Diversity-Oriented Assembly of *C*-Glycosides *via* Late-Stage C−H Glycosylation

Dissertation

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Submitted by

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Deutsche Zusammenfassung

C-Glycoside sind weit verbreite Strukturmotive, welche in Naturprodukten und kommerziell erhältlichen Arzneimittelmolekülen vorhanden sind. Aufgrund der Stabilität glykosidischer C−C-Bindungen gegenüber chemischer und enzymatischer Hydrolyse, wurden ausschließlich *C*-Glykoside als synthetische Ersatzstoffe von *O*-Glykosiden verwendet und synthetisiert. Die Forschung zur Entwicklung einer stereoselektiven *C*-Glykosylierung für den Zugang von Kohlenhydratanaloga hat an großer Bedeutung gewonnen. Dennoch ist der präzise Aufbau glykosidischer C−C-Bindungen seit langem eine große Herausforderung in der stereokontrollierten Synthese von Kohlenhydraten. In den letzten Jahren haben sich übergangsmetallkatalysierte Glykoslierungsreaktionen auf Grund ihrer Vielseitigkeit, Effizienz und Stereoselektivität für die Synthese verschiedener *C*-Glykoside und Glykokonjugate etabliert. Die langwierige Synthese von Glykosyldonoren und der Bedarf an toxischen und empfindlichen metallorganischen Reagenzien mindern jedoch eine breite Anwendbarkeit dieser Reaktionen.

Daher wurde die C−H-Glykosylierung im späten Stadium der Synthese entwickelt. Zunächst wurde eine Palladium-katalysierte C(sp^3)−H-Glykosylierung von Aminosäuren mithilfe von Triazol als Isoster für Peptide etabliert. Dies ermöglichte die vielseitige Synthese von Glykoaminosäuren, Glykopeptiden und BODIPY-markierten Glykoaminosäuren. Des Weiteren entwarfen wir einen konzeptionell neuen *C*-Glykosyl-Akzeptor mittels Palladium−katalysierter C−H-Aktivierung von Glykosiden. Ausgestattet mit Glykaliodid-Donoren wurde die selektive Palladium-katalysierte C−H-Glykosylierung von Glykosiden zum effizienten Aufbau von Oligosacchariden erforscht. Darüber hinaus wurde die Methode zur selektiven C(sp^2)−H-Glykosylierung von Arenen mit einem stabilen Glykosylbromid-Donor mittels Ruthenium-Katalyse entwickelt. Bemerkenswerterweise ermöglichte die entfernte *meta*-*C*(sp^2)−H-Glykosylierung den effizienten Aufbau biologisch wichtiger *meta*-*C*-Arylglykoside. Weiterhin wurde eine Domino-Reaktion für den Aufbau von *meta*-*C*-Alkylglykosiden in einer einzigen katalytischen Reaktion mit leicht verfügbaren Ausgangsmaterialien entwickelt. Abschließend wurde die rhodiumkatalysierte positionsselektive Tryptophanpeptid-C7-Amidierung mit leicht zugänglichen Dioxazolonen erreicht.

Contents

List of Abbreviations

Ac	acetyl
Alk	alkyl
AMLA	ambiphilic metal-ligand activation
AQ	amino quinoline
aq.	aqueous
Ar	aryl
atm	atmospheric pressure
BIES	base-assisted internal electrophilic substitution
Bn	benzyl
Boc	*tert*-butyloxycarbonyl
Bu	butyl
Bz	benzoyl
calc.	calculated
cat.	catalytic
CMD	concerted-metalation-deprotonation
conv.	conversion
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
δ	chemical shift
d	doublet

DCE	1,2-dichloroethane
dd	doublet of doublet
DFT	density functional theory
DG	directing group
dt	doublet of triplet
EI	electron ionization
equiv	equivalent
ES	electrophilic substitution
ESI	electrospray ionization
Et	ethyl
FG	functional group
g	gram
GPC	gel permeation chromatography
h	hour
Hal	halogen
Het	heteroatom
Hept	heptyl
Hex	hexyl
HFIP	1,1,1,3,3,3-hexafluoro-2-propanol
HPLC	high performance liquid chromatography
HR-MS	high resolution mass spectrometry

Hz	Hertz
i	*iso*
IR	infrared spectroscopy
IES	internal electrophilic substitution
J	coupling constant
KIE	kinetic isotope effect
L	ligand
m	*meta*
m	multiplet
M	molar
$[M]^+$	molecular ion peak
Me	methyl
Mes	mesityl
mg	milligram
MHz	megahertz
min	minute
mL	milliliter
mmol	millimol
M. p.	melting point
MS	mass spectrometry
m/z	mass-to-charge ratio

NMP	*N*-methylpyrrolidinone
NMR	nuclear magnetic resonance
o	*ortho*
OA	oxidative addition
p	*para*
Ph	phenyl
PhMe	toluene
PMP	*para*-methoxyphenyl
Piv	pivaloyl
ppm	parts per million
Pr	propyl
py	pyridyl
pym	pyrimidyl
pyr	pyrazol
q	quartet
RT	ambient temperature
s	singlet
sat.	saturated
SPS	solvent purification system
t	*tert*
t	triplet

T	temperature
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromatography
TM	transition metal
TS	transition state
t_r	retention time
wt%	weight percentage
UV	ultraviolet
X	(pseudo)halide

1. Introduction

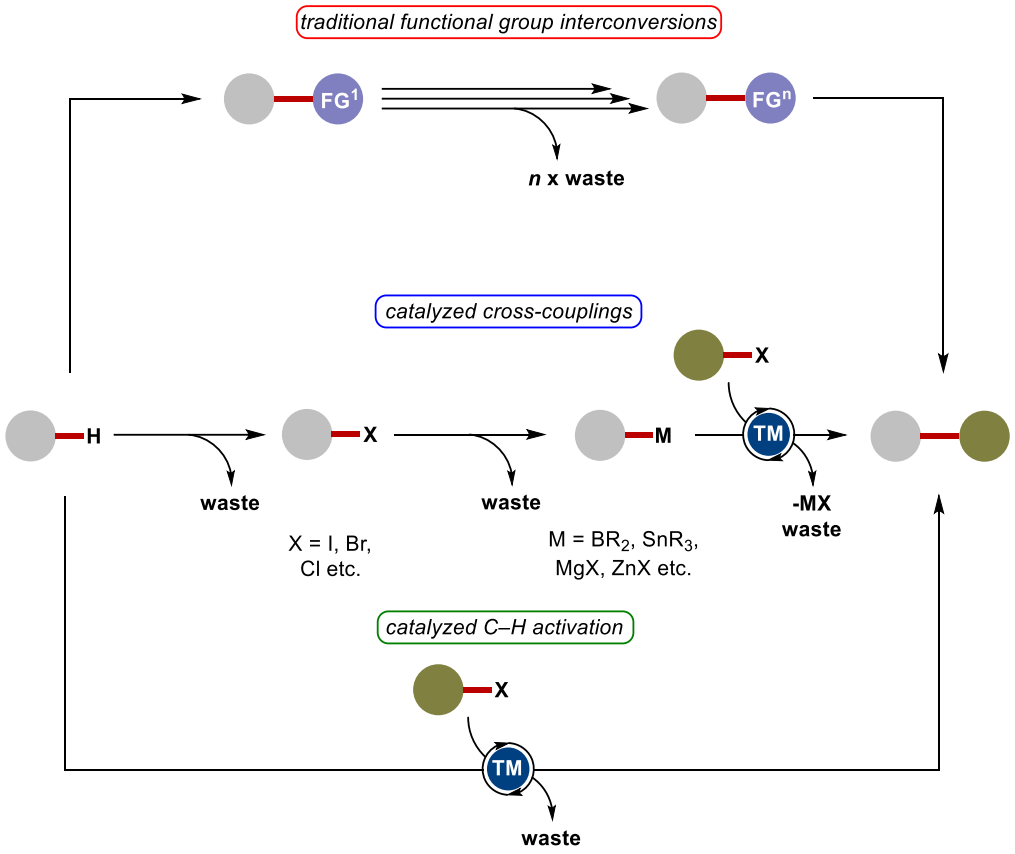
During the last decades, there has been an increasing focus on the environmental issues. Correspondingly, new and efficient processes that aimed to modify or replace traditional technologies are increasingly emerging. This trend is also evident in the molecular assembly of compounds with transformative applications in drug developments, energy storage and material science. In this context, Catalysis represents a significant approach that allows for efficient, green and economic transformations to minimize the environmental footprint, as was defined by Anastas and Werner in their *12 Principles of Green Chemistry*.[1] Additionally, catalysis offers new disconnections from simple precursors, making it an attractive option for the practitioners.[2] From an atom- and step-economy perspective, the direct functionalization of C−H bond to C−C and C−Het bonds is among the most straightforward and valuable approach in molecular synthesis.

1.1. Transition Metal-Catalyzed C–H Functionalization

Since the discovery and extensive exploration of metathesis[3] and palladium-catalyzed cross-couplings[4], both in catalytic modes and in industrial applications, the way we synthesize organic compounds has been revolutionized. A shift from step-intensive functional group interconversions to palladium-catalyzed cross-couplings reaction has emerged, for example with the Kumada-Corriu,[5] Negishi,[6] Magita-Kosogi-Stille,[7] Suzuki-Miyaura,[8] Hiyama[9] cross-couplings *via* the cross-coupling of aryl halides or pseudo-halides with various organometallic nucleophiles (Scheme 1.1.1). These valuable synthetic methods for the formation of C−C bonds were honored with the Nobel Prize in Chemistry in 2010, not only for their efficiency in organic synthesis, but also for revolutionizing the way we think about these bond-formation.[10] However, the requirement of pre-functionalized starting materials leads to additional processes for their preparation. Furthermore, some organometallic nucleophiles are either air- or moisture-sensitive, such as organomagnesium reagents for Kumada-Corriu cross-couplings, organozinc reagents for Negishi cross-couplings and toxic organostannane reagents for Stille couplings. In addition, the chemical waste associated with the preparation of those starting materials and the stoichiometric byproducts of these reaction significantly limits further applications.

In this context, the combination of direct C−H functionalization and catalysis provides an efficient and environmentally benign platform for developing novel and valuable

products in synthetic chemistry.[11] In this approach, the organometallic nucleophile is replaced by an inert C–H bond, therefore eliminating the need for multi-step sequences for accessing the sensitive and potentially toxic organic nucleophile (Scheme 1.1.1).

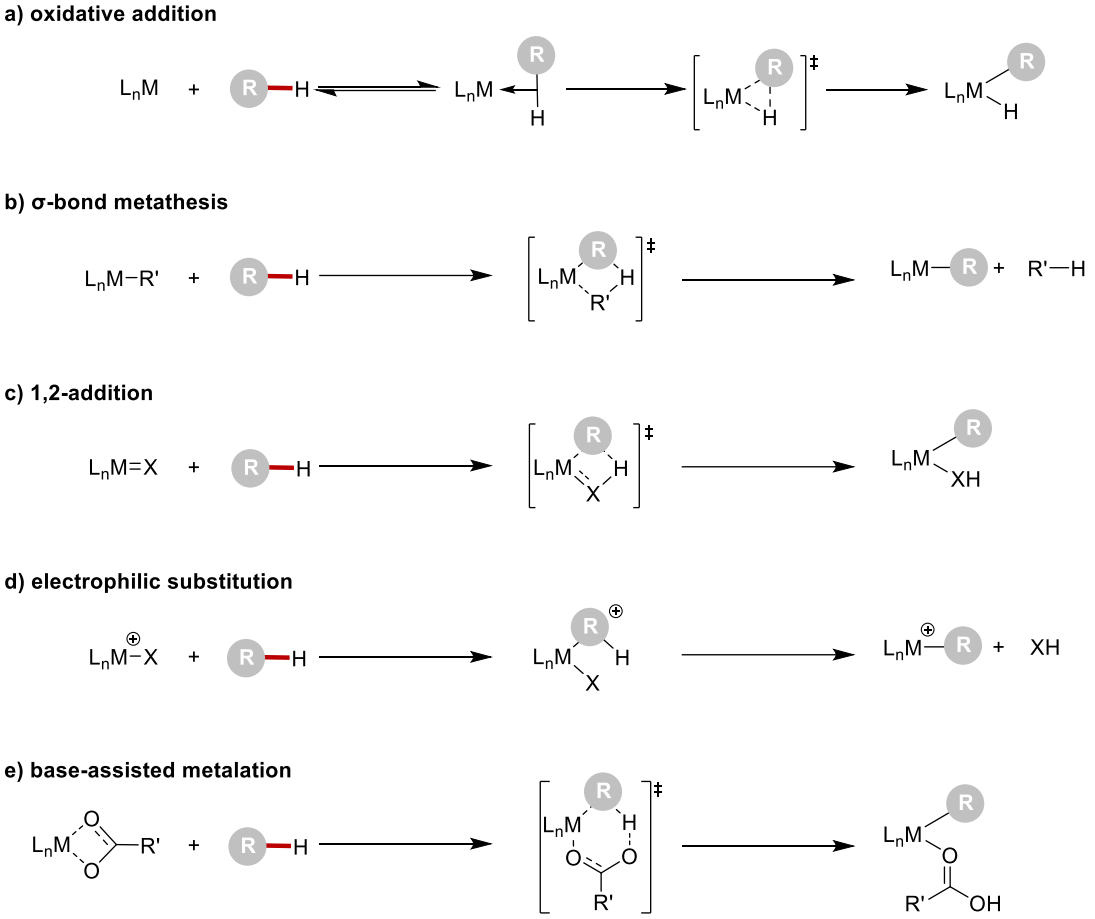


Scheme 1.1.1. Conceptual advantages of C–H functionalization over classical cross-couplings.

1.2. Mechanistic Manifolds

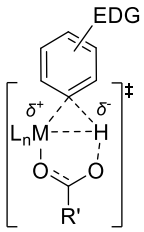
Due to the inherent benefits of the C–H functionalization approach, efforts on the mechanistic and computational studies for transition metal-catalyzed C−H functionalization have been devoted to the understanding of the C–H cleavage step. Several distinct transition states could be considered in the C−H metalation step (Scheme 1.2.1). The mechanistic modes[12] include: oxidative addition (OA), σ-bond metathesis, 1,2-addition, electrophilic substitution and base-assisted metalation. C–H bond cleavage by oxidative addition is typically observed at electron-rich metal centers (Scheme 1.2.1a). The key interaction of the σ^* orbital of the C–H bond with the metal center induces a formal two-electron transfer from the metal to the ligand. σ-bond metathesis proceeds with high-valent early transition metals, especially for metal hydride and metal alkyl complexes (Scheme 1.2.1b). The 1,2-addition with a M=X bond mostly observed with group IV and V metal imido-complexes (Scheme 1.2.1c). C–H

cleavage *via* electrophilic substitution is generally observed with cationic electron-poor late-transition metals (Scheme 1.2.1d). The base-assisted metalation is related to complexes bearing a carboxylate chelating base (Scheme 1.2.1e).



Scheme 1.2.1. Different modes of C–H bond metalation step.

C–H cleavage mediated by the base-assisted metalation pathway can be further categorized (Scheme 1.2.2).[13] For a deprotonation transition state as first put forward by Sakaki,[14] Fagnou coined the term ‘concerted metalation-deprotonation’ (CMD).[15] The agostic interaction between the C–H bond and the metal center was also studied by Macgregor and Davies and the named ambiphilic metal ligand activation (AMLA).[16] Due to the deprotonation, a preferential activation of electron-deficient substrates is observed through kinetic C–H acidity control. In contrast, the base-assisted internal electrophilic substitution (BIES) was introduced by Ackermann for the preferred and predominant activation of electron-neutron and electron-rich substrates and proceeds in a deprotonative/electrophilic substitution-type pathway.[17]

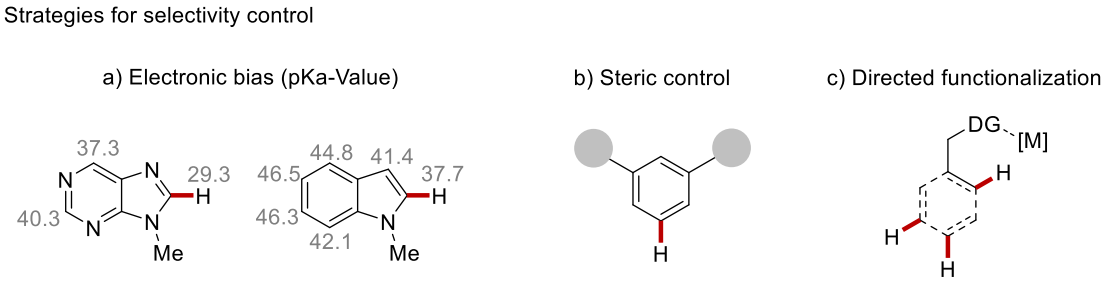


BIES

Scheme 1.2.2. Transition state structure in base-assisted metalation.

1.3. Selectivity Control of C−H Functionalization

Functionalization of unreactive C−H bonds utilized as latent functional groups allowed for a straightforward approach towards molecules complexity. However, organic molecules typically embody multiple C−H bonds with similar dissociation energies. Thus, the selective functionalization of a specific C−H bonds of given molecules is highly challenging. During the last decade, various approaches have been developed for addressing this position-selectivity (Scheme 1.3.1). Selective modification can be achieved through the inherent properties of the molecule based on the electronic or steric differences. Alternatively, the installation of functional groups with Lewis-basic functionalities enabled the site-selective *ortho*-C−H functionalization of aromatics or remote C−H transformation.

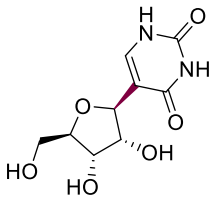


Scheme 1.3.1. Strategies for regioselectivity control. a) Electronic bias; b) Steric control; c) Directed functionalization.

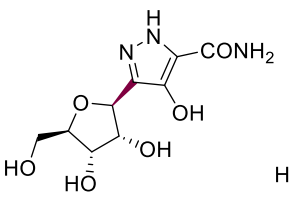
1.4. The Importance of *C*-Glycosides

Together with nucleic acids, proteins and lipids, carbohydrates belong to the most important classes of organic natural products. They contribute to a great variety of functions. First, they constitute the major source of metabolic energy. Second, versatile glycoconjugates exist in the cell wall and the extracellular matrix. Third, they provide recognition sites on the cell surfaces, and are therefore involved in numerous biologic processes. After the first isolation of *pseudouridine* from *t*-RNA in 1957, many natural *C*-glycosides, such as *showdomycin*, *minimycin*, *pyrazomycin*, *formycin*, *papulacandin*

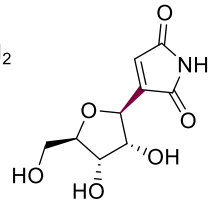
and *chaetiacandin*, have been isolated and shown potent biological activities (Scheme 1.4.1).[18] For example, compared to KRN7000, its *C*-glycoside analogue was reported to be 1000 and 100 times more effective against mouse malaria and mouse melanoma, respectively (Scheme 1.4.2).[19] Furthermore, compared with *O*- and *N*-glycoconjugates, *C*-glycosides have been considered as more chemically and enzymatically stable. Thus, research on *C*-glycosides synthesis has recently attracted wide interest because of the great importance of their potent biological activities. In particular, *C*-glycosides are well known to have potent antiviral, antibacterial, and antitumor activities.[20]



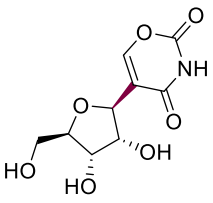
Pseudouridine



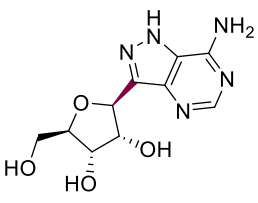
Pirazomycin
(antiviral)



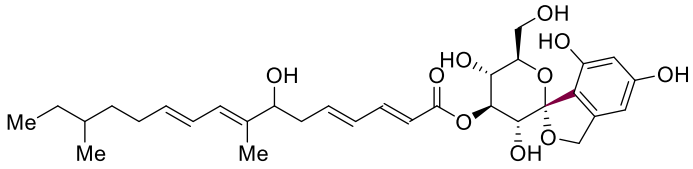
Showdomycin
(antibacterial, antitumor)



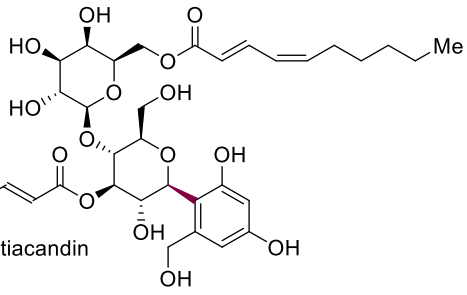
Minimycin
(antibiotic)



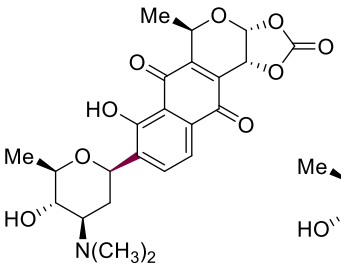
Formycin
(antiviral)



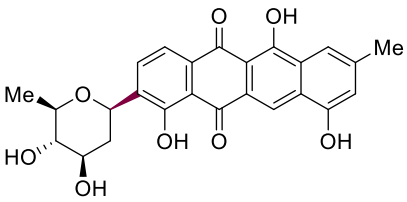
Papulacandin D



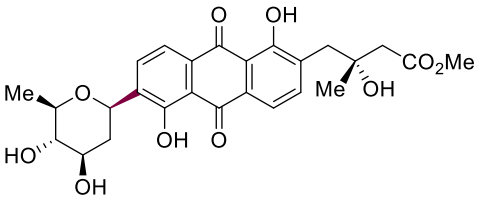
Chaetiacandin



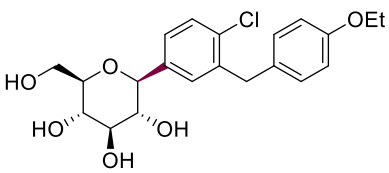
Medermycin
(antibiotic)



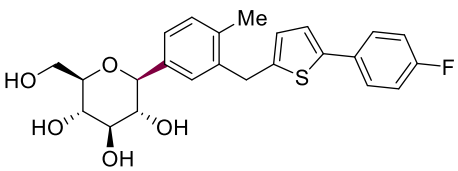
Galtamycinone
(antibiotic and antitumor)



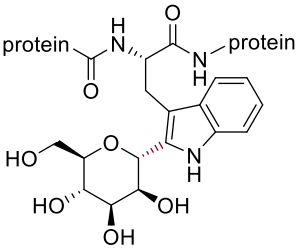
Vineomycinone B2 methyl ester
(antibiotic and antitumor)



Dapagliflozin
(antidiabetic)

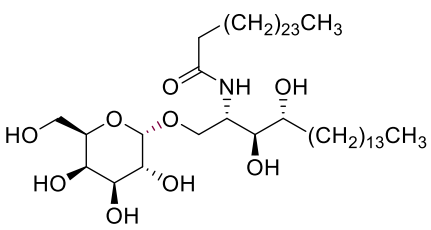


Canagliflozin
(against type 2 diabetes)

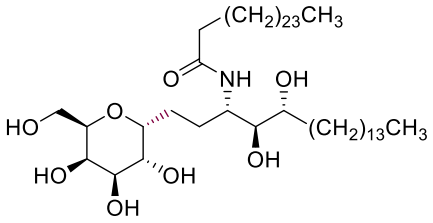


C-mannosyl-Trp

Scheme 1.4.1. Selected examples of *C*-glycosides.



KRN7000



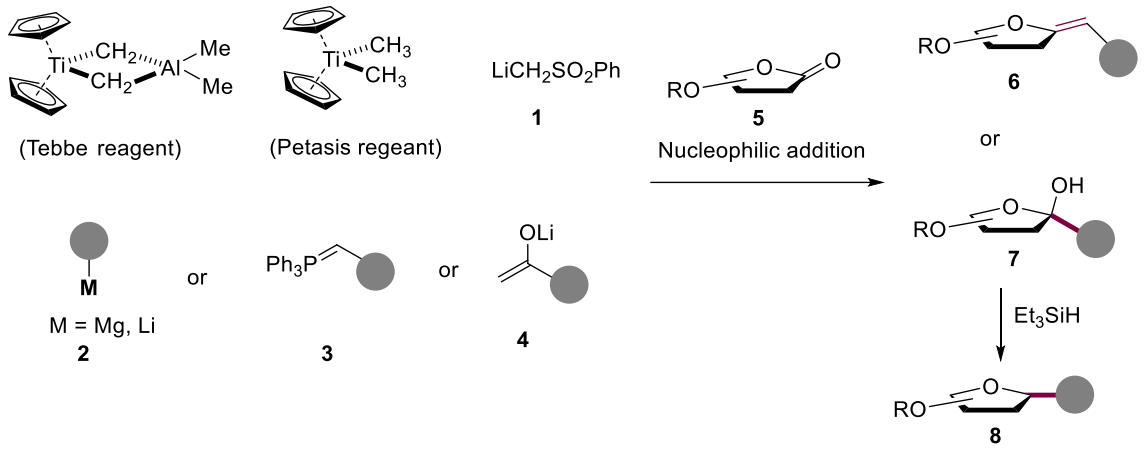
C-glycosides of KRN7000

1000-fold activity against mouse malaria
100-fold activity against mouse melanoma

Scheme 1.4.2. Comparison of KRN7000 and its' *C*-glycoside.

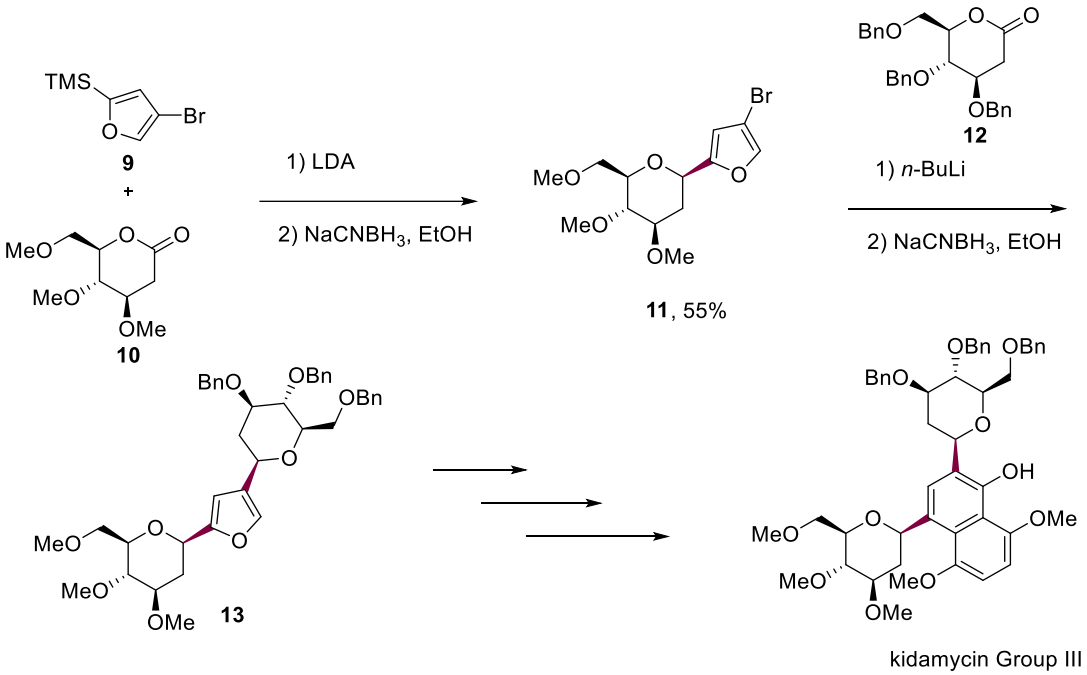
1.5. *C*-Glycosylation through Nucleophilic Addition

1.5.1 Lactone as an Electrophilic Carbohydrate



Scheme 1.5.1.1 Traditional methods for *C*-aryl glycosides assembly.

Traditionally, *C*-glycosylation have been wildly explored with glyconolactones **5**, featuring a anomeric carbonyl group (Scheme 1.5.1.1). The direct nucleophilic addition of organometallic reagents (e.g., aryl lithium, aryl and alkyl Grignard reagents) or nucleophiles, such as enolate **4**[21] and carbanion **1** stabilized by a sulfonyl group[22] or Wittig reagents **3**,[23] to protected glyconolactones at the anomeric C1 position. The resulting hemiacetal **7** could be further reduced with Et_3SiH in the presence of Lewis acids such as TMSOTf or $BF_3{\cdot}OEt_2$ to afford *C*-glycosides.[24] In addition, simple methylation of sugar lactone was carried out by titanium-based reagents, including the Tebbe and Petasis reagents (Me_2TiCp_2)[25] or the methylation of lactone by a Julia coupling.[26]

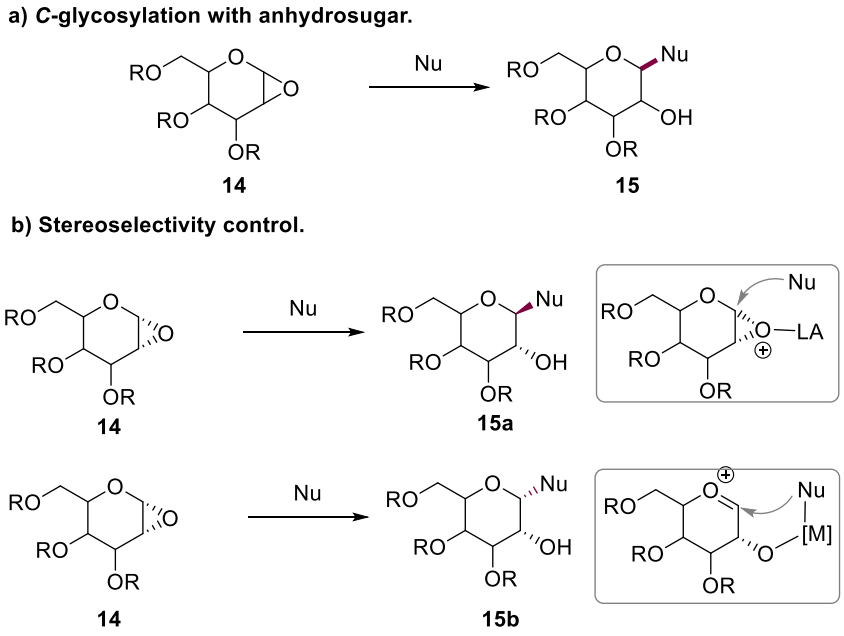


Scheme 1.5.1.2 *C*-Glycosylation for kidamycin group III synthesis.

This method was greatly exemplified by the total synthesis of kidamycin group III, a *C*-aryl glycoside antibiotic.[27] The key intermediate 2,4-diglycosyl furan **13** could be prepared by sequential addition of metalated furan to the glucosyl lactone, followed by hydride reduction of the resulting lactol intermediates. Then, a Diels-Alder reaction with benzynes and acid-catalyzed rearrangement delivered the Group III *C*-aryl glycoside (Scheme 1.5.1.2).

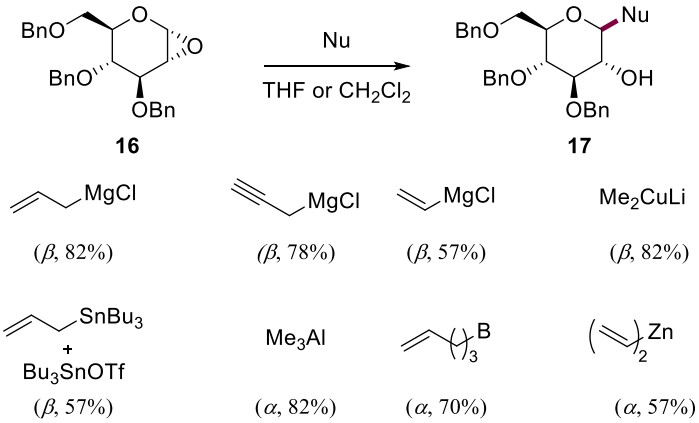
1.5.2 Anhydrosugar as an Electrophilic Carbohydrate

1,2-Anhydrosugar has been used as an efficient glycosyl donor for *C*-glycosylation, especially for oligosaccharide assembly[28] and glycosylated natural product synthesis.[29] It could be easily prepared by a epoxidation reaction of glycal with dimethyldioxorane (DMDO). The thus formed glycal epoxide is well-explored due to its high reactivity with organometallic reagents (Scheme 1.5.2.1a). The stereoselectivity with organometallic reagents is predictable based on the Lewis acidity and nucleophilicity of organometallic reagents. It was found that a S_N2 reaction pathway might be involved at the anomeric position when Grignard reagents and mild Lewis acids were probed,[30] giving *β*-stereoselectivities (Scheme 1.5.2.1b). Noteworthily, the use of strong Lewis acids, such as aluminum reagents,[31] afforded *α*-*C*-glycosides, through the formation of oxocarbenium ion (Scheme 1.5.2.1b).



Scheme 1.5.2.1 *C*-Glycosylation with anhydrosugar and stereoselectivity.

Selected examples for the *C*-glycosylation with glucal epoxide **16** are shown using different nucleophiles (Scheme 1.5.2.2).



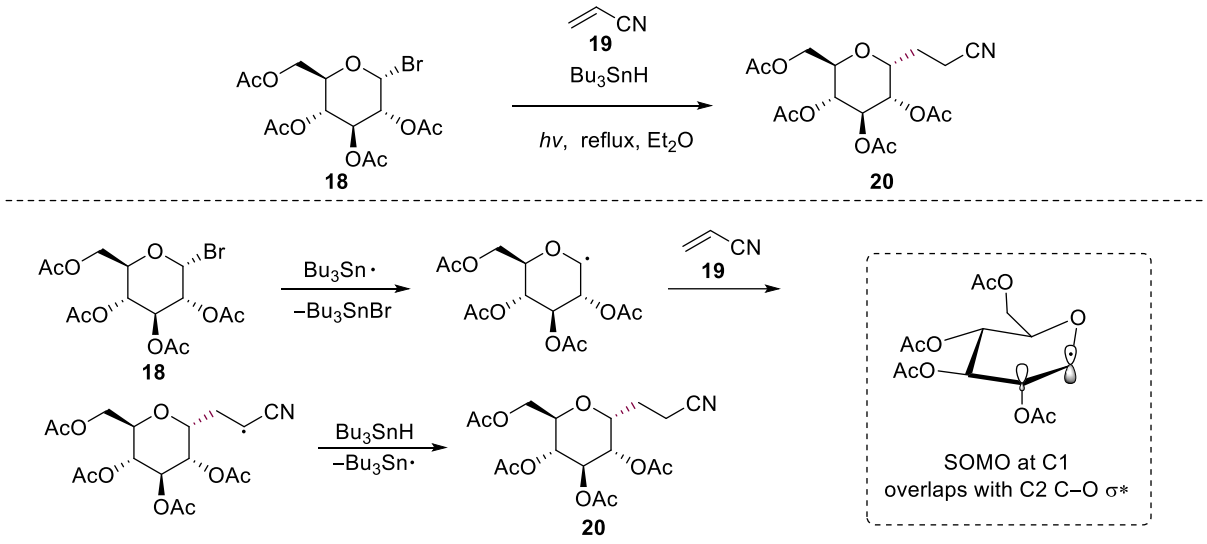
Scheme 1.5.2.2 *C*-Glycosylation with versatile organometallic reagents.

1.6. *C*-Glycosylation through Anomeric Radical Addition

1.6.1 Giese-Type Addition for *C*-Glycosylation

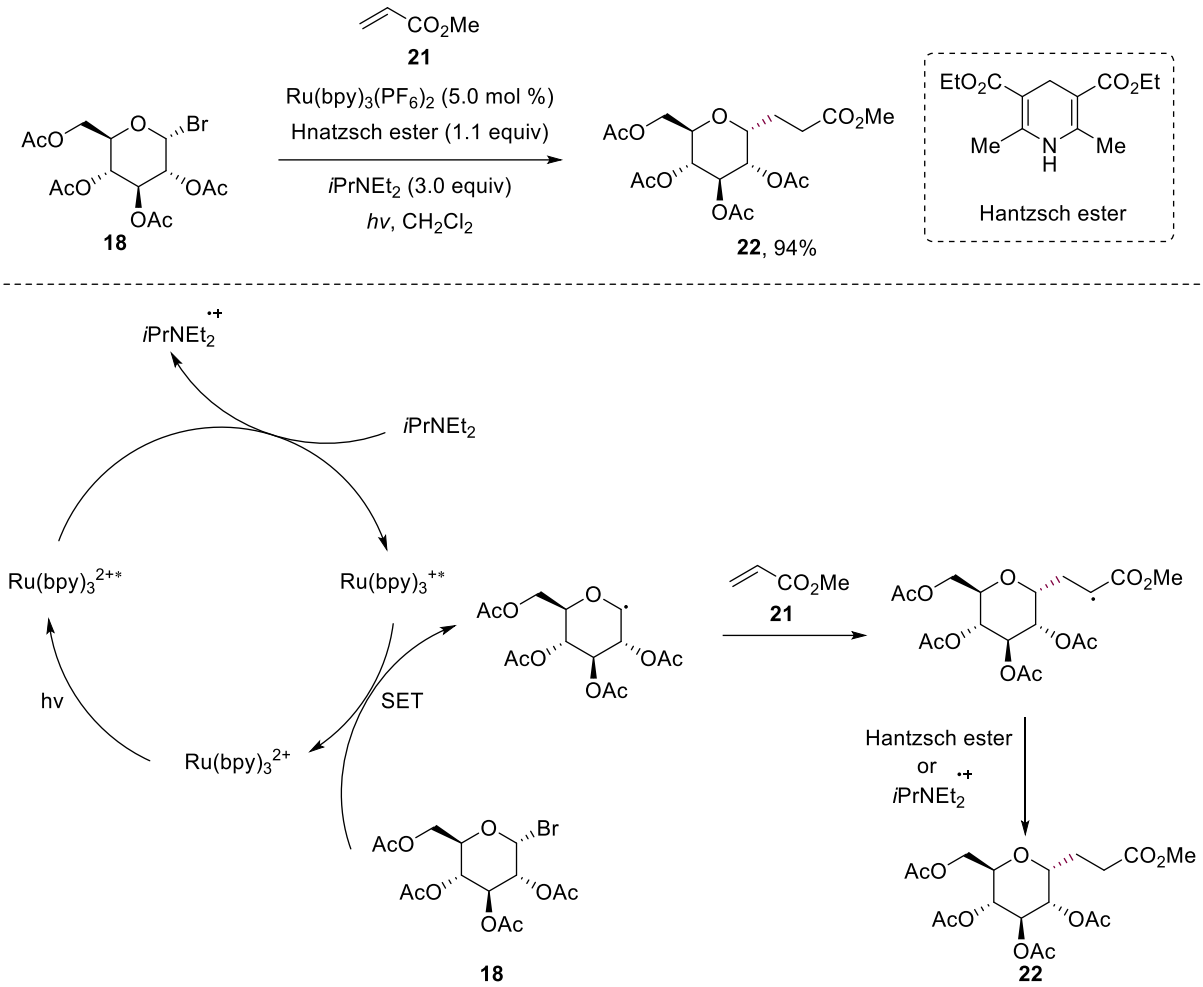
The pioneering work on anomeric radical addition for *C*-glycosides synthesis was exploited by treatment of glycosyl halides with allyl-*n*-butylstannane.[32] In 1983, Giese reported a highly α-selective *C*-glycosylation of acrylonitrile with acetyl protected glucosyl bromide **18**.[33] The transformation occurred *via* UV photolysis in the presence of acrylonitrile **19** and Bu_3SnH in refluxing Et_2O. The authors proposed that halophilic tributylstannyl radical may abstract bromine atom from glycosyl bromide to generate

glycosyl radical. Subsequent polarity-match addition of nucleophilic glycosyl radical to electro-deficient acrylonitrile and newly formed radical abstract hydrogen atom from Bu_3SnH deliver *C*-alkyl glycoside product **20** (Scheme 1.6.1). EPR studies suggested a boat ($B_{2,5}$) conformation for the glucosyl radical, in which the electron-rich SOMO overlaps with the σ* orbital of the pseudoaxial C−O bond at *C*(2) which affects the stereochemical outcome.



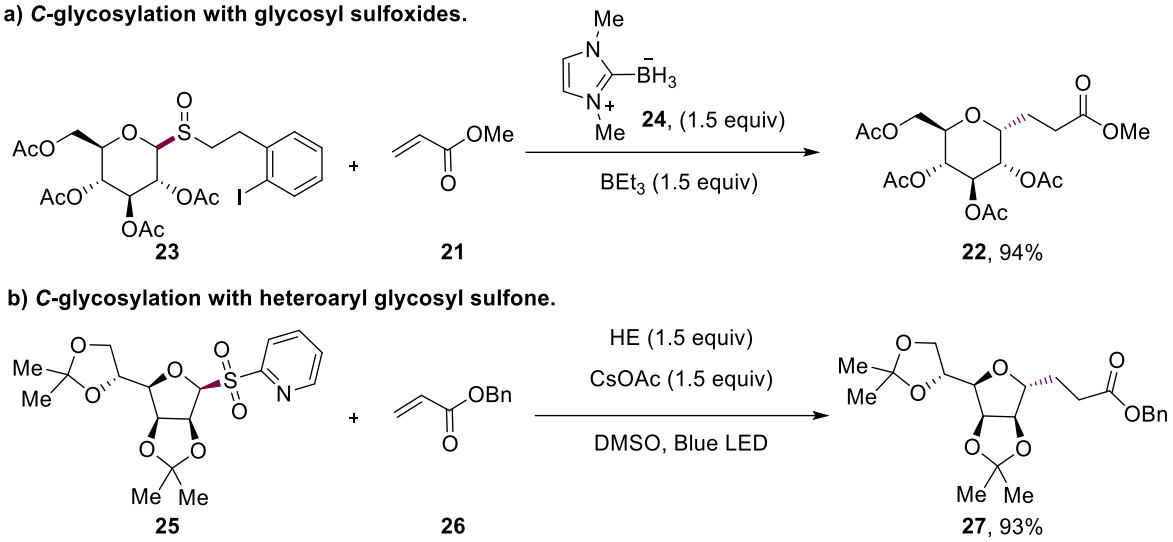
Scheme 1.6.1.1 *C*-Glycosylation with Giese-type addition.

Giese's seminal contributions in the area of *C*-glycosylation set the stage for a number of additional contributions with the use of thioglycoside, glycosyl selenide or nitroglycoside as glycosyl radical precursors.[34] Among these reports, the combination of BEt_3 and air as the radical initiator to replace tin reagents greatly improved its utility. Another important tin-free variant of the early *C*-glycosylation with visible-light photoredox catalysis was made by the Gagné group (Scheme 1.6.1.2).[35] Irradiation of the photosensitizer $Ru(bpy)_3(PF_6)_2$ in the presence of glycosyl bromide **18**, diisopropylethylamine (*i*PrNEt$_2$), Hantzsch ester and Michael acceptors **21** resulted in the *C*-glycosylation product **22**. The reaction pathway was suggested that the oxidizing excited state $Ru(bpy)_3^{2+*}$ accepts an electron by SET from the *i*PrNEt$_2$ to generate strongly reducing $Ru(bpy)_3^{+}$ catalyst. Then, ruthenium(I) species donates an electron to glycosyl bromide to deliver bromide anion and expected glycosyl radical, which is mechanistically different for the tin-mediated anomeric radical formation. Subsequent addition to electron-deficient alkene and hydrogen atom transfer from the Hantzsch ester form the desired Giese-type addition reaction product **22**.



Scheme 1.6.1.2 *C*-Glycosylation with photoredox catalysis.

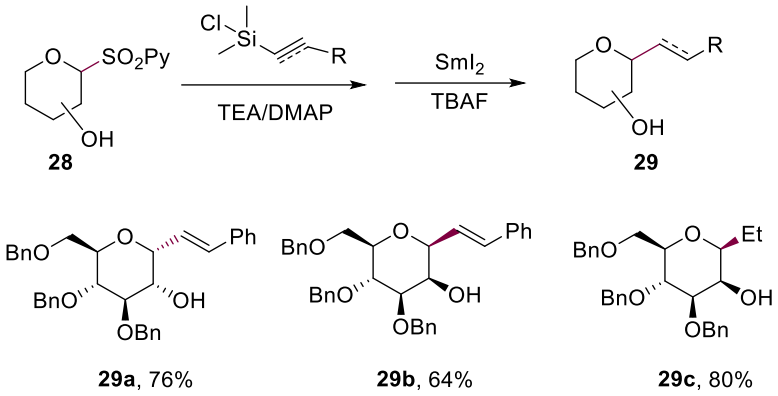
In 2021, the Niu group firstly employed the glycosyl sulfoxides donor **23** as anomeric radical precursor in the presence of Et_3B and air, along with a boron-carbene complex **24**.[36] Capitalizing on a facile radical substitution reaction at the sulfur atom, this method likewise allowed the generation of valuable glycosyl radicals with completely free hydroxyl group in aqueous media and enabled the same transformation (Scheme 1.6.1.3a). Also recently, the Koh group[37] explored that heteroaryl glycosyl sulfones donor **25** can undergo desulfonylative anomeric radical addition by the use of Hantzsch ester and CsOAc under photo irradiation.[38] The *in-situ* formed Hantzsch ester-CsOAc complex contributes to trigger single electron transfer that activate the sulfone and further generate the glycosyl radical. This approach featured broad substrate scope and great applicability and scalability (Scheme 1.6.1.3b).



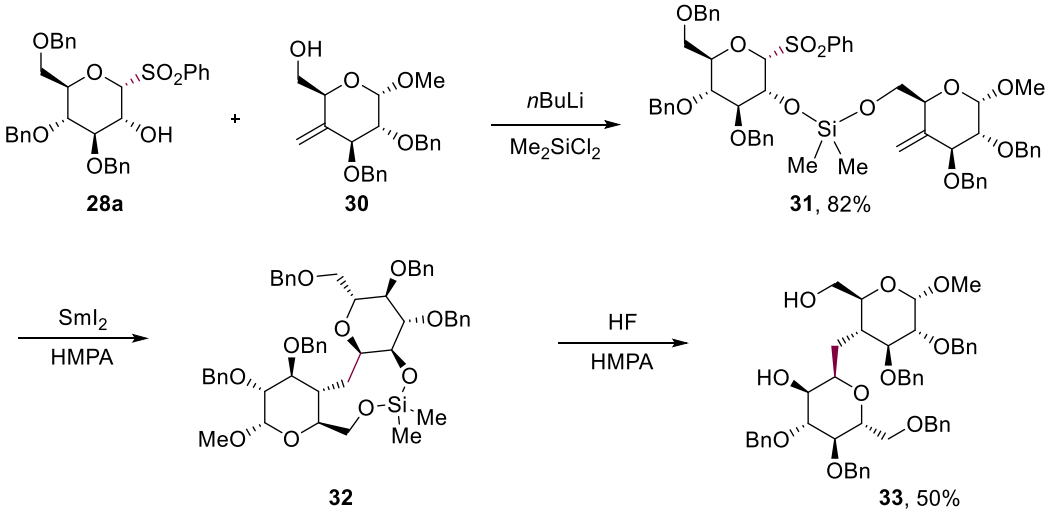
Scheme 1.6.1.3 *C*-Glycosylation with different glycosyl donors.

1.6.2 Samarium Mediated *C*-Glycosylation

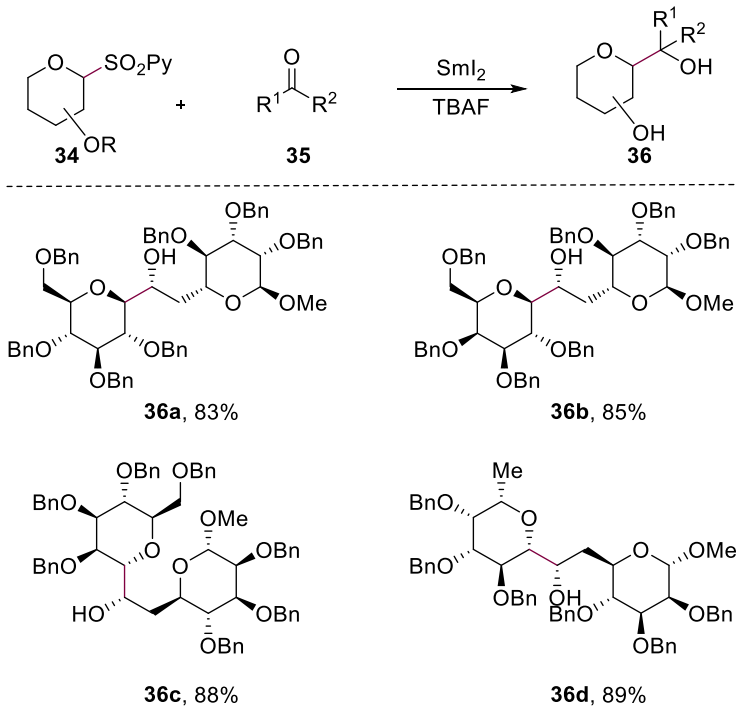
Samarium diiodide (SmI_2) has long been used for C−C bond formation in the total synthesis of natural product.[39] Likewise, it was proved efficient for the reduction of glycosyl pyridyl sulfone, glycosyl phenyl sulfone and glycosyl phosphate[40] to the corresponding anomeric radicals,[41] thus enabling diversified *C*-glycosides construction. By virtue of installation of radical acceptors through a tether,[42] intramolecular radical *C*-glycosylation was secured with high stereoselectivity controlled by the configuration of the hydroxyl group (Scheme 1.6.2.1). In 1994, the Sinay group reported a disaccharide synthesis with glycosyl phenyl sulfone **28a** by treatment of a solution of SmI_2 in THF containing HMPA (Scheme 1.6.2.2).[43] The resulting anomeric radical proceeded with a 9-endo-trig mode of radical cyclization, giving silicon-tethered disaccharide **32**. Thereafter, SmI_2-mediated intermolecular radical addition with aldehyde or ketones **35** has been well-exploited for *C*-disaccharide assembly **36** (Scheme 1.6.2.3).[44]



Scheme 1.6.2.1 SmI_2-mediated intramolecular *C*-glycosylation.

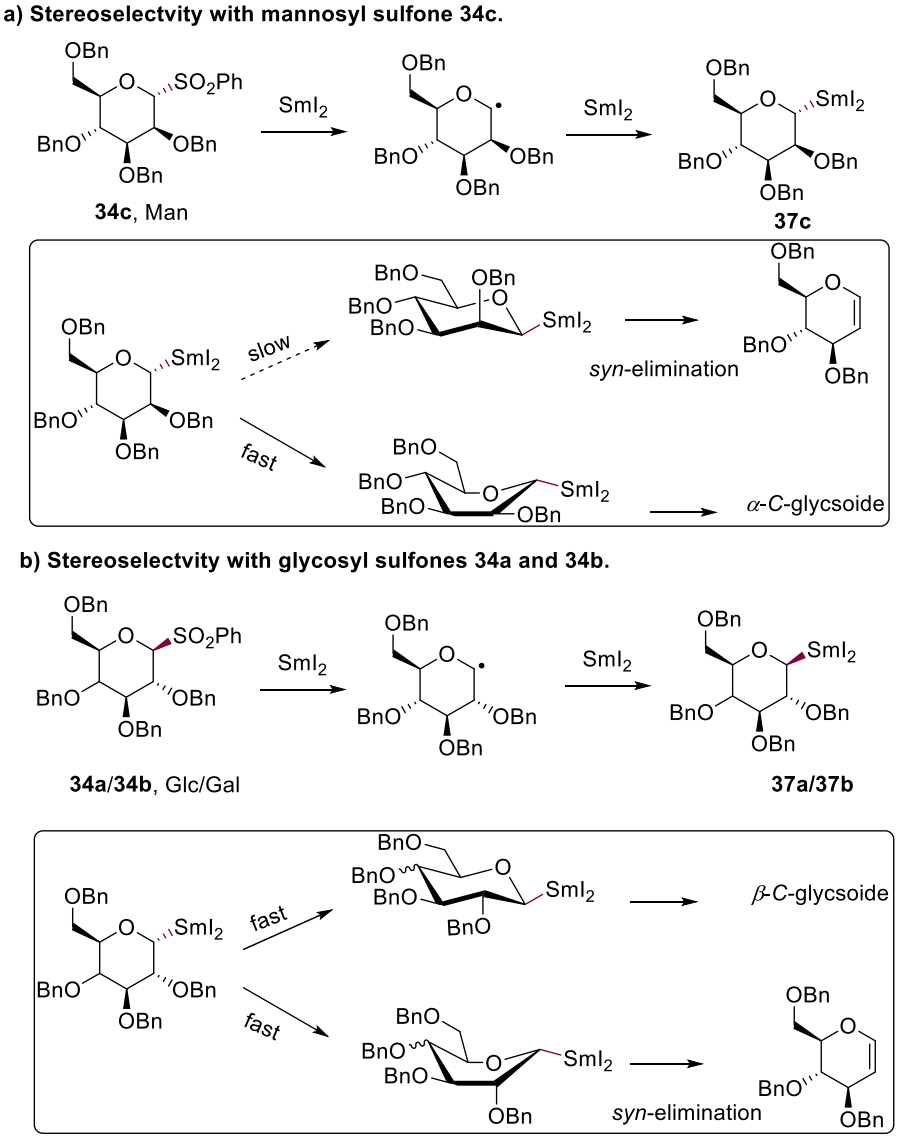


Scheme 1.6.2.2 SmI_2-mediated intramolecular *C*-glycosylation.



Scheme 1.6.2.3 SmI_2-mediated intermolecular *C*-glycosylation.

The stereoselectivity of intermolecular *C*-glycosylation strongly depends on the given carbohydrates (Scheme 1.6.2.4). It was proposed that the SET from SmI_2 to glycosyl sulfone generates thermodynamically stable *α*-anomeric radical. It could be further reduced by SmI_2 to glycosyl anion, which adopts a boat-like conformation in the case of mannose to avoid the repulsive interactions between the Sm-anion and endocyclic lone-pair of the ring oxygen, resulting in *α*-*C*-glycosides (Scheme 1.6.2.4b). Regarding glucose and galactose, there is an equilibrium of boat-like conformation of samarium anion **37a** and **37b**, samarium positioned at axial position will deliver the glycal byproduct *via* a *syn*-elimination. By contrast, the equatorial samarium anion gives a *β*-*C*-glycosides (Scheme 1.6.2.4b).[41c]

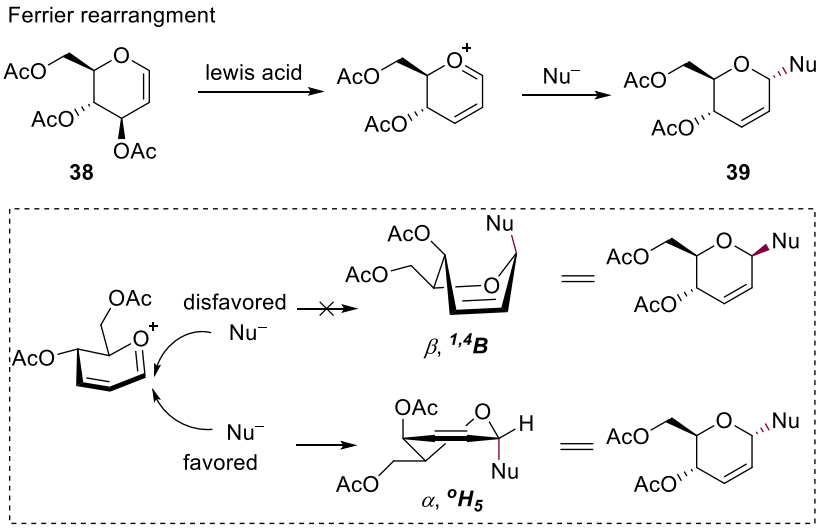


Scheme 1.6.2.4 Stereoselectivity rational.

1.7. *C*-Glycosylation with Glycal

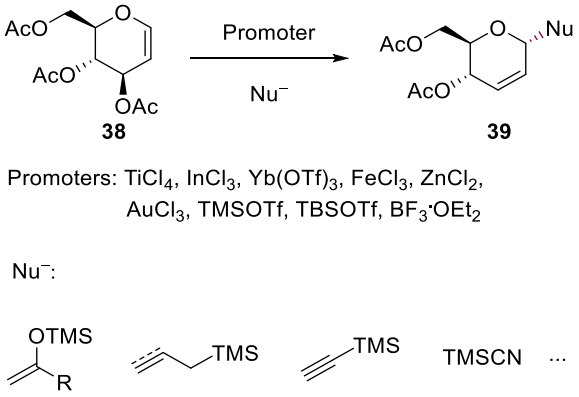
1.7.1 Ferrier-Type *C*-Glycosylation with Glycal

Glycal donors with an endocyclic 1,2-double bond, have been likewise exploited for the construction of anomeric carbon-carbon bonds. The majority of *C*-glycosylation reaction types employing glycals include Ferrier-type rearrangement and palladium-catalyzed Heck-type reaction. It was found that glycals bearing an acetoxyl group at the C3 position will generate oxocarbenium ion with Lewis acid as promoters. The formed oxocarbenium ion can be attacked by a carbon nucleophile. The stereoselectivity is mainly governed by the conformation of oxocarbenium intermediate and the attack pathway. The bottom face attack leads to favored half-chair conformation $^{o}H_{5}$, instead of the top face attack, giving the disfavored boat conformation $^{1,4}B$. Thus, the *α*-anomer is typically the major product (Scheme 1.7.1.1).



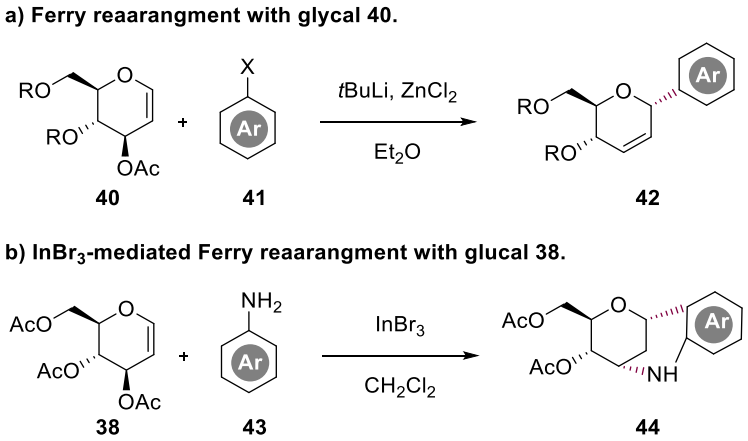
Scheme 1.7.1.1 Ferrier-type *C*-glycosylation.

Silyl nucleophiles, such as allylic silanes, propargyl silanes and also vinyl silyl ethers, were ideal nucleophiles. The reaction with acetyl-protected glucal **38** which can be activated with Lewis acids such as $TiCl_4$, $InCl_3$ and $BF_3.OEt_2$, led to the formation of 2,3-unsaturated glycosides **39**. The stereochemical outcome of the reactions generally favors the *α*-isomer (Scheme 1.7.1.2).



Scheme 1.7.1.2 Lewis acid promoted *C*-glycosylation.

The Du Bois group found that the halide-lithium exchange of aryl halide enabled the in-situ formation of aryl zinc reagents, and proved amenable for the Ferrier rearrangement, giving the C1 arylated glycosides. **42** (Scheme 1.7.1.3a).[45] In 2003, Yadav disclosed a novel one-pot synthesis of new benzo-fused heterobicycles from glucal **38** and aryl amines **43** using a catalytic amount of $InBr_3$ under mild reaction conditions (Scheme 1.7.1.3b).[46]

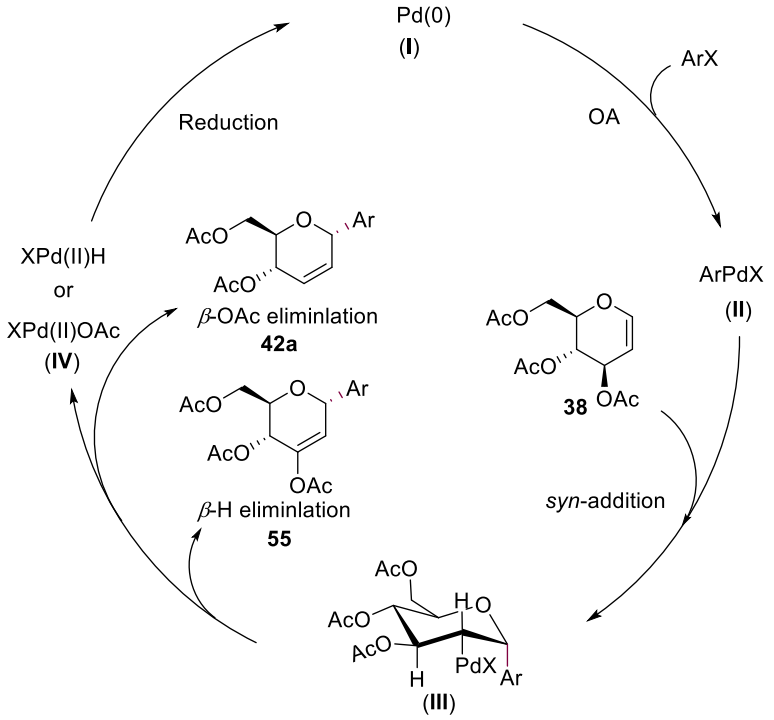


Scheme 1.7.1.3 Ferrier rearrangement for *C*-glycosylation.

1.7.2 Mizoroki-Heck Type *C*-Glycosylation with Glycal

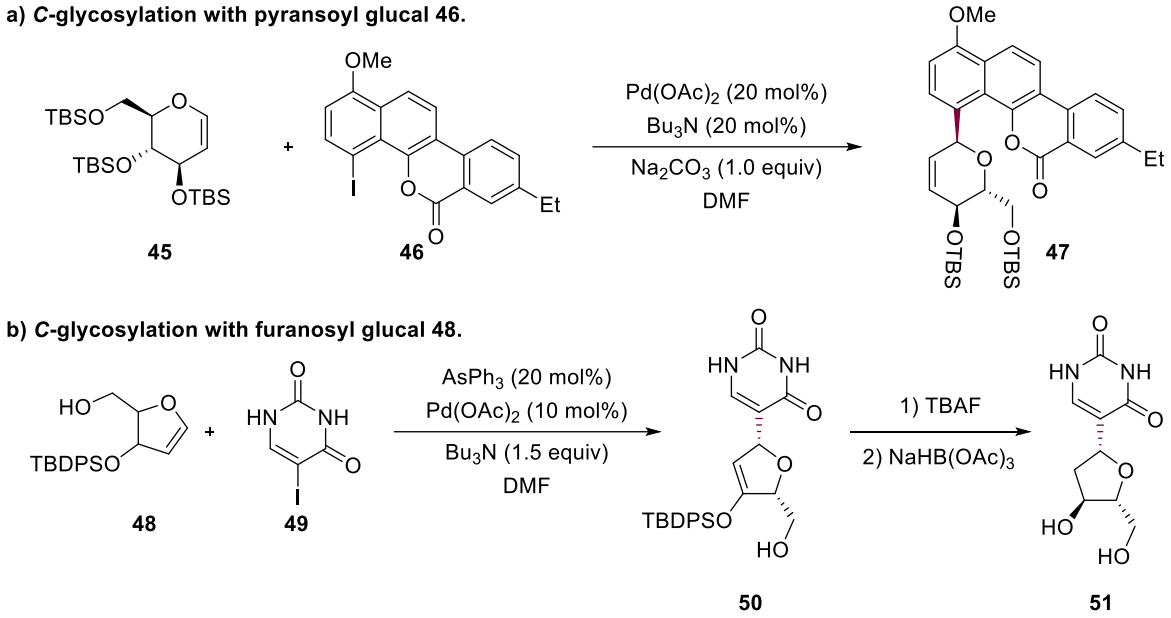
The 2010 Nobel-winning Mizoroki–Heck reaction is commonly used to construct C–C bond in organic syntheses. Given the vinyl motif of glycals, the Mizoroki–Heck reaction is expected to be a reliable synthetic method toward *C*-glycosides. A general mechanism of Mizoroki–Heck C-glycosylation reaction is shown below (Scheme 1.7.2.1). The oxidative addition is initiated by palladium(0), generating organopalladium(II) complex. Then coordination and subsequent migratory insertion followed to form glycosyl palladium complex **III**. This intermediate can undergo either

β-hydride elimination or *β*-acetoxyl elimination. The released palladium(II) can be reduced to regenerate palladium(0) for the next catalytic cycle.



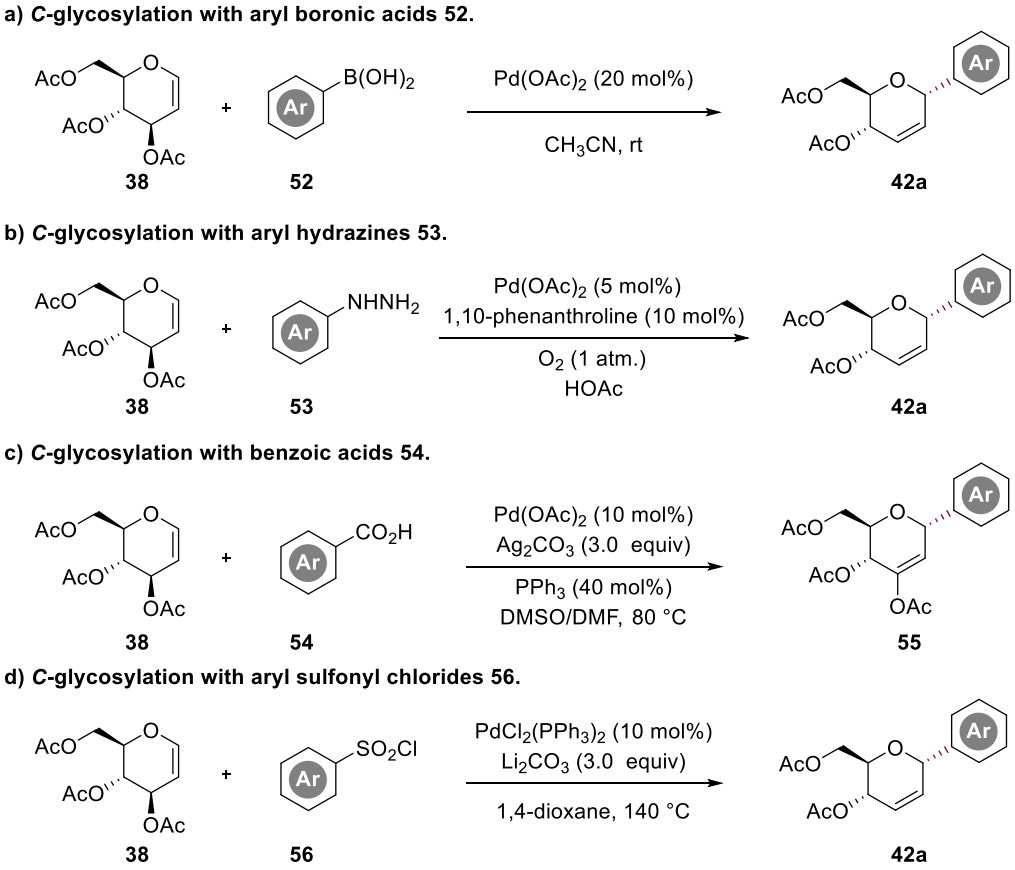
Scheme 1.7.2.1 Catalytic cycle of Mozoroki-Heck type *C*-glycosylation.

Mozoroki-Heck type *C*-glycosylation has emerged as an efficient method for biological molecular synthesis. Efficient coupling of iodo-derivatives of anthracycline aglycons with furanose and pyranose with pyranosyl glycals was achieved in the presence of palladium acetate and a tertiary amine in DMF solution (Scheme 1.7.2.2a).[47] It provided an effective route to 2,3-unsaturated aryl glycosides **47** *via* β-heteroatom elimination. Similarly, 5-iodouracil **49** as the coupling electrophile undergoes regio- and stereoselective coupling with ribofuranoid glycal **48**.[48] The resulting enolate *C*-glycoside **50** derived from a *β*-hydride elimination could be further converted to 2'-deoxypseudouridineby **51** by a desilylation/reduction sequences (Scheme 1.7.2.2b).



Scheme 1.7.2.2 Examples of Mozoroki-Heck type *C*-glycosylation.

Thereafter, Maddaford devised a practical and convenient stereoselective method for the synthesis of *C*-aryl glycosides with the use of aryl boronic acids **52** in the presence of catalytic amounts of palladium acetate.[49] It was proposed that the *syn*- addition of aryl palladium(II) complex and anti-*β*-elimination will generate the *C*-Ferrier products **42a** preferentially under mild condition (Scheme 1.7.2.3a). Furthermore, the substrate scope for *C*-aryl glycosides was extended to aryl hydrazine **53** as the coupling partner,[50] which avoids the use of highly explosive and decomposable diazonium salts (Scheme 1.7.2.3b). The pure *α*-*C*-glycosides were obtained with glycal bearing an equatorial *C*3-acetoxyl group, whereas *α*/*β* mixtures were observed with *C*3 axial acetoxyl protected glycals. Liu found that replacing aryl hydrazine with commercially available benzoic acids will deliver *C*-aryl glycosides in the presence of silver carboxylate and catalytic palladium acetate in DMSO/DMF *via* a *β*-hydride elimination pathway (Scheme 1.7.2.3c).[51] However, the palladium-catalyzed decarboxylative *C*-glycosylation is limited to electron-rich benzoic acids. Aryl sulfonyl chlorides as aryl source were involved in various transformations. The desulfitative direct *C*-arylation of glycal was thus disclosed by Mukherjee with the use of $Pd(PPh_3)_2Cl_2$ as catalyst and Li_2CO_3 in dioxane, albeit at high temperature (Scheme 1.7.2.3d).[52]



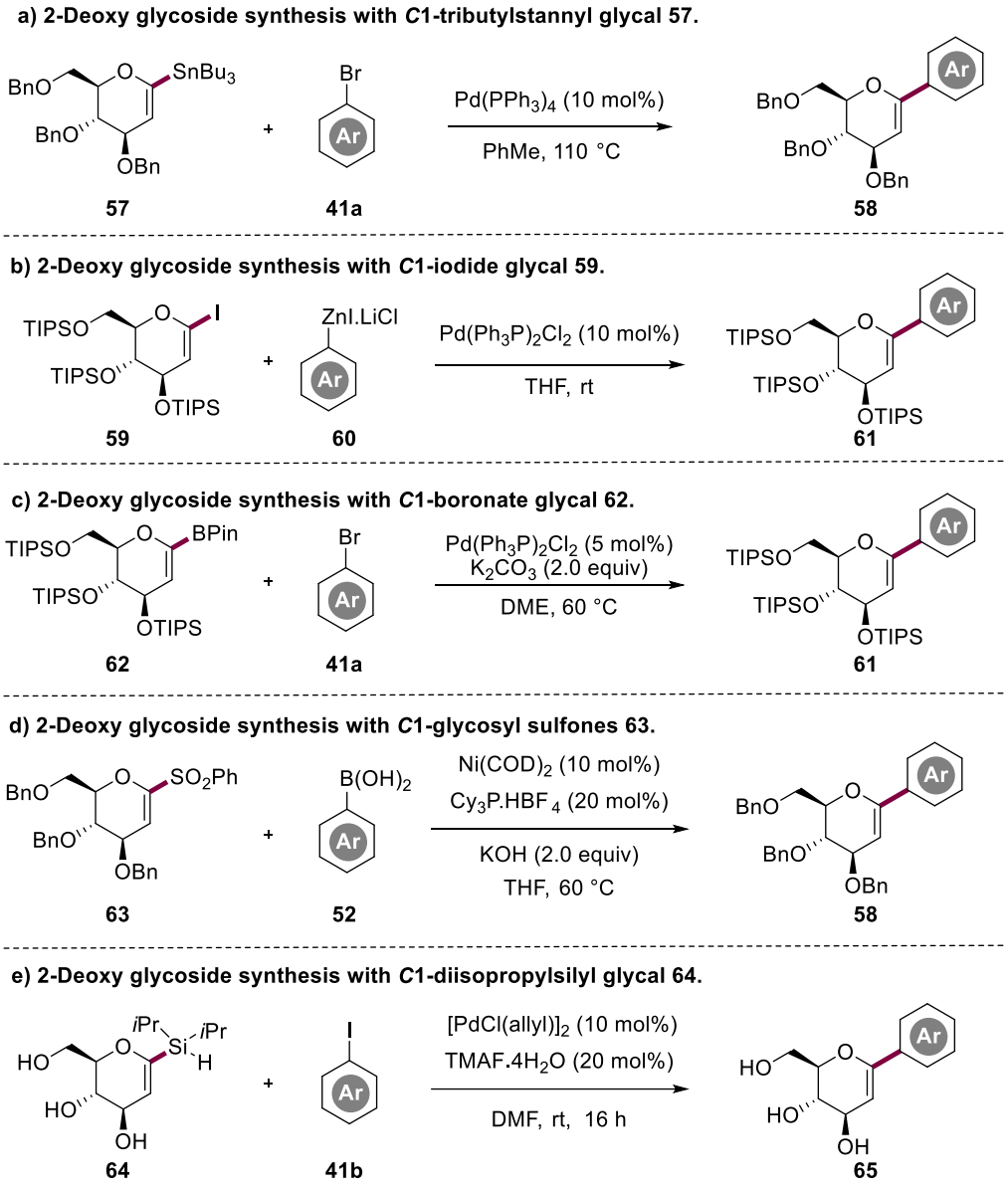
Scheme 1.7.2.3 Mozoroki-Heck type *C*-glycosylation with versatile coupling partners.

1.8. *C*-Aryl Glycosides Synthesis by Cross Couplings

1.8.1. 2-Deoxy *C*-Aryl Glycosides Synthesis by Cross Couplings

Cross-couplings have been utilized as an efficient tool for the 2-deoxy *C*-aryl glycosides assembly, especially *Stille* cross-coupling reactions, which was well documented with the benzyl protected 1-tributylstannyl glycal **57** and aryl bromide **41a** under palladium(0) catalysis (Scheme 1.8.1.1a).[53] The limitation is the lengthy synthesis for the preparation of tributylstannyl glycal **57** derived from unsaturated sulphones, thus triisopropyl silyl protected glycosyl iodide **59** as electrophile was employed for pseudo-*C*-glycoside synthesis with aryl zinc nucleophiles **60** (Scheme 1.8.1.1b).[54] The 1-iodo-glycal **59** could be readily available *via* a one-pot two-step sequence with selective *C*1-stannylation and tin-iodide exchange, but they are inherently unstable. In 2012, Sakamaki adopted non-toxic, easy-to-hand glucal boronates as nucleophiles,[55] and its robustness was further demonstrated by the synthesis of bergenin derivative (Scheme 1.8.1.1c).[56] In 2019, bench-stable 1-sulfonyl glycals **63** was used as an alternative to the 1-iodo-glycal **59** as the electrophilic

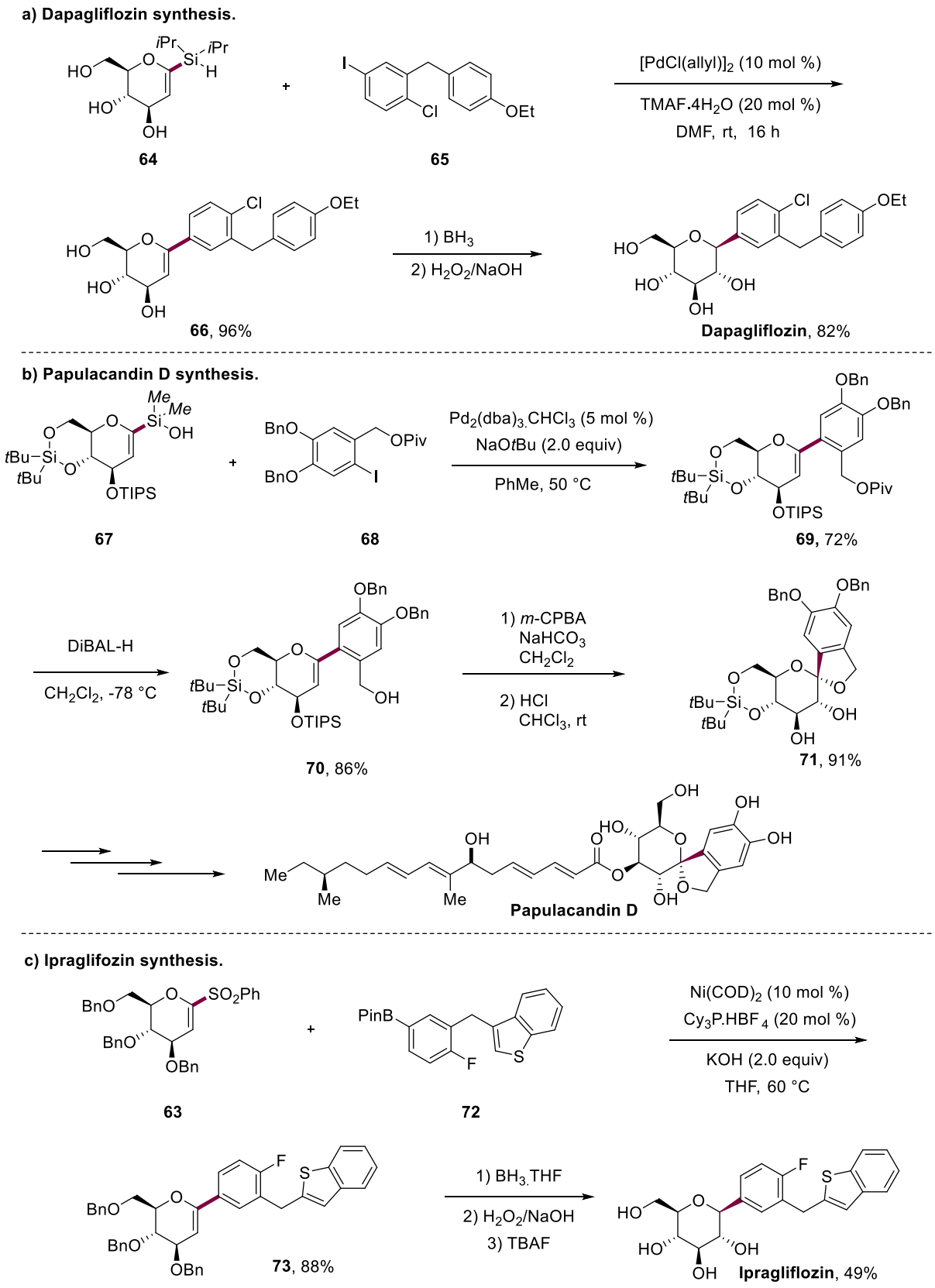
coupling partners for a nickel-catalyzed Suzuki-Miyaura cross-coupling reaction with phenyl boronic acid **52** (Scheme 1.8.1.1d).[57] Very recently, a facile approach to *C*-aryl glycosides was updated with Hiyama cross-coupling reaction, in which a protecting group-free and scalable 1-diisopropylsilyl-D-glucal **64** was used under mild reaction conditions (Scheme 1.8.1.1e).[58]



Scheme 1.8.1.1 Cross couplings for 2-deoxy *C*-aryl glycoside assembly.

In addition, the unsaturated pseudo-*C*-glycoside bearing an endocyclic vinyl moiety could be stereo-selectively converted into diversified glycosides, such as *α*- and *β*-*C*-aryl glycosides, as well as 2-deoxy-glycosides, and thus emerged as important precursors for the synthesis of targeted natural products and drugs. For example, *dapagliflozin*, an approved inhibitor for the treatment of type 2 diabetes, could be

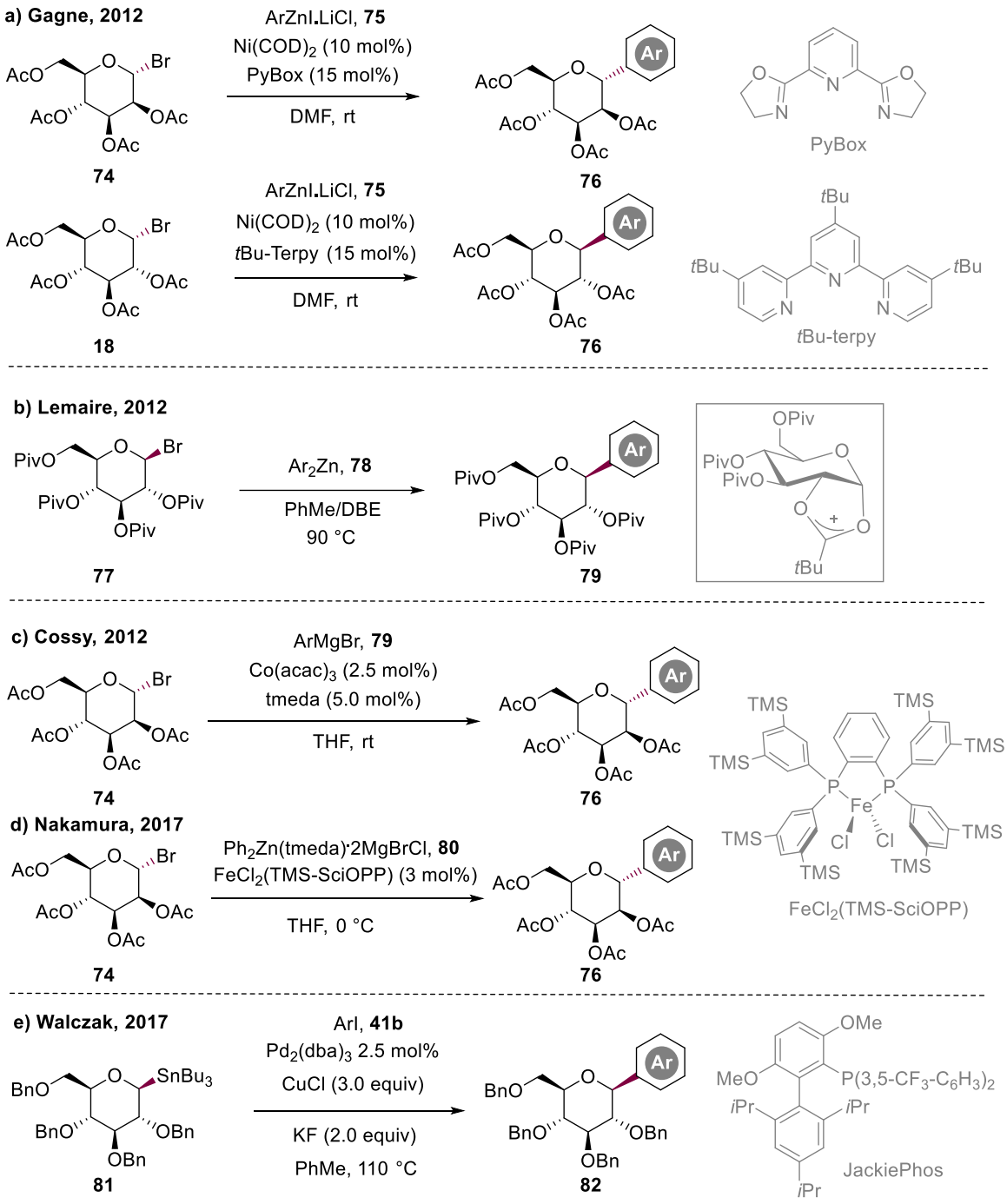
efficiently constructed via a Hiyama cross-coupling and hydroboration-oxidation sequences (Scheme 1.8.1.2a).[58] Since the high cost of organic soluble and corrosive fluoride reagents used for nucleophilic activation of glycosyl silanol donors **67** to form pentacoordinate siliconate, a fluoride-free Denmark-Hiyama cross-coupling reaction was developed and offered an efficient tool for the total synthesis of *Papulacandin D* (Scheme 1.8.1.2b).[59] The potential utility of Suzuki-Miyaura cross-coupling was also demonstrated by the synthesis of *Ipragliflozin* with sulfonyl glycal **63** and aryl boronate **72** (Scheme 1.8.1.2c).[60]



Scheme 1.8.1.2 Synthetic application of cross-couplings to bioactive saccharides.

1.8.2 *C*-Aryl Glycosides by Cross-Couplings

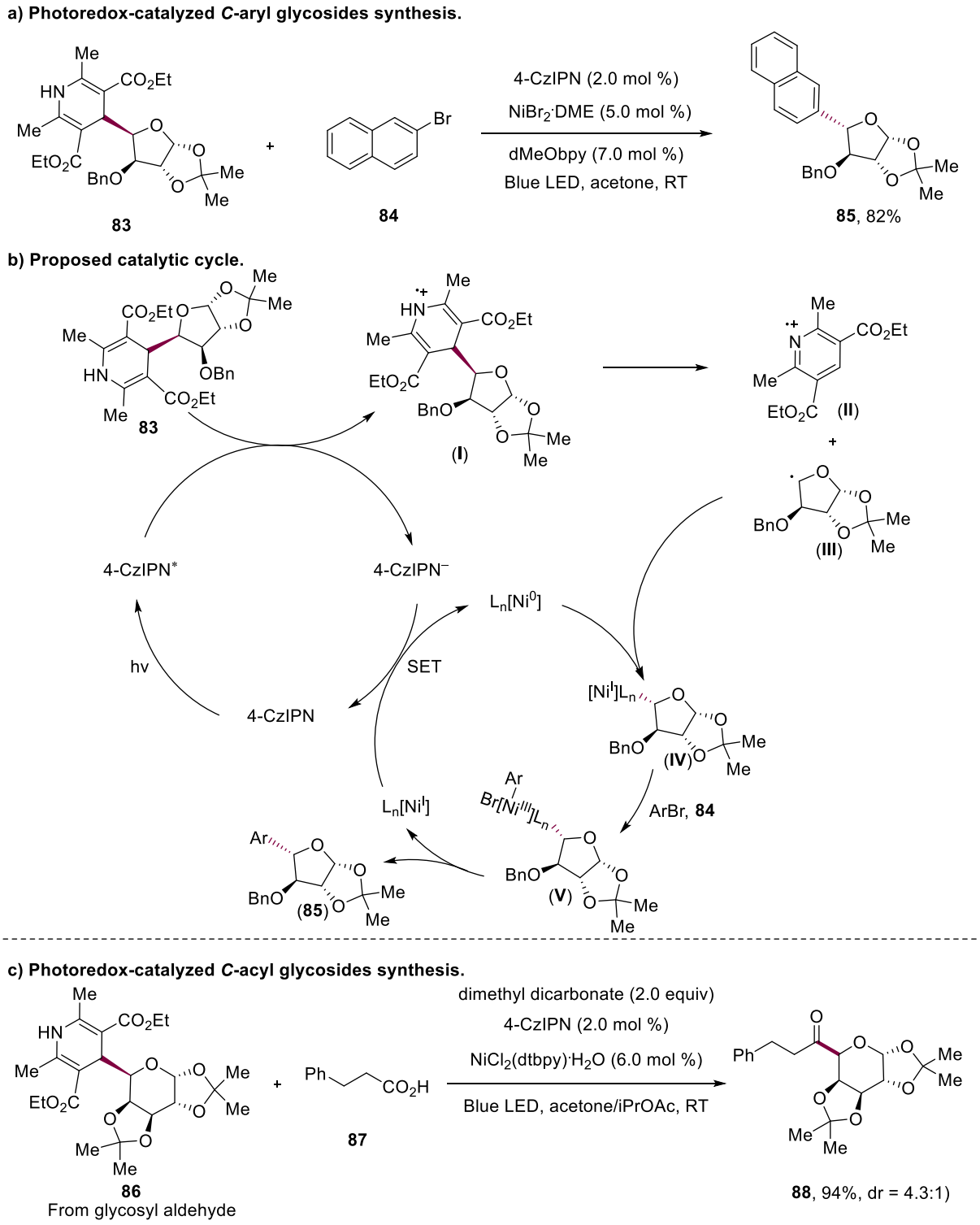
Although pseudo *C*-glycoside could be easily transformed into *C*-aryl glycosides, and also readily available *via* cross-couplings with versatile electrophilic or nucleophilic glycal, the tedious synthetic steps restricted its further application. Alternatively, the glycosyl halide as electrophiles was directly utilized. The pioneering work from Gagne group was developed with the nickel-catalyzed Negishi cross-coupling reaction to fully oxygenated *C*-aryl glycosides **76**. Reactions employing $Ni(COD)_2$ as catalyst and *t*Bu-Terpy as ligand in DMF provided *C*-glucosides with high *β*-selectivity (Scheme 1.8.2.1a). Noteworthily, when mannosyl bromide as electrophile gave *C*-aryl mannoside **76** with moderate selectivity by the combination of a $Ni(COD)_2$ and PyBox ligand. These findings indicated that the stereochemical control of *C*-aryl glycsoides relied on the substrate and the catalyst. Meanwhile, Lemaire and Knochel found that *C*-aryl glycosides could be obtained directly with aryl zinc reagents **78** and pivaloyl protected glycosyl bromides **77** (Scheme 1.8.2.1b).[61] The metal-free approach was explained by the anchimeric assistance of the *C*2 pivaloyl group. Thereafter, 3d metal catalysis was also reported for the *C*-aryl glycoside synthesis, such as cobalt catalysis (Scheme 1.8.2.1c)[62] and iron catalysis (Scheme 1.8.2.1d).[63] In 2017, Walczak described the preparation of glycosyl anomeric stannanes **81**, and allowed the synthesis of pure *α*- or *β*-glycosyl stannanes nucleophiles.[64] Equipped with such glycosyl donor reagents, the coupling partner of the often toxic or dangerous organometallic aryl nucleophile could be replaced with commercially available aryl halides (Scheme 1.8.2.1e). Thus, glycosyl cross-coupling was established with catalytic $Pd_2(dba)_3$ and a bulky JackiePhos ligand, resulting in high anomeric selectivity.



Scheme 1.8.2.1 Cross-couplings for *C*-glycosylation.

In 2018, Molander reported cross-coupling reactions of glycosyl dihydropyridine **83** with aryl halides **84** in the presence of photoredox and nickel catalysts.[65] The dual catalysis reaction proceeded by visible-light irradiation with inexpensive organic dye 4-CzIPN, along with $NiBr_2$·DME and dMeObpy with dihydropyridine glycosides and aryl halides in acetone to generate aryl-*C*-glycosides **85** (Scheme 1.8.2.2a). The proposed mechanism involved two interdependent catalytic cycles. Irradiation of 4-CzIPN with

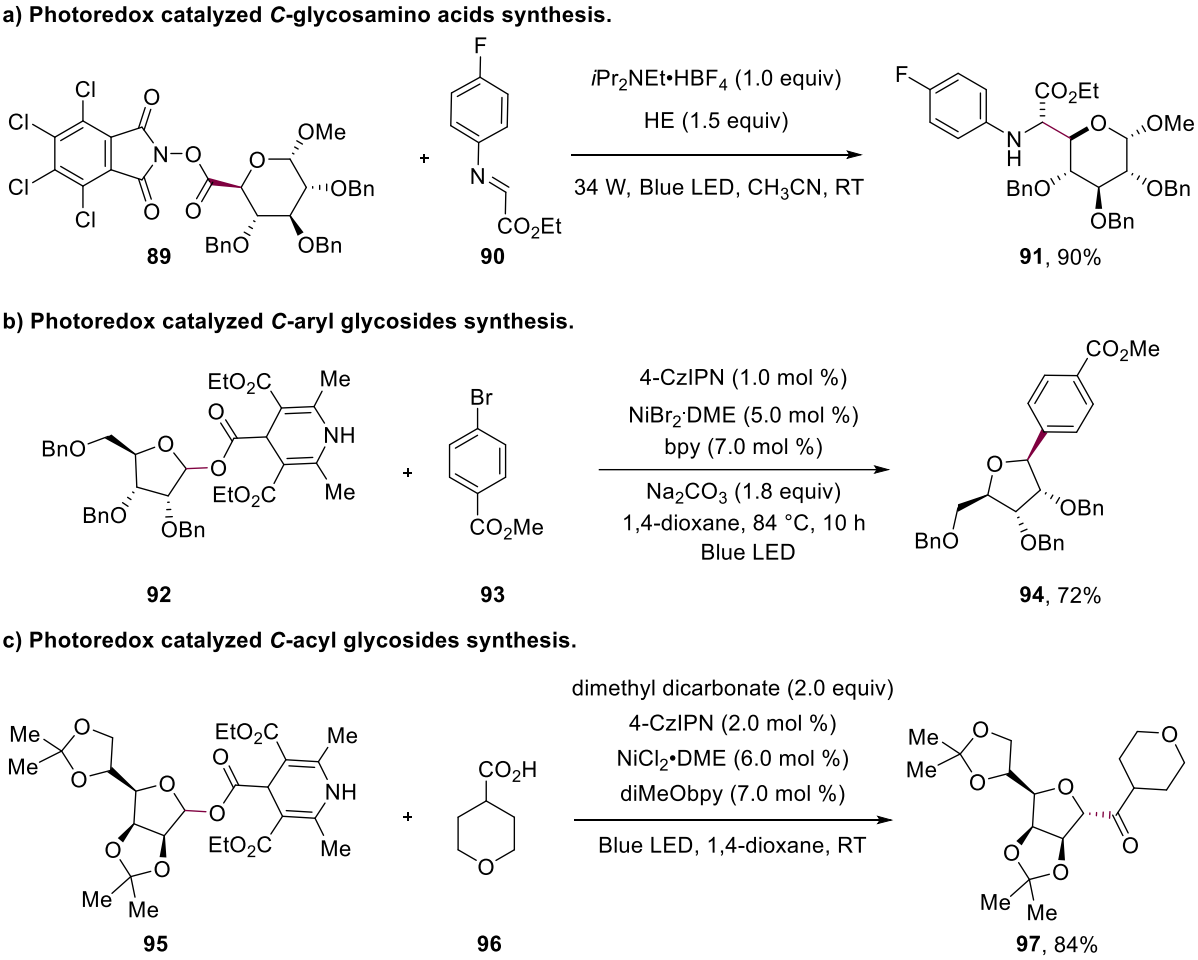
blue LEDs results in the strongly oxidizing excited state 4-CzIPN*, and then the SET reduction by glycosyl dihydropyridine to afford a radical cation (I), followed with fragmentation to a generate glycosyl radical (**III**). Meanwhile, the nickel complex $L_n[Ni^0]$, generated from $NiBr_2$·DME, undergoes rapid reaction with the glycosyl radical (**III**) to generate nickel(I). Then oxidative addition proceeds with aryl bromide to generate nickel(III) complex. The high oxidation state of the nickel complex then follows with a reductive elimination to deliver *C*-aryl-glycoside **85** and nickel(I) complex. The SET process between photo-reduced 4-CzIPN radical anion and $Ln[Ni^I]$ to finish the catalytic cycle, and regenerate the $L_n[Ni^0]$ (Scheme 1.8.2.2b). A silmilar transformation for the synthesis of *C*-acyl glycoside **88** was also developed with carboxylic acids **87** through *in-situ* formation of acyl carbonate with dimethyl dicarbonate under photoredox and nickel catalysis (Scheme 1.8.2.2c).[66]



Scheme 1.8.2.2 *C*-Glycosylation with glycosyl dihydropyridine.

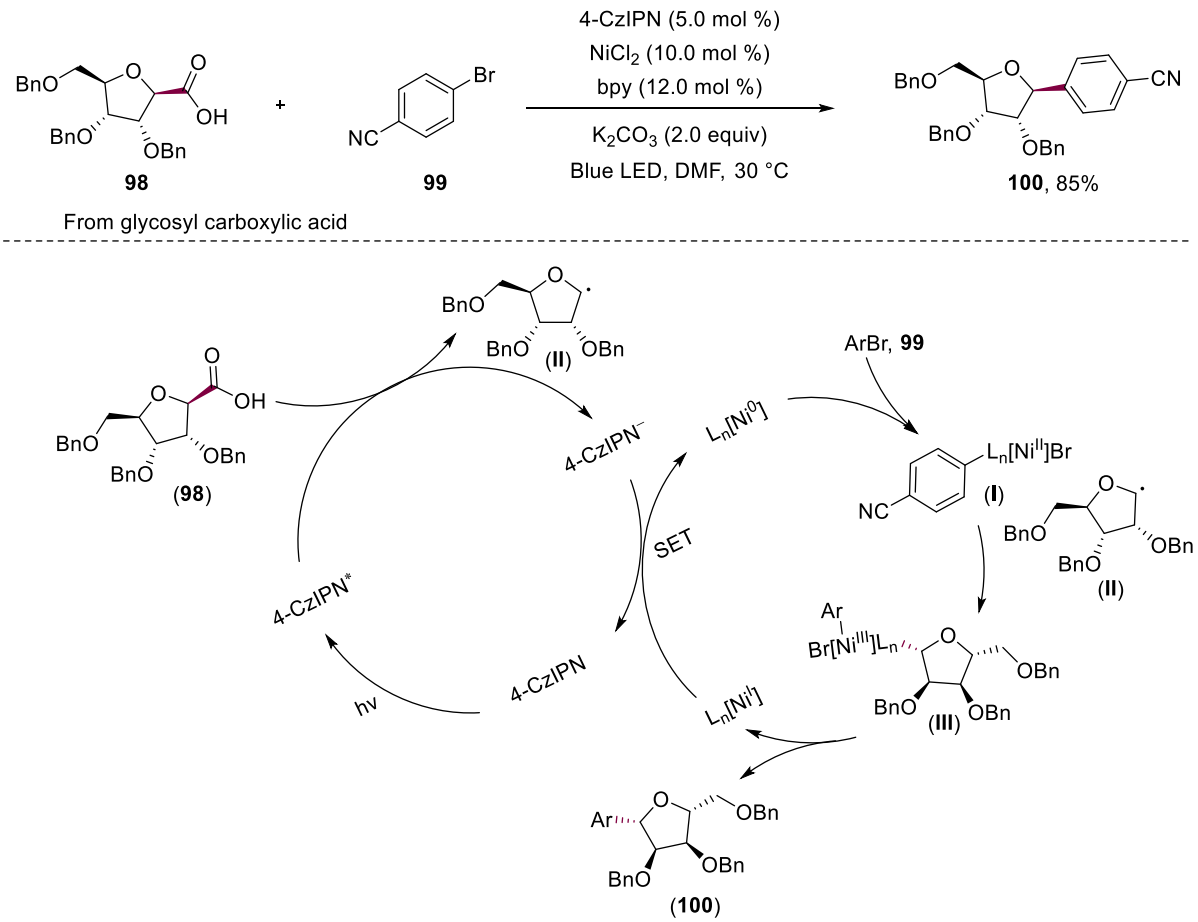
Subsequently, Wang devised a glycosylation redox ester **89** derived from glycsoyl carboxylic acids.[67] It allowed the efficient synthesis of *C*-glycosyl amino acids **91** with HE under visible light irradiation, in which *α*-imino esters serve as electrophiles in a

chemo-selective addition reaction with nucleophilic glycosyl radicals (Scheme 1.8.2.3a).



Scheme 1.8.2.3 *C*-Glycosylation with glycosyl dihydropyridine-derived glycosyl ester.

Although those transformation enabled the synthesis of *C*-aryl glycosides, the synthesis of dihydropyridine-derived glycoside or glycosyl redox ester **89** involved labor-intensive and time-consuming multiple synthetic procedures. In this context, a simpler and more efficient synthetic protocol was disclosed by the Diao group.[68] The easily available glycosyl anomeric hydroxide was utilized for the preparation of dihydropyridine-based glycosyl anomeric ester **92**, and involved in the photoredox/nickel cross-coupling reaction, demonstrating the applicability for the *C*-aryl and *C*-acyl glycosides assembly **94** and **97** (Scheme 1.8.2.3b and 1.8.2.3c).

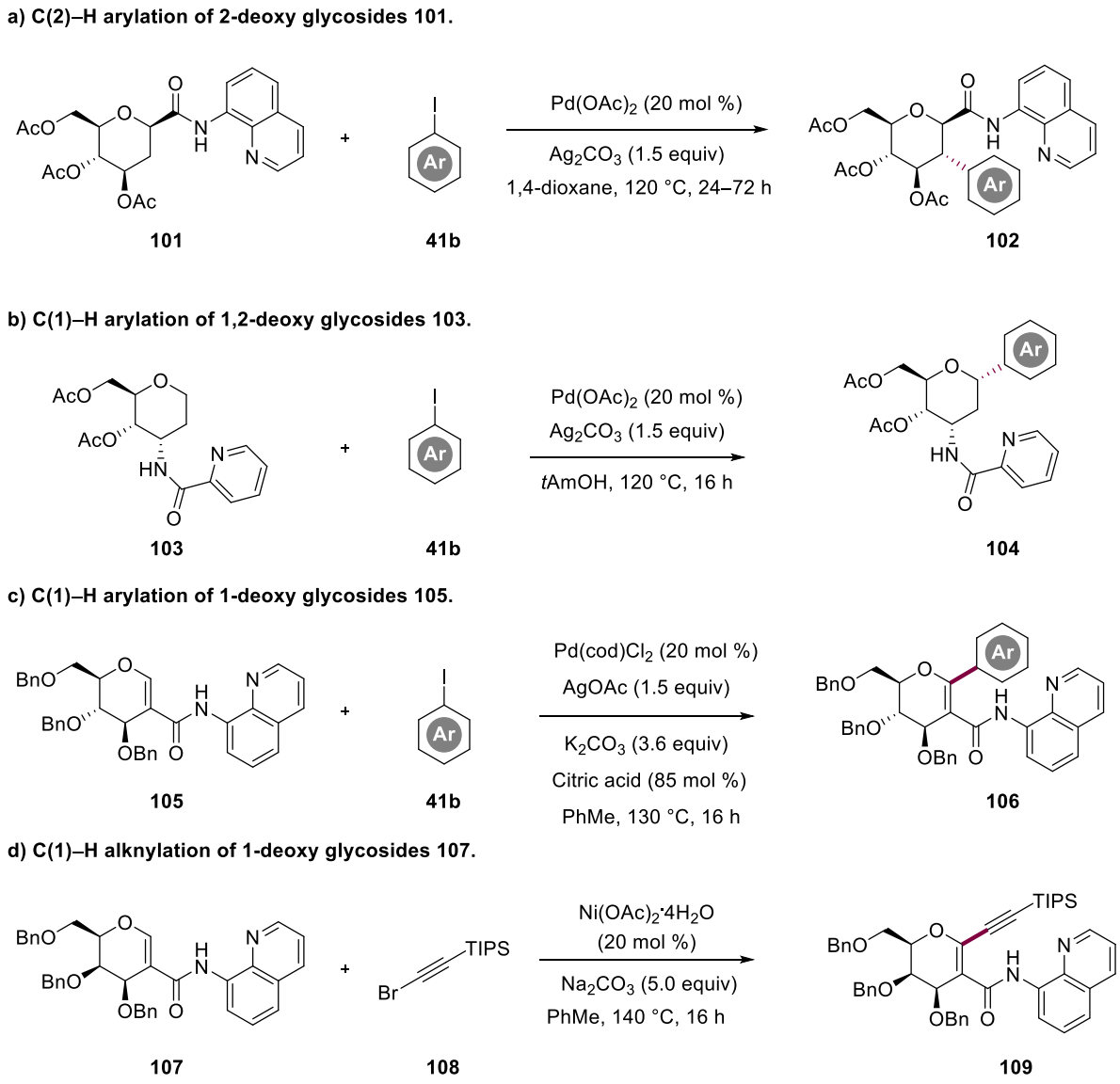


Scheme 1.8.2.4 *C*-Glycosylation with glycosyl carboxylic acid **98**.

In 2019, the Wang group reported on the decarboxylative arylation of ribosyl carboxylic acid **98** through a photoredox/nickel dual catalysis.[69] The reaction proceeded smoothly with the cost-effective and user-friendly catalyst, allowing stereoselective synthesis of diverse *C*-aryl nucleosides **100**. It was proposed that the nucleophilic ribosyl radical was formed by the SET reduction of glycosyl carboxylic acid **98**. Concurrent with generation of reducing photocatalyst, the active Ni(0) species *in-situ* formed *via* two SET reductions of the (bpy)Ni(II)Br_2. The following oxidative addition of aryl bromide **99** delivers ArylNi(II)Br (**I**), and then rapidly intercept anomeric ribosyl radical (**II**), give aryl Ni(III)-ribosy complex (**III**), which should undergo reductive elimination to produce the desired product **100** (Scheme 1.8.2.4).

1.9. *C*-Glycosylation by C−H Functionalization

1.9.1. Directed C−H Functionalization of Glycosides

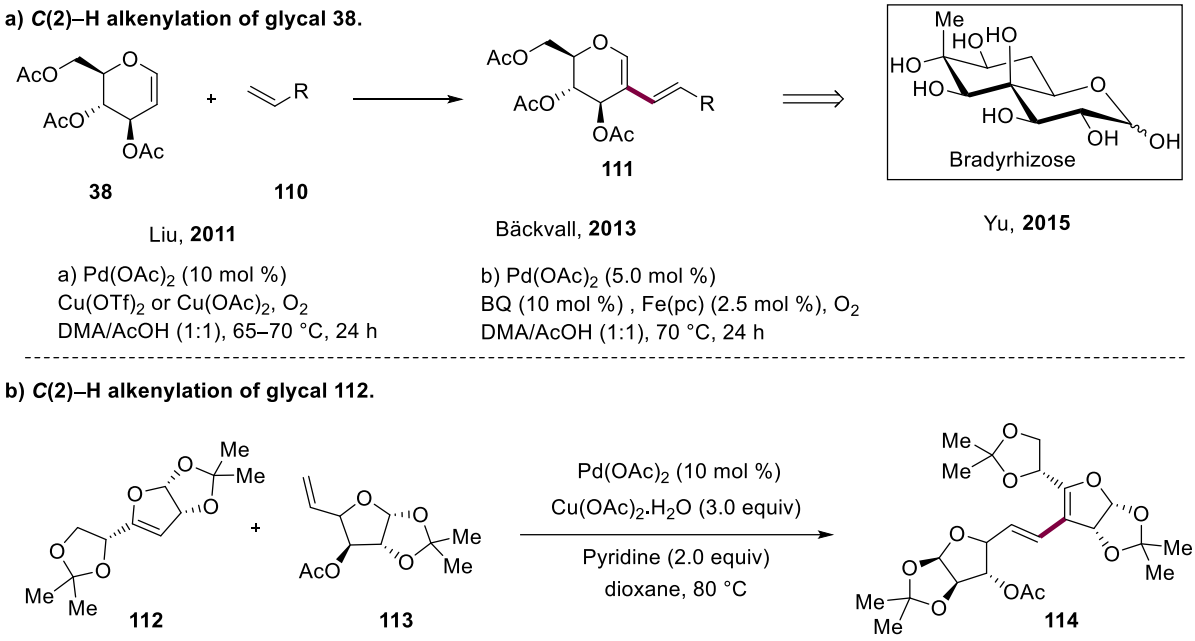


Scheme 1.9.1.1 *C*-Glycosylation by C−H functionalization of glycosides.

By rational design of glycosides, the selective functionalization of glycosides enabled the late-stage modification of glycosides. Here, the Messaoudi group reported the diastereoselective C(sp^3)−H arylation of glycosides **101**, paving the avenue to access series of *C*(2)-aryl glycosides **102** (Scheme 1.9.1.1a).[70] This approach exhibited for the first time a 2,3-*trans* arylation selectivity. Then, by introducing the picolinic amide auxiliary at the *C*(3) axial position of glycosides **103**, the same group developed a new approach to the anomeric selective arylation (Scheme 1.9.1.1b).[71] Detailed experimental and computational mechanistic studies proved that the anomeric arylation control is governed by the spatial positioning of the directing group. Installation of the bidentate aminoquinoline auxiliary at the *C*(2) position of 1,2-unsaturated glycal **105** and **107**, Ferry group likewise accomplished *C*(1)-arylation

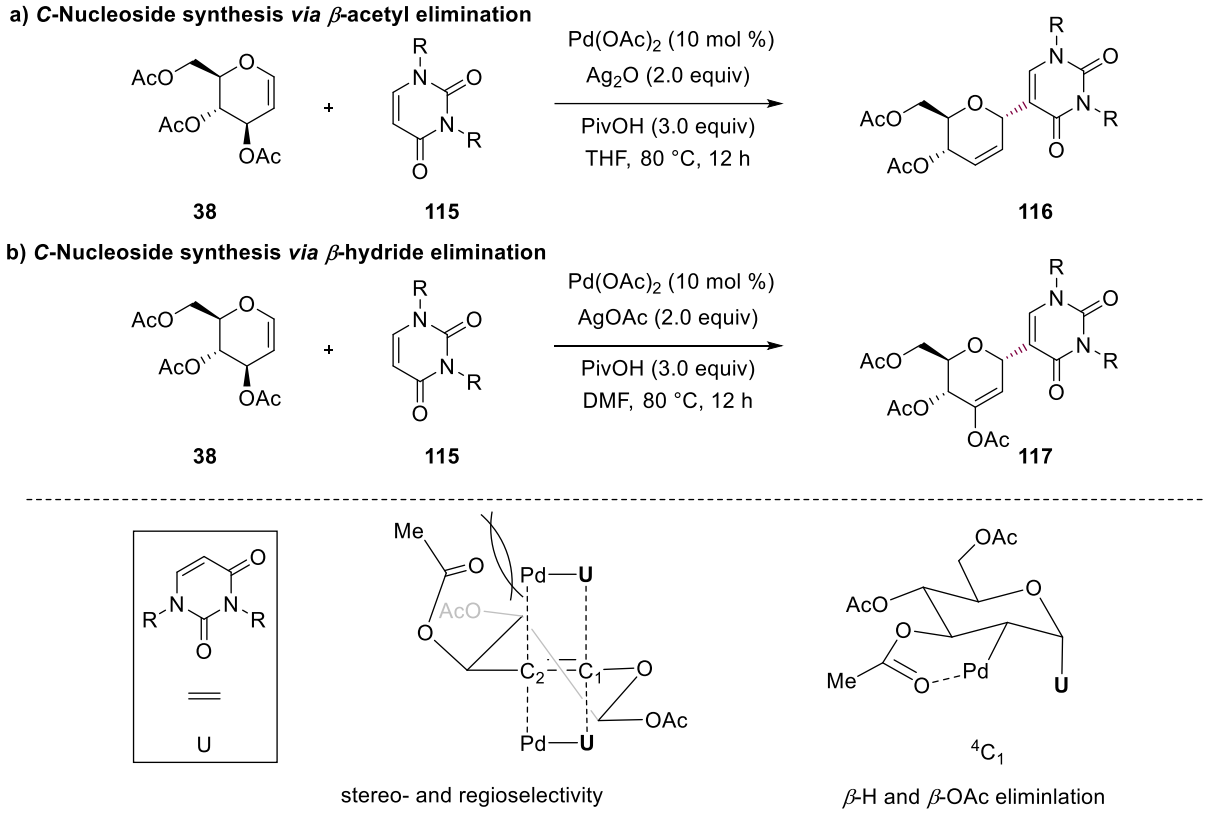
(Scheme 1.9.1.1c)[72] and *C*(1)-alkynylation (Scheme 1.9.1.1d)[73] by palladium catalysis and nickel catalysis, respectively.

1.9.2. Non-Directed C−H Functionalization of Glycal



Scheme 1.9.2.1 *C*-Vinyl glycoside by C−H alkenylation of glycal.

The Liu group reported on the palladium(II)-catalyzed cross-coupling reaction of glycal **38** with activated alkene **110** (Scheme 1.9.2.1aa).[74] Sine the *C*(2) position is more electron-rich, the electrophilic C–H palladation allowed the selective activation of glycal **38**, and then followed with migratory insertion, *β*-hydride elimination and regeneration of palladium(II) catalyst by stochiometric amounts of copper oxidant under an O_2 atmosphere. The non-directed C–H glycosylation featured excellent *E*-selectivity and its robustness was further exemplified by the total synthesis of bradyrhizose by Yu group.[75] Thereafter, a more general protocol was devised by Bäckvall for non-directed *C*(2)-glycal alkenylation with activated and inactivated olefins (Scheme 1.9.2.1ab).[76] The reaction condition is more environmentally benign with the use of catalytic amounts of catalyst and oxidant loading. The BQ and Fe(Pc) were utilized as redox moderators in the presence of O_2, and thus avoided the stoichiometric amount of the copper oxidant. Then, Mukherjee also developed the cross dehydrogenative coupling strategy for the *C*(2)-pyran and *C*(2)-furan alkenylation (Scheme 1.9.2.1b).[77]



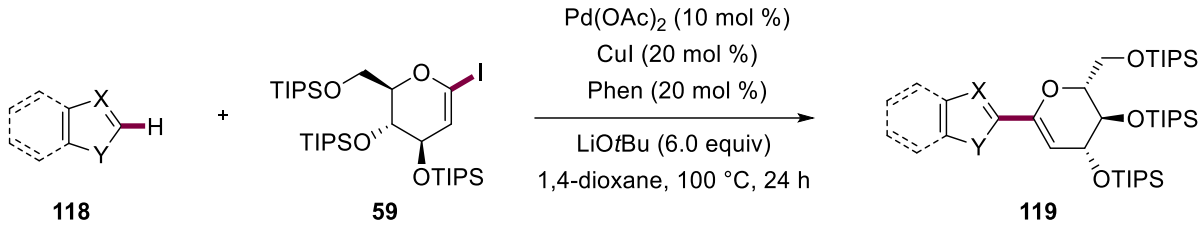
Scheme 1.9.2.2 *C*-Vinyl glycoside by C−H alkenylation of glycal.

Palladium(II)-catalyzed regio- and stereo-selective *C*-nucleoside synthesis was explored by the Mukherjee group with pyranoid glycal **38** and uracils **115** (Scheme 1.9.2.2).[78] Slightly different reaction conditions allowed to access *β*-hydride or *β*-acetyl eliminated *C*-nucleosides **116** and **117** selectively. Mechanistic studies revealed that the first electrophilic C–H palladation selectively occurred at the *C*5 position of uracil, instead of the *C*2 position of glycal. The formed organopalladium species then attacked the glycal regio-selectively and stereo-selectively. Due to the steric hindrance of *C*3 acetyl group, the migratory addition was only favored from the *α*-face. Meanwhile, the *C*(2) glycosyl palladacycle in $^4C_1$ conformer feature lower activation energy due to the *C*(3) acetyl coordination. The *anti*-elimination of acetate and palladium gave the Ferrier *C*-nucleosides product **116** (Scheme 1.9.2.2a). When changing the solvent from THF to polar DMF, it undergoes *syn*-hydride elimination to give **117** (Scheme 1.9.2.2b).

1.9.3. Non-Directed C−H Glycosylation

Heteroaryl *C*-glycosides possess a wide range of biological activity, such as glycosidase inhibition, antibacterial and antifungal activity. Hence, a general synthetic

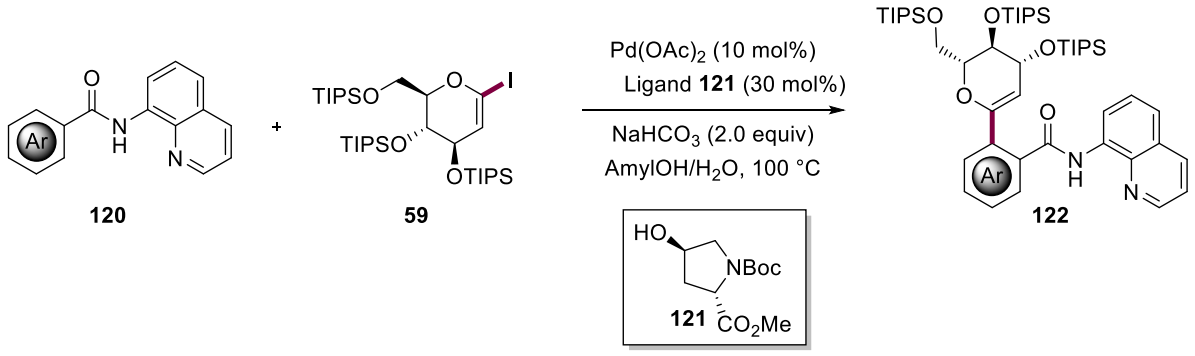
approach for heteroaryl *C*-glycoside synthesis is valuable. Based on various methods for the arylation of heterocycles with palladium and copper catalysis, the non-directed glycosylation of heteroarenes was envisioned.[79] It was demonstrated that a set of heteroarenes **118** including thiazoles, benzothiazoles, imidazole, benzimidazoles and benzoxazoles were compatible with a $Pd(OAc)_2$ and CuI catalytic system in a highly regioselective C–H activation manner with glycal iodide **59** as the electrophile (Scheme 1.9.3.1).



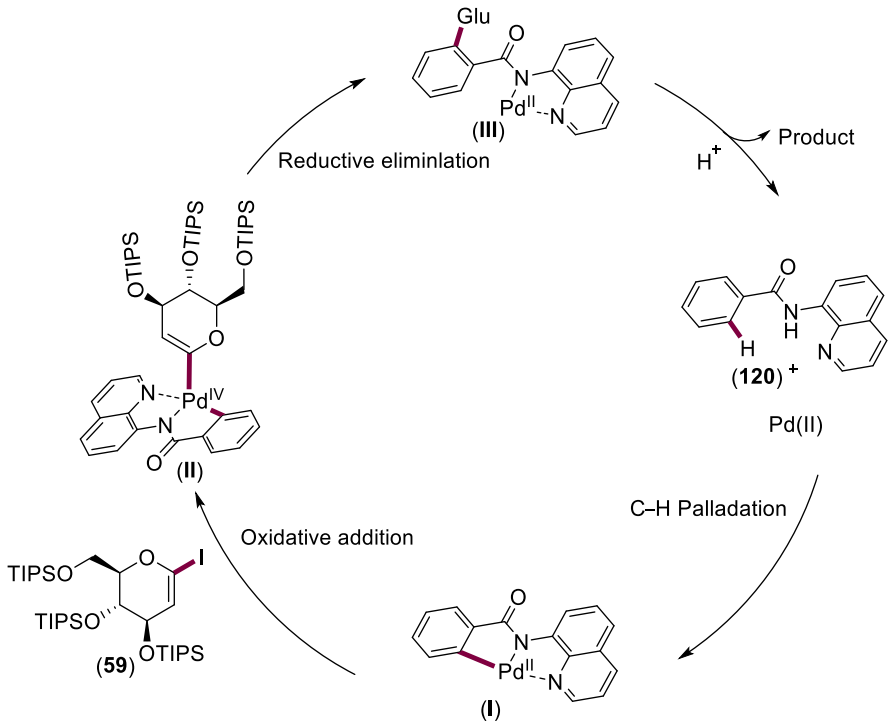
Scheme 1.9.3.1 *C*-Aryl glycoside by C−H glycosylation.

1.9.4. Directed C−H Glycosylation

Equipped with a bidentate quinoline auxiliary, Ye developed a straightforward strategy for *ortho*-C(sp^2)–H glycosylation of benzamides with triisopropylsilyl-protected 1-iodo-glycal **59** (Scheme 1.9.4.1).[80] The utility of amino acid ligand **121** proved crucial to afford mono-selective glycosylation product **122**. This ligand-controlled C–H glycosylation protocol was efficient for late-stage glycosylation of various heteroaromatic amides **120** and enabled to applied to rhamnose- and galactose-based 1-iodo-glycal coupling partners.

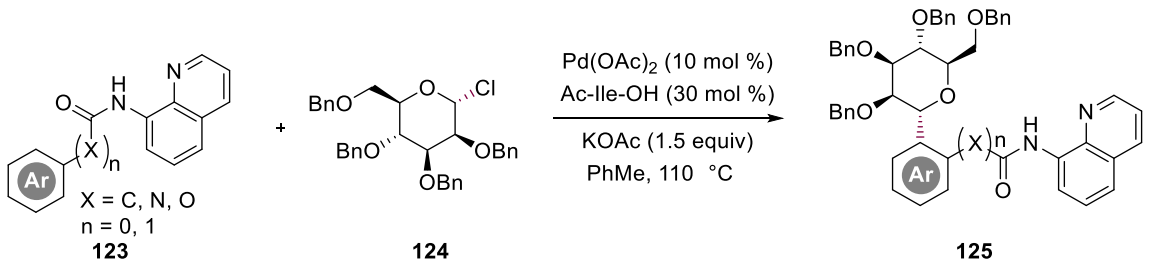


Scheme 1.9.4.1 2-Deoxy *C*-aryl glycoside synthesis by C−H glycosylation.

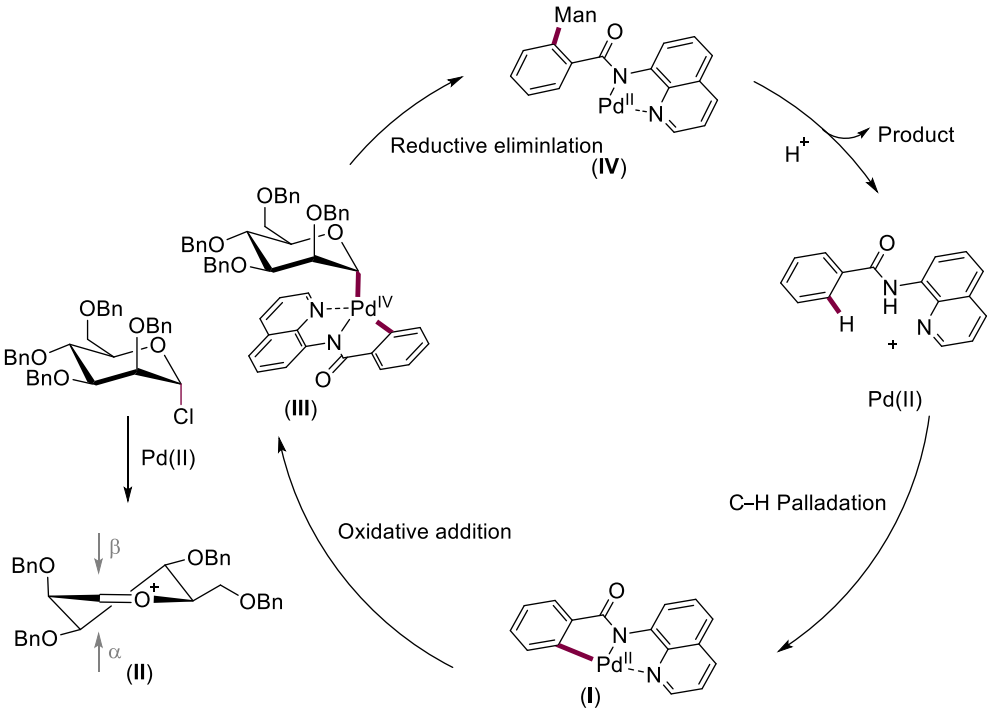


Scheme 1.9.4.2 Catalytic cycle of C−H glycosylation.

This proposed catalytic cycle starts with C–H palladation at the *ortho*-position of arene to form a five-membered palladium(II) palladacycle intermediate (**I**). Duo to the stabilizing effect of the auxiliary, the formed palladacycle intermediate (**I**) reacts with 1-iodo-glycal **59** *via* oxidative addition and followed reductive elimination to give *C*-glycosylated product (Scheme 1.9.4.2).

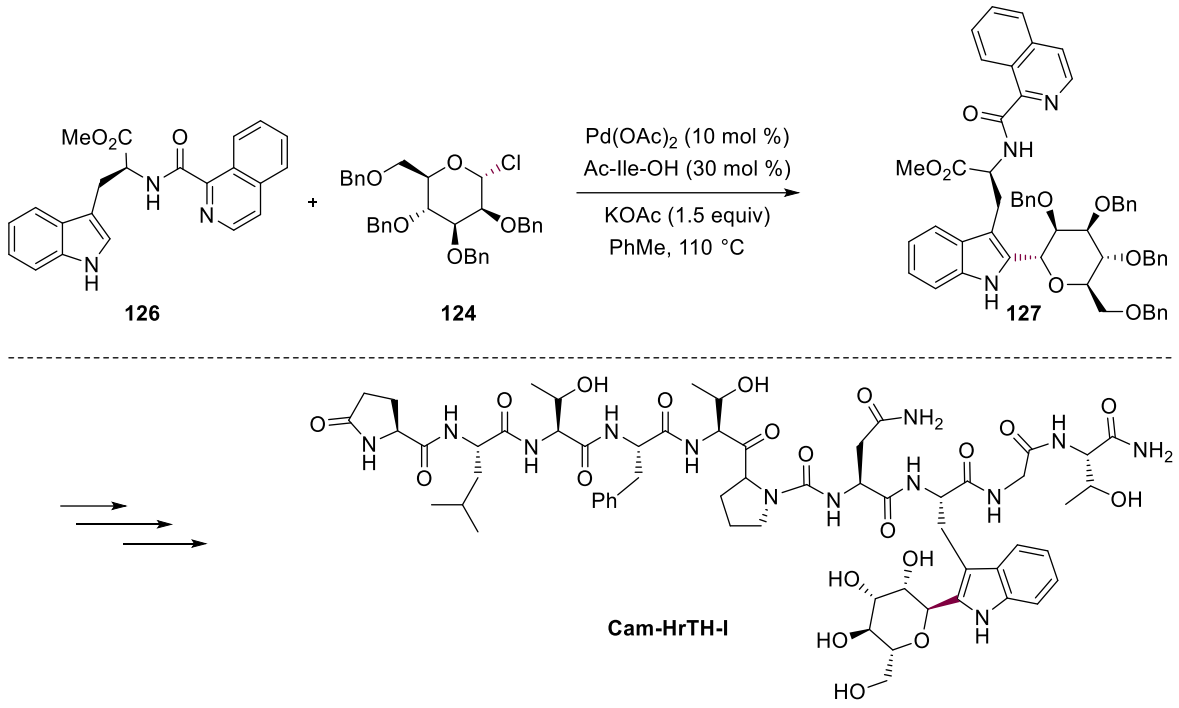


Scheme 1.9.4.3 *C*-Aryl glycoside synthesis by C−H glycosylation.



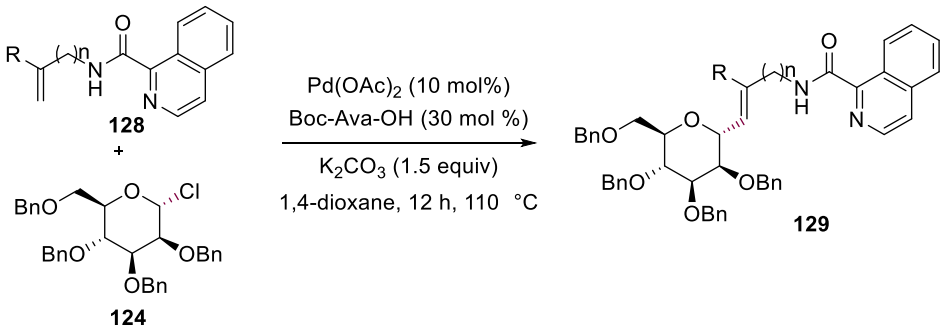
Scheme 1.9.4.4 Catalytic cycle of C−H glycosylation.

A related simple, yet powerful strategy for the stereoselective synthesis of *C*-aryl glycosides **125** *via* palladium-catalyzed *ortho*-directed C(sp^2)–H glycosylation of arenes and heteroarenes **123** with easily accessible glycosyl chloride donors **124** was reported by the Chen group (Scheme 1.9.4.3).[81] They proposed that the palladium acetate works as a Lewis acid to allow the activation of the glycosyl chloride donor into oxocarbenium ion (**II**). Meanwhile, the catalytic palladacycle intermediate (**I**) is generated *via* the directed C–H palladation provides a soft aryl nucleophile, and then followed with a stepwise oxidative addition of palladacycle intermediate to oxocarbenium ion to give palladium(IV) intermediate (**III**). Reductive elimination, protonation regenerated the palladium(II) intermediate and the desired *C*-aryl glycosides (Scheme 1.9.4.4). After that, the Liang group also achieved the same transformation with nickel catalysis, albeit with limited scope and lower catalytic efficiency.[82]



Scheme 1.9.4.5 C−H glycosylation for synthesizing Cam-HrTH-I .

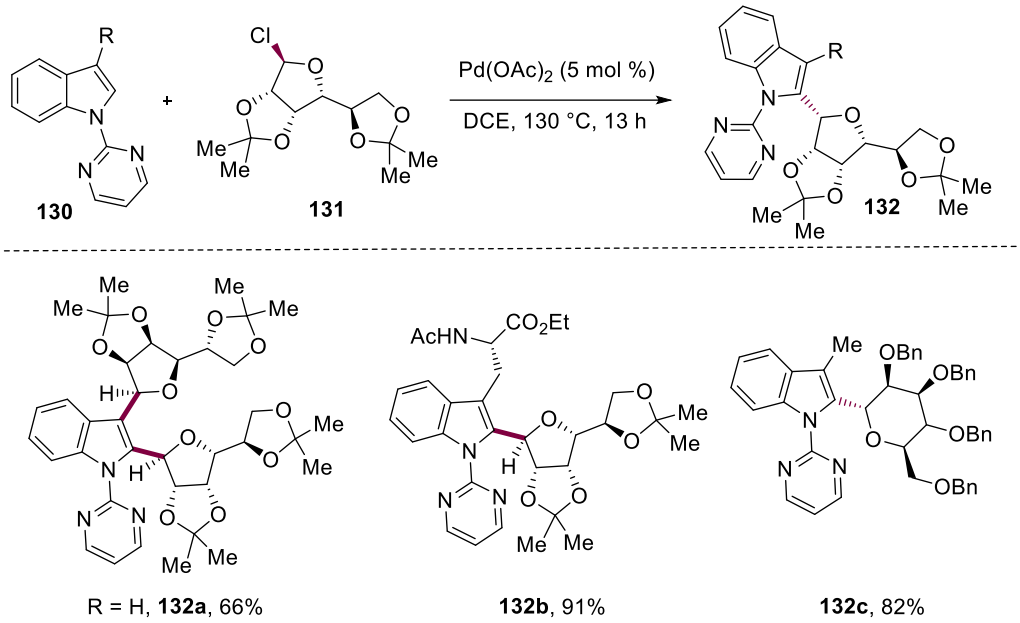
Cam-HrTH-I, a decamer glycopeptide hormone, from the stick insect *Carausius morosus* featured a *C*(2)-*α*-Man-Trp unit. Equipped with a bidentate isoquinoline-1-carboxylic acid auxiliary at the *N*-terminus **126**. A streamlined stereoselective synthesis of *C*-α-mannosyl tryptophan **127** *via* palladium-catalyzed C–H glycosylation of tryptophan with mannosyl chloride donor **124** was achieved (Scheme 1.9.4.5).[83]



Scheme 1.9.4.6 *C*-Vinyl aryl glycoside synthesis by C−H glycosylation.

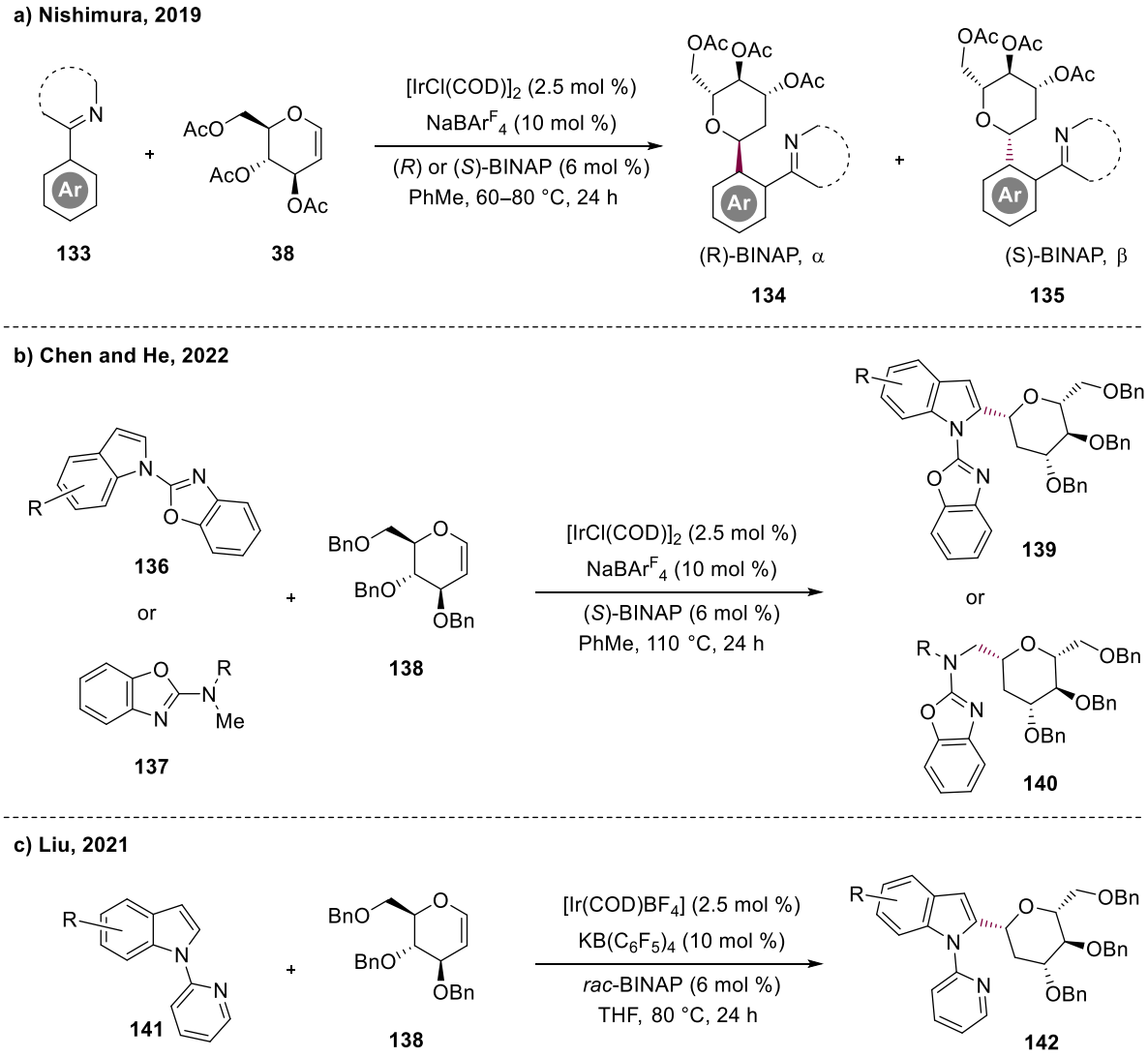
To expand the palladium-catalyzed glycosylation strategy, the vinyl C–H glycosylation was exploited with removable auxiliary, which allows the late-stage functionalization of *γ*-C–H bonds of allylamine and *δ*-C–H bond of homoallyl amine **128** (Scheme 1.9.4.6).[84] The resulting *C*-vinyl glycosides **129** can be further converted to a variety of *C*-alkyl glycosides. Compared to the developed cross-couplings by employing vinyl

Grignard reagents[62] or stochiometric amounts of reductant,[85] such as zinc. The C–H glycosylation featured mild and benign reaction medium and broad substrate scope.



Scheme 1.9.4.7 C−H glycosylation of indole derivatives.

Given the bifunctional roles of palladium acetate as Lewis acid for glycosyl chloride activation and C–H activation for selective C–H cleavage, selective C–H glycosylation of indole moiety **130** was developed (Scheme 1.9.4.7).[86] It was found that the diglycosylated products **132a** were obtained when there was no substituents at *C*(3) position. Mechanistic studies revealed that the *C*(3) electrophilic palladation preferentially occurred. Moreover, this transformation was successfully extended to the late-stage C–H glycosylation of tryptophan **132b**.



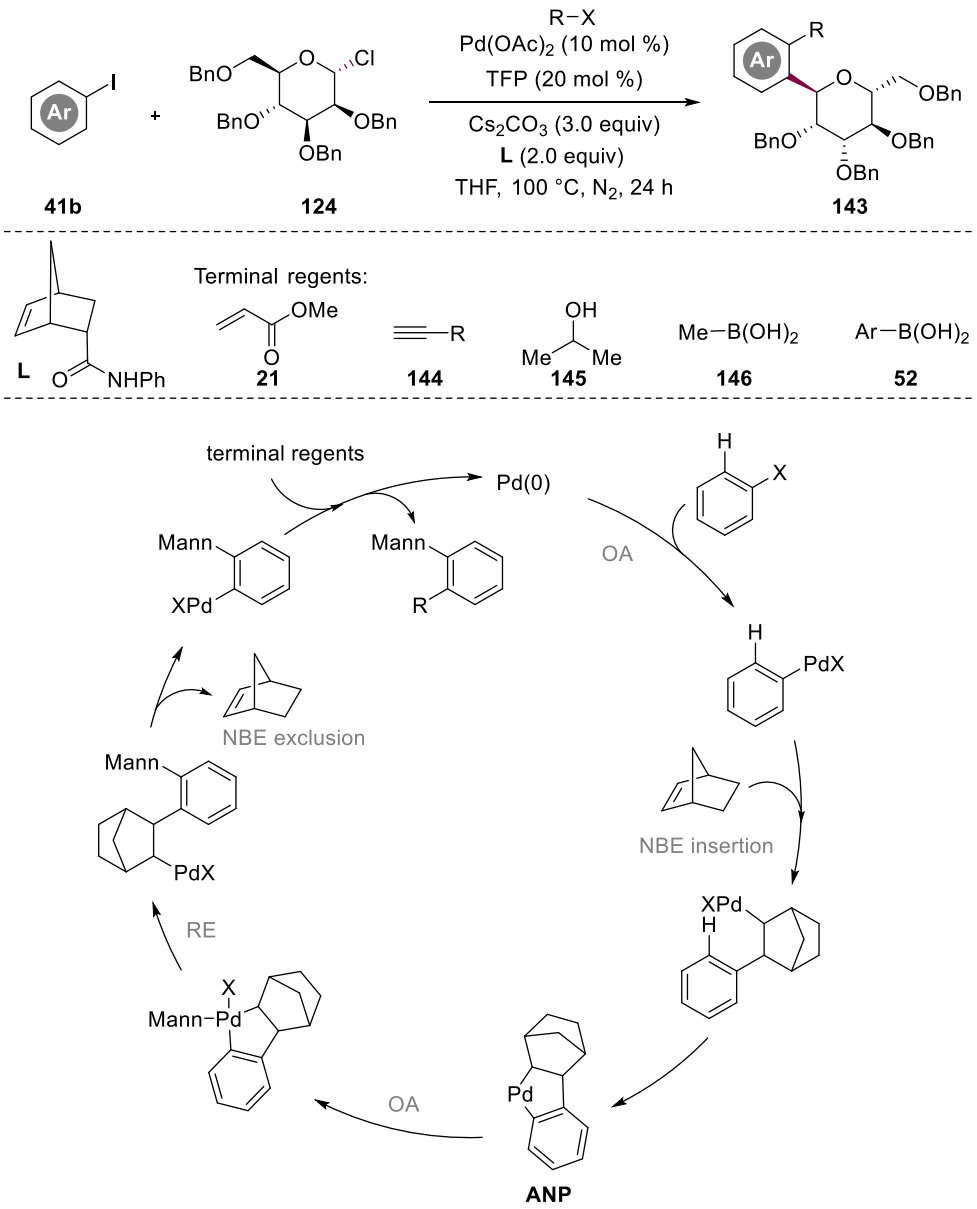
Scheme 1.9.4.8 Iridium(I)-catalyzed 2-deoxy *C*-glycoside synthesis.

2-deoxyl *C*-aryl glycosides represent a class of carbohydrates and its stereoselective synthesis has two major challenges. One is the anomeric selectivity control due to the lack of a *C*(2) participating group. Another problem is the formation of Ferrier-type *C*(aryl)-glycosides byproduct due to *β*-elimination pathway. The Nishimura group provided an elegant strategy for the efficient synthesis of 2-deoxyl *C*(aryl)-glycosides **134** and **135** *via* iridium(I)-catalyzed hydroarylation of glycals **38** (Scheme 1.9.4.8a).[87] It was found that the stereoselectivity can be well-controlled by the chiral BINAP. However, the limitation is the removal of directing group. Thus, a removable auxiliary (benzoxazole) **136** was devised for iridium-catalyzed C–H glycosylation under similar reaction conditions by Chen group (Scheme 1.9.4.8b).[88] In addition, this method also enabled the methyl C–H glycosylation of methyl substituted secondary amines **137**. The *N*-linked benzoxazole group could be easily removed by nucleophilic cleavage.

Alternatively, 2-indolyl-*C*-deoxyglycosides **142** could also be generated *via* iridium catalysis under a slightly different reaction conditions with *rac*-BINAP as ligand, featuring exclusive *β*-anomeric selectivity (Scheme 1.9.4.8c).[89]

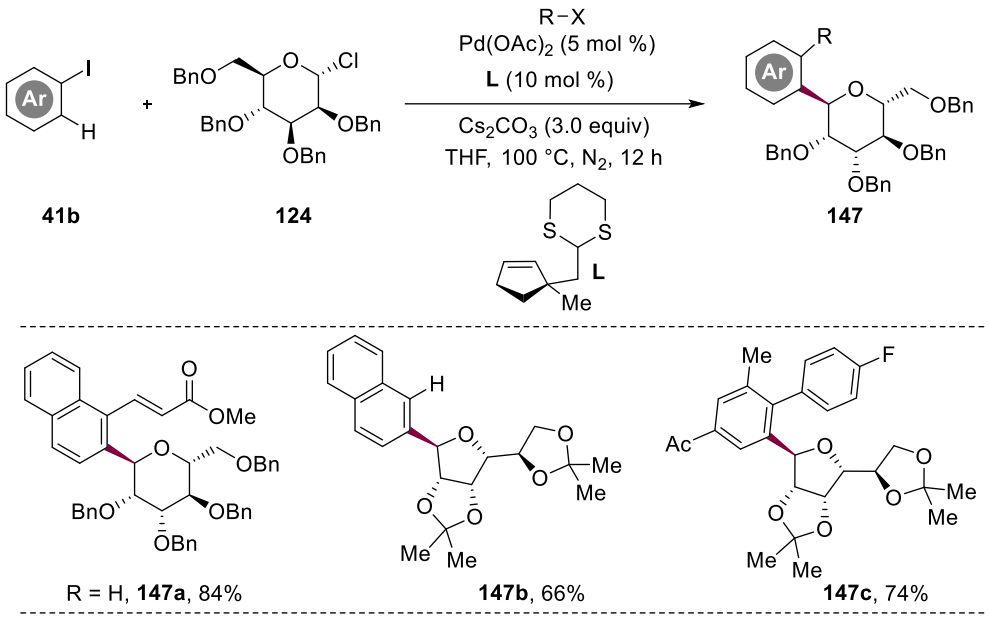
1.9.5. C−H Glycosylation by Catellani-Type Reaction

Since the discovery of the Catellani reaction,[90] it has been wildly employed for streamlined synthesis of polysubstituted arenes.[91] By use of the unique aryl norbornyl palladacycle (ANP) intermediate, versatile electrophiles can be installed at the *ortho*-position, while nucleophiles could be coupled at the *ipso*-position. In addition, the chiral norbornene (NBE) design recently enabled the efficient introduction of chiral elements in molecular synthesis.[92] In this context, key contributions were made by Cheng[93] and Liang[94] independently for the modular and stereoselective synthesis of *C*-aryl glycosides **143** *via* Catellani reaction (Scheme 1.9.5.1). Although a range of functionalized alkyl halides as electrophiles were previously examined,[95] but alkylating reagents are generally limited to less sterically hindered primary alkyl halides due to the facile hydride elimination of secondary alkyl palladium intermediates.[96] Based on oxocarbenium ion generated from the glycosyl chloride activation by palladium acetate. The reaction of ANP intermediate with oxocarbenium ion was favored *via* S_N1 pathway, combined with the terminal *ipso*-Heck reaction, hydrogenation, Sonogashira and Suzuki couplings, thus affording diversified *C*-aryl glycosides.



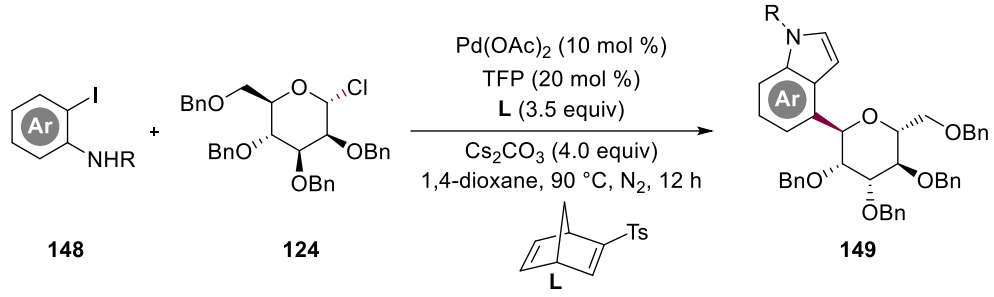
Scheme 1.9.5.1 C−H glycosylation and catalytic cycle.

Very recently, unstrained hybrid cycloolefin ligands were designed for the Catellani reaction by Jiao.[97] The ligands bear a P or S coordination site to mimic the function of phosphine ligand and a cyclopentenyl moiety as an alternative to NBE. The robustness of new ligands was also demonstrated by the *ortho*-glycosylated difunctionalization of iodoarenes **41b** in a highly efficient and selective manner.



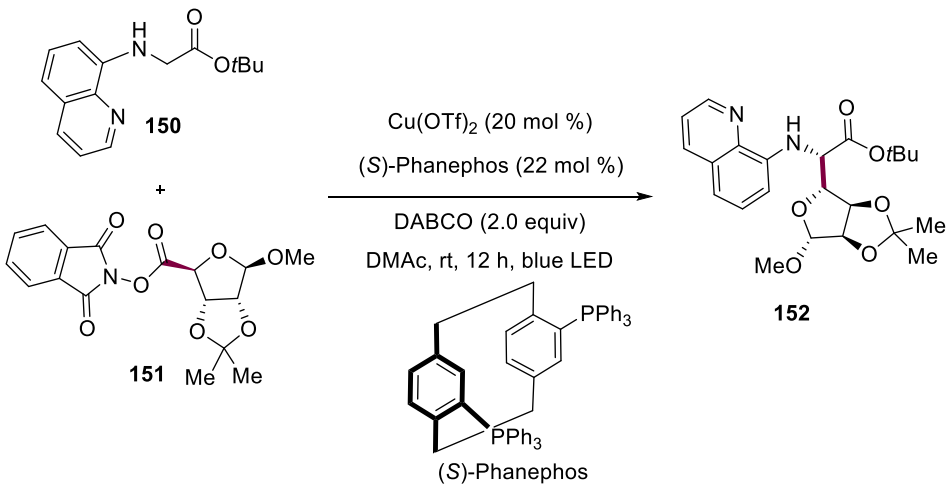
Scheme 1.9.5.2 C−H glycosylation by Catellani-type reaction.

Although the Indolyl-*C*-glycoside skeleton could be formed by transition metal-catalyzed C–H glycosylation *via* C–H activation.[88-89] The employment of strong directing group limited its application, and the current methods mainly focus on the *C*(2) selective glycosylation. Regarding the naturally and biologically important indolyl-*C*-glycosides, strategies for the synthesis of diversified glycosyl indole skeletons, such as 3-indole-*C*-glycosides[98] and 4-indole-*C*-glycoside, remain to be in demand. The Liang group used structurally modified norbornadiene as the coupling partner in the Catellani reaction to realize the construction of *C*(4)-glycosylated indoles **149**, combined with a reverse Diels-Alder reaction of the norbornadiene (Scheme 1.9.5.3).[99]



Scheme 1.9.5.3 C−H glycosylation by Catellani-type reaction.

1.9.6. *C*-Alkyl Glycosides Assembly by C(sp^3)−H Glycosylation



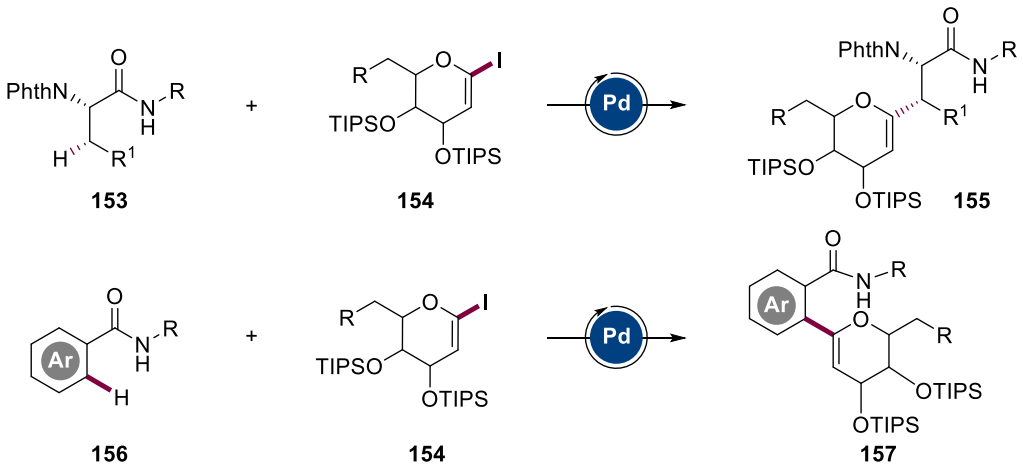
Scheme 1.9.6.1 C(sp^3)−H glycosylation for the synthesis of glycoamino acids.

Glycine is the simplest amino acid and the late-stage glycosylation of the glycine residue could provide a variety of glycoamino acids. However, the selectivity control of both the stereocenters of the two coupling partners is quite challenging. In this context, Xu and Liang developed the visible-light-promoted copper-catalyzed stereoselective C(sp^3)–H glycosylation of glycine residue **150** towards glycoamino acids **152** (Scheme 1.9.6.1).[100] It was proved that the radical coupling product was determined by the chiral copper catalyst[101] and the stable conformation of the resulting glycosyl radical intermediate. It is noteworthy that it could be also amenable for more structurally complex molecules, such as peptides and disaccharides.

2. Objectives

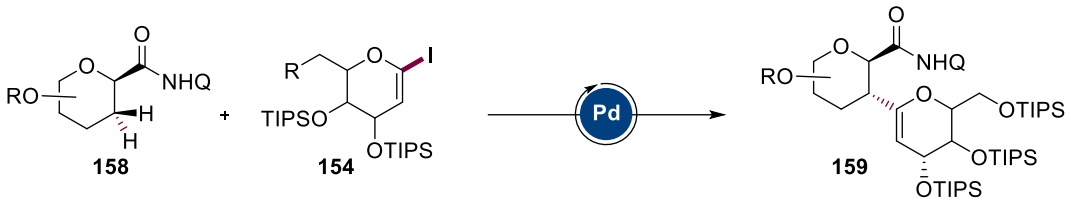
Late-stage saccharide C−H activation as a special case in the area of late-stage functionalization is challenging because it involves selectively functionalizing inert C−H bonds of a given molecule in the presence of a myriad of other functionalities. Despite the difficulties, the modular nature of the late-stage C–H activation strategy allows for an atom- and step-economical exploration of the chemical space. Therefore, the development of novel and robust C–H functionalization strategies is crucial for the efficient late-stage functionalization of biomolecules, such as amino acids, peptides,[11h, 102] and carbohydrates.[103] As such, the aim of this thesis is to develop effective strategies for the late-stage C−H functionalization of biomolecules, which will ultimately lead to the creation of structurally complex molecular architectures.

The direct manipulation of a side chain onto a peptide for the synthesis of *O*- or *N*-glycoamino acids, mediated by the nucleophilic nature of the side chains, has been well established. *C*-glycosides, which are stable isosteres of *O*/*N*-glycosides, embody improved metabolic stability. However, efficient and sustainable methods for the synthesis of *C*-alkyl glycopeptides **155** continue to be rare. To address this issue, palladium catalyzed peptide-saccharide conjugation was envisioned by the assistance of peptide bond isosteric triazole in a selective C(sp^3)−H glycosylation manner. Meanwhile, equipped with *C*(1)-glycal iodides **154** and **59** as glycosylation reagents, the C(sp^2)−H glycosylation was also explored for the modular assembly of *C*-aryl glycosides **157** (Scheme 2.1). These methods complement the numerous strategies of metal-catalyzed cross-couplings for the construction of *C*-aryl glycoside with two prefunctionalized substrates.



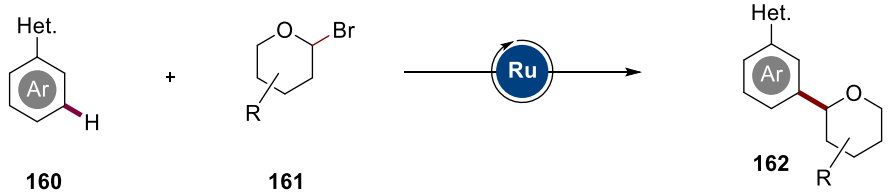
Scheme 2.1. Envisioned palladium-catalyzed C(sp^3)−H/C(sp^2)−H glycosylation.

Despite of indisputable advances in the assembly of *O*-oligosaccharides, such as enzymatic biosynthesis and solid-phase synthesis, the methodologies for the construction of *C*-oligosaccharides remain rare, likely due to a lack of efficient and selective strategies for the assembly of the interglycosidic C–C linkages. In the context of late-stage C−H functionalization, we decided to explore the selective C−H functionalization of carbohydrates **158** in order to provide a versatile and robust strategy for the synthesis of structurally complex *C*-oligosaccharides. The *C*(1)-glycal iodide **154** as the glycosylation partner was employed for palladium-catalysed saccharides stitching strategy (Scheme 2.2).



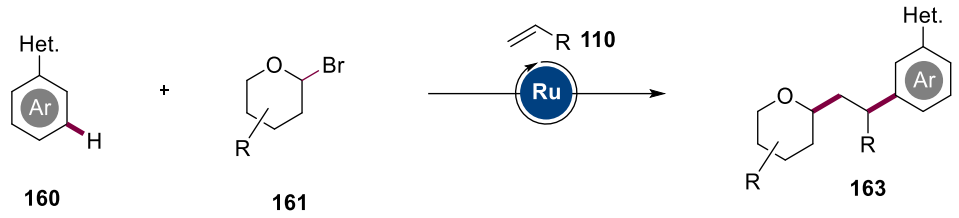
Scheme 2.2. Palladium-catalyzed C(sp^3)−H glycosylation of glycosides for first di- and oligosaccharide synthesis.

Although the activation of C(sp^2)−H bonds, adjacent to a directing group, has been well explored, the remote C(sp^2)−H functionalization is more challenging due to the intrinsic inertness of C−H bonds and the difficulty of regioselectivity control. Based on the pioneering studies on ruthenium-catalyzed remote C−H alkylation.[104] We proposed a ruthenium-catalyzed C–H glycosylation (Scheme 2.3). *C*-Aryl glycosides, especially *meta*-*C*-aryl glycosides **162**, represent an important carbohydrate scaffold, which were widely exploited in a variety of pharmacologically relevant drugs. Therefore, we wondered whether a versatile ruthenium(II)-catalyzed *meta*-C–H glycosylation could be established to construct *meta*-*C*-aryl glycosides **162** from readily available glycosyl bromide donors **161**.



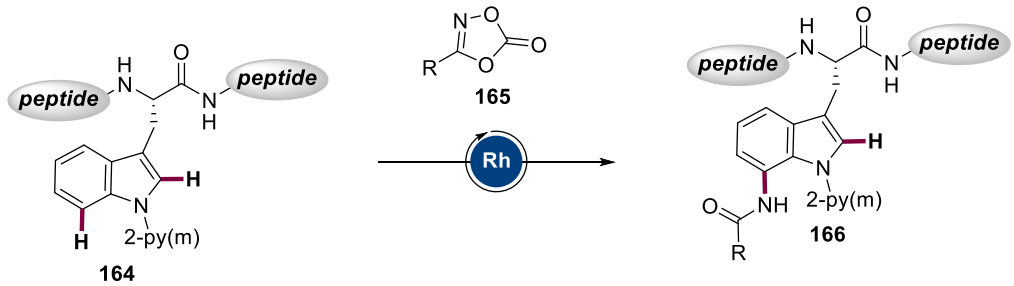
Scheme 2.3. Ruthenium-catalyzed *meta*-C−H glycosylation.

Anomeric radical involved Giese-type reaction provided the access to *C*-alkyl glycoside synthesis, the anomeric radical mediated multicomponent reaction is rare. To enrich the viable *C*-alkyl glycoside, robust and efficient approaches with readily available starting materials are still demanding. Given the robustness of the ruthenium catalysis for *meta*-C−H functionalization of arenes, we combine the ruthenium catalysis and Giese-type addition to achieve diverse *meta-C*-alkyl glycosides **163** synthesis in one-pot reaction with readily available heteroarenes **160**, glycosyl bromides **161** and vinyl arenes **110** (Scheme 2.4).



Scheme 2.4. Ruthenium-catalyzed *meta*-C(sp^2)−H Domino ethyl glycosylation.

Tryptophan (Trp) residues are of particular interest in the modification of peptides due to their unique chemical reactivity and biological function. Although few examples are developed for *C*(7)−H transformations of indole moiety with bulky auxiliaries, such as pivaloyl and phosphine-derived directing groups, the methods available for tryptophan C–H functionalization are currently severely limited to the activated *C*(2)-position. Herein, the highly modular and easily accessible dioxazolones **165** were chosen as amidation reagents. We decided to probe a strategy for the *C*(7)-selective amidation of tryptophan-containing peptides **164** with pyrimidine at *N*(1)-position as directing group under rhodium(III)-catalysis (Scheme 2.5).



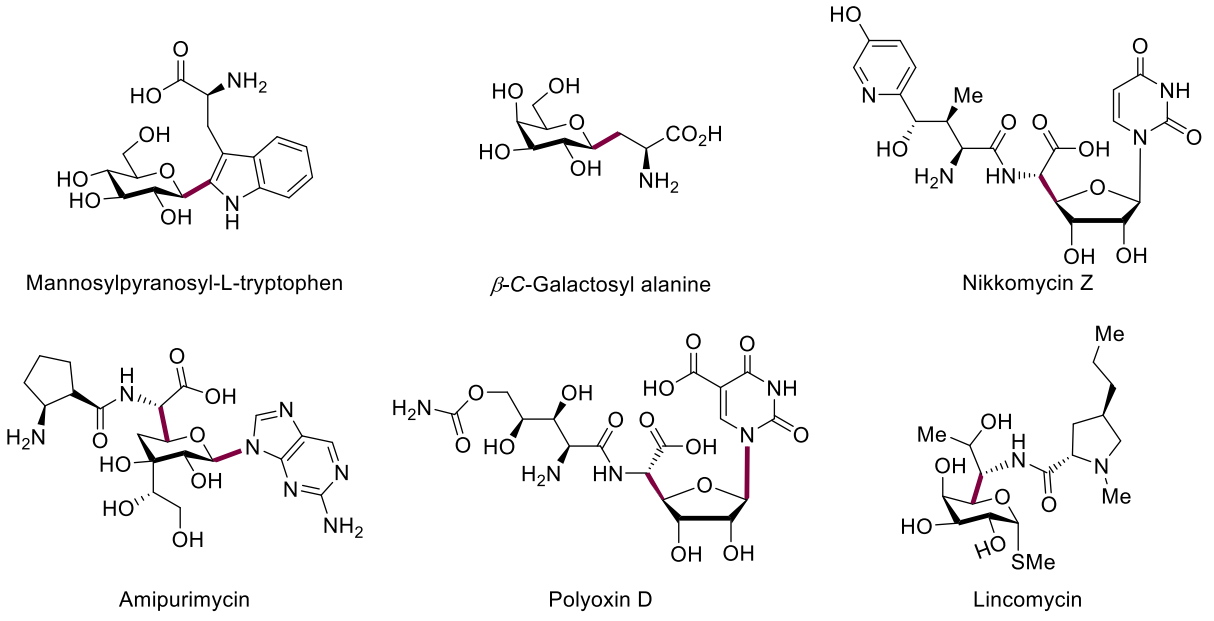
Scheme 2.5. Rhodium-catalyzed tryptophan *C*(7) amidation.

3. Results and Discussion

3.1. Late-Stage C(sp^3)−H Glycosylation for Glycopeptides Synthesis

3.1.1. Introduction

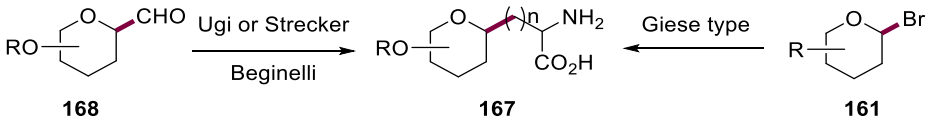
Glycoamino acids are key building blocks of the glycopeptides and glycoprotein which play essential roles in the cell-cell recognition, fertilization and the docking of viruses and bacteria on cells. The incorporation of glycosyl scaffold into the analgesic peptide could significantly improve metabolic stability and enhanced drug delivery.[105] As estimated that more than half of all the proteins carry carbohydrate side chain, with the majority being *N/O*-glycopeptides due to the high nucleophilicity of side residue of the amino acids. However, the instability of *N*/*O*-glycosides on account of the chemical and enzymatic hydrolysis under physiological conditions limits the utilities in the drug discoveries.[106] Instead, *C*-glyco-amino acids bearing glycosidic C−C bonds have been proved more stable to chemical and enzymatic conditions, thus being promising inhibitors of cell-surface recognition events and regulators of glycoside metabolism, but the methods for the synthesis of such privileged glycopeptides are rare due to the challenging associated with the selective glycosylation of aliphatic side.[103a, 107]



Scheme 3.1.1.1 Selected examples of *C*-glycoamino acids.

The available strategies for the synthesis of *C*-glycosyl amino acids through the installation of amino acid moiety to the glycoside relied on the use of well-known α-amino acids synthesis, such as alkylation of α-amino acids, Giese type addition,[108]

Strecker reactions,[109] hydrogenation of dehydroamino acids,[110] Beginelli reaction[111] and multicomponent Ugi reaction[112] with sugar derivatives (Scheme 3.1.1.2). Despite of these advances, the lengthy synthetic steps and harsh reaction conditions limited further applications. Thus, we devised a modular assembly strategy with C−H glycosylation to efficiently stitch amino acids and glycosyl framework.



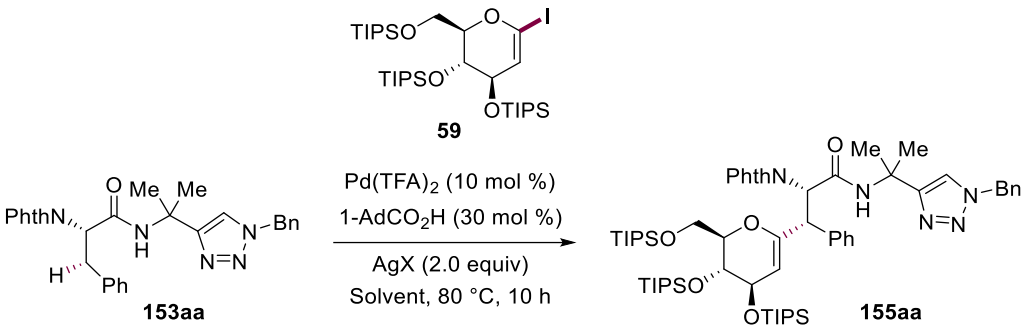
168 **167** **161**

Scheme 3.1.1.2 Conventional methods for the synthesis of *C*-glyco-amino acids.

3.1.2. Optimization Studies for C(sp^3)−H Glycosylation

We initiated our studies by exploring reaction conditions for the challenging secondary C(sp^3)−H glycosylation of triazolyldimethylmethyl (TAM) amide **153aa** (Table 3.1.2.1). Preliminary optimization indicated that 60 °C was not suitable temperature for this transformation (entry 1), but a slight increase the temperature to 80 °C led to the formation of product **155aa** in 85% yield with $Pd(TFA)_2$ as the catalyst, 1,4-dioxane as the solvent and AgOAc as the additive (entry 2). When replacing AgOAc with other silver salts (AgTFA, Ag_2CO_3, $AgBF_4$), Ag_2CO_3 stood out, providing glycopeptide **155aa** in 95% yield (entries 3−5). Notably, further optimization indicated that 1,4-dioxane was the solvent of choice, while DCE, PhMe, THF provided diminished yields or trace amounts of the product (entries 6−8).

Table 3.1.2.1 Optimization of C(sp^3)–H glycosylation of amino acids.

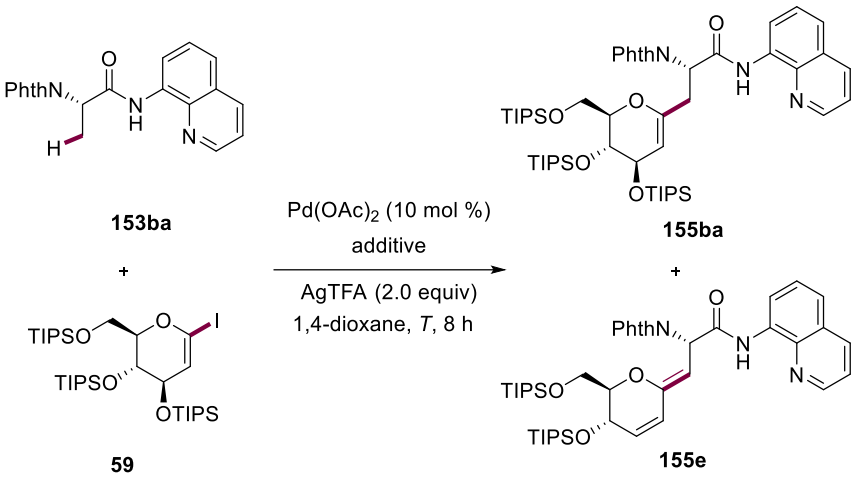


Entry	[Ag]	Solvent	Yield (%)
1	AgOAc	1,4-dioxane	49[a]
2	AgOAc	1,4-dioxane	85
3	AgTFA	1,4-dioxane	trace
4	**Ag_2CO_3**	**1,4-dioxane**	**95**
5	$AgBF_4$	1,4-dioxane	trace
6	Ag_2CO_3	DCE	45
7	Ag_2CO_3	PhMe	28
8	Ag_2CO_3	1,4-dioxane	<5

Reaction conditions: **153aa** (0.10 mmol), **59** (0.15 mmol), $Pd(TFA)_2$ (10 mol %), Ag_2CO_3 (0.2 mmol), 1-$AdCO_2H$ (30 mol %), solvent (0.5 mL), 80 °C, 10 h. Yields of isolated product. [a] Reaction at 60 °C.

We wondered whether the powerful palladium-catalyzed C(sp^3)−H glycosylation could be applicable with 8-aminoquinoline (AQ) as the auxiliary. When 8-aminoquinoline (AQ) was installed at the *C*-terminal of alanine, the reaction also efficiently proceeded, albeit under modified reaction conditions (Table 3.1.2.2). We found that the reaction generated a dien-byproduct **155e** in 79% yield, which might derived from the *C*(3)-OTIPS-elimination (entry 1). Lowering the reaction to 40 °C efficiently afforded the desired product **155ba** in 85 yield after 8 h (entries 2 and 3). Further optimization of different additives, the combination of K_2CO_3 and catalytic amount of BQ gave the product in 93% yield (entries 4−7).

Table 3.1.2.2 Optimization of C(sp^3)–H glycosylation of amino acids.



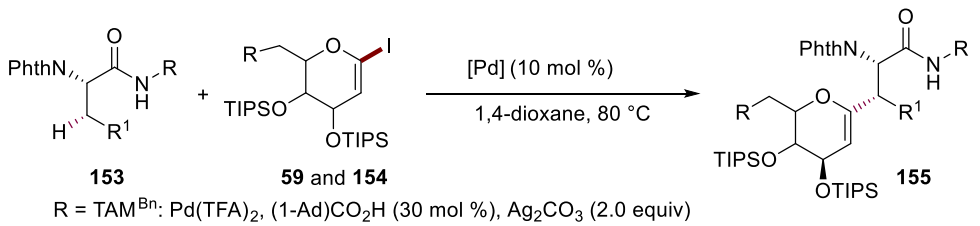
Entry	Addtive	*T*/°C	Yield (%)
1	/	100	/[a]
2	/	40	69
3	/	40	85[b]
4	K_2CO_3	40	82[c]
5	$(BnO)_2PO_2H$	40	27
6	**K_2CO_3/BQ**	**60**	**93[d]**
7	K_2CO_3/Ac-Gly	60	88

[a] Reaction conditions: **153ba** (0.10 mmol), **59** (0.15 mmol), $Pd(OAc)_2$ (10 mol %), AgTFA (0.2 mmol), 1,4-dioxane (0.5 mL), 100 °C, 16 h, isolated **155e**, 79%. Yields of isolated product. [b] Reaction time, 8 h. [c] Addition of K_2CO_3 (0.10 mmol). [d] Addition of BQ (50 mol %), K_2CO_3 (0.10 mmol).

3.1.3. Scope of the Late-Stage C(sp^3)−H Glycosylation

With the best reaction condition in hand, we first probed the generality of *C*-terminal triazole-directed C(sp^3)−H glycosylation (Scheme 3.1.3.1). Phenylalanine derivatives bearing a variety of functional groups, such as, arene, ester or aldehyde, were well tolerated, leading to the formation of products **155aa**-**155ae** with high yields and high level of diastereoselectivities. Besides the glucal **59**, the reaction with rhamanose-derived glycal **154a** as coupling partner also proceeded efficiently. Furthermore, primary C(sp^3)−H bonds of deuterated or non-deuterated alanine were likewise amenable to generate products **155ag** and **155ah** in 88% and 91% yield, respectively.

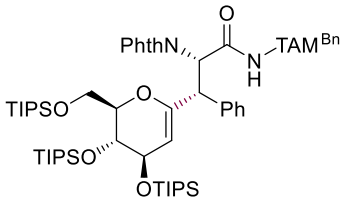
In addition, when amino acids with the 8-amino quinolone installed at the *C*-terminal as the auxiliary were also examined with our C(sp^3)−H glycosylation (**155ba**-**155bf**). It was proved that both primary and secondary C(sp^3)−H bonds could be functionalized selectively without any racemization at the stereo-center. Noteworthy, when deuterated *L*-*α*-aminobutyramide was utilized as substrate, deuterium-labelled glycoamino acid **155bg** was obtained.



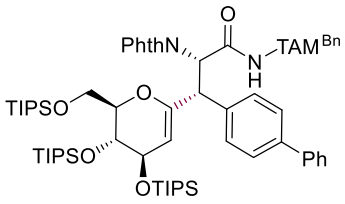
153 **59** and **154** **155**

R = TAM^{Bn}: $Pd(TFA)_2$, (1-Ad)CO_2H (30 mol %), Ag_2CO_3 (2.0 equiv)

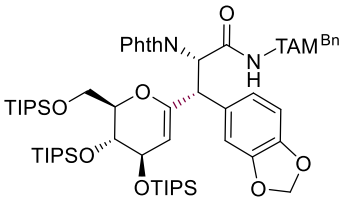
R = AQ: $Pd(OAc)_2$, K_2CO_3 (1.0 equiv), BQ (50 mol %), AgTFA (2.0 equiv)



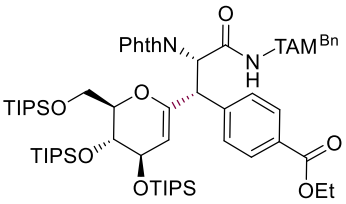
155aa: 95%, d.r. > 20:1



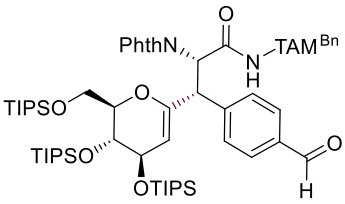
155ab: 62%, d.r. = 10:1



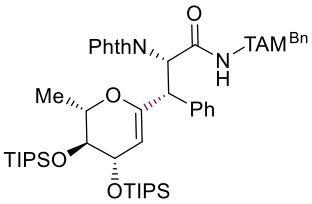
155ac: 65%, d.r. > 20:1*



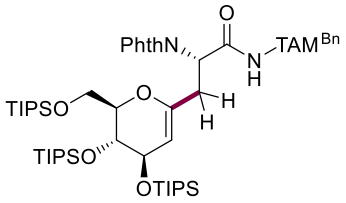
155ad: 51%, d.r. > 20:1



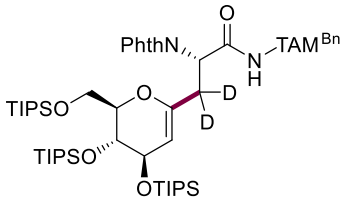
155ae: 56%, d.r. > 20:1*



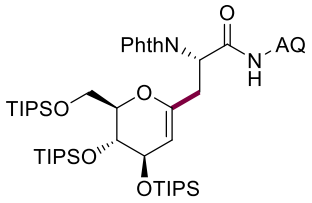
155af: 86%, d.r. >20:1



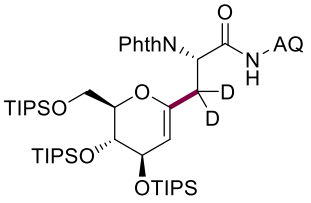
155ag: 88%



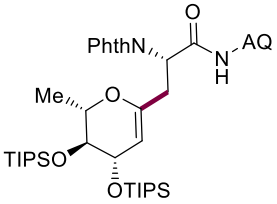
155ah: 91%



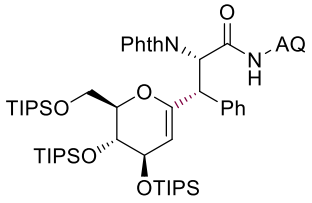
155ba: 85%



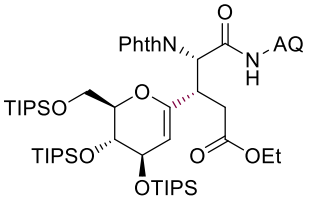
155bb: 79%



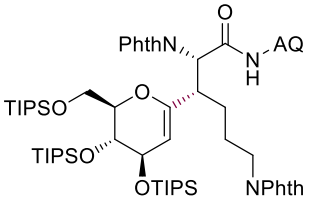
155bc: 52%



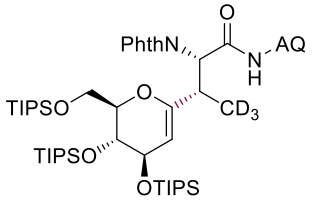
155bd: 93%, d.r. = 10:1



155be: 92%, d.r. = 6:1

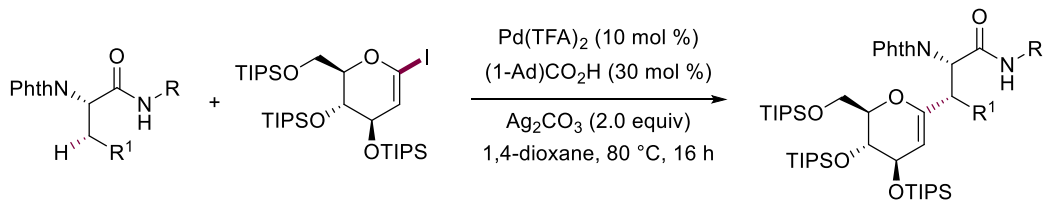


155bf: 92%, d.r. = 6:1

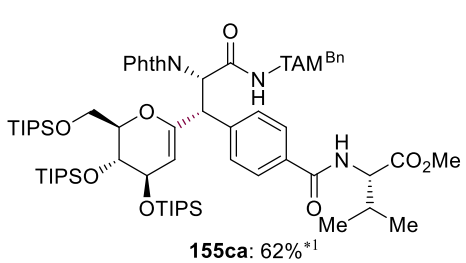


155bg: 90%, d.r. = 4:1

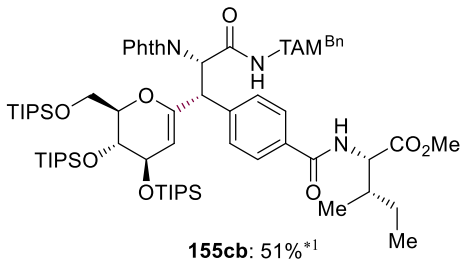
Scheme 3.1.3.1. Palladium-catalyzed C(sp^3)−H glycosylation. *Done by Felix Kaltenhäuser.



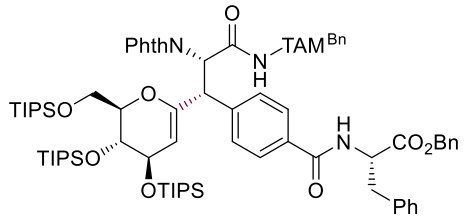
153 **59** **155c**



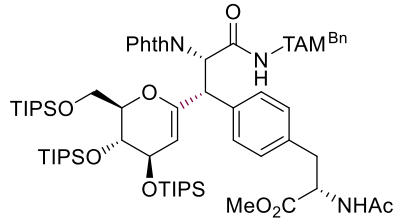
155ca: 62%*1



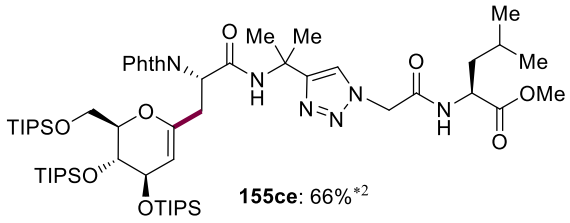
155cb: 51%*1



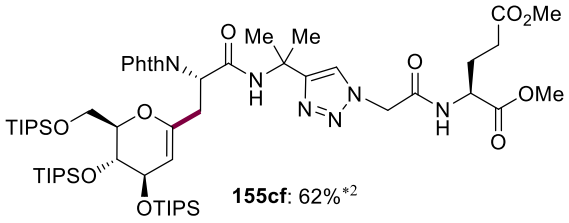
155cc: 50%



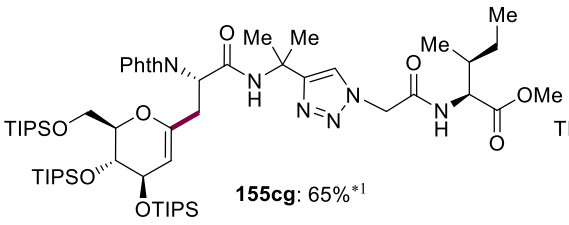
155cd: 32%



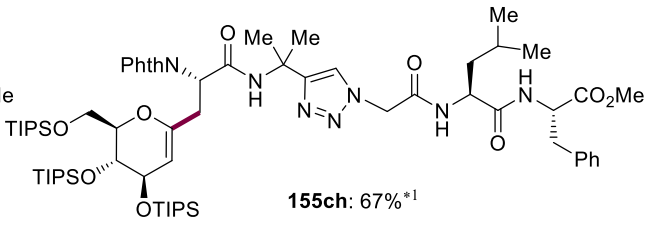
155ce: 66%*2



155cf: 62%*2



155cg: 65%*1



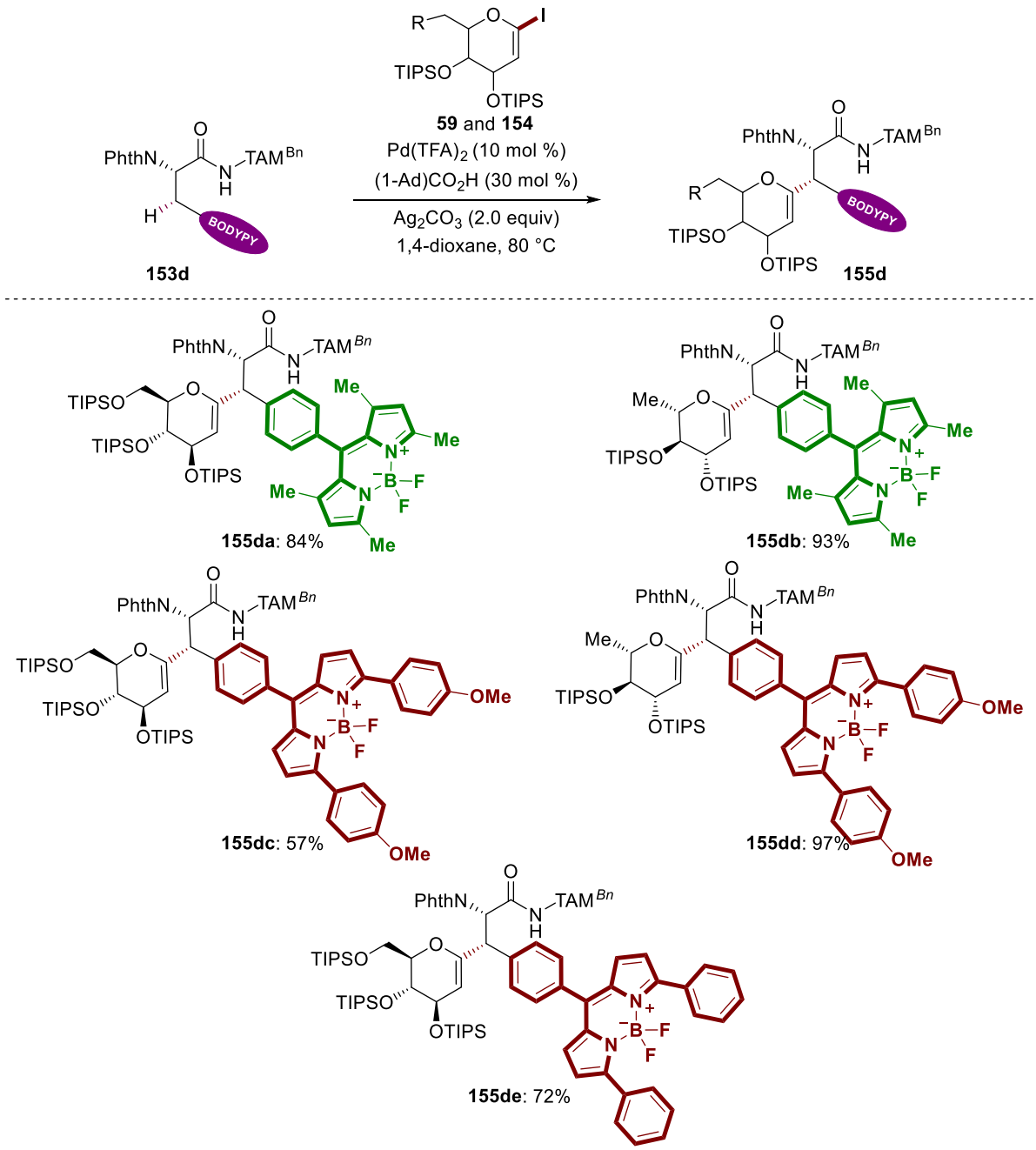
155ch: 67%*1

Scheme 3.1.3.2 Late-stage C(sp^3)−H glycosylation of terminal peptides. *1 Done by Dr. Nikolaos Kaplaneris,; *2 Done by Felix Kaltenhäuser.

Next, we studied the C(sp^3)−H glycosylation for bio-conjugations to form versatile glycopeptides (Scheme 3.1.3.2). When alanine derivatives, bearing amino acids at the alanine side chain, employed in this reaction, products **155ca-155cd** were obtained by late-stage C−H glycosylation, thereby expanding the possibilities for synthesizing structural complex peptides. Then, the robustness of C(sp^3)−H glycosylation was explored with triazole as isosteric peptide bond at the internal. Various value-added peptides **155ce**-**155ch** were formed under significantly mild reaction condition. It is

noteworthy that the sterically congested *gem*-disubstituted substrates are required for the high conversion.

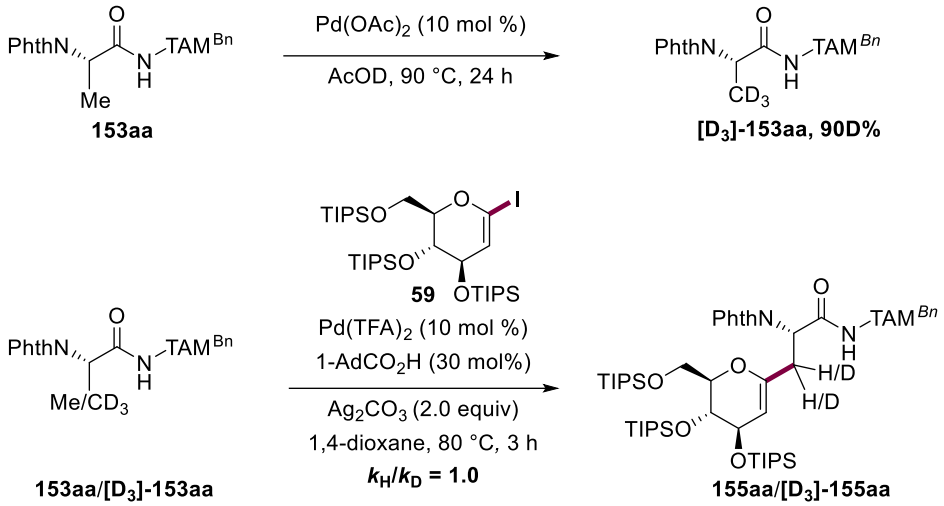
Among various fluorescent labels, BODIPYs as colour-tunable and biocompatible dyes were found to be crucial for biochemistry and molecular biology studies, such as biology sensors and cell imaging fluorescein, due to their structural diversity, high cell-permeability, large stock-shift, broad emission wavelength and high quantum yields.[113] By virtue of palladium-catalyzed C(sp^3)−H activation, versatile BODIPY labelled amino acids were synthesized. Then, the C(sp^3)−H glycosylation was explored for the preparation of important BODIPY labelled glycoamino acids **155da**-**155de** (Scheme 3.1.3.3). As a result, the excellent conversion and high level of stereoselectivities (d.r. > 20:1) were observed.



Scheme 3.1.3.3. Late-stage C(sp^3)−H glycosylation of BODIPY labelled amino acids

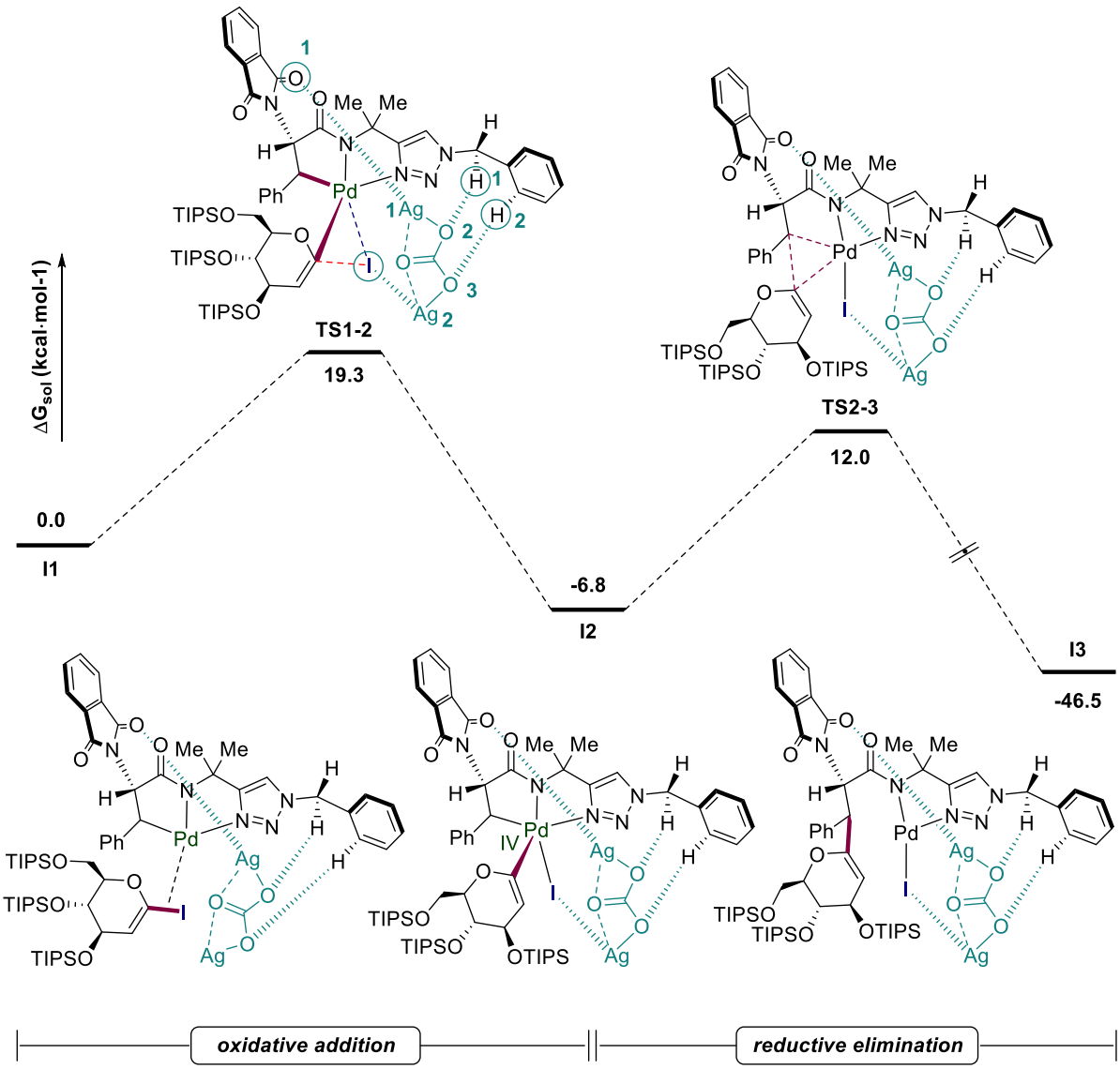
3.1.4. Mechanistic Studies

To shed light into the working mode of the palladium(II)-catalyzed C(sp^3)−H glycosylation, mechanistic studies were conducted (Scheme 3.1.4.1). First, deuterated alanine **[D$_3$]-153aa** was synthesized with 90%D incorporation. Then, the kinetic isotope effect (KIE) experiment with k_H/k_D = 1.0 indicated that the C(sp^3)−H cleavage is not the kinetically relevant step of the palladium-catalyzed C−H glycosylation.

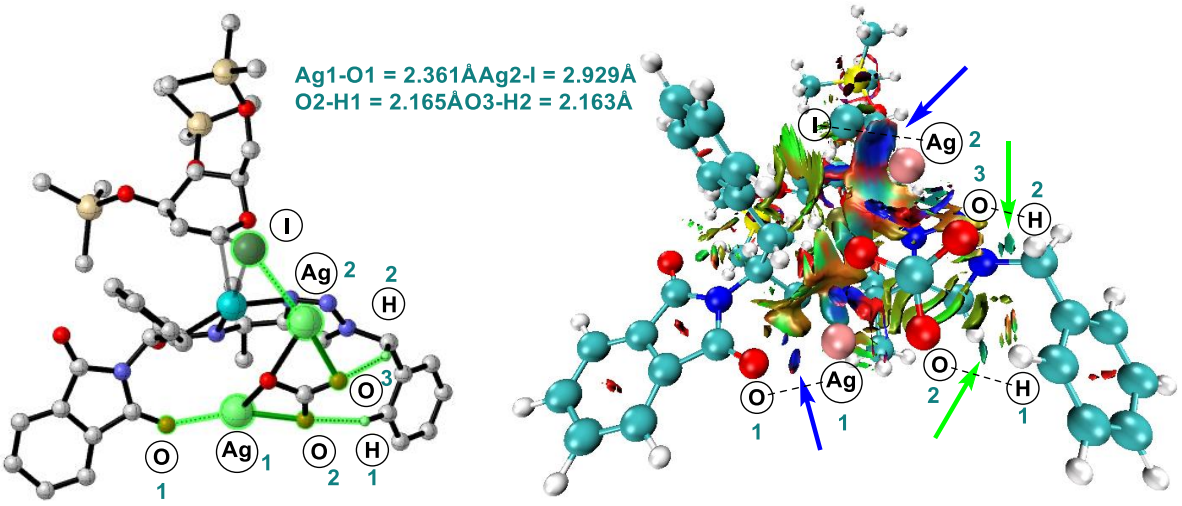


Scheme 3.1.4.1. H/D exchange and KIE experiment.

In order to gain further insights into the mechanism of the C−H glycosylation, DFT calculations were performed at the ωB97X-D/6-311++G(d,p), SDD(Pd, I, Ag) + SMD(1,4-dioxane)//ωB97X-D/6-31G(d), LANL2DZ(Pd, I, Ag) level of theory by Dr. Shao-Fei Ni. The calculated barrier for the initial C−H activation is 19.4 kcal·mol^{-1}. After the C−H activation, the dissociation of acetic acid and association of **59** lead to afford the stable intermediate **I1**, which could be stabilized by Ag_2CO_3. This process is highly exergonic by 36.8 kcal·mol^{-1}, thus making the step irreversible. In **I1** as shown in scheme 3.1.4.2, C−I bond cleavage occurs with the assistance of silver *via* bimetallic transition state **TS1-2** to afford the oxidized Pd(IV) intermediate **I2**, with a barrier of 19.3 kcal·mol^{-1} with respect to **I1**. In this transition state, it is possible to observe attractive dispersive interactions between the imide of the substrate and Ag_2CO_3, which subsequently becomes evident by the bond distances between both moieties as shown in scheme 3.1.4.3. This could be further confirmed by visualizing the NCI (non-covalent interactions) plot. The reaction continues with the reductive elimination *via* **TS2-3** with a barrier of 18.8 kcal·mol^{-1} to finalize the C−C formation process, followed by subsequent protonation to release the desired product.



Scheme 3.1.4.2. Calculated Gibbs free energy profiles for the oxidative addition and reductive elimination steps in kcal·mol^{-1} at the ωB97X-D/6-311++G(d,p), SDD(Pd, I, Ag) + SMD(1,4-dioxane)//ωB97X-D/6-31G(d), LANL2DZ(Pd, I, Ag) level of theory. *Done by Dr. Shao-Fei Ni.

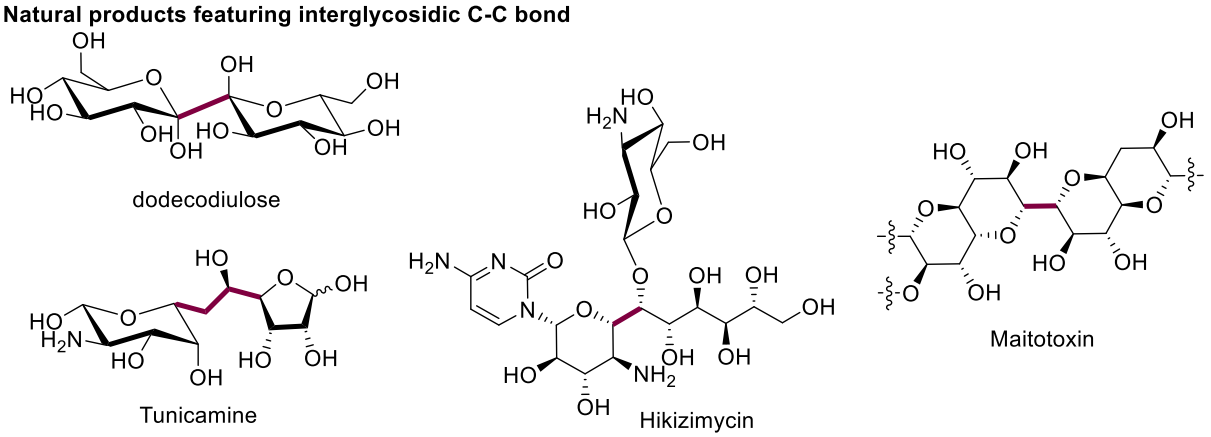


Scheme 3.1.4.3. The 3D structures and the non-covalent interactions visualized through NCI-plots of transition state **TS1-2** (strong and week attractive interactions are given in blue and green, respectively, while red corresponds to strong repulsive interactions). *Done by Dr. Shao-fei Ni.

3.2. Synthesis of *C*-Oligosaccharides *via* C(sp^3)−H Glycosylation of Glycosides

3.2.1. Introduction

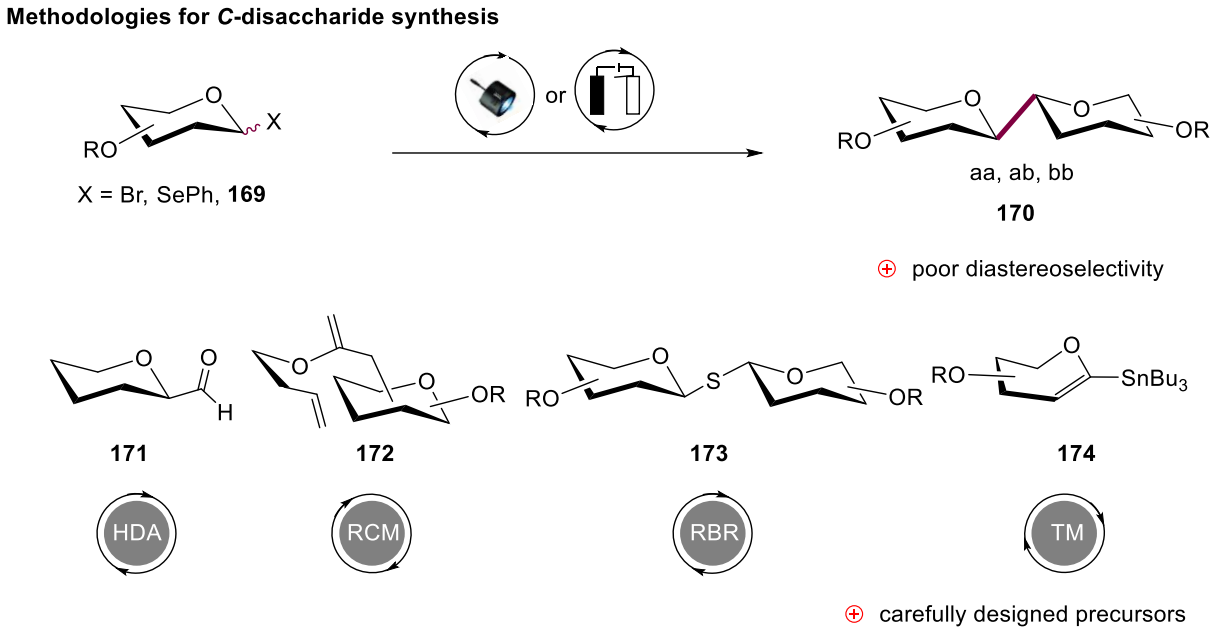
The occurrence of complex oligosaccharides motifs as epitopes at the cell surface interferes with cell-cell and antibody-cell adhesion.[114] The integration of oligosaccharides into the repertoire of therapeutic, diagnostic and nutritional agents facilitates the pharmacological investigation of carbohydrate-based drugs.[115] Practical syntheses of *O*-oligosaccharides are well exploited to provide opportunities for a comprehensive understanding of structure and function of *O*-oligo- and *O*-polysaccharides. Of particular interest are *C*-oligosaccharides as nonhydrolyzing antimetabolites due to their significantly improved stability to chemical hydrolysis and enzymatic degradation. Oligosaccharides with a glycosidic *C*-linkage are embedded in numerous naturally occurring biomolecules, such as, dodecodiulose, (an analogue of trehalose),[116] structurally complex natural products, such as anthelmintic hikizimycin[117] and neurotoxic Maitotoxin[118] embody interglycosidic C–C bonds. Thus glycosidic C–C bond formation strategies are of current topical interest for the discovery of new therapeutic agents (Scheme 3.2.1.1).[119]



Scheme 3.2.1.1. Selective examples of *C*-glycosides.

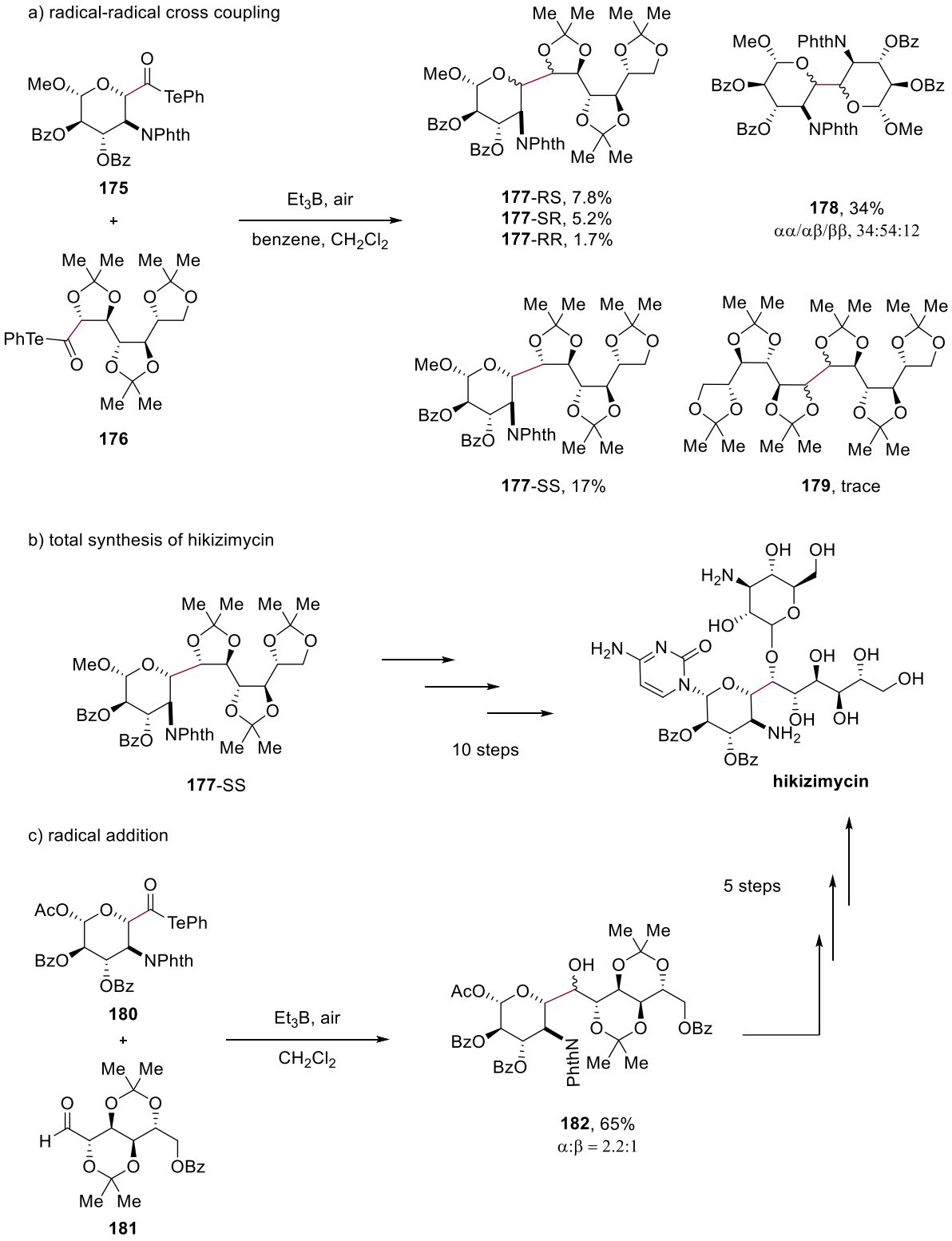
Commonly used *C*-disaccharides construction strategies were developed *via* photoinduced radical mediated C–C bond formation[35] or electrochemical reductive radical dimerization.[120] However, both approaches showed limited diastereoselectivity and restricted substrate scope. The central synthetic step for interglycosidic linked C–C bond formation also realized *via* ring closing metathesis (RCM),[121] hetero-Diels-Alder cycloaddition (HDA),[122] Stille-like cross-coupling[123] or Ramberg-Bäcklund

rearrangement reactions,[124] which greatly relied on the use of specifically designed glycosyl precursors (Scheme 3.2.1.2).



Scheme 3.2.1.2. Methods for the *C*-oligosaccharide synthesis.

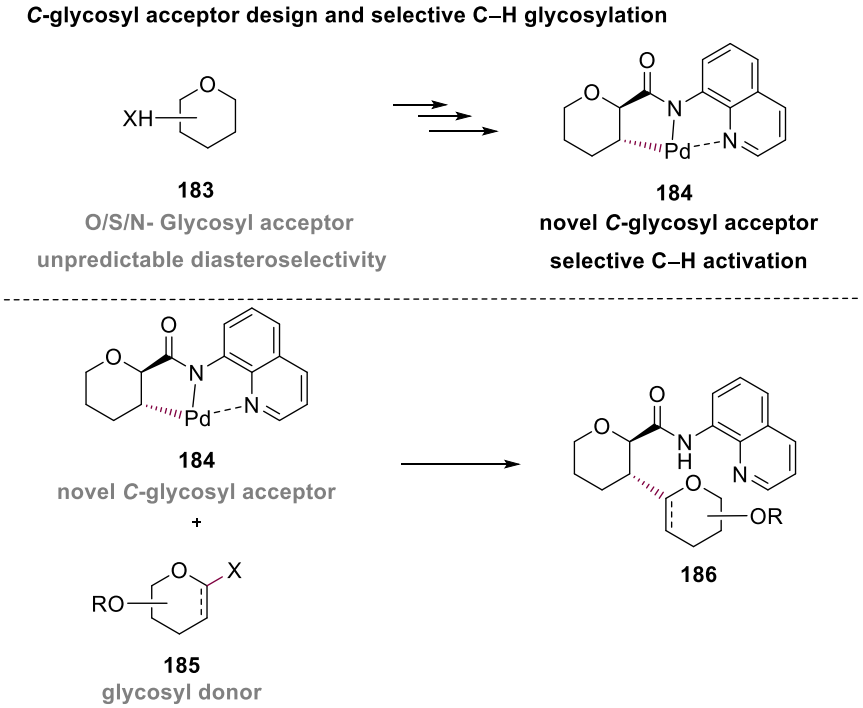
Alternatively, Inoue unprecedentedly devised a radical-radical homo-coupling/cross-coupling of sugar-derived α-alkoxyacyl tellurides **175** and **176** using Et_3B/O_2 at room temperature (Scheme 3.2.1.3a),[125] which exemplified the remarkable utility of the dimerization by one-step assembly of the protected *C*1–*C*11 oxygenated carbon chain of the anthelmintic *hikizimycin* (Scheme 3.2.1.3b), but the diastereoselectivity of the dimerization could still not be well controlled. And then this methodology was well extended to the convergent total synthesis of *hikizimycin* enabled by intermolecular anomeric radical addition to aldehyde **181**, affording interglycosidic C–C bond of **182** (Scheme 3.2.1.3c).[126]



Scheme 3.2.1.3. *C*-oligosaccharides synthesis with glycosyl acyl tellurides.

Thus, we became interested into the efficient construction of glycosidic C−C bonds. We envisioned that initial C–H activation of deoxy sugar with palladium(II) acetate would give the cyclopalladaglycoside complex **184**. This palladacycle would serve as the key *C*-glycosyl acceptor for the saccharide assembly by the subsequent reaction

with 1-iodo-glucal donor **185** (Scheme 3.2.1.4). Thus, the chemical space of the oligosaccharide library will be expanded by the selective C−H palladation to form *C*-oligosaccharides **186**.



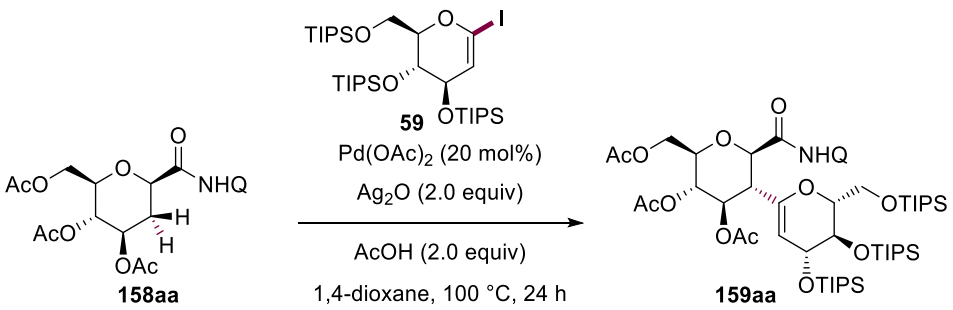
Scheme 3.2.1.4. *C*-glycosyl acceptor design and selective C−H glycosylation

3.2.2. Optimization Studies for C(sp^3)−H Glycosylation

We initiated our studies by exploring reaction conditions with 2-deoxy-*β*-glycoside **158aa** and glycosyl donor 1-iodo-glucal **59** as model substrates for the C−H glycosylation for saccharide assembly. After brief optimization of all reaction parameters (Table 3.2.2.1), we observed that the C(sp^3)–H activation of glycoside **158aa** in 1,4-dioxane delivered the equatorial C(sp^3)–H glycosylated product **159aa** in 73% yield with Ag_2O and AcOH as additives (entry 1). A slightly reduced catalytic efficiency was observed in the absence of AcOH when other silver salts were probed (entries 2-4). Additives, such as acetyl protected glycine and trifluoroacetic acid, were also examined, giving the product in 56% yield with Ac-Gly-OH (entries 5 and 6). Then, the base showed that acetate salts performed better for the C−H glycosylation (entry 7). Furthermore, different solvents, such as THF, DCE and PhMe, were tested, delivering the product in moderate yields (entry 8). Lower loadings of the palladium catalyst or silver salt proved less efficient for the saccharide assembly (entries 9 and

10). In addition, control experiments verified the essential roles of the catalyst and the silver salt (entries 11 and 12).

Table 3.2.2.1 Optimization of C(sp^3)–H glycosylation of glycoside **158aa**.



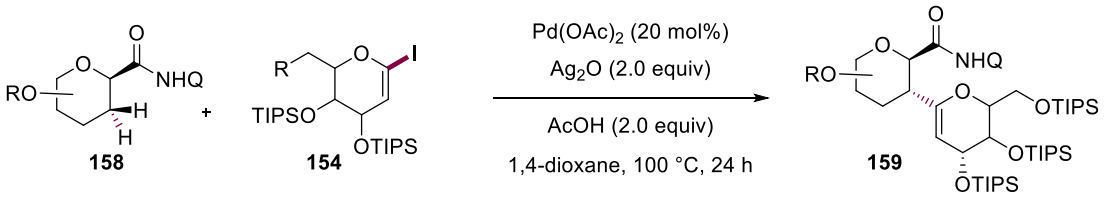
Entry	Deviation from standard conditions	Yield (%)
1	None	73
2	Ag_2O instead of Ag_2O/HOAc	59
3	AgOAc instead of Ag_2O/HOAc	53
4	Ag_2CO_3 instead of Ag_2O/HOAc	51
5	Ac-Gly-OH instead of HOAc	56
6	TFA instead of HOAc	trace
7	K_2CO_3 or NaOAc instead of HOAc	19/63
8	THF or DCE or PhMe as solvent	62/68/61
9	5 mol % or 10 mol % of $Pd(OAc)_2$	29/65
10	0.5 equiv or 1.0 equiv of Ag_2O	45/65
11	No $Pd(OAc)_2$	-
12	No Ag_2O	-

Reaction conditions: **158aa** (0.10 mmol), **59** (0.15 mmol), $Pd(OAc)_2$ (20 mol %), Ag_2O (0.2 mmol), AcOH (0.2 mmol), 1,4-dioxane (1.0 mL), 100 °C, 24 h. Yields of isolated product.

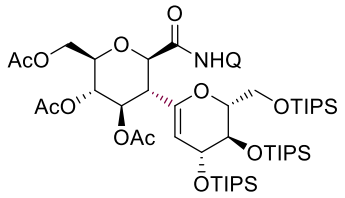
3.2.3. Scope for C(sp^3)−H Glycosylation

With the best reaction condition in hand, we examined the generality of the C(sp^3)–H glycosylation (Scheme 3.2.3.1). First, quinolines with different substituents (**158aa**-

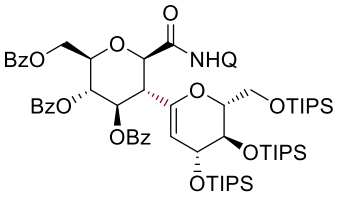
158ac) were found to be compatible. Second, 2-deoxy-glucoside with benzoyl groups delivered the desired glucosyl-*C*-[2→1]-glucal **159ba**. Third, methyl and benzyl ethers proved feasible (**159bb**-**159bc**). When the C(sp^3)–H glycosides glycosylation was applied to galactosides, excellent catalytic efficiencies were observed for the galactosyl-*C*-[2→1]-glucal **159ca-159cc** construction. 2,6-Deoxy-rhamnoside and 2,6-deoxy-fucose, important components of naturally occurred *C*-glycosides, could be used for the preparation of rhamnosyl-*C*-[2→1]-glucal **159d** and fucosyl-*C*-[2→1]-glucal **159e**. 1-Iodo-galactal **154b** was utilized for the saccharide assembly, and proved powerful for the construction of various *C*-disaccharides, such as glucosyl-*C*-[2→1]-galactal **159fa-159fc**, galactosyl-*C*-[2→1]-galactal **159g**, rhamnosyl-*C*-[2→1]-galactal **159h** and fucosyl-*C*-[2→1]-galactal **159i** with selective *trans*- C(sp^3)–H glycosylation. In addition to the glycals **59** and **154b,** glycosyl donor **154a** derived from rhamnose also proved amenable to 2-deoxy-glucosides, galacotosides, delivering disaccharides **159ja-159jd** and **159k** in moderate to excellent yields. Especially, this approach provided facile access to the rhamnosyl-*C*-[2→1]-rhamnal **159l** that would be challenging to prepare by conventional methods. Arabinoside bearing a *C3* equatorial group was investigated, and the elimination product was not formed (**159m**). The catalytic efficiency of 2-deoxy-xyloside with an *axial*-OAc functional group at *C3* position was suppressed due to the steric effect of the *C3* axial protecting group along with *β*-eliminated product **159n**. To demonstrate transition-metal catalyzed diversification of our saccharide assembly strategy with C(sp^3)–H glycosylation of glycosides, elaborately designed glycosides with the removable picolinic acid was employed and precisely aimed for the anomeric C(sp^3)–H glycosylation for the construction of interglycosidic (1→1)-*C*-oligosaccharides. To our delight, we observed that glycosides bearing an axial picolinic amide at *C3* position allowed for the formation of altrose-*C*-[1→1]-glucal **159oa** and **159ob** with exclusive α-selectivity.



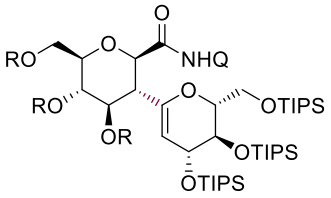
158 + **154** → **159**



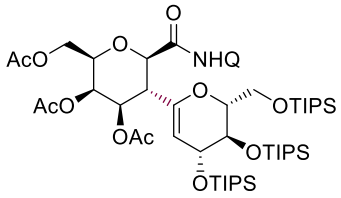
R = H **(159aa)**: 73%
R = OMe **(159ab)**: 76%
R = Cl **(159ac)**: 70%*



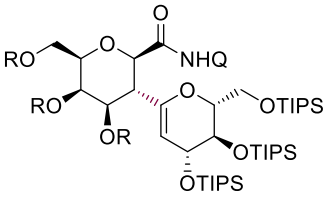
159ba: 61%



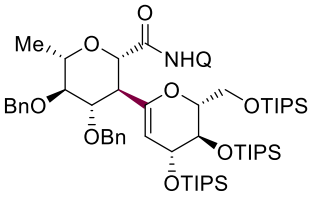
R = Me **(159bb)**: 90%
R = Bn **(159bc)**: 64%



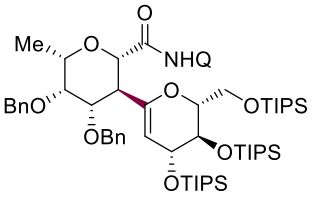
159ca: 82%



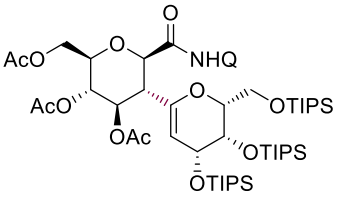
R = Me **(159cb)**: 95%
R = Bn **(159cc)**: 90%



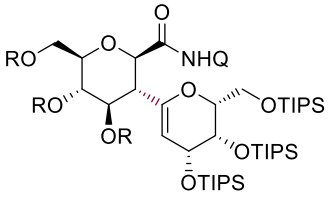
159d: 64%



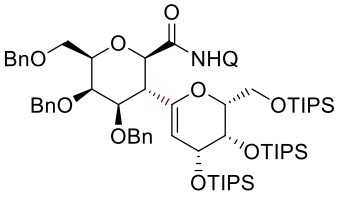
159e: 80%



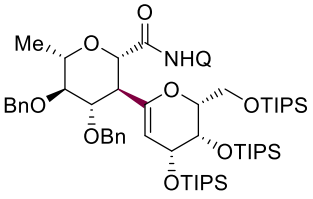
159fa: 66%



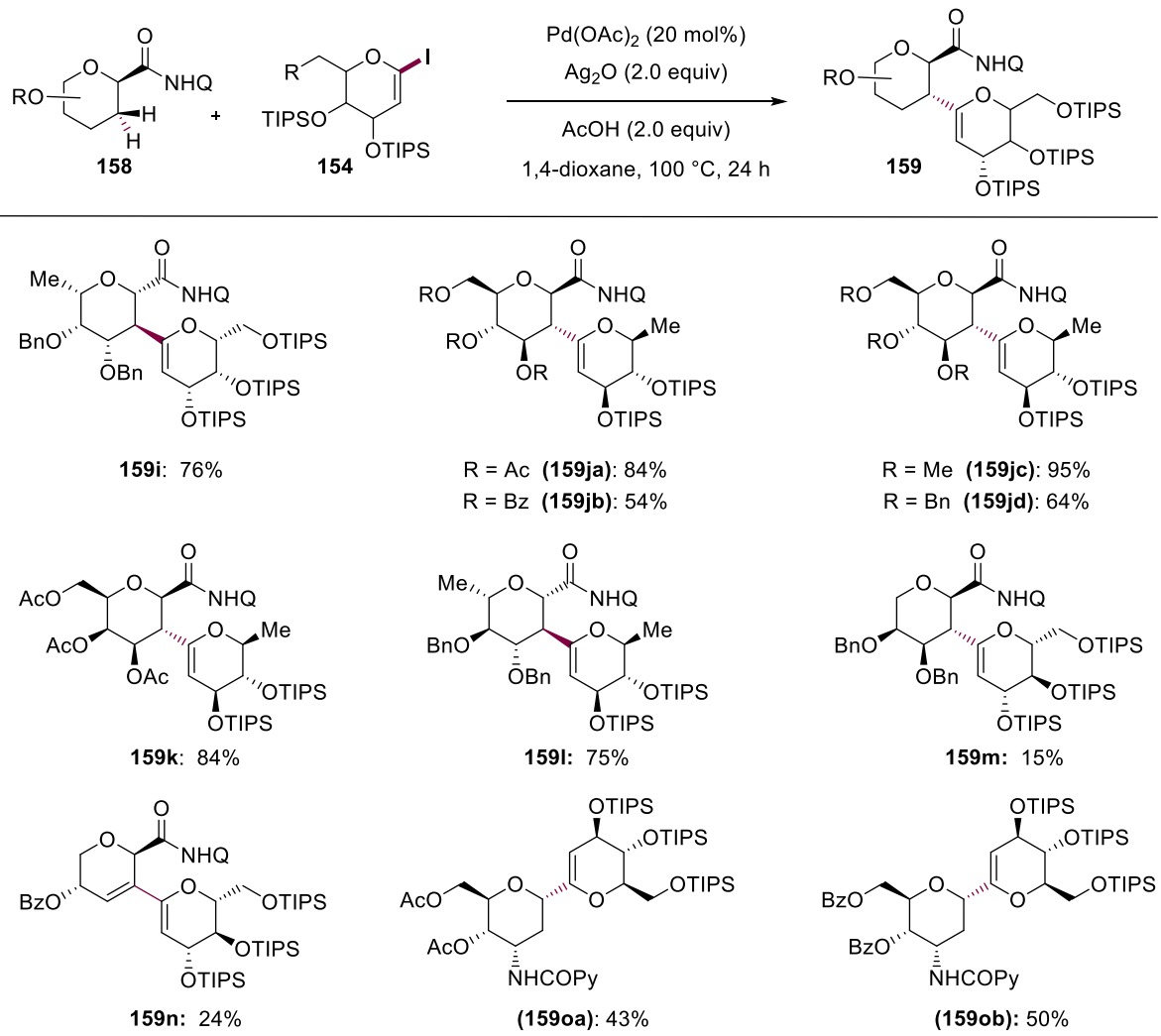
R = Me **(159fb)**: 97%
R = Bn **(159fc)**: 64%



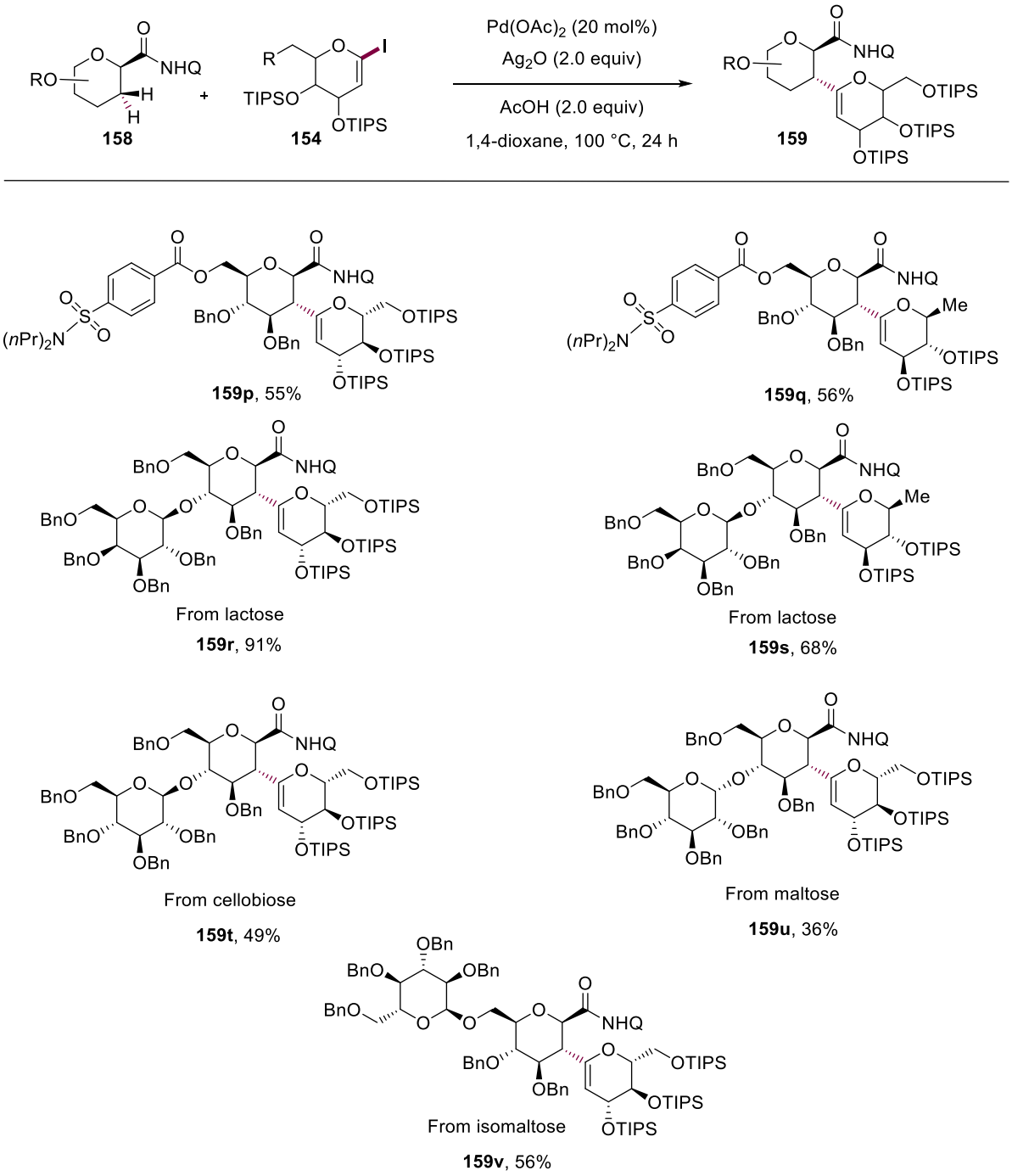
159g: 66%



159h: 69%



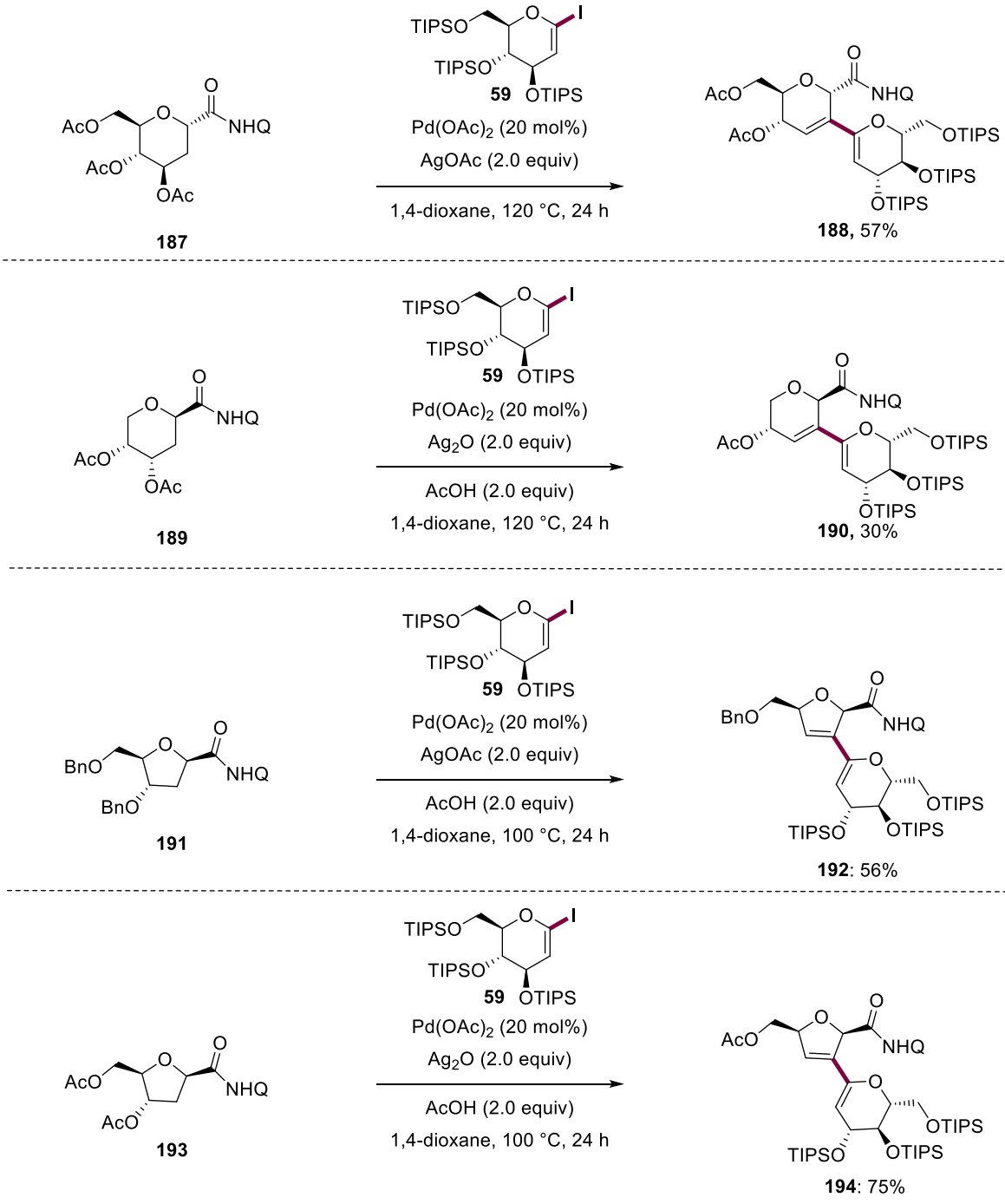
Scheme 3.2.3.1. Versatile and robustness of C(sp^3)–H glycosylation of glycosides. *Performed by Adelina Kopp.



Scheme 3.2.3.2. Late-stage C–H glycosylation for saccharide assembly.

Then, we examined the influence of the absolute configuration at the anomeric center. When anomeric *α*-glucoside **187** was subjected to the modified conditions, the *β*-OAc eliminated product **188** was selectively formed (Scheme 3.2.3.3). In this case, a *cis*-C–H activation[70] favored a C(sp^3)–H activation along with a *β*-acetoxyl- elimination. 2-Deoxy-xyloside **189** with an axial acetoxyl group at *C*(3) position gave a suppressed catalytic efficiency due to the steric effect of the *C*(3) axial substituent. Furanosides

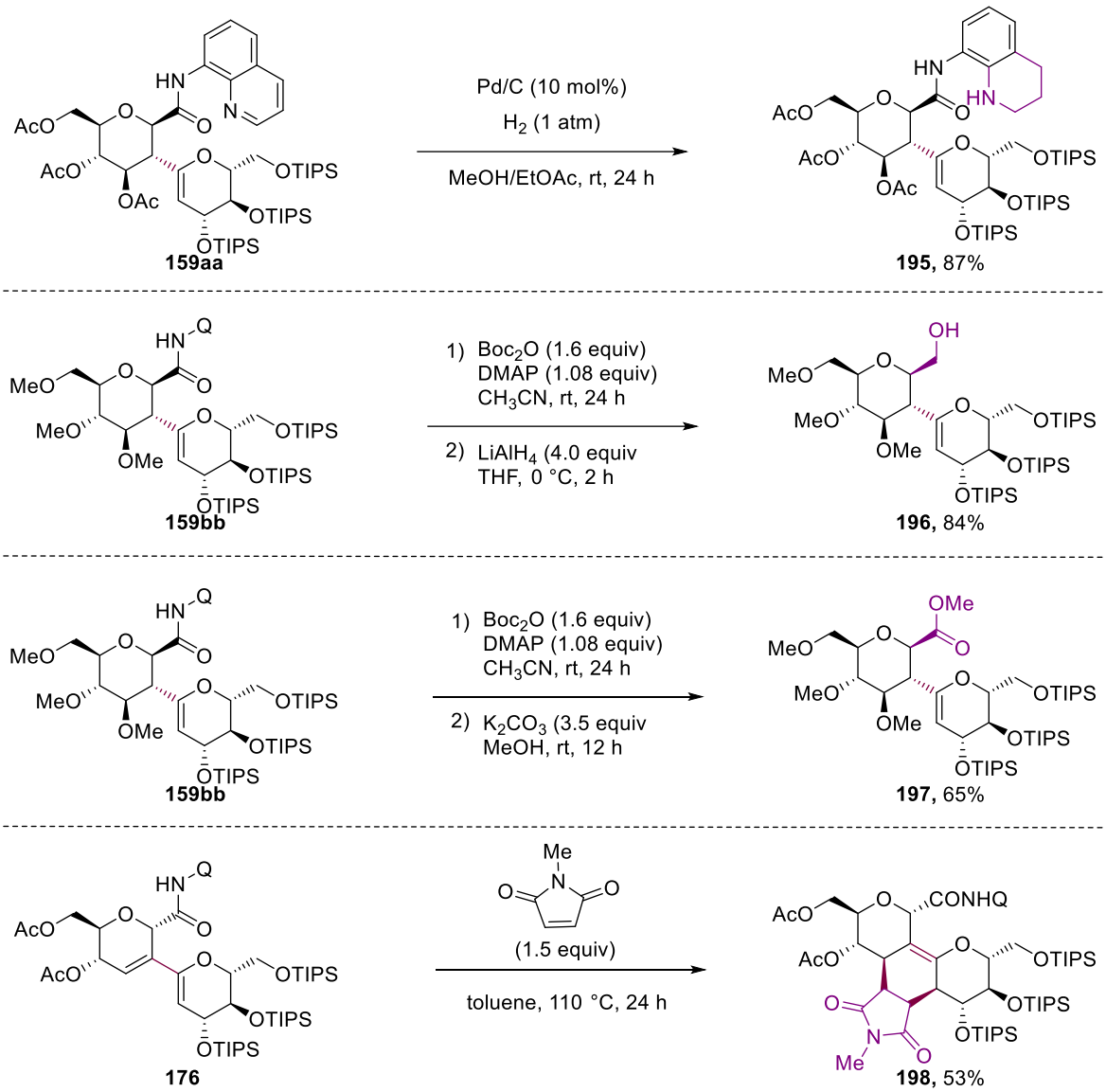
derived from 2-deoxy ribose with different leaving groups gave the *β*-eliminated products **192** and **194** with excellent selectivities.



Scheme 3.2.3.3. *β*-Elimination of various glycosides.

Treatment of disaccharide **159aa** with a palladium catalyst and molecular hydrogen afforded product **195** bearing a newly formed tetrahydroquinoe hydrogen bond donor. The amide-linked quinoline could also be successfully cleaved under mild reaction conditions *via* a two-step sequence, resulting in either the primary alcohol **196** or the ester **197**. Finally, a Diels-Alder reaction set the stage for the efficient construction of

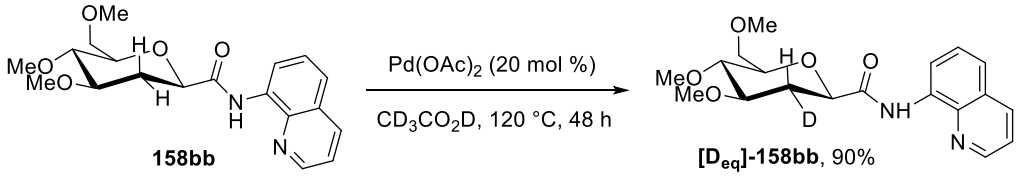
polycyclic product **198** with four newly formed stereocenters with defined configuration in a single step (Scheme 3.2.3.4).



Scheme 3.2.3.4. Quinoline amide transformation.

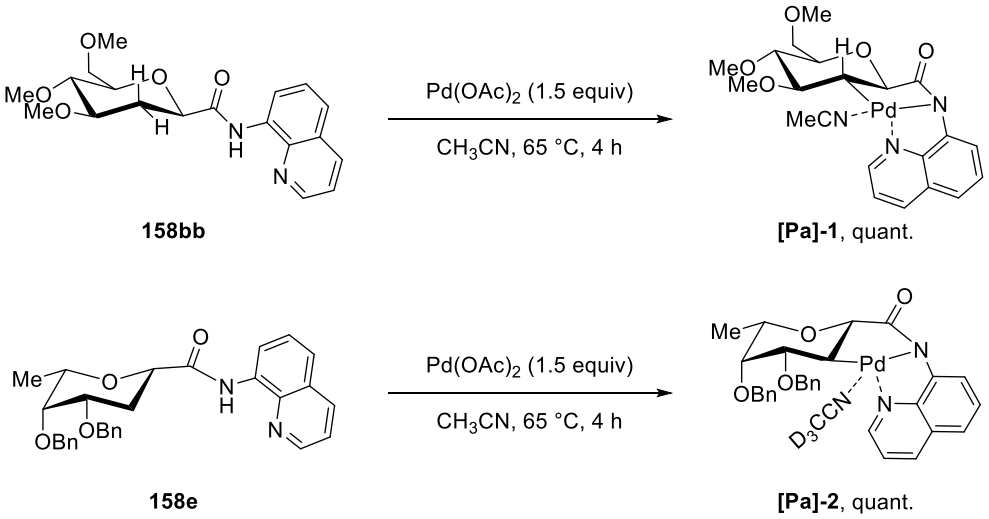
3.2.4. Mechanistic Studies

To gain insights into the C(sp^3)–H palladation, we conducted transformations with isotopically labelled CD_3CO_2D as the solvent. The H/D exchange experiment showed that the equatorial hydrogen was selectively deuterated to give compound [**D_{eq}]-158bb** (Scheme 3.2.4.1). This finding was indicative of a *trans*-C(sp^3)–H palladation.



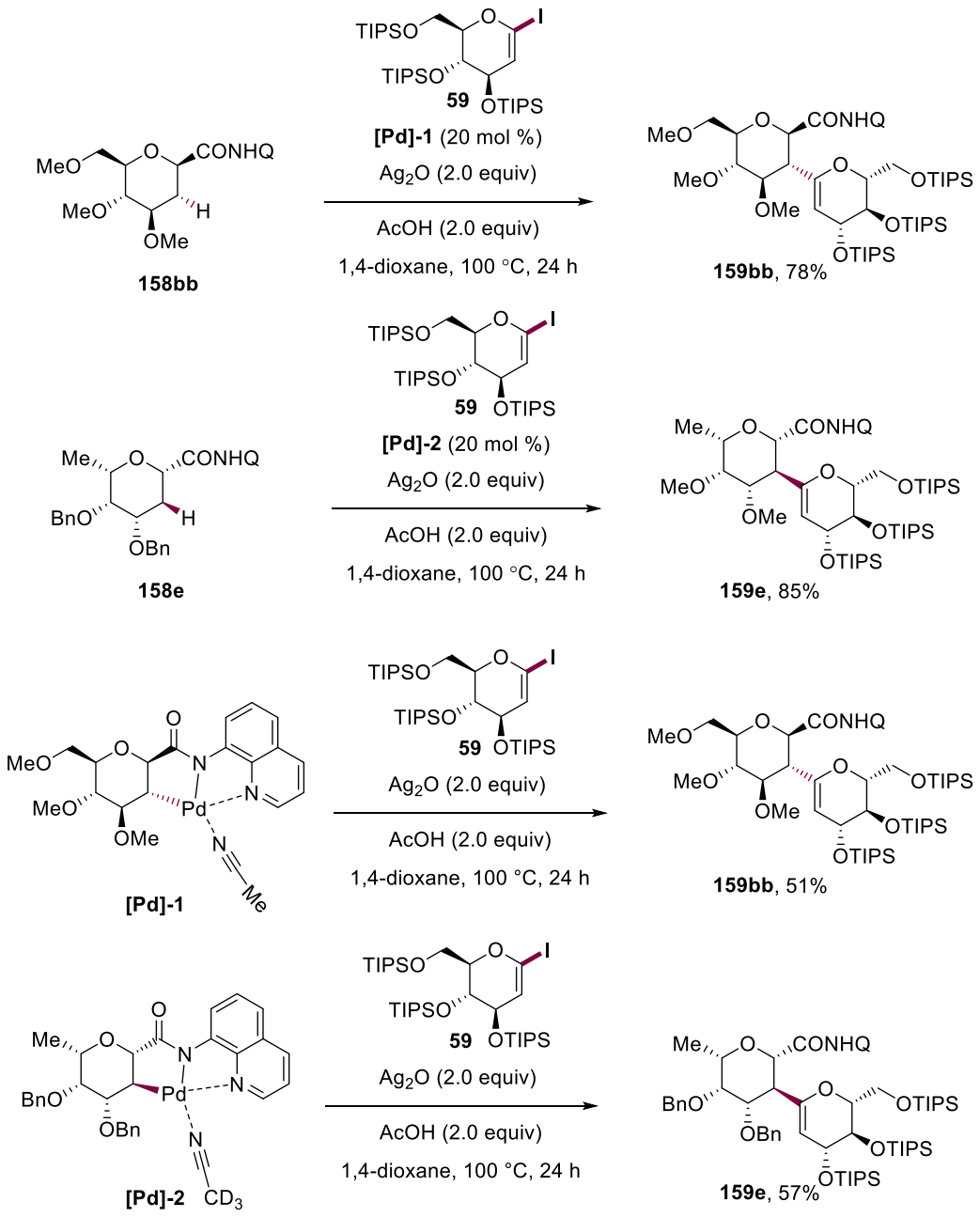
Scheme 3.2.4.1. H/D exchange of 2-deoxy-glucoside **158bb**.

Furthermore, cyclopalladaglycoside complexes [**Pd]-1** and **[Pd]-2** were independently prepared with 2-deoxy-glucoside **158bb** and 2-deoxy-rhamanoside **158e** via C–H activation (Scheme 3.2.4.2). The selective C−H bond cleavage was further demonstrated.



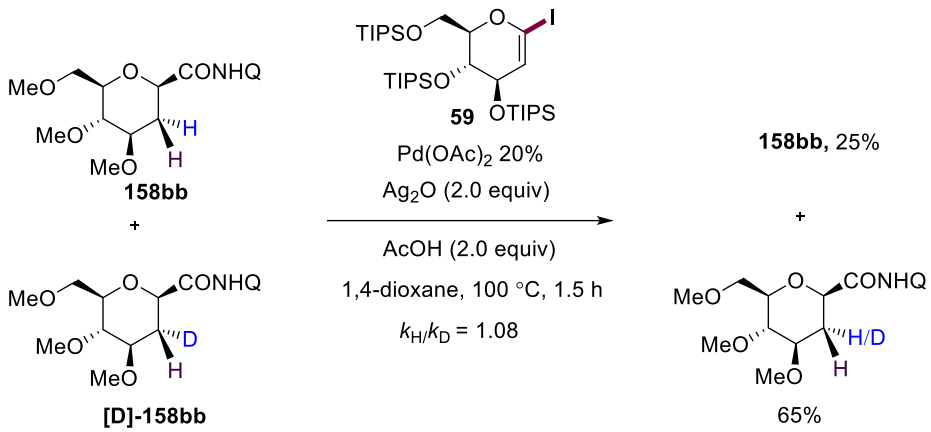
Scheme 3.2.4.2. Cyclopalldaglycosides synthesis.

The cyclopalladacycle intermediates were utilized for the catalytic C−H glycosylation, the desired products **159bb** and **159e** were isolated in comparable yields and exclusive *trans*-C−H glycosylation products (Scheme 3.2.4.3). In addition. Then, the stochiometric amounts of the cyclopalladaglycoside complexes were identified as catalytic relevant for the saccharide assembly of **159bb** and **159e**.



Scheme 3.2.4.3. Catalytic and stoichiometric reactions with cyclopalldacycle intermediates.

Intermolecular competition experiments provided strong support for a facile C–H metalation with a minor kinetic isotopic effect (KIE) of $k_H/k_D \approx 1.1$, which suggested that the *trans*-C−H cleavage is not be the rate-determination step (Scheme 3.2.4.4).

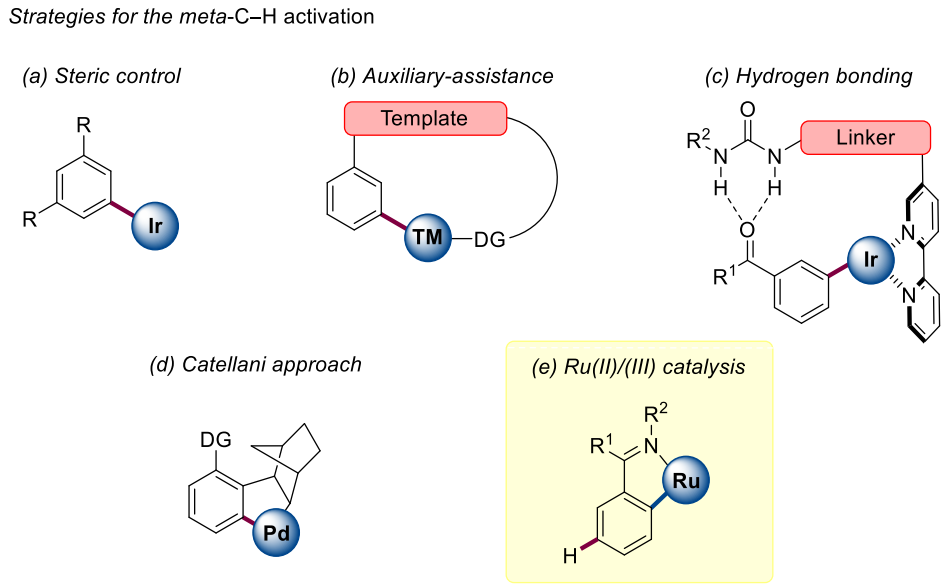


Scheme 3.2.4.4. Kinetic isotope effect experiment.

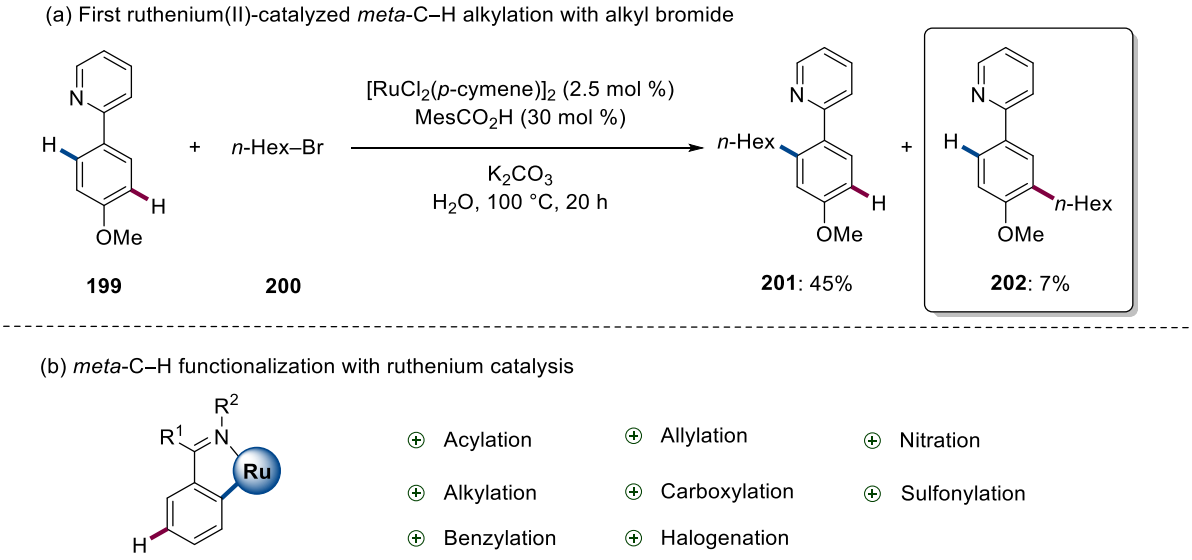
3.3. C(sp²)−H Glycosylation by Ruthenium (II) Catalysis towards *meta-C*-Aryl Glycosides

3.3.1. Introduction

In contrast to numerous reports on *ortho*-selective C–H activations of arenes,[11l, 127] procedures for remote *meta*-selective C–H functionalization remain underdeveloped and were thus far largely realized through a limited number of viable strategies (Scheme 3.3.1.1).[104, 128] Unfortunately, most approaches are either limited to specific substrates, requiring the installation of elaborate templates[128b, 129] and the use of transient mediator, such as norbornene derivatives in a Catellani-type manifold,[91, 128e] or are restricted to the use of expensive rhodium[130] and iridium complex.[131] A mechanistically different approach for the *meta*-C–H functionalization was unraveled in a stoichiometric[132] and catalytic fashion by ruthenium catalysis,[104, 128h] in which the reaction proceeded in a remote C–H functionalization manner. In 2011, the Ackermann group reported on the regioselective intermolecular alkylation of pyridine, pyrazole or ketimine with primary and secondary alkyl halides by using ruthenium(II) carboxylate complex.[133] Interestingly, the reaction of *para*-methoxy phenyl pyridine **199** with primary hexyl bromide **200** under ruthenium catalysis gave the desired *ortho*-alkylation product **201**, along with 7% of *meta*-alkylated byproduct **202** (Scheme 3.3.1.2a).[134] Later, the Frost group reported the ruthenium-catalyzed sulfonation.[135] We proposed new XAT/SET mechanism that proximity-induced, directing group-enabled *ortho*-selective C–H ruthenation leads to a considerable electronic bias towards an electrophilic arene activation and consequently allowed further functionalization to take place at the remote *para*-position with respect to the Ru–C bond, thus resulting in the formation of overall *meta*-functionalized products.[136] Thereafter, a series of *meta*-C−H functionalizations were reported *via* ruthenium(II/III) catalysis (Scheme 3.3.1.2b), such as acylation,[137] formylation,[138] alkylation,[136, 139] allylation,[140] halogenation,[141] carboxylation,[142] nitration,[143] and sulfonylation.[135, 144]

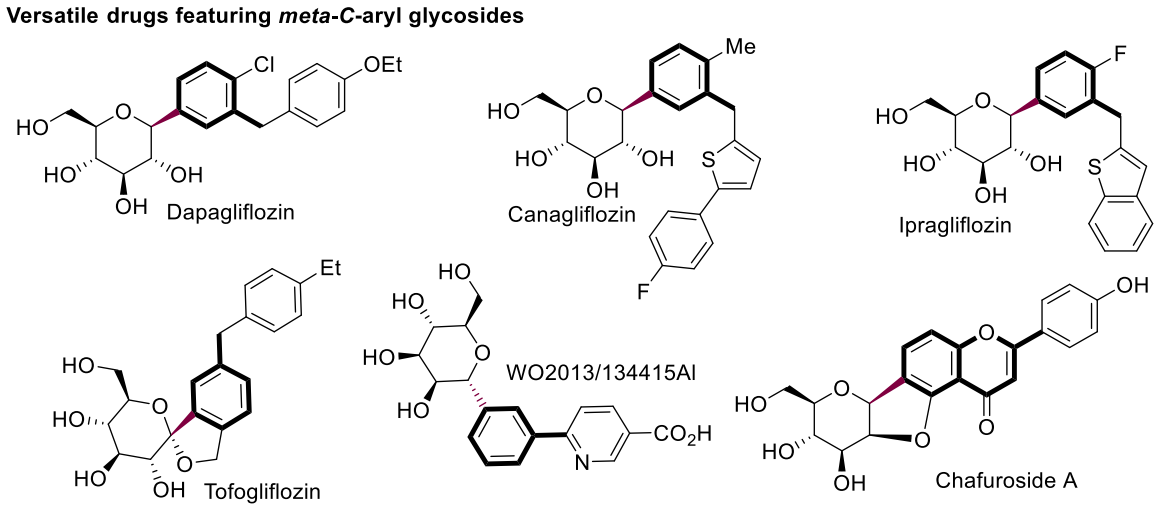


Scheme 3.3.1.1. Strategies for *meta*-C−H functionalization.



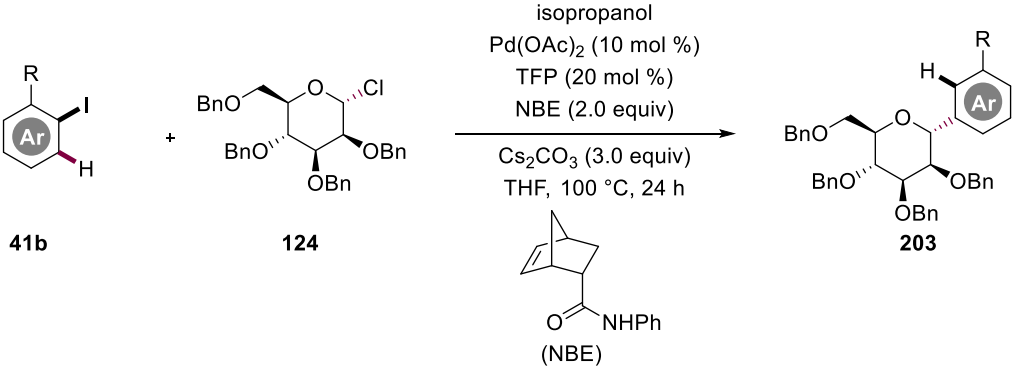
Scheme 3.3.1.2. Versatile *meta*-C−H functionalization by ruthenium catalysis.

meta-C-aryl glycosides represent an important carbohydrate scaffold in which the glycosidic C–C bond confers a remarkable stability to both enzymatic and chemical hydrolysis.[145] As a consequence, *C*-aryl glycosides were widely exploited in a variety of pharmacologically relevant drugs, such as *Dapagliflozin*, *Canagliflozin* and *Ipragliflozin* (Scheme 3.3.1.3).



Scheme 3.3.1.3. Selected examples featuring *meta*-*C*-aryl glycosides.

Unlike the proximal C–H glycosylation,[81, 83, 86, 146] the *meta*-C–H glycosylation is more challenging and only few established methods are thus far available for indirect *meta*-C–H glycosylation.[93, 97, 147] Combined with the role of palladium(II) as Lewis acid promoter,[81] palladium/norbornene cooperative catalysis was designed to achieve remote C–H glycosylation with glycosyl chloride donor **124**, targeting the efficient and site-selective synthesis of stable *C*-aryl glycosides **203** (Scheme 3.3.1.4). We wondered whether a ruthenium-catalyzed C–H glycosylation could be amenable for the construction of *meta*-C-aryl glycosides **203**.[139m, 141d, 148]



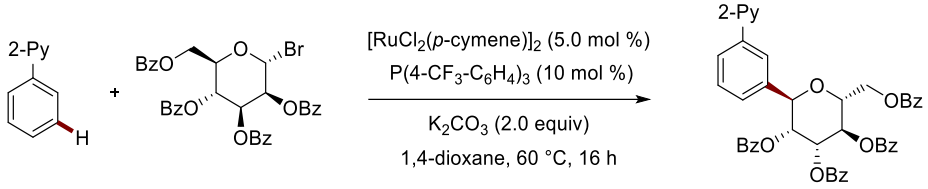
Scheme 3.3.1.4. Catellani-type reaction for *meta*-*C*-aryl glycosides **203** synthesis.

3.3.2. Optimization Studies for *meta*-C(sp^2)−H Glycosylation

We initiated our studies for the *meta*-C(sp^2)–H glycosylation with mannosyl bromide donor **161aa** as the glycosylation reagent (Table 3.3.2.1). The reaction with [$RuCl_2$(*p*-cymene)]$_2$ as the catalyst and $MesCO_2H$ as the additive failed to deliver the desired product **162aa** (entry 2). Instead, P(4-CF_3-C_6H_4)$_3$ provided the *meta*-glycosylation

product **162aa** in 29% yield at 100 °C (entry 3).[139c] Decreasing the reaction temperature improved the catalytic efficiency, with 60 °C being the best choice to give the product **162aa** in 75% yield with exclusive *meta*- and *α*-selectivity (entries 1-3). Next, $[RuCl_2(PPh_3)_3]$ as catalyst in the absence of $P(4\text{-}CF_3\text{-}C_6H_4)_3$ was tested, delivering product in 37% yield (entry 4). When replacing the $P(4\text{-}CF_3\text{-}C_6H_4)_3$ with different phosphine ligands, the yield could not be improved (entries 5-7). An optimization of the base demonstrated that K_2CO_3 was optimal (entry 8). A set of typical solvents, such as NMP, toluene and THF, was probed, but with no further improvement (entry 9). Control experiments verified the essential roles of the ruthenium catalyst and the phosphine ligand (entries 10 and 11).

Table 3.3.2.1 Optimization of *meta*-C(sp^2)–H glycosylation.

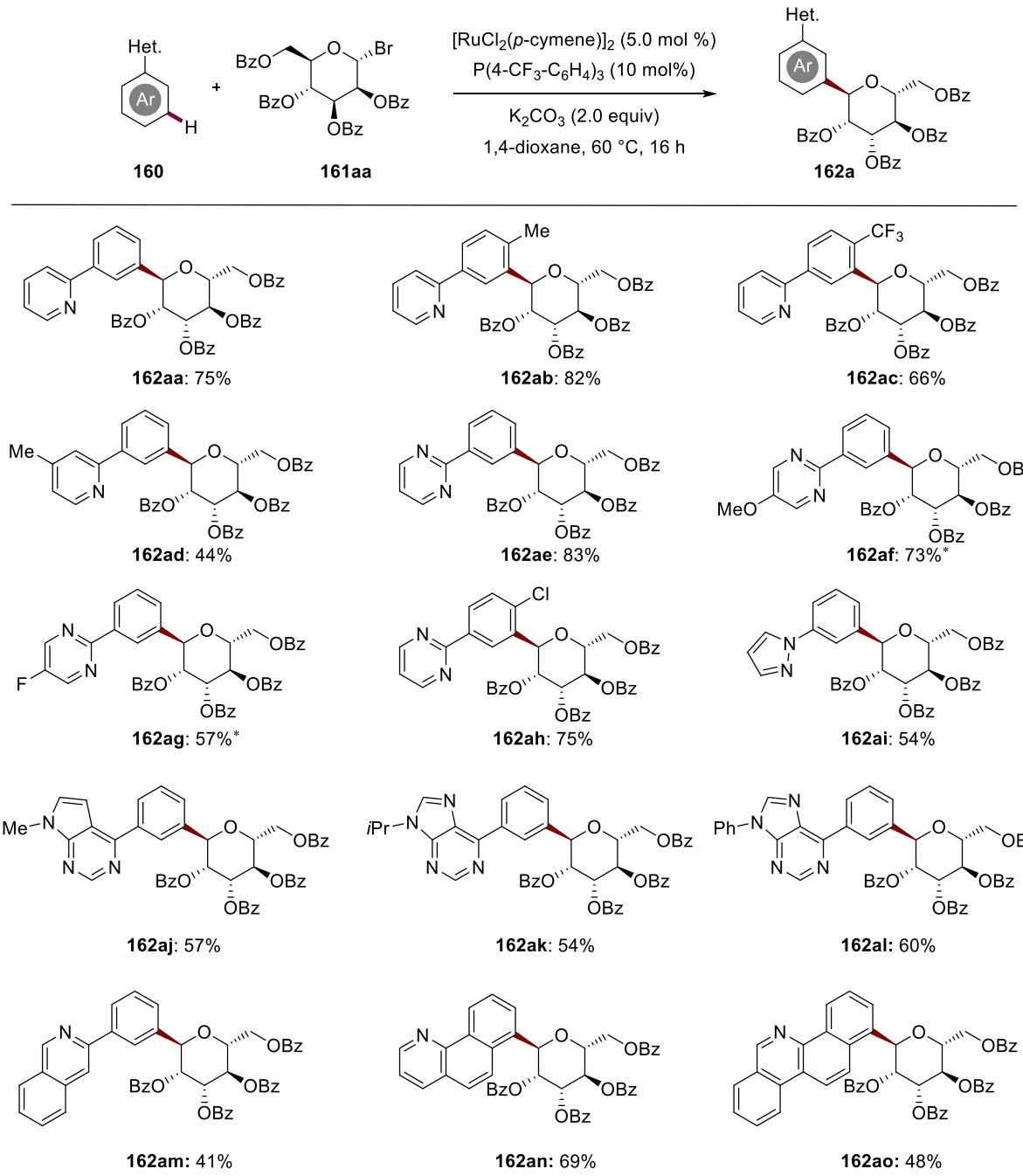


160aa **161aa** **162aa**

Entry	Deviation from standard conditions	Yield (%)
1	None	75
2	$MesCO_2H$ as ligand	NR
3	At 100 °C, 80 °C, 40 °C	29/57/12
4	$[RuCl_2(PPh_3)_3]$ as catalyst	37[a]
5	$P(4\text{-}OMe\text{-}C_6H_4)_3$ as ligand	40
6	$P(4\text{-}F\text{-}C_6H_4)_3$ as ligand	59
7	$P(3,5\text{-}CF_3\text{-}C_6H_3)_3$ as ligand	NR
8	Na_2CO_3 or K_3PO_4 or KOAc	28/49/NR
9	NMP/toluene/THF as solvents	NR/NR/27
10	Without $[RuCl_2(p\text{-cymene})]_2$	NR
11	Without $P(4\text{-}CF_3\text{-}C_6H_4)_3$	NR

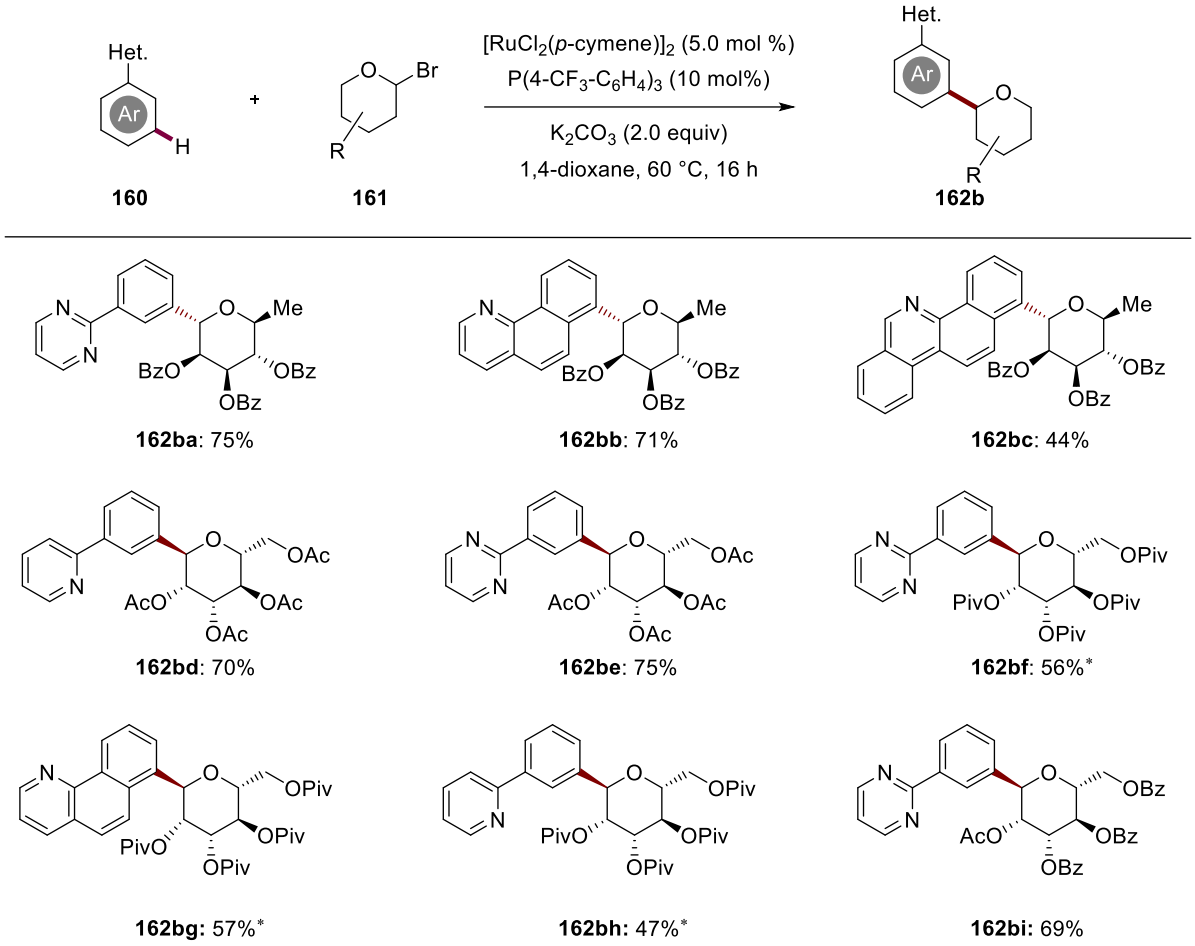
Reaction conditions: **160a** (0.10 mmol), **161aa** (0.15 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (10 mol %), K_2CO_3 (0.2 mmol), 1,4-dioxane (1.0 mL), 60 °C, 16 h. Yields of isolated product.

With the optimized reaction conditions for the *meta*-C(sp^2)–H glycosylation in hand, we examined its generality (Scheme 3.3.2.1). Initially, the substitution pattern on the arene moiety was tested, and *para*-decorated arenes **160b** and **160c** were well tolerated (**162ab** and **162ac**). Electron-rich pyridine **160d** exhibited a lower efficiency (**162ad**). When methyl substituent was installed at the *meta*-position of pyridine, desired product was not observed. Then, pyrimidine derivatives **160e**-**160h** were used in the *meta*-C–H glycosylation and high catalytic efficiencies were observed (**162ae**-**162ah**). The electrophilic chloro-group at the *para*-position of phenyl **160h** also proved to be feasible (**162ah**), without any *ortho*-arylation being observed.[149] The *meta*-C–H glycosylation was not restricted to pyridine-guided functionalization. Indeed, a plethora of heterocycles, such as pyrazole **160i**, purine derivatives **160k** and **160l** and quinoline **160m**, was identified as amenable substrates for the challenging *meta*-*C*-aryl glycosides assembly (**162ak**-**162am**). In addition, fluorescent scaffolds, such as benzo[*h*]quinoline **160n** and benzo[*c*]phenanthridine **160o**, afforded products **162an** and **162ao** irrespectively in a remote C–H glycosylation manner.



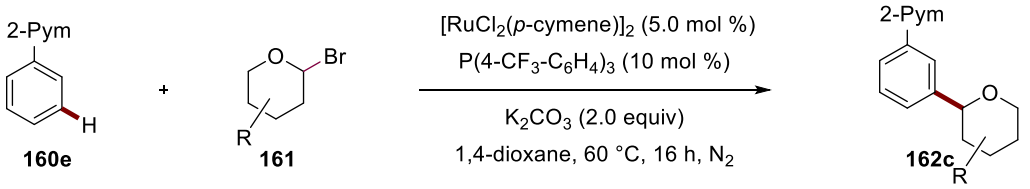
Scheme 3.3.2.1. Ruthenium-catalysed *meta*-C−H glycosylation of heteroarenes **160**. *Done by Takuya Michiyuki.

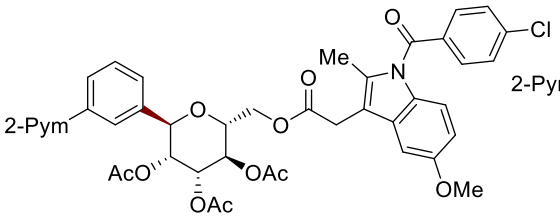
Subsequently, the ruthenium-catalyzed *meta*-C–H glycosylation strategy was probed with different glycosyl bromides (Scheme 3.3.2.2). Rhamnosyl bromide **161ba** proved efficient to site- and stereo-selectively stitch rhamnose moiety into the *meta*-position of a series of heteroarenes (**162ba-162bc**). Diversely protected mannosyl bromides **161bb-161bd**, containing acetyl and pivaloyl group, generated **162bd-162bi** with exclusive α-anomeric selectivity.



Scheme 3.3.2.2. Ruthenium-catalyzed *meta*-C−H glycosylation of heteroarenes. * Done by Dr. Nikolaos Kaplaneris.

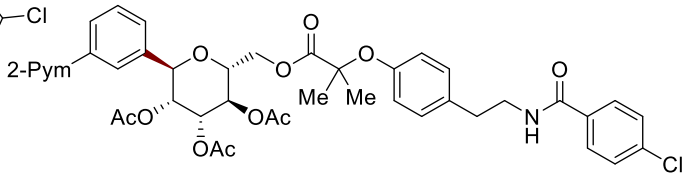
Finally, the robustness of the *meta-C*-aryl glycoside assembly was exploited for the *meta*-C–H glycosylation with structurally complex glycosyl bromides (Scheme 3.3.2.3). Hybrid glycosyl donors bearing natural products and drug derivatives, such as indomethacin, bezafibrate, naproxen, fenofibric acid, dehydrochloric acid, ibuprofen, repaglinide, ciprofibrate, and tolmetin, were thereby selectively converted to *C*-aryl glycosides **162ca-162ci**, leading to highly functionalized conjugates with excellent levels of chemo-, site- and stereoselectivities.





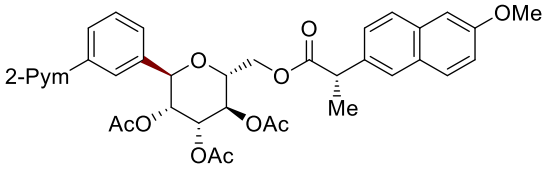
From Indomethacin

162ca: 75%



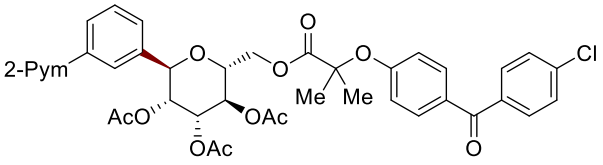
From Bezafibrate

162cb: 55%



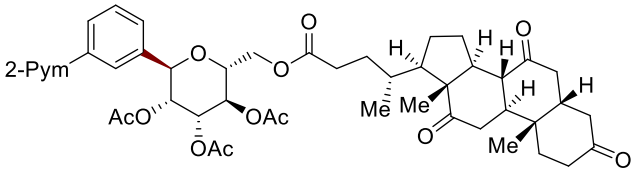
From Naproxen

162cc: 68%



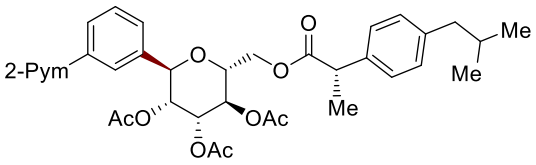
From Fenofibric acid

162cd: 52%



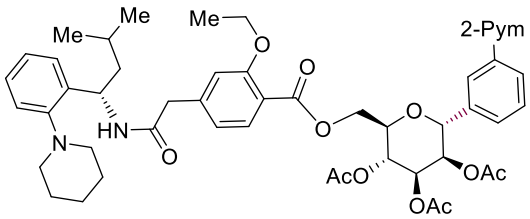
From Dehydrocholic acid

162ce: 65%



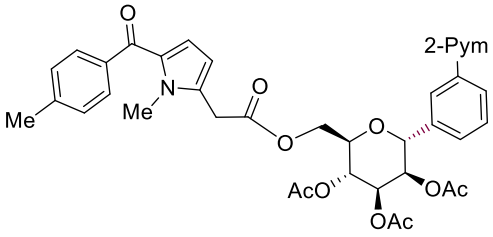
From Ibuprofen

162cf: 59%



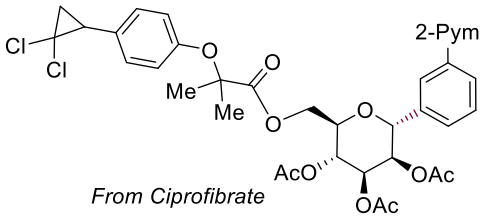
From Repaglinide

162cg: 79%



From Tolmetin

162ch: 50%

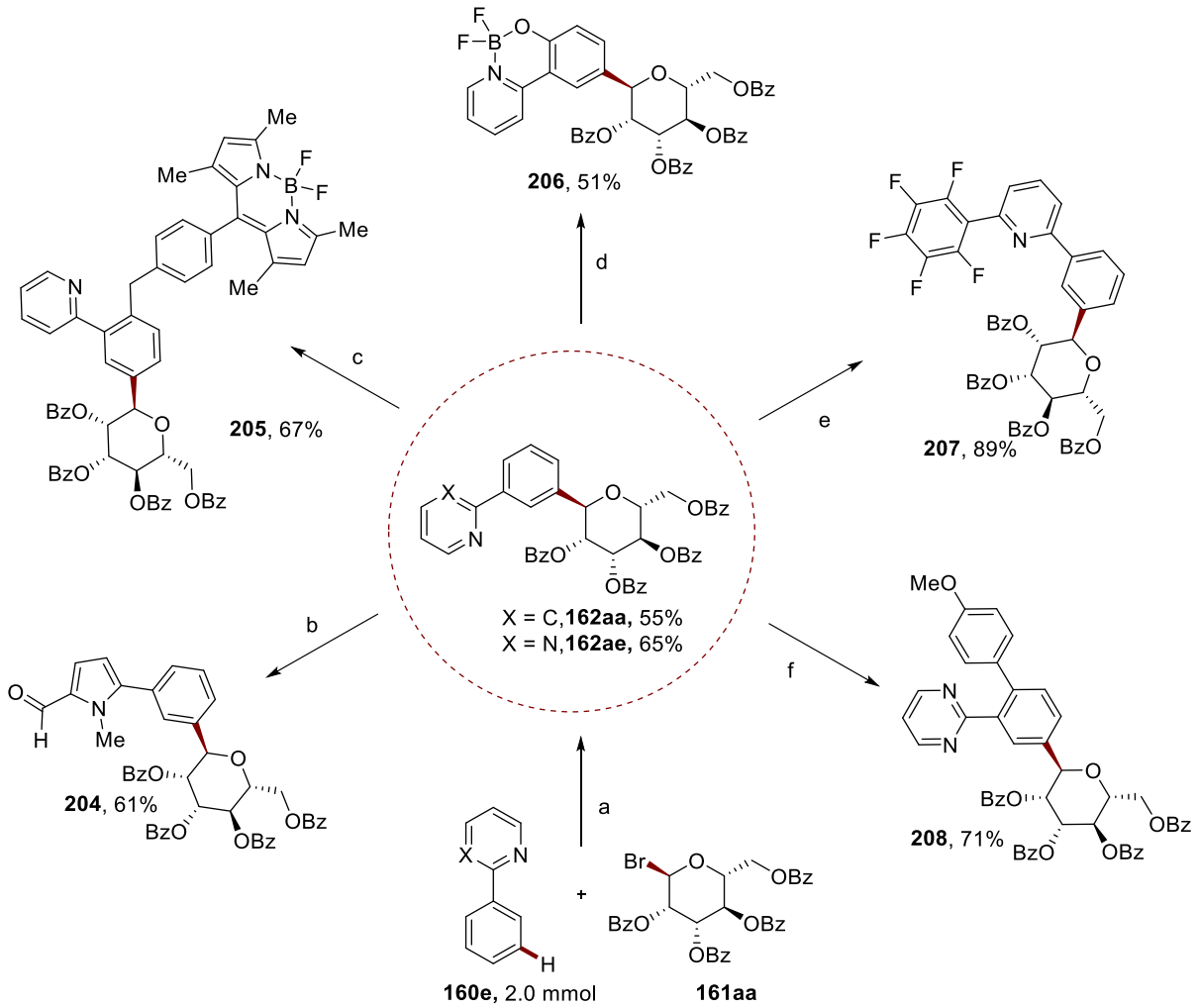


From Ciprofibrate

162ci: 62%

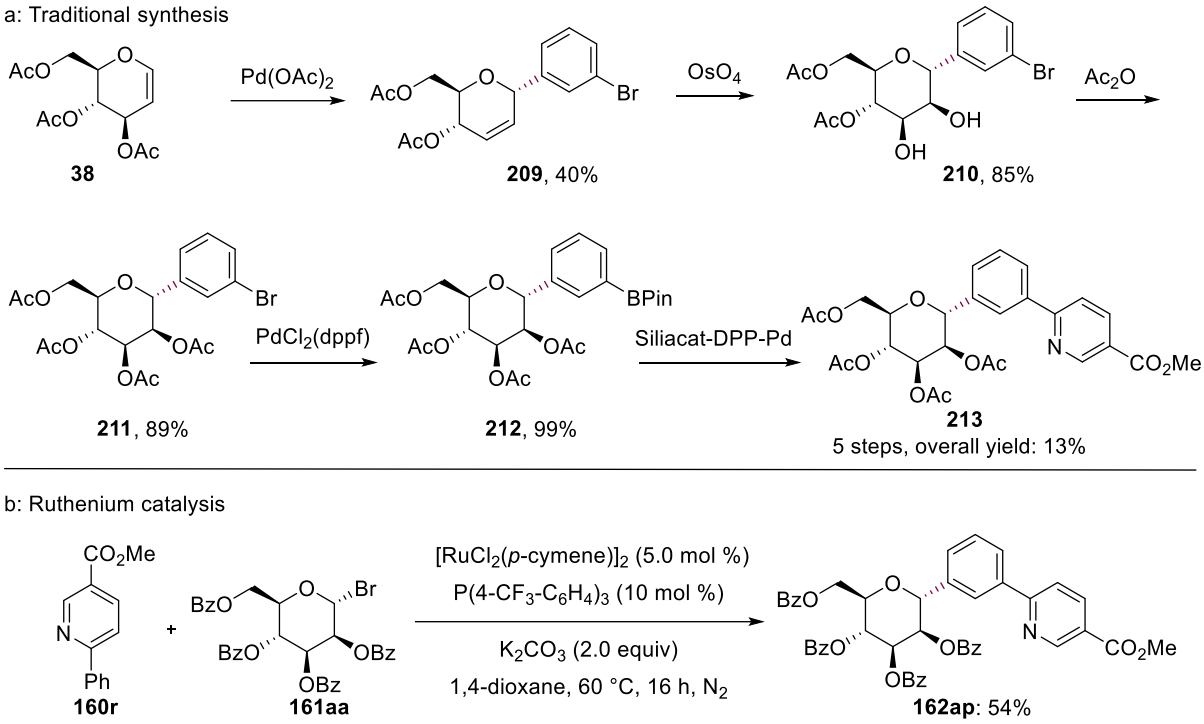
Scheme 3.3.2.3. Late-stage *meta*-C−H glycosylation.

The practical utility of the ruthenium-catalyzed *meta*-C–H glycosylation was illustrated by a gram-scale synthesis of *C*-aryl glycosides **162aa** and **162ae**. (Scheme 3.3.2.4a). Likewise, a two-step sequence enabled the efficient transformation of the pyridyl group into useful 2-formylpyrrole **204** (Scheme 3.3.2.4b). Late-stage diversification of product **162aa** allowed the construction of fluorescent labelled *C*-aryl glycosides **205** and **206** by ruthenium[150] and copper[151] catalysis (3.3.2.4c and 4d). In addition, to enrich the structural diversity of the products, the selective arylations of the arene scaffolds were featured in the synthesis of biaryl **207** and **208** (Scheme 3.3.2.4e and 4f).



Scheme 3.3.2.4. Gram-scale reaction and late-stage transformation.

In addition, the versatility of the ruthenium catalysis was mirrored by the one-pot synthesis of product **162ap** in 54% yield with the commercially available substrate **160p** and easily prepared **161aa**. Noteworthily, the synthesis of product **213** with established cross coupling strategy involved multiple synthetic steps and much lower overall yield.

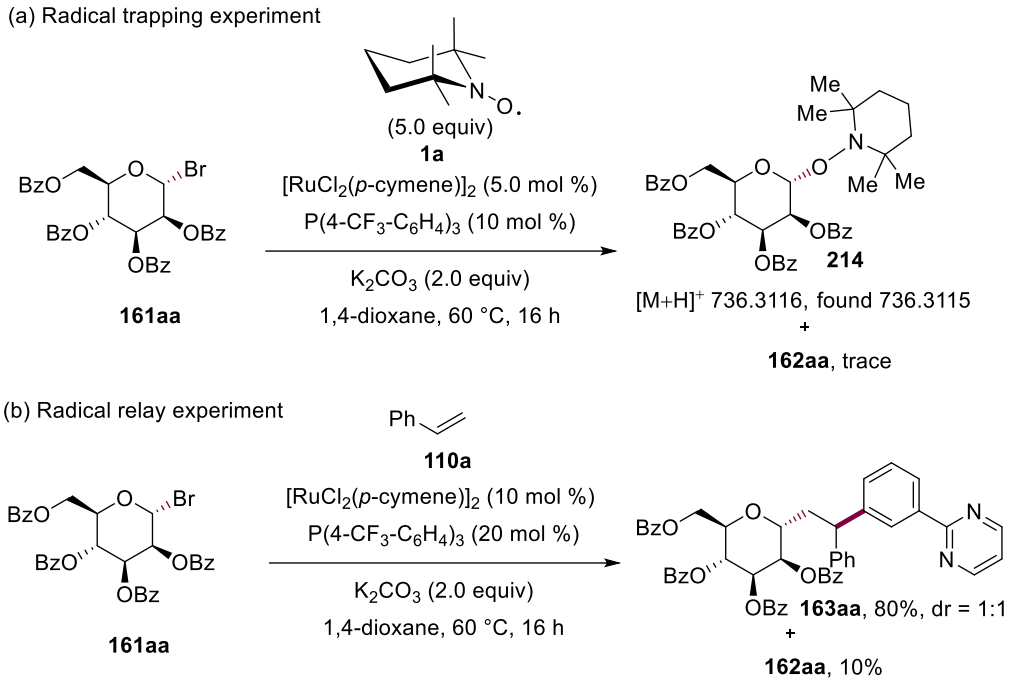


Scheme 3.2.2.4. Synthetic application.

3.3.3. Mechanistic Studies

3.3.3.1 Radical Trapping Experiments

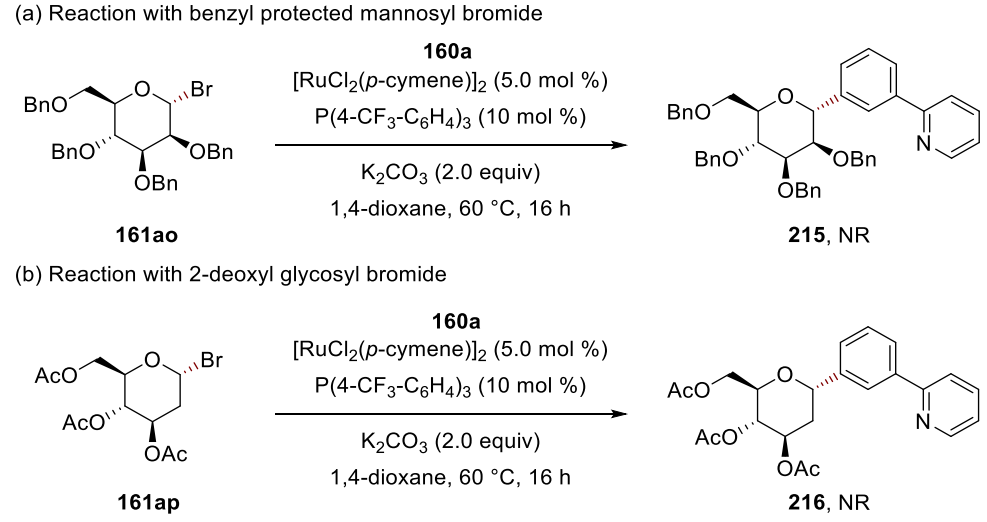
To gain insight into the reaction mechanism, we conducted a series of mechanistic experiments. The involvement of radical intermediate was supported by the detection of the glycosyl radical-TEMPO adduct **214** *via* high resolution mass-spectrometry (Scheme 3.3.3.1.1a). The involvement of mannosyl radical was further demonstrated by a ruthenium-catalyzed radical relay experiment, with three-component product **163aa** formed in 80% yield as well as 10% of direct *meta*-C−H glycosylation product **162aa** (Scheme 3.3.3.1.1b).



Scheme 3.3.3.1.1 Radical trapping experiments.

3.3.3.2 Investigation of Neighboring Effect

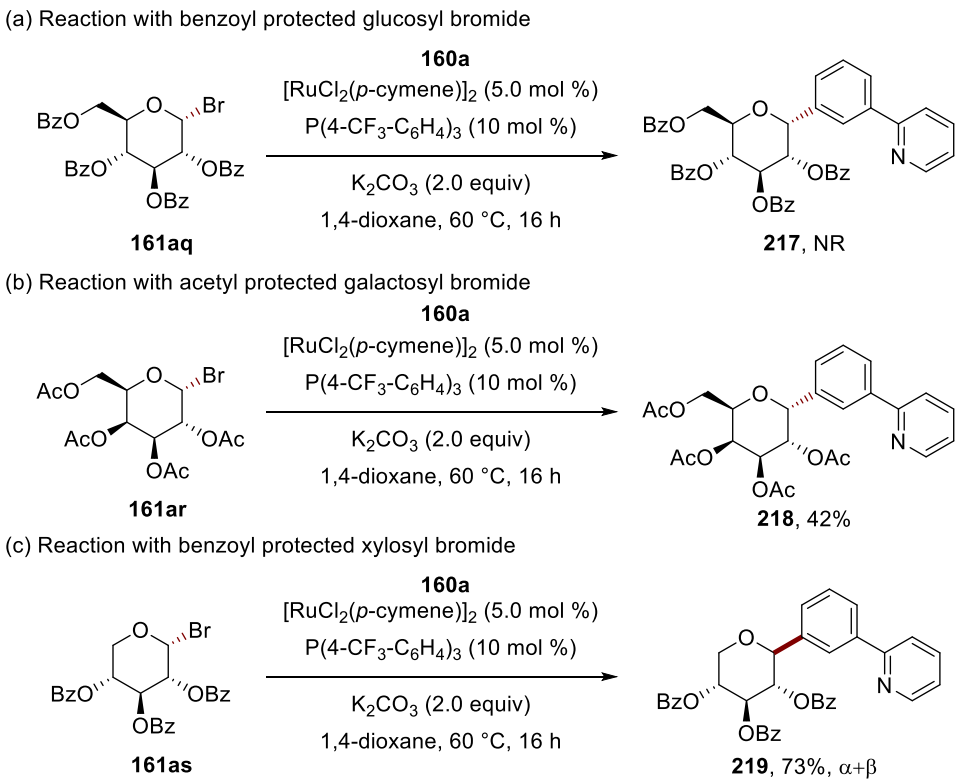
To examine whether there is a neighboring effect of the *C*2-benzoyl group, substrate **161ao** was utilized under otherwise identical reaction conditions and product **215** was not detected (Scheme 3.3.3.2.1a). Similarly, 2-deoxyl glycosyl bromide **161ap** featuring no substituent at the *C*(2)-position proved not suitable for the *meta*-C–H glycosylation, suggesting that the *C*(2)-carboxyl protecting group might be crucial for an efficient transformation (Scheme 3.3.3.2.1b).



Scheme 3.3.3.2.1 Neighbouring effect investigation.

3.3.3.3 Investigation of Versatile of Glycosyl Donors.

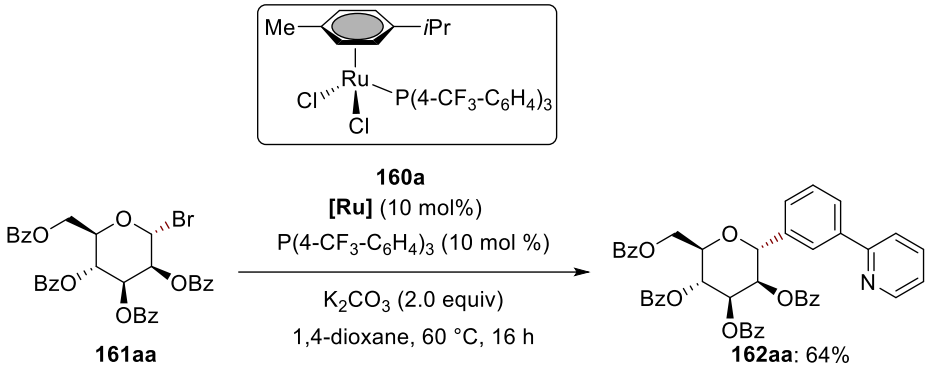
Glucosyl bromide **161aq** failed to generate the desired *meta*-C–H glycosylation product **217** (Scheme 3.3.3.3.1a). Compared to the $^4C_1$ and $^1C_4$ conformers, the slightly distorted $B_{2,5}$ boat conformation of glucopyranosyl radical is more stable.[152] The C2 benzoyl group and lone pair electrons of the endocyclic oxygen hence may block the attack of a glucosyl radical to the *para*-position of the cyclometalated C–Ru bond.[127f] In contrast, when acetyl protected galactosyl bromide **161ar** was employed, the product **218** was formed with α-anomeric selectivity in 42% yield (Scheme 3.3.3.3.1b). This α-selectivity may be caused by the C4 acetyl group, instead of the α-selectivity control derived from the sterically encumbered catalyst. Interestingly, when conformationally unrestricted benzoyl protected xylosyl bromide **161as** was employed, product **219** was isolated, albeit with poor stereoselectivity (Scheme 3.3.3.3.1c). We assume that the $B_{2,5}$ boat conformer of xylosyl radical is more flexible than its chair conformers. It features a planar C1 carbon center and allows the attack from either the *α*- or the *β*-side.[153]



Scheme 3.3.3.3.1 Investigations of versatile glycosyl donors.

3.3.3.4 Investigation of Key Ruthenium Catalyst.

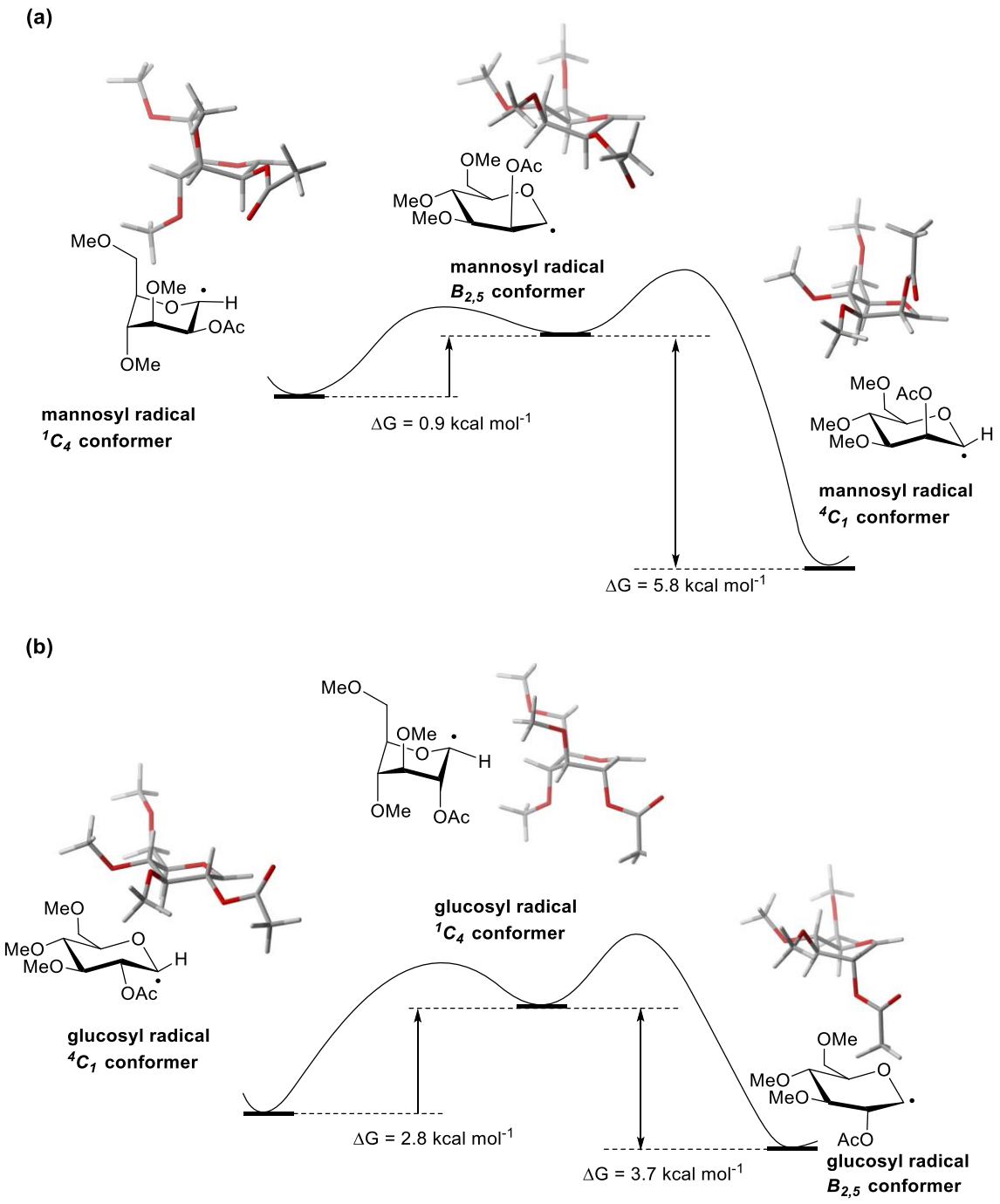
In addition, the ruthenium catalyst **[Ru]** was employed for the challenging *meta*-C–H transformation (Scheme 3.3.3.4.1). The *meta*-glycosylation product **162aa** was obtained in 64% yield, which indicates that this catalyst could be catalytically relevant.

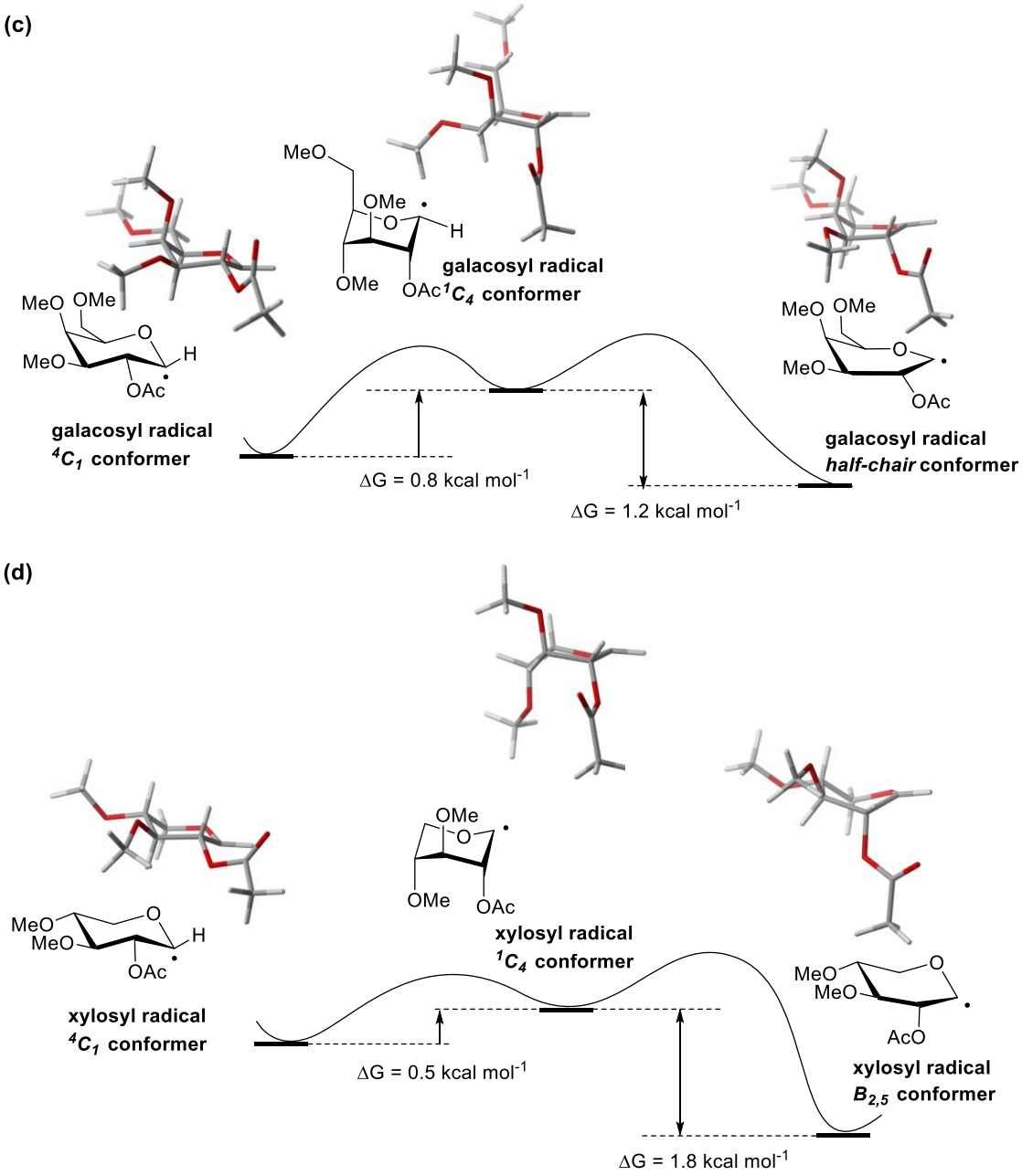


Scheme 3.3.3.4.1 Reaction with key catalytic intermediate.

3.3.3.5 DFT Calculation

Further DFT calculations studies on the pyranosyl radical conformations analysis were carried out (Done by Bin-Bin Yuan). It was found that $^4C_1$ conformer of the mannosyl radical is more stable than the $^1C_4$ and $B_{2,5}$-boat conformer by 4.9 and 5.8 kcal mol^{-1} (Scheme. 3.3.3.5.1a). The mannosyl radical was stabilized by the interaction between the anomeric radical orbital (SOMO), the σ*-orbital of the adjacent C–O bond, and the p-orbital of a lone pair of the ring oxygen in their periplanar arrangement. The *C*(2) axial benzoyl group and lone pair electrons of ring oxygen force the formation of the *meta*-C–H glycosylation product with complete *α*-stereoselectivity (Scheme 3.3.3.5.1b). We also found that the $B_{2,5}$-boat conformation of the glucosyl radical is slightly more favorable than the other conformers, which had also been disclosed by the Giese group.[152, 154] Interestingly, galactosyl radicals display two stable conformers, the half-chair conformation and a flattened $^4C_1$-chair conformation with similar energies (Scheme 3.3.3.5.1c). It is noted that the reaction with xylosyl bromide generated the mixture of *α*- and *β*-products. This was probably due to the $B_{2,5}$-boat conformation of the pyranosyl radical intermediates, which provides *α* planar carbon center with potential to form both anomers through *α*- and *β*-attacks (Scheme 3.3.3.5.1d).


(a)
MeO
OMe
O
H
OAc
OMe
mannosyl radical
$^1C_4$ conformer
OMe
OAc
O
MeO
MeO
mannosyl radical
$B_{2,5}$ conformer
ΔG = 0.9 kcal mol^{-1}
MeO
AcO
O
MeO
MeO
H
mannosyl radical
$^4C_1$ conformer
ΔG = 5.8 kcal mol^{-1}
(b)
MeO
OMe
O
H
OMe
OAc
glucosyl radical
$^1C_4$ conformer
MeO
MeO
O
H
OAc
glucosyl radical
$^4C_1$ conformer
ΔG = 2.8 kcal mol^{-1}
OMe
MeO
MeO
O
AcO
ΔG = 3.7 kcal mol^{-1}
glucosyl radical
$B_{2,5}$ conformer



Scheme 3.3.3.5.1. Relative stabilities of different pyranosyl radical intermediates Done by Bin-Bin Yuan.

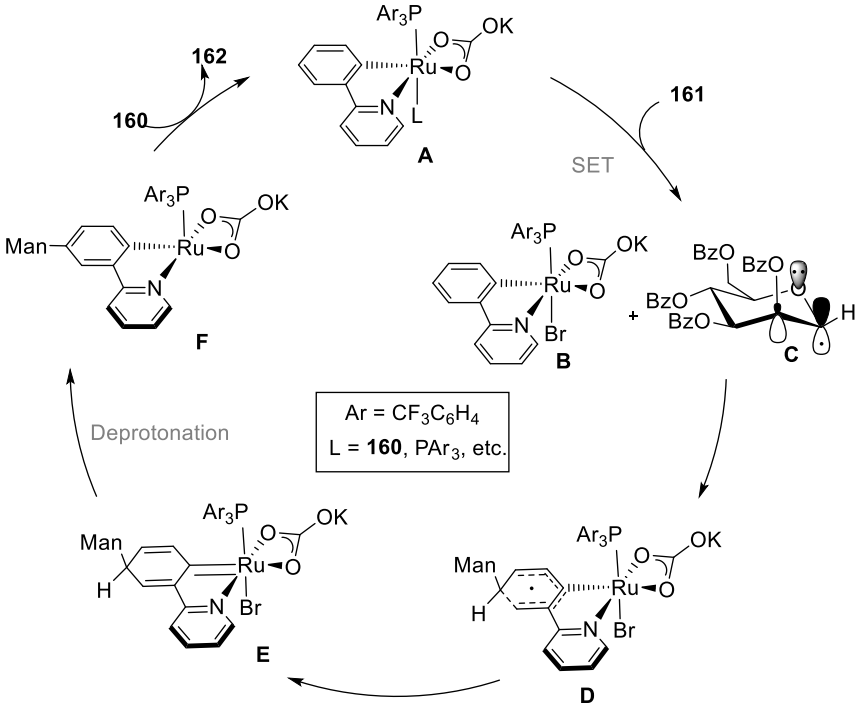
Stabilization energies of the orbital interactions between the anomeric carbon, which is adjacent C–O bond and the p-orbital of the ring oxygen were calculated based on the NBO theory for several conformations (Table 3.3.5.1). The results shown that all conformers were significantly stabilized by the interaction between the LP(2) O5 orbital and the LP*(1) *C*(1) orbital by 42 up to 48 kcal mol^{-1}. Additionally, the interaction between the antibonding orbital BD*(C2–O2) and the LP (1) *C*(1) orbital also contributes significantly for the stabilization of both boat-like and chair-like conformations by 10 up to 14 kcal mol^{-1}.

Table 3.3.5.1 Stabilization energies by second-order perturbation theory of the Fock matrix within NBO calculation between the LP(2) O5 and the LP*(1) C1 and between the LP (1) C1 and BD* (C2–O2) for the full mannosyl, glucosyl, galactosyl and xylosyl radical conformers.

		Stabilization energy (kcal mol^{-1})			
Donor	Acceptor	**Mannosyl**	**Glucosyl**	**Galacosyl**	**Xylosyl**
LP(2) O5	LP*(1) C1	42.70	47.01	42.74	48.11
LP(1) C1	BD*(C2-O2)	12.87	14.41	10.22	14.46

3.3.6 Proposed Catalytic Cycle

Based on our findings, a plausible catalytic cycle (Scheme 3.3.6.1) commences with a *ortho*-C–H ruthenation to form intermediate **A**. Subsequently, single electron transfer (SET) from the ruthenium(II) complex to the mannosyl bromide occurs, generating ruthenium(III) intermediate **B** and radical **C**, followed by addition of the radical **C** to the *para*-position of intermediate **B** to give intermediate **D**. The reactive triplet radical **D** is stabilized by singlet metallacycle **E** *via* ligand to metal charge transfer. Finally, proton abstraction and ligand exchange deliver the desired *meta*-glycosylation product **162** and regenerate ruthenium(II) complex **A**.

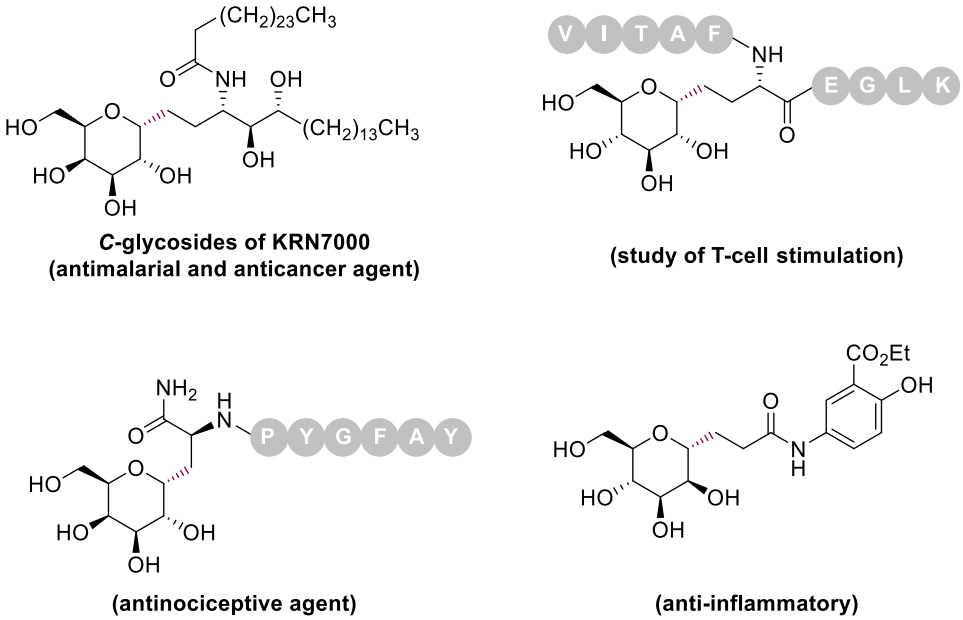


Scheme 3.3.6.1. Proposed catalytic cycle.

3.4. Ruthenium-Catalyzed *meta*-C−H Domino Ethyl Glycosylation towards *C*−Alkyl Glycoside

3.4.1. Introduction

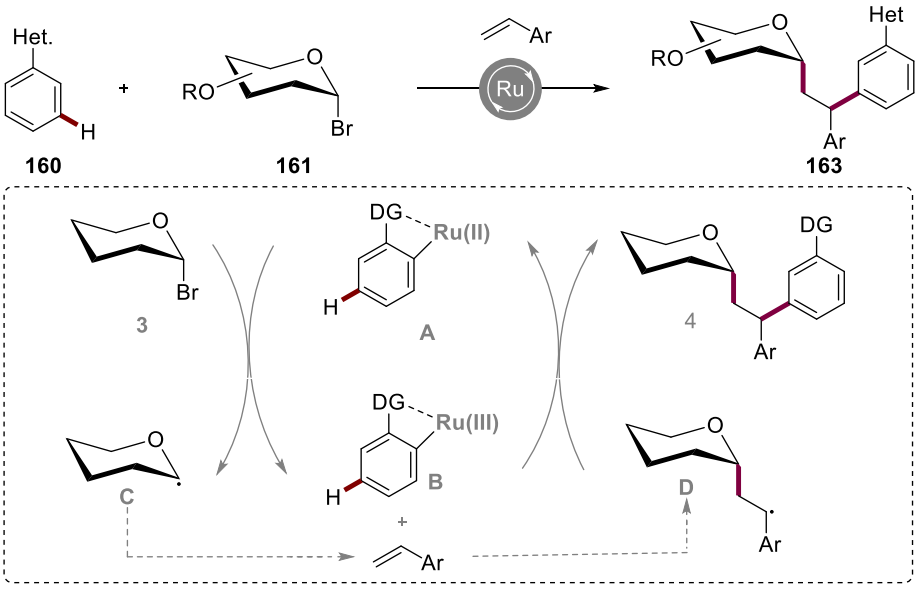
Compared to the studies on the synthesis of *C*-aryl glycoside, the studies on *C*-alkyl glycoside are rare due to the challenges of overcoming *β*-hydride elimination. Indeed, such scaffolds are valuable drug candidates because of its biological activities after the incorporation into aliphatic C−H bond, especially for installation to the side chain of amino acids and peptides.



Scheme 3.4.1.1. Selected examples of *C*-alkyl glycosides.

As discussed in the introduction (*vide supra*), the Giese-type addition has been well exploited for the efficient synthesis of *C*-alkyl glycosides and tin-free variants were also recently well-documented, such as transition metal-catalysed cross coupling, photo-induced radical addition and photo-induced metal-catalysis. Despite of the advances made during the last decade, the Giese-type anomeric addition was still restricted to two-component transformation. The Domino C−H ethyl glycosylation reaction has not yet been established. Thus, we wondered whether it would be possible to combine the Giese addition with our ruthenium-catalysed C−H glycosylation. With the aid of external styrene, we proposed that the Giese addition intermediate could be intercepted by the benzyl radical addition to the *para*-C−H position of C−Ru bond. The overall *meta*-C−H functionalized product was thus formed in a multicomponent manner.

The resulting diversified *C*-alkyl glycosides could be generated within a single step (Scheme 3.4.1.2).

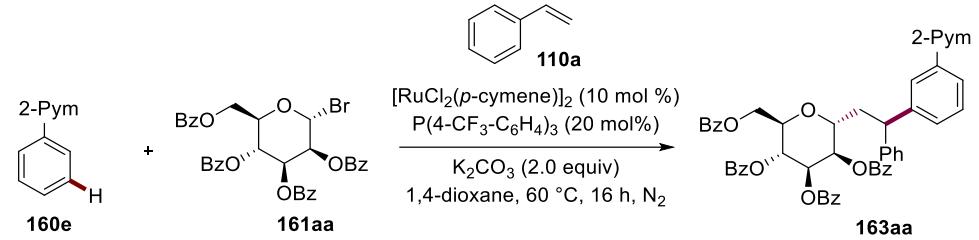


Scheme 3.4.1.2. Ruthenium-catalysed Domino C−H ethyl glycosylation for *meta*-*C*-alkyl glycoside **163**.

3.4.2. Optimization Studies for *meta*-C−H Domino Ethyl Glycosylation

We initiated our studies for the ruthenium-catalyzed multicomponent reaction with phenyl pyrimidine **160e**, styrene **110a** and mannosyl bromide donor **161aa** (Table 3.4.2.1). After an extensive optimization, the desired Domino C−H ethyl glycosylation product **163aa** was obtained in 80% yield in a site- and stereoselective manner by using $[RuCl_2(p\text{-cymene})]_2$ as the catalyst, $P(4\text{-}CF_3\text{-}C_6H_4)_3$ as the ligand and K_2CO_3 as the base under 60°C for 16 h (entry 1). Replacing the $P(4\text{-}CF_3\text{-}C_6H_4)_3$ ligand with electron-deficient $P(4\text{-F-}C_6H_4)_3$ or electron-rich $P(4\text{-OMe-}C_6H_4)_3$ and $P(furyl)_3$ ligands could not further improve the yield (entries 2-4). Ruthenium catalysts, such as $[RuCl_2(PPh_3)_2]$ and $[Ru(OAc)_2(PPh_3)_2]$, were examined, yet showing no catalytic efficiencies (entries 6 and 7). When $[Ru(MesCO_2)_2(p\text{-cymene})]$ was utilized, product **163aa** could be isolated in 65% yield (entry 5). Then, different acid additives were probed, indicating that only $MesCO_2H$ enabled the formation of *C*-alkyl glycoside, albeit with a relatively lower yield (entries 8 and 9). In addition, experiments win different solvents were performed, the reaction showed significantly decrease in the conversion (entry 10). The control experiments proved that the catalyst and ligand were essential for this multicomponent transformation (entries 11 and 12).

Table 3.4.2.1 Optimization of *meta*-C(sp^2)–H Domino ethyl glycosylation.[a]



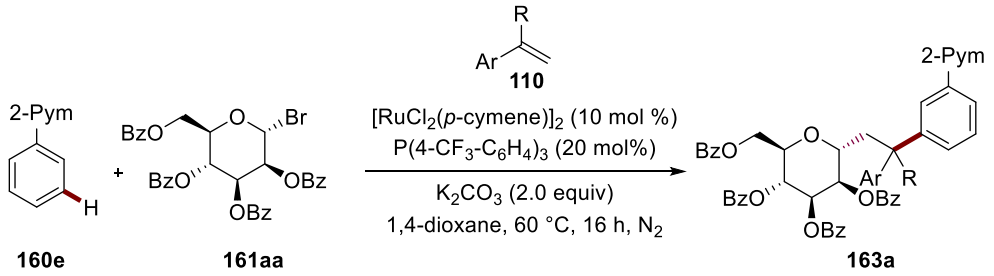
Entry	Deviations from standard conditions	Yield (%)[b]
1	None	80 (76)[c]
2	$P(4\text{-}F\text{-}C_6H_4)_3$ used as ligand	62
3	$P(4\text{-}OMe\text{-}C_6H_4)_3$ used as ligand	50
4	$P(furyl)_3$ used as ligand	trace
5	$[Ru(MesCO_2)_2(p\text{-cymene})]$ as catalyst	65
6	$[RuCl_2(PPh_3)_2]$ as catalyst	trace
7	$[Ru(OAc)_2(PPh_3)_2$ as catalyst	trace
8	PivOH/AcOH/$AdCO_2H$ as additives	trace
9	$MesCO_2H$ as additive	70
10	Toluene/NMP	45/32
11	Without $[RuCl_2(p\text{-cymene})]_2$	NR
12	Without $P(4\text{-}CF_3\text{-}C_6H_4)_3$	NR

[a] Reaction conditions: **160e** (0.20 mmol), **110a** (0.3 mmol), **161aa** (0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol %), ligand (20 mol %), K_2CO_3 (0.4 mmol), solvent (2.0 mL), 60 °C, 16 h. [b] Yields of isolated product. [c] Gram scale reaction with 1.0 mmol

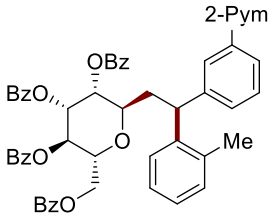
3.4.3. Scope for *meta*-C−H Domino Ethyl Glycosylation

With the optimal reaction conditions in hand, we examined its generality of our three-component transformation (Scheme 3.4.3.1). First, the substitution pattern on the vinyl arenes **110** was probed, indicating that the substituents at the *ortho*- or *meta*-position of styrene led to variable conversions (**163ab**-**163af**). Functional group, such as electrophilic bromo, at the *ortho*-position also proved feasible, giving the product **163ad** in 81% yield. Second, styrenes bearing different substituents at the *para*-

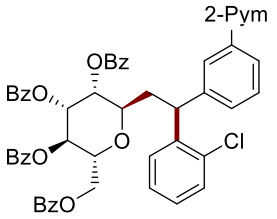
position, such as trifluoromethyl, halides or dimethylamino, was likewise amenable (**163ag**-**163an**). Notably, the ally oxygen group was compatible to ruthenium system and thus allowed further application (**163am**). Third, the challenging 1,1-disubstituted styrene were identified as feasible coupling partners for the synthesis of a plethora of *C*-alkyl glycosides **163ao**-**163aq** with a quaternary centre.



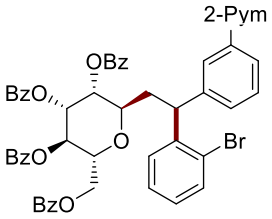
160e **161aa** **163a**



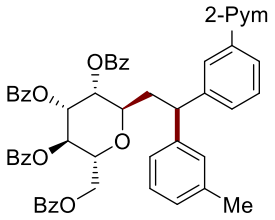
163ab: 77%



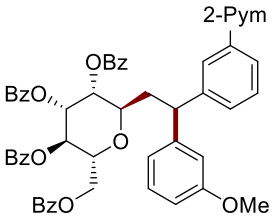
163ac: 35%



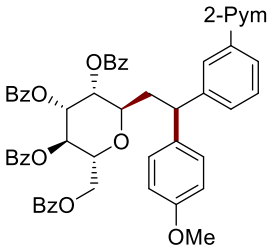
163ad: 81%



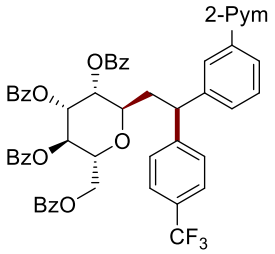
163ae: 43%



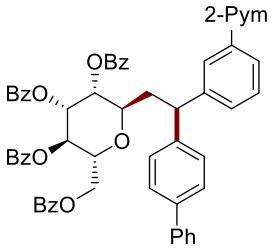
163af: 44%*



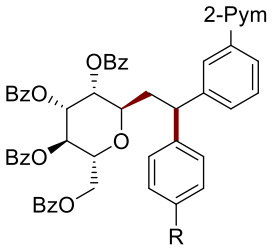
163ag: 85%*



163ah: 80%

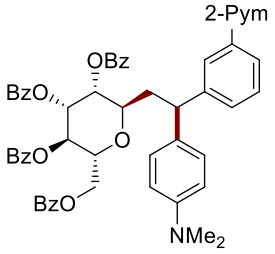


163ai: 85%*

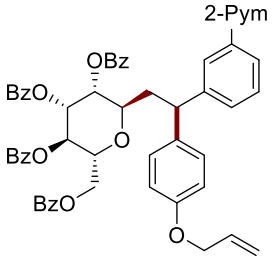


163aj: R = Cl, 82%*

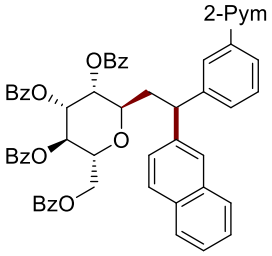
163ak: R = Br, 71%



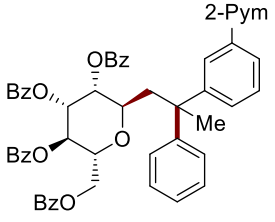
163al: 81%



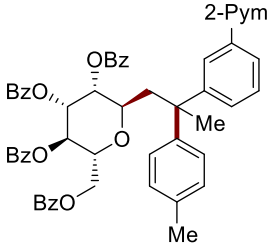
163am: 73%



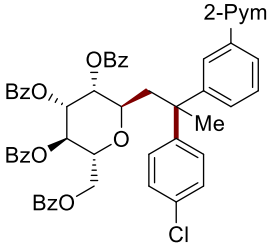
163an: 85%



163ao: 82%

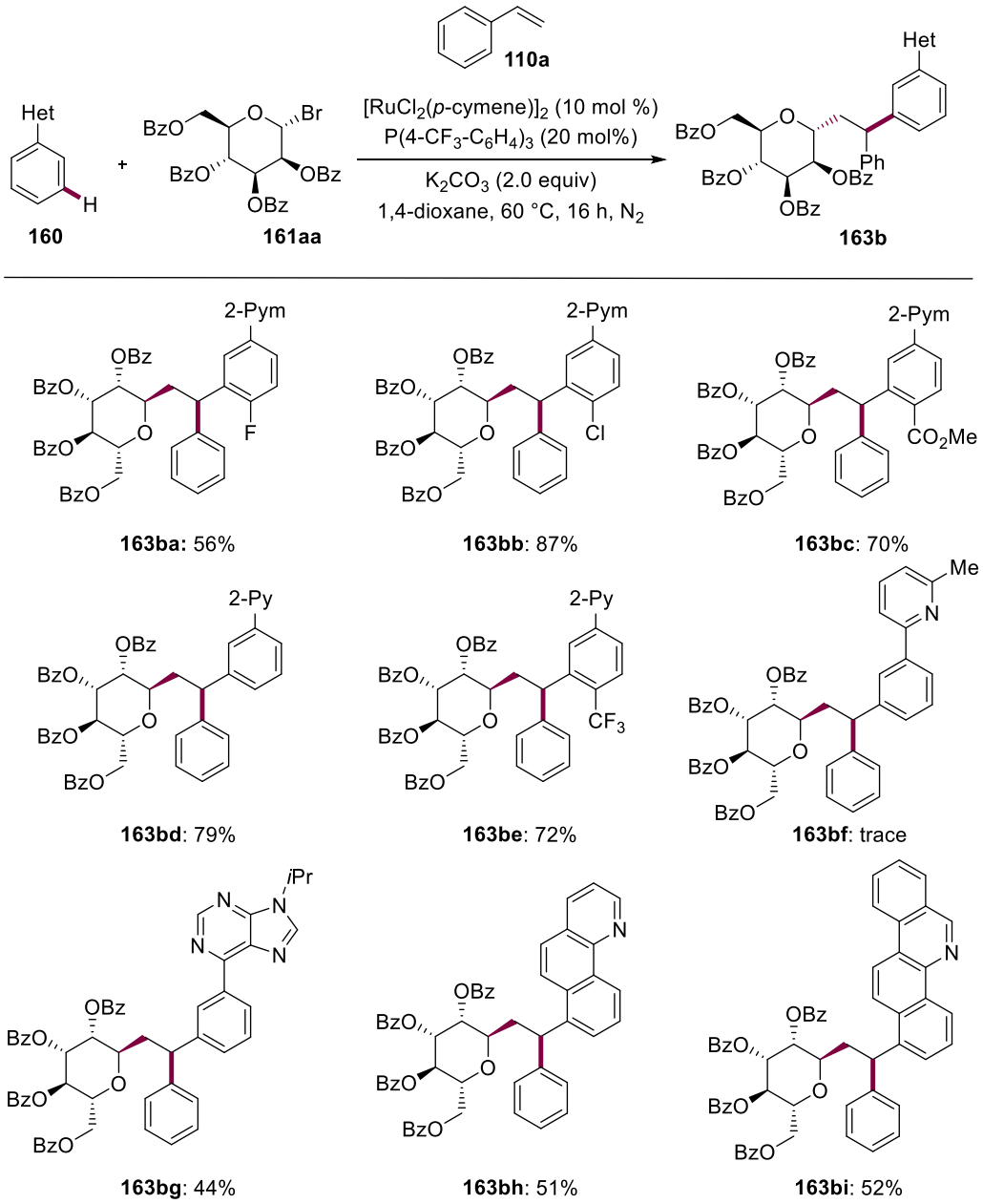


163ap: 78%



163aq: 64%

Scheme 3.4.3.1. Scope of vinyl arenes. * Done by Julia Pöhlmann.

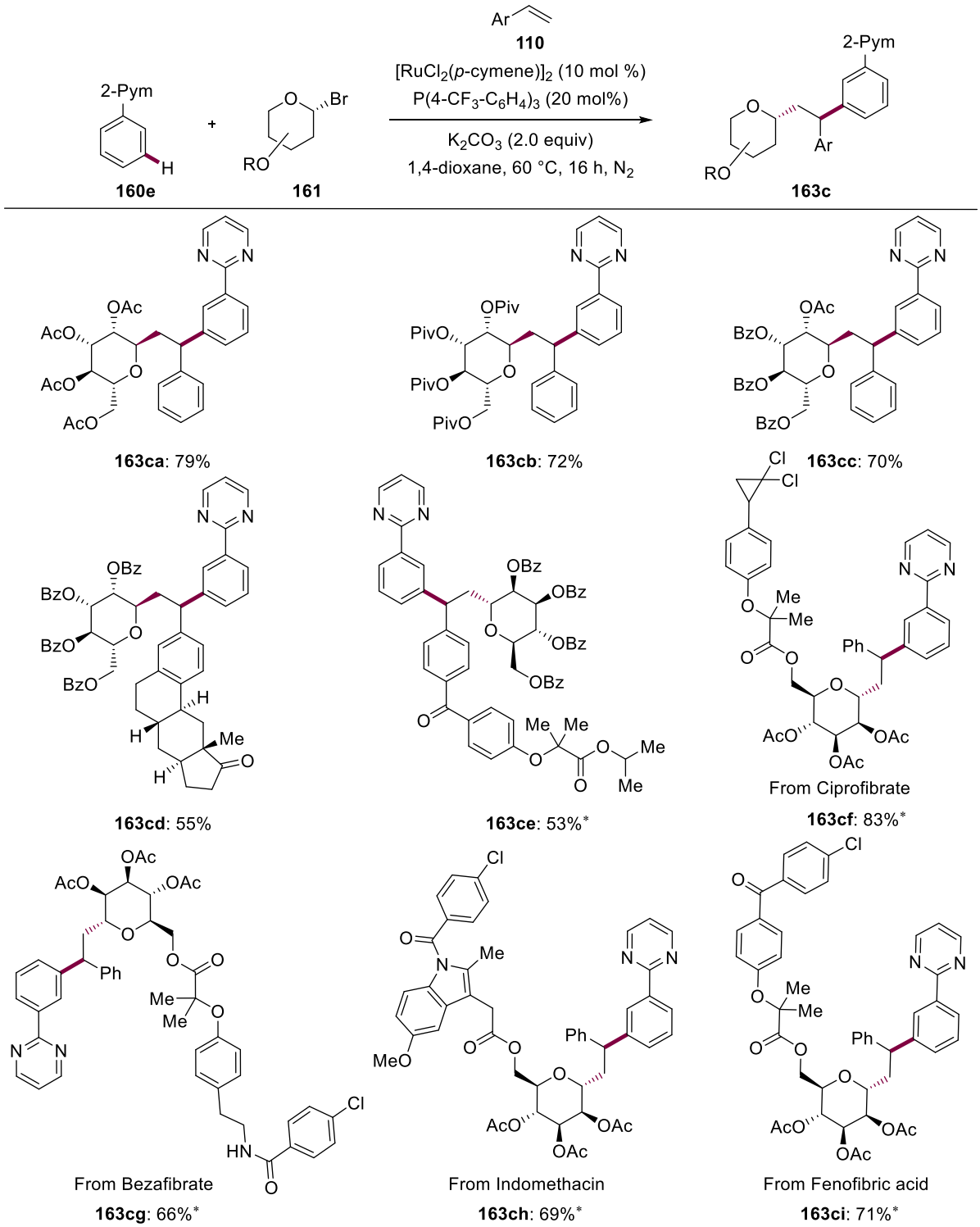


Scheme 3.4.3.2. Scope of heteroarenes.

Further examinations indicated that this ruthenium-catalyzed Domino C−H ethyl glycosylation tolerated a series of heteroarenes (Scheme 3.4.3.2). Functional groups, such as fluoro or ester, at the *para*-position of phenyl worked well, giving products **163ba**-**163bc** in moderate yields. Similarly, phenyl pyridine derivatives resulted in the formation of corresponding *C*-alkyl glycosides **163bd** and **163be** with exclusive α-and *meta*-selectivity. When methyl substituent was installed at the *ortho*-position of pyridine, the product **163bf** cannot be formed. Subsequently, the ruthenium-catalyzed Domino *meta*-C−H glycosylation was probed with versatile heteroarenes, such as purine derivatives, benzo[*h*]quinoline and benzo[*c*]phenanthridine, which were well-tolerated

and delivered the desired products **163bg**-**163bi** in moderate to good yields, along with excellent *meta*-selectivity control.

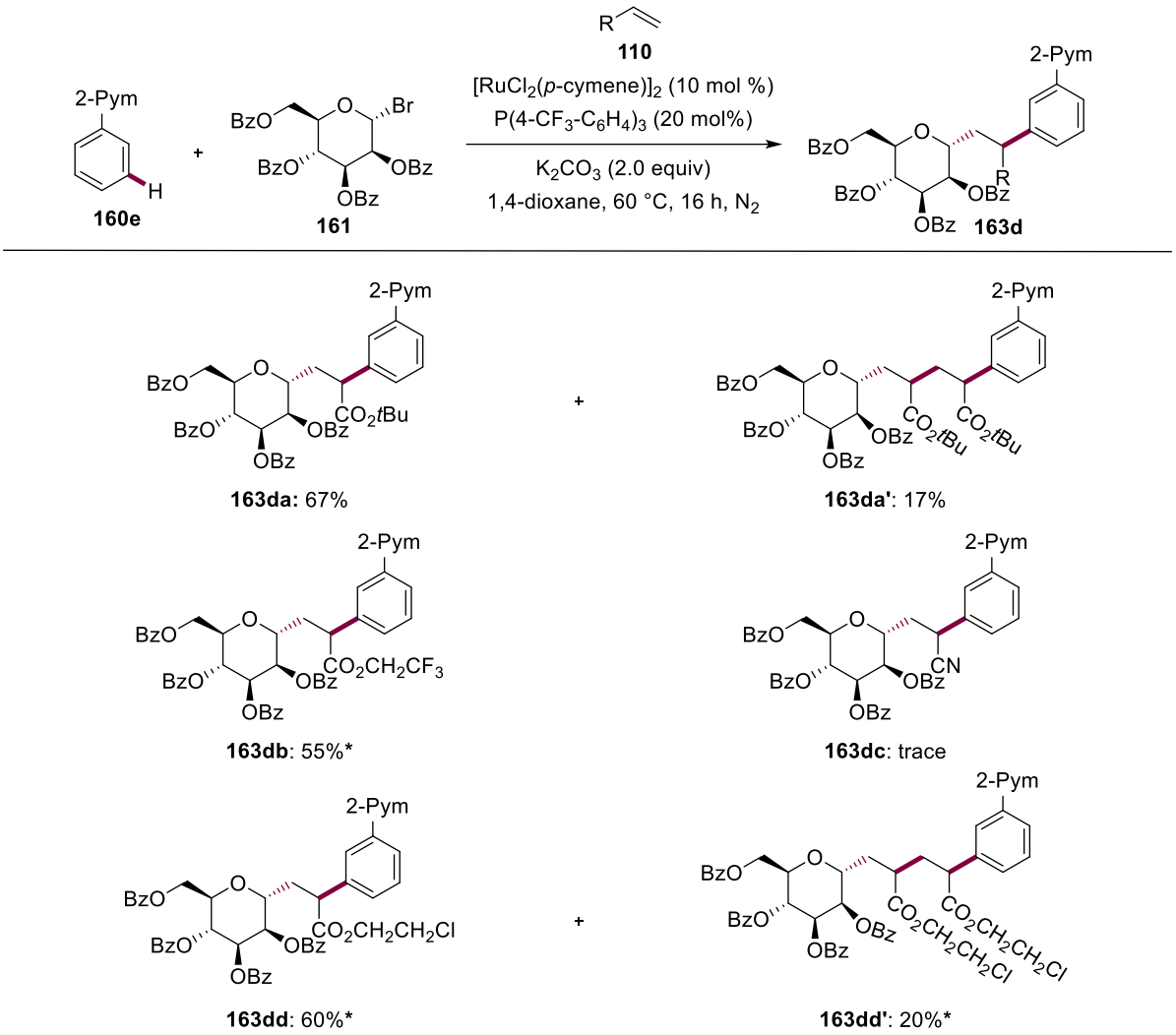
To demonstrate the applicability of the ruthenium-catalyzed *meta*-C–H sequential addition reaction (Scheme 3.4.3.3), diversely protected mannosyl bromides were adopted as glycosyl coupling regents and generated products **163ca**-**163cc** in good yields. Then, the late-stage transformation of the complex molecules derived from pharmaceuticals and natural products was carried out. For example, vinyl arenes derived from *estrone* and *fenofibric acid* were well incorporated into the *C*-alkyl glycosides **163cd**-**163ce**. In addition, the rapid and modular transformation of hybrid glycosyl bromides bearing *indomethacin*, *bezafibrate*, *naproxen*, *fenofibric acid*, *dehydrochloric acid*, *ibuprofen*, *repaglinide*, *ciprofibrate*, and *tolmetin* to the target *C*-alkyl glycosides products **163cf**-**163ck** demonstrate the excellent functional group tolerance and unique stereo- and position-selectivity control.



Scheme 3.4.3.3. Scope of glycosyl bromides. * Done by Wen Wei.

Next, the Domino *meta*-C(sp^2)−H ethyl glycosylation was probed with acrylates as coupling partners (Scheme 3.4.3.4). The desired products **163da** and **163db** were formed in 67% and 55% yields, respectively. Notably, a four-component byproduct **163da'** bearing a 1,5-ester motif was also isolated in 17% yield. In contrast, our method was not compatible with acrylonitrile. The experiment with 2-chloroethyl acrylate

delivered multicomponent reaction products **163dd** in 60% yield and **163dd'** in 20% yield with the chloro-functionality intact.



Scheme 3.4.3.4. Scope of acylates. * Done by Wen Wei.

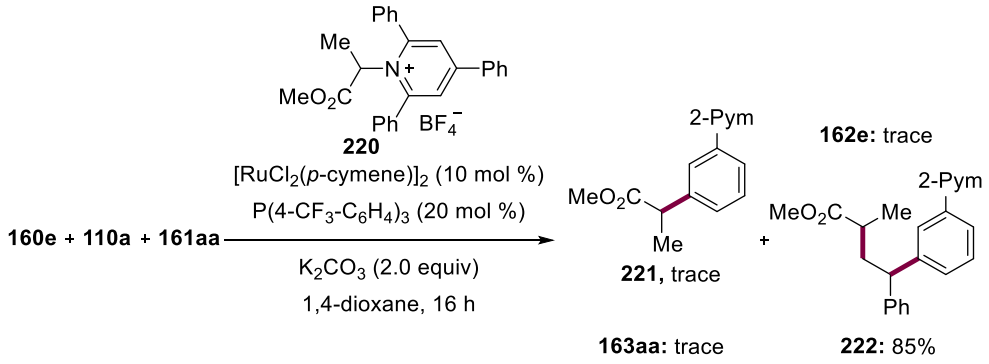
3.4.4. Mechanistic Studies

3.4.4.1 Radical Competition Experiments

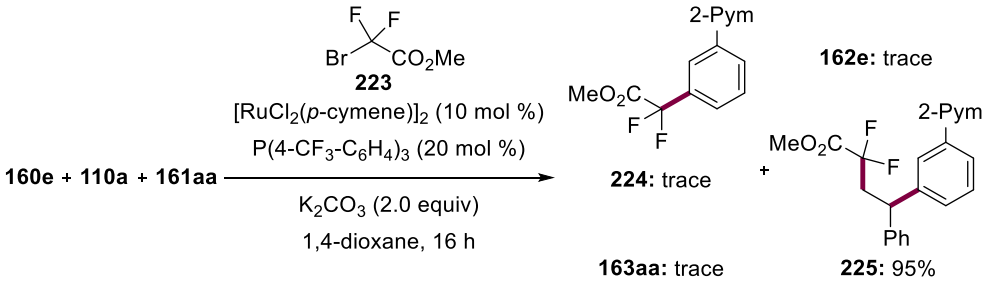
To compare the reactivity of glycosyl bromides **161** with different radical precursors, we conducted series of competition experiments with reported alkyl precursors for ruthenium catalysis (Scheme 3.4.4.1). First, Katritzky salt **220** was utilized and found that desired *C*-alkyl glycosides **163aa** and direct *meta*-deaminative alkylation product **221** were not formed (Scheme 3.4.4.1a). Instead, excellent three-component addition product **222** was isolated in 85% yield, which indicated that the addition to styrene of α-ester alkyl radical is favored compared to the electron-rich mannosyl radical. Second,

when the radical precursor 2-bromo-2,2-difluoroacetate **223** was employed, the desired product **163aa** was also inhibited (Scheme 3.4.4.1b). In contrast, only three-component addition product **225** was generated in 95% yield, which suggests that the electron-deficient radical led to a higher catalytic efficiency. Third, the use of 2-bromo-2-methylpropane **226** furnished the product **163aa** in 49% yield, along with direct *meta*-alkylation product **227** in 42% yield (Scheme 3.4.4.1c). There is no three-component alkylation product **228** formed. Those competition experiments indicated that the preferential addition of electron-deficient radical to styrene to form benzyl radical intermediate occurred instead of the electro-rich radical addition to styrene, although all those electrophilic radical precursors could be reduced to radical species *via* single electron transfer under ruthenium catalysis.

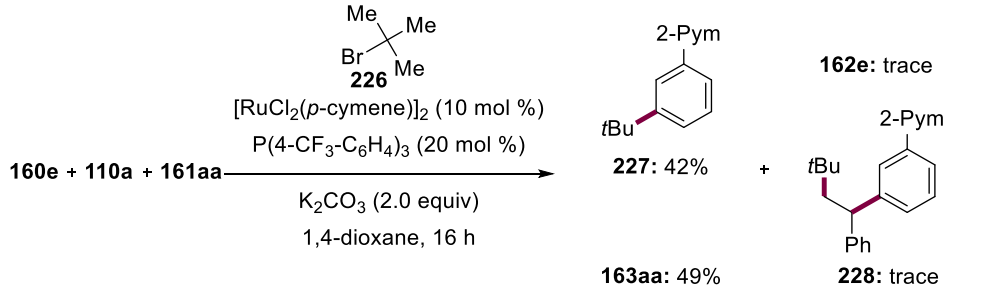
a) Competition experiment with Katritzky salt **220.**



b) Competition experiment with 2-bromo-2,2-difluoroacetate **223.**



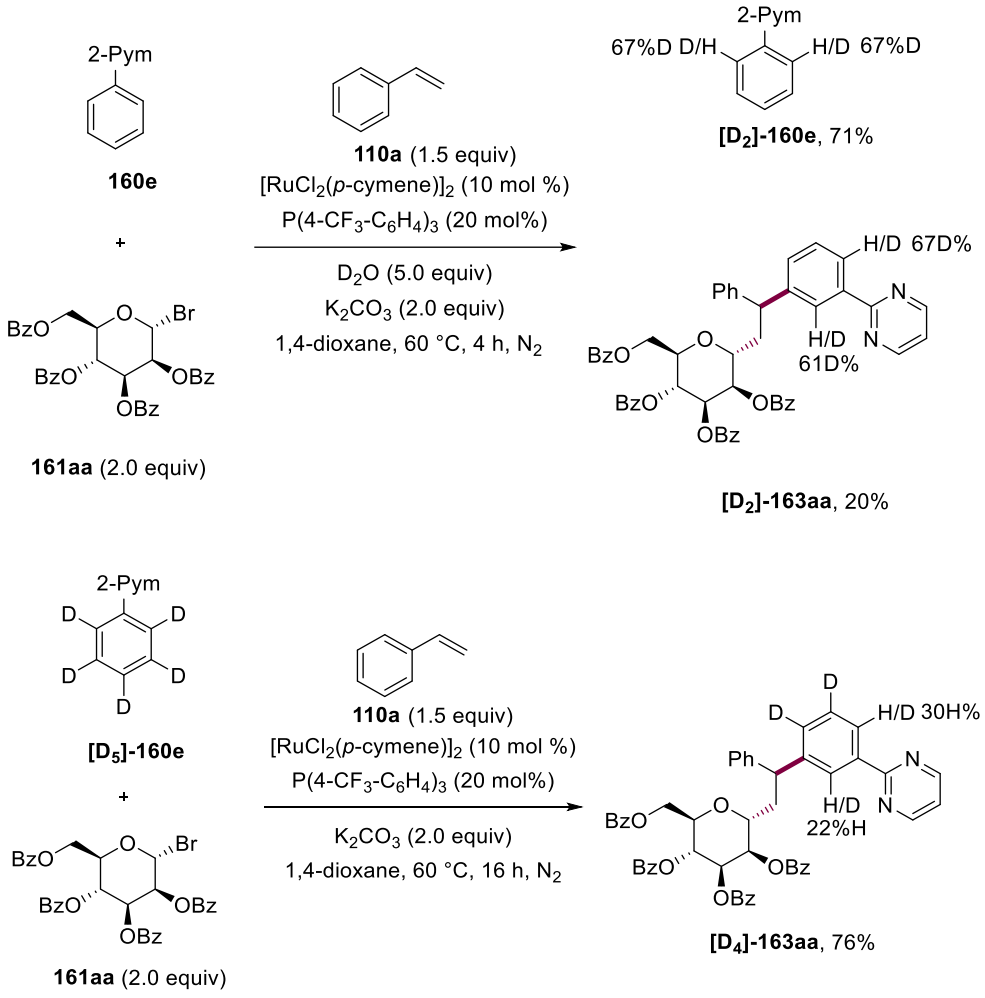
c) Competition experiment with 2-bromo-2-methylpropane **226.**



Scheme 3.4.4.1.1 Comparison with versatile radical precursors.

3.4.4.2 Deuterium Labelling Experiments

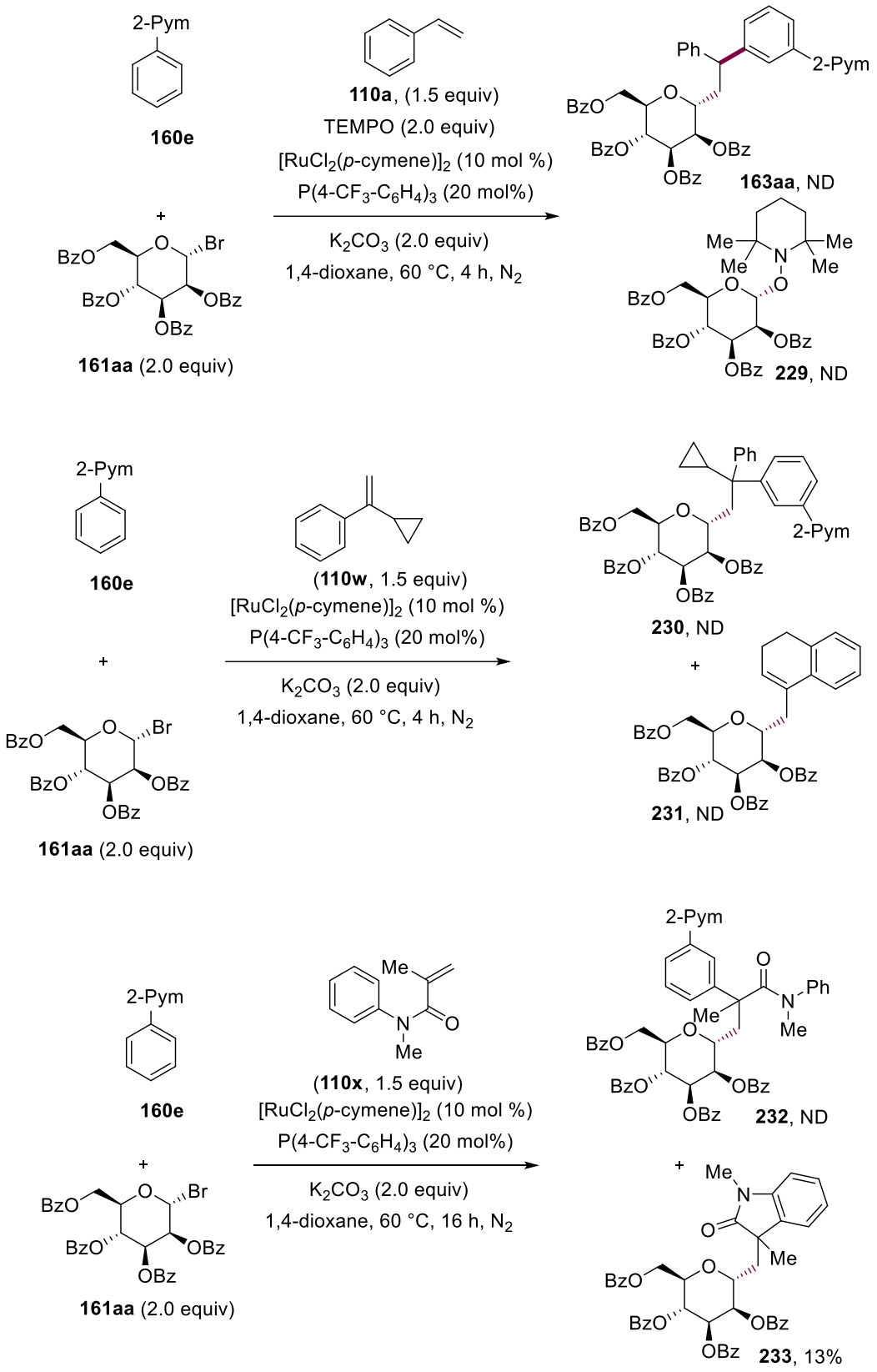
Next, the H/D exchange experiment with D_2O or the use of deuterated phenyl pyrimidine as substrate led to significant H/D scrambling in the *ortho*-position, suggesting the formation of cycloruthenacycles (Scheme 3.4.4.2).



Scheme 3.4.4.2.1 Deuterium-labelling experiments.

3.4.4.3 Anomeric Radical Trapping Experiments

Furthermore, to elucidate the involvement of glycosyl anomeric radical, radical trapping experiments were conducted. The reaction with TEMPO or (1-cyclopropylvinyl)benzene **110w** inhibited the formation of desired products **163aa** or **230** (Scheme 3.4.4.3). Notably, the desired glycosyl anomeric radical was reflected by the formation of **233** in 13% yield when *N*-methyl-*N*-phenyl methacrylamide **110x** was employed.

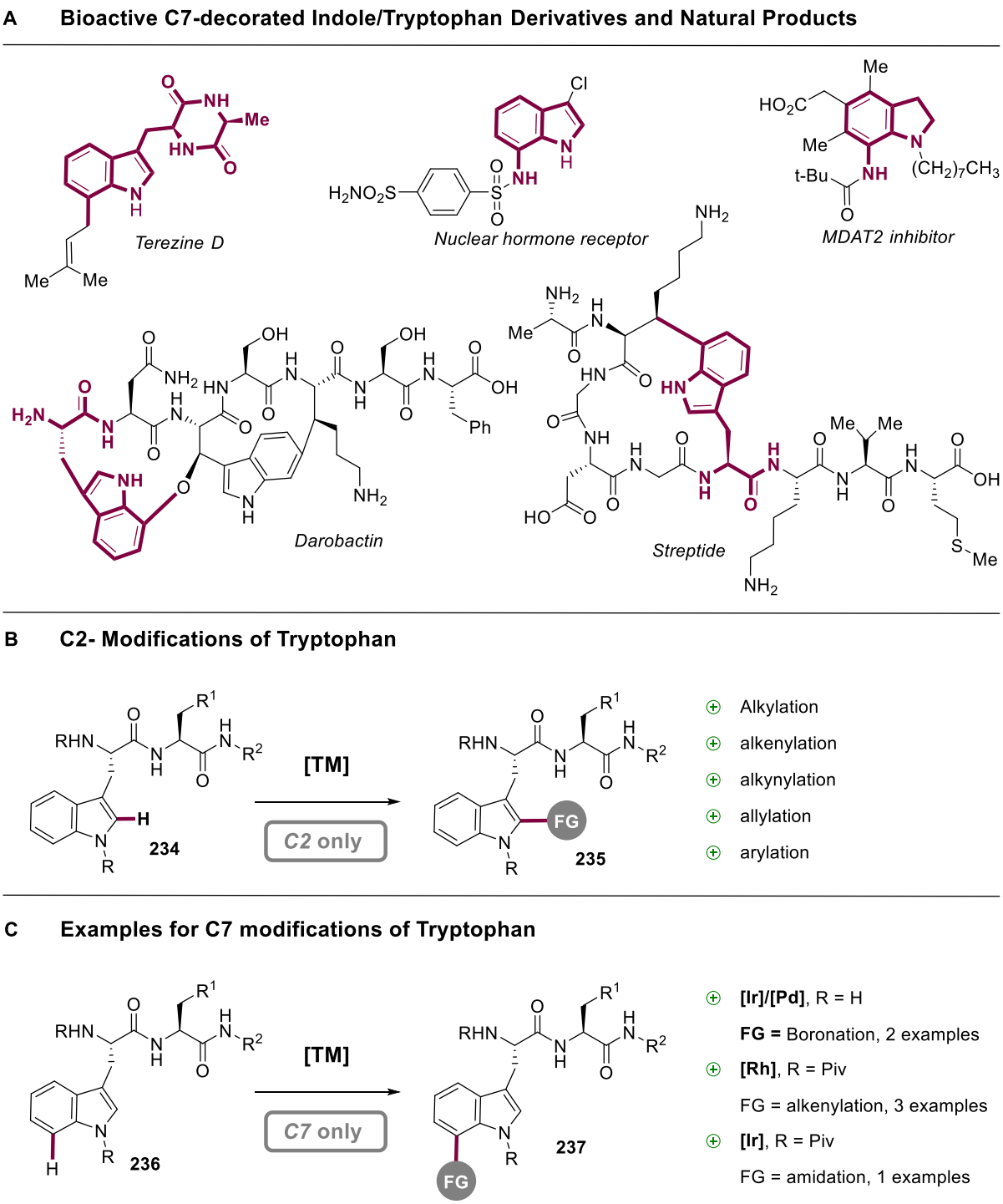


Scheme 3.4.4.3.1 Anomeric radical trapping experiments. * Performed by Wen Wei. ** Performed by Julia Pöhlmann.

3.5. Rhodium-Catalyzed Peptide Tryptophan C(7)−H Amidation

3.5.1. Introduction

The indole motifs are important structural element of versatile biologically active natural products and drugs, among which the tryptophan-containing peptides hold a special place, such as the *Darobactin* and *Streptide* (Scheme 3.5.1.1a). Thus, the development of effective methods for the selective functionalization of indoles and indole-containing peptides has recently received intensive attention. The introduction of a directing group on the *N*-atom center, such as acetyl, pivaloyl, and pyridine groups, has been a powerful strategy to secure *C*2 selectivity (Scheme 3.5.1.1b). General methods to selective access the *C*7 position of tryptophan continue to be rare, despite of few examples were showcased for tryptophan derivatives, such as *C*7-boronation,[155] C7-alkenylation,[156] *C*7 amination[157] (Scheme 3.5.1.1c). Although the significance of *C*7-decorated tryptophan-peptides, to the best of our knowledge, no chemical strategy was developed for the direct late-stage tryptophan-peptide *C*(7)─H functionalizations to date. We, hence, questioned whether *C*7 activation for the diversification of structurally more complex peptide would indeed be viable, ideally via amide bond formation, which is the most important reaction for both chemistry and biology field. In this context, we became interested in the development of a general strategy for the late-stage amidation of tryptophan-containing peptides. To this end, we report on a highly-selective and robust direct late-stage peptide amidation reaction.[158]

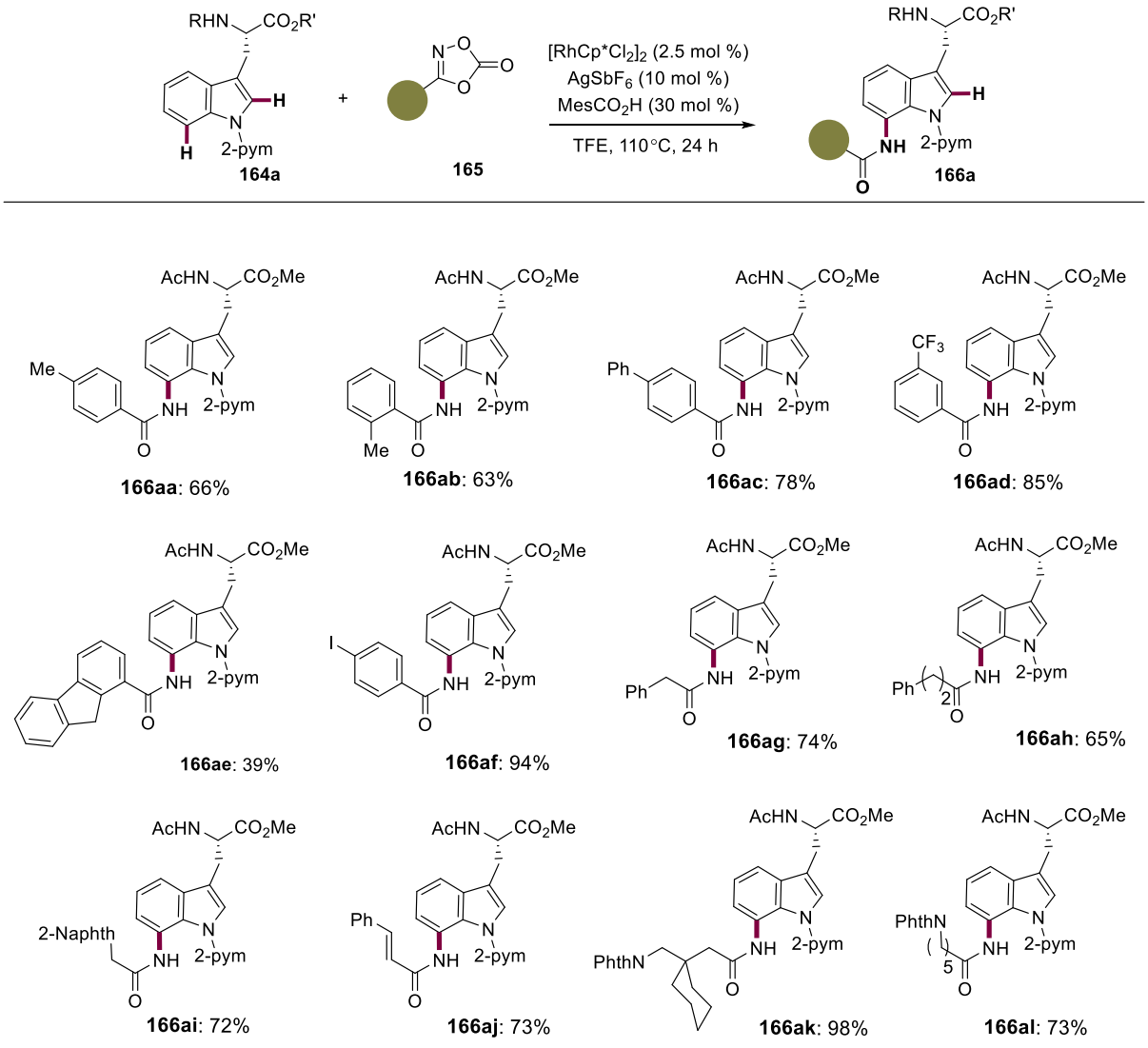


Scheme 3.5.1.1. Bioactive *C*7 decorated indole and tryptophan derivatives and selective *C*(2)/*C*(7) modification of tryptophan.

3.5.2. Scope for Tryptophan C(7)−H Amidation

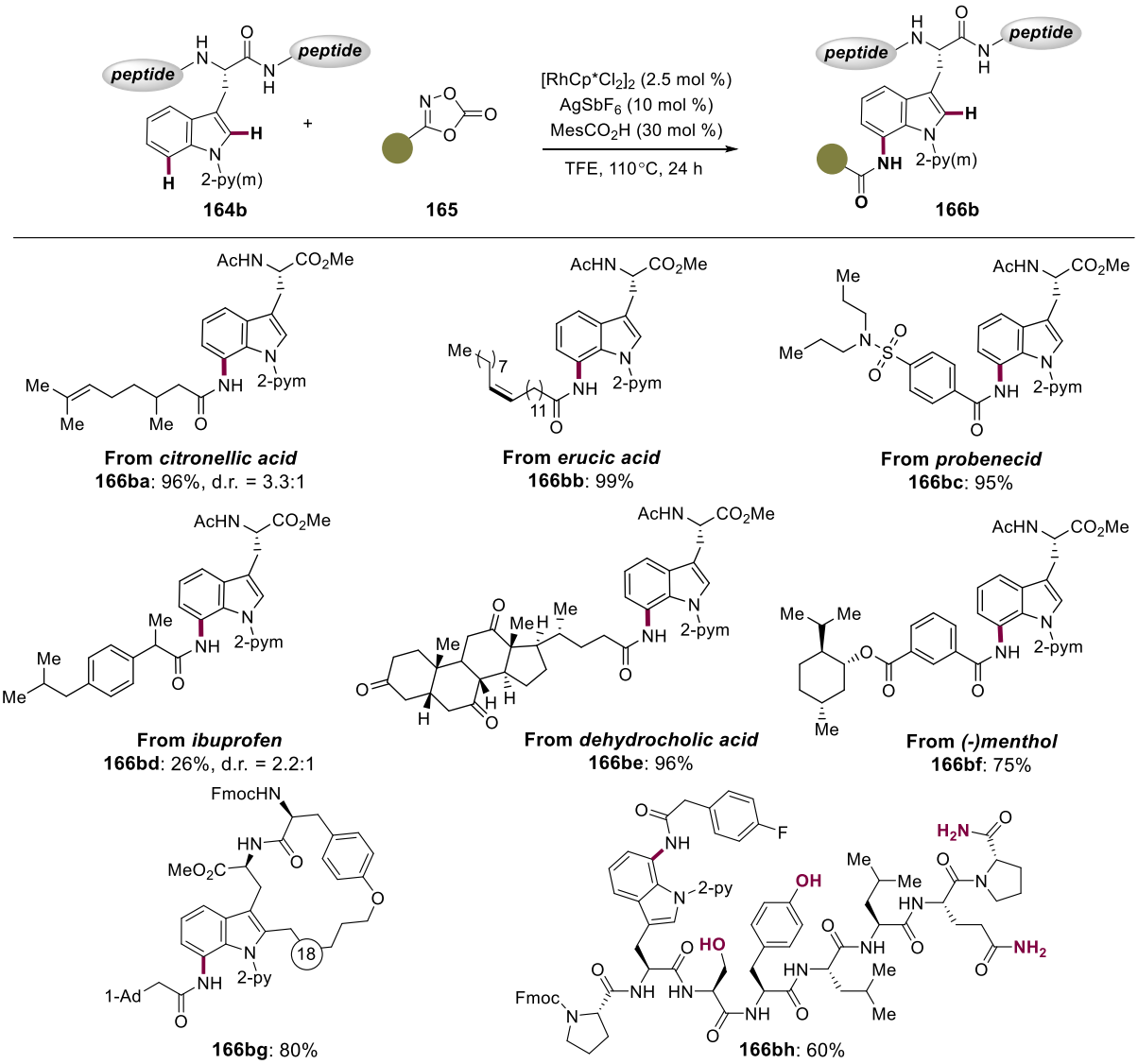
Initial optimization studies, performed by Dr. W. Wei, established optimal reaction conditions with 2.5 mol % of $[Cp^*RhCl_2]_2$ as the catalyst, 10 mol % of $AgSbF_6$, and 30 mol % of $MesCO_2H$ as the additive in TFE under 110 °C afforded the product in 92%

yield. With these optimized reaction conditions in hand, we explored the scope of the tryptophan diversification using a set of 1,4,2-dioxazol-5-ones **165**. Both aryl and alkyl dioxazolones were thus well tolerated (Scheme 3.5.2.1). Electron-rich and electron-poor arenes were also compatible (**166aa**-**166ad**). Furthermore, fluorene was introduced successfully by the C7-amidation to yield product **166ae**. Notably, iodide-substituted dioxazolone was characterized by an excellent chemo-selectivity, without any cross-coupling products being observed (**166af**). Various alkyl and vinyl dioxazolones could also be employed (**166ag**-**166aj**). Intrigued by the compatibility of alkyl groups, we employed the reaction for the direct chemical ligation with various amino acid-derived dioxazolones, thus enabling new disconnections towards dipeptides (**166ak** and **166al**).



Scheme 3.5.2.1. Tryptophan *C*(7)-amidations with various dioxazolones **165**.

We studied the amidation for the bio-conjugation to form versatile amino acid-natural product and -drug hybrids in a chemo- and site-selective manner (Scheme 3.5.2.2). Hence, hybrid conjugates **164ba–164bg** with *citronellic acid*, *erucic acid*, *probenecid acid*, *ibuprofen*, *dehydrocholic acid* and *(-)menthol* were selectively assembled, reflecting the versatility of our approach towards structurally complex drugs and natural products. Furthermore, the late-stage C7 amidation reaction delivered amidation product of a *Leuprorelin* derivative without decompositions (**166bh**), importantly with free C-terminus and various functional amino acid side-chains compatible such as serine, tyrosine and glutamine, thereby highlighting the potential to assemble structurally complex peptides.

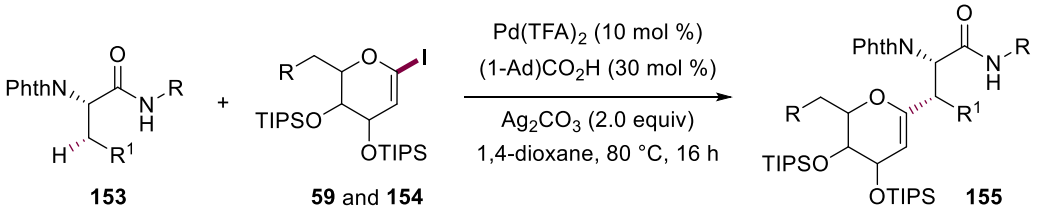


Scheme 3.5.2.2. Tryptophan *C*(7) conjugations for the assembly of natural product hybrids.

4. Summary and Outlook

The late-stage modification of peptides and carbohydrates is of significance to drug discovery and medicinal chemistry. Traditional organic synthesis has relied on step-, time- and resource-intensive strategies, namely the functional group interconversion. Transition-metal catalyzed cross-coupling reaction has allowed the (bio)chemistry community to synthesize new molecule, however two prefunctionalized starting materials are required. Thus, the next major challenge in the field of organic synthesis are the efficiency, scalability, and sustainability. In this context, transition metal-catalyzed C–H activation has emerged as a uniquely powerful tool. Inert and omnipresent C–H bonds are utilized as latent functional groups, avoiding the time- and resource-consuming preparation of prefunctionalized starting materials. In this thesis, the primary focus was the development of versatile C−H glycosylation for increasing the molecular complexity of readily available amino acids, peptides and carbohydrates

Within the first project, a highly efficient C(sp^3)−H glycosylation of amino acids and peptides under palladium catalysis was developed (Scheme 4.1).[159] Mild and robust reaction conditions ensured ample substrate scope featuring a plethora of valuable functional groups. The robust catalytic system allowed the formation of glycoamino acids and BODIPY labeled glycoamino acids by stitching the glycosylation regents and amino acids *via* selective C−H glycosylation.

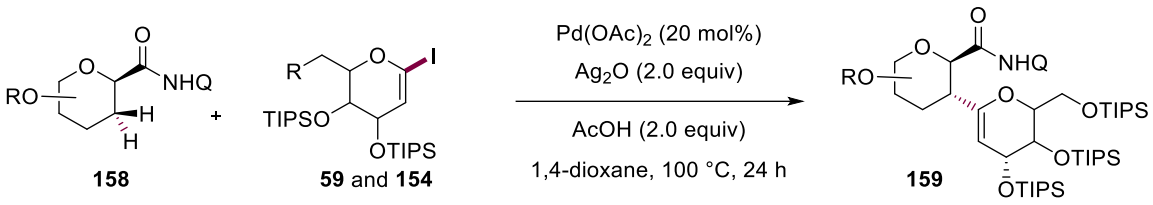


153 **59** and **154** **155**

Scheme 4.1. C(sp^3)−H glycosylation of amino acids towards glycoamino acids **155**.

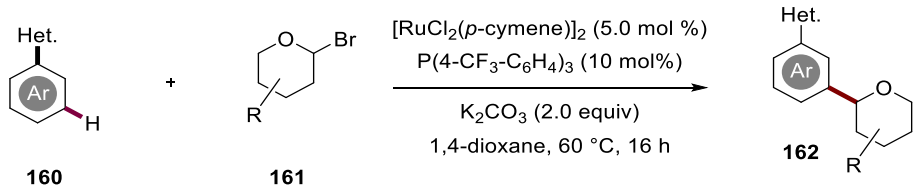
In the second part, we reported on the first saccharide assembly strategy by C(sp^3)−H glycosylation of 2-deoxy glycosides.[160] Through 1,2-*trans*-C−H activation of glycosides, we were able to access various *C*-disaccharides and *C*-trisaccharides. Our strategy proved to be efficient, diastereoselective, broadly applicable and operationally simple. In addition, detailed mechanistic studies unravelled the unique reaction mode of our palladium-catalyzed selective C−H glycosylation and probed the reactivity of versatile glycosides. Notably, cyclopalladaglycosides derived from C−H palladation

demonstrated its robustness for the saccharide assembly, which expanded the chemical space of *C*-oligosaccharides.



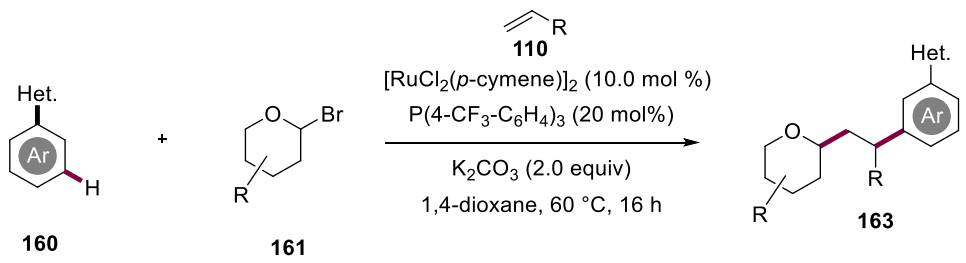
Scheme 4.2. C(sp^3)−H glycosylation of glycosides towards *C*-oligosaccharides **159**.

In the third project, a *meta*-C(sp^2)−H glycosylation was developed to the targeted synthesis of privileged *meta*-C-aryl glycosides.[139m] The precise and efficient selective *meta*-C−H activation was achieved with combination of commercially available and cheap ruthenium catalyst and phosphine ligand under extremely mild reaction conditions. Meanwhile, the high level of *meta*-selectivity and anomeric control were examined with structurally complex carbohydrate-drug hybrid, delivering corresponding 1,2-*trans*-*C*-aryl glycosides. In addition, the investigation of versatile glycosyl donors were performed to unravel the anomeric selectivity.



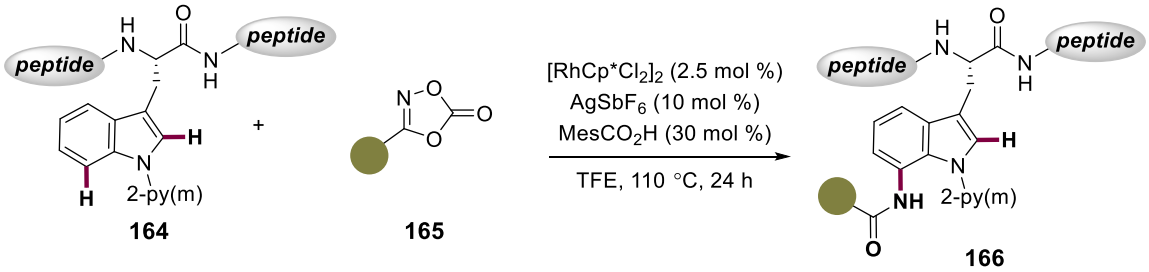
Scheme 4.3. C(sp^2)−H glycosylation of arenes towards *meta*-*C*-glycosides **162**.

In the fourth project, an anomeric radical involved multicomponent transformation was described with ruthenium catalysis. Versatile *C*-alkyl glycosides were generated with a highly *meta*- and anomeric selectivity. Our ruthenium-catalysed multicomponent reaction featured exceedingly mild reaction conditions and broad substrate scope, which greatly complement the Giese-type addition for *C*-alkyl glycosides synthesis.



Scheme 4.4. Ruthenium-catalysed multicomponent transformation for *meta*-*C*-alkyl glycosides synthesis.

In the fifth project, a robust positional-selective *C*(7)−H amidation reaction was developed by rhodium(III) catalysis.[158] Versatile amides were installed on the tryptophan derivatives. It is noteworthy that the robustness of the catalytic system could be demonstrated by the application of tryptophan containing peptide with a broad functional group tolerance. In sharp contrast to the *C*(2)−H functionalizations of indole and tryptophan, the pyrimidine auxiliary secured the unique *C*(7) selectivity.



Scheme 4.5. C(7)−H amidation of tryptophan by rhodium catalysis

5. Experimental Part

5.1. General Remarks

All reactions involving air- and/or moisture-sensitive compounds were conducted under a dry nitrogen atmosphere using pre-dried glassware and standard Schlenk techniques. If not otherwise noted, yields refer to isolated compounds, which were estimated to be >95% pure based on ^{1}H-NMR.

Vacuum

The following average pressure was measured on the used rotary vane pump RD4 from Vacuubrand®: 0.8·10–1 mbar (uncorrected value).

Melting Points

Melting points were measured on a Stuart® Melting Point Apparatus SMP3 from Barloworld Scientific. Values are uncorrected.

Chromatography

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminium sheets from Merck. Plates were either visualized under irradiation at 254 nm or 365 nm or developed by treatment with a potassium permanganate solution followed by careful warming. Chromatographic purifications were accomplished by column chromatography on Merck Geduran® silica gel, grade 60 (40–63 µm, 70–230 mesh ASTM).

Gel permeation chromatography (GPC)

GPC purifications were performed on a JAI system (JAI-*LC-9260 II NEXT*) equipped with two sequential columns (*JAIGEL-2HR*, gradient rate: 5.000; *JAIGEL-2.5HR*, gradient rate: 20.000; internal diameter = 20 mm; length = 600 mm; Flush rate = 10.0 mL/min and $CHCl_3$ (HPLC-quality with 0.6% EtOH as stabilizer) was used as the eluent.

Infrared Spectroscopy

IR spectra were recorded using a Bruker® Alpha-P ATR spectrometer. Liquid samples were measured as film and solid samples neat. Spectra were recorded in the range from 4000 to 400 cm^{-1}. Analysis of the spectral data was carried out using Opus 6. Absorption is given in wave numbers (cm^{-1}).

Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on Mercury Plus 300, VNMRS 300, Inova 500 and 600 from Varian®, or Avance 300, Avance III 300 and 400, Avance III HD 400 and 500 from Bruker®. Chemical shifts are reported in *δ*-values in ppm relative to the residual proton peak or carbon peak of the deuterated solvent.

The coupling constants *J* are reported in hertz (Hz). Analysis of the recorded spectra was carried out using MestReNova 10.0 software.

	^{1}H-NMR	^{13}C-NMR
$CDCl_3$	7.26	77.16
$(CD_3)_2SO$	2.50	39.51

Gas Chromatography

Monitoring of reaction process *via* gas chromatography or coupled gas chromatography-mass spectrometry was performed using a 7890 GC-system with/without mass detector 5975C (Triple-Axis-Detector) or a 7890B GC-system coupled with a 5977A mass detector, both from Agilent Technologies®.

Mass Spectrometry

Electron ionization (EI) and EI high resolution mass spectra (HR-MS) were measured on a time-of-flight mass spectrometer AccuTOF from JEOL. Electrospray ionization (ESI) mass spectra were recorded on an Io-Trap mass spectrometer LCQ from Finnigan, a quadrupole time-of-flight maXis from Bruker Daltonic or on a time-of-flight mass spectrometer microTOF from Bruker Daltonic. ESI-HR-MS spectra were recorded on a Bruker Apex IV or Bruker Daltonic 7T, Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. The ratios of mass to charge (*m/z*) are indicated, intensities relative to the base peak (I = 100) are written in parentheses.

Solvents

All solvents for reactions involving air- and/or moisture-sensitive reagents were dried, distilled and stored under an N_2 atmosphere according to the following standard procedures.

1,2-Dichloroethane (DCE) and toluene (PhMe) were dried over CaH_2 for 8 h, degassed and distilled under reduced pressure. 1,4-Dioxane and di-*n*-butylether (*n*Bu_2O) were dried over Na for 8 h, degassed and distilled under reduced pressure. 1,1,1,3,3,3-

hexafluoropropane-2-ol (HFIP) was distilled from 3 Å molecular sieves. 2,2,2-trifluoroethanol (TFE) was stirred over CaSO4 and distilled under reduced pressure. CH_2Cl_2, DMF, THF, Et_2O were obtained from a MBRAUN MB SPS-800 solvent purification system.

Chemicals

Chemicals obtained from commercial sources with a purity >95% were used as received without further purification.

The following compounds were known from the literature and synthesized according to previously known methods: 1,4,2-dioxazo-5-ones **165**,[161] 2-deoxy-glycal-1-iodide **95 and 154**,[79] , 2-deoxy glycosides **158**,[70-71] triazole-containing peptides **153a**,[162] quinoline-containing peptides **153b**,[163] glycosyl bromide **161**.[164]

The following compounds were kindly synthesized and provided by the persons listed below:

Karsten Rauch: $[RuCl_2(p\text{-cymene})]_2$, $[Ru(MesCO_2)_2(p\text{-cymene})]$, $[Ru(OAc)_2(p\text{-cymene})]$, dry and/or degassed solvents.

Dr. Wang Wei: tryptophan peptides **164**, and dioxazolone **165al**.

Adelina Kopp: 2-deoxy glycoside **158ac** and dioxazolone **165bh**.

Nikolaos Kaplaneris: glycosyl bromide **161aq**,**161bc** and **153ca, 153cb, 153cg, 153ch**.

Felix Kaltenhäuser: peptides **153ac**, **153ae**, **153ce-153cf**.

Takuya Michiyuki: heteroarenes **160af** and **160ag**.

Wen Wei: Katritzky salt **220**.

5.2. General Procedures

General Procedure A: Palladium-Catalyzed C(sp^3)−H Glycoylation of Amino Acids with TAM^{Bn}

Amide **153a**, **153c** or **153d** (0.1 mmol), $Pd(TFA)_2$ (10 mol %), Ag_2CO_3 (0.2 mmol), 1-$AdCO_2H$ (30 mol %) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, 1-iodo glycal **59** or **154a** (0.15 mmol) in 1,4-dioxane (0.5 mL) was added. The tube was sealed and stirred at 80 °C for 10 h (for glycosylation of peptides: 16 h). After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the

residue by column chromatography on silica gel yielded the product **155a**, **155c** or **155d**.

General Procedure B: Palladium-catalyzed primary C(sp^3)−H Glycosylation of Amino Acids with AQ

Amide **153ba** (0.1 mmol), $Pd(OAc)_2$ (10 mol %), AgTFA or Ag_2CO_3 (0.2 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, 1-iodo glycal **59 or 154a** (0.15 mmol) in dioxane (1.0 mL) was added. The tube was sealed and stirred at 40 °C for 8 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product **155ba**-**155bc**.

General Procedure C: Palladium-Catalyzed Secondary C(sp^3)−H Glycosylation of Amino Acids with AQ

Amide **153bd**-**153bg** (0.1 mmol), $Pd(OAc)_2$ (10 mol %), AgTFA (0.2 mmol), K_2CO_3 (0.1 mmol), BQ (50 mol %) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, 1-iodo glycal **59** (0.15 mmol) in dioxane (1.0 mL) was added. The tube was sealed and stirred at 60 °C for 8 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product **155bd**-**155bg**.

General Procedure D: Palladium-Catalyzed C(sp^3)–H Glycosylation of 2-Deoxy Pyranoside

A suspension of deoxysugar **158** (0.10 mmol), glycal **59 or 154** (0.15-0.30 mmol), $Pd(OAc)_2$ (20 mol %), Ag_2O (0.20 mmol) and HOAc (0.20 mmol) in 1,4-dioxane (1.0 mL) was stirred at 100-120 °C under N_2 for 24 h. After cooling to ambient temperature, CH_2Cl_2 (10 mL) was added and the mixture was concentrated *in vacuo*. Purification by column chromatography on silica gel afforded the desired products **159aa-159n, 159ob, 159p-159v**, **190**.

General Procedure E: Palladium-Catalyzed C(sp^3)–H Glycosylation of 1,2-Deoxy Pyranoside

A suspension of deoxysugar **158oa** (0.10 mmol), glucal **59** (0.15 mmol), $Pd(OAc)_2$ (20 mol %) and Ag_2CO_3 (0.20 mmol, 2.0 equiv) in 1,4-dioxane (1.0 mL) was stirred at 120 °C under N_2 for 24 h. After cooling to ambient temperature, CH_2Cl_2 (10 mL) was added and the mixture was concentrated *in vacuo*. Purification by column chromatography on silica gel afforded the desired products **159oa**.

General Procedure F: Palladium-Catalyzed C(sp^3)–H Glycosylation of 2-Deoxy Pyranoside

A suspension of deoxysugar **187** (0.10 mmol), glucal **59** (0.15 mmol), $Pd(OAc)_2$ (20 mol %) and AgOAc (0.2 mmol) in 1,4-dioxane (1.0 mL) was stirred at 120 °C under N_2 for 24 h. After cooling to ambient temperature, CH_2Cl_2 (10 mL) was added and the mixture was concentrated *in vacuo*. Purification by column chromatography on silica gel afforded the desired products **188**.

General Procedure G: Palladium-Catalyzed C(sp^3)–H Glycosylation of 2-Deoxy Furanoside

A suspension of deoxysugar **191 or 193** (0.10 mmol, 1.0 equiv), glucal **S2a** (0.15 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.4 mg, 20 mol %) and AgOAc (0.20 mmol, 2.0 equiv) and HOAc (0.20 mmol, 2.0 equiv) in 1,4-dioxane (1.0 mL) was stirred at 100 °C under N_2 for 24 h. After cooling to ambient temperature, CH_2Cl_2 (10 mL) was added and the mixture was concentrated *in vacuo*. Purification by column chromatography on silica gel afforded the desired products **192, 194**.

General Procedure H: Ruthenium-Catalyzed *meta*-C−H Glycosylation

Arene **160** (0.10 mmol), glycoside bromide **161** (0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (1.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product **162**.

General Procedure I: Ruthenium-Catalyzed Domino C−H Ethyl Glycosylation

Arene **160** (0.10 mmol), glycoside bromide **161** (0.20 mmol), vinyl arenes **110**, $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 10.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (9.4 mg, 20 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (1.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product **163**.

General Procedure J: Rhodium-Catalyzed C(7)–H Amidation of Tryptophan Peptides

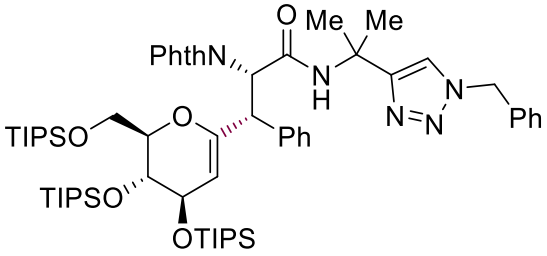
Tryptophan peptide derivatives **164** (0.2 mmol), 1,4,2-dioxazol-5-one **165** (0.4 mmol), $[RhCp^*Cl_2]_2$ (3.0 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $MesCO_2H$ (5.4 mg, 15 mol %) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, TFE (0.4 mL) was added. The tube was sealed and stirred at 110 °C for 24 h. After cooling to room temperature, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the products **166**.

5.3. Experimental Procedures and Analytic Data

5.3.1 Palladium-Catalyzed C(sp^3)−H/C(sp^2)−H Glycosylation

5.3.1.1 Characterization Data

(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-((2*S*,3*S*,4*S*)-3,4-bis{(triisopropylsilyl)oxy-2-[((triisopropylsilyl)oxy)methyl]-3,4-dihydro-2*H*-pyran-6-yl}-2- (1,3-dioxoisoindolin-2-yl)-3-phenylpropanamide (155aa)

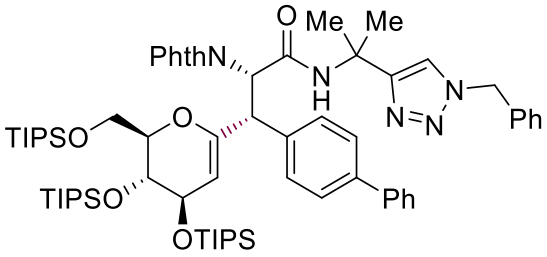


The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**153aa**) (49 mg, 0.10 mmol) and 1-iodo glycal **59** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **155aa** (105 mg, 95%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.56 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.44 (s, 1H), 7.33 – 7.25 (m, 3H), 7.26 – 7.17 (m, 4H), 7.04 (d, *J* = 5.6 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 5.49 (d, *J* = 11.8 Hz, 1H), 5.41 (s, 2H), 5.06 (d, *J* = 5.4, 1H), 4.55 (d, *J* = 11.8 Hz, 1H), 4.35 (t, *J* = 6.6 Hz, 1H), 4.10 (t, *J* = 2.0 Hz, 1H), 4.06 – 3.93 (m, 3H), 1.76 (s, 3H), 1.73 (s, 3H), 1.11 – 1.04 (m, 42H), 0.91 – 0.78 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 166.7 (C_q), 153.1 (C_q), 151.4 (C_q), 138.5 (C_q), 135.0 (C_q), 133.7 (CH), 131.4 (C_q), 128.9 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.9 (CH), 126.8 (CH), 123.2 (CH), 121.0 (CH), 98.8 (CH), 80.9 (CH), 69.5 (CH), 66.7 (CH), 61.2 (CH_2), 55.4 (CH), 53.9 (CH_2), 52.1 (C_q), 50.1 (CH), 28.7 (CH_3), 28.0 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 3053, 2943, 2867, 1716, 1264, 895, 737, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1128 (85) $[M+Na]^+$, 1106 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{62}H_{95}N_5NaO_7Si_3^+$ $[M+Na]^+$:1128.6432, found: 1128.6436.

_N_-((_R_)-[1,1'-Biphenyl]-4-yl((2_R_,3_R_,4_R_)-3,4-bis((triisopropylsilyl)oxy)-2{[(triisopropylsilyl)oxy)methyl]-3,4-dihydro-2_H_-pyran-6-yl}methyl)-_N_-[2-(1-benzyl-1_H_-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)acetamide (155ab)



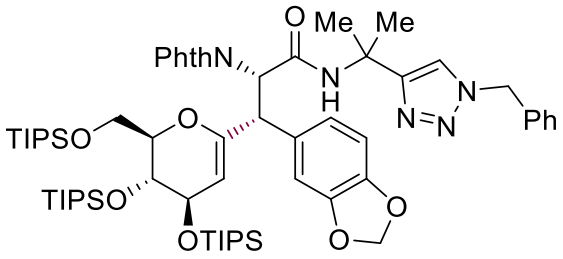
The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**153ab**) (57 mg, 0.10 mmol) and 1-iodo glycal **59** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **155ab** (73 mg, 62%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.55 (t, *J* = 5.4, 3.1 Hz, 2H), 7.44 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.24 (m, 8H), 7.21 (dd, *J* = 7.2, 2.2 Hz, 2H) 7.04 (s, 1H), 5.55 (d, *J* = 11.8 Hz, 1H), 5.41 (s, 2H), 5.10 (d, *J* = 5.3 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.37 (t, *J* = 6.8 Hz, 1H), 4.10 (m, 1H), 4.04 (d, *J* = 6.8 Hz, 2H), 4.00 (d, *J* = 5.3 Hz, 1H), 1.78 (s, 3H), 1.74 (s, 3H), 1.11 – 1.04 (m, 42H), 0.90 – 0.81 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 166.7 (C_q), 153.1 (C_q), 151.4 (C_q), 140.8 (C_q), 139.4 (C_q), 137.7 (C_q), 135.0 (C_q), 133.7 (CH), 131.4 (C_q), 128.9 (CH), 128.5 (CH), 128.5 (CH), 128.3 (CH), 127.9 (CH), 126.9 (CH), 126.7 (CH), 126.6 (CH), 123.2 (CH), 120.9 (CH), 98.8 (CH), 80.9 (CH), 69.4 (CH), 66.7 (CH), 61.2 (CH_2), 55.2 (CH), 53.9 (CH_2), 52.2 (C_q), 49.9 (CH), 28.6 (CH_3), 28.1 (CH_3), 18.24 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 3018, 2943, 2866, 1715, 1387, 1215, 908, 751, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1204 (100) $[M+Na]^+$, 1182 (80) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{68}H_{100}N_5O_7Si_3^+$ $[M+H]^+$: 1182.6925, found: 1182.6914.

(2_S_,3_S_)-3-(Benzo[d][1,3]dioxol-5-yl)-_N_-[2-(1-benzyl-1_H_-1,2,3-triazol-4-yl)propan-2-yl]-3-{(2_R_,3_R_,4_R_)-3,4-bis[(triisopropylsilyl)oxy]-2 [((triisopropylsilyl)oxy)methyl]-3,4-dihydro-2_H_-pyran-6-yl}-2-(1,3-dioxoisoindolin-2-yl)propenamide (155ac)



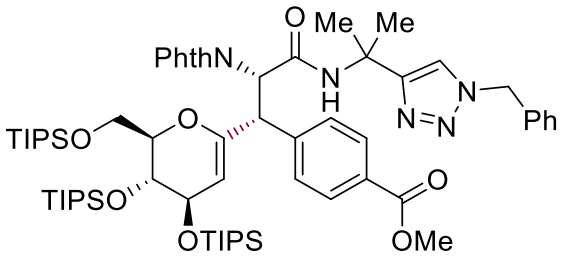
The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**153ac**) (54 mg, 0.10 mmol) and 1-iodo glycal **59** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **155ac** (75 mg, 65%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 – 7.65 (m, 2H), 7.62 – 7.59 (m, 2H), 7.42 (s, 1H), 7.33 – 7.25 (m, 3H), 7.23 – 7.15 (m, 2H), 6.98 (s, 1H), 6.79 (s, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 5.74 (m, 2H), 5.51 – 5.27 (m, 3H), 5.03 (d, *J* = 5.3 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.43 – 4.30 (m, 1H), 4.10 (s, 1H), 4.03 – 3.92 (m, 3H), 1.74 (s, 3H), 1.72 (s, 3H), 1.14 – 0.99 (m, 42H), 0.94 – 0.87 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 166.6 (C_q), 153.1 (C_q), 151.5 (C_q), 147.0 (C_q), 146.3 (C_q), 135.0 (C_q), 133.8 (CH), 132.5 (C_q), 131.4 (C_q), 128.9 (CH), 128.3 (CH), 127.9 (CH), 123.3 (CH), 121.6 (CH), 120.9 (CH), 108.6 (CH), 107.6 (CH), 100.6 (CH_2), 98.6 (CH), 80.9 (CH), 69.4 (CH), 66.7 (CH), 61.2 (CH_2), 55.4 (CH), 53.9 (CH_2), 52.1 (C_q), 49.7 (CH), 28.6 (CH_3), 28.0 (CH_3), 18.2 (CH_3) , 18.19 (CH_3), 18.1 (CH_3), 18.02 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.4 (CH), 12.30 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 3019, 2867, 1715, 1385, 1264, 1215, 908, 754, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1172 (100) $[M+Na]^+$, 1150 (75) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{63}H_{95}N_5NaO_9Si_3^+$ $[M+Na]^+$: 1172.6330, found: 1172.6319.

Methyl 4-[(1*S*,2*S*)-3-{[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]amino}-1-{(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl}-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]benzoate (155ad)



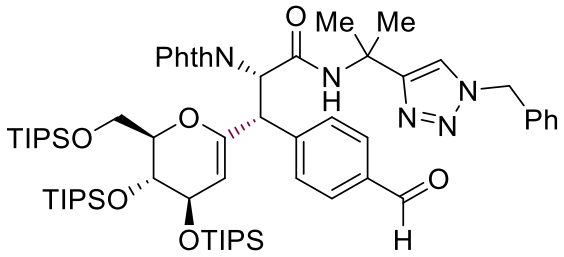
The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**153ad**) (28 mg, 0.05 mmol) and 1-iodo glycal **59** (55 mg, 0.08 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **155ad** (30 mg, 51%, d.r. > 20:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 8.3 Hz, 2H), 7.66 – 7.53 (m, 4H), 7.40 (s, 1H), 7.37 – 7.27 (m, 5H), 7.22 – 7.16 (m, 2H), 6.95 (s, 1H), 5.52 (d, *J* = 11.9 Hz, 1H), 5.40 (s, 2H), 5.08 (dd, *J* = 5.4, 1.4 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.34 (t, *J* = 6.7 Hz, 1H), 4.13 – 3.91 (m, 4H), 3.79 (s, 3H), 1.76 (s, 3H), 1.71 (s, 3H), 1.13 – 0.98 (m, 42H), 0.93 – 0.73 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.7 (C_q), 166.9 (C_q), 166.3 (C_q), 153.0 (C_q), 150.6 (C_q), 143.9 (C_q), 134.9 (C_q), 133.9 (CH), 131.3 (C_q), 129.4 (C_q), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 123.3 (CH), 120.8 (CH), 99.3 (CH), 81.1 (CH), 69.4 (CH), 66.6 (CH), 61.2 (CH), 54.9 (CH), 53.9 (CH_2), 52.2 (CH), 51.9 (CH_3), 50.1 (CH), 28.4 (CH_3), 28.2 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 12.3 (CH), 12.2 (CH), 12.1 (CH)

IR (ATR): $\tilde{\nu}$ = 2865, 1718, 1463, 1382, 1279, 1062, 883, 757, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1186 (100) $[M+Na]^+$, 1164 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{64}H_{97}N_5NaO_9Si_3^+$ $[M+Na]^+$: 1186.6486, found: 1186.6486.

(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(4-formylphenyl)propenamide (155ae)



The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**153ae**) (52 mg, 0.10 mmol) and 1-iodo glycal **59** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **155ae** (63 mg, 56%, d.r. >20:1).

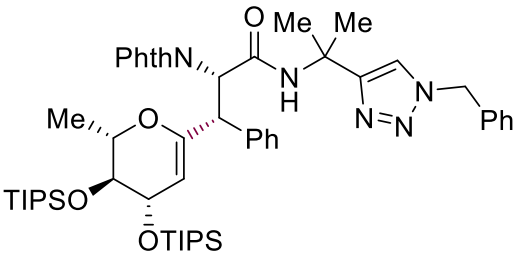
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 7.66 – 7.61 (m, 2H), 7.60 – 7.54 (m, 4H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.39 (s, 1H), 7.32 – 7.24 (m, 3H), 7.23 – 7.16 (m, 2H), 6.92 (s, 1H), 5.54 (d, *J* = 11.8 Hz, 1H), 5.40 (s, 2H), 5.10 (d, *J* = 5.4 Hz, 1H), 4.74 (d, *J* =

11.8 Hz, 1H), 4.35 (t, *J* = 6.3 Hz, 1H), 4.11 – 4.04 (m, 2H), 4.02 – 3.93 (m, 2H), 1.76 (s, 3H), 1.71 (s, 3H), 1.07 (m, *J* = 7.8 Hz, 42H), 0.83 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 191.8 (CH), 167.7 (C_q), 166.2 (C_q), 153.0 (C_q), 150.2 (C_q), 145.7 (C_q), 135.1 (C_q), 134.9 (C_q), 133.9 (CH), 131.2 (C_q), 129.5 (CH), 128.9 (CH), 128.9 (CH), 128.4 (CH), 127.9 (CH), 123.3 (CH), 120.8 (CH), 99.5 (CH), 81.1 (CH), 69.3 (CH), 66.5 (CH), 61.2 (CH_2), 54.8 (CH), 53.9 (CH_2), 52.2 (C_q), 50.2 (CH), 28.3 (CH_3), 28.2(CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 12.3 (CH), 12.2 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 3020, 1714, 1265, 1216, 909, 755, 706, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1156 (100) $[M+Na]^+$, 1134 (15) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{63}H_{95}N_5NaO_8Si_3^+$ $[M+Na]^+$: 1156.6381, found: 1156.6374.

(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-{(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl}-3-phenylpropanamide (155af)



The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**153aa**) (49 mg, 0.10 mmol) and 1-iodo glycal **154a** (85 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **155af** (80 mg, 86%, d.r. > 20:1).

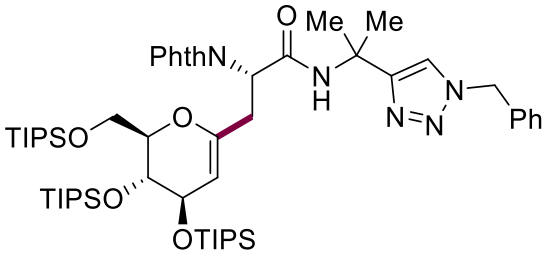
^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 7.76 – 7.72 (m, 2H), 7.69 – 7.63 (m, 3H), 7.45 – 7.41 (m, 3H), 7.40 – 7.36 (m, 2H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.26 (s, 1H), 7.17 (dd, *J* = 7.3 Hz, 2H), 7.10 (dd, *J* = 7.3 Hz, 1H), 5.61 (d, *J* = 11.4 Hz, 1H), 5.56 (s, 2H), 5.28 (d, *J* = 4.3 Hz, 1H), 4.60 (d, *J* = 11.4 Hz, 1H), 4.49 (dt, *J* = 7.0 Hz, 1H), 4.23 (d, *J* = 4.3 Hz, 1H), 3.94 (q, *J* = 1.8 Hz, 1H), 1.86 (s, 3H), 1.82 (s, 3H), 1.18 – 1.02 (m, 45H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 167.8 (C_q), 166.8 (C_q), 153.0 (C_q), 151.2 (C_q), 138.0 (C_q), 135.0 (C_q), 133.7 (CH), 131.5 (C_q), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 126.9 (CH), 123.1 (CH), 121.1 (CH), 100.7 (CH), 75.8 (CH), 74.0

(CH), 67.3 (CH), 53.9 (CH_2), 53.5 (CH), 52.4 (C_q), 51.3 (CH), 29.0 (CH_3), 27.6 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 15.2 (CH_3), 12.5 (CH), 12.5 (CH).

IR (ATR): $\tilde{\nu}$ = 3054, 2867, 1715, 1386, 1265, 1092, 884, 737, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 956 (100) $[M+Na]^+$, 934 (40) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{75}N_5NaO_6Si_2^+$ $[M+Na]^+$: 956.5148, found: 956.5129.

(*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4 bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)propenamide (155ag)



The general procedure **A** was followed using Phth-Ala-TAM^{Bn} (**153af**) (42 mg, 0.10 mmol) and 1-iodo glycal **59** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **155ag** (91 mg, 88%).

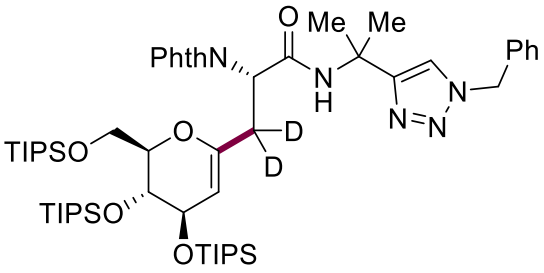
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.43 (s, 1H), 7.38 – 7.28 (m, 3H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.24 (m, 1H), 7.07 (s, 1H), 5.45 (s, 2H), 5.00 (t, *J* = 8.0, 6.0 Hz, 1H), 4.76 (dd, *J* = 5.4, 1.3 Hz, 1H), 4.27 – 4.21 (m, 1H), 4.01 (d, *J* = 2.0 Hz, 1H), 3.95 – 3.88 (m, 2H), 3.85 (dd, *J* = 11.1, 5.0 Hz, 1H), 3.08 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.96 (dd, *J* = 14.8, 6.0 Hz, 1H), 1.72 (s, 3H), 1.71 (s, 3H), 1.07 – 0.97 (m, 42H), 0.98 – 0.90 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9 (C_q), 167.5 (C_q), 153.2 (C_q), 149.2 (C_q), 134.8 (C_q), 133.8 (CH), 132.0 (C_q), 128.9 (CH), 128.4 (CH), 128.0 (CH), 123.3 (CH), 120.6 (CH), 99.1 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 54.0 (CH_2), 53.1 (CH), 52.0 (C_q), 35.0 (CH_2), 28.4 (CH_3), 27.9 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.3 (CH), 11.9 (CH). (1 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 2867, 2012, 1716, 1384, 1265, 1054, 895, 737, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1052 (100) $[M+Na]^+$, 1030 (25) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{56}H_{91}N_5NaO_7Si_3^+$ [M+Na]$^+$: 1052.6119, found: 1052.6120.

(*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)propenamide (155ah)



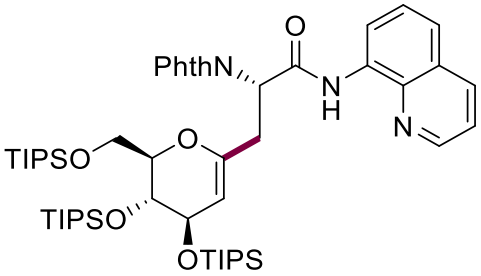
The general procedure **A** was followed using Phth-[**D$_3$**]-Ala-TAM^{Bn} **(153ag**) (42 mg, 0.10 mmol) and 1-iodo glycal **59** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **155ah** (93 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.68 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.42 (s, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.21 (m, 2H), 7.06 (s, 1H), 5.45 (s, 2H), 4.98 (s, 1H), 4.75 (d, *J* = 4.4 Hz, 1H), 4.24 (dt, *J* = 7.0, 3.8 Hz, 1H), 4.00 (d, *J* = 2.0 Hz, 1H), 3.95 – 3.81 (m, 3H), 1.71 (s, 3H), 1.70 (s, 3H), 1.05 – 0.97 (m, 42H), 0.96 – 0.91 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9 (C_q), 167.5 (C_q), 153.2 (C_q), 149.2 (C_q), 134.8 (C_q), 133.8 (CH), 132.0 (C_q), 128.9 (CH), 128.4 (CH), 128.0 (CH), 123.3 (CH), 120.6 (CH), 99.1 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 54.0 (CH_2), 53.0 (CH), 52.0(C_q), 28.4 (CH_3), 27.8 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.3 (CH), 11.9 (CH). (2 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019, 2945, 2866, 1716, 1387, 1265, 1215, 909, 754, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1054 (100) [M+Na]$^+$, 1032 (20) [M+H]$^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{56}H_{89}D_2N_5NaO_7Si_3^+$ [M+Na]$^+$: 1054.6244, found: 1054.6244.

(*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)propenamide (155ba)



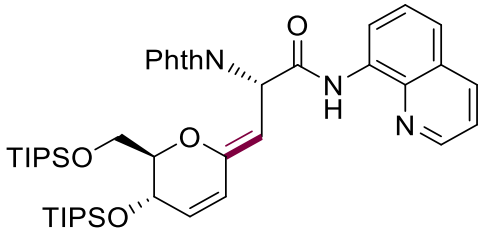
The general procedure **B** was followed using Phth-Ala-AQ (**153ba**) (35 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **155ba** (81 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.32 (s, 1H), 8.75 – 8.56 (m, 2H), 8.11 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.48 (m, 2H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.51 (dd, *J* = 11.2, 4.6 Hz, 1H), 4.82 (d, *J* = 5.1 Hz, 1H), 4.28 (t, *J* = 5.9 Hz, 1H), 4.01 (t, *J* = 2.0 Hz, 1H), 3.95 (dd, *J* = 10.9, 7.0 Hz, 1H), 3.89 (m, 2H), 3.53 (dd, *J* = 14.6, 11.2 Hz, 1H), 3.17 (dd, *J* = 14.6, 4.6 Hz, 1H), 1.08 – 1.04 (m, 21H), 1.02 – 0.98 (m, 21H), 0.95 – 0.87 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.84 (C_q), 166.78 (C_q), 148.94 (C_q), 148.20 (CH), 138.47 (C_q), 136.13 (CH), 133.98 (C_q), 133.81 (CH), 132.07 (C_q), 127.77 (C_q), 127.18 (CH), 123.40 (CH), 121.81 (CH), 121.52 (CH), 116.76 (CH), 98.97 (CH), 81.14 (CH), 69.34 (CH), 66.20 (CH), 62.16 (CH_2), 52.91 (CH), 33.78 (CH_2), 18.13 (CH_3), 18.09 (CH_3), 18.00 ($2CH_3$), 17.94 (CH_3), 17.93 (CH_3), 12.40 (CH), 12.33 (CH), 12.01 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 2943, 1720, 1532, 1464, 1384, 1264, 1060, 883, 738 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 980 (100) $[M+Na]^+$, 958 (40) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{83}N_3NaO_7Si_3^+$ $[M+Na]^+$: 980.5431, found: 980.5426.

(*S*,*Z*)-2-(1,3-Dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)-3-[(5*S*,6*R*)-5-[(triisopropylsilyl)oxy]-6-{[(triisopropylsilyl)oxy]methyl}-5,6-dihydro-2*H*-pyran-2-ylidene]propenamide (155e)



The general procedure **B** was followed using Phth-Ala-AQ **(153ba)** (35 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol). After 8 h at 100 °C, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **155e** (62 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.63 (s, 1H), 8.72 – 8.66 (m, 2H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.48 (m, 2H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.31 (d, *J* = 9.4 Hz, 1H), 6.20 (dd, *J* = 10.0, 1.4 Hz, 1H), 6.13 (dd, *J* = 10.0, 2.6 Hz, 1H), 5.51 (d, *J* = 9.4 Hz, 1H), 4.80 (d, *J* = 6.6 Hz, 1H), 4.07 – 3.96 (m, 2H), 3.90 (dd, *J* = 7.3, 2.6 Hz, 1H), 1.26 – 0.97 (m, 21H), 0.94 – 0.76 (m, 21H).

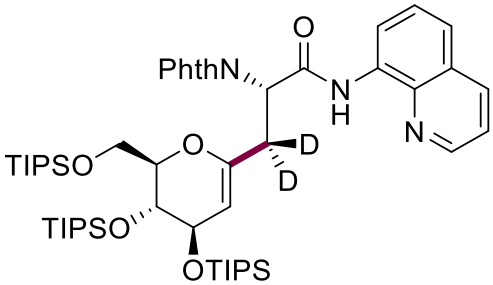
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 165.8 (C_q), 152.3 (C_q), 148.0 (CH), 138.8 (C_q), 136.0 (CH), 134.2 (C_q), 133.9 (CH), 132.4 (CH), 132.2 (C_q), 127.8 (C_q), 127.3 (CH), 123.4 (CH), 122.7 (CH), 121.6 (CH), 121.4 (CH), 116.4 (CH), 100.5 (CH), 81.0 (CH), 63.3 (CH), 62.1 (CH_2), 50.3 (CH), 18.12 (CH_3) , 18.1 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 12.6 (CH), 11.8 (CH).

IR (ATR): $\tilde{\nu}$ = 3004, 1711, 1420, 1359, 1220, 1092, 902, 530 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 806 (100) $[M+Na]^+$, 784 (70) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{61}N_3NaO_6Si_2^+$ $[M+Na]^+$: 806.3991, found: 806.3987.

(*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)propenamide (155bb)



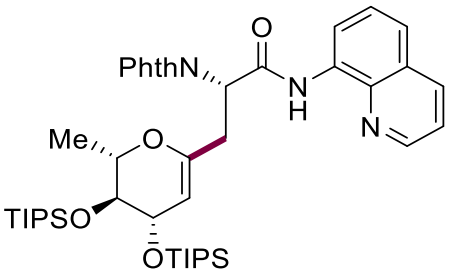
The general procedure **B** was followed using Phth-[**D$_3$**]Ala-AQ (**153bb**) (35 mg, 0.10 mmol) and 1-iodo glycal **59** (111 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **155bb** (76 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.32 (s, 1H), 8.72 – 8.66 (m, 2H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.48 (d, *J* = 4.5 Hz, 2H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.50 (s, 1H), 4.81 (dd, *J* = 5.2, 1.4 Hz, 1H), 4.28 (dt, *J* = 9.0, 3.4 Hz, 1H), 4.00 (d, *J* = 1.9 Hz, 1H), 3.95 (dd, *J* = 10.9, 7.1 Hz, 1H), 3.91 – 3.86 (m, 2H), 1.06 (m, 21H), 1.00 (m, 21H), 0.94 – 0.88 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9 (C_q), 166.8 (C_q), 148.9 (C_q), 148.2 (CH), 138.5 (C_q), 136.1 (CH), 134.0 (C_q), 133.8 (CH), 132.1 (C_q), 127.8 (C_q), 127.2 (CH), 123.4 (CH), 121.8 (CH), 121.5 (CH), 116.8 (CH), 99.0 (CH), 81.2 (CH), 69.4 (CH), 66.2 (CH), 62.2 (CH_2), 52.8 (CH), 18.2 (CH_3), 18.1 (CH_3), 18.0 ($2CH_3$), 17.96 (CH_3), 17.9 (CH_3), 12.4 (CH_3), 12.3 (CH_3), 12.0 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2866, 2254, 1720, 1531, 1464, 1382, 905, 730, 650 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 982 (55) $[M+Na]^+$, 960 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{82}D_2N_3O_7Si_3^+$ $[M+H]^+$:960.5737, found: 960.5723.

(*S*)-2-(1,3-Dioxoisoindolin-2-yl)-3-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)propenamide (155bc)



The general procedure **B** was followed using Phth-Ala-AQ (**153ba**) (35 mg, 0.10 mmol) and 1-iodo glycal **154a** (85 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **155bc** (41 mg, 52%).

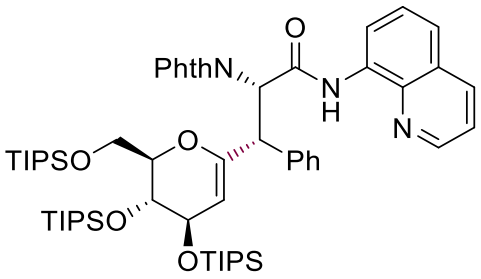
^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.33 (s, 1H), 8.70 (dd, *J* = 5.5, 3.6 Hz, 1H), 8.64 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.49 (s, 1H), 7.39 (dd, *J* = 8.3, 4.2

Hz, 1H), 5.52 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.76 (d, *J* = 5.1 Hz, 1H), 4.35 (dtd, *J* = 7.1, 5.1, 1.9 Hz, 1H), 4.07 – 3.89 (m, 1H), 3.82 (d, *J* = 1.9 Hz, 1H), 3.43 (dd, *J* = 14.5, 11.5 Hz, 1H), 3.16 (dd, *J* = 14.5, 4.5, Hz, 1H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.06 – 0.95 (m, 21H), 0.89 – 0.80 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 167.8 (C_q), 166.8 (C_q), 148.2 (CH), 147.7 (C_q), 138.5 (C_q), 136.2 (C_q), 133.9 (CH), 131.9 (C_q), 127.8 (C_q), 127.3 (CH), 123.5 (CH), 121.8 (CH), 121.5 (CH), 116.7 (CH), 99.4 (CH), 75.2 (CH) , 72.8 (CH), 66.6 (CH), 52.7 (CH), 33.8 (CH_2), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 15.7 (CH_3), 12.6 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 2948, 1718, 1535, 1464, 1388, 1262, 885, 740 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 808 (30) $[M+Na]^+$, 786 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{64}N_3O_6Si_2^+$ $[M+H]^+$: 786.4328, found: 786.4312.

(2*S*,3*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-phenyl-*N*-(quinolin-8-yl)propenamide (155bd)



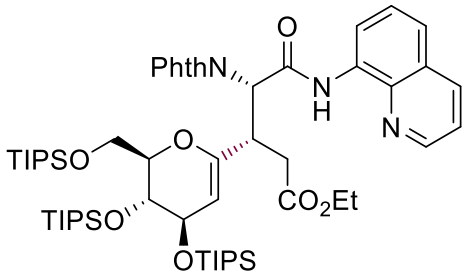
The general procedure **C** was followed using Phth-Phe-AQ (**153bc**) (42 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **155bd** (96 mg, 93%, d.r. = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 10.51 (s, 1H), 8.90 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.82 (dd, *J* = 5.4, 3.7 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.58 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.49 (s, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.45 (m, 3H), 7.11 (m, 2H), 7.04 (m, 1H), 5.85 (d, *J* = 12.1 Hz, 1H), 5.22 – 5.01 (m, 2H), 4.29 (dt, *J* = 7.8, 4.0 Hz, 1H), 4.17 (d, *J* = 1.9 Hz, 1H), 4.03 (dd, *J* = 10.2, 8.1 Hz, 1H), 3.99 (dt, *J* = 4.7, 1.9 Hz, 1H), 3.71 (dd, *J* = 10.2, 5.8 Hz, 1H), 1.02 – 0.83 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.6 (C_q), 165.1 (C_q), 151.2 (C_q), 148.4 (CH), 138.7 (C_q), 138.6 (C_q), 135.9 (CH), 134.4 (C_q), 133.8 (CH), 131.3 (C_q) 128.2 (CH), 128.1 (CH), 127.8 (C_q), 127.2 (CH), 126.8 (CH), 123.3 (CH), 121.6 (CH), 121.4 (CH), 117.1 (CH), 99.0 (CH), 80.5 (CH), 69.2 (CH), 66.7 (CH), 60.8 (CH_2), 57.1 (CH), 48.7 (CH), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.93 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 12.3 (CH), 11.7 (CH). (1 CH resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum)

IR (ATR): $\tilde{\nu}$ = 3019, 2022, 1719, 1530, 1215, 750, 1215, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1056 (75) $[M+Na]^+$, 1034 (50) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{59}H_{87}N_3NaO_7Si_3^+$ $[M+Na]^+$: 1056.5744, found: 1056.5738.

Ethyl (3*S*,4*S*)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4-(1,3-dioxoisoindolin-2-yl)-5-oxo-5-(quinolin-8-ylamino)pentanoate (155be)



The general procedure **C** was followed using Phth-Glu(OEt)-AQ (**153bd**) (43 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **155be** (96 mg, 92%, d.r. = 6:1).

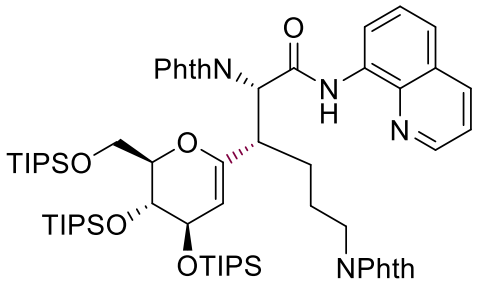
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.47 (s, 1H), 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 6.8, 2.3 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.51 – 7.37 (m, 3H), 5.39 (d, *J* = 11.5 Hz, 1H), 5.11 (d, *J* = 5.2 Hz, 1H), 4.30 (dd, *J* = 11.5, 6.0 Hz, 1H), 4.27 – 4.23 (m, 1H), 4.21 – 4.07 (m, 1H), 4.06 – 3.91 (m, 2H), 3.93 – 3.77 (m, 2H), 3.71 (dd, *J* = 10.3, 5.8 Hz, 1H), 2.70 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.48 (dd, *J* = 16.2, 6.0 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H), 1.07 – 0.95 (m, 21H), 0.92 – 0.77 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.1 (C_q), 167.7 (C_q), 164.6 (C_q), 150.2 (C_q), 148.4 (CH), 138.7 (C_q), 135.9 (CH), 134.3 (C_q), 134.1 (CH), 131.7 (C_q), 127.8 (C_q), 127.2 (CH), 123.6 (CH), 121.6 (CH), 121.4 (CH), 117.1 (CH), 100.0 (CH), 80.3 (CH), 69.3

(CH), 66.5 (CH), 60.8 (CH_2), 60.4 (CH_2), 57.2 (CH), 39.5 (CH), 35.7 (CH_2), 18.1 (CH_3), 18.1 ($2CH_3$), 18.0 (CH_3), 17.93 (CH_3), 17.9 (CH_3), 13.9 (CH_3), 12.4 (CH), 12.2 (CH), 11.8 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019,2317, 2182, 1722, 1530, 1214, 751, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1066 (100) $[M+Na]^+$, 1044 (55) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{57}H_{89}N_3NaO_9Si_3^+$ $[M+Na]^+$:1066.5799, found: 1066.5794.

(2*S*,3*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2,6-bis(1,3-dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)hexanamide (155bf)



The general procedure **C** was followed using Phth-Lys(Phth)-AQ (**153be**) (27 mg, 0.05 mmol) and 1-iodo glycal **59** (55 mg, 0.08 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **155bf** (53 mg, 92%, d.r. = 6:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.45 (s, 1H), 8.88 (dd, *J* = 4.1, 1.9 Hz, 1H), 8.71 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.10 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.73 – 7.68 (m, 2H), 7.68 – 7.62 (m, 4H), 7.48 – 7.38 (m, 3H), 5.29 (d, *J* = 11.2 Hz, 1H), 5.07 (d, *J* = 5.2 Hz, 1H), 4.25 (t, *J* = 7.1 Hz, 1H), 4.16 (d, *J* = 1.9 Hz, 1H), 4.05 – 3.91 (m, 2H), 3.79 (td, *J* = 11.2, 3.8 Hz, 1H), 3.70 (dd, *J* = 10.1, 5.7 Hz, 1H), 3.59 (t, *J* = 7.2 Hz, 2H), 1.90 – 1.73 (m, 2H), 1.74 – 1.58 (m, 2H), 1.00 – 0.92 (m, 21H), 0.90 – 0.77 (m, 42H).

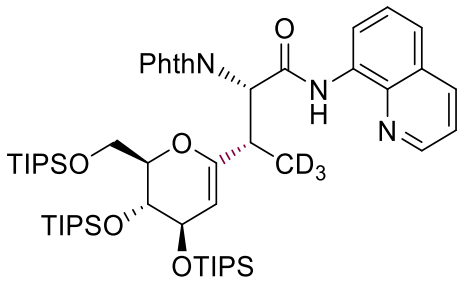
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.0 (C_q), 167.9 (C_q), 165.1 (C_q), 149.3 (C_q), 148.4 (CH), 138.8 (C_q), 135.9 (CH), 134.3 (C_q), 134.0 (CH), 133.5 (CH), 132.1 (C_q), 131.6 (C_q), 127.8 (C_q), 127.2 (CH), 123.5 (CH), 122.9 (CH), 121.5 (CH), 121.4 (CH), 117.1 (CH), 101.2 (CH), 80.1 (CH), 69.4 (CH), 66.4 (CH), 60.8 (CH_2), 58.1 (CH), 42.2 (CH), 37.7 (CH_2), 26.1 (CH_2), 25.4 (CH_2), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.3 (CH), 12.2 (CH), 11.8 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019, 2399, 1716, 1530 1214, 751, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1167 (100) $[M+Na]^+$, 1145 (20) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{64}H_{92}N_4NaO_9Si_3^+$ $[M+Na]^+$: 1167.6064, found: 1167.6064.

(2*S*,3*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)butanamide (155bg)



The general procedure **C** was followed using **153bf** (36 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol). After 8 h, Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded inseparable diastereomers **155bg** (87 mg, 90%, d.r. = 4:1).

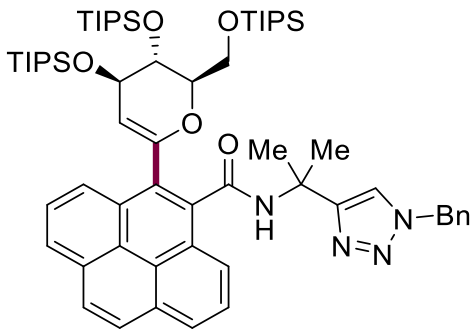
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.48 (s, 1H), 8.97 – 8.80 (m, 1H), 8.78 – 8.62 (m, 1H), 8.20 – 8.01 (m, 1H), 7.90 – 7.76 (m, 2H), 7.72 – 7.59 (m, 2H), 7.52 – 7.32 (m, 3H), 5.32 – 5.14 (m, 1H), 5.04 – 4.79 (m, 1H), 4.31 – 4.11 (m, 2H), 4.07 – 3.93 (m, 2H), 3.88 (d, *J* = 11.9 Hz, 1H), 3.79 – 3.69 (m, 1H), 1.09 – 0.94 (m, 21H), 0.92 – 0.77 (m, 42H)

^{13}C NMR (101 MHz, $CDCl_3$): the major isomer: δ = 168.0 (C_q), 165.5 (C_q), 152.8 (C_q), 148.4 (CH), 138.8 (C_q), 135.9 (CH), 134.3 (C_q), 134.1 (CH), 131.7 (C_q), 127.8 (C_q), 127.2 (CH), 123.5 (CH), 121.6 (CH), 121.3 (CH), 117.2 (CH), 98.2 (CH), 80.3 (CH), 69.4 (CH), 66.6 (CH), 61.0 (CH_2), 58.7 (CH), 37.4 (CH), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9(CH_3), 12.5 (CH), 12.2 (CH), 11.8 (CH). the minor isomer: **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 167.7 (C_q), 166.8 (C_q), 152.6 (C_q), 148.5 (CH), 138.6 (C_q), 136.1 (CH), 134.3 (C_q), 133.7 (CH), 131.9 (C_q), 127.8 (C_q), 127.1 (CH), 123.4 (CH), 121.9 (CH), 121.6 (CH), 117.0 (CH), 98.3 (CH), 80.6 (CH), 69.7 (CH), 66.2 (CH), 61.7 (CH_2), 58.4 (CH), 37.3 (CH), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.5 (CH), 12.2 (CH), 11.8 (CH).

IR (ATR): $\tilde{\nu}$ = 3019, 2867, 1719, 1531, 1381, 1215, 751, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 997 (100) $[M+Na]^+$, 975 (70) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{54}H_{82}D_3N_3NaO_7Si_3^+$ $[M+Na]^+$: 997.5776, found: 997.5773.

***N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-5-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]pyrene-4-carboxamide (157a)**



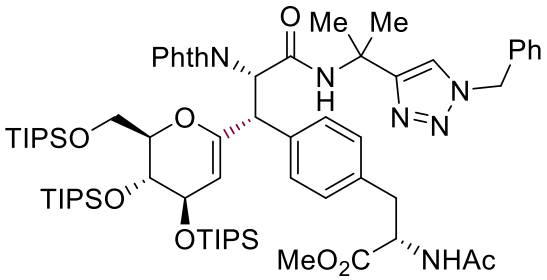
The general procedure **B** was followed using pyrene-TAM^{Bn} (**156a**) (44 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol), Ag_2CO_3 (2.0 equiv). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **157a**(83 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H), 8.15 (dd, *J* = 7.4 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.95 (m, 2H), 7.65 (s, 1H), 7.43 – 7.38 (m, 3H), 7.37 – 7.33 (m, 2H), 6.48 (s, 1H), 5.77 (d, *J* = 3.9 Hz, 1H), 5.59 (s,1H), 5.58 (s, 1H), 4.66 – 4.56 (m, 1H), 4.41 (dd, *J* = 11.4, 8.5 Hz, 1H), 4.29 (d, *J* = 4.4 Hz, 1H), 4.17 – 4.16 (m, 1H), 3.91 (dd, *J* = 11.4, 3.5 Hz, 1H), 2.04 (s, 3H), 1.78 (s, 3H), 1.37 – 0.92 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1 (C_q), 153.7 (C_q), 148.1 (C_q), 134.9 (C_q), 131.2 (C_q), 131.1 (C_q), 131.0 (C_q), 130.8 (C_q), 130.6 (C_q), 129.1 (CH), 128.6 (CH), 128.5 (CH), 128.3(C_q), 128.2 (CH), 128.1 (CH), 127.3 (CH), 126.2 (CH), 125.4 (CH), 125.3 (CH), 125.0 (CH), 124.6 (CH), 124.3 (C_q), 124.2 (C_q), 120.6 (CH), 103.3 (CH), 81.7 (CH), 71.3 (CH), 67.2 (CH), 61.1 (CH_2), 54.2 (CH_2), 52.1 (C_q), 28.8 (CH_3), 26.8 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 12.5 (CH), 12.4 (CH), 12.1 (CH).). (3 CH_3 resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019, 1716, 1215, 908, 752, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1079 (100) $[M+Na]^+$, 1057 (40) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{62}H_{92}N_4NaO_5Si_3^+$ $[M+Na]^+$: 1079.6268, found: 1079.6252.

Methyl (*S*)-2-acetamido-3-{4-[(1*S*,2*S*)-3-{[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]amino}-1-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]phenyl}propanoate (155cd)



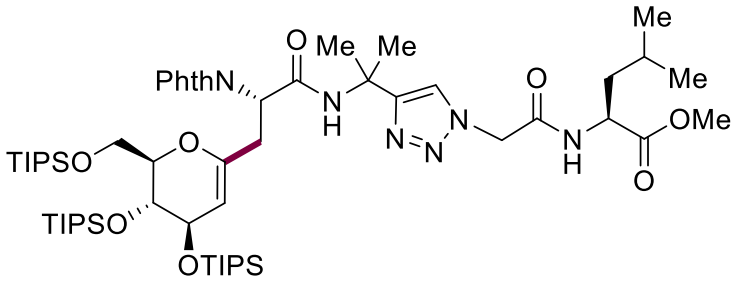
The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**153cd**) (64 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:2) yielded **155cd** (40 mg, 32 %, d.r. >20 :1).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.59 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.42 (s, 1H), 7.33 – 7.25 (m, 3H), 7.20 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.00 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 2H), 5.51 (d, *J* = 7.7 Hz, 1H), 5.45 (d, *J* = 11.7 Hz, 1H), 5.40 (s, 2H), 5.03 (dd, *J* = 5.4, 1.4 Hz, 1H), 4.63 (dt, *J* = 7.7, 5.8 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.33 (tt, *J* = 6.5, 1.9 Hz, 1H), 4.09 (q, *J* = 1.8 Hz, 1H), 4.05 – 3.99 (m, 2H), 3.97 (dq, *J* = 5.2, 1.8 Hz, 1H), 3.43 (s, 3H), 2.89 (dd, *J* = 14.1, 5.8 Hz, 1H), 2.83 (dd, *J* = 14.1, 5.8 Hz, 1H), 1.77 (s, 3H), 1.74 (s, 3H), 1.71 (s, 3H), 1.12 – 0.99 (m, 42H), 0.91 – 0.84 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.5 (C_q), 169.2 (C_q), 167.7 (C_q), 166.4 (C_q), 153.0 (C_q), 151.1 (C_q), 137.5 (C_q), 134.9 (C_q), 134.2 (C_q), 133.7 (CH), 131.3 (C_q), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 123.2 (CH), 120.9 (CH), 99.0 (CH), 80.9 (CH), 69.5 (CH), 66.7 (CH), 61.2 (CH_2), 55.4 (CH), 53.9 (CH_2), 52.8 (CH), 52.1 (C_q), 51.9 (CH_3), 49.7 (CH), 37.1 (CH_2), 28.5 (CH_3), 28.0 (CH_3), 22.9 (CH_3), 18.23 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.02 (CH_3), 18.0 (CH_3), 17.95 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 2942, 1717, 1669, 1514, 1463, 1383, 1215, 1051, 883, 682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1271 (100) $[M+Na]^+$, 1249 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{68}H_{104}N_6NaO_{10}Si_3^+$ $[M+Na]^+$: 1271.7014, found: 1271.7006.

Methyl (2-{4-[2-((*S*)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)propanamido)propan-2-yl]-1*H*-1,2,3-triazol-1-yl}acetyl)-*L*-leucinate (155ce)



The general procedure **A** was followed using Phth-Ala-Tzl-Gly-Leu-OMe (**153ce**) (51 mg, 0.10 mmol) and 1-iodo glycal **59** (111 mg, 0.15 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:1) yielded **155ce** (81 mg, 72%)

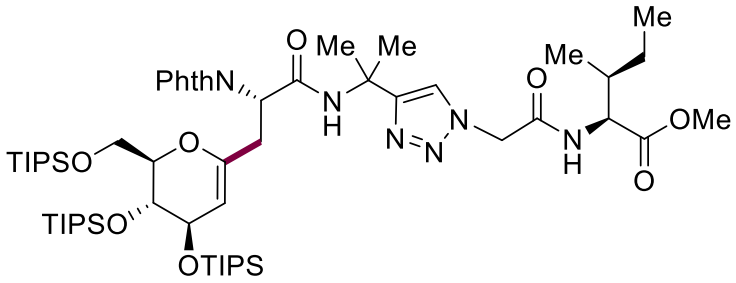
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.62 (s, 1H), 7.02 (s, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 5.24 – 4.88 (m, 3H), 4.75 (d, *J* = 5.0 Hz, 1H), 4.55 (t, *J* = 6.2 Hz, 1H), 4.24 (t, *J* = 5.0 Hz, 1H), 4.14 – 3.96 (m, 1H), 3.93 – 3.83 (m, 3H), 3.68 (s, 3H), 3.05 (dd, *J* = 14.9, 5.9 Hz, 1H), 2.96 (dd, *J* = 14.9, 5.9 Hz, 1H), 1.74 (s, 3H), 1.72 (s, 3H), 1.61 – 1.45 (m, 3H), 1.08 – 0.91 (m, 63H), 0.87 – 0.81 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4 (C_q), 167.8 (C_q), 167.7 (C_q), 165.2 (C_q), 153.3 (C_q), 149.2 (C_q), 133.9 (CH), 131.9 (C_q), 123.4 (CH), 122.6 (CH), 99.2 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 53.0 (CH), 52.8 (CH_2), 52.3 (CH_3), 51.8 (C_q), 51.1 (CH), 40.8 (CH_2), 34.9 (CH_2), 28.3 (CH_3), 28.0 (CH_3), 24.8 (CH), 22.6 (CH_3), 21.7 (CH_3), 18.11 (CH_3), 18.1 (CH_3), 17.97 (CH_3), 12.3 (CH), 11.9 (CH).). (3 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum):

IR (ATR): $\tilde{\nu}$ = 2943, 1714, 1661, 1384, 1056, 881, 731, 680 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1147 (100) $[M+Na]^+$, 1125 (5) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{58}H_{100}N_6NaO_{10}Si_3^+$ $[M+Na]^+$: 1147.6701, found: 1147.6697.

Methyl (2-{4-[2-((*S*)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-

dioxoisoindolin-2- yl)propanamido)propan-2-yl]-1*H*-1,2,3-triazol-1-yl}acetyl)-*L*-isoleucinate (155cg)



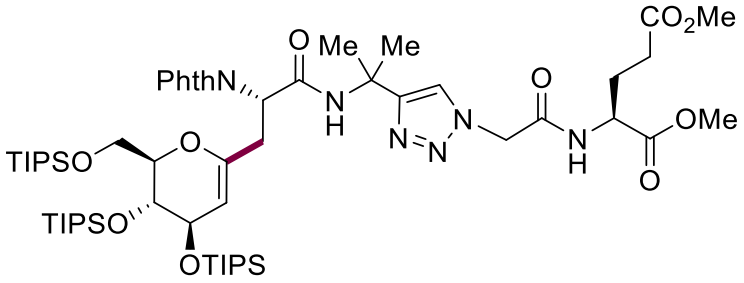
The general procedure **A** was followed using Phth-Ala-Tzl-Gly-Ile-Ome (**153cg**) (51 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:2) yielded **155cg** (74 mg, 65%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.68 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.62 (s, 1H), 7.06 (s, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 5.11 – 4.92 (m, 3H), 4.76 (d, *J* = 4.7 Hz, 1H), 4.49 (dd, *J* = 8.4, 4.9 Hz, 1H), 4.25 (td, *J* = 5.1, 2.6 Hz, 1H), 4.01 (d, *J* = 1.9 Hz, 1H), 3.96 – 3.82 (m, 3H), 3.68 (s, 3H), 3.06 (dd, *J* = 14.8, 7.8 Hz, 1H), 2.97 (dd, *J* = 14.8, 6.2 Hz, 1H), 1.86 – 1.79 (m, 1H), 1.73 (s, 6H), 1.39 – 1.20 (m, 2H), 1.06 – 0.92 (m, 63H), 0.86 – 0.74 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ= 171.3 (C_q), 167.9 (C_q), 167.7 (C_q), 165.1 (C_q), 153.4 (C_q), 149.2 (C_q), 133.9 (CH), 131.92 (C_q), 123.4 (CH), 122.5 (CH), 99.2 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 56.7 (CH), 53.1 (CH), 52.8 (CH_2), 52.1 (CH_3), 51.8 (C_q), 37.5 (CH), 35.0 (CH_2), 28.4 (CH_3), 27.9 (CH_3), 25.0 (CH_2), 18.1 (CH_3), 18.1 (CH_3), 18.0 ($4CH_3$), 15.3 (CH_3), 12.3 (CH), 11.9 (CH), 11.4 (CH).

IR (ATR): $\tilde{\nu}$ = 3019, 1716, 1665, 1215, 908, 753, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1147 (100) $[M+Na]^+$, 1125 (15) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{58}H_{100}N_6NaO_{10}Si_3^+$ $[M+Na]^+$: 1147.6701, found: 1147.6686.

Dimethyl [2-(4-{2-[(*R*)-3-((2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-2-(1,3-dioxoisoindolin-2-yl)propanamido]propan-2-yl}-1*H*-1,2,3-triazol-1-yl)acetyl]-*L*-glutamate (155cf)



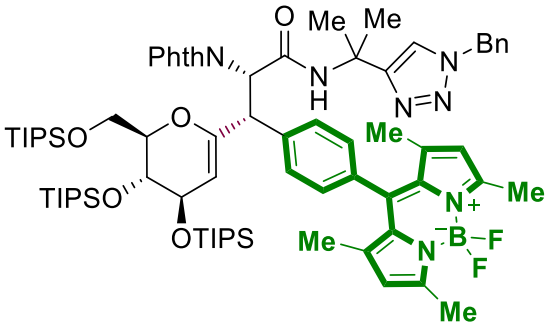
The general procedure **A** was followed using Phth-Ala-Tzl-Gly-Glu(OMe)-OMe (**153cf**) (53 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:2) yielded **155cf** (72 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.63 (s, 1H), 7.01 (s, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.07 – 4.89 (m, 3H), 4.75 (d, *J* = 5.1 Hz, 1H), 4.54 (q, *J* = 7.7, 6.8 Hz, 1H), 4.27 – 4.20 (m, 1H), 4.08 – 3.96 (m, 1H), 3.93 – 3.82 (m, 3H), 3.70 (s, 3H), 3.63 (s, 3H), 3.06 (dd, *J* = 15.0, 8.1 Hz, 1H), 2.95 (dd, *J* = 15.0, 5.9 Hz, 1H), 2.39 – 2.24 (m, 2H), 2.14 (dq, *J* = 13.8, 6.8 Hz, 1H), 1.94 (dq, *J* = 13.8, 7.7 Hz, 1H), 1.74 (s, 6H), 1.11 – 1.01 (m, 21H), 1.00 – 0.97 (m, 21H), 0.96 – 0.91 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0 (C_q), 171.3 (C_q), 167.9 (C_q), 167.7 (C_q), 165.4 (C_q), 153.3 (C_q), 149.2 (C_q), 133.9 (CH), 131.9 (C_q), 123.4 (CH), 122.5 (CH), 99.2 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 53.0 (CH), 52.7 (CH_2), 52.6 (CH_3), 52.0 (CH), 51.9 (CH_3), 51.8 (C_q), 34.8 (CH_2), 29.8 (CH_2), 28.3 (CH_3), 27.9 (CH_3), 26.6 (CH_2), 18.11 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 12.3 (CH), 11.9 (CH).). (3 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019, 1716, 1663, 1215, 908, 752, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1177 (100) $[M+Na]^+$, 1155 (5) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{58}H_{98}N_6NaO_{12}Si_3^+$ $[M+Na]^+$: 1177.6443, found: 1177.6436.

(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-((2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-3-[4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)phenyl]-2-(1,3-dioxoisoindolin-2-yl)propenamide (155da)



The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**153da**) (74 mg, 0.10 mmol) and 1-iodo glycal **59** (110 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 1:1) yielded **155da** (111 mg, 84%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 – 7.60 (m, 4H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.41 (s, 1H), 7.35 – 7.28 (m, 3H), 7.20 (dd, *J* = 6.8, 2.7 Hz, 2H), 7.05 – 6.93 (m, 3H), 5.82 (s, 2H), 5.46 (d, *J* = 11.7 Hz, 1H), 5.41 (s, 2H), 5.01 (d, *J* = 5.0 Hz, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.40 (t, *J* = 7.1 Hz, 1H), 4.25 – 4.21 (m, 1H), 4.16 (t, *J* = 10.5, 7.1 Hz, 1H), 4.03 (d, *J* = 5.0 Hz, 1H), 3.93 (t, *J* = 10.5, 7.1 Hz, 1H), 2.48 (s, 6H), 1.75 (s, 3H), 1.71 (s, 3H), 1.11 – 1.05 (m, 42H), 1.02 – 0.98 (m, 21H), 0.86 (s, 6H).

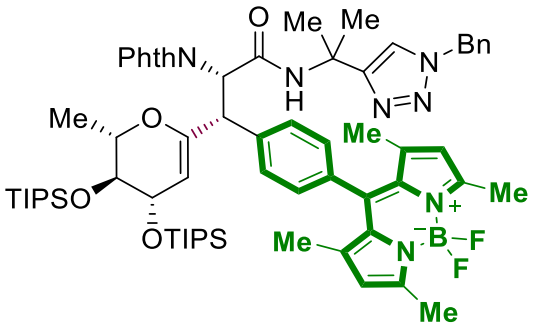
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 155.2 (C_q), 153.0 (C_q), 151.0 (C_q), 142.8 (C_q), 141.5 (C_q), 140.4 (C_q), 134.9 (C_q), 134.0 (CH), 133.6 (C_q), 131.3 (C_q), 131.2 (C_q), 129.2 (CH), 128.9 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 123.4 (CH), 121.0 (CH), 120.7 (CH), 99.8 (CH), 80.9 (CH), 69.6 (CH), 66.8 (CH), 61.0 (CH_2), 56.0 (CH), 53.9 (CH_2), 52.0 (C_q), 49.2 (CH), 28.5 (CH_3), 27.9 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1(CH_3), 14.5 (CH_3), 13.9 (CH_3), 12.5 (CH), 12.4 (CH), 12.1 (CH). (2 CH_3 resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

^{19}F NMR (282 MHz, $CDCl_3$): δ = -146.41 (dd, $J_{B\text{-}F}$ = 68.8, 32.4 Hz).

IR (ATR): $\tilde{\nu}$ = 2946, 1717, 1544, 1510, 1382, 1214, 984, 883, 751, 668 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1374 (100) $[M+Na]^+$, 1352 (55) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{75}H_{108}BF_2N_7NaO_7Si_3^+$ $[M+Na]^+$: 1374.7584, found: 1374.7546.

(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-

yl)phenyl]-2-(1,3-dioxoisoindolin-2-yl)-3-{(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl}propenamide (155db)



The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**153da**) (37 mg, 0.05 mmol) and 1-iodo glycal **154a** (43 mg, 0.08 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 1:1) yielded **155db** (55 mg, 93%, d.r. > 20:1).

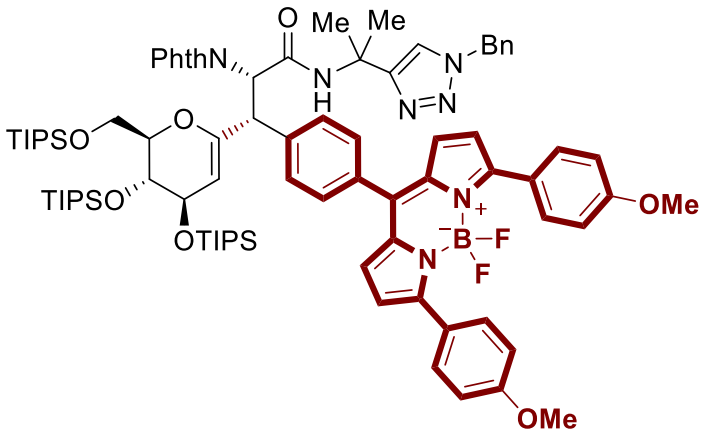
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 – 7.68 (m, 1H), 7.68 – 7.58 (m, 3H), 7.57 – 7.47 (m, 1H), 7.43 (d, J = 7.7 Hz, 2H), 7.37 – 7.25 (m, 5H), 7.19 (s, 1H), 7.02 (d, J = 7.7 Hz, 2H), 5.80 (s, 2H), 5.58 (d, J = 11.2 Hz, 1H), 5.45 (s, 2H), 5.29 (d, J = 4.3 Hz, 1H), 4.59 (d, J = 11.2 Hz, 1H), 4.50 (d, J = 7.4 Hz, 1H), 4.12 (d, J = 4.3 Hz, 1H), 3.88 (s, 1H), 2.47 (s, 6H), 1.75 (s, 3H), 1.72 (s, 3H), 1.18 – 0.92 (m, 48H), 0.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.5 (C_q), 166.5 (C_q), 155.3 (C_q), 152.9 (C_q), 150.2 (C_q), 142.7 (C_q), 141.2 (C_q), 139.5 (C_q), 135.0 (C_q), 133.8 (CH), 133.7 (C_q), 131.5 (C_q), 131.2 (C_q), 129.5 (CH), 128.4 (CH), 128.0 (CH), 127.4 (CH), 123.4 (CH), 123.1 (CH), 121.1 (CH), 121.0 (CH), 101.7 (CH), 75.7 (CH), 73.7 (CH), 66.8 (CH), 53.9 (CH_2), 52.7 (CH), 52.50 (C_q), 51.9 (CH), 28.9 (CH_3), 27.6 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 15.0 (CH_3), 14.5 (CH_3), 13.4 (CH_3), 12.5 (CH), 12.4 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

^{19}F NMR (377 MHz, $CDCl_3$): δ = -146.42 (dd, $J_{B\text{-}F}$ = 65.6, 30.6 Hz).

IR (ATR): $\tilde{\nu}$ = 2866, 1715, 1545, 1511, 1214, 983, 883, 751, 668 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1202 (100) $[M+Na]^+$, 1180 (30) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{66}H_{88}BF_2N_7NaO_6Si_2^+$ $[M+Na]^+$ 1202.6299, found: 1202.6285.

(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-3- {4-[5,5-difluoro-3,7-bis(4-methoxyphenyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl]phenyl}-2-(1,3-dioxoisoindolin-2-yl)propenamide (155dc).



The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**153db**) (45 mg, 0.10 mmol) and 1-iodo glycal **59** (55 mg, 0.08 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 1:3) yielded **155dc** (43 mg, 57%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.8 Hz, 4H), 7.68 (dd, J = 5.5, 3.2 Hz, 2H), 7.62 (dd, J = 5.5, 3.0 Hz, 2H), 7.48 (s, 1H), 7.42 (d, J = 8.3 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.26 – 7.23 (m, 2H), 7.19 (d, J = 8.3 Hz, 2H), 6.99 (s, 1H), 6.93 (d, J = 8.8 Hz, 4H), 6.42 (d, J = 4.3 Hz, 2H), 6.18 (d, J = 4.3 Hz, 2H), 5.57 (d, J = 11.4 Hz, 1H), 5.45 (s, 2H), 5.14 (d, J = 5.2 Hz, 1H), 4.64 (d, J = 11.4 Hz, 1H), 4.46 (t, J = 6.5 Hz, 1H), 4.18 (t, J = 1.9 Hz, 1H), 4.11 (d, J = 6.5 Hz, 2H), 4.04 (m, 1H), 3.84 (s, 6H), 1.79 (s, 3H), 1.76 (s, 3H), 1.14 – 1.07 (m, 42H), 1.04 – 0.87 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 160.7 (C_q), 158.0 (C_q), 153.1 (C_q), 150.4 (C_q), 142.1 (C_q), 140.8 (C_q), 136.0 (C_q), 134.9 (C_q), 134.0 (CH), 133.0 (C_q), 131.1 (C_q), 131.01 (C_q), 131.0 (CH), 130.0 (CH), 129.9 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 125.1 (C_q), 123.2 (CH), 120.9 (CH), 120.1 (CH), 113.7 (CH), 99.6 (CH), 81.1 (CH), 69.5 (CH), 66.6 (CH), 61.2 (CH_2), 55.3 (CH_3), 53.9 (CH_2), 52.1 (C_q), 50.2 (CH), 28.5 (CH_3), 28.0 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.05 (CH_3), 18.0 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

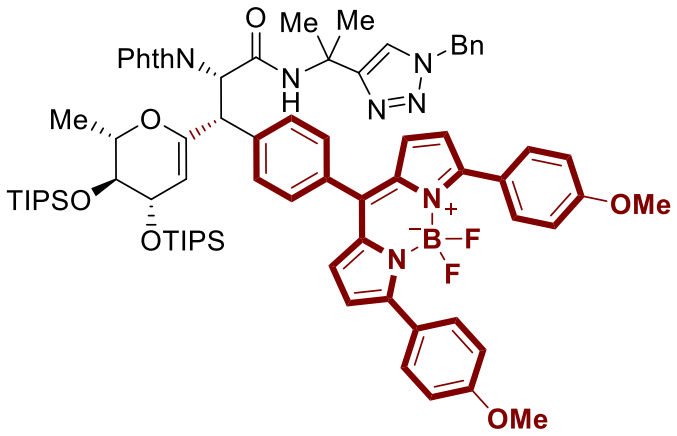
^{19}F NMR (377 MHz, $CDCl_3$): δ = -133.08 (dd, $J_{B\text{-}F}$ = 64.8, 32.1 Hz).

IR (ATR): $\tilde{\nu}$ = 2923, 1717, 1550, 1466, 1214, 1142, 1071, 749, 668 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1530 (100) $[M+Na]^+$, 1508 (40) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{85}H_{112}BF_2N_7NaO_9Si_3^+$ $[M+Na]^+$: 1530.7796, found: 1530.7785.

(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-{4-[5,5-difluoro-3,7-bis(4-methoxyphenyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl]phenyl}-2-(1,3-dioxoisoindolin-2-yl)-3-{(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl}propenamide (155dd)



The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**153db**) (40 mg, 0.045 mmol) and 1-iodo glycal **154a** (38 mg, 0.067 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 1:3) yielded **155dd** (58 mg, 97%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.5 Hz, 4H), 7.73 – 7.67 (m, 2H), 7.67 – 7.60 (m, 2H), 7.56 (s, 1H), 7.46 – 7.22 (m, 9H), 7.09 (s, 1H), 6.93 (d, *J* = 8.5 Hz, 4H), 6.45 (d, *J* = 4.4 Hz, 2H), 6.22 (d, *J* = 4.4 Hz, 2H), 5.54 (d, *J* = 11.2 Hz, 1H), 5.48 (s, 2H), 5.27 (d, *J* = 4.7 Hz, 1H), 4.62 (d, *J* = 11.2 Hz, 1H), 4.46 (d, *J* = 7.4 Hz, 1H), 4.19 (d, *J* = 4.7 Hz, 1H), 3.91 (s, 1H), 3.84 (s, 6H), 1.78 (s, 3H), 1.76 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.10 – 0.98 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.6 (C_q), 166.3 (C_q), 160.7 (C_q), 158.1 (C_q), 153.0 (C_q), 150.5 (C_q), 141.9 (C_q), 140.4 (C_q), 136.0 (C_q), 135.0 (C_q), 134.0 (CH), 133.2 (C_q), 131.3 (C_q), 131.0 (CH), 129.9 (CH), 129.8 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 125.1 (C_q), 123.2 (CH), 121.0 (CH), 120.2 (CH), 113.8 (CH), 100.8 (CH), 75.9 (CH), 73.6 (CH), 67.1 (CH), 55.2 (CH_3), 54.0 (CH_2), 53.6 (CH), 52.4(C_q), 50.9

(CH), 28.72 (CH_3), 27.7 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 15.6 (CH_3), 12.5 (CH), 12.5 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

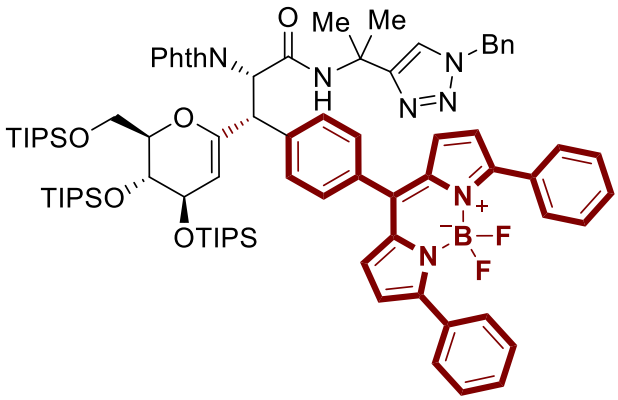
^{19}F NMR (377 MHz, $CDCl_3$): δ = -133.10 (dd, $J_{B\text{-}F}$ = 64.9, 32.3 Hz).

IR (ATR): $\tilde{\nu}$ = 2940, 1715, 1547, 1464, 1255, 1137, 1057, 883, 794, 718, 681 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1358 (100) $[M+Na]^+$, 1336 (35) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{76}H_{92}BF_2N_7NaO_8Si_2^+$ $[M+Na]^+$:1358.6512, found: 1358.6506.

(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-3-[4-(5,5-difluoro-3,7-diphenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)phenyl]-2-(1,3-dioxoisoindolin-2-yl)propenamide (155de)



The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**153dc**) (56 mg, 0.067 mmol) and 1-iodo glycal **59** (74 mg, 0.10 mmol). After 10 h, purification by column chromatography (n-hexane/EtOAc 1:1) yielded **155de** (70 mg, 72%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 – 7.78 (m, 4H), 7.72 – 7.67 (m, 2H), 7.66 – 7.60 (m, 2H), 7.49 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.42 – 7.37 (m, 7H), 7.35 – 7.30 (m, 3H), 7.26 – 7.19 (m, 3H), 7.01 (s, 1H), 6.46 (d, *J* = 4.3 Hz, 2H), 6.25 (d, *J* = 4.3 Hz, 2H), 5.60 (d, *J* = 11.3 Hz, 1H), 5.45 (s, 2H), 5.17 (d, *J* = 5.2 Hz, 1H), 4.67 (d, *J* = 11.3 Hz, 1H), 4.48 (d, *J* = 6.7 Hz, 1H), 4.19 (s, 1H), 4.13 (d, *J* = 6.7 Hz, 2H), 4.06 (d, *J* = 5.2 Hz, 1H), 1.81 (s, 3H), 1.77 (s, 3H), 1.19 – 1.05 (m, 42H), 0.98 – 0.91 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.6 (C_q), 166.0 (C_q), 158.6 (C_q), 153.1 (C_q), 150.4 (C_q), 143.8 (C_q), 141.1 (C_q), 136.1 (C_q), 134.9 (C_q), 134.0 (CH), 132.8 (C_q), 132.5 (C_q), 131.1 (C_q), 130.3 (CH), 130.0 (CH), 129.4 (CH), 129.4 (CH), 129.3 (CH), 128.9 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 123.2 (CH), 120.9 (CH), 120.5 (CH), 99.6 (CH), 81.1 (CH), 69.4 (CH), 66.6 (CH), 61.2 (CH_2), 55.2 (CH), 53.9 (CH_2), 52.1 (C_q), 50.2 (CH), 28.5 (CH_3), 28.0 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.03 (CH_3), 18.0 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

^{19}F NMR (377 MHz, $CDCl_3$): δ = -132.60 (dd, $J_{B\text{-}F}$ = 63.9, 32.1 Hz).

IR (ATR): $\tilde{\nu}$ = 2941, 1717, 1546, 1467, 1274, 1068, 998, 882,718, 683 cm^{-1}.

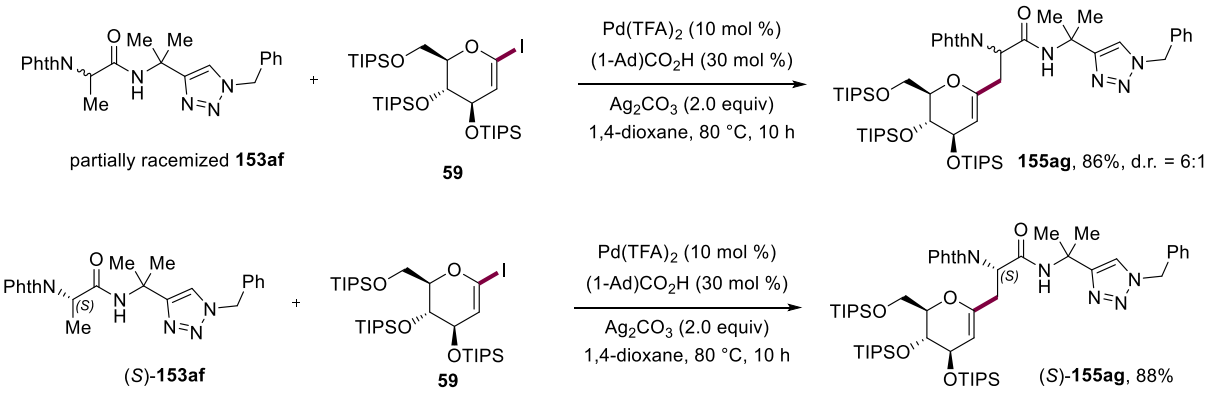
MS (ESI) *m/z* (relative intensity): 1470 (100) $[M+Na]^+$, 1448 (50) $[M+H]^+$.

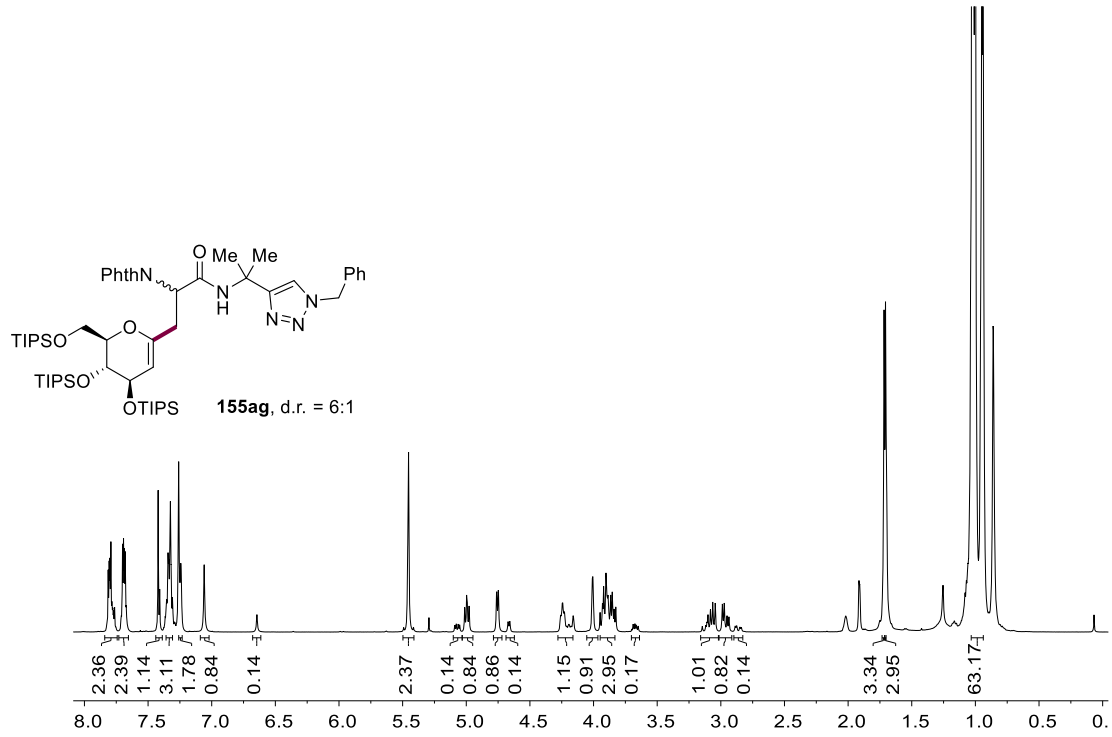
HR-MS (ESI): *m/z* calcd for $C_{83}H_{109}BF_2N_7O_7Si_3^+$ $[M+H]^+$: 1448.7765, found: 1448.7748.

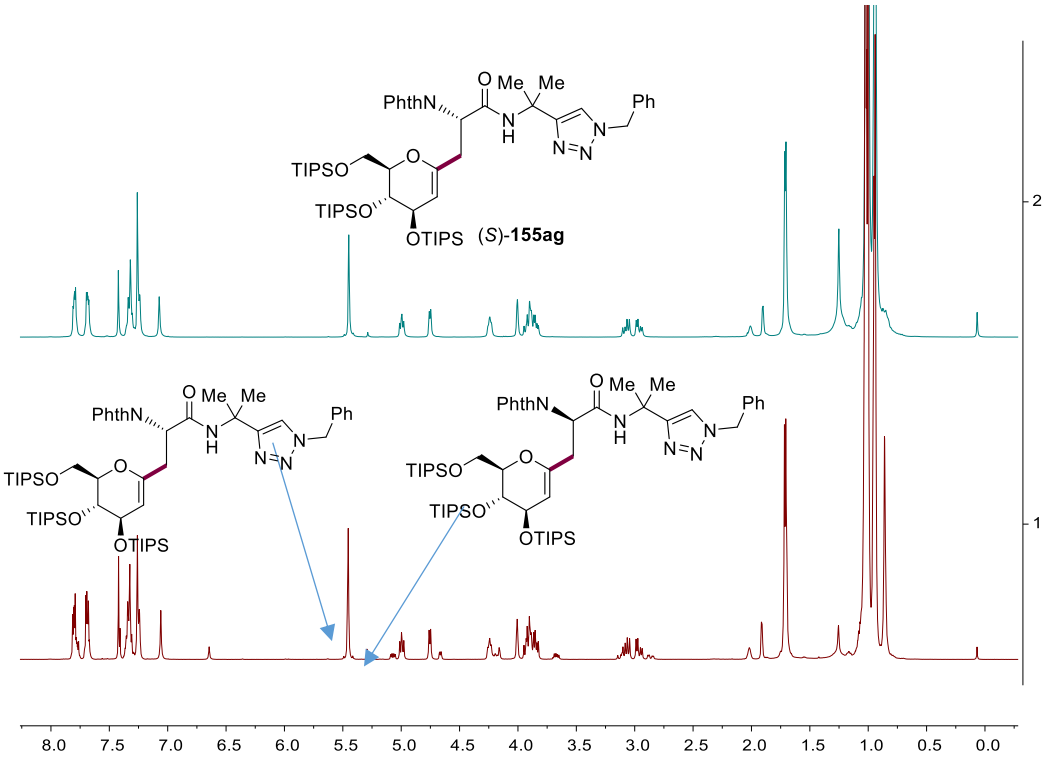
5.3.1.2 Mechanism Studies.

5.3.1.2.1 Studies on Potential Racemization

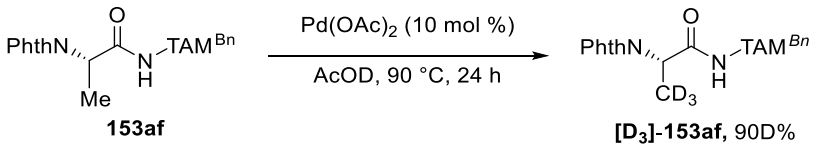
Substrates (*S*)-**153af**, partially racemized **153af** were subjected to the C–H glycosylation reaction under the optimized reaction conditions. ^{1}H NMR analysis of the obtained products showed that no racemization occurred during the C–H glycosylation process.







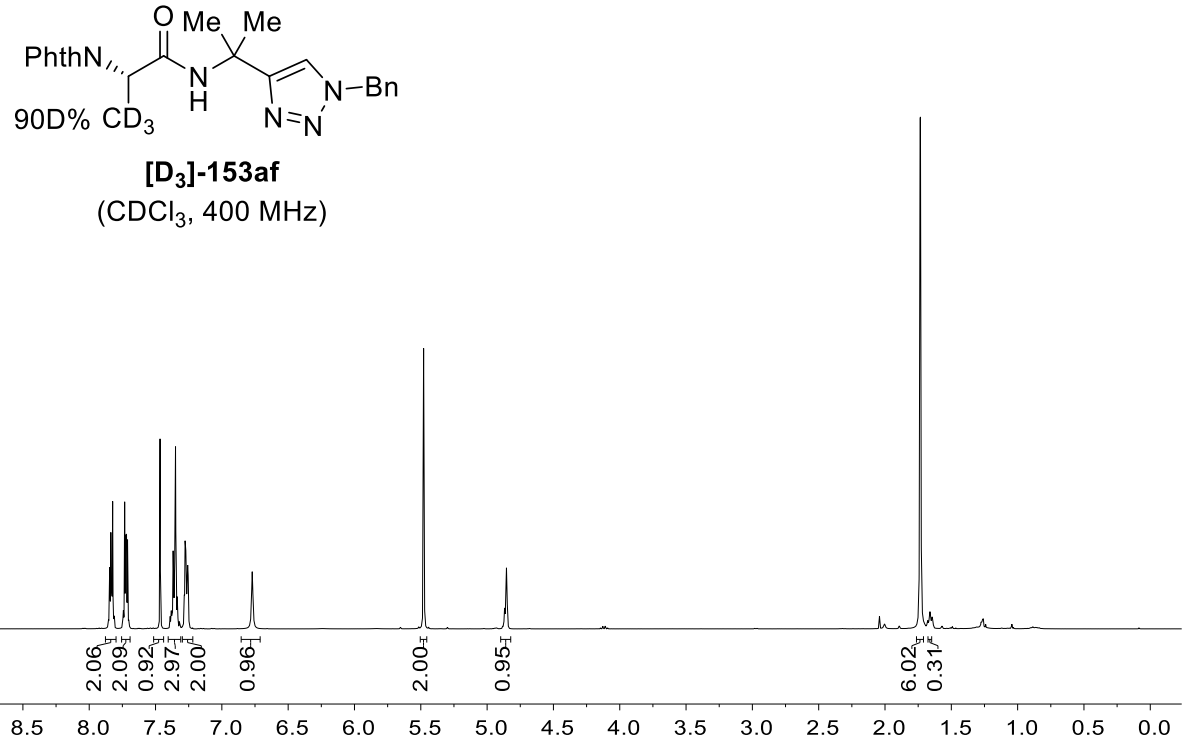
5.3.1.2.2 H/D Exchange

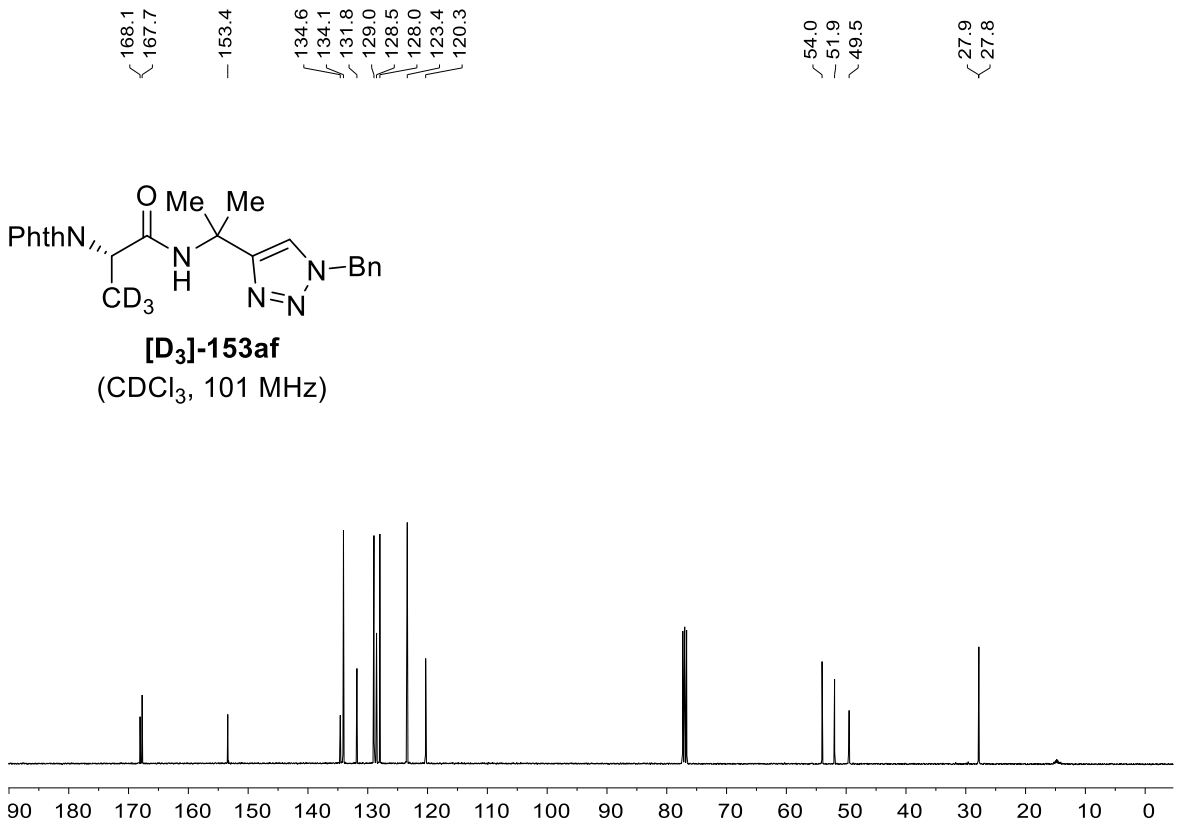


A solution of alanine substrate **153af** (417 mg, 1.0 mmol) and $Pd(OAc)_2$ (22 mg, 10 mol %) in deuterated acetic acid (AcOD) (3.0 mL) was stirred at 90 ºC for 24 h. Then, the reaction was filtrated and concentrated. This procedure was repeated twice. The product was purified by column chromatography (*n*-hexane/EtOAc 1:1), yielding deuterated alanine substrate **[D]-153af** in 94% yield with 90D%. The deuterium incorporation was determined by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.47 (s, 1H), 7.40 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 6.77 (s, 1H), 5.48 (s, 2H), 4.85 (s, 1H), 1.73 (s, 6H).

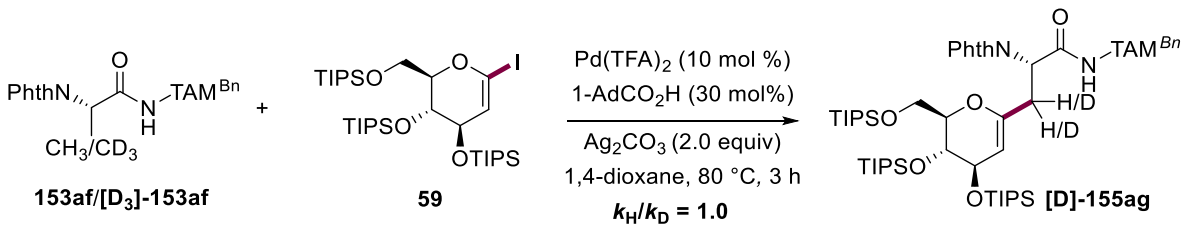
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.1 (C_q), 167.7 (C_q), 153.4 (C_q), 134.6 (C_q), 134.1 (CH), 131.8 (C_q), 129.0 (CH), 128.5 (CH), 128.0 (CH), 123.4 (CH), 120.3 (CH), 54.0 (CH_2), 51.9 (C_q), 49.5 (CH), 27.9 (CH_3), 27.8 (CH_3).





[D$_3$]-153af
(CDCl$_3$, 101 MHz)

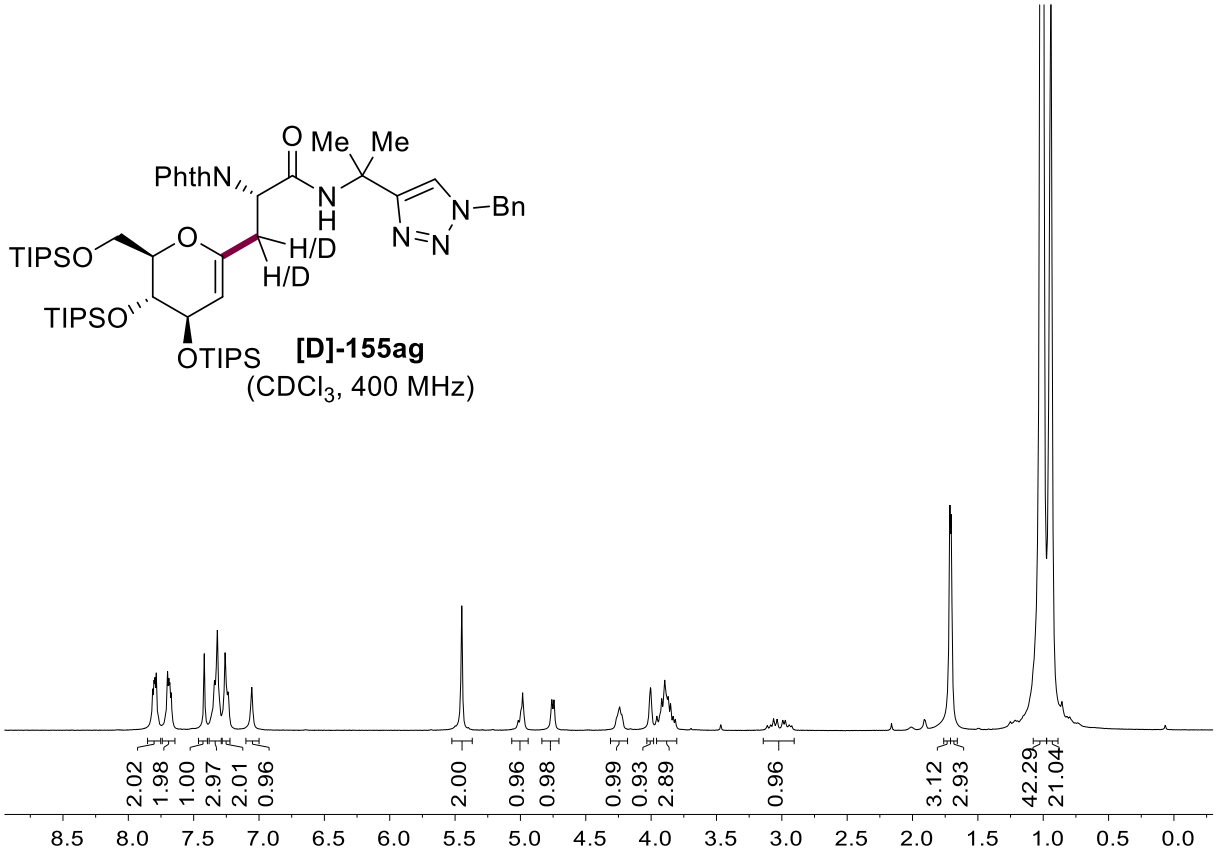
5.3.1.2.3 Kinetic Isotope Effect



Deuterated substrate **[D$_3$]-1f** (21 mg, 0.05 mmol) and non-deuterated substrate **1f** (21 mg, 0.05 mmol), Pd(OAc)$_2$ (2.2 mg, 10 mol %), Ag$_2$CO$_3$ (55 mg, 0.1 mmol), and (1-Ad)CO$_2$H (5.4 mg, 30 mol %) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, a solution of 1-iodo glycal **2a** (110 mg, 0.15 mmol) in 1,4-dioxane (0.5 mL) was added. The resulting reaction mixture was stirred at 80 ºC for 3 h. After cooling to ambient temperature, the mixture was diluted with CH_2Cl_2 (10 mL) and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel isolated the product **10** in 87%yield. A k_H/k_D = 1.0 was determined by ^{1}H NMR spectroscopy.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.80 (dd, J = 5.5, 3.1 Hz, 2H), 7.69 (dd, J = 5.5, 3.1 Hz, 2H), 7.42 (s, 1H), 7.37 – 7.28 (m, 3H), 7.28 – 7.21 (m, 2H), 7.06 (s, 1H), 5.45 (s,

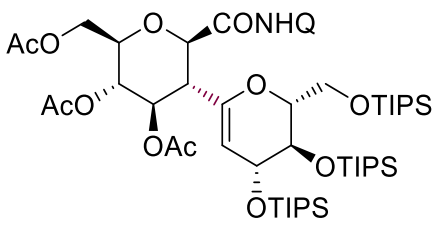
2H), 5.01 – 4.95 (m, 1H), 4.75 (d, *J* = 5.2 Hz, 1H), 4.24 (t, *J* = 5.4 Hz, 1H), 4.11 – 3.96 (m, 1H), 3.98 – 3.76 (m, 3H), 3.14 – 2.89 (m, 1H), 1.71 (s, 3H), 1.70 (s, 3H), 1.01 (m, 42H), 0.94 (m, 21H).



5.3.2 Palladium-Catalyzed C(sp^3)−H Glycosylation of Glycosides.

5.3.2.1 Characterization Data

(2*R*,3*S*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-5-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (159aa)



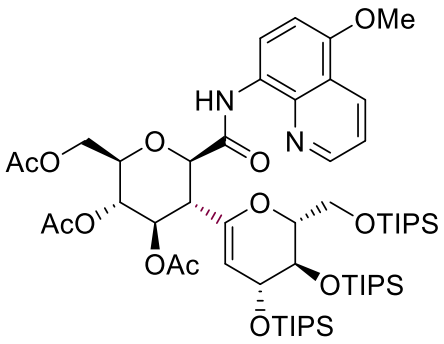
The general procedure **D** was followed using (2*R*,3*S*,4*R,6R*)-2-(acetoxymethyl)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (**158aa**) (22.2 mg, 0.05 mmol), 1-iodo-glucal (**59**) (55.0 mg, 0.075 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159aa** (38.7 mg, 73%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.15 (s, 1H), 9.05 – 8.56 (m, 2H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.38 (m, 3H), 5.52 (t, *J* = 10.7, 9.7 Hz, 1H), 5.11 (t, *J* = 9.7 Hz, 1H), 4.86 (d, *J* = 4.9 Hz, 1H), 4.42 – 4.25 (m, 2H), 4.27 – 4.15 (m, 3H), 4.05 (t, *J* = 9.7 Hz, 1H), 3.96 (d, *J* = 4.9 Hz, 1H), 3.92 – 3.82 (m, 1H), 3.62 (dd, *J* = 9.7, 4.9 Hz, 1H), 3.00 (t, *J* = 10.7 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 1.95 (s, 3H), 1.09 – 0.92 (m, 42H), 0.89 – 0.78 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.8 (C_q), 170.0 (C_q), 169.8 (C_q), 164.8 (C_q), 148.1 (CH), 146.0 (C_q), 138.6 (C_q), 136.2 (CH), 134.2 (C_q), 127.9 (C_q), 127.2 (CH), 121.7 (CH), 121.5 (CH), 117.0 (CH), 101.8 (CH), 80.0 (CH), 79.2 (CH), 75.6 (CH), 71.6 (CH), 69.7 (CH), 69.0 (CH), 66.4 (CH), 62.5 (CH_2), 60.7 (CH_2), 49.2 (CH), 20.8 (CH_3), 20.8 (CH_3), 20.7 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.4 (CH), 12.4 (CH), 11.9 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1751, 1531, 1422, 1264, 896, 733, 702 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1079 (100) $[M+Na]^+$, 1057 (60) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{55}H_{92}N_2NaO_{12}Si_3^+$ $[M+Na]^+$ 1079.5850, found 1079.5833.

(2*R*,3*S*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-5-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-6-[(5-methoxyquinolin-8-yl)carbamoyl]tetrahydro-2*H*-pyran-3,4-diyl diacetate (159ab)



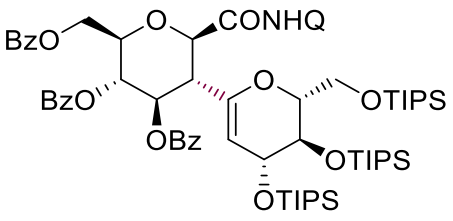
The general procedure **D** was followed using (2*R*,3*S*,4*R,6R*)-2-(acetoxymethyl)-6-[(5-methoxyquinolin-8-yl)carbamoyl]tetrahydro-2*H*-pyran-3,4-diyl diacetate (**158aa**) (47.4 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159ab** (82.3 mg, 76%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.89 (s, 1H), 8.81 (t, *J* = 4.3, 1.7 Hz, 1H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.56 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.43 (dd, *J* = 8.4, 4.3 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 5.52 (t, *J* = 10.1, 9.6 Hz, 1H), 5.10 (t, *J* = 9.6 Hz, 1H), 4.87 (d, *J* = 5.1 Hz, 1H), 4.40 – 4.25 (m, 2H), 4.22 – 4.12 (m, 3H), 4.05 (t, *J* = 9.6 Hz, 1H), 3.98 (s, 3H), 3.97 – 3.94 (m, 1H), 3.86 (dt, *J* = 9.6, 5.0, 2.3 Hz, 1H), 3.61 (dd, *J* = 9.6, 4.9 Hz, 1H), 3.02 (t, *J* = 10.7, 10.1 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.08 – 0.95 (m, 42H), 0.84 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.8 (C_q), 170.0 (C_q), 169.8 (C_q), 164.3 (C_q), 150.4 (C_q), 148.5 (CH), 146.1 (C_q), 139.3 (C_q), 131.1 (CH), 127.7 (C_q), 120.6 (CH), 120.3 (C_q), 117.1 (CH), 104.2 (CH), 101.8 (CH), 80.0 (CH), 79.3 (CH), 75.6 (CH), 71.6 (CH), 69.8 (CH), 69.0 (CH), 66.4 (CH), 62.5 (CH_2), 60.6 (CH_2), 55.7 (CH_3), 49.1 (CH), 20.8 (CH_3), 20.8 (CH_3), 20.7 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.4 (CH), 11.9 (CH). (1 CH resonance of TIPS group is overlapped).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1752, 1699, 1531, 1241, 1091, 881, 736, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1109 (100) $[M+Na]^+$, 1087 (20) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{56}H_{94}N_2NaO_{13}Si_3^+$ $[M+Na]^+$ 1109.5956, found 1109.5987.

(2*R*,3*S*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-5-((2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy)]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl dibenzoate (159ba)



The general procedure **D** was followed using (2*R*,3*S*,4*R,6R*)-2-[(benzoyloxy)methyl)]6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl dibenzoate (**158ba**) (63.0 mg, 0.10 mmol), 1--iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159ba** (76.0 mg, 61%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.33 (s, 1H), 8.79 (t, *J* = 4.5 Hz, 1H), 8.60 (d, *J* = 3.9 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.88 (t, *J* = 6.9 Hz, 4H), 7.54 – 7.44 (m, 4H), 7.43 – 7.37 (m, 2H), 7.37 – 7.32 (m, 3H), 7.31 – 7.23 (m, 3H), 6.08 (t, *J* = 10.2, 9.7 Hz, 1H), 5.63 (t, *J* = 9.7 Hz, 1H), 4.94 (d, *J* = 5.1 Hz, 1H), 4.65 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.59 (d, *J* = 10.7 Hz, 1H), 4.51 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.30 – 4.21 (m, 2H), 4.20 – 4.14 (m, 1H), 4.05 – 3.93 (m, 2H), 3.70 (dd, *J* = 9.9, 5.2 Hz, 1H), 3.28 (t, *J* = 10.7, 10.2 Hz, 1H), 1.17 – 0.96 (m, 21H), 0.90 – 0.80 (m, 42H).

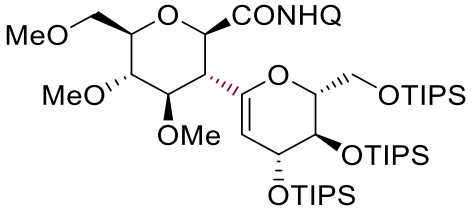
^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2 (C_q), 165.6 (C_q), 165.2 (C_q), 165.0 (C_q), 148.2 (CH), 146.1 (C_q), 138.6 (C_q), 136.1 (CH), 134.3 (C_q), 133.1 (CH), 132.9 (CH), 132.7 (CH), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.4 (C_q), 129.1 (C_q), 128.2 (CH), 128.0 (CH), 127.8 (C_q), 127.2 (CH), 121.6 (CH), 121.4 (CH), 116.9 (CH), 101.8 (CH), 80.3 (CH), 79.4 (CH), 76.0 (CH), 71.6 (CH), 71.0 (CH), 69.1 (CH), 66.4 (CH), 63.6 (CH_2), 60.8 (CH_2), 49.7 (CH), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.4 (CH), 12.2 (CH), 11.9 (CH). (2 CH_3 resonances of TIPS, 1 C_q and 1 CH group are overlapped).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1730, 1530, 1451, 1267, 1091, 1068, 882, 754, 707, 682 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 2486 (100) $[2M+Na]^+$, 1265 (10) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{70}H_{98}N_2NaO_{12}Si_3^+$ $[M+Na]^+$ 1265.6320, found 1265.6285.

(2*R*,3*R*,4*R*,5*S*,6*R*)-3-((2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy)-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4,5-dimethoxy-6-(methoxymethyl)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamid (159bb)



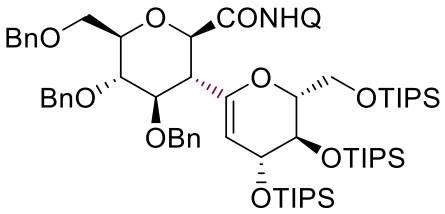
The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4,5-dimethoxy-6-(methoxymethyl)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158bb**) (36.0 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159bb** (87.5 mg, 90%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.24 (s, 1H), 8.75 (t, *J* = 4.5 Hz, 2H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.46 (d, *J* = 4.5 Hz, 2H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.88 (d, *J* = 4.9 Hz, 1H), 4.34 – 4.18 (m, 2H), 4.04 – 3.97 (m, 2H), 3.75 – 3.67 (m, 4H), 3.66 – 3.61 (m, 1H), 3.60 (s, 3H), 3.58 (s, 3H), 3.49 (m, 4H), 3.26 (t, *J* = 9.3 Hz, 1H), 2.68 (t, *J* = 10.4 Hz, 1H), 1.15 – 1.00 (m, 42H), 0.97 – 0.84 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1 (C_q), 148.5 (C_q), 147.9 (CH), 138.6 (C_q), 136.0 (CH), 134.5 (C_q), 127.8 (C_q), 127.2 (CH), 121.3 (CH), 121.3 (CH), 116.8 (CH), 100.7 (CH), 83.2 (CH), 81.0 (CH), 80.6 (CH), 79.3 (CH), 78.9 (CH), 71.8 (CH_2), 69.8 (CH), 67.1 (CH_2), 67.0 (CH), 60.5 (CH_3), 60.3 (CH_3), 59.7 (CH_3), 50.9 (CH), 18.2 (CH_3), 18.2 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.5 (CH), 12.5 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1704, 1526, 1462, 1387, 1122, 883, 755, 682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1968 (100) $[2M+Na]^+$, 995 (20) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{92}N_2NaO_9Si_3^+$ $[M+Na]^+$ 995.6003, found 995.5987.

(2*R*,3*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159bc)



The general procedure **D** was followed using (2*R*,4*R*,5S,6*R*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158bc**) (58.8 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0

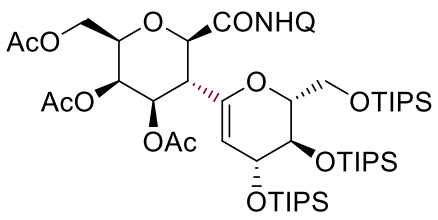
mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159bc** (77.0 mg, 64%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.34 (s, 1H), 8.79 (dd, *J* = 5.4, 3.6 Hz, 1H), 8.63 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.43 – 7.35 (m, 3H), 7.33 – 7.28 (m, 4H), 7.26 – 7.21 (m, 7H), 7.16 (dd, *J* = 7.1, 2.6 Hz, 2H), 5.01 (d, *J* = 11.1 Hz, 1H), 4.95 (d, *J* = 4.3 Hz, 1H), 4.77 (dd, *J* = 11.1, 6.7 Hz, 3H), 4.65 (d, *J* = 12.6 Hz, 1H), 4.60 (d, *J* = 11.1 Hz, 1H), 4.33 (d, *J* = 10.5 Hz, 1H), 4.31 – 4.26 (m, 1H), 4.13 (dd, *J* = 10.2, 9.2 Hz, 1H), 4.09 – 4.06 (m, 3H), 4.01 (dd, *J* = 10.9, 6.8 Hz, 1H), 3.85 (d, *J* = 2.9 Hz, 2H), 3.75 (t, *J* = 9.2 Hz, 1H), 3.67 (dt, *J* = 9.9, 3.0 Hz, 1H), 2.92 (t, *J* = 10.5 Hz, 1H), 1.06 – 1.02 (m, 21H), 1.01 – 0.97 (m, 21H), 0.96 – 0.91 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.3 (C_q), 148.7 (C_q), 148.1 (CH), 139.0 (C_q), 138.7 (C_q), 138.6 (C_q), 138.5 (C_q), 136.0 (CH), 134.6 (C_q), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.9 (C_q), 127.8 (CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 127.4 (CH), 127.2 (CH), 127.1 (CH), 121.4 (CH), 121.3 (CH), 116.8 (CH), 101.0 (CH), 81.6 (CH), 81.1 (CH), 79.4 (CH), 79.3 (CH), 78.6 (CH), 74.7 (CH_2), 74.5 (CH_2), 73.8 (CH_2), 70.0 (CH), 69.4 (CH_2), 67.4 (CH), 61.9 (CH_2), 51.4 (CH), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.6 (CH), 12.5 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1705, 1526, 1463, 1385, 1086, 882, 753, 682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2402 (35) $[2M+Na]^+$, 1201 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{70}H_{105}N_2O_9Si_3^+$ $[M+H]^+$ 1201.7122, found 1201.7121.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-5-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (159bd)



The general procedure **D** was followed using (2*R*,3*R*,4*R,6R*)-2-(acetoxymethyl)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (**158bd**) (44.4 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O

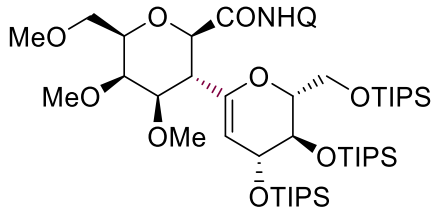
(46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159bd** (87.0 mg, 82%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.20 (s, 1H), 8.81 (d, *J* = 4.2 Hz, 1H), 8.77 (t, *J* = 4.5 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 4.5 Hz, 2H), 7.44 (t, *J* = 8.2, 4.2 Hz, 1H), 5.45 (d, *J* = 3.2 Hz, 1H), 5.36 (dd, *J* = 11.4, 3.2 Hz, 1H), 4.89 (d, *J* = 5.0 Hz, 1H), 4.42 (d, *J* = 10.4 Hz, 1H), 4.26 – 4.13 (m, 4H), 4.11 – 4.02 (m, 2H), 4.00 – 3.96 (m, 2H), 3.61 (dd, *J* = 9.9, 5.2 Hz, 1H), 3.11 (t, *J* = 11.4, 10.4 Hz, 1H), 2.17 (s, 3H), 2.05 (s, 3H), 1.92 (s, 3H), 1.10 – 0.94 (m, 42H), 0.97 – 0.77 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.5 (C_q), 170.4 (C_q), 169.8 (C_q), 165.1 (C_q), 148.1 (CH), 146.7 (C_q), 138.6 (C_q), 136.2 (CH), 134.3 (C_q), 127.8 (C_q), 127.2 (CH), 121.6 (CH), 121.5 (CH), 116.9 (CH), 101.9 (CH), 80.2 (CH), 79.0 (CH), 74.2 (CH), 69.8 (CH), 69.3 (CH), 66.3 (CH), 66.0 (CH), 62.2 (CH_2), 61.0 (CH_2), 43.6 (CH), 20.8 (CH_3), 20.7 (CH_3), 20.6 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.4 (CH), 12.3 (CH), 11.9 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1712, 1526, 1422, 1264, 1122, 895, 735, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2136 (100) $[2M+Na]^+$, 1079 (30) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{55}H_{92}N_2NaO_{12}Si_3^+$ $[M+Na]^+$ 1079.5850, found 1079.5832.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4,5-dimethoxy-6-(methoxymethyl)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159ca)



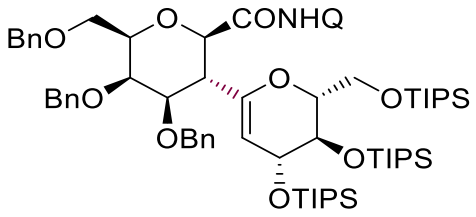
The general procedure **D** was followed using (2*R*,4*R*,5*R*,6*R*)-4,5-dimethoxy-6-(methoxymethyl)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158ca**) (36.0 mg, 0.10- mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159ca** (92.0 mg, 95%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.22 (s, 1H), 9.05 – 8.54 (m, 2H), 8.11 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.89 (dd, *J* = 4.8, 1.5 Hz, 1H), 4.35 (d, *J* = 10.6 Hz, 1H), 4.22 (td, *J* = 5.0, 2.5 Hz, 1H), 4.06 – 3.96 (m, 3H), 3.93 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.75 – 3.62 (m, 5H), 3.60 (s, 3H), 3.45 (s, 6H), 2.99 (t, *J* = 10.6 Hz, 1H), 1.07 – 0.95 (m, 42H), 0.95 – 0.86 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1 (C_q), 148.7 (C_q), 147.9 (CH), 138.7 (C_q), 136.0 (CH), 134.7 (C_q), 127.8 (C_q), 127.3 (CH), 121.3 (CH), 121.1 (CH), 116.8 (CH), 101.1 (CH), 81.1 (CH), 80.5 (CH), 78.7 (CH), 77.3 (CH), 72.8 (CH), 71.7 (CH_2), 70.1 (CH), 66.8 (CH), 62.1 (CH_2), 61.0 (CH_3), 59.3 (CH_3), 57.0 (CH_3), 45.3 (CH), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.5 (CH), 12.4 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1705, 1526, 1461, 1122, 1098, 882, 756, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1968 (100) $[2M+Na]^+$, 995 (80) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{92}N_2NaO_9Si_3^+$ $[M+Na]^+$ 995.6003, found 995.5999.

(2*R*,3*R*,4*R*,5*R*,6*R*)-4,5-Bis(benzyloxy)-6-[(benzyloxy)methyl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159cb)



The general procedure **D** was followed using (2*R*,4*R*,5*R*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158cb**) (58.8 mg, 0.10 -mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159cb** (108 mg, 90%) as a syrup.

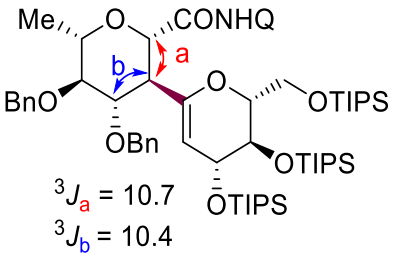
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.34 (s, 1H), 8.77 (dd, *J* = 6.6, 2.4 Hz, 1H), 8.71 (d, *J* = 3.9 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.32 – 7.28 (m, 7H), 7.28 – 7.22 (m, 5H), 4.98 – 4.87 (m, 2H), 4.80 (d, *J* -= 11.8 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.60 – 4.52 (m, 2H), 4.48

(d, *J* = 11.8 Hz, 1H), 4.36 (d, *J* = 10.4 Hz, 1H), 4.30 – 4.23 (m, 1H), 4.13 – 3.89 (m, 6H), 3.89 – 3.59 (m, 3H), 3.25 (t, *J* = 10.4 Hz, 1H), 1.09 – 0.92 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 166.4 (C_q), 148.9 (C_q), 148.0 (CH), 139.2 (C_q), 138.7 (C_q), 138.7 (C_q), 138.1 (C_q), 136.0 (CH), 134.7 (C_q), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (C_q), 127.6 (CH), 127.6 (CH), 127.2 (CH), 127.1 (CH), 127.1 (CH), 127.1 (CH), 121.3 (CH), 121.1 (CH), 116.7 (CH), 101.5 (CH), 81.1 (CH), 79.4 (CH), 79.2 (CH), 77.4 (CH), 74.0 (CH_2), 73.6 (CH_2), 71.7 (CH), 71.6 (CH_2), 70.4 (CH), 69.9 (CH_2), 67.5 (CH), 62.2 (CH_2), 45.9 (CH), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 12.6 (CH), 12.6 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1703, 1529, 1463, 1387, 1094, 883, 755, 682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2402 (100) $[2M+H]^+$, 1223 (50) $[M+Na]^+$, 1201 (30) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{70}H_{104}N_2NaO_9Si_3^+$ $[M+Na]^+$ 1223.6942, found 1223.6915.

(2*S*,3*S*,4*S*,5*S*,6*S*)-4,5-Bis(benzyloxy)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-6-methyl-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159d)



The general procedure **D** was followed using (2*S*,4*S*,5*S*,6*S*)-4,5-bis(benzyloxy)-6-methyl-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158d**) (48.2 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159d** (70.0 mg, 64%) as a syrup.

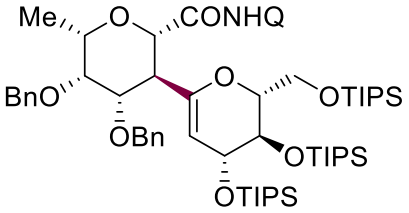
^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 10.36 (s, 1H), 8.80 (ddd, *J* = 9.0, 4.7, 2.8 Hz, 2H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.39 – 7.29 (m, 7H), 7.28 – 7.23 (m, 3H), 5.03 – 4.95 (m, 2H), 4.90 (d, *J* = 11.0 Hz, 1H), 4.65 (d, *J* = 11.0 Hz, 1H), 4.56 (d, *J* = 9.9 Hz, 1H), 4.38 (d, *J* = 10.7 Hz, 1H), 4.35 – 4.28

(m, 1H), 4.27 (d, *J* = 1.6 Hz, 1H), 4.21 (dd, *J* = 10.4, 8.2 Hz, 1H), 4.15 (dd, *J* = 4.5, 1.9 Hz, 1H), 4.09 – 4.03 (m, 1H), 4.03 – 3.97 (m, 1H), 3.59 (dq, *J* = 9.5, 6.1 Hz, 1H), 3.26 (t, *J* = 9.1 Hz, 1H), 2.69 (t, *J* = 10.4 Hz, 1H), 1.42 (d, *J* = 6.1 Hz, 3H), 1.06 – 0.90 (m, 63H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 166.6 (C_q), 148.2 (CH), 148.0 (C_q), 138.8 (C_q), 138.7 (C_q), 138.6 (C_q), 136.0 (CH), 134.6 (C_q), 128.6 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.8 (C_q), 127.6 (CH), 127.5 (CH), 127.2 (CH), 121.3 (CH), 121.1 (CH), 116.7 (CH), 102.1 (CH), 83.9 (CH), 81.0 (CH), 80.8 (CH), 78.6 (CH), 75.4 (CH_2), 75.3 (CH_2), 75.3 (CH), 70.7 (CH), 67.0 (CH), 61.4 (CH_2), 53.1 (CH), 18.5 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.4 (CH), 12.4 (CH), 11.9 (CH).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1702, 1526, 1488, 1463, 1384, 1096, 883, 754, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2190 (100) $[2M+H]^+$, 1117 (45) $[M+Na]^+$, 1095 (15) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{64}H_{99}NNaO_8Si_3^+$ $[M+Na]^+$ 1117.6523, found 1117.6517.

(2*S*,3*S*,4*S*,5*R*,6*S*)-4,5-Bis(benzyloxy)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2H-pyran-6-yl]-6-methyl-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159e)



The general procedure **D** was followed using (2*S*,4*S*,5*R*,6*S*)-4,5-bis(benzyloxy)-6-methyl-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158e**) (48.2 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159e** (87.5 mg, 80%) as a syrup.

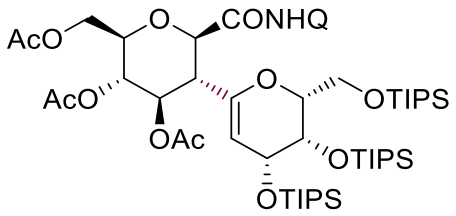
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 10.54 (s, 1H), 8.78 (dd, *J* = 6.0, 3.1 Hz, 2H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.43 – 7.37 (m, 5H), 7.38 – 7.26 (m, 5H), 7.26 – 7.20 (m, 1H), 5.03 (d, *J* = 12.2 Hz, 1H), 4.92 (d, *J* = 4.7 Hz, 1H), 4.86 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.33 (d, *J* = 10.8 Hz, 2H), 4.28 – 4.20 (m, 2H), 4.14 (dd, *J* = 10.5, 5.7 Hz, 1H), 4.09 (d, *J* = 4.7 Hz, 1H), 3.93 (dd,

J = 10.6, 2.7 Hz, 1H), 3.60 (q, *J* = 6.3 Hz, 1H), 3.42 (d, *J* = 2.7 Hz, 1H), 2.95 (t, *J* = 10.6 Hz, 1H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.12 – 0.93 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9 (C_q), 148.4 (C_q), 148.1 (CH), 139.4 (C_q), 139.2 (C_q), 138.9 (C_q), 135.9 (CH), 134.8 (C_q), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.8 (C_q), 127.7 (CH), 127.4 (CH), 127.2 (CH), 127.0 (CH), 121.2 (CH), 120.8 (CH), 116.6 (CH), 102.3 (CH), 81.0 (CH), 78.8 (CH), 78.5 (CH), 76.4 (CH), 74.4 (CH_2), 74.1 (CH), 73.5 (CH_2), 70.8 (CH), 66.9 (CH), 61.8 (CH_2), 47.0 (CH), 18.3 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.6 (CH_3), 12.5 (CH), 12.4 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1696, 1526, 1488, 1463, 1096, 883, 754, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2190 (100) $[2M+H]^+$, 1095 (30) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{64}H_{100}NO_8Si_3^+$ $[M+H]^+$ 1095.6704, found 1095.6693.

(2*R*,3*S*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-5-[(2*R*,3*S*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (159fa)



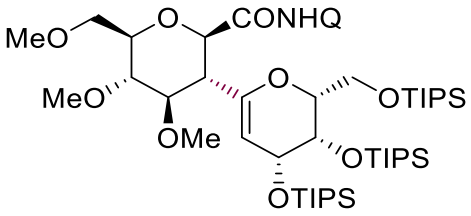
The general procedure **D** was followed using (2*R*,3*S*,4*R,6R*)-2-(acetoxymethyl)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (**158aa**) (22.2 mg, 0.050 mmol), 1-iodo-galacal (**154b**) (55.5 mg, 0.075 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.2 mmol) in 1,4-dioxane (0.5 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159fa** (35 mg, 66%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.34 (s, 1H), 8.81 (d, *J* = 4.3 Hz, 1H), 8.79 – 8.65 (m, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.46 (dd, *J* = 8.2, 4.3 Hz, 1H), 5.65 – 5.05 (m, 2H), 4.81 – 4.40 (m, 2H), 4.39 – 4.20 (m, 3H), 4.18 – 3.93 (m, 3H), 3.87 – 3.74 (m, 1H), 3.20 -– 2.56 (m, 1H), 2.12 (s, 3H), 2.05 (s, 3H), 1.95 (s, 3H), 1.15 – 0.76 (m, 63H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8 (C_q), 170.2 (C_q), 148.4 (CH), 138.6 (C_q), 136.2 (CH), 133.9 (C_q), 127.9 (C_q), 127.2 (CH), 121.9 (CH), 121.7 (CH), 116.7 (CH), 102.6 (CH), 81.6 (CH), 79.3 (CH), 75.6 (CH), 72.8 (CH), 69.7 (CH), 69.5 (CH), 64.6 (CH), 62.5 (CH_2), 61.4 (CH_2), 49.6 (CH), 21.1 (CH_3), 20.8 (CH_3), 18.1 (CH_3), 12.5 (CH), 12.1 (CH). (3 C_q from OAc, amide and quinoline as well as 5 CH_3 and 1 CH resonances of TIPS group are missing due to overlap).

IR (ATR): $\tilde{\nu}$ = 2943, 2865, 1757, 1696, 1527, 1462, 1235. 1067, 1011, 882, 682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2136 (85) $[2M+Na]^+$, 1079 (100) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{55}H_{92}N_2NaO_{12}Si_3^+$ $[M+Na]^+$ 1079.5850, found 1079.5829.

(2*R*,3*R*,4*R*,5*S*,6*R*)-3-[(2*R*,3*S*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4,5-dimethoxy-6-(methoxymethyl)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159fb)



The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4,5-dimethoxy-6-(methoxymethyl)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158bb**) (36.0 mg, 0.10 mmol), 1-iodo-galacal (**154b**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159fb** (92.3 mg, 95%) as a syrup.

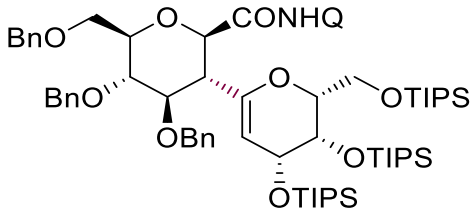
^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.31 (s, 1H), 8.78 (d, *J* = 4.2 Hz, 1H), 8.72 (t, *J* = 4.5 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.51 (d, *J* = 4.5 Hz, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.75 (d, *J* = 6.3 Hz, 1H), 4.46 – 4.26 (m, 3H), 4.22 – 4.12 (m, 2H), 4.06 (m, 1H), 3.83 – 3.66 (m, 3H), 3.63 (s, 3H), 3.61 (s, 3H), 3.56 (s, 3H), 3.53 – 3.48 (m, 1H), 3.28 (t, *J* = 9.3 Hz, 1H), 2.49 (t, *J* = 10.6 Hz, 1H), 1.27 – 0.70 (m, 63H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 148.5 (C_q), 148.2 (CH), 138.6 (C_q), 136.1 (CH), 134.2 (C_q), 127.9 (C_q), 127.3 (CH), 121.5 (CH), 116.6 (CH), 102.1 (CH), 82.1 (CH), 81.0 (CH), 80.5 (CH), 79.5 (CH), 79.4 (CH), 71.9 (CH_2), 69.9 (CH), 64.8 (CH), 61.1 (CH_2), 60.5 (CH_3), 60.4 (CH_3), 59.8 (CH_3), 52.3 (CH), 18.3 (CH_3), 18.1 (CH_3), 18.1

(CH_3), 12.5 (CH), 12.3 (CH), 12.1 (CH) (3 CH_3 resonances of the TIPS group and 1 CH at 121.5 is missing due to overlap. The overlap was determined by analysis of the HSQC spectroscopic analysis).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1695, 1525, 1462, 1385, 1107, 1011, 882, 790, 680 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1968 (100) $[2M+H]^+$, 995 (65) $[M+Na]^+$, 973 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{93}N_2O_9Si_3^+$ $[M+H]^+$ 973.6183, found 973.6174.

(2*R*,3*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-6-[(benzyloxy)methyl)-3-[(2*R*,3*S*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159fc)



The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158bc**) (36.0 mg, 0.10 mmol), 1-iodo-galacal (**154b**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 50/1 to 20/1) yielded **159fc** (76.8 mg, 64%) as a syrup.

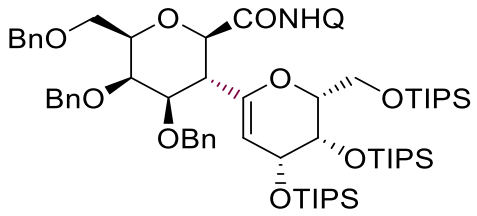
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.44 (s, 1H), 8.72 (d, *J* = 4.4 Hz, 1H), 8.60 (d, *J* = 4.2 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 4.4 Hz, 2H), 7.45 – 7.35 (m, 3H), 7.35 – 7.27 (m, 6H), 7.25 – 7.20 (m, 5H), 7.20 – 7.07 (m, 2H), 5.09 (d, *J* = 11.3 Hz, 1H), 4.91 – 4.64 (m, 5H), 4.58 (m, 1H), 4.52 – 4.00 (m, 7H), 3.93 – 3.75 (m, 3H), 3.67 (d, *J* = 9.8 Hz, 1H), 2.68 (t, *J* = 10.6 Hz, 1H), 1.13 – 0.81 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.0 (C_q), 148.8 (C_q), 148.3 (CH), 139.1 (C_q), 138.7 (C_q), 138.7 (C_q), 138.5 (C_q), 136.1 (CH), 134.3 (C_q), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.9 (CH), 127.8 (CH), 127.7 (2 CH), 127.5 (CH), 127.4 (CH), 127.2 (CH), 127.0 (C_q), 121.5 (2 CH), 116.5 (CH), 102.0 (CH), 81.2 (CH), 81.1 (CH), 80.2 (CH), 79.5 (CH), 78.5 (CH), 74.9 (CH_2), 74.5 (CH_2), 73.8 (CH_2), 70.0 (CH), 69.2 (CH_2), 65.0 (CH), 61.1 (CH_2), 53.0 (CH), 18.3 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0

(CH_3), 12.6 (CH), 12.5 (CH), 12.2 (CH) (2 CH of resonances of arene are missing due to overlap. The overlap was dertermined by analysis of the HSQC spectroscopic analysis).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1694, 1525, 1463, 1091, 1012, 883, 733, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1223 (20) $[M+Na]^+$, 1201 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{70}H_{105}N_2O_9Si_3^+$ $[M+H]^+$ 1201.7122, found 1201.7114.

(2*R*,3*R*,4*R*,5*R*,6*R*)-4,5-Bis(benzyloxy)-6-[(benzyloxy)methyl]-3-[(2*R*,3*S*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159g)



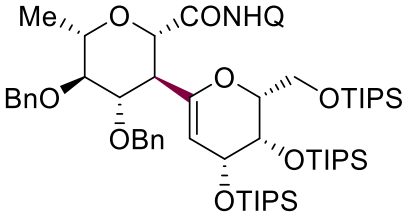
The general procedure **D** was followed using (2*R*,4*R*,5*R*,6*R*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158cb**) (58.8 mg, 0.10 -mmol), 1-iodo-galacal (**154b**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159g** (79.3 mg, 66%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.44 (s, 1H), 8.78 (d, *J* = 4.3 Hz, 1H), 8.73 (t, *J* = 4.7 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.47 (m, 2H), 7.45 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.41 – 7.24 (m, 14H), 5.00 – 4.85 (m, 2H), 4.82 – 4.63 (m, 2H), 4.60 – 4.45 (m, 3H), 4.41 – 4.26 (m, 4H), 4.15 (dd, *J* = 14.6, 7.5 Hz, 2H), 3.99 (d, *J* = 10.4 Hz, 1H), 3.89 – 3.66 (m, 4H), 3.06 (t, *J* = 10.5 Hz, 1H), 1.11 – 0.97 (m, 63H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2 (C_q), 149.3 (C_q), 148.3 (CH), 139.4 (C_q), 139.1 (C_q), 138.8 (C_q), 138.1 (C_q), 136.0 (CH), 134.4 (C_q), 128.3 (CH), 128.0 (CH), 127.9 (C_q), 127.8 (2 CH), 127.6 (CH), 127.6 (CH), 127.5 (CH), 127.2 (CH), 127.1 (CH), 127.1 (CH), 121.4 (CH), 121.4 (CH), 116.6 (CH), 102.2 (CH), 81.1 (CH), 80.3 (CH), 79.3 (CH), 77.6 (CH), 74.3 (CH_2), 73.6 (CH_2), 72.9 (CH), 72.5 (CH_2), 70.0 (CH), 69.6 (CH_2), 64.9 (CH), 61.4 (CH_2), 47.2 (CH), 18.3 (CH_3), 18.2 (CH_3), 12.6(CH), 12.2 (CH). (1 CH and 4 CH_3 of resonances of TIPS are overlapped).

IR (ATR): $\tilde{\nu}$ = 2943, 2865, 1694, 1526, 1464, 1106, 1012, 883, 753, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2402 (100) $[2M+H]^+$, 1201 (15) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{70}H_{105}N_2O_9Si_3^+$ $[M+H]^+$ 1201.7122, found 1201.7116.

(2*S*,3*S*,4*S*,5*S*,6*S*)-4,5-Bis(benzyloxy)-3-[(2*R*,3*S*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-6-methyl-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159h)



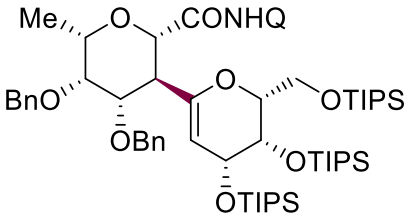
The general procedure **D** was followed using (2*S*,4*S*,5*S*,6*S*)-4,5-bis(benzyloxy)-6-methyl-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158d**) (48.2 mg, 0.10 mmol), 1-iodo-galacal (**154b**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159h** (75 mg, 69%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.54 (s, 1H), 9.04 – 8.66 (m, 2H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.38 – 7.31 (m, 5H), 7.28 (m, 5H), 5.00 – 4.80 (m, 3H), 4.79 – 4.57 (m, 3H), 4.40 – 4.28 (m, 2H), 4.24 – 4.15 (m, 2H), 4.13 – 4.02 (m, 2H), 3.60 (dt, *J* = 12.2, 6.1 Hz, 1H), 3.28 (t, *J* = 9.1 Hz, 1H), 2.63 (t, *J* = 10.5 Hz, 1H), 1.47 (d, *J* = 6.1 Hz, 3H), 1.18 – 0.90 (m, 63H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0 (C_q), 148.8 (C_q), 148.2 (CH), 138.8 (C_q), 138.7 (C_q), 138.5 (C_q), 136.1 (CH), 134.7 (C_q), 128.4 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 121.3 (CH), 121.0 (CH), 116.6 (CH), 102.7 (CH), 84.1 (CH), 82.1 (CH), 81.7 (CH), 77.2 (CH), 75.1 (CH_2), 70.6 (CH_2), 64.7 (CH), 61.0 (CH_2), 52.4 (CH), 18.4 (CH_3), 18.3 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 12.7 (CH), 12.3 (CH), 12.1 (CH) (One Cq and 2 CH_3 of resonances of TIPS are overlapped).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1700, 1524, 1462, 1383, 1086, 882, 696, 673 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2190 (100) $[2M+H]^+$, 1117 (25) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{64}H_{99}NNaO_8Si_3^+$ $[M+Na]^+$ 1117.6523, found 1117.6498.

(2*S*,3*R*,4*S*,5*R*,6*R*)-2-Methyl-5-[(2*S*,3*R*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (159i)



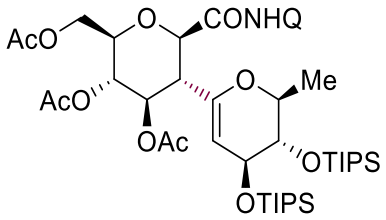
The general procedure **D** was followed using (2*S*,4*S*,5*R*,6*S*)-4,5-bis(benzyloxy)-6-methyl-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158d**) (48.2 mg, 0.10 mmol), 1-iodo-galacal (**154b**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159i** (83.3 mg, 76%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.65 (s, 1H), 8.83 (dd, *J* = 6.9, 2.2 Hz, 1H), 8.78 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.44 – 7.38 (m, 4H), 7.37 – 7.34 (m, 3H), 7.33 – 7.29 (m, 3H), 7.28 – 7.26 (m, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 4.86 (d, *J* = 5.8 Hz, 1H), 4.77 – 4.59 (m, 4H), 4.36 – 4.26 (m, 2H), 4.24 – 4.18 (m, 2H), 4.15 (dd, *J* = 5.1, 3.8 Hz, 1H), 4.00 (dd, *J* = 10.7, 2.5 Hz, 1H), 3.88 – 3.52 (m, 2H), 2.97 (t, *J* = 10.7 Hz, 1H), 1.36 (d, *J* = 6.2 Hz, 3H), 1.11 – 0.97 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.3 (C_q), 149.2 (C_q), 148.1 (CH), 139.1 (C_q), 138.9 (C_q), 138.6 (C_q), 135.9 (CH), 134.9 (C_q), 128.3 (CH), 128.1 (CH), 127.8 (C_q), 127.8 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 127.2 (CH), 121.2 (CH), 120.8 (CH), 116.5 (CH), 102.9 (CH), 82.1 (CH), 80.2 (CH), 77.7 (CH), 75.5 (CH), 74.3 (CH_2), 74.0 (CH), 73.0 (CH_2), 70.7 (CH), 64.7 (CH), 61.1 (CH_2), 46.2 (CH), 18.4 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 17.7 (CH_3), 12.7 (CH), 12.4 (CH), 12.1 (CH) (2 CH_3 of resonances of TIPS are overlapped).

IR (ATR): $\tilde{\nu}$ = 2942, 2866, 1698, 1528, 1462, 1097, 1066, 882, 791, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2190 (100) $[2M+H]^+$, 1095 (20) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{63}H_{99}N_2O_8Si_3^+$ $[M+H]^+$ 1095.6704, found 1095.6693.

(2*R*,3*S*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-5-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (159ja)



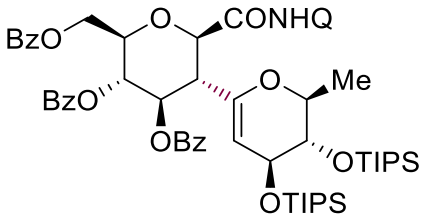
The general procedure **D** was followed using (2*R*,3*S*,4*R*,6*R*)-2-(acetoxymethyl)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (**158aa**) (44.4 mg, 0.10 mmol), 1-iodo-rhamanal (**154a**) (85.2 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159ja** (74.4 mg, 84%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.31 (s, 1H), 8.81 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.76 (dd, *J* = 6.1, 3.0 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.3, 4.3 Hz, 1H), 5.46 (td, *J* = 10.7, 9.7 Hz, 1H), 5.14 (td, *J* = 9.7, 2.6 Hz, 1H), 4.76 (d, *J* = 4.5 Hz, 1H), 4.39 (d, *J* = 10.7 Hz, 1H), 4.29 – 4.20 (m, 3H), 3.96 (t, *J* = 4.5, 2.3 Hz, 1H), 3.86 (ddd, *J* = 10.3, 4.8, 2.6 Hz, 1H), 3.73 (t, *J* = 3.1 Hz, 1H), 2.84 (td, *J* = 10.7 Hz, 1H), 2.11 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.39 (d, *J* = 7.0 Hz, 3H), 1.01 (m, 21H), 0.88 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.8 (C_q), 170.1 (C_q), 169.6 (C_q), 165.5 (C_q), 148.2 (CH), 145.2 (C_q), 138.6 (C_q), 136.2 (CH), 133.9 (C_q), 127.8 (C_q), 127.2 (CH), 121.7 (CH), 121.5 (CH), 117.1 (CH), 102.4 (CH), 79.2 (CH), 75.9 (CH), 75.3 (CH), 73.6 (CH), 71.2 (CH), 69.7 (CH), 67.3 (CH), 62.5 (CH_2), 50.3 (CH), 20.8 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 16.5 (CH_3), 12.5 (CH), 12.5 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1712, 1421, 1522, 1264, 909, 734, 704, 651 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1770 (100) $[2M+Na]^+$, 907 (20) $[M+Na]^+$, 885 (40) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{46}H_{73}N_2O_{11}Si_2^+$ $[M+H]^+$ 885.4747, found 885.4736.

(2*R*,3*S*,4*R*,5*R*,6*R*)-2-((Benzoyloxy)methyl)-5-((2*S*,3*S*,4*S*)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2*H*-pyran-6-yl)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl dibenzoate (159jb)



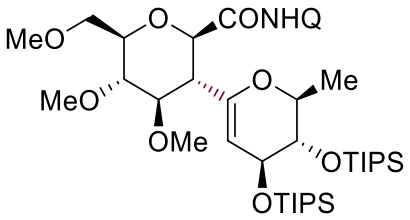
The general procedure **D** was followed using (2*R*,3*S*,4*R*,6*R*)-2-((benzoyloxy)methyl)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl dibenzoate (**158ba**) (31.5 mg, 0.05 mmol), 1-iodo-rhamanal (**154a**) (42.6 mg, 0.075 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159jb** (29.0 mg, 54%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.48 (s, 1H), 8.79 (t, *J* = 4.5 Hz, 1H), 8.54 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.07 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.93 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.86 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.55 – 7.47 (m, 4H), 7.42 (td, *J* = 7.3, 1.3 Hz, 1H), 7.40 – 7.32 (m, 5H), 7.30 – 7.26 (m, 2H), 5.98 (dd, *J* = 10.7, 9.7 Hz, 1H), 5.66 (dd, *J* = 9.7 Hz, 1H), 4.81 (dd, *J* = 4.4, 1.1 Hz, 1H), 4.69 (dd, *J* = 12.3, 2.9 Hz, 1H), 4.62 (d, *J* = 10.7 Hz, 1H), 4.53 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.32 – 4.15 (m, 2H), 3.92 – 3.78 (m, 1H), 3.71 – 3.60 (m, 1H), 3.10 (t, *J* = 10.7 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 3H), 0.99 – 0.72 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2 (C_q), 165.6 (C_q), 165.6 (C_q), 165.0 (C_q), 148.3 (CH), 145.6 (C_q), 138.6 (C_q), 136.1 (CH), 134.0 (C_q), 133.2 (CH), 132.9 (CH), 132.7 (CH), 129.9 (CH), 129.9 (CH), 129.8 (C_q), 129.8 (C_q), 129.7 (CH), 129.2 (C_q), 128.3 (CH), 128.3 (CH), 128.0 (CH), 127.8 (C_q), 127.2 (CH), 121.7 (CH), 121.5 (CH), 117.1 (CH), 102.8 (CH), 79.2 (CH), 76.1 (CH), 75.7 (CH), 73.8 (CH), 71.4 (CH), 70.8 (CH), 67.8 (CH), 63.4 (CH_2), 50.9 (CH), 18.0 (CH_3), 17.9 (CH_3), 16.7 (CH_3), 12.6 (CH), 12.5 (CH) (2 CH_3 of resonances of TIPS are overlapped).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1735, 1530, 1269, 1122, 1069, 882, 754, 708, 684 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1093 (100) $[M+Na]^+$, 1071 (50) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{61}H_{79}N2O_{11}Si_2^+$ $[M+H]^+$ 1071.5217, found 1071.5194.

(2*R*,3*R*,4*R*,5*S*,6*R*)-4,5-Dimethoxy-6-(methoxymethyl)-3-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159jc)



The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4,5-dimethoxy-6-(methoxymethyl)-*N*-(quinolin-8-yl)tetrahydro-2H-pyran-2-carboxamide (**158bb**) (36.0 mg, 0.10 mmol), 1-iodo-rhamanal (**154a**) (85.2 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159jc** (76.0 mg, 95%) as a syrup.

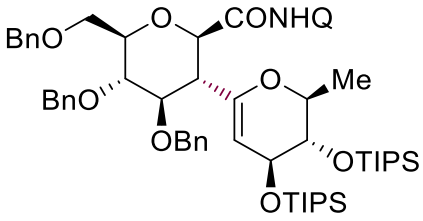
^{1}H NMR (400 MHz, $CDCl_3$): δ =10.36 (s, 1H), 9.09 – 8.43 (m, 2H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 4.5 Hz, 2H), 7.41 (dd, *J* = 8.2, 4.2 Hz, 1H), 4.83 (d, *J* = 4.8 Hz, 1H), 4.40 (q, *J* = 7.3 Hz, 1H), 4.24 (d, *J* = 10.5 Hz, 1H), 4.00 (d, *J* = 4.8 Hz, 1H), 3.87 – 3.82 (m, 1H), 3.77 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.73 – 3.69 (m, 1H), 3.67 – 3.62 (m, 1H), 3.60 (s, 3H), 3.59 (s, 3H), 3.54 (s, 3H), 3.52 – 3.47 (m, 1H), 3.22 (t, *J* = 9.3 Hz, 1H), 2.48 (t, *J* = 10.5 Hz, 1H), 1.44 (d, *J* = 7.3 Hz, 3H), 1.11 – 0.90 (m, 21H), 0.96 – 0.82 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6 (C_q), 148.0 (CH), 146.7 (C_q), 138.7 (C_q), 136.1 (CH), 134.2 (C_q), 127.8 (C_q), 127.2 (CH), 121.4 (CH), 121.3 (CH), 117.0 (CH), 101.5 (CH), 82.8 (CH), 80.0 (CH), 79.3 (CH), 79.0 (CH), 75.8 (CH), 73.7 (CH), 72.0 (CH_2), 66.7 (CH), 61.1 (CH_3), 60.7 (CH_3), 59.8 (CH_3), 53.0 (CH), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH), 16.3 (CH_3), 12.3 (CH) (1 CH_3 and 1 CH of resonances of TIPS are overlapped).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1703, 1525, 1462, 1384, 1119, 1095, 882, 680 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1602 (100) $[2M+H]^+$, 823 (60) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{43}H_{73}N_2O_8Si_2^+$ $[M+H]^+$ 801.4900, found 801.4892.

(2*R*,3*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)-3-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159jd)



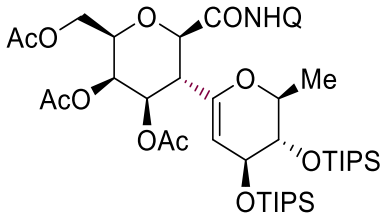
The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158bc**) (29.4 mg, 0.05 mmol), 1-iodo-rhamanal (**154a**) (42.6 mg, 0.075 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159jd** (33.0 mg, 64%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.47 (s, 1H), 8.77 (dd, *J* = 5.9, 3.1 Hz, 1H), 8.54 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.39 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.34 – 7.27 (m, 8H), 7.23 (m, 5H), 5.08 – 4.93 (m, 2H), 4.83 (dd, *J* = 11.5, 7.8 Hz, 2H), 4.65 (dd, *J* = 13.6, 11.5 Hz, 2H), 4.56 (d, *J* = 9.9 Hz, 1H), 4.43 (dt, *J* = 7.1, 1.9 Hz, 1H), 4.38 (d, *J* = 10.8 Hz, 1H), 4.10 (d, *J* = 4.7 Hz, 1H), 4.06 (t, *J* = 10.4, 8.7 Hz, 1H), 3.95 – 3.88 (m, 2H), 3.85 (dd, *J* = 11.5, 1.7 Hz, 1H), 3.76 (t, *J* = 9.3, 8.7 Hz, 1H), 3.65 (ddd, *J* = 10.0, 4.2, 1.8 Hz, 1H), 2.72 (t, *J* = 10.4 Hz, 1H), 1.50 (d, *J* = 7.1 Hz, 3H), 0.98 – 0.90 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9 (C_q), 148.2 (CH), 146.9 (C_q), 138.8 (C_q), 138.7 (C_q), 138.5 (C_q), 136.0 (CH), 134.3 (C_q), 128.6 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.8 (C_q), 127.6 (2 CH), 127.5 (CH), 127.4 (CH), 127.2 (CH), 121.3 (CH), 121.3 (CH), 116.9 (CH), 102.0 (CH), 81.1 (CH), 79.3 (CH), 79.1 (CH), 78.1 (CH), 76.0 (CH), 75.4 (CH_2), 75.2 (CH_2), 74.2 (CH), 73.8 (CH_2), 69.3 (CH_2), 67.2 (CH), 53.4 (CH), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 16.3 (CH_3), 12.4 (CH), 12.4 (CH).

IR (ATR): $\tilde{\nu}$ = 2924, 2866, 1702, 1524, 1463, 1094, 882, 753, 697, 680 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2058 (50) $[2M+H]^+$, 1029 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{61}H_{85}N_2O_8Si_2^+$ $[M+H]^+$ 1029.5839, found 1029.5839.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-5-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (159k)



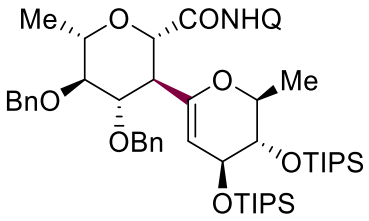
The general procedure **D** was followed using (2*R*,3*R*,4*R*,6*R*)-2-(acetoxymethyl)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (**158bd**) (44.4 mg, 0.10 mmol), 1-iodo-rhamanal (**154a**) (85.2 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159k** (74.4 mg, 84%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.36 (s, 1H), 8.89 – 8.67 (m, 2H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.50 (d, *J* = 3.0 Hz, 1H), 5.31 (dd, *J* = 11.4, 3.0 Hz, 1H), 4.80 (d, *J* = 4.8 Hz, 1H), 4.40 (d, *J* = 10.5 Hz, 1H), 4.30 (q, *J* = 7.3 Hz, 1H), 4.21 (d, *J* = 6.4 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.79 (d, *J* = 2.1 Hz, 1H), 2.96 (t, *J* = 11.4, 10.5 Hz, 1H), 2.22 (s, 3H), 2.04 (s, 3H), 1.93 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 3H), 1.05 – 0.91 (m, 21H), 0.93 – 0.76 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6 (C_q), 170.4 (C_q), 169.7 (C_q), 165.7 (C_q), 148.2 (CH), 145.5 (C_q), 138.6 (C_q), 136.2 (CH), 134.0 (C_q), 127.8 (C_q), 127.2 (CH), 121.6 (CH), 121.5 (CH), 117.0 (CH), 102.0 (CH), 79.6 (CH), 75.6 (CH), 73.9 (CH), 73.3 (CH), 69.3 (CH), 66.6 (CH), 65.9 (CH), 62.4 (CH_2), 44.7 (CH), 20.8 (CH_3), 20.8 (CH_3), 20.7 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 16.2 (CH_3), 12.4 (CH), 12.3 (CH). (1 CH_3 of resonances of TIPS is overlapped).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1748, 1534, 1422, 1264, 1094, 908, 734, 704 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1792 (100) $[2M+Na]^+$, 885 (70) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{46}H_{73}N_2O_{11}Si_2^+$ $[M+H]^+$ 885.4747, found 885.4732.

(2*S*,3*S*,4*S*,5*S*,6*S*)-4,5-Bis(benzyloxy)-6-methyl-3-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159l)



The general procedure **D** was followed using (2*S*,4*S*,5*S*,6*S*)-4,5-bis(benzyloxy)-6-methyl-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158d**) (24.1 mg, 0.05 mmol), 1-iodo-rhamanal (**154a**) (42.6 mg, 0.075 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %),

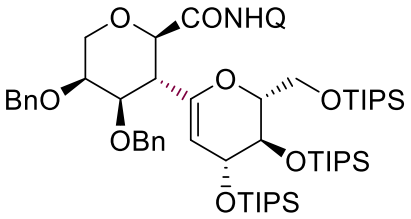
Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159l** (34.5 mg, 75%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.19 (s, 1H), 8.85 (d, *J* = 3.4 Hz, 1H), 8.80 (dd, *J* = 6.1, 2.6 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.38 – 7.34 (m, 4H), 7.33 – 7.29 (m, 4H), 7.29 – 7.24 (m, 2H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.92 – 4.87 (m, 2H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.69 (d, *J* = 10.8 Hz, 1H), 4.32 (q, *J* = 6.2 Hz, 1H), 4.27 (d, *J* = 10.5 Hz, 1H), 4.17 – 3.99 (m, 2H), 3.81 (t, *J* = 4.2 Hz, 1H), 3.63 (dt, *J* = 12.2, 6.2 Hz, 1H), 3.37 (t, *J* = 9.1 Hz, 1H), 2.89 (t, *J* = 10.3 Hz, 1H), 1.45 (d, *J* = 6.2 Hz, 6H), 1.01 – 0.92 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6 (C_q), 148.1 (CH), 148.0 (C_q), 138.8 (C_q), 138.7 (C_q), 138.4 (C_q), 136.1 (CH), 134.3 (C_q), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.9 (C_q), 127.7 (CH), 127.6 (CH), 127.3 (CH), 127.3 (CH), 121.5 (CH), 121.4 (CH), 116.9 (CH), 102.1 (CH), 84.4 (CH), 81.0 (CH), 79.7 (CH), 75.7 (CH), 75.7 (CH), 75.3 (CH_2), 74.6 (CH_2), 74.2 (CH), 69.0 (CH), 51.7 (CH), 18.4 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.2 (CH_3), 12.8 (CH) (1 CH of resonances of TIPS and 1 CH_3 are missing due to overlap).

IR (ATR): $\tilde{\nu}$ = 2942, 2866, 1705, 1527, 1463, 1382, 1108, 882, 753, 682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 945 (100) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{54}H_{78}N_2NaO_7Si_2^+$ $[M+Na]^+$ 945.5240, found 945.5233.

(2*R*,3*R*,4*R*,5*S*)-4,5-Bis(benzyloxy)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (159m)



The general procedure **D** was followed using (2*R*,4*R*,5*S*)-4,5-bis(benzyloxy)-*N*-(quinolin-8-yl)tetrahydro-2*H*-pyran-2-carboxamide (**158f**) (46.8 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification

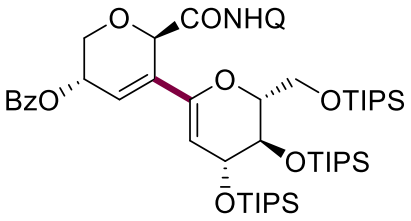
by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159m** (16.1 mg, 15%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.74 (s, 1H), 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.81 (t, *J* = 4.5 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.48 (d, *J* = 4.5 Hz, 2H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.40 – 7.27 (m, 8H), 7.25 – 7.19 (m, 2H), 5.40 (d, *J* = 4.7 Hz, 1H), 4.99 (d, *J* = 12.7 Hz, 1H), 4.91 (d, *J* = 13.7 Hz, 1H), 4.76 (d, *J* = 13.7 Hz, 1H), 4.67 (d, *J* = 12.7 Hz, 1H), 4.36 (dd, *J* = 11.8, 2.8 Hz, 1H), 4.26 – 4.10 (m, 4H), 3.81 (dd, *J* = 5.2, 2.9 Hz, 2H), 3.74 (dd, *J* = 8.0, 2.9 Hz, 1H), 3.68 – 3.57 (m, 2H), 3.49 – 3.32 (m, 1H), 1.17 – 0.52 (m, 63H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.7 (C_q), 149.3 (C_q), 148.2 (CH), 139.5 (C_q), 138.9 (C_q), 138.9 (C_q), 136.0 (CH), 134.2 (C_q), 128.2 (CH), 128.1 (CH), 127.9 (C_q), 127.7 (CH), 127.3 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 121.3 (CH), 116.8 (CH), 99.8 (CH), 79.9 (CH), 78.4 (CH), 78.1 (CH), 72.8 (CH), 71.4 (CH_2), 70.8 (CH_2), 70.6 (CH), 70.1 (CH_2), 67.4 (CH), 61.2 (CH_2), 42.1 (CH), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.6 (CH), 12.4 (CH), 11.8 (CH) (2 CH_3 of resonances of TIPS are missing due to overlap).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1694, 1526, 1463, 1385, 1089, 882, 734, 682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1103 (15) $[M+Na]^+$, 1081 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{62}H_{97}N_2O_8Si_3^+$ $[M+H]^+$ 1081.6547, found 1081.6539.

(2'*R*,4*R*,5*R*,5'*S*,6*R*)-2'-(Quinolin-8-ylcarbamoyl)-4,5-bis[(triisopropylsilyl)oxy]-6-{[(triisopropylsilyl)oxy]methyl}-5,5',6,6'-tetrahydro-2'*H*,4*H*-[2,3'-bipyran]-5'-yl benzoate (159n)



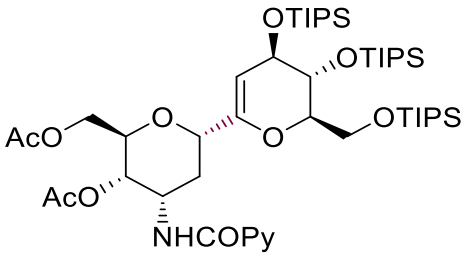
The general procedure **D** was followed using (**158g**) (49.6 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4--dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159n** (23.6 mg, 24%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.56 (s, 1H), 8.77 (d, *J* = 4.2 Hz, 1H), 8.69 (dd, *J* = 5.8, 3.2 -Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.37 (m, 5H), 6.57 – 6.26 (m, 1H), 5.74 (dd, *J* = 5.5, 5.0 Hz, 1H), 5.59 (d, *J* = 5.4 Hz, 1H), 5.51 (dd, *J* = 5.5, 1.9 Hz, 1H), 4.49 (qd, *J* = 11.5, 5.0 Hz, 2H), 4.30 (t, *J* = 7.0, 3.6 Hz, 1H), 4.23 – 3.95 (m, 3H), 3.81 (dd, *J* = 11.3, 3.6 Hz, 1H), 1.13 – 0.97 (m, 42H), 0.91 – 0.82 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.4 (C_q), 166.4 (C_q), 148.4 (CH), 143.3 (C_q), 138.7 (C_q), 137.8 (C_q), 136.1 (CH), 134.2 (C_q), 133.1 (CH), 129.9 (C_q), 129.7 (CH), 128.4 (CH), 127.9 (C_q), 127.2 (CH), 125.0 (CH), 121.5 (CH), 121.5 (CH), 116.4 (CH), 103.4 (CH), 86.7 (CH), 85.1 (CH), 81.2 (CH), 69.6 (CH), 66.5 (CH_2), 66.0 (CH), 62.1 (CH_2), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 12.5 (CH), 12.4 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2942, 2965, 1727, 1695, 1535, 1463, 1270, 882, 711, 682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1009 (20) $[M+Na]^+$, 987 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{55}H_{87}N_2O_8Si_3^+$ $[M+H]^+$ 987.5765, found 987.5756.

[(2*R*,3*S*,4*S*,6*S*)-3-Acetoxy-6-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4-(picolinamido)tetrahydro-2*H*-pyran-2-yl]methyl acetate (159oa)



The general procedure **E** was followed using [(2*R*,3*S*,4*S*)-3-acetoxy-4-(picolinamido)tetrahydro-2*H*-pyran-2-yl]methyl acetate (**158ha**) (33.6 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2CO_3 (55.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159oa** (37 mg, 43%) as a syrup.

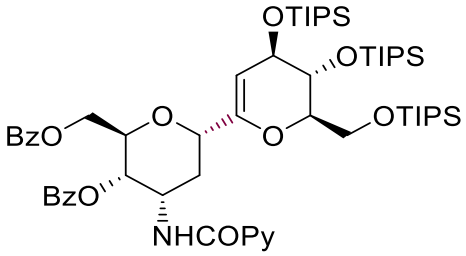
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 4.7 Hz, 1H), 8.18 (,d, *J* = 8.2 Hz, 2H), 7.85 (t, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.54 (d, 2.8 Hz, 1H), 5.15 – 4.93 (m, 1H), 4.67 (tt, *J* = 12.8, 8.2, 4.0 Hz, 1H), 4.47 (dd, *J* = 11.0, 5.6 Hz, 1H), 4.41 (dd, *J* =

10.8, 2.8 Hz, 1H), 4.23 (d, *J* = 7.8 Hz, 1H), 4.21 – 4.13 (m, 3H), 4.11 – 4.09 (m, 1H), 4.08 – 4.02 (m, 1H), 3.80 (dd, *J* = 11.5, 3.3 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 2.08 – 1.98 (q, 11.6, 10.8 Hz 1H), 1.86 (dt, *J* = 11.6, 3.8 Hz, 1H), 1.19 – 0.92 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.5 (C_q), 170.4 (C_q), 163.6 (C_q), 149.5 (C_q), 148.1 (CH), 142.1 (CH), 137.4 (CH), 126.3 (CH), 122.3 (CH), 111.4 (C_q), 81.3 (CH), 73.0 (CH), 70.3 (CH), 69.5 (CH), 69.2 (CH), 65.7 (CH), 62.9 (CH_2), 62.4 (CH_2), 44.7 (CH), 31.4 (CH_2), 21.0 (CH_3), 20.8 (CH_3), 18.4 (CH_3), 18.3 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.9 (CH), 12.5 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1747, 1668, 1518, 1464, 1367, 1222, 882, 680 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 971 (75) $[M+Na]^+$, 949 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{49}H_{89}N_2O_{10}Si_3^+$ $[M+H]^+$ 949.5820, found 949.5796.

[(2*R*,3*S*,4*S*,6*S*)-3-(benzoyloxy)-6-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4-(picolinamido)tetrahydro-2*H*-pyran-2-yl]methyl benzoate (159ob)



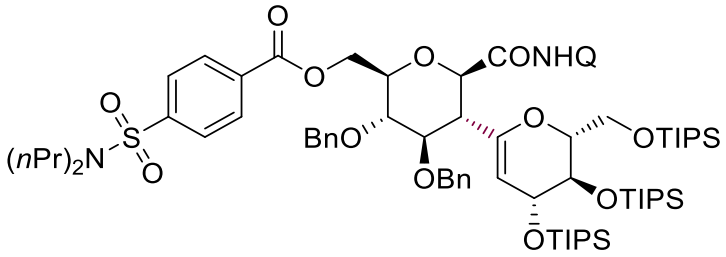
The general procedure **D** was followed using [(2*R*,3*S*,4*S*)-3-(benzoyloxy)-4-(picolinamido)tetrahydro-2*H*-pyran-2-yl]methyl benzoate (**158hb**) (23.0 mg, 0.05 mmol), 1-iodo-glucal (**59**) (55.0 mg, 0.075 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1) yielded **159ob** (27.0 mg, 50%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 4.7 Hz, 1H), 8.36 (d, *J* = 8.9 Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 2H), 8.09 (d, *J* = 7.6 Hz, 2H), 7.81 (dd, *J* = 7.8, 7.7 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.37 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.60 (s, 1H), 5.43 (d, *J* = 2.3 Hz, 1H), 4.92 – 4.83 (m, 1H), 4.74 (ddd, *J* = 10.0, 9.4, 5.8 Hz, 1H), 4.63 – 4.46 (m, 3H), 4.24 (dd, *J* = 5.3, 3.1 Hz, 2H), 4.18 – 3.97 (m, 2H), 3.80 (dd, *J* = 11.4, 2.9 Hz, 1H), 2.29 – 2.16 (m, 1H), 2.09 – 1.97 (m, 1H), 1.10 – 0.95 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2 (C_q), 166.0 (C_q), 163.7 (C_q), 149.4 (C_q), 148.1 (CH), 142.0 (CH), 137.3 (CH), 133.3 (CH), 133.1 (CH), 129.9 (CH), 129.8 (CH), 129.7 (2 C_q), 128.5 (CH), 128.4 (CH), 126.2 (CH), 122.3 (CH), 111.6 (C_q), 81.4 (CH), 73.3 (CH), 70.4 (CH), 70.1 (CH), 69.5 (CH), 65.5 (CH), 63.0 (CH_2), 62.8 (CH_2), 45.1 (CH), 32.0 (CH_2), 18.3 (CH_3), 18.3 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.9 (CH), 12.5 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1726, 1686, 1512, 1466, 1265, 1067, 882, 710, 689 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1095 (60) $[M+Na]^+$, 1073 (90) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{59}H_{93}N_2O_{10}Si_3^+$ $[M+H]^+$ 1073.6133, found 1073.6118.

[(2*R*,3*S*,4*R*,5*R*,6*R*)-3,4-Bis(benzyloxy)-5-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-2-yl]methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (159p)



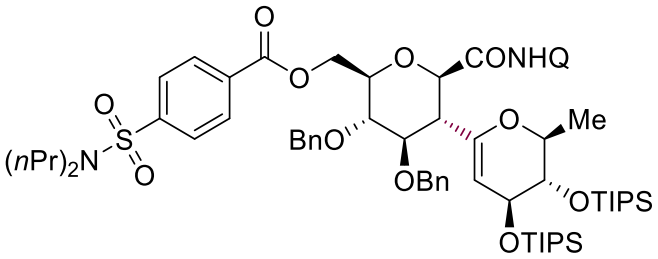
The general procedure **D** was followed using ((2*R*,3*S*,4*R*,6*R*)-3,4-bis(benzyloxy)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-2-yl)methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**158i**) (76.5 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159p** (76.0 mg, 55%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.25 (s, 1H), 8.76 (t, *J* = 4.5 Hz, 1H), 8.53 (d, *J* = 4.3 Hz, 1H), 8.27 – 8.03 (m, 3H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 4.5 Hz, 2H), 7.38 (dd, *J* = 8.2, 4.3 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.29 – 7.27 (m, 2H), 7.25 – 7.19 (m, 6H), 5.07 (d, *J* = 11.0 Hz, 1H), 5.02 (d, *J* = 4.6 Hz, 1H), 4.81 (dd, *J* = 15.4, 11.0 Hz, 2H), 4.69 (dd, *J* = 11.9, 2.0 Hz, 1H), 4.56 (dd, *J* = 11.6, 4.1 Hz, 2H), 4.42 (d, *J* = 10.3 Hz, 1H), 4.34 (t, *J* = 5.7 Hz, 1H), 4.23 (t, *J* = 9.1 Hz, 1H), 4.10 – 4.00 (m, 4H), 3.95 – 3.84 (m, 1H), 3.81 – 3.67 (m, 1H), 3.26 – 2.69 (m, 5H), 1.53 (q, *J* = 7.5 Hz, 4H), 1.10 – 0.87 (m, 63H), 0.85 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.9 (C_q), 164.9 (C_q), 148.3 (C_q), 148.1 (CH), 144.1 (C_q), 138.6 (C_q), 138.6 (C_q), 137.9 (C_q), 136.1 (CH), 134.3 (C_q), 133.3 (C_q), 130.4 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.8 (C_q), 127.7 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 126.9 (CH), 121.5 (CH), 121.4 (CH), 116.8 (CH), 101.1 (CH), 81.6 (CH), 81.3 (CH), 79.2 (CH), 78.1 (CH), 74.8 (CH_2), 74.6 (CH_2), 69.8 (CH), 67.0 (CH), 64.4 (CH_2), 61.9 (CH_2), 51.0 (CH), 50.0 (CH_2), 21.9 (CH_2), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.5 (CH), 12.5 (CH), 12.0 (CH), 11.1 (CH_3) (1 CH_3 of resonance of TIPS is overlapped).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1730, 1704, 1526, 1483 , 1086, 882, 745, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1400 (10) $[M+Na]^+$, 1378 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{76}H_{116}N_3O_{12}SSi_3^+$ $[M+H]^+$ 1378.7582, found 1378.7569.

[(2*R*,3*S*,4*R*,5*R*,6*R*)-3,4-Bis(benzyloxy)-5-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-2-yl]methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (159q)



The general procedure **D** was followed using ((2*R*,3*S*,4*R*,6*R*)-3,4-bis(benzyloxy)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-2-yl)methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**158i**) (38.3 mg, 0.05 mmol), 1-iodo-rhamanal (**154a**) (42.6 mg, 0.075 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159q** (33.6 mg, 56%) as a syrup.

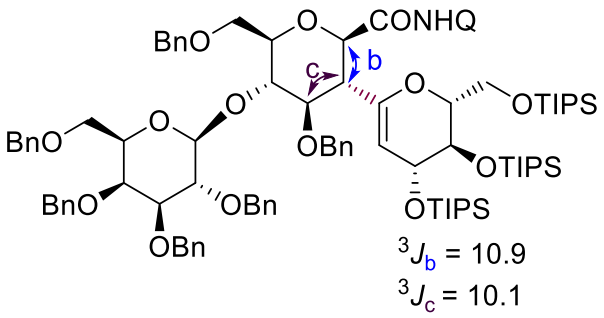
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.37 (s, 1H), 8.76 – 8.73 (m, 1H), 8.39 (d, *J* = 3.7 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 2H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 4.5 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.30 – 7.25 (m, 7H), 7.25 – 7.17 (m, 1H), 5.05 (dd, *J* = 11.7, 7.2 Hz, 2H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.67 – 4.54 (m, 4H), 4.49 – 4.40 (m, 2H), 4.17 – 4.07 (m, 2H), 3.97 – 3.85 (m, 1H), 3.86 – 3.78 (m, 1H), 3.73 (t, *J* = 9.2

Hz, 1H), 3.10 – 3.04 (m, 4H), 2.77 (t, *J* = 10.4 Hz, 1H), 1.53 (dd, *J* = 15.2, 7.4 Hz, 4H), 1.49 (d, *J* = 7.3 Hz, 3H), 1.01 – 0.90 (m, 42H), 0.85 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 166.4 (C_q), 164.9 (C_q), 148.1 (CH), 146.5 (C_q), 144.2 (C_q), 138.6 (C_q), 138.4 (C_q), 137.9 (C_q), 136.1 (CH), 134.1 (C_q), 133.3 (C_q), 130.4 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.8 (C_q), 127.8 (CH), 127.2 (CH), 126.9 (CH), 121.5 (CH), 121.4 (CH), 116.9 (CH), 102.3 (CH), 81.2 (CH), 79.3 (CH), 77.2 (CH), 76.4 (CH), 76.1 (CH), 75.4 (CH_2), 75.1 (CH_2), 74.1 (CH), 67.0 (CH), 64.0 (CH_2), 53.2 (CH), 50.0 (CH_2), 22.0 (CH_2), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 16.2 (CH_3), 12.4 (CH), 12.4 (CH), 11.1 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1730, 1701, 1526, 1456, 1104, 882, 744, 680 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1206 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{67}H_{96}N_3O_{11}SSi_2^+$ $[M+H]^+$ 1206.6299, found 1206.6288.

(2*R*,3*R*,4*R*,5*S*,6*R*)-4-(Benzyloxy)-6-[(benzyloxy)methyl]-3-[(2*R*,3*R*,4*R*)-3,4 bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)-5-{[(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-[(benzyloxy)methyl]tetrahydro-2H-pyran-2-yl]oxy}tetrahydro-2*H*-pyran-2-carboxamide (159r)



The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4-(benzyloxy)-6-[(benzyloxy)methyl]-*N*-(quinolin-8-yl)-5-{[(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-[(benzyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]oxy}tetrahydro-2*H*-pyran-2-carboxamide (**158j**) (102.0 mg, 0.10 mmol), 1-iodo-glucal (**59**) (222 mg, 0.30 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159r** (148 mg, 91%) as a syrup.

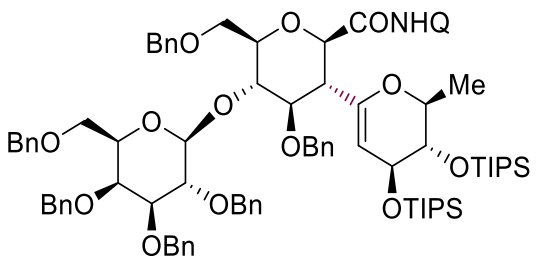
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 10.30 (s, 1H), 8.78 (dd, *J* = 6.5, 2.5 Hz, 1H), 8.59 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.40 – 7.27

(m, 24H), 7.24 – 7.17 (m, 4H), 7.14 – 7.02 (m, 3H), 5.16 (d, *J* = 10.5 Hz, 1H), 4.99 (d, *J* = 11.5 Hz, 1H), 4.93 (dd, *J* = 6.2, 3.1 Hz, 1H), 4.90 – 4.81 (m, 2H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.73 (s, 2H), 4.71 (d, *J* = 11.9 Hz, 1H), 4.56 (t, *J* = 9.5, 6.5 Hz, 2H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.36 (d, *J* = 10.9 Hz, 1H), 4.34 – 4.30 (m, 1H), 4.26 (d, *J* = 11.8 Hz, 1H), 4.15 (d, *J* = 12.1 Hz, 2H), 4.13 – 4.06 (m, 2H), 4.04 (t, *J* = 2.5 Hz, 2H), 4.02 – 3.95 (m, 2H), 3.91 (d, *J* = 2.9 Hz, 1H), 3.82 (dt, *J* = 9.5, 3.2 Hz, 2H), 3.61 (q, *J* = 3.9 Hz, 1H), 3.47 (dd, *J* = 9.8, 2.9 Hz, 1H), 3.41 – 3.27 (m, 2H), 3.18 (dd, *J* = 7.7, 3.5 Hz, 1H), 2.90 (t, *J* = 10.1 Hz, 1H), 1.07 – 0.88 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 166.3 (C_q), 148.1 (CH), 148.0 (C_q), 139.6 (C_q), 139.2 (C_q), 138.8 (C_q), 138.7 (C_q), 138.7 (C_q), 138.6 (C_q), 138.2 (C_q), 136.0 (CH), 134.6 (C_q), 128.3 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 127.9 (CH), 127.8 (C_q), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.5 (CH), 127.5 (CH), 127.4 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 127.2 (CH), 126.4 (CH), 121.3 (CH), 121.2 (CH), 116.7 (CH), 102.9 (CH), 101.3 (CH), 82.4 (CH), 81.1 (CH), 80.4 (CH), 79.7 (CH), 79.4 (CH), 78.4 (CH), 77.4 (CH), 75.4 (CH_2), 74.7 (CH_2), 74.2 (CH_2), 73.7 (CH), 73.4 (CH_2), 73.3 (CH_2), 72.9 (CH), 72.7 (CH_2), 70.3 (CH), 68.5 (CH_2), 68.0 (CH_2), 67.3 (CH), 61.8 (CH_2), 51.1 (CH), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.6 (CH), 12.5 (CH), 12.0 (CH) (2 CH_3 of resonances of TIPS are missing due to overlap).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1705, 1665, 1526, 1487, 1364, 882, 697, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1633 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{97}H_{133}N_2O_{14}Si_3^+$ $[M+H]^+$ 1633.9059, found 1633.9050.

(2*R*,3*R*,4*R*,5*S*,6*R*)-4-(Benzyloxy)-6-[(benzyloxy)methyl]-3-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)-5{[(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-[(benzyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]oxy}tetrahydro-2*H*-pyran-2-carboxamide (159s)



The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4-(benzyloxy)-6-[(benzyloxy)methyl]-*N*-(quinolin-8-yl)-5-{[(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6

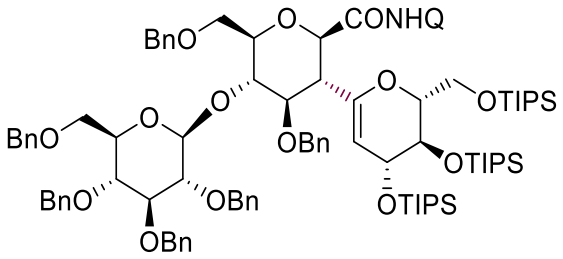
[(benzyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]oxy}tetrahydro-2*H*-pyran-2-carboxamide (**158j**) (51.0 mg, 0.05 mmol), 1-iodo-rhamanal (**154a**) (85.2 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159s** (49.7 mg, 68%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.45 (s, 1H), 8.75 (dd, *J* = 6.2, 2.8 Hz, 1H), 8.45 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.36 – 7.27 (m, 22H), 7.23 – 7.16 (m, 4H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 2H), 5.01 (d, *J* = 11.5 Hz, 1H), 4.93 (d, *J* = 4.6 Hz, 1H), 4.85 – 4.83 (m, 2H), 4.80 (dd, *J* = 13.6, 10.9 Hz, 2H), 4.71 (d, *J* = 10.9 Hz, 3H), 4.60 (d, *J* = 4.9 Hz, 1H), 4.58 (m, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.45 – 4.38 (m, 1H), 4.37 (d, *J* = 10.9 Hz, 1H), 4.27 (d, *J* = 11.7 Hz, 1H), 4.17 (d, *J* = 11.9 Hz, 1H), 4.10 (dd, *J* = 10.5, 7.4 Hz, 2H), 4.01 (dd, *J* = 11.8, 3.7 Hz, 1H), 3.94 (d, *J* = 2.9 Hz, 1H), 3.94 – 3.85 (m, 2H), 3.83 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.77 (d, *J* = 11.7 Hz, 1H), 3.61 – 3.53 (m, 1H), 3.53 – 3.43 (m, 2H), 3.39 (dd, *J* = 8.7, 4.8 Hz, 1H), 3.24 (dd, *J* = 8.9, 4.7 Hz, 1H), 2.65 (t, *J* = 10.5 Hz, 1H), 1.51 (d, *J* = 7.0 Hz, 3H), 1.09 – 0.74 (m, 42H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1 (C_q), 148.2 (CH), 146.8 (C_q), 139.2 (C_q), 138.9 (C_q), 138.9 (C_q), 138.7 (C_q), 138.7 (C_q), 138.2 (C_q), 135.9 (CH), 134.4 (C_q), 128.7 (CH), 128.3 (CH), 128.2 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 127.8 (CH), 127.6 (CH), 127.6 (CH), 127.4 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 127.2 (CH), 126.9 (CH), 121.3 (CH), 121.2 (CH), 116.8 (CH), 103.0 (CH), 102.0 (CH), 82.6 (CH), 80.2 (CH), 79.3 (CH), 79.2 (CH), 78.4 (CH), 76.9 (CH), 75.9 (CH), 75.3 (CH_2), 75.1 (CH_2), 74.8 (CH_2), 74.3 (CH), 73.9 (CH), 73.5 (CH_2), 73.3 (CH_2), 72.9 (CH), 72.6 (CH_2), 68.5 (CH_2), 68.1 (CH_2), 67.4 (CH), 52.8 (CH), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 16.3 (CH_3), 12.5 (CH), 12.4 (CH) (2 C_q and 4 CH resonances of the OBn groups are overlapped).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1700, 1526, 1453, 1363, 1095, 882, 733, 697 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1461 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{88}H_{113}N_2O_{13}Si_2^+$ $[M+H]^+$ 1461.7776, found 1461.7769.

(2*R*,3*R*,4*R*,5*S*,6*R*)-4-(Benzyloxy)-6-[(benzyloxy)methyl]-3-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)-5-

{[(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-[(benzyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]oxy}tetrahydro-2*H*-pyran-2-carboxamide (159t)



The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4-(benzyloxy)-6-[(benzyloxy)methyl]-*N*-(quinolin-8-yl)-5-{[(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6 [(benzyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]oxy}tetrahydro-2*H*-pyran-2-carboxamide (**158k**) (51.0 mg, 0.05 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159t** (40.0 mg, 49%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.32 (s, 1H), 8.76 (dd, *J* = 5.7, 3.3 Hz, 1H), 8.57 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.41 – 7.35 (m, 4H), 7.34 – 7.27 (m, 14H), 7.23 – 7.19 (m, 7H), 7.18 – 7.10 (m, 6H), 5.13 (d, *J* = 10.9 Hz, 1H), 4.90 (td, *J* = 10.7, 10.3, 4.5 Hz, 3H), 4.83 – 4.71 (m, 5H), 4.63 (d, *J* = 7.8 Hz, 1H), 4.54 (dd, *J* = 11.5, 7.9 Hz, 2H), 4.37 – 4.25 (m, 3H), 4.22 – 4.14 (m, 2H), 4.10 – 3.94 (m, 6H), 3.79 (d, *J* = 11.5 Hz, 1H), 3.65 – 3.50 (m, 4H), 3.43 (t, *J* = 8.1 Hz, 1H), 3.37 – 3.28 (m, 2H), 2.83 (t, *J* = 10.3 Hz, 1H), 1.04 – 0.94 (m, 63H).

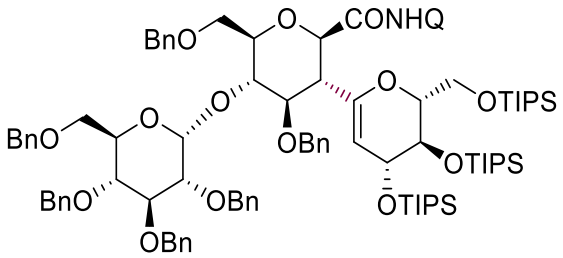
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.4 (C_q), 148.1 (CH), 148.1 (C_q), 139.6 (C_q), 138.7 (C_q), 138.7 (C_q), 138.7 (C_q), 138.5 (C_q), 138.2 (C_q), 136.0 (CH), 134.6 (C_q), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.6 (CH), 127.6 (CH), 127.5 (CH), 127.5 (CH), 127.4 (CH), 127.2 (CH), 127.1 (CH), 126.6 (CH), 121.4 (CH), 121.3 (CH), 116.7 (CH), 102.5 (CH), 101.6 (CH), 84.9 (CH), 83.2 (CH), 81.2 (CH), 79.6 (CH), 79.4 (CH), 78.6 (CH), 78.4 (CH), 76.9 (CH), 75.7 (CH_2), 75.2 (CH), 75.1 (CH_2), 74.8 (CH_2), 74.1 (CH_2), 73.6 (CH_2), 73.2 (CH_2), 70.5 (CH), 69.1 (CH_2), 68.4 (CH_2), 67.7 (CH), 62.0 (CH_2), 51.3 (CH), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 12.7 (CH), 12.6 (CH), 12.0 (CH) (1 CH_3 of resonances of TIPS and 2 C_q are overlapped).

IR (ATR): $\tilde{\nu}$ = 2942, 2864, 1705, 1525, 1453, 1363, 1068, 882, 697,681 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1633 (100) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{97}H_{133}N_2O_{14}Si_3^+$ $[M+H]^+$ 1633.9059, found 1633.9053.

(2*R*,3*R*,4*R*,5*S*,6*R*)-4-(Benzyloxy)-6-[(benzyloxy)methyl]-3-[(2*R*,3*R*,4*R*)-3,4 bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N* (quinolin-8-yl)-5-{[(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6 [(benzyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]oxy}tetrahydro-2*H*-pyran-2-carboxamide (159u)



The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4-(benzyloxy)-6-[(benzyloxy)methyl]-*N*-(quinolin-8-yl)-5-{[(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6 [(benzyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]oxy}tetrahydro-2*H*-pyran-2-carboxamide (**158l**) (102.0 mg, 0.10 mmol), 1-iodo-glucal (**59**) (222 mg, 0.30 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159u** (59.0 mg, 36%) as a syrup.

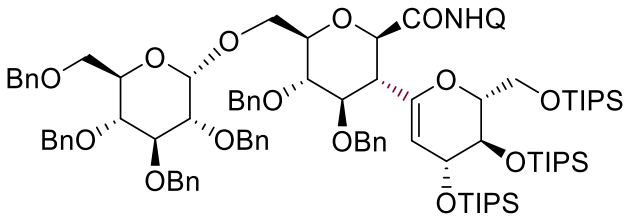
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.40 (s, 1H), 8.80 (t, *J* = 4.5 Hz, 1H), 8.61 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.38 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.30 – 7.22 (m, 15H), 7.21 – 7.15 (m, 9H), 7.15 – 7.10 (m, 4H), 5.59 (d, *J* = 3.5 Hz, 1H), 5.04 – 4.94 (m, 2H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.84 – 4.71 (m, 4H), 4.63 (d, *J* = 12.3 Hz, 1H), 4.52 (d, *J* = 12.3 Hz, 2H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.38 (d, *J* = 12.3 Hz, 1H), 4.34 – 4.20 (m, 6H), 4.17 (d, *J* = 3.4 Hz, 1H), 4.11 (dt, *J* = 4.3, 1.9 Hz, 1H), 4.02 (dd, *J* = 11.7, 3.8 Hz, 1H), 3.91 (dd, *J* = 9.6, 4.7 Hz, 2H), 3.88 – 3.80 (m, 2H), 3.75 – 3.67 (m, 1H), 3.66 – 3.50 (m, 2H), 3.41 (td, *J* = 10.3, 2.8 Hz, 2H), 3.02 (t, *J* = 9.8 Hz, 1H), 1.15 – 1.01 (m, 21H), 0.98 – 0.88 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.4 (C_q), 149.2 (C_q), 148.2 (CH), 138.9 (C_q), 138.8 (C_q), 138.7 (C_q), 138.7 (C_q), 138.6 (C_q), 138.1 (C_q), 138.0 (C_q), 136.1 (CH), 134.6 (C_q), 128.3 (CH), 128.3 (CH), 128.2 (CH), 128.2 (CH), 128.2 (CH), 127.9 (CH), 127.9 (CH), 127.9 (C_q), 127.8 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.5 (CH),

127.4 (CH), 127.3 (CH), 127.2 (CH), 126.9 (CH), 126.8 (CH), 121.4 (CH), 121.4 (CH), 116.8 (CH), 100.8 (CH), 96.7 (CH), 81.9 (CH), 81.9 (CH), 80.8 (CH), 79.8 (CH), 78.9 (CH), 78.7 (CH), 77.6 (CH), 75.5 (CH_2), 74.9 (CH_2), 73.8 (CH_2), 73.4 (CH_2), 72.9 (CH), 72.3 (CH_2), 71.8 (CH_2), 70.9 (CH), 69.8 (CH), 69.3 (CH_2), 68.4 (CH_2), 67.4 (CH), 61.8 (CH_2), 50.8 (CH), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 12.6 (CH), 12.5 (CH), 12.0 (CH) (2 CH_3 of resonances of TIPS are overlapped).

IR (ATR): $\tilde{\nu}$ = 2943, 2865, 1705, 1526, 1453, 1385, 1088, 883, 697,682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1633 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{97}H_{133}N_2O_{14}Si_3^+$ $[M+H]^+$ 1633.9059, found 1633.9063.

(2*R*,3*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)-6-({[(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-[(benzyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]oxy}methyl)tetrahydro-2*H*-pyran-2-carboxamide (159v)



The general procedure **D** was followed using (2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-*N*-(quinolin-8-yl)-6-({[(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-[(benzyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]oxy}methyl)tetrahydro-2*H*-pyran-2-carboxamide (**158m**) (51.0 mg, 0.05 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **159v** (45.0 mg, 56%) as a syrup.

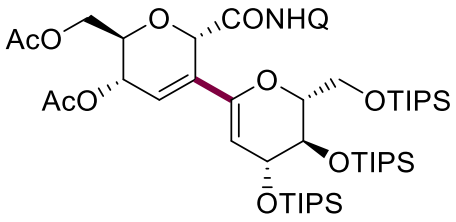
^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.42 (s, 1H), 8.85 – 8.79 (m, 1H), 8.63 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.40 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.28 (h, *J* = 2.6 Hz, 14H), 7.23 – 7.12 (m, 14H), 5.61 (d, *J* = 3.6 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.89 (t, *J* = 10.4 Hz, 2H), 4.82 (d, *J* = 3.1 Hz, 1H), 4.81 – 4.73 (m, 3H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.3 Hz, 2H), 4.47 (d, *J* = 11.0 Hz, 1H), 4.41 (d, *J* = 12.3 Hz, 1H), 4.34 (d, *J* = 3.0 Hz, 1H), 4.33 – 4.28 (m, 3H),

4.25 (t, *J* = 6.3 Hz, 1H), 4.22 – 4.17 (m, 1H), 4.16 – 4.12 (m, 1H), 4.05 (dd, *J* = 11.7, 3.8 Hz, 1H), 3.98 – 3.94 (m, 1H), 3.92 (t, *J* = 2.3 Hz, 1H), 3.90 – 3.83 (m, 2H), 3.75 (d, *J* = 8.5 Hz, 1H), 3.67 – 3.53 (m, 2H), 3.44 (td, *J* = 9.8, 8.7, 2.8 Hz, 2H), 3.05 (t, *J* = 9.8 Hz, 1H), 1.11 – 0.85 (m, 63H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 166.4 (C_q), 149.1 (C_q), 148.2 (CH), 138.9 (C_q), 138.7 (C_q), 138.7 (C_q), 138.7 (C_q), 138.6 (C_q), 138.1 (C_q), 138.0 (C_q), 136.1 (CH), 134.6 (C_q), 128.3 (CH), 128.3 (CH), 128.2 (CH), 128.2 (CH), 128.2 (CH), 127.9 (CH), 127.9 (CH), 127.8 (C_q), 127.8 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 126.9 (CH), 126.8 (CH), 121.4 (CH), 116.8 (CH), 100.8 (CH), 96.7 (CH), 81.9 (CH), 81.9 (CH), 80.8 (CH), 79.8 (CH), 78.9 (CH), 78.7 (CH), 77.6 (CH), 75.5 (CH_2), 74.9 (CH_2), 73.8 (CH_2), 73.4 (CH_2), 72.9 (CH), 72.3 (CH_2), 71.8 (CH_2), 70.9 (CH), 69.8 (CH), 69.3 (CH_2), 68.4 (CH_2), 67.4 (CH), 61.8 (CH_2), 50.8 (CH), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 12.6 (CH), 12.5 (CH), 12.0 (CH) (2 CH_3 of resonances of TIPS are overlapped).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1704, 1525, 1453, 1088, 882, 732, 697,681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1633 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{97}H_{133}N_2O_{14}Si_3^+$ $[M+H]^+$ 1633.9059, found 1633.9048.

[(2*′S*,4*R*,5*R*,5*′S*,6*R*,6*′R*)-5'-Acetoxy-2'-(quinolin-8-ylcarbamoyl)-4,5-bis[(triisopropylsilyl)oxy]-6-{[(triisopropylsilyl)oxy]methyl}-5,5',6,6'-tetrahydro-2*′H*,4*H*-[2,3'-bipyran]-6'-yl]methyl acetate (188)



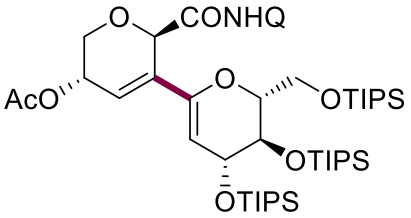
The general procedure **F** was followed using (2*R*,3*S*,4*R*,6*S*)-2-(acetoxymethyl)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (**187**) (47.4 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), AgOAc (33.4 mg, 0.20 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **188** (56.8 mg, 57%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.45 (s, 1H), 8.81 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.73 (dd, *J* = 5.3, 3.6 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.45 (dd, *J* = 8.2, 4.3 Hz, 1H), 6.41 (s, 1H), 5.51 (dt, *J* = 8.6, 2.4 Hz, 1H), 5.27 – 5.14 (m, 1H), 5.09 (d, *J* = 5.2 Hz, 1H), 4.48 – 4.17 (m, 4H), 4.13 – 4.02 (m, 2H), 3.91 (d, *J* = 6.0 Hz, 2H), 2.09 (s, 3H), 2.01 (s, 3H), 1.13 – 1.00 (m, 21H), 1.00 – 0.87 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9 (C_q), 170.3 (C_q), 166.6 (C_q), 148.3 (CH), 147.6 (C_q), 138.7 (C_q), 136.2 (CH), 134.3 (C_q), 134.2 (C_q), 127.9 (C_q), 127.2 (CH), 123.4 (CH), 121.8 (CH), 121.6 (CH), 116.7 (CH), 99.1 (CH), 80.9 (CH), 75.0 (CH), 70.9 (CH), 69.9 (CH), 66.5 (CH), 64.5 (CH), 62.8 (CH_2), 61.4 (CH_2), 21.0 (CH_3), 20.7 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.5 (CH), 12.4 (CH), 11.9 (CH). (1 CH_3 resonance of TIPS group is overlapped).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1746, 1523, 1462, 1234, 1085, 1052, 882, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1019 (65) $[M+Na]^+$, 997 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{89}N_2O_{10}Si_3^+$ $[M+H]^+$ 997.5820, found 997.5816.

(2'*R*,4*R*,5*R*,5'*S*,6*R*)-2'-(Quinolin-8-ylcarbamoyl)-4,5-bis[(triisopropylsilyl)oxy]-6-{[(triisopropylsilyl)oxy]methyl}-5,5',6,6'-tetrahydro-2'*H*,4*H*-[2,3'-bipyran]-5'-yl acetate (190)



The general procedure **D** was followed using (3*R*,4*S*,6*R*)-6-(quinolin-8-ylcarbamoyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (**189**) (37.2 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 120 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **190** (27.7 mg, 30%) as a syrup.

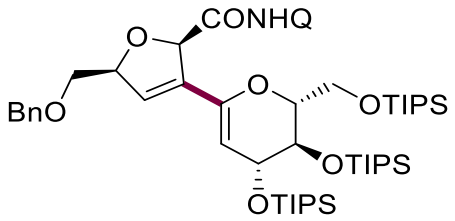
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.39 (s, 1H), 8.81 (t, *J* = 4.3, 1.7 Hz, 1H), 8.74 (t, *J* = 4.5 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.51 (d, *J* = 4.5 Hz, 2H), 7.44 (t, *J* = 8.3, 4.5 Hz, 1H), 6.49 (d, *J* = 5.2 Hz, 1H), 5.26 (d, *J* = 5.2 Hz, 2H), 5.17 (d, *J* = 5.2 Hz, 1H), 4.32 (d, *J* = 5.9 Hz, 1H), 4.18 (dd, *J* = 13.1, 3.2 Hz, 1H), 4.13 – 4.06 (m, 2H), 4.03 –

3.94 (m, 2H), 3.89 (dd, *J* = 10.9, 5.2 Hz, 1H), 2.12 (s, 3H), 1.11 – 1.00 (m, 21H), 1.00 – 0.92 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 170.6 (C_q), 166.5 (C_q), 148.3 (CH), 148.1 (C_q), 138.6 (C_q), 136.2 (C_q), 136.1 (CH), 134.2 (C_q), 127.9 (C_q), 127.2 (CH), 121.7 (CH), 121.5 (CH), 120.8 (CH), 116.7 (CH), 98.9 (CH), 81.2 (CH), 74.2 (CH), 69.6 (CH), 66.2 (CH), 65.3 (CH_2), 64.3 (CH), 61.9 (CH_2), 21.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.5 (CH), 12.4 (CH), 12.0 (CH). (2 CH_3 resonances of TIPS group are overlapped).

IR (ATR): $\tilde{\nu}$ = 3053, 2986, 1711, 1422, 1264, 1217, 896, 735, 704, 669 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1850 (100) $[2M+H]^+$, 947 (71) $[M+Na]^+$, 925 (30) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{50}H_{84}N_2NaO_8Si_3^+$ $[M+Na]^+$ 947.5428, found 947.5416.

(2*R*,5*S*)-5-[(Benzyloxy)methyl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)-2,5-dihydrofuran-2-carboxamide (192)



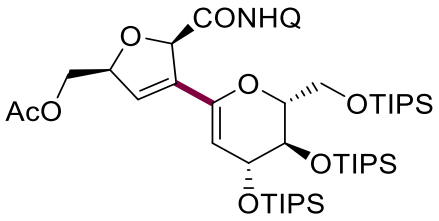
The general procedure **G** was followed using (2*R*,4*S*,5*R*)-4-(benzyloxy)-5-[(benzyloxy)methyl]-*N*-(quinolin-8-yl)tetrahydrofuran-2-carboxamide (**191**) (46.8 mg, 0.10 mmol), 1-iodo-glucal (**59**) (111.0 mg, 0.15 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), AgOAc (33.4 mg, 0.20 mmol), HOAc (12.0 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **192** (54.0 mg, 56%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 10.54 (s, 1H), 8.78 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.69 (dd, *J* = 5.9, 3.1 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.44 – 7.40 (m, 1H), 7.40 – 7.36 (m, 3H), 7.35 – 7.29 (m, 2H), 6.37 (d, *J* = 1.9 Hz, 1H), 5.62 (d, *J* = 5.4 Hz, 1H), 5.57 (d, *J* = 5.6 Hz, 1H), 5.45 (dd, *J* = 5.6, 1.9 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.33 – 4.23 (m, 1H), 4.14 – 4.00 (m, 3H), 3.81 (dd, *J* = 11.3, 3.7 Hz, 1H), 3.65 (d, *J* = 5.4 Hz, 2H), 1.14 – 1.01 (m, 42H), 0.87 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8 (C_q), 148.4 (CH), 143.5 (C_q), 138.7 (C_q), 138.1 (C_q), 136.9 (C_q), 136.0 (CH), 134.3 (C_q), 128.4 (CH), 127.8 (CH), 127.8 (CH), 127.7 (CH), 127.2 (CH), 126.1 (CH), 121.4 (CH), 116.4 (CH), 103.0 (CH), 86.6 (CH), 86.5 (CH), 81.1 (CH), 73.5 (CH_2), 72.9 (CH_2), 69.7 (CH), 66.0 (CH), 62.1 (CH_2), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 12.5 (CH), 12.4 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1711, 1526, 1422, 1264, 1216, 896, 736, 704 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1946 (100) $[2M+H]^+$, 973 (75) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{55}H_{89}N_2O_7Si_3^+$ $[M+H]^+$ 973.5972, found 973.5948.

[(2*S*,5*R*)-4-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2H-pyran-6-yl]-5-(quinolin-8-ylcarbamoyl)-2,5-dihydrofuran-2-yl]methyl acetate (194)



The general procedure **G** was followed using [(2*R*,3*S*,5*R*)-3-acetoxy-5-(quinolin-8-ylcarbamoyl)tetrahydrofuran-2-yl]methyl acetate (**193**) (19.0 mg, 0.05 mmol), 1-iodo-glucal (**59**) (55.0 mg, 0.075 mmol), $Pd(OAc)_2$ (2.2 mg, 20 mol %), Ag_2O (23.2 mg, 0.10 mmol), HOAc (6.0 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL) at 100 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 5/1) yielded **194** (34.5 mg, 75%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.49 (s, 1H), 8.79 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.68 (dd, *J* = 5.6, 3.4 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.42 (dd, *J* = 8.3, 4.3 Hz, 1H), 6.32 (t, *J* = 1.9 Hz, 1H), 5.62 – 5.53 (m, 2H), 5.46 (dd, *J* = 5.6, 2.0 Hz, 1H), 4.29 (dd, *J* = 11.5, 4.2 Hz, 2H), 4.19 (dd, *J* = 11.5, 6.0 Hz, 1H), 4.11 – 4.05 (m, 2H), 4.03 (q, *J* = 1.9 Hz, 1H), 3.81 (dd, *J* = 11.3, 3.7 Hz, 1H), 2.12 (s, 3H), 1.25 – 0.95 (m, 42H), 0.95 – 0.73 (m, 21H).

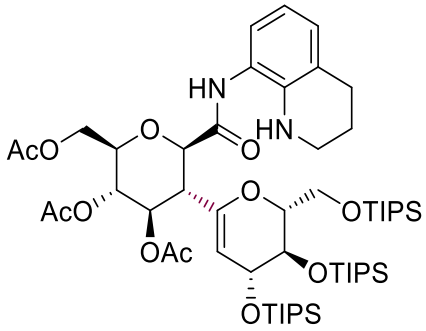
^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.8 (C_q), 168.3 (C_q), 148.4 (C_q), 143.3 (CH), 138.6 (C_q), 137.8 (C_q), 136.1 (CH), 134.2 (C_q), 127.8 (C_q), 127.2 (CH), 124.8 (CH), 121.5 (CH), 121.4 (CH), 116.4 (CH), 103.3 (CH), 86.7 (CH), 85.1 (CH), 81.2 (CH), 69.6 (CH),

66.1 (CH_2), 65.9 (CH), 62.1 (CH_2), 20.8 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 12.4 (CH), 12.4 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1747, 1695, 1530, 1462, 1222, 1064, 882, 790, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1872 (70) $[2M+Na]^+$, 947 (100) $[M+Na]^+$, 925 (20) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{50}H_{84}N_2NaO_8Si_3^+$ $[M+Na]^+$ 947.5428, found 947.5408.

5.3.2.2 Amide Transformation

(2*R*,3*S*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-5-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-6-[(1,2,3,4-tetrahydroquinolin-8-yl)carbamoyl]tetrahydro-2*H*-pyran-3,4-diyl diacetate (195)



Compound **159aa** (53.0 mg, 0.05 mmol, 1.0 equiv) was dissolved in MeOH (3.0 mL) and EtOAc (15 mL), then Pd/C (75.0 mg, 10 mol %) was added under 1 atm. H_2. The reaction was allowed to stir for 24 h at ambient temperature. The solvent was filtered and then was evaporated *in vacuo*. The residue was purified by column chromatography to give product **195** (46.6 mg, 87% yield).

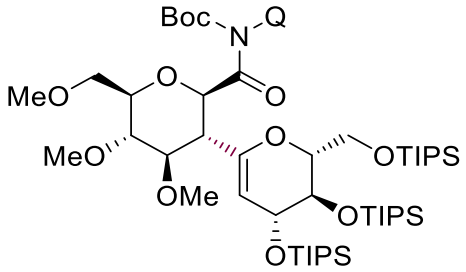
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.4 Hz, 1H), 6.57 (dd, *J* = 7.8 Hz, 7.4 Hz, 1H), 5.47 (dd, *J* = 10.0 Hz, 9.7 Hz, 1H), 5.04 (dd, *J* = 9.7 Hz, 9.6 Hz, 1H), 4.86 (d, *J* = 4.8 Hz, 1H), 4.37 – 4.16 (m, 5H), 4.11 – 3.98 (m, 2H), 3.86 – 3.74 (m, 1H), 3.62 (dd, *J* = 9.7, 5.1 Hz, 1H), 3.28 (dd, *J* = 7.7, 3.9 Hz, 2H), 2.86 – 2.64 (m, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.89 – 1.83 (m, 2H), 1.09 – 1.00 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.8 (C_q), 169.9 (C_q), 169.8 (C_q), 165.7 (C_q), 146.1 (C_q), 138.9 (C_q), 127.3 (CH), 123.8 (C_q), 123.0 (CH), 122.5 (C_q), 116.9 (CH), 102.3 (CH), 80.1 (CH), 77.9 (CH), 75.2 (CH), 71.5 (CH), 69.6 (CH), 69.5 (CH), 66.6 (CH), 62.3 (CH_2), 60.5 (CH_2), 50.2 (CH), 42.2 (CH_2), 27.4 (CH_2), 21.9 (CH_2), 20.8 (CH_3), 20.7

(CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 12.5 (CH), 12.4 (CH), 11.9 (CH) (1 CH_3 resonances of the OAc group is overlapped).

IR (ATR): $\tilde{\nu}$ = 2942, 2866, 1753, 1462, 1365, 1242, 1089, 1063, 882, 680 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2122 (100) $[2M+H]^+$, 1083 (40) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{55}H_{96}N_2NaO_{12}Si_3^+$ $[M+Na]^+$ 1083.6163, found 1083.6151.

Tert-butyl [(2*R*,3*R*,4*R*,5*S*,6*R*)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4,5-dimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-carbonyl](quinolin-8-yl)carbamate (159bb')



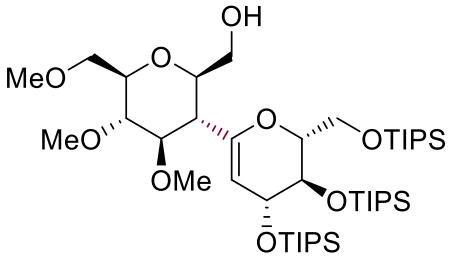
Compound **159bb** (97.3 mg, 0.1 mmol, 1.0 equiv) was dissolved in CH_3CN (1.5 mL), and then DMAP (13.0 mg, 0.35 mmol, 1.08 equiv), Boc_2O (35.0 mg, 0.16 mmol, 1.6 equiv) was added. The reaction was allowed to stir for 24 h at room temperature. The solvent was then evaporated *in vacuo* and the residue purified by column chromatography to give product **159bb'** (99.8 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 4.1 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 8.3, 4.1 Hz, 1H), 5.22 (d, *J* = 10.6 Hz, 1H), 4.85 (d, *J* = 5.0 Hz, 1H), 4.23 (d, *J* = 6.2 Hz, 1H), 4.11 – 4.05 (m, 1H), 4.04 – 3.98 (m, 1H), 3.95 (d, *J* = 6.2 Hz, 2H), 3.66 – 3.52 (m, 9H), 3.42 (s, 3H), 3.31 (d, *J* = 9.9 Hz, 1H), 3.22 (t, *J* = 9.3 Hz, 1H), 2.78 (t, *J* = 10.6 Hz, 1H), 1.25 (s, 9H), 1.07 – 0.85 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.9 (C_q), 152.1 (C_q), 149.7 (CH), 148.9 (C_q), 144.3 (C_q), 136.9 (C_q), 135.5 (CH), 128.9 (CH), 128.6 (C_q), 127.5 (CH), 125.9 (CH), 121.1 (CH), 100.7 (CH), 83.6 (CH), 82.1 (C_q), 80.6 (CH), 80.5 (CH), 79.7 (CH), 75.6 (CH), 71.4 (CH_2), 70.0 (CH), 67.0 (CH), 61.7 (CH_2), 60.3 (CH_3), 60.1 (CH_3), 59.6 (CH_3), 49.8 (CH), 27.6 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.5 (CH), 12.4 (CH), 11.9 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1726, 1686, 1512, 1466, 1265, 1067, 882, 710, 689 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 2146 (95) $[2M+H]^+$, 1073 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{57}H_{101}N_2O_{11}Si_3^+$ $[M+H]^+$ 1073.6708, found 1073.6711.

[(2*R*,3*S*,4*R*,5*S*,6*R*)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4,5-dimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl]methanol (196)



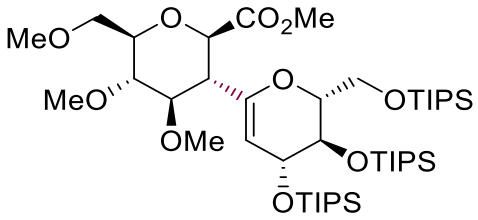
$LiAlH_4$ (15.1 mg in 125 uL THF) was added in flask at 0 °C under N_2, and then compound **159bb** (106.1 mg, 0.1 mmol, 1.0 equiv) in THF (0.45 mL) was dropwisely added at 0 °C. The reaction was allowed to stir for 2 h at 0 °C. The solution was quenched with NH_4Cl at 0 °C, and stir for 30 min at room temperature. The solvent was then extracted and evaporated in vacuo and the residue purified by column chromatography to give product **196** (70.2 mg, 84% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.78 (dd, *J* = 5.5, 1.5 Hz, 1H), 4.30 – 4.22 (m, 1H), 4.09 – 3.97 (m, 3H), 3.93 (dd, *J* = 11.1, 5.1 Hz, 1H), 3.72 (d, *J* = 9.7 Hz, 1H), 3.68 – 3.55 (m, 5H), 3.55 (s, 3H), 3.53 (s, 3H), 3.39 (s, 3H), 3.33 (m, 1H), 3.11 (t, *J* = 9.3 Hz, 1H), 2.16 (t, *J* = 10.2 Hz, 1H), 1.05 (m, 63H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.1 (C_q), 99.6 (CH), 82.9 (CH), 81.3 (CH), 81.0 (CH), 78.5 (CH), 77.5 (CH), 71.8 (CH_2), 69.4 (CH), 65.8 (CH), 63.4 (CH_2), 61.9 (CH_2), 60.3 (CH_3), 60.2 (CH_3), 59.2 (CH_3), 50.7 (CH), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.3 (CH), 12.0 (CH) (1 CH_3 and 1 CH resonances of the TIPS groups are overlapped).

IR (ATR): $\tilde{\nu}$ = 2943, 2865, 1466, 1382, 1112, 1067, 999, 980, 882, 682 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 850 (100) $[M+NH_4]^+$, 833 (35) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{43}H_{89}O_9Si_3^+$ $[M+H]^+$ 833.5809, found 833.5805.

Methyl (2*R*,3*R*,4*R*,5*S*,6*R*)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4,5-dimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-carboxylate (197)



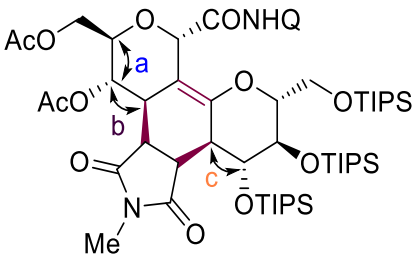
Compound **159bb** (62.2 mg, 0.058 mmol) was dissolved in MeOH (1.5 mL), K_2CO_3 (16.0 mg, 0.2 mmol) was added under N_2. The reaction was allowed to stir for 12 h at room temperature. The solvent was then evaporated *in vacuo* and the residue purified by column chromatography to give product **197** (32.4 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.76 (d, J = 5.1 Hz, 1H), 4.23 (t, J = 5.5 Hz, 1H), 4.11 (d, J = 10.8 Hz, 1H), 4.06 (t, J = 1.9 Hz, 1H), 3.99 – 3.89 (m, 3H), 3.64 (s, 3H), 3.62 – 3.57 (m, 3H), 3.55 (s, 3H), 3.52 (s, 3H), 3.44 – 3.29 (m, 4H), 3.16 (t, J = 9.2 Hz, 1H), 2.56 (t, J = 10.8 Hz, 1H), 1.38 – 0.87 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.8 (C_q), 147.9 (C_q), 100.8 (CH), 82.1 (CH), 81.2 (CH), 80.7 (CH), 79.1 (CH), 77.5 (CH), 71.5 (CH_2), 69.8 (CH), 66.4 (CH), 61.9 (CH_2), 60.2 (CH_3), 60.1 (CH_3), 59.3 (CH_3), 51.9 (CH_3), 50.7 (CH), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.4 (CH), 12.4 (CH), 12.0 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2866, 1756, 1675, 1462, 1383, 1107, 882, 756, 681 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1744 (100) $[2M+Na]^+$, 861 (95) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{89}O_{10}Si_3^+$ $[M+H]^+$ 861.5758, found 861.5749.

[(2*R*,3*R*,4*R*,4a*R*,4b*S*,7a*R*,7b*R*,8*S*,9*R*,11*S*)-8-Acetoxy-6-methyl-5,7-dioxo-11-(quinolin-8-ylcarbamoyl)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4,4a,4b,5,6,7,7a,7b,8,9,11-dodecahydro-2*H*-dipyrano[3,2-*e*:3',4'-*g*]isoindol-9-yl]methyl acetate (198)



^3Ja = 10.2 Hz
^3Jb = 10.1 Hz
^3Jc = 11.4 Hz

Compound **188** (23.8 mg, 0.024 mmol, 1.0 equiv) was dissolved in toluene (0.23 mL) and then *N*-methyl maleic imide (4.0 mg, 1.5 equiv) was added. The reaction was allowed to stir 24 h at RT. The solvent was then evaporated *in vacuo* and the residue was purified by column chromatography to give product **198** (14.0 mg, 53% yield).

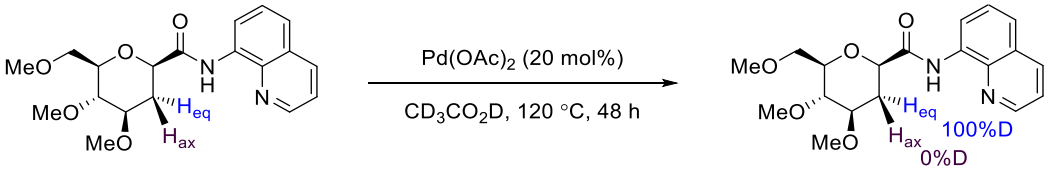
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.57 (s, 1H), 8.88 – 8.56 (m, 2H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.60 – 7.47 (m, 2H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.75 (s, 1H), 4.94 (t, *J* = 10.1 Hz, 1H), 4.82 (d, *J* = 3.8 Hz, 1H), 4.41 (dd, *J* = 12.5, 3.8 Hz, 1H), 4.32 (d, *J* = 3.9 Hz, 1H), 4.27 – 4.18 (m, 3H), 4.08 (d, *J* = 6.3 Hz, 2H), 3.47 (dd, *J* = 11.4, 8.6 Hz, 1H), 3.17 (dt, *J* = 10.2, 3.4 Hz, 1H), 3.06 (dd, *J* = 8.6, 3.3 Hz, 1H), 2.94 (s, 3H), 2.50 (dd, *J* = 11.4, 3.1 Hz, 1H), 2.07 (s, 6H), 1.20 – 1.10 (m, 21H), 1.08 – 0.90 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.7 (C_q), 177.6 (C_q), 171.4 (C_q), 170.8 (C_q), 167.8 (C_q), 148.9 (C_q), 148.3 (CH), 138.8 (C_q), 136.2 (CH), 134.2 (C_q), 127.9 (C_q), 127.2 (CH), 121.8 (CH), 121.5 (CH), 116.8 (CH), 108.6 (C_q), 86.4 (CH), 73.3 (CH), 73.0 (CH), 71.2 (CH), 70.8 (CH), 69.8 (CH), 65.4 (CH_2), 62.6 (CH_2), 42.5 (CH), 41.8 (CH), 41.7 (CH), 34.9 (CH), 24.6 (CH_3), 21.1 (CH_3), 20.8 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 17.8 (CH_3), 12.4 (CH), 12.2 (CH), 12.0 (CH). (1 CH_3 of resonances of TIPS is overlapped)

IR (ATR): $\tilde{\nu}$ = 2984, 1737, 1372, 1234, 1098, 1043, 938, 847, 634, 607 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1130 (15) $[M+Na]^+$, 1108 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{58}H_{94}N_3O_{12}Si_3^+$ $[M+H]^+$ 1108.6140, found 1108.6140.

5.3.2.3 Mechanistic Investigations

5.3.2.3.1 H/D Exchange Experiment

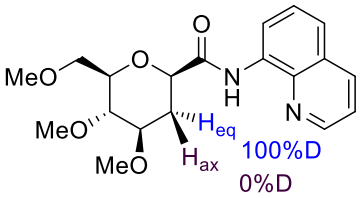


158bb **[D]-158bb,** 90%

A solution of substrate **158bb** (36.0 mg, 0.1 mmol) and $Pd(OAc)_2$ (4.4 mg, 20 mol%) in deuterated acetic acid (CD_3CO_2D) (1.0 mL) was stirred at 120 °C for 24 h. Then, the reaction was filtrated and concentrated *in vacuo*. The same procedure was repeated with the same reaction conditions. After another 24 h, the product was purified by column chromatography (*n*hexane/EtOAc 3:1), yielding deuterated substrate **[D]-**

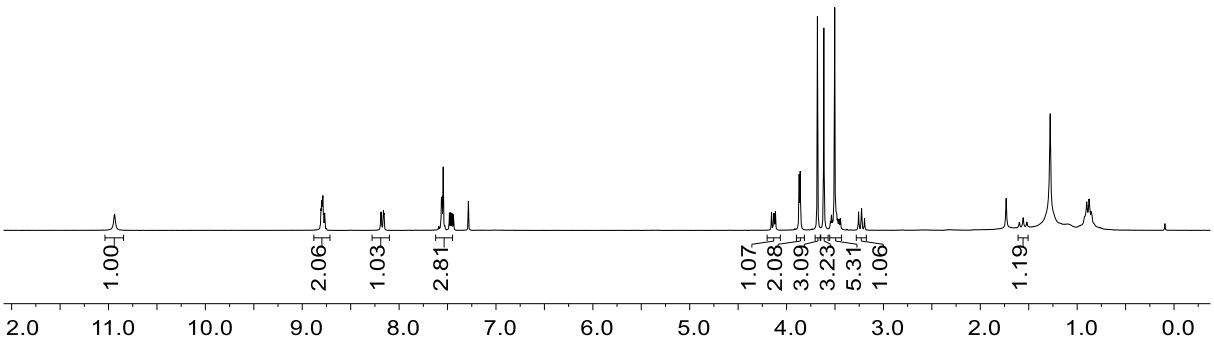
158bb in 90% yield The deuterium incorporation was determined by ^{1}H NMR spectroscopy. This result suggests that the equatorial hydrogen is preferentially accessible than the axial hydrogen, thus the 2,3-*trans*-C–H activation manifold is proposed for the palladium-catalyzed glycosylation of 2-deoxyl sugars.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.91 (s, 1H), 8.83 – 8.71 (m, 2H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.59 – 7.48 (m, 2H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.17 – 4.04 (m, 1H), 3.84 (d, *J* = 3.2 -Hz, 2H), 3.65 (s, 3H), 3.59 (s, 3H), 3.53 – 3.39 (m, 5H), 3.24 – 3.15 (m, 1H), 1.55 (q, *J* = 11.7 Hz, 1H).

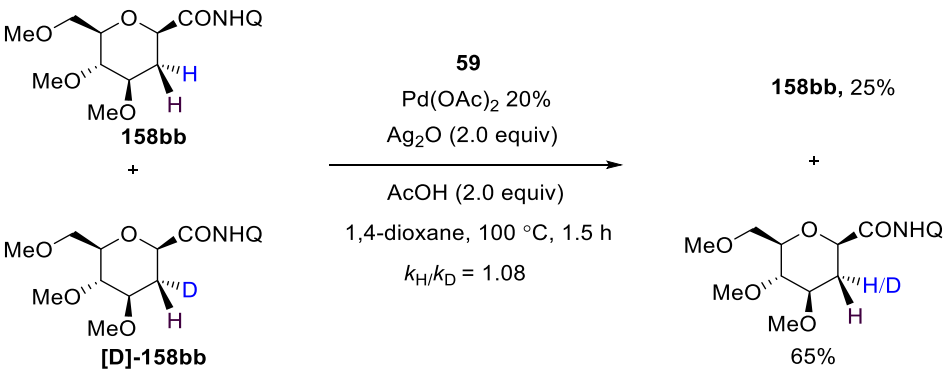


[D]-S1e

$CDCl_3$, 300 MHz

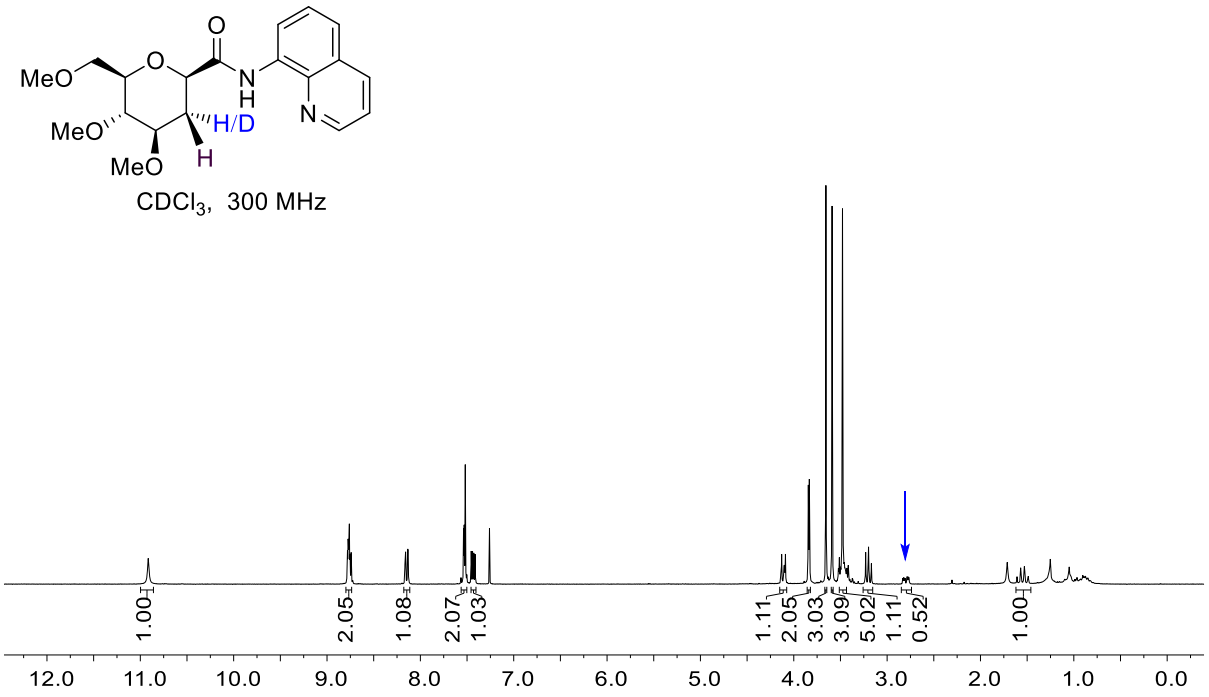


5.3.2.3.2 KIE Experiment

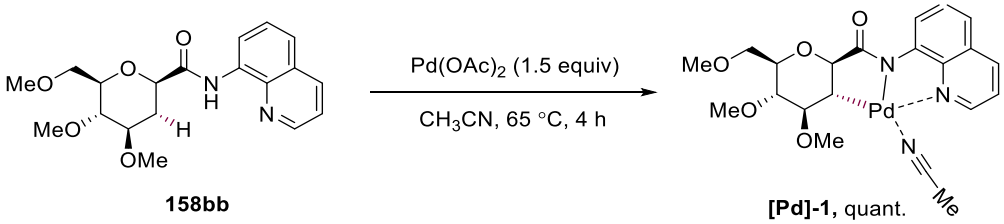


Deuterated substrate **[D]-158bb** (18.0 mg, 0.05 mmol) and substrate **158bb** (18.0 mg, 0.05 mmol), $Pd(OAc)_2$ (4.4 mg, 20 mol %), Ag_2O (46.0 mg, 0.2 mmol), and HOAc (12.0 mg, 0.2 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, a solution of 1-iodo glycal **59** (110 mg, 0.15 mmol) in 1,4-dioxane (1.0 mL) was added. The resulting reaction mixture was stirred at 100 ºC for 1.5 h. After cooling to ambient temperature, the mixture was diluted with CH_2Cl_2 (10 mL) and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel afforded the product **1bb** in 25% yield and isolated substrates in 65% yield. A k_H/k_D = 1.08 was determined by ^{1}H NMR spectroscopy based on the mixture of reisolated substrates **158bb** and **[D]-158bb**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.91 (s, 1H), 9.25 – 8.61 (m, 2H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.20 – 4.04 (m, 1H), 3.84 (d, *J* = 3.2 Hz, 2H), 3.66 (s, 3H), 3.59 (s, 3H), 3.54 – 3.31 (m, 5H), 3.20 (dd, *J* = 9.7, 8.7 Hz, 1H), 2.80 (ddd, *J* = 13.1, 4.9, 2.3 Hz, 0.52H), 1.55 (q, *J* = 12.8, 12.3 Hz, 1H).

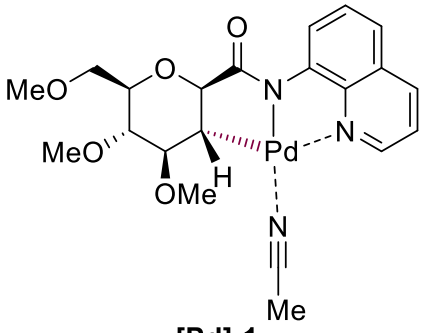


5.3.2.3.3 Palladacycle Intermediates Synthesis



158bb **[Pd]-1,** quant.

A solution of substrate **158bb** (36 mg, 0.10 mmol) and $Pd(OAc)_2$ (33 mg, 0.15 mmol) in CH_3CN (1.0 mL) was stirred at 65 ºC for 4 h. Then, the reaction mixture was filtrated through the Celite and concentrated, yielding palladacycle intermediate **[Pd]-1** in quantitative yield. This intermediate was fully characterized by ^{1}H NMR, ^{13}C NMR and 2D NMR spectra. The 2,3-*trans*- C–H activation manifold was demonstrated by the isolated intermediate.

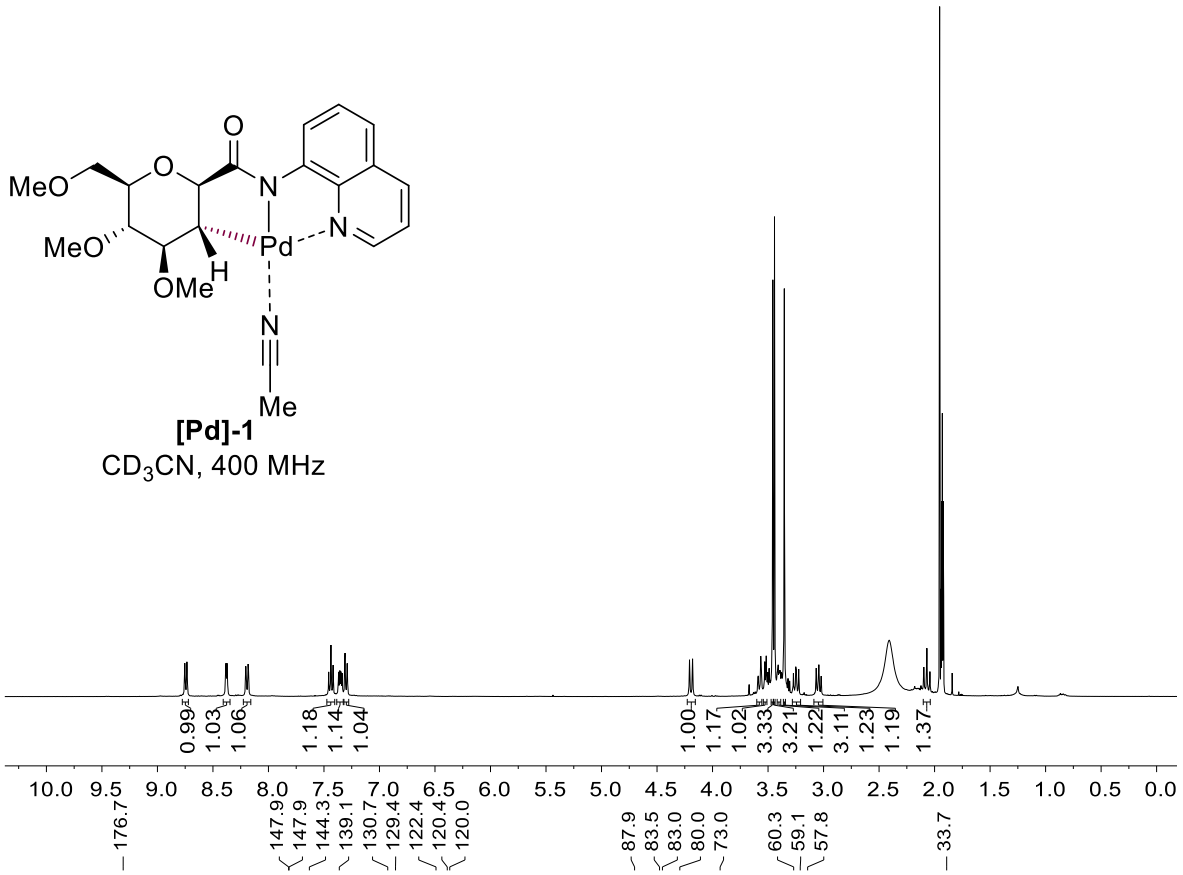


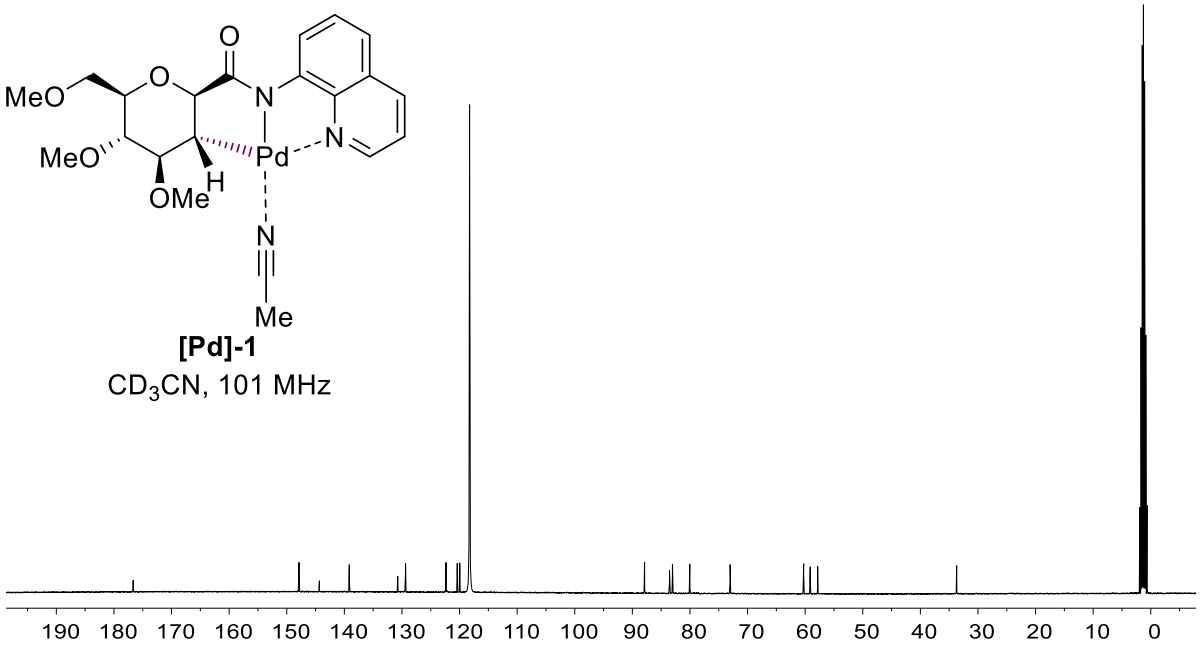
[Pd]-1

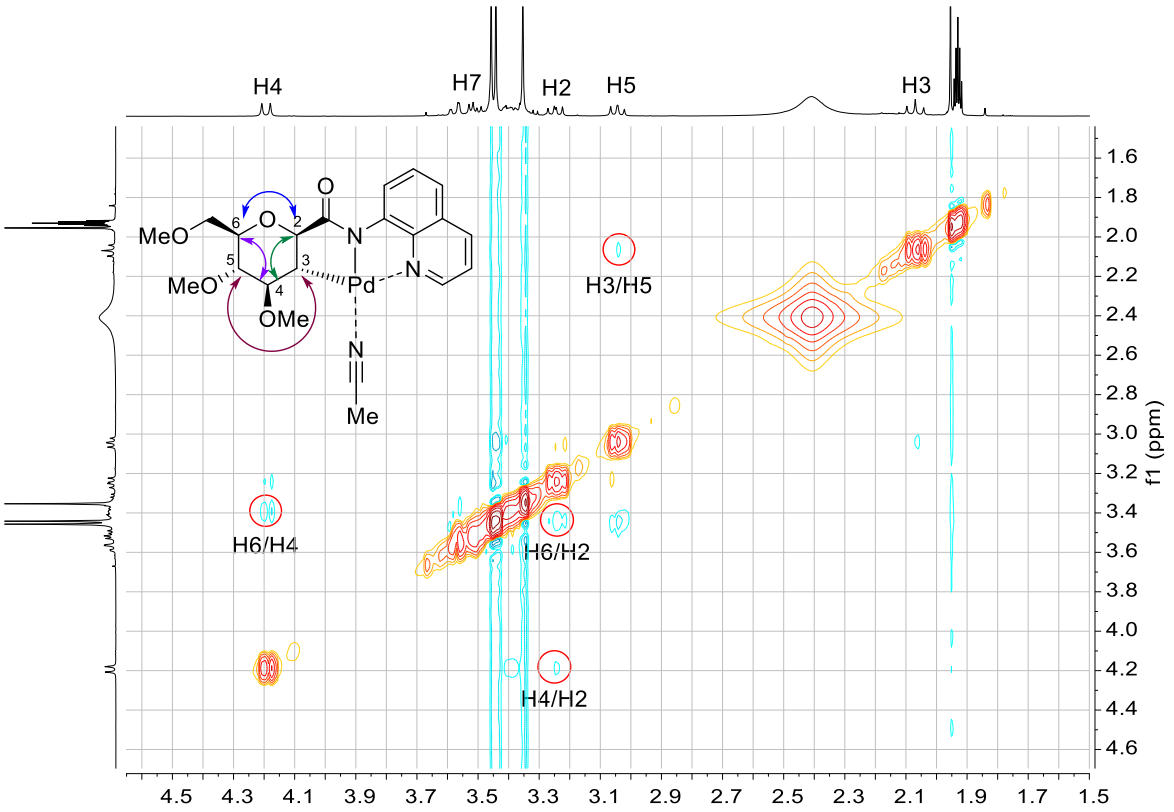
^{1}H NMR (400 MHz, CD_3CN): δ = 8.74 (dd, *J* = 7.8, 1.3 Hz, 1H), 8.38 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.35 (dd, *J* = 8.3, 4.6 Hz, 1H), 7.30 (dd, *J* = 7.9, 1.1 Hz, 1H), 4.19 (d, *J* = 11.1 Hz, 1H), 3.58 (dd, *J* = 10.5, 1.9 Hz, 1H), 3.51 (dd, *J* = 10.5, 5.4 Hz, 1H), 3.46 (s, 3H), 3.44 (s, 3H), 3.42 – 3.39 (m, 1H), 3.35 (s, 3H), 3.25 (dd, *J* = 10.8, 8.2 Hz, 1H), 3.04 (dd, *J* = 9.7, 8.2 Hz, 1H), 2.07 (t, *J* = 11.0 -Hz, 1H).

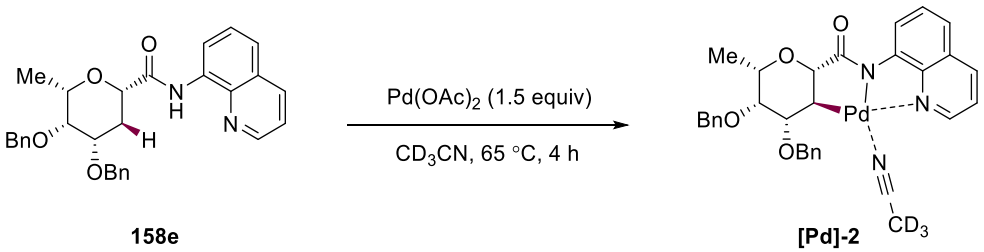
^{13}C NMR (101 MHz, CD_3CN): δ = 176.7 (C_q), 147.9 (C_q), 147.9 (CH), 144.3 (C_q), 139.1 (CH), 130.7 (C_q), 129.4 (CH), 122.4 (CH), 120.4 (CH), 120.0 (CH), 87.9 (CH), 83.6 (CH), 83.0 (CH), 80.0 (CH), 73.0 (CH), 60.3 (CH_3), 59.1 (CH_3), 57.8 (CH_3), 33.7 (CH).

IR (ATR): $\tilde{\nu}$ = 2929, 2829, 1617, 1571, 1501, 1464, 1397, 1119, 1074, 825, 785 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 487 (50) $[M+Na]^+$, 465 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{19}H_{23}N_2O_5Pd^+$ $[M+H]^+$ 465.0642, found 465.0633.


MeO
O
O
N
MeO
Pd
N
H
OMe
N
Me
[Pd]-1
CD3CN, 400 MHz
0.99
1.03
1.06
1.18
1.14
1.04
1.00
1.17
1.02
3.33
3.21
1.22
3.11
1.23
1.19
1.37
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
176.7
147.9
147.9
144.3
139.1
130.7
129.4
122.4
120.4
120.0
87.9
83.5
83.0
80.0
73.0
60.3
59.1
57.8
33.7


MeO
O
O
N
MeO
Pd
N
H
OMe
N
Me
[Pd]-1
CD3CN, 101 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



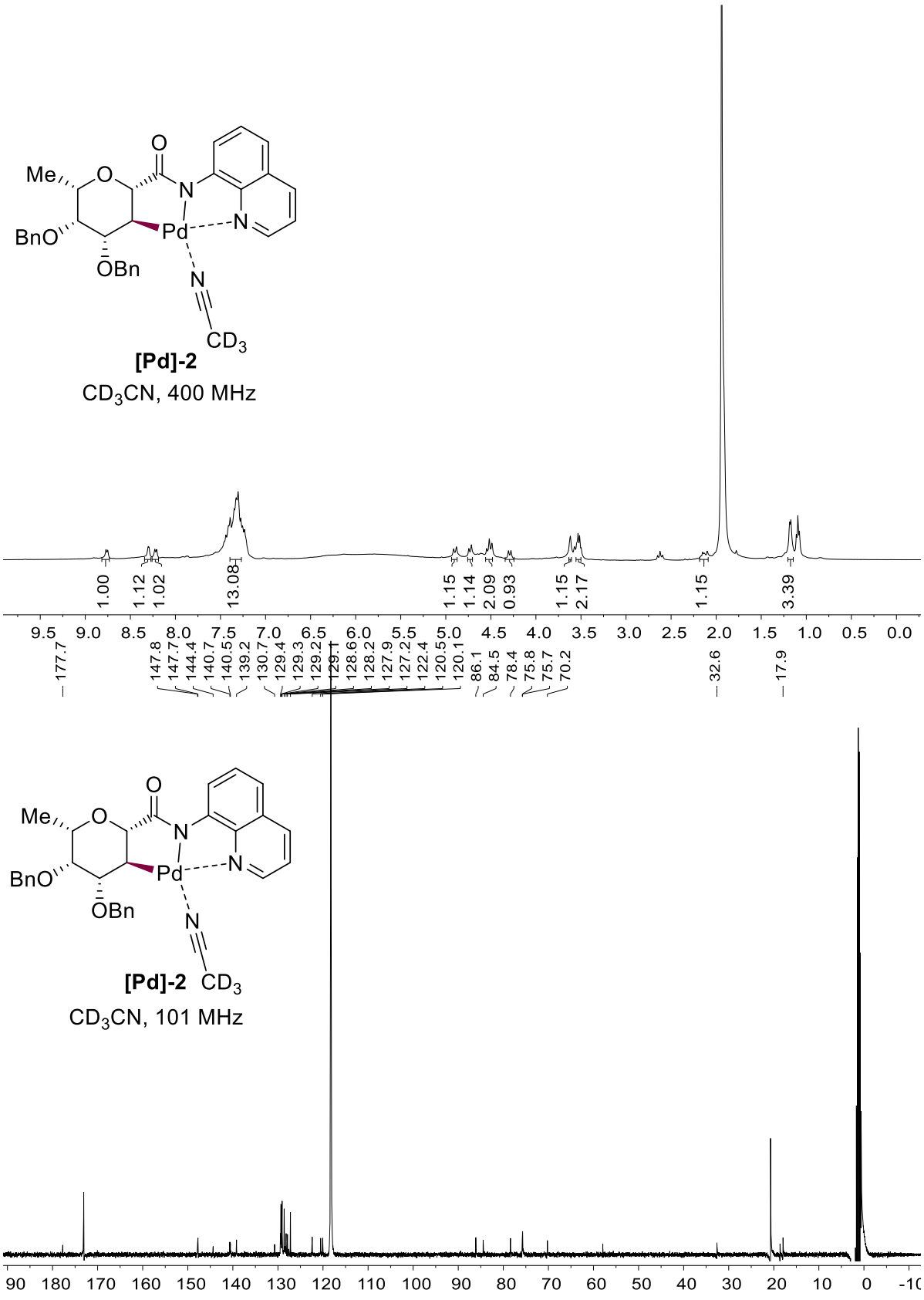


158e **[Pd]-2**

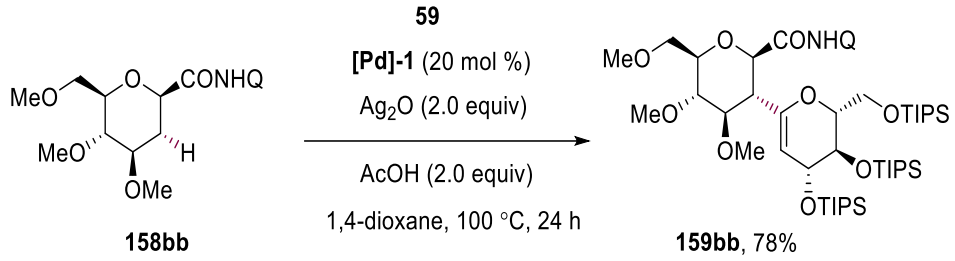
A solution of substrate **158e** (48.2 mg, 0.1 mmol) and $Pd(OAc)_2$ (33 mg, 0.15 mmol) in CD_3CN (1.0 mL) was stirred at 65 ºC for 4 h. The reaction mixture was filtrated through the Celite and this intermediate **[Pd]-2** was directly characterized by ^1H NMR and ^{13}C NMR spectra.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 7.9 Hz, 1H), 8.30 (d, J = 4.5 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 7.56 – 7.14 (m, 13H), 4.90 (d, J = 12.7 Hz, 1H), 4.73 (d, J = 11.1 Hz, 1H), 4.64 -– 4.40 (m, 2H), 4.29 (d, J = 11.2 Hz, 1H), 3.72 – 3.59 (m, 1H), 3.58 – 3.43 (m, 2H), 2.22 – 2.06 (m, 1H), 1.18 (d, J = 6.2 Hz, 3H).

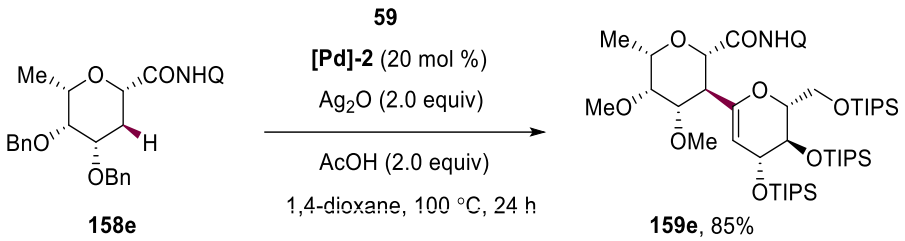
^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.7 (C_q) , 147.8 (C_q), 147.8 (CH), 144.4 (C_q), 140.7 (C_q), 140.5 (C_q), 139.2 (CH), 130.7 (C_q), 129.4 (CH), 129.3 (CH), 129.2 (CH), 129.1 (CH), 128.6 (CH), 128.2 (CH), 127.9 (CH), 127.2 (CH), 122.4 (CH), 120.5 (CH), 120.1 (CH), 86.1 (CH), 84.5 (CH), 78.4 (CH), 75.8 (CH), 75.7 (CH_2), 70.2 (CH_2), 32.6 (CH), 17.9 (CH_3).



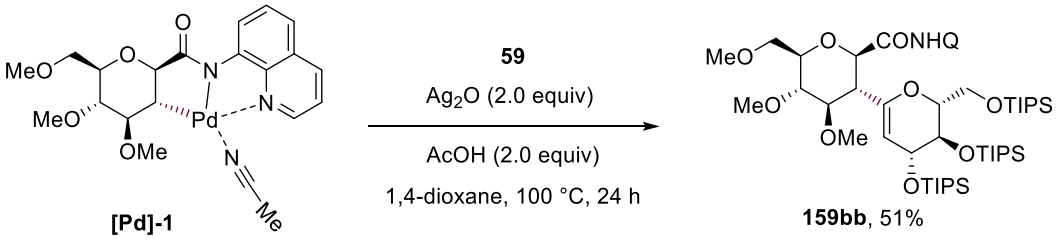
5.3.2.3.4 Catalytic and Stoichiometric Reactions of [Pd]-1 and [Pd]-2



A suspension of deoxysugar **158bb** (0.10 mmol, 1.0 equiv), glucal **59** (0.15mmol, 1.5 equiv), **[Pd]-1** (20 mol %), Ag_2O (0.20 mmol, 2.0 equiv) and HOAc (0.20 mmol, 2.0 equiv) in 1,4-dioxane (1.0 mL) was stirred at 100 °C under N_2 for 24 h. After cooling to ambient temperature, CH_2Cl_2 (10 mL) was added and the mixture was concentrated *in vacuo*. Purification by column chromatography on silica gel afforded the desired products **159bb** in 78% yield, which suggested that the isolated palladacycle specie **[Pd]-1** could be the active intermediate of catalytic system.

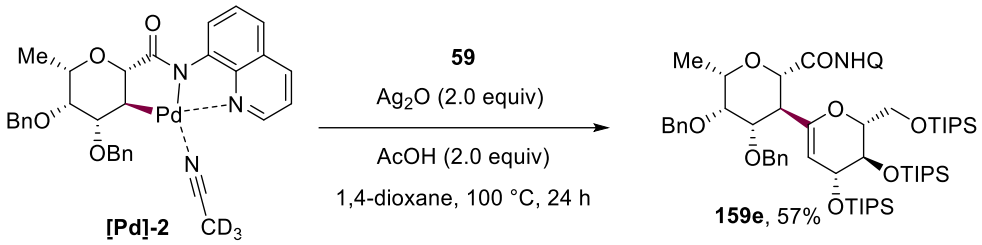


A suspension of deoxysugar **158e** (0.05 mmol, 1.0 equiv), glucal **59** (0.075 mmol, 1.5 equiv), **[Pd]-2** (20 mol %), Ag_2O (0.10 mmol, 2.0 equiv) and HOAc (0.10 mmol, 2.0 equiv) in 1,4-dioxane (0.5 mL) was stirred at 100 °C under N_2 for 24 h. After cooling to ambient temperature, CH_2Cl_2 (10 mL) was added and the mixture was concentrated *in vacuo*. Purification by column chromatography on silica gel afforded the desired products **159e** in 85% yield, which suggested that the isolated palladacycle specie **[Pd]-2** could be catalytically relevant intermediate.



Likewise, a stochiometric reaction was performed with stochiometric amount of **[Pd]-1**. A suspension of **[Pd]-1** (0.05 mmol, 1.0 equiv), glucal **59** (0.075 mmol, 1.5 equiv), Ag_2O (0.10 mmol, 2.0 equal) and HOAc (0.10 mmol, 2.0 equiv) in 1,4-dioxane (0.5 mL) was stirred at 100 °C under N_2 for 24 h. After cooling to ambient temperature, CH_2Cl_2

(10 mL) was added and the mixture was concentrated *in vacuo*. Purification by column chromatography on silica gel afforded the desired products **159bb** in 51% yield.

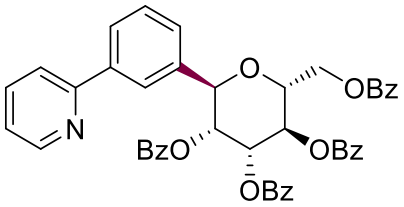


A stochiometric reaction was performed with stochiometric amount of **[Pd]-2**. A suspension of **[Pd]-2** (0.10 mmol, 1.0 equiv), glucal **59** (0.15mmol, 1.5 equiv), Ag_2O (0.20 mmol, 2.0 equiv) and HOAc (0.20 mmol, 2.0 equiv) in 1,4-dioxane (1.0 mL) was stirred at 100 °C under N_2 for 24 h. After cooling to ambient temperature, CH_2Cl_2 (10 mL) was added and the mixture was concentrated *in vacuo*. Purification by column chromatography on silica gel afforded the desired products **159e** in 57% yield.

5.3.3 Ruthenium-Catalyzed *meta*-C(sp^2)−H Glycosylation.

5.3.3.1 Characterization Data

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(pyridin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162aa)



The general procedure **H** was followed using 2-phenylpyridine (**160a**) (15.5 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 4/1) yielded **162aa** (55.0 mg, 75%) as a syrup.

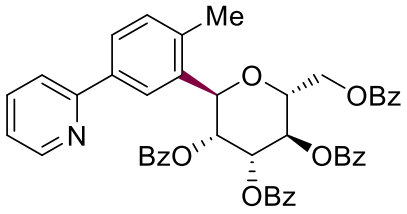
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 4.8 Hz, 1H), 8.34 (s, 1H), 8.13 (t, *J* = 8.1 Hz, 5H), 7.93 (d, *J* = 7.8 Hz, 4H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.67 – 7.55 (m, 3H), 7.51 – 7.38 (m, 6H), 7.36 – 7.29 (m, 4H), 7.29 – 7.21 (m, 1H), 6.64 (dd, *J* = 2.9, 2.4 Hz, 1H, H_2), 6.22 (t, *J* = 9.5 Hz, 1H, H_4), 5.75

(dd, *J* = 9.5, 2.9 Hz, 1H, H_3), 5.54 (d, *J* = 2.4 Hz, 1H, H_1), 4.75 (dd, *J* = 12.1, 2.5 Hz, 1H, H_6), 4.62 (dd, *J* = 12.1, 5.6 Hz, 1H, H_6), 4.29 (ddd, *J* = 8.9, 5.6, 2.5 Hz, 1H, H_5).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 166.20 (C_q), 165.94 (C_q), 165.65 (C_q), 165.37 (C_q), 156.81 (C_q), 149.74 (CH), 140.54 (C_q), 136.87 (CH), 135.81 (C_q), 133.41 (CH), 133.38 (CH), 133.29 (CH), 133.02 (CH), 129.86 (CH), 129.83 (C_q), 129.79 (CH), 129.75 (CH), 129.45 (C_q), 128.95 (C_q), 128.86 (C_q), 128.53 (CH), 128.41 (CH), 128.37 (CH), 127.29 (CH), 126.92 (CH), 125.08 (CH), 122.37 (CH), 120.75 (CH), 76.30 (CH, C_1), 71.26 (CH, C_5), 70.97 (CH, C_3), 70.36 (CH, C_2), 67.40 (CH, C_4), 63.28 (CH_2, C_6). 3 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1716, 1584, 1451, 1263, 1177, 1088, 1068, 1025, 706, 685 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 756 (15) $[M+Na]^+$, 734 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{45}H_{36}NO_9^+$ $[M+H]^+$ 734.2385, found 734.2352.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-methyl-5-(pyridin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ab)



The general procedure **H** was followed using 2-(*p*-tolyl)pyridine (**160b**) (16.9 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 4/1) yielded **162ab** (61.3 mg, 82%) as a syrup.

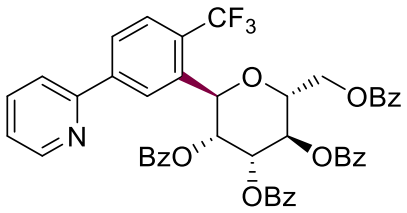
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 8.74 (d, *J* = 4.8 Hz, 1H), 8.45 (s, 1H), 8.13 (t, *J* = 8.4 Hz, 2H), 8.07 (t, *J* = 7.2 Hz, 4H), 7.98 (d, *J* = 7.4 Hz, 4H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.46 – 7.41 (m, 4H), 7.40 – 7.31 (m, 5H), 7.32 – 7.27 (m, 1H), 6.57 (t, *J* = 2.9 Hz, 1H), 6.20 – 6.02 (m, 2H), 5.58 (d, *J* = 2.9 Hz, 1H), 4.86 – 4.47 (m, 2H), 4.13 (ddd, *J* = 8.4, 5.7, 3.1 Hz, 1H), 2.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 166.15 (C_q), 166.01 (C_q), 165.49 (C_q), 165.40 (C_q), 156.59 (C_q), 149.56 (CH), 139.57 (C_q), 137.22 (C_q), 137.06 (CH), 133.84 (C_q), 133.43

(CH), 133.37 (CH), 133.34 (CH), 133.06 (CH), 132.24 (CH), 129.86 (CH), 129.82 (2 CH), 129.79 (C_q), 129.74 (CH), 129.47 (C_q), 129.00 (C_q) , 128.96 (C_q), 128.49 (CH), 128.44 (CH), 128.42, 128.36 (CH), 127.49 (CH), 125.65 (CH), 122.21 (CH), 120.59 (CH), 74.96 (CH), 71.64 (CH), 71.37 (CH), 70.60 (CH), 67.86 (CH), 62.87 (CH_2), 20.26 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1718, 1602, 1451, 1262, 1177, 1091, 1069, 1026, 780, 707 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 770 (20) $[M+Na]^+$, 748 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{46}H_{38}NO_9^+$ $[M+H]^+$ 748.2541, found 748.2544.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[5-(pyridin-2-yl)-2-(trifluoromethyl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ac)



The general procedure **H** was followed using 2-[4-(trifluoromethyl)phenyl]pyridine (**160c**) (22.3 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 4/1) yielded **162ac** (52.9 mg, 66%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 4.4 Hz, 0H), 8.30 – 8.16 (m, 1H), 8.11 – 8.06 (m, 2H), 8.06 – 8.01 (m, 2H), 7.87 – 7.80 (m, 2H), 7.77 – 7.73 (m, 2H), 7.69 (td, *J* = 7.7, 1.8 Hz, 2H), 7.63 – 7.44 (m, 7H), 7.44 – 7.35 (m, 5H), 7.32 – 7.27 (m, 3H), 6.22 (d, *J* = 6.9 Hz, 1H), 6.08 (dd, *J* = 6.9, 2.7 Hz, 1H), 5.88 – 5.75 (m, 2H), 4.89 – 4.72 (m, 1H), 4.45 (dd, *J* = 8.9, 4.1 Hz, 2H).

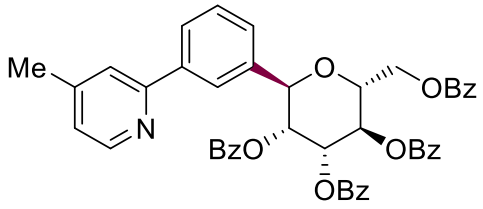
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.08 (C_q), 165.22 (C_q), 165.15 (C_q), 164.86 (C_q), 158.19 (C_q), 149.40 (CH), 144.01 (C_q), 136.77 (CH), 135.73 (C_q), 133.61 (CH), 133.42 (CH), 133.21 (CH), 133.08 (CH), 131.06 (C_q, d, *J* = 32.8 Hz), 131.06 (CH), 129.90 (CH), 129.77 (CH), 129.71 (CH), 129.61 (C_q), 129.08 (C_q), 128.99 (C_q), 128.87 (C_q), 128.57 (CH), 128.48 (CH), 128.36 (CH), 128.24 (CH), 125.10 (dd, *J* = 89.1, 3.9 Hz).

123.82 (CH), 122.55 (CH), 73.38 (CH), 70.21 (CH), 69.48 (CH), 69.45 (CH), 68.52 (CH), 61.86 (CH_2).

^{19}F NMR (377 MHz, $CDCl_3$): δ = -62.47.

IR (ATR): $\tilde{\nu}$ = 1719, 1602, 1452, 1314, 1259, 1086, 1067, 1025, 705, 685 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 824 (30) $[M+Na]^+$, 802 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{46}H_{35}F_3NO_9^+$ $[M+H]^+$ 802.2258, found 802.2267.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(4-methylpyridin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ad)



The general procedure **H** was followed using 4-methyl-2-phenylpyridine (**160d**) (22.3 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 4/1) yielded **162ad** (32.9 mg, 44%) as a syrup.

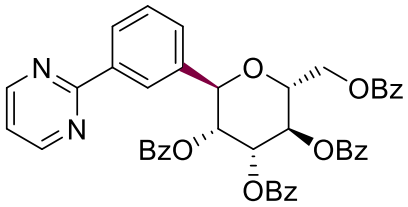
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 4.4 Hz, 1H), 8.32 (s, 1H), 8.24 – 8.05 (m, 5H), 7.98 – 7.87 (m, 4H), 7.82 – 7.74 (m, 2H), 7.71 – 7.53 (m, 3H), 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 4H), 7.36 – 7.30 (m, 4H), 7.12 (d, *J* = 4.4 Hz, 1H), 6.64 (dd, *J* = 3.0, 2.4 Hz, 1H), 6.22 (t, *J* = 9.5 Hz, 1H), 5.75 (dd, *J* = 9.5, 3.0 Hz, 1H), 5.52 (d, *J* = 2.4 Hz, 1H), 4.73 (dd, *J* = 12.1, 2.5 Hz, 1H), 4.60 (dd, *J* = 12.1, 5.3 Hz, 1H), 4.26 (ddd, *J* = 9.5, 5.3, 2.5 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.24 (C_q), 165.99 (C_q), 165.68 (C_q), 165.37 (C_q), 156.57 (C_q), 149.24 (CH), 148.42 (C_q), 140.37 (C_q), 135.79 (C_q), 133.41 (CH), 133.32 (CH), 133.02 (CH), 129.88 (CH), 129.83 (C_q), 129.81 (CH), 129.78 (CH), 129.76 (CH), 129.47 (C_q), 128.98 (C_q), 128.89 (C_q), 128.55 (CH), 128.41 (CH), 128.39 (CH), 127.43 (CH), 127.02 (CH), 125.17 (CH), 123.52 (CH), 122.06 (CH), 76.33 (CH), 71.25 (CH),

71.08 (CH), 70.38 (CH) , 67.35 (CH), 63.25 (CH_2), 21.27 (CH). 3 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1716, 1601, 1451, 1315, 1263, 1177, 1088, 1068, 1025, 707 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 770 (15) $[M+Na]^+$, 748 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{46}H_{38}NO_9^+$ $[M+H]^+$ 748.2541, found 748.2547.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ae)



The general procedure **H** was followed using methyl 2-phenylpyrimidine (**160e**) (22.3 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162ae** (60.9 mg, 83%) as a syrup.

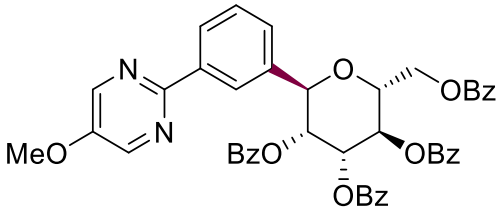
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.84 (s, 1H), 8.77 (d, *J* = 4.8 Hz, 2H), 8.50 (d, *J* = 7.8 Hz, 1H), 8.17 (d, *J* = 7.3 Hz, 2H), 8.11 (d, *J* = 7.3 Hz, 2H), 7.97 – 7.82 (m, 5H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.51 – 7.39 (m, 6H), 7.37 – 7.29 (m, 4H), 7.20 (t, *J* = 4.8 Hz, 1H), 6.61 (dd, *J* = 2.9, 2.6 Hz, 1H, H_2), 6.19 (t, *J* = 9.3 Hz, 1H, H_4), 5.74 (dd, *J* = 9.3, 2.9 Hz, 1H, H_3), 5.55 (d, *J* = 2.6 Hz, 1H, H_1), 4.77 (dd, *J* = 12.1, 2.7 Hz, 1H, H_6), 4.61 (dd, *J* = 12.1, 5.7 Hz, 1H, H_6), 4.33 (ddd, *J* = 8.9, 5.7, 2.7 Hz, 1H, H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.28 (C_q), 165.85 (C_q), 165.66 (C_q), 165.40 (C_q), 164.23 (C_q), 157.28 (CH), 138.76 (C_q), 135.82 (C_q), 133.41 (CH), 133.37 (CH), 133.28 (CH), 132.99 (CH), 129.93 (C_q), 129.89 (CH), 129.85 (CH), 129.78 (CH), 129.60 (CH), 129.51 (C_q), 129.00 (C_q), 128.89 (C_q), 128.58 (CH), 128.54 (CH), 128.38 (CH), 128.30 (CH), 126.54 (CH), 119.31 (CH), 76.24 (CH, C_1), 71.29 (CH, C_5), 70.78 (CH, C_3), 70.60 (CH, C_2), 67.53 (CH, C_4), 63.28 (CH_2, C_6).

IR (ATR): $\tilde{\nu}$ = 1720, 1601, 1451, 1410, 1265, 1178, 1093, 1070, 1027, 709 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 757 (50) $[M+Na]^+$, 735 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{35}N_2O_9^+$ $[M+H]^+$ 735.2337, found 735.2315.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(5-methoxypyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162af)



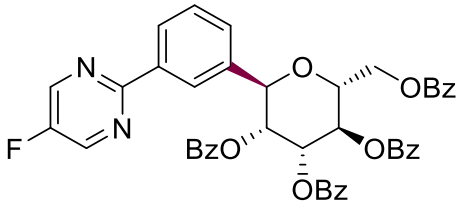
The general procedure **H** was followed using 5-methoxy-2-phenylpyrimidine (**160f**) (18.6 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162af** (55.8 mg, 73%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 1H), 8.44 – 8.39 (m, 1H), 8.41 (s, 2H), 8.18 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.12 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.92 (dd, *J* = 8.3, 2.6 Hz, 2H), 7.92 (dd, *J* = 8.4, 2.6 Hz, 2H), 7.84 – 7.79 (m, 1H), 7.67 – 7.55 (m, 3H), 7.51 – 7.38 (m, 6H), 7.36 – 7.29 (m, 4H), 6.62 (dd, *J* = 3.1, 1.7 Hz, 1H), 6.20 (dd, *J* = 9.6, 9.4 Hz, 1H), 5.75 (dd, *J* = 9.6, 3.1 Hz, 1H), 5.55 (d, *J* = 1.7 Hz, 1H), 4.77 (dd, *J* = 12.0, 2.6 Hz, 1H), 4.60 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.33 (ddd, *J* = 9.4, 5.7, 2.6 Hz, 1H), 3.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.41 (C_q), 166.00 (C_q), 165.82 (C_q), 165.56 (C_q), 157.42 (C_q), 152.25 (C_q), 143.54 (CH), 138.75 (C_q), 135.82 (C_q), 133.54 (CH), 133.51 (CH), 133.41 (CH), 133.10 (CH), 130.13 (C_q), 130.03 (CH), 129.93 (CH), 129.92 (CH), 129.88 (CH), 129.71 (CH), 129.69 (C_q), 129.17 (C_q), 129.05 (C_q), 128.69 (CH), 128.53 (CH), 128.51 (CH), 127.82 (CH), 127.72 (CH), 126.06 (CH), 76.51 (CH), 71.36 (CH), 70.99 (CH), 70.78 (CH), 67.68 (CH), 63.49 (CH_2), 56.12 (CH_3). 10 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1452, 1424, 1315, 1264, 1178, 1092, 1070, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 787 (100) $[M+Na]^+$, 765 (70) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{45}H_{37}N_2O_{10}^+$ $[M+H]^+$ 765.2443, found 765.2436.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(5-fluoropyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ag)



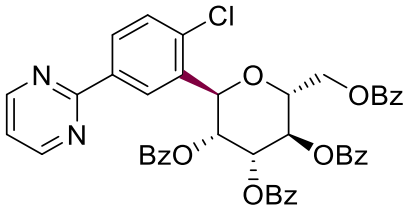
The general procedure **H** was followed using 5-fluoro-2-phenylpyrimidine (**160g**) (17.4 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.8 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 4/1) yielded **162ag** (42.9 mg, 57%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 1H), 8.57 (s, 2H), 8.44 (d, *J* = 7.9 Hz, 1H), 8.16 (dd, *J* = 8.4, 1.4 Hz, 2H), 8.12 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.93 (dd, *J* = 8.3, 3.9 Hz, 2H), 7.92 (dd, *J* = 8.4, 3.9 Hz, 2H), 7.87 – 7.83 (m, 1H), 7.68 – 7.58 (m, 3H), 7.51 – 7.40 (m, 6H), 7.36 – 7.30 (m, 4H), 6.60 (dd, *J* = 3.1, 1.7 Hz, 1H), 6.18 (dd, *J* = 9.5, 8.7 Hz, 1H), 5.73 (dd, *J* = 9.5, 3.1 Hz, 1H), 5.54 (d, *J* = 1.7 Hz, 1H), 4.77 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.61 (dd, *J* = 12.1, 5.8 Hz, 1H), 4.31 (ddd, *J* = 8.7, 5.8, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.40 (C_q), 166.02 (C_q), 165.84 (C_q), 165.57 (C_q), 160.62 (d, *J* = 5.4 Hz, C_q), 156.95 (d, *J* = 265.0 Hz, C_q), 145.11 (d, *J* = 20.2 Hz, CH), 137.93 (d, *J* = 1.3 Hz, C_q), 136.07 (C_q), 133.59 (CH), 133.57 (CH), 133.47 (CH), 133.19 (CH), 130.10 (C_q), 130.05 (CH), 130.01 (CH), 129.94 (CH), 129.93 (CH), 129.83 (CH), 129.64 (C_q), 129.13 (C_q), 129.04 (C_q), 128.71 (CH), 128.58 (CH), 128.56 (CH), 128.55 (CH), 128.39 (CH), 126.62 (CH), 76.36 (CH), 71.50 (CH), 70.90 (CH), 70.72 (CH), 67.68 (CH), 63.46 (CH_2). 10 CH resonances are missing due to the overlap.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -140.15 (s, 1F).
IR (ATR): $\tilde{\nu}$ = 1722, 1451, 1423, 1267, 1245, 1178, 1092, 1070, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 775 (100) $[M+Na]^+$, 753 (45) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{34}FN_2O_9^+$ $[M+H]^+$ 753.2243, found 753.2237.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(5-chloropyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ah)



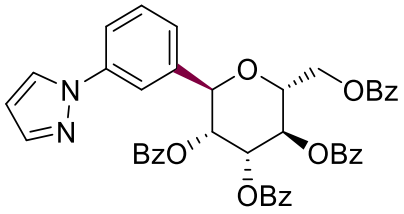
The general procedure **H** was followed using methyl 2-(4-chlorophenyl)pyrimidine (**160h**) (22.3 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162ah** (57.6 mg, 75%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.94 (d, *J* = 2.0 Hz, 1H), 8.81 (d, *J* = 4.8 Hz, 2H), 8.36 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 4H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.67 – 7.53 (m, 2H), 7.55 – 7.37 (m, 9H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 4.8 Hz, 1H), 6.16 (dd, *J* = 7.3, 3.0 Hz, 1H), 6.10 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.98 (d, *J* = 7.3 Hz, 1H), 5.85 (dd, *J* = 5.6, 3.8 Hz, 1H), 5.12 (dd, *J* = 11.8, 7.7 Hz, 1H), 4.75 (dd, *J* = 11.8, 4.7 Hz, 1H), 4.64 (dt, *J* = 8.2, 4.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.14 (C_q), 165.28 (C_q), 165.08 (C_q), 163.39 (C_q), 157.27 (CH), 136.86 (C_q), 136.72 (C_q), 134.95 (C_q), 133.55 (CH), 133.23 (CH), 133.05 (CH), 130.20 (CH), 130.07 (CH), 129.78 (CH), 129.64 (C_q), 129.38 (CH), 129.12 (C_q), 129.01 (C_q), 128.65 (CH), 128.54 (CH), 128.42 (CH), 128.33 (CH), 128.30 (CH), 119.37 (CH), 73.94 (CH), 70.85 (CH), 69.70 (CH), 69.39 (CH), 68.94 (CH), 61.69 (CH_2). 2 C_q resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1722, 1568, 1452, 1420, 1260, 1178, 1092, 1069, 1026, 709 cm^{-1}
MS (ESI) *m*/*z* (relative intensity): 791 (100) $[M+Na]^+$, 769 (20) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{34}ClN_2O_9^+$ $[M+H]^+$ 769.1947, found 769.1937.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[3-(1*H*-Pyrazol-1-yl)phenyl]-6-[(benzoyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ai)



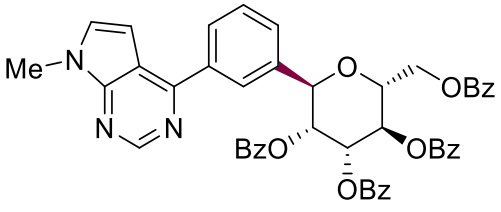
The general procedure **H** was followed using 1-phenyl-1*H*-pyrazole (**160i**) (14.4 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162ai** (39.0 mg, 54%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 – 8.04 (m, 6H), 8.01 – 7.89 (m, 4H), 7.89 – 7.80 (m, 1H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.69 – 7.55 (m, 4H), 7.54 – 7.45 (m, 3H), 7.44 – 7.39 (m, 3H), 7.39 – 7.28 (m, 4H), 6.56 (dd, *J* = 2.9, 2.4 Hz, 1H), 6.48 (t, *J* = 2.1 Hz, 1H), 6.19 (t, *J* = 9.5 Hz, 1H), 5.70 (dd, *J* = 9.5, 2.9 Hz, 1H), 5.49 (d, *J* = 2.4 Hz, 1H), 4.72 (dd, *J* = 12.1, 2.8 Hz, 1H), 4.63 (dd, *J* = 12.1, 5.5 Hz, 1H), 4.26 (ddd, *J* = 8.7, 5.5, 2.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.22 (C_q), 166.05 (C_q), 165.64 (C_q), 165.37 (C_q), 141.37 (CH), 141.09 (C_q), 136.98 (2 C_q), 133.47 (CH), 133.39 (CH), 133.09 (CH), 130.55 (CH), 129.87 (CH), 129.78 (4 CH), 129.35 (C_q), 128.87 (C_q), 128.82 (C_q), 128.57 (CH), 128.45 (CH), 128.41 (2 CH), 126.95 (CH), 124.28 (CH), 119.47 (CH), 117.04 (CH), 107.99 (CH), 75.94 (CH), 71.47 (CH), 70.94 (CH), 70.18 (CH), 67.28 (CH), 63.26 (CH_2).

IR (ATR): $\tilde{\nu}$ = 1716, 1601, 1451, 1393, 1262, 1091, 1068, 1026, 706, 686 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 745 (75) $[M+Na]^+$, 723 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{43}H_{35}N_2O_9^+$ $[M+H]^+$ 723.2337, found 723.2335.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162aj)



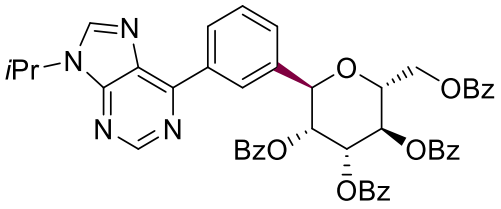
The general procedure **H** was followed using 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (**160j**) (20.9 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 10.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (9.5 mg, 20 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162aj** (44.9 mg, 57%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.02 (s, 1H), 8.51 (s, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 8.21 – 8.13 (m, 2H), 8.13 – 8.05 (m, 2H), 8.03 – 7.87 (m, 5H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.62 – 7.56 (m, 1H), 7.55 – 7.44 (m, 4H), 7.41 – 7.34 (m, 6H), 7.27 (d, *J* = 3.6 Hz, 1H), 6.93 (d, *J* = 3.6 Hz, 1H), 6.66 (dd, *J* = 3.0, 2.5 Hz, 1H), 6.24 (dd, *J* = 9.4, 8.7 Hz, 1H), 5.79 (dd, *J* = 9.4, 3.0 Hz, 1H), 5.62 (d, *J* = 2.5 Hz, 1H), 4.75 (dd, *J* = 12.1, 2.7 Hz, 1H), 4.68 (dd, *J* = 12.1, 5.5 Hz, 1H), 4.37 (ddd, *J* = 8.7, 5.5, 2.7 Hz, 1H), 3.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.19 (C_q), 165.87 (C_q), 165.65 (C_q), 165.37 (C_q), 156.59 (C_q), 151.87 (C_q), 151.42 (CH), 139.38 (C_q), 136.01 (C_q), 133.43 (CH), 133.33 (CH), 132.94 (CH), 130.24 (CH), 129.87 (CH), 129.84 (CH), 129.78 (CH), 129.75 (CH), 129.71 (C_q), 129.68 (CH), 129.42 (C_q), 129.16 (CH), 128.92 (C_q), 128.84 (C_q), 128.55 (CH), 128.39 (3CH), 128.26 (CH), 127.85 (CH), 127.08 (CH), 115.69 (C_q), 100.14 (CH), 76.26 (CH), 71.38 (CH), 70.86 (CH), 70.37 (CH), 67.42 (CH), 63.24 (CH_2), 31.26 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1721, 1564, 1451, 1315, 1265, 1177, 1092, 1070, 1027, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 810 (15) $[M+Na]^+$, 788 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{47}H_{38}N_3O_9^+$ $[M+H]^+$ 788.2603, found 788.2596.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(9-isopropyl-9*H*-purin-6-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ak)



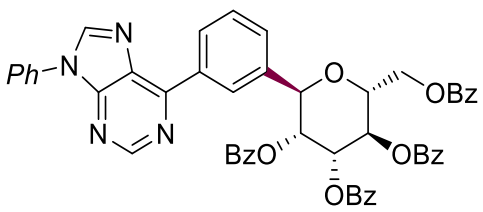
The general procedure **H** was followed using 9-isopropyl-6-phenyl-9*H*-purine (**160k**) (23.8 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162ak** (44.1 mg, 54%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (s, 1H), 9.00 (s, 1H), 8.81 (d, *J* = 7.8 Hz, 1H), 8.17 (s, 1H), 8.13 (d, *J* = 7.7 Hz, 4H), 7.95 – 7.85 (m, 4H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.65 – 7.53 (m, 2H), 7.50 – 7.42 (m, 4H), 7.41 – 7.35 (m, 3H), 7.34 – 7.29 (m, 4H), 6.62 (dd, *J* = 2.9, 2.1 Hz, 1H), 6.24 (t, *J* = 9.4 Hz, 1H), 5.74 (dd, *J* = 9.4, 2.9 Hz, 1H), 5.66 – 5.37 (d, *J* = 2.1 Hz, 1H), 4.99 (hept, *J* = 6.8 Hz, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.62 (dd, *J* = 12.0, 5.0 Hz, 1H), 4.49 – 4.29 (m, 1H), 1.68 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.31 (C_q), 165.82 (C_q), 165.66 (C_q), 165.36 (C_q), 154.16 (C_q), 152.17 (C_q), 152.11 (CH), 142.21 (CH), 136.90 (C_q), 135.73 (C_q), 133.35 (CH), 133.25 (CH), 132.96 (CH), 131.65 (C_q), 129.91 (C_q), 129.89 (CH), 129.78 (CH), 129.75 (CH), 129.64 (CH), 129.54, 129.01 (C_q), 128.92 (C_q), 128.53 (CH), 128.46 (CH), 128.35 (CH), 128.32 (CH), 128.29 (CH), 76.40 (CH), 71.21 (CH), 70.87 (CH), 70.71 (CH), 67.45 (CH), 63.20 (CH_2), 47.25 (CH), 22.57 (CH_3), 22.55 (CH_3). 4 CH resonance are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1718, 1570, 1451, 1262, 1178, 1091, 1069, 1026, 707, 647 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 839(30) $[M+Na]^+$, 817 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{48}H_{41}N_4O_9^+$ $[M+H]^+$ 817.2868, found 817.2869.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(9-phenyl-9*H*-purin-6-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162al)



The general procedure **H** was followed using 9-isopropyl-6-phenyl-9*H*-purine (**160l**) (23.8 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$

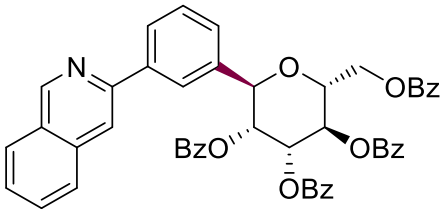
(3.1 mg, 5.0 mol %), (4-CF_3-C_6H_4)$_3$P (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162al** (51.0 mg, 60%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.23 (s, 1H), 9.07 (s, 1H), 8.85 (d, *J* = 7.9 Hz, 1H), 8.37 (s, 1H), 8.18 – 8.04 (m, 4H), 7.98 – 7.85 (m, 5H), 7.81 – 7.70 (m, 3H), 7.68 – 7.57 (m, 3H), 7.54 – 7.40 (m, 6H), 7.39 – 7.29 (m, 6H), 6.63 (dd, *J* = 3.0, 2.4 Hz, 1H), 6.24 (t, *J* = 9.4 Hz, 1H), 5.76 (dd, *J* = 9.4, 3.0 Hz, 1H), 5.62 (d, *J* = 2.4 Hz, 1H), 4.82 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.65 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.40 (ddd, *J* = 8.7, 5.2, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.29 (C_q), 165.85 (C_q), 165.68 (C_q), 165.39 (C_q), 154.88 (C_q), 153.14 (CH), 152.29 (C_q), 143.46 (CH), 136.67 (C_q), 135.89 (C_q), 134.38 (C_q), 133.39 (CH), 133.29 (CH), 132.98 (CH), 131.68 (C_q), 129.99 (CH), 129.90 (CH), 129.88 (CH), 129.80 (CH), 129.77 (CH), 129.72 (CH), 129.67 (CH), 129.54 (C_q), 129.01 (C_q), 128.92 (C_q), 128.76 (CH), 128.55 (CH), 128.53 (CH), 128.45 (CH), 128.38 (CH), 128.30 (CH), 123.66 (CH), 76.39 (CH), 71.29 (CH), 70.86 (CH), 70.68 (CH), 67.51 (CH), 63.24 (CH_2). 2 CH and 1 C_q resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1563, 1451, 1263, 1178, 1092, 1069, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 873 (40) $[M+Na]^+$, 851 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{51}H_{39}N_4O_9^+$ $[M+H]^+$ 851.2712, found 851.2710.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(isoquinolin-3-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162am)



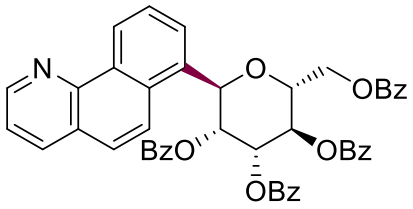
The general procedure **H** was followed using 3-phenylisoquinoline (**160m**) (20.5 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (3.1 mg, 5.0 mol %), (4-CF_3-C_6H_4)$_3$P (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162am** (32.1 mg, 41%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.32 (s, 1H), 8.48 (s, 1H), 8.35 – 8.20 (m, 2H), 8.16 – 8.06 (m, 4H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.96 – 7.85 (m, 5H), 7.78 (t, *J* = 7.3 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.65 – 7.58 (m, 2H), 7.52 – 7.44 (m, 3H), 7.45 – 7.39 (m, 2H), 7.38 – 7.28 (m, 6H), 6.68 (dd, *J* = 3.0, 2.2 Hz, 1H), 6.22 (t, *J* = 9.6 Hz, 1H), 5.79 (dd, *J* = 9.6, 3.0 Hz, 1H), 5.56 (d, *J* = 2.2 Hz, 1H), 4.73 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.61 (dd, *J* = 12.0, 5.4 Hz, 1H), 4.29 (ddd, *J* = 8.5, 5.4, 2.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.26 (C_q), 166.02 (C_q), 165.72 (C_q), 165.42 (C_q), 152.46 (CH), 150.60 (C_q), 140.72 (C_q), 136.72 (C_q), 135.86 (C_q), 133.41 (CH), 133.32 (CH), 132.97 (CH), 130.59 (CH), 129.91 (CH), 129.86 (CH), 129.79 (CH), 129.74 (CH), 129.52 (C_q), 129.03 (C_q), 128.91 (C_q), 128.56 (CH), 128.40 (CH), 128.37 (CH), 127.90 (C_q), 127.54 (CH), 127.43 (CH), 127.28 (CH), 127.19 (CH), 126.57 (CH), 125.18 (CH), 117.10 (CH), 76.45 (CH), 71.27 (CH), 71.12 (CH), 70.45 (CH), 67.44 (CH), 63.36 (CH_2). 3 CH and 1 C_q resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1718, 1451, 1260, 1177, 1089, 1068, 1026, 908, 802, 703 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 806(10) $[M+Na]^+$, 784 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{49}H_{38}NO_9^+$ $[M+H]^+$ 784.2541, found 784.2544.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-(Benzo[*h*]quinolin-7-yl)-6-[(benzoyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162an)



The general procedure **H** was followed using benzo[*h*]quinoline (**160n**) (17.9 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162an** (52.2 mg, 69%) as a syrup.

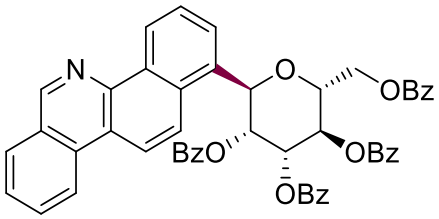
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.52 (d, *J* = 8.3 Hz, 1H), 9.05 (dd, *J* = 4.4, 1.7 Hz, 1H), 8.48 (d, *J* = 9.3 Hz, 1H), 8.29 (d, *J* = 7.3 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 2H), 8.08 (d, *J* = 7.9 Hz, 1H), 8.01 – 7.87 (m, 5H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.58

– 7.53 (m, 2H), 7.52 – 7.43 (m, 5H), 7.39 – 7.31 (m, 4H), 7.18 (t, *J* = 7.7 Hz, 2H), 6.72 (dd, *J* = 2.9, 2.1 Hz, 1H), 6.24 – 6.16 (m, 2H), 6.09 (d, *J* = 2.1 Hz, 1H), 4.59 (dd, *J* = 12.0, 6.5 Hz, 1H), 4.44 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.99 (dt, *J* = 6.5, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.29 (C_q), 166.02 (C_q), 165.61 (C_q), 165.43 (C_q), 148.98 (CH), 146.36 (C_q), 135.71 (CH), 133.48 (CH), 133.44 (CH), 133.42 (CH), 132.82 (CH), 132.63 (C_q), 132.36 (C_q), 130.87 (C_q), 129.93 (CH), 129.81 (CH), 129.77 (CH), 129.67 (C_q), 129.64 (CH), 129.46 (C_q), 128.89 (C_q), 128.85 (C_q), 128.55 (CH), 128.46 (CH), 128.44 (CH), 128.09 (CH), 127.90 (CH), 126.31 (CH), 126.13 (CH), 125.95 (CH), 125.88 (C_q), 124.52 (CH), 122.08 (CH), 75.76 (CH), 71.77 (CH), 71.34 (CH), 70.65 (CH), 67.84 (CH), 63.13 (CH_2).

IR (ATR): $\tilde{\nu}$ = 1718, 1601, 1451, 1262, 1177, 1091, 1069, 1026, 707, 686 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 780 (20) $[M+Na]^+$, 758 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{47}H_{36}NO_9^+$ $[M+H]^+$ 758.2385, found 758.2387.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-(Benzo[*c*]phenanthridin-1-yl)-6-[(benzoyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ao)



The general procedure **H** was followed using benzo[*c*]phenanthridine (**160o**) (22.9 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162ao** (38.7 mg, 48%) as a syrup.

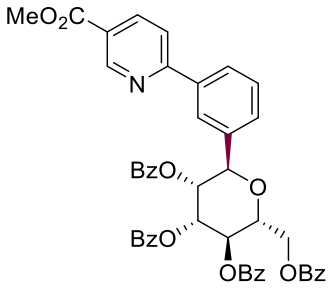
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.63 (d, *J* = 8.5 Hz, 1H), 9.52 (s, 1H), 8.68 (d, *J* = 9.4 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 9.4 Hz, 1H), 8.28 (d, *J* = 7.2 Hz, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.02 – 7.86 (m, 6H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.43 (m, 4H), 7.42 – 7.31 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 2H), 6.75 (dd, *J* = 2.8, 2.0

Hz, 1H), 6.27 – 6.17 (m, 2H), 6.14 (d, *J* = 2.0 Hz, 1H), 4.61 (dd, *J* = 12.0, 6.7 Hz, 1H), 4.43 (dd, *J* = 12.0, 2.3 Hz, 1H), 4.02 (td, *J* = 6.7, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 166.32 (C_q), 166.07 (C_q), 165.67 (C_q), 165.47 (C_q), 152.08 (CH), 141.40 (C_q), 133.49 (CH), 133.45 (CH), 133.42 (CH), 133.13 (C_q), 132.69 (CH), 132.53 (C_q), 131.87 (C_q), 130.81 (CH), 130.67 (C_q), 129.97 (CH), 129.83 (CH), 129.78 (CH), 129.57 (C_q), 129.54 (CH), 129.52 (C_q), 128.93 (C_q), 128.87 (C_q), 128.65 (CH), 128.58 (CH), 128.47 (CH), 128.44 (C_q), 128.00 (CH), 127.44 (CH), 127.19 (CH), 126.95 (C_q), 126.65 (CH), 126.16 (CH), 124.82 (CH), 122.47 (CH), 120.85 (C_q), 120.62 (CH), 75.94 (CH), 71.86 (CH), 71.32 (CH), 70.72 (CH), 67.91 (CH), 63.22 (CH_2).

IR (ATR): $\tilde{\nu}$ = 1713, 1601, 1451, 1261, 1177, 1089, 1067, 1026, 907, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 830(10) $[M+Na]^+$, 808 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{51}H_{38}NO_9^+$ $[M+H]^+$ 808.2541, found 808.2542.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{3-[5-(methoxycarbonyl)pyridin-2-yl]phenyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ap)



The general procedure **H** was followed using methyl 6-phenylnicotinate (**160r**) (21.3 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (131.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 4/1) yielded **162ap** (42.7 mg, 54%) as a syrup.

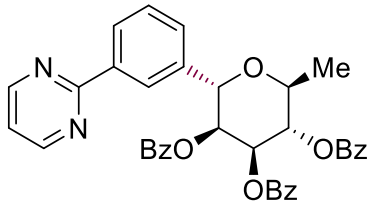
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 9.25 (s, 1H), 8.39 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.17 – 8.06 (m, 4H), 7.93 (d, *J* = 7.9 Hz, 5H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.60 (q, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (q, *J* = 7.2 Hz, 4H), 7.33 (t, *J* = 7.5 Hz, 4H), 6.61 (dd, *J* = 2.8, 2.4 Hz, 1H), 6.19 (t, *J* = 9.4 Hz, 1H), 5.72 (dd, *J* = 9.4, 2.8 Hz, 1H), 5.53 (d, *J* = 2.4 Hz, 1H), 4.74 (dd, *J* = 12.2,

2.5 Hz, 1H), 4.63 (dd, *J* = 12.2, 5.8 Hz, 1H), 4.26 (ddd, *J* = 8.9, 5.8, 2.6 Hz, 1H), 4.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.20 (C_q), 166.00 (C_q), 165.80 (C_q), 165.68 (C_q), 165.40 (C_q), 160.23 (C_q), 150.98 (CH), 139.40 (C_q), 138.06 (CH), 136.12 (C_q), 133.46 (CH), 133.37 (CH), 133.09 (CH), 129.96 (CH), 129.81 (CH), 129.78 (CH), 129.75 (CH), 129.41 (C_q), 128.91 (C_q), 128.85 (C_q), 128.56 (CH), 128.44 (CH), 128.41 (CH), 127.95 (CH), 127.72 (CH), 125.53 (CH), 124.43 (C_q), 120.09 (CH), 76.14 (CH), 71.43 (CH), 70.92 (CH), 70.30 (CH), 67.40 (CH), 63.26 (CH_2), 52.37 (CH_3). 3 CH and 1 C_q resonances is missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1713, 1596, 1451, 1262, 1177, 1087, 1068, 1025, 908, 704 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 814 (45) $[M+Na]^+$, 792 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{47}H_{38}NO_{11}^+$ [M+H] 792.2439, found 792.2444.

(2*S*,3*S*,4*R*,5*S*,6*S*)-2-Methyl-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162ba)



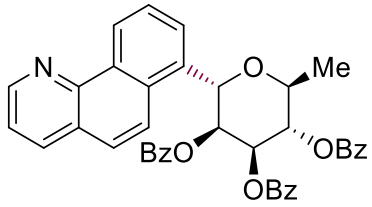
The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*S*,3*R*,4*R*,5*S*,6*S*)-2-bromo-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161ba**) (107.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162ba** (43.6 mg, 75%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85 (d, *J* = 4.8 Hz, 2H), 8.77 (s, 1H), 8.48 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.3 Hz, 2H), 8.04 – 7.86 (m, 4H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.72 – 7.54 (m, 2H), 7.53 – 7.42 (m, 4H), 7.34 (dt, *J* = 9.3, 7.7 Hz, 4H), 7.22 (t, *J* = 4.8 Hz, 1H), 6.50 (t, *J* = 3.1 Hz, 1H), 5.79 (t, *J* = 8.6 Hz, 1H), 5.69 (dd, *J* = 9.1, 3.1 Hz, 1H), 5.45 (d, *J* = 3.0 Hz, 1H), 4.17 – 3.98 (m, 1H), 1.50 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.79, 165.75, 165.65, 164.35, 157.30 (CH), 138.51, 136.72, 133.29 (CH), 133.26 (CH), 133.19 (CH), 129.90 (CH), 129.72 (2 CH), 129.44 (CH), 129.27, 129.20, 128.59 (CH), 128.48 (CH), 128.36 (CH), 128.35 (CH), 128.09 (CH), 126.55 (CH), 119.30 (CH), 75.59 (CH), 72.28 (CH), 70.99 (CH), 70.65 (CH), 69.52 (CH), 17.66(CH_3).

IR (ATR): $\tilde{\nu}$ = 1718, 1555, 1451, 1240, 1177, 1089, 1068, 1026, 706 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 637 (90) $[M+Na]^+$, 615 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{37}H_{30}N_2O_7^+$ $[M+H]^+$ 615.2126, found 615.2127.

(2*S*,3*S*,4*R*,5*S*,6*S*)-2-(Benzo[*h*]quinolin-7-yl)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162bb)



The general procedure **H** was followed using benzo[*h*]quinoline (**160n**) (17.9 mg, 0.10 mmol), (2*S*,3*R*,4*R*,5*S*,6*S*)-2-bromo-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161ba**) (107.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162bb** (45.2 mg, 71%) as a syrup.

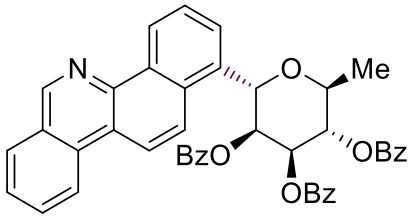
^{1}H NMR (400 MHz, $CHCl_3$): δ = 9.49 (d, *J* = 8.3 Hz, 1H), 9.04 (d, *J* = 4.2 Hz, 1H), 8.53 (d, *J* = 9.3 Hz, 1H), 8.22 (dd, *J* = 10.2, 7.7 Hz, 2H), 8.10 (d, *J* = 7.7 Hz, 2H), 8.04 – 7.90 (m, 4H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 9.3 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.54 – 7.44 (m, 4H), 7.42 – 7.30 (m, 4H), 6.63 (dd, *J* = 3.2, 2.7 Hz, 1H), 6.10 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.02 (d, *J* = 2.7 Hz, 1H), 5.83 (t, *J* = 8.7 Hz, 1H), 3.78 (dq, *J* = 8.7, 6.3 Hz, 1H), 1.34 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.20 (C_q), 165.68 (C_q), 165.66 (C_q), 148.95 (CH), 146.47 (C_q), 135.65 (CH), 133.34 (CH), 133.32 (CH), 132.58 (C_q), 132.34 (C_q), 131.73 (C_q), 129.89 (CH), 129.75 (CH), 129.69 (CH), 129.52 (C_q), 129.24 (C_q), 129.08 (C_q), 128.48 (CH), 128.42 (CH), 128.40 (CH), 127.72 (CH), 126.33 (CH), 125.93 (C_q),

125.78 (CH), 125.61 (CH), 124.53 (CH), 122.12 (CH), 74.88 (CH), 72.46 (CH), 71.51 (CH), 70.96 (CH), 69.41 (CH), 17.61 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1718, 1601, 1451, 1261, 1177, 1089, 1067, 1026, 833, 704 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1275(80) $[2M+H]^+$, 660 (20) $[M+Na]^+$, 638 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{40}H_{32}NO_7^+$ $[M+H]^+$ 638.2173, found 638.2174.

(2*S*,3*S*,4*R*,5*S*,6*S*)-2-(Benzo[*c*]phenanthridin-1-yl)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (162bc)



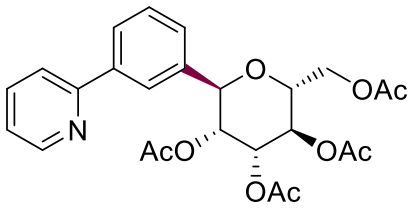
The general procedure **H** was followed using benzo[*c*]phenanthridine (**160o**) (22.9 mg, 0.10 mmol), (2*S*,3*R*,4*R*,5*S*,6*S*)-2-bromo-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161ba**) (107.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162bc** (30.2 mg, 71%) as a syrup.

^{1}H NMR (400 MHz, $CHCl_3$): δ = 9.60 (d, *J* = 8.4 Hz, 1H), 9.50 (s, 1H), 8.85 – 8.67 (m, 2H), 8.62 (d, *J* = 9.5 Hz, 1H), 8.23 (d, *J* = 7.2 Hz, 1H), 8.19 – 8.03 (m, 3H), 8.03 – 7.96 (m, 4H), 7.92 (t, *J* = 7.9 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.44 (m, 4H), 7.41 – 7.31 (m, 4H), 6.68 (t, *J* = 2.9 Hz, 1H), 6.14 (dd, *J* = 9.2, 2.9 Hz, 1H), 6.07 (d, *J* = 2.9 Hz, 1H), 5.86 (t, *J* = 8.9 Hz, 1H), 3.79 (dq, *J* = 8.9, 6.3 Hz, 1H), 1.34 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.25 (C_q), 165.75 (C_q), 165.70 (C_q), 152.07 (CH), 141.52 (C_q), 133.35 (CH), 133.31 (CH), 133.11 (C_q), 132.57 (C_q), 131.89 (C_q), 131.51 (C_q), 130.90 (CH), 129.94 (CH), 129.77 (CH), 129.71 (CH), 129.59 (C_q), 129.27 (C_q), 129.12 (C_q), 128.68 (CH), 128.50 (CH), 128.43 (CH), 128.40 (CH), 127.37 (CH), 126.98 (CH), 126.95 (C_q), 126.30 (CH), 126.18 (CH), 124.78 (CH), 122.25 (CH), 120.83 (C_q), 120.28 (CH), 75.15 (CH), 72.53 (CH), 71.63 (CH), 71.06 (CH), 69.37 (CH), 17.71 (CH_2).

IR (ATR): $\tilde{\nu}$ = 1717, 1452, 1281, 1260, 1177, 1091, 1068, 907, 706, 685 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1397 (35) [2M+Na]$^+$, 710 (100) [M+Na]$^+$, 688 (55) [M+H]$^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{34}NO_7^+$ [M+H]$^+$ 688.2330, found 688.2319.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-6-[3-(pyridin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162bd)

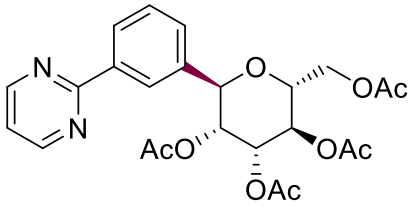


The general procedure **H** was followed using 2-phenylpyridine (**160a**) (15.5 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-(acetoxymethyl)-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161bb**) (82.0 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 2/1) yielded **162bd** (33.9 mg, 70%) as a syrup

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (dt, *J* = 4.7, 1.3 Hz, 1H), 8.14 (s, 1H), 8.08 – 7.98 (m, 1H), 7.87 – 7.71 (m, 2H), 7.63 – 7.48 (m, 2H), 7.26 (dd, *J* = 11.8, 1.3 Hz, 1H), 6.08 (t, *J* = 3.1 Hz, 1H), 5.36 (t, *J* = 8.8 Hz, 1H), 5.27 – 5.15 (m, 2H), 4.38 (dd, *J* = 12.0, 6.6 Hz, 1H), 4.16 (dd, *J* = 12.0, 2.8 Hz, 1H), 3.84 (ddd, *J* = 9.1, 6.6, 2.7 Hz, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.44 – 1.31 (m, 2H), 1.32 – 1.19 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.67 (C_q), 170.30 (C_q), 170.26 (C_q), 169.63 (C_q), 156.81 (C_q), 149.66 (CH), 140.20 (C_q), 136.95 (CH), 135.82 (C_q), 129.61 (CH), 127.14 (CH), 126.91 (CH), 125.14 (CH), 122.45 (CH), 120.71 (CH), 75.65 (CH), 71.37 (CH), 69.73 (CH), 69.24 (CH), 66.86 (CH), 62.54 (CH_2), 20.98 (CH_3), 20.74 (CH_3), 20.71 (CH_3).
IR (ATR): $\tilde{\nu}$ = 1742, 1585, 1463, 1435, 1368, 1223, 1079, 1049, 919, 767 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 508 (60) [M+Na]$^+$, 486 (100) [M+H]$^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{25}H_{28}NO_9^+$ [M+H]$^+$ 486.1755, found 486.1759.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-6-(3-(pyrimidin-2-yl)phenyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162be)



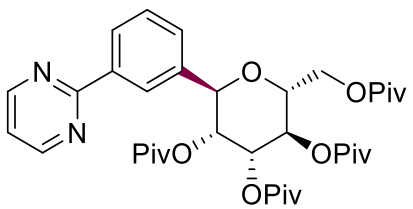
The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-(acetoxymethyl)-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161bb**) (82.0 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 2/1) yielded **162be** (36.4 mg, 75%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 4.9 Hz, 2H), 8.62 (s, 1H), 8.43 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 4.9 Hz, 1H), 6.03 (t, *J* = 3.3 Hz, 1H), 5.33 (t, *J* = 8.5 Hz, 1H), 5.27 – 5.13 (m, 2H), 4.41 (dd, *J* = 12.0, 6.8 Hz, 1H), 4.18 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.00 – 3.81 (m, 1H), 2.15 (s, 3H), 2.14 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.71 (C_q), 170.21 (C_q), 170.10 (C_q), 169.64 (C_q), 164.21 (C_q), 157.24 (CH), 138.45 (C_q), 135.86 (C_q), 129.37 (CH), 128.53 (CH), 128.24 (CH), 126.52 (CH), 119.35 (CH), 75.37 (CH), 71.48 (CH), 69.49 (CH), 69.35 (CH), 67.05 (CH), 62.37 (CH_2), 20.95 (CH_3), 20.74 (CH_3), 20.72 (CH_3), 20.70 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1737, 1556, 1411, 1367, 1211, 1048, 1020, 1051, 731, 700 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 509 (100) $[M+Na]^+$, 487 (70) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{24}H_{27}N_2O_9^+$ $[M+H]^+$ 487.1711, found 487.1712.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(pivaloyloxy)methyl]-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (162bf)



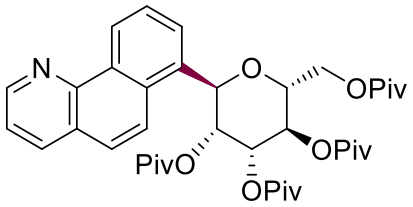
The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-[(pivaloyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (**161bc**) (115.9 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 4/1) yielded **162bf** (36.7 mg, 56%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (d, *J* = 4.8 Hz, 2H), 8.66 (s, 1H), 8.44 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.58 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.22 (t, *J* = 4.8 Hz, 1H), 6.08 (t, *J* = 3.2 Hz, 1H), 5.54 (t, *J* = 8.7 Hz, 1H), 5.23 (dd, *J* = 9.1, 2.9 Hz, 1H), 5.18 (d, *J* = 3.3 Hz, 1H), 4.37 (dd, *J* = 12.3, 5.6 Hz, 1H), 4.21 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.94 – 3.84 (m, 1H), 1.27 (s, 9H), 1.26 (s, 9H)1.21 (s, 9H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.2 (C_q), 177.5 (C_q), 177.3 (C_q), 176.7 (C_q), 164.3 (C_q), 157.3 (CH), 138.6 (C_q), 136.1 (C_q), 129.4 (CH), 128.6 (CH), 128.2 (CH), 126.8 (CH), 119.3 (CH), 75.8 (CH), 71.7 (CH), 70.0 (CH), 69.3 (CH), 66.2 (CH), 62.2 (CH_2), 38.9 (C_q), 38.9 (C_q), 38.8 (C_q), 38.8 (C_q), 27.2 (CH_3), 27.2 (CH_3), 27.1 (CH_3), 27.0 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2973, 1729, 1569, 1555, 1410, 1278, 1174, 1129, 731 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 677 (100) $[M+Na]^+$, 655 (70) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{36}H_{51}N_2O_9^+$ $[M+H]^+$ 655.3589, found 655.3592.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-(benzo[*h*]quinolin-7-yl)-6-[(pivaloyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (162bg)



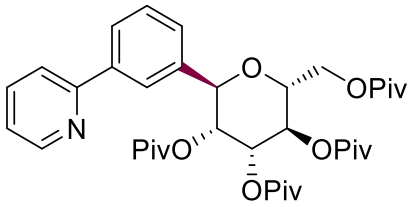
The general procedure **H** was followed using benzo[*h*]quinoline (**160n**) (17.9 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-[(pivaloyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (**161bc**) (115.9 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol)

in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 4/1) yielded **162bg** (38.6 mg, 57%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.44 (d, *J* = 8.1 Hz, 1H), 9.03 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.45 (d, *J* = 9.3 Hz, 1H), 8.21 (dt, *J* = 8.1, 1.4 Hz, 1H), 8.03 (d, *J* = 7.3 Hz, 1H), 7.87 – 7.74 (m, 2H), 7.56 (dd, *J* = 8.1, 4.5 Hz, 1H), 6.13 (t, *J* = 3.6 Hz, 1H), 5.74 (d, *J* = 4.0 Hz, 1H), 5.63 (dd, *J* = 8.3, 2.9 Hz, 1H), 5.54 (t, *J* = 7.8 Hz, 1H), 4.52 – 4.31 (m, 1H), 4.06 (dd, *J* = 12.2, 2.5 Hz, 1H), 3.80 – 3.66 (m, 1H), 1.29 (s, 9H), 1.21 (s, 9H), 1.18 (s, 9H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.2 (C_q), 177.8 (C_q), 177.1 (C_q), 176.7 (C_q), 149.0 (CH), 146.5 (C_q), 135.6 (CH), 132.4 (C_q), 132.2 (C_q), 131.5 (C_q), 128.0 (CH), 126.3 (CH), 125.9 (C_q), 125.8 (CH), 125.7 (CH), 124.4 (CH), 122.1 (CH), 74.0 (CH), 72.2 (CH), 70.6 (CH), 69.6 (CH), 66.6 (CH), 61.5 (CH_2), 38.9 (C_q), 38.8 (C_q), 38.8 (C_q), 27.2 (CH_3), 27.2 (CH_3), 27.1 (CH_3), 27.0 (CH_3).
IR (ATR): $\tilde{\nu}$ = 2976, 1729, 1479, 1397, 1278, 1169, 1144, 1123, 762 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 700 (60) $[M+Na]^+$, 678 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{36}H_{52}NO_9^+$ $[M+H]^+$ 678.3637, found 678.3636.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(pivaloyloxy)methyl]-6-[3-(pyridin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (162bh)



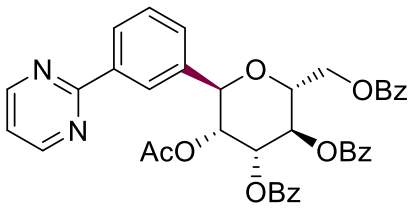
The general procedure **H** was followed using 2-phenylpyridine (**160a**) (15.5 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-[(pivaloyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (**161bc**) (115.9 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 4/1) yielded **162bh** (30.7 mg, 47%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.18 (dd, *J* = 2.1, 1.2 Hz, 1H), 8.12 – 8.04 (m, 1H), 7.90 – 7.76 (m, 2H), 7.71 – 7.63 (m, 1H), 7.60 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.33 – 7.27 (m, 1H), 6.14 (t, *J* = 3.0 Hz, 1H), 5.58 (t, *J* = 9.2 Hz, 1H),

5.24 (dd, *J* = 9.2, 3.0 Hz, 1H), 5.20 (d, *J* = 3.0 Hz, 1H), 4.35 (dd, *J* = 12.2, 5.6 Hz, 1H), 4.21 (dd, *J* = 12.2, 2.2 Hz, 1H), 3.87 (ddd, *J* = 9.2, 5.6, 2.2 Hz, 1H), 1.31 (s, 9H), 1.26 (s, 9H), 1.23 (s, 9H), 1.18 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.2 (C_q), 177.7 (C_q), 177.4 (C_q), 176.8 (C_q), 156.9 (C_q), 149.8(CH), 140.4 (C_q), 136.9 (CH), 136.1 (C_q), 129.6 (CH), 127.2 (CH), 127.0 (CH), 125.3 (CH), 122.4 (CH), 120.8 (CH), 76.0 (CH), 71.7 (CH), 70.3 (CH), 69.2 (CH), 66.0 (CH), 62.3 (CH_2), 39.0 (C_q), 38.9 (C_q), 38.9 (C_q), 38.8(C_q), 27.2 (CH_3), 27.2 (CH_3), 27.1 (CH_3). 1 CH resonances are missing due to the overlap.
IR (ATR): $\tilde{\nu}$ = 2974, 1729, 1585, 1479, 1279, 1130, 1076, 762, 730 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 676 (10) $[M+Na]^+$, 654 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{37}H_{52}NO_9^+$ $[M+H]^+$ 654.3637, found 654.3639.

(2*R*,3*R*,4*R*,5*R*,6*R*)-5-Acetoxy-2-[(benzoyloxy)methyl]-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4-diyl dibenzoate (162bi)



The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-5-acetoxy-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4-diyl dibenzoate (**161bd**) (119.2 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **162bi** (46.4 mg, 69%) as a syrup.

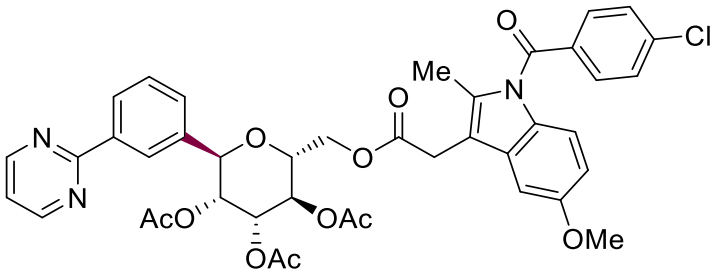
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 1H), 8.73 (d, *J* = 4.8 Hz, 2H), 8.48 (d, *J* = 7.8 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 3H), 7.93 (d, *J* = 8.0 Hz, 3H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.51 – 7.45 (m, 1H), 7.44 – 7.37 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 4.8 Hz, 1H), 6.33 (t, *J* = 3.1 Hz, 1H), 5.97 (d, *J* = 9.0 Hz, 1H), 5.62 (dd, *J* = 9.0, 3.1 Hz, 1H), 5.38 (d, *J* = 3.1 Hz, 1H), 4.99 – 4.46 (m, 2H), 4.29 (dt, *J* = 9.0, 5.5, 4.2 Hz, 1H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.13 (C_q), 166.22 (C_q), 165.76 (C_q), 165.45 (C_q), 164.22 (C_q), 157.25 (CH), 138.65 (C_q), 135.90 (C_q), 133.43 (CH), 133.40 (CH), 132.99

(CH), 129.85 (C_q), 129.82 (CH), 129.81 (CH), 129.71 (CH), 129.51 (CH), 129.07 (C_q), 128.87 (C_q), 128.58 (CH), 128.49 (CH), 128.39 (CH), 128.30 (CH), 126.54 (CH), 119.27 (CH), 75.83 (CH), 71.43 (CH), 70.46 (CH), 69.88 (CH), 67.76 (CH), 63.47 (CH_2), 20.91 (CH_3). 1 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1717, 1555, 1410, 1267, 1220, 1091, 1069, 1027, 908, 707 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1367 (45) $[2M+Na]^+$, 695 (100) $[M+Na]^+$, 673 (20) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{39}H_{33}N_2O_9^+$ $[M+H]^+$ 673.2181, found 673.2177.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-({2-[1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl]acetoxy}methyl)-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162ca)



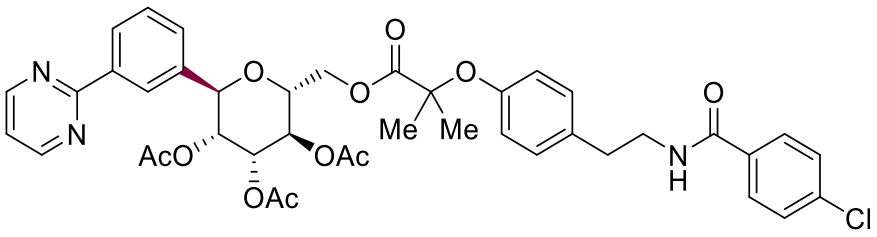
The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-({2-[1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl]acetoxy}methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161ca**) (141.4 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 2/1) yielded **162ca** (58.7 mg, 75%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 4.8 Hz, 2H), 8.66 (d, *J* = 2.0 Hz, 1H), 8.45 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.59 (dt, *J* = 7.7, 2.0 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.46 (m, 1H), 7.46 – 7.43 (m, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 7.00 (d, *J* = 2.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.64 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.02 (dd, *J* = 3.8, 3.1 Hz, 1H), 5.33 (dd, *J* = 8.5, 7.8 Hz, 1H), 5.24 (dd, *J* = 8.5, 3.1 Hz, 1H), 5.18 (d, *J* = 3.8 Hz, 1H), 4.50 (dd, *J* = 12.1, 7.0 Hz, 1H), 4.21 (dd, *J* = 12.1, 2.8 Hz, 1H), 3.92 (td, *J* = 7.5, 2.8 Hz, 1H), 3.87 – 3.80 (m, 1H), 3.79 – 3.72 (m, 4H), 2.36 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.58 (C_q), 170.14 (C_q), 170.03 (C_q), 169.60 (C_q), 168.24 (C_q), 164.03 (C_q), 157.26 (CH), 156.04 (C_q), 139.17 (C_q), 138.21 (C_q), 136.11 (C_q), 135.95 (C_q), 133.87 (C_q), 131.16 (CH), 130.76 (C_q), 130.62 (C_q), 129.38 (CH), 129.05 (CH), 128.70 (CH), 128.32 (CH), 126.55 (CH), 119.39 (CH), 114.91 (CH), 112.23 (C_q), 111.69 (CH), 101.20 (CH), 75.10 (CH), 71.64 (CH), 69.39 (CH), 69.28 (CH), 67.02 (CH), 62.69 (CH_2), 55.61 (CH), 29.85 (CH_2), 20.90 (CH_3), 20.71 (CH_3), 13.32 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1737, 1683, 1529, 1495, 1366, 1215, 1091, 1051, 917, 732 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 806 (100) $[M+Na]^+$, 784 (20) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{41}H_{39}ClN_3O_{11}^+$ $[M+H]^+$ 784.2268, found 784.2263.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-{[(2-{4-[2-(4-Chlorobenzamido)ethyl]phenoxy}-2-methylpropanoyl)oxy]methyl}-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162cb)



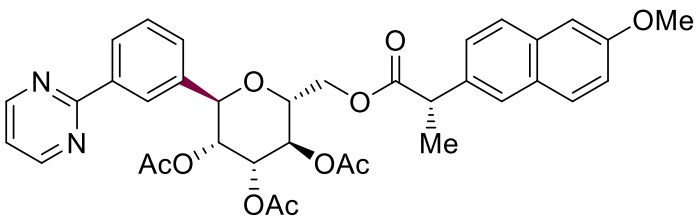
The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-{[(2-{4-[2-(4-chlorobenzamido)ethyl]phenoxy}-2-methylpropanoyl)oxy]methyl}tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161cb**) (142.2 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 2/1) yielded **162cb** (43.3 mg, 55%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 4.8 Hz, 2H), 8.58 (s, 1H), 8.41 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.54 (m, 3H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.20 (t, *J* = 4.8 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.16 (t, *J* = 5.7 Hz, 1H), 5.93 (t, *J* = 4.4 Hz, 1H), 5.40 – 5.24 (m, 2H), 5.16 (d, *J* = 4.4 Hz, 1H), 4.57 (dd, *J* = 12.0, 6.8 Hz, 1H), 4.31 (dd, *J* = 12.0, 3.1 Hz, 1H), 4.02 – 3.89 (m, 1H), 3.59 (dd, *J* = 6.8, 5.7 Hz, 2H), 2.79 (t, *J* = 6.8 Hz, 2H), 2.09 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.60 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.81 (C_q), 170.01 (C_q), 169.98 (C_q), 169.63 (C_q), 166.29 (C_q), 164.14 (C_q), 157.27 (CH), 153.93 (C_q), 138.32 (C_q), 137.54 (C_q), 136.11 (C_q), 133.00 (C_q), 132.58 (C_q), 129.38 (CH), 129.27 (CH), 128.87 (CH), 128.75 (CH), 128.29 (CH), 128.24 (CH), 126.63 (CH), 120.00 (CH), 119.35 (CH), 79.21 (C_q), 74.54 (CH), 71.80 (CH), 69.32 (CH), 69.17 (CH), 67.22 (CH), 62.77 (CH_2), 41.16 (CH_2), 34.69 (CH_2), 25.43 (CH_3), 25.31 (CH_3), 20.83 (CH_3), 20.76 ($2CH_3$).

IR (ATR): $\tilde{\nu}$ = 1748, 1639, 1556, 1509, 1412, 1368, 1222, 1146, 1073, 1014 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 810 (100) $[M+Na]^+$, 788 (40) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{41}H_{43}ClN_3O_{11}^+$ $[M+H]^+$ 788.2581, found 788.2577.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-({[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]oxy}methyl)-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162cc)



The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-({[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]oxy}methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161cc**) (116.0 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 2/1) yielded **162cc** (44.6 mg, 68%) as a syrup.

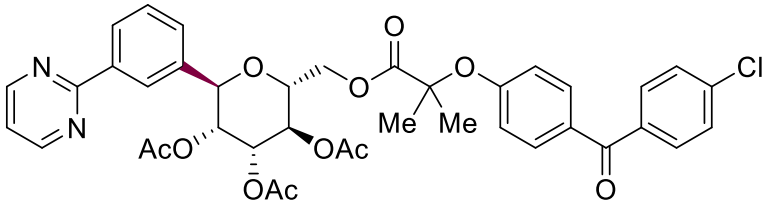
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 4.8 Hz, 2H), 8.67 (t, *J* = 1.4 Hz, 1H), 8.48 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.68 (t, *J* = 8.7 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 7.24 (t, *J* = 4.8 Hz, 1H), 7.14 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.01 (dd, *J* = 4.0, 2.9 Hz, 1H), 5.34 – 5.29 (m, 1H), 5.26 (dd, *J* = 8.3, 2.9 Hz, 1H), 5.17 (d, *J* = 4.0 Hz, 1H), 4.44 (dd, *J* = 12.0, 7.6 Hz, 1H), 4.29 (dd, *J* = 12.0, 2.9 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 1H), 3.98 – 3.89 (m, 4H), 2.11 (s, 6H), 2.04 (s, 3H), 1.62 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.26 (C_q), 170.10 (C_q), 170.02 (C_q), 169.59 (C_q), 164.15 (C_q), 157.56 (C_q), 157.24 (CH), 138.18 (C_q), 136.09 (C_q), 135.28 (C_q), 133.66

(C_q), 129.25 (CH), 128.87 (C_q), 128.80 (CH), 128.23 (CH), 127.08 (CH), 126.55 (CH), 126.28 (CH), 126.01 (CH), 119.32 (CH), 118.86 (CH), 105.51 (CH), 74.74 (CH), 71.74 (CH), 69.34 (CH), 69.28 (CH), 67.26 (CH), 62.67 (CH_2), 55.25 (CH_3), 45.33 (CH), 20.83 (CH_3), 20.72 (CH_3), 20.70 (CH_3), 18.38 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1745, 1607, 1569, 1412, 1370, 1247, 1217, 1074, 690 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 679 (100) $[M+Na]^+$, 657 (60) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{36}H_{37}N_2O_{10}^+$ $[M+H]^+$ 657.2443, found 657.2441.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[({2-[4-(4-Chlorobenzoyl)phenoxy]-2-methylpropanoyl}oxy)methyl]-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162cd)



The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-[({2-[4-(4-chlorobenzoyl)phenoxy]-2-methylpropanoyl}oxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161cd**) (133.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 2/1) yielded **162cd** (38.7 mg, 52%) as a syrup.

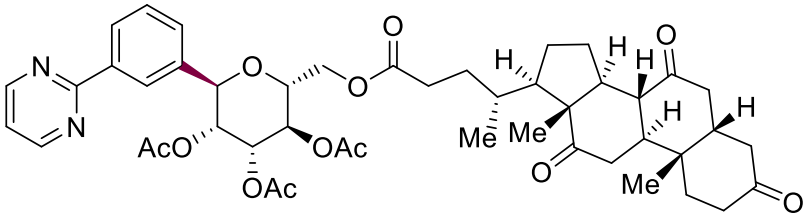
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 4.8 Hz, 2H), 8.57 (t, *J* = 1.6 Hz, 2H), 8.38 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.69 – 7.60 (m, 4H), 7.57 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.20 (t, *J* = 4.8 Hz, 1H), 6.92 – 6.83 (m, 2H), 5.94 (dd, *J* = 4.4, 2.8 Hz, 1H), 5.29 (t, *J* = 8.1, 7.0 Hz, 1H), 5.25 (dd, *J* = 7.9, 2.8 Hz, 1H), 5.15 (d, *J* = 4.4 Hz, 1H), 4.62 (dd, *J* = 12.0, 7.0 Hz, 1H), 4.28 (dd, *J* = 12.0, 2.8 Hz, 1H), 3.93 (td, *J* = 7.0, 2.8 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.70 (s, 3H), 1.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.15 (C_q), 173.20 (C_q), 169.96 (C_q), 169.95 (C_q), 169.62 (C_q), 164.08 (C_q), 159.35 (C_q), 157.25 (CH), 138.31 ($2C_q$), 136.28 (C_q), 135.99 (C_q), 131.85 (CH), 131.14 (CH), 130.49 (C_q), 129.24 (CH), 128.81 (CH), 128.48 (CH),

128.34 (CH), 126.61 (CH), 119.34 (CH), 117.81 (CH), 79.36 (CH_2), 74.56 (CH), 71.77 (CH), 69.23 (CH), 69.16 (CH), 67.14 (CH), 62.92 (CH_2), 25.44 (CH_3), 20.83 (CH_3), 20.77 (CH_3), 20.75 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1747, 1655, 1599, 1411, 1247, 1220, 1143, 1048, 928, 764 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 767(100) $[M+Na]^+$, 745 (35) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{39}H_{38}ClN_2O_{11}^+$ $[M+Na]^+$ 745.2159, found 745.2153

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-({[(*R*)-4-[(5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl]pentanoyl]oxy}methyl)-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162ce)



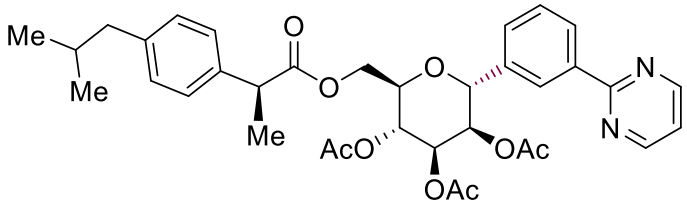
The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-({[(*R*)-4-[(5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl]pentanoyl]oxy}methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161ce**) (151.4 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 2/1) yielded **162ce** (53.8 mg, 65%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85 (d, *J* = 4.7 Hz, 2H), 8.63 (s, 1H), 8.45 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 4.7 Hz, 1H), 6.02 (dd, *J* = 3.7, 3.3 Hz, 1H), 5.33 (t, *J* = 8.1 Hz, 1H), 5.24 (dd, *J* = 8.3, 3.3 Hz, 2H), 5.20 (d, *J* = 3.7 Hz, 2H), 4.46 (dd, *J* = 12.0, 6.9 Hz, 1H), 4.19 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.04 – 3.83 (m, 1H), 3.10 – 2.68 (m, 3H), 2.54 – 2.41 (m, 1H), 2.38 – 2.29 (m, 4H), 2.26 – 2.20 (m, 3H), 2.15 (s, 3H), 2.10 (s, 3H), 2.09 – 2.05 (m, 2H), 2.04 (s, 3H), 2.02 – 1.94 (m, 4H), 1.90 – 1.77 (m, 2H), 1.63 (td, *J* = 13.8, 5.4 Hz, 1H), 1.41 (s, 3H), 1.36 – 1.21 (m, 4H), 1.05 (s, 3H), 0.86 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.86 (C_q), 208.96 (C_q), 208.62 (C_q), 173.73 (C_q), 170.15 (C_q), 170.04 (C_q), 169.56 (C_q), 164.19 (C_q), 157.29 (CH), 138.38 (C_q), 136.00 (C_q), 129.32 (CH), 128.65 (CH), 128.26 (CH), 126.55 (CH), 119.36 (CH), 75.07 (CH), 71.66 (CH), 69.40 (CH), 69.37 (CH), 67.14 (CH), 62.13 (CH_2), 56.84 (C_q), 51.71 (CH), 48.95 (CH), 46.80 (CH), 45.61 (CH), 45.51 (CH), 44.94 (CH_2), 42.76 (CH_2), 38.59 (C_q), 36.45 (CH_2), 35.97 (CH_2), 35.39 (CH), 35.24 (CH_2), 31.15 (CH_2), 30.27 (CH_2), 27.52 (CH_2), 25.08 (CH_2), 21.87 (CH_3), 20.93 (CH_3), 20.73 ($2CH_3$), 18.63 (CH_3), 11.79 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1746, 1714, 1556, 1412, 1369, 1247, 1221, 1048, 751 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 851 (100) $[M+Na]^+$, 829 (50) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{46}H_{57}N_2O_{12}^+$ $[M+Na]^+$ 829.3906, found 829.3900

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-({[(*S*)-2-(4-Isobutylphenyl)propanoyl]oxy}methyl)-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162cf)



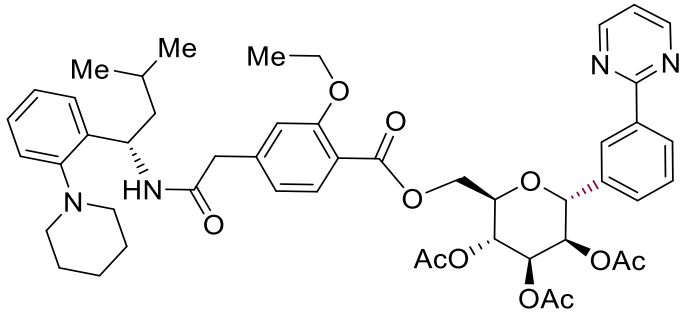
The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-({[(*S*)-2-(4-isobutylphenyl)propanoyl]oxy}methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161cf**) (111.2 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 2/1) yielded **162cf** (37.3 mg, 59%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 4.8 Hz, 2H), 8.64 (t, *J* = 1.7 Hz, 1H), 8.44 (dt, *J* = 7.0, 1.5 Hz, 1H), 7.67 – 7.39 (m, 2H), 7.25 – 7.16 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.99 (dd, *J* = 3.9, 3.0 Hz, 1H), 5.27 (t, *J* = 8.4, 7.6 Hz, 1H), 5.22 (dd, *J* = 8.4, 3.0 Hz, 1H), 5.14 (d, *J* = 3.9 Hz, 1H), 4.33 (dd, *J* = 11.9, 7.5 Hz, 1H), 4.25 (dd, *J* = 11.9, 3.1 Hz, 1H), 3.88 (td, *J* = 7.5, 3.0 Hz, 1H), 3.81 (q, *J* = 7.2 Hz, 1H), 2.40 (d, *J* = 7.1 Hz, 2H), 2.12 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.81 (dq, *J* = 13.8, 7.1, 6.6 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.39 (C_q), 170.18 (C_q), 170.10 (C_q), 169.63 (C_q), 164.27 (C_q), 157.30 (CH), 140.58 (C_q), 138.35 (C_q), 137.39 (C_q), 136.12 (C_q), 129.34 (CH), 129.32 (CH), 128.83 (CH), 128.28 (CH), 127.26 (CH), 126.60 (CH), 119.38 (CH), 74.92 (CH), 71.74 (CH), 69.45 (CH), 69.38 (CH), 67.31 (CH), 62.77 (CH_2), 45.06 (CH), 45.04 (CH_2), 30.16 (CH), 22.40 (CH_3), 20.96 (CH_3), 20.78 (CH_3), 20.76 (CH_3), 18.41 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1737, 1569, 1555, 1411, 1368, 1246, 1213, 1075, 1047, 753cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 655 (100) $[M+Na]^+$, 633 (50) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{35}H_{41}N_2O_9^+$ $[M+H]^+$ 633.2807, found 633.2801.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-({[2-Ethoxy-4-(2-{[(*S*)-3-methyl-1-[2-(piperidin-1-yl)phenyl]butyl]amino}-2-oxoethyl)benzoyl]oxy}methyl)-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162cg)



The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-({[2-ethoxy-4-(2-{[(*S*)-3-methyl-1-[2-(piperidin-1-yl)phenyl]butyl]amino}-2-oxoethyl)benzoyl]oxy}methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161cg**) (160.4 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), (4-CF_3-C_6H_4)$_3$P (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 1/1) yielded **162cg** (69.4 mg, 79%) as a syrup.

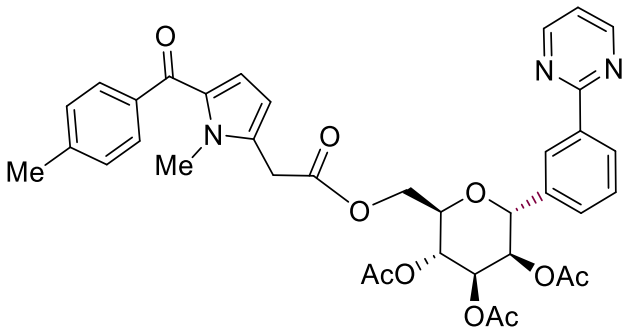
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 4.4 Hz, 2H), 8.64 – 8.60 (m, 1H), 8.40 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.12 (t, *J* = 4.4 Hz, 1H), 7.10 – 6.98 (m, 2H), 6.85 (s, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.00 (dd, *J* = 3.9, 3.0 Hz, 1H), 5.46 – 5.33 (m, 2H), 5.26 (dd, *J* = 8.3, 3.0 Hz, 1H), 5.20 (d, *J* = 3.9 Hz, 1H), 4.64 – 4.39 (m, 2H), 4.14 – 3.86 (m, 3H),

3.53 (s, 2H), 2.12 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.78 – 1.47 (m, 10H), 1.41 (d, *J* = 6.2 Hz, 1H), 1.35 (t, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 170.07 (C_q), 169.99 (C_q), 169.57 (C_q), 168.54 (C_q), 165.16 (C_q), 164.04 (C_q), 159.15 (C_q), 157.17 (CH), 152.40 (C_q), 141.35 (C_q), 138.58 (C_q), 138.36 (C_q), 135.98 (C_q), 132.28 (CH), 129.19 (CH), 128.57 (CH), 128.08 (CH), 127.86 (CH), 127.61 (CH), 126.49 (CH), 125.03 (CH), 122.75 (CH), 120.60 (CH), 119.25 (CH), 118.41 (C_q), 113.74 (CH), 74.88 (CH), 71.64 (CH), 69.43 (CH), 69.33 (CH), 67.38 (CH), 64.44 (CH_2), 62.63 (CH_2), 49.73 (CH), 46.65 (CH_2), 44.24 (CH_2), 26.68 (CH_2), 25.26 (CH_3), 24.04 (CH_2), 22.71 (CH_3), 22.46 (CH_3), 20.87 (CH_3), 20.71 (CH_3), 14.50 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1747, 1609, 1529, 1410, 1368, 1213, 1177, 1041, 750 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 901 (10) $[M+Na]^+$, 879 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{49}H_{59}N_4O_{11}^+$ $[M+H]^+$ 879.4175, found 879.4170.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-({2-[1-methyl-5-(4-methylbenzoyl)-1*H*-pyrrol-2-yl]acetoxy}methyl)-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162ch)



The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-({2-[1-methyl-5-(4-methylbenzoyl)-1*H*-pyrrol-2-yl]acetoxy}methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161ch**) (121.4 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 1/1) yielded **162ch** (34.2 mg, 50%) as a syrup.

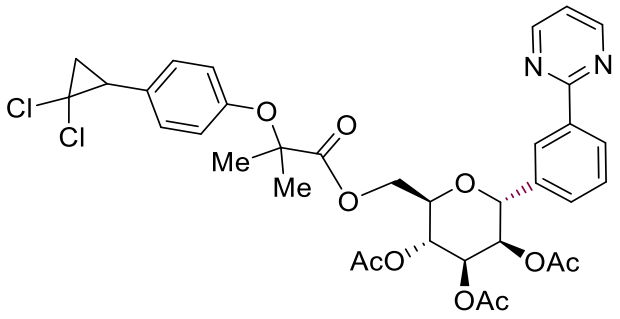
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 8.85 (d, *J* = 4.8 Hz, 2H), 8.68 (t, *J* = 2.1 Hz, 1H), 8.49 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.69 – 7.63 (m, 1H), 7.60 (t, *J* = 7.7

Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 3H), 7.24 (t, *J* = 4.8 Hz, 1H), 6.69 (d, *J* = 4.1 Hz, 1H), 6.14 (d, *J* = 4.1 Hz, 1H), 6.08 (t, *J* = 3.4 Hz, 1H), 5.37 (t, *J* = 8.3 Hz, 1H), 5.29 (dd, *J* = 8.6, 3.1 Hz, 1H), 5.23 (d, *J* = 3.4 Hz, 1H), 4.60 (dd, *J* = 12.1, 7.1 Hz, 1H), 4.25 (dd, *J* = 12.1, 2.6 Hz, 1H), 3.96 – 3.93 (m, 1H), 3.93 – 3.83 (m, 2H), 2.46 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.82 (C_q), 170.14 (C_q), 170.04 (C_q), 169.67 (C_q), 169.19 (C_q), 164.13 (C_q), 157.26 (CH), 141.83 (C_q), 138.38 (C_q), 137.28 (C_q), 135.85 (C_q), 134.06 (C_q), 131.42 (C_q), 129.38 (3CH), 128.63 (4CH), 128.34 (CH), 126.56 (CH), 122.17 (CH), 119.40 (CH), 109.53 (CH), 75.21 (CH), 71.53 (CH), 69.40 (CH), 69.22 (CH), 66.97 (CH), 62.99 (CH_2), 33.16 (CH_3), 32.46 (CH_2), 21.50 (CH_3), 20.93 (CH_3), 20.71 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1746, 1625, 1568, 1454, 1374, 1246, 1219, 1047, 750 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 706 (100) $[M+Na]^+$, 684 (40) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{37}H_{38}N_3O_{10}^+$ $[M+H]^+$ 684.2552, found 684.2544

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[({2-[4-(2,2-dichlorocyclopropyl)phenoxy]-2-methylpropanoyl}oxy)methyl]-6-[3-(pyrimidin-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162ci)



The general procedure **H** was followed using 2-phenylpyrimidine (**160e**) (15.6 mg, 0.10 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-[({2-[4-(2,2-dichlorocyclopropyl)phenoxy]-2-methylpropanoyl}oxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161ci**) (127.6 mg, 0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (4.7 mg, 10 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 5/1 to 2/1) yielded **162ci** (44.4 mg, 62%) as a syrup.

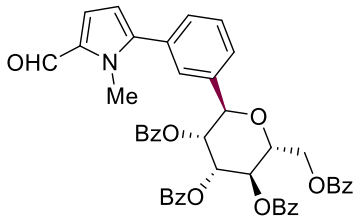
^{1}H NMR (400 MHz,$CDCl_3$): δ = 8.85 (d, *J* = 4.8 Hz, 2H), 8.64 (d, *J* = 1.8 Hz, 1H), 8.47 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.24 (td, *J* = 4.8, 0.8 Hz, 1H), 7.04 (d, *J* = 6.9 Hz, 2H), 6.86 (d, *J* = 6.9 Hz, 2H), 5.99 (dd, *J* = 4.3, 3.0 Hz, 1H), 5.34 (t, *J* = 8.2, 6.9 Hz, 1H), 5.29 (ddd, *J* = 8.1, 3.0, 1.8 Hz, 1H), 5.21 (d, *J* = 4.3 Hz, 1H), 4.63 (dd, *J* = 12.0, 6.9 Hz, 1H), 4.33 (dt, *J* = 12.0, 2.9, 1.5 Hz, 1H), 3.97 (tt, *J* = 6.9, 3.0 Hz, 1H), 2.80 (dd, *J* = 7.7, 7.3 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H), 1.92 (dd, *J* = 11.0, 7.7 Hz, 1H), 1.76 (t, *J* = 7.3 Hz, 1H), 1.65 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.70 (C_q), 170.00 (C_q), 169.95 (C_q), 169.57 (C_q), 164.14 (C_q), 157.24 (CH), 154.67 (C_q), 138.35 (C_q), 136.05 (C_q), 129.49 (CH), 129.23 (CH), 128.85 (CH), 128.29 (C_q), 128.27 (CH), 128.25 (CH), 126.57 (CH), 126.55 (CH), 119.31 (CH), 119.28 (CH), 79.20 (C_q), 74.55 (CH), 74.53 (CH), 71.77 (CH), 69.27 (CH), 69.19 (CH), 67.16 (CH), 62.74 (CH_2), 60.80 (C_q), 34.74 (CH), 25.73 (CH_2), 25.43 (CH_3), 25.32 (CH_3), 20.81 (CH_3), 20.74 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1745, 1569, 1556, 1412, 1368, 1218, 1143, 1047, 760 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 737 (100) $[M+Na]^+$, 715 (60) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{35}H_{37}Cl_2N_2O_{10}^+$ $[M+H]^+$ 715.1820, found 715.1814

5.3.3.2 Post-Functionalization and Synthetic Application

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(5-formyl-1-methyl-1*H*-pyrrol-2-yl)phenyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (204)



To a solution of **162aa** (530 mg, 0.7 mmol) in acetonitrile (4 mL) was added CH_3I (3.5 mmol, 5.0 equiv) under argon in a sealed flask. The mixture was stirred at 70 °C for 12 h, and then cooled to room temperature. After removal of the solvent under reduced pressure to afford the crude pyridinium salt, which was purified by fast column chromatography on silica gel. Then, to an oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was sequentially charged with pyridinium salt (218.8 mg, 0.25 mmol), I_2 (40 mg, 0.16 mmol), K_2CO_3 (138 mg, 1.0 mmol), Methyl Methacrylate

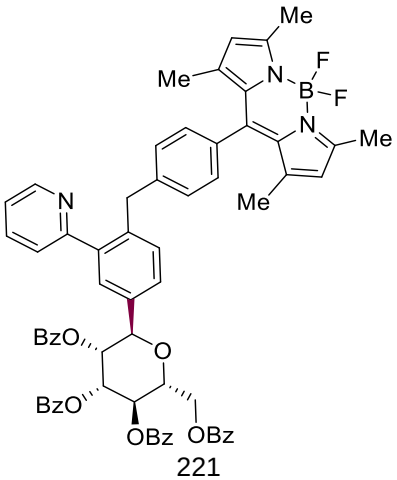
(28 µL, 0.25 mmol), H_2O (0.5 mL) and DCE (0.5 mL) in the air. The mixture was stirred at 80 °C for 17 hours.[165] After cooling to room temperature, the mixture was diluted with DCM and the volatiles were removed under vacuum. The residue was purified by column chromatography on silica gel (hexane/ ethyl acetate) to afford **204** (130 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.61 (s, 1H), 8.13 – 8.06 (m, 4H), 8.01 – 7.88 (m, 4H), 7.82 – 7.76 (m, 2H), 7.65 – 7.56 (m, 3H), 7.53 – 7.47 (m, 3H), 7.46 – 7.40 (m, 4H), 7.38 (d, *J* = 4.2 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 3H), 6.98 (d, *J* = 4.1 Hz, 1H), 6.52 (dd, *J* = 3.0, 2.8 Hz, 1H), 6.38 (d, *J* = 4.1 Hz, 1H), 6.18 (t, *J* = 9.2 Hz, 1H), 5.73 (dd, *J* = 9.2, 3.0 Hz, 1H), 5.51 (d, *J* = 2.8 Hz, 1H), 4.79 – 4.58 (m, 2H), 4.28 (ddd, *J* = 8.8, 5.6, 3.2 Hz, 1H), 3.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 179.60 (CHO), 166.10 (C_q), 165.85 (C_q), 165.56 (C_q), 165.36 (C_q), 143.35 (C_q), 136.19 (C_q), 133.49 (CH), 133.46 (CH), 133.39 (CH), 133.17 (C_q), 133.11 (CH), 132.18 (C_q), 129.80 (CH), 129.72 (CH), 129.61 (CH), 129.53 (CH), 129.27 (C_q), 129.24 (CH), 128.79 (C_q), 128.53 (CH), 128.41 (CH), 127.35 (CH), 126.56 (CH), 124.37 (CH), 111.10 (CH), 77.00, 75.82 (CH), 71.63 (CH), 70.62 (CH), 70.18 (CH), 67.43 (CH), 63.03 (CH_2), 34.35 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1718, 1657, 1601, 1451, 1262, 1090, 1069, 1026, 751, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1549 (15) $[2M+Na]^+$, 786 (100) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{46}H_{37}NO_{10}Na^+$ $[M+Na]^+$ 786.2310, found 786.2299.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{4-[4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4 λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)benzyl]-3-(pyridin-2-yl)phenyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (205)

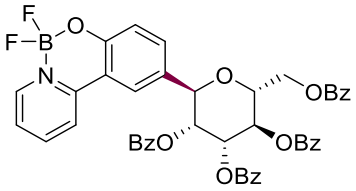


221

To an oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was sequentially charged with **162aa** (36.5 mg, 0.05 mmol), benzyl chloride (28 mg, 0.075 mmol), $[RuCl_2(p\text{-cymene})]_2$ (1.6 mg, 5.0 % mol), $(1\text{-Ad})CO_2H$ (2.7 mg, 30% mol), K_2CO_3 (13.8 mg, 2.0 equiv), toluene (0.5 mL) under the N_2. The mixture was stirred at 110 °C for 20 h, and then cooled to room temperature.[166] After removal of the solvent under reduced pressure to afford the crude residue, which was purified by column chromatography on silica gel to afford **205** (36 mg, 67%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 4.7 Hz, 1H), 8.16 – 7.99 (m, 4H), 8.00 – 7.85 (m, 4H), 7.74 (d, *J* = 6.3 Hz, 2H), 7.68 – 7.52 (m, 3H), 7.51 – 7.43 (m, 3H), 7.42 – 7.27 (m, 10H), 7.19 – 7.04 (m, 4H), 6.55 (dd, *J* = 3.0, 2.4 Hz, 1H), 6.19 (t, *J* = 9.6 Hz, 1H), 5.96 (s, 2H), 5.72 (dd, *J* = 9.6, 3.0 Hz, 1H), 5.49 (d, *J* = 2.4 Hz, 1H), 4.72 (dd, *J* = 12.1, 2.7 Hz, 1H), 4.58 (dd, *J* = 12.1, 5.4 Hz, 1H), 4.45 – 4.19 (m, 3H), 2.55 (s, 6H), 1.33 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.15 (C_q), 165.87 (C_q), 165.64 (C_q), 165.39 (C_q), 155.25 (C_q), 142.99 (C_q), 141.78 (C_q), 141.71 (C_q), 139.08 (C_q), 133.84 (C_q), 133.45 (CH), 133.41 (CH), 133.32 (CH), 132.98 (CH), 132.51 (C_q), 131.79 (CH), 131.44 (C_q), 129.84 (CH), 129.77 (CH), 129.71 (2 CH), 129.68 (CH), 129.58 (CH), 129.40 (C_q), 128.91 (C_q), 128.86 (C_q), 128.53 (CH), 128.42 (CH), 128.39 (3 CH), 128.35 (CH), 127.78 (CH), 126.59 (CH), 124.26 (CH), 122.18 (CH), 121.07 (CH), 76.03 (CH), 71.25 (CH), 70.83 (CH), 70.32 (CH), 67.41 (CH), 63.15 (CH_2), 38.72 (CH_2), 14.53 (CH_3). 2 C_q resonances are missing due to the overlap.
^{19}F NMR (282 MHz, $CDCl_3$): δ = -146.30 (dd, *J* = 65.2, 31.8 Hz).
^{11}B NMR (96 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 33.3 Hz).
IR (ATR): $\tilde{\nu}$ = 1718, 1601, 1451, 1264, 1177, 1091, 1068, 1027, 979, 706 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1092 (20) $[M+Na]^+$, 1070 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{65}H_{55}BF_2N_3O_9^+$ $[M+H]^+$ 1070.4004, found 1070.3992.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-(6,6-difluoro-6*H*-6λ^4,7λ^4-benzo[*e*]pyrido[1,2-*c*][1,3,2]oxazaborinin-4-yl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (206)



To a 25 mL Schlenk tube with a magnetic stir bar was charged with $Cu(OAc)_2$ (3.7 mg, 20 mol %), $AgBF_4$ (29.2 mg, 1.5 equiv), PivOH (15.3 mg, 1.5 equiv), and **162aa** (73.3 mg, 0.1 mmol) in toluene (0.5 mL) under air atmosphere. The resulting mixture was stirred at 145 °C for 24 h and then diluted with 3 mL of dichloromethane.[167] The solution was filtered through a celite pad and washed with dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired products **206** (41 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 5.0 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.36 – 8.33 (m, 1H), 8.28 – 8.19 (m, 1H), 8.17 – 8.03 (m, 4H), 8.01 – 7.89 (m, 4H), 7.82 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.69 – 7.55 (m, 3H), 7.54 – 7.39 (m, 6H), 7.38 – 7.28 (m, 5H), 6.64 (t, *J* = 2.6 Hz, 1H), 6.23 (t, *J* = 9.7 Hz, 1H), 5.70 (dd, *J* = 9.7, 2.9 Hz, 1H), 5.53 – 5.33 (m, 1H), 4.71 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.61 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.15 (ddd, *J* = 9.7, 5.2, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.44 (C_q), 166.12 (C_q), 165.69 (C_q), 165.34 (C_q), 156.08 (C_q), 149.88 (C_q), 142.70 (CH), 141.24 (CH), 133.53 (CH), 133.50 (CH), 133.30 (CH), 133.17 (CH), 129.88 (CH), 129.77 (CH), 129.73 (CH), 129.26 (C_q), 128.81 (C_q), 128.79 (C_q), 128.58 (CH), 128.50 (CH), 128.45 (CH), 128.42 (CH), 127.49 (C_q), 123.73 (CH), 123.30 (CH), 121.96 (CH), 121.07 (CH), 116.24 (C_q), 75.79 (CH), 71.39 (CH), 71.29 (CH), 69.72 (CH), 67.10 (CH), 63.10 (CH_2).2 CH and 1 C_q resonances are missing due to the overlap.

^{19}F NMR (377 MHz, $CDCl_3$): δ = -143.06 – -148.08 (m).

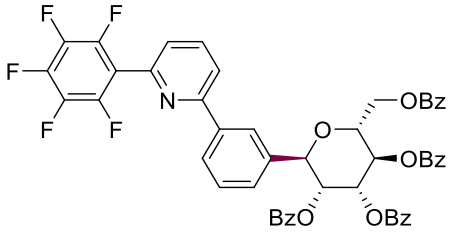
^{11}B NMR (96 MHz, $CDCl_3$): δ = 1.21 (s).

IR (ATR): $\tilde{\nu}$ = 1717, 1621, 1500, 1452, 1261, 1089, 1067, 1026, 917, 707 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 820 (100) $[M+Na]^+$, 798 (15) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{45}H_{34}BF_2NNaO_{10}^+$ $[M+Na]^+$ 820.2144, found 820.2140.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(benzoyloxy)methyl]-6-{3-[6-(perfluorophenyl)pyridin-2-yl]phenyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (207)



To a solution of **162aa** (530 mg, 0.7 mmol) in acetonitrile (4 mL) was added CH_3I (3.5 mmol, 5.0 equiv) under argon in a sealed flask. The mixture was stirred at 70 °C for 12 h, and then cooled to room temperature. After removal of the solvent under reduced pressure to afford the crude pyridinium salt, which was purified by fast column chromatography on silica gel. Then, to an oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was sequentially charged with pyridinium salt (218.8 mg, 0.25 mmol), pentafluorbenzoic acid (0.5 mmol), $CuBr_2$ (0.5 mmol), TBAB (161 mg, 0.5 mmol), diglyme (1.5 mL) in the air. The mixture was stirred at 130 °C for 12 hours.[168] After cooling to room temperature, the mixture was diluted with DCM and filtered through a short pad of celite, the volatiles were removed under vacuum and the residue was purified by column chromatography on silica gel with hexane/ethyl acetate to give pure product **207** (214.5 mg, 89%).

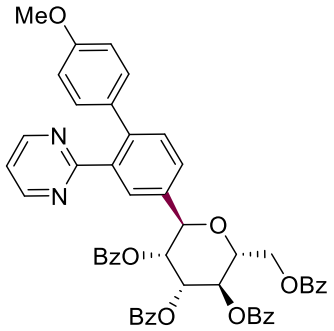
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 8.16 – 8.09 (m, 5H), 8.00 – 7.87 (m, 6H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.59 (dd, *J* = 7.4, 5.6 Hz, 2H), 7.54 – 7.44 (m, 4H), 7.41 (dd, *J* = 7.8, 2.9 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 4H), 6.65 (t, *J* = 2.7 Hz, 1H), 6.25 (d, *J* = 9.5 Hz, 1H), 5.77 (dd, *J* = 9.5, 2.7 Hz, 1H), 5.58 – 5.53 (m, 1H), 4.76 (dd, *J* = 12.2, 2.7 Hz, 1H), 4.63 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.27 (ddd, *J* = 9.5, 5.2, 2.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.13 (C_q), 165.93 (C_q), 165.64 (C_q), 165.36 (C_q), 157.19 (C_q), 139.63 (C_q), 137.65 (CH), 135.95 (C_q), 133.40 (CH), 133.30 (CH), 133.02 (CH), 129.92 (CH), 129.84 (CH), 129.79 (C_q), 129.73 (CH), 129.71 (CH), 129.43 (C_q), 128.93 (C_q), 128.86 (C_q), 128.53 (CH), 128.39 (CH), 128.36 (CH), 127.53 (CH), 127.45 (CH), 125.09 (CH), 124.36 (CH), 120.54 (CH), 76.30 (CH), 71.31 (CH), 70.99 (CH), 70.33 (CH), 67.33 (CH), 63.14 (CH_2). 3 CH and 2 C_q resonances are missing due to the overlap.

^{19}F NMR (282 MHz, $CDCl_3$): δ = -142.92 (dd, *J* = 23.6, 9.2 Hz), -154.11 (t, *J* = 21.4 Hz), -161.93 (td, *J* = 22.3, 8.3 Hz).

IR (ATR): $\tilde{\nu}$ = 1719, 1522, 1499, 1451, 1262, 1091, 1068, 1026, 988, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 922 (100) $[M+Na]^+$, 900 (30) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{51}H_{34}F_5NO_9Na^+$ $[M+Na]^+$ 922.2046, found 922.2053.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[4'-methoxy-2-(pyrimidin-2-yl)-[1,1'-biphenyl]-4-yl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (208)



To an oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was sequentially charged with **162ae** (73.4 mg, 0.1 mmol), *para*-methoxy phenyl iodide (35.0 mg, 0.15 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.0 mg, 2.5% mol), $MesCO_2H$ (4.9 mg, 30% mol), K_2CO_3 (58 mg, 2.0 equiv), toluene (0.5 mL) under the N_2. The mixture was stirred at 120 °C for 24 h, and then cooled to room temperature.[169] After removal of the solvent under reduced pressure to afford the crude residue, which was purified by column chromatography on silica gel to afford **208** (60 mg, 71%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 4.8 Hz, 2H), 8.13 (dd, *J* = 7.8, 1.4 Hz, 5H), 8.05 – 7.95 (m, 2H), 7.95 – 7.84 (m, 3H), 7.68 – 7.56 (m, 3H), 7.55 – 7.36 (m, 8H), 7.36 – 7.30 (m, 2H), 7.21 – 6.98 (m, 3H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.64 (dd, *J* = 2.9, 2.2 Hz, 1H), 6.24 (t, *J* = 9.6 Hz, 1H), 5.75 (dd, *J* = 9.6, 2.9 Hz, 1H), 5.56 (d, *J* = 2.2 Hz, 1H), 4.77 (dd, *J* = 12.1, 2.5 Hz, 1H), 4.56 (dd, *J* = 12.1, 5.3 Hz, 1H), 4.37 (ddd, *J* = 8.2, 5.3, 2.5 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.88 (C_q), 166.17 (C_q), 165.86 (C_q), 165.65 (C_q), 165.39 (C_q), 158.61 (C_q), 156.85 (CH), 141.23 (C_q), 139.12 (C_q), 134.03 (C_q), 133.40 (CH), 133.37 (CH), 133.24 (CH), 133.15 (C_q), 132.94 (CH), 131.62 (CH), 130.18 (CH), 129.91 (CH), 129.85 (CH), 129.77 (CH), 129.75 (CH), 129.51 (C_q), 129.02 (C_q), 128.89 (C_q), 128.75 (CH), 128.53 (CH), 128.39 (CH), 128.35 (CH), 127.23 (CH), 118.65 (CH), 113.59 (CH), 76.24 (CH), 71.12 (CH), 70.97 (CH), 70.42 (CH), 67.34 (CH), 63.24 (CH_2), 55.19 (CH). 4 CH and 1 C_q resonances are missing due to the overlap.

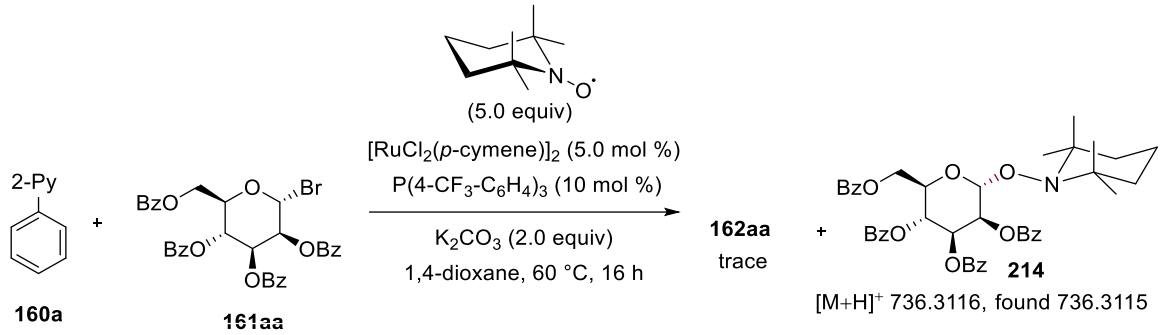
IR (ATR): $\tilde{\nu}$ = 1720, 1555, 1452, 1266, 1178, 1093, 1069, 1027, 709 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 863 (100) $[M+Na]^+$, 841 (10) $[M+H]^+$.

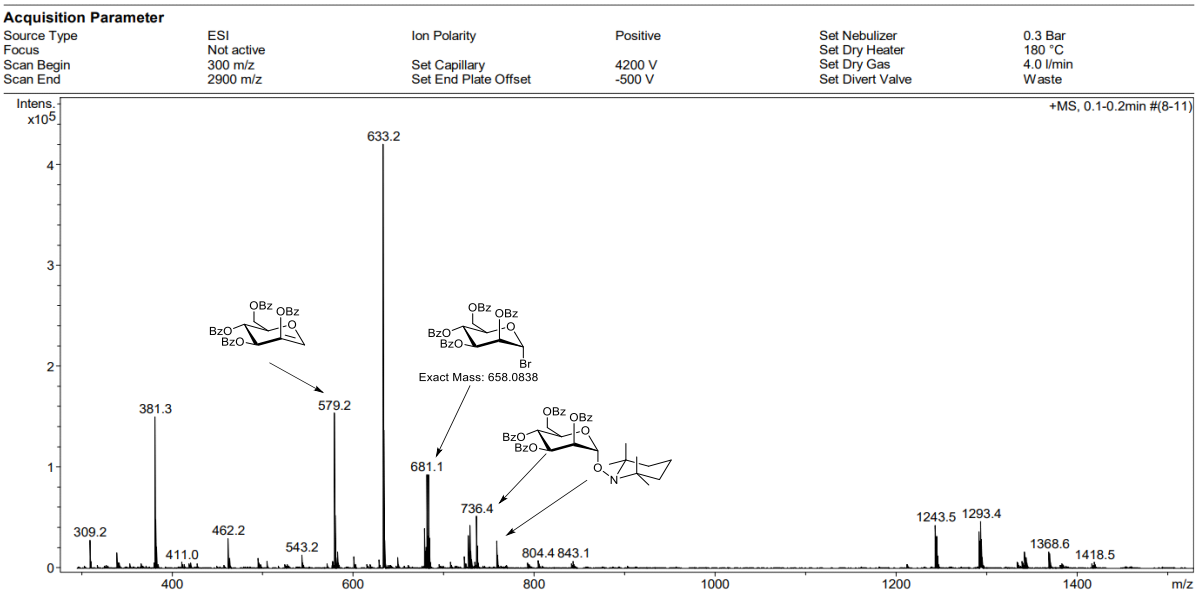
HR-MS (ESI): *m*/*z* calcd for $C_{51}H_{40}N_2O_{10}Na^+$ $[M+Na]^+$ 863.2575, found 863.2570.

5.3.3.3 Mechanistic Studies

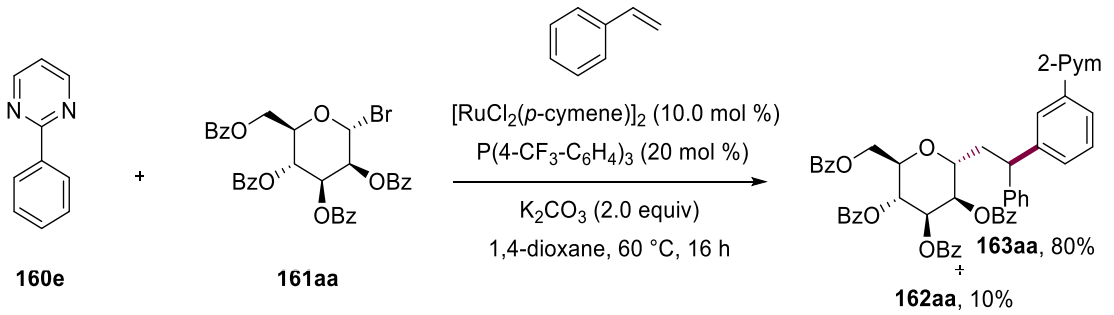
5.3.3.3.1 Radical Trapping Experiment



Phenyl pyridine **160a** (0.20 mmol), OBz-mannosyl bromide **161aa** (0.40 mmol), TEMPO (1.0 mmol, 5.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (9.3 mg, 10 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2, filtered. and concentrated *in vacuo*. Based on TLC, only trace amount mount of **162aa** could be observed and the residue was checked with ESI-HRMS, the desired glycosyl radical-TEMPO adduct **214** was detected at 736.3115[M+H] and 758.2937 [M+Na], which means that this ruthenium catalyzed C–H glycosylation might involves radical species.



5.3.3.3.2 Radical Relay Experiment



Arene **160e** (0.10 mmol), OBz-mannosyl bromide **161aa** (0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 10.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (9.4 mg, 20 mol %), K_2CO_3 (27.6 mg, 0.2 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, styrene (0.15 mmol) and 1,4-dioxane (1.0 mL) was added under N_2 and then stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product **163aa** in 80% yield and **162aa** in 10% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 4.8 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.52 (t, *J* = 1.8 Hz, 0.5H), 8.47 (t, *J* = 1.8 Hz, 0.5H),, 8.35 – 8.25 (m, 1H), 8.21 – 8.15 (m, 2H), 8.03 – 7.94 (m, 4H), 7.80 (ddd, *J* = 8.3, 6.6, 1.4 Hz, 2H), 7.65 – 7.54 (m, 2H), 7.51 – 7.26 (m, 15H), 7.25 – 7.21 (m, 1H), 7.21 – 7.11 (m, 2H), 5.97 (t, *J* = 9.1 Hz, 1H), 5.86 (dd, *J* = 4.7, 3.3 Hz, 1H), 5.75 (td, *J* = 3.0, 1.7 Hz, 1H), 4.74 – 4.48 (m, 2H), 4.46 – 4.28 (m, 2H), 4.17 (ddt, *J* = 15.4, 11.6, 3.0 Hz, 1H), 3.05 – 2.77 (m, 1H), 2.74 – 2.48 (m, 1H).

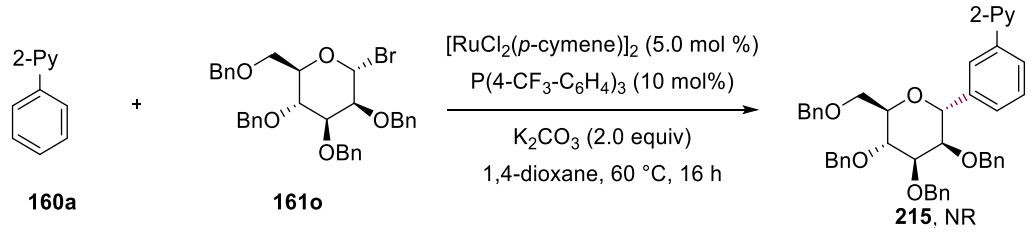
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.13 (C_q), 165.62 (C_q), 165.57 (C_q), 165.45 (C_q), 165.41 (C_q), 165.39 (3C_q), 164.54 (C_q), 164.46 (C_q), 157.18 (CH), 157.09 (CH), 144.65 (C_q), 144.16 (C_q), 143.11 (C_q), 142.56 (C_q), 138.05 (C_q), 137.96 (C_q), 133.43 (CH), 133.42 (CH), 133.27 (CH), 133.23 (CH), 133.20 (CH), 133.10 (CH), 130.61 (CH), 130.39 (CH), 129.88 (C_q), 129.86 (C_q), 129.79 (CH), 129.77 (CH), 129.68 (CH), 129.66 (CH), 129.46 (C_q), 129.45 (C_q), 129.08 (CH), 128.95 (CH), 128.92 (C_q), 128.90 (C_q), 128.81 (CH), 128.69 (CH), 128.48 (CH), 128.44 (CH), 128.41 (CH), 128.31 (CH), 128.28 (CH), 128.09 (CH), 127.71 (CH), 127.65 (CH), 127.01 (CH), 126.69 (CH), 126.61 (CH), 126.55 (CH), 126.49 (CH), 119.12 (CH), 119.02 (CH), 73.56 (CH), 73.36 (CH), 71.85 (CH), 71.66 (CH), 70.66 (CH), 70.38 (CH), 70.35 (CH), 70.23 (CH), 67.79 (CH), 67.75 (CH), 63.56 (CH_2), 63.38 (CH_2), 46.89 (CH), 46.68 (CH), 34.31 (CH_2), 34.01 (CH_2). 1Cq is missing

IR (ATR): $\tilde{\nu}$ = 1721, 1555, 1452, 1264, 1178, 1093, 1069, 1027, 708 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 861 (100) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{42}N_2O_9Na^+$ $[M+Na]^+$ 861.2783, found 861.2777.

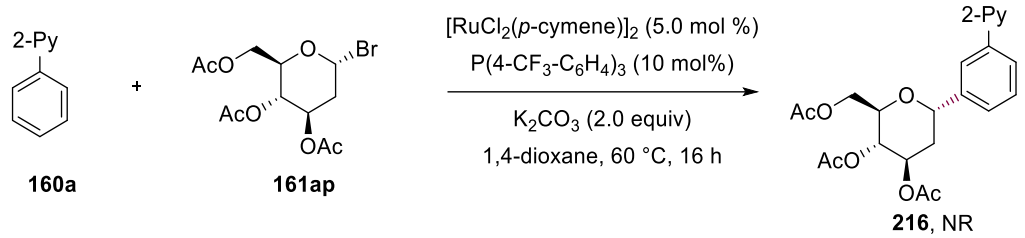
5.3.3.3.3 Reaction with Benzyl Protected Mannosyl Bromide 161ao



160a **161o** **215**, NR

Phenyl pyridine **160a** (0.20 mmol), OBn-mannosyl bromide **161o** (0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (9.3 mg, 10 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2, filtered. and concentrated *in vacuo*. The residue was checked with ESI-HRMS, but no desired product **215** was observed.

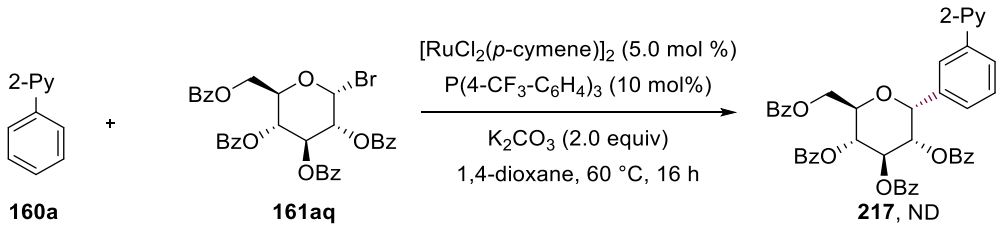
5.3.3.3.4 Reaction with 2-Deoxyl Glycosyl Bromide 161ap



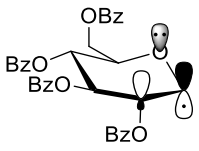
160a **161ap** **216**, NR

Phenyl pyridine **160a** (0.20 mmol), 2-deoxyl-OAc-glycoside bromide **161ap** (0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (9.3 mg, 10 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2, filtered. and concentrated *in vacuo*. The residue was checked with ESI-HRMS, but no desired product **216** was observed.

5.3.3.3.5 Reaction with Benzyl Protected Glucosyl Bromide 161aq



160a **161aq** **217**, ND

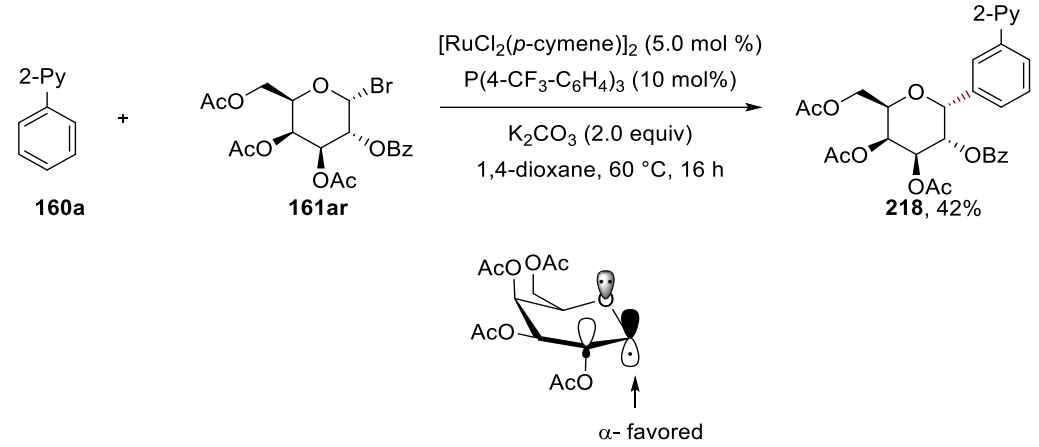


$B_{2,5}$
more stable

Phenyl pyridine **160a** (0.20 mmol), OBz-glucosyl bromide **161aq** (0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (9.3 mg, 10 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2, filtered. and concentrated *in vacuo*. The residue was checked with ESI-HRMS, but no desired product **217** was observed. It was reported that the glucopyranosyl radical in $B_{2,5}$ conformer is slightly stable than the $^1C_4$ and $^4C_1$ conformers as showed below, but the C2 benzoyl group and the lone pair electron of

the oxygen may block the attack of both sides to the cyclometallated ruthenium complex.

5.3.3.3.6 Reaction with Acetyl Protected Galactosyl Bromide 161ar



Phenyl pyridine **160a** (0.20 mmol), OAc-galactosyl bromide **161ar** (0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (9.3 mg, 10 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2, filtered. and concentrated *in vacuo*. The residue was purified by column chromatography to give desired product **218** in 42% yield with α-selectivity. This selectivity may be caused by the C4-acetyl group, which favors the axial radical addition to the para position of ruthenium complex.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 (dd, *J* = 4.7, 1.4 Hz, 1H), 8.15 (d, *J* = 1.9 Hz, 1H), 7.97 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.89 – 7.70 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.29 – 7.26 (m, 1H), 5.56 (t, *J* = 3.8 Hz, 1H), 5.52 – 5.48 (m, 1H), 5.48 – 5.43 (m, 1H), 5.41 (d, *J* = 3.0 Hz, 1H), 4.63 (dd, *J* = 12.0, 8.5 Hz, 1H), 4.32 (dt, *J* = 8.5, 4.1 Hz, 1H), 4.23 (dd, *J* = 12.0, 3.8 Hz, 1H), 2.20 (s, 3H), 2.18 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H).

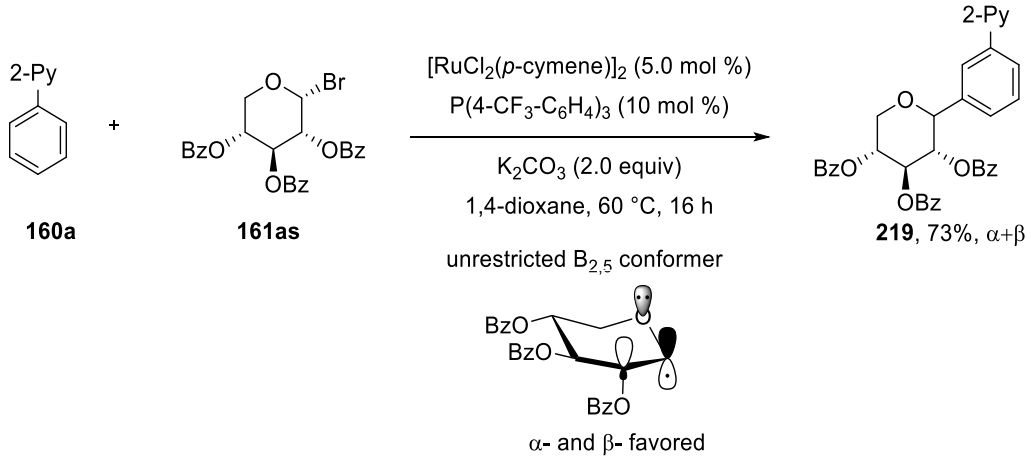
^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.74 (C_q), 169.81 (C_q), 169.42 (C_q), 169.31 (C_q), 156.95 (C_q), 149.68 (CH), 139.50 (C_q), 136.75 (CH), 136.56 (C_q), 128.72 (CH), 127.66 (CH), 126.60 (CH), 125.97 (CH), 122.27 (CH), 120.50 (CH), 71.09 (CH), 71.05 (CH), 70.12 (CH), 67.81 (CH), 66.69 (CH), 60.29 (CH_2), 20.89 (CH_3), 20.75 (CH_3), 20.74 (CH_3), 20.63 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1746, 1585, 1462, 1436, 1371, 1213, 1082, 1044, 778 cm^{-1}.

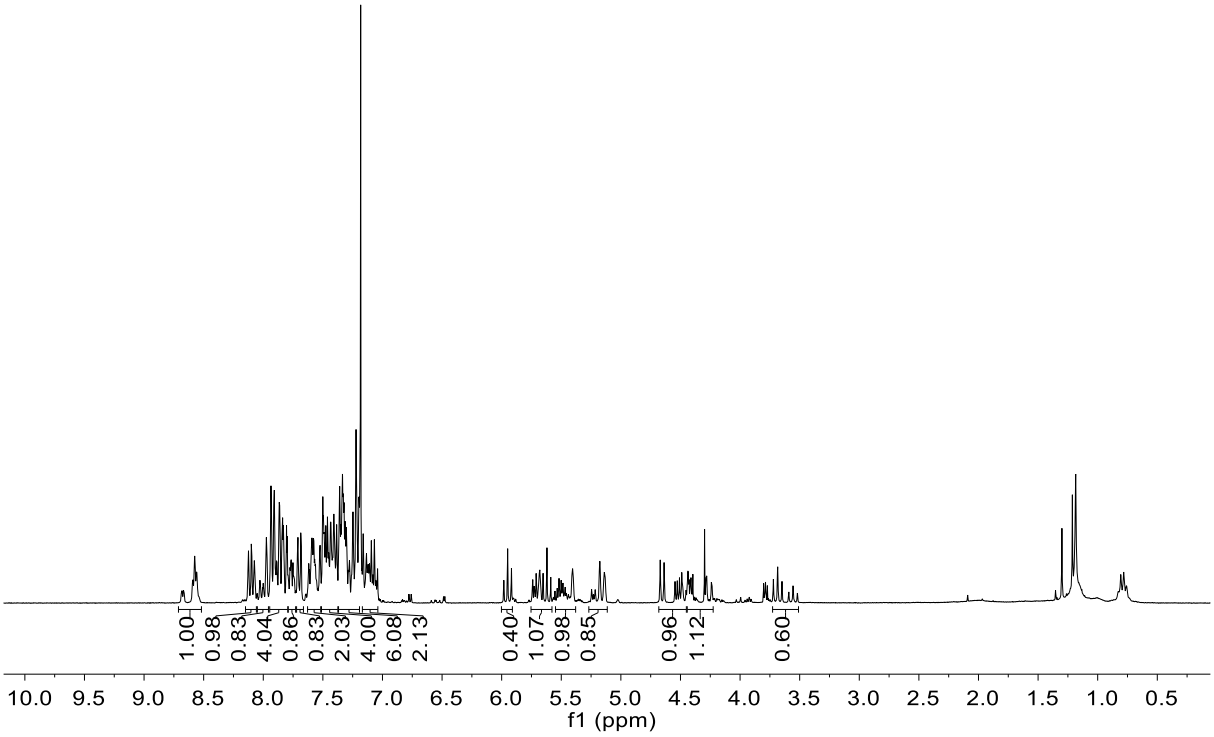
MS (ESI) *m*/*z* (relative intensity): 508 (60) $[M+Na]^+$, 486 (100) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{25}H_{28}NO_9^+$ $[M+H]^+$ 486.1755, found 486.1759.

5.3.3.3.7 Reaction with Benzyl Protected Xylosyl Bromide 161as

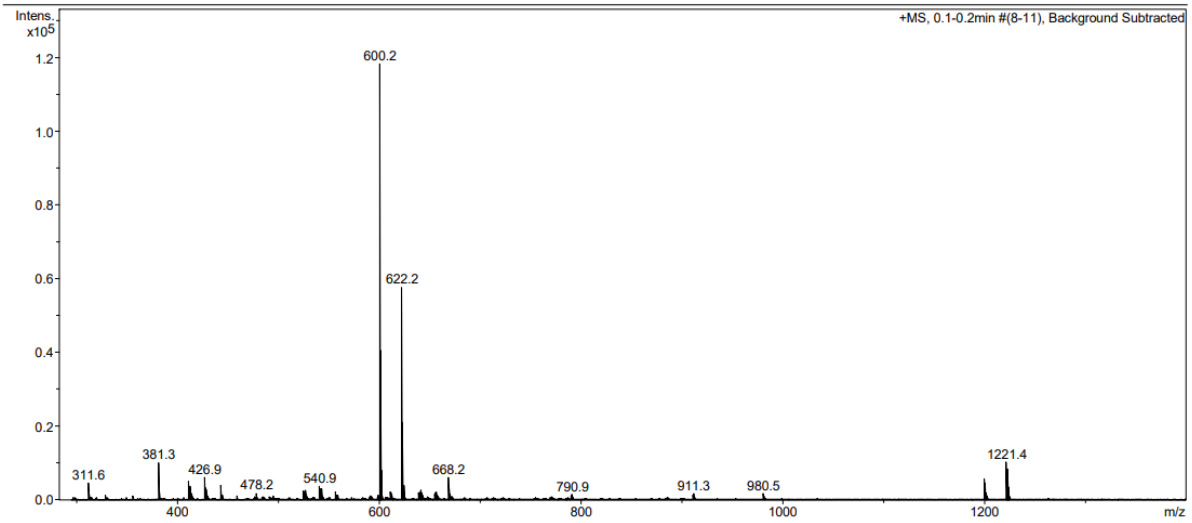


Phenyl pyridine **160e** (0.20 mmol), OBz-xylosyl bromide **161as** (0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (9.3 mg, 10 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2, filtered. and concentrated *in vacuo*. The residue was purified by column chromatography to give desired product **219** in 73% yield with a mixture of *α*- and *β*-selectivity. This selectivity may be caused by the formed stable $B_{2,5}$ boat conformer, and the C1 a planar carbon center allowed to form *α*-anomer and *β*-anomer, thus giving the mixture of isomers which are inseparable. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.80 – 8.50 (m, 1H), 8.19 – 8.05 (m, 1H), 8.05 – 7.96 (m, 1H), 7.96 – 7.83 (m, 4H), 7.81 – 7.73 (m, 1H), 7.73 – 7.66 (m, 1H), 7.64 – 7.55 (m, 2H), 7.54 – 7.38 (m, 4H), 7.37 – 7.19 (m, 6H), 7.17 – 7.01 (m, 2H), 5.95 (t, *J* = 9.6 Hz, 0.4H), 5.80 – 5.58 (m, 1H), 5.56 – 5.37 (m, 1H), 5.28 – 5.06 (m, 1H), 4.74 – 4.47 (m, 1H), 4.46 – 4.22 (m, 1H), 3.62 (t, *J* = 10.8 Hz, 0.6H). **IR** (ATR): $\tilde{\nu}$ = 1719, 1584, 1451, 1316, 1280, 1260, 1091, 1068, 1026, 708 cm^{-1}. **HR-MS** (ESI): *m*/*z* calcd for $C_{37}H_{30}NO_7^+$ $[M+H]^+$ 600.2017, found 600.2012.

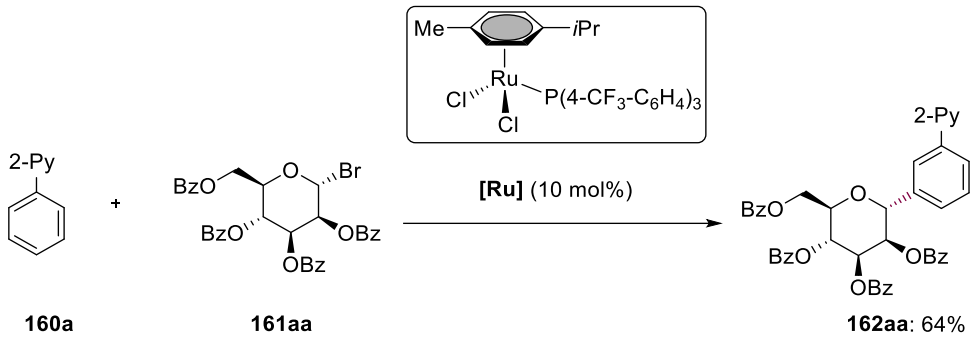


Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	300 m/z	Set Capillary	4200 V	Set Dry Gas	4.0 l/min
Scan End	2900 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



5.3.3.3.8 Key Ruthenium Catalyst Investigation



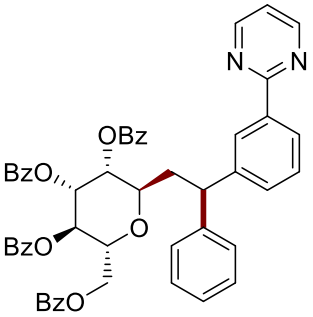
160a **161aa** **162aa**: 64%

Phenyl pyridine **160a** (0.20 mmol), OBz-mannosyl bromide **161aa** (0.40 mmol), **[Ru]** (5.0 mol %), (4-CF_3-C_6H_4)$_3$P (9.3 mg, 10 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2, filtered. and concentrated *in vacuo*. The residue was purified by column chromatography to afford product **162aa** in 64% yield, which means [Ru2] might be catalytic relevant for the *meta*-C–H glycosylation.

5.3.4 Ruthenium-Catalyzed *meta*-C−H Domino Ethyl Glycosylation

5.3.4.1 Characterization Data

(2*R*,3*R*,4*R*,5*R*,6R)-2-[(Benzoyloxy)methyl]-6-{2-phenyl-2-[3-(pyrimidin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163aa)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (12.2 mg, 10.0 mol %), P(4-CF_3-C_6H_4)$_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1)

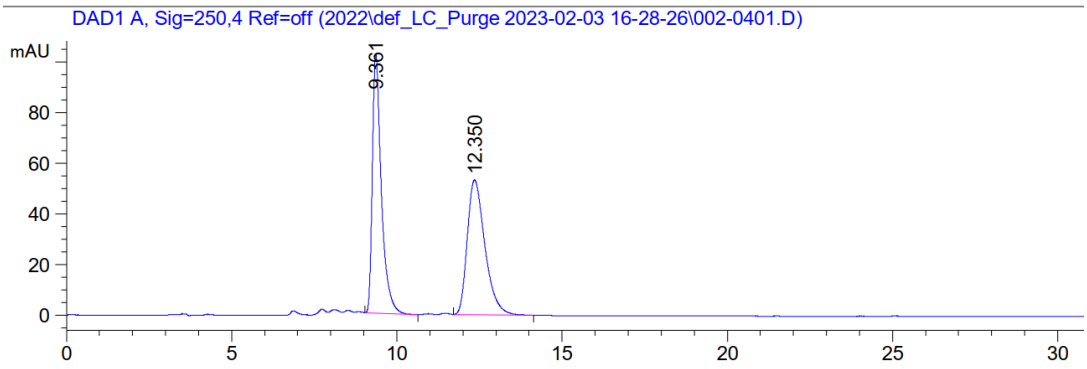
yielded **163aa** (134.1 mg, 80%) as a syrup, d.r. = 1:1, HPLC analysis also suggested the diastereoisomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 4.8 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.52 (t, *J* = 1.8 Hz, 0.5H), 8.47 (t, *J* = 1.8 Hz, 0.5H),, 8.35 – 8.25 (m, 1H), 8.21 – 8.15 (m, 2H), 8.03 – 7.94 (m, 4H), 7.80 (ddd, *J* = 8.3, 6.6, 1.4 Hz, 2H), 7.65 – 7.54 (m, 2H), 7.51 – 7.26 (m, 15H), 7.25 – 7.21 (m, 1H), 7.21 – 7.11 (m, 2H), 5.97 (t, *J* = 9.1 Hz, 1H), 5.86 (dd, *J* = 4.7, 3.3 Hz, 1H), 5.75 (td, *J* = 3.0, 1.7 Hz, 1H), 4.74 – 4.48 (m, 2H), 4.46 – 4.28 (m, 2H), 4.17 (ddt, *J* = 15.4, 11.6, 3.0 Hz, 1H), 3.05 – 2.77 (m, 1H), 2.74 – 2.48 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 165.6 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (3C_q), 164.5 (C_q), 164.5 (C_q), 157.2 (CH), 157.1 (CH), 144.7 (C_q), 144.2 (C_q), 143.1 (C_q), 142.6 (C_q), 138.1 (C_q), 138.0 (C_q), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.1 (CH), 130.6 (CH), 130.4 (CH), 129.9 (C_q), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.5 (C_q), 129.5 (C_q), 129.1 (CH), 129.0 (CH), 128.9 (C_q), 128.9 (C_q), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 127.7 (CH), 127.7 (CH), 127.0 (CH), 126.7 (CH), 126.6 (CH), 126.6 (CH), 126.5 (CH), 119.1 (CH), 119.0 (CH), 73.6 (CH), 73.4 (CH), 71.9 (CH), 71.7 (CH), 70.7 (CH), 70.4 (CH), 70.4 (CH), 70.2 (CH), 67.8 (CH), 67.8 (CH), 63.6 (CH_2), 63.4 (CH_2), 46.9 (CH), 46.7 (CH), 34.3 (CH_2), 34.0 (CH_2). 1 Cq and 4 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1721, 1555, 1452, 1264, 1178, 1093, 1069, 1027, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 861 (100) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{42}N_2O_9Na^+$ $[M+Na]^+$ 861.2783, found 861.2777.

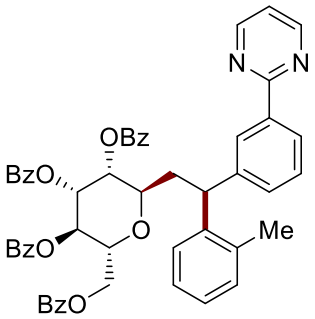
HPLC separation (Chiralpak® IA, *n*-hexane/*i*-PrOH 70:30, 1.0 mL/min, detection at 250 nm, 25 °C)



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.361	BB	0.2816	1940.07202	102.61768	49.5527
2	12.350	BB	0.5482	1975.09753	53.31678	50.4473

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{2-[3-(pyrimidin-2-yl)phenyl]-2-(*o*-tolyl)ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ab)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-methyl-2-vinylbenzene (**110b**) (35.4 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ab** (131.3 mg, 77% d.r. = 1:1) as a syrup.

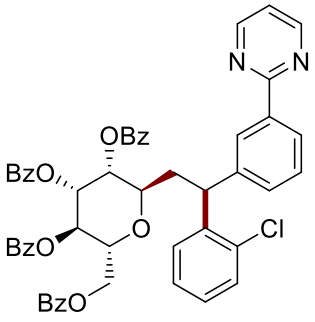
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 4.8 Hz, 1H), 8.74 (d, *J* = 4.8 Hz, 1H), 8.50 (t, *J* = 1.4 Hz, 0.49H), 8.46 (t, *J* = 1.4 Hz, 0.51H),, 8.37 – 8.23 (m, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.06 – 7.92 (m, 4H), 7.80 (t, *J* = 8.3 Hz, 2H), 7.54 (p,

J = 7.1 Hz, 3H), 7.51 – 7.32 (m, 10H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.25 – 7.04 (m, 4H), 5.98 (t, *J* = 8.9 Hz, 1H), 5.86 (d, *J* = 3.2 Hz, 0.54H), 5.83 (d, *J* = 3.0 Hz, 0.46H), 5.75 (t, *J* = 2.7 Hz, 0.48H), 5.71 (t, *J* = 3.1 Hz, 0.52H), 4.76 – 4.51 (m, 3H), 4.50 – 4.32 (m, 1H), 4.21 (t, *J* = 3.0 Hz, 1H), 3.09 – 2.49 (m, 2H), 2.31 (s, 1.46H), 2.24 (s, 1.54H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2 (C_q), 166.2 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 165.4 (C_q), 165.4 (C_q), 164.6 (C_q), 164.5 (C_q), 157.2 (CH), 157.1 (CH), 144.6 (C_q), 142.7 (C_q), 142.0 (C_q), 140.2 (C_q), 138.0 (C_q), 138.0 (C_q), 136.9 (C_q), 136.3 (C_q), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.1 (CH), 133.0 (CH), 131.1 (CH), 130.9 (CH), 130.7 (CH), 130.5 (CH), 129.9 (C_q), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.5 (C_q), 129.5 (C_q), 128.9 (C_q), 128.9 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 127.3 (CH), 126.6 (CH), 126.5 (CH), 126.5 (CH), 126.5 (CH), 126.5 (CH), 126.4 (CH), 126.3 (CH), 119.1 (CH), 119.0 (CH), 74.0 (CH), 72.8 (CH), 72.0 (CH), 71.6 (CH), 70.9 (CH), 70.5 (CH), 70.3 (CH), 70.1 (CH), 67.9 (CH), 67.7 (CH), 63.6 (CH_2), 63.3 (CH_2), 42.4 (CH), 42.2 (CH), 35.1 (CH_2), 34.5 (CH_2), 20.0 (CH_3), 19.9 (CH_3). 2 Cq and 6 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1727, 1555, 1411, 1264, 1108, 1093, 1069, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 875(95) $[M+Na]^+$, 853 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{45}N_2O_9^+$ $[M+H]^+$ 853.3120, found 853.3117.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-(2-chlorophenyl)-2-[3-(pyrimidin-2-yl)phenyl]ethyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ac)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1- 1-chloro-2-vinylbenzene (**110c**) (41.4 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$

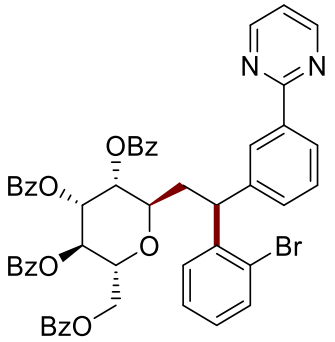
(18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ac** (61.1 mg, 35%) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 4.8 Hz, 1H), 8.74 (d, *J* = 4.8 Hz, 1H), 8.54 (t, *J* = 1.9 Hz, 0.5H), 8.49 (t, *J* = 1.9 Hz, 0.5H), 8.40 – 8.27 (m, 1H), 8.19 (d, *J* = 7.4 Hz, 1H), 8.13 (d, *J* = 7.4 Hz, 1H), 8.05 – 7.89 (m, 4H), 7.86 – 7.73 (m, 2H), 7.64 – 7.27 (m, 16H), 7.25 – 7.07 (m, 3H), 6.03 (t, *J* = 8.9 Hz, 0.5H), 5.95 (d, *J* = 8.9 Hz, 0.5H), 5.84 (td, *J* = 9.6, 3.2 Hz, 1H), 5.76 (t, *J* = 3.0 Hz, 0.5H), 5.73 (t, *J* = 3.0 Hz, 0.5H), 4.99 (dt, *J* = 8.7, 4.3 Hz, 1H), 4.76 – 4.33 (m, 3H), 4.32 – 4.13 (m, 1H), 2.97 – 2.45 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.3 (C_q), 166.2 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.3 (C_q), 164.5 (C_q), 164.4 (C_q), 157.2 (CH), 157.1 (CH), 143.2 (C_q), 141.6 (C_q), 141.1 (C_q), 139.8 C_q), 138.1 (C_q), 138.0 (C_q), 134.7 (C_q), 133.8 (C_q), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.0 (CH), 133.0 (CH), 131.3 (CH), 130.8 (CH), 130.2 (CH), 129.9 (C_q), 129.9 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.5 (C_q), 129.5 (C_q), 129.0 (CH), 129.0 (C_q), 129.0 (CH), 128.9 (C_q), 128.9 (C_q), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.3 (CH), 127.9 (CH), 127.8 (CH), 127.3 (CH), 127.3 (CH), 127.2 (CH), 126.8 (CH), 126.7 (CH), 119.1 (CH), 119.1 (CH), 74.0 (CH), 72.9 (CH), 71.9 (CH), 71.7 (CH), 70.9 (CH), 70.6 (CH), 70.3 (CH), 70.2 (CH), 67.6 (CH), 67.6 (CH), 63.4 (CH_2), 63.3 (CH_2), 42.9 (CH), 42.7 (CH), 34.0 (CH_2), 33.9 (CH_2). 1 Cq and 4 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1555, 1451, 1411, 1263, 1093, 1069, 1027, 909, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 895 (80) $[M+Na]^+$, 873 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{42}ClN_2O_9^+$ $[M+H]^+$ 873.2573, found 873.2571.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-(2-bromophenyl)-2-[3-(pyrimidin-2-yl)phenyl]ethyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ad)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-1-bromo-2-vinylbenzene (**110d**) (54.6 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ad** (148.4 mg, 81%, d.r. = 1:1) as a syrup.

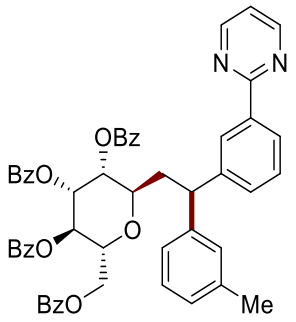
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (d, *J* = 4.8 Hz, 1H), 8.80 (d, *J* = 4.8 Hz, 1H), 8.60 (t, *J* = 1.4 Hz, 0.53H), 8.55 (d, *J* = 1.4 Hz, 0.47H), 8.37 (d, *J* = 6.1 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.00 (t, *J* = 8.3 Hz, 3H), 7.85 (dd, *J* = 11.4, 7.9 Hz, 2H), 7.64 – 7.51 (m, 5H), 7.51 – 7.46 (m, 4H), 7.42 (d, *J* = 6.8 Hz, 4H), 7.39 – 7.32 (m, 3H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 4.9 Hz, 0.5H), 7.18 (t, *J* = 4.9 Hz, 0.5H), 7.12 (q, *J* = 8.2 Hz, 1H), 6.06 (t, *J* = 9.0 Hz, 1H), 5.91 (dd, *J* = 9.3, 2.5 Hz, 0.5H), 5.87 (dd, *J* = 9.3, 2.0 Hz, 0.5H), 5.79 (d, *J* = 2.9 Hz, 1H), 5.10 – 4.96 (m, 1H), 4.83 – 4.41 (m, 3H), 4.32 (d, *J* = 11.1 Hz, 0.5H), 4.27 (d, *J* = 9.8 Hz, 0.5H), 3.08 – 2.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.3 (C_q), 166.2 (C_q), 165.6 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.3 (C_q), 165.3 (C_q), 164.5 (C_q), 164.4 (C_q), 157.2 (CH), 157.1 (CH), 143.2 (C_q), 143.1 (C_q), 141.4 (C_q), 141.2 (C_q), 138.1 (C_q), 138.0 (C_q), 133.6 (CH), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.0 (CH), 133.0 (CH), 131.3 (CH), 130.8 (CH), 130.0 (C_q), 129.9 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.5 (C_q), 129.5 (C_q), 129.0 (CH), 129.0 (C_q), 128.9 (C_q), 128.9 (C_q), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.9 (CH), 127.4 (CH), 126.8 (CH), 126.7 (CH), 125.6 (C_q), 124.7 (C_q), 119.1 (CH), 119.1 (CH), 74.0 (CH), 72.9 (CH), 71.8 (CH), 71.7 (CH), 70.9 (CH), 70.6 (CH),

70.3 (CH), 70.3 (CH), 67.6 (CH), 63.5 (CH_2), 63.3 (CH_2), 45.6 (CH), 45.3 (CH), 34.3 (CH_2), 34.2 (CH_2). 5 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1568, 1411, 1264, 1108, 1093, 1069, 1026, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 941(100) $[M+Na]^+$, 917 (15) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{41}{}^{79}BrNaO_9^+$ $[M+Na]^+$ 939.1888, found, 939.1879. *m*/*z* calcd for $C_{52}H_{41}{}^{81}BrO_9Na^+$ $[M+Na]^+$ 941.1871, found, 941.1871.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{2-[3-(pyrimidin-2-yl)phenyl]-2-(*m*-tolyl)ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ae)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-1-methyl-3-vinylbenzene (**110e**) (35.4 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ae** (73.3 mg, 43%, d.r. = 1:1) as a syrup.

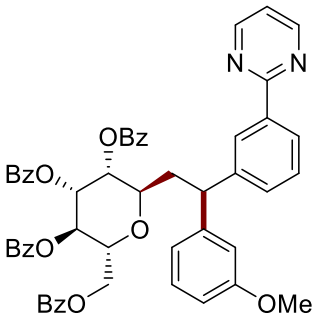
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 4.8 Hz, 1H), 8.70 (d, *J* = 4.8 Hz, 1H), 8.46 (d, *J* = 1.4 Hz, 0.5H), 8.42 (d, *J* = 1.4 Hz, 0.5H), 8.31 – 8.21 (m, 1H), 8.20 – 8.09 (m, 2H), 8.01 – 7.86 (m, 4H), 7.75 (dd, *J* = 7.7, 3.3 Hz, 2H), 7.52 (q, *J* = 7.1 Hz, 2H), 7.45 – 7.29 (m, 10H), 7.27 – 7.21 (m, 1H), 7.17 – 7.01 (m, 5H), 6.94 (d, *J* = 6.5 Hz, 1H), 5.92 (q, *J* = 9.1 Hz, 1H), 5.81 (dt, *J* = 9.5, 3.3 Hz, 1H), 5.69 (d, *J* = 2.9 Hz, 1H), 4.67 – 4.44 (m, 2H), 4.41 – 4.24 (m, 2H), 4.18 – 4.06 (m, 1H), 2.94 – 2.69 (m, 1H), 2.68 – 2.49 (m, 1H), 2.26 (s, 1.6H), 2.20 (s, 1.4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1 (C_q), 165.6 (C_q), 165.6 (C_q), 165.4 (C_q), 165.4 (C_q), 164.6 (C_q), 164.5 (C_q), 157.2 (CH), 157.1 (CH), 144.8 (C_q), 144.1 (C_q), 143.2 (C_q),

142.4 (C_q), 138.3 (C_q), 138.2 (C_q), 138.0 (C_q), 137.9 (C_q), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.1 (CH), 130.5 (CH), 130.3 (CH), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.5 (C_q), 129.5 (C_q), 129.0 (CH), 128.9 (CH), 128.9 (C_q), 128.6 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.8 (CH), 127.5 (CH), 127.3 (CH), 127.0 (CH), 126.6 (CH), 126.4 (CH), 125.0 (CH), 124.5 (CH), 119.1 (CH), 119.0 (CH), 73.6 (CH), 73.4 (CH), 71.8 (CH), 71.7 (CH), 70.6 (CH), 70.3 (CH), 70.3 (CH), 67.8 (CH), 63.5 (CH_2), 63.4 (CH_2), 46.7 (CH), 46.7 (CH), 34.2 (CH_2), 34.0 (CH_2), 21.5 (CH_3). 2 Cq and 6 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1721, 1556, 1452, 1265, 1108, 1093, 1069, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 875 (100) $[M+Na]^+$, 853 (70) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{45}N_2O_9^+$ $[M+H]^+$ 853.3120, found 853.3115.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-(3-methoxyphenyl)-2-[3-(pyrimidin-2-yl)phenyl]ethyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163af)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-1-methoxy-3-vinylbenzene (**110f**) (35.4 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163af** (76.4 mg, 44%, d.r. = 1:1) as a syrup.

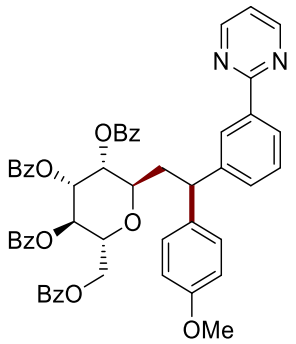
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 4.8 Hz, 1H), 8.79 (d, *J* = 4.8 Hz, 1H), 8.57 (d, *J* = 1.8 Hz, 0.5H), 8.53 (d, *J* = 1.8 Hz, 0.5H), 8.40 – 8.33 (m, 1H), 8.23 (d, *J* = 7.3 Hz, 2H), 8.10 – 7.96 (m, 4H), 7.90 – 7.81 (m, 2H), 7.69 – 7.36 (m, 12H), 7.35 – 7.31 (m, 1H), 7.30 – 7.27 (m, 1H), 7.27 – 7.15 (m, 2H), 6.99 (t, *J* = 7.0 Hz, 1H), 6.95 (t, *J* =

2.1 Hz, 0.5H), 6.91 (t, *J* = 2.1 Hz, 0.5H), 6.78 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.02 (t, *J* = 9.1 Hz, 1H), 5.91 (t, *J* = 3.5 Hz, 1H), 5.80 (t, *J* = 2.8 Hz, 1H), 4.76 – 4.56 (m, 2H), 4.50 – 4.37 (m, 2H), 4.23 (d, *J* = 2.9 Hz, 1H), 3.81 (s, 1.5H), 3.75 (s, 1.5H), 3.06 – 2.81 (m, 1H), 2.77 – 2.56 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 164.5 (C_q), 164.4 (C_q), 159.8 (C_q), 159.8 (C_q), 157.2 (CH), 157.1 (CH), 145.8 (C_q), 144.5 (C_q), 144.2 (C_q), 142.9 (C_q), 138.0 (C_q), 137.9 (C_q), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.0 (CH), 130.5 (CH), 130.3 (CH), 129.8 (C_q), 129.8 (C_q), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.6 (CH), 129.5 (C_q), 129.4 (C_q), 129.1 (CH), 128.9 (CH), 128.9 (C_q), 128.9 (C_q), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.7 (CH), 127.0 (CH), 126.6 (CH), 126.5 (CH), 120.3 (CH), 119.9 (CH), 119.1 (CH), 119.0 (CH), 114.0 (CH), 113.8 (CH), 112.0 (CH), 111.6 (CH), 73.6 (CH), 73.3 (CH), 71.8 (CH), 71.6 (CH), 70.7 (CH), 70.4 (CH), 70.4 (CH), 70.2 (CH), 67.8 (CH), 67.7 (CH), 63.5 (CH_2), 63.4 (CH_2), 55.2 (CH_3), 55.0 (CH_3), 46.9 (CH), 46.7 (CH), 34.3 (CH_2), 33.9 (CH_2). 1 Cq and 5 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1716, 1583, 1410, 1261, 1244, 1090, 1068, 906, 781, 704 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 891 (67) $[M+Na]^+$, 869 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{44}N_2O_{10}^+$ $[M+H]^+$ 869.3069, found 869.3064.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-(4-methoxyphenyl)-2-[3-(pyrimidin-2-yl)phenyl]ethyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ag)



The general pr^{oc}edure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-1-methoxy-4-vinylbenzene (**110g**) (35.4 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**)

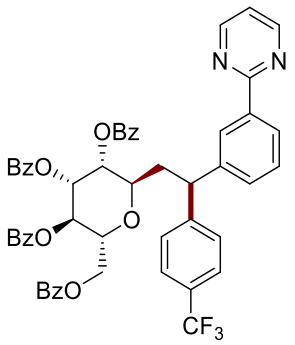
(263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ag** (147.6 mg, 85%, d.r. = 1:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 4.8 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.51 (t, *J* = 1.8 Hz, 0.46H), 8.46 (t, *J* = 1.8 Hz, 0.54H), 8.37 – 8.26 (m, 1H), 8.20 (t, *J* = 1.2 Hz, 1H), 8.18 (t, *J* = 1.2 Hz, 1H), 8.08 – 7.91 (m, 4H), 7.81 (td, *J* = 8.0, 1.4 Hz, 2H), 7.64 – 7.53 (m, 2H), 7.53 – 7.33 (m, 10H), 7.31 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 7.19 (t, *J* = 4.8 Hz, 0.52H), 7.13 (t, *J* = 4.8 Hz, 0.48H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 5.98 (t, *J* = 9.2 Hz, 1H), 5.87 (t, *J* = 3.3 Hz, 1H), 5.76 (q, *J* = 2.7 Hz, 1H), 4.71 – 4.51 (m, 2H), 4.46 – 4.38 (m, 1H), 4.35 (d, *J* = 4.4 Hz, 1H), 4.24 – 4.08 (m, 1H), 3.77 (s, 1.56H), 3.73 (s, 1.44H), 3.03 – 2.72 (m, 1H), 2.74 – 2.45 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 166.1 (C_q), 165.6 (C_q), 165.6 (C_q), 165.4 (C_q), 165.4 ($3C_q$), 164.5 (C_q), 164.5 (C_q), 158.2 (C_q), 158.2 (C_q), 157.2 (CH), 157.1 (CH), 145.0 (C_q), 143.5 (C_q), 138.0 (C_q), 137.9 (C_q), 136.3 (C_q), 134.6 (C_q), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.1 (CH), 130.5 (CH), 130.3 (CH), 129.9 (C_q), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.6 (CH), 129.5 (C_q), 129.4 (C_q), 129.0 (CH), 128.9 (CH), 128.9 (C_q), 128.9 (C_q), 128.8 (C_q), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.6 (CH), 126.9 (CH), 126.5 (CH), 126.4 (CH), 119.1 (CH), 119.0 (CH), 114.2 (CH), 114.0 (CH), 73.6 (CH), 73.4 (CH), 71.9 (CH), 71.6 (CH), 70.6 (CH), 70.4 (CH), 70.3 (CH), 70.2 (CH), 67.8 (CH), 67.7 (CH), 63.6 (CH_2), 63.4 (CH_2), 55.2 (CH_3), 55.1 (CH_3), 46.0 (CH), 45.8 (CH), 34.5 (CH_2), 34.1 (CH_2). 4 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1511, 1411, 1266, 1178, 1108, 1093, 1069, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 891 (50) $[M+Na]^+$, 869 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{45}N_2O_{10}^+$ $[M+H]^+$ 869.3069, found 869.3064.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{2-[3-(pyrimidin-2-yl)phenyl]-2-[4-(trifluoromethyl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ah)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1- 1-(trifluoromethyl)-4-vinylbenzene (**110h**) (51.6 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ah** (145.0 mg, 80%, d.r. = 1:1) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.83 (d, *J* = 4.8 Hz, 1H), 8.76 (d, *J* = 4.8 Hz, 1H), 8.50 (t, *J* = 1.4 Hz, 0.48H), 8.45 (t, *J* = 1.4 Hz, 0.52H), 8.35 (t, *J* = 7.2 Hz, 1H), 8.27 – 8.11 (m, 2H), 8.08 – 7.93 (m, 4H), 7.81 (t, *J* = 8.2 Hz, 2H), 7.65 – 7.25 (m, 18H), 7.18 (t, *J* = 4.8 Hz, 1H), 6.05 – 5.80 (m, 2H),, 5.74 (t, *J* = 2.9 Hz, 1H), 4.87 – 4.52 (m, 2H), 4.53 – 4.31 (m, 2H), 4.19 (dt, *J* = 10.8, 3.3 Hz, 0.51H), 4.10 (dt, *J* = 10.8, 3.3 Hz, 0.49H), 2.93 (ddd, *J* = 13.2, 11.7, 4.0 Hz, 0.48H), 2.80 (ddd, *J* = 15.1, 10.9, 4.4 Hz, 0.52H), 2.73 – 2.49 (m, 1H).

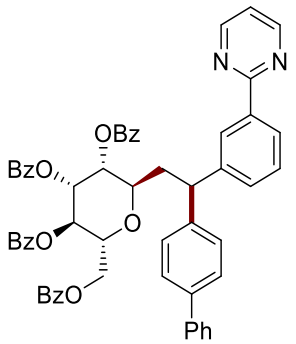
^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1 (C_q), 166.1 (C_q), 165.6 (C_q), 165.5 (C_q), 165.5 (C_q), 165.4 ($3C_q$), 164.3 (C_q), 164.3 (C_q), 157.2 (CH), 157.1 (CH), 148.1 (C_q), 146.7 (C_q), 143.6 (C_q), 142.1 (C_q), 138.3 (C_q), 138.2 (C_q), 133.5 (CH), 133.5 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 130.6 (CH), 130.2 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.3 ($2C_q$), 129.3 (CH), 129.1 (CH), 128.9 (C_q), 128.8 ($3C_q$), 128.5 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 127.0 (CH), 126.9 (CH), 125.8 (d, *J* = 3.3 Hz), 125.6 (d, *J* = 3.3 Hz), 119.3 (CH), 119.1 (CH), 73.3 (CH), 72.8 (CH), 71.7 (CH), 71.4 (CH), 70.9 (CH), 70.5 (CH), 70.2 (CH), 70.0 (CH), 67.9 (CH), 67.7 (CH), 63.5 (CH_2), 63.3 (CH_2), 46.6 (CH), 46.4 (CH), 34.2 (CH_2), 33.8 (CH_2). 2 Cq and 6 CH resonances are missing due to the overlap.

^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.41 (*s*)

IR (ATR): $\tilde{\nu}$ = 1727, 1569, 1452, 1326, 1265, 1108, 1069, 1027, 709 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 929 (90) $[M+Na]^+$, 907 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{42}F_3N_2O_9^+$ $[M+H]^+$ 907.2837, found 907.2839.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[2-([1,1'-Biphenyl]-4-yl)-2-[3-(pyrimidin-2-yl)phenyl]ethyl]-6-[(benzoyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ai)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1- 4-vinyl-1,1'-biphenyl (**110i**) (54.0 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ai** (155.4 mg, 85%, d.r. = 1:1) as a syrup.

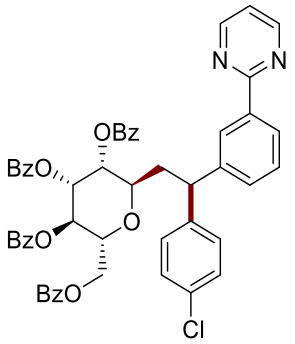
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (d, *J* = 4.8 Hz, 1H), 8.76 (d, *J* = 4.8 Hz, 1H), 8.58 (d, *J* = 1.7 Hz, 0.5H), 8.53 (d, *J* = 1.7 Hz, 0.5H), 8.42 – 8.32 (m, 1H), 8.22 (ddd, *J* = 8.5, 2.5, 1.4 Hz, 2H), 8.08 – 7.96 (m, 4H), 7.83 (ddd, *J* = 7.9, 6.3, 1.4 Hz, 2H), 7.65 – 7.49 (m, 9H), 7.48 – 7.35 (m, 12H), 7.34 – 7.28 (m, 1H), 7.25 – 7.23 (m, 1H), 7.20 (t, *J* = 4.8 Hz, 0.5H), 7.14 (t, *J* = 4.8 Hz, 0.5H), 6.01 (t, *J* = 9.1 Hz, 1H), 5.91 (dt, *J* = 9.1, 3.5 Hz, 1H), 5.80 (t, *J* = 2.6 Hz, 1H), 4.78 – 4.55 (m, 2H), 4.53 – 4.41 (m, 2H), 4.24 (t, *J* = 3.2 Hz, 1H), 3.19 – 2.84 (m, 1H), 2.79 – 2.60 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 166.1 (C_q), 165.6 (C_q), 165.6 (C_q), 165.4 (C_q), 165.4 (C_q), 165.4 (C_q), 164.5 (C_q), 164.4 (C_q), 157.2 (CH), 157.1 (CH), 144.6 (C_q), 143.2 (C_q), 143.0 (C_q), 141.6 (C_q), 140.7 (C_q), 140.7 (C_q), 139.5 (C_q), 139.5 (C_q), 138.1 (C_q), 138.0 (C_q), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.1 (CH), 130.6 (CH), 130.3 (CH), 129.8 (C_q), 129.8 (CH), 129.8 (CH), 129.6 (CH), 129.4 (C_q), 129.4 (C_q), 129.1 (CH), 129.0 (CH), 128.9 (C_q), 128.9 (C_q), 128.7 (CH), 128.6 (CH), 128.5

(CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 127.1 (CH), 127.0 (CH), 127.0 (CH), 126.9 (CH), 126.7 (CH), 126.6 (CH), 119.1 (CH), 119.0 (CH), 73.6 (CH), 73.3 (CH), 71.8 (CH), 71.6 (CH), 70.7 (CH), 70.4 (CH), 70.3 (CH), 70.2 (CH), 67.8 (CH), 67.7 (CH), 63.6 (CH_2), 63.4 (CH_2), 46.5 (CH), 46.3 (CH), 34.3 (CH_2), 34.0 (CH_2). 5 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1721, 1555, 1451, 1264, 1108, 1093, 1069, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 937 (45) $[M+Na]^+$, 915 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{58}H_{47}N_2O_9^+$ $[M+H]^+$ 915.3276, found 915.3279.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-(4-chlorophenyl)-2-[3-(pyrimidin-2-yl)phenyl]ethyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163aj)



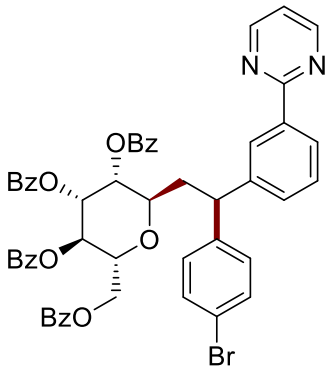
The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1- 1-chloro-4-vinylbenzene (**110j**) (41.4 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163aj** (143.0 mg, 82%, d.r. = 1:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 4.8 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.49 (d, *J* = 1.8 Hz, 0.5H), 8.44 (d, *J* = 1.8 Hz, 0.5H), 8.34 (t, *J* = 8.7 Hz, 1H), 8.23 – 8.10 (m, 2H), 8.05 – 7.94 (m, 4H), 7.89 – 7.78 (m, 2H), 7.63 – 7.54 (m, 2H), 7.53 – 7.28 (m, 12H), 7.25 – 7.22 (m, 4H), 7.20 (t, *J* = 4.8 Hz, 0.5H), 7.14 (t, *J* = 4.8 Hz, 0.5H), 5.97 (t, *J* = 9.0 Hz, 1H), 5.86 (t, *J* = 3.6 Hz, 1H), 5.74 (t, *J* = 2.7 Hz, 1H), 4.70 – 4.55 (m, 2H), 4.46 – 4.31 (m, 2H), 4.22 – 4.08 (m, 1H), 2.97 – 2.72 (m, 1H), 2.69 – 2.50 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 166.1 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 ($3C_q$), 164.4 (C_q), 164.3 (C_q), 157.2 (CH), 157.1 (CH), 144.1 (C_q), 142.6 (C_q), 142.6 (C_q), 141.1 (C_q), 138.2 (C_q), 138.1 (C_q), 133.5 (CH), 133.4 (CH), 133.3 (CH), 133.3 (CH), 133.3 (CH), 133.2 (CH), 133.1 (CH), 132.5 (C_q), 132.3 (C_q), 130.5 (CH), 130.2 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.6 (CH), 129.5 (CH), 129.4 (C_q), 129.4 (C_q), 129.2 (CH), 129.0 (CH), 129.0 (CH), 128.9 (CH), 128.9 (C_q), 128.8 ($3C_q$), 128.7 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.6 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 119.2 (CH), 119.1 (CH), 73.3 (CH), 73.0 (CH), 71.8 (CH), 71.5 (CH), 70.8 (CH), 70.4 (CH), 70.2 (CH), 70.1 (CH), 67.8 (CH), 67.7 (CH), 63.5 (CH_2), 63.3 (CH_2), 46.1 (CH), 46.0 (CH), 34.3 (CH_2), 33.9 (CH_2). 1 Cq and 2 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1556, 1452, 1411, 1264, 1108, 1094, 1070, 710 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 895 (100) $[M+Na]^+$, 873 (73) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{42}ClN_2O_9^+$ $[M+H]^+$ 873.2573, found 873.2531.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-(4-bromophenyl)-2-[3-(pyrimidin-2-yl)phenyl]ethyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ak)



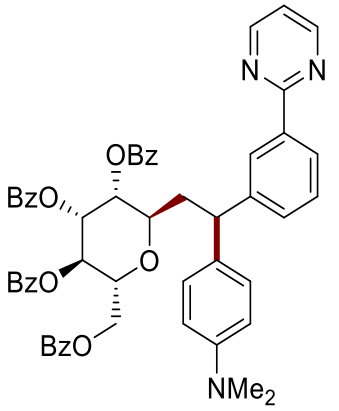
The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1- 1-bromo-4-vinylbenzene (**110k**) (54.6 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ak** (130.1 mg, 71%, d.r. = 1:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, *J* = 4.8 Hz, 1H), 8.80 (d, *J* = 4.8 Hz, 1H), 8.51 (d, *J* = 1.4 Hz, 0.5H), 8.46 (*J* = 1.4 Hz, 0.5H), 8.37 (t, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 2H), 8.12 – 7.97 (m, 4H), 7.84 (t, *J* = 9.1 Hz, 2H), 7.69 – 7.49 (m, 6H), 7.49 – 7.32 (m, 10H), 7.30 – 7.16 (m, 3H), 5.99 (t, 8.9 Hz, 1H), 5.88 (d, *J* = 9.1 Hz, 1H), 5.77 (d, *J* = 3.6 Hz, 1H), 4.76 – 4.53 (m, 2H), 4.48 – 4.33 (m, 2H), 4.19 (t, *J* = 10.5 Hz, 1H), 3.02 – 2.77 (m, 1H), 2.71 – 2.54 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 165.6 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 164.4 (C_q), 164.3 (C_q), 157.2 (CH), 157.1 (CH), 146.5 (C_q), 145.0 (C_q), 143.8 (C_q), 142.3 (C_q), 138.2 (C_q), 138.1 (C_q), 133.5 (CH), 133.5 (CH), 133.3 (CH), 133.3 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 131.2 (CH), 130.8 (CH), 130.5 (CH), 130.4 (CH), 130.3 (CH), 130.3 (CH), 130.0 (CH), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.7 (CH), 129.4 (C_q), 129.4 (C_q), 129.2 (CH), 129.1 (CH), 128.9 (C_q), 128.9 (C_q), 128.9 (C_q), 128.5 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 127.7 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 126.2 (CH), 122.9 (C_q), 122.8 (C_q), 119.2 (CH), 119.1 (CH), 73.2 (CH), 72.9 (CH), 71.7 (CH), 71.5 (CH), 70.8 (CH), 70.5 (CH), 70.2 (CH), 70.1 (CH), 67.9 (CH), 67.7 (CH), 63.4 (CH_2), 63.4 (CH_2), 46.5 (CH), 46.4 (CH), 34.1 (CH_2), 33.9 (CH_2). 2 Cq and 1 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1555, 1451, 1411, 1264, 1108, 1093, 1069, 1027, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 941(100) $[M+Na]^+$, 917 (20) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{41}{}^{79}BrNaO_9^+$ $[M+Na]^+$ 939.1888, found, 939.1883. *m*/*z* calcd for $C_{52}H_{41}{}^{81}BrO_9Na^+$ $[M+Na]^+$ 941.1871, found, 941.1875.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{(R)-2-[4-(dimethylamino)phenyl]-2-[3-(pyrimidin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163al)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1- *N*,*N*-dimethyl-4-vinylaniline (**110l**) (44.1 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163al** (142.8 mg, 81%, d.r. = 1:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 4.8 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.49 (d, *J* = 1.8 Hz, 0.53H), 8.45 (d, *J* = 1.9 Hz, 0.47H), 8.35 – 8.27 (m, 1H), 8.24 – 8.16 (m, 2H), 8.07 – 7.92 (m, 4H), 7.80 (td, *J* = 8.2, 1.4 Hz, 2H), 7.64 – 7.54 (m, 2H), 7.52 – 7.31 (m, 11H), 7.30 – 7.22 (m, 5H), 7.19 (t, *J* = 4.8 Hz, 0.53H), 7.13 (t, *J* = 4.8 Hz, 0.47H), 5.98 (dt, *J* = 15.8, 9.2 Hz, 1H), 5.85 (dt, *J* = 9.2, 3.0 Hz, 1H), 5.74 (t, *J* = 2.9 Hz, 1H), 4.80 – 4.50 (m, 2H), 4.46 – 4.27 (m, 2H), 4.24 – 4.11 (m, 1H), 2.93 (s, 6H), 2.86 – 2.39 (m, 2H).

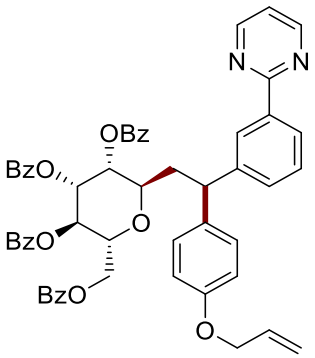
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 166.1 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 165.4 (C_q), 164.5 (C_q), 164.4 (C_q), 157.2 (CH), 157.1 (CH), 138.0 (C_q), 137.9 (C_q), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.1 (CH), 130.5 (CH), 130.2 (CH), 129.8 (C_q), 129.8 (CH), 129.8 (CH), 129.6 (CH), 129.6 (CH), 129.4 (C_q), 129.4 (C_q), 129.0 (CH), 128.9 (CH), 128.9 (C_q), 128.8 (C_q), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.5 (CH), 126.9 (CH), 126.5 (CH), 126.4 (CH), 119.1 (CH), 119.0 (CH), 73.7 (CH), 73.4 (CH), 71.9 (CH), 71.6 (CH), 70.6 (CH), 70.4 (CH), 70.3 (CH), 70.2 (CH), 67.8 (CH), 67.7 (CH), 63.6 (CH_2), 63.4 (CH_2), 46.0 (CH), 45.8 (CH_3), 34.4 (CH_2), 34.0 (CH_2). 4 Cq and 5 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1721, 1520, 1451, 1264, 1178, 1093, 1069, 1027, 709 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 904 (100) $[M+Na]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{54}H_{47}N_3NaO_9^+$ $[M+Na]^+$ 904.3205, found 904.3201.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-{2-[4-(Allyloxy)phenyl]-2-[3-(pyrimidin-2-yl)phenyl]ethyl}-6-[(benzoyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163am)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1- 1-(allyloxy)-4-vinylbenzene (**110m**) (48.0 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163am** (130.6 mg, 73%, d.r. = 1:1) as a syrup.

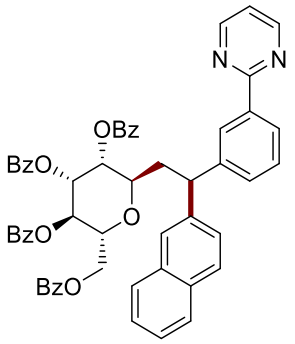
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 4.8 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.52 (t, *J* = 1.6 Hz, 0.46H), 8.47 (t, *J* = 1.6 Hz, 0.46H), 8.37 – 8.27 (m, 1H), 8.18 (dt, *J* = 8.5, 1.6 Hz, 2H), 8.09 – 7.92 (m, 4H), 7.80 (td, *J* = 8.1, 1.4 Hz, 2H), 7.63 – 7.32 (m, 12H), 7.31 – 7.26 (m, 1H), 7.25 – 7.11 (m, 3H), 7.02 – 6.84 (m, 2H), 6.74 (dddd, *J* = 13.8, 8.2, 2.6, 0.9 Hz, 1H), 6.11 – 5.91 (m, 2H), 5.89 – 5.82 (m, 1H), 5.79 – 5.70 (m, 1H), 5.40 (dd, *J* = 17.3, 1.6 Hz, 0.51H), 5.35 (dd, *J* = 17.3, 1.6 Hz, 0.49H), 5.27 (dd, *J* = 10.5, 1.5 Hz, 0.51H), 5.21 (dd, *J* = 10.5, 1.5 Hz, 0.49H), 4.70 – 4.52 (m, 2H), 4.49 (dt, *J* = 5.4, 1.5 Hz, 1H), 4.45 – 4.32 (m, 3H), 4.18 (dd, *J* = 11.3, 3.0 Hz, 1H), 2.98 – 2.76 (m, 1H), 2.72 – 2.55 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 164.5 (C_q), 164.5 (C_q), 158.8 (C_q), 158.8 (C_q), 157.2 (CH), 157.1 (CH), 145.8 (C_q), 144.5 (C_q), 144.2 (C_q), 142.9 (C_q), 138.1 (C_q), 138.0 (C_q), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.2 (CH), 133.1 (CH), 130.5 (CH), 130.3 (CH),

129.9 (C_q), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.6 (CH), 129.5 (C_q), 129.4 (C_q), 129.1 (CH), 128.9 (CH), 128.9 (C_q), 128.9 (C_q), 128.9 (C_q), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.8 (CH), 127.0 (CH), 126.6 (CH), 126.5 (CH), 120.6 (CH), 120.2 (CH), 119.1 (CH), 119.0 (CH), 117.7 (C_q), 117.7 (C_q), 114.7 (CH), 114.6 (CH), 112.9 (CH), 112.4 (CH), 73.6 (CH), 73.3 (CH), 71.8 (CH), 71.6 (CH), 70.7 (CH), 70.4 (CH), 70.2 (CH), 68.7 (CH_2), 68.6 (CH_2), 67.8 (CH), 67.7 (CH), 63.6 (CH_2), 63.4 (CH_2), 46.8 (CH), 46.7 (CH), 34.3 (CH_2), 33.9 (CH_2). 1 CH resonance is missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1722, 1601, 1452, 1266, 1107, 1092, 1070, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 917 (90) $[M+Na]^+$, 895 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{55}H_{47}N_2O_{10}^+$ $[M+H]^+$ 895.3225, found 895.3225.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-(naphthalen-2-yl)-2-[3-(pyrimidin-2-yl)phenyl]ethyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163an)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1- 2-vinylnaphthalene (**110n**) (412.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163an** (151.0 mg, 85%, d.r. = 1:1) as a syrup.

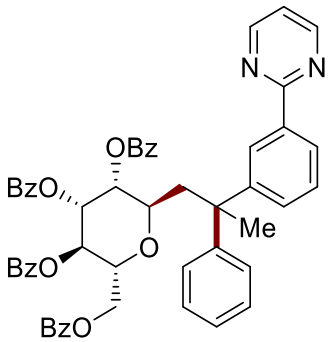
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, *J* = 4.8 Hz, 1H), 8.79 (d, *J* = 4.8 Hz, 1H), 8.61 (d, *J* 7.96 (m, 4H), 7.90 – 7.74 (m, 6H), 7.68 – 7.37 (m, 16H), 7.30 – 7.26 (m, 1H), 7.24 (t, *J* = 4.8 = 1.8 Hz, 0.41H), 8.55 (d, *J* = 1.8 Hz, 0.43H), 8.41 – 8.32 (m, 1H), 8.32 – 8.19 (m, 2H), 8.09 –Hz, 0.48H), 7.18 (t, *J* = 4.8 Hz, 0.48H), 6.02 (q, *J* = 9.2 Hz, 1H),

5.93 (dt, *J* = 9.2, 2.6 Hz, 1H), 5.84 (t, *J* = 2.9 Hz, 0.45H), 5.82 (t, *J* = 2.9 Hz, 0.45H), 4.80 – 4.16 (m, 5H), 3.16 – 2.95 (m, 1H), 2.89 – 2.71 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 166.1 (C_q), 166.1 (C_q), 165.6 (C_q), 165.6 (C_q), 165.4 (C_q), 165.4 (C_q), 164.5 (C_q), 164.4 (C_q), 157.2 (CH), 157.1 (CH), 144.5 (C_q), 143.0 (C_q), 141.6 (C_q), 140.0 (C_q), 138.1 (C_q), 138.0 (C_q), 133.5 (C_q), 133.4 (CH), 133.2 (CH), 133.1 (CH), 132.4 (C_q), 132.2 (C_q), 130.8 (CH), 130.5 (CH), 129.9 (C_q), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.7 (CH), 129.7 (CH), 129.4 (C_q), 129.4 (C_q), 129.1 (CH), 129.0 (CH), 128.9 (C_q), 128.7 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.9 (CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 127.1 (CH), 126.9 (CH), 126.7 (CH), 126.6 (CH), 126.6 (CH), 126.1 (CH), 126.1 (CH), 126.0 (CH), 125.6 (CH), 125.6 (CH), 125.4 (CH), 119.1 (CH), 119.0 (CH), 73.5 (CH), 73.3 (CH), 71.8 (CH), 71.7 (CH), 70.7 (CH), 70.4 (CH), 70.4 (CH), 70.3 (CH), 67.8 (CH), 67.8 (CH), 63.5 (CH_2), 63.5 (CH_2), 46.7 (CH), 34.1 (CH_2), 33.7 (CH_2). 2 Cq and 4 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1722, 1555, 1451, 1264, 1108, 1093, 1069, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 911 (50) $[M+Na]^+$, 889 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{56}H_{45}N_2O_9^+$ $[M+H]^+$ 889.3120, found 889.3120.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{2-phenyl-2-[3-(pyrimidin-2-yl)phenyl]propyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ao)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), prop-1-en-2-ylbenzene (**110o**) (35.4 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C.

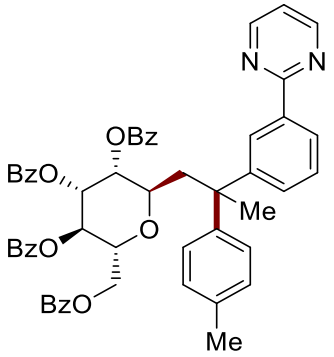
Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ao** (139.8 mg, 82%, d.r. = 1:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 4.9 Hz, 1.18H), 8.75 (d, *J* = 4.9 Hz, 0.82H), 8.54 (d, *J* = 1.4 Hz, 0.41H), 8.46 (d, *J* = 1.4 Hz, 0.59H), 8.32 (d, *J* = 7.6 Hz, 0.41H), 8.27 (d, *J* = 7.6 Hz, 0.59H), 8.09 (d, *J* = 8.0 Hz, 0.82H), 8.06 (d, *J* = 8.0 Hz, 1.18H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.93 (dd, *J* = 7.7, 5.4 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 1.18H), 7.76 (d, *J* = 8.1 Hz, 0.82H), 7.58 – 7.44 (m, 4H), 7.44 – 7.28 (m, 14H), 7.25 – 7.17 (m, 1H), 7.14 (t, *J* = 4.3 Hz, 1H), 6.01 – 5.79 (m, 2H), 5.59 (t, *J* = 3.4 Hz, 0.41H), 5.55 (t, *J* = 3.4 Hz, 0.59H), 4.52 – 4.19 (m, 4H), 2.98 (dd, *J* = 14.4, 8.2 Hz, 1H), 2.74 – 2.54 (m, 1H), 1.96 (s, 1.23H), 1.93 (s, 1.77H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 166.1 (C_q), 165.6 (C_q), 165.5 (C_q), 165.3 (C_q), 165.3 (C_q), 164.8 (C_q), 164.7 (C_q), 157.2 (CH), 157.1 (CH), 149.8 (C_q), 149.3 (C_q), 148.4 (C_q), 147.8 (C_q), 137.6 (C_q), 137.5 (C_q), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.2 (CH), 133.0 (CH), 130.6 (CH), 130.0 (CH), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.7 (CH), 129.6 (CH), 129.4 (C_q), 129.4 (C_q), 129.1 (C_q), 129.0 (C_q), 128.9 (C_q), 128.9 (C_q), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.2 (CH), 127.5 (CH), 127.2 (CH), 126.8 (CH), 126.4 (CH), 126.2 (CH), 126.2 (CH), 126.1 (CH), 119.0 (CH), 72.3 (CH), 72.2 (CH), 71.2 (CH), 71.1 (CH), 69.9 (CH), 69.8 (CH), 67.9 (CH), 67.9 (CH), 62.9 (CH_2), 62.8 (CH_2), 46.4 (C_q), 46.4 (C_q), 39.9 (CH_2), 39.8 (CH_2), 27.9 (CH_3), 27.7 (CH_3). 1 Cq and 6 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1730, 1373, 1236, 1045, 909, 729, 648, 608 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 875(100) $[M+Na]^+$, 853 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{45}N_2O_9^+$ $[M+H]^+$ 853.3120, found 853.3122.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{2-[3-(pyrimidin-2-yl)phenyl]-2-(p-tolyl)propyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ap)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-methyl-4-(prop-1-en-2-yl)benzene (**110p**) (39.6 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ap** (135.1 mg, 78%, d.r. = 1.4:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 4.7 Hz, 1.18H), 8.75 (d, *J* = 4.7 Hz, 0.82H), 8.53 (d, *J* = 1.9 Hz, 0.41H), 8.46 (d, *J* = 1.9 Hz, 0.59H), 8.31 (d, *J* = 7.8 Hz, 0.41H), 8.26 (d, *J* = 7.8 Hz, 0.59H), 8.09 (d, *J* = 8.1 Hz, 0.81H), 8.05 (d, *J* = 8.1 Hz, 1.19H), 8.02 – 7.97 (m, 2H), 7.93 (t, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 1.17H), 7.75 (d, *J* = 7.9 Hz, 0.83H), 7.62 – 7.44 (m, 4H), 7.44 – 7.27 (m, 10H), 7.23 – 7.13 (m, 3H), 7.13 – 7.05 (m, 2H), 6.00 – 5.79 (m, 2H), 5.62 – 5.50 (m, 1H), 4.49 – 4.24 (m, 4H), 3.00 (dd, *J* = 14.4, 8.2 Hz, 0.59H), 2.91 (dd, *J* = 14.4, 8.2 Hz, 0.41H), 2.59 (t, *J* = 13.4 Hz, 1H), 2.28 (s, 3H), 1.94 (s, 1.23H), 1.90 (s, 1.77H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 165.6 (C_q), 165.5 (C_q), 165.3 (C_q), 165.3 (C_q), 165.3 (C_q), 164.8 (C_q), 164.8 (C_q), 157.2 (CH), 149.9 (C_q), 148.6 (C_q), 146.4 (C_q), 144.9 (C_q), 137.5 (C_q), 137.5 (C_q), 135.7 (C_q), 135.6 (C_q), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.0 (CH), 133.0 (CH), 130.6 (CH), 130.1 (CH), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.7 (CH), 129.6 (CH), 129.5 (C_q), 129.4 (C_q), 129.1 (CH), 129.0 (C_q), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 127.3 (CH), 127.0 (CH), 126.7 (CH), 126.4 (CH), 126.1 (CH), 126.0 (CH), 119.0 (CH), 72.5 (CH), 72.4 (CH), 72.2 (CH), 71.2 (CH), 70.9 (CH), 70.0 (CH), 69.9 (CH), 68.0 (CH), 67.9 (CH), 62.9 (CH_2), 62.8 (CH_2), 46.1 (C_q), 46.0 (C_q), 39.9 (CH_2), 39.8 (CH_2), 27.9 (CH_3),

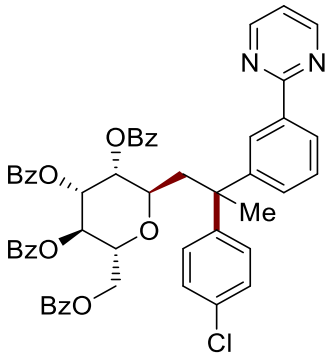
27.6 (CH_3), 20.9 (CH_3), 20.9 (CH_3). 2 Cq and 1 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1729, 1555, 1452, 1267, 1109, 1094, 1069, 1027, 709 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 889(100) $[M+Na]^+$, 867 (15) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{54}H_{46}N_2NaO_9^+$ [M+Na] 889.3096, found 889.3090.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-(4-chlorophenyl)-2-[3-(pyrimidin-2-yl)phenyl]propyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163aq)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-chloro-4-(prop-1-en-2-yl)benzene (**110q**) (45.6mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163aq** (138.3 mg, 78%, d.r. = 1.6:1) as a syrup.

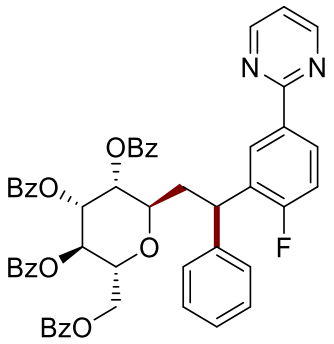
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 4.8 Hz, 1.22H), 8.74 (d, *J* = 4.8 Hz, 0.78H), 8.47 (s, 0.39H), 8.39 (s, 0.61H), 8.33 (d, *J* = 7.8 Hz, 0.39H), 8.27 (d, *J* = 7.7 Hz, 0.61H), 8.08 (d, *J* = 7.9 Hz, 0.78H), 8.05 (d, *J* = 7.9 Hz, 1.22H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 1.22H), 7.74 (d, *J* = 7.8 Hz, 0.78H), 7.66 – 7.27 (m, 14H), 7.25 – 7.13 (m, 5H), 5.97 – 5.74 (m, 2H), 5.55 (d, *J* = 4.2 Hz, 1H), 4.61 – 4.16 (m, 4H), 2.98 (dd, *J* = 14.3, 8.4 Hz, 0.61H), 2.86 (dd, *J* = 14.3, 8.4 Hz, 0.39H), 2.69 – 2.43 (m, 1H), 1.92 (s, 1.17H), 1.88 (s, 1.83H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 165.6 (C_q), 165.5 (C_q), 165.3 (C_q), 165.3 (C_q), 165.3 (C_q), 164.6 (C_q), 164.5 (C_q), 157.2 (CH), 157.2 (CH), 149.4 (C_q), 148.0 (C_q), 147.8 (C_q), 146.5 (C_q), 137.7 (C_q), 137.7 (C_q), 133.5 (CH), 133.5 (CH), 133.4 (CH),

133.3 (CH), 133.2 (CH), 133.0 (CH), 132.1 (C_q), 131.9 (C_q), 130.3 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.7 (CH), 129.7 (CH), 129.6 (CH), 129.3 (C_q), 129.0 (CH), 128.9 (C_q), 128.8 (C_q), 128.8 (CH), 128.6 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 126.8 (CH), 126.4 (CH), 126.3 (CH), 119.1 (CH), 72.1 (CH), 72.0 (CH), 71.9 (CH), 71.8 (CH), 71.4 (CH), 71.2 (CH), 69.7 (CH), 69.7 (CH), 68.0 (CH), 67.9 (CH), 62.7 (CH_2), 46.3 (C_q), 46.2 (C_q), 40.0 (CH_2), 39.9 (CH_2), 27.9 (CH_3), 27.7 (CH_3). 3 Cq and 4 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1555, 1407, 1265, 1108, 1093, 1069, 1026, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 909(100) $[M+Na]^+$, 887 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{43}ClN_2NaO_9^+$ $[M+Na]^+$ 909.2549, found 909.2548.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{(*R*)-2-[2-fluoro-5-(pyrimidin-2-yl)phenyl]-2-phenylethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ba)



The general procedure **I** was followed using 2-(4-fluorophenyl)pyrimidine (**160p**) (34.8 mg, 0.20 mmol), styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ba** (95.9 mg, 56%, d.r. = 1:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 4.9 Hz, 1H), 8.74 (d, *J* = 4.8 Hz, 1H), 8.60 (d, *J* = 7.0 Hz, 1H), 8.44 – 8.29 (m, J1H), 8.17 (d, *J* = 8.0 Hz, 2H), 8.06 – 7.92 (m, 4H), 7.85 – 7.76 (m, 2H), 7.62 – 7.54 (m, 2H), 7.54 – 7.49 (m, 1H), 7.48 – 7.41 (m, 3H), 7.41 – 7.33 (m, 6H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 2H), 7.18 – 7.07 (m, 2H),

5.97 (t, *J* = 9.0 Hz, 1H), 5.86 (dt, *J* = 8.6, 4.0 Hz, 1H), 5.78 (d, *J* = 3.1 Hz, 0.5H), 5.74 (d, *J* = 2.9 Hz, 0.5H), 4.70 (dt, *J* = 9.3, 4.8 Hz, 1H), 4.65 – 4.47 (m, 2H), 4.46 – 4.41 (m, 0.5H), 4.40 – 4.32 (m, 0.5H), 4.25 (d, *J* = 9.6 Hz, 0.5H), 4.17 (d, *J* = 11.3 Hz, 0.5H), 2.96 – 2.56 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 166.2 (C_q), 166.2 (C_q), 165.7 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 164.1 (C_q), 163.7 (C_q), 163.7 (C_q), 163.6 (C_q), 161.6 (C_q), 161.2 (C_q), 157.2 (CH), 157.1 (CH), 143.0 (C_q), 141.0 (C_q), 134.0 (C_q), 134.0 (C_q), 134.0 (C_q), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.1 (CH), 133.0 (CH), 131.6 (C_q), 131.5 (C_q), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.5 (C_q), 128.9 (C_q), 128.9 (C_q), 128.9 (C_q), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.8 (CH), 126.9 (CH), 126.7 (CH), 119.0 (CH), 118.9 (CH), 116.4 (CH), 116.2 (CH), 116.0 (CH), 115.8 (CH), 73.5 (CH), 71.9 (CH), 71.6 (CH), 70.8 (CH), 70.4 (CH), 70.3 (CH), 70.2 (CH), 67.7 (CH), 67.7, 63.7 (CH_2), 63.2 (CH_2), 40.3 (CH), 40.3 (CH), 39.6 (CH), 39.5 (CH), 33.3 (CH_2), 33.1 (CH_2), 30.3 (CH), 29.7 (CH). 4 CH resonances are missing due to the overlap.

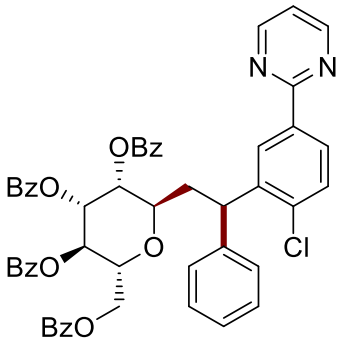
^{19}F NMR (377 MHz, $CDCl_3$): *δ* = -113.48 (q, *J* = 7.4 Hz).

IR (ATR): $\tilde{\nu}$ = 1721, 1556, 1452, 1420, 1264, 1108, 1069, 1027, 802, 708 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 879(100) $[M+Na]^+$, 857 (5) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{41}FN_2NaO_9^+$ $[M+Na]^+$ 879.2688, found 879.2686.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2[((Benzoyloxy)methyl)-6-{(R)-2-[2-chloro-5-(pyrimidin-2-yl)phenyl]-2-phenylethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163bb)



The general procedure **I** was followed using 2-(4-chlorophenyl)pyrimidine (**160h**) (38.0 mg, 0.20 mmol), styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-

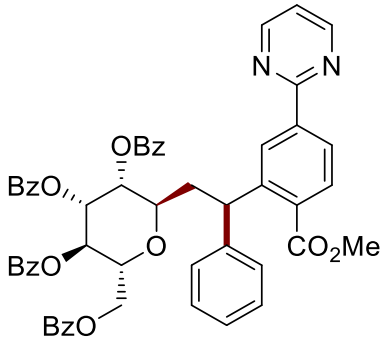
[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163bb** (151.8 mg, 87%, d.r. = 1:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 4.8 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.65 (d, *J* = 2.0 Hz, 1H), 8.27 (td, *J* = 8.1, 2.0 Hz, 1H), 8.17 (d, *J* = 7.4 Hz, 1H), 8.13 (d, *J* = 7.4 Hz, 1H), 8.05 – 7.92 (m, 4H), 7.88 – 7.78 (m, 2H), 7.63 – 7.37 (m, 11H), 7.40 – 7.25 (m, 6H), 7.27 – 7.12 (m, 3H), 6.01 (dt, *J* = 14.6, 9.0 Hz, 1H), 5.87 (dt, *J* = 9.5, 3.4 Hz, 1H), 5.81 (t, *J* = 3.1 Hz, 0.51H), 5.75 (t, *J* = 2.8 Hz, 0.49H), 4.92 (ddd, *J* = 16.1, 10.5, 4.9 Hz, 1H), 4.69 (dd, *J* = 12.0, 2.7 Hz, 0.49H), 4.57 (dd, *J* = 12.0, 5.6 Hz, 0.51H), 4.53 (d, *J* = 4.2 Hz, 1H), 4.46 (ddd, *J* = 8.6, 5.5, 2.7 Hz, 0.49H), 4.37 (dt, *J* = 8.5, 4.2 Hz, 0.51H), 4.31-4.17 (m, 1H), 3.01 – 2.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2 (C_q), 166.2 (C_q), 165.7 (C_q), 165.6 (C_q), 165.4 (C_q), 165.4 (C_q), 165.4 (C_q), 165.3 (C_q), 163.7 (C_q), 163.5 (C_q), 157.3 (CH), 157.1 (CH), 142.7 (C_q), 141.7 (C_q), 140.7 (C_q), 140.1 (C_q), 137.5 (C_q), 136.7 (C_q), 136.6 (C_q), 136.6 (C_q), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.0 (CH), 133.0 (CH), 130.4 (CH), 130.1 (CH), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.5 (C_q), 129.0 (C_q), 128.9 (C_q), 128.7 (CH), 128.7 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.5 (CH), 127.5 (CH), 126.9 (CH), 126.7 (CH), 119.3 (CH), 119.2 (CH), 73.5 (CH), 73.5 (CH), 71.9 (CH), 71.5 (CH), 70.8 (CH), 70.4 (CH), 70.4 (CH), 70.2 (CH), 67.7 (CH), 67.6 (CH), 63.6 (CH_2), 63.2 (CH_2), 42.9 (CH), 42.6 (CH), 34.4 (CH_2), 33.9 (CH_2). 2 Cq and 4 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1568, 1452, 1418, 1262, 1093, 1069, 1027, 799, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 895(100) $[M+Na]^+$, 873 (5) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{52}H_{41}ClN_2NaO_9^+$ $[M+Na]^+$ 895.2393, found 895.2392.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{(*R*)-2-[2-(methoxycarbonyl)-5-(pyrimidin-2-yl)phenyl]-2-phenylethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163bc)



The general procedure **I** was followed using methyl 4-(pyrimidin-2-yl)benzoate (**160q**) (42.8 mg, 0.20 mmol), styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163bc** (125.5 mg, 70%, d.r. = 1:1) as a syrup.

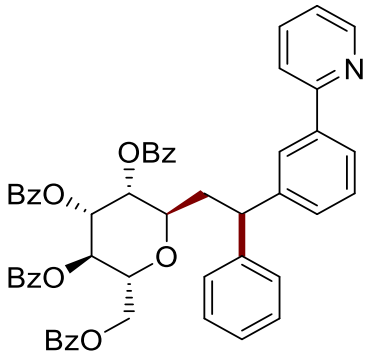
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (d, *J* = 4.8 Hz, 1H), 8.79 (d, *J* = 4.8 Hz, 1H), 8.69 (d, *J* = 1.7 Hz, 0.5H), 8.67 (d, *J* = 1.7 Hz, 0.5H), 8.35 (ddd, *J* = 8.0, 6.1, 1.7 Hz, 1H), 8.13 (t, *J* = 7.5 Hz, 2H), 8.01 (dd, *J* = 12.7, 7.4 Hz, 2H), 7.97 – 7.89 (m, 3H), 7.81 (t, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 3H), 7.53 – 7.46 (m, 1H), 7.45 – 7.38 (m, 4H), 7.39 – 7.31 (m, 5H), 7.31 – 7.27 (m, 1H), 7.25 – 7.14 (m, 3H), 6.14 (t, *J* = 9.3 Hz, 0.5H), 6.08 (t, *J* = 9.3 Hz, 0.5H), 5.87 (ddd, *J* = 9.5, 5.9, 3.2 Hz, 1H), 5.80 (t, *J* = 2.9 Hz, 0.5H), 5.76 (t, *J* = 2.9 Hz, 0.5H), 5.57 (dd, *J* = 9.9, 5.5 Hz, 0.5H), 5.50 (dd, *J* = 9.9, 4.3 Hz, 0.5H), 4.81 – 4.68 (m, 0.5H), 4.63 – 4.42 (m, 2H), 4.38 – 4.24 (m, 1H), 4.22 – 4.11 (m, 0.5H), 3.88 (s, 3H), 3.01 – 2.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.1 (C_q), 168.0 (C_q), 166.2 (C_q), 166.1 (C_q), 165.7 (C_q), 165.6 (C_q), 165.4 (C_q), 165.4 (C_q), 165.3 (C_q), 165.2 (C_q), 163.5 (C_q), 163.4 (C_q), 157.3 (CH), 157.2 (CH), 145.5 (C_q), 144.3 (C_q), 143.8 (C_q), 142.1 (C_q), 140.7 (C_q), 140.6 (C_q), 133.3 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 132.9 (CH), 132.8 (CH), 132.5 (C_q), 131.8 (C_q), 131.0 (CH), 130.6 (CH), 130.1 (C_q), 129.9 (C_q), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.7 (CH), 129.6 (C_q), 129.5 (C_q), 129.1 (C_q), 129.0 (C_q), 129.0 (C_q), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 126.6 (CH), 126.5 (CH), 125.9 (CH), 125.8 (CH), 119.6 (CH), 119.5 (CH), 74.0 (CH), 72.2 (CH), 71.7 (CH), 70.6 (CH), 70.4 (CH), 70.4 (CH), 70.1 (CH), 67.4 (CH), 67.4 (CH), 63.2 (CH_2), 63.0 (CH_2),

52.2 (CH), 41.3 (CH), 40.9 (CH), 34.8 (CH_2), 34.1 (CH_2). 4 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1717, 1568, 1452, 1262, 1178, 1106, 1070, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 919 (100) $[M+Na]^+$, 897 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{54}H_{44}N_2NaO_{11}^+$ $[M+Na]^+$ 919.2837, found 919.2832.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(benzoyloxy)methyl]-6-{(*R*)-2-phenyl-2-[3-(pyridin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163bd)



The general procedure **I** was followed using 2-phenylpyridine (**160a**) (31.0 mg, 0.20 mmol), styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163bd** (132.3 mg, 79%, d.r. = 1.5:1) as a syrup.

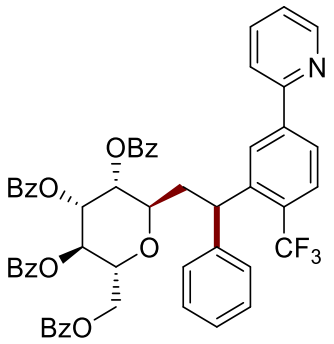
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 4.7 Hz, 0.4H), 8.66 (d, *J* = 4.7 Hz, 0.6H), 8.17 (dd, *J* = 6.8, 1.7 Hz, 2H), 8.04 – 7.88 (m, 5H), 7.88 – 7.71 (m, 3H), 7.76 – 7.67 (m, 1H), 7.67 – 7.48 (m, 4H), 7.48 – 7.41 (m, 4H), 7.41 – 7.27 (m, 11H), 7.24 – 7.14 (m, 2H), 5.98 (td, *J* = 9.2, 5.6 Hz, 1H), 5.87 (t, *J* = 3.0 Hz, 0.6H), 5.85 (t, *J* = 3.0 Hz, 0.4H), 5.75 (q, *J* = 2.4 Hz, 1H), 4.72 – 4.53 (m, 2H), 4.49 – 4.33 (m, 2H), 4.27 – 4.10 (m, 1H), 3.12 – 2.78 (m, 1H), 2.75 – 2.49 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 157.3 (C_q), 157.2 (C_q), 149.6 (CH), 149.5 (CH), 144.8 (C_q), 144.1 (C_q), 143.1 (C_q), 142.5 (C_q), 139.8 (C_q), 136.8 (CH), 136.7 (CH), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH),

133.2 (CH), 133.1 (CH), 133.1 (CH), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.4 (C_q), 129.4 (C_q), 129.2 (CH), 129.1 (CH), 128.9 (C_q), 128.9 (C_q), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 127.7 (CH), 126.7 (CH), 126.6 (CH), 126.2 (CH), 125.5 (CH), 125.2 (CH), 122.2 (CH), 122.1 (CH), 120.8 (CH), 120.7 (CH), 73.5 (CH), 71.8 (CH), 71.7 (CH), 70.5 (CH), 70.4 (CH), 70.3 (CH), 70.3 (CH), 67.8 (CH), 67.7 (CH), 63.6 (CH_2), 63.5 (CH_2), 46.8 (CH), 46.7 (CH), 34.2 (CH_2), 34.1 (CH_2). 3 Cq and 3 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1719, 1584, 1451, 1315, 1262, 1178, 1069, 1027, 707 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 860 (100) $[M+Na]^+$, 838 (25) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{43}NNaO_9^+$ $[M+Na]^+$ 860.2830, found 860.2847.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{(R)-2-phenyl-2-[5-(pyridin-2-yl)-2-(trifluoromethyl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163be)



The general procedure **I** was followed using 2-(4-(trifluoromethyl)phenyl)pyridine (**160c**) (44.6 mg, 0.20 mmol), styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163be** (130.3 mg, 72%, d.r. = 1:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 4.4 Hz, 1H), 8.33 (s, 0.5H), 8.27 (s, 0.5H), 8.15 (d, *J* = 7.7 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 8.05 – 7.90 (m, 5H), 7.85 – 7.74 (m, 4H), 7.75 – 7.68 (m, 1H), 7.62 – 7.52 (m, 2H), 7.51 – 7.45 (m, 2H), 7.43 – 7.29 (m, 12H), 7.25 – 7.17 (m, 2H), 6.12 (t, *J* = 9.5 Hz, 0.5H), 6.03 (t, *J* = 8.9 Hz, 0.5H), 5.89 –

5.65 (m, 2H), 4.99 – 4.82 (m, 1H), 4.78 – 4.44 (m, 2H), 4.41 – 4.22 (m, 2H), 2.98 – 2.63 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2 (C_q), 166.2 (C_q), 165.7 (C_q), 165.5 (C_q), 165.5 (C_q), 165.4 (C_q), 165.3 (C_q), 165.3 (C_q), 155.7 (C_q), 155.6 (C_q), 150.0 (CH), 149.9 (CH), 143.1 (C_q), 143.0 (C_q), 142.9 (C_q), 142.7 ($^1J_{C–CF3}$, d, J = 227.9 Hz) 140.7 (C_q), 136.9 (CH), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.3 (CH), 133.2 (CH), 133.0 (CH), 132.9 (CH), 130.0 (C_q), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.7 (CH), 129.5 (C_q), 129.5 (C_q), 129.0 (C_q), 129.0 (C_q), 128.9 (CH), 128.9 (C_q), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 127.8 (CH), 127.4 (CH), 127.0 (CH), 126.8 (CH), 125.1 (CH), 124.8 (CH), 123.0 (CH), 123.0 (CH), 121.0 (CH), 120.9 (CH), 73.8 (CH), 73.8 (CH), 72.2 (CH), 71.7 (CH), 70.8 (CH), 70.5 (CH), 70.2 (CH), 70.1 (CH), 67.6 (CH), 67.1 (CH), 63.1 (CH_2), 42.5 (CH), 41.6 (CH), 36.3 (CH_2), 34.5 (CH_2). 2 Cq and 4 CH resonances are missing due to the overlap.

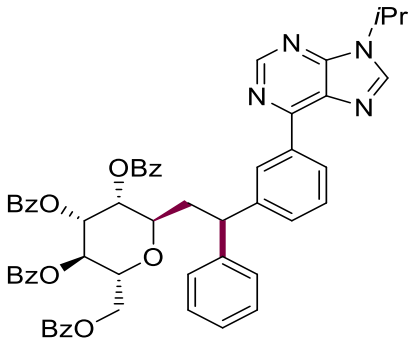
^{19}F NMR (377 MHz, $CDCl_3$): δ = -57.63 (s)

IR (ATR): $\tilde{\nu}$ = 1720, 1586, 1452, 1314, 1263, 1107, 1069, 1027, 784, 708 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 928(100) $[M+Na]^+$, 906 (25) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{54}H_{42}F_3NNaO_9^+$ $[M+Na]^+$ 928.2704, found 928.2703.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{(*R*)-2-[3-(9-isopropyl-9*H*-purin-6-yl)phenyl]-2-phenylethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163bg)



The general procedure **I** was followed using 9-isopropyl-6-phenyl-9H-purine (**160k**) (47.6 mg, 0.20 mmol), styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), P(4-CF_3-C_6H_4)$_3$

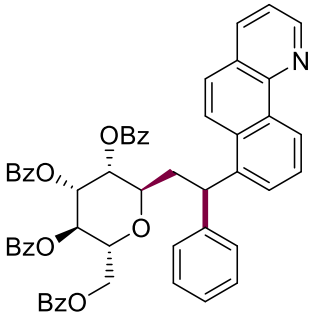
(18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163bg** (81.0 mg, 44%, d.r. = 1.5:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.08 (s, 0.6H), 9.01 (s, 0.4H), 8.95 (d, *J* = 1.9 Hz, 0.4H), 8.93 (d, *J* = 1.9 Hz, 0.6H), 8.72 (dt, *J* = 7.8, 1.4 Hz, 0.6H), 8.67 (dt, *J* = 7.8, 1.4 Hz, 0.4H), 8.27 – 8.12 (m, 3H), 8.07 – 7.95 (m, 4H), 7.91 – 7.81 (m, 2H), 7.66 – 7.54 (m, 3H), 7.53 – 7.45 (m, 4H), 7.45 – 7.37 (m, 7H), 7.37 – 7.32 (m, 3H), 7.30 – 7.26 (m, 2H), 7.25 – 7.17 (m, 1H), 6.01 (dt, *J* = 13.6, 9.2 Hz, 1H), 5.91 (ddd, *J* = 12.4, 9.2, 3.2 Hz, 1H), 5.84 (t, *J* = 2.8 Hz, 0.4H), 5.79 (t, *J* = 3.3, 2.4 Hz, 0.6H), 5.19 – 4.93 (m, 1H), 4.71 – 4.56 (m, 2H), 4.52 – 4.40 (m, 2H), 4.32 (dt, *J* = 11.0, 2.9 Hz, 0.4H), 4.22 (dt, *J* = 11.0, 2.8 Hz, 0.6H), 3.08 – 2.83 (m, 1H), 2.81 – 2.59 (m, 1H), 1.80 – 1.53 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2 (C_q), 166.2 (C_q), 165.6 (C_q), 165.5 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 152.2 (C_q), 151.9 (CH), 144.7 (C_q), 144.3 (C_q), 142.9 (C_q), 142.5 (C_q), 142.1 (CH), 133.4 (CH), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.1 (CH), 133.1 (CH), 131.6 (C_q), 130.7 (CH), 129.9 (C_q), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.5 (C_q), 129.3 (CH), 129.1 (CH), 129.0 (C_q), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 126.7 (CH), 126.6 (CH), 73.7 (CH), 73.6 (CH), 72.0 (CH), 71.8 (CH), 70.6 (CH), 70.4 (CH), 67.8 (CH), 63.6 (CH_2), 47.2 (CH), 47.1 (CH), 46.8 (CH), 46.8 (CH), 34.3 (CH_2), 34.2 (CH_2), 22.6 (CH_3), 22.5 (CH_3). 4 Cq and 4 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1721, 1581, 1315, 1264, 1108, 1093, 1069, 1027, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 943 (80) $[M+Na]^+$, 921 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{56}H_{49}N_4O_9^+$ $[M+H]^+$ 921.3494, found 921.3490.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[2-(Benzo[*h*]quinolin-7-yl)-2-phenylethyl]-6-[(benzoyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163bh)



The general procedure **I** was followed using benzo[*h*]quinoline (**160n**) (35.8 mg, 0.20 mmol), 1- styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163bh** (87.9 mg, 51%, d.r. = 1.2:1) as a syrup.

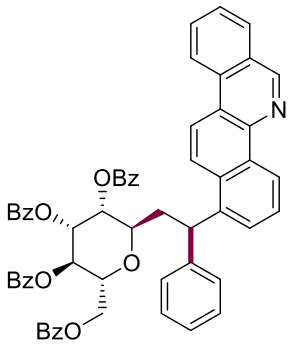
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.49 – 9.27 (m, 1H), 9.00 (d, *J* = 3.3 Hz, 0.45H), 8.98 (d, *J* = 3.1 Hz, 0.55H), 8.26 – 8.06 (m, 4H), 8.04 – 7.97 (m, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.91 – 7.79 (m, 3H), 7.78 – 7.73 (m, 1H), 7.65 – 7.25 (m, 19H), 7.23 – 7.10 (m, 1H), 6.02 (t, *J* = 8.9 Hz, 0.45H), 5.96 (t, *J* = 8.9 Hz, 0.55H), 5.88 (t, *J* = 3.2 Hz, 0.55H), 5.86 (t, *J* = 3.2 Hz, 0.45H), 5.80 (t, *J* = 3.0 Hz, 0.55H), 5.76 (t, *J* = 3.0 Hz, 0.45H), 5.23 (dd, *J* = 10.3, 4.8 Hz, 0.56H), 5.15 (dd, *J* = 11.5, 3.4 Hz, 0.44H), 4.75 (dd, *J* = 12.0, 2.9 Hz, 0.44H), 4.65 (dd, *J* = 12.0, 5.8 Hz, 0.46H), 4.58 (d, *J* = 4.4 Hz, 1H), 4.54 – 4.40 (m, 1H), 4.35 – 4.18 (m, 1H), 3.09 – 2.88 (m, 1H), 2.80 (ddd, *J* = 14.3, 10.3, 3.6 Hz, 0.55H), 2.64 (ddd, *J* = 14.3, 11.4, 3.2 Hz, 0.45H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2 (C_q), 166.1 (C_q), 165.6 (C_q), 165.6 (C_q), 165.4 (C_q), 165.4 (C_q), 165.4 (C_q), 148.8 (CH), 148.6 (CH), 144.3 (C_q), 142.5 (C_q), 139.8 (C_q), 138.3 (C_q), 135.7 (CH), 133.5 (CH), 133.5 (CH), 133.3 (CH), 133.3 (CH), 133.1 (CH), 132.1 (C_q), 131.6 (C_q), 129.9 (C_q), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.4 (C_q), 129.4 (C_q), 128.9 (C_q), 128.9 (C_q), 128.9 (C_q), 128.9 (C_q), 128.8 (CH), 128.8 (CH), 128.5 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 127.7 (CH), 126.7 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 125.8 (C_q), 125.7 (C_q), 125.6 (CH), 125.5 (CH), 123.6 (CH), 123.6 (CH), 123.2 (CH), 123.0 (CH), 121.8 (CH), 121.8 (CH), 73.6 (CH), 73.0 (CH), 71.7 (CH), 71.6 (CH), 70.8 (CH), 70.8 (CH), 70.3 (CH), 70.2 (CH), 67.8 (CH), 67.7 (CH), 63.6 (CH_2),

63.5 (CH_2), 41.8 (CH), 41.8 (CH), 35.2 (CH_2), 35.0 (CH_2). 2 Cq and 5 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1728, 1601, 1315, 1266, 1107, 1093, 1069, 1027, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 884 (45) $[M+Na]^+$, 862 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{55}H_{44}NO_9^+$ $[M+H]^+$ 862.3011, found 862.3001.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[2-(Benzo[*c*]phenanthridin-1-yl)-2-phenylethyl]-6-[(benzoyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163bi)



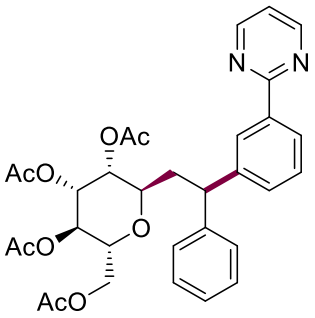
The general procedure **I** was followed using benzo[*c*]phenanthridine (**160o**) (45.8 mg, 0.20 mmol), 1-styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163bi** (94.8 mg, 51%, d.r. = 1.3:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.55 – 9.42 (m, 2H), 8.59 (dd, *J* = 8.4, 3.8 Hz, 1H), 8.45 – 8.29 (m, 2H), 8.26 – 8.13 (m, 3H), 8.10 – 8.01 (m, 2H), 8.02 – 7.96 (m, 2H), 7.98 – 7.80 (m, 5H), 7.82 – 7.72 (m, 1H), 7.69 – 7.51 (m, 3H), 7.53 – 7.41 (m, 7H), 7.43 – 7.29 (m, 6H), 7.30 – 7.16 (m, 1H), 6.06 (t, *J* = 8.8 Hz, 0.43H), 6.00 (t, *J* = 8.7 Hz, 0.57H), 5.95 (t, *J* = 3.4 Hz, 0.57H), 5.92 (t, *J* = 3.4 Hz, 0.43H), 5.86 (t, *J* = 2.9 Hz, 0.57H), 5.83 (t, *J* = 3.0 Hz, 0.43H), 5.34 (dd, *J* = 10.4, 4.7 Hz, 0.57H), 5.26 (dd, *J* = 11.5, 3.3 Hz, 0.43H), 4.82 (dd, *J* = 12.0, 2.9 Hz, 0.43H), 4.77 – 4.65 (m, 0.57H), 4.68 – 4.58 (m, 1H), 4.57 (ddd, *J* = 8.7, 5.7, 3.2 Hz, 0.57H), 4.52 (ddd, *J* = 8.8, 5.9, 2.9 Hz, 0.43H), 4.43 – 4.26 (m, 1H), 3.13 – 2.95 (m, 1H), 2.88 (ddd, *J* = 14.2, 10.4, 3.6 Hz, 0.57H), 2.71 (ddd, *J* = 14.4, 11.5, 3.1 Hz, 0.43H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2 (C_q), 166.2 (C_q), 165.6 (C_q), 165.6 (C_q), 165.5 ($2C_q$), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 152.0 (CH), 151.8 (CH), 144.4 (C_q), 142.6 (C_q), 141.7 (C_q), 139.6 (C_q), 138.0 (C_q), 133.5 (CH), 133.4 (CH), 133.3 (CH), 133.3 (CH), 133.3 (CH), 133.1 (CH), 133.1 (CH), 132.7 (C_q), 132.6 (C_q), 132.6 (C_q), 131.8 (C_q), 131.3 (C_q), 130.8 (CH), 130.8 (CH), 129.9 (C_q), 129.9 (CH), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.7 (CH), 129.4 (C_q), 129.4 (C_q), 128.9 (C_q), 128.9 (C_q), 128.9 (C_q), 128.8 (C_q), 128.8 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 127.8 (CH), 127.2 (CH), 127.2 (CH), 126.8 (C_q), 126.8 (C_q), 126.7 (CH), 126.6 (CH), 126.5 (CH), 125.6 (CH), 124.0 (CH), 123.3 (CH), 123.1 (CH), 122.2 (CH), 122.1 (CH), 120.5 (C_q), 120.4 (C_q), 120.2 (CH), 120.2 (CH), 73.5 (CH), 73.1 (CH), 71.8 (CH), 71.6 (CH), 70.8 (CH), 70.3 (CH), 70.2 (CH), 67.9 (CH), 67.8 (CH), 63.7 (CH_2), 63.6 (CH_2), 41.9 (CH), 41.8 (CH), 35.1 (CH_2), 35.1 (CH_2). 1 CH resonance is missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1601, 1451, 1263, 1107, 1092, 1069, 1027, 752, 708 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 934 (100) $[M+Na]^+$, 912 (55) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{59}H_{45}NO_9Na^+$ $[M+Na]^+$ 934.2987, found 934.2983.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-(Acetoxymethyl)-6-{2-phenyl-2-[3-(pyrimidin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (163ca)



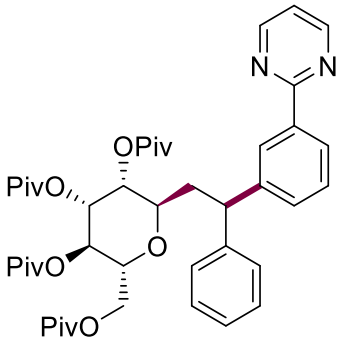
The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-(acetoxymethyl)-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161bb**) (164.0 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ca** (93.3 mg, 79%, d.r. = 1:1) as a syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (t, *J* = 5.5 Hz, 2H), 8.40 (d, *J* = 6.6 Hz, 1H), 8.29 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.36 – 7.28 (m, 4H), 7.18 (p, *J* = 5.1 Hz, 2H), 5.42 – 5.07 (m, 3H), 4.35 – 4.21 (m, 2H), 4.11 (dd, *J* = 12.0, 2.6 Hz, 0.5H), 4.04 (dd, *J* = 12.0, 2.6 Hz, 0.5H), 3.97 – 3.69 (m, 2H), 2.73 – 2.50 (m, 1H), 2.49 – 2.29 (m, 1H), 2.19 (s, 1.5H), 2.18 (s, 1.5H), 2.08 (s, 1.5H), 2.06 (s, 1.5H), 2.04 (s, 1.5H), 2.03 (s, 1.5H), 1.99 (s, 1.5H), 1.98 (s, 1.5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7 (C_q), 170.6 (C_q), 170.2 (C_q), 170.0 (C_q), 169.6 (C_q), 164.5 (C_q), 157.2 (CH), 157.1 (CH), 144.5 (C_q), 144.0 (C_q), 143.0 (C_q), 142.5 (C_q), 138.1 (C_q), 137.9 (C_q), 130.4 (CH), 130.2 (CH), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 127.1 (CH), 126.7 (CH), 126.6 (CH), 126.6 (CH), 126.5 (CH), 119.1 (CH), 119.1 (CH), 73.4 (CH), 73.4 (CH), 70.9 (CH), 70.7 (CH), 70.2 (CH), 70.1 (CH), 69.4 (CH), 69.3 (CH), 66.8 (CH), 66.8 (CH), 62.8 (CH_2), 46.8 (CH), 46.6 (CH), 34.1 (CH_2), 34.0 (CH_2), 20.9 (CH_3), 20.9 (CH_3), 20.8 (CH_3), 20.7 (CH_3), 20.7 (CH_3). 2 Cq resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1738, 1569, 1555, 1411, 1368, 1222, 1048, 755, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 613 (100) $[M+Na]^+$, 591 (70) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{32}H_{35}N_2O_9^+$ $[M+H]^+$ 591.2337, found 591.2336.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-{2-Phenyl-2-[3-(pyrimidin-2-yl)phenyl]ethyl}-6-[(pivaloyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (163cb)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-[(pivaloyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (**161bc**) (231.8 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), P(4-CF_3-

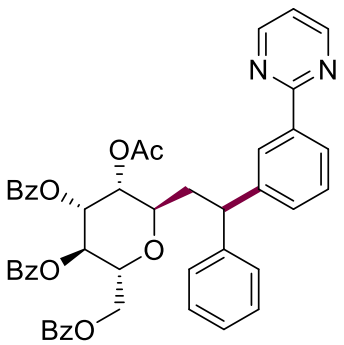
$C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163cb** (109.2 mg, 72%, d.r. = 1.3:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (ddd, *J* = 7.5, 5.0, 1.3 Hz, 2H), 8.45 – 8.41 (m, 0.57H), 8.41 – 8.36 (m, 0.43H), 8.28 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.35 (m, 2H), 7.34 – 7.27 (m, 4H), 7.23 – 7.13 (m, 2H), 5.33 (dd, *J* = 10.5, 7.2 Hz, 2H), 5.23 (q, *J* = 3.4, 2.9 Hz, 1H), 4.32 – 4.24 (m, 1H), 4.18 (dt, *J* = 11.8, 5.7 Hz, 1H), 4.13 – 4.02 (m, 1H), 3.94 (q, *J* = 7.1 Hz, 1H), 3.82 (t, *J* = 11.4 Hz, 1H), 2.68 – 2.51 (m, 1H), 2.49 – 2.35 (m, 1H), 1.28 (s, 9H), 1.18 (s, 18H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.1 (C_q), 178.1 (C_q), 177.3 (C_q), 177.2 (C_q), 177.1 (C_q), 177.1 (C_q), 176.7 (C_q), 176.7 (C_q), 164.5 (C_q), 164.5 (C_q), 157.2 (CH), 157.1 (CH), 144.7 (C_q), 144.2 (C_q), 143.4 (C_q), 142.9 (C_q), 138.0 (C_q), 137.9 (C_q), 130.5 (CH), 130.3 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.7 (CH), 127.1 (CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 119.1 (CH), 119.1 (CH), 73.1 (CH), 72.8 (CH), 71.1 (CH), 70.9 (CH), 70.7 (CH), 70.5 (CH), 69.4 (CH), 69.3 (CH), 66.3 (CH), 66.2 (CH), 62.5 (CH_2), 62.3 (CH_2), 46.9 (CH), 46.8 (CH), 38.9 (C_q), 38.8 (C_q), 38.8 (C_q), 38.8 (C_q), 38.7 (C_q), 38.7 (C_q), 34.6 (CH_2), 34.3 (CH_2), 27.2 (CH_3), 27.1 (CH_3), 27.1 (CH_3), 27.0 (CH_3), 27.0 (CH_3). 1 CH resonance is missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1733, 1569, 1556, 1480, 1411, 1367, 1279, 1132, 732, 704 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 781(100) $[M+Na]^+$, 759 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{58}N_2NaO_9^+$ $[M+Na]^+$ 781.4035, found 781.4033.

(2*R*,3*R*,4*R*,5*R*,6*R*)-5-Acetoxy-2-[(benzoyloxy)methyl]-6-{2-phenyl-2-[3-(pyrimidin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4-diyl dibenzoate (163cc)



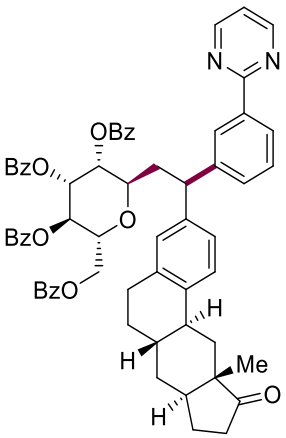
The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-5-acetoxy-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4-diyl dibenzoate (**161bd**) (238.0 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163cc** (108.7 mg, 70%, d.r. = 1:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 4.8 Hz, 1H), 8.76 (d, *J* = 4.8 Hz, 1H), 8.49 (s, 0.5H), 8.43 (s, 0.5H), 8.30 (t, *J* = 7.3 Hz, 1H), 8.16 (dd, *J* = 7.7, 2.9 Hz, 2H), 7.97 (dd, *J* = 7.8, 3.5 Hz, 2H), 7.88 (t, J = 7.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.54 – 7.42 (m, 4H), 7.41 – 7.27 (m, 10H), 7.17 (t, *J* = 4.9 Hz, 2H), 6.02 – 5.66 (m, 2H), 5.59 – 5.35 (m, 1H), 4.78 – 4.46 (m, 2H), 4.34 (d, *J* = 10.3 Hz, 2H), 3.98 (t, *J* = 10.1 Hz, 1H), 2.96 – 2.69 (m, 1H), 2.66 – 2.45 (m, 1H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0 (C_q), 169.9 (C_q), 166.1 (C_q), 165.6 (C_q), 165.6 (C_q), 165.5 (C_q), 164.6 (C_q), 164.5 (C_q), 157.2 (CH), 157.1 (CH), 144.6 (C_q), 144.1 (C_q), 143.0 (C_q), 142.5 (C_q), 138.1 (C_q), 138.0 (C_q), 133.5 (CH), 133.3 (CH), 133.3 (CH), 133.2 (CH), 130.6 (CH), 130.4 (CH), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.6 (CH), 129.6 (CH), 129.1 (CH), 129.0 (C_q), 129.0 (C_q), 128.9 (CH), 128.9 (CH), 128.9 (C_q), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.6 (CH), 126.9 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 126.5 (CH), 119.1 (CH), 119.0 (CH), 73.3 (CH), 73.2 (CH), 71.3 (CH), 71.1 (CH), 70.6 (CH), 70.4 (CH), 70.2 (CH), 70.1 (CH), 67.9 (CH), 63.8 (CH_2), 63.7 (CH_2), 46.6 (CH), 46.4 (CH), 34.2 (CH_2), 33.9 (CH_2), 20.8 (CH_3), 20.8 (CH_3). 2 Cq and 2 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1719, 1555, 1452, 1411, 1266, 1093, 1069, 1027, 908, 707 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 799 (100) $[M+Na]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{47}H_{40}N_2NaO_9^+$ $[M+Na]^+$ 799.2626, found 799.2637.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{2-[(6a*S*,7a*S*,10a*S*,11a*S*)-10a-methyl-10-oxo-6,6a,7,7a,8,9,10,10a,11,11a-decahydro-5*H*-cyclopenta[*b*]phenanthren-3-yl]-2-[3-(pyrimidin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163cd)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), (6a*S*,7a*S*,10a*S*,11a*S*)-10a-methyl-3-vinyl-5,6,6a,7,7a,8,9,10a,11,11a-decahydro-10*H*-cyclopenta[*b*]phenanthren-10-one (**110r**) (84.1 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163cd** (111.6 mg, 55%, d.r. = 1.1:1) as a syrup.

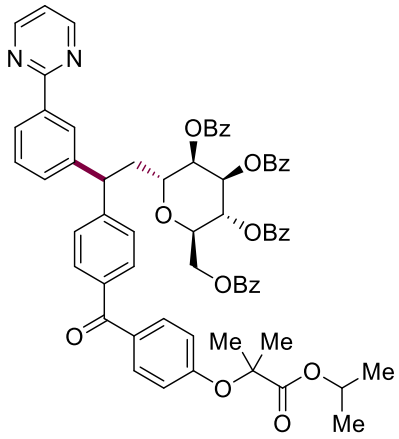
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 4.8 Hz, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.53 (d, *J* = 1.5 Hz, 0.48H), 8.49 (d, *J* = 1.5 Hz, 0.52H), 8.38 – 8.27 (m, 1H), 8.21 (d, *J* = 7.7 Hz, 2H), 8.10 – 7.92 (m, 5H), 7.81 (t, *J* = 7.0 Hz, 2H), 7.63 – 7.31 (m, 14H), 7.22 – 7.11 (m, 3H), 7.07 – 7.01 (m, 0.52H), 7.01 – 6.95 (m, 0.48H), 5.99 (dt, *J* = 18.1, 9.3 Hz, 1H), 5.91 – 5.81 (m, 1H), 5.76 (t, *J* = 2.7 Hz, 1H), 4.77 – 4.49 (m, 2H), 4.46 – 4.24 (m, 2H), 4.24 – 4.11 (m, 1H), 2.95 – 2.78 (m, 3H)), 2.73 – 2.56 (m, 1H), 2.56 – 2.30 (m, 2H), 2.20 (dd, *J* = 25.4, 9.7 Hz, 1H), 2.12 – 1.89 (m, 4H), 1.67 – 1.40 (m, 5H), 1.32 – 1.21 (m, 1H), 0.90 (s, 1.56H), 0.86 (s, 1.44H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 220.8 (C_q), 220.8 (C_q), 166.1 (C_q), 166.0 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 164.5 (C_q), 164.5 (C_q), 157.1 (CH), 157.0 (CH), 144.9 (C_q), 143.2 (C_q), 141.6 (C_q), 139.8 (C_q), 138.1 (C_q), 138.0 (C_q), 137.9 (C_q), 136.8 (C_q), 136.7 (C_q), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 133.1 (CH), 133.0 (CH), 130.4 (CH), 130.3 (CH), 129.9 (C_q), 129.8 (CH), 129.7 (CH), 129.6 (CH), 129.6 (CH), 129.5 (C_q), 129.4 (C_q), 129.0 (CH), 128.9 (CH), 128.9 (C_q), 128.9 (C_q), 128.8 (C_q), 128.6 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 126.9 (CH), 126.5 (CH), 126.4 (CH), 125.7 (CH), 125.6 (CH), 125.1 (CH), 124.8 (CH), 119.1 (CH), 119.0 (CH), 74.0 (CH), 73.4 (CH), 72.0 (CH), 71.7 (CH), 70.5 (CH),

70.5 (CH), 70.2 (CH), 70.1 (CH), 67.8 (CH), 67.6 (CH), 63.6 (CH_2), 63.4 (CH_2), 50.4 (CH), 47.9 (C_q), 46.3 (CH), 44.2 (CH), 44.2 (CH), 38.0 (CH), 37.9 (CH), 35.8 (CH_2), 34.2 (CH_2), 33.8 (CH_2), 31.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.4 (CH_2), 26.4 (CH_2), 25.6 (CH_2), 25.5 (CH_2), 21.5 (CH_2), 13.8 (CH_3). 5 CH resonance is missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1720, 1601, 1451, 1410, 1263, 1107, 1093, 1026, 753, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1037 (100) $[M+Na]^+$, 1015 (80) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{64}H_{59}N_2O_{10}^+$ $[M+H]^+$ 1015.4164, found 1015.4165.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[2-(4-{4-[(1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy]benzoyl}phenyl)-2-[3-(pyrimidin-2-yl)phenyl]ethyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163ce)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), isopropyl 2-methyl-2-(4-(4-vinylbenzoyl)phenoxy)propanoate (**110s**) (105.7 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa**) (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ce** (115.2 mg, 53%, d.r. = 1:1) as a syrup.

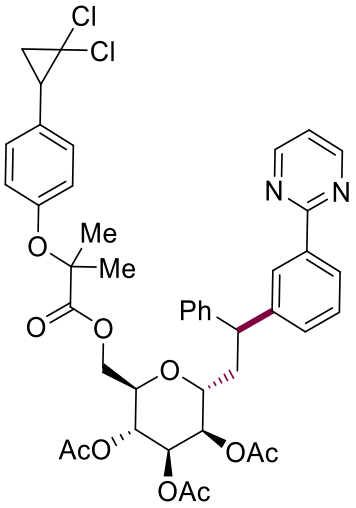
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 4.8 Hz, 1H), 8.70 (d, *J* = 4.8 Hz, 1H), 8.45 (d, *J* = 1.8 Hz, 0.49H), 8.40 (d, *J* = 1.8 Hz, 0.51H), 8.27 (tt, *J* = 7.6, 1.6 Hz, 1H), 8.19 – 8.07 (m, 2H), 8.03 – 7.87 (m, 4H), 7.83 – 7.69 (m, 2H), 7.72 – 7.57 (m, 4H), 7.57 – 7.39 (m, 2H), 7.48 – 7.36 (m, 5H), 7.36 – 7.28 (m, 7H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.18

(d, *J* = 8.1 Hz, 1H), 7.15 (t, *J* = 4.8 Hz, 0.51H), 7.09 (t, *J* = 4.8 Hz, 0.49H), 6.87 – 6.71 (m, 2H), 5.92 (t, *J* = 9.3 Hz, 0.53H), 5.87 (t, *J* = 8.7 Hz, 0.47H), 5.81 (t, *J* = 3.2 Hz, 0.6H), 5.78 (t, *J* = 3.2 Hz, 0.4H), 5.68 (q, *J* = 2.7 Hz, 1H), 5.08 – 4.93 (m, 1H), 4.66 – 4.49 (m, 2H), 4.45 – 4.31 (m, 2H), 4.20 – 4.05 (m, 1H), 3.10 – 2.70 (m, 1H), 2.69 – 2.49 (m, 1H), 1.60 (s, 3H), 1.58 (s, 3H), 1.14 (s, 1.53H), 1.13 (s, 1.53H), 1.12 (s, 1.47H), 1.10 (s, 1.47H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.0 (C_q), 173.1 (C_q), 173.1 (C_q), 166.1 (C_q), 166.1 (C_q), 165.6 (C_q), 165.6 (C_q), 165.5 (C_q), 165.4 (C_q), 165.4 (C_q), 164.4 (C_q), 164.3 (C_q), 159.4 (C_q), 159.4 (C_q), 157.2 (CH), 157.1 (CH), 148.4 (C_q), 146.9 (C_q), 143.8 (C_q), 142.3 (C_q), 138.2 (C_q), 138.2 (C_q), 136.6 (C_q), 136.4 (C_q), 133.5 (CH), 133.5 (CH), 133.4 (CH), 133.3 (CH), 133.3 (CH), 133.2 (CH), 133.2 (CH), 132.0 (CH), 132.0 (CH), 130.6 (C_q), 130.6 (CH), 130.5 (CH), 130.3 (CH), 130.3 (CH), 129.8 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 129.4 (C_q), 129.2 (CH), 129.1 (CH), 128.9 (C_q), 128.8 (C_q), 128.5 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 127.5 (CH), 127.1 (CH), 126.9 (CH), 126.8 (CH), 119.2 (CH), 119.1 (CH), 117.1 (CH), 117.1 (CH), 79.3 (C_q), 79.3 (C_q), 73.4 (CH), 72.9 (CH), 71.8 (CH), 71.5 (CH), 70.9 (CH), 70.5 (CH), 70.2 (CH), 70.1 (CH), 69.3 (CH), 69.2 (CH), 67.9 (CH), 67.7 (CH), 63.5 (CH_2), 63.3 (CH_2), 46.8 (CH), 46.6 (CH), 34.2 (CH_2), 33.8 (CH_2), 25.4 (CH_3), 25.3 (CH_3), 21.5 (CH_3), 21.5 (CH_3). 3 Cq and 3 CH resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1728, 1600, 1452, 1412, 1267, 1178, 1105, 1027, 930, 710 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1109 (60) $[M+Na]^+$, 1087 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{66}H_{59}N_2O_{13}^+$ $[M+H]^+$ 1087.4012, found 1087.4005.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[({2-[4-(2,2-Dichlorocyclopropyl)phenoxy]-2-methylpropanoyl}oxy)methyl]-6-{2-phenyl-2-[3-(pyrimidin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (163cf)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-[({2-[4-(2,2-dichlorocyclopropyl)phenoxy]-2-methylpropanoyl}oxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161ci**) (255.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163cf** (135.8 mg, 83%, d.r. = 1:1) as a syrup.

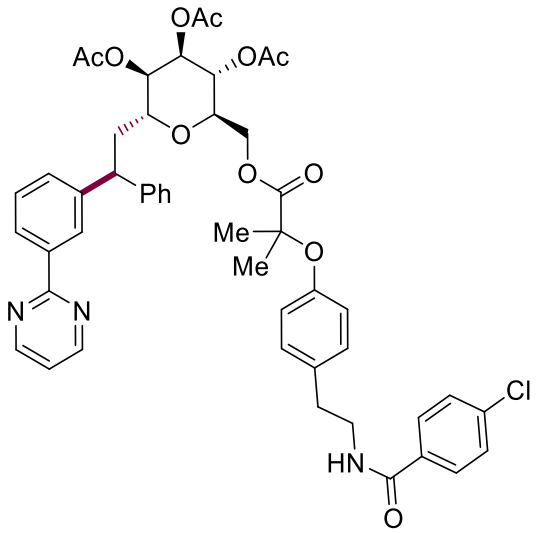
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 4.9 Hz, 1H), 8.76 (d, *J* = 4.8 Hz, 1H), 8.42 (d, *J* = 1.9 Hz, 0.5H), 8.38 (d, *J* = 1.9 Hz, 0.5H), 8.34 – 8.26 (m, 1H), 7.47 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 7.26 – 7.12 (m, 3H), 7.01 (t, *J* = 3.2 Hz, 2H), 6.87 (d, *J* = 2.0 Hz, 2H), 5.32 – 5.15 (m, 3H), 4.58 – 4.10 (m, 3H), 3.99 – 3.73 (m, 2H), 2.88 – 2.72 (m, 1H), 2.68 – 2.49 (m, 1H), 2.47 – 2.30 (m, 1H), 2.05 (s, 3H), 1.98 (s, 6H), 1.94 – 1.85 (m, 1H), 1.77 – 1.70 (m, 1H), 1.67 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.7 (C_q), 170.1 (C_q), 170.0 (C_q), 170.0 (C_q), 169.6 (C_q), 164.5 (C_q), 164.5 (C_q), 157.2 (CH), 157.1 (CH), 154.8 (C_q), 154.7 (C_q), 144.5 (C_q), 144.0 (C_q), 143.1 (C_q), 142.6 (C_q), 142.5 (C_q), 138.0 (C_q), 137.9 (C_q), 130.8 (CH), 130.4 (CH), 129.6 (CH), 129.6 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.5 (C_q), 128.4 (C_q), 128.2 (CH), 127.7 (CH), 127.6 (CH), 127.0 (CH), 126.7 (CH), 126.7 (CH), 126.6 (CH), 126.6 (CH), 126.5 (CH), 119.5 (CH), 119.1 (CH), 119.1 (CH), 79.3 (C_q), 79.3 (C_q), 73.2 (CH), 73.2 (CH), 70.9 (CH), 70.8 (CH), 70.7 (CH), 70.7 (CH), 70.2 (CH), 70.2 (CH), 69.3 (CH), 69.3 (CH), 66.8 (CH), 66.7 (CH), 63.5 (CH_2), 63.4 (CH_2), 60.8 (C_q), 60.8 (C_q), 46.5 (CH), 46.4 (CH), 34.8 (CH), 34.2 (CH_2), 33.9 (CH_2), 25.8

(CH_2), 25.7 (CH_2), 25.7 (CH_3), 25.4 (CH_3), 25.2 (CH_3), 25.1 (CH_3), 20.8 (CH_3), 20.7 (CH_3), 20.6 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1746, 1569, 1556, 1511, 1411, 1369, 1247, 1223, 1049, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 841(100) $[M+Na]^+$, 819 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{43}H_{44}Cl_2N_2NaO_{10}^+$ $[M+Na]^+$ 841.2265, found 841.2263.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-{[(2-{4-[2-(4-Chlorobenzamido)ethyl]phenoxy}-2-methylpropanoyl)oxy]methyl}-6-{2-phenyl-2-[3-(pyrimidin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (163cg)



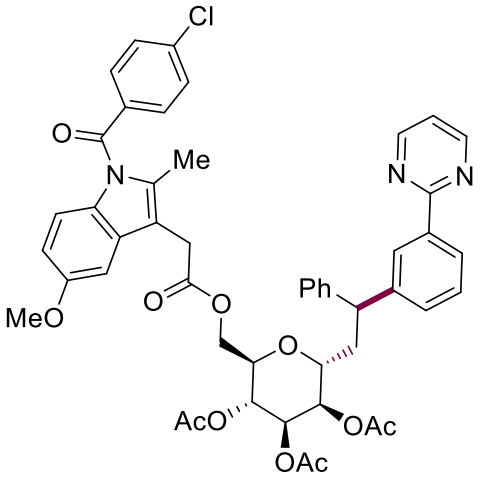
The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-{[(2-{4-[2-(4-chlorobenzamido)ethyl]phenoxy}-2-methylpropanoyl)oxy]methyl}tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161cb**) (284.4 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), P(4-CF_3-C_6H_4)$_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163cg** (117.7 mg, 66%, d.r. = 1.3:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (dd, *J* = 5.0, 2.1 Hz, 2H), 8.41 (s, 0.44H), 8.38 (s, 0.56H), 8.28 (t, *J* = 8.1 Hz, 1H), 7.72 – 7.54 (m, 2H), 7.44 – 7.27 (m, 7H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.21 – 7.10 (m, 2H), 6.97 (t, *J* = 8.4 Hz, 2H), 6.84 (t, *J* = 6.5 Hz, 2H), 6.31 (t, *J* = 6.0 Hz, 0.5H), 6.22 (t, *J* = 6.0 Hz, 0.5H), 5.36 – 5.07 (m, 3H), 4.57 – 4.07 (m, 3H), 4.03 – 3.76 (m, 2H), 3.71 – 3.52 (m, 2H), 3.02 – 2.71 (m, 2H), 2.56 (q, *J* = 11.2 Hz, 1H), 2.38 (q, *J* = 11.2 Hz, 1H), 1.98 (s, 9H), 1.69 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.8 (C_q), 173.8 (C_q), 170.1 (C_q), 170.1 (C_q), 170.0 (C_q), 169.6 (C_q), 169.6 (C_q), 166.4 (C_q), 166.3 (C_q), 164.5 (C_q), 164.4 (C_q), 157.2 (CH), 157.1 (CH), 153.9 (C_q), 153.9 (C_q), 144.5 (C_q), 143.9 (C_q), 143.1 (C_q), 142.6 (C_q), 138.0 (C_q), 137.9 (C_q), 137.5 (C_q), 137.5 (C_q), 133.0 (C_q), 133.0 (C_q), 132.7 (C_q), 130.7 (CH), 130.4 (CH), 129.4 (CH), 129.4 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 127.8 (CH), 127.6 (CH), 127.0 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 126.5 (CH), 120.2 (CH), 119.2 (CH), 119.1 (CH), 79.3 (C_q), 79.3 (C_q), 73.1 (CH), 70.9 (CH), 70.7 (CH), 70.2 (CH), 70.2 (CH), 69.2 (CH), 69.2 (CH), 66.8 (CH), 66.7 (CH), 63.5 (CH_2), 63.4 (CH_2), 46.5 (CH), 46.4 (CH), 41.2 (CH_2), 34.7 (CH_2), 34.1 (CH_2), 33.9 (CH_2), 25.6 (CH_3), 25.5 (CH_3), 25.3 (CH_3), 25.2 (CH_3), 20.8 (CH_3), 20.8 (CH_3), 20.7 (CH_3), 20.6 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1745, 1640, 1569, 1508, 1486, 1368, 1221, 1047, 734 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 892 (20) $[M+Na]^+$, 914 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{49}H_{50}ClN_3NaO_{11}^+$ $[M+Na]^+$ 914.3026, found 914.3023.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-({2-[1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl]acetoxy}methyl)-6-{2-phenyl-2-[3-(pyrimidin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (163ch)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-({2-[1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl]acetoxy}methyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161ca**) (282.8 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), P(4-CF_3-C_6H_4)$_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in

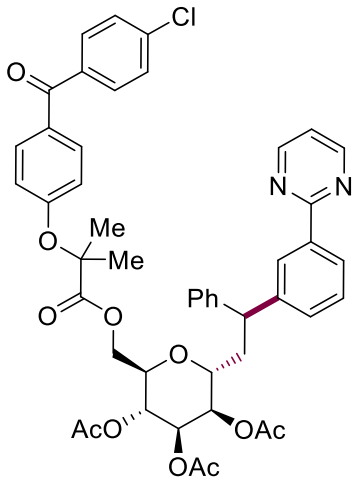
1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ch** (122.4 mg, 69%, d.r. = 1.5:1) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (dd, *J* = 9.0, 4.8 Hz, 2H), 8.41 (d, *J* = 1.8 Hz, 0.6H), 8.40 (d, *J* = 1.8 Hz, 0.4H), 8.30 (t, *J* = 1.6 Hz, 0.6H), 8.28 (t, *J* = 1.6 Hz, 0.4H), 7.63 (dd, *J* = 8.5, 2.9 Hz, 2H), 7.46 – 7.38 (m, 3H), 7.36 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.23 – 7.11 (m, 2H), 7.00 (t, *J* = 2.3 Hz, 1H), 6.89 (d, *J* = 1.0 Hz, 0.4H), 6.87 (d, *J* = 1.0 Hz, 0.6H), 6.67 (t, *J* = 2.5 Hz, 0.6H), 6.65 (t, *J* = 2.5 Hz, 0.4H), 5.38 – 5.19 (m, 3H), 4.33 (dd, *J* = 5.7, 2.9 Hz, 0.4H), 4.30 (dd, *J* = 5.6, 2.9 Hz, 0.6H), 4.27 – 4.21 (m, 1H), 4.18 (dd, *J* = 12.2, 2.6 Hz, 0.6H), 4.12 (dd, *J* = 12.1, 2.8 Hz, 0.4H), 3.99 – 3.92 (m, 1H), 3.90 – 3.78 (m, 3H), 3.76 (s, 3H), 2.74 – 2.53 (m, 1H), 2.46 – 2.33 (m, 4H), 2.05 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6 (C_q), 170.1 (C_q), 170.1 (C_q), 170.0 (C_q), 169.5 (C_q), 169.5 (C_q), 168.2 (C_q), 164.4 (C_q), 157.2 (CH), 157.1 (CH), 156.0 (C_q), 144.4 (C_q), 143.9 (C_q), 143.0 (C_q), 142.6 (C_q), 139.1 (C_q), 138.0 (C_q), 137.9 (C_q), 136.1 (C_q), 136.1 (C_q), 133.9 (C_q), 131.1 (CH), 130.8 (C_q), 130.8 (C_q), 130.6 (C_q), 130.4 (CH), 130.1 (CH), 129.1 (CH), 129.0 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 127.1 (CH), 126.7 (CH), 126.6 (CH), 126.6 (CH), 126.5 (CH), 119.1 (CH), 119.1 (CH), 114.9 (CH), 112.2 (C_q), 112.1 (C_q), 111.6 (CH), 101.3 (CH), 73.2 (CH), 73.2 (CH), 70.8 (CH), 70.6 (CH), 70.3 (CH), 70.2 (CH), 69.2 (CH), 69.2 (CH), 66.7 (CH), 66.6 (CH), 63.1 (CH_2), 55.6 (CH), 55.6 (CH_3), 46.9 (CH), 46.7 (CH), 34.3 (CH_2), 34.1 (CH_2), 29.9 (CH_2), 20.9 (CH_3), 20.9 (CH_3), 20.7 (CH_3), 20.7 (CH_3), 20.6 (CH_3), 20.6 (CH_3), 13.4 (CH_3), 13.4 (CH_3). 4 Cq resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1734, 1680, 1555, 1478, 1411, 1371, 1218, 1045, 911, 731 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 910 (100) $[M+Na]^+$, 887 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{49}H_{46}ClN_3NaO_{11}^+$ $[M+Na]^+$ 910.2713, found 910.2710.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[({2-[4-(4-Chlorobenzoyl)phenoxy]-2-methylpropanoyl}oxy)methyl]-6-{2-phenyl-2-[3-(pyrimidin-2-yl)phenyl]ethyl}tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (163ci)



The general procedure **I** was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 1-styrene (**110a**) (31.2 mg, 0.30 mmol), (2*R*,3*S*,4*S*,5*R*,6*R*)-2-bromo-6-[({2-[4-(4-chlorobenzoyl)phenoxy]-2-methylpropanoyl}oxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**161cd**) (267.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163ci** (120.5 mg, 71%, d.r. = 1:1) as a syrup.

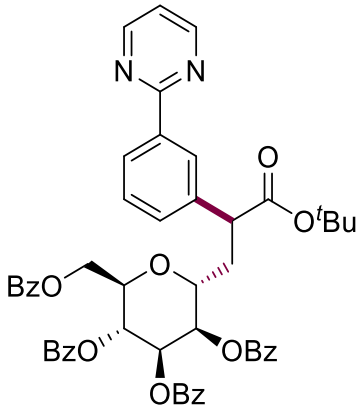
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 4.9 Hz, 1H), 8.75 (d, *J* = 4.9 Hz, 1H), 8.40 (s, 0.5H), 8.36 (s, 0.5H), 8.27 (t, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 4H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.12 (m, 4H), 6.91 (dd, *J* = 7.1, 4.6 Hz, 2H), 5.37 – 5.14 (m, 3H), 4.47 – 4.37 (m, 0.5H), 4.36 – 4.29 (m, 0.5H), 4.28 – 4.16 (m, 2H), 3.91 (dd, *J* = 7.7, 4.0 Hz, 1H), 3.80 (t, *J* = 8.8 Hz, 1H), 2.66 – 2.50 (m, 1H), 2.45 – 2.29 (m, 1H), 2.04 (s, 3H), 2.02 (s, 1.5H), 2.01 (s, 1.5H), 1.98 (s, 1.5H), 1.97 (s, 1.5H), 1.75 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.2 (C_q), 173.2 (C_q), 173.2 (C_q), 170.0 (C_q), 170.0 (C_q), 170.0 (C_q), 169.6 (C_q), 169.6 (C_q), 164.5 (C_q), 164.4 (C_q), 159.4 (C_q), 159.4 (C_q), 157.2 (CH), 157.1 (CH), 144.4 (C_q), 143.9 (C_q), 143.0 (C_q), 142.5 (C_q), 138.4 (C_q), 138.1 (C_q), 137.9 (C_q), 136.3 (C_q), 132.0 (CH), 131.9 (CH), 131.1 (CH), 130.7 (C_q), 130.6 (CH), 130.3 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.1 (CH), 127.7 (CH), 127.6 (CH), 127.0 (CH), 126.7 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 119.2 (CH), 119.1 (CH), 118.0 (CH), 79.5 (C_q), 79.4 (C_q), 73.3 (CH), 73.2 (CH), 70.8 (CH), 70.7 (CH), 70.1 (CH), 70.1 (CH), 69.3 (CH), 69.2 (CH), 66.7 (CH), 66.7 (CH), 63.7 (CH_2), 46.6 (CH), 46.4 (CH), 34.2 (CH_2), 33.9 (CH_2), 25.7

(CH_3), 25.6 (CH_3), 25.4 (CH_3), 25.3 (CH_3), 20.8 (CH_3), 20.8 (CH_3), 20.7 (CH_3), 20.7 (CH_3), 20.7 (CH_3), 20.6 (CH_3). 2 Cq resonances are missing due to the overlap.

IR (ATR): $\tilde{\nu}$ = 1745, 1656, 1599, 1411, 1369, 1248, 1146, 1047, 928, 731 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 871(100) $[M+Na]^+$, 849 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{47}H_{45}ClN_2NaO_{11}^+$ $[M+Na]^+$ 871.2604, found 871.2603.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-{3-(tert-butoxy)-3-oxo-2-[3-(pyrimidin-2-yl)phenyl]propyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163da)



The general procedure was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), *tert*-butyl acrylate (**110t**) (38.4 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa)** (263.2 mg, 0.40 mmol) $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}F_3CC_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 °C. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163da** (115.5 mg, 67%, d.r. = 1.3:1) and **163da'** in 17% yield.

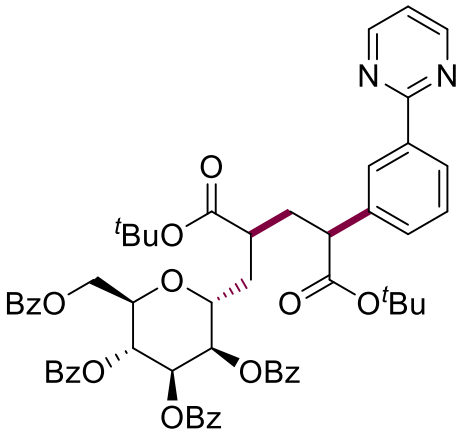
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (dd, *J* = 5.9, 4.8 Hz, 2H), 8.48 (s, 1H), 8.43 – 8.33 (m, 1H), 8.16 (td, *J* = 8.4, 1.4 Hz, 2H), 8.10 – 7.91 (m, 4H), 7.87 – 7.76 (m, 2H), 7.63 – 7.27 (m, 13H), 7.25 – 7.12 (m, 2H), 6.03 (dt, *J* = 20.5, 8.9 Hz, 1H), 5.82 (ddd, *J* = 13.6, 9.3, 3.2 Hz, 1H), 5.74 (t, *J* = 2.9 Hz, 0.44H), 5.64 (t, *J* = 3.0 Hz, 0.56H), 4.80 – 4.42 (m, 3H), 4.38 – 4.09 (m, 1H), jj3.96 (dd, *J* = 10.3, 4.1 Hz, 0.44H), 3.88 (dd, *J* = 7.9, 6.3 Hz, 0.56H), 2.98 (td, *J* = 13.2, 12.0, 6.4 Hz, 0.44H), 2.71 (ddd, *J* = 14.1, 10.3, 3.6 Hz, 0.44H), 2.59 – 2.32 (m, 0.56H), 2.20 (ddd, *J* = 14.5, 8.0, 2.8 Hz, 0.56H), 1.40 (s, 5.04H), 1.37 (s, 3.96H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.45 (C_q), 171.76 (C_q), 166.17 (C_q), 166.14 (C_q), 165.51 (C_q), 165.40 (C_q), 165.39 (C_q), 165.35 (C_q), 164.37 (C_q), 164.34 (C_q), 157.19 (CH), 157.16 (CH), 139.69 (C_q), 138.76 (C_q), 138.13 (C_q), 133.42 (CH), 133.39 (CH),

133.27 (CH), 133.23 (CH), 133.18 (CH), 132.98 (CH), 130.27 (CH), 130.05 (CH), 129.94 (C_q), 129.84 (CH), 129.82 (CH), 129.78 (CH), 129.70 (CH), 129.67 (CH), 129.58 (C_q), 129.45 (C_q) (C_q), 129.05 (CH), 129.04 (CH), 129.00 (C_q), 128.94 (C_q), 128.92 (C_q), 128.90 (C_q), 128.48 (CH), 128.42 (CH), 128.39 (CH), 128.31 (CH), 128.28 (CH), 127.93 (CH), 127.63 (CH), 127.21 (CH), 127.18 (CH), 119.18 (CH), 119.13 (CH), 81.38 (C_q), 81.25 (C_q), 74.13 (CH), 74.07(CH), 71.82 (CH), 71.69 (CH), 70.58 (CH), 70.54 (CH), 70.22 (CH), 70.02 (CH), 67.62 (CH), 67.39 (CH), 63.19 (CH_2), 63.03 (CH_2), 49.54 (CH), 48.38 (CH), 32.23 (CH_2), 31.79 (CH_2), 27.92 (CH_3), 27.86 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1719, 1555, 1452, 1412, 1263, 1147, 1108, 1069, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 885 (100) $[M+Na]^+$, 863 (45) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{51}H_{47}N_2O_{11}^+$ $[M+H]^+$ 863.3174, found 863.3170.

Di-tert-butyl 2-[3-(pyrimidin-2-yl)phenyl]-4-{[(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzoyloxy)-6-[(benzoyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]methyl}pentanedioate (163da')



^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.74 – 8.61 (m, 2H), 8.51 – 8.21 (m, 2H), 8.12 – 7.83 (m, 6H), 7.81 – 7.68 (m, 2H), 7.56 – 7.20 (m, 14H), 7.03 (dq, *J* = 12.7, 5.0 Hz, 1H), 6.05 (dt, *J* = 18.2, 9.2 Hz, 0.6H), 5.90 (dt, *J* = 16.4, 8.6 Hz, 0.4H), 5.79 – 5.41 (m, 2H), 4.74 – 4.06 (m, 4H), 3.85 – 3.54 (m, 1H), 2.66 – 2.24 (m, 2H), 2.19 – 1.87 (m, 1H), 1.82 – 1.65 (m, 1H), 1.45 (s, 5H), 1.40 (s, 3H), 1.32 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.38 (C_q), 174.25 (C_q), 173.78 (C_q), 173.68 (C_q), 172.45 (C_q), 172.35 (C_q), 172.07 (C_q), 166.14 (CH), 166.07 (CH), 166.01 (CH), 165.61(C_q), 165.60 (C_q), 165.5 (C_q), 165.44 (C_q), 165.40 (C_q), 165.38 (C_q), 165.32 (C_q), 165.29 (C_q), 165.23 (C_q), 164.44 (C_q), 164.42 (C_q), 164.40 (C_q), 164.35 (C_q), 157.14 (CH), 157.06 (CH), 139.66 (C_q), 139.41 (C_q), 138.97 (C_q), 138.83 (C_q), 138.00 (C_q),

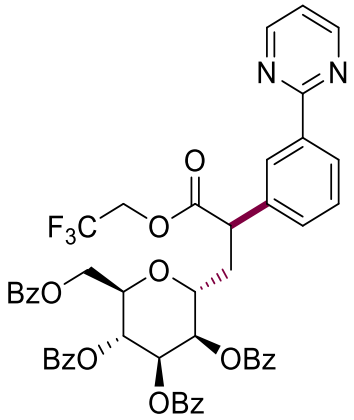
137.97 (C_q), 137.84 (C_q), 133.39 (CH), 133.33 (CH), 133.22 (CH), 132.88 (CH), 132.82 (CH), 130.51 (CH), 130.21 (CH), 129.97 (C_q), 129.95 (C_q), 129.88 (CH), 129.83 (CH), 129.78 (CH), 129.73 (CH), 129.60 (CH), 129.58 (C_q), 129.55 (C_q), 129.09 (C_q), 129.06 (C_q), 129.05 (C_q), 129.01 (C_q), 128.98 (CH), 128.95 (CH), 128.93 (CH), 128.46 (CH), 128.38 (CH), 128.33 (CH), 128.31 (CH), 128.22 (CH), 128.08 (CH), 127.84 (CH), 127.65 (CH), 127.18 (CH), 127.14 (CH), 127.12 (CH), 127.06 (CH), 119.06 (CH), 119.01 (CH), 81.26 (C_q), 81.17 (C_q), 81.13 (C_q), 81.03 (C_q), 81.00 (C_q), 75.14 (CH), 74.47 (CH), 73.19 (CH), 73.17 (CH), 73.11 (CH), 73.09 (CH), 72.09 (CH), 71.99 (CH), 71.71 (CH), 71.63 (CH), 70.52 (CH), 70.46 (CH), 70.32 (CH), 70.26 (CH), 69.97 (CH), 69.82 (CH), 67.56 (CH), 67.48 (CH), 67.04 (CH), 66.98 (CH), 62.79 (CH_2), 62.73 (CH_2), 62.66 (CH_2), 62.62 (CH_2), 62.54 (CH_2), 62.51 (CH), 50.71 (CH), 50.43 (CH), 50.35 (CH), 50.12 (CH), 42.36 (CH), 41.30 (CH), 40.43 (CH), 39.90 (CH), 36.96 (CH_2), 36.73 (CH_2), 36.30 (CH_2), 35.67 (CH_2), 31.86 (CH_2), 31.13 (CH_2), 30.86 (CH_2), 30.55 (CH_2), 29.68 (CH_2), 29.51 (CH_2), 29.27 (CH_2), 28.18 (CH_3), 28.08 (CH_3), 28.07 (CH_3), 27.92 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1719, 1555, 1452, 1412, 1368, 1264, 1146, 1108, 1027, 709 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1013 (100) $[M+Na]^+$, 991 (45) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{58}H_{59}N_2O_{13}^+$ $[M+H]^+$ 991.4012, found 991.4004.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(benzoyloxy)methyl]-6-{3-oxo-2-[3-(pyrimidin-2-yl)phenyl]-3-(2,2,2-trifluoroethoxy)propyl}tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163db)



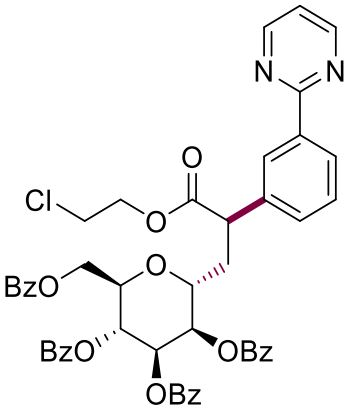
The general procedure was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 2,2,2-trifluoroethyl acrylate (**110u**) (46.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**161aa)** (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}F_3CC_6H_4)_3$

(18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 ℃. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163db** (97.7 mg, 55%, d.r. = 1.3:1) and **163db'** in 17% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (dd, *J* = 4.8, 3.7 Hz, 2H), 8.48 (d, *J* = 6.7 Hz, 1H), 8.44 – 8.36 (m, 1H), 8.14 (ddd, *J* = 7.7, 6.2, 1.4 Hz, 2H), 8.08 – 7.91 (m, 4H), 7.82 (ddd, *J* = 16.6, 8.3, 1.4 Hz, 2H), 7.66 – 7.27 (m, 14H), 7.19 (q, *J* = 4.7 Hz, 1H), 6.02 (t, *J* = 8.7 Hz, 0.52H), 5.94 (t, *J* = 8.6 Hz, 0.48H), 5.87 – 5.74 (m, 1H), 5.72 (t, *J* = 3.2 Hz, 0.48H), 5.63 (t, *J* = 3.1 Hz, 0.52H), 4.74 – 4.39 (m, 5H), 4.34 – 4.01 (m, 2H), 3.20 – 2.93 (m, 0.52H), 2.89 – 2.67 (m, 0.48H), 2.63 – 2.41 (m, 0.48H), 2.40 – 2.21 (m, 0.52H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.98 (C_q), 171.28 (C_q), 166.15 (C_q), 165.50 (C_q), 165.49 (C_q), 165.42 (C_q), 165.38 (C_q), 165.35 (C_q), 164.08 (C_q), 157.23 (CH), 157.21 (CH), 138.46 (C_q), 137.90 (C_q), 137.01 (C_q), 133.51 (CH), 133.48 (CH), 133.37 (CH), 133.33 (CH), 133.29 (CH), 133.10 (CH), 133.08 (CH), 130.38 (CH), 130.13 (CH), 129.85 (CH), 129.78 (CH), 129.75 (CH), 129.69 (CH), 129.42 (C_q), 129.36 (CH), 129.35 (CH), 129.32 (C_q), 128.94 (C_q), 128.87 (C_q), 128.85 (C_q), 128.52 (CH), 128.49 (CH), 128.44 (CH), 128.38 (CH), 128.34 (CH), 127.86 (CH), 127.81 (CH), 127.68 (CH), 127.48 (CH), 119.32 (CH), 119.28 (CH), 73.59 (CH), 73.14 (CH), 71.54 (CH), 71.32 (CH), 71.09 (CH), 70.89 (CH), 69.98 (CH), 69.74 (CH), 67.69 (CH), 67.44 (CH), 62.95 (CH_2), 62.73 (CH_2), 61.05 (CH_2), 60.96 (CH_2), 60.56 (CH_2), 60.47 (CH_2), 48.18 (CH), 46.82 (CH), 32.45 (CH_2), 32.16 (CH_2).
^{19}F NMR (282 MHz, $CDCl_3$): δ = -73.58 (t, *J* = 8.4 Hz), -73.64 (t, *J* = 8.4 Hz).

IR (ATR): $\tilde{\nu}$ = 1722, 1555, 1485, 1413, 1266, 1179, 1070, 1027, 709 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 911 (100) $[M+Na]^+$, 889 (45) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{49}H_{40}F_3N_2O_{11}^+$ $[M+H]^+$ 889.2579, found 889.2577.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(Benzoyloxy)methyl]-6-[3-(2-chloroethoxy)-3-oxo-2-[3-(pyrimidin-2-yl)phenyl]propyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (163dd)



The general procedure was followed using 2-phenylpyrimidine (**160e**) (31.2 mg, 0.20 mmol), 2-chloroethyl acrylate (**110v**) (40.2 mg, 0.30 mmol), (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(benzoyloxy)methyl]-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate **(161aa)** (263.2 mg, 0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}F_3CC_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.2 mmol) in 1,4-dioxane (2.0 mL) at 60 ℃. Purification by column chromatography on silica gel (*n*hexane/EtOAc: 10/1 to 3/1) yielded **163dd** (104.2 mg, 60%, d.r. = 1.2:1) and **163dd'** in 20% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.82 (t, *J* = 4.6 Hz, 2H), 8.52 (dd, *J* = 3.7, 1.7 Hz, 1H), 8.42 (dt, *J* = 7.4, 2.0 Hz, 1H), 8.18 (ddd, *J* = 6.9, 5.9, 1.4 Hz, 2H), 8.12 – 7.93 (m, 4H), 7.85 (ddd, *J* = 12.9, 8.3, 1.4 Hz, 2H), 7.64 – 7.30 (m, 14H), 7.22 (q, *J* = 4.9 Hz, 1H), 6.08 (t, *J* = 8.8 Hz, 0.55H), 6.00 (t, *J* = 8.9 Hz, 0.45H), 5.83 (ddd, *J* = 11.8, 9.2, 3.2 Hz, 1H), 5.76 (t, *J* = 3.0 Hz, 1H), 5.66 (t, *J* = 3.0 Hz, 1H), 4.76 – 4.47 (m, 3H), 4.45 – 4.18 (m, 3H), 4.18 – 3.94 (m, 1H), 3.78 – 3.44 (m, 2H), 3.06 (td, *J* = 13.2, 12.7, 6.9 Hz, 0.45H), 2.92 – 2.71 (m, 0.45H), 2.62 – 2.39 (m, 0.55H), 2.37 – 2.23 (m, 0.45H).

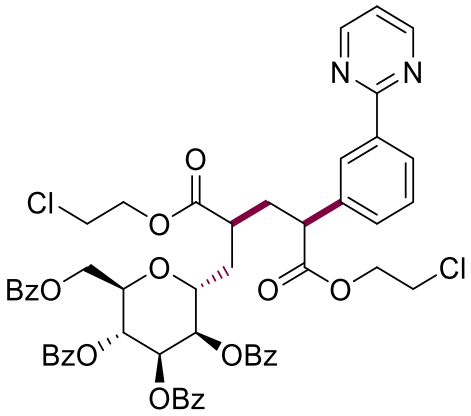
^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.01 (C_q), 172.25 (C_q), 166.15 (C_q), 165.53 (C_q), 165.51 (C_q), 165.42 (C_q), 165.40 (C_q), 165.36 (C_q), 164.20 (C_q), 157.22 (CH), 157.20 (CH), 138.64 (C_q), 138.34 (C_q), 137.76 (C_q), 133.47 (CH), 133.45 (CH), 133.33 (CH), 133.29 (CH), 133.25 (CH), 133.07 (CH), 133.04 (CH), 130.46 (CH), 130.22, 129.91 (CH), 129.85 (CH), 129.79 (CH), 129.73 (CH), 129.69 (CH), 129.50 (C_q), 129.38 (C_q), 129.25 (CH), 128.97 (C_q), 128.90 (C_q), 128.88 (CH), 128.51 (CH), 128.44 (CH), 128.35 (CH), 128.32 (CH), 127.80 (CH), 127.64 (CH), 127.61 (CH), 127.58 (CH), 119.28 (CH), 119.23 (CH), 73.99 (CH), 73.69 (CH), 71.69 (CH), 71.51 (CH), 70.82 (CH), 70.70 (CH), 70.12 (CH), 69.90 (CH), 67.64 (CH), 67.38 (CH), 64.54 (CH_2), 64.47 (CH_2), 63.11 (CH_2), 62.86 (CH_2), 48.49 (CH), 47.20 (CH), 41.19 (CH_2), 41.02 (CH_2), 32.30 (CH_2), 32.13 (CH_2).

IR (ATR): $\tilde{\nu}$ = 1721, 1555, 1452, 1412, 1265, 1109, 1093, 1069, 1027, 709 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 891 (100) $[M+Na]^+$, 869 (50) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{49}H_{42}ClN_2O_{11}^+$ $[M+H]^+$ 869.2472, found 869.2464.

Bis(2-chloroethyl) 2-[3-(pyrimidin-2-yl)phenyl]-4-{[(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzoyloxy)-6-[(benzoyloxy)methyl]tetrahydro-2*H*-pyran-2-yl]methyl}pentanedioate (163dd')



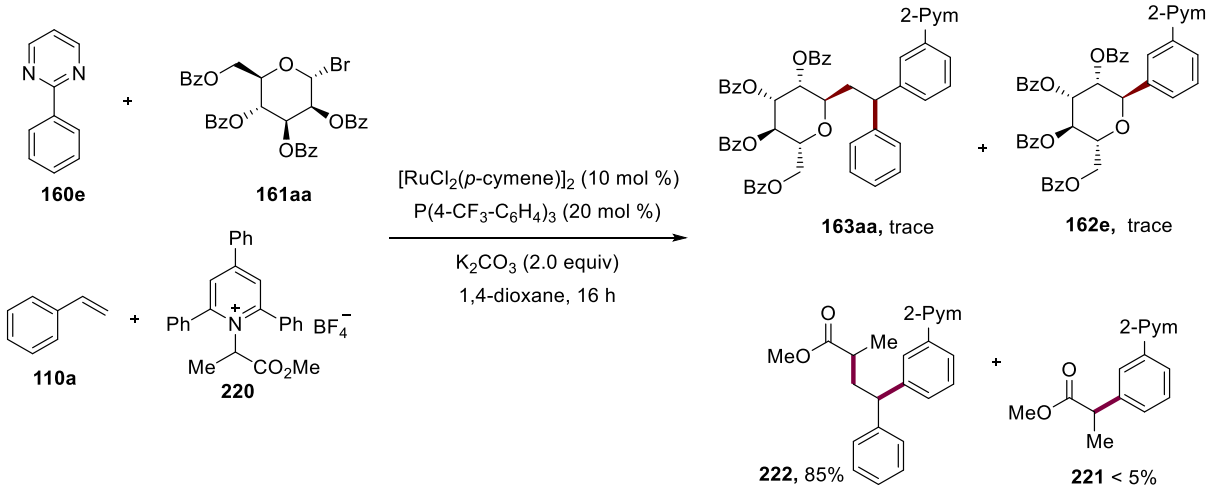
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.93 – 8.65 (m, 2H), 8.57 – 8.32 (m, 2H), 8.27 – 7.93 (m, 6H), 7.87 (dd, *J* = 7.8, 6.2 Hz, 2H), 7.65 – 7.30 (m, 14H), 7.24 – 7.09 (m, 1H), 6.14 (td, *J* = 9.4, 5.4 Hz, 0.59H), 5.96 (q, *J* = 9.1 Hz, 0.41H), 5.87 – 5.55 (m, 2H), 4.77 – 4.50 (m, 1H), 4.48 – 4.11 (m, 6H), 3.92 (ddd, *J* = 31.6, 9.8, 5.6 Hz, 1H), 3.82 – 3.52 (m, 4H), 3.01 – 2.47 (m, 3H), 2.45 – 2.14 (m, 2H), 2.08 – 1.77 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.72 (C_q), 174.68 (C_q), 173.82 (C_q), 173.71 (C_q), 172.68 (C_q), 172.47 (C_q), 166.10 (C_q), 166.08 (C_q), 166.04 (C_q), 166.02 (C_q), 165.61 (C_q), 165.60 (C_q), 165.54 (C_q), 165.49 (C_q), 165.45 (C_q), 165.42 (C_q), 165.36 (C_q), 165.33 (C_q), 165.30 (C_q), 165.27 (C_q), 164.22 (C_q), 164.20 (C_q), 164.17 (C_q), 164.14 (C_q), 157.20, 157.18, 157.15, 138.43 (C_q), 138.27 (C_q), 138.26 (C_q), 138.20 (C_q), 138.17 (C_q), 138.16 (C_q), 137.81 (C_q), 137.67 (C_q), 133.48 (CH), 133.42 (CH), 133.31 (CH), 133.29 (CH), 132.99 (CH), 132.93 (CH), 130.69 (CH), 130.37 (CH), 130.07 (CH), 130.02 (CH), 129.92 (CH), 129.89 (CH), 129.85 (CH), 129.78 (CH), 129.74 (CH), 129.44 (C_q), 129.43 (C_q), 129.38 (CH), 129.22 (CH), 129.17 (CH), 128.97 (C_q), 128.91 (C_q), 128.89 (C_q), 128.48 (CH), 128.46 (CH), 128.43 (CH), 128.39 (CH), 128.38 (CH), 128.35 (CH), 128.34 (CH), 128.23 (CH), 127.85 (CH), 127.82 (CH), 127.71 (CH), 127.65 (CH), 127.62 (CH), 127.55 (CH), 127.51 (CH), 119.22 (CH), 119.18 (CH), 74.88 (CH), 74.86 (CH), 72.82 (CH), 72.73 (CH), 71.93 (CH), 71.90 (CH), 71.43 (CH), 71.41 (CH), 70.76 (CH), 70.66 (CH), 70.47 (CH), 70.34 (CH), 70.18 (CH), 69.81 (CH), 69.73

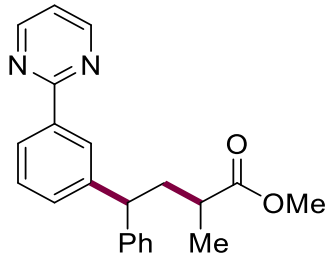
(CH), 67.59 (CH), 67.44 (CH), 67.00 (CH), 66.82 (CH), 64.52 (CH_2), 64.46 (CH_2), 64.42 (CH_2), 64.39 (CH_2), 64.36 (CH_2), 64.34 (CH_2), 62.78 (CH_2), 62.58 (CH_2), 62.40 (CH_2), 62.24 (CH_2), 49.28 (CH), 49.25 (CH), 48.87 (CH), 41.73 (CH), 41.58 (CH_2), 41.51 (CH_2), 41.46 (CH_2), 41.43 (CH_2), 41.26 (CH_2), 41.22 (CH_2), 41.20 (CH_2), 41.16 (CH_2), 40.82 (CH), 39.43 (CH), 38.84 (CH), 36.30 (CH_2), 36.10 (CH_2), 35.67 (CH_2), 35.51 (CH_2), 31.32 (CH_2), 31.28 (CH_2), 31.24 (CH_2), 31.03 (CH_2).

IR (ATR): $\tilde{\nu}$ = 1722, 1558, 1542, 1412, 1266, 1108, 1098, 1070, 1024, 710 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 1025 (100) $[M+Na]^+$, 1003 (40) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{54}H_{49}Cl_2N_2O_{13}^+$ $[M+H]^+$ 1003.2606, found 1003.2606.

5.3.4.2 Mechanism Studies



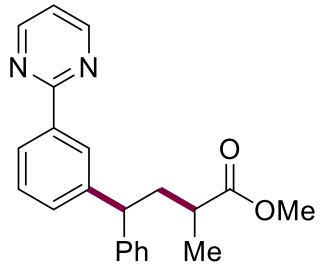
Phenyl pyrimidine **160e** (0.20 mmol), styrene **110a** (0.30 mmol), glycoside bromide **161aa** (0.40 mmol), Katritzky salt **220** (0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product **222** in 85% yield. It was found that the desired glycosylation product **163aa** and direct two-component glycosylation byproduct **162e** were not isolated, indicating that the Katritzky salt is much reactive that the glycosyl bromide as SET radical precursor under ruthenium catalysis.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 4.8 Hz, 2H), 8.40 (s, 1H), 8.30 (d, *J* = 7.4 Hz, 1H), 7.49 – 7.35 (m, 2H), 7.31 (dd, *J* = 8.7, 4.4 Hz, 4H), 7.20 (t, *J* = 4.8 Hz, 2H), 4.13 (td, *J* = 8.0, 3.3 Hz, 1H), 3.65 (s, 3H), 2.62 (dt, *J* = 14.0, 7.8 Hz, 1H), 2.43 (h, *J* = 6.9 Hz, 1H), 2.19 (dt, *J* = 14.0, 7.2 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 3H).

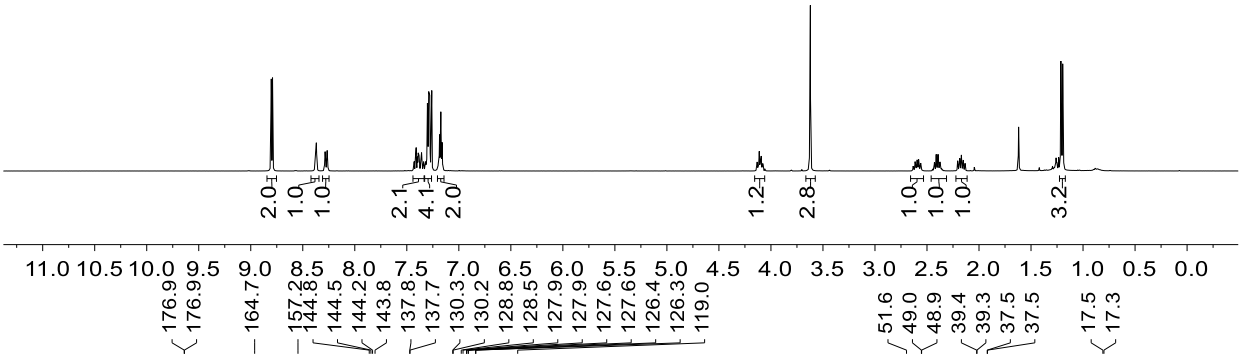
^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.9 (C_q), 176.9 (C_q), 164.7 (C_q), 157.2 (CH), 144.8 (C_q), 144.5 (C_q), 144.2 (C_q), 143.8 (C_q), 137.8 (C_q), 137.7 (C_q), 130.3 (CH), 130.2 (CH), 128.8 (CH), 128.5 (CH), 127.9 (CH), 127.9 (CH), 127.6 (CH), 127.6 (CH), 126.4 (CH), 126.3 (CH), 119.0 (CH), 51.6 (CH_3), 49.0 (CH), 49.0 (CH), 39.4 (CH_2), 39.3 (CH_2), 37.6 (CH), 37.5 (CH), 17.5 (CH_3), 17.3 (CH_3).

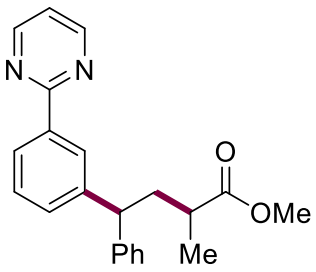
MS (ESI) *m*/*z* (relative intensity): 369 (100) $[M+Na]^+$, 347 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{22}H_{22}N_2NaO_2^+$ $[M+Na]^+$ 369.1573, found 369.1576.



225

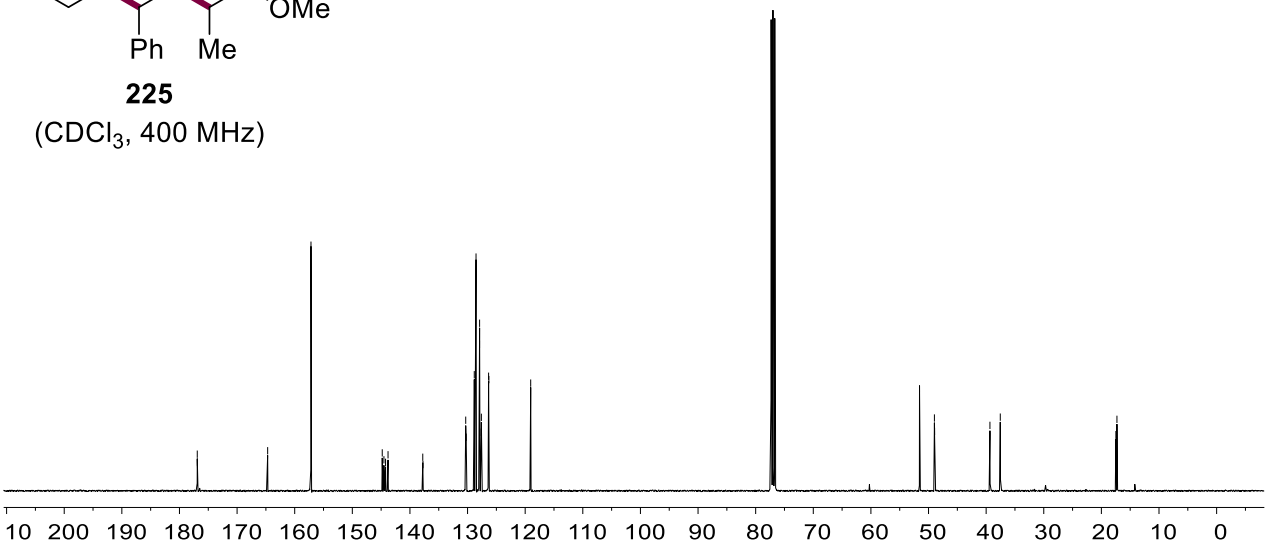
($CDCl_3$, 400 MHz)

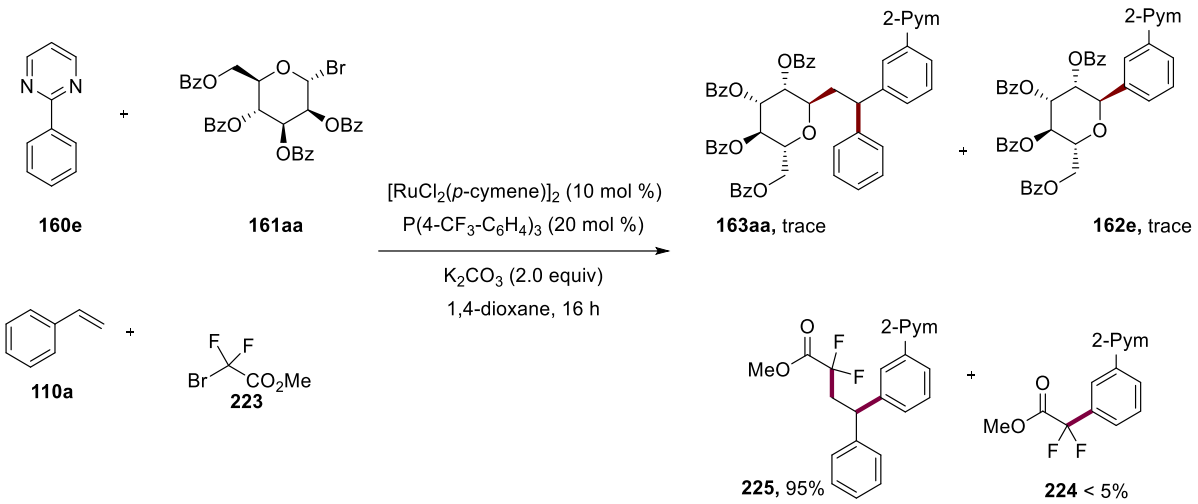




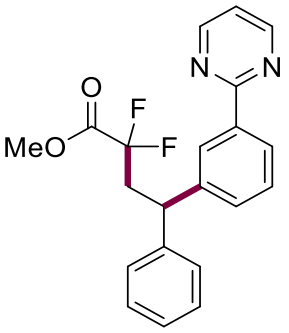
225

($CDCl_3$, 400 MHz)





Phenyl pyrimidine **160e** (0.20 mmol), styrene **110a** (0.30 mmol), glycoside bromide **161aa** (0.40 mmol), methyl 2-bromo-2,2-difluoroacetate **223** (0.4 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (12.2 mg, 10.0 mol %), P(4-CF_3-C_6H_4)$_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product **225** in 95% yield. It was found that the desired glycosylation product **162e** and direct two-component glycosylation byproduct **163aa** were not isolated, indicating that the methyl 2-bromo-2,2-difluoroacetate is much more reactive.



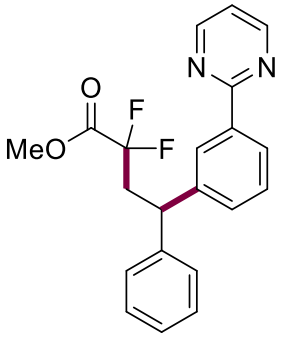
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 4.8 Hz, 2H), 8.41 (s, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.25 (m, 4H), 7.28–7.19 (m, 2H), 4.40 (t, *J* = 7.4 Hz, 1H), 3.43 (s, 3H), 3.03 (td, *J* = 15.4, 7.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.4 (C_q), 164.1 (C_q, d, *J* = 32.6 Hz), 157.2 (CH), 143.3 (C_q), 142.6 (C_q), 137.9 (C_q), 130.2 (CH), 128.9 (CH), 128.6 (CH), 127.8 (CH),

127.2 (CH), 126.8 (CH), 126.7 (CH), 119.2 (CH), 115.7 (C_q, t, J = 250.6 Hz), 52.9 (CH_3), 44.9 (CH, t, J = 4.8 Hz), 40.2 (CH_2, t, J = 23.3 Hz).

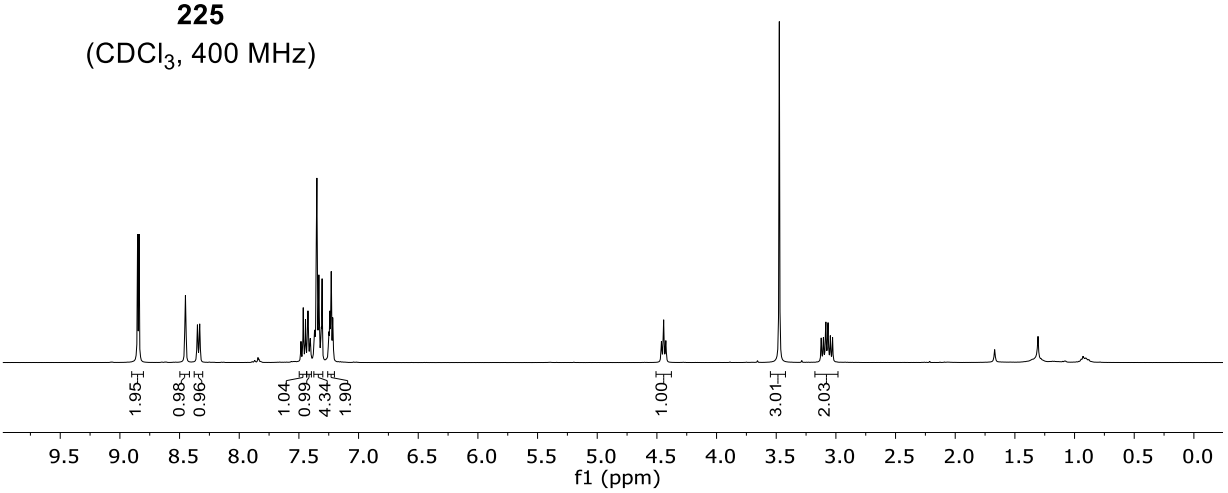
MS (ESI) *m*/*z* (relative intensity): 391 (100) $[M+Na]^+$, 369 (10) $[M+H]^+$.

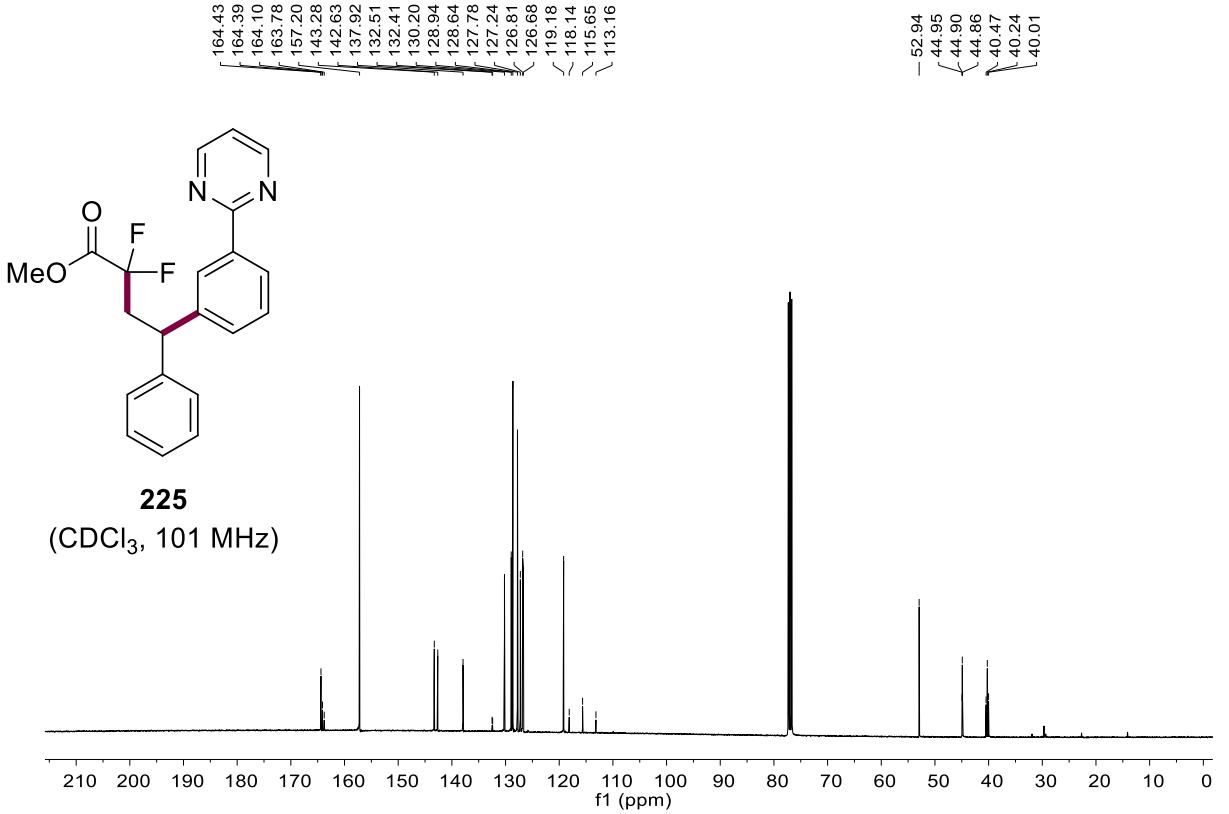
HR-MS (ESI): *m*/*z* calcd for $C_{21}H_{18}F_2N_2NaO_2^+$ $[M+Na]^+$ 391.1229, found 391.1228.

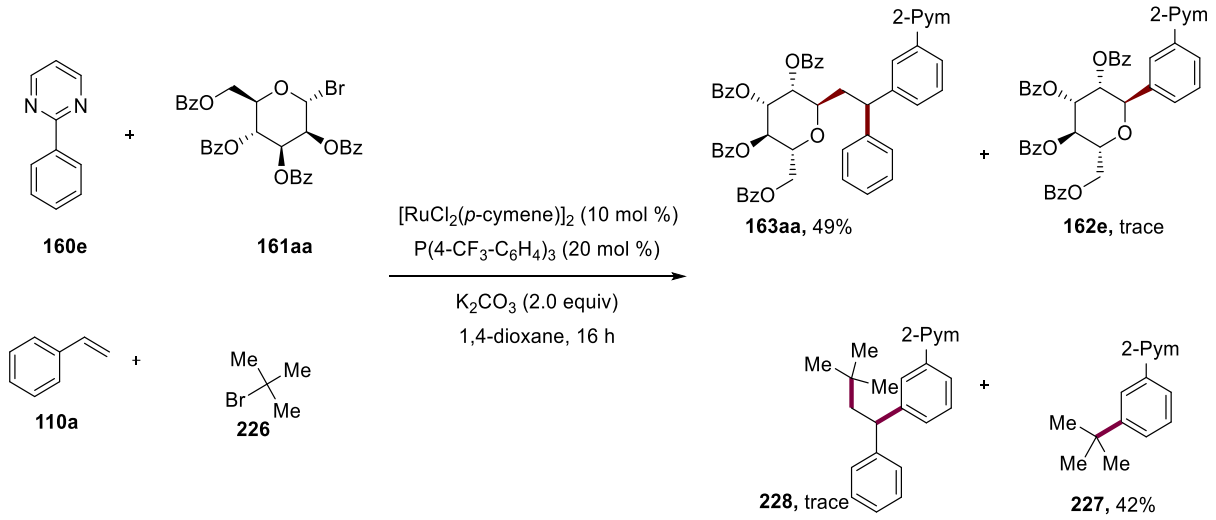


225

($CDCl_3$, 400 MHz)



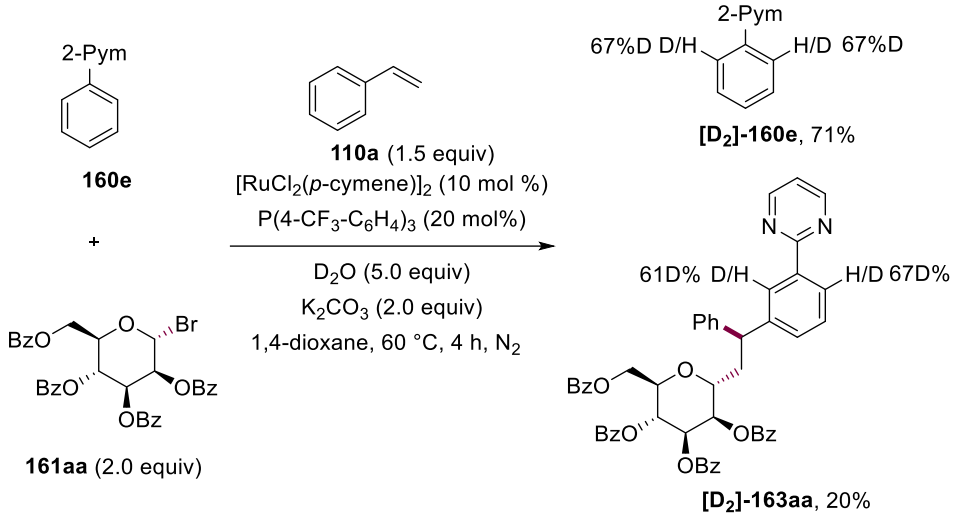




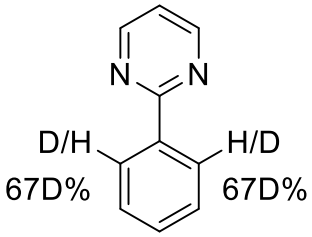
Phenyl pyrimidine **160e** (0.20 mmol), styrene **110a** (0.30 mmol), glycoside bromide **161aa** (0.40 mmol), *tert*-butyl bromide (0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $(4\text{-}CF_3\text{-}C_6H_4)_3P$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and stirred at 60 °C for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product **227** in **42%** yield and **163aa** in 49% yield. It was found that **228** and direct two-component glycosylation byproduct **162e** were not isolated, indicating

that the tert-butyl bromide is much less reactive than Katritzky salt **220** and methyl 2-bromo-2,2-difluoroacetate **223**.

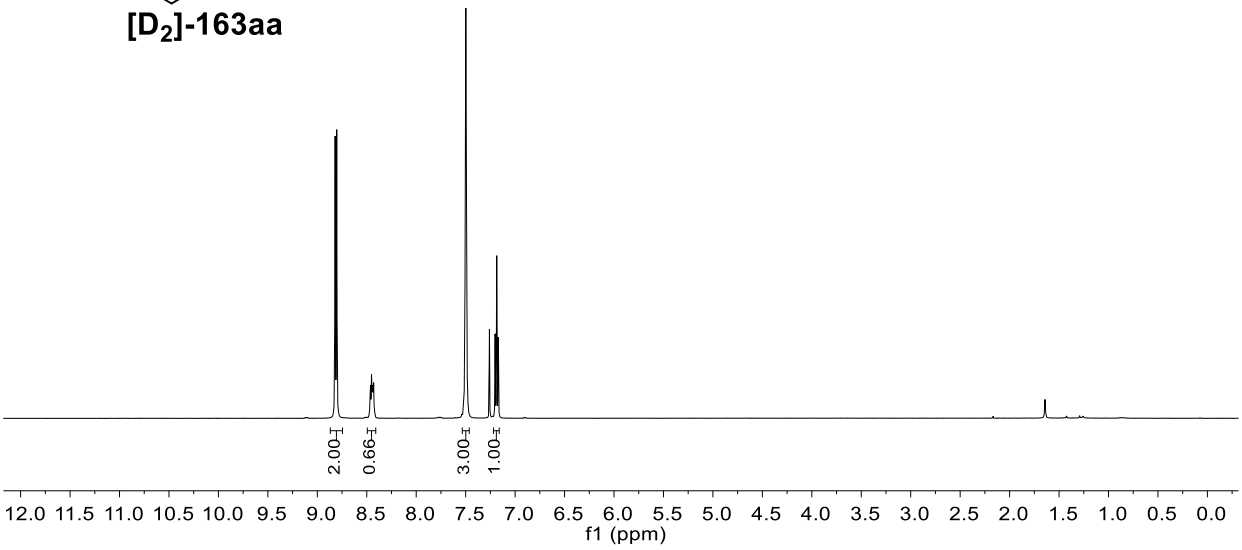
Deuterium labelling experiment

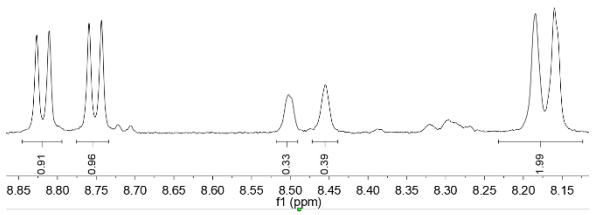


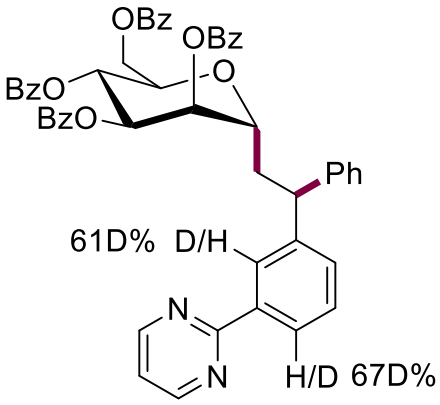
Phenyl pyrimidine **160e** (0.20 mmol), styrene **110a** (0.30 mmol), glycoside bromide **161aa** (0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}F_3CC_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.4 mmol), D_2O (2.0 equiv) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and heated at 60 ℃ for 4 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the multicomponent reaction product **[D₂]-163aa** in 20% yield with 61D%/67D% and recovered phenyl pyrimidine **[D₂]-160e** in 71% yields with 67D%.



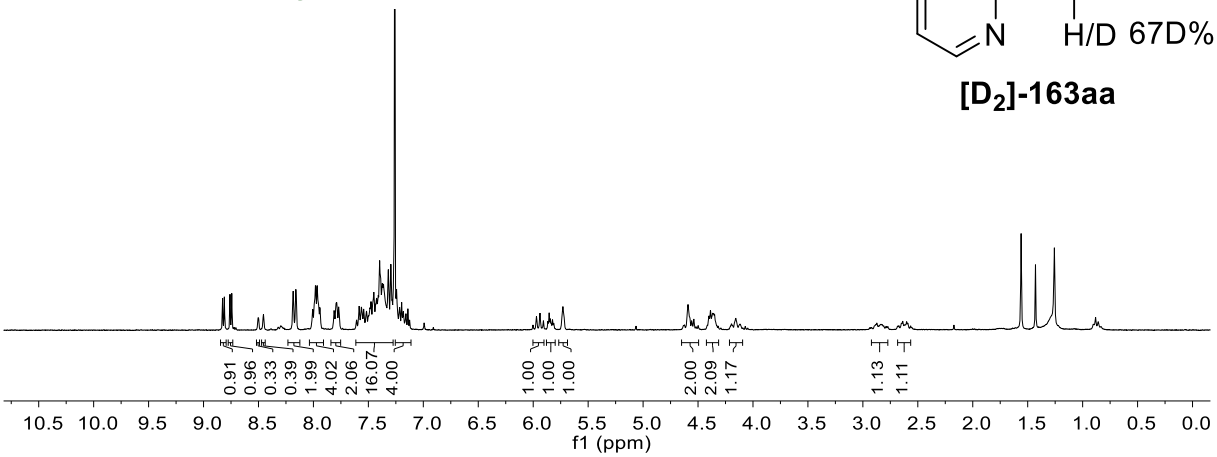
[D_2]-163aa

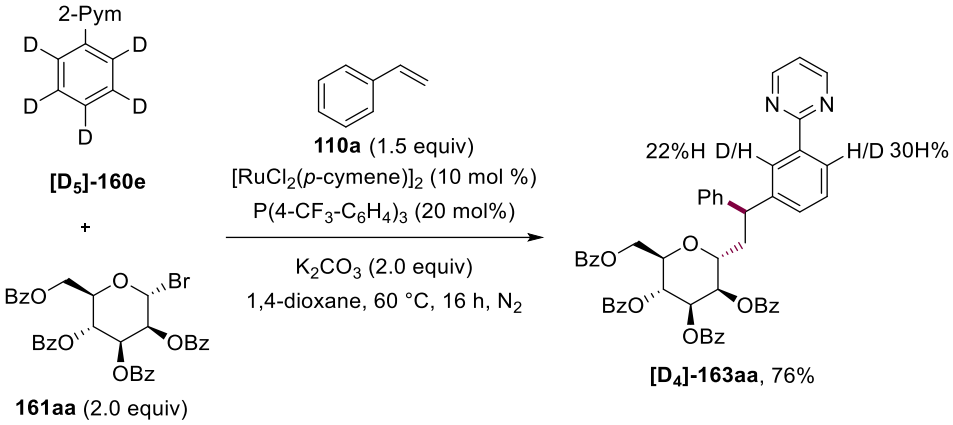




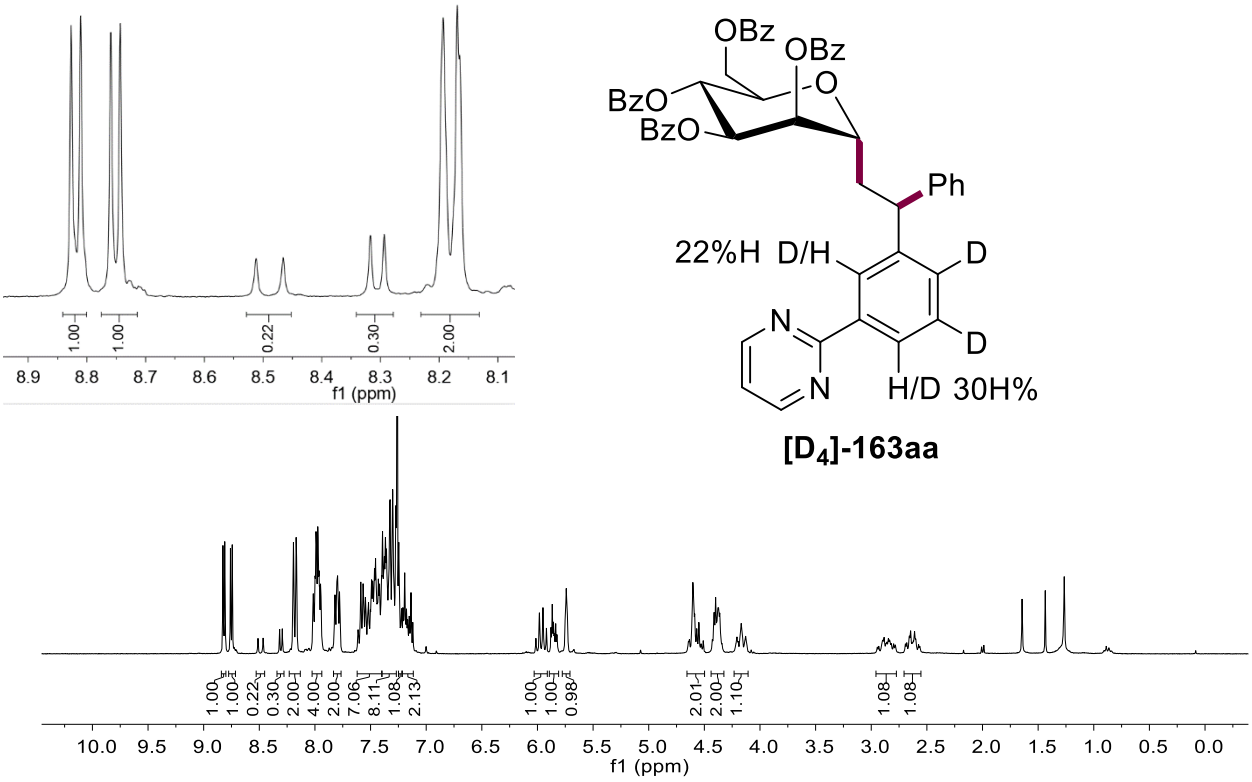


[D_2]-163aa

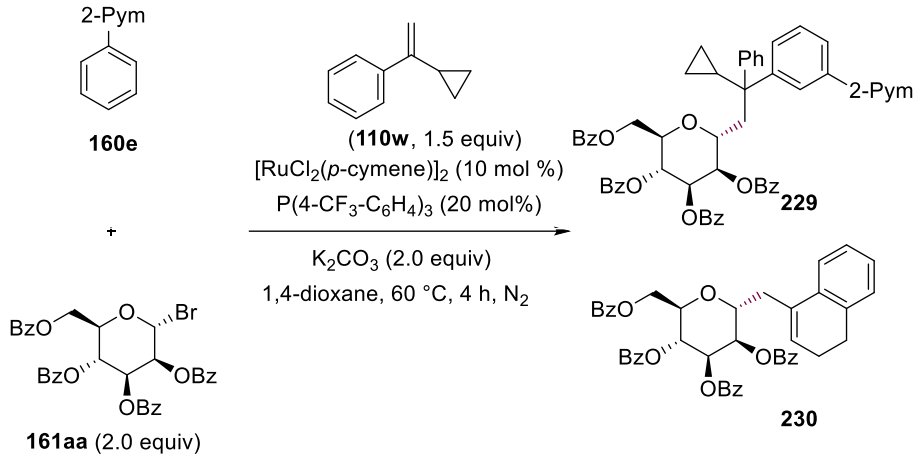




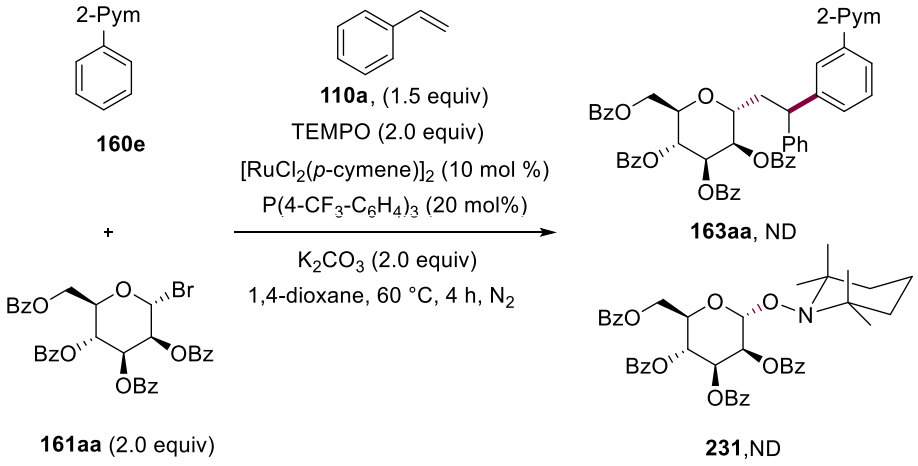
Phenyl pyrimidine **[D$_5$]-160e** (0.20 mmol), styrene **110a** (0.30 mmol), glycoside bromide **161aa** (0.40 mmol), [RuCl$_2$(*p*-cymene)]$_2$ (12.2 mg, 10.0 mol %), P(4-F$_3$CC$_6$H$_4$)$_3$ (18.6 mg, 20 mol %), K$_2$CO$_3$ (55.2 mg, 0.4 mmol), were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N$_2$ three time. Then, 1,4-dioxane (2.0 mL) was added and heated at 60 ℃ for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH$_2$Cl$_2$ and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the multicomponent reaction product **[D$_4$]-163aa** in 76% yield with 22H%/30H%.



Radical Trapping experiments

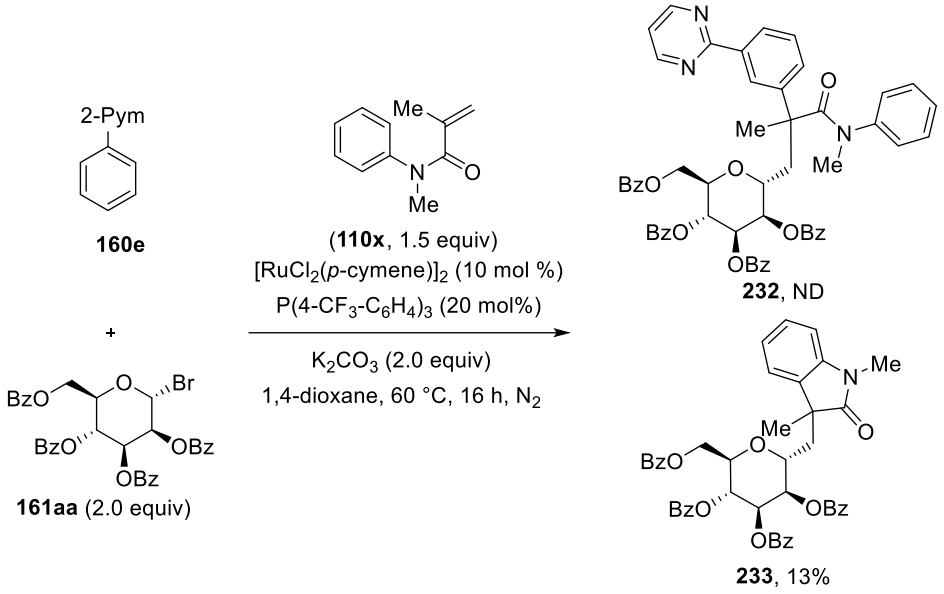


Phenyl pyrimidine **160e** (0.20 mmol), (1-cyclopropylvinyl)benzene (**110w**, 0.30 mmol), glycoside bromide **161aa** (0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}F_3CC_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.4 mmol), were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and heated at 60 ℃ for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. The multicomponent reaction product **229** was not formed and the glycosyl anomeric radical was not trapped (**230**).



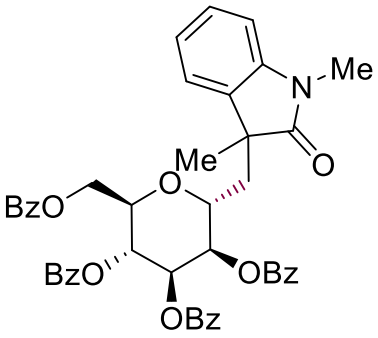
Phenyl pyrimidine **160e** (0.20 mmol), styrene **110a** (0.30 mmol), glycoside bromide **161aa** (0.40 mmol), TEMPO (2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}F_3CC_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.4 mmol), were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and heated at 60 ℃ for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and

concentrated *in vacuo*. The multicomponent reaction product **163aa** was not formed and the glycosyl anomeric radical was also not trapped by TEMPO (**231**).



Phenyl pyrimidine **160e** (0.20 mmol), *N*-methyl-*N*-phenylmethacrylamide **110x** (0.30 mmol), glycoside bromide **161aa** (0.40 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10.0 mol %), $P(4\text{-}F_3CC_6H_4)_3$ (18.6 mg, 20 mol %), K_2CO_3 (55.2 mg, 0.4 mmol), were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three time. Then, 1,4-dioxane (2.0 mL) was added and heated at 60 ℃ for 16 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded **233** in 13% yield. The multicomponent reaction product **232** was not formed.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-[(benzoyloxy)methyl]-6-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (233)



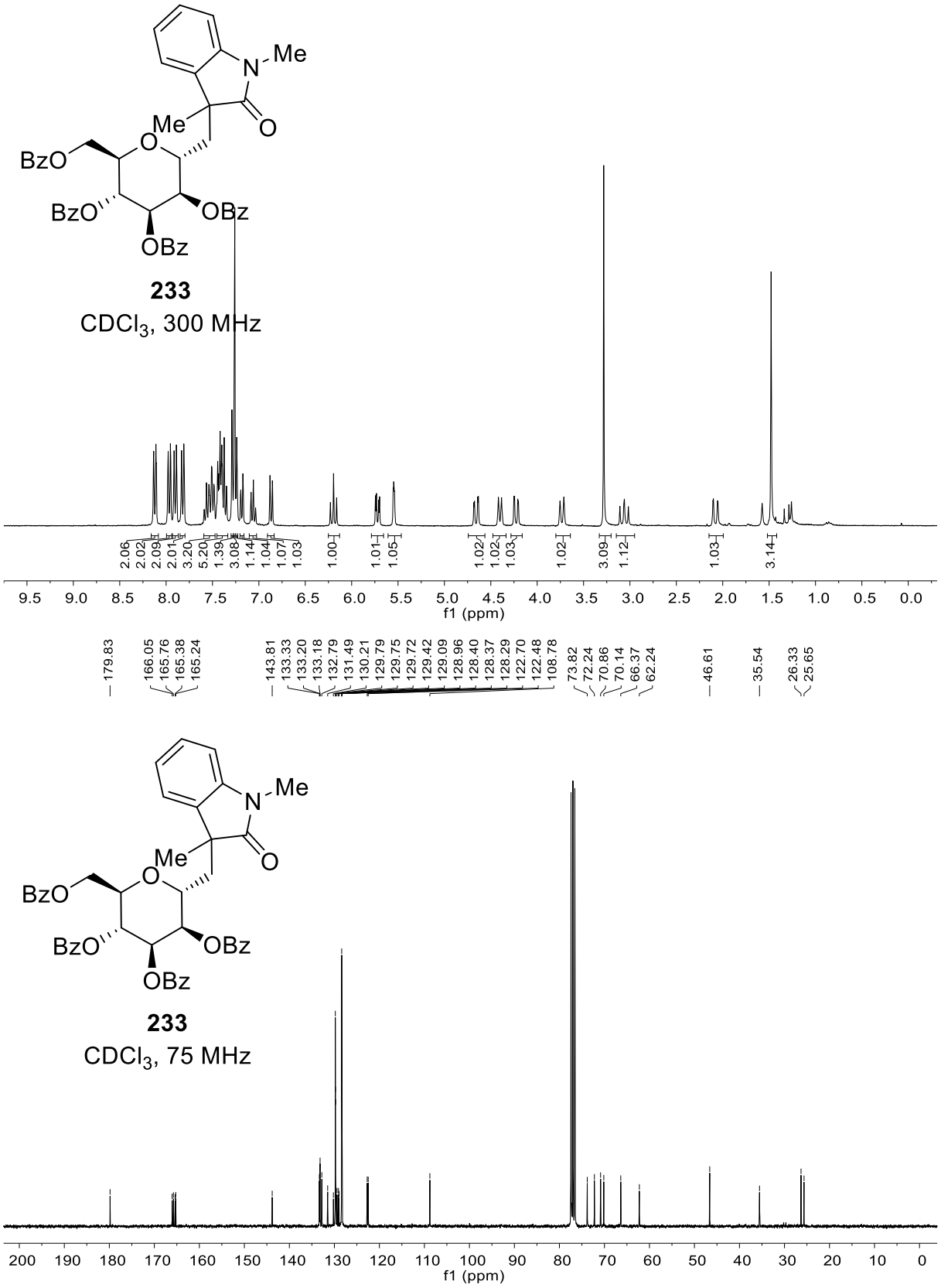
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 – 8.10 (m, 2H), 8.02 – 7.94 (m, 2H), 7.94 – 7.88 (m, 2H), 7.86 – 7.76 (m, 2H), 7.64 – 7.47 (m, 3H), 7.46 – 7.34 (m, 5H), 7.29 (d, *J* = 1.6 Hz, 1H), 7.28 – 7.25 (m, 3H), 7.24 (t, *J* = 1.7 Hz, 1H), 7.18 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.20 (t, *J* = 10.1 Hz, 1H), 5.72 (dd, *J* = 10.2, 3.1 Hz, 1H), 5.54 (dd, *J* = 3.1, 1.7 Hz, 1H), 4.66 (dd, *J* = 12.5, 2.3 Hz, 1H), 4.40 (d, *J* = 10.0 Hz, 1H), 4.23 (dd, *J* = 12.5, 2.2 Hz, 1H), 3.73 (d, *J* = 12.4 Hz, 1H), 3.28 (s, 3H), 3.06 (dd, *J* = 14.6, 12.7 Hz, 1H), 2.08 (dd, *J* = 14.6, 2.0 Hz, 1H), 1.48 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 179.83 (C_q), 166.05 (C_q), 165.76 (C_q), 165.38 (C_q), 165.24 (C_q), 143.81 (C_q), 133.33 (CH), 133.20 (CH), 133.18 (CH), 132.79 (CH), 131.49 (C_q), 130.21 (C_q), 129.79 (CH), 129.75 (CH), 129.72 (CH), 129.42 (C_q), 129.09 (C_q), 128.96 (C_q), 128.40 (CH), 128.37 (CH), 128.29 (CH), 122.70 (CH), 122.48 (CH), 108.78 (CH), 73.82 (CH), 72.24 (CH), 70.86 (CH), 70.14 (CH), 66.37 (CH), 62.24 (CH_2), 46.61 (C_q), 35.54 (CH_2), 26.33 (CH_3), 25.65 (CH_3).

IR (ATR): $\tilde{\nu}$ = 1698, 1653, 1558, 1457, 1358, 1093, 902, 708, 649 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 776 (100) $[M+Na]^+$, 754 (10) $[M+H]^+$.

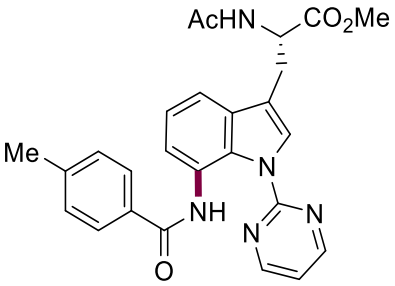
HR-MS (ESI): *m*/*z* calcd for $C_{45}H_{39}NNaO_{10}^+$ $[M+Na]^+$ 776.2466, found 776.2461.



5.3.5 Rhodium-Catalyzed Tryptophan *C*(7) Amdiation.

5.3.5.1 Characterization Data

Methyl (*S*)-2-acetamido-3-[7-(4-methylbenzamido)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]propanoate (166aa)



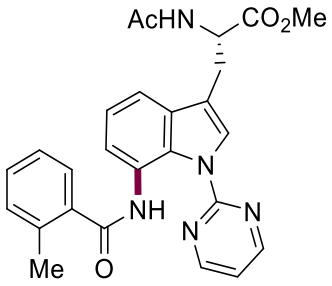
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**165aa**) (71 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 3:1 to 1:5) yielded **166aa** (62 mg, 66%) as an orange solid (M.p.: 145─146 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.89 (s, 1H), 8.50 (d, *J* = 4.9 Hz, 2H), 8.31 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.10 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.34–7.27 (m, 4H), 6.99 (t, *J* = 4.9 Hz, 1H), 6.15 (d, *J* = 7.7 Hz, 1H), 4.97 (dt, *J* = 7.7, 5.5 Hz, 1H), 3.71 (s, 3H), 3.32 (dd, *J* = 14.7, 5.5 Hz, 1H), 3.24 (dd, *J* = 14.7, 5.5 Hz, 1H), 2.43 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.8 (C_q), 166.4 (C_q), 158.1 (CH), 156.7 (C_q), 141.8 (C_q), 134.1 (C_q), 134.1 (C_q), 129.2 (CH), 127.4 (CH), 127.0 (CH), 126.5 (C_q), 126.2 (C_q), 123.4 (CH), 118.8 (CH), 116.2 (CH), 115.5 (C_q), 114.7 (CH), 52.6 (CH), 52.5 (CH_3), 27.2 (CH_2), 23.2 (CH_3), 21.5 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3052, 1742, 1671, 1566, 1492, 1421, 1370, 1265, 1220, 736, 704 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 494 (60) $[M+Na]^+$, 472 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{26}H_{26}N_5O_4^+$ $[M+H]^+$ 472.1979, found 472.1971.

Methyl (*S*)-2-acetamido-3-[7-(2-methylbenzamido)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]propanoate (166ab)



The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-(*o*-tolyl)-1,4,2-dioxazol-5-one (**165ab**) (71 mg, 0.4 mmol). After 24 h,

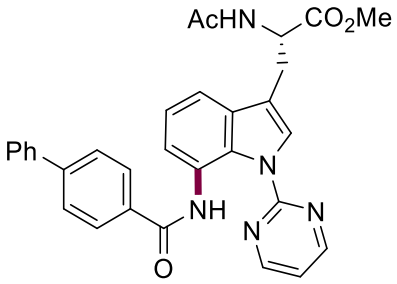
purification by column chromatography (*n*-hexane/EtOAc 3:1 to 0:100) yielded **166ab** (59 mg, 63%) as a white solid (M.p.: 184─185 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.20 (s, 1H), 8.53 (d, *J* = 7.5 Hz, 1H), 8.20 (d, *J* = 4.9 Hz, 2H), 8.12 (s, 1H), 7.53 (d, *J* = 7.1 Hz, 1H), 7.39–7.30 (m, 2H), 7.29–7.26 (m, 3H), 6.91 (t, *J* = 4.9 Hz, 1H), 6.11 (d, *J* = 7.7 Hz, 1H), 4.97 (dt, *J* = 7.7, 5.4 Hz, 1H), 3.72 (s, 3H), 3.33 (dd, *J* = 14.8, 5.4 Hz, 1H), 3.25 (dd, *J* = 14.8, 5.4 Hz, 1H), 2.48 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.7 (C_q), 167.8 (C_q), 157.9 (CH), 156.5 (C_q), 137.9 (C_q), 136.6 (C_q), 134.1 (C_q), 131.1 (CH), 129.8 (CH), 126.8 (CH), 126.8 (CH), 125.8 (2 × C_q), 125.5 (CH), 123.6 (CH), 117.5 (CH), 116.2 (CH), 115.5 (C_q), 114.7 (CH), 52.6 (CH), 52.5 (CH_3), 27.3 (CH_2), 23.2 (CH_3), 19.8 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3053, 1743, 1579, 1422, 1371, 1334, 1215, 800, 739, 703 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 494 (100) $[M+Na]^+$, 472 (30) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{26}H_{26}N_5O_4^+$ $[M+H]^+$ 472.1979, found 472.1977.

Methyl (*S*)-3-[7-([1,1'-biphenyl]-4-carboxamido)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]-2-acetamidopropanoate (166ac)



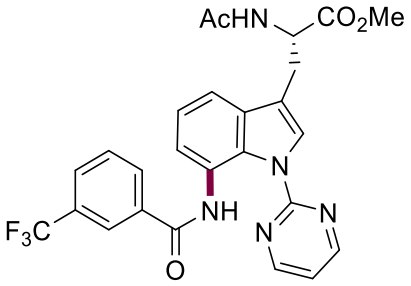
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-([1,1'-biphenyl]-4-yl)-1,4,2-dioxazol-5-one (**165ac**) (96 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 3:1 to 0:100) yielded **166ac** (83 mg, 78%) as an orange solid (M.p.: 174─175 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.04 (s, 1H), 8.49 (d, *J* = 4.7 Hz, 2H), 8.35 (d, *J* = 7.3 Hz, 1H), 8.11 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.45–7.38 (m, 1H), 7.34–7.27 (m, 2H), 6.97 (t, *J* = 4.7 Hz, 1H), 6.23 (d, *J* = 7.2 Hz, 1H), 4.97 (dt, *J* = 7.2, 5.4 Hz, 1H), 3.72 (s, 3H), 3.31 (dd, *J* = 14.8, 5.4 Hz, 1H), 3.23 (dd, *J* = 14.8, 5.4 Hz, 1H), 1.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.8 (C_q), 166.1 (C_q), 158.1 (CH), 156.7 (C_q), 144.2 (C_q), 139.9 (C_q), 135.6 (C_q), 134.1 (C_q), 128.9 (CH), 128.0 (CH), 128.0 (CH), 127.1 (CH), 127.1 (CH), 127.0 (CH), 126.4 (C_q), 126.2 (C_q), 123.4 (CH), 118.7 (CH), 116.2 (CH), 115.6 (C_q), 114.9 (CH), 52.6 (CH), 52.4 (CH_3), 27.2 (CH_2), 23.2 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3052, 1740, 1667, 1580, 1421, 1265, 744, 700 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 556 (100) $[M+Na]^+$, 534 (25) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{28}N_5O_4^+$ $[M+H]^+$ 534.2136, found 534.2127.

Methyl (*S*)-2-acetamido-3-{1-(pyrimidin-2-yl)-7-[4-(trifluoromethyl)benzamido]-1*H*-indol-3-yl}propanoate (166ad)



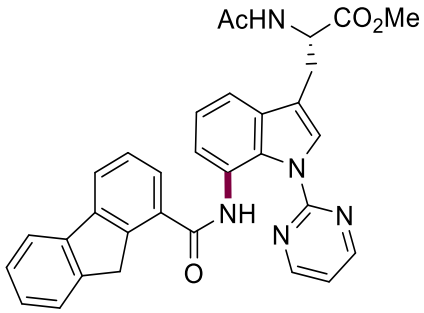
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-[3-(trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (**165ad**) (92 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 0:100) yielded **166ad** (89 mg, 85%) as a white solid (M.p.: 200─202 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.02 (s, 1H), 8.45 (d, *J* = 4.9 Hz, 2H), 8.27 (dd, *J* = 5.9, 3.1 Hz, 1H), 8.13–8.07 (m, 3H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.33–7.26 (m, 2H), 6.98 (t, *J* = 4.9 Hz, 1H), 6.18 (d, *J* = 7.7 Hz, 1H), 4.94 (dt, *J* = 7.7, 5.5 Hz, 1H), 3.69 (s, 3H), 3.29 (ddd, *J* = 14.8, 5.5, 0.9 Hz, 1H), 3.21 (ddd, *J* = 14.8, 5.5, 0.9 Hz, 1H), 1.96 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0 (C_q), 169.8 (C_q), 164.7 (C_q), 158.0 (CH), 156.7 (C_q), 137.7 (C_q), 134.2 (C_q), 131.2 (CH), 130.8 (q, $^2J_{C–F}$ = 32.6 Hz, C_q), 129.3 (CH), 127.9 (q, $^3J_{C–F}$ = 3.6 Hz, CH), 127.1 (CH), 126.2 (C_q), 125.9 (C_q), 123.8 (q, $^3J_{C–F}$ = 3.7 Hz, CH), 123.4 (CH), 122.4 (q, $^1J_{C–F}$ = 272.5 Hz, C_q), 118.8 (CH), 116.3 (CH), 115.7 (C_q), 115.3 (CH), 52.6 (CH), 52.4 (CH_3), 27.3 (CH_2), 23.1 (CH_3).
^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.4 (s).

IR (ATR): $\tilde{\nu}$ = 3054, 1745, 1566, 1421, 1332, 1249, 1126, 738, 701, 673 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 548 (100) $[M+Na]^+$, 526 (15) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{26}H_{22}F_3N_5NaO_4^+$ $[M+Na]^+$ 548.1516, found 548.1517.

Methyl (*S*)-3-[7-(9*H*-fluorene-1-carboxamido)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]-2-acetamidopropanoate (166ae)



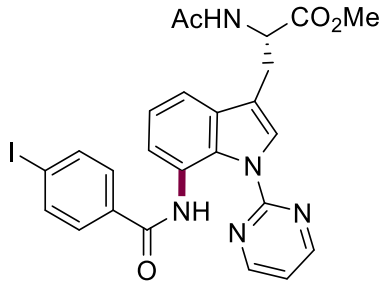
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-(9*H*-fluoren-1-yl)-1,4,2-dioxazol-5-one (**165ae**) (100 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 3:1 to 0:100) yielded **166ae** (43 mg, 39%) as a white solid (M.p.: 250─252 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.14 (s, 1H), 8.39 (d, *J* = 7.5 Hz, 1H), 8.33 (d, *J* = 4.9 Hz, 2H), 8.10 (s, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.56–7.48 (m, 2H), 7.40–7.27 (m, 4H), 6.88 (t, *J* = 4.9 Hz, 1H), 6.08 (d, *J* = 7.7 Hz, 1H), 4.97 (dt, *J* = 7.7, 5.5 Hz, 1H), 4.24 (s, 2H), 3.71 (s, 3H), 3.33 (dd, *J* = 14.8, 5.5 Hz, 1H), 3.24 (dd, *J* = 14.8, 5.5 Hz, 1H), 1.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.7 (C_q), 166.8 (C_q), 158.0 (CH), 156.6 (C_q), 143.9 (C_q), 143.4 (C_q), 143.3 (C_q), 140.4 (C_q), 134.2 (C_q), 133.8 (C_q), 127.4 (CH), 127.0 (CH), 126.9 (CH), 126.7 (CH), 126.4 (C_q), 126.2 (C_q), 125.1 (CH), 124.7 (CH), 123.5 (CH), 122.2 (CH), 119.9 (CH), 118.5 (CH), 116.2 (CH), 115.5 (C_q), 114.9 (CH), 52.6 (CH), 52.5 (CH_3), 37.4 (CH_2), 27.3 (CH_2), 23.2 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3055, 1746, 1667, 1584, 1526, 1422, 1371, 1265, 741, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 568 (100) $[M+Na]^+$, 546 (20) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{32}H_{28}N_5O_4^+$ $[M+H]^+$ 546.2136, found 546.2130.

Methyl (*S*)-2-acetamido-3-[7-(4-iodobenzamido)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]propanoate (166af)



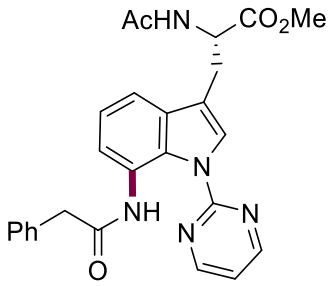
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-(4-iodophenyl)-1,4,2-dioxazol-5-one (**165af**) (116 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 1:5) yielded **166af** (110 mg, 94%) as an orange solid (M.p.: 145─147 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.05 (s, 1H), 8.50 (d, *J* = 4.8 Hz, 2H), 8.29 (d, *J* = 6.4 Hz, 1H), 8.12 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.37–7.27 (m, 2H), 7.04 (t, *J* = 4.8 Hz, 1H), 6.11 (d, *J* = 7.7 Hz, 1H), 4.97 (dt, *J* = 7.7, 5.5 Hz, 1H), 3.72 (s, 3H), 3.33 (dd, *J* = 14.8, 5.5 Hz, 1H), 3.24 (dd, *J* = 14.8, 5.5 Hz, 1H), 1.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.8 (C_q), 165.6 (C_q), 158.1 (CH), 156.7 (C_q), 137.7 (CH), 136.4 (C_q), 134.2 (C_q), 129.1 (CH), 127.1 (CH), 126.2 (C_q), 126.1 (C_q), 123.5 (CH), 118.7 (CH), 116.3 (CH), 115.7 (C_q), 115.1 (CH), 98.3 (C_q), 52.6 (CH), 52.5 (CH_3), 27.3 (CH_2), 23.2 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3053, 1741, 1665, 1583, 1421, 1370, 1265, 1007, 738, 704 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 606 (100) $[M+Na]^+$, 584 (20) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{25}H_{23}IN_5O_4^+$ $[M+H]^+$ 584.0789, found 584.0791.

Methyl (*S*)-2-acetamido-3-[7-(2-phenylacetamido)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]propanoate (166ag)



The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-benzyl-1,4,2-dioxazol-5-one (**165ag**) (71 mg, 0.4 mmol). After 24 h,

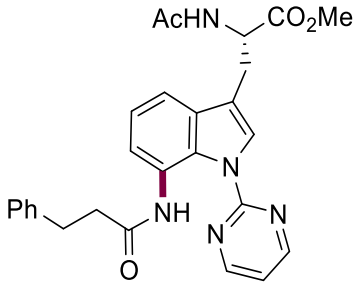
purification by column chromatography (*n*-hexane/EtOAc 3:1 to 1:5) yielded **166ag** (70 mg, 74%) as an orange solid (M.p.: 183─184 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.88 (s, 1H), 8.39 (d, *J* = 4.8 Hz, 2H), 8.17 (dd, *J* = 6.0, 2.5 Hz, 1H), 8.03 (s, 1H), 7.32–7.26 (m, 7H), 6.97 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 7.7 Hz, 1H), 4.96 (dt, *J* = 7.7, 5.5 Hz, 1H), 3.72 (s, 2H), 3.71 (s, 3H), 3.31 (dd, *J* = 14.9, 5.5 Hz, 1H), 3.23 (dd, *J* = 14.9, 5.5 Hz, 1H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.8 (C_q), 168.8 (C_q), 157.9 (CH), 156.7 (C_q), 135.1 (C_q), 133.9 (C_q), 129.1 (CH), 128.7 (CH), 127.2 (CH), 127.1 (CH), 126.2 (C_q), 126.0 (C_q), 123.4 (CH), 119.1 (CH), 116.2 (CH), 115.6 (C_q), 115.0 (CH), 52.6 (CH), 52.5 (CH_3), 45.4 (CH_2), 27.2 (CH_2), 23.2 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3053, 1743, 1668, 1566, 1422, 1370, 1265, 1212, 896, 736 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 494 (60) $[M+Na]^+$, 472 (100) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{26}H_{26}N_5O_4^+$ $[M+H]^+$ 472.1979, found 472.1977.

Methyl (*S*)-2-acetamido-3-[7-(3-phenylpropanamido)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]propanoate (166ah)



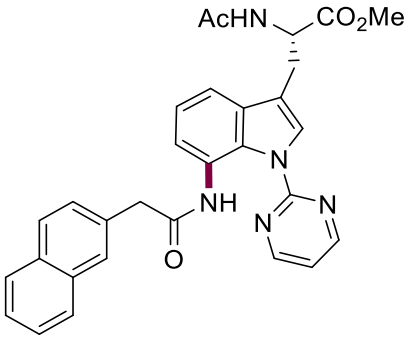
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-phenethyl-1,4,2-dioxazol-5-one (**165ah**) (76 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 0:100) yielded **166ah** (63 mg, 65%) as a white solid (M.p.: 109─111 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.16 (s, 1H), 8.54 (d, *J* = 4.8 Hz, 2H), 8.20 (dd, *J* = 7.2, 2.0 Hz, 1H), 8.04 (s, 1H), 7.26–7.23 (m, 1H), 7.23–7.21 (m, 2H), 7.20–7.19 (m, 1H), 7.20–7.13 (m, 2H), 7.18–7.09 (m, 1H), 7.02 (t, *J* = 4.8 Hz, 1H), 6.15 (d, *J* = 7.7 Hz, 1H), 4.93 (dt, *J* = 7.7, 5.4 Hz, 1H), 3.68 (s, 3H), 3.27 (ddd, *J* = 14.8, 5.4, 0.9 Hz, 1H), 3.19 (ddd, *J* = 14.8, 5.4, 0.9 Hz, 1H), 3.02 (t, *J* = 7.7 Hz, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.9 (C_q), 169.8 (C_q), 157.9 (CH), 156.7 (C_q), 141.0 (C_q), 133.9 (C_q), 128.4 (CH), 128.2 (CH), 127.0 (CH), 126.1 (CH), 126.1 (C_q), 125.9 (C_q), 123.4 (CH), 118.4 (CH), 116.3 (CH), 115.5 (C_q), 114.6 (CH), 52.6 (CH), 52.4 (CH_3), 40.4 (CH_2), 31.7 (CH_2), 27.2 (CH_2), 23.2 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3054, 1743, 1659, 1579, 1420, 1372, 1294, 1217, 800, 701 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 508 (100) $[M+Na]^+$, 486 (16) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{27}H_{27}N_5NaO_4^+$ $[M+Na]^+$ 508.1955, found 508.1960.

Methyl (*S*)-2-acetamido-3-{7-[2-(naphthalen-2-yl)acetamido]-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}propanoate (166ai)



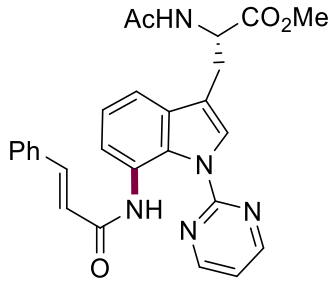
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-(naphthalen-2-ylmethyl)-1,4,2-dioxazol-5-one (**165ai**) (91 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 3:1 to 0:100) yielded **166ai** (75 mg, 72%) as an orange solid (M.p.: 153─155 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.23 (s, 1H), 8.10–8.03 (m, 3H), 7.99–7.95 (m, 1H), 7.89 (s, 1H), 7.84–7.80 (m, 1H), 7.77 (dd, *J* = 6.2, 2.6 Hz, 1H), 7.47 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.44–7.37 (m, 2H), 7.28 (d, *J* = 2.6 Hz, 1H), 7.27 (d, *J* = 4.7 Hz, 1H), 6.70 (t, *J* = 4.7 Hz, 1H), 6.08 (d, *J* = 7.5 Hz, 1H), 4.94 (dt, *J* = 7.5, 5.5 Hz, 1H), 4.17 (s, 2H), 3.69 (s, 3H), 3.28 (dd, *J* = 14.8, 5.5 Hz, 1H), 3.21 (dd, *J* = 14.8, 5.5 Hz, 1H), 1.96 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0 (C_q), 169.7 (C_q), 169.1 (C_q), 157.6 (CH), 156.5 (C_q), 133.8 (2 × C_q), 132.3 (C_q), 131.1 (C_q), 128.6 (CH), 128.2 (CH), 127.9 (CH), 127.4 (CH), 126.7 (CH), 126.6 (C_q), 126.0 (CH), 125.6 (C_q), 125.5 (CH), 123.7 (CH), 123.2 (CH), 120.1 (CH), 115.8 (CH), 115.6 (C_q), 115.3 (CH), 52.5 (CH), 52.4 (CH_3), 43.1 (CH_2), 27.2 (CH_2), 23.2 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3052, 1742, 1673, 1566, 1491, 1371, 1265, 791, 734, 704 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 544 (100) $[M+Na]^+$, 522 (25) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{30}H_{28}N_5O_4^+$ $[M+H]^+$ 522.2136, found 522.2140.

Methyl (*S*)-2-acetamido-3-[7-cinnamamido-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]propanoate (166aj)



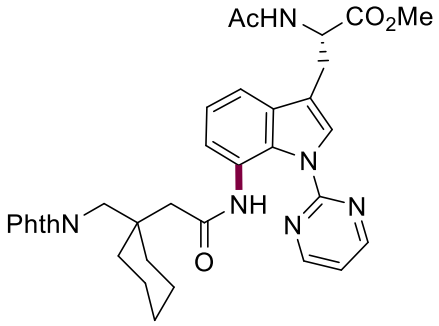
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and (*E*)-3-styryl-1,4,2-dioxazol-5-one (**165aj**) (76 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 3:1 to 0:100) yielded **166aj** (71 mg, 73%) as a white solid (M.p.: 209–211 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.71 (s, 1H), 8.70 (d, *J* = 4.8 Hz, 2H), 8.40–8.36 (m, 1H), 8.12 (s, 1H), 7.70 (d, *J* = 15.6 Hz, 1H), 7.51 (d, *J* = 6.4 Hz, 2H), 7.43–7.36 (m, 3H), 7.33–7.24 (m, 2H), 7.15 (t, *J* = 4.8 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.16 (d, *J* = 7.7 Hz, 1H), 4.97 (dt, *J* = 7.7, 5.2 Hz, 1H), 3.72 (s, 3H), 3.31 (dd, *J* = 14.9, 5.2 Hz, 1H), 3.24 (dd, *J* = 14.9, 5.2 Hz, 1H), 2.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.8 (C_q), 163.8 (C_q), 158.0 (CH), 156.8 (C_q), 140.8 (CH), 134.9 (C_q), 134.0 (C_q), 129.7 (CH), 128.9 (CH), 127.7 (CH), 127.0 (CH), 126.5 (C_q), 126.0 (C_q), 123.5 (CH), 122.6 (CH), 118.4 (CH), 116.5 (CH), 115.6 (C_q), 114.8 (CH), 52.6 (CH), 52.5 (CH_3), 27.2 (CH_2), 23.2 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3053, 1742, 1578, 1421, 1370, 1265, 1215, 1001, 803, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 506 (75) $[M+Na]^+$, 484 (100) $[M+H]^+$
HR-MS (ESI): *m*/*z* calcd for $C_{27}H_{26}N_5O_4^+$ $[M+H]^+$ 484.1979, found 484.1977.

Methyl (*S*)-2-acetamido-3-{7-{2-{1-[(1,3-dioxoisoindolin-2-yl)methyl]cyclohexyl}acetamido}-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}propanoate (166ak)



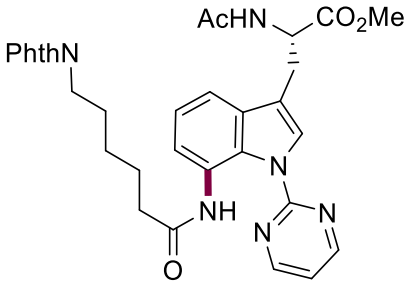
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 2-{{1-[(5-oxo-1,4,2-dioxazol-3-yl)methyl]cyclohexyl}methyl}isoindoline-1,3-dione (**165ak**) (137 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 0:100) yielded **166ak** (125 mg, 98%) as a white solid (M.p.: 142─144 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.16 (s, 1H), 8.72 (d, *J* = 4.8 Hz, 2H), 8.17 (t, *J* = 4.6 Hz, 1H), 8.06 (s, 1H), 7.79–7.76 (m, 2H), 7.70–7.67 (m, 2H), 7.23–7.18 (m, 2H), 7.07 (t, *J* = 4.8 Hz, 1H), 6.19 (d, *J* = 7.7 Hz, 1H), 4.94 (dt, *J* = 7.7, 5.5 Hz, 1H), 3.83 (s, 2H), 3.70 (s, 3H), 3.29 (dd, *J* = 14.8, 5.5 Hz, 1H), 3.21 (dd, *J* = 14.8, 5.5 Hz, 1H), 2.38 (s, 2H), 1.96 (s, 3H), 1.87–1.77 (m, 2H), 1.72–1.58 (m, 2H), 1.54–1.42 (m, 2H), 1.43–1.32 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0 (C_q), 169.8 (C_q), 169.1 (C_q), 169.0 (C_q), 158.1 (CH), 156.8 (C_q), 133.9 (CH), 133.8 (C_q), 131.9 (C_q), 127.0 (CH), 126.2 (C_q), 125.8 (C_q), 123.2 (CH), 123.1 (CH), 118.3 (CH), 116.4 (CH), 115.4 (C_q), 114.5 (CH), 52.5 (CH_3), 52.4 (CH), 45.8 (CH_2), 45.2 (CH_2), 39.1 (C_q), 33.2 (CH_2), 27.2 (CH_2), 25.5 (CH_2), 23.1 (CH_3), 21.7 (CH_2).

IR (ATR): $\tilde{\nu}$ = 3055, 1714, 1423, 1264, 1053, 896, 732, 703 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 659 (100) $[M+Na]^+$, 637 (10) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{35}H_{36}N_6NaO_6^+$ $[M+Na]^+$ 659.2589, found 659.2592.

Methyl (*S*)-2-acetamido-3-{7-[6-(1,3-dioxoisoindolin-2-yl)hexanamido]-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}propanoate (166al)



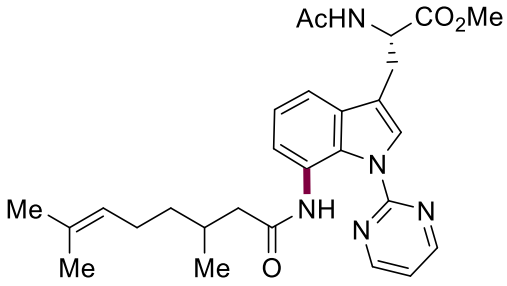
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 2-[5-(5-oxo-1,4,2-dioxazol-3-yl)pentyl]isoindoline-1,3-dione (**165al**) (121 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 0:100) yielded **166al** (87 mg, 73%) as a white solid (M.p.: 215─216 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.35 (s, 1H), 8.88 (d, J = 4.9 Hz, 2H), 8.42 (d, J = 7.6 Hz, 1H), 8.04 (s, 1H), 7.89–7.74 (m, 5H), 7.37 (t, J = 4.9 Hz, 1H), 7.35 (d, J = 7.3 Hz, 1H), 7.21 (dd, J = 7.8, 7.8 Hz, 1H), 4.56 (ddd, J = 8.1, 7.6, 5.5 Hz, 1H), 3.61 (s, 3H), 3.53 (t, J = 7.1 Hz, 2H), 3.17 (dd, J = 14.8, 5.5 Hz, 1H), 3.05 (dd, J = 14.8, 8.1 Hz, 1H), 2.23 (t, J = 7.3 Hz, 2H), 1.81 (s, 3H), 1.57 (tt, J = 7.7, 7.1 Hz, 2H), 1.51 (tt, J = 7.7, 7.3 Hz, 2H), 1.34–1.17 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 172.2 (C_q), 170.0 (C_q), 169.4 (C_q), 167.9 (C_q), 158.7 (CH), 156.1 (C_q), 134.3 (CH), 132.8 (C_q), 131.5 (C_q), 127.2 (CH), 126.0 (C_q), 125.7 (C_q), 122.9 (CH), 122.3 (CH), 118.4 (CH), 117.4 (CH), 115.4 (C_q), 114.6 (CH), 52.2 (CH_3), 51.9 (CH), 37.2 (CH_2), 36.5 (CH_2), 27.7 (CH_2), 26.4 (CH_2), 25.8 (CH_2), 24.5 (CH_2), 22.3 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3054, 1422, 1265, 896, 736, 706 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 619 (100) $[M+Na]^+$, 597 (12) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{32}H_{32}N_6NaO_6^+$ $[M+Na]^+$ 619.2276, found 619.2284.

Methyl (2*S*)-2-acetamido-3-[7-(3,7-dimethyloct-6-enamido)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]propanoate (166ba)



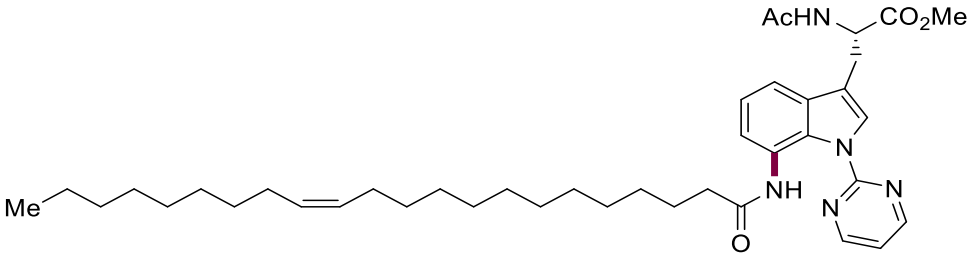
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-(2,6-dimethylhept-5-en-1-yl)-1,4,2-dioxazol-5-one (**165ba**) (84 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 3:1 to 1:1) yielded **166ba** (97 mg, 96%) as a white solid (M.p.: 116─118 °C). d.r. = 3.3:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.11 (s, 1H), 8.63 (d, *J* = 4.8 Hz, 2H), 8.21 (d, *J* = 5.5 Hz, 1H), 8.05 (s, 1H), 7.28–7.18 (m, 2H), 7.12–7.05 (m, 1H), 6.20 (d, *J* = 7.7 Hz, 1H), 5.03 (t, *J* = 6.9 Hz, 1H), 4.92 (dt, *J* = 7.7, 5.5 Hz, 1H), 3.68 (s, 3H), 3.27 (dd, *J* = 14.8, 5.5 Hz, 1H), 3.18 (dd, *J* = 14.8, 5.5 Hz, 1H), 2.39–2.26 (m, 1H), 2.13–2.03 (m, 1H), 1.96–1.91 (m, 5H), 1.62 (s, 3H), 1.54 (s, 3H), 1.46–1.30 (m, 1H), 1.24–1.14 (m, 1H), 1.14–1.11 (m, 1H), 0.92 (d, *J* = 5.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0 (C_q), 170.4 (C_q), 169.7 (C_q), 157.9 (CH), 156.8 (C_q), 133.9 (C_q), 131.4 (C_q), 127.0 (CH), 126.3 (C_q), 125.8 (C_q), 124.2 (CH), 123.3 (CH), 118.3 (CH), 116.3 (CH), 115.5 (C_q), 114.5 (CH), 52.5 (CH), 52.4 (CH_3), 46.5 (CH_2), 37.0 (CH_2), 30.5 (CH), 27.2 (CH_2), 25.6 (CH_3), 25.4 (CH_2), 23.1 (CH_3), 19.6 (CH_3), 17.6 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3055, 1678, 1579, 1423, 1264, 733, 703 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 528 (100) $[M+Na]^+$, 506 (40) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{28}H_{36}N_5O_4^+$ $[M+H]^+$ 506.2762, found 506.2761.

Methyl (*S*,*Z*)-2-acetamido-3-[7-(docos-13-enamido)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl]propanoate (166bb)



The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and (*Z*)-3-(henicos-12-en-1-yl)-1,4,2-dioxazol-5-one (**165bb**) (152 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 0:100) yielded **166bb** (133 mg, 99%) as a white solid (M.p.: 138─140 °C).

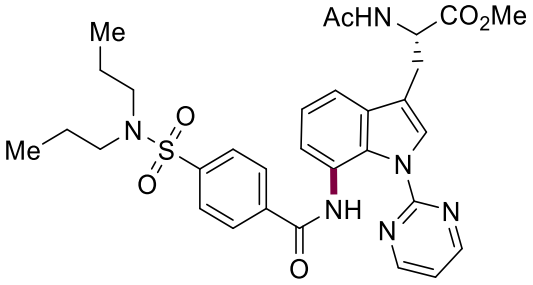
^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.12 (s, 1H), 8.66 (d, *J* = 4.8 Hz, 2H), 8.21 (d, *J* = 6.8 Hz, 1H), 8.06 (s, 1H), 7.25–7.21 (m, 2H), 7.11 (t, *J* = 4.8 Hz, 1H), 6.06 (d, *J* = 7.7 Hz,

1H), 5.48–5.13 (m, 2H), 4.94 (dt, *J* = 7.7, 5.4 Hz, 1H), 3.69 (s, 3H), 3.30 (ddd, *J* = 14.8, 5.4, 0.9 Hz, 1H), 3.22 (ddd, *J* = 14.8, 5.4, 0.9 Hz, 1H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.01–1.97 (m, 4H), 1.96 (s, 3H), 1.75–1.64 (m, 2H), 1.39–1.12 (m, 28H), 0.85 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 171.0 (C_q), 169.7 (C_q), 158.0 (CH), 157.0 (C_q), 134.0 (C_q), 129.9 (CH), 129.8 (CH), 127.0 (CH), 126.4 (C_q), 125.9 (C_q), 123.5 (CH), 118.4 (CH), 116.3 (CH), 115.6 (C_q), 114.5 (CH), 52.6 (CH), 52.5 (CH_3), 38.6 (CH_2), 31.9 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2) 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 27.3 (CH_2), 27.2 (3 × CH_2), 25.8 (2 × CH_2), 23.2 (CH_3), 22.7 (CH_2), 14.1 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3053, 1422, 1264, 896, 734, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 696 (100) $[M+Na]^+$, 674 (13) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{40}H_{59}N_5NaO_4^+$ $[M+Na]^+$ 696.4459, found 696.4455.

Methyl (*S*)-2-acetamido-3-{7-[4-(*N*,*N*-dipropylsulfamoyl)benzamido]-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}propanoate (166bc)



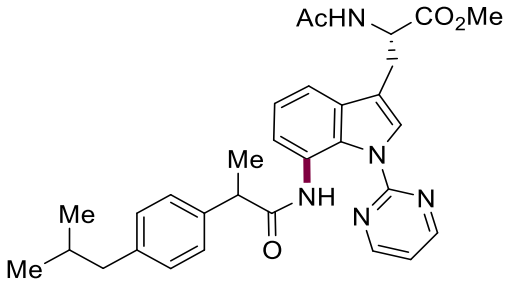
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 4-(5-oxo-1,4,2-dioxazol-3-yl)-*N*,*N*-dipropylbenzenesulfonamide (**165bc**) (130 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 1:5) yielded **166bc** (118 mg, 95%) as a white solid (M.p.: 173─175 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.28 (s, 1H), 8.45 (d, *J* = 4.9 Hz, 2H), 8.32 (dd, *J* = 5.6, 3.3 Hz, 1H), 8.13 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.33–7.30 (m, 2H), 7.02 (t, *J* = 4.9 Hz, 1H), 6.15 (d, *J* = 7.7 Hz, 1H), 4.97 (dt, *J* = 7.7, 5.4 Hz, 1H), 3.71 (s, 3H), 3.32 (dd, *J* = 14.8, 5.4 Hz, 1H), 3.23 (dd, *J* = 14.8, 5.4 Hz, 1H), 3.14–3.09 (m, 4H), 1.98 (s, 3H), 1.59–1.53 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0 (C_q), 169.8 (C_q), 165.0 (C_q), 158.1 (CH), 156.6 (C_q), 142.9 (C_q), 140.6 (C_q), 134.2 (C_q), 128.1 (CH), 127.2 (CH), 127.1 (CH), 126.1 (C_q), 125.9 (C_q), 123.5 (CH), 118.5 (CH), 116.4 (CH), 115.7 (C_q), 115.4 (CH), 52.6 (CH), 52.5 (CH_3), 49.9 (CH_2), 27.3 (CH_2), 23.2 (CH_3), 21.9 (CH_2), 11.1 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2967, 1745, 1566, 1422, 1337, 1265, 1156, 798, 740, 605 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 643 (100) $[M+Na]^+$, 621 (77) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{37}N_6O_6S^+$ $[M+H]^+$ 621.2490, found 621.2490.

Methyl (2*S*)-2-acetamido-3-{7-[2-(4-isobutylphenyl)propanamido]-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}propanoate (166bd)



The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and 3-[1-(4-isobutylphenyl)ethyl]-1,4,2-dioxazol-5-one (**165bd**) (99 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 1:5) yielded **166bd** (28 mg, 26%) as a white solid (M.p.: 160─162 °C). d.r. = 2.2:1.

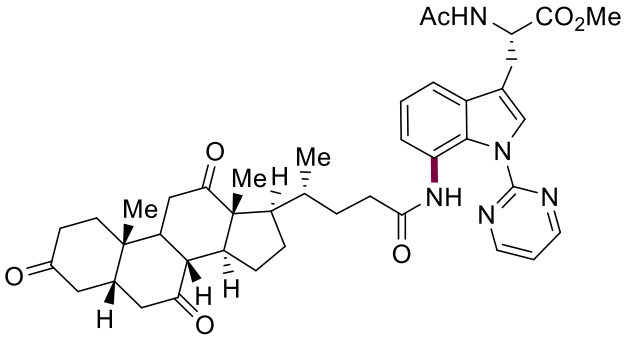
^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.76 (s, 1H), 8.45 (d, *J* = 4.8 Hz, 2H), 8.21 (d, *J* = 7.4 Hz, 1H), 8.00 (s, 1H), 7.31–7.25 (m, 2H), 7.22–7.16 (m, 2H), 7.07–7.01 (m, 2H), 6.98 (t, *J* = 4.8 Hz, 1H), 6.03 (d, *J* = 7.5 Hz, 1H), 4.95 (dt, *J* = 7.5, 5.2 Hz, 1H), 3.76–3.59 (m, 4H), 3.30 (dd, *J* = 14.9, 5.2 Hz, 1H), 3.23 (dd, *J* = 14.9, 5.2 Hz, 1H), 2.41 (d, *J* = 6.8 Hz, 2H), 1.97 (s, 3H), 1.85–1.76 (m, 1H), 1.53 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2 (C_q), 172.0 (C_q), 169.7 (C_q), 157.9 (CH), 156.7 (C_q), 140.4 (C_q), 139.0 (C_q), 133.9 (C_q), 133.9 (C_q), 129.4 (CH), 127.2 (CH), 127.1 (CH), 126.3 (C_q), 123.3 (CH), 119.0 (CH), 116.0 (CH), 115.6 (C_q), 114.7 (CH), 52.6 (CH), 52.5 (CH_3), 48.3 (CH), 45.0 (CH_2), 30.1 (CH), 27.2 (CH_2), 23.2 (CH_3), 22.4 (CH_3), 19.6 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3325, 1587, 1544, 1503, 1471, 1264, 908, 844, 730, 649 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 564 (60) $[M+Na]^+$, 542 (100) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{31}H_{36}N_5O_4^+$ $[M+H]^+$ 542.2762, found 542.2761.

Methyl (2*S*)-2-acetamido-3-{7-[(4*R*)-4-((10*S*,13*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanamido]-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}propanoate (166be)



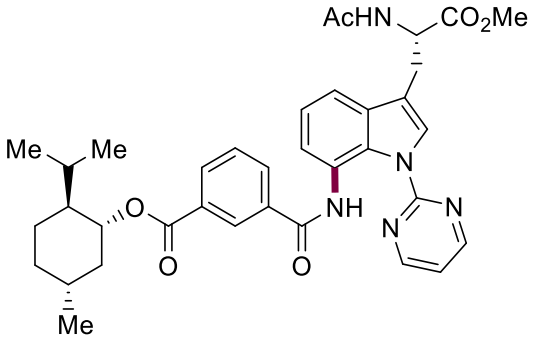
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and (5*S*,8*R*,9 *S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-[(*R*)-4-(5-oxo-1,4,2-dioxazol-3-yl)butan-2-yl]dodecahydro-3*H*-cyclopenta[a]phenanthrene-3,7,12(2*H*,4*H*)-trione (**165be**) (177 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 0:100) yielded **166be** (142 mg, 96%) as an orange solid (M.p.: 154─156 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 12.14 (s, 1H), 8.67 (d, *J* = 4.9 Hz, 2H), 8.27–8.13 (m, 1H), 8.06 (s, 1H), 7.27–7.18 (m, 2H), 7.13 (t, *J* = 4.9 Hz, 1H), 6.12 (d, *J* = 7.7 Hz, 1H), 4.93 (dt, *J* = 7.7, 5.3 Hz, 1H), 3.69 (s, 3H), 3.29 (dd, *J* = 14.8, 5.3 Hz, 1H), 3.20 (dd, *J* = 14.8, 5.3 Hz, 1H), 2.96–2.72 (m, 3H), 2.49–2.19 (m, 8H), 2.17–2.05 (m, 3H), 1.95 (m, 9H), 1.86–1.71 (m, 2H), 1.66–1.50 (m, 2H), 1.36 (s, 3H), 1.02 (s, 3H), 0.83 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.2 (C_q), 209.0 (C_q), 208.7 (C_q), 172.0 (C_q), 171.1 (C_q), 169.7 (C_q), 158.0 (CH), 156.9 (C_q), 133.9 (C_q), 127.0 (CH), 126.3 (C_q), 125.9 (C_q), 123.4 (CH), 118.3 (CH), 116.4 (CH), 115.5 (C_q), 114.5 (CH), 56.8 (C_q), 52.5 (CH_3), 52.4 (CH), 51.7 (CH), 48.9 (CH), 46.7 (CH), 45.7 (CH), 45.5 (CH), 44.9 (CH_2), 42.7 (CH_2), 38.6 (CH_2), 36.4 (CH_2), 35.9 (CH_2), 35.20 (CH), 35.2 (2 × CH_2), 31.1 (CH_2), 27.5 (C_q), 27.2 (CH_2), 25.0 (CH_2), 23.2 (CH_3), 21.8 (CH_3), 18.8 (CH_3), 11.9 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3053, 2929, 1711, 1675, 1578, 1421, 1265, 801, 736, 704 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 760 (100) $[M+Na]^+$, 738 (5) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{42}H_{51}N_5NaO_7^+$ $[M+Na]^+$ 760.3681, found 760.3677.

(1*S*,2*R*,5*S*)-2-*iso*-propyl-5-methylcyclohexyl 3-{[3-((*S*)-2-acetamido-3-methoxy-3-oxopropyl)-1-(pyrimidin-2-yl)-1*H*-indol-7-yl]carbamoyl}benzoate (166bf)



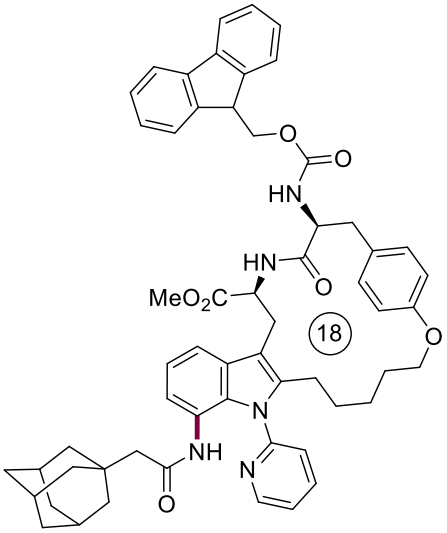
The general procedure **J** was followed using Ac-Trp^{pym}-OMe (**164aa**) (68 mg, 0.2 mmol) and (1*S*,2*R*,5*S*)-2-*iso*-propyl-5-methylcyclohexyl 3-(5-oxo-1,4,2-dioxazol-3-yl)benzoate (**165bf**) (138 mg, 0.4 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 0:100) yielded **166bf** (96 mg, 75%) as a white solid (M.p.: 161─162 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.07 (s, 1H), 8.65 (d, *J* = 4.9 Hz, 2H), 8.61 (s, 1H), 8.29 (dd, *J* = 6.9, 2.2 Hz, 1H), 8.25–8.17 (m, 2H), 8.12 (s, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.38–7.28 (m, 2H), 6.99 (t, *J* = 4.9 Hz, 1H), 6.12 (d, *J* = 7.7 Hz, 1H), 5.09–4.92 (m, 2H), 3.72 (s, 3H), 3.34 (dd, *J* = 14.7, 5.2 Hz, 1H), 3.26 (dd, *J* = 14.7, 5.2 Hz, 1H), 2.19–2.10 (m, 1H), 1.99 (s, 3H), 1.97–1.89 (m, 1H), 1.82–1.71 (m, 2H), 1.64–1.49 (m, 2H), 1.28–1.06 (m, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.7 (C_q), 165.6 (C_q), 165.1 (C_q), 158.4 (CH), 156.7 (C_q), 136.9 (C_q), 134.2 (C_q), 132.6 (CH), 132.3 (CH), 130.9 (C_q), 129.0 (CH), 127.6 (CH), 127.2 (CH), 126.4 (C_q), 126.1 (C_q), 123.4 (CH), 119.1 (CH), 116.3 (CH), 115.6 (C_q), 115.2 (CH), 75.4 (CH), 52.6 (CH), 52.5 (CH_3), 47.2 (CH), 41.0 (CH_2), 34.2 (CH_2), 31.5 (CH), 27.3 (CH_2), 26.5 (CH), 23.5 (CH_2), 23.2 (CH_3), 22.0 (CH_3), 20.8 (CH_3), 16.4 (CH_3).

IR (ATR): $\tilde{\nu}$ = 3053, 1711, 1672, 1566, 1421, 1370, 1265, 1133, 736, 705 cm^{-1}.
MS (ESI) *m*/*z* (relative intensity): 662 (100) $[M+Na]^+$, 640 (15) $[M+H]^+$.
HR-MS (ESI): *m*/*z* calcd for $C_{36}H_{41}N_5NaO_6^+$ $[M+Na]^+$ 662.2949, found 662.2940.

Methyl (3*S*,6*S*)-6-({[(9*H*-fluoren-9-yl)methoxy]carbonyl}amino)-17-{2-[(1*S*,3*R*)-adamantan-1-yl]acetamido}-5-oxo-11-(pyridin-2-yl)-11*H*-9-oxa-4-aza-1(3,2)-indola-8(1,4)-benzenacyclotetradecaphane-3-carboxylate (166bg)



The general procedure **J** was followed using cyclic peptide (**164ba**) (75 mg, 0.1 mmol) and 3-[(3r,5r,7r)-adamantan-1-yl)methyl]-1,4,2-dioxazol-5-one (**165bg**) (94 mg, 0.2 mmol). After 24 h, purification by column chromatography (*n*-hexane/EtOAc 1:3 to 1:1) yielded **166bg** (75 mg, 80%) as a white solid (M.p.: 128─129 °C).

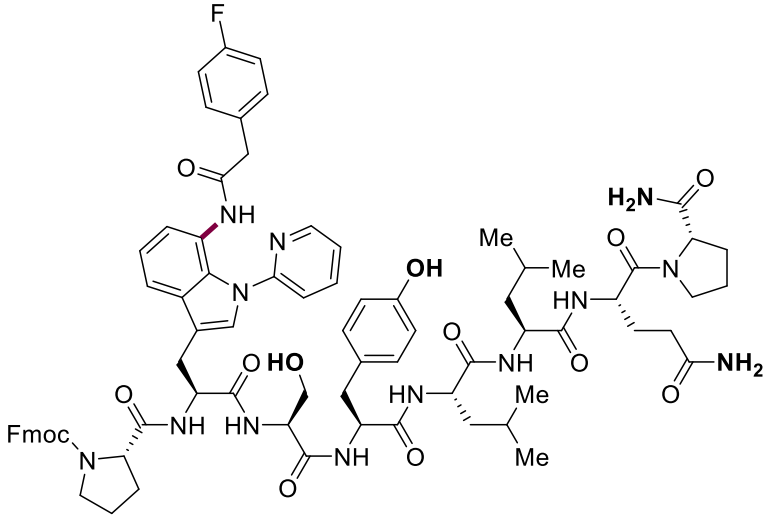
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.84 (t, *J* = 7.0 Hz, 2H), 7.76 (d, *J* = 6.3 Hz, 3H), 7.67–7.55 (m, 5H), 7.44 (dd, *J* = 7.8, 4.1 Hz, 2H), 7.41–7.36 (m, 2H), 7.35–7.27 (m, 4H), 7.17 (q, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.82–5.58 (m, 1H), 5.55–5.40 (m, 1H), 4.77–4.57 (m, 1H), 4.48 (dd, *J* = 10.5, 7.2 Hz, 1H), 4.43–4.32 (m, 2H), 4.24 (t, *J* = 7.3 Hz, 2H), 4.18–4.06 (m, 1H), 3.69 (s, 3H), 3.41 (d, *J* = 12.1 Hz, 1H), 2.97–2.48 (m, 3H), 2.23–2.08 (m, 1H), 2.06–1.96 (m, 1H), 1.94–1.82 (m, 3H), 1.69–1.61 (m, 3H), 1.59–1.56 (m, 2H), 1.55–1.49 (m, 3H), 1.48–1.42 (m, 6H), 1.33–1.21 (m, 1H), 1.18–1.07 (m, 1H), 1.03–0.91 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 170.0 (C_q), 169.0 (C_q), 156.6 (C_q), 155.5 (C_q), 152.7 (C_q), 149.1 (CH), 143.6 (C_q), 141.3 (C_q), 141.3 (C_q), 138.7 (CH), 138.5 (C_q), 131.1 (CH), 129.7 (C_q), 129.4 (C_q), 127.7 (CH), 127.1 (CH), 125.0 (CH), 123.8 (CH), 123.4 (CH), 122.6 (C_q), 121.0 (CH), 120.0 (CH), 119.0 (CH), 116.6 (CH), 115.6 (CH), 108.8 (C_q), 67.0 (CH_2), 66.4 (CH_2), 56.3 (CH), 52.9 (CH), 52.3 (CH_3), 52.2 (CH_2), 47.2

(CH), 42.4 (CH_2), 36.6 (CH_2), 32.8 (C_q), 28.5 (CH), 28.4 (2 × CH_2), 27.9 (CH_2), 26.4 (CH_2), 23.5 (CH_2), 23.4 (CH_2).

IR (ATR): $\tilde{\nu}$ = 3403, 2902, 1733, 1683, 1508, 1361, 1239, 1044, 741, 513 cm^{-1}.
MS (ESI) *m/z* (relative intensity): 962 (100) $[M+Na]^+$, 940 (10) $[M+H]^+$.
HR-MS (ESI): *m/z* calcd for $C_{58}H_{62}N_5O_7$ $[M+H]^+$ 940.4644, found 940.4615.

(9*H*-fluoren-9-yl) Methyl (*S*)-2-[((2*S*,5*S*,8*S*,11*S*,14*S*,17*S*)-20-amino-17-((*S*)-2-carbamoylpyrrolidine-1-carbonyl)-1-[7-(2-(4-fluorophenyl)acetamido)-1-(pyridin-2-yl)-1*H*-indol-3-yl]-8-(4-hydroxybenzyl)-5-(hydroxymethyl)-11,14-diisobutyl-3,6,9,12,15,20-hexaoxo-4,7,10,13,16-pentaazaicosan-2-yl)carbamoyl]pyrrolidine-1-carboxylate (166bh)



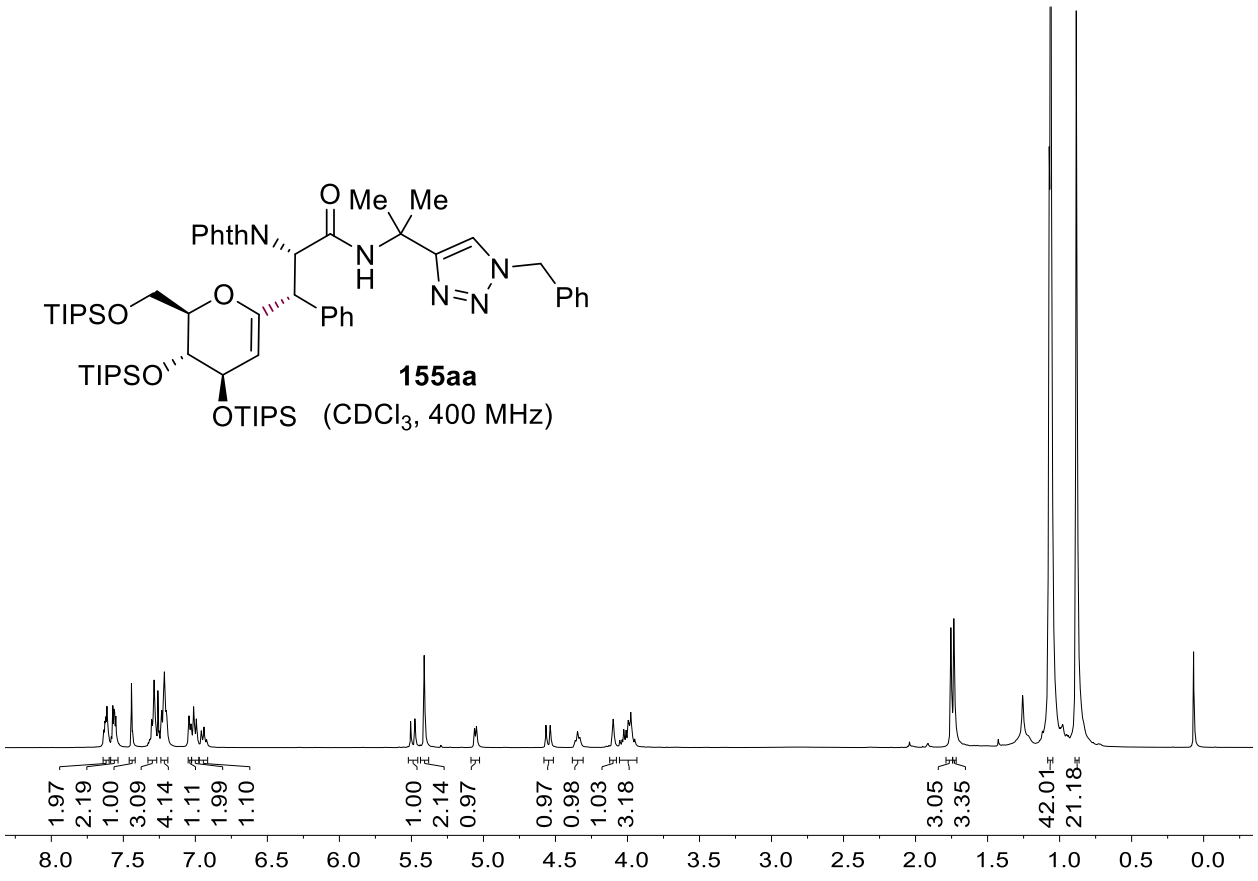
The general procedure **J** was followed using Fmoc-Pro-Trp^{py}-Ser-Tyr-Leu-Leu-Gln-Pro-NH_2 (**164bb**) (130 mg, 0.1 mmol) and 3-(4-fluorobenzyl)-1,4,2-dioxazol-5-one (**165bh**) (39 mg, 0.2 mmol). After 24 h, purification by column chromatography (EtOAc/MeOH 50:1 to 6:1) yielded **166bh** (87 mg, 60%) as a white solid (M.p.: 185─186 °C).

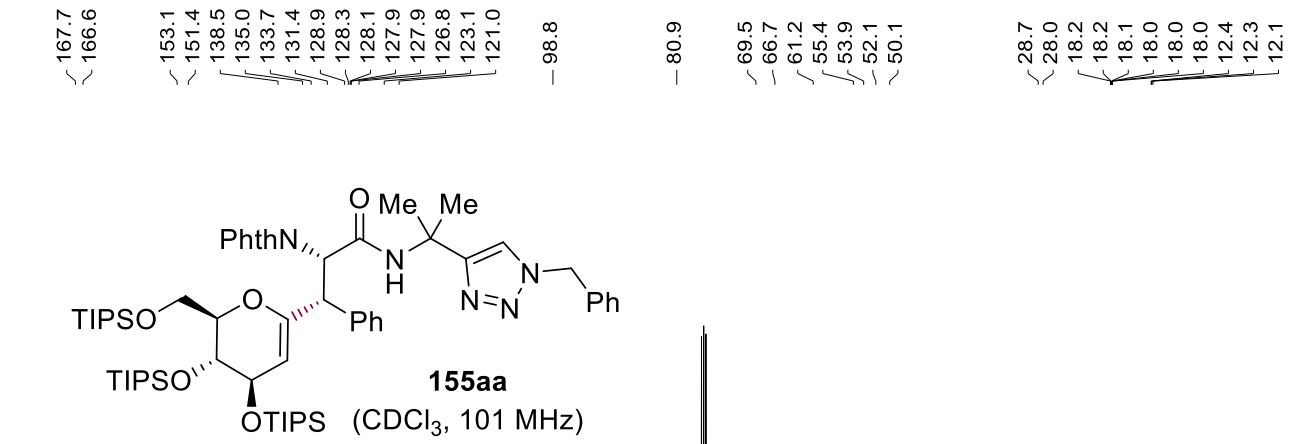
^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.17 (s, 1H), 8.53–8.38 (m, 1H), 8.36–8.22 (m, 1H), 8.12–8.00 (m, 2H), 7.96 (s, 1H), 7.93–7.81 (m, 3H), 7.80–7.69 (m, 2H), 7.68–7.56 (m, 2H), 7.54–7.38 (m, 4H), 7.36–7.25 (m, 5H), 7.23–7.13 (m, 3H), 7.13–6.93 (m, 7H), 6.91 (s, 1H), 6.80 (s, 1H), 6.66–6.56 (m, 2H), 5.21–5.04 (m, 1H), 4.86–4.60 (m, 1H), 4.54–4.42 (m, 2H), 4.40–4.10 (m, 8H), 3.68–3.51 (m, 5H), 3.25–2.84 (m, 4H), 2.81–2.68 (m, 1H), 2.21–2.06 (m, 3H), 1.97–1.87 (m, 2H), 1.84–1.67 (m, 5H), 1.65–1.50 (m, 4H), 1.49–1.36 (m, 4H), 0.95–0.74 (m, 14H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 174.0 (C_q), 173.7 (C_q), 171.7 (C_q), 171.6 (C_q), 170.7 (C_q), 169.6 (C_q), 168.2 (C_q), 161.0 (d, $^1J_{C\text{-}F}$ = 242.1 Hz, C_q), 155.8 (C_q), 154.3 (C_q), 153.9 (C_q), 143.8 (C_q), 142.5 (C_q), 140.7 (C_q), 139.4 (C_q), 137.4 (C_q), 133.9 (C_q), 131.6 (C_q), 131.3 (C_q), 131.0 (CH), 130.9 (CH), 130.8 (d, $^3J_{C\text{-}F}$ = 7.8 Hz, CH), 130.1 (CH), 128.9 (CH), 127.7 (CH), 127.5 (C_q), 127.3 (CH), 127.1 (CH), 127.1 (CH), 127.0 (CH), 125.1 (CH), 124.2 (d, $^4J_{C\text{-}F}$ = 2.1 Hz, C_q), 123.8 (C_q), 121.4 (CH), 120.1 (CH), 120.0 (CH), 114.8 (d, $^2J_{C\text{-}F}$ = 20 Hz, CH), 114.8 (CH), 66.9 (CH_2), 66.7 (CH_2), 66.6 (CH_2), 61.8 (CH_2), 59.9 (CH), 59.8 (CH), 59.7 (CH_2), 59.3 (CH), 54.4 (CH), 54.3 (CH), 52.7 (CH), 51.0 (CH), 50.8 (CH), 49.8 (CH), 46.7 (CH_2), 46.6 (CH), 42.0 (CH_2), 41.1 (CH_2), 40.7 (CH_2), 36.2 (CH_2), 31.0 (CH_2), 29.7 (CH_2), 29.3 (CH_2), 27.2 (CH_2), 24.4 (CH_2), 24.1 (CH), 23.1 (CH_3), 23.1 (CH_3), 21.6 (CH_3), 21.5 (CH_3).
^{19}F NMR (282 MHz, DMSO-d_6): δ = –73.47 (s).

IR (ATR): $\tilde{\nu}$ = 3310, 2816, 1648, 1509, 1467, 1023, 990, 761, 737, 571 cm^{-1}.
MS (ESI) *m/z* (relative intensity): 1474 (100) $[M+Na]^+$.
HR-MS (ESI): *m/z* calcd for $C_{78}H_{91}FN_{13}O_{14}^+$ $[M+H]^+$ 1452.6787, found 1452.6767.

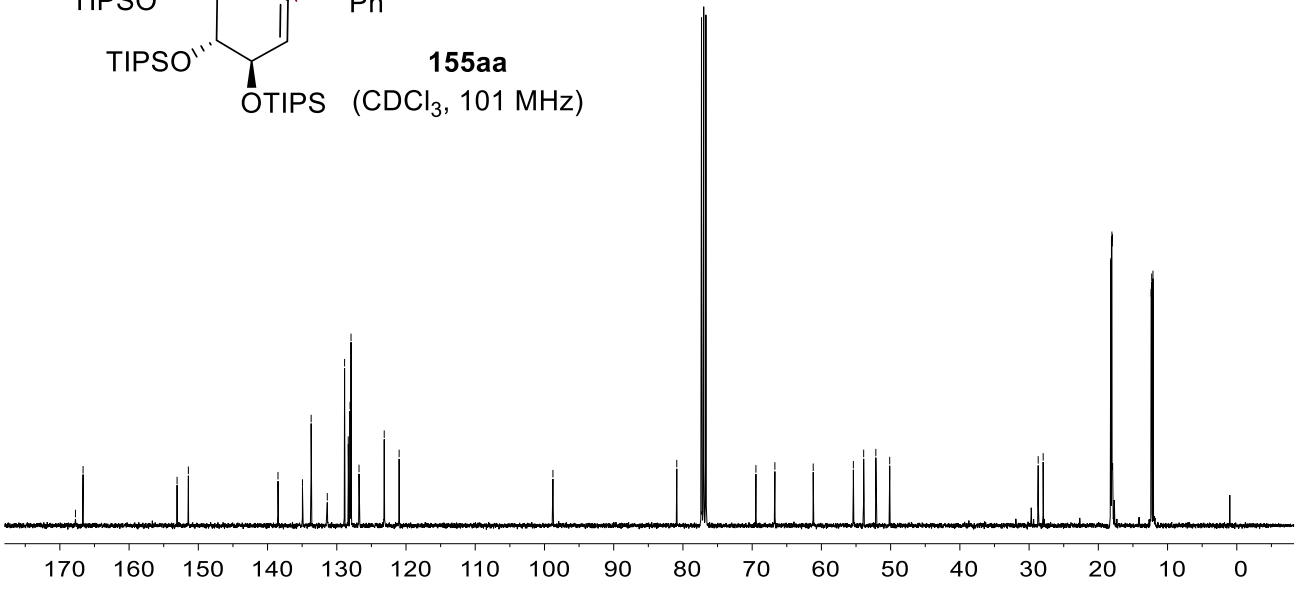
6. NMR Spectra

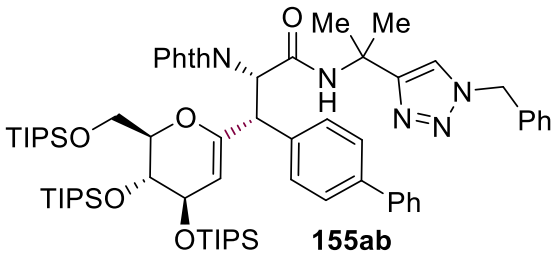




155aa

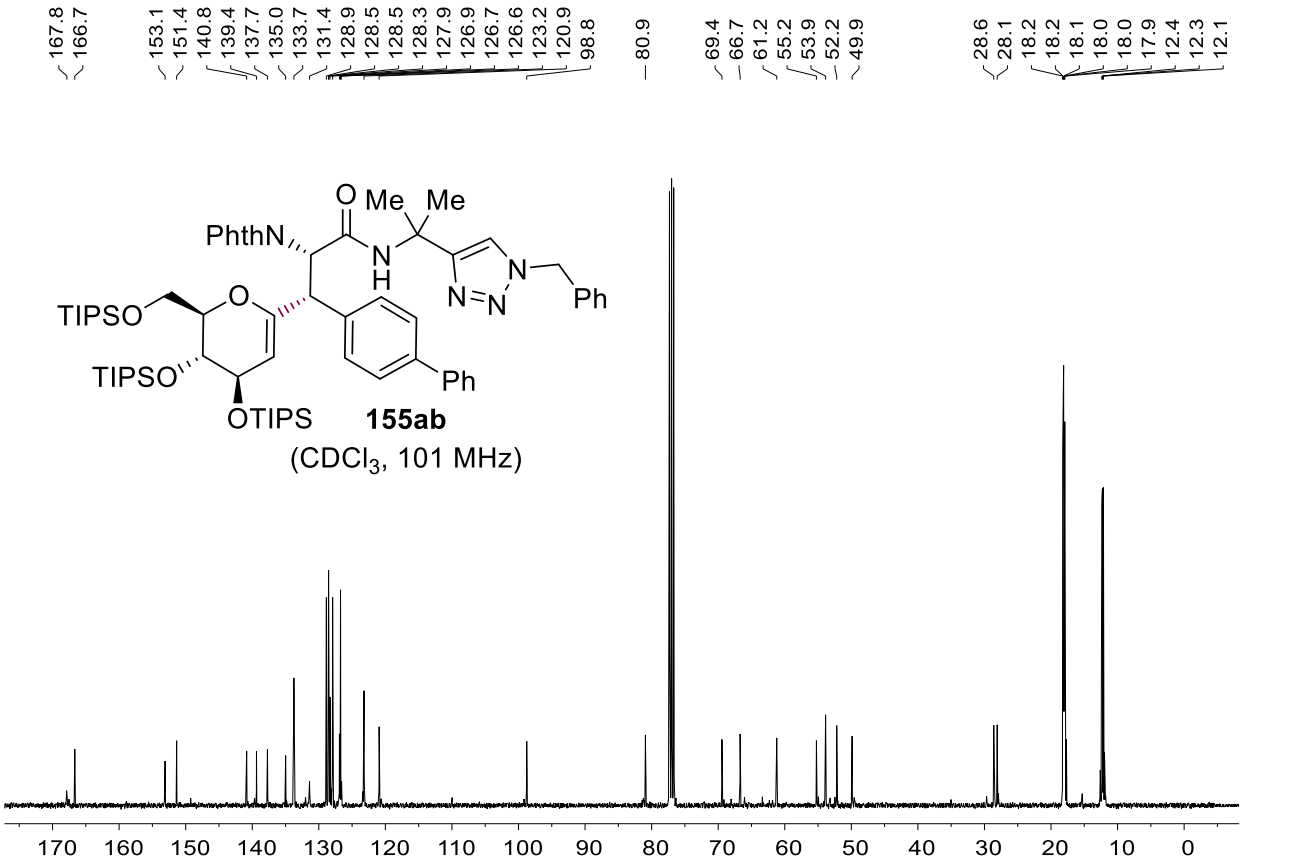
($CDCl_3$, 101 MHz)





155ab

($CDCl_3$, 400 MHz)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166.7
153.1
151.4
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139.4
137.7
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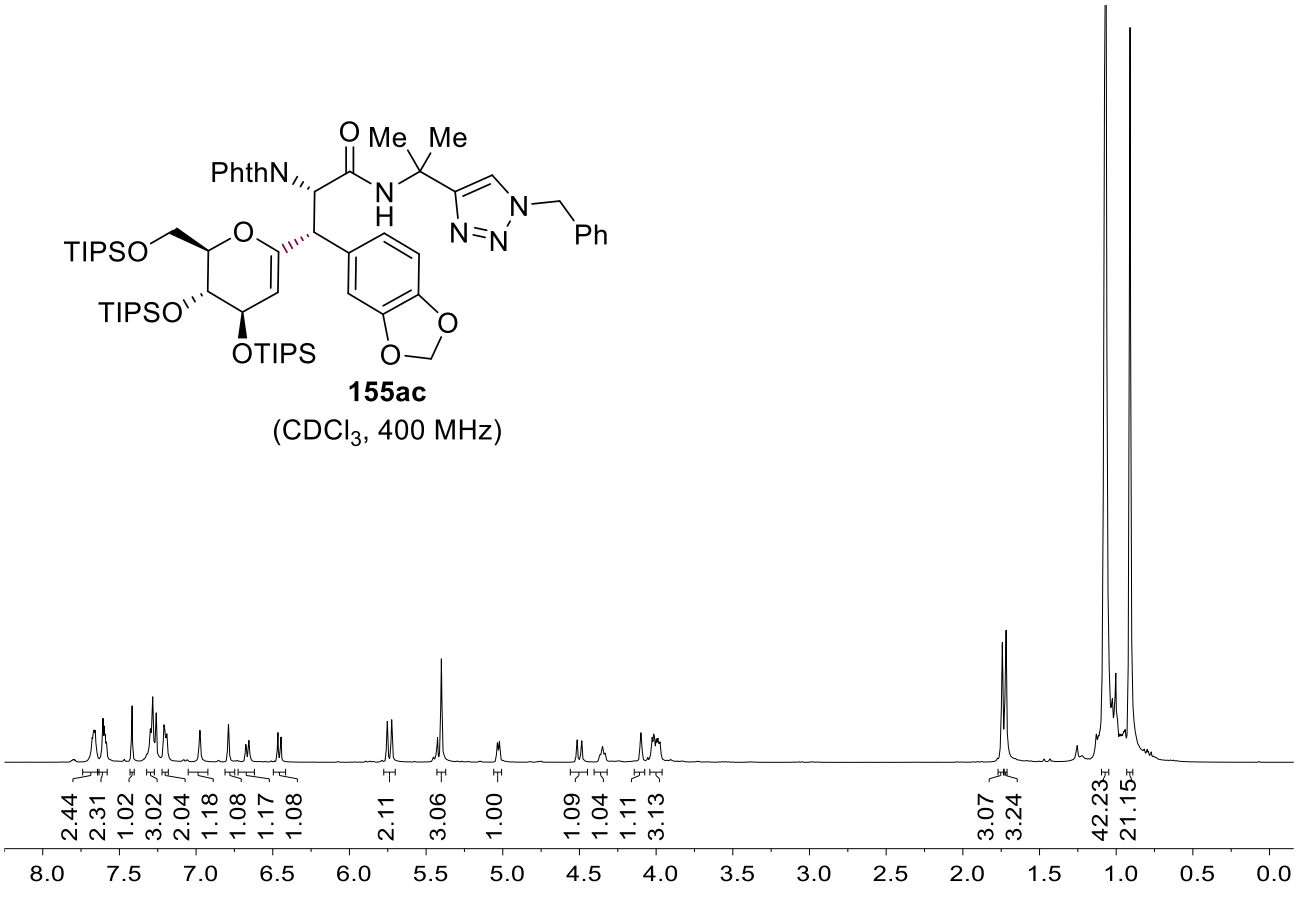
133.7
131.4
128.9
128.5
128.5
128.3
127.9
126.9
126.7
126.6
123.2
120.9
98.8
80.9
69.4
66.7
61.2
55.2
53.9
52.2
49.9
28.6
28.1
18.2
18.2
18.1
18.0
18.0
17.9
12.4
12.3
12.1
O
Me
Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
Ph
OTIPS
155ab
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
Me
Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
O
O
OTIPS
155ac
(CDCl3, 400 MHz)
2.44
2.31
1.02
3.02
2.04
1.18
1.08
1.17
1.08
2.11
3.06
1.00
1.09
1.04
1.11
3.13
3.07
3.24
42.23
21.15
8.0
7.5
7.0
6.5
6.0
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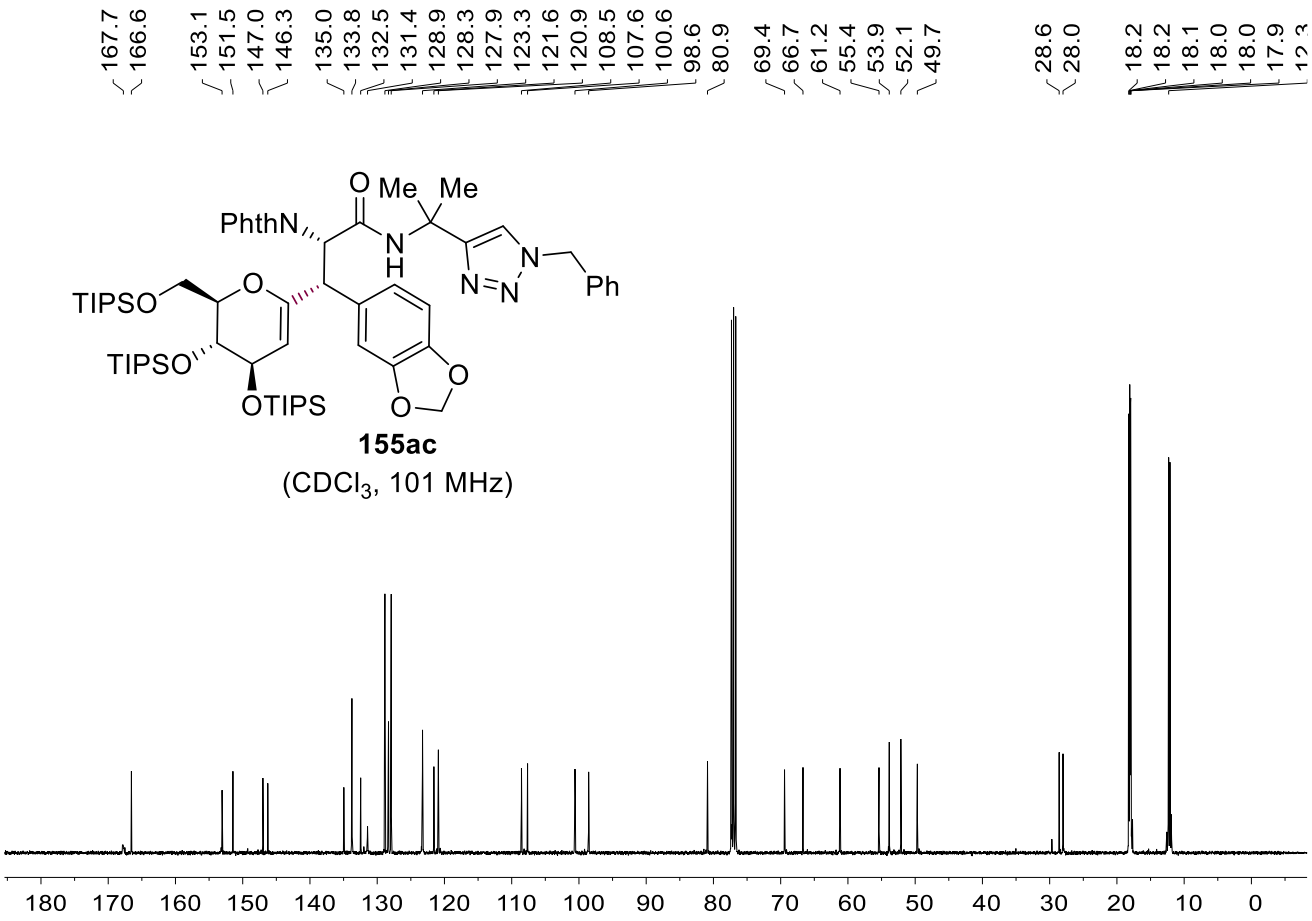
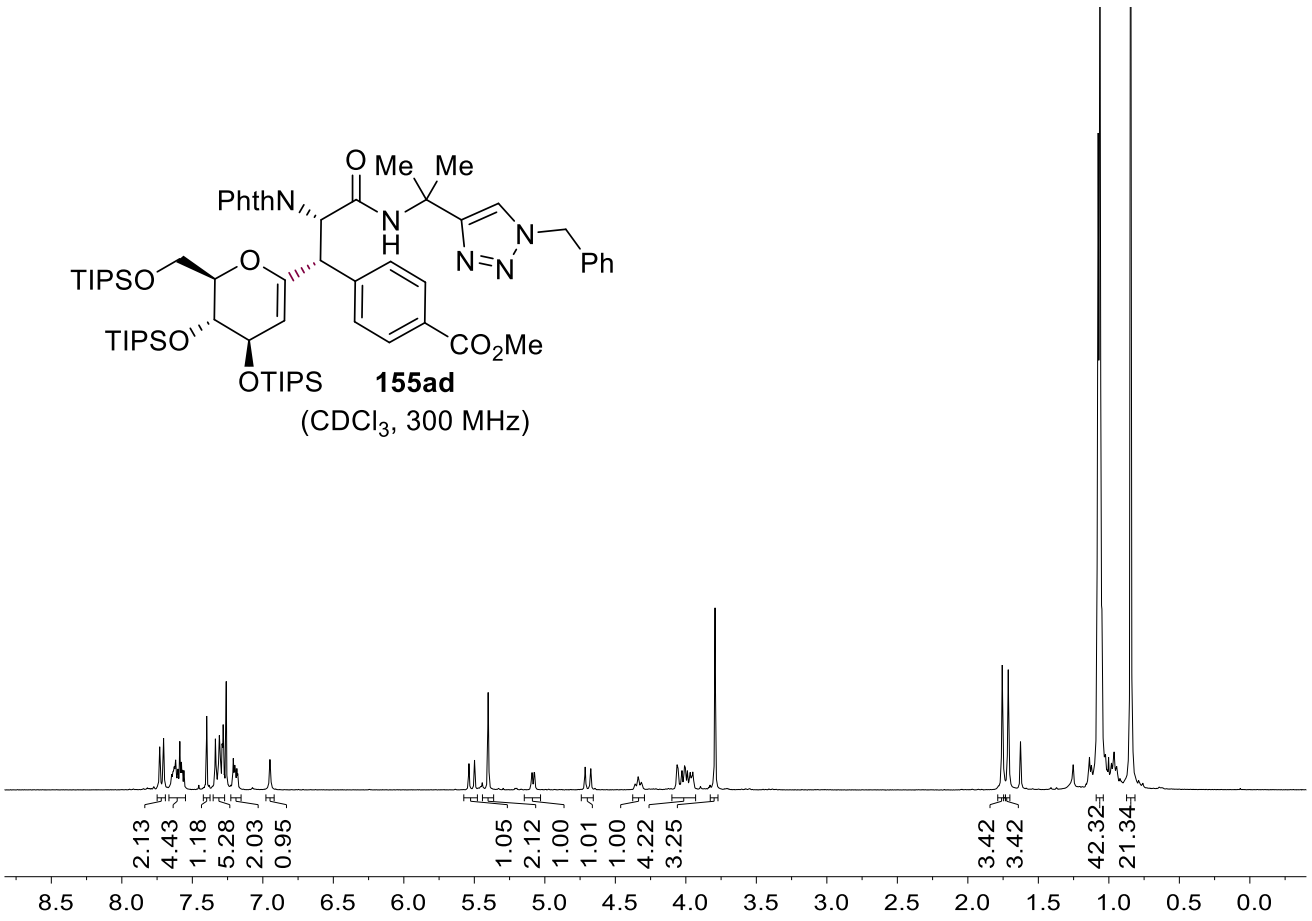


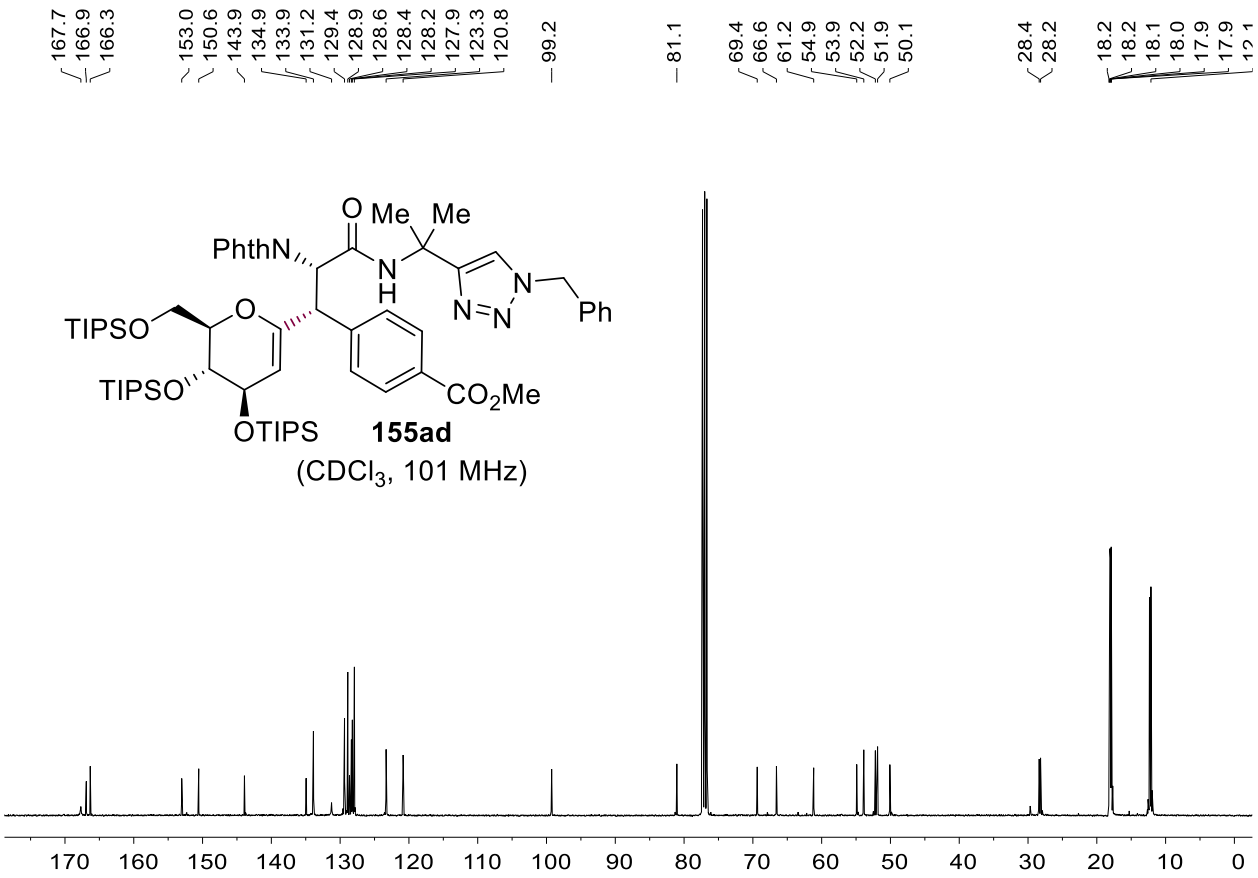
155ac

($CDCl_3$, 101 MHz)



155ad

($CDCl_3$, 300 MHz)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166.9
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143.9
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133.9
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128.9
128.6
128.4
128.2
127.9
123.3
120.8
99.2
81.1
69.4
66.6
61.2
54.9
53.9
52.2
51.9
50.1
28.4
28.2
18.2
18.2
18.1
18.0
17.9
17.9
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Me
Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
CO2Me
OTIPS
155ad
(CDCl3, 101 MHz)
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130
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70
60
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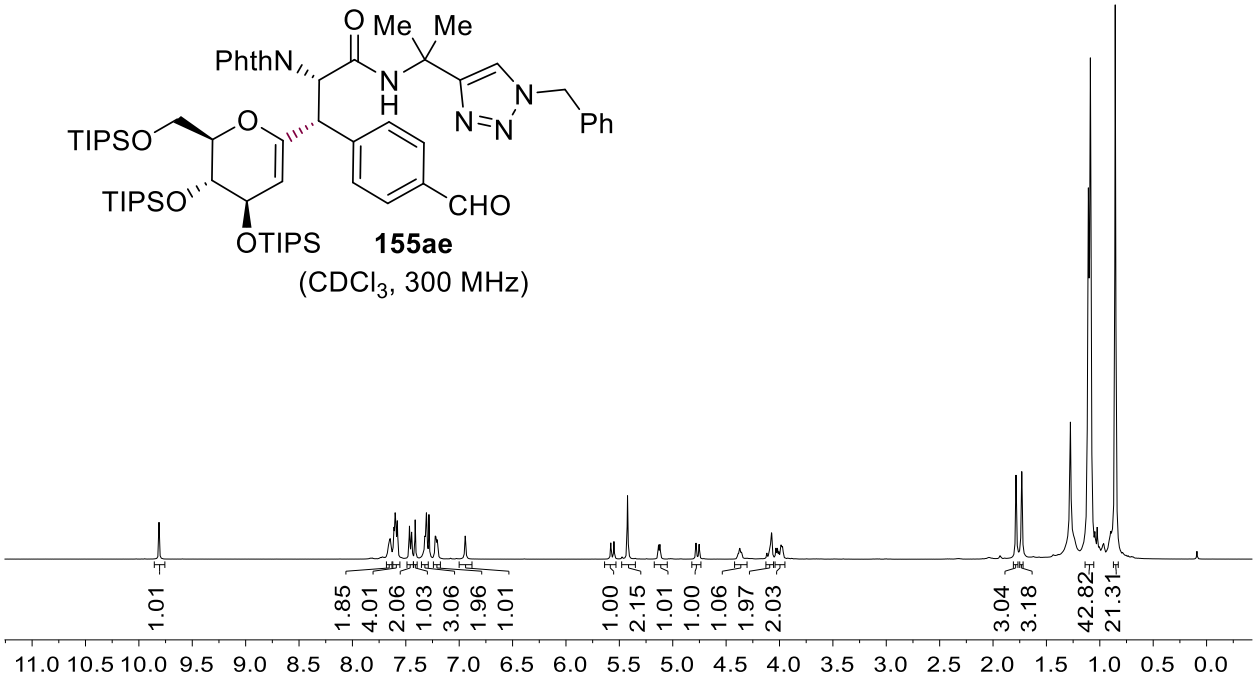
10
0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Me
Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
CHO
OTIPS
155ae
(CDCl3, 300 MHz)
1.01
1.85
4.01
2.06
1.03
3.06
1.96
1.01
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2.15
1.01
1.00
1.06
1.97
2.03
3.04
3.18
42.82
21.31
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
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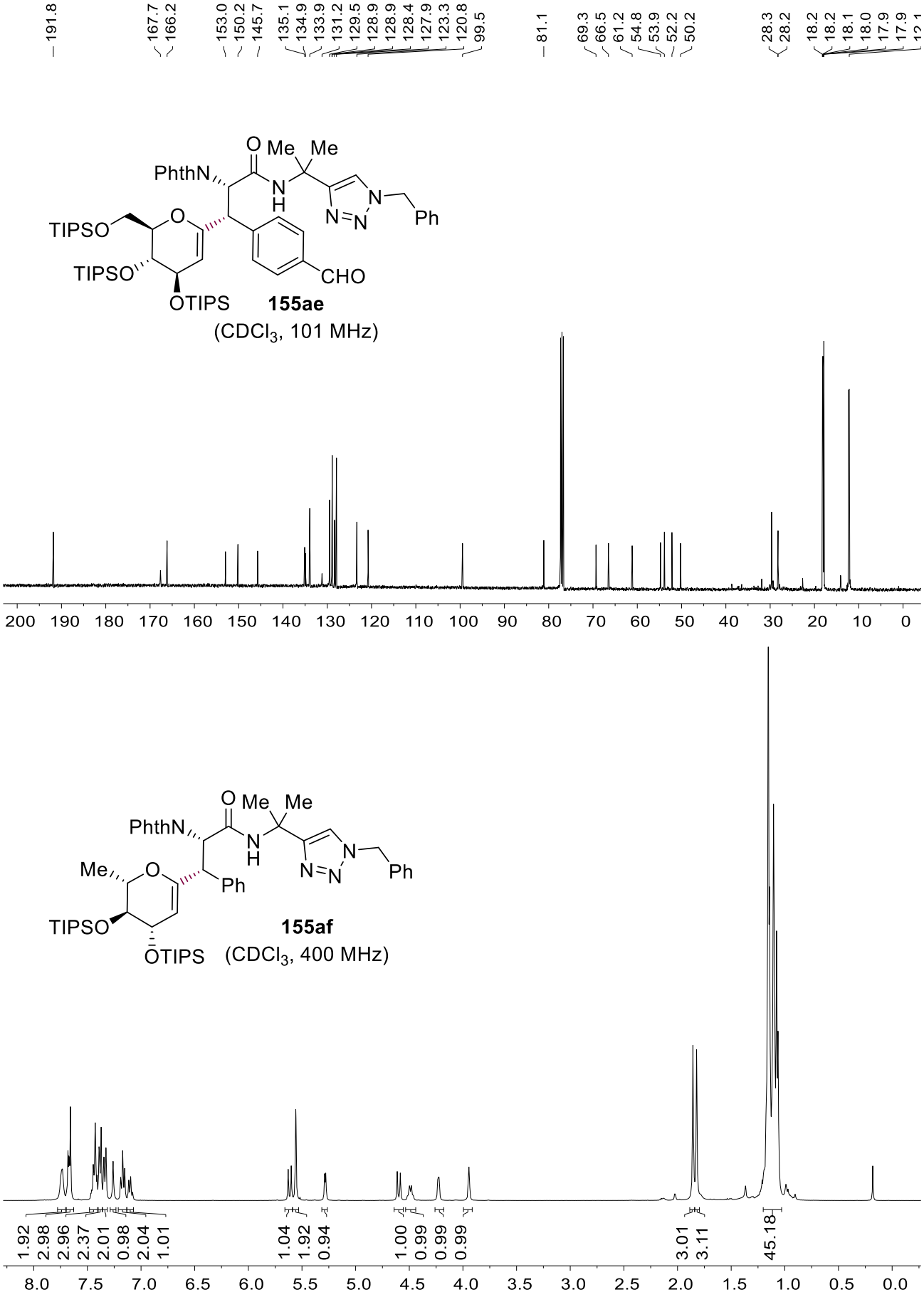
2.0
1.5
1.0
0.5
0.0


191.8
167.7
166.2
153.0
150.2
145.7
135.1
134.9
133.9
131.2
129.5
128.9
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128.4
127.9
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120.8
99.5
81.1
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61.2
54.8
53.9
52.2
50.2
28.3
28.2
18.2
18.2
18.1
18.0
17.9
17.9
PhthN
O
Me
Me
N
H
N
N=N
Ph
TIPSO
O
TIPSO
CHO
OTIPS
155ae
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
PhthN
O
Me
Me
N
H
N
N=N
Ph
Me
O
Ph
TIPSO
OTIPS
155af
(CDCl3, 400 MHz)
1.92
2.98
2.96
2.37
2.01
0.98
2.04
1.01
1.04
1.92
0.94
1.00
0.99
0.99
0.99
3.01
3.11
45.18
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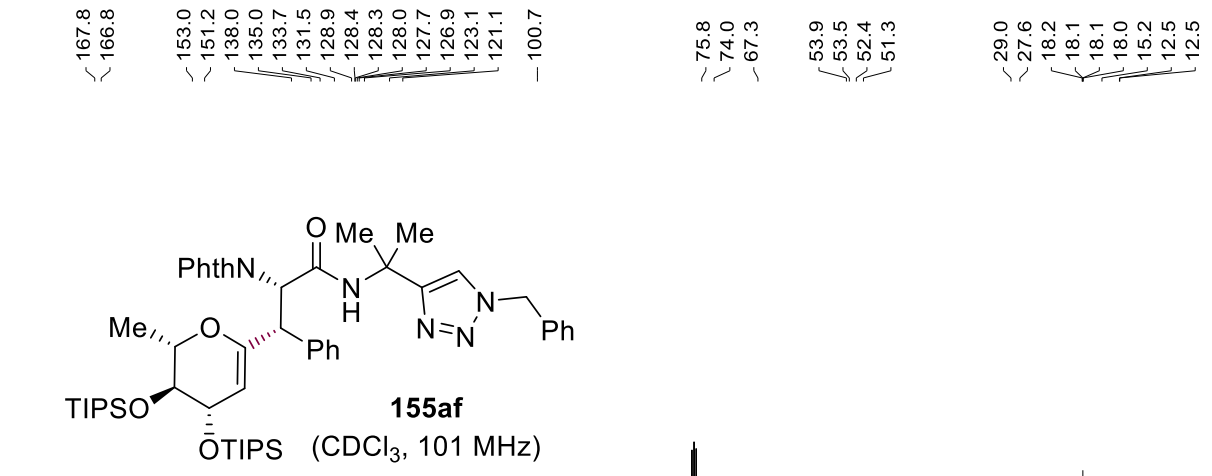
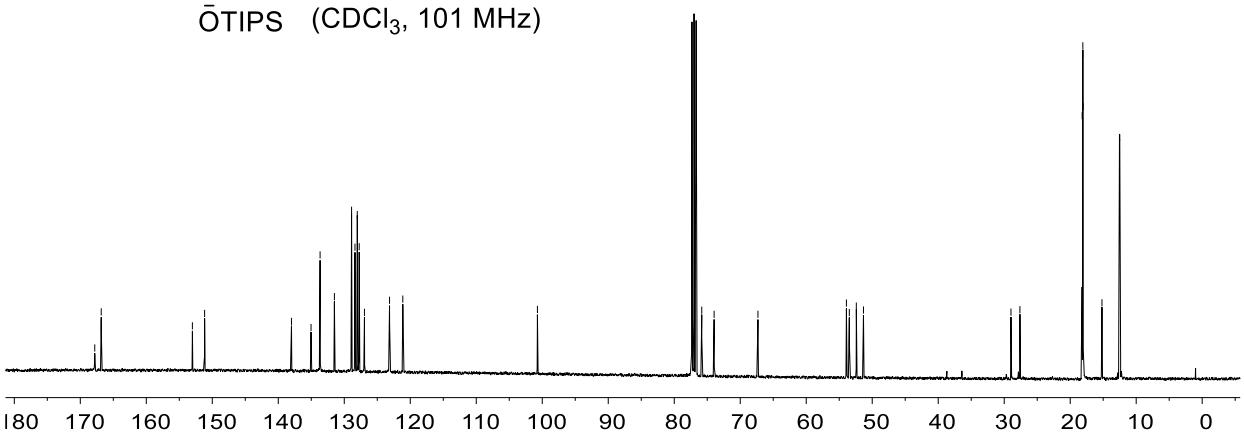
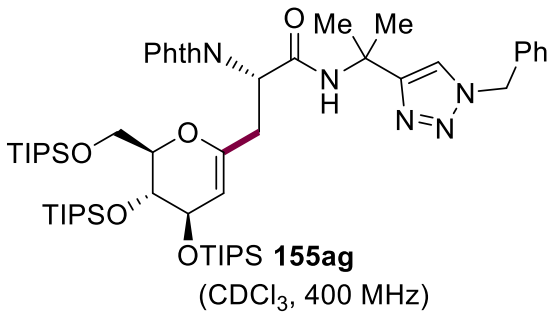
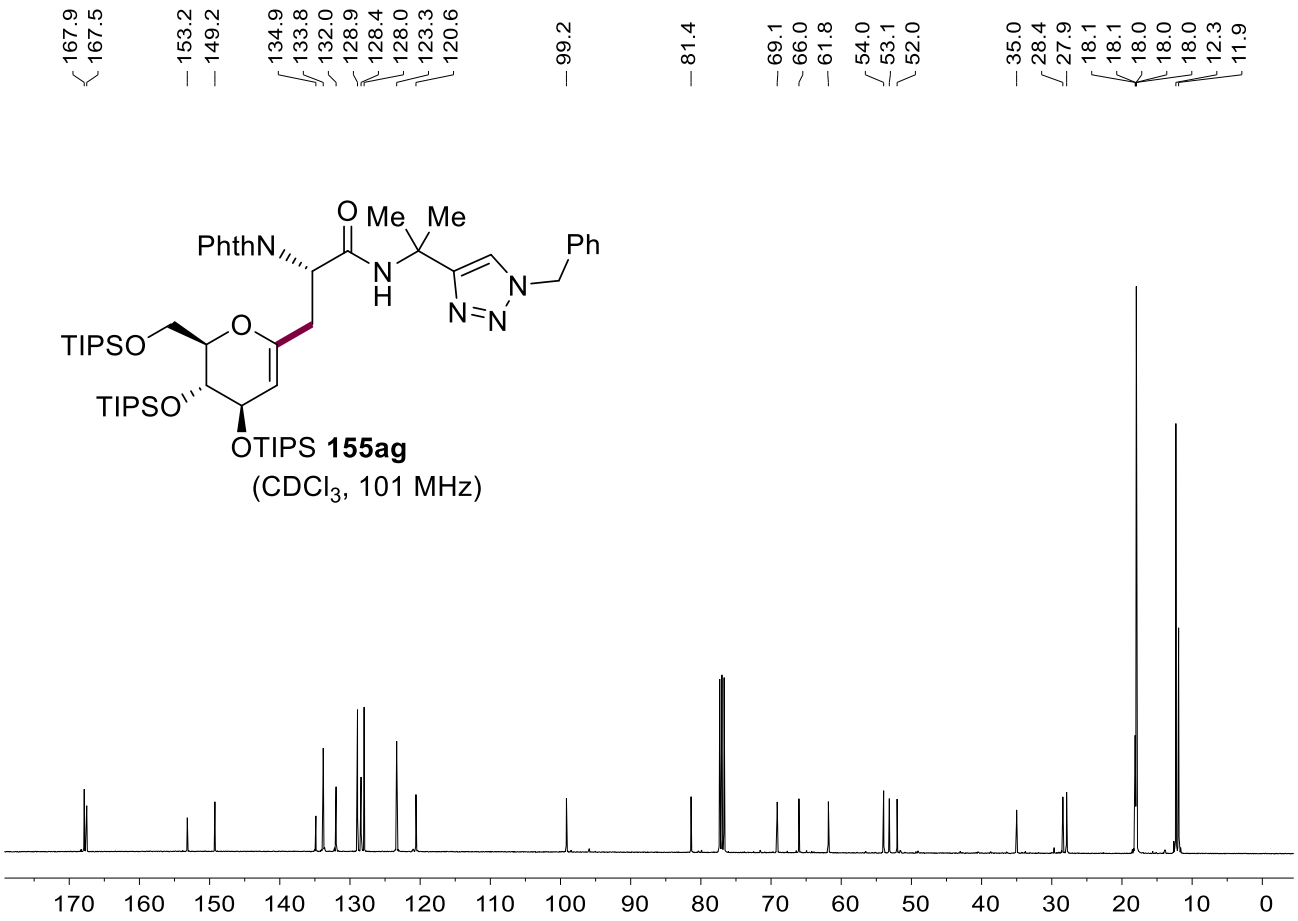


155af
($CDCl_3$, 101 MHz)





155ag
($CDCl_3$, 400 MHz)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132.0
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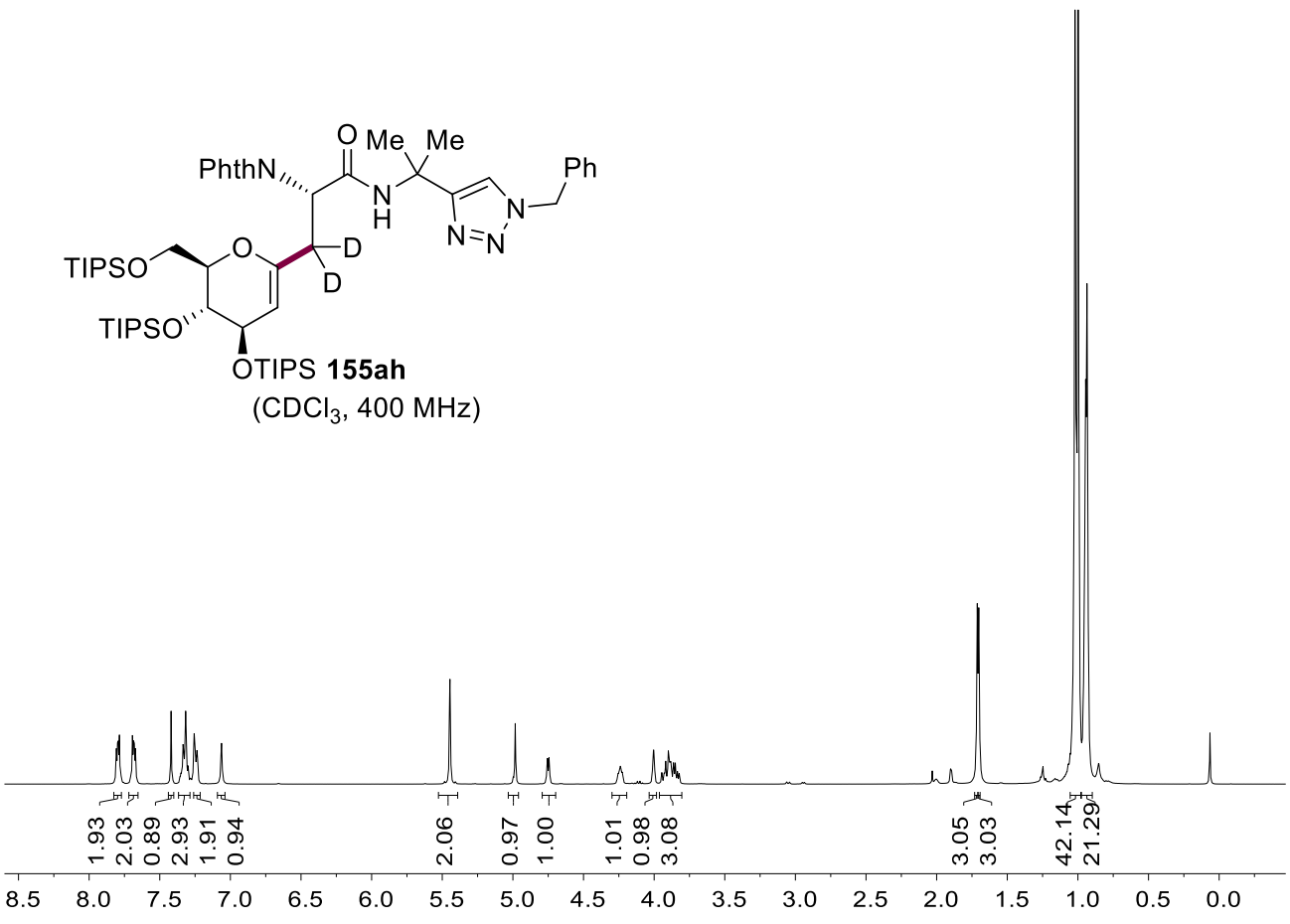
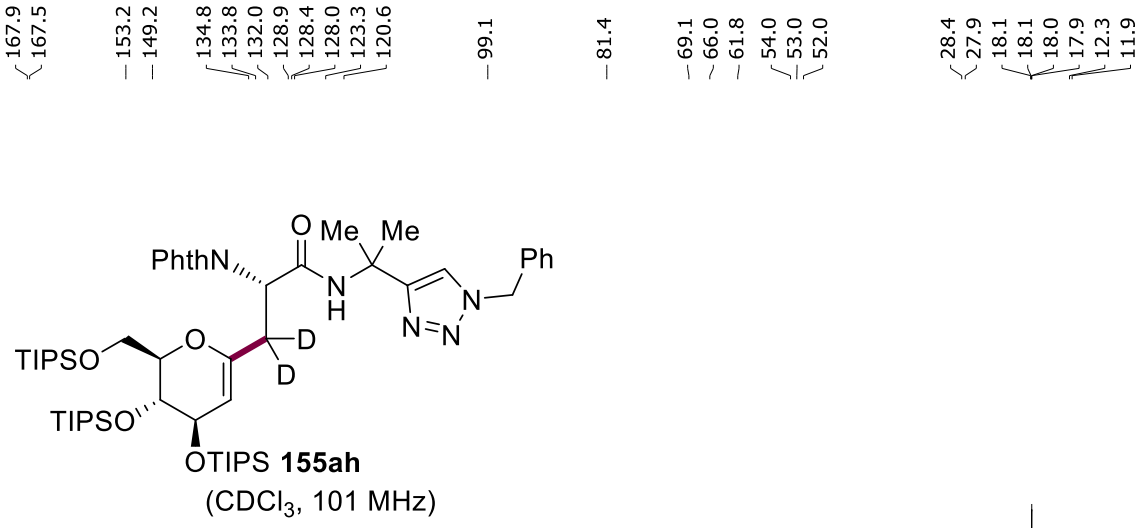
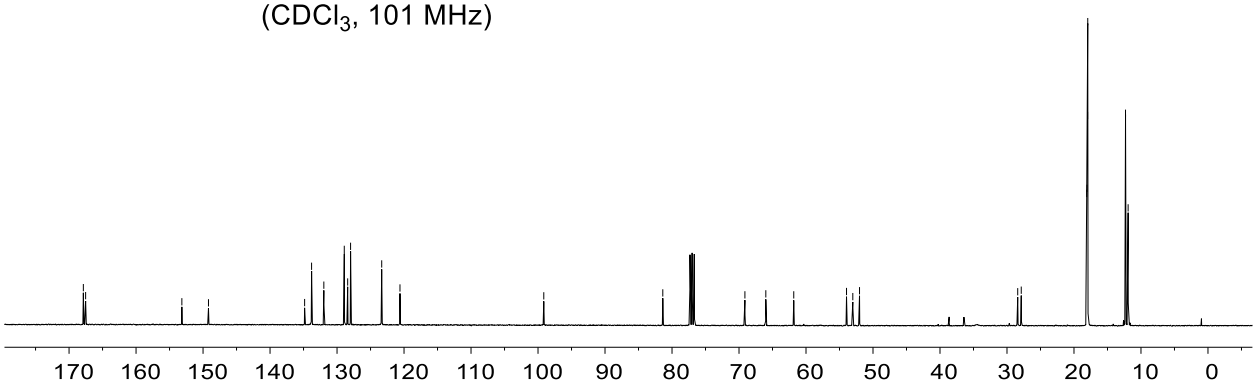
123.3
120.6
99.2
81.4
69.1
66.0
61.8
54.0
53.1
52.0
35.0
28.4
27.9
18.1
18.1
18.0
18.0
18.0
12.3
11.9
O
Me
Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
OTIPS **155ag**
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

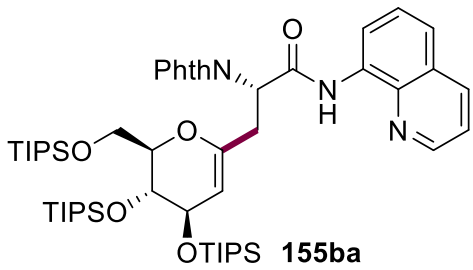

O
Me
Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
D
D
TIPSO
OTIPS **155ah**
(CDCl3, 400 MHz)
1.93
2.03
0.89
2.93
1.91
0.94
2.06
0.97
1.00
1.01
0.98
3.08
3.05
3.03
42.14
21.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



155ah

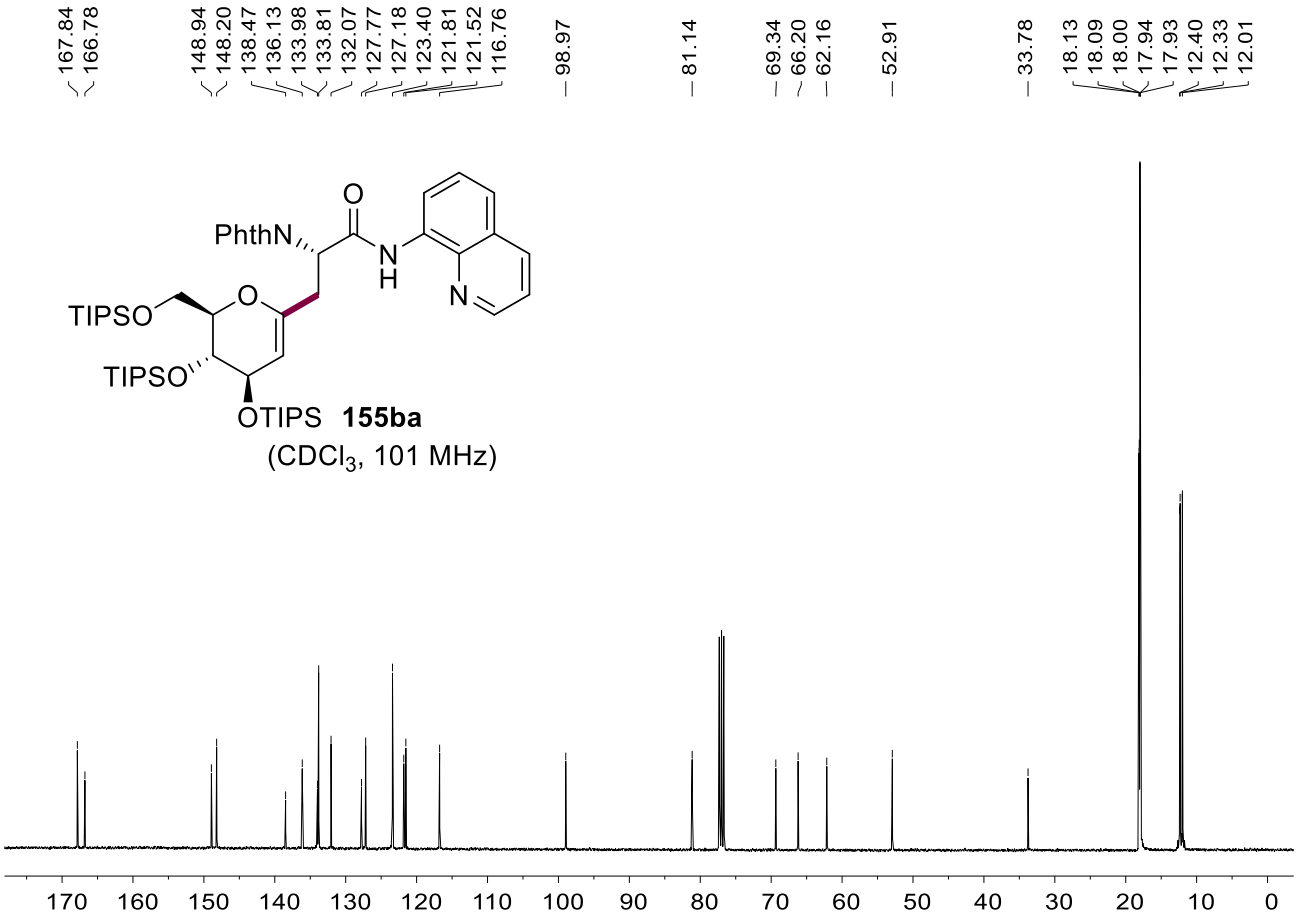
($CDCl_3$, 101 MHz)





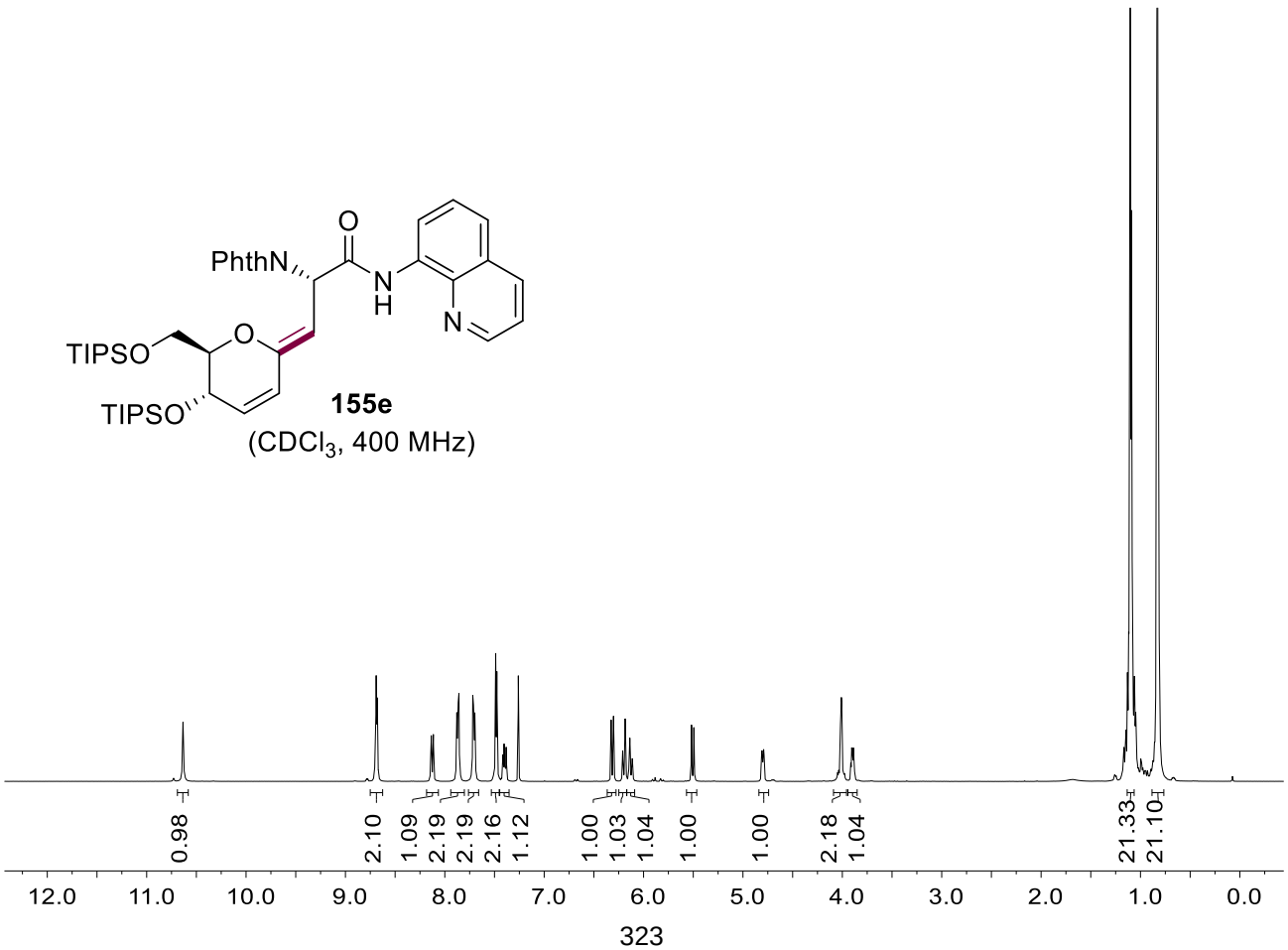
155ba

($CDCl_3$, 400 MHz)



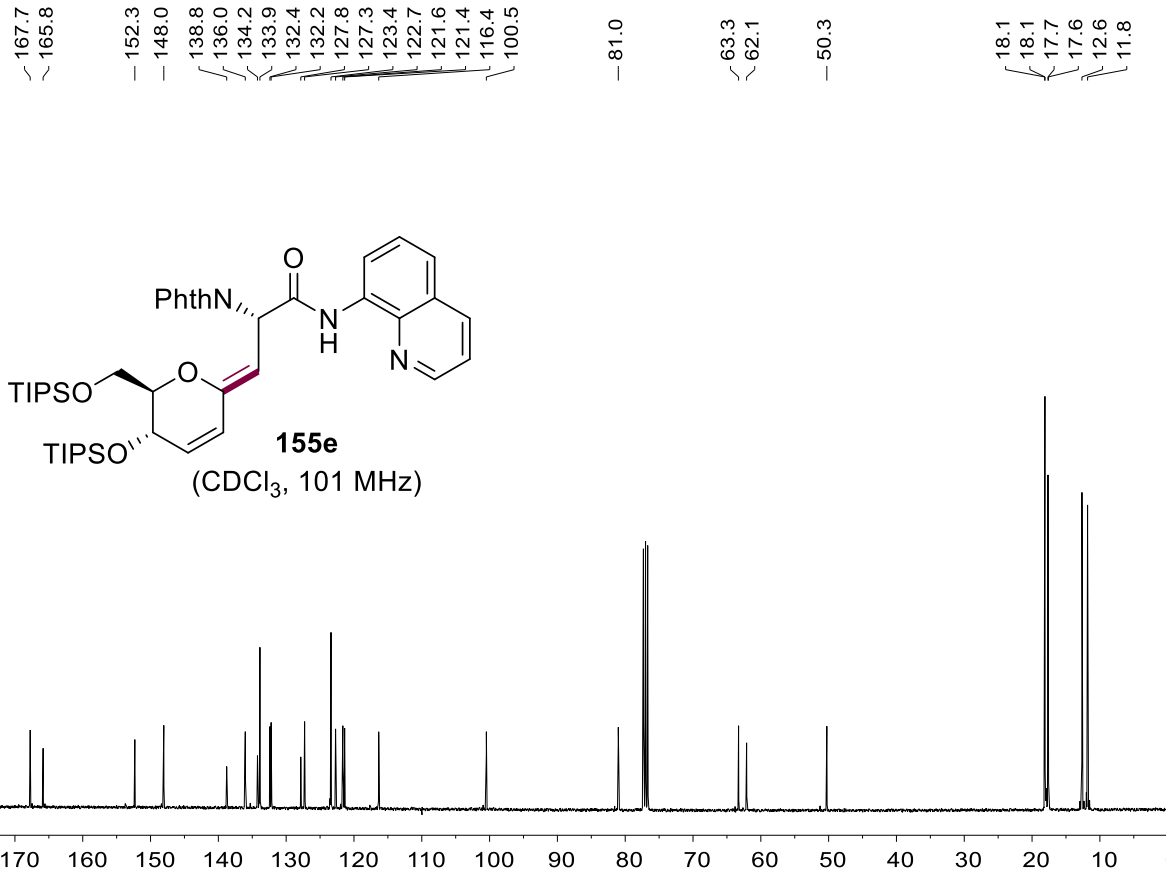
155ba

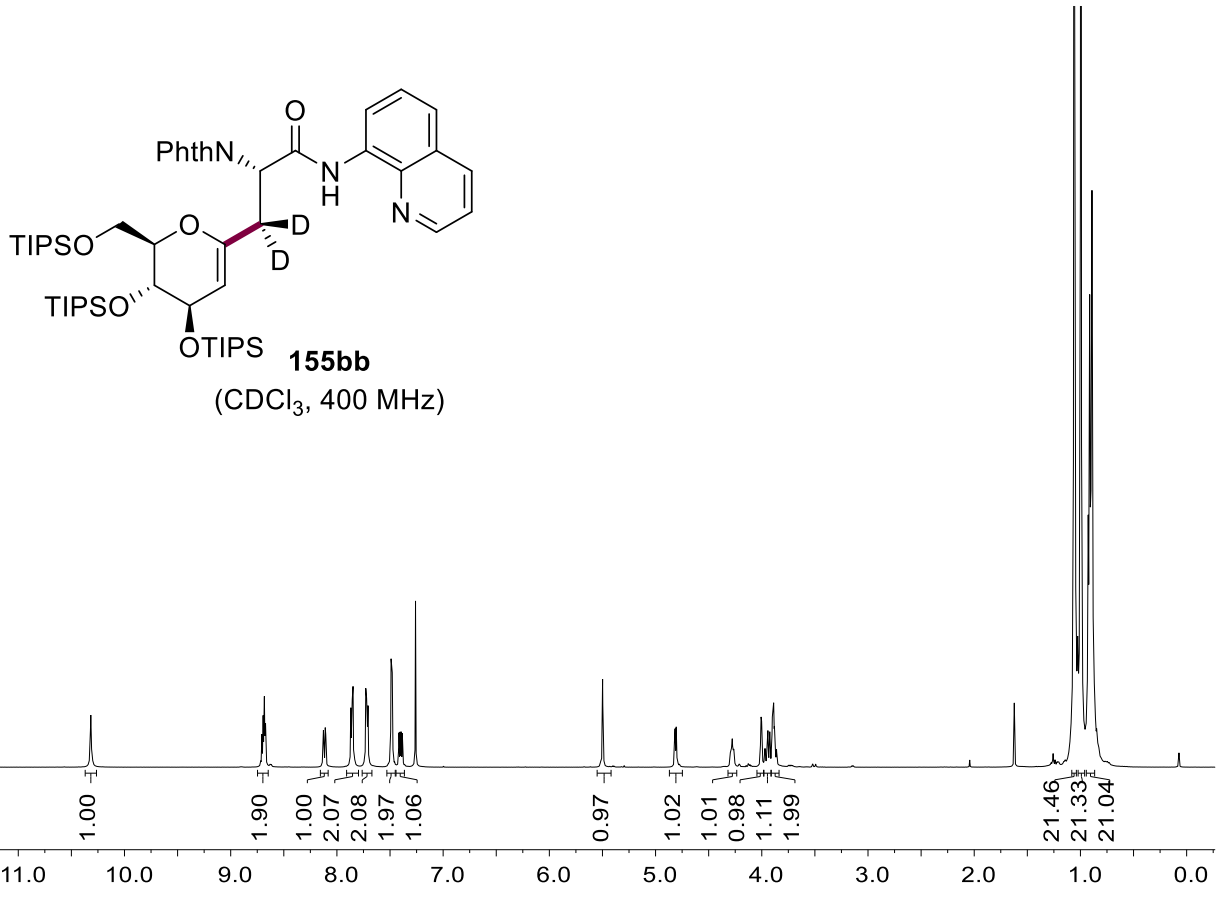
($CDCl_3$, 101 MHz)

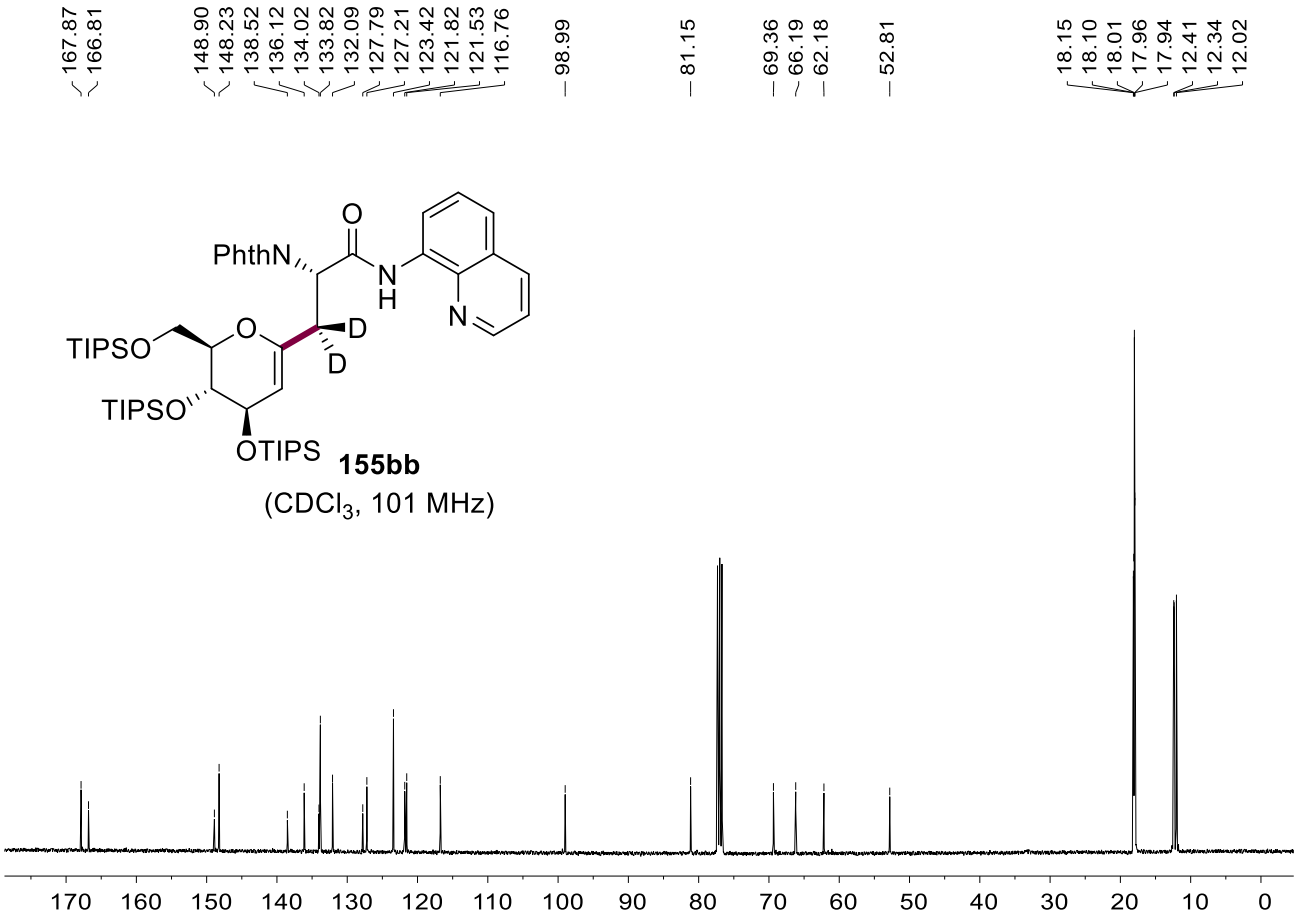


155e

($CDCl_3$, 400 MHz)

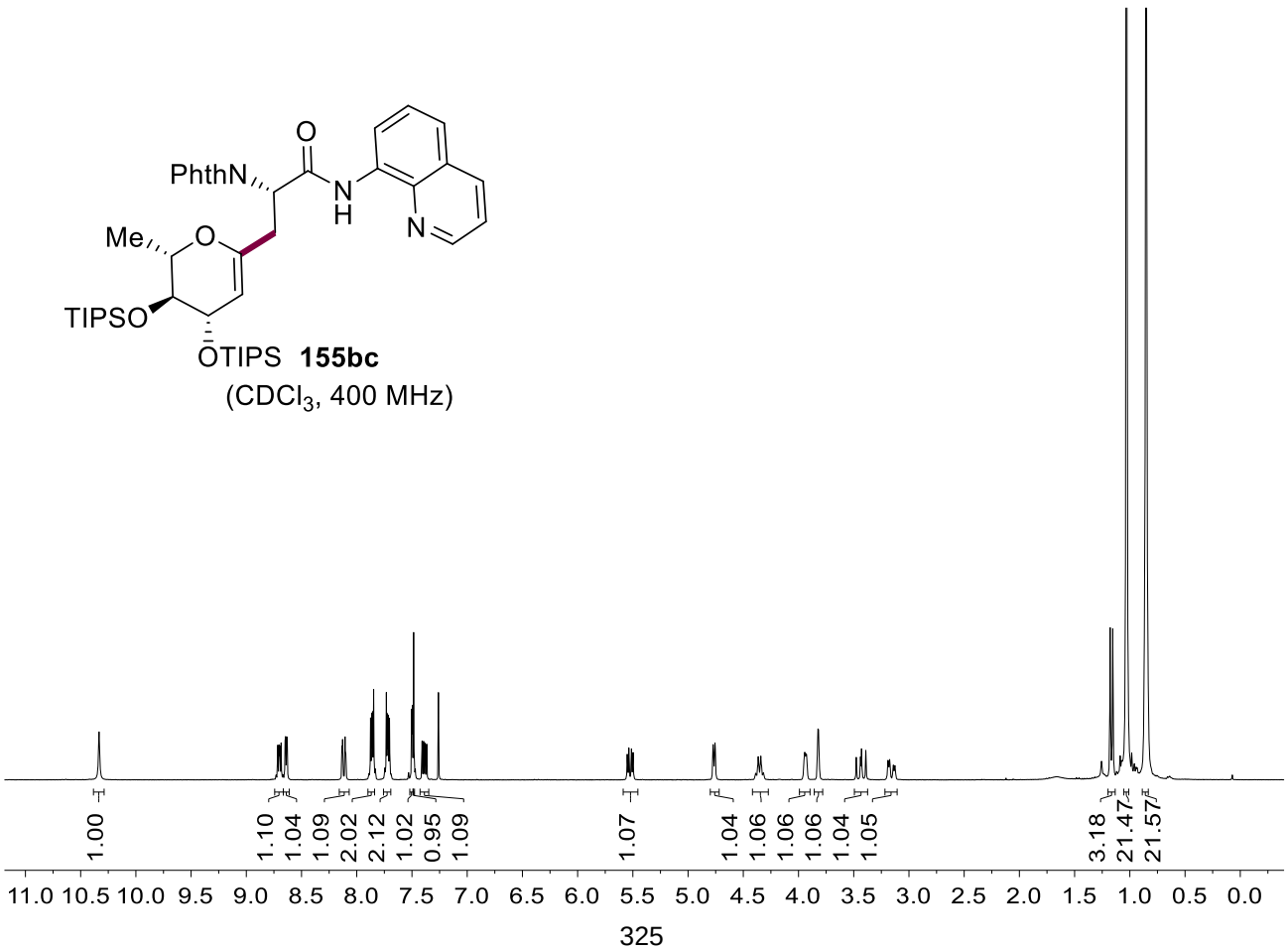

167.7
165.8
152.3
148.0
138.8
136.0
134.2
133.9
132.4
132.2
127.8
127.3
123.4
122.7
121.6
121.4
116.4
100.5
81.0
63.3
62.1
50.3
18.1
18.1
17.7
17.6
12.6
11.8
PhthN
O
N
H
N
TIPSO
O
TIPSO
155e
(CDCl3, 101 MHz)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


PhthN
O
N
H
N
D
D
TIPSO
O
TIPSO
OTIPS
155bb
(CDCl3, 400 MHz)
1.00
1.90
1.00
2.07
2.08
1.97
1.06
0.97
1.02
1.01
0.98
1.11
1.99
21.46
21.33
21.04
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0



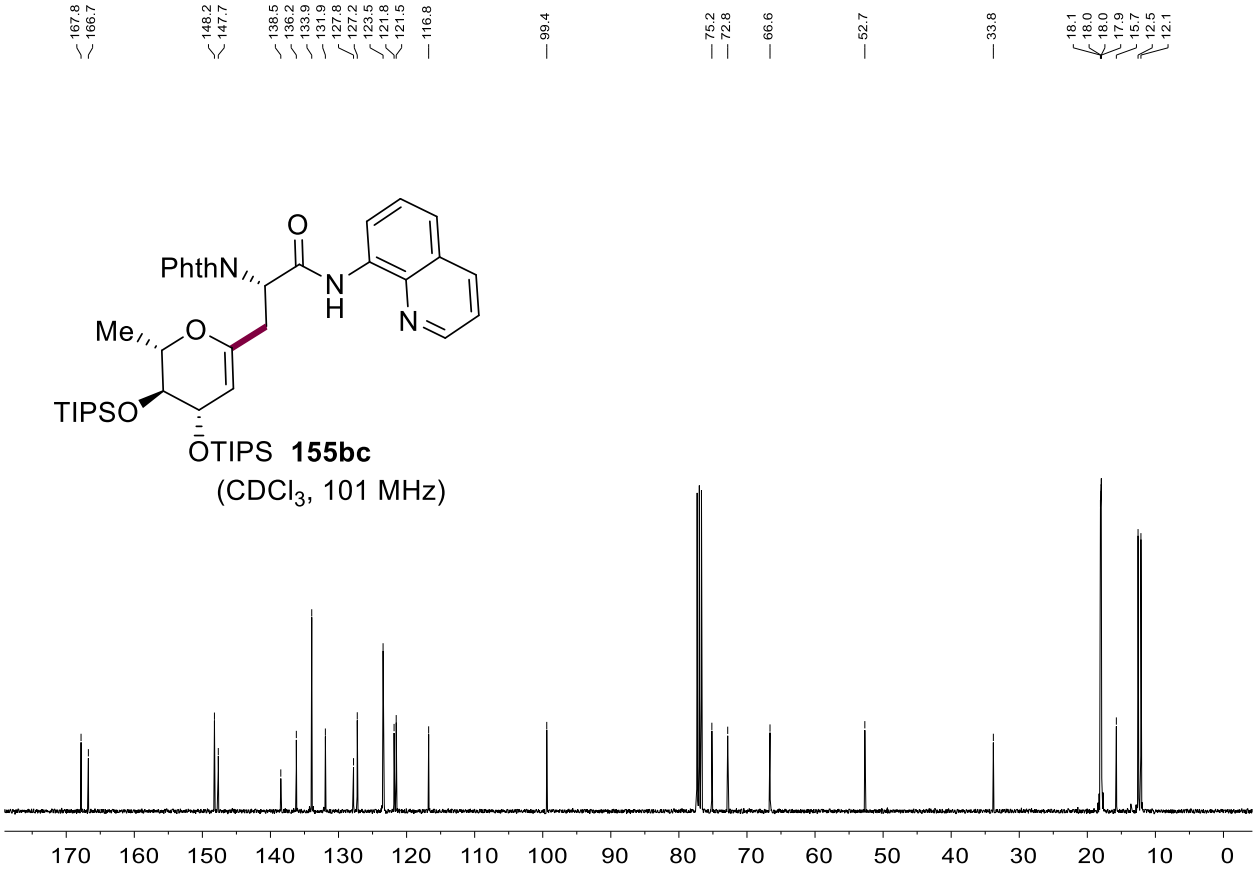
155bb

($CDCl_3$, 101 MHz)



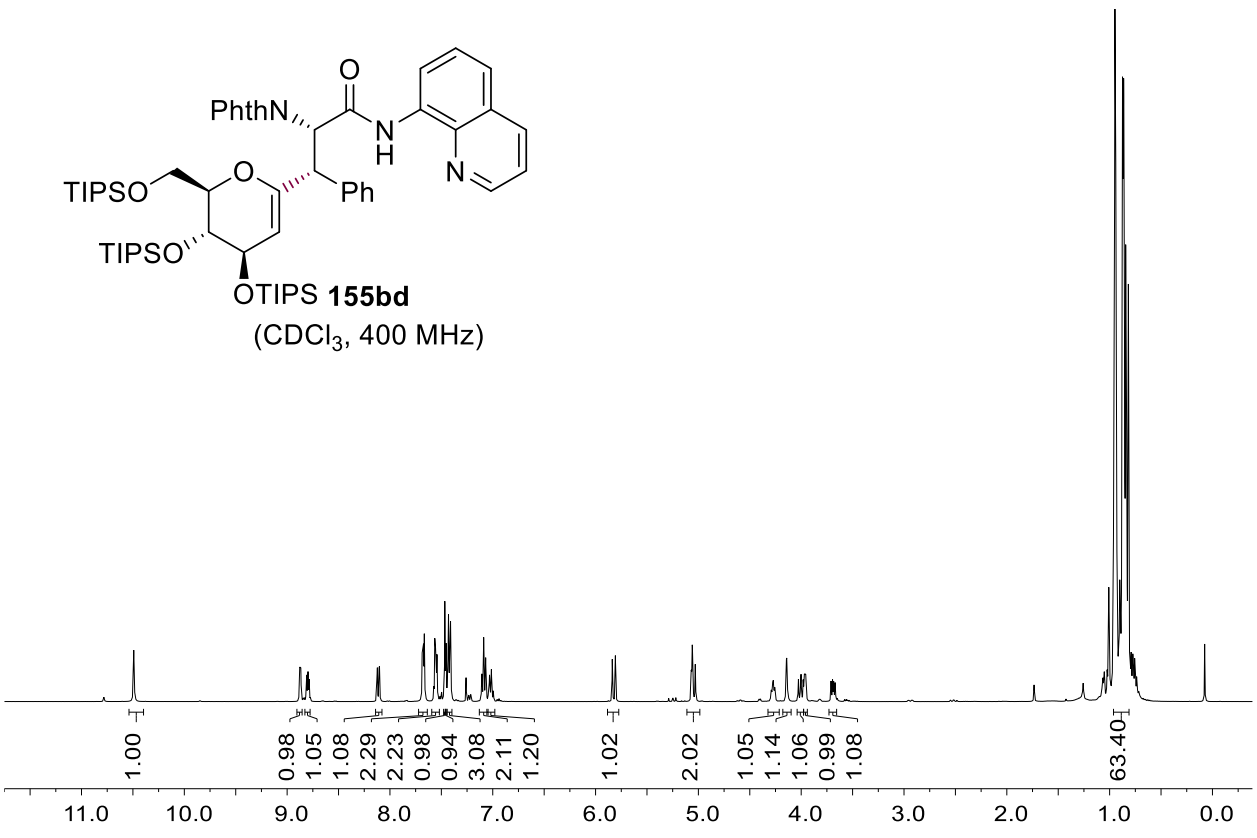
155bc

($CDCl_3$, 400 MHz)



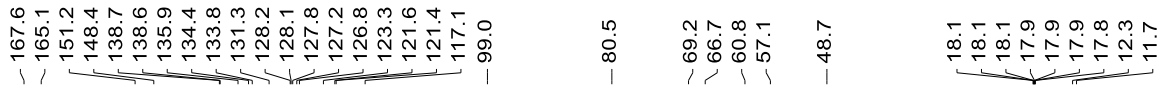
155bc

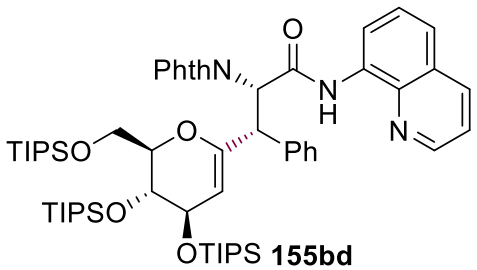
($CDCl_3$, 101 MHz)



155bd

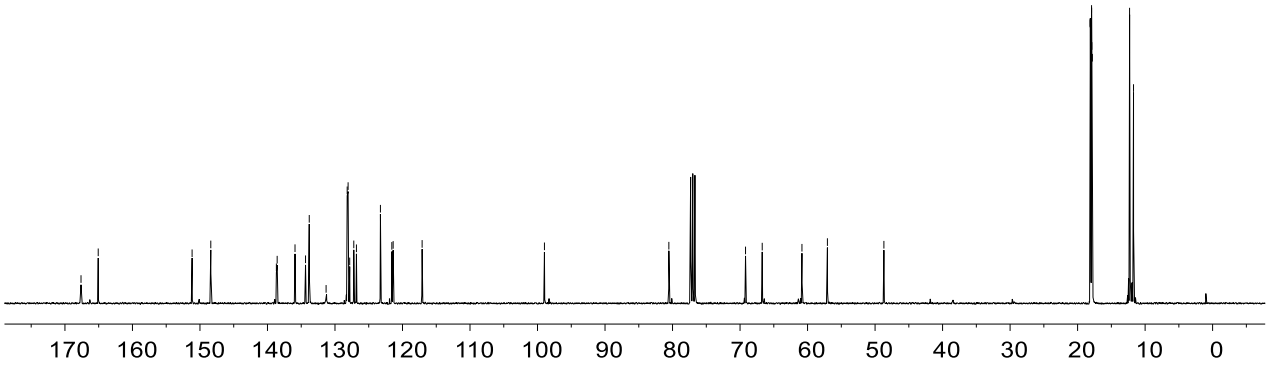
($CDCl_3$, 400 MHz)

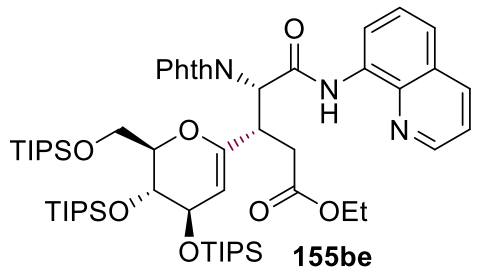




155bd

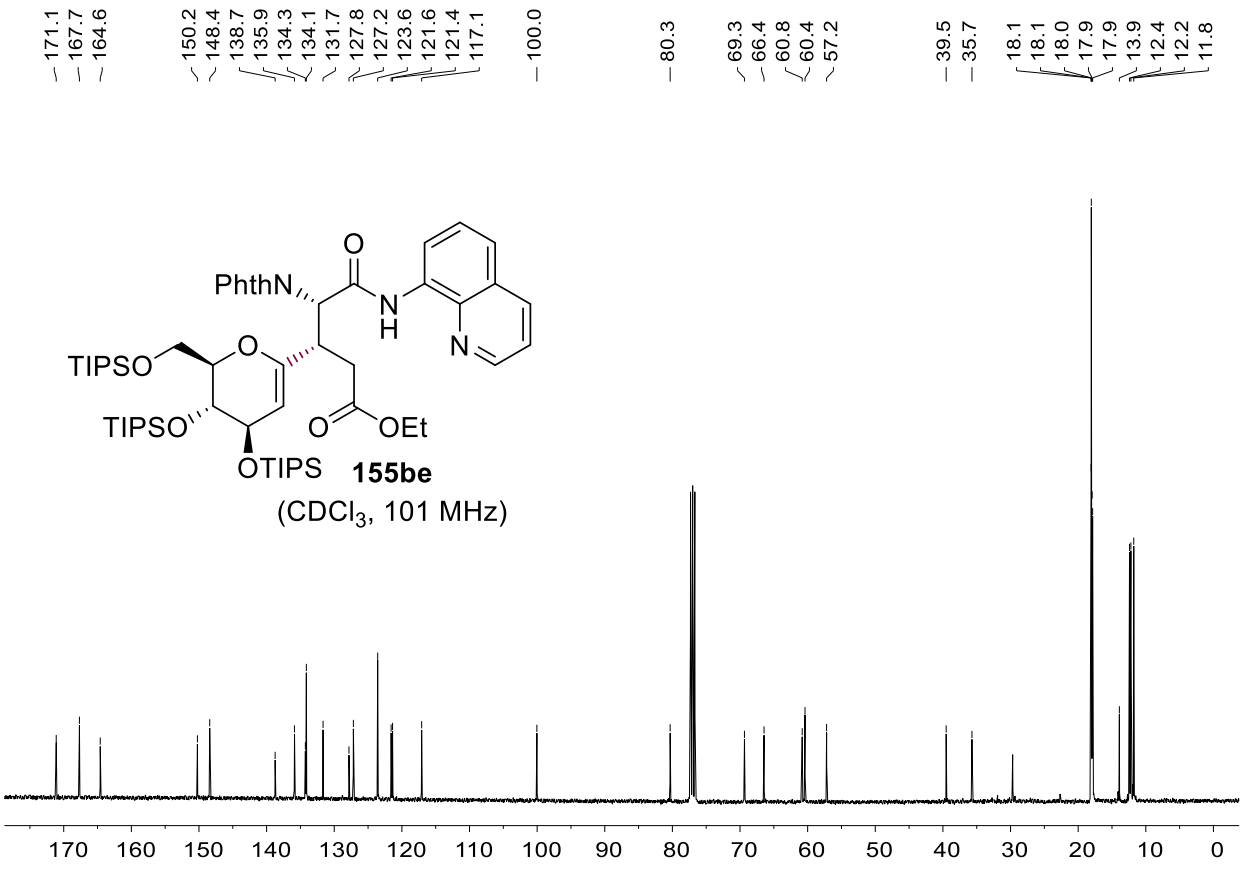
($CDCl_3$, 101 MHz)

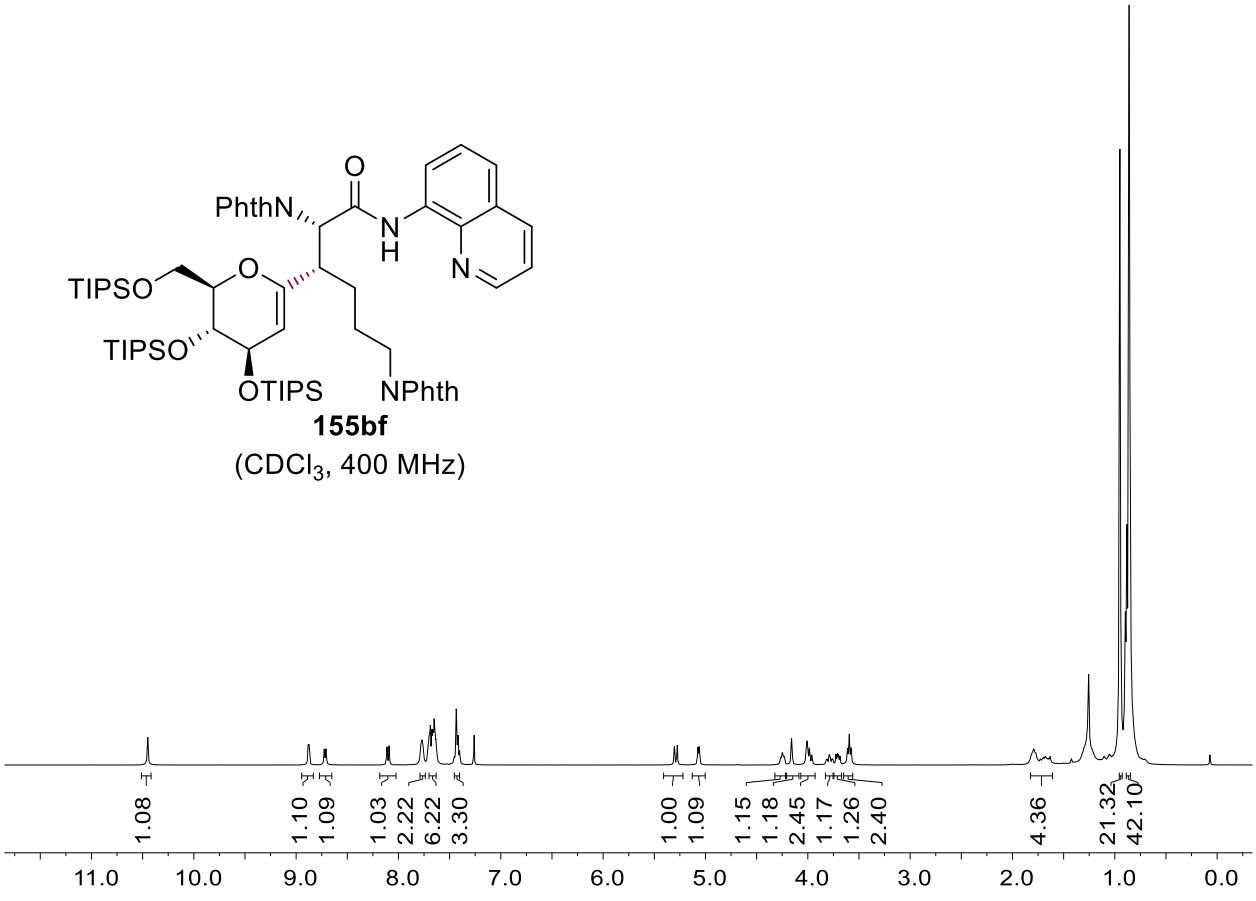


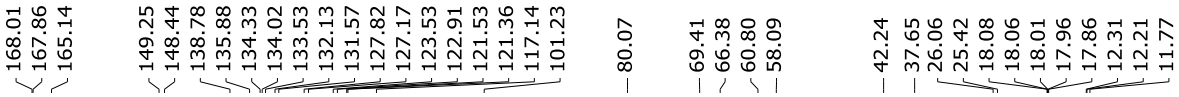


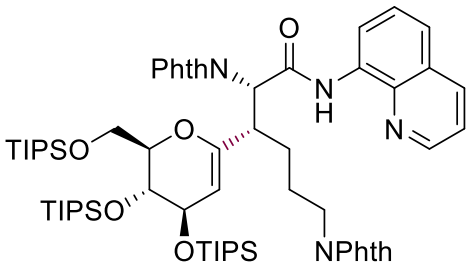
155be

($CDCl_3$, 400 MHz)


171.1
167.7
164.6
150.2
148.4
138.7
135.9
134.3
134.1
131.7
127.8
127.2
123.6
121.6
121.4
117.1
100.0
80.3
69.3
66.4
60.8
60.4
57.2
39.5
35.7
18.1
18.1
18.0
17.9
17.9
13.9
12.4
12.2
11.8
PhthN
O
N
H
N
TIPSO
O
TIPSO
O
OEt
OTIPS
155be
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

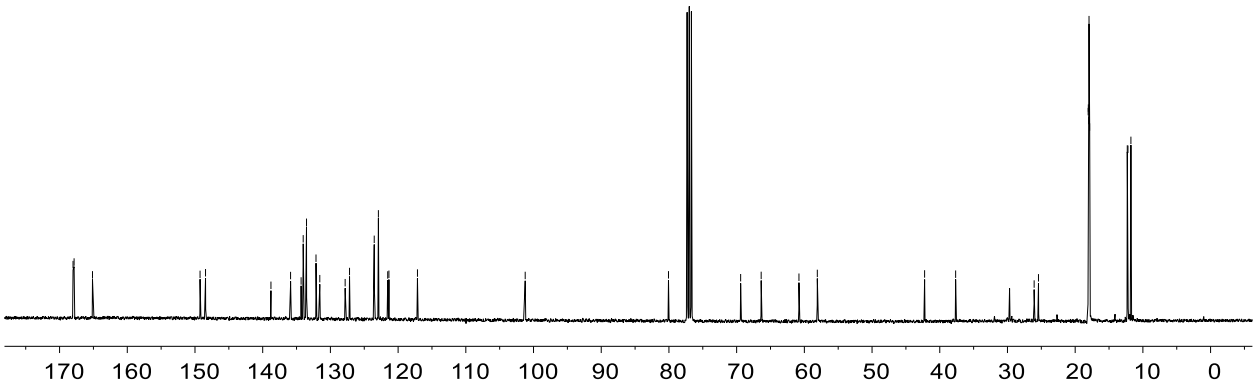

PhthN
O
N
H
N
TIPSO
O
TIPSO
OTIPS
NPhth
155bf
(CDCl3, 400 MHz)
1.08
1.10
1.09
1.03
2.22
6.22
3.30
1.00
1.09
1.15
1.18
2.45
1.17
1.26
2.40
4.36
21.32
42.10
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

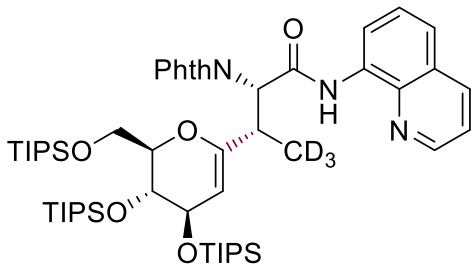




155bf

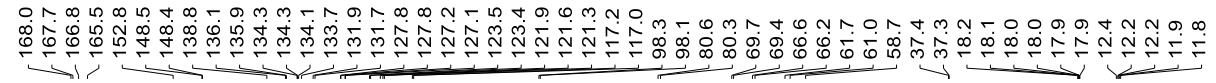
($CDCl_3$, 101 MHz)

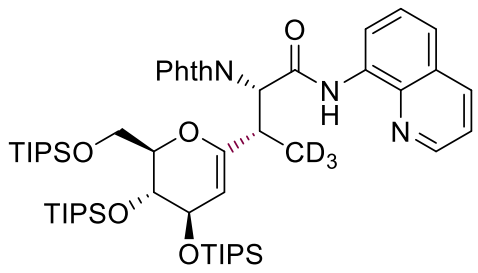




155bg

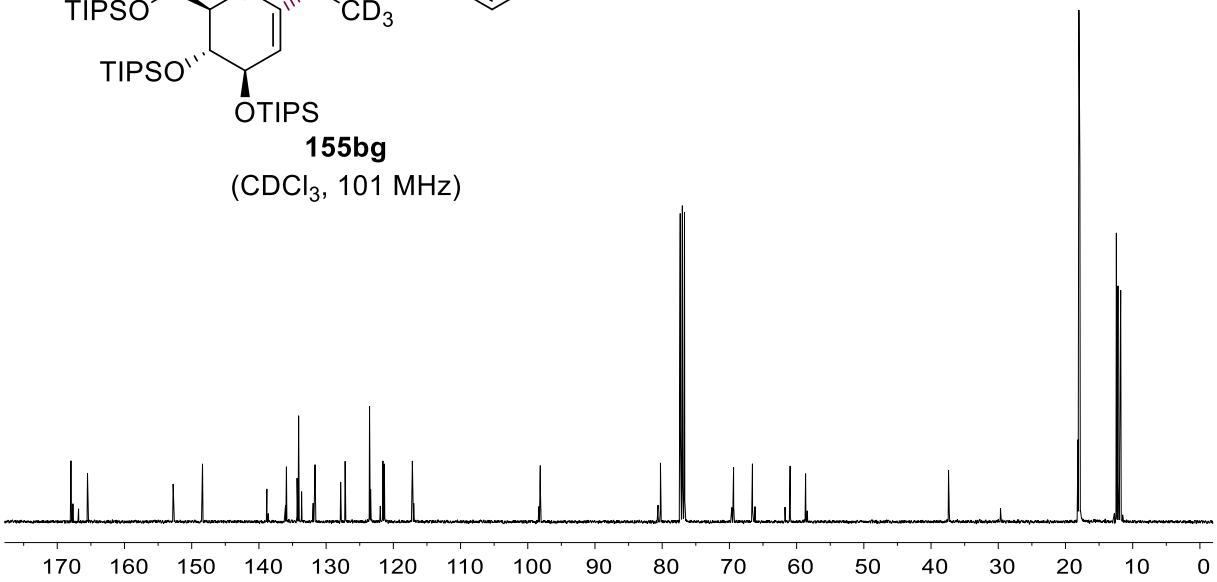
($CDCl_3$, 400 MHz)

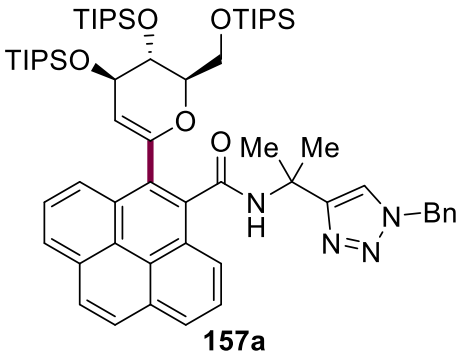




155bg

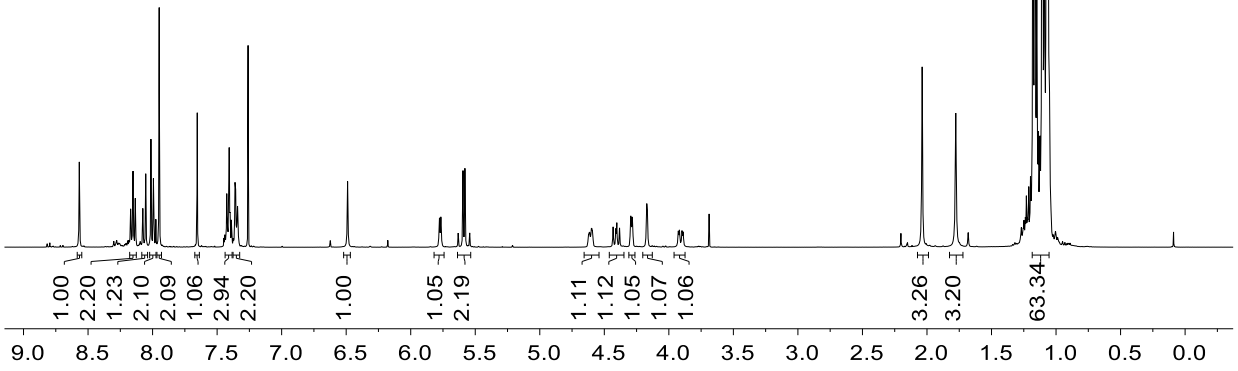
($CDCl_3$, 101 MHz)

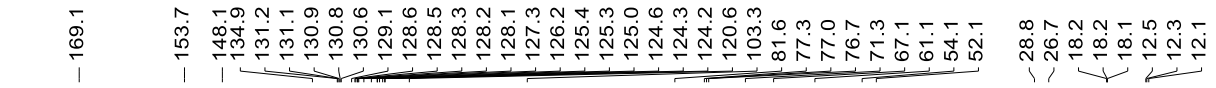


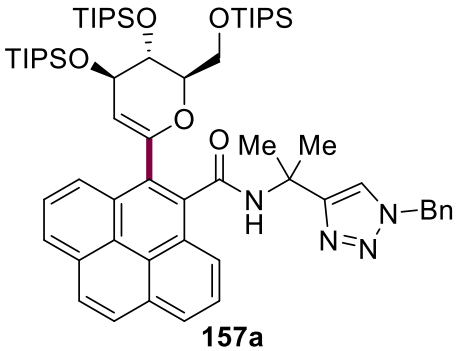


157a

($CDCl_3$, 400 MHz)

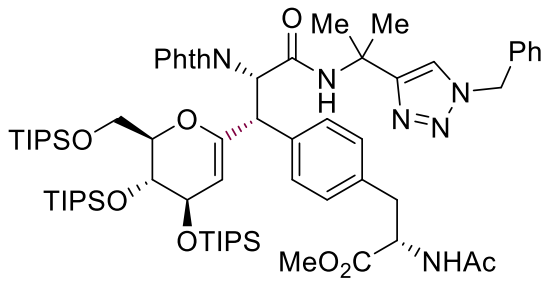






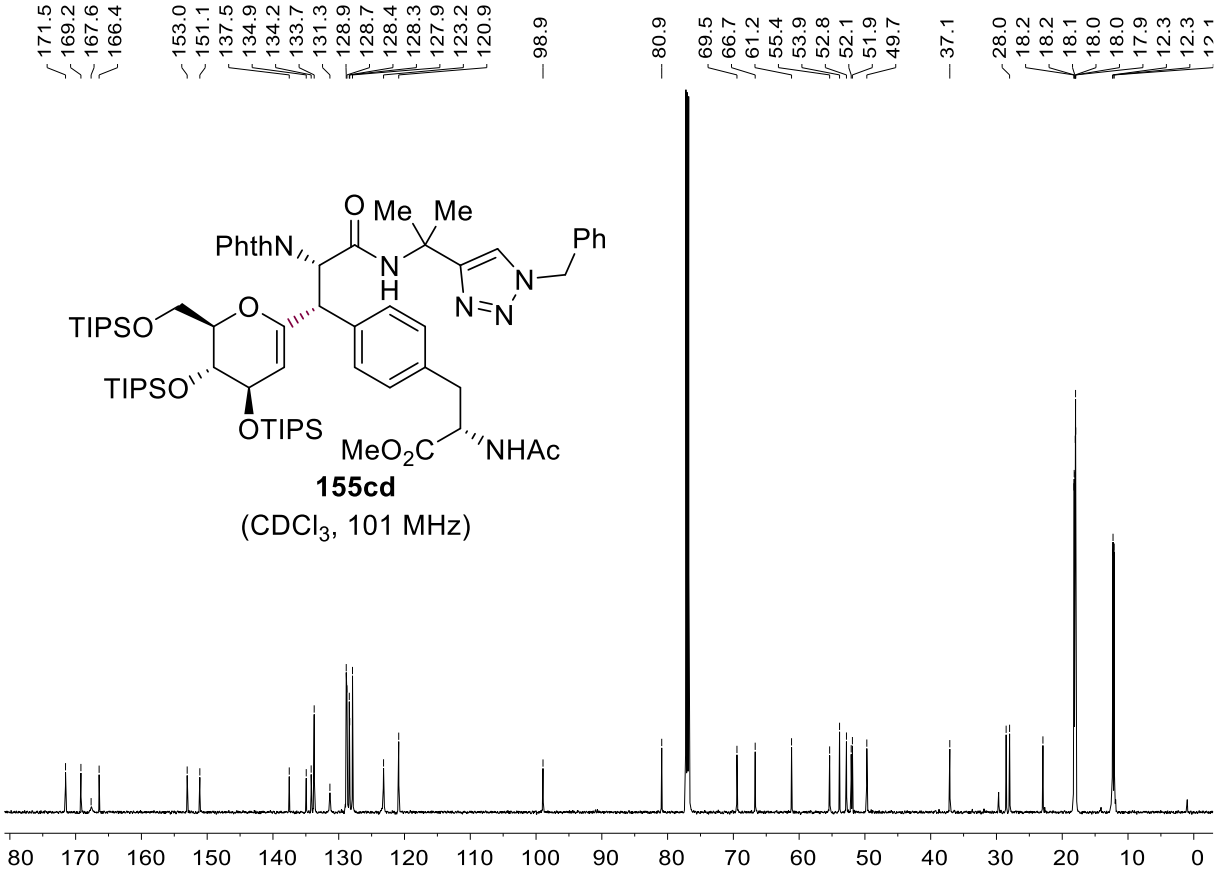
157a

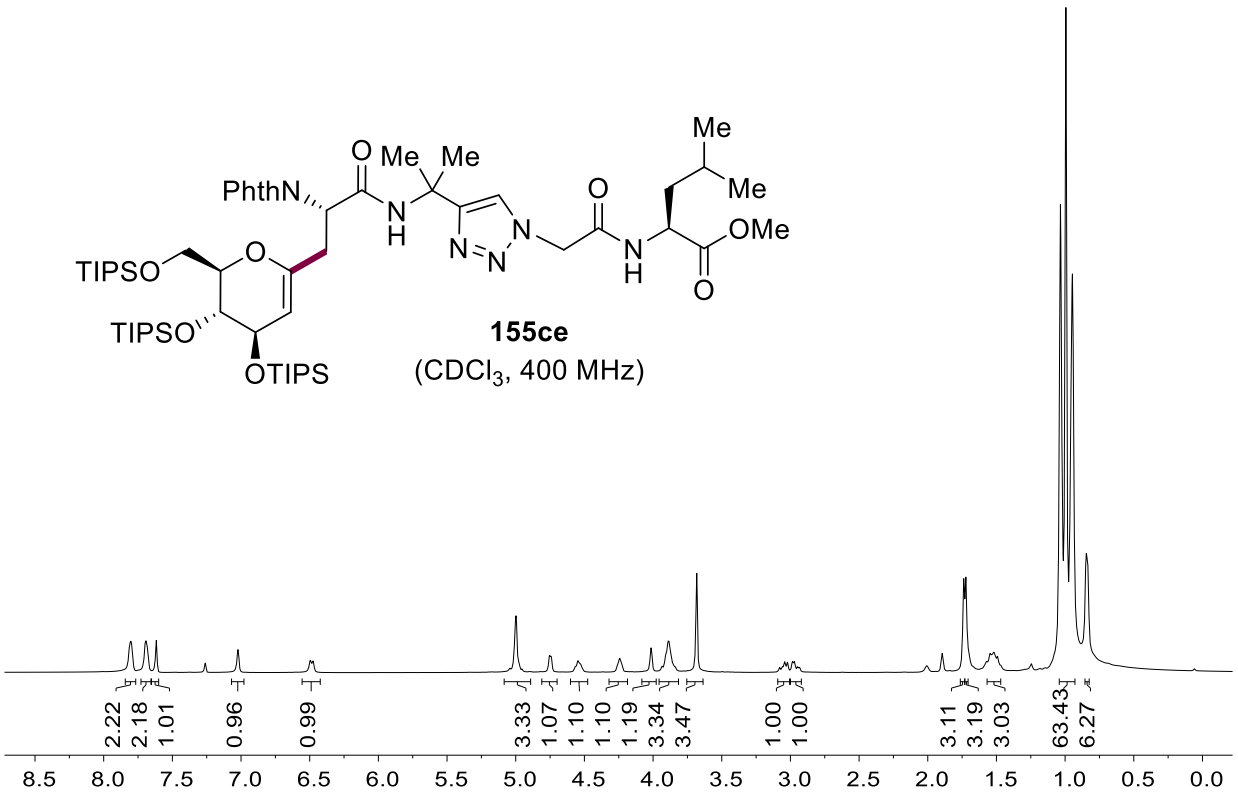
($CDCl_3$, 101 MHz)

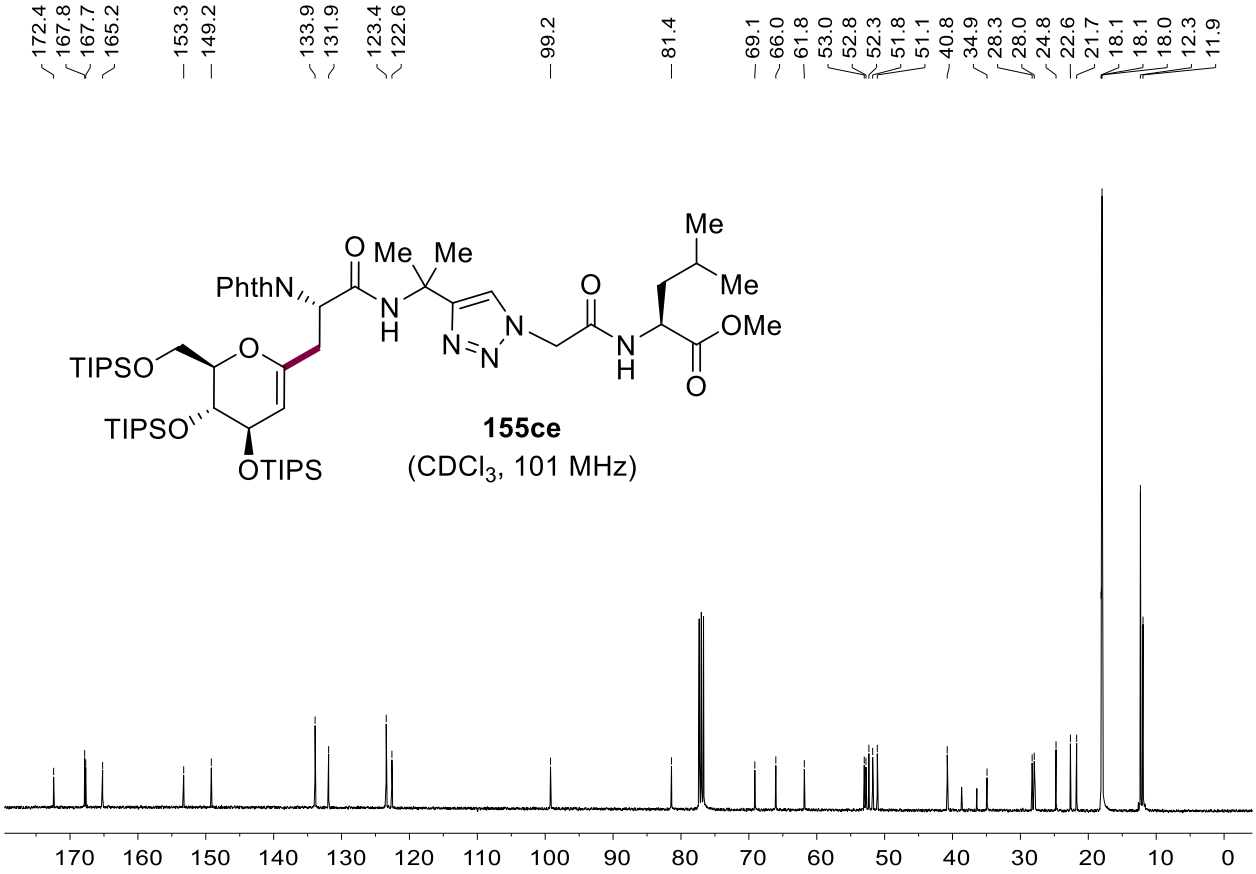


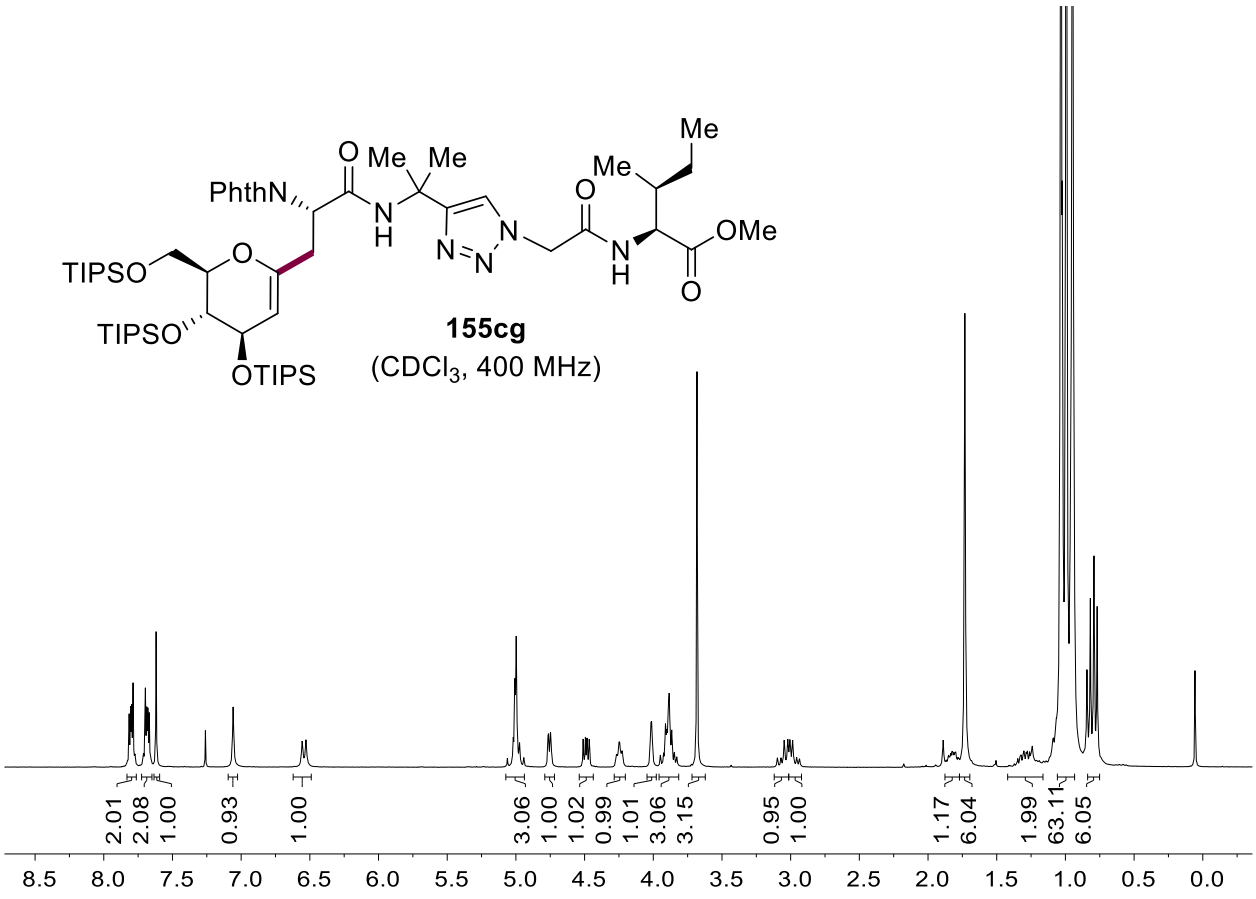
155cd

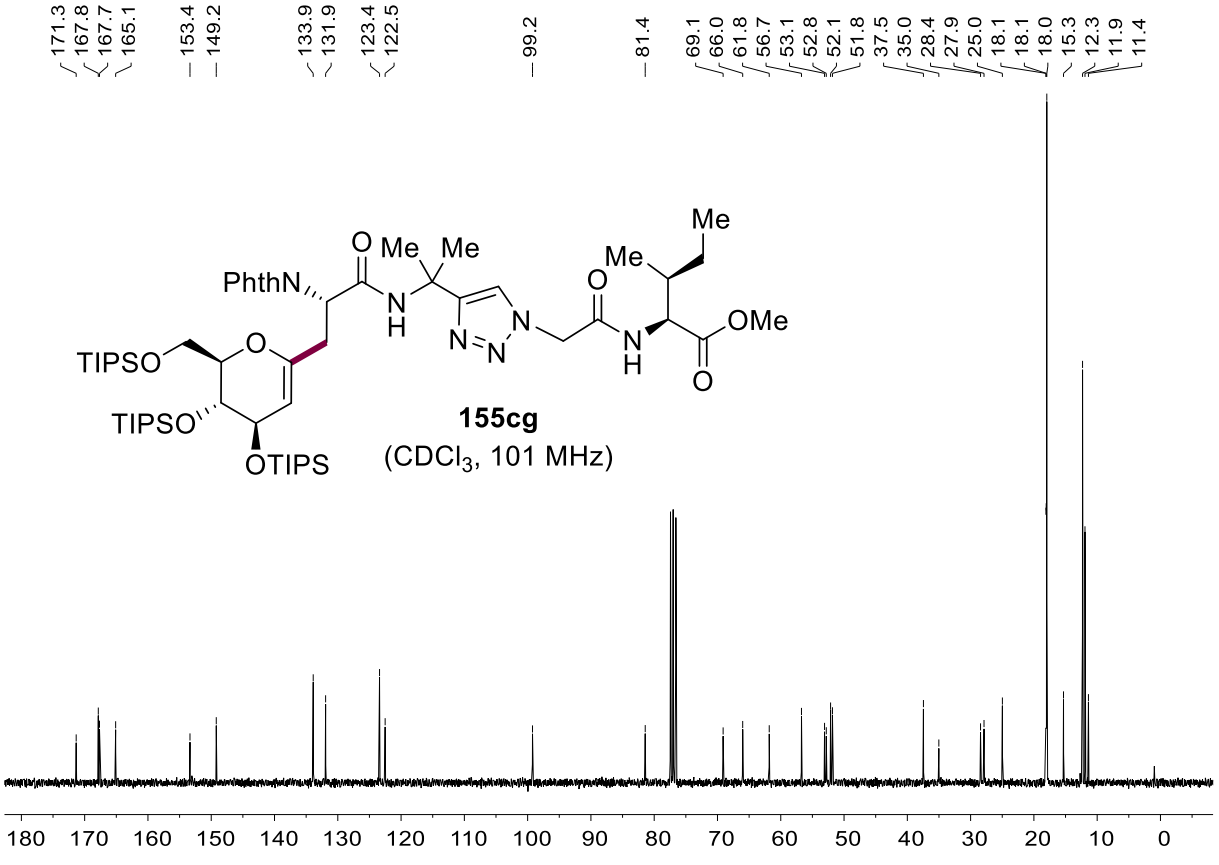
($CDCl_3$, 400 MHz)

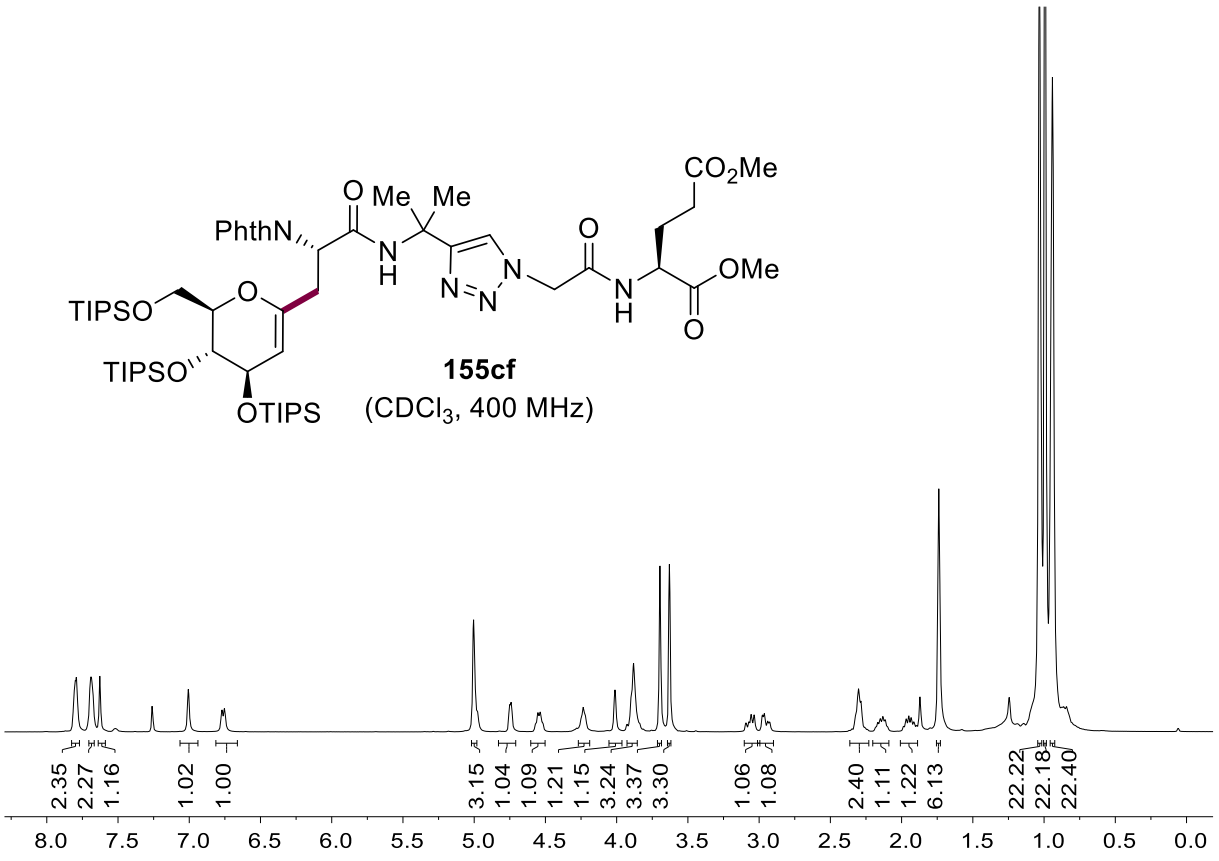

171.5
169.2
167.6
166.4
153.0
151.1
137.5
134.9
134.2
133.7
131.3
128.9
128.7
128.4
128.3
127.9
123.2
120.9
98.9
80.9
69.5
66.7
61.2
55.4
53.9
52.8
52.1
51.9
49.7
37.1
28.0
18.2
18.2
18.1
18.0
18.0
17.9
12.3
12.3
O Me Me
PhthN
N
H
Ph
N
N=N
TIPSO
O
TIPSO
OTIPS
MeO2C
NHAc
155cd
(CDCl3, 101 MHz)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

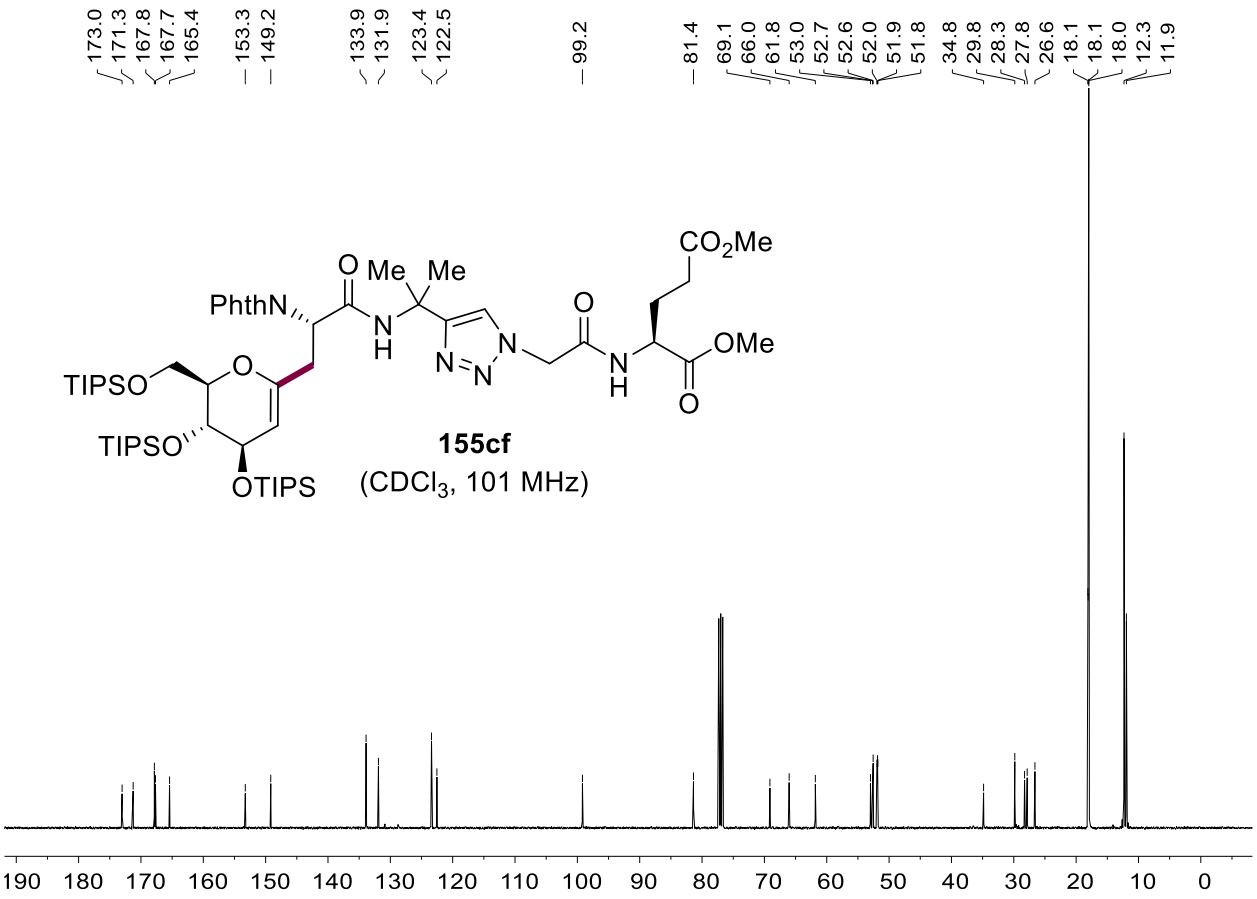

Me
O Me Me
PhthN
N
H
O
Me
N
N=N
N
H
OMe
O
TIPSO
O
TIPSO
OTIPS
155ce
(CDCl3, 400 MHz)
2.22
2.18
1.01
0.96
0.99
3.33
1.07
1.10
1.10
1.19
3.34
3.47
1.00
1.00
3.11
3.19
3.03
63.43
6.27
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

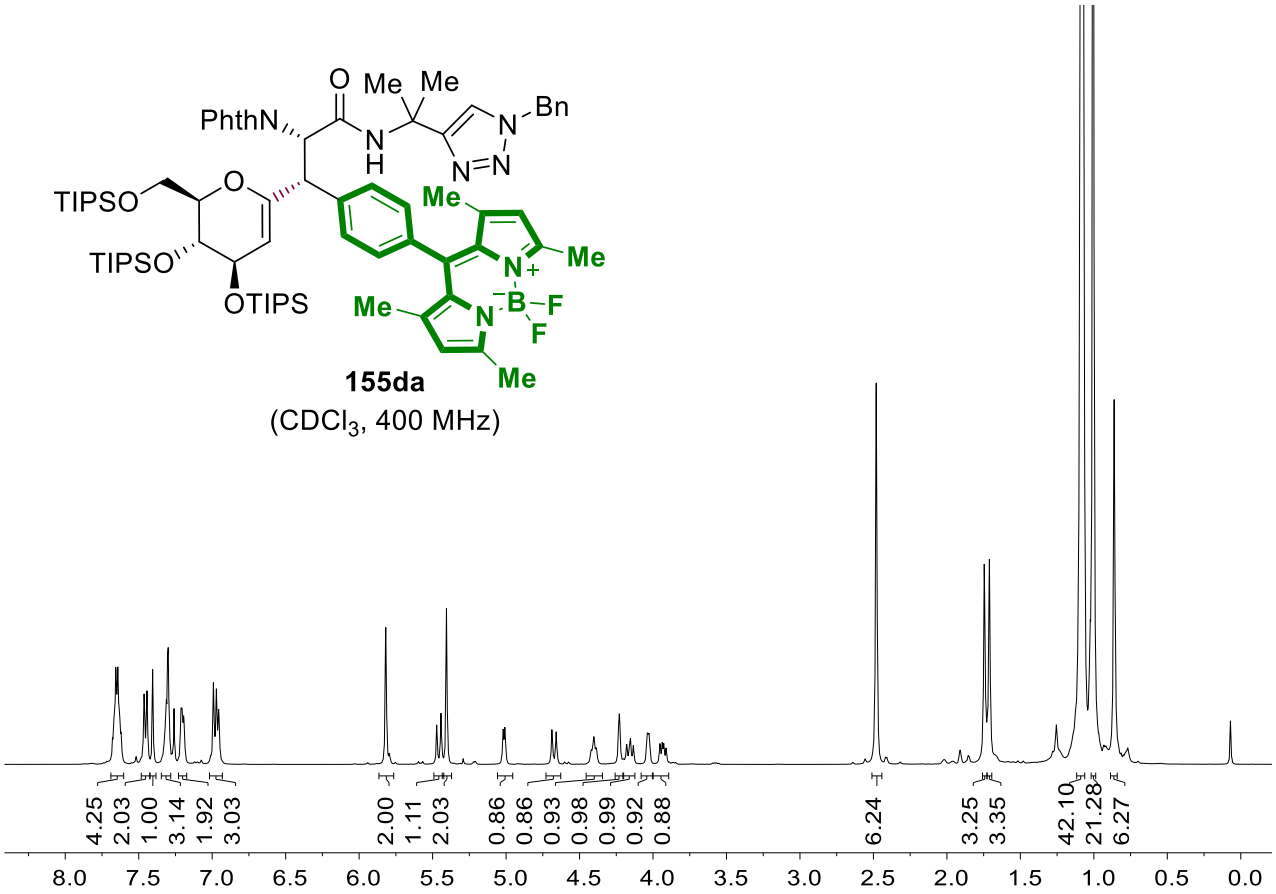

172.4
167.8
167.7
165.2
153.3
149.2
133.9
131.9
123.4
122.6
99.2
81.4
69.1
66.0
61.8
53.0
52.8
52.3
51.8
51.1
40.8
34.9
28.3
28.0
24.8
22.6
21.7
18.1
18.1
18.0
12.3
11.9
PhthN
O
Me
Me
N
H
N
N
N
O
N
H
Me
Me
OMe
O
TIPSO
O
TIPSO
OTIPS
155ce
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

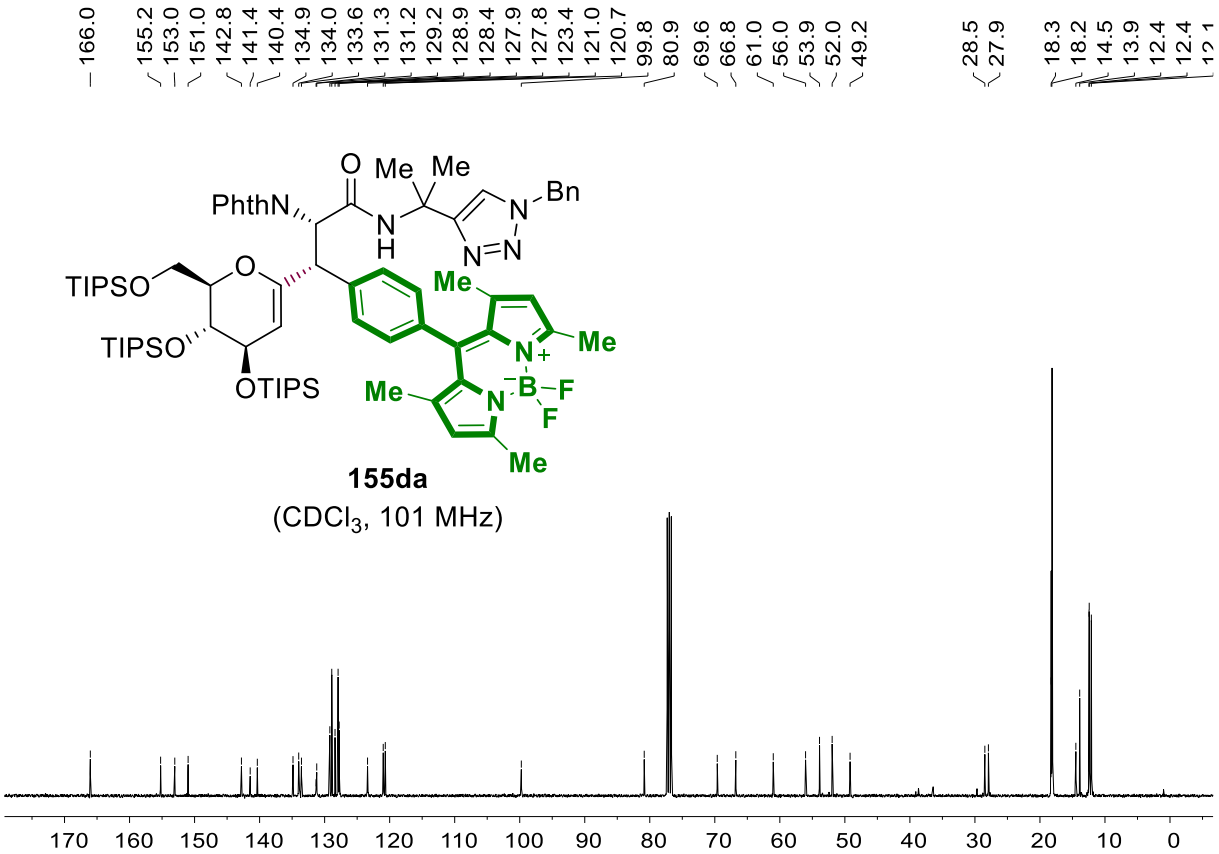

PhthN
O
Me
Me
N
H
N
N
N
O
N
H
Me
Me
OMe
O
TIPSO
O
TIPSO
OTIPS
155cg
(CDCl3, 400 MHz)
2.01
2.08
1.00
0.93
1.00
3.06
1.00
1.02
0.99
1.01
3.06
3.15
0.95
1.00
1.17
6.04
1.99
63.11
6.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

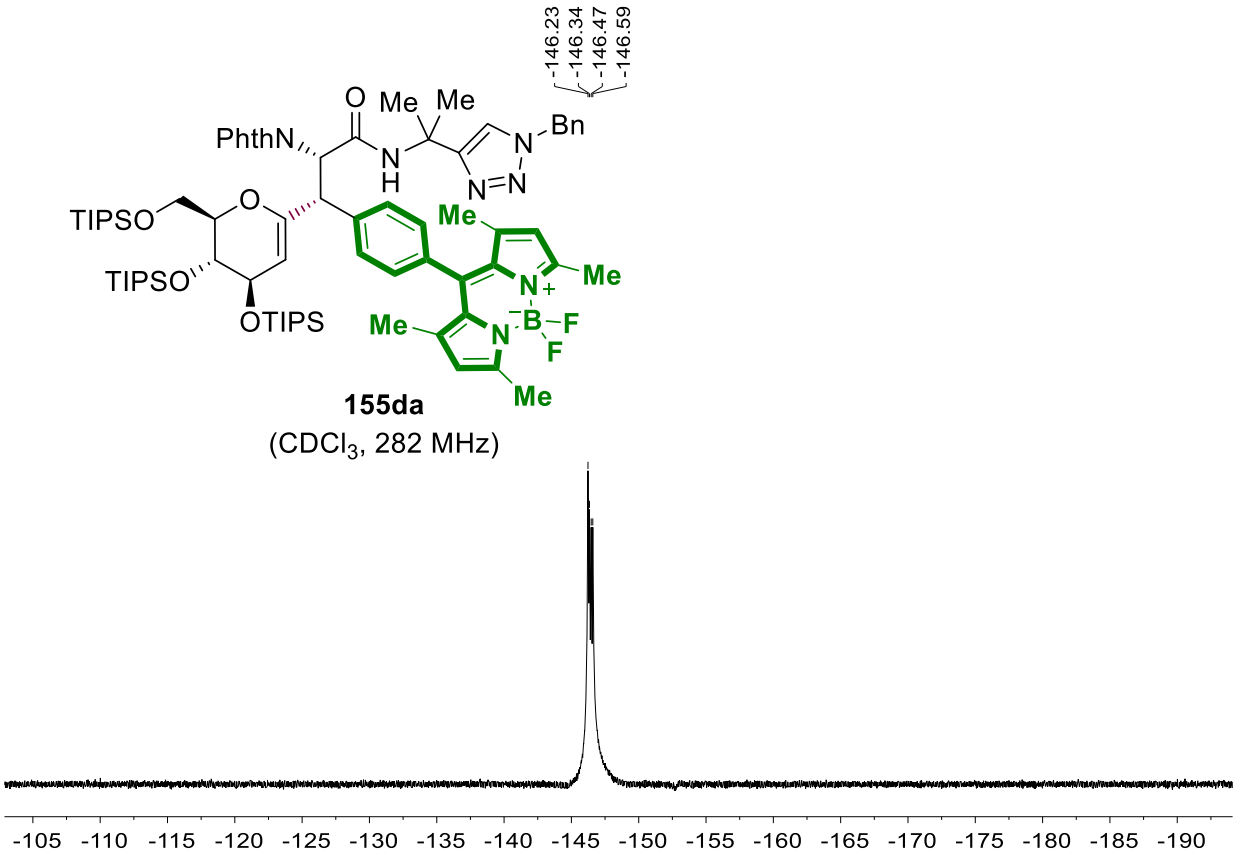

171.3
167.8
167.7
165.1
153.4
149.2
133.9
131.9
123.4
122.5
99.2
81.4
69.1
66.0
61.8
56.7
53.1
52.8
52.1
51.8
37.5
35.0
28.4
27.9
25.0
18.1
18.1
18.0
15.3
12.3
11.9
11.4
PhthN
TIPSO
TIPSO
OTIPS
Me
Me
Me
OMe
155cg
(CDCl3, 101 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

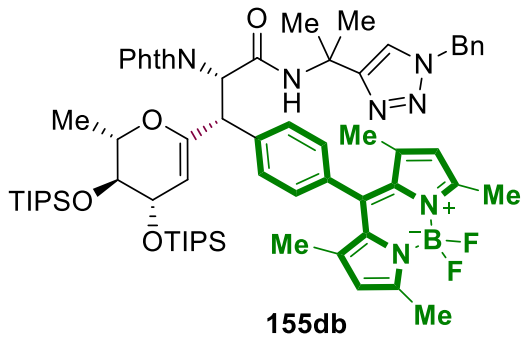

CO2Me
PhthN
TIPSO
TIPSO
OTIPS
Me
Me
OMe
155cf
(CDCl3, 400 MHz)
2.35
2.27
1.16
1.02
1.00
3.15
1.04
1.09
1.21
1.15
3.24
3.37
3.30
1.06
1.08
2.40
1.11
1.22
6.13
22.22
22.18
22.40
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


173.0
171.3
167.8
167.7
165.4
153.3
149.2
133.9
131.9
123.4
122.5
99.2
81.4
69.1
66.0
61.8
53.0
52.7
52.6
52.0
51.9
51.8
34.8
29.8
28.3
27.8
26.6
18.1
18.1
18.0
12.3
11.9
CO2Me
O
Me
Me
PhthN
N
H
N
N=N
O
N
H
OMe
O
TIPSO
O
TIPSO
OTIPS
155cf
(CDCl3, 101 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
Me
Me
PhthN
N
H
N
Bn
N=N
TIPSO
O
TIPSO
OTIPS
Me
Me
N+
Me
Me
N
B
F
F
Me
155da
(CDCl3, 400 MHz)
4.25
2.03
1.00
3.14
1.92
3.03
2.00
1.11
2.03
0.86
0.86
0.93
0.98
0.99
0.92
0.88
6.24
3.25
3.35
42.10
21.28
6.27
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

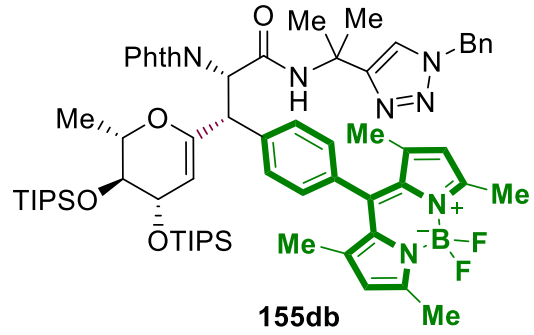

166.0
155.2
153.0
151.0
142.8
141.4
140.4
134.9
134.0
133.6
131.3
131.2
129.2
128.9
128.4
127.9
127.8
123.4
121.0
120.7
99.8
80.9
69.6
66.8
61.0
56.0
53.9
52.0
49.2
28.5
27.9
18.3
18.2
14.5
13.9
12.4
12.4
PhthN
O
Me
Me
N
H
N
Bn
N=N
TIPSO
O
TIPSO
OTIPS
Me
Me
N+
Me
Me
N
B
F
F
Me
155da
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


-146.23
-146.34
-146.47
-146.59
PhthN
O
Me
Me
N
H
N
Bn
N=N
TIPSO
O
TIPSO
OTIPS
Me
Me
N+
Me
Me
N
B
F
F
Me
155da
(CDCl3, 282 MHz)
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190



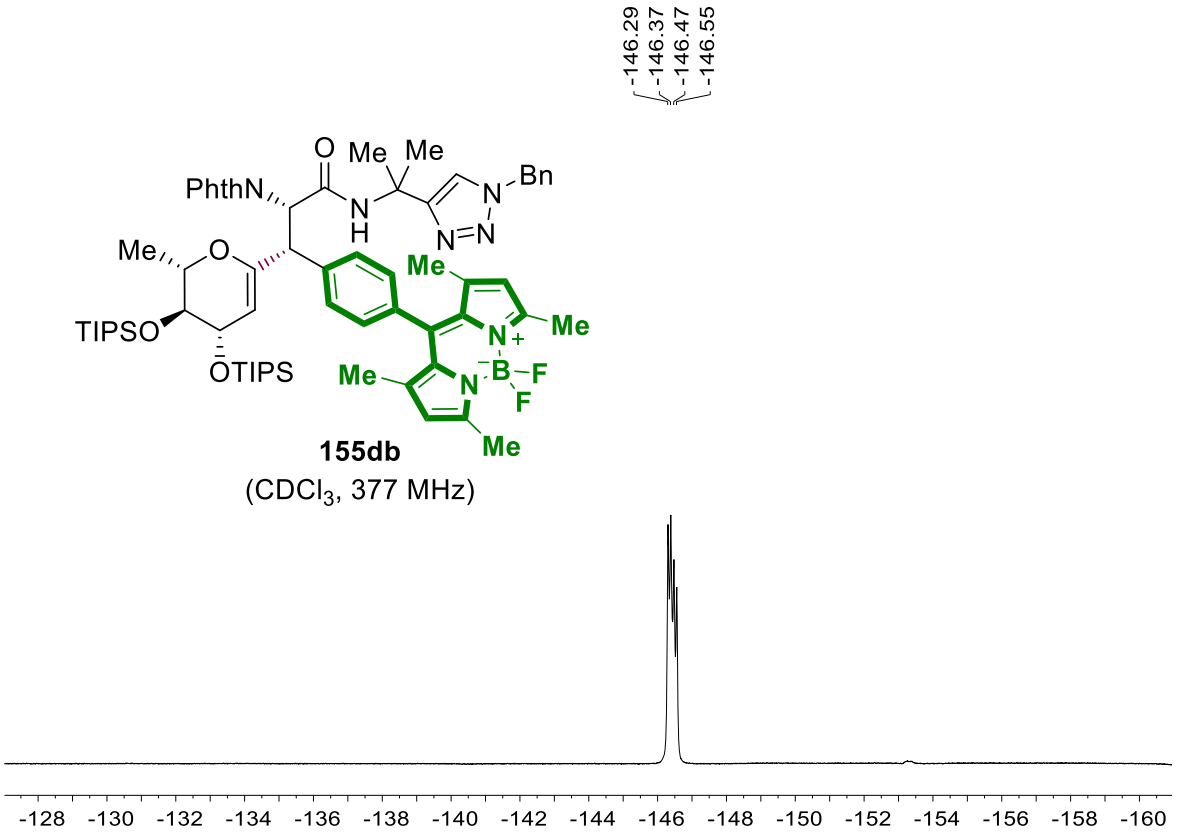
155db

($CDCl_3$, 400 MHz)



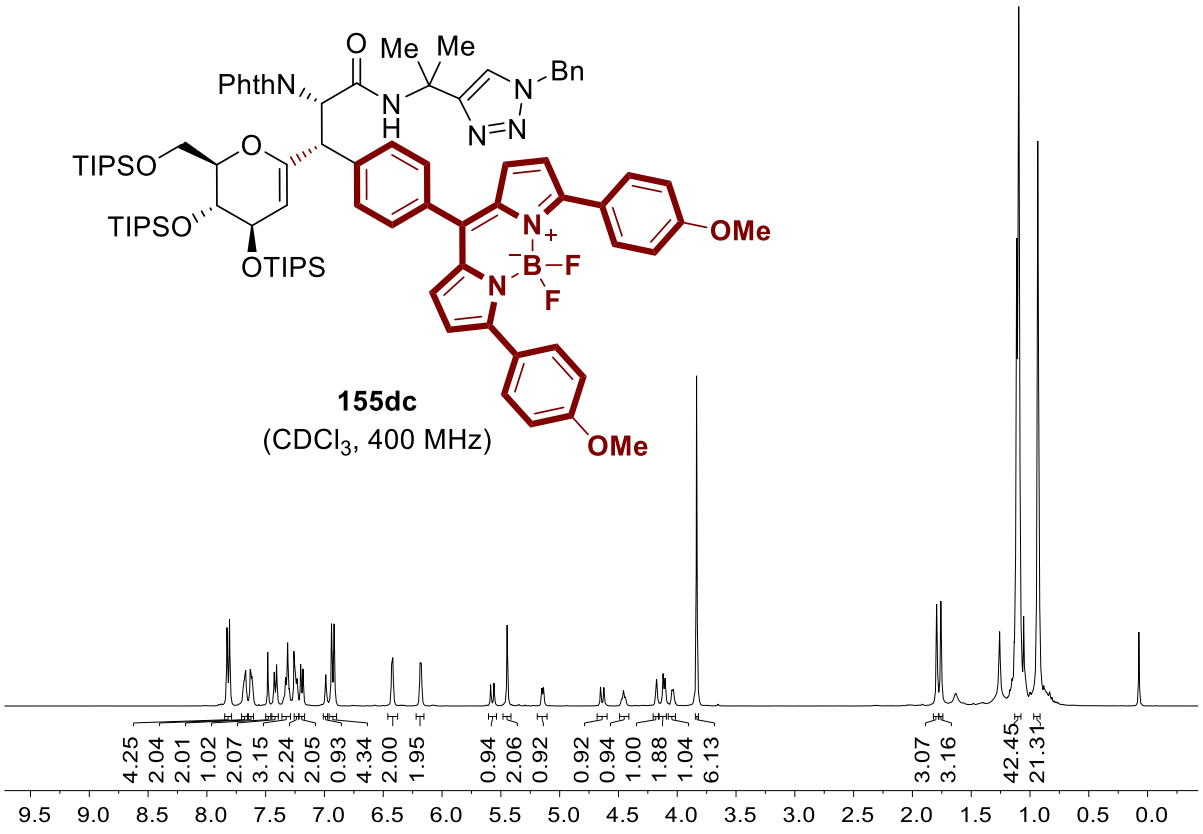
155db

($CDCl_3$, 101 MHz)



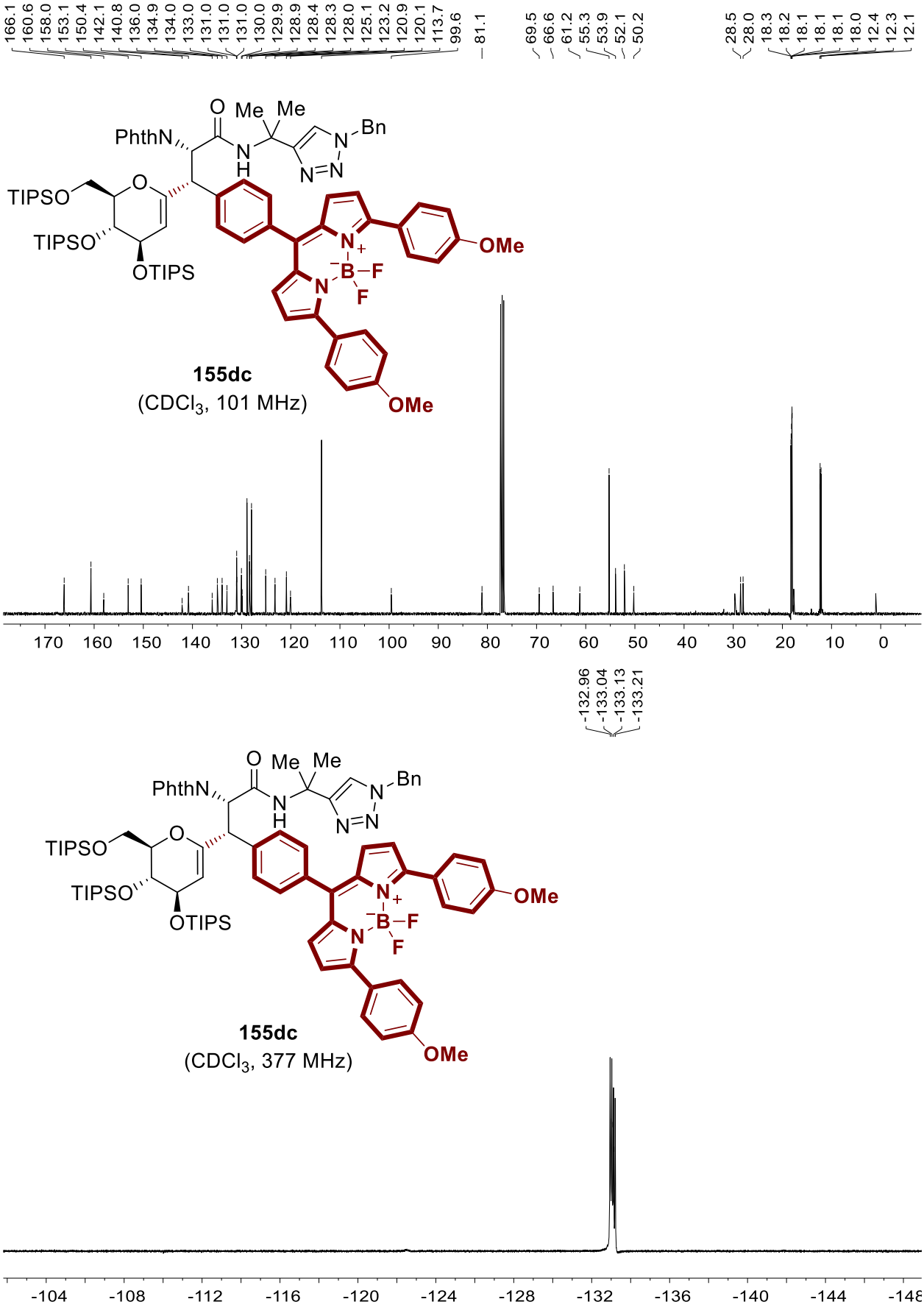
155db

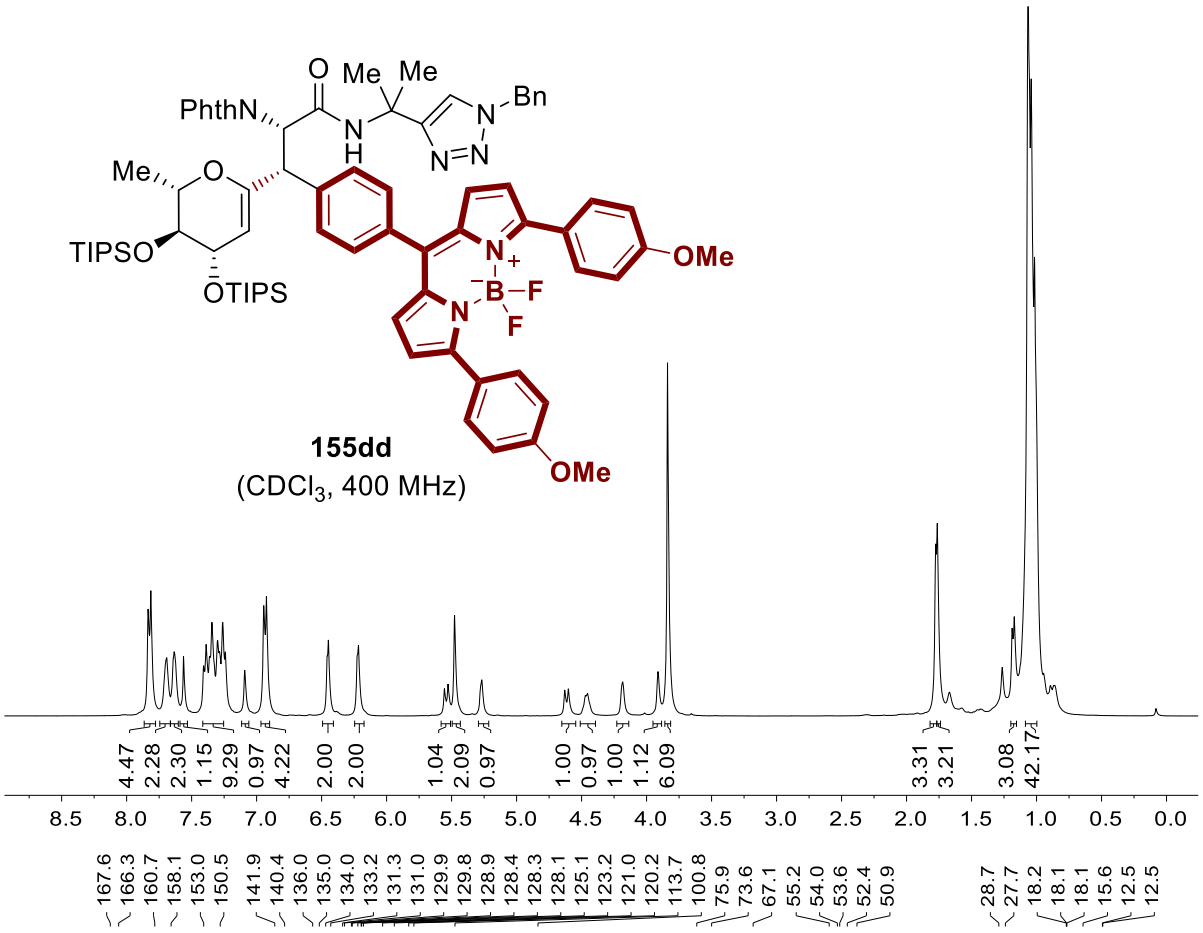
($CDCl_3$, 377 MHz)

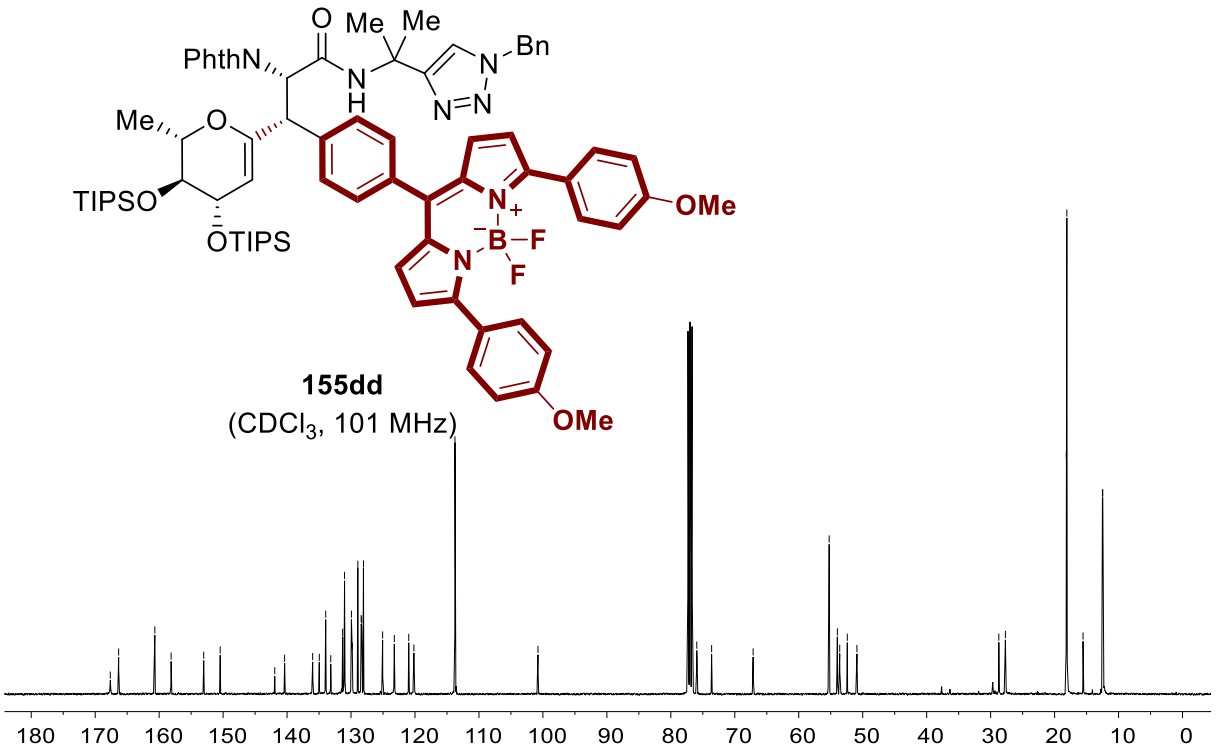


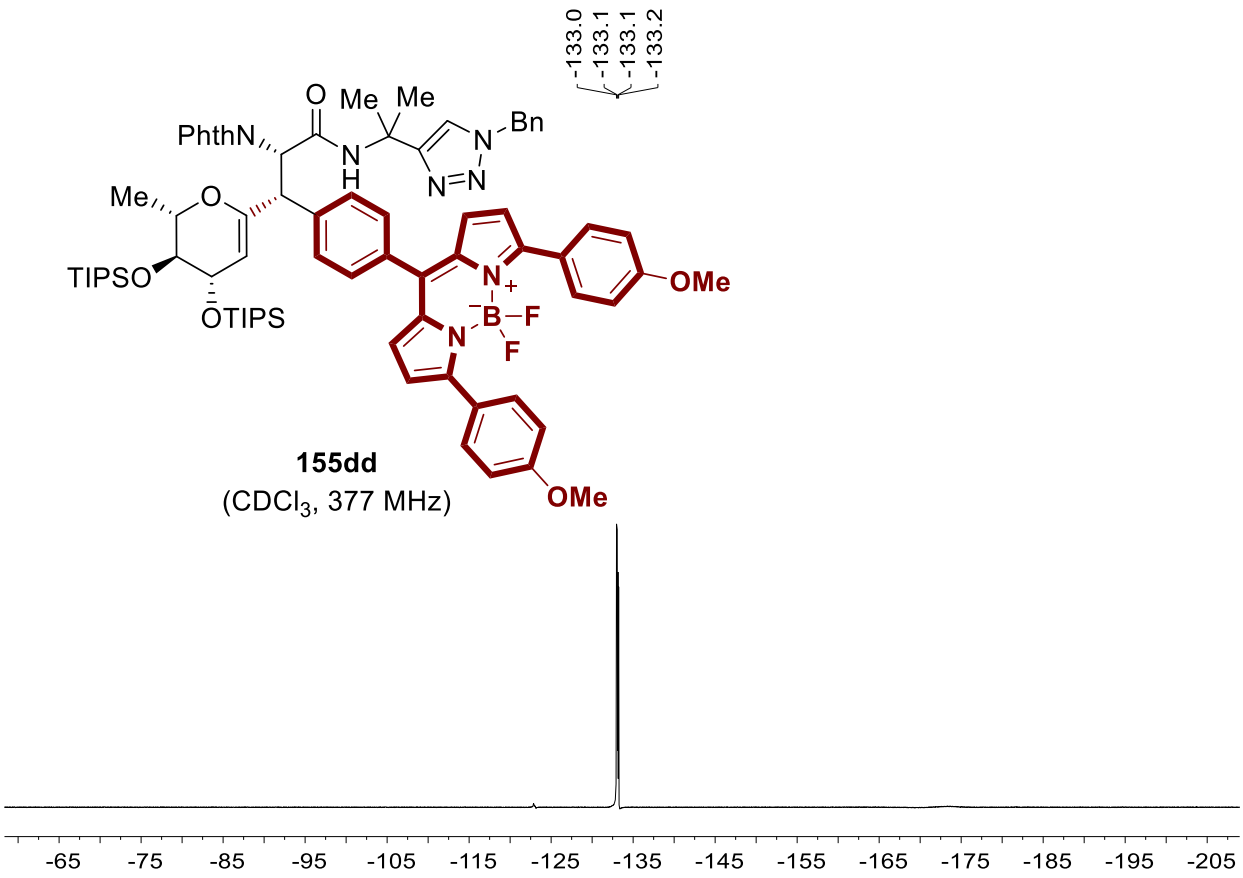
155dc

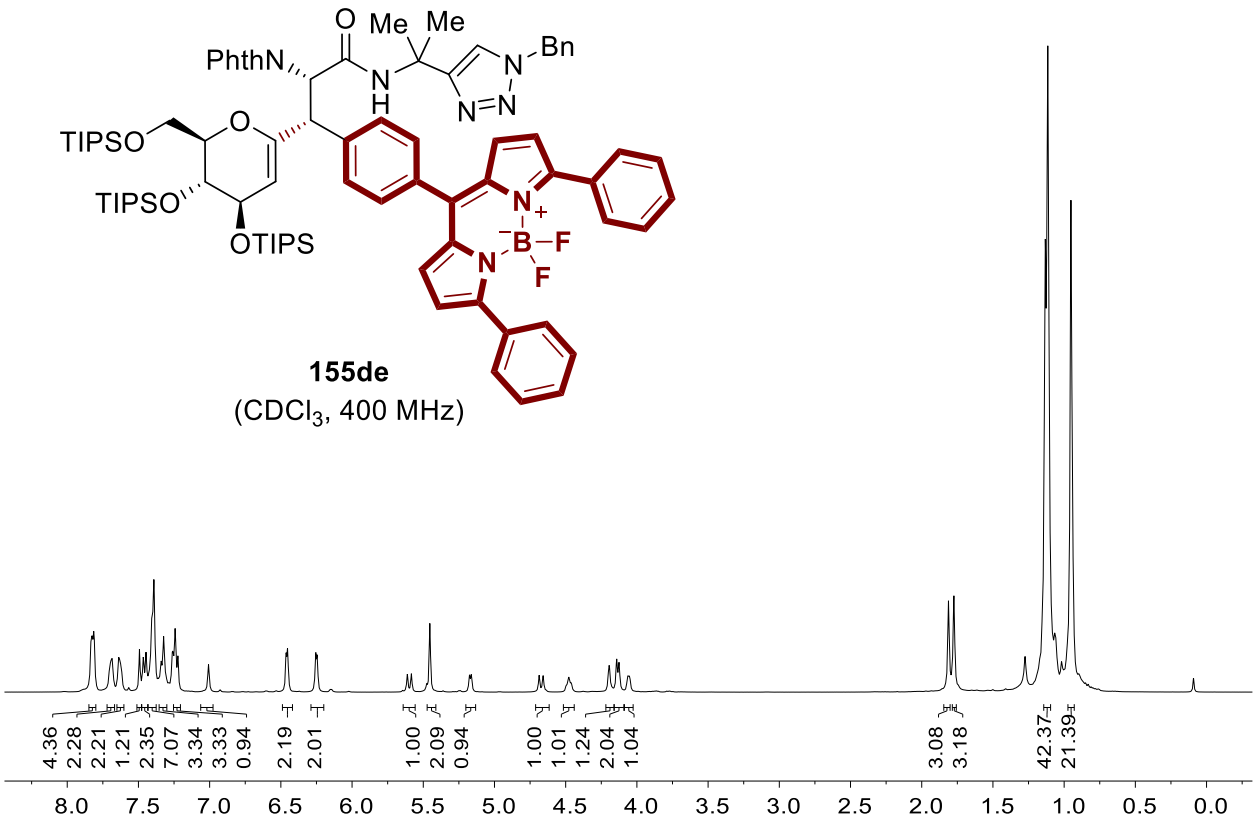
($CDCl_3$, 400 MHz)

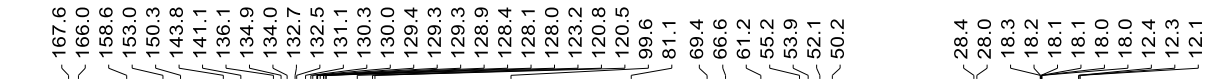

166.1
160.6
158.0
153.1
150.4
142.1
140.8
136.0
134.9
134.0
133.0
131.0
131.0
131.0
130.0
129.9
128.9
128.4
128.3
128.0
125.1
123.2
120.9
120.1
113.7
99.6
81.1
69.5
66.6
61.2
55.3
53.9
52.1
50.2
28.5
28.0
18.3
18.2
18.1
18.1
18.1
18.0
12.4
12.3
12.1
O
Me
Me
PhthN
N
H
N
N=N
Bn
TIPSO
O
TIPSO
OTIPS
N+
B
F
F
N
OMe
OMe
155dc
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-132.96
-133.04
-133.13
-133.21
155dc
(CDCl3, 377 MHz)
-104
-108
-112
-116
-120
-124
-128
-132
-136
-140
-144

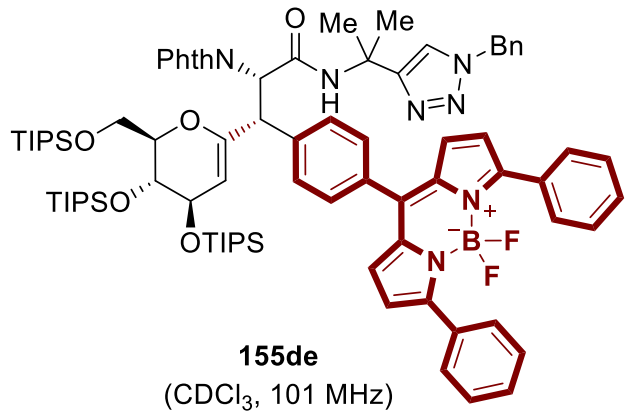

155dd
(CDCl3, 400 MHz)
4.47 2.28 2.30 1.15 9.29 0.97 4.22 2.00 2.00 1.04 2.09 0.97 1.00 0.97 1.00 1.12 6.09 3.31 3.21 3.08 42.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
167.6 166.3 160.7 158.1 153.0 150.5 141.9 140.4 136.0 135.0 134.0 133.2 131.3 131.0 129.9 129.8 128.9 128.4 128.3 128.1 125.1 123.2 121.0 120.2 113.7 100.8 75.9 73.6 67.1 55.2 54.0 53.6 52.4 50.9 28.7 27.7 18.2 18.1 18.1 15.6 12.5 12.5


155dd
(CDCl3, 101 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

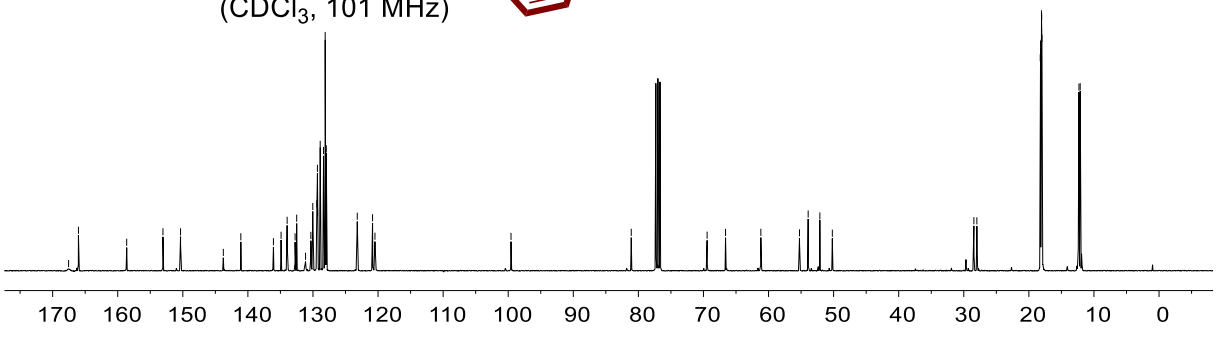

-133.0
-133.1
-133.1
-133.2
O
Me
Me
PhthN
N
H
N
Bn
N=N
Me
O
TIPSO
OTIPS
N+
B−F
F
N
OMe
OMe
155dd
(CDCl3, 377 MHz)
-65
-75
-85
-95
-105
-115
-125
-135
-145
-155
-165
-175
-185
-195
-205

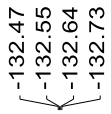

O
Me
Me
PhthN
N
H
N
Bn
N=N
TIPSO
O
TIPSO
OTIPS
N+
B−F
F
N
155de
(CDCl3, 400 MHz)
4.36
2.28
2.21
1.21
2.35
7.07
3.34
3.33
0.94
2.19
2.01
1.00
2.09
0.94
1.00
1.01
1.24
2.04
1.04
3.08
3.18
42.37
21.39
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

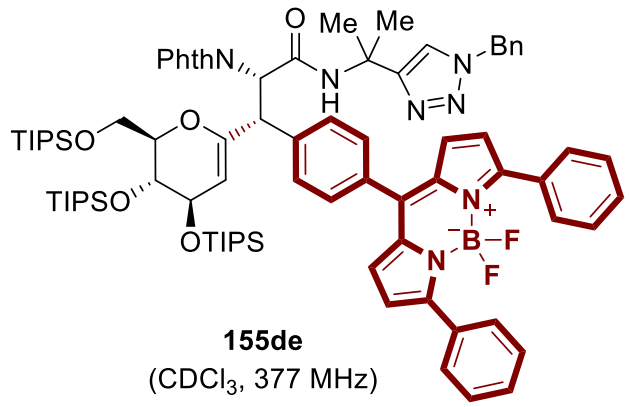




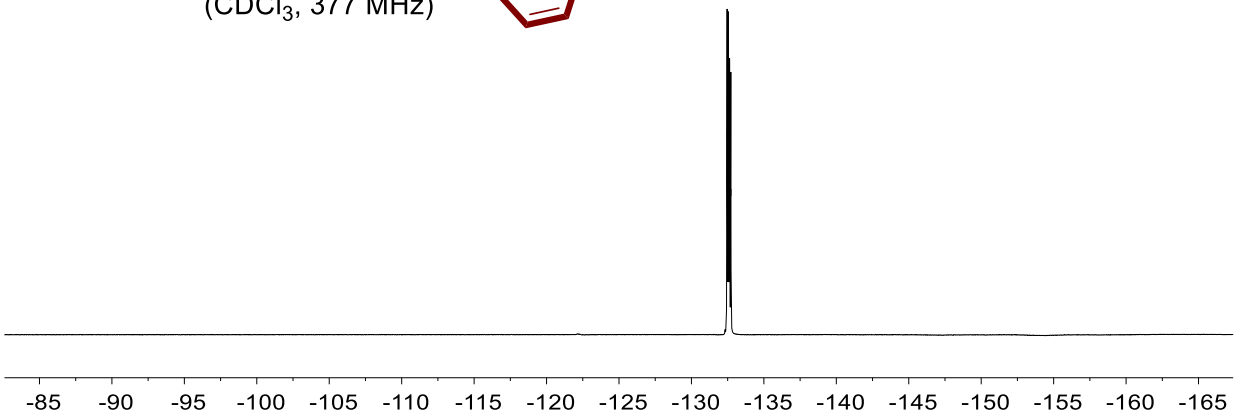
155de
($CDCl_3$, 101 MHz)

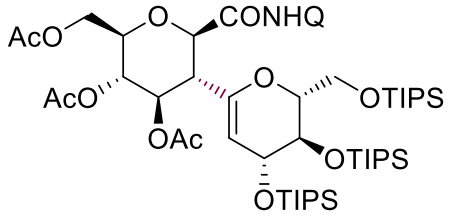






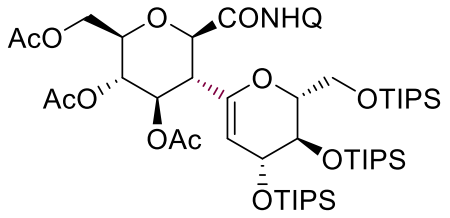
155de
($CDCl_3$, 377 MHz)





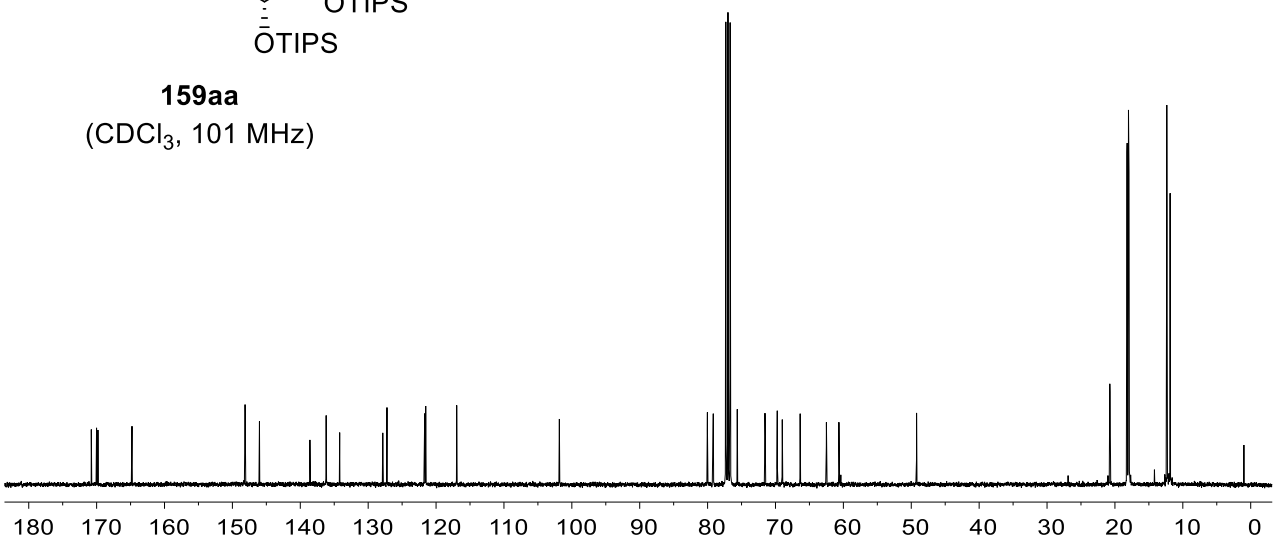
159aa

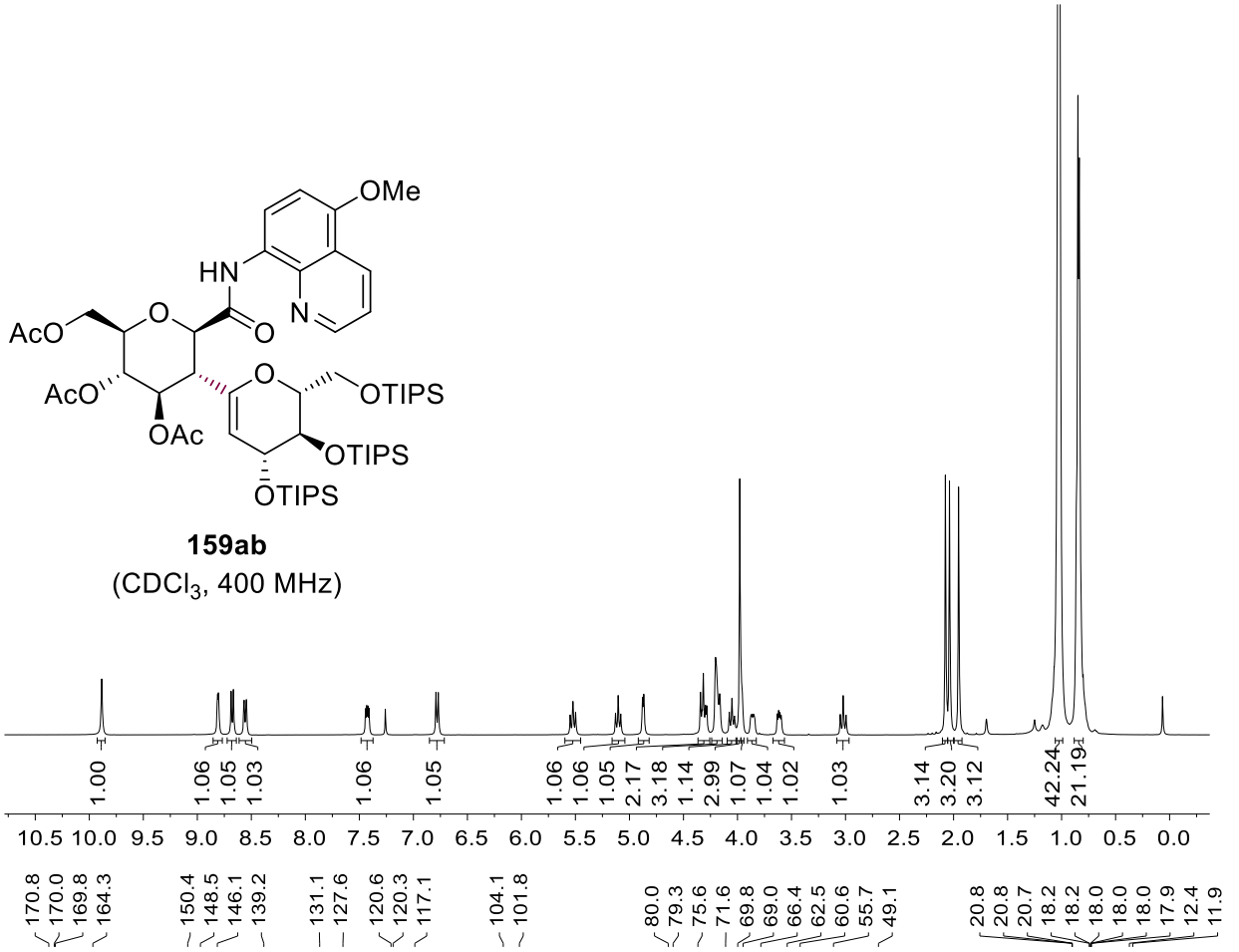
($CDCl_3$, 400 MHz)



159aa

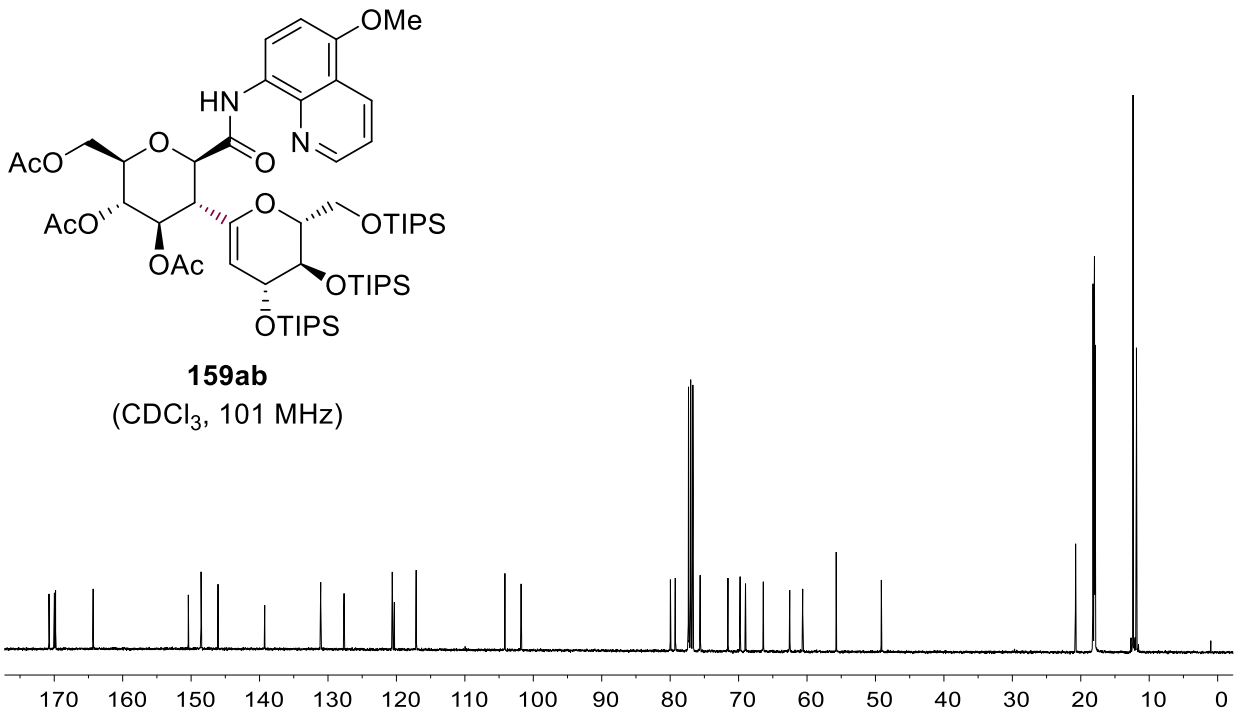
($CDCl_3$, 101 MHz)





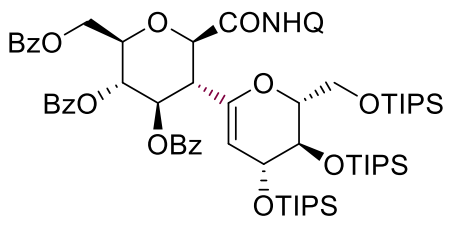
159ab

($CDCl_3$, 400 MHz)



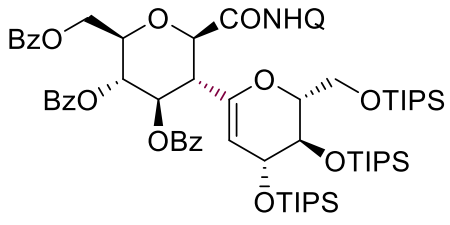
159ab

($CDCl_3$, 101 MHz)



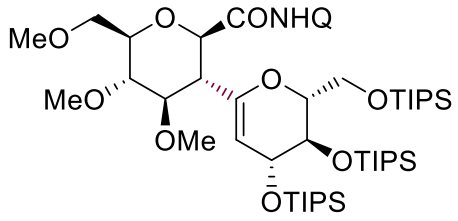
159ba

($CDCl_3$, 300 MHz)



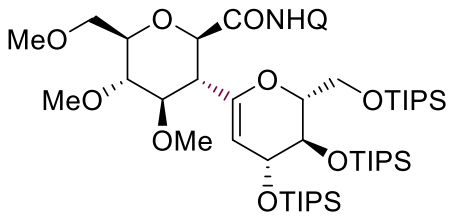
159ba

($CDCl_3$, 75 MHz)



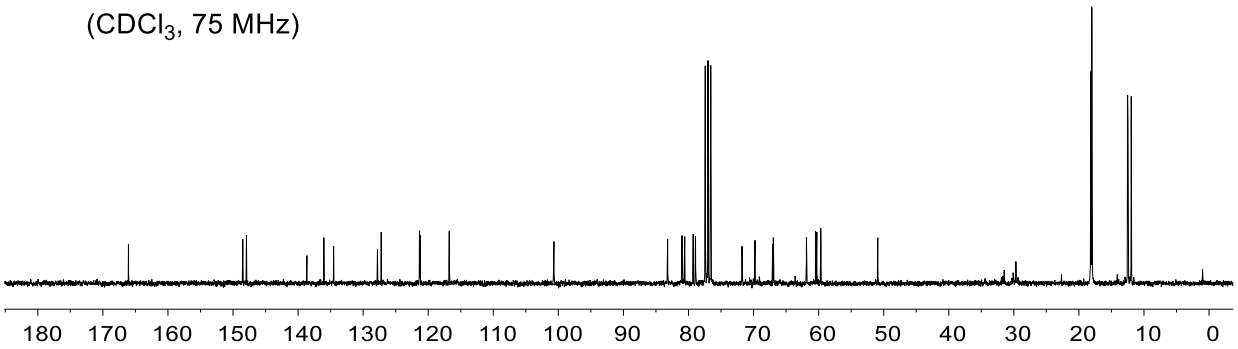
159bb

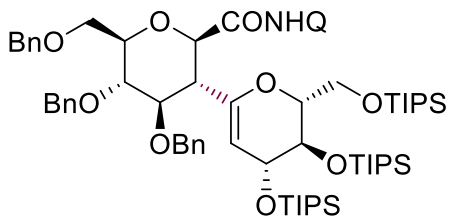
($CDCl_3$, 300 MHz)



159bb

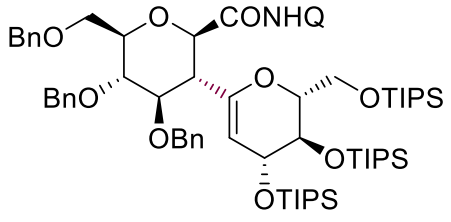
($CDCl_3$, 75 MHz)





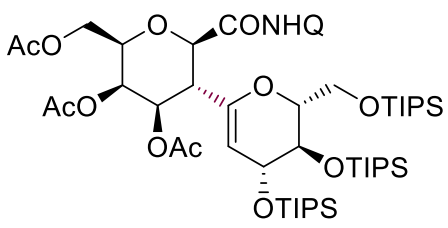
159bc

($CDCl_3$, 300 MHz)



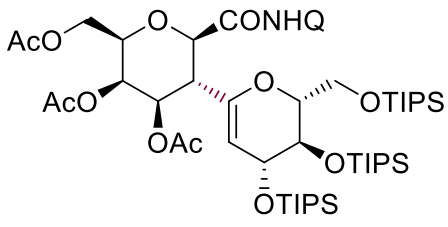
159bc

($CDCl_3$, 75 MHz)



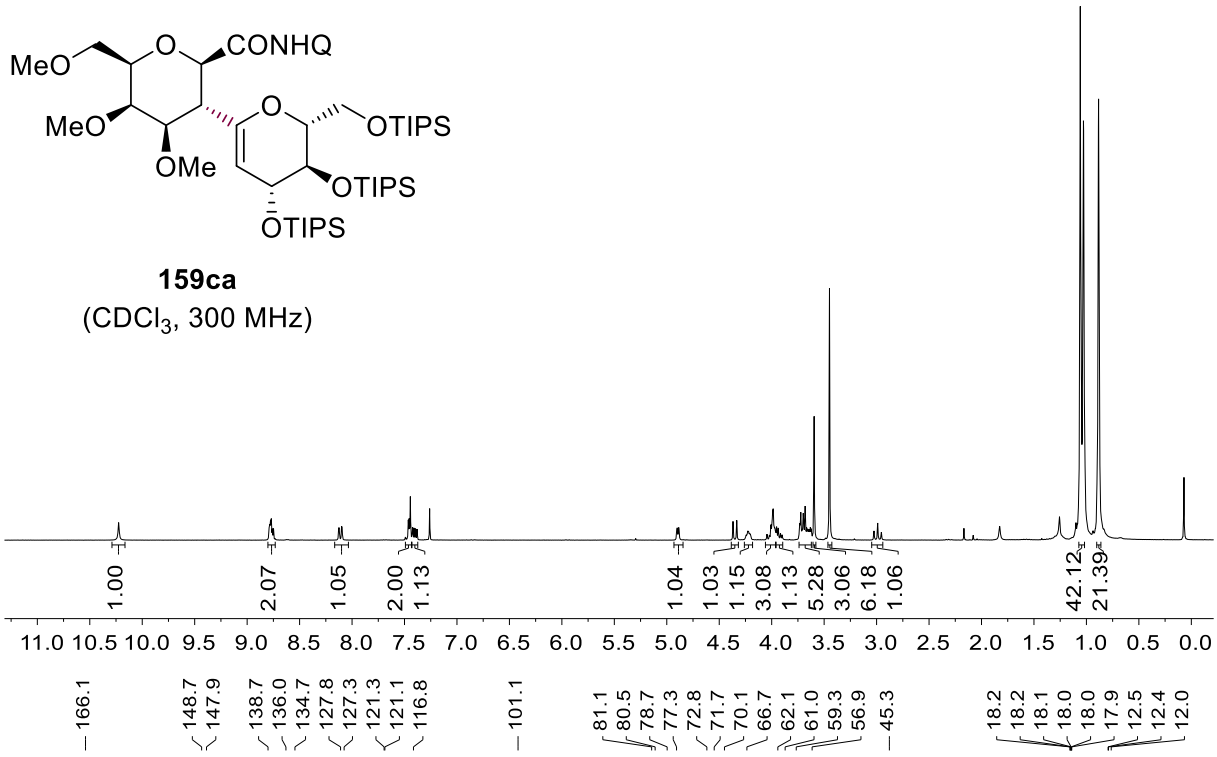
159bd

($CDCl_3$, 400 MHz)



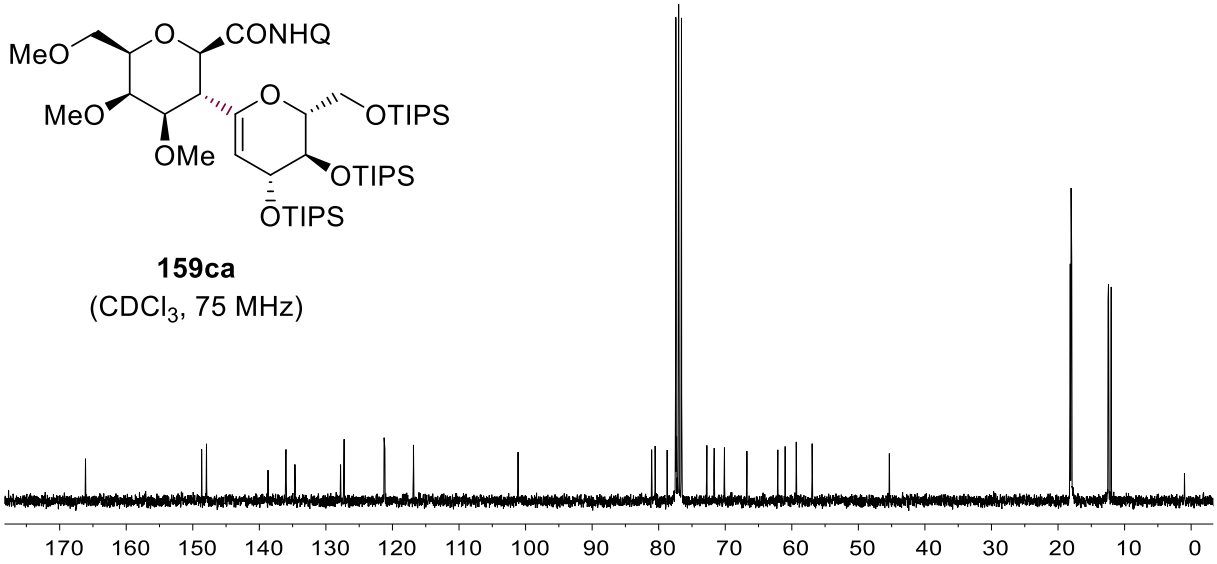
159bd

($CDCl_3$, 101 MHz)



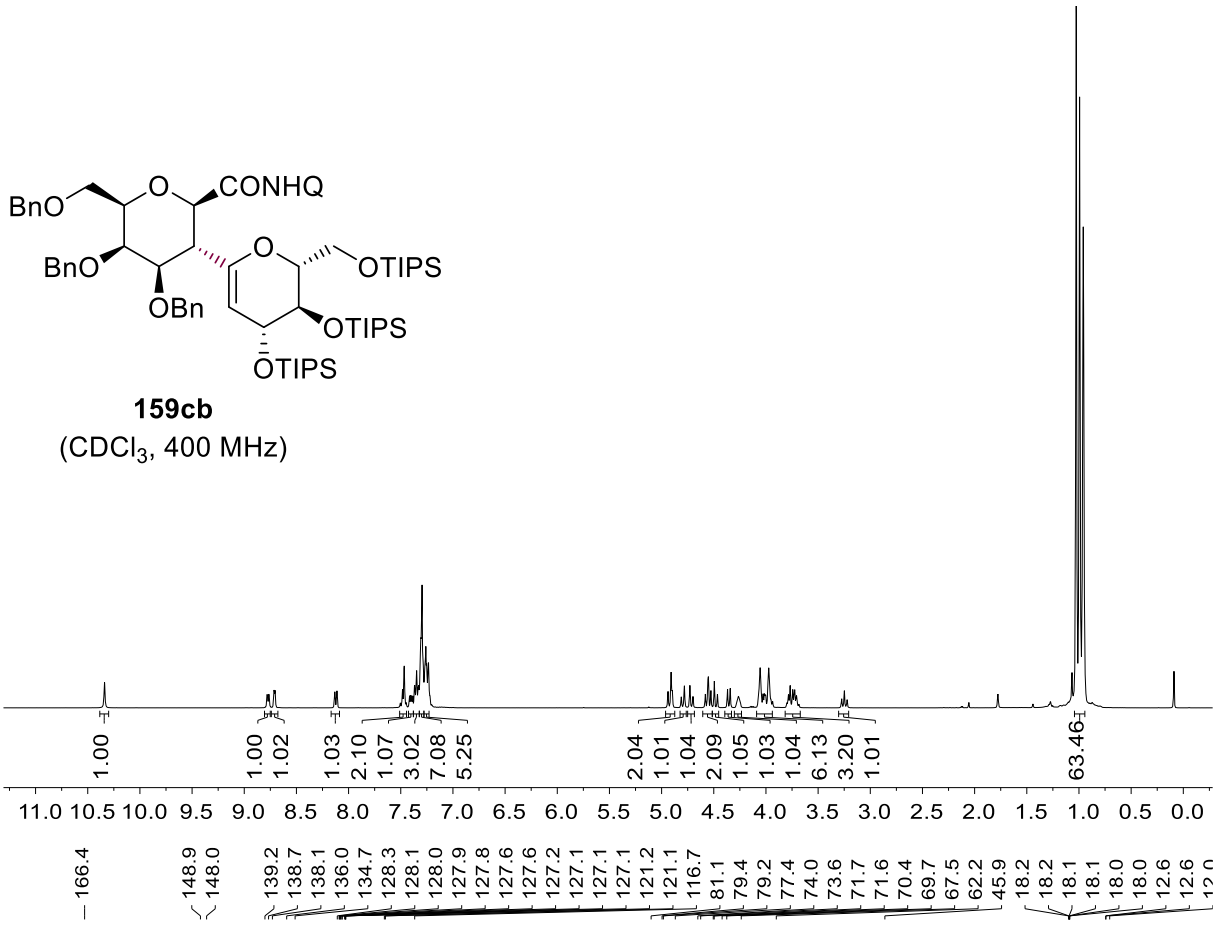
159ca

($CDCl_3$, 300 MHz)



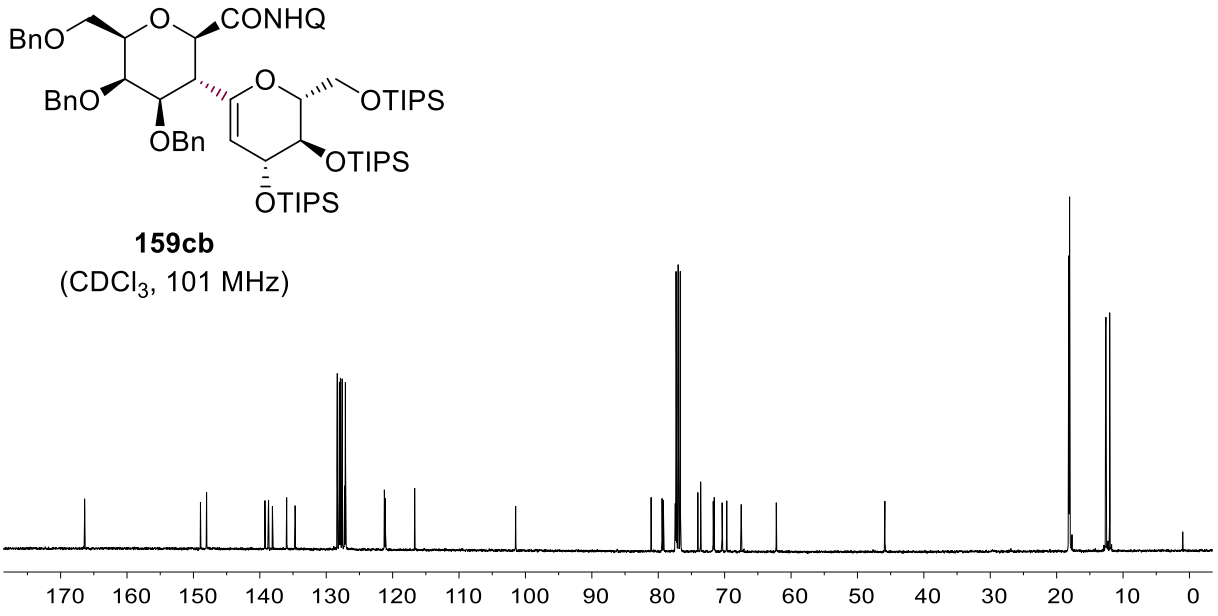
159ca

($CDCl_3$, 75 MHz)



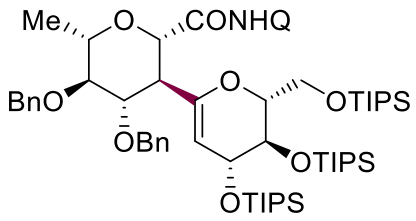
159cb

($CDCl_3$, 400 MHz)



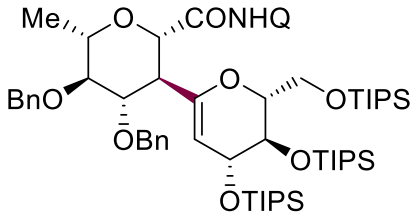
159cb

($CDCl_3$, 101 MHz)



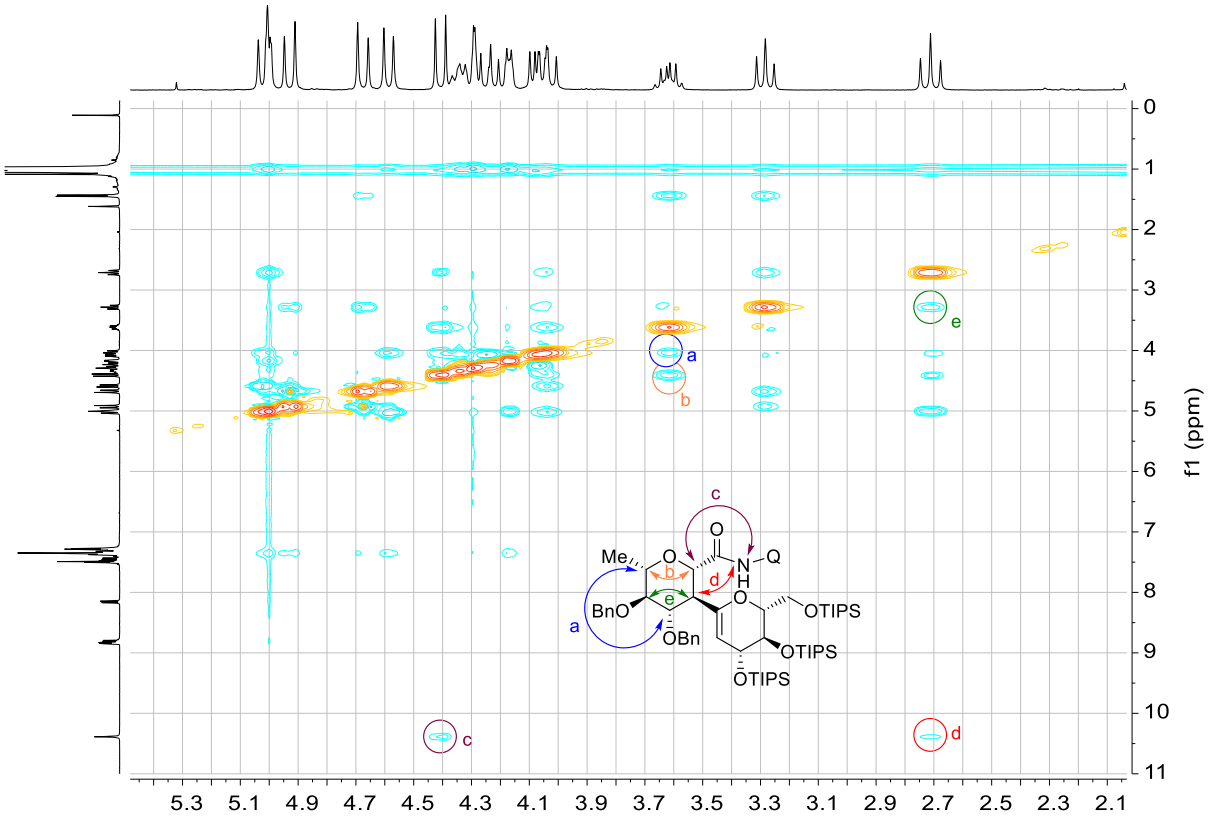
159d

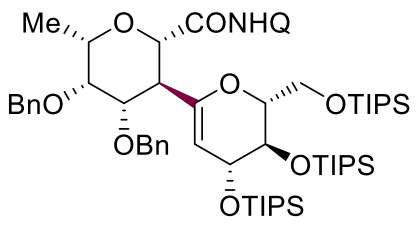
($CDCl_3$, 300 MHz)



159d

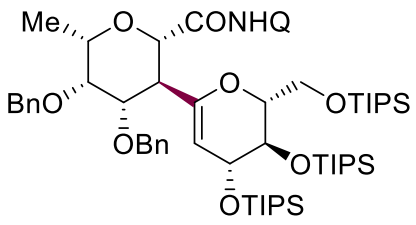
($CDCl_3$, 75 MHz)


f1 (ppm)
5.3 5.1 4.9 4.7 4.5 4.3 4.1 3.9 3.7 3.5 3.3 3.1 2.9 2.7 2.5 2.3 2.1
0 1 2 3 4 5 6 7 8 9 10 11
a
b
c
d
e
Me
O
N
H
Q
BnO
OBn
OTIPS
OTIPS
OTIPS



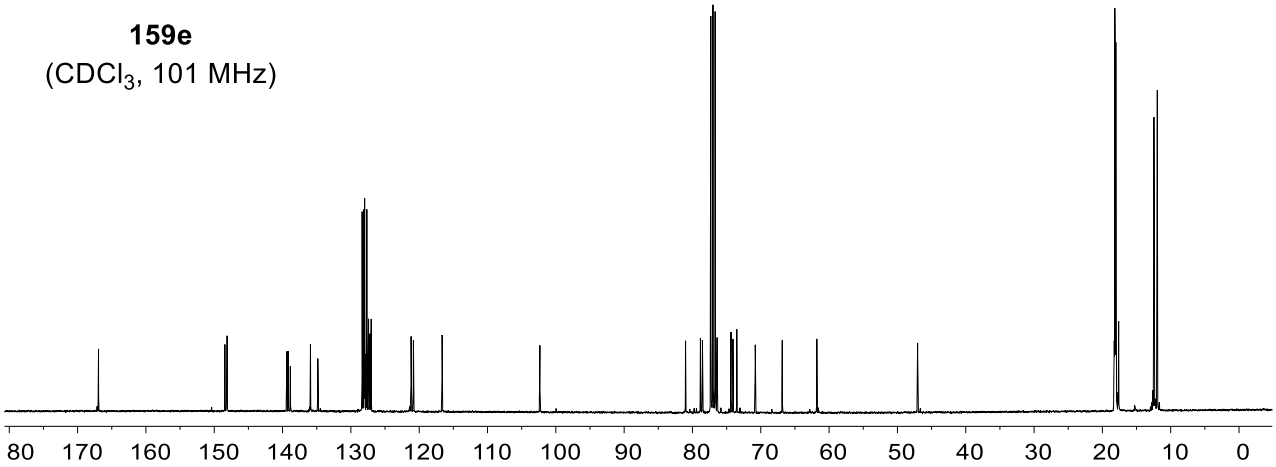
159e

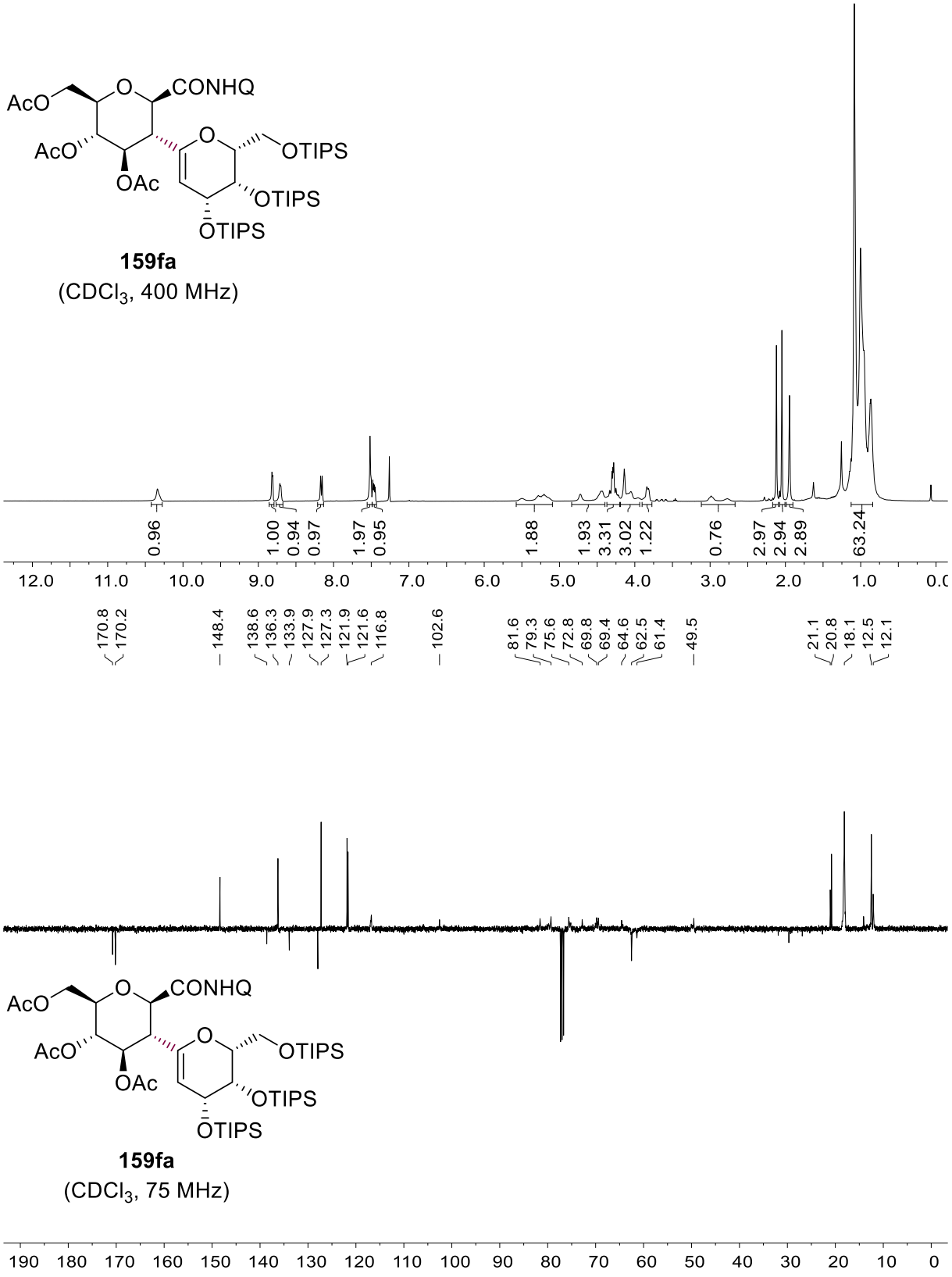
($CDCl_3$, 400 MHz)



159e

($CDCl_3$, 101 MHz)



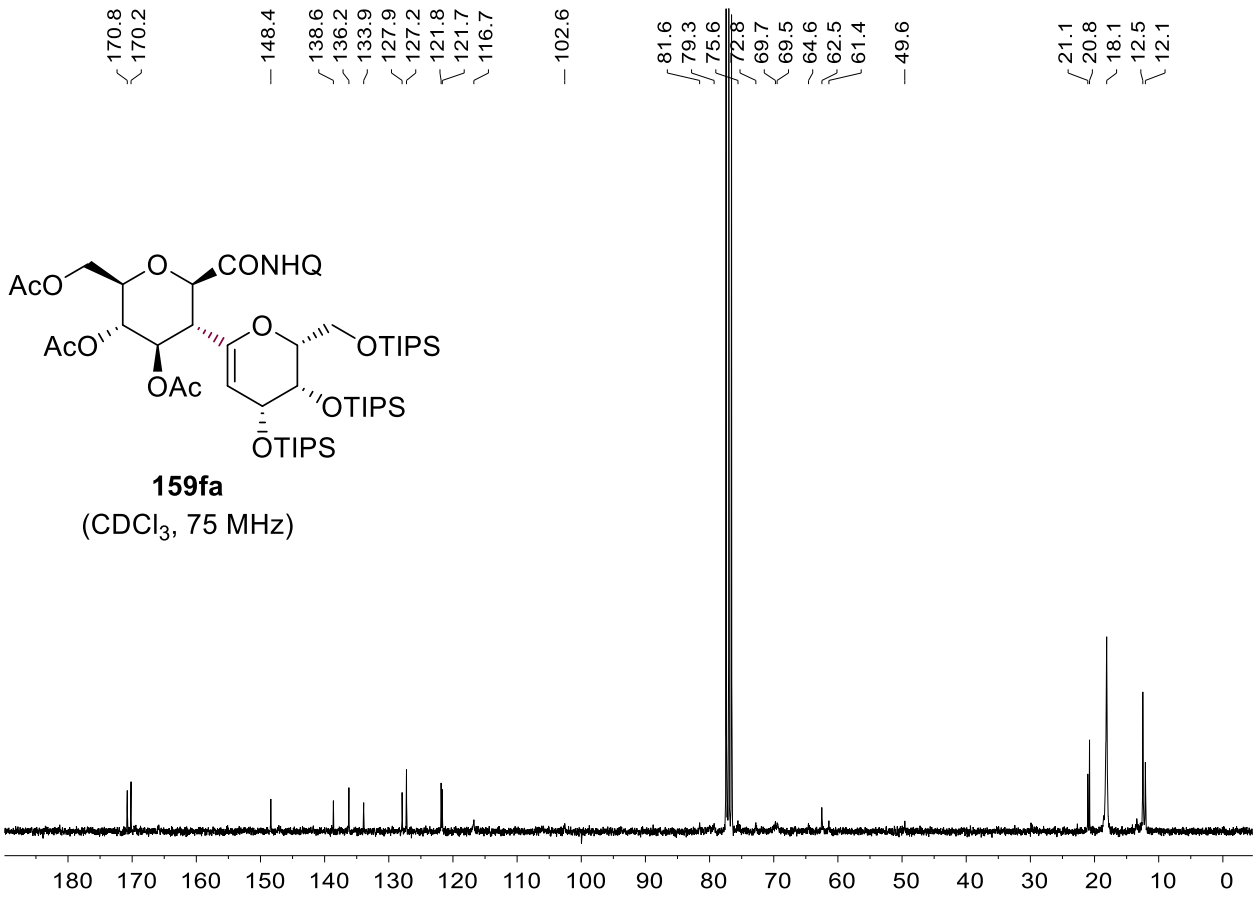


159fa

($CDCl_3$, 400 MHz)

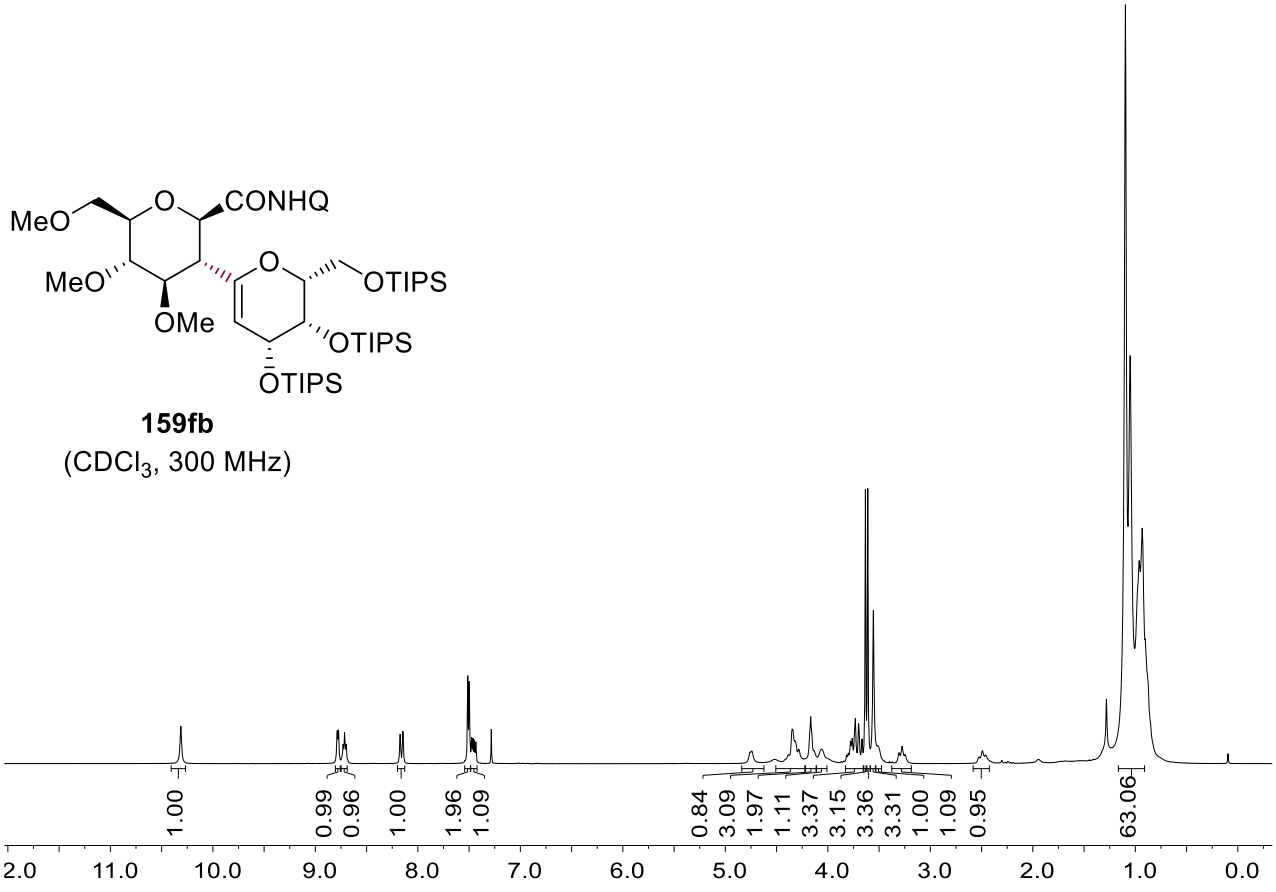
159fa

($CDCl_3$, 75 MHz)



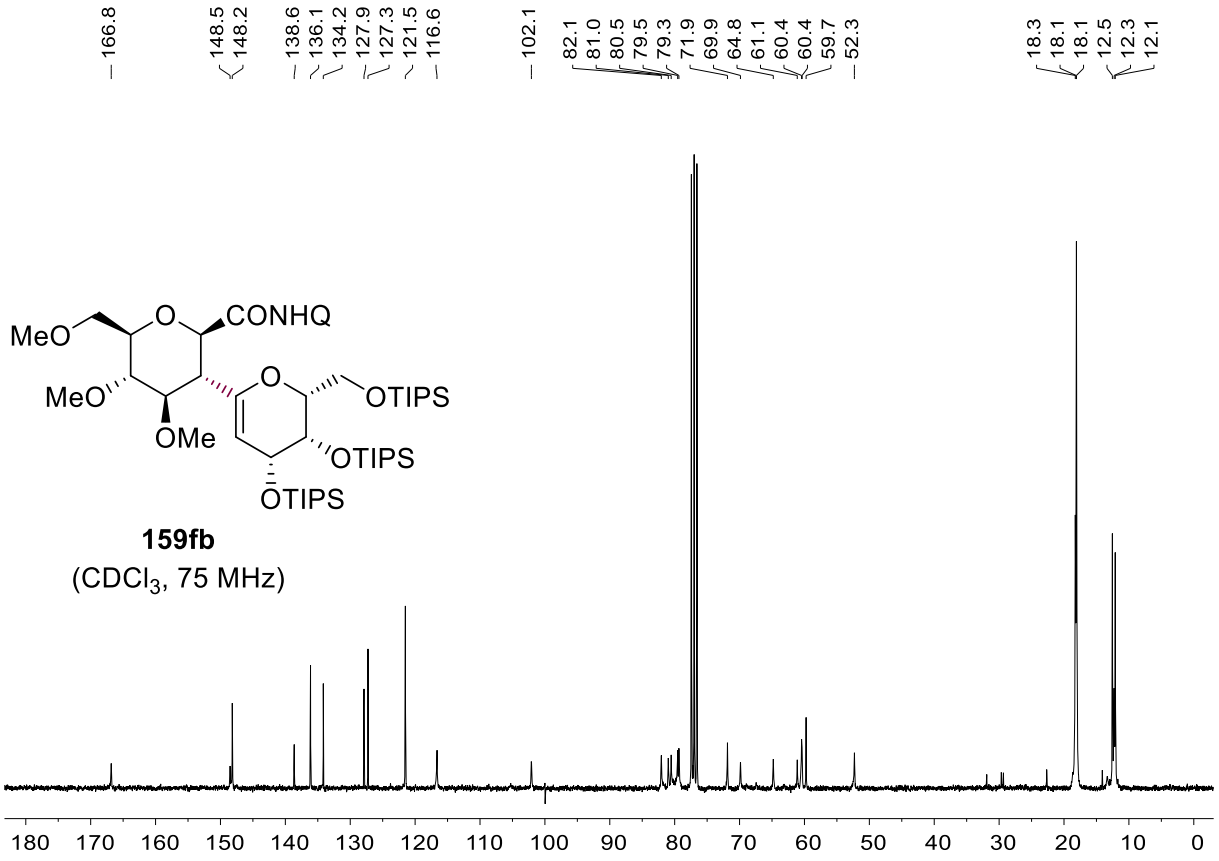
159fa

($CDCl_3$, 75 MHz)



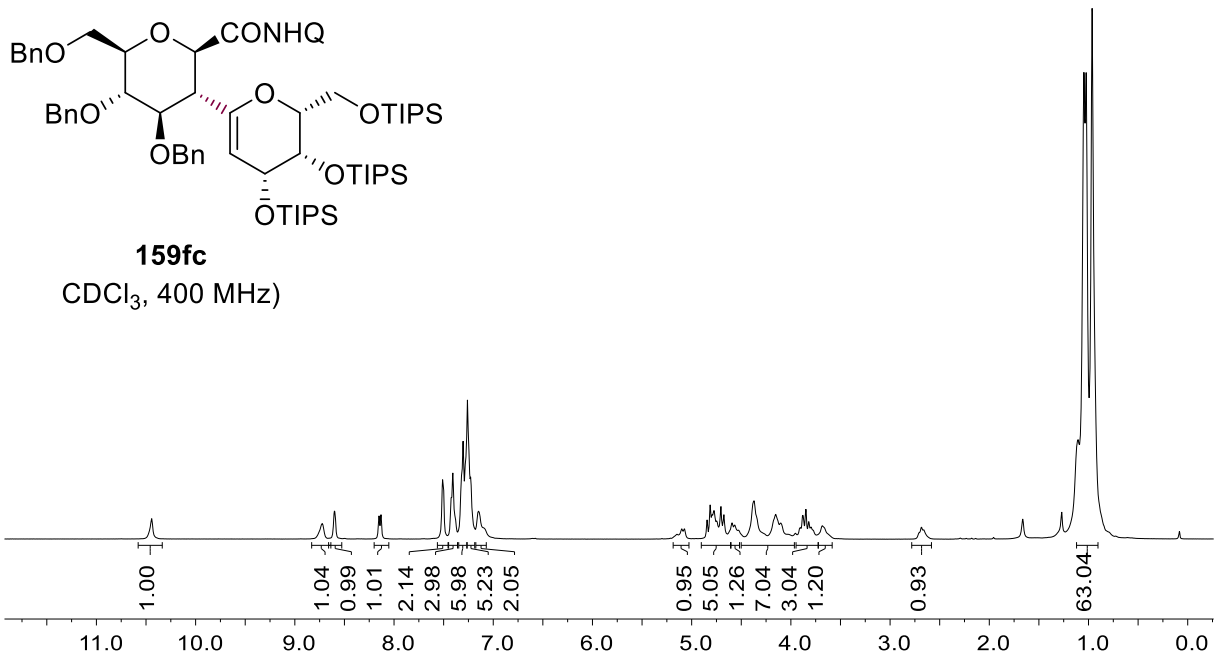
159fb

($CDCl_3$, 300 MHz)



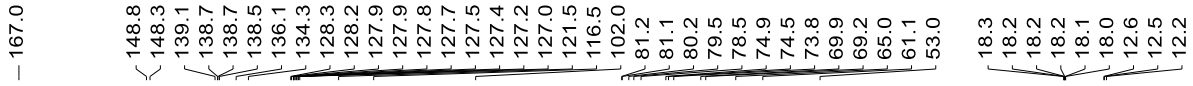
159fb

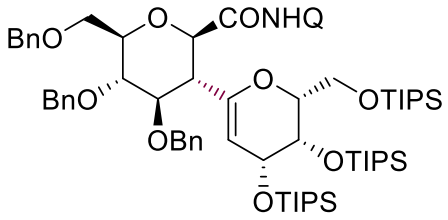
($CDCl_3$, 75 MHz)



159fc

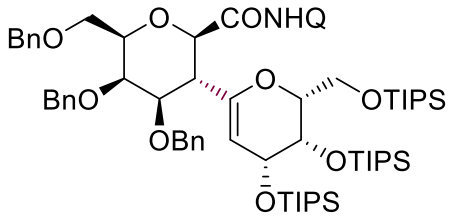
$CDCl_3$, 400 MHz)





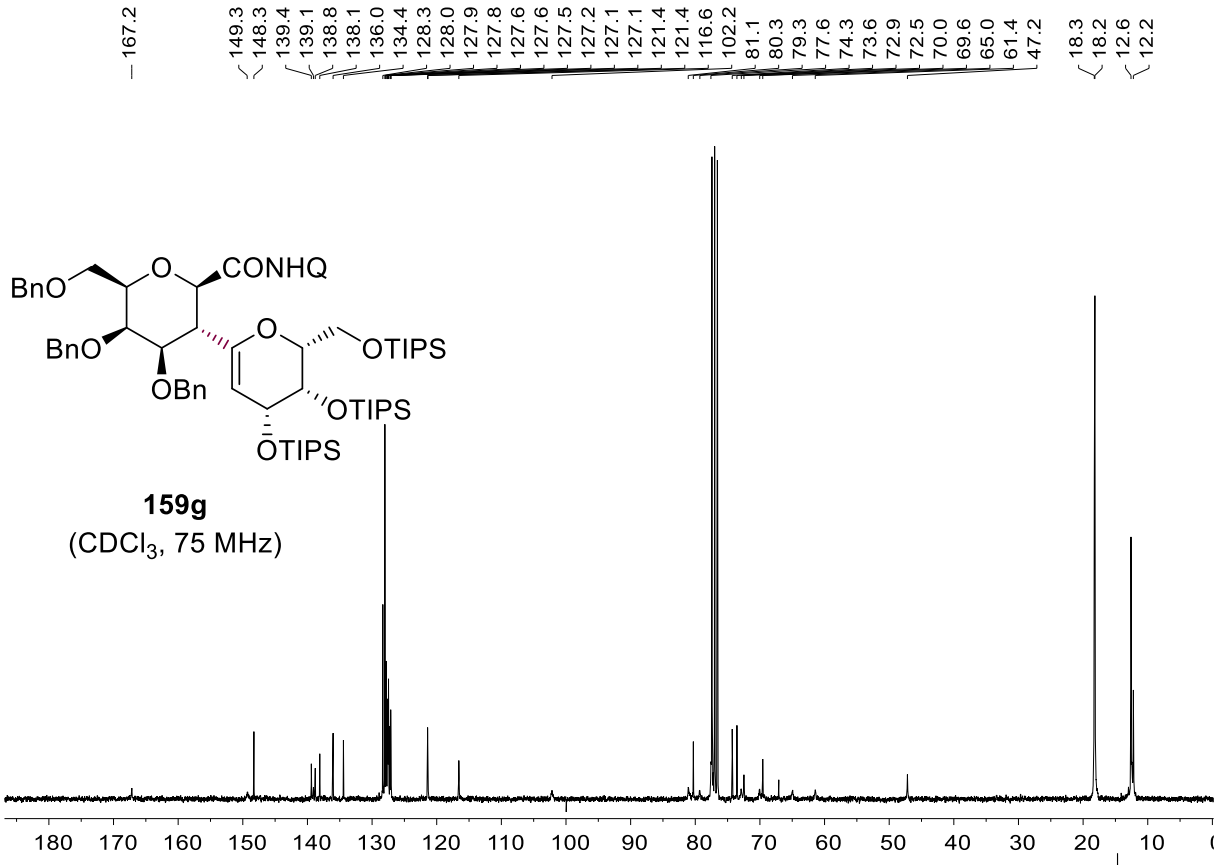
159fc

($CDCl_3$, 101 MHz)

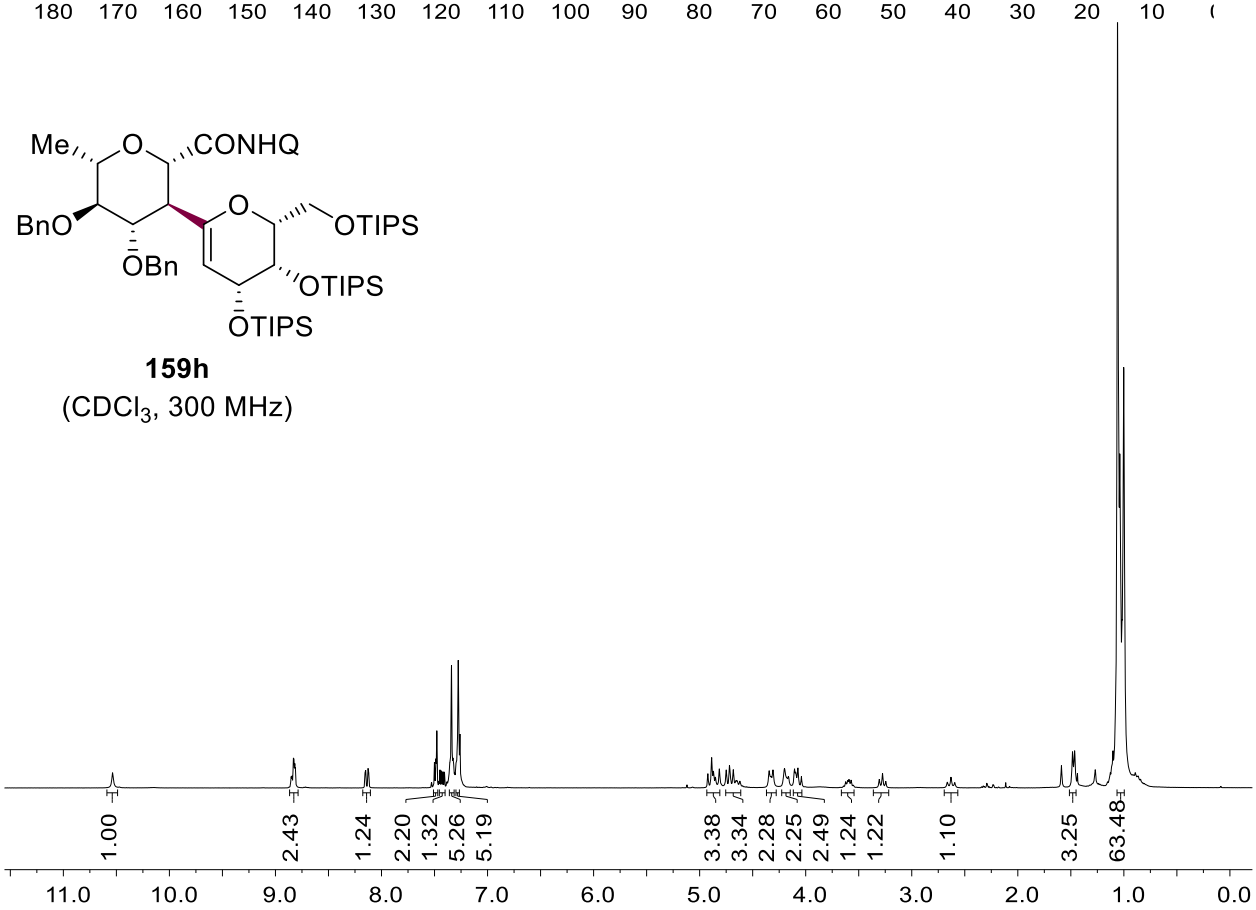


159g

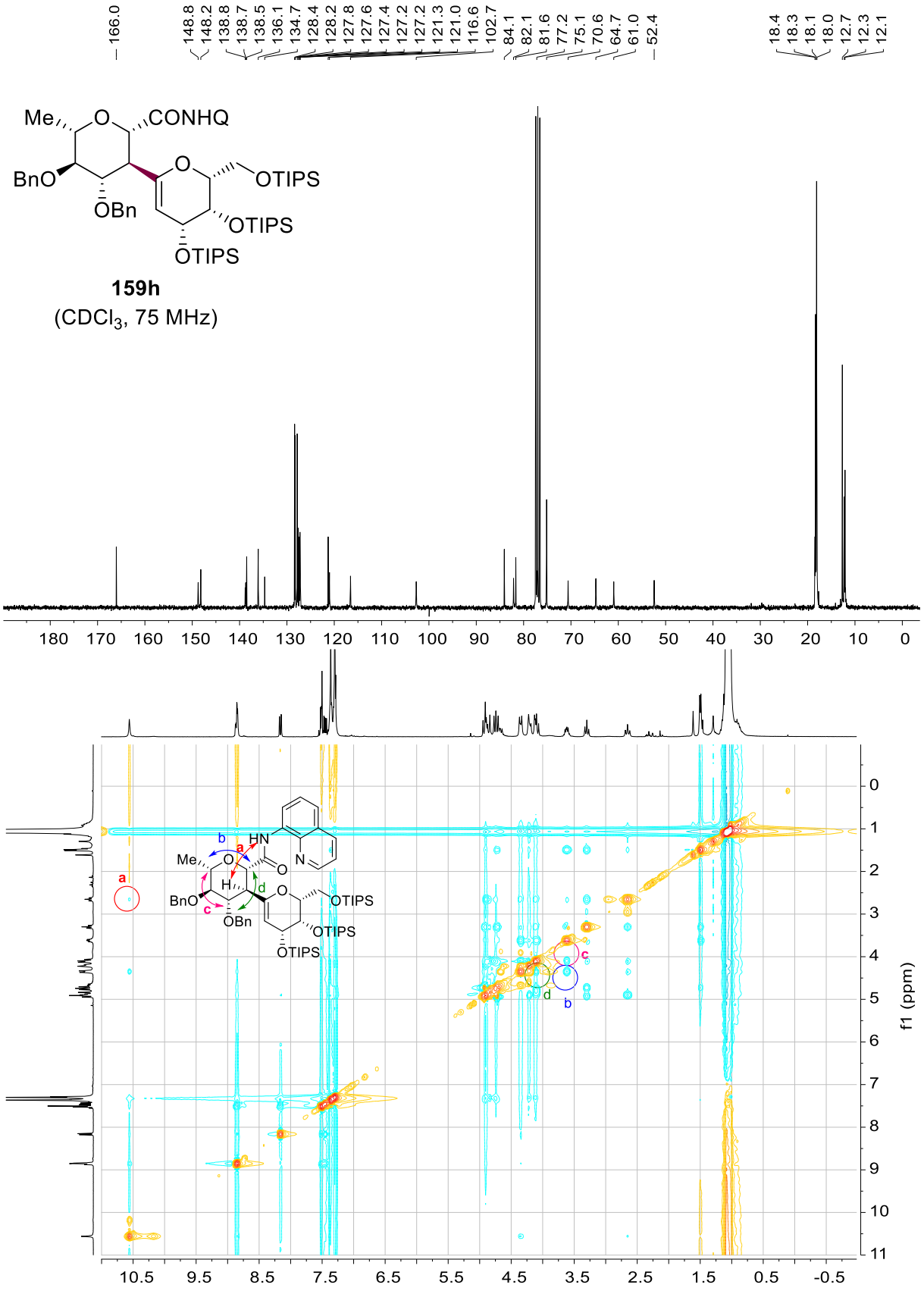
($CDCl_3$, 300 MHz)

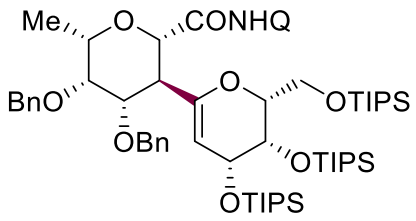


159g
($CDCl_3$, 75 MHz)



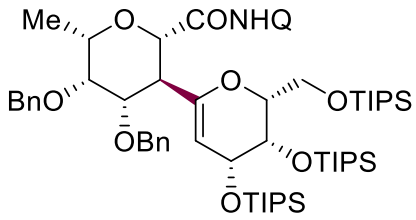
159h
($CDCl_3$, 300 MHz)


166.0
148.8
148.2
138.8
138.7
138.5
136.1
134.7
128.4
128.2
127.8
127.6
127.4
127.2
121.3
121.0
116.6
102.7
84.1
82.1
81.6
77.2
75.1
70.6
64.7
61.0
52.4
18.4
18.3
18.1
18.0
12.7
12.3
12.1
Me
O
CONHQ
BnO
OBn
O
OTIPS
OTIPS
OTIPS
159h
(CDCl3, 75 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
HN
N
O
H
a
b
c
d
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)
0 1 2 3 4 5 6 7 8 9 10 11



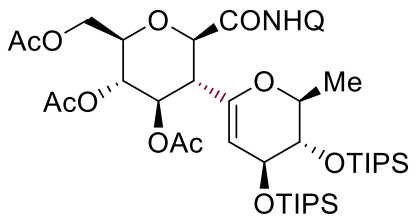
159i

($CDCl_3$, 300 MHz)



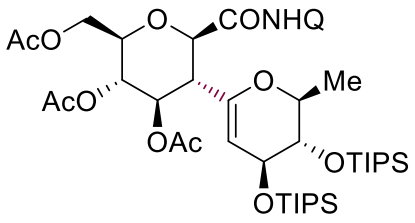
159i

($CDCl_3$, 101 MHz)



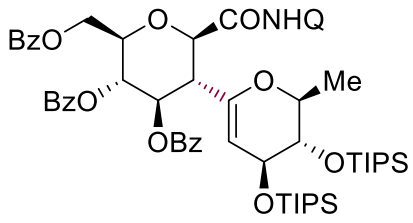
159ja

($CDCl_3$, 400 MHz)



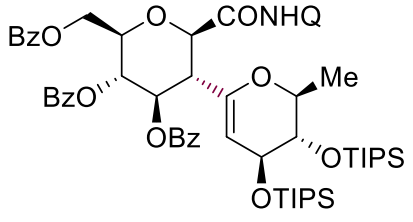
159ja

($CDCl_3$, 101 MHz)



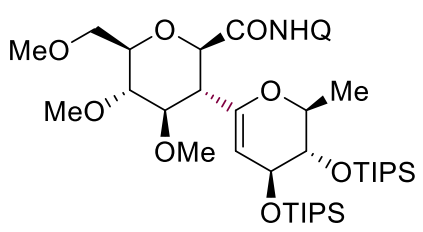
159jb

($CDCl_3$, 400 MHz)



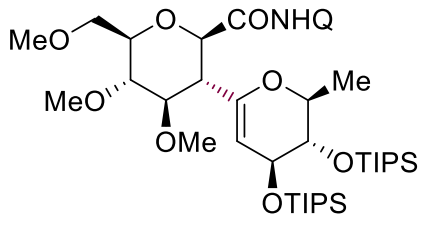
159jb

($CDCl_3$, 101 MHz)



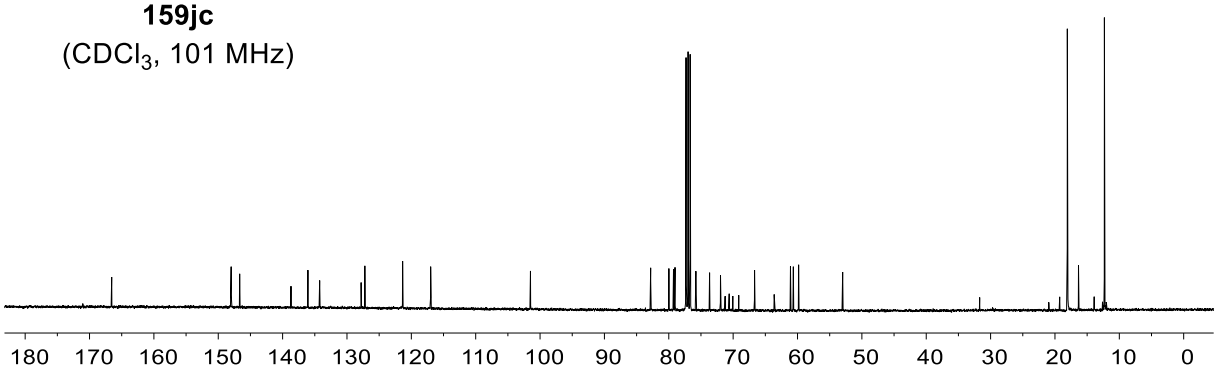
159jc

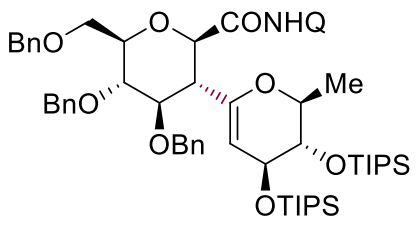
($CDCl_3$, 400 MHz)



159jc

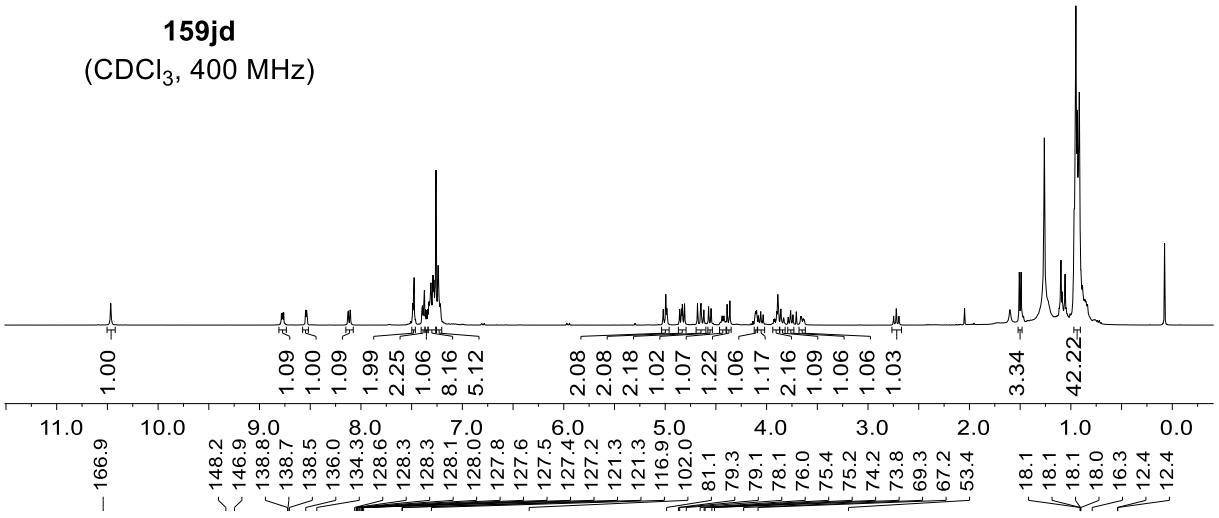
($CDCl_3$, 101 MHz)

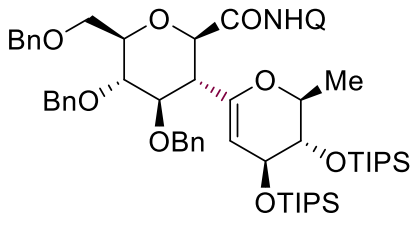




159jd

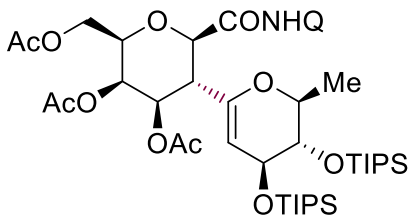
($CDCl_3$, 400 MHz)





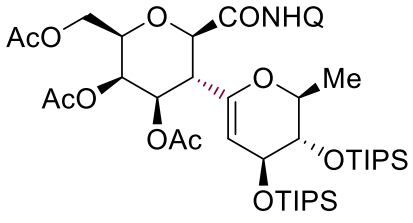
159jd

($CDCl_3$, 101 MHz)



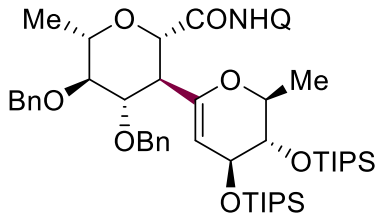
159k

($CDCl_3$, 400 MHz)



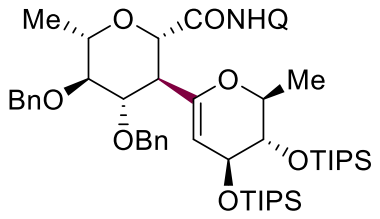
159k

($CDCl_3$, 101 MHz)



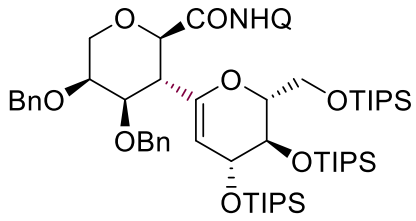
159l

($CDCl_3$, 400 MHz)



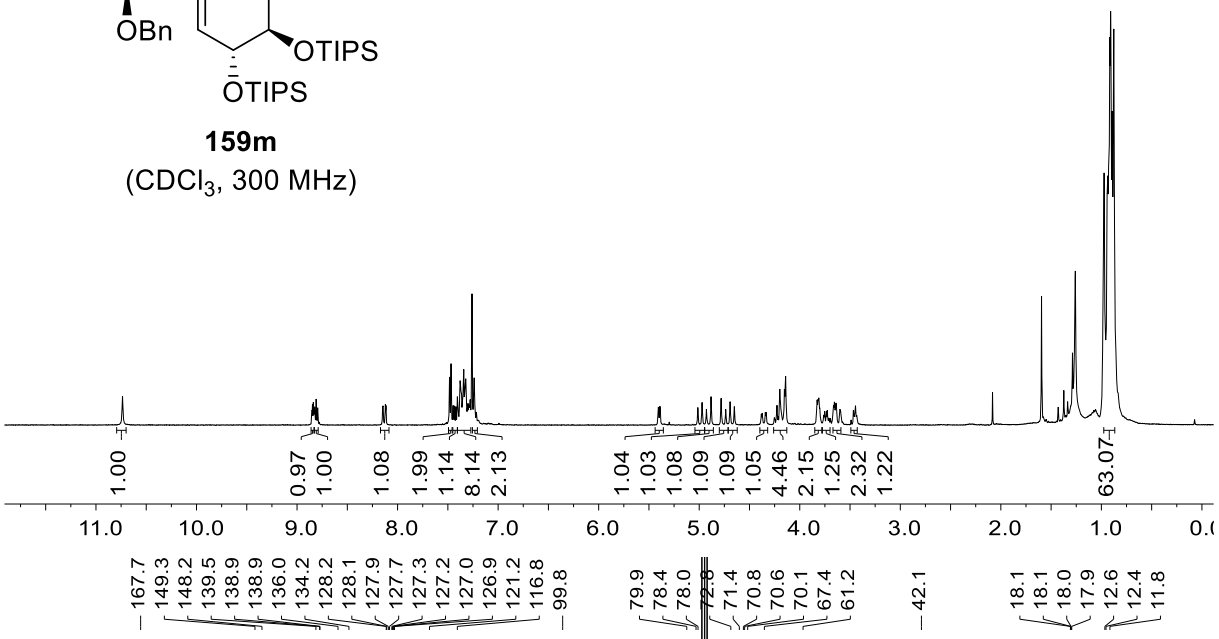
159l

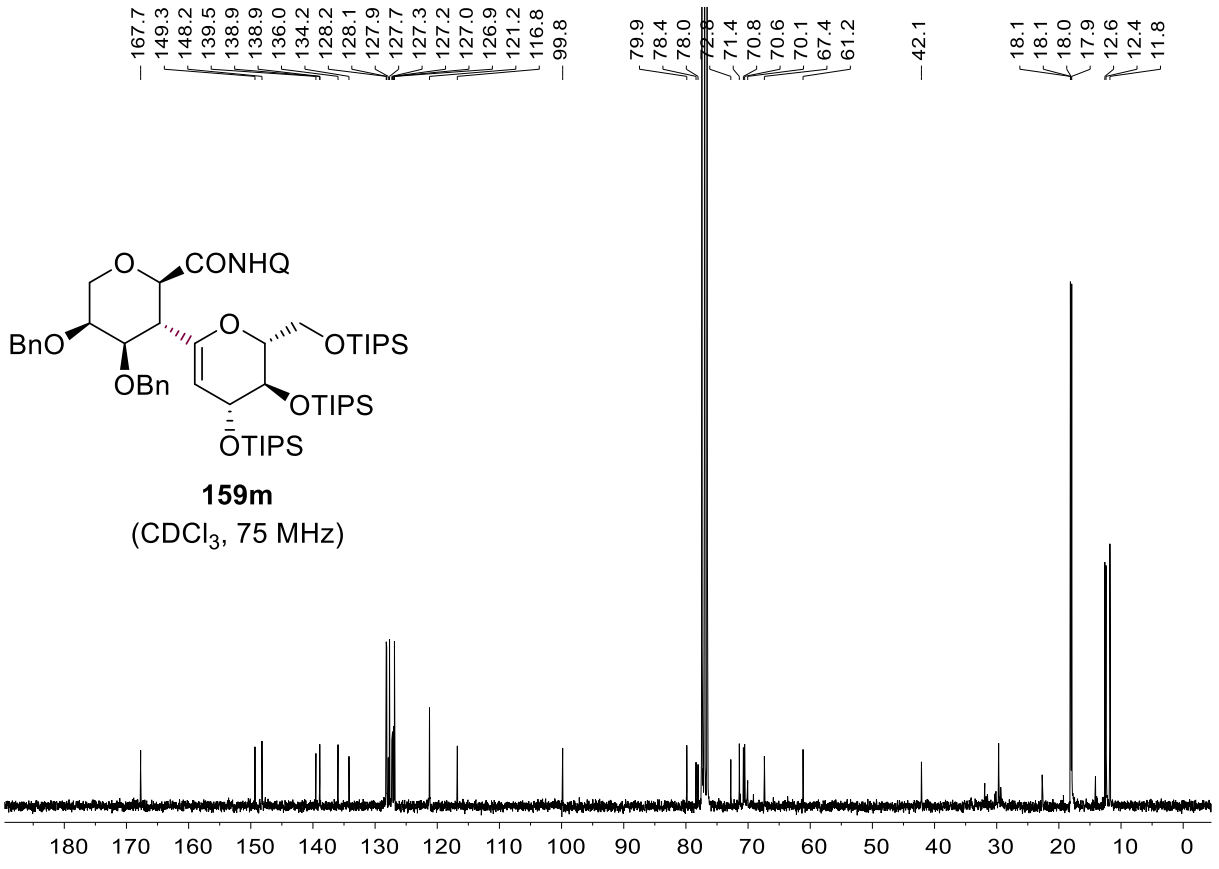
($CDCl_3$, 101 MHz)



159m

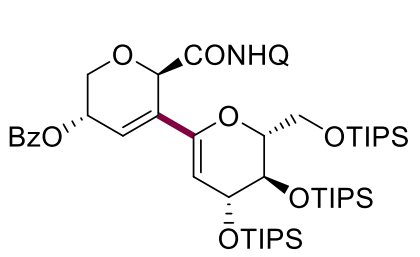
($CDCl_3$, 300 MHz)





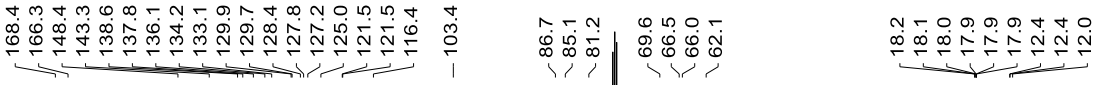
159m

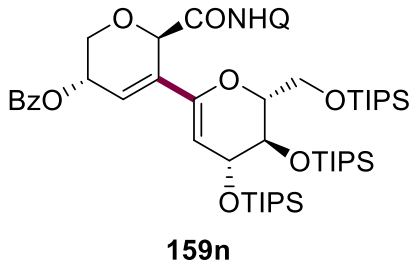
($CDCl_3$, 75 MHz)



159n

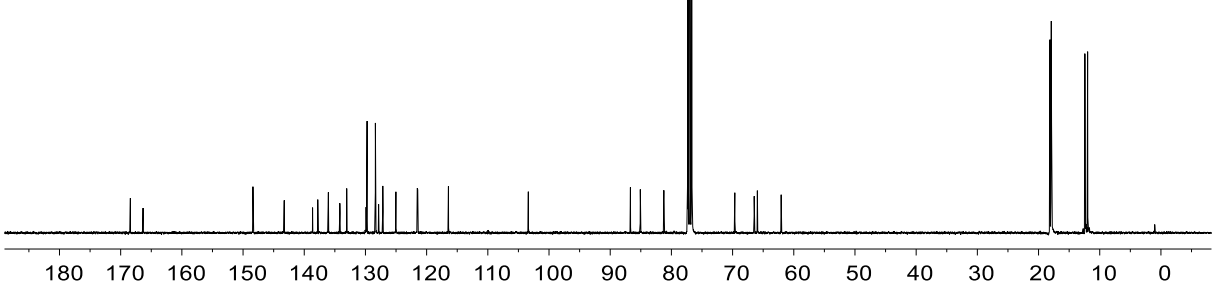
($CDCl_3$, 400 MHz)

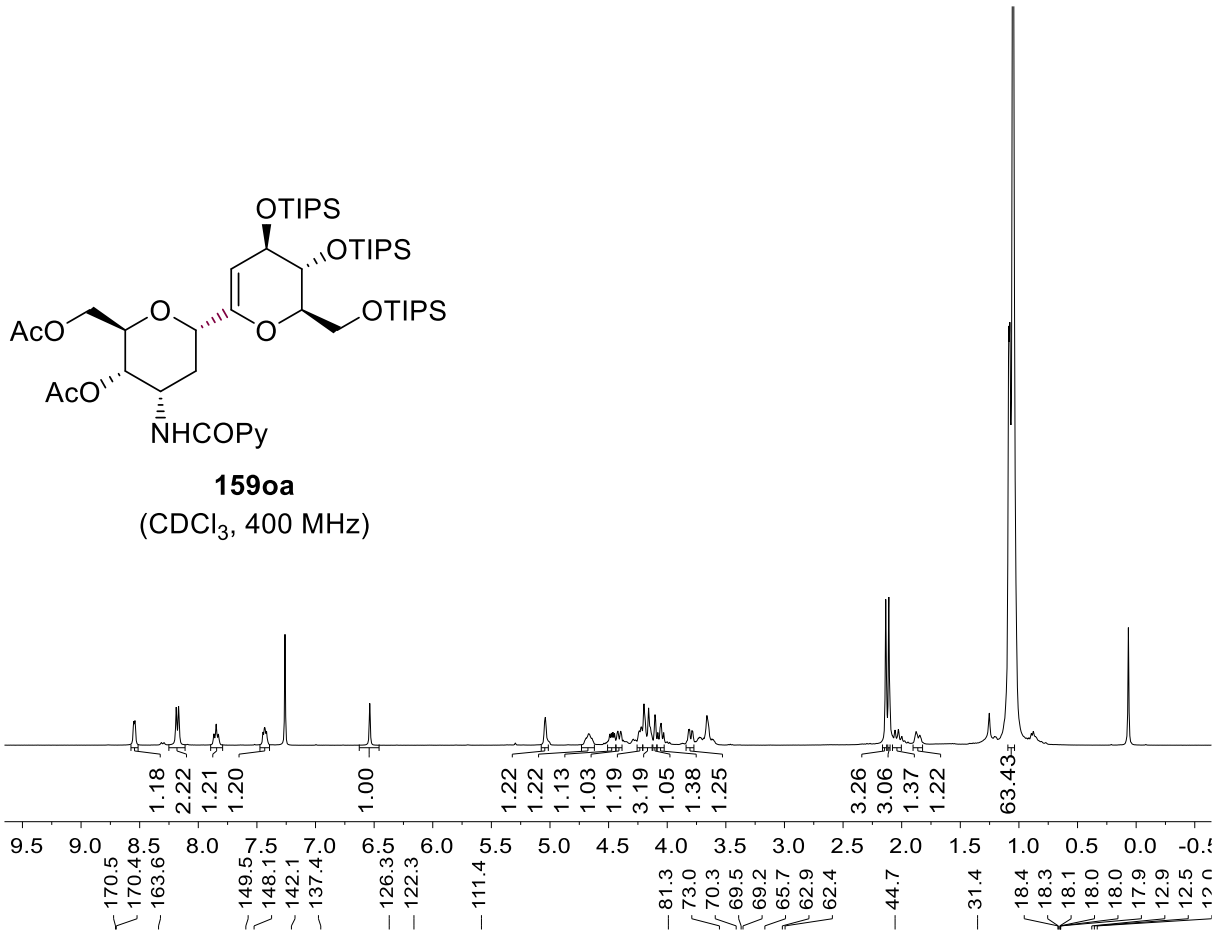




159n

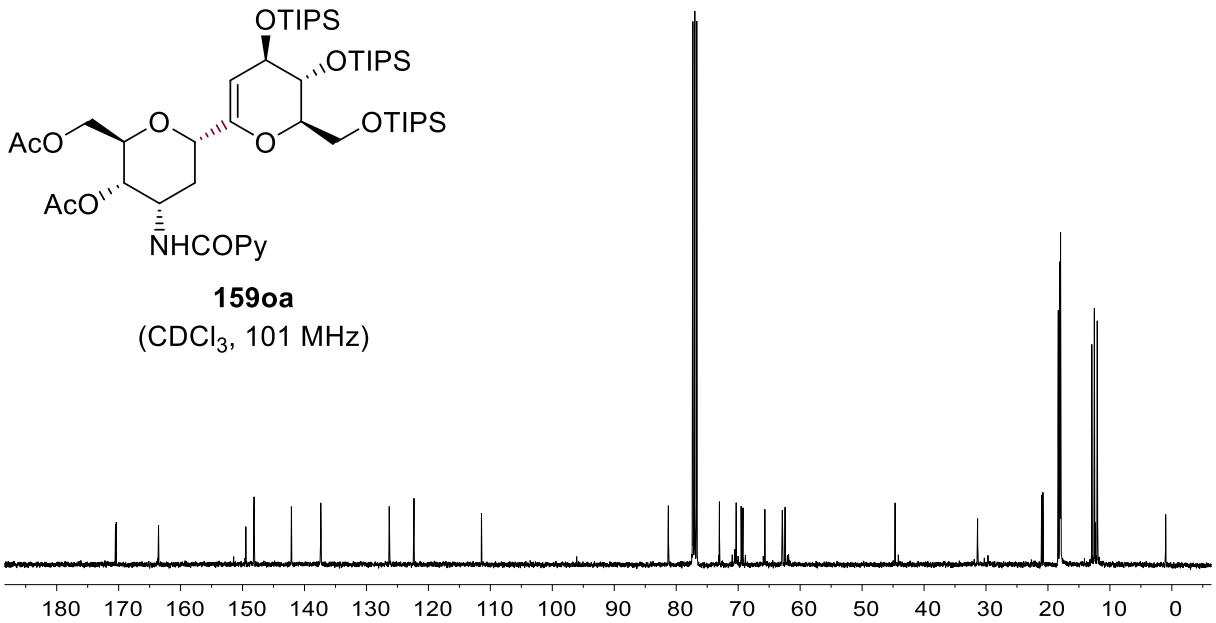
($CDCl_3$, 101 MHz)





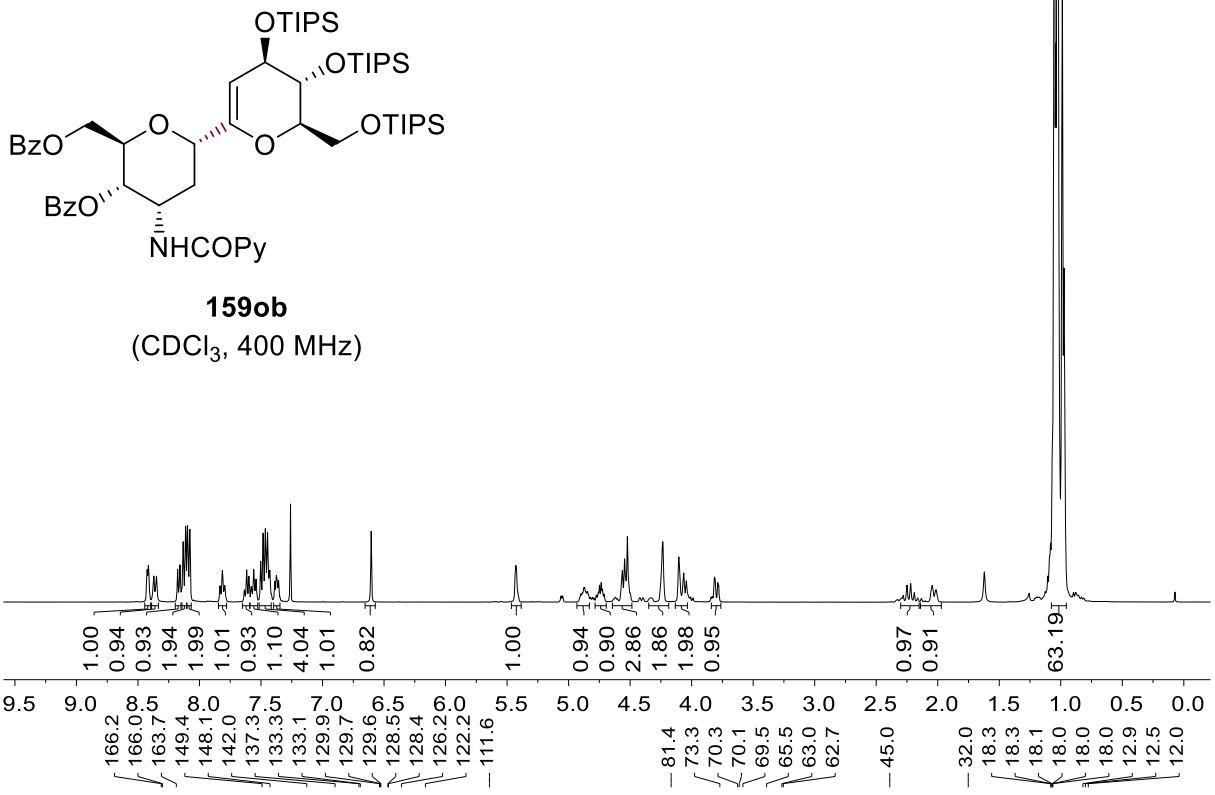
159oa

($CDCl_3$, 400 MHz)

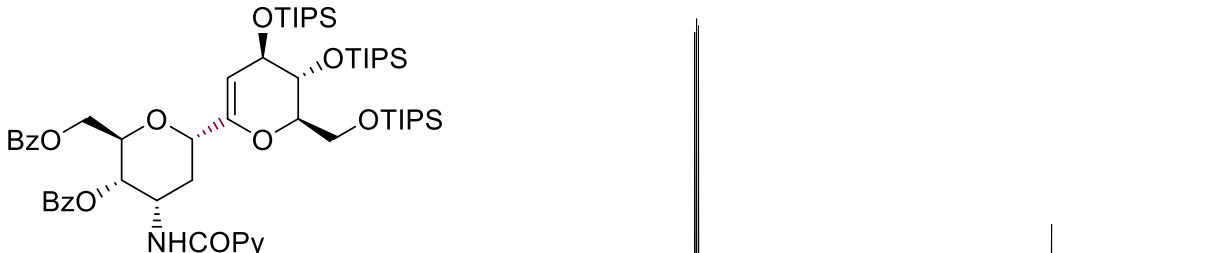


159oa

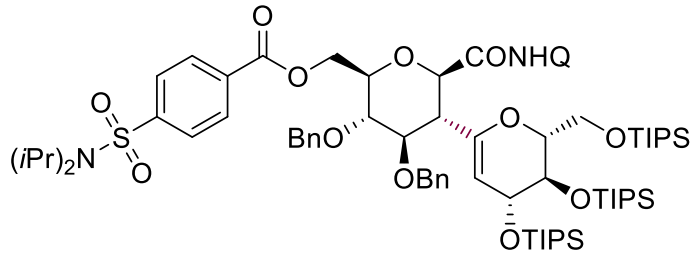
($CDCl_3$, 101 MHz)



159ob
($CDCl_3$, 400 MHz)

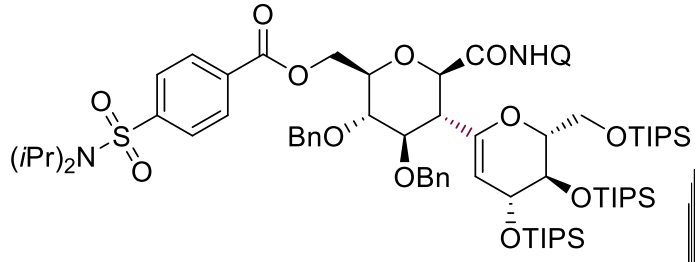


159ob
($CDCl_3$, 101 MHz)



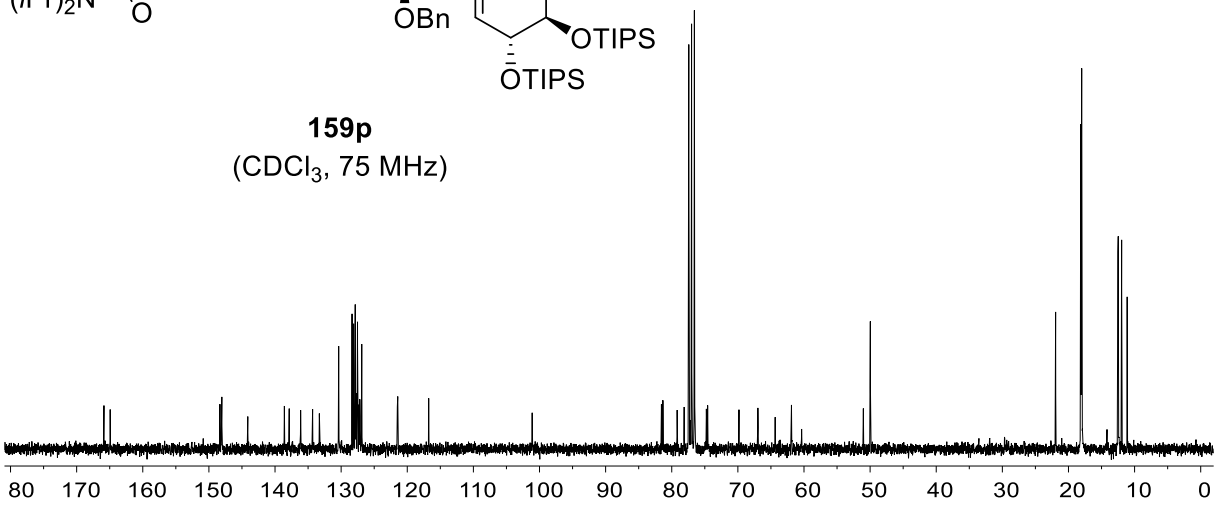
159p

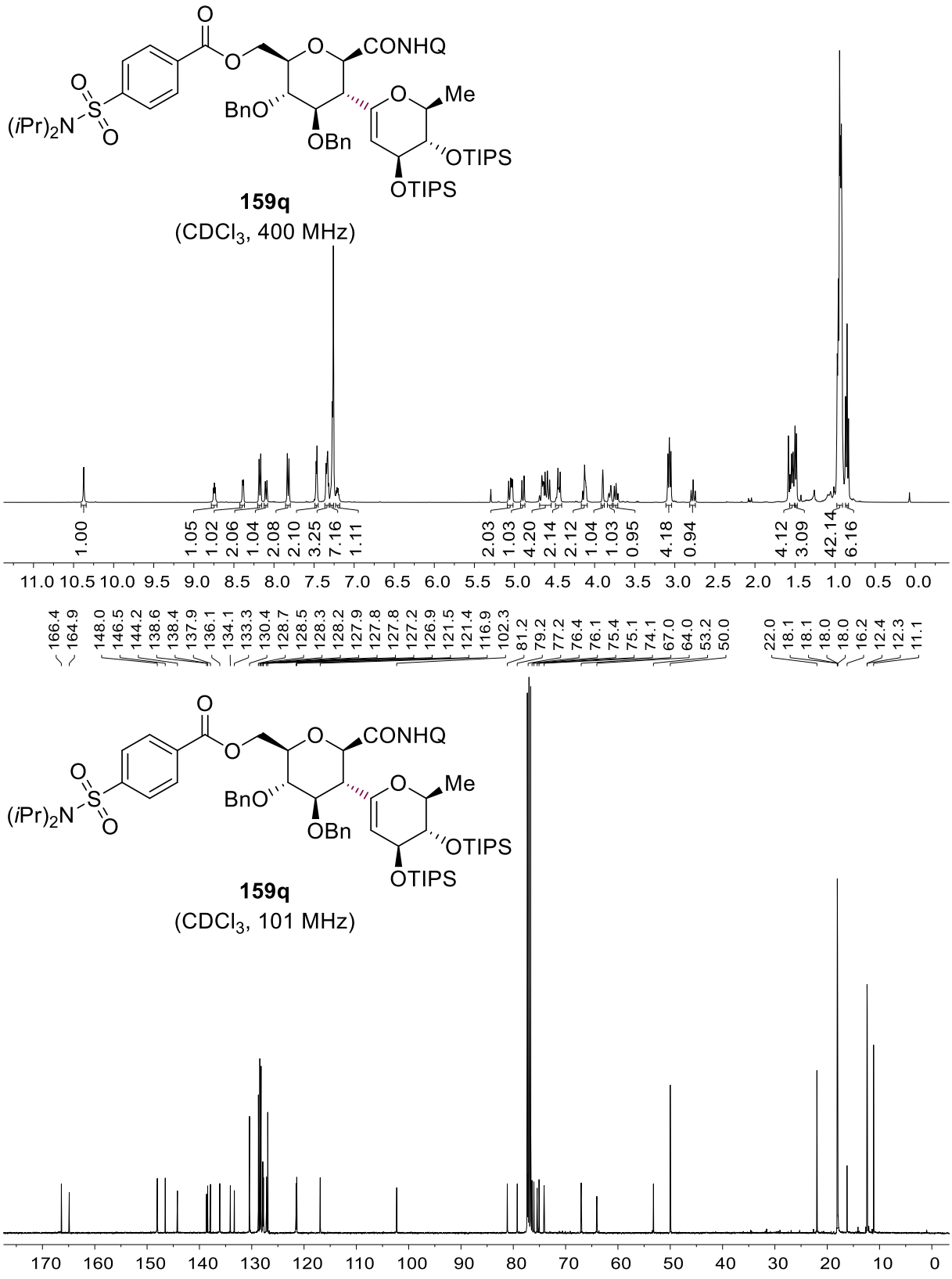
($CDCl_3$, 300 MHz)

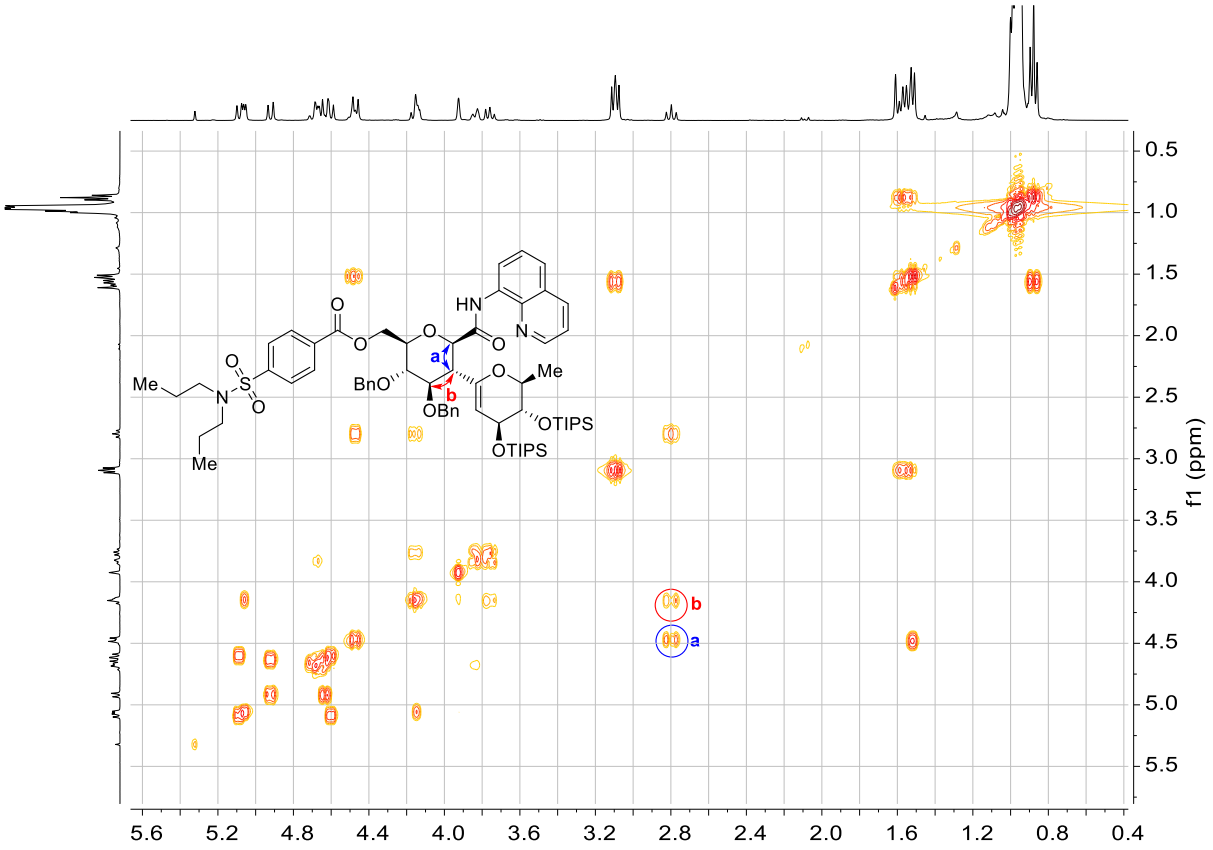


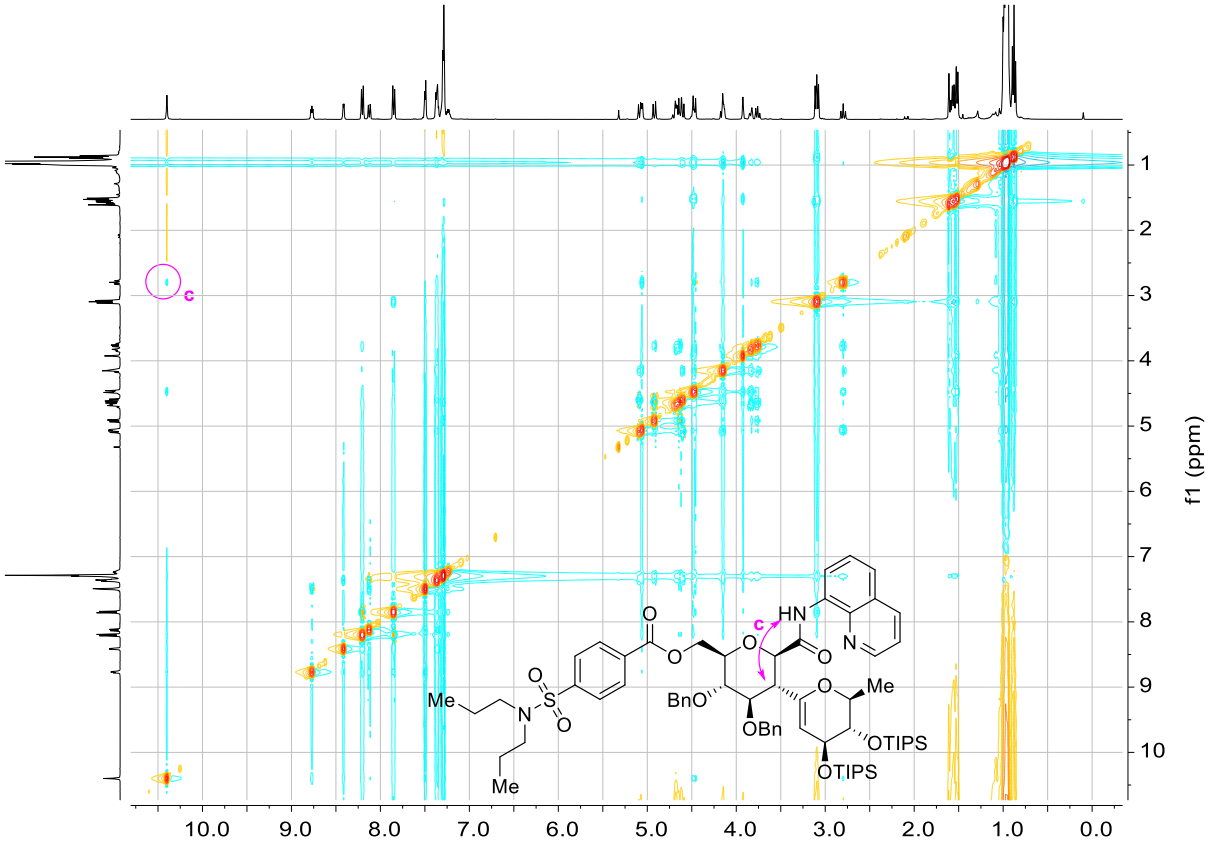
159p

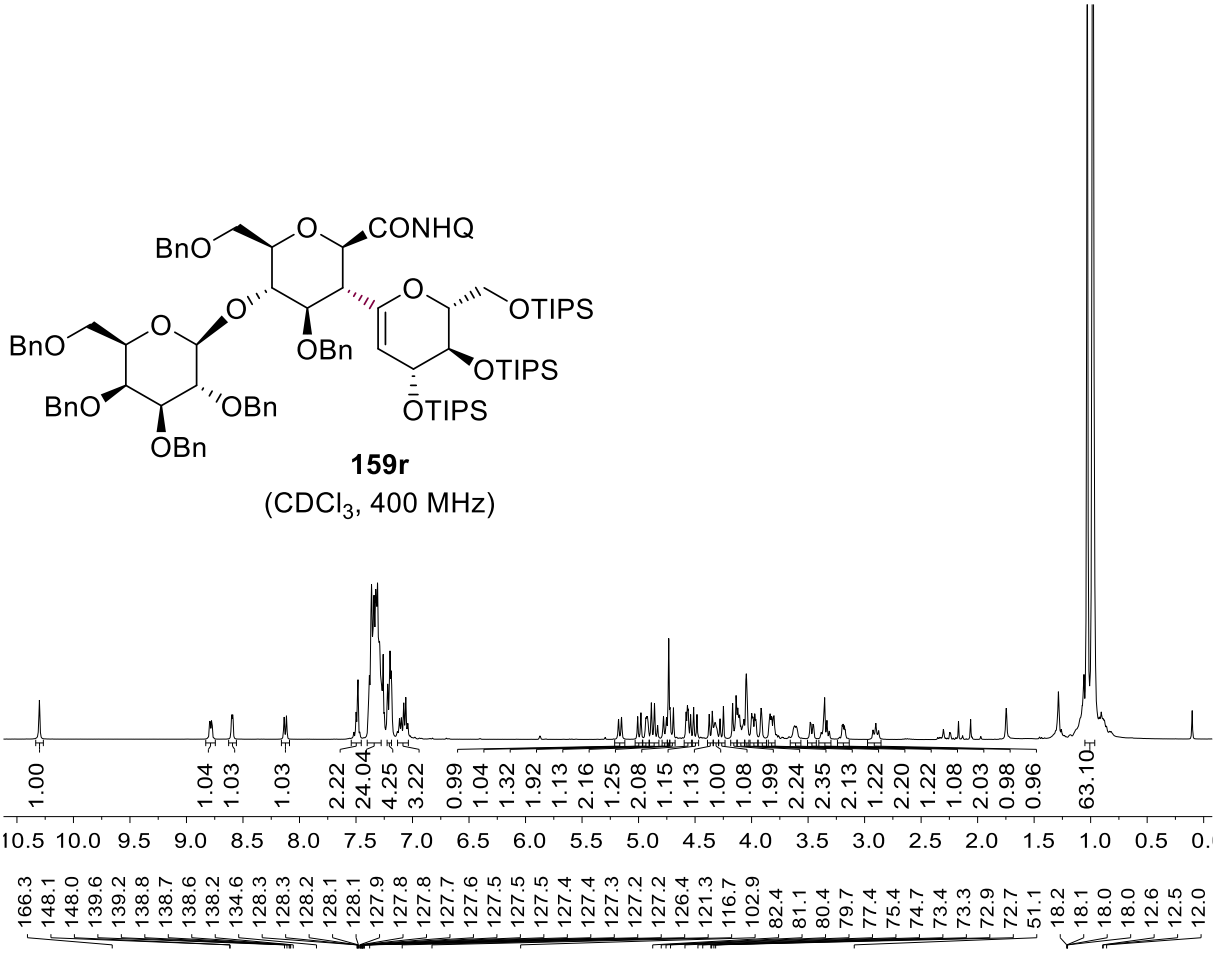
($CDCl_3$, 75 MHz)




CONHQ
Me
BnO
OBn
OTIPS
OTIPS
(iPr)2N
159q
(CDCl3, 400 MHz)
1.00 1.05 1.02 2.06 1.04 2.08 2.10 3.25 7.16 1.11 2.03 1.03 4.20 2.14 2.12 1.04 1.03 0.95 4.18 0.94 4.12 3.09 42.14 6.16
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
166.4 164.9 148.0 146.5 144.2 138.6 138.4 137.9 136.1 134.1 133.3 130.4 128.7 128.5 128.3 128.2 127.9 127.8 127.8 127.2 126.9 121.5 121.4 116.9 102.3 81.2 79.2 77.2 76.4 76.1 75.4 75.1 74.1 67.0 64.0 53.2 50.0 22.0 18.1 18.1 18.0 18.0 16.2 12.4 12.3 11.1
CONHQ
Me
BnO
OBn
OTIPS
OTIPS
(iPr)2N
159q
(CDCl3, 101 MHz)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

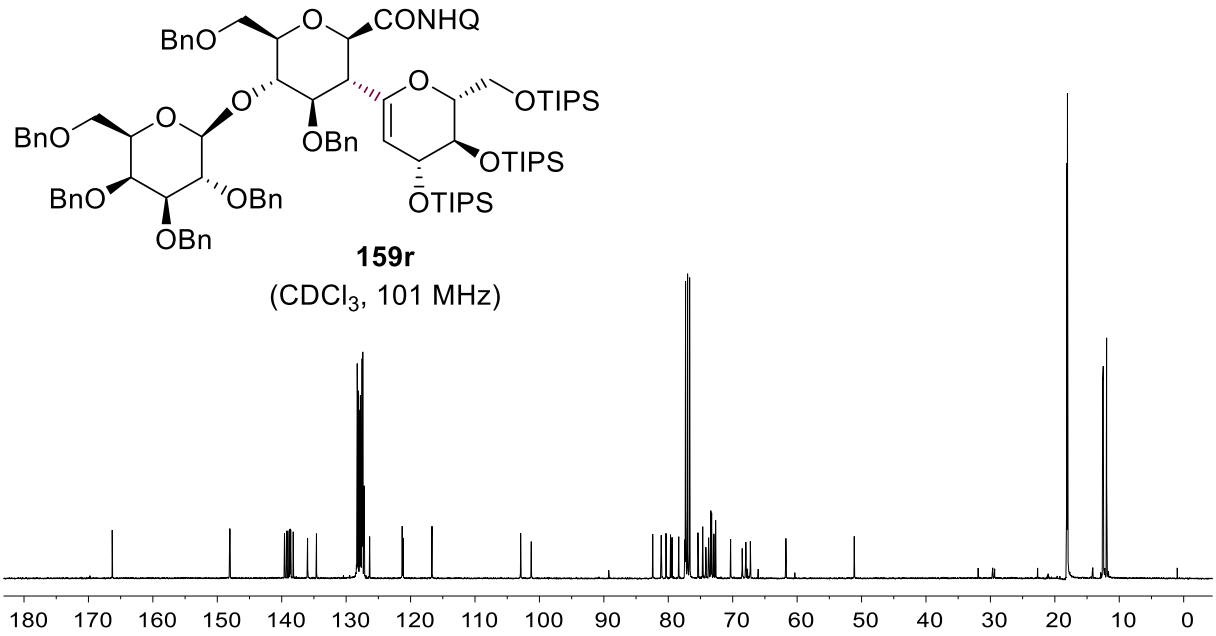

f1 (ppm)
5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
a
b
Me
N
S
O
Me
BnO
OBn
OTIPS
OTIPS
HN
N
Me


f1 (ppm)
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
1 2 3 4 5 6 7 8 9 10
c
HN
N
Me
N
Me
BnO
OBn
OTIPS
OTIPS



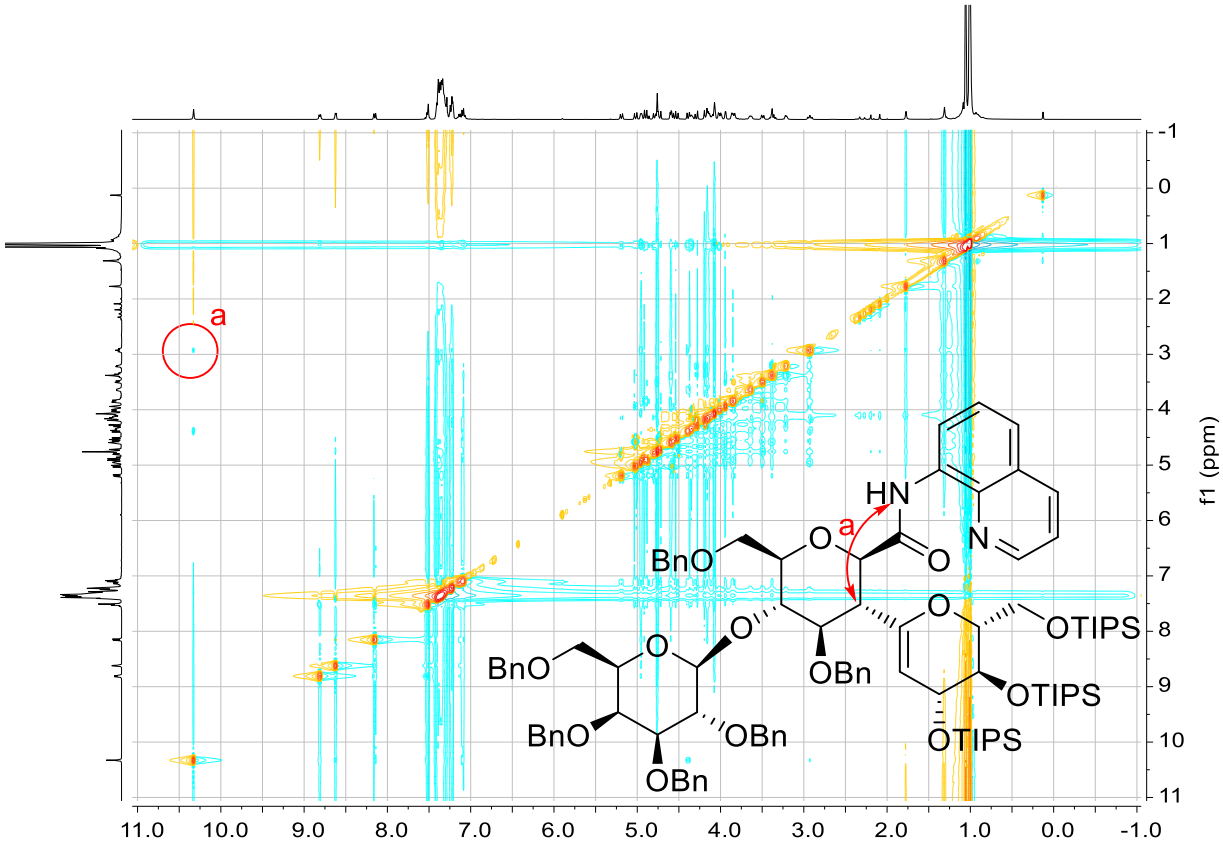
159r

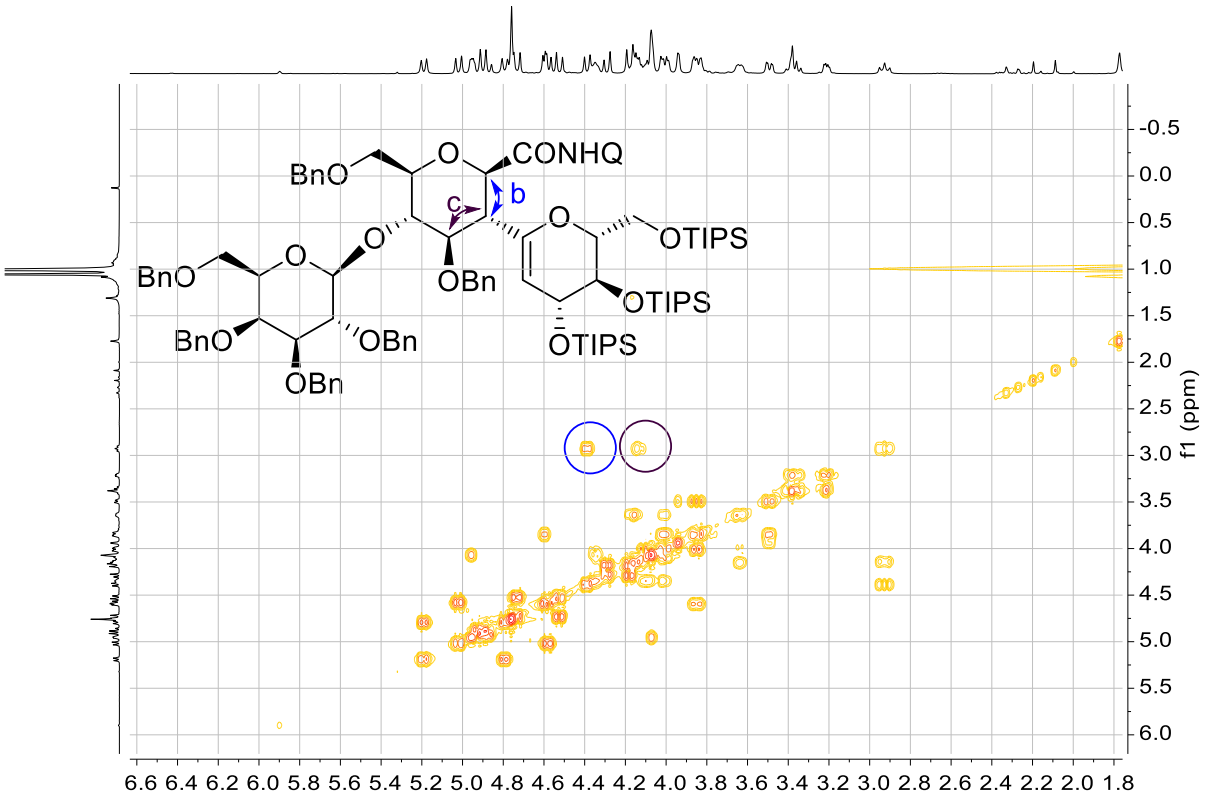
($CDCl_3$, 400 MHz)

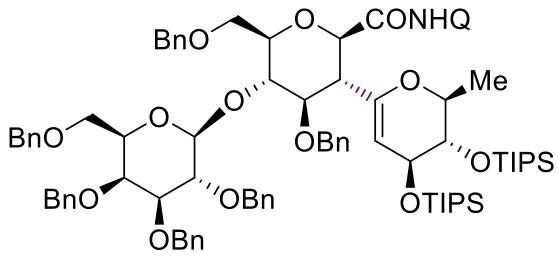


159r

($CDCl_3$, 101 MHz)

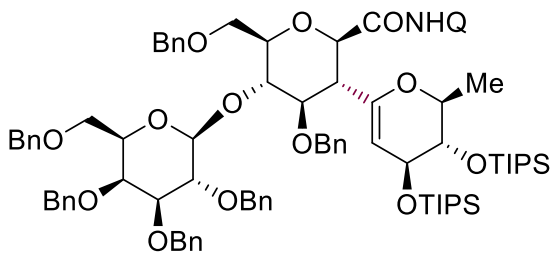

a
HN
N
O
BnO
OBn
OTIPS
f1 (ppm)
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


CONHQ
BnO
OBn
OTIPS
a
b
c
f1 (ppm)
6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8



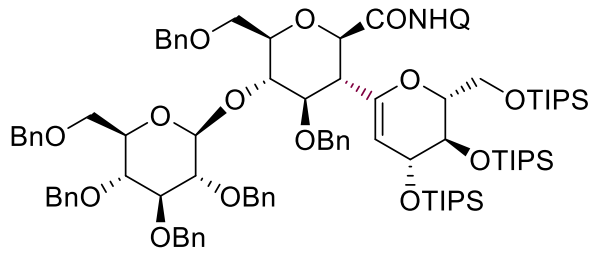
159s

($CDCl_3$, 400 MHz)



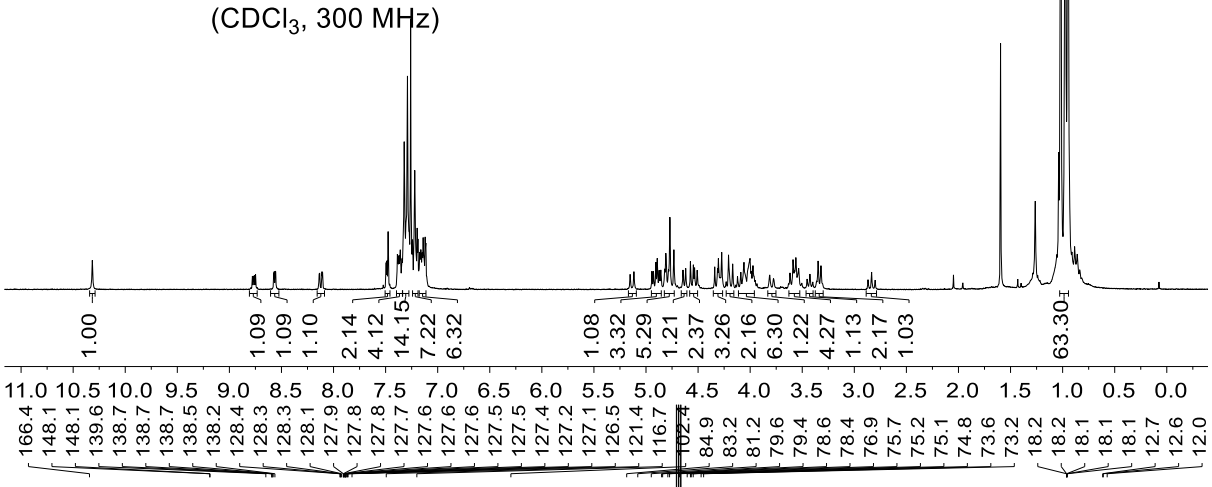
159s

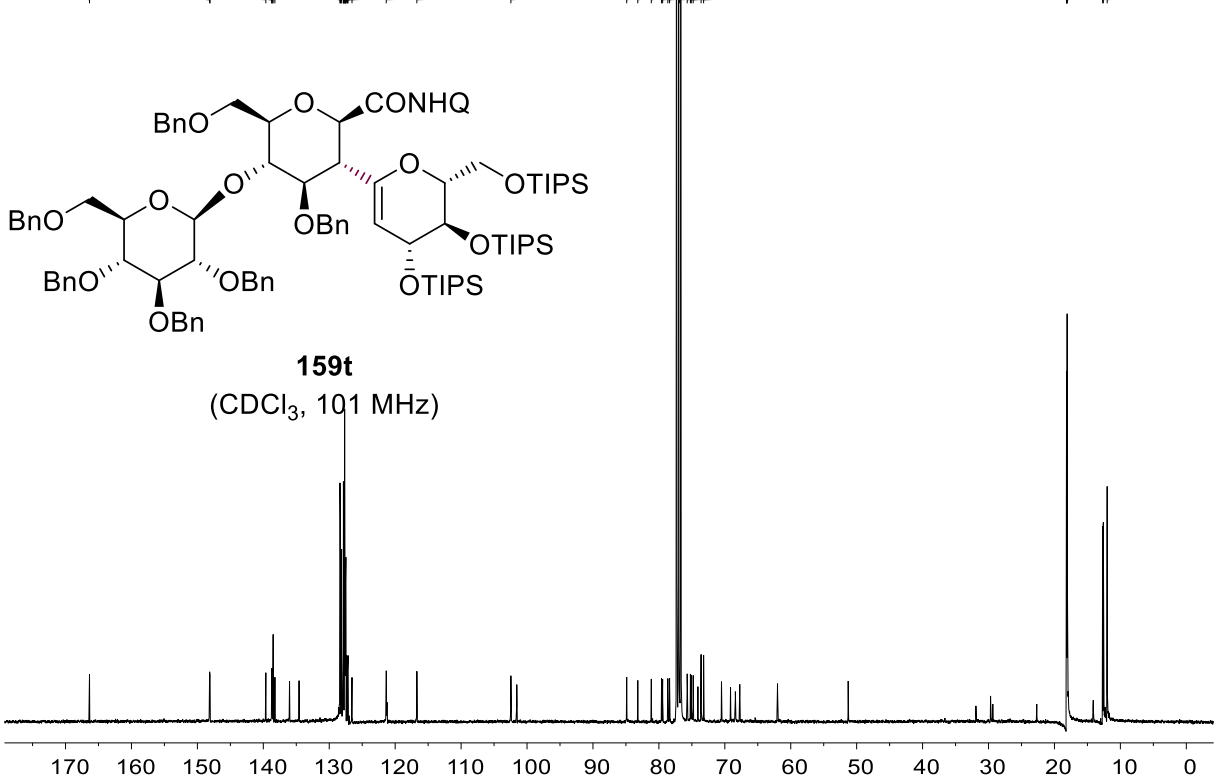
($CDCl_3$, 101 MHz)



159t

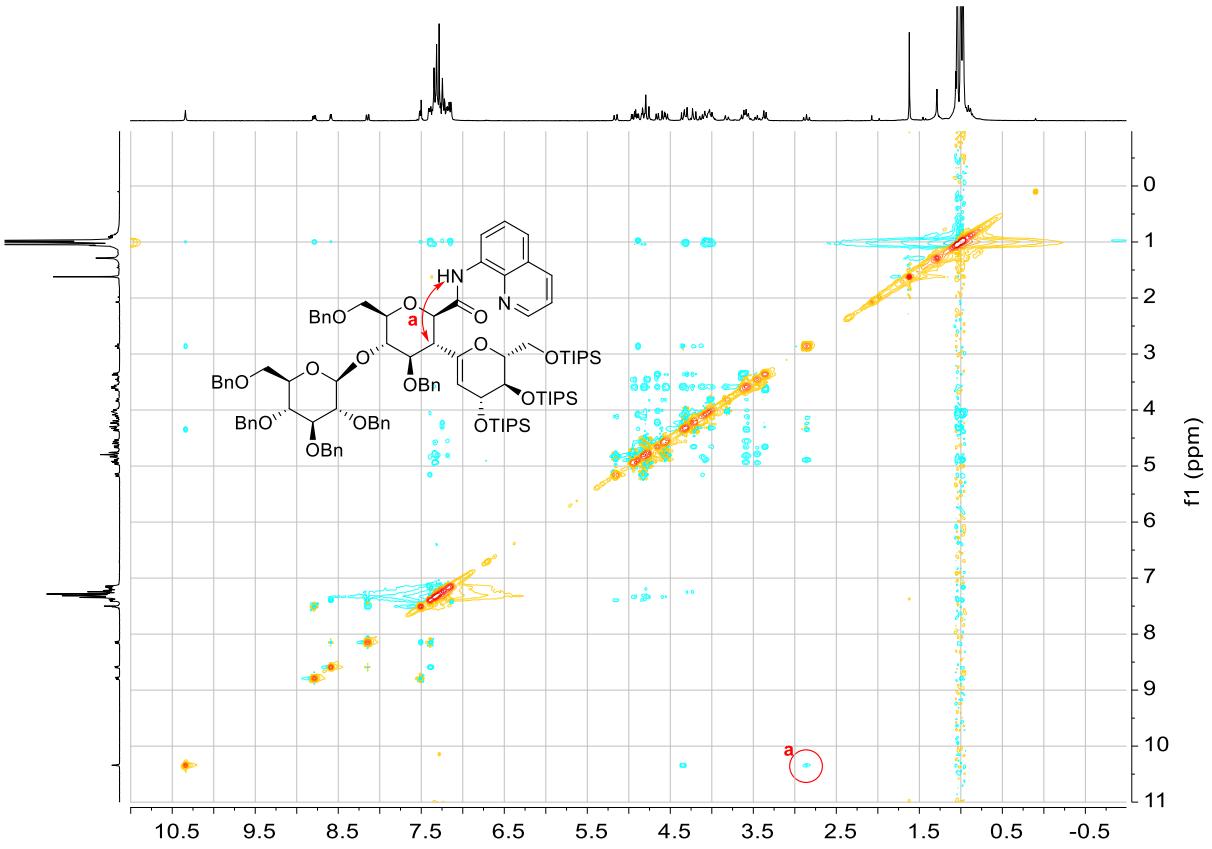
($CDCl_3$, 300 MHz)

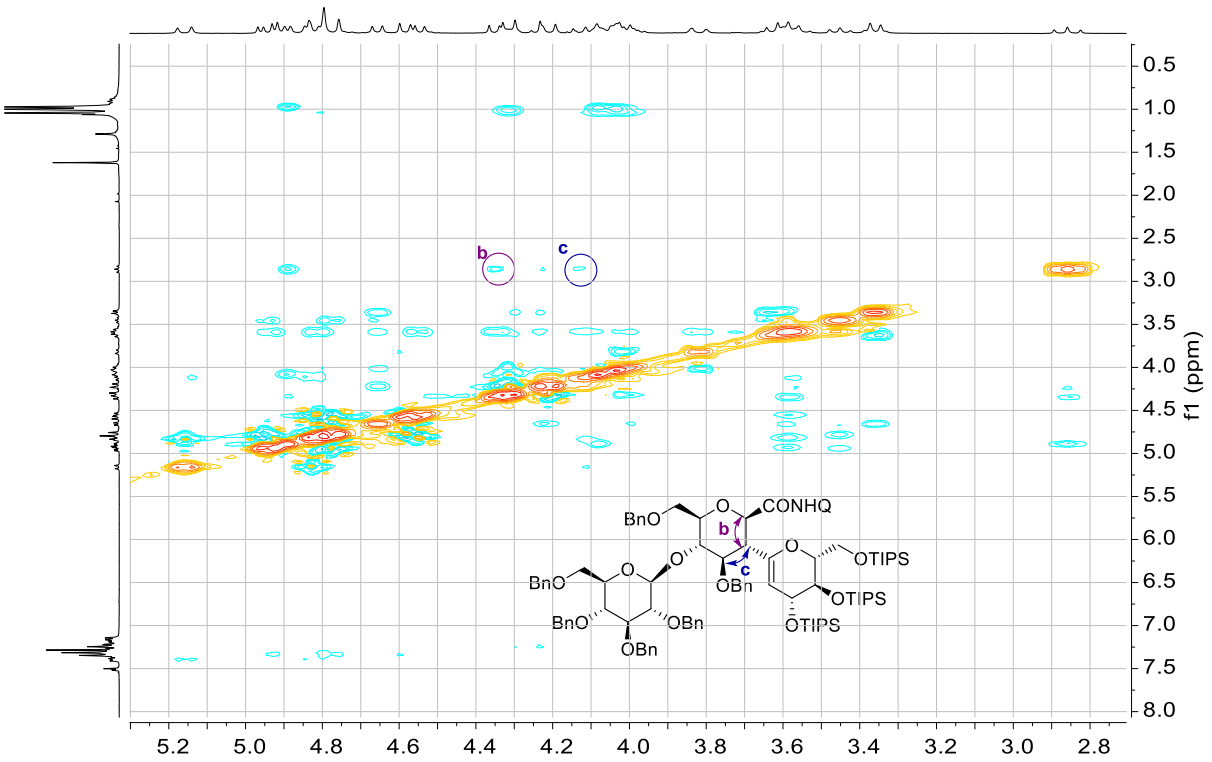


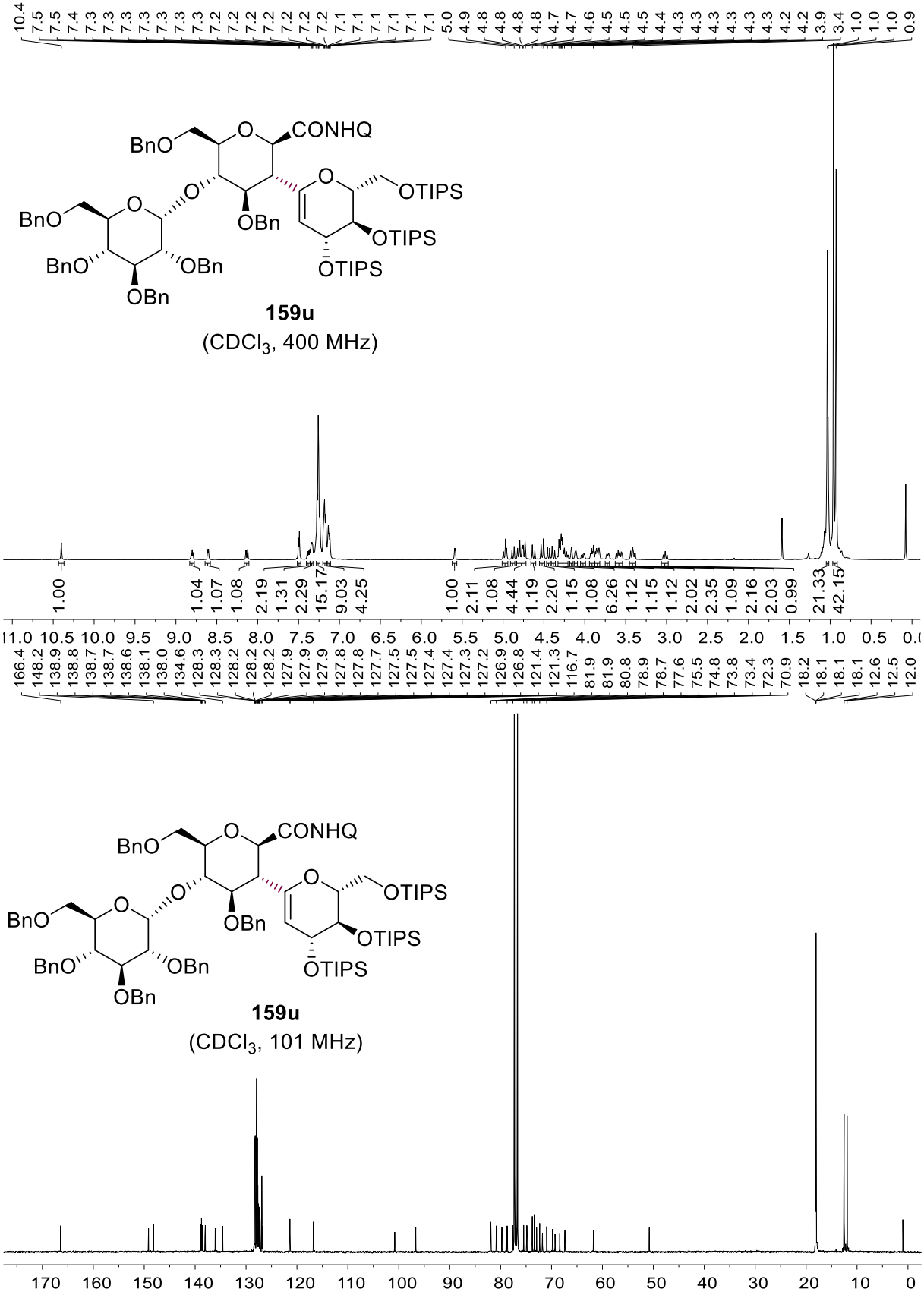


159t

($CDCl_3$, 101 MHz)


HN
N
O
BnO
a
OBn
OTIPS
f1 (ppm)
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


b
c
CONHQ
BnO
OBn
OTIPS
f1 (ppm)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8

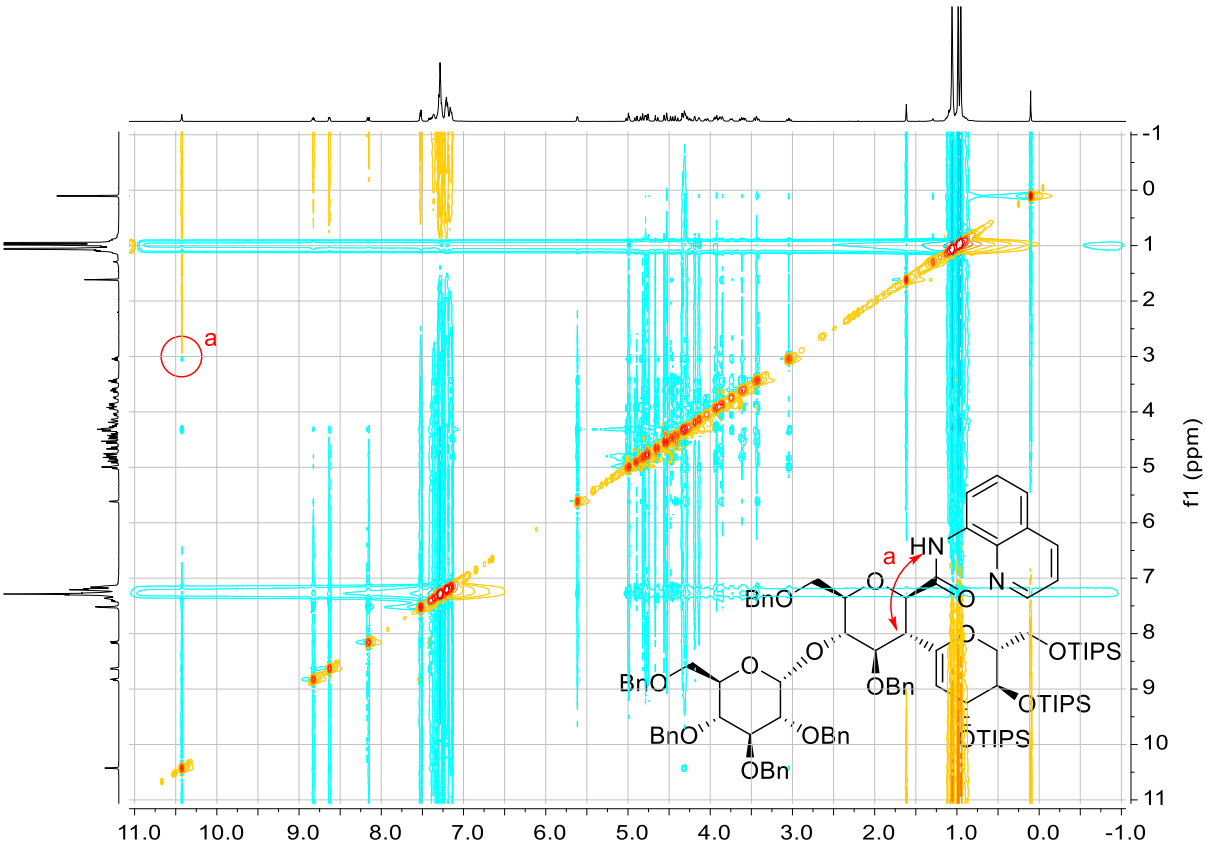


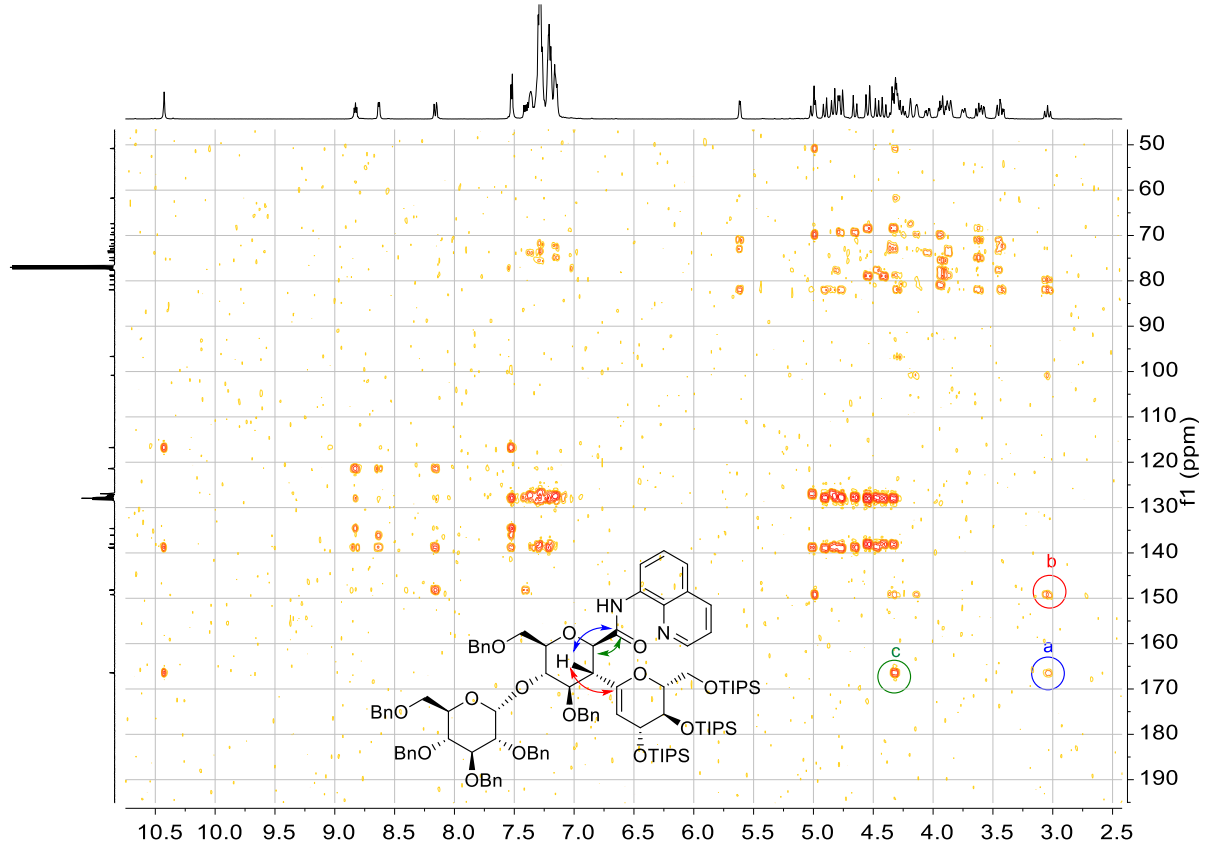
159u

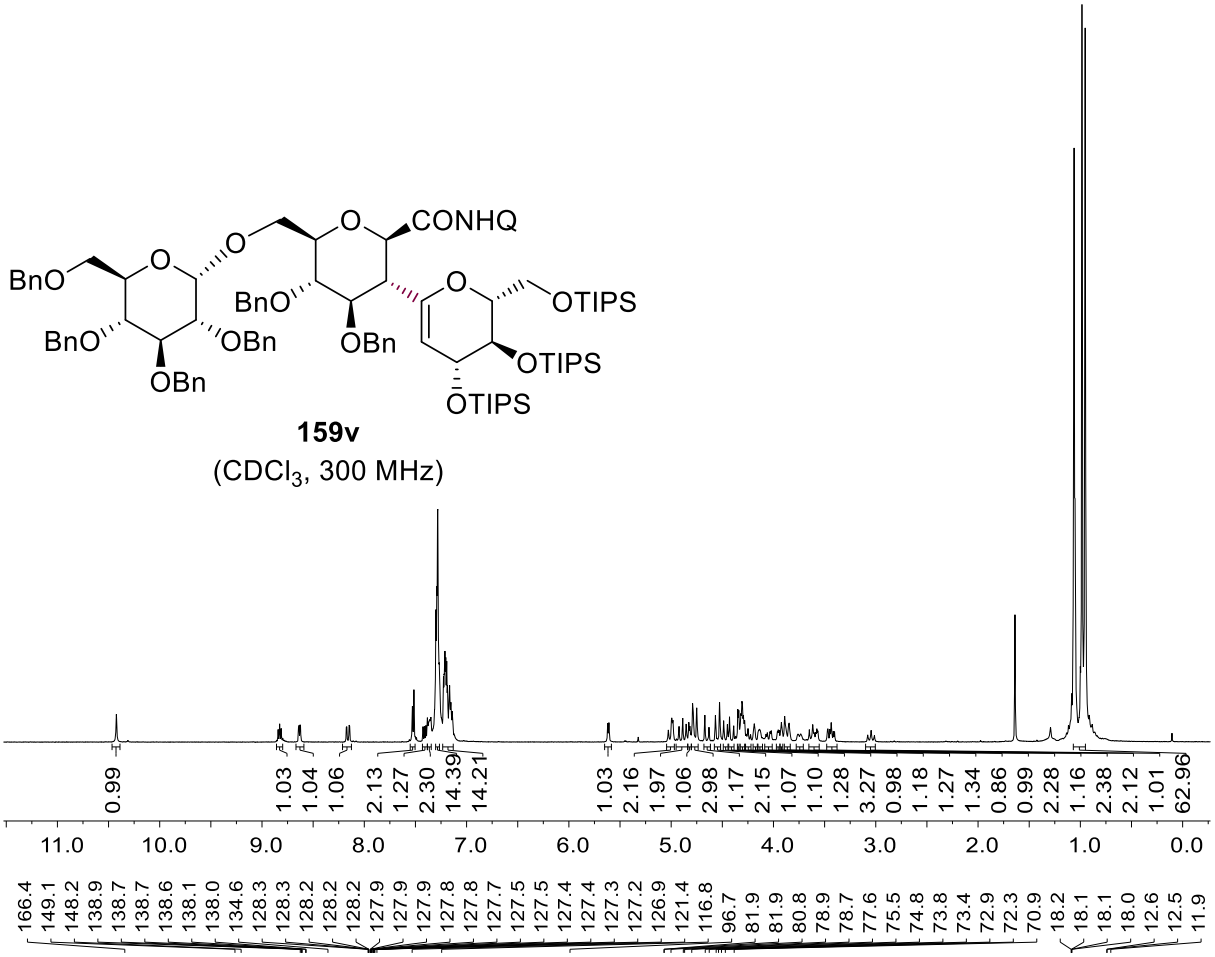
($CDCl_3$, 400 MHz)

159u

($CDCl_3$, 101 MHz)

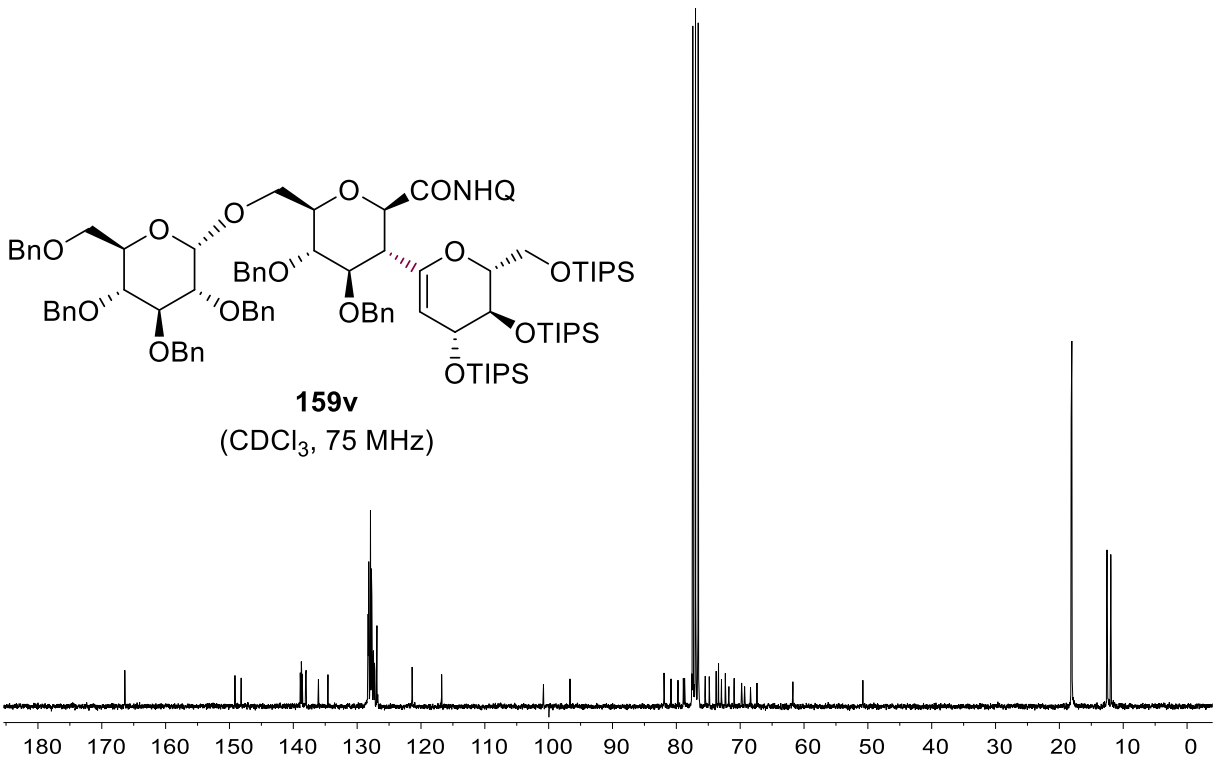

a
HN
N
BnO
O
OBn
OTIPS
f1 (ppm)
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


HN
N
BnO
OBn
OTIPS
a
b
c
f1 (ppm)
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



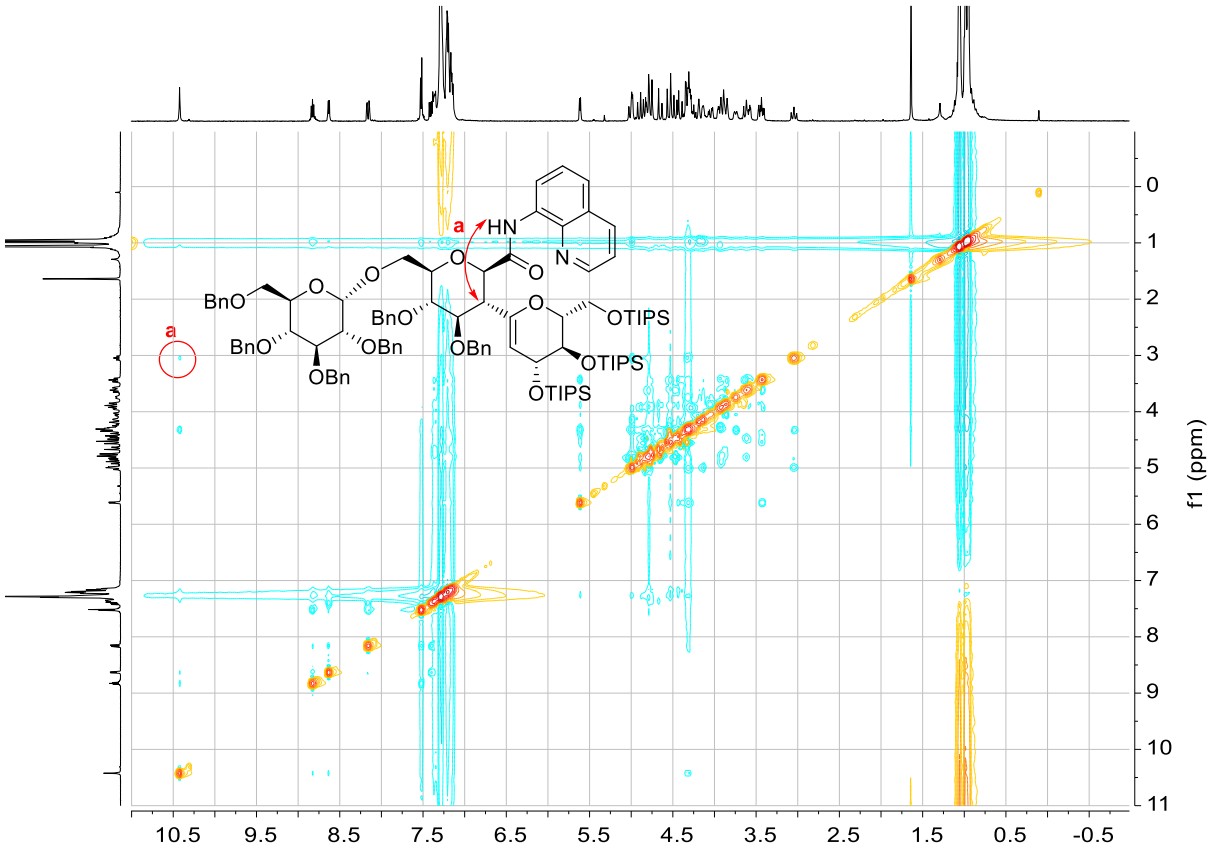
159v

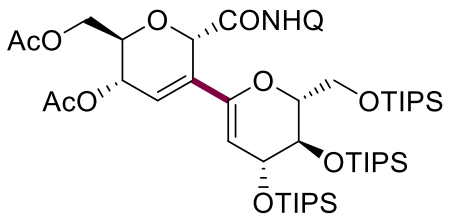
($CDCl_3$, 300 MHz)



159v

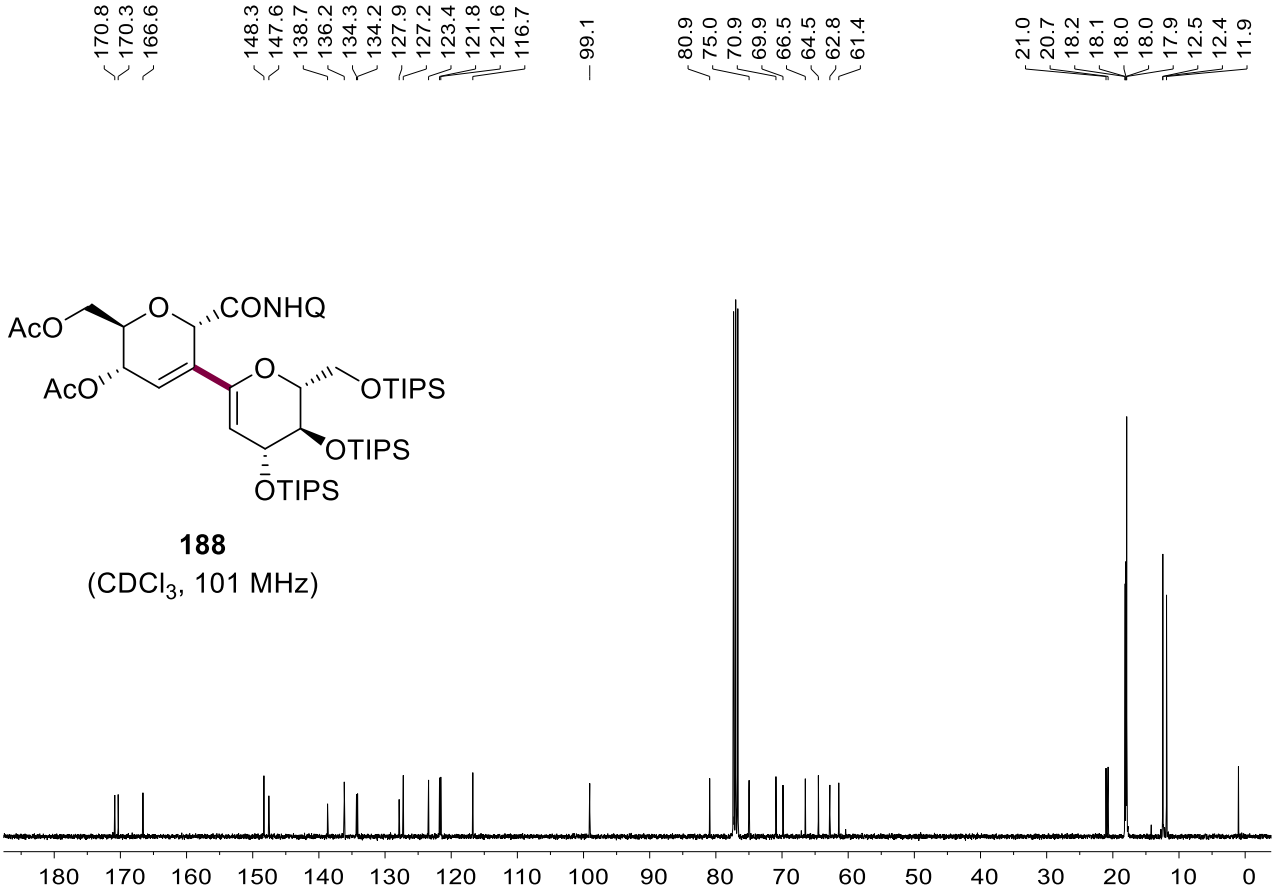
($CDCl_3$, 75 MHz)



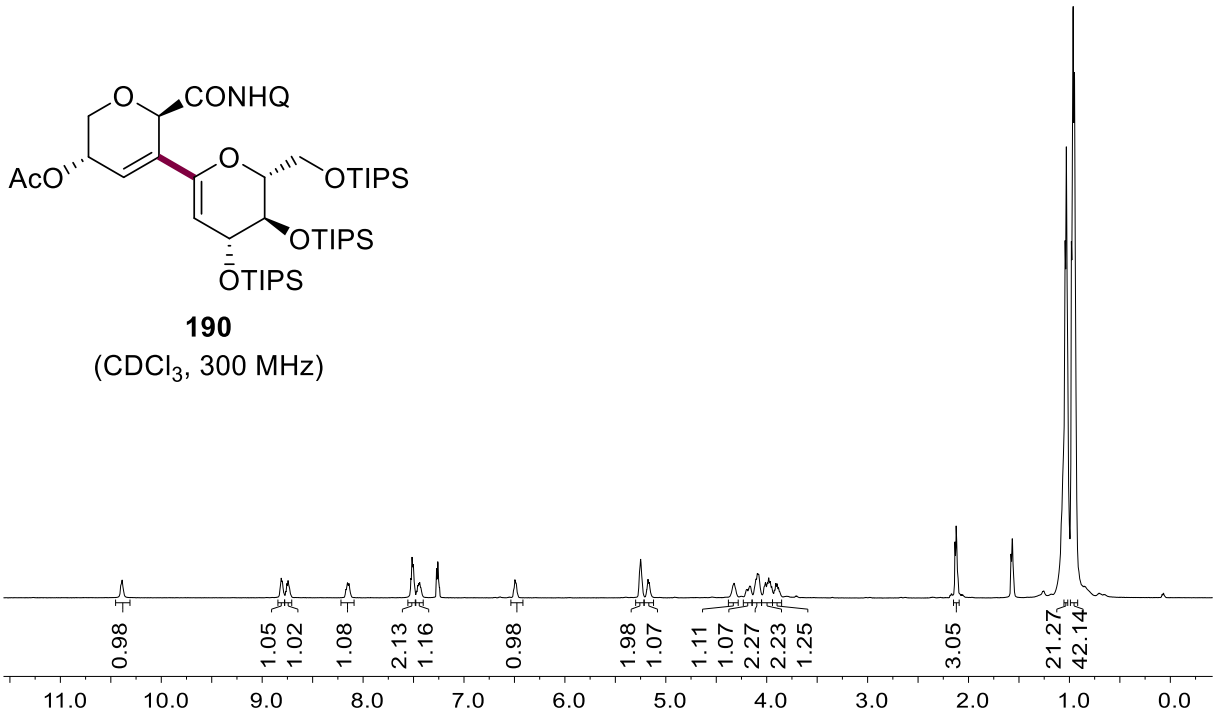


188

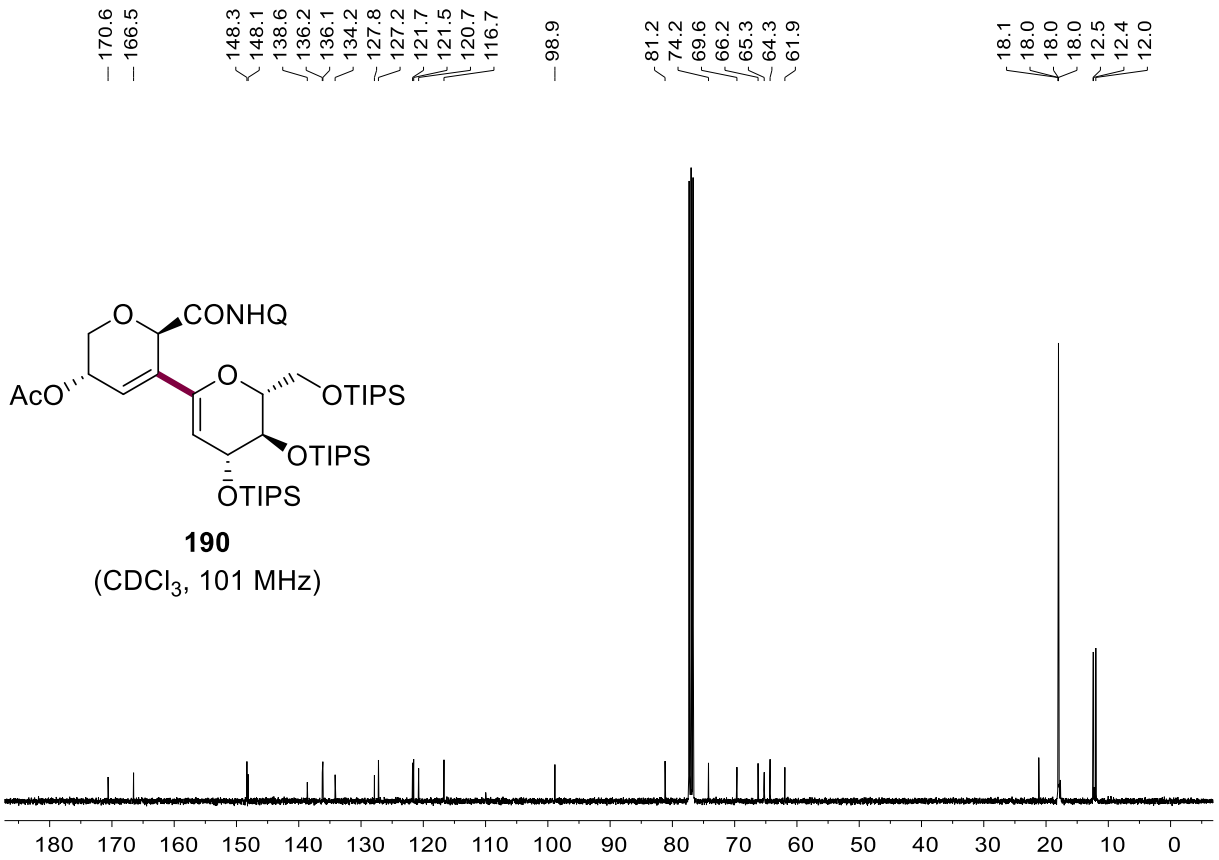
($CDCl_3$, 400 MHz)



188
($CDCl_3$, 101 MHz)

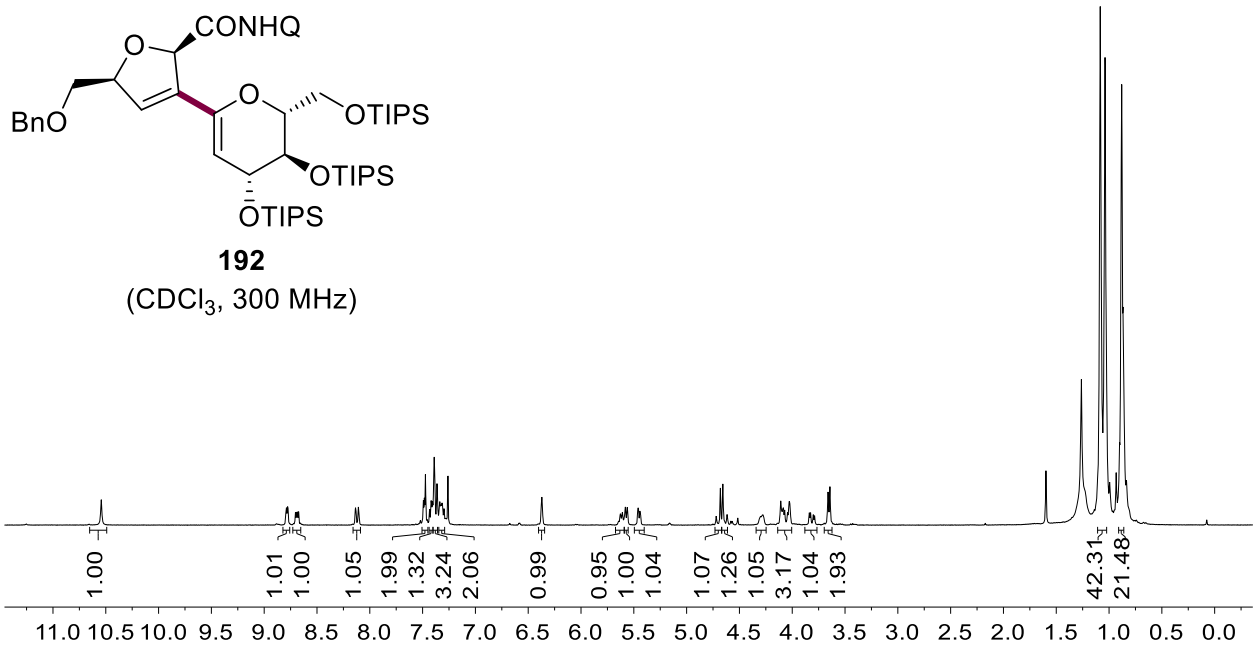


190
($CDCl_3$, 300 MHz)



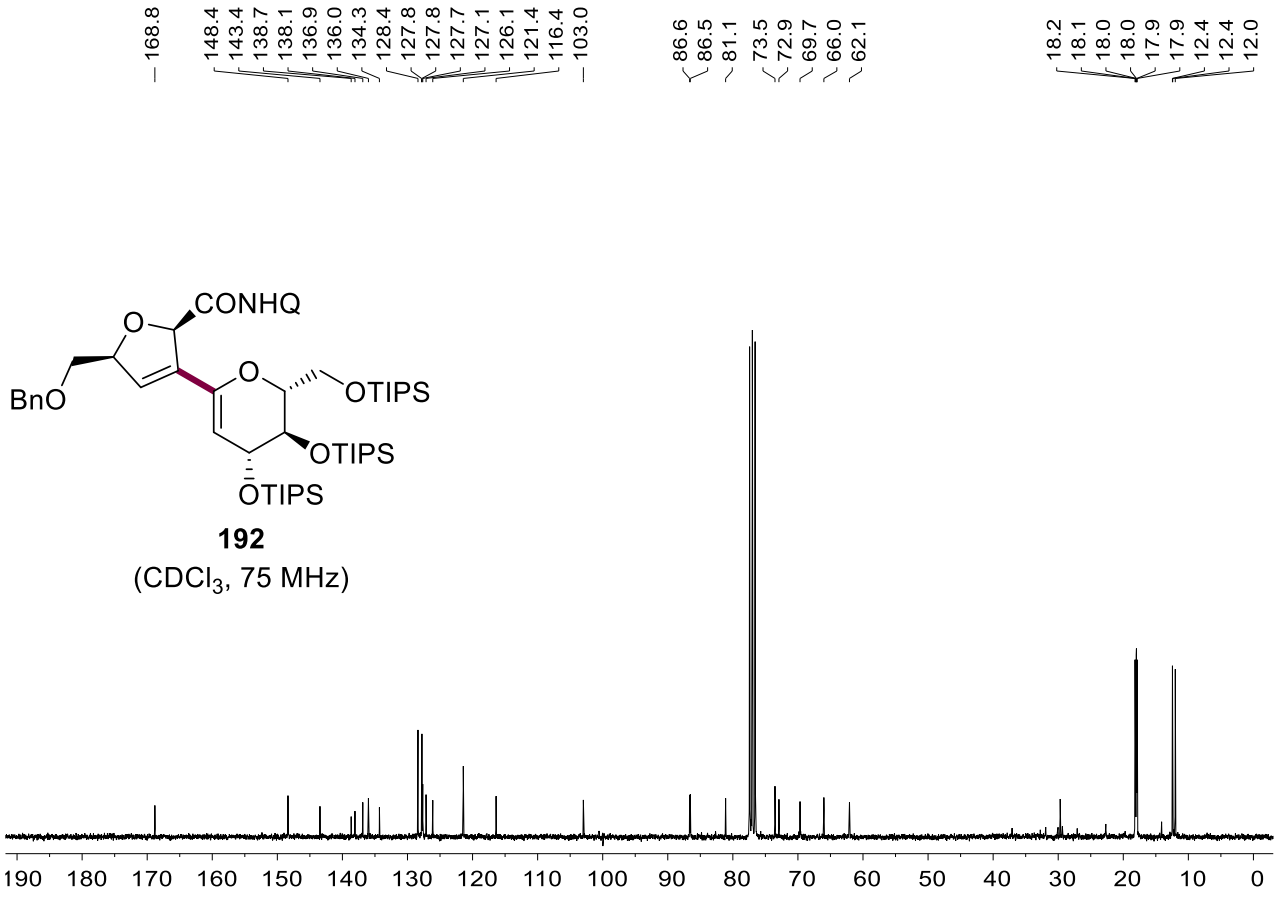
190

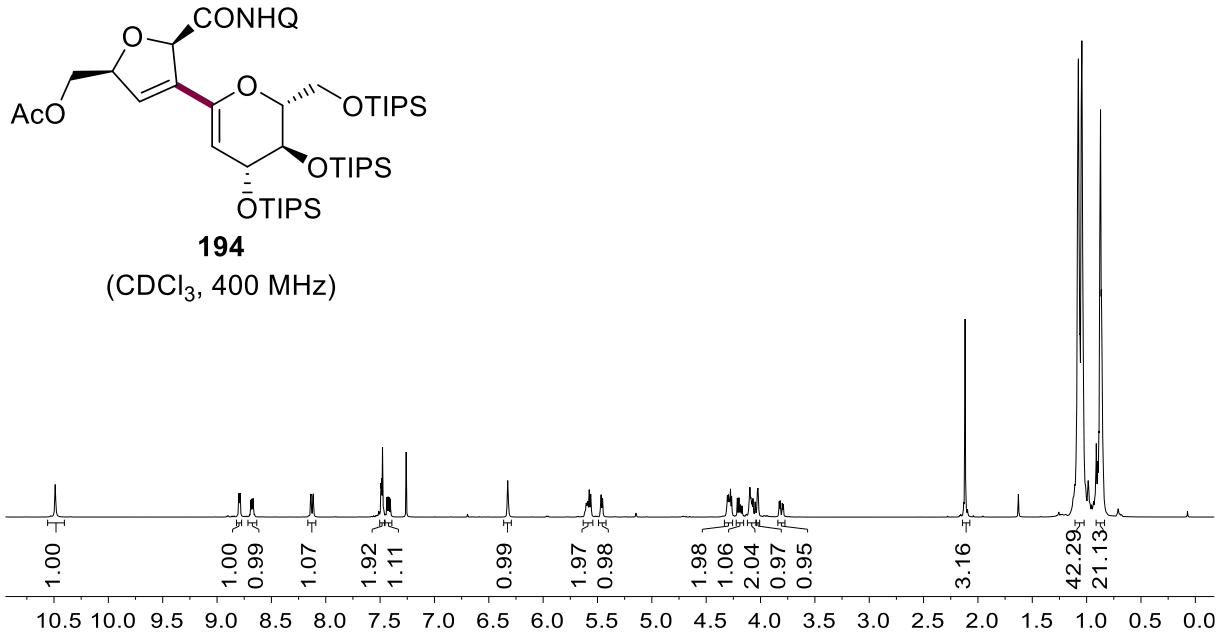
($CDCl_3$, 101 MHz)

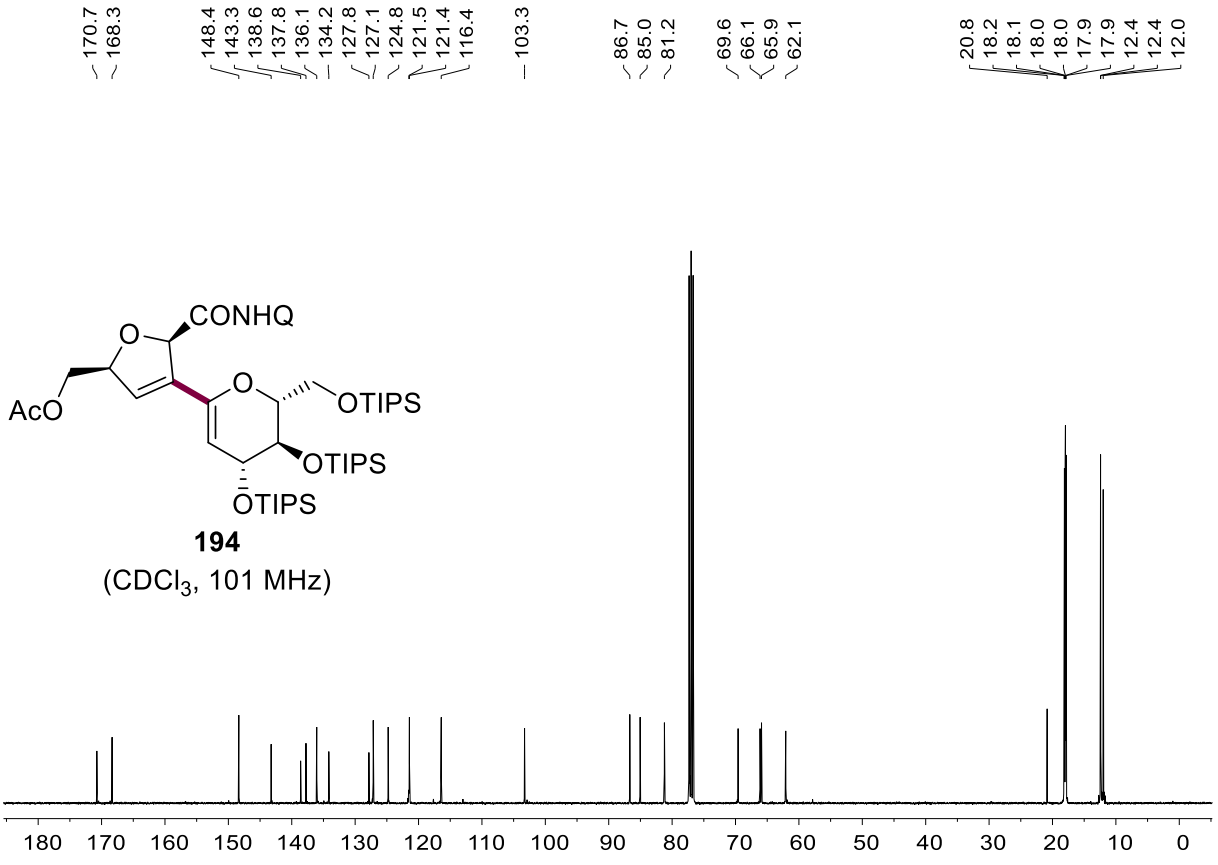


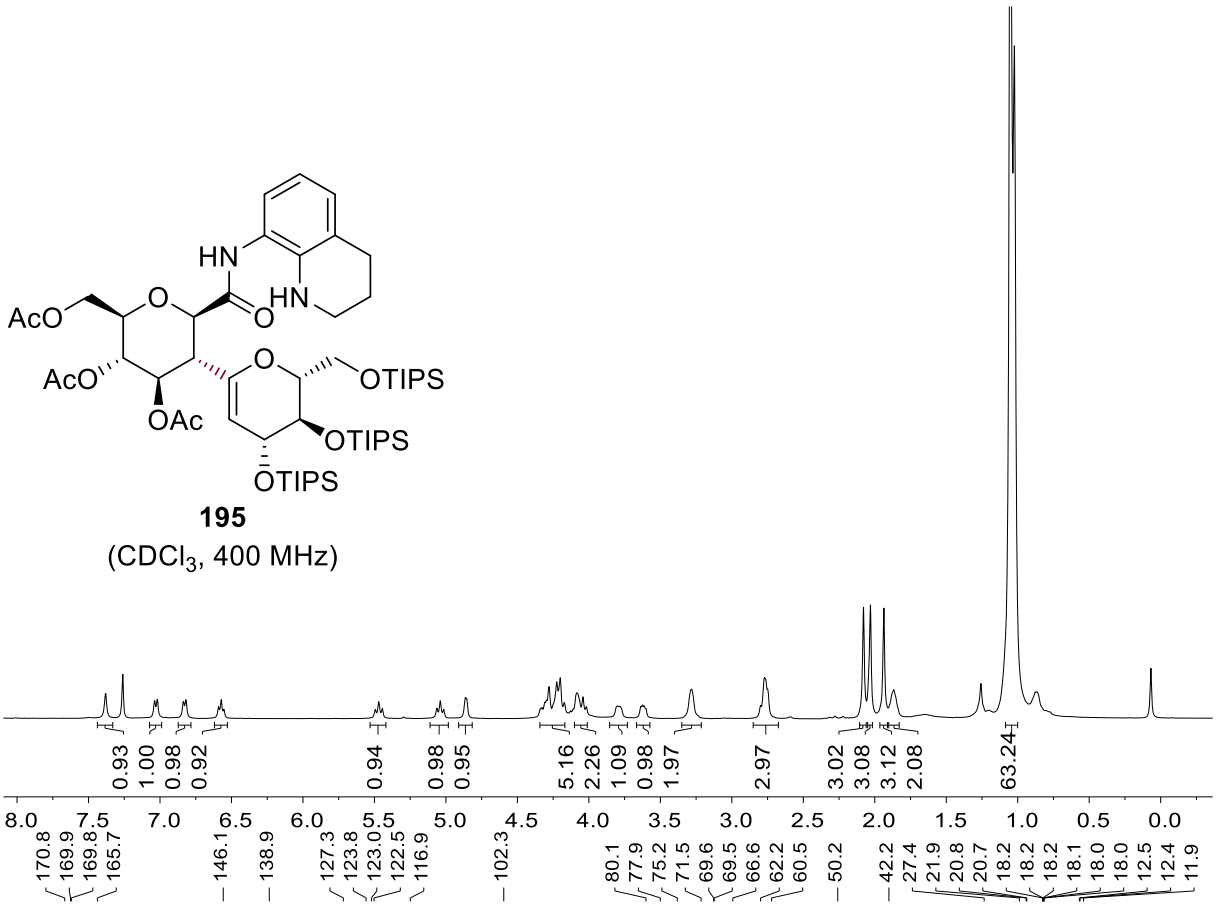
192

($CDCl_3$, 300 MHz)


168.8
148.4
143.4
138.7
138.1
136.9
136.0
134.3
128.4
127.8
127.8
127.7
127.1
126.1
121.4
116.4
103.0
86.6
86.5
81.1
73.5
72.9
69.7
66.0
62.1
18.2
18.1
18.0
18.0
17.9
17.9
12.4
12.4
12.0
CONHQ
O
O
BnO
OTIPS
OTIPS
OTIPS
192
(CDCl3, 75 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

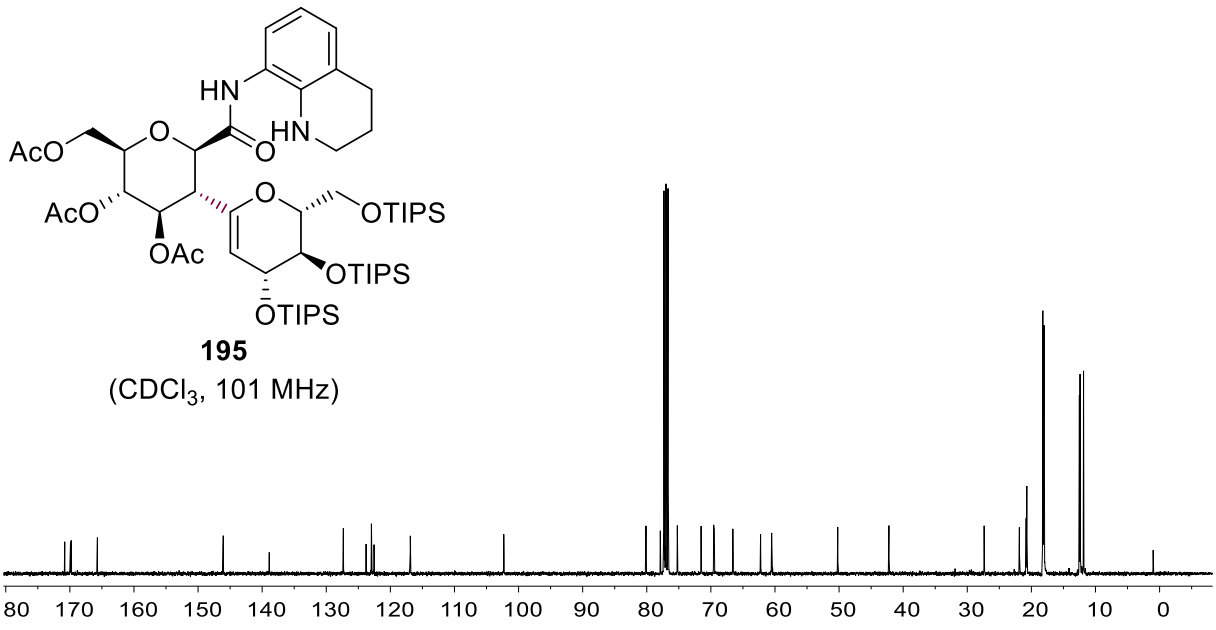

CONHQ
O
O
AcO
OTIPS
OTIPS
OTIPS
194
(CDCl3, 400 MHz)
1.00
1.00
0.99
1.07
1.92
1.11
0.99
1.97
0.98
1.98
1.06
2.04
0.97
0.95
3.16
42.29
21.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


170.7
168.3
148.4
143.3
138.6
137.8
136.1
134.2
127.8
127.1
124.8
121.5
121.4
116.4
103.3
86.7
85.0
81.2
69.6
66.1
65.9
62.1
20.8
18.2
18.1
18.0
18.0
17.9
17.9
12.4
12.4
12.0
CONHQ
O
O
AcO
OTIPS
OTIPS
OTIPS
194
(CDCl3, 101 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



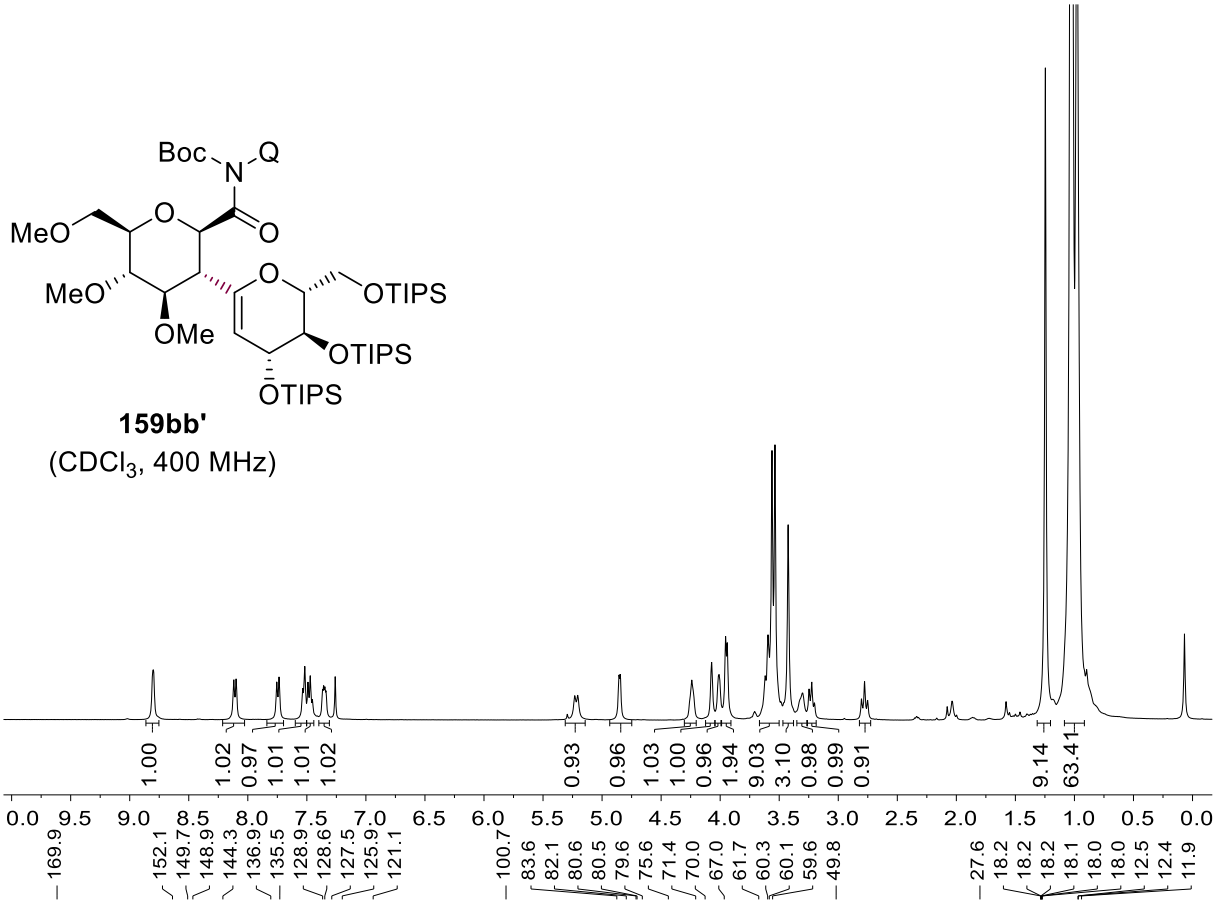
195

($CDCl_3$, 400 MHz)



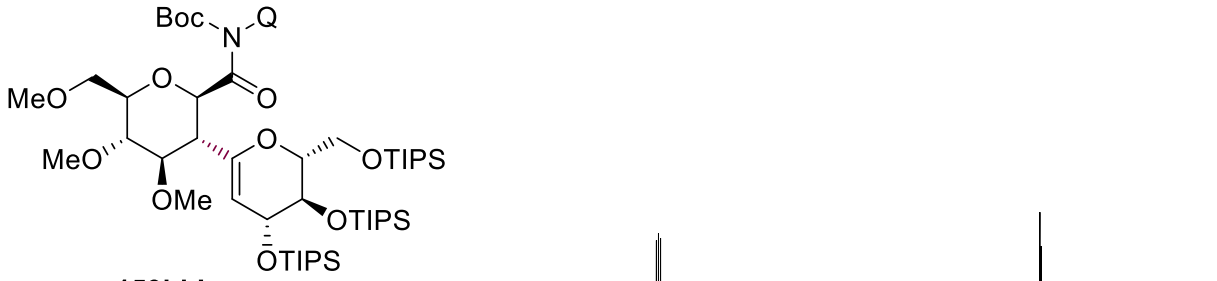
195

($CDCl_3$, 101 MHz)



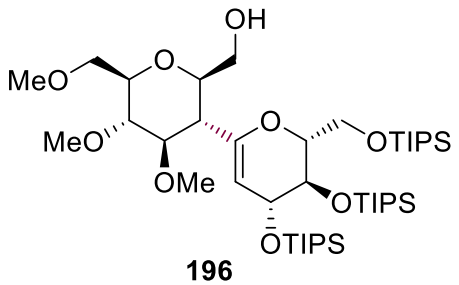
159bb'

($CDCl_3$, 400 MHz)



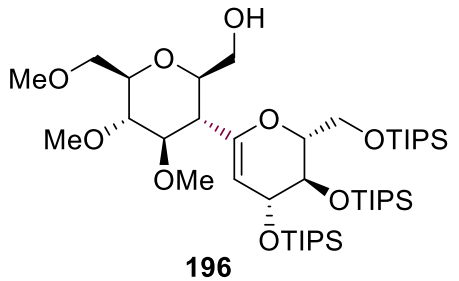
159bb'

($CDCl_3$, 101 MHz)



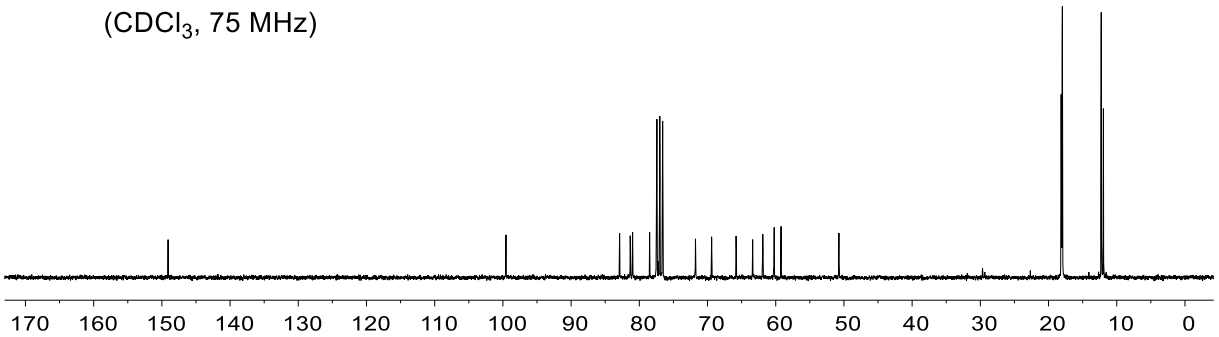
196

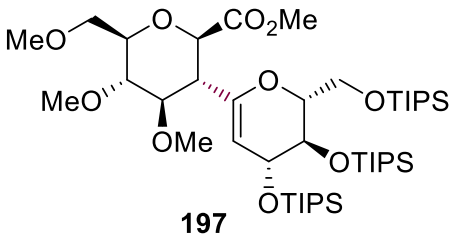
($CDCl_3$, 300 MHz)



196

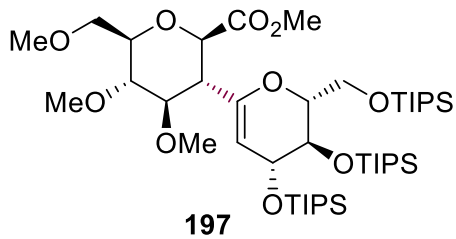
($CDCl_3$, 75 MHz)





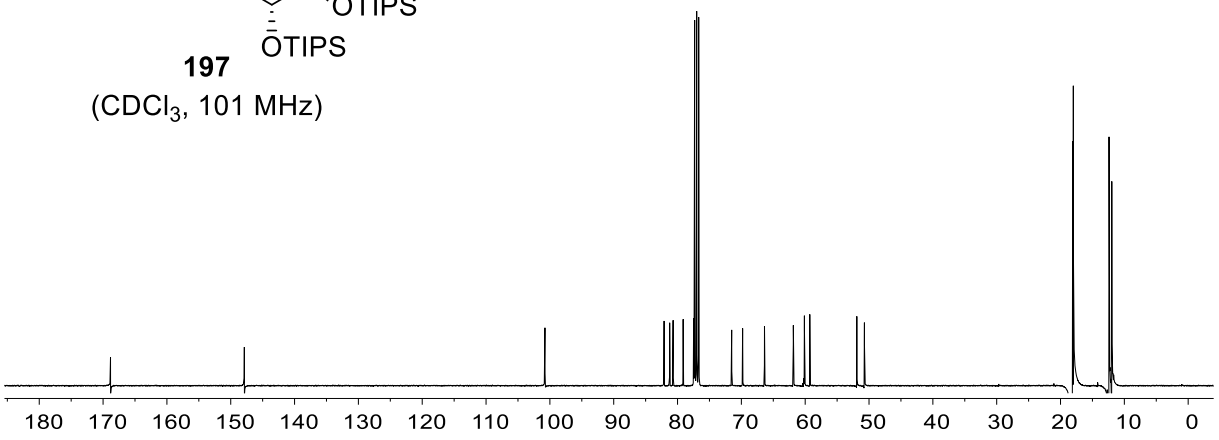
197

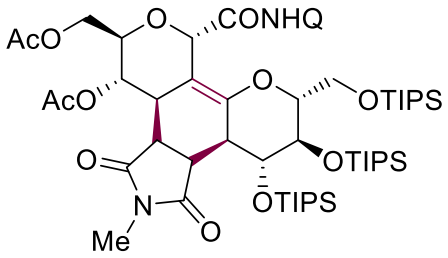
($CDCl_3$, 400 MHz)



197

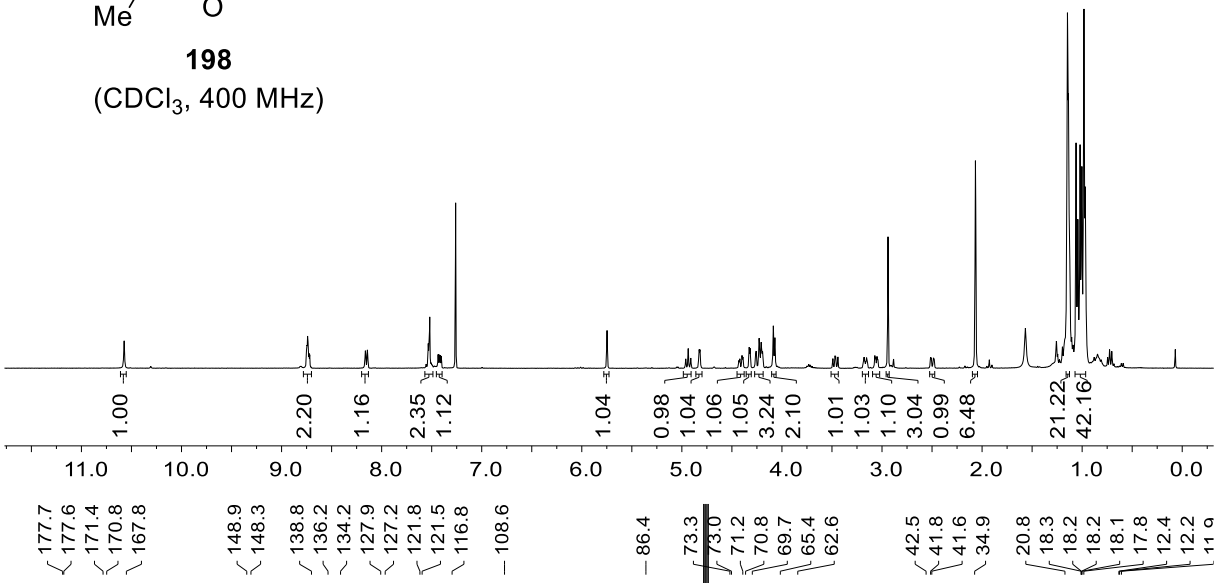
($CDCl_3$, 101 MHz)

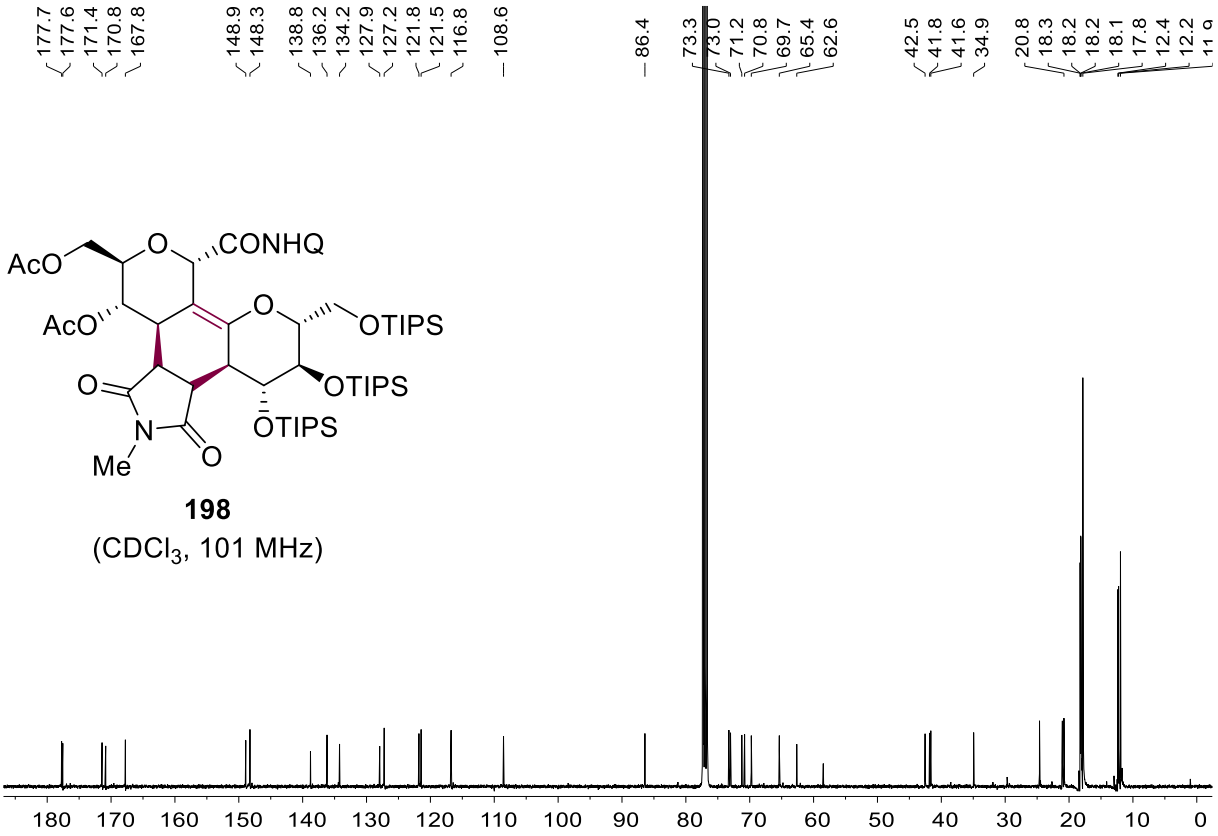




198

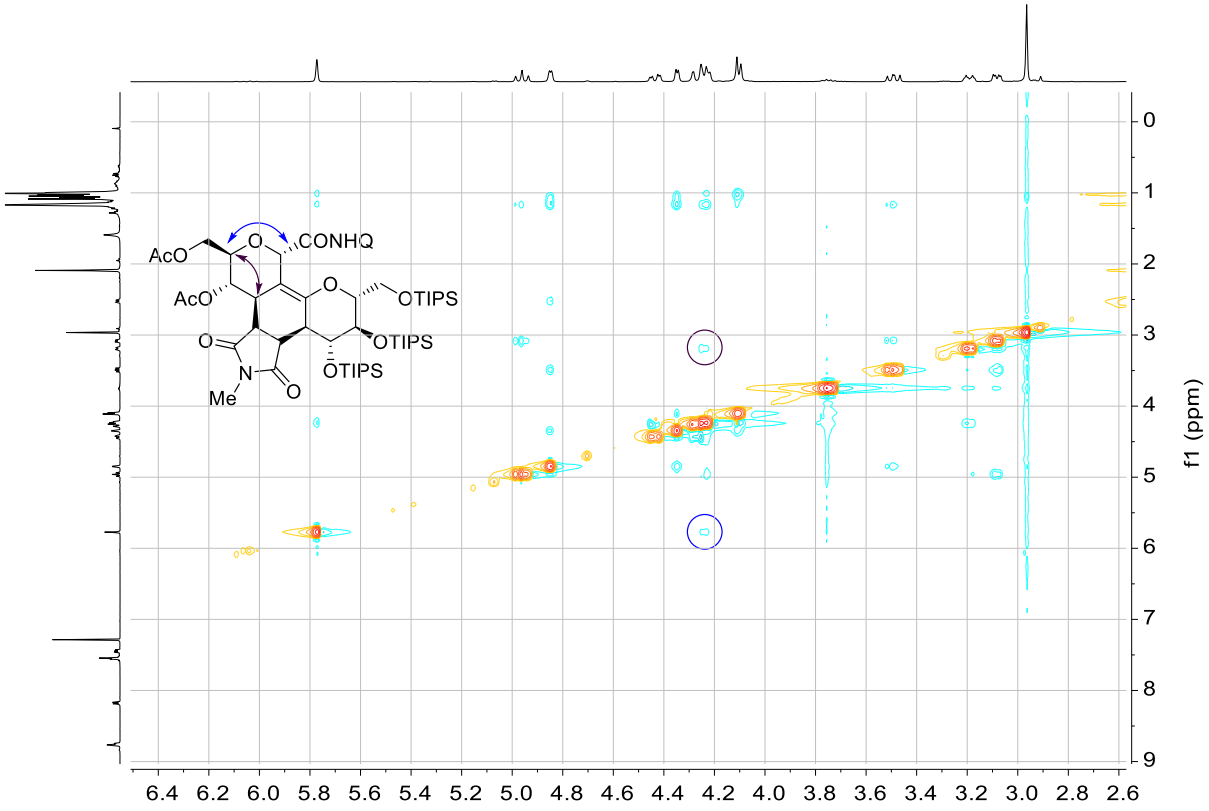
($CDCl_3$, 400 MHz)

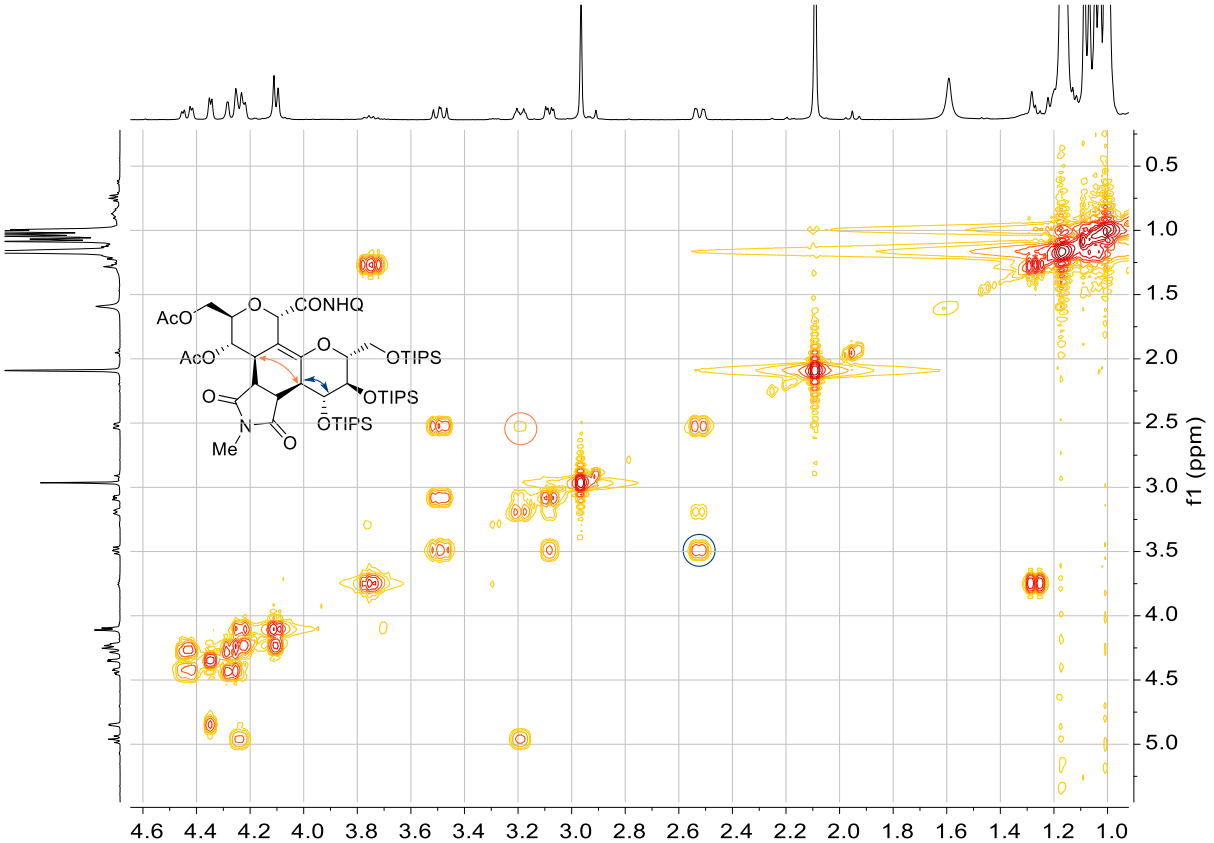


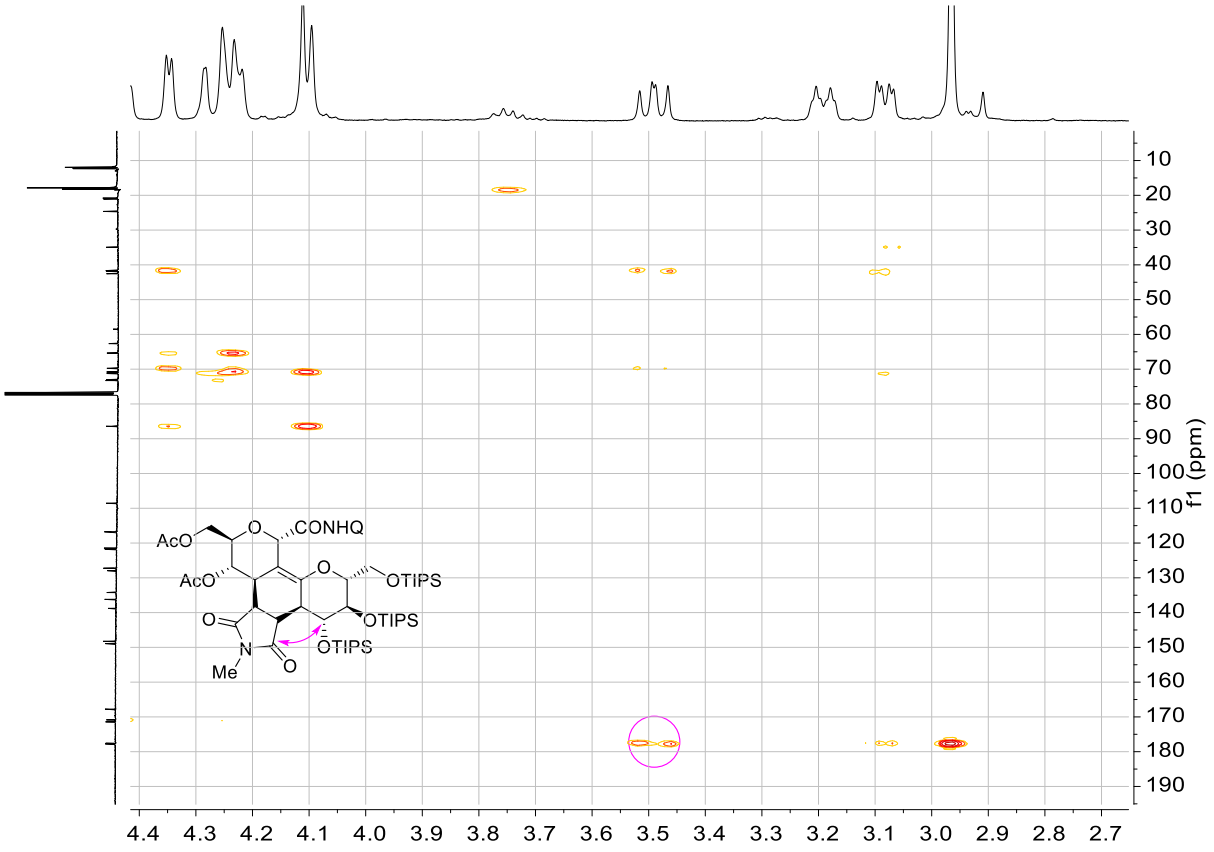


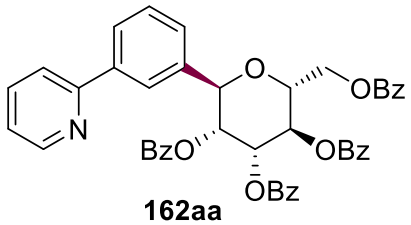
198

($CDCl_3$, 101 MHz)


AcO
O
CONHQ
AcO
O
OTIPS
OTIPS
OTIPS
O
N
Me
O
f1 (ppm)
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6
0 1 2 3 4 5 6 7 8 9

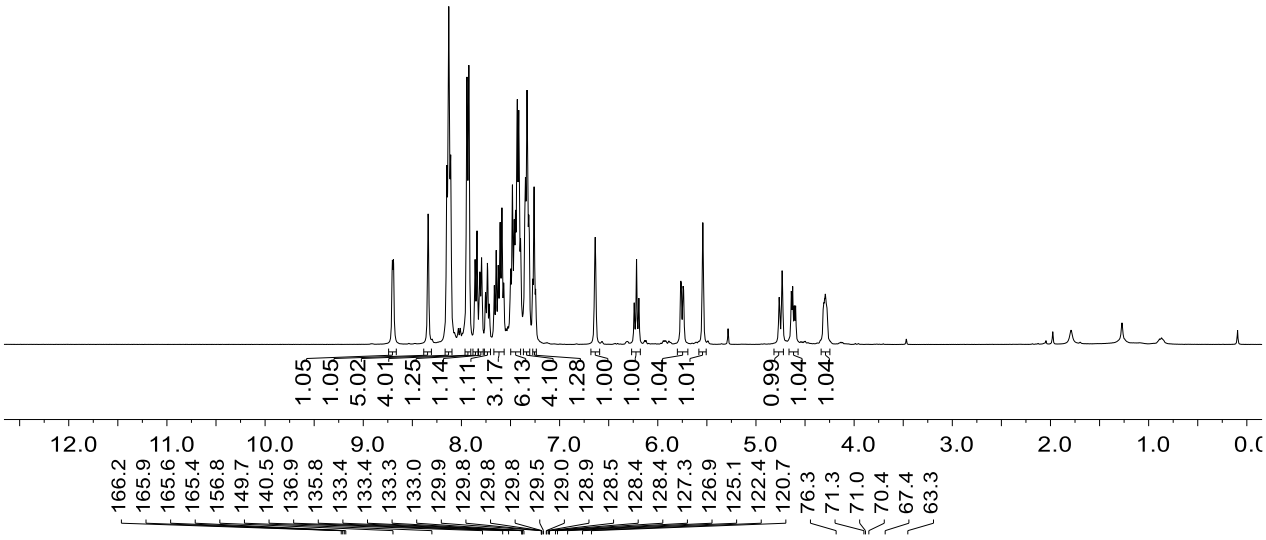

AcO
O
CONHQ
AcO
O
OTIPS
OTIPS
OTIPS
O
N
Me
O
f1 (ppm)
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0

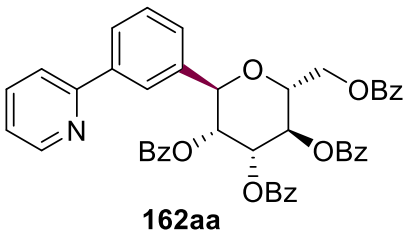

AcO
O
CONHQ
AcO
O
OTIPS
O
OTIPS
N
OTIPS
Me
O
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7



162aa

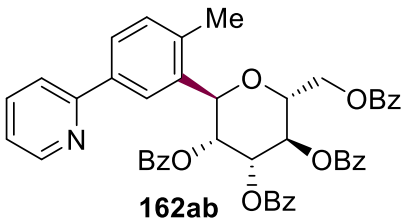
($CDCl_3$, 400 MHz)





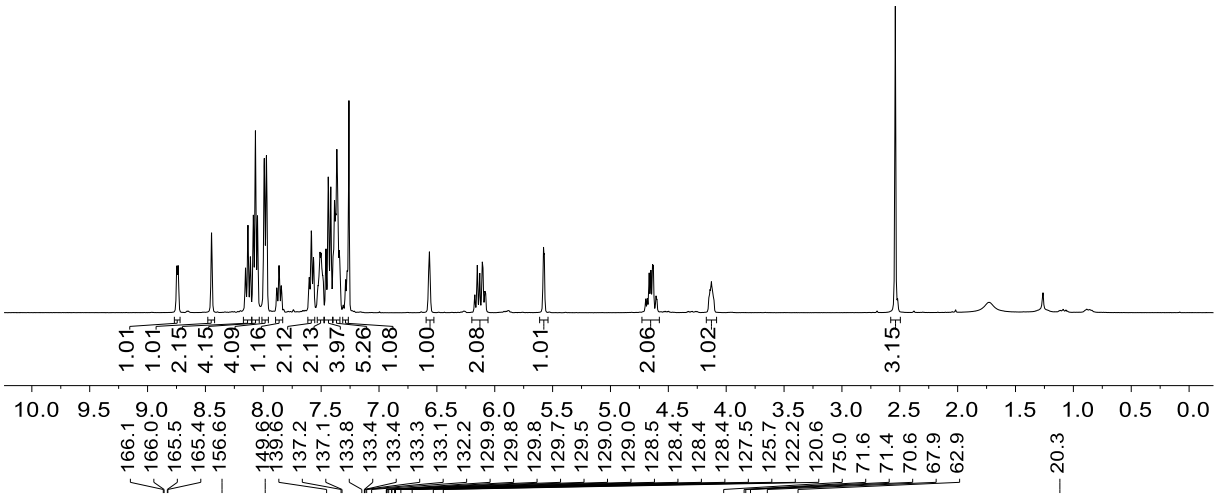
162aa

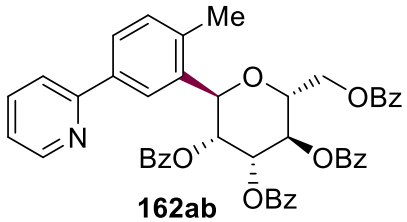
($CDCl_3$, 101 MHz)



162ab

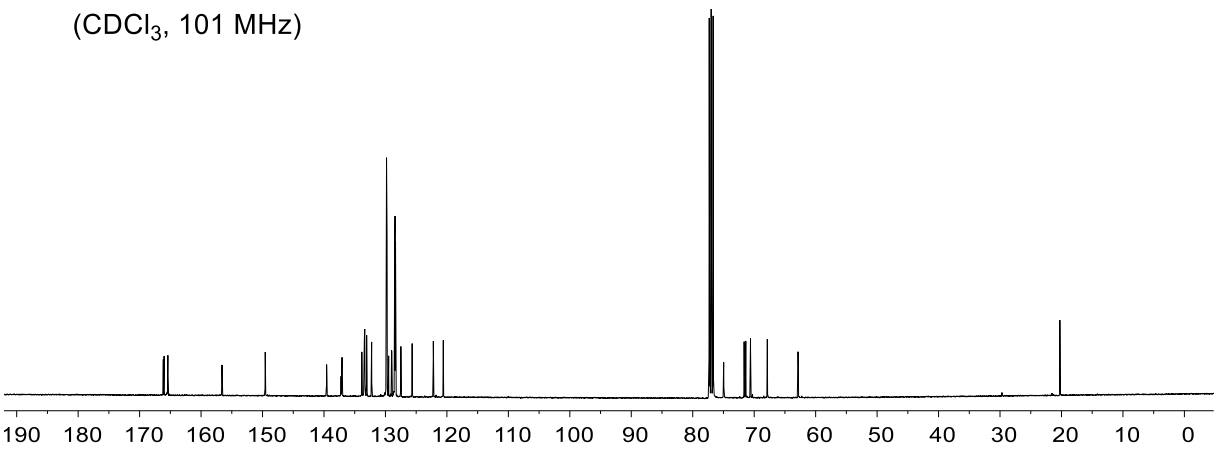
($CDCl_3$, 400 MHz)

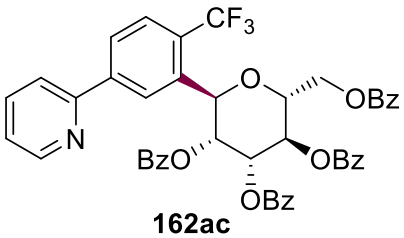




162ab

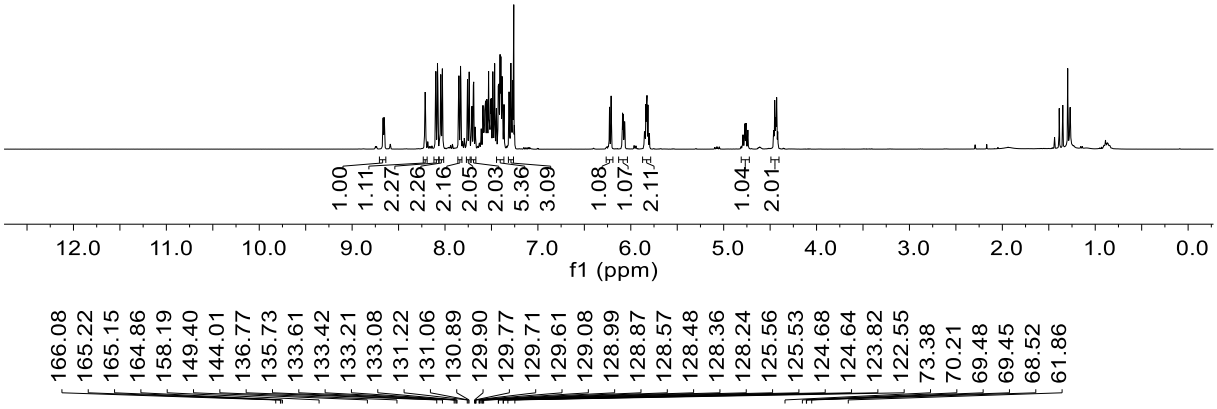
($CDCl_3$, 101 MHz)

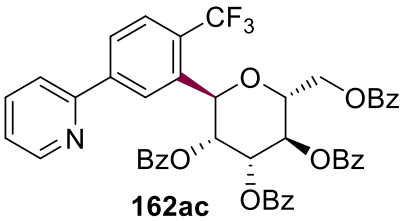




162ac

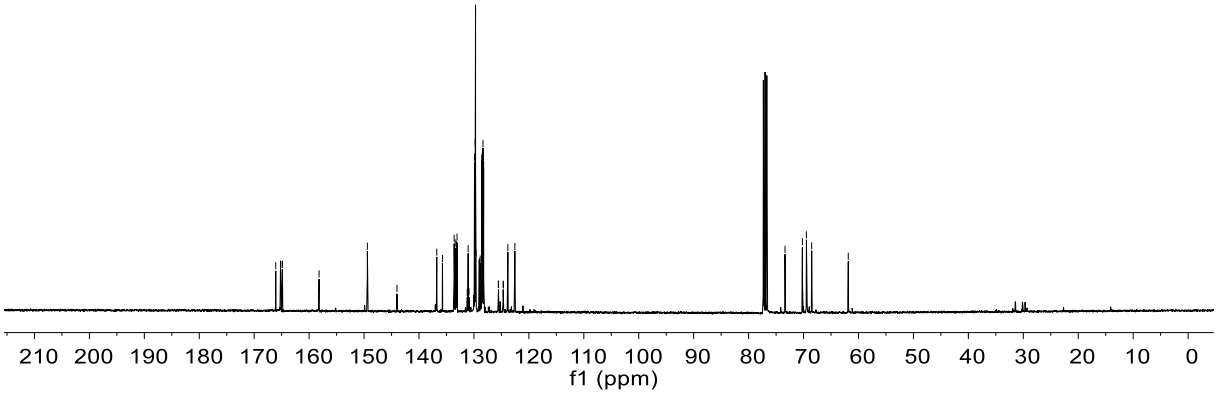
($CDCl_3$, 400 MHz)

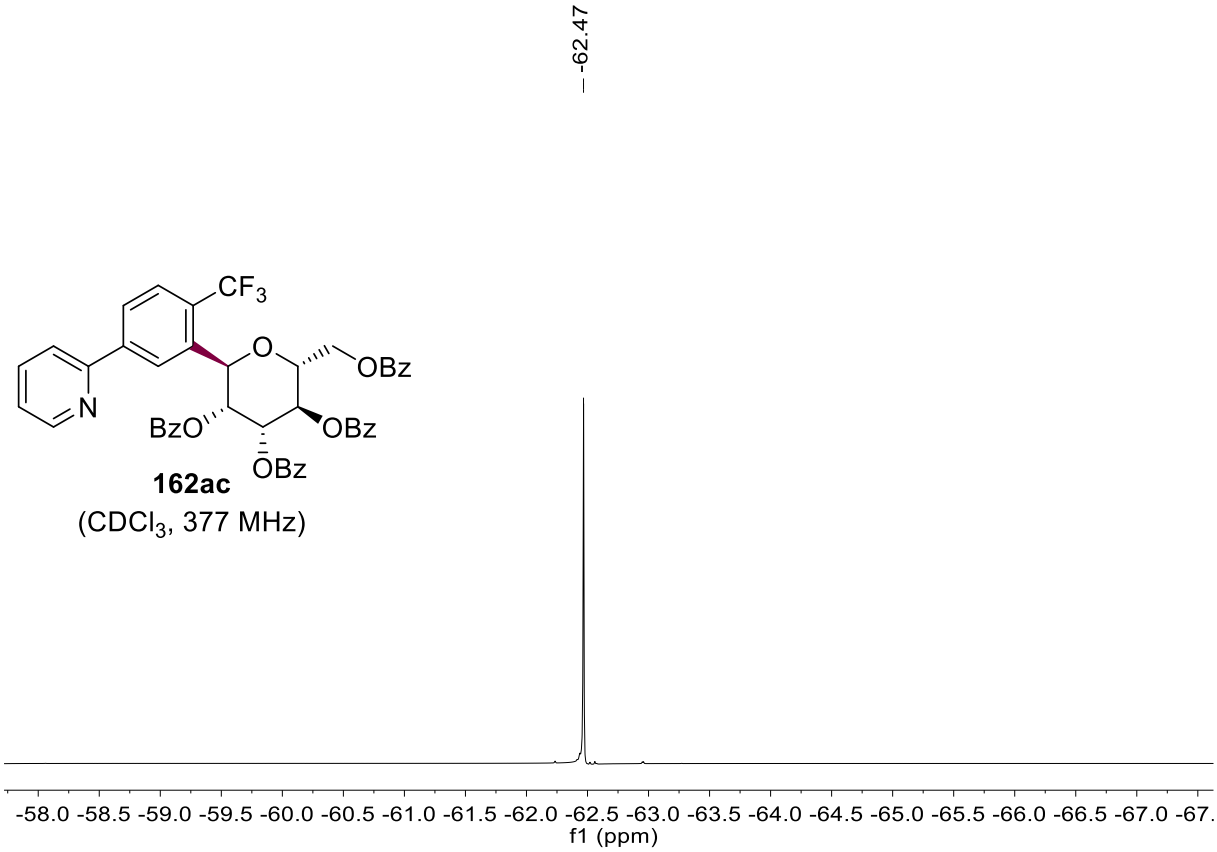




162ac

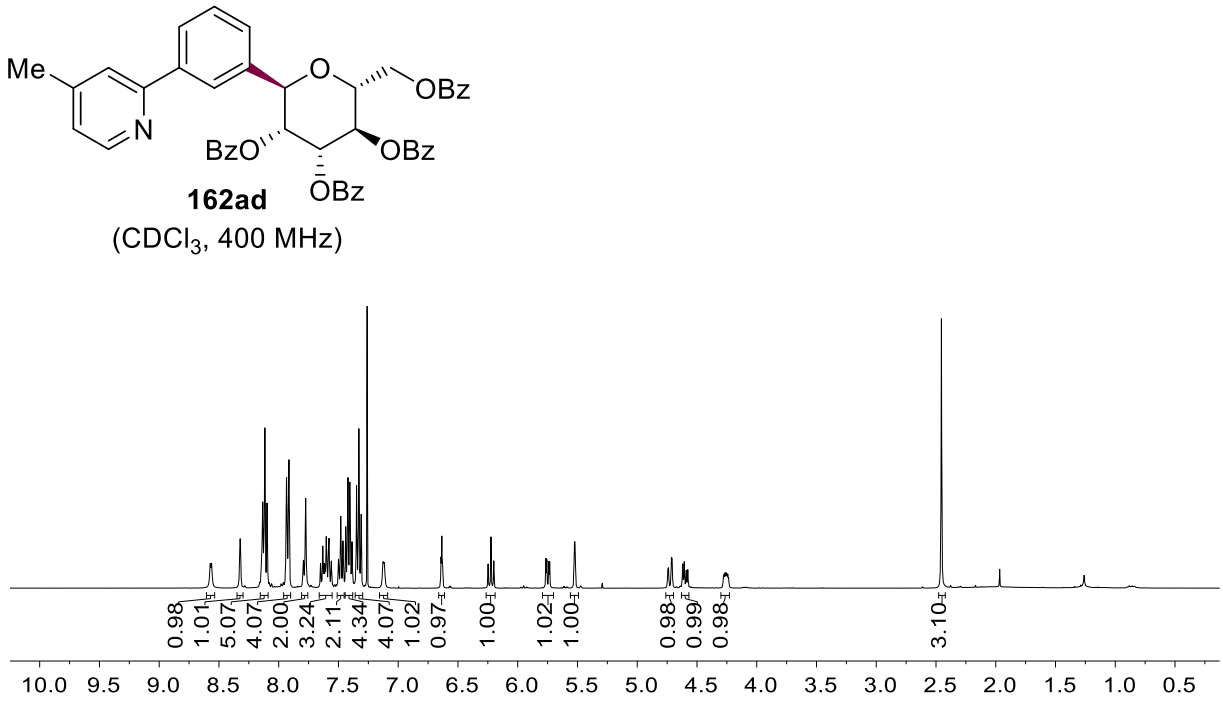
($CDCl_3$, 101 MHz)





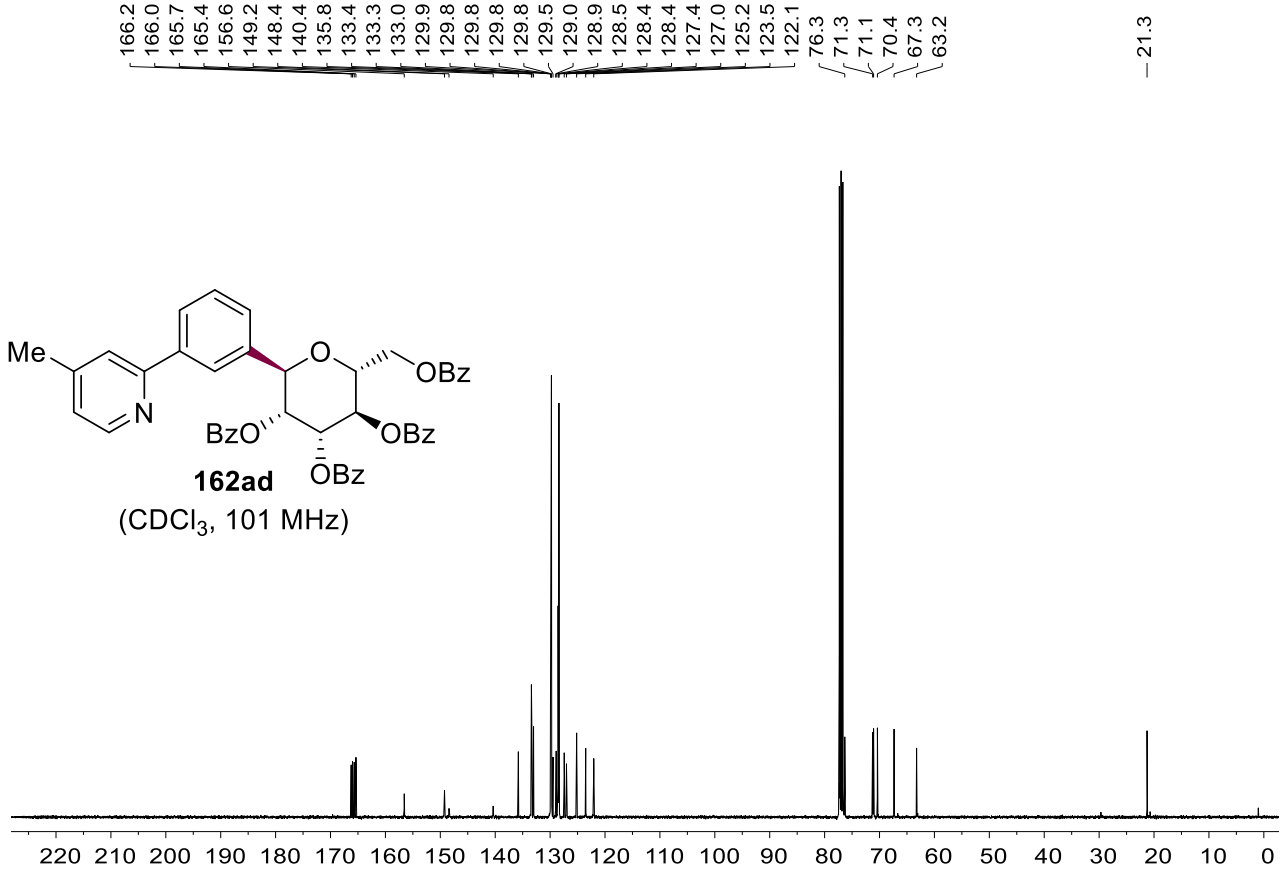
162ac

($CDCl_3$, 377 MHz)



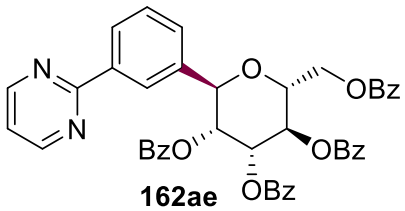
162ad

($CDCl_3$, 400 MHz)



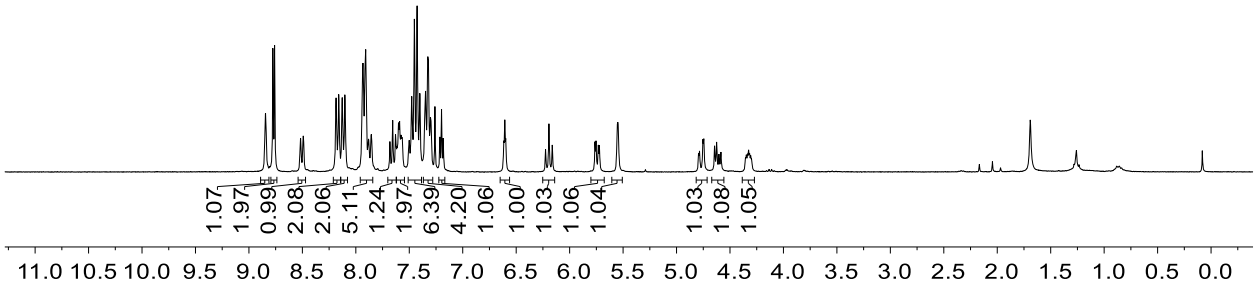
162ad

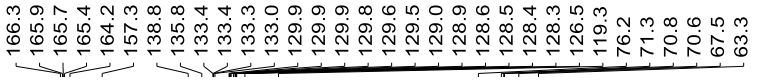
($CDCl_3$, 101 MHz)

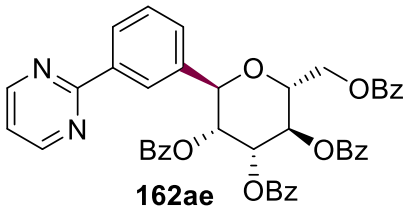


162ae

($CDCl_3$, 300 MHz)

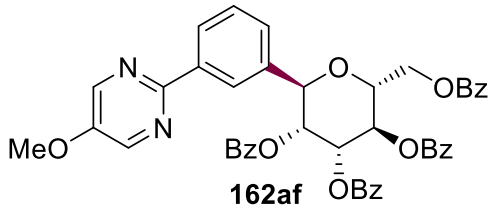






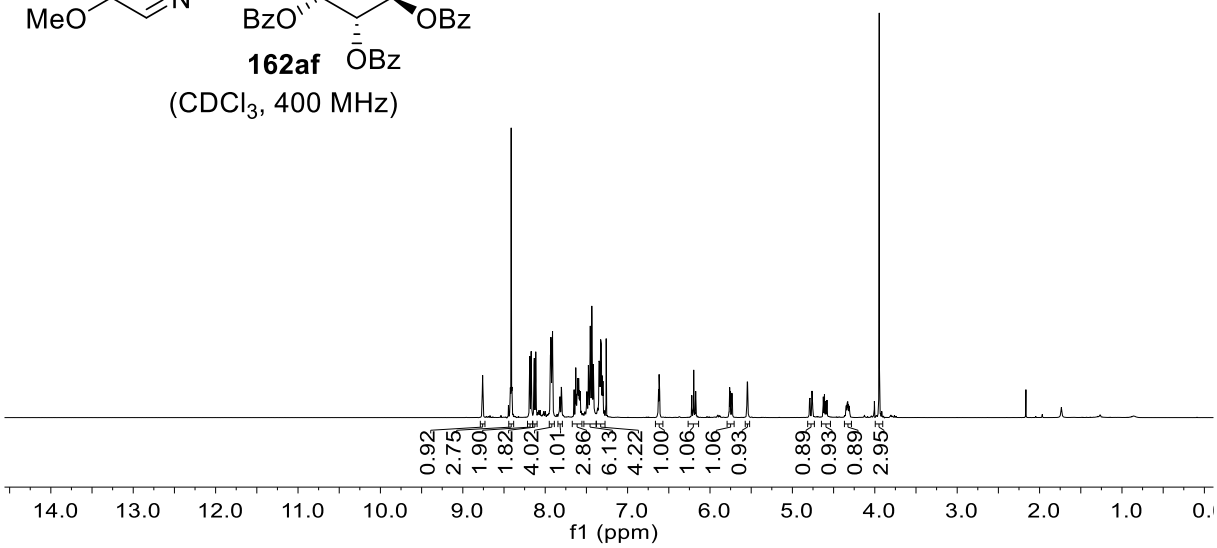
162ae

($CDCl_3$, 75 MHz)

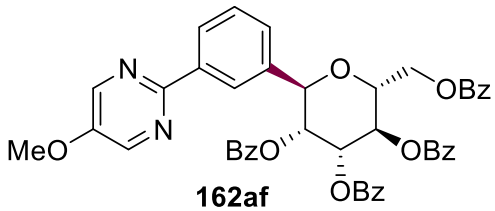


162af

($CDCl_3$, 400 MHz)

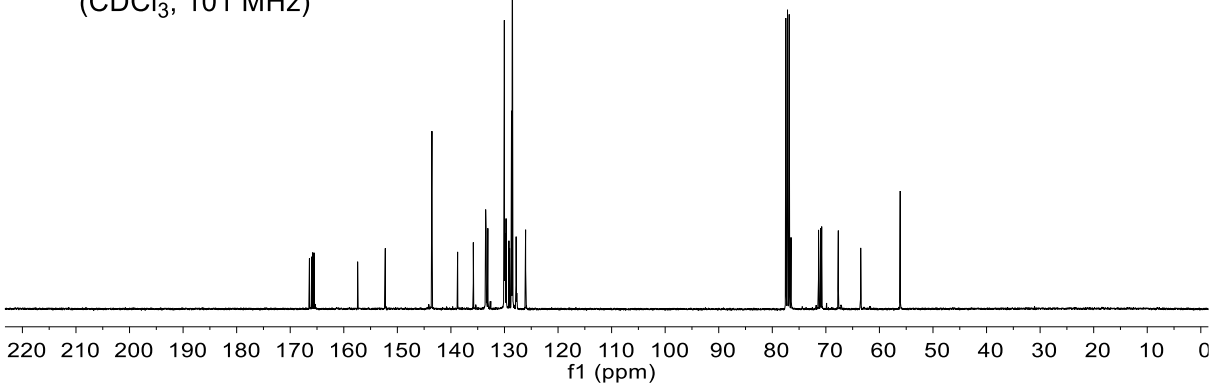


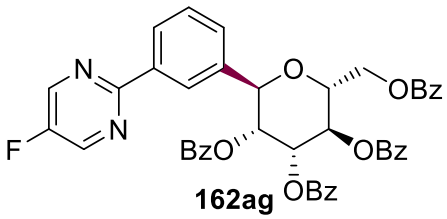
166.41
166.00
165.82
165.56
157.42
152.25
143.54
138.75
135.82
133.54
133.51
133.41
133.10
130.13
130.03
129.93
129.92
129.88
129.71
129.69
129.17
129.05
128.69
128.53
128.51
127.82
127.72
126.06
76.51
71.36
70.99
70.78
67.68
63.49
56.12



162af

($CDCl_3$, 101 MHz)

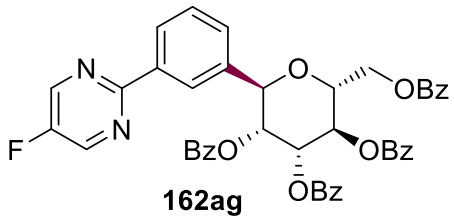




162ag

($CDCl_3$, 400 MHz)

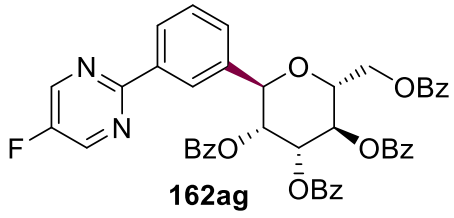
166.40
166.02
165.84
165.57
160.65
160.60
158.27
155.63
145.21
145.01
137.93
137.92
136.07
133.59
133.57
133.47
133.19
130.10
130.05
130.01
129.94
129.93
129.83
129.64
129.13
129.04
128.71
128.58
128.56
128.55
128.39
126.62
76.36
71.50
70.90
70.72
67.68
63.46



162ag

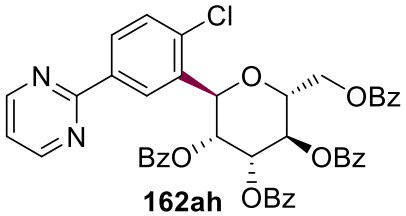
($CDCl_3$, 101 MHz)

-140.15



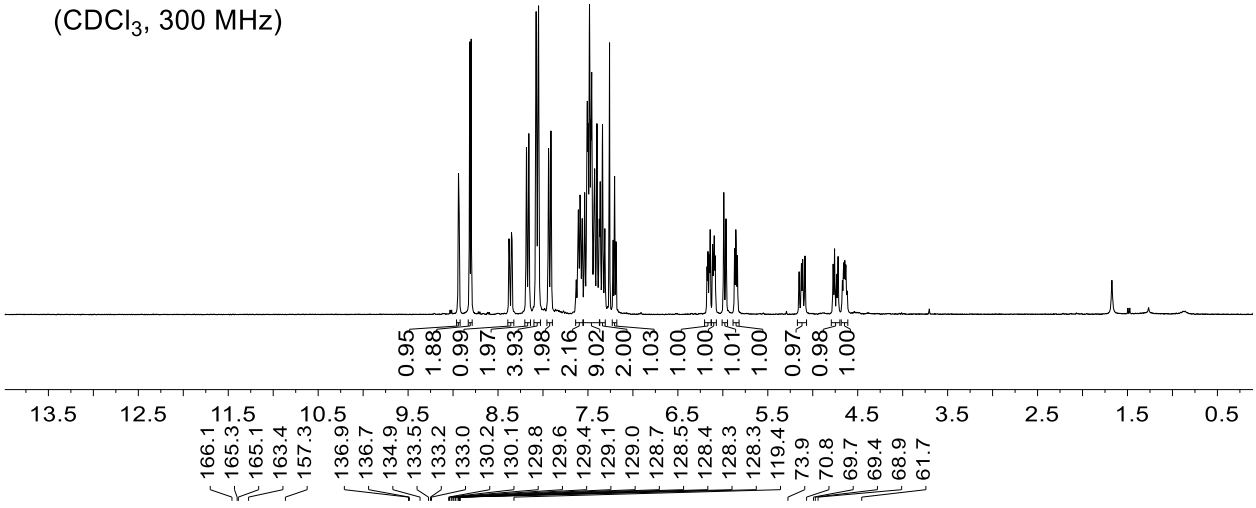
162ag

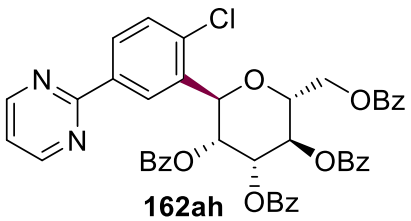
($CDCl_3$, 377 MHz)



162ah

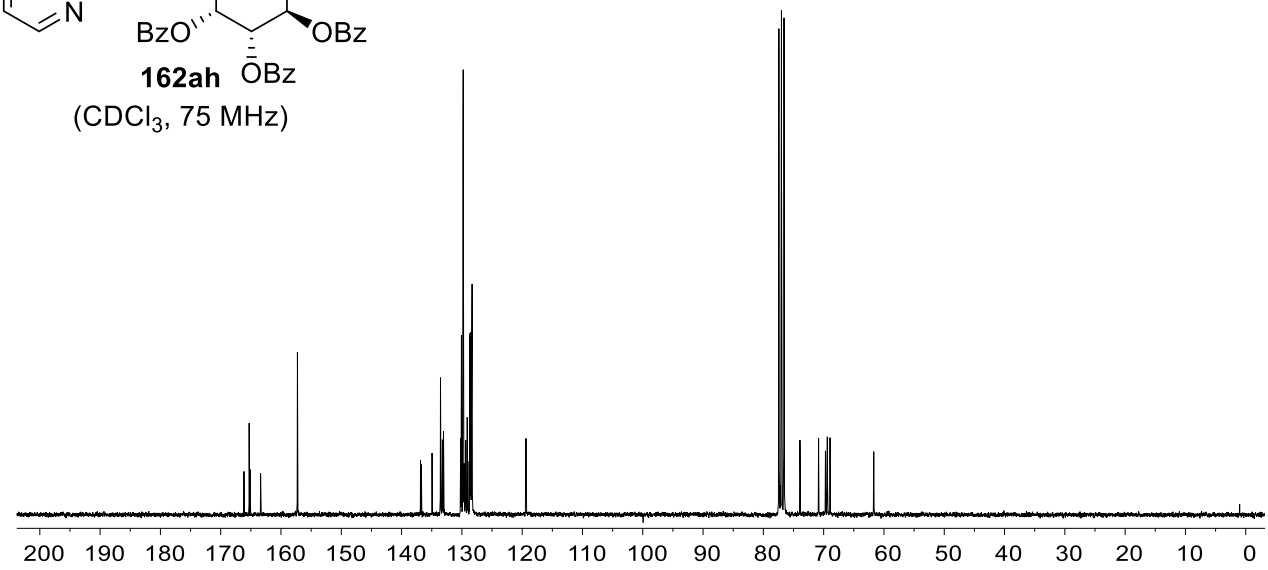
($CDCl_3$, 300 MHz)

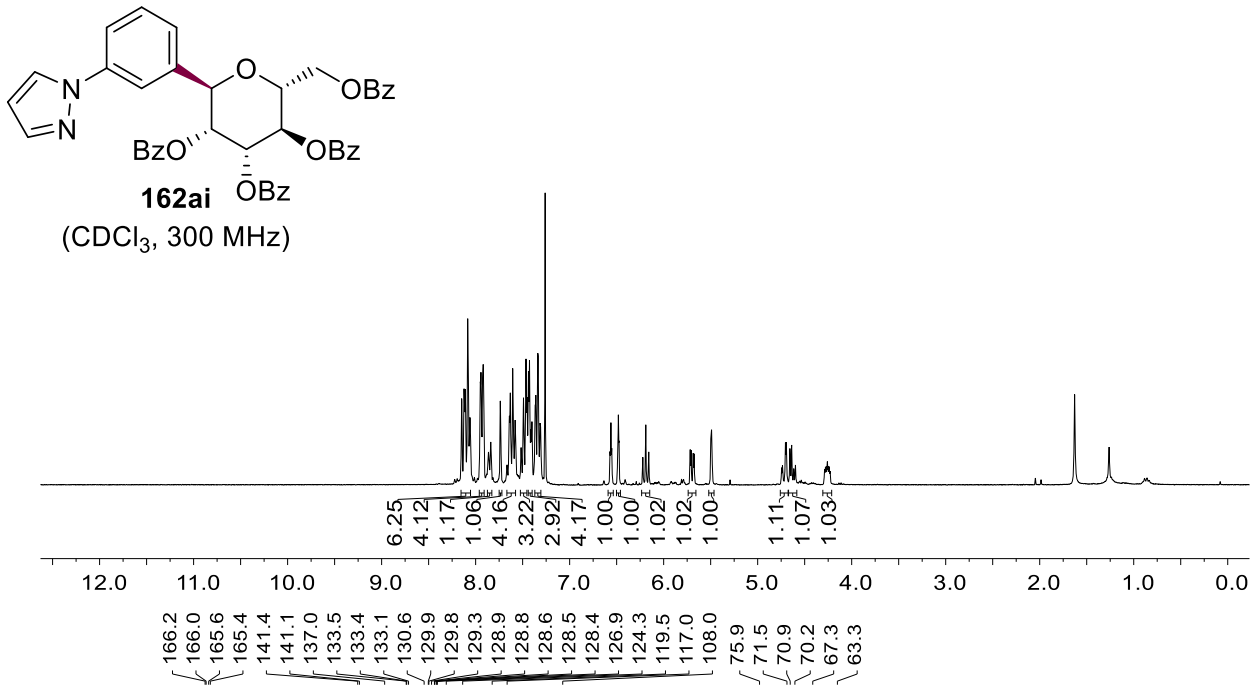




162ah

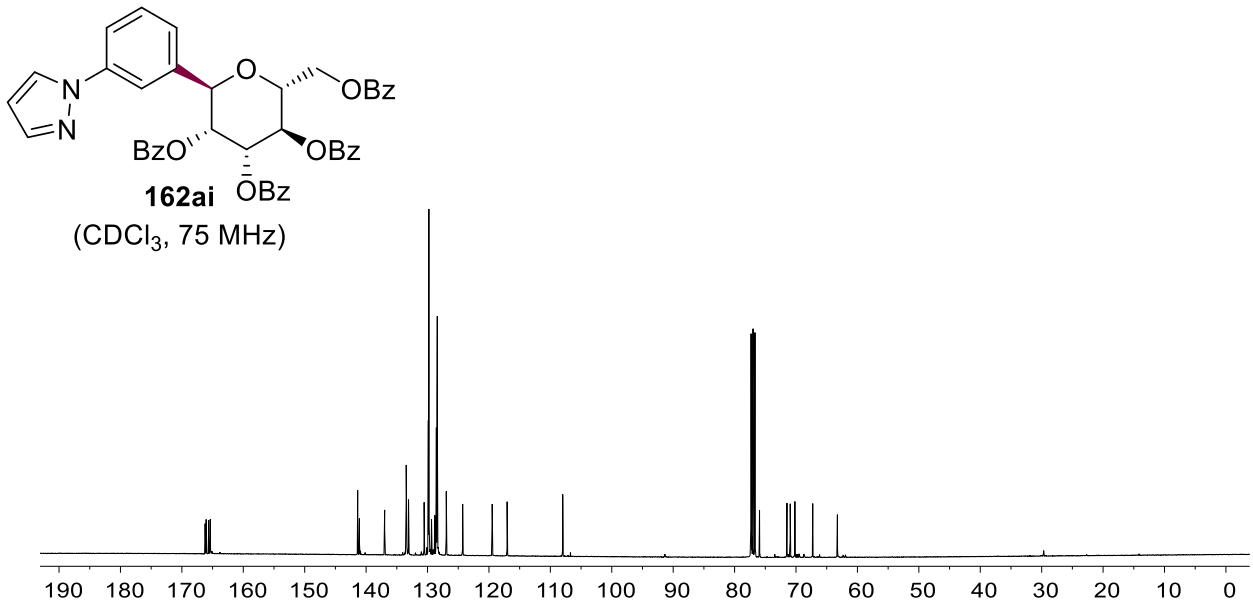
($CDCl_3$, 75 MHz)





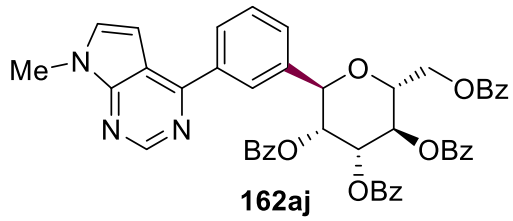
162ai

($CDCl_3$, 300 MHz)



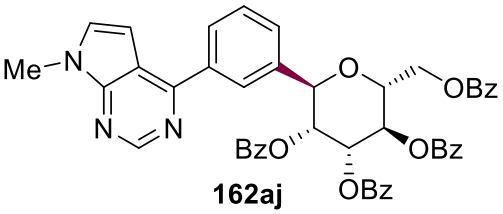
162ai

($CDCl_3$, 75 MHz)



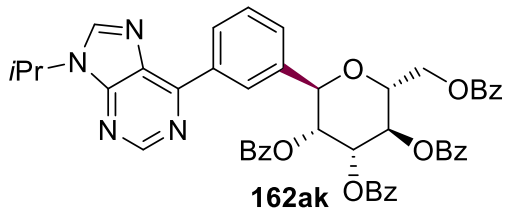
162aj

($CDCl_3$, 400 MHz)



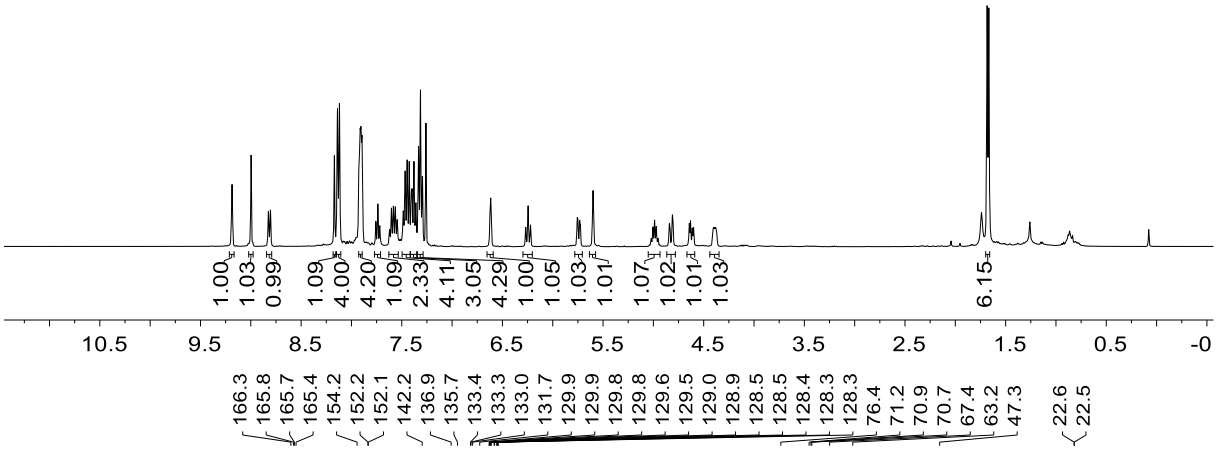
162aj

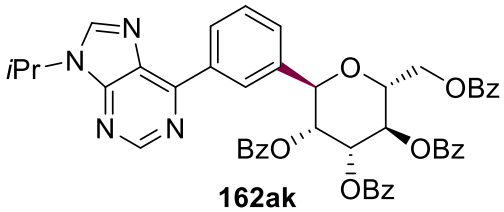
($CDCl_3$,101 MHz)



162ak

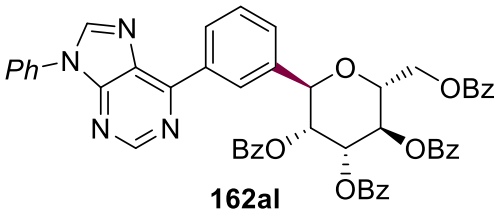
($CDCl_3$, 400 MHz)





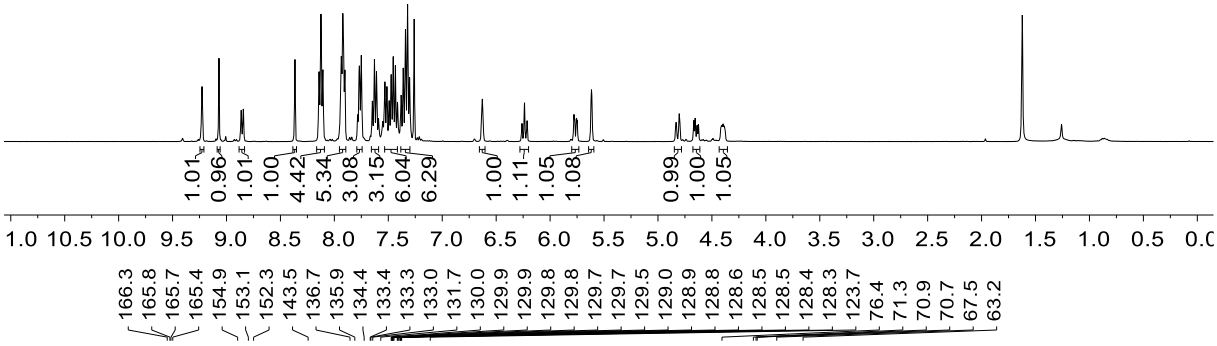
162ak

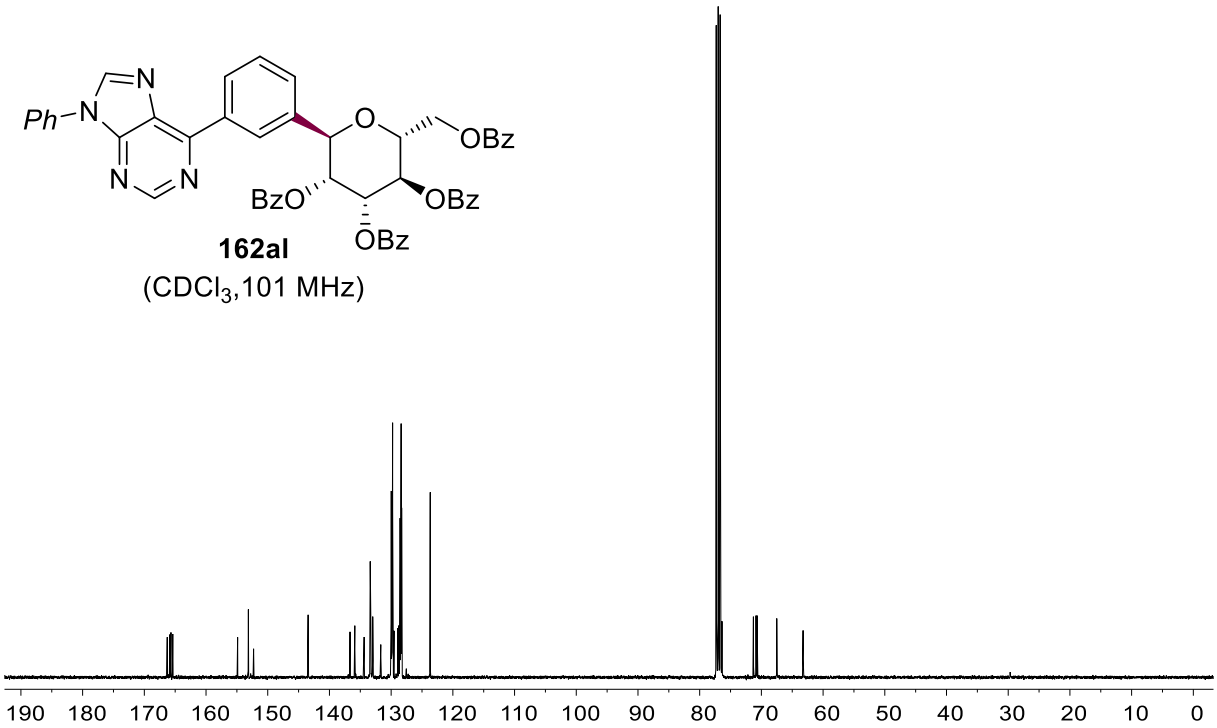
($CDCl_3$,101 MHz)



162al

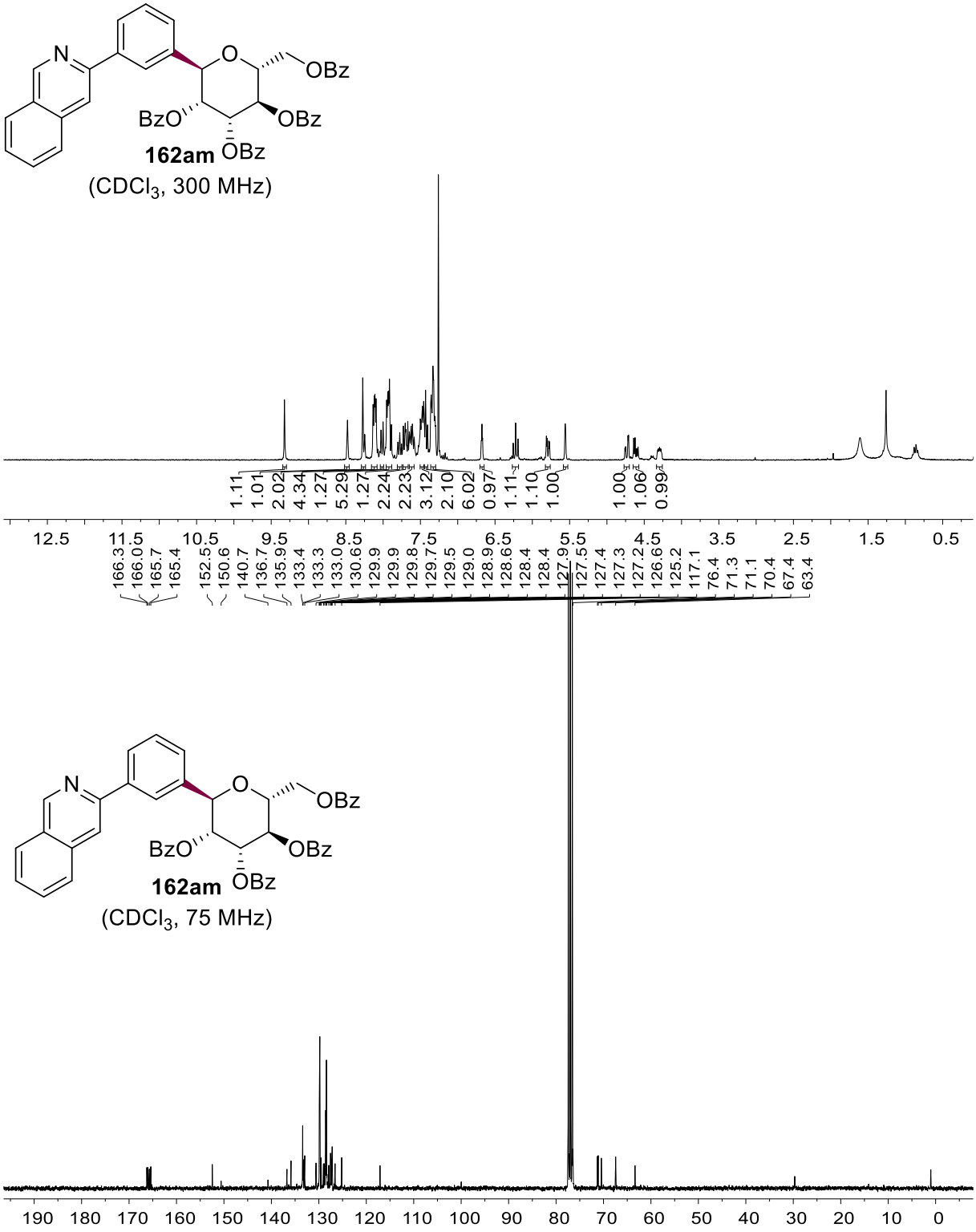
($CDCl_3$, 400 MHz)

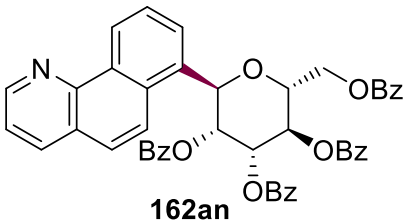




162al

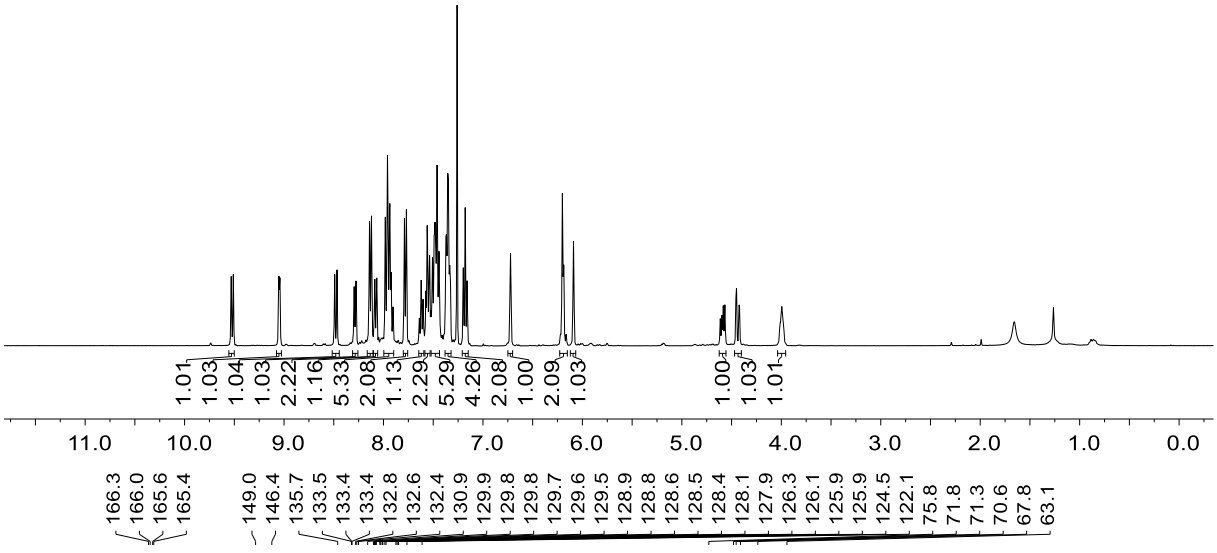
($CDCl_3$,101 MHz)

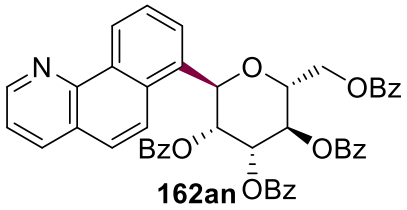

N
O
OBz
BzO
OBz
OBz
162am
(CDCl3, 300 MHz)
1.11
1.01
2.02
4.34
1.27
5.29
1.27
2.24
2.23
3.12
2.10
6.02
0.97
1.11
1.10
1.00
1.00
1.06
0.99
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
166.3
166.0
165.7
165.4
152.5
150.6
140.7
136.7
135.9
133.4
133.3
133.0
130.6
129.9
129.9
129.8
129.7
129.5
129.0
128.9
128.6
128.4
128.4
127.9
127.5
127.4
127.3
127.2
126.6
125.2
117.1
76.4
71.3
71.1
70.4
67.4
63.4
N
O
OBz
BzO
OBz
OBz
162am
(CDCl3, 75 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



162an

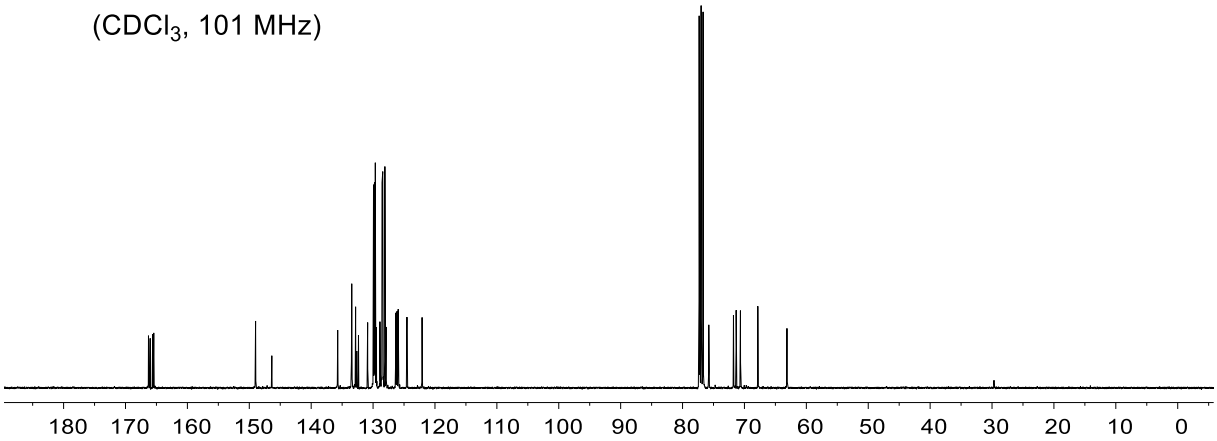
($CDCl_3$, 400 MHz)

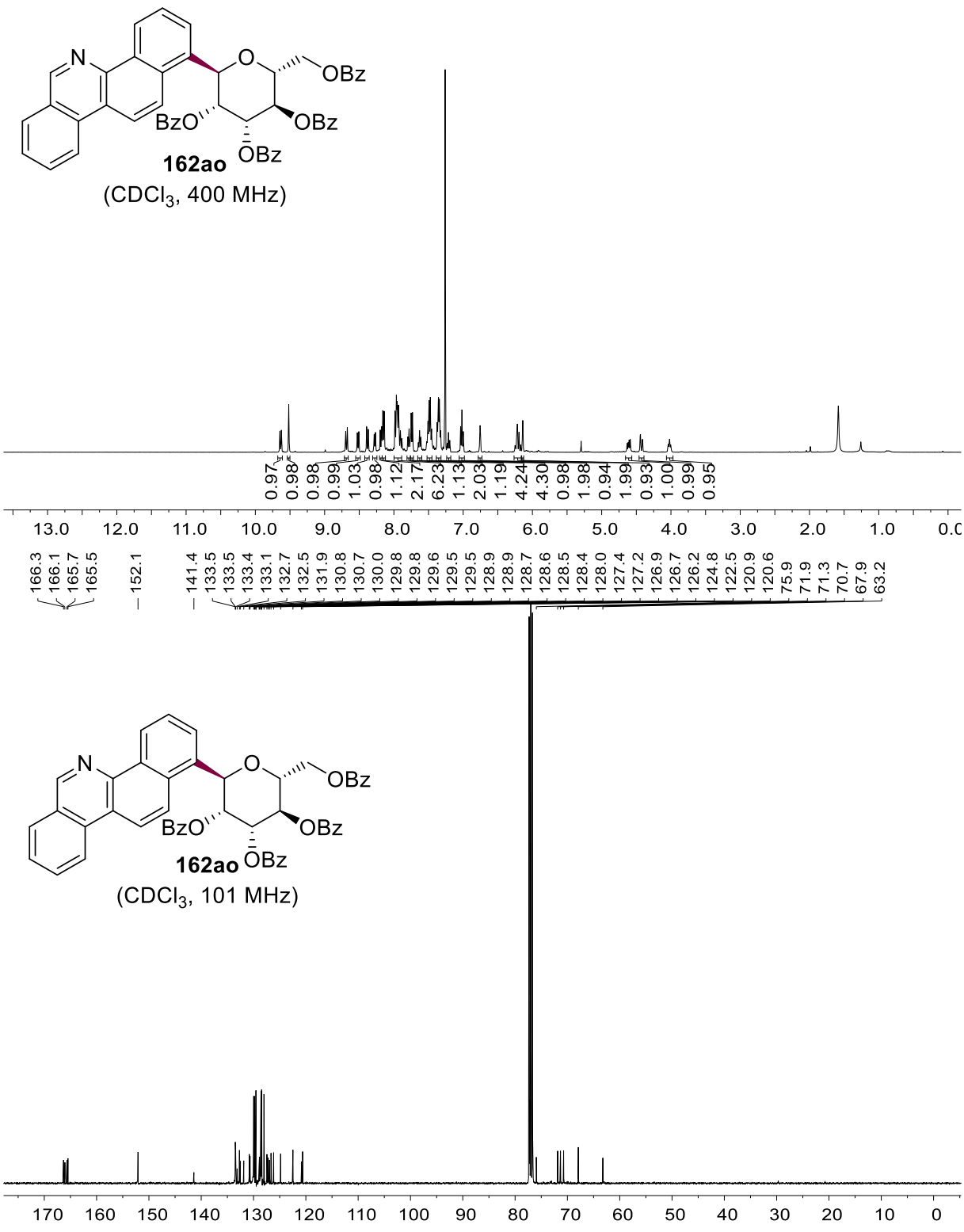


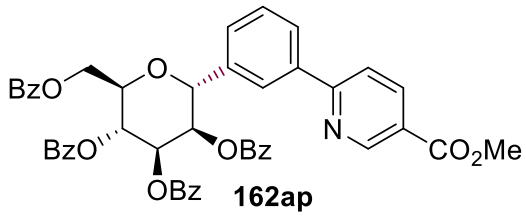


162an

($CDCl_3$, 101 MHz)

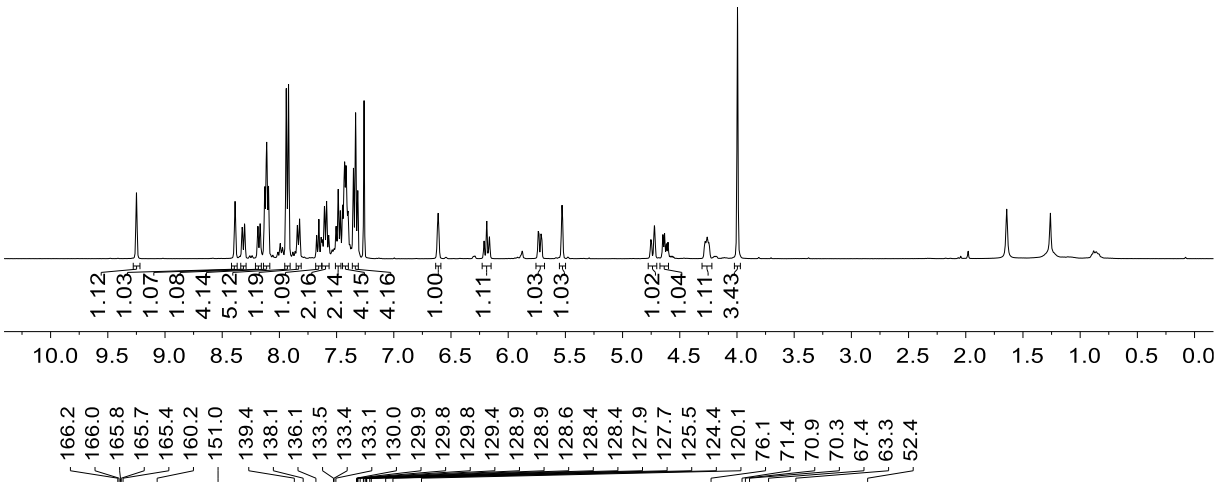


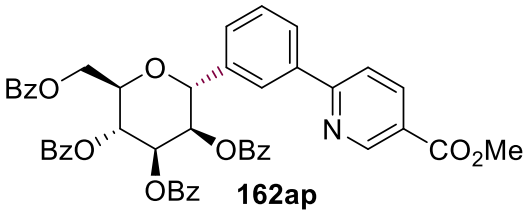

N
O
OBz
BzO
OBz
OBz
162ao
(CDCl3, 400 MHz)
0.97 0.98 0.98 0.99 1.03 0.98 1.12 2.17 6.23 1.13 2.03 1.19 4.24 4.30 0.98 1.98 0.94 1.99 0.93 1.00 0.99 0.95
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
166.3 166.1 165.7 165.5 152.1 141.4 133.5 133.5 133.4 133.1 132.7 132.5 131.9 130.8 130.7 130.0 129.8 129.8 129.6 129.5 129.5 128.9 128.9 128.7 128.6 128.5 128.4 128.0 127.4 127.2 126.9 126.7 126.2 124.8 122.5 120.9 120.6 75.9 71.9 71.3 70.7 67.9 63.2
N
O
OBz
BzO
OBz
OBz
162ao
(CDCl3, 101 MHz)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



162ap

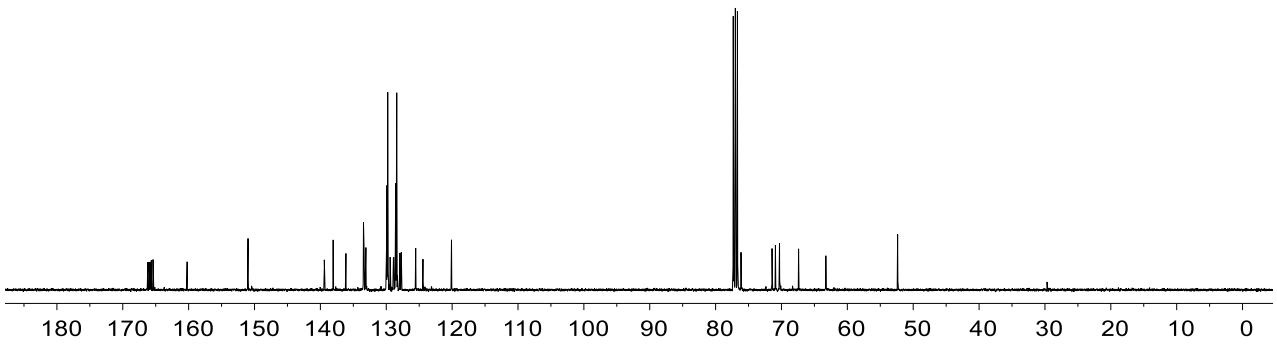
($CDCl_3$, 400 MHz)

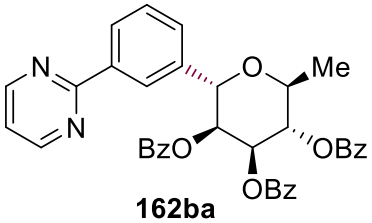




162ap

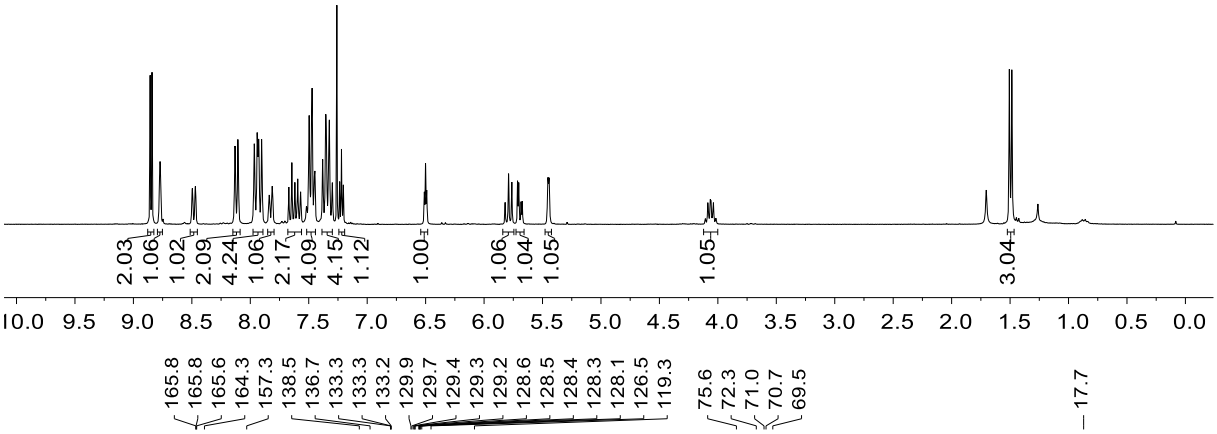
($CDCl_3$, 101 MHz)

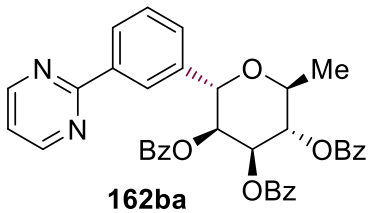




162ba

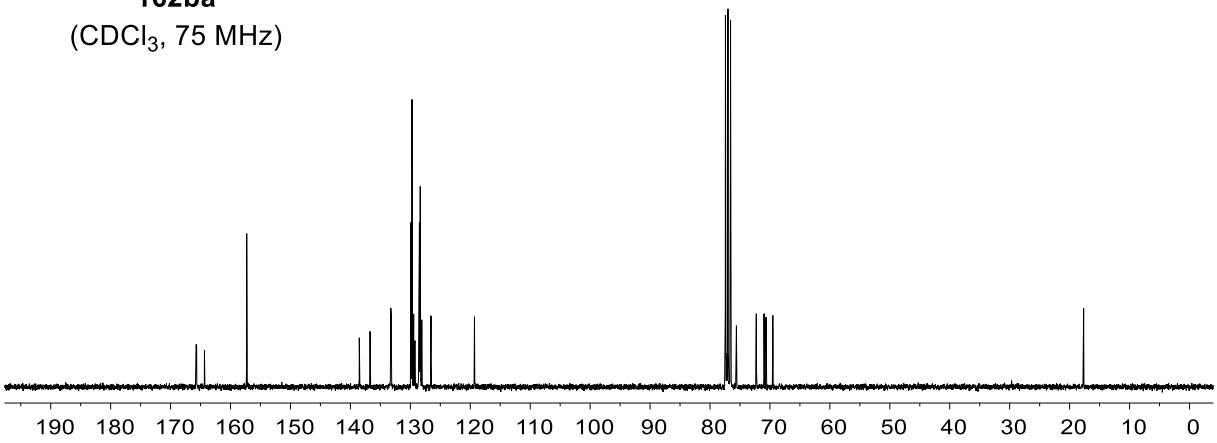
($CDCl_3$, 300 MHz)

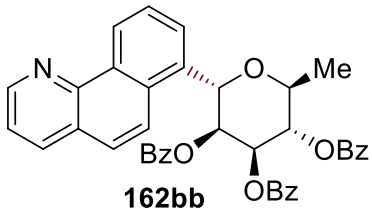




162ba

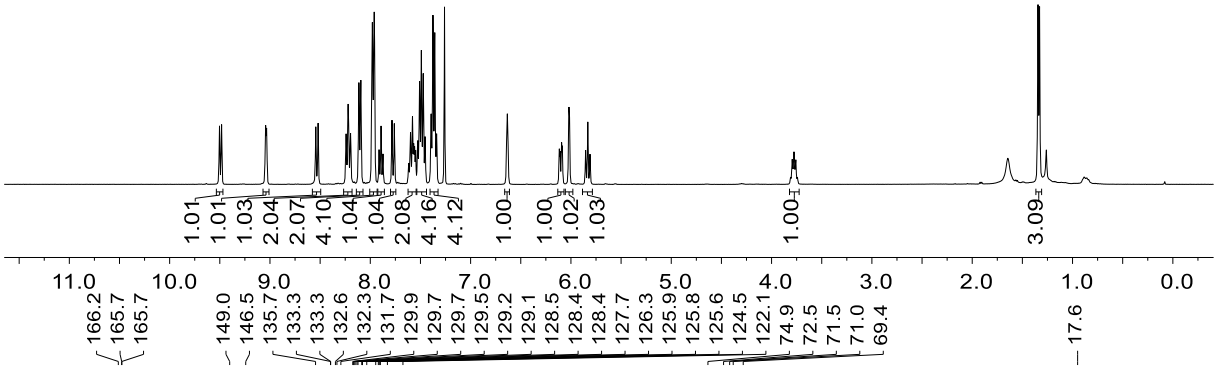
($CDCl_3$, 75 MHz)

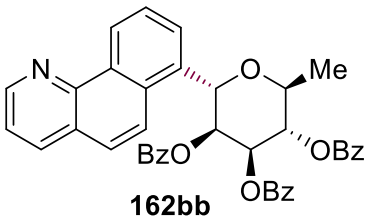




162bb

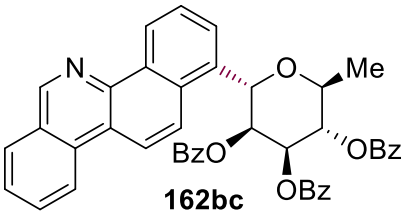
($CDCl_3$, 400 MHz)





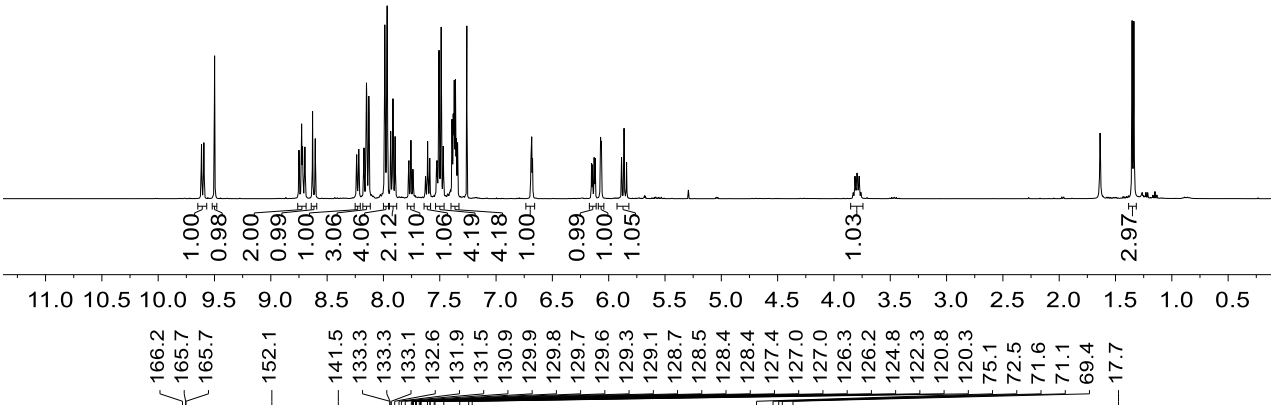
162bb

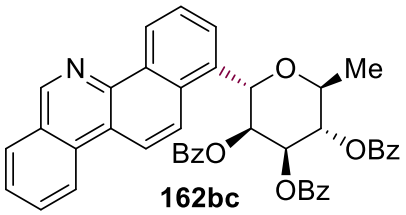
($CDCl_3$, 101 MHz)



162bc

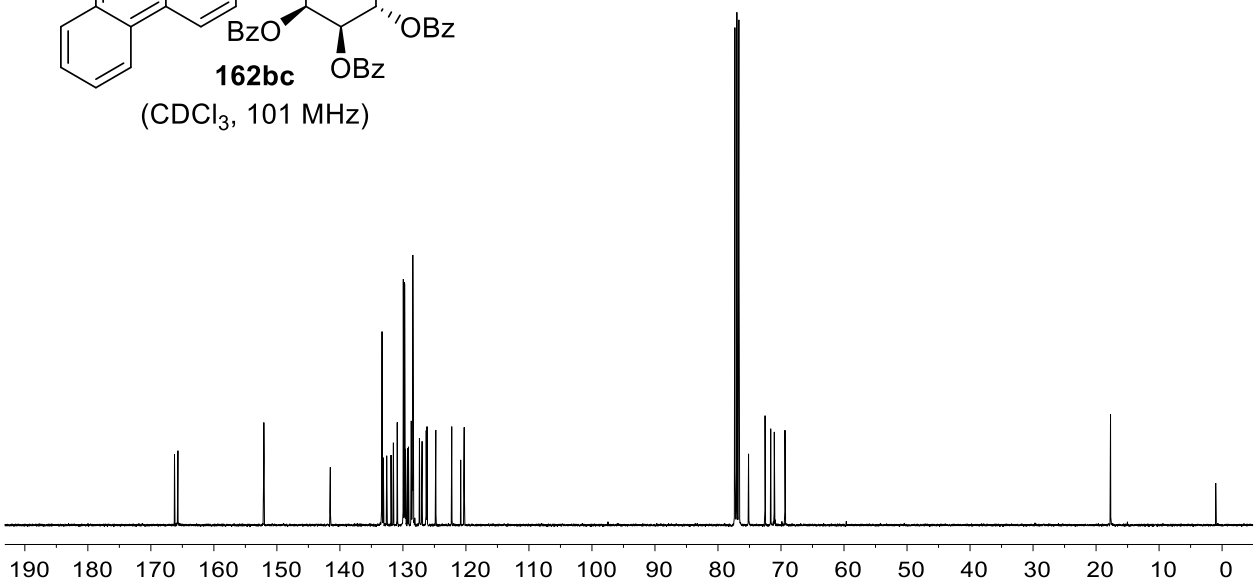
($CDCl_3$, 400 MHz)

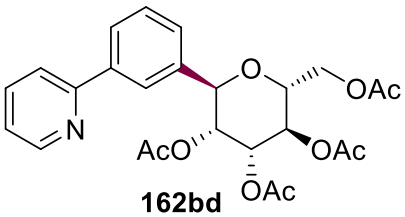




162bc

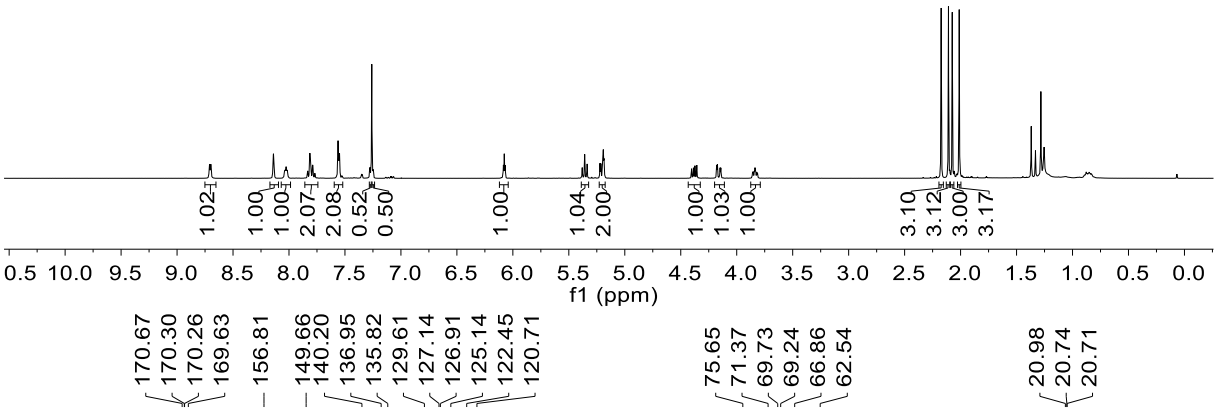
($CDCl_3$, 101 MHz)

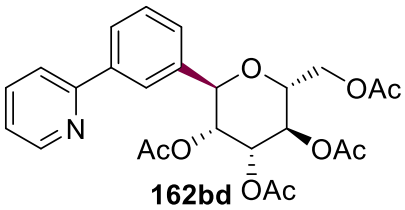




162bd

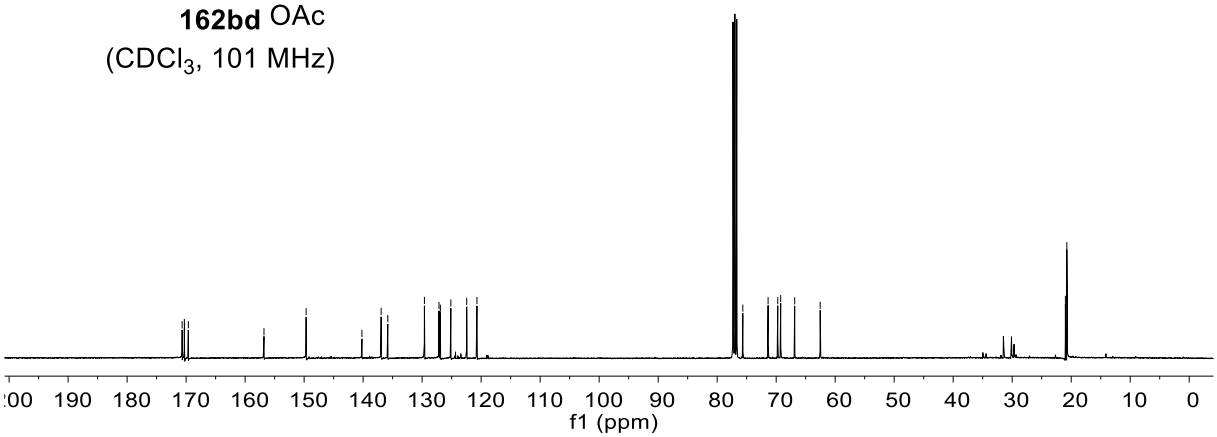
($CDCl_3$, 400 MHz)

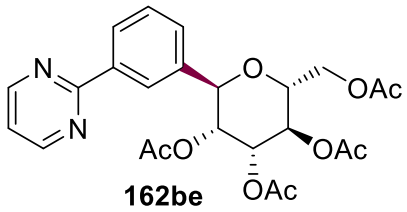




162bd

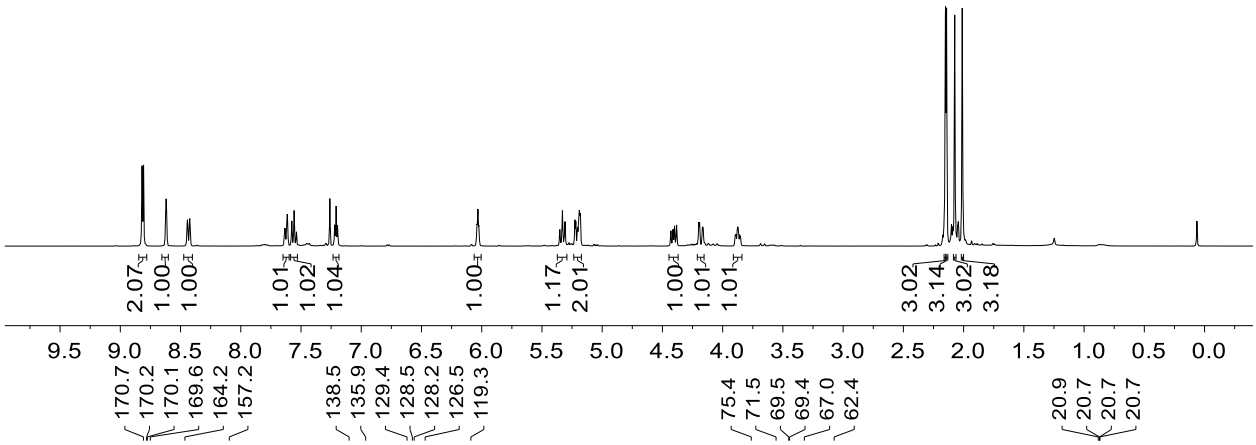
($CDCl_3$, 101 MHz)

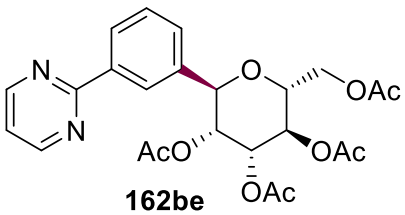




162be

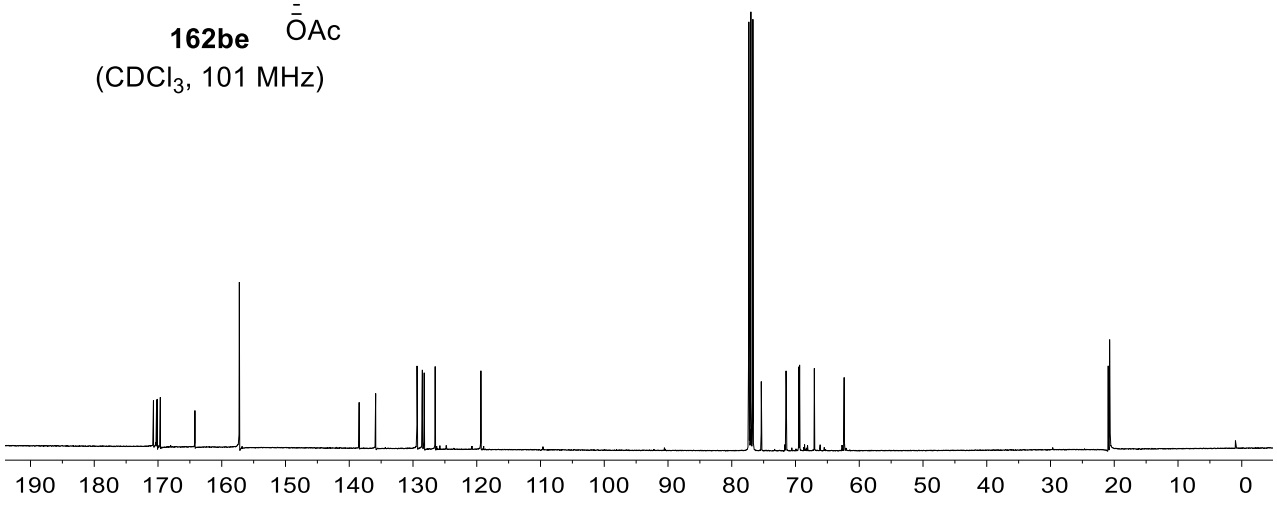
($CDCl_3$, 400 MHz)

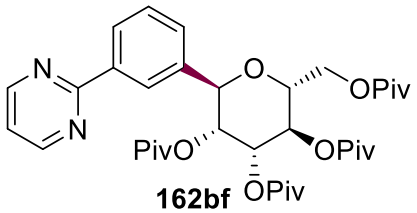




162be

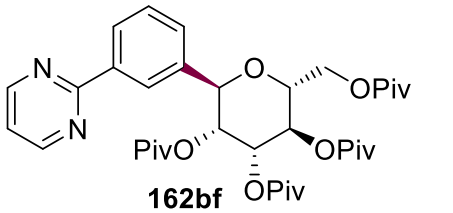
($CDCl_3$, 101 MHz)





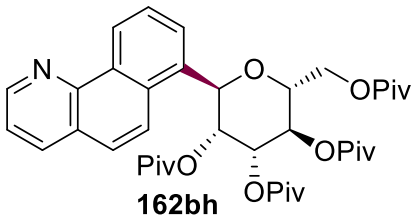
162bf

($CDCl_3$, 400 MHz)



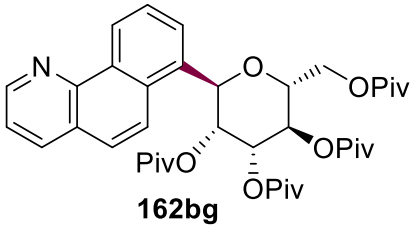
162bf

($CDCl_3$, 101 MHz)



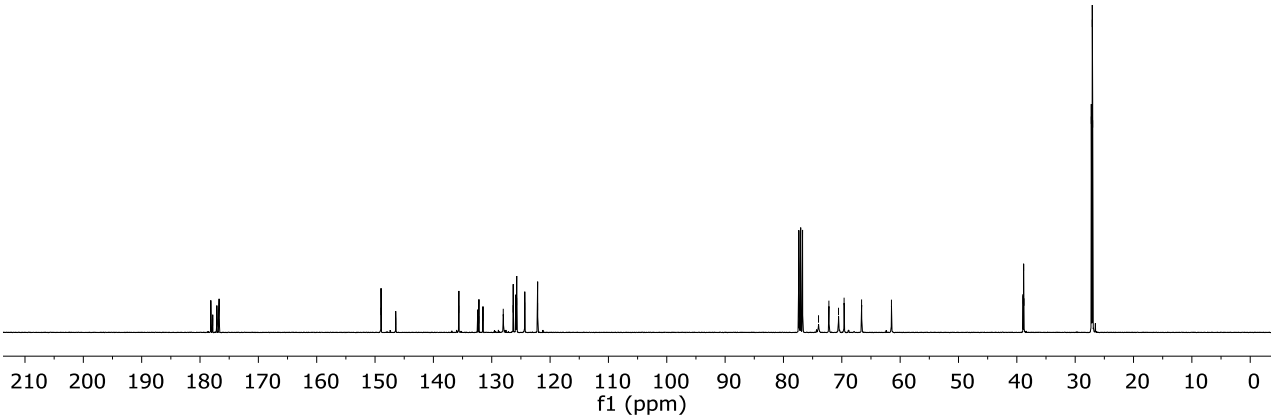
162bh

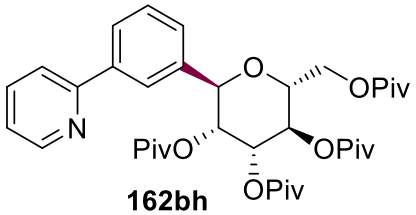
($CDCl_3$, 400 MHz)



162bg

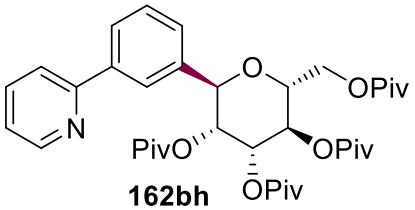
($CDCl_3$, 101 MHz)





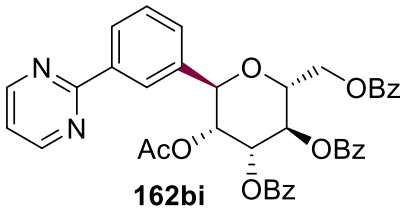
162bh

($CDCl_3$, 400 MHz)



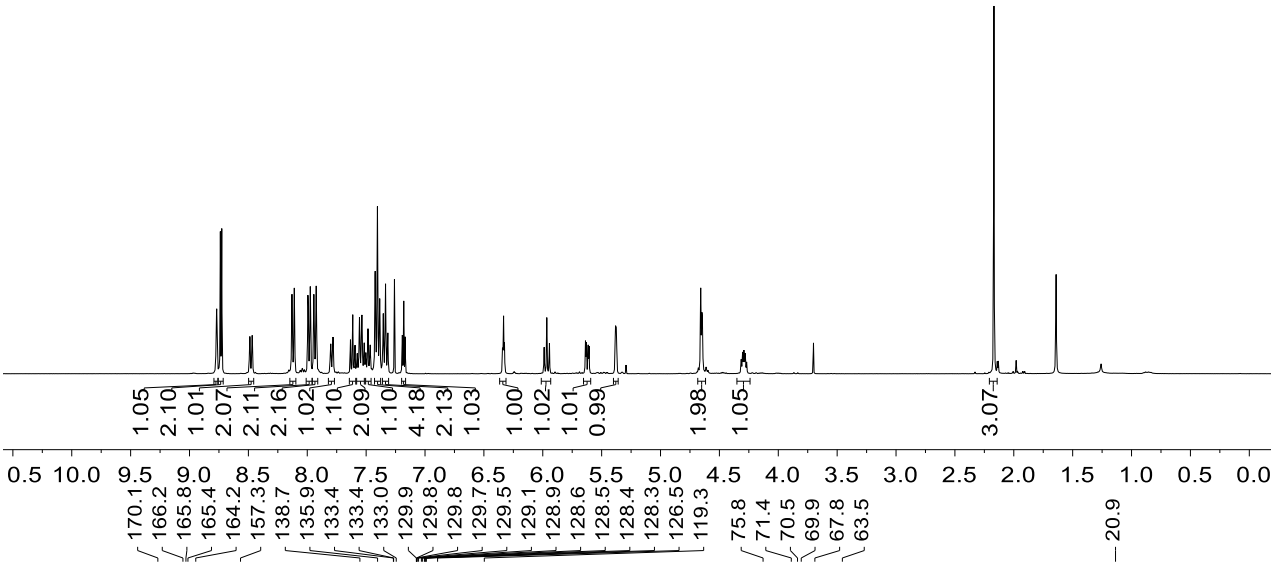
162bh

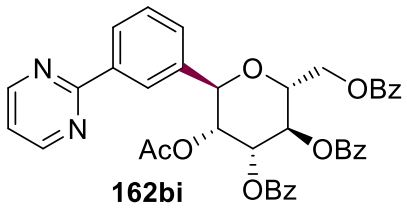
($CDCl_3$, 101 MHz)



162bi

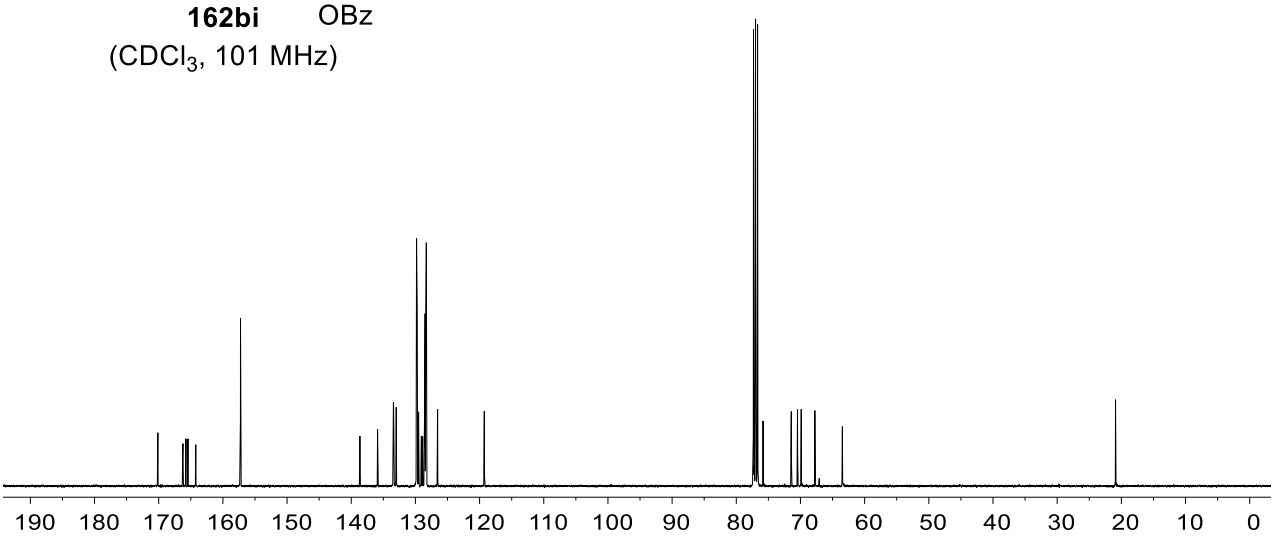
($CDCl_3$, 400 MHz)

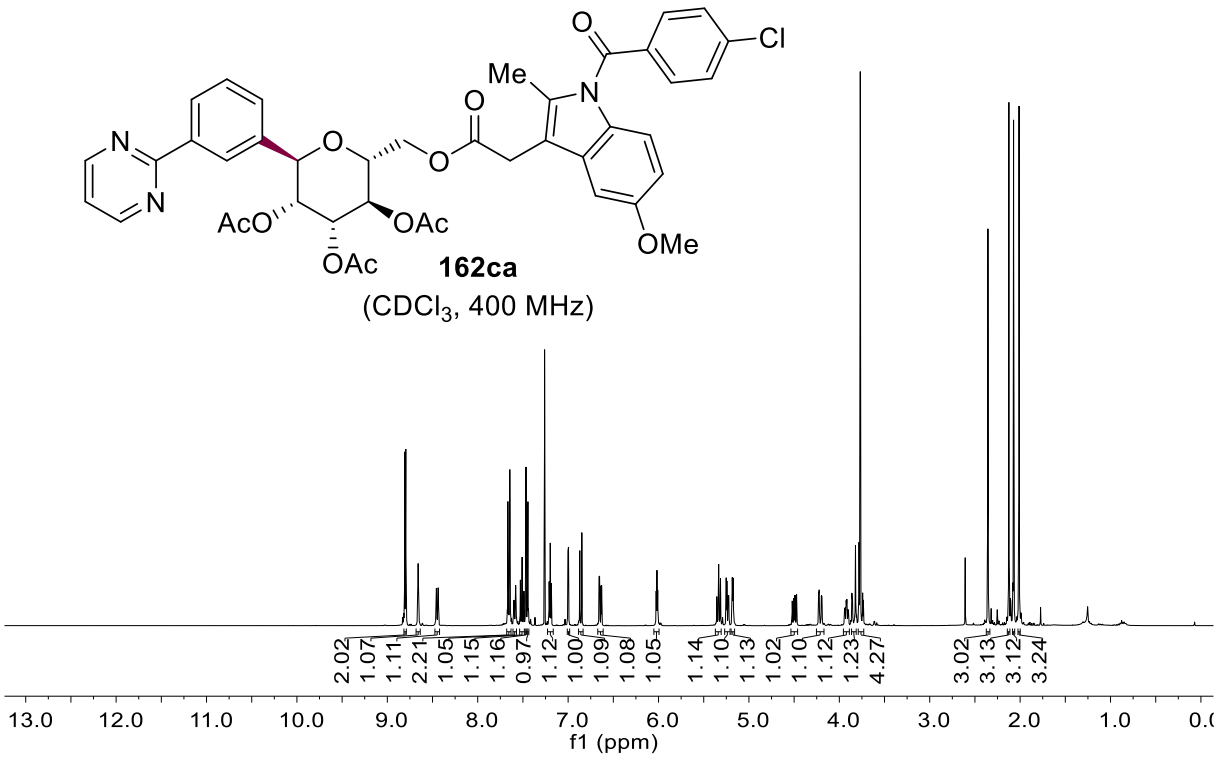


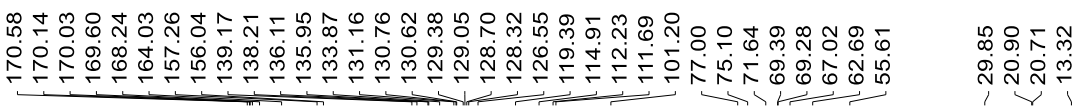


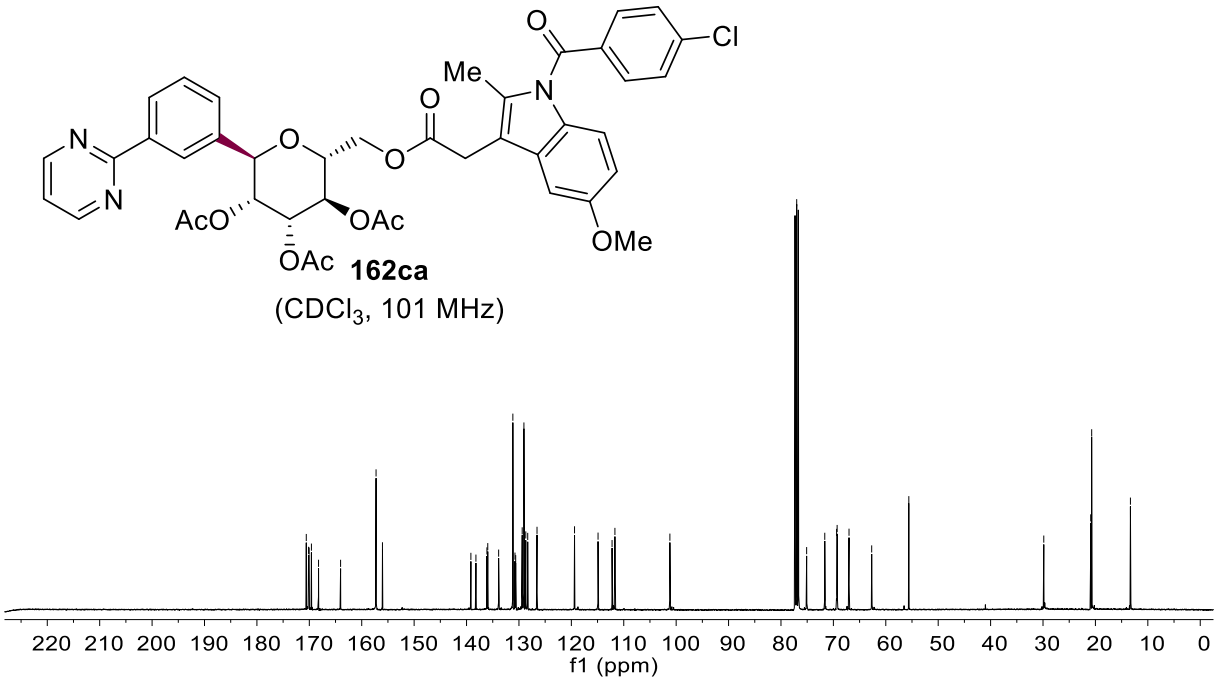
162bi

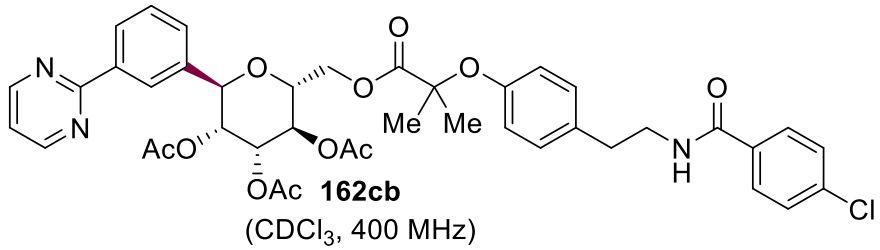
($CDCl_3$, 101 MHz)




Me
N
O
Cl
O
O
N
N
O
AcO
OAc
OAc
OMe
162ca
(CDCl3, 400 MHz)
2.02 1.07 1.11 2.21 1.05 1.15 1.16 0.97 1.12 1.00 1.09 1.08 1.05 1.14 1.10 1.13 1.02 1.10 1.12 1.23 4.27 3.02 3.13 3.12 3.24
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

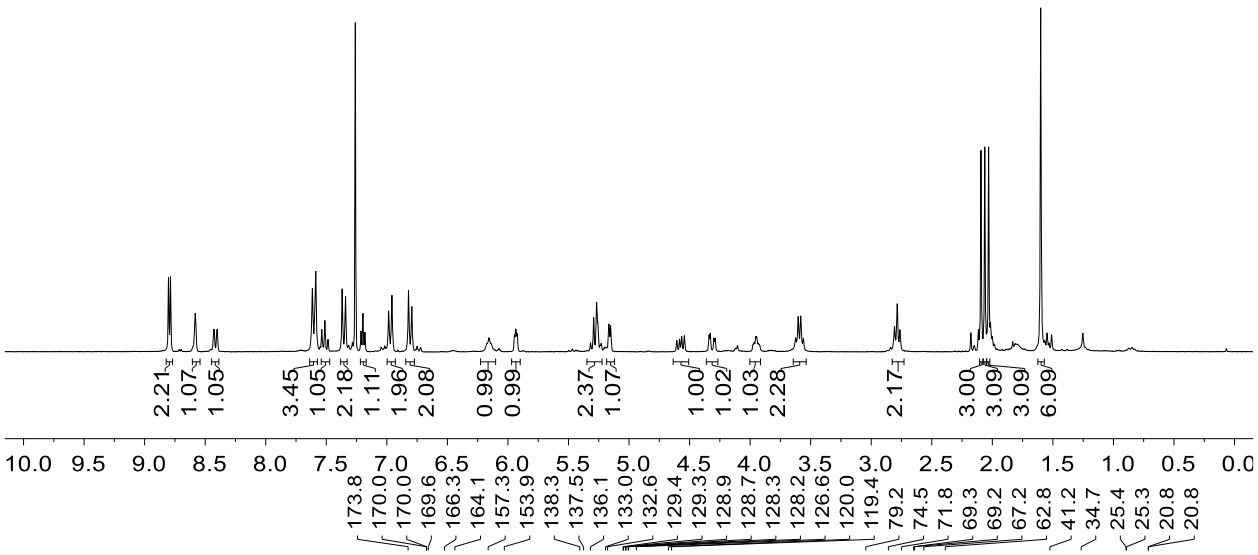

170.58 170.14 170.03 169.60 168.24 164.03 157.26 156.04 139.17 138.21 136.11 135.95 133.87 131.16 130.76 130.62 129.38 129.05 128.70 128.32 126.55 119.39 114.91 112.23 111.69 101.20 77.00 75.10 71.64 69.39 69.28 67.02 62.69 55.61 29.85 20.90 20.71 13.32

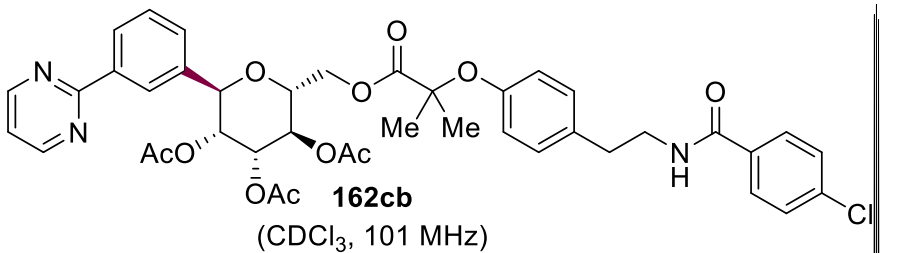

Me
N
O
Cl
O
O
N
N
O
AcO
OAc
OAc
OMe
162ca
(CDCl3, 101 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



162cb

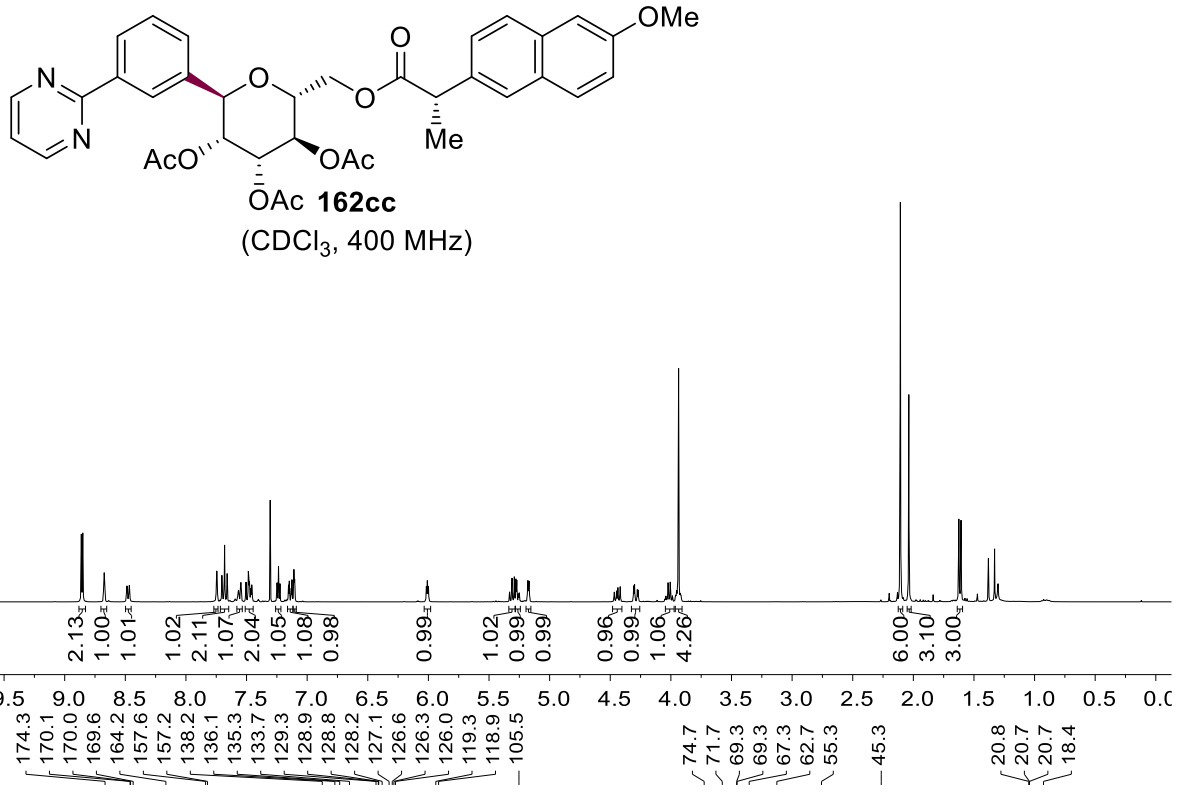
($CDCl_3$, 400 MHz)

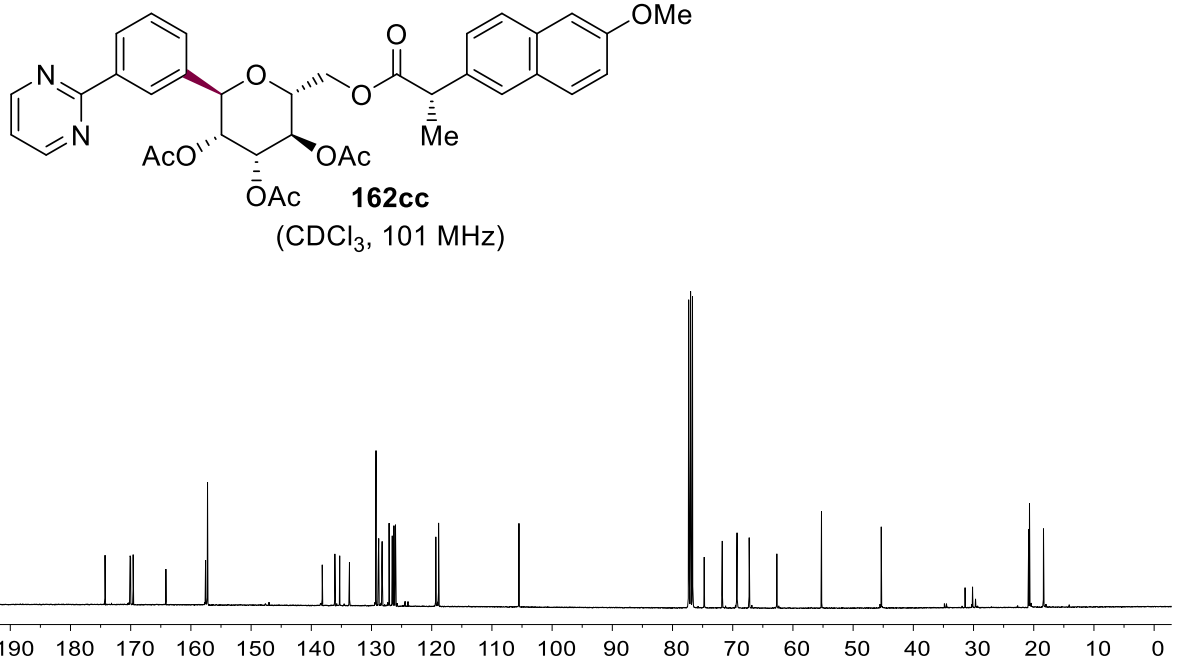


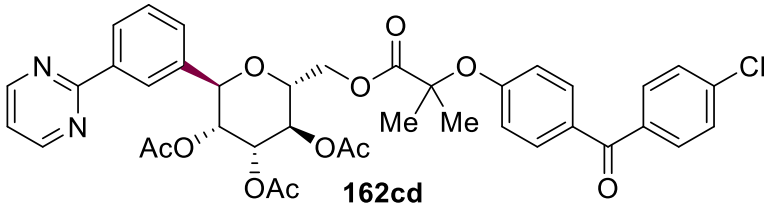


162cb

($CDCl_3$, 101 MHz)

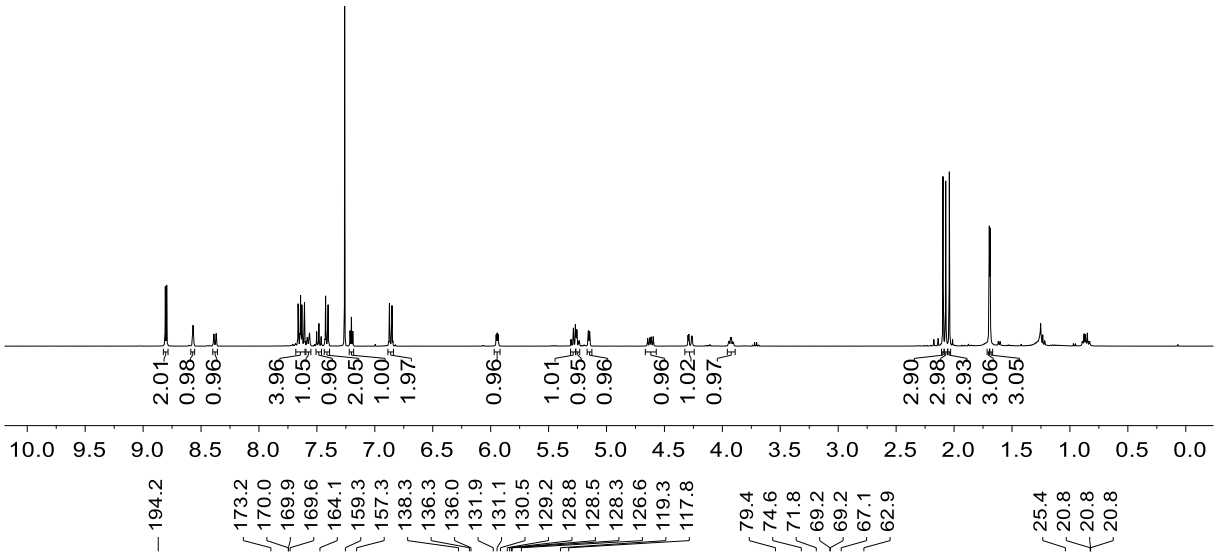

OMe
O
N
N
O
O
Me
AcO
OAc
OAc
162cc
(CDCl3, 400 MHz)
2.13
1.00
1.01
1.02
2.11
1.07
2.04
1.05
1.08
0.98
0.99
1.02
0.99
0.99
0.96
0.99
1.06
4.26
6.00
3.10
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
174.3
170.1
170.0
169.6
164.2
157.6
157.2
138.2
136.1
135.3
133.7
129.3
128.9
128.8
128.2
127.1
126.6
126.3
126.0
119.3
118.9
105.5
74.7
71.7
69.3
69.3
67.3
62.7
55.3
45.3
20.8
20.7
20.7
18.4

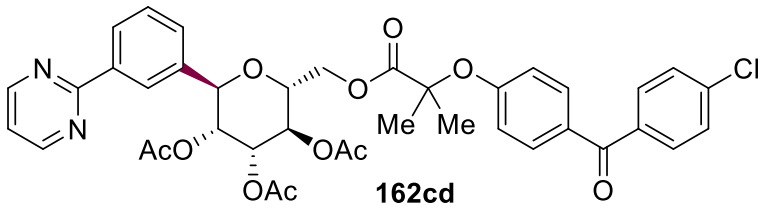

OMe
O
N
N
O
O
Me
AcO
OAc
OAc
162cc
(CDCl3, 101 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



162cd

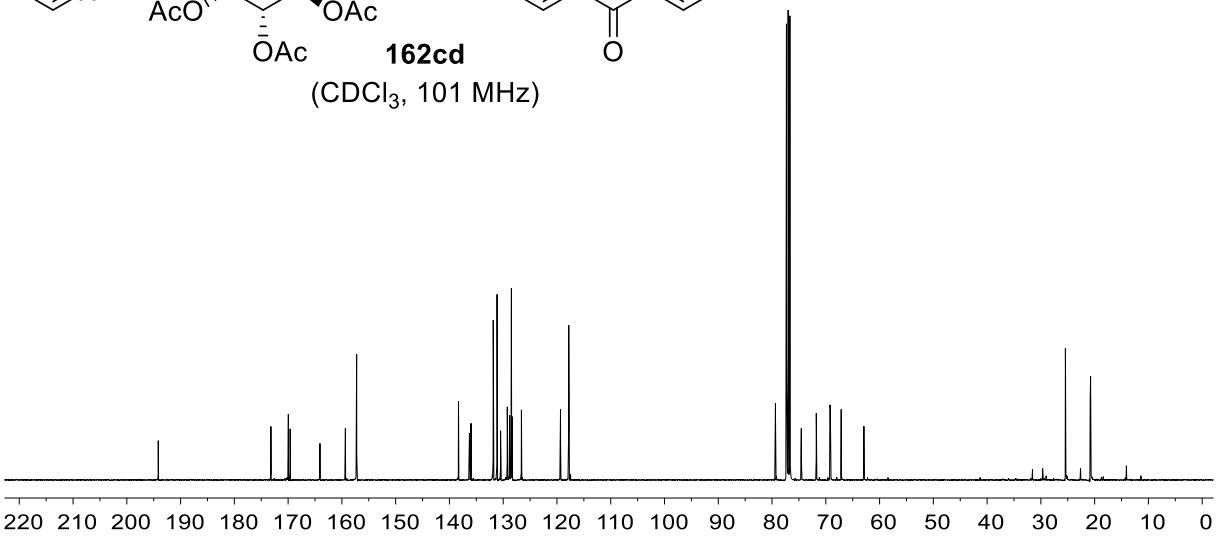
($CDCl_3$, 400 MHz)

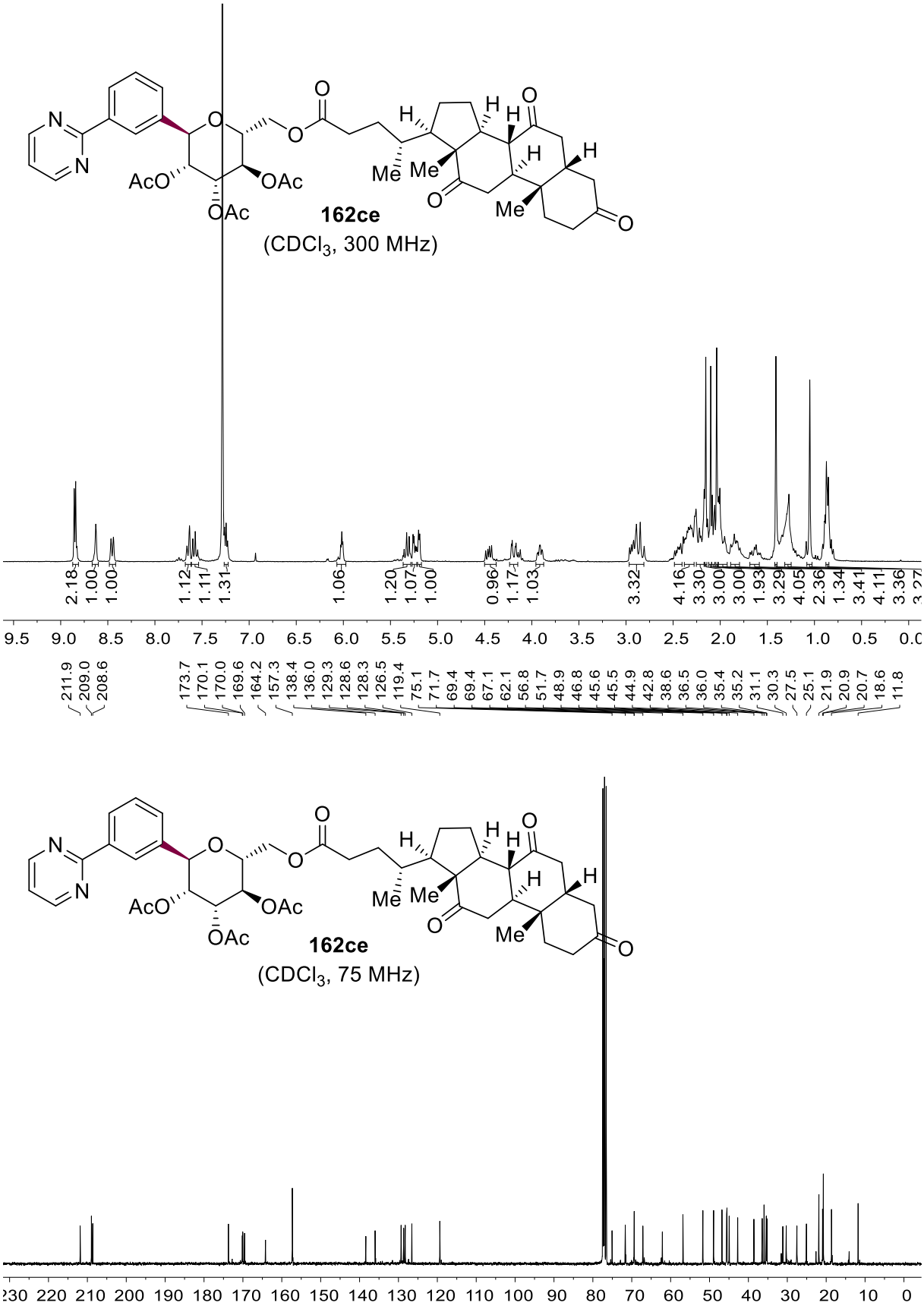


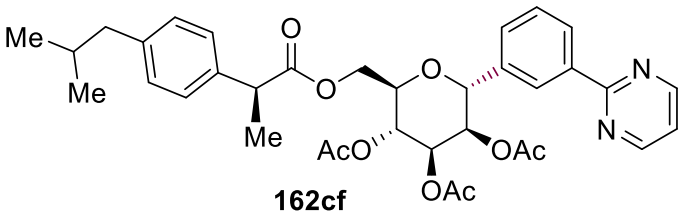


162cd

($CDCl_3$, 101 MHz)

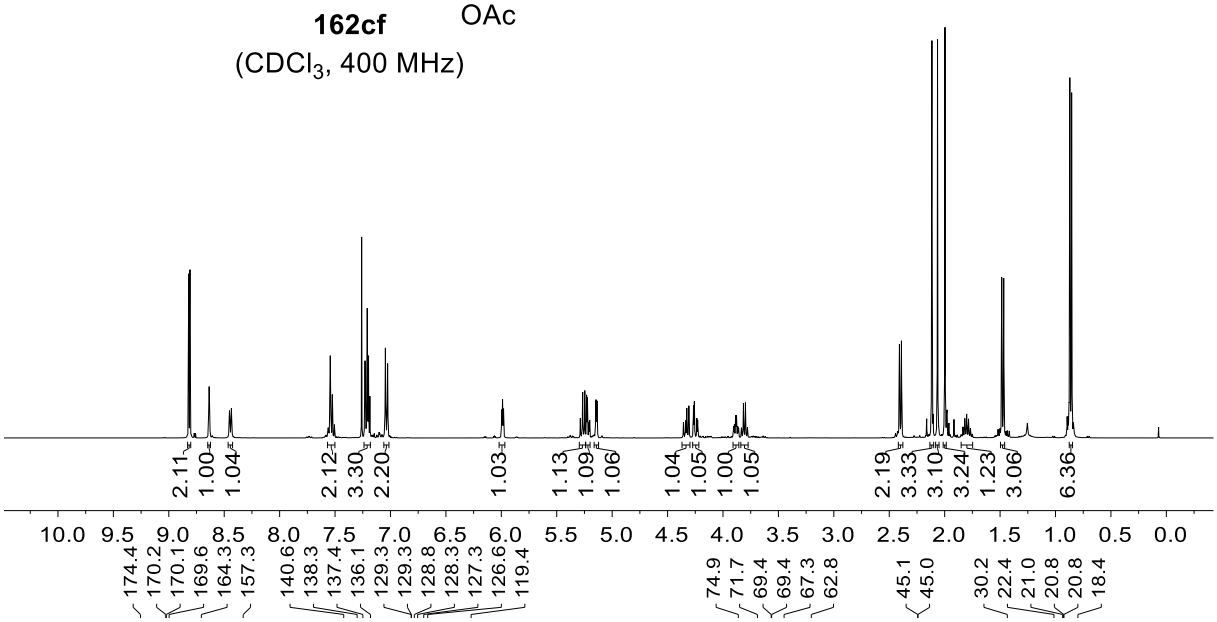


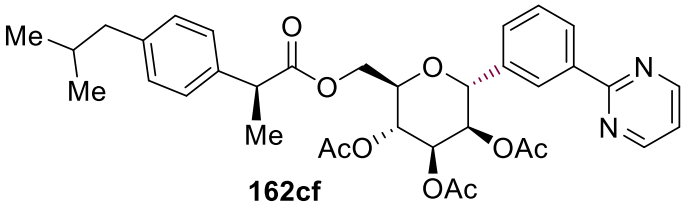

162ce
(CDCl3, 300 MHz)
2.18 1.00 1.00 1.12 1.11 1.31 1.06 1.20 1.07 1.00 0.96 1.17 1.03 3.32 4.16 3.30 3.00 3.00 1.93 3.29 4.05 2.36 1.34 3.41 4.11 3.36
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
211.9 209.0 208.6 173.7 170.1 170.0 169.6 164.2 157.3 138.4 136.0 129.3 128.6 128.3 126.5 119.4 75.1 71.7 69.4 69.4 67.1 62.1 56.8 51.7 48.9 46.8 45.6 45.5 44.9 42.8 38.6 36.5 36.0 35.4 35.2 31.1 30.3 27.5 25.1 21.9 20.9 20.7 18.6 11.8
162ce
(CDCl3, 75 MHz)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



162cf

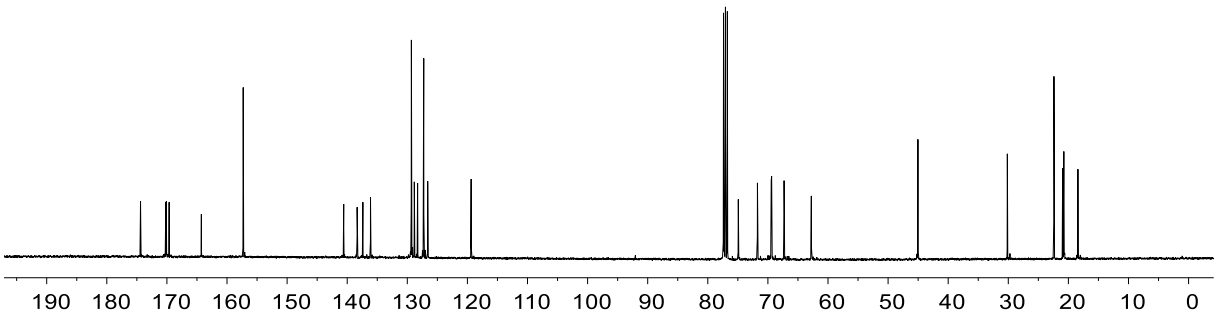
($CDCl_3$, 400 MHz)

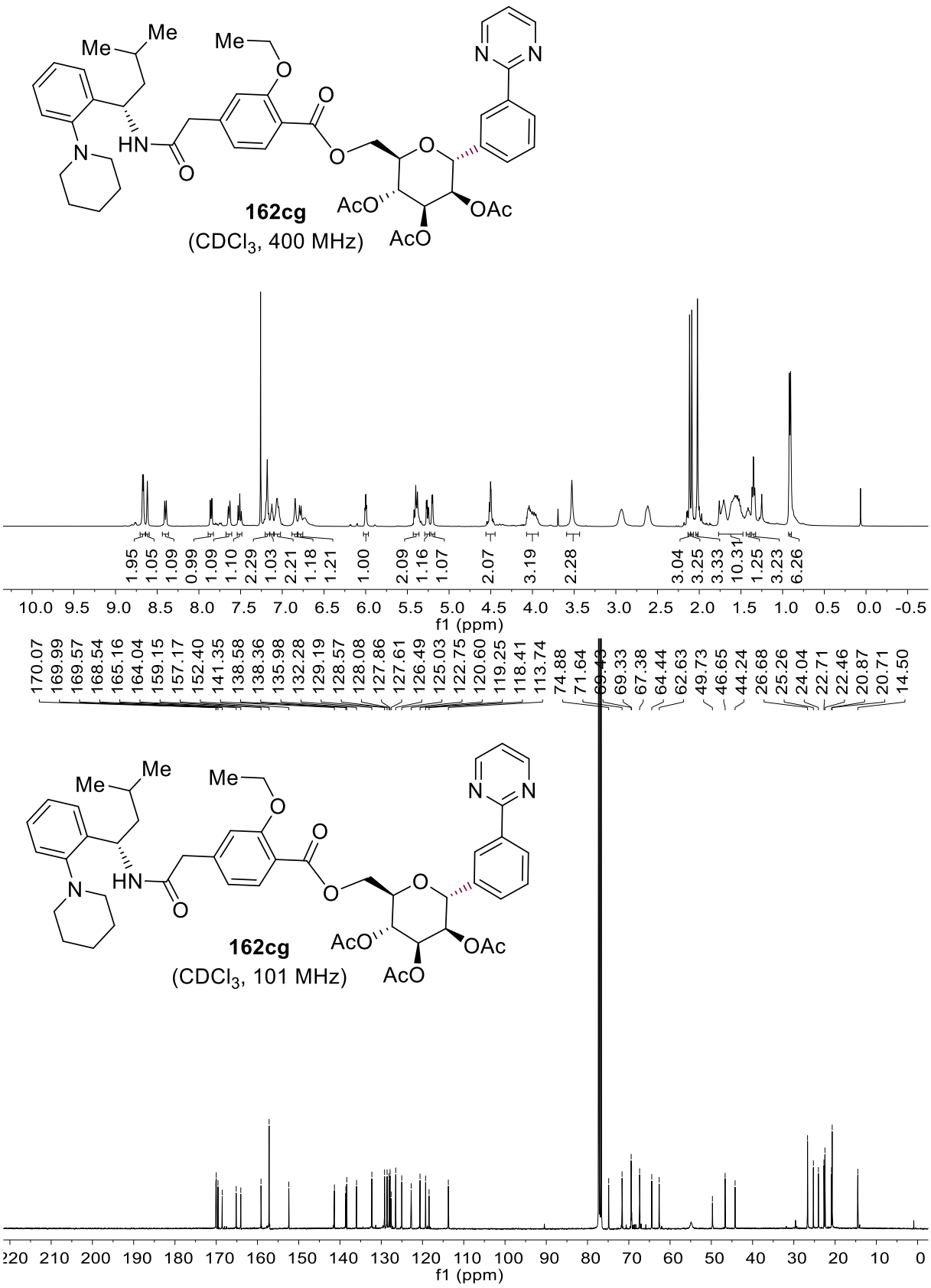


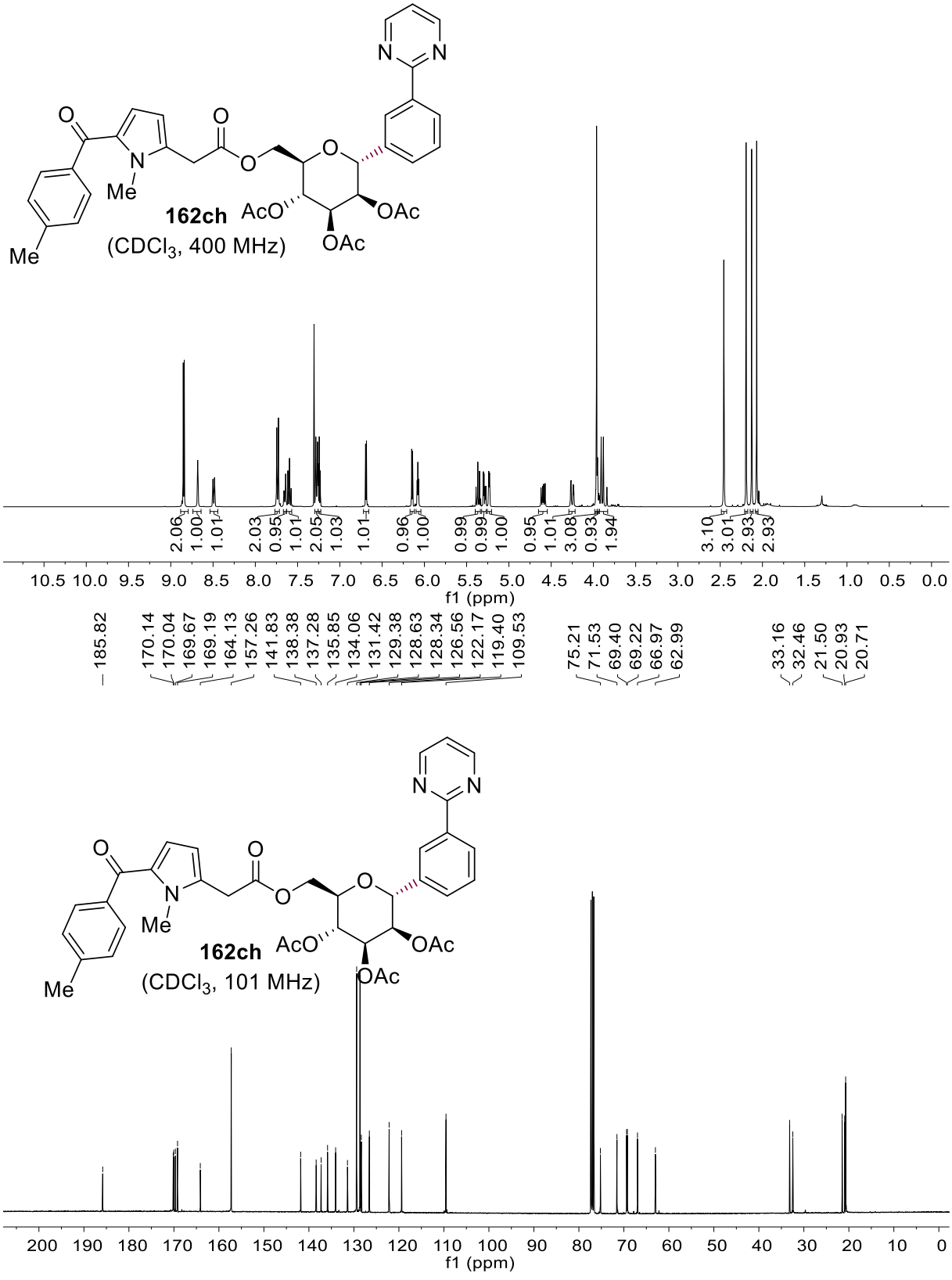


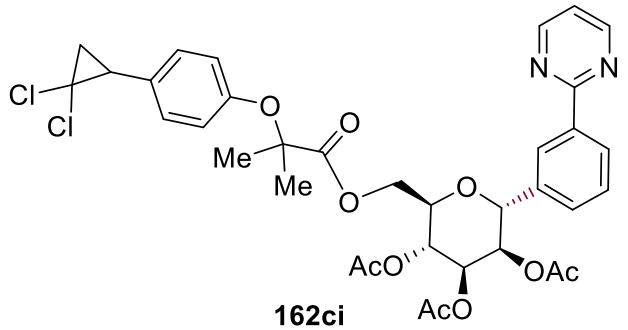
162cf

($CDCl_3$, 101 MHz)



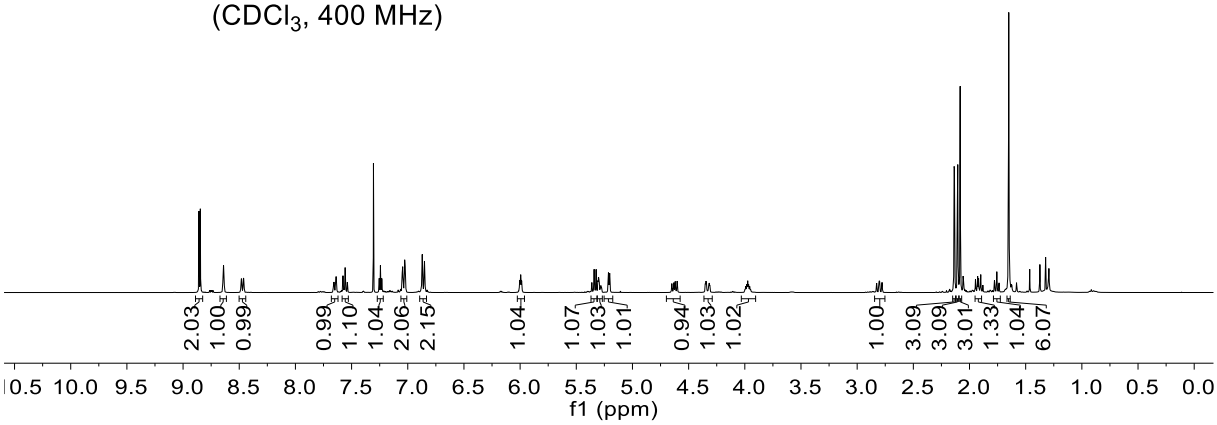

Me
Me
Me
O
N
N
HN
O
O
O
O
N
AcO
OAc
AcO
162cg
(CDCl3, 400 MHz)
1.95 1.05 1.09 0.99 1.09 1.10 2.29 1.03 2.21 1.18 1.21 1.00 2.09 1.16 1.07 2.07 3.19 2.28 3.04 3.25 3.33 10.31 1.25 3.23 6.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
170.07 169.99 169.57 168.54 165.16 164.04 159.15 157.17 152.40 141.35 138.58 138.36 135.98 132.28 129.19 128.57 128.08 127.86 127.61 126.49 125.03 122.75 120.60 119.25 118.41 113.74 74.88 71.64 69.33 67.38 64.44 62.63 49.73 46.65 44.24 26.68 25.26 24.04 22.71 22.46 20.87 20.71 14.50
Me
Me
Me
O
N
N
HN
O
O
O
O
N
AcO
OAc
AcO
162cg
(CDCl3, 101 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

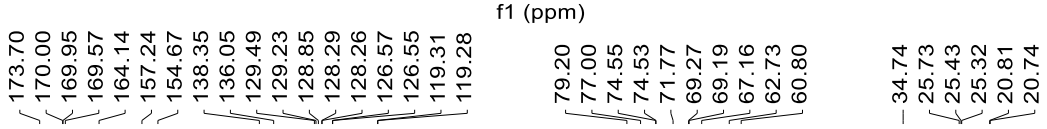

162ch
(CDCl3, 400 MHz)
f1 (ppm)
162ch
(CDCl3, 101 MHz)
f1 (ppm)

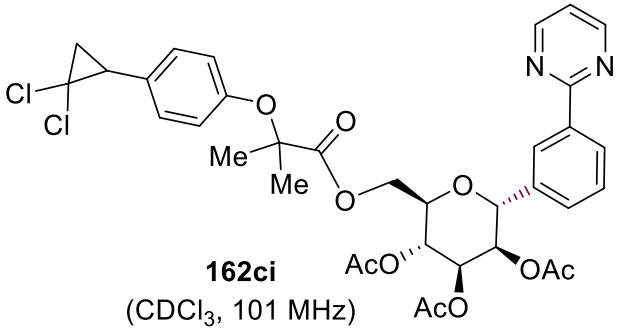


162ci

($CDCl_3$, 400 MHz)

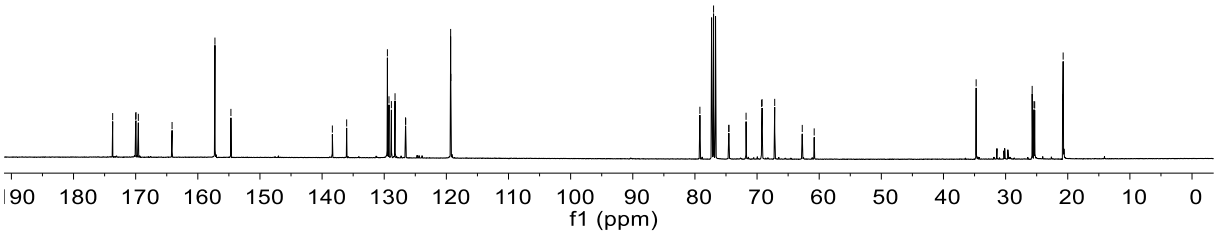


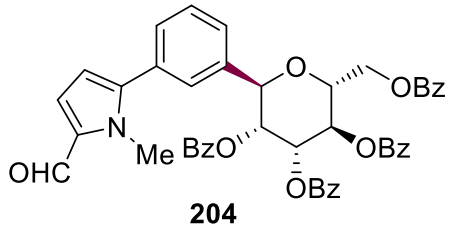




162ci

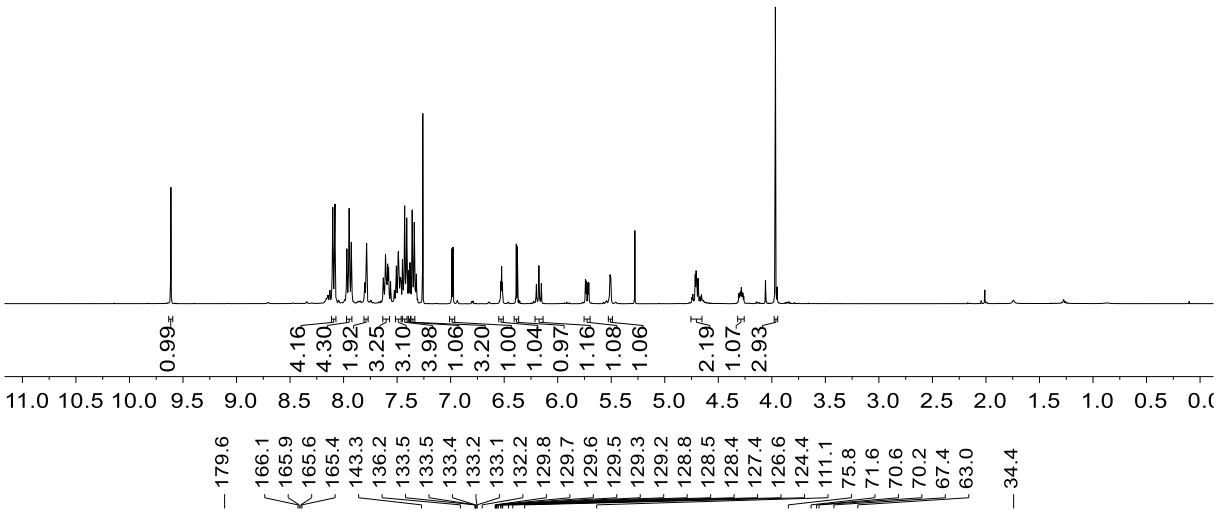
($CDCl_3$, 101 MHz)

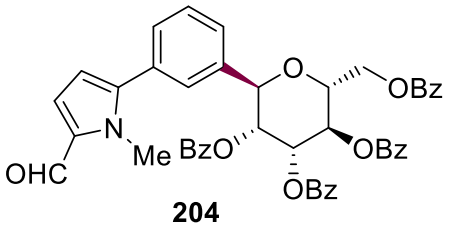




204

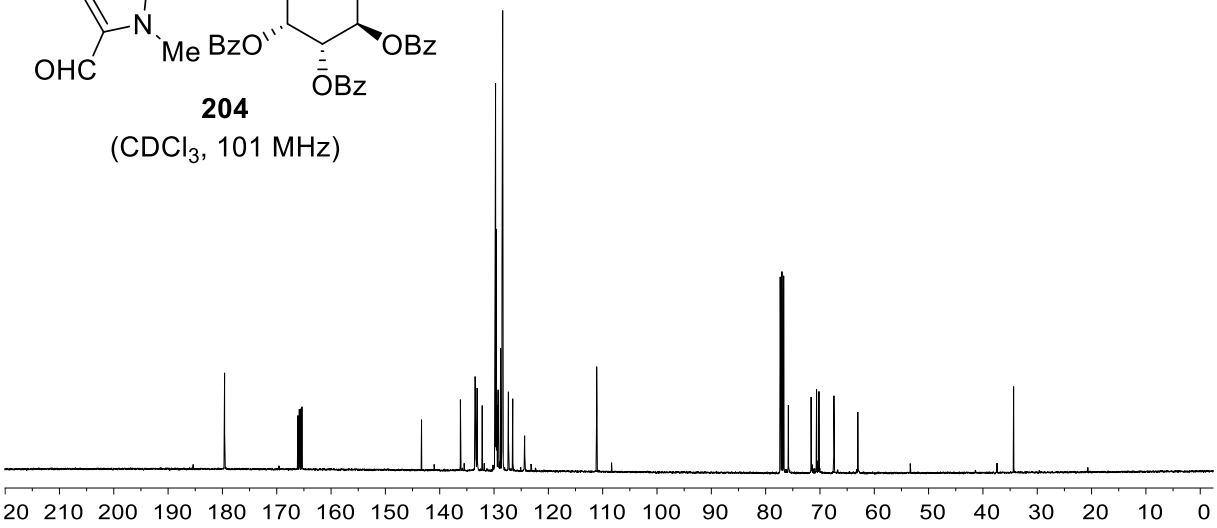
($CDCl_3$, 400 MHz)

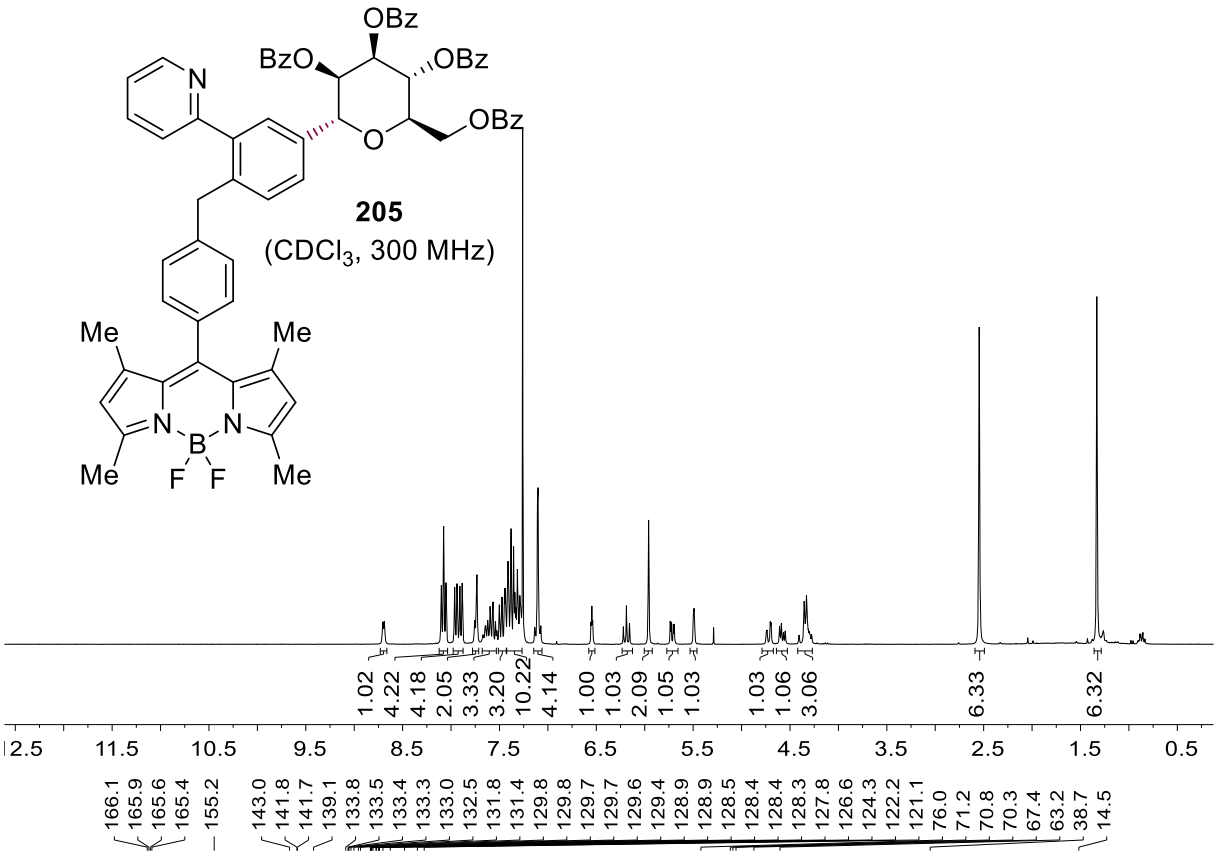


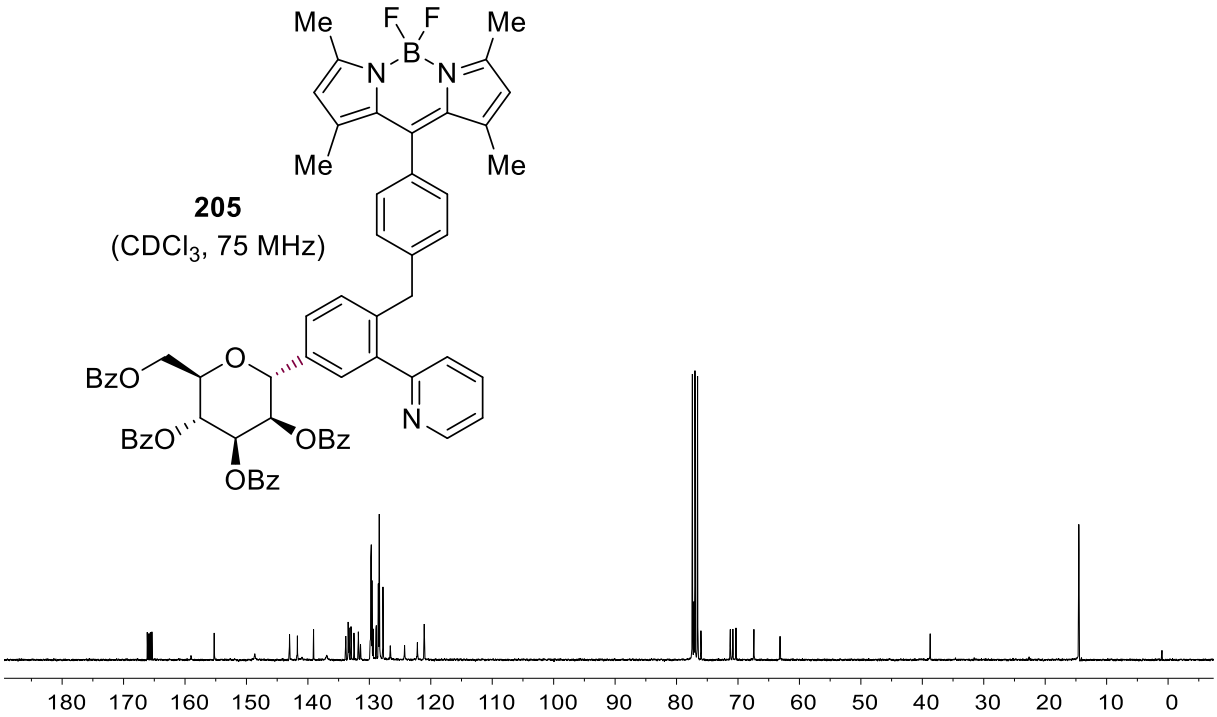


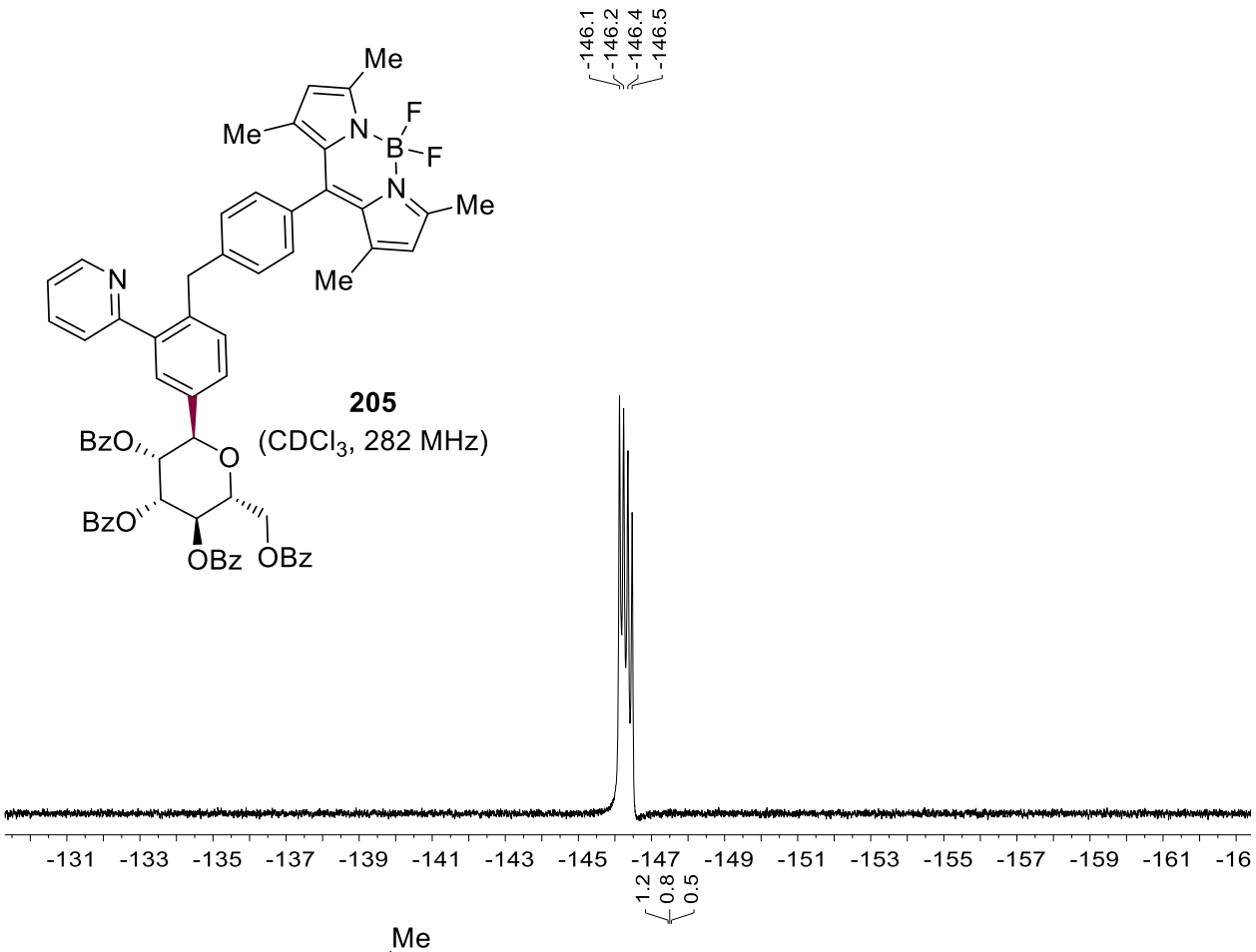
204

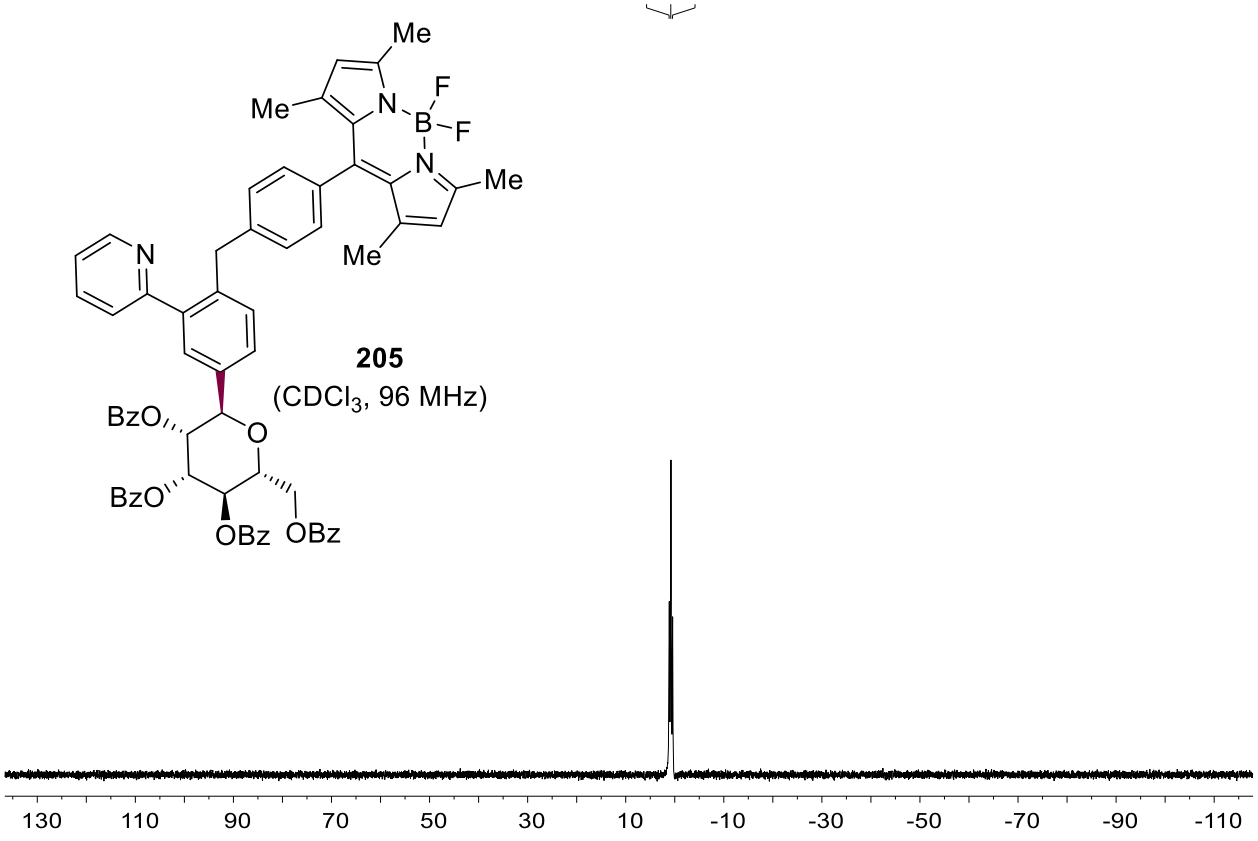
($CDCl_3$, 101 MHz)

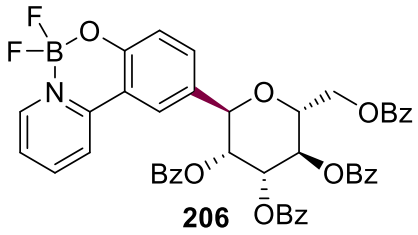



OBz
BzO
OBz
OBz
O
N
205
(CDCl3, 300 MHz)
Me
Me
Me
Me
N
B
N
F
F
1.02
4.22
4.18
2.05
3.33
3.20
10.22
4.14
1.00
1.03
2.09
1.05
1.03
1.03
1.06
3.06
6.33
6.32
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
166.1
165.9
165.6
165.4
155.2
143.0
141.8
141.7
139.1
133.8
133.5
133.4
133.3
133.0
132.5
131.8
131.4
129.8
129.8
129.7
129.7
129.6
129.4
128.9
128.9
128.5
128.4
128.4
128.3
127.8
126.6
124.3
122.2
121.1
76.0
71.2
70.8
70.3
67.4
63.2
38.7
14.5


Me
F
F
Me
B
N
N
Me
Me
205
(CDCl3, 75 MHz)
BzO
O
N
BzO
OBz
OBz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

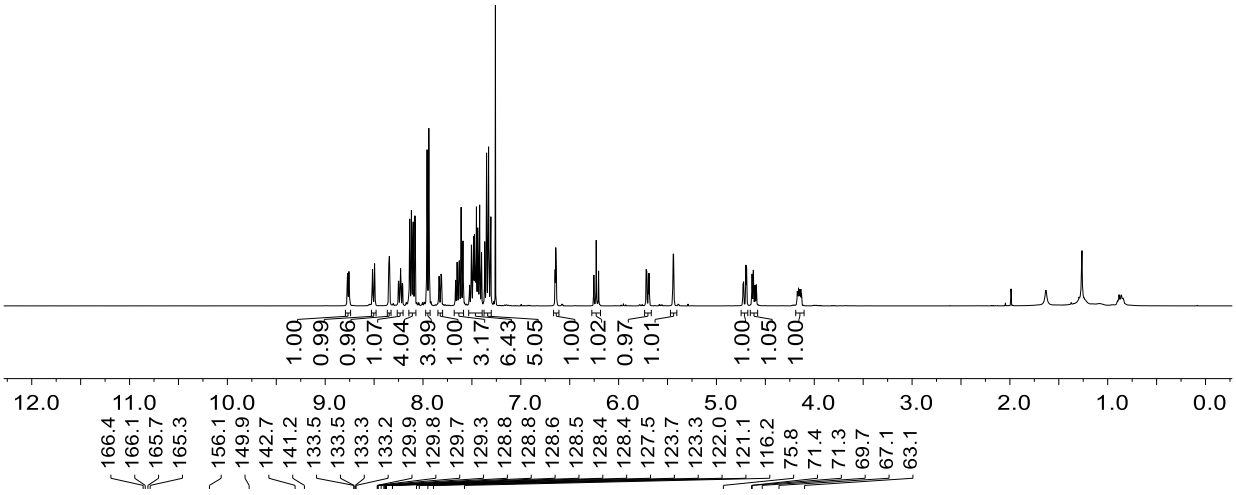

-146.1
-146.2
-146.4
-146.5
Me
Me
N
B
F
F
N
Me
Me
N
BzO
O
BzO
OBz
OBz
205
(CDCl3, 282 MHz)
-131 -133 -135 -137 -139 -141 -143 -145 -147 -149 -151 -153 -155 -157 -159 -161 -16
1.2
0.8
0.5

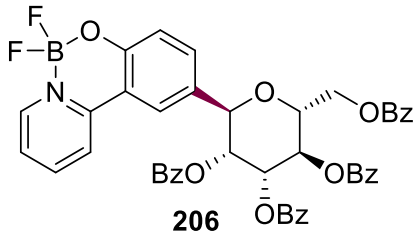

Me
Me
N
B
F
F
N
Me
Me
N
BzO
O
BzO
OBz
OBz
205
(CDCl3, 96 MHz)
130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110



206

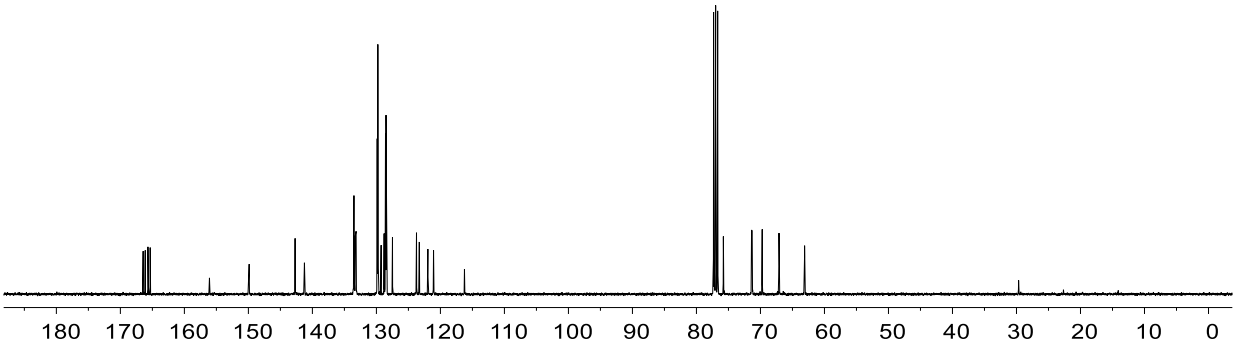
($CDCl_3$, 400 MHz)

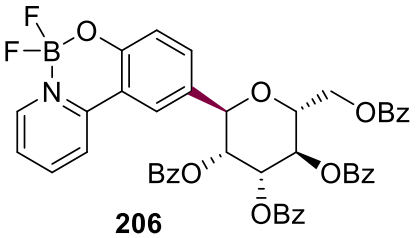




206

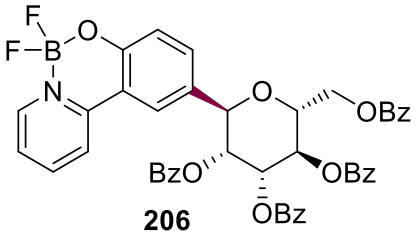
($CDCl_3$, 101 MHz)





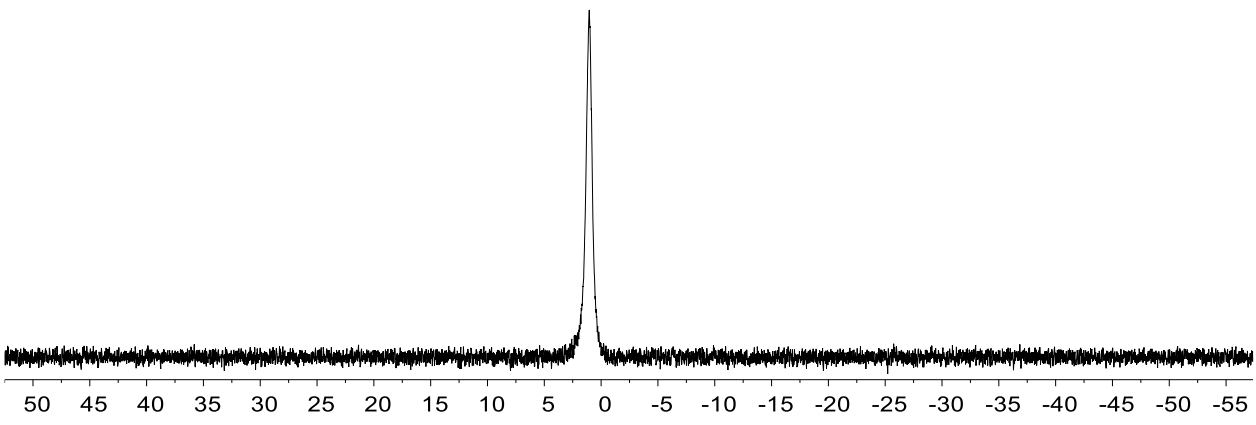
206

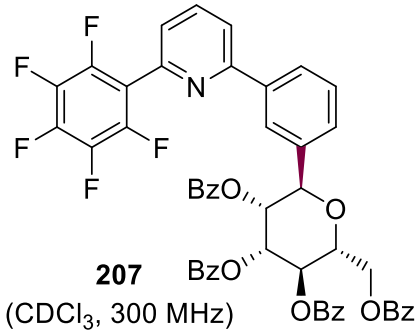
($CDCl_3$, 377 MHz)



206

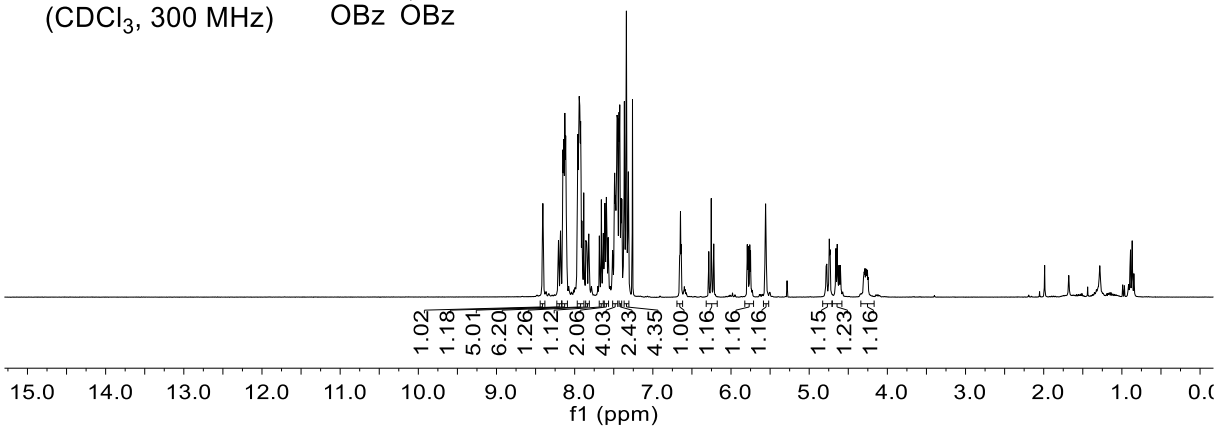
($CDCl_3$, 96 MHz)

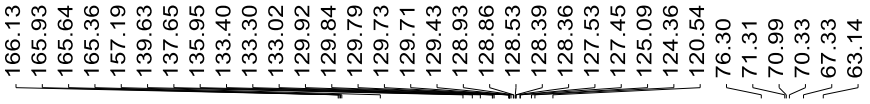


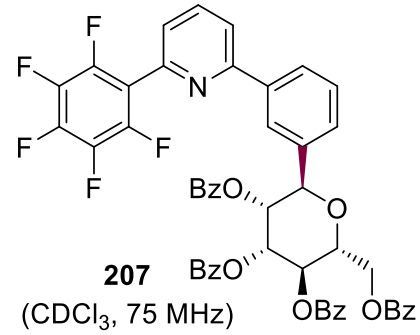


207

($CDCl_3$, 300 MHz)

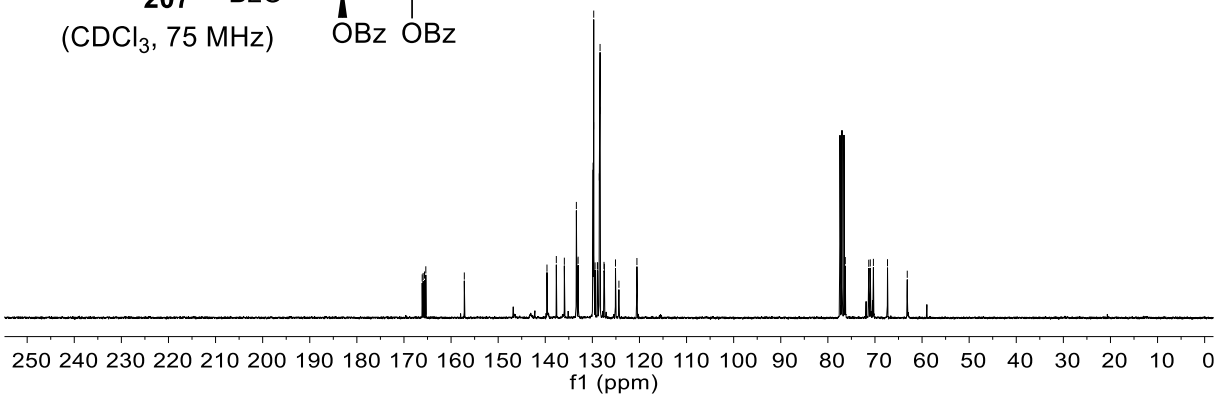


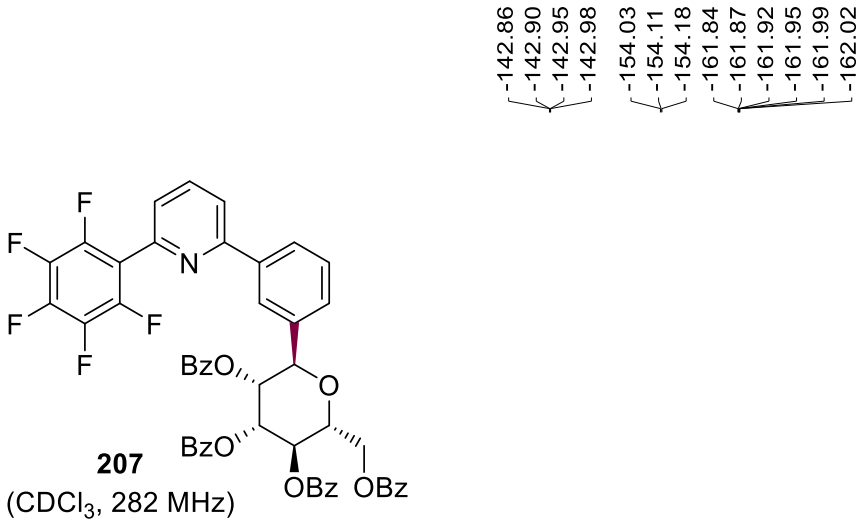




207

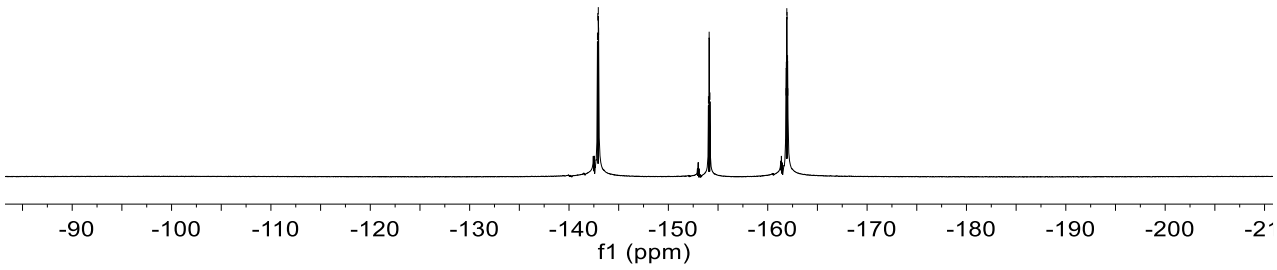
($CDCl_3$, 75 MHz)

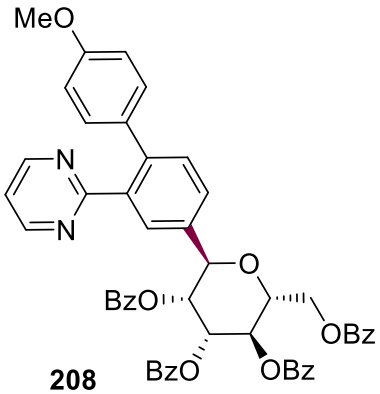




207

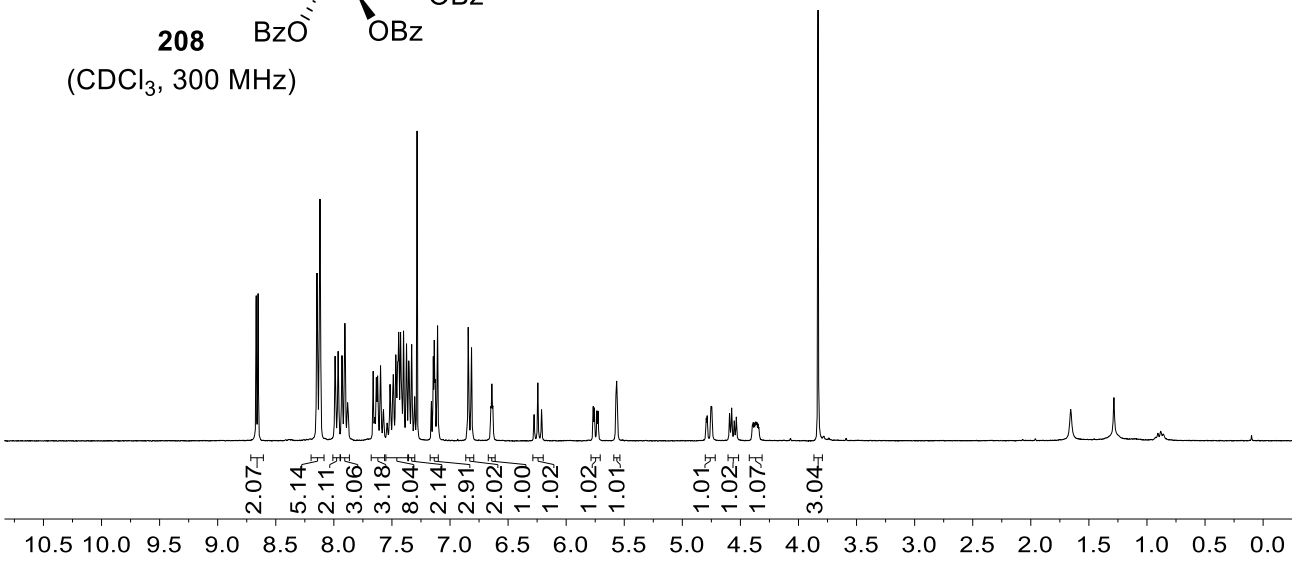
($CDCl_3$, 282 MHz)

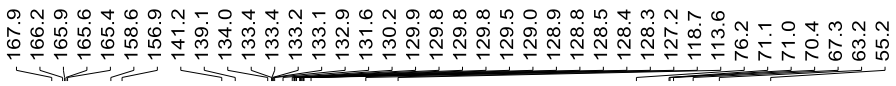


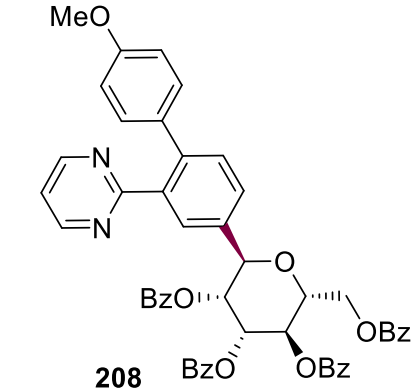


208

($CDCl_3$, 300 MHz)

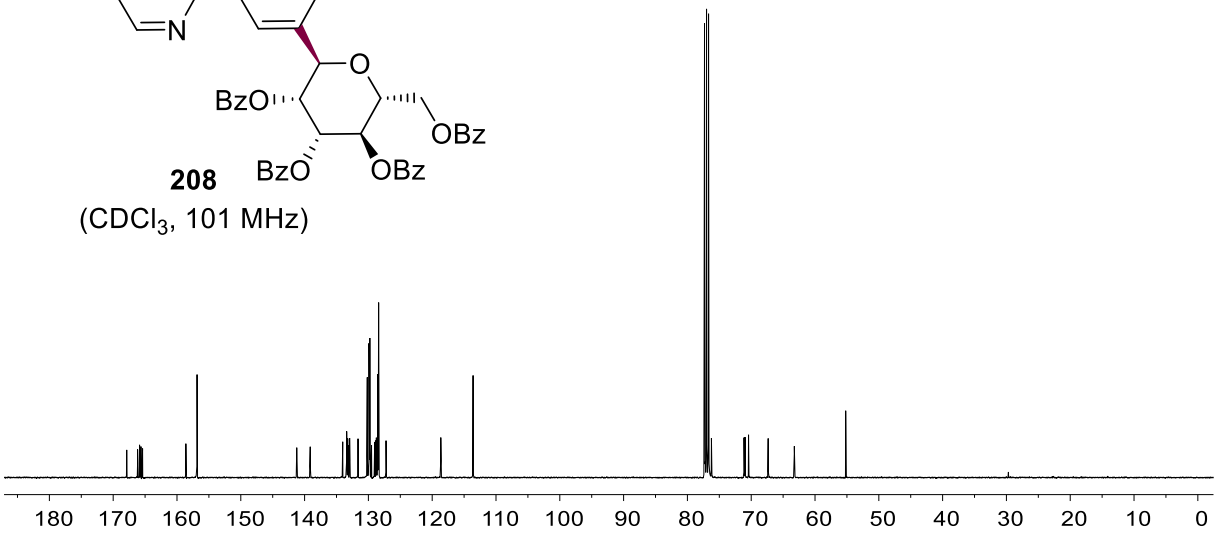


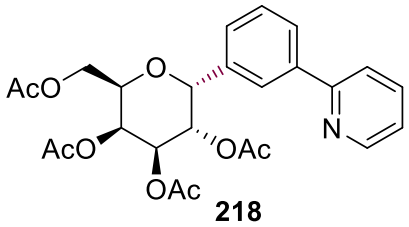




208

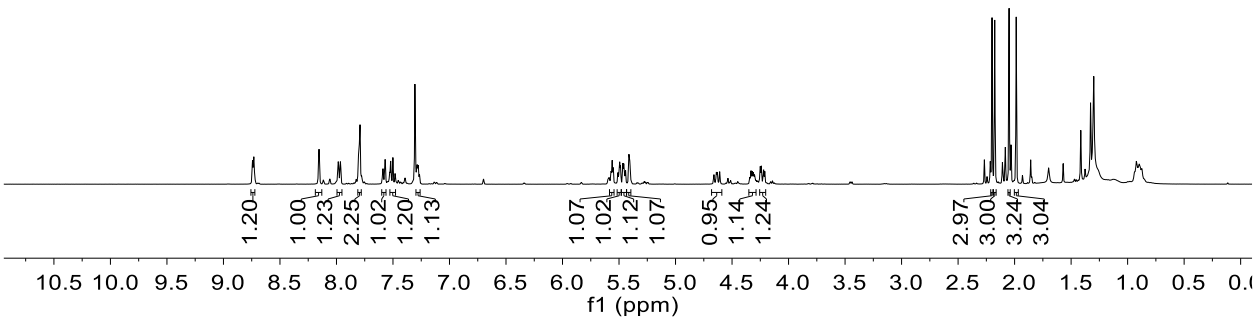
($CDCl_3$, 101 MHz)

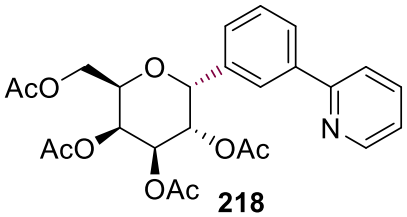




218

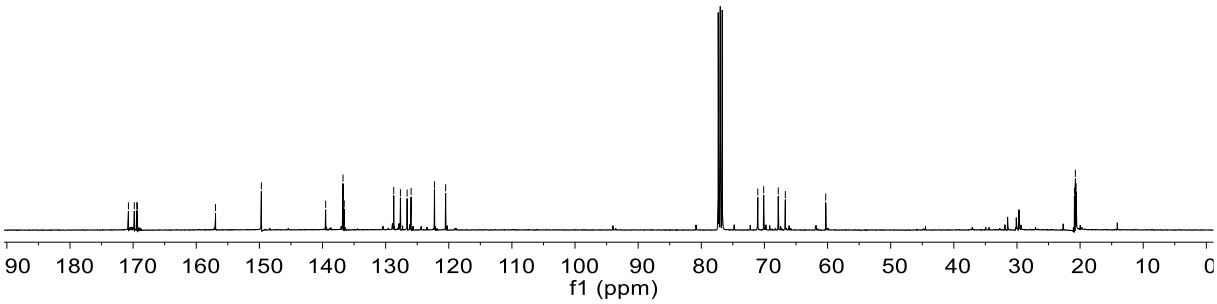
($CDCl_3$, 400 MHz)

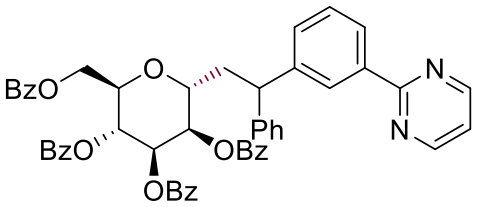




218

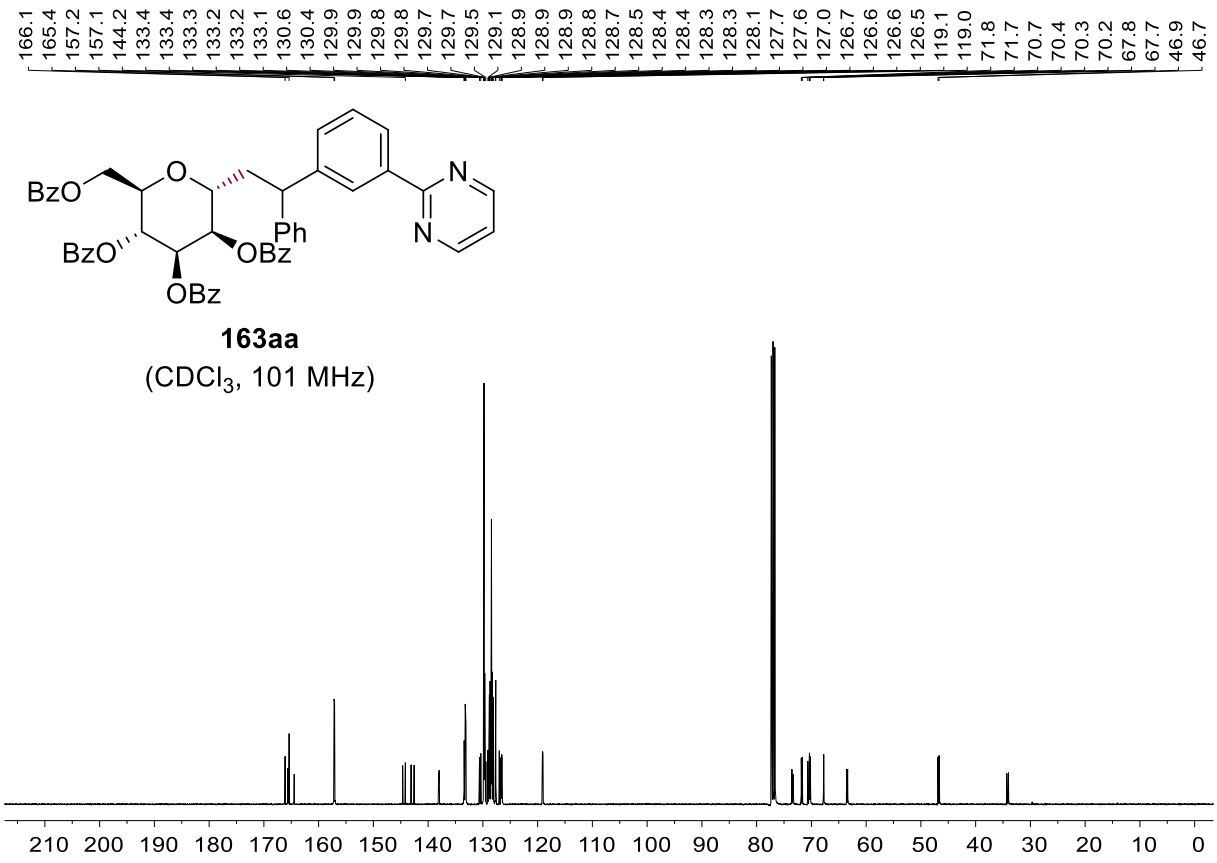
($CDCl_3$, 101 MHz)





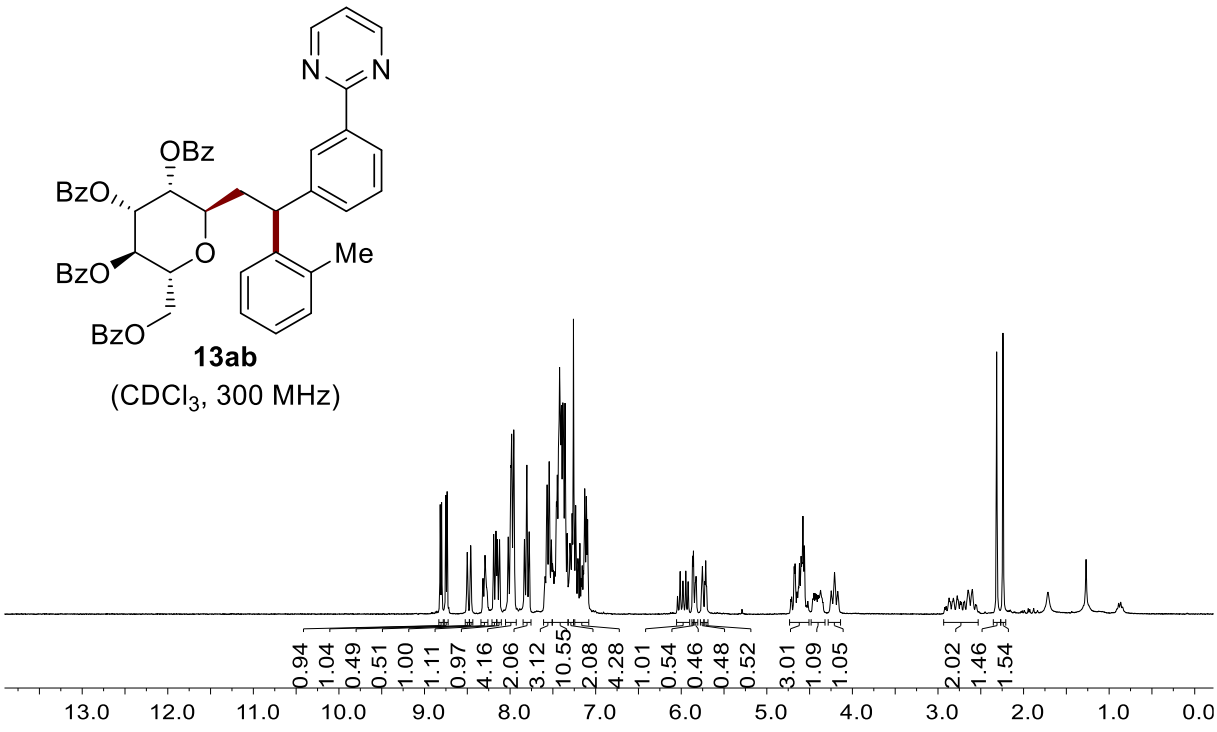
163aa

($CDCl_3$, 400 MHz)



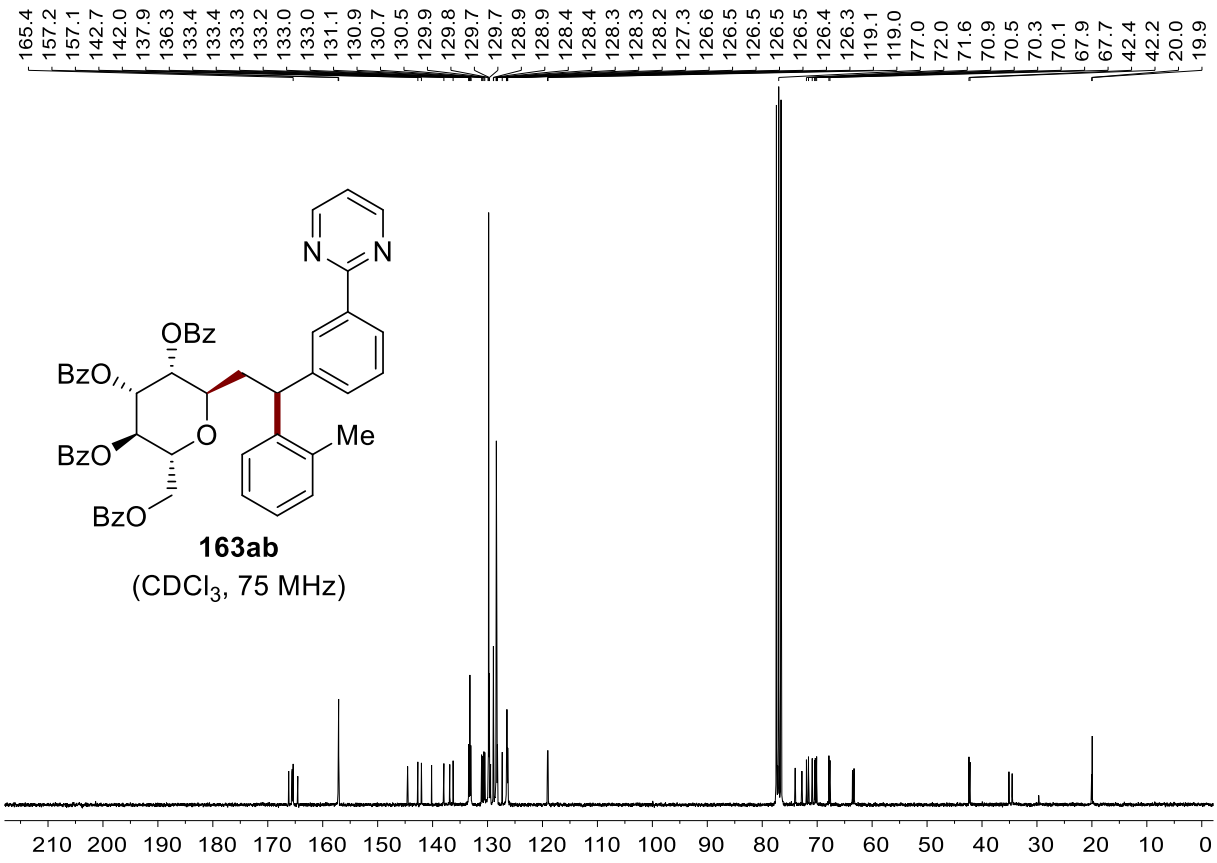
163aa

($CDCl_3$, 101 MHz)



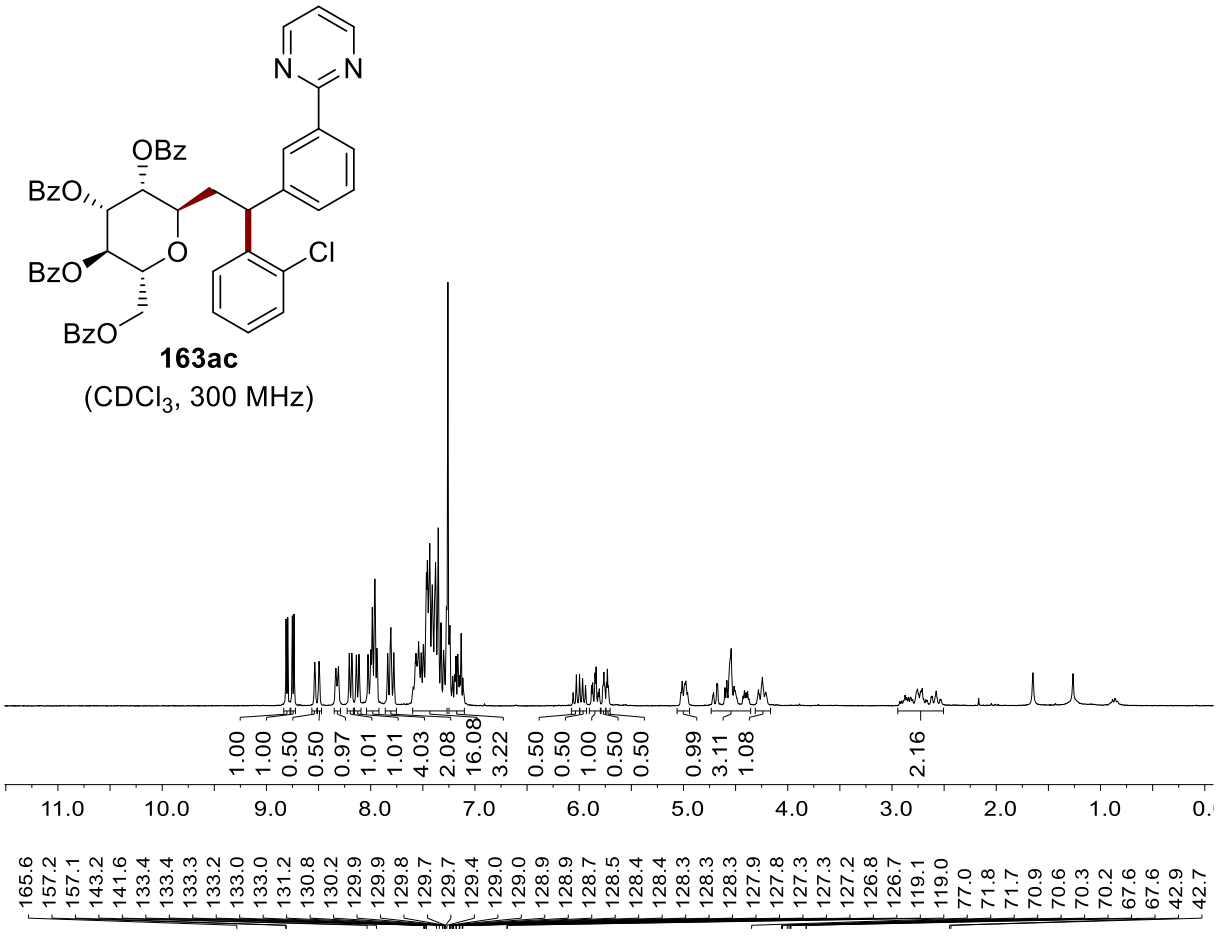
13ab

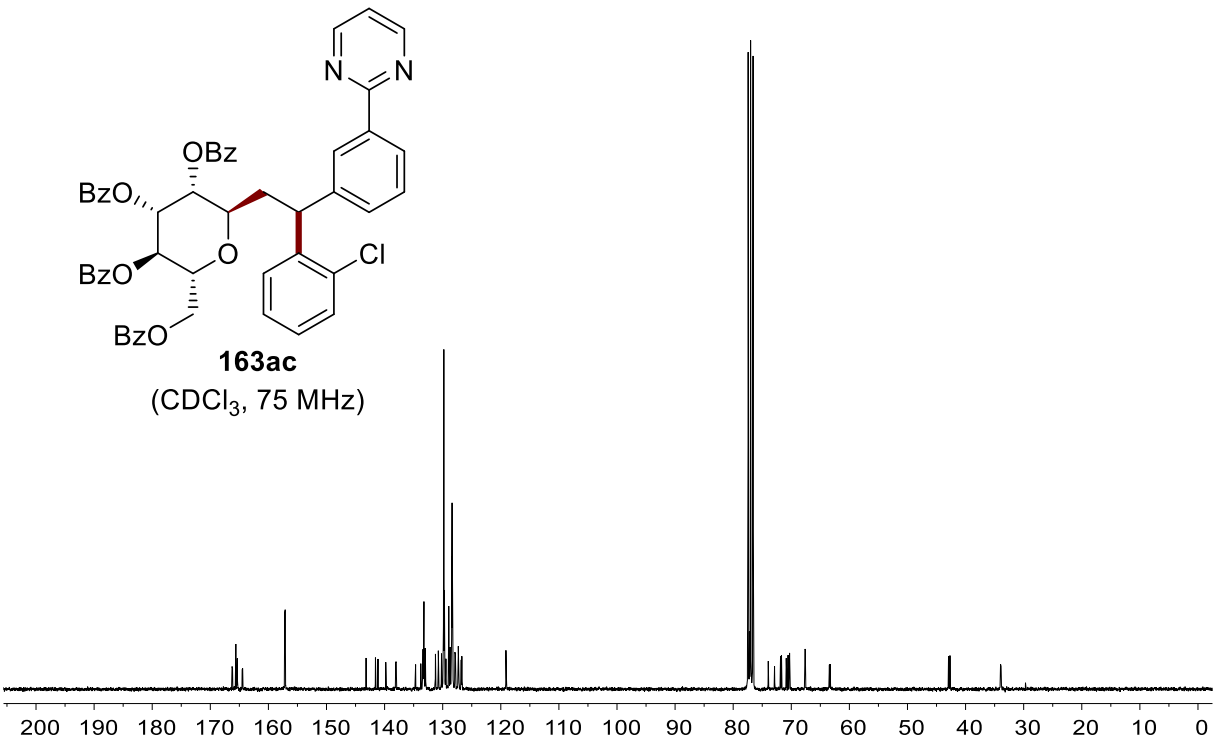
($CDCl_3$, 300 MHz)

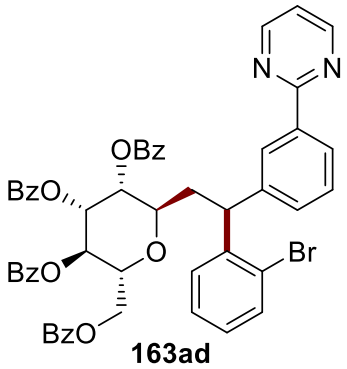


163ab

($CDCl_3$, 75 MHz)

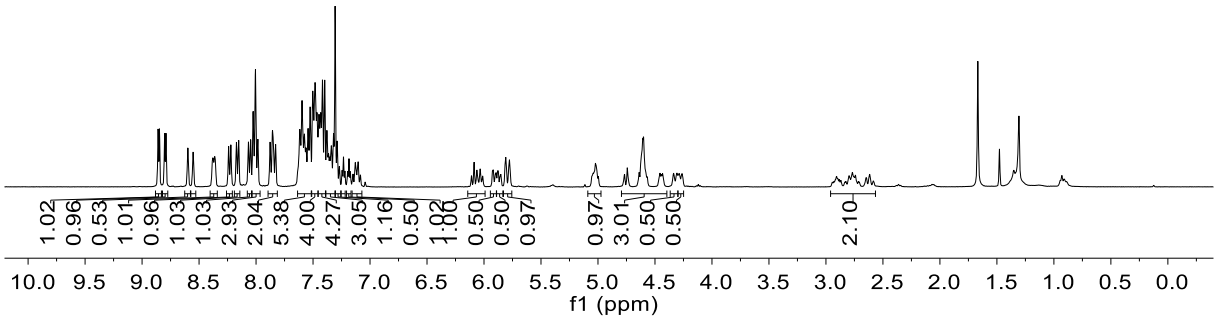

OBz
BzO
BzO
BzO
O
Cl
N
N
163ac
(CDCl3, 300 MHz)
1.00 1.00 0.50 0.50 0.97 1.01 1.01 4.03 2.08 16.08 3.22 0.50 0.50 1.00 0.50 0.50 0.99 3.11 1.08 2.16
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.

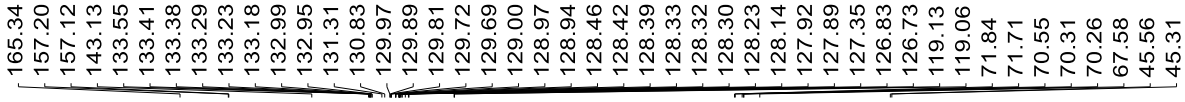

OBz
BzO
BzO
BzO
O
Cl
N
N
163ac
(CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

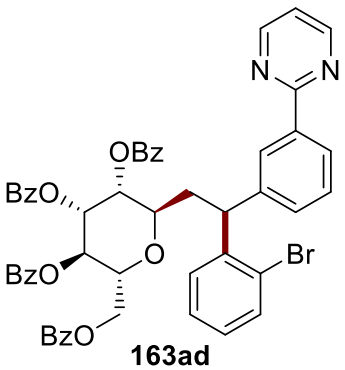


163ad

($CDCl_3$, 400 MHz)

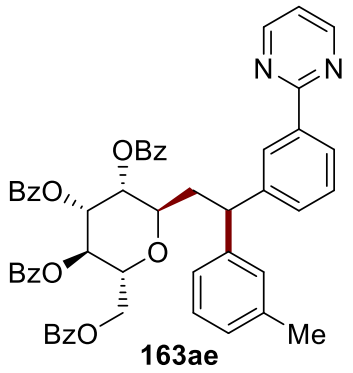






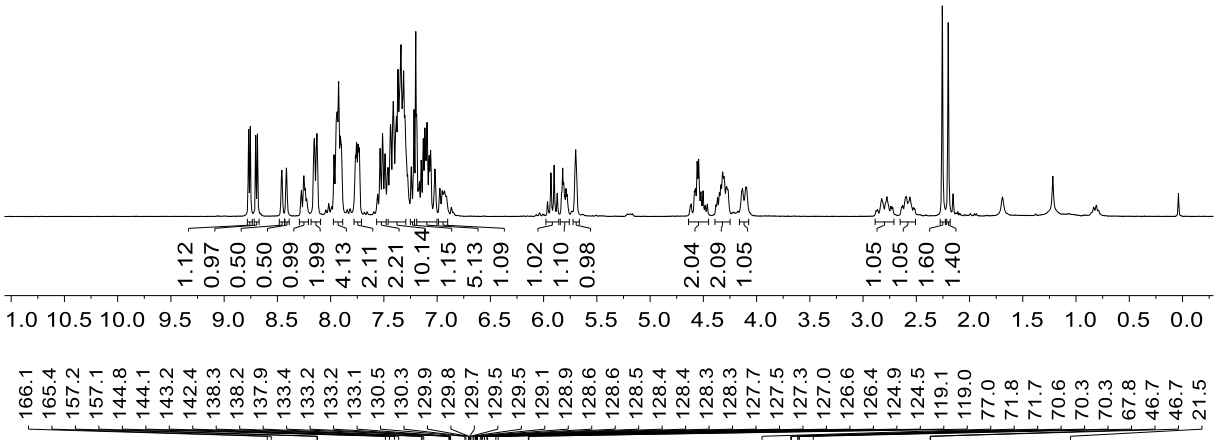
163ad

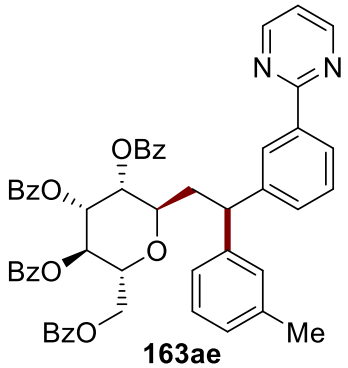
($CDCl_3$, 101 MHz)



163ae

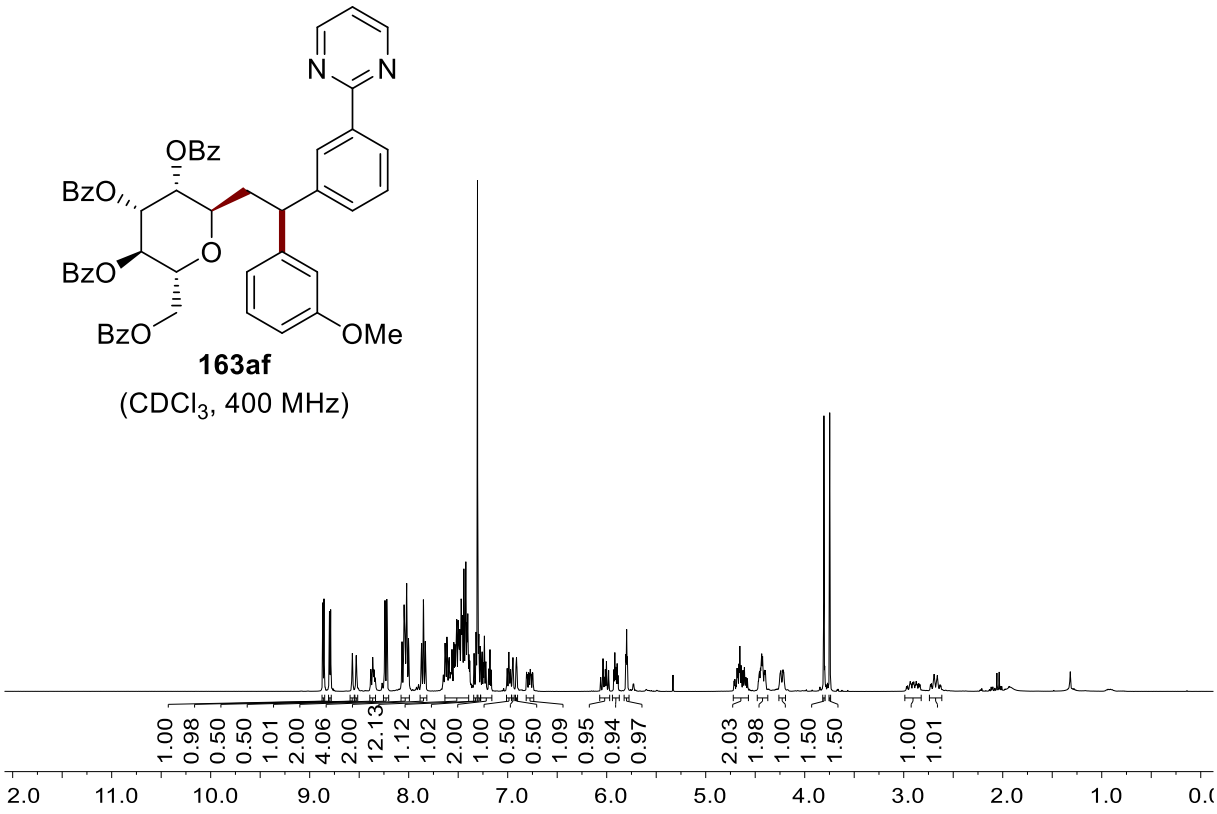
($CDCl_3$, 300 MHz)

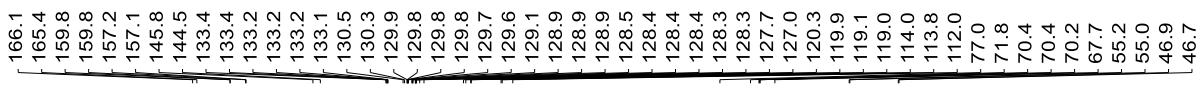


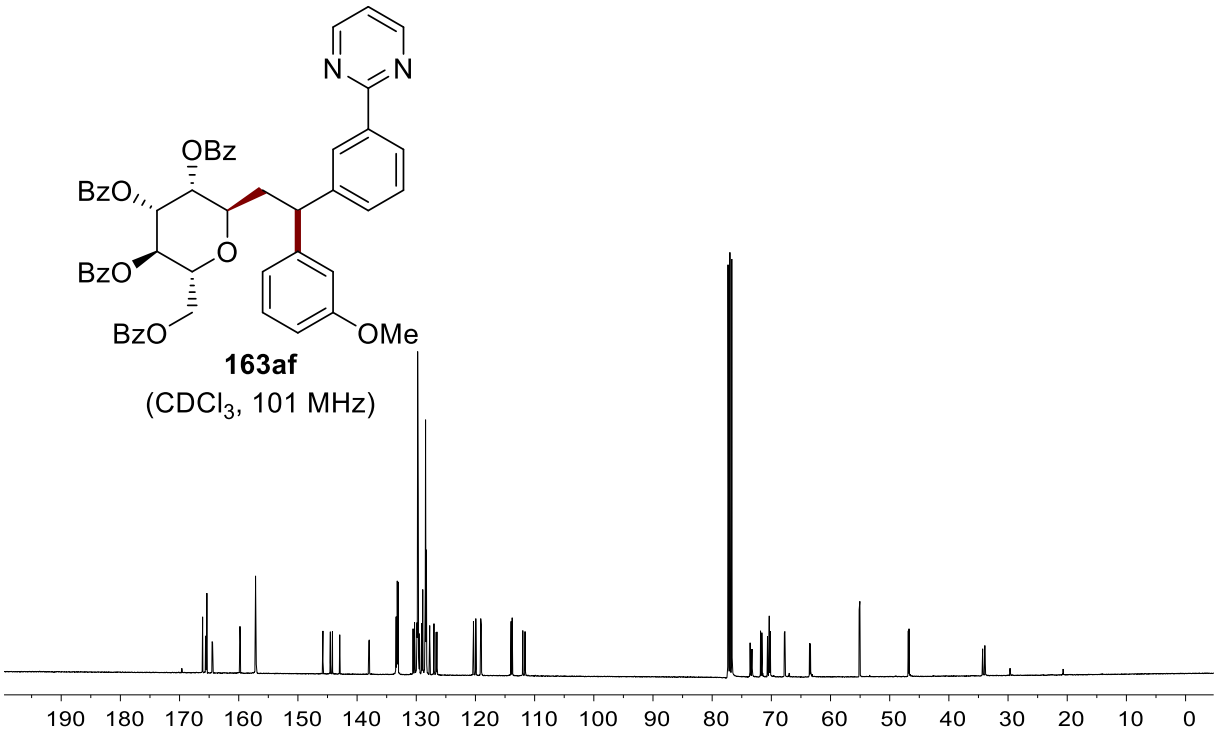


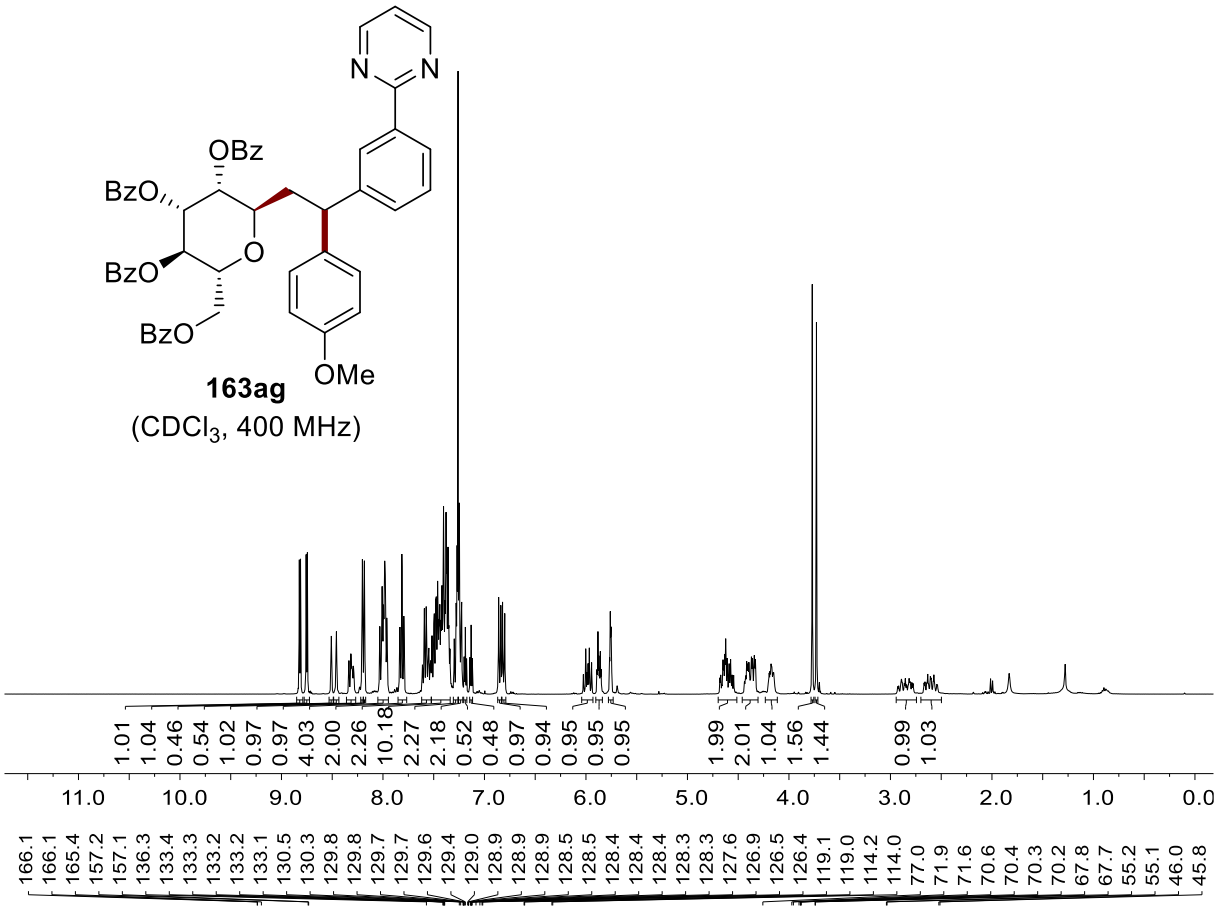
163ae

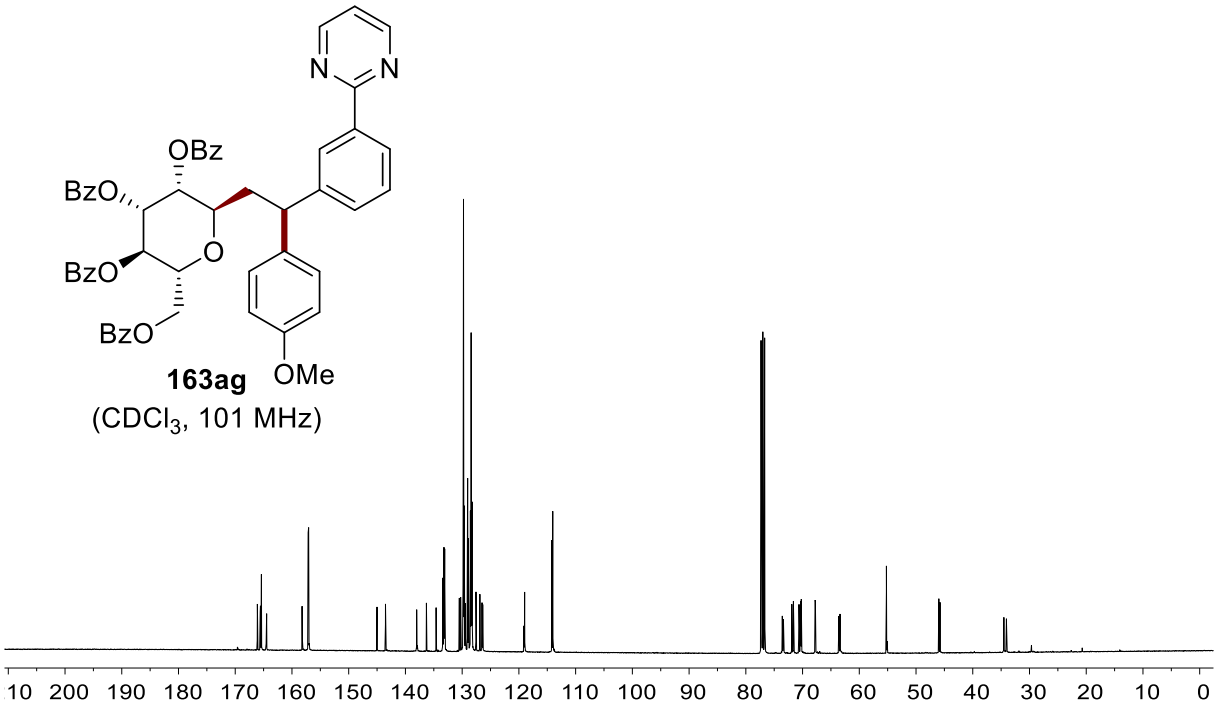
($CDCl_3$, 75 MHz)

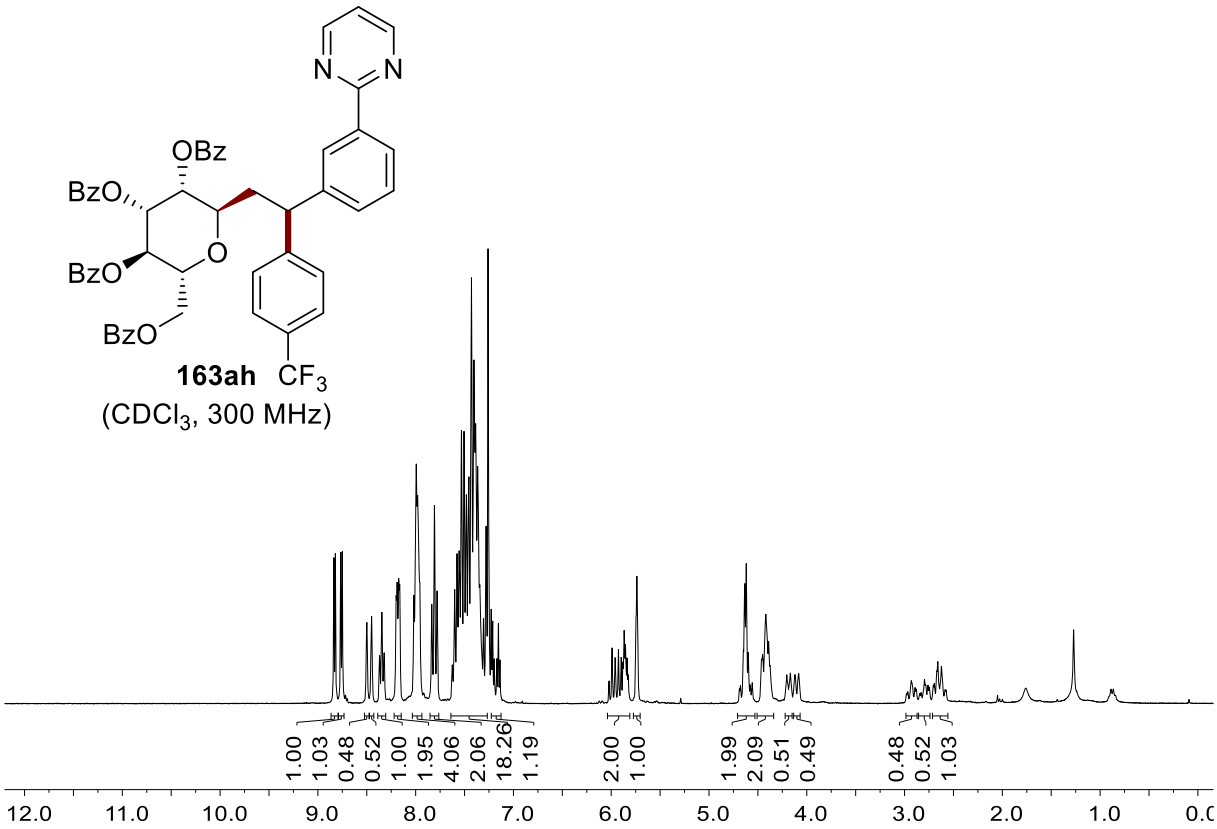

N
N
OBz
BzO
BzO
O
BzO
OMe
163af
(CDCl3, 400 MHz)
1.00 0.98 0.50 0.50 1.01 2.00 4.06 2.00 12.13 1.12 1.02 2.00 1.00 0.50 0.50 1.09 0.95 0.94 0.97 2.03 1.98 1.00 1.50 1.50 1.00 1.01
2.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

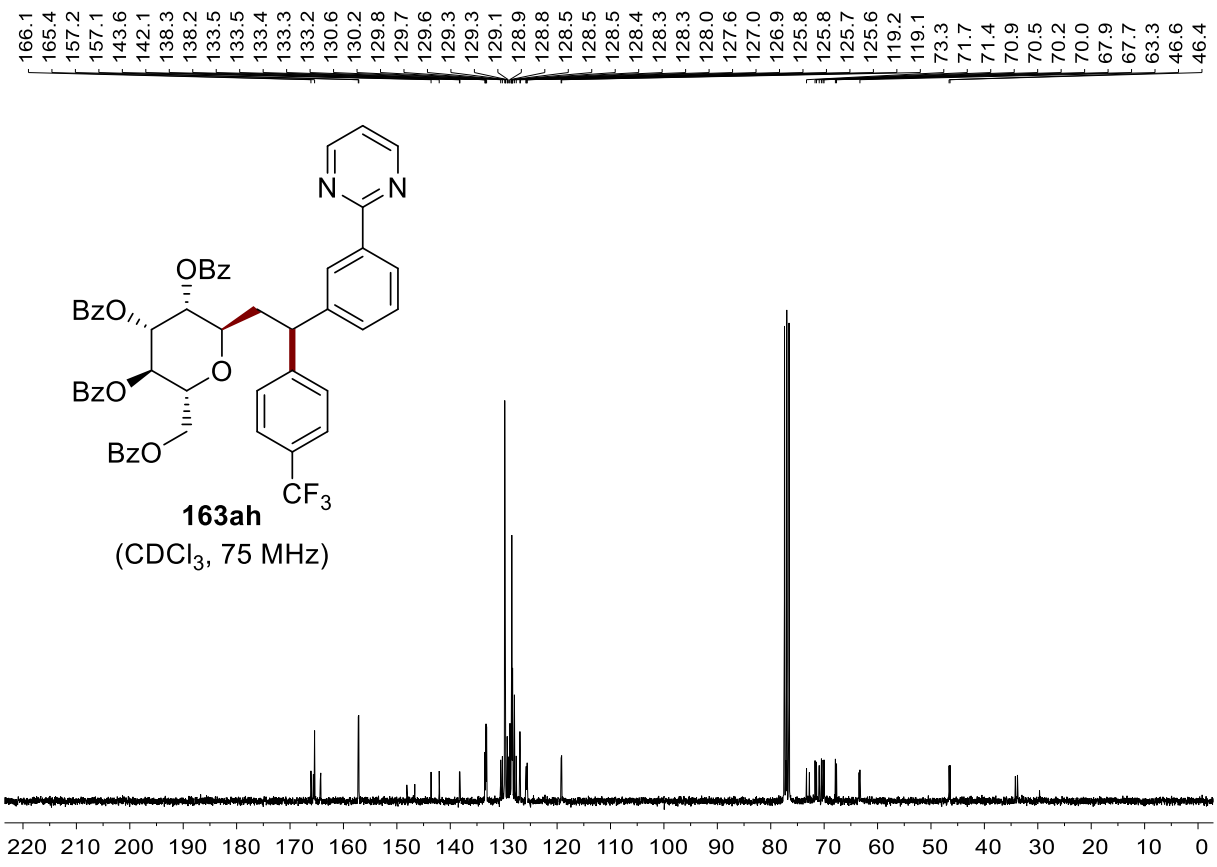

166.1 165.4 159.8 159.8 157.2 157.1 145.8 144.5 133.4 133.4 133.2 133.2 133.2 133.1 130.5 130.3 129.9 129.8 129.8 129.8 129.7 129.6 129.1 128.9 128.9 128.9 128.5 128.4 128.4 128.4 128.3 128.3 127.7 127.0 120.3 119.9 119.1 119.0 114.0 113.8 112.0 77.0 71.8 70.4 70.4 70.2 67.7 55.2 55.0 46.9 46.7

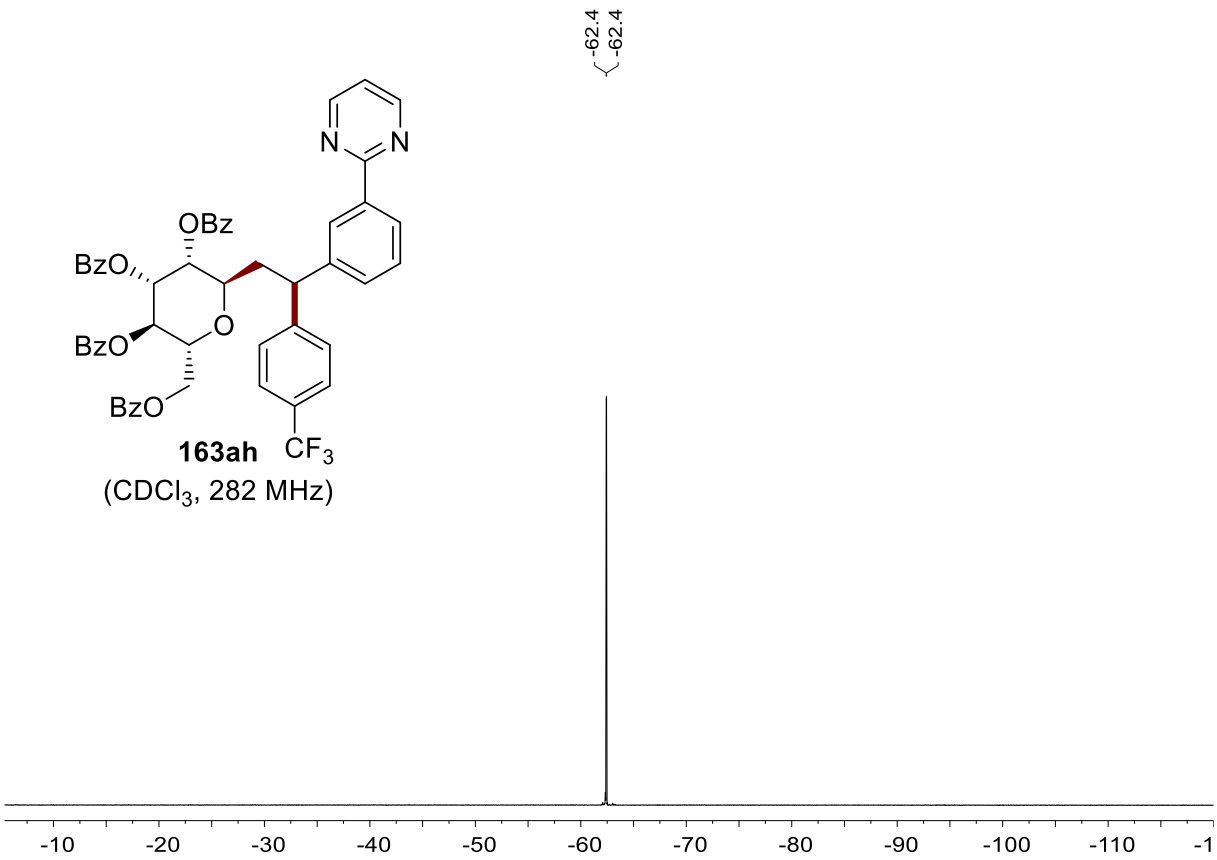

N
N
OBz
BzO
BzO
O
BzO
OMe
163af
(CDCl3, 101 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


OBz
BzO
BzO
BzO
O
N
N
OMe
163ag
(CDCl3, 400 MHz)
1.01 1.04 0.46 0.54 1.02 0.97 0.97 4.03 2.00 2.26 10.18 2.27 2.18 0.52 0.48 0.97 0.94 0.95 0.95 0.95 1.99 2.01 1.04 1.56 1.44 0.99 1.03
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
166.1 166.1 165.4 157.2 157.1 136.3 133.4 133.3 133.2 133.2 133.1 130.5 130.3 129.8 129.8 129.7 129.7 129.6 129.4 129.0 128.9 128.9 128.9 128.5 128.5 128.4 128.4 128.4 128.3 128.3 127.6 126.9 126.5 126.4 119.1 119.0 114.2 114.0 77.0 71.9 71.6 70.6 70.4 70.3 70.2 67.8 67.7 55.2 55.1 46.0 45.8

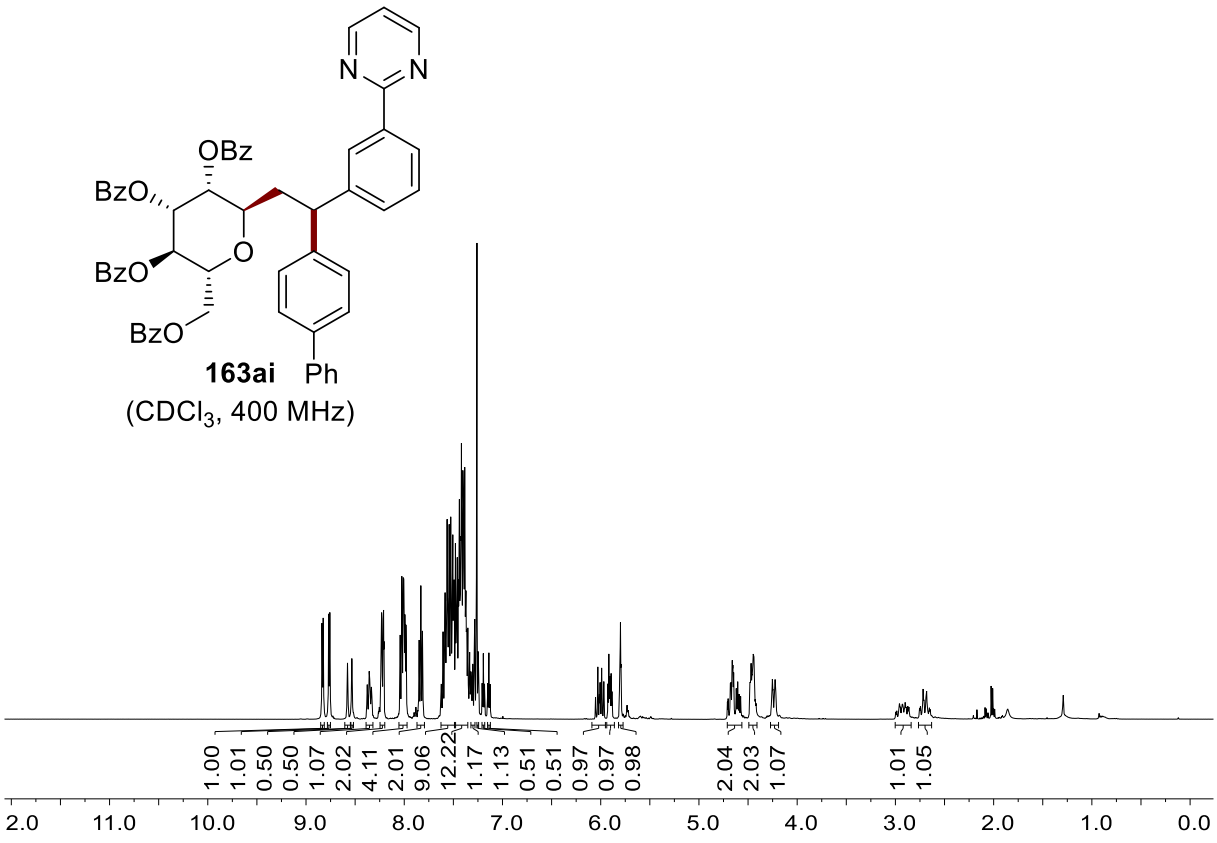

OBz
BzO
BzO
BzO
O
N
N
OMe
163ag
(CDCl3, 101 MHz)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


OBz
BzO
BzO
BzO
CF3
163ah
(CDCl3, 300 MHz)
1.00 1.03 0.48 0.52 1.00 1.95 4.06 2.06 18.26 1.19 2.00 1.00 1.99 2.09 0.51 0.49 0.48 0.52 1.03
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

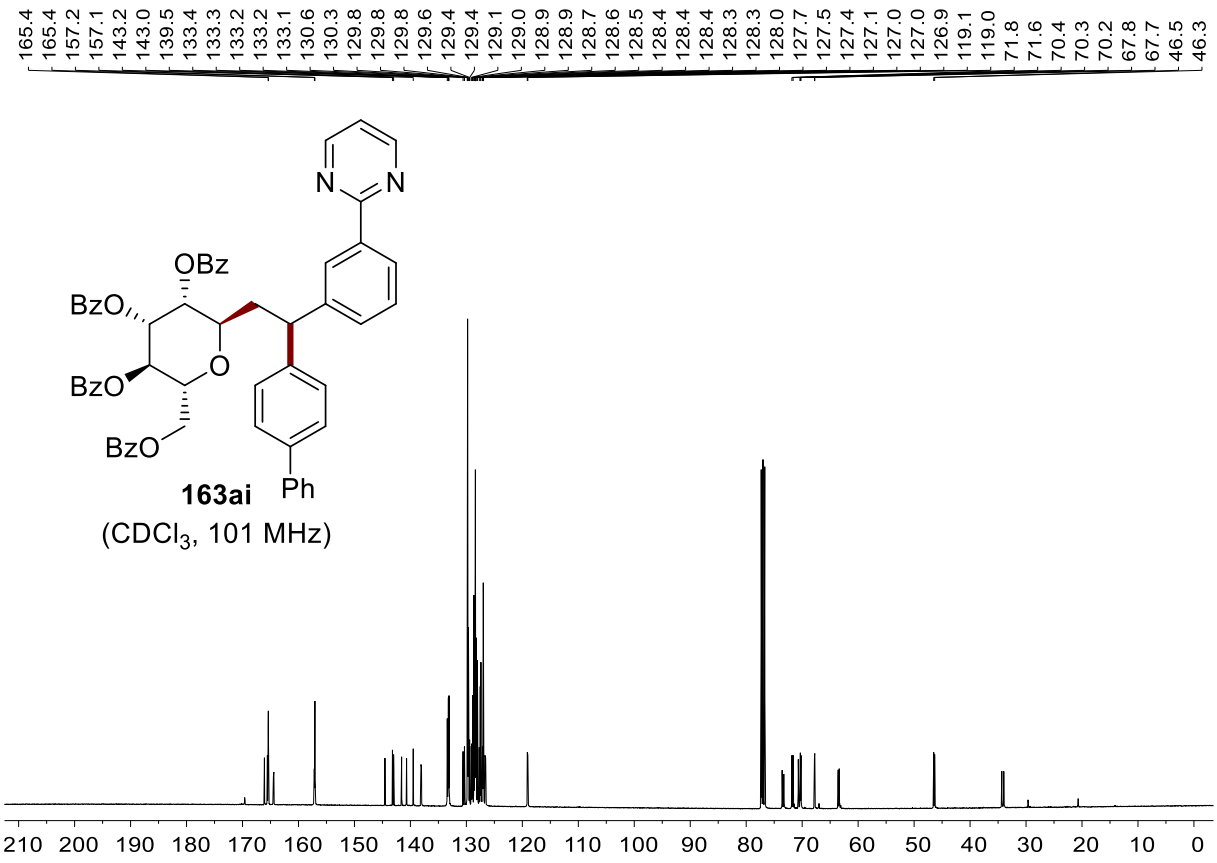

166.1 165.4 157.2 157.1 143.6 142.1 138.3 138.2 133.5 133.5 133.4 133.3 133.2 130.6 130.2 129.8 129.7 129.6 129.3 129.3 129.1 128.9 128.8 128.5 128.5 128.5 128.4 128.3 128.3 128.0 127.6 127.0 126.9 125.8 125.8 125.7 125.6 119.2 119.1 73.3 71.7 71.4 70.9 70.5 70.2 70.0 67.9 67.7 63.3 46.6 46.4
OBz
BzO
BzO
BzO
CF3
163ah
(CDCl3, 75 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

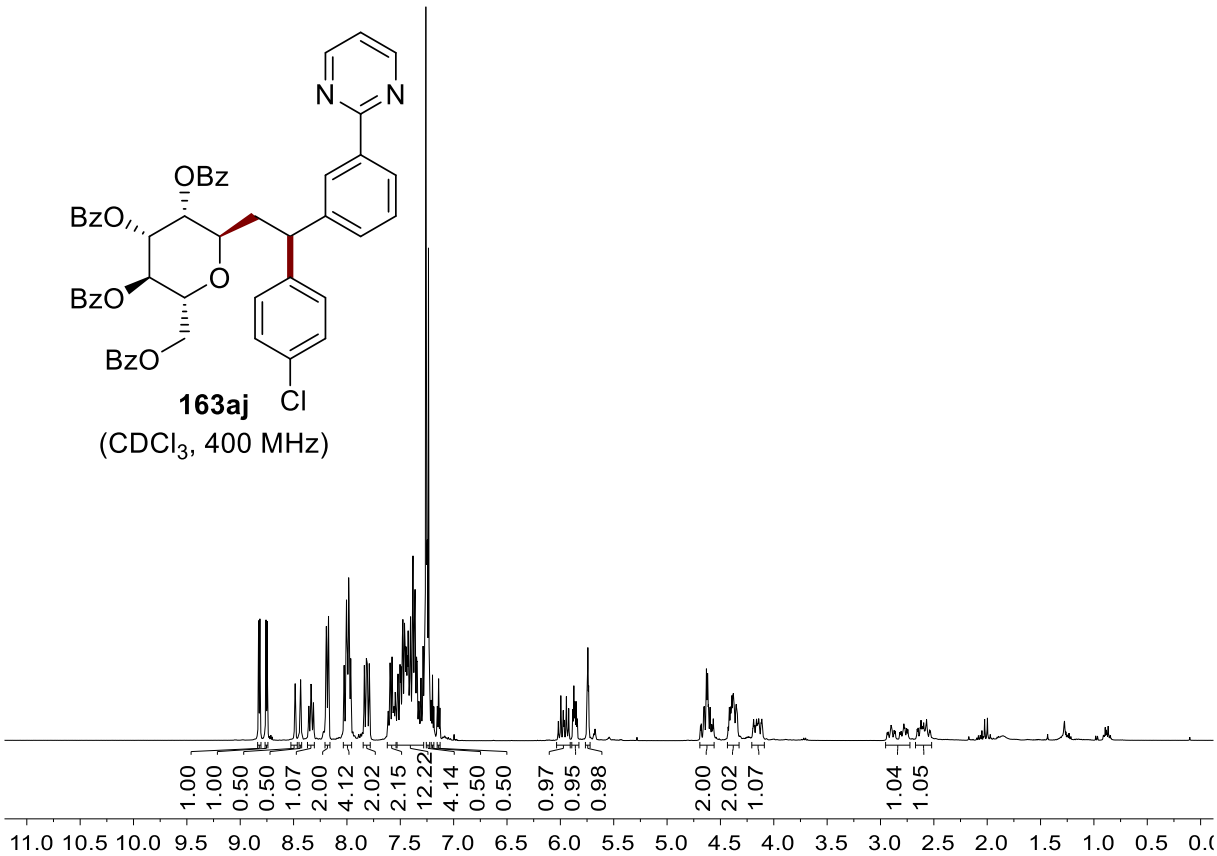


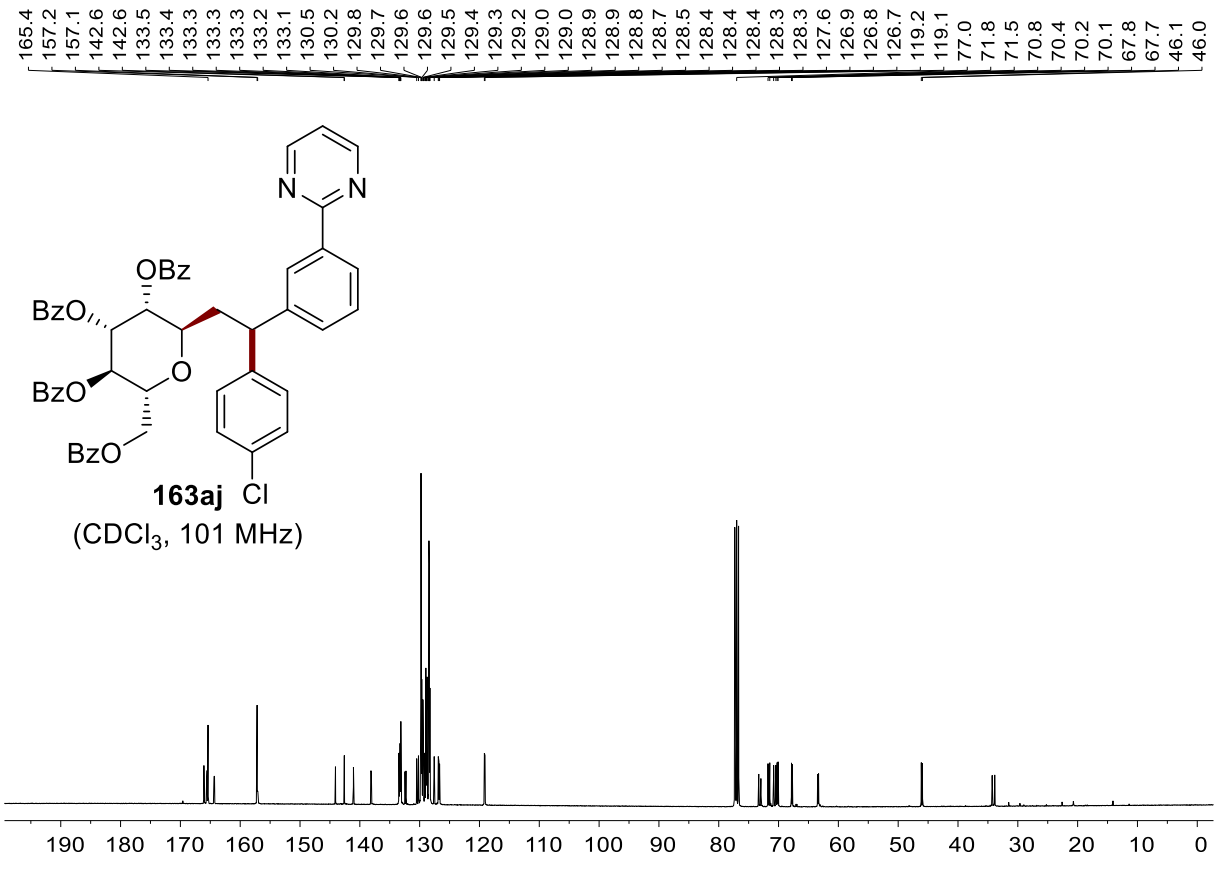
163ah
($CDCl_3$, 282 MHz)

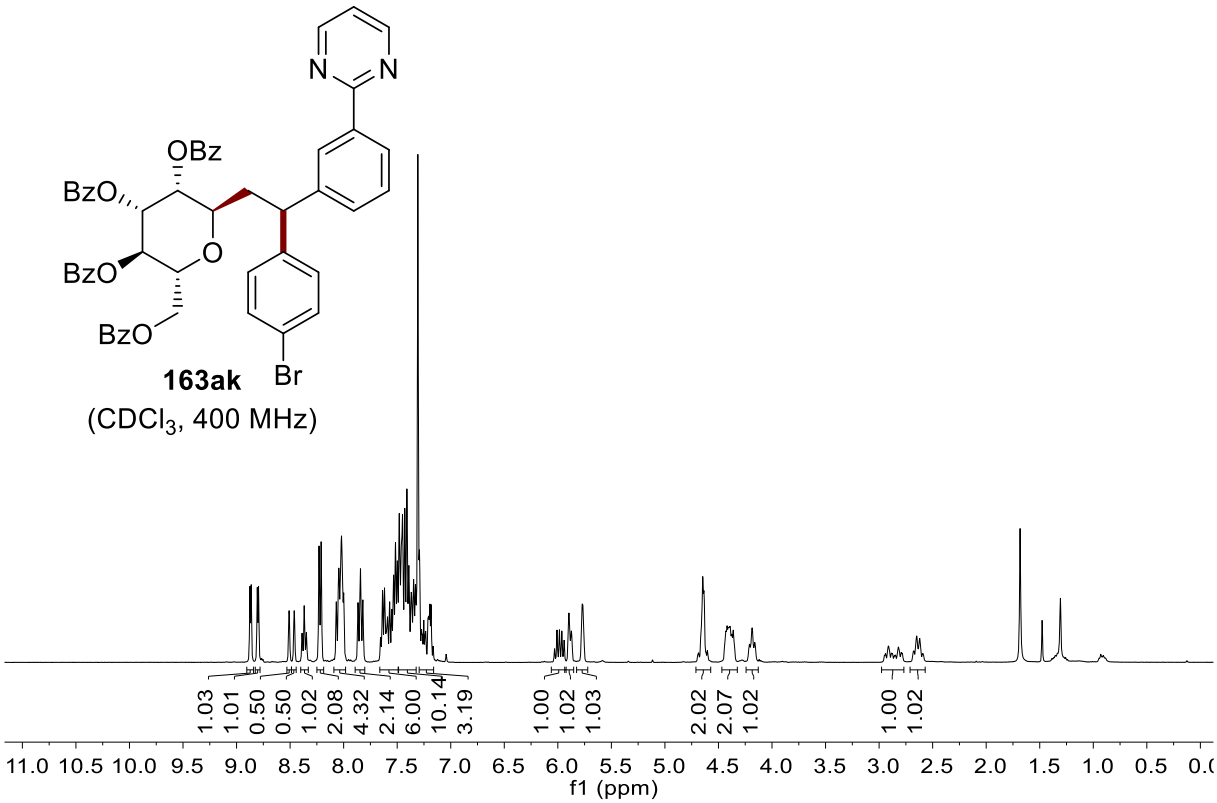


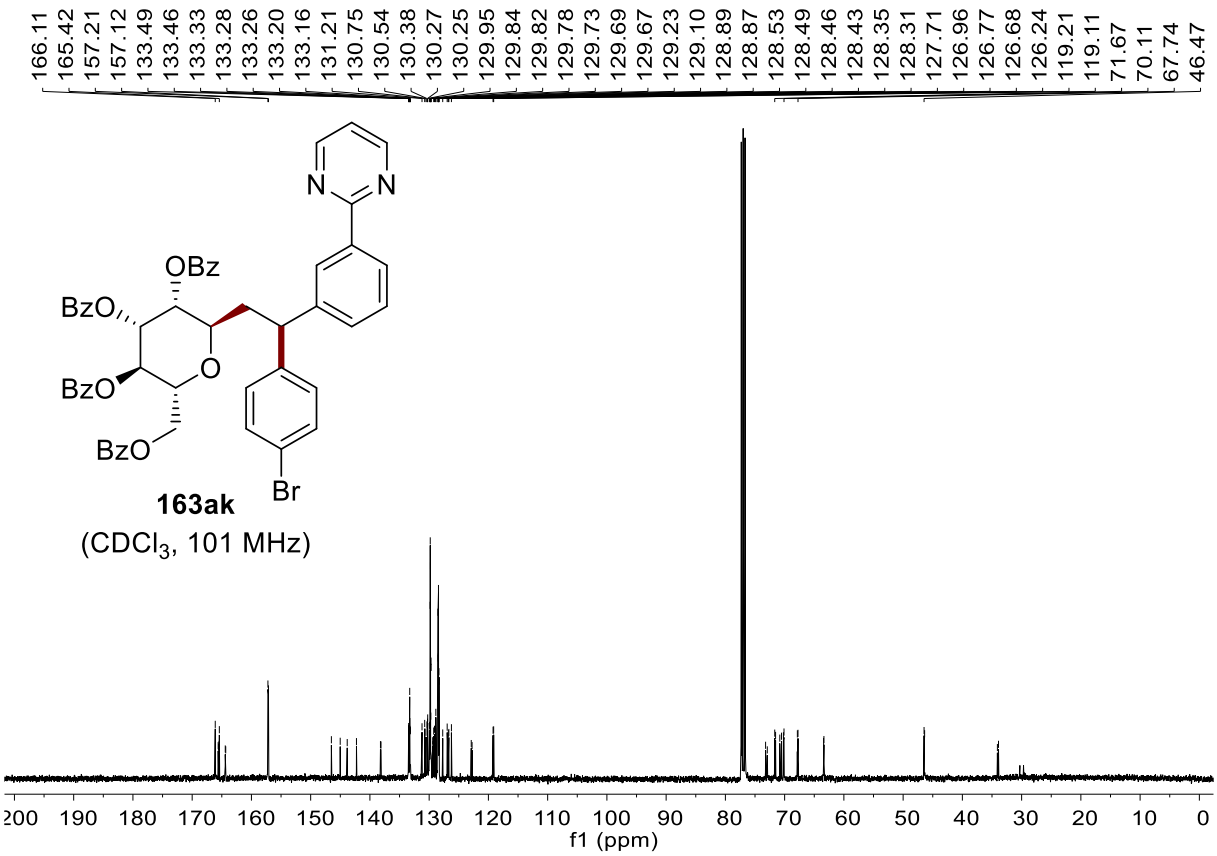
163ai
($CDCl_3$, 400 MHz)

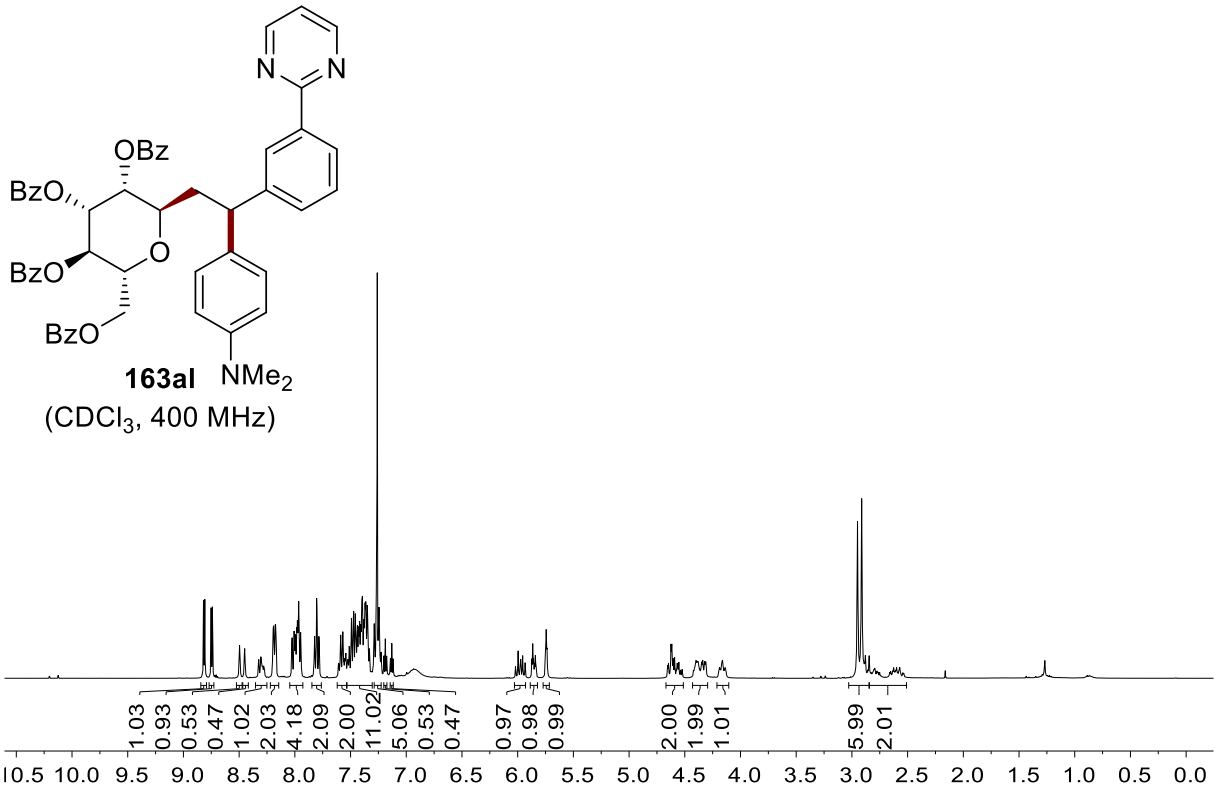

165.4
165.4
157.2
157.1
143.2
143.0
139.5
133.4
133.3
133.2
133.2
133.1
130.6
130.3
129.8
129.8
129.8
129.6
129.4
129.4
129.1
129.0
128.9
128.9
128.7
128.6
128.5
128.4
128.4
128.4
128.3
128.3
128.0
127.7
127.5
127.4
127.1
127.0
127.0
126.9
119.1
119.0
71.8
71.6
70.4
70.3
70.2
67.8
67.7
46.5
46.3
N
N
OBz
BzO
BzO
O
BzO
Ph
163ai
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

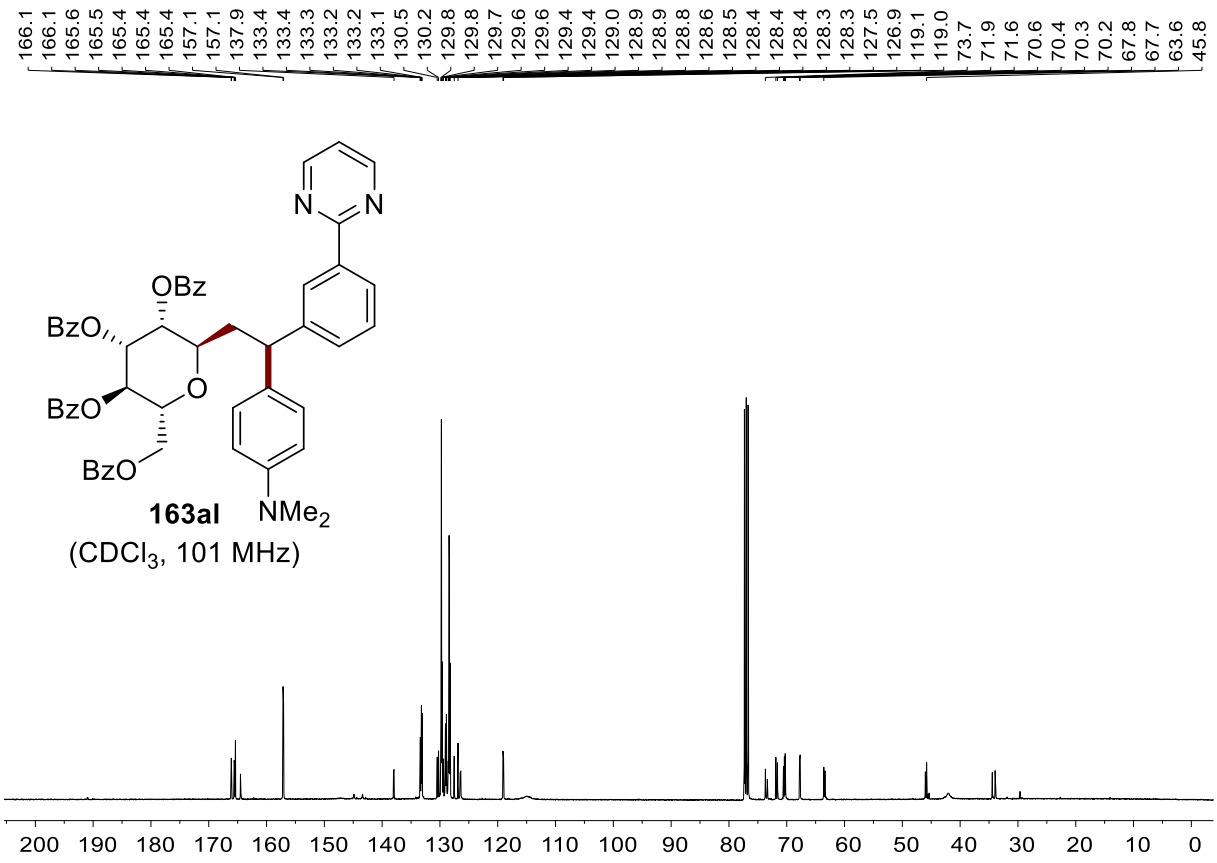

N
N
OBz
BzO
BzO
O
BzO
Cl
163aj
(CDCl3, 400 MHz)
1.00
1.00
0.50
0.50
1.07
2.00
4.12
2.02
2.15
12.22
4.14
0.50
0.50
0.97
0.95
0.98
2.00
2.02
1.07
1.04
1.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

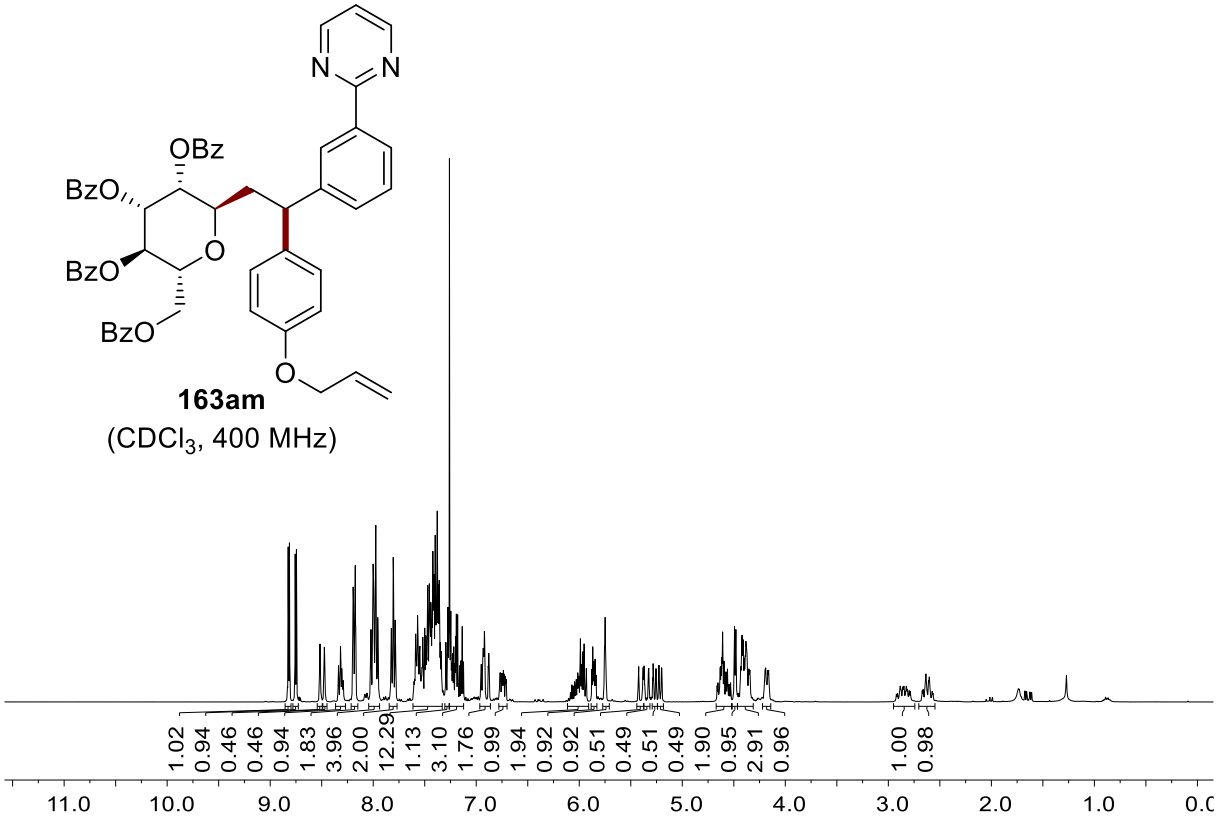

165.4
157.2
157.1
142.6
142.6
133.5
133.4
133.3
133.3
133.3
133.2
133.1
130.5
130.2
129.8
129.7
129.6
129.6
129.5
129.4
129.3
129.2
129.0
129.0
128.9
128.9
128.8
128.7
128.5
128.4
128.4
128.4
128.3
128.3
127.6
126.9
126.8
126.7
119.2
119.1
77.0
71.8
71.5
70.8
70.4
70.2
70.1
67.8
67.7
46.1
46.0
OBz
BzO
BzO
BzO
O
N
N
Cl
163aj
(CDCl3, 101 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

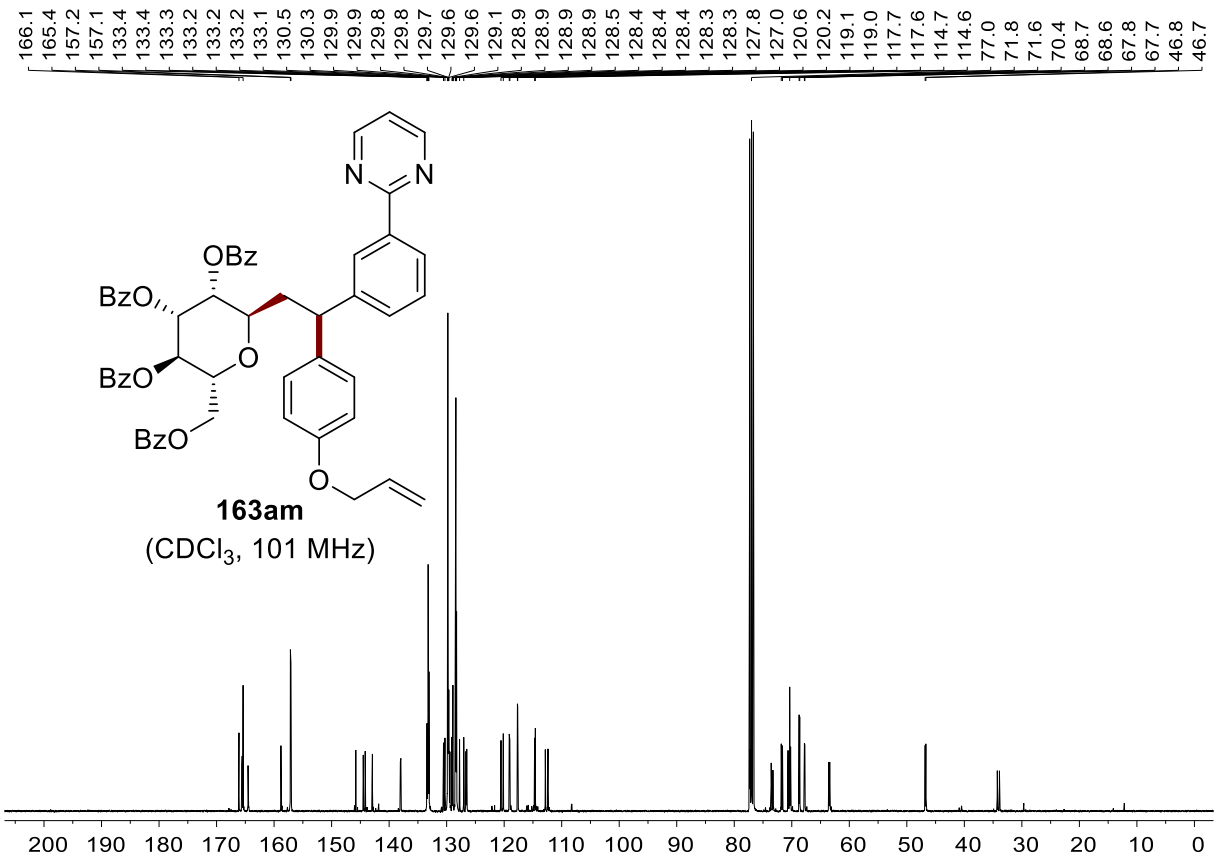

OBz
BzO
BzO
BzO
O
N
N
Br
163ak
(CDCl3, 400 MHz)
1.03
1.01
0.50
0.50
1.02
2.08
4.32
2.14
6.00
10.14
3.19
1.00
1.02
1.03
2.02
2.07
1.02
1.00
1.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

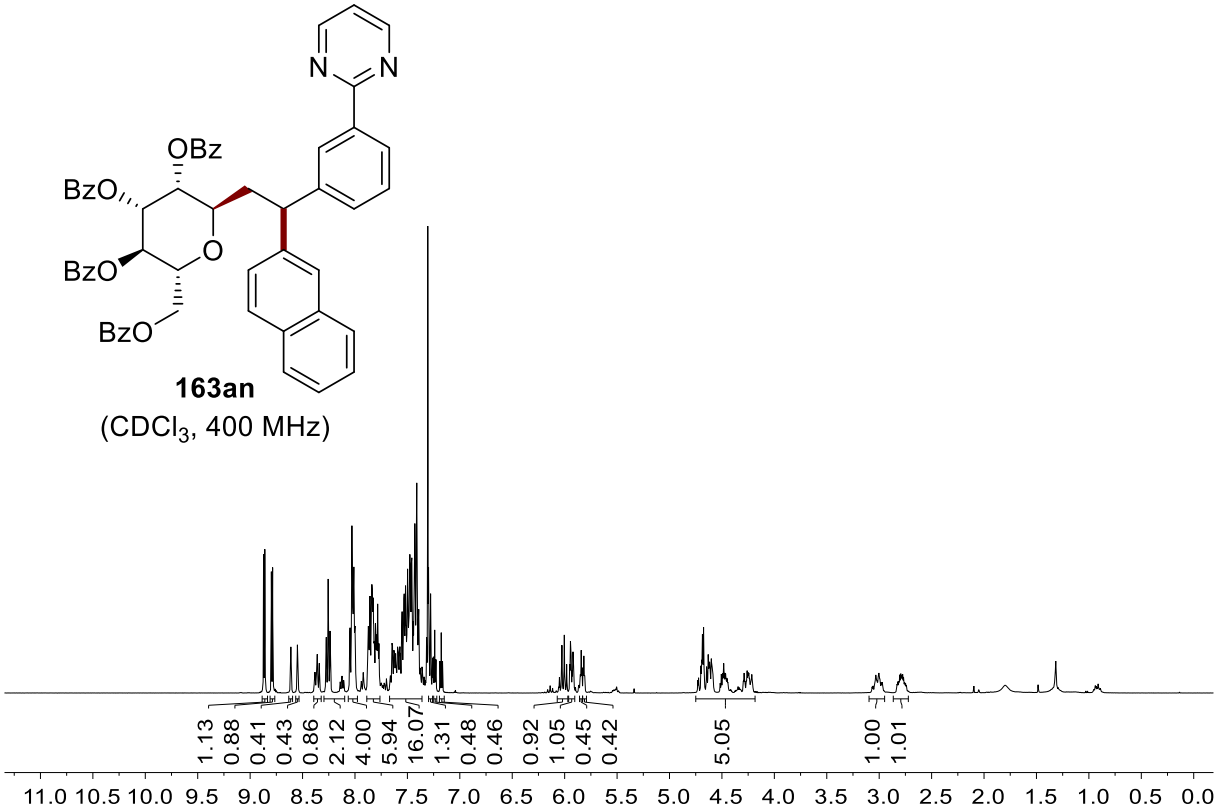

166.11
165.42
157.21
157.12
133.49
133.46
133.33
133.28
133.26
133.20
133.16
131.21
130.75
130.54
130.38
130.27
130.25
129.95
129.84
129.82
129.78
129.73
129.69
129.67
129.23
129.10
128.89
128.87
128.53
128.49
128.46
128.43
128.35
128.31
127.71
126.96
126.77
126.68
126.24
119.21
119.11
71.67
70.11
67.74
46.47
OBz
BzO
BzO
BzO
O
N
N
Br
163ak
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

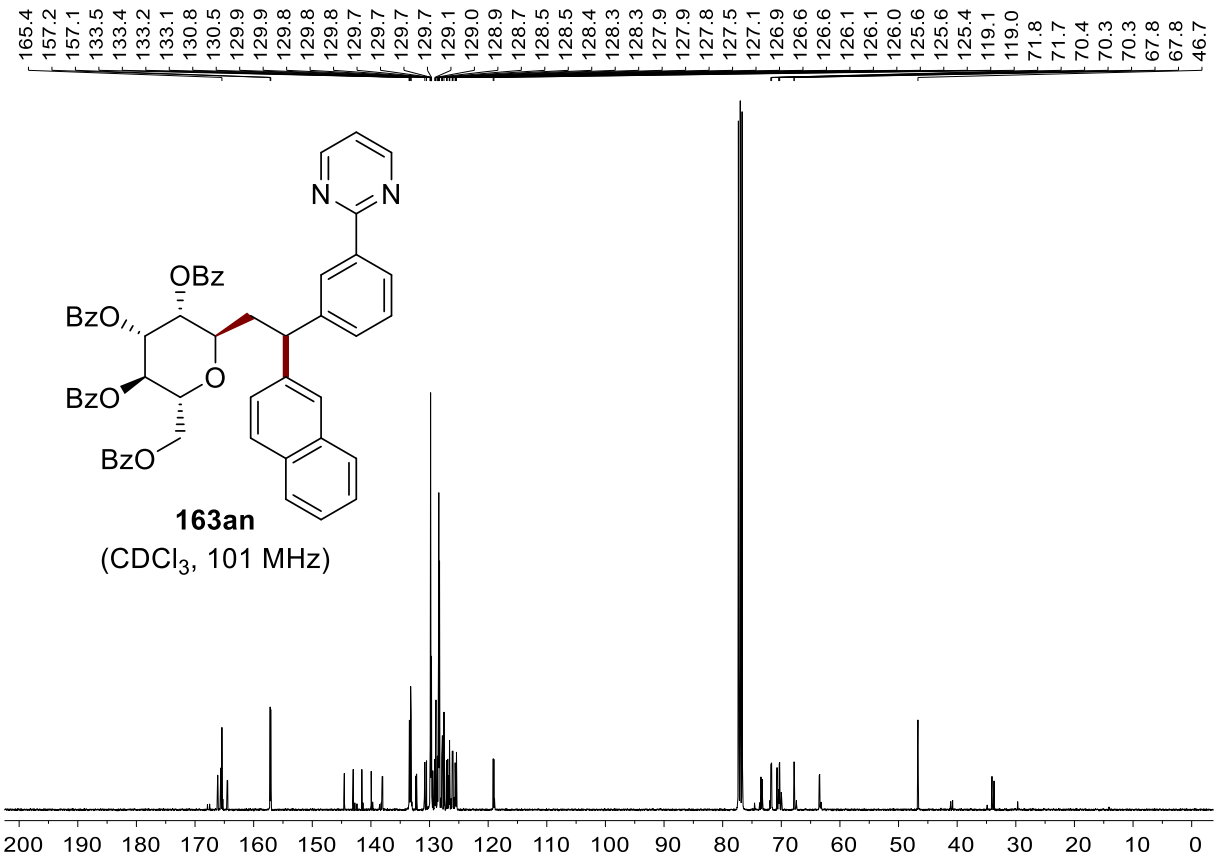

OBz
BzO
BzO
BzO
O
N
N
NMe2
163al
(CDCl3, 400 MHz)
1.03
0.93
0.53
0.47
1.02
2.03
4.18
2.09
2.00
11.02
5.06
0.53
0.47
0.97
0.98
0.99
2.00
1.99
1.01
5.99
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

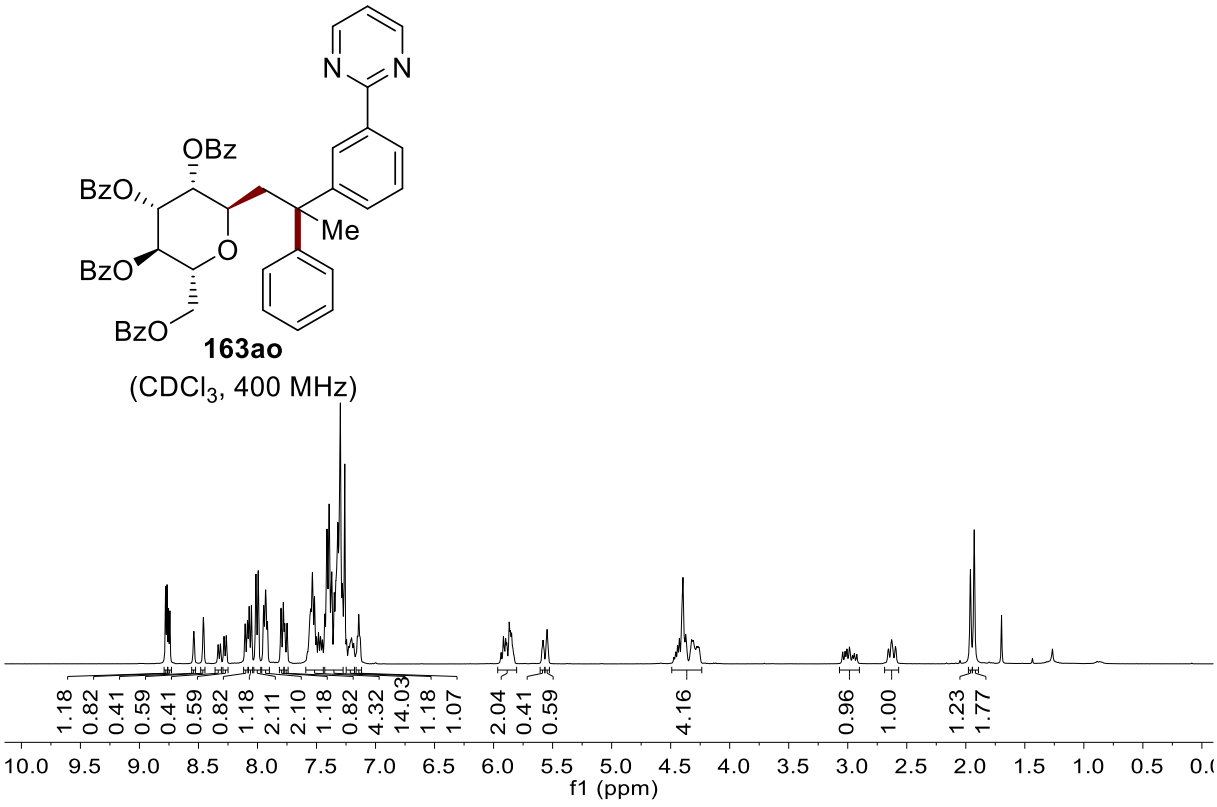

166.1 166.1 165.6 165.5 165.4 165.4 165.4 165.4 157.1 157.1 137.9 133.4 133.4 133.3 133.2 133.2 133.1 130.5 130.2 129.8 129.8 129.7 129.6 129.6 129.4 129.4 129.0 128.9 128.9 128.8 128.6 128.5 128.4 128.4 128.4 128.3 128.3 127.5 126.9 119.1 119.0 73.7 71.9 71.6 70.6 70.4 70.3 70.2 67.8 67.7 63.6 45.8
OBz
BzO
BzO
BzO
O
N
N
NMe2
163al
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

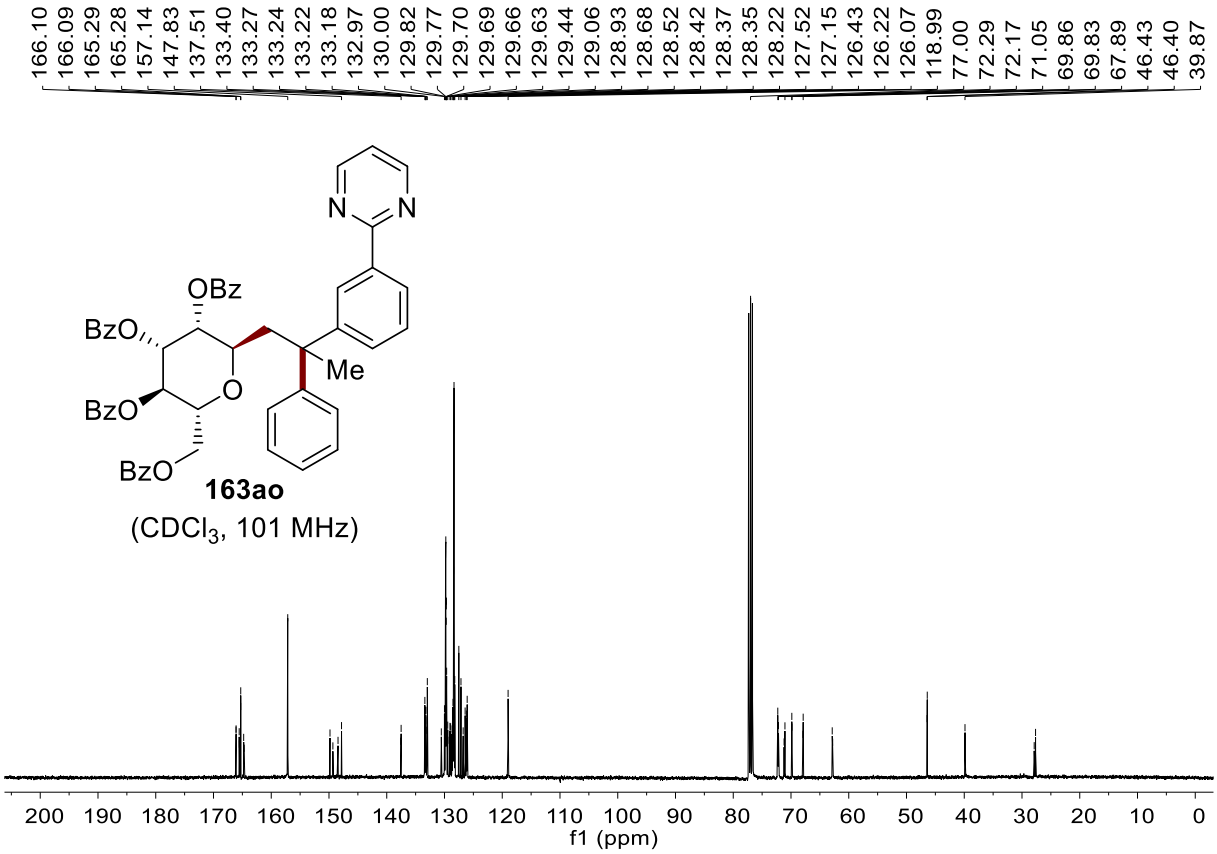

OBz
BzO
BzO
BzO
O
N
N
O
163am
(CDCl3, 400 MHz)
1.02 0.94 0.46 0.46 0.94 1.83 3.96 2.00 12.29 1.13 3.10 1.76 0.99 1.94 0.92 0.92 0.51 0.49 0.51 0.49 1.90 0.95 2.91 0.96 1.00 0.98
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

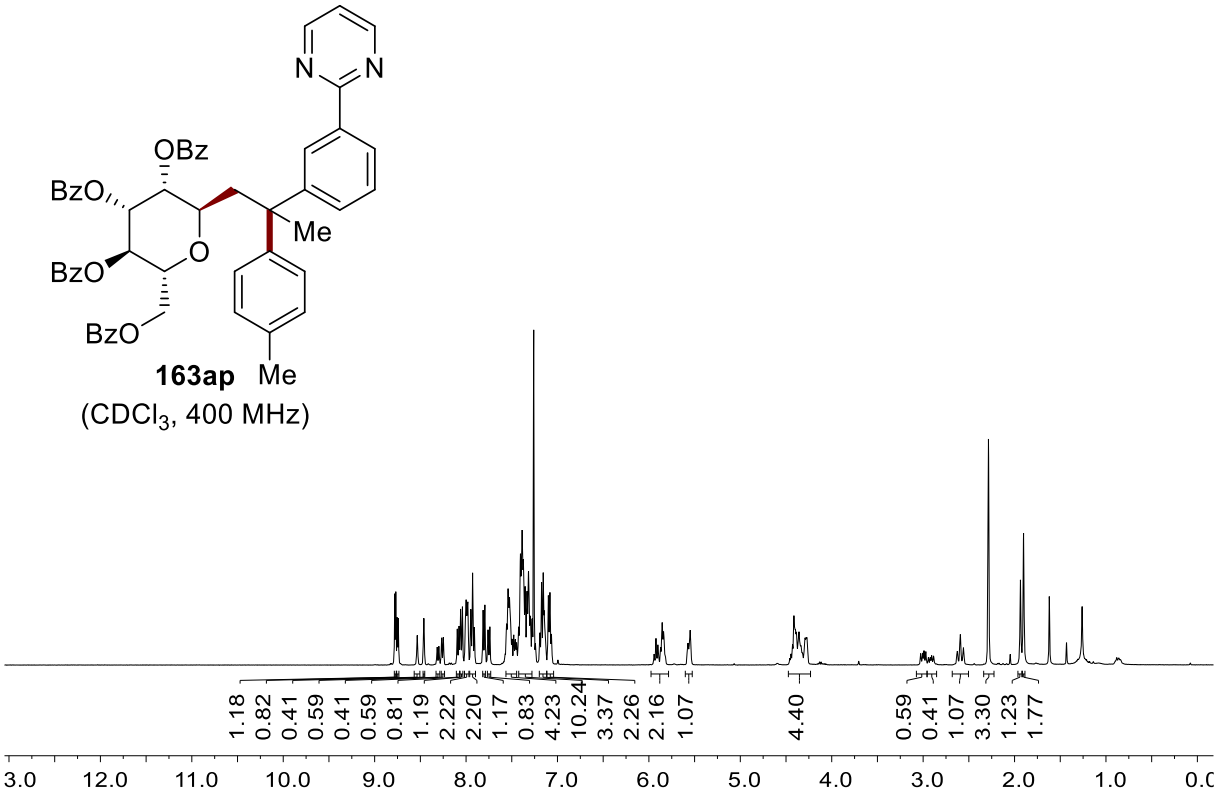

166.1 165.4 157.2 157.1 133.4 133.4 133.3 133.2 133.2 133.2 133.1 130.5 130.3 129.9 129.9 129.8 129.8 129.7 129.6 129.6 129.1 128.9 128.9 128.9 128.9 128.5 128.4 128.4 128.3 128.3 127.8 127.0 120.6 120.2 119.1 119.0 117.7 117.6 114.7 114.6 77.0 71.8 71.6 70.4 68.7 68.6 67.8 67.7 46.8 46.7
N
N
OBz
BzO
BzO
BzO
O
O
163am
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

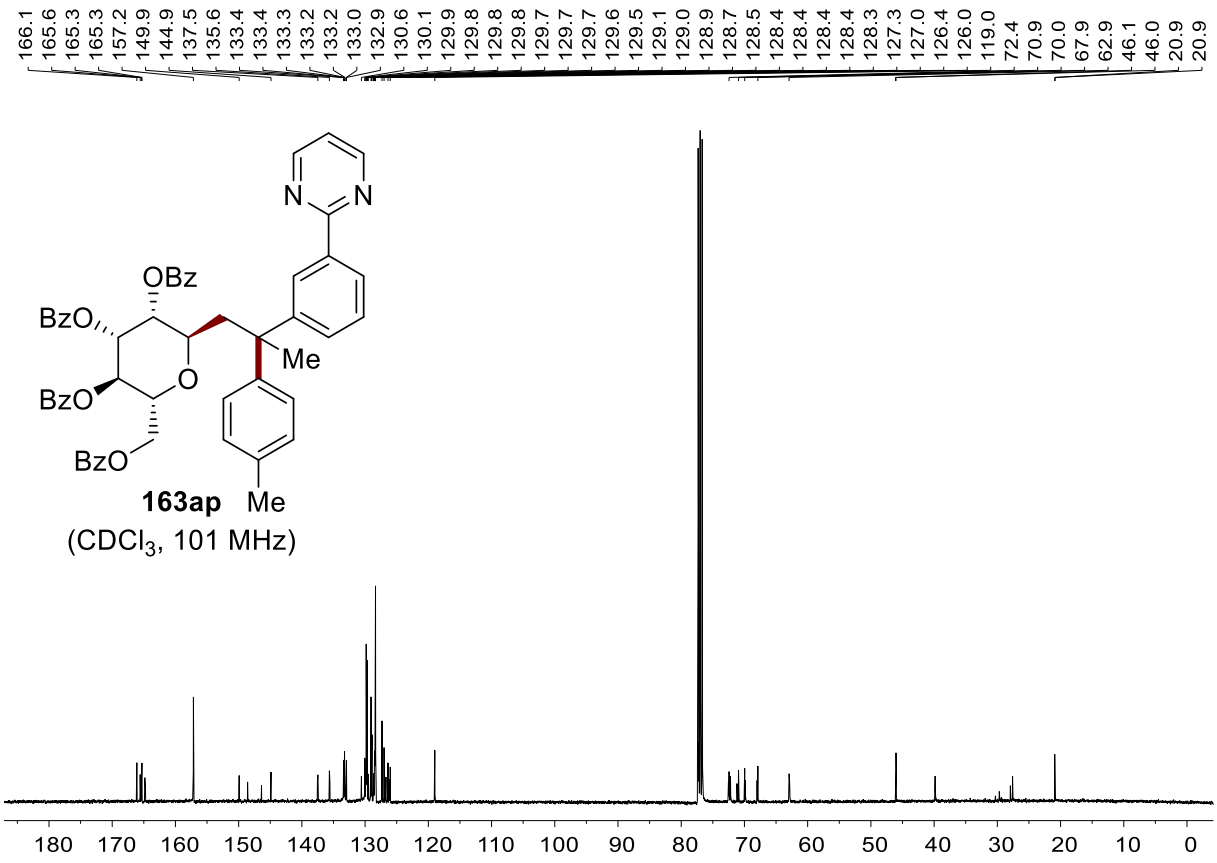

N
N
OBz
BzO
BzO
BzO
O
163an
(CDCl3, 400 MHz)
1.13 0.88 0.41 0.43 0.86 2.12 4.00 5.94 16.07 1.31 0.48 0.46 0.92 1.05 0.45 0.42 5.05 1.00 1.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

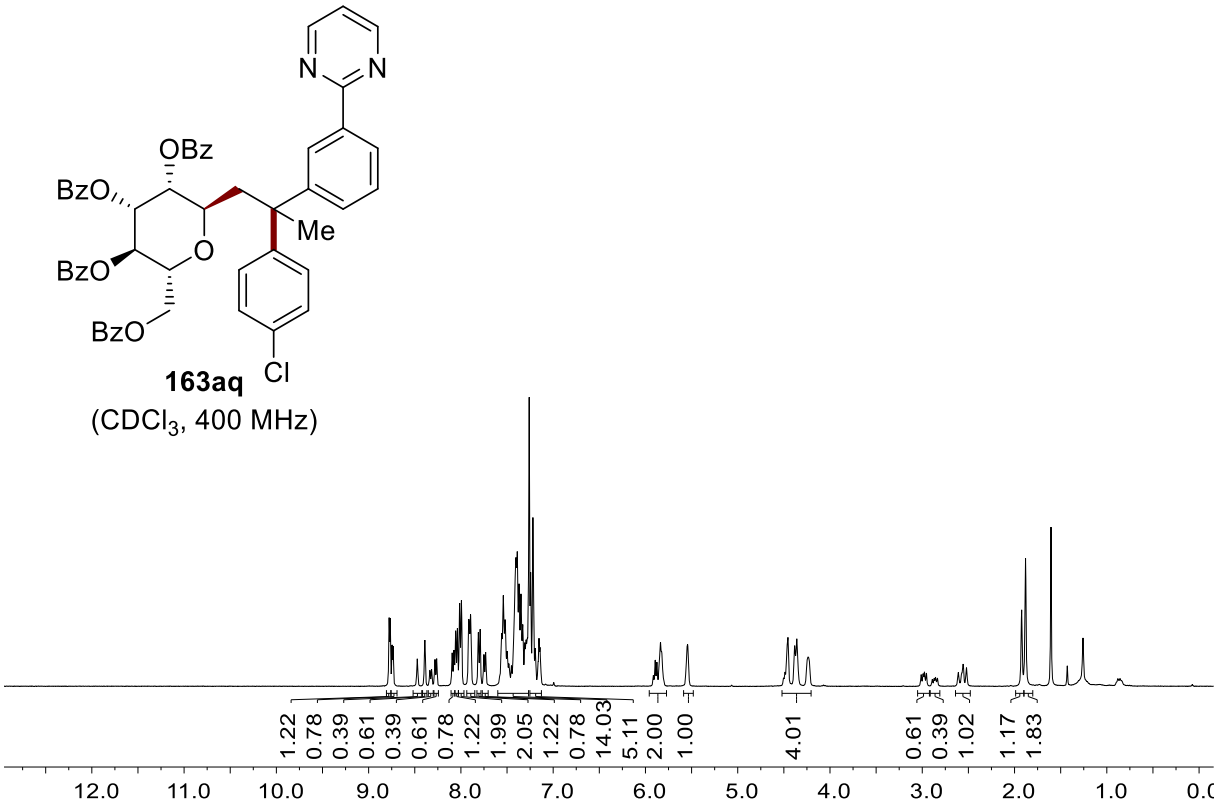

165.4 157.2 157.1 133.5 133.4 133.2 133.1 130.8 130.5 129.9 129.9 129.8 129.8 129.8 129.7 129.7 129.7 129.7 129.1 129.0 128.9 128.7 128.5 128.5 128.4 128.3 128.3 127.9 127.9 127.8 127.5 127.1 126.9 126.6 126.6 126.1 126.1 126.0 125.6 125.6 125.4 119.1 119.0 71.8 71.7 70.4 70.3 70.3 67.8 67.8 46.7
N
N
OBz
BzO
BzO
O
BzO
163an
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

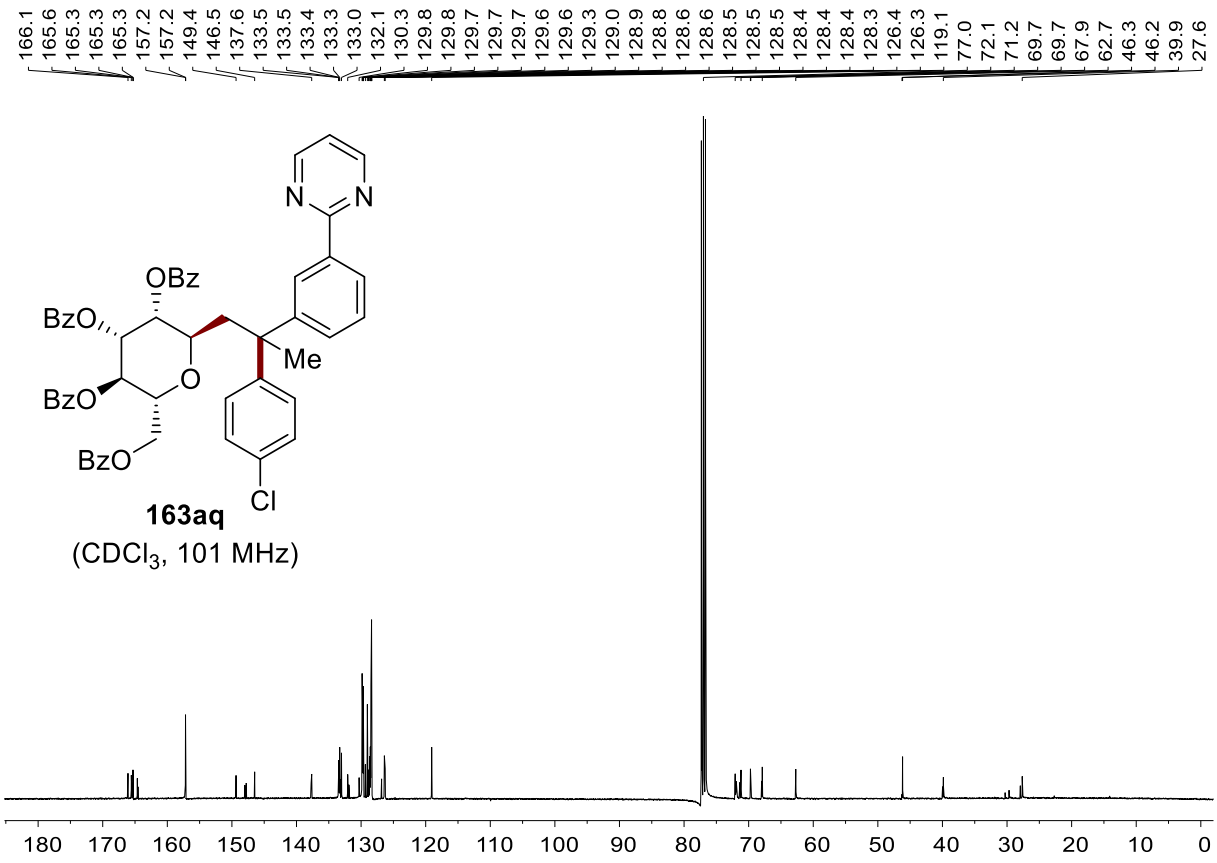

N
N
OBz
BzO
Me
BzO
O
BzO
163ao
(CDCl3, 400 MHz)
1.18 0.82 0.41 0.59 0.41 0.59 0.82 1.18 2.11 2.10 1.18 0.82 4.32 14.03 1.18 1.07 2.04 0.41 0.59 4.16 0.96 1.00 1.23 1.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

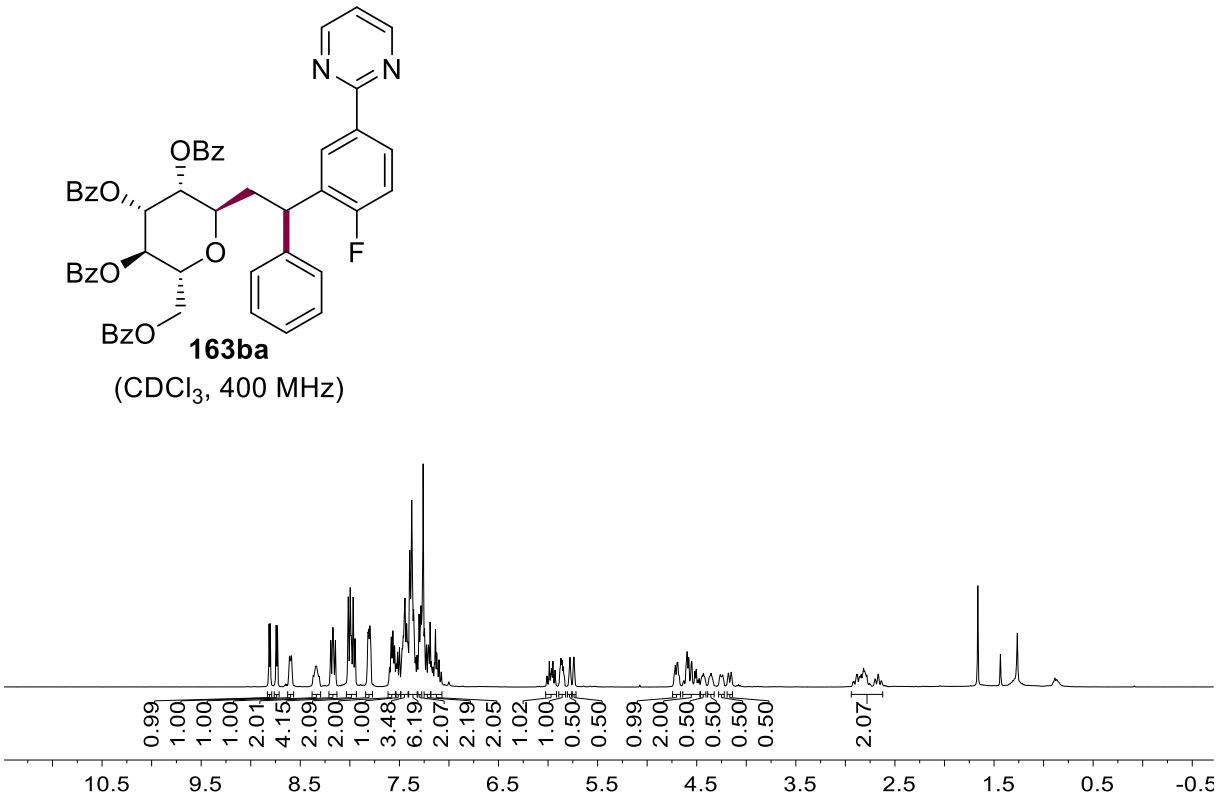

166.10
166.09
165.29
165.28
157.14
147.83
137.51
133.40
133.27
133.24
133.22
133.18
132.97
130.00
129.82
129.77
129.70
129.69
129.66
129.63
129.44
129.06
128.93
128.68
128.52
128.42
128.37
128.35
128.22
127.52
127.15
126.43
126.22
126.07
118.99
77.00
72.29
72.17
71.05
69.86
69.83
67.89
46.43
46.40
39.87
N
N
OBz
BzO
Me
O
BzO
BzO
163ao
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

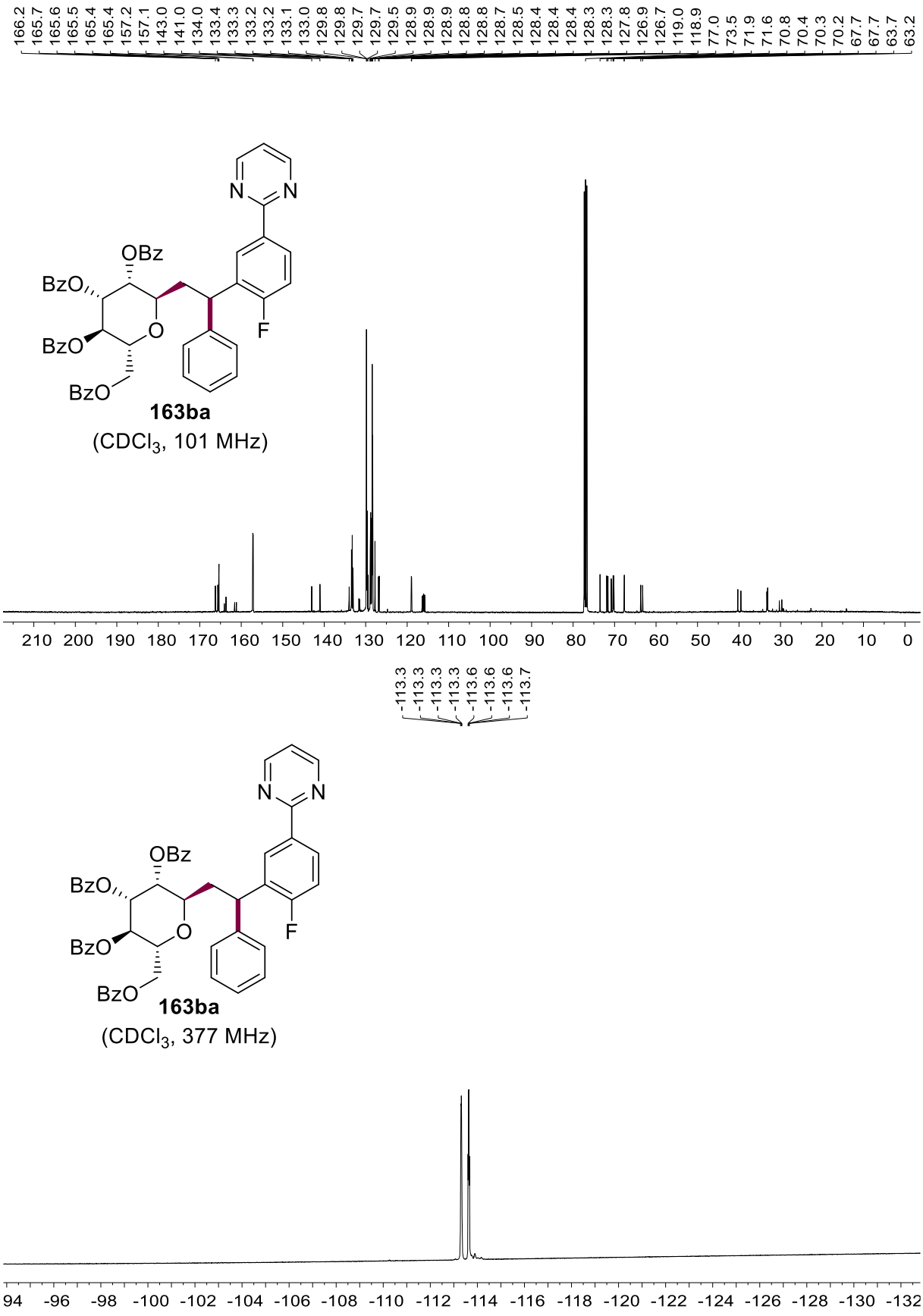

N
N
OBz
BzO
Me
O
BzO
BzO
163ap Me
(CDCl3, 400 MHz)
1.18
0.82
0.41
0.59
0.41
0.59
0.81
1.19
2.22
2.20
1.17
0.83
4.23
10.24
3.37
2.26
2.16
1.07
4.40
0.59
0.41
1.07
3.30
1.23
1.77
3.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

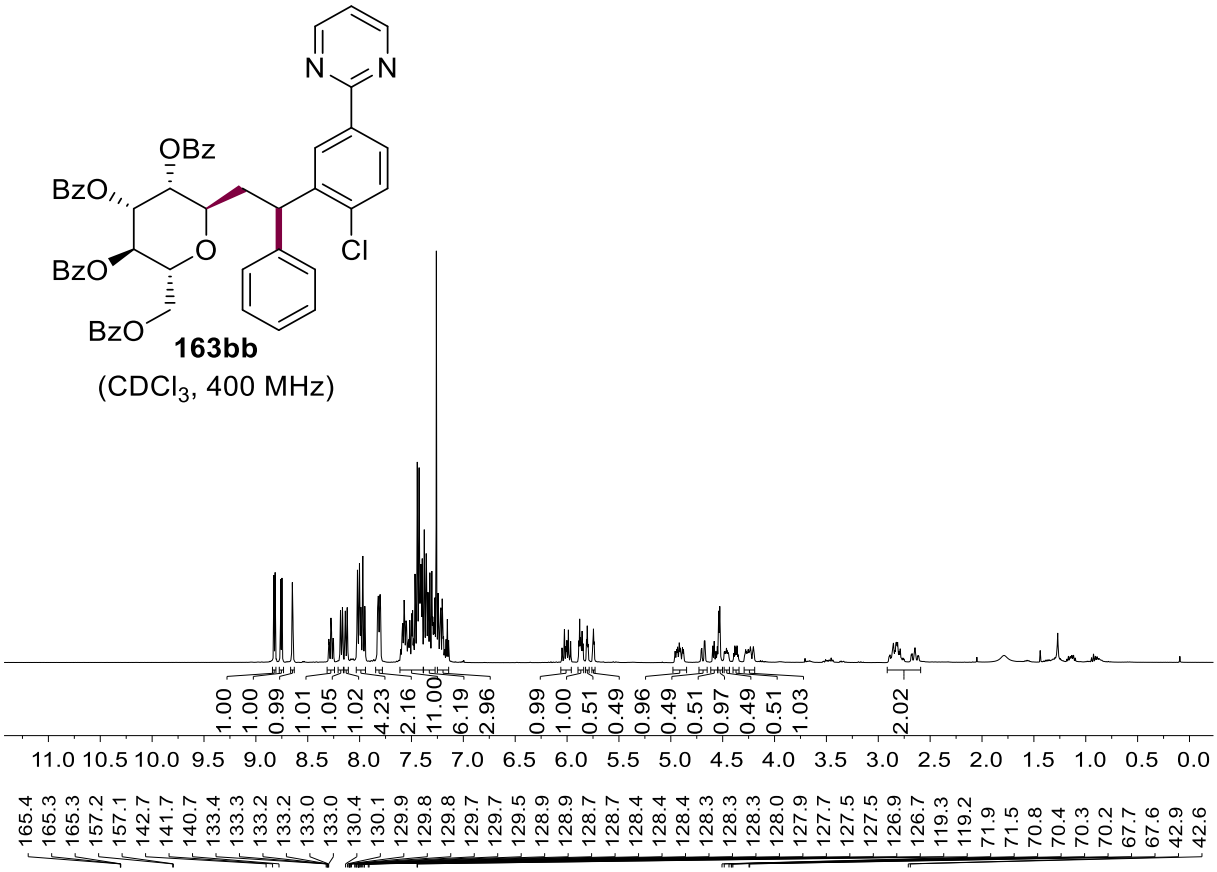

166.1
165.6
165.3
165.3
157.2
149.9
144.9
137.5
135.6
133.4
133.4
133.3
133.2
133.2
133.0
132.9
130.6
130.1
129.9
129.8
129.8
129.8
129.7
129.7
129.7
129.6
129.5
129.1
129.0
128.9
128.7
128.5
128.4
128.4
128.4
128.4
128.3
127.3
127.0
126.4
126.0
119.0
72.4
70.9
70.0
67.9
62.9
46.1
46.0
20.9
20.9
N
N
OBz
BzO
BzO
BzO
O
Me
Me
163ap
(CDCl3, 101 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

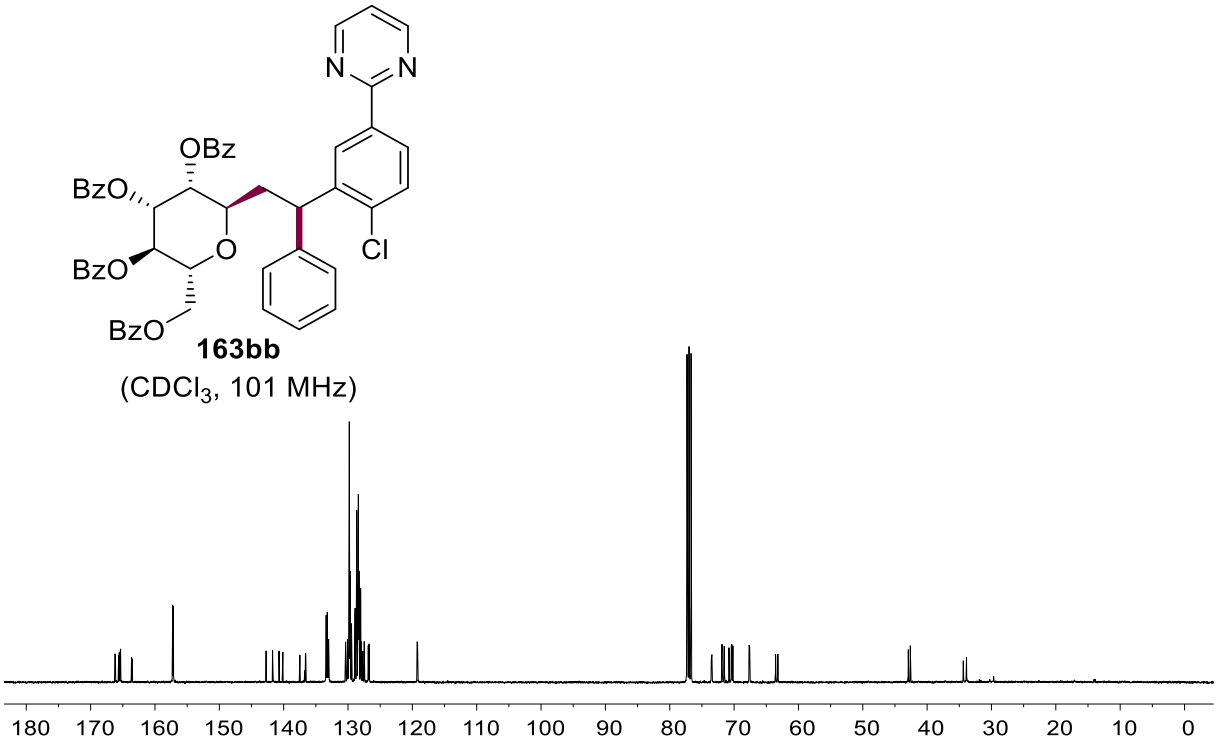

N
N
OBz
BzO
BzO
BzO
O
Me
Cl
163aq
(CDCl3, 400 MHz)
1.22
0.78
0.39
0.61
0.39
0.61
0.78
1.22
1.99
2.05
1.22
0.78
14.03
5.11
2.00
1.00
4.01
0.61
0.39
1.02
1.17
1.83
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

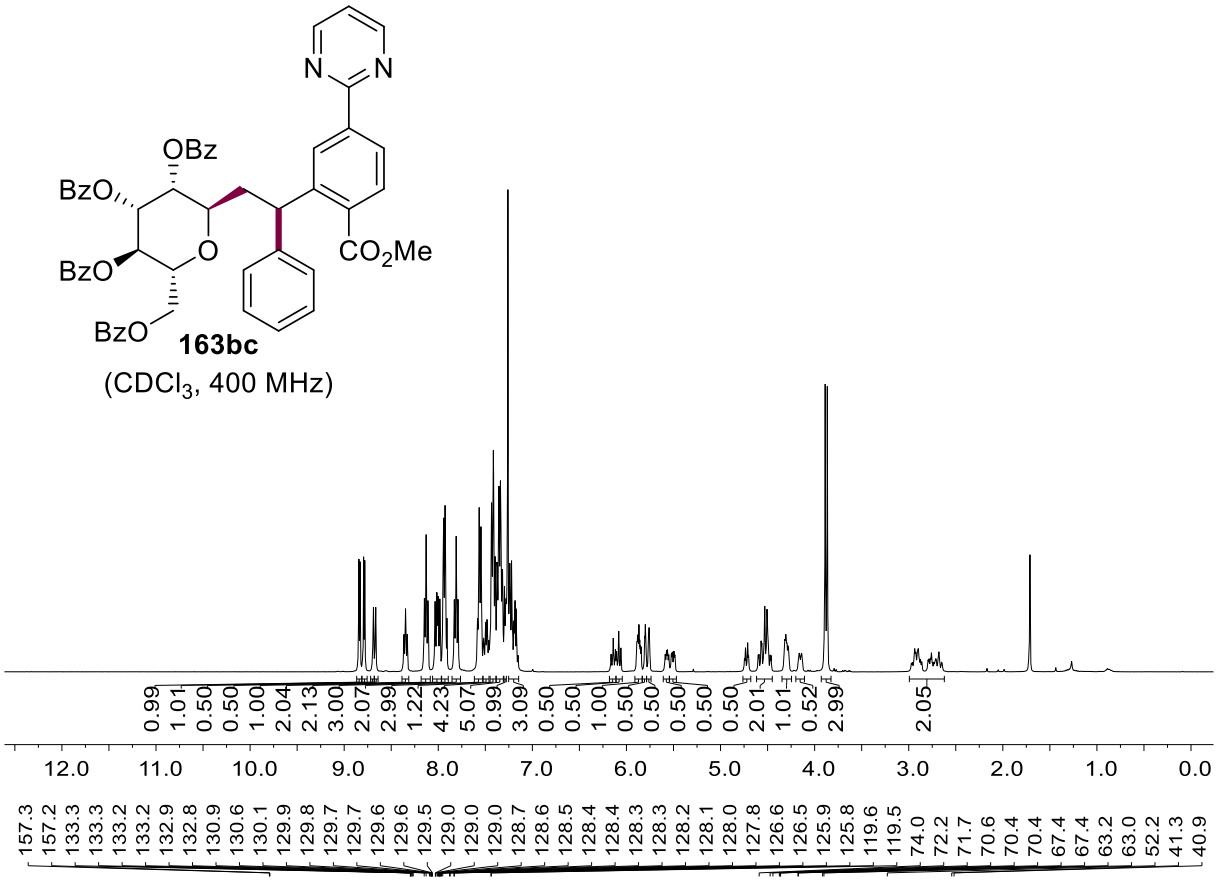

166.1
165.6
165.3
165.3
165.3
157.2
157.2
149.4
146.5
137.6
133.5
133.5
133.4
133.3
133.0
132.1
130.3
129.8
129.8
129.7
129.7
129.7
129.6
129.6
129.3
129.0
128.9
128.8
128.6
128.6
128.5
128.5
128.5
128.4
128.4
128.4
128.3
126.4
126.3
119.1
77.0
72.1
71.2
69.7
69.7
67.9
62.7
46.3
46.2
39.9
27.6
N
N
OBz
BzO
BzO
BzO
O
Me
Cl
163aq
(CDCl3, 101 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

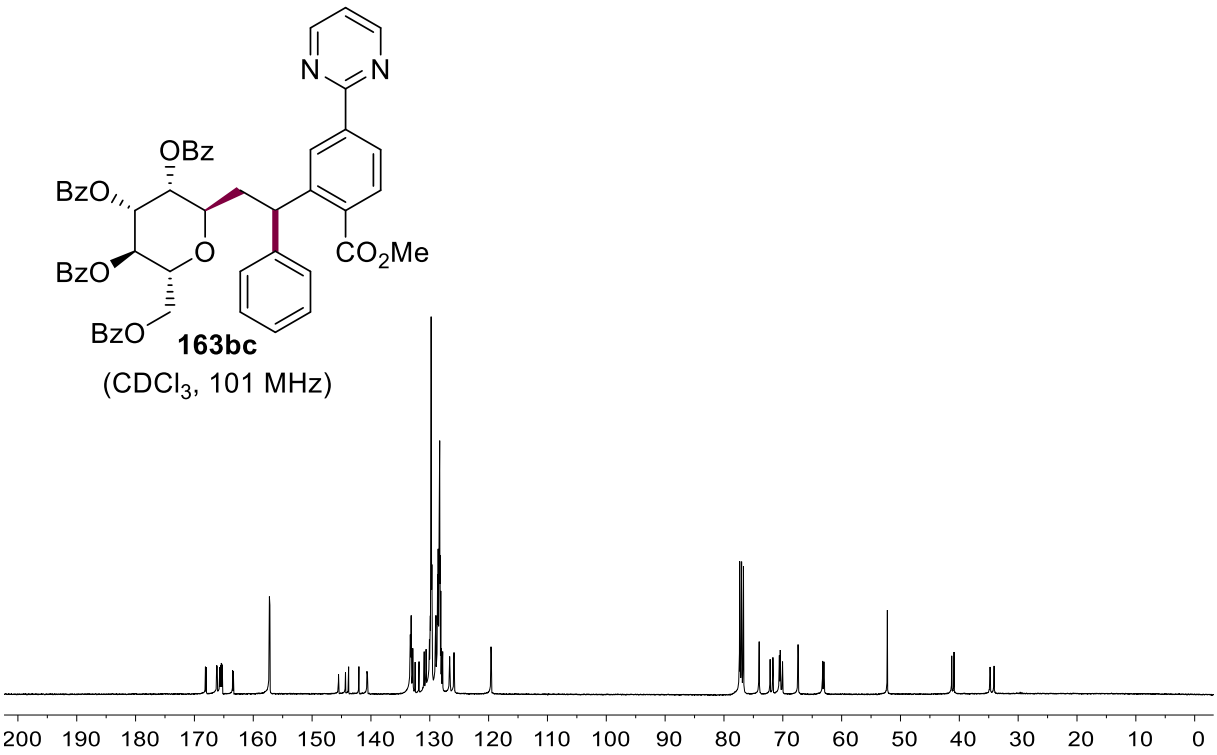

N
N
OBz
BzO
BzO
BzO
O
F
163ba
(CDCl3, 400 MHz)
0.99
1.00
1.00
1.00
2.01
4.15
2.09
2.00
1.00
3.48
6.19
2.07
2.19
2.05
1.02
1.00
0.50
0.50
0.99
2.00
0.50
0.50
0.50
0.50
2.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

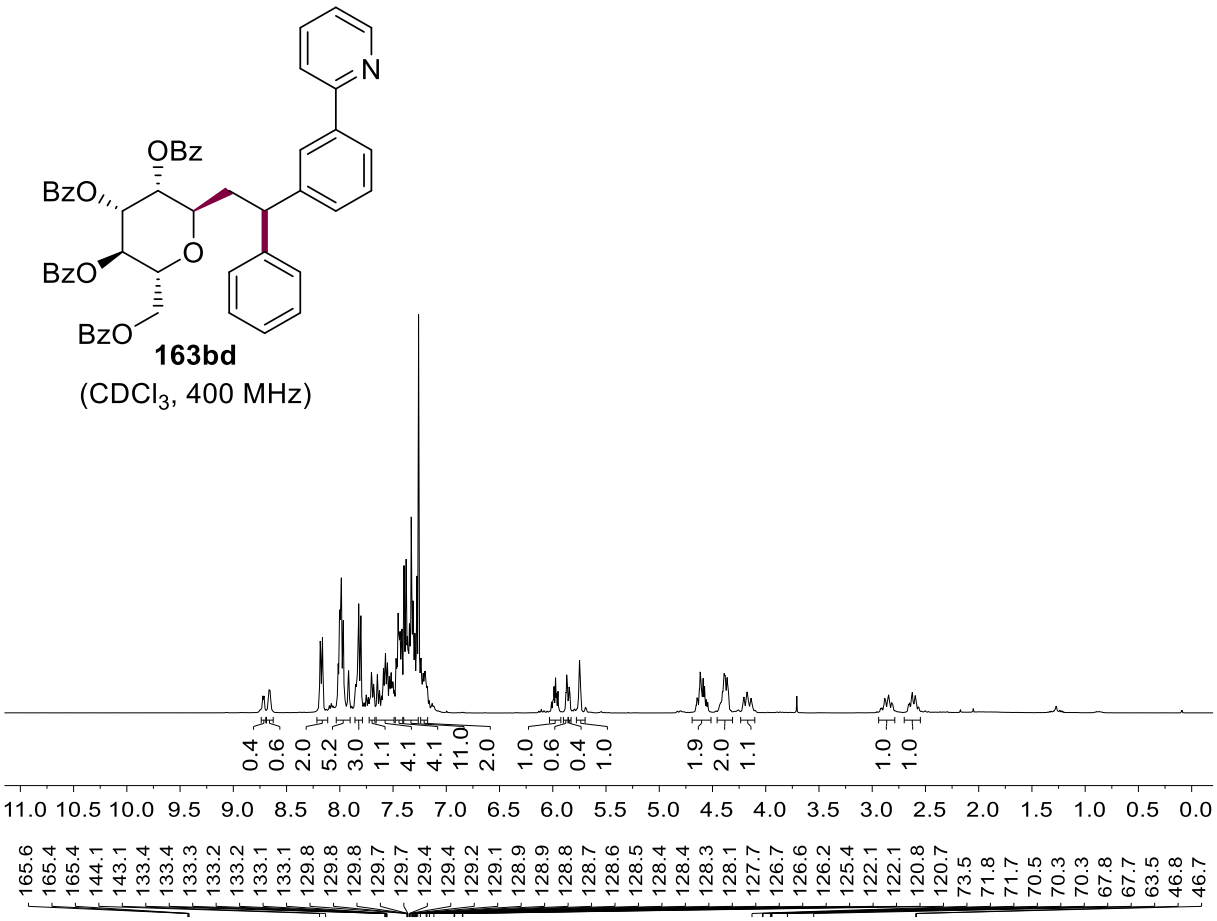

166.2
165.7
165.6
165.5
165.4
165.4
157.2
157.1
143.0
141.0
134.0
133.4
133.3
133.2
133.2
133.1
133.0
129.8
129.8
129.7
129.7
129.5
128.9
128.9
128.9
128.8
128.8
128.7
128.5
128.4
128.4
128.4
128.3
128.3
127.8
126.9
126.7
119.0
118.9
77.0
73.5
71.9
71.6
70.8
70.4
70.3
70.2
67.7
67.7
63.7
63.2
N
N
OBz
BzO
BzO
BzO
O
F
163ba
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
-113.3
-113.3
-113.3
-113.3
-113.6
-113.6
-113.6
-113.7
N
N
OBz
BzO
BzO
BzO
O
F
163ba
(CDCl3, 377 MHz)
94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132

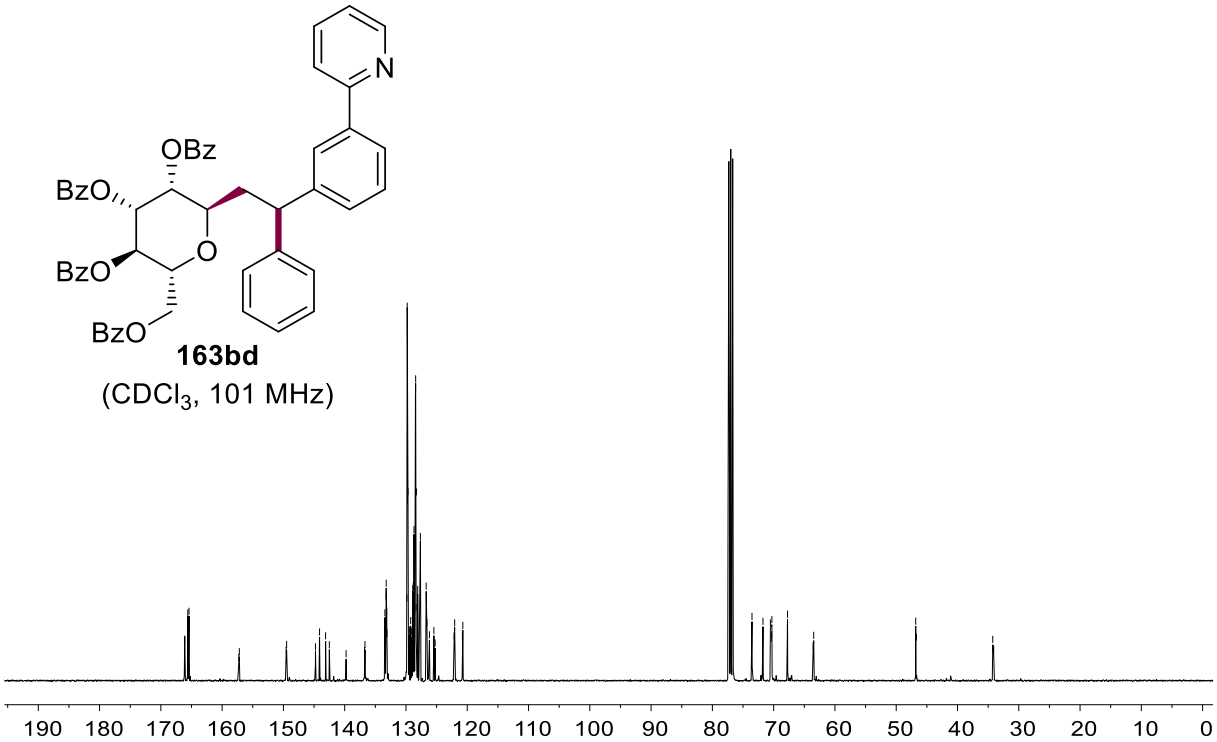

OBz
BzO
BzO
BzO
O
Cl
N
N
163bb
(CDCl3, 400 MHz)
1.00 1.00 0.99 1.01 1.05 1.02 4.23 2.16 11.00 6.19 2.96 0.99 1.00 0.51 0.49 0.96 0.49 0.51 0.97 0.49 0.51 1.03 2.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
165.4 165.3 165.3 157.2 157.1 142.7 141.7 140.7 133.4 133.3 133.2 133.2 133.0 133.0 130.4 130.1 129.9 129.8 129.8 129.7 129.7 129.5 128.9 128.9 128.7 128.7 128.4 128.4 128.4 128.3 128.3 128.3 128.0 127.9 127.7 127.5 127.5 126.9 126.7 119.3 119.2 71.9 71.5 70.8 70.4 70.3 70.2 67.7 67.6 42.9 42.6

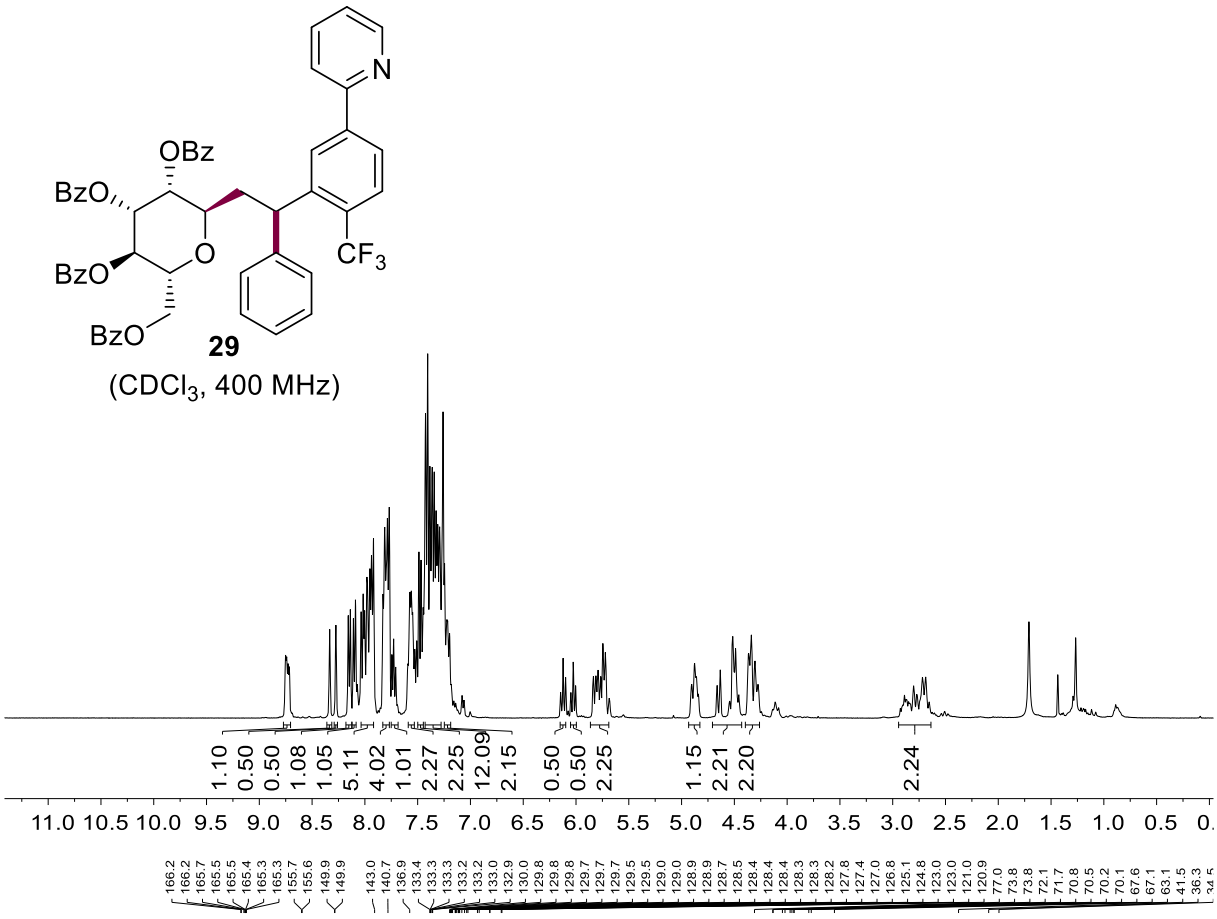

OBz
BzO
BzO
BzO
O
Cl
N
N
163bb
(CDCl3, 101 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

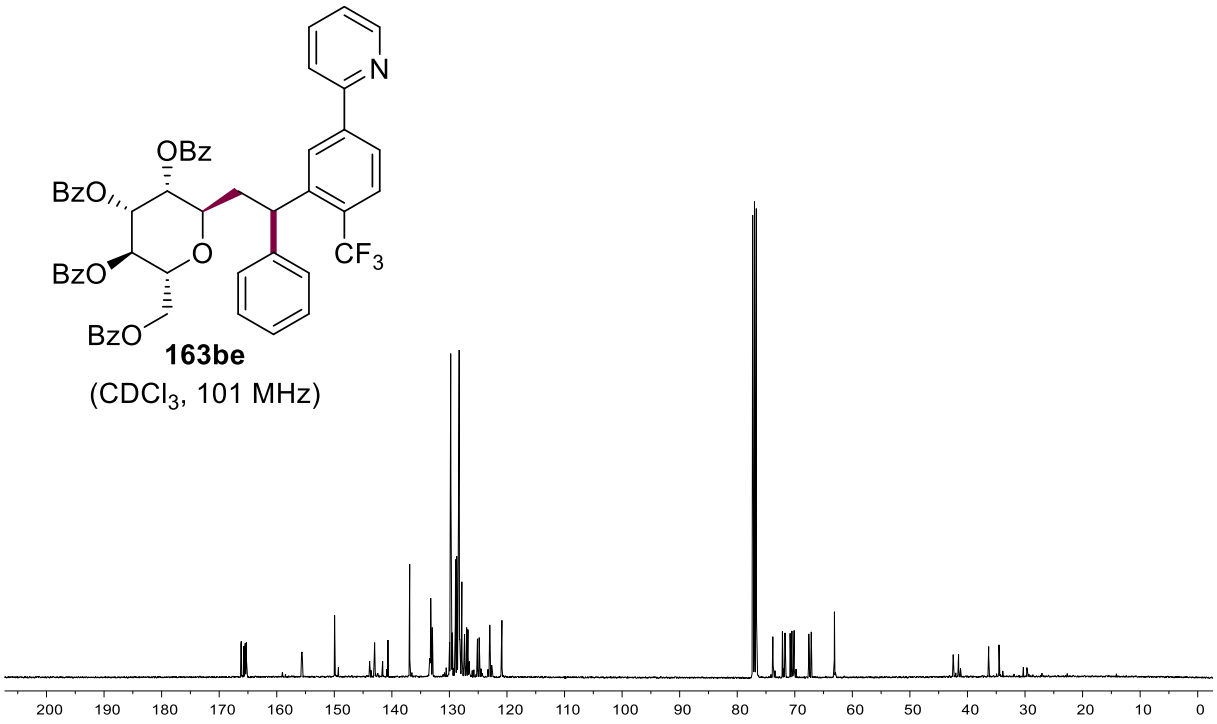

OBz
BzO
BzO
BzO
O
N
N
CO2Me
163bc
(CDCl3, 400 MHz)
0.99 1.01 0.50 0.50 1.00 2.04 2.13 3.00 2.07 2.99 1.22 4.23 5.07 0.99 3.09 0.50 0.50 1.00 0.50 0.50 0.50 0.50 0.50 2.01 1.01 0.52 2.99 2.05
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
157.3 157.2 133.3 133.3 133.2 133.2 132.9 132.8 130.9 130.6 130.1 129.9 129.8 129.7 129.7 129.6 129.6 129.5 129.0 129.0 129.0 128.7 128.6 128.5 128.4 128.4 128.3 128.3 128.2 128.1 128.0 127.8 126.6 126.5 125.9 125.8 119.6 119.5 74.0 72.2 71.7 70.6 70.4 70.4 67.4 67.4 63.2 63.0 52.2 41.3 40.9

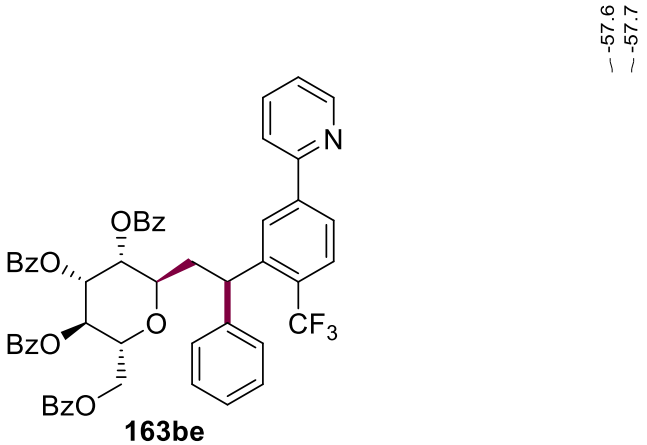

OBz
BzO
BzO
BzO
O
N
N
CO2Me
163bc
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


N
OBz
BzO
BzO
O
BzO
163bd
(CDCl3, 400 MHz)
0.4 0.6 2.0 5.2 3.0 1.1 4.1 4.1 11.0 2.0 1.0 0.6 0.4 1.0 1.9 2.0 1.1 1.0 1.0
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
165.6 165.4 165.4 144.1 143.1 133.4 133.4 133.3 133.2 133.2 133.1 133.1 129.8 129.8 129.7 129.7 129.4 129.4 129.2 129.1 128.9 128.9 128.8 128.7 128.6 128.5 128.4 128.4 128.3 128.1 127.7 126.7 126.6 126.2 125.4 122.1 122.1 120.8 120.7 73.5 71.8 71.7 70.5 70.3 70.3 67.8 67.7 63.5 46.8 46.7


N
OBz
BzO
BzO
O
BzO
163bd
(CDCl3, 101 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

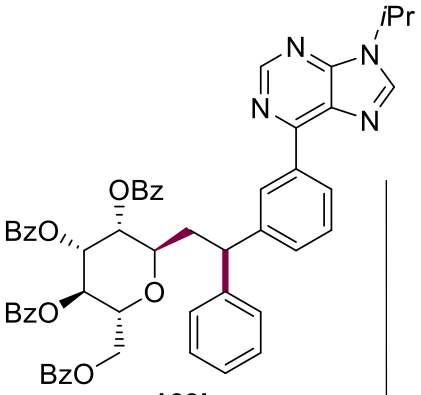

N
OBz
BzO
BzO
BzO
O
CF3
29
(CDCl3, 400 MHz)
1.10
0.50
0.50
1.08
1.05
5.11
4.02
1.01
2.27
2.25
12.09
2.15
0.50
0.50
2.25
1.15
2.21
2.20
2.24
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.


N
OBz
BzO
BzO
BzO
O
CF3
163be
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



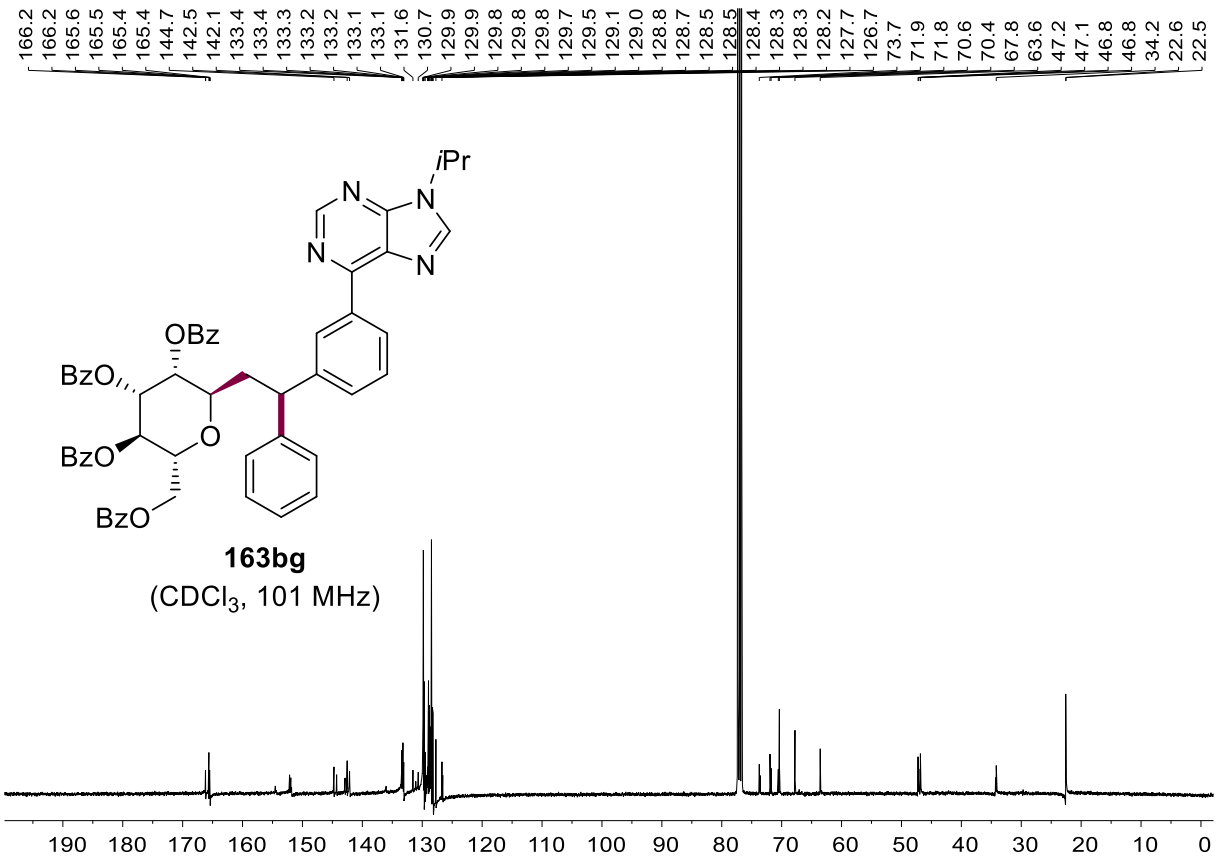
163be

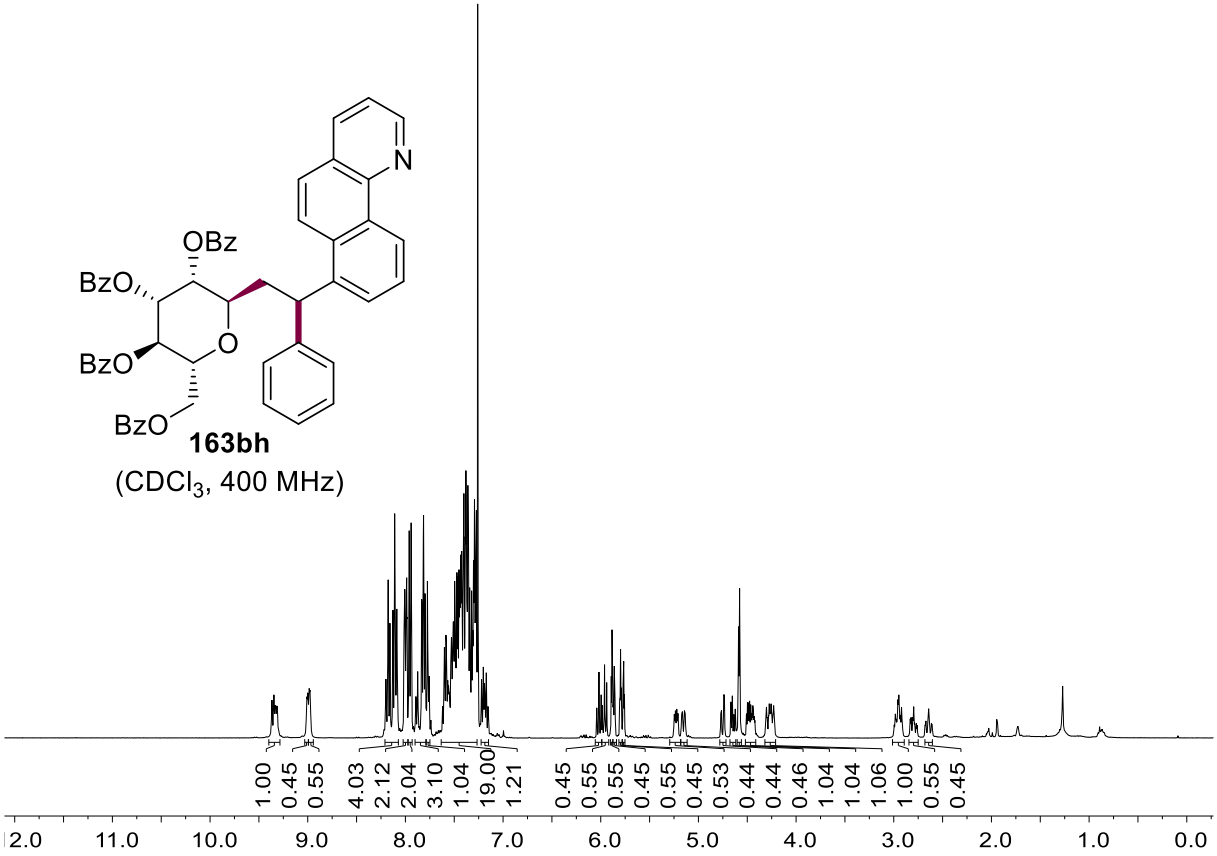
($CDCl_3$, 377 MHz)

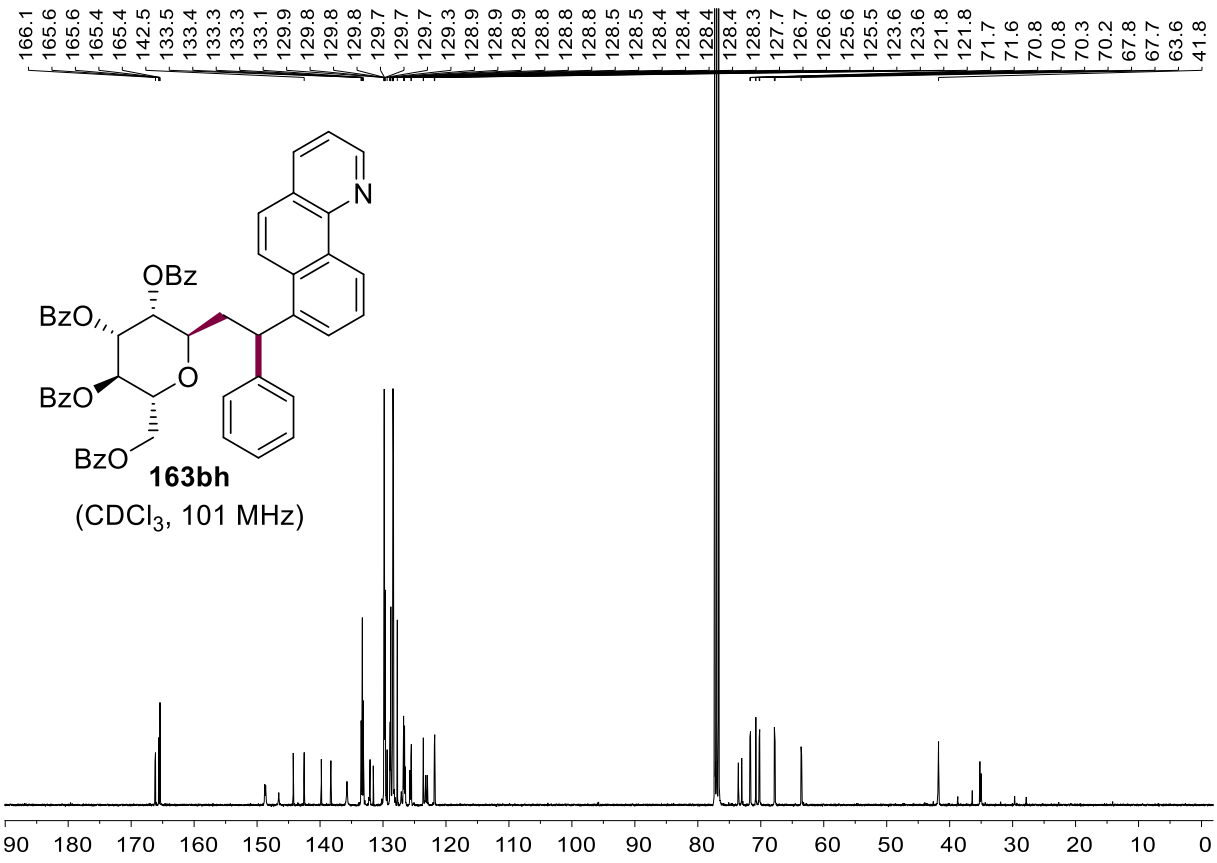


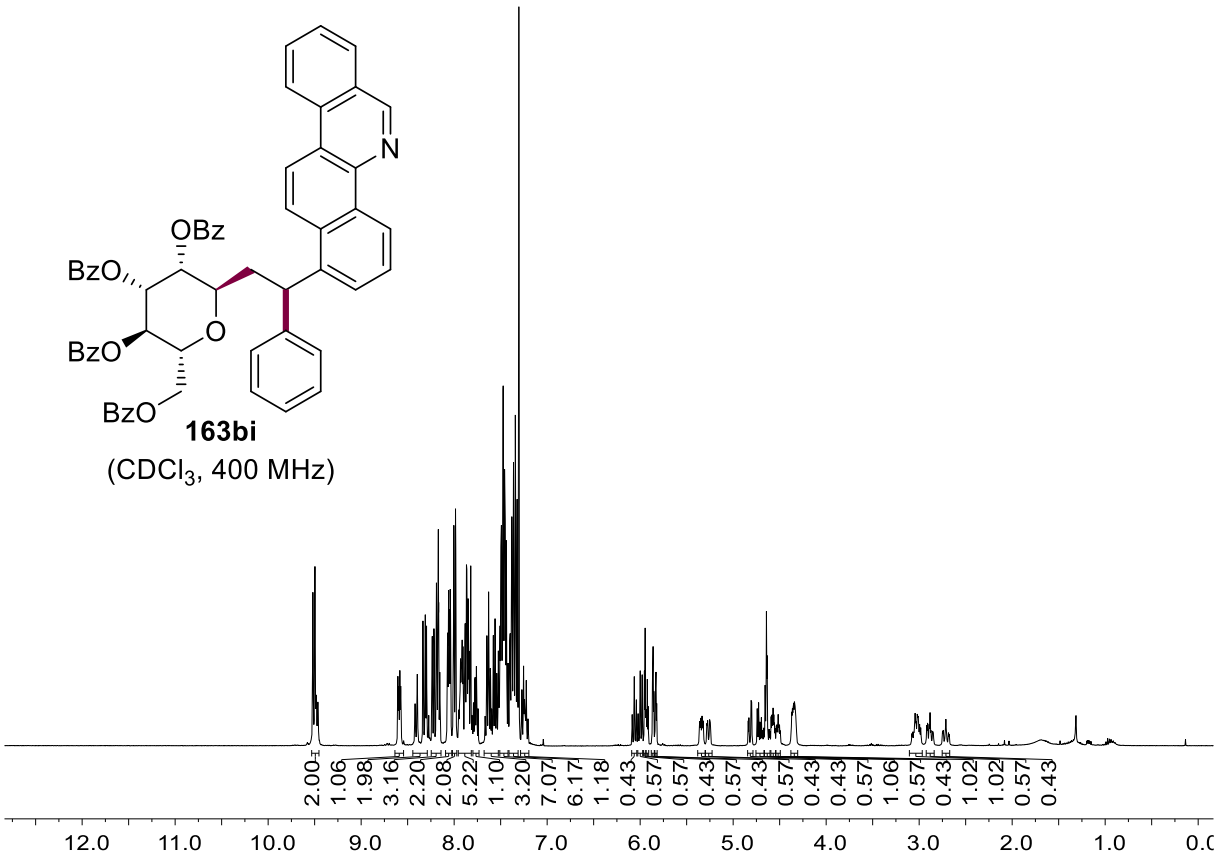
163bg

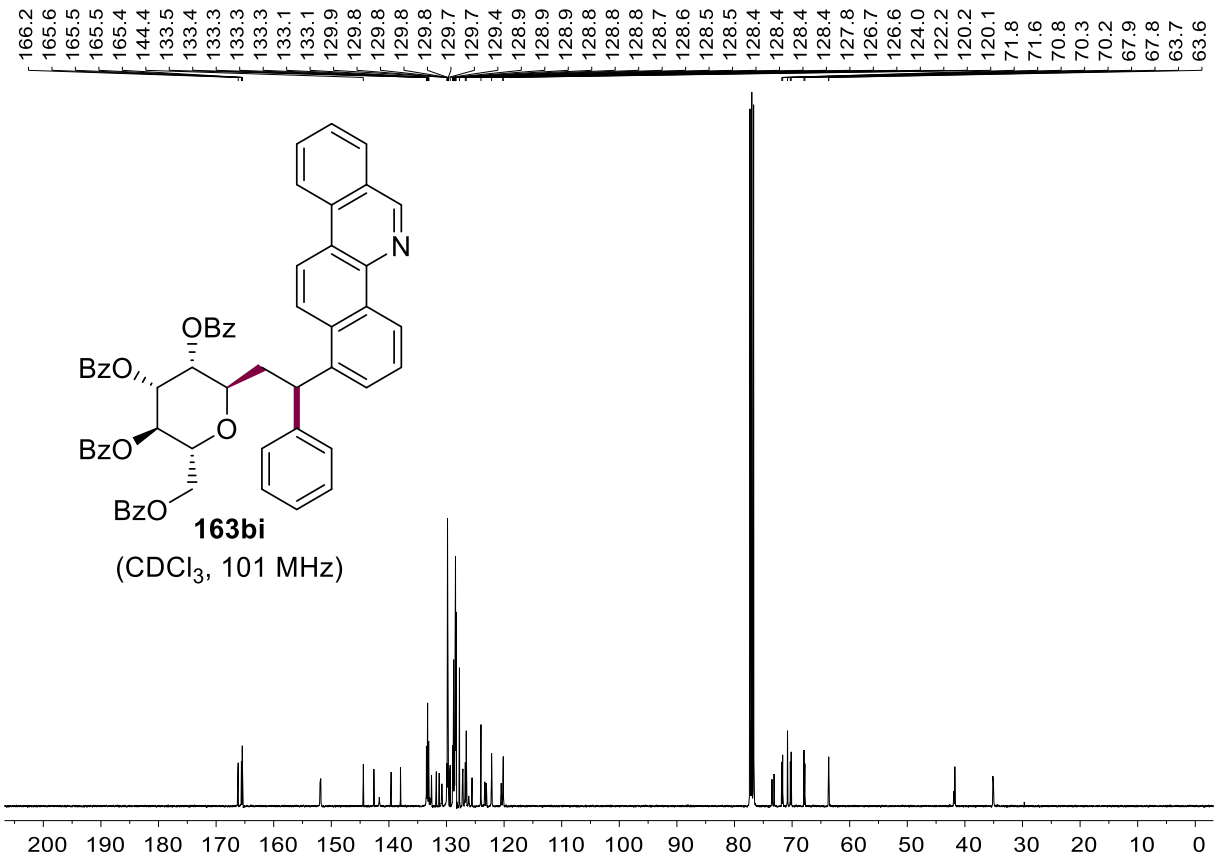
($CDCl_3$, 400 MHz)

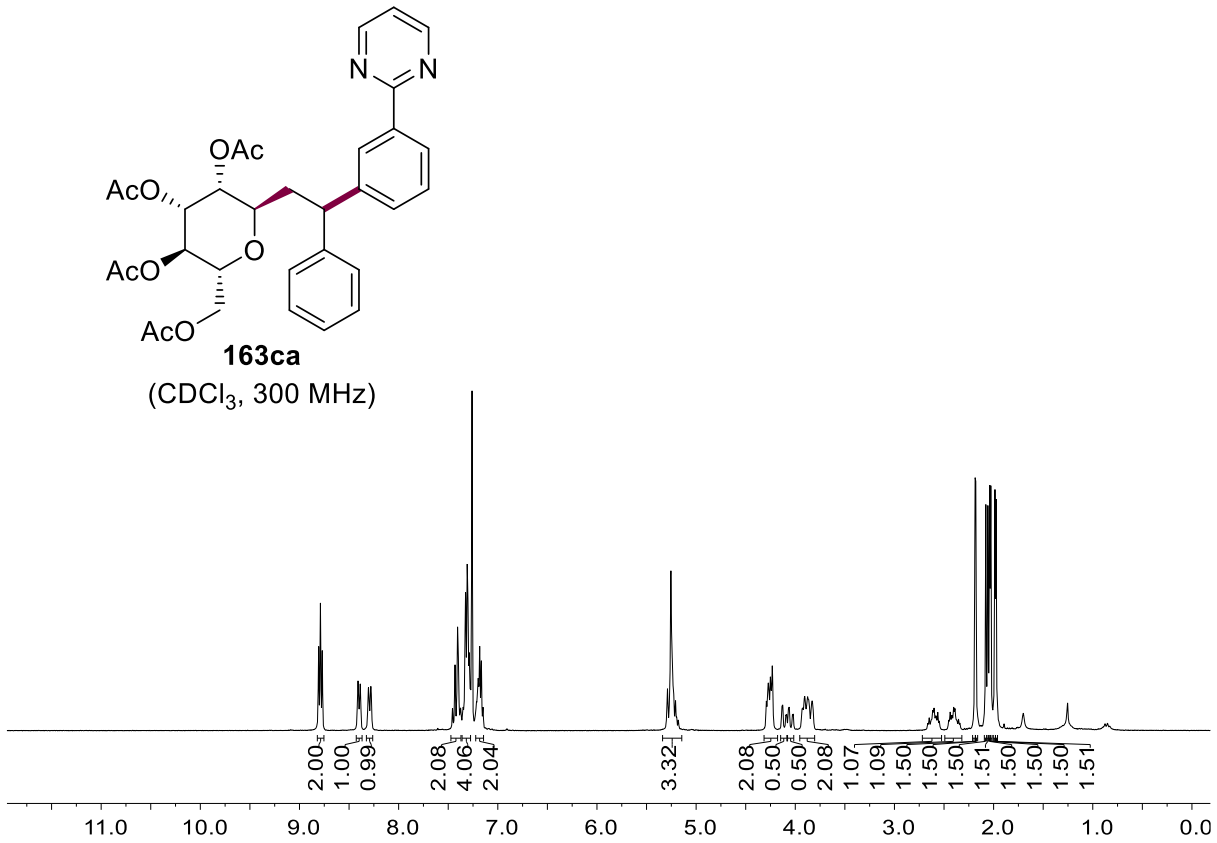

166.2
166.2
165.6
165.5
165.4
165.4
144.7
142.5
142.1
133.4
133.4
133.3
133.2
133.2
133.1
133.1
131.6
130.7
129.9
129.9
129.8
129.8
129.8
129.7
129.5
129.1
129.0
128.8
128.7
128.5
128.5
128.4
128.3
128.3
128.2
127.7
126.7
73.7
71.9
71.8
70.6
70.4
67.8
63.6
47.2
47.1
46.8
46.8
34.2
22.6
22.5
iPr
N
N
N
N
OBz
BzO
BzO
O
BzO
163bg
(CDCl3, 101 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

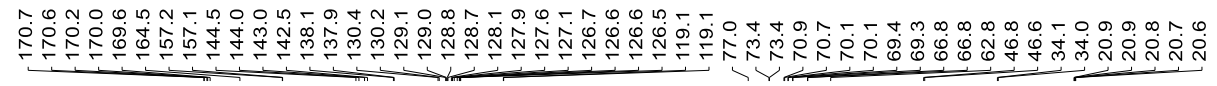

N
OBz
BzO
BzO
O
BzO
163bh
(CDCl3, 400 MHz)
1.00
0.45
0.55
4.03
2.12
2.04
3.10
1.04
19.00
1.21
0.45
0.55
0.55
0.45
0.55
0.45
0.53
0.44
0.44
0.46
1.04
1.04
1.06
1.00
0.55
0.45
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

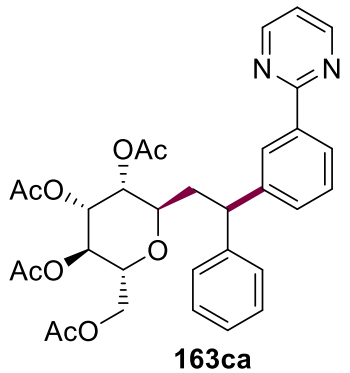

166.1
165.6
165.6
165.4
165.4
142.5
133.5
133.4
133.3
133.3
133.1
129.9
129.8
129.8
129.8
129.7
129.7
129.7
129.3
128.9
128.9
128.8
128.8
128.8
128.5
128.5
128.4
128.4
128.4
128.4
128.3
127.7
126.7
126.6
125.6
125.5
123.6
123.6
121.8
121.8
71.7
71.6
70.8
70.8
70.3
70.2
67.8
67.7
63.6
41.8
N
OBz
BzO
O
BzO
BzO
163bh
(CDCl3, 101 MHz)
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


N
OBz
BzO
O
BzO
BzO
163bi
(CDCl3, 400 MHz)
2.00
1.06
1.98
3.16
2.20
2.08
5.22
1.10
3.20
7.07
6.17
1.18
0.43
0.57
0.57
0.43
0.57
0.43
0.57
0.43
0.43
0.57
1.06
0.57
0.43
1.02
1.02
0.57
0.43
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


166.2
165.6
165.5
165.5
165.4
144.4
133.5
133.4
133.3
133.3
133.3
133.1
133.1
129.9
129.8
129.8
129.8
129.8
129.7
129.7
129.4
128.9
128.9
128.9
128.8
128.8
128.8
128.7
128.6
128.5
128.5
128.4
128.4
128.4
128.4
127.8
126.7
126.6
124.0
122.2
120.2
120.1
71.8
71.6
70.8
70.3
70.2
67.9
67.8
63.7
63.6
N
OBz
BzO
BzO
O
BzO
163bi
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

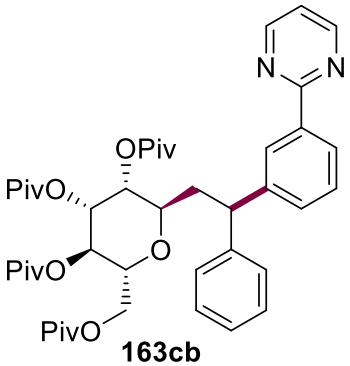

N
N
OAc
AcO
AcO
O
AcO
163ca
(CDCl3, 300 MHz)
2.00
1.00
0.99
2.08
4.06
2.04
3.32
2.08
0.50
0.50
2.08
1.07
1.09
1.50
1.50
1.50
1.51
1.50
1.50
1.50
1.51
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0





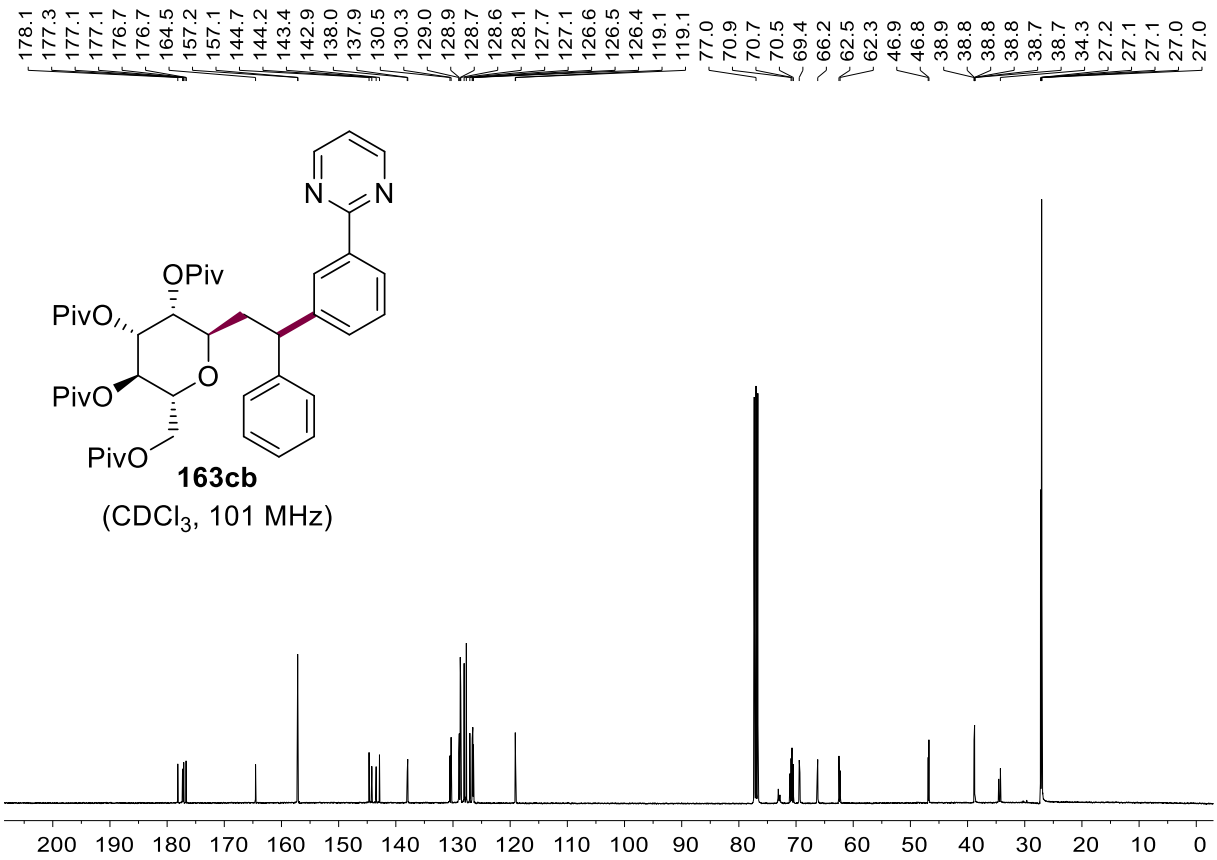
163ca

($CDCl_3$, 75 MHz)



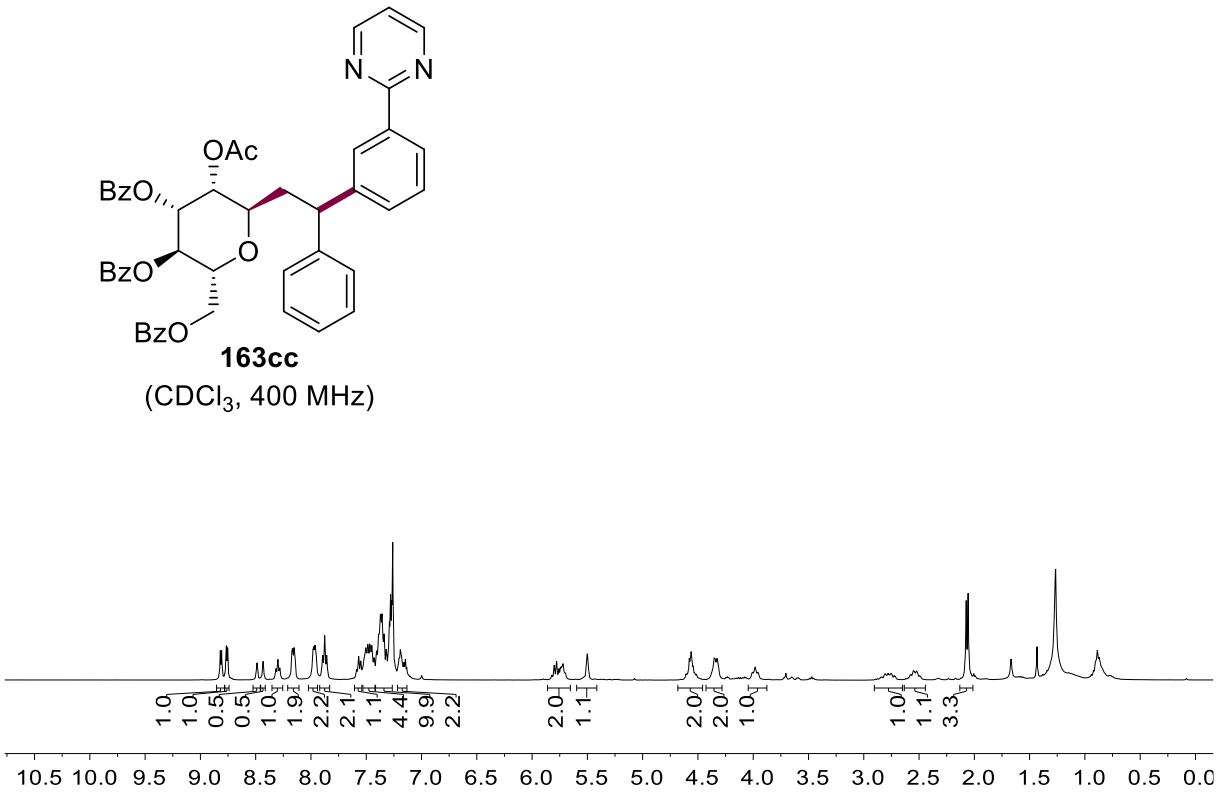
163cb

($CDCl_3$, 400 MHz)



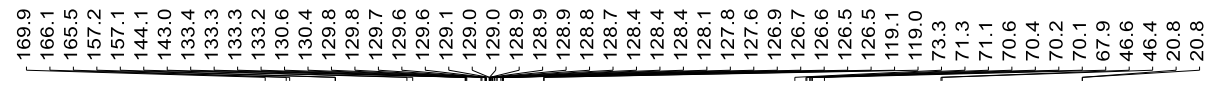
163cb

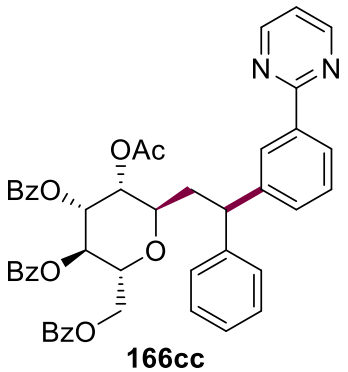
($CDCl_3$, 101 MHz)



163cc

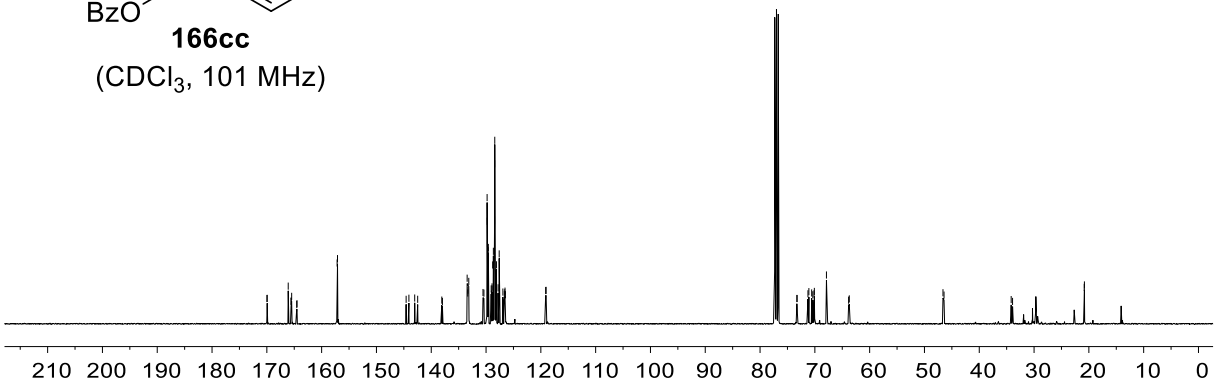
($CDCl_3$, 400 MHz)

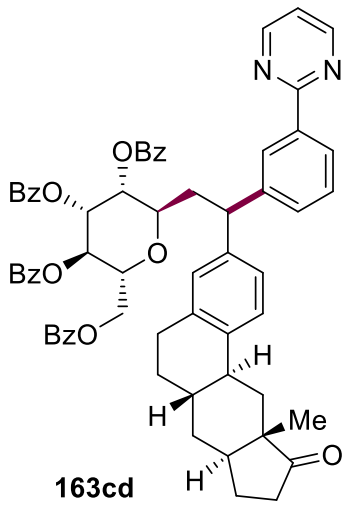




166cc

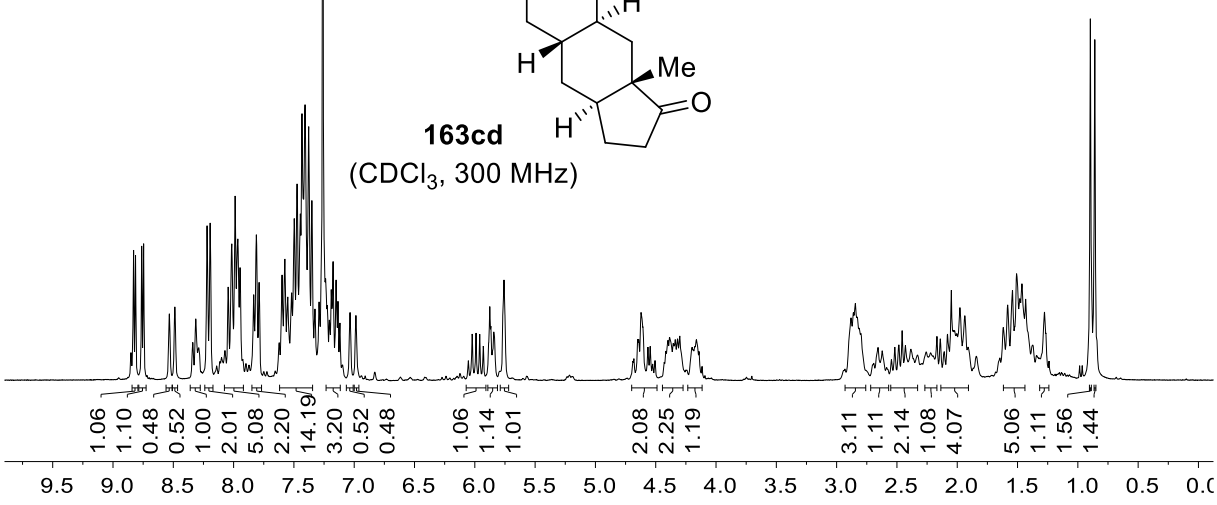
($CDCl_3$, 101 MHz)

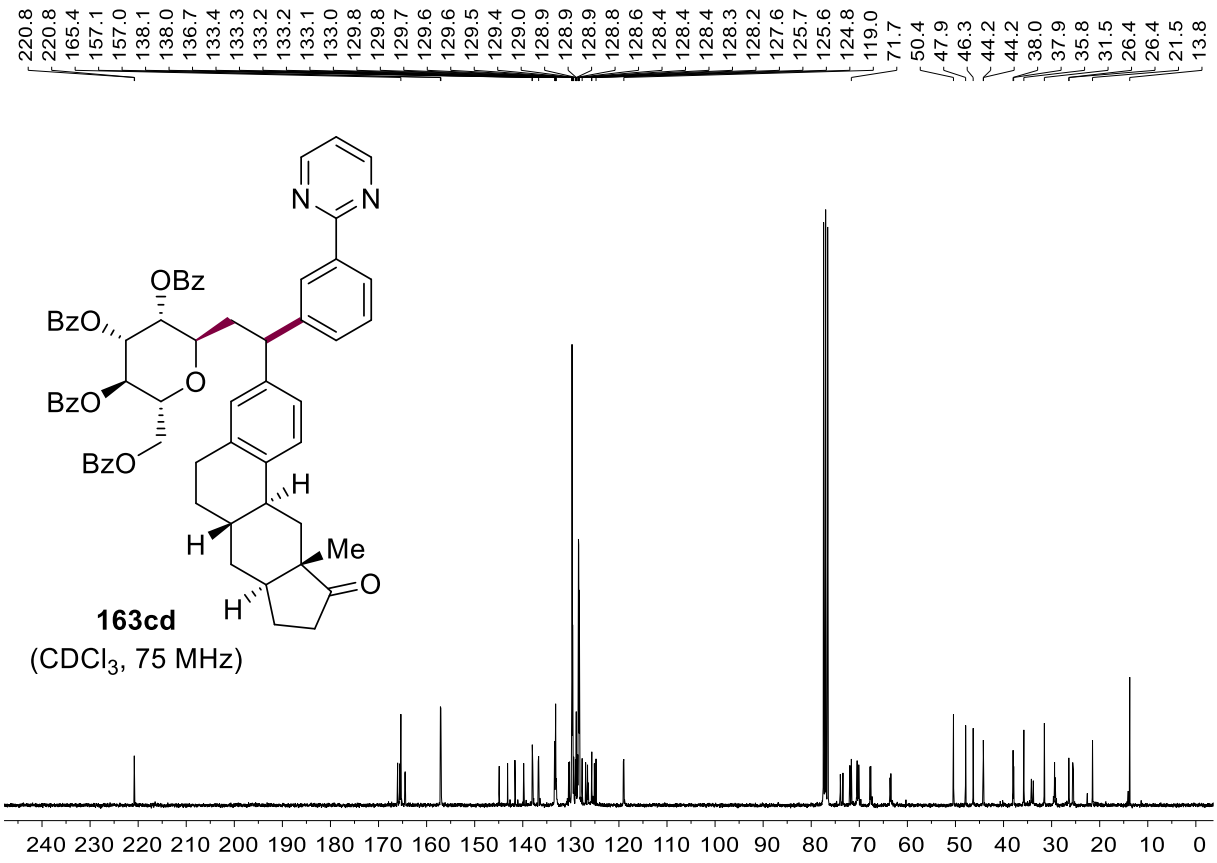


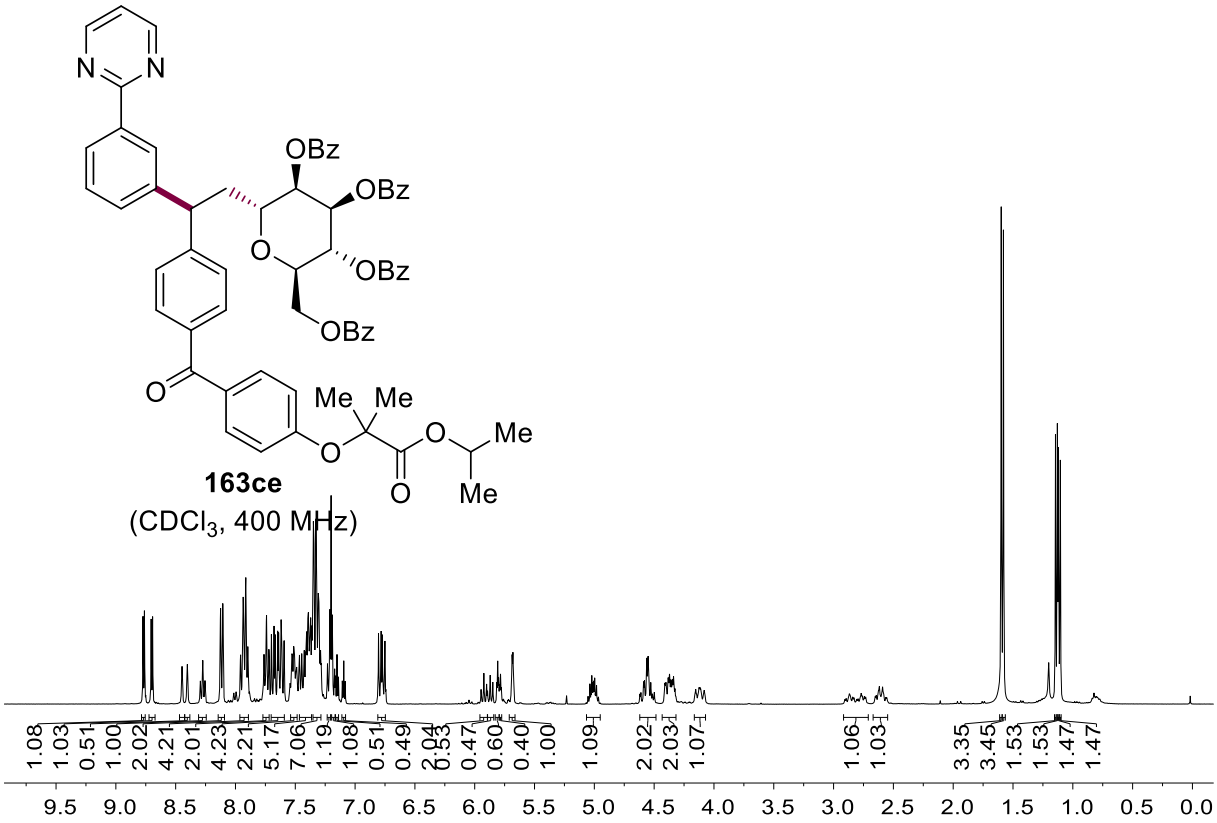


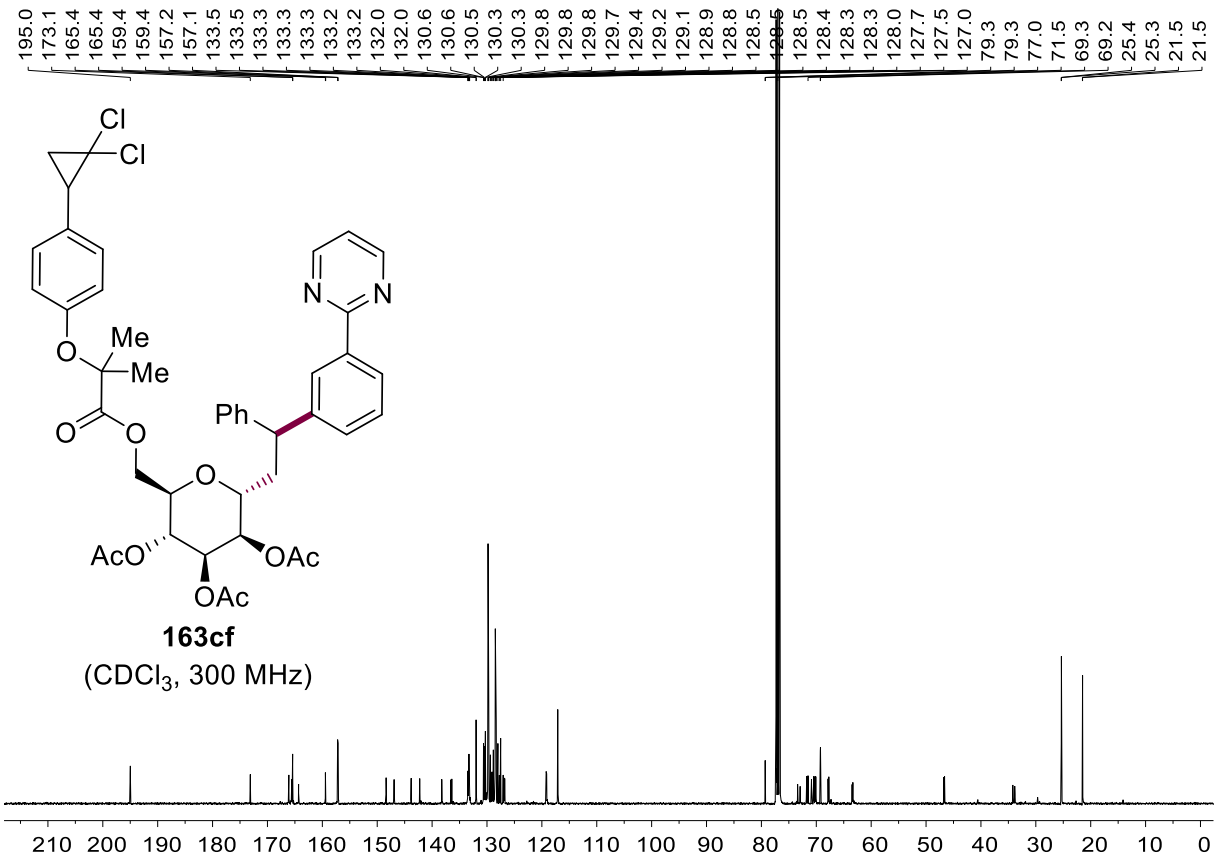
163cd

($CDCl_3$, 300 MHz)



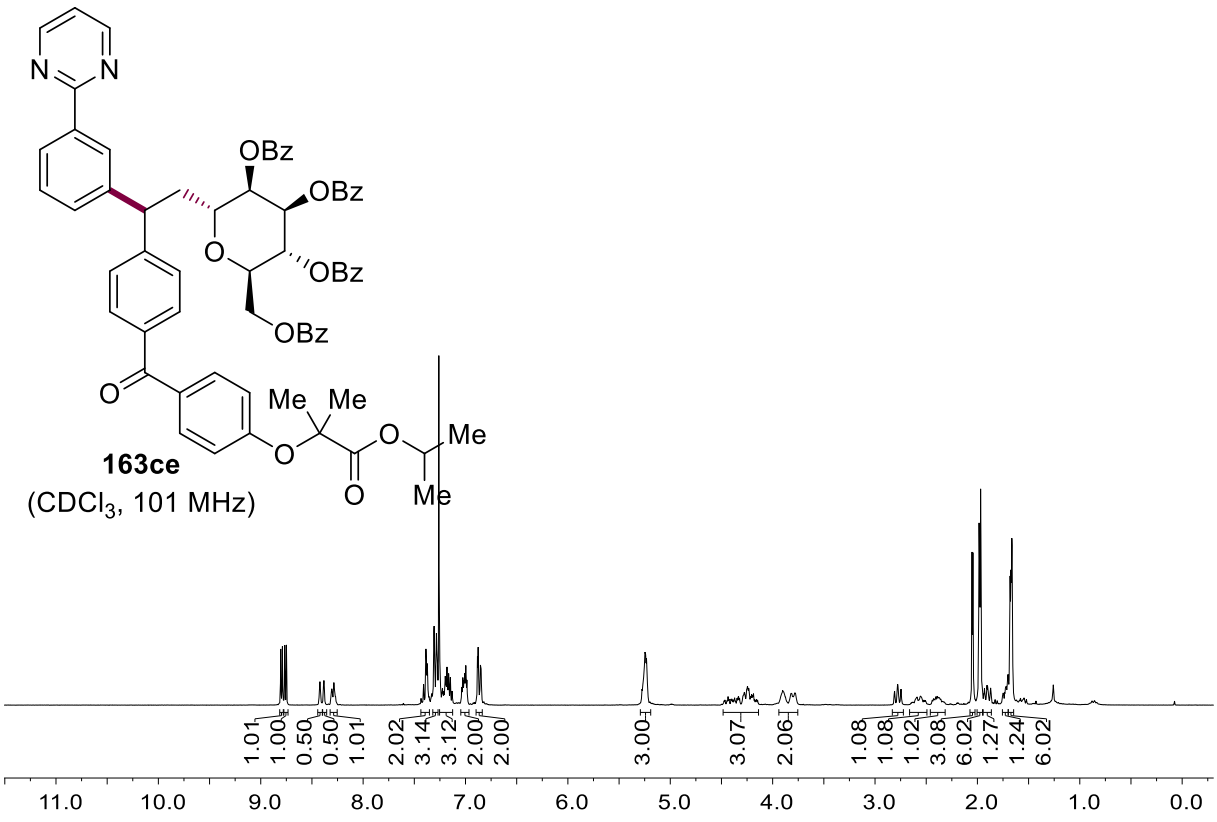

220.8 220.8 165.4 157.1 157.0 138.1 138.0 136.7 133.4 133.3 133.2 133.2 133.1 133.0 129.8 129.8 129.7 129.6 129.6 129.5 129.4 129.0 128.9 128.9 128.9 128.8 128.6 128.4 128.4 128.4 128.3 128.2 127.6 125.7 125.6 124.8 119.0 71.7 50.4 47.9 46.3 44.2 44.2 38.0 37.9 35.8 31.5 26.4 26.4 21.5 13.8
OBz
BzO
BzO
BzO
O
H
H
H
Me
O
163cd
(CDCl3, 75 MHz)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


OBz
OBz
OBz
OBz
O
O
Me Me
O
Me
O
Me
163ce
(CDCl3, 400 MHz)
1.08 1.03 0.51 1.00 2.02 4.21 2.01 4.23 2.21 5.17 7.06 1.19 1.08 0.51 0.49 2.04 0.53 0.47 0.60 0.40 1.00 1.09 2.02 2.03 1.07 1.06 1.03 3.35 3.45 1.53 1.53 1.47 1.47
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



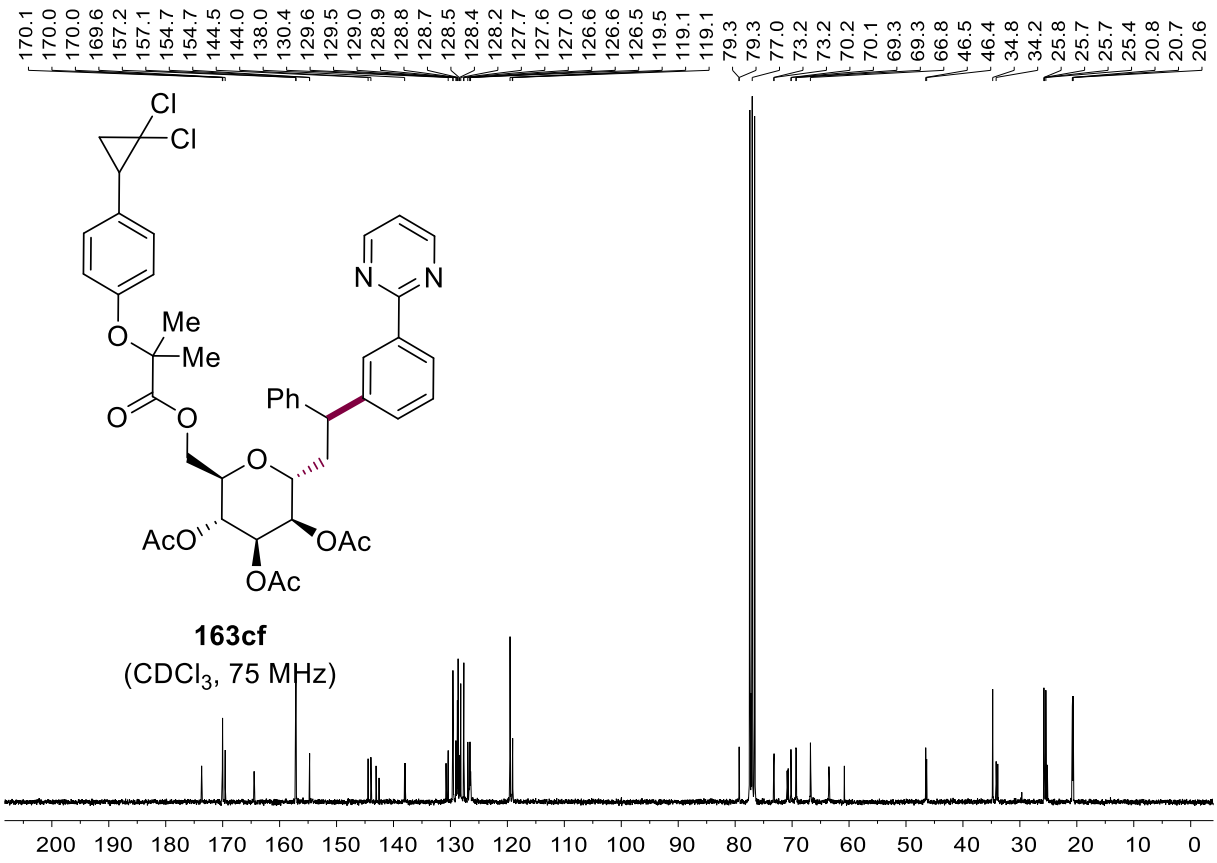
163cf

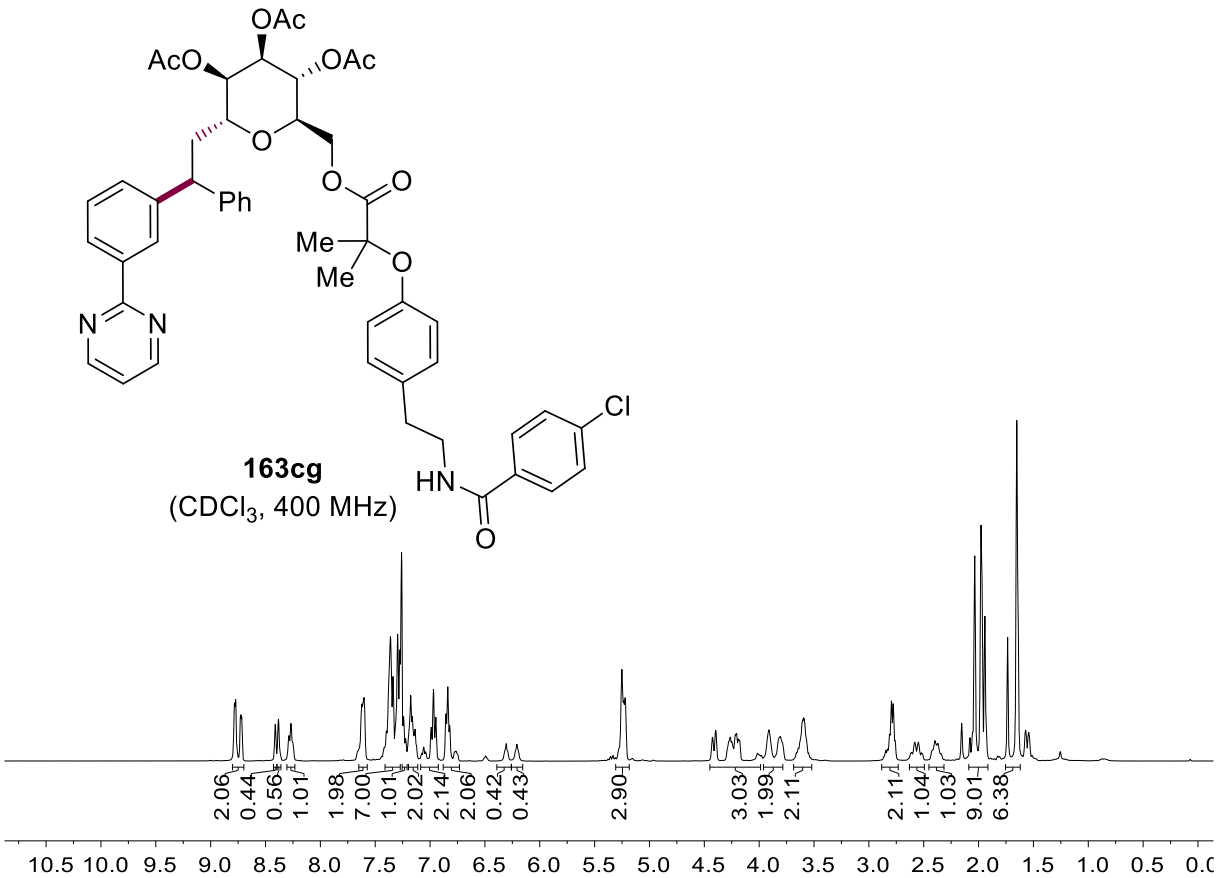
($CDCl_3$, 300 MHz)

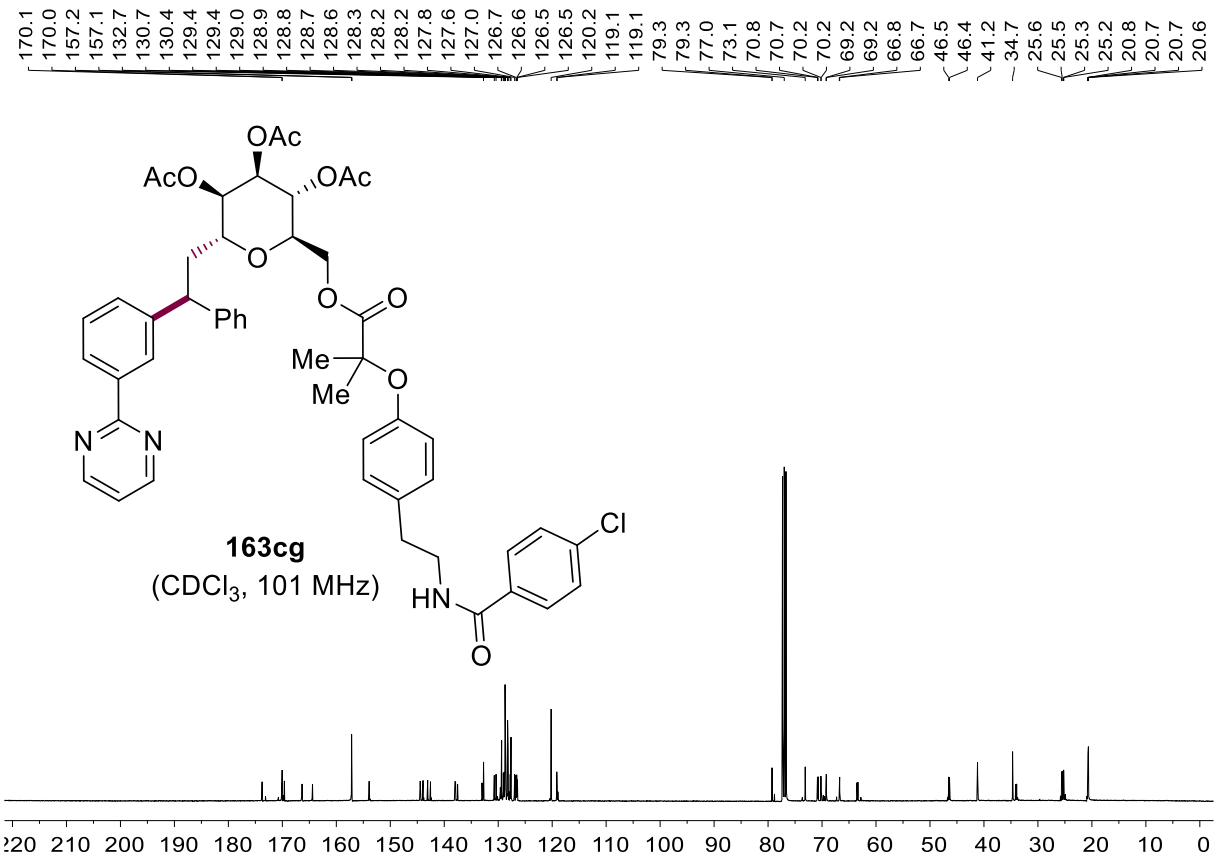


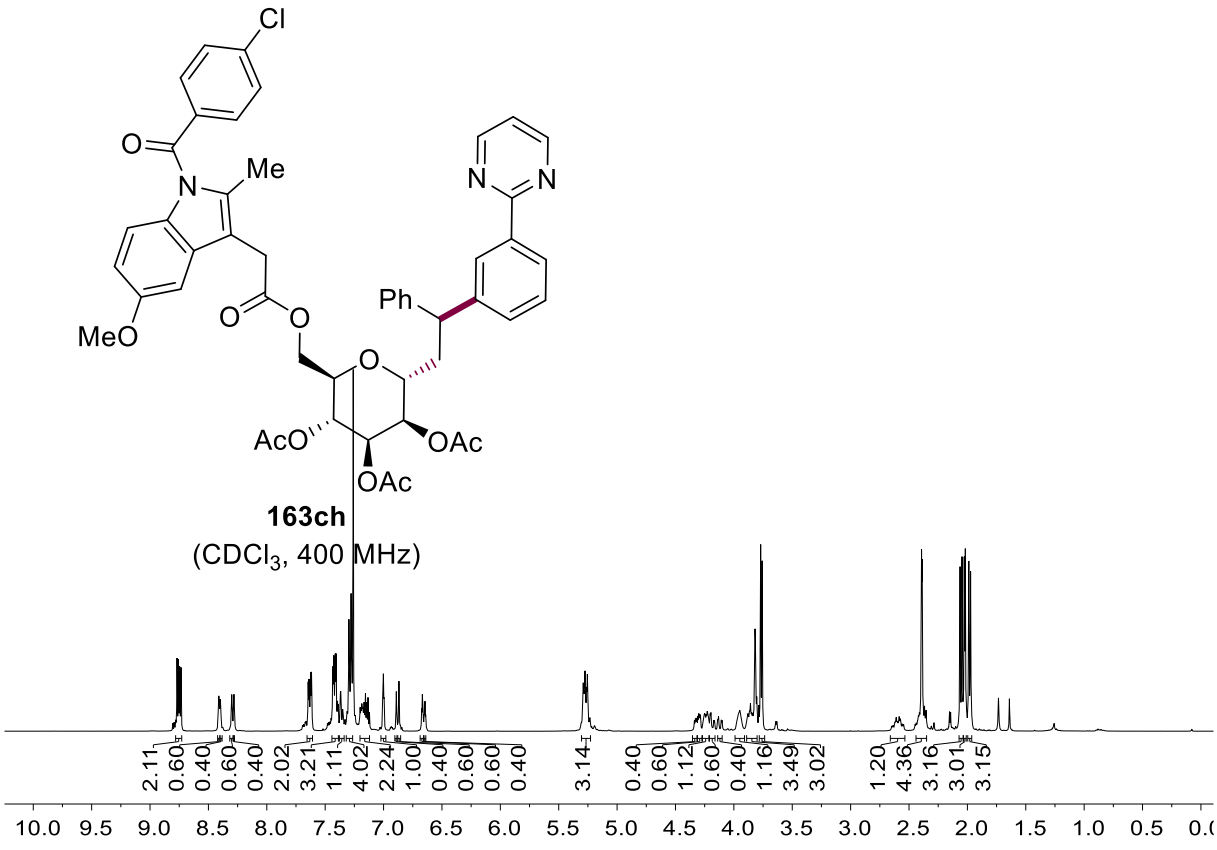
163ce

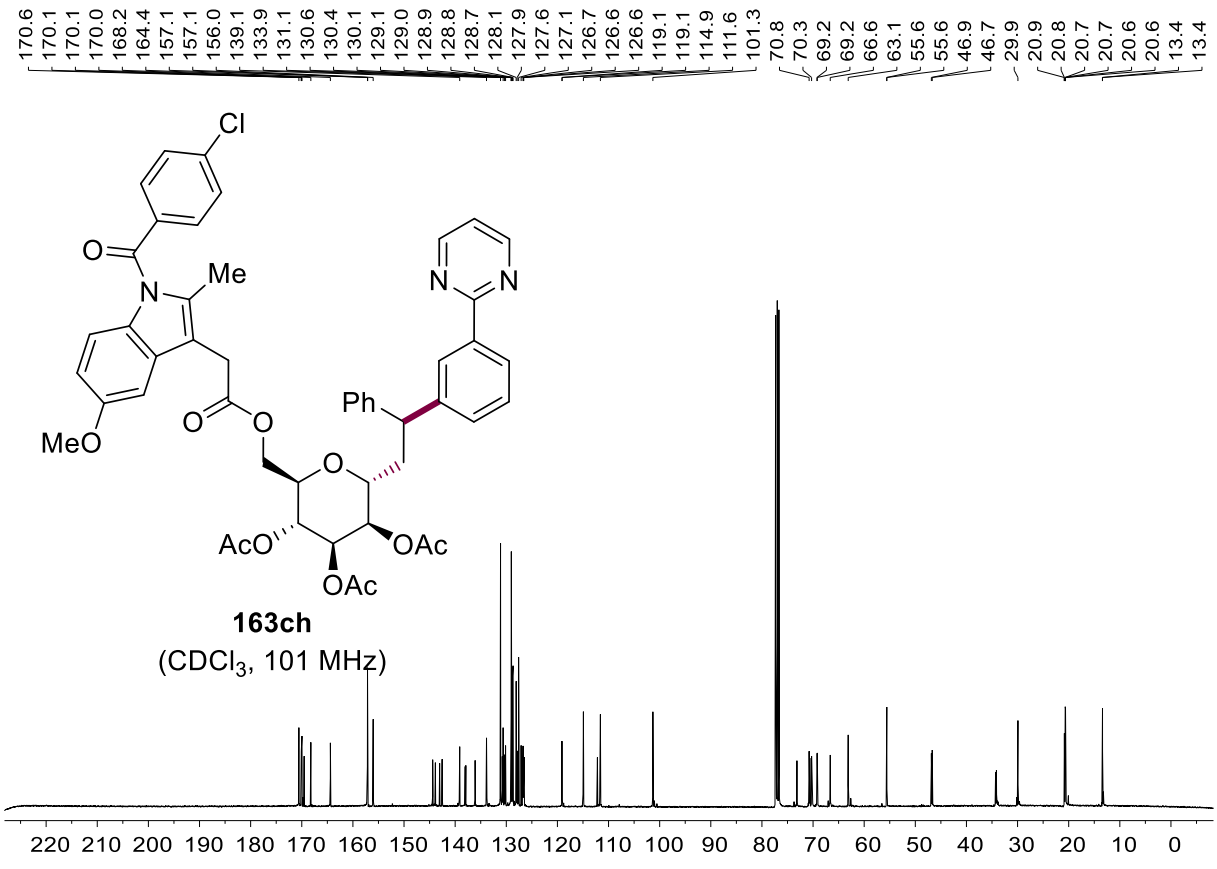
($CDCl_3$, 101 MHz)


170.1 170.0 170.0 169.6 157.2 157.1 154.7 154.7 144.5 144.0 138.0 130.4 129.6 129.5 129.0 128.9 128.8 128.7 128.5 128.4 128.2 127.7 127.6 127.0 126.6 126.6 126.5 119.5 119.1 119.1 79.3 79.3 77.0 73.2 73.2 70.2 70.1 69.3 69.3 66.8 46.5 46.4 34.8 34.2 25.8 25.7 25.7 25.4 20.8 20.7 20.6
Cl
Cl
Me
Me
O
O
O
O
N
N
Ph
AcO
OAc
OAc
163cf
(CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


OAc
AcO
OAc
O
Ph
O
O
Me
Me
O
N
N
Cl
HN
O
163cg
(CDCl3, 400 MHz)
2.06 0.44 0.56 1.01 1.98 7.00 1.01 2.02 2.14 2.06 0.42 0.43 2.90 3.03 1.99 2.11 2.11 1.04 1.03 9.01 6.38
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

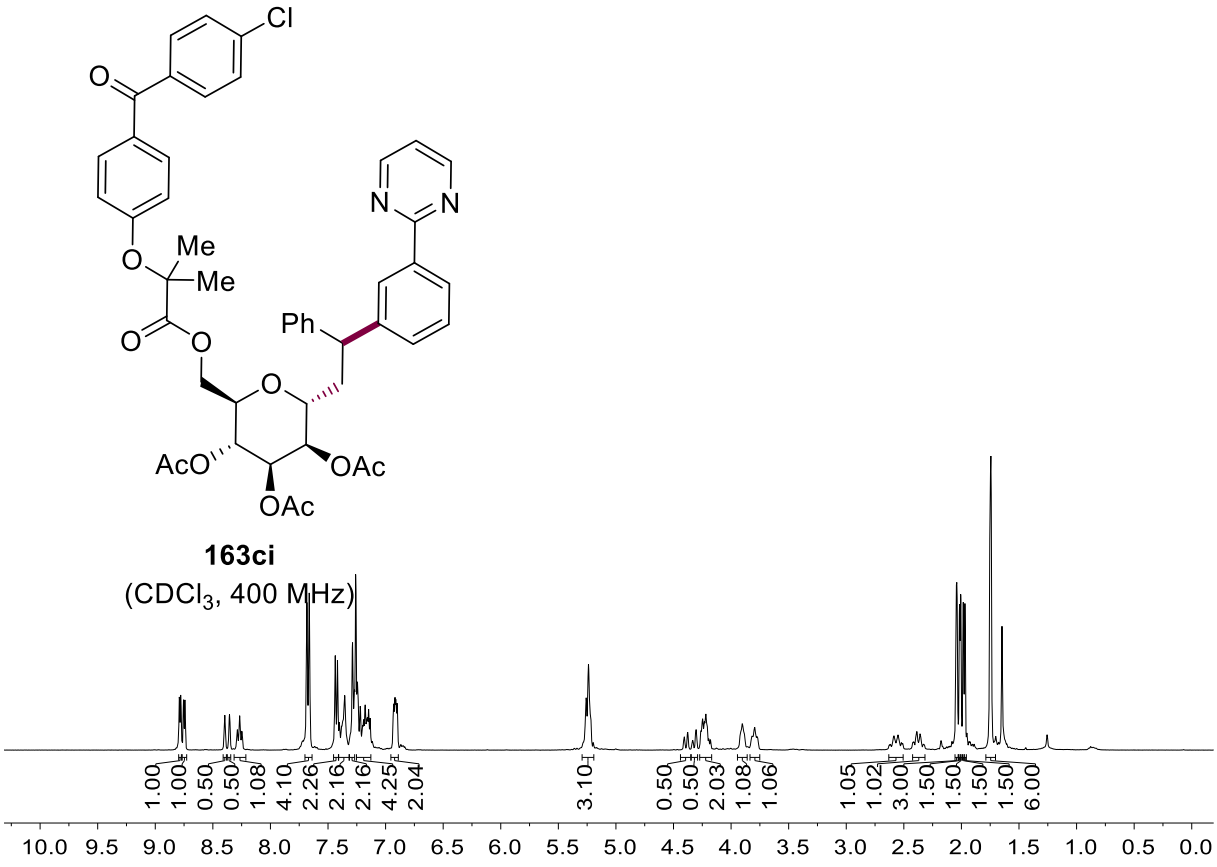

170.1
170.0
157.2
157.1
132.7
130.7
130.4
129.4
129.4
129.0
128.9
128.8
128.7
128.6
128.3
128.2
128.2
127.8
127.6
127.0
126.7
126.6
126.5
126.5
120.2
119.1
79.3
79.3
77.0
73.1
70.8
70.7
70.2
70.2
69.2
69.2
66.8
66.7
46.5
46.4
41.2
34.7
25.6
25.5
25.3
25.2
20.8
20.7
20.7
20.6
OAc
AcO
OAc
O
O
O
Ph
Me
Me
O
N
N
Cl
HN
O
163cg
(CDCl3, 101 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Cl
O
N
Me
N
N
Ph
MeO
O
O
O
AcO
OAc
OAc
163ch
(CDCl3, 400 MHz)
2.11
0.60
0.40
0.60
0.40
2.02
3.21
1.11
4.02
2.24
1.00
0.40
0.60
0.60
0.40
3.14
0.40
0.60
1.12
0.60
0.40
1.16
3.49
3.02
1.20
4.36
3.16
3.01
3.15
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



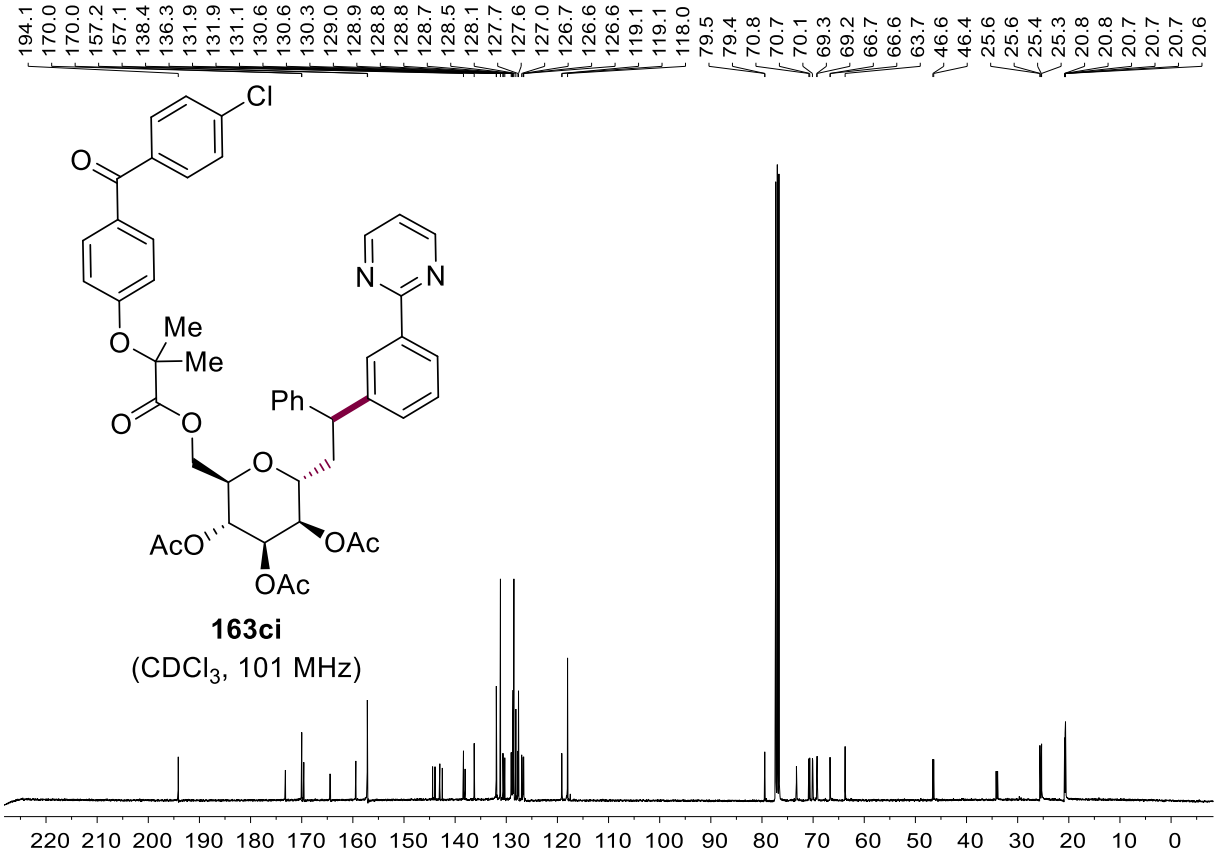
163ch

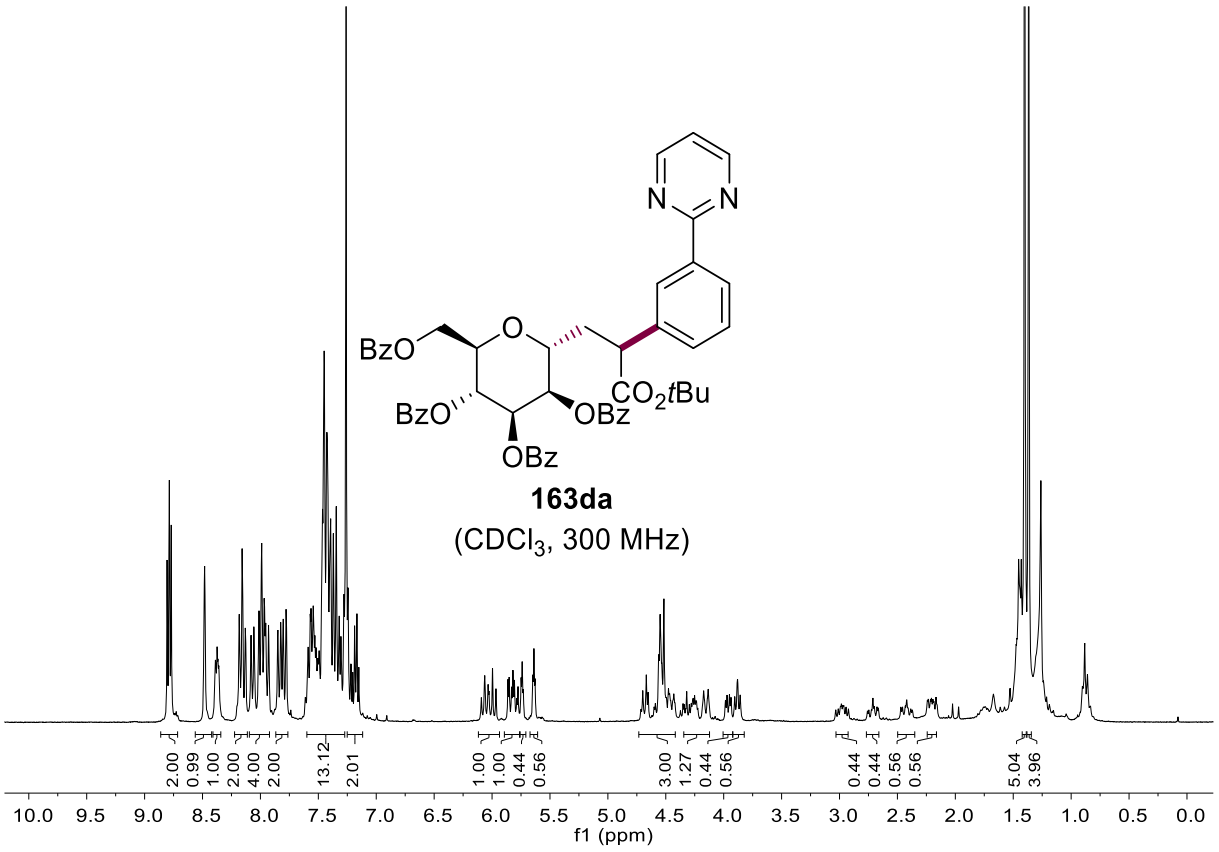
($CDCl_3$, 101 MHz)

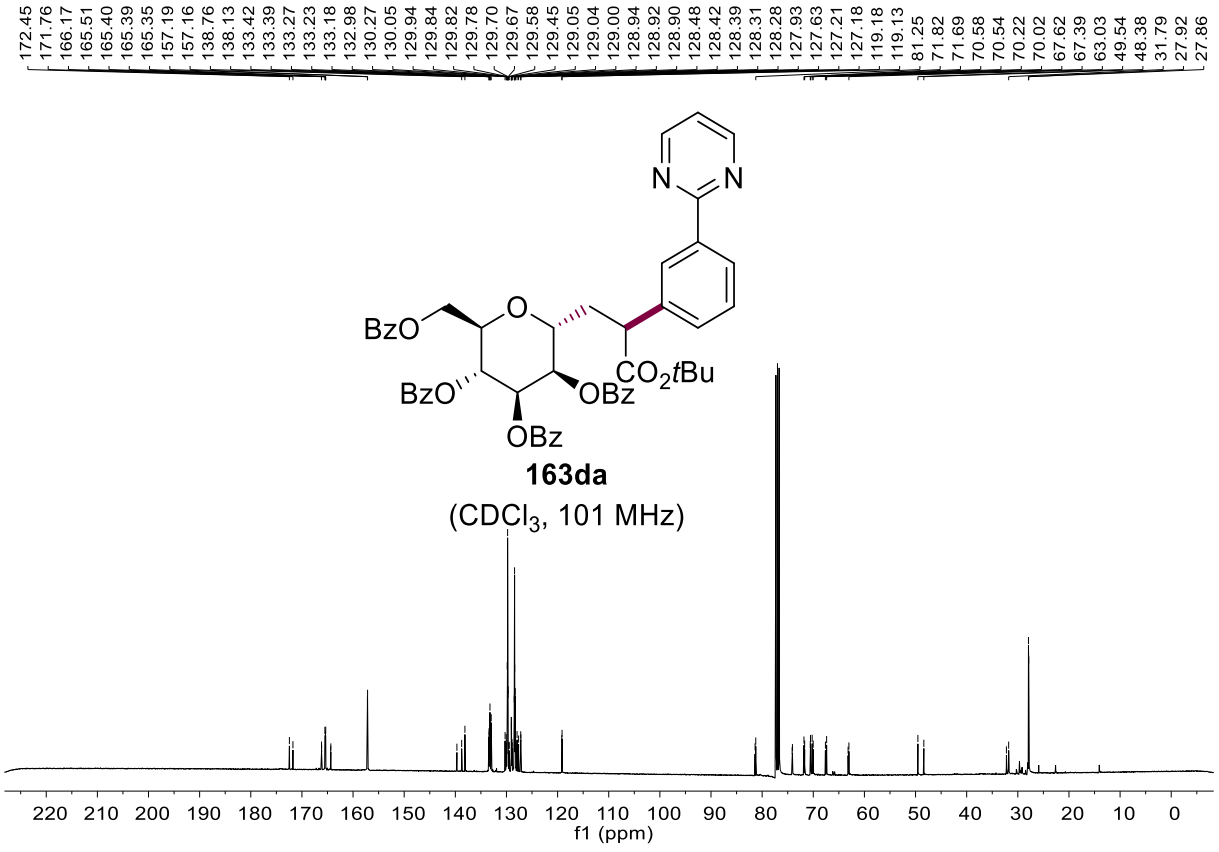


163ci

($CDCl_3$, 400 MHz)

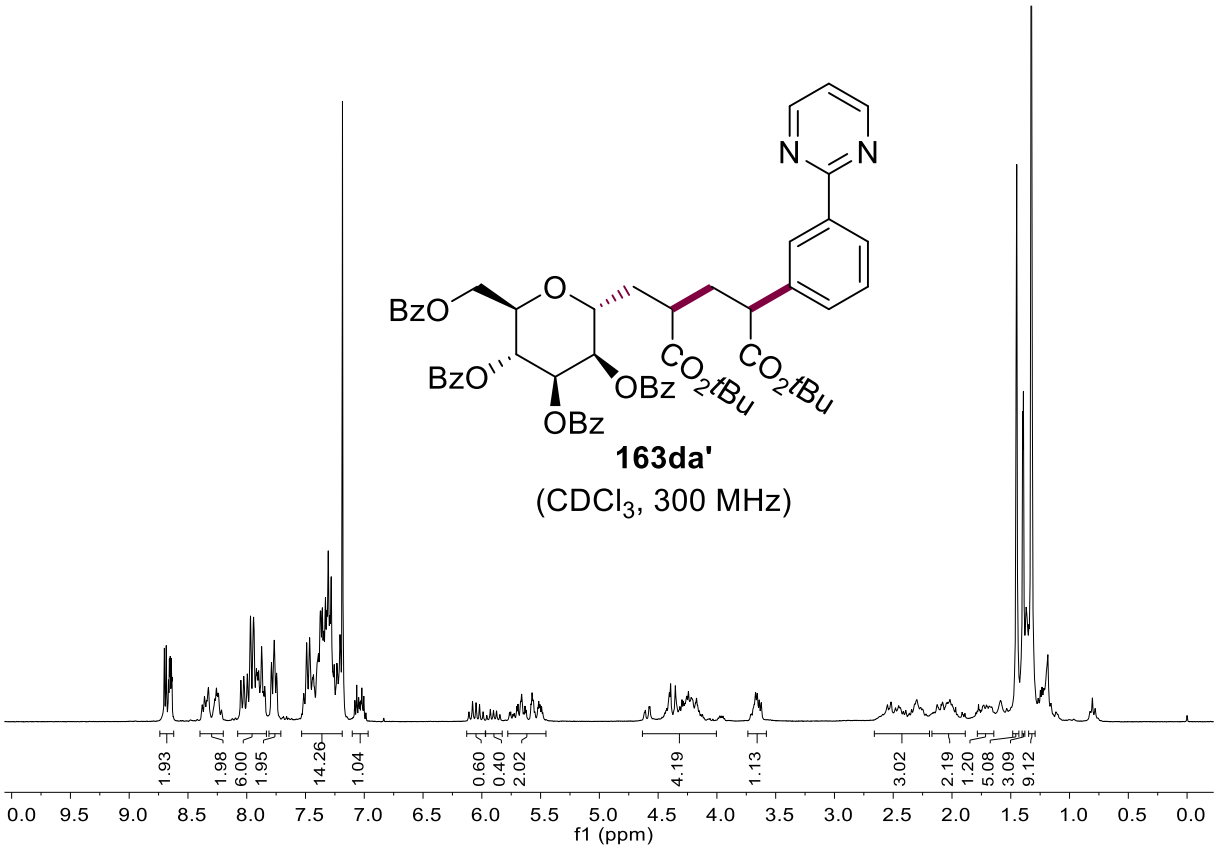

194.1 170.0 170.0 157.2 157.1 138.4 136.3 131.9 131.9 131.1 130.6 130.6 130.3 129.0 128.9 128.8 128.8 128.7 128.5 128.1 127.7 127.6 127.0 126.7 126.6 126.6 119.1 119.1 118.0 79.5 79.4 70.8 70.7 70.1 69.3 69.2 66.7 66.6 63.7 46.6 46.4 25.6 25.6 25.4 25.3 20.8 20.8 20.7 20.7 20.7 20.6
Cl
O
O
Me
Me
O
O
Ph
N
N
O
AcO
OAc
OAc
163ci
(CDCl3, 101 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


N
N
BzO
O
BzO
OBz
CO2tBu
OBz
163da
(CDCl3, 300 MHz)
2.00 0.99 1.00 2.00 4.00 2.00 13.12 2.01 1.00 1.00 0.44 0.56 3.00 1.27 0.44 0.56 0.44 0.44 0.56 0.56 5.04 3.96
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
f1 (ppm)



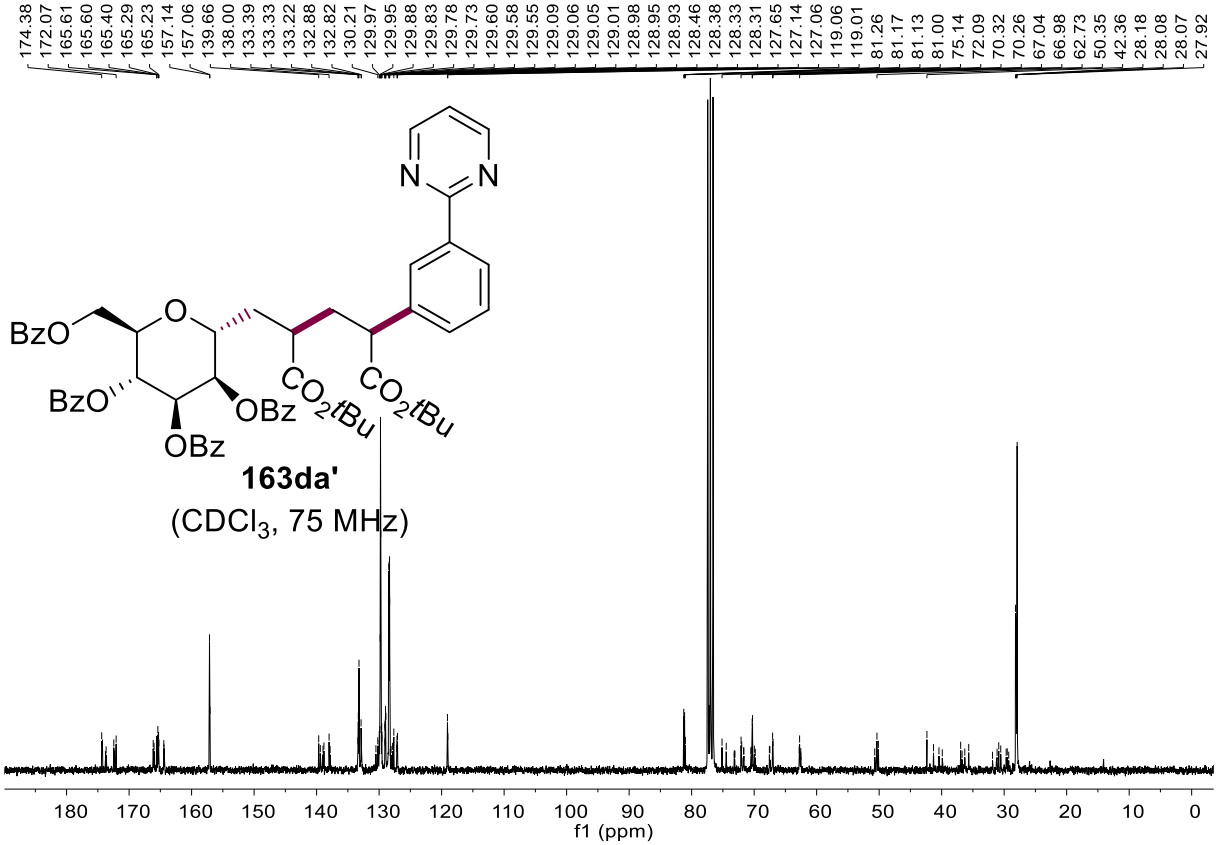
163da

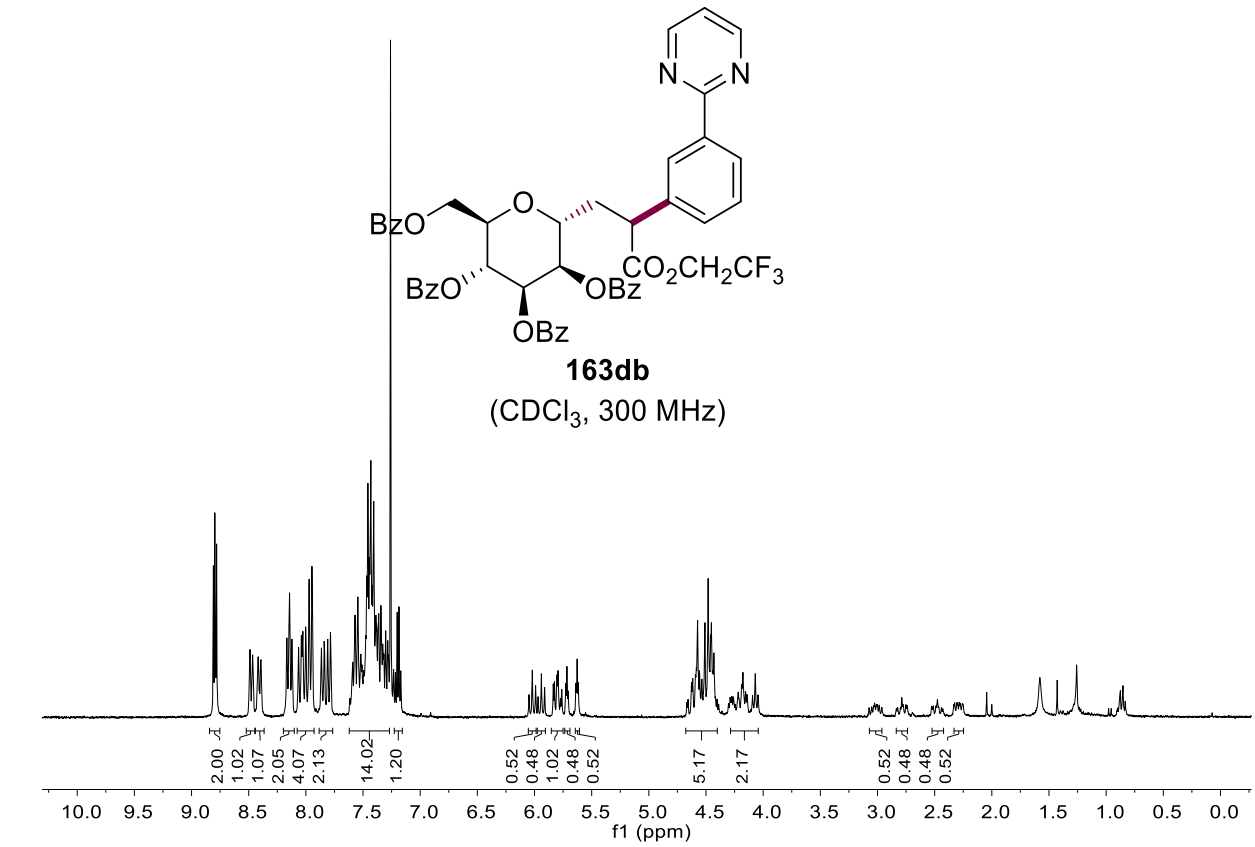
($CDCl_3$, 101 MHz)

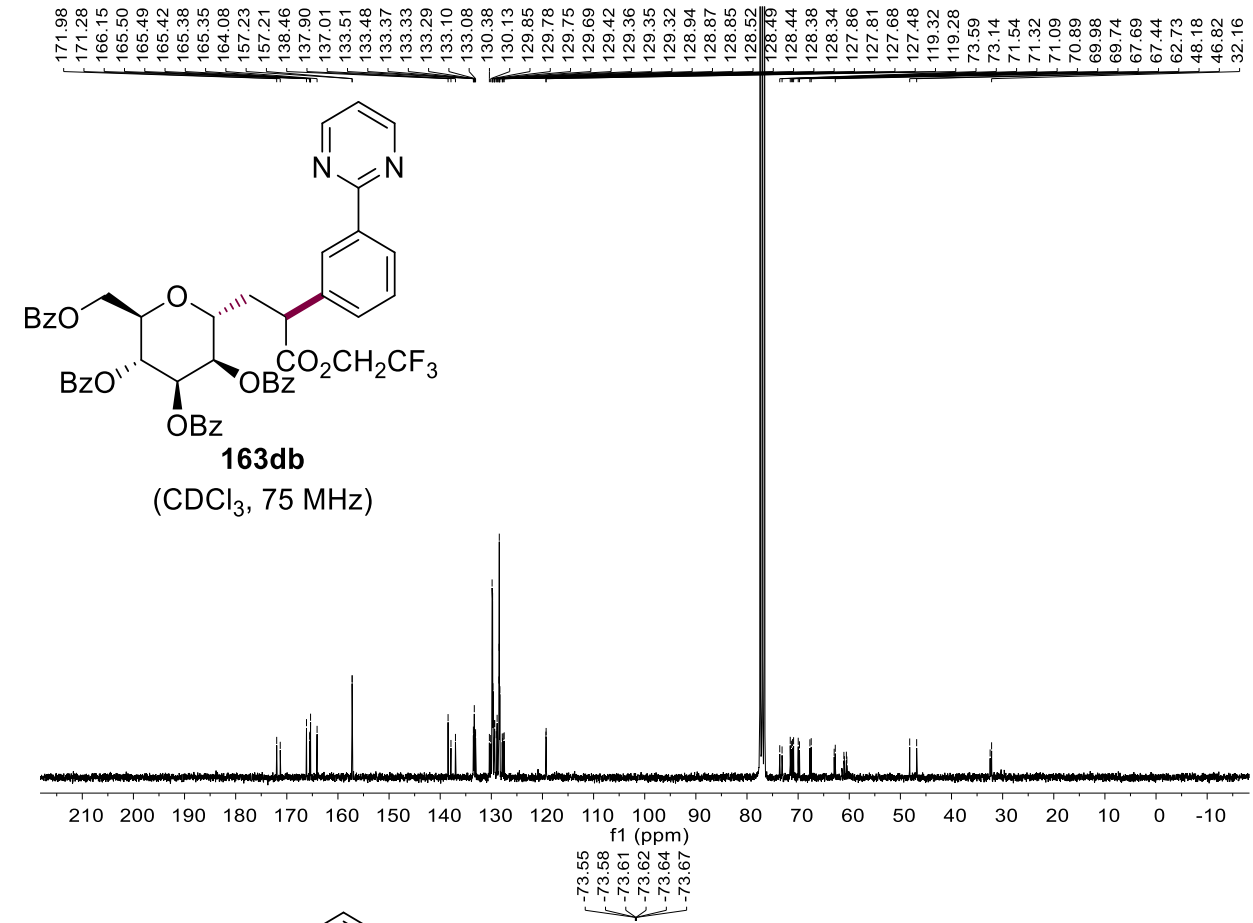


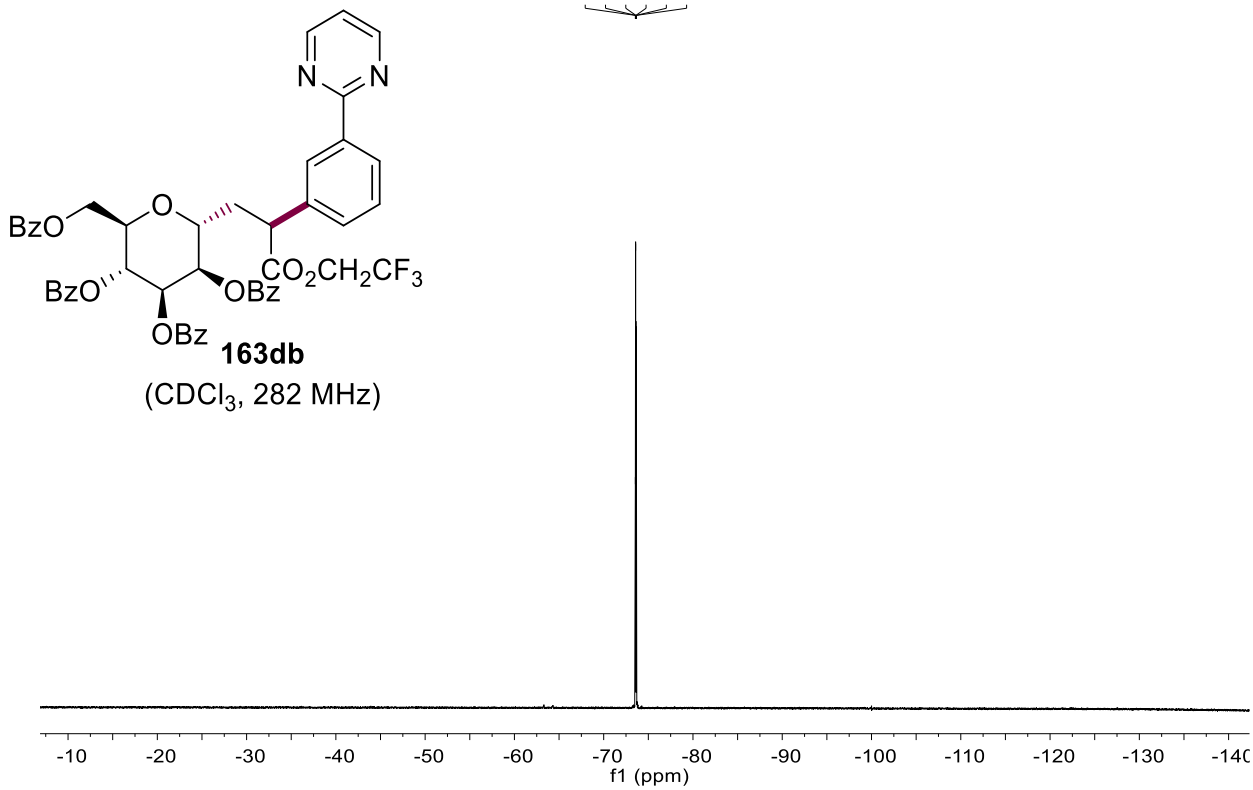
163da'

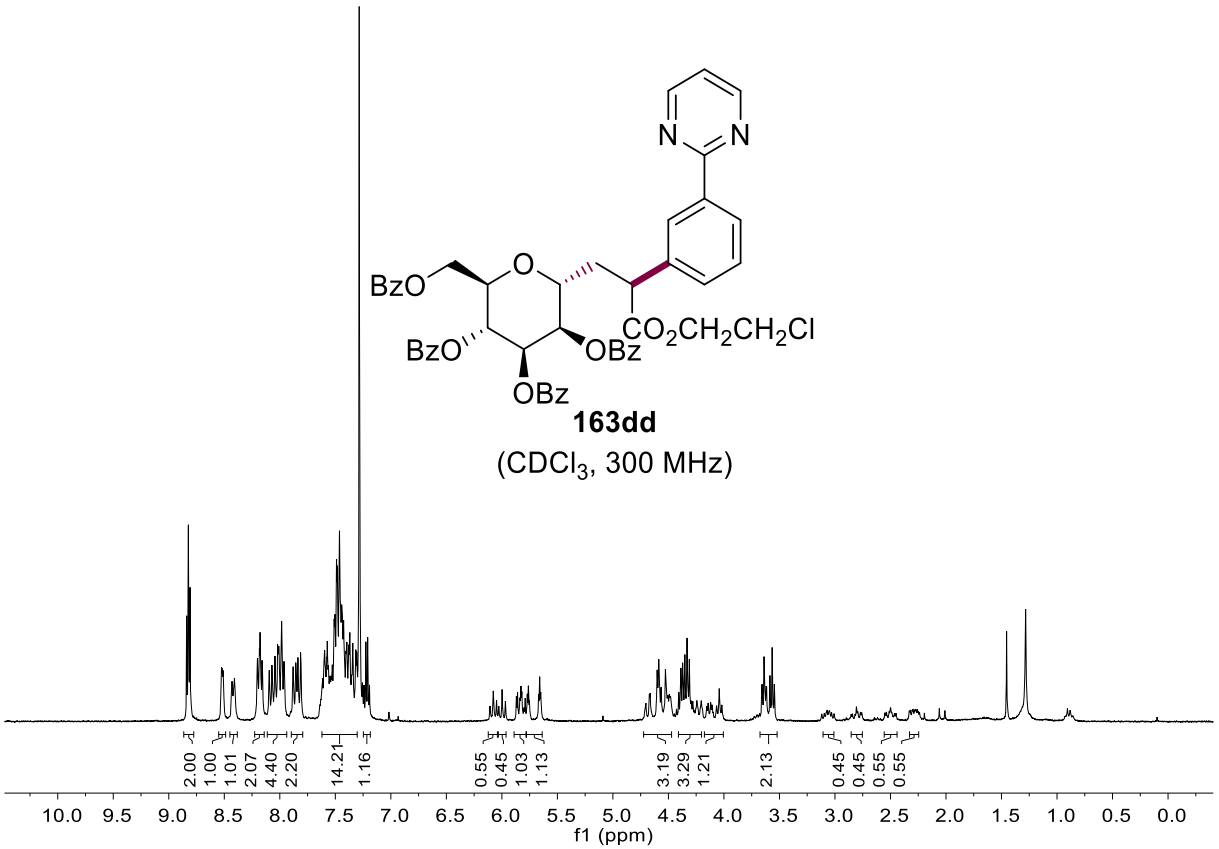
($CDCl_3$, 300 MHz)

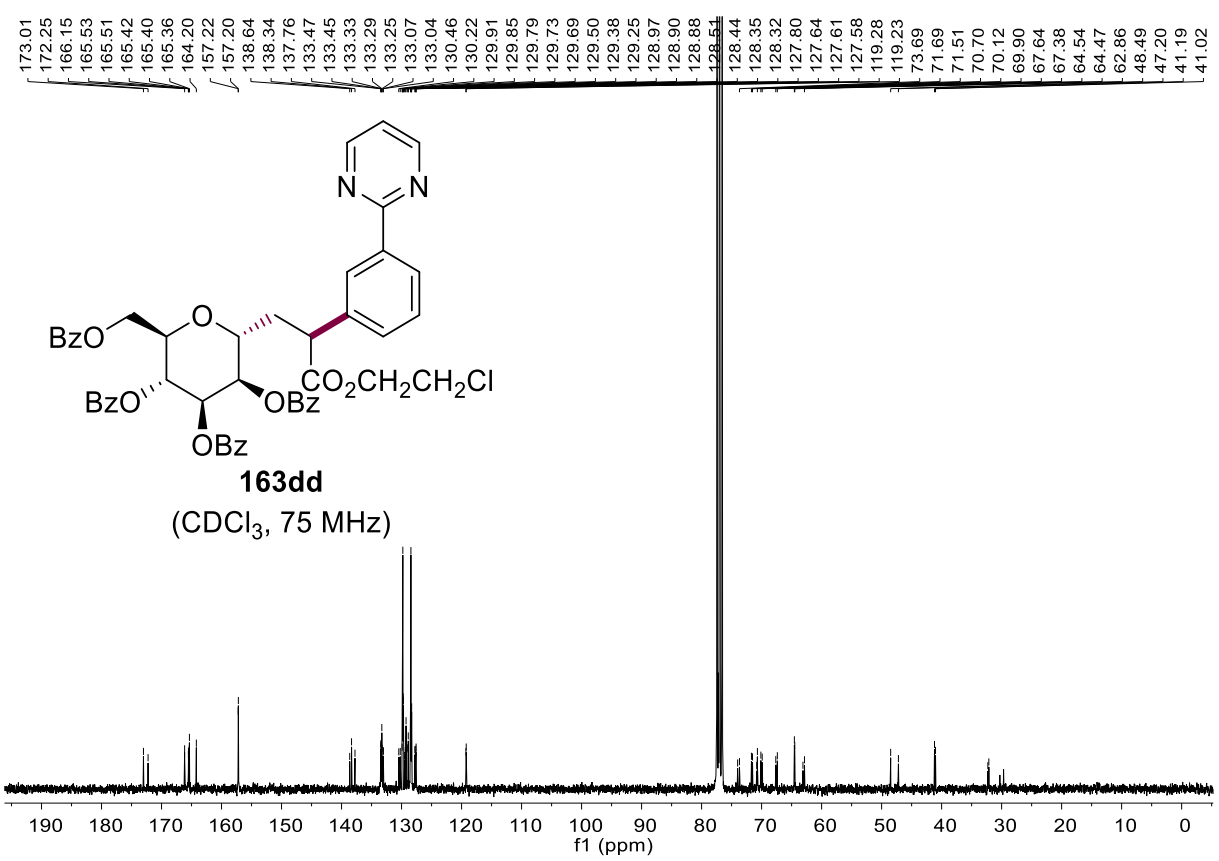

174.38
172.07
165.61
165.60
165.40
165.29
165.23
157.14
157.06
139.66
138.00
133.39
133.33
133.22
132.88
132.82
130.21
129.97
129.95
129.88
129.83
129.78
129.73
129.60
129.58
129.55
129.09
129.06
129.05
129.01
128.98
128.95
128.93
128.46
128.38
128.33
128.31
127.65
127.14
127.06
119.06
119.01
81.26
81.17
81.13
81.00
75.14
72.09
70.32
70.26
67.04
66.98
62.73
50.35
42.36
28.18
28.08
28.07
27.92
N
N
O
BzO
BzO
OBz
OBz
CO2tBu
CO2tBu
163da'
(CDCl3, 75 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

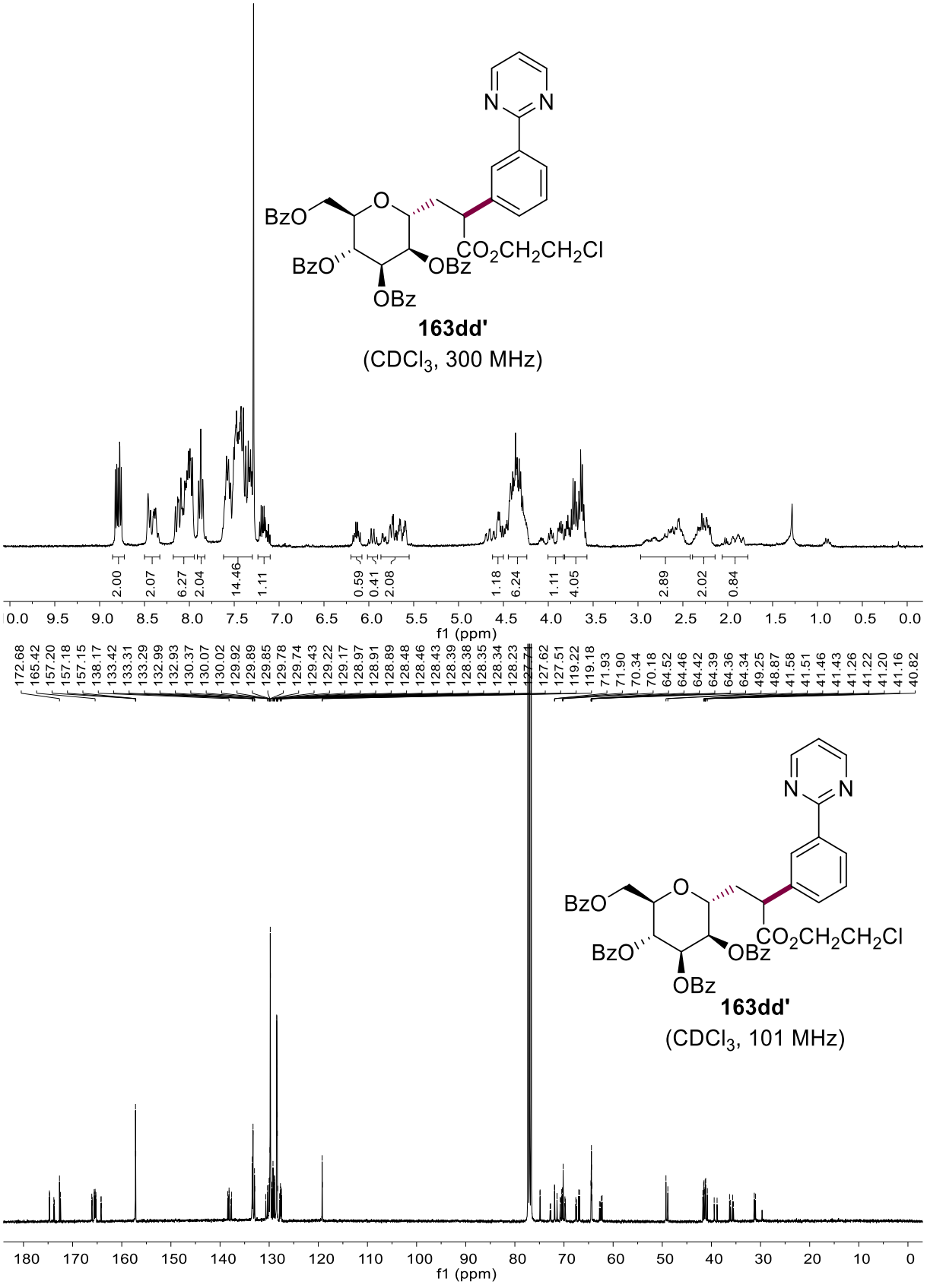

N
N
O
BzO
BzO
OBz
OBz
CO2CH2CF3
163db
(CDCl3, 300 MHz)
2.00
1.02
1.07
2.05
4.07
2.13
14.02
1.20
0.52
0.48
1.02
0.48
0.52
5.17
2.17
0.52
0.48
0.52
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

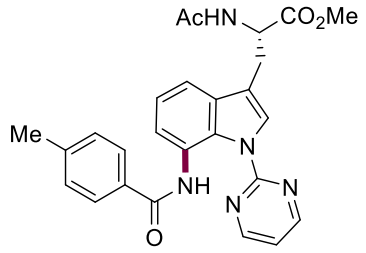

171.98
171.28
166.15
165.50
165.49
165.42
165.38
165.35
164.08
157.23
157.21
138.46
137.90
137.01
133.51
133.48
133.37
133.33
133.29
133.10
133.08
130.38
130.13
129.85
129.78
129.75
129.69
129.42
129.36
129.35
129.32
128.94
128.87
128.85
128.52
128.49
128.44
128.38
128.34
127.86
127.81
127.68
127.48
119.32
119.28
73.59
73.14
71.54
71.32
71.09
70.89
69.98
69.74
67.69
67.44
62.73
48.18
46.82
32.16
N
N
BzO
O
BzO
OBz
CO2CH2CF3
OBz
163db
(CDCl3, 75 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-73.55
-73.58
-73.61
-73.62
-73.64
-73.67
N
N
BzO
O
BzO
OBz
CO2CH2CF3
OBz
163db
(CDCl3, 282 MHz)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

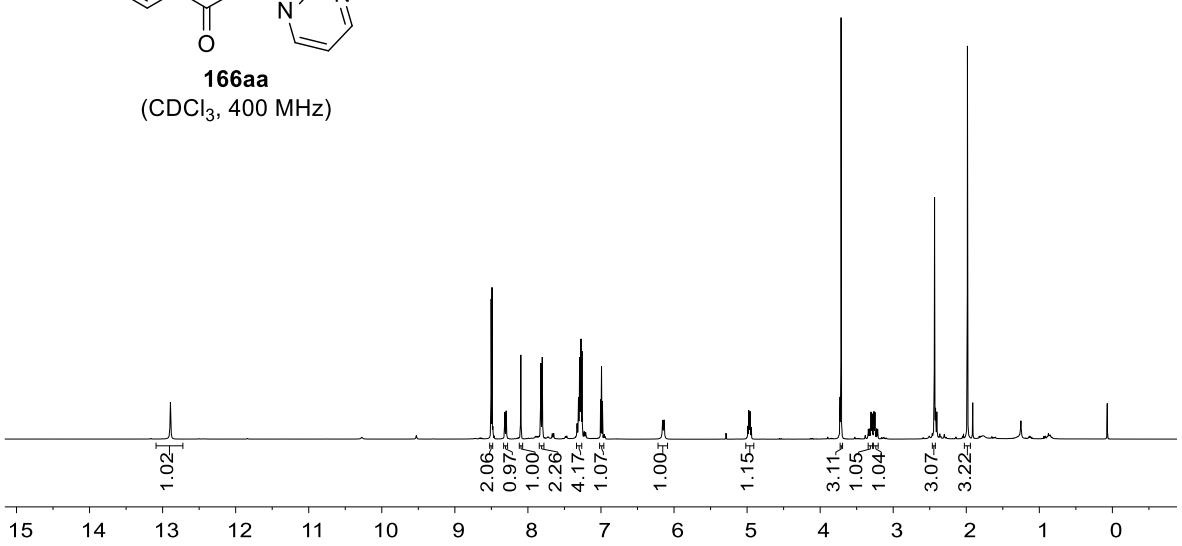

BzO
BzO
OBz
OBz
O
N
N
CO2CH2CH2Cl
163dd
(CDCl3, 300 MHz)
2.00
1.00
1.01
2.07
4.40
2.20
14.21
1.16
0.55
0.45
1.03
1.13
3.19
3.29
1.21
2.13
0.45
0.45
0.55
0.55
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

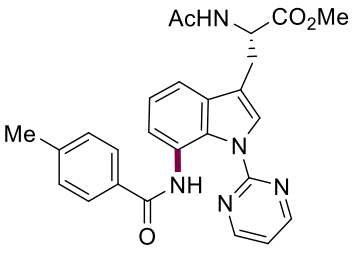

173.01
172.25
166.15
165.53
165.51
165.42
165.40
165.36
164.20
157.22
157.20
138.64
138.34
137.76
133.47
133.45
133.33
133.29
133.25
133.07
133.04
130.46
130.22
129.91
129.85
129.79
129.73
129.69
129.50
129.38
129.25
128.97
128.90
128.88
128.51
128.44
128.35
128.32
127.80
127.64
127.61
127.58
119.28
119.23
73.69
71.69
71.51
70.70
70.12
69.90
67.64
67.38
64.54
64.47
62.86
48.49
47.20
41.19
41.02
BzO
BzO
OBz
OBz
O
N
N
CO2CH2CH2Cl
163dd
(CDCl3, 75 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


BzO
BzO
OBz
OBz
O
N
N
CO2CH2CH2Cl
163dd'
(CDCl3, 300 MHz)
2.00
2.07
6.27
2.04
14.46
1.11
0.59
0.41
2.08
1.18
6.24
1.11
4.05
2.89
2.02
0.84
f1 (ppm)
172.68
165.42
157.20
157.18
157.15
138.17
133.42
133.31
133.29
132.99
132.93
130.37
130.07
130.02
129.92
129.89
129.85
129.78
129.74
129.43
129.22
129.17
128.97
128.91
128.89
128.48
128.46
128.43
128.39
128.38
128.35
128.34
128.23
127.74
127.62
127.51
119.22
119.18
71.93
71.90
70.34
70.18
64.52
64.46
64.42
64.39
64.36
64.34
49.25
48.87
41.58
41.51
41.46
41.43
41.26
41.22
41.20
41.16
40.82
BzO
BzO
OBz
OBz
O
N
N
CO2CH2CH2Cl
163dd'
(CDCl3, 101 MHz)
f1 (ppm)

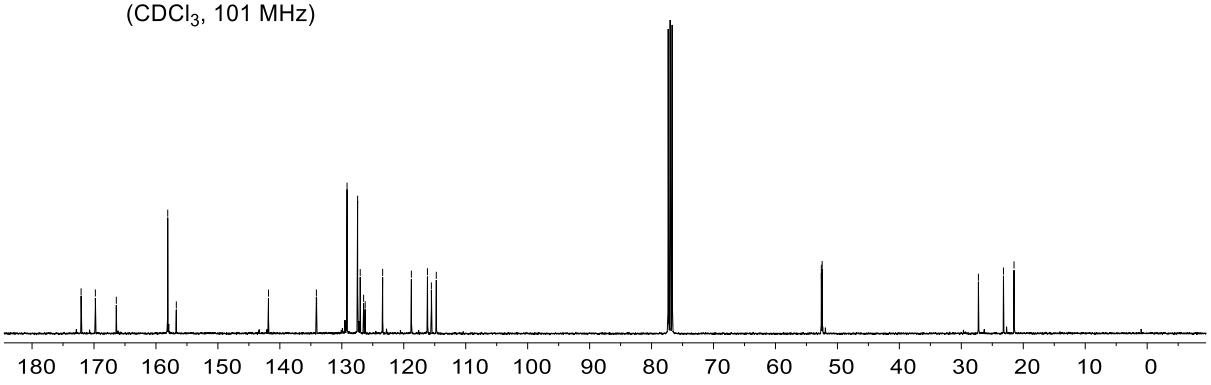


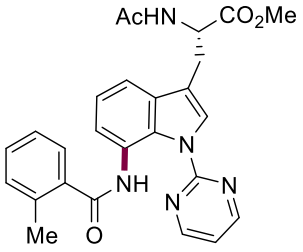
166aa
($CDCl_3$, 400 MHz)



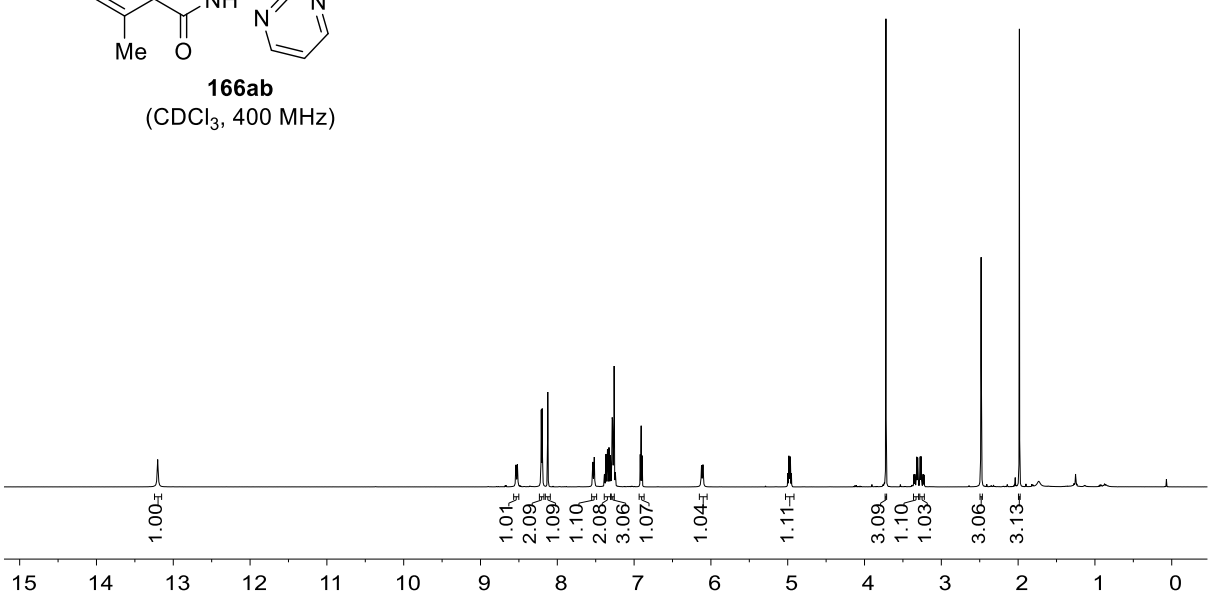


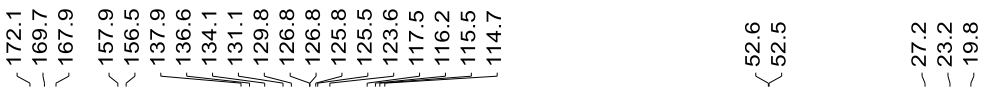
166aa
($CDCl_3$, 101 MHz)

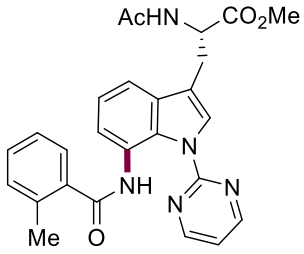




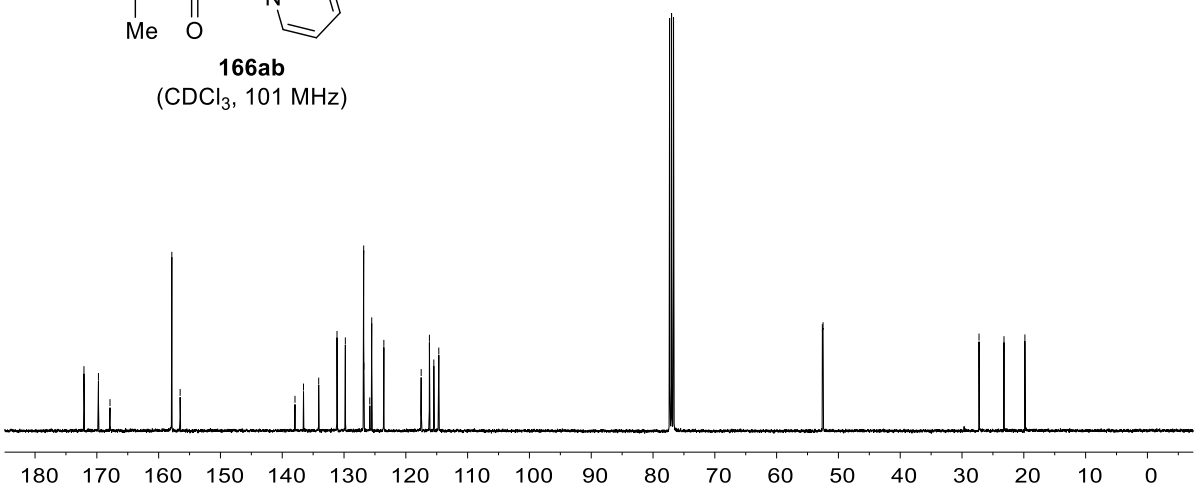
166ab
($CDCl_3$, 400 MHz)

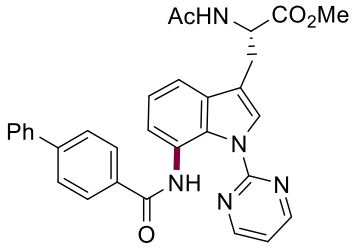




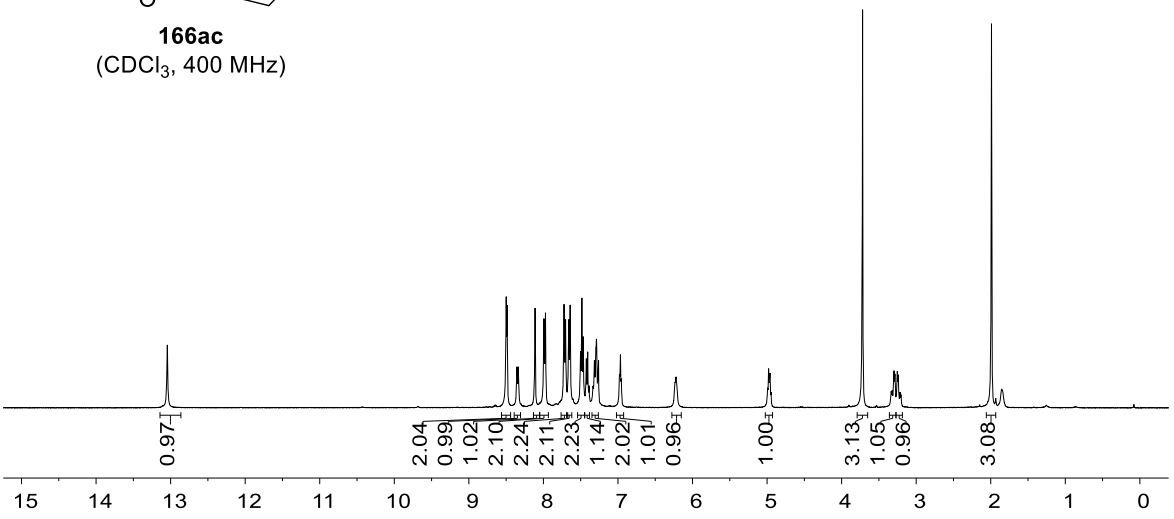


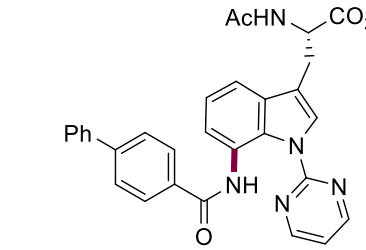
166ab
($CDCl_3$, 101 MHz)



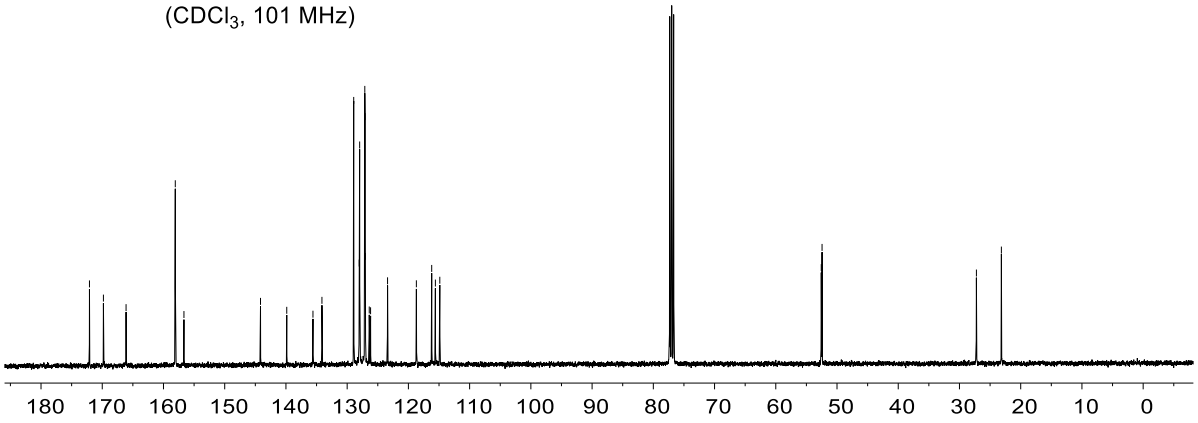


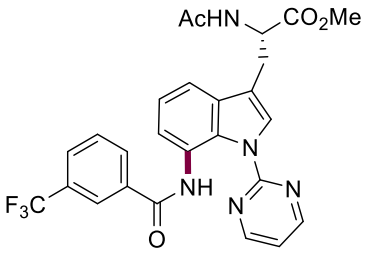
166ac
($CDCl_3$, 400 MHz)





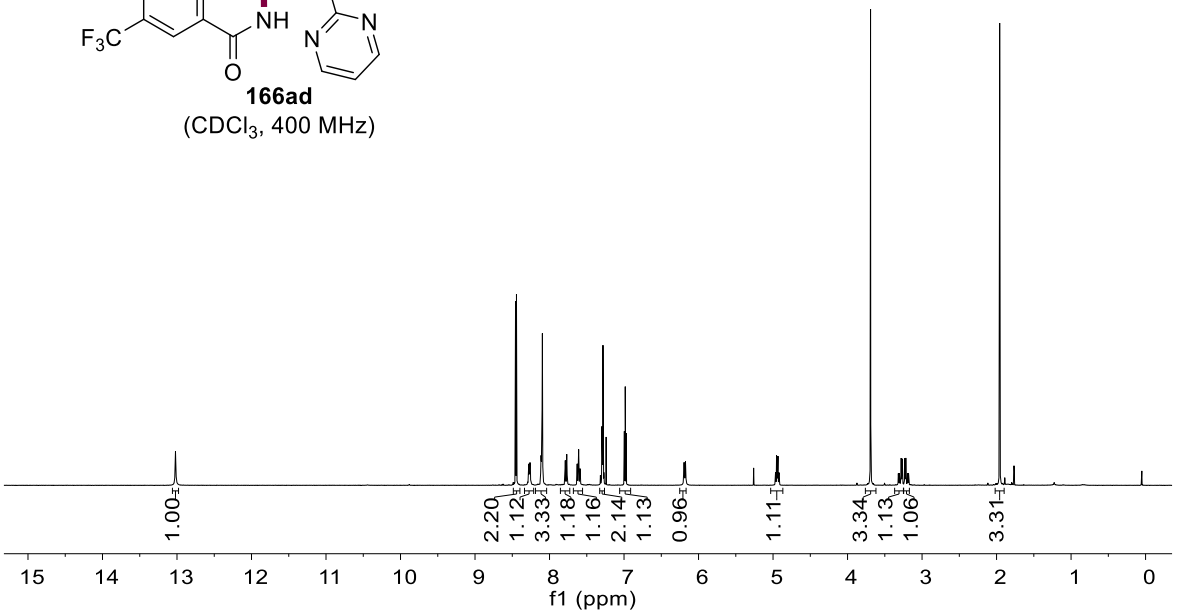
166ac
($CDCl_3$, 101 MHz)

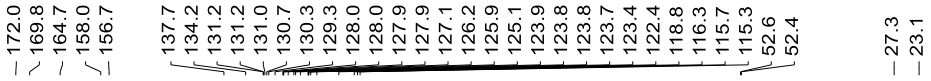


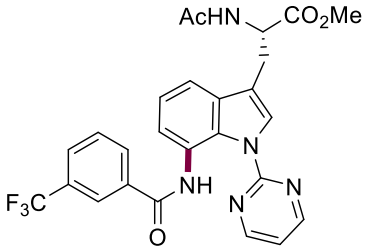


166ad

($CDCl_3$, 400 MHz)

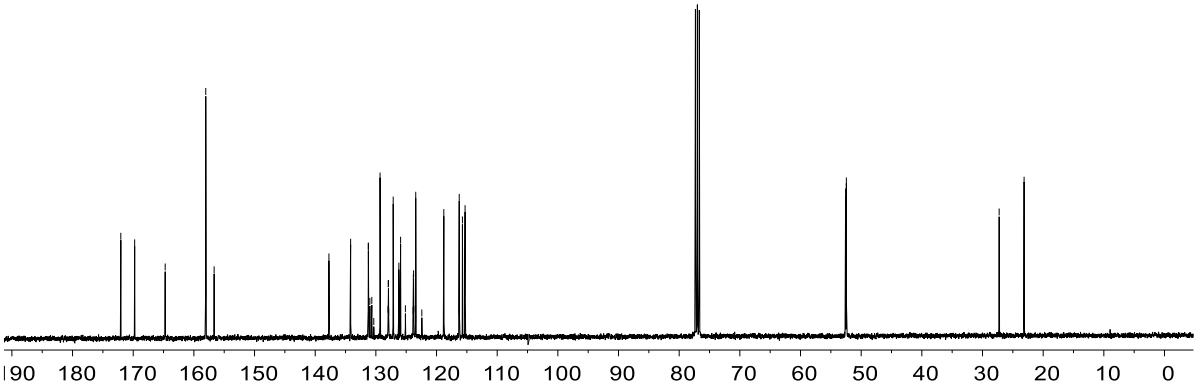


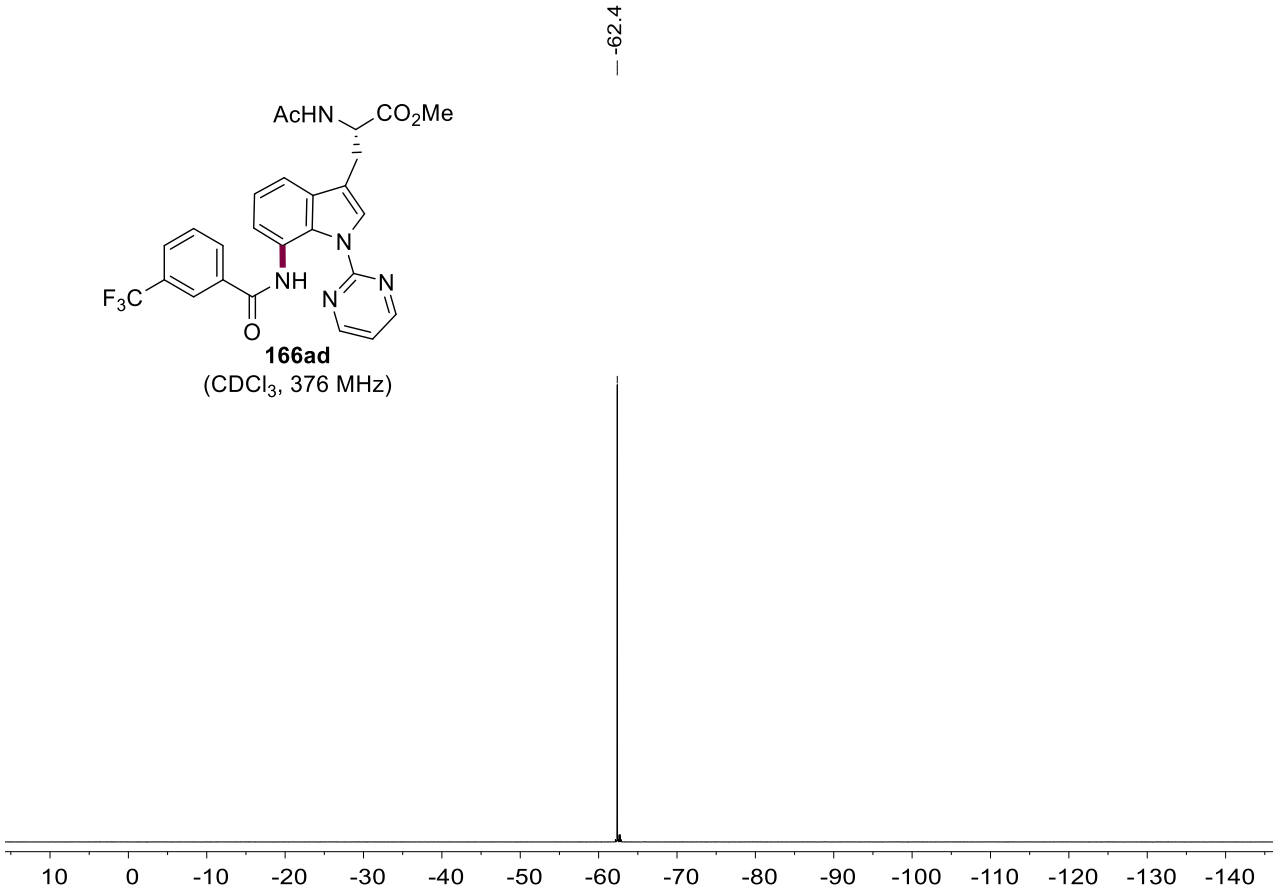


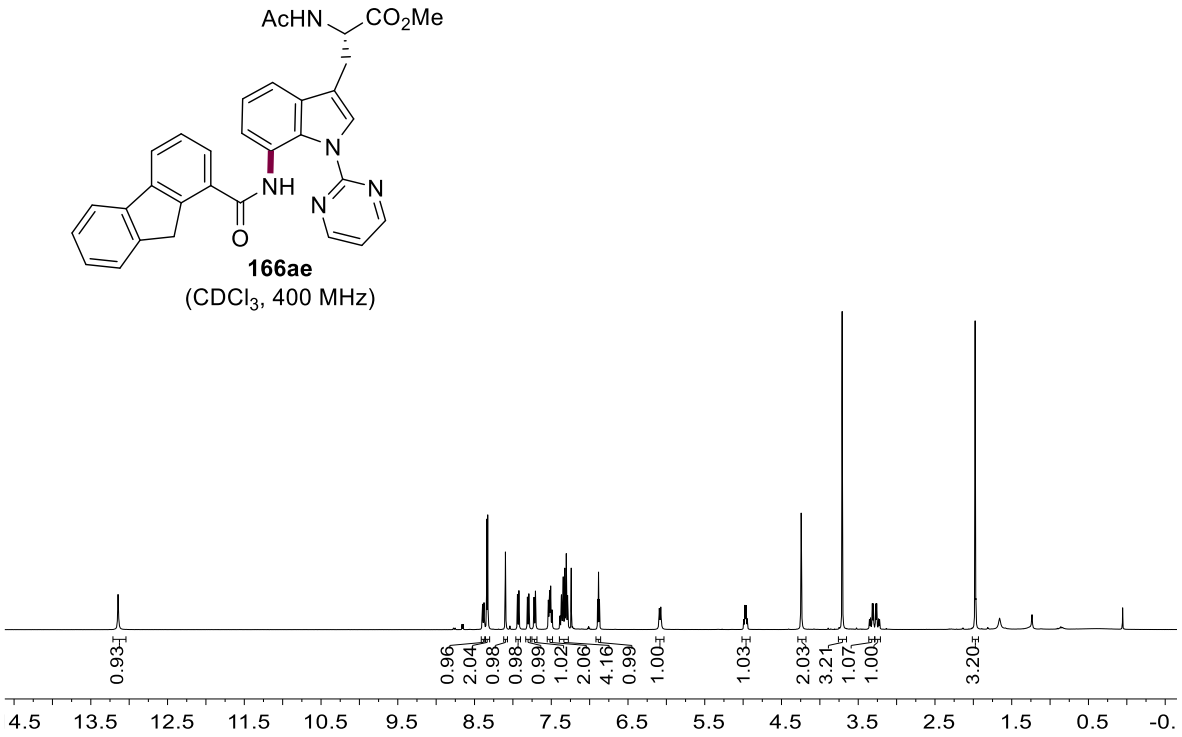


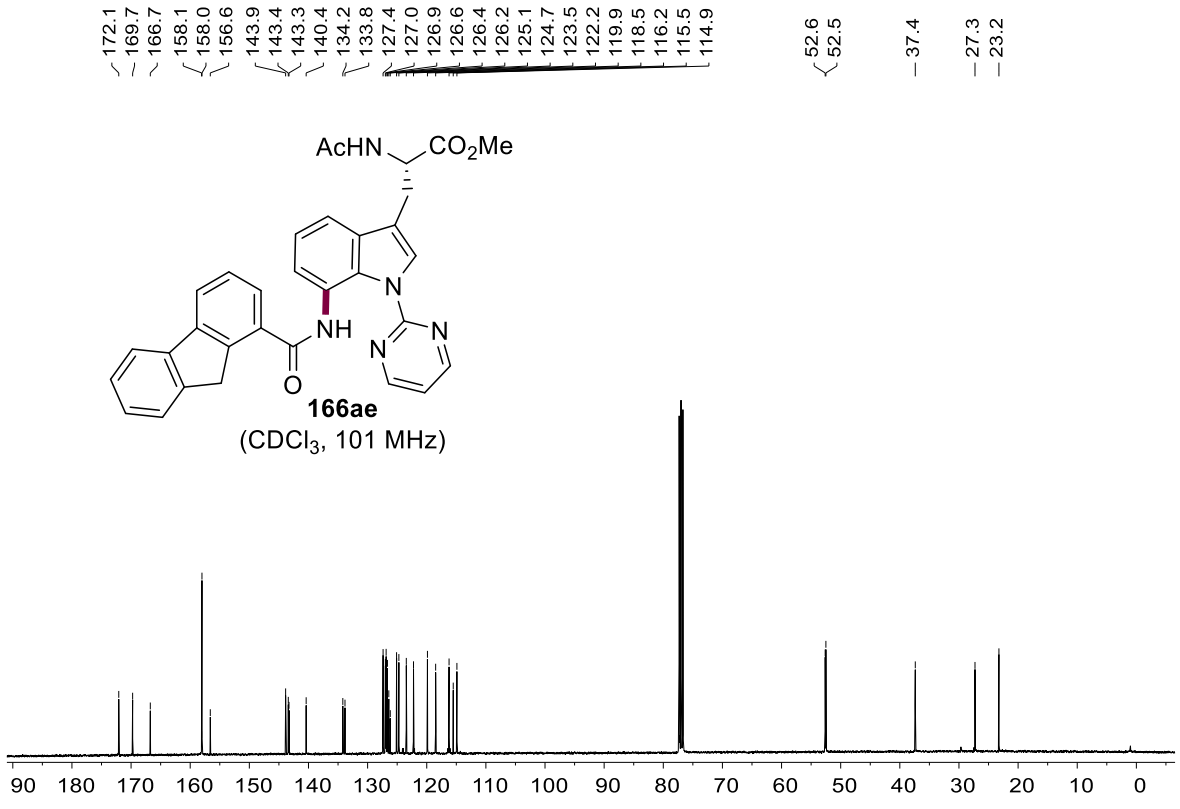
166ad

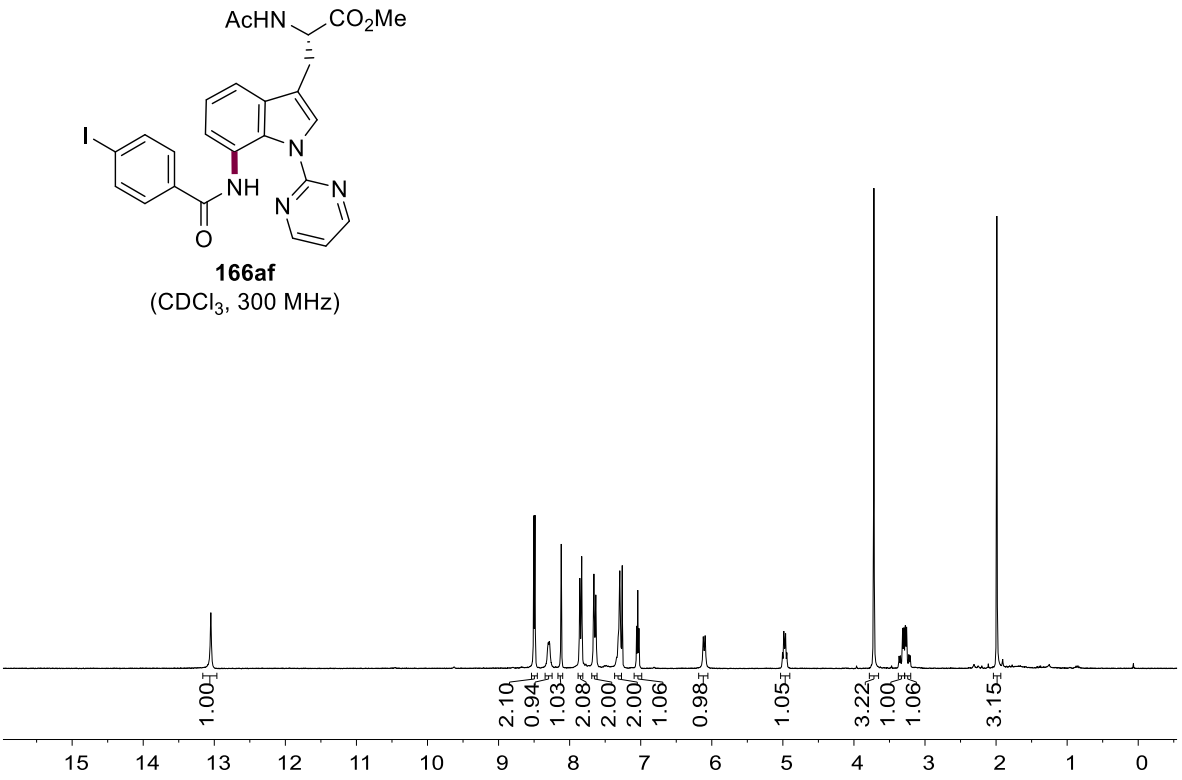
($CDCl_3$, 101 MHz)

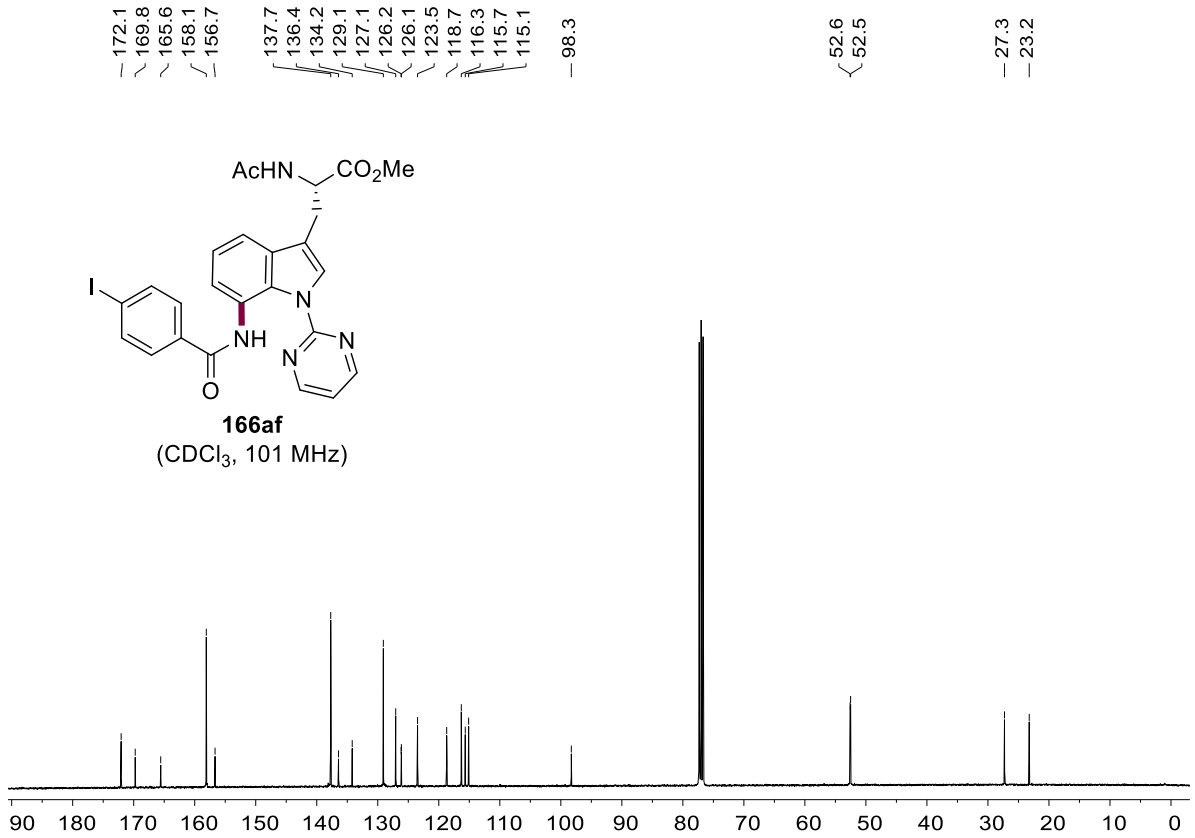



-62.4
AcHN
CO2Me
F3C
NH
N
N
N
O
166ad
(CDCl3, 376 MHz)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140

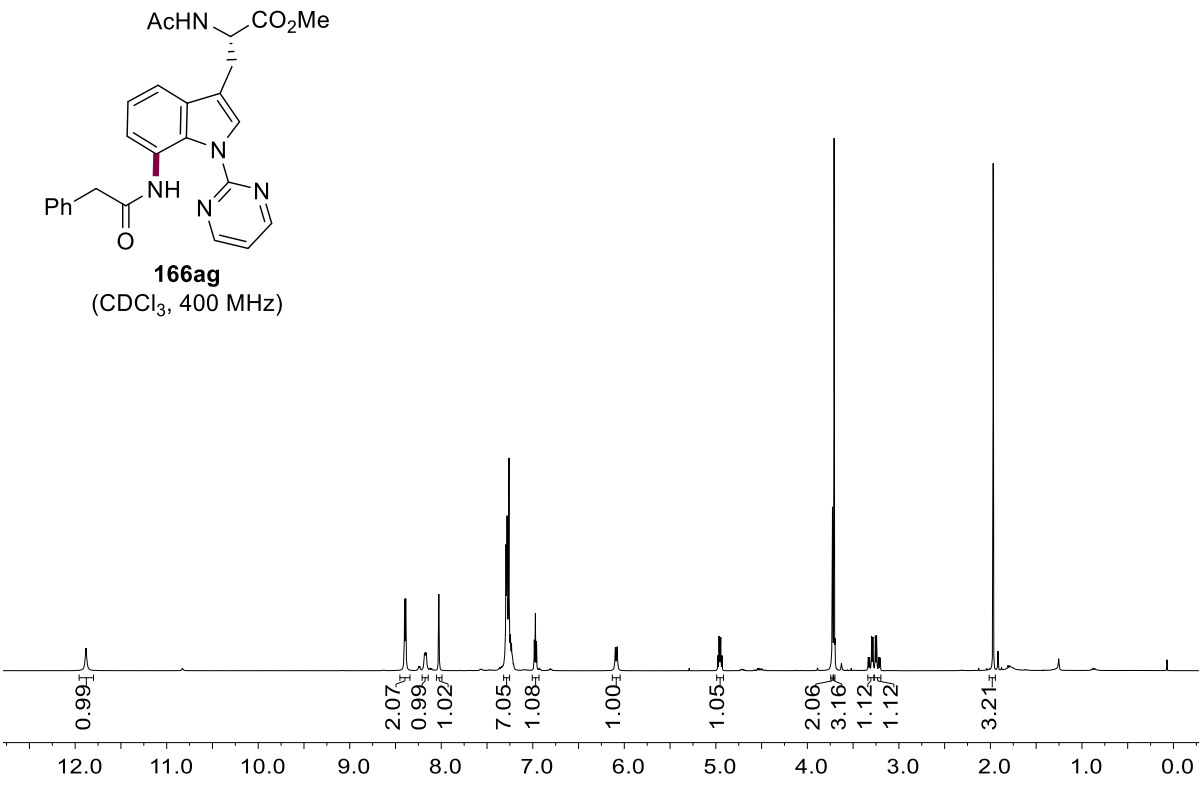

AcHN
CO2Me
NH
N
N
N
O
166ae
(CDCl3, 400 MHz)
0.93
0.96
2.04
0.98
0.98
0.99
1.02
2.06
4.16
0.99
1.00
1.03
2.03
3.21
1.07
1.00
3.20
4.5
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.


172.1
169.7
166.7
158.1
158.0
156.6
143.9
143.4
143.3
140.4
134.2
133.8
127.4
127.0
126.9
126.6
126.4
126.2
125.1
124.7
123.5
122.2
119.9
118.5
116.2
115.5
114.9
52.6
52.5
37.4
27.3
23.2
AcHN
CO2Me
NH
N
N
O
166ae
(CDCl3, 101 MHz)
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

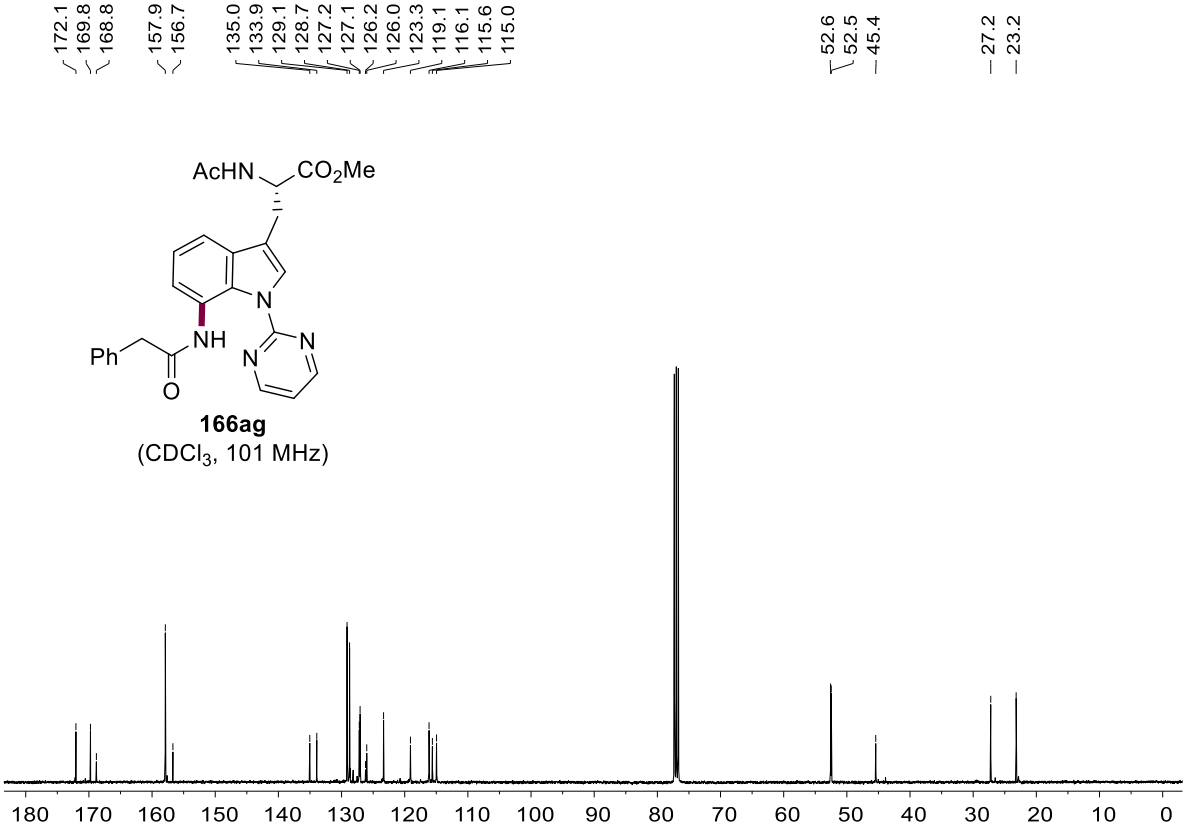

AcHN
CO2Me
I
NH
N
N
O
166af
(CDCl3, 300 MHz)
1.00
2.10
0.94
1.03
2.08
2.00
2.00
1.06
0.98
1.05
3.22
1.00
1.06
3.15
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0



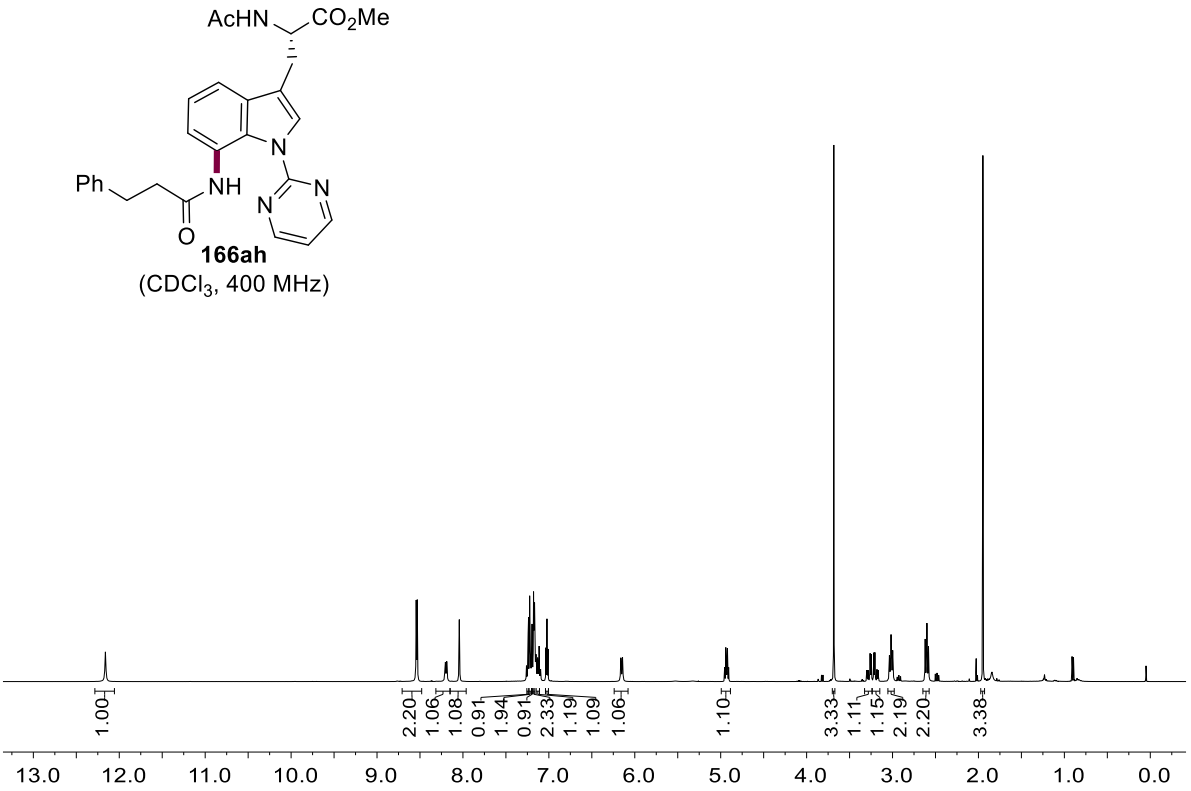
166af
($CDCl_3$, 101 MHz)



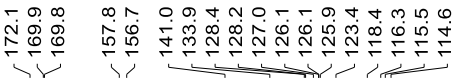
166ag
($CDCl_3$, 400 MHz)

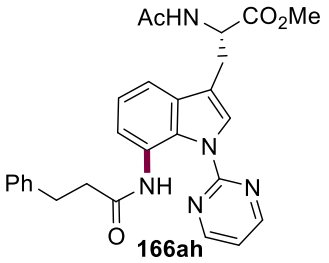


166ag
($CDCl_3$, 101 MHz)



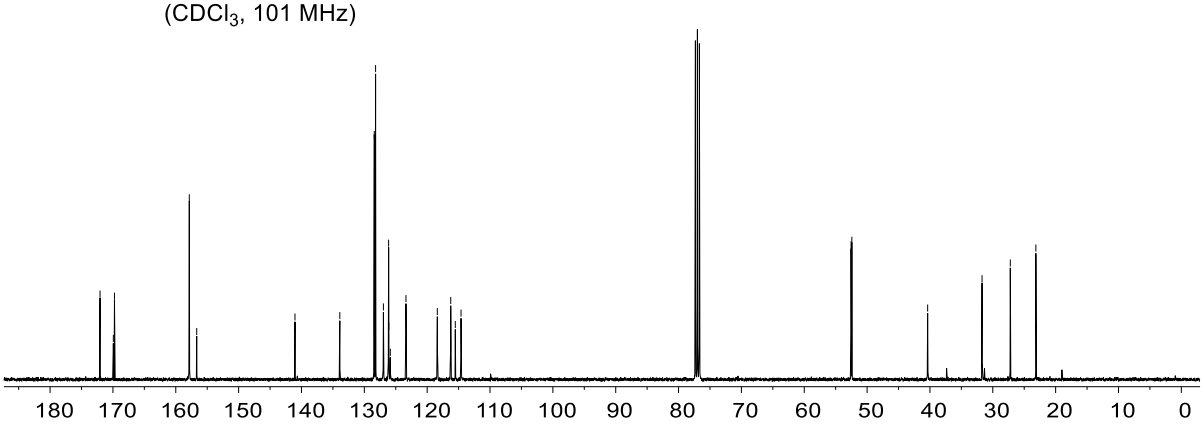
166ah
($CDCl_3$, 400 MHz)

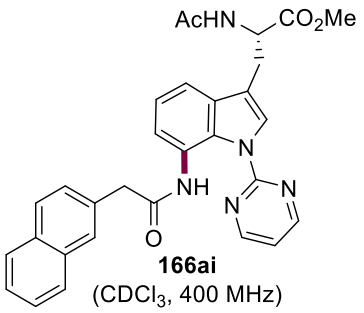




166ah

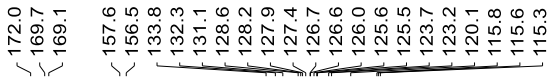
($CDCl_3$, 101 MHz)

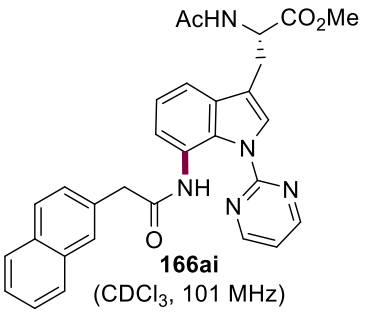




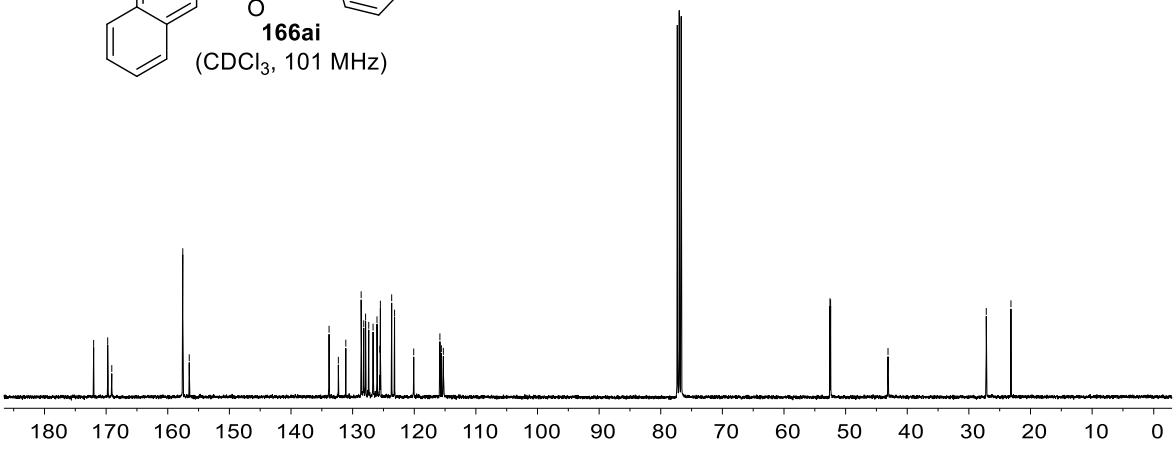
166ai

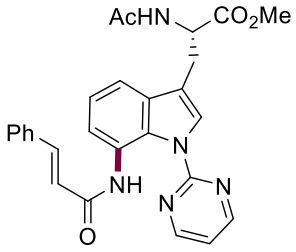
($CDCl_3$, 400 MHz)



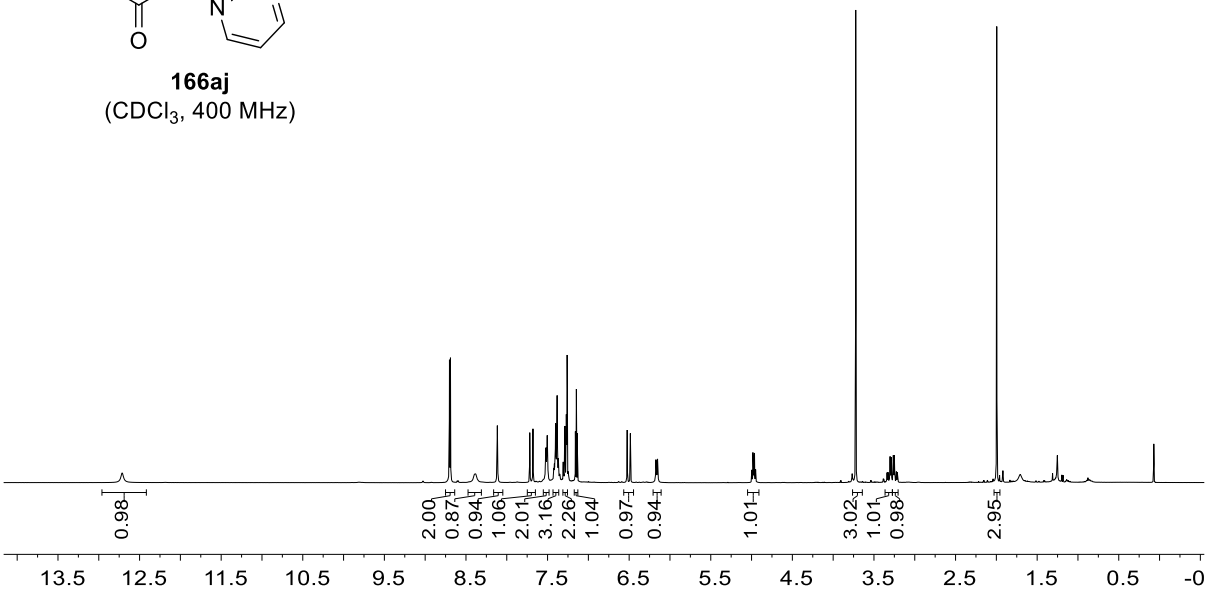


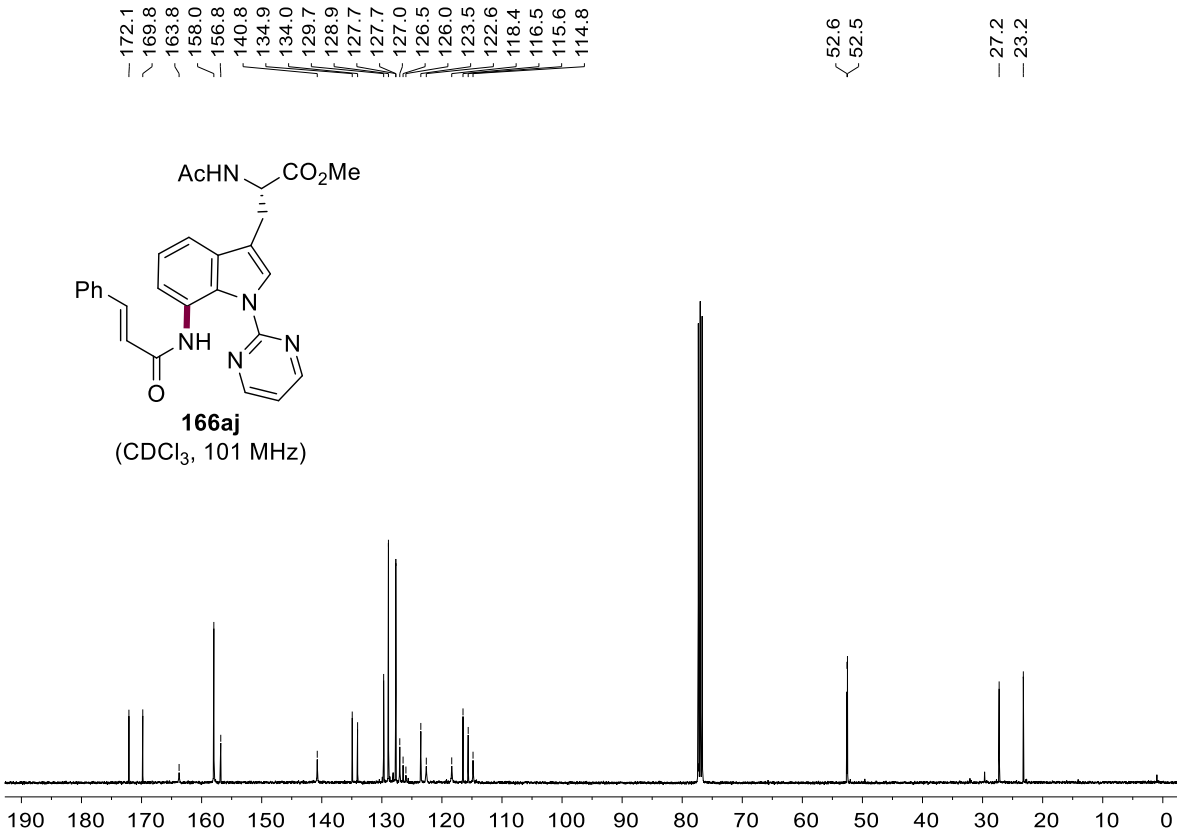
166ai
($CDCl_3$, 101 MHz)



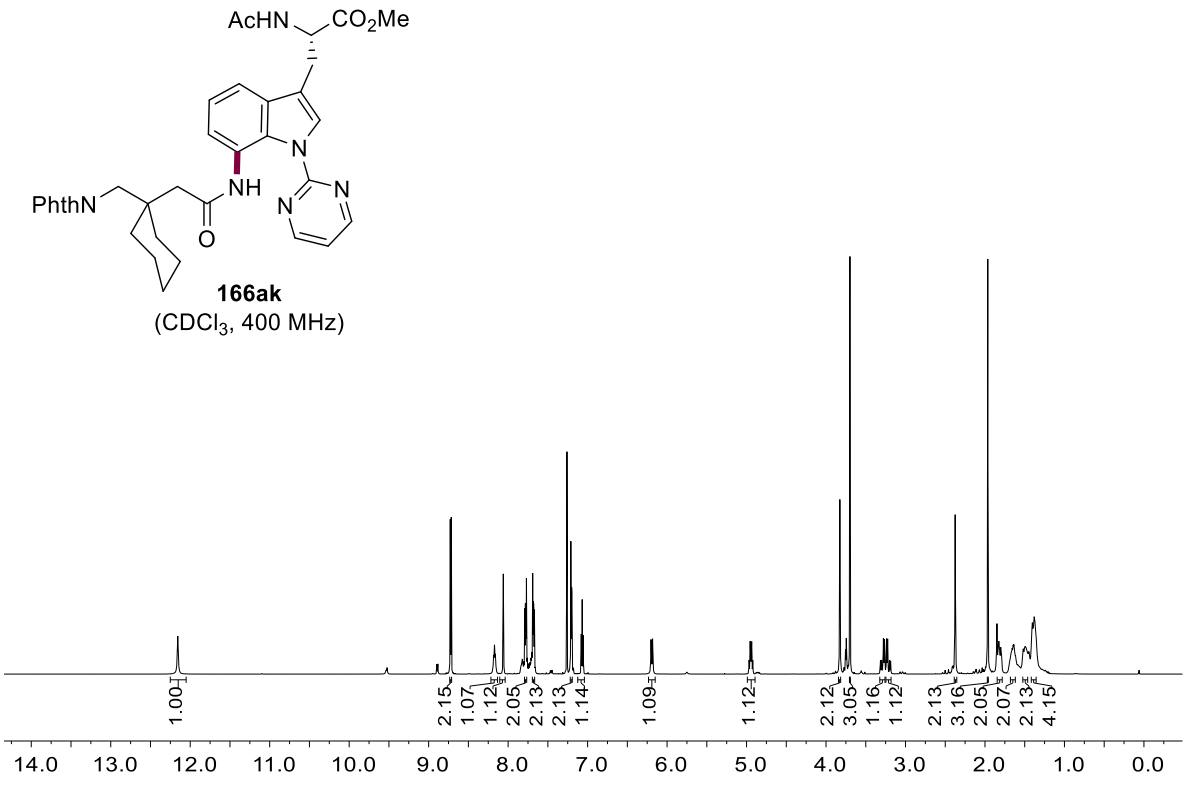


166aj
($CDCl_3$, 400 MHz)

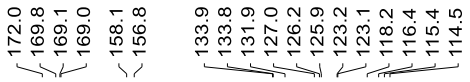


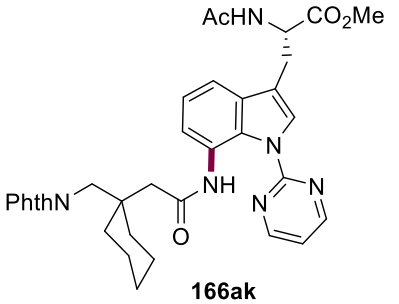


166aj
($CDCl_3$, 101 MHz)

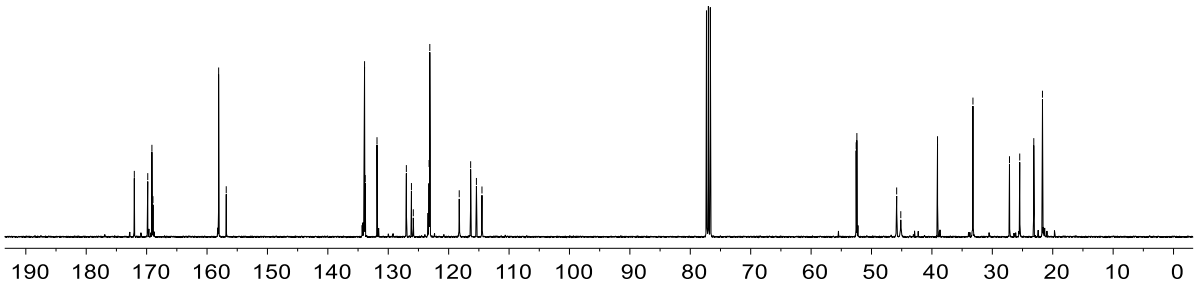


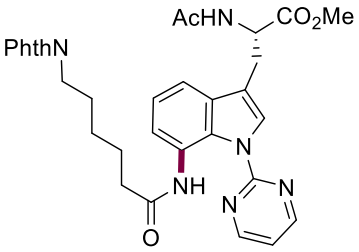
166ak
($CDCl_3$, 400 MHz)



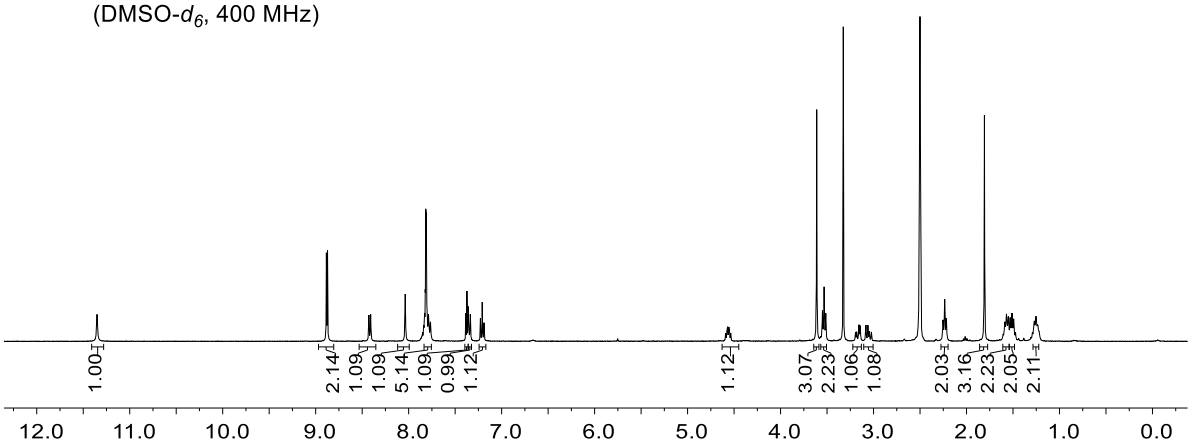


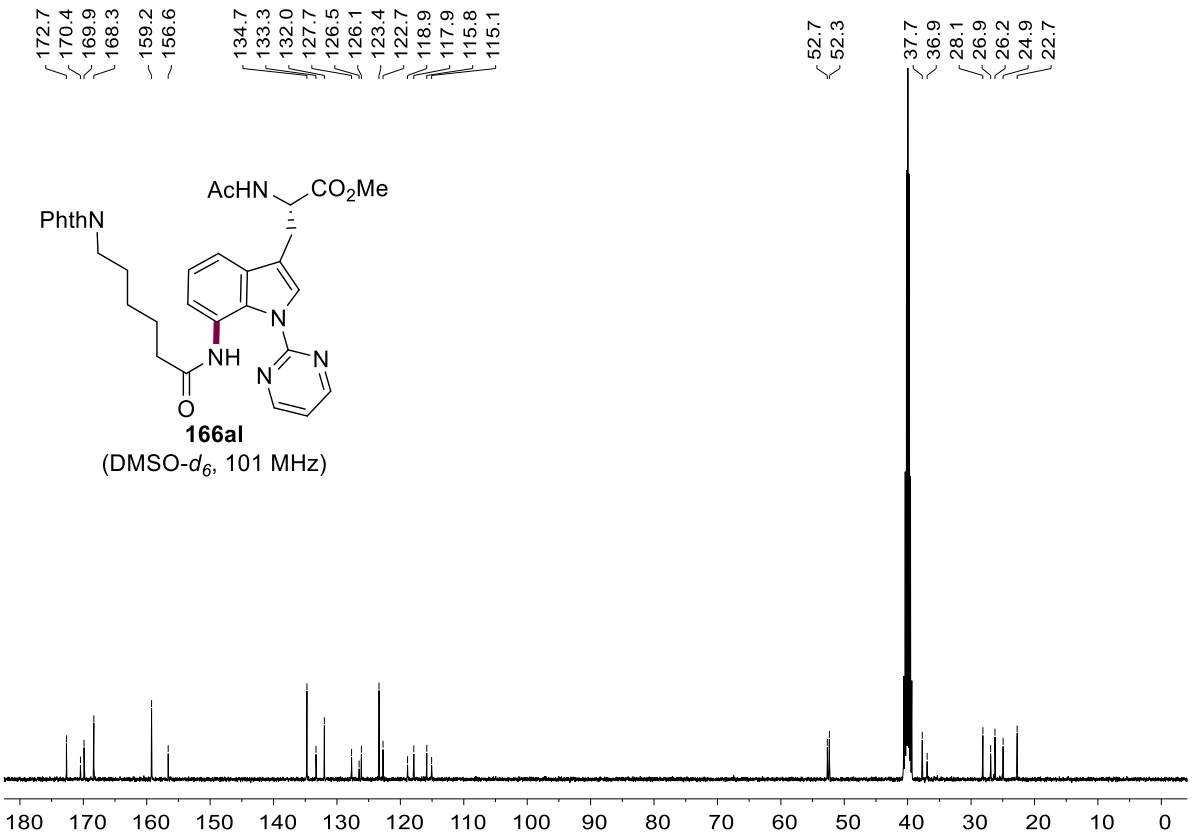
166ak
($CDCl_3$, 101 MHz)



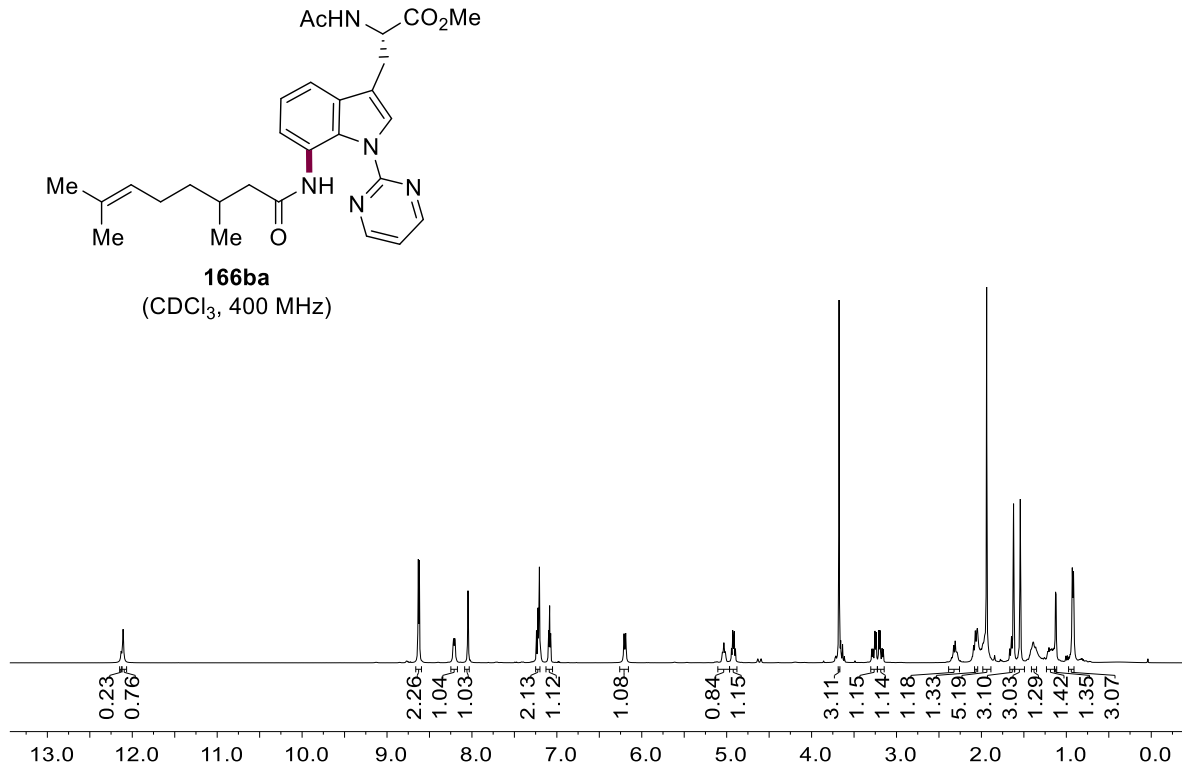


166al
(DMSO-d_6, 400 MHz)

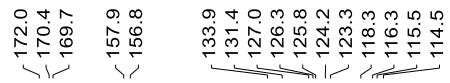


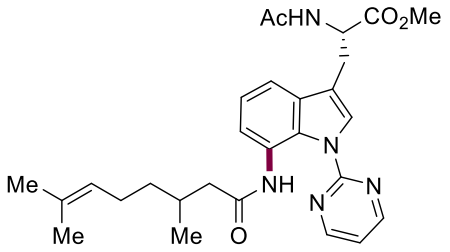


166al
(DMSO-d_6, 101 MHz)

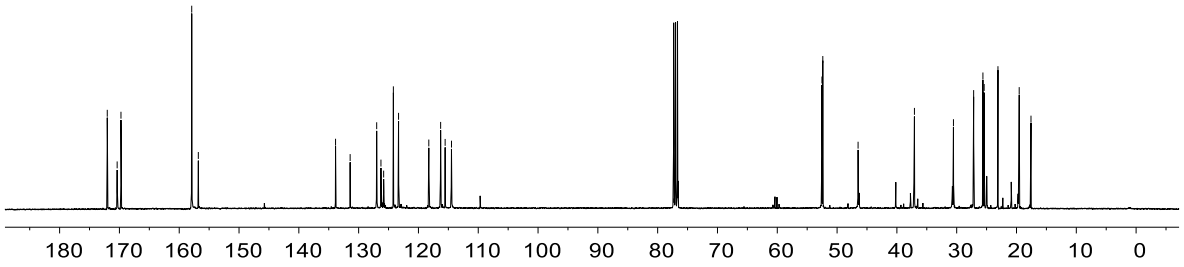


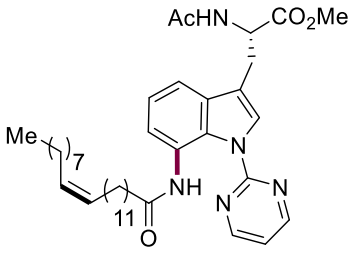
166ba
($CDCl_3$, 400 MHz)



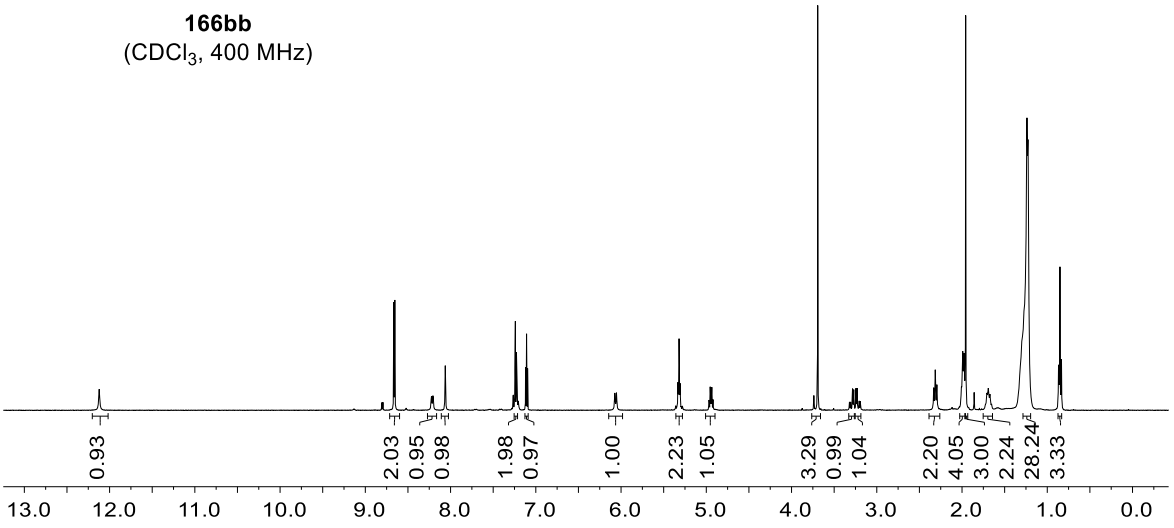


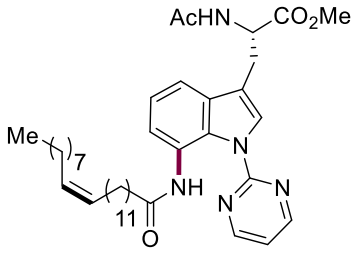
166ba
($CDCl_3$, 101 MHz)



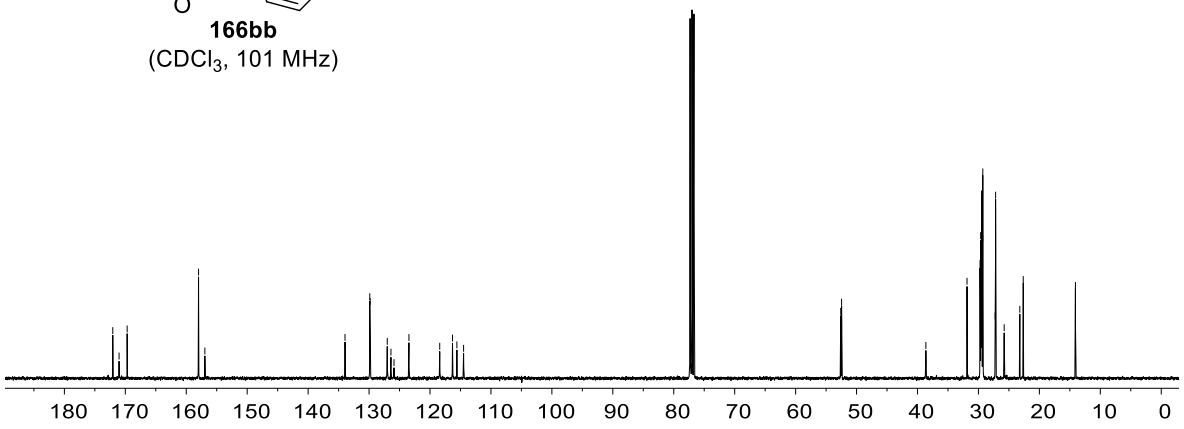


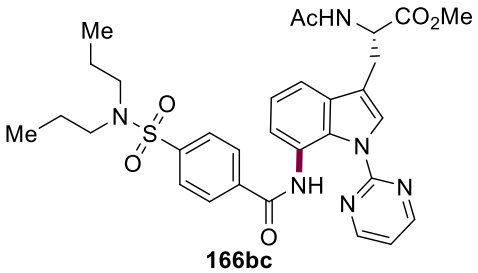
166bb
($CDCl_3$, 400 MHz)



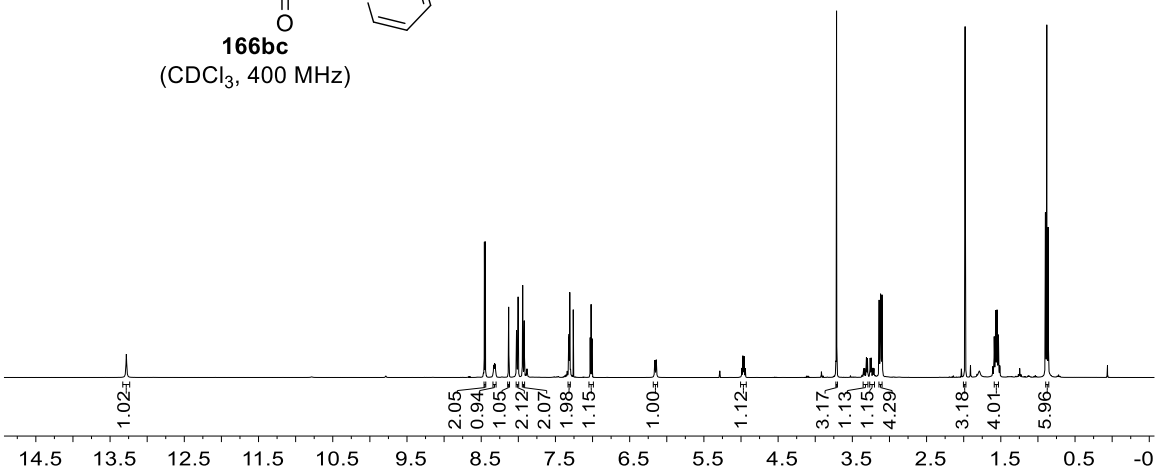


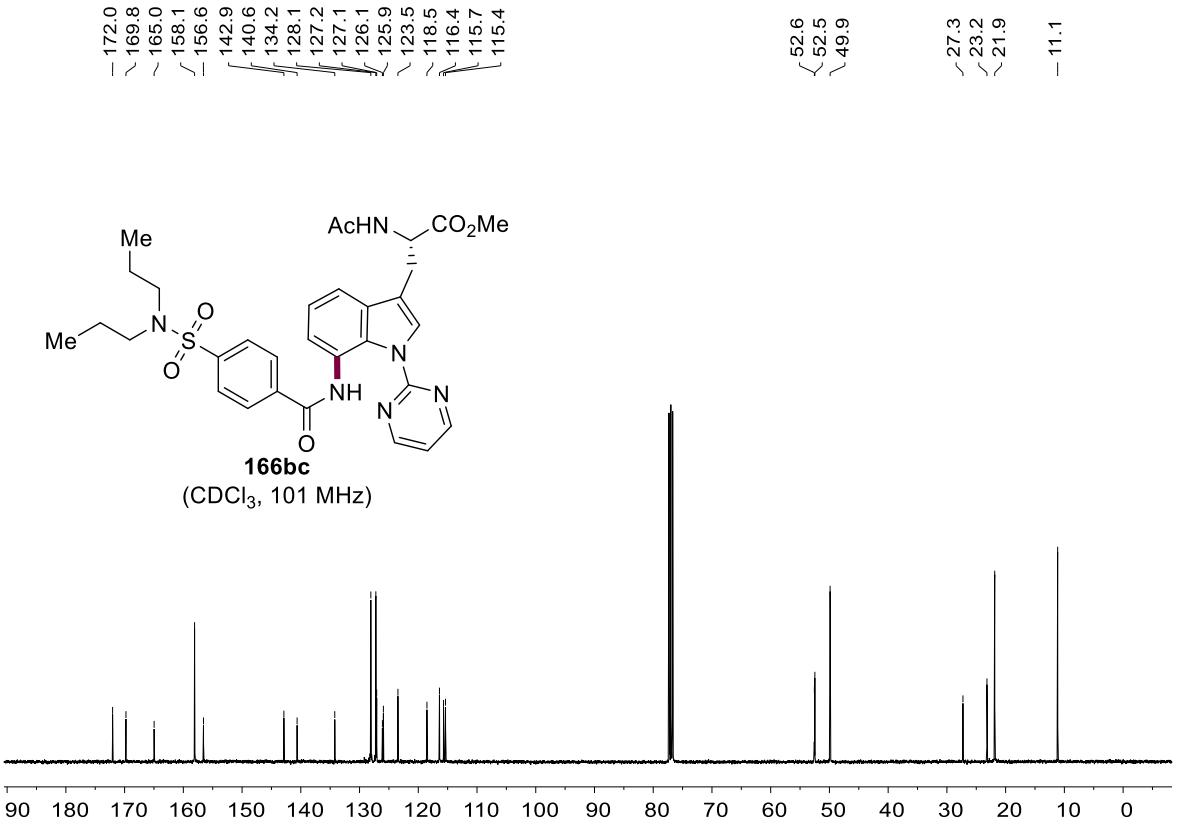
166bb
($CDCl_3$, 101 MHz)



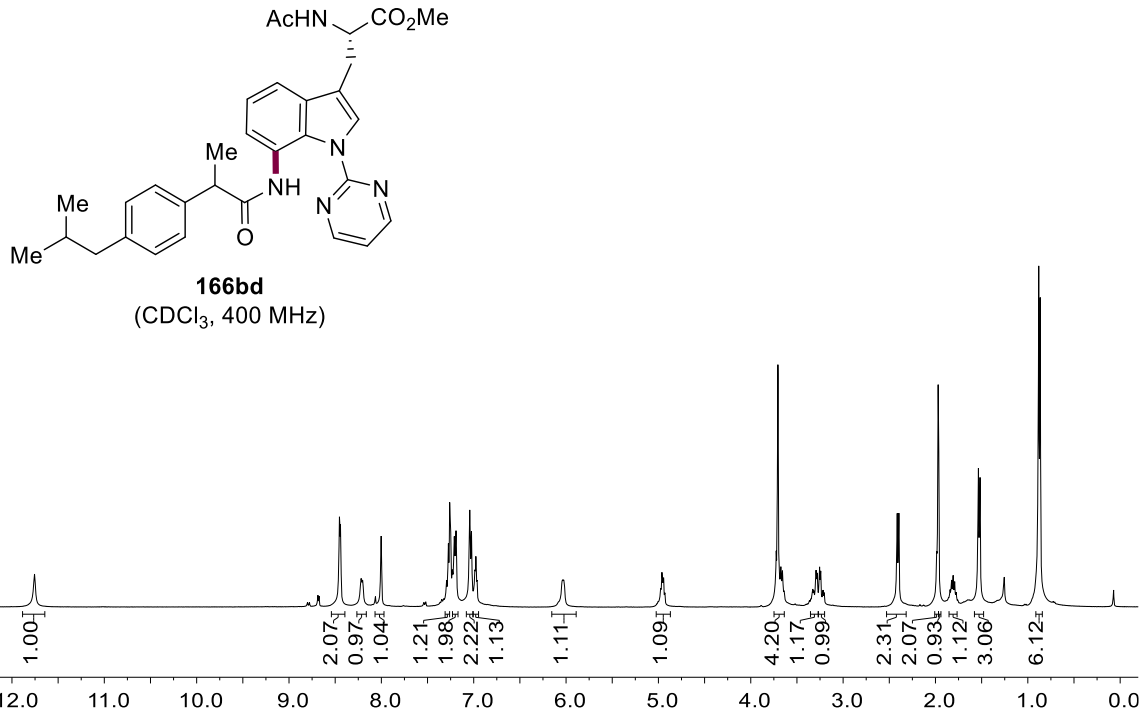


166bc
($CDCl_3$, 400 MHz)

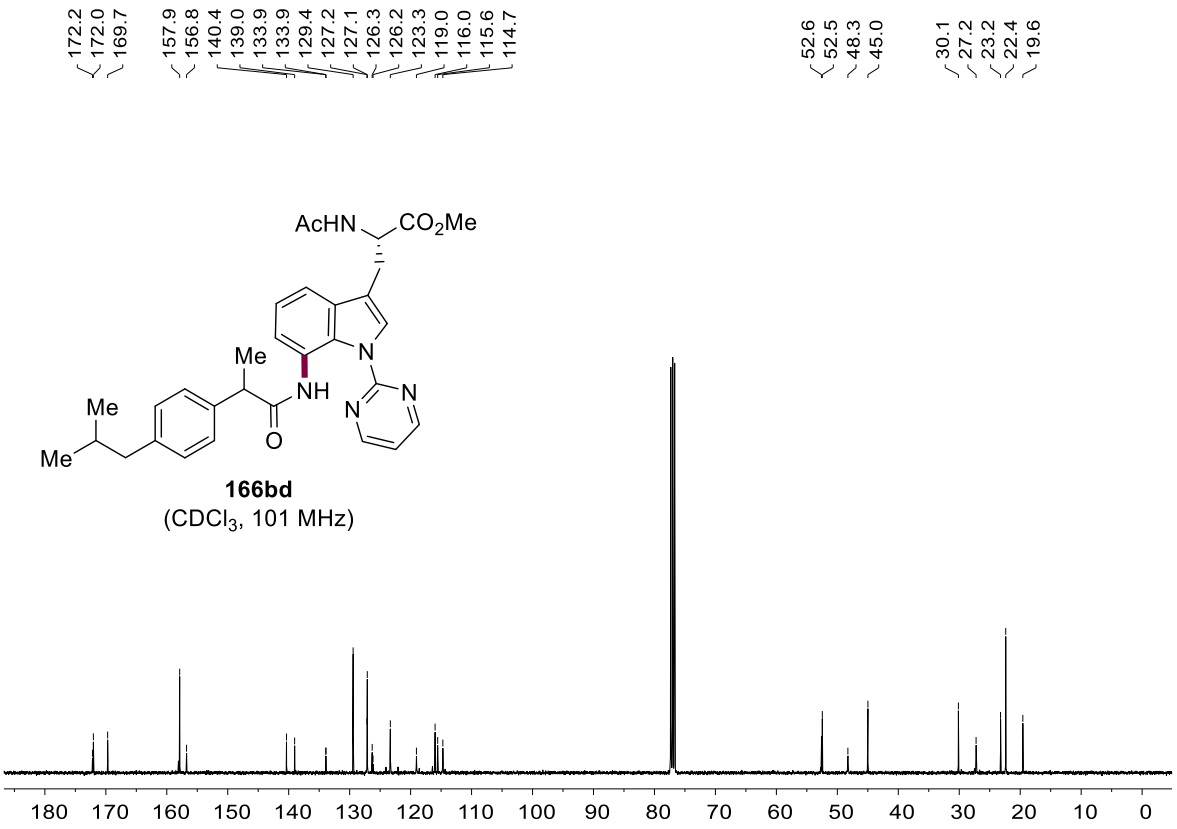


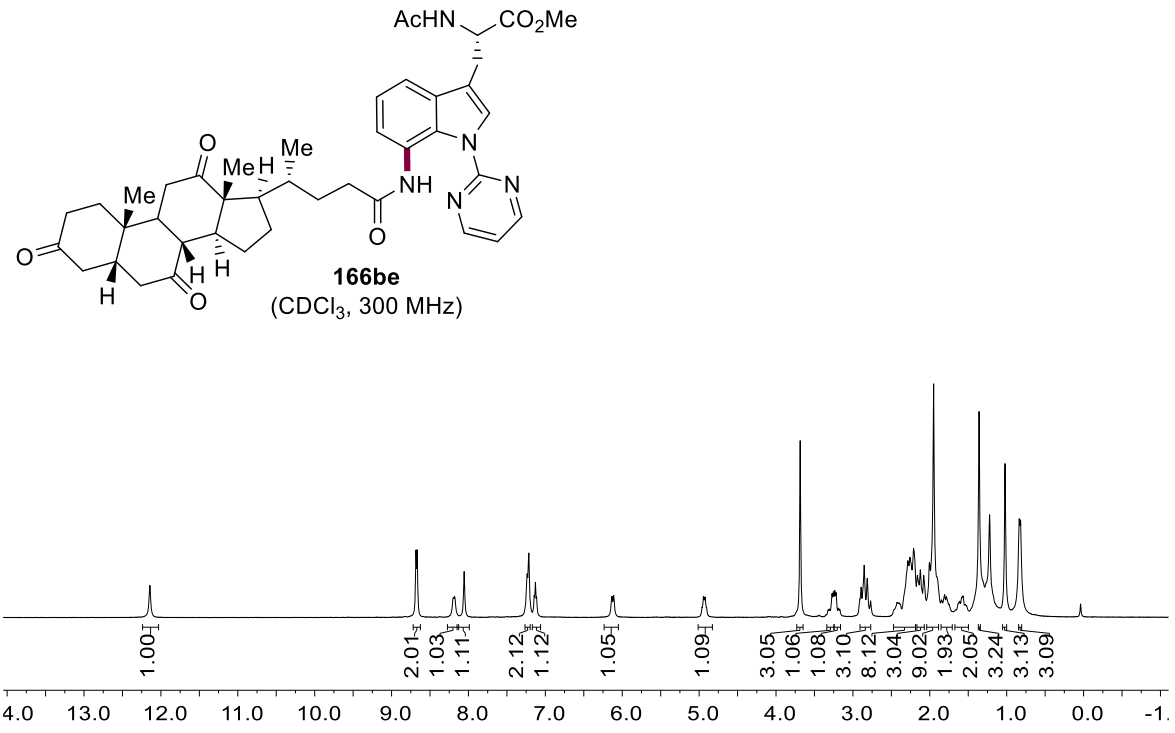


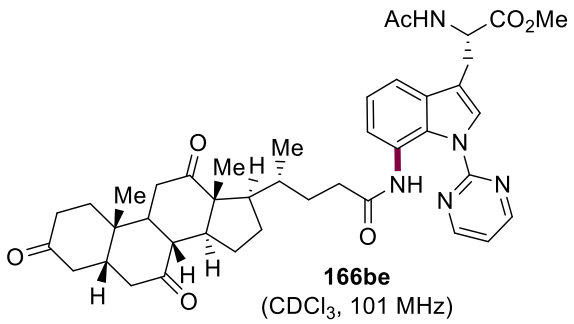
166bc
($CDCl_3$, 101 MHz)



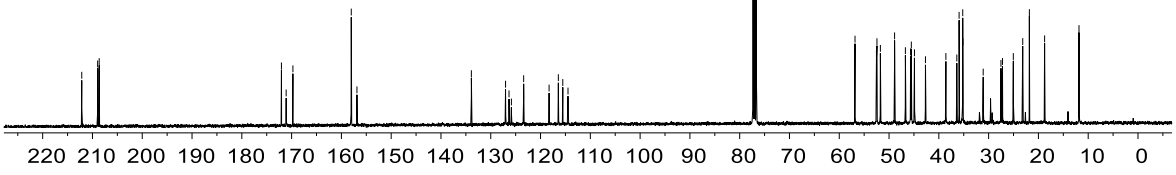
166bd
($CDCl_3$, 400 MHz)

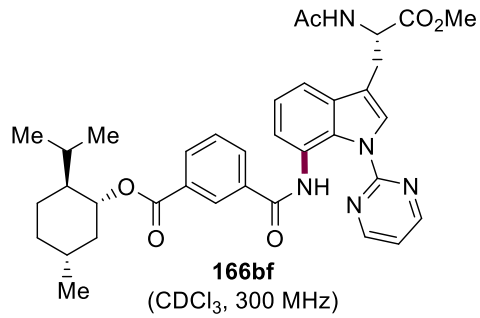

172.2
172.0
169.7
157.9
156.8
140.4
139.0
133.9
133.9
129.4
127.2
127.1
126.3
126.2
123.3
119.0
116.0
115.6
114.7
52.6
52.5
48.3
45.0
30.1
27.2
23.2
22.4
19.6
AcHN
CO2Me
Me
NH
N
N
N
Me
Me
O
166bd
(CDCl3, 101 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


AcHN
CO2Me
O
Me
H
Me
Me
NH
N
N
N
O
O
H
H
H
O
166be
(CDCl3, 300 MHz)
1.00
2.01
1.03
1.11
2.12
1.12
1.05
1.09
3.05
1.06
1.08
3.10
8.12
3.04
9.02
1.93
2.05
3.24
3.13
3.09
4.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.

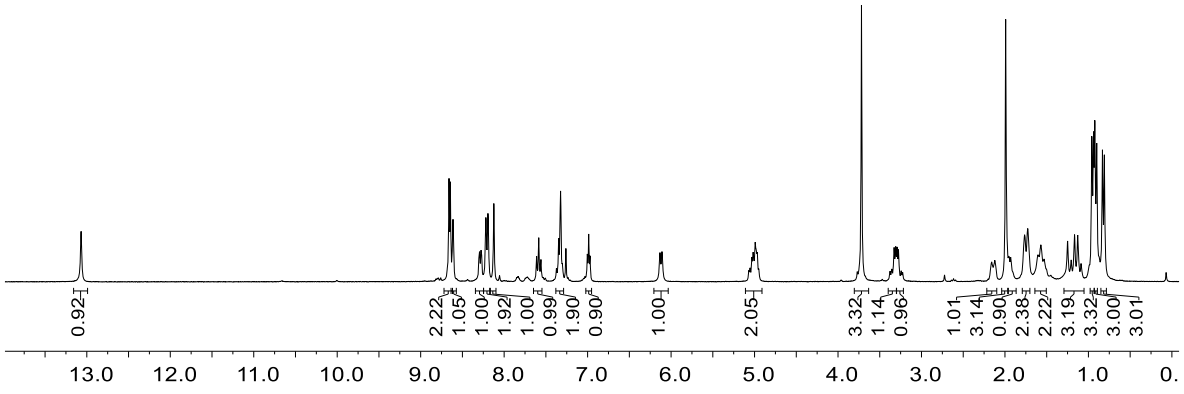


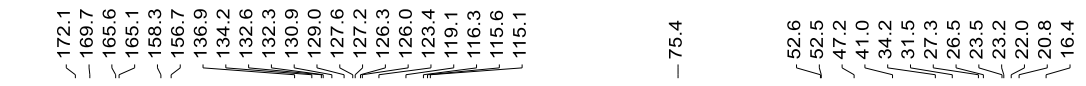
166be
($CDCl_3$, 101 MHz)

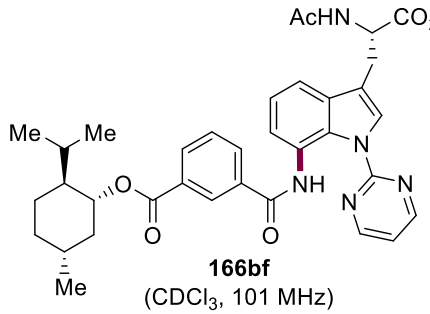




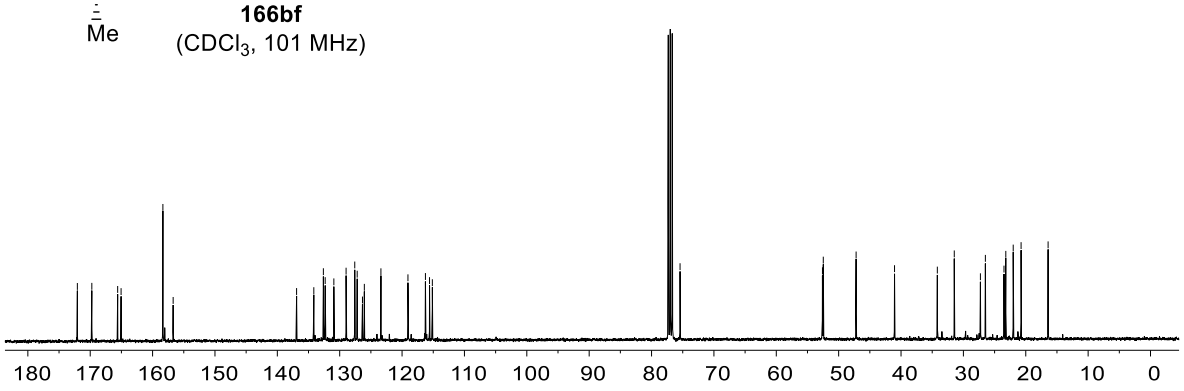
166bf
($CDCl_3$, 300 MHz)

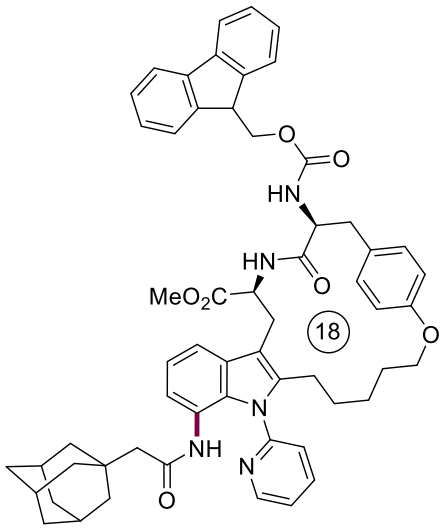




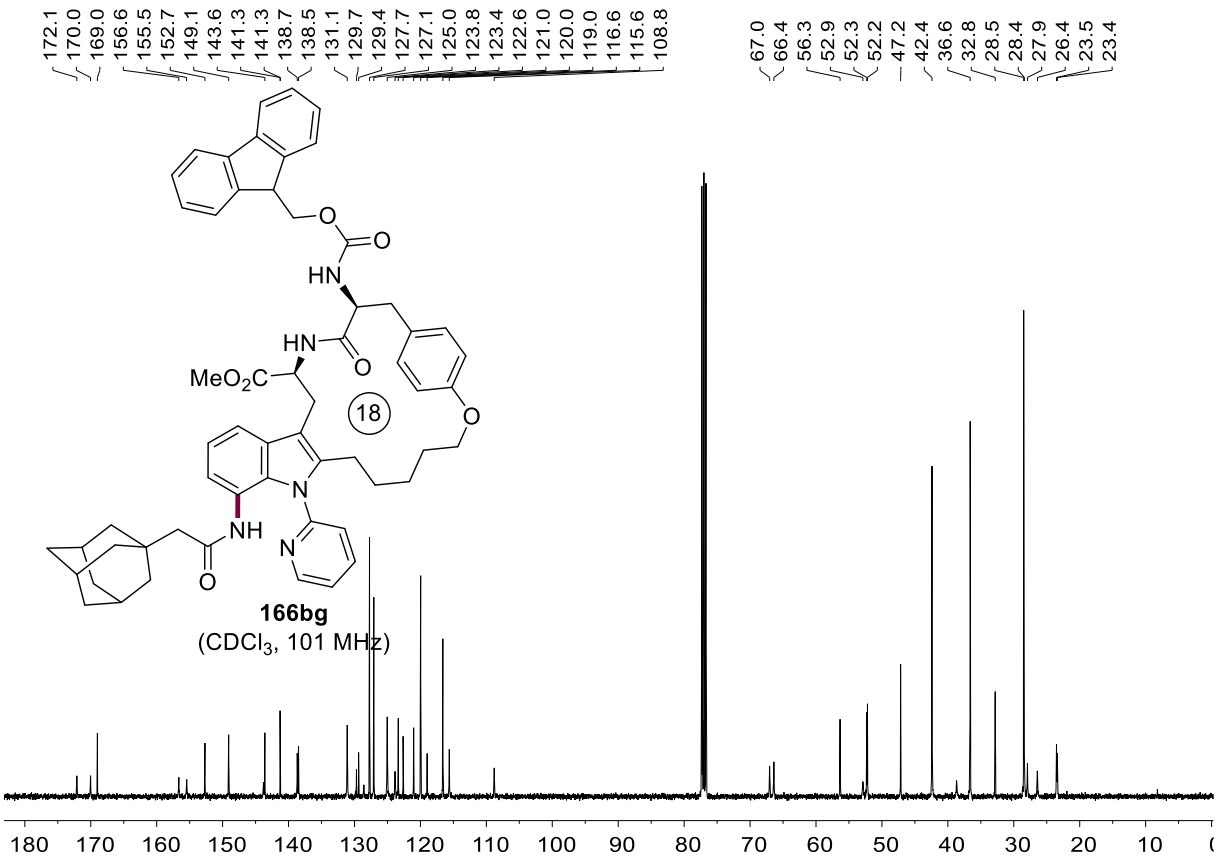


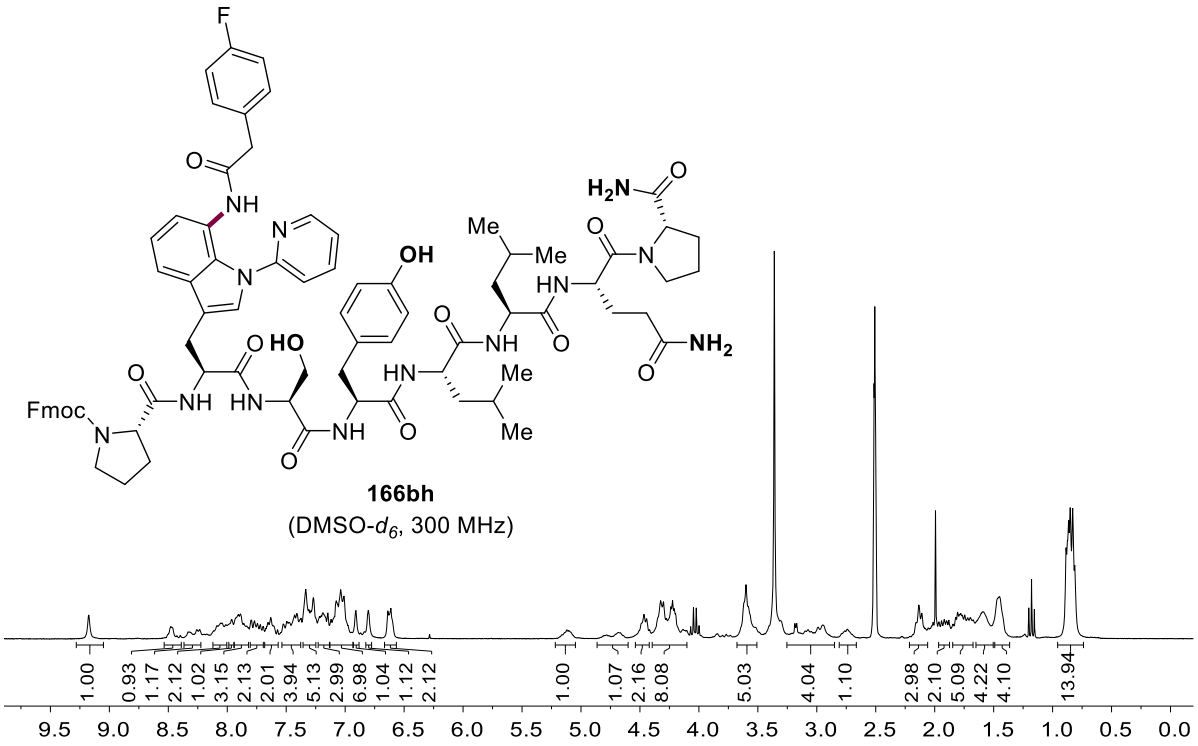
166bf
($CDCl_3$, 101 MHz)

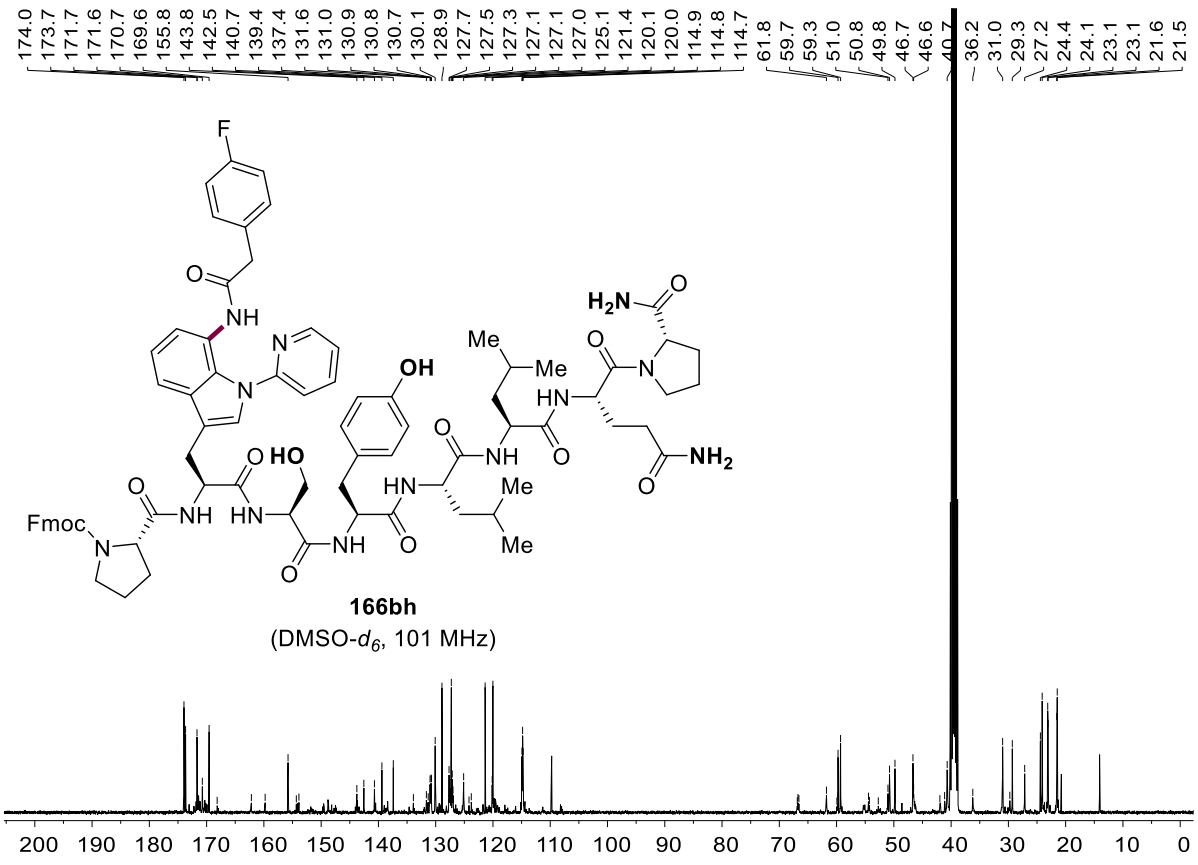




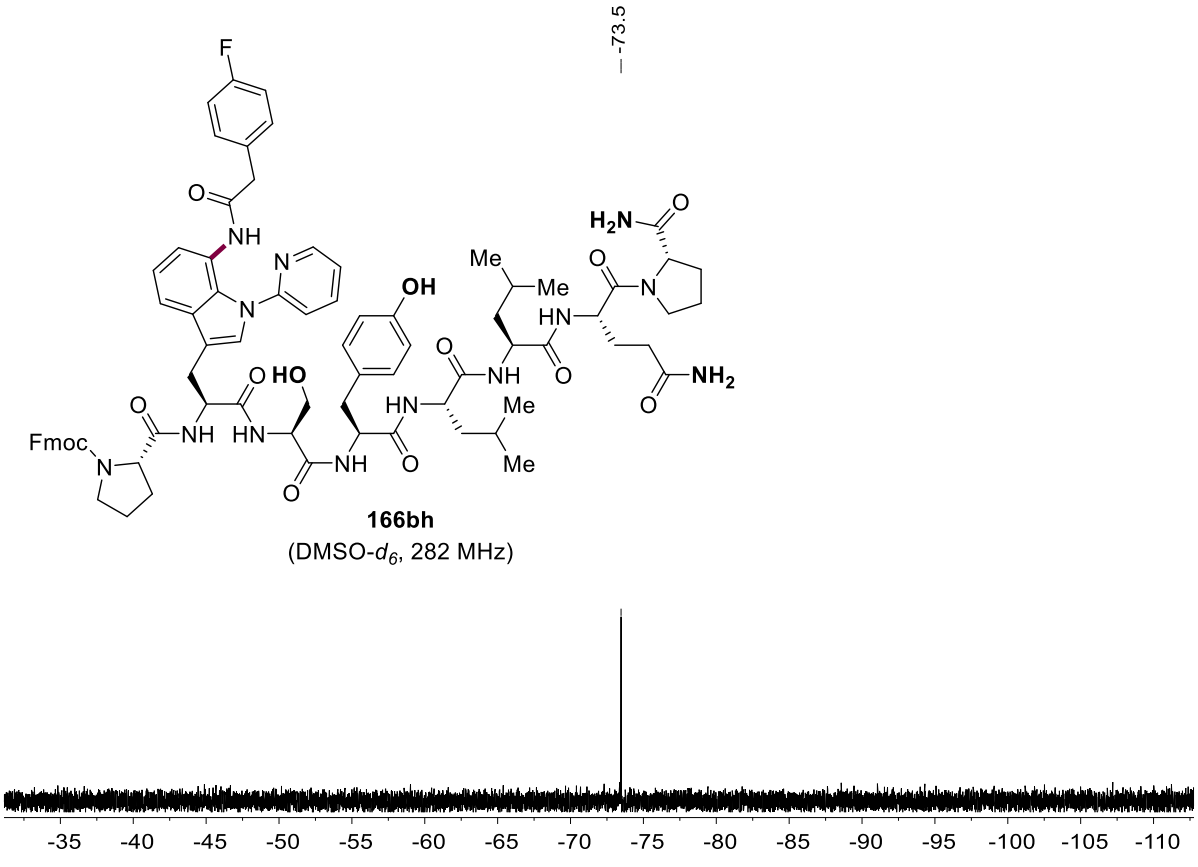
166bg
($CDCl_3$, 400 MHz)


172.1
170.0
169.0
156.6
155.5
152.7
149.1
143.6
141.3
141.3
138.7
138.5
131.1
129.7
129.4
127.7
127.1
125.0
123.8
123.4
122.6
121.0
120.0
119.0
116.6
115.6
108.8
67.0
66.4
56.3
52.9
52.3
52.2
47.2
42.4
36.6
32.8
28.5
28.4
27.9
26.4
23.5
23.4
MeO2C
18
HN
NH
N
O
166bg
(CDCl3, 101 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


F
Fmoc
OH
HO
H2N
NH2
Me
166bh
(DMSO-d6, 300 MHz)
1.00 0.93 1.17 2.12 1.02 3.15 2.13 2.01 3.94 5.13 2.99 6.98 1.04 1.12 2.12 1.00 1.07 2.16 8.08 5.03 4.04 1.10 2.98 2.10 5.09 4.22 4.10 13.94
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



166bh
(DMSO-d_6, 101 MHz)



166bh
(DMSO-d_6, 282 MHz)

Reference

[1] a) P. T. Anastas, M. M. Kirchhoff, *Acc. Chem. Res.* **2002**, *35*, 686−694; b) J. C. W. P. T. Anastas, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, **1998**.

[2] a) P. Gandeepan, L. H. Finger, T. H. Meyer, L. Ackermann, *Chem. Soc. Rev.* **2020**, *49*, 4254-4272; b) T. H. Meyer, L. H. Finger, P. Gandeepan, L. Ackermann, *Trends Chem.* **2019**, *1*, 63−76; c) B. Trost, *Science* **1991**, *254*, 1471−1477.

[3] a) A. Fürstner, *Angew. Chem. Int. Ed.* **2013**, *52*, 2794−2819; b) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem. Int. Ed.* **2005**, *44*, 4490−4527.

[4] K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem. Int. Ed.* **2005**, *44*, 4442−4489.

[5] a) K. Tamao, K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 4374−4376; b) R. J. P. Corriu, J. P. Masse, *J. Chem. Soc., Chem. Commun.* **1972**, 144a−144a.

[6] a) A. O. King, N. Okukado, E.-i. Negishi, *J. Chem. Soc., Chem. Commun.* **1977**, 683−684; b) E. Negishi, A. O. King, N. Okukado, *J. Org. Chem.* **1977**, *42*, 1821−1823; c) E. Negishi, *Acc. Chem. Res.* **1982**, *15*, 340−348; d) E. Negishi, T. Takahashi, S. Baba, D. E. Van Horn, N. Okukado, *J. Am. Chem. Soc.* **1987**, *109*, 2393−2401.

[7] a) M. Kosugi, K. Sasazawa, Y. Shimizu, T. Migita, *Chem. Lett.* **1977**, *6*, 301−302; b) M. Kosugi, Y. Shimizu, T. Migita, *Chem. Lett.* **1977**, *6*, 1423−1424; c) D. Milstein, J. K. Stille, *J. Am. Chem. Soc.* **1978**, *100*, 3636−3638; d) D. Milstein, J. K. Stille, *J. Am. Chem. Soc.* **1979**, *101*, 4992−4998; e) J. K. Stille, *Angew. Chem. Int. Ed.* **1986**, *25*, 508−524.

[8] a) N. Miyaura, A. Suzuki, *J. Chem. Soc., Chem. Commun.* **1979**, 866−867; b) N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* **1979**, *20*, 3437−3440; c) A. Suzuki, *Acc. Chem. Res.* **1982**, *15*, 178−184; d) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457−2483.

[9] a) Y. Hatanaka, T. Hiyama, *J. Org. Chem.* **1988**, *53*, 918−920; b) T. Hiyama, *J. Organomet. Chem.* **2002**, *653*, 58−61.

[10] a) S. B. A. de Meijere, M. Oestreich, *Metal-Catalyzed Cross-Coupling Reactions and More*, Wiley-VCH, Weinheim, **2014**; b) *M. A. M.* L. Ackermann, Wiley-VCH,

Weinheim, **2009**; c) C. C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem. Int. Ed.* **2012**, *51*, 5062−5085.

[11] a) R. G. Bergman, *Nature* **2007**, *446*, 391−393; b) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792−9826; c) W. R. Gutekunst, P. S. Baran, *Chem. Soc. Rev.* **2011**, *40*, 1976−1991; d) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem Soc Rev* **2011**, *40*, 1885−1898; e) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960−9009; f) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369−375; g) J. F. Hartwig, M. A. Larsen, *ACS Cent Sci* **2016**, *2*, 281−292; h) W. Wang, M. M. Lorion, J. Shah, A. R. Kapdi, L. Ackermann, *Angew. Chem. Int. Ed.* **2018**, *57*, 14700−14717; i) P. Gandeepan, T. Muller, D. Zell, G. Cera, S. Warratz, L. Ackermann, *Chem. Rev.* **2019**, *119*, 2192−2452; j) J. Wang, G. Dong, *Chem. Rev.* **2019**, *119*, 7478−7528; k) G. Meng, N. Y. S. Lam, E. L. Lucas, T. G. Saint-Denis, P. Verma, N. Chekshin, J. Q. Yu, *J. Am. Chem. Soc.* **2020**, *142*, 10571−10591; l) L. Guillemard, N. Kaplaneris, L. Ackermann, M. J. Johansson, *Nat. Rev. Chem.* **2021**, *5*, 522−545; m) S. Shabani, Y. Wu, H. G. Ryan, C. A. Hutton, *Chem Soc Rev* **2021**, *50*, 9278−9343.

[12] a) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315−1345; b) D. Balcells, E. Clot, O. Eisenstein, *Chem. Rev.* **2010**, *110*, 749−823; c) M. Albrecht, *Chem. Rev.* **2010**, *110*, 576−623.

[13] T. Rogge, J. C. A. Oliveira, R. Kuniyil, L. Hu, L. Ackermann, *ACS Catal.* **2020**, *10*, 10551−10558.

[14] B. Biswas, M. Sugimoto, S. Sakaki, *Organometallics* **2000**, *19*, 3895−3908.

[15] a) D. Lapointe, K. Fagnou, *Chem. Lett.* **2010**, *39*, 1118−1126; b) S. I. Gorelsky, D. Lapointe, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 10848−10849.

[16] a) Y. Boutadla, D. L. Davies, S. A. Macgregor, A. I. Poblador-Bahamonde, *Dalton Trans.* **2009**, 5820−5831; b) Y. Boutadla, D. L. Davies, S. A. Macgregor, A. I. Poblador-Bahamonde, *Dalton Trans.* **2009**, 5887−5893.

[17] a) D. Zell, M. Bursch, V. Müller, S. Grimme, L. Ackermann, *Angew. Chem. Int. Ed.* **2017**, *56*, 10378−10382; b) R. Mei, H. Wang, S. Warratz, S. A. Macgregor, L. Ackermann, *Chem. Eur. J.* **2016**, *22*, 6759−6763; c) W. Ma, R. Mei, G. Tenti, L. Ackermann, *Chem. Eur. J.* **2014**, *20*, 15248−15251.

[18] S. I. Elshahawi, K. A. Shaaban, M. K. Kharel, J. S. Thorson, *Chem. Soc. Rev.* **2015**, *44*, 7591−7697.

[19] G. Yang, J. Schmieg, M. Tsuji, R. W. Franck, *Angew. Chem. Int. Ed.* **2004**, *43*, 3818−3822.

[20] B. La Ferla, C. Airoldi, C. Zona, A. Orsato, F. Cardona, S. Merlo, E. Sironi, G. D'Orazio, F. Nicotra, *Nat. Prod. Rep.* **2011**, *28*, 630−648.

[21] F. Schweizer, A. Otter, O. Hindsgaul, *Synlett* **2001**, *2001*, 1743−1746.

[22] K. Tatsuta, H. Mukai, M. Takahashi, *J. Antibiot.* **2000**, *53*, 430−435.

[23] a) M. Lakhrissi, Y. Chapleur, *Angew. Chem. Int. Ed.* **1996**, *35*, 750−752; b) Y. Lakhrissi, C. Taillefumier, M. Lakhrissi, Y. Chapleur, *Tetrahedron Asymmetry* **2000**, *11*, 417−421; c) G. S. Coumbarides, M. Motevalli, W. A. Muse, P. B. Wyatt, *J. Org. Chem.* **2006**, *71*, 7888−7891.

[24] a) M. D. Lewis, J. K. Cha, Y. Kishi, *J. Am. Chem. Soc.* **2002**, *104*, 4976−4978; b) M. Terauchi, H. Abe, A. Matsuda, S. Shuto, *Org. Lett.* **2004**, *6*, 3751−3754.

[25] a) T. V. Rajanbabu, G. S. Reddy, *J. Org. Chem.* **1986**, *51*, 5458−5461; b) B. A. Johns, Y. T. Pan, A. D. Elbein, C. R. Johnson, *J. Am. Chem. Soc.* **1997**, *119*, 4856−4865; c) A. M. Gómez, A. Pedregosa, S. n. Valverde, J. C. López, *Tetrahedron Lett.* **2003**, *44*, 6111−6116.

[26] D. Gueyrard, R. Haddoub, A. Salem, N. S. Bacar, P. G. Goekjian, *Synlett* **2005**, *2005*, 520−522.

[27] D. E. Kaelin, Jr., O. D. Lopez, S. F. Martin, *J. Am. Chem. Soc.* **2001**, *123*, 6937−6938.

[28] S. J. Danishefsky, K. F. McClure, J. T. Randolph, R. B. Ruggeri, *Science* **1993**, *260*, 1307−1309.

[29] a) H. W. Johnson, U. Majumder, J. D. Rainier, *J. Am. Chem. Soc.* **2005**, *127*, 848−849; b) C. O. Akoto, J. D. Rainier, *Angew. Chem. Int. Ed.* **2008**, *47*, 8055−8058.

[30] S. P. Allwein, J. M. Cox, B. E. Howard, H. W. B. Johnson, J. D. Rainier, *Tetrahedron* **2002**, *58*, 1997−2009.

[31] J. D. Rainier, J. M. Cox, *Org. Lett.* **2000**, *2*, 2707−2709.

[32] G. E. Keck, J. B. Yates, *J. Am. Chem. Soc.* **1982**, *104*, 5829−5831.

[33] B. Giese, J. Dupuis, *Angew. Chem. Int. Ed.* **1983**, *22*, 622−623.

[34] J. R. Ragains, in *Comprehensive Glycoscience* (Ed.: J. J. Barchi), Elsevier, Oxford, **2021**, pp. 327−364.

[35] R. S. Andrews, J. J. Becker, M. R. Gagne, *Angew. Chem. Int. Ed.* **2010**, *49*, 7274−7276.

[36] W. Shang, S. N. Su, R. Shi, Z. D. Mou, G. Q. Yu, X. Zhang, D. Niu, *Angew. Chem. Int. Ed.* **2021**, *60*, 385−390.

[37] Y. Jiang, Q. Q. Wang, X. L. Zhang, M. J. Koh, *Chem* **2021**, *7*, 3377−3392.

[38] Q. Wang, B. C. Lee, T. J. Tan, Y. Jiang, W. H. Ser, M. J. Koh, *Nat. Synth.* **2022**, *1*, 967−974.

[39] a) M. M. Heravi, A. Nazari, *RSC Adv.* **2022**, *12*, 9944−9994; b) K. C. Nicolaou, S. P. Ellery, J. S. Chen, *Angew. Chem. Int. Ed.* **2009**, *48*, 7140−7165; c) D. J. Edmonds, D. Johnston, D. J. Procter, *Chem. Rev.* **2004**, *104*, 3371−3404.

[40] S. C. Hung, C. H. Wong, *Angew. Chem. Int. Ed.* **1996**, *35*, 2671−2674.

[41] a) G. A. Molander, *Chem. Rev.* **1992**, *92*, 29−68; b) G. A. Molander, C. R. Harris, *Chem. Rev.* **1996**, *96*, 307−338; c) T. Skrydstrup, O. Jarreton, D. Mazeas, D. Urban, J. M. Beau, *Chem. Eur. J.* **1998**, *4*, 655−671.

[42] D. Mazéas, T. Skrydstrup, O. Doumeix, J.-M. Beau, *Angew. Chem. Int. Ed.* **1994**, *33*, 1383−1386.

[43] A. Chénedé, E. Perrin, E. D. Rekaï, P. Sinaÿ, *Synlett* **1994**, *1994*, 420−422.

[44] a) D. Mazéas, T. Skrydstrup, J.-M. Beau, *Angew. Chem. Int. Ed.* **1995**, *34*, 909−912; b) N. Miquel, G. Doisneau, J. M. Beau, *Angew. Chem. Int. Ed.* **2000**, *39*, 4111−4114; c) Z. Abdallah, G. Doisneau, J. M. Beau, *Angew. Chem. Int. Ed.* **2003**, *42*, 5209−5212; d) A. Malapelle, Z. Abdallah, G. Doisneau, J. M. Beau, *Angew. Chem. Int. Ed.* **2006**, *45*, 6016−6020.

[45] D. P. Steinhuebel, J. J. Fleming, J. Du Bois, *Org. Lett.* **2002**, *4*, 293−295.

[46] J. S. Yadav, B. V. S. Reddy, K. V. Rao, K. Saritha Raj, A. R. Prasad, S. Kiran Kumar, A. C. Kunwar, P. Jayaprakash, B. Jagannath, *Angew. Chem. Int. Ed.* **2003**, *42*, 5198−5201.

[47] R. N. Farr, R. A. Outten, J. C. Y. Cheng, G. D. Daves, *Organometallics* **1990**, *9*, 3151−3156.

[48] H. C. Zhang, G. D. Daves, *J. Org. Chem.* **1992**, *57*, 4690−4696.

[49] J. Ramnauth, O. Poulin, S. Rakhit, S. P. Maddaford, *Org. Lett.* **2001**, *3*, 2013−2015.

[50] Y. Bai, L. M. H. Kim, H. Liao, X.-W. Liu, *J. Org. Chem.y* **2013**, *78*, 8821−8825.

[51] S. Xiang, S. Cai, J. Zeng, X.-W. Liu, *Org. Lett.* **2011**, *13*, 4608−4611.

[52] A. K. Kusunuru, S. K. Yousuf, M. Tatina, D. Mukherjee, *Eur. J. Org. Chem.* **2015**, *2015*, 459−462.

[53] E. Dubois, J. M. Beau, *J. Chem. Soc.-Chem. Commun.* **1990**, 1191−1192.

[54] R. W. Friesen, R. W. Loo, *J. Org. Chem.* **1991**, *56*, 4821−4823.

[55] S. Sakamaki, E. Kawanishi, S. Nomura, T. Ishikawa, *Tetrahedron* **2012**, *68*, 5744−5753.

[56] K. Parkan, R. Pohl, M. Kotora, *Chem. Eur. J.* **2014**, *20*, 4414−4419.

[57] L. Gong, H. B. Sun, L. F. Deng, X. Zhang, J. Liu, S. Yang, D. Niu, *J. Am. Chem. Soc.* **2019**, *141*, 7680−7686.

[58] K. Vaňková, M. Rahm, J. Choutka, R. Pohl, K. Parkan, *Chem. Eur. J.* **2021**, *27*, 10583−10588.

[59] M. van der Kaaden, E. Breukink, R. J. Pieters, *Beilstein J. Org. Chem.* **2012**, *8*, 732−737.

[60] L. Gong, H.-B. Sun, L.-F. Deng, X. Zhang, J. Liu, S. Yang, D. Niu, *J. Am. Chem. Soc.* **2019**, *141*, 7680−7686.

[61] S. Lemaire, I. N. Houpis, T. Xiao, J. Li, E. Digard, C. Gozlan, R. Liu, A. Gavryushin, C. Diene, Y. Wang, V. Farina, P. Knochel, *Org. Lett.* **2012**, *14*, 1480−1483.

[62] L. Nicolas, P. Angibaud, I. Stansfield, P. Bonnet, L. Meerpoel, S. Reymond, J. Cossy, *Angew. Chem. Int. Ed.* **2012**, *51*, 11101−11104.

[63] L. Adak, S. Kawamura, G. Toma, T. Takenaka, K. Isozaki, H. Takaya, A. Orita, H. C. Li, T. K. M. Shing, M. Nakamura, *J. Am. Chem. Soc.* **2017**, *139*, 10693−10701.

[64] F. Zhu, J. Rodriguez, T. Yang, I. Kevlishvili, E. Miller, D. Yi, S. O'Neill, M. J. Rourke, P. Liu, M. A. Walczak, *J. Am. Chem.l Soc.* **2017**, *139*, 17908−17922.

[65] A. Dumoulin, J. K. Matsui, A. Gutierrez-Bonet, G. A. Molander, *Angew. Chem. Int. Ed.* **2018**, *57*, 6614−6618.

[66] S. O. Badir, A. Dumoulin, J. K. Matsui, G. A. Molander, *Angew. Chem. Int. Ed.* **2018**, *57*, 6610−6613.

[67] P. Ji, Y. Zhang, Y. Wei, H. Huang, W. Hu, P. A. Mariano, W. Wang, *Org. Lett.* **2019**, *21*, 3086−3092.

[68] a) Y. Wei, B. Ben-Zvi, T. Diao, *Angew. Chem. Int. Ed.* **2021**, *60*, 9433−9438; b) Y. Wei, J. Lam, T. Diao, *Chem. Sci.* **2021**, *12*, 11414−11419.

[69] Y. Ma, S. Liu, Y. Xi, H. Li, K. Yang, Z. Cheng, W. Wang, Y. Zhang, *Chem. Commun.* **2019**, *55*, 14657−14660.

[70] N. Probst, G. Grelier, S. Dahaoui, M. Alami, V. Gandon, S. Messaoudi, *ACS Catal.* **2018**, *8*, 7781−7786.

[71] J. Ghouilem, C. Tran, N. Grimblat, P. Retailleau, M. Alami, V. Gandon, S. Messaoudi, *ACS Catal.* **2021**, *11*, 1818−1826.

[72] M. de Robichon, A. Bordessa, M. Malinowski, J. Uziel, N. Lubin-Germain, A. Ferry, *Chem. Commun.* **2019**, *55*, 11806−11808.

[73] M. Robichon, D. Branquet, J. Uziel, N. Lubin-Germain, A. Ferry, *Adv. Synth. Catal* **2021**, *363*, 5138−5148.

[74] Y. Bai, J. Zeng, S. Cai, X.-W. Liu, *Org. Lett.* **2011**, *13*, 4394−4397.

[75] W. Li, A. Silipo, A. Molinaro, B. Yu, *Chem. Commun.* **2015**, *51*, 6964−6967.

[76] N. Gigant, J.-E. Bäckvall, *Chem. Eur. J.* **2013**, *19*, 10799−10803.

[77] N. Hussain, M. Babu Tatina, D. Mukherjee, *Org. Biomol. Chem.* **2018**, *16*, 2666−2677.

[78] F. Rasool, D. Mukherjee, *Org. Lett.* **2017**, *19*, 4936−4939.

[79] S. Zhang, Y. H. Niu, X. S. Ye, *Org. Lett.* **2017**, *19*, 3608−3611.

[80] M. Liu, Y. Niu, Y.-F. Wu, X.-S. Ye, *Org. Lett.* **2016**, *18*, 1836−1839.

[81] Q. Wang, S. An, Z. Deng, W. Zhu, Z. Huang, G. He, G. Chen, *Nat. Catal.* **2019**, *2*, 793−800.

[82] W.-Y. Shi, Y.-N. Ding, N. Zheng, X.-Y. Gou, Z. Zhang, X. Chen, Y.-Y. Luan, Z.-J. Niu, Y.-M. Liang, *Chem. Commun.* **2021**, *57*, 8945−8948.

[83] Q. Wang, Y. Fu, W. Zhu, S. An, Q. Zhou, S.-F. Zhu, G. He, P. Liu, G. Chen, *CCS Chem.* **2021**, *3*, 1729−1736.

[84] Q. Sun, H. Zhang, Q. Wang, T. Qiao, G. He, G. Chen, *Angew. Chem. Int. Ed.* **2021**, *60*, 19620−19625.

[85] J. Liu, H. Gong, *Org. Lett.* **2018**, *20*, 7991−7995.

[86] Y. N. Ding, N. Li, Y. C. Huang, W. Y. Shi, N. Zheng, C. T. Wang, Y. An, X. Y. Liu, Y. M. Liang, *Org. Lett.* **2022**, *24*, 2381−2386.

[87] K. Sakamoto, M. Nagai, Y. Ebe, H. Yorimitsu, T. Nishimura, *ACS Catalysis* **2019**, *9*, 1347−1352.

[88] W. Zhu, Q. Sun, H. Chang, H.-X. Zhang, Q. Wang, G. Chen, G. He, *Chinese J. Chem.* **2022**, *40*, 571−576.

[89] C. Yu, Y. Liu, X. Xie, S. Hu, S. Zhang, M. Zeng, D. Zhang, J. Wang, H. Liu, *Adv. Syn. Catal.* **2021**, *363*, 4926−4931.

[90] M. Catellani, F. Frignani, A. Rangoni, *Angew. Chem. Int. Ed.* **1997**, *36*, 119−122.

[91] a) N. Della Ca, M. Fontana, E. Motti, M. Catellani, *Acc. Chem. Res.* **2016**, *49*, 1389−1400; b) J. Wang, G. Dong, *Chem. Rev.* **2019**, *119*, 7478−7528.

[92] R. Li, G. Dong, *J. Am. Chem. Soc.* **2020**, *142*, 17859−17875.

[93] W. Lv, Y. Chen, S. Wen, D. Ba, G. Cheng, *J. Am. Chem. Soc.* **2020**, *142*, 14864−14870.

[94] Y.-N. Ding, W.-Y. Shi, C. Liu, N. Zheng, M. Li, Y. An, Z. Zhang, C.-T. Wang, B.- , *Angew. Chem. Int. Ed.* **2013**, *52*, 6080−6083.

[97] Y.-X. Zheng, L. Jiao, *Nat* S. Zhang, Y.-M. Liang, *J. Org. Chem.* **2020**, *85*, 11280−11296.

[95] a) D. A. Candito, M. Lautens, *Angew. Chem. Int. Ed.* **2009**, *48*, 6713-6716; b) H. Liu, M. El-Salfiti, M. Lautens, *Angew. Chem. Int. Ed.* **2012**, *51*, 9846-9850; c) H. Weinstabl, M. Suhartono, Z. Qureshi, M. Lautens, *Angew. Chem. Int. Ed.* **2013**, *52*, 5305-5308; d) J. Ye, M. Lautens, *Nat. Chem.* **2015**, *7*, 863-870; e) J. Ye, Z. Shi, T. Sperger, Y. Yasukawa, C. Kingston, F. Schoenebeck, M. Lautens, *Nat. Chem.* **2017**, *9*, 361-368.

[96] a) L. Jiao, T. Bach, *J. Am. Chem. Soc.* **2011**, *133*, 12990−12993; b) L. Jiao, T. Bach

. Synth. **2022**, *1*, 180−187.

[98] T. Nishikawa, *Synlett* **1999**, *1999*, 123−125.

[99] Y. An, B.-S. Zhang, Y.-N. Ding, Z. Zhang, X.-Y. Gou, X.-S. Li, X. Wang, Y. Li, Y.-M. Liang, *Chem. Sci.* **2021**, *12*, 13144−13150.

[100] a) R. Qi, C. Wang, Z. Ma, H. Wang, Q. Chen, L. Liu, D. Pan, X. Ren, R. Wang, Z. Xu, *Angew. Chem. Int. Ed.* **2022**, *61*, e202200822; b) Y. N. Ding, N. Li, Y. C. Huang, Y. An, Y. M. Liang, *Org. Lett.* **2022**, *24*, 4519−4523; c) R. Qi, C. Wang, Z. Ma, H. Wang, Q. Chen, L. Liu, D. Pan, X. Ren, R. Wang, Z. Xu, *Angew. Chem. Int. Ed.* **2022**, *61*, e202200822.

[101] R. Qi, C. Wang, Y. Huo, H. Chai, H. Wang, Z. Ma, L. Liu, R. Wang, Z. Xu, *J. Am. Chem. Soc.* **2021**, *143*, 12777−12783.

[102] a) H.-R. Tong, B. Li, G. Li, G. He, G. Chen, *CCS Chem.* **2021**, *3*, 1797v1820; b) B. B. Zhan, M. X. Jiang, B. F. Shi, *Chem. Commun.* **2020**, *56*, 13950−13958; c) Z. B. Bai, H. Wang, *Synlett* **2020**, *31*, 199−204; d) G. He, B. Wang, W. A. Nack, G. Chen, *Acc. Chem. Res.* **2016**, *49*, 635−645.

[103] a) Z. Yuan, C. Zhu, Y. Zhang, Y. Rao, *Eur. J. Org. Chem.* **2022**, *2022,* e202201036; b) J. Ghouilem, M. de Robichon, F. Le Bideau, A. Ferry, S. Messaoudi, *Chem. Eur J.* **2021**, *27*, 491−511.

[104] K. Korvorapun, R. C. Samanta, T. Rogge, L. Ackermann, *Synthesis* **2021**, *53*, 2911−2946.

[105] a) R. A. Dwek, *Chem. Rev.* **1996**, *96*, 683−720; b) A. Varki, *Glycobiology* **1993**, *3*, 97-130; c) D. H. R. Barton, S. D. Gero, B. Quicletsire, M. Samadi, *Tetrahedron-Asymmetry* **1994**, *5*, 2123−2136.

[106] a) P. Sears, C. H. Wong, *Angew. Chem. Int. Ed.* **1999**, *38*, 2300−2324; b) L. A. Marcaurelle, C. R. Bertozzi, *Chem. Eur. J.* **1999**, *5*, 1384−1390.

[107] a) J. Revuelta, R. Fuentes, L. Lagartera, M. J. Hernaiz, A. Bastida, E. Garcia-Junceda, A. Fernandez-Mayoralas, *Chem. Commun.* **2018**, *54*, 13455−13458; b) A. Dondoni, A. Massi, *Acc. Chem. Res.* **2006**, *39*, 451−463; c) M. Bejugam, S. L. Flitsch, *Org. Lett.* **2004**, *6*, 4001−4004; d) A. Dondoni, A. Marra, *Chem. Rev.* **2000**, *100*, 4395−4422; e) M. Monsigny, C. Quetard, S. Bourgerie, D. Delay, C. Pichon, P. Midoux, R. Mayer, A. C. Roche, *Biochimie* **1998**, *80*, 99−108.

[108] J. R. Axon, A. L. J. Beckwith, *J. Chem. Soc., Chem. Commun.* **1995**, 549−550.

[109] S. P. Vincent, A. Schleyer, C. H. Wong, *J. Org. Chem.* **2000**, *65*, 4440−4443.

[110] S. D. Debenham, J. S. Debenham, M. J. Burk, E. J. Toone, *J. Am. Chem. Soc.* **1997**, *119*, 9897−9898.

[111] a) A. Dondoni, A. Massi, S. Sabbatini, *Tetrahedron Lett.* **2001**, *42*, 4495−4497; b) C. Oliver Kappe, *Tetrahedron* **1993**, *49*, 6937−6963.

[112] H. Kunz, W. Pfrengle, *J. Am. Chem. Soc.* **1988**, *110*, 651−652.

[113] a) Z. Shi, X. Han, W. Hu, H. Bai, B. Peng, L. Ji, Q. Fan, L. Li, W. Huang, *Chem. Soc. Rev.* **2020**, *49*, 7533−7567; b) Z. Liu, Z. Jiang, M. Yan, X. Wang, *Front*

Chem **2019**, *7*, 712; c) A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891−4932.

[114] R. A. Dwek, *Chem. Rev.* **1996**, *96*, 683−720.

[115] P. M. Simon, *Drug Discov. Today* **1996**, *1*, 522−528.

[116] T. Mochizuki, M. Shiozaki, *Chem. Lett.* **1997**, *26*, 801−802.

[117] N. Ikemoto, S. L. Schreiber, *J. Am. Chem. Soc.* **2002**, *114*, 2524−2536.

[118] a) K. C. Nicolaou, M. O. Frederick, A. C. Burtoloso, R. M. Denton, F. Rivas, K. P. Cole, R. J. Aversa, R. Gibe, T. Umezawa, T. Suzuki, *J. Am. Chem. Soc.* **2008**, *130*, 7466−7476; b) K. C. Nicolaou, P. Heretsch, T. Nakamura, A. Rudo, M. Murata, K. Konoki, *J. Am. Chem. Soc.* **2014**, *136*, 16444−16451.

[119] a) X. Yuan, R. J. Linhardt, *Curr. Top. Med. Chem.* **2005**, *5*, 1393−1430; b) L. Lei, M. Michael, H. D. P. Maarten, *Curr. Org. Chem.* **2001**, *5*, 1133−1167; c) P. Sinaÿ, *Pure Appl. Chem.* **1997**, *69*, 459−464.

[120] M. Guerrini, S. Guglierl, R. Santarsiero, E. Vismara, *Tetrahedron-Asymmetry* **2005**, *16*, 243−253.

[121] L. Liu, M. H. Postema, *J. Am. Chem. Soc.* **2001**, *123*, 8602−8603.

[122] D. C. Myles, S. J. Danishefsky, G. Schulte, *J. Org. Chem.* **1990**, *55*, 1636−1648.

[123] D. C. Koester, E. Kriemen, D. B. Werz, *Angew. Chem. Int. Ed.* **2013**, *52*, 2985−2989.

[124] G. D. McAllister, D. E. Paterson, R. J. Taylor, *Angew. Chem. Int. Ed.* **2003**, *42*, 1387−1391.

[125] K. Masuda, M. Nagatomo, M. Inoue, *Nat. Chem.* **2017**, *9*, 207−212.

[126] H. Fujino, T. Fukuda, M. Nagatomo, M. Inoue, *J. Am. Chem. Soc.* **2020**, *142*, 13227−13234.

[127] a) Q. Zhang, L.-S. Wu, B.-F. Shi, *Chem* **2022**, *8*, 384−413; b) L. Zhang, T. Ritter, *J. Am. Chem. Soc.* **2022**, *144*, 2399−2414; c) D. S. Brandes, J. A. Ellman, *Chem. Soc. Rev.* **2022**, *51*, 6738−6756; d) Z. Shen, I. Maksso, R. Kuniyil, T. Rogge, L. Ackermann, *Chem. Commun.* **2021**, *57*, 3668−3671; e) N. Y. S. Lam, K. Wu, J. Q. Yu, *Angew. Chem. Int. Ed.* **2021**, *60*, 15767−15790; f) C. Shan, L. Zhu, L. B. Qu, R. Bai, Y. Lan, *Chem. Soc. Rev.* **2018**, *47*, 7552−7576; g) J. R. Hummel, J. A. Boerth, J. A. Ellman, *Chem. Rev.* **2017**, *117*, 9163−9227; h) T. Gensch, M. N. Hopkinson, F. Glorius, J. Wencel-Delord, *Chem. Soc. Rev.* **2016**, *45*, 2900−2936; i) L. Yang, H. Huang, *Chem. Rev.* **2015**, *115*, 3468−3517; j) J.

Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369−375; k) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960−9009; l) B. J. Li, Z. J. Shi, *Chem. Soc. Rev.* **2012**, *41*, 5588−5598; m) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879−5918.

[128] a) S. K. Sinha, S. Guin, S. Maiti, J. P. Biswas, S. Porey, D. Maiti, *Chem. Rev.* **2022**, *122*, 5682−5841; b) U. Dutta, D. Maiti, *Acc. Chem. Res.* **2022**, *55*, 354−372; c) W. Guo, Q. Wang, J. Zhu, *Chem. Soc. Rev.* **2021**, *50*, 7359−7377; d) G. Meng, N. Y. S. Lam, E. L. Lucas, T. G. Saint-Denis, P. Verma, N. Chekshin, J. Q. Yu, *J. Am. Chem. Soc.* **2020**, *142*, 10571−10591; e) H. G. Cheng, S. Chen, R. Chen, Q. Zhou, *Angew. Chem. Int. Ed.* **2019**, *58*, 5832−5844; f) M. T. Mihai, G. R. Genov, R. J. Phipps, *Chem. Soc. Rev.* **2018**, *47*, 149−171; g) F. F. Khan, S. K. Sinha, G. K. Lahiri, D. Maiti, *Chem. Asian J.* **2018**, *13*, 2243−2256; h) J. A. Leitch, C. G. Frost, *Chem. Soc. Rev.* **2017**, *46*, 7145−7153.

[129] N. Y. S. Lam, Z. Fan, K. Wu, H. S. Park, S. Y. Shim, D. A. Strassfeld, J. Q. Yu, *J. Am. Chem. Soc.* **2022**, *144*, 2793−2803.

[130] H. M. Davies, D. Morton, *Chem. Soc. Rev.* **2011**, *40*, 1857−1869.

[131] I. A. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890−931.

[132] a) A. M. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, *Organometallics* **1999**, *18*, 2813−2820; b) C. Coudret, S. Fraysse, J. P. Launay, *Chem. Commun.* **1998**, 663−664.

[133] L. Ackermann, P. Novak, R. Vicente, N. Hofmann, *Angew. Chem. Int. Ed.* **2009**, *48*, 6045−6048.

[134] L. Ackermann, N. Hofmann, R. Vicente, *Org. Lett.* **2011**, *13*, 1875−1877.

[135] O. Saidi, J. Marafie, A. E. Ledger, P. M. Liu, M. F. Mahon, G. Kociok-Kohn, M. K. Whittlesey, C. G. Frost, *J. Am. Chem. Soc.* **2011**, *133*, 19298−19301.

[136] a) J. Li, K. Korvorapun, S. De Sarkar, T. Rogge, D. J. Burns, S. Warratz, L. Ackermann, *Nat. Commun.* **2017**, *8*, 15430; b) J. Li, S. Warratz, D. Zell, S. De Sarkar, E. E. Ishikawa, L. Ackermann, *J. Am. Chem. Soc.* **2015**, *137*, 13894−13901; c) N. Hofmann, L. Ackermann, *J. Am. Chem. Soc.* **2013**, *135*, 5877−5884.

[137] K. Jing, Z. Y. Li, G. W. Wang, *ACS Catal.* **2018**, *8*, 11875−11881.

[138] C. Jia, N. Wu, X. Cai, G. Li, L. Zhong, L. Zou, X. Cui, *J. Org. Chem.* **2020**, *85*, 4536−4542.

[139] a) A. J. Paterson, S. St John-Campbell, M. F. Mahon, N. J. Press, C. G. Frost, *Chem. Commun.* **2015**, *51*, 12807−12810; b) Z. Y. Li, L. Li, Q. L. Li, K. Jing, H. Xu, G. W. Wang, *Chem. Eur. J.* **2017**, *23*, 3285−3290; c) Z. Ruan, S. K. Zhang, C. Zhu, P. N. Ruth, D. Stalke, L. Ackermann, *Angew. Chem. Int. Ed.* **2017**, *56*, 2045−2049; d) F. Fumagalli, S. Warratz, S. K. Zhang, T. Rogge, C. Zhu, A. C. Stuckl, L. Ackermann, *Chem. Eur. J.* **2018**, *24*, 3984−3988; e) K. Korvorapun, N. Kaplaneris, T. Rogge, S. Warratz, A. C. Stückl, L. Ackermann, *ACS Catal.* **2018**, *8*, 886−892; f) X. G. Wang, Y. Li, L. L. Zhang, B. S. Zhang, Q. Wang, J. W. Ma, Y. M. Liang, *Chem. Commun.* **2018**, *54*, 9541−9544; g) P. Gandeepan, J. Koeller, K. Korvorapun, J. Mohr, L. Ackermann, *Angew. Chem. Int. Ed.* **2019**, *58*, 9820−9825; h) I. Choi, V. Muller, Y. Wang, K. Xue, R. Kuniyil, L. B. Andreas, V. Karius, J. G. Alauzun, L. Ackermann, *Chem. Eur. J.* **2020**, *26*, 15290−15297; i) K. Korvorapun, M. Moselage, J. Struwe, T. Rogge, A. M. Messinis, L. Ackermann, *Angew. Chem. Int. Ed.* **2020**, *59*, 18795−18803; j) W. Wei, H. Yu, A. Zangarelli, L. Ackermann, *Chem. Sci.* **2021**, *12*, 8073−8078; k) H. C. Liu, X. Kong, X. P. Gong, Y. Li, Z. J. Niu, X. Y. Gou, X. S. Li, Y. Z. Wang, W. Y. Shi, Y. C. Huang, X. Y. Liu, Y. M. Liang, *Chem. Sci.* **2022**, *13*, 5382−5389; l) Y. Wang, S. Chen, X. Chen, A. Zangarelli, L. Ackermann, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205562; m) J. Wu, N. Kaplaneris, J. Pohlmann, T. Michiyuki, B. Yuan, L. Ackermann, *Angew. Chem. Int. Ed.* **2022**, *61*, e202208620; n) S. Yang, B. Yan, L. Zhong, C. Jia, D. Yao, C. Yang, K. Sun, G. Li, *Org. Chem. Front.* **2020**, *7*, 2474−2479; o) G. Li, C. Jia, X. Cai, L. Zhong, L. Zou, X. Cui, *Chem. Commun.* **2019**, *56*, 293−296.

[140] C. Jia, N. Wu, G. Li, X. Cui, *J. Org. Chem.* **2022**, *87*, 6934−6941.

[141] a) C. J. Teskey, A. Y. Lui, M. F. Greaney, *Angew. Chem. Int. Ed.* **2015**, *54*, 11677−11680; b) Q. Yu, L. Hu, Y. Wang, S. Zheng, J. Huang, *Angew. Chem. Int. Ed.* **2015**, *54*, 15284−15288; c) S. Warratz, D. J. Burns, C. Zhu, K. Korvorapun, T. Rogge, J. Scholz, C. Jooss, D. Gelman, L. Ackermann, *Angew. Chem. Int. Ed.* **2017**, *56*, 1557−1560; d) X. Y. Gou, Y. Li, W. Y. Shi, Y. Y. Luan, Y. N. Ding, Y. An, Y. C. Huang, B. S. Zhang, X. Y. Liu, Y. M. Liang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205656; e) Y. Wang, H. Simon, X. Chen, Z. Lin,

S. Chen, L. Ackermann, *Angew. Chem. Int. Ed.* **2022**, *61*, e202201595; f) Z. Fan, H. Lu, Z. Cheng, A. Zhang, *Chem. Commun.* **2018**, *54*, 6008-6011.

[142] G. L. Tu, G. D. Ju, Z. B. Huang, S. J. Ji, Y. S. Zhao, *Org. Chem. Front.* **2022**, *9*, 3876−3881.

[143] a) Z. Fan, J. Ni, A. Zhang, *J. Am. Chem. Soc.* **2016**, *138*, 8470−8475; b) S. Sasmal, S. K. Sinha, G. K. Lahiri, D. Maiti, *Chem. Commun.* **2020**, *56*, 7100−7103; c) D. Liu, P. Luo, J. Ge, Z. Jiang, Y. Peng, Q. Ding, *J. Org. Chem.* **2019**, *84*, 12784−12791.

[144] P. Marcé, A. J. Paterson, M. F. Mahon, C. G. Frost, *Catal. Sci. Technol.* **2016**, *6*, 7068−7076.

[145] a) T. Bililign, B. R. Griffith, J. S. Thorson, *Nat. Prod. Rep.* **2005**, *22*, 742−760; b) K. Kitamura, Y. Ando, T. Matsumoto, K. Suzuki, *Chem. Rev.* **2018**, *118*, 1495−1598; c) D. Y. Lee, M. He, *Curr. Top. Med. Chem.* **2005**, *5*, 1333−1350.

[146] a) W. Y. Shi, Y. N. Ding, N. Zheng, X. Y. Gou, Z. Zhang, X. Chen, Y. Y. Luan, Z. J. Niu, Y. M. Liang, *Chem. Commun.* **2021**, *57*, 8945−8948; b) Q. Q. Wang, W. J. Zhu, Q. K. Sun, G. He, G. Chen, *Chin. J. Chem.* **2021**, *39*, 571−576; c) W. Zhu, Q. Sun, H. Chang, H. X. Zhang, Q. Wang, G. Chen, G. He, *Chin. J. Chem.* **2021**, *40*, 571−576; d) S. Cai, Q. Sun, Q. Wang, G. He, G. Chen, *J. Org. Chem.* **2022**, *87*, 8811−8818.

[147] a) Y. N. Ding, W. Y. Shi, C. Liu, N. Zheng, M. Li, Y. An, Z. Zhang, C. T. Wang, B. S. Zhang, Y. M. Liang, *J. Org. Chem.* **2020**, *85*, 11280−11296; b) Y. An, B. S. Zhang, Y. N. Ding, Z. Zhang, X. Y. Gou, X. S. Li, X. Wang, Y. Li, Y. M. Liang, *Chem. Sci.* **2021**, *12*, 13144v13150; c) Y. N. Ding, Y. C. Huang, W. Y. Shi, N. Zheng, C. T. Wang, X. Chen, Y. An, Z. Zhang, Y. M. Liang, *Org. Lett.* **2021**, *23*, 5641−5646.

[148] W. Y. Shi, H. Y. Li, X. Y. Gou, Y. Y. Luan, N. Zheng, Z. J. Niu, Z. Zhang, X. Y. Liu, Y. M. Liang, *Adv. Synth. Catal* **2022**, *364*, 2796−2800.

[149] L. Ackermann, A. V. Lygin, *Org. Lett.* **2011**, *13*, 3332−3335.

[150] L. Ackermann, P. Novak, *Org. Lett.* **2009**, *11*, 4966−4969.

[151] G. Tan, M. L. Schrader, C. Daniliuc, F. Strieth-Kalthoff, F. Glorius, *Angew. Chem. Int. Ed.* **2020**, *59*, 21541−21545.

[152] B. Giese, *Angew. Chem. Int. Ed.* **1989**, *28*, 969−980.

[153] H. Abe, S. Shuto, A. Matsuda, *J. Am. Chem. Soc.* **2001**, *123*, 11870-11882.

[154] a) B. Giese, J. Dupuis, M. Leising, M. Nix, H. J. Lindner, *Carbohydr. Res.* **1987**, *171*, 329−341; b) J. Dupuis, B. Giese, D. Rüegge, H. Fischer, H.-G. Korth, R. Sustmann, *Angew. Chem. Int. Ed.* **1984**, *23*, 896−898.

[155] R. P. Loach, O. S. Fenton, K. Amaike, D. S. Siegel, E. Ozkal, M. Movassaghi, *J. Org. Chem.* **2014**, *79*, 11254−11263.

[156] a) L. Xu, C. Zhang, Y. He, L. Tan, D. Ma, *Angew. Chem. Int. Ed.* **2016**, *55*, 321−325; b) L. Liu, X. Fan, B. Wang, H. Deng, T. Wang, J. Zheng, J. Chen, Z. Shi, H. Wang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202206177.

[157] L. Xu, L. Tan, D. Ma, *J. Org. Chem.* **2016**, *81*, 10476−10483.

[158] W. Wang, J. Wu, R. Kuniyil, A. Kopp, R. N. Lima, L. Ackermann, *Chem* **2020**, *6*, 3428−3439.

[159] J. Wu, N. Kaplaneris, S. Ni, F. Kaltenhauser, L. Ackermann, *Chem. Sci.* **2020**, *11*, 6521−6526.

[160] J. Wu, A. Kopp, L. Ackermann, *Angew. Chem. Int. Ed.* **2022**, *61*, e202114993.

[161] a) K. Schwekendiek, F. Glorius, *Synthesis* **2006**, 2996-3002; b) N. Mori, H. Togo, *Tetrahedron* **2005**, *61*, 5915−5925.

[162] a) H. H. Al Mamari, E. Diers, L. Ackermann, *Chem. Eur. J.* **2014**, *20*, 9739−9743; b) Q. Gu, H. H. Al Mamari, K. Graczyk, E. Diers, L. Ackermann, *Angew. Chem. Int. Ed.* **2014**, *53*, 3868−3871; c) W. Wang, M. M. Lorion, O. Martinazzoli, L. Ackermann, *Angew. Chem. Int. Ed.* **2018**, *57*, 10554−10558.

[163] a) B. Wang, W. A. Nack, G. He, S.-Y. Zhang, G. Chen, *Chem. Sci.* **2014**, *5*, 3952−3957; b) B. Wang, X. Wu, R. Jiao, S. Y. Zhang, W. A. Nack, G. He, G. Chen, *Org. Chem. Front.* **2015**, *2*, 1318−1321.

[164] G. Zhao, W. Yao, J. N. Mauro, M. Y. Ngai, *J. Am. Chem. Soc.* **2021**, *143*, 1728−1734.

[165] K. Xu, W. Li, R. Sun, L. Luo, X. Chen, C. Zhang, X. Zheng, M. Yuan, H. Fu, R. Li, H. Chen, *Org. Lett.* **2020**, *22*, 6107−6111.

[166] L. Ackermann, P. Novák, *Org. Lett.* **2009**, *11*, 4966−4969.

[167] G. Tan, M. L. Schrader, C. Daniliuc, F. Strieth-Kalthoff, F. Glorius, *Angew. Chem. Int. Ed.* **2020**, *59*, 21541−21545.

[168] S. Li, W.-J. Li, X. Yang, R. Sun, J. Tang, X.-L. Zheng, M.-L. Yuan, R.-X. Li, H. Chen, H.-Y. Fu, *Org. Chem. Front.* **2020**, *7*, 3887−3895.

[169] L. Ackermann, R. Vicente, A. Althammer, *Org. Lett.* **2008**, *10*, 2299−2302.

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Publications

1. **Wu. J.[+]**, Wei. W.[+], Pöhlmann. J., Purushothaman R., Ackermann L., Domino meta-C−H Ethyl Glycosylation by Ruthenium(II/III) Catalysis: Modular Assembly of meta-*C*-Alkyl Glycoside. *Angew. Chem. Int. Ed.* **2023**, *62*, e202219319. (co-first author)
2. **Wu, J**.; Kaplaneris, N.; Pöhlmann, J.; Michiyuki, T.; Yuan, B.; Ackermann, L., Remote C-H Glycosylation by Ruthenium(II) Catalysis: Modular Assembly of meta-*C*-Aryl Glycosides. *Angew. Chem. Int. Ed.* **2022,** *61* (42), e202208620.
3. **Wu, J**.; Kopp, A.; Ackermann, L. Synthesis of *C*-Oligosaccharides through Versatile C(sp^3)−H Glycosylation of Glycosides. *Angew. Chem. Int. Ed.* **2022**, *61*, e202114993.
4. **Wu, J.[+]**; Kaplaneris, N.[+]; Ni, S.; Kaltenhauser, F.; Ackermann, L. Late-stage C(sp^2)-H and C(sp^3)-H glycosylation of *C*-aryl/alkyl glycopeptides: mechanistic insights and fluorescence labeling. *Chem. Sci.* **2020**, *11*, 6521−6526. (co-first author)
5. Wang, W.[+]; **Wu, J.[+]**; Kuniyil, R.; Kopp, A.; Lima, R. N.; Ackermann, L. Peptide Late-Stage Diversifications by Rhodium-Catalyzed Tryptophan C7 Amidation. *Chem* **2020**, *6*, 3428−3439. (co-first author)
6. **Wu, J**.; Tang, Y.; Wei, W.; Wu, Y.; Li, Y.; Zhang, J.; Zheng, Y.; Xu, S. Phosphine-Catalyzed Activation of Vinylcyclopropanes: Rearrangement of Vinylcyclopropylketones to Cycloheptenones. *Angew. Chem. Int. Ed.* **2018**, *57*, 6284−6288.
7. **Wu, J.[+]**; Zhang, J.-Y.[+]; Gao, P.; Xu, S.-L.; Guo, L.-N. Copper-Catalyzed Redox-Neutral Cyanoalkylarylation of Activated Alkenes with Cyclobutanone Oxime Esters. *J. Org. Chem.* **2018**, *83*, 1046−1055. (co-first author)
8. X. Chen, H. C. Gülen, **J. Wu**, Z.-J. Zhang, X. Hong, L. Ackermann, Close-Shell Reductive Elimination versus Open-Shell Radical Coupling

for Site-Selective Ruthenium-Catalyzed C–H Activations by Computation and Experiments. *Angew. Chem. Int. Ed.* **2023**, *62*, e202302021.

9. Kaplaneris, N.; Vilches-Herrera, M.; **Wu, J**.; Ackermann, L. Sustainable Ruthenium(II)-Catalyzed C–H Activations in and on H_2O. *ACS Sustain. Chem. Eng.* **2022**, *10*, 6871−6888;
10. Mendive-Tapia, L.; Mendive-Tapia, D.; Zhao, C.; Gordon, D.; Benson, S.; Bromley, M. J.; Wang, W.; **Wu, J.**; Kopp, A.; Ackermann, L.; Vendrell, M. Rational Design of Phe-BODIPY Amino Acids as Fluorogenic Building Blocks for Peptide-Based Detection of Urinary Tract Candida Infections. *Angew. Chem. Int. Ed.* **2022**, *61*, e202117218
11. Wang, W.; Subramanian, P.; Martinazzoli, O.; **Wu, J.**; Ackermann, L. Glycopeptides by Linch-Pin C−H Activations for Peptide-Carbohydrate Conjugation by Manganese(I)-Catalysis. *Chem. Eur.J.* **2019**, *25*, 10585−10589;
12. Virelli, M.; Wang, W.; Kuniyil, R.; **Wu, J.**; Zanoni, G.; Fernandez, A.; Scott, J.; Vendrell, M.; Ackermann, L. BODIPY-Labeled Cyclobutanes by Secondary C(sp^3)−H Arylations for Live-Cell Imaging. *Chem. Eur.J.* **2019**, *25*, 12712−12718;
13. Wei, W.; Tang, Y.; Zhou, Y.; Deng, G.; Liu, Z.; **Wu, J.**; Li, Y.; Zhang, J.; Xu, S. Recycling Catalyst as Reactant: A Sustainable Strategy To Improve Atom Efficiency of Organocatalytic Tandem Reactions. *Org. Lett.* **2018**, *20*, 6559−6563;
14. Li, Y.; Tang, Y.; He, X.; Shi, D.; **Wu, J.**; Xu, S. Rhodium(III)-Catalyzed Annulative Carbooxygenation of 1,1-Disubstituted Alkenes Triggered by C−H Activation. *Chem. Eur.J.* **2017**, *23*, 7453−7457

Erklärung

Ich versichere, dass ich die vorliegende Dissertation in dem Zeitraum von Oktober 2018 bis Juni 2023 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 16.06.2023