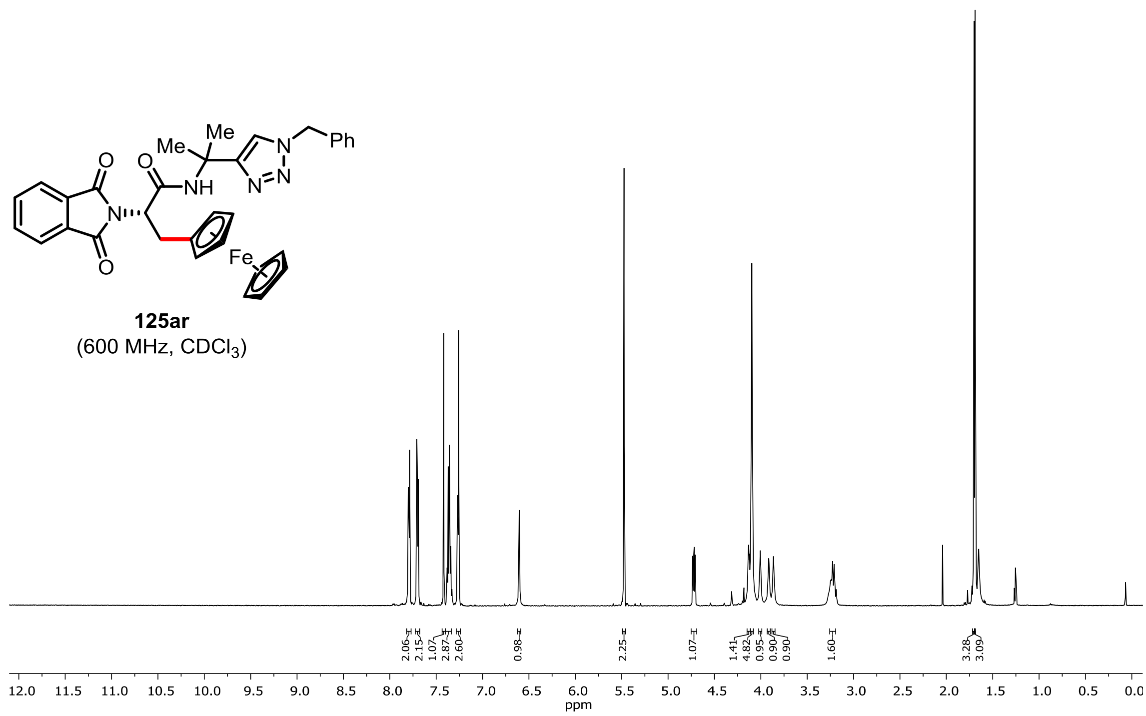
125ap
(126 MHz, $CDCl_3$)



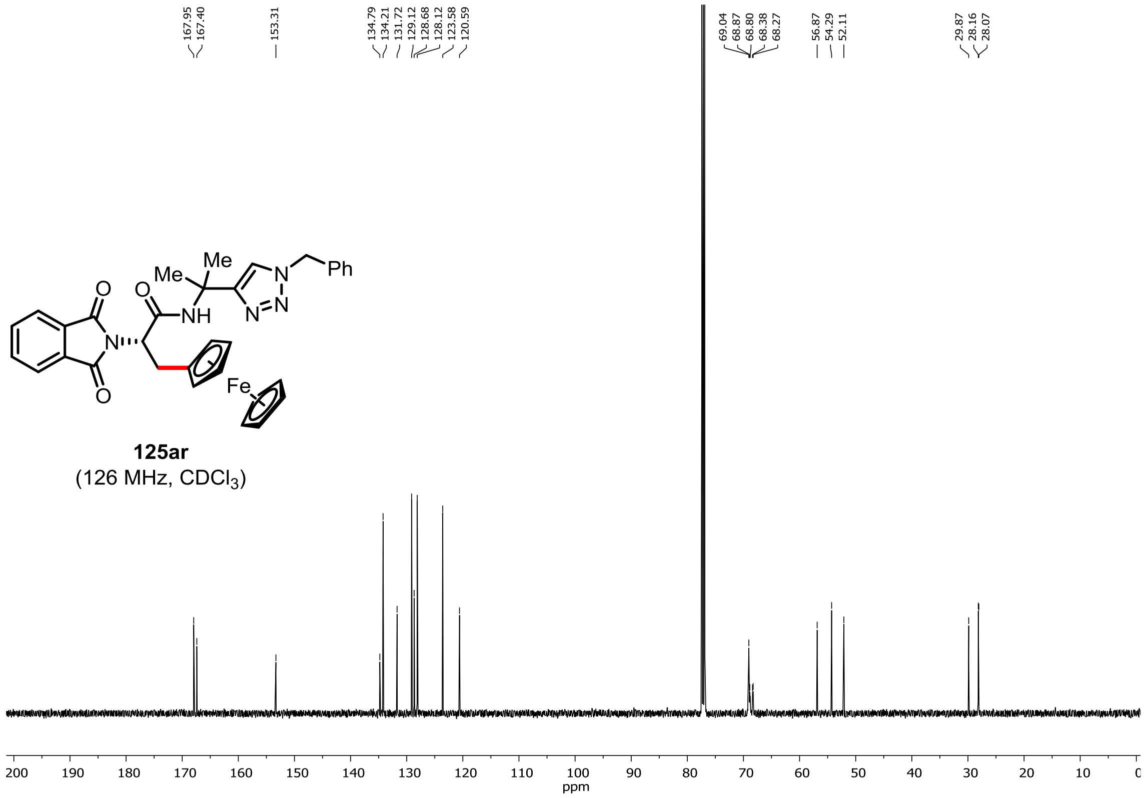
125aq
(600 MHz, $CDCl_3$)



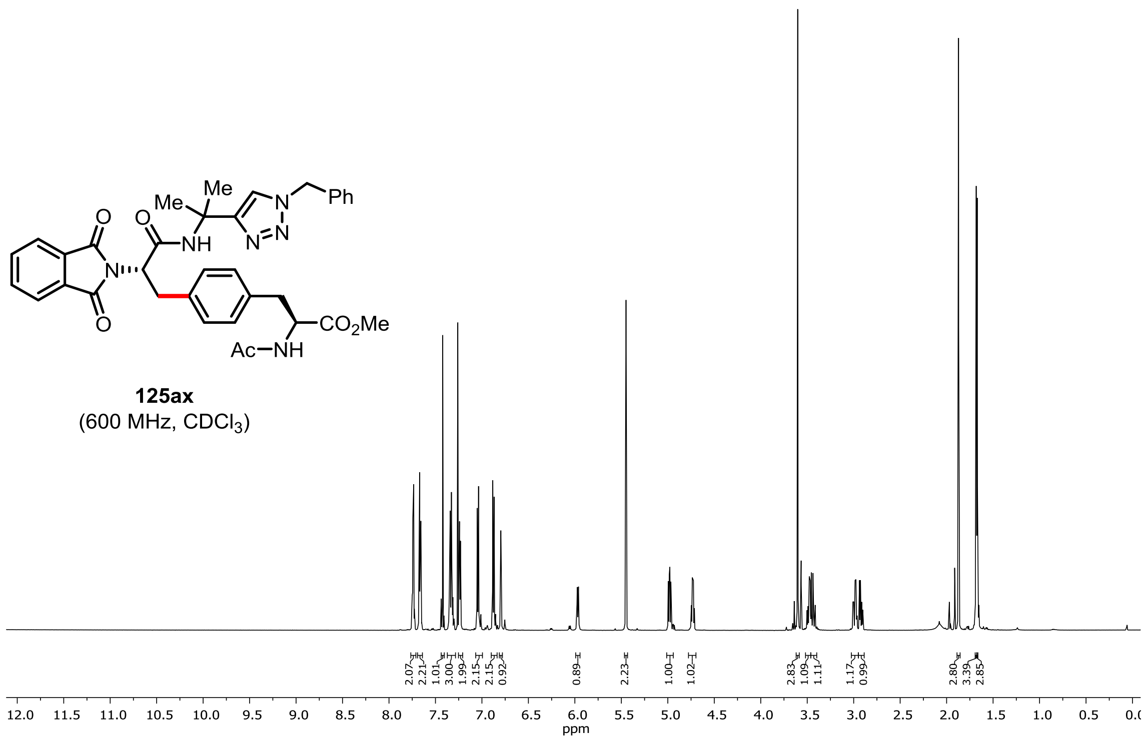
125aq
(126 MHz, $CDCl_3$)



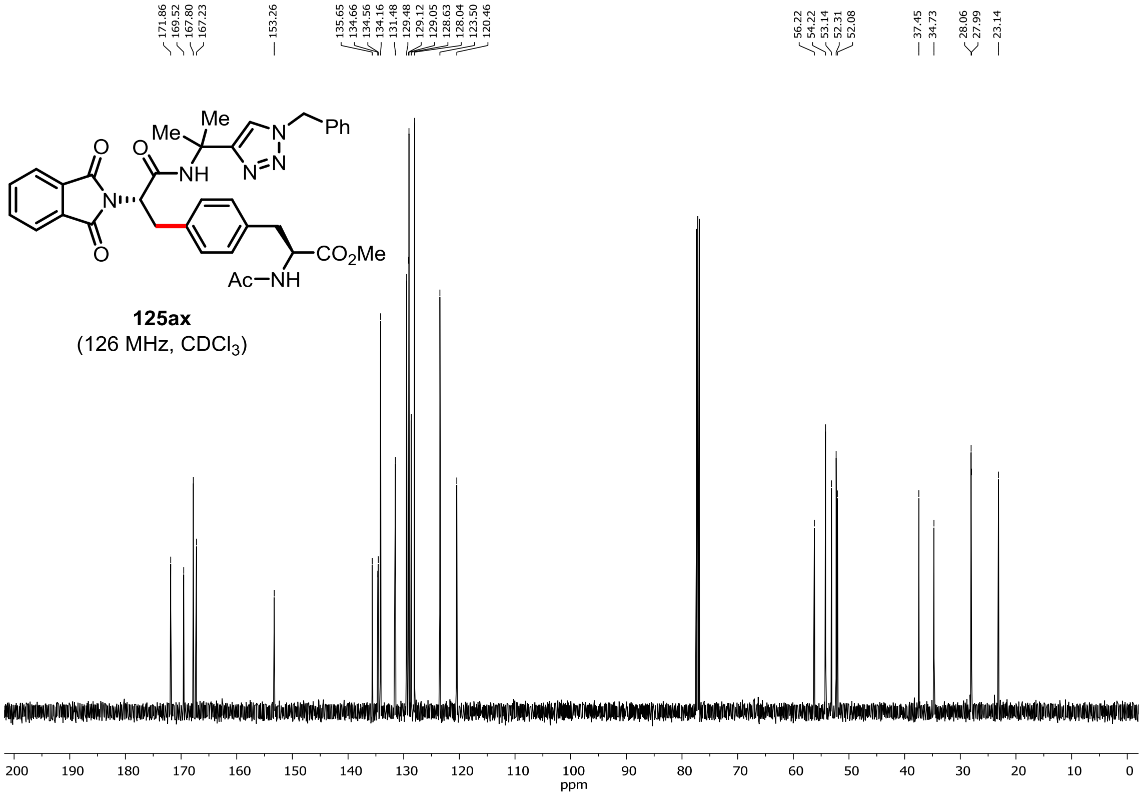
125ar
(600 MHz, $CDCl_3$)



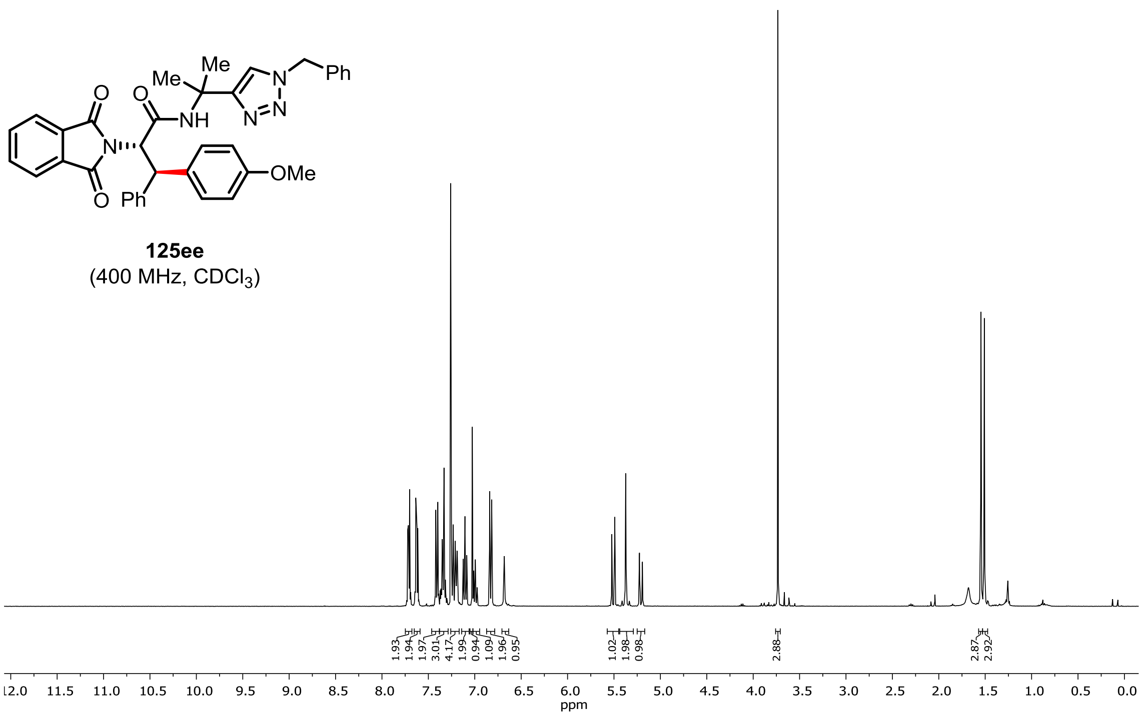
125ar
(126 MHz, $CDCl_3$)



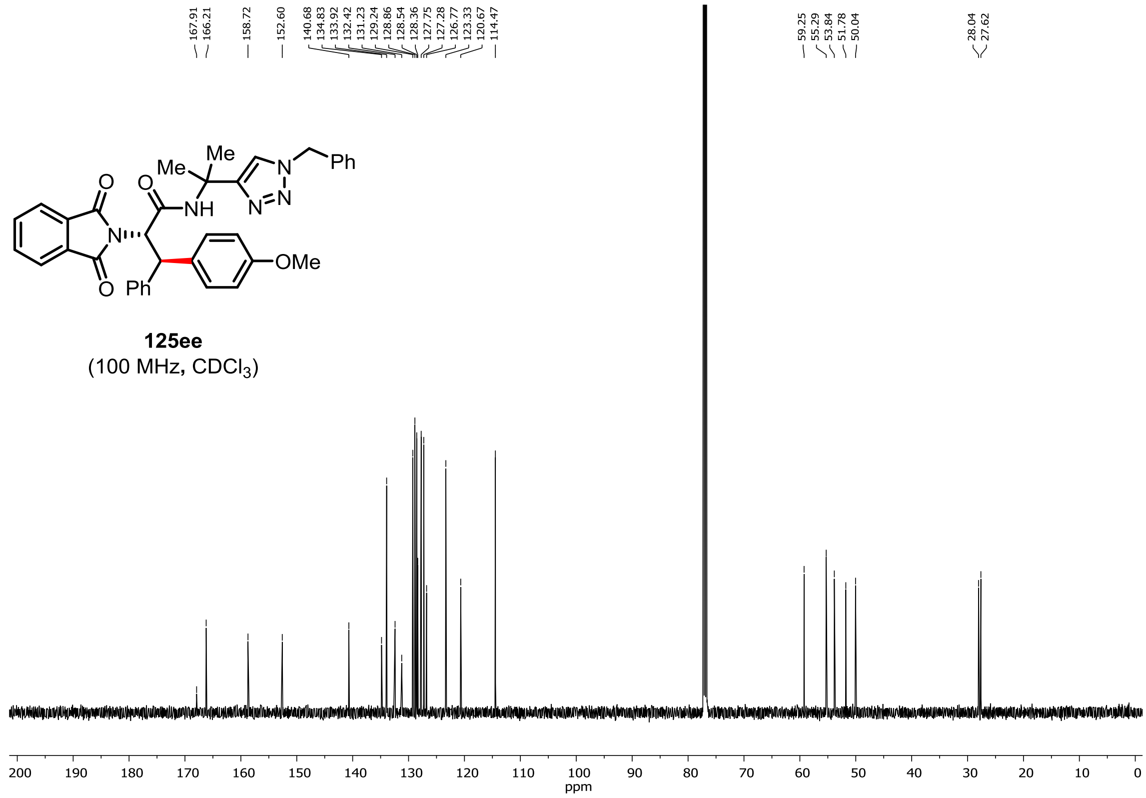
125ax
(600 MHz, $CDCl_3$)



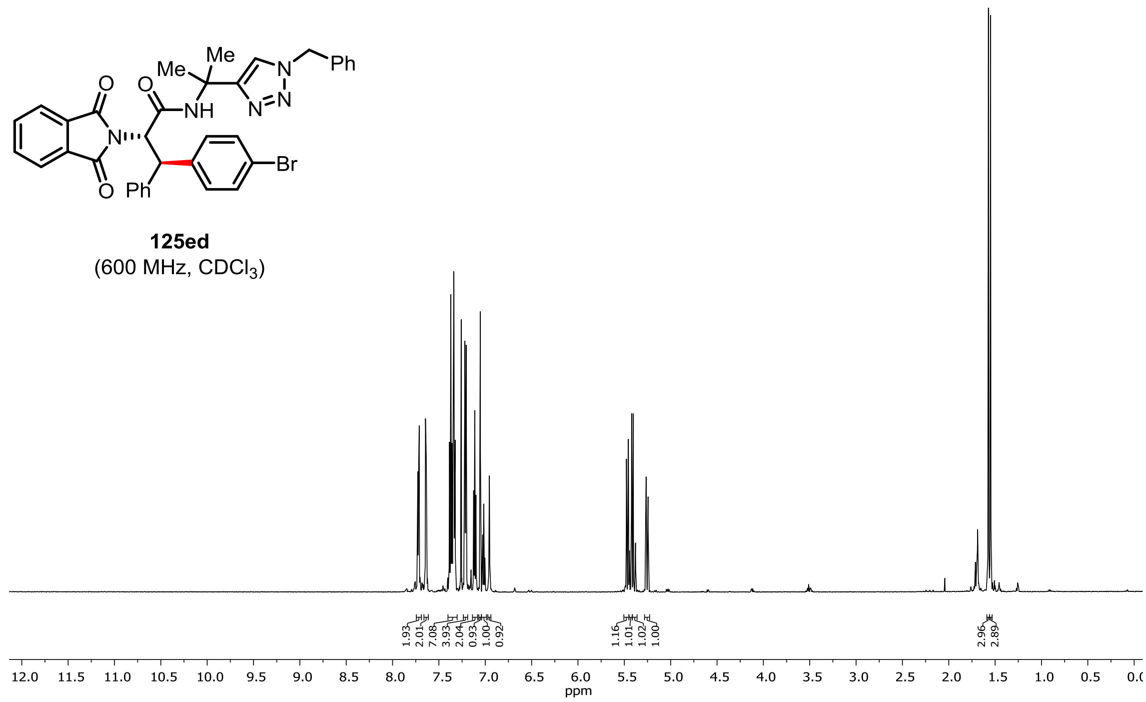
125ax
(126 MHz, $CDCl_3$)



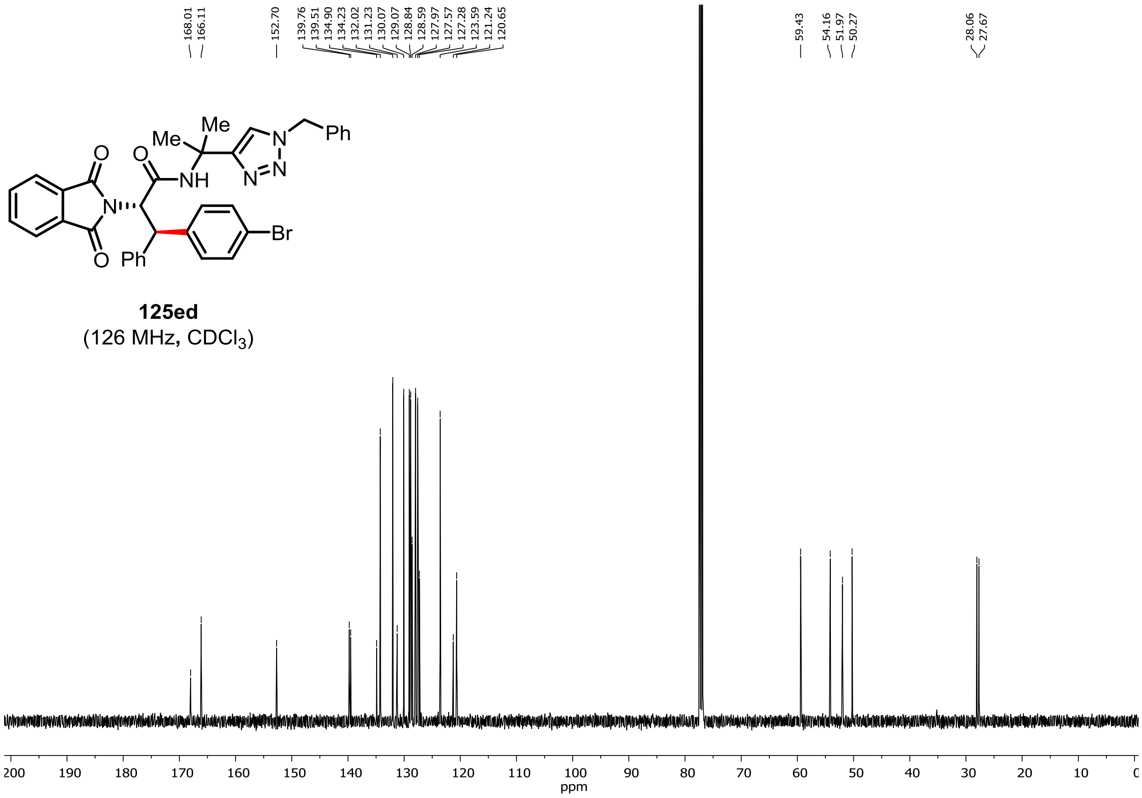
125ee
(400 MHz, $CDCl_3$)



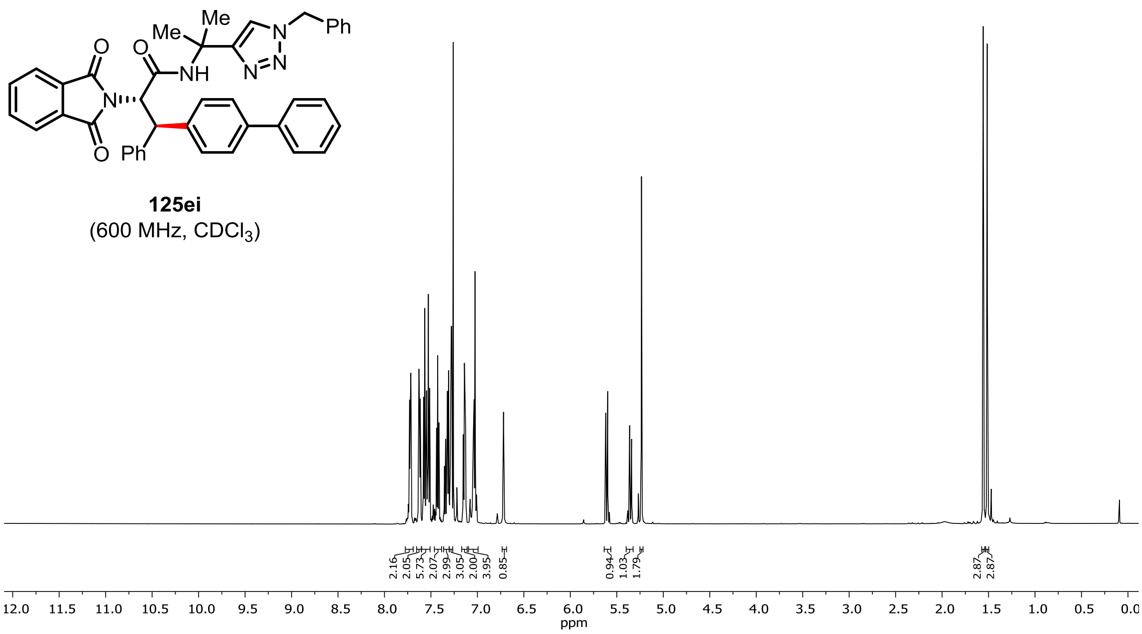
125ee
(100 MHz, $CDCl_3$)



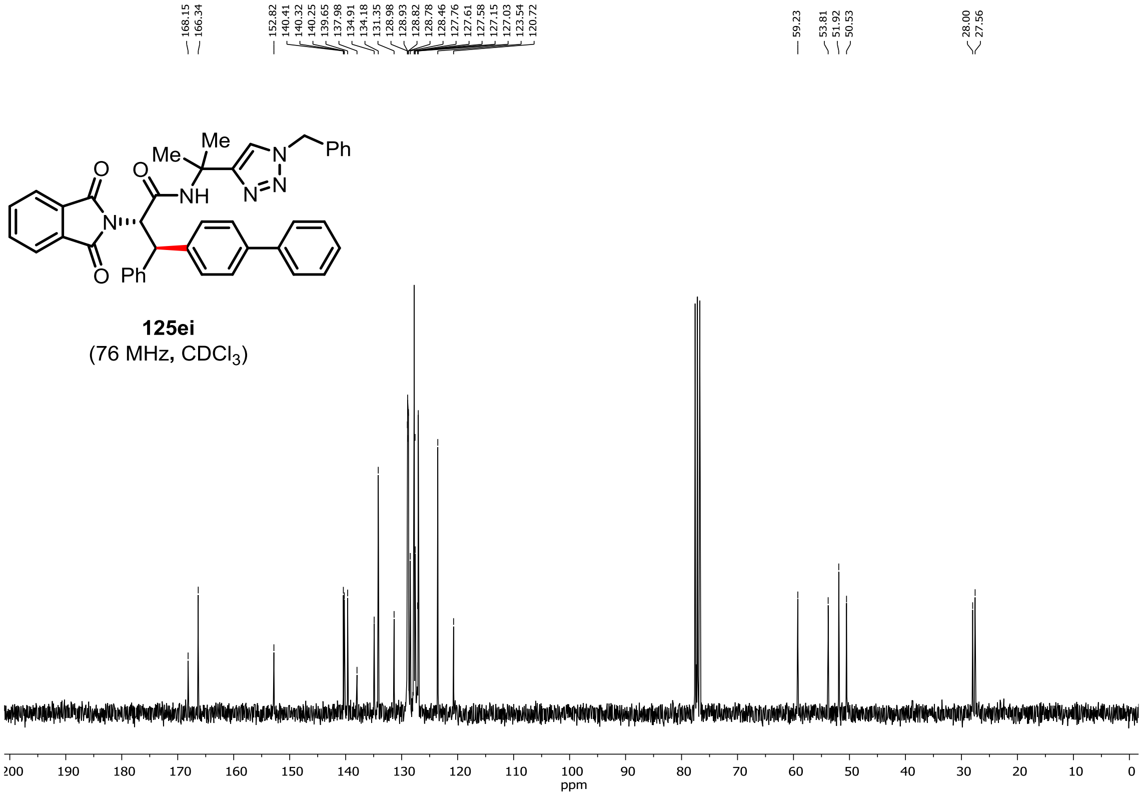
125ed
(600 MHz, $CDCl_3$)



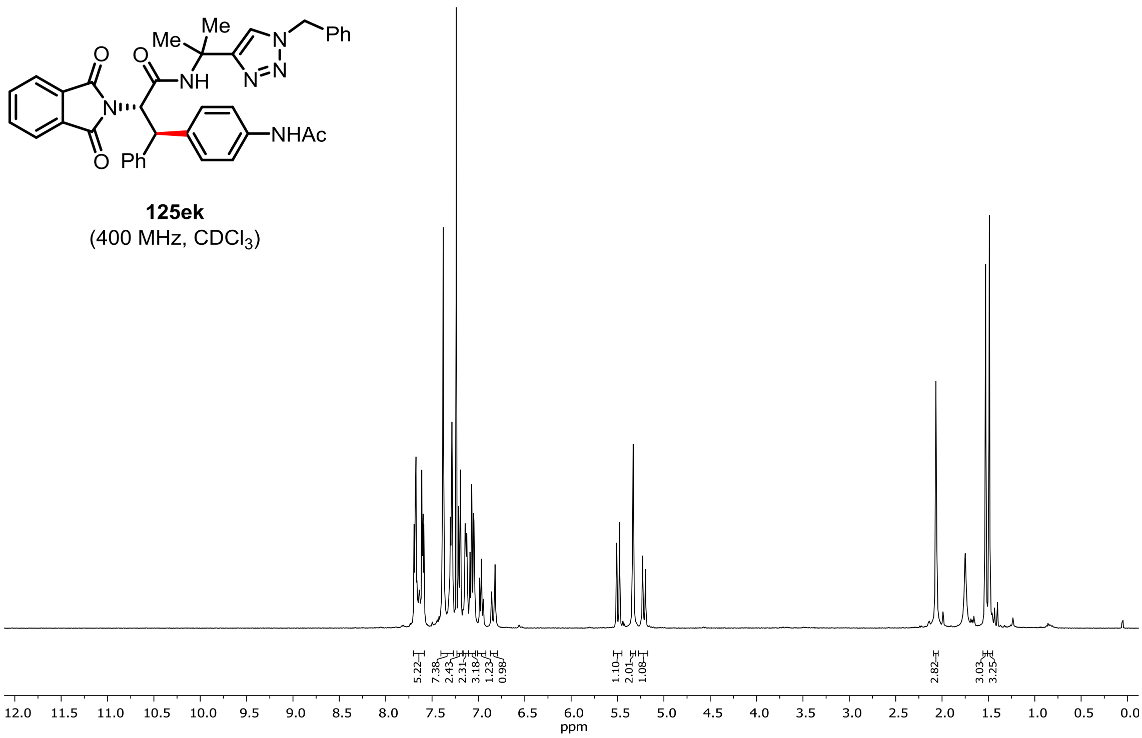
125ed
(126 MHz, $CDCl_3$)



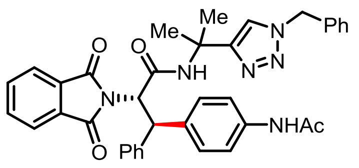
125ei
(600 MHz, $CDCl_3$)



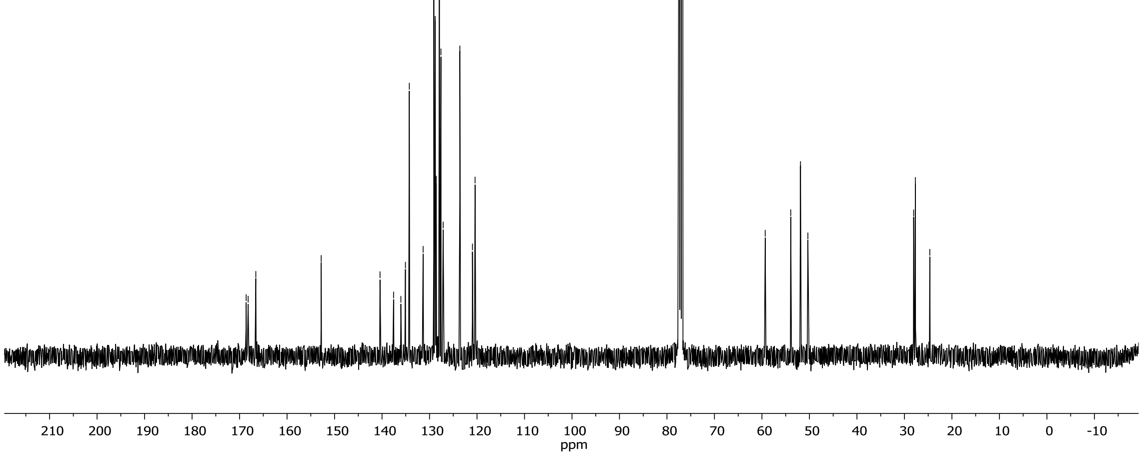
125ei
(76 MHz, $CDCl_3$)

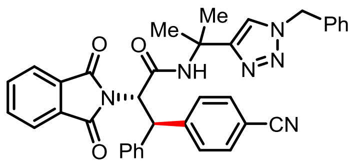


125ek
(400 MHz, $CDCl_3$)

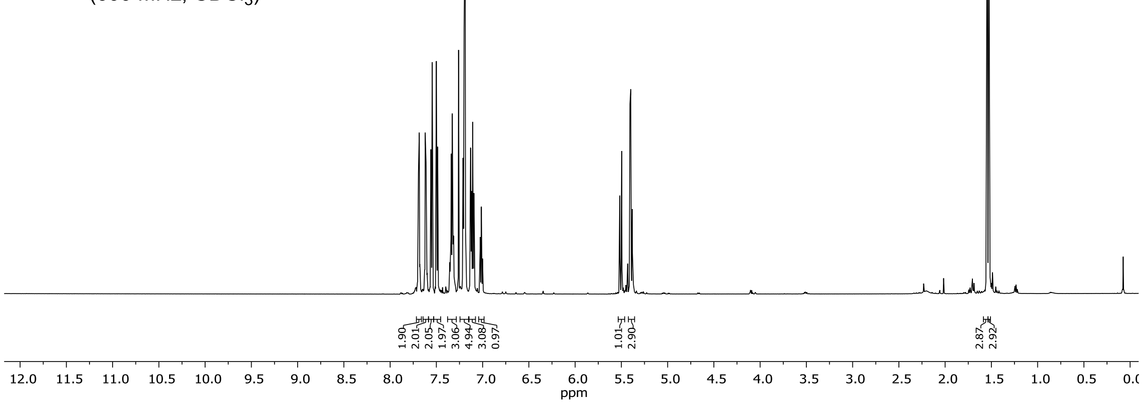


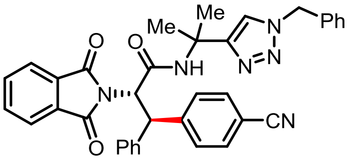
125ek
(101 MHz, $CDCl_3$)



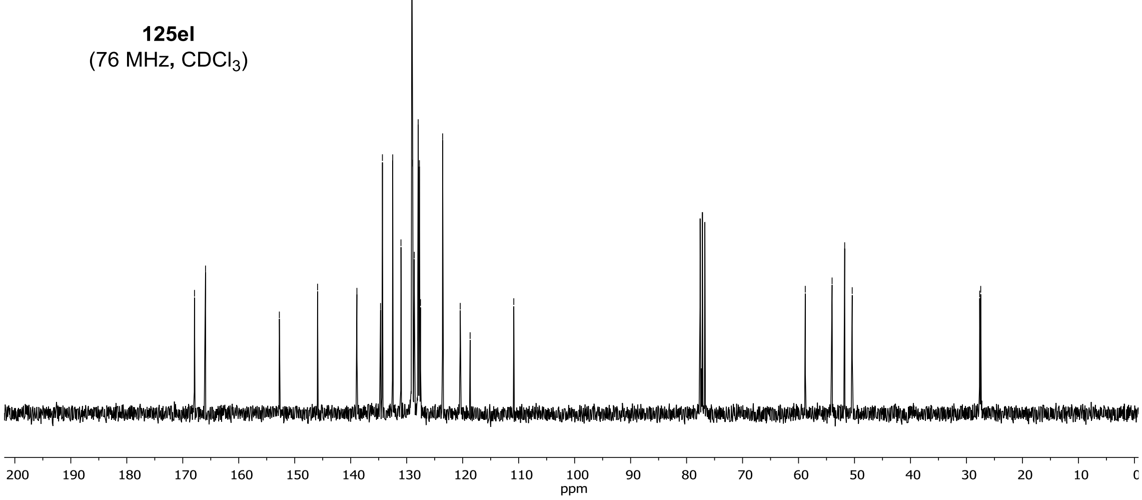


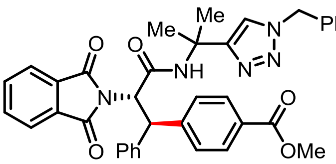
125el
(600 MHz, $CDCl_3$)



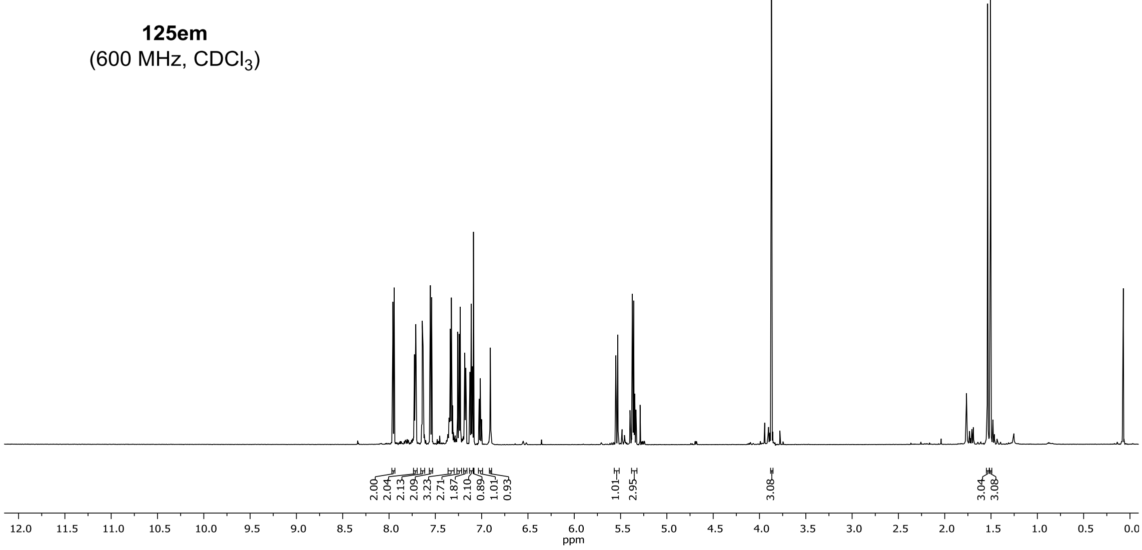


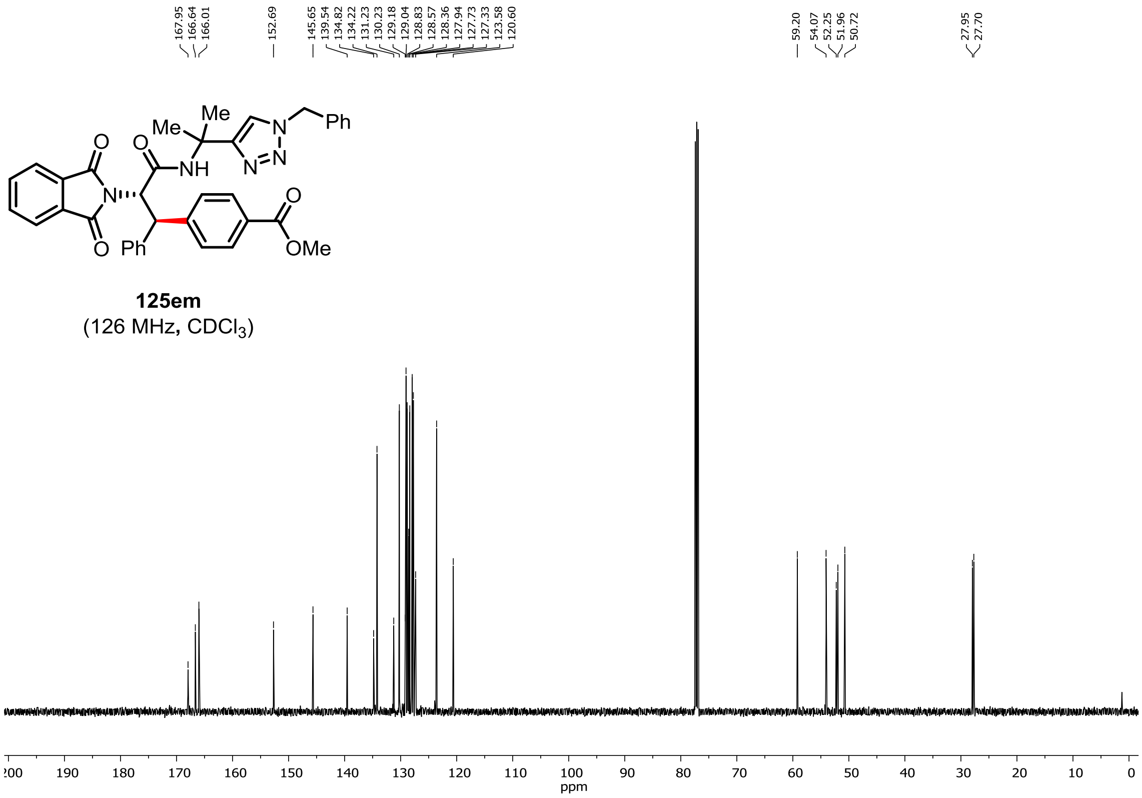
125el
(76 MHz, $CDCl_3$)



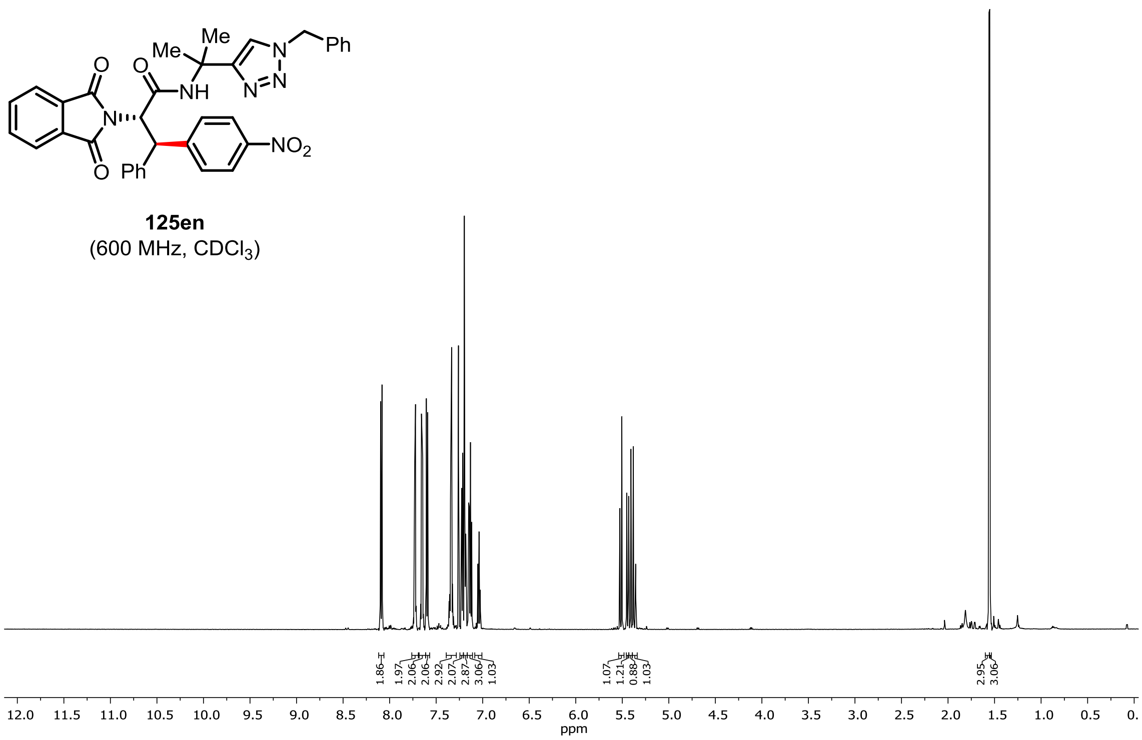


125em
(600 MHz, $CDCl_3$)

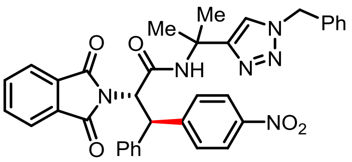




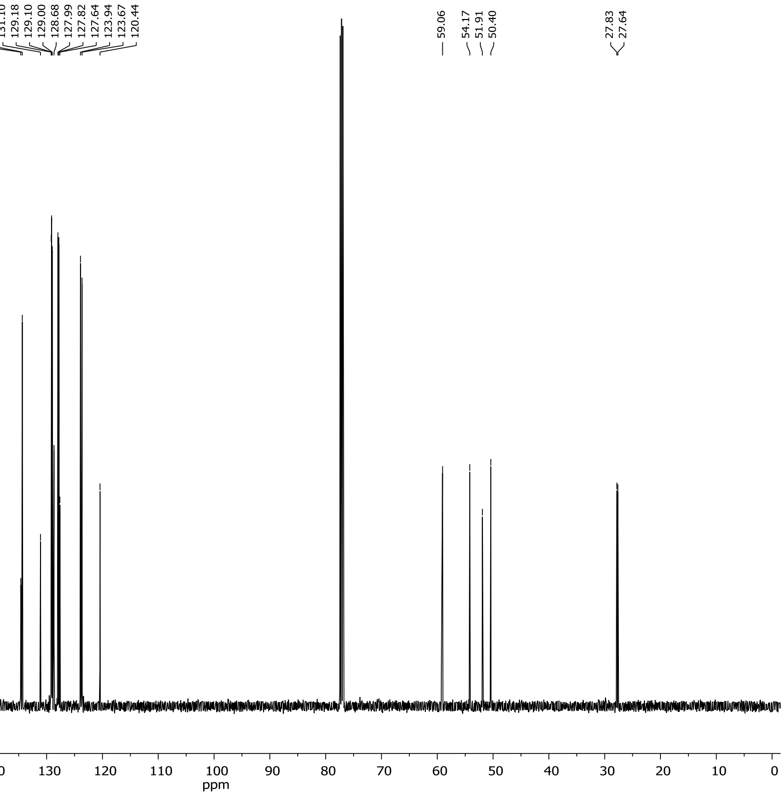
125em
(126 MHz, $CDCl_3$)

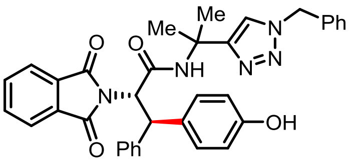


125en
(600 MHz, $CDCl_3$)

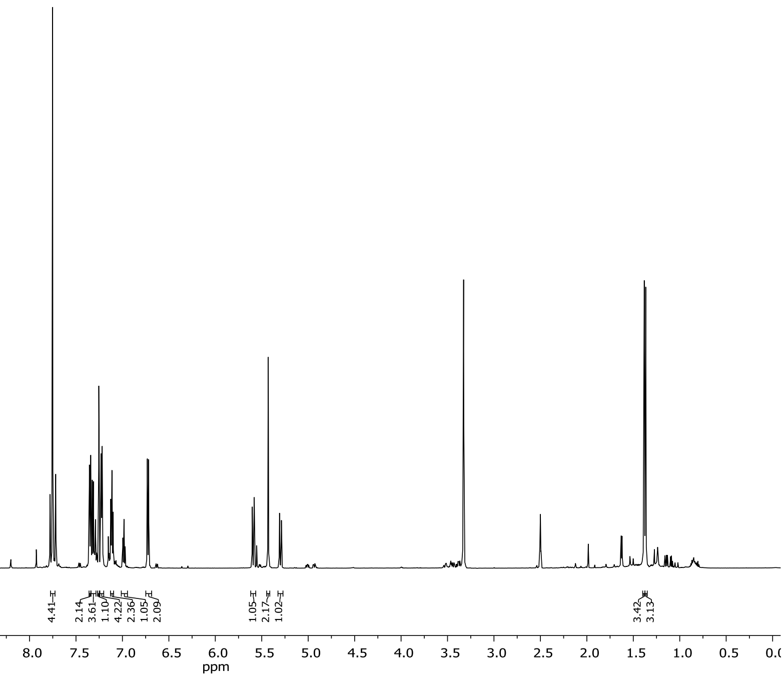


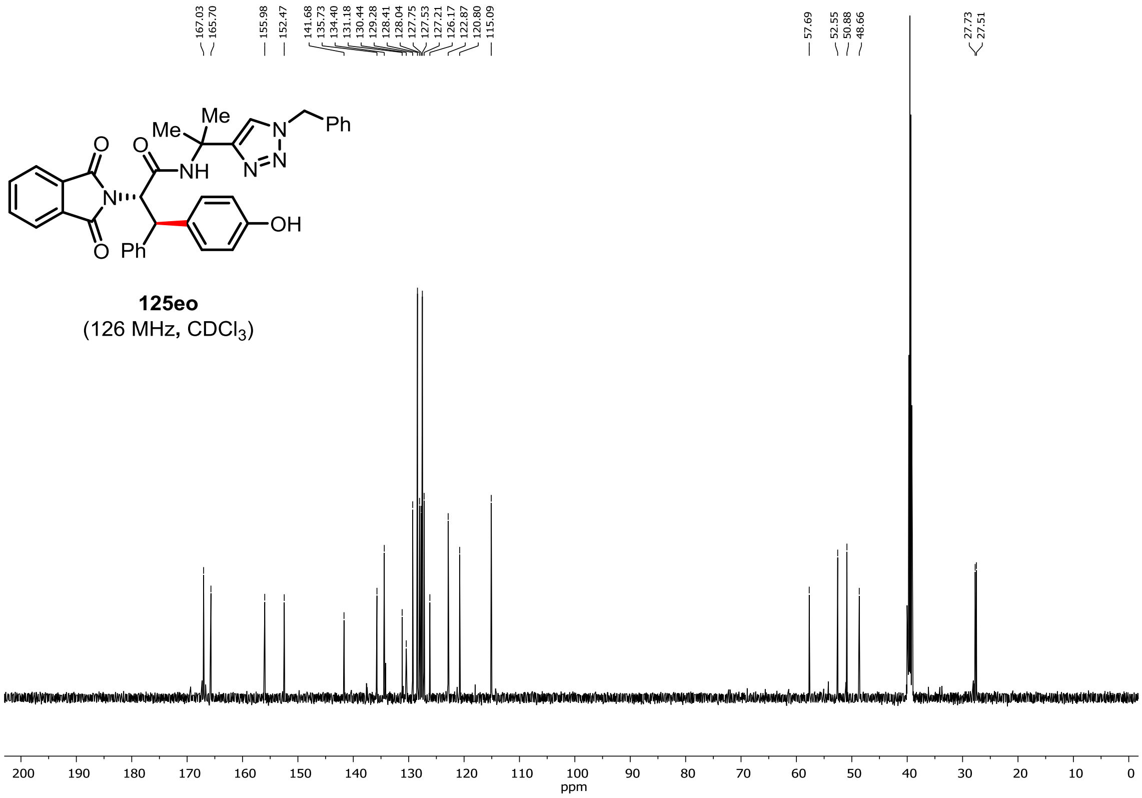
125en
(126 MHz, $CDCl_3$)



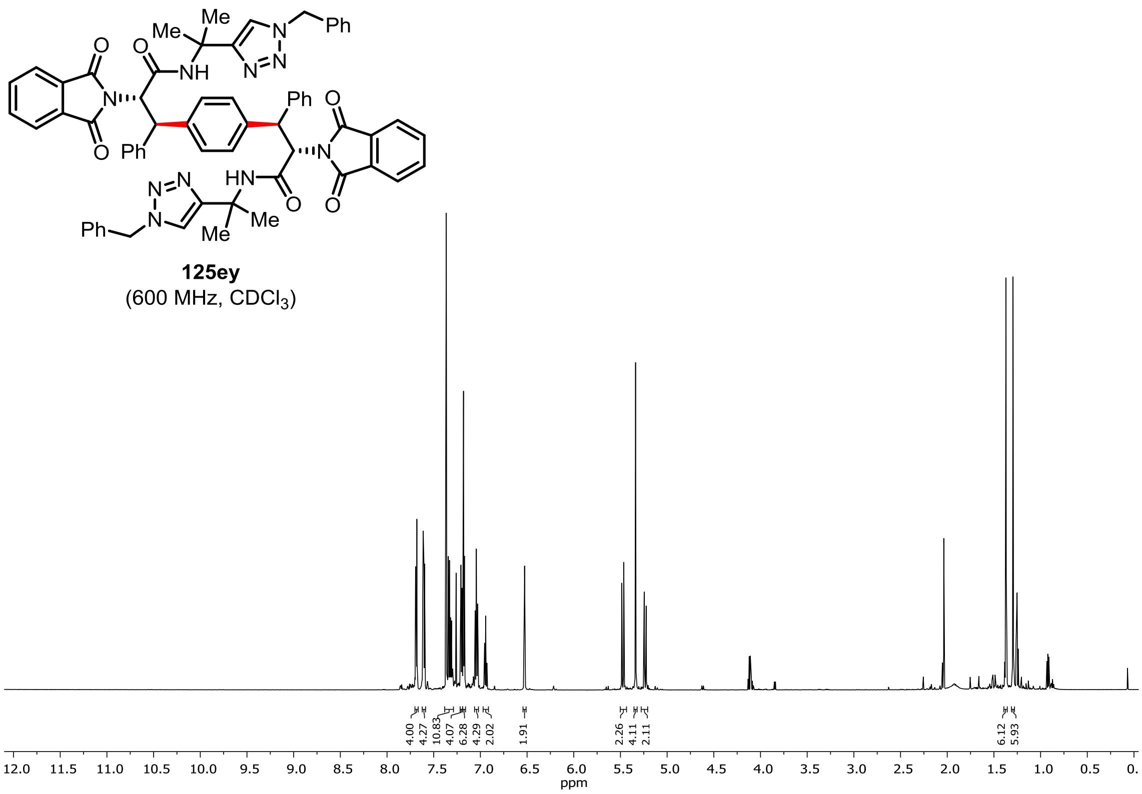


125eo
(600 MHz, $CDCl_3$)

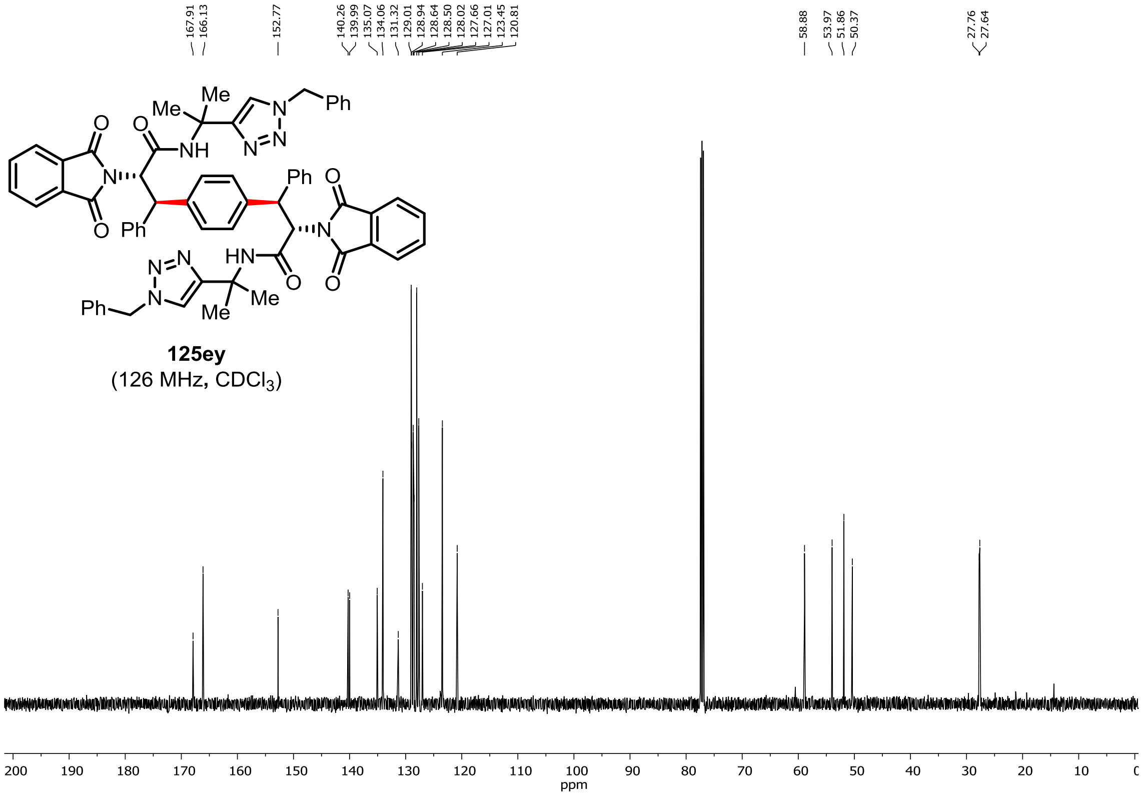




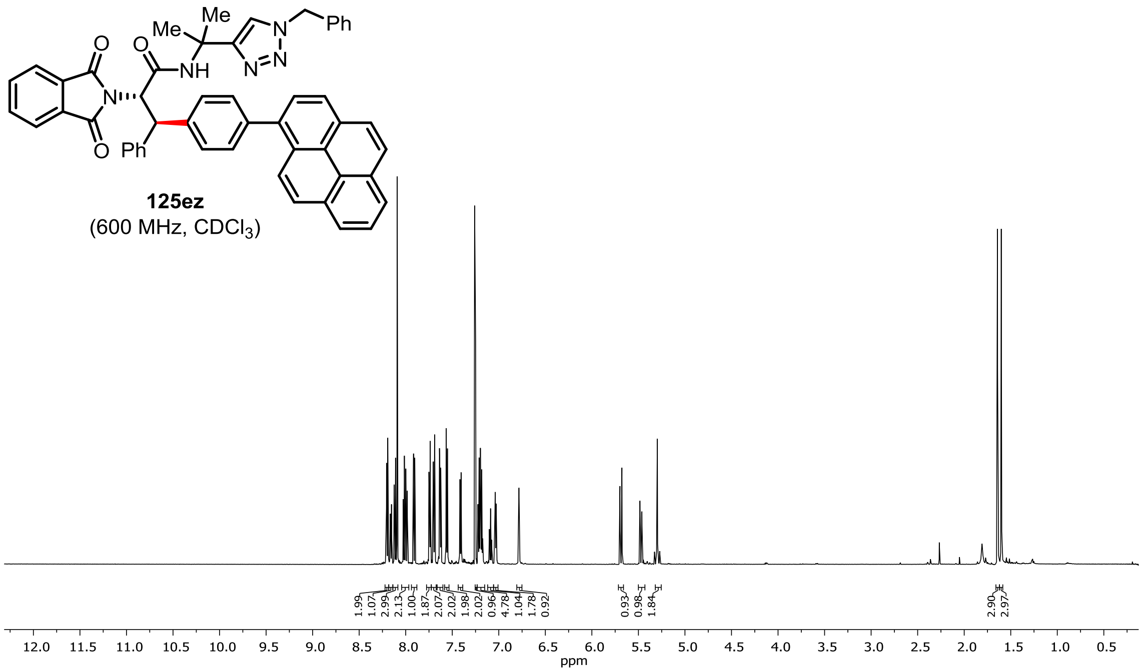
125eo
(126 MHz, $CDCl_3$)



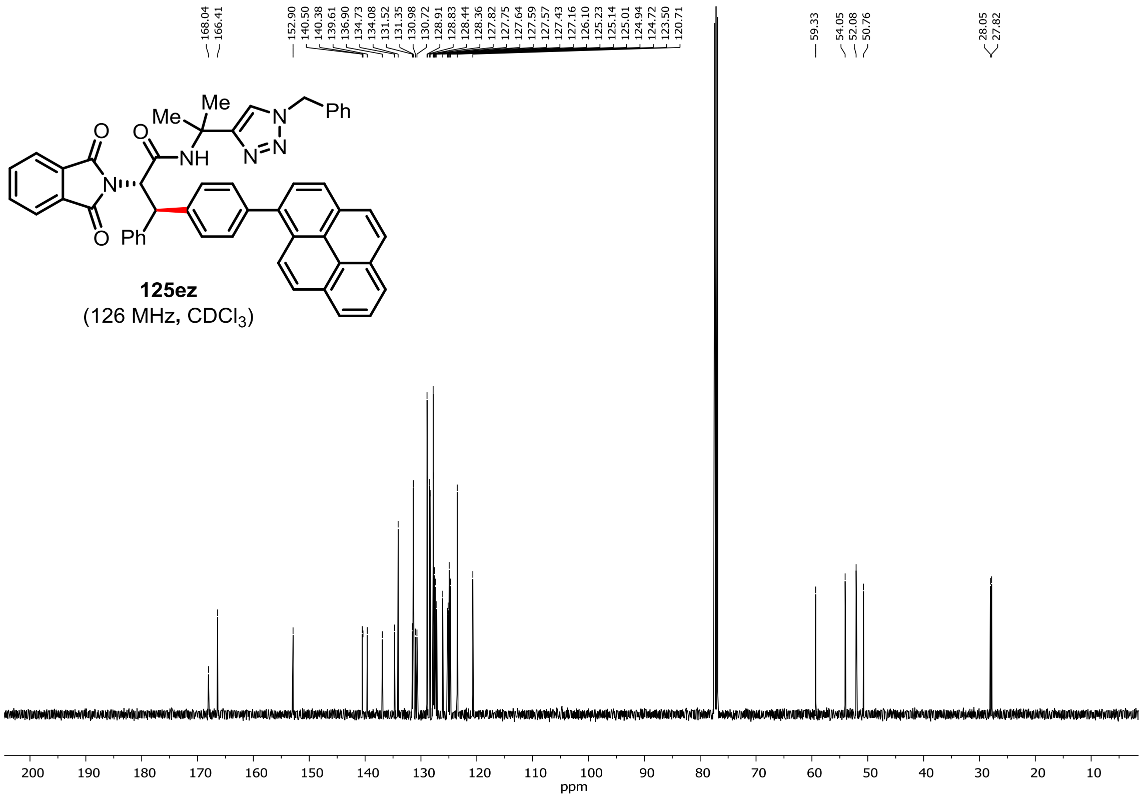
125ey
(600 MHz, $CDCl_3$)



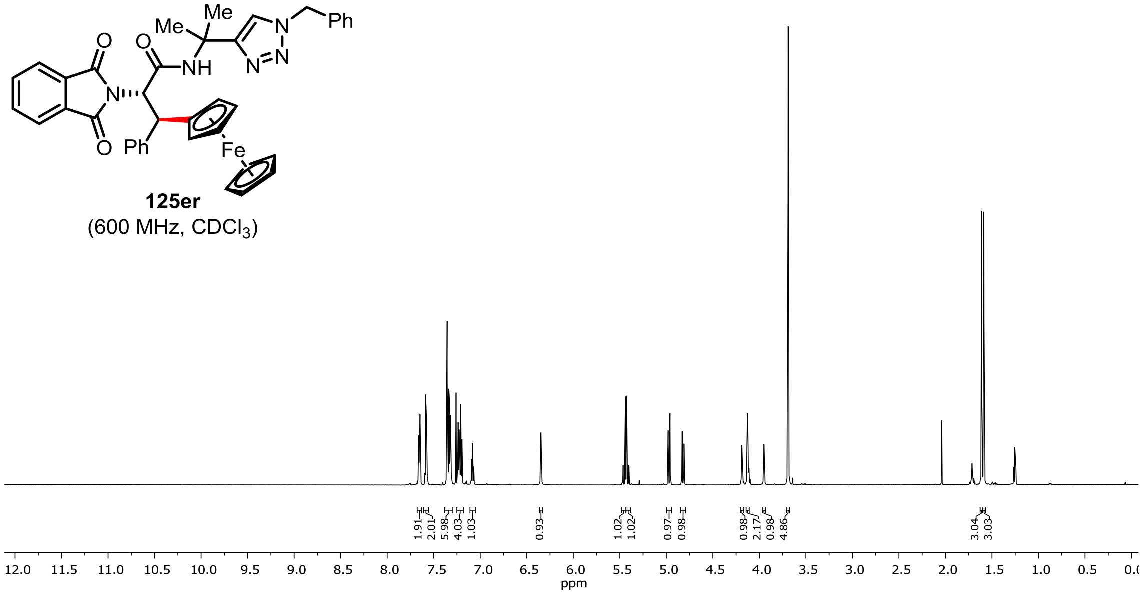
125ey
(126 MHz, $CDCl_3$)



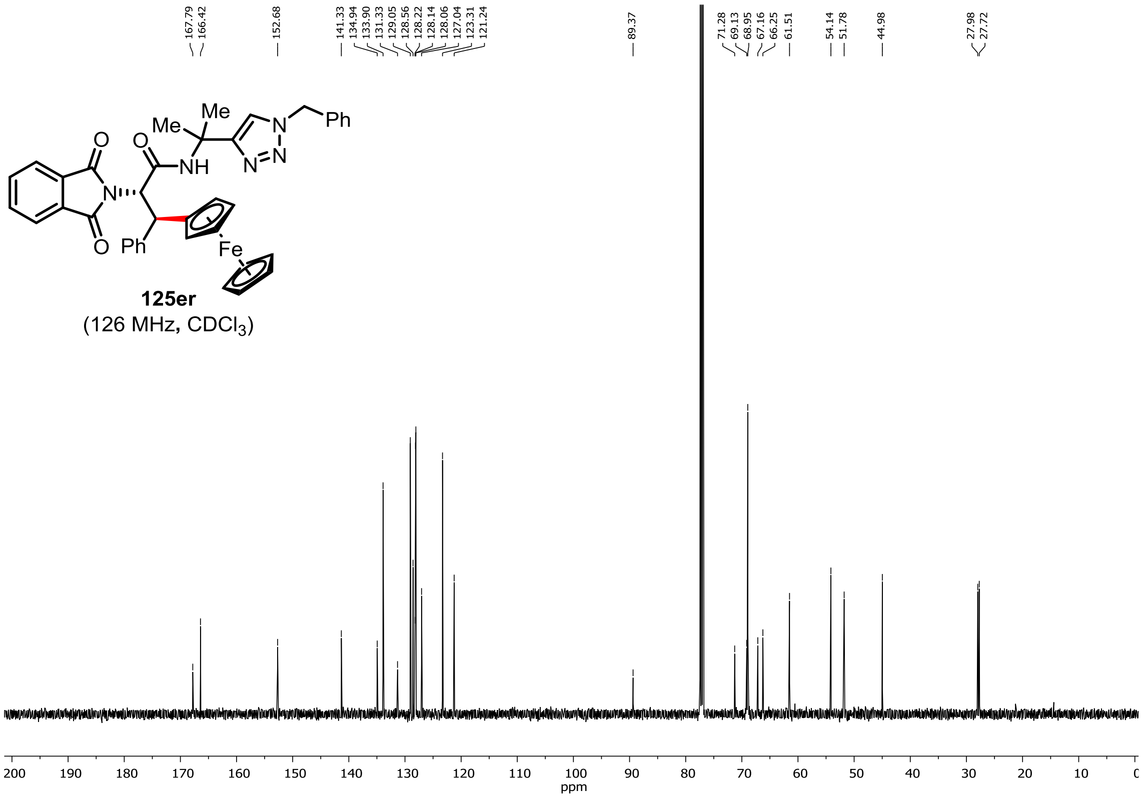
125ez
(600 MHz, $CDCl_3$)



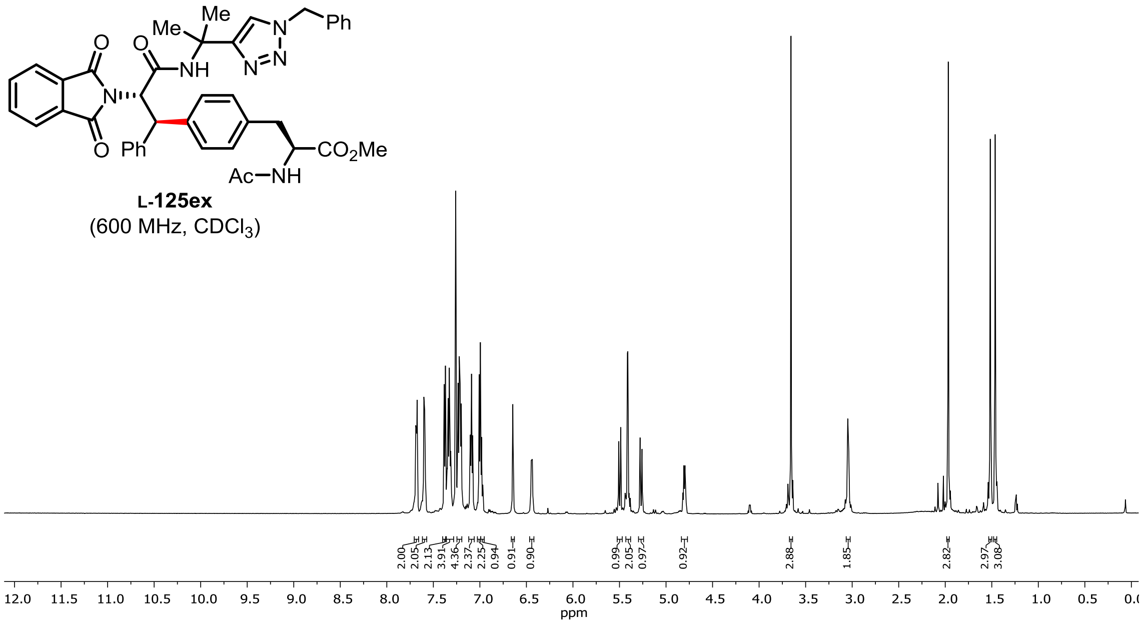
125ez
(126 MHz, $CDCl_3$)



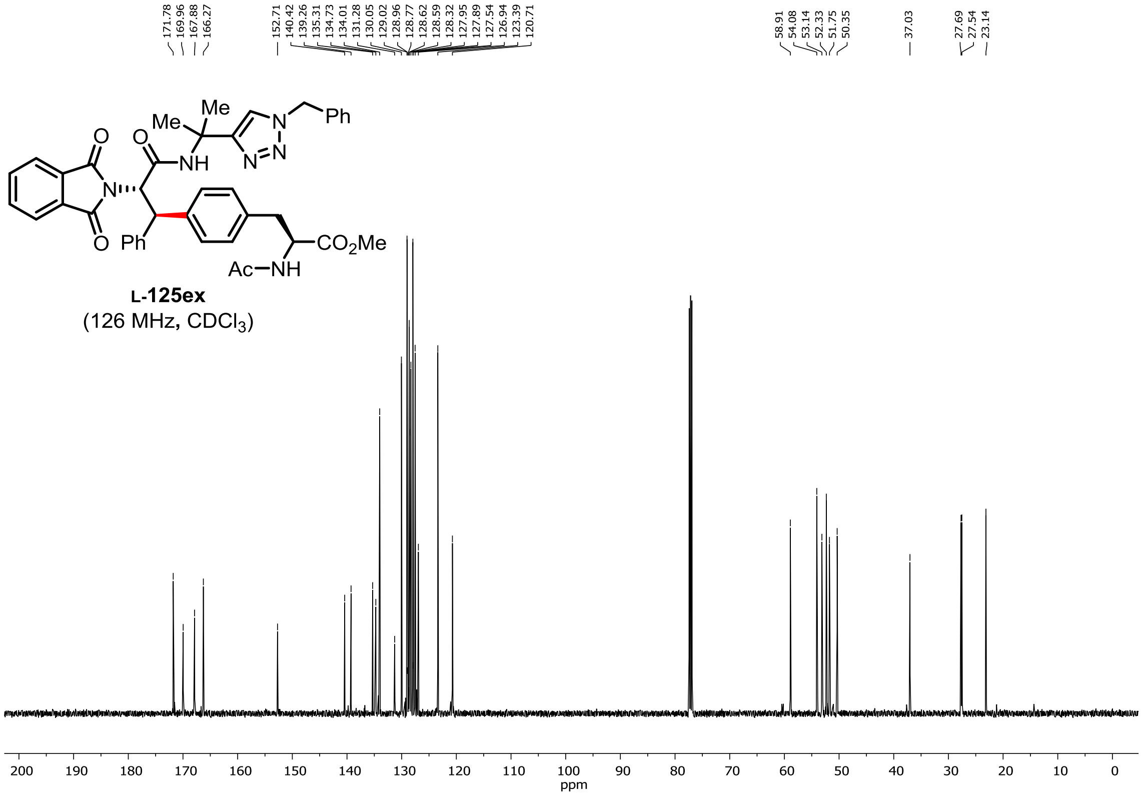
125er
(600 MHz, $CDCl_3$)



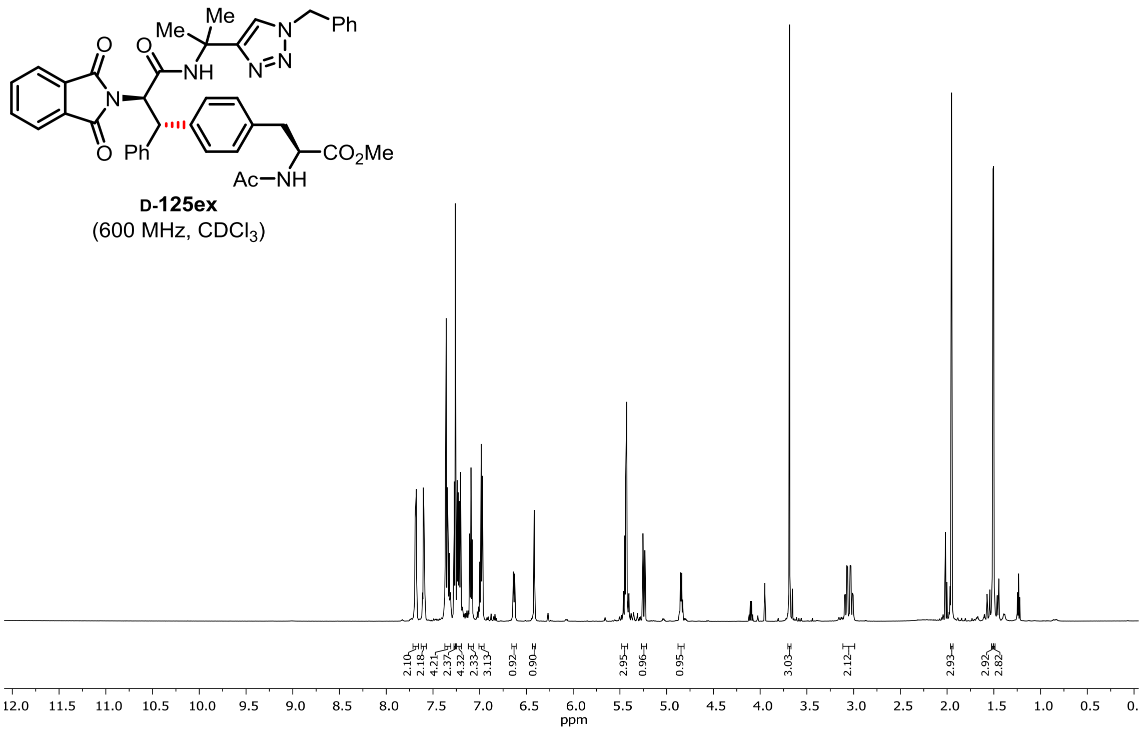
125er
(126 MHz, $CDCl_3$)



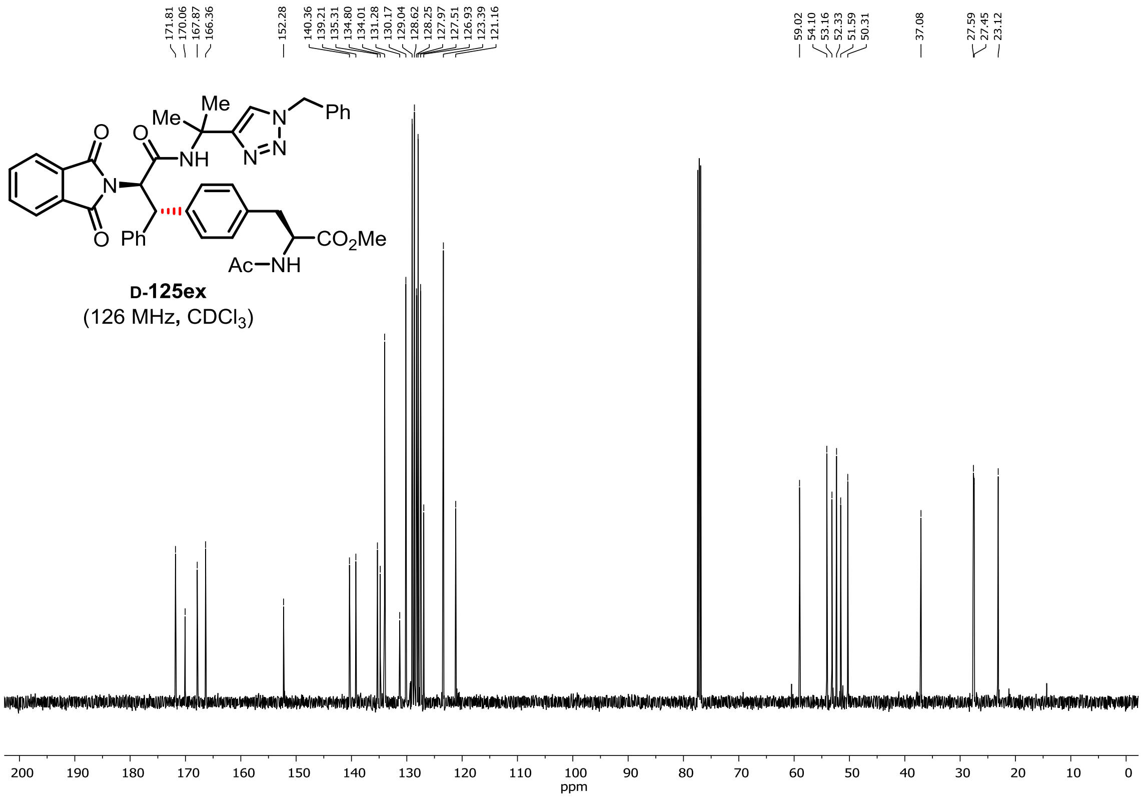
L-125ex
(600 MHz, $CDCl_3$)



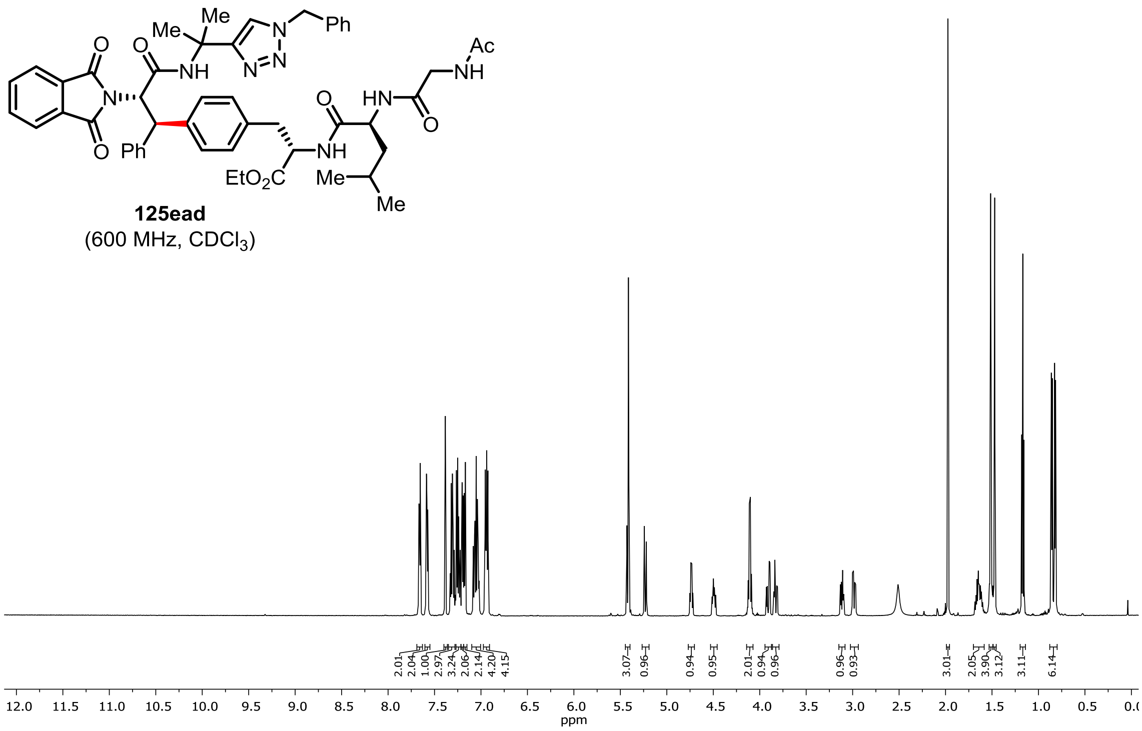
L-125ex
(126 MHz, $CDCl_3$)



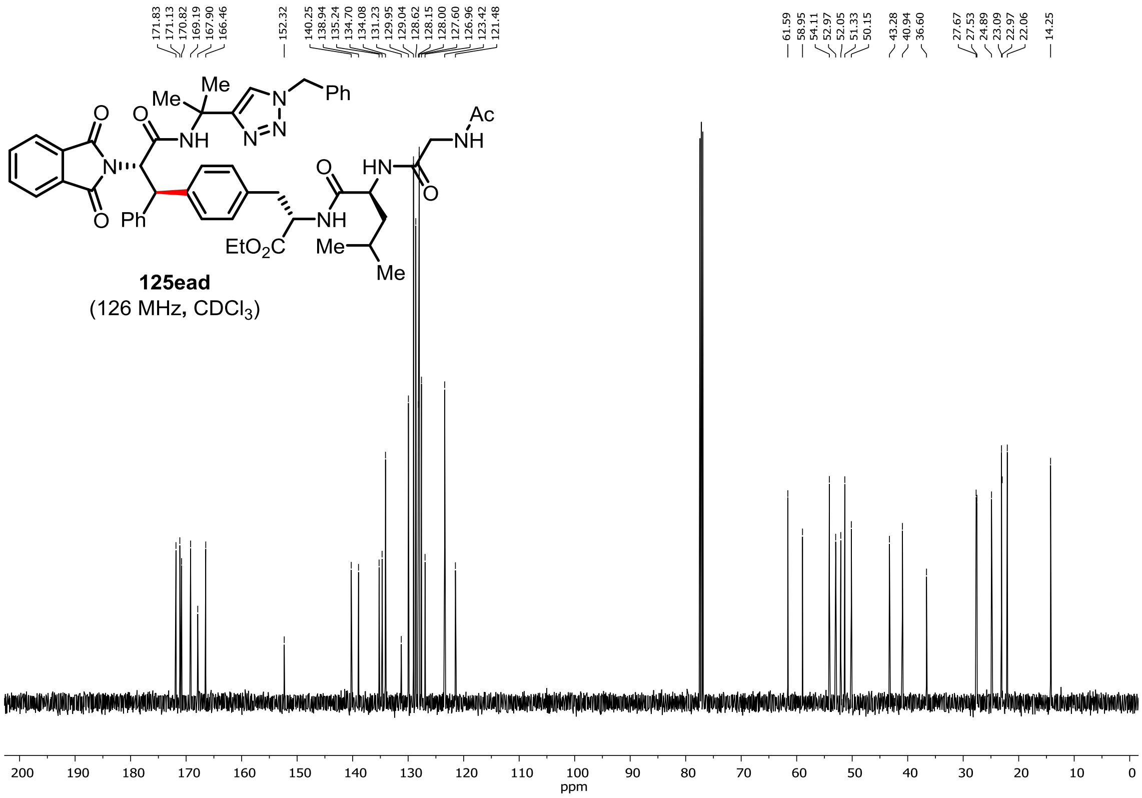
D-125ex
(600 MHz, $CDCl_3$)



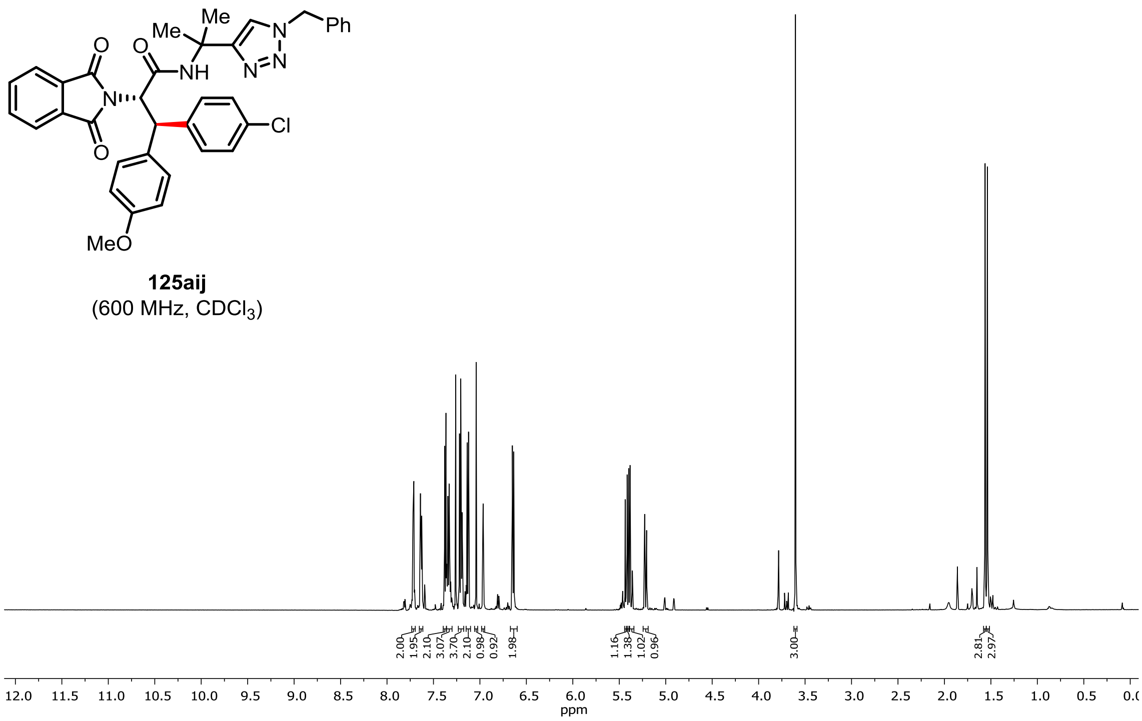
D-125ex
(126 MHz, $CDCl_3$)



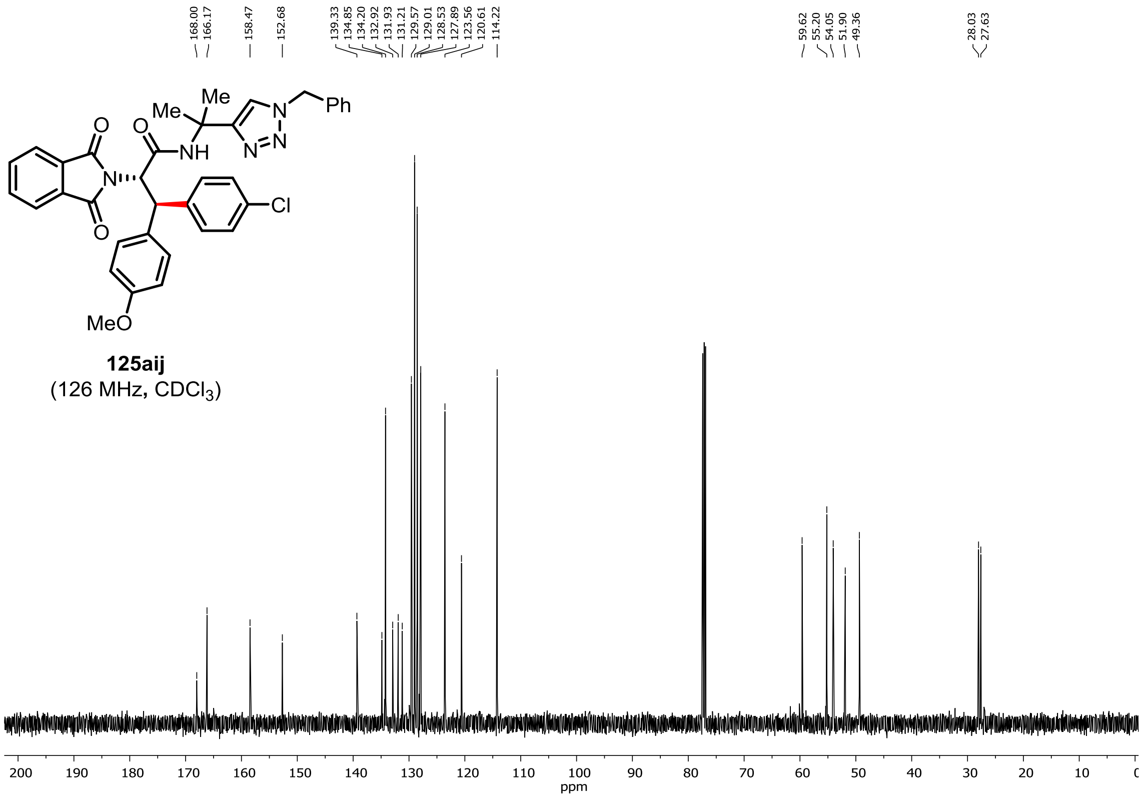
125ead
(600 MHz, $CDCl_3$)



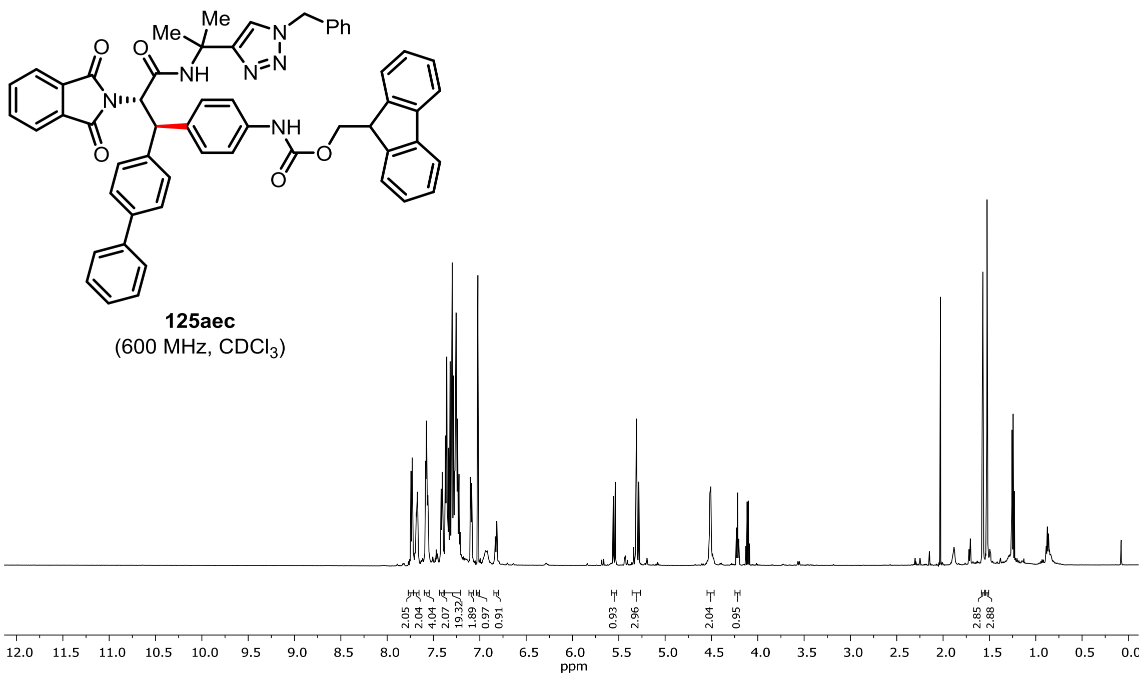
125ead
(126 MHz, $CDCl_3$)



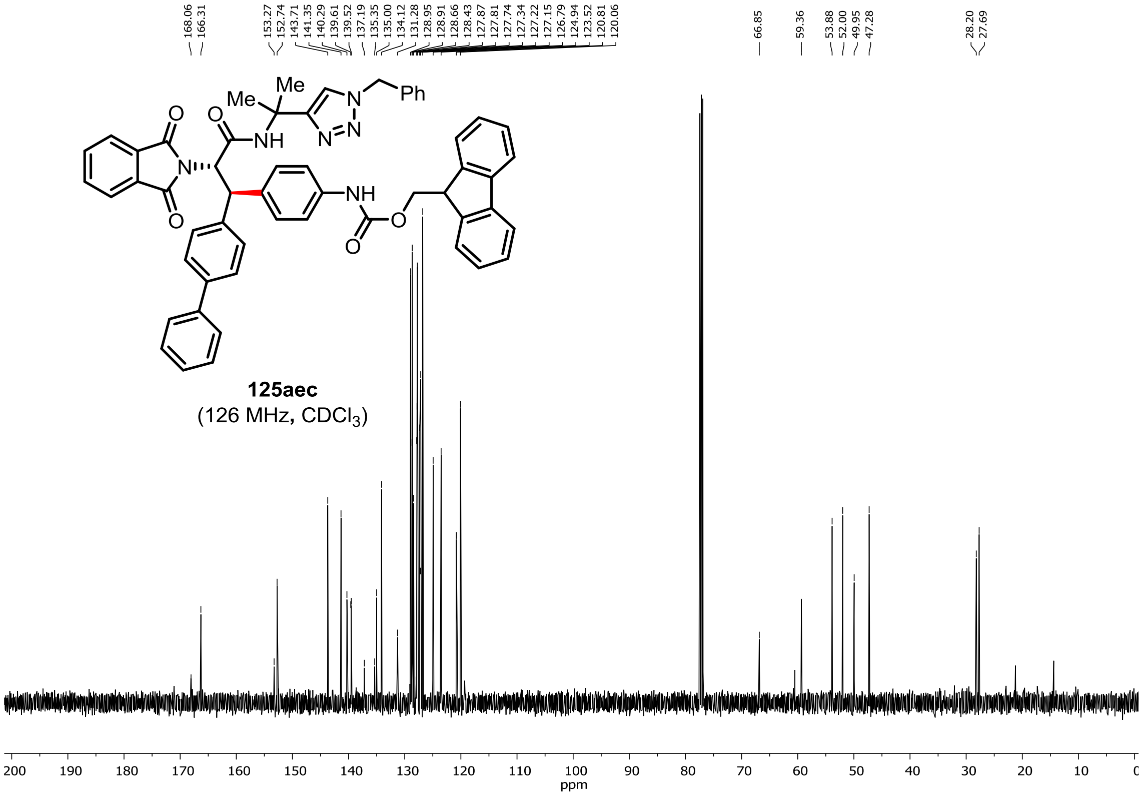
125aij
(600 MHz, $CDCl_3$)



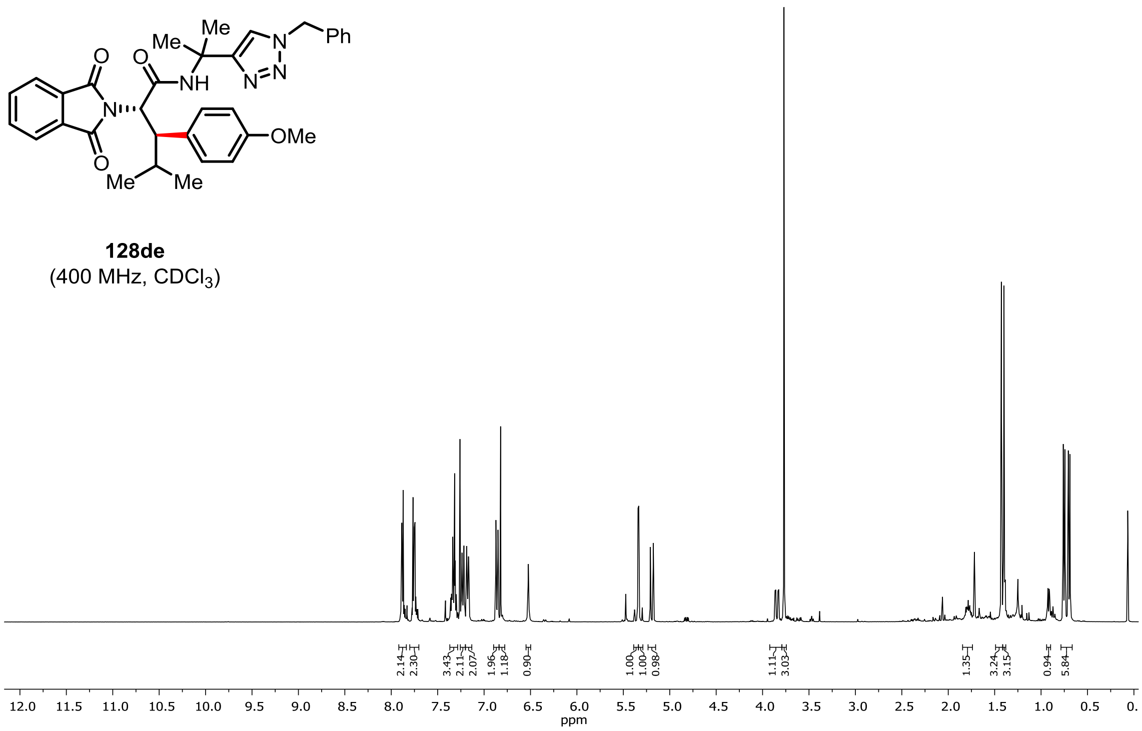
125aij
(126 MHz, $CDCl_3$)



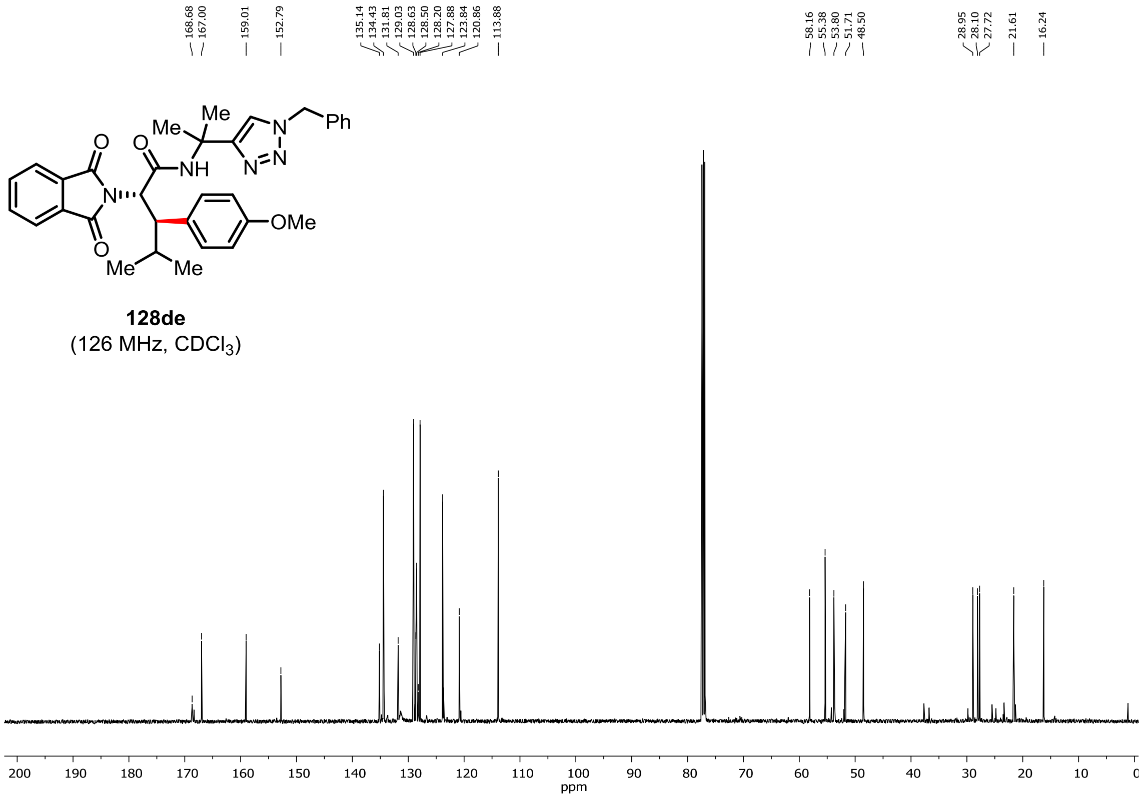
125aec
(600 MHz, $CDCl_3$)



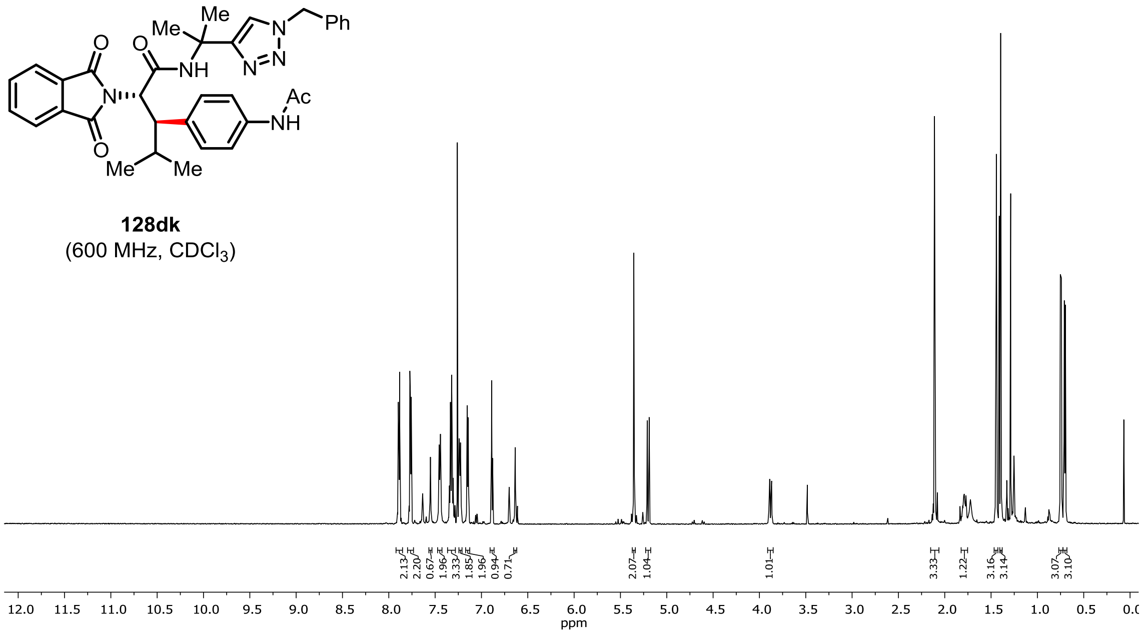
125aec
(126 MHz, $CDCl_3$)



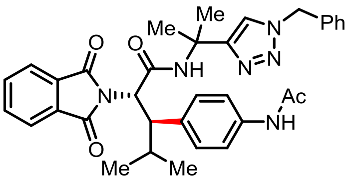
128de
(400 MHz, $CDCl_3$)



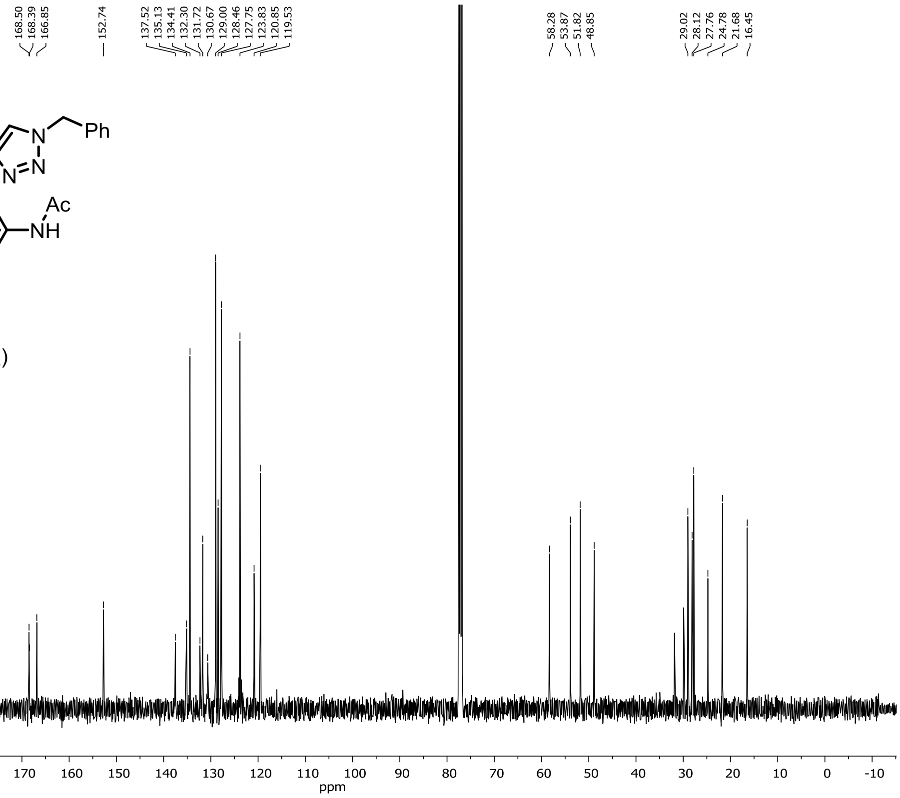
128de
(126 MHz, $CDCl_3$)

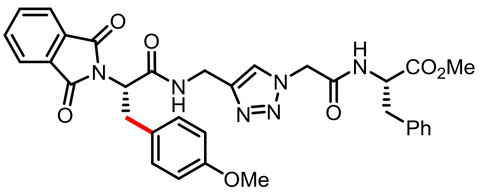


128dk
(600 MHz, $CDCl_3$)

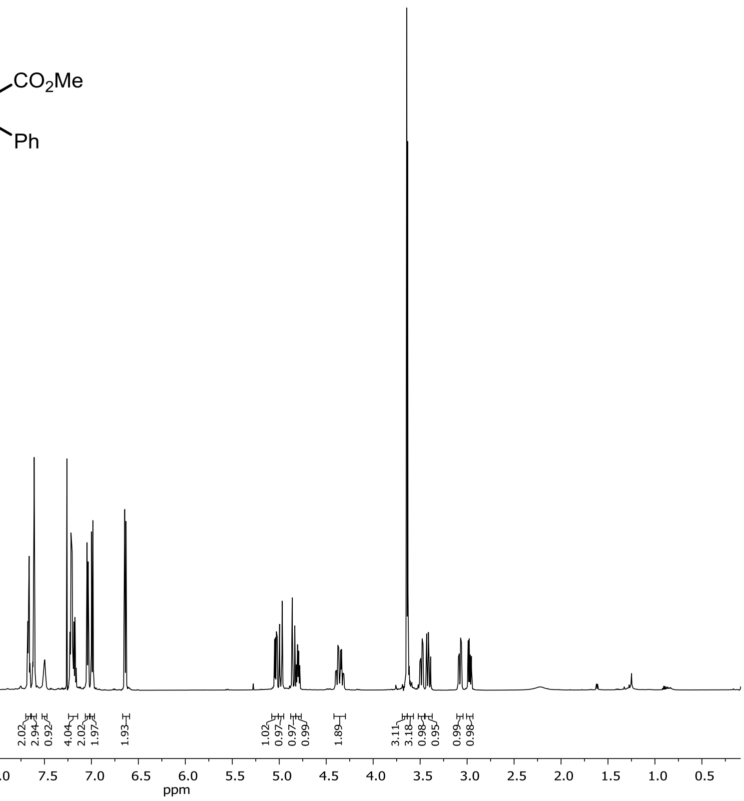


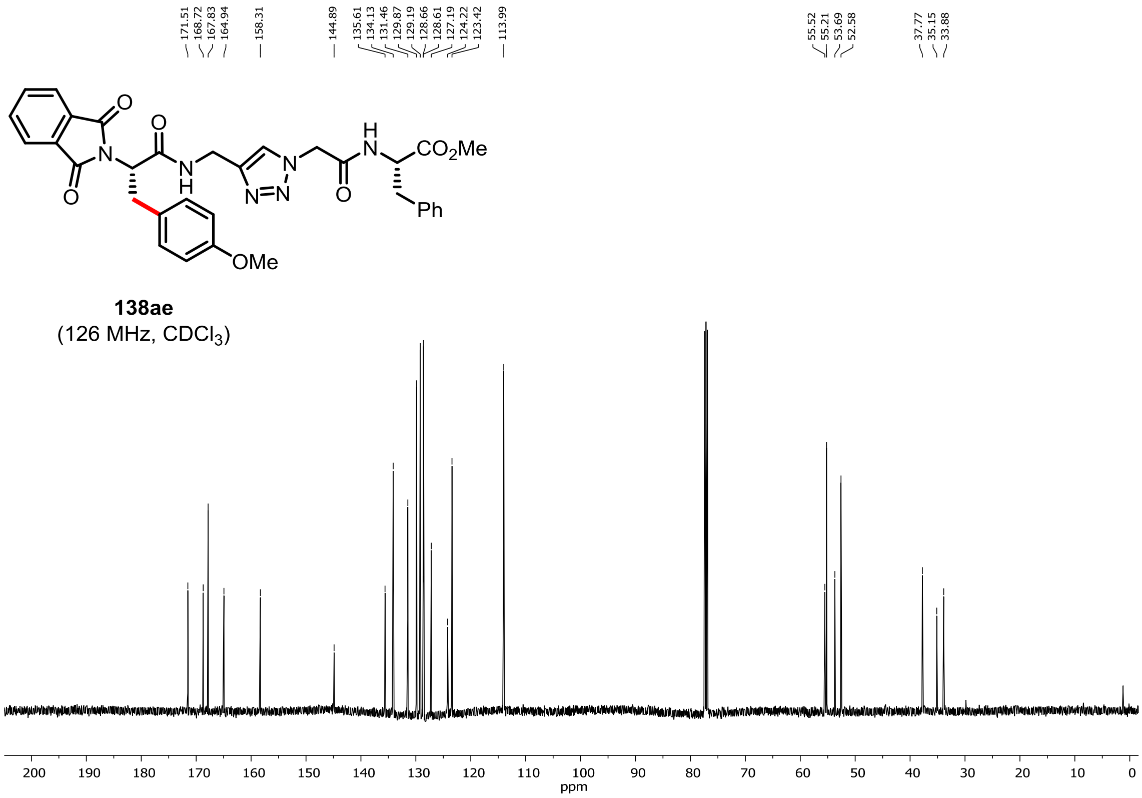
128dk
(126 MHz, $CDCl_3$)



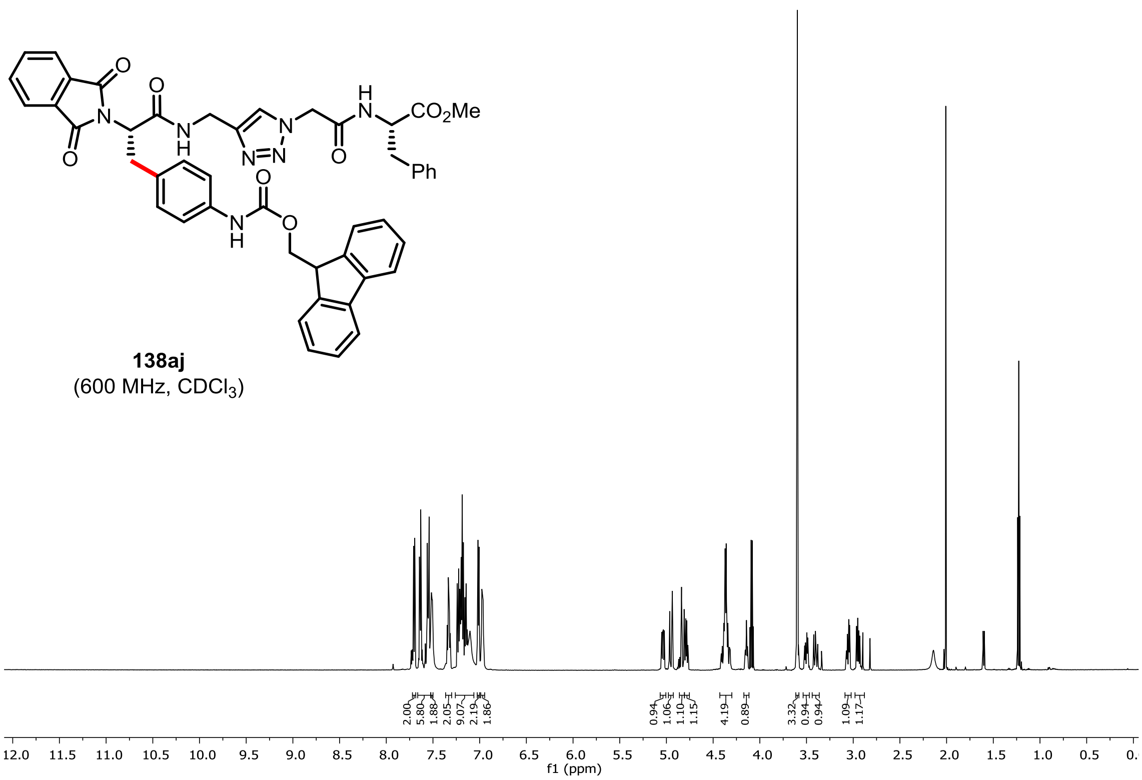


138ae
(600 MHz, $CDCl_3$)

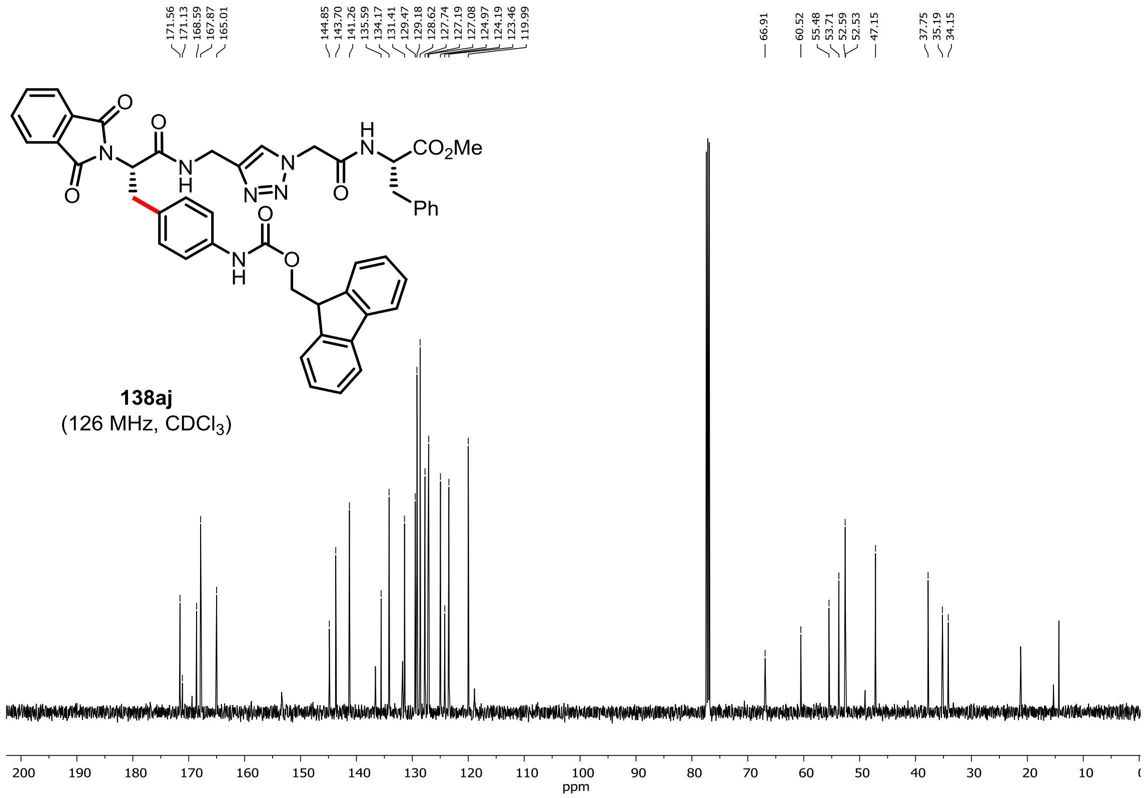




138ae
(126 MHz, $CDCl_3$)



138aj
(600 MHz, $CDCl_3$)



138aj
(126 MHz, $CDCl_3$)

9. Cartesian coordinates of the optimized structures

HOAc
Lowest frequency = 62.31 cm^{-1}.
Charge = 0, Multiplicity = 1

8

C	0.01386539738274	-0.00001288730978	-0.06982627029382
C	0.03349263451411	-0.00010839690389	1.43662475697787
O	1.01704192799225	0.00000932427211	2.14416473977445
H	-0.52265861071899	-0.88203621980867	-0.43318547531624
H	-0.52270843959308	0.88202439734249	-0.43308363650109
H	1.03560942426338	0.00003953167765	-0.44686307947512
O	-1.23658804503719	0.00000886535275	1.94558102712696
H	-1.13798728880322	0.00007538537734	2.91758393770698

TFA
Lowest frequency = 32.78 cm^{-1}.
Charge = 0, Multiplicity = 1

8

C	0.01248649705550	-0.00001318242199	-0.03697222734077
C	0.03470554472972	-0.00007091587864	1.51582711064201
O	-1.22964577000666	-0.00000372546672	1.98101419291640
O	1.04140700736756	0.00001882550226	2.17349788282903
F	-0.62934489665151	-1.09470089496449	-0.50377036414621
F	-0.62937306414917	1.09469841663606	-0.50367595197213
F	1.25967788090341	0.00002380432099	-0.52227480648670
H	-1.17984619924885	0.00004767227253	2.95735016355837

AgI
Lowest frequency = 197.06 cm^{-1}.
Charge = 0, Multiplicity = 1

2

Ag	0.00000000000000	0.00000000000000	0.37793116805170
I	0.00000000000000	0.00000000000000	2.94426883194830

AgOAc
Lowest frequency = 16.73 cm^{-1}.
Charge = 0, Multiplicity = 1

16

C	0.01096316446098	0.00001349453737	0.35328680689111
C	0.01678080700028	-0.00007303675998	1.86979302797657
O	-1.12934907975106	-0.00002945634077	2.42671388493392
O	1.15675856843843	-0.00003307084068	2.43760387242508
H	-0.53033509542208	-0.88164857884844	-0.00253721437232
H	-0.53033588797512	0.88171350059396	-0.00244568720187
H	1.02722372027572	0.00003520744648	-0.03996685833929
Ag	-1.35091047298919	0.00001860365073	4.52589598040504
Ag	1.35091776994082	0.00000716776478	4.54063466593050
O	-1.15675136807557	-0.00002719795408	6.62892656211313
O	1.12935632295581	-0.00001866632781	6.63981666489442
C	-0.01677361647043	-0.00005870596345	7.19673744592517
C	-0.01095609631055	0.00001292728153	8.71324365409584
H	-1.02721672836162	0.00002759259482	9.10649714339953
H	0.53034481915437	-0.88165093147390	9.06905959693188
H	0.53034017312921	0.88171115063943	9.06898445399128

C_6H_5I
Lowest frequency = 148.21 cm^{-1}.
Charge = 0, Multiplicity = 1

12

C	-0.01217052414376	0.00000339876382	0.06578896900130
C	0.00555878632339	0.00000539738514	1.46040984703332
C	1.23513009753412	0.00000235730859	2.12113384413588
C	2.42731555699526	-0.00000141918514	1.39709900756954
C	2.39123253007998	0.00000243345135	0.00269181527778
C	1.17032321440014	0.00000504734934	-0.67385995619206

H	-0.92197354104044	0.00000241669706	2.02253916765882
H	1.25435072243305	-0.00000196994461	3.20732708281906
H	3.38038350760921	-0.00000716896613	1.91733648472415
H	3.31495853524281	-0.00000165156379	-0.56906430565724
H	1.14159679519339	0.00000224596168	-1.75805657157022
I	-1.86673268062715	-0.00001108725731	-0.94617838480035

4-F-C_6H_4I
Lowest frequency = 100.85 cm^{-1}.
Charge = 0, Multiplicity = 1

12

C	1.15109307091406	-0.00000416542918	-0.68344444723633
C	-0.03360355901068	-0.00000285455968	0.05407044498479
C	-0.01289614732491	-0.00000404671904	1.44942524863702
C	1.21061784645266	-0.00000245582399	2.11946088475392
C	2.38026436061385	-0.00000038109701	1.37139455586820
C	2.37655648102867	-0.00000238558618	-0.01699501413238
I	-1.88508897463700	0.00000672575303	-0.95637470013633
H	-0.93806902707590	-0.00000004370694	2.01484637878947
H	1.25899066995150	0.00000136910243	3.20325176474240
F	3.57185177818749	0.00000488287803	2.02162767707823
H	3.31419971493829	0.00000124734189	-0.56266645978184
H	1.12605478596197	0.00000010784663	-1.76742933356715

$Pd_3(OAc)_6$
Lowest frequency = 28.50 cm^{-1}.
Charge = 0, Multiplicity = 1

45

Pd	1.54813951434509	0.88422042101521	-0.01295628784363
C	-0.07525372133987	2.56328645590793	-1.85944207851389
O	1.01173145672186	2.42497813356315	-1.22001248553477
O	-1.16748858709412	1.94383944843334	-1.66080401890802
C	-2.24098622230126	-1.23733575851264	1.88220415146984
O	-1.58216418051184	-2.10603649398015	1.23359697707482
O	-2.25615828555929	0.01898566087196	1.68833476438784
C	-3.13027459765960	-1.75595881952077	2.98939947013292
H	-3.32484832317619	-0.96619216493502	3.71627853379948
H	-4.08387320012039	-2.06626195845085	2.54796940386506
H	-2.67107370108496	-2.62368444728626	3.46565961334972
C	-0.08258934318868	3.60091842891328	-2.95888178709136
H	0.89333822306629	3.64076041576109	-3.44534599797829
H	-0.87154828073421	3.37998704906296	-3.67905113416702
H	-0.28592849335018	4.57866257689855	-2.50811976400203
Pd	-0.00134136243576	-1.79655558330944	-0.00011814582639
C	-2.21005967520373	-1.34110702789340	-1.84586243324469
O	-2.62871646875841	-0.34017499417449	-1.18714310242765
O	-1.13429242521282	-1.98986157680166	-1.65575931950235
C	0.07909195090193	2.56289682762840	1.85995633280406
O	1.17036477918254	1.94176583489624	1.66127229439525
O	-1.00811373774425	2.42631365048017	1.22053419600764
C	0.08815610383252	3.60047204915854	2.95943611321915
H	-0.88865822940455	3.64437587473261	3.44372797513342
H	0.87460515395949	3.37624158302299	3.68135026647573
H	0.29678600317495	4.57733919701729	2.50918249368694
C	-3.08968197495258	-1.80282443321288	-2.98537173432678
H	-3.05366466866900	-1.05202044284118	-3.78126354065802
H	-2.74897535587797	-2.76475507377245	-3.36830029195879
H	-4.12429740023157	-1.87188810732080	-2.63986978063555
Pd	-1.54679744504315	0.88655915283982	0.01323385581199
C	2.20801952409482	-1.34471135321834	1.84578143314813
O	2.62822418485744	-0.34431043505697	1.18723825910140
O	1.13130394760330	-1.99183336513891	1.65549769914797
C	3.08672009603573	-1.80778318645788	2.98544800737889
H	3.04914749319952	-1.05834777791216	3.78257705884386
H	2.74615967551760	-2.77052937919791	3.36646272062716
H	4.12178790891753	-1.87550472312439	2.64109253195822
C	2.23916200744304	-1.24037351495431	-1.88231556270745
O	2.25624776729498	0.01588499684413	-1.68819591783933
O	1.57901679724574	-2.10820100404154	-1.23388490940995
C	3.12764357532824	-1.76014910766121	-2.98961815647589
H	4.08044790394779	-2.07280942305379	-2.54813867379522
H	2.66671445578154	-2.62659324839672	-3.46655031452197
H	3.32407915720241	-0.97033735682153	-3.71594271445046

$Pd_3(TFA)_6$
Lowest frequency = -5.69 cm^{-1}.
Charge = 0, Multiplicity = 1

45

C	-3.12274802191158	-1.77635535319880	3.01701972213283
C	-2.21761898994510	-1.23662370025982	1.87101799882997
O	-2.31670082054959	-0.00164768224177	1.65049800826048
Pd	-1.58497672450995	0.90750238147541	0.01159617340990
O	-1.04146920987723	2.39321291607010	1.26965642798125
C	0.06777720427953	2.54873349802704	1.84103375261864
C	0.07506107621009	3.62283834892376	2.96775380143951
O	-1.53108213334607	-2.11788682161469	1.29291505473956
Pd	-0.00154976727767	-1.84210072640540	0.00011148532019
O	1.52745104304294	-2.12025118915793	-1.29282332872107
C	2.21529082898091	-1.24007870678958	-1.87102652270448
C	3.11956550481904	-1.78099035825899	-3.01714844194086
Pd	1.58628659785283	0.90485603826117	-0.01136659182440
O	2.31639680175606	-0.00526335873758	-1.65047338602020
O	1.04516978762058	2.39181203834661	-1.26901177978135
C	-0.06380508581538	2.54932604066056	-1.84036398137787
C	-0.06943978693873	3.62380334500050	-2.96673014638418
O	1.18226491399992	2.00512797361408	1.62364791742475
O	2.62309297624893	-0.30021431129285	1.23719421351205
C	2.21502333363848	-1.34044311530605	1.81504324867668
C	3.11378954935581	-1.80567757130249	2.99800287431941
O	-1.17917519374226	2.00744396983173	-1.62318464412679
O	-1.19513343286817	-2.04048305714296	-1.60703497130391
C	-2.21702960468813	-1.33659550921884	-1.81515609467469
C	-3.11608447593864	-1.80009443999480	-2.99856957669891
O	1.19177152903807	-2.04245862373450	1.60725261580682
O	-2.62343151875242	-0.29566166502067	-1.23741186767048
F	-3.47007333028502	-0.79971637398830	3.86719169279906
F	-4.24761287674935	-2.29285710026182	2.47227451243428
F	-2.49864898499074	-2.74485880282038	3.70593008455153
F	1.12297333516810	3.69547908506123	-3.57619512102673
F	-1.00787775641313	3.35607385001648	-3.88723996815894
F	-0.34197948564913	4.82677853616499	-2.41146691621587
F	-1.11698095534488	3.69545720359522	3.57784580002838
F	1.01369673826099	3.35390835546075	3.88770518855055
F	0.34847493493012	4.82573628191198	2.41275435229749
F	-2.88072146923816	-0.99835417022750	-4.06134263335946
F	-2.85376214641870	-3.06513836177330	-3.35304620961233
F	-4.41593161091402	-1.70461712954739	-2.67104538299946
F	2.88167463217932	-1.00254239798197	4.06043907618258
F	2.84818671640150	-3.06970887244102	3.35360061517243
F	4.41360639481379	-1.71410714635475	2.66922542631257
F	4.24579588741639	-2.29493796288982	-2.47272917097743
F	2.49601704394568	-2.75159863044294	-3.70345525229502
F	3.46457455220494	-0.80547372401473	-3.86960705492649

Phenylalanine

124e
Lowest frequency = 5.52 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	1.25281821464624	8.61082376762097	0.50520629790995
C	0.79820103241728	8.24888775606100	-0.76753030958272
C	-0.45706113893465	8.70357735301869	-1.18785080461223
C	-1.24124568944611	9.49953909175538	-0.35551973612193
C	-0.78026991266783	9.85247954609336	0.91377319922649
C	0.47011326430173	9.40704788306112	1.34152855210871
C	1.62388290011292	7.33398025907377	-1.64060255495127
C	1.06103479936121	5.88866499900680	-1.63813012786973
N	0.76820025918355	5.43740222390816	-0.29071412253020
C	-0.53057447145632	5.12425313840703	0.14778475445881
C	-0.37472535442951	4.69890507209341	1.56766209023412
C	0.98114432103418	4.76403122960038	1.89945790230781
C	1.73488700832870	5.24070842545792	0.70479608398088
C	1.43281177734209	4.42825698314144	3.16660226820948
C	0.47756397642750	4.01893464134370	4.10503617166049
C	-0.88046345135683	3.95452359744015	3.77268528918239

C	-1.32786570822077	4.29638465677212	2.49066493115485
O	-1.53704328546404	5.20816965184162	-0.53068709202485
O	2.92808949359661	5.45389924927091	0.57746206614314
C	1.94424279269776	4.82029927510253	-2.33270967237325
O	1.89327010027630	3.64126781616003	-1.99006682664405
N	2.70263153934030	5.29683370870796	-3.34639030881860
C	3.61700692273263	4.48973112165142	-4.17222239450821
C	4.70753692338785	3.84694536474868	-3.28983476649677
C	4.24007932851296	5.46673893917409	-5.14418961475493
C	5.17584781283278	5.26194642664975	-6.13749142237327
N	5.35686797504061	6.48841518349516	-6.69459450938644
N	4.57803926262878	7.41561495367578	-6.09245135461507
N	3.90507247733296	6.79146414462620	-5.15270209421383
C	6.23113023728889	6.87006341108223	-7.80939995202825
C	5.98626897130401	6.01796478776984	-9.03382304796563
C	4.70867185464023	5.94799262023448	-9.60237299533715
C	4.48394224517012	5.16090893654118	-10.72846810155176
C	5.53356125270196	4.43711919125140	-11.29989829103886
C	6.80749056038073	4.50305422722890	-10.73879327615304
C	7.03065274057438	5.28923624392480	-9.60695317523891
C	2.83349591576998	3.40569000730994	-4.94118237421135
H	0.08822664344248	5.87862432560509	-2.14514068715892
H	5.69612005068113	4.38794010835154	-6.49586559460165
H	-2.37881417283237	4.25057848336550	2.22321255293809
H	-1.59697981599942	3.63368529517418	4.52325482264008
H	0.79292663298285	3.74650453975837	5.10807065886353
H	2.48819277957882	4.48183349779513	3.41471769587909
H	6.00724578946332	7.92454137892951	-7.99103111141282
H	7.27349329013720	6.78718861581474	-7.48604422632158
H	3.51634115300963	2.83572659237892	-5.57966330417115
H	2.35615791447714	2.72811263610170	-4.23057827877749
H	2.06881584583624	3.86849127982666	-5.57150500148870
H	5.40640079149565	3.28174213489898	-3.91535841870424
H	5.26146703396841	4.62052244827090	-2.75113808473693
H	4.24239695019351	3.17145010117318	-2.56944077012077
H	3.89046708401922	6.50658718912233	-9.15464789065297
H	3.48972774774058	5.11172814363574	-11.16293975884565
H	5.35625625999305	3.82338595538914	-12.17820342562536
H	7.62702827074538	3.94063279338712	-11.17663554077431
H	8.02381380320288	5.33701505094553	-9.16593736711649
H	2.22497266236353	8.25886815850539	0.84112509634886
H	0.83768315906415	9.67821071032655	2.32746583623530
H	-1.39184979940049	10.47188498850021	1.56369732490203
H	-2.21394859092206	9.84263785071477	-0.69665315324350
H	-0.82741270598415	8.42560303678974	-2.17205645334303
H	2.65881431279480	7.31381246349994	-1.29014524604392
H	1.61746047816843	7.70732562035868	-2.67163060253304
H	2.71131748439091	6.29102071707813	-3.55739375330921

1.1
Lowest frequency = 15.02 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	6.91326988967130	7.51736687314519	-5.75327395989052
C	7.11131976583429	8.88587187906572	-5.97517145997025
C	6.76914702146893	9.78639818439962	-4.95797169664945
C	6.23207283968664	9.33597220523006	-3.75147044078050
C	6.02774268416603	7.97131385931233	-3.54826056970085
C	6.37201776212299	7.06574588506208	-4.55150135516140
C	7.65076737997760	9.38358799199297	-7.29508246703578
C	6.72815851407355	9.09559657903864	-8.51435138779710
N	7.41475073514245	9.41347564695156	-9.75849334519638
C	7.38283181310068	8.55388480895648	-10.87414799130118
C	8.01450701780303	9.31338114049170	-11.98840271396312
C	8.34761859152827	10.58402071397087	-11.51784174838427
C	7.94856557953829	10.67812840797384	-10.08394146730373
C	8.94831843523036	11.52574134035951	-12.33987947749695
C	9.20631531426981	11.15419705253943	-13.66475254686326
C	8.87171009366169	9.87913238821458	-14.13655395472586
C	8.26771529173091	8.93447231819593	-13.29856307655812
O	6.92302975885565	7.42714743870798	-10.87932590423255
O	8.07425252539635	11.62123677002194	-9.32529034861096
C	5.38679850763879	9.87065354503891	-8.49904358339385
O	5.07764891058668	10.64740132981035	-9.40112497396789
N	4.61380501509774	9.61951100750954	-7.41112778861559

C	3.39762760198102	10.38102642392947	-7.06352538014556
C	3.72893744845587	11.88873927375641	-7.06349464789381
C	2.99294062722525	9.98438642114768	-5.66081545078573
C	2.71022911292806	10.84492519702289	-4.61923228663348
N	2.33803203777650	10.05937502961963	-3.58055750663131
N	2.38995941761611	8.76814592050845	-3.90331593392763
N	2.78542563722134	8.71446914882736	-5.16553346882862
C	2.05127526752843	10.43573974444773	-2.18368638451252
C	3.30964832636123	10.43607742398305	-1.34676470800542
C	3.98794001477930	11.63015139896086	-1.08816343774789
C	5.17548890071845	11.62142207702519	-0.35664170547196
C	5.68862868202691	10.41577372954321	0.12129187572937
C	5.01135058033883	9.22144275015783	-0.13074122909874
C	3.82666107356817	9.22950437117308	-0.86359941161703
C	2.24362618054599	10.10921374998103	-8.05370052203870
H	2.75498206046580	11.91818777771947	-4.54435918318725
H	8.00274495563770	7.94365071818032	-13.65401723705926
H	9.08380204500777	9.62215313058850	-15.17035728836712
H	9.67212276787285	11.86540565097446	-14.34082392564994
H	9.20187621266068	12.51224528288019	-11.96469133360913
H	1.58596785264455	11.42349408843445	-2.20801775919291
H	1.32549234220385	9.70580065155168	-1.82088055171991
H	1.37207186162484	10.70820607605370	-7.76894231460306
H	2.56959186049895	10.40524874180145	-9.05328612809651
H	1.97812854929803	9.05167587503034	-8.04862926251170
H	2.83497698574110	12.47008663935449	-6.81555811727101
H	4.52236346092693	12.11082905851011	-6.34307982949132
H	4.06657598708799	12.17544849725766	-8.05895657010039
H	3.58723831708920	12.57098461320993	-1.45924058213080
H	5.69833195129512	12.55297292696248	-0.16148599357897
H	6.61497337490245	10.40607263688629	0.68777969090891
H	5.41123776475465	8.28165633916199	0.23810692880388
H	3.31183774172751	8.29814434627554	-1.08343111990896
H	7.14352441143860	6.80372261289159	-6.53738027518380
H	6.20782038213609	6.00302367143720	-4.40618389779751
H	5.58497545569813	7.61478582585623	-2.62483301633259
H	5.96674494466337	10.04709505784169	-2.97430540167699
H	6.91522781659537	10.85129025628844	-5.12453093584978
H	8.60306942532621	8.88503742237762	-7.51237559772410
H	7.84726403505008	10.45602528749190	-7.24506246092855
H	6.49510592639313	8.02451254124948	-8.55606034530123
H	4.89150419925169	8.85618428817537	-6.80050145224777
Pd	3.08199590689444	6.76793169397173	-5.67375448830973
O	2.78985096751475	7.05051773406599	-7.62819351919182
C	3.85124247747495	6.75176108073139	-8.34991708152470
O	4.95981893677489	6.49395739347517	-7.87526232258482
C	3.57726590098710	6.75663576632405	-9.84191269921014
H	4.52314451767232	6.74159805439101	-10.38394233007084
H	2.99180295014484	5.86686040364944	-10.09802427253576
H	2.98824403422667	7.63434978921668	-10.12169854471440
O	3.36473103574227	4.72984482267159	-5.64132423137025
C	3.44586021282455	4.75379092795902	-4.36150923706178
O	3.30407137143969	5.89006899141176	-3.78352780556761
C	3.72729737759189	3.50762179468829	-3.58154537270992
H	3.26810716537007	3.57151603936121	-2.59263070279161
H	3.36045262252249	2.63385700573140	-4.12375589163130
H	4.81130947917291	3.40569946183553	-3.45433708570892

1.2
Lowest frequency = 4.19 cm^{-1}
Charge = 0, Multipicity = 1

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C	4.68087309736752	5.38436269233289	-9.89413489096319
C	5.83288689369894	5.85968003455795	-9.25248549499446
C	7.06617941407777	5.28609595350439	-9.57890319860546
C	7.15020189825681	4.25556866541681	-10.51653564500573
C	5.99787859123124	3.78723946072466	-11.14632560198454
C	4.76237997246808	4.35747242974518	-10.83218291137529
C	5.75786264913639	6.99457053985288	-8.25847378186748
C	5.20480967897319	8.28884312079029	-8.90227528853830
C	5.30499200826260	9.52373660434216	-7.97866077688560
O	5.89961369019151	10.53664338187867	-8.37325130725736
N	5.88681570423995	8.58292800002107	-10.15345618041309
C	5.18744960050780	8.83563480619046	-11.34480346503375
C	6.22942892628230	9.14686155222815	-12.36403455636646

C	7.47816260882551	9.08286933514261	-11.74370910756034
C	7.27575054179333	8.72041879413150	-10.31005311835069
C	8.64832970149139	9.32548488363869	-12.44672064741923
C	8.53158835499170	9.64149860289974	-13.80582302947158
C	7.27912945886372	9.70537433571682	-14.42769660893562
C	6.10305934035206	9.45597349621212	-13.71001547735031
O	3.97688117093351	8.79157383360699	-11.47214164883553
O	8.11674100132739	8.54178203487422	-9.44776180256553
N	4.76320482466698	9.39590160293389	-6.74049401299683
Pd	3.27175875899610	8.12038086649564	-6.24000775488520
O	1.69888523605638	6.76128582757396	-5.99814240024245
C	1.69375276367482	6.55352471295750	-7.26000728487933
C	0.77567254339873	5.56155835617183	-7.90041724203805
C	5.03059361874861	10.49671939802463	-5.76240166045789
C	6.54201932797014	10.76767268048842	-5.59375778695367
C	4.27091015309565	11.78608436286713	-6.14999137161235
C	4.49790487374547	9.98367944294145	-4.45954284047740
C	4.60032567388772	10.35551304748060	-3.13758044050569
N	3.84060168264059	9.45210931371302	-2.45558702107820
N	3.27317022007526	8.55177476921978	-3.27130653001845
N	3.68323842245431	8.89000509553375	-4.47675889343686
C	3.57831982479311	9.38392733770373	-1.00867036468900
C	3.00302572527054	10.68025966364507	-0.48832837771039
C	3.68824137985791	11.41642068160235	0.48051301381638
C	3.15892762793034	12.61544668668907	0.96087273206634
C	1.94338177112545	13.08595839749166	0.46765727642157
C	1.25576193915814	12.35484572165706	-0.50434714839692
C	1.78162927683322	11.15682152543905	-0.97960005411520
O	2.53536480697287	7.22237540770054	-7.96503038350990
H	4.15935036546557	8.13652293869022	-9.18245325559395
H	5.11695391720159	11.16030820669953	-2.64064840278206
H	5.12680811155574	9.50172720780845	-14.18250453321398
H	7.22168704018011	9.95271142518977	-15.48388651369077
H	9.42568604144151	9.84084917631219	-14.38973032816735
H	9.61464179340275	9.27235543129441	-11.95495336314121
H	2.88790862289218	8.54593790062303	-0.88914096593424
H	4.51586112553584	9.14150239249765	-0.49988609745085
H	4.42143153650196	12.56217657317281	-5.39075967356999
H	4.64713470656576	12.13809090689097	-7.11149326626728
H	3.20025874166463	11.57595344723113	-6.23312427119658
H	6.69558478663620	11.47485775147201	-4.77010875839063
H	7.06459196458320	9.83561145050376	-5.36029646926666
H	6.95031890533352	11.18761045595510	-6.51110945870475
H	1.24758401371962	10.58969633482957	-1.73813150494765
H	0.30796629380666	12.71876128278102	-0.88969872718114
H	1.53098857957364	14.01993997834544	0.83764334343075
H	3.69780069678350	13.18034640509177	1.71571765767119
H	4.63805778959938	11.04952417205465	0.86299519057593
H	7.96728740404329	5.66527750652072	-9.10404167527860
H	8.11780596795501	3.82413267028453	-10.75907398622178
H	6.06104902464773	2.98849876814755	-11.88025887632260
H	3.86016950723900	4.00475880729618	-11.32530486443912
H	3.72066872119739	5.83782762399249	-9.66460911312105
H	6.74755713287808	7.19294296940489	-7.84244311079420
H	5.09172055131369	6.73570466309110	-7.42667381705958
H	0.35618182746945	5.98286879730530	-8.81766909162811
H	1.35340091879276	4.67103562412836	-8.17314480075215
H	-0.01778784260477	5.27695667624694	-7.20783518108253

1.3
Lowest frequency = 3.14 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.44612151453458	6.23385448330542	-10.18254222445760
C	4.68167360930523	6.41926421941307	-9.55388037093286
C	5.76185448104820	5.60285106450428	-9.90581458938203
C	5.61486807794760	4.62549552475585	-10.88942691421929
C	4.38381562678445	4.45220496784416	-11.52213992377355
C	3.30013167290687	5.25575104354952	-11.16329482914922
C	4.88356166678740	7.52772105842210	-8.54556531602608
C	5.00568496258385	8.93698362594520	-9.16485798210841
C	5.44168397438841	10.04694871241405	-8.17029565010824
O	5.96726471779146	11.07862305346314	-8.61132349361445
N	5.91770831997511	8.92939852986435	-10.29040832749202
C	5.53023355779564	9.25082587380614	-11.60498353670246

C	6.77944061238084	9.16185830891177	-12.41377364460220
C	7.83121469849363	8.81064455905192	-11.56294708911028
C	7.28738467285164	8.65725288417210	-10.18398663228597
C	9.12353675165181	8.64881220244512	-12.03871908867913
C	9.33798783194334	8.85281275425154	-13.40726606569018
C	8.28448264468186	9.20393580616238	-14.25916890953184
C	6.98206942057627	9.36356954381556	-13.77046811046111
O	4.39862165919159	9.52680656569137	-11.95292748191451
O	7.85960035653582	8.33795646865089	-9.15538697858917
N	5.15641309186651	9.79086510372970	-6.88002191781658
Pd	4.38438521310026	8.04507956453318	-6.29089960108951
O	3.61767456675467	6.29191376339769	-5.62224041790938
C	2.54930375098809	5.95036641181747	-6.29752496403038
C	1.94409634505945	4.62629548913401	-5.86647580341247
C	5.49518461713494	10.79388260356223	-5.83485195905116
C	7.02252503186009	11.01838556675979	-5.76942842946289
C	4.74728681710002	12.12358940258464	-6.07645037538032
C	5.02333569327370	10.19331029950546	-4.54011096394303
C	4.98215464390445	10.62823917041143	-3.23419870335613
N	4.44057457105296	9.59448380120988	-2.53048213192369
N	4.13253036645738	8.55476528458801	-3.31760060942840
N	4.49447079644879	8.92989883856523	-4.52585178799390
C	4.07612324495739	9.54630041552483	-1.10543394204862
C	2.91540942352541	10.46527041878525	-0.79759650372110
C	3.06162428738007	11.49993681264904	0.12859908384301
C	1.98999297616332	12.34790892401038	0.41283843030015
C	0.76946405192121	12.16717940281436	-0.23513321679503
C	0.62016115407835	11.13552149225336	-1.16523782211192
C	1.68713123069141	10.28612034654538	-1.44479198430966
O	2.07116731336148	6.61159461102518	-7.23106807853422
H	4.03923699731666	9.23521045576068	-9.58723747308842
H	5.26954594485559	11.55473826200321	-2.76429404425052
H	6.15818428683507	9.63476786243179	-14.42296979963935
H	8.48312106079483	9.35463593934636	-15.31629437157100
H	10.33722025910381	8.73734854308893	-13.81708673320536
H	9.93393236001338	8.37594810340947	-11.37008017305583
H	3.83372405529191	8.49878355205136	-0.91276898014346
H	4.95838311072780	9.81866242045168	-0.52034042120643
H	4.95741206242827	12.82645749020514	-5.26233332970869
H	5.08080273661094	12.55393520010476	-7.02117805013720
H	3.66919798428690	11.94427641086171	-6.11871181521276
H	7.26821623492739	11.71314259627325	-4.95829650806924
H	7.53311769388828	10.06790616525279	-5.59166110496512
H	7.35986491235715	11.43475059679228	-6.71946977227675
H	1.57181924650680	9.48514112209327	-2.17082213228130
H	-0.32971419697479	10.99221119247813	-1.67157803897386
H	-0.06456488916421	12.82797951128104	-0.01825267475778
H	2.11147625770583	13.14896617814957	1.13597701220636
H	4.01529240704798	11.64190401918702	0.63223797470738
H	6.72047060543163	5.74404978805413	-9.41332354465668
H	6.46122246891191	3.99982001134316	-11.15894819182487
H	4.26774374654267	3.68943648081965	-12.28698639739837
H	2.33648312770671	5.11712686903931	-11.64492216002708
H	2.59671873641345	6.84148946250780	-9.88606481166243
H	5.78925586231107	7.31005901342706	-7.96583516631135
H	3.89003327283522	7.49223642328882	-7.96449931633148
H	0.86899734948286	4.63513796160906	-6.05614912627773
H	2.39294260625396	3.82911579650978	-6.47015679633040
H	2.15149668231541	4.41808559833235	-4.81477219654442

TS1.(3-4)
Lowest frequency = -1150.35 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	4.11360101306756	6.31310807238110	-10.57176117949242
C	4.86627118646339	6.30078273283765	-9.39033255489004
C	5.52190391373603	5.11871381285815	-9.02132150978104
C	5.42884037118398	3.97496012063769	-9.81085644666891
C	4.68363276762781	3.99871210073736	-10.99076835020480
C	4.03149865543387	5.17364322006520	-11.36825604038512
C	4.98930045338766	7.50670660095939	-8.49763214572597
C	4.95111421455181	8.87606272872868	-9.18585335495363
C	5.30237723905797	10.03851719867833	-8.22134524976542
O	5.75482059114839	11.10419875119147	-8.66030709588428
N	5.84933532058451	8.93373065554024	-10.32964769364984

C	5.43487494703811	9.26663047452445	-11.62890752565655
C	6.68167765466987	9.31084725737215	-12.44463660830386
C	7.76402919534185	9.02734146172057	-11.60771736352891
C	7.24252865684434	8.79469197012380	-10.23028621826903
C	9.06295810581436	8.99336505788666	-12.09138798632007
C	9.25174273498888	9.25631571140800	-13.45374260728559
C	8.16743494017317	9.54019777881105	-14.29190325019756
C	6.85861219471531	9.57056688078633	-13.79511334928257
O	4.28105574303134	9.45399507135081	-11.97165853493122
O	7.85025973273449	8.52502512706403	-9.20958160751879
N	5.02858743834943	9.75091573737263	-6.93626644347240
Pd	4.35899403908986	7.94690996232585	-6.44536481776221
O	3.54474890283838	6.11006523436526	-5.94746867407236
C	2.68366101050870	5.76610984619477	-6.82928910166985
C	1.89873433729103	4.50040392016077	-6.59726857509765
C	5.25905976496833	10.75266323301827	-5.86720595423403
C	6.76338684245143	11.08525877953654	-5.75622329558838
C	4.42753346933087	12.03081760091377	-6.11672825258076
C	4.78693921456756	10.10059248426922	-4.59617238142777
C	4.69069708924629	10.52252641994041	-3.28864836289177
N	4.16913702571880	9.46185499399253	-2.61136005583820
N	3.93424475840596	8.41644732796520	-3.41846815576306
N	4.31396553822066	8.81495966056053	-4.61467897802999
C	3.84367988823956	9.36210295012689	-1.17956150235350
C	2.98524124002523	10.51887116953376	-0.72503125975871
C	3.44040052034198	11.38451948447666	0.27187342464949
C	2.64981639573705	12.45550872329094	0.69210291611068
C	1.40155603095179	12.66876279461061	0.11034458907333
C	0.94299728791133	11.80789165511952	-0.89006039789763
C	1.72971171527161	10.73719673131912	-1.30515470458699
O	2.48628224607869	6.42144375763254	-7.89945081414082
H	3.95713811049803	9.08676121107472	-9.59722075469727
H	4.91993163719781	11.45614846008850	-2.80125702146391
H	6.01092589449686	9.78986928219889	-14.43663812352019
H	8.34686864380878	9.74032242710899	-15.34430035578200
H	10.25512629654775	9.24061167637000	-13.86945250369204
H	9.89727847587616	8.77194335287971	-11.43326534337063
H	3.33534452617157	8.40078283147735	-1.07453665881416
H	4.77905721042710	9.32668451485472	-0.61307257533004
H	4.56307929529240	12.73592504049042	-5.28882655183107
H	4.75765754410431	12.49488096288423	-7.04683897017299
H	3.36637327375934	11.77716644814750	-6.19460612230358
H	6.93835312537589	11.78863723623569	-4.93410743674430
H	7.33603760835464	10.17199532677290	-5.57268026814018
H	7.09484001089657	11.53331748224738	-6.69432554656355
H	1.37378266278117	10.07019026660931	-2.08654261468933
H	-0.02941742404536	11.97143192464143	-1.34497405568556
H	0.78614718664006	13.50329645415030	0.43303184584026
H	3.01165109954002	13.12241276531587	1.46905902543884
H	4.41631566184284	11.21936202251505	0.72277437250901
H	6.10962241322007	5.10338349900353	-8.10655552544464
H	5.94701631478950	3.06824926781967	-9.51031026980473
H	4.61501010011890	3.11058553163476	-11.61266463566651
H	3.45066612955699	5.20357434105897	-12.28598254990266
H	3.58880637088691	7.21428269930413	-10.87428109406234
H	5.95059110846599	7.40868602185190	-7.97888530797301
H	3.64528677568696	7.19885526745949	-7.96755062175097
H	0.84942759809518	4.66389368377443	-6.85393942477850
H	2.28993919946094	3.72894342545352	-7.26957239187660
H	1.99627176301362	4.16523632418689	-5.56437804969894

1.4
Lowest frequency = 4.45 cm^{-1}.
Charge = 0,, Multiplicity = 1

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C	3.65189422895293	6.58960806980053	-9.94019155912783
C	4.81856735591809	6.42204626069074	-9.17338499011666
C	5.32664609396054	5.11597858161919	-9.03915093632166
C	4.69306231793419	4.02596325002593	-9.62895437676502
C	3.52879454429148	4.21096463619637	-10.37908319373273
C	3.01723696733394	5.50042012057814	-10.53328136714739
C	5.51215580638155	7.54406212647946	-8.48924095194846
C	5.42010442237815	8.91706094249067	-9.15275215512745
C	5.80026709196401	10.05494838436045	-8.18286206941705
O	6.30537789868371	11.11589962828252	-8.56605551964844

N	6.19691125599774	9.01212734938057	-10.38233137596466
C	5.62875734383402	9.34648993649740	-11.62127658349280
C	6.77185502989360	9.43859281449854	-12.57455768559364
C	7.95006373120228	9.18193961366800	-11.86952928749828
C	7.59644664446831	8.91204479806327	-10.44442749632707
C	9.18652229531077	9.19990974076772	-12.49643024067503
C	9.21214055746624	9.48751830268171	-13.86668107638774
C	8.03152087216488	9.74435242723268	-14.57301333993645
C	6.78687954988439	9.72240051064962	-13.93178423888801
O	4.43875086663019	9.51074251700676	-11.82776487779195
O	8.32972807392599	8.63910345437492	-9.51155445196631
N	5.43002045975261	9.73132000916536	-6.92544994194494
Pd	4.90325632350659	7.86559432927082	-6.54664400572670
O	4.34898225432910	5.85197043682394	-6.17964347091364
C	3.17325874935990	5.55988820993074	-6.44821814799602
C	2.64801507454620	4.16328094869237	-6.37088544237562
C	5.59772827863865	10.68051900589261	-5.80279222335970
C	7.09828987253125	10.94910057078822	-5.54799389176598
C	4.84534077919100	12.00084414924606	-6.07864445911765
C	4.98929156954777	10.01339692304464	-4.59448682216679
C	4.72026528502600	10.46358099799173	-3.32028930098544
N	4.16023571104659	9.40130089918601	-2.67895145618053
N	4.06510698767990	8.32881825475221	-3.48474629194739
N	4.57315942367343	8.70837714015851	-4.63925120538110
C	3.65661962147308	9.32927449138062	-1.30017018988339
C	2.68431684903910	10.44771939211796	-1.00422957775486
C	2.93144240343921	11.33758927489929	0.04312878641748
C	2.03537228427192	12.37211040400199	0.31779674595954
C	0.88967250003481	12.52513253521823	-0.46056034468953
C	0.63952780069068	11.64008434261621	-1.51226340229309
C	1.53103953253448	10.60569507999495	-1.78220449021720
O	2.29571700256218	6.46701136615270	-6.85771171848523
H	4.39138951221894	9.12617215709806	-9.46501152545079
H	4.85269272220285	11.41782265296083	-2.83667677042722
H	5.86550978672275	9.92112366209996	-14.47025401496572
H	8.08450203881380	9.96502231254074	-15.63528335131291
H	10.16244730162052	9.51313240515855	-14.39228715071286
H	10.09650448964178	9.00026464928653	-11.93923738870802
H	3.18994099480835	8.34413141982500	-1.22288458018524
H	4.50822509386973	9.36589467252690	-0.61401940432938
H	4.93076432953799	12.67200254958323	-5.21638338097790
H	5.27773118957834	12.48224412331173	-6.95654889810585
H	3.78655416640594	11.79674329054681	-6.26318908519761
H	7.22899889073431	11.62493952866271	-4.69505154641781
H	7.61537181315705	10.00829911315379	-5.33911509942637
H	7.52938761575024	11.40364016706539	-6.44202930279864
H	1.33851205186139	9.92122286874014	-2.60472429955597
H	-0.25176466383801	11.75727860431500	-2.12157683157481
H	0.19348282017187	13.33207930415254	-0.25199021332319
H	2.23653868947121	13.05885783619398	1.13470875576613
H	3.82875000202083	11.22116950249640	0.64669181454067
H	6.23181515037162	4.96631837001610	-8.45580858193363
H	5.11300144418780	3.03011428079898	-9.51092981436093
H	3.03568041265759	3.36395848518476	-10.84797077346888
H	2.12097169294151	5.66279339584294	-11.12595732754727
H	3.23864303128934	7.58251186003882	-10.09034121978463
H	6.56396552205317	7.29461936903457	-8.31286019952932
H	2.82674428457184	7.32575160026152	-6.93821131228078
H	1.62136929251842	4.15611364063609	-5.99906712786681
H	2.64926721925829	3.75545192706968	-7.38844019383154
H	3.29903439394930	3.55690902472678	-5.74202955155015

1.3'
Lowest frequency = 7.00 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.38643504597565	5.78312760743688	-10.23529793243053
C	4.62117771367138	6.22575413810830	-9.78367082221954
C	5.79805305971120	5.94579066052338	-10.48026198434081
C	5.78496725967283	5.21128996158596	-11.65638031067522
C	4.54362276484723	4.76072503260896	-12.12138181163447
C	3.36363084826049	5.04163949786008	-11.42236017855067
C	6.94855252045734	6.54188519752358	-9.74129463601629
N	6.37774703060883	7.16424529240063	-8.60920425122397
C	4.97646565286624	7.02274734674057	-8.57936989240212

C	7.06039922564564	7.95415743233976	-7.58938942807401
C	8.18596137954716	8.79865219357927	-8.22085452278930
O	7.98124720793657	9.37068653063549	-9.29882968883578
O	4.25505204733338	7.48311723072653	-7.71241085627156
O	8.12856822404290	6.49720508290242	-10.02527450007996
C	7.35512227949648	7.10737174898907	-6.33557402640832
H	6.38260845395799	6.91161864245486	-5.86455315832482
Pd	9.39153310418044	8.10354608855560	-5.62843844243206
N	9.29508136362717	8.89677207275095	-7.46276675567083
C	10.42973371523390	9.73901775068445	-7.92522601809456
C	10.99841573916891	9.19874827545758	-9.25547621035653
C	11.47164395635286	9.62156130579427	-6.84858066382615
C	12.75556865538443	10.09427579814981	-6.69458725299525
N	13.15380363382840	9.64814009300397	-5.46996612952627
N	12.19970471820557	8.93649202919059	-4.85535116707711
N	11.19145739076600	8.92843054554396	-5.70075896132225
C	14.43462415352115	9.88550899215277	-4.78269421573539
C	14.73694171117048	11.36164492900591	-4.67718202909065
C	13.87915195480977	12.20683293564032	-3.96282640125477
C	14.15149382816926	13.56918800880278	-3.87633426595295
C	15.28409580694857	14.09893811810328	-4.49982262174713
C	16.14216346149164	13.26177660473468	-5.21052449054584
C	15.86620146003369	11.89639946621420	-5.30097814339627
C	10.01117296447689	11.22089136121284	-8.05893852139340
O	9.66946160244727	7.31810054608074	-3.78416802780960
C	8.60345994134768	7.18900340458653	-3.03833742989576
C	8.88001610770029	6.49824116018888	-1.71193812526101
O	7.46087300866208	7.54559987373680	-3.35412136809196
H	6.31009100997423	8.68960189358799	-7.27129460324637
H	13.39138810923403	10.70085690328374	-7.31864389747426
H	2.47767104539565	6.00652635432035	-9.68542484902819
H	2.41659382049265	4.67697626474080	-11.80934312388843
H	4.49231477937934	4.18275249831989	-13.03956128308444
H	6.70550056061166	4.99848585004364	-12.19059689194047
H	14.31788112330958	9.41299789916899	-3.80488184906774
H	15.22244044816706	9.36377614971928	-5.33371601012722
H	10.87602338277444	11.83399132498975	-8.33618822778338
H	9.24349648292411	11.30518450023635	-8.82907197409132
H	9.61272107584094	11.58348907130903	-7.10688778519091
H	11.86678725758658	9.79255738788057	-9.56288913231975
H	11.30557951772889	8.15608979421822	-9.13607217328624
H	10.22700914265685	9.25813100443110	-10.02383376784734
H	12.99596712100218	11.79564160712670	-3.48000687895475
H	13.48199769065766	14.21903480745146	-3.32074767552284
H	15.49502337974375	15.16194759198389	-4.43052210003177
H	17.02364252536413	13.66868773657753	-5.69708048654010
H	16.53397297666887	11.24239258148427	-5.85726669312687
C	8.07016328432309	5.77494753782145	-6.43202878464882
H	7.64973794670739	7.78118052216646	-5.41512538811837
H	8.15545932493632	6.82973771399203	-0.96580225597781
H	8.75997692301450	5.41831625182675	-1.85695764941979
H	9.90107676310505	6.68444953727582	-1.37280199551808
C	7.69012744414564	4.76730371871096	-5.53487622845561
C	8.32647702970162	3.52813532096828	-5.54463018875913
C	9.34298311360783	3.27193980250713	-6.46503785234928
C	9.71834421885066	4.26561225061143	-7.36930691628501
C	9.09548184348810	5.51220935787336	-7.34944715221579
H	6.90178437834657	4.97081502728942	-4.81482404439071
H	8.02209880836544	2.76064646257435	-4.83837529682559
H	9.83648460863013	2.30416752758692	-6.47927836446466
H	10.50296486090272	4.07425785633818	-8.09600208732103
H	9.39300901080460	6.27494993557719	-8.05819315094481

TS1.(3-4)’
Lowest frequency = -1035.46 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.28862217862704	5.88926421239902	-10.00799333815932
C	4.56521423779053	6.27365896363880	-9.62460936451208
C	5.69139246946911	5.91079986911853	-10.36531053362956
C	5.58354423211376	5.14809384408131	-11.51831346824575
C	4.29935918905080	4.75528017997841	-11.91427665230041
C	3.17013781883265	5.11973472757727	-11.17134052129215
C	6.90530522847927	6.46192767644126	-9.69454715587802
N	6.42098982732280	7.14476057053366	-8.55755914794103

C	5.01929156610254	7.07846170759201	-8.45820180687286
C	7.20445189632739	7.89615365357532	-7.58081484040079
C	8.29844310042663	8.72457736464538	-8.26894181721860
O	8.09710828407025	9.27043092130649	-9.35984664171210
O	4.36165068176257	7.59301903026586	-7.57026659612445
O	8.06711113697737	6.34560972394360	-10.02743821998764
C	7.61019942040726	7.01880728861682	-6.37882032111303
H	6.66137389373386	6.81988239310965	-5.86226930247473
Pd	9.43408695561694	8.03745359816120	-5.67270912537068
N	9.39997036821718	8.83582623540364	-7.50094486351337
C	10.53266831028404	9.68917281245009	-7.93870417916993
C	11.14191991422668	9.14393791610996	-9.24873400443457
C	11.54712994459928	9.60482908078390	-6.83308544394624
C	12.81746350545816	10.10744617233089	-6.65884951035577
N	13.19550484083783	9.69056076296198	-5.41805610930812
N	12.23896913010616	8.96867721610911	-4.81628292321719
N	11.24925056043588	8.92414952878598	-5.68332656584031
C	14.45322229471786	9.96455606196300	-4.70528593893930
C	14.72563883761966	11.44781725436831	-4.61397368292018
C	13.81632846082227	12.29305690550265	-3.96660596101724
C	14.06407739135337	13.66070721458233	-3.89013940738985
C	15.22346117130948	14.19625818567572	-4.45678149744025
C	16.13257633021033	13.35926323239137	-5.10104814836555
C	15.88119742832013	11.98850097403275	-5.18173772741541
C	10.09159463068982	11.16160312929496	-8.10385626542222
O	9.61127994098727	7.30386772628631	-3.75190418099825
C	8.49055085404290	7.23462532977019	-3.13962516071188
C	8.50821618151386	6.75684612508991	-1.70750484383421
O	7.38345666212133	7.51973793620814	-3.68328873354732
H	6.49711329439538	8.63488657074170	-7.18235792094954
H	13.45562763924869	10.71652861682234	-7.27811634296552
H	2.41984015270187	6.17720130911356	-9.42440443181785
H	2.18759460720320	4.79864698265100	-11.50493918020694
H	4.17402753604698	4.15720829097199	-12.81231444227207
H	6.46565563406478	4.87050246763564	-12.08660178549012
H	14.32289738650890	9.50497789999933	-3.72279791443768
H	15.26570691175435	9.45092665701871	-5.22753226812488
H	10.95213497694157	11.78675949465305	-8.36752241446658
H	9.34185611495276	11.22159787819988	-8.89389322044213
H	9.66239352075814	11.52927586926977	-7.16720629068306
H	12.00229652621069	9.75300809568727	-9.54895802528422
H	11.47141589370045	8.11066817795954	-9.10799460604559
H	10.38398478705544	9.17480671811811	-10.03253033620991
H	12.91197813544431	11.87745254018513	-3.52888062596727
H	13.35404261449312	14.31043830726951	-3.38714042841866
H	15.41496919438793	15.26345890221286	-4.39581524139969
H	17.03463035574626	13.77052330677537	-5.54434027649266
H	16.58845636434752	11.33493326451805	-5.68739086656040
C	8.25393353032355	5.67315672447344	-6.58903166551042
H	7.74903181642014	7.60718900542118	-5.08135493462605
H	7.82485696669321	7.36159112440328	-1.10701304610833
H	8.14863364328452	5.72228215832240	-1.68403268977616
H	9.51850856598472	6.79303452464973	-1.29909181219238
C	7.79369181193479	4.59376406616396	-5.81927102774129
C	8.36955548963088	3.32984664783069	-5.93517369939777
C	9.41183818784385	3.11873941643091	-6.83705479535066
C	9.87114173799032	4.18268768091509	-7.61619080362815
C	9.30791037859552	5.44906403967861	-7.48855436900014
H	6.97616987080550	4.75542155034677	-5.12009364160004
H	7.99720012275447	2.50945728882850	-5.32754343032253
H	9.86009806686518	2.13399655208745	-6.93549789317525
H	10.67598352730917	4.02686346746252	-8.32929899372853
H	9.67054576261777	6.26666187809676	-8.09890857858715

1.4'
Lowest frequency = 7.83 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	4.83091268850284	4.79167463009610	-10.64725450826587
C	5.74625699355179	5.63911981561902	-10.04164161208255
C	7.10426141201482	5.59410443926734	-10.35991722200352
C	7.59952771254320	4.69980009205601	-11.29660590176731
C	6.68330664112658	3.83974020353207	-11.91460060512754
C	5.32133505107628	3.88466927392955	-11.59472320324204
C	7.82038302064584	6.60260824936655	-9.52504723072272

N	6.82887216616128	7.22225614918204	-8.74997247892445
C	5.54847896328097	6.68625526801600	-9.00114908169884
C	7.03047248341592	8.24177457563289	-7.72317617305640
C	7.99799302103931	9.32558770354644	-8.24760461362623
O	7.69257964955661	10.04042383751919	-9.20993543139122
O	4.52314305833994	7.03842100857768	-8.44965142996126
O	9.01554536247271	6.83735046955375	-9.48548330767413
C	7.47060831874637	7.67084042082155	-6.34611605332666
H	7.03752252945552	8.35243232465608	-5.60196852031293
Pd	9.49495946184396	7.97404936292650	-6.19511135184927
N	9.14679816555102	9.37825086293030	-7.53616298159612
C	10.25941790714886	10.25682139807494	-7.97343821597017
C	10.66544347266396	9.95290756980803	-9.43648061817941
C	11.43361831237640	9.92821210892395	-7.08669430928023
C	12.66423287406146	10.52551041787295	-6.91834857790610
N	13.30811232771421	9.75670529472619	-5.99749820686602
N	12.54468447948183	8.72793383963180	-5.58766064507154
N	11.41524865930030	8.83810507162303	-6.25653341226388
C	14.65612554110591	9.93478473015590	-5.44070657745697
C	14.87334914395753	11.34756786746623	-4.95104811222750
C	14.03939560822147	11.89082574563657	-3.96620097397805
C	14.23657269296069	13.19503126801954	-3.52140686833949
C	15.27067080413197	13.96901625263410	-4.05405697124885
C	16.10451722068176	13.43356413535042	-5.03385146247703
C	15.90286389701611	12.12714869380278	-5.48264046090121
C	9.87501382491627	11.74135998137827	-7.80841112351754
O	9.82675206293254	6.37896796049949	-4.84713205854467
C	9.31329017688782	6.47738502000925	-3.72376884630256
C	9.25997058047330	5.33706654103925	-2.75983058031791
O	8.73265525001531	7.59954176170311	-3.31117803847608
H	6.04033674393480	8.70016455999130	-7.62266793066878
H	13.11597512859850	11.40734340922862	-7.34275193767528
H	3.77725416686242	4.83286827805389	-10.38983861302733
H	4.63610457895257	3.20283744501091	-12.09012723426119
H	7.03248412077479	3.12416406485197	-12.65351418396160
H	8.65812689027302	4.67213932738941	-11.53544678058901
H	14.72611851201330	9.20176058885878	-4.63320098279091
H	15.39049629205632	9.67594723652229	-6.20975016335923
H	10.71186417007521	12.38970154106592	-8.09370878246991
H	9.02072063326107	11.95627918813862	-8.45261467573917
H	9.60641203491782	11.94758781224690	-6.76818817267237
H	11.54040935880701	10.55384806076313	-9.70984677677414
H	10.90803677182083	8.89268233731314	-9.54113487507020
H	9.83336560774913	10.19413998027359	-10.09857660149908
H	13.23040539275157	11.29149749248767	-3.55583659438481
H	13.58432911617099	13.60973364100240	-2.75849081529380
H	15.42250076992213	14.98661499445255	-3.70649336103080
H	16.90814434204933	14.03137449045709	-5.45366519913579
H	16.54974425821109	11.71056741054868	-6.25134827203653
C	7.03411226347152	6.28028241793436	-6.02360781090005
H	8.79032441871544	8.22286777855309	-4.10545154637075
H	9.27555614808445	5.69222033605582	-1.72819886991408
H	8.31502144848703	4.80857465229962	-2.93489633403251
H	10.08411825828869	4.65091305642236	-2.95506735915613
C	6.05833027561314	6.05803351407462	-5.03901301311602
C	5.64341472595555	4.76823106759149	-4.70742013281321
C	6.19541339514205	3.66586045346095	-5.36024155303907
C	7.17460241804998	3.86808225865270	-6.33615889614684
C	7.59437620899872	5.15609012883732	-6.65546045239793
H	5.61457106796256	6.91405326656712	-4.53601930537493
H	4.88107875293242	4.62614764805538	-3.94573409875268
H	5.87014049472506	2.66001240423223	-5.10953534301056
H	7.62288193499165	3.01687401189919	-6.84180347118351
H	8.39681776400747	5.29960380112174	-7.37302409539739

1.1a
Lowest frequency = 13.27 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.73644057659153	9.18015352472372	-0.91994373195099
C	3.37493156225264	10.45263107795107	-1.37624250484165
C	4.19158769548496	11.54876630862292	-1.08570299477826
C	5.36285568761992	11.37762523090139	-0.34761990679955
C	5.72077603522129	10.10740105003388	0.10371060160140
C	4.90507459445929	9.01076180686624	-0.18097632037303

C	2.13112083121897	10.62838050207182	-2.21661322359233
N	2.37174528934305	10.21978850866899	-3.61662892454001
C	2.73318000870289	10.97321482760911	-4.68423057464449
C	2.97490155885961	10.08305479373519	-5.71187710123406
N	2.75400924602613	8.83284463014886	-5.17633494209684
N	2.38809952156238	8.92353019552750	-3.90820950912128
C	3.35950785524128	10.41994045817915	-7.13402349185372
C	2.17408448170631	10.13905648999684	-8.08271756648108
Pd	3.03899662511807	6.87937702398583	-5.61038814430644
O	3.29534779816896	6.07820661109400	-3.67568718035253
C	3.44396102062131	4.94656855750753	-4.23215208332905
C	3.79866755942817	3.71731216351951	-3.37760594773936
N	4.54801088020725	9.60541530489620	-7.46491410596384
C	5.28730644693081	9.77142003258665	-8.59748681964306
O	4.90043526392040	10.40157599398662	-9.57577699668081
C	6.67552786851504	9.07911694201239	-8.56170495870505
N	7.38723411536686	9.44475715232889	-9.77366911190656
C	7.66483349346234	8.52484169188065	-10.80666946827855
C	8.24052479379232	9.33663197017110	-11.91539945196192
C	8.28102423782705	10.67211403797232	-11.50867337128756
C	7.73715631618851	10.76226121246474	-10.12334963178401
C	8.77293369388702	11.66677986196560	-12.34073742477495
C	9.22259536747773	11.28277206134297	-13.60966839970855
C	9.18124426581831	9.94401039064257	-14.01699169993341
C	8.68885885421331	8.94553465149350	-13.16834629525988
O	7.47344572508755	7.32657168813378	-10.74449727111071
O	7.63784848980233	11.73899026447273	-9.40244246334269
C	7.54615532276211	9.41249693114407	-7.31647228917035
C	7.04011390285370	8.85199272905202	-6.00770083444329
C	6.90818943712864	7.46952156293703	-5.82034610459392
C	6.43102413363084	6.96001080585100	-4.61444324133228
C	6.07614699562533	7.82154032475531	-3.57540264512012
C	6.20330516010341	9.19944124679651	-3.74741847340520
C	6.68319763264655	9.70721839073328	-4.95530018821479
C	3.73266024107499	11.91603339994864	-7.20883437740819
O	2.68168953994534	7.06761362039658	-7.55981968602902
C	3.68235561176078	6.69588467115356	-8.30393640791857
C	3.27941495517670	6.59108185541207	-9.80608612640795
O	3.34957255502458	4.83066224403552	-5.49312857140737
O	4.81878664432037	6.40600840817080	-7.96626706763286
H	2.79960306579995	12.04723545241373	-4.63912607526729
H	8.65169179138835	7.90467639838624	-13.47394268283678
H	9.53614090496790	9.67865619065336	-15.00862040991161
H	9.60906648314822	12.03409418962269	-14.29227091550877
H	8.80057553861294	12.70211544585936	-12.01591031450578
H	1.80778149366799	11.67064371362932	-2.24493977140266
H	1.30893925467580	10.00689064788692	-1.85691109139868
H	1.33362109385763	10.78310530797962	-7.80355628354479
H	2.48110779761614	10.36916147145621	-9.10418086126058
H	1.86631104918846	9.09601264480509	-8.02388687817306
H	2.86146697883563	12.54002077411804	-6.98397072730360
H	4.54244384409386	12.15094424700687	-6.51091116575083
H	4.06716742077810	12.14026074452299	-8.22218065318436
H	3.91223747352331	12.53989656066429	-1.43629637539417
H	5.99376225292450	12.23340574808287	-0.12713976258505
H	6.63395556102034	9.97134827174286	0.67520710958532
H	5.18240727415630	8.02079504507597	0.16853846602622
H	3.11623257307103	8.32226444774985	-1.16389308218108
H	7.15673945047436	6.78845108982201	-6.62825878029364
H	6.33657186009228	5.88583035911945	-4.48975124586772
H	5.68972846111349	7.42143270812022	-2.64445529148073
H	5.93052903827480	9.87539676936485	-2.94241213593162
H	6.77971616277686	10.78189895714006	-5.09344493917386
H	8.53776214229807	8.99415475906599	-7.52579134285399
H	7.65786567002576	10.49699124112667	-7.24766474612159
H	6.51285321947007	7.99660257795237	-8.62460291927231
H	4.97073779340991	9.07610009397869	-6.70855572052801
F	4.30284320056156	6.95035876089377	-10.60023600798223
F	2.95659714343789	5.30389906191942	-10.09340507031101
F	2.21416882172793	7.35905503730255	-10.13119272533519
F	3.30413115994856	3.83718154483277	-2.13016324713901
F	3.32471245596488	2.58565159267126	-3.92215328125349
F	5.14856466692019	3.60912193715296	-3.28163104199936

1.2a
Lowest frequency = 11.41 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	1.64663709958921	10.52705414338270	-1.10052705854912
C	2.93194390391507	10.61559390190425	-0.55298138777728
C	3.24571627153296	11.67368877375549	0.30262778886474
C	2.28438056839426	12.63624169327611	0.61411826955047
C	1.00664424915343	12.54621669884518	0.06454559185057
C	0.68966062189450	11.49071204197436	-0.79372820748865
C	3.97475542789672	9.57381933627140	-0.89211096892915
N	4.29286674746020	9.57288153877971	-2.33078054052450
C	5.07535633009361	10.44109042135276	-3.03303569664411
C	4.92915053849280	10.07050736178490	-4.35226165604423
N	4.06426434023075	9.01807115890492	-4.34364729556893
N	3.66562377580159	8.70027733597383	-3.12939544013836
C	5.45579889971119	10.54219079564164	-5.67280732139549
C	4.79493739140631	11.89306354313429	-6.02909179381356
Pd	3.53236877137785	8.28823982433639	-6.07849724638615
O	2.59574453664724	7.44224827565069	-7.77613275705049
C	1.78184205612692	6.86299851858875	-6.99084300440318
C	0.71732129618432	5.91957757856734	-7.58120320711682
N	5.05928229549400	9.47113503673970	-6.64530293912489
C	5.54778314995758	9.56510209114504	-7.91146351501635
O	6.20364918914953	10.53361191560931	-8.31516450424379
C	5.29929627635558	8.36133641803473	-8.84507388503122
N	5.92645504159471	8.62651681555156	-10.12968396946648
C	5.17549018630277	8.92616068317520	-11.27939087135800
C	6.17368940136199	9.14448686785049	-12.36363939540398
C	7.44975083083766	8.98300458137374	-11.82067489112684
C	7.30959580019074	8.64808679056949	-10.37320238962343
C	8.58926713708497	9.12195964988662	-12.59827340304851
C	8.41328650261691	9.43379873145596	-13.95192112952499
C	7.13366416933844	9.59541231763640	-14.49590249611480
C	5.98857093898592	9.45105390115416	-13.70341238657699
O	3.96006636913754	8.97898265207885	-11.32791412666385
O	8.18377780794764	8.40868644745068	-9.56024569178402
C	5.78648256666608	7.01331500985140	-8.25732183376156
C	5.73591086929295	5.90310556161989	-9.28146405903118
C	4.52545796018623	5.51880368851610	-9.87367559787832
C	4.49443968336581	4.51618095906633	-10.84037083820070
C	5.67422680906351	3.88122762385627	-11.23341294878378
C	6.88424029422750	4.25814202504956	-10.65227546306696
C	6.91286924836456	5.26360686030978	-9.68481824109488
O	1.86339894327348	7.03012053407534	-5.73878160008756
C	6.99068431053431	10.67717044385039	-5.56297625597759
H	4.23068414519962	8.29715585742678	-9.06784738791926
H	5.64417445641337	11.21965442798992	-2.55156533799403
H	4.99159161076022	9.57193053854200	-14.11540665382128
H	7.03035372321846	9.83596714001956	-15.55011364499604
H	9.28211417532201	9.55211547422602	-14.59312047795725
H	9.57706165526583	8.99265228376361	-12.16713941235487
H	3.62684934656642	8.56162784616511	-0.67473720545602
H	4.90485365249612	9.75421576217814	-0.34829425918105
H	5.03910890277184	12.64722925196084	-5.27237398779653
H	5.16428659317569	12.21975269088258	-7.00176017345971
H	3.70793310131122	11.77642144049976	-6.07258620144111
H	7.23740360788974	11.36461013836887	-4.74553953849064
H	7.43722296683448	9.70174252060295	-5.35032028367088
H	7.39855676084532	11.06342132646316	-6.49519133994920
H	1.40115394375413	9.70703824505253	-1.77061203568667
H	-0.30548107582754	11.41716034315599	-1.22208488249235
H	0.25787444560287	13.29556166037101	0.30349838160380
H	2.53528639943937	13.45442205742994	1.28259094873157
H	4.24308532970491	11.74370436556107	0.73118078804184
H	7.85882472276861	5.57099492860180	-9.24680806593198
H	7.80902251305420	3.77416877725803	-10.95502455678627
H	5.64952625840291	3.10103415855188	-11.98924239665294
H	3.54679066218412	4.23223118649744	-11.28989581626293
H	3.60537259470056	6.01736239726114	-9.58403268047476
H	6.80595338316708	7.13091301664127	-7.88473574314319
H	5.14426246153195	6.77720238013209	-7.39949493084962
F	0.20143398201412	6.42436379763479	-8.71821345166696
F	1.28200118473738	4.72221177747171	-7.87176942053256
F	-0.28739211054436	5.70918666125826	-6.71234086985421

1.3a

Lowest frequency = -2.91 cm^{-1}.

Charge = 0, Multiplicity = 1

71

C	1.74729361886240	9.79936218338474	-1.36725027456449
C	2.92998568969281	10.32045689103396	-0.82929636139438
C	2.88016011429827	11.46682850043265	-0.03308860891141
C	1.65911010887784	12.08960294065828	0.22875493356550
C	0.48390389951984	11.56950854222297	-0.31104597768223
C	0.52999302460861	10.42446462712643	-1.10976043497743
C	4.25320894075714	9.64620509952096	-1.11328770331706
N	4.60484478523750	9.71239755212193	-2.54387121644929
C	5.14457452886646	10.74921433775412	-3.24530749658821
C	5.15705636378137	10.32945698693254	-4.55779464258524
N	4.61216517830465	9.07448640782263	-4.54542231792003
N	4.27101733106093	8.68714336103123	-3.33550483521070
C	5.62273820074751	10.92435680211251	-5.85776518818596
C	4.89225624383345	12.26383331392778	-6.09512103187811
Pd	4.45533978425158	8.20499046120962	-6.30973643978371
O	3.63673362365803	6.47020259320569	-5.62037612403494
C	2.54967258462815	6.15887737994101	-6.24559613292337
O	2.01489948583210	6.73382994698604	-7.19000312180437
C	4.87344473491453	7.67447114273024	-8.56149405009190
C	5.05749029096014	9.07296862990553	-9.18778012229951
N	5.96993501152982	9.00930983414559	-10.30949236087662
C	5.58890903877012	9.28748130773337	-11.63687897044496
C	6.82354590931421	9.08600450599710	-12.44682841247247
C	7.85949447609348	8.70944862202588	-11.58677341462540
C	7.31954086138766	8.65107279904115	-10.19949184912525
C	9.13372431956599	8.44084540813937	-12.06316634837845
C	9.34625633693809	8.56225439655385	-13.44178815836479
C	8.30881781671942	8.93848450754320	-14.30260922063305
C	7.02462001753699	9.20682003396992	-13.81332442666591
O	4.47064241323590	9.60771400303760	-11.98896543145513
O	7.87531182219362	8.33724999563809	-9.16015340404750
C	4.60703159242109	6.56573173358093	-9.55387471057759
C	3.37227098517276	6.45930817561328	-10.20186274413740
C	3.16953398983097	5.47119117023209	-11.16170169299646
C	4.19590853236270	4.58006407844398	-11.48000864446762
C	5.42589940715162	4.67661269964554	-10.82958180716613
C	5.62937964011822	5.66379741757699	-9.86628475116595
C	5.53424425758349	10.16971908040558	-8.19833483234555
N	5.25589439187783	9.92541335959874	-6.90159983773490
O	6.07986568200972	11.18796528095822	-8.64155940859149
C	1.89363161837688	4.88483422209527	-5.63856502462407
C	7.15405554376363	11.12298267369933	-5.80962015547888
H	4.10675310239714	9.41112411359209	-9.61607474508355
H	5.45764587476309	11.66415192544788	-2.76930490554456
H	6.21287727815493	9.49669092518451	-14.47291393182607
H	8.50532165597858	9.02191376701459	-15.36748054677162
H	10.33117182523286	8.36046310681727	-13.85265239538964
H	9.93148051380750	8.14759506872924	-11.38805351708835
H	4.22714910098416	8.58094238919515	-0.87427106179257
H	5.06519596343858	10.11697869954526	-0.55446447954394
H	5.12269661244921	12.96482115249153	-5.28513194829115
H	5.22181335623833	12.68779952435200	-7.04409136001815
H	3.81116253767347	12.10133531737481	-6.12439804140521
H	7.41908510323881	11.81170099426893	-4.99968008101078
H	7.65103625791332	10.16408658030428	-5.63890760936538
H	7.48849786718499	11.53617644308695	-6.76191092597675
H	1.78376034334099	8.90924575929589	-1.99019310425334
H	-0.38421990409399	10.01579437857474	-1.52959988478028
H	-0.46730156533198	12.05330033477689	-0.10983099695017
H	1.62786845072226	12.97849679390175	0.85183550625410
H	3.79754494448128	11.87123106196597	0.38924537245001
H	6.58673922985948	5.74390136374574	-9.35791911183379
H	6.22644680393816	3.98194152397079	-11.06755328574992
H	4.03398222415635	3.80792478977810	-12.22670411876559
H	2.20602944770643	5.39194518039677	-11.65630628568983
H	2.56572151907174	7.13783979752774	-9.94105304422011
H	5.77527253321080	7.41565128501003	-7.99085023561200
H	3.88742786423458	7.69545426225616	-7.96679336098296
F	0.85733193912797	4.45276565158350	-6.38020250531862
F	2.77730372707791	3.86330979800305	-5.53282538305734
F	1.42136319639553	5.14624200607252	-4.38867025897004

TS1.(3-4)a

Lowest frequency = -1084.94 cm^{-1}.
Charge = 0, Multiplicity = 1

71

C	1.80474092882148	9.99735942073474	-1.38964107260117
C	3.03512112229024	10.25595542159037	-0.77408818230479
C	3.13785641949920	11.29948975439835	0.14815506972051
C	2.02188116178031	12.07805103290763	0.45895119737336
C	0.79935622105378	11.81841681783614	-0.15788219385213
C	0.69286428719561	10.77734925258032	-1.08333486592305
C	4.24416573025153	9.41176682476656	-1.10929576602937
N	4.59677325201419	9.50716430983853	-2.53538261705213
C	5.12262349567833	10.56505561458795	-3.21401847790819
C	5.15670916686690	10.16506967288987	-4.53234916009211
N	4.64113778411904	8.89767031179580	-4.55486788354473
N	4.29524809205676	8.48836338017895	-3.35226218229486
C	5.61388206985975	10.81939290095858	-5.80845152384941
C	4.84382467585274	12.14448680339347	-6.00072700057188
Pd	4.54459243320087	8.08454643175810	-6.42287763489436
O	3.59855269243445	6.27641950302632	-5.94653645853207
C	2.65879117941014	6.11118922815880	-6.77229416630880
O	2.41811555742890	6.83143715268693	-7.78195348780808
C	5.06133124675502	7.66631807653467	-8.48239372011948
C	5.08183125089597	9.04053115779599	-9.15453725358198
N	5.93540220005349	9.05173963223622	-10.33178354126598
C	5.48636492040122	9.40185174466098	-11.61597822881945
C	6.69442811112013	9.34768018337119	-12.48657478902027
C	7.79069476364443	8.99283338101099	-11.69577605976690
C	7.31798301445350	8.80981646705087	-10.29390395885237
C	9.05945389725062	8.85581244560532	-12.23779473821682
C	9.20304193888366	9.08796041230149	-13.61120509740664
C	8.10496377905512	9.44313187924772	-14.40296698029330
C	6.82677139323570	9.57814062197071	-13.84742079960040
O	4.33414259561905	9.66844032065508	-11.90684166680041
O	7.94881251663916	8.50195479608104	-9.29830360331842
C	4.73131872004018	6.48107649435842	-9.34024679855253
C	3.91672551112756	6.57191503690424	-10.47711255780276
C	3.63634792623669	5.43859181732334	-11.23631447726631
C	4.14871937490155	4.19473669208706	-10.86546968856613
C	4.95712050512548	4.09318936098255	-9.73229084020706
C	5.24951331434720	5.22829879395956	-8.98110230791745
C	5.53783924560202	10.15869606757825	-8.18396056200559
N	5.29038183961126	9.85797840170043	-6.89368952796604
O	6.03707803466751	11.20546856098909	-8.61258180332180
C	1.70369281516014	4.91956643912721	-6.54146962501624
C	7.13748048309628	11.06656985517708	-5.74836240067902
H	4.08817000555742	9.32053686952955	-9.52379812229586
H	5.40564461793916	11.48026859348478	-2.71989520347949
H	5.96859584066958	9.85227171542349	-14.45283729691565
H	8.24919284376599	9.61599741303753	-15.46548787636119
H	10.18161139921415	8.99088010311815	-14.07235714864116
H	9.90466205143225	8.57865613499841	-11.61573622423404
H	4.06221124736396	8.34892762247532	-0.93483138710256
H	5.11397632258033	9.72256340931598	-0.52506430212805
H	5.04922565878839	12.82291628946276	-5.16511532380427
H	5.16333082857922	12.61134708772485	-6.93308354499971
H	3.76828140070405	11.95013682707123	-6.04140790448189
H	7.38024562883341	11.73920316666758	-4.91803492501165
H	7.66526845950528	10.11954688354092	-5.60606654897681
H	7.45919734298810	11.51847937598638	-6.68787483022972
H	1.72266092153170	9.18824165372285	-2.11108423769138
H	-0.25883005556116	10.57187886420186	-1.56427507950201
H	-0.06967422255874	12.42447661170271	0.08043964252129
H	2.10991619162491	12.88608024371433	1.17917424087966
H	4.09247547392010	11.50203337209140	0.62876924211010
H	5.88375657950467	5.15067786930936	-8.10111892715788
H	5.36451104662083	3.13045300625815	-9.43648902996506
H	3.92052678889458	3.31141054298233	-11.45494642725659
H	3.00769739346702	5.52780679007364	-12.11777626255448
H	3.49696137049451	7.52854844708896	-10.77338557959052
H	6.04897886959220	7.48091529798560	-8.04322841717849
H	3.60723422116347	7.52465864045663	-7.84881045799639
F	1.62450045440469	4.15052663487304	-7.64662114676136
F	2.09891042460687	4.14208137966974	-5.51776074630828
F	0.45939922663604	5.37839968123521	-6.25940074204990

1.4a
Lowest frequency = 7.55 cm^{-1}.
Charge = 0, Multiplicity = 1

71

C	1.56707768085237	9.87233311775679	-1.96611818950438
C	2.65744299086587	10.23874048607308	-1.16836576934934
C	2.53134612830790	11.31053387753688	-0.28230153365833
C	1.32708501286552	12.00993333558277	-0.18771154031020
C	0.24493845453434	11.64277881025605	-0.98554431464261
C	0.36745669400700	10.57313472513876	-1.87571884038863
C	3.96201784677160	9.47942583586713	-1.26899995426635
N	4.51769993631021	9.52675062531393	-2.62927583520105
C	5.06408103930141	10.58423529412865	-3.29094090808803
C	5.31425702684471	10.12225768125991	-4.56552753574226
N	4.89541256712738	8.81888810990240	-4.58993882288970
N	4.40593400618247	8.44958460448612	-3.42467239642256
C	5.91766852189451	10.76449130232521	-5.79073895308818
C	5.23033565394389	12.12398521929310	-6.03883771566168
Pd	5.10255667275073	7.98434668085074	-6.51372732392575
O	4.47907006179609	5.98681543292462	-6.05739862507377
C	3.27332204120464	5.81743813082048	-6.22682956880912
O	2.42652744924934	6.72913929596071	-6.64030729008313
C	5.54305855244355	7.65055617272253	-8.49868471568250
C	5.52996894805827	9.03370003590769	-9.14604807900758
N	6.26926052856955	9.07878302706822	-10.39922290684240
C	5.68231911612866	9.43819891157088	-11.62309755943408
C	6.79473246235320	9.43440960646537	-12.61576864803152
C	7.97556049270873	9.09934915666422	-11.94827560443782
C	7.65440901522557	8.87260375031349	-10.50859488925436
C	9.18648112573065	9.01557495418523	-12.61838444605937
C	9.18357582363253	9.28134514757487	-13.99325354967265
C	8.00060494722039	9.61662598150007	-14.66181485736679
C	6.78177389534459	9.69764367526474	-13.97719620808261
O	4.50052373604126	9.68493664418376	-11.78910923169081
O	8.39570110686796	8.55477447148882	-9.59642270626970
C	4.68022216026936	6.60877921990722	-9.11598065221752
C	3.49686714654194	6.90218428418612	-9.81783330440976
C	2.69423338602748	5.88545305011770	-10.33057525802807
C	3.04689469306309	4.54702820233865	-10.15603485600857
C	4.22551357772598	4.23616817840641	-9.47417635994296
C	5.03100234824524	5.25287509457465	-8.96954017418892
C	6.01369898130504	10.13793658844305	-8.18405931447728
N	5.66241088495585	9.83190962222281	-6.91440906144231
O	6.56607125718674	11.16990745104040	-8.57600654374111
C	2.60876298456026	4.46842476279351	-5.88876750616260
C	7.43835630541634	10.94740551311276	-5.58254881989468
H	4.50913139061644	9.31896369137092	-9.42192585217629
H	5.21034024360193	11.54175368529912	-2.81782313695649
H	5.85889593815991	9.95688571904348	-14.48647103117773
H	8.03126258009029	9.81718295120303	-15.72888391741496
H	10.11323150816720	9.22717994621683	-14.55242898218513
H	10.09844721963223	8.75470595191857	-12.09057610989425
H	3.83184871517575	8.41622303281306	-1.05356189719121
H	4.70703149153475	9.88932406397218	-0.58224227637314
H	5.38103283063645	12.78508207143667	-5.17779173322916
H	5.66070496843226	12.58642222723250	-6.92772408926571
H	4.15653436047373	11.97995960112012	-6.18948929465124
H	7.63205437797804	11.60954686054766	-4.73108860785117
H	7.90843663656988	9.97820206089287	-5.39327964965536
H	7.86671809652541	11.38257224857946	-6.48738419535225
H	1.66381829487579	9.04147543129304	-2.66054756640354
H	-0.47425034324264	10.28416988070772	-2.49817068368125
H	-0.69192999590073	12.18757986279857	-0.91617886711829
H	1.23766932379450	12.84120947343047	0.50539922461362
H	3.37676967602120	11.59845700523966	0.33871008547705
H	5.94595124862825	5.00423707918163	-8.43728685735045
H	4.51995636607832	3.19883191448907	-9.33904403969188
H	2.41663849034328	3.75618638183155	-10.55218065108539
H	1.78825373477686	6.14306274711028	-10.87228671281599
H	3.20247273085922	7.93423220777330	-9.98293956954804
H	6.57554597699484	7.29759147692268	-8.40360930643591
H	3.00759103326375	7.55342496280483	-6.81363928138320
F	2.03891719373134	4.56008640983679	-4.66086618793531
F	1.65007591245774	4.15060826117671	-6.77356818783027
F	3.51693073929172	3.48485972622665	-5.85940225598592

1.3a'
Lowest frequency = -6.90 cm^{-1}.
Charge = 0, Multiplicity = 1

71

C	9.01723674487875	5.60195873105450	-7.35457508620777
C	8.03691312956177	5.96938818822335	-6.42314834609426
C	7.66692640618494	5.05235886905391	-5.43001510457026
C	8.27407478859668	3.80101322877071	-5.35644731155287
C	9.24573047883822	3.43998654336058	-6.28980171147185
C	9.60756034452551	4.34105166426631	-7.29137833070709
C	7.36496499938081	7.32870475931181	-6.41420109304154
Pd	9.46952716052908	8.26141436884130	-5.84610284913352
O	9.76701960263092	7.57106108959875	-3.95248278613106
C	8.73729812709334	7.55717533712157	-3.17614007562349
O	7.58830773257979	7.92793753234857	-3.39811180395075
C	7.06756596077858	8.08372337816152	-7.72485390473529
C	8.19680441893987	8.87578464155923	-8.41592779293805
N	9.34067242117544	8.96299605863158	-7.70470100580687
C	10.48215072981561	9.76262307438738	-8.23206187742094
C	10.10221199894101	11.25445485729362	-8.36431795074899
N	6.37940753654232	7.22034867786815	-8.67727904014090
C	6.93282094545623	6.53455033837049	-9.78049293342147
C	5.78114857194697	5.83761702525581	-10.42261054786921
C	4.62174947105032	6.11895140891486	-9.69692079981187
C	4.98841232499868	7.01835386699299	-8.57181255817808
C	5.75412651158439	5.01173973175798	-11.53615099865409
C	4.51760218073438	4.46966724301491	-11.90692876919389
C	3.35585266346008	4.75148105093096	-11.17844299338192
C	3.39220986637301	5.58600634133797	-10.05523726785226
O	8.10318345656985	6.51499715091171	-10.10570629828399
O	4.28704534378746	7.50791296204283	-7.70463510778457
O	7.97382540366489	9.42389864423970	-9.50068109383536
N	11.30239194048918	8.97537149040481	-6.02557468079140
C	11.56844770376683	9.62012591881802	-7.20305293214406
C	12.88807084433401	10.00708706704986	-7.12190131017482
N	13.31781695076003	9.55575665567197	-5.90946177504944
N	12.35038462480992	8.92716166852968	-5.23228633976409
C	14.62017917874395	9.77123517927134	-5.25291923724429
C	14.72319119773185	11.15730119558901	-4.65834763610168
C	13.88913607029777	11.52851760121218	-3.59718251227941
C	13.97788441311655	12.80827062654024	-3.05563919754051
C	14.90084263685821	13.72406512387799	-3.56626803542674
C	15.73479160662470	13.35732780030065	-4.62128248908097
C	15.64332930268274	12.07637323504291	-5.16745532702129
C	10.97071600545857	9.18664730188956	-9.57859743614424
C	9.08880730526124	6.92869955572661	-1.79487514784838
H	6.40282225921173	7.20639716246100	-5.89990098361040
H	6.32380504399142	8.84582197697347	-7.45884321206388
H	13.53261716063791	10.54704468683154	-7.79618453280828
H	2.49795193312901	5.80973409581188	-9.48226557424610
H	2.41259409316541	4.31327281838999	-11.49097894079328
H	4.45605959264536	3.81755592213936	-12.77325940351444
H	6.66064071227857	4.79738096043719	-12.09313923210056
H	14.68626162046258	8.99303988100976	-4.48972796638847
H	15.39790218320470	9.60331336371824	-6.00162250987993
H	10.97025619363932	11.83689716298548	-8.69220080941615
H	9.30055579174583	11.35391796976672	-9.09721917147222
H	9.76326900375263	11.64096650362900	-7.39879275084586
H	11.84772357842454	9.74348057002198	-9.92747156611158
H	11.24127281052264	8.13390919065835	-9.46079480483559
H	10.17151596383735	9.26911741477249	-10.31529015618048
H	13.16988813735903	10.81570580913845	-3.20172602609614
H	13.32913049354194	13.09063926068757	-2.23194268421013
H	14.96948330587485	14.72066764630002	-3.14034739956473
H	16.45517950960268	14.06536042369103	-5.02012935407684
H	16.29513599225628	11.78876212159113	-5.98959266465499
H	7.71790188677977	8.08136043773100	-5.58401436866869
F	8.10134876149436	7.10783516415866	-0.89708823519683
F	9.28604883923745	5.58903255076313	-1.92337154714301
F	10.22091008896780	7.45719671932736	-1.26802084123656
H	6.91353195043501	5.33512695488693	-4.69958392003794
H	7.98516121353185	3.10866089834185	-4.57117809455188
H	9.71720397398730	2.46275996085481	-6.23706702137232
H	10.35787910372771	4.06697384337100	-8.02763852056923

H	9.30608270100046	6.29386634600270	-8.13643321319996

TS1.(3-4)a’
Lowest frequency = -1078.77 cm^{-1}.
Charge = 0, Multiplicity = 1

71

C	9.24738827177120	5.41456853023024	-7.52598010748270
C	8.26200383965457	5.78246921969299	-6.59506448353113
C	7.78953122676214	4.80708957891923	-5.70219915744048
C	8.28742667299242	3.50602445124303	-5.72984620446333
C	9.26027580590639	3.15152531112262	-6.66393354318768
C	9.73053594402557	4.10995955330254	-7.56432631605816
C	7.71713161447478	7.17822030885616	-6.47496646342998
Pd	9.60466028576736	8.09971556090571	-5.91262423917702
O	9.80479384115521	7.41790314609216	-3.94235868818619
C	8.71879300459115	7.56018696273421	-3.32349457063950
O	7.62942541109703	7.97152594452229	-3.81433060258040
C	7.29800956583474	7.97931378805509	-7.72264646091806
C	8.39947168069829	8.72622381420231	-8.48648805960760
N	9.53016525660887	8.83594797437333	-7.75620651306493
C	10.67944509956670	9.63069757115771	-8.26451925201197
C	10.28053193734189	11.10846828667774	-8.47582671733808
N	6.46060237604300	7.19057541949728	-8.61993065193755
C	6.87860753028084	6.42121568394502	-9.72735963512314
C	5.62592341240805	5.83786699387910	-10.29107022869212
C	4.54410678903593	6.26271937635906	-9.51731752175951
C	5.06601229736665	7.14154954659098	-8.43684869039251
C	5.44997501627026	4.99512816626497	-11.37804659356697
C	4.14371845904475	4.58567076862674	-11.67222345739061
C	3.05952522179776	5.01203778037490	-10.89602944469735
C	3.24631987209977	5.86246510870083	-9.79998337547474
O	8.02104594036607	6.26741788558192	-10.10922596799813
O	4.46449276211792	7.71969225045333	-7.54843002975593
O	8.18969685862478	9.22660820081083	-9.59542081905481
N	11.46808272425267	8.89250611835105	-6.02532875278559
C	11.73141559761488	9.55455415377293	-7.19244041338872
C	13.01608152499631	10.03876323582190	-7.07120948242013
N	13.43688068632576	9.62422475581399	-5.84322819127115
N	12.49160247251004	8.92746098413561	-5.19828570868393
C	14.68988994410315	9.94532371392029	-5.14018485549815
C	14.66832899952075	11.34534018975548	-4.56788985176255
C	13.72318293392124	11.69171069443416	-3.59510591779551
C	13.70041848638545	12.98180086258234	-3.07185410413139
C	14.62270713214062	13.93412027179158	-3.51206487717151
C	15.56701891995303	13.59273789987814	-4.47869012467544
C	15.58683202357630	12.30109730611315	-5.00713966833409
C	11.22392965215819	9.00888346732161	-9.56919322837049
C	8.69140137306984	7.17202257229504	-1.82868298505184
H	6.80107173925125	7.09738025171583	-5.87599020877575
H	6.62824501762220	8.76810479598095	-7.35618937393640
H	13.64103618896926	10.62520445387126	-7.72489979406157
H	2.41311364203104	6.19816960060911	-9.19066750250774
H	2.05856556649630	4.67531100742625	-11.14970279421606
H	3.96570197274502	3.92492270896008	-12.51569825354657
H	6.29735763988739	4.66884350855521	-11.97263005692020
H	14.78031049005715	9.18745286899029	-4.35882408699270
H	15.51140253321446	9.82281342829112	-5.85000606318910
H	11.15100364771076	11.69266600023183	-8.79459100044625
H	9.50656870837498	11.16259071328457	-9.24250935835912
H	9.89720692980690	11.52885154395450	-7.54156436288620
H	12.09694186602301	9.57107381253084	-9.91954961465678
H	11.51798442122957	7.97009110832935	-9.39514015072368
H	10.44348548096245	9.03780329748345	-10.33044270910640
H	13.00442812011632	10.95056743042938	-3.25476547262823
H	12.96460334124615	13.24449254986189	-2.31762968202216
H	14.60392724088881	14.93916214459723	-3.10111234955962
H	16.28655671839089	14.32931201373608	-4.82378574865168
H	16.32355181375483	12.03435346016363	-5.76175015401387
H	7.93322688200893	7.94100302802149	-5.15683694104707
F	8.21229483950410	8.19181286654016	-1.08213859305644
F	7.88010549547423	6.10311641514266	-1.64761317151754
F	9.91058771213773	6.85261284721258	-1.36220280184222
H	7.02498562261354	5.07826628824282	-4.97737435084027
H	7.90921795686901	2.76921746284504	-5.02666688868078
H	9.64765634583466	2.13702840498503	-6.69236998282999

H	10.48222949779114	3.84143822829328	-8.30134639459364
H	9.61773110475539	6.14991835055448	-8.22985718209082

1.4a'

Lowest frequency = -6.66 cm^{-1}.

Charge = 0, Multiplicity = 1

71

C	7.63909627792067	5.25804743199354	-6.68875396958384
C	7.13055843577809	6.41250738426520	-6.06671327741159
C	6.26009119088970	6.24101512432258	-4.97863089635747
C	5.89591368925329	4.96947654534992	-4.53686893494346
C	6.39113772148030	3.83629432888817	-5.18124908917930
C	7.26613266475131	3.98823506730605	-6.25925449334242
C	7.53346722528829	7.78452527508140	-6.48847826284133
Pd	9.56784679835474	8.04348832927982	-6.43966246795959
O	9.92883592647418	6.55335323131050	-4.94175252854156
C	9.55815449619264	6.91211050312106	-3.82713109282933
O	9.05672317350311	8.09137353472073	-3.53750669430770
C	7.05092357007459	8.29429562902602	-7.87329119059162
C	8.01757846303878	9.33418810094881	-8.48408523983875
N	9.19394222072852	9.39990027024440	-7.81607159861616
C	10.30778520694416	10.24154525352356	-8.32299724260826
C	9.94782300901494	11.73662418173124	-8.21229365023958
N	6.79206720225913	7.23064453572045	-8.83855480419753
C	7.74202235921056	6.56079880427969	-9.62296823652552
C	6.98193335037353	5.51347104802672	-10.36498916172037
C	5.64094929328531	5.58518988359115	-9.98385119427168
C	5.49771511698078	6.68988214726427	-8.99580459760207
C	7.42800811705100	4.56212899124173	-11.26969952680971
C	6.47999669219679	3.67215947142489	-11.78955412557066
C	5.13558419128862	3.74378337856856	-11.40660598893463
C	4.69470182536920	4.70833794293401	-10.49221645379941
O	8.93958405747177	6.78751564054256	-9.64743710081607
O	4.50421110216577	7.08050046212827	-8.41366428030634
O	7.69341645677795	10.01165133819165	-9.46482595018783
N	11.50349783214009	8.85611830241510	-6.60975212596714
C	11.50272233683562	9.93386605110582	-7.45500772636733
C	12.73846705734772	10.53057123383062	-7.32245073487781
N	13.40537991047455	9.76946009376794	-6.41125935257140
N	12.64834349276885	8.75165395696644	-5.96720435501078
C	14.73080882988622	9.99493715759230	-5.81801701925314
C	14.72634903895926	11.16367747951352	-4.85736771108560
C	13.88524112717917	11.15114149278949	-3.73844195516500
C	13.87921528828162	12.22754620214491	-2.85541591909844
C	14.71519230178153	13.32406942853992	-3.07987669408514
C	15.55558166735371	13.34052504958318	-4.19156984869070
C	15.55788139829177	12.26326116423041	-5.07923817577233
C	10.66518246110443	9.86474099161936	-9.78148653381181
C	9.68322108649699	5.98315668133969	-2.60442164250855
H	7.14157253934445	8.50562854419916	-5.75966943140724
H	6.07458468179559	8.77752943314524	-7.75591508417509
H	13.18185682615882	11.40316956269612	-7.77410889041541
H	3.65532858892408	4.76979758686492	-10.18558969658047
H	4.42513784562283	3.03691988009665	-11.82535940232331
H	6.79060405823279	2.91133032553798	-12.49984206694027
H	8.47365468184586	4.51314609709557	-11.55712431419181
H	14.97946745840149	9.05699791126333	-5.31582796290049
H	15.44410449154953	10.15939533021792	-6.62976800255294
H	10.78435357823163	12.35908995962975	-8.55072934357157
H	9.07798124074508	11.93650000307955	-8.84013862359810
H	9.71350942720462	11.99261701237109	-7.17490694807085
H	11.53871646206162	10.43998910162476	-10.10866151847008
H	10.89084173010981	8.79752307735170	-9.84440484223769
H	9.81637426347108	10.08697860958177	-10.42887880596570
H	13.23308611979398	10.29857595857740	-3.56591826437895
H	13.22391119947896	12.21128993375775	-1.98951198504132
H	14.70950380403501	14.16231340927123	-2.38944547164055
H	16.20684752962272	14.19078383308768	-4.37151990201090
H	16.21230924719180	12.27701105848869	-5.94803851680706
H	9.04599087768655	8.58057006941332	-4.44179041739949
F	10.64726732754241	6.45792926162020	-1.77831981726217
F	8.52712796908959	5.93416601587845	-1.91692857762956
F	10.01788662072116	4.74416711229281	-2.97864283840885
H	5.86075249240229	7.12101883295165	-4.47951679233243
H	5.22108164288175	4.86537449982792	-3.69159492530219

H	6.10801247033239	2.84443093648470	-4.84073654823895
H	7.67438649579578	3.11251906833421	-6.75652245504485
H	8.36895166670705	5.36236245479269	-7.48598771090268

1.4-4
Lowest frequency = 11.76 cm^{-1}.
Charge = 0, Multiplicity = 1

71

C	3.54869178775161	6.89744280575437	-10.74357179269065
C	4.33617492841290	6.64089982788522	-9.61603394309049
C	4.71929389438660	5.32541455433181	-9.33311307812495
C	4.32644716455333	4.28080358384366	-10.16694017385194
C	3.54930380177139	4.54186465976141	-11.29615631258163
C	3.16419280936781	5.85178706559440	-11.58197031753417
C	4.77418599735673	7.74924558430357	-8.68434289930412
C	5.04417674209175	9.13089292982369	-9.29847511115242
C	5.57138466318580	10.20781347710887	-8.30238792486061
O	6.11090228949497	11.22147996032140	-8.76680367385684
N	5.97048475322725	9.02943415356019	-10.40952165846901
C	5.67222685902497	9.46420912933934	-11.71350975986588
C	6.93710470073514	9.29678556018092	-12.48267165561787
C	7.91651261942255	8.79789139959136	-11.61878998006412
C	7.30941410579987	8.63199125180153	-10.26845416041582
C	9.20517448471817	8.53710179253322	-12.05929846335350
C	9.49143093550551	8.79485293812105	-13.40544938108368
C	8.51077381086907	9.29412791468637	-14.27023691776051
C	7.21118620897726	9.55252690803838	-13.81761524892059
O	4.58556448449145	9.86716064933838	-12.08486954330334
O	7.81002119186096	8.23026022558182	-9.23279881250647
N	5.33047708090804	9.95477558407339	-7.00357599026520
Pd	4.63529456815122	8.18818060649350	-6.38163987301663
O	3.95720875566250	6.39332410228439	-5.75240020165722
C	2.81264687728800	6.44451465467370	-5.10533377600490
C	2.37691549788003	5.08882494358295	-4.57108264431677
C	5.73758838633213	10.94311852040381	-5.96414546111869
C	7.27071858140052	11.14086191312277	-5.96883152524011
C	5.00177876183827	12.28398791877747	-6.16245260487821
C	5.32519501147392	10.33030560397470	-4.65312752410343
C	5.23539879892549	10.77660605892979	-3.35289961229969
N	4.82147286666935	9.69444931400170	-2.63189225133305
N	4.63448714368207	8.61885714321354	-3.40415374974556
N	4.93928582927570	9.01756205799063	-4.61674013455590
C	4.35059131985580	9.63414006076268	-1.24022577250895
C	2.90122797229234	10.06397481935077	-1.13068767529261
C	2.53217274386810	11.01307600133560	-0.17433732147117
C	1.19826524951440	11.40247410855175	-0.04756512601758
C	0.23100574910056	10.84954349404854	-0.88569845136337
C	0.59987675134170	9.90651516623703	-1.84745273995762
C	1.92915076208707	9.50848804422550	-1.97235870155456
O	2.15387140314625	7.46947142881647	-4.91168669821543
H	4.12571691540486	9.54199933659254	-9.73248251780677
H	5.40912054984870	11.73783559012683	-2.89739271553284
H	6.44407908172454	9.94028753792849	-14.48035988195313
H	8.76470768680026	9.48421306650628	-15.30895357063822
H	10.49041333011490	8.60558892694885	-13.78730044799046
H	9.95903356341456	8.14994686197804	-11.38113591228417
H	4.49114439465936	8.59532746416548	-0.93070107164855
H	4.99984578476370	10.27384169908765	-0.63800708609777
H	5.26459466352971	12.97957185968977	-5.35742776379166
H	5.29681946116333	12.71585609419506	-7.11939861178091
H	3.92014939741563	12.12361696904290	-6.15172569454963
H	7.56495636338528	11.81773723479316	-5.15916239777620
H	7.77196663456258	10.17914315125756	-5.82826378133194
H	7.57174263150476	11.56571362951534	-6.92733518209914
H	2.20030160224963	8.77916194348412	-2.73268567395149
H	-0.14623489020688	9.47544018906279	-2.50813284593671
H	-0.80708394766152	11.15569554758561	-0.79326457985541
H	0.91908514374731	12.14021509119334	0.69916156470456
H	3.28878876846524	11.44883058218814	0.47497626743154
H	5.32177860711212	5.12395889370375	-8.45134429610525
H	4.63118687016979	3.26388377140284	-9.93665700268363
H	3.24699570836148	3.72918911070829	-11.95044957470619
H	2.56226630197710	6.06467815659263	-12.46073548858010
H	3.24981785578379	7.91295780467605	-10.98637006820683
H	5.68220183045109	7.41064922886317	-8.16062841397340

H	3.85649239533441	7.87841437305336	-8.00266146426120
H	1.29733889038238	5.08523645390035	-4.41075736167187
H	2.66895856336399	4.28357426132503	-5.24930025511815
H	2.87612049847959	4.91819925408106	-3.61016252847914

TS1.(3-4)-4
Lowest frequency = -1255.73 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.56234536890510	6.56012469950269	-9.70727790504711
C	4.87789722173426	6.45224032644901	-9.23320427849562
C	5.66630140338722	5.37505758952049	-9.65778116489956
C	5.15906927823945	4.43558456359774	-10.55380682912503
C	3.85266962429499	4.55572760987370	-11.02861745502353
C	3.05662395933900	5.62077705504950	-10.60144018818787
C	5.46019459579812	7.47830566223776	-8.28139689595699
C	5.40942539535923	8.89791407515571	-8.89365270348924
C	5.95078832887166	10.02292220733417	-7.97626557967831
O	6.52873651914255	11.01376165654251	-8.43604448186726
N	6.10259807771807	8.91972082964347	-10.17200855213807
C	5.47303287791919	9.27715976589667	-11.37790794854872
C	6.54335754204678	9.22646994654272	-12.41399567102099
C	7.73950171535117	8.86093190717289	-11.79150808068417
C	7.47143838895294	8.65813817004301	-10.33820750957534
C	8.91813280978560	8.72939027577242	-12.51005158549982
C	8.86629517651337	8.97893545860111	-13.88685151295187
C	7.66757704029243	9.34413617566178	-14.51042842185903
C	6.48172903547381	9.47298106095227	-13.77724269264304
O	4.29367881587021	9.55253303723330	-11.49730909439687
O	8.23705606608415	8.31100236021500	-9.45640742425653
N	5.63008807613892	9.79554963471673	-6.68944152985203
Pd	4.84134112819786	8.03554937495105	-6.27087724465625
O	4.09537393113986	6.01989802872272	-6.34067926717097
C	2.74503863036043	5.96812112273283	-6.45519304021174
C	2.23955914638437	4.54348791026666	-6.45729003676227
C	5.90070845389937	10.77167960033399	-5.61166009858584
C	7.42125292696671	10.91863404072899	-5.38944460466827
C	5.25515067425381	12.13826229469968	-5.92885233867136
C	5.24495809599411	10.18524388631145	-4.38879025333316
C	5.04712135433943	10.62806424278585	-3.09971901258558
N	4.38283204867743	9.61614235966243	-2.47406471541593
N	4.14825170659020	8.58633271994170	-3.30167545026964
N	4.67525944467117	8.94084627106587	-4.45342075292028
C	3.81679268315647	9.58846214957938	-1.11821243448633
C	2.59678103301749	10.47579526702058	-1.00141628328084
C	2.54150738067299	11.46883717291583	-0.02135398638102
C	1.41256768584745	12.28109959157694	0.09606742962680
C	0.33722695783267	12.10705657421363	-0.77335939838176
C	0.39099126039603	11.11801575050281	-1.75840034362788
C	1.51429962936809	10.30323457773515	-1.87203746575916
O	2.03978581586802	6.95485038319896	-6.55780969869699
H	4.37453176207264	9.16271930899289	-9.13550140423674
H	5.30050354791514	11.54613335326912	-2.59478954768273
H	5.54690249485043	9.75530281465132	-14.25115315911828
H	7.66004364456470	9.53057607622836	-15.58045868192376
H	9.76964964948079	8.88854409401746	-14.48319821156352
H	9.84269227568045	8.44554522408876	-12.01718158660536
H	3.57656280827461	8.53865654102219	-0.93303813603324
H	4.59611647997068	9.90013843452991	-0.41799633991084
H	5.41117638247082	12.82952855626787	-5.09299741176961
H	5.71157866186867	12.54983737276751	-6.82984817112481
H	4.18058552770627	12.01622451964876	-6.09130410904938
H	7.62499339553979	11.61058107409191	-4.56438566982647
H	7.86207354247246	9.94554594089992	-5.15590219322484
H	7.87198846483344	11.30537524087265	-6.30565627186527
H	1.55638882175684	9.53601117216251	-2.64117797323778
H	-0.44422057929706	10.98054017977726	-2.43863962380997
H	-0.54040433040912	12.74082596544349	-0.68686198463806
H	1.37734667886583	13.05030767925076	0.86194614895689
H	3.38291307666877	11.60706403693145	0.65414666305547
H	6.68559052672570	5.28764117272423	-9.29069055077082
H	5.78568532301448	3.61101557219235	-10.88235525903244
H	3.45617959314590	3.82391076871894	-11.72664091582327
H	2.03782870390801	5.72003744336280	-10.96465036463788
H	2.93296474558200	7.37756236926618	-9.36771855254559

H	6.49712467549673	7.21554816901086	-8.06409616992413
H	4.61721051697978	6.70574603795630	-7.33810955034196
H	1.14957564450729	4.53513467439155	-6.43750418628501
H	2.59898984981490	4.04600282821332	-7.36467326328365
H	2.64367381068726	3.99676799258826	-5.60048402231141

1.4-4
Lowest frequency = 7.69 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.84045244348085	6.42258444705354	-10.20182144735835
C	4.96530849000451	6.35762841519700	-9.35884243354506
C	5.54124919197713	5.08649690270959	-9.13614796982951
C	5.00276962823951	3.93284762707067	-9.70939548406391
C	3.87957599968662	4.01948695570630	-10.53022956330322
C	3.31153600351428	5.27164035857468	-10.77843148366907
C	5.51983903529783	7.52842608579138	-8.64531360641918
C	5.40360100605565	8.89653321891508	-9.30849554981070
C	5.68061384690502	10.02372618405744	-8.29117268738120
O	6.15882275721491	11.11553444364064	-8.61967823867375
N	6.25753818228474	9.04545166330482	-10.48133405569547
C	5.75717557433599	9.35323670727144	-11.75588085768727
C	6.95554857329640	9.52406797154686	-12.62667057949488
C	8.09582558249846	9.33104451030211	-11.84310493764997
C	7.66182668351181	9.02402728536431	-10.44802241239752
C	9.36920867745595	9.43053475085288	-12.38260821053383
C	9.47144121942878	9.73486635031478	-13.74571197978999
C	8.32883540978578	9.92753520808029	-14.53067638155005
C	7.04657027034465	9.82295751843794	-13.97777292336483
O	4.57619618853808	9.44274106018269	-12.04460639731815
O	8.34367304444545	8.77809374728926	-9.46974465324572
N	5.27304312697537	9.64780586639404	-7.06076990050191
Pd	4.64625822241156	7.79378729201059	-6.79853188987034
O	3.92072368579699	5.73599490636583	-6.69892119094774
C	2.63483886290066	5.23678194893157	-6.47861029251969
C	1.80993120520951	6.16449657435321	-5.64086952370407
C	5.35250176949262	10.56890669788883	-5.90810607563261
C	6.82644687080019	10.90278357357805	-5.58855034198730
C	4.54455754457932	11.85952115398270	-6.17688020146821
C	4.73197141632194	9.84192266696953	-4.74257289237514
C	4.54050271033655	10.20601332019137	-3.42705786611482
N	3.92895284433832	9.13820142202131	-2.84722870677565
N	3.73222942738854	8.14331191915720	-3.72965193604628
N	4.22045665833066	8.57700022615924	-4.87571218870128
C	3.49730939042522	8.97947971171349	-1.45030351377978
C	2.69647505364307	10.17032753486927	-0.97909816688922
C	3.14440765535101	10.93953942583104	0.09693151044480
C	2.40866410973864	12.04364065766343	0.53092026017695
C	1.22277296515499	12.38700703688259	-0.11540383245341
C	0.77168232935458	11.62314541680223	-1.19479517975909
C	1.50377074263963	10.51977530384497	-1.62385343032842
O	2.31275082757747	4.17351265489557	-6.94193724848533
H	4.38920978316217	9.06336506375473	-9.68611973097192
H	4.76212709917914	11.10566384902046	-2.87613369854647
H	6.15407581597346	9.97143514647987	-14.57756578166298
H	8.44135425055763	10.16303409205008	-15.58508020865268
H	10.45232870220089	9.82429183666587	-14.20378685138421
H	10.24923827626315	9.28013303308947	-11.76512640263236
H	2.91299771302837	8.05616697132390	-1.43794590910006
H	4.38404734963113	8.83782854519345	-0.82480323224555
H	4.56605692064368	12.50910566023453	-5.29443784003559
H	4.98289081862952	12.38472725618686	-7.02643119757611
H	3.50448806813717	11.60809580341361	-6.40455166655177
H	6.89187893152609	11.55649201114384	-4.71094004598734
H	7.38284234689662	9.98251789760623	-5.39020319775251
H	7.26595752473200	11.40835113252282	-6.45029814488614
H	1.15502665807377	9.92967241145445	-2.46787425691467
H	-0.15187882563805	11.88845909674720	-1.70074093803187
H	0.65062063720530	13.24772518007375	0.21788947535049
H	2.76509810044383	12.63515268331014	1.36901900832920
H	4.07244369404959	10.67369668739292	0.59790890097008
H	6.44019988182051	5.02130800696506	-8.52493789013070
H	5.46595892762689	2.96910632053886	-9.51642077002875
H	3.45363668100872	3.12516848914957	-10.97435925288845
H	2.44399661257235	5.35185774552672	-11.42786449863195

H	3.38367597750181	7.38357844788530	-10.41780787791632
H	6.56049868514098	7.35082600264029	-8.35518336139817
H	4.34389699135705	5.18654429831827	-7.41056784133948
H	0.84010020501337	5.70560649199051	-5.45226187906188
H	2.32494228861358	6.39180187045335	-4.70302527519639
H	1.68601765758048	7.11367324669819	-6.17364217462531

1.3'-4
Lowest frequency = 10.00 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.25751345128849	5.79609565477197	-10.10796564119228
C	4.53473071449431	6.19860139054883	-9.74564730036134
C	5.66105706965245	5.79386310891147	-10.46474009666127
C	5.55236717473669	4.96962491253706	-11.57450635909017
C	4.26743935153388	4.55909948349546	-11.94949235613061
C	3.13844336911486	4.96530207114687	-11.22818822386925
C	6.87692222210014	6.37448858381621	-9.82455923203425
N	6.39235013359817	7.12359860409274	-8.72768216535995
C	4.98946558876860	7.06389749336894	-8.62595108773518
C	7.15650197117311	7.95396861700006	-7.80484405327458
C	8.32634536933803	8.65707119110877	-8.53321625358456
O	8.11443650001610	9.15706160179081	-9.64510320676683
O	4.33818826160743	7.62851254559539	-7.76381707534005
O	8.03864322344856	6.22989683241266	-10.14525872766369
C	7.41052192444302	7.20619681889553	-6.47833940552729
H	6.43644204498102	7.12521309810922	-5.97726054228131
Pd	9.58844547118091	8.07349722049976	-5.93602052315622
N	9.46450686674133	8.74127473109618	-7.81966807832190
C	10.62195063130248	9.50758079741120	-8.36329649998243
C	11.14074499929859	8.85049589869161	-9.66071803480430
C	11.68092906643473	9.43051617498870	-7.29776379647422
C	12.95051653235715	9.94369593532559	-7.14635095533850
N	13.37378624733824	9.49569928992863	-5.92903187311709
N	12.44451680976161	8.75500459498097	-5.31574176384986
N	11.43185843094747	8.72959879716466	-6.14966943203248
C	14.55343169274235	9.90376744433334	-5.15257620632166
C	14.31137379327194	11.21723804903281	-4.43575063100253
C	13.14989802210087	11.40998802183722	-3.67716285939262
C	12.95198203506779	12.61971541389725	-3.01486600043680
C	13.90564020620865	13.63650019977547	-3.09778329643570
C	15.06197572680850	13.44472411598525	-3.85282185270735
C	15.26097669833775	12.23805738199211	-4.52459337234222
C	10.25116561455968	10.98913338060774	-8.59497781908560
O	9.74044637512110	7.41422787934756	-4.03148871069822
C	10.03588939169177	8.33904131967421	-3.14486945583014
C	10.24805222780133	7.76964560086677	-1.74987527991636
O	10.16619935015502	9.54219997356891	-3.38572372964978
H	6.47285355139293	8.77373097072729	-7.54820208160538
H	13.56073472684576	10.57736163159109	-7.76901865245919
H	2.38883845813656	6.11660947161113	-9.54159942730616
H	2.15553349891118	4.62883708957419	-11.54474145026451
H	4.14146769540510	3.91399872183689	-12.81414082562169
H	6.43392323036645	4.65969642354337	-12.12658359866249
H	14.73674739224466	9.08504806014420	-4.45196971711812
H	15.39960707766727	9.97773248617043	-5.83966593861606
H	11.13170129928202	11.54830553851790	-8.93057186974901
H	9.47288398384643	11.04872082482460	-9.35652007042158
H	9.88732753924464	11.43212464709285	-7.66360420926658
H	12.02105475115686	9.38840734678109	-10.02994664705948
H	11.41603020297677	7.80948102010463	-9.46979766700899
H	10.35354774009646	8.87979448878292	-10.41505835394608
H	12.39128104335247	10.63305435505483	-3.60803700301315
H	12.04563461933035	12.76283201246905	-2.43429169416658
H	13.74516413443684	14.57741272057938	-2.57928511220335
H	15.80536020181700	14.23326261159005	-3.92628773668223
H	16.15979586393068	12.09014059083881	-5.11975188020205
C	8.02927167972205	5.82192751292206	-6.47878079177293
H	7.82495607846336	7.97039958981294	-5.70214430880930
H	10.03549220146698	8.53645816619920	-1.00248470607067
H	9.63123589602224	6.88386069155530	-1.58220115656973
H	11.29914576763552	7.47266744415382	-1.65602343939864
C	7.60227610036717	4.90989814480380	-5.50564619585568
C	8.14018637811370	3.62637557510108	-5.44622536374070
C	9.10535467725188	3.23150873405737	-6.37223542923016

C	9.52731582313187	4.12983674081329	-7.35260567098256
C	9.00141402940347	5.41916791259319	-7.40380825360016
H	6.84826950375680	5.21404098995368	-4.78373287565302
H	7.80086548236287	2.93464067214976	-4.68054728881494
H	9.52346385393418	2.22968243090114	-6.33186664729255
H	10.27210424135044	3.82985585829935	-8.08416202708402
H	9.33198671705294	6.10594729624106	-8.17298201198398

TS1.(3-4)'-4
Lowest frequency = -1245.62 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.19897218318104	6.09563746411316	-9.60379033632947
C	4.53774645521630	6.37113435972003	-9.36634940310755
C	5.54690578964513	5.84659803824911	-10.17613516014176
C	5.25476772358757	5.02537211138461	-11.25455369896928
C	3.90641075540705	4.74244869003378	-11.50365102941686
C	2.89474509608963	5.26887500227154	-10.69161908475191
C	6.86789244198759	6.30846274326714	-9.65753828252190
N	6.56073742217186	7.12150311624891	-8.54246140963289
C	5.17782844069707	7.19452051890179	-8.30491584948350
C	7.50671766725664	7.82049712163288	-7.67999601909373
C	8.61950513938632	8.49873274732417	-8.50744439237051
O	8.39199268091023	8.96827915040210	-9.62555447102939
O	4.66267347089439	7.81484043231214	-7.38977067551129
O	7.97673010100158	6.04090983012895	-10.07079366186065
C	7.92253130891035	6.92883641992024	-6.47685519997465
H	7.02412126774535	6.90862126857666	-5.83630499579824
Pd	9.75053189210946	7.94140239614526	-5.94435467205166
N	9.77107930945398	8.60259709863224	-7.81004592727960
C	10.90603627371118	9.42327931788878	-8.29779955473467
C	11.53708193896951	8.76722972952873	-9.54285287656925
C	11.88758538837796	9.45190346496265	-7.15575665362815
C	13.13202155539644	10.01460457350196	-6.97282893209424
N	13.47806183630403	9.70293996396368	-5.69213655682473
N	12.51976447023890	8.99667653132240	-5.07415035368399
N	11.56624662634070	8.85243727784896	-5.96783766038728
C	14.63334906997516	10.16582210506246	-4.91111268985478
C	14.45083553624674	11.59092812586793	-4.43365422238902
C	13.30730026821876	11.95119419574340	-3.71088619963489
C	13.14765620930651	13.26150996802414	-3.26743141272574
C	14.12814312896834	14.21927024453483	-3.53644939688740
C	15.26832093781592	13.86362831177315	-4.25502913705450
C	15.42629005734348	12.55229408391001	-4.70600113125877
C	10.46349329542464	10.87391109019227	-8.59918924037735
O	9.19470822882725	7.11811663355546	-4.02168594905027
C	9.07538999379353	8.10215919079930	-3.10064582832655
C	8.92183289424201	7.53887773851299	-1.70368918156794
O	9.11183757969938	9.29015982828117	-3.36461317580638
H	6.92978991356981	8.65240776499584	-7.25786562731393
H	13.77266391979461	10.59744133564351	-7.61455791484436
H	2.42251638185752	6.50816014564790	-8.96722227645734
H	1.85816856827672	5.02982426288960	-10.91093915279632
H	3.63770921980957	4.10328755508870	-12.33977611521390
H	6.04694166672760	4.62092284816400	-11.87663715246233
H	14.71397716904340	9.46535623150351	-4.07614953052728
H	15.52408704610387	10.07213954062887	-5.53712459675998
H	11.33183866643215	11.47698734592680	-8.88703899637833
H	9.73756920343305	10.86781005403201	-9.41288942111183
H	10.00722757630610	11.31638337483556	-7.70903754143041
H	12.39742847055249	9.35053373391274	-9.89039037545192
H	11.86859164335940	7.75223312904814	-9.30664116647833
H	10.78707906798921	8.72401650750427	-10.33472763567627
H	12.54028100660870	11.20881168106814	-3.50473648195244
H	12.25623771096350	13.53484170901704	-2.71080529239024
H	14.00066502850631	15.24024126207556	-3.18884671231863
H	16.03227252868702	14.60497693019549	-4.47023883274482
H	16.31380834853178	12.27557542324343	-5.27100424520780
C	8.30427938218629	5.50186832150707	-6.75966991204149
H	8.43383586081861	7.24133141048992	-5.11184620246914
H	8.79662724714160	8.35149208684413	-0.98784621039715
H	8.06201556841204	6.86313642698351	-1.66630895114594
H	9.80902934100459	6.94962951274721	-1.45026881801826
C	7.58885370953772	4.47046562019259	-6.13639791547681
C	7.90976992856650	3.13282513625846	-6.36509230296271

C 8.95535162017680 2.80651649777843 -7.22739413130434
C 9.67406595840159 3.82598989889325 -7.85565763896930
C 9.35769238886804 5.16000209426350 -7.62038422754231
H 6.76899813083595 4.72274640798041 -5.46718585756549
H 7.34131443479974 2.34879730277374 -5.87243009753056
H 9.20897511405955 1.76599521183189 -7.41005261845556
H 10.48549939522875 3.58023537201653 -8.53486045568928
H 9.91547434855757 5.94771997947895 -8.11393317073456

1.4'-4
Lowest frequency = 6.88 cm^{-1}.
Charge = 0, Multiplicity = 1

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C 3.56589624068219 5.60203997884560 -10.41364442293259
C 4.77571223874592 6.07664811594946 -9.92872240122146
C 5.98858606941101 5.72958631007961 -10.52534503712223
C 6.03827712782373 4.89323952901407 -11.63007603798751
C 4.82243052228269 4.40910546324441 -12.12814309507735
C 3.60589777064239 4.75752622381539 -11.52961260580284
C 7.09756093178885 6.38575191590968 -9.77166919392128
N 6.46808742309201 7.11373642996032 -8.74192852939045
C 5.06881102736099 6.97922863143746 -8.78137838231904
C 7.10583199985126 7.97499374925299 -7.74459874527010
C 8.27567046865618 8.76641571883517 -8.35820986562176
O 8.21604883438201 9.24993840669935 -9.49303525162625
O 4.29577572365681 7.51759654717668 -8.00761911837362
O 8.29299344617210 6.30278367624542 -9.97664485027225
C 7.41008079343835 7.28933421307712 -6.39812936407685
H 6.56160314460376 7.44475236481493 -5.72215557401432
Pd 9.06096793338536 8.22472988359919 -5.63459175967985
N 9.27727351809958 8.93070264184713 -7.46247825234666
C 10.44818142434053 9.77938128962709 -7.78362054448065
C 11.23712660854929 9.17342897938196 -8.96463277274122
C 11.31522920031282 9.79284229468341 -6.54967372621614
C 12.55542379118057 10.33883162668261 -6.29712611197581
N 12.81192034698196 10.05083634591916 -4.99208943270242
N 11.80251891289161 9.36212426883512 -4.42841228443902
N 10.90138258253396 9.21264143812303 -5.37936279043051
C 13.99913813605257 10.39940602054603 -4.19724290007415
C 14.37218304291977 11.85302440767350 -4.36977300520826
C 13.46739729619237 12.86182343380843 -4.01700954943506
C 13.80796403751034 14.20059099722476 -4.18866529552102
C 15.05685572849330 14.54503312201776 -4.71186542079125
C 15.96207338529210 13.54555396972325 -5.06340786579604
C 15.61782089762978 12.20318763841869 -4.89533572019065
C 10.01643531539575 11.23103144142144 -8.09751885107781
O 8.71270889181065 7.44285959922511 -3.62958162291478
C 9.15040108686546 6.23626382368412 -3.05940654896005
C 10.34322149346470 5.69491764401553 -3.77778164521361
O 8.57250291705883 5.79375760746842 -2.10150362107904
H 6.34400410565845 8.73372341179446 -7.52903627652228
H 13.24516209773862 10.90378549971156 -6.90300481309098
H 2.62806642256820 5.87892030766415 -9.94228002274315
H 2.67972202097306 4.36519016894821 -11.93967761259806
H 4.82006536877325 3.75214155424314 -12.99322168629366
H 6.98719630062273 4.62975826262398 -12.08655793631186
H 13.72929298000552 10.16011295627812 -3.16569625923619
H 14.82671369781864 9.75046553914471 -4.50043561476295
H 10.89758851851581 11.85749276113203 -8.27719026487898
H 9.38196328097204 11.23058230360599 -8.98487000137718
H 9.45771149422871 11.64375990390717 -7.25222093517993
H 12.12641027237650 9.77728791963889 -9.18000089169475
H 11.54957966114024 8.15410250946819 -8.72120243224946
H 10.59327835871279 9.14896019955915 -9.84498393737458
H 12.49286100638274 12.59479693283196 -3.61568092826970
H 13.10030697906972 14.97724737206858 -3.91413962905348
H 15.32050334902728 15.59000323891685 -4.84572711337475
H 16.93339020293515 13.80740151070687 -5.47254779133378
H 16.32177629514315 11.42255254783027 -5.17456546787709
C 7.81295443102362 5.85687010936220 -6.36599769109279
H 7.89786410462997 7.70695042247374 -3.16148462037047
H 10.73086500327375 4.83838869237449 -3.22793307202778
H 10.04244416769012 5.38951084254656 -4.78686094955415
H 11.10358073976414 6.47528087491907 -3.87845906240401
C 7.21080353640099 4.99059050251030 -5.43525637878198

C	7.62218948022066	3.66443533694118	-5.30398201164499
C	8.63847667265147	3.16363958894920	-6.11719998378995
C	9.23829496905204	4.00680428336073	-7.05851064697081
C	8.84115722874080	5.33527647084184	-7.17614332638595
H	6.40809219580001	5.36967724027699	-4.80639547265763
H	7.14403447391795	3.02329494544857	-4.56846782214150
H	8.95970734262002	2.13038847965337	-6.02144865316247
H	10.02905100571159	3.62843687173811	-7.70099029751597
H	9.32538192628896	5.98343769024551	-7.89768020097291

1.4-OA
Lowest frequency = 7.57 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.41031009105848	6.50109499761624	-9.69554878428815
C	4.68074867585130	6.30898807494430	-9.12844224907979
C	5.19851344714348	5.00541026950002	-9.08011065468995
C	4.47008675386222	3.93275245442100	-9.58472879932221
C	3.21027180526278	4.13916533359481	-10.15122048866495
C	2.68158739472665	5.42957050135214	-10.20350656815626
C	5.41475902791836	7.48468045235021	-8.60837487124833
C	6.22573285900932	7.30536941324054	-7.32671749566915
C	7.20822065029935	8.47443383246366	-7.09565246788734
O	7.57470785520109	8.81615274371889	-5.96751313969398
Pd	6.77757596130512	8.29441568942441	-9.93293583862178
N	7.61310151272827	9.00406914150102	-8.26915174331364
C	8.70115228672826	10.00451169272272	-8.35229844049651
C	8.23582714411087	11.32628585208781	-7.70172784793123
C	8.98263080563652	10.23107565329471	-9.81818943045720
C	9.85763736614404	11.07837197713205	-10.46512042532767
N	9.67657242815752	10.82583627893214	-11.79024016259261
N	8.74894703576145	9.87607540604566	-11.99271036977426
N	8.33864576014890	9.52497839210924	-10.79494107738362
C	10.35778311772923	11.44046577876431	-12.94090158777955
C	11.85994941145977	11.38225061468534	-12.79337262734893
C	12.51327575389475	10.14691572909648	-12.70615063461408
C	13.89681186908508	10.09456317769413	-12.56174152375034
C	14.64128991492244	11.27553833731184	-12.50571921948307
C	13.99656825468333	12.50793544740303	-12.59333440232926
C	12.60865648503058	12.55967043924475	-12.73369323039189
C	9.98727889637855	9.47877102104581	-7.67585426350347
O	5.75643854390437	7.76160861703119	-11.66957686386639
N	5.37539557533857	7.11221152730682	-6.16419663346224
C	5.43622551136248	5.96308990899208	-5.35638506851575
C	4.47376083287596	6.20816923822719	-4.24505353014142
C	3.90909602443703	7.47372268148963	-4.42407079387475
C	4.48622691964728	8.07733424928890	-5.66022571703394
C	2.97132681844729	7.97950734828019	-3.53667908900637
C	2.61034334073702	7.17363492573091	-2.45004283831839
C	3.17568266571157	5.90573537934439	-2.27118704604105
C	4.12130349505968	5.40245199584764	-3.17275422136082
O	6.14297582620559	4.99439557571788	-5.56814161269895
O	4.25356500824816	9.15664809382449	-6.17209151157260
H	6.83390718421757	6.39537405111601	-7.37826152111994
H	10.57771884050392	11.79935772845159	-10.11351414218291
H	4.56599564463336	4.42083758199115	-3.04282766720267
H	2.87462700677510	5.30478188048665	-1.41798609072106
H	1.87996986704157	7.53597596134068	-1.73236760892857
H	2.53906506536402	8.96420694237764	-3.68412651504797
H	10.00409699137691	10.87772916150310	-13.80801087787139
H	10.01648972252536	12.47586202827500	-13.03285372637427
H	10.79250672800359	10.21416713330428	-7.78048731309714
H	9.79185581393435	9.30291412451038	-6.61715674700379
H	10.30302919324690	8.54339008522425	-8.14718946286154
H	9.01910202484233	12.08804322685462	-7.78807068874967
H	7.32990259933368	11.68682347709410	-8.19584587094540
H	8.02299316906502	11.14423122751369	-6.64699577134281
H	11.93425364263420	9.22752665253811	-12.74608703853273
H	14.39654970214821	9.13272628740944	-12.49484009755383
H	15.72061465916508	11.23265726727343	-12.39364433512898
H	14.57025409436158	13.42899755371335	-12.54948511518135
H	12.10437866708183	13.52112306777654	-12.79931933313780
H	2.99775461615844	7.50688840344276	-9.72645217829779
H	1.69865764498788	5.59912134429868	-10.63488897624153
H	2.64463449623283	3.29966768959895	-10.54542695976088

H	4.88574049416173	2.93025854736921	-9.53475493462322
H	6.17557678778040	4.82611214107757	-8.64109780015964
H	4.75773668445671	8.35313043591786	-8.51617510816392
H	7.66895575968456	7.08818765450571	-9.66642145777569
C	5.04989234675366	8.84073868750801	-11.69832982067654
C	4.05428137613798	9.01483790716019	-12.81222962474369
H	3.62079144212805	10.01525461953280	-12.77902930564931
H	4.54052682556884	8.84136400122759	-13.77639284080154
H	3.26337272122867	8.26545653225221	-12.70063152992284
O	5.19630806225294	9.70967535457574	-10.78802527050769

1.4'-OA
Lowest frequency = 10.54 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	6.43450964674238	6.59840728286361	-8.64246733580020
C	5.12414801982942	6.55841438959473	-9.14400064925499
C	4.65859286434159	5.35966537780999	-9.70881396480850
C	5.48214687263536	4.23899099050732	-9.78923853862714
C	6.78875946843227	4.29881718642349	-9.30278101610525
C	7.25890954476261	5.48239801886997	-8.72950896480789
C	4.19648761897467	7.71451509905407	-9.06602039878052
C	4.67475179161679	9.10184609593464	-9.54323795498367
C	5.24843341022737	10.03340059618373	-8.45846623489322
O	5.83431254221975	11.07913439347996	-8.74203557294837
Pd	3.73556356154434	8.01609116118894	-7.07400459700272
N	4.94185216565123	9.59993975765450	-7.20984900227226
C	5.12833503952538	10.48344019982938	-6.03194699838669
C	6.63565995126806	10.70334151432444	-5.78764256200512
C	4.51444075833105	9.76956316697689	-4.85364177286854
C	4.59913516630077	9.98342466260268	-3.49435334097855
N	3.77696777956481	9.04972089632531	-2.94136723799785
N	3.19868615069200	8.27964379426470	-3.87724633158995
N	3.64878916898331	8.72681139096598	-5.02710190508784
C	3.49030965253300	8.81253999268450	-1.51753967133650
C	3.14608234716236	10.09662731215124	-0.80137601258528
C	2.02207046301782	10.83917510699422	-1.18324562349211
C	1.71324123039094	12.02937422297576	-0.53071157521542
C	2.52282576789811	12.48816902040731	0.51149502882830
C	3.64196208291655	11.75265323847203	0.89712386786225
C	3.95327073018456	10.56145742470500	0.23927345942055
C	4.39270542280759	11.83180318537586	-6.21553197335351
O	4.76761282227128	6.18133567012820	-6.13020360839260
C	3.68599486174739	5.57707210330926	-6.37130029311613
C	3.51476470387475	4.11423621318077	-6.06931302474258
O	2.70290341144841	6.21602632418644	-6.92314881384997
N	5.53391381724798	9.05307202124995	-10.72070237016239
C	4.96960859113475	9.04684090429180	-12.01061307962833
C	6.11641681499690	9.01583543529420	-12.95766757996364
C	7.29541436974334	9.01936352932329	-12.21045621894662
C	6.94576395018131	9.03990375682855	-10.75996051764285
C	8.53949257990719	8.99363560799825	-12.82223278029411
C	8.56965429445099	8.96466630845670	-14.22170909224301
C	7.38691989097606	8.96116844645610	-14.97084315690780
C	6.13531456266443	8.98701694693016	-14.34453357611834
O	3.77366897766589	9.06584027692826	-12.24362999639599
O	7.69693643054894	9.02929118619300	-9.80600147712363
H	3.77209806136168	9.62090432150442	-9.89110489858421
H	5.13710906423762	10.69891068648246	-2.89404846785956
H	5.21229774904126	8.98433346207518	-14.91575142210589
H	7.44431260855442	8.93753173146402	-16.05523387177778
H	9.52526223672914	8.94388594577346	-14.73766032163172
H	9.45030611267289	8.99601005960786	-12.23184276818195
H	2.66328137943205	8.09867960722885	-1.51254381100945
H	4.36460937718754	8.33699184629893	-1.06286113002688
H	4.50197261697096	12.44162362068362	-5.31225618890004
H	4.81564910836912	12.36435377693662	-7.06832361291558
H	3.32707448281218	11.65382843872525	-6.38966873177290
H	6.78743143619934	11.32041942268870	-4.89460180378450
H	7.13573885720023	9.74158693236709	-5.64658044691254
H	7.06630467262929	11.20998784974407	-6.65225462633750
H	1.39395937977089	10.48499720603818	-1.99699903670536
H	0.83978450344506	12.59973223084557	-0.83259394495149
H	2.28010667506110	13.41669895913264	1.01970287104583
H	4.27513198380057	12.10500148756482	1.70603510231476

H	4.82845810584698	9.98849429961598	0.53707855367611
H	6.80097176428508	7.50621738555835	-8.17797992262161
H	8.27141904124113	5.53363055382091	-8.33955170763985
H	7.43517609174253	3.42765541964055	-9.36549257067654
H	5.10619405589459	3.32244785891527	-10.23615858232214
H	3.64033239522760	5.31624103079490	-10.08702271389333
H	2.69329578162968	8.96066548039972	-7.66164118527086
H	3.25194217684373	7.46599001892796	-9.55213834580388
H	4.00703050042881	3.54270385534212	-6.86386481747209
H	4.00402504589285	3.87093005692245	-5.12326528621616
H	2.45787443807795	3.84366524552464	-6.03817784706386

1.5
Lowest frequency = -2.19 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	9.90900502562666	6.41401165380064	-2.22748535594878
C	10.62456502384507	7.60953024902314	-2.22418284550891
C	11.14304103761037	8.16312514525970	-3.38989806593037
C	10.94775487513638	7.49550499331249	-4.59899798239254
C	10.23516231566593	6.30470204947830	-4.59416491194100
C	9.71135676354330	5.74745507770457	-3.43452499846414
I	10.87947932081453	8.61978090061704	-0.37862111544496
Pd	8.67587542404201	7.85607005094641	0.83417735279826
N	9.53497743669801	6.47807283651681	2.18552055580283
C	8.60720356461231	5.98418102568254	3.06469569710041
C	9.25912062911891	5.04006347468976	3.82795581353508
N	10.53961266600810	5.03028351870211	3.36479219903018
N	10.70747708169542	5.90270454677424	2.35539474402136
C	7.18864596412144	6.49493680728955	3.06056990530449
C	6.21804080411309	5.29484973200640	3.08070659295776
C	11.64946864011666	4.15100854193703	3.75539616375082
C	11.36260621155938	2.70418184692744	3.42011569170457
C	11.38498399187928	1.73040367940962	4.42055148302923
C	11.12241904051183	0.39457209446208	4.11194714306241
C	10.82921165714733	0.02840550606174	2.79966499869440
C	10.80204993767326	0.99962858858667	1.79578676682641
C	11.06888823879966	2.33095048524896	2.10319658007217
C	7.36134010651783	9.11228807044181	-0.15433344991371
C	7.67290069613147	9.39689015441963	-1.58133411962258
C	7.33399436473334	8.51625810932497	-2.62307874538036
C	7.62623455763548	8.82057342177849	-3.94990613742305
C	8.27621342951778	10.01159737288900	-4.27449139218066
C	8.62836885178849	10.89669478049990	-3.25379919855183
C	8.32639707276586	10.59305104944385	-1.92853176494099
C	5.97976337191142	8.49648835479883	0.08513902292763
C	5.85560579796982	7.82711986562772	1.46516882048346
N	7.03892203231289	7.27550467961217	1.81229775743465
N	4.90001072013969	9.45043430905203	-0.13007151225319
C	3.88170709795318	9.25013300465546	-1.07649478380709
C	2.96000987887704	10.41240345366946	-0.92394772255329
C	3.44869300749316	11.22591644887788	0.10093030227210
C	4.70203830242487	10.61271273322046	0.63184777250280
C	2.79578376146302	12.39108274314336	0.47306036233142
C	1.62379274006555	12.72363938962442	-0.21742745194055
C	1.13447086511399	11.90848959003190	-1.24456578288747
C	1.80108808487702	10.73387059244360	-1.61421720889908
O	3.81216245624130	8.30816170800042	-1.84588423288477
O	5.43495476289301	11.01443527071683	1.51769124675097
O	4.78818363417558	7.76159412070206	2.08393146119462
C	6.96455518396583	7.40295281206218	4.29167843867363
H	5.78658448473024	7.70339027799114	-0.64514424579508
H	8.93179277603863	4.38560738064113	4.61960187105926
H	1.43003101269811	10.09458077751317	-2.40919809442665
H	0.22248697743780	12.19363759521132	-1.76118454708052
H	1.08343487807501	13.62826304448436	0.04650058648480
H	3.18350667133115	13.01612285015888	1.27142063306003
H	12.51558564826732	4.53329087428782	3.20962925767745
H	11.82811952729574	4.27346094138308	4.82732944431288
H	6.37782245734669	4.69444692332984	3.98378948666438
H	5.19206747605747	5.66421008522968	3.07040043488811
H	6.38411187503675	4.66346134332531	2.20300519156511
H	7.11418934653655	6.83744930095510	5.21850926676048
H	7.66745545321732	8.24057790813431	4.26805722296357
H	5.94447614582495	7.79046910009277	4.26117941715565

H	11.04386986561363	3.08752733566805	1.32273374232039
H	10.57362295519669	0.71736148483257	0.77223883232967
H	10.62033178336075	-1.00949800233138	2.55779598748589
H	11.14265816032208	-0.35569222627691	4.89691489632322
H	11.60969253703510	2.01702895759550	5.44550342774789
H	8.58872608537651	11.29342280977798	-1.13903573184445
H	9.12751990280954	11.83256816962300	-3.49201449191640
H	8.50432390117989	10.24765621089007	-5.31012173711828
H	7.34553261211821	8.12259083460182	-4.73376534391596
H	6.82657998336578	7.58342836170964	-2.39671686279831
H	7.46134311197582	10.01975580316602	0.44934163861322
H	11.67291942761501	9.10877366107022	-3.37211922727887
H	11.32358197982261	7.89976794638302	-5.53263036404347
F	10.03217934615128	5.66306511441671	-5.77347063871220
H	9.14924732655282	4.82088107190623	-3.48183948246216
H	9.49075086430400	6.02582222475581	-1.30362566341203

TS1.(5-6)
Lowest frequency = -93.61 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	10.28272472633475	5.47138621801623	-0.89404158380346
C	9.84184221060316	6.73525679474688	-1.30788954873330
C	9.08021957500775	6.88899371829832	-2.46778629917004
C	8.65563710512384	5.75669657438739	-3.16181714943478
C	9.04601625002700	4.50527941557147	-2.70510525873699
C	9.86091394271683	4.34228058830859	-1.59047118936669
I	11.13768057285176	8.51641963437081	-0.66759815152761
Pd	8.83754173708532	7.81519277366282	0.46879687455114
N	9.64143300085233	6.50738260330782	1.97466756590693
C	8.67908719280637	6.05521307195845	2.83240669698229
C	9.31037717421910	5.19706645870019	3.70931185887899
N	10.61609286882737	5.19756232762360	3.32759885854274
N	10.81814424188314	5.99290383084738	2.26545919206907
C	7.24546283537217	6.49502801653988	2.70519464609133
C	6.35551418332592	5.24030785933395	2.54950764979654
C	11.71395605175290	4.33573839456509	3.79790608846762
C	11.65375012754810	2.97375735705395	3.14230507008868
C	11.19401183798594	1.86304542002303	3.85368612516553
C	11.09494979874628	0.61804781178590	3.23148483438124
C	11.45387707493188	0.47899514698922	1.89150727397645
C	11.91881597086329	1.58516096146022	1.17683292631268
C	12.01988433318831	2.82684446714956	1.79955026090174
C	7.54067339727686	9.25563007105949	-0.33744135043129
C	7.85372569185013	9.93701148246484	-1.61482043969111
C	7.24053430184037	9.59516912935901	-2.83440951720403
C	7.54557311251355	10.28159531481186	-4.00934388156587
C	8.46671855000050	11.32832789130159	-3.99680252133877
C	9.06976079495474	11.69453375361933	-2.79041954235058
C	8.76286135276597	11.01089662069881	-1.61990386383430
C	6.17170986772307	8.58563055281974	-0.25989552549357
C	5.98899789845500	7.83301934850176	1.06911265544327
N	7.17074570901257	7.34336145742536	1.49511590830618
N	5.07070099215693	9.51968153309534	-0.46192336536914
C	4.08462551982742	9.34718230091920	-1.44464612752131
C	3.10483059274645	10.44897105464133	-1.22768097779435
C	3.53069086019391	11.20338093912925	-0.13183424486973
C	4.79699336755961	10.60749736479159	0.38538921189536
C	2.81494601573408	12.30565740454066	0.30955507559104
C	1.64413222955557	12.63532335718029	-0.38428711623610
C	1.21740001309046	11.87908468020916	-1.48193792609328
C	1.94770265640113	10.76833830132252	-1.92188775155053
O	4.08116509653140	8.46872836106618	-2.29037550936753
O	5.48670264727119	10.96404686460879	1.32278470357380
O	4.88231592617922	7.68744912739430	1.60053090263447
C	6.84016329495465	7.30759691301664	3.95551943337818
H	6.05752503703991	7.84137398913719	-1.05722299642544
H	8.95306757596355	4.60364807886194	4.53533703252824
H	1.62510060891281	10.17502177493988	-2.77171006505438
H	0.30430508901579	12.16014374709130	-1.99871364471020
H	1.05529725347952	13.49125562179282	-0.06726571950581
H	3.15433197999182	12.88549649472055	1.16210906230771
H	12.63327244303875	4.86775428360938	3.54566511230484
H	11.63232671050951	4.25794924151654	4.88446663153414
H	6.45971467637101	4.59320068837837	3.42788427549543

H	5.31454817699952	5.54955126055532	2.44941294120055
H	6.65533544638243	4.67833932683435	1.66018239816097
H	6.93492494352461	6.69249561801112	4.85773004276351
H	7.48461890427668	8.18554042077943	4.05463961663417
H	5.80451473632066	7.63309243274071	3.84501501674952
H	12.37871177512670	3.68929245894852	1.24406582120893
H	12.20642629654929	1.47815381008069	0.13490549276126
H	11.37476598756829	-0.48859087675971	1.40489860009369
H	10.73722976113020	-0.24018982999028	3.79258757156501
H	10.91346603789452	1.97035528167681	4.89922400737453
H	9.22852477805088	11.30396417509397	-0.68253089726145
H	9.77738738984692	12.51876492935349	-2.76407577648674
H	8.70376525815464	11.86197073642154	-4.91275325831361
H	7.05201266249740	9.99982623410642	-4.93556727271497
H	6.50239528248970	8.79921556863143	-2.86830886978241
H	7.65308120475420	9.95643002900085	0.49629530821388
H	8.80338687373468	7.87490573844822	-2.81938074985031
H	8.03437440306529	5.84704980230771	-4.04686423719079
F	8.63675153426674	3.39950620102214	-3.38213358745185
H	10.15814717532663	3.34774237300949	-1.27358274327335
H	10.92176829706916	5.37021012100157	-0.02687108432602

1.6
Lowest frequency = 9.44 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	3.15035570221601	-4.56654212648775	1.10275017051934
C	3.04871542312638	-4.74735300668658	2.48732693217653
C	2.86161693805518	-6.03148162338281	3.00352767552083
C	2.78163968002642	-7.13017750519792	2.14639572354474
C	2.88094613224860	-6.94577230186550	0.76806191831922
C	3.06442006867075	-5.66244037687139	0.24798556629883
C	3.12345588002840	-3.55280801176872	3.41539036088065
N	2.08141069315390	-2.56750108212819	3.08465523961231
C	0.73603065253502	-2.65203469935754	3.28940632249557
C	0.20258158004600	-1.59403793294758	2.58680314424643
N	1.25913447450394	-0.94564131905660	2.00454671672639
N	2.39722053212796	-1.53514993040809	2.28991356359644
Pd	0.59993012831470	0.31110243960262	0.35735206431119
N	-1.16833541079712	-0.36425915403661	1.06913516330454
C	-1.20949423489940	-1.12295383657696	2.34610812573426
C	-1.65677720661386	-0.18255579403206	3.48901827547420
C	0.87193280777332	-1.09870804078933	-1.05177101923359
C	0.47416407943437	-2.39453792489083	-0.73142891866639
C	0.67455141375706	-3.42494268609828	-1.65422290590860
C	1.27728439223918	-3.12306159415820	-2.86571574021967
C	1.67808898980673	-1.83680487635723	-3.19524593201883
C	1.47179107631304	-0.80733301660916	-2.27306601422210
F	1.48748034119742	-4.12842581532376	-3.76020400334238
I	2.92822206019610	1.46753143798039	-0.02652645498911
C	-0.62942636616452	1.48731919899295	-0.86522265225925
C	-1.94573234201444	0.71082403159036	-0.90083617230267
N	-3.04930416150727	1.53244407518020	-1.36413720816626
C	-3.87062178941942	1.17802532336856	-2.44865474343736
C	-4.92582380368589	2.22809495165921	-2.50580855487391
C	-4.70663378689190	3.12928020215697	-1.46017491812403
C	-3.50138876842296	2.68705555889731	-0.70228715115703
C	-5.53757566816739	4.22101651413233	-1.25997748388713
C	-6.60924562494116	4.38737778762253	-2.14563618324951
C	-6.82874289747808	3.48470626371434	-3.19250496379514
C	-5.98382647343899	2.38556800976188	-3.38832626442177
O	-3.70355060399163	0.20665517008010	-3.16386365995319
O	-2.97221575107792	3.19117285540873	0.27149610272359
C	-0.14379693643454	1.98662859851784	-2.16953991667304
C	-0.46451851392462	1.35814024523783	-3.38565482024954
C	-0.01738745972992	1.87986826475896	-4.59693230908033
C	0.75886530804591	3.03906353772417	-4.62040566296824
C	1.07772325132872	3.67990697680687	-3.42094218343529
C	0.63002555719636	3.15991120495622	-2.21184886518744
C	-2.29077626530201	0.06479466012302	0.45318267400033
O	-3.45047038300739	-0.05762989648534	0.85484057256610
C	-2.14769367767071	-2.34408486017464	2.25419932376980
H	-1.87893798264403	-0.11262813662437	-1.62126089805311
H	0.29301049963531	-3.44107769829075	3.87509747371896
H	-6.14590329561455	1.67975195135477	-4.19683441776479

H	-7.66928482073240	3.64134601160971	-3.86225720196065
H	-7.28309535280052	5.22989130190556	-2.02016362784087
H	-5.35923039990318	4.91534519566773	-0.44500545709729
H	4.06851328857475	-3.01416947536238	3.31497663477236
H	2.99232133257235	-3.85230956396272	4.45786397006383
H	-2.10955098857017	-2.91174038377793	3.19063601692001
H	-3.16861166249703	-2.00441093541005	2.08157464596591
H	-1.84814063726575	-3.00103309256529	1.43252058840040
H	-1.66905335952787	-0.72198908249294	4.44224220189986
H	-0.96871655852995	0.66363624482671	3.57033192772448
H	-2.65951778484949	0.18876650947988	3.26794594549659
H	3.28289595323945	-3.56752209994090	0.69567693259104
H	3.13784237383701	-5.51334266127112	-0.82509898201986
H	2.81451973576418	-7.79879927816076	0.09911608303222
H	2.63682190073485	-8.12566779811375	2.55574824197406
H	2.77991983782504	-6.17455500098267	4.07883938815164
H	0.88255258088317	3.65629000298601	-1.28003132995549
H	1.67717069344344	4.58562449106604	-3.42875199201804
H	1.10853939945342	3.44371601079472	-5.56604417514582
H	-0.28053207194616	1.37909837426938	-5.52436592236950
H	-1.07371912627426	0.46039530870159	-3.39420913002565
H	-0.68878672938075	2.30244474203053	-0.13297639781079
H	1.78878192925827	0.19739641079826	-2.51591585918500
H	2.15405398996763	-1.63891248523220	-4.15004269174846
H	0.36368461550262	-4.44052950398351	-1.43265794767242
H	0.00809260308427	-2.62381425590185	0.21701904595686

TS1.(6-7)
Lowest frequency = -253.51 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	3.80507752920083	-4.56896504814061	2.39835247688921
C	3.38284163294506	-4.26735921664039	3.69872845996070
C	3.23616071292551	-5.29515931717769	4.63260657557490
C	3.51230152594050	-6.61594495803917	4.27572759702168
C	3.92994732358495	-6.91290689885187	2.97951327272506
C	4.07497659628858	-5.88763825576654	2.04175296522541
C	3.07814229798690	-2.83610517408342	4.08273056280459
N	1.98400712780042	-2.28483841104233	3.26602018789366
C	0.64798940696688	-2.54194115104238	3.34391049232571
C	0.09750921670068	-1.89983550383104	2.25699901210409
N	1.14238963778166	-1.30803403053295	1.59785915150552
N	2.29154464949370	-1.54150629370062	2.19865368365972
Pd	0.66025530565636	-0.55952292763146	-0.24290183491445
N	-1.20398239666771	-1.03603653673570	0.45360004569422
C	-1.31046834080250	-1.74085749429024	1.75870982231900
C	-2.09170606337005	-0.89024287486582	2.78932679136524
C	0.26093346676480	-1.01227986221252	-2.25732958709107
C	-0.53375609594801	-2.16440571506403	-2.35137116222747
C	-0.40126728370289	-3.02819982942243	-3.44029604600172
C	0.52606947722282	-2.71824329478555	-4.42314146367148
C	1.31615470718884	-1.57603713404350	-4.36497076838464
C	1.16620765777001	-0.71528348513084	-3.28483648311279
F	0.66122306194986	-3.55419308920669	-5.48510585095055
I	3.12974221517537	0.28094277570791	-0.69127666467316
C	-0.64047329260644	0.73558129602806	-1.58086366155788
C	-2.06943640775843	0.22361024279158	-1.44299286382760
N	-3.00439227956770	1.33856267230707	-1.46423511261226
C	-4.02463074169815	1.46939854291649	-2.42484942250205
C	-4.79539931624702	2.67696244006831	-2.01724878992576
C	-4.22724569383083	3.18961933034014	-0.84735181076006
C	-3.07398751078121	2.32588266048371	-0.46812594538272
C	-4.73666698259958	4.32328395871277	-0.23245631815457
C	-5.84588724965160	4.93662867520526	-0.82740654690165
C	-6.41474092863623	4.42276649901786	-1.99844049847052
C	-5.89325891948016	3.27828769980646	-2.61370034845770
O	-4.19036893751727	0.72811986085206	-3.37543363997373
O	-2.31422693818726	2.41508716787037	0.47986203160970
C	-0.32379691370621	1.60411417294133	-2.74164622446121
C	-0.96541728790947	1.45701301428763	-3.98116017009008
C	-0.66498326051076	2.31616265524483	-5.03216171401449
C	0.29310931050834	3.32094834682680	-4.86917035417585
C	0.93968682473532	3.46969350246069	-3.64227646918776
C	0.62764103416226	2.62052583167192	-2.58239609838065
C	-2.31905420664419	-0.60098635289249	-0.15696041665382

O	-3.48627518573762	-0.81213199778259	0.20326150853030
C	-1.96328601447718	-3.12673478568206	1.57273468830079
H	-2.35834879812059	-0.39399890049984	-2.29831722602216
H	0.22151636112101	-3.14220108782823	4.13116770239498
H	-6.32720437994816	2.87174341362497	-3.52169810485845
H	-7.27496500368431	4.92169141931875	-2.43504872515494
H	-6.27401332862608	5.82613208652112	-0.37459071392517
H	-4.28859459789520	4.71460145132108	0.67535870828931
H	3.92841946914578	-2.17454183892252	3.90299871066406
H	2.78379996682761	-2.76231508823510	5.13230409050830
H	-2.01163607532282	-3.65896186458123	2.52942536080472
H	-2.97552723078053	-2.98980925720764	1.18847392648080
H	-1.38056544589680	-3.72697086709925	0.86770948445199
H	-2.06361985689664	-1.38158877966443	3.76822696664419
H	-1.63615717094497	0.10004430968777	2.87446131718833
H	-3.12576071155786	-0.78128503406721	2.46355046008555
H	3.91399353323657	-3.77114458669383	1.66778619274379
H	4.40097685837241	-6.11579939561545	1.03134640587146
H	4.14214976439844	-7.94030266439641	2.69859586794584
H	3.39806056875317	-7.40938347038376	5.00846938663927
H	2.90847443538204	-5.06290270894611	5.64360539975194
H	1.13758090277478	2.72276939862068	-1.62868242773822
H	1.68690724948359	4.24639258363514	-3.50813670809974
H	0.53261077952742	3.98368349738395	-5.69598211278885
H	-1.17496761352102	2.19837905673507	-5.98395032756724
H	-1.70226539985333	0.67266187834784	-4.12336856790234
H	-0.37595189094049	1.28768288360956	-0.66584994363375
H	1.75904209797825	0.18931083975763	-3.24269253968978
H	2.02602924488739	-1.36262255339035	-5.15701859653885
H	-1.00503610244794	-3.92593891104275	-3.52029275885201
H	-1.24426109616301	-2.41167651693580	-1.57296028668481

1.7

Lowest frequency = 8.12 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	7.76867260706315	6.03672959432474	-2.19108455406010
C	8.32071907675350	7.34847707216161	-2.08549311735556
C	9.39470595003591	7.67880447832492	-2.96353824419207
C	9.84746947375922	6.79398428951385	-3.91237762593921
C	9.24873317920899	5.52803963368127	-4.00144727060785
C	8.24219024224266	5.12446022918964	-3.16070398740699
C	7.60141411824002	8.50299244239349	-1.37937089625679
C	7.48936670211816	9.70523892436523	-2.30514019727756
C	6.89066255868735	9.58856827589572	-3.56547760781727
C	6.75839050198206	10.70238506093603	-4.39026858525249
C	7.22691201302193	11.94828481688001	-3.96743185991282
C	7.82719110669932	12.07187064478996	-2.71512010885905
C	7.95693854002214	10.95432540411093	-1.88891307136655
Pd	9.03052208533495	6.19510298071253	-0.25179720647125
I	11.37847868913345	5.39481209224171	-1.15077376082396
C	6.19955542980709	8.06596272849160	-0.90190363984930
C	6.12198749075139	7.13227889453364	0.32923985935233
N	7.26912963635357	6.59989285490453	0.79563284324161
C	7.16312509000332	5.83318398267374	2.07822479124082
C	6.43663749910466	4.48769698029420	1.85394267594989
N	5.36718098877144	9.22832023903197	-0.62818450324261
C	4.24027177348104	9.55297639001152	-1.40408361750175
C	3.70930348999701	10.81533022459351	-0.81788201278968
C	4.52051688108668	11.17304385798582	0.26230336863806
C	5.59776457145989	10.15142473203320	0.39925781961365
C	4.27918752387468	12.32295192726400	0.99827483801154
C	3.18852607268446	13.11520318581268	0.61901848935290
C	2.37630373185134	12.75646628858665	-0.46279326011501
C	2.62775784643695	11.59341958315231	-1.20099880094359
O	3.83750339348743	8.91079422463298	-2.35585778011359
O	6.51533134625572	10.09750055528136	1.20013220156661
O	4.99386753649183	6.96828016405031	0.82329168631463
N	9.59526355393034	5.69813661012242	1.60693011838747
C	8.57514146057782	5.56711544452217	2.50472575886651
C	9.16212278866212	5.18446897022779	3.69078682470409
N	10.49704329183109	5.13205958927189	3.42259087004422
N	10.76864289483452	5.44336934831870	2.15180511535984
C	11.59584636250613	4.64940606075353	4.27418324106835
C	11.69115310277731	3.13920713869741	4.24886976864962

C	11.57046983952556	2.40697315490274	5.43179066625372
C	11.66047908524015	1.01439004598903	5.41023724614933
C	11.86440133678605	0.35002905684964	4.20198179794672
C	11.98170762425490	1.07959074861229	3.01644766948383
C	11.89828971939236	2.46954935837068	3.03672582046205
C	6.48580719863870	6.65811236943758	3.19725098869947
H	5.67630584383686	7.56796503058378	-1.72707869459854
H	8.75992818195403	4.95492004894072	4.66388167996109
H	2.00578843692117	11.30770424606832	-2.04338917063129
H	1.53872457037174	13.39292610534164	-0.73301073377880
H	2.96794526751801	14.02436588646499	1.17080576724156
H	4.91647821405594	12.59431018865504	1.83402820394106
H	12.49738994966818	5.12020689810992	3.87549486189429
H	11.41894097677864	5.01795241037115	5.28719016631545
H	6.40546659079446	3.90876722039615	2.78365517724287
H	5.41793633151970	4.69055827962673	1.51914364588906
H	6.96463511039233	3.90186455178311	1.09485037313838
H	6.60883275488949	6.13764300840712	4.15420123551150
H	6.95335659962457	7.64415571269923	3.26625292734657
H	5.42565810526040	6.77938511903585	2.98681123511853
H	11.98412857428786	3.03663894403545	2.11282251550288
H	12.14029619709043	0.56508895823648	2.07336604477819
H	11.93088304760435	-0.73384363951528	4.18215548143735
H	11.56744961703984	0.45204180285012	6.33473300048811
H	11.40863459870629	2.92621288768057	6.37398306356293
H	8.41348545330299	11.04975824208836	-0.90708997008354
H	8.19455512963925	13.03739520936758	-2.37870741311557
H	7.12409655185047	12.81658232951657	-4.61200082191429
H	6.28524771013756	10.59927550915489	-5.36258820139384
H	6.51659425489433	8.62418626676730	-3.89857419219622
H	8.17284806886772	8.81278349809349	-0.49817240908606
H	9.83222683448879	8.66906626080311	-2.89837930509971
H	10.66275082236392	7.04568563339512	-4.58118106510958
F	9.69784262682339	4.67931145502624	-4.95311200051890
H	7.80901013168783	4.13526524146096	-3.25209279650830
H	6.85254404247102	5.78076304562374	-1.67164835653736

1.5'
Lowest frequency = 4.02 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	-1.79930880563546	8.73449451126258	-2.45587039799434
C	-0.81233921099105	8.83030549344453	-3.43465271748414
C	-0.07116880365075	7.72241628604994	-3.83878390725760
C	-0.32546580848538	6.48251373584644	-3.24986882047711
C	-1.31365774433384	6.39939234836421	-2.27828117999495
C	-2.05668402136126	7.49796983117182	-1.86660760547600
I	-0.44736143822129	10.73239654080573	-4.30387659429144
Pd	-1.40522196387809	12.24374726530314	-2.37654895320265
C	-2.54490922054203	13.37079069229419	-3.65914547874540
C	-1.53189986572820	14.06784012731788	-4.50179923898625
C	-0.59411342205430	14.97418070299119	-3.97226184687389
C	0.37764639146069	15.54997030788456	-4.78427769471041
C	0.45480246104531	15.22555266712476	-6.14191865489552
C	-0.46265740443801	14.32545652587894	-6.68269816503715
C	-1.44774515568001	13.75963541747504	-5.87297608161524
N	-0.38961103550485	11.47329428686395	-0.70540354167910
N	0.53046903435075	10.55765839950871	-0.48113384630574
N	0.74701010255637	10.58038499781483	0.84447536914198
C	-0.04034146494640	11.50114834629625	1.46554886489350
C	-0.77506020806155	12.08769416280343	0.45649689527276
C	1.65198259741046	9.58716744765972	1.44259667998577
C	0.89829561754682	8.38985500672005	1.97768844371026
C	0.24680312315562	7.52158560664566	1.09413022471200
C	-0.46158236250972	6.42668365062966	1.58322039731884
C	-0.52317375033306	6.19046045686045	2.95876423805859
C	0.12536029438351	7.05138049176354	3.84280325230903
C	0.83340960568824	8.14934294632818	3.35189574899821
C	-1.82224976799366	13.17434698856819	0.45869047993124
C	-1.21621603076306	14.47419269735145	1.03264403926288
C	-3.02245470249306	12.70281169188593	1.31147298150478
N	-2.21643772833952	13.37637837112756	-0.95461201052506
C	-3.18957112998683	14.25716042587985	-1.28332498716204
C	-3.51493645583171	14.20211409619911	-2.78848137649060
N	-3.78810598533371	15.53867969869136	-3.31272100901446

C	-3.12521883375745	16.73395719892791	-2.97332204541864
C	-3.78474084318949	17.79527267767322	-3.78985436723117
C	-4.77949602655287	17.20436053708766	-4.57069077284176
C	-4.79797877786539	15.74636933004052	-4.26836506649150
C	-5.55307734701580	17.95025757422780	-5.44750213672007
C	-5.29828658718382	19.32495867099172	-5.52210318572508
C	-4.30047090699150	19.91772610083411	-4.73956805886412
C	-3.52490418265982	19.15542023843169	-3.85736751651938
O	-2.19879407614212	16.85104340841463	-2.19440015369938
O	-5.51467233110148	14.87266357532424	-4.72510583238093
O	-3.83342519985516	14.96839935044657	-0.50574635083884
H	-4.48458777003164	13.69329467244277	-2.84365112813206
H	-3.13340840681434	12.69667387124492	-4.28782530697504
H	-0.01333241662729	11.65224757914415	2.53263100744306
H	-6.32356413010841	17.48014619106127	-6.05058551605198
H	-5.88203381008951	19.94342240263170	-6.19783120331760
H	-4.12637346647832	20.98684353684315	-4.82096328269547
H	-2.74778728631198	19.60462611681817	-3.24699796162762
H	2.34045751919407	9.30598687555259	0.64273491942188
H	2.21471014837817	10.08460319375830	2.23623088035279
H	-2.70131302472376	12.50263900794675	2.34012039498275
H	-3.78688958556144	13.48083308259169	1.31345805332380
H	-3.44138396390333	11.78415565926169	0.88963306292407
H	-0.88572655584161	14.31812926374198	2.06620129436476
H	-0.36000366477013	14.78494601888211	0.42775051527046
H	-1.97398018622700	15.25874692611288	1.00733698475932
H	-2.17577449075361	13.07498781668300	-6.30242343583922
H	-0.42129775292594	14.07096567252795	-7.73860608732765
H	1.22086068946321	15.67156016367777	-6.76993484906226
H	1.08665474162951	16.25138469094820	-4.35260258174966
H	-0.63705870563523	15.22181099883736	-2.91722753463732
H	0.28824451838380	7.71288518335601	0.02543705865287
H	-0.96071165950286	5.75459503861329	0.89179313041416
H	-1.07470014733448	5.33551881526795	3.33889188965382
H	0.08115070678588	6.87073977289756	4.91286010058076
H	1.34098363895559	8.82037747578950	4.04153632395817
H	0.70015857694635	7.81185273155943	-4.59640401195106
H	0.23230372516609	5.59697183734266	-3.53525544178191
F	-1.55692884757224	5.19325533814610	-1.69778330524823
H	-2.81502120326788	7.38759235267351	-1.09876852424335
H	-2.34873981860774	9.62115082843261	-2.14991046561209

TS1.(5-6)'
Lowest frequency = -103.35 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	-3.05982056566299	10.37652463222185	-4.19976242302206
C	-1.81767324113191	9.99026264205607	-3.68223498837281
C	-1.71658485481728	8.96810445593160	-2.72903543743718
C	-2.87978860379682	8.39845292457299	-2.21785221366865
C	-4.10981874262194	8.83713020339013	-2.69411376534528
C	-4.22148860481290	9.80766924877719	-3.68129313381079
I	0.04727231121458	10.46139057991462	-4.84067277985209
Pd	-0.77234899462359	11.89742535997854	-2.74627572777306
C	-1.67243251212966	13.33124072676268	-3.92312671425339
C	-0.58213924928472	14.28791899573044	-4.24990142318958
C	0.05014480527096	15.10048893934195	-3.29178021571139
C	1.09326839855699	15.94549885088979	-3.65551696503520
C	1.53921589727367	15.99624938350602	-4.97821823697752
C	0.92251875440703	15.19602980368248	-5.94120389375375
C	-0.12481544695815	14.35412000165113	-5.57801555595352
N	0.15394042281187	10.97365411654611	-1.05608280495409
N	1.01671786903345	10.00191442360627	-0.84592629436514
N	1.21591161168869	9.97416115227807	0.48355078500225
C	0.47667705776310	10.92283513276508	1.11974739591431
C	-0.21412713957257	11.57266936367810	0.11882477997346
C	2.09145695066025	8.95213155181092	1.07067081922746
C	1.35199964501882	8.09709486616193	2.07554137616320
C	0.14355877808701	7.48133390698522	1.72842762579917
C	-0.53312726093623	6.69247934166316	2.65461235281750
C	-0.00734022808959	6.50784230132771	3.93568359032076
C	1.19546899989847	7.11800485685841	4.28645283882461
C	1.87018968697251	7.91392188118372	3.35915000054013
C	-1.24900822514774	12.66943785826963	0.15796980139519
C	-0.68541157481668	13.91024616500376	0.88180334986052

C	-2.49478130253056	12.12014628077773	0.89550171019385
N	-1.56655257167498	12.99609395708768	-1.24764149833719
C	-2.58362898759753	13.83256993933268	-1.55805115447305
C	-2.86651407670813	13.76559611441962	-3.06813577401279
N	-3.56500636871504	14.94664979453133	-3.56697264434416
C	-3.26948950915670	16.30130478169706	-3.29520943634190
C	-4.32333456584972	17.08068794104939	-4.01119990022227
C	-5.17410820559451	16.18849988587185	-4.66617819917102
C	-4.69699583996981	14.80710089853701	-4.38595693447442
C	-6.24989708597716	16.63229523238548	-5.42141075932475
C	-6.45223149125709	18.01505539462271	-5.50386936917644
C	-5.59764717213539	18.91006435666188	-4.84930225150885
C	-4.51502910955102	18.45164648892218	-4.08883805230878
O	-2.34184342294988	16.72041923316852	-2.63528274059390
O	-5.15446923001521	13.74110830049605	-4.76797842826762
O	-3.27971450418027	14.48655278578648	-0.77549702491149
H	-3.61161736138935	12.96530252855038	-3.17045232920102
H	-2.03626348648475	12.87286022877797	-4.84677717932850
H	0.49021716547668	11.03460700878852	2.19190015011347
H	-6.90631445814812	15.92977068703749	-5.92532792576055
H	-7.28419948212069	18.40232300875935	-6.08494943261765
H	-5.77988862258786	19.97751535547114	-4.93420922994620
H	-3.84685076941403	19.13663264671825	-3.57647088814884
H	2.45202907760470	8.36890934973179	0.21931663524712
H	2.94651205075573	9.44839149285098	1.53905595972418
H	-2.22825579246045	11.82032174289727	1.91521116201483
H	-3.26169184492281	12.89489076104439	0.93084943045521
H	-2.88571261468520	11.24757336198599	0.36320077052954
H	-0.42244078683250	13.66653195786606	1.91776952625032
H	0.20879678891552	14.27136770737048	0.36583894263808
H	-1.44488379661482	14.69419273388563	0.87841574928735
H	-0.60446329558109	13.73042650484796	-6.32917192221315
H	1.25446324774319	15.23101752123674	-6.97550787254854
H	2.35715183731631	16.65518876197668	-5.25598242420808
H	1.56095386133621	16.57161877638976	-2.90063322727706
H	-0.28584446459624	15.06835830655709	-2.26297834421145
H	-0.27064962183490	7.63015573293909	0.73422112902008
H	-1.47187974023259	6.22106524158169	2.37894728188876
H	-0.53715667874179	5.89334130242683	4.65744507827376
H	1.60685334213873	6.98210702021264	5.28229582684721
H	2.80513645861843	8.39601241982810	3.63557061146747
H	-0.74567551826524	8.64939097301876	-2.36918713124347
H	-2.83724553709528	7.62187108523103	-1.46088459198537
F	-5.24145807779048	8.28324197954931	-2.18476375983658
H	-5.19706796590407	10.12407895301481	-4.03463454789278
H	-3.13637841459486	11.13128379756075	-4.97250413242650

1.6’

Lowest frequency = 10.04 cm^{-1}.

Charge = 0, Multiplicity = 1

75

C	-3.11876637327154	10.41027341761532	-3.31791653369942
C	-2.06798411628619	10.54671373766011	-2.41510854947583
C	-1.95607579794126	9.68230065745406	-1.32829245080637
C	-2.91932986635429	8.69195604457997	-1.11957851910497
C	-3.97277609694746	8.58941968450509	-2.01510015240825
C	-4.09034248544155	9.42644940253074	-3.11392163742755
Pd	-0.67049615998416	12.01102349871463	-2.56879668129194
C	-1.76702555738820	13.21339645035498	-3.83347116428726
C	-0.63954641598028	14.09916631771857	-4.20338350163325
C	0.00386055304314	14.95199416897025	-3.28291831234761
C	1.11653598012250	15.69711577816079	-3.66911362267989
C	1.60563150132547	15.61014807638345	-4.97039130910236
C	0.97437717424650	14.77153934545351	-5.89626916280130
C	-0.12584159216263	14.01930114630223	-5.51446524847035
N	0.54175939609429	11.49657863875362	-0.83304409346608
N	1.45482841116088	10.58512052818081	-0.57841536513056
N	1.50763800928489	10.48862396890616	0.75778826253686
C	0.61608798077710	11.32588892956561	1.35809306524112
C	-0.00994288699325	11.98494764420386	0.32100376792055
C	2.27623090016649	9.38393951751346	1.35667970192190
C	1.38480501805542	8.17878744075539	1.57132677874060
C	0.80004593113555	7.53964313938820	0.47113427684412
C	-0.05707056042296	6.45948705319464	0.66593898275693
C	-0.33179261801202	6.00562647179849	1.95830582547739

C 0.25426779680859 6.63478934660216 3.05563099855831
C 1.10808982534413 7.72181689185111 2.86156414803055
C -1.12656391646234 13.00006000560419 0.29724146979801
C -0.60930431518214 14.35595533093667 0.83098222259919
C -2.29396771098798 12.48002739256896 1.16556803782251
N -1.53188119319458 13.14580892554209 -1.11889521892954
C -2.59953210524210 13.89558157005970 -1.47524015714579
C -2.92993204051958 13.69782129372450 -2.96680883115806
N -3.63885766052319 14.83545842774162 -3.53516777456362
C -3.32020413554015 16.20357240285291 -3.38855743773688
C -4.40472227194970 16.93502254891429 -4.10674027914315
C -5.29799914591878 16.00378850020568 -4.64057534199679
C -4.82156686649364 14.64318231004938 -4.27561061368470
C -6.40911027456361 16.39876603730643 -5.37141089015257
C -6.60361250306355 17.77275339258946 -5.55460955363674
C -5.70840594839434 18.70674870505952 -5.01960915028829
C -4.58934143207463 18.29785266728771 -4.28429038546506
O -2.35353257167988 16.65932139365231 -2.81276040192312
O -5.30599617357206 13.55578480764574 -4.53719772609014
I 0.46899626950695 10.52421178438635 -4.41313344201950
O -3.29408282309604 14.59799295614779 -0.73712472067712
H -3.67519733366114 12.89251459164300 -2.97967406234065
H -2.12095477588350 12.65075327878789 -4.69755930291991
H 0.49552636268408 11.36403572696679 2.42866641577543
H -7.09724928834488 15.66628341797803 -5.78138073707408
H -7.46217872429230 18.12251899529461 -6.12038212870325
H -5.88761722277022 19.76601445966897 -5.17929769319232
H -3.88954324143908 19.01390122372001 -3.86522774049391
H 3.08492975142720 9.17589093677819 0.65292703570211
H 2.70130787594844 9.73857078006296 2.29823939180189
H -1.95716892833117 12.32822439416984 2.19725913685622
H -3.10199937137554 13.21242200249053 1.15544866485881
H -2.66209146090870 11.53017390543001 0.76916982883554
H -0.28543677877819 14.25331902537026 1.87254906760095
H 0.23931228338119 14.69777993349961 0.23155438051265
H -1.41418399845475 15.09078051766088 0.77206435902781
H -0.59942767799425 13.34530107941287 -6.22205369963204
H 1.35154877769156 14.70005250461293 -6.91222945673706
H 2.47436706234157 16.19096728908000 -5.26711446401267
H 1.59500964328429 16.35391894949508 -2.94860032904811
H -0.38451942320610 15.04571595450760 -2.27813129040040
H 1.00646142870910 7.89828998626349 -0.53411750234502
H -0.51044523962859 5.97207690100356 -0.19203849595033
H -1.00069833217567 5.16320100313003 2.10788573372986
H 0.04469767372458 6.28485325121741 4.06216608620737
H 1.56087248706852 8.21607961186396 3.71839487358138
H -1.12899004744154 9.74736615544467 -0.63507957901242
H -2.84761956263095 8.01499482042502 -0.27435331044594
F -4.91595234319737 7.62921452441805 -1.81199493810044
H -4.91886099511922 9.31186718262390 -3.80483380621575
H -3.20412373205517 11.03952384758733 -4.19456974736967

TS1.(6-7)‘
Lowest frequency = -254.79 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C -3.04743316147584 10.05027867258545 -4.44960345402023
C -3.08118900805473 10.79814648853193 -3.25880072682968
C -4.11729490601905 10.57033678370212 -2.33868657066472
C -5.06415403303562 9.57113611316247 -2.56886639863151
C -4.97542511500368 8.83215346360187 -3.73879509112717
C -3.98600640641069 9.05766790649509 -4.69152783466389
Pd -1.33039885582843 11.39787947488370 -2.24682170696694
C -2.63033663178333 12.71759863345682 -3.70337745013509
C -1.31825080953543 13.28263356536127 -4.15331703376008
C -0.46932806158591 14.05428970739694 -3.33892455920490
C 0.71772728439221 14.56624609984042 -3.85099666724598
C 1.09202356387412 14.30706175105307 -5.17143691121212
C 0.25415663602494 13.55097039580726 -5.99054861019737
C -0.94410611489995 13.05440033410662 -5.48806530227321
N -0.00175544231721 11.37247714751052 -0.69973556912538
N 1.17924492560112 10.81564910845944 -0.54004005610591
N 1.46929966694579 10.97275510345088 0.75533194145214
C 0.47539532119710 11.62017353986785 1.42704047412918
C -0.48188102573991 11.88936605177433 0.47407517274945

C	2.66273692402441	10.29701065820799	1.28938633075617
C	2.32890621380954	8.90502398034699	1.78209267085011
C	1.78087244414422	7.96278482429210	0.90304765480632
C	1.46641399132894	6.68586322305400	1.36120096755346
C	1.70034847603464	6.33882168835892	2.69394568871649
C	2.24852484398969	7.27395573117622	3.57026864039819
C	2.55845511719020	8.55627954200092	3.11466230215218
C	-1.81530476881309	12.58391841423994	0.50339796029780
C	-1.63116861418126	13.97310998488465	1.15457032744746
C	-2.83588221567158	11.73349902666396	1.29061933592481
N	-2.22119076132294	12.69536718977733	-0.92091622459803
C	-3.27846233656630	13.45372594528975	-1.25656500712700
C	-3.55687111960880	13.49825321475877	-2.76917547491903
N	-3.70131087916230	14.87649746076692	-3.23118180777073
C	-3.05933559042120	16.02909714579233	-2.73026309764450
C	-3.61862748523717	17.16195799155632	-3.52317475304487
C	-4.53891263719646	16.65636828359477	-4.44402569174043
C	-4.60748531797621	15.18197970662065	-4.26700252289393
C	-5.21444207861652	17.48596805275788	-5.32702657976437
C	-4.93863159039282	18.85670458027158	-5.26070949030059
C	-4.01602042595609	19.36408360472755	-4.33818292935416
C	-3.33868713109986	18.51813715948052	-3.45160925036616
O	-2.22238820444536	16.06246715904608	-1.85015945915257
O	-5.27820955418256	14.35638639959638	-4.86022189968057
I	0.17201402672515	9.71854295987591	-3.65102578851764
O	-4.04492751888722	14.04986574393513	-0.48777609641570
H	-4.55335005773282	13.06261836695922	-2.89866550898057
H	-3.19738757107059	12.48473581480377	-4.59881715010504
H	0.53171875797690	11.82371998757865	2.48410752582283
H	-5.92786932418863	17.08209691126700	-6.03834329289269
H	-5.44716882868711	19.53962544110237	-5.93487044196916
H	-3.82403381522388	20.43274841582295	-4.31214205172200
H	-2.62165720736629	18.90201592183562	-2.73294787485755
H	3.37754545221959	10.27515444199903	0.46352184800196
H	3.06509448049894	10.91659581496177	2.09392824512522
H	-2.51737619180973	11.61333258562447	2.33192014558635
H	-3.80365946637141	12.23940026570112	1.26816178271156
H	-2.92818829666173	10.74216499069987	0.83653821005936
H	-1.20452366234645	13.85243669339656	2.15687922906796
H	-0.95542280165422	14.58439520551015	0.55081247429211
H	-2.59324122998724	14.47835957949309	1.22503098376573
H	-1.59998365355590	12.47195968806514	-6.12981983910706
H	0.53162237420198	13.34956872430670	-7.02100587445883
H	2.02883464766024	14.69598240211339	-5.55993845218158
H	1.35843132823485	15.16622420274565	-3.21113874234649
H	-0.75288166012649	14.25767462096448	-2.31377153507942
H	1.59182425619716	8.23437909329578	-0.13271332433373
H	1.03859150172981	5.96039255196587	0.67574558934817
H	1.45403371999998	5.34181965011744	3.04740804278534
H	2.43142835477149	7.00974918293554	4.60774583262728
H	2.98317348750542	9.28774966660028	3.79893130501984
H	-4.18019016860481	11.14613797908055	-1.42342708564639
H	-5.85527506206878	9.36985231401830	-1.85441269848102
F	-5.89642319908668	7.86387437247500	-3.97361896435961
H	-3.96142871932498	8.46557124192922	-5.60020154197943
H	-2.27561307898312	10.24513786050959	-5.18495028749244

1.7'

Lowest frequency = 9.28 cm^{-1}.

Charge = 0, Multiplicity = 1

75

C	-2.77614050960503	10.42535382739937	-4.94311300323627
C	-3.12978502128720	11.19944476823944	-3.79681395644934
C	-3.87404952975583	10.54649582550406	-2.76886810689560
C	-4.27716161912269	9.19804204960655	-2.90846823470538
C	-3.94421977873368	8.53247488300956	-4.06068660414899
C	-3.18674437156749	9.12281214936444	-5.08593385061950
Pd	-1.69802690271007	10.82172022882974	-2.06739914268453
N	-2.34065598233901	12.50126118018106	-1.01459275873727
C	-3.35762852762964	13.32656552397255	-1.32415549297930
C	-3.78394229155623	13.47447803521263	-2.80239371028651
N	-3.82607030468667	14.89857347668823	-3.13427249029076
C	-2.90428573424991	15.88568019946081	-2.73383136889108
C	-3.38560919726009	17.14839455788460	-3.36669699192727
C	-4.53933251197902	16.86813555304745	-4.10206994833452

C	-4.83564715805109	15.41659429252750	-3.96159505994554
C	-5.20513120601677	17.85489411549155	-4.81358680487263
C	-4.67528815510341	19.15008603195855	-4.76796520414965
C	-3.51848465199616	19.43141674955852	-4.03192824229940
C	-2.85365358661006	18.42762896845433	-3.31674288008985
O	-1.92893716793160	15.71215902429472	-2.03031525697343
O	-5.73893291444779	14.75787713275112	-4.44890552909360
C	-3.12003216009891	12.71796450491095	-3.97329087901320
C	-1.80412529857309	13.27691929913700	-4.49234132001166
C	-0.66741070525944	13.44192061804737	-3.69301133668777
C	0.51771276716279	13.92612112581664	-4.24210343750801
C	0.58906476372518	14.25733316549744	-5.59549910320101
C	-0.54164613781941	14.11485156782235	-6.39803717845088
C	-1.72740955523918	13.63084041891032	-5.84501608170650
N	-0.27029571805362	10.95569474631567	-0.65327821007850
N	0.91557699030661	10.40026393775701	-0.50974655713719
N	1.34956478423330	10.81776119044635	0.68329948176081
C	0.44910573350427	11.63450599107578	1.30013162454101
C	-0.60424293673051	11.73423766497122	0.41798126435873
C	2.59220563586120	10.23466939589288	1.21366371935155
C	2.31555986719756	8.97247407033333	2.00272116459011
C	1.65902427357091	7.89444137952125	1.39621760646171
C	1.40587492982787	6.73617338661268	2.12690022161781
C	1.80886682140409	6.64276554579423	3.46112614469470
C	2.46444142173133	7.71378266505686	4.06619636398450
C	2.71341613720877	8.87807494692368	3.33798933818543
C	-1.91083349450880	12.47194339531893	0.42032711332091
C	-1.65135330276365	13.88341635186554	0.99397861539215
C	-2.94166721535702	11.70144092385089	1.27442032606711
I	-0.55095677787001	8.61014787954835	-2.94376866787714
O	-4.02347530596410	13.99386820542488	-0.51475038551957
H	-4.83868535327619	13.17299373510955	-2.81129244320292
H	-3.83615108969641	12.88252449337110	-4.79220815368998
H	0.62860230546606	12.05906175102837	2.27422680014310
H	-6.10083793338823	17.62554995270563	-5.38221073863198
H	-5.16730232270041	19.95069366583387	-5.31253331301085
H	-3.13144841302139	20.44614455533288	-4.01800989967852
H	-1.95487307339390	18.63532054871171	-2.74481435797068
H	3.21713849424317	10.03721513278769	0.33947728333921
H	3.07610045202188	10.99205438811975	1.83427993181234
H	-2.60770737391211	11.63461095625573	2.31568576123025
H	-3.89425258199009	12.23346668845333	1.23429409456543
H	-3.06841325640301	10.68758872957829	0.88123491156331
H	-1.14002904406297	13.78803858945779	1.95924609587661
H	-1.02126632165055	14.45626372625343	0.30917295749719
H	-2.59065107858243	14.41326385874975	1.13281957406410
H	-2.61141317558612	13.52630932704612	-6.47110746925207
H	-0.50448389337702	14.38066747947089	-7.45079268932160
H	1.51666834191113	14.63163936260464	-6.01945248364736
H	1.38891975788692	14.05057606911048	-3.60518607033883
H	-0.72405442156232	13.21987770591551	-2.63406419884205
H	1.33816946059890	7.96811163717837	0.35977399294605
H	0.89359385677936	5.90453150861843	1.65233337518382
H	1.61012526719553	5.73730989616401	4.02707319216488
H	2.77834190870857	7.64741032156428	5.10381756350443
H	3.22200092287620	9.71566652860013	3.81061403331798
H	-4.32038947884032	11.12174476444255	-1.96613242462927
H	-4.85292363948781	8.70637198113726	-2.13299451708272
F	-4.34266168440468	7.25134201253070	-4.22477050074863
H	-2.92232118459828	8.53490415912244	-5.95766489309177
H	-2.18970484261015	10.89942652445681	-5.72358360359418

1.5a
Lowest frequency = 8.04 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	10.31007974300262	10.83363517784706	1.36971387599751
C	11.03717964312748	10.42836335730634	0.25331500830234
C	11.66664574510889	11.34099824046354	-0.58852923844869
C	11.56780550394227	12.70266107264870	-0.30357233373789
C	10.83414142660446	13.09945437902372	0.80750264729050
C	10.20128828400174	12.19483849258527	1.65067584526087
I	11.09921336667517	8.36301713882146	-0.21821702665402
Pd	8.82803945128393	7.60319681972140	0.86903400583086
N	9.57772477989445	6.09968769143152	2.14467141837721

C	8.62038347245404	5.64877002319524	3.01486864855434
C	9.23194972404528	4.70186459518875	3.80814637212461
N	10.51978301217556	4.64810959524299	3.36968647066741
N	10.73083706682129	5.49712092197854	2.34863573950643
C	7.21795802005620	6.20278597851908	2.98476586609630
C	6.21493627395443	5.03415603721009	2.86794813741750
C	11.60806363957072	3.77268952883616	3.82337702932926
C	11.29139868138928	2.31246139534182	3.59143868224085
C	11.32864162551095	1.40642882280205	4.65322620760987
C	11.04647950057855	0.05618657802553	4.43939100319098
C	10.71817226878669	-0.39196782224599	3.16128052975137
C	10.67465068339446	0.51168387596850	2.09671302185407
C	10.96131120597750	1.85722719330737	2.30951134826364
C	7.62115067159128	9.03065719013221	-0.01024473385023
C	7.98015232885558	9.40792635463906	-1.40490706244593
C	7.91003852400574	8.48498951005713	-2.46255997745828
C	8.26701370837809	8.84847553922293	-3.75621445474412
C	8.70419448301610	10.14854108424881	-4.02839948439452
C	8.76764732062082	11.07996040085189	-2.99310937097287
C	8.40505069264369	10.71302972778974	-1.69727836825593
C	6.19514090392475	8.48618274604573	0.14084825290354
C	5.99726950664827	7.70214603985453	1.45087774109361
N	7.14524957969079	7.07920932976153	1.79500362633151
N	5.19360554800578	9.53839625550798	0.01993494257016
C	4.17695118589290	9.52449142008880	-0.95132133919890
C	3.34282650825094	10.72924154843159	-0.67265418941408
C	3.87662777545070	11.38258688447522	0.44049308767163
C	5.07322401745670	10.62024667157289	0.90423144839397
C	3.30558332794352	12.54290678083602	0.94069194485887
C	2.16960107487909	13.03742902599675	0.28795271116340
C	1.63559333776359	12.38306522434920	-0.82808553843005
C	2.21970016734329	11.21222146930037	-1.32694543916887
O	4.04830475198045	8.68408363031918	-1.82233534291899
O	5.82322892982106	10.86634399446635	1.83354682511276
O	4.90737267513217	7.63306873556075	2.02959919281515
C	6.96084489182583	7.01978623975505	4.27150181051662
H	5.96671307965211	7.79409664463312	-0.67750360774671
H	8.87330320715724	4.07407978576476	4.60785161071069
H	1.81328943428494	10.69649072256910	-2.19134129907160
H	0.75325548265365	12.79148419543403	-1.31244504566626
H	1.69261613744227	13.94296623840767	0.65194310646965
H	3.72671283928335	13.04255286260987	1.80755065283743
H	12.48313020968665	4.09714562071329	3.25465478223292
H	11.78975697960039	3.96639249346478	4.88448061920964
H	6.31769770863622	4.36041941158131	3.72637795753871
H	5.20082292242478	5.43466445890662	2.84172139673125
H	6.40483084572898	4.46889551861468	1.95097041334120
H	7.05217887841038	6.38073469280515	5.15727190409534
H	7.68618991697111	7.83522604235362	4.34521353445609
H	5.95397197077942	7.43880219223470	4.22659844334920
H	10.92322498992543	2.56096821334798	1.48169441104372
H	10.41774211745995	0.16602113382305	1.09976173124881
H	10.49419288416873	-1.44119688638728	2.99312594976986
H	11.07871422481265	-0.64110868034883	5.27137549565986
H	11.58051592981292	1.75748572530670	5.65147784775989
H	8.44636405608732	11.44474815656743	-0.89458641114058
H	9.09348321125259	12.09760825828428	-3.19309431347650
H	8.98410254232937	10.43143456986939	-5.03932365770927
H	8.20649649189793	8.11729708733517	-4.55790521319141
H	7.58640685436641	7.46745154820183	-2.25716596370575
H	7.73947913048404	9.88657301907257	0.66040797824349
H	12.20661712532629	11.00908080091781	-1.46840305391196
H	12.03679392192552	13.44681320659799	-0.93838612795374
F	10.72792200846337	14.42542031673244	1.07517273261272
H	9.62645970094538	12.54815553535309	2.49993308984463
H	9.80838316855347	10.10015621875080	1.99331149541494

TS1.(5-6)a
Lowest frequency = -59.45 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	11.51873178622482	9.00560812576414	1.75845641165177
C	10.72333979778031	9.26226065633010	0.63185888559936
C	10.42774000696337	10.57577657384422	0.25055185944807
C	10.82677265307588	11.63482411721118	1.06034897189447

C	11.55826437449656	11.35906291093564	2.20888865890059
C	11.92151472152824	10.06608179873325	2.56600451088666
I	10.82859602403788	7.74255965532333	-1.08422756773002
Pd	8.87752488617457	7.92249193037120	0.74437259644746
N	9.68897994831237	6.47471148531105	2.10686230631818
C	8.80194662066517	6.14453092622784	3.09251559087402
C	9.43539870403214	5.21673497281678	3.89308501173736
N	10.66960267415718	5.05770530874058	3.34288279567600
N	10.82169775310720	5.81890598640895	2.24648288587839
C	7.43848372730541	6.78058384670281	3.15335866870896
C	6.37873040768215	5.66740413452048	3.30981347501481
C	11.73757728677854	4.12306131748783	3.72572019251784
C	11.39783761464877	2.69567011088517	3.35901128245281
C	11.34233746794648	1.70891490909693	4.34534548721040
C	11.03502627719911	0.39016996313344	4.00685764315481
C	10.77533870073753	0.05562116029065	2.67903789109663
C	10.82568433889836	1.04072466458685	1.68981821790082
C	11.13739283329454	2.35520788377484	2.02653302220498
C	7.54846687818567	9.24255433205823	-0.17036316355739
C	7.72115045300095	9.53418236965338	-1.62066225209025
C	7.62841825910712	8.52777436340530	-2.59549820226102
C	7.74862461598137	8.82692913640980	-3.94716941338650
C	7.96247167132556	10.14500011990518	-4.36196852143943
C	8.03808642802437	11.16000979042314	-3.41038690022048
C	7.91320393322650	10.85538144756141	-2.05423634582310
C	6.16268271960129	8.66432240862929	0.13983798558332
C	6.08701884736822	8.08540084687152	1.55877883166865
N	7.26881316437907	7.50801197619859	1.87551916117779
N	5.10674541136006	9.64040595980672	-0.08605028913233
C	4.05405225484024	9.42934920820393	-0.99479131150172
C	3.18068622512260	10.63203135135340	-0.87913900369114
C	3.73081550806943	11.48142294442971	0.08358390991437
C	4.97938135762527	10.85416000298389	0.60787488502396
C	3.13117480004254	12.68801453055091	0.41117203318871
C	1.94944482838969	13.02508912615020	-0.26015990869506
C	1.39928208764377	12.17443705931079	-1.22599799867361
C	2.01214697102503	10.95812959373850	-1.55081055974695
O	3.92913830879234	8.45164374442019	-1.70889254806052
O	5.76047129985550	11.28368533256074	1.43835990355710
O	5.05753044086372	8.10558936918676	2.23935670748075
C	7.37830978926444	7.77046074398987	4.33893971079687
H	5.93232490167505	7.84465064637304	-0.55062884092180
H	9.12172073255180	4.66815701376533	4.76651989542231
H	1.59378285789128	10.29104570874842	-2.29797400704836
H	0.48161396990524	12.46456201979124	-1.72953232861290
H	1.44913983634664	13.96120658147927	-0.02930820353972
H	3.56556201631201	13.34041832819727	1.16220371627376
H	12.62617207125972	4.47732505197994	3.19759950103333
H	11.90445080836334	4.22090483768978	4.80155863958229
H	6.57337694574955	5.09374836706292	4.22323413412530
H	5.38707617345269	6.11554825488111	3.36854667716792
H	6.41922078392091	4.98879678405032	2.45286813760546
H	7.54414502877804	7.24697380189481	5.28733249510683
H	8.14477180239601	8.54165744331995	4.21916882780774
H	6.39376767374000	8.24200496829824	4.35213558151927
H	11.17310647653554	3.12333896946849	1.25797605110436
H	10.62337596557880	0.78301679708175	0.65445367562466
H	10.53286623802253	-0.96913337896111	2.41368397362973
H	10.99559467605149	-0.37137631375724	4.78011475394751
H	11.54293531525636	1.97110516394026	5.38186863518036
H	7.93511068707795	11.65362169713796	-1.31525039128650
H	8.18436063013697	12.19104610175854	-3.72113790159315
H	8.05995949986810	10.37673572874805	-5.41871766658497
H	7.67781735366122	8.03132974372702	-4.68369332950563
H	7.47699635629340	7.49875676796813	-2.28013954091482
H	7.69029217459073	10.14560195221700	0.42822706076880
H	9.87948808886118	10.76589902330889	-0.66367065669956
H	10.58058267786633	12.65994810348578	0.80383307425314
F	11.95357561203032	12.39080036558181	2.99909699073319
H	12.51598571751654	9.89653938267634	3.45790150821891
H	11.80861507016834	7.99238589178822	2.00580402964619

1.6a
Lowest frequency = 4.87 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	2.45352197343051	-6.28574707958993	2.06636066530420
C	2.91255474569623	-5.37898692097524	3.02952002781314
C	3.01043572934966	-5.78525145873429	4.36249804513343
C	2.65675088661244	-7.08365371264894	4.73315581872544
C	2.19796460459380	-7.98085671398957	3.77030400180577
C	2.09690251850377	-7.57974121781969	2.43585893948324
C	3.28023447681452	-3.96959913721988	2.63464835848420
N	2.10077604245776	-3.21509167570424	2.17321661828042
C	0.86315071875180	-3.15234259222079	2.73625484122388
C	0.14808335738828	-2.29603279048852	1.92573976384338
N	0.99984821628320	-1.90671236947529	0.92955923824314
N	2.18637472619759	-2.45608406726559	1.07081877401540
Pd	0.11030566457074	-0.34945437092688	-0.31171833029920
N	-1.47364733166407	-0.97235577230460	0.77507540483239
C	-1.26913019025298	-1.78659223319955	1.99469048666444
C	-1.45616556695911	-0.94922642724785	3.27960200657351
C	0.64459162630813	1.04619184218841	1.04888966633642
C	1.95212853095169	0.97758464469935	1.52781089061648
C	2.34144212718709	1.83167940988535	2.56221475343466
C	1.41145361962016	2.72081698722430	3.08333927254107
C	0.10955707553155	2.78950935943959	2.61467351120516
C	-0.28334671502967	1.93302545814302	1.57929639361461
F	1.79463283724923	3.55073350866548	4.09235362016115
I	2.17011054205696	0.12853322270482	-1.88294061359993
C	-1.27135800204253	0.91844659301019	-1.24986958298266
C	-2.61893242253256	0.27105624558823	-0.88975289864663
N	-3.72687620947351	1.19143773377692	-1.08088771604124
C	-4.76356605562707	0.94127948379914	-2.00581819716749
C	-5.71612213768444	2.07521887507936	-1.85082422560007
C	-5.23358795987503	2.91788698884557	-0.84626097667813
C	-3.95408739824701	2.35351679980784	-0.33217191411323
C	-5.91592539176326	4.06615739510744	-0.47407182925945
C	-7.11113293256944	4.35159675974099	-1.14515459666631
C	-7.59420331443887	3.50783241434472	-2.15207763407999
C	-6.89872211924162	2.34993697488989	-2.52091799835370
O	-4.81517626915969	-0.01952156732972	-2.74924562950597
O	-3.22301961017990	2.79077499966676	0.54071961204623
C	-1.03773489303316	1.08558344347196	-2.70360179357596
C	-1.35210660720993	0.08781170191531	-3.64002666357862
C	-1.10260841667772	0.28060184159184	-4.99461311808140
C	-0.54348322926128	1.47854976039168	-5.44243714675545
C	-0.23473919834418	2.48378318610490	-4.52389592285458
C	-0.47552313266717	2.28588620557031	-3.16933557778628
C	-2.66416362335602	-0.38849627932355	0.50138990566858
O	-3.69786621081417	-0.45307355099358	1.16988649487172
C	-2.23807126201658	-2.99143482344717	1.98781364288509
H	-2.83118815265298	-0.54099499744635	-1.59446452985702
H	0.60742090650312	-3.71570046455672	3.61893841305120
H	-7.26539463684988	1.68922283969324	-3.30002786253945
H	-8.52445714962210	3.75751426481656	-2.65386962867082
H	-7.67471315653462	5.24190690194616	-0.88191894694135
H	-5.53326400804059	4.71377588049635	0.30837616991668
H	3.97972102379450	-3.93882477749817	1.79631379080443
H	3.72194549433942	-3.43225146953046	3.47928196318337
H	-2.03650892254391	-3.63498992506006	2.85099752008541
H	-3.26545649150134	-2.62912338538139	2.04033210447867
H	-2.10484803322127	-3.57617032605853	1.07323532243938
H	-1.29830018532158	-1.57948297131070	4.16183964747019
H	-0.74210937067556	-0.12346525526876	3.30241824848934
H	-2.47217621314639	-0.55099555657397	3.29950600122785
H	2.37274138541079	-5.97338654775749	1.02807908843034
H	1.74272388460240	-8.27787623502924	1.68323205182152
H	1.92049468853448	-8.99108216256064	4.05629402999688
H	2.73866163965643	-7.39108728975493	5.77147640574733
H	3.36719806808670	-5.08349906291865	5.11296587824633
H	-0.21729435830086	3.05828562269187	-2.44975243192582
H	0.20128063314828	3.41855627532509	-4.86463864496841
H	-0.35043965479302	1.62803439388725	-6.50089965158100
H	-1.34770691594118	-0.50457337843673	-5.70393152361029
H	-1.78918765471515	-0.85087019080333	-3.31140619606582
H	-1.14748406781497	1.86798868850376	-0.73354144639746
H	-1.31110501527233	1.98344234797873	1.23998921560050
H	-0.59828613829328	3.48712278554349	3.04995130266819
H	3.35623620534499	1.81433085772076	2.94648024379706
H	2.66888237638575	0.28665106259438	1.10286107692192

TS1.(6-7)a
Lowest frequency = -225.30 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	1.63443529947957	-6.38179362539318	1.30984873653836
C	2.36152004155959	-5.91009149962324	2.40948928706085
C	2.48054089546677	-6.71003901266771	3.54802375591834
C	1.88420594060972	-7.97143063607487	3.59015558570214
C	1.15973325582371	-8.43495235902777	2.49359344634258
C	1.03540815969402	-7.63757206248581	1.35305020373887
C	3.00034241658612	-4.54253380976976	2.36894139492695
N	1.99057073633510	-3.48162192894883	2.21370268425673
C	0.86365920605199	-3.26703391241064	2.95071154732730
C	0.27124291660570	-2.16469919751694	2.37934680826733
N	1.08164118155203	-1.79341885403244	1.33636318448068
N	2.12524855613368	-2.58710814376063	1.22775750005886
Pd	0.53333839543445	-0.00456797331922	0.47360392691266
N	-1.16539584974733	-0.55711719716173	1.44949030139154
C	-0.99004680521639	-1.38663729912919	2.66089873843072
C	-0.80625881415964	-0.50005290375493	3.91096236263868
C	0.20207481048870	2.05859442187435	0.59972463889452
C	1.07322169711929	2.96173478961556	-0.03017223566972
C	1.36112817529384	4.18783363030012	0.55654781613591
C	0.73674431484636	4.51391291447627	1.75622422980309
C	-0.17617205837691	3.67120153263469	2.37263398402209
C	-0.46003870328689	2.44427699843659	1.77599725421104
F	1.01573234535900	5.71210757091540	2.33232550886918
I	2.90927416715135	0.23248682459272	-0.70508047792009
C	-1.04690034648811	1.24789558111563	-0.84370578032874
C	-2.26388424186680	0.42045587164169	-0.41129661362537
N	-3.48315703284615	1.11379329157476	-0.78773338870145
C	-4.48038675358999	0.50515338971167	-1.57804382536405
C	-5.61974250110101	1.46461766863069	-1.58634163381609
C	-5.27741765564123	2.56058089571727	-0.79010984995688
C	-3.90451448023188	2.34399943878104	-0.25324315709067
C	-6.14978061970792	3.62255685205735	-0.60516327201451
C	-7.39249221338908	3.55512187725219	-1.24631512563138
C	-7.73540646891832	2.45752013980025	-2.04460050146136
C	-6.84754727296581	1.39052158031441	-2.22723114304816
O	-4.37562913853179	-0.57993707420038	-2.11745905660531
O	-3.23676096449855	3.06439151639597	0.46649776501488
C	-0.44218187107660	0.93129811882411	-2.16206919542951
C	-0.27189750032172	-0.38519519719650	-2.61998444884026
C	0.27732375337974	-0.63282069705381	-3.87021067243303
C	0.67519377797899	0.42931390076888	-4.68669936019622
C	0.50121054405830	1.74133376424129	-4.25024194894672
C	-0.06019262269408	1.98924719798177	-2.99976847139089
C	-2.34559149797652	-0.05525891117900	1.05945836327172
O	-3.41692201643354	-0.05496952427798	1.67435453624324
C	-2.14921960778863	-2.38397398677428	2.86842677922361
H	-2.28579482615370	-0.50502117510830	-0.99573198366148
H	0.58375364538737	-3.90896043756783	3.77010917656110
H	-7.10459148908792	0.53513382731437	-2.84390084010458
H	-8.70742530041298	2.43542337504557	-2.52859686761142
H	-8.10433363337519	4.36619214179366	-1.12354270908639
H	-5.87418344769648	4.46878669854045	0.01618879723987
H	3.66825260000881	-4.41748636300726	1.51368411638016
H	3.56468712814430	-4.34822667418319	3.28572594406300
H	-1.89758894386005	-3.06577627758236	3.68851553733494
H	-3.06633344249150	-1.84816494066703	3.10898991781847
H	-2.31022399778143	-2.97144447311641	1.96008180976505
H	-0.61329083531601	-1.11499050415177	4.79680835772802
H	0.03235749476767	0.18729186179620	3.76803938726267
H	-1.72114280521250	0.07628503616184	4.07294091564018
H	1.53569766447374	-5.76059438523583	0.42296136046461
H	0.47298289224548	-7.99711103702199	0.49650248338060
H	0.69243649976722	-9.41472163474448	2.52499803578647
H	1.98415081784913	-8.58733011230265	4.47900340382240
H	3.04453071170348	-6.34612897734386	4.40391419430900
H	-0.20798797119935	3.01166671120605	-2.66169862173982
H	0.79927921388345	2.57221702319564	-4.88306134873627
H	1.11739772098738	0.23218528485773	-5.65889615612941
H	0.41082778320943	-1.65662578621771	-4.20618133980316
H	-0.55060298446002	-1.21813904447757	-1.98031678084220
H	-1.33676897716200	2.29170881692089	-0.81392586055931

H -1.19816638763523 1.80126897927829 2.23334777474012
H -0.66793190846217 3.97601926968252 3.29014942636282
H 2.05719416896144 4.88267740034773 0.09828552070394
H 1.54347505876449 2.69437643469150 -0.96886783230087

1.7a
Lowest frequency = 12.97 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C 10.05574273894452 10.84057617386411 -0.12260836011309
C 8.92771842994315 10.27226379882666 0.54589913698061
C 8.64921594381721 10.74714666663981 1.86123840976049
C 9.45257483242284 11.74236487136371 2.46291331291972
C 10.49181314159843 12.27182453482533 1.74266680602570
C 10.81329791366191 11.83294322341176 0.44900732286087
C 7.89814629140527 9.57028658407878 -0.35721711135933
C 8.55226853598544 8.49296341695658 -1.21662996607592
C 8.74852057768918 7.19025653632804 -0.74125945404089
C 9.38642852714053 6.23524732212041 -1.52993802475131
C 9.83441268044609 6.56351343001819 -2.80999644803843
C 9.62130571095364 7.84957972466627 -3.30335670592531
C 8.97982294607962 8.80322177477015 -2.51146495535396
Pd 9.56493127916200 8.64031620397567 1.99198218994219
I 12.16699084328648 9.03233609051342 1.94603868382157
C 6.58120152134229 9.06142770931143 0.29779067137145
C 6.51249628145045 8.64663130894684 1.79341274994753
N 7.59888835521157 7.99129046602497 2.25295780631048
C 7.47062637978636 7.22149996038397 3.52656091066424
C 6.24918921833152 6.28181854231002 3.52347564736277
N 5.45153461420496 9.92932586370197 -0.00995635946834
C 4.27038948271147 9.40730202988696 -0.58117974557689
C 3.29079983354547 10.52819376186283 -0.57335481543293
C 3.90050955105318 11.63540741422634 0.01988927165415
C 5.28802594603261 11.25709823387785 0.41030966900335
C 3.22862041650333 12.83904896074625 0.17110125736675
C 1.90918673777094 12.90287878667432 -0.29278294856290
C 1.29779791149165 11.79302320662437 -0.88782345143180
C 1.98524877357343 10.58259711496928 -1.03834930820813
O 4.14032327554304 8.26997310732732 -0.99198512888894
O 6.13647440125394 11.93852059211091 0.95900406296430
O 5.43435916716218 8.79283179890075 2.38697810841194
N 9.84767854349153 6.88661194755648 2.95627432242450
C 8.71956735853869 6.38604362894359 3.54766387479695
C 9.05732786242556 5.13500239091428 4.00958938907526
N 10.36990842223349 4.97610626525157 3.67065106602672
N 10.85184807054367 6.04058329652876 3.01907952589862
C 11.20186732283518 3.76258039527082 3.72740060588288
C 11.00656311634849 2.91134628853168 2.49051753082810
C 10.46775377480396 1.62727691884100 2.59414453511004
C 10.27460145812268 0.84963442072619 1.45130794536526
C 10.61533605840137 1.35760646030641 0.19883209936159
C 11.15322824907657 2.64227778040766 0.09129978639378
C 11.35096474928502 3.41754409964112 1.23106336921814
C 7.44176488635435 8.16763722495740 4.74656489993017
H 6.31800838552610 8.13180534864155 -0.22167304925971
H 8.49629110708993 4.36813698354486 4.51819424172653
H 1.51928527877621 9.71638178486177 -1.49726148680333
H 0.27238884750340 11.87457005782626 -1.23638118400351
H 1.34799335470818 13.82701141827024 -0.18924710133036
H 3.71169794473499 13.69322836656229 0.63504007968356
H 12.23149758849160 4.11534553042168 3.81942458245506
H 10.92873588077518 3.21670733347009 4.63294459345952
H 6.29276161616896 5.62664084887458 4.40132084267183
H 5.32902862259898 6.86214433909608 3.55740395704160
H 6.24995097414479 5.66297216636215 2.62117576439296
H 7.41247131408212 7.59616398639274 5.68069530833765
H 8.33625962399121 8.79905209237276 4.74805007411301
H 6.55207516926890 8.79734956176125 4.67902104378250
H 11.76023519668433 4.42087092604496 1.14730148694652
H 11.42304978527972 3.04034134106726 -0.88260507349214
H 10.46249962948911 0.75556194105466 -0.69204278583812
H 9.85583297947046 -0.14839073955711 1.54075706134623
H 10.19931529241915 1.23148657880978 3.57125312544292
H 8.80421455431275 9.80161420186389 -2.90673966981091
H 9.94837134606011 8.11208331339265 -4.30551034361953

H	10.33482451877019	5.81962970374351	-3.42353439882609
H	9.53002995031758	5.23081824266537	-1.14108191653332
H	8.39018261567966	6.92578496440931	0.24943903313729
H	7.57430405074810	10.35530402846457	-1.05175442058864
H	7.70279405307232	10.52653000096796	2.33234837818661
H	9.22422757878909	12.10862306866724	3.45695927971706
F	11.25199243453457	13.24789516800461	2.28945765197627
H	11.66875268915372	12.25976946028517	-0.06217272510276
H	10.30810748539332	10.47983365353559	-1.11352753366067

1.5a’

Lowest frequency = 6.39 cm^{-1}.

Charge = 0, Multiplicity = 1

75

C	2.00234791449259	12.38423919106137	-3.72902843782677
C	1.57273972983729	11.39629700266240	-4.60919596859273
C	2.28097413262813	11.07150726831489	-5.76283880200016
C	3.46268814221739	11.75833157452050	-6.04389409288701
C	3.88467048391384	12.74349989569681	-5.16084995126144
C	3.18014030335261	13.07240830562579	-4.01094717809836
I	-0.25218273318185	10.39429973454321	-4.18584465208549
Pd	-1.22708595822673	11.96681086594416	-2.32459784980562
C	-2.14257796241949	13.23574727191962	-3.65541398170204
C	-1.02066389218272	14.08149847401311	-4.15448076942971
C	-0.31568963756589	14.97693517448171	-3.32798122902596
C	0.73720580224058	15.73451146784623	-3.83121583078096
C	1.13434013551207	15.60266529857260	-5.16443141698369
C	0.45706944572753	14.70832378077017	-5.99323611185210
C	-0.61026504104781	13.96430139783917	-5.49456254715482
N	-0.32591558093920	11.17761246648133	-0.58515673801117
N	0.63652337114318	10.32040140222477	-0.31256153970175
N	0.86917818143790	10.44512857828016	1.00568557724152
C	0.05654802209652	11.37867995771672	1.57306159190010
C	-0.71796604167763	11.85808742694655	0.53854286379106
C	1.89415238514336	9.60985754893416	1.64741314241335
C	1.32507042703732	8.80493342588907	2.79249441092895
C	0.28180331542871	7.89883393839648	2.56748238974352
C	-0.24393950871216	7.15947009404073	3.62324979037443
C	0.26892660922160	7.31632743684155	4.91337086971876
C	1.30760432402486	8.21659603828724	5.14308874810689
C	1.83131911735056	8.96083909690210	4.08454409928506
C	-1.82106282714350	12.88581080090274	0.48467403836390
C	-1.35482818816108	14.18775357224976	1.16976053613539
C	-3.06744792578105	12.30605908675039	1.19470639608114
N	-2.09029449109822	13.12987151119451	-0.95029171437694
C	-3.08640355583165	13.96149626088152	-1.33893526381352
C	-3.28399924101639	13.90178749604487	-2.86452119138336
N	-3.70398918494756	15.19524513964438	-3.40740614673212
C	-3.25241874304552	16.47572598585883	-3.02576967282982
C	-4.00501896270849	17.43179948793254	-3.89130337499380
C	-4.84336090452768	16.70504122426814	-4.73763158443025
C	-4.66442205337847	15.25898028031150	-4.43207446800175
C	-5.65808349955159	17.33347738929898	-5.66793664033889
C	-5.60867187662449	18.73133906784475	-5.72735602334843
C	-4.76803479324440	19.46074254036884	-4.87822536198062
C	-3.94910633284932	18.81621928295655	-3.94299360178697
O	-2.41393921444633	16.72991230665021	-2.18401375107357
O	-5.21039875860601	14.29219146494461	-4.93599959513355
O	-3.82943325689109	14.61941547106943	-0.60494778923327
H	-4.16197966119231	13.25981630647850	-3.00469675824842
H	-2.57008906314309	12.66613582807077	-4.48509365705371
H	0.09131347988109	11.60194887578037	2.62715459044836
H	-6.30579623295407	16.75799961520901	-6.32190191312639
H	-6.23098507128794	19.26085347891740	-6.44307150374367
H	-4.75232809624193	20.54460115825717	-4.94892417648272
H	-3.29281475009620	19.37179406109907	-3.28052280106600
H	2.27686942404473	8.97304531925104	0.84612419338229
H	2.70418482811769	10.25827284042675	1.99484438802498
H	-2.83536417897405	12.07773775182091	2.24106010438698
H	-3.87572982856267	13.03747324020073	1.15038602286540
H	-3.38374422338784	11.38532575631301	0.69537144328505
H	-1.11881768505249	14.00275306592555	2.22427240868843
H	-0.46311667966054	14.57565373157292	0.66908878366370
H	-2.15301237447381	14.92842402682726	1.10254344608131
H	-1.14347229185945	13.27739956987702	-6.14789531362206

H	0.75621692216534	14.59369558969072	-7.03170752575693
H	1.96489316777710	16.18684769532571	-5.55072030934136
H	1.25354092039772	16.43175890879316	-3.17641266479079
H	-0.61135648813675	15.08152928051982	-2.29060111740541
H	-0.12045467355249	7.77988210060735	1.56439879563847
H	-1.05337816987919	6.45874002078423	3.44109053759704
H	-0.14237324985229	6.73840394302702	5.73567356180423
H	1.70866787787159	8.34415258804934	6.14424764267601
H	2.63981457521148	9.66610071011356	4.26365068798319
H	1.92503559718799	10.30533902434016	-6.44338168111755
H	4.04323094960756	11.54110145336307	-6.93411781144027
F	5.02891129105567	13.42013029067773	-5.44085235857851
H	3.53514846000335	13.86453907371992	-3.36138145483036
H	1.40919954798606	12.63602321103546	-2.85561373734872

TS1.(5-6)a’
Lowest frequency = -60.71 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	1.49617854904464	10.57257670030770	-2.64516565420502
C	0.64726732023991	11.12849929867277	-3.61328964922463
C	1.14396682987084	12.05372818253701	-4.54208447494904
C	2.44249914368024	12.53229650066663	-4.41772650147629
C	3.24012154611273	12.03236864092252	-3.39567147449034
C	2.79855923049061	11.05039349563300	-2.51735217094304
Pd	-1.30573886018623	11.61227774231865	-2.65667449508256
C	-1.70115205588997	13.22904052416250	-3.88626392002049
C	-0.63935842351306	14.28065649285299	-3.74882114678217
C	-0.03719615073333	14.60635468419423	-2.52588561215921
C	0.95528062137536	15.57876248380523	-2.45650182571304
C	1.35937313480230	16.26049763955312	-3.60586633095181
C	0.75277332128060	15.96576589547460	-4.82657161915747
C	-0.23464266423315	14.98338482467351	-4.89392180784661
N	-1.17730243458637	10.40077460604514	-0.86532042645043
N	-0.42822982151756	9.40354619522350	-0.44443000372698
N	-0.61038738526677	9.33745413117870	0.88407945525568
C	-1.46970253976593	10.29998172211463	1.31551018347301
C	-1.84377350002980	10.98406134617180	0.17801186350896
C	0.22698951377379	8.43184153828815	1.67671480893291
C	1.36338511533442	9.16985657628203	2.35616706051880
C	1.69595594044225	8.87102442014597	3.67934163372181
C	2.75823423882891	9.52531044642789	4.30453871397805
C	3.48830281864438	10.48967516271282	3.61139121263630
C	3.15430790395729	10.79674329775591	2.29081734079081
C	2.09834749427465	10.13906615629680	1.66431995194560
C	-2.80529182445971	12.11917666957041	-0.04470478876689
C	-2.53208720164167	13.25472331755018	0.96266129898138
C	-4.24064231972258	11.56119109565713	0.12736903122051
N	-2.57426284127125	12.59164917741547	-1.42860464210602
C	-3.40411199585499	13.51736550147675	-1.97322204005787
C	-3.11320828886243	13.68640713962743	-3.46957291452021
N	-3.42216510115433	15.03752846864183	-3.92400048641258
C	-3.07975641336380	16.23811157644197	-3.26217757251583
C	-3.56165400209052	17.32854624863465	-4.15981375534096
C	-4.13836773779985	16.75271080189859	-5.29334970344861
C	-4.04931927246763	15.27208166576174	-5.15824221564253
C	-4.66308461224827	17.53036411677654	-6.31537447088425
C	-4.59346479340074	18.92076985166506	-6.16793210063280
C	-4.01519432824164	19.49830786041487	-5.03125427892037
C	-3.48780410821467	18.70451121485411	-4.00555920433226
O	-2.50119933496637	16.33260721771256	-2.19955359183436
O	-4.41570867724637	14.40372375072093	-5.93202142531918
I	-1.02175899159017	9.74804715798180	-4.52655210772902
O	-4.34064704951404	14.08942702642116	-1.41203443479433
H	-3.83396718503713	13.04528515811326	-3.99081545070414
H	-1.73923608906733	12.87675818269791	-4.92200297269584
H	-1.72245350640426	10.41919247272415	2.35666876036755
H	-5.10834487353158	17.07223735358892	-7.19301369945210
H	-4.99304037481749	19.56404784790887	-6.94663819832970
H	-3.97560968846045	20.58056281944377	-4.94695532738964
H	-3.03522083014026	19.14149273066262	-3.12102285623883
H	-0.40678003628523	7.92926795158369	2.41192863139867
H	0.59563997466874	7.68609892461777	0.96699259215148
H	-4.35773331847115	11.14013377775316	1.13205287846420
H	-4.96238436152530	12.36458559892590	-0.02050909276321

H	-4.42107681078888	10.77111024499551	-0.60773122598780
H	-2.67642077172761	12.90117099123147	1.99021492663054
H	-1.50583876347296	13.61685920793668	0.85393775944139
H	-3.22369597988392	14.07505266614983	0.76505906472263
H	-0.70231076547483	14.75124104479216	-5.84878497187592
H	1.04780628940278	16.49816850633335	-5.72697482457620
H	2.13677580805833	17.01721995234306	-3.54925231089731
H	1.41392303621397	15.81005084058435	-1.49910432207675
H	-0.35491799738381	14.08526474958084	-1.62915759365887
H	1.12202368300892	8.12514927862948	4.22474081901017
H	3.00803031434562	9.28675804066052	5.33419003556095
H	4.31059148558368	11.00487308220754	4.09889611720970
H	3.71546350288073	11.55159241900609	1.74771217140913
H	1.83795933940079	10.38640234191511	0.63874269542434
H	0.51387665488265	12.41882687185983	-5.34190324096870
H	2.82646288863195	13.29004954141397	-5.09168195261078
F	4.50701894880254	12.50331696280556	-3.26371404946843
H	3.46707932540622	10.66179732765269	-1.75554797944019
H	1.14035610886553	9.79074354824041	-1.98629109118279

1.6a’
Lowest frequency = 5.21 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	0.79280044638049	13.68538841702999	-1.84748923397403
C	0.49369554978319	12.79486562028291	-2.87262757899538
C	1.30401236861255	12.68545982391637	-4.00121694508458
C	2.45294353247028	13.47452225868927	-4.08948679727134
C	2.74390547653360	14.35793196563360	-3.06102527636253
C	1.93459066038034	14.48643202161520	-1.94332425815665
Pd	-1.15660353124427	11.66700569250265	-2.63184288794437
C	-2.31540026088151	12.74848738167977	-3.99405338906578
C	-1.62096076719458	13.31190938590559	-5.17901791138409
C	-0.82877072775633	14.47250855554821	-5.13580586679335
C	-0.24011774697943	14.97970319728299	-6.28950977717934
C	-0.40932515330997	14.32854674345290	-7.51243118188370
C	-1.16898088325030	13.15959194196400	-7.56798125897417
C	-1.76748136159712	12.66000973458036	-6.41440359958732
N	-0.33006211417710	10.80915132212026	-0.81761586021116
N	0.71437264446410	10.06306685546152	-0.53721200487184
N	0.93911842468016	10.23857756517477	0.77278389478211
C	0.04504488532566	11.10245305262361	1.32990072645790
C	-0.77831083331717	11.47679304941118	0.29025647810893
C	2.07313547284378	9.55256183868168	1.41676428509271
C	1.66204805824937	8.91005564848229	2.71903369646460
C	0.73107217877630	7.86420409066786	2.72738986258618
C	0.34154111613470	7.28243289497467	3.93060765598305
C	0.87996349337055	7.73833693253475	5.13656855270022
C	1.80855400052087	8.77761576232320	5.13441888566675
C	2.19575278092358	9.36295931858728	3.92781545896782
C	-1.98067891034079	12.38285780897798	0.21315616472112
C	-1.74422171448426	13.65526421026609	1.05321575089074
C	-3.21364582344005	11.61368633364453	0.75000102375278
N	-2.17739021364908	12.68595618172625	-1.22972371301147
C	-3.15126169174852	13.53821228139672	-1.63037461399290
C	-3.23611608187903	13.68886871871154	-3.16322851041303
N	-3.17164639153219	15.10108291998423	-3.50338831879762
C	-2.36252050779671	16.06729885454546	-2.88629130604677
C	-2.64880921296532	17.34157046857554	-3.60331192996162
C	-3.58916831068325	17.08662920941920	-4.60450954322519
C	-3.94954275128032	15.64329242518826	-4.54796454873911
C	-4.03106327856039	18.08846955011182	-5.45533574051183
C	-3.49755876943806	19.37022119244874	-5.27350057864171
C	-2.55576686594973	19.62588056464356	-4.27005785381747
C	-2.11524095276581	18.60767242226371	-3.41585762467073
O	-1.57534209870756	15.86070716651409	-1.97938110028087
O	-4.73610374568883	15.00983479440967	-5.22449885008904
I	-0.53287766215515	9.70794436926883	-4.29040621793918
O	-3.96535223159924	14.10249999893160	-0.89613945655124
H	-4.26181228912869	13.40511460379483	-3.42735292285363
H	-2.92388688046950	11.89777309817358	-4.31908712559394
H	0.06857301393278	11.35258644182468	2.37802367648825
H	-4.75939141774074	17.87978554789124	-6.23245571227431
H	-3.81687211653816	20.18105743295609	-5.92170764756187
H	-2.16045409400759	20.63100773202862	-4.15557978229425

H	-1.38336719956883	18.79480260344587	-2.63641674678889
H	2.41440072499132	8.82262856173679	0.67932648632068
H	2.86987768778889	10.28485959253424	1.57834148490381
H	-3.05577250457454	11.34222186735125	1.79921981585042
H	-4.09562619344623	12.25095118369919	0.66747657285112
H	-3.36645834021484	10.69987113577776	0.16871595878367
H	-1.55525656774251	13.37677956581389	2.09603647088280
H	-0.88783479025463	14.22276575293215	0.68167007840942
H	-2.62960577896354	14.28842651671814	1.00345412744122
H	-2.35797594814537	11.74976084544259	-6.46129784570635
H	-1.29935527300725	12.63681084732995	-8.51117233275187
H	0.05551758003818	14.72321451840525	-8.41156269974828
H	0.37036490478003	15.87625872883661	-6.22716282373876
H	-0.62940441805413	14.95515167804010	-4.18665563995602
H	0.31035712071094	7.51041523916802	1.78929524675366
H	-0.37975138275994	6.47062690698108	3.92917525306701
H	0.57595298037881	7.28225671290827	6.07406276997198
H	2.23090766335507	9.13492786065056	6.06893328479989
H	2.91947036570776	10.17488509412784	3.92476721177579
H	1.05120013299811	12.01924942573249	-4.81355210986130
H	3.10197372657509	13.40985876214568	-4.95651407386142
F	3.85739305699657	15.13630164556649	-3.15817978685444
H	2.17474737324231	15.20807602669461	-1.16956151293263
H	0.13816436804317	13.80155252913719	-0.99769737726723

TS1.(6-7)a’
Lowest frequency = -229.28 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	1.01346558810473	14.87010374053187	-2.43212519667234
C	0.84563114700247	13.67247061162656	-3.13134101517974
C	1.63565889428730	13.40910666766633	-4.26098592793089
C	2.62903179641011	14.29943210531187	-4.64522508662518
C	2.78832453183885	15.47577168184095	-3.91876532315263
C	1.99425793784296	15.78440694352867	-2.82817638590096
Pd	0.15586951433442	12.09316918922627	-1.95215975186326
C	-1.18245922518160	13.07619270332120	-3.48910693012381
C	-1.12004853471532	13.35515183047523	-4.95127863158053
C	-0.83613574760721	14.62331446012424	-5.48591073072303
C	-0.87850273551406	14.83524759068208	-6.85761388163257
C	-1.17859716908826	13.78051752361063	-7.72590955332758
C	-1.42919882310187	12.51145885979488	-7.20932224398674
C	-1.40162733723941	12.30193161331401	-5.83073524965116
N	0.51706825405528	11.14035427654035	-0.16842824591076
N	1.18827578482202	10.05825117373201	0.16691463895635
N	1.23273644044435	10.07346249983202	1.50337242642680
C	0.58643970346293	11.15393080636685	2.02518260112336
C	0.12552512809641	11.85511469926409	0.93344803869647
C	1.83269048368038	8.92873723444691	2.20866630812587
C	0.77373074513232	8.00866982832489	2.77281542140012
C	-0.12437190914573	7.36464231765122	1.91351707180025
C	-1.10596380866436	6.52485423268279	2.43293138137999
C	-1.19595733814797	6.31862895797254	3.81169867904170
C	-0.30188556090292	6.95597662775817	4.67024479592984
C	0.67898866502580	7.80204593315749	4.15056623903982
C	-0.65718650122093	13.13140685617508	0.77715803894623
C	0.18008990052618	14.33606751529488	1.25779451754278
C	-1.95708651093011	13.00135578724636	1.60440380191628
N	-0.93192862742207	13.24244807483884	-0.67669138259044
C	-1.82745790624955	14.13202149441876	-1.14373767305420
C	-2.16395667861922	13.91547522461624	-2.63656860892279
N	-2.67302997565139	15.12799608299359	-3.24782455542501
C	-2.17862760152992	16.44345544108327	-3.14043449037500
C	-3.13222670661187	17.28717620921623	-3.91545388964935
C	-4.13355937058277	16.46937268685005	-4.44066043843219
C	-3.86706010211901	15.07561741554065	-4.00234416415326
C	-5.15398218101026	16.98417274667607	-5.22697129164923
C	-5.14145586136349	18.36149976661880	-5.47562673946505
C	-4.13717050973486	19.18250494182354	-4.94829680769442
C	-3.11172218110023	18.65285733433965	-4.15615428761907
O	-1.16473443273395	16.79217158364862	-2.56904968808989
O	-4.50607641253003	14.06125969899753	-4.21006441303992
I	1.16158120686351	10.10856951971696	-3.40489651271865
O	-2.45179808672247	14.96864856423159	-0.48283314257234
H	-3.05948022681066	13.27694146910158	-2.60003500968952

H	-1.48804685699023	12.02542913107465	-3.39389202064976
H	0.50317550470030	11.31662477230059	3.08753597706261
H	-5.92711012863926	16.33892795780884	-5.63176848961442
H	-5.92215674304692	18.80341192889369	-6.08781620301431
H	-4.15626941961424	20.24769733875285	-5.15966107647194
H	-2.32801958961026	19.27989174094260	-3.74291527777490
H	2.45234577550571	8.43029030341532	1.45999234230404
H	2.47640058883925	9.32137616720323	2.99967656998327
H	-1.70378894247426	12.79675209143968	2.65059241059997
H	-2.53080524252026	13.92487661319462	1.54186653269288
H	-2.56222411762430	12.17373336732810	1.22315086974190
H	0.40944745118334	14.24521072020882	2.32526175430025
H	1.11889091482471	14.39100667948954	0.69954445447862
H	-0.39523676474302	15.24983391493095	1.09213841604042
H	-1.59000825352396	11.31146819677584	-5.42604752102932
H	-1.64666279129775	11.68175019209187	-7.87546237496270
H	-1.20193946927017	13.94834310468315	-8.79892764059301
H	-0.65815228309627	15.82206707797186	-7.25474439628844
H	-0.53783182610630	15.43079945490158	-4.82596858058810
H	-0.05481522212540	7.52773008170854	0.84082024576612
H	-1.80015185868196	6.02807149319189	1.76169805825527
H	-1.96170166565874	5.66196954876739	4.21396795102931
H	-0.36732952929081	6.79836509430821	5.74277039630377
H	1.37678913499021	8.30061038965453	4.81984411513863
H	1.47447050616781	12.51007356153882	-4.84177092347139
H	3.26053143203615	14.09775657057177	-5.50402281622250
F	3.74844540938082	16.35765722520317	-4.30659709713244
H	2.12362526831319	16.72204652030790	-2.29891068059271
H	0.39036005869408	15.12077223912761	-1.58889470621546

1.7a'
Lowest frequency = 8.93 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	1.10396347048961	14.69327829032236	-2.57988037625405
C	0.62770879978111	13.65819532514111	-3.43358937937097
C	1.50841405232288	13.19226818107665	-4.45664035019405
C	2.74698468156962	13.75281347646255	-4.65158032017718
C	3.16065085900953	14.79157761061192	-3.80314658831317
C	2.38687312558296	15.25579870468471	-2.77078439418609
Pd	1.09794034609718	12.70630632720827	-1.40745853543131
N	-0.71444628081603	13.34070030994458	-0.58513537589684
C	-1.60281305260554	14.18291055464730	-1.15477324344741
C	-1.88741679366625	13.95303212749731	-2.65616109075846
N	-2.46665935086296	15.15302457500962	-3.24927853287718
C	-1.95312734919584	16.45864096597588	-3.24841836827887
C	-2.96486911465355	17.28887643058707	-3.96103999422222
C	-4.03074346066390	16.47009175784791	-4.33442075885135
C	-3.74185087212608	15.09308841122671	-3.85639738746253
C	-5.11937257454651	16.96929281402523	-5.03383814811930
C	-5.10770227235830	18.33205202236465	-5.35415302682088
C	-4.03866288214887	19.15427933899792	-4.97819324524568
C	-2.94510493433327	18.64030323192064	-4.27104689499863
O	-0.88730912521180	16.81949442411793	-2.78212172782789
O	-4.42428670434345	14.08949194617413	-3.93834113289300
C	-0.83987525846734	13.23485084404061	-3.56045468649652
C	-1.29893480920714	13.31603679511747	-5.01087554722431
C	-1.00464890978502	14.43921218749618	-5.79442788573094
C	-1.47594581887371	14.53448595257497	-7.10127730963357
C	-2.24259612155025	13.50254506365768	-7.64661440903244
C	-2.53302382618033	12.37771679368286	-6.87623528839927
C	-2.06423084051880	12.28849531955028	-5.56538963998556
N	1.08645222920723	11.67538777401332	0.32360532785960
N	1.75305198747128	10.63043006241597	0.76948703088454
N	1.28738847742681	10.42647840533686	2.00708131458379
C	0.31741239126428	11.32310055727772	2.34486126586635
C	0.19021813797838	12.14062306219818	1.24528916048726
C	1.75967838542846	9.25204390729758	2.75811449823688
C	0.74174467559847	8.13401176458438	2.74051061751581
C	0.37298780557837	7.54158176075806	1.52698509410113
C	-0.57159110597888	6.51887103350781	1.50836227077021
C	-1.15214208031931	6.07741032490380	2.69986728363130
C	-0.78592750653838	6.66293232716628	3.91051458737974
C	0.15741990139610	7.69142458085155	3.92906255470089
C	-0.65697755224016	13.33280345600966	0.90928502049751

C	0.02307623679721	14.61733027547166	1.43476310055506
C	-2.04284486646625	13.13225462930870	1.55845381277626
I	3.43396978464369	11.65099010032568	-2.01343630937626
O	-2.31808970868783	15.00372018018403	-0.56176191789990
H	-2.74467699215543	13.26698837246494	-2.64715395632673
H	-0.89641097540860	12.17941481811504	-3.26818650924488
H	-0.18755880842747	11.29404468516489	3.29647669581332
H	-5.94289016479010	16.32327069073828	-5.32088049556278
H	-5.94047485375160	18.76135245420172	-5.90352763507698
H	-4.06041338432905	20.20784660286053	-5.24133305560112
H	-2.11099081171123	19.26843560752262	-3.97456688032338
H	2.69392261521134	8.96304852195415	2.27177956867081
H	1.97520508101015	9.57243077755798	3.78044869374593
H	-1.91736461142017	12.96392243136385	2.63440244502586
H	-2.66281102585111	14.01273871080058	1.40390348238857
H	-2.53869758459369	12.25937016280531	1.12345762180699
H	0.11467406957464	14.58767668824164	2.52613015377695
H	1.02360570955973	14.71106073005183	1.00044914369097
H	-0.58239905671118	15.47793180417494	1.14393738425299
H	-2.30228182316790	11.41539525984662	-4.96255621081902
H	-3.12702785814579	11.56936399476908	-7.29281725366504
H	-2.60756478936875	13.57483682049232	-8.66712158594894
H	-1.24291833808496	15.41386397731766	-7.69516356381491
H	-0.39882950452876	15.24042546089671	-5.37914570193018
H	0.82367505185206	7.88818741603345	0.60031263789271
H	-0.85378151754432	6.06303211507617	0.56394754394974
H	-1.88780066127865	5.27870096818880	2.68261114038206
H	-1.23401241944363	6.32308958990054	4.83959244877246
H	0.44323805989570	8.14944449493358	4.87348133033386
H	1.17099509314908	12.39566059497959	-5.11113413690819
H	3.41600869066497	13.39865937923908	-5.42756000036125
F	4.37811367109079	15.34044622199339	-4.02138235313042
H	2.73354454264908	16.06473193293682	-2.13847850244314
H	0.41946342075743	15.22291573180214	-1.93383052378684

1.7b
Lowest frequency = 13.38 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	11.00727241699948	3.08024403710155	0.99603394802723
C	11.28544469218061	2.81107527942628	2.34162504598806
C	11.23091639964735	1.49531551681473	2.80717377965642
C	10.91135690186945	0.45232261741431	1.93665669246604
C	10.63803754483124	0.72401044593292	0.59705955954071
C	10.68443310757508	2.03914958662583	0.12891633581337
C	11.65258167250159	3.93500872914076	3.28906611607504
N	10.68172929768274	5.03515623754177	3.21941554848197
C	9.38547468711296	5.05516997701628	3.64207012859287
C	8.86655614667831	6.23063014129557	3.14729276306005
N	9.87932999372627	6.83941945501854	2.45774019801833
N	10.97577893089852	6.11994463890003	2.48336474546930
Pd	9.01295999792729	8.22005106616142	1.00792784334273
O	9.69591469612095	10.04850340772163	2.16865633253586
C	10.67463591725084	10.09712635895223	1.36656935185266
C	11.75817768496972	11.13141504199815	1.49295857196017
C	7.49319104682060	6.85842493140892	3.18428232614060
C	7.41105074951785	7.90748748786335	4.31516887793159
C	9.00337820868903	6.73031006550907	-0.33234901995175
C	8.09538008209737	5.67360743729036	-0.35697351365037
C	8.24540931479513	4.64882137829272	-1.29662765748171
C	9.31193319796414	4.70928621551877	-2.17943005362008
C	10.22806680874909	5.75154115502779	-2.17137669630149
C	10.06527184850504	6.77547665639370	-1.23574728470400
O	10.75225894807569	9.23296867602019	0.40974268823158
C	7.69944791229714	9.37179582008785	-0.12590389023088
C	6.37882328203703	8.62032975594950	-0.00661096999819
N	5.24347124686644	9.43523408203518	-0.39711991127073
C	4.33829050412302	9.04136064144193	-1.39823700272244
C	3.28226969234554	10.09209912210087	-1.41500755093475
C	3.58681191370490	11.03600120387901	-0.43075406821672
C	4.85210680179269	10.62443167430877	0.24404799133255
C	2.77535879446841	12.13844318842010	-0.21020878723468
C	1.63451419296182	12.27082739927848	-1.01106266026867
C	1.32980638221944	11.32535785040736	-1.99713388455240
C	2.15571193139474	10.21591734521578	-2.21426238476135

O	4.44650144294594	8.04068571462667	-2.08405455896409
O	5.46256537587140	11.17829345258741	1.13894105261646
N	7.34273465977024	7.53490799660280	1.87026424531734
C	6.17462682664887	8.02649043755446	1.40517651082438
O	5.07026187640815	7.96452443036569	1.95012489589189
C	8.18954908834301	9.67772372253638	-1.48687131486157
C	7.92735402881619	8.85373471348432	-2.59446004542811
C	8.42051334748013	9.17904399443135	-3.85431716375384
C	9.18720046430393	10.33134279445363	-4.03681876321834
C	9.44888611993478	11.16473670916649	-2.94754602614787
C	8.95307373439654	10.84027888140755	-1.68915808306407
C	6.43843101601739	5.75301925782865	3.38053603991284
H	6.36265517111461	7.77012114530195	-0.69755905437705
H	8.95694745670666	4.24752976374129	4.21276321435816
H	1.92819845281696	9.47698998272083	-2.97611192922433
H	0.43719195504645	11.45646974693381	-2.60190347706588
H	0.97302295573378	13.12011818800053	-0.86652477047273
H	3.02029171035609	12.86577107795657	0.55737736271764
H	12.61347231349859	4.38713242090575	3.03034827246288
H	11.69743567815111	3.57849094074196	4.32127281822834
H	6.61863899654035	5.24238476565806	4.33352259946593
H	5.44267719029530	6.19415989665988	3.39043030385690
H	6.49560290645339	5.01789263253059	2.57218055458192
H	7.55978113403579	7.43283152760348	5.29123486608374
H	8.17531547689770	8.67548190576943	4.16910701892985
H	6.42390145449287	8.37538712758047	4.28761234478436
H	11.03260048180442	4.10302590290406	0.62886280513829
H	10.46792899363822	2.25453664453150	-0.91256454047820
H	10.38505068179996	-0.08521371310190	-0.08175029529479
H	10.87136343051286	-0.56788674671837	2.30720566402682
H	11.43992939293393	1.28432758687085	3.85375667691058
H	9.14723025532398	11.49340030038815	-0.84231087386332
H	10.03554047942530	12.06943349450727	-3.08166687182200
H	9.57199434706924	10.58142175154851	-5.02152515549590
H	8.20530305286600	8.52855087194805	-4.69731509092984
H	7.33434111700172	7.95297307119480	-2.47531924246855
H	7.69914384286355	10.25613376557453	0.51529728955989
H	10.76480199230735	7.60471591772386	-1.22106823933406
H	11.04587688801319	5.76460234400781	-2.88469193644876
F	9.47512315680901	3.69799675333112	-3.08296253352126
H	7.54977945189465	3.81690113298158	-1.33720923336772
H	7.27072328063804	5.63460814723493	0.34328281906946
H	11.49674909809316	11.86214610227137	2.25922728445866
H	12.69790277165116	10.63699690778799	1.76037297009487
H	11.90807150488052	11.62673491435220	0.52907508169418

TS1.(7-8)b
Lowest frequency = -289.72 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	11.99077930913404	2.92015115669179	2.83217012393416
C	11.74434953084580	3.33964002223037	4.14492863433264
C	11.68083568705015	2.39311606943404	5.16955873544137
C	11.86680817667821	1.03815621539091	4.89030021565063
C	12.10994421964721	0.62474302594328	3.58171448079207
C	12.17065651204826	1.56809029483494	2.55303299245402
C	11.54198993439820	4.80781089385937	4.44730180565921
N	10.41736271549436	5.36457006826340	3.67974014497025
C	9.09014840851042	5.07368540162203	3.78709179003776
C	8.48684443405490	5.77321127897340	2.76518217425451
N	9.49442867231893	6.42954992230731	2.11372278881914
N	10.66967624198788	6.18639169514394	2.65239824891262
Pd	8.90733943875998	7.36082112327170	0.39956353687293
N	7.10962816220350	6.75651116441770	1.07610792508716
C	7.06040902184548	5.93498495031935	2.31751617685830
C	6.28632852372884	6.67023997270449	3.43763533512757
C	8.48904618707993	7.07022728429634	-1.63633301875794
C	7.67534669329023	5.96078109238875	-1.90313844807012
C	7.85739645262728	5.21435254098368	-3.06872961346117
C	8.85826985614573	5.59395070518206	-3.94970845219388
C	9.68058109222396	6.68967901620427	-3.71210063649808
C	9.48095832862807	7.43490378079180	-2.55671845764541
O	10.79047827968126	7.97105801991310	-0.09081699167695
C	11.07931759190147	9.10938423023633	0.49512379278780
C	12.49943597158825	9.57961728960614	0.22272999759309

C	7.57466659732608	8.69750932953768	-0.82224544707359
C	6.15450727709826	8.16243719926571	-0.67181267140906
N	5.21688151655704	9.26752671535099	-0.54842494372721
C	4.19550838366485	9.51976945957101	-1.48230051979706
C	3.44652440672007	10.68758092736910	-0.93891274052357
C	4.02585234629555	11.05656769124628	0.27860178500823
C	5.16562317626081	10.13709977343907	0.55443917961975
C	3.53852937935084	12.12354889546674	1.01803422507508
C	2.44036605608894	12.82000738972014	0.49906244093555
C	1.86004728611170	12.45015757016054	-0.71977274221754
C	2.35868621123726	11.37154795998368	-1.46019331666416
O	4.01064134600335	8.88955471564203	-2.50688945109844
O	5.92647146524722	10.10405963544672	1.50371213128524
C	7.83642685438101	9.66214930912925	-1.92497437408455
C	7.22242840901708	9.54442097658759	-3.18079693510431
C	7.47052542672076	10.48665027442119	-4.17264019891365
C	8.34764515551353	11.54840841726374	-3.93235293089164
C	8.96277171056131	11.67025654863958	-2.68656679544395
C	8.70346728631787	10.73640248858811	-1.68391132196151
C	5.96425586639941	7.21042426718964	0.53587550562158
O	4.81456485199236	6.92434152828212	0.89937611542775
C	6.44070889189994	4.55264414571401	2.02489974695693
O	10.28634875809000	9.77095506452313	1.17337037763190
H	5.83119105914908	7.63085261242126	-1.57160487431305
H	8.70745789056098	4.41082377144499	4.54601462355238
H	1.91584741336085	11.07695814632294	-2.40635176883893
H	1.00913442943301	13.01092639629984	-1.09541285309483
H	2.03037502572975	13.66199020403466	1.04914969094050
H	3.99628965736152	12.40306839311662	1.96165231675699
H	12.40581931362005	5.41030708270478	4.15723082954070
H	11.34152053504190	4.96596240437015	5.51012411469333
H	6.43718674130022	3.93480604928855	2.93001698805947
H	5.41362800774222	4.69332136710281	1.68377365911299
H	7.01693480713088	4.03757986495012	1.25054856317143
H	6.35013396907949	6.09448321550447	4.36776852747501
H	6.72038876450257	7.66050071557094	3.59930465512307
H	5.24201039129747	6.78047196474756	3.14668348422633
H	12.03468760268301	3.65386513075366	2.03100965417313
H	12.36006509231052	1.24905260368873	1.53241631243003
H	12.25093125416010	-0.42930408215116	3.36146712492515
H	11.81737775389037	0.30886201054810	5.69349893479943
H	11.48777920633633	2.71599351190398	6.19019452179053
H	9.17093407818094	10.82707657848496	-0.70643675299915
H	9.63933495082186	12.49729862769675	-2.48988750833096
H	8.54518423547379	12.27793287111493	-4.71285066345012
H	6.98256169860322	10.39085525421241	-5.13839004365558
H	6.54816499909485	8.71750790713314	-3.38088551611048
H	7.86676601923425	9.19456300805834	0.11941327866315
H	10.10305670448627	8.29951073961674	-2.36627478284666
H	10.45143776650682	6.95647814951534	-4.42738063038722
F	9.04256747055168	4.87064835685820	-5.08581492448670
H	7.23929550823076	4.34889427627483	-3.28299239398977
H	6.91322950112901	5.64959214967026	-1.19947505622872
H	12.81161344363216	10.27610093390148	1.00278117524578
H	13.18928817820325	8.73501043998834	0.15846269235545
H	12.51545243043315	10.10367484730269	-0.74031477823614

1.8b
Lowest frequency = 8.98 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	11.71151483754446	2.38908665522391	3.22285786190769
C	11.68861848284889	3.18381914778079	4.37511763716206
C	11.60457174762813	2.57546318643251	5.62917472043992
C	11.54900965336454	1.18484727312135	5.73619437709250
C	11.57019121536750	0.39750722269740	4.58637763930055
C	11.65036674880588	1.00221943990604	3.32956810019555
C	11.75491179868568	4.69061807229711	4.26069277246665
N	10.65258581072292	5.22356954929818	3.44632098086705
C	9.32298098747236	5.27597812927830	3.74197604945266
C	8.72490331916729	5.77800453774158	2.60590491137025
N	9.73259822190618	5.98096973232391	1.71393290838307
N	10.90900343825915	5.65065388409419	2.20340831065688
Pd	9.17874883234305	6.75526186901313	-0.05105983141837
N	7.37837031738890	6.86227288668662	0.93200169108367

C	7.30940150043851	6.07968437156066	2.21351173600799
C	6.67388522384134	6.91057338256679	3.35222665477525
C	8.17164995928434	6.64506552606918	-2.09642824536232
C	8.50850556958837	7.99639359706546	-1.77750281617432
C	9.66337324012394	8.55651430128935	-2.40658481624129
C	10.41501463420297	7.83080794462949	-3.29621267414264
C	10.03903087270383	6.50723008609728	-3.58339088225419
C	8.94605122443859	5.90217203009556	-3.01689533503994
C	7.53118036997789	8.97266939854232	-1.12657531726719
C	6.20261369095829	8.28462046569537	-0.74594986076378
N	5.16258500018075	9.28002919862878	-0.53945442713071
C	4.03658067108187	9.38674373201448	-1.37116680461818
C	3.24749689828651	10.52503459644187	-0.82159067331027
C	3.91876534592311	11.02387781309010	0.29799572760614
C	5.16019134093505	10.22242269915349	0.49657330329843
C	3.42661205452360	12.10355207514182	1.01487734743817
C	2.22716639418399	12.67751503104362	0.57566883575615
C	1.55497854946790	12.17753911352252	-0.54541608836967
C	2.05997339217524	11.08701488263385	-1.26418421118984
O	3.80941942377603	8.68046029677995	-2.33656602160668
O	6.02816067281977	10.33724313521484	1.34414300333729
O	11.04146876040186	6.45097135308403	-0.78265407446057
C	11.86104071947972	7.41772357894331	-0.43426265213871
C	13.30505982194365	7.13190075573108	-0.81399169405195
C	7.26830031317437	10.13936161221025	-2.06930392767055
C	6.79816453277025	9.91809228221081	-3.36912983693525
C	6.53119060419949	10.99063592359235	-4.21594736872609
C	6.73596095384347	12.29984268477888	-3.77518074238055
C	7.20922266418444	12.52778770791583	-2.48353100853585
C	7.47397782108405	11.45146153788454	-1.63537422153789
C	6.20007033366766	7.34528673244017	0.48730842689414
O	5.09085705157419	7.11651448724521	0.99799847913079
C	6.56527780487912	4.73982360060106	2.00676946124337
O	11.51930145942010	8.45020793365321	0.14684740471436
H	5.83217401969455	7.71012847583060	-1.60376037386071
H	8.93397076250496	4.95856465570478	4.69558440468817
H	1.54779562735396	10.69340608787170	-2.13648651060878
H	0.62731640007100	12.64555233524187	-0.86182666689191
H	1.81019951866004	13.52552325976723	1.11118420688822
H	3.95683837149855	12.48550860107567	1.88162955023180
H	12.66447564632807	5.02339327815520	3.75532371895965
H	11.70683299674730	5.16140290098360	5.24591858033586
H	6.57092292311537	4.15618887465502	2.93429790238589
H	5.53575910816507	4.94673347341682	1.71311465472314
H	7.06143189791426	4.15668164661059	1.22451708846969
H	6.78175999199954	6.37049092287095	4.30010732554038
H	7.18157108619622	7.87548815524535	3.43359050412111
H	5.61787369837727	7.07677565446683	3.14983911278886
H	11.77143053171230	2.86007483322423	2.24474667234424
H	11.66753990112036	0.39123504468316	2.43190722963431
H	11.52354852027080	-0.68450571502642	4.66697941515647
H	11.48560843837805	0.72007134986868	6.71568750895292
H	11.58536569206946	3.19053109698949	6.52613875678667
H	7.83365025365569	11.62571331955022	-0.62470035445672
H	7.37294209131314	13.54325137636123	-2.13358407290536
H	6.52861074030906	13.13626617943645	-4.43660453568201
H	6.15975095349517	10.80513774280989	-5.21978824721259
H	6.63058523732337	8.90216683261135	-3.71722210837921
H	7.98146192975909	9.37368449089615	-0.21296991177572
H	9.92755221427651	9.58351804297457	-2.18151592013670
H	11.29373587225671	8.24999896313521	-3.77442074025655
F	10.79521296503067	5.81516961134295	-4.46881547666955
H	8.68353832777802	4.88223010216596	-3.27276325796751
H	7.22417370168276	6.22522909096988	-1.77872792214581
H	13.87645667582659	8.06165424795211	-0.82004557722081
H	13.73576031038056	6.45418809083402	-0.06831831638840
H	13.36261531369631	6.63661052386210	-1.78696444870282

1.9b

Lowest frequency = 11.72 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	11.88333263684220	2.44230748182532	1.20106811156004
C	12.22992172879394	3.39971042281923	2.16146040299733
C	12.56321760273846	2.98416189570337	3.45489493332467

C	12.55018353253362	1.63005614963372	3.78519127587957
C	12.19953450101257	0.68089276933938	2.82410287570896
C	11.86585932704613	1.08821925910069	1.53184835194372
C	12.21298640504080	4.86520627723238	1.81526614329313
N	10.87258988708721	5.45387769338115	2.03486150988896
C	9.68458461078741	4.81726172800680	2.24403654499193
C	8.74632078289178	5.82141292937599	2.28805413923938
N	9.43311417073257	6.98769213963167	2.10102667321654
N	10.72336556515239	6.78520073227601	1.94199291231457
Pd	8.25961467879041	8.59004212717032	2.11719593056568
O	7.12137581716728	10.28156789784957	2.50240020391819
C	8.18582186836793	10.92198902529858	2.83559949043431
C	8.12853389405056	12.36646342651090	3.22326869441767
C	7.24424159970509	5.91639481285038	2.40796510330895
C	6.82655534760381	6.15660253063449	3.87292693099971
C	7.95459727643940	6.54335868586252	-1.40198201252629
C	7.08132605938141	5.49481268904832	-1.71178920368895
C	7.54908681057705	4.18615462212301	-1.84252474013969
C	8.90417027871094	3.94704129308623	-1.67196250582209
C	9.80473266585999	4.96140820817314	-1.38155892935988
C	9.31515679351787	6.25744378633337	-1.24255124000570
O	9.29148598969702	10.28095335782290	2.81069741617262
C	7.51461953364113	7.99316171222791	-1.28581374498521
C	6.16552145469416	8.16093004508067	-0.55043985225101
N	5.87586026455109	9.57972964117265	-0.28655731948191
C	4.52045280642294	10.00268909329698	-0.25853971403603
C	4.55063196305355	11.47854680854890	-0.08718389624375
C	5.88340371555605	11.88203702905579	-0.07789451541169
C	6.75251151167546	10.67993140838289	-0.20962861440800
C	6.23567133255236	13.21863450476145	0.03156158310325
C	5.19779570490245	14.15075874332565	0.14722114641836
C	3.85781458614504	13.74390318237005	0.14720769154556
C	3.51322178718849	12.39267097957111	0.02455437098564
O	3.56430061752223	9.26585569706053	-0.38910798054645
O	7.97189818561160	10.66600295497753	-0.24870318252013
N	6.96334426820693	7.14436463607831	1.59784854471951
C	6.00663825810641	7.17345883579299	0.64732221120385
O	5.06703066265404	6.36899152935024	0.57298271813948
C	7.47945010231969	8.64725667115140	-2.66391927497118
C	6.45649216474508	8.37333482507495	-3.57886080295212
C	6.46312238692514	8.94873056419938	-4.84837707254428
C	7.49839934580966	9.80527775219756	-5.22476141114839
C	8.52329322637043	10.08306336166902	-4.32046893829517
C	8.51093291106651	9.50904383136110	-3.04964334029824
C	6.63784716852339	4.59775164212729	1.89844839488633
H	5.34296202080377	7.84302507551170	-1.19668548461472
H	9.61638007193109	3.74596972561349	2.32511935890664
H	2.47798179098405	12.06665535267827	0.01440237623893
H	3.07531539785124	14.49158825407984	0.23837296514292
H	5.43215314331739	15.20779911472842	0.23498158535331
H	7.27751851031639	13.52313340571234	0.02109206354337
H	12.46834507452460	5.02667541393948	0.76426500700661
H	12.90973523255356	5.43584700376063	2.43292259214113
H	7.08721713441814	3.77986497949139	2.47718690453623
H	5.55930828187569	4.58442086121704	2.03632484101439
H	6.85790617910331	4.44445654066105	0.84112091161808
H	7.11433852073179	5.30739409762013	4.50278958361487
H	7.30081846609861	7.06496808715636	4.25823339483200
H	5.74128381485936	6.28186528035392	3.91277820238202
H	11.61634283092237	2.75446627954240	0.19505319031658
H	11.59350887335876	0.35389334662675	0.77986162638614
H	12.18958624269691	-0.37425526395745	3.08102788990448
H	12.81545910761903	1.31609695869212	4.79035994499743
H	12.83453764217577	3.72435637250592	4.20371965763428
H	9.29619225480093	9.74423715427201	-2.33753857164264
H	9.33163825281945	10.75284093284731	-4.60134412650114
H	7.50408943835007	10.25389777339718	-6.21419551062259
H	5.65882711015947	8.72637254522169	-5.54426803814976
H	5.64598456120971	7.70284768184654	-3.30556462928757
H	8.27906430157641	8.50399698756976	-0.69740223179909
H	10.00161377786060	7.06437175225457	-1.00239424057938
H	10.86153621465663	4.73792109172310	-1.27828870596820
F	9.37354439736001	2.66871115347817	-1.78554322919285
H	6.87641447416121	3.36425192179574	-2.06384844107982
H	6.01794489135657	5.68174326560218	-1.81614952610734
H	7.09274400941222	12.70455625998773	3.27641537537156
H	8.62775950574380	12.51141594848519	4.18563196286771

H	8.66942268561924	12.95347025566078	2.47405428819473

1.7c
Lowest frequency = 5.09 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	10.91752407296497	1.88127308285959	3.14811591706504
C	11.47607701470094	2.91033387903005	3.91608378381951
C	11.63961419412394	2.72761368628837	5.29129308979093
C	11.25437002451074	1.52996192347427	5.89590698110269
C	10.69769750864590	0.51005402505063	5.12630606482956
C	10.52936520739970	0.68791468754946	3.75079211219128
C	11.88487430289847	4.21029342064629	3.26813717517924
N	10.72221042368681	4.93343598417000	2.72457604058326
C	9.50309747379430	5.12958209992158	3.29806722730369
C	8.80978302669817	5.91348434061836	2.40012476474119
N	9.65331904186479	6.13138561637050	1.34765353364446
N	10.81597971605955	5.54907751389438	1.53498988943658
Pd	8.89041883016417	7.75617958811602	0.11086729265337
O	8.65489935686589	6.51304193416597	-1.77235390364522
C	9.77035228028337	6.99603019559497	-2.13188218573354
C	10.38240113292999	6.67445249970650	-3.46410929181893
C	7.40818676698822	6.47116434795101	2.41766896968753
C	7.13684105592974	7.17898056196354	3.76072225930483
C	9.67645709143881	9.02637538632156	1.44525273773084
C	11.06990735500957	9.00787888907082	1.48841374785348
C	11.74756148080286	9.83894456709116	2.38452415390210
C	11.00225013000216	10.66755364008291	3.21254385985716
C	9.61651075506422	10.70698157936521	3.17459448725551
C	8.94465491900728	9.87170382769156	2.27615261206810
O	10.38590221098133	7.81880429690917	-1.34776605549952
C	7.71756776130709	9.30312242810421	-0.64820407946003
C	6.30750290795122	8.76018023052581	-0.41663325676786
N	5.30489296737580	9.80910511633085	-0.52262855880159
C	4.27428119167421	9.80139698297367	-1.48094946408385
C	3.43298693062351	10.99129415715094	-1.16803147017815
C	3.97087241329281	11.62623794993062	-0.04552491864345
C	5.17590361925253	10.86599672672585	0.39159600306853
C	3.39405932961901	12.76987786422137	0.48536904322882
C	2.24788216527658	13.26724547701262	-0.14668226118736
C	1.70940219616568	12.63156529685613	-1.27137141070911
C	2.29876392132410	11.47700398926613	-1.80084065093677
O	4.14419332732078	8.97295924128068	-2.36294113111994
O	5.92709144195825	11.08745681277185	1.32560827429836
N	7.31451975181482	7.42068734104312	1.28420285174897
C	6.15868287456210	8.01501206898787	0.92933873526329
O	5.07537751191271	7.93419354146197	1.51683939305678
C	8.09953069704153	9.69406010536904	-2.02447613894461
C	7.49464341591884	9.16341658929029	-3.17483719864426
C	7.90263123772895	9.57387378464785	-4.44283497431646
C	8.92542536651533	10.51205100055995	-4.58770484874236
C	9.53772304711914	11.04553776471756	-3.45058748424594
C	9.12614994521295	10.64199007049188	-2.18614762268797
C	6.41594185334764	5.30206727495893	2.20541838895192
H	6.04351179101351	8.03143654126328	-1.19085163801361
H	9.24482865460898	4.69916186155832	4.25185270103863
H	1.88809279367374	10.97607992098162	-2.67177131272118
H	0.81911558644593	13.04211448664635	-1.73878475974145
H	1.76650972971439	14.16061668936463	0.24043065022102
H	3.81882100645787	13.25497832882857	1.35854241113105
H	12.54961635380438	4.05939938080360	2.41444732852040
H	12.38732475619063	4.86166911836383	3.98985968161115
H	6.52870512398486	4.56924395226664	3.01175376791887
H	5.39624526475005	5.68976081002661	2.20499052582110
H	6.61859410872867	4.81103706757946	1.24947667235415
H	7.19725418971595	6.45940966971200	4.58531684469317
H	7.87058534799481	7.97097146354984	3.92726494080459
H	6.13443125910345	7.61001887905286	3.73601952202627
H	10.78272102016314	2.02015608176186	2.07821952157303
H	10.09759541779470	-0.10579518232828	3.14838092737991
H	10.39541265272170	-0.42196555343198	5.59460433344018
H	11.38747294064657	1.39691861007728	6.96545662733269
H	12.07173373704357	3.52528266923858	5.89113019631171
H	9.60784399864986	11.04752809636941	-1.29998425532481
H	10.33445432518365	11.77719053354150	-3.55222793334059

H	9.24077893571601	10.82883522335829	-5.57800234942248
H	7.41491046006178	9.15978575453981	-5.32100676498028
H	6.69473188377959	8.43653410403278	-3.08567517335945
H	7.92217506894513	10.11535621124387	0.04709426286407
H	7.86261934301300	9.91435896679956	2.22759229705580
H	9.07083088339375	11.38107605603767	3.82699769351487
F	11.66021889553961	11.47807446925590	4.08993450801601
H	12.83168543121642	9.84888538369805	2.43734351937605
H	11.63386500424012	8.35872543821087	0.82583718634146
H	9.98172672823816	5.73497812417265	-3.84840026890861
H	10.12327176773350	7.48197778166340	-4.15794553995593
H	11.47096329260107	6.62912467317809	-3.38321660702789

TS1.(7-8)c
Lowest frequency = -305.51 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	11.52018184956338	2.80800936401986	4.72914562223015
C	11.32327631480873	3.53110504101278	3.55071528671456
C	11.56234847717365	4.91097362562273	3.53952221417702
C	11.99370209410164	5.55536594134836	4.69650261063985
C	12.19548781510443	4.82664833281906	5.87108273421012
C	11.96047068608609	3.45274078538823	5.88619158076670
C	10.84896897963679	2.82535611568762	2.29560245340253
N	9.72631454274383	3.54669592778513	1.68241313763683
C	8.46583246880930	3.72081153088671	2.17376576245420
C	7.90202232689768	4.69067287651900	1.37776491692031
N	8.85893600610287	5.04168427065953	0.46063033349051
N	9.96945865196687	4.36611081116626	0.64507709256142
Pd	8.58478568985859	7.04531773345734	-0.18077814746032
O	8.80096741610069	6.16318755107253	-2.57284835970123
C	9.95083248729656	6.61489045639478	-2.40599193285429
C	11.02532184116136	6.53302456333038	-3.46325616610893
C	6.57888460251042	5.40574134320425	1.38343304223698
C	6.08824482014432	5.58684516084971	2.83296660378223
C	9.08613489276600	8.57245294966389	1.15568076030086
C	10.41361144797683	8.98062937381674	0.95478215531855
C	11.24936935439217	9.21682945153348	2.04433627941799
C	10.73123766481572	9.07436887339934	3.32350337555356
C	9.40504776947380	8.72774554593540	3.55579524526404
C	8.57722806929501	8.48651883340339	2.46630767908851
O	10.29433472781111	7.21515575134836	-1.29798758299128
C	7.84763572438983	9.30550806826851	-0.11545272366013
C	6.39666253911685	8.79909055542044	-0.33840144938784
N	5.48946317364081	9.92871591408213	-0.22759535238326
C	4.63650049997343	10.34263435871333	-1.26991700363078
C	3.80976346415153	11.43881414379272	-0.68860335368586
C	4.17659427508226	11.60546389824141	0.64975346204374
C	5.25603136688094	10.62860916073686	0.96593215183939
C	3.57145654765817	12.55999302337177	1.45329166871366
C	2.57410750162486	13.35315117034106	0.87329697356342
C	2.20746847929576	13.18719846208454	-0.46727580923686
C	2.82488344386102	12.22170617831953	-1.27180557194340
O	4.62307853891060	9.87065209528701	-2.39007440948471
O	5.86283730843697	10.45797499229036	2.01016680271032
N	6.84856706468127	6.71625275611502	0.73571648170717
C	5.89495859820109	7.64200512014363	0.56003141932604
O	4.72557366646518	7.59660434617106	0.95942079643393
C	8.50206138019789	9.92857494950368	-1.30854443465435
C	8.38891774824238	9.39779018299949	-2.59936879054950
C	8.99322443690640	10.03262100377045	-3.68036762616945
C	9.72687849693298	11.20554625203727	-3.49019066176091
C	9.84446765300805	11.74539133183969	-2.20946569643816
C	9.23162601551394	11.11255814987979	-1.12993697938665
C	5.54973937377428	4.61301894644317	0.54619841880073
H	6.28258844386095	8.44442350981422	-1.36788150288823
H	8.10620553499491	3.17988280534095	3.03399285640846
H	2.54729084936565	12.08542503030123	-2.31220073392150
H	1.43027477572893	13.81861554834500	-0.88783994466753
H	2.07493676152496	14.11005111058843	1.47129939178728
H	3.86291448940728	12.68066638528610	2.49188566515273
H	10.52852291349962	1.80396635690909	2.51631272113137
H	11.62379092638455	2.79361937085623	1.52531859396570
H	5.38300408207756	3.62598502278576	0.99084073003859
H	4.60732897461138	5.16373426656174	0.52326564199816

H	5.92090323136363	4.48510920139276	-0.47429092714222
H	5.89743149667561	4.60873111045664	3.28916216336564
H	6.84105338615900	6.11010791572838	3.42886958997235
H	5.16300365175955	6.16436550358024	2.82769219579303
H	11.32775185382905	1.73738814292134	4.74392035850682
H	12.11092846968655	2.88227229887159	6.79815725393062
H	12.53030211098565	5.33156777121286	6.77247197410633
H	12.16927036536637	6.62655884062152	4.68277642209806
H	11.40135325347132	5.48257098875129	2.62903754309192
H	9.31775968446369	11.53478868847689	-0.13123867420444
H	10.40621490254468	12.66176504167765	-2.05124621874687
H	10.19949930962901	11.69749491395019	-4.33561983690066
H	8.89015447516920	9.60829056895845	-4.67490915989146
H	7.84426180195247	8.47272425105196	-2.76281712110163
H	7.75085706315694	10.07004127086546	0.65165996562666
H	7.53502198481223	8.24950680763371	2.62961158558057
H	9.03191886469924	8.65398233747999	4.57204313339495
F	11.55079161044227	9.28493524340445	4.39350631389610
H	12.28774802712875	9.49976262283332	1.90501899745992
H	10.80209738881601	9.06887746775396	-0.05259945003449
H	10.69961980012271	5.88534893476134	-4.27848680759204
H	11.21722068311569	7.53983214964690	-3.85067006441514
H	11.95740953965015	6.16061025100258	-3.02887566561652

1.8c
Lowest frequency = 8.32 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	6.98561919525339	3.61222448770570	1.50133199339536
C	7.75067788112687	2.84370356522538	2.38768788165489
C	7.15675609045882	1.78095594479613	3.07255234566959
C	5.80970125325585	1.47702357508693	2.87055979771686
C	5.04830438714721	2.24635638341959	1.99213069885956
C	5.63843517967734	3.31410662586220	1.31214533509478
C	9.21344775682002	3.16188677221847	2.60979492493088
N	9.40938251124942	4.59766896769113	2.85661120645565
C	8.77500640357087	5.39103937572594	3.77236240788262
C	9.19415504357880	6.66703768798200	3.48780256089606
N	10.05188888891104	6.55310720722450	2.42362282544262
N	10.18297277301394	5.31097385294793	2.02585931419494
Pd	10.53191050323343	8.34060157751471	1.58777015428445
N	8.82952979487889	8.81199829876340	2.62301241011813
C	8.87638885130742	8.07632409792753	3.92887465951845
C	10.05401863682556	8.64901925767954	4.74411933694971
C	10.68044892037273	10.32409177492496	0.55616238764633
C	9.46333972834685	10.99614319603602	0.85342935733419
C	9.39270340917231	11.79717362796263	1.98087284712411
C	10.48433928739462	11.93205059464486	2.85397893052624
C	11.62917969699529	11.21077671627371	2.59765162070013
C	11.76741889251216	10.39974625837210	1.46240907202205
C	8.21764900256186	10.67863372588320	0.06065868123991
C	7.84383338308284	9.20760641890604	0.40135910348773
N	6.63715416367859	8.77069242198766	-0.28522212441106
C	6.45000246038430	7.40112649212929	-0.54642283753740
C	5.08622991315992	7.27631451534502	-1.12610218920874
C	4.49078693816041	8.53767685887878	-1.10018019799477
C	5.46141988100106	9.51265209235660	-0.52034163701634
C	3.19939590035304	8.73849976450313	-1.56289760746838
C	2.51294775875354	7.62513146679912	-2.06260788319190
C	3.11267205826011	6.36056629001744	-2.09504236208874
C	4.41668585335263	6.16801702418872	-1.62364144904783
O	7.26767679905405	6.53045429652641	-0.30412653912669
O	5.29203690516233	10.69766140955472	-0.30661585051269
O	12.18482777707019	7.66096297309216	0.60380082813518
C	11.88759450989341	7.29855995682269	-0.62056973672911
C	13.02357961099962	6.59471805499665	-1.34214612755477
C	8.37295414674990	10.90489088004237	-1.43458503079955
C	8.96280165116777	9.95797433469160	-2.27979805756379
C	9.11785282064696	10.23031475741384	-3.63978056740131
C	8.68134677012827	11.44302356268293	-4.17204453144969
C	8.08217749391125	12.38627706622581	-3.33573856534026
C	7.92889250178564	12.11556904079478	-1.97759894386806
C	7.66684941181753	8.93334457619512	1.92612069044191
O	6.52180699941687	8.84666323289942	2.38116929649587
C	7.61270973741820	8.12455149198666	4.80224573682100

O	10.78649364227929	7.47898242894435	-1.15556016799922
H	8.64568348230267	8.55106737357791	0.03464877211446
H	8.07662868806671	4.99235746577713	4.48973641940254
H	4.89320387245043	5.19292291582683	-1.65256544552899
H	2.55566704559082	5.51781768035853	-2.49416521322123
H	1.49890490106482	7.74187359017987	-2.43378009129009
H	2.74488187225080	9.72377197987630	-1.53522834123479
H	9.82394394922553	2.94370801681192	1.72979105328885
H	9.61041878847263	2.59978540276742	3.46042220373422
H	7.84725095955080	7.64648132595885	5.76210551364959
H	7.33312320430700	9.16257575465026	4.99173740298503
H	6.76648027836856	7.62732895114260	4.33334579711739
H	10.18759480406034	8.07676811543050	5.66771948805229
H	10.98356746931972	8.61271326364798	4.16727243312262
H	9.84088776908441	9.69131515916524	4.99556890400209
H	7.42756044454444	4.45013982279619	0.96818392676201
H	5.04765614926980	3.92419774086463	0.63587683322329
H	3.99663344617471	2.01972963570535	1.84226500152715
H	5.35608473465419	0.64853602508233	3.40678847405965
H	7.74847950958315	1.18968048797142	3.76809614664559
H	7.44756002297552	12.84301613917922	-1.32885517191743
H	7.72833130731399	13.33002759446384	-3.74175594964896
H	8.80058127502269	11.65027193367786	-5.23195362445951
H	9.58104327712408	9.48553885051864	-4.28101407351205
H	9.31282688600636	9.00500276696639	-1.89237852383339
H	7.41189947176938	11.32221996522797	0.41827289114219
H	8.45906221567798	12.29872700421972	2.21833091347863
H	10.42518230891123	12.55497530077533	3.74042647295181
F	12.67653754603189	11.29110690954721	3.45793371710206
H	12.72672564921567	9.95528627328917	1.22340531166787
H	10.82560511847281	9.87944740923561	-0.42496966832980
H	12.92937012673139	6.74934719469539	-2.41869789115389
H	13.99664754707780	6.93841512100752	-0.98443087039692
H	12.94498470397530	5.52081384975490	-1.13789581023113

1.9c
Lowest frequency = 7.69 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	11.02519791233032	2.14705930448702	5.21056818648996
C	11.25946336159999	2.94277028523952	4.08705841644706
C	11.95496960029351	4.14965295649142	4.22685585608721
C	12.40795794378978	4.55200006297988	5.48025600632762
C	12.17400872733622	3.75241335250176	6.60196040486489
C	11.48433464191537	2.54872240180179	6.46619765603462
C	10.75449536337682	2.51555934552274	2.72860205175860
N	9.77365004704723	3.47545051197886	2.19479337619936
C	8.59447154941804	3.87783942724510	2.74861977787854
C	8.10061099624495	4.83078802888939	1.88614695018837
N	9.01897336217558	4.93678156700058	0.88455032023094
N	10.04321964624290	4.12773548179349	1.05479397501328
Pd	8.64630508224780	6.24903845411092	-0.52708435837251
O	8.45058872841993	7.40596421414951	-2.26399643096462
C	9.44062813724258	6.77926700426461	-2.78696517062976
C	9.95012580198903	7.14605113025562	-4.14533272579538
C	6.88330099553176	5.70312162683447	1.82972372367332
C	6.62966216382681	6.24449513818701	3.25411200908443
C	9.24762659219035	9.11803925226995	0.95173335930022
C	10.29013611871957	8.81703733674817	0.06866528295427
C	11.38757101721033	8.05854686604867	0.47760469100242
C	11.42434287455668	7.61262217866083	1.78906290832563
C	10.42243796166701	7.90086724138134	2.70374641941609
C	9.33827977542966	8.66212759660487	2.27104731167387
O	9.97980207561944	5.85306609586952	-2.08829925926686
C	8.02239962962843	9.90744099031079	0.52594523198011
C	6.90717317921041	9.01690504272366	-0.11336202374298
N	5.76485336448458	9.85960061326619	-0.45618028164787
C	5.13653872277817	9.76621944991036	-1.71206804121249
C	3.99747012970198	10.72374743207104	-1.66961350797427
C	3.98692517743593	11.33044961400720	-0.41392874751340
C	5.12358014516372	10.78928904817437	0.38726176324079
C	3.03713023189680	12.28296311832568	-0.07760796030026
C	2.08233466711514	12.61167762497962	-1.04730275665525
C	2.09303041152627	12.00265093698527	-2.30790334443599
C	3.05864297580455	11.04470504743758	-2.63893763306762

O 5.49504675597917 9.04113422918895 -2.62233422482815
O 5.46041451771670 11.10914267882002 1.51200059455684
N 7.23143114765993 6.76991919245457 0.83599746173198
C 6.42308893017280 7.85479655396432 0.77798305030121
O 5.35955494568332 7.97137089877921 1.40643231408227
C 8.37700469755924 11.06177355801332 -0.39837687028797
C 8.46740611567623 10.91360886572795 -1.78837270283688
C 8.82923119476233 11.99370355145280 -2.59392261940566
C 9.10413967114914 13.23715004632224 -2.02501797566599
C 9.00705368327705 13.39603541627667 -0.64214441530912
C 8.64362384188371 12.31621450100882 0.16076260567780
C 5.67108072097630 4.88693944991227 1.32901590636962
H 7.25975431756137 8.61007569637944 -1.06106688081551
H 8.23662098528889 3.48021336475464 3.68414573108161
H 3.07789509835225 10.56810196118058 -3.61405054340857
H 1.33914179346884 12.28035867123684 -3.03895665596628
H 1.31988488709455 13.35160184442556 -0.82110093802461
H 3.04034004816234 12.75045577299663 0.90204886142252
H 10.27967440744363 1.53148210589465 2.77777975781539
H 11.55079656829957 2.48617197319476 1.98168273733617
H 5.44871913739609 4.06382961196727 2.01775450689016
H 4.80732093136203 5.55147226493772 1.26682844146117
H 5.88395239971203 4.47451870764884 0.33835606054236
H 6.50780769391921 5.39761171443728 3.93980720279108
H 7.48317143736352 6.83988557258029 3.58752104416445
H 5.73091658683534 6.85697871846026 3.27180143181324
H 10.48506659752205 1.20884190719727 5.10378720448494
H 11.30058001705784 1.92314873951902 7.33476490745295
H 12.52982513969005 4.06764083292850 7.57846632136566
H 12.94733772248526 5.48932687991345 5.58001683390917
H 12.13711187413446 4.77575772502285 3.35812514187933
H 8.55543692309320 12.44442135476949 1.23677116175807
H 9.20685774534262 14.36313056658808 -0.18870834340315
H 9.38191653464768 14.07802467966608 -2.65443270800817
H 8.88756540097003 11.86266144208881 -3.67126376467887
H 8.24093389287501 9.95707707440241 -2.25103692959922
H 7.58647282857573 10.33618858221855 1.43122155663945
H 8.54046220857323 8.90273774581040 2.96776512270069
H 10.49688524032288 7.54170916940808 3.72518651559599
F 12.49601301679414 6.86888269929646 2.20073989984466
H 12.19311968050742 7.80903463797091 -0.20416406142103
H 10.25016066679456 9.18666003792384 -0.95045581380272
H 9.10910764623980 7.34072059785070 -4.81548229781245
H 10.53838486836075 8.06769282416831 -4.06684538349863
H 10.58437937008965 6.35088880173214 -4.54042068148807

1.7b'
Lowest frequency = 2.14 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C -4.99318794805160 17.93740334819476 -4.00928029044442
C -4.61503451892160 16.62107366514667 -3.79144080263665
C -5.43818127837348 15.55709115343225 -4.16140017915561
C -6.67109470573756 15.76585433145380 -4.76279782160955
C -7.06120130910141 17.09120852188275 -4.98632379096240
C -6.23545829406021 18.15947683582862 -4.61530685246285
C -4.75117563926786 14.29224540433764 -3.79121099143472
N -3.51641173419238 14.67056850339797 -3.22444776455502
C -3.36638524776852 16.07692308232034 -3.18095240603130
C -2.62236757824888 13.64627003709460 -2.70076255503074
C -2.12776794991553 13.96288982320372 -1.27466177548550
O -2.71083654386110 14.74247534159626 -0.52079989579714
O -2.41431315641845 16.69553492476774 -2.75408297035093
O -5.13002685934574 13.14168550709180 -3.92395356886880
N -1.06472263450408 13.18169038588925 -0.97130877770432
C -0.38073534461014 13.16574940271594 0.34892682068934
C -1.35675313293439 13.22225332839591 1.54010867879118
C 0.36505512241884 11.85108421124302 0.39367855641228
N 0.84517428346988 11.29259920049643 -0.75894891786676
N 1.41027492696140 10.13220395715441 -0.52944241887800
N 1.31735717479351 9.93775765367915 0.79711550566200
C 0.66867385792484 10.96962191532135 1.40783969544782
Pd -0.21296907342042 12.15468196518508 -2.46118888459588
O 1.76303280748379 13.15839112309719 -3.04576928306698
C 1.83451130250108 12.28711536861615 -3.95636454730312

C	2.95923365964898	12.27128436031114	-4.95129461480230
C	1.70105490513209	8.63384895457495	1.35488449505607
C	0.49261075096570	7.74613623821358	1.57173715623950
C	-0.41192823149220	7.51525867182734	0.52843610447612
C	-1.51615811328609	6.69118865253919	0.73126072182700
C	-1.72410074046439	6.08990014331237	1.97470184697246
C	-0.82682210129030	6.31853185925658	3.01680520595212
C	0.27712976715978	7.14837472602097	2.81557690824671
C	-1.58925203328375	10.70315174985325	-2.33708405602613
C	-1.58102141900057	9.78995559719219	-3.39107825968646
C	-2.40080133084545	8.65915582267305	-3.34038163762514
C	-3.21430659828791	8.48000469475950	-2.23118839973052
C	-3.24794858824537	9.38186997108913	-1.17913684955252
C	-2.42184604855365	10.50699200403284	-1.23609950780815
C	-1.53234749492694	13.19416664342374	-3.68647269932743
C	-0.74656310258419	14.19152046661616	-4.44919882895568
C	-0.14077393397829	15.30845623642255	-3.85239965386827
C	0.60837007577633	16.19720006334384	-4.61439922887167
C	0.78046750822525	15.98370928397445	-5.98373247254935
C	0.19769080431437	14.86892331609631	-6.58872181278342
C	-0.55528719777693	13.98042134229586	-5.82524003979894
O	0.89535638802751	11.39866052505960	-4.06122709125851
C	0.61382619789853	14.34704146483631	0.40325566604847
H	-3.27564683363908	12.77316680915898	-2.57620785028743
H	-1.93988688625993	12.43748758711496	-4.35978389360283
H	0.46733155111215	10.97222020300917	2.46660412183060
H	-7.30332155378830	14.93000211385738	-5.04543768645849
H	-8.01934000362611	17.29726831632515	-5.45455953295365
H	-6.56729061607971	19.17674358517840	-4.80205647517659
H	-4.34557028200854	18.75800598840470	-3.71722815555313
H	2.39423381095183	8.20509648681957	0.62674385972148
H	2.23570381628116	8.80479168802517	2.29256499748788
H	-0.78961168303061	13.11592822828325	2.47230367614684
H	-1.88773172192428	14.17205773147211	1.54380716935222
H	-2.08985266683207	12.41206973001749	1.48334432025261
H	1.17154228846018	14.34087792923871	1.34618760618702
H	1.31842120759394	14.28032516301815	-0.43016953089222
H	0.05155516302413	15.28157889949813	0.32592704041635
H	-1.00797622343957	13.10882918774262	-6.29150358753560
H	0.32618447559986	14.69386137247751	-7.65349540111583
H	1.36813160988855	16.68047799662980	-6.57514069914595
H	1.06577508300359	17.05818794272213	-4.13608332949272
H	-0.25428090573354	15.47437685640281	-2.78834049285671
H	-0.25887163590141	7.98945362246565	-0.43739999285020
H	-2.21606827475251	6.52066880484492	-0.08065475972144
H	-2.58637956265111	5.44805403652037	2.13004559699502
H	-0.98650917174048	5.85736546612430	3.98713481332209
H	0.97497808352692	7.33077351044412	3.63000426737204
H	-2.43645514587918	11.21663765030496	-0.41902771126229
H	-3.89973247597939	9.20501925194507	-0.32976201015881
F	-4.00156002766221	7.36708447961275	-2.16559777646300
H	-2.40705009868263	7.93021061536155	-4.14439226738359
H	-0.92411624979028	9.93887899422241	-4.24215076777565
H	3.88589042745437	12.59529680357288	-4.47264897390412
H	3.07584091088775	11.27807182797658	-5.38896381105718
H	2.71690894166398	12.98372034194051	-5.74771747837259

TS1.(7-8)b’
Lowest frequency = -277.12 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	-3.64627268570919	18.59744406380925	-3.31994462831480
C	-3.83682093837556	17.22610216777672	-3.39476084792097
C	-4.75305134886632	16.66618939269490	-4.28737950919422
C	-5.51408529483422	17.45450266346807	-5.13798008363735
C	-5.32902938493709	18.84029101954411	-5.06824045224514
C	-4.41025794278547	19.40213912216103	-4.17392104546884
C	-4.71270391955555	15.18927818585494	-4.12372697224606
N	-3.74943669580309	14.93770237866577	-3.12750903747256
C	-3.16972918802565	16.12799421049196	-2.63679616001643
C	-3.48546520395374	13.56567682668393	-2.70148062842196
C	-3.10820956426112	13.51445832838504	-1.20900440952879
O	-3.84355574748893	14.07325382414925	-0.38428076534893
O	-2.30248145069449	16.21391614854292	-1.79077657860589
O	-5.34830309250844	14.32437484836660	-4.70073982671564

N	-2.01487052026592	12.77579678779872	-0.94441811021707
C	-1.54208507471363	12.64954293047136	0.46156455994091
C	-2.57404093107479	11.88913411999538	1.32390970191272
C	-0.27132875160660	11.84997063458992	0.39201386304615
N	0.17707781950903	11.37519077829042	-0.80976560725962
N	1.27882951469068	10.67098818157059	-0.68165809188599
N	1.55976952999613	10.70177515470378	0.62689850699273
C	0.63307987562662	11.41005160388559	1.33289887925364
Pd	-1.06089148233731	11.72137629301654	-2.37624986200418
O	1.70894619630523	12.18079195153688	-3.32718600964037
C	1.24330269810070	11.22195110806074	-3.93777818914244
C	2.00876639195599	10.51623147239078	-5.04879669305144
C	2.69096470888580	9.90991649593514	1.13174813198716
C	2.21979753262115	8.65348892087798	1.83037887637445
C	1.43429320414499	7.72031689891759	1.14321535285702
C	0.99524169130951	6.56706248177124	1.78801142397939
C	1.33971321682856	6.33381438612373	3.12167030065645
C	2.12333333248799	7.25912790922390	3.80885366493393
C	2.55886455419897	8.41815812530728	3.16429880777885
C	-2.79806596614217	10.93390656944326	-3.30778597276618
C	-2.59393885164843	10.13540766259298	-4.44327494416099
C	-3.37337549224284	9.00638464087917	-4.66080905487506
C	-4.37242371028110	8.69764101709823	-3.74299121569456
C	-4.61317748489059	9.47546127059386	-2.62123676239138
C	-3.82338343226910	10.60651369983128	-2.40880616652726
C	-2.58348396828708	12.84786923407938	-3.71506409035145
C	-1.38264469762631	13.54995602267729	-4.28735738017189
C	-0.56599810417277	14.42593840418894	-3.55325213452482
C	0.49560822714676	15.07955983194443	-4.17036295166290
C	0.77863206968013	14.85666385226903	-5.51723191460790
C	-0.02150388942734	13.98423901564561	-6.25562589771695
C	-1.09892244426409	13.34630952272228	-5.64817714742958
O	0.04503589517136	10.70201226217069	-3.74715277918028
C	-1.23187494398680	14.04039055730220	1.05832572309514
H	-4.46128136697701	13.07175651489843	-2.76798789474436
H	-3.21248269410366	12.58772152173145	-4.56200680640476
H	0.69176310718274	11.52746986844968	2.40273455241128
H	-6.22293545864633	17.00838973810894	-5.82837561460418
H	-5.90564550198775	19.49209194426685	-5.71802502084925
H	-4.28919642261921	20.48108331601744	-4.14489021363384
H	-2.93041527648922	19.02324992159742	-2.62409473077372
H	3.29512688834145	9.68720380225233	0.24929937235181
H	3.27261775287123	10.54137435399749	1.80804289754099
H	-2.19698321476394	11.76320674724915	2.34487620868332
H	-3.50341421982603	12.46035897347710	1.35065835899163
H	-2.76286396712125	10.89922191649020	0.89747736796218
H	-0.81684672740061	13.92614558629312	2.06612131359721
H	-0.50387651274292	14.56149279382148	0.43120911861147
H	-2.14769917027533	14.62923811522943	1.10500849180753
H	-1.73631560706825	12.68476307541104	-6.22963978393875
H	0.18490874297322	13.80998717092752	-7.30804684533235
H	1.62016923981968	15.35595199641186	-5.98848189409913
H	1.11736807032692	15.75083435257277	-3.58623091226661
H	-0.77181141264584	14.60187072676684	-2.50440932098960
H	1.16347778122937	7.90385926946037	0.10638316459316
H	0.38479060070580	5.84801104873192	1.24974324569129
H	0.99631154600750	5.43328704155843	3.62225382633776
H	2.39311103907957	7.08339987739916	4.84607844996263
H	3.16771474444132	9.14222810042341	3.70121636265415
H	-3.99574866426034	11.20236113340369	-1.52097809246830
H	-5.39598597811391	9.19866094158361	-1.92285404420698
F	-5.13797124080901	7.59455114203204	-3.95509875240204
H	-3.21818780830059	8.37159050730522	-5.52711664745391
H	-1.79919377477780	10.38484245431661	-5.13612594744982
H	1.76147226941964	9.45280533829627	-5.09073431539361
H	1.72638488908568	10.97145504774322	-6.00500423737897
H	3.08107909182099	10.65746368327497	-4.90069452921484

1.8b‘

Lowest frequency = 12.95 cm^{-1}.

Charge = 0, Multiplicity = 1

81

C	-4.36751650547900	18.50943535159247	-3.68606389020857
C	-4.36901694487173	17.13252760074236	-3.52350304856917
C	-5.47340227099436	16.35793297996879	-3.88085837422354

C	-6.62014785201636	16.92810699336976	-4.41359686482302
C	-6.62847625723365	18.31810090793415	-4.58049931832513
C	-5.52078468872287	19.09548836589067	-4.22225415317218
C	-5.15496028091117	14.94030394419764	-3.57134864169970
N	-3.83437893161775	14.92908752582678	-3.08047953219058
C	-3.30325994310416	16.23307499134669	-2.99496926387481
C	-3.28684685646669	13.67283037262493	-2.55177818130009
C	-2.47257557684052	13.92594568880615	-1.26345368343748
O	-3.01909847695598	14.65350090095427	-0.41942154685175
O	-2.19622267740747	16.54351957908088	-2.59751585393279
O	-5.85404754911174	13.94694773092977	-3.68682063084956
N	-1.34703774491099	13.20874426598697	-1.09535602421913
C	-0.73975603600950	13.19069613715495	0.27668108922301
C	-1.76768704833507	12.92540292044236	1.39613787110267
C	0.21025971453165	12.02582090041541	0.24554553087845
N	0.71852918565696	11.62877515262104	-0.95516898988499
N	1.50382694223737	10.58258298791441	-0.84533248321820
N	1.51739743961624	10.30109237474657	0.46681512928539
C	0.72785425492932	11.15620887077375	1.17859481845664
Pd	0.00860382391535	12.66174075478076	-2.53176597481887
O	2.81238163794693	13.37575932575147	-2.72199232802476
C	2.60570483125977	12.47354862930066	-3.53619673669902
C	3.71341262045717	11.85999010639011	-4.37897757068836
C	2.16906251975929	9.06968114702526	0.92550180972240
C	1.15346429213906	8.00510111985509	1.28907694792669
C	0.02839389467818	7.79155044856282	0.48487398828243
C	-0.89234118747424	6.79963935573729	0.81443618413369
C	-0.69256448909364	6.00928367026971	1.94834425291306
C	0.42682482054786	6.21817320327003	2.75288672649965
C	1.34470255317288	7.21744187498424	2.42650457925703
C	-2.92096918872511	11.26922512348798	-3.25603854948132
C	-1.85982074797428	10.35734779697231	-3.27031915813315
C	-2.02493815551699	9.04675412032315	-2.81996118729653
C	-3.27167536473779	8.65628327605138	-2.36054060508306
C	-4.36430168511522	9.51169824410065	-2.37357729739516
C	-4.17881785796159	10.81343956660679	-2.83448263463782
C	-2.78960205252860	12.73525596818331	-3.68468899551204
C	-1.45507955806977	13.10734038360596	-4.30576120911305
C	-0.69874323963292	14.24827249312709	-3.90553139594488
C	0.39453077754917	14.69215156136664	-4.69791011524654
C	0.73723414059217	14.02508741427570	-5.85129155273374
C	-0.00725966648906	12.89601224339123	-6.25356624285112
C	-1.07551368764942	12.45048010516313	-5.50651914749919
O	1.43093488071968	11.93325588015639	-3.77318215042104
C	0.03446345450056	14.50345043822803	0.52306220353020
H	-4.17300694202742	13.17019849295200	-2.15155860350559
H	-3.53588101463075	12.87215702413288	-4.48200703105258
H	0.59215115726161	11.05707099512969	2.24295967081369
H	-7.47425644593001	16.31640571127374	-4.68642325091732
H	-7.50786197253025	18.80370336561274	-4.99323573349240
H	-5.55958684409350	20.17173356552825	-4.36268184443700
H	-3.50420790993037	19.10343849896213	-3.40355532419124
H	2.80659184878610	8.75844250458729	0.09359471573512
H	2.80550822629928	9.31233966217487	1.78077221534126
H	-1.23067922502389	12.72681597930158	2.33127145421525
H	-2.41755092978750	13.78659068755463	1.53049775091014
H	-2.37668413598591	12.05015465483514	1.15007789736652
H	0.51680500441349	14.48934749926296	1.50686342290288
H	0.80235495289036	14.63307919194622	-0.24574738444876
H	-0.67199859825157	15.33508488023544	0.47603027499542
H	-1.65516802482029	11.59443767257323	-5.83985958372646
H	0.25869139936084	12.37695652315641	-7.17015160067889
H	1.57520494240833	14.36339437261746	-6.45322313549117
H	0.94515588338736	15.56878212276275	-4.37412198774288
H	-1.07137208857871	14.92165659221140	-3.14095557073355
H	-0.13356107943548	8.40837527589042	-0.39470181540898
H	-1.76519749148815	6.64802224515622	0.18661968197501
H	-1.41142343532418	5.23715573549870	2.20627050190689
H	0.58319587944572	5.61105847911553	3.63984410920404
H	2.21235372072718	7.38588308641398	3.06066421512788
H	-5.03371448514662	11.48412404814833	-2.87156476935419
H	-5.33427227324378	9.16236126237406	-2.03591806487465
F	-3.43518116094604	7.38292093632315	-1.89596519262571
H	-1.20005484059697	8.34192707967665	-2.83221714010305
H	-0.88252222710038	10.65164660132794	-3.63868092503566
H	4.63352889683560	12.43241263081306	-4.25380780008509
H	3.87888990682305	10.82498028533651	-4.06132986187105

H	3.42029504398079	11.83744254282700	-5.43292408956895

1.9b‘
Lowest frequency = 8.66 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	3.68597757331341	11.55014410279001	-4.28217221529643
C	3.58293539894001	10.68188754433456	-5.37410513462090
C	2.61996671413406	9.66611219648783	-5.32838019181678
C	1.76894345194646	9.52341575936165	-4.23559199679340
C	1.91136564762445	10.40484704367059	-3.17290162874113
C	2.85620719320945	11.41480589078586	-3.16676702679670
C	4.50664787731997	10.78809782153635	-6.58202987625617
C	5.67885396313849	11.72739673193733	-6.37197754401919
C	5.79640297635969	12.98120131912579	-6.96771383181389
C	6.91259541638861	13.78441159888611	-6.71884150870134
C	7.92412729058975	13.34712546253327	-5.86706752985474
C	7.81858357081984	12.08904679861865	-5.26801012866847
C	6.71034012263532	11.28825853384024	-5.52679273444883
H	8.79190164923128	13.97269059113078	-5.67596728800842
C	3.72548707865806	10.86346408995185	-7.94233686046975
N	4.65454000837098	10.99944679591845	-9.06149910051974
C	5.37996332051572	9.88890129307733	-9.52009649752993
C	6.13482291118838	10.35606863850650	-10.71379592751742
C	5.79695497618805	11.69135531547330	-10.94165663675641
C	4.83315725349225	12.12668464016106	-9.88932771170445
C	6.34266870817216	12.40513451937232	-11.99740862632862
C	7.24744396808968	11.73488127920712	-12.83007643619038
C	7.58594868796514	10.39618467329590	-12.60115367740479
C	7.02982916722846	9.68328955185840	-11.53207204416844
O	5.34989128852647	8.78230816422802	-9.00620813508761
O	4.31939546086291	13.21717932852591	-9.73843893267814
C	2.37902134647527	11.57913088434578	-8.27589937444080
O	1.97406252719066	11.36721350814728	-9.42794579505727
N	1.60471671011850	12.07175522419946	-7.28046890653645
Pd	2.04970857434508	13.49576625977840	-5.89452150042658
O	3.55866388000691	14.73379942637995	-6.60828242461658
C	3.49804836537812	15.42747143415710	-5.53315904846311
C	4.43676932576116	16.56785077795687	-5.29743406183509
N	0.38328559863708	12.73468057911409	-5.15415321207199
N	-0.14986828393710	12.74176122467139	-3.95337342203387
N	-1.30823335160011	12.08081759956690	-4.09252840477525
C	-1.50654248693647	11.65838746855116	-5.37499660429378
C	-0.39814341329229	12.09082844866869	-6.06762609710335
C	-2.18923079712425	11.91466190404158	-2.91915669662727
C	-2.93227102779512	10.60378043980451	-2.97723457267899
C	-4.28313155949311	10.57598166235175	-3.33509614025043
C	-4.96780872684087	9.36272377123741	-3.41651839580226
C	-4.30204217507480	8.16938314286221	-3.14025638133133
C	-2.95314501162145	8.19182584745287	-2.77823637380757
C	-2.26968875947717	9.40256996153067	-2.69627209950793
C	0.11914302012145	11.99807222585335	-7.47818275326464
C	-0.39500064525699	13.18114592770167	-8.32390343740429
C	-0.35465767997178	10.65414982490468	-8.06619174244346
O	2.62280239657680	15.08036471362982	-4.66201663787592
H	3.36605301796513	9.83094732718819	-8.05398422660186
H	4.97349268808083	9.79632029847943	-6.66626867199093
H	-2.37492009728251	11.08717621860689	-5.65817642697013
H	7.28531273916753	8.64490735299142	-11.34565589720412
H	8.29152805128984	9.90482214422731	-13.26481995504465
H	7.69580637651773	12.26034225262200	-13.66832138513101
H	6.07324493170106	13.44296719366008	-12.16608829724181
H	-1.52770125167242	11.97780955439613	-2.05316606327367
H	-2.88681259826068	12.75757340543608	-2.89421820529924
H	-1.44492896936383	10.58989024459298	-7.97106834185952
H	-0.08243457223744	10.57472311208636	-9.11644045632745
H	0.09162890639388	9.82161702613795	-7.51365599491658
H	-1.48844939895402	13.16169980792836	-8.39934466792220
H	-0.08632817924800	14.12662676971909	-7.86649714145638
H	0.04347214780320	13.10706927379111	-9.32114245025240
H	6.63494332468174	10.30601411174944	-5.06479504042854
H	8.60389679090326	11.72932964225452	-4.60867274426772
H	6.98367903440642	14.75568868947075	-7.20123086354033
H	5.02007714244474	13.34829818149306	-7.62329461531775
H	-1.22142596499453	9.42182644284950	-2.41208036222841

H	-2.43479922275813	7.26399038299332	-2.55454047493204
H	-4.83282160502126	7.22386377439403	-3.20181852092329
H	-6.01802515215954	9.35121624238544	-3.69281501576040
H	-4.80149132489186	11.50818291579577	-3.54816772020260
H	2.52780731249451	8.97094102408903	-6.15825929368458
H	1.01897756653604	8.73991606485097	-4.19871360174303
F	1.08124197810255	10.26629198537951	-2.09171942896961
H	2.92453089429557	12.09473361798321	-2.32503975877504
H	4.43651796263285	12.33318436495371	-4.29079243648068
H	4.56813918693079	17.13847480877929	-6.22020473402550
H	4.06444773297806	17.20840302861045	-4.49625558950681
H	5.41333105041992	16.16080679858176	-5.01073131288131

1.7c’
Lowest frequency = 2.14 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C	-2.56458105178146	18.78072877166356	-3.62170037062061
C	-2.96123425758135	17.45760146855998	-3.74148972113156
C	-3.89484228779845	17.05980304794987	-4.70089811004566
C	-4.46716752351225	17.97003972027832	-5.57658152402224
C	-4.07337942040643	19.30888670745305	-5.46247496937999
C	-3.13814520961140	19.70774691657763	-4.50047500194149
C	-4.09305544915752	15.59007483700186	-4.57248532540391
N	-3.23344131759182	15.17929888946558	-3.53306624380491
C	-2.51536288925422	16.25366494193102	-2.98442595607931
C	-3.17146025679259	13.78443678476592	-3.11965919900336
C	-2.99349523356425	13.69020621341633	-1.58724698660208
O	-3.73986084189998	14.31587762465203	-0.82906260187329
O	-1.67684850001461	16.17945447023770	-2.10367062749892
O	-4.82454125339792	14.84671329071185	-5.19862388774522
N	-2.03846297152896	12.81157899507041	-1.21274794475636
C	-1.87016219082369	12.41363567628944	0.21097341143371
C	-3.15541841364270	11.70808599405285	0.70817401774200
C	-0.73361452672696	11.42337948089307	0.24484329758023
N	-0.39238221061694	10.70745621213235	-0.86820946933196
N	0.60832673979936	9.89205093681378	-0.62728243764370
N	0.91286743842691	10.07060454950440	0.66838080642338
C	0.11343529694310	11.00807461015454	1.24949704969498
Pd	-1.23129150789841	11.66592715518577	-2.62992239589696
O	-2.70824893253836	9.97090265699077	-3.03808432857338
C	-1.87111782371943	9.55677620167109	-3.89284024249162
C	-2.08680156605041	8.28153682330252	-4.66098291994768
C	2.03477148711211	9.32650832657826	1.26480939097094
C	1.68103308967822	8.78655668636256	2.62909863217792
C	0.65590464332580	7.84367273253573	2.77321638472387
C	0.32498921623486	7.35445033513814	4.03379755174949
C	1.01683392781912	7.80054020057157	5.16270207465527
C	2.03901473038065	8.73789559523996	5.02565848468972
C	2.36724064474902	9.23091628092833	3.76165346678343
C	0.43721852844558	12.77155653907829	-2.69601548147102
C	0.65651539734621	13.93838522441276	-1.97087968548155
C	1.88204096125612	14.60143551686071	-2.09077485009194
C	2.84885783621032	14.06943803544556	-2.92982091494490
C	2.64523300309300	12.90437930128735	-3.65610555712445
C	1.41938672361307	12.24691619553264	-3.53345952458433
C	-2.26155987080967	12.87087529516403	-3.98161032595431
C	-1.39947629421044	13.43008315241600	-5.04994468478979
C	-0.61481793833054	14.58811007149831	-4.91000149611836
C	0.19338664603853	15.03336293125596	-5.95004165755141
C	0.24514906971558	14.33285796343803	-7.15675876814953
C	-0.52362921517389	13.17941817865843	-7.31207943853418
C	-1.33566978367881	12.73765343342578	-6.27125859426003
O	-0.79046420116918	10.23191193221067	-4.10572285606981
C	-1.53131693732741	13.62333206662261	1.10466928025685
H	-4.18993867169858	13.41643022037938	-3.29033588923021
H	-2.88769041806707	12.08526288411103	-4.40950861657631
H	0.21146317697484	11.27785209872754	2.28822321540135
H	-5.18929637754423	17.65033058826691	-6.32112964485964
H	-4.49780465920893	20.05185665382588	-6.13140938135471
H	-2.85295520604208	20.75392331858521	-4.43810072655010
H	-1.83650151574121	19.07899407429283	-2.87395468553776
H	2.26011216533226	8.53294058148458	0.54855611156939
H	2.89824799606424	9.99612696248992	1.32454275066895
H	-3.01984231136963	11.36305868454432	1.73892491623652

H	-3.98729674519001	12.41368832367124	0.66791667180988
H	-3.37624716543941	10.84738282154156	0.07060187358389
H	-1.41851598135071	13.29349570452696	2.14392414093470
H	-0.59805603005231	14.09141406540273	0.78235578556412
H	-2.33973364080689	14.35177202930371	1.04498424901037
H	-1.93227380869600	11.83814664354946	-6.39572401085643
H	-0.49272942916559	12.62364183936381	-8.24520241133203
H	0.88232248735387	14.68035629063290	-7.96515481876635
H	0.79895723545772	15.92450964579401	-5.81019738117472
H	-0.59451437147491	15.11701533894682	-3.96674355883157
H	0.11447991044219	7.49873034751313	1.89569472712099
H	-0.47096960310273	6.62295271064359	4.13731274898496
H	0.75808888275088	7.41711663376290	6.14524366046507
H	2.57972654834169	9.08839026916347	5.89981879660811
H	3.16288709478043	9.96451087367324	3.65383117421557
H	1.23311288401721	11.34504878027454	-4.10703180926055
H	3.42450173780507	12.52646254194837	-4.31009463566259
F	4.04377742166042	14.71727106577738	-3.05141148365365
H	2.07320684593393	15.52444072139934	-1.55266469812732
H	-0.12400418452021	14.37067810141269	-1.36130317795652
H	-3.14455058502653	8.01360561347916	-4.65890558433262
H	-1.71630328603909	8.38847868921537	-5.68338335230864
H	-1.51711289995617	7.47959391090866	-4.17809170576412

TS1.(7-8)c'
Lowest frequency = -240.80 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	-2.54559875240391	18.94661496638589	-3.40638490979695
C	-2.80319946206892	17.59029631133746	-3.53874303338849
C	-3.64522240712347	17.10244292426213	-4.53824282157160
C	-4.26279328442482	17.95036571221901	-5.44601252872546
C	-4.00768592738700	19.32094499633125	-5.32150624603548
C	-3.16358575378650	19.81115613725937	-4.31750822185025
C	-3.70450573750780	15.62410863177309	-4.40855693982112
N	-2.84655386740490	15.29321784789551	-3.33366847753759
C	-2.27720609966640	16.44095994566474	-2.74825652178126
C	-2.69409346318734	13.90023766962890	-2.95266270596634
C	-2.82143169230574	13.70743406151562	-1.42413960428253
O	-3.54232680585664	14.46088745010206	-0.76142249769856
O	-1.49387959568753	16.47346938280491	-1.81945188380223
O	-4.34102088867589	14.81475284339981	-5.05581314609430
N	-2.19195939920198	12.60192116553646	-0.98044770907347
C	-2.39677787112285	12.12682302559432	0.41288346462933
C	-3.89839335117498	11.98127853178101	0.75298589713744
C	-1.76946962251481	10.75889413490659	0.46679974875155
N	-1.19911354095250	10.21725238764764	-0.65368359647702
N	-0.70240737832882	9.02124769057233	-0.42088337086482
N	-0.96541622451818	8.77883522211484	0.87057604156242
C	-1.61328004438009	9.82133899645100	1.46344408320912
Pd	-0.95032492307701	11.57377653249001	-2.17029948544947
O	-1.73047083817183	9.94639519152950	-4.45441913213422
C	-0.53172486791853	9.72687983570360	-4.23910458358542
C	0.25944092193652	8.73568284464379	-5.07781753058881
C	-0.44180793878745	7.55294530105847	1.49263529350102
C	0.70152431381075	7.85895238641581	2.43469588099680
C	0.62987015255884	7.48049794465991	3.77685635599935
C	1.68459685928637	7.76349100003320	4.64631422517514
C	2.81249139576734	8.43395260759578	4.17643029592770
C	2.88643314468090	8.81785972645984	2.83519144413376
C	1.83719267314828	8.53055230764946	1.96633049489415
C	0.24945854736479	13.19462191748323	-2.68370583238383
C	0.34811667161924	14.21951595817600	-1.74028902302814
C	1.52020425880553	14.97459041991831	-1.64203312142556
C	2.57355189585706	14.67820985283494	-2.49027458105367
C	2.50223128558620	13.66225248988564	-3.43925250382460
C	1.32621168797502	12.93193569191210	-3.54460008399517
C	-1.59317918306580	13.10819302147347	-3.69642391821711
C	-1.05635904289001	13.69730293232859	-4.95908163684502
C	-0.44876774669748	14.96208749610635	-5.02765073167885
C	-0.04909371500111	15.48653028292943	-6.25014487765775
C	-0.22646397297007	14.74974484400025	-7.42567584312865
C	-0.80476404821508	13.48379101382792	-7.36556189021872
C	-1.21996237847004	12.96123729131257	-6.14019399273846
O	0.18733443015132	10.32666040733057	-3.32198615835765

C	-1.69466955975722	13.07402799958750	1.40865834145646
H	-3.61815470012377	13.44531012326826	-3.33999202171985
H	-2.01511127704356	12.12994053825231	-3.97403289889638
H	-1.88465306641855	9.80923850178261	2.50657992747376
H	-4.91408710433917	17.55972792479178	-6.22135171348110
H	-4.47009350002924	20.01805190606678	-6.01421074600777
H	-2.98629387124232	20.88047766527667	-4.24768081125591
H	-1.88859938739982	19.31543427666351	-2.62503506831420
H	-1.26230836682081	7.05783806443597	2.01844831186434
H	-0.12819659288243	6.92487478509586	0.65556854891277
H	-4.00606350267797	11.52924774524583	1.74524717467159
H	-4.37562187263680	12.96052351852654	0.74409025099627
H	-4.38611238401083	11.33437607811418	0.01801953289270
H	-1.81448465938338	12.71193793182200	2.43592787975849
H	-0.62710108415900	13.13761934487669	1.17969477558189
H	-2.14395169706612	14.06571095625621	1.32362058337698
H	-1.67765432049451	11.97693625846411	-6.08761749028923
H	-0.94005647002584	12.90069685551577	-8.27208571352517
H	0.09446948752169	15.16009738324766	-8.37905233192987
H	0.41786020480984	16.46679767083823	-6.28648833800554
H	-0.25411003766582	15.51595143944924	-4.11505866681094
H	-0.25233190802511	6.96065562135863	4.14393166843236
H	1.62135363266297	7.46421322011293	5.68836562358022
H	3.63229436540950	8.65923768814186	4.85212409191132
H	3.76362724947660	9.34096347773812	2.46618463005277
H	1.89349805827685	8.83288987076615	0.92346571214384
H	1.24660375898484	12.15375275506440	-4.29200566568986
H	3.34834169004460	13.46421471393384	-4.08897898953175
F	3.71953608624162	15.40691711531056	-2.40006083936940
H	1.60227273545521	15.78114395503567	-0.92160245530498
H	-0.47524528906469	14.46001493660443	-1.08633298055013
H	-0.38238138603953	7.89528329632833	-5.35072755916484
H	0.57182684408401	9.23698299922255	-6.00153392532250
H	1.15068251073611	8.38705204986201	-4.55266992277545

1.8c’

Lowest frequency = 9.82 cm^{-1}.

Charge = 0, Multiplicity = 1

81

C	-2.54873741283054	18.86806346089812	-4.21142612632347
C	-2.80692728977394	17.53601717105599	-3.92465400864911
C	-3.98945215893758	16.91839184592386	-4.33158884447440
C	-4.96092437132885	17.60635066166089	-5.04321296899156
C	-4.70722940448442	18.95001244117843	-5.34292505296403
C	-3.52120130452392	19.57093688182863	-4.93275304784020
C	-3.95847629763716	15.51101916743280	-3.85713512150288
N	-2.69163446940799	15.33321142939879	-3.24842373388338
C	-1.97428706941058	16.53739073978488	-3.19669536496524
C	-2.36725265177540	14.05609652132203	-2.61460592624897
C	-1.96589853844640	14.28551790824093	-1.13938090879336
O	-2.60217406881132	15.16077406430291	-0.53284491786896
O	-0.88842081591281	16.71818827971097	-2.67227782771072
O	-4.81894006410370	14.65559208247953	-3.92769202292084
N	-1.10443933852491	13.40487261073411	-0.58785987825906
C	-1.02775788202641	13.41354196967007	0.91289509807689
C	-2.41441503614037	13.24161193628648	1.56615036346006
C	-0.18962675339749	12.22103693278047	1.27192120616762
N	0.71519851390257	11.76794548855785	0.36031039574239
N	1.40361717186602	10.74274139225653	0.80713702076981
N	0.93416347914608	10.52367817068247	2.04103545153069
C	-0.05790935351165	11.40158527330235	2.37191048397389
Pd	0.52571485864037	12.53377550350165	-1.48608141025995
O	2.20391148879950	11.56350420049760	-2.07767524711794
C	1.97568001827649	10.28571489911969	-2.26629790958774
C	3.24034141895190	9.48880497271479	-2.53992167195106
C	1.36375042509340	9.30277392938454	2.73702309605968
C	0.49488713446805	8.11585183029364	2.36993221527011
C	0.24109315952765	7.80623406430027	1.02784669740984
C	-0.54435032419475	6.70066678548881	0.70912405785506
C	-1.07467424594234	5.89574781639577	1.71957139247878
C	-0.82275052309232	6.20261170965485	3.05595711678493
C	-0.04298549777235	7.31372647461814	3.37928797203381
C	0.70002111264398	14.21235811602060	-3.00519472001151
C	-0.06329547774239	13.13956393748789	-3.54998110986529
C	0.58604364261940	12.25708778667768	-4.47155839289393

C 1.89652018096911 12.44025068744100 -4.83110835270936
C 2.60850871039372 13.51840899469980 -4.27454209170920
C 2.05079664288595 14.39952752019796 -3.38455716091111
C -1.58690827184702 13.05918710870205 -3.52065181276533
C -2.13042403606422 13.13029845175415 -4.94259720777933
C -1.66646665523032 14.10500507243790 -5.83448277464005
C -2.19629343930460 14.20031906224796 -7.11911970430397
C -3.19196635104181 13.31343578300273 -7.53292255185573
C -3.65097562150308 12.33266662322754 -6.65466037611128
C -3.12293041285566 12.24483671856806 -5.36695798580154
C -0.32248880439664 14.69303763092330 1.41868665618774
O 0.86095241635764 9.75430647691058 -2.21171307637112
H -3.35790007608206 13.59196671165988 -2.52054493908988
H -1.84100640140989 12.06822007817253 -3.12673588411397
H -0.57052554554825 11.35794589489214 3.31883210812032
H -5.87798080862436 17.11593341448038 -5.35377316514289
H -5.44141286139015 19.52325018017254 -5.90149760880050
H -3.35579847968400 20.61577918405341 -5.17904906981404
H -1.62733903873633 19.34056752221579 -3.88597706944802
H 2.40459363610189 9.14758979963185 2.44107341077653
H 1.32847724145906 9.49991733529982 3.81081979017217
H -2.29136643433760 13.10734848189663 2.64718708027045
H -3.02857718514396 14.12128471142907 1.38443783628384
H -2.91367163564560 12.35765659861402 1.15821312897121
H -0.21934545294103 14.66750720754110 2.50931436694757
H 0.67380539317438 14.76727228581200 0.97197503630964
H -0.91593163376179 15.56066733207072 1.12668107991034
H -3.49062718204194 11.48679295587995 -4.67974838753086
H -4.42336535933042 11.63683105658090 -6.96950005694998
H -3.60338092781365 13.38454376629755 -8.53573801731774
H -1.82886641825376 14.96426909737107 -7.79870768509673
H -0.88201581635267 14.78964685515763 -5.52200722238360
H 0.64068633239160 8.42954237869065 0.23153308269388
H -0.74015817515321 6.47156751089379 -0.33408694271469
H -1.68599622906901 5.03463705005307 1.46545297792503
H -1.23644745284709 5.58404598030633 3.84714813193283
H 0.14878545530291 7.55668481994859 4.42236484923473
H 0.01416950648126 11.44078651447168 -4.89996648826302
H 2.39767830236645 11.77221960060177 -5.52333701538448
F 3.89879540922807 13.68167541809619 -4.65563668351236
H 2.62621862929388 15.22929566595046 -2.99045762897824
H 0.20420931149642 15.01023350227606 -2.46463601855701
H 2.99407248372555 8.58660319497597 -3.10316350736535
H 3.97968270504434 10.08991552015029 -3.07454819333561
H 3.67645527553207 9.19383178859809 -1.57853121150925

1.9c'
Lowest frequency = 14.05 cm^{-1}.
Charge = 0, Multiplicity = 1

81

C -2.69729985520064 18.65096042062032 -3.86753348826898
C -2.81567567359851 17.27188308444258 -3.94571969267146
C -3.72157276777877 16.66599216908627 -4.81513491740851
C -4.54635103129906 17.41423207793494 -5.64194328085758
C -4.43610682970203 18.80790226028159 -5.56943285649493
C -3.52660915475189 19.41632341160264 -4.69599879936608
C -3.58986116230852 15.19303158949898 -4.66243135305023
N -2.58368672503577 14.99009201152291 -3.69400966508555
C -2.06939154716322 16.20697881100657 -3.21725145307796
C -2.20230029799353 13.63762561734376 -3.30939947598297
C -2.56989517281209 13.39613652900700 -1.82894537423762
O -3.11150831118244 14.29989467383518 -1.17707974162791
O -1.17422013967993 16.35626391084095 -2.40630844556557
O -4.19486492579992 14.30590964830667 -5.23661083951257
N -2.26370219291238 12.17392909629475 -1.33831686254997
C -2.42063635783473 11.92826987571987 0.12887683115263
C -3.90335529013524 11.66247295496710 0.46568849514632
C -1.59622896272466 10.69757012545641 0.37080221467720
N -1.29025074253616 9.90899207781916 -0.69967060054046
N -0.53312093105527 8.88524640048632 -0.36862966235523
N -0.35106055859322 9.01282083964993 0.95379378199770
C -0.98157872821767 10.11319811478014 1.45479192546902
Pd -1.99389603421575 10.50024128429160 -2.44171660241566
O -2.78187118876399 10.81743635131596 -4.34315831845151
C -2.44908311898573 9.62221097258903 -4.68166630406262

C	-2.69614097282037	9.12100875792805	-6.06942555805038
C	0.47546750300875	8.02863501989699	1.67264848632953
C	1.43539820659486	8.70584641761492	2.62170126942496
C	1.44493486692295	8.36078364684416	3.97513429699420
C	2.33518925094452	8.98049438854013	4.85363954105819
C	3.21179746802681	9.95658357552763	4.38241572861394
C	3.20076001767378	10.31036457006923	3.03088675526758
C	2.31935064436834	9.68526540072968	2.15346490892930
C	0.30616640959868	13.00982483588017	-2.70132172644922
C	0.55356938525803	13.91248854019866	-1.66244647750567
C	1.54620544346049	13.65912030897474	-0.71468543094932
C	2.28353855338457	12.49030935584294	-0.82047777895590
C	2.07044855996613	11.56629436008147	-1.83176667233723
C	1.07542366197768	11.84152645753551	-2.76816979142745
C	-0.74504803758813	13.21766868671034	-3.77466239763847
C	-0.29005178489804	14.10571148602165	-4.92745924689816
C	0.66934169513358	15.10955204559334	-4.77676087896217
C	1.01348039193035	15.92858745084853	-5.85315950122224
C	0.40513578360296	15.75308265008874	-7.09508076058509
C	-0.54812474668162	14.74581000108987	-7.25725542393607
C	-0.88860984627338	13.92810143880676	-6.18251538039844
O	-1.87871613417738	8.90161284626073	-3.79230227737444
C	-1.85169968354327	13.05627152907806	1.01562379698019
H	-2.87881911474131	13.01864224702441	-3.90749152333797
H	-0.89866934175627	12.22786460407755	-4.21542623814074
H	-0.91107718456569	10.38699432053893	2.49444789784521
H	-5.24639286443144	16.93224780486358	-6.31709035231336
H	-5.06450017415120	19.42988683677786	-6.20034530417807
H	-3.46501678309321	20.50034119520552	-4.66358486548593
H	-1.98648583752987	19.11139957833423	-3.18860454014722
H	-0.18711566466253	7.34495542328376	2.21226044493701
H	0.99005018454608	7.46705859709687	0.88896784541038
H	-4.02447623994969	11.41937691593330	1.52745225339188
H	-4.47558605856708	12.56337437577200	0.23360261433326
H	-4.28089280148995	10.82990704947845	-0.13582975129271
H	-1.85034416149637	12.71723664431925	2.05859623671375
H	-0.82580996420619	13.28582484286599	0.71934538373609
H	-2.46035784655454	13.95312744738834	0.92728630875620
H	-1.64418481608347	13.15569947494031	-6.30615439888844
H	-1.02755639248513	14.59743600264172	-8.22104365970461
H	0.67338445445481	16.39240331244000	-7.93152709036614
H	1.75917876192149	16.70715774884690	-5.71679643458386
H	1.14389262106152	15.25791733738991	-3.81253221152373
H	0.75462208071395	7.60517425739774	4.34334771672548
H	2.33723497471554	8.70502490396052	5.90419188446192
H	3.90014039689270	10.44456330046475	5.06624490416718
H	3.87471603900035	11.07429269214161	2.65637115698875
H	2.31062784678364	9.97133008980673	1.10575963612226
H	0.88753289413601	11.12489113488877	-3.56380356181390
H	2.66465343882588	10.65973157499990	-1.88173515140819
F	3.25598068343942	12.23392618634492	0.10980678888856
H	1.74425641056579	14.35436746758324	0.09488585786114
H	-0.04201299502724	14.81626525140231	-1.58869259089812
H	-3.60428593380233	9.57288475962853	-6.47400925298975
H	-1.85366695280573	9.41659098069647	-6.70567580780755
H	-2.76780559524715	8.03182556260279	-6.07059219122594

1.8 (125eb)
Lowest frequency = 12.33 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	6.48224770501935	8.56600606356923	-5.66010963391703
C	7.35288440092336	7.84263265117266	-6.47902160666355
C	7.62149639667981	6.50239709120390	-6.17888189155330
C	7.02729901133820	5.89745994049367	-5.07359729285235
C	6.15908910866869	6.62600377474913	-4.25744439066824
C	5.88648413756756	7.96156545862067	-4.55206179194752
C	8.01790056543492	8.49991696273798	-7.66882287801185
N	9.43015868175048	8.81545874737958	-7.41866167474403
C	9.97634658398834	9.92065356286183	-6.84555633421062
C	11.32700745708444	9.65039186483985	-6.78624213204880
N	11.53030751564671	8.40042504833031	-7.30558224935618
N	10.38345885495829	7.89042158159502	-7.68480058244854
C	12.47938577290403	10.47025606712030	-6.25741714451005
C	11.96266517769798	11.66350339761526	-5.43891486165531

N	13.23941370746111	9.53697705592839	-5.39522979526317
C	14.27440164398833	9.84962023371514	-4.58059906066898
O	14.80966888455426	10.95186717721742	-4.49891774818525
C	14.72082222637815	8.64492088963824	-3.71623219140625
N	16.13121180704410	8.75789966218463	-3.38548680049080
C	17.09612880426596	7.99090803209028	-4.06535806448509
C	18.40613369261000	8.36965471750046	-3.47394925446142
C	18.17495772220674	9.31761695521909	-2.47554769106842
C	16.70765600756150	9.57500037780244	-2.38822256226955
C	19.21543599674323	9.85084879149988	-1.73020267646340
C	20.51085470742250	9.40580196280514	-2.02058369434232
C	20.74208650411280	8.45532808553847	-3.02200330483114
C	19.68499676450325	7.91870731735916	-3.76632751482179
O	16.84555233030517	7.17820102266964	-4.93869304579657
O	16.11249594072542	10.29174285080095	-1.60824825851569
C	13.85153204617578	8.47381431997039	-2.43675258297151
C	12.38825635803244	8.26983429450202	-2.79766037852251
C	11.45356656560658	9.25718103939202	-2.47489672120891
C	10.11506487933762	9.11905238316923	-2.84216447499344
C	9.69492987458747	7.99237362887336	-3.54721235786131
C	10.61936238341358	6.99648388675430	-3.86581993695130
C	11.95290654498020	7.12914518362427	-3.48353051198611
C	14.38024485116680	7.35473707430280	-1.55373866826881
C	14.91934091319844	6.17213022034091	-2.07338703061093
C	15.36045669746730	5.15085379578830	-1.23279636295817
C	15.25500996776070	5.33177903248569	0.13846367964860
C	14.73704428578905	6.49313029196986	0.69485654522067
C	14.30517488387942	7.50099897341248	-0.16446998973674
C	13.37924936760442	10.94745505061894	-7.41608451972940
H	9.38021573908827	10.76402883200461	-6.53638311196352
H	19.85253120525781	7.17835814938980	-4.54217709888118
H	21.75873570597541	8.12959007493108	-3.22167258886955
H	21.35244187800263	9.80189647080675	-1.45979161460918
H	19.02523221239387	10.58425639004339	-0.95305988898323
H	7.51258299926849	9.43204544413155	-7.93276990505206
H	8.01233899207496	7.83752005334478	-8.53719010650848
H	12.82028092036101	11.62660902034349	-8.06800602294051
H	14.24626721622278	11.47192725820272	-7.00711726546746
H	13.71467483306711	10.08904863022135	-8.00334955861811
H	11.39437502075185	12.33801352769031	-6.08815218905759
H	11.31711969553363	11.31740859253541	-4.62691409714449
H	12.80624641916832	12.21040141695433	-5.01532390377838
H	6.26712863894740	9.60733424503661	-5.88963348956264
H	5.21238126750049	8.53289995719395	-3.92056912611699
H	5.69942758720934	6.15429715523726	-3.39402262082509
H	7.24318304562572	4.85777619703989	-4.84546002705969
H	8.30992053174383	5.94320762251145	-6.80665557599588
H	12.66094674178290	6.34002958119733	-3.72469179603655
H	10.29961764532838	6.11698046240504	-4.41641797965063
H	8.65693729877763	7.88656338151564	-3.84272011244869
H	9.40078917494478	9.89623039387472	-2.58288493261443
H	11.78518429861495	10.14700560028512	-1.94530808998858
H	13.93024927183464	9.40541238683188	-1.87172764484280
H	14.64988694129328	7.74141054590110	-4.33194982451009
H	12.92134070812876	8.57464664820493	-5.41925802263918
H	13.90901528692613	8.42335478618538	0.25142780087477
H	14.68458429350965	6.60134922801253	1.77306033016569
F	15.68516334071912	4.34114833260436	0.96665552539739
H	15.78579438691582	4.23472760374284	-1.62868331369604
H	15.02358097448652	6.03686549215719	-3.14621530998967

1.8‘
Lowest frequency = 10.13 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	8.48327618094488	9.87072461454981	-3.18917939376852
C	7.86406860609532	9.70592504978310	-4.43276485604051
C	7.07103431927993	8.57544926290540	-4.65607445486116
C	6.90223510126090	7.62321890127223	-3.65139202367672
C	7.53351955597692	7.78849101631042	-2.41757895410345
C	8.32457097457600	8.91420995695603	-2.18715775006965
C	8.08301603780571	10.71370083313879	-5.53933792255208
N	9.26511118685503	10.38909052497114	-6.34883680772382
C	10.57253680799324	10.42351972816216	-5.98884985289523
C	11.25049641189705	9.93943147199561	-7.09165264818278

N	10.33114886719921	9.63809736364184	-8.05641310601621
N	9.12587569528160	9.90617411164597	-7.60977487853255
C	12.74069594373907	9.76597535917184	-7.27665171162664
C	13.38214083243710	11.12938597129451	-7.60490861404069
N	13.22776082237593	9.27458088209120	-5.96139145306316
C	14.52057422175916	9.08674316046586	-5.60406252822568
O	15.49918560731904	9.40140422529435	-6.27249082138675
C	14.74595361087416	8.33431280128372	-4.26335259450092
N	15.81733929125425	8.98108289280989	-3.51486858368025
C	16.79131201914587	8.20585831746130	-2.85874877631195
C	17.74257222809520	9.17478124220934	-2.25366933564397
C	17.31750468078266	10.46370426608195	-2.58443962746967
C	16.07413511180004	10.36317376599817	-3.40226078808572
C	18.01315666635219	11.58512158457287	-2.15910327697492
C	19.16093108844933	11.37668863869188	-1.38437317545053
C	19.58627869165468	10.08487402732110	-1.05343436686523
C	18.87772847277432	8.95791392082425	-1.48676203743140
O	16.79452736192427	6.98688738391035	-2.82803529659941
O	15.39883606293906	11.25796634676044	-3.87109845372298
C	13.58570711678679	7.90591406790945	-3.30473122476467
C	12.57851153676207	7.02021290728421	-4.03912627522015
C	11.23101417824109	7.37562815570485	-4.16649558428603
C	10.34122150398857	6.58874869875112	-4.89882369385948
C	10.82004347813845	5.43088901636383	-5.48970058697614
C	12.14448513963388	5.02664772326974	-5.36483441460317
C	13.01674168101604	5.82862998886735	-4.63544678226767
C	12.92040202951913	8.98635132992918	-2.46974434700274
C	12.71194562827425	10.29916167255160	-2.90342796502878
C	12.04282615454876	11.21840329807874	-2.09188472251819
C	11.56243235276314	10.83952085435399	-0.83975935985863
C	11.76774041300818	9.53196205167828	-0.39521009631193
C	12.44172442379863	8.62006418259019	-1.20363997574391
C	13.04721123374695	8.73518613664600	-8.37416457628234
H	10.89804726264158	10.76120126162438	-5.01740356742111
H	19.19974885307262	7.95188821195369	-1.23713754898746
H	20.48115104693363	9.95723973371958	-0.45147998942259
H	19.73329470716016	12.23038567824518	-1.03356273284606
H	17.67660294917982	12.58292809022360	-2.42182507559434
H	8.21904100297498	11.71945522447579	-5.13089941645610
H	7.24794317562621	10.72541202002770	-6.24190252558245
H	12.64345692602889	9.07608967097597	-9.33033383075517
H	14.12990881625021	8.61284527093521	-8.45532011313733
H	12.58760887784197	7.77270031398441	-8.13239829642614
H	12.93201282059190	11.51832878186964	-8.52287125480014
H	13.19822879603017	11.83970569551647	-6.79355190930606
H	14.45887068519399	11.01765639885634	-7.73887948484483
H	9.10074927670807	10.74566364396679	-3.00067812731516
H	8.82513894755517	9.04821476262193	-1.23338010666352
H	7.40862093473031	7.04219606701361	-1.63856109190779
H	6.28390990339832	6.74919077818613	-3.83430412898502
H	6.59282062214388	8.43928574117586	-5.62274518427222
H	14.05257257544110	5.51785903695896	-4.52550148570404
H	12.47497171443930	4.10417758844402	-5.83036311148790
F	9.96604865274805	4.65448471629797	-6.20563339254128
H	9.30009439771701	6.86938248993679	-5.00543812961297
H	10.86197746223504	8.27679429566489	-3.68880789373089
H	14.10215838431824	7.24862741805305	-2.59246719204257
H	15.19221243847344	7.38750875578184	-4.59014680277429
H	12.52867025559450	8.78902895065285	-5.40828968605459
H	12.59936605879999	7.60249948714010	-0.85289569970012
H	11.41128054560164	9.22515457789286	0.58436355555706
H	11.04536868695740	11.55754390678044	-0.20938566293917
H	11.91258018955142	12.23980948839420	-2.43982796797179
H	13.10273970499279	10.62127323707577	-3.86054045204761

Leucin

127a
Lowest frequency = 5.11 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	6.63411140493253	6.99259734415755	-5.52136017309786
C	7.17911350928269	8.28604683795931	-6.14389348677826
C	6.97724124316452	9.46521644908347	-5.18273612184045
H	7.43578835182171	9.25387524994367	-4.21083621810656

C	6.50579343796466	8.50579650902518	-7.51141795696099
C	6.98193337402138	9.74402384552274	-8.30512458719487
N	6.09845001927271	10.04443652443081	-9.42482228099868
C	5.79608740436172	11.37995932706286	-9.75655542863630
C	5.01533538574988	11.31932070171295	-11.02118850627913
C	4.91642288570960	9.98163801016466	-11.40646995714000
C	5.62191825582247	9.13734214937145	-10.39688243722171
C	4.24152242853165	9.60909677902740	-12.55916840991872
C	3.66419697823795	10.62810724169447	-13.32633956877619
C	3.76370498803795	11.96992818829845	-12.93935765340858
C	4.44458940186341	12.33638946128971	-11.77257397973701
O	6.12967826533540	12.35080340576557	-9.10005763757336
O	5.73924179186537	7.92796161544929	-10.37904455183137
C	8.43107014455816	9.60859027196014	-8.83461193415458
O	8.68536449362865	9.31463527117643	-9.99896668664995
N	9.35197222045387	9.81383659802874	-7.86003819351944
C	10.81924087405217	9.66031225300962	-7.97128798342010
C	11.18000890143920	8.31020435577850	-8.60936550329986
C	11.29655953380223	9.70599189416702	-6.53788734606022
C	12.21700012713830	8.93674717252774	-5.85989117691646
N	12.17825594160442	9.40107892664276	-4.58172657215700
N	11.26528613047683	10.39518585911560	-4.45827778053984
N	10.74155791617281	10.58293623412100	-5.64490439359611
C	12.80605165033133	8.83824002536897	-3.38427311959363
C	12.19322646233953	7.50252617477421	-3.01447908311967
C	10.80235078207448	7.36637707680071	-2.93081745390123
C	10.23738630603924	6.13912663469599	-2.59421226053328
C	11.05531364480019	5.03709670155611	-2.33362953359971
C	12.44058539716269	5.16802614350867	-2.41411957258575
C	13.00656966076100	6.39708729983400	-2.75776584029529
C	11.40731067945514	10.82843424811848	-8.78976325422845
H	12.85409620822593	8.11829344271081	-6.15443200033958
H	4.52810361477405	13.37352250259372	-11.46334834820904
H	3.30535961335346	12.73693706418561	-13.55685602010452
H	3.13046748593826	10.37650738385637	-14.23826611060533
H	4.17075850094198	8.56589672722759	-12.85054874708517
H	13.88039095270049	8.73772477870727	-3.56176056969124
H	12.64891201264136	9.58564932598141	-2.60176499521978
H	12.49610066244805	10.73301725593974	-8.85566078111028
H	10.98358391722640	10.81067256796583	-9.79729720619336
H	11.16467506809543	11.78082692794428	-8.31127970441879
H	12.26906579697825	8.19866439827668	-8.63792522280841
H	10.75361310230903	7.48558316961025	-8.03013859305389
H	10.79193603257638	8.26483322455671	-9.62723015424541
H	14.08760598452574	6.49575120504382	-2.82858495642164
H	13.08209557862777	4.31389744137070	-2.21746099806886
H	10.61276416621910	4.08016502825816	-2.07300423495510
H	9.15721561165896	6.04104964618015	-2.53457565121846
H	10.16645886269580	8.22331357218863	-3.13827430797619
H	5.42564149464124	8.62597517052434	-7.35279496844870
H	6.63597749333834	7.61740246608123	-8.13406830275029
H	6.92966584874639	10.63566761205140	-7.67049132456256
H	9.04345790041979	10.22409725812981	-6.98406819866567
H	5.90823031578277	9.65013223908315	-5.01968284478096
H	7.42141279445660	10.39746389308914	-5.54893661053010
H	6.79243546559694	6.13690414695086	-6.18647912429291
H	7.13076040415602	6.78069725921186	-4.56773111351369
H	5.55738367451194	7.07628551945828	-5.32910543637460
H	8.25541644414771	8.14719299167797	-6.30365083068486

2.1
Lowest frequency = 11.11 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	18.56114932100573	3.45152045532004	12.61309602935112
C	17.57221455971306	4.40582255413508	12.86300714815648
C	16.22662997786359	4.06921954152997	12.67491813202873
C	15.87952344285778	2.79242394436953	12.24150743180397
C	16.87085037242884	1.83896055257408	12.00090292204188
C	18.21221340369431	2.16858776704454	12.18927168634560
C	17.96021669860811	5.78734062489743	13.33930758338241
N	17.25880361934907	6.83640363130482	12.58925607828110
C	17.07575619964387	6.94283375576250	11.24973524402436
C	16.32861665313415	8.08410305923551	11.06928921270550
N	16.10361044429093	8.58666375462015	12.32591039264699

N	16.66297665403692	7.83695673376147	13.25162292272832
C	15.73312156726271	8.63152952528262	9.78938057718164
C	15.79110257568870	10.16269643192970	9.71905750957961
Pd	15.10289416739764	10.21600479374779	12.90635896499430
O	16.68992270425142	10.81214737263952	13.93381324853319
C	17.82469486761735	10.98979966118646	13.28976357112973
O	18.02829249311246	10.77523288367173	12.09565299231766
N	14.29762499761468	8.23246506220984	9.75435913591861
C	13.90331487303635	6.92950288576464	9.76446583405788
O	14.66353613231531	5.97296544351310	9.62861118086272
C	12.37904916523068	6.66681608163380	9.88278245385205
C	11.48119782449334	7.87009809107065	10.19896398287616
C	9.96884262434351	7.54942372489123	10.25418546346610
C	9.51325242705652	7.10904235897198	11.65375751464216
N	12.21642804107746	5.56229792557146	10.82380622085039
C	11.63732277528823	4.32609088602137	10.48393083277523
C	11.78989632150466	3.47173643877372	11.69779655331344
C	12.45060089526565	4.21643136991800	12.67903129263701
C	12.76581885038723	5.55798593562955	12.11287172274175
C	12.73276773998093	3.68324544302480	13.92778258472257
C	12.33815295051441	2.36160877193349	14.16839130508231
C	11.68256120604852	1.61314428932873	13.18398272499798
C	11.39500892328850	2.16234234561186	11.92781055817193
O	11.12114888829498	4.06303208616938	9.41433978080073
O	13.38069259568794	6.48284372778278	12.61464477775982
C	9.16123846728477	8.77908152779131	9.81341252924979
C	16.47803321483748	8.06457440072993	8.56896856718111
O	13.75234296498718	11.74085508114655	13.32793999119183
C	12.86080665436196	11.15643585426666	12.62530029999249
O	13.18744202025390	10.04932256849006	12.05476126524331
C	11.47904420313494	11.71660175068236	12.48316530325577
C	18.90907580755428	11.54041568692531	14.20946682693052
H	12.07901197770377	6.24247811014571	8.91661167176402
H	11.65130971708125	8.59864384284563	9.39579642647535
H	17.43730027287083	6.20453688561989	10.55511236742262
H	10.88615895954264	1.58935209765211	11.15916347707180
H	11.39242326295794	0.58922597245061	13.40043726420344
H	12.54623629801239	1.90668410592764	15.13220882822940
H	13.24692112911363	4.26969798986496	14.68262488986854
H	11.79739397420591	8.34230860934555	11.13486889926702
H	13.66200604975215	8.90528939570639	10.17705176149455
H	19.03850202127096	5.94327347691751	13.23517892153335
H	17.68663998109620	5.95786690470336	14.38408615777509
H	18.82087066222905	12.63220173782016	14.23708674152870
H	18.79447188452582	11.16481268226361	15.22850916609466
H	19.89010068358298	11.28032239512773	13.80740633236795
H	11.15147785446535	11.64317718456011	11.44267806838823
H	10.79016765925237	11.12380979482602	13.09536131496064
H	11.45488917682762	12.75395409736127	12.81986368718835
H	15.45705838305761	4.81577499373460	12.84697734956561
H	14.83493202526504	2.54246034532226	12.08601628814711
H	16.59740048823127	0.84508630947272	11.65863088764757
H	18.98835819481589	1.43381919484515	11.99587633036491
H	19.60829585298827	3.71372904521661	12.74658502714779
H	10.01747883724046	6.20058021916684	11.99141938408508
H	9.72135002436156	7.89842642021289	12.38636962892068
H	8.43515006166642	6.91464688957094	11.66283658732818
H	8.08539378467850	8.57512106213111	9.84507845887512
H	9.35988991501853	9.62897176205390	10.47851457938227
H	9.42171563794202	9.08071772570545	8.79281231778081
H	9.76234836461964	6.73376947564390	9.54750508166644
H	15.41485808814759	10.48719722098430	8.74369075320577
H	15.18834922069687	10.62668800930812	10.50744279166759
H	16.81839763624918	10.50207077647883	9.85916117170870
H	15.99612936666314	8.43567142195050	7.66019775400776
H	17.51239822692292	8.42058193393169	8.58601765898008
H	16.45851004114423	6.97517713026640	8.55171462407848

2.2
Lowest frequency = 8.16 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	4.68166198384252	5.53377952434549	-9.79725460094118
C	5.85310440618095	5.92109797597226	-9.13559057091043
C	7.06683776889865	5.32252426005835	-9.47980480462002

C	7.11510617173845	4.34920952444528	-10.47924764268024
C	5.94600220131821	3.96619389955347	-11.13397115372542
C	4.72869108574744	4.55967861109346	-10.79055425076815
C	5.80176487826489	6.97443156998069	-8.05312293411013
N	4.92686565792749	6.56692970455223	-6.94265410371429
C	5.02899503013958	5.46921323886594	-6.14005729688142
C	3.94218571918365	5.53853230037668	-5.29809968430587
N	3.26324947811541	6.66719849142047	-5.65741495165250
N	3.84367320607276	7.30353917428624	-6.65322966028216
C	3.38655702477248	4.70366532144886	-4.18213998047500
C	2.65754649148835	3.47460623283326	-4.77059038948245
Pd	1.58711206001257	7.01511264111092	-4.67747063367643
O	-0.30075312185665	7.41601562370393	-3.93685627415443
C	-0.50834773425211	8.25003459821812	-4.89267352963466
C	-1.79296978843655	9.01125572660550	-4.97771030869126
N	2.43196397744473	5.61909180832807	-3.48712002287331
C	1.92927110784756	5.22110056109023	-2.29135604140489
O	2.09214596893980	4.08798118972430	-1.81718047737319
C	1.17817020647589	6.30032780958871	-1.46255697169192
N	0.80536777686185	5.68801588170636	-0.19288377602486
C	-0.50837117691915	5.27526602980224	0.07994387783008
C	-0.44249654197834	4.54256724064884	1.37595229264915
C	0.88847017557668	4.51881849136327	1.79490440240343
C	1.71458739814445	5.24431436775955	0.78593903974542
C	1.26344371498501	3.90144007633510	2.97861749313574
C	0.25536774337291	3.29596055731546	3.73853204313722
C	-1.07976529366746	3.31995566075906	3.31800995429213
C	-1.44935000701535	3.94974905502326	2.12353023934133
O	-1.47871943308719	5.50526926856358	-0.62109293702698
O	2.91128269566291	5.46378778686707	0.80762578047573
C	2.00302815968286	7.59288790107096	-1.29613117945634
C	1.35297739044432	8.75491831996697	-0.51119945796462
C	-0.03273638474135	9.13503036440149	-1.04805011415912
O	0.43553541674583	8.40845469292800	-5.74216578735272
C	4.55268439912505	4.27417155947980	-3.26658842530092
H	0.22992552365948	6.52602345411325	-1.95811414553001
H	5.83157144340856	4.75727832983626	-6.24293422347102
H	-2.48153165438340	3.97467334854369	1.78822325656487
H	-1.83873739149517	2.84084987389583	3.92991109781441
H	0.51024929775091	2.79818038702844	4.66984354626647
H	2.30162680488374	3.88927336764597	3.29553060652458
H	5.37779914635979	7.91511367029972	-8.41187380085921
H	6.79994488716703	7.16967492716774	-7.65095488415217
H	3.35560067342648	2.84504781840574	-5.33431988676599
H	2.22833700024160	2.89923914210205	-3.94870353419039
H	1.85678021611870	3.80304529594177	-5.44039734097400
H	5.30173130971641	3.73669424457648	-3.86007475855372
H	5.02163153437927	5.15506891728059	-2.81904659123767
H	4.18630923737000	3.62398495391962	-2.47440172080656
H	3.73367750488788	5.99326307426759	-9.52821508965689
H	3.81622256107465	4.26367464262296	-11.29954152761583
H	5.98053757258140	3.20693974281441	-11.90963322884473
H	8.06372806128378	3.89024156512836	-10.74156711867884
H	7.97845309889163	5.62018364852655	-8.96650627182826
H	2.96644934857350	7.34033841293568	-0.84353352721260
H	2.21028395501652	7.94332067218855	-2.31523803283143
H	-2.63160864838436	8.34974849024012	-4.74656751493801
H	-1.78094797184647	9.81002511702494	-4.22744386746794
H	-1.90759810424991	9.45187142666688	-5.96928512554319
H	-0.41733153182185	10.01543129256151	-0.52024812137044
H	0.00905509378490	9.36579754920804	-2.11694601073452
H	-0.75221584982472	8.32031747760486	-0.91116062796731
C	1.30930904038583	8.54400763270868	1.01117518429070
H	1.06498398006644	9.48792518177801	1.51217526475129
H	0.54428312995935	7.81606058463563	1.29715329269394
H	2.27281170747741	8.19240748823609	1.39330539635674
H	2.02018521048146	9.61161022850049	-0.68779685570763

2.3
Lowest frequency = 3.85 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	6.57803012527608	11.29115202641159	2.81459158305840
C	5.81577021868759	10.25822228859186	3.33916602013899
C	4.60155059574867	10.50269968476836	3.98645668982676

C	4.10564774401240	11.78956796178227	4.13248152943469
C	4.86734500662381	12.83861109777073	3.60355020370654
C	6.08361919699414	12.59349021854800	2.95554838439725
C	4.03646970190401	9.19695541445037	4.43000271252762
N	4.97748718077789	8.22946426876082	4.04274783739127
C	6.06447995147279	8.78857487702698	3.34596058941442
C	4.73619081738383	6.79936372442473	4.13138923938149
C	3.51054093328800	6.46655619204123	3.23704063056906
O	3.29486489911691	7.15097090825627	2.22625944739235
O	6.99582140073465	8.16021131433489	2.87887071237388
O	2.99846297559304	8.96304234154345	5.02372394377582
C	4.61907958731752	6.33174070120589	5.59103504042889
C	5.71721721314544	6.84677154985409	6.55514121784745
C	7.11530151599989	6.37295843763217	6.14343382677327
Pd	3.18534280559261	4.43845380813335	5.34436690432815
N	2.79570021849230	5.40017933107093	3.63779533333224
C	1.61780626522532	4.96159316946151	2.84109098803998
C	0.53329996164571	6.06205563255996	2.81893176159111
N	1.65635106585627	3.34553298716738	4.73016262895626
C	1.08487012131756	3.75114065423055	3.55359922783076
C	0.07401089918929	2.85118850340892	3.30033474751913
N	0.11015556065285	1.97362499497393	4.34221892203005
N	1.07978538812992	2.26788549041828	5.21891310131366
C	-0.74158781415909	0.79398168173952	4.57274605315004
C	-0.76897123615387	-0.10947735531551	3.36287305597015
C	0.40952714679837	-0.71220051695516	2.90615408851243
C	0.38519436494071	-1.53536234023893	1.78388067476524
C	-0.81651632165886	-1.76615850074811	1.10941043929865
C	-1.99268189066317	-1.17006944065286	1.56058292026137
C	-1.96700865716385	-0.34093242986763	2.68335060274058
O	3.46803665531275	3.38695623008270	7.05407278534172
C	4.70308841293026	2.97738087726615	7.18733983724647
C	4.93269145534365	2.13745027262798	8.43272184371720
O	5.62318156149564	3.25889671202428	6.40611995487519
C	2.03276078204896	4.56037738217942	1.40827993230424
C	5.38817313878857	6.44619642931190	7.99670142794611
H	6.10596203465913	6.90059372365246	8.68789744927602
H	3.64602032837853	6.63618841914228	5.99670193232136
H	5.61065605216848	6.33674275082436	3.66022330243876
H	-0.62948006039546	2.74982073359043	2.49009680294643
H	7.51919420164805	11.09028129967558	2.31258576934363
H	6.65057491819390	13.42888551429902	2.55512325906866
H	4.51037210180792	13.86032041155726	3.69520039772697
H	3.16081021711857	11.96938883218808	4.63563046575220
H	5.88974366965007	1.61920861686532	8.35836464537560
H	4.94998046621005	2.79700237697848	9.30792184997597
H	4.11671281632377	1.42374000873297	8.57278549459605
H	-0.31038396506418	0.30491078122176	5.44905418603497
H	-1.74851588382025	1.14013125172546	4.82394250999467
H	4.83278937826985	5.20196270756811	5.61740370077193
H	1.16470772249596	4.17822926063834	0.85920430915052
H	2.43042182117276	5.43529423813322	0.89328023478844
H	2.79873086030845	3.78054058578624	1.44526603948536
H	-0.35370827561620	5.70765569565326	2.28163802993750
H	0.24869747353198	6.32718813831048	3.84091692851729
H	0.93388738820639	6.94393982041096	2.31749456067736
H	1.34571133774872	-0.53038855753365	3.42837704580413
H	1.30288541695205	-1.99949934258346	1.43516586093517
H	-0.83342533115165	-2.40922770820156	0.23450457322236
H	-2.92915364191180	-1.34601173715823	1.03963131825913
H	-2.88390644461115	0.12670058462142	3.03499842742568
H	7.37514491127009	6.70082340791083	5.13195146796872
H	7.86595302741024	6.78021709129017	6.82952947055067
H	7.16866714708391	5.27977504467457	6.18345163437500
H	4.38248032676630	6.77350577473765	8.28186219500962
H	5.44461111680265	5.36074438215260	8.11617010772899
H	5.67588192035432	7.94212131285313	6.48885719103179

TS2.(3-4)
Lowest frequency = -1212.27 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	6.77970691561863	11.09131511836895	2.84177967968511
C	5.94907305688246	10.11250886281217	3.36617388620033
C	4.72556147958575	10.43406039192364	3.95828512224800

C	4.28758560068844	11.74668209892894	4.04792625509264
C	5.11847541248466	12.74198210344243	3.51904246004903
C	6.34454329645520	12.41959679956963	2.92577334902598
C	4.07959781594604	9.16928728136486	4.41320324960063
N	4.98752333100711	8.14630006813960	4.09648177990795
C	6.12203165487583	8.63254233107411	3.42423995185554
C	4.66507404742066	6.72549185040144	4.20041545915555
C	3.47273531668504	6.44754048898310	3.25209246635389
O	3.29821108804611	7.12909256508137	2.23177394133228
O	7.03925173758770	7.94903727487175	3.00661963746661
O	3.00521451222248	9.01048114787618	4.96589189484397
C	4.39346083727690	6.26614934582824	5.64194019894221
C	5.36981021637222	6.86823211644598	6.69490035501358
C	6.86916768233487	6.66449759140212	6.43729429654117
Pd	3.16411403996577	4.47920578732903	5.35549953412498
N	2.72171966932324	5.41149954825106	3.66148221372338
C	1.55674725483031	4.95625962544507	2.86469777891579
C	0.47078206701359	6.05374477590044	2.82908103180300
N	1.63006993716531	3.30439823986317	4.72750469380270
C	1.03232166810846	3.73881255061977	3.57469510440425
C	0.00912930745873	2.85330733286483	3.31785376352888
N	0.05982941729828	1.94868726031618	4.33506134426929
N	1.05187140401162	2.21870872211706	5.19787376202023
C	-0.79090992529741	0.76879298875831	4.55232768918875
C	-0.82312254523699	-0.12441397759407	3.33409042663426
C	0.36240192419098	-0.67063690812553	2.82757460335410
C	0.33168030201210	-1.48936185460989	1.70221412294039
C	-0.88367193915403	-1.77273560564814	1.07397866920746
C	-2.06679767504140	-1.23254942274274	1.57441865860513
C	-2.03465616983249	-0.40741164887113	2.69996896518898
O	3.68214418719504	3.32050924512781	6.99950160910412
C	4.94327408847480	3.20141290475800	7.05531692715624
C	5.54544619233795	2.22125767587585	8.02631367477905
O	5.73911536901188	3.90053080711296	6.33280596141672
C	1.98304673532997	4.55487128057430	1.43437054752943
C	4.97331496932063	6.48150131221700	8.12413873058497
H	5.51820637779520	7.09985031760283	8.84612833479911
H	3.41767578756725	6.67264405639458	5.93979408343518
H	5.54127970684141	6.21500056694217	3.78410192431729
H	-0.71180301343006	2.77815811184091	2.52008587117957
H	7.72773753354796	10.83056483686414	2.38185235676987
H	6.96568325757716	13.21447718290014	2.52302133799710
H	4.80824299589858	13.78187366668408	3.56696356784329
H	3.33402550343844	11.98604961770201	4.50812718946034
H	6.30735184346114	1.62341942602330	7.51962794487889
H	6.04264254155976	2.77938394871442	8.82699441521941
H	4.77399394653765	1.57998472731316	8.45242542589584
H	-0.35821885990513	0.26846145144394	5.42193807750753
H	-1.79808375377816	1.10936585616240	4.81056297687939
H	4.97838861499088	4.83721265067513	5.84878618227580
H	1.12097738137900	4.16527671959129	0.88104219095507
H	2.37997273473901	5.43116716968514	0.92084676261706
H	2.75395472252420	3.78005184205895	1.47800431837652
H	-0.40937986827989	5.70251247835364	2.27825671606434
H	0.17275281789948	6.31846834424213	3.84727301727188
H	0.88009844018980	6.93623113600410	2.33460433758110
H	1.30915666580656	-0.44691701080037	3.31312917274441
H	1.25538489621882	-1.90846328935934	1.31432647763172
H	-0.90556359925541	-2.41167530938517	0.19614799598072
H	-3.01401410338088	-1.44776976816694	1.08878820211658
H	-2.95712608251782	0.01802568448988	3.08862261218830
H	7.14297121339018	6.91760763943253	5.40854672505464
H	7.44176263312099	7.32026963042934	7.10360646936442
H	7.17720773991830	5.63433245973418	6.62804407909192
H	3.90052393420718	6.62818573325752	8.28916278508266
H	5.21054478234869	5.43631481586518	8.34013997644175
H	5.18189092961339	7.94857923125070	6.60872267738157

2.4
Lowest frequency = 6.04 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	6.81672432372377	11.41246500061801	2.96434357652008
C	5.91959497485781	10.44549383796291	3.39246021081056
C	4.67511581672079	10.78897440450913	3.92524116215310

C	4.28214366530197	12.11284075011409	4.04948344211843
C	5.18034728328167	13.09676219705879	3.61780173904069
C	6.42751381215837	12.75230246525035	3.08404919959540
C	3.95754282807340	9.53188210646426	4.29198039580784
N	4.83724451245655	8.48812323468703	3.95831443177146
C	6.03421425732973	8.95804512108388	3.39735829996941
C	4.50184504708154	7.07005427672099	4.06186922322598
C	3.26979543670997	6.76301526221243	3.19453566750024
O	2.97642709291254	7.42418427231048	2.19090019918109
O	6.95719715018753	8.25799817447048	3.01781191073497
O	2.85765992746530	9.39893385275281	4.79652937824586
C	4.34174022914801	6.59988329136250	5.51262184854899
C	5.67470753877602	6.59497898970093	6.27278243201187
C	6.61797970630232	5.45935664695882	5.85626976705441
Pd	3.17692601541253	4.90834541718795	5.39916833287602
N	2.63603429078880	5.66541084064532	3.65857974544396
C	1.45480240251641	5.11417959594931	2.95690457178955
C	0.28640583662607	6.12527254522278	3.00244207780081
N	1.69330882575535	3.49350125537266	4.85518783625214
C	1.06355958913491	3.86015679698351	3.69615802278772
C	0.11868193098244	2.88891230026513	3.44315903956354
N	0.23877007900032	1.99997830786920	4.46700992668981
N	1.20436142214345	2.36503539344670	5.32905953124726
C	-0.50054468389438	0.74823416448753	4.68048411469918
C	-0.41374204229725	-0.16158873663087	3.47659292707091
C	0.83327120569519	-0.57483526443565	2.99230107039219
C	0.91201434091248	-1.40745249646677	1.87951654022512
C	-0.25410854018417	-1.83785483269127	1.24152866341601
C	-1.49799722939956	-1.43052713834606	1.71989819358410
C	-1.57597357254285	-0.59143499654853	2.83282885902018
O	3.68790357723256	3.98555187665375	7.24570191347409
C	4.24177529250685	2.87984123688548	7.15652376866366
C	4.53167950409726	2.01904897094592	8.34492802334321
O	4.62645389425228	2.37148170251874	5.99112609253736
C	1.80145199933474	4.74349769825644	1.49740886581167
C	5.47458423887293	6.63519759694260	7.79297752341303
H	6.43906145178862	6.71397317052567	8.30871629490559
H	3.63397821783672	7.27455395886941	6.01274377131505
H	5.34917083145221	6.55625871435705	3.59252203808801
H	-0.58978928725482	2.74625079904409	2.64329552222122
H	7.78132783500414	11.13436401106170	2.55123241133294
H	7.10190688794090	13.53872395422327	2.75739209797081
H	4.90707897200293	14.14516292174343	3.69664234722855
H	3.31228750857157	12.36930841780213	4.46426093632741
H	3.95686706108970	1.09066043859555	8.26490079091337
H	5.59259045481801	1.75296510364191	8.35724988266069
H	4.26006130556054	2.54712850324379	9.25774858576152
H	-0.04625032065608	0.30192471850839	5.56858350575006
H	-1.54288558119074	0.99163552366829	4.90732932134637
H	4.36378110304014	3.06796486952836	5.30301728663332
H	0.93348040254886	4.28858240342012	1.00635072428841
H	2.09104464728120	5.64675995826346	0.95927476031251
H	2.63067204525189	4.03004363264925	1.47956428998251
H	-0.60199234157147	5.70746591146264	2.51466276691667
H	0.04314598441435	6.36680424572475	4.04086648818492
H	0.59159582218229	7.03659862711724	2.48522596921257
H	1.74148503718331	-0.23512693043149	3.48424437514540
H	1.88292426595649	-1.72185537742315	1.50820569720985
H	-0.19065213109792	-2.48647492236200	0.37285164662139
H	-2.40763456346618	-1.75932924475354	1.22606538988763
H	-2.54640657347254	-0.26853770125864	3.20298173691472
H	6.76255301882871	5.43480327881301	4.77149050971695
H	7.60369200644771	5.58449763791145	6.31909702131331
H	6.22099076040696	4.48724795430690	6.16652711936223
H	4.86515366943895	7.49986102006500	8.07872292729008
H	4.96632711880664	5.73571001695558	8.15128323268288
H	6.18013441142324	7.53666026597460	5.99739002811108

2.3a
Lowest frequency = 6.49 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	0.35099414938569	-0.31757468862928	3.97053725664100
C	-0.82021226370609	0.43661195633196	3.82898980908702
C	-1.79850268139733	0.02204708909834	2.92260638948867

C	-1.61449741125625	-1.13667527940671	2.16621576416859
C	-0.44609250668110	-1.88257235268301	2.30981614489179
C	0.53690548596260	-1.47070102026830	3.21329853827651
C	-1.01660216476835	1.69548458508808	4.64036290336942
N	0.01251789902802	2.70111618264240	4.32696277941317
C	0.37045701175351	3.19191330162113	3.10704533751528
C	1.38966391753743	4.08130996268039	3.36403467740710
N	1.57233357784213	4.05594105851299	4.72034453595682
N	0.74837680769955	3.22232834643886	5.31827422879492
Pd	3.06477768648442	5.17881366730355	5.38906980441204
O	2.74738841422420	4.66242869797882	7.32158817172223
C	3.05268974449367	5.57297446988078	8.21332310778481
O	3.57861572153665	6.66323714524108	7.96250661112266
C	2.23114622634345	4.99071315946822	2.51572379422084
C	2.88623510343111	4.17709894720617	1.37966280604528
C	5.25724543579353	6.39770093287495	5.37746748171763
C	5.09617762508493	7.07122708872672	4.00822837751361
C	4.12573429193054	6.46380659258349	2.96947223511496
N	3.25898814855731	5.54796358564347	3.43714508994362
C	6.24765201234674	5.22140820196143	5.43202680386980
C	6.29938548058067	4.63335221888327	6.84753339144234
C	6.01578734869170	4.11844428991785	4.39396176605998
N	4.77052528482731	8.49241610459059	4.15772279839123
C	5.73657012551792	9.50289532641650	3.98361224160195
C	5.00765083885504	10.78885936818174	4.17041087725769
C	3.66926838156300	10.49770289349157	4.44406630543846
C	3.49542094224246	9.01681779087506	4.43825273890212
C	2.74129437320830	11.50239237601582	4.67210205574409
C	3.19619101118850	12.82531471790083	4.61479412239553
C	4.53718036977148	13.11726802489893	4.33958514342978
C	5.46788516121477	12.09597090084227	4.11333201342780
O	6.91409853673437	9.30828191025633	3.74439990656533
O	2.48641341713267	8.36467414210669	4.63165630384844
O	4.20712810069575	6.85400464390584	1.79456792334073
C	2.67744620179752	5.17049684288359	9.63097391840588
C	1.32659193073535	6.11272984489084	1.95263963636759
H	7.10582218032825	3.89645167465187	6.92542419312860
H	5.64419050016393	7.16670071270278	6.06020902536091
H	6.08248225459783	7.07778469859625	3.53053427389925
H	-0.10241223944885	2.86384255578097	2.19578495946603
H	6.50997556608141	12.31215046612047	3.90019791941487
H	4.85872881585209	14.15402904643948	4.30234723245436
H	2.49931161789214	13.64034140468049	4.78748733158832
H	1.70433333223102	11.26482459610972	4.88750191565517
H	2.83811028221316	4.10148046280341	9.79018603338403
H	3.25409172168073	5.75910774583557	10.34648345429360
H	1.61180968707977	5.37621926087941	9.78297506881593
H	-0.91738132391337	1.51938255221584	5.71375673926667
H	-1.99911916079169	2.13532298217551	4.44572136398773
H	4.29626701886504	6.29247558608524	6.01805710580966
H	2.11553846094811	3.71999528319958	0.74846679871923
H	3.49906678895666	4.84443841629373	0.77284350542358
H	3.51450094643942	3.38548202876016	1.79814429492605
H	0.51762597978621	5.67655213184204	1.35567913383458
H	0.89696357077511	6.68919074317284	2.77603301796439
H	1.92632230775055	6.77391016607508	1.32645194938033
H	1.11770453457745	0.00426716362692	4.67108128108667
H	1.44762820261621	-2.05093098471909	3.32825102838173
H	-0.29929203211548	-2.78274454243968	1.72035166672093
H	-2.38146791259434	-1.45229844477378	1.46515034767616
H	-2.70897317795943	0.60624432716593	2.80946330824881
H	5.98962712964039	4.50807723654185	3.37195916556238
H	6.82168929821523	3.37876168076304	4.45733141675438
H	5.06250014177617	3.60872489517359	4.58172104633944
H	6.46495510942787	5.41158137355895	7.59931994152223
H	5.35321943891880	4.13308597283853	7.08363230268080
H	7.22469622362642	5.67907278149011	5.21312238715631

TS2.(3-4)a
Lowest frequency = -1093.70 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	0.50148574655604	-0.29285759953739	4.04084671698339
C	-0.72606835662691	0.34478384036864	3.82485417060975
C	-1.64736658041476	-0.22053138973946	2.94084541202064

C	-1.35163293743238	-1.41468406994954	2.28114358239440
C	-0.12787260598473	-2.04485322021374	2.49883942804725
C	0.79880786928379	-1.48111770248793	3.37944072916494
C	-1.04749917337346	1.63777707478787	4.53892212905194
N	-0.05902690838529	2.68307230796503	4.23568006904641
C	0.28528800708221	3.19698413059479	3.02174195583698
C	1.29103576400851	4.09941753995292	3.28850614511062
N	1.48584299450803	4.06152451118343	4.64221165310438
N	0.67779042890750	3.20343730560374	5.22897248188182
Pd	3.03312158105322	5.20344427048705	5.29106360821991
O	2.70359072483675	4.76971858462381	7.28721108420791
C	3.02794427831817	5.73759829649341	8.05533488858802
O	3.60374615559526	6.78654191364742	7.63601418841148
C	2.10546464018022	5.03563314830302	2.44190796393149
C	2.73372431924224	4.26152686787203	1.26441002722435
C	4.97513886452736	6.25807267675330	5.30434448232296
C	4.97015961519218	7.02821823248944	3.96993131597162
C	4.00494762688538	6.51669404854739	2.88841932613978
N	3.15925201105217	5.57215186748647	3.34176733044471
C	6.02470335929694	5.12156764348877	5.35433771566130
C	6.08077191079852	4.48246340489602	6.74731335347179
C	5.87747450802018	4.04682576024554	4.27073908786542
N	4.74092577336841	8.46071746717841	4.17332527271203
C	5.79512118969092	9.39364493768933	4.15079225630717
C	5.15965791570778	10.72386153829227	4.36805185717177
C	3.78391118260567	10.53224484178730	4.51069758141153
C	3.49309529713544	9.07388626534952	4.38776327397418
C	2.92377650711836	11.59686891810057	4.73249512403283
C	3.48703110663254	12.87669119731260	4.80680171280381
C	4.86604766586062	13.06875682841712	4.66328112324957
C	5.72719873715419	11.98723864322180	4.44108074216822
O	6.97074342503794	9.11696898923940	3.99526858806937
O	2.42094341280372	8.50294018939473	4.45927484261015
O	4.06638844016036	6.95894013963672	1.73276946882659
C	2.73288913331377	5.59929136560639	9.52823391415150
C	1.18304604971919	6.17042386213077	1.93596112380690
H	6.92181793967636	3.78348369009454	6.81340303100977
H	5.34663861681323	6.98989986320374	6.03694474272965
H	5.98102114878702	6.98517480614801	3.54503393974898
H	-0.18739278768189	2.87553572916948	2.10796581682810
H	6.79792677877532	12.12551733469478	4.32878156716282
H	5.27226262378944	14.07413976466358	4.72603939719000
H	2.84572063297874	13.73629331002422	4.97901857782134
H	1.85596089502490	11.43655086188537	4.84351852426999
H	3.67697359358715	5.43923133639295	10.06021192919335
H	2.29341444854903	6.52657388278651	9.90384547908203
H	2.06664310234836	4.75617369225935	9.71215219106227
H	-1.01383325974411	1.52853397415634	5.62546133464148
H	-2.03768293505385	2.00433147306245	4.25331611459332
H	3.93910739683144	6.43073039466349	6.31738147524915
H	1.94967391488814	3.82384936233207	0.63566308110619
H	3.33043021467045	4.95128547989401	0.66609614057030
H	3.37414828591395	3.45877767297162	1.64104173294113
H	0.35953079938849	5.74893571002986	1.34824425621894
H	0.77510969080946	6.72226622200255	2.78663953824385
H	1.76472961595571	6.85223601724852	1.31463307547941
H	1.22446106315375	0.14760634786573	4.72309142997564
H	1.75331887180129	-1.96980624307503	3.55100998592484
H	0.10609522216348	-2.97192647618038	1.98391097684014
H	-2.07486135558786	-1.84744366217777	1.59623231186420
H	-2.60085402914526	0.27377552761526	2.76857157563817
H	5.83546393636977	4.47813692745836	3.26608451462345
H	6.73205480279442	3.36136040651815	4.31212492481002
H	4.95907650915370	3.46811434763170	4.42266162524451
H	6.20372884609627	5.24087454384690	7.52836981526632
H	5.15839985112835	3.92792091122317	6.95218160716997
H	6.98866088632869	5.62772916437142	5.17975656049167

2.4a
Lowest frequency = 6.83 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	0.80069638793063	-0.58237521516153	3.02867262301715
C	-0.46861900282784	-0.14623810873603	3.42715893408445
C	-1.59535372208602	-0.58563205716991	2.72911078793388

C	-1.46048438282131	-1.45732266508496	1.64710051265372
C	-0.19463375218437	-1.88792827120887	1.25439860206112
C	0.93624789885781	-1.44774288910446	1.94678322616719
C	-0.61645259544124	0.79734116106879	4.59877293250204
N	0.14428665826654	2.03757939932797	4.39536220729787
C	0.07302963988543	2.91369724289494	3.35592186503436
C	1.02094245598724	3.87570216987497	3.63116484385739
N	1.60758840437384	3.51395144961689	4.81426025298190
N	1.08518697551456	2.40031654033865	5.28587544070977
Pd	3.10409108982455	4.90203495630965	5.38257479447071
O	3.51135389539664	4.04385748105730	7.28322903924722
C	2.77079890884445	4.43010151218639	8.20070245847696
O	1.85569069778011	5.37321566985044	8.02301414466697
C	1.44274302112364	5.12586978421184	2.90248018389804
C	1.80576046786344	4.76197222777113	1.44591586228228
C	4.33330414506435	6.54901467233310	5.51937436793735
C	4.48489014145863	7.05001769336481	4.07549977502198
C	3.26109657114170	6.76207635931748	3.19060958423768
N	2.62427306692748	5.65291138185744	3.62287796121498
C	5.70530129848288	6.38986110909377	6.19689874067473
C	5.63860810707161	6.51358171463527	7.72442963942134
C	6.43137837808747	5.10442297670236	5.77616479547922
N	4.82099440973642	8.46933731832758	4.00454523589198
C	6.00855638646178	8.95616714361221	3.43581098405579
C	5.88123058177435	10.44250319937161	3.45045112666722
C	4.63867524529178	10.76903207022481	3.99829683580287
C	3.93557571106585	9.50141580245892	4.35600171678388
C	4.23450939104691	12.08796647408806	4.13859740843443
C	5.11928035778126	13.08434060523365	3.70766567876746
C	6.36470087486915	12.75677144689532	3.15943927007660
C	6.76536023794757	11.42186871021218	3.02358541994326
O	6.93235605312944	8.26869817655933	3.03730755609861
O	2.83979866783755	9.35215514834493	4.86647615066513
O	2.98341507264437	7.44052347465433	2.19436117465226
C	2.85744100200224	3.88811830527387	9.59251910804583
C	0.28732514535658	6.15248259776667	2.93932534138525
H	6.64614235926143	6.59097352824923	8.14915777020286
H	3.72343249595438	7.27874107494695	6.06608138082185
H	5.33420733213099	6.54533682826805	3.59870591717076
H	-0.60817433113479	2.76984817646693	2.53287624414685
H	7.72833904008126	11.15667198822977	2.59838907822316
H	7.02835534609429	13.55253280487433	2.83341931296789
H	4.83652651503635	14.12929830908124	3.79792083014127
H	3.26583481174970	12.33163588340694	4.56372134815282
H	3.23033978800841	4.67578525841713	10.25607397581499
H	1.86306536899600	3.60088064728146	9.94464026313231
H	3.53519960194764	3.03596771479944	9.61529616422404
H	-0.21688462747448	0.37212661571923	5.52279777922741
H	-1.66807094062962	1.05407175694503	4.75836292842208
H	1.94287936734723	5.64135521638382	7.04545454096364
H	0.93880328686752	4.32403554568188	0.93783603234226
H	2.11561727159172	5.66536264818635	0.91922502082525
H	2.62476127162983	4.03697990373687	1.43485141357323
H	-0.60052123961162	5.74829795595033	2.43945656973922
H	0.03429483522152	6.39093267326744	3.97638390214770
H	0.60967066581821	7.06314508212132	2.43160355919522
H	1.68161462323792	-0.23526107644305	3.56304221651358
H	1.92425580847633	-1.78022765145579	1.64236742174657
H	-0.08667270775573	-2.56246764040085	0.41018282588816
H	-2.34279526912808	-1.79365632387504	1.11056381672264
H	-2.58272961895922	-0.24505718076720	3.03281241674748
H	6.49116060078917	5.02096712237293	4.68580752987782
H	7.45521404306342	5.08784250862547	6.16810713420449
H	5.90134724556973	4.22434875607106	6.15679654498944
H	5.07531212896739	7.40551051076833	8.02193478434637
H	5.16181879953527	5.63699548061793	8.17175524953122
H	6.31605723585038	7.23710611410155	5.84162244539661

2.3’
Lowest frequency = 3.36 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	5.19147349702939	9.25165349110335	-6.85249472901078
C	4.55992896133596	9.15515762836185	-5.62091722771477
C	3.23982681659227	8.71705801786471	-5.50830786469505

C	2.49904535150377	8.35803918801976	-6.62451417159306
C	3.12759686956330	8.44963801896103	-7.87198056627336
C	4.45200495483006	8.88998137227577	-7.98440968620194
C	2.85143680641318	8.73263597470250	-4.06847066329759
N	3.98477932216262	9.21453066797497	-3.37965633258421
C	5.06825987250446	9.44925136762312	-4.25495479574004
C	4.18805969698997	9.22855052693772	-1.93680920233693
C	3.49660029084688	10.42697565784258	-1.26094926455250
C	1.97209132672980	10.60835388083111	-1.29742354100241
C	1.61642161232575	11.95650564240681	-0.65202410382807
O	6.17569654574860	9.81491448110120	-3.90691602287866
O	1.78084330941924	8.43730363776245	-3.57519662780708
Pd	3.81647447853294	9.46496651769544	1.06857217986626
O	3.65126322280439	11.06398782161176	2.30110015034973
C	4.37477212697097	12.09083788219406	1.92710324327446
O	5.07365826495586	12.11949798094739	0.90671409633492
N	3.82355973059413	8.14007832024811	2.54263310133284
C	3.83125870016806	6.82716358887143	2.15577548924936
C	3.84639339089038	6.09464578704531	3.32185268285041
N	3.84359443085317	7.02011808895799	4.32219007814535
N	3.83416364088469	8.27441250176969	3.85163432179157
C	3.86998576147290	6.79374339951371	5.77783279588228
C	4.99744439751349	5.86920284048957	6.17082010026260
C	4.72242506771944	4.63345251396063	6.76062805454581
C	5.76339525796621	3.77506658713135	7.11858662703689
C	7.08501807572626	4.14824845632336	6.88132400866096
C	7.36536324702821	5.38214074495150	6.28883936260537
C	6.32719374146140	6.23975481316273	5.93618506546779
C	3.82989584519180	6.48151501735379	0.69432508870718
C	5.05633131819331	5.59315165914993	0.38836317455580
N	3.91875232123894	7.78560948162515	-0.01507014636641
C	3.97700351404830	7.81091502394040	-1.35940592081069
O	3.98018405869401	6.82382648442263	-2.10819826933069
C	2.51461159256132	5.75253532080942	0.33890857332951
C	1.15543042618530	9.48060318661047	-0.66195320029923
C	4.24999673359396	13.29087060705708	2.85053798879259
H	5.26567298255693	9.41622839452433	-1.83726082183694
H	3.94382528298476	11.31934927578653	-1.72295988559488
H	3.87792832821245	5.03588059218085	3.52094688900953
H	6.21905764786594	9.59299516250093	-6.92792202205894
H	4.91082334961280	8.94983313914057	-8.96704442972088
H	2.58155057180194	8.17431660889817	-8.76964831987389
H	1.47337299898631	8.01674607145682	-6.52628022517943
H	5.13970330118420	13.91680052417331	2.76219361164235
H	3.37846593592657	13.87954153303980	2.54127157685645
H	4.09670235431032	12.97778340735757	3.88573887815271
H	3.97646722122354	7.78988207679991	6.21298555758946
H	2.90314580124833	6.38020238633339	6.07941597096908
H	3.97698950633880	10.67946059760543	-0.23717506059697
H	5.00887346797410	4.67154698549460	0.97957648163006
H	5.06193248243236	5.34314553206965	-0.67275208326245
H	5.97688029376294	6.12725960285354	0.64057164855518
H	2.43774366631066	4.81399136430032	0.89937493384022
H	1.65694402772326	6.38396979150903	0.58662449344754
H	2.50785113980420	5.53744249672566	-0.73067240162904
H	6.54604346038794	7.19854318846458	5.47249337196776
H	8.39431934201891	5.67596090408261	6.10419330375882
H	7.89647389044577	3.48108386928161	7.15645652141895
H	5.54029583928611	2.81704778288171	7.57872649188165
H	3.69047889585219	4.34250217405343	6.94357633214798
H	2.17711515234535	12.78161113593756	-1.10463887072756
H	0.54719274763991	12.16259401848117	-0.76689569760352
H	1.84528682086782	11.93674940724474	0.41982440812215
H	0.08648999108214	9.68022177350779	-0.79792327695749
H	1.38022041568399	8.51437682867681	-1.11425914780323
H	1.35659490596826	9.42530710148121	0.41777543969830
H	1.70368559891633	10.65224209354484	-2.36059651456119

TS2.(3-4)'

Lowest frequency = -1104.78 cm^{-1}.

Charge = 0, Multiplicity = 1

70

C	4.97322592267957	9.69938318776546	-6.85496249363916
C	4.43329847738635	9.40469007338610	-5.61142738797968
C	3.17455115846095	8.81669227560246	-5.48182416456989

C	2.40579630534497	8.50067740209315	-6.59196262235038
C	2.94210277555305	8.79230703978928	-7.85190796608138
C	4.20507303049864	9.38257787551992	-7.98146878910384
C	2.87712579637479	8.63822538896572	-4.03019063529792
N	4.00137086267799	9.15354259369177	-3.35144156806348
C	4.99130364646808	9.60701525040307	-4.24692634179858
C	4.27385461434181	9.07852570415524	-1.91755436775615
C	3.60119263493328	10.19761488936436	-1.09791802629871
C	2.07502519932522	10.41422327386203	-1.21134744936495
C	1.69440691998232	11.75597000311067	-0.56674324305815
O	6.07172359353084	10.06368672757469	-3.91824174533624
O	1.87222940787877	8.18260757551824	-3.52131622978626
Pd	3.86838972807008	9.36291898657402	0.94183718425148
O	3.83521098662341	11.03373185317013	2.15847343348141
C	4.45918948824467	12.02736943526923	1.65345202569521
O	4.94138474196032	12.01254634695132	0.48105912740323
N	3.82121712878141	8.06227706239577	2.49825265402353
C	3.80514581383483	6.74235478644343	2.13742442079104
C	3.73517299672438	6.02661156627591	3.31216092356406
N	3.70967227468687	6.96677948249930	4.29775888594331
N	3.76592394509568	8.21318822979517	3.80513176097580
C	3.67676837213390	6.76437788115316	5.75400228255323
C	4.83866800685357	5.92010129827772	6.22431378488347
C	4.60931079880867	4.72859370636421	6.91540883129261
C	5.68123702425670	3.94850086153762	7.35246743394603
C	6.98869863154502	4.35478868164136	7.09242956498281
C	7.22327989046249	5.54402814120765	6.39765623635853
C	6.15412281486929	6.32442336745476	5.96683481069454
C	3.87834759108160	6.36100584266850	0.68620510480851
C	5.14970557036533	5.51219365278813	0.45631983842493
N	3.94972985421325	7.64193731867384	-0.05854501096393
C	4.09037314660252	7.64686395210316	-1.39732259319333
O	4.16487443615644	6.66024115071410	-2.14059081200031
C	2.61071961818369	5.57413266663604	0.28644413061450
C	1.18462974186074	9.29465604284256	-0.66060273123554
C	4.58746837235989	13.27745782237639	2.48750700766556
H	5.35337081974517	9.26970660909681	-1.85877755618294
H	4.03344622906089	11.11641095430583	-1.52637249909040
H	3.71989182048495	4.97044231111213	3.52674887009310
H	5.95394471338654	10.15603753675562	-6.94389502399020
H	4.59301478951126	9.59616561354262	-8.97327053786393
H	2.37148511920487	8.55717200868294	-8.74577474041917
H	1.42825761336886	8.04225222022280	-6.48019869743493
H	5.58301365373792	13.70830084861764	2.36046257887536
H	3.85695279000833	14.00984223186238	2.12612912522423
H	4.38836890467663	13.06360270506572	3.53800878805042
H	3.69947591425577	7.77190471972726	6.17610882122192
H	2.72397989878198	6.29578804310407	6.01713096084547
H	4.37432265133893	10.85303792631187	-0.06034403036235
H	5.10808076014019	4.59991761863369	1.06226695782462
H	5.21476635249270	5.24553216145503	-0.59912442650501
H	6.03713302805773	6.08482032623102	0.74119234124967
H	2.54230914763657	4.64383932035800	0.86196694126186
H	1.71894101179427	6.17679048515620	0.47848947393107
H	2.66383361142375	5.33853644699562	-0.77773521954854
H	6.33738026937978	7.24779111244651	5.42283819746749
H	8.24096689898124	5.86302108463567	6.19303038742256
H	7.82422263813456	3.74747144555899	7.42764693027760
H	5.49308985646252	3.02400504020344	7.89032359603036
H	3.58852254110883	4.40996983221266	7.11428865249798
H	2.30164255532789	12.57942624736771	-0.95899446118862
H	0.64059507100239	11.98393681114107	-0.75978450336589
H	1.83569379306055	11.71251266442492	0.51930672910335
H	0.13756302092154	9.50855194158077	-0.90614128968821
H	1.44116049714448	8.32698483537231	-1.09158250609217
H	1.27525054085098	9.23404818071322	0.43171018709469
H	1.86816416930641	10.49487132048993	-2.28850831121529

2.4’
Lowest frequency = -4.72 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	4.81181923765245	9.85009622540174	-6.86036323730916
C	4.30697184523562	9.49164013968745	-5.61889885466700
C	3.12942970217573	8.75395040886860	-5.49459123406248

C	2.40958247760603	8.34673753545359	-6.60758681108390
C	2.91118691951197	8.70178348278869	-7.86573052261522
C	4.09307197847473	9.44180708231482	-7.99025751639089
C	2.85264750013593	8.53802773429843	-4.04300453851539
N	3.90635641860831	9.18073706168525	-3.36057678266277
C	4.83030521355022	9.75820475603418	-4.25049225400629
C	4.17708014695423	9.14391603739599	-1.92188095297633
C	3.41299051753079	10.16543882804206	-1.05739439165833
C	1.91230131316117	10.35255575566039	-1.34296505120775
C	1.42771320724519	11.70891235233609	-0.81083601624132
O	5.84562064754259	10.34796495231796	-3.92118821387561
O	1.90750516600320	7.96373165219193	-3.53979188340633
Pd	3.69883781973444	9.46419083098871	0.85326184997174
O	3.47901270017262	11.36545139470094	1.76212480422922
C	4.48931252972577	12.08539152474627	1.73278508714301
O	5.62851302841909	11.68247730239896	1.18629128538116
N	3.89414456917861	8.22534016870344	2.56399556052049
C	3.96493350026300	6.90441377281792	2.20784488125455
C	3.98708498908240	6.18375968046110	3.38281623015990
N	3.93054294684811	7.11744734201144	4.37163333028204
N	3.87378100319903	8.36544179921069	3.87418048771828
C	3.90125755333111	6.90654990849561	5.82728275429612
C	4.89794418351660	5.85577130223309	6.25407080058823
C	4.46102538550920	4.67560527728139	6.85994343124615
C	5.37877496480629	3.69789428044446	7.24784875047212
C	6.74027279245901	3.89436692908722	7.02481343830361
C	7.18327646274649	5.07153415605706	6.41639755028673
C	6.26749637230900	6.04781955340370	6.03430228913252
C	4.03309538806325	6.48246547089365	0.76149251366076
C	5.36885134775761	5.73742133747396	0.53238829478990
N	3.96899479856499	7.72422758885890	-0.03934096123579
C	4.12237775833207	7.70284995010767	-1.38270491609922
O	4.29558300343461	6.70808263727553	-2.09527602503284
C	2.83392581388314	5.56988982387027	0.42290533585048
C	1.02094323976981	9.22346723240664	-0.80360775375757
C	4.51253459553175	13.47084044932227	2.29790090212771
H	5.23653277223641	9.42287021990977	-1.86454361743413
H	3.91027335782259	11.13916515465146	-1.16406449650315
H	4.05654046198000	5.12956977703780	3.59645384304764
H	5.73017412628768	10.42262278931637	-6.94555842603694
H	4.45650632483728	9.70079636525122	-8.98061151897002
H	2.37731514306948	8.39847563074191	-8.76184986483149
H	1.49519318826578	7.77185061907830	-6.49922311570193
H	5.35631931935916	13.57889481573070	2.98512444957409
H	4.65711914839973	14.18620336347906	1.48153516407179
H	3.57310666880687	13.67685902314451	2.80882711821130
H	4.11896051948991	7.88574727806773	6.26069953018541
H	2.88672588684605	6.61624594206645	6.11785111005702
H	5.42885468449013	10.74622926205879	0.83659625292972
H	5.42159624716724	4.85213753188048	1.17642580685156
H	5.43511101417272	5.43321205382285	-0.51279792572211
H	6.20874171263812	6.39668203636056	0.77125449611182
H	2.85725266832859	4.65974260092860	1.03358848083723
H	1.89614248115504	6.10004386266991	0.61057539514087
H	2.88751828544984	5.29835937127028	-0.63307374912148
H	6.61288456139525	6.96066630712957	5.55519181757684
H	8.24362677704894	5.22748130383861	6.24112706319471
H	7.45599551344923	3.13357004164802	7.32195404320056
H	5.02854344510656	2.78414019372437	7.71879605475320
H	3.39785711282167	4.52087286882910	7.02890636346448
H	2.02785298933725	12.53170987828024	-1.21835511824036
H	0.38210369918114	11.88095014835631	-1.09052678250605
H	1.49694830929251	11.74544311904568	0.28150460026858
H	-0.01331503745883	9.36447180114713	-1.13993767970185
H	1.36009074076432	8.24703276131233	-1.15141804297931
H	1.02945044894867	9.22879796818823	0.29478913533161
H	1.79124039128446	10.37246219330553	-2.43704104767013

2.3b

Lowest frequency = 7.14 cm^{-1}.

Charge = 0, Multiplicity = 1

70

C	3.78180187457340	7.26045907801828	-6.77884923885650
C	4.42627132691930	6.70794202971870	-7.88800466484022
C	3.91622196924110	6.94625792518422	-9.17013373995649

C	2.77616033113355	7.72748130624364	-9.33603331089587
C	2.13362028799864	8.27536140917561	-8.22284586187048
C	2.63583563588606	8.04012783209583	-6.94430688948642
C	5.67004308359625	5.87183957252902	-7.70723744185182
N	6.83831173632428	6.50386242878289	-8.34606675295890
C	7.25762383667951	7.79677632378278	-8.24987654284569
C	8.39142081923121	7.86349056426717	-9.03006966235761
N	8.56613969135715	6.60943152023792	-9.53468138384043
N	7.63371747076667	5.76897385556267	-9.13357639377214
Pd	10.13601893902952	6.32894692966835	-10.68499911547740
O	9.66963788290293	4.38494253251175	-10.98590052875130
C	9.63372961309660	4.06942675162557	-12.25888230018707
C	9.33971741837590	8.95510736454288	-9.41598519667231
C	8.54908098951223	9.99224743312202	-10.25038972730518
C	12.55562853918440	5.91137699552456	-11.61454478117166
C	13.10619898620417	5.76055261738644	-13.04292066882883
C	13.08262762746648	7.17492908144375	-10.93302534858498
C	12.48423047896468	8.45128747819483	-11.55770448354604
C	11.37873146197148	9.12120131513304	-10.70377677497603
N	10.41710728702257	8.30225004856624	-10.22699415622354
N	13.49693747531996	9.44712514626925	-11.85897465523812
C	14.33546363242710	10.03396578037746	-10.89472342995220
C	15.03850229055764	11.14197509735673	-11.60500313351046
C	14.57912440799064	11.18238795539777	-12.92365735343839
C	13.56180320161430	10.10703573734731	-13.09704456506720
C	15.99499707479083	12.03439937521555	-11.14513792607592
C	16.48212298229560	12.98344101413494	-12.05218233637862
C	16.02179339412635	13.02334180931975	-13.37346542852441
C	15.05865167956829	12.11571861350794	-13.83050015736309
O	14.45740725525982	9.65848574678675	-9.74357127214064
O	12.90867507540073	9.81289384900077	-14.08246820451762
C	12.81448569745782	4.65276274992326	-10.78942089782569
O	11.42809449238340	10.34829276079461	-10.52213981512883
C	9.91645343936505	9.58978880831143	-8.13082570959665
H	12.03876851699371	8.21576206635702	-12.53174478365689
H	6.72135529632860	8.53190279029548	-7.67245775809558
H	14.69407823672005	12.13861705522429	-14.85269327899427
H	16.41850741936867	13.77250492216814	-14.05256587837674
H	17.22846935880921	13.70277217341273	-11.72750251558170
H	16.34495287223860	11.99597934911876	-10.11831091610608
H	5.58745654226332	4.89140343699718	-8.18146923361903
H	5.89343344241454	5.72996454567946	-6.64564563559989
H	7.71487814884176	10.38786393805169	-9.65970688295725
H	9.21268584108791	10.80753930879785	-10.53642272666043
H	8.14775166746064	9.51525021153864	-11.14945600021527
H	9.10357913827752	9.99407275773896	-7.51631157663604
H	10.45440767220911	8.83396943513297	-7.55133544809291
H	10.60008789154376	10.39427218799686	-8.39996752111828
H	4.41742210295700	6.52306498958626	-10.03725014165910
H	2.38613681383204	7.90816109887016	-10.33322012027446
H	1.24382871954934	8.88384167162460	-8.35435764670648
H	2.14011366133358	8.46386140058302	-6.07598464342467
H	4.17622368934154	7.07809373955068	-5.78179177220122
H	14.17213139907714	7.19481046009811	-11.04517597105964
H	12.87191484905244	7.15295003066062	-9.86049366972992
H	12.62789331242443	4.92151243472102	-13.55211242403868
H	12.94207744954304	6.66091141248282	-13.64138363091708
H	14.18637953416353	5.57910681284280	-12.97798254298960
H	12.37927337458726	3.77003676725842	-11.26335339008987
H	13.89874450462829	4.50333368432952	-10.71073153800187
H	12.40368450434966	4.73806816642621	-9.77948222332818
O	9.91984642796077	4.84428463804591	-13.17853748960872
H	11.43743059109240	6.01730342977982	-11.88659125313325
C	9.23732849740720	2.62364634752650	-12.50915332447812
H	10.10545107008067	1.97965859739338	-12.32720246848996
H	8.44406259437766	2.31363414496154	-11.82445083372194
H	8.92112447368903	2.50373315768687	-13.54652391042210

TS2.(3-4)b
Lowest frequency = -1097.97 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	4.25332273980308	7.66569991121653	-6.38779498336583
C	5.05712053991999	6.87968762693833	-7.21600981696765
C	4.51246179838957	6.32899736576544	-8.38225322165037

C	3.18023304941597	6.56313918479897	-8.71116310784141
C	2.37893075750388	7.34668096673691	-7.87693897362530
C	2.91590857653747	7.89655642563067	-6.71446568402018
C	6.50386720794772	6.62732821356995	-6.85848933488465
N	7.41208380466810	7.07989968391475	-7.92234860629193
C	7.53734798518683	8.32716532084264	-8.45639321101533
C	8.50026379789751	8.19998774901017	-9.43433853817167
N	8.88073167791439	6.89319374586680	-9.42143224112999
N	8.23088326337477	6.19602348008049	-8.51170807417300
Pd	10.23439403226125	6.38905779680805	-10.84606361579292
O	9.80877448327655	4.37421908881799	-10.61322807037282
C	9.52374563445239	3.85719140255236	-11.74552746177992
C	9.12346987597935	9.14526979661393	-10.41752725491214
C	8.09532852944763	9.47807768794693	-11.52228254607745
C	11.94460973017227	6.01249468755101	-12.22125423843082
C	11.92883109716338	6.11888821108208	-13.76228872826704
C	12.80852993200053	7.15210158100849	-11.64492601870105
C	12.47249889311681	8.53971501897024	-12.17670552690577
C	11.14051245044569	9.17637961566880	-11.73908714968428
N	10.30704013289388	8.42828495031955	-10.99284548505857
N	13.53884837009990	9.48660360565155	-11.84310916150850
C	13.76007999945133	10.02638366988774	-10.56707658653199
C	14.85143136022868	11.02909251831477	-10.74195825599808
C	15.21604016893121	11.05199973223186	-12.09000325892825
C	14.36766844763082	10.06596386471925	-12.81942450884217
C	15.47116347723298	11.84831095237927	-9.81052859684224
C	16.47799327809973	12.70485519299072	-10.27261619063065
C	16.84319158191036	12.72768259009757	-11.62358279129661
C	16.21352845951882	11.89476637471254	-12.55670692506481
O	13.16912401895017	9.70754473439188	-9.55045821001604
O	14.36564314436942	9.77869193428205	-14.00264011634928
C	12.59056026292304	4.68740877160514	-11.79745806001742
O	10.94950718514280	10.35850841877551	-12.07584169029381
C	9.53765595604718	10.41513561792320	-9.63615563464950
H	12.47610055866782	8.52836477512743	-13.27080029120440
H	6.94421058006445	9.15921037133588	-8.11385173115263
H	16.48823043727846	11.90606677453511	-13.60678281156751
H	17.62709922194512	13.40444495932866	-11.95112512216459
H	16.98466394492024	13.36422482017697	-9.57374187037865
H	15.17986685833672	11.82364151472945	-8.76507663520888
H	6.72039631365431	5.56287949678832	-6.74076668422746
H	6.77123743251698	7.14370141338264	-5.93200662135409
H	7.20973196590533	9.95834810164068	-11.09029405352395
H	8.56194144005022	10.15460429536426	-12.24000506100057
H	7.78615635001908	8.56022499772198	-12.03187209543102
H	8.67201596438952	10.79342348537547	-9.07943570708043
H	10.33746951407342	10.17203845830504	-8.93173661723279
H	9.88895788826238	11.18143356243511	-10.32362197498702
H	5.13687536402942	5.72260904679449	-9.03386106697040
H	2.76481259483689	6.13391486198067	-9.61811360542464
H	1.33986614106995	7.52816786754908	-8.13531433776823
H	2.29832210809717	8.50845025073443	-6.06362498995997
H	4.67416678871893	8.09811713134108	-5.48282954251331
H	13.84392867382161	6.93349206050619	-11.95570991061835
H	12.79640280799831	7.15519545572291	-10.55054903843298
H	11.55163169648254	5.19981343597650	-14.21531908445306
H	11.30849836960960	6.94664905177196	-14.11644819309732
H	12.95633010912167	6.28727710750207	-14.11433712138115
H	12.06299865401573	3.82433567548241	-12.20980608346201
H	13.61984955321398	4.66043834957254	-12.18380420561477
H	12.63389596136126	4.58642686152534	-10.70922666230397
O	9.69790235412463	4.46718244618513	-12.84610207472097
H	10.47385207110283	5.57431702787813	-12.38166200951318
C	8.99461816689579	2.44495350096638	-11.76501685627376
H	9.80074378571506	1.77531198670182	-12.08464477349605
H	8.65441033848504	2.14645183677592	-10.77309545329481
H	8.18535929091029	2.36307552911155	-12.49407483809755

2.4b
Lowest frequency = 5.07 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.68009864383700	7.28656006386492	-7.16894939820038
C	4.41494914797468	6.82029725841303	-8.26112506722088
C	4.06251823169131	7.23265476396464	-9.55206889923329

C	2.98916994819623	8.09820174192058	-9.74344003482196
C	2.25490903110267	8.55801690415930	-8.64725962478431
C	2.60023445651492	8.15033755977879	-7.36022556378994
C	5.58316299775835	5.88649242878009	-8.04922068217986
N	6.83161543462042	6.45080456866424	-8.58200991496325
C	7.32736909726060	7.70796288523323	-8.41964936049446
C	8.52132053555212	7.71331095253506	-9.11178525952809
N	8.66684456717940	6.46727370398815	-9.63961027128516
N	7.64890762701550	5.68744741942073	-9.32904843310993
Pd	10.59219005392217	6.18947218067013	-10.46867438795217
O	10.24075849406129	4.10425437284192	-10.79765399912820
C	9.50100451283437	3.85569835247985	-11.76202751127074
C	9.52900567540921	8.79554591626781	-9.38148006975830
C	8.78447909068499	9.88675466361593	-10.19447877178602
C	12.55579786062781	5.94805670681709	-11.05001859277353
C	12.59654887152124	5.47365268875267	-12.50475768415574
C	13.35330011452014	7.23216193887542	-10.86442534841631
C	12.67692620985935	8.44123936868521	-11.51616701136220
C	11.57969045999442	9.06424492526676	-10.62731926385678
N	10.66030362885212	8.19532649600896	-10.15674911332962
N	13.62216744457877	9.48344134359728	-11.88923678225680
C	14.49186337151709	10.13553445876381	-10.99588630935626
C	15.08104960478813	11.26704643233875	-11.77193323667719
C	14.52794127439141	11.25899066085960	-13.05347515341860
C	13.56126108763810	10.12691560061011	-13.13450734597846
C	16.01693528025066	12.21765765557617	-11.39394504185444
C	16.38551360653814	13.17572992025563	-12.34627164524053
C	15.83042789640152	13.16777601276778	-13.63126347761087
C	14.88866731576982	12.20144006920240	-14.00498246763070
O	14.72106738374443	9.80140639507952	-9.84877182784572
O	12.85278357658034	9.78851347957450	-14.06760108391398
C	13.11105697473748	4.87060595335289	-10.11587238741401
O	11.59296864317251	10.28972872431372	-10.42188254248243
C	10.04209543037621	9.35915435792669	-8.03846858337998
H	12.21070705558235	8.14356725781473	-12.46123127382283
H	6.79538592799620	8.46346451792170	-7.86473684633175
H	14.45090317059553	12.18707623369412	-14.99826891981918
H	16.13564374257908	13.92565308379973	-14.34717780347820
H	17.11241942204841	13.93992356057664	-12.08596952631310
H	16.43985202011277	12.21553414666558	-10.39415176461481
H	5.45463498067660	4.93701900928487	-8.57507131746712
H	5.72026004716206	5.67659262924373	-6.98380148432525
H	7.90473629507961	10.22387162029236	-9.63419974822473
H	9.44774014144197	10.72972776289019	-10.37971659156693
H	8.44980014544780	9.46999049964454	-11.14962527016893
H	9.21003138853997	9.76712449562620	-7.45213709098388
H	10.52392859089882	8.56418682141082	-7.46180806895377
H	10.76396317312070	10.15152891492336	-8.23905562813675
H	4.63734572925990	6.88154819631009	-10.40554669727518
H	2.72383735558822	8.41539409449427	-10.74760936065987
H	1.41846943111290	9.23390481789264	-8.79825423129781
H	2.03533405564545	8.50711800147052	-6.50407099252910
H	3.95421330215351	6.97331177740713	-6.16416718828785
H	14.34857679450297	7.10047210372584	-11.31898574107524
H	13.51526127756835	7.43585427136036	-9.80259273261610
H	12.05328462190004	4.53293435146105	-12.63787325852214
H	12.18202916565713	6.20876089268327	-13.20191476222073
H	13.64125148324882	5.28855580185308	-12.80653747715549
H	12.58511050242213	3.91810290271652	-10.22534737371316
H	14.17507835154684	4.69383943491850	-10.34775684391025
H	13.05419903230559	5.18251412310268	-9.06726938617408
O	9.07434575412223	4.79874563330753	-12.59117046810738
H	9.47346090142643	5.66352337791689	-12.23442132360901
C	9.01788390765356	2.47526650067459	-12.07872030957443
H	9.22837122978023	2.23948862854316	-13.12563897240674
H	9.49872448788751	1.75462287098100	-11.41884486151243
H	7.93218193346155	2.43884674016912	-11.94137353668455

2.3c
Lowest frequency = 3.82 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	13.40677010193949	12.24737824181440	-13.98494284038150
C	13.54614746230844	11.21607262041271	-13.06756093060994
C	14.62935000308826	11.16158712641798	-12.18903657979862

C	15.61518018822812	12.13670730497887	-12.19439257220167
C	15.48153805862936	13.18424007139413	-13.11365329069320
C	14.39519599430461	13.23855146248801	-13.99507322128627
C	12.67429639461649	10.03923252889841	-12.80136158794248
N	13.32223262339567	9.30057513668366	-11.79443080130805
C	14.49347921144605	9.94172904618699	-11.33940800665598
C	12.64451578575992	8.18974198003357	-11.13534101269519
C	11.81734845958217	8.77161790085490	-9.95721764230303
O	12.12741985573074	9.87334309255313	-9.47811171595431
O	15.24020521492906	9.54180837474687	-10.46745057743072
O	11.61433091024975	9.73198053655291	-13.31892750346542
C	13.62816370202380	7.07466572474224	-10.73974502439352
C	13.02011553872300	5.67016681235085	-10.74288748497597
C	14.02586248153230	4.65161245058780	-10.18322324055247
Pd	10.51849207440337	6.05218815902676	-9.95565011695392
N	10.75145847126030	8.03099414975587	-9.59617457476711
C	9.78078984623489	8.60448663797821	-8.61649984228919
C	10.37411342306054	8.57284571157353	-7.19128985752591
N	8.69869565667289	6.49823415567363	-9.33587531045854
C	8.58267737291000	7.70216895225867	-8.70043675082201
C	7.27285288518789	7.77571403256414	-8.28251744600633
N	6.70224096383633	6.60788161921091	-8.69394642388171
N	7.57095220607308	5.82097079552275	-9.34338373216362
C	5.30759973747545	6.16361864849320	-8.52595344939036
C	4.33382445403773	7.23681587202092	-8.95059729497637
C	3.44026192171752	7.78218742110966	-8.02611843302718
C	2.54287874115988	8.77830348292589	-8.41483764859458
C	2.54138012759916	9.23801743262337	-9.73044150589486
C	3.43561702384357	8.69823055813978	-10.65839873851530
C	4.32670578176036	7.70127929197406	-10.27159316106205
O	10.12285295773068	4.09605960922233	-10.27674167477116
C	10.62820290168432	3.32090834357526	-9.34251559285440
C	10.27300113168265	1.85475140278909	-9.53401192177132
O	11.32537552219627	3.71865943963946	-8.40492542499270
C	9.32502388843665	10.03067300795231	-8.99800283297757
C	12.51090231882547	5.21754507361456	-12.11449030177117
H	11.93440514583287	7.81666479047378	-11.88011242554705
H	6.70976055137537	8.53706851960465	-7.76816851713232
H	12.56009676590254	12.28043268547740	-14.66348740954163
H	14.31968401384833	14.06518138381896	-14.69566444079839
H	16.23060303367437	13.97026775217578	-13.14443414553653
H	16.45263440308083	12.08561939566648	-11.50569334347741
H	5.22575333695614	5.26084943999445	-9.13549860927665
H	5.15626566325089	5.89281581739280	-7.47683723036281
H	8.49479799347731	10.33105427385916	-8.34809781934253
H	10.14928538106983	10.73122375621357	-8.88029650772595
H	8.98323121672415	10.04932553042576	-10.03693443088268
H	9.64931902458849	8.94897768312223	-6.46034979579464
H	10.65087592579499	7.54874853081211	-6.92410468945571
H	11.26409024649965	9.20542868155261	-7.17502116451653
H	5.02480156901752	7.28490426747702	-10.99370833524800
H	3.43643808621644	9.05429725733414	-11.68426274325465
H	1.84672100440853	10.01543461040604	-10.03435038661584
H	1.85049679417593	9.19517931127688	-7.68950195656627
H	3.44473177543996	7.42511176714181	-6.99878636690033
H	14.45306993898119	7.07101732835613	-11.46216921120537
H	14.06964565344731	7.29325766562013	-9.76470774097313
H	12.02251074858866	4.24348746554425	-12.04481039575907
H	11.79734383921054	5.91700417799456	-12.56037693993341
H	13.36975698858502	5.13380128010423	-12.79237387588645
H	13.58359602858918	3.65494409783457	-10.12730776449871
H	14.89697835948744	4.61820702810491	-10.84943828087365
H	14.35974148271201	4.93671108713508	-9.18240297740054
H	12.23765930419092	5.61649224862136	-9.90011303119422
H	10.73472696366676	1.25624217736106	-8.74772255540380
H	9.18560544555317	1.73219950614039	-9.50812376572769
H	10.61613192137720	1.51151827361542	-10.51535407505250

TS2.(3-4)c
Lowest frequency = -782.19 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	15.00419561175273	12.26533196470458	-13.59396220895908
C	14.56184966916812	11.21785014350240	-12.79973980939695
C	15.13231851950403	10.95633380229302	-11.55234045046059

C	16.16716049669891	11.73241941681201	-11.05279445437485
C	16.61867961902434	12.79421189677974	-11.84587151419094
C	16.04662911244788	13.05638982994592	-13.09631977740118
C	13.47979209129431	10.22048659172637	-13.03493222959977
N	13.49545672699575	9.37265982830592	-11.91639699190240
C	14.43836881260688	9.77897655702998	-10.95387541031143
C	12.44319961060641	8.39471828056610	-11.67152352892427
C	11.49316660864563	8.97999351725854	-10.59424851308263
O	11.61553565867487	10.18690885157780	-10.32754708015438
O	14.63556434128505	9.23984682710690	-9.88115710272290
O	12.72078584648057	10.11626426847013	-13.98305532149110
C	13.06223962801487	7.01420851295841	-11.44835854581356
C	12.07975449109563	5.84987537397242	-11.44439944719680
C	12.85656962624805	4.53002865370553	-11.52692966776039
Pd	10.49449961427529	6.12428234902085	-9.98956183368085
N	10.51517761229419	8.17877019070791	-10.11357439227363
C	9.51631395787258	8.86677484441401	-9.22328984052599
C	10.18025582187403	9.32849337761656	-7.90349394803777
N	8.69008550092712	6.53336849046077	-9.10541231191849
C	8.46314986794240	7.85554289236098	-8.88227805295159
C	7.20681175262782	7.93934210207875	-8.31997229414537
N	6.77155196482246	6.65038366559775	-8.24284438405417
N	7.67236888060273	5.78518031636144	-8.72761441289274
C	5.48121907864307	6.15076284781650	-7.74030767821492
C	4.31863481391267	6.84866073037139	-8.40623940100738
C	3.40984222104154	7.58637440122772	-7.64452781274713
C	2.33593588761887	8.23361104972153	-8.25804877962979
C	2.17103883538916	8.15056278821692	-9.63935386910689
C	3.07939241779474	7.41673814985280	-10.40644758135022
C	4.14726833888870	6.76742396799715	-9.79345748722767
O	10.37939442477513	4.11903623505585	-9.57081249135847
C	11.41095661937532	3.74418212617512	-8.88218514453209
C	11.36993590853459	2.32203623565112	-8.36378413294060
O	12.41367001444122	4.46237012542738	-8.66578154456593
C	8.81370577393019	10.04092211752560	-9.94309287203758
C	11.09053077555927	5.88522321391865	-12.62321228973642
H	11.86851478356913	8.38632670720131	-12.60500644932753
H	6.59878338494962	8.76865826350669	-7.99777768715048
H	14.55229466089408	12.46163988239164	-14.56125025720915
H	16.41799875981069	13.88893650950567	-13.68695349996681
H	17.42452245606218	13.42787710006793	-11.48667310379825
H	16.60213579753708	11.52184111599847	-10.08080583301361
H	5.49664401054511	5.07843063710677	-7.94849888336078
H	5.45299794160678	6.29706560402630	-6.65654077217679
H	8.01146675088173	10.43194888893152	-9.30631310726682
H	9.52768500863094	10.83533636251737	-10.14928120201136
H	8.37380504133177	9.69172870370237	-10.88216054653423
H	9.42988157364543	9.77245030573132	-7.23913494019961
H	10.63453001344802	8.47021284877313	-7.39940745881657
H	10.95011956765171	10.06602969578308	-8.12996237732117
H	4.85574040039573	6.19955033419890	-10.39158105684524
H	2.95318574639564	7.35004841457097	-11.48298005029437
H	1.33843286818385	8.65614333711578	-10.11942226007260
H	1.63356488531231	8.80374540758433	-7.65724713626735
H	3.54121428761557	7.65353893196711	-6.56693633002082
H	13.76130343279028	6.84612927620260	-12.28251847415216
H	13.65714340497778	7.01906821945238	-10.53119542832531
H	10.45281673790025	4.99638118595845	-12.62281729133181
H	10.45270963058677	6.77215372578478	-12.63455712292232
H	11.67500099289652	5.87573648934863	-13.55821160958616
H	12.19176613648876	3.66927978169305	-11.41969824009909
H	13.31361176329223	4.48027687555282	-12.52512135011335
H	13.64745475458662	4.46376738908361	-10.77846017646853
H	12.02264984316606	5.66200080516658	-9.80230148710320
H	11.83036732190192	2.27808309971763	-7.37475434864587
H	10.34706649559769	1.94430610506559	-8.33265667732739
H	11.96039499366046	1.69177346200029	-9.03840723359242

2.4c
Lowest frequency = 5.99 cm^{-1}.
Charge = 0, Multiplicity = 1

70

C	14.79990045871498	12.25675149224461	-14.02442996000893
C	14.47927783408924	11.30395836958446	-13.06899564915752
C	15.09236782961566	11.29162423367736	-11.81517370973527

C	16.05033291783364	12.23259156970041	-11.46967145758664
C	16.37892190273847	13.20122981070815	-12.42597986437491
C	15.76393614513448	13.21304786335637	-13.68341366195667
C	13.50457784376933	10.17756603276980	-13.11992643426507
N	13.62167879808788	9.51548748610965	-11.88774840652120
C	14.53618524248426	10.15062235440634	-11.02805881852953
C	12.69478206491139	8.46461622753965	-11.49321265767394
C	11.62811455158334	9.06731945521518	-10.55594111170039
O	11.65758687471439	10.28465304705036	-10.30897537714684
O	14.82089361639233	9.79876879200547	-9.89867425668475
O	12.75113622982593	9.85556767864565	-14.02275643343042
C	13.40151567566671	7.25048061901281	-10.88674342962235
C	12.60447996861634	5.96244825679385	-11.04302034479796
C	13.26760646670887	4.88131507655247	-10.18509830734468
Pd	10.64392428632485	6.18880500299720	-10.43534362257495
N	10.70605370336507	8.19180737964196	-10.10215342559119
C	9.58814143447243	8.77771214768456	-9.29810008674732
C	10.11522769091339	9.28522620906610	-7.93829314952057
N	8.70684058935508	6.46394858789264	-9.61772826018590
C	8.56776552590116	7.69945463288121	-9.06332007311474
C	7.37240579986613	7.68706093337876	-8.37354760906091
N	6.87259844329745	6.43446349677817	-8.55606152687158
N	7.68662272252944	5.68207202723476	-9.31809256592981
C	5.61815409674602	5.86758680786254	-8.04062811563877
C	4.44144024108079	6.77476062856883	-8.31399916818703
C	3.67274788107489	7.26839786238066	-7.25774021011676
C	2.58492064691914	8.10697722437214	-7.50699696606206
C	2.26552759992798	8.46125971326241	-8.81638594327877
C	3.03384583635079	7.97378512685782	-9.87662981742606
C	4.11546956036745	7.13368963011226	-9.62752557639099
O	10.30097406874152	4.10729040703651	-10.72991908312216
C	10.20369298981438	3.43471004560061	-9.69226967256310
C	9.79350123962020	1.99629638792203	-9.69333665356804
O	10.45410303292730	3.94304528016517	-8.49265460515155
C	8.85294076450962	9.90762414662793	-10.06579202481052
C	12.53037837480946	5.50782214140512	-12.50322479660771
H	12.19521430577927	8.17862834697831	-12.42473741542793
H	6.84197768625841	8.43581176822773	-7.80790081819217
H	14.31581215860201	12.25704084736751	-14.99611173595252
H	16.03978427617300	13.97828339388488	-14.40339712741855
H	17.12183407997373	13.95807625249827	-12.19063062078580
H	16.52041150662975	12.21508545512357	-10.49131661172207
H	5.51925001097007	4.90123924329965	-8.54138267383941
H	5.72874432556727	5.69311311562313	-6.96577731609996
H	7.97828284530668	10.23085703588456	-9.48953009513228
H	9.52344954424348	10.75098847934116	-10.21965436320211
H	8.51163798382378	9.53163366089603	-11.03514672509171
H	9.29252133495061	9.68190086343843	-7.33136857043377
H	10.59098040473484	8.46378045981657	-7.39414630872399
H	10.84626255258171	10.07505268577573	-8.11497893625541
H	4.71664977252225	6.76036093344638	-10.45291064821384
H	2.78852768546591	8.24922192331285	-10.89803317830408
H	1.42249794850066	9.11707178690477	-9.01271409245098
H	1.99318735635905	8.48550110010130	-6.67874913029689
H	3.92597455831397	6.99603830131307	-6.23562607720532
H	14.37344689777912	7.12558428251062	-11.39127276762843
H	13.61680309988890	7.44471724802433	-9.83238985632840
H	11.95197304234567	4.58418402075536	-12.60264989797508
H	12.07885815212265	6.26083603853938	-13.15699481799500
H	13.54622882761504	5.30824555292034	-12.88474834516563
H	12.79220183837247	3.90335226869411	-10.30481489059762
H	14.32019938498697	4.76471223812256	-10.49339083672115
H	13.27066644734524	5.14946953630327	-9.12312031320879
H	10.69954763975456	4.91199179428989	-8.66658751580975
H	8.81638389046947	1.90724943905981	-9.20701668009186
H	9.73032667002778	1.63081406154960	-10.71724645047499
H	10.50860282273382	1.40432568089481	-9.11546935019693

2.5
Lowest frequency = 6.41 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	-0.01507907525335	-0.20035830595372	2.35472453963696
C	-1.18564347248465	0.22061253299332	2.96700445613708
C	-2.43891976899271	-0.06159554351872	2.41843220303302

C	-2.56670045769277	-0.77720935165085	1.23781704317831
C	-1.39003955466975	-1.20934814258264	0.61306805813529
C	-0.13467009632337	-0.92519409527810	1.16229406695976
C	-3.48241562006033	0.52545756172286	3.30902301285821
N	-2.78239052914209	1.14432083465194	4.35349475749336
C	-1.39111914162203	0.99346436440121	4.22685938598528
C	-3.43240903947725	1.76088026944161	5.50581236164152
C	-4.26207678056044	0.70507905974436	6.25205317818594
O	-3.92949330671466	-0.48606883160313	6.28950078555696
O	-0.56146705529930	1.43270223480741	5.00244836307708
O	-4.69547735565448	0.51101743147090	3.17908892394826
C	-4.19267930787625	3.04176144035820	5.11471505873010
C	-3.24884726140207	4.25601957714825	5.22889825434180
C	-3.12902582640382	4.76734850119921	6.67171771681693
Pd	-5.92554336698191	3.06620874884430	6.24584662427035
N	-5.30130335438204	1.28172975343774	6.89156858376729
C	-6.23672262365688	0.45450460217771	7.69222883406402
C	-6.92000233020974	-0.61280668099580	6.80339575050004
N	-7.46476360588764	2.62833106119278	7.63385579358737
C	-7.29426846078685	1.39590668655068	8.20516178359953
C	-8.24587138881043	1.28939649740455	9.19597165014745
N	-8.93317857629366	2.46451797268655	9.15543960024120
N	-8.45160017878588	3.28653547301643	8.20545245424469
C	-10.03421083020101	2.91070092829181	10.01845135795162
C	-9.65433839419242	2.86420710653486	11.48106996199994
C	-8.52077848403991	3.54656955520383	11.93880525989154
C	-8.17380755004824	3.50386427738940	13.28629035623283
C	-8.95707896690287	2.78168055222687	14.19010576917210
C	-10.08649270797279	2.10060242187192	13.73991016494034
C	-10.43088831481604	2.13960928570494	12.38766106604334
I	-7.15304007460344	5.08213600486132	5.09642925746979
C	-6.89588245804999	4.54245574489468	3.05024224538426
C	-5.50491880993208	-0.20363144618756	8.87906413602069
C	-3.57848743035052	5.39993444632971	4.26505318357537
H	-2.76490873564952	6.13478143814259	4.25612627168854
H	-4.54574194565305	2.93245303636568	4.08532637517947
H	-2.60541532895752	2.01754117383259	6.17966080091411
H	-8.47421297911005	0.51836264566271	9.91391308316535
H	0.95366667196785	0.02352340468316	2.79033851236737
H	0.75957286793268	-1.27547652897459	0.65486960695908
H	-1.44986113424717	-1.77617969397536	-0.31163833143360
H	-3.54502834780302	-0.99591472453168	0.82116085092565
H	-10.25782639745655	3.92693736757262	9.68397718733280
H	-10.90800697048805	2.28082222467213	9.82601779991939
H	-6.21199759852191	-0.77048540370853	9.49613850873818
H	-4.74206335437672	-0.88191608447220	8.49476270805238
H	-5.02984058931315	0.56256009906699	9.49854253342790
H	-7.64921630504139	-1.18396730393593	7.38922291080547
H	-7.43662110318805	-0.12425009239702	5.97204400056119
H	-6.15861878006504	-1.28593103618321	6.40656222975828
H	-7.90714942036767	4.10381395975187	11.23529077139114
H	-7.29180456946097	4.03404821608884	13.63326827631376
H	-8.68426389132806	2.74899644776651	15.24077063745452
H	-10.69706591355492	1.53435737636611	14.43710546198038
H	-11.30912143343612	1.60347341837949	12.03498824238750
H	-2.88108654328656	3.95562016972251	7.36422431164172
H	-2.35028585251531	5.53497101199795	6.75380663107946
H	-4.08228050817210	5.20186174258411	6.99735760463051
H	-3.71545948674302	5.02963827474961	3.24316470617567
H	-4.49141194889258	5.92564178484513	4.56130785795845
H	-2.25306653707694	3.88127634126346	4.93641108651235
C	-6.87292157133002	5.54400053758686	2.08427787808225
C	-6.67158258565315	5.17548128401387	0.75220634230958
C	-6.48947499735266	3.83474712387564	0.41116227883330
C	-6.51372557807384	2.85104014188857	1.40030949606747
C	-6.72414557023233	3.19833459239990	2.73584816986012
H	-6.99525530715737	6.58713019800807	2.35640966500746
H	-6.64644710392485	5.94495557140488	-0.01421167052976
H	-6.32146356495832	3.55835561007009	-0.62559805158433
H	-6.35381966435168	1.80645022183857	1.15239673019207
H	-6.71913936562713	2.44028792478919	3.51282452705518

TS2.(5-6)
Lowest frequency = -114.12 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	0.61798108927894	0.07779252413605	2.81355713642858
C	-0.64362348826255	0.50544965213086	3.19896970976873
C	-1.76327999653551	0.29947864216404	2.38968079545716
C	-1.66204623484676	-0.34261967176154	1.16489542797540
C	-0.39259919959067	-0.78089813539617	0.76822554708797
C	0.72925531208062	-0.57381104834996	1.57910940591869
C	-2.95532429099424	0.87267982745617	3.08070798588888
N	-2.46761347557015	1.41050398102068	4.28447208943968
C	-1.08475486964767	1.21265066247421	4.43557121788884
C	-3.31921932794005	1.96267158830105	5.33100594357514
C	-4.28281028908274	0.88674341972920	5.84292700125410
O	-4.04199623311059	-0.32147278784640	5.75590234099648
O	-0.42349263437914	1.57417902978931	5.39259231736101
O	-4.11345488432195	0.91069290183090	2.70592444812879
C	-4.00883444352767	3.25681133211470	4.87572268663746
C	-3.01647620183727	4.42955006043517	4.96738176645625
C	-2.88752436441329	5.01078549178578	6.38256732868868
Pd	-5.79603071558212	3.36219209982828	5.95290811403948
N	-5.34035382093093	1.46849981617671	6.45263776935554
C	-6.40390448641211	0.63057142363745	7.05951328148507
C	-7.14840009204749	-0.15642940047789	5.95511211155578
N	-7.38789507809824	2.90451843332453	7.34274674024696
C	-7.36076663188487	1.58961920468365	7.71454704379249
C	-8.32550305921739	1.43732686752048	8.68715255106971
N	-8.87795407831266	2.67331623984909	8.83272370719822
N	-8.29933319260822	3.57223094729128	8.01667060638705
C	-9.91367015540663	3.10950821320670	9.77942481980618
C	-9.50350880732840	2.85915758947929	11.21290190852459
C	-8.31103728537696	3.39831825625318	11.71017918231489
C	-7.93477339728597	3.16602624538837	13.03022282818221
C	-8.74709979560233	2.39620497511794	13.86653163520151
C	-9.93549957059895	1.85785440099887	13.37662562392979
C	-10.30972700960104	2.08657314980794	12.05138404146792
I	-6.65684618200244	5.85274656331593	5.53537074887434
C	-7.19020704732034	4.03116935818389	4.21948764154522
C	-5.83026498612337	-0.32050177416163	8.12968957856903
C	-3.25474522921108	5.52324889671935	3.92149230620465
H	-2.45399541189286	6.27088195122340	3.95998341258515
H	-4.35625944991425	3.10820730264634	3.85226701899762
H	-2.63362962639247	2.17949527362309	6.15984440730938
H	-8.64054283022191	0.59582175052693	9.28264479108348
H	1.48137043356515	0.24217725796387	3.45064326149601
H	1.70029262064176	-0.92669775809189	1.24389083712191
H	-0.27383508123905	-1.29142870412913	-0.18317468124500
H	-2.53860220700270	-0.49997458134088	0.54417906797035
H	-10.05187286504712	4.17338750626334	9.57091468406090
H	-10.84377602693860	2.58321396523100	9.54543600093238
H	-6.64498628232399	-0.87050239727561	8.61514900457642
H	-5.14941740749051	-1.02891706954634	7.65868325336220
H	-5.28905249352414	0.25093331937907	8.88950004381101
H	-7.97216657350685	-0.73660208215192	6.38618316241928
H	-7.55137701631917	0.53912887745391	5.21330594649551
H	-6.44264782460487	-0.83157341562640	5.46750262859430
H	-7.67601600305504	3.99365154984393	11.05871581910425
H	-7.00743961974531	3.58584992417775	13.40856111697224
H	-8.45143672896329	2.21596806224330	14.89583838156403
H	-10.56950419725550	1.25623718126902	14.02129210761233
H	-11.23481520203698	1.66255811610444	11.66716107966530
H	-2.72996433470283	4.21937025690087	7.12369434212006
H	-2.03741252136869	5.70011495117206	6.43975154622974
H	-3.79551696204155	5.55524905415899	6.66136684989102
H	-3.26735291020799	5.09724856823161	2.91114083445049
H	-4.20205649050342	6.04373177476451	4.08855522721617
H	-2.03615662226036	3.98353633435020	4.72763412491172
C	-6.57884017950805	3.97356372549500	2.96460875406198
C	-7.17706098089532	3.21620135474881	1.95976661999455
C	-8.39526256475380	2.57293361492120	2.18136250322360
C	-9.02888744252368	2.70676720823604	3.41739586598413
C	-8.44490094796857	3.45201047665238	4.44130389352925
H	-5.64046280583549	4.48141717932678	2.78316759861595
H	-6.67592593549309	3.12908864936230	1.00018555233809
H	-8.85329770889928	1.98412491102727	1.39288733164670
H	-9.98995343283174	2.23165218594153	3.59586436907569
H	-8.94262721328609	3.56651974876580	5.39555985351949

2.6

Lowest frequency = 3.47 cm^{-1}.
Charge = 0, Multiplicity = 1

74

C	0.74103454965618	0.21618376508025	2.95755744106734
C	-0.55442413507139	0.63537085176867	3.22164254202351
C	-1.58503080820346	0.44969942972617	2.29780685254661
C	-1.35929373935784	-0.16238603293149	1.07424338045158
C	-0.05491193672230	-0.59050209253911	0.79895701610350
C	0.97812527977870	-0.40416267704790	1.72503340791321
C	-2.84208125185242	1.00452098514833	2.87521478834197
N	-2.48748373818712	1.52116557448840	4.13028296269222
C	-1.12151193705835	1.31160504706407	4.41992182827077
C	-3.40674585739537	2.06029192457595	5.12318282630046
C	-4.40620968334788	0.99168486253744	5.58804587300904
O	-4.20897692935828	-0.21633182810458	5.43808024165241
O	-0.57091329568803	1.64420414451720	5.45285551646119
O	-3.95421924271375	1.03704081560478	2.37799534739756
C	-4.01787082002908	3.41648394314117	4.70996082330333
C	-2.94187047191609	4.50944786789691	4.80525117782944
C	-2.63863216056275	4.97571205647795	6.23688966242815
Pd	-5.71838643877142	3.54495453959906	5.93860641027613
N	-5.41011812569799	1.57705292199424	6.28320401279192
C	-6.44902755083193	0.76600014605684	6.96126692577019
C	-7.27696195441673	-0.06492789579732	5.95461090361380
N	-7.25390797811645	3.08850322884725	7.42916698337674
C	-7.34979961803007	1.74640620326384	7.66498991774445
C	-8.36770338488778	1.58361966349212	8.58076680931358
N	-8.82123600838665	2.84342877985178	8.82706180279781
N	-8.13882883425047	3.76318175044963	8.12868595230613
C	-9.86640061181433	3.27452778561844	9.76958049168377
C	-9.53724051039773	2.86752879555579	11.18713137046310
C	-8.38151473396527	3.35535578093985	11.80879088724749
C	-8.07220895421989	2.97133683234865	13.11068643847364
C	-8.91543525316755	2.09954662256431	13.80419120052187
C	-10.06821256776662	1.61274654825120	13.19065051606861
C	-10.37562919551684	1.99441979881134	11.88360482731425
I	-6.20172026277526	6.14325621872134	5.89741942798718
C	-7.02398906706617	3.15818089096263	4.44098930109004
C	-5.78932240268960	-0.15505044488385	8.01258205321795
C	-3.16663631011011	5.67692825383306	3.84049210448873
H	-2.29767856592278	6.34492162366754	3.84964849138923
H	-4.42013419859595	3.36694728085151	3.69813653788305
H	-2.76242278273868	2.23482273231003	5.99503231821163
H	-8.78187198342518	0.71878858033892	9.07342514263069
H	1.53491065792777	0.36452777818309	3.68269005935237
H	1.97899929043076	-0.74821247207718	1.48128703974085
H	0.16166246853102	-1.07620436867142	-0.14803726989458
H	-2.16718386708230	-0.30310851263818	0.36321323852103
H	-9.91633160710265	4.35940587643815	9.65147370624288
H	-10.81801972330016	2.84042049252100	9.45006163995457
H	-6.56266000712070	-0.69555856231355	8.56937435115933
H	-5.14108421312572	-0.87289891333015	7.50920194478474
H	-5.19836086626797	0.43864650057945	8.71571604485752
H	-8.03170715056033	-0.65171745293254	6.48998727568676
H	-7.77941086385075	0.59145465145427	5.24124871760152
H	-6.60892881885096	-0.74057458025765	5.41756531571274
H	-7.72395591065095	4.03194391565321	11.26838009359850
H	-7.17427299007611	3.35361049542754	13.58702513795645
H	-8.67262137409637	1.80199030040091	14.82000490996056
H	-10.72714291836120	0.93493997945845	13.72529009828942
H	-11.27424631799400	1.61358019965441	11.40333487345797
H	-2.49907093083254	4.12620020651095	6.91668647109371
H	-1.71338588365868	5.56121253420051	6.25404571325415
H	-3.44920494640636	5.60164145242829	6.62085577490467
H	-3.30262644870961	5.30901871626059	2.81708435802167
H	-4.04860888445988	6.25902772032556	4.11658262000781
H	-2.03070376151113	3.99311781094077	4.45632452297369
C	-6.68073310720141	2.32531877134357	3.38806751669462
C	-7.66958412312330	1.99087064618064	2.45318726103482
C	-8.96672600087402	2.47822853346789	2.58267194063104
C	-9.28503007865108	3.30718046422155	3.65781562017330
C	-8.31567021916318	3.65467468472719	4.60373650919579
H	-5.69235826422199	1.90023955784152	3.26638858971122
H	-7.40128004342961	1.33088314907887	1.63289149123169
H	-9.72665184425473	2.21436940492720	1.85273565234699

H	-10.29032249980394	3.70493387020957	3.77014228658976
H	-8.56900828055720	4.30701687473309	5.42862598069834

TS2.(6-7)
Lowest frequency = -242.22 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	0.51992986796583	0.27104090570248	3.77361778258562
C	-0.80794893403656	0.67220124273850	3.76694494080135
C	-1.62242843724552	0.48362135296789	2.64812340418215
C	-1.13928780908304	-0.11308281645936	1.49337519140120
C	0.19884647753733	-0.52485362930371	1.49182562072348
C	1.01516485515699	-0.33559044206651	2.61325664783933
C	-2.97900457423259	1.02228366974966	2.95275332783824
N	-2.89644364764787	1.52454436911798	4.26538429669249
C	-1.61803506063203	1.33082124149974	4.82752911441566
C	-4.01145851908081	2.00636564965631	5.06393674112933
C	-4.99297341457869	0.86348594574981	5.39024369928323
O	-4.69068169836949	-0.32062536952475	5.20599698937878
O	-1.29486978845604	1.66394063849710	5.95334535662277
O	-3.96059225533444	1.07213111186729	2.23690093049664
C	-4.55977913248960	3.33252236240559	4.51293952620294
C	-3.88951626750984	4.54719335545530	5.18427819680813
C	-4.11430324375477	4.71209450436353	6.69084299356938
Pd	-6.67910245918872	3.27263597579786	5.65562300045252
N	-6.07916048614447	1.35331517939568	6.00649382131044
C	-7.04968981024116	0.49445043879375	6.72107787892221
C	-8.04959152729104	-0.14373485134841	5.73317604014243
N	-7.66806879344360	2.80202051076645	7.40497026779626
C	-7.75733592397039	1.45501683806324	7.64131662180255
C	-8.52733881716700	1.31450035387613	8.77270637925126
N	-8.85411184916684	2.58762787729834	9.13569643072263
N	-8.32660453572635	3.49648597944951	8.30671606155918
C	-9.58386371013259	3.04575490286935	10.32828341782131
C	-8.79075554713291	2.80343695964360	11.59266762944783
C	-7.53109049167881	3.39229212921237	11.75476177632595
C	-6.79746708261582	3.16414907518184	12.91582176201828
C	-7.31656320415479	2.35005179600218	13.92559115751472
C	-8.57118410110116	1.76353485707055	13.76939946977373
C	-9.30444195532833	1.98788549069071	12.60302961802228
I	-7.79013625285682	5.69398520802071	5.65944627075129
C	-6.39451531072027	3.25377020331176	3.58368806592655
C	-6.35922349835948	-0.58935257690890	7.57504203835788
C	-4.09439181752366	5.87588901033094	4.45275891519771
H	-3.38133636283617	6.61536640118146	4.83271684385247
H	-4.30864546022856	3.37063038425891	3.45696641874791
H	-3.55410583911241	2.22550582389180	6.03595599385919
H	-8.84456291641287	0.45525808085649	9.34099097733704
H	1.14450771245223	0.42204666526193	4.64838417559298
H	2.04905919227499	-0.66655325500259	2.58018410609276
H	0.61301823174642	-0.99995333534104	0.60729628568519
H	-1.78050195708200	-0.25520896184652	0.62922337938205
H	-9.76530825121926	4.10868226863890	10.15357753500728
H	-10.54357702061253	2.52332724649682	10.36082665173794
H	-7.10934088430677	-1.09924313227483	8.19025483979162
H	-5.86523505150292	-1.31485188054868	6.93042651717040
H	-5.61467701573573	-0.13385699730350	8.23418263401295
H	-8.80716390265315	-0.72520301307010	6.27000874105233
H	-8.54827669144848	0.63260458424009	5.14579125295260
H	-7.50297918147349	-0.80888606551248	5.05934809343285
H	-7.12690082530605	4.02419590141993	10.96775457657455
H	-5.82059716030281	3.62323221997366	13.03520202398350
H	-6.74277185830500	2.17431440567392	14.83073051977096
H	-8.97916890358879	1.12955020470030	14.55114044499901
H	-10.28291088958737	1.52884926586813	12.47958683027062
H	-4.03209389463348	3.76350237074073	7.23177892935446
H	-3.36037120485180	5.39465387395753	7.09911346344576
H	-5.10387897098527	5.13805901082287	6.88565194247633
H	-3.93412621297644	5.77052452186215	3.37444452438130
H	-5.10212734138666	6.26409924182028	4.63122347457707
H	-2.82704789296499	4.27146282033338	5.04720670956874
C	-6.70848324942516	1.99618284067829	3.04289799104220
C	-7.30629513153167	1.90290700617905	1.78596235248512
C	-7.55434601838167	3.04805773137251	1.03427404514306
C	-7.19070177053599	4.29692506858196	1.54495836881687

C	-6.60510119177429	4.40361408512651	2.80104114120272
H	-6.49454909929366	1.08700693294889	3.58451246764916
H	-7.55872258985369	0.92133286184091	1.39533876871113
H	-8.01253992875826	2.97076270518537	0.05236023008458
H	-7.36851400453552	5.19933110384769	0.96652155152549
H	-6.34033070713530	5.37864656320481	3.18190581514188

2.7
Lowest frequency = 7.77 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	0.07680526816282	0.62873020393050	1.86022043181102
C	-1.11861214485024	0.73385113707538	2.55577051622976
C	-2.21449339292631	-0.07452363663831	2.25206130469437
C	-2.15867908499381	-1.02029759852699	1.23976280189577
C	-0.95586306046010	-1.13563221382047	0.53197337203274
C	0.14347049211278	-0.32439499221996	0.83667857979542
C	-3.34120351087099	0.28550608481229	3.16044130278772
N	-2.85281660635305	1.32711795158927	3.97339209227280
C	-1.50693260326389	1.62533306720014	3.68085560725460
C	-3.49802729868940	1.97589086177068	5.13003652325053
C	-4.41856988997738	0.94255459912944	5.82768384480621
O	-3.87928755237646	-0.14828327933363	6.08106352683295
O	-0.84212887941338	2.45893675993058	4.27198362170379
O	-4.45919035375397	-0.19640736252374	3.18386848676758
C	-3.90097164107204	3.43246152121088	4.79251339404065
C	-3.68286173333169	4.35348413802464	6.04473464910247
C	-4.47803772256787	4.02497767043900	7.31423443120108
Pd	-6.80352704338059	2.89056749289192	5.48062486196817
N	-5.65138494750374	1.31723642740423	6.21295996336253
C	-6.42477753438157	0.35528668173548	7.05667728842344
C	-6.97670639078615	-0.78089204755052	6.16874905389101
N	-7.88840970100425	2.36879899362888	7.10425130774021
C	-7.55205429971486	1.15718579030898	7.64071005779734
C	-8.40802980228109	0.96163001390368	8.70155808016102
N	-9.20328718333738	2.06755289840468	8.72263594399768
N	-8.88398533990296	2.93549025933685	7.75561863225922
C	-10.21039972221122	2.45665227474879	9.72196257957764
C	-9.56293883589450	2.84783916841148	11.03169477326371
C	-8.65890640972198	3.91592240534016	11.07441038694972
C	-8.05169808593409	4.26844004120779	12.27663682934050
C	-8.34448151413334	3.56107399164967	13.44526019325197
C	-9.24595586181101	2.49881148214664	13.40745412453865
C	-9.85093848772142	2.14168799910429	12.20132953779200
I	-8.41117493523768	4.91521720128845	4.99353264062772
C	-5.16393720918125	3.56802328721820	3.94279959313607
C	-5.61746349735443	-0.21741356644458	8.24628855287949
C	-3.83305770118533	5.85085022109105	5.74719844478833
H	-3.47609447492769	6.42491659486418	6.60929479190266
H	-3.09738013422613	3.76667634508098	4.12029802308626
H	-2.67569664628088	2.07725698134992	5.84954047389008
H	-8.50555448026712	0.16943979116682	9.42564831845942
H	0.92376330874721	1.26198106231313	2.10472116204545
H	1.06210069773167	-0.43849941854411	0.26863043329041
H	-0.87168468146102	-1.86627658145898	-0.26723345668226
H	-3.01676748653899	-1.64466825236511	1.01190747910804
H	-10.75273627134803	3.28849615946582	9.26697746386914
H	-10.89590079884770	1.61620182799914	9.85700561612513
H	-6.30312408485342	-0.74480096095053	8.91982792514221
H	-4.85344167069402	-0.90518456609299	7.89359244469857
H	-5.14113209179993	0.59429220441546	8.80430153104332
H	-7.57389369952043	-1.48245711526727	6.76209370776471
H	-7.60458871396515	-0.36312237181640	5.37609628776896
H	-6.13375085268692	-1.30919286701787	5.71857450243711
H	-8.42903233007257	4.46337765842530	10.16359987625348
H	-7.35029674875123	5.09709387791763	12.30328613143224
H	-7.86955388866656	3.83828959052499	14.38176252222755
H	-9.47656398420526	1.94524553822639	14.31293312060804
H	-10.55236659340409	1.31076511340805	12.17040662682040
H	-4.37402183350167	2.98278851404007	7.62058511745218
H	-4.11602498402207	4.66422980209583	8.12869218048748
H	-5.54695365380478	4.23279080171506	7.17774587019105
H	-3.24359338929906	6.15915124922518	4.87629285689129
H	-4.88177358254849	6.12056446569044	5.58366749215374
H	-2.62254854565420	4.17989092932716	6.27701021157765

C	-5.91401732073850	2.43569385212470	3.49961133969001
C	-6.85748177065033	2.55344024381670	2.44411648424046
C	-7.03735768338063	3.75185570959140	1.79622239322802
C	-6.28079921309030	4.87219113390013	2.19545943797164
C	-5.38260627231879	4.78703008051170	3.23461052729955
H	-5.61245442641097	1.43207228766198	3.77093314684311
H	-7.39515375297574	1.66294845774204	2.13372741258719
H	-7.74763193110538	3.83856922911018	0.97985981916460
H	-6.40570327116772	5.81779571931959	1.67647680782074
H	-4.79639152598930	5.65857598460740	3.49139858888428

2.5a
Lowest frequency = 11.19 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	0.96397377498282	-0.66554068771154	3.14319215655301
C	-0.31426488824900	-0.23091395981331	3.46013140721731
C	-1.42837418437848	-0.64133390601263	2.72465299488874
C	-1.30475140347773	-1.50240480186520	1.64489629662631
C	-0.01821096495461	-1.94905007448506	1.31856007955128
C	1.09817518239513	-1.53706739054297	2.05540556304355
C	-2.64215312748046	0.00014346978576	3.31221917934793
N	-2.17168717502216	0.78246616624991	4.38070028930121
C	-0.78158790658017	0.68108300449648	4.54399198370072
C	-3.03645537621741	1.49953713601401	5.31450576672830
C	-3.97099708236513	0.50607731414421	6.01927930730262
O	-3.68099284038931	-0.68552524096785	6.18132276303830
O	-0.13033060605975	1.25066526914643	5.40267543060941
O	-3.80273879432341	-0.09022968205169	2.95621644427117
C	-3.77212588837690	2.67849589116940	4.66069851235103
C	-2.78429766617667	3.79910601795293	4.29810751546966
C	-2.34781561998410	4.65206738835369	5.49710277458423
Pd	-5.41958952225830	3.01054790484573	5.86887226039410
N	-5.07110770018495	1.14363808913304	6.46993390507571
C	-6.09511843295876	0.42621184357193	7.26379761518247
C	-6.77293866441265	-0.66380594630668	6.40251857348100
N	-7.07457560492532	2.72398061859511	7.15358500169517
C	-7.11721255990867	1.45674056650859	7.66722018719068
C	-8.20559180828921	1.41720377288226	8.51292809477043
N	-8.75502806782805	2.66141605350606	8.44314430187034
N	-8.05992596802504	3.46259266529479	7.61903737272541
C	-9.85548089851555	3.22976150602051	9.23263715138606
C	-9.40605290370455	3.61043831077979	10.62662992363850
C	-8.38741774596066	4.55450724821053	10.80177847166640
C	-7.96892576677063	4.89723609398464	12.08452550168581
C	-8.56415834260866	4.30574381273634	13.20123552066847
C	-9.58008489053614	3.36681319284213	13.03071074562946
C	-9.99705172586389	3.01877321068003	11.74499869140815
I	-6.09518241292984	5.51539867128592	5.39645066288726
C	-5.93022769931845	6.21534394114720	7.39923215503862
C	-5.47401077687834	-0.18798484790374	8.53796418105446
C	-3.26381872489311	4.65958820856810	3.12415186326362
H	-2.48623746924014	5.37013178394144	2.82052112043640
H	-4.27068511501414	2.30930651640624	3.75519333683306
H	-2.34973234531288	1.87515835567551	6.08312393985202
H	-8.61742984160725	0.64281318308952	9.13979483213801
H	1.82294703849032	-0.34079313019457	3.72211058771329
H	2.08297789806161	-1.90181355028201	1.77774646006473
H	0.11845997145172	-2.62717501497906	0.48100196973703
H	-2.17709152296155	-1.81686574361130	1.08049272763790
H	-10.19624421972817	4.09966555195837	8.66615157793549
H	-10.66187492298786	2.49312427187113	9.26791244459803
H	-6.25254866428594	-0.66545650339844	9.14416454955306
H	-4.73042900460835	-0.93229188593507	8.25141455700766
H	-4.99360040586646	0.59365325648175	9.13387044990841
H	-7.55745690843222	-1.17228863540534	6.97486004617499
H	-7.21777040588921	-0.21093566146648	5.51206909398069
H	-6.01697678038338	-1.38892390493882	6.09588791106667
H	-7.91718993259922	5.01092901207353	9.93499647819448
H	-7.17693710890851	5.62870571505434	12.21132321852384
H	-8.23502523919747	4.57545254756914	14.20052882806841
H	-10.04554419802742	2.90183040163271	13.89483649414412
H	-10.78755053186513	2.28346912386777	11.61121191272108
H	-2.00680668250074	4.02343892957777	6.32639715250269
H	-1.52043382069168	5.31549752195843	5.22017673908793

H	-3.17459823919875	5.27237263363119	5.85839791319690
H	-3.51124671352666	4.03238875017300	2.26065300912604
H	-4.15350031714346	5.24249131477231	3.38361131132227
H	-1.87714739679106	3.28217961139881	3.94181022817516
C	-6.59084610254167	7.38368998156831	7.76976819053384
C	-6.45240924803208	7.84078377760653	9.08205998420982
C	-5.66526214173677	7.13769948897700	9.99484262833840
C	-5.01995213878798	5.96448096673057	9.60159025601262
C	-5.14842029689547	5.49083396177172	8.29495412569846
H	-7.20168164234429	7.92989440565345	7.05844261177886
H	-6.96239973507947	8.75067327015759	9.38523810079964
H	-5.55526040111457	7.50535689136633	11.01086668026086
H	-4.41066695813391	5.40943663569384	10.30912199962463
H	-4.66058767314172	4.57401133930792	7.97304288774559

TS2.(5-6)a
Lowest frequency = -131.15 cm^{-1}.
Charge = 0, Multiplicity = 1

74

C	1.02722481795969	-0.00919834740672	3.77747006165954
C	-0.30819430873533	0.31689728123925	3.96037397241426
C	-1.32206426413186	-0.32996205075059	3.24942518016641
C	-1.03676637034318	-1.32702070306771	2.32914325382108
C	0.30889478412862	-1.66554579442991	2.13976746950081
C	1.32437501213775	-1.01709150720690	2.85191630031562
C	-2.63259759420488	0.25197317940935	3.66511605905418
N	-2.31801161356284	1.23961976229140	4.61429388979114
C	-0.93929354872302	1.32765446165484	4.85638307738041
C	-3.30623531257191	1.98915551904604	5.38327022958728
C	-4.15432418055684	1.02308925481719	6.23553618159265
O	-3.73258037205631	-0.08156927347300	6.60131629287461
O	-0.40976549494752	2.10041268726260	5.63762005657920
O	-3.75177648107620	-0.01729716369845	3.26992576706170
C	-4.21210828366090	2.89157988700502	4.54742935266559
C	-3.51125067071113	3.76300412629757	3.50625434404600
C	-2.48444467754342	4.76856451017791	4.03727943635555
Pd	-5.60618429177811	3.50563565344312	5.96653466817261
N	-5.34544709010317	1.58214482200495	6.52612237655394
C	-6.26445340991364	0.95817371356979	7.50138626488717
C	-6.80498984912650	-0.37644130395380	6.94810058693816
N	-7.35416168796902	3.19732206002310	7.20503905561356
C	-7.39595402217044	1.92989316582147	7.71523489980786
C	-8.57265657243863	1.83647137341434	8.42919121759138
N	-9.16730650583835	3.05304988330744	8.29415310757817
N	-8.42038717178703	3.88669390584506	7.55040615362312
C	-10.36756482966043	3.56972241835893	8.96805267467800
C	-10.06633020905710	3.94966350194670	10.40153040642232
C	-9.19267888984494	5.00853255183256	10.67516404404525
C	-8.88302574895577	5.33944965377095	11.99159152573086
C	-9.44749256303505	4.61845996539250	13.04669162847947
C	-10.32279677978631	3.56704205549531	12.77980649985913
C	-10.62866264218884	3.23274985844480	11.45957701219455
I	-5.68240680016955	6.13765442680984	5.74674460961819
C	-4.68582332785701	5.00010916825420	7.48830742894292
C	-5.55238927460168	0.74663878460985	8.86047419659467
C	-4.50275776588613	4.42347938273391	2.54089514156097
H	-3.96971244903688	4.89039237826873	1.70498919819994
H	-4.92919830582013	2.25441842411239	4.01228327446023
H	-2.70574205009424	2.58711268266028	6.08071757048042
H	-9.01694220355953	1.04099486238537	9.00548658406838
H	1.80718866042058	0.49981350243139	4.33506879689787
H	2.35860425249924	-1.30263273759034	2.68260046419439
H	0.57172626310361	-2.44414853629142	1.42941850347299
H	-1.83153634444060	-1.82408652898847	1.78179511141522
H	-10.68466436868996	4.43119169384813	8.37638425347221
H	-11.14119231095962	2.79973371267911	8.91811678433200
H	-6.25462132568404	0.33463294133166	9.59396922205010
H	-4.72030383540571	0.05461190189082	8.72270287241525
H	-5.17299292383478	1.70267863893851	9.23249712686242
H	-7.51256917311315	-0.82646533175840	7.65451953287057
H	-7.31189959679004	-0.20886616448682	5.99377869484317
H	-5.96672892812589	-1.05786294004067	6.79409978749305
H	-8.75311379539970	5.56677947931290	9.85258924886835
H	-8.20389052444577	6.16214699885311	12.19572868647498
H	-9.20574222407858	4.87771055411161	14.07319578230376

H	-10.76588923480450	3.00473477999843	13.59646657584613
H	-11.30943919997247	2.41014728493749	11.25174229846797
H	-1.75546978161612	4.29145569354807	4.70118078828200
H	-1.92957815054644	5.21177578324635	3.20266341103056
H	-2.97736221215370	5.58570198436660	4.57357630557257
H	-5.19876209901203	3.68288293217554	2.13219943410616
H	-5.08914667210309	5.19868761166207	3.04297491900275
H	-2.94547425746527	3.03183386828300	2.90214174784259
C	-5.40939601170115	5.01984858411213	8.68647864906174
C	-4.74253401539968	4.73423219813516	9.87613179099359
C	-3.37157041194717	4.46733084171223	9.88015230452953
C	-2.65857101906817	4.51697244432915	8.68249917931418
C	-3.30214742900597	4.81250321101974	7.47946558337595
H	-6.47280074458819	5.21993759099075	8.68239105377725
H	-5.30902356113681	4.71952965923476	10.80385719483708
H	-2.86182498579082	4.23711313382316	10.81043683552771
H	-1.59054574966169	4.31951983241478	8.66548928414671
H	-2.74003928980448	4.86157216404972	6.55788372535170

2.6a
Lowest frequency = 11.26 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	0.84903900222006	-0.21721345342648	3.27466103500122
C	-0.43527714507312	0.17309312764496	3.62304097298762
C	-1.55931017742897	-0.36521017614162	2.98984465361566
C	-1.43884787606346	-1.31371002633842	1.98551206621992
C	-0.14573268714905	-1.71495277733061	1.62840917462571
C	0.97957558014901	-1.17550927973223	2.26217103525044
C	-2.77734593766359	0.25627524981625	3.58404732056573
N	-2.30025582130400	1.16479433178175	4.54531058221516
C	-0.89732698490945	1.15409933651604	4.64527158371060
C	-3.16304252068240	1.91503823000664	5.44680981739553
C	-4.00238118358635	0.93075035820095	6.28136843722216
O	-3.56720241434788	-0.17619413847705	6.61456244023957
O	-0.24740227994544	1.83425762823419	5.41811930756275
O	-3.95079805882824	0.06768964854521	3.32068522181047
C	-3.96753508636407	2.98029707100487	4.69539986453305
C	-3.06872843601823	4.10977923665597	4.16755673582323
C	-2.92687079211906	5.31549872574572	5.10586091828997
Pd	-5.69618855811394	3.23408720564924	5.81280915389408
N	-5.20520027375149	1.45026377564617	6.60920418975110
C	-6.12223196447525	0.74868480939425	7.53999228152179
C	-6.59768067633186	-0.57723532529923	6.90056579761491
N	-7.47569903533405	2.78337976750667	6.98718066335871
C	-7.30395958252473	1.65963490274853	7.74543006239735
C	-8.34962934428052	1.63338095915759	8.64307660815580
N	-9.08107866599745	2.74752214623631	8.36256668622613
N	-8.54020196064151	3.45580308586344	7.35943215889576
C	-10.20086467270907	3.31690836935665	9.11925100809693
C	-9.75245743641347	3.80607862520753	10.48184247536340
C	-8.52755698132714	4.46569656009815	10.63127328778075
C	-8.13086082791352	4.92881075754477	11.88324634284419
C	-8.95521315542685	4.74278554809337	12.99472163299962
C	-10.17649291265389	4.08575417764936	12.84961394454618
C	-10.57112096335447	3.61391815265498	11.59703651392459
I	-6.74067584488995	5.20255430981714	4.39397620336313
C	-5.03466478356839	4.26428444015056	7.41242647844668
C	-5.44359809082823	0.49180997850647	8.90278439555306
C	-3.44639924348679	4.54020176657220	2.74477972698274
H	-2.70192456554955	5.24439011092611	2.35631449388193
H	-4.51491185425880	2.49490745371751	3.87244886034120
H	-2.46243405307000	2.40997018558412	6.13261016327012
H	-8.61460623400548	0.95972334341868	9.44187385950059
H	1.71541363740827	0.20653248293339	3.77262065660622
H	1.96916284829702	-1.50779119456807	1.96235820214739
H	-0.01091060522124	-2.45726989124139	0.84712623595226
H	-2.31751146126361	-1.72661610595019	1.50015668833922
H	-10.57792064384607	4.13305851117515	8.49686121221511
H	-10.98247947695164	2.55800325822333	9.21193510750007
H	-6.14444623354007	-0.00585635323290	9.58203704000931
H	-4.57328990266352	-0.14913152563807	8.75611176883147
H	-5.13153189546613	1.43854041315271	9.35186413250545
H	-7.31655737821392	-1.07326777879502	7.56183440122364
H	-7.07801365035900	-0.37793854366091	5.93883988207444

H	-5.73562911360010	-1.22720698586436	6.74425851668221
H	-7.87705342691206	4.61032112264933	9.77324973858640
H	-7.17413247875832	5.43204831970986	11.98806946640894
H	-8.64384826862741	5.10298149255457	13.97080964278275
H	-10.81931807656851	3.93129173886955	13.71129539542315
H	-11.51964991336515	3.09276417292308	11.48776719153951
H	-2.57401575294276	5.01380546242320	6.09593530438947
H	-2.20176414304245	6.02266805601842	4.68848023557165
H	-3.88674896899010	5.82649217981308	5.22326887713530
H	-3.48126697150366	3.67541388910679	2.07233174851331
H	-4.42385546531412	5.02853283699543	2.72632710893551
H	-2.06689445275849	3.65560602511237	4.10475331675229
C	-5.80897170143171	5.34277916685890	7.83849019636112
C	-5.42025308773293	6.03792337680402	8.98824840551045
C	-4.29320633109406	5.64962418089817	9.71064719944816
C	-3.54751481773178	4.55561525754060	9.27950828102887
C	-3.91568911546880	3.85237773075107	8.12672549816565
H	-6.68804350953716	5.65054646465519	7.28779203584510
H	-6.01141387344868	6.89335014591911	9.30535776953233
H	-3.99746083992445	6.19666046965707	10.60117606167311
H	-2.67099752962082	4.23037369539009	9.83315718091118
H	-3.32438689978582	3.00031572990963	7.82271434561930

TS2.(6-7)a
Lowest frequency = -277.08 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	0.04901281584019	-0.39273920830704	2.69231071860452
C	-1.01977823872302	0.14693861361215	3.39208136052825
C	-2.33945837498473	-0.20292962529469	3.09298416451042
C	-2.63838845420327	-1.10469545924241	2.08270650015208
C	-1.56533841029235	-1.65601767508936	1.37219932611568
C	-0.24367409742874	-1.30585680017356	1.67202661908996
C	-3.24368957281831	0.54750714314912	4.00877273196871
N	-2.39699831253552	1.33494521262078	4.80853737775068
C	-1.03590028348128	1.13126872365910	4.51074960947074
C	-2.85764318964812	2.15503145925343	5.92606961218492
C	-3.69132409676893	1.23826088817187	6.85670646787007
O	-3.21927370210572	0.14351511399127	7.19995557028260
O	-0.10637211965021	1.68139743884751	5.07086837900594
O	-4.45905968283915	0.53515604090112	4.07908884314731
C	-3.54658552505182	3.42403647555682	5.41798566893285
C	-2.61925513002068	4.29217269754073	4.51917389625552
C	-2.57327599962476	5.81439678407852	4.68279142285701
Pd	-5.45630455473047	3.55134580943769	6.53826565897056
N	-4.87656428830101	1.74292053767956	7.22788450770738
C	-5.82178525928128	0.94900972925600	8.05050551332418
C	-6.08261161778223	-0.44103633889492	7.42180618196462
N	-7.22642088243436	2.88133241697066	7.32250099782153
C	-7.11402943227432	1.71767402216098	8.03750047718346
C	-8.34617288621598	1.50549431490215	8.61417919389777
N	-9.11432301896876	2.55245321140648	8.20086230929834
N	-8.43355783842710	3.39819436683716	7.41899310279790
C	-10.49437965025487	2.88789893612336	8.58731174194365
C	-10.57982787558071	3.27652836633489	10.04595449040979
C	-9.85485825663660	4.37522159407887	10.52269679508175
C	-9.92530037626858	4.72760327919059	11.86774398306580
C	-10.72206150189237	3.98912376622873	12.74621394867753
C	-11.44722264318902	2.89602751837481	12.27532907217729
C	-11.37268848623500	2.53932001397740	10.92789459490483
I	-6.59764362530418	5.51176503093729	5.12528087499241
C	-3.70708885999020	4.48137560855295	7.27267959308146
C	-5.29133951093422	0.81690456342920	9.49327830462937
C	-2.99635785879408	3.99155171199284	3.05259239615928
H	-2.27884898538475	4.46743342223569	2.37544672954406
H	-4.39724242470964	3.11807124759280	4.78171120616503
H	-1.93615321297320	2.41988320465854	6.45353963050068
H	-8.72639154373518	0.73447172591826	9.26450016766745
H	1.07040863271588	-0.11467134181801	2.93203923388439
H	0.56654495736083	-1.75115800923876	1.10211551835880
H	-1.75886679249159	-2.36714666448145	0.57444053281740
H	-3.66671960580563	-1.36882683503126	1.85716914140771
H	-10.77861785960470	3.70839621970341	7.92467101031104
H	-11.12754208796338	2.02295799605663	8.37308842891217
H	-6.00354001769449	0.26521544856919	10.11705962756772

H	-4.34407421519577	0.27422704277980	9.46814221790317
H	-5.13290619400128	1.80754917908697	9.92891789161785
H	-6.87213060373960	-0.95308588017912	7.98331780183378
H	-6.40024287130708	-0.32470687882468	6.38231376731904
H	-5.16836983370599	-1.03268302162331	7.45097111466416
H	-9.23295094410543	4.94813060376642	9.83921010820570
H	-9.36016942448260	5.58053673723105	12.23163117162055
H	-10.77596485502569	4.26662760484926	13.79478752756610
H	-12.06802352381145	2.31863577028476	12.95408009120209
H	-11.93685812110029	1.68515094642527	10.55987946974850
H	-2.14160963328444	6.11557633131822	5.63733588776323
H	-1.94319845772351	6.22118166862367	3.88360575053340
H	-3.57099147564342	6.25148727580591	4.58130117159705
H	-3.01087075907398	2.92078544423073	2.83544006774279
H	-3.99267282256427	4.39557889914910	2.84014289837471
H	-1.60413362877797	3.92006215518899	4.70968433078543
C	-3.86272694004693	5.87522254793948	7.31321148940699
C	-3.26047703209324	6.62456470836796	8.32468112963589
C	-2.47096135703451	6.01076871183062	9.29368463594743
C	-2.30941432180832	4.62784254642127	9.25340244443705
C	-2.92809562645659	3.86463679186037	8.26216660080024
H	-4.47066037936309	6.37817532153315	6.57574164284892
H	-3.41535187361056	7.70006751167192	8.33797180767038
H	-1.99458898375433	6.59879052513516	10.07276738048007
H	-1.71201475271207	4.11987728840920	10.00551682181382
H	-2.81132563146005	2.79192347230055	8.31502854452869

2.7a
Lowest frequency = -12.45 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	-3.29312401653074	-1.39970148516035	3.01150756847908
C	-3.33297288910894	-0.15725660262407	3.62709387604924
C	-4.40410997658094	0.71748161343362	3.43439465506933
C	-5.47948813849386	0.38466000937488	2.62398244125269
C	-5.45097782990869	-0.87073557319668	2.00428554109544
C	-4.37560963090707	-1.74727206409322	2.19359196844031
C	-4.14418561011036	1.95716215731382	4.21051888351129
N	-2.92239038108139	1.75904978429509	4.86484171488485
C	-2.35985441559064	0.49841009226148	4.54297938789296
C	-2.27142136032109	2.65454412054889	5.82609637571067
C	-2.79652978776170	2.42314381590232	7.27289568329251
O	-1.94066640301099	2.14267706347592	8.12911342112665
O	-1.28831138425754	0.09099662190769	4.94839828672007
O	-4.83624563936322	2.96509955187077	4.26220411170289
C	-2.24384302135543	4.14072855396188	5.32992033835887
C	-0.81597292148823	4.56455836744930	4.90835162013404
C	-0.79120046066758	6.04170049358859	4.49594331172554
Pd	-5.53063013750594	3.76911624825910	6.66669125109507
N	-4.13351040349877	2.43495826192748	7.46686989765960
C	-4.65545186701450	1.85749231818974	8.74142480197360
C	-4.01875504386448	0.49567289054107	9.09157282535053
N	-6.71617870701579	2.35099953643059	7.46382922427827
C	-6.11443381266468	1.62533113047914	8.45446148032740
C	-7.08929852307633	0.79496213755376	8.95974387529952
N	-8.20482032391715	1.06950654417404	8.22460025434561
N	-7.97966426598914	2.02412899103780	7.31047577958212
C	-9.58079503580603	0.58890955986167	8.41278609371641
C	-10.30108426996055	1.36761755376216	9.49290949151494
C	-10.42682975806436	2.75846748593914	9.39161702354798
C	-11.09121496974597	3.47063778716430	10.38705474046323
C	-11.63770888111886	2.80259403287504	11.48550657631086
C	-11.51557029943867	1.41788589037710	11.58800765332046
C	-10.84491401724394	0.70322452252627	10.59428957833706
I	-7.59714946986041	5.06631746708204	5.64119244470612
C	-2.85425414973287	5.01476175497331	6.39589326335312
C	-4.49597782811184	2.85637197521295	9.90621511055679
C	-0.30707768937463	3.68268307408263	3.75969698801843
H	0.70025998735013	3.99120522470273	3.46081740799537
H	-2.88311711919125	4.21312948339407	4.44636565510462
H	-1.24803092008540	2.27856367705431	5.88821644816634
H	-7.08659191295486	0.05947956516295	9.74762824769330
H	-2.45485079844821	-2.07236156810566	3.16325502744434
H	-4.38340210477108	-2.71293488880127	1.69648179013283
H	-6.27524679650078	-1.17154122434453	1.36411557725527

H	-6.30598979185093	1.07436122457414	2.48417481423743
H	-10.06409539593595	0.70582841778535	7.43978467488202
H	-9.53326019474527	-0.47436432753255	8.65978188219529
H	-4.94290061240334	2.45878882302378	10.82437427846922
H	-3.43048812249606	3.03403362300657	10.06698514140880
H	-4.98522045164093	3.80142319012510	9.65142649209377
H	-4.58085374372055	0.03759741627871	9.91388898740595
H	-4.05807310950565	-0.17275704449041	8.22601818244510
H	-2.98189705562980	0.62578904188479	9.39397668510712
H	-9.99751383855423	3.27963740083396	8.53930812949594
H	-11.18408608949888	4.54945046611169	10.30388245755104
H	-12.15597393870408	3.36147986727794	12.25928315450198
H	-11.93690178890575	0.89326237583955	12.44062883873876
H	-10.74640054816195	-0.37722598856872	10.67534633426556
H	-1.10976177700122	6.69450120722572	5.31435544112349
H	0.21772101356358	6.34031833479632	4.19210859611199
H	-1.46315183588522	6.21296079597705	3.64575179690160
H	-0.26131960730136	2.62432868778580	4.03418303557082
H	-0.96235490273102	3.78124398066264	2.88520901929366
H	-0.15022137511161	4.42760563881865	5.77222226223497
C	-4.15861960848202	5.53579540675063	6.20372798955019
C	-4.79642793081860	6.23767934116775	7.25687786026849
C	-4.14106687236456	6.41996289808794	8.47754926877944
C	-2.84708919327152	5.93553091159810	8.64088121112293
C	-2.21149238115197	5.23308256730969	7.61215686194645
H	-4.58198354820887	5.56753717537504	5.20016578818818
H	-5.76881703506662	6.68197367106505	7.07850963925860
H	-4.63569717567492	6.95409744420115	9.28292205213512
H	-2.32671718796725	6.08633410001210	9.58278800033708
H	-1.22143691662848	4.82196340119453	7.77909043138258

2.5’

Lowest frequency = 10.05 cm^{-1}.

Charge = 0, Multiplicity = 1

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C	4.57293571030317	4.56863374706253	6.77784819797196
C	4.96708578992103	5.76354284244794	6.19344647392158
C	6.31390016687077	6.09339301685080	6.04192229427453
C	7.32037627517607	5.24067899283343	6.46947095544935
C	6.93376778022466	4.03103966651605	7.05930899255205
C	5.58186922028761	3.70045843966240	7.21167501309973
C	6.40685225018153	7.43676906839071	5.39562411896155
N	5.07354296262877	7.84935815246107	5.19362411912117
C	4.15432900875945	6.87774499849664	5.63265652407708
C	4.60864474542751	9.04410622858694	4.48381301789065
C	4.56331161193440	10.34517334632174	5.30797168329826
C	5.80042740093167	10.68739940291169	6.15351113916197
C	5.45590015282136	11.72468737681581	7.23082253414271
O	2.94163727690177	6.97205977904873	5.54846283104169
O	7.41068885153286	8.06693715437086	5.12775629321387
Pd	4.24147957634578	11.77761131284767	3.85965300824601
I	2.85023800487105	13.39881800080724	5.35876436863435
C	1.22859213988088	13.73845324143914	4.01893938074642
N	4.33252624954292	12.91142647162435	2.08413321175490
C	5.00478302079453	12.25268919380991	1.08884524577728
C	5.05674241252221	13.12015727402654	0.01794825083262
N	4.42399880608357	14.24885670841751	0.44231598537308
N	3.97560208223946	14.11977526220628	1.70230434599536
C	4.07813815844672	15.45593032213848	-0.32003484759818
C	2.85060682607249	15.24523389126172	-1.17951911108123
C	2.93263419821722	15.35721543446970	-2.56897142349482
C	1.80062162089538	15.15860327443412	-3.36102721518403
C	0.58169700045321	14.84135778064148	-2.76411115215218
C	0.49686976953551	14.72597281096273	-1.37456562385617
C	1.62433166474311	14.92852789306727	-0.58339571760995
C	5.51479824445322	10.84606904980384	1.28864945870763
C	4.85155365478047	9.93257412212630	0.23150348452966
N	5.12193158973411	10.45323365812664	2.65843591152865
C	5.29086247013291	9.19020393798098	3.11160807958741
O	5.81147633303060	8.24570152624062	2.50828927060066
C	7.05233776315347	10.81586626161242	1.14895939866764
C	7.01592242620025	11.16196020715395	5.34391336780909
H	3.56554792241783	8.79840491296348	4.25017445369850
H	3.68599717413539	10.29678126578397	5.96454358521725
H	5.46959916587310	13.03315870694025	-0.97416921794278

H	3.52175671580139	4.32196282252568	6.89002259364845
H	5.31451218309961	2.75429641404020	7.67347433696507
H	7.69301848565024	3.33525828154152	7.40495963844212
H	8.36542127762236	5.50690553873285	6.34556199206731
H	3.91638897347043	16.23403721982810	0.42966801103964
H	4.94271759244703	15.72761268197039	-0.93053788255518
H	5.10472843756337	10.27877974957840	-0.77714898487036
H	5.20557054090186	8.91009710919112	0.36673647430060
H	3.76388595878885	9.95650852356198	0.34832548046044
H	7.35721164534405	11.13448002046196	0.14524357487723
H	7.50767557179150	11.48138863084054	1.88742431895429
H	7.39817234464363	9.79516405381735	1.32442419383626
H	1.55766122528748	14.83025183362898	0.49659589384589
H	-0.45080318801161	14.47946316549337	-0.90511766460990
H	-0.29985004126193	14.68309777014867	-3.37847957112352
H	1.87344501451804	15.24829309856198	-4.44093335727714
H	3.88465863048183	15.60233335219144	-3.03480485571714
H	4.56486992160590	11.43677968335161	7.80066045716355
H	6.28728776969268	11.84798027384773	7.93392781705218
H	5.27520369808510	12.70831889906303	6.77450588444764
H	7.88329227158212	11.28809587714488	6.00310770830019
H	7.28353587388113	10.44548272299089	4.56687996251570
H	6.79428044059843	12.12760029547812	4.87048642451553
H	6.09313294390010	9.76615365798474	6.68164106122704
C	0.47909055260720	14.90581429501267	4.13613386496195
C	-0.58543938796847	15.10800893634540	3.25474111085796
C	-0.88516046796218	14.15522860875981	2.28089857577520
C	-0.11574303186965	12.99515091147034	2.17927561720198
C	0.95230583746207	12.77715649912633	3.05051480985419
H	0.71577044392024	15.64777818758833	4.89179503885055
H	-1.17775679000587	16.01507062937015	3.33443395550821
H	-1.71816909294644	14.31750320245087	1.60311553338178
H	-0.34111738039242	12.25184224827523	1.41982118773855
H	1.56829355121394	11.88507507196141	2.97708411139839

TS2.(5-6)'
Lowest frequency = -115.97 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.89394398150030	5.13212299336522	6.90936797296315
C	4.40855018820066	6.24197582623592	6.25522748179168
C	5.76862189897660	6.35251890879467	5.96260225371839
C	6.66706574791150	5.35631391560139	6.31312866022674
C	6.15753325092973	4.23021534008559	6.97131186558394
C	4.79330538664330	4.12005046184138	7.26542212209884
C	6.00513179974874	7.65849665394208	5.27714243141113
N	4.73558327887103	8.26794265320056	5.18760148293309
C	3.72792768211861	7.46526915294277	5.74980240995201
C	4.39254791654986	9.51863011354556	4.50997055205928
C	4.61217546686612	10.79933455755797	5.32464494924266
C	5.99526111984248	11.01849985439434	5.95412210196336
C	5.94417454114039	12.10505498475445	7.03651044167086
O	2.54340153385410	7.75742696095100	5.79424147044031
O	7.06100252440100	8.12935304727365	4.90473962943464
Pd	4.17346643633106	12.24109282821551	3.91514775548176
I	2.88271340753233	13.83948478442594	5.58547391636761
C	1.83971254653499	12.35609163780919	4.23114767617013
N	4.30957371133437	13.40483600369750	2.11525409413015
C	4.86624421426478	12.68408459472354	1.09345767711639
C	4.99571773679656	13.55282177892348	0.03007992457605
N	4.51476733710417	14.74279548272415	0.48229234455073
N	4.08999432079879	14.65148694748097	1.75471412897793
C	4.30297251676679	15.99089056460074	-0.26252958425541
C	3.14276509719004	15.87182699579665	-1.22658768131812
C	3.34117359731145	16.04519789157985	-2.59769836128370
C	2.27110975037258	15.92718902731068	-3.48632618081308
C	0.99729538631124	15.62889204217256	-3.00597381091815
C	0.79418706365596	15.45247305502714	-1.63505997757325
C	1.86090571428607	15.57475394780962	-0.74895554906834
C	5.16523987898032	11.21271128588558	1.23715538735481
C	4.18133473548957	10.43878835281757	0.32497784184218
N	4.93919686739656	10.87240410489932	2.65723391564985
C	4.95959591149015	9.58857512984664	3.08322240261048
O	5.27194986666758	8.58871066595453	2.42776832553541
C	6.62777986433778	10.92267079175403	0.84163295158698

C	7.12903110154302	11.32024918060583	4.96338625968022
H	3.30724288719716	9.43278546724631	4.36782065274387
H	3.85552790355222	10.84889790011985	6.11679766795968
H	5.36577216816219	13.42855313179411	-0.97487037480005
H	2.83432078664240	5.05693188140324	7.13278891273823
H	4.42951197272970	3.23417675170111	7.77796886970052
H	6.82970253244906	3.42722043948171	7.25990697974093
H	7.72305348429940	5.45209952701221	6.08080823789765
H	4.12208422891308	16.75139986475663	0.50073550352753
H	5.22776558056291	16.23506467858466	-0.79160260092355
H	4.31308077733886	10.74562127130552	-0.71870144935048
H	4.37214290613525	9.36887828517819	0.41871353657637
H	3.15165486861395	10.65169798285718	0.62815013264880
H	6.80762367150682	11.20171750268865	-0.20332176960224
H	7.30912675904861	11.48815050446320	1.48315625428890
H	6.81960085200613	9.85552816912792	0.96683011047199
H	1.70494885640499	15.43495417297846	0.31772791390225
H	-0.19774503439621	15.22210235961338	-1.25728973548856
H	0.16409893919903	15.53324696647358	-3.69588459233433
H	2.43498117078386	16.06469993785581	-4.55108766286840
H	4.33597825669063	16.27477176101857	-2.97307576175891
H	5.13250941066890	11.92464150460751	7.75057068312907
H	6.88908258343226	12.13504441828195	7.59049559461472
H	5.78588622984353	13.09205766611733	6.58725956802662
H	8.07962665003447	11.39426490909875	5.50465284218002
H	7.22740882722240	10.53773023847904	4.21088523731512
H	6.94565568071730	12.27603968023476	4.45652983523556
H	6.25002834158668	10.07312367948276	6.45952325683749
C	1.29373684860722	12.86824190390471	3.04799570088302
C	0.35162318003877	12.10350477496645	2.36275553528722
C	-0.06611972514982	10.86840748491387	2.86376989642821
C	0.44883464155539	10.40440059998260	4.07489220373244
C	1.38767996668130	11.15444791710103	4.78353458999837
H	1.62714268187930	13.82293422642398	2.65973901206218
H	-0.05363717561314	12.48177697868444	1.42767507867414
H	-0.79551069172579	10.27694911323532	2.31922621919487
H	0.13795344466971	9.44633110822998	4.48066423229484
H	1.77867815766094	10.78590772204734	5.72414840714512

2.6'
Lowest frequency = 6.08 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	4.19384327277465	5.05529428654597	6.88867356384144
C	4.57325635608151	6.22443380778329	6.24572701470610
C	5.90154893614291	6.46275653632326	5.88600210837123
C	6.90076806666617	5.53996581912024	6.15637485990557
C	6.52716013933033	4.35515912829584	6.80209305379987
C	5.19573487202082	4.11691671353280	7.16309674256875
C	5.98541471162079	7.79922057589086	5.22946767087312
N	4.66601029896058	8.29959423981502	5.23234751472316
C	3.75778885380862	7.39157394989697	5.81211425113226
C	4.20001101791639	9.49699347777903	4.54312394611673
C	4.35287402312718	10.79773020354359	5.34612187996663
C	5.71103023134948	11.06879559238180	6.01541784313026
C	5.54572940752376	11.80765671286526	7.34842072225561
O	2.55779300042685	7.57555322948306	5.90966730195571
O	6.96863910827817	8.37963502472605	4.81035747684746
Pd	4.11027297217937	12.25666052027722	3.90482906126708
I	3.25084661851535	14.17937928268688	5.46619218952555
C	2.16554401121559	11.83061186706479	3.54781742985438
N	4.56526246599111	13.41917151315138	2.09317968646653
C	4.98786215619933	12.61250048295548	1.07209943607554
C	5.14285035357096	13.42904356238585	-0.02882935754036
N	4.80994010442070	14.67519973143220	0.40739444102629
N	4.44982353891293	14.66847241702670	1.69944365747240
C	4.62397986692370	15.90366842997547	-0.37984945749257
C	3.33099395135168	15.84918263104173	-1.16519592409255
C	3.34508496805885	15.93083374725778	-2.55891028366159
C	2.15221648876715	15.86336792830659	-3.28080366028771
C	0.94078587768800	15.70618518290689	-2.60969180043941
C	0.92278289879039	15.62201453512840	-1.21522935890946
C	2.11165942908830	15.69558090133814	-0.49429047920094
C	5.15703855826343	11.12453503334837	1.25266595504080
C	4.19924423710862	10.39369606620750	0.28253823584333

N	4.83106851602357	10.82619250351918	2.66557274909949
C	4.76859006521940	9.55089001651765	3.11294447797639
O	5.05222235884144	8.53076413143742	2.48029363461950
C	6.62400436452164	10.73043606494753	0.96599495049794
C	6.71406755613020	11.80192759239903	5.10262293852209
H	3.12412710962334	9.32579994358451	4.41509599287452
H	3.54479274605775	10.89271057471737	6.07304140745342
H	5.43661968233524	13.23706658553359	-1.04822462169456
H	3.15848346963715	4.87996359110672	7.16337534477079
H	4.93843935466135	3.18777917536033	7.66321897331787
H	7.28081356539774	3.60619817030201	7.02740057795648
H	7.93011313842938	5.73387539633742	5.87182313903384
H	4.62570923337874	16.71606273877214	0.35040424020892
H	5.48496104560873	16.01796204550845	-1.04273911374986
H	4.42170556323289	10.68211948873718	-0.75085741235006
H	4.32955924333790	9.31672993054590	0.39441876227467
H	3.16243080106919	10.65603329011750	0.50790749529391
H	6.88322483786620	10.97105671652817	-0.07120933554323
H	7.29852386149154	11.27330690058394	1.63370447487504
H	6.74107752577040	9.65789229134452	1.12883842608921
H	2.09835771901174	15.62730067851109	0.59075410178461
H	-0.01929772303940	15.50191586181872	-0.68830392730035
H	0.01220374737456	15.64912184418616	-3.16996593077418
H	2.17189379899639	15.92906215478736	-4.36468943264031
H	4.29104122312687	16.04873125017608	-3.08296858164221
H	4.86975736261269	11.26195079133451	8.01572825279796
H	6.51713914814751	11.89939327357189	7.84726765012397
H	5.13760370685347	12.81160031271728	7.19835399356500
H	7.63847809823257	12.00266348898472	5.65568257622066
H	6.95662393349852	11.21132777730073	4.21829452018026
H	6.32621403215346	12.78763176416073	4.78765004095991
H	6.15426917619394	10.09049969819212	6.23312234563026
C	1.66915986990875	12.23007795066214	2.31008215127395
C	0.35201882757330	11.90996693319905	1.96657500144022
C	-0.45955734405066	11.20657758737012	2.85379847019609
C	0.04721777242352	10.83458685003025	4.09668622036831
C	1.36117051852854	11.15228390495766	4.45526772130261
H	2.27804822899993	12.78833826283693	1.61199163544911
H	-0.02666987168201	12.21695687696408	0.99487419266490
H	-1.48111417691526	10.95752165011086	2.58240650883518
H	-0.57346587251177	10.29773112201182	4.80844400695788
H	1.71858899285600	10.87414468774040	5.43849365993844

TS2.(6-7)'
Lowest frequency = -262.48 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	5.31933634009654	5.28421853570604	7.03701462238314
C	5.26113412971365	6.38661839142065	6.19692251616992
C	6.40027611250551	6.87664286980084	5.55408074730746
C	7.64114635259650	6.28217285118627	5.72788745225045
C	7.70981557725812	5.16820819919745	6.57316574417681
C	6.56789874458594	4.67740685959746	7.21739323235689
C	6.01400135127220	8.06228712200441	4.73623460313280
N	4.62864026656687	8.22253590016797	4.94466549669684
C	4.10379916206752	7.23587025056250	5.80446903974320
C	3.75495943094684	9.18017835561618	4.27471340114605
C	3.61520179171106	10.48343976944370	5.07202363348844
C	4.86563052659585	11.13711056927766	5.71026723217869
C	4.46802756411093	12.10199635722250	6.83472621043954
O	2.93368322661244	7.14965178689969	6.12834017400696
O	6.71899097888364	8.77364403090819	4.04776916129745
Pd	3.36703973262606	12.12634254782200	3.36257171267182
I	2.59499260440771	14.46814854144151	4.33840392237563
C	1.82370950721145	11.16819163414682	4.38877909460822
N	4.34567562859644	13.06973455160780	1.82528533216974
C	4.71422080674313	12.25569296142413	0.78993344223779
C	5.23129287286086	13.08321777332788	-0.18221340127558
N	5.14885252361365	14.33721048245010	0.34429348799299
N	4.60401272326614	14.33404841574513	1.56502153567988
C	5.43085439385829	15.63009378324088	-0.29875794775374
C	4.28939317120471	16.06208870997464	-1.19321130440232
C	4.50721346841777	16.28605031978125	-2.55416750872341
C	3.45473779961300	16.68444489706899	-3.37966210471520
C	2.17829212483624	16.85282286217844	-2.84564769390639

C	1.95636288543953	16.62612113710236	-1.48516812339447
C	3.00670879066716	16.23438792425176	-0.65905644875908
C	4.53344607753127	10.76925272611722	0.90006518573845
C	3.42056404406914	10.29505553607550	-0.05955185118970
N	4.13682158111039	10.53125397326058	2.31232775181763
C	4.13027941588359	9.27653067120066	2.79001343995556
O	4.34399324166986	8.23640554197336	2.15015753641671
C	5.88291777778068	10.09536229187947	0.55927682893684
C	5.94488939297042	11.76356823296787	4.82094403873015
H	2.77285568392779	8.69618795213765	4.30694729910792
H	2.98263368157621	10.24329728992736	5.92348723875930
H	5.63497510285513	12.89539470537137	-1.16391080528146
H	4.42785210490347	4.91080448896008	7.53088856428439
H	6.65471752036877	3.81124023404727	7.86682472648727
H	8.66374301491797	4.67426060640076	6.73335860478487
H	8.52041102177566	6.66960907877294	5.22303883992910
H	5.59143272002177	16.33101073009071	0.52359177879348
H	6.35930538556383	15.52575999597341	-0.86509721713615
H	3.69047307138623	10.50746597797975	-1.10001141933370
H	3.28920192545336	9.21796227085481	0.06450248620310
H	2.48188837322664	10.80818693909585	0.17063672911999
H	6.20627923491074	10.41473841641249	-0.43817043294338
H	6.64229873885697	10.38733795924829	1.28946493175145
H	5.77256844636485	9.01254941071949	0.57870143983100
H	2.83303195899125	16.05315444605895	0.39899898161298
H	0.96307684691603	16.75619697712722	-1.06594374118168
H	1.35682688363048	17.15891318928697	-3.48678830365387
H	3.63256916284084	16.85840284422569	-4.43686691239707
H	5.50321578091133	16.15148507122601	-2.97055536034200
H	3.77351199360434	11.63147986647589	7.54022621390207
H	5.35991393286992	12.40956773289196	7.39059174487844
H	3.99869786222389	13.00253998754522	6.42452053658910
H	6.86220917501576	11.87899707359149	5.41102029254082
H	6.17223428454354	11.14134414118437	3.95547878720463
H	5.63555904992410	12.76003044088903	4.48630492576820
H	5.31915020604837	10.25743712105355	6.19857258080638
C	1.13398518856101	10.36958327779076	3.46071123725254
C	-0.24688601781090	10.19363508824918	3.57756633098915
C	-0.94267847055265	10.77450337717161	4.63479087742497
C	-0.25272257448517	11.53758258726057	5.58212385111740
C	1.11763770028578	11.73111630116780	5.46715121416139
H	1.65989802269523	9.91039534628069	2.63162503023179
H	-0.76983251371439	9.59494883886544	2.83712650059572
H	-2.01436424997597	10.62603496453660	4.73025038689756
H	-0.78516759775499	11.98672615404639	6.41566742397680
H	1.64469122922176	12.31764675303187	6.20940244528122

2.7'

Lowest frequency = 9.28 cm^{-1}.

Charge = 0, Multiplicity = 1

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C	5.72080845990369	5.05135668678885	6.60408817580225
C	5.50357412013818	6.24347192829872	5.92933224328155
C	6.55363308100327	6.95224305695035	5.34170906135241
C	7.86126002928685	6.49559862796545	5.40789155366826
C	8.09070322083526	5.29185836708853	6.08541558907412
C	7.03794508385306	4.58154074349415	6.67407865409315
C	5.99916259865698	8.18252337808009	4.70687528333569
N	4.61631850138422	8.14640286304946	4.96647510289060
C	4.24092466519250	6.99116193071616	5.67622194483516
C	3.61333404758342	9.06390096717192	4.42407167153952
C	3.32200438515817	10.21222506597003	5.42234554860491
C	4.57982340172407	10.98536400015736	5.93371689105065
C	4.36072646820718	11.65300611936882	7.30376317148640
O	3.09886226381035	6.71133090742036	5.99464609051396
O	6.58988662172900	9.06259694039121	4.10965572239198
Pd	2.76074757970485	12.13179451692235	3.10137226577292
I	1.49771304288337	14.40807291628963	3.54297011219192
C	2.06409769240387	10.98154273978015	5.00521948849009
N	3.90248152098374	13.04885748806192	1.71668759956815
C	4.52857179493765	12.20005068942911	0.84865880571010
C	5.22211735279148	13.00241851057848	-0.03013724434536
N	4.97689648867895	14.27677234271197	0.38684722399895
N	4.17036319224379	14.31087468368521	1.45283578149611
C	5.34663305913036	15.55003644915315	-0.25029678771461

C	4.36207329166839	15.93430272317747	-1.33380385185926
C	4.80091629666145	16.13011337565530	-2.64494029208408
C	3.89559687522172	16.49002869737243	-3.64428600520607
C	2.54571165141507	16.64784190260231	-3.33473792521563
C	2.10315217266472	16.44845379751044	-2.02486298714827
C	3.00585222321121	16.09532466149145	-1.02494113283045
C	4.36617033742586	10.71690295325194	1.01392356912980
C	3.29220317402340	10.19582313371317	0.03400520018786
N	3.91340344637736	10.53681604809550	2.42932533179941
C	3.95477580306030	9.28853903588495	2.92836382980651
O	4.23871896618377	8.26260295535844	2.28556516902904
C	5.73841649015732	10.06141075485292	0.73766699552311
C	5.23200605032821	11.99054091642371	4.98087026353452
H	2.70488856107741	8.44870717732542	4.41120257511558
H	2.98507349638707	9.66171036536839	6.31576874325604
H	5.84762476486101	12.78475285145077	-0.88025086177770
H	4.89740657108899	4.50721147220675	7.05582930547920
H	7.24879489049071	3.65049643922103	7.19208151533300
H	9.10121363493350	4.89997729519195	6.15622708570732
H	8.67049827439928	7.05331791067943	4.94714355254211
H	5.36544563669120	16.28418813939346	0.55861062963130
H	6.35558991645451	15.43896242878298	-0.65384367661567
H	3.59702897850270	10.37110243445542	-1.00367874796776
H	3.16449786713919	9.12374247320366	0.19723743688768
H	2.34298326266018	10.71099663302257	0.21302609525324
H	6.11292645556769	10.41097868744388	-0.23181567630523
H	6.45147917987413	10.33974283860988	1.51781636038044
H	5.64322628788906	8.97844409225837	0.71922870249755
H	2.65969845014340	15.93412893881274	-0.00677553546404
H	1.05209347463057	16.56962931409392	-1.78013978336230
H	1.83861851826088	16.92415989624119	-4.11146274788975
H	4.24499547659596	16.64217589841290	-4.66134010373753
H	5.85420417820284	16.00384466248440	-2.88624438267899
H	3.80096172180082	11.00913074908405	7.99235904650076
H	5.33332458416521	11.86762284228594	7.75972475685197
H	3.83554893520658	12.60895186208369	7.21035294679534
H	6.13138856570552	12.39881310499053	5.45802574667526
H	5.52256568084130	11.52372795758974	4.04024415844912
H	4.55756365476055	12.83155804404352	4.77172631693824
H	5.31084527659025	10.18749922935205	6.10671895207275
C	1.28716502628969	10.61192264434933	3.86028075601757
C	-0.06116449848399	11.03295526635810	3.72458212112628
C	-0.65584615033238	11.79483089947797	4.70211106198358
C	0.09259173861756	12.17598235270545	5.83313539989739
C	1.40722246268420	11.79319556995489	5.97587528673553
H	1.62207422956670	9.82380456781100	3.19702189904944
H	-0.61765560990923	10.71674079978118	2.84795053138454
H	-1.68987953574026	12.10918207613503	4.60361320677641
H	-0.37200449859868	12.78123714968631	6.60550057235092
H	1.94343109036289	12.07640706073777	6.87110264035493

2.5a‘

Lowest frequency = 7.68 cm^{-1}.

Charge = 0, Multiplicity = 1

74

C	4.68986902087828	4.70269349970274	6.87222292176638
C	5.02093345533109	5.89064550455063	6.23677510979019
C	6.34563945895668	6.22247184900784	5.95257976765746
C	7.39224690881047	5.37922862759159	6.29390874535887
C	7.06924163093521	4.17667008525085	6.93421803019325
C	5.73954052020541	3.84380031088037	7.21923292526784
C	6.37001198611975	7.55537798732970	5.27943686825930
N	5.02179255530179	7.96099850419813	5.19977954958125
C	4.15303083969653	6.99342717318543	5.73917137791666
C	4.48764019656212	9.13409421227790	4.50197580737953
C	4.51159204935919	10.45955398254909	5.28782507228988
C	5.82851678444849	10.82231355993130	5.99589941025364
C	5.60434167951364	11.86694965769445	7.09714080798897
O	2.93749931289701	7.08213388094831	5.76866894893892
O	7.34045705743030	8.18469439461226	4.90649546323299
Pd	4.03556117677503	11.84032151430851	3.83059220943905
I	2.67025311790644	13.43995470458763	5.36925124514975
C	3.88630706491484	15.18465164931684	5.45015306914412
N	4.02247367945195	12.94235374249600	2.01782708026110
C	4.67323903261116	12.27008415542232	1.01627786568462

C	4.72483208275080	13.12971726606857	-0.06020010745199
N	4.10322536462375	14.26494007269983	0.36220181659915
N	3.67312440049519	14.15256454421511	1.63102595666411
C	3.87607821952355	15.51374869566255	-0.37959245883502
C	3.32133399392083	15.24594770649683	-1.75873122972181
C	4.02251546151286	15.66102448008428	-2.89293584885859
C	3.51549297812129	15.40971044877216	-4.16907387742048
C	2.30539888464256	14.73436147344800	-4.31606842652623
C	1.60123241529163	14.31360364085084	-3.18503020210768
C	2.10528008210730	14.56903719603194	-1.91284141486447
C	5.14761634665180	10.85072078011953	1.20326197947406
C	4.35977229917938	9.94245460066896	0.22928979148011
N	4.86435115388385	10.49850131430355	2.61003305366483
C	5.05246713342798	9.24298023468221	3.07486445101640
O	5.50675358924654	8.27798057135374	2.45031452209155
C	6.66408335223927	10.75996490824778	0.92746713936415
C	6.95401892236855	11.28510934913121	5.05944234050680
H	3.42995322691880	8.87775794383339	4.36596886794471
H	3.70787827706352	10.42628065199709	6.03377954606550
H	5.11564859998494	13.03103404000342	-1.05997743096036
H	3.65530020807793	4.45389360756521	7.08710345867213
H	5.52174511616942	2.90296946290206	7.71659303128179
H	7.86115510792963	3.48805893362459	7.21484026671426
H	8.41943532435566	5.64691380179528	6.06675419148772
H	3.18485578470420	16.08863352793976	0.24168391918837
H	4.82220553976342	16.06028639353427	-0.44396903901253
H	4.53681741687183	10.25671629964116	-0.80565359595690
H	4.68619291145162	8.90990340043285	0.35917748819595
H	3.28855805907965	10.01235101752046	0.44031359848285
H	6.88714932418740	11.04988543876710	-0.10602990321161
H	7.20838403466305	11.42072108728765	1.60787553494915
H	6.98859031253336	9.73067353122251	1.09157672757854
H	1.55971077355382	14.23543201619716	-1.03357635296445
H	0.65832552148451	13.78639450931267	-3.29622471556968
H	1.91097276227544	14.53347802512289	-5.30775947332578
H	4.06844805833211	15.73691528460308	-5.04464267213350
H	4.96971197772017	16.18300525134074	-2.77750023718096
H	4.78548826958734	11.57824326878488	7.76588760951595
H	6.51218662351700	11.98774336816646	7.69914055256784
H	5.36108567617513	12.84490534490681	6.66697243772208
H	7.88031747283804	11.43145890048120	5.62794218587768
H	7.14956024648951	10.55554954225430	4.27352965833911
H	6.68034941683093	12.23911162446692	4.58972460336717
H	6.17776728879599	9.90502009502967	6.49499847427449
C	3.41419117439914	16.31504997250012	6.11226810764381
C	4.22734150869766	17.44912923464544	6.15767452325583
C	5.48426622245841	17.44153896868742	5.55175862614993
C	5.93460397455602	16.29613028824772	4.89458208550328
C	5.13506356736572	15.15381915626195	4.83701791102409
H	2.43721309950968	16.31945060793216	6.58472559944547
H	3.87228493499216	18.33775744521446	6.67179254490916
H	6.11209878986291	18.32647673610458	5.59438376101040
H	6.91415802237019	16.28248312849523	4.42509447012980
H	5.46978816634119	14.25426581449836	4.32859687839002

TS2.(5-6)a’
Lowest frequency = -96.66 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	3.56292347971536	5.06586013511813	5.14469317634749
C	4.22200755098091	6.27538345368081	4.97839521879753
C	5.60916224674559	6.37327385444805	5.09094337064412
C	6.39220276367502	5.26444156892234	5.37498160248721
C	5.73732132804887	4.03837131088280	5.54228650746099
C	4.34513403535465	3.94058919141935	5.42976342474236
C	6.00819933059962	7.79446977462435	4.87117275692251
N	4.80157258913474	8.49174909451608	4.63945725325738
C	3.68781818859955	7.62728860256685	4.66078578935418
C	4.65382734419076	9.87455001982727	4.18536085812886
C	4.69924011149595	10.94502337867757	5.29442675755206
C	5.83982257298055	10.83355948988387	6.30871763345753
C	5.38974993398529	11.39639611251753	7.66960321093696
O	2.53699931930616	7.96614169142290	4.44750285565677
O	7.12322759703371	8.27471554106744	4.92086579321074
Pd	4.56590034773928	12.67145026810354	4.09058613983206

I	2.72807524197748	13.77187878464719	5.62234539050298
C	4.95978188581042	14.59369213682980	5.14309108710099
N	4.37112306484158	13.72760798990952	2.15712606911101
C	5.22413989576540	13.19349662889160	1.23246515740454
C	4.84724500246873	13.69937102358112	0.00871973714917
N	3.78743122595575	14.51434051688551	0.27556249769090
N	3.49311109550680	14.52075744662055	1.58844677419702
C	2.91087893864633	15.21921474716808	-0.66900991130083
C	2.14150490942912	14.25390394930362	-1.54372292477113
C	2.20040042324967	14.36337466737495	-2.93448007040050
C	1.48774261423954	13.47609978850467	-3.74276014043138
C	0.71896766417785	12.46948149775118	-3.16129951116301
C	0.66107836596784	12.35325703459743	-1.77036074237028
C	1.36702321190001	13.24203649898619	-0.96414910229099
C	6.28586229161681	12.22410687488328	1.69471289346775
C	6.72281056595530	11.33829930715464	0.51550934999983
N	5.66353969863324	11.51514134951440	2.83813255658302
C	5.57744358901533	10.17137461611405	2.99162500288590
O	6.04593275053483	9.28574482888332	2.27619913160984
C	7.49751129471599	13.01866348130098	2.23382354370377
C	7.19655114801624	11.35946252253874	5.81894693891248
H	3.63706508357439	9.89104588140576	3.77348228043946
H	3.74256568872132	10.92767113842525	5.82388384275099
H	5.20805049617302	13.53788587765015	-0.99403257221059
H	2.48316275857070	5.00118268723980	5.05391163621453
H	3.86722284030241	2.97463132489065	5.56520127106918
H	6.31638377077792	3.14607698546942	5.76228310776465
H	7.47091528286637	5.35135510805679	5.45880975826449
H	2.24767178814424	15.82050676271071	-0.04192691619208
H	3.52399566019072	15.89070390058390	-1.27660936307026
H	7.10768215473825	11.99153933083881	-0.27848986403102
H	7.51020677127252	10.65194329454554	0.82246252556076
H	5.89056758117560	10.74901010168772	0.12745836229577
H	7.94446138997247	13.62896953233098	1.44139385467821
H	7.18383202348685	13.67335895747124	3.05266652601521
H	8.24519223117049	12.31641698047170	2.61206163845065
H	1.32566526546751	13.14732683064324	0.11811508200002
H	0.06577345164081	11.56814990771279	-1.31379769667775
H	0.16855110808720	11.77416378861667	-3.78815203706987
H	1.53951632956905	13.56876816586724	-4.82363079127648
H	2.80565200259583	15.14519724028859	-3.38809882851487
H	4.67601085176137	10.71130489966491	8.14041841804018
H	6.23905359140387	11.52076483420118	8.35068179465623
H	4.87409746069692	12.35698420128671	7.57412674465737
H	7.94942026881815	11.24550234134446	6.60774611264428
H	7.52886980408156	10.78416590437746	4.95306368490973
H	7.14534830456532	12.41277015505304	5.53232684713256
H	5.98945135655749	9.75731011065698	6.47030163173087
C	4.90718847984596	15.70547220480204	4.29308629438040
C	5.90919707606309	16.66954977292453	4.38013705340556
C	6.92746070876012	16.55843114302235	5.32945014018104
C	6.92000687485353	15.48403782940818	6.21571934846257
C	5.91948706271478	14.51037100986060	6.14950277042082
H	4.10889625517240	15.81113298304299	3.57095033096868
H	5.87894938764018	17.51953746713607	3.70352309942233
H	7.70292243901565	17.31574909680861	5.39262942164883
H	7.68944878518209	15.39060615086859	6.97711731153924
H	5.91336099635965	13.70006091951484	6.86104410295837

2.6a'
Lowest frequency = 5.53 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	5.20516405910403	5.09205366717060	6.36126887689891
C	5.31432420768643	6.40012669111605	5.91303105551440
C	6.54670527094200	7.05373102770358	5.85809424695858
C	7.71837010278581	6.42376938382217	6.24947125838059
C	7.61905273217228	5.10271843042432	6.70254068702306
C	6.38301438590696	4.44779255707774	6.75808772783911
C	6.32820032330242	8.43352378416060	5.34140440216081
N	4.94260312632753	8.55113796968939	5.14441121592010
C	4.27115942209355	7.33922783881986	5.42230712303874
C	4.26147991602669	9.64250674237556	4.45791514326400
C	3.93516041028266	10.91919910366179	5.29655491131444
C	4.68803063037592	11.05297778342345	6.62976466042353

C	4.03194098685809	10.10387351112296	7.66384687690751
O	3.07715507473508	7.15930134788386	5.27346967508855
O	7.15702799681085	9.30599249623544	5.14801164351303
Pd	3.90234535373644	12.42772458261020	3.84974709871620
I	2.23603778278816	13.99597162366218	5.16163830837807
C	5.69549953251607	13.23658679155970	4.25398289156370
N	3.89081652198942	13.52156084406966	1.96111645190953
C	4.59820677725854	12.86262910756511	0.99541165457830
C	4.64319544774308	13.70387582299740	-0.09624880995846
N	3.96608870274202	14.81880020491066	0.29298666186210
N	3.50369909444240	14.70713776023635	1.54759989184856
C	3.64727356189461	16.02003596336077	-0.49463885949041
C	2.80007149693568	15.68445372488227	-1.70045959930832
C	3.27183654268540	15.94368578572544	-2.98898308978473
C	2.49161846480899	15.62877154489499	-4.10284307949447
C	1.23711785109200	15.04654385733616	-3.93089335914549
C	0.76199364071980	14.78282406402555	-2.64375944994084
C	1.53830724925449	15.10131497507911	-1.53288745043144
C	5.15061262245849	11.48029518997139	1.23295313755017
C	4.54387190962301	10.52247410742667	0.17996034881912
N	4.70921225730370	11.08828455101008	2.59191600723339
C	4.95966080621246	9.86039042383368	3.09272676839348
O	5.54612278953667	8.94023383914519	2.51747188914774
C	6.69045259783047	11.50198343396072	1.12472551378092
C	4.70076436045223	12.44926297617596	7.26464955783202
H	3.29645783632734	9.19478291856484	4.18782604409492
H	2.85832383222196	10.93807654415623	5.50532326579699
H	5.06645035842396	13.60563700030413	-1.08285611540229
H	4.24213980054422	4.59283244764455	6.39875071746541
H	6.34004520713657	3.42269338572974	7.11425756304689
H	8.51468429654160	4.57437195952378	7.01611008270144
H	8.67213304498278	6.93953373811623	6.20105633116892
H	3.12824200962095	16.68068843151708	0.20366655090728
H	4.58631456050160	16.49250906900205	-0.79619903291183
H	4.80367597056662	10.86933976640094	-0.82606596310214
H	4.93942284785426	9.51787546281124	0.33110418343619
H	3.45435773838968	10.50254170416398	0.27416638225759
H	6.99061829939564	11.79594970218036	0.11268840248749
H	7.11082707101720	12.21178648001216	1.84029576594516
H	7.07479401593058	10.50259394979721	1.33695743314176
H	1.16943216662450	14.89385469597290	-0.53134019914012
H	-0.21582424631000	14.33071781859261	-2.50667480231750
H	0.62943230623130	14.79802910574140	-4.79596545112671
H	2.86575256150755	15.83576845681815	-5.10116710156136
H	4.25193288689725	16.39632329258331	-3.12236712987840
H	3.94321451558849	9.07464050687246	7.31492661016707
H	4.62109608975158	10.10322701179955	8.58765336103894
H	3.02567210048020	10.46534247175798	7.90460740867028
H	5.27181152105354	12.40558385044132	8.19959166548721
H	5.15672123283912	13.19801194111867	6.61711357488345
H	3.68561919696233	12.78121538475458	7.49779281948034
H	5.72513361423135	10.74200502933904	6.47159982544956
C	5.77250169069283	14.62424381761200	4.17395288671536
C	7.01112255173340	15.23151601069694	4.40670989685150
C	8.13696643378447	14.46140239940222	4.69717612743009
C	8.02768794033359	13.07372415725033	4.75589260304762
C	6.79863053814118	12.44281217261639	4.52872981091695
H	4.89692698783459	15.22464056080775	3.96054110768625
H	7.07915334950858	16.31560644434384	4.36791901501699
H	9.09390922198412	14.94234718466701	4.87849692517346
H	8.89540431975851	12.45673261411845	4.97303082143353
H	6.74158912148223	11.36249300364211	4.57762962523716

TS2.(6-7)a'
Lowest frequency = -248.02 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	4.56366340009631	5.39789043166044	5.65840973979732
C	4.96615364868837	6.71227337739509	5.46959540656484
C	6.27183190633993	7.12306552027857	5.73536845036296
C	7.22959388224056	6.23533200001174	6.20209727707908
C	6.83527779731043	4.90590200789569	6.39397000305131
C	5.52379908947569	4.49387507071225	6.12700580302436
C	6.38660452285452	8.57867127249050	5.43716915227150
N	5.09811916696134	8.98768879781798	5.03323265887116

C	4.20483503754607	7.88969064320660	4.98475846494840
C	4.69953400459073	10.23789833947303	4.39522322607568
C	4.54370966477387	11.49536418303496	5.30165836147718
C	4.84267405981886	11.27005804657584	6.79634828988302
C	3.66018023923196	10.42988808746058	7.34442428737955
O	3.04652344871741	7.95756171975729	4.61522804868698
O	7.36824985605158	9.28579899221962	5.55463125384117
Pd	4.47561259134609	13.02069871365417	3.64972474524157
I	2.83583363264099	14.71974753146834	4.91681530985553
C	6.14369939096669	12.91346435334009	4.91999236520477
N	4.09578035085907	13.77718336539078	1.76678141905309
C	4.80321128802186	13.14260664441145	0.77686299685783
C	4.52819045768298	13.82548068824662	-0.38537782833900
N	3.67953377112238	14.82613874479813	-0.01427542852879
N	3.41004252042961	14.79636469074399	1.29660862663443
C	3.01545880745921	15.82761436416229	-0.86580092204664
C	2.16541209378160	15.17068861088300	-1.92832013914548
C	2.45417867863568	15.36223104719077	-3.28118465913964
C	1.67375134045713	14.74928295240293	-4.26290071353688
C	0.60400282073250	13.93610580004068	-3.89319950671845
C	0.31274227589766	13.73949134042401	-2.54095923212299
C	1.08818959040246	14.35472810092304	-1.56208864520481
C	5.65176061553421	11.94103883076663	1.11178729557524
C	5.36078362939809	10.82501832233251	0.08553743717947
N	5.21956249704986	11.56902440880908	2.47398178076622
C	5.46117386529922	10.38026281346104	3.04261709098368
O	6.08804461250207	9.42923894394037	2.56324573514970
C	7.14821858505555	12.31851871094228	1.10444463504367
C	4.93952573286829	12.52252800534145	7.67734756195851
H	3.67674648171549	10.00974087969715	4.06630814038566
H	3.50062878682460	11.83591081370448	5.26251107131201
H	4.83014846586740	13.68027547395321	-1.40990608433505
H	3.54476908290877	5.08920480844449	5.44733599763228
H	5.25031586147163	3.45490511450402	6.28601454645674
H	7.55701396976228	4.17894403128160	6.75494607495450
H	8.24367728145961	6.56485920372380	6.40468728273155
H	2.42349590258701	16.43106004041718	-0.17405926113898
H	3.78566497770319	16.45990691934541	-1.31638258117134
H	5.57784425742990	11.19363590705986	-0.92331680825251
H	5.98184956682338	9.95569207941389	0.29717184594985
H	4.30845110123991	10.53153529658313	0.13455879934821
H	7.45725489412458	12.65236545748083	0.10785394073106
H	7.34024557062063	13.11718634896206	1.82580648123261
H	7.73415895897842	11.43931151819520	1.38386650621916
H	0.86245337585581	14.19986714889569	-0.50982681170432
H	-0.52136221145919	13.10785925452645	-2.25018855072764
H	-0.00289433806077	13.45582416585809	-4.65502398726435
H	1.90404267814970	14.90566800988737	-5.31263609137619
H	3.29030342465497	15.99588642912451	-3.56857713689013
H	3.39103409817478	9.58299755379726	6.71207866053977
H	3.91556420282625	10.04954037182340	8.33936145915858
H	2.77575191430272	11.07002535631597	7.44048091090055
H	4.78437219497714	12.23033922536536	8.72196603216878
H	5.91459910892104	13.00199067485639	7.60295001512085
H	4.16706039882351	13.25109627303409	7.40877990687140
H	5.77488763390582	10.70437653417424	6.88041222637856
C	6.29431733869235	14.16006926430453	5.55110609075069
C	7.57019345734004	14.62671830905188	5.87114755832332
C	8.69820799698708	13.84797451187809	5.61849885406860
C	8.53853347797440	12.59490920176060	5.03174106047842
C	7.27191645145059	12.13145284567793	4.67257803425972
H	5.43135732638024	14.76948418172427	5.78184695907514
H	7.66600560529027	15.60453792420619	6.33565822681603
H	9.68759162200552	14.20969926635450	5.88386592436217
H	9.39767269972766	11.95816104164744	4.84109225328826
H	7.20723451072235	11.15279708930566	4.22381510531031

2.7a'

Lowest frequency = 7.66 cm^{-1}.

Charge = 0, Multiplicity = 1

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C	3.74437974760061	5.83428072603696	4.50247794588819
C	4.37233254690550	7.05247578042642	4.71846843750968
C	5.69161427155309	7.12587560839155	5.16405320834915
C	6.43704640712686	5.98322865581168	5.41261451200744

C	5.81509381908246	4.74849601543339	5.19268082953550
C	4.49008964808642	4.67502466254722	4.74575225345404
C	6.06746963511505	8.56049209216797	5.30480376675758
N	4.91686789896275	9.29427341580314	4.95435120088696
C	3.87036009705333	8.43912764960166	4.54033154432440
C	4.84239197544167	10.71714402369092	4.63402971017038
C	5.02515165932220	11.70443444107441	5.84076323911331
C	5.00501788672307	11.02709542475978	7.24094487033149
C	3.59791498506139	10.49673396181528	7.55002332961089
O	2.78768509175201	8.81543394820505	4.12792054645357
O	7.12405022854882	9.01245575882297	5.70878222941631
Pd	5.09376882974974	14.01338430950012	3.60262317118543
I	4.08004836496420	16.36003464453148	4.26982678880600
C	6.21366748650383	12.61056567421318	5.62402727548299
N	4.54010326829998	14.22709016407480	1.68755299056622
C	5.21531651009123	13.40017986526092	0.83294850508621
C	4.77984508355583	13.72892841981751	-0.43015469148457
N	3.87629030056647	14.73352596643358	-0.24313617179559
N	3.72181510702526	15.03597439307913	1.05334548648105
C	3.03754732474975	15.41173111357071	-1.24317930393314
C	2.11845473461348	14.44052933797245	-1.94838065836477
C	2.17173585368693	14.30152755536740	-3.33688012838568
C	1.32265516754924	13.40609060389167	-3.98944923979799
C	0.42145208004476	12.63973396754151	-3.25269287317640
C	0.36753924593081	12.77231652364316	-1.86293626968651
C	1.21022974177814	13.66969040582219	-1.21287928874307
C	6.16161403922098	12.37745701818245	1.40883830587175
C	6.12351255550107	11.14693498947206	0.47720821249914
N	5.63157402071148	12.16595914837517	2.79115980397254
C	5.73537542136180	10.95332891680384	3.36950246529718
O	6.36639413804169	9.98821798916455	2.91223330602402
C	7.59322694157179	12.94616073673866	1.48826185788968
C	5.43428143664326	12.01401701339413	8.33560251115690
H	3.81356170001902	10.83504747894590	4.28119063508322
H	4.14662459283299	12.36125245261383	5.82148827424948
H	5.00470654427727	13.33633325659839	-1.40818989435356
H	2.71687311371352	5.78875452071104	4.15566476639666
H	4.03667214308400	3.70130364168770	4.58471194880975
H	6.36753897918459	3.83018179488196	5.36949323698475
H	7.46360981467464	6.05168814587351	5.75835542978059
H	2.48617097766940	16.16662376830245	-0.67771957357111
H	3.69409085282657	15.91698980531662	-1.95711905411487
H	6.29565010067174	11.49058538547738	-0.55072668860727
H	6.89003932824817	10.42620956579607	0.74821383950191
H	5.14812098354443	10.65588124742520	0.52324945775519
H	7.97356556450591	13.19475838356000	0.49113785490562
H	7.60476362965126	13.84613555504519	2.11132095539674
H	8.24185377768691	12.19279488322339	1.94268957100585
H	1.16970064902220	13.77010365775322	-0.13106408451369
H	-0.33298046693733	12.17610177972530	-1.28587704483963
H	-0.23716446440516	11.93926318904948	-3.75763216183278
H	1.36983726050500	13.30583516419301	-5.06982979891702
H	2.87794967631876	14.89736564292472	-3.91087188221376
H	3.21825058667175	9.83157373463615	6.77091908879498
H	3.59691202655760	9.94590525999587	8.49679896230943
H	2.89472163764373	11.33327700613366	7.64726058880215
H	5.36637654651380	11.53401741118497	9.31773270094229
H	6.46413990931361	12.35543014461647	8.19505620489942
H	4.78176611968861	12.89578965584757	8.34810744573955
H	5.72025485350100	10.19952820469412	7.23353261151068
C	6.00687959341438	14.00954960196150	5.66926732187370
C	7.08064782852077	14.89886977147566	5.40163252558897
C	8.34374047421209	14.39613917029594	5.13202639660402
C	8.55088577312530	13.00901112093321	5.13864646645892
C	7.50388470878903	12.12385198132240	5.36372028914318
H	5.09030709969122	14.40357120898002	6.10455807420762
H	6.89056747013985	15.96616128768776	5.43478646456403
H	9.16826975533869	15.07174058495934	4.92566267554957
H	9.54457698074041	12.61458533873252	4.94275638687095
H	7.66928732854712	11.05206227599925	5.33689333047410

2.5b
Lowest frequency = 4.17 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	10.97639594699517	2.54287424534992	-13.51514441193951
C	11.39020888567060	1.49718505329083	-12.69477975715784
C	12.38789078546208	0.60582085706614	-13.07874006888929
C	12.98867077797694	0.77520573833822	-14.32812383444890
C	12.59319104842378	1.81784902672914	-15.16674516215546
C	11.58859179331991	2.69708128809958	-14.75937522942458
I	10.48905242646895	1.29415089857465	-10.78130781551094
Pd	9.47114241504285	3.73131292639900	-10.55768719450606
N	11.42069673003389	4.55611874584603	-10.72627599129955
C	11.37658616546372	5.90172442983488	-10.93505993106453
C	12.61767623476856	6.26646268029967	-11.41505912458465
N	13.33046822733094	5.10677134704652	-11.46176832116036
N	12.60183576038530	4.06030615966667	-11.04119076008752
C	10.15294988639120	6.69386897037329	-10.57631334875793
C	10.52450804456373	7.50543501265338	-9.30641370598388
C	14.70851133644969	4.89320035439807	-11.92447440253825
C	15.66459991102352	5.88956808909995	-11.31291773594190
C	16.42300012924878	6.73068291251506	-12.12995923156573
C	17.30819911355929	7.65239099239921	-11.56823435968738
C	17.43309377524438	7.74164936897600	-10.18314451060719
C	16.67360545797513	6.90577323232561	-9.36060041571309
C	15.79502721345334	5.98340368103455	-9.92194831561867
C	7.49903841000956	3.09325158147457	-10.69538291517681
C	7.20841511137727	2.12787420503848	-9.54205958525633
C	6.53981524163036	4.27822255345044	-10.65917253315605
C	6.80406882239524	5.22927214532451	-9.48946104971926
C	7.90225985735188	6.25789477162454	-9.82271315597658
N	9.04004016015879	5.72860465073861	-10.31787202378002
N	5.61013710167396	5.93995279922075	-9.05595903141356
C	5.28837072302416	6.08768553037422	-7.69770984196841
C	4.14702987209712	7.04576284928969	-7.65389897436771
C	3.87107679121127	7.45323679799203	-8.96013881609735
C	4.82146497050191	6.76185493836428	-9.88139804216141
C	2.85576727509783	8.35611990972716	-9.23677167950356
C	2.11718753477876	8.84946906498559	-8.15426697677212
C	2.39418688142497	8.44066269532176	-6.84444039328850
C	3.41917766261884	7.52564481567422	-6.57521083383675
O	5.85012838139136	5.52094591649593	-6.77602331765857
O	4.89837980706432	6.84239812180734	-11.09306626344401
O	7.68798890812405	7.46436373525201	-9.61636877702208
C	7.32792448182908	2.39727720116798	-12.04949250568801
C	9.78391437020386	7.63146867412993	-11.74481137988313
H	7.12374546051040	4.66437304073747	-8.60762885498312
H	13.04833223644349	7.21347244924681	-11.69723414696531
H	3.64342124939899	7.20310512907621	-5.56319566999199
H	1.80425635024477	8.84280242194392	-6.02570600257700
H	1.31684181947844	9.56258642430888	-8.33045657244090
H	2.65033370685665	8.66769381964454	-10.25617166853960
H	14.94328582107432	3.86429332206427	-11.64043752296685
H	14.72395984076718	4.96164726838494	-13.01681770705571
H	11.40745191939445	8.12143132678251	-9.51222948392819
H	9.69020167689329	8.14129391159789	-9.01513836439053
H	10.76207087409280	6.81785540072234	-8.48887976436307
H	10.61342462401544	8.31435216136764	-11.96461663319850
H	9.56497684459207	7.04158231455471	-12.63988243636331
H	8.90380454704627	8.21355108233734	-11.46984800118365
H	15.19975120130815	5.33798682159078	-9.28076805601813
H	16.76743746751715	6.97379827364901	-8.28080507315203
H	18.11748554803695	8.46109101807176	-9.74338189424357
H	17.89352291582225	8.30179810066558	-12.21254857647563
H	16.32042764331384	6.66455061265088	-13.21074489948582
H	5.51273885076342	3.88925762435162	-10.57086213361923
H	6.58497976834611	4.83861220134541	-11.59672400752614
H	7.81564545823580	1.21862519027290	-9.60848292868565
H	7.38357740583482	2.57944866818206	-8.56058742572883
H	6.15146524728181	1.81409522159391	-9.57693843752149
H	7.90675404863352	1.47262482510593	-12.12658710048154
H	6.26589409026842	2.13481770472392	-12.19307077514080
H	7.61167992949533	3.05780594070270	-12.87600584190205
H	12.70026324377588	-0.20013100753838	-12.42280193616114
H	13.76884155818889	0.08682294900708	-14.64049537158360
H	13.06445412969191	1.94223301301842	-16.13716631645439
H	11.27289736066113	3.50849759113447	-15.40915263688627
H	10.20334173279958	3.22707721093206	-13.17530403517251

TS2.(5-6)b
Lowest frequency = -133.15 cm^{-1}.

Charge = 0, Multiplicity = 1

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C	8.79395890977140	3.96297112503830	-13.49441401306806
C	10.05585010440284	3.72488060721290	-12.95011110435708
C	11.11743047175098	4.61081769558645	-13.16796979121748
C	10.86710629531004	5.80181291587635	-13.84689295494749
C	9.59002847210787	6.09468725887814	-14.32789151172443
C	8.56247426238049	5.16902399086222	-14.15588358000055
I	10.67791001964620	1.53696588459615	-12.53350554949328
Pd	9.87674552054956	3.24657645647051	-10.67110100769450
N	11.89129565567478	3.88213519005049	-10.29603621648503
C	11.94885687656672	4.96511610654401	-9.47798968830122
C	13.28526926956635	5.17137940604763	-9.19628436551447
N	13.94210322082990	4.18345687610879	-9.86249951406790
N	13.09132200464120	3.39383318266439	-10.53885753663268
C	10.71480354265070	5.73344955917457	-9.10219390129375
C	10.78324345776462	6.02569558241309	-7.58635949246171
C	15.38886970268346	3.99400440890432	-10.03901645842236
C	15.93717388478417	4.91098883927952	-11.11087486855692
C	15.52509717166791	4.75850940634356	-12.43999482491716
C	16.00582345704404	5.61741009794441	-13.42487161231898
C	16.90572221824223	6.63265662263654	-13.09172865315696
C	17.32280788429133	6.78535413713778	-11.77056437204084
C	16.83671056256840	5.92727969571046	-10.78281440346088
C	7.95136813706361	2.52411585046145	-10.37123052865691
C	8.06875612043070	2.00461120462665	-8.93349833536483
C	6.96872423961062	3.67129635861039	-10.53172583705637
C	7.01733960744218	4.72975628403253	-9.43600986180089
C	8.32948871808573	5.50856986737551	-9.18155200618683
N	9.50781481427667	4.90637091832706	-9.44526662681056
N	5.95786542358360	5.71038358493464	-9.65770179257196
C	4.92971995327459	5.94357051333596	-8.73154921998736
C	4.18170805665645	7.12456931227451	-9.25225098971085
C	4.80724089622659	7.55446723212864	-10.42457895221972
C	5.97049103927255	6.65875357980570	-10.69095345095394
C	4.33571737199805	8.64577440398628	-11.13815900930890
C	3.20644514446600	9.30568152365660	-10.63808906369840
C	2.57943466436814	8.87454651471258	-9.46334736321768
C	3.06156332254243	7.76986967754255	-8.75043532000975
O	4.72225695445494	5.28243111483019	-7.72961902109131
O	6.77166982043164	6.69727078104209	-11.60841419366967
O	8.19641422604335	6.63135566813337	-8.65890339443156
C	7.52937683246769	1.37172136616353	-11.27963242788543
C	10.74117114688370	7.04123242609735	-9.93669279147999
H	6.75305565084693	4.27185406135831	-8.47537642038034
H	13.80443284407617	5.90955301731143	-8.60677835588443
H	2.58374284049375	7.42898131547409	-7.83728421671825
H	1.70605006476363	9.40848689793316	-9.10003355195238
H	2.80950554421252	10.16733139052910	-11.16723056813656
H	4.83080282100295	8.97346610519862	-12.04702495192316
H	15.87236763988042	4.17951022697353	-9.07699054436526
H	15.51484396447208	2.94161612353595	-10.30288557801846
H	11.70680380395954	6.56923595626614	-7.35363095110506
H	9.92824723618913	6.62990379890017	-7.28854199713722
H	10.78229191007891	5.08504099881788	-7.02703423346181
H	11.66971584595925	7.58902316905249	-9.73797396323754
H	10.69830696246086	6.79499342760954	-11.00138369687068
H	9.88487212150821	7.66003192505825	-9.67254949574667
H	17.16024041948649	6.04852857323784	-9.75133159370301
H	18.02307963401845	7.57232953466824	-11.50636878272514
H	17.28031356504685	7.30133517896235	-13.86113864396001
H	15.68086376046734	5.49366415802528	-14.45382637443157
H	14.82242008741084	3.96963636779890	-12.69621623080302
H	5.94623696221726	3.25563275353174	-10.52382877516702
H	7.10500904910397	4.15382704769700	-11.50377354654185
H	8.76721245565312	1.16250063721291	-8.88156097850437
H	8.40463255518201	2.77042230665642	-8.23065428300457
H	7.08595265466261	1.63474433026504	-8.59399302698521
H	8.17446576943337	0.49823433459259	-11.16134663649199
H	6.50334013233718	1.07563234174014	-11.00780283688365
H	7.51648727902138	1.64058819767446	-12.33986175203500
H	12.10791267433697	4.38665036705543	-12.79498869844859
H	11.68408039167116	6.50411065869529	-13.99107868266727
H	9.39915269863740	7.03271404959420	-14.83917124266666
H	7.56323728777745	5.38256800831248	-14.52266167498839

H	7.99469291915720	3.24235051270284	-13.38036410880772

2.6b
Lowest frequency = 8.78 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	9.74944732951518	5.08279510072520	-12.28849159781610
C	10.28532194101805	3.84999167007650	-11.92603378738488
C	11.13940780699509	3.14919013282771	-12.77791110384603
C	11.42120611621448	3.68672925161645	-14.03881167518901
C	10.87896544755186	4.90942509296649	-14.43117144266077
C	10.05132936192520	5.60384868069421	-13.55276292532217
I	10.80535167127661	0.58088179624506	-10.27575340837056
Pd	9.93687420791775	3.09374068265893	-10.08353249568307
N	11.93308812598004	3.77242774172421	-9.57342247123136
C	11.92439444575551	5.08766838206186	-9.22557685722480
C	13.20766403196365	5.55317687694248	-9.41484313096981
N	13.90409303138905	4.47447077320918	-9.87051948564697
N	13.12281257814160	3.39015073068720	-9.98384086319957
C	10.67056933064205	5.74332404497344	-8.72953925600148
C	10.73052533497443	5.73262329497940	-7.18050446649940
C	15.27842427904898	4.42862348772622	-10.38097785881424
C	15.43931989975568	5.30191695266464	-11.60823838891445
C	14.45149266127075	5.32061286268977	-12.59911220545990
C	14.61389393738393	6.11328409400759	-13.73236790872942
C	15.76417907024300	6.88925789865932	-13.88869882084797
C	16.75057180297537	6.87311914726165	-12.90336510986709
C	16.58528806859553	6.08522186977124	-11.76349989906253
C	7.95581012636641	2.56508418510328	-10.52278360000407
C	7.56217048114765	1.76454328853805	-9.27919626947936
C	7.13309973826115	3.83268288843521	-10.67859521267292
C	7.01670807511674	4.71495393617638	-9.44074273304293
C	8.27822483610093	5.42345297486884	-8.90535082723530
N	9.49824138028685	4.93292814330913	-9.21984776228417
N	6.01668441506328	5.75407502700246	-9.67276128129396
C	4.80920590408756	5.83884540104452	-8.95751905419626
C	4.17374330210942	7.11247863567959	-9.40308272413004
C	5.02737751481099	7.72971929430114	-10.32161044914120
C	6.23149343788590	6.86848276543973	-10.49189586394029
C	4.70326227742307	8.94308283359461	-10.90908367988807
C	3.48524629748750	9.53097471816981	-10.54602790778298
C	2.63046955289331	8.91281239875708	-9.62643735882938
C	2.96519828361657	7.68627731522026	-9.03911112382360
O	4.40965477464893	5.01121383323845	-8.15987401618073
O	7.21563926971524	7.04996236989385	-11.19103865603048
O	8.08943501996966	6.40624186440457	-8.16961424607632
C	7.82874012890532	1.74863267213354	-11.80456566826108
C	10.63049322889918	7.18428203803064	-9.28196341055123
H	6.60893587518670	4.13228359743024	-8.60651084019269
H	13.66401447624428	6.52232457166105	-9.29680277235945
H	2.30982981997940	7.20047073952991	-8.32313809886156
H	1.69336180349517	9.39517078187290	-9.36420956326663
H	3.19752039939603	10.48296479547852	-10.98259848890807
H	5.37369844761471	9.41590641405741	-11.61985303193267
H	15.96021046194308	4.74240497454226	-9.58545818926503
H	15.46121187962121	3.37350734514105	-10.60209923401756
H	11.63295620473896	6.25682931851062	-6.84725296825199
H	9.84789906004666	6.22583694049003	-6.77545487435044
H	10.77560868137315	4.70065481598626	-6.81948422053105
H	11.51238746447387	7.73253346818538	-8.93106882699288
H	10.64063399533091	7.16871137056476	-10.37469563512184
H	9.73510034987565	7.69401845349685	-8.93192609018043
H	17.35102392720949	6.08124309813720	-10.99087805265776
H	17.64465449109931	7.47954596047891	-13.01530588251216
H	15.88813218257651	7.50852887915313	-14.77231502920736
H	13.83632773501093	6.12450121365387	-14.49015784857777
H	13.55078238087494	4.72394942955251	-12.48503012497888
H	6.10920708725922	3.51254521633269	-10.93166884003899
H	7.48686325869295	4.41985155295853	-11.52854541351479
H	8.00056986581570	0.76559669879855	-9.30103362376677
H	7.86882386257162	2.24991446087013	-8.34348693428669
H	6.46501822045519	1.67105317426524	-9.24219458735418
H	8.39660143595448	0.81901068789081	-11.75774415139112
H	6.76558008086881	1.50112756337193	-11.95246196208826
H	8.16134102837649	2.32128860245234	-12.67477403605795

H	11.57305800672128	2.20385307093544	-12.48239011050366
H	12.07218199952965	3.13057426853669	-14.70857980611751
H	11.09975318843650	5.31624067349482	-15.41417716729662
H	9.62435929265192	6.56364640558327	-13.83096303555819
H	9.10677351124571	5.65055530807689	-11.62981555627270

TS2.(6-7)b
Lowest frequency = -247.18 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	8.63500063217117	5.31381334648222	-13.05130852883612
C	9.11190107597164	4.01353012312870	-12.81103538321937
C	9.56111980613951	3.26425284464809	-13.91383202255790
C	9.59057352788130	3.81751218830025	-15.19081096861683
C	9.14196623358109	5.11957216163997	-15.41141354081952
C	8.65682318889642	5.85832346769039	-14.33454067298827
I	11.58509532656595	1.57859681384316	-11.77659116693078
Pd	10.29186984720113	3.81250388252394	-11.04684016827554
N	11.94135439971687	4.38423594754648	-10.01552879064903
C	11.96728072046910	5.71615492072549	-9.71466881493101
C	13.21251009736037	5.95975693001737	-9.17914986952147
N	13.84054814950748	4.74976373205990	-9.18313986683366
N	13.07012207095696	3.78561624872737	-9.69700932721263
C	10.75263651045375	6.55780223510616	-9.98545436304441
C	10.57069285708709	7.50498406532498	-8.77696414285118
C	15.24001924493713	4.43042643032240	-8.86050616184336
C	16.15572986499289	4.72258724413873	-10.02980837508861
C	15.93458995716843	4.10375861743119	-11.26621773635521
C	16.77740087313229	4.37739171613906	-12.34051135832650
C	17.84668415457751	5.26336870406245	-12.18853794348085
C	18.07037796527082	5.87883414643086	-10.95808359508492
C	17.22296084014699	5.61095687767878	-9.88197388038346
C	8.04188525316582	2.97834895037686	-11.42861563616684
C	8.40391308549326	2.14815939586958	-10.16710659783539
C	6.96856254146244	3.99869664160273	-11.07583237110900
C	7.25993510285492	4.95253966971032	-9.90611120361457
C	8.37914348370145	6.02772465223001	-10.04525825753466
N	9.64168750154073	5.56595687656101	-10.12600605263675
N	6.02956535647395	5.64864782442589	-9.54912309159491
C	5.62689954525554	5.78949199724128	-8.20888065108557
C	4.49960596136406	6.76238587068706	-8.22573270805778
C	4.32056130279504	7.19869039076232	-9.53991076992423
C	5.31975153210545	6.51158509271748	-10.40805052723599
C	3.34231614622659	8.12510741697810	-9.86801742931595
C	2.53971301101916	8.61134347717097	-8.82905639695949
C	2.71912904688145	8.17358846855227	-7.51147433920633
C	3.70760831069943	7.23585994565386	-7.18997543336499
O	6.13204938981884	5.20915210436100	-7.26410687352763
O	5.48662733631549	6.62315136741533	-11.60859357619921
O	8.06201416737466	7.22527989634526	-9.95487352284629
C	7.49402687906550	1.97775234508751	-12.44783257510054
C	10.94179693883306	7.36108331823413	-11.28944315312706
H	7.51323628027749	4.36540305821620	-9.01788894359685
H	13.68769267898976	6.85357283270827	-8.80929095080366
H	3.85603826489513	6.89165481801501	-6.17127766528813
H	2.08101875078431	8.57123436112804	-6.72760928824482
H	1.76560845498206	9.34190716592385	-9.04554944229279
H	3.21297886225676	8.45956348766510	-10.89253764852515
H	15.52170388365562	5.01487696847446	-7.98167021912484
H	15.24156340039560	3.36979095129978	-8.59849835710653
H	11.51205939409909	8.03771708386413	-8.59802748657619
H	9.78002759626082	8.22555357782625	-8.97065926017494
H	10.31958484720431	6.92881609498384	-7.88159608958199
H	11.79147041643817	8.04693852564272	-11.19916510753287
H	11.12121408064714	6.68234642480328	-12.12823090199839
H	10.03359431029168	7.93733111509697	-11.47911780362013
H	17.39477188844008	6.09357022615652	-8.92221906249069
H	18.89927437205786	6.56971476190273	-10.83469695625719
H	18.50210176408571	5.47374472504587	-13.02863628421461
H	16.59934411162373	3.89688960563733	-13.29793688585521
H	15.09913577552742	3.41831860050035	-11.38699370531228
H	6.10682455634948	3.39472712728995	-10.75247988706386
H	6.64271690317094	4.55810988906436	-11.95147758596454
H	9.06060694112252	1.31223757974421	-10.40678111701863
H	8.84535388817740	2.72050380443826	-9.34684814603774

H	7.44339829752807	1.74588067062515	-9.80549942032162
H	8.26609237124294	1.26849836834957	-12.75368538770834
H	6.69750592810428	1.40885895743508	-11.94706650038204
H	7.07778315403132	2.46910695693367	-13.32901741581611
H	9.90366031735581	2.24794452849385	-13.77693556978525
H	9.96276480729354	3.21542074616426	-16.01524591836193
H	9.15784494869033	5.54673389702888	-16.41003818035675
H	8.28600066783803	6.86920500452506	-14.47738330395775
H	8.24251784954966	5.93539073906603	-12.26016366433342

2.7b
Lowest frequency = 9.14 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	8.90947127430905	4.01313418727212	-13.84397317264964
C	8.01433232596712	3.09819536108711	-13.22115063689194
C	8.23381412614124	1.73229808277121	-13.43649399381023
C	9.24317297989612	1.28509057902338	-14.28593176104741
C	10.09656016680304	2.18425674266894	-14.92887390988052
C	9.94538751444359	3.54202950077143	-14.69245711051494
I	11.55941401356348	2.03269068815740	-11.75800140453954
Pd	10.32917349940831	4.32480412349557	-12.09668389919165
N	11.59881603282281	5.25447887141842	-10.81145247655577
C	11.62391872434661	6.62085209764690	-10.95454312367513
C	12.47943316082339	7.08556262434791	-9.98726637674264
N	12.89508341347517	5.97064967594790	-9.31704308339687
N	12.36221358202918	4.85054484251990	-9.82153163343317
C	10.72342099103966	7.18196814863557	-12.02327055318000
C	10.38337082434763	8.66753905197734	-11.82574055292932
C	13.88674262722090	5.85880517515869	-8.23785733635851
C	15.29796367402862	6.01593946024289	-8.75932495897001
C	15.78762506317069	5.13683081099988	-9.73276850961460
C	17.08517415785348	5.28464642258000	-10.21585956076498
C	17.90429234140291	6.30668320938374	-9.72970924795303
C	17.42077194157037	7.18264862727121	-8.75936008702941
C	16.11849181882413	7.03825292969043	-8.27834671410513
C	6.72923688156340	3.58617919640054	-12.54927994773042
C	6.27480452911845	2.65068046900589	-11.41225727173835
C	6.83365810829237	5.03342755703202	-12.02279727682877
C	7.71371634033818	5.20432113143209	-10.76764348089969
C	8.78150546117018	6.32410330463764	-10.85386686504990
N	9.52982191085471	6.28334715533718	-12.00428587601852
N	6.92053378353055	5.39600200357685	-9.56316003841629
C	7.13781201190357	4.65499425055114	-8.38849459810699
C	6.27616578046583	5.28741619653606	-7.34983214134172
C	5.63187172993058	6.38491645172014	-7.92499437366620
C	6.05437001482822	6.48510401605394	-9.35236113373888
C	4.76190855139700	7.17866725307263	-7.19279635246804
C	4.55405120717029	6.84015183582085	-5.85010613593008
C	5.19926804699109	5.73955876983900	-5.27402558719896
C	6.07419355379037	4.94216129130213	-6.02177276899689
O	7.88091462537174	3.69496764063868	-8.29357626078941
O	5.72104330945417	7.29832191562630	-10.19425421363630
O	8.92056703752935	7.11309300282256	-9.91573804441184
C	5.64468123470376	3.58557206951284	-13.65770831027220
C	11.39716708265554	7.01332757628058	-13.40049030048703
H	8.27913160793882	4.28010432267254	-10.57703313538954
H	12.80181723494824	8.07719040996749	-9.71516027496996
H	6.58001662811636	4.08700660194893	-5.58451125012152
H	5.01730947678980	5.50330534311314	-4.22956354644482
H	3.88228354288987	7.44014314988269	-5.24295508632216
H	4.26703199719324	8.03046816827661	-7.64870984894648
H	13.65592936536402	6.62058760668396	-7.48901396890601
H	13.72072701882161	4.87123503932907	-7.80145200297645
H	11.27980513759865	9.27355329516789	-12.00252880878444
H	9.62778277633194	8.95537679861024	-12.56263860281413
H	9.99185166565648	8.85619191167456	-10.82811313320702
H	12.29117334200316	7.64140610614811	-13.46556527706874
H	11.68715335282411	5.96946185119782	-13.56451343265998
H	10.69141552137280	7.31078545499430	-14.18183572162426
H	15.73922714276811	7.72281707384158	-7.52271076915076
H	18.05289796057227	7.97950864098445	-8.37840342994398
H	18.91633342854626	6.41864057885442	-10.10771016393710
H	17.45935301820012	4.59981066433300	-10.97113137299054
H	15.14856011621128	4.34351768049456	-10.11316547884034

H	5.82463175669373	5.37549523741113	-11.78157340502620
H	7.19567048288369	5.70260466924271	-12.80609256008788
H	5.99473366164674	1.66403348190172	-11.79271428944318
H	7.05261003989287	2.51660542328766	-10.65499711060145
H	5.39089027412596	3.07700621813929	-10.92582974316281
H	5.52522027195157	2.58432706627530	-14.08319832571023
H	4.68497050628721	3.90489378593808	-13.23606254311558
H	5.91337440282893	4.27349091871908	-14.46650204511753
H	7.59394099843782	1.00223649000214	-12.95349681661263
H	9.37183681479745	0.21807074891219	-14.44100760619418
H	10.89207987255703	1.82235391935789	-15.57114562392968
H	10.58919663659989	4.26454252362328	-15.18437219106189
H	8.66464749260309	5.06886551874694	-13.87136335387695

2.5c
Lowest frequency = 8.70 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	11.72492632649255	2.86458724725824	-9.59067647256605
C	11.97478405540538	1.89335641653549	-10.55595748667801
C	13.12704818720604	1.11206593718506	-10.54003032832389
C	14.05229713386930	1.30936299315110	-9.51228461282126
C	13.81976653180779	2.27139519398792	-8.52897150615314
C	12.66200643668630	3.04947428121133	-8.57310135443650
I	10.53475210982314	1.59447382179591	-12.09407553962494
Pd	9.36791430882279	3.96166670672911	-11.87818837011777
N	11.20781698319573	4.90322872940028	-12.29505467123088
C	11.15498282780905	6.25855370805304	-12.20531662763697
C	12.38999977372412	6.72552326482337	-12.60929356523746
N	13.10158540275777	5.60958420490762	-12.92756896367140
N	12.38248173465393	4.49254248815798	-12.73187719862992
C	9.92271744953022	6.95443227783143	-11.70548252003076
C	10.32699206555367	7.67023366390133	-10.39059094640550
C	14.51455304647337	5.49274165052781	-13.30597102273709
C	15.43294846556577	5.64519424112916	-12.11239274743549
C	16.44671794474188	6.60542750805233	-12.12363330183586
C	17.30207884194684	6.74177547073366	-11.02916273500599
C	17.14080323886893	5.92039279535140	-9.91479762580896
C	16.12472109013819	4.96205911388766	-9.89860471502162
C	15.27439000336516	4.82142508833378	-10.99186532252905
C	7.46856886953479	3.16689427539296	-11.66025218694755
C	7.38058397199786	2.32470444623688	-10.38481064634181
C	6.43556552194098	4.28797120029811	-11.65672571721647
C	6.67299493822419	5.31569709003550	-10.54968195753487
C	7.72624826050434	6.38352129826466	-10.90449764412308
N	8.86314833620432	5.92121379976549	-11.46743941127825
N	5.44749831674306	5.98999496878385	-10.14481855408769
C	5.09169916152335	6.13936468207769	-8.79597316261189
C	3.91507225319136	7.05495379369418	-8.78749922858683
C	3.65417126146671	7.44021692879164	-10.10376654236199
C	4.65093527342896	6.77627289215975	-10.99557141912464
C	2.61306928769356	8.30259968068054	-10.41194242923600
C	1.83205898202329	8.77762654599134	-9.35120504498588
C	2.09379460483591	8.39099175630676	-8.03159226835421
C	3.14560665745409	7.51727296405474	-7.73034585698844
O	5.65407197269112	5.60344580791218	-7.85620114154612
O	4.75942477258361	6.85157531757649	-12.20528874571617
O	7.48429714671131	7.57150950538580	-10.62866360729230
C	7.21509139481078	2.30048046346391	-12.89896877712270
C	9.45976115907531	7.96875613662896	-12.77544899942818
H	7.01314555902762	4.81036017901273	-9.63968056809479
H	12.81035697071051	7.71515728806692	-12.68767024016459
H	3.35841699230663	7.21240923708519	-6.71041386611406
H	1.47063849670061	8.77795950435014	-7.23035933592035
H	1.01007669243600	9.45878284890967	-9.55237413302481
H	2.41970541686299	8.59754568676840	-11.43861768604644
H	14.60810083849713	4.50452214894060	-13.76323465057029
H	14.72810634064642	6.25179182565977	-14.06271453067823
H	11.16298151282596	8.35221092418154	-10.58425645770372
H	9.48038038396388	8.23091344671135	-9.99805005321819
H	10.64903340739813	6.92821094242975	-9.65301247592789
H	10.25801370757881	8.69206628046912	-12.98093889529954
H	9.21486306580710	7.44184600865703	-13.70228837479151
H	8.57784701326743	8.49658245155136	-12.41307652166872
H	14.48161726008881	4.07854660599819	-10.97337770444900

H	15.99282940890204	4.32087570078753	-9.03264961315018
H	17.80203038510508	6.02744406847521	-9.05981858824726
H	18.08766869566511	7.49152596660193	-11.04682463279981
H	16.56918424838612	7.24950232743476	-12.99169371292470
H	5.44022867139480	3.83964782907100	-11.50123394129450
H	6.40766984399475	4.79343604004153	-12.62606850940856
H	8.03891993823845	1.45254514663522	-10.43606767856144
H	7.64674884207670	2.88867792566441	-9.48574192470288
H	6.34919420123234	1.95763734194868	-10.24927732315003
H	7.83173845928898	1.39347259701697	-12.90988492302105
H	6.16314772208659	1.96829330075955	-12.90984535836801
H	7.39237194173097	2.85537443304749	-13.82644463033221
H	13.30773454582779	0.36673504009073	-11.30760077826733
H	14.95588133257599	0.70703274018851	-9.48716903372356
H	14.54016311453308	2.41389545890433	-7.72882070665781
H	12.47825982884943	3.80418875212496	-7.81388488769571
H	10.82144806091683	3.46713459596896	-9.64551128919917

TS2.(5-6)c
Lowest frequency = -134.48 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	9.36386426678163	2.68011314456435	-8.83237679421697
C	10.42910230210142	2.76732366239710	-9.72832152725099
C	11.63981269933446	3.36789999353037	-9.36395992452707
C	11.72863439956464	3.98671314660145	-8.11829757949636
C	10.64192653129236	3.98826126883726	-7.24155427517537
C	9.46730619284723	3.32846772865838	-7.60032050409977
I	10.61559308568309	1.18533233055877	-11.41437010140442
Pd	9.68655658254444	3.65986285226501	-11.73509851736222
N	11.60757964006205	4.51311604305873	-12.22957945692388
C	11.55664626166258	5.87202611602561	-12.31406575328490
C	12.72329916361269	6.27037026613693	-12.93309590848102
N	13.39863866327385	5.11623518491504	-13.18919413718699
N	12.71835793190839	4.04001158797931	-12.75724711494492
C	10.41457349958102	6.63605152459021	-11.70970941270794
C	10.92046314012230	7.16966469222028	-10.34269567090836
C	14.74956290164669	4.94325510702559	-13.73910302546727
C	15.81386440834462	5.31004987484851	-12.72806875462281
C	16.70679169971427	6.35189033800323	-12.98630925781312
C	17.68296277421519	6.69357791852068	-12.04886310194716
C	17.76577490270283	5.99627807495943	-10.84499171950387
C	16.87336539887730	4.95426587640278	-10.58131050329880
C	15.90273259581177	4.61105690376309	-11.51853024474498
C	7.68142441359135	3.11177066794097	-12.08079077444466
C	7.08862142951095	2.01283379722938	-11.20883214767576
C	6.80872786680228	4.35667342740959	-11.98835502800891
C	7.07946934185460	5.11742776677344	-10.68342112984829
C	8.19541003652163	6.16204088241125	-10.87970895959088
N	9.27041401155942	5.69036356806716	-11.54416001831335
N	5.90688007944638	5.76359450146291	-10.12156545377562
C	5.57433574666828	5.65118139548749	-8.76420153617790
C	4.45932990334036	6.61468694140508	-8.54052953127719
C	4.20135416489480	7.27059166927044	-9.74620860909531
C	5.13737671170326	6.73975314398646	-10.78140742082709
C	3.21065389511207	8.23538911737949	-9.84639372118293
C	2.47908538506393	8.53310326711129	-8.68998635442038
C	2.73768535191521	7.87529073681221	-7.48191091913964
C	3.73713717114124	6.89890101550077	-7.39114864377598
O	6.10781365791196	4.89504010048631	-7.96850560180650
O	5.22005500876800	7.03083445466818	-11.95939358746292
O	8.03729367236918	7.31719431753634	-10.45169964338886
C	7.82445506667704	2.65323389319890	-13.53370479761930
C	10.01451668613298	7.79579850114559	-12.64382380522663
H	7.40787026541629	4.41701575074581	-9.90745150154413
H	13.11877432483063	7.23772715978022	-13.19756205812319
H	3.94625621054478	6.38328213773956	-6.45902336727556
H	2.15343974721354	8.12931607723263	-6.60211401663047
H	1.69846312041445	9.28755359734826	-8.72779706433681
H	3.01829430448799	8.74042685951859	-10.78782689519092
H	14.80862532354150	3.89110877277294	-14.02728471923094
H	14.83349576405510	5.56076240399796	-14.63702320535853
H	11.81999132860617	7.77726478846353	-10.49410587477345
H	10.14219021522418	7.77152059584917	-9.87504487099604
H	11.17068387731434	6.32794973697060	-9.69093152029910

H	10.86329851144312	8.47383612419437	-12.79435745328680
H	9.69807965430358	7.40301438960948	-13.61447355311043
H	9.19227902890159	8.35106784818556	-12.19211096571643
H	15.20595752052517	3.80188974697951	-11.31429434439983
H	16.93663481738864	4.40758911369263	-9.64495870143242
H	18.52250200776365	6.26240876556083	-10.11291273122341
H	18.37383915587001	7.50481375392688	-12.25885928423176
H	16.64029261054448	6.89803594924958	-13.92470837797179
H	5.75279508380410	4.04819244907633	-12.01584066013869
H	6.97408571357581	5.02227896469672	-12.83877567136750
H	7.74322880580898	1.14380792929560	-11.10797433184939
H	6.82719300599511	2.38159057979091	-10.21224081519941
H	6.15065082483500	1.66982655993572	-11.67401083182812
H	8.34795326251095	1.69662959437889	-13.61309564782897
H	6.81855255034013	2.52984433716725	-13.97094520211607
H	8.35145771111369	3.39336398985979	-14.14713357942531
H	12.47786384466612	3.37761329090027	-10.04873601080122
H	12.65865393174069	4.47640790220381	-7.84136785188301
H	10.71513233309159	4.48874688472100	-6.28121548522645
H	8.60985933569810	3.32085126634734	-6.93447313534932
H	8.46060616576051	2.14762087866302	-9.09273330342738

2.6c
Lowest frequency = 6.81 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	9.01746510053118	2.97081910456598	-8.65652891446550
C	10.01630890763936	3.28607753798015	-9.56350097151250
C	11.32253114307660	3.51872229458001	-9.13675391238302
C	11.60917806748166	3.48522556436433	-7.76994938365357
C	10.60556619875913	3.21249499828049	-6.84148460037476
C	9.31451209935953	2.94996677598359	-7.28844813742464
I	10.59243486101571	1.03445487980360	-11.76430493358384
Pd	9.71595674289182	3.52737453209182	-11.55705144035409
N	11.65538566597136	4.39658186355013	-12.13265792713440
C	11.60092976590730	5.75806614450640	-12.16112792017484
C	12.73690879803357	6.18240223995427	-12.81876473811447
N	13.39661098828064	5.03825493835637	-13.14958099637274
N	12.73857223604310	3.94617700983057	-12.73245562498615
C	10.48629231085135	6.50534415797392	-11.48759863676788
C	11.02865364160137	7.00310370538862	-10.12266379041270
C	14.70214452548450	4.88911603443648	-13.81084437473987
C	15.82398540740630	5.42414043934968	-12.95028004020615
C	16.60541854577865	6.49369102181267	-13.39214440030786
C	17.63638662712007	6.99165265436263	-12.59365980288783
C	17.88550150252470	6.42358450215049	-11.34562059929323
C	17.10493269084445	5.35469952747345	-10.89840080513296
C	16.07948633934837	4.85554878198934	-11.69684744640373
C	7.70917466589189	3.03633307288876	-11.96018038488796
C	7.08526150385947	1.86775863010212	-11.22373185175734
C	6.85470840430264	4.29462457808241	-11.85156823324233
C	7.07322716383049	5.06366319586108	-10.54630254822467
C	8.25653253790385	6.04656856011075	-10.66395174315501
N	9.32974661572612	5.56652724191146	-11.33878109720095
N	5.89523622129904	5.79191816861991	-10.11133298835749
C	5.39279626621862	5.69032105216427	-8.80417819787171
C	4.33238896930805	6.73238014403589	-8.70094364023675
C	4.26968650793560	7.41485532142211	-9.91845901214574
C	5.28254026782809	6.82575874684715	-10.84223448950071
C	3.37105343446943	8.45126875296993	-10.12082716272137
C	2.52924311028194	8.79355521906441	-9.05550345595520
C	2.59215721515694	8.10949604875557	-7.83597940007850
C	3.49964955245352	7.06112459842917	-7.64171305741718
O	5.77252069528352	4.88798827769454	-7.96864273240720
O	5.53278421515488	7.11882534423672	-11.99647198505779
O	8.14189285488096	7.18768807402955	-10.19721273160559
C	8.02242913190374	2.74278010355210	-13.42810571996727
C	10.07110879105496	7.69550835718234	-12.37984121494084
H	7.28417504373921	4.37219940981219	-9.72634550795053
H	13.12341520627432	7.15892063811943	-13.06169569886813
H	3.55707272926606	6.52509592122127	-6.69956729249003
H	1.92632552244378	8.39974178192782	-7.02841126237831
H	1.81572242539103	9.60389195507563	-9.17411813104420
H	3.33054637499231	8.97634607868426	-11.06999725126739
H	14.80095771138288	3.81712456738864	-13.99611942532389

H	14.66200987479954	5.41211050275684	-14.77019597347254
H	11.92882579623052	7.60599745128668	-10.28701676027475
H	10.26952027218382	7.60449108291848	-9.62449889168231
H	11.28724546474921	6.15067069438066	-9.48998048909729
H	10.92745933239723	8.36215122971388	-12.53491613434678
H	9.72295883650636	7.33397171990700	-13.35162085179532
H	9.27180974927467	8.25300712958096	-11.89264403899360
H	15.47055381087932	4.02461731383222	-11.34903439306025
H	17.29843574391720	4.90872595948137	-9.92728907022225
H	18.68539356150591	6.81090730591240	-10.72149251930823
H	18.24022881911532	7.82270164973624	-12.94609658042703
H	16.40925279920340	6.93768110504588	-14.36564095516020
H	5.80179105911609	3.98220872680443	-11.90684570960438
H	7.03932772815822	4.96578481364934	-12.69342207543888
H	7.77146094634355	1.02607051162280	-11.11783778939890
H	6.71367738330959	2.16076301864751	-10.23754821687244
H	6.20912096027545	1.53199947708606	-11.79997298915327
H	8.35890886606379	1.71830779689459	-13.58719984945192
H	7.12266663220730	2.94557645318379	-14.02981159016358
H	8.79519577681241	3.42330810547514	-13.83188346721900
H	12.11484237670262	3.70908374868197	-9.84892934963131
H	12.62885364108295	3.66950013648664	-7.44172828232773
H	10.83187679353949	3.19404483125442	-5.77953551926501
H	8.51708570384655	2.72739600631763	-6.58538483387200
H	8.01243176759532	2.73004568036863	-8.97078205702027

TS2.(6-7)c
Lowest frequency = -269.22 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	9.76674788829163	1.31678089485278	-9.89096908109326
C	9.51846172592135	2.68656015501888	-10.07809930930894
C	9.90889215590463	3.57005977331551	-9.05108470142025
C	10.49886776244387	3.09456781041800	-7.88022126732367
C	10.71106997071712	1.72997786248243	-7.69839057345931
C	10.35048436331777	0.84841755983648	-8.71684235730517
I	10.80320130313994	1.53386350521615	-13.10629036853532
Pd	10.09373724336625	3.73952026710095	-11.82448571796229
N	11.58410901798868	4.75142484712899	-12.72385350865827
C	11.53997245906955	6.10637741995146	-12.57173095329666
C	12.76540974994588	6.57678611223395	-12.98789765751015
N	13.45864821749926	5.46585311815291	-13.36693876238828
N	12.74762506205798	4.34606186657906	-13.19472797403576
C	10.27652703207804	6.76381396995416	-12.11465194364033
C	10.65134813557350	7.98013025213074	-11.24246868346416
C	14.86725548014706	5.35371734491480	-13.77603307848968
C	15.80046869432371	5.52632210819680	-12.59807833639217
C	16.75073065177553	6.54939066137848	-12.59492987940423
C	17.61098083329069	6.70875950611415	-11.50742785350782
C	17.51767962604537	5.84793793814742	-10.41527353366015
C	16.56583106871448	4.82539231527259	-10.41330926811213
C	15.71124242307529	4.66222649266201	-11.50027283576807
C	7.88162809503963	3.01049277816384	-11.17221838301206
C	7.33514827820958	1.58260556842417	-11.18757947006404
C	7.10607692113426	3.82856957612175	-10.14813800982028
C	7.50844411245432	5.28864024380000	-9.85044872239203
C	8.32019630134578	6.17265196598480	-10.85100975433700
N	9.50974733683907	5.73092784231919	-11.32841727091937
N	6.30980396766485	6.03394826976317	-9.48799306377310
C	6.25821256533500	6.82684982039876	-8.32799812497852
C	5.00640582610228	7.62579989655922	-8.44109631333217
C	4.40914416073536	7.32843976581353	-9.66802463322779
C	5.25681973730642	6.32506310394655	-10.37371777719712
C	3.22565222342788	7.93407994345510	-10.06246168854065
C	2.65043536709346	8.85994726138868	-9.18378843599074
C	3.24881531484494	9.15734721526597	-7.95372438014356
C	4.44247869569627	8.53903852631614	-7.56269001467879
O	7.09308803436103	6.82057805681625	-7.44085235560463
O	5.09117198940236	5.82015629006547	-11.46977337970874
O	7.88588646006056	7.32415769747237	-11.02954985132199
C	7.58578629929690	3.55904785326915	-12.60446115061907
C	9.51462006458211	7.19085614145780	-13.39663449125288
H	8.09436644164242	5.30635965595894	-8.92837932673823
H	13.19034965552737	7.56594216428130	-13.03644434710299
H	4.91565410392963	8.76475826998891	-6.61220439232141

H	2.77865293458736	9.88185844132144	-7.29509496008057
H	1.72591269694185	9.35902365237071	-9.45949687374157
H	2.77099977408207	7.69869892883251	-11.01962092892478
H	14.95357012785110	4.36149415164492	-14.22474237548514
H	15.05737985318225	6.10855740722004	-14.54301782618424
H	11.29635256359458	8.65909949797736	-11.81286359567905
H	9.75262482149098	8.51530160431816	-10.94277225400112
H	11.19382141765211	7.64701608859384	-10.35275572526849
H	10.13247940023859	7.88201406703077	-13.98077730017767
H	9.30782755787489	6.30941982820018	-14.01196000485116
H	8.57861088090768	7.67630610055423	-13.12450329381425
H	14.96795431143693	3.86878766994374	-11.49790784317486
H	16.49073904353858	4.15295460320718	-9.56389640385991
H	18.18340219185978	5.97244449828685	-9.56628950724577
H	18.34851681523202	7.50594870419142	-11.51363039098155
H	16.82097389229848	7.22268839030465	-13.44645680338817
H	7.08599707699870	3.29052162389181	-9.19547437055593
H	6.08137007796741	3.84833799053352	-10.53770846372137
H	7.32653608548183	1.12566713154727	-10.19637938957691
H	6.30227842096606	1.64211348093271	-11.55405968788332
H	7.89677467903631	0.95289078276257	-11.88284436487477
H	8.05146651615016	2.94704313275302	-13.37981345857543
H	6.49371779502737	3.48160550580723	-12.70980878879833
H	7.84027947682123	4.60632788824347	-12.75476761558816
H	9.81972062276670	4.63831628751615	-9.18616935170356
H	10.79619893865342	3.80739477891717	-7.11609967985759
H	11.16186898075458	1.35917214755945	-6.78240849039457
H	10.53125655835853	-0.21765056077046	-8.61031884223573
H	9.53194267152919	0.60733148821827	-10.67097242756300

2.7c
Lowest frequency = 14.53 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	8.72926656219136	1.20873671952489	-11.89071084255839
C	7.92257878441376	1.83371080257002	-10.90110809191813
C	7.91467480400082	1.24336199746949	-9.61176027395972
C	8.52332226690211	0.02409683249239	-9.37724943911644
C	9.20465840670743	-0.64751974952114	-10.40576763335492
C	9.33779640217452	-0.04408916301987	-11.64022129721891
I	11.74275315867166	1.43357779336874	-9.42868828477536
Pd	10.29032679552607	2.82013255674154	-11.13444840068034
N	11.82043279382638	4.13419624955499	-11.36825752668986
C	11.71764870802855	4.90031783130429	-12.50691877485806
C	12.69802878298766	5.85423866107662	-12.40990601090910
N	13.32384215998431	5.59713182715039	-11.22194249177581
N	12.78366168543782	4.55281798120785	-10.58176297979155
C	10.54483501067869	4.58488517493119	-13.39696951385266
C	10.21320317983377	5.70686847615078	-14.39434532074571
C	14.36596291212777	6.38872045900192	-10.55077977446454
C	13.94085671090359	7.83395183335216	-10.41619659802580
C	14.77323742022040	8.85550393536194	-10.87869879667844
C	14.38113414028905	10.19035568575396	-10.76556667095637
C	13.14612885061792	10.50554423521103	-10.20170326356318
C	12.30836047136421	9.48583033965701	-9.74348624957667
C	12.70357152935129	8.15428593530758	-9.84302582753005
C	6.80913172212057	2.83261181840738	-11.27154614539717
C	5.46774419267985	2.16692806804080	-10.85143535590150
C	6.86922278222156	4.17029821268836	-10.49264866956647
C	8.21934110033820	4.89177899935875	-10.38206217953545
C	8.95393331173058	5.31342667485936	-11.68615422906913
N	9.47134616883112	4.27266072961031	-12.39938895486553
N	8.09589137126469	6.08322968501635	-9.54281122980375
C	9.18443279349219	6.48899532649445	-8.74716923795584
C	8.84514515471902	7.84587209132154	-8.24211608449843
C	7.64183244762389	8.23603785427817	-8.82946725318233
C	7.16026240748098	7.12906100445039	-9.70888700552779
C	7.08005091046992	9.47736038867866	-8.57064866208702
C	7.76728019951247	10.32606522867076	-7.69420602390421
C	8.97181586372267	9.93093533852001	-7.09930438052645
C	9.53071039827883	8.67551655517785	-7.36640673985456
O	10.19459497752184	5.83363196405790	-8.55993567763293
O	6.16355281907324	7.10817138761600	-10.40494141787014
O	9.06279334355144	6.51443820258468	-11.95561040411763
C	6.68676043613649	3.05993531385575	-12.79160112113536

C	10.81968215085332	3.29641848683279	-14.19837163329476
H	8.92006518277002	4.24190447591468	-9.83583249854823
H	12.96732254939893	6.69010583628955	-13.03439834524601
H	10.46467667132911	8.35946191623448	-6.91208705703478
H	9.47879078213221	10.61124424766435	-6.42107543072162
H	7.36114736585230	11.30802035792056	-7.46926586956109
H	6.14577709800738	9.77452482773349	-9.03647346225111
H	14.50399150307458	5.90171471482867	-9.58232368475106
H	15.29473054833668	6.30592873187021	-11.12292638193460
H	10.98103015382380	5.72445087417271	-15.17701420921516
H	9.25119063405772	5.48912437185216	-14.86714800833324
H	10.14438935018587	6.67606145590223	-13.90626932929891
H	11.63761521970589	3.46140297170805	-14.90642061183044
H	11.09099756892529	2.46984797532126	-13.53260809659446
H	9.91878328687969	3.02080505875410	-14.75531131709260
H	12.04805258199325	7.36312331061333	-9.48755226307364
H	11.34138624079969	9.72738320387066	-9.31337163986827
H	12.83249824925430	11.54257881356703	-10.12392182666911
H	15.03511331791842	10.97862297151198	-11.12707119880449
H	15.73087025479375	8.60672840822985	-11.33090077816852
H	6.55223714729101	3.98096826854634	-9.45908429569670
H	6.12958997769515	4.84634279909382	-10.92665928438820
H	5.41245810653229	2.00167906956283	-9.77218228328640
H	4.63842284392012	2.82153836644466	-11.14111403866901
H	5.34216273388965	1.20385084675058	-11.35624855578195
H	6.45166833840739	2.11587462199168	-13.29610306480529
H	5.85832561953110	3.75234382685099	-12.97419000799883
H	7.59152651267948	3.48317198431214	-13.22422122036141
H	7.36643192398609	1.72891805562590	-8.81013168123030
H	8.47574695172957	-0.41692140078352	-8.38652621488391
H	9.66913566259420	-1.60833910805118	-10.21174345811911
H	9.91072203746701	-0.51874559836555	-12.43043575154606
H	8.68978649717608	1.57713899889393	-12.90935566550926

2.8
Lowest frequency = 9.45 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	11.34248320467461	8.90521156142353	-2.23488884941212
C	12.42146437935216	8.09946541741704	-2.96763159900847
C	12.07242023159504	6.60605974830420	-2.97706100512029
H	11.09724273382886	6.44443689591241	-3.44916841541159
C	13.86910029449645	8.30220995361288	-2.43024912372290
C	14.32032658416598	9.78899275426244	-2.50118007712997
C	15.83416109620341	9.94938020073248	-2.19777945723033
N	16.10528912530862	9.98884048962102	-0.87319055863158
C	17.44755759742328	9.95759832378013	-0.24985834326022
C	18.18788886256396	11.27792473901677	-0.54709264561328
C	14.08504317631222	7.74657169106442	-1.03524722369314
C	14.87377018362503	6.60238995513404	-0.87092996334898
C	15.13526275779170	6.08138498450157	0.39579203984296
C	14.61339444660114	6.70167870999822	1.53016843989909
C	13.81897299261714	7.83860765773231	1.38295390993877
C	13.55270794407936	8.35145540703670	0.11360840979019
N	14.03966816048390	10.40272748726280	-3.79131532227599
C	13.56225865280139	11.72640406300505	-3.86588187572543
C	13.56848408904627	12.08073574772811	-5.31005194758919
C	14.05959168070216	10.98660465037461	-6.02413707781795
C	14.37001874323446	9.88676448575364	-5.06387093144170
C	14.18369083601793	11.02123374048800	-7.40483774320554
C	13.80363813806994	12.20042539902515	-8.05712179076581
C	13.31129847991688	13.29760388396280	-7.34026454157104
C	13.18377013553543	13.25154843610256	-5.94709763365207
O	13.21956291987747	12.39576313717492	-2.90712708998086
O	14.76385197906312	8.76325104586496	-5.30881940110438
O	16.67366798407090	10.01365623141648	-3.09328143872817
C	18.24808102542470	8.75089109369593	-0.76514661414787
C	17.18313514770405	9.82402485765867	1.23064639107588
C	17.72341680702298	8.97139295803758	2.16988956193661
N	17.10858595915951	9.30911868724399	3.33419744154022
N	16.21307980129951	10.30610222732380	3.13371151333573
N	16.26419535983711	10.61868346051964	1.86134646500986
C	17.23117523711083	8.69332844231571	4.66141070617459
C	16.28992377608683	7.52296192653009	4.84592334985551
C	14.92669548208891	7.74903267415674	5.06676154515122

C	14.05273015190484	6.67540711148477	5.22223788317025
C	14.53274397247946	5.36534016879524	5.15797168165500
C	15.89016970924936	5.13360006107211	4.93768836171616
C	16.76436996431991	6.21045003895711	4.78281908572533
H	18.45541723327155	8.18198344146219	2.11239594665258
H	12.80256409813380	14.09581930715816	-5.38132328567571
H	13.02546475254132	14.19811487654774	-7.87599612056568
H	13.89215411349233	12.26841843078099	-9.13752035583574
H	14.56592387756237	10.16485186447589	-7.95130075079179
H	18.27085761502691	8.38113612250972	4.78630602390794
H	17.01340145745089	9.48872304068147	5.37749560263431
H	19.17568851354072	11.26583732487271	-0.07494289631357
H	18.30476862801316	11.39120955725556	-1.62742003703495
H	17.61636303061645	12.12084638441128	-0.15068162599341
H	19.23287453119200	8.72686669714448	-0.28649118815279
H	17.71733560502849	7.82017474844998	-0.54452779137404
H	18.38393018566257	8.83623662642751	-1.84434013736699
H	17.82337012870981	6.02812429547459	4.61385074450373
H	16.26879394997838	4.11691190151526	4.88616503787251
H	13.85004982228605	4.52914993488397	5.27656609930535
H	12.99565805980180	6.85916184778184	5.39063733919473
H	14.55447470680243	8.76935110995353	5.10189310148907
H	12.94800852780901	9.24995640525640	0.02520804385396
H	13.41924406427805	8.33837929336059	2.26017401228912
H	14.82613800415722	6.30839212869413	2.51829591815449
H	15.75643801325927	5.19519359530829	0.49725064352541
H	15.30043972425378	6.12806344544795	-1.75130765958655
H	14.52131868792410	7.74405488970573	-3.10825501139766
H	13.75294221862350	10.38676777055571	-1.78037491215522
H	15.32731522198771	9.98109401932193	-0.22396282451496
H	12.02645164652642	6.20846395700108	-1.95712289258225
H	12.81999731357352	6.03056293503345	-3.53380009136264
H	11.57728487247940	9.97432188042163	-2.19177495969945
H	10.38580382291375	8.79889390282249	-2.75794317560512
H	11.19924400540270	8.53989561700066	-1.21264214705349
H	12.44376876455364	8.43780014278245	-4.00980976654972

2.8‘
Lowest frequency = 6.32 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	17.70267385395954	6.05402112363824	4.56012588029089
C	16.71504305229420	7.05121651300011	4.61727851627002
C	15.38023849408751	6.63867669022360	4.72385699442780
C	15.04321609831682	5.28493908408848	4.75926587546828
C	16.03460733877485	4.31115431642575	4.68116589493211
C	17.37052628215623	4.70187322226065	4.58518424075820
C	17.17039944731875	8.50783703861749	4.53272557792613
C	16.22230515180652	9.60363058804423	5.08310593919929
C	14.99133340355552	9.95579427763124	4.23380113364547
C	17.78743582541573	8.78694974662919	3.11724789471193
N	18.70472106459278	9.92169181770490	3.11118813799701
C	20.08927802050057	9.68333415212878	2.97329569787709
C	20.72700916344006	11.01673022387917	2.82873116055273
C	19.72065490587273	11.98211548942879	2.85805034005716
C	18.40529072497761	11.30350269859838	3.04578557811368
C	20.01072695983856	13.33310224316223	2.73948474352943
C	21.35477670725384	13.69214176370869	2.58318466209297
C	22.36454829955577	12.72247771649984	2.55395794880910
C	22.06270311060881	11.36160451557657	2.67886564514324
O	20.60655751269831	8.57932867267282	2.97932726155714
O	17.31429677693074	11.82052470749003	3.17263218495641
C	16.87047938315601	8.85316011829019	1.86856570699818
O	16.97284245122107	9.75112716471258	1.03617860941754
N	16.03593535022007	7.79184007157542	1.75699684854042
C	15.10871793727360	7.53585250725958	0.62508607122602
C	15.90223641742012	7.38918817931388	-0.68790967907812
C	14.42293691772742	6.23166242805861	0.95559782521658
C	13.11454122563297	5.97160170743105	1.30827196217910
N	13.06795251164947	4.62626206732564	1.49258732181432
N	14.28855218064775	4.07119993665709	1.28381265040266
N	15.10327959445334	5.04229912649399	0.95545866352839
C	11.94954386101715	3.78968407873438	1.94722091178740
C	11.89497701690696	3.68100527051135	3.45512265587223
C	11.19798957177229	4.62721666483070	4.21295316461756

C	11.19275270213375	4.55342015356035	5.60552217927544
C	11.88163110111748	3.52616141046540	6.25158660532501
C	12.57242502336027	2.57398294018356	5.50093708505591
C	12.58021926433714	2.65247292476225	4.10914874117545
C	14.08767784607569	8.68019554908599	0.52323763983435
H	18.05606939720801	8.55513082757933	5.18261063566891
C	15.84805470019893	9.31493103474926	6.54640375344289
H	12.24739345465604	6.60090741278128	1.42934862602147
H	22.83723470173356	10.60150284824910	2.65723702562758
H	23.39769790250616	13.03413817311075	2.43122885270659
H	21.62195474177081	14.74002284420800	2.48177569625470
H	19.22030933900716	14.07655836537256	2.76347231015387
H	11.03088001569458	4.22857531167952	1.54952098540194
H	12.10074241793675	2.81010868221239	1.48980850560442
H	15.21037031550344	7.19374063377140	-1.51351947433196
H	16.45279205524688	8.31050138246340	-0.88692072289747
H	16.59719678505778	6.55036927049820	-0.60863934031727
H	13.38734573251757	8.48479455026441	-0.29525173723358
H	13.52726225762313	8.78460828982479	1.45768099427684
H	14.61198493897735	9.61696052828046	0.32695920675748
H	10.65800224011092	5.42804922229093	3.71254029827868
H	10.65153314839108	5.29552850237552	6.18513362547078
H	11.88099713961138	3.46891683779491	7.33598500543926
H	13.11075156513223	1.77377532534461	6.00030976074086
H	13.13380904991805	1.92350020862356	3.52354100423802
H	18.74843937162759	6.34661430023310	4.48656359398303
H	18.15612490764766	3.95407666449806	4.52563867778635
H	15.76794758038357	3.25888890977182	4.68736661433547
H	14.00065804587088	4.99678277002898	4.83925999897268
H	14.58716758471318	7.37342921895830	4.77010192485205
H	18.45700192256023	7.93840772756228	2.92928296291748
H	16.07789667384919	7.07519085660572	2.47394923321512
H	16.83282441436478	10.51300084372079	5.09405416465972
H	14.46405772346244	10.79165018815119	4.70719285974892
H	15.28281981404065	10.28478784879957	3.23515766990452
H	14.28115974087711	9.13018905804925	4.13661832437722
H	15.34243925489983	10.18448022438702	6.98015608125761
H	15.17976921322918	8.45435141669122	6.64377164747264
H	16.74211230359388	9.10944282040708	7.14670796370859

2.8b
Lowest frequency = 10.19 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	10.40392066590450	8.39241821819153	-1.62739075522645
C	11.29743254033624	7.34192845405554	-1.84330642988641
C	10.85021001372353	6.02143115577787	-1.71043737625664
C	9.53059115052943	5.75677934903062	-1.35593123991604
C	8.64090155155502	6.81245063943219	-1.14252908606812
C	9.07602659238134	8.12882900229114	-1.28375125628069
C	12.74840479076434	7.61701133036172	-2.18254716210399
N	13.63948761080300	6.93366589365887	-1.23935196753643
C	13.78297677966705	7.14924995935957	0.09417250926397
C	14.54407830839960	6.08960431456020	0.54061564562277
N	14.81376900067315	5.28068737163003	-0.53252345607657
N	14.26189281865342	5.78465882279731	-1.60883821911690
C	14.92747174609324	5.67814676191781	1.94189938840392
C	14.62538619516729	6.80019614999974	2.94593640522057
N	14.04775051748745	4.50830038205618	2.21225979956647
C	13.90923422955167	3.83901154287572	3.38457682422039
O	14.51059382992534	4.09171878271290	4.42230966008211
C	12.89692838924447	2.66533748887155	3.26585694157901
N	12.80500938701684	1.98950530069201	4.54556011146714
C	13.46331648671030	0.77274926231684	4.79792026514520
C	13.26606923790419	0.50283440357574	6.24834185053631
C	12.54332878787555	1.56527123895324	6.79676869463528
C	12.24709177830847	2.54692401705672	5.71351660352337
C	12.20790432866305	1.59328964575000	8.14188652894111
C	12.62433022656425	0.51598786087969	8.93346086360257
C	13.34801732190364	-0.54847021394722	8.38347209656809
C	13.67980287712573	-0.57026772585343	7.02353034379499
O	14.04860885413805	0.11134934245794	3.95824428033707
O	11.63000370856528	3.59349854067560	5.77370258137674
C	11.50820570404136	3.07817548988112	2.71108498982112
H	11.54432190194425	4.13076008627183	2.41264484539112

C	11.00694103375830	2.22995429443635	1.52096202348808
C	11.96991162646812	2.39404123658645	0.32452642398120
C	16.40457424196667	5.25310094061547	2.01390401079307
H	13.33267723686040	7.99336833331315	0.59141341703605
H	14.24122086493053	-1.39044976775411	6.58735817297680
H	13.65732524457272	-1.36881543781728	9.02450474414091
H	12.38413080285372	0.50410566400680	9.99262168460782
H	11.64696391149864	2.42347943065011	8.55932142374994
H	12.96004863242522	8.68952152151542	-2.15728681756988
H	13.02039741871840	7.22683768860926	-3.16680967872135
H	17.05035895362029	6.11629842433463	1.82353892702831
H	16.61813969567705	4.85808666439227	3.01000364537844
H	16.61088577745743	4.48870215498662	1.26143810857281
H	15.22750875159673	7.68186433406084	2.70461579611849
H	13.56534731270933	7.07148812227377	2.91721398510924
H	14.86775888606659	6.46533491431970	3.95535008192877
H	10.74699776460623	9.42040338095804	-1.72297323643294
H	8.38823633323640	8.95288917335708	-1.11633088390337
H	7.61371643402675	6.60283438924770	-0.85974925490265
H	9.19483093453036	4.73182478655449	-1.23484102236897
H	11.54671738412914	5.20278083084470	-1.87352527271577
H	10.79290533736648	3.01726828508842	3.53333781833424
H	13.36909108190206	1.92696680096281	2.60677681742597
H	13.59102058458386	4.11970599490642	1.39597364454043
H	11.64374170210865	1.79727715580407	-0.53158129722811
H	12.01280678181900	3.44025901050729	0.00075793337713
H	12.98286894940647	2.05961140690861	0.57754077502977
C	10.94198683141670	0.74301516977193	1.93403262533729
H	10.57599741906294	0.12574812703742	1.10826546577278
H	11.93140737522966	0.36834796603359	2.21724305244056
H	10.26405565713789	0.61084974582938	2.78371347479725
C	9.60608877029709	2.68971992706830	1.08816770685382
C	8.98506196460187	2.06485980862198	-0.00551196241214
C	7.71366039595665	2.43919114367881	-0.43302856498750
C	7.02240002209298	3.45631646290941	0.22854891574434
C	7.62319146547212	4.08813247513623	1.31373752859967
C	8.90012643916747	3.71034945488076	1.73643086574948
H	9.50143674401698	1.26769296856919	-0.53354564501130
H	7.26162286557116	1.93520480349159	-1.28297629536531
H	6.02953964775086	3.74963164646469	-0.10048402949252
H	7.10219865760558	4.88382870184208	1.83922188442800
H	9.33663673410358	4.22710999670496	2.58371672714003

Internal Triazole

137a
Lowest frequency = 9.99 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	16.96090269474682	3.82154799015273	11.91669626510582
C	15.67194085483057	3.88402844632243	11.37430596367029
C	14.97784793782568	2.68787863634593	11.14105867446887
C	15.56711388916166	1.45824287300826	11.43226524463382
C	16.86096165588535	1.40581340498329	11.95726285448821
C	17.55410437261257	2.59141443203071	12.20453128201203
C	15.07007233516916	5.19639153526066	10.94351085503492
C	15.38568360243342	5.44584032566400	9.43572264734317
C	14.57354739714578	6.63152272782593	8.92848974335101
O	15.19907222109238	7.80460318227635	9.19318029792026
C	14.48140942199697	8.99058596368288	8.76303423036932
N	16.81015262086595	5.66217981190672	9.20810206241620
C	17.80668126561707	4.77691964590679	8.90931660592696
O	18.98872855462769	5.09266735323693	9.00314444993185
C	17.46687212129783	3.34705135162379	8.46341418634424
N	16.33835579676761	3.22165940172684	7.54687350692887
C	15.26413503012195	2.39346589702478	7.63271643570748
C	14.49414159025515	2.71538405740841	6.53549195463195
N	15.12880338838398	3.71048321696432	5.84126311776600
N	16.24737160696725	4.01956703362291	6.44985294156046
C	13.16144490337709	2.18611915532922	6.10937960789908
N	12.03421543886414	2.90776204592321	6.71340311821879
C	11.54004058592555	2.55544072738029	7.93004161831492
O	11.96469262379411	1.60204574705120	8.57805226175428
C	10.31034728848176	3.37794290051622	8.38998351363253
C	10.37402252863873	4.88399410633930	8.09676123238338

N	10.06712140410592	3.10348467853512	9.79842725869803
C	8.99255936559381	2.30372551222338	10.24214301597238
C	9.19458166502785	2.14520881580188	11.70990736745134
C	10.36889596904718	2.81441805218973	12.06432210305690
C	10.94770921773318	3.42649098429046	10.83644416852284
C	10.82671492744743	2.83305641414961	13.37306992604782
C	10.06422702922421	2.15442229440284	14.33163016449715
C	8.88582853059151	1.48722053645910	13.97763481804145
C	8.43161738471854	1.47323090555332	12.65297695679759
O	8.10885928033072	1.86880972446217	9.52883287521628
O	11.96458321512800	4.08911733844230	10.71454473610120
O	13.48461409443044	6.55024434174012	8.40283033261525
H	9.44365647039305	2.93886752956492	7.87988721534941
H	9.50705421213808	5.37498927467362	8.54752850715904
H	10.32000912335326	5.06646901589303	7.01809040460044
H	15.13186008715484	1.69315313117087	8.44159393618089
H	17.16509935082955	6.57032046574151	9.49196268370263
H	15.04394073387684	4.58379119417733	8.86870344359752
H	15.48026894336107	6.02898251902430	11.52501530421340
H	13.98442735920593	5.17625618729470	11.06658004715928
H	13.97492332226313	2.72705240650633	10.72602996686698
H	15.01421303402680	0.54071811125412	11.24877521598132
H	17.32266817071619	0.44763630710825	12.17803158354429
H	18.55978617901880	2.56025083184517	12.61365311809820
H	17.51155254723729	4.74080389100089	12.09837764517104
H	15.12072941012519	9.82623309181728	9.04407409299511
H	14.32859875579138	8.95632897061183	7.68248689625562
H	13.51550344679855	9.04261563831328	9.27007021636637
H	7.52092177104858	0.95543554601360	12.36920996558631
H	8.31713480988612	0.97001251779789	14.74478192877454
H	10.39102665312961	2.14298020895826	15.36725345148501
H	11.74353814787760	3.35070283382301	13.63740123924401
H	11.28783007478761	5.33240288532985	8.48895596676957
H	11.79549625457017	3.81260107802238	6.32958808305991
H	17.24476160483330	2.73675518735920	9.34332571992563
H	18.37121829666875	2.96854871740428	7.98453154332226
H	13.05363043755423	1.13946587426793	6.39929404389034
H	13.06975499308898	2.27259501726215	5.02404538586782

3.1
Lowest frequency = 11.91 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	16.99490097898641	3.55119605097692	11.74188433412632
C	15.70605742530548	3.69063974288788	11.24871140428042
C	14.94318159465905	2.58189010086797	10.87630895085012
C	15.43873787232007	1.29145718962052	10.98538071675625
C	16.73797361398422	1.14008456627867	11.48481464228131
C	17.50366401799726	2.25164699153997	11.85577439296997
C	14.88782206739627	4.91428142076640	11.02224059679813
N	13.66652479667668	4.46092917628728	10.48060856864945
C	13.61783710505602	3.06151685280252	10.39208320372009
C	12.54641885822943	5.36221629492065	10.24768066629260
C	11.99779897335151	5.26112928257603	8.81564817719881
O	12.67673687852928	2.40612644751223	9.98041736900106
O	15.16320288117035	6.07989977278385	11.23703864127211
C	11.48130982436976	5.12360653026307	11.34126578645933
O	11.63868900905140	4.31938489218676	12.25963528246540
N	10.38227095331864	5.91206734730131	11.23221561855600
C	9.25091506091458	5.72649081396607	12.12945728281410
C	8.36268621326592	4.59489176159388	11.71089285934340
C	8.10787842326153	3.42312253173156	12.38412237150297
N	7.26425811359431	2.72137740068913	11.58549757894853
N	6.98497434258963	3.38906490613388	10.45926047057622
N	7.66555864447966	4.51841622899629	10.52976181856741
C	6.73080380716679	1.37596151216419	11.79630609019760
C	6.72311786400926	0.43114034091680	10.58506005358831
O	5.80515766511332	-0.38256276744905	10.52809604687958
Pd	7.68439189825245	5.55551659908834	8.80277067111406
O	8.53117877959809	7.20173020085298	9.57965679039592
C	7.73388461969823	7.99987343902508	10.27883503411902
C	8.39959779248204	9.33370634149231	10.58812015087597
N	7.69698441968857	0.47145065599746	9.63509289856297
C	8.98389130798671	1.15700871862222	9.56386128883812
C	9.26574523409279	1.62218513166814	8.13811642223458

O	9.90725508400876	2.60778842389273	7.85382003350735
C	10.14840050298625	0.25311233969410	10.07085977325277
C	10.01586941361010	0.05484976535046	11.55849298486365
C	10.53266656473908	1.01959215948804	12.43509891671180
C	10.33520726043449	0.90184049739744	13.81066720791237
C	9.61244772959412	-0.17571965900070	14.32898236551272
C	9.10252175581682	-1.14539818245876	13.46358885159930
C	9.30655930278209	-1.03059193060319	12.08750630789465
O	8.75976260145235	0.75670931136202	7.22590067782920
C	8.99307319456307	1.12991510775173	5.84369756597995
O	7.57146603771785	6.17240850698709	6.84415146325277
C	7.09864715512129	5.02568045685087	6.51146745474732
C	6.75954254187976	4.71334016073599	5.08788592487934
O	6.94219566855076	4.16252959198636	7.44642588616222
O	6.60044162425202	7.71439038411448	10.64570868695084
H	12.96486100276440	6.36190330825935	10.41576352407286
H	12.81947524196565	5.39473906132071	8.10608431511078
H	11.26647677247962	6.05352383893484	8.63012827655732
H	8.47816672019395	3.03701057457836	13.31950875314065
H	7.53312207074682	-0.20260816190033	8.89298246288183
H	8.97426486616097	2.05611894589092	10.17215104090399
H	10.10667854742852	-0.70210343766290	9.53660972978780
H	11.09139978422343	0.75290955790474	9.83558759365009
H	11.08566108895470	1.86844876595913	12.04193947978168
H	10.75203104698093	1.65400447093685	14.47536690599518
H	9.45793159162090	-0.26607377633287	15.40057836502045
H	8.54477039523170	-1.99001178102634	13.85809991533997
H	8.90127057232167	-1.78460041781528	11.41752498675268
H	8.53399016493950	0.33774509012291	5.25392143499854
H	8.52192854383503	2.09420623869808	5.64556182956685
H	10.06631358577278	1.19623212770835	5.65318062452839
H	17.58041707472880	4.41876103143160	12.02916396694885
H	18.50818987423847	2.10060921333598	12.23997226172974
H	17.16073561320896	0.14500422942162	11.58825058012741
H	14.83660692296516	0.43558867683517	10.69680274034168
H	11.52053764053424	4.29681422257580	8.63882832628724
H	10.18346850418307	6.46011632846853	10.39648592231896
H	7.32442913545232	0.92157218018090	12.59464640829595
H	5.69008134312638	1.44625489128748	12.11628145714158
H	9.64010483084393	5.50354333723409	13.12473323172948
H	8.67946425637109	6.65458334877418	12.16922754590219
H	7.76863548088194	9.91068176996914	11.26488505985904
H	9.38786512284676	9.17874276862400	11.03321769951237
H	8.54502394896666	9.88878338416897	9.65582329947823
H	7.68659847722157	4.59927626892705	4.51503839484437
H	6.17931079502479	3.79064138205279	5.03216052355549
H	6.19793550968072	5.54317115252606	4.65087506254587

3.2
Lowest frequency = 7.76 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	-3.96288792531910	1.27344752628574	9.65719028895703
C	-3.77628916005026	2.23722139828349	8.65636580075193
C	-4.17769813153510	3.55405765097153	8.90907485864083
C	-4.73719480845607	3.90564211905380	10.13842513504240
C	-4.90638906311539	2.94108601467207	11.13241958292442
C	-4.52571548102632	1.61987050249676	10.88503498584286
C	-3.03694463431785	1.87362191066238	7.39484603376530
C	-1.51113001978750	2.02262688014119	7.65289591216391
C	-0.69104677380955	1.29016655625038	6.58688999603123
O	0.27794124983457	2.05894488718348	6.05644666620951
C	1.16114735343842	1.36749451135710	5.12959146294632
N	-1.12240616714707	3.41186033781910	7.82849257138637
C	-0.91669533702411	4.14904244950277	8.95675366531305
O	-0.78047128777334	5.36652665669046	8.91926234023868
C	-0.87192093001667	3.46795889257097	10.33761613089540
N	-0.19029210969645	2.17205076172888	10.36639029528397
C	-0.63112358097088	0.99571193848256	10.90650042738300
C	0.26492319780228	0.04559414000640	10.47501987948324
N	1.17707851665891	0.71486245308241	9.70438678708693
N	0.91917576180650	2.00175622679912	9.63077062049320
C	0.44273445663022	-1.42692607054006	10.58426905081257
N	1.31823872477374	-1.82479094923813	9.46886630858199
Pd	2.52022378480366	-0.37995130370668	8.75198458926391

C	4.57891699518119	-0.12833097795816	7.46160266418505
C	5.85498440303162	-0.00092317893878	6.69142493676468
C	1.21313893692712	-3.12988312580544	9.11385952437180
O	0.51971197181289	-3.93193672347412	9.75324709098055
C	1.97979681546752	-3.55861643243767	7.84743474006114
C	1.46558205515006	-2.86687089568103	6.57690016454299
N	1.92764853505298	-5.01355698289102	7.73861926992189
C	0.79355975277829	-5.77855008959836	7.39824731463526
C	1.20005635732329	-7.20077587184565	7.60394770513640
C	2.51494968913194	-7.22481728836184	8.06932326351313
C	2.99141101523998	-5.81807033961635	8.18554539308654
C	0.48381360284793	-8.37013006160672	7.39750010919864
C	1.12964791335065	-9.58035584130104	7.67735296255894
C	2.44931161827648	-9.60425434821219	8.14439677907534
C	3.16506003454111	-8.41835690723753	8.34709242732079
O	-0.27085120809983	-5.35430352970141	6.99080983036153
O	4.06913709878581	-5.40409085145815	8.57500214398340
O	4.07574183798152	-1.28218262042097	7.71950035199109
O	3.94232197150660	0.89463765606284	7.89523961102418
O	-0.90160302386406	0.13406359113210	6.28921363477181
H	3.03807085852335	-3.32333201937457	7.98908883241123
H	2.05282413313749	-3.19632288790996	5.71430457350616
H	1.58261448135174	-1.78572177283546	6.68709724897224
H	-1.52680257812680	0.94404624840470	11.50377002267596
H	-1.06778765311251	3.97483122445574	6.98552139600014
H	-1.30639212377218	1.47340392404536	8.57089559691297
H	-3.32783056248422	2.52080199583908	6.56050367723264
H	-3.22432005904281	0.83504355062943	7.10885178573050
H	-3.66500483553516	0.24426627717316	9.46784367457209
H	-4.67614424907341	0.85839797337565	11.64568994927242
H	-5.34350347103809	3.21316248777623	12.08865611077915
H	-5.03656240754530	4.93371871838358	10.31987706474034
H	-4.03818434775955	4.31294847936417	8.14393801517619
H	1.84679899523787	2.13384089169242	4.77254477214468
H	1.69624804711671	0.58169207212063	5.66606826851014
H	0.57944336270170	0.93397619874595	4.31391313105920
H	4.18830936616749	-8.42525709042084	8.70952279774250
H	2.92227689444708	-10.55958234629956	8.35324038048325
H	0.60039942897248	-10.51780758820445	7.53194076581046
H	-0.53925676165454	-8.33968553120268	7.03579666065281
H	0.41265184941693	-3.08983029977997	6.40455263463222
H	0.88310868364693	-1.69253651323400	11.55706136007787
H	-0.51143322439189	-1.95921740592122	10.51281059181158
H	-0.35802922334816	4.16947393091779	10.99584959805233
H	-1.89055091610612	3.30515088878017	10.70148843348090
H	6.08989280359401	1.05054237709766	6.52061800707691
H	6.66436273067796	-0.47633235892982	7.25473290419912
H	5.76224776987328	-0.52935509589343	5.73774643930079

3.3
Lowest frequency = 10.08 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	0.54859431333469	-7.91704342513390	8.20214819054657
C	0.73787502413436	-6.54645412676492	8.29473983582342
C	-0.16337846789559	-5.64532724626554	7.72035020837018
C	-1.28658631444919	-6.08132536122213	7.03394683515734
C	-1.48642733457627	-7.46370936267647	6.93735566955146
C	-0.58369976020237	-8.36621679904862	7.51139478219612
C	0.31913173835687	-4.26344327908675	7.99130544389410
N	1.51488831907086	-4.41414943974120	8.70686824597660
C	1.82547397616972	-5.76806162556655	8.95330750117656
C	2.26174805510661	-3.30222576079903	9.27434627795464
C	2.91357329221144	-2.47132149463888	8.16716254519106
O	2.79697595128907	-6.15839154381027	9.57047226849440
O	-0.17293645986575	-3.19402117888485	7.67100344068065
C	1.33741384227879	-2.51518977161419	10.23462477726796
O	0.51815830518600	-3.10758786375270	10.94801580652269
N	1.56044497006052	-1.18803610920351	10.24956030873961
Pd	2.62700767545552	-0.22627316568962	8.86958676953706
O	5.37381492827855	-0.45103297460699	8.02280304442733
C	0.75779008351971	-0.35572511019155	11.15470945516497
C	0.59846618541107	0.96335843985463	10.47962393100983
C	-0.32123888150060	1.98546795272623	10.48633959081456
N	0.11375795372187	2.86104214034214	9.53083862835211

N	1.24040279822056	2.43775734169332	8.93492686757480
N	1.52193542734513	1.29426693648590	9.51508557651635
C	-0.59415419326888	3.99357272238391	8.94600297488619
C	-1.73906927272631	3.70888803187253	7.95485779293842
O	-2.47278953679032	4.66338086306902	7.71576270046878
N	-1.93805948656387	2.49562036705271	7.36866690245641
C	-1.19464019638047	1.23710146763297	7.33211544431390
C	-0.10918977012632	1.16853608040953	6.24496500068535
O	0.35364637818624	0.12616001340086	5.83437382950124
C	-2.17718333094690	0.04835474907910	7.25928392208196
C	-2.78687784709021	-0.21504037338742	8.61690476293961
C	-3.84730631673116	0.55474827873264	9.11214040721833
C	-4.33063269195388	0.35022564969633	10.40530371252831
C	-3.76539926018455	-0.63458727977034	11.21795233723833
C	-2.71949053606826	-1.41797866677578	10.72726697828997
C	-2.23186683991420	-1.20491293569165	9.43767733872184
O	0.31664695130269	2.39350112632997	5.88513555633262
C	1.51690182462197	2.39228738386499	5.05762080015548
O	3.61928624136516	0.84460714427844	7.46374410587223
H	3.03629596039449	-3.76976705649821	9.89317182502679
H	3.59725573268343	-3.07078334500936	7.55716144499760
H	3.69331004295391	-1.73978633154677	8.57900685230906
H	-1.24008258461609	2.13160650098407	11.03185987056139
H	-2.71004499243644	2.54706818564046	6.70893290567807
H	-0.64717196574366	1.11228272815886	8.26541485816307
H	-2.94649561447706	0.26392142658813	6.50614488823461
H	-1.61098762490825	-0.82258070319183	6.92187468708145
H	-1.41547860957336	-1.81480562418681	9.06209705564483
H	-2.27422649953922	-2.19797565451308	11.33881171456344
H	-4.14800775156876	-0.79890734723794	12.22152501506853
H	-5.15535473380400	0.95417755647741	10.77419097551564
H	-4.30143197641907	1.31873728912817	8.48610282836080
H	1.70523122801321	3.44277791843782	4.84014412829344
H	2.33559438381737	1.94581207704570	5.62650865097264
H	1.33292539575956	1.82594611896613	4.14257956065506
H	1.25321506494212	-8.60961708944446	8.65138775651755
H	-0.76715708666326	-9.43261373637602	7.41887264435998
H	-2.35560202835307	-7.84451408347854	6.40914853634378
H	-1.98085507324677	-5.37323001529483	6.59265545708886
H	2.16569773897743	-2.04262819282794	7.48828216038511
H	1.26554911330923	-0.23211015296022	12.12246065186011
H	-0.21086105659038	-0.82550624129581	11.34268386448966
H	0.15256708181134	4.58768436664489	8.41607302390275
H	-1.02479272453799	4.59631674693969	9.74654210574221
C	4.87085405515107	0.46449972932486	7.35994040746516
C	5.65950789159556	1.25021167741355	6.32682918392632
H	5.55813896239364	2.32372461798250	6.51228535497773
H	6.70992163411221	0.95947701419873	6.36255548879318
H	5.25746929917044	1.04722282534837	5.32830153545179

TS3.(3-4)
Lowest frequency = -1123.78 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	1.17345361421238	-8.30442604901461	8.84878897917128
C	1.10364236203681	-6.92114655593359	8.78135484296590
C	0.01197569259980	-6.27362592091977	8.19680350470117
C	-1.04976837183923	-6.98505797391225	7.65892167732068
C	-0.98879349611367	-8.38240560625040	7.72452681529299
C	0.10482707228537	-9.03119234751395	8.30934747131941
C	0.24010331633952	-4.80331630109689	8.27866504829324
N	1.48479611163710	-4.64856006732454	8.90507117902970
C	2.06246761062112	-5.88371643914280	9.25956451374891
C	2.04519626176645	-3.35784228011761	9.28703799390043
C	2.43937135685079	-2.53457584988876	8.05721909939713
O	3.12937875980978	-6.01907135385982	9.82766937940342
O	-0.46722288114434	-3.89213631953377	7.88263584189956
C	1.06451449394346	-2.63410533647379	10.22930465192252
O	0.34227436713290	-3.23066518918323	11.03574802660296
N	1.14110103838435	-1.30080272788958	10.08788836686396
Pd	2.27762617770343	-0.46035632748078	8.70678575033166
O	4.78771353554404	-1.25560409517881	7.50680619092418
C	0.35683634091010	-0.43886529339218	10.97454925637190
C	0.42098800520173	0.93518577983686	10.39953768894249
C	-0.32392084357060	2.08566238518828	10.51447208528534

N	0.25477055795609	2.97115444240015	9.65162511776365
N	1.30500960840250	2.43062361384638	9.00845207950356
N	1.39568480045474	1.20244052106488	9.46737568705820
C	-0.25069775516542	4.26522598122795	9.21172399649262
C	-1.56866782779988	4.25721228969339	8.41850653429479
O	-2.24930501777654	5.27654703466321	8.46817225014816
N	-1.96546648959838	3.17010145059758	7.69330269865224
C	-1.28239082134723	1.95049415497981	7.25940594083008
C	-0.26032449765681	2.15515889925740	6.12918159525807
O	0.11063581333044	1.26877817797639	5.39165486924720
C	-2.32207704919611	0.86526957883214	6.90637696148655
C	-2.80800340058986	0.14608585785768	8.14312457627698
C	-3.77471193925548	0.70708553595401	8.98730735702398
C	-4.15313700379762	0.05674231958522	10.16237107087317
C	-3.57475307845203	-1.16768253868137	10.50305450670858
C	-2.61986763800747	-1.74133112345552	9.66210788614259
C	-2.23755158484101	-1.08404675183840	8.49256801855283
O	0.23367290514342	3.41146911682364	6.11934653698613
C	1.36289167048240	3.60106621098279	5.22233247008414
O	3.45711339441262	0.53866185471249	7.33579554754579
H	2.93682155080022	-3.60354099299982	9.87546054706269
H	3.17427538179137	-3.10539275770381	7.47522710562346
H	3.58302659316798	-1.67048482412921	8.04047862424260
H	-1.20666372032523	2.32701675213921	11.08456494721202
H	-2.82645132661795	3.37156803282397	7.19186890125392
H	-0.69350457879912	1.54883315448685	8.08517336769601
H	-3.15210074364806	1.32965394849855	6.35748207636774
H	-1.83402350557098	0.16065351380188	6.22964157727791
H	-1.48760335025507	-1.53989446150144	7.85284481893063
H	-2.15485223954648	-2.68824486609824	9.91730398194118
H	-3.87072221754815	-1.67580060039312	11.41656370019673
H	-4.90734348716748	0.50171206194417	10.80609750635690
H	-4.23700585685805	1.65607136542611	8.72627289660033
H	1.62825995778053	4.65273139743434	5.32146654968629
H	2.18173557958012	2.95056003108981	5.53712942227787
H	1.06750709685576	3.36284109632017	4.19885569020754
H	2.02517998405588	-8.79876032003990	9.30519132982197
H	0.12207758158211	-10.11656018423593	8.34500125934987
H	-1.80236502153669	-8.97483880812505	7.31612750132385
H	-1.89352270050182	-6.47215232103309	7.20803277509233
H	1.58418162501920	-2.37790023175321	7.39253141861185
H	0.76810239030264	-0.45042277303458	11.99490169136708
H	-0.67904774227988	-0.78752176415080	11.03482707147582
H	0.52742484511006	4.70132407569027	8.58259933857733
H	-0.41890053735284	4.90672280316117	10.07772371731837
C	4.53443495859560	-0.09200219620830	7.06549097971216
C	5.53528742255119	0.57721103216791	6.15648741677959
H	5.31396784619043	1.63982300338230	6.05290572186489
H	6.54469694016828	0.42998195126240	6.54723499120719
H	5.48573310344659	0.09984312437945	5.17186500994542

3.4
Lowest frequency = 8.60 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	1.27634077298726	-8.90246574009305	10.00173868859128
C	1.13670552184445	-7.54730051649795	9.74348786455237
C	0.01023062738909	-7.04152018378571	9.09014278910364
C	-1.01767642982094	-7.87220140831864	8.67101547798966
C	-0.88650593453177	-9.24236531590093	8.92929497369506
C	0.24197495099850	-9.74914625979893	9.58372640941089
C	0.16511402391143	-5.56310824210162	8.96694535843655
N	1.40315364674928	-5.26293661389696	9.55157688451589
C	2.04415322181457	-6.40601352599039	10.06081883721734
C	1.89926321469168	-3.90414452833669	9.74303126898910
C	2.24620690061464	-3.19340435265633	8.43008359390992
O	3.12191669682457	-6.41373960895357	10.62715175518698
O	-0.59011587215775	-4.75345507023580	8.45539734028451
C	0.89319298151638	-3.10396311787050	10.59841991236962
O	0.17873073632301	-3.60308594678197	11.47161083416512
N	0.96133270647599	-1.79072323701911	10.29847450611471
Pd	1.87963400607164	-1.20139722010870	8.66940540233111
O	4.76379609208523	-0.81304499306572	8.13747038064387
C	0.12452203365559	-0.84861143539172	11.03641281201523
C	0.25826366400881	0.49566135977926	10.39548366441820

C	-0.30630021707181	1.72512441407481	10.64972720612422
N	0.20609071071927	2.55138872236876	9.69670357674865
N	1.04391319547123	1.89660354274378	8.86852253571394
N	1.07104240941111	0.65592862958293	9.30143320454688
C	-0.11037828618446	3.95645866301962	9.45090631254714
C	-1.61458244015419	4.13388575065501	9.18664595378827
O	-2.34095379719390	4.62859855842226	10.04250638514752
N	-2.09444695162241	3.67865462864510	7.99515142617806
C	-1.35415972561674	3.17799513118880	6.83158939967957
C	-1.19733177468812	4.34763596418748	5.85258664975868
O	-1.97779028732725	4.63802170198675	4.97238212325515
C	-2.09741387481620	2.00188824043176	6.17377988801017
C	-2.08770108720461	0.74018927684304	7.00575428015873
C	-2.97180523323937	0.56195260997618	8.07775927453411
C	-2.96161520329129	-0.62002440142939	8.82014841799786
C	-2.07572032504360	-1.64760155014367	8.49649072912030
C	-1.18927792764542	-1.47864300308596	7.43288873226355
C	-1.19311853757724	-0.29244402471662	6.69991039986975
O	-0.08001047411554	5.06001635272447	6.14541147668663
C	0.11096863107965	6.25366300338331	5.33729136883221
O	2.89821122403104	-0.65669128196460	6.89353129143162
H	2.79971937349758	-4.02236943844936	10.35625054852460
H	3.27228135395700	-3.41028413117041	8.11345394135467
H	4.02556451325607	-1.06070841752263	8.79559649378839
H	-1.01377160280667	2.07273073233421	11.38586926689328
H	-3.08985746853039	3.83673087844460	7.86450606773118
H	-0.36612340628654	2.85297111307578	7.16143823082639
H	-3.12118425046832	2.32485159496787	5.95096874567321
H	-1.61801710744347	1.80994454157809	5.20862171175934
H	-0.49648138340722	-0.16872152255370	5.87357491681734
H	-0.50928573711014	-2.28299333397271	7.17532349475591
H	-2.06420239787407	-2.57651442094552	9.05748938485316
H	-3.66006220924860	-0.74283696587326	9.64377306310275
H	-3.68785753863940	1.34185430031358	8.32455269326644
H	1.04253066837387	6.69081936878017	5.69381467936599
H	0.18104637810040	5.97911025686267	4.28293462653061
H	-0.72817688387135	6.93703068923539	5.48387255762289
H	2.15463253592711	-9.28570636297419	10.51167714996584
H	0.31350962930849	-10.81672205946410	9.77075536932112
H	-1.67252339289584	-9.92484354636433	8.61901833025509
H	-1.88961007807821	-7.46884308690595	8.16562750396200
H	1.55358433368969	-3.48802009748945	7.63538966584080
H	0.42786911160076	-0.80445749486506	12.09187293760633
H	-0.92497778732190	-1.17069418911075	11.02066492720130
H	0.50831378743165	4.27419986470605	8.60996348300667
H	0.12818881105123	4.54549046750868	10.33730370363698
C	4.13332651629696	-0.57931467868940	6.99517154525147
C	5.02089924607997	-0.22312597023747	5.84382517280856
H	4.41600511326986	0.02254757511196	4.97218960545035
H	5.65992798168403	0.62135778007939	6.11746492236349
H	5.67486930108569	-1.07165541827882	5.61806187412979

3.5
Lowest frequency = 9.61 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	3.63889523626718	9.38329057207948	8.45833271842078
C	4.27692809978867	8.60170921055957	7.48779042937938
C	3.51624447254332	8.09700438790696	6.42417226011267
C	2.14853808730948	8.35459082932593	6.33926194425355
C	1.51892807305579	9.12020914918449	7.32339512888591
C	2.26933182401122	9.63937758124145	8.37913857441199
C	5.72323363499997	8.20736514345048	7.63204388376046
C	5.81676983852980	6.86617427051303	8.42345700741222
C	7.23771862975353	6.30775448089742	8.38229593623180
O	8.02855362296722	6.35806543619272	9.30280995049167
N	5.41050529078390	7.02293967078485	9.80786459870141
C	4.21731543734974	6.79029616698097	10.42493167972773
O	4.00570813542546	7.13951238368774	11.58076891878835
C	3.07657449246257	6.08077020077947	9.66759407526177
N	3.51183179516399	4.96906514738412	8.82075520269896
C	3.24884635389078	4.75815873936578	7.49778423480046
C	4.09889531587080	3.74380457952831	7.11851052235779
N	4.82029842076337	3.40261506699358	8.23829263610714
N	4.47121618599020	4.13970886771238	9.26967130661351

Pd	6.50681120509382	2.21873335548657	7.75093058171018
C	8.01215814015089	1.33653429236622	6.68146773477993
C	7.43369252344969	0.90498921828111	5.33091636735160
N	8.42695922188208	0.87945152135914	4.26101892914943
C	8.78430220802055	-0.28993646254264	3.56559633053661
C	9.72462300267530	0.15229336679881	2.49537341859587
C	9.87103697277341	1.53831409394133	2.58856897226557
C	9.03371502512022	2.02260853434077	3.72435781296869
C	10.68804694138374	2.24004497546950	1.71538210852168
C	11.36245869312876	1.50647303280127	0.73136267706276
C	11.21638383875566	0.11774878614022	0.63866926337686
C	10.39020591373207	-0.58290489604051	1.52633843182083
O	8.38768223952969	-1.41090343849924	3.82704406810196
O	8.89796131471607	3.16134478557757	4.14125863810992
C	4.40118406741722	3.07624964354877	5.81261027339111
N	5.62772608883306	2.30158475309019	5.97958599959268
C	6.22312406088279	1.75829755159485	4.89822444978519
O	5.83011068167629	1.85947661325172	3.73341609084228
I	7.74186490589118	2.03798828484545	10.04210811402269
C	8.09232911748819	-0.05810412693680	10.17985153372188
C	9.05894888946248	-0.52250972282402	11.06759413073976
C	9.28277584118489	-1.89863226920432	11.14624598650720
C	8.55425835945454	-2.77919377240588	10.34632498228493
C	7.59182287224433	-2.28772913806392	9.46371182537957
C	7.34896718170175	-0.91620584745429	9.37502503269608
O	7.47683824954022	5.78059494714300	7.17177076164297
C	8.80193426485088	5.20561134875198	6.97068770952301
H	7.07259964934044	-0.12795529102065	5.39282858594764
H	8.47614498201869	0.49738433108371	7.20743194950027
H	2.52757646629367	5.35233149569888	6.96044691389216
H	6.12906612575455	7.38619590049887	10.42923634847259
H	5.17662109725314	6.15145940708569	7.91320974761279
H	6.29464007311638	8.97379325564414	8.16563231505601
H	6.18253409903975	8.05395974715309	6.65081310163983
H	4.00370712660190	7.49815442457209	5.65772925015931
H	1.57500011223492	7.96538553936299	5.50221048632146
H	0.45338619848646	9.32055020746995	7.26019472977321
H	1.78885941567783	10.24159885967000	9.14460840843324
H	4.21517166549423	9.78181345112474	9.28868072502059
H	8.75293132656866	4.71438872340690	6.00105868143358
H	9.54703073076594	6.00445813498596	6.98674195503506
H	9.00675355803936	4.48771740023678	7.76654505242198
H	10.26882961256383	-1.65963116959534	1.46154731200751
H	11.75211411641643	-0.42279376608039	-0.13629647009127
H	12.00889020664560	2.02131273094438	0.02643535606670
H	10.79327941849600	3.31758806295730	1.79408549044106
H	8.74522074146335	2.13656806663399	6.54694285233300
H	2.55357797932909	6.79492315314020	9.02554133600095
H	2.39484462358837	5.71691874899622	10.43715584058499
H	4.52491538552358	3.82511782688006	5.01878595271167
H	3.56713316414878	2.42714939804154	5.50746492247808
H	9.63115076611288	0.16475053336465	11.68222527979291
H	10.03505983940553	-2.27610469472792	11.83283217841631
H	8.73867636516672	-3.84732040999840	10.40863553110657
H	7.02479240234499	-2.96845540608993	8.83552659532333
H	6.60950498414214	-0.51583297682512	8.68724233920964

TS3.(5-6)
Lowest frequency = -89.14 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	6.44579144105325	5.86020104838287	6.94158721195014
C	5.24508397111082	6.12242350600375	6.27094203731760
C	4.30042537414765	6.95664459504528	6.88445846890721
C	4.54120931723710	7.50179943938149	8.14512224126636
C	5.73398498578058	7.21643208090018	8.81383026823798
C	6.68847224547527	6.40046260951695	8.20513941615654
C	4.91521779916933	5.43830972527440	4.97111112049993
C	4.17892746371617	4.09265906624091	5.26067824806623
C	3.65123353401358	3.49213479331489	3.96027056865727
O	4.20185478538683	2.60988500521353	3.33352331172171
N	5.04641379212180	3.12660060798943	5.90980486062124
C	5.22873702077477	2.83472937094877	7.22887709282582
O	6.13761721612056	2.10840801260799	7.61477034741032
C	4.28183175826384	3.43010451834702	8.29197885277954

N	2.86989005729763	3.43574768451346	7.90431965825981
C	1.99746891290908	4.48563178434718	7.88606825407944
C	0.90048451318225	4.03013340357114	7.18899651995617
N	1.17731291950016	2.73308265281305	6.83355343008717
N	2.36430951998230	2.36818269593886	7.26134540692477
Pd	-0.15290903128292	2.03224417929838	5.31312367930524
N	-0.97584511180655	3.79176713729321	5.72542194638311
C	-0.37378514629415	4.66619252728827	6.72903973282324
C	-0.27110931964389	-0.29070544043796	5.97439323712950
C	-1.56413009472411	-0.73654487183096	5.68264209435258
C	-2.36823635437780	-1.18824826689346	6.72848504041047
C	-1.88008072769991	-1.22542623186077	8.03524534072696
C	-0.57223829964221	-0.81335180585217	8.29902724737265
C	0.25103165808718	-0.35624117345346	7.27166450818348
I	1.18809075816740	-0.07066343252552	4.31543437693359
C	-1.47747465312196	2.09641906744728	3.74946219851502
C	-2.56677054013881	3.10815623537241	4.10449506498162
N	-3.20789728878961	3.69422025944475	2.93130999956583
C	-4.57918814886586	3.55300359100214	2.64820012019176
C	-4.82920623099481	4.40300829650032	1.44848240964683
C	-3.62557147866978	5.01255310454980	1.08622731703437
C	-2.56852216667579	4.56644280858530	2.03939259314895
C	-3.54738653063874	5.87109289190324	0.00027663542310
C	-4.72369365808835	6.10772071685249	-0.72184394221833
C	-5.92921599601776	5.49630077090590	-0.35929654984737
C	-5.99834344765337	4.62886866287699	0.73798222784476
O	-5.35704751315157	2.85965346056141	3.27737155617940
O	-1.38397264192148	4.85827249363182	2.05826395656826
C	-2.04448769011290	4.22727734582114	5.02685631314907
O	-2.57417162941771	5.33470148378152	5.14211965076562
O	2.51764965210876	4.11764240416737	3.60671075310631
C	1.90292994006367	3.68017708801433	2.35922588328486
H	-3.37961139459569	2.61100624380893	4.64609924461764
H	-1.89381713787748	1.11424920336689	3.51452892499414
H	2.24529644678541	5.43705476378298	8.32813240612589
H	5.64960925855810	2.60036883086223	5.28199966136696
H	3.32058866450123	4.32152365228411	5.88637533959864
H	5.81915321391959	5.22608621680546	4.39118489071503
H	4.25280500732648	6.06185629178361	4.36261262334568
H	3.37008420457323	7.17907717671422	6.36605394403853
H	3.80327592211871	8.15516535896556	8.60295405912299
H	5.92256222820731	7.63789538789965	9.79681353252991
H	7.62163112500135	6.17983409809122	8.71496543102250
H	7.18849334534878	5.21681518752661	6.47814276449765
H	0.96096354893751	4.22192297017201	2.30291256567417
H	2.56487645207348	3.92500474917880	1.52536125578876
H	1.73642179844454	2.60263126950738	2.40065013547734
H	-6.92881337804480	4.15119625934741	1.02827691156563
H	-6.82464868538690	5.70089443991405	-0.93899339815574
H	-4.70323473491160	6.77729996613097	-1.57685447208082
H	-2.60807432139731	6.34211218393419	-0.27205043828045
H	-0.87714700896649	2.45514263845783	2.91027666880319
H	4.56408545787416	4.46304309230375	8.51279175332742
H	4.41888100885318	2.81716050487403	9.18349377463913
H	-0.17603501690024	5.65885691310409	6.30335891742671
H	-1.05997247316573	4.81534268944837	7.57583450031376
H	-1.93992825783443	-0.71868411901124	4.66705424864177
H	-3.38206191617599	-1.51198865731113	6.51114781266798
H	-2.51253392805034	-1.58150191635429	8.84248984230607
H	-0.17954884677746	-0.85021468143763	9.31137783565352
H	1.26693148162147	-0.03643361694499	7.47204555756985

3.6
Lowest frequency = 16.51 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	5.45991531616899	7.04553682786887	7.07249928937508
C	6.59173875560154	7.02100138316055	7.89986477623819
C	7.66221781646931	6.19721627756689	7.54065214437026
C	7.61946936776092	5.44037054279237	6.36776511816358
C	6.49385371289466	5.48032349403334	5.53979640097917
C	5.40980426214526	6.27832716266445	5.90750932054942
C	6.69878070490846	7.89041341919504	9.13076301194664
C	5.90451847461155	7.36899455338514	10.36053644533847
C	6.33032286827705	8.18120725677570	11.58617018905274

O	5.76948744988871	9.18447795289556	11.97437415206013
N	4.47061486588808	7.51713229957156	10.15298612877663
C	3.46942420614736	6.64919511754721	10.46379455814622
O	2.28228235981677	6.93917111677828	10.36045830254247
C	3.87410329954015	5.22837416741614	10.89691684831918
N	4.32547229566502	4.45467605928254	9.74204725537299
C	3.61978042592606	4.12220935843027	8.62631682814799
C	4.53027924264474	3.48413990165532	7.81387847933784
N	5.72292621407666	3.47923482087773	8.48988828242352
N	5.60957714324611	4.06866942596755	9.65609357472700
Pd	7.31786067335674	2.59323383772802	7.28213500165648
C	8.33455950078068	1.93278796473150	5.63267896338049
C	7.33431509721889	1.15681369133446	4.77861452764828
N	7.72134454180951	1.12738059000562	3.37611051363781
C	8.01844195354869	-0.05735099243745	2.67211904480176
C	8.22389652495958	0.36630220839638	1.25732933926523
C	8.02702811490725	1.74788308825241	1.17800531548075
C	7.69287954281902	2.25301305944400	2.53906133814034
C	8.14789135505226	2.42890560702328	-0.02387837470477
C	8.47363446025641	1.67876725247838	-1.16039567104001
C	8.67078035235609	0.29540421704183	-1.08109440731754
C	8.54850399851267	-0.38403793259739	0.13724419107640
O	8.08611666121909	-1.16565153807316	3.16748577191570
O	7.45463733800042	3.39262107599773	2.90262235664987
C	4.42486322598438	2.85719829505749	6.45887421615494
N	5.74666287780119	2.39686523724341	6.05568068969061
C	5.89721284514583	1.70186324233223	4.90935698981438
O	5.00811328160636	1.49789353600692	4.08216270526467
C	7.19205508138044	0.68333965139101	7.91623241843411
C	8.29467287927397	-0.16473738318018	7.94543937249791
C	8.12120452788541	-1.48230131581876	8.37982998571404
C	6.86690267796339	-1.94173398913500	8.77566442333446
C	5.77639336560749	-1.07582528563256	8.74369522984856
C	5.93144112890228	0.24470788618731	8.30945698739462
I	9.45968177137448	3.07307163065258	8.74190011624231
O	7.44212967955853	7.65584989256309	12.14120395166176
C	7.98340019355296	8.40827966717602	13.26239818288272
H	7.30732239091494	0.10818089082991	5.09549375450772
H	9.21275206778976	1.35102219997967	5.90558962101436
H	2.57770398741851	4.37608046087719	8.51230970345593
H	4.14485129398804	8.46182264430687	9.96590341925434
H	6.15320934257392	6.31754118403882	10.51015448608348
H	6.35099857480707	8.90908486952383	8.91801513309625
H	7.74940115476665	7.96191888543981	9.42802164009301
H	8.54315478042096	6.14344197015893	8.17380973554688
H	8.49472182899750	4.86476573784433	6.08045926504298
H	6.47618850603155	4.89996362383391	4.62312356564959
H	4.52946522501793	6.32385630459730	5.27219109957042
H	4.61875359483230	7.68435007805126	7.32893284549630
H	8.86105616824569	7.84740900242729	13.57922066547560
H	8.25252898452766	9.41498440744553	12.93585435566641
H	7.24049600222930	8.46728241163261	14.06036292909244
H	8.69771437829566	-1.45677568267358	0.20818754301900
H	8.92127656336895	-0.25828751083948	-1.98121161469714
H	8.57426888210721	2.17599247338587	-2.12071861568763
H	7.99141962162924	3.50174882944120	-0.07543827994106
H	8.62333835919661	2.87126772767690	5.15417284982799
H	2.98508498008551	4.76060407221416	11.32031903625223
H	4.68921032312079	5.20312559108905	11.62177334458218
H	4.04370953011352	3.58868687795179	5.73377965811079
H	3.70857883771530	2.02293120691871	6.46922450968171
H	9.28034136949266	0.18530583925236	7.66715408025488
H	8.98405649734507	-2.14193872628229	8.40996586467905
H	6.74014293716285	-2.96798484313719	9.10717043688826
H	4.79051113958349	-1.41875515194232	9.04598099226628
H	5.07088424080993	0.90125129392386	8.28776569032437

TS3.(6-7)
Lowest frequency = -320.11 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	5.34118119564733	7.24281555959097	6.93865858692969
C	6.50618635291150	7.08857112703841	7.70222276256908
C	7.42645246811499	6.10124701808121	7.33254106334886
C	7.20248458026130	5.30375394948437	6.21217732297200

C	6.04477059612274	5.46742891796583	5.45211548625870
C	5.10931186411736	6.43322090375111	5.82590324406786
C	6.79508222374624	7.97692950245863	8.88829026466146
C	6.03788594405134	7.56366099718046	10.18231132787457
C	6.57076061607651	8.40629524882097	11.34229818853967
O	6.10071043324678	9.46881170033252	11.69195914877383
N	4.60728126310247	7.78883302701812	10.03750801480813
C	3.57219668173855	6.95386622810785	10.31021291085359
O	2.39734683691032	7.27441352657162	10.15553780258537
C	3.91420004163786	5.53772500880931	10.80480427047050
N	4.27211659526165	4.66830734422092	9.68462175042736
C	3.51248542869716	4.32666603522147	8.60653329260129
C	4.32023739951195	3.50362454027953	7.85651140765964
N	5.51103327558609	3.41484674485739	8.53136046613175
N	5.49216948724432	4.11822579167734	9.64221343365586
Pd	6.86312353920435	2.09310651221768	7.71819504620430
C	7.96654350298424	1.22648104351013	6.02974046900539
C	6.96611028157405	0.84591040261628	4.94978499236694
N	7.52398755159504	1.03550956600866	3.62131245723758
C	7.59599363175875	-0.00766890731455	2.67135334577274
C	8.03274096379797	0.64256320163616	1.40437427620790
C	8.17285404521338	2.01344444772038	1.63814931018824
C	7.83451529342838	2.28485327625714	3.06236306502379
C	8.56565489962343	2.88377450211339	0.63246002827920
C	8.81461277530017	2.33681327359470	-0.63199111091023
C	8.67419640235287	0.96394041258895	-0.86635286940981
C	8.27975934083082	0.09199406872527	0.15562879159922
O	7.34666396785630	-1.17489775064880	2.90040131833813
O	7.83287362460721	3.34287142220986	3.66686429767500
C	4.14604011726394	2.75046991346475	6.58338868050055
N	5.36174481690499	1.96697261502449	6.34674236189328
C	5.63177997831614	1.61141959515088	5.07589042420535
O	4.89422133780935	1.80927909286024	4.10477737671421
C	7.44003152801125	0.07337696261881	7.62754146573515
C	8.59886415122665	-0.42684612588760	8.23443318058671
C	8.60339041690035	-1.71833827225302	8.75253029950271
C	7.47127862930140	-2.53028329414218	8.64827427968031
C	6.33244230554644	-2.04112825772980	8.01427223435826
C	6.31227165710793	-0.74510717046555	7.49085550668316
I	8.81634131914274	2.83887384105989	9.34309828496501
O	7.66529700800545	7.83252920348736	11.88354350306929
C	8.30607971703442	8.60424899889653	12.93650933403064
H	6.74135250337094	-0.22511838417988	5.00335504158430
H	8.86756559389568	0.62310896931796	6.01304377935144
H	2.50981899911352	4.70031738001769	8.47272319289728
H	4.32377731496106	8.73588985382073	9.80222774421849
H	6.23254514257923	6.50738986626847	10.37236206119234
H	6.53246391247311	9.01941947611425	8.66911546942030
H	7.86550941495361	7.94966656663796	9.11399177955056
H	8.32525712021413	5.95155299695296	7.92489436268620
H	7.93708482457740	4.56434234058212	5.91543620522606
H	5.88737261932658	4.84701061919817	4.57571220507747
H	4.20467420616226	6.57178706877554	5.23959459904347
H	4.61942140534968	8.01187112871014	7.20197124150792
H	9.15624075514067	8.00037102237997	13.24931814874479
H	8.62909210335115	9.57008990451897	12.54226546836835
H	7.60534183310217	8.75935842149636	13.75940135216053
H	8.16622359210940	-0.97343873248804	-0.01733130692507
H	8.87340388071761	0.57121244097361	-1.85909045917011
H	9.12030307124236	2.98656825999878	-1.44676590345602
H	8.66986720749290	3.94705175085025	0.82389009328594
H	8.25652905970357	2.28268227900128	5.95756216162532
H	3.01635628741087	5.14735153921741	11.28527342548661
H	4.75380609825394	5.49942533145886	11.49974437098289
H	3.97612157334813	3.43319054644799	5.74163142868610
H	3.26595945760097	2.09514891424617	6.64837180133389
H	9.48344753255438	0.19431963110211	8.31180481204745
H	9.50331526284809	-2.09114966562074	9.23362051792811
H	7.48354253681837	-3.53939952187726	9.04935556094549
H	5.44554340283293	-2.66137980164414	7.91957396651811
H	5.41905220181085	-0.37198794706576	7.00484278498955

3.7
Lowest frequency = 12.52 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	6.30352246074409	7.06944364426012	7.08885085680901
C	7.11928630299367	6.80363415007195	8.19638672105276
C	7.99040422508717	5.71086621298719	8.13952707419741
C	8.04975631237411	4.90633852729426	7.00306928807978
C	7.23305784705445	5.17314895477953	5.90365675694752
C	6.35684624408241	6.25789998282591	5.95497632357252
C	7.04894435510427	7.63294291686223	9.45877442408928
C	5.83254152678053	7.24227324375611	10.33013119796290
C	5.91341761979972	7.68977288687866	11.79937518271725
O	4.96528639877774	8.08153853145684	12.44720322348983
N	4.60908501350440	7.74238906636130	9.72079167372750
C	3.36399796175664	7.19792892995441	9.73460675923820
O	2.37893234518395	7.76957557827809	9.28028253849299
C	3.24096447428469	5.76593217225428	10.28218014842801
N	3.75436117826952	4.80685554801968	9.30255725068101
C	3.25531826773713	4.50527059845952	8.07187829059140
C	4.15782201641480	3.61481160167752	7.53613900380305
N	5.13953208380014	3.45088690921276	8.47279300831470
N	4.90689450148424	4.17211521602227	9.55121034738602
Pd	6.56894463046520	2.09576953702419	7.99314635084685
N	5.50625214344213	2.11568880405259	6.21385423298647
C	4.23720532643643	2.86448084289971	6.26018494565864
C	8.22918585418368	0.77247429227593	7.01807502709992
C	9.46117906599415	0.82768616079234	7.72930300833959
C	9.67437606455305	0.05824628796539	8.85013400387889
C	8.65769743194733	-0.78526347954163	9.34404286757157
C	7.43200634397702	-0.82573724655862	8.71832098057227
C	7.19874568776638	-0.05614924523497	7.55107400691178
C	8.23921885049764	1.26807716925121	5.58261309302093
C	7.03550303594894	0.82227379338732	4.74970441027036
N	7.33918236168753	0.88317570582973	3.32667565874140
C	7.19992452475850	-0.23383869009355	2.48023584083046
C	7.38429209141766	0.28931431852041	1.09780579622139
C	7.58079621982737	1.67059551181962	1.17476662179487
C	7.53285237673937	2.07300648998364	2.60869226587672
C	7.77558945011944	2.43857848449703	0.03672984773791
C	7.76464776332225	1.77719238092499	-1.19728632211823
C	7.56761173419683	0.39355370314167	-1.27423727844374
C	7.37467312461952	-0.37463307468957	-0.11966318136933
O	6.98348441615908	-1.37050862157749	2.85722399201048
O	7.65539609520277	3.18137266066239	3.10053327208940
I	7.70723915213311	2.48895732184826	10.34507681510652
C	5.72276397896502	1.59316221151135	4.99029887952435
O	4.91255233721257	1.70344158910400	4.05523381972324
O	7.15638412056997	7.52268819131520	12.29539807814346
C	7.29355844668611	7.81584560636198	13.71237523165908
H	6.84017988500421	-0.24299252185432	4.92625271870435
H	9.13807358472679	0.85373848904291	5.10979046296751
H	2.34410304810547	4.94411962506485	7.69789730449291
H	4.62491960920291	8.70344116883964	9.39281064893665
H	5.79854011856827	6.14652284856646	10.35671842946257
H	6.98515087729297	8.70471336343548	9.22772354221976
H	7.95231612253062	7.48029949484085	10.05172535678065
H	8.61306019289055	5.47303952142131	8.99735315165550
H	8.74096236793089	4.06912667771617	6.98500132894437
H	7.27812645548174	4.54695151564525	5.01829476466919
H	5.71946945669931	6.47897495603948	5.10307902231208
H	5.62521333014683	7.91869746554386	7.10695348371372
H	8.34066530863958	7.62183201584184	13.93918264220568
H	7.03274383268057	8.85911504691591	13.90158660272168
H	6.63645471062724	7.16183766675542	14.28925716026781
H	7.21853126274233	-1.44759293619870	-0.16927516549629
H	7.56246509694639	-0.08943370501989	-2.24700063639988
H	7.90903808561450	2.34511142521711	-2.11174613643254
H	7.92523892723811	3.51136189679619	0.10647440664024
H	8.33511225759621	2.35598546756594	5.53897928582320
H	2.18121374660061	5.57305037450353	10.44727775842722
H	3.79896773525630	5.60358725717052	11.20467766182401
H	4.18656176296331	3.54906318555265	5.40479024553747
H	3.37990258486034	2.18462072566999	6.15761650049250
H	10.25491193740327	1.46068777793646	7.34174124172376
H	10.63043691833954	0.10418049684884	9.36195809502327
H	8.83899603535204	-1.38549435755660	10.22987156552432
H	6.63767924145079	-1.46286309330321	9.09345946408875
H	6.31406674304554	-0.27463922588374	6.96260775890313

3.5a
Lowest frequency = 9.24 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	7.94638351981323	7.04941299916876	6.27829638241011
C	6.77560706077092	6.40505223056164	6.66632728141103
C	6.59005020511385	5.90901691818837	7.95305914283647
C	7.62582526877865	6.04730454163138	8.87751096512997
C	8.80979331773033	6.68995713320183	8.51393326381327
C	8.96573445972870	7.19393737634057	7.22258983799634
I	5.21992031428052	6.13392592373226	5.23568318363925
Pd	4.07465098845821	3.98032292136372	6.15792567549823
N	3.29182189308731	2.32537686865866	6.99741670585287
C	4.06602036244899	1.78031404006644	7.99203578757955
O	3.65695783246023	1.03877331358238	8.87914452513021
C	5.80604554552967	2.96861910248434	6.56657781303412
C	5.51083710407641	2.30987226849127	7.91212526363843
N	6.47744796308691	1.29250157479211	8.31528636937189
C	7.38025110498231	1.47875577466712	9.37370746686802
C	8.15118937584426	0.20616033656453	9.47138433450792
C	7.67924612147552	-0.66789564457119	8.48839873640210
C	6.59414475046139	0.02084343977412	7.72840455608336
C	8.21049929818669	-1.93958245646478	8.33640959076936
C	9.24017373271941	-2.31799529216670	9.20697764284673
C	9.71287349900502	-1.44233473408332	10.19110088232679
C	9.17093937116055	-0.15945138367929	10.33724360054260
O	7.48238259699694	2.49507174625658	10.04030707526921
O	5.93476781037352	-0.38193500954669	6.78885120810997
N	2.02509301326854	4.41427745899425	5.89849302633587
C	1.23833072266162	3.37742651325115	6.33526818093030
C	-0.00025368239835	3.56248861987595	5.76466810898998
N	0.11283137903615	4.70582520621750	5.03142596543210
N	1.34918925451587	5.22763110646861	5.11413043108564
C	1.82914927225871	2.31646407199296	7.20654639967972
C	-0.87559596729098	5.30883974963099	4.13462125481626
C	-0.29242811871736	5.89729103527254	2.83842394082262
N	0.62909421988137	5.19537973561365	2.12200668101984
C	1.17984048028373	3.86300219035671	2.30290399353732
C	0.44872465289288	2.80377060034462	1.42160666114834
C	-0.98648620295219	2.68636640135235	1.86612758691506
C	-1.32107233417279	1.85173738797408	2.94204275928123
C	-2.62706047388303	1.82364285298498	3.43170080621533
C	-3.61274011875059	2.63130743373200	2.85901622314022
C	-3.28839416433191	3.45667629549649	1.78145362428075
C	-1.98341347779517	3.48082910960397	1.28769047445983
O	-0.70611553579951	6.98976645308185	2.46488125346843
C	2.66333395264285	3.93171127368029	1.94908054750448
O	3.33630260011142	2.93173876992861	2.54389285976710
C	4.76867021507689	2.89472564515823	2.29318377105855
O	3.15896378573156	4.76313591687130	1.21500478056958
O	3.66641667020281	0.64721267563998	4.70545148497736
C	2.50335250715813	0.36820855166152	4.11144816952631
C	2.69001149575467	-0.51930663348192	2.90360623915153
O	1.41764802291917	0.78392252583990	4.49511044191220
H	5.58483399487437	3.06253175017508	8.70655905195450
H	6.69632303992432	3.59980260254586	6.61336577584723
H	-0.90774245292089	2.98198771169918	5.78120519881101
H	1.01742263235609	5.71113982979881	1.33570234936035
H	1.09572561290427	3.53603614161622	3.33648489966392
H	0.51480289092714	3.11078320311508	0.37257808745948
H	0.96924832820150	1.84895458649276	1.53986195438373
H	-0.54985689568318	1.23904085077104	3.40365553015551
H	-2.87671208299748	1.16600871309940	4.26049875186186
H	-4.62822339132645	2.61078772752267	3.24417113780811
H	-4.04877903513624	4.08535660301042	1.32739103411480
H	-1.73319822148528	4.13389402136552	0.45591793930426
H	5.12982958324222	2.06081606120245	2.89167733890142
H	4.95292513829783	2.74127074283094	1.22755414257348
H	5.21955529465183	3.83447360818414	2.61680954709712
H	9.52940532889604	0.52636776974949	11.09846910444425
H	10.51209449822865	-1.76591886181040	10.85160388086421
H	9.68036027036085	-3.30714830415942	9.11986303942448
H	7.83624388356728	-2.61216425151308	7.57101524190537
H	3.33632792918719	-1.36519791262058	3.15219189006735
H	1.72129033142935	-0.87141158620919	2.54867015206225
H	3.18384857675763	0.05239230343853	2.11069191137753

H	5.91495242831258	2.22363599800797	5.77213879515718
H	-1.61071605932994	4.53490634126186	3.89580225132193
H	-1.37172796673448	6.13930057468005	4.63887421596679
H	1.40265701944130	1.34456062809395	6.94050395565174
H	1.60916078689573	2.50201928741301	8.26655549982109
H	3.52447522737958	1.24239228328909	5.50571358924223
H	8.07295917588617	7.42307699260601	5.26762083920810
H	9.88720147722326	7.69254062026649	6.93599812764610
H	9.61396497481665	6.79214959053716	9.23613625191795
H	7.50466609662520	5.63307867429230	9.87341386519804
H	5.66528592035287	5.40572376269054	8.21699869233293

TS3.(5-6)a
Lowest frequency = -86.55 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	6.74208190128091	5.70393006991637	7.41055116596247
C	5.66458637020827	5.96333182692083	6.55785375495994
C	4.61299755407516	6.80484417010880	6.93938173782632
C	4.61039308780580	7.31833520652327	8.23520906045245
C	5.64839987756961	7.02531394524216	9.12223283830958
C	6.71090245396859	6.22343173113791	8.70472005527737
Pd	4.73524187013231	3.95009110346664	5.85663025893404
I	5.98207021293413	5.71614975540043	4.32101128858138
C	6.37701489164496	2.75805073143022	6.13245479253865
C	6.18135340965250	2.25086349813936	7.55605741296741
C	4.71363874452825	1.87041661036984	7.82431410670213
O	4.33612755719128	1.23891727978706	8.80418643461370
N	7.09225295993621	1.18172935117659	7.94760939299624
C	8.13485988957386	1.37043238962736	8.86974133191060
C	8.78296977668264	0.03606647860593	9.01819405801341
C	8.11116233939525	-0.87164850379266	8.19454366201711
C	7.01386995593593	-0.14542491648230	7.48977956246702
C	8.49400422102200	-2.20242723418412	8.12238691345770
C	9.58069558582721	-2.60558032243280	8.90826324082398
C	10.25336851796529	-1.69633926791569	9.73266945942895
C	9.86107393737342	-0.35381410583540	9.79861948226796
O	8.41729349280603	2.43072418737554	9.40092542884689
O	6.21057571482123	-0.56007419215123	6.67580682336575
N	2.68049177157731	4.53578491530235	5.75029864073696
C	1.86774787844049	3.60129530060299	6.33850414900451
C	0.59125602452072	3.86009950872209	5.89253584616266
N	0.71384202086821	4.94340587249632	5.07527033353624
N	1.98997068921664	5.35752145637273	4.99044291813166
C	2.46062156702727	2.55439131307949	7.22436195547189
N	3.88802871598197	2.41731078981772	6.87026066101332
C	-0.31565689772249	5.57999563404205	4.25087181832314
C	0.15508487076270	6.01352810403029	2.85157566355791
N	0.91896112905757	5.17794738402973	2.09478373848267
C	1.36060324825945	3.81057934420613	2.31274273898938
C	0.41438901371358	2.77281811015771	1.63207093051854
C	-0.95158512981572	2.84026322625495	2.26340163550005
C	-1.21900401628828	2.11951966856092	3.43596482838668
C	-2.44381729576475	2.26476175298745	4.08782387622700
C	-3.41336732849264	3.13415452190406	3.58172269453770
C	-3.15799878617675	3.84523032668980	2.40830120093426
C	-1.93525921011804	3.69565744258440	1.75280449540134
O	-0.20452737114905	7.11192375133453	2.44092745723691
C	2.76914680127488	3.69143793455940	1.73756299214065
O	3.44013240861525	2.69161370252634	2.33633468842477
C	4.79690762934008	2.47009083709430	1.86262295889891
O	3.20575684260112	4.38379898953386	0.84060540922432
O	3.85990195145723	0.55996925416334	4.67400233651791
C	2.61656822953468	0.34391264650057	4.23253939815370
C	2.59162136280080	-0.63993837227040	3.08731845621983
O	1.62022776015870	0.88166918018122	4.69718754229323
H	6.40480944457031	3.06492382696957	8.25803781717237
H	7.32220294666471	3.28926553751704	6.00141862254037
H	-0.35281418893859	3.36432699467375	6.04620767959329
H	1.24732112201381	5.59351013912569	1.22581357052754
H	1.40360049664882	3.56999823464457	3.37222454881202
H	0.36634177433561	2.99270001103159	0.56048227787094
H	0.85261392310261	1.77941600654113	1.76572626170452
H	-0.45634469830333	1.45871662030039	3.84199148925439
H	-2.64385004933218	1.69417934099528	4.99123469595318

H	-4.36486601291398	3.24898342213273	4.09296773594223
H	-3.90751540751817	4.51978670780585	2.00488540581364
H	-1.73657229938443	4.26004744580368	0.84567256357265
H	5.18939000404746	1.68741059170530	2.50898973520836
H	4.77559463928845	2.15864258009991	0.81575597999054
H	5.37322507079462	3.39084865553646	1.96455544740105
H	10.37567870916138	0.35881759834631	10.43549330255842
H	11.09235055615759	-2.04031945007971	10.33053306130271
H	9.90869623005715	-3.64063117325834	8.88001687648301
H	7.96557501827481	-2.90049012348331	7.48075676070554
H	3.20436095734747	-1.51345975683568	3.32469923821250
H	1.56446789986834	-0.93953358802510	2.87888320599161
H	3.02026736900688	-0.16613050875537	2.19789906200652
H	6.29249581177710	1.95333716994283	5.39666728212638
H	-1.14445432248228	4.87177223866493	4.16446556366509
H	-0.66509122365824	6.49082170838401	4.73906700911913
H	1.93073031774838	1.60784143626863	7.08124881336159
H	2.37289728698663	2.83345789151302	8.28316812009550
H	3.85538881426749	1.21557769422896	5.43651747574925
H	7.57703977984231	5.09494015619345	7.08751317963250
H	7.52650841513525	5.98710353429344	9.38176388737505
H	5.63350968938947	7.42752149921331	10.13033203881816
H	3.78632678441761	7.95455425129397	8.54607237222649
H	3.80868893961521	7.02928091931323	6.24910729246622

3.6a
Lowest frequency = 17.69 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	6.65072269008758	5.86882855208499	7.40283260796779
C	5.35468034977709	5.39549482266872	7.22983915842859
C	4.32472694125252	5.74291685218883	8.09519458447011
C	4.61049526006954	6.58051207724790	9.17909543801752
C	5.90313702165500	7.05747600978725	9.38152609721293
C	6.91580039329545	6.70446692010533	8.49210181497587
Pd	4.86567130237915	4.11999844991450	5.74722435470643
I	5.99350436824006	5.58648477539493	3.90709084752248
C	6.51057192813667	2.99181082709597	6.19539767876730
C	6.25665973261244	2.46668727873847	7.60689038065890
C	4.77188996409614	2.13646394482659	7.85299777688183
O	4.36257250177062	1.49664223176896	8.81230332441431
N	7.10935432896790	1.34611166654875	7.96610220509344
C	8.13291099928539	1.43332912268856	8.93094458275102
C	8.70024586231207	0.05860226983544	9.02772009860068
C	8.00073867093978	-0.77112260487350	8.14606685498780
C	6.96422049610364	0.04624994613176	7.45341989664348
C	8.31053019219419	-2.11702508676840	8.02010930445265
C	9.35237525719649	-2.61635063594211	8.81111446926769
C	10.05252216292601	-1.78547070682765	9.69344988534275
C	9.73381576347165	-0.42750441126421	9.81439525855851
O	8.44811605882640	2.44758123642068	9.52376825948923
O	6.14957299178754	-0.28156404979458	6.61022869766164
N	2.77250515486146	4.66218773340147	5.49358239820253
C	1.95559725527834	3.80909320199926	6.19244840525526
C	0.67545213115648	4.04458023314626	5.74583256415473
N	0.80437582001398	5.03133004678528	4.81500781176408
N	2.08243561786134	5.41060801155783	4.66258506889874
C	2.54017377492657	2.86288588258616	7.19277154469644
N	3.97109728831058	2.70389055063660	6.88790442107860
C	-0.24393073690991	5.62243342271119	3.97777074623226
C	0.15088494930759	5.91621891791093	2.51993321164449
N	0.89244115573462	5.02279370050896	1.81000211248803
C	1.34333211613243	3.67632546323720	2.12305081822676
C	0.35811897461846	2.59094001091019	1.58838031620423
C	-0.97514316301410	2.72536125353658	2.27608191364430
C	-1.19389606301752	2.10991705464761	3.51661999284494
C	-2.38689983894980	2.32196641688697	4.20824496257966
C	-3.37282236327819	3.15546657616251	3.67434473989916
C	-3.16641575545021	3.76192391584333	2.43436576470437
C	-1.97626355807788	3.54422121326734	1.73951959466903
O	-0.25496826810284	6.96210005961473	2.02497677108065
C	2.71087708719562	3.50000453511773	1.46897534588987
O	3.47734737526430	2.65539850182870	2.18241823903000
C	4.80523975091297	2.40487134237848	1.63534161401835
O	3.03430824326771	4.02350561957464	0.42315965227561

O	3.92259113222302	0.68760506346435	4.69380174846122
C	2.65964874345746	0.42777965205333	4.32226901829212
C	2.60688560732251	-0.57489227392665	3.19692770864786
O	1.67994126563538	0.94044149329721	4.84296713414707
H	6.50927712076655	3.25223899874262	8.32918550350597
H	7.43641719947798	3.55756359566697	6.10746796525559
H	-0.27544114608446	3.59044447620322	5.97025942106038
H	1.15579202729856	5.34888460308909	0.88237775572096
H	1.44865685875205	3.53357181121431	3.19503776737268
H	0.25943464305927	2.71550542041187	0.50522240167810
H	0.79753888366975	1.60841992064666	1.78585033464782
H	-0.41966628325186	1.47767520597441	3.94536735437592
H	-2.54953291780422	1.83088029647908	5.16439356711179
H	-4.29935422972022	3.32275277329596	4.21601808585041
H	-3.92873736958604	4.40806573839866	2.00915100776706
H	-1.81597027195812	4.02734239602200	0.77951245516858
H	5.24273237445137	1.66605416739668	2.30467422753319
H	4.71720635948500	2.02552467616482	0.61518748410630
H	5.37783253926035	3.33342333899004	1.64993088948195
H	10.27007790669656	0.22459056929465	10.49650439814935
H	10.85536633865642	-2.20352794645125	10.29357517765668
H	9.62345598687513	-3.66571095686421	8.74123636781053
H	7.76140451945555	-2.75410759186709	7.33407195189087
H	3.15813573913138	-1.47643060630451	3.47922631436071
H	1.57022960813017	-0.82349269024055	2.97065635820984
H	3.09207396056793	-0.15618346480805	2.31015667250996
H	6.46558072362626	2.19788812581437	5.44298063850734
H	-1.09571929091444	4.93685149959334	3.99886187984601
H	-0.54122736589809	6.58385343793381	4.39866953835121
H	2.02955918636040	1.89681309630349	7.12910295101132
H	2.41460083460247	3.23725695267726	8.21875489039689
H	3.92857948296969	1.31497055517231	5.46729318641278
H	7.44091433854748	5.61782728423686	6.70750236307629
H	7.92625273863891	7.07855050275062	8.63043905966108
H	6.12001879620162	7.70319201444366	10.22698979789870
H	3.80925019410242	6.84739270628568	9.86273670285580
H	3.31314858037052	5.38555100621782	7.94869633485458

TS3.(6-7)a
Lowest frequency = -312.65 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	6.91326137532319	6.66898628052558	7.29425088987669
C	5.87270365827079	5.79810645730481	7.64343037219322
C	5.37057843347246	5.79973856796706	8.95121772278557
C	5.87054051793461	6.71356725675424	9.88305873300519
C	6.87947831329576	7.60464596534561	9.52764266599091
C	7.39941090285653	7.57538360470725	8.23122727101773
Pd	4.40302612672781	5.15772923287463	6.28510235841014
I	5.27346841088940	6.59893463526038	4.25507271374972
C	6.18934596834735	3.98397732797528	6.75903057226785
C	5.82985916823416	2.96692035634042	7.83159142623759
C	4.31356897001473	2.72330783795149	7.94548716327870
O	3.87579887594578	1.66739880127538	8.45607763391885
N	6.51788261330426	1.70681385467253	7.59627170152042
C	7.34956544228548	1.09752775533297	8.56446992652029
C	7.69669374595953	-0.23615095889169	7.99981739449233
C	7.05700628431115	-0.37272218620610	6.76420672513427
C	6.28562989624827	0.87006600419626	6.49351618370538
C	7.18754398051500	-1.52540656957983	6.00465124207846
C	7.98735616976684	-2.55121225042620	6.52182454811574
C	8.62998112588438	-2.41349882512244	7.75775836748349
C	8.49271151951242	-1.24638050363427	8.51878240274561
O	7.68028407028865	1.60962994128856	9.61502506321768
O	5.59565571588135	1.16030558919735	5.53055170969487
N	2.45582769467358	5.14748092333435	5.59821423131767
C	1.61954458241500	4.31028697384798	6.29332557717876
C	0.43890251829691	4.27979929788234	5.59214712477787
N	0.64037744843601	5.10876366561112	4.52839510616764
N	1.86632702493860	5.64433664917541	4.53009868214948
C	2.12003106860801	3.64420752899822	7.52843366597869
N	3.58224680686281	3.74927033876619	7.51887460503760
C	-0.28413477348826	5.38520061720716	3.42421438977344
C	0.33524675459772	5.45574555065572	2.01727563997810
N	1.30905220475665	4.58678758677944	1.63825834268902

C	1.89736214692647	3.43020144697294	2.29543397659936
C	1.19738897322392	2.09860547514195	1.88369162406901
C	-0.24465800866639	2.11091830083585	2.31853289987545
C	-0.59345667049227	1.70124352677731	3.61306370463121
C	-1.91370740083695	1.80380661705212	4.05325529145122
C	-2.89997396089328	2.32382522496619	3.21160016373354
C	-2.56120247861017	2.72481689580609	1.91813567483429
C	-1.24282301458983	2.61444965564177	1.47484275284719
O	-0.11484007065873	6.30374418755358	1.25336728003800
C	3.36673517453319	3.38991974402062	1.88155113559026
O	4.11046837668408	2.79987558796810	2.82718235785133
C	5.53535966234092	2.71549063309024	2.53670540345815
O	3.77692769487435	3.80293596154512	0.81498001247268
O	3.22164822979911	-0.39863572227269	6.95663498244060
C	2.44732764814584	-0.07913101926114	5.91666354084359
C	2.45004691037076	-1.15125789018856	4.85331802772748
O	1.82571534437501	0.97206237208898	5.81996049597413
H	6.18650778672050	3.29942180962578	8.81307178578327
H	7.23677232551528	4.26498289696623	6.77136076904702
H	-0.47925753537634	3.73291446138303	5.72665909405527
H	1.70153280801070	4.78259881423759	0.71908515696476
H	1.84594187050802	3.51541468741892	3.37692421253717
H	1.28014859882394	1.98448690240525	0.79786252665085
H	1.73923474152450	1.27757881288970	2.36339414126764
H	0.17537414644988	1.31788396277460	4.28151481628395
H	-2.17361856780054	1.47148622030213	5.05540576690889
H	-3.92658540092959	2.40602466652114	3.55710075867274
H	-3.32160044660347	3.12637765344146	1.25469660421225
H	-0.98308740331519	2.93589216853924	0.46985670473707
H	5.93727804322471	2.08623841396048	3.32769364270766
H	5.68509483294842	2.27499836259364	1.54900276090048
H	5.95889132173749	3.72181123188421	2.56956183137993
H	8.98436277192856	-1.13226622733677	9.47957944686132
H	9.24277514172742	-3.22831475861948	8.13172815307162
H	8.11142432681171	-3.47104790204632	5.95802985214682
H	6.68222426538228	-1.62494289929962	5.04934146649926
H	2.55916476356111	-2.14440409552303	5.29406734040895
H	1.53919304205002	-1.09179108770634	4.25577951713370
H	3.31265330152420	-0.97121526929200	4.20101428780803
H	5.93629280337554	3.61167215933165	5.75812977133975
H	-1.04823598071386	4.60304539576708	3.44914731919010
H	-0.75329395758278	6.35671351962431	3.58488309216404
H	1.82409756934983	2.59182967840035	7.54142132834206
H	1.71034022432444	4.14134526447152	8.41956480671730
H	3.33905890261105	0.40224828636694	7.56091436921687
H	7.32603390529001	6.64678289972749	6.29251405917702
H	8.19450908565777	8.25748660074603	7.94373802053538
H	7.26720124776531	8.31054930063696	10.25608476489252
H	5.46001220225095	6.71918454654460	10.88882345936292
H	4.58207109135512	5.11582221815745	9.23998289609689

3.7a
Lowest frequency = 12.92 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	7.21035171580139	5.34870576370872	5.98721356129795
C	6.43349958416844	4.59230595107598	6.90989498556050
C	5.82326667055206	5.29793052838698	7.98748480313703
C	6.05832048360556	6.68391508219838	8.16051898430914
C	6.87452866655633	7.36383317296713	7.28401560158314
C	7.43761015949568	6.69265654375732	6.17927877297648
C	6.65967628238028	3.08975124220192	6.92766065314637
C	6.07645790024988	2.38229103917651	8.15267235384893
C	4.55475018546896	2.15881955894554	8.16044567010425
O	4.07591920944710	1.30772431130126	8.91536396252937
Pd	4.13344673226701	4.82869670686097	6.50186800280327
I	4.15305607550933	7.04034501022737	5.08542071814074
N	6.73543414009080	1.10621293017496	8.39270952728274
C	7.49975490753066	0.86334010524866	9.54958873231339
C	7.87001714298844	-0.57773922545762	9.48558859869973
C	7.29697261428554	-1.12759096340325	8.33552284283807
C	6.54449220535479	-0.05485599332529	7.62387140573184
C	7.46811403391188	-2.46499361571997	8.01127614661648
C	8.23734497406774	-3.24692715053065	8.88154089678069
C	8.81116291155865	-2.69571619807374	10.03306439458325

C	8.63434124496916	-1.34415772935293	10.35272651728529
O	7.77621767337500	1.70009917964741	10.38933153865085
O	5.90205529644510	-0.11378476759817	6.59221292030678
N	2.17346068967775	4.59246733378011	6.04361712684208
C	1.58742077460764	3.46367441271020	6.54593475047776
C	0.31993490831422	3.42085589330229	6.01551420100349
N	0.22617956784454	4.53764421112924	5.24134286634510
N	1.35018321952370	5.26160325240278	5.25713185326683
C	2.36047620185047	2.60149404691162	7.46896279638515
N	3.80056119203343	2.91156350182802	7.30553490087077
C	-0.91955643617413	4.97604688273549	4.43522269147099
C	-0.57906977286657	5.81096284858990	3.18884354737943
N	0.38196378884690	5.39056601265520	2.32313766869847
C	1.24596625021334	4.22135654734280	2.34297250294345
C	0.70225440624966	3.07452304687536	1.43948265504701
C	-0.60975753800177	2.58152423609731	1.99268055993934
C	-0.62617704783516	1.64404807711636	3.03530948818213
C	-1.83174416704422	1.27473910501144	3.63233740594541
C	-3.03447681086287	1.84066138583259	3.20219176354375
C	-3.02633628177412	2.76742538545225	2.15864318620281
C	-1.82112952277247	3.13202098633285	1.55717213706480
O	-1.24439105487016	6.82031405083170	2.98270958531690
C	2.62312436097918	4.67894613381541	1.86868624097302
O	3.58934106418904	3.94862144064896	2.44984693124282
C	4.95196922133263	4.34424306147703	2.12727978030151
O	2.80392450592799	5.56334572564505	1.05725467234166
O	4.45687563373075	1.87308450156613	4.67309766137651
C	3.44407395200299	1.19548337875215	4.11460356565723
C	3.87022487720689	0.49075174989858	2.85148268476657
O	2.31814033621304	1.15316534115691	4.58796333509623
H	6.32251193217784	2.96238265834982	9.05170695312433
H	7.74648973009785	2.94212235738477	6.95965433729735
H	-0.47873370913028	2.70153831278922	6.08876195337159
H	0.58403230248199	6.05063341765160	1.57500958371988
H	1.34692658439618	3.82755770538585	3.35020899288132
H	0.58678374590477	3.45330339438587	0.41901943625084
H	1.44494415365604	2.27044351977179	1.42906800539240
H	0.30802819610806	1.21878423275127	3.39530964135479
H	-1.83146707095246	0.54024002297054	4.43372689403435
H	-3.97179107434297	1.55526938977012	3.67119253618130
H	-3.95651054547216	3.21095048487598	1.81560530108467
H	-1.81808187873892	3.86390946088536	0.75393838843100
H	5.57720393628143	3.62901943229529	2.65924817568229
H	5.10768529055354	4.29457450572929	1.04748273333805
H	5.11920629311280	5.35893104036817	2.49386535951915
H	9.07315982742437	-0.90792299399916	11.24446474014273
H	9.40135465767723	-3.32926678995324	10.68864412468566
H	8.39161679596023	-4.29947515510036	8.66265634046484
H	7.01728907300510	-2.88451018488895	7.11749421015932
H	4.64024009160092	-0.24747809853805	3.09710667528222
H	3.01358424960978	-0.00577955158033	2.39606700243932
H	4.30771701465927	1.20778624828856	2.15141746898125
H	6.31033471534325	2.61848498052690	6.00523769844013
H	-1.46744023523927	4.07512835634338	4.14401674341201
H	-1.56111780755421	5.61236100607271	5.04636200706939
H	2.18348015665418	1.54503363738385	7.24664079015445
H	2.05161109484159	2.76799397742923	8.50982765676526
H	4.16728012949138	2.24754315939770	5.55662709675839
H	7.67018643245479	4.82895414664789	5.15098038233150
H	8.05344850686898	7.24207630164778	5.47427315879555
H	7.06489939336802	8.42280021398691	7.42520988942831
H	5.60145288235986	7.19304400531041	9.00274611942794
H	5.35904800671837	4.75481277334456	8.80435645439093

3.8
Lowest frequency = 12.03 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	8.28383277350061	1.78672910546325	12.74260793867730
C	9.11374749999414	2.23582718627080	11.72699510461997
C	10.34774776022026	2.83145593938775	12.00304235120175
C	10.79829301127121	2.99664045862436	13.30364165547627
C	9.96705484541578	2.54451242556778	14.33598486241408
C	8.73023438650293	1.95078463992664	14.05992990690255
C	10.98056337258039	3.21290681683348	10.71092675188252

N	10.08702298166063	2.81111643663346	9.71791180533390
C	8.92692095363333	2.21234019653516	10.24874092144339
C	10.28820763748065	3.02356886415533	8.29662583646858
C	10.34665684625717	4.53622110193792	7.94260830958114
O	7.99674887844747	1.79123703513273	9.58856371910092
O	12.04444230789480	3.77596455983757	10.50692293994934
C	11.51357794144678	2.20482073514496	7.82956375034974
O	11.93572601941255	1.24527698095162	8.46748924859086
N	12.02156442960603	2.58519929338996	6.62481728446133
C	13.21046310325567	1.93332454902536	6.06169876021226
C	14.48408617027341	2.59704712827428	6.48270008492697
C	15.28438335825014	2.36721887185506	7.58169267562851
N	16.26762975791896	3.30112618951956	7.48640754570596
N	16.09333487081721	4.07531361917104	6.38269312652055
N	15.01118373490920	3.64772606389050	5.77998839177264
C	17.40025474159674	3.52552103608310	8.37970990218659
C	17.65081444776862	4.98519602741986	8.78445288081150
O	18.80841066474501	5.38947795903023	8.82703382215255
N	16.60283242996060	5.80005424993231	9.10742051245031
C	15.20888599522467	5.48018256396137	9.39125272083139
C	14.29453608512064	6.59973702862251	8.90954394324166
O	13.19313720349853	6.43644292239228	8.42952324158908
C	14.96662731700669	5.22464589529410	10.91235678842947
C	15.70243579897167	3.98114899678874	11.33943565083120
C	17.01019738261299	4.04978583102279	11.83390813313096
C	17.72736424007782	2.88624086993927	12.11584488630837
C	17.14107730913077	1.63669524717738	11.91084153246988
C	15.82983273606328	1.55809429621903	11.43469553999696
C	15.11610531580812	2.72138132807281	11.14888680926108
O	14.84033018814539	7.81759635635174	9.14089999036552
C	14.01864214552195	8.94269861662635	8.73078717041143
H	9.40438722836764	2.57110251180777	7.83098176062100
C	9.34979453400681	5.34262708433025	8.74298967828587
H	10.12855395847568	4.63974932781104	6.87151778817928
H	15.22813072867025	1.66300889002100	8.39632409293541
H	16.89866328996278	6.73716253664557	9.36321656819737
H	14.91090603855674	4.58929710083000	8.84372949006244
H	15.31556891752990	6.10038395093854	11.47004798981763
H	13.89148446547867	5.10475475641816	11.06850517783347
H	14.09908349352796	2.66140672491303	10.77225966875377
H	15.36058186269095	0.58913626060716	11.28586335546601
H	17.69918253399752	0.73016690349544	12.12686342220403
H	18.74564529431241	2.95700013578604	12.48697879524384
H	17.47760072097966	5.01976051885430	11.98189355084682
H	14.60509088062266	9.82632473882406	8.97791697570688
H	13.82442070167620	8.88403452246454	7.65809855361626
H	13.07288754995726	8.92884682174781	9.27682314491286
H	7.32606725863220	1.32755195961110	12.51945835300499
H	8.10789805844727	1.61206505066372	14.88298443096776
H	10.28473373461214	2.65591560593872	15.36852914187918
H	11.75926207132154	3.45821468737555	13.50850703517346
H	11.35260917640407	4.91934593508583	8.12667049003558
H	11.77460318941665	3.49533651874445	6.25732438707950
H	17.23456448005930	2.92374201425967	9.27763809902098
H	18.31978622418355	3.19630510320279	7.89325799267735
H	13.18512980378727	0.89597506318206	6.39879767589748
H	13.12926705004400	1.96360656411382	4.97232840886615
C	9.80506285374840	6.25347503979353	9.70244194219773
C	8.90149175067794	6.96953055093723	10.48829218907712
C	7.52940206473313	6.78185357556613	10.32489802604105
C	7.06600909324578	5.87745791818961	9.36761740795733
C	7.97015286814194	5.16416260985478	8.58304977886491
H	10.87500140125264	6.39233188388409	9.82794404578221
H	9.27034254001851	7.67270633714444	11.23034187017139
H	6.82438414927263	7.33648285248672	10.93768319830975
H	5.99875491966011	5.72469153801458	9.23419073019488
H	7.59829147152512	4.45125398399396	7.85098928842979

3.1’
Lowest frequency = 9.59 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	7.54138106930933	1.76128145998694	8.13261131092412
C	6.96924272138040	0.50635571022434	7.88653923244654
C	6.31386086817187	-0.14746647053370	8.93611520896580

C	6.21616110146856	0.44060133967070	10.19677359739044
C	6.77524915996703	1.69841568387452	10.42582548040898
C	7.44271513452030	2.35447052522808	9.39071943134808
C	7.01669805480332	-0.11403206292205	6.51295133494790
C	5.87102436255996	0.39442112442765	5.59218349491727
C	6.06284680863101	1.87980926145747	5.31843386412094
O	7.00591653985937	2.34484149251600	4.71548594688094
N	5.89007580671300	-0.31119299395933	4.31645358365164
C	5.26868806414113	-1.50186181717049	4.18693149478240
O	4.65181189937422	-2.08909661015908	5.07431764652742
C	5.42795663667231	-2.11934534254952	2.78341495171547
N	4.12019183294612	-2.43942822759459	2.22518155298819
N	3.27550124509985	-1.46399075386772	1.81165794075758
N	2.13347975398865	-1.99854373188598	1.45849646443613
C	2.22755176771209	-3.34243853219561	1.64880411047691
C	3.48944679875396	-3.63120593773594	2.14250169579947
C	1.04227391336572	-4.24895117505579	1.49979729616010
N	0.45261259569481	-4.51437341332072	2.81805222305857
C	1.12743743823048	-5.31683961613679	3.68923721096501
O	2.04875385082797	-6.05755163651041	3.34839137714321
Pd	3.58003727239886	0.50554513215517	2.03695888686196
O	3.52256780073465	2.48313529748716	2.63142062851694
C	2.60373512000363	2.19005320466981	3.47957076604621
C	1.97016350128299	3.22999903467609	4.34671830638798
C	0.66868808086489	-5.23399124286022	5.16121699123899
C	-0.81713728865796	-5.54312101930293	5.37407740094789
N	1.05424732393608	-3.93385476245117	5.73759624948057
C	0.51251975858093	-2.68103326962951	5.42783569999446
C	1.21202524294117	-1.70101807947421	6.29592374496104
C	2.11940108929993	-2.39144442420167	7.10169539738939
C	2.03549635578176	-3.83694531633826	6.76697454803046
C	1.08244699543120	-0.32232118045897	6.36246020525408
C	1.89366479177451	0.35255494601003	7.28133366158379
C	2.79817345591315	-0.33798469401217	8.09555897006868
C	2.92557758976817	-1.72961131501150	8.01340699159263
O	-0.36610345425937	-2.46812886727515	4.59789713812155
O	2.62495871270577	-4.78412123137915	7.24366821903173
O	2.24881617676164	0.95935317571007	3.55286171616648
O	4.82424739089670	0.57299273276851	0.47158973421790
C	6.10924992266139	0.69554306890518	0.66251617093664
C	6.86687017899402	1.06075992674269	-0.60219355072783
O	5.07479463605756	2.62565433596549	5.86777450329728
C	5.25945323633100	4.05705847507886	5.69803603301874
O	6.70740765712014	0.54950103016420	1.74032391516759
H	-0.11358247960128	-3.76933629240104	3.23447900682340
H	0.28876333972444	-3.77156253485421	0.87165429827474
H	1.33459699857334	-5.20427765449239	1.06063464422029
H	3.94725202877842	-4.55515794970187	2.45575454063858
H	6.28304446223221	0.13843820043027	3.47327387259674
H	7.00461728660945	2.14773955011598	-0.61196455346643
H	7.85334235227387	0.59294380772105	-0.58519935809918
H	6.31260287794377	0.77267547538950	-1.49681894650530
H	5.95013103407472	-1.44389307211605	2.10363844881746
H	5.97288327195366	-3.06055053737738	2.87600222348692
H	3.63364483734155	-2.27488831339990	8.62834607567004
H	3.42169671802797	0.21869081053774	8.78819959745219
H	1.82749657622858	1.43315858651436	7.36538573537643
H	0.39235674389804	0.20418482171042	5.71290496382079
H	1.28781746416474	-5.95771280210564	5.69567058268567
H	-1.04186440720283	-5.55241869489958	6.44481997284271
H	-1.45822135800183	-4.80573659658822	4.88709937801596
H	-1.04144994047675	-6.53143475903362	4.96229271624793
H	4.43150180934830	4.51678631257559	6.23629066613814
H	6.21834321669651	4.35800752207808	6.12439780238370
H	5.23277953595543	4.30705201861367	4.63544875839589
H	4.90694757721349	0.21469851459646	6.07213978803294
H	8.07257314263279	2.27122295379820	7.33244600626137
H	7.89528409444900	3.32672438798486	9.56579530673909
H	6.70286389517198	2.15804703548182	11.40734714730093
H	5.71060489347686	-0.08576482974183	11.00204233377390
H	5.88593452688112	-1.13089491811831	8.75917014620393
H	6.90411836867157	-1.19979150880225	6.58149344503344
H	7.96381697015964	0.10913812243405	6.01163325397154
H	2.28789488075905	3.06803643820626	5.38117472195158
H	2.27065616775328	4.22747321393776	4.02299360854494
H	0.88212814277459	3.12980345777982	4.30432103797140

3.2’
Lowest frequency = 3.33 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	15.89216598774997	9.19461855802022	12.22331334061053
C	14.97204746815505	8.16274139034880	12.11573856309979
C	15.19104415288312	7.07561993231751	11.26413537301596
C	16.33777675869595	6.98141105924172	10.49007114505516
C	17.27240304614773	8.01900762975518	10.59297639587372
C	17.05323459558070	9.10723535311245	11.44526010551445
C	14.02634444521433	6.15278484165043	11.37398808419560
N	13.15532847168005	6.75584821623018	12.29363178285860
C	13.65918340412132	7.97075298521522	12.79701954725440
C	11.89045672266847	6.16338387914195	12.71971912242444
C	10.82191827488345	6.29764080797256	11.62985524661777
O	13.09261194401631	8.68008514400154	13.60626384397625
O	13.81599744834390	5.09266042064455	10.81005329354242
C	12.18642975966510	4.73592669878303	13.23447929650167
O	13.01287745482982	4.54149407362544	14.11929349932921
N	11.43449847747880	3.74004126333082	12.69320402580788
C	11.73582722612822	2.35203200716065	13.02360273618418
C	10.77743316994005	1.46085314883040	12.29849693774244
C	10.18744957684562	0.26586106119966	12.67310434913977
N	9.42813619654581	-0.10315658447554	11.61236073334879
N	9.54019426902423	0.83236038923255	10.65000432969676
N	10.35053472135508	1.78031264866267	11.04585300454666
C	8.49685578034403	-1.21928243071615	11.41839605607642
C	7.06130396477648	-0.68054469974633	11.23167964929593
N	6.92415528508957	0.18321943316494	10.21186996683408
H	11.59558278878222	6.74393659691024	13.60082779720602
H	10.67754452221806	7.35457004577973	11.39053825334018
H	9.86572715197637	5.89652574946893	11.97923112672882
H	10.24232045803508	-0.33173767671311	13.56900917321395
H	15.71401023019165	10.03438298716759	12.88745311212570
H	17.79773936369304	9.89581945720800	11.50268569507199
H	18.18323780431534	7.98095878148935	10.00269343446779
H	16.49895171487541	6.13339432311067	9.83203647474632
H	11.12031108048853	5.77704410838070	10.71452235015399
H	10.97816549266108	3.89370974877277	11.80084065916690
H	8.83015327766710	-1.78672408595619	10.54412463149864
H	8.52830121438926	-1.83897813481848	12.31276198866768
H	12.77196867422206	2.11540820272752	12.74277136814263
H	11.65615101893881	2.21086079308181	14.10485373453947
C	5.62737293863438	0.88035845463745	10.15026593198873
O	6.17598240409292	-1.04288151790730	12.01927579086894
C	5.44383353801280	1.53298805072779	8.78328623440553
O	4.64336317897342	0.79167236825702	7.99255385414600
O	5.93567044869661	2.59447209989141	8.45086806005884
C	4.43801354321558	1.33339448696538	6.66303978687217
H	3.75992142147327	0.63442730285088	6.17494817889395
H	3.99539952653133	2.32950730830639	6.73347915866467
H	5.39665593755793	1.38510512493387	6.14379029835449
H	4.84071929897255	0.13395851984454	10.29290595716112
C	5.52558517374013	1.95890555039443	11.25524491940855
C	4.11820230378603	2.48837591711805	11.37331343482916
C	3.73655771732579	3.68584325988660	10.75746747015199
C	2.41897544487695	4.13812736477803	10.83757195766124
C	1.46388705307320	3.39590372377956	11.53227015675902
C	1.83399937587582	2.19874736522694	12.14791252460005
C	3.15055757230053	1.74917084820069	12.06728481085992
H	4.47863662159063	4.25923988858699	10.20835656729646
H	2.13880632220416	5.07198220716008	10.35747237802370
H	0.43817617277562	3.74838211881530	11.59619727759522
H	1.09638133846037	1.61614487445868	12.69327361915199
H	3.43946137922692	0.81586374444012	12.54579590542877
H	6.22961376409307	2.76026963965983	11.01309308065036
H	5.82811190432290	1.48397769949469	12.19247661392008
Pd	8.45137175731281	0.67422874563324	8.99610283271173
O	9.75288831755263	1.08472746615200	7.42161904964937
O	7.67652546862913	0.47447163493810	7.08857717050219
C	8.80452325817786	0.84496308265623	6.59504087149323
C	8.98426212871031	1.01164075471891	5.12020673039668
H	8.41657505458353	0.24719709947188	4.58442605033645
H	8.59596861951781	1.99412148732342	4.82840304181239
H	10.04321962108579	0.96083920528482	4.86127305773390

TS3.(2-3)’
Lowest frequency = -1086.95 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	10.97332217701843	2.90463772856307	8.00630986662106
C	11.68971830739807	2.80328939306182	9.18933827047085
C	12.18596324274687	3.93646899952082	9.83857637673122
C	11.98860634941065	5.21070405950072	9.32829439626839
C	11.26716847068275	5.31937461978454	8.13402825006718
C	10.76159044837417	4.18669637402765	7.48829077115025
C	12.88215447682979	3.50325631113471	11.07435008475000
N	12.78336196656443	2.10496265380243	11.11097866821479
C	12.06835627493371	1.60828053638934	9.98632255675992
C	13.32122419959420	1.20046746869791	12.14443038861384
C	14.82631123948366	1.39132889524449	12.36077394768551
O	11.85874546276733	0.43014002145387	9.77242034206249
O	13.43049598265035	4.20079752993344	11.92132714917464
C	12.48409581463381	1.31715468206453	13.43636381842533
O	11.83575533304736	0.36778145875371	13.87092392564675
N	12.49675489927360	2.54320374722210	14.03170240997395
C	11.42251716735592	2.88252885637416	14.96987478016381
C	10.09882071744186	2.84930244721002	14.26364658625742
C	9.12318672877619	1.87018442493098	14.26434105048600
N	8.21142208952374	2.26529415015280	13.34670003971256
N	8.62138419065990	3.44336187784408	12.80360321349451
N	9.76231812714378	3.79326622698904	13.34346116556674
C	6.92304854969429	1.63661364411783	13.02664370105763
C	6.59587985192004	1.39223515219959	11.54313733937485
N	7.23936548762440	2.17225110185157	10.66360044498157
H	13.11625560610459	0.19908714914009	11.76023953485752
H	15.36057557689410	1.22088999573441	11.42133932144290
H	15.17472881032775	0.66130310684552	13.09706712026669
H	9.02455414162236	0.94782864602406	14.81322702352829
H	10.57729762402729	2.03076247289969	7.50384698956202
H	10.17947999734296	4.30281825854037	6.58009972595752
H	11.07628333018377	6.29861773656947	7.70758150933676
H	12.37404020337507	6.08411868416434	9.84442045102464
H	15.05909826698326	2.39499863708227	12.72080256602440
H	12.92818923211775	3.31030400999959	13.51007921021532
H	6.90764087982989	0.67711196004027	13.54345343275313
H	6.12701029685127	2.26790388887411	13.43716554122126
H	11.42408259483134	2.16666167921618	15.79430258088815
H	11.62526035926493	3.88103939056460	15.36174618224296
C	6.76598245049617	2.31647571691767	9.29847942778471
O	5.74129815756225	0.53923648425862	11.28131485625788
C	7.67158734769153	1.63480872264866	8.27283507619414
O	8.14826286512076	0.47995790353925	8.76423505715437
O	7.88176676496821	2.06781359914783	7.15446208326475
C	8.95729144884466	-0.34772706283433	7.88687882848034
H	8.88314465337100	0.01526463501169	6.86054364198955
H	9.98538735209312	-0.30944718153390	8.25254038045668
H	8.56047664006905	-1.35985578732698	7.97636987052862
H	5.77309079993655	1.85549362520503	9.17179758725683
C	6.70904301954043	3.85011518710076	9.09482989432829
C	5.40416941866884	4.50224772879482	9.44739644359380
C	4.45289428599901	3.88109357417223	10.27245405256994
C	3.25553659409376	4.52171326883124	10.58554037432710
C	2.98417284115886	5.79635735113791	10.08822697052917
C	3.91918874933899	6.42071553729733	9.26133865632604
C	5.11450243806796	5.78109778810461	8.94384525535116
H	4.63571618777210	2.88673077299132	10.66936510381452
H	2.53169254551019	4.01882269283009	11.22097596518185
H	2.05145647872722	6.29466402966977	10.33625983075048
H	3.71457791495445	7.40832455901633	8.85680644043046
H	5.83940484510743	6.27308692257681	8.30188871620677
H	6.98684846557959	4.05835484663986	8.05417060170292
H	7.74101484096844	4.82524176433684	9.27635086948323
Pd	7.89420162459411	4.00397855484556	10.97681977104425
O	8.56932935333965	5.93892194437152	11.17926843681327
O	8.29982810332513	6.07081565774261	8.95839819382362
C	8.63492695162104	6.57362261922604	10.07545392548705
C	9.11344474004709	8.00350767381288	10.12069006215486
H	8.23634789824016	8.66008932931559	10.14143337971067
H	9.70578539247838	8.18141730937208	11.01892071586901

H	9.68715635540705	8.23823625626013	9.22181179810012

3.3’
Lowest frequency = 13.25 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	10.36914851618926	2.45561692099256	7.23167261633764
C	11.04432513964084	2.55511305796205	8.43880799318591
C	11.22070110527870	3.78475749658878	9.07450489403818
C	10.73694398279804	4.96250547848574	8.52577602298810
C	10.05919290056845	4.87232498983220	7.30496162103660
C	9.87245163377091	3.63849748467450	6.67101813465442
C	11.98995386027856	3.56128636049207	10.32611446664744
N	12.22167451619676	2.18570758217019	10.40400343365237
C	11.71331064570051	1.50975709651859	9.25925576640839
C	13.03659983037857	1.46551737826388	11.39961932580442
C	14.50071472290969	1.92321529704113	11.35999748627161
O	11.88066773402813	0.33152518039946	9.02384224609675
O	12.37400121379727	4.40600638974574	11.13028872314751
C	12.43406019907576	1.51764696854076	12.82256306310648
O	12.05574546911302	0.49649543993915	13.39080477827779
N	12.42482009011154	2.74829109525462	13.40733938347186
C	11.69278938138818	2.94657811619661	14.65942597248395
C	10.21656648266055	2.98582824242388	14.40067288143307
C	9.26305603896058	1.98899734053718	14.52874728386086
N	8.12184380475458	2.51533910435892	14.03452648711018
N	8.36555565888355	3.78222521701778	13.58337818788363
N	9.63461077203831	4.06553914676139	13.82354489505023
C	6.82483936877764	1.86410089298141	13.83902377340761
C	6.63107155445067	1.35145424967208	12.38907247931928
N	6.68952073173974	2.33552451008542	11.48340336757394
H	12.96039415847718	0.41977828613348	11.09605375402854
H	14.91624386647278	1.74875951157585	10.36294567670344
H	15.08033834388277	1.34571681350587	12.08593655931329
H	9.31828640530348	0.97832620370024	14.90056134606090
H	10.23305316081250	1.49744855429279	6.74134305319502
H	9.33146477341015	3.60061479411369	5.73039719638466
H	9.66648915119208	5.77193682426360	6.84052425942980
H	10.87424032313332	5.91068061988258	9.03262517753988
H	14.59382708079115	2.98421304912468	11.60266403639223
H	12.53616187010603	3.55475732663570	12.78608859677031
H	6.77514479157875	1.01964138870954	14.52504190850044
H	6.05041268569516	2.59533235098612	14.08232306640809
H	11.93864370922332	2.12417451942895	15.33317671818284
H	12.02541638877624	3.88879954999633	15.10067810001654
C	6.77732305271480	2.07398880438795	10.05031687834395
O	6.38969749169024	0.16000083376881	12.17093976482189
C	7.91014823901398	1.08852989290014	9.76864099954748
O	7.57732965567334	0.21531075994397	8.79479809901361
O	8.98639357779276	1.09750774222124	10.33388586905976
C	8.56935256230863	-0.81762227751075	8.54480747944585
H	8.17427631428715	-1.39039466052259	7.70645015519006
H	9.53824530189534	-0.37551811178530	8.30897543354000
H	8.66732491667123	-1.44182366466360	9.43571000627530
H	5.84921977831367	1.68561236028319	9.61492158101266
C	7.15656124883611	3.50400984361256	9.59089478562423
C	6.08072569555399	4.39787499029139	9.12920387158776
C	4.73083178770767	4.20278546375719	9.47930222834591
C	3.74595737090895	5.08339895963586	9.04291021789366
C	4.07773697759289	6.18379615937365	8.24870185713519
C	5.41219891482316	6.39147815076507	7.89326072875628
C	6.39814915204143	5.51077562284506	8.32687497030488
H	4.46051931222134	3.36781681386476	10.11886052206154
H	2.71090451876327	4.91276076008800	9.32709928458269
H	3.30603799146969	6.86958530149602	7.91121927181010
H	5.68308519295288	7.24177915016936	7.27234457412023
H	7.43661643883890	5.67644725845487	8.05360410514908
H	8.06448815173011	3.56119772747716	8.98949157737981
H	7.75994115720305	5.84371315172335	13.19019907587636
Pd	7.70111511773951	4.02699989253354	11.50776285861908
O	8.76277673814880	5.80804628102148	11.09766430607776
O	8.15976785368780	6.74368825552678	13.06515422475301
C	8.80283181837941	6.74782413825293	11.90182473399683
C	9.61074259081257	7.98222582386866	11.64869500003492
H	9.68270118251707	8.16208452070884	10.57564115772439

H	9.17887293589243	8.84318762080785	12.16103384012412
H	10.61943689947244	7.81110560541726	12.04259880961666

3.4’
Lowest frequency = 19.64 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	9.76672309046635	2.60129909830899	7.58196557723716
C	10.55438080395171	2.70635899256962	8.74535374276124
C	10.55904073838630	3.93685558910270	9.42899792660049
C	9.81145495594023	5.01325774160664	8.96298958027374
C	9.04219491324344	4.89619750885484	7.80188817483891
C	9.02354750247208	3.68187060227507	7.11411406546176
C	11.36476886140860	1.55647354720466	9.18260607926300
Pd	13.34364271212778	1.83013646734041	8.63895340246661
I	12.95773006460542	1.87409107295006	6.04372373199650
C	14.76966658336186	1.24563994586523	5.12032726112289
C	11.73073941171138	1.43771526105454	10.68255763940706
C	11.75346309388947	-0.02001957843661	11.14073593541801
O	12.51306225998358	-0.86289932670068	10.70209065561565
N	13.09399146152429	1.95414382807925	10.61777146535042
C	13.97175496410118	1.73512252440240	11.60706894530471
O	13.70344605979068	1.34301553542990	12.74816055968579
C	15.42425099483609	2.08577387386413	11.20863847953000
N	15.89110023501035	1.26618828882754	10.08997117103031
C	16.61699276359284	0.12643224383978	10.11959450730162
C	16.67715234570052	-0.30076029330700	8.80385802615261
N	15.98455028763289	0.57614506941277	8.03368203881683
N	15.49212136895217	1.52347119350087	8.80813493896897
C	17.22306440534463	-1.57106940658406	8.22625956048532
N	16.17112601007975	-2.58734826771800	8.12319496905807
C	15.72797749393143	-3.22240348530018	9.24167379940859
O	16.29109631326632	-3.14283063643263	10.33117854238941
C	14.49957139886480	-4.14477880901910	9.05161686674266
C	14.78932687737537	-5.31623643145498	8.10348447434264
N	13.27867750305110	-3.41962802498630	8.65493004785668
C	13.03482965218962	-2.76482152578944	7.45029284339773
C	11.63168191275841	-2.28207408910778	7.50744104682878
C	11.07481468350841	-2.69187896005363	8.71947334267478
C	12.10635166389130	-3.46514014158397	9.46391560751895
C	10.90134642646072	-1.55369984673420	6.58019941871413
C	9.57947808762421	-1.23390100376719	6.91097412445143
C	9.02240931418792	-1.63684422965317	8.13001698170552
C	9.76534138093685	-2.38209257987051	9.05362040486133
O	13.83411290138831	-2.63678999239044	6.52473415560643
O	12.01289243248667	-4.07937296990654	10.50504250224105
O	10.82108104101351	-0.26147174228257	12.08468737190458
C	10.90060168585530	-1.57936027136087	12.69232064301014
H	14.27087791897551	-4.51841613645459	10.05137951758942
H	13.94246047113164	-6.00910471388040	8.09978751874877
H	15.67685874062842	-5.85138429985455	8.45306782565131
H	17.00167026348356	-0.29218266458002	11.03576939012495
H	9.33526471080513	-2.70153516388264	9.99689609740070
H	7.99709260007975	-1.36483341587518	8.36150443648824
H	8.97427132300257	-0.66336414826949	6.21287114338434
H	11.34131199763293	-1.24057066496003	5.63960290369557
H	14.96846903262512	-4.96825140015971	7.08372293269496
H	15.54077760303634	-2.55577591244109	7.31897107466730
H	16.08373933475138	1.90064823654434	12.05545621537583
H	15.48797091981588	3.13136919714057	10.89849733043225
H	18.01931781806339	-1.96966576979333	8.85740884634637
H	17.60981363329287	-1.38662027098038	7.22184130533815
H	10.06245344973180	-1.62035912332270	13.38715858651404
H	10.83371355455367	-2.36228886659388	11.93615886126784
H	11.85286045318379	-1.66870626112751	13.21965415452178
H	11.07876835420606	2.01141603241749	11.35151547220207
H	11.17801965002209	4.05049944137592	10.31419727232220
H	9.83289823330799	5.95492390202802	9.50506775961997
H	8.46390853801018	5.74108010895982	7.43971215788213
H	8.42273011868473	3.57478006907260	6.21469047082272
H	9.73830078650730	1.65126956054701	7.05341108608290
H	11.05916673861718	0.61209508817619	8.72983364345064
C	14.93607718746593	-0.09954619685980	4.80966559054067
C	16.14679340018120	-0.50416640314619	4.24508336138614
C	17.16007089541032	0.42386009981828	4.00380755829520

C 16.96688722150315 1.76786485574873 4.32409881796311
C 15.76264832907643 2.19204449473961 4.88786549941693
H 14.16662618866332 -0.82898022040121 5.03273730536858
H 16.29247917639266 -1.55310194926453 4.00220148925664
H 18.10048864023880 0.10057514330528 3.56706303119560
H 17.75424100856987 2.49350211821366 4.14140641743215
H 15.61219805144516 3.23269646171023 5.15341231871805

TS3.(4-5)'
Lowest frequency = -101.69 cm^{-1}.
Charge = 0, Multiplicity = 1

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C 10.36837520223713 2.52839164438115 7.20011319219718
C 11.04959441074926 2.67917761930329 8.42321376279552
C 11.02637441514292 3.94113066409634 9.04616542839698
C 10.34645421771198 5.00738007107123 8.46680859168498
C 9.67619230487363 4.84363921371425 7.25185376402721
C 9.68988779898192 3.59690080529505 6.62153976704120
C 11.78848147720713 1.54577657464382 8.98365888727377
Pd 13.85445686077888 1.60420365479394 8.60111593473395
I 13.85528925632880 1.02351717804390 6.03455006238389
C 12.01592521094758 1.50344987912878 10.51118541458722
C 11.83387710984486 0.08682712690976 11.05902302923415
O 12.52355636628960 -0.85978071569661 10.72980850833334
N 13.42720836780606 1.87103612976361 10.54246022795621
C 14.16828345036157 1.61930385474302 11.63662124736273
O 13.72378361992818 1.32507750960158 12.75022199533678
C 15.68284592413307 1.75196932795535 11.38598889605861
N 16.14030070551869 0.72689541180362 10.44865228414390
C 16.67413773877390 -0.48931858644914 10.70126339209138
C 16.82601901482683 -1.08063458468684 9.45883486313153
N 16.36907830734222 -0.21925465670705 8.51215983101785
N 15.94226774400995 0.87415103483408 9.10828054478796
C 17.26100083416593 -2.46975734915392 9.10148309081230
N 16.10422100133110 -3.35129096278102 8.93091517487236
C 15.42694165255028 -3.80074054455847 10.02100090724004
O 15.83509354746583 -3.66882963599954 11.17314003626168
C 14.12380697097118 -4.57964161771803 9.72383188727668
C 14.37611428094573 -5.86292693677837 8.92131809201930
N 13.08368100499230 -3.74608199390160 9.09460170361053
C 13.10403938625060 -3.18217090396931 7.81575184646379
C 11.78579257207731 -2.52162764773251 7.63056584794472
C 11.02451880663801 -2.72512682119738 8.78191069105233
C 11.82747458665659 -3.54808267070810 9.72725469242014
C 11.29239272349194 -1.80718144645475 6.54921874920871
C 9.99956563577121 -1.28235729545333 6.66134346370673
C 9.23985715079439 -1.47433325232319 7.82110075695347
C 9.74266714442134 -2.20997019162077 8.90130779654383
O 14.03238303836610 -3.24006309499305 7.01622993753208
O 11.50950353831122 -4.02635712814698 10.79684426057358
O 10.81064133434188 0.01837496882579 11.92998725645593
C 10.67894794525960 -1.25706382504926 12.61734849233319
H 13.71000053686578 -4.82369764547859 10.70397743769717
H 13.45020275386807 -6.44109815615260 8.84543745182525
H 15.12534444988338 -6.46973957800959 9.43790669007528
H 16.87613950006172 -0.83954599977896 11.70088719741515
H 9.15411208400829 -2.36938840662019 9.79877250041283
H 8.24375924629443 -1.04624861353796 7.88101296016009
H 9.57694114334472 -0.71720479996655 5.83596744303315
H 11.88858817789593 -1.66473257052153 5.65458614367518
H 14.73877120258613 -5.63944568846838 7.91559478010920
H 15.60221335815168 -3.32889320094698 8.03955350824567
H 16.22034918674011 1.61839276725655 12.32371134186394
H 15.91457451292276 2.72440105585292 10.94535624844461
H 17.89182926780334 -2.88570530967822 9.88918003494685
H 17.81493955084799 -2.45687745425752 8.16046167213891
H 9.81945053516442 -1.13324494573943 13.27498856819452
H 10.52510084765085 -2.06827436308067 11.90541572051900
H 11.58929530151917 -1.44650012880597 13.18977679063740
H 11.37498289986343 2.18846333289736 11.07649139953242
H 11.57516778664489 4.09083909265077 9.97095822234273
H 10.34672757454324 5.97552199102635 8.95986133136060
H 9.15080382587300 5.67957761867643 6.79946873705613
H 9.17351634469442 3.46005224514013 5.67534014157544
H 10.39324402210820 1.56262400428472 6.70448175465842

H	11.51525021714732	0.58339123419244	8.55067860569487
C	14.39974558383562	3.09549903134102	7.01091223619432
C	15.77143905179699	3.34978259748144	7.12723270011779
C	16.20033531173649	4.67666149460975	7.15862464396838
C	15.28652378033499	5.72447624286279	7.03162522007147
C	13.93147358015799	5.44192793538755	6.85631466003877
C	13.47674605801249	4.12346658267205	6.81892402417753
H	16.47775275495027	2.53408102270637	7.21534179075676
H	17.26100275228090	4.88325415516710	7.27380471504222
H	15.63159025767246	6.75380595913512	7.05072834202231
H	13.21079397621922	6.24617472200878	6.73833936842829
H	12.42857590792312	3.90794396886414	6.65633130970916

3.5’
Lowest frequency = 11.62 cm^{-1}.
Charge = 0, Multiplicity = 1

75

C	10.32224714284852	2.60910228078919	7.10820307879203
C	10.96912839442186	2.78180475493868	8.34743444155385
C	10.83780875207616	4.01529882559040	9.01045571950977
C	10.07273579541941	5.03670946805466	8.45705978766872
C	9.43112163457948	4.85050206265775	7.23073419531022
C	9.56009909455884	3.63278256670001	6.55689805611215
C	11.77932427318604	1.69171821935749	8.88031062782606
Pd	13.83772897853351	1.56253225042210	8.42832837529373
I	13.73051559903028	0.82969063142131	5.92271466605407
C	12.09746769076533	1.66023755564367	10.38778164238603
C	11.99321081679995	0.21896541941446	10.88914407057896
O	12.67081040622145	-0.67820821634555	10.41315638737062
N	13.51537879784273	2.04103082114282	10.37261422181931
C	14.28797353203833	1.72769555240452	11.43447297581572
O	13.86796466919914	1.41241312409556	12.55055391973769
C	15.79456405077930	1.77804411280742	11.13247042172959
N	16.16693629882618	0.65400141772136	10.27072371633582
C	16.70336430542437	-0.54129402996547	10.60311970037878
C	16.76902150871673	-1.24992622534753	9.41583160677493
N	16.25968916611593	-0.47545157469123	8.42211707700379
N	15.88995729570859	0.67581552950472	8.93276876537936
C	17.19573914135708	-2.66445715412487	9.15738949044308
N	16.04108375456242	-3.55199028575734	9.02166519620114
C	15.33384615825667	-3.92353319406759	10.12147270926008
O	15.70604825697102	-3.70136151199166	11.27232665447469
C	14.03738468337357	-4.71973255325769	9.84111883016744
C	14.30141651219809	-6.05705512423094	9.13766795941326
N	13.03047254555480	-3.91594983630305	9.12689328012089
C	13.09740264714883	-3.44537909029618	7.80821444150378
C	11.82455305622026	-2.72015768635090	7.56277217001204
C	11.04009960714536	-2.80435001547847	8.71479017427234
C	11.78438486601119	-3.60413406876235	9.72357880340639
C	11.40073913627965	-2.02204788991594	6.44262181624161
C	10.15051297070511	-1.39489674980888	6.51350839194156
C	9.36426251401512	-1.47542055706116	7.66805751938969
C	9.79893767004482	-2.19163789779092	8.79119211920660
O	14.03324328221898	-3.61570275771135	7.03626195644058
O	11.43468154737517	-3.97525089360709	10.82765265344298
O	11.09511394996516	0.07919730414312	11.86669331910598
C	11.07489937868175	-1.22368912115418	12.52051486280266
H	13.59251398116177	-4.89237507524474	10.82294704882858
H	13.37160801518857	-6.62993271164539	9.07003344874623
H	15.02492277627262	-6.63370340196725	9.72124231197844
H	16.96658522358026	-0.79662808166327	11.61726647071399
H	9.19173279516233	-2.25958717135703	9.68820968673941
H	8.40219060947972	-0.97201343055211	7.69295804185435
H	9.78814811265491	-0.83061983701996	5.65946707061736
H	12.02310100958646	-1.95223612700157	5.55850025240960
H	14.69963819760430	-5.90802293513532	8.13196445275762
H	15.57353211735603	-3.61046387750271	8.11345180089858
H	16.35570183839862	1.69026075624505	12.06161373698062
H	16.05535767388067	2.70211001987003	10.61280696169040
H	17.81125584135171	-3.02729232629315	9.98281643577306
H	17.76799093300473	-2.71628006601244	8.22866296651818
H	10.43192378885740	-1.08722969644179	13.38862323928295
H	10.67808405177633	-1.98268267510783	11.84713628603799
H	12.09079597819209	-1.48982335160964	12.81640634642902
H	11.47375139519046	2.31813186798273	10.99972974311102

H	11.36156503622451	4.18274716333906	9.94615886867057
H	9.98509489212935	5.98585665322100	8.97758792525629
H	8.83907504545422	5.65204083404422	6.79866367326283
H	9.07086109506553	3.48658111839856	5.59823560398247
H	10.45337857078715	1.67080576959911	6.57756636536709
H	11.52078096431431	0.71790717751811	8.45948275320961
C	14.32442068584126	3.41268346548102	7.77338729792988
C	15.64071367701889	3.77982437818050	8.03077126467589
C	16.06474892792747	5.06353086941089	7.66941487524256
C	15.18793957659880	5.94565665249870	7.04165222515445
C	13.88750254564160	5.53552973611120	6.75491166308696
C	13.44776188577554	4.25612972889072	7.11192990091516
H	16.34209415865973	3.08140787563593	8.47145441810936
H	17.08971557778607	5.35814239315140	7.87853174499774
H	15.52260625408421	6.93961936359741	6.75970311017533
H	13.20189143403144	6.19859982196440	6.23445415627626
H	12.44746145278391	3.93976065662527	6.84769205104211

TS3.(5-6)'
Lowest frequency = -209.94 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	11.16599316170795	2.05151843855203	6.86638619914198
C	11.64787779259355	2.58644786657197	8.07391600891039
C	10.94400732143537	3.64298563297264	8.67807723861974
C	9.78316172623606	4.13566599381998	8.09584560784624
C	9.31442614991879	3.59781789653956	6.89349643482481
C	10.01078533344135	2.55444434192984	6.28013939510896
C	12.85141497867394	2.00429559813158	8.66364516076473
Pd	15.28279970601932	1.94800232041226	8.39447593005856
I	16.27077243263989	1.89891066791753	5.96217240065076
C	13.08022457691416	1.99549389334168	10.16277376901165
C	12.45717045388281	0.71079320768684	10.74876322529126
O	12.81538971244145	-0.40630716205460	10.43419042427687
N	14.52804217407931	1.96339853630480	10.28465103816946
C	15.08518883854719	1.50922874079721	11.41522522474105
O	14.49230538821310	1.30278077500269	12.48156837319377
C	16.58671600052545	1.22127580030599	11.25340736926529
N	16.75771998798894	0.12680412704719	10.29615619235906
C	17.06177303061272	-1.17054074501298	10.52080527367330
C	16.94649541757747	-1.78662616040596	9.28782329523544
N	16.56496294114185	-0.85795578039107	8.37071748348684
N	16.44821454248966	0.29289212094004	8.98256151470931
C	17.05768700959288	-3.23908945764791	8.93560119970484
N	15.74420949474209	-3.88570480860016	8.95484335332656
C	15.08947998281903	-4.06384730552534	10.13037706635596
O	15.61173436445522	-3.87572005793444	11.22859057878115
C	13.64266825153992	-4.59890689067725	10.02411932402893
C	13.59452386728787	-6.03642974863473	9.48833339041879
N	12.74413016096677	-3.70954887657684	9.26511918152235
C	12.78900555420855	-3.42336874339791	7.89770523797132
C	11.61084042596489	-2.56541414283315	7.61085229609390
C	10.89194781758705	-2.39289852048673	8.79380996268057
C	11.58767165117492	-3.14714587820568	9.87203786078138
C	11.19841266366101	-1.99383782617042	6.41605534287762
C	10.02600376270322	-1.23024385416393	6.44255108895257
C	9.30626964162478	-1.05051694126465	7.62924278119933
C	9.72906933667262	-1.63791472181193	8.82721907294622
O	13.63701044032366	-3.81911819134719	7.10467730408043
O	11.25841364467822	-3.32262480003058	11.02706361349293
O	11.46770935954654	0.99399585810981	11.61076746475141
C	10.95555875587569	-0.15368011059364	12.34460910278806
H	13.25222139854541	-4.56408580677496	11.04287327284141
H	12.57191707290368	-6.42114582663740	9.54738359026238
H	14.24186824974492	-6.67005508342873	10.10134090886169
H	17.29972847119803	-1.54934653372247	11.50146555000952
H	9.16850819296730	-1.50905365138475	9.74727917804065
H	8.40736917315464	-0.44174969261702	7.61800308119871
H	9.66786299491598	-0.76513573063618	5.52902182078090
H	11.76708138123300	-2.13721427542985	5.50277493591156
H	13.93408077476754	-6.08570693999710	8.45138297787353
H	15.19988527070471	-3.92739323444147	8.08964375848291
H	17.01099014094097	0.90284695377402	12.20416299317215
H	17.11782814894068	2.09596083369492	10.86793149048123
H	17.70850855590535	-3.74858042526888	9.64987111567003

H	17.46795797769440	-3.34894031877187	7.93015161359563
H	10.14113405915044	0.24083040653476	12.95052230242306
H	10.60945697966221	-0.92646315667660	11.65866217094872
H	11.75515654349242	-0.55570389040683	12.96981499602132
H	12.63987648604269	2.85808718327884	10.66933812973427
H	11.32257123741794	4.09176869212765	9.59042319977901
H	9.24673447027594	4.95157485439767	8.57105008610122
H	8.41464531368863	3.99667786749399	6.43417379283510
H	9.65182770850413	2.13637604136613	5.34400174246039
H	11.71441136828026	1.24086807892117	6.39548415982236
H	13.10890325773951	1.04214218976280	8.21897085574696
C	14.18022177132459	3.64991350394367	8.03351944835180
C	14.26712730865745	4.63394690290864	9.03544639852962
C	14.01866605285116	5.97122252817783	8.72877553855161
C	13.66038143465036	6.33795107721913	7.43044784922222
C	13.55562277676763	5.36282989250188	6.43290000286264
C	13.79466565732817	4.02898673603590	6.73384660486640
H	14.54446425378139	4.35222569518422	10.04536251437806
H	14.10728771824527	6.72599587747268	9.50554796455892
H	13.45330421310624	7.37858480677590	7.19697783839722
H	13.27471792327071	5.64350706394727	5.42175842210791
H	13.67354380964115	3.27331728805851	5.96603691302470

3.6’
Lowest frequency = 8.59 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	10.41150145447567	1.91308534569412	7.88370994450913
C	11.34144073346459	2.84540331900437	8.35310026709454
C	10.93382953766710	4.16798939625522	8.55722912741150
C	9.61912978592302	4.55063410234366	8.29839761670875
C	8.69492081967794	3.61383078906182	7.83304086973391
C	9.09501506384249	2.29377444557106	7.62648943829314
C	12.75652249325774	2.39644340618671	8.67782346731132
Pd	15.66937491982692	2.38610094765875	8.99456244047628
I	17.59225068026944	3.05773970971949	7.33872559390777
C	12.91050090486292	2.08181371006333	10.17932629348119
C	12.08563093592367	0.83206033809414	10.50497715000664
O	12.32838328125180	-0.27513483570501	10.06399252897800
N	14.32387608681426	1.83883239881450	10.43087984324306
C	14.66514229245188	1.39623977132564	11.64850320663800
O	13.88514283876889	1.18025260305979	12.58545583169183
C	16.17422444915705	1.12759484178941	11.81347247990411
N	16.64487290954707	0.24658872153697	10.74858122451662
C	16.89441907670347	-1.08068124998069	10.76624527978290
C	17.08422824915110	-1.42950949356463	9.43842593244877
N	16.93832449588944	-0.32037129753933	8.66699333879152
N	16.67615443982677	0.68420306081707	9.46571177679806
C	17.27161029324625	-2.78770185950320	8.83442405735322
N	15.98711357889955	-3.47792147919064	8.69288615852122
C	15.33535992042902	-3.93107565725951	9.79183419049973
O	15.82861490529787	-3.91777863213278	10.92094637987093
C	13.95183943082386	-4.57338519101274	9.55366686330038
C	14.06945570252019	-5.89432764748816	8.77879282428701
N	12.95528768273292	-3.68163922156759	8.93168124182343
C	12.96901446716316	-3.16831890825059	7.63235424511270
C	11.64164349135264	-2.53543969644896	7.41662500948065
C	10.87457524789595	-2.71798484354609	8.56692867884566
C	11.69895669302703	-3.45177730830885	9.56373506321807
C	11.13641082048646	-1.88426788108588	6.30074289546210
C	9.81461982966692	-1.42746670347665	6.36713681150579
C	9.03932981900019	-1.62495229438812	7.51600432709208
C	9.56304130707728	-2.27553907686123	8.63928919842618
O	13.89693960965421	-3.25138436313358	6.83365290184637
O	11.40485267649215	-3.83730603764392	10.67561065935934
O	11.02814487867736	1.13126951686757	11.27907190120001
C	10.19722845605946	-0.00055703215288	11.63632256810248
H	13.55281882639428	-4.75870086648961	10.55266048097555
H	13.09753554788022	-6.39590595522159	8.74943105428773
H	14.78457638180904	-6.54789235848729	9.28641602517570
H	16.89506650279330	-1.66432794420673	11.67214423397959
H	8.96746889751798	-2.43754095772752	9.53167998268664
H	8.01432037316216	-1.26651740858931	7.53404417264044
H	9.38123754860482	-0.91341360199162	5.51433352327722
H	11.74362718933405	-1.74411784303578	5.41218560703041

H	14.41440825731066	-5.72361929926467	7.75633373170010
H	15.45761553432286	-3.38778243251559	7.82116637961066
H	16.34836541068365	0.62952389148083	12.76575460937938
H	16.74706423142703	2.05857856086548	11.76043678948729
H	17.92284849631813	-3.39826346019487	9.46426830643118
H	17.71356048614565	-2.68810428507809	7.84186686577432
H	9.50503996161108	0.38051246511300	12.38594167248964
H	9.65949036319200	-0.35121052351712	10.75244939899342
H	10.81628546664467	-0.80517911028663	12.03698047956447
H	12.52895531359726	2.90786833948470	10.79212787571790
H	11.65024787546553	4.90476683101532	8.91166334449020
H	9.31576898894098	5.58143199883669	8.45824567783009
H	7.67083572433005	3.91324647116172	7.62945022550482
H	8.38244657470510	1.55941500867135	7.26104973292353
H	10.72259845604088	0.88414843957741	7.72754249425011
H	12.94603025205876	1.45384177638460	8.14990729986455
C	13.78803185426853	3.41060765575883	8.18984378820897
C	14.44493603624470	4.34226057620051	9.04864194136824
C	15.11361974969219	5.46446978613338	8.50276481726648
C	15.14578076852780	5.65990985957253	7.13892283612698
C	14.52356903798932	4.73242221327177	6.27951279859832
C	13.86846112804120	3.63276968677204	6.78789079745098
H	14.26472631608558	4.30978171076166	10.11830919286134
H	15.59975757101664	6.16478567621080	9.17413365625513
H	15.66582315735716	6.51626520310461	6.72230167110781
H	14.57245712353300	4.88097094556309	5.20528298643015
H	13.37401633769783	2.93001423704358	6.12368592322600

3.7’
Lowest frequency = 2.95 cm^{-1}.
Charge = 0, Multiplicity = 1

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C	13.94469027031884	3.81893234277245	6.93923828076223
C	13.62668893485847	3.62936684547478	8.28904409019900
C	14.09188814005438	4.55889523285923	9.22575100378722
C	14.85191575187136	5.65570151127213	8.81746234847914
C	15.15672823890067	5.83931960124161	7.46958793481500
C	14.70103479346343	4.91440900691092	6.52923313924968
C	12.76740256425660	2.43780124160009	8.67155217824676
C	13.11255485950106	1.87665725051441	10.07915578814365
N	14.52488151559628	1.55862901305925	10.18901863499087
C	15.32584990653667	2.09812447785347	11.14247004076436
C	16.79898508205472	1.66692981623331	11.08088223979658
N	17.03918169130258	0.45695417394168	10.31144281984105
C	16.86816863583060	-0.84014303607195	10.67874731336577
C	17.10444992906740	-1.56001937523707	9.52612233045932
N	17.39586340797234	-0.67910287208056	8.51938466660431
N	17.35470629580763	0.54424936360723	8.98476414180378
C	17.04598153399075	-3.03852824986885	9.29381312175330
N	15.68672268529962	-3.54149187714854	9.08280889463727
C	14.84938772004354	-3.74844559558296	10.12562245067299
C	13.48025034887905	-4.38530657699198	9.78600772912034
N	12.62571613859479	-3.59470402150917	8.88251257885018
C	12.87065371890883	-3.25920335532177	7.54827145458258
C	11.63991579832842	-2.58643068104673	7.05394555636502
C	10.69684690585690	-2.58412122263493	8.08191212158343
C	11.30860469659355	-3.23533739471191	9.27059422663969
C	9.42811909989539	-2.05636129878011	7.89876349605297
C	9.13143648286822	-1.51435569493429	6.64219827129047
C	10.08396010702337	-1.49926459371373	5.61706886484956
C	11.36071782921780	-2.04177957414794	5.80955257043003
O	13.89529602688129	-3.49949617721623	6.91909793551362
O	10.81698111367301	-3.47474701622636	10.35578690203849
C	11.27380684345502	2.72889908780204	8.59836160403684
C	10.41052053429779	1.79646169766175	8.01325621288513
C	9.03403459395226	2.02170038553000	7.99048095516686
C	8.50460275829686	3.18238390606608	8.55289415990796
C	9.36084738080578	4.11885749999271	9.13477169552654
C	10.73544237153006	3.89366090618483	9.15574540348864
C	12.30265577568667	0.60159553576431	10.30957550860638
O	11.38420731473705	0.76696061535249	11.27202081644877
C	10.52408954220903	-0.38201536634947	11.51226329915008
O	12.47691889195198	-0.42666411905987	9.68050846890173
O	14.95834198656911	2.89990259109103	11.99531366433649
O	15.16509314415080	-3.55432879239669	11.30074891358710

C	13.64528242997647	-5.82201635122252	9.26845972215816
H	12.93166916160608	-4.39046984645758	10.72940229337373
H	12.66525642044627	-6.30078002501062	9.18089490444296
H	14.25161615910869	-6.39393306189990	9.97662651872640
H	16.58254773428686	-1.14387391652636	11.67362534862632
H	8.69403724278301	-2.06938059816954	8.69810534368204
H	8.14578021533341	-1.09801527375922	6.45669320367375
H	9.82444062896770	-1.06432647979180	4.65654068484783
H	12.10378255233669	-2.04423188431612	5.01853020549946
H	14.13801547764259	-5.83663957942354	8.29337347374790
H	15.30603998111735	-3.59896170228939	8.13606661331962
H	17.15144574045590	1.53148597997723	12.10458090238341
H	17.37064970109883	2.47027762317034	10.60927302457694
H	17.46368293707985	-3.56990394619078	10.15286819302185
H	17.62951153679593	-3.27888993661688	8.40264412928060
H	9.88699017308298	-0.08565460604699	12.34375846518055
H	9.93324367450600	-0.58223617128236	10.61693158064810
H	11.12576624412362	-1.25671085735156	11.75982864861840
H	12.88447864687262	2.60021000189707	10.86264339292729
H	11.39821287801908	4.63305070661494	9.59654828453930
H	8.95729307815489	5.02883952402625	9.56986156126175
H	7.43317580845778	3.36039685757349	8.53329513934586
H	8.37639283704399	1.29112922967447	7.52866525433736
H	10.81995823570021	0.88731772081413	7.58098978414053
H	12.97616256260805	1.62843157543215	7.96041788472222
H	13.89195302724539	4.42188731861057	10.28457701148742
H	15.21224080166374	6.36216098012282	9.56001573634658
H	15.75254078316823	6.69107372417569	7.15432749734706
H	14.94187082847257	5.04122943116191	5.47752372804096
H	13.59633059955542	3.09655737995566	6.20446161829205
H	14.92126554119993	0.92197497139374	9.50692102367232

Curriculum Vitae

Personal Information

Name:	Michaela Bauer
Date of Birth:	06.11.1984
Place of Birth:	Kassel, Germany
Nationality:	German

Academic Education

11.2013 – Present	**PhD Candidate in Organic Chemistry** Institut für Organische und Biomolekulare Chemie Georg-August Universität Göttingen Supervisor: Prof. Dr. Lutz Ackermann Thesis: *Late-Stage Peptide Functionalization by Transition Metal-free and Palladium-Catalyzed C–H Arylations*
10.2011 – 9.2013	**M. Sc. in Chemistry** Georg-August Universität Göttingen Final grade: very good, 1.5 Supervisor: Prof. Dr. Lutz Ackermann Thesis: *Synthese und Anwendung sekundärer Phosphinoxid-Präliganden*
10.2008 – 7.2011	**B. Sc. in Chemistry** Georg-August Universität Göttingen Final grade: good, 1.7 Supervisor: Prof. Dr. Lutz Ackermann Thesis: *Metallfreie direkte Arylierung elektronenreicher (Hetero) Arene*

Parental leave

4.2017 – present	Parental leave to bring up my son (born may 2017) and daughter (born october 2020) until they are old enough to enter kindergarten

Working Experience

6.2007 – 6.2008	Chemielaborantin, Landesbetrieb Hessisches Landeslabor (LHL), Kassel Sachgebiet: Untersuchungen von Milch und Milchprodukten

Education

9.2004 – 6.2007	Ausbildung zur Chemielaborantin, Landesbetrieb Hessisches Landeslabor (LHL), Kassel Abschlussnote: sehr gut
1995 – 2004	Albert-Schweitzer-Schule Kassel, Abitur grade: 2.0
1991 – 1995	Ernst-Leinius-Schule Kassel

Teaching Experience

4.2014 – 9.2014	Assistant of the practical course ”Organisch-Chemisches Grundpraktikum für Lehrarmtskandidaten und Biochemiker“
10.2014 – 3.2015	Assistant of the practical course ”Organisch-Chemisches Fort-geschrittenen Praktikum für Chemiker”
4.2015 – 9.2015	Assistant of the practical course ”Organisch-Chemisches Grundpraktikum für Lehrarmtskandidaten und Biochemiker“
10.2015 – 3.2016	Assistant of the practical course ”Organisch-Chemisches Fort-geschrittenen Praktikum für Chemiker”
4.2016 – 9.2016	Assistant of the practical course ”Organisch-Chemisches Grundpraktikum für Chemiker“
10.2016 – 3.2017	Assistant within the FoLL Program (Forschungsorientiertes Lehren und Lernen)

Publications

4) M. Bauer,' W. Wang,' M. M. Lorion, C. Dong, L. Ackermann, *"Internal Peptide Late-Stage Diversification: Peptide Isosteric Triazoles for Primary and Secondary C(sp^3)–H Activation" Angew. Chem. Int. Ed.* **2018**, 57, 203-207. 'Both authors contributed equally.
3) X. Tian, F. Yang, D. Rasina, M. Bauer, S. Warratz, F. Ferlin, L. Vaccaro, L. Ackermann, *"C-H Arylations of 1,2,3-Triazoles by Reusable Heterogeneous Palladium Catalysts in Biomass-Derived γ-Valerolactone" Chem. Commun.* **2016**, 52, 9777-9780.
2) Y. Zhu, M. Bauer, L. Ackermann, *"Late-Stage Peptide Diversification by Bioorthogonal Catalytic C-H Arylation at 23 °C in H_2O" Chem. Eur. J.* **2015**, 21, 9980-9983.
1) Y. Zhu, M. Bauer, J. Ploog, L. Ackermann, *"Late-Stage Diversification of Peptides by Metal-free C-H Arylation" Chem. Eur. J.* **2014**, 20, 13099-13102.

Conferences

5) *ECHC XXVII*, Amsterdam (Netherlands), **July 3-6 2016**, Poster presentation.
4) *Jungchemikerforum 2015*, Göttingen (Germany), **July 1, 2015**, Poster presentation.
3) *IRTG Münster-Nagoya*, Münster (Germany), **November 28, 2014**, Poster presentation.
2) *Niedersächsisches Katalyse Symposium*, Göttingen (Germany), **October, 16-17, 2014**, Poster presentation.
1) *ORCHEM*, Weimar (Germany), **September, 15-17, 2014**, Poster presentation.

Göttingen, den 1.02.2022

Erklärung

Hiermit versichere ich, dass ich die vorliegende Dissertation in dem Zeitraum von November 2013 bis Januar 2022 am Institut für Organische und Biomolekulare Chemie der Georg-August Universität Göttingen auf Anregung und unter Anleitung von

Herrn Prof. Dr. Lutz Ackermann

Selbstständig durchgeführt und keine anderen als die angegebenen Hilfsmittel und Quellen verwendet habe.

Göttingen, den 1.02.2022

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