Studies Toward Selenium-π-Acid Catalyzed Oxidative Functionalizations of Olefinic and Acetylenic Multiple Bonds

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“Ja, aber Pippi”, sagte Thomas. “Du kannst ja wohl nicht Klavier spielen!”
“Wie soll ich das wissen, wenn ich es noch nie versucht hab?”, fragte Pippi.

«–»

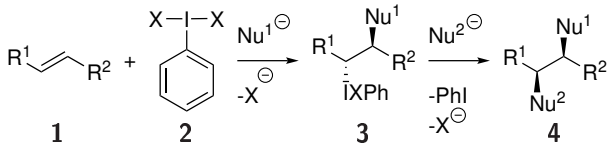
Kapitän Langstrumpf stand eine Weile still. “Mach es wie du willst”, sagte er schließlich. “Das hast du immer getan.”
Pippi nickte zustimmend. “Ja, das habe ich immer getan”, sagte sie ruhig.

Pippi Langstrumpf /Pippi geht an Bord
Astrid Lindgren

Contents

1 Introduction

Simple olefins are important starting materials for organic syntheses. Due to their easy availability from petrochemical industrial processes, they are abundant and inexpensive. Therefore, the functionalization of alkenes, especially oxidative functionalizations, which are a step-economic,[1–3] versatile tool for the formation of new C−C,[4–6] C−N,[7,8] C−O,[7,9] C−S[10] and C−Hal[11,12] bonds, has been the subject of extensive research in the last decades. The larger part of the methods developed thus far involve the use of transition metal catalysts such as palladium[4,7,13,14] or copper complexes.[9] Although a large variety of different methods for the functionalization of terminal alkenes has been developed, the functionalization of internal alkenes remains challenging.[13] This is due to many transition metal catalysts being prone to isomerization of the double bond to the terminal position, which often leads to mixtures of products.[13] During the last decades, the use of organocatalytic alternatives for the oxidative functionalization of terminal and internal alkenes has been explored. Especially the use of electrophilic, hypervalent iodine(III) reagents turned out to be a versatile and mild method for the formation of C-O,[15–18] C-N[19–22] and C-Hal[23–25] bonds. In most cases, vicinal difunctionalizations of alkenes **1** took place by forming iodofunctionalized intermediate **3** followed by a substitution of the iodo-moiety with a second nucleophile, yielding the *syn*-product **4** (Scheme 1.1).[26,27]



Scheme 1.1: Iodine(III)-mediated oxidative vicinal functionalization of alkenes.

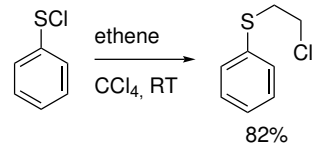
Furthermore, an allylic amination of α-methyl styrene derivatives was accomplished by Muñiz *et al.* by eliminating the iodine moiety from intermediate **3** instead of substituting it.[28] The elimination was preferred due to the iodo-moiety being attached to a tertiary carbon. The iodine(III)-mediated functionalizations were further improved by the development of catalytic variants of the previous reactions.[27,29–31] Because in the elimination step an iodide(I) species is formed, a suitable oxidant is needed to facilitate the reformation of the catalytically active iodine(III) species. The group of Fuchigami was able to perform the reoxidation electrochemically,[29] while the groups of Kita and Ochiai employed *m*CPBA as the terminal oxidant.[30,31] Another important achievement was the development of stereo- and enantioselective variants. Fujita and colleagues were able to perform intramolecular oxylactonizations of *ortho*-alkenylbenzoates with *ee*'s up to 98%,[32,33] and Wirth and colleagues were able to achieve the cyclization of bisnucleophilic urea derivatives to isourea derivatives with up to 99% *ee* by using chiral non-racemic hypervalent iodine(III) species at low reaction temperatures.[34] The application of a chiral iodine(III) catalyst was first realized by Muñiz and colleagues.[35] They were able to

accomplish the catalytic intermolecular diacetoxylation of styrenes using peracetic acid as the terminal oxidant with up to 94% *ee*.

A method that is conceptually cognate to the iodine(III)-mediated reactions is the application of electrophilic sulfur and selenium compounds in the oxidative functionalization of alkenes. After the development of stoichiometric methods for the oxidative chalcogenofunctionalization of alkenes, the identification of suitable oxidants facilitated the investigation of several catalytic methods.[36,37] As chalcogen-catalyzed reactions usually afford allylic or vinylic products, they beneficially complement the available repertoire of transition-metal and iodine(III)-catalyzed oxidative functionalizations of alkenes.

1.1 Chalcogens in oxidative alkene functionalization reactions

The first functionalization reactions of alkenes with chalcogens were addition reactions of electrophilic sulfenyl chlorides. In 1925, Lecher and colleagues described the addition of phenyl-, *p*-tolyl- and 2-nitrobenzenesulfenyl chloride to ethene which yielded chlorosulfenylated adducts **6** (Equation 1.1).[38] This reactivity was further examined by Kharasch *et al.*, who added 2,4-dinitrophenylsulfenyl chloride to cyclohexene (Equation 1.2), and by Turner and Connor, who added 2-nitro-4-chlorobenzenesulfenyl chloride to several alkenes.[39,40]



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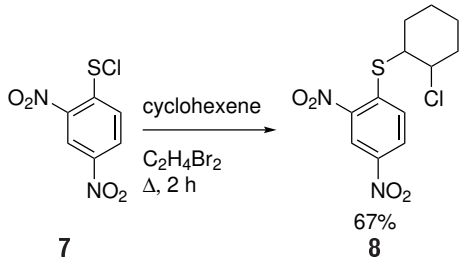
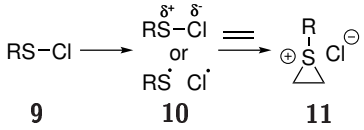


(1.2)

Shortly after these findings, Jenny und Hölzle expanded this methodology to selenium electrophiles, when they showed that selenenylacetates readily add to alkenes.[41,42] For both chalcogens, the addition reaction was found to be stereospecific (*trans*-addition) and following Markovnikov's rule.[40,43–45] Based on this, Kharasch and Buess proposed a thiiranium ion as an intermediate in the addition of sulfenyl chlorides to nonsymmetric alkenes.[43] Such an ion could be formed either by homolytic cleavage of the S-Cl bond of a sulfenyl chloride followed by a radical reaction, or by a polarization of the S-Cl bond which enables an electrophilic attack of the sulfur (Scheme 1.2).[46]



Scheme 1.2: Formation of thiiranium ion **11** *via* an ionic or a radical pathway.

Evidence for the existence of thiiranium ions was provided in the 1960s, when PETTIT and HELMKAMP isolated several thiiranium compounds (e.g., Figure 1.1, **12**).[47,48] Similarly, GARATT and SCHMID isolated and characterized a series of seleniranium ions as well as episelenurane **14**, which is one of only few examples of this compound class ever reported (Figure 1.1, **13** and **14**).[49,50]

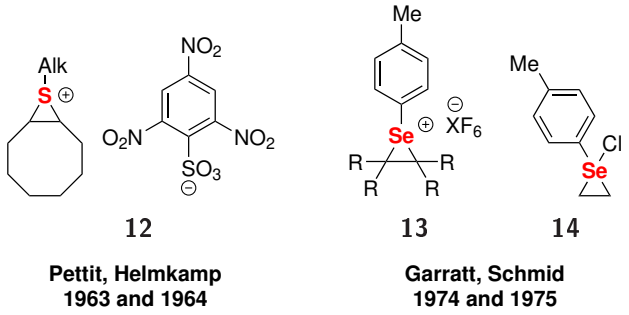
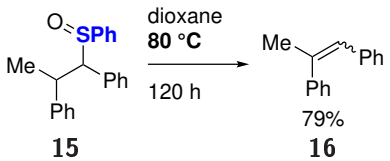


Figure 1.1: First synthesized thiiranium and seleniranium ions.

When the chalcogeniranium ions were subjected to nucleophiles, they gave way to the same products that were obtained in the functionalization of the respective alkenes with the chalcogen compounds.[50,51] This supports the assumption that chalcogeniranium ions are intermediates in the functionalization reaction of alkenes.

An important reactivity of the chalcogenofunctionalized products is the possibility to eliminate the chalcogen moieties under oxidative conditions, which results in the formation of alkenes. This was first found by KINGSBURY and CRAM in 1960, when they showed that sulfoxides **15** eliminate to alkenes **16** in good yields when they are heated (Equation 1.3).[52] JONES and colleagues observed a similar behavior in the case of selenoxides (Equation 1.4).[53] However, a striking difference between sulfur and selenium is that for the elimination reaction of sulfur, high temperatures are needed, whereas selenium compounds readily eliminate at room temperature or even at 0 °C.[53]



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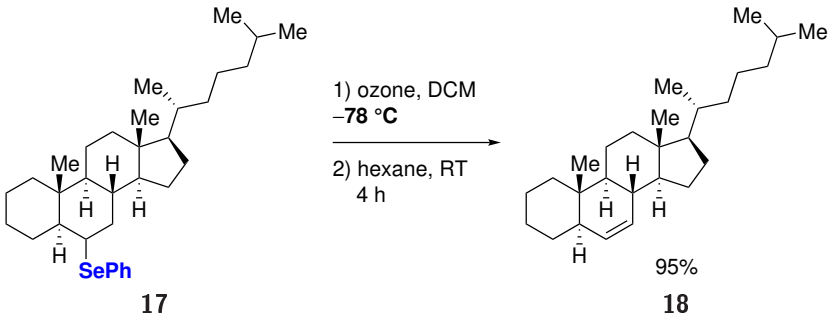
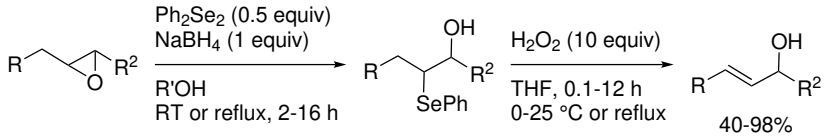


17 18 (1.4)

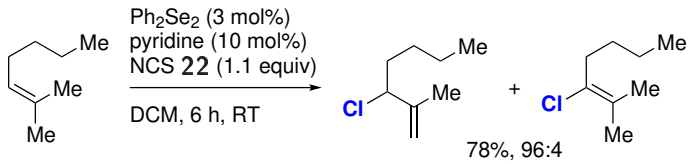
Sharpless and Lauer exploited this reactivity when they converted epoxides **19** into allyl alcohols **21** (Scheme 1.3). They opened the epoxide with a phenylselenyl anion to form hydroxy selenide **20**. The subsequent oxidation of the selenide by H_2O_2 afforded the corresponding allylic alcohols **21** in yields ranging from 40-98%.



19 **20** **21**

Scheme 1.3: Allylic alcohol synthesis by Sharpless and Lauer.

A few years later, Sharpless advanced this methodology further, when he and Hori developed the first selenium-catalyzed chlorination of olefins with 3 mol% diphenyl diselenide, 1.1 equiv *N*-chlorosuccinimide (NCS, **22**) as the oxidant and chloride source and 10 mol% pyridine (Equation 1.5).[11]

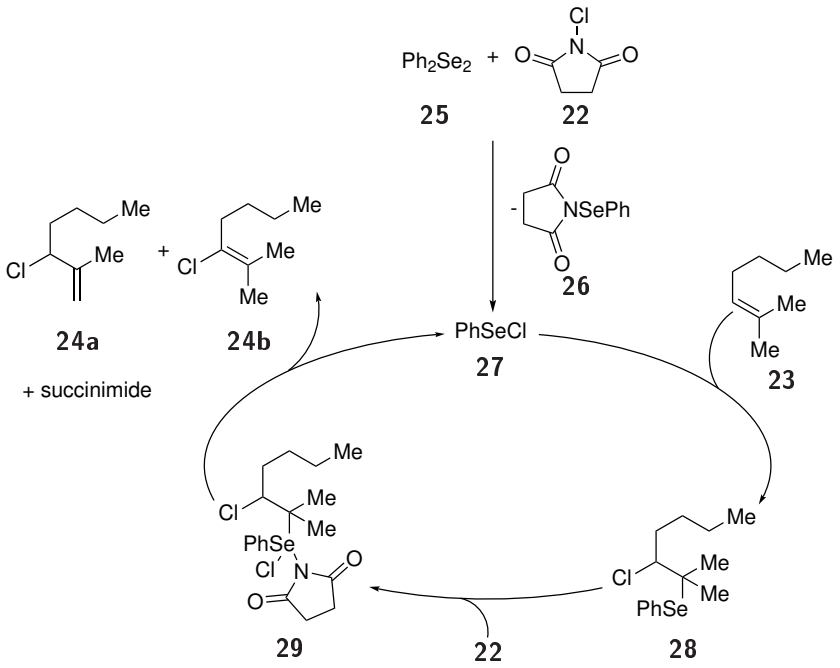


23 **24a** **24b** (1.5)

They hypothesized that diphenyl diselenide (**25**) and NCS (**22**) react with each other to form PhSeCl (**27**), which adds to the double bond of alkene **23** (Scheme 1.4). The reaction of selenide **28** with NCS eventually results in product formation by the elimination of PhSeCl along with succinimide. Following this first catalytic reaction, different methods for the selenium-catalyzed oxidative functionalization of alkenes were developed.

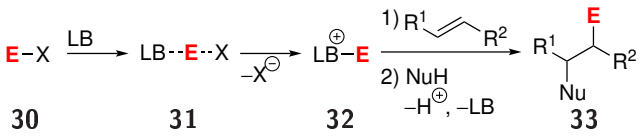
1.1.1 Activation modes in chalcogen-mediated reactions

The activation modes in chalcogen-mediated reactions are based on two distinct roles of the chalcogen atom. In the first activation mode, the chalcogen atom acts as a Lewis base and



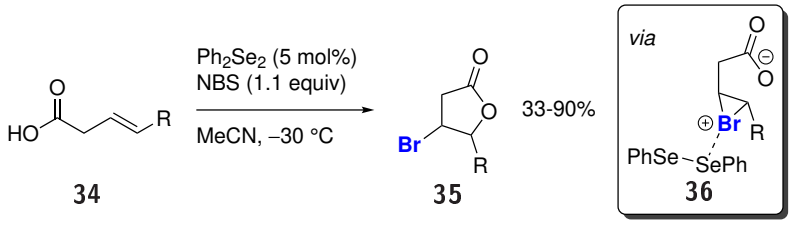
Scheme 1.4: Proposed mechanism of the catalytic chlorination by HORI and SHARPLESS.

activates an electrophile **30**, which can react in its activated form **32** with an unactivated alkene (Scheme 1.5).[54]



Scheme 1.5: LEWIS base activation of an electrophile and subsequent alkene functionalization.

Important examples for this kind of activation are the chlorination of alkenes with NCS by SHARPLESS and HORI (Scheme 1.4) and cognate halogenations,[11,12] as well as halocyclization reactions.[55–59] One of the first examples of a selenium-catalyzed bromolactonization was described by TUNGE and MELLEGAARD.[57] The reaction of β,γ-unsaturated acids **34** to bromolactones **35** was realized by the LEWIS base activation of *N*-bromosuccinimide (NBS) by diphenyl diselenide (Equation 1.6). The authors first suspected a reaction of diphenyl diselenide and NBS to PhSeBr and phenylselenyl succinimide, reminiscent of the reaction with NCS in the chlorination reaction by SHARPLESS and HORI (cf. Scheme 1.4). As both PhSeBr and phenylselenyl succinimide did not reproduce the results with diphenyl diselenide, they hypothesized that the Se-Se bond remains intact and proposed the formation of bromonium ion **36** and the subsequent attack of the carboxylate moiety.



(1.6)

In the other activation mode of chxalcogen-mediated reactions, the electrophilic chalcogen atom activates the double bond of an olefin for a nucleophilic attack by acting as a LEWIS acid. In the transition state of this activation, the antibonding σ*-orbital of the Ch−X bond receives electron density from the binding π-orbital of the double bond (donation) and the non-bonding n orbitals of the chalcogen donate electrons into the antibonding π*-orbital of the double bond (back-donation) (Figure 1.2a).[37,60] This interaction is somewhat reminiscent of the binding situation found in certain transition metal-olefin complexes, which has been described by the DEWAR-CHATT-DUNCANSON model. In these systems, the donating interaction is between a π-orbital of the double bond and a σ*-orbital of a metal-ligand bond or an empty d orbital of the metal. The back-donation into the π*-orbital of the double bond results from a filled d orbital of the metal (Figure 1.2b).[61]

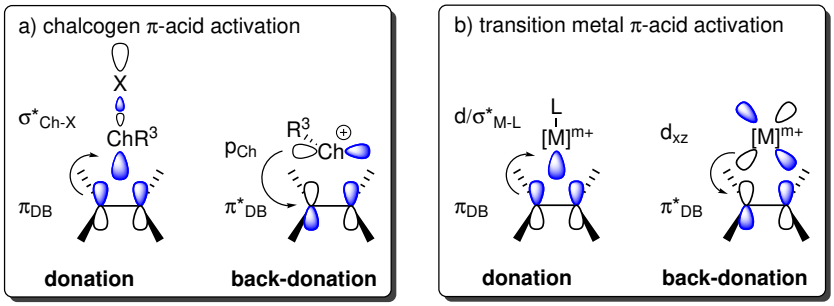
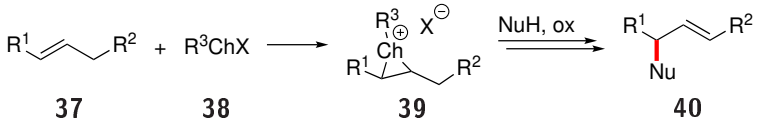


Figure 1.2: Proposed orbital interactions in the π-acid activation of olefins by a) chalcogenium ions and b) transition metals.

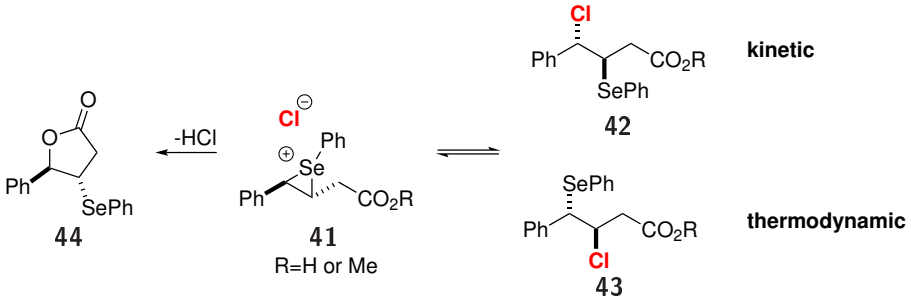
The overall mechanism of the π-acid activation of an alkene **37** with a chalcogen atom and the following functionalization with a nucleophile is depicted in Scheme 1.6. During the electrophilic attack of the chalcogen LEWIS acid **38** on the π-bond, chalcogeniranium ion **39** is formed, which is activated for a nucleophilic attack. Subsequent oxidation and elimination of the chalcogen species affords functionalized product **40**.[62]



Scheme 1.6: Oxidative functionalization of alkene **37** *via* π-acid activation.

1.1.2 Endogenous and exogenous nucleophiles

In the course of their close examination of the mechanism of the PhSeCl-mediated selenolactonization reaction, Denmark and Edwards were able to provide NMR evidence for the formation of seleniranium ion **41** as an intermediate of the reaction.[62] Furthermore, they observed the reversible formation of chlorinated side products **42** and **43** from this intermediate by attack of the nucleophilic chloride counter ion (Scheme 1.7). By conducting NMR experiments at low temperatures, they were able to identify adduct **42** as the kinetic adduct. When instead of the free acid the methyl ester was used and the reaction mixture was warmed to room temperature, lactone formation could not occur and they observed the preferred formation of adduct **43**, and thus identified this species as the thermodynamic adduct.



Scheme 1.7: Formation of selenolactone **44** and adducts **42** and **43** from seleniranium ion **41**.

The observation that the attack of the counterion can in certain cases be faster than the attack of the intramolecular nucleophile illustrates a challenge in the selenium-π-acid catalyzed functionalization of alkenes. In some cases, nucleophiles originating from the oxidant (*endogenous nucleophiles*) outcompete intramolecular or intermolecular external nucleophiles (*exogenous nucleophiles*), leading to the formation of an undesired side product. Therefore, the choice of the nucleophile and the oxidant can be crucial for the course of the reaction.

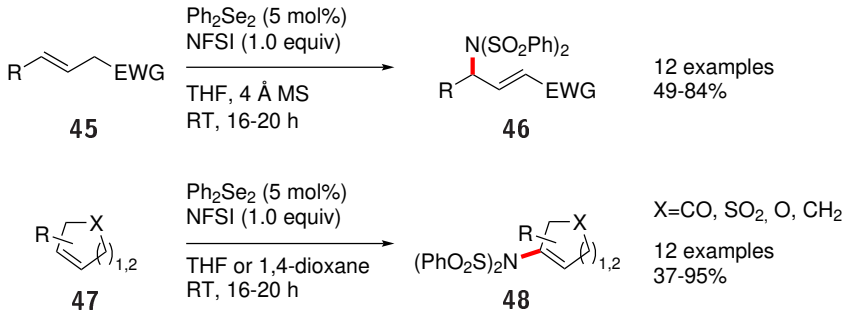
1.2 Examples for selenium-catalyzed oxidative functionalizations of alkenes

Following the catalytic chlorination by Sharpless and Hori, various other selenium-catalyzed oxidative functionalizations of alkenes were developed, which promote the formation of C−N, C−O and C−X bonds and differ in the oxidants and nucleophiles used.

1.2.1 Formation of C−N bonds

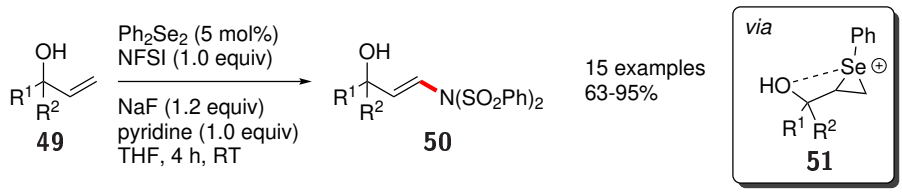
The first allylic and vinylic amination of alkenes *via* selenium-π-catalysis was reported in 2013 by Breder *et al.*[63] Remarkably, they were able to use *N*-fluorobenzenesulfonimide (NFSI) as the oxidant and nitrogen source, whereas other *N*-halogenated oxidants usually serve as a halogen source (e.g. allylic chlorinations with NCS by Sharpless *et al.* and Tunge *et al.*).[11,12] Allyl imides **46** were obtained from alkenes **45**, bearing an electron-withdrawing group (EWG) in the

allylic position, in yields between 49 and 84% using 5 mol% diphenyldiselenide (**25**) and 1 equiv NFSI at room temperature (Scheme 1.8, top). The imidation of cyclic alkenes **47** was realized under slightly changed conditions and afforded vinylic imides **48** in yields between 37 and 95% (Scheme 1.8, bottom).



Scheme 1.8: Selenium-π-acid catalyzed allylic and vinylic imidation by Breder *et al.*[63]

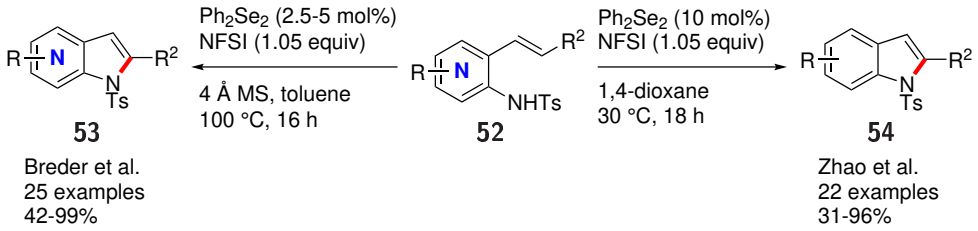
The use of NFSI as the nitrogen source and oxidant in selenium-catalyzed amination reactions turned out to be a groundbreaking discovery and led to several following reactions using *N*-fluorinated oxidants. In 2015, Zhao et al. were able to use NFSI in the amination of allylic alcohols **49** to obtain 3-amino-allylalcohols **50** in good yields between 63 and 95% (Equation 1.7).[64] The high selectivity for the formation of the anti-Markovnikov product was rationalized by the authors to originate from a stabilizing interaction of the hydroxy group with a cationic seleniranium intermediate.



(1.7)

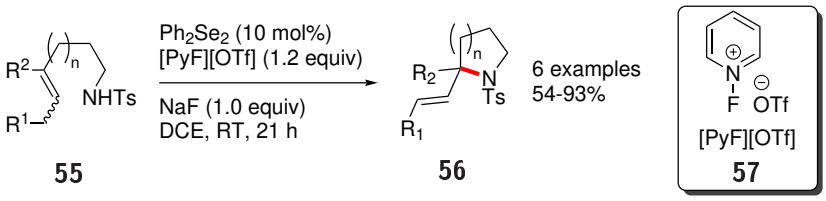
In the same year, the groups of both Breder and Zhao independently discovered that the intramolecular C–H amination of simple alkenes, which was previously dominated by metal-catalyzed methods, could also be facilitated by the use of diphenyl diselenide and NFSI as the oxidant.[65,66] Both groups were able to catalyze the formation of indoles from *ortho*-vinylated anilines under conditions that differ in solvent, temperature and catalyst loading (Scheme 1.9). While Zhao *et al.* conducted the reaction in 1,4-dioxane at 30 °C with 10 mol% of diphenyl diselenide, Breder *et al.* were able to decrease the loading to 2.5 mol% in most cases, but needed to perform the reaction in toluene at 100 °C. Futhermore, they showed that with their method azaindoles could also be obtained in good yields between 57 and 81%.

During their attempt to expand this methodology to non-aromatic amines, Zhao *et al.* tested several oxidants for the formation of tetrahydrofurans, tetrahydropyrans and cyclic tosyl amides.[67] They found out that *N*-fluoropyridinium triflate (**57**), first disclosed by Denmark and colleagues



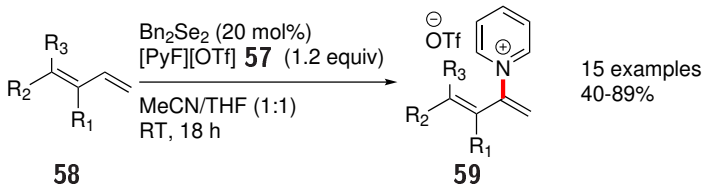
Scheme 1.9: Indole formation under different conditions by Breder *et al.* and Zhao *et al.*[65,66]

in their work on selenium-catalyzed dichlorinations,[68] was a potent oxidant for this reaction. The formation of cyclic tosyl amides **56** from tosyl amides **55** in yields between 54 and 93% was performed by treating them with 10 mol% of diphenyl diselenide, 1.2 equiv of **57** and 1.0 equiv NaF (Equation 1.8).



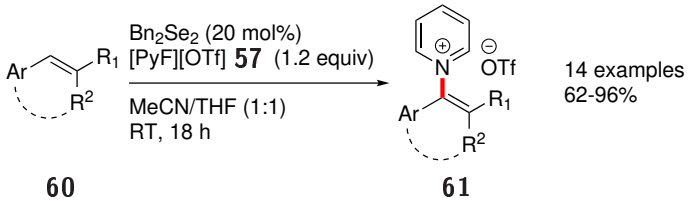
(1.8)

This new *N*-fluorinated oxidant could also be used in the pyridination reaction of 1,3-dienes and alkenes.[69] Interestingly, the reaction of dienes **58** with 20 mol% of dibenzyl diselenide and 1.2 equiv of [PyF][OTf] **57** selectively afforded products **59** with the pyridinium moiety at C-2 in yields between 40 and 89% (Equation 1.9). In previous studies that rely on transition metal catalysts, the functionalization usually occurs with *anti*-Markovnikov selectivity.[70–73]



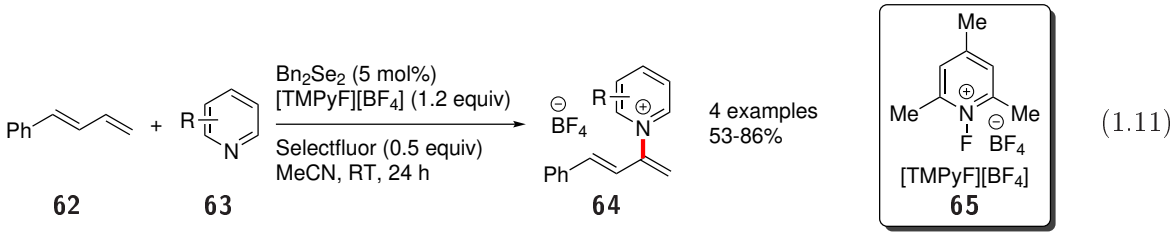
(1.9)

The selectivity holds true for styrene derivatives as well and products **61** were obtained under otherwise unaltered conditions in good yields between 62-96% (Equation 1.10). However, when a non-styrenic alkene was used, the selectivity changed to C-1 pyridination.



(1.10)

During their experiments for the pyridination of dienes with different *N*-fluoropyridinium salts as oxidants and nitrogen source (Equation 1.9), Zhao *et al.* noticed that bulky *N*-fluorinated pyridinium salts like *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**65**) did not lead to product formation and attributed this to them being unsuitable nucleophiles due to the steric shielding of the nitrogen lone pair. As a consequence, they tried to use pyridines **63** as exogenous nucleophiles together with pyridinium salt **65** (1.2 equiv) as the oxidant and Selectfluor (0.5 equiv) as the co-oxidant for a faster deselenenylation. Under these conditions, they were able to obtain pyridinium salts **64** in good yields (Equation 1.11). Remarkably, this transformation is one of only few examples for a selenium-catalyzed reaction with an exogenous nucleophile.

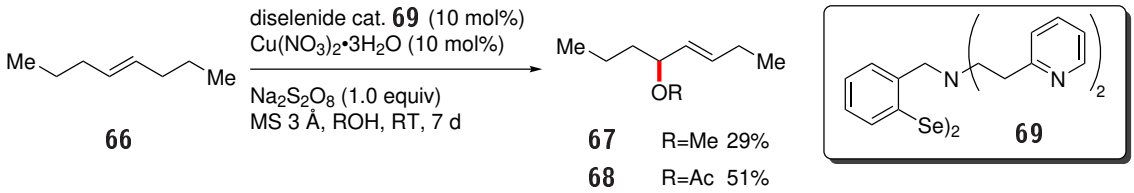


62 63 64 65 (1.11)

Although the employment of pyridine derivatives **63** as exogenous nitrogen nucleophiles is an exciting finding, it is important to develop further methods that can use different nitrogen sources in the selenium-catalyzed allylic and vinylic functionalization of alkenes. In the design of the established methods, the choice of oxidant played a key role. Therefore it is important to further examine different oxidants, especially concerning competing reactions between exogenous and endogenous nucleophiles.

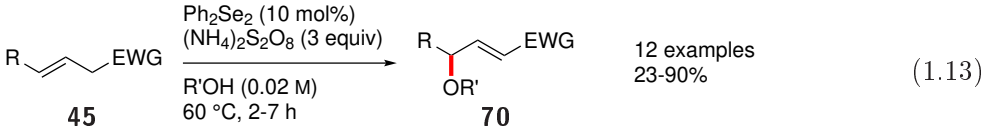
1.2.2 Formation of C–O bonds

One of the first selenium-catalyzed allylic oxyfunctionalizations of alkenes was realized as early as in 1992 by Iwaoka and Tomoda. They were able to insert a methoxy- or acetoxy moiety into simple alkenes like 4-octene (**66**) by using 10 mol% of diselenide catalyst **69** together with the same amount of copper(II) nitrate and 1.0 equiv sodium peroxodisulfate as the oxidant in methanol or acetic acid as the solvent (Equation 1.12).[74] In previous reactions, the selenium compound could not be used catalytically. This was attributed to the formation of selenenic acid during oxidative elimination using oxidants such as O_3, $NaIO_4$ or peroxides, which could not be reintroduced into the catalytic cycle. As a possible reason, the subsequent disproportionation reaction was suggested. To avoid this, the amine backbone of diselenide **69** served to stabilize the respective selenenic acid after its elimination from the functionalized alkene. The allylic ethers or esters were obtained in low to moderate yields between 16 and 51% and the scope remained limited.



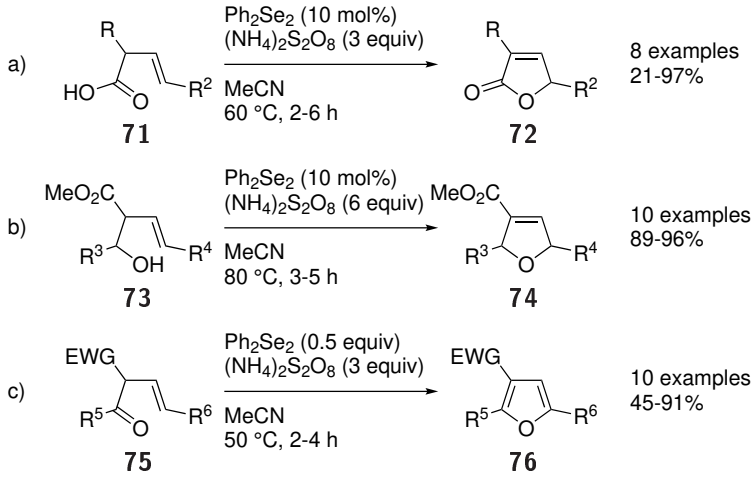
(1.12)

Shortly after, Tiecco and colleagues reported a procedure for the alkoxy and hydroxy functionalization of alkenes using simple diphenyl diselenide (**25**) as the catalyst and an excess of ammonium peroxodisulfate as the oxidant (Equation 1.13).[75] They obtained allylic alcohols and ethers **70** in 23-90% yield in short reaction times of 2-7 hours. In contrast to Iwaoka and Tomoda, they used substrates that contained electron-withdrawing groups and heated the reaction mixture to 60 °C.



(1.13)

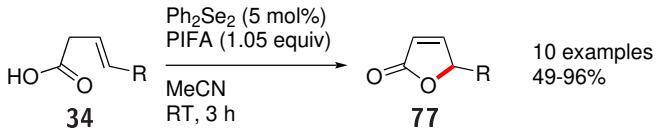
Having identified ammonium peroxodisulfate as a suitable oxidant for selenylation-deselenylation reactions, the group of Tiecco applied this strategy to several other functionalization reactions. Under slightly modified conditions, they were able to catalyze the formation of butenolides **72** from β,γ-unsaturated acids **71** in high yields (Scheme 1.10a).[76] Furthermore, the formation of dihydrofuranes **74** was catalyzed in excellent yields (Scheme 1.10b).[77] The reaction of β,γ-unsaturated ketones **75** to furanes **76** was also realized, but the diselenide had to be used stoichiometrically to prevent the decomposition by the starting material by the oxidant (Scheme 1.10c).[78]



Scheme 1.10: Subsequent oxygenation reactions by Tiecco *et al.*

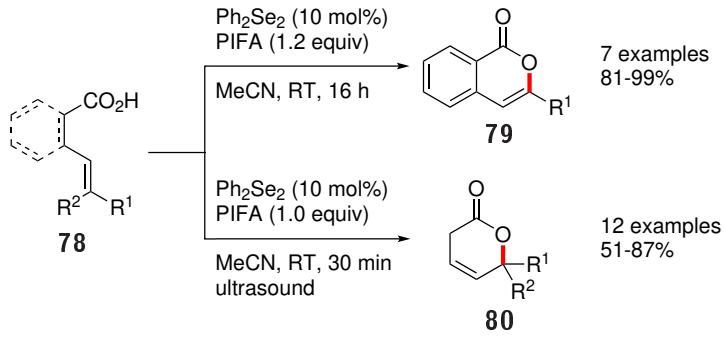
Although ammonium peroxodisulfate has the advantages that no endogenous nucleophile can arise from it and only non-toxic sulfate is formed as a side product, the reactions need elevated temperatures and in some cases, e.g., the formation of furans (Scheme 1.10c), the oxidant is potent enough to oxidize the substrate.[78]

As an alternative to peroxodisulfate, hypervalent iodine compounds have been found to work equally well as oxidants in phenylselenylation reactions with diphenyl diselenide.[79–81] Their application in catalytic selenation-deselenylation reactions was first disclosed by the group of Wirth in 2007. The lactonization of β,γ-unsaturated acids **34** with 5 mol% of diphenyl diselenide and 1.05 equiv of [bis(trifluoroacetoxy)iodo]benzene (PIFA) as the oxidant afforded lactones **77** in moderate to excellent yields between 49 and 96% (Equation 1.14).[82] Compared to the previous works, lower catalyst and oxidant loadings could be used and the reaction worked at room temperature. Electronically neutral acids worked well (R = *n*-propyl, *n*-butyl or *n*-decyl, yield >65%), however, as only simple alkyl and aryl moieties are present in the scope, the functional group tolerance of the method could not be evaluated.



(1.14)

The conditions for the formation of butenolides **77** were also applied to other lactonization reactions. When styrylbenzoic acids **78** (R^1=Ar, R^2=H) were subjected to PIFA and a catalytic amount of diphenyl diselenide, isocoumarins **79** were obtained. However, in order to ensure complete conversion of the selenofunctionalized intermediate into the product, the catalyst loading had to be increased to 10 mol% and the reaction time to 16 h (Scheme 1.11, top).[83] When the cyclization of aryl-substituted β,γ-unsaturated acids **78** (R^1, R^2=Ar) was examined, it was realized that the reaction time could be reduced to 30 min when ultrasound was used (Scheme 1.11, bottom).[84]

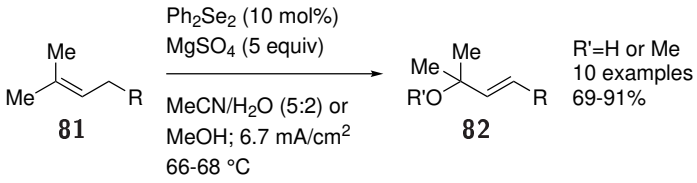


Scheme 1.11: Formation of isocoumarins **79** and dihydropyranones **80** by Wirth *et al.*

Hypervalent iodine reagents are a valuable addition to the oxidants available for selenium-catalyzed functionalization reactions, as only equimolar amounts are needed (compared to the

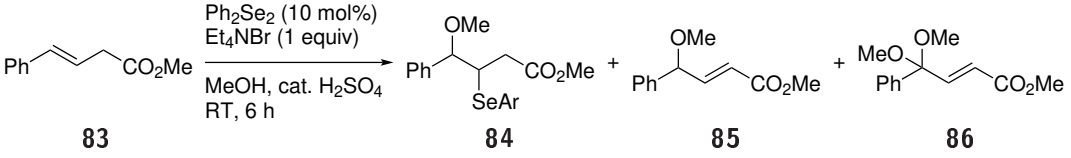
high excess that is needed when peroxodisulfates are used). Furthermore, they usually need low reaction temperatures. Unfortunately, only functionalizations with acid nucleophiles were examined.

The possibility of using electrochemistry for the formation of phenylselenium cations from diphenyl diselenide for oxyselenylation reactions as well as the oxidation of selenides with the following elimination of the selenium moiety came up in the early 1980s.[85–87] In contrast to the conventional methods, where the oxidations are two-electron processes, electrochemical oxidations take place as one-electron oxidations. Torii and colleagues were the first to disclose such an electrochemical oxyselenylation/elimination sequence using only a catalytic amount of diphenyl diselenide (Equation 1.15).[88] With water or methanol as the nucleophiles, allylic alcohols and methyl ethers **82** were obtained from alkenes **81** in good yields between 69 and 91%.



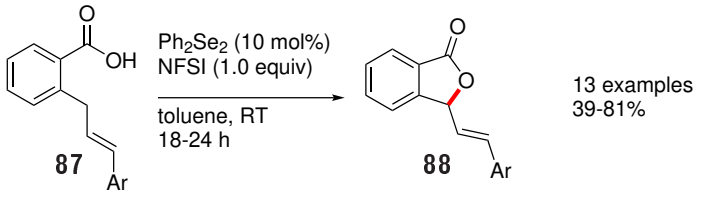
(1.15)

Although a promising alternative to reactions with conventional oxidants, selenium-catalyzed electrochemical functionalizations of alkenes remain sparse. A later example by the group of Wirth depicts potential difficulties that arise with the method. They examined the allylic methoxylation of alkene **83** using 10 mol% of diphenyl diselenide along with 1.0 equiv of Et_4NBr, which served both as the electrolyte and a redox catalyst. The reactive selenium species PhSeBr was presumably formed by the reaction of diphenyl diselenide and bromine, which originated from the oxidation of bromide ions. Wirth and colleagues observed that the ratio of the formed products depended strongly on the applied current (Equation 1.16).[89] When only 0.5 mA was used, the mixture contained 64% of the desired product **85**, but also 19% of the selenofunctionalized intermediate **84** and 17% of additional side products. The product formation could be increased when the current was raised to 3 mA (83% of **85**, 5% of **84** and 12% side products), but with higher currents, overfunctionalized product **86** began to form (36% at 10 mA, together with 46% of desired product **85** and 18% side products). The desired product **85** was isolated from the reaction under a 3 mA current, with a 50% yield. Further experiments with water, ethanol, isopropanol and acetic acid led to moderate yields between 48 and 62%.



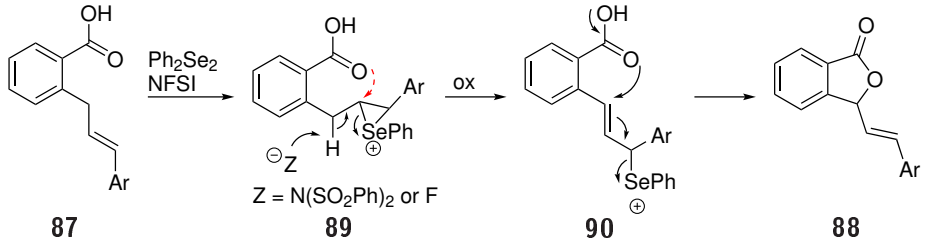
(1.16)

As demonstrated by these last reports, electrochemistry can be used in the functionalization of alkenes with exogenous nucleophiles under mild conditions. The formation of side products can be controlled by tuning the applied current. Nevertheless, the yields in WIRTH's experiments were only moderate and the development of more efficient conditions is desirable.
While in previous studies *N*-fluorinated oxidants were successfully applied in amination reactions, in which these reagents were also the source for endogenous nitrogen nucleophiles, BREDER *et al.* succeeded in using NFSI to promote a selenium-catalyzed allylic oxyfunctionalization. The synthesis of isobenzufuranones **88** from benzoic acid derivatives **87** was achieved with 10 mol% diphenyl diselenide and 1.0 equiv NFSI in yields of up to 81% (Equation 1.17).[90] Interestingly, the substrates did not undergo the expected 6-*exo*-trig cyclization, but formed the corresponding 5-membered ring.



(1.17)

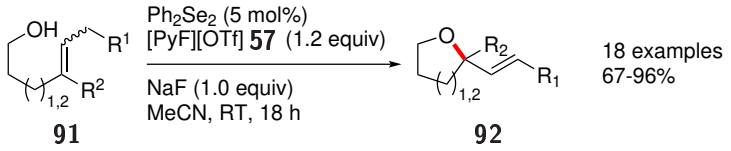
The mechanism for the product formation was therefore examined more closely. Through their following experiments, the authors were able to rule out different hypothesized scenarios and developed the following mechanistic rationale for the formation of isobenzofuranones **88** (Scheme 1.12). According to this hypothesis, the reaction starts with an attack of an electrophilic selenium-species on the double bond, leading to the formation of seleniranium ion **89**. Instead of the direct nucleophilic attack of the carboxy group (red arrow), the opening of the seleniranium ion occurs *via* the elimination of a benzylic hydrogen atom, leading to the formation of styrene derivative **90**. After a subsequent oxidation of the selenium moiety, an S_N2' reaction by attack of the carboxy group on the double bond leads to elimination of the selenium species and formation of product **88**.



Scheme 1.12: Suggested mechanism for the formation of isobenzofuranones **88**.

In the course of their investigation of the cyclization of tosylamides **55**, ZHAO *et al.* were also able to perform the corresponding oxyfunctionalizations with *N*-fluoropyridinium triflate as the oxidant, resulting in the formation of tetrahydrofuranes and -pyranes **92** from unsaturated

alcohols **91** (Equation 1.18).[67] The reaction tolerated a lower catalyst loading than the amination reaction (5 instead of 10 mol% diphenyl diselenide) and proceeded in good yields of 67-96%.

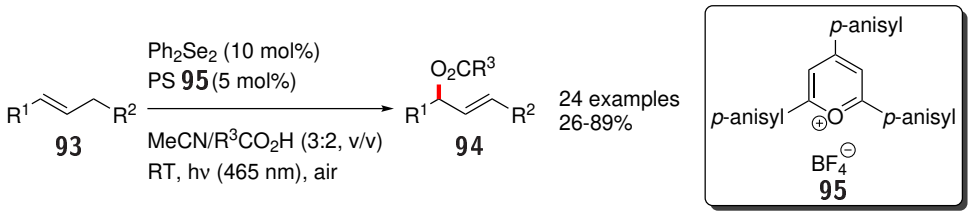


(1.18)

In the presented reactions, the intramolecular nucleophiles outcompete the endogenous nucleophiles originating from the oxidant. However, this competition still poses a problem for intermolecular functionalization reactions. Therefore, the identification of a different oxidant, which does not release strong endogenous nucleophiles, is necessary.

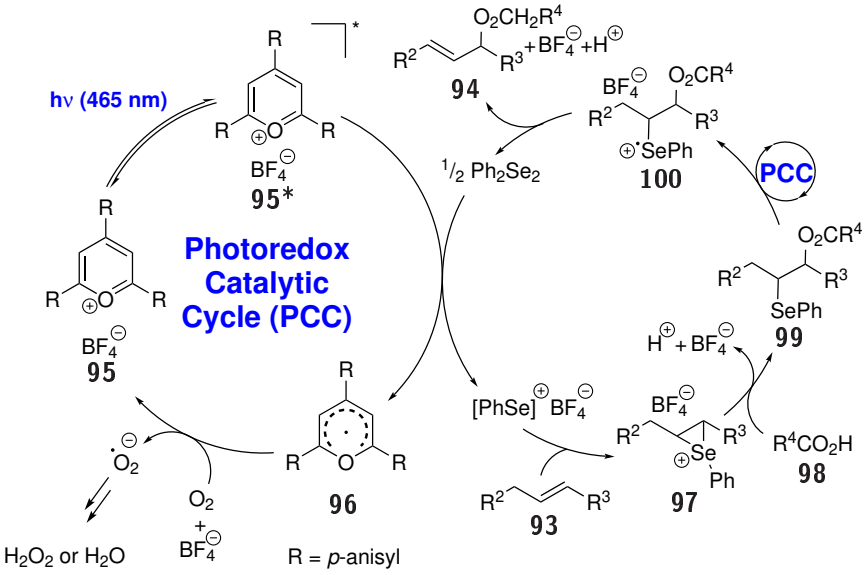
In this context, Breder *et al.* disclosed a new approach that was based on a photoredox catalyst that permits the use of ambient air as the terminal oxidant and therefore enables the use of exogenous nucleophiles.[91] Their idea was based on findings by Pandey and Ragains, who were able to facilitate the oxidative cleavage of diphenyl diselenide as well as the cleavage of selenides under photoredox conditions.[92–96] While Pandey and colleagues used 1,4-dicyanonaphthalene (DCN), which acts as a one-electron acceptor in its excited state, Ragains *et al.* initiated the homolytic cleavage of diphenyl diselenide by irradiation with blue light (λ=455 nm).

Breder and colleagues speculated that a selenylation-deselenylation reaction of alkenes could be performed if a photosensitizer with a suitable redox potential (reduction potential of the excited state is higher than the oxidation potential of diphenyl diselenide, $E_{ox} = 1.35$ V vs. SCE)[97] was used as a one-electron-shuttle together with air as the terminal oxidant.[91] They identified 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (**95**, *p*-MeO-TPT) as a suitable photocatalyst and achieved the intermolecular esterification of alkenes **93** with different carboxylic acids in good yields using 10 mol% of diphenyl diselenide and 5 mol% of photosensitizer **95** under an atmosphere of air and irradiation with blue light (Equation 1.19).



(1.19)

The oxidation steps involving photosensitizer **95** were envisioned to proceed *via* its excitated state after irradiation with blue light (intermediate **95***, Scheme 1.13). In this state, a single electron transfer (SET) from either diphenyl diselenide or the selenofunctionalized intermediate **99** can occur and radical **96** is formed, which is reconverted to its ground state **95** by an oxidation by oxygen. The superoxide, which is formed by the reduction of oxygen, undergoes further reactions to finally give water as the terminal reduction product of oxygen reduction.

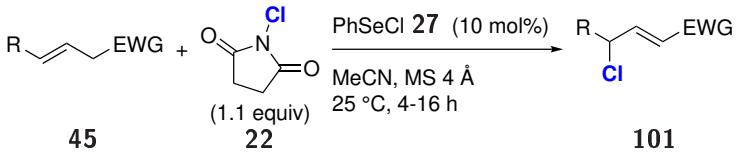


Scheme 1.13: Envisioned catalytic cycle for the intermolecular esterification.

These last results show a new possibility for the incorporation of exogenous nucleophiles into alkenes *via* selenium-catalysis. It is an important task to further examine the scope of this reaction regarding different nucleophiles and types of bond formation.

1.2.3 Formation of C–X bonds

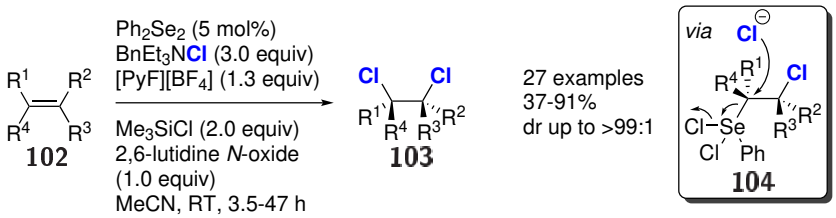
As discussed, the first selenium-catalyzed oxidative functionalizations of alkenes was the allylic chlorination of alkenes, where NCS (**22**) was activated by the reaction with diphenyl diselenide (cf. Equation 1.5).[11] This method was further studied by Tunge and Mellegaard who directly used PhSeCl (**27**) (10 mol%) and NCS for the allylic chlorination of allylic acids, esters, arenes and nitriles **45** in yields of 62-89% (Equation 1.20).[12]



(1.20)

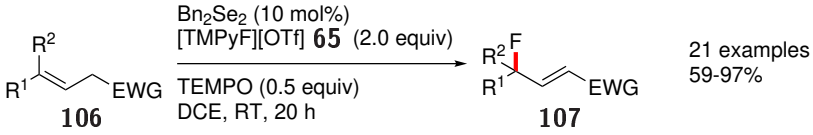
A seminal work concerning selenium-catalyzed dichlorinations of alkenes was published in 2015 by Denmark *et al.*[68] This work was remarkable in several points, as on the one hand, it was the first selenium-catalyzed difunctionalization reaction, and on the other hand the reaction was *syn*-stereospecific, while in the traditional dichlorination methods using Cl_2 an *anti*-dichlorination takes place.[98] The *syn*-dichloro motif is especially common in chlorosulfolipids, a class of polychlorinated marine natural products.[99–102] The selectivity for a *syn*-dichlorination was achieved by the judicious choice of the oxidant and chloride as the nucleophile. The authors reasoned that the oxidant had to fulfill several criteria: it must not oxidize the substrate or chloride ions, it

must not release endogenous nucleophiles that outcompete chloride, and it must not transform the selenium moiety to a species that is capable of a fast *syn*-elimination, which would lead to the allylic product. They identified *N*-fluoropyridinium tetrafluoroborate as a suitable oxidant and obtained *syn*-dichlorides **103** in up to 91% yield and up to >99:1 dr using 5 mol% diphenyl diselenide, 3.0 equiv $BnEt_3NCl$ as the chloride source, 1.3 equiv $[PyF][BF_4]$ as the oxidant, 2.0 equiv Me_3SiCl as a fluoride scavenger and 1.0 equiv 2,6-lutidine *N*-oxide as a LEWIS base additive (Equation 1.21). In the proposed mechanism, the *syn*-selectivity was rationalized by the intermediate formation of chloroselenenylated product **104** and a subsequent S_N2-reaction at the selenium moiety by a chloride ion.



(1.21)

Until recently, *N*-fluorinated compounds could only be used as oxidant and/or nitrogen source and not for fluorination reactions, as the endogenous nitrogen nucleophiles react faster than the fluorides. ZHAO *et al.* observed that bulky *N*-fluorinated pyridinium salts like *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**65**) were weak nucleophiles and used them to promote a pyridination reaction with exogenous pyridine nucleophiles (Equation 1.11, Subsection 1.2.1).[69] They realized that they could also apply this idea to fluorination reactions and were successful in promoting the allylic fluorination of electron-poor alkenes **106** using 2.0 equiv of [TMPyF][OTf] (**105**) as the oxidant and fluoride source along with 10 mol% of dibenzyl diselenide as the catalyst (Equation 1.22).[103] Additionally, 0.5 equiv of TEMPO were used as an additive to prevent the decomposition of the diselenide catalyst. Under these conditions, fluorides **107** were obtained in good yields between 59 and 97%.

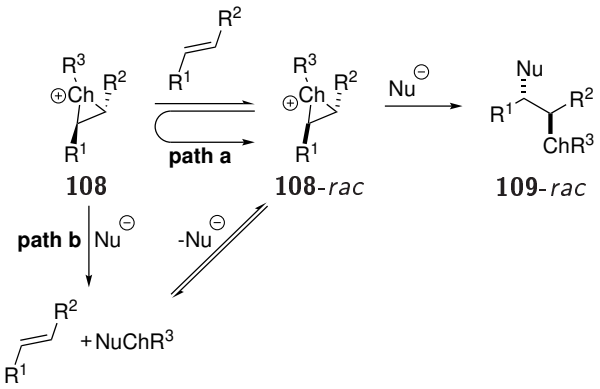


(1.22)

1.2.4 Asymmetric selenium-catalysis

Ever since the first successful selenium-catalyzed reactions were found, the endeavor to develop asymmetric reactions has been ongoing. As the reactions with electrophilic selenium reagents were found to proceed *via* a seleniranium ion that is opened in a *trans*-fashion, the efforts were directed towards the synthesis of chiral selenium species that allow for the stereoselective formation of these intermediates (see Subsection 1.1.1).[62,104] In this context, the configurational stability of chalcogeniranium ions is an important aspect and was therefore examined more closely. Com-

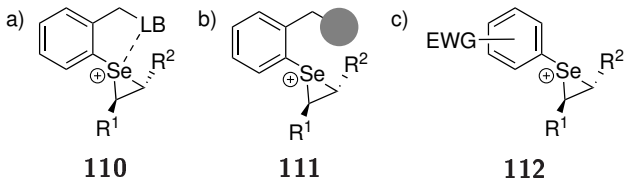
putational studies by the groups of RADOM and BORODKIN suggest that it is possible to transfer the chalcogenium ion from a chalcogeniranium ion to another olefin.[105–107] WIRTH *et al.* and DENMARK *et al.* were able to support this hypothesis by NMR studies and additionally showed that the formation of chalcogeniranium ions is reversible.[62,108,109] The olefin-to-olefin transfer of chalcogenium ions is a mechanism that leads to racemization of enantioenriched chalcogeniranium ions and therefore prevents the formation of enantioenriched chalcogenofunctionalization products (Scheme 1.14, path a).[37,110] Another pathway that leads to racemization of enantioenriched chalcogeniranium ions is the attack of a nucleophile on the chalcogenium moiety and the following dissociation of the chalcogeniranium ion, leading to the loss of the stereoinformation (Scheme 1.14, path b).[37,110]



Scheme 1.14: Erosion of enantioenriched chalcogeniranium ion **108** *via* a) olefin-to-olefin transfer and b) nucleophilic attack on the chalcogenium.[37,110]

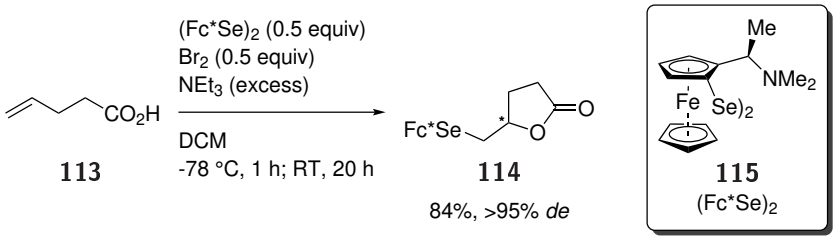
In the course of asymmetric selenium-catalyzed reactions, several strategies for the stabilization of seleniranium ions and the consequential synthesis of enantioenriched selenofunctionalized products were developed.[37,104,110,111] A frequently applied method is the use of LEWIS basic side chains in vicinity to the selenium atom. The interaction of a lone pair from these side chains with the LUMO of the selenium cation is supposed to block the free coordination site and prevent the attack of another alkene on the selenium ion (Figure 1.3a). A similar approach is the use of sterically demanding groups, which would prevent attack on the selenium atom by alkenes as well as nucleophiles (Figure 1.3b). For the third strategy, electron-withdrawing groups are attached to the selenium-moiety, polarizing the endocyclic Se−C bonds (Figure 1.3c). On the one hand, this polarization leads to a higher electrophilicity of the selenium atom and thus a stronger binding to the carbon centers. On the other hand, it increases the probability of a nucleophilic attack at these carbon centers instead of the selenium atom.

The application of chiral selenium compounds with the mentioned features in the synthesis of enantioenriched selenofunctionalized products was successful and products with high diastereomeric excess were obtained.[104] For example, the selenolactonization of acid **113** with diferrocenyldiselenide **115** afforded selenolactone **114** in 84% yield with a diastereomeric excess of >95% (Equation 1.23).[112]



110 **111** **112**

Figure 1.3: Strategies for the stabilization of enantioenriched seleniranium ions: a) Lewis basic side chains, b) steric bulk, c) electron-withdrawing substituents at the selenium moiety.



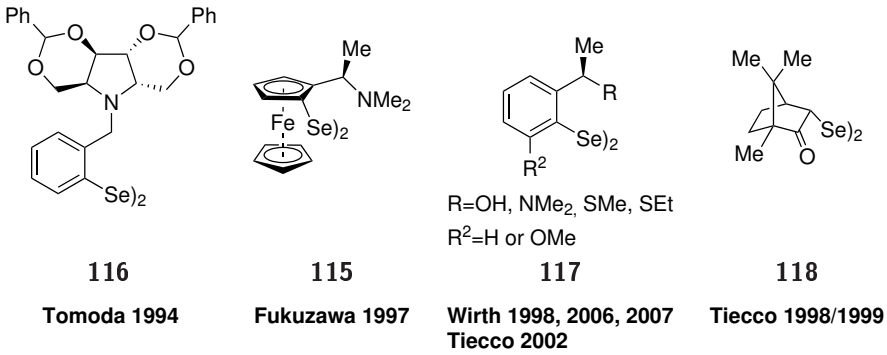
113 **114** **115**

84%, >95% *de*

(Fc*Se)2

(1.23)

Unfortunately, these findings could not be translated into a catalytic processes. The efforts by Tomoda,[113] Fukuzawa,[114] Wirth,[82,89] Tiecco[115,116] and their respective groups using diselenides **115**, **116**, **117** and **118** (Figure 1.4) in the catalytic oxyfunctionalization of alkenes led to low enantiomeric excesses (20-66% *ee*), an exception being *ee*'s of 75 and 82% that were achieved in methoxylation reactions by Wirth[117] and Tiecco[118] when they used catalyst **117** with R^2=OMe.



116 **115** **117** **118**

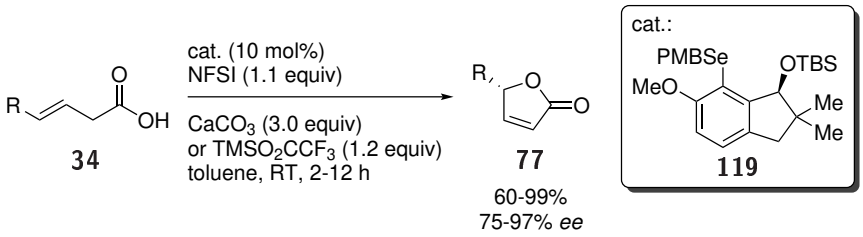
Tomoda 1994 **Fukuzawa 1997** **Wirth 1998, 2006, 2007** **Tiecco 1998/1999**
Tiecco 2002

Figure 1.4: Chiral selenium catalysts synthesized by Tomoda, Fukuzawa, Wirth, and Tiecco.

The difference in selectivity between the selenofunctionalization reactions and the selenylation-desenylation sequences can be explained by the temperatures that were applied during the reactions. While the selenylation reactions could be conducted at low temperatures (−78 °C), the catalytic reactions were conducted at room temperature because they need higher temperatures for the elimination of the selenium species from the selenylated intermediates (0 °C or higher; cf. Subsection 1.1).[53] As Denmark and colleagues showed in their NMR studies, the transfer of selenium ions between olefins already proceeds at −70 °C.[109] It is therefore safe to assume

that this transfer is even faster at room temperature, degrading the enantiomeric excess of the formed seleniranium ions.

Despite these challenges, MARUOKA *et al.* accomplished the enantioselective lactonization of unsaturated acids **34** in high yields (60-99%) and excellent selectivities (75-97%) using 10 mol% of chiral selenide **119**, 1.1 equiv NFSI and a base (Equation 1.24) at room temperature.[119] Their catalyst features a sterically demanding side chain (OTBS) and a rigid structure based on indanol.



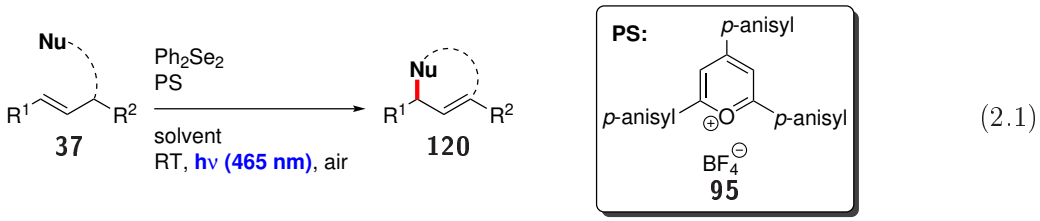
(1.24)

Although MARUOKA's work is groundbreaking, it is still of interest to find further reliable ways for the stabilization of enantioenriched seleniranium ions in order to find general methods for asymmetric selenium-catalyzed functionalization reactions.

2 Objectives

The work during this thesis was focused on the development of new selenium-catalyzed functionalizations. As described in the previous section (Subsection 1.2), the choice of the right oxidant for these transformations is crucial. Conventional oxidants, especially *N*-halogenated oxidants, are the source of endogenous nucleophiles that compete with the intended nucleophile.[37,62] To be able to use weak exogenous nucleophiles in these reactions, an alternative to conventional oxidants is necessary. In this context, the recently developed dual selenium/photoredox catalysis by Breder *et al.* is a promising method for the functionalization of alkenes with exogenous nucleophiles.[91]

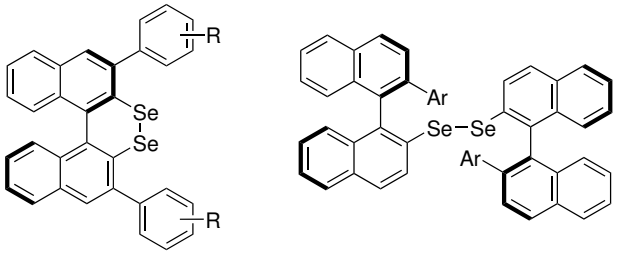
In the first experiments with dual selenium/photoredox catalysis, acids were used as nucleophiles. Therefore the question occurred whether the reaction conditions would also promote reactions with weak and challenging nucleophiles. As suitable candidates, a number of different nucleophiles come to mind. Alcohols have been used in selenium-catalyzed oxidative functionalizations, but the reactions often needed special substrates or had selectivity issues (cf. Subsection 1.2.2).[67,74,75,88,89] In this context, it was to be investigated if selenium/photoredox catalysis allows for simple substrates and high selectivity. Other interesting nucleophiles are amines, which in conventional transformations are often limited to endogenous nucleophiles originating from the *N*-halogenated oxidant (an exception being the pyridination by Zhao *et al.*).[69] Selenium/photoredox catalysis could allow for new types of nitrogen nucleophiles that are not derived from oxidants. For the above-mentioned nucleophiles, intramolecular as well as intermolecular transformations were to be investigated in this work (Equation 2.1). Furthermore, it was to be determined if instead of alkenes, alkynes could be used as substrates for the described transformations.



(2.1)

In addition to the development of new selenium-catalyzed functionalizations, the possibility to conduct these reactions in an asymmetric fashion should be examined. For this purpose, asymmetric diselenides should be synthesized and used as catalysts. As already explained in the previous section (Subsection 1.2.4), methods for asymmetric selenium-catalyzed oxidative functionalizations are sparse. Most of the attempts made focus on the use of diselenides bearing Lewis basic side chains for the stabilization of the seleniranium intermediate in order to prevent its racemization. Another option to prevent racemization of the seleniranium ion by olefin-to-olefin transfer is the application of diselenides with attached bulky groups, which would block the free coordination site from the attack of a second alkene. Additionally, a rigid structure was

expected to keep the steric bulk in place. A suitable structure motif that could fulfill these requirements is the binaphthyl moiety. As binaphthyl-derived catalysts have been applied as chiral brønsted acids in MANNICH-type reactions or transfer hydrogenations,[120–123] the question arose if binaphthyl-derived diselenides could be selective catalysts in selenium-catalyzed transformations. Therefore, two possible binaphthyl-based catalyst structures were envisioned and were to be synthesized during this work (Figure 2.1).



121 **122**

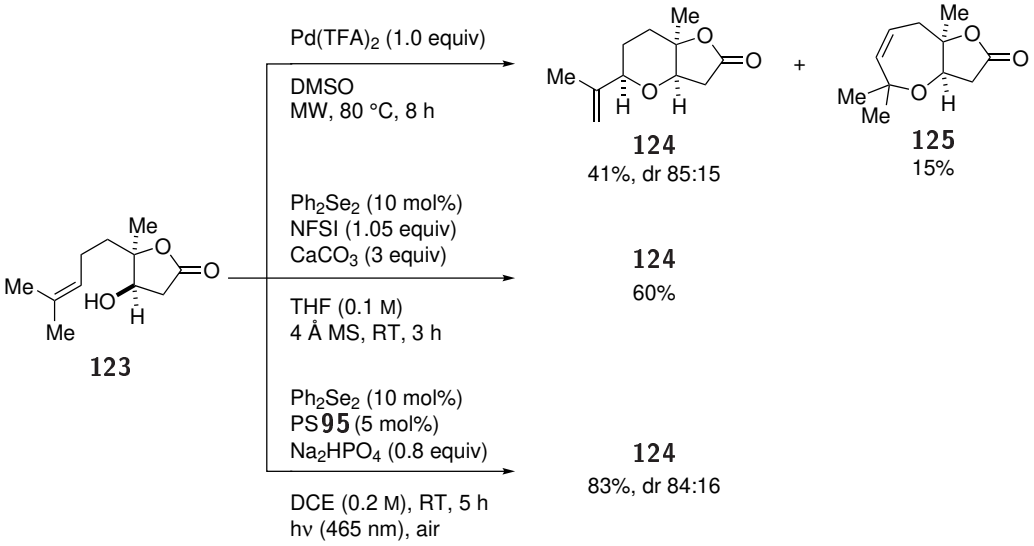
Figure 2.1: Binaphthyl derived chiral diselenides.

3 Results and Discussion

3.1 Intra- and intermolecular etherification *via* photo-aerobic selenium-π-acid catalysis

3.1.1 Intramolecular etherification - Preliminary investigations and optimization of reaction conditions

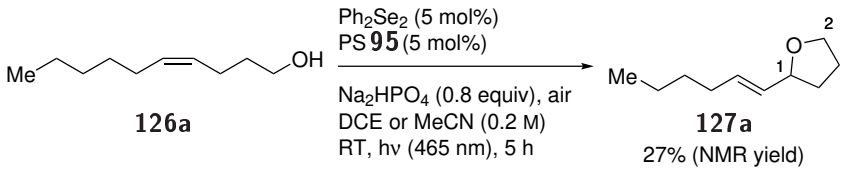
During the total synthesis of (+)-Greek tobacco lactone (**124**), the groups of Stark, Breder and Christmann investigated the selenium-catalyzed cyclization of alcohol **123** as an alternative to the reaction with palladium trifluoroacetate.[124] While in the palladium-mediated reaction the desired product **124** was obtained in only 41% isolated yield and 15% of tetrahydrooxepin side product **125** was formed (Scheme 3.1, top), the selenium-π-acid-catalyzed transformation led to the clean formation of lactone **124** in 60% yield when NFSI was used as the oxidant (Scheme 3.1, middle). Moreover, under the conditions of selenium-π-acid/photoredox catalysis, the yield was even higher (83%) and the dr of 84:16 was comparable to that of the product of the palladium-catalyzed reaction (Scheme 3.1, bottom).



Scheme 3.1: Palladium-mediated (top), selenium/NFSI-mediated (middle) and selenium-photoredox-mediated (bottom) formation of (+)-Greek tobacco lactone (**124**).

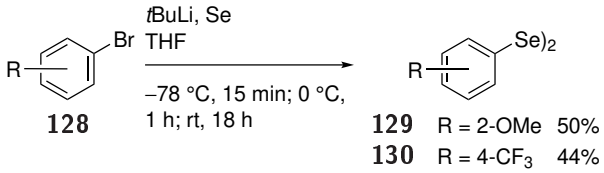
These impressive findings raised the question if the selenium-π-acid/photoredox-catalyzed intramolecular etherification, which worked well for a rigid system such as alcohol **123**, was also possible for more flexible substrates. To find an answer to this question, (*Z*)-dec-4-en-1-ol (**126a**) was subjected to the conditions that were used in the synthesis of (+)-Greek tobacco lactone (**124**). Gratifyingly, when the alcohol was treated with diphenyl diselenide (10 mol%), *p*-MeO-TPT (5 mol%), Na_2HPO_4 (0.8 equiv) and irradiation at $\lambda = 465$ nm under air in DCE (0.2 M), 27% of a product was observed in ^{1}H NMR (Equation 3.1), and identified as (*E*)-2-(hex-1-en-

1-yl)tetrahydrofuran (**127a**) *via* ^{1}H NMR spectroscopy by the characteristic shift and splitting of the signals of the three carbinol protons. While the signal of the proton at C-1 was observed as a quartet at 4.22 ppm, the two protons at C-2 appeared as a doublet of doublets of doublets at 3.89 ppm and a triplet of doublets at 3.75 ppm. The formation of product **127a** was also confirmed by comparison with literature data.[125] Intrigued by this result, it was examined whether the reaction would run more efficiently in MeCN, which had been the best solvent in the intermolecular selenium-π-acid/photoredox-catalyzed esterification.[91] Unfortunately, the reaction in MeCN but under otherwise unchanged conditions led to the same yield as in DCE (Equation 3.1).



(3.1)

Following these initial results, it was hypothesized that a different combination of diselenide and photosensitizer could lead to improved yields due to a better match of the reduction potential of the excited state of the photosensitizer with the oxidation potential of the diselenide on the one hand, and the one of the selenofunctionalization intermediate on the other hand. For further investigations, diselenides **129** ($E_{ox} = 1.22$ V vs. SCE)[126] and **130** ($E_{ox} = 1.53$ V vs. SCE)[126] were synthesized according to a procedure by Denmark and obtained in yields of 50 and 44% (Equation 3.2).[68]

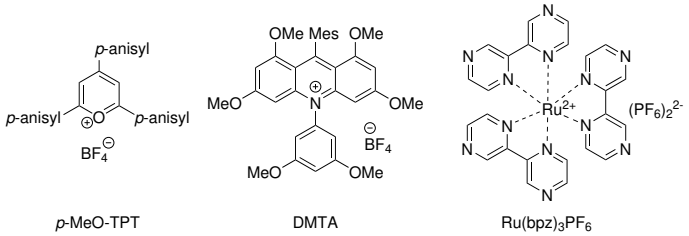


(3.2)

In order to identify potent combinations of the synthesized diselenides with different photosensitizers, their interactions were examined in fluorescence quenching experiments by Dr. S. Ortgies.[127] The Stern-Volmer constants were determined for the combination of diselenides **25**, **129** and **130** with photosensitizers *p*-MeO-TPT (**95**), 10-(3,5-dimethoxyphenyl)-9-mesityl-1,3,6,8-tetramethoxyacridinium tetrafluoroborate (**131**, DMTA) and Ru(bpz)$_3$PF$_6$ (**132**) (Table 3.1).[127] The Stern-Volmer constant for the combination of diphenyl diselenide (R=H) and *p*-MeO-TPT, which was used in the starting experiment for the intramolecular etherification, was determined to be $K_{SV} = (116 \pm 2.52)\ \mathrm{L \cdot mol^{-1}}$. The quenching of *p*-MeO-TPT with electron-poor diselenide **130** (R = 4-CF$_3$) was less efficient with a constant of $K_{SV} = (85.1 \pm 4.70)\ \mathrm{L \cdot mol^{-1}}$. For DMTA, both diselenides **129** and **130** showed higher quenching than diphenyl diselenide ($K_{SV} = (76.9 \pm 4.12)\ \mathrm{L \cdot mol^{-1}}$), with Stern-Volmer constants of $K_{SV} = (103 \pm 5.61)\ \mathrm{L \cdot mol^{-1}}$ (R = 2-OMe) and $K_{SV} = (96.3 \pm 6.00)\ \mathrm{L \cdot mol^{-1}}$ (R = 4-CF$_3$), respectively. Using ruthenium

complex **132**, higher quenching than in the other experiments was observed, with diselenide **129** (R = 2-OMe) having the highest observed constant (K_{SV} = (992 ± 18.8) L · mol^{-1}) and diphenyl diselenide having a constant of K_{SV} = (140±29.6) L·mol^{-1}. The high values can be attributed to the significantly longer lifetime of the excited triplet state of photocatalyst **132** (τ_f = 1.04 µs)[128] compared to the excited states of photocatalysts **95** and **131** (τ_f =4-12 ns).[129,130] Due to the quenching of the different photosensitizers with electron-poor diselenide **130** being lower than that of *p*-MeO-TPT with diphenyl diselenide, **130** was ruled out as a potential catalyst. Electron-rich diselenide **129** quenched photosensitizers **131** and **132** more efficiently than diphenyl diselenide in the respective combinations, indicating stronger interactions. Therefore, it was applied in further test reactions for the intramolecular etherification.

Table 3.1: Stern-Volmer constants for different diselenide/photosensitizer combinations, determined by Dr. S. Ortgies.[127]



p-MeO-TPT **95** | DMTA **131** | $Ru(bpz)_3PF_6$ **132**

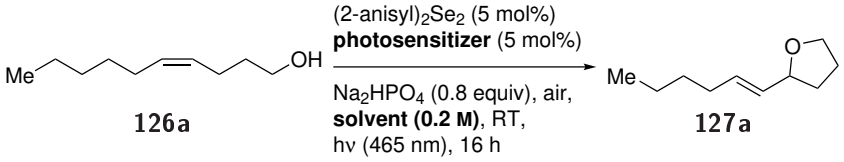
$(R-C_6H_4)_2Se_2$	*p*-MeO-TPT (**95**)	DMTA (**131**)	$Ru(bpz)_3PF_6$ (**132**)
2-OMe	-[a]	(103±5.61) M^{-1}	(992±18.8) M^{-1}
H	(116±2.52) M^{-1}	(76.9±4.12) M^{-1}	(140±29.6) M^{-1}
4-CF_3	(85.1±4.70) M^{-1}	(96.3±6.00) M^{-1}	-[a]

[a] Values not determined. bpz = 2,2′-bipyrazine

In the following experiments, the cycloetherification of alcohol **126a** with $(2\text{-anisyl})_2Se_2$ (**129**) and photosensitizers **95**, **131** and **132** was examined. For both the diselenide and the photosensitizers, an amount of 5 mol% was used. With the new diselenide catalyst, the yield of the transformation with *p*-MeO-TPT increased to 31% in DCE and 45% in MeCN (Table 3.2, entries 1 and 2). With the other photosensitizers, product **127a** was observed in lower yields. With DMTA, it was formed in 27% in DCE and 6% in MeCN (Table 3.2, entries 3 and 4). With $Ru(bpz)_3PF_6$, the product was formed in 24% in MeCN and no reaction occurred in DCE (Table 3.2, entries 5 and 6). In both solvents, the quenching of the fluorescence was observed. This suggests the decomposition of the photosensitizer, possibly by a selenium species.

As it was assumed that the product decomposed when exposed to the photoconditions for too long, the reaction time was shortened (5 h instead of 16 h) and the product development monitored during the reaction by 1,1,2,2-tetrachloroethane (TCE) as an internal NMR standard in MeCN-d_3. These changes of the reaction conditions increased the yield with *p*-MeO-TPT to 69% (Table 3.3, entry 1), whereas with DMTA, tetrahydrofuran **127a** was formed in 29%, a similar

Table 3.2: Comparison of photosensitizers in different solvents in the intramolecular etherification.



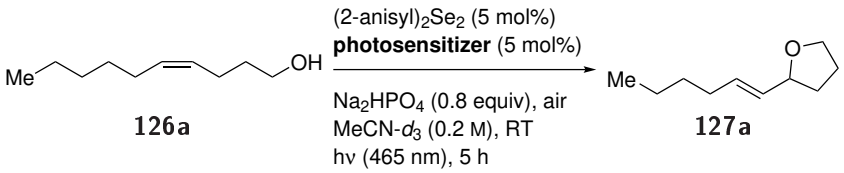
126a **127a**

entry	photosensitizer	solvent	NMR yield[a]
1	*p*-MeO-TPT	DCE	31%
2	*p*-MeO-TPT	MeCN	45%
3	DMTA	DCE	27%
4	DMTA	MeCN	6%
5	$Ru(bpz)_3PF_6$	DCE	-
6	$Ru(bpz)_3PF_6$	MeCN	24%

[a] Standard: 1,3,5-trimethoxybenzene (TMB).

yield as after 16 h reaction time (Table 3.3, entry 2). The yield with $Ru(bpz)_3PF_6$ decreased to 9% (Table 3.3, entry 3).

Table 3.3: Comparison of photosensitizers in the intramolecular etherification.



126a **127a**

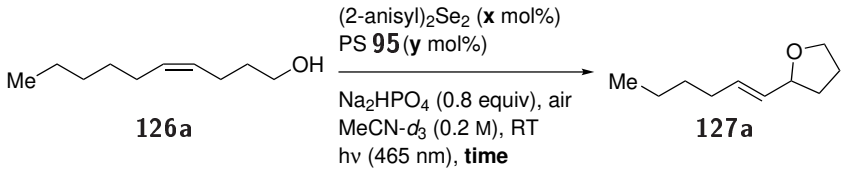
entry	photosensitizer	NMR yield[a]
1	*p*-MeO-TPT	69%
2	DMTA	31%
3	$Ru(bpz)_3PF_6$	9%

[a] Internal standard TCE.

As the combination of pyrylium derivative **95** and $(2\text{-anisyl})_2Se_2$ showed the best results in MeCN (69% yield, Table 3.4, entry 1), these conditions were used to optimize the catalyst loadings. In an initial experiment, the influence of the amount of the photosensitizer on the yield was investigated. In fact, decreasing the photosensitizer loading to 3 mol% decreased the yield only slightly to 65% after 5 h reaction time (Table 3.4, entry 2). In combination with a higher loading of diselenide **129** (10 mol%), the formation of tetrahydrofuran **127a** with a yield of 68% was observed after 7 h (Table 3.4, entry 3). Because the difference between the yields was very small, it was decided to go with the lower catalyst loadings of 5 mol% diselenide and 3 mol% photosensitizer for further reactions. During all preceding experiments, air was used as the oxidant. Alternatively, using pure oxygen could increase the reaction rate and yield, but it could also lead to the formation of oxidized side products. In the experiments on the selenium-π-acid/photoredox-catalyzed esterification by Dr. S. Ortgies, the formation of an allylic

hydroperoxide was observed as the probable consequence of the SCHENCK-ene reaction of the alkene with $^1O_2$.[127,131,132] In the following investigations, the addition of molecular sieves was found to reduce the hydroperoxide formation.[127] Therefore, to examine the influence of oxygen on the intramolecular etherification, 4 Å molecular sieves and oxygen instead of air were used with 5 mol% (2-anisyl)$_2$Se$_2$ and 3 mol% *p*-MeO-TPT. The reaction resulted in a yield of 67%, which is comparable to the yield obtained with air (Table 3.4, entry 4). Air was chosen in further experiments to minimize the formation of side products by the SCHENCK-ene reaction. To make sure that both catalysts and air were neccessary for the reaction, two control experiments leaving out one of the catalysts and one experiment under an argon atmosphere were conducted. No product development was observed in either case (Table 3.4, entries 5-7). As irradiation of the reaction mixture could lead to elevated temperatures in the reaction flask, the influence of higher or lower reaction temperatures was examined during reactions using a double-walled flask with a cryostat. Increasing the temperature to 60 °C led to a decreased yield of 57% (Table 3.4, entry 8). Decreasing the temperature to 0 °C led to the shutdown of the reaction and no product formation was observed (Table 3.4, entry 9).

Table 3.4: Optimization of catalyst loading and control experiments in the intramolecular etherification.



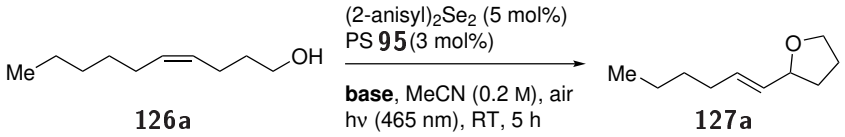
entry	x mol%	y mol%	time	NMR yield[a]
1	5	5	5 h	69%
2	5	3	5 h	65%
3	10	3	7 h	68%
4[b]	5	3	5 h	67%
5	-	3	5 h	0%
6	5	-	5 h	0%
7[c]	5	3	5 h	0%
8[d]	5	3	5 h	57%
9[e]	5	3	5 h	0%

[a] Standard: TCE. [b] Reaction with oxygen and molecular sieves instead of air. [c] Reaction under an argon atmosphere using degassed solvents. [d] Reaction at 60 °C. [e] Reaction at 0 °C.

As the last step of the optimization of the reaction conditions, the effect of different bases on the yield was investigated with TMB as an external NMR standard. The use of different phosphate bases led to good yields of 47 and 53% with sodium phosphates Na_2HPO_4 and NaH_2PO_4, respectively, and to significantly lower yields of 0-14% with potassium phosphates (Table 3.5, entries 1-5). This observation is probably due to the deactivation of the photosensitizer, as in these last reactions, complete quenching of fluorescence was observed. While with KF no reac-

tion occurred and fluorescence quenching was observed, using CaF_2 afforded the product in 51% yield (Table 3.5, entries 6 and 7). When carbonate bases were used, the yields were between 14 and 50%, with Li_2CO_3 giving the best result (Table 3.5, entries 8-10). Acetates were no effective bases for the reaction. Only with NaOAc the reaction occurred and led to only 9% yield (Table 3.5, entries 11-13). In order to check if the base was important for the reaction, an experiment without any added base was conducted. The product was observed in 33% yield, indicating a possible inhibition of the reaction by some bases as in the case of potassium phosphates, sodium carbonates and acetates (Table 3.5, entry 14). As some bases proved to be beneficial for the reaction, the influence of the loading was examined. With 0.5 equiv of Na_2HPO_4, the product was obtained in 47% yield, whereas an increase of the loading to 1 or 1.5 equiv resulted in a lower yield of 41%, respectively (Table 3.5, entries 15-17).

Table 3.5: Optimization of bases used in the intramolecular etherification.



126a **127a**

entry	base	amount	NMR yield[a]
1	Na_2HPO_4	0.8 equiv	47%
2	NaH_2PO_4	0.8 equiv	53%
3	KH_2PO_4	0.8 equiv	14%
4	K_2HPO_4	0.8 equiv	12%
5	K_3PO_4	0.8 equiv	-
6	KF	0.8 equiv	-
7	CaF_2	0.8 equiv	51%
8	$NaHCO_3$	0.8 equiv	28%
9	Na_2CO_3	0.8 equiv	14%
10	Li_2CO_3	0.8 equiv	50%
11	$LiOAc \cdot 2\,H_2O$	0.8 equiv	-
12	NaOAc	0.8 equiv	9%
13	KOAc	0.8 equiv	-
14	-	0.8 equiv	33%
15	Na_2HPO_4	0.5 equiv	47%
16	Na_2HPO_4	1.0 equiv	41%
17	Na_2HPO_4	1.5 equiv	41%

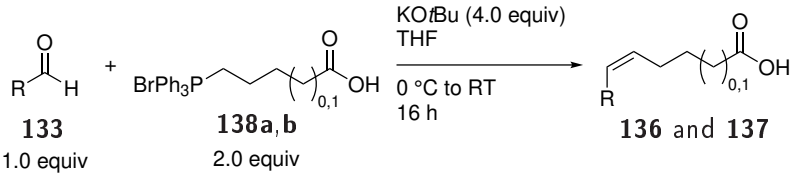
[a] Standard: TMB.

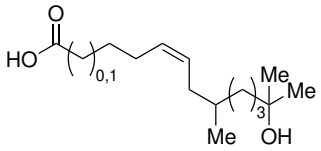
3.1.2 Intramolecular etherification - Synthesis and cyclization of unsaturated alcohols

For the evaluation of the scope and limitations of the selenium-π-acid/photoredox-catalyzed intramolecular etherification, a series of unsaturated alcohols was synthesized. In order to investigate the formation of cyclic ethers with different ring sizes, it was intended to synthesize

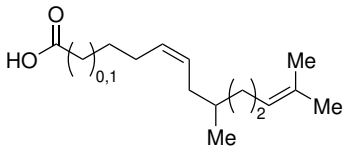
4-alken-1-ol derivatives as well as 5-alken-1-ol derivatives. The first path that allowed for the synthesis of both kinds of alcohols was the synthesis and reduction of unsaturated acids **136** and **137**. The WITTIG reaction of 1.0 equiv of aldehyde **133** with 2.0 equiv of either 3-carboxypropyl triphenylphosphonium bromide (**138a**) or 4-carboxybutyl triphenylphosphonium bromide (**138b**) and 4.0 equiv potassium *tert*-butoxide afforded alkenoic acids **136a–d** and **137a–j** in high yields between 54 and 99% (Table 3.6; products **136** (n=0) with yields in gray synthesized by Dr. M. Palomba).[133,134] Acid **136f** was obtained in only 20%, presumably due to the formation of dechlorinated side products. The isolation of acid **136e** was supposedly impaired by the volatility of the product, which was obtained in 38%. In the reaction with 3,3,3-trifluoropropanal, no transformation into acid **137k** was observed. The product formation of unsaturated acids **136** and **137** was confirmed in the ^{1}H NMR spectrum, where the singlet of the aldehyde proton at around 9-10 ppm disappeared and a new multiplet signal indicative of the protons corresponding to the double bond between 5 and 6 ppm appeared.

Table 3.6: WITTIG reaction of aldehydes **133** to carboxylic acids **136** and **137**. Products **136** (n=0) with yields in gray synthesized by Dr. M. Palomba.[133,134]

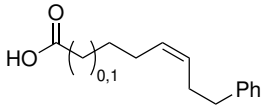




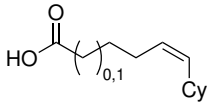
n=0 **136a** 99%
n=1 **137a** 79%



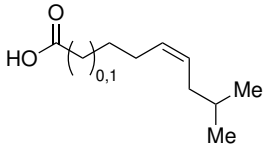
n=0 **136b** 71%
n=1 **137b** 79%



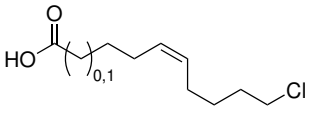
n=0 **136c** 96%
n=1 **137c** 82%



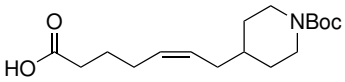
n=0 **136d** 75%
n=1 **137d** 77%



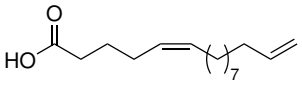
n=0 **136e** 38%
n=1 **137e** 84%



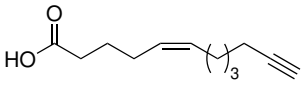
n=0 **136f** 20%
n=1 **137f** 60%



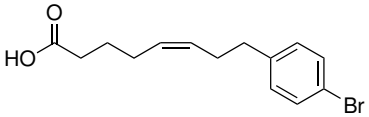
137g 62%



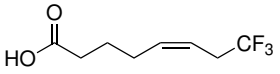
137h 73%



137i 54%



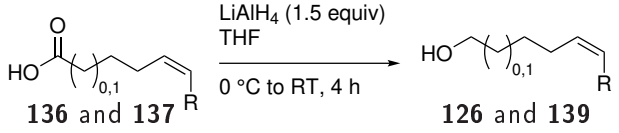
137j 81%

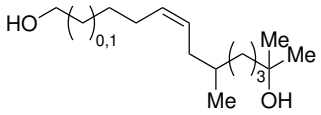
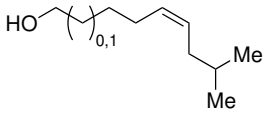
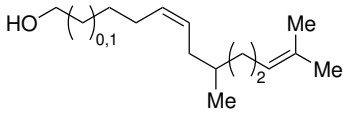
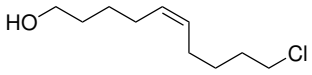
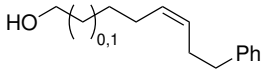
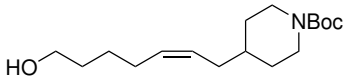
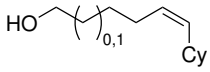
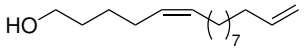
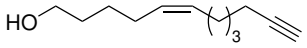


137k nr

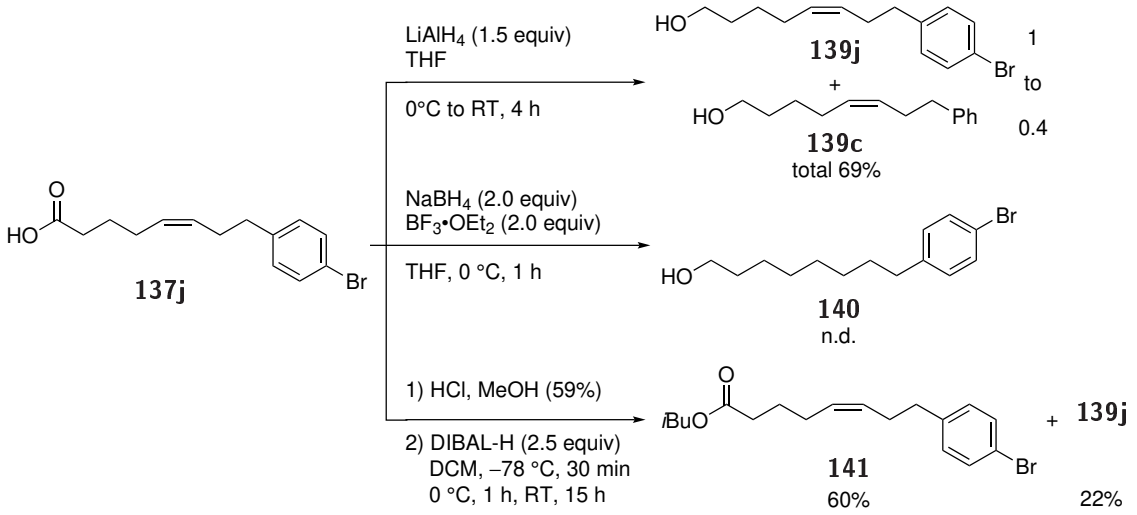
The following reduction of alkenoic acids **136** and **137** was achieved by the reaction with 1.5 equiv $LiAlH_4$ in THF. Alcohols **126** and **139** were synthesized in overall good yields between 36 and 99% (Table 3.7; products **126** (n=0) with yields in gray synthesized by Dr. M. Palomba).[133,134] The lowest yield was obtained for chloride **139f**, which suffered from partial dehalogenation during the reaction. The successful formation of alcohols **126** and **139** was observed in ^{1}H NMR, where the triplet of the newly formed methylene moiety next to the hydroxyl group was observed at around 3.6 ppm.

Table 3.7: Reduction of carboxylic acids **136** and **137** to alcohols **126** and **139**. Products **126** (n=0) with yields in gray synthesized by Dr. M. Palomba.[133,134]



	n=0 **126b** 83% n=1 **139a** 68%			n=0 **126f** 49% n=1 **139e** 71%	
	n=0 **126c** 99% n=1 **139b** 76%			**139f** 36%	
	n=0 **126d** 40% n=1 **139c** 51%			**139g** 61%	
	n=0 **126e** 88% n=1 **139d** 91%			**139h** 73%	
				**139i** 54%	

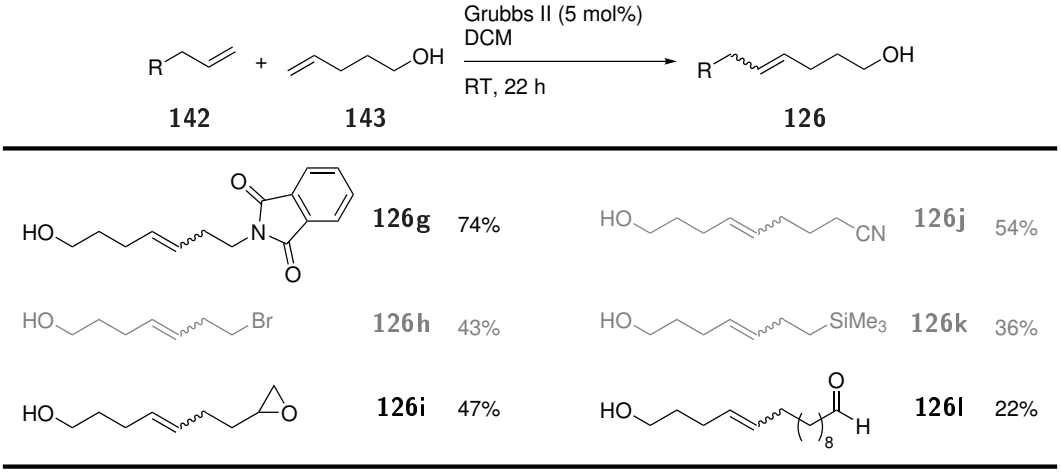
When the reduction of alkenoic acid **137j** was attempted with $LiAlH_4$, the desired alcohol **139j** was obtained in 69% as an inseparable mixture with the debrominated alcohol **139c** (Equation 3.3, top). Therefore, other reduction methods were tested. In the reaction with $NaBH_4$ (2.0 equiv) and boron trifluoride diethyl etherate (2.0 equiv), the double bond was also reduced along with the acid moieties (Equation 3.3, middle). The formation of the methyl ester followed by treatment with DIBAL-H (2.5 equiv) afforded an impure fraction of the desired product **139j** in 22% yield, but most starting material underwent a transesterification to isobutyl ester **141** (Equation 3.3, bottom).



(3.3)

In order to avoid problems with halogenated substances and to be able to access substrates with functional groups that would not tolerate the conditions of the WITTIG reaction and the reduction (e.g. aldehydes, nitriles), another synthetic path to unsaturated alcohols **126** and **139** was needed. An easy and step-economic alternative to the previous route was provided by the cross-metathesis of terminal alkenes **142** with alkenol **143**. Terminal alkenes **142** were reacted with 4-pentene-1-ol (**143**) (3.0 equiv) using the 2nd generation GRUBBS catalyst (5 mol%) to give alcohols **126g–l** as *E/Z* mixtures in 22-74% yield (Table 3.8; grayed alcohols were synthesized by Dr. M. Palomba).[133,134] Possible side products in this reaction are the products of the homocoupling of the two starting materials. In order to assure easy separation of the desired product from the side products by column chromatography, an excess of the alcohol was used, so that the homocoupling of alkene **142** was avoided. The diol that results from the homocoupling of alcohol **143** is very polar and therefore easier to separate. The discrimination between the starting material and the products is also easy in ^{1}H NMR. The olefinic protons of terminal alkene 4-pentene-1-ol (**143**) result in three signals between 4.8 and 6.0 ppm (Figure 3.1, red). The signal of H^a, a doublet of doublets of triplets at 5.84 ppm, has coupling constants of 17.0, 10.2 and 6.7 Hz that correspond to the *trans*-coupling to H^b, the *cis*-coupling to H^c and the coupling to the neighboring CH_2 group, respectively. The signal of H^b, a doublet of quartets at 5.05 ppm, shows coupling to H^a with 17.0 Hz and to H^c with 1.7 Hz. The coupling constants of the doublet of doublets of triplets at 4.98 ppm (H^c) are 10.2 Hz (coupling to H^a), 1.7 Hz (coupling to H^b) and 1.3 Hz (coupling to the CH_2 group). The olefinic protons of alcohol **126j**, however, show two signals at 5.50 and 5.36 ppm (Figure 3.1, green) and in the spectrum of diol **126m**, there is only one multiplet at 5.43 ppm for both double bond protons, resulting from the symmetry of the molecule (Figure 3.1, blue).

Table 3.8: Synthesis of alcohols **126g–l**. Grayed products were synthesized by Dr. M. Palomba.[133,134]



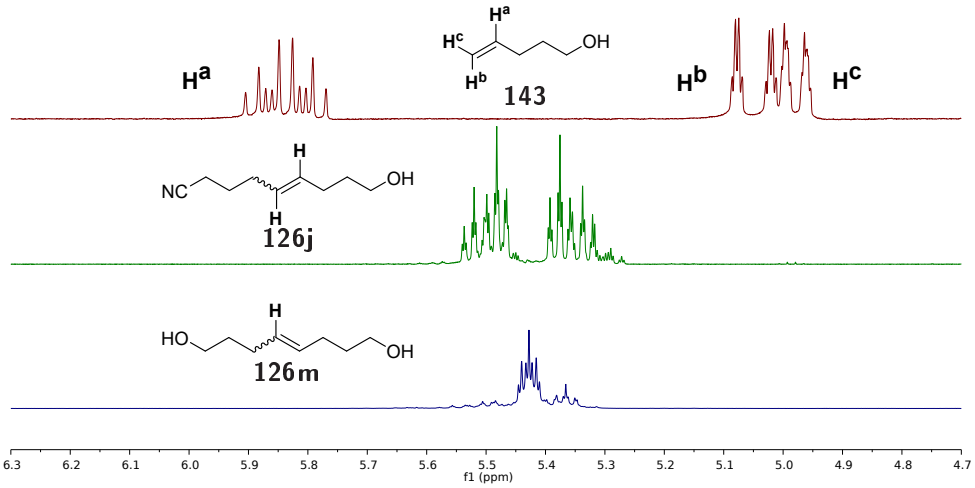
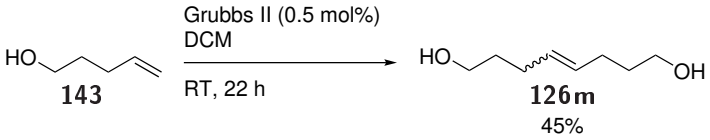


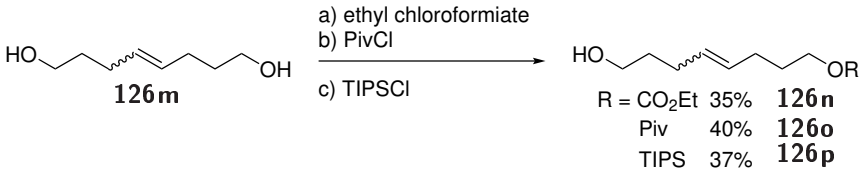
Figure 3.1: Comparison of the ^{1}H NMR spectra of 4-pentene-1-ol (**143**), alcohol **126j** and diol **126m**.

The homocoupling of 4-pentene-1-ol (**143**) was also a useful path to substrates with additional free or functionalized hydroxyl groups. Oct-4-ene-1,8-diol (**126m**) was synthesized in 45% from alcohol **143** using the 2nd generation Grubbs catalyst (0.5 mol%) following a procedure by Marshall and Sabatini (Equation 3.4).[135]



(3.4)

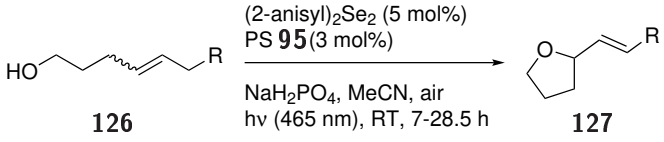
Diol **126m** was then transformed to monocarbonate **126n**, monopivalic ester **126o** and monosilylether **126p** in yields between 35 and 40% (Equation 3.5).

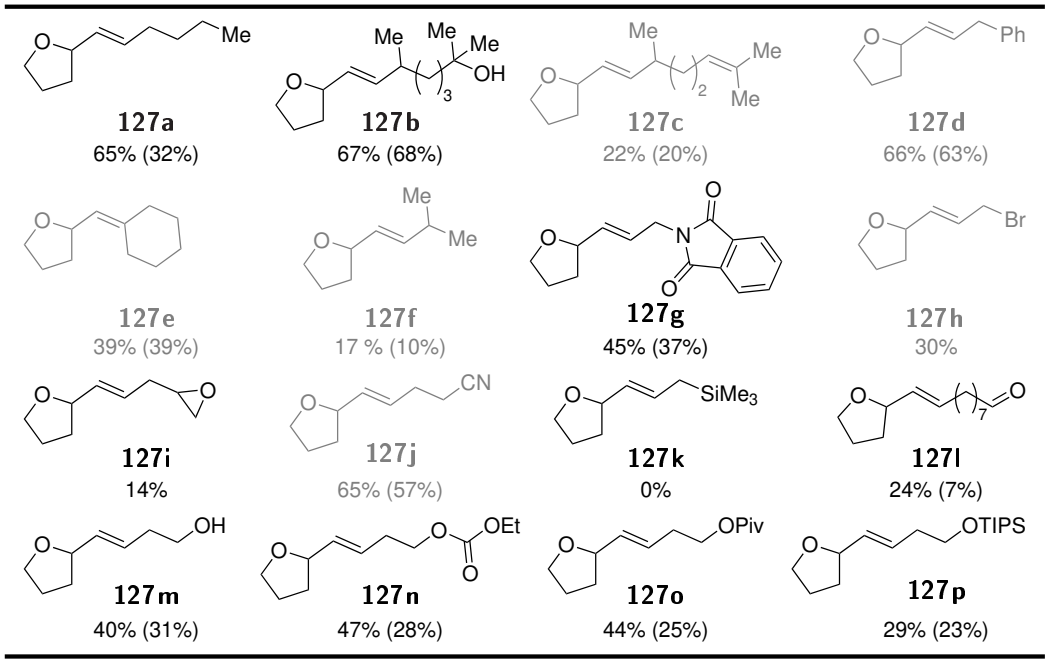


(3.5)

With the substrates in hand, the cycloetherification was attempted using (2-anisyl)$_2$Se$_2$ (5 mol%), photosensitizer **95** (3 mol%) and NaH_2PO_4 (0.8 equiv) in MeCN under irradiation at $\lambda = 465$ nm and air at room temperature. Tetrahydrofurans **127a–j,l–p** were formed in yields between 14 and 67% (Table 3.9; grayed products were synthesized by Dr. M. Palomba).[133,134] Their formation was easily observable by ^{1}H NMR, where the carbinol proton typically resonates at around 4.2 ppm as a quartet with a coupling constant of 7 Hz. The newly formed double bonds have two signals between 5 and 6 ppm and show a coupling of 15 Hz, meaning they are (*E*)-configured. The method tolerated various functional groups very well (aryl, imide, nitrile, free alcohol, carbonate, ester). The formation of ether **127e** with a trisubstituted double bond resulted in a moderate yield of 39%. Other substrates proved to be more challenging. Ether **127c** was obtained in

Table 3.9: Synthesis of tetrahydrofurans **127**.[a] Grayed products were synthesized by Dr. M. Palomba.[133,134]





[a] NMR yield, standard: TMB or TCE, isolated yield in brackets.

only 22% yield, presumably due to side reactions with the second double bond. Compound **127f** was volatile, which diminished both the NMR and isolated yield. The same was assumed for aldehyde **127l**, the formation of which was observed in 24% yield in NMR, but only 7% was isolated. Bromide **126h** and epoxide **126i** seemed to tolerate the reaction conditions and product formation was determined via NMR with yields of 30 and 14%, respectively. However, the products could not be isolated, as the bromide degraded during isolation attempts and the epoxide could only be isolated as a mixture with unidentifiable side products. The NMR yields were based on the signals of the assumed carbinol protons as a quartet at 4.32 and 4.26 ppm, respectively (Figure 3.2). In the case of assumed bromide **127h**, there were also two clear signals that were assigned to the double bond, a doublet of triplets of doublets at 5.90 ppm (J = 15.3, 7.3 and 0.9 Hz) and a doublet of doublets at 5.76 ppm (J = 15.3 and 6.5 Hz).

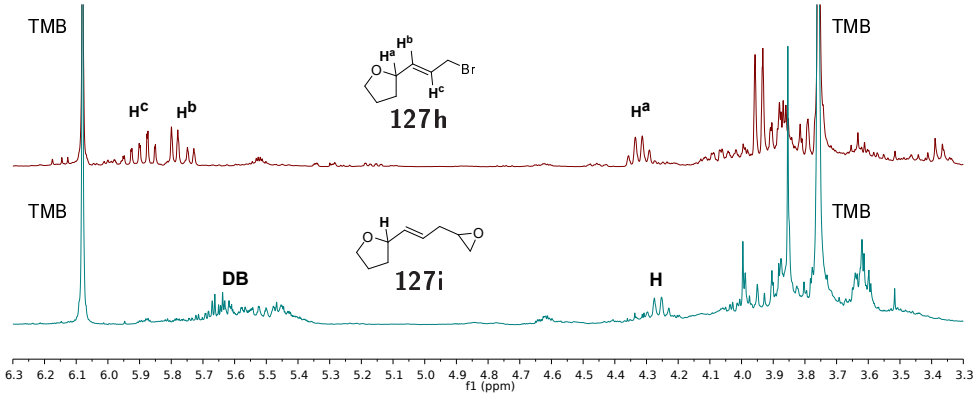
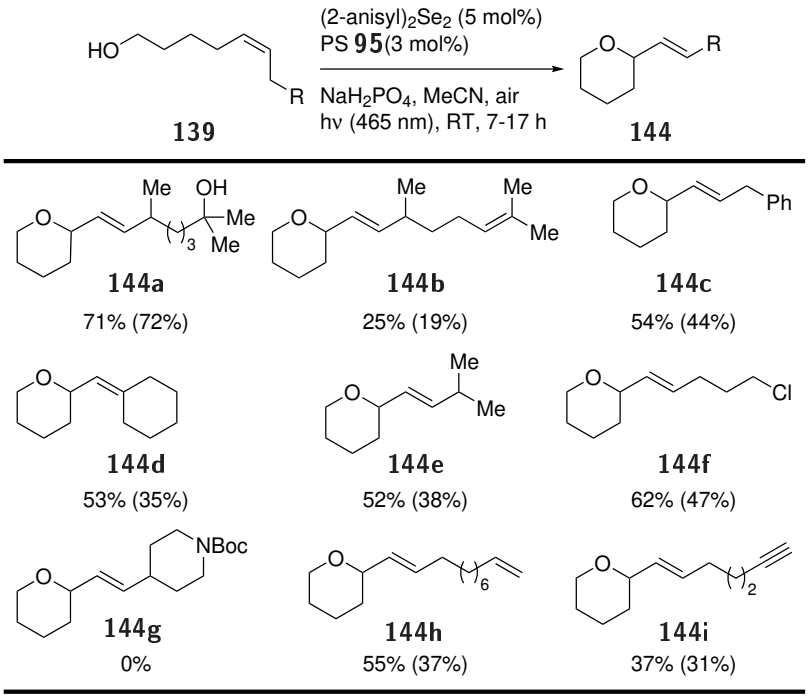


Figure 3.2: Crude ^{1}H NMR spectra of assumed products **127h** and **127i**.

Substrates containing silyl moieties turned out to be problematic. With silyl ether **126p**, the reaction to ether **127p** proceeded in a low yield of 29% and the fluorescence was partly quenched. During the attempted cyclization of silane **126k**, the fluorescence was quenched completely and in the ^{1}H NMR spectrum, no signals for the product **127k**, but new signals around 0 ppm were observed. As at the same time, the signals of the starting material disappeared, it was assumed that it decomposed under the applied conditions.

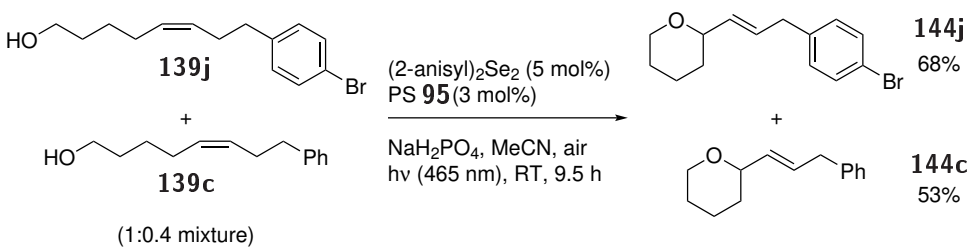
The cycloetherification of alcohols **139** under the same conditions proceeded smoothly and delivered tetrahydropyrans **144** in mostly high yields between and 19 and 72% (Table 3.10).[134] In contrast to tetrahydrofuran derivatives **127**, the carbinol proton is shifted to higher field (4.0 ppm). Compounds with functional groups that were well tolerated in the formation of tetrahydrofurans delivered ethers **144** in high yields as well (compounds **144a**,**c**,**d**), while an additional internal double bond seemed to also inhibit the reaction (compound **144b**). Moreover, ether **144e** was less volatile than its furan-equivalent and chloride **144f** and alkene **144h** were also obtained in very good yields. Alkyne **144i** was obtained in moderate yield. Unfortunately, the protected piperidine derivative **139g** showed no conversion and also showed partial quenching of the fluorescence.

Table 3.10: Synthesis of tetrahydropyrans **144**.[a][134]



[a] NMR yield, standard: TMB or TCE, isolated yield in brackets.

In order to evaluate the performance of an aryl bromide, the reaction of the mixture of alcohols **139j** and **139c** under the established conditions was examined (Equation 3.6). As it was also not possible to separate the formed ethers from each other, only the NMR yield was determined. The differentiation of the signals of the two ethers was simplified by comparison with the previously obtained clean NMR spectrum of compound **144c** (Figure 3.3, bottom). As the signals of the double bond protons and the carbinol proton of both compounds overlapped, the NMR yield was determined by integration of the signal of the benzylic protons, a doublet of doublets at 3.37 or 3.31 ppm, respectively (Figure 3.3, top). Bromide **144j** was obtained in an excellent yield of 68%, the formation of ether **144c** was observed in 53%, consistent with the result of pure alcohol **139c** (Table 3.10).



(3.6)

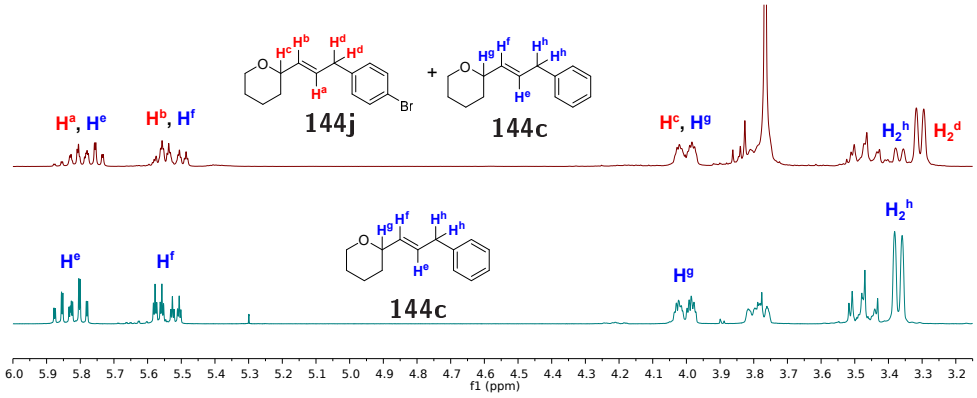
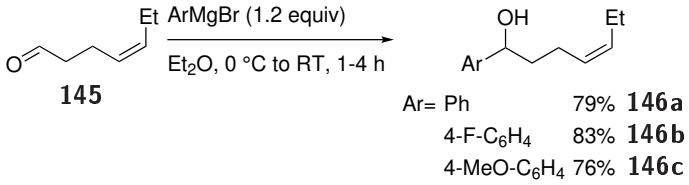


Figure 3.3: Crude ^{1}H NMR spectrum of ethers **144j** and **144c** compared with a clean spectrum of compound **144c**.

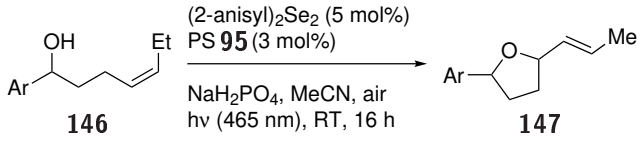
As the cyclization of primary alcohols proceeded well under the established conditions, the question came up whether secondary alcohols would perform equally well and if one diastereomer would be formed preferentially. For this purpose, secondary alcohols **146a–c** were synthesized by Dr. S. Ortgies *via* the reaction of *cis*-4-hepten-1-al (**145**) with aryl magnesium bromide derivatives (1.2 equiv) in 76 to 83% yield (Equation 3.7).[134,136]

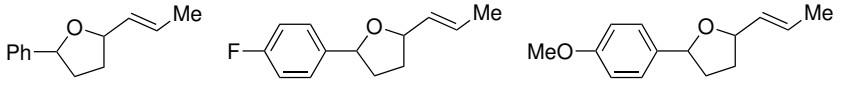


(3.7)

Gratifyingly, the selenium/photoredox catalyzed cyclization of alcohols **146a–c** yielded tetrahydrofurans **147a–c** in good yields with approx. 1:1 diastereomeric ratios (Table 3.11, experiments by Dr. S. Ortgies).[134,136] Electron-rich product **147c** was obtained in the lowest yield (56%), electron-poor product **147b** in the highest (69%).

Table 3.11: Synthesis of tetrahydrofurans **147**.[a] All syntheses by Dr. S. Ortgies.[134,136]



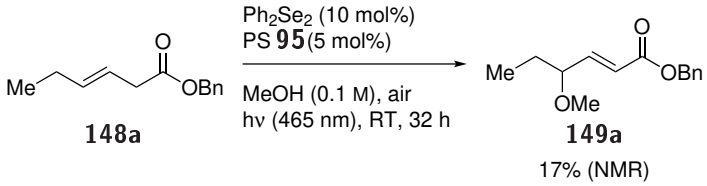


147a	**147b**	**147c**
65% (62%)	69% (66%)	56% (42%)
dr = 1:1.19	dr = 1:1.05	dr = 1:1.16

[a] NMR yield, standard: TCE, isolated yield in brackets.

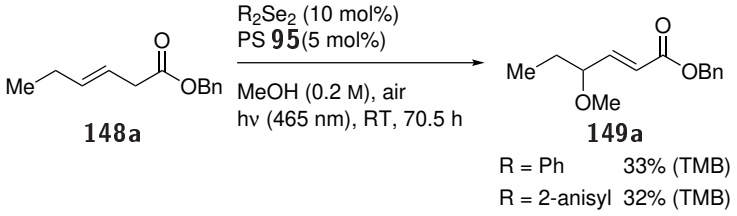
3.1.3 Intermolecular etherification - Preliminary investigations and optimization of reaction conditions

As the aerobic intramolecular etherification reactions proceeded in good yields, it was hypothesized that it was also possible to accomplish the alkoxylation of alkenes with selenium/photoredox catalysis. This reaction had been previously conducted using selenium catalysts together with high amounts of persulfate oxidants or in electrochemical reactions, which lacked selectivity (see Subsection 1.2.2).[74,75,88,89] In an initial experiment, R. Rieger examined the reaction of hex-3-enoic acid benzyl ester (**148a**) with diphenyl diselenide (10 mol%) and *p*-MeO-TPT (5 mol%) in methanol under air (Equation 3.8).[137] He observed an NMR yield of ether **149a** of 17%. The product was identified by the characteristic ^{1}H NMR signals of the double bond, the carbinol and the matching signal of the methoxy group. The signals of the double bond are doublets of doublets at 6.85 and 6.05 ppm. This splitting and chemical shift is typical for a double bond that is conjugated to a carbonyl group.[138] The carbinol proton is shifted to higher field, compared to the cyclic ethers. It is a quartet of doublets at 3.67 ppm. The methoxy group appears as a singlet at 3.31 ppm, which is slightly shifted compared to methanol (3.49 ppm).[139]



(3.8)

In order to find out if concentration had an impact on the reaction, as a first measure, it was increased to 0.2 M, which was the used concentration in the intramolecular reaction. Indeed, ether **149a** was observed in 33% yield (Equation 3.9). As (2-anisyl)$_2$Se$_2$ proved to furnish good yields in the intramolecular etherification, the reaction was repeated using this catalyst and the product was obtained in 32% yield, indicating that the used selenium-catalyst did not have an influence on this reaction (Equation 3.9).

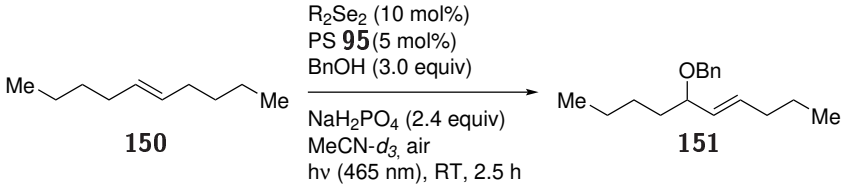


(3.9)

As the reactions by Tiecco *et al.* needed electron-poor substrates like ester **148a**, it was interesting to find out if under selenium/photoredox catalyzed conditions, simple alkenes could be used as substrates instead. Therefore, 5-decene (**150**) was chosen as a suitable substrate for further investigations. As the resulting methoxy ether would probably be volatile, benzyl alcohol was used as the nucleophile. When the reaction was tested under previous conditions in benzyl alcohol

as the solvent, it turned out that the solubility of *p*-MeO-TPT in benzyl alcohol was too low to catalyze the reaction and no conversion was observed (Table 3.12, entry 1). For this reason, the next experiments were conducted in MeCN-d_3 with 3.0 equiv BnOH and 2.4 equiv NaH_2PO_4. The solvent was used as an internal NMR standard and the integral of its signal compared to one of the doublets of the benzyl group at 4.34 ppm. This signal was chosen because the signals of the double bond between 5.3 and 5.7 ppm were expected to overlap with the SCHENCK-ene side product (allyl alcohol or hydroperoxide) and the signal of the carbinol proton, which was expected to be between 3.5 and 4 ppm, could not be identified due to several overlapping signals in this region. The reaction turned out to work more efficiently with (2-anisyl)$_2$Se$_2$, where the ratio of product to solvent was 0.22 to 1, compared to 0.10 to 1 with diphenyl diselenide (Table 3.12, entries 2 and 3).

Table 3.12: Comparison of diselenides in the intermolecular etherification of 5-*trans*-decen.



150 **151**

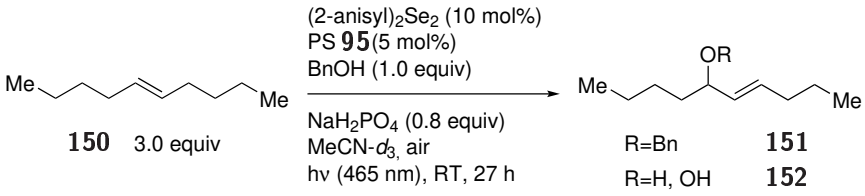
entry	R	ratio product to solvent[a]
1[b]	Ph	-
2	Ph	0.10 to 1
3	2-anisyl	0.22:1

[a] Yields not determined. [b] BnOH as the solvent, no base.

An important observation in the last reactions was the formation of benzaldehyde as a side product. In order to avoid the loss of nucleophile by oxidation, the ratio of alkene and benzyl alcohol was reversed, so that the excess of alkene would lead to preferred attack of the alcohol. Unfortunately, in the reaction of benzyl alcohol with 3 equiv 5-decene (**150**) with 10 mol% (2-anisyl)$_2$Se$_2$, 5 mol% *p*-MeO-TPT and 0.8 equiv NaH_2PO_4, only traces of product **151** were formed, but 15% of the alkene underwent a SCHENK-ene reaction to the allyl alcohol or the allylic hydroperoxide **152** (Table 3.13, entry 1). The formation of the target product **151** could be achieved in 14% when no base was added to the reaction mixture, but still 15% of the side product was formed (Table 3.13, entry 2).

Since the functionalization of a simple alkene proved challenging due to overoxidation of either the substrate or the nucleophile, further investigations focused again on alkenes that contained electron-withdrawing groups. However, it was concluded that the reaction proceeded more efficiently with catalyst (2-anisyl)$_2$Se$_2$ and without a base.

Table 3.13: Influence of base on the intermolecular etherification of 5-*trans*-decen.

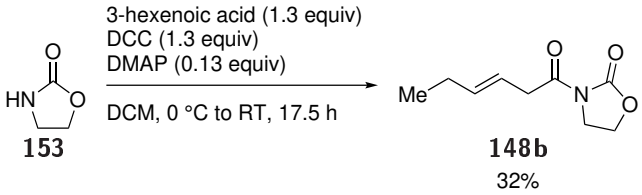


entry	yield ether **151**[a]	yield product **152**[b]
1	traces	19%
2[c]	14%	15%

[a] NMR yield based on BnOH with internal standard TCE. [b] NMR yield based on 5-decene with internal standard TCE. [c] No base was used.

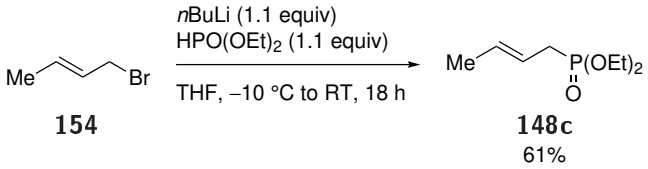
3.1.4 Intermolecular etherification - Synthesis and etherification of alkenes

For the evaluation of the scope and limitations of the intermolecular etherification, two additional substrates were synthesized according to literature procedures. Imide **148b** was obtained in 32% in a reaction of 2-oxazolidinone (**153**) with 3-hexenoic acid (1.3 equiv), using DCC (1.31 equiv) and DMAP (0.13 equiv) as coupling reagents (Equation 3.10).[63]



(3.10)

The reaction of (*E*)-crotylbromide (**154**) with 1.1 equiv *n*BuLi and 1.1 equiv diethyl phosphite afforded phosphonate **148c** in 61% yield (Equation 3.11).[140] The success of the reaction was confirmed by ^{31}P NMR by the shift of the phosphorus signal from 7.27 ppm to 28.1 ppm and by the additional coupling of the protons to the phosphorus in ^{1}H NMR (e.g., the coupling of the CH_2 group at 2.52 ppm, $^{2}J_{HP} = 21.4$ Hz).[141]

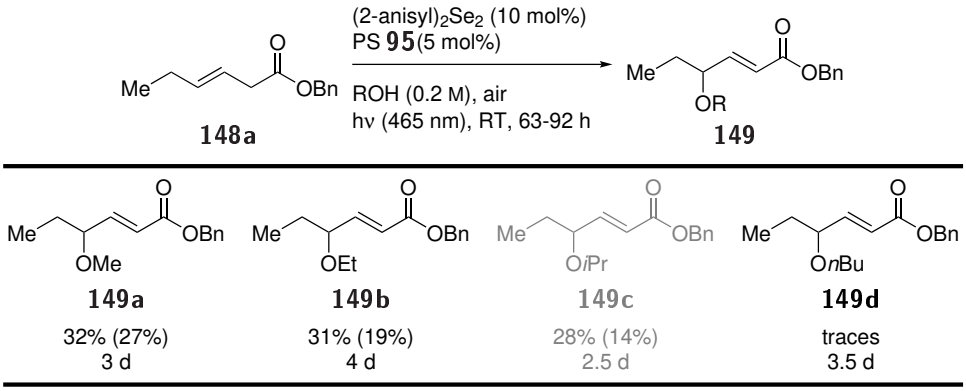


(3.11)

With the substrates in hand, the reactions with alcohols of different carbon chain length were tested using 10 mol% of (2-anisyl)$_2$Se$_2$ and 5 mol% of *p*-MeO-TPT under irradiation with blue light with the respective alcohol as the solvent. The functionalization of benzyl ester **148a** in methanol, ethanol and isopropanol afforded the respective ethers **149a**–**c** in similar yields of 28 to 32% (Table 3.14; grayed product **149c** synthesized by R. Rieger).[134,142] With *n*-butanol, only

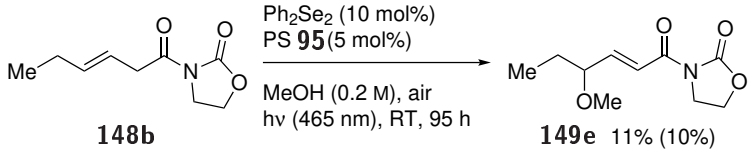
traces of product formation and later decomposition of the substrate was observed. The reactions were run until completion was determined *via* NMR or TLC, which often took several days. The same observation was made by IWAOKA and TOMODA, whose oxyfunctionalization of 5-decene ran for 7 days (cf. Equation 1.12, Subsection 1.2.2).[74]

Table 3.14: Synthesis of allylic ethers **149a–d**.[a] Grayed product **149c** was synthesized by R. Rieger.[134,142]



[a] NMR yield with standard TCE or TMB, isolated yield in brackets.

Unfortunately, imide **148b** proved to be less reactive under the established conditions than ester **148a**. Therefore, the reaction was conducted with diphenyl diselenide (10 mol%) as the catalyst instead. After 4 days, ether **149e** was obtained in 11% NMR yield (10% isolated yield) (Equation 3.12). Similar to ethers **149a–c**, the change of the signals of the double bond protons in NMR from multiplets around 5.6 ppm to the characteristic doublets of doublets at 7.36 and 6.96 ppm along with a singlet at 3.32 ppm with the integral 3 from the methoxy group indicated the product formation.

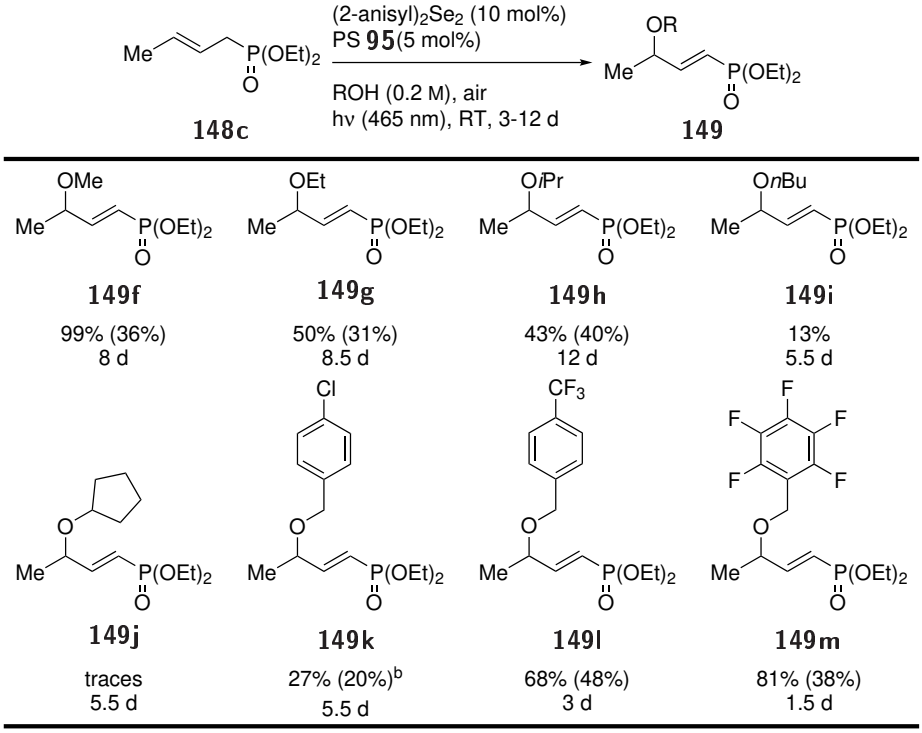


(3.12)

In contrast to imide **148b**, phosphonate **148c** turned out to be a high-yielding substrate for the intermolecular etherification. The functionalization with simple alcohols methanol, ethanol and isopropanol afforded ethers **149f–h** in good to excellent NMR yields of 43 to 99%, functionalization with benzyl alcohol derivatives led to yields between 27 and 81% (products **149k–m**, Table 3.15). The occasionally high difference between NMR yields and isolated yields (e.g. for products **149f** and **149m**) resulted from difficulties during chromatographic purification due to the high polarity of both products and starting materials. The progress of the reactions was determined *via* ^{31}P NMR because the signal of the phosphorus atom was shifted to high field from 28.1 ppm in the alkene to around 18 ppm in the products. The yields of ethers **149f–h** were decreasing with increasing carbon chain length of the alcohol, which is confirmed by the results with *n*-

butanol (13%) and cyclopentanol (traces), where the reactions stagnated after 5.5 days (**149i,j**). This trend could be attributed to a lower reactivity of longer-chained alcohols, leading to longer reaction times. At first glance, the results with benzyl ester **148a** and methanol, ethanol and isopropanol contradict these assumptions, because they do not show decreasing yields, although the reaction with *n*-butanol afforded only traces of the desired product. While the reactions with ester **148a** showed complete conversion (caused by reaction to the product or by oxidative decomposition) after 3-4 days, the reactions with phosphonate **148c** needed more than twice this time for full conversion but also afforded higher yields of the products. A possible explanation for these findings is the different susceptibility of the substrates to oxidation which leads to a high amount of the ester being oxidized before the reaction can occur. The phosphonate seems to be less prone to oxidation, being available for the functionalization with isopropanol for as long as 12 days. The reaction times were shorter (up to 5.5 days) with electron-poor benzyl alcohol derivatives, which we attributed to them being more easily deprotonated by side products of the oxidation cycle, which would increase their nucleophilicity. The reaction with 4-chlorobenzyl alcohol had to be conducted in MeCN due to the alcohol being a solid. The lower yield from this reaction, compared to the other benzyl alcohol derivatives, was attributed to the lower amount of alcohol used (1.5 equiv vs. >10-fold excess with the alcohol as the solvent). Due to the high

Table 3.15: Synthesis of allylic ethers **149f–m**.[a][134]

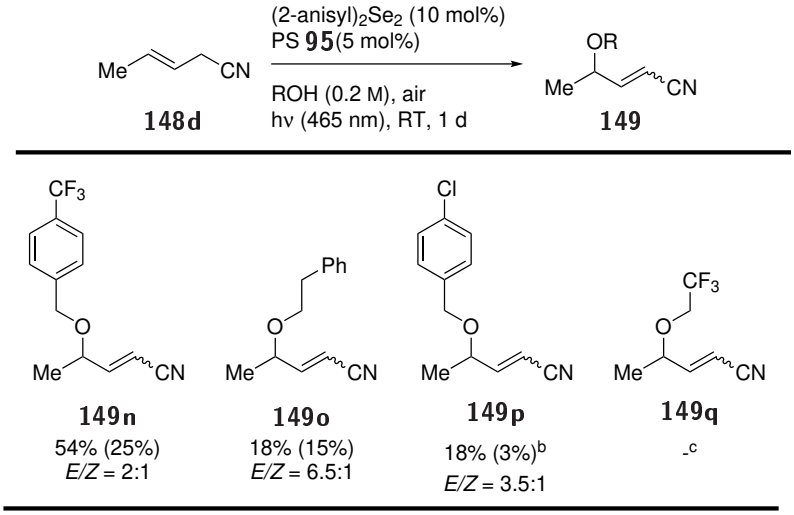


[a] NMR yield with standard TCE, TMB, phthalide or benzaldehyde, isolated yield in brackets. [b] Reaction in MeCN (0.4 M), 1.5 equiv ROH.

polarity of the products, the isolated yields sometimes differ from the NMR yields because of difficulties in the separation from the alcohols.

Being intrigued by the results with phosphonate **148c**, the reactivity of a nitrile was examined with commercially available 3-pentenenitrile (**148d**). Under the established conditions, ethers **149n–p** were obtained in 18 to 54% yield (Table 3.16). Interestingly, in contrast to the previous products, not only the (*E*)-configured ethers were obtained, but in all cases, also significant amounts of the (*Z*)-configured product were formed. A possible explanation is the smaller steric bulk of the nitrile moiety compared to the phosphonate, the imide and the ester group. While the ^{1}H NMR shifts of the double bond protons are similar for both isomers (6.3-6.7 ppm and 5.4-5.6 ppm), the carbinol proton has a shift of 4.0 ppm in the (*E*)-isomer and a shift of 4.5 ppm in the (*Z*)-isomer. Furthermore, the reactions showed complete conversion after 1 day, which could be attributed to fast oxidation of the substrate. While the use of 4-(trifluoromethyl)benzyl alcohol led to a good yield, probably due to the higher nucleophilicity, the reactions with 2-phenylethanol and 4-chlorobenzyl alcohol afforded the products in lower yields. In the latter case, the lower amount of alcohol (1.5 equiv) could be the reason. In the experiment with trifluoroethanol, the desired product was not obtained. Instead, a mixture of the (*E*) and the (*Z*)-configured allylic alcohols **155** (ratio 3.5:1) was isolated. This conclusion was based on the appearance of two doublets at 1.95 and 1.37 ppm (J = ~4 Hz), that were attributed to the O−H protons, and the appearance of the carbinol proton as a doublet of doublets of doublets of a quartet at 4.48 ppm (J = 8.7, 6.7, 4.5, 2.3 Hz) and a multiplet at 4.81 ppm (Figure 3.4). The matching coupling constant of 4.5 ppm and the roof effect of the doublets in question supported this assumption.

Table 3.16: Synthesis of allylic ethers **149n–q**.[a][134]



[a] NMR yield with standard TCE or TMB, isolated yield in brackets. [b] Reaction in MeCN (0.4 M), 1.5 equiv ROH. [c] (*E*/*Z*) mixture (3.5:1) of the respective allyl alcohol was isolated.

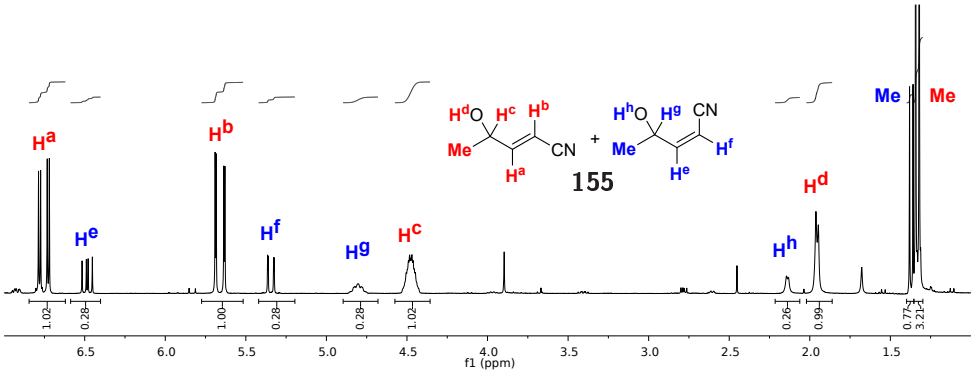
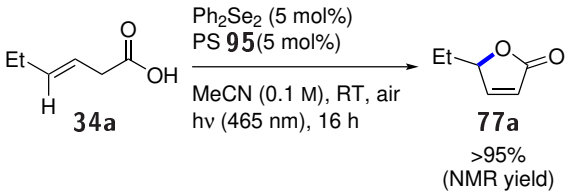


Figure 3.4: ^{1}H NMR spectrum of assumed allyl alcohols **155**.

3.2 Lactonization of unsaturated acids *via* photo-aerobic selenium-π-acid catalysis

After the successful application of the dual selenium-π-acid/photoredox catalysis in the intermolecular acyloxylation[91] and in the etherification,[134] it was speculated that the lactonization of unsaturated acids could also be accomplished with this method. Due to lactones being an important group of natural products with different biological activities, various synthetic methods for their preparation have been developed, amongst others selenium-catalyzed variants.[76,82,83,89,90,143] Compared to these methods, the selenium/photoredox catalysis would have the advantage of a high atom economy through consequential prevention of waste from the used oxidants, as air would be the terminal oxidant and water the sole co-product. The examination and optimization of the lactonization of 3-hexenoic acid (**34a**) under selenium/photoredox conditions was performed by R. Rieger.[137,144] He was able to obtain lactone **77a** in >95% NMR yield using 5 mol% diphenyl diselenide and 5 mol% *p*-MeO-TPT in MeCN (0.1 M) under air and irradiation with blue light (465 nm). A lower loading of the diselenide or the photosensitizer resulted in lower yields. In toluene or ethereal solvents such as THF or 1,4-dioxane, no product formation was observed, probably due to low solubility of the photosensitizer in these solvents. Using acetone or DCE led to good and very good yields, respectively, but both did not reach the level of product formation observed with MeCN.



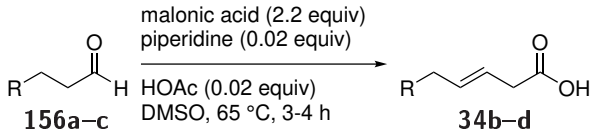
(3.13)

3.2.1 Synthesis of unsaturated acids

With the optimized reaction conditions in hand, the synthesis of unsaturated acids was pursued. In addition to the formation of butenolides **77** from 3-alkenoic acids **34**, the formation of 6- and 7-membered ring lactones was to be examined by using 4-, 5- or 6-alkenoic acids. The DOEBNER-type KNOEVENAGEL reaction was identified as an easy way to obtain β,γ-unsaturated acids from aldehydes. In order to examine the applicability of aromatic substrates in the selenium-catalyzed lactonization, 3-arylpropanal derivatives **156a** and **156b** were transformed to acids **34b** and **34c** in 28 and 43% yield using 2.2 equiv malonic acid and 0.02 equiv piperidine and acetic acid, respectively (Table 3.17, entries 1 and 2). The success of the reaction was visible *via* the appearance of two signals for the newly formed double bond in the ^{1}H NMR spectrum, two doublets of triplets of triplets at around 5.6 and 5.75 ppm with couplings of approx. 15, 6.5 and 1.0 Hz. Other characteristic signals are the doublets at around 3.1 and 3.4 ppm, which are caused by the methylene groups next to the double bond. With aldehyde **156c**, no reaction occurred

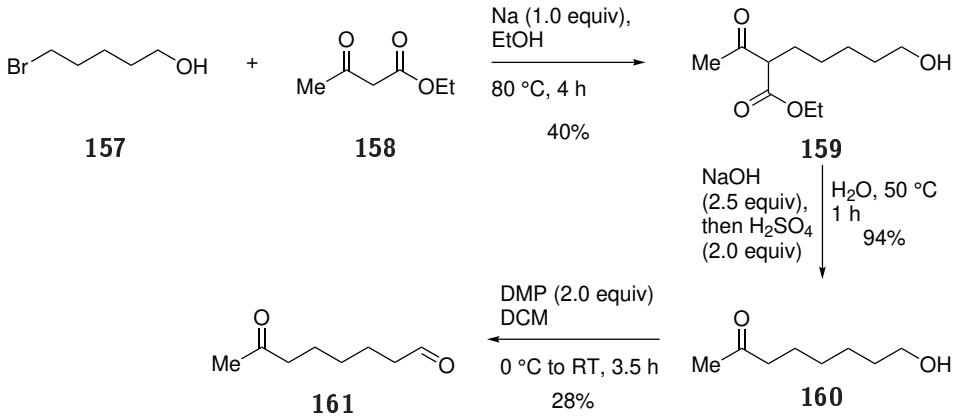
and only the starting material was observed in the ^{1}H NMR spectrum of the crude reaction, a very characteristic signal being the triplet of the aldehyde proton at 9.7 ppm.

Table 3.17: Synthesis of carboxylic acids **34b–d**.[144]



entry	substrate	R	product	yield
1	**156a**	Ph	**34b**	28%
2	**156b**	4-MeO-C_6H_4	**34c**	43%
3	**156c**	BnO	**34d**	nr

In addition to aromatic substrates, it was interesting to find out if ketones and aldehydes would react under photocatalytic conditions. Therefore, the synthesis of a ketone-containing acid was conducted following a procedure of Castellano *et al.*[145] In order to obtain 7-oxooctanal (**161**) for a Knoevenagel reaction, 5-bromopentanol (**157**) was transformed to β-keto ester **159** in 40% yield by coupling it to ethyl acetoacetate (**158**) using 1.0 equiv NaOEt (Scheme 3.2). The hydrolysis of the ethyl ester with aq. NaOH (2.5 equiv), followed by the decarboxylation with aq. H_2SO_4 (2.0 equiv) gave ketone **160** in 94% yield. Aldehyde **161** was obtained in 28% yield after a Dess-Martin oxidation using 2.0 equiv Dess-Martin periodinane.[146]



Scheme 3.2: Synthesis of 7-oxooctanal (**161**).[145]

In order to selectively synthesize the β,γ-unsaturated acid, a procedure of List and coworkers was applied to the aldehyde.[147] The Knoevenagel reaction proceeded with 1.0 equiv malonic acid and 0.1 equiv DMAP and provided the β,γ-unsaturated acid **34e** in a 1.5:1 mixture with the α,β-unsaturated acid **162** in 23% yield (Figure 3.5, top). The ratio of the products was determined in ^{1}H NMR spectroscopy by comparison of the signals of the protons of the double bond. The α,β-unsaturated acid **162** shows two doublets of triplets at 7.04 and 5.80 ppm with an identical integral (Figure 3.5, bottom). They have coupling constants of 15.6 and 7.0 Hz, and

15.6 and 1.5 Hz, respectively. The protons at the double bond of the β,γ-unsaturated acid **34e** have only one multiplet signal at 5.68-5.40 ppm.

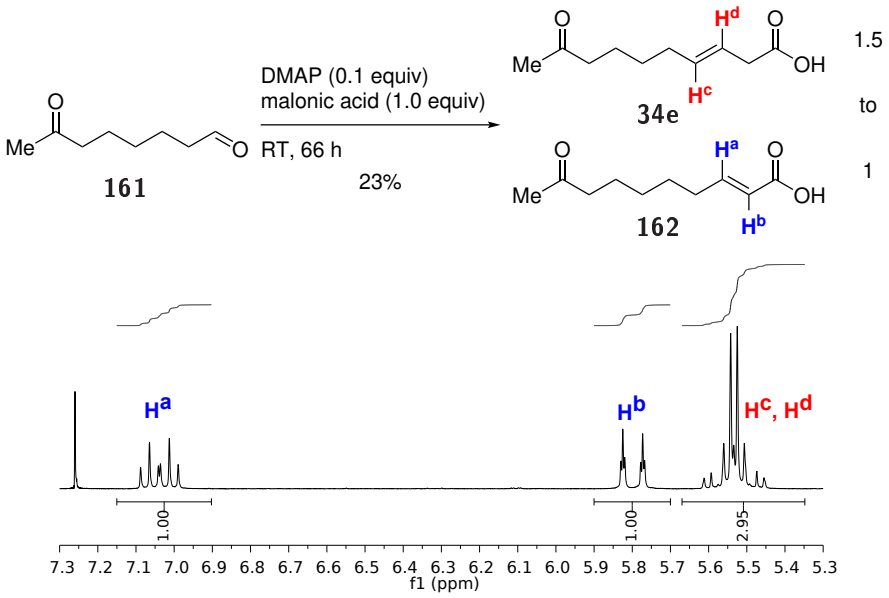
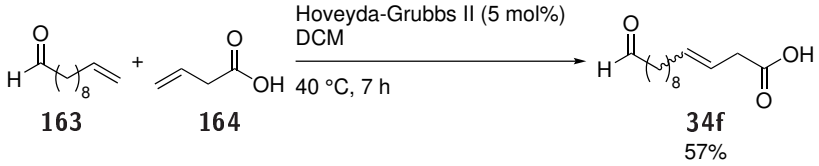


Figure 3.5: KNOEVENAGEL reaction of aldehyde **161** (top), extract from the ^{1}H NMR spectrum of the mixture of **34e** and **162** (bottom).

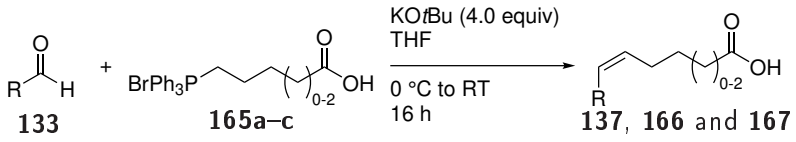
For the synthesis of the aldehyde substrate, the KNOEVENAGEL reaction was not an option, as it uses an aldehyde as the starting material and a second aldehyde moiety could lead to selectivity problems. In order to avoid the introduction and removal of protecting groups, a step-economic cross-metathesis reaction was used. Acid **34f** was obtained in 57% yield from the reaction of 10-undecenyl aldehyde (**163**, 3.0 equiv) and 4-butenoic acid (**164**, 1.0 equiv) using 5 mol% 2nd generation Hoveyda-Grubbs catalyst (Equation 3.14).

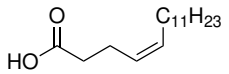
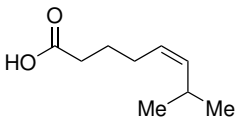
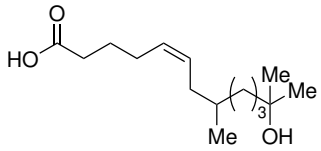
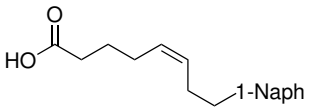
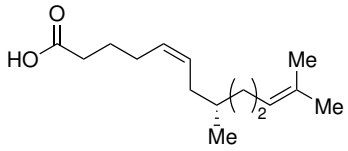
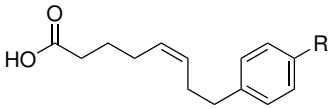
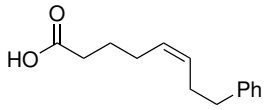
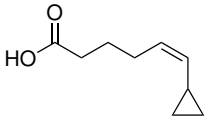
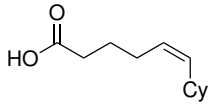
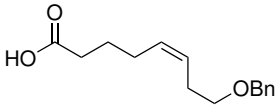
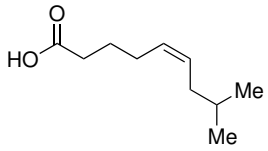
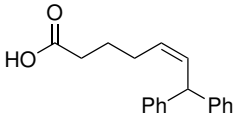
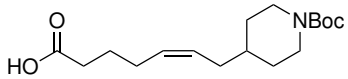
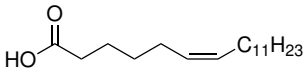


(3.14)

The synthesis of 5-alkenoic acids *via* a WITTIG reaction was already performed during the synthesis of unsaturated alcohols (see Subsection 3.1.2). Therefore, alkenoic acids **137**, **166** and **167** were synthesized according to the established procedure using 2.0 equiv of either (3-carboxypropyl)-triphenylphosphoniumbromide, (4-carboxybutyl)triphenylphosphoniumbromide or (5-carboxypentyl)triphenylphosphoniumbromide (**138a–c**) and KO*t*Bu (4.0 equiv) as the base in THF at 0 °C (Table 3.18; products with yields in gray were synthesized by L. Löffler and Dr. S. Ortgies).[144,148,149] The acids were obtained in moderate to excellent yields of 37-92%. The lowest yield of 12% was obtained for ether **137t**. No reaction occurred with diphenylacetaldehyde (product **137u**).

Table 3.18: WITTIG reaction of aldehydes **133** to carboxylic acids **137**, **166** and **167**. Acids with yield in gray synthesized by L. Löffler and Dr. S. Ortgies.[144,148,149]



	**166**	37%		**137l**	71%
	**137a**	79%		**137m**	47%
	**137b**	79%		R = *t*Bu **137n** 92% R = CF_3 **137o** 58% R = F **137p** 7% (2 steps) R = CN **137q** 51% R = OMe **137r** 75%	
	**137c**	82%		**137s**	55% *Z*/*E* 7:1
	**137d**	74%		**137t**	12%
	**137e**	60%		**137u**	nr
	**137g**	42%		**167**	82%

For all of the synthesized acids, the configuration of the double bond could not be determined by the coupling constants of the double bond protons in ^{1}H NMR. Instead, substrate **137l** was examined in 2D-NMR spectroscopy. All signals were assigned to the protons by COSY. In the NOESY spectrum, a coupling of the CH_2 group **c** to the $CHMe_2$ group **a** was observed. This coupling would not be possible if the molecule was in (*E*)-configuration (Figure 3.6). To further support these findings, analytical data of acid **167** were compared to those of petroselinic acid, which is the same molecule with the double bond in (*Z*)-configuration. The data were in

agreement with each other, meaning acid **167** is in fact petroselinic acid. From this evidence, it was concluded that in all cases, the WITTIG reaction was selective for the (*Z*)-alkene.

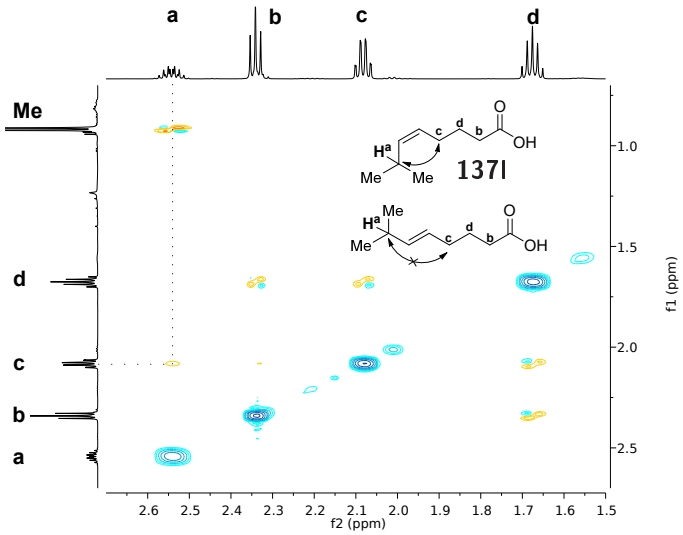
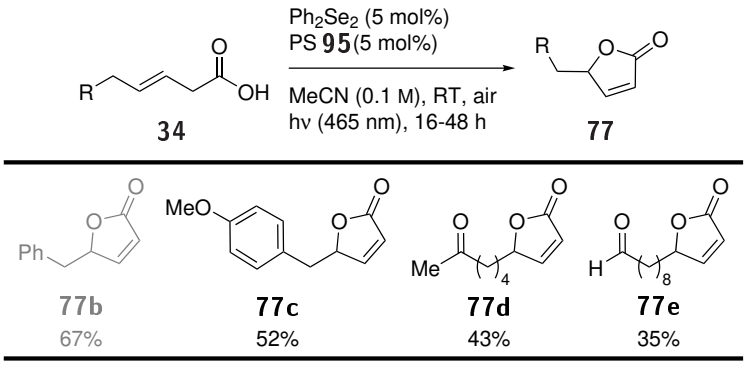


Figure 3.6: NOESY spectrum of unsaturated acid **137l**.

3.2.2 Lactonization of unsaturated acids

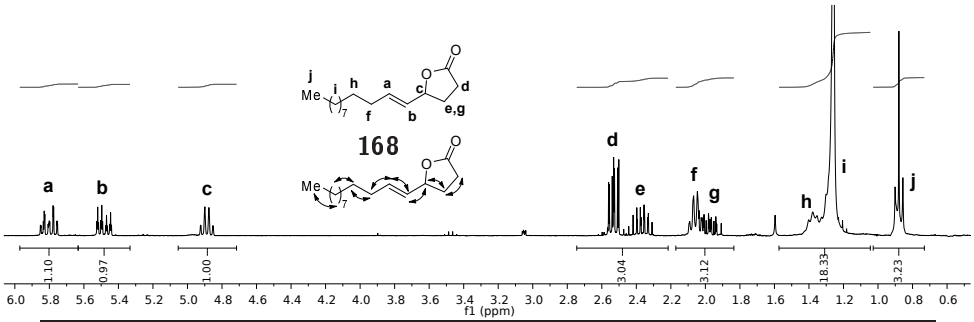
The lactonization of 3-alkenoic acids **34** was performed under the established conditions with 5 mol% diphenyl diselenide and photosensitizer **95**, respectively, in acetonitrile at room temperature under air for 16 h and under irradiation with blue light.[137] Butenolides **77b–e** were obtained with 35-67% yield (Table 3.19; grayed product **77b** was synthesized by R. Rieger).[137,144] The products were identified by their NMR signals. The protons of the double bond are a doublet of doublet of triplets at 6.1 ppm and a doublet of doublets at 7.4 ppm and show only a small coupling to each other (J = 5.7 Hz), which can be justified by the (*Z*)-configuration needed in the ring. The protons of the double bond in the unsaturated acid had signals between 5.4 and 5.9 ppm. The changes are also visible in the ^{13}C spectrum, where the former double bond

Table 3.19: Synthesis of lactones **77**. Grayed product **77b** synthesized by R. Rieger.[137,144]



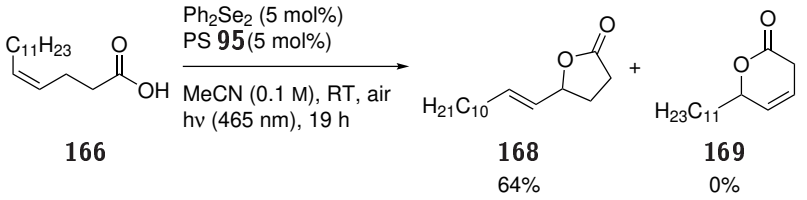
had two signals at 120 and 135 ppm and the signals of the new double bond are at 121 and 156 ppm. Additionally, the carbinol proton and carbon show a shift to low field and have signals at around 5 ppm (proton) and 83 ppm (carbon). Lactones **77b** and **77c** with aromatic groups were obtained in good yields of 52 and 67%, which is similar to the yield that was obtained in the intramolecular etherification (cf. Table 3.9 in Subsection 3.1.2, **127d**). Gratifyingly, ketone **34e** and aldehyde **34f** were also reactive under the photoredox conditions and afforded products **77d** and **77e** in moderate yields of 35 and 43%. In the intramolecular etherification, the use of an aldehyde led to only low yield (cf. Table 3.9 in Subsection 3.1.2, **127l**).
In the lactonization of 4-alkenoic acid **166**, there is the possibility of a 5-*exo-trig*-cyclization or a 6-*endo-trig*-cyclization. Under the standard conditions, the formation of a product was observed in a good yield of 64% (Equation 3.15). The constitution and configuration of the molecule were deduced from the signals in ^{1}H NMR and the COSY couplings (Table 3.20). The coupling constants of the double bond protons with signals at 5.80 ppm (dtd, J = 15.3, 6.6, 1.0 Hz) and 5.48 ppm (ddt, J = 15.3, 7.1, 1.5 Hz) indicate an (*E*)-configuration. This hints already at the *exo*-product, since the *endo*-product needs a (*Z*)-configured double bond because of the ring geometry. Furthermore, in COSY it was visible that the double bond protons **a** and **b** couple to the carbinol proton **c** at 4.89 ppm, but also to the CH_2 group **f**. In the 6-membered ring lactone **169**, this would be the CH_2 group next to the carbonyl moiety, which would have no further coupling partners. However, protons **f** couple to the alkyl chain (**h** and **i**), revealing that indeed,

Table 3.20: Assignment of ^{1}H NMR signals of lactone **168** and COSY couplings.



proton	coupling partner
a (5.80 ppm)	b (5.48 ppm), f (2.0 ppm)
b (5.48 ppm)	a (5.80 ppm), c (4.89 ppm)
c (4.89 ppm)	b (5.48 ppm), e (2.36 ppm), g (1.99 ppm)
d (2.54, 2.52 ppm)	e (2.36 ppm), g (1.99 ppm)
e (2.36 ppm)	c (4.89 ppm), d (2.54, 2.52 ppm), g (1.99 ppm)
f (2.0 ppm)	a (5.80 ppm), h (1.4 ppm)
g (1.99 ppm)	c (4.89 ppm), d (2.54, 2.52 ppm), e (2.36 ppm)
h (1.4 ppm)	f (2.0 ppm), i (1.2-1.3 ppm)
i (1.2-1.3 ppm)	h (1.4 ppm), j (0.88 ppm)
j (0.88 ppm)	i (1.2-1.3 ppm)

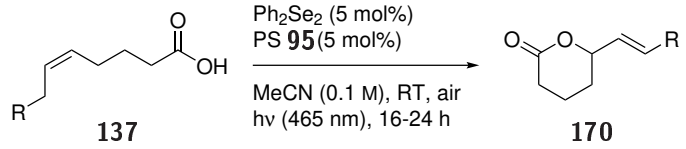
the 5-membered ring product **168** was formed. The signals **d**, **e** and **g** at 2.54, 2.52, 2.36 and 1.99 ppm with a combined integral of four were assigned to the methylene groups in the lactone ring, as **e** and **g** both couple to carbinol **c**. The multiplets **h** and **i** at 1.49-1.15 ppm belong to the alkyl chain and the triplet at 0.88 ppm (**j**) to the methyl group.

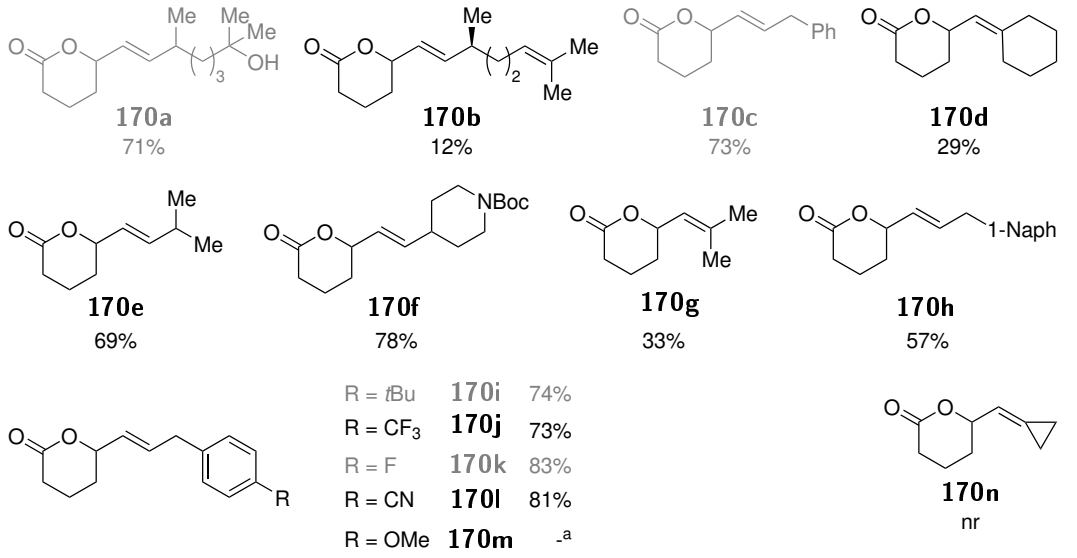


(3.15)

The lactonization of δ,ε-unsaturated acids **137** under the same conditions led to the formation of six-membered ring lactones with an exocyclic double bond (Table 3.21; grayed products were synthesized by L. Löffler, Dr. S. Ortgies and R. Rieger).[137,144,148,149] This was visible from similar aspects of the ^{1}H NMR spectrum as for lactone **168**. The protons at the double bond show two characteristic multiplets at around 5.5 and 5.7 ppm that couple with each other with a coupling constant of approx. 15 Hz. The proton in the carbinol position can be found in the spectra as a doublet of doublets of doublets of doublets at around 4.7 ppm. It couples with the

Table 3.21: Lactonization of acids **137**. Grayed products synthesized by L. Löffler, Dr. S. Ortgies and R. Rieger.[137,144,148,149]

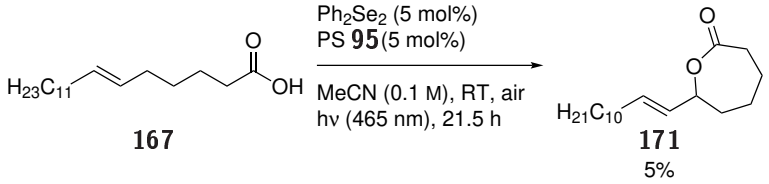




[a] Decomposition of the starting material.

two protons at the double bond and the two protons in the adjacent CH_2-group. The signals of the CH_2 groups in the lactone ring are multiplets between 1.5 and 2.7 ppm. The reactions proceeded with yields between 12 and 81%. The functional group tolerance is comparable to that observed in the formation of tetrahydropyrans (cf. Table 3.10 in Subsection 3.1.2). Lactones **170a** and **170e** were obtained in good yields of 71 and 69%. The formation of lactone **170b** proceeded only with a low yield of 12%, probably due to side reactions of the additional double bond. Similarly, the formation of lactones with trisubstituted double bonds was impaired and products **170d** and **170g** were formed in 29 and 33% yield, while the cyclopropyl-substituted acid **137s** did not react at all. Aryl moieties were well tolerated and products **170c**,**h**–**l** were obtained in very good yields of 73-81%, an exception being methoxy-substituted lactone **170m**, which decomposed under the applied conditions. In contrast to the intramolecular etherification, piperidine derivative **137g** reacted in a high yield of 78% to the respective lactone **170f**.

As the formation of 5- and 6-membered ring lactones proceeded smoothly under selenium/photoredox catalysis, the possible reaction of petroselinic acid (**167**) in a 7-*exo*-*trig*-cyclization was examined. Indeed, the subjection of the acid to the established conditions led to the formation of 7-membered ring lactone **171**, albeit in 5% yield (Equation 3.16). The configuration of the double bond was determined to be (*E*) by the coupling constant of 15.4 Hz of the two protons at 5.74 and 5.53 ppm, which suggested again an exocyclic double bond. The signal of the carbinol proton, a doublet of doublets at 4.70 ppm, has a similar shift as in the 5- and 6-membered ring lactones.



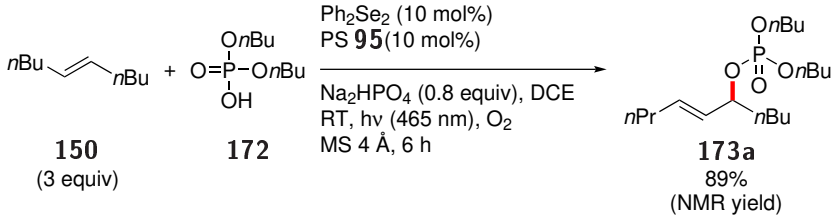
167 **171** 5% (3.16)

3.3 Photo-aerobic selenium-π-acid catalysed phosphatation of alkenes

After the successful use of acids and alcohols as exogenous nucleophiles in selenium-π-acid-catalyzed reactions, the question came up if other oxygen nucleophiles could be applied as well. Phosphoric acids came to mind, as their acidity is comparable to that of carboxylic acids, which suggests the feasibility of the reaction.[150]

Phosphate esters have several biological, synthetical and industrial applications, e.g. they are found in the DNA, as phospholipids in cell membranes and in the ATP-based energy transfer of organisms, they serve as chiral brønsted acid catalysts and substrates in cross-coupling reactions, and they are used in flame retardants and plastisizers.[151–155] Previous methods for their synthesis needed prefunctionalized or preactivated reagents, such as alcohols or phosphoric acid chlorides, and the synthesis *via* selenium-π-acid-catalysis was unprecedented at the outset of this project.[156,157]

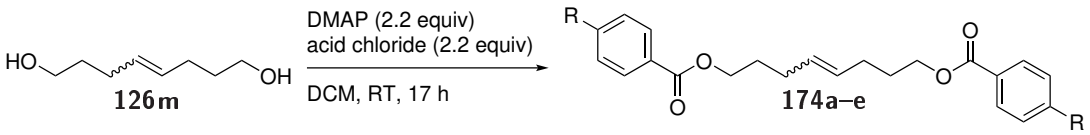
Therefore, the direct phosphatation of alkenes with phosphoric acids under photo-aerobic selenium-π-acid catalysis was investigated by our group. C. Depken and R. Rieger were able to optimize conditions for the functionalization of *trans*-dec-5-ene (**150**) with dibutyl phosphate (**172**). The use of the alkene in an excess of 3.0 equiv, 10 mol% of diphenyl diselenide and *p*-MeO-TPT (**95**), respectively, 4 Å MS and 0.8 equiv Na_2HPO_4 in DCE under irradiation at 465 nm and an oxygen atmosphere led to the formation of phosphate **173a** in 89% yield (Equation 3.17).[142,158,159] When MeCN was used as the solvent, the phosphate was still obtained in a good yield of 81%, other solvents led to low or moderate yields. With excess of the phosphate or the base, lower yields were achieved. The reaction only proceeded with Na_2HPO_4, $NaHCO_3$ or KF, other carbonate or fluoride bases did not lead to product formation.



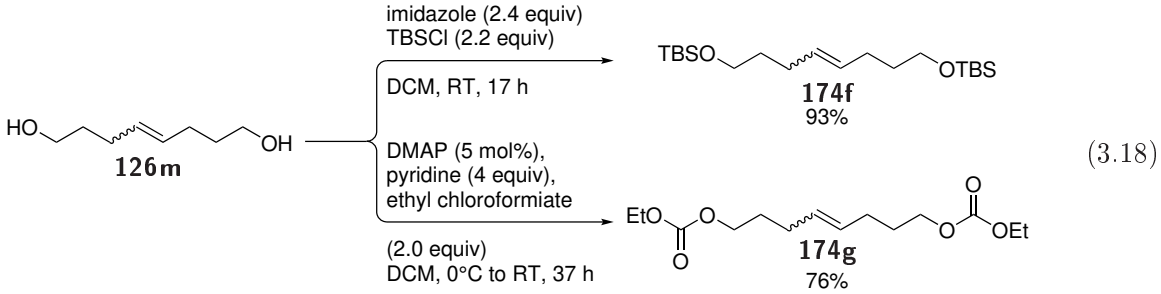
(3.17)

The reaction of *trans*-dec-5-ene (**150**) with different phosphates was examined by C. Depken and F. Krätzschmar.[158–160] In order to evaluate the reactivity of different alkenes, a series of symmetric olefins was to be synthesized. For this purpose, oct-4-ene-1,8-diol (**126m**) was functionalized with different groups. First, diesters **174a–e** were synthesized in yields between 89 and >99% by performing an esterification of diol **126m** with 2.2 equiv of benzoic acid chlorides and 2.2 equiv DMAP (Table 3.22). Additionally, the two hydroxy groups of diol **126m** were transformed into silyl ether or carbonate groups to obtain alkenes **174f** and **174g**. The reactions with TBSCl (2.2 equiv) or ethyl chloroformiate (2.0 equiv) afforded the products in 93 and 76% yield, respectively (Equation 3.18).[161]

Table 3.22: Esterification of diol **126m**.

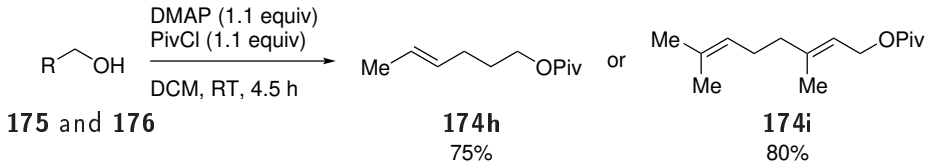


entry	R	product	yield
1	CF_3	**174a**	89%
2	NO_2	**174b**	>99%
3	Br	**174c**	94%
4	CN	**174d**	95%
5	MeO	**174e**	91%



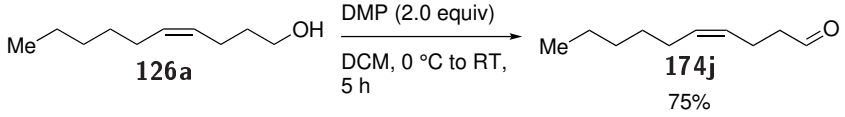
(3.18)

As further substrates, a number of unsymmetric alkenes were to be synthesized. For this purpose, three alcohols and one acid were functionalized in different ways. The pivalic acid esters of 4-hexene-1-ol (**175**) and geraniol (**176**) were formed with 1.1 equiv DMAP and 1.1 equiv pivalic acid chloride in 75% and 80% yield (Equation 3.19).

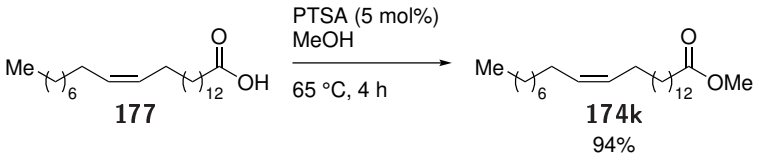


(3.19)

In order to examine the reactivity of an aldehyde in the selenium-catalyzed phosphatation reaction, (*Z*)-dec-4-en-1-ol (**126a**) was oxidized to aldehyde **174j** with 2.0 equiv DMP in 75% yield (Equation 3.20). Finally, the methyl ester of (*Z*)-15-tetracosenoic acid (**177**) was afforded in a reaction in MeOH with 5 mol% PTSA as a catalyst in 94% yield (Equation 3.21).



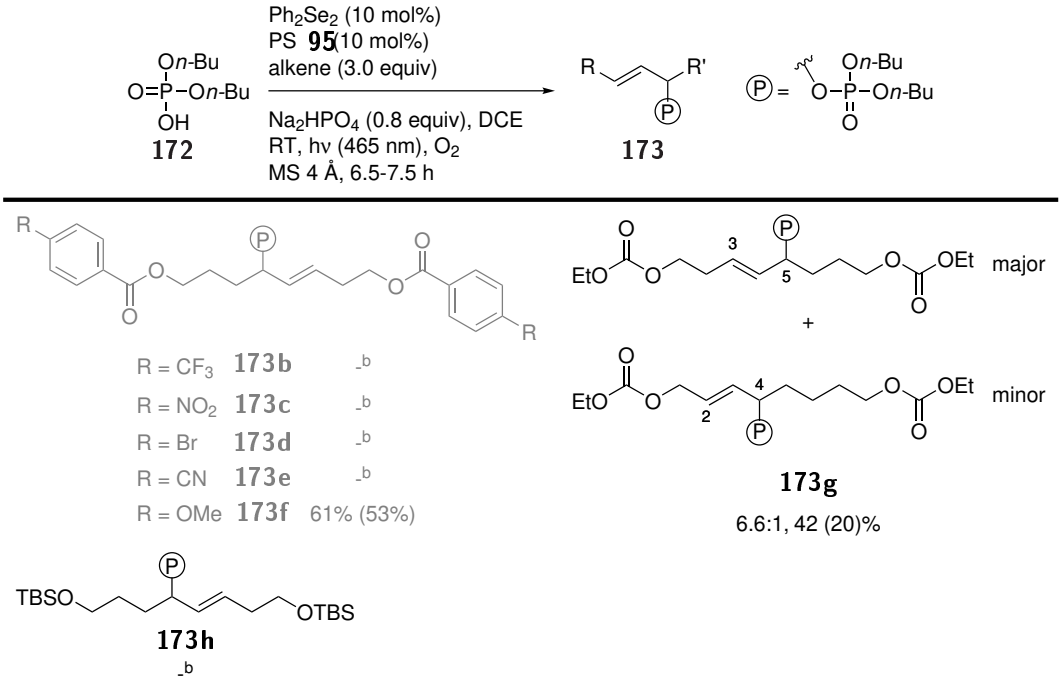
(3.20)



(3.21)

With the aforementioned substrates in hand, the phosphatation with dibutyl phosphate (**172**) was conducted under the established conditions using alkenes **174a**–**g** in an excess of 3.0 equiv, 10 mol% of diphenyl diselenide and *p*-MeO-TPT, respectively, 4 Å MS and 0.8 equiv Na_2HPO_4 in DCE under irradiation at 465 nm and an oxygen atmosphere (Table 3.23; reactions for products highlighted in gray were conducted by F. Krätzschmar and R. Rieger).[142,159,160] In the reactions with the benzoic acid esters, only methoxylated product **173f** was isolated in 53%, in the reactions of **174a**–**d**, decomposition of the starting material was observed.[142,159,160] The allylic phosphate was identified in ^{31}P NMR, where the phosphorus atom was shifted to higher field from 1.3 ppm in dibutyl phosphate to −1.42 ppm in the product. In the ^{1}H NMR spectrum, the double bond protons were shifted to lower field, compared to alkene **174e**, and appeared as a doublet of doublets of doublets at 5.84 ppm and a doublet of doublets of triplets at 5.63 ppm. The signal of the carbinol proton was a quintet at 4.80 ppm. The loss of symmetry of the product compared to the starting material was visible in the appearance of two singlets for the methoxy

Table 3.23: Phosphatation reactions of asymmetric alkenes **174**.[a] Reactions for products in gray conducted by F. Krätzschmar and R. Rieger.[142,159,160]



[a] NMR yields, standard: TMB or PPh_3, (isolated yields). [b] Decomposition.

groups at 3.86 and 3.83 ppm and two triplets for the CH_2O groups next to the ester units at 4.33 and 4.25 ppm. In the reaction of disilyl ether **174f**, the crude ^{31}P NMR spectrum showed two signals at −1.49 and −8.94 ppm. As the target products usually had a signal at around −1.4 ppm, the signal at −1.49 ppm probably belonged to the expected product, the signal at −8.49 ppm probably belonged to a side product that resulted from an attack of the phophorus at silicon. This assumption was supported by literature data of a TMS phosphite, where the signal in the ^{31}P NMR was at −7.70 ppm.[162] In the ^{1}H NMR spectrum, a complete shift of the signals of the TBS group from 0.90 and 0.05 ppm to 0.84 and 0.00 ppm was observed, indicating a complete consumption of the alkene by a side reaction. Unfortunately, none of the phosphate species was isolated due to problems in the chromatographic purification. A similar problem was observed in the intramolecular etherification when silylated alkene **126k** was used and the alcohol decomposed under the used conditions. Other silyl compounds seemed to tolerate the photoconditions better, as the intramolecular etherification of triisopropylsilyl ether **126p** afforded the product in 29%. Following this observation, F. Krätzschmar achieved the phosphatation of a triisopropylsilyl ether in 71% yield.[159,160] The reaction with carbonate **174g** led to the formation of an inseparable mixture of two products **173g** with the ratio of 6.6:1 in 42% yield, which was isolated in 20% yield. When the products were examined closely, the major product was identified as the expected product with the double bond in 3-position and the phosphate moiety in 5-position. Surprisingly, the minor product had the double bond in 2-position and the phosphate moiety in 4-position. The assignment of the structures was done by 1D and 2D-NMR spectroscopy and started from the signals of the carbinol protons at 4.73 (major product) and 4.83 ppm (minor product), which were assigned because of their chemical shift and by P,H-HMBC couplings (Figure 3.7). The ^{13}C NMR signals of the carbinol carbons were assigned by HSQC to be at 78 ppm. *Via* HMBC, the coupling of the carbinol moiety to the double bond and the sequential coupling to CH_2 groups was determined. For the major product, two methylene units were found to be between the double bond and the carbonate group. For the minor product, only one unit with a doublet at 4.62 ppm connected the double bond with the carbonate moiety. The position of the double bond of the side product was explained by the possible impureness of the used alkene. During the synthesis, the double bond could have partly isomerized from the 4-position to the 3-position which would lead to the formation of the minor product.

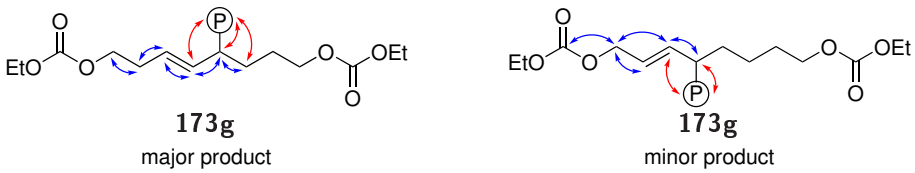
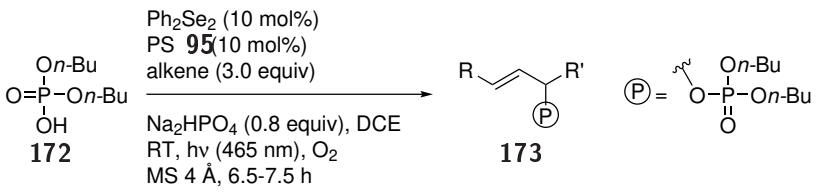
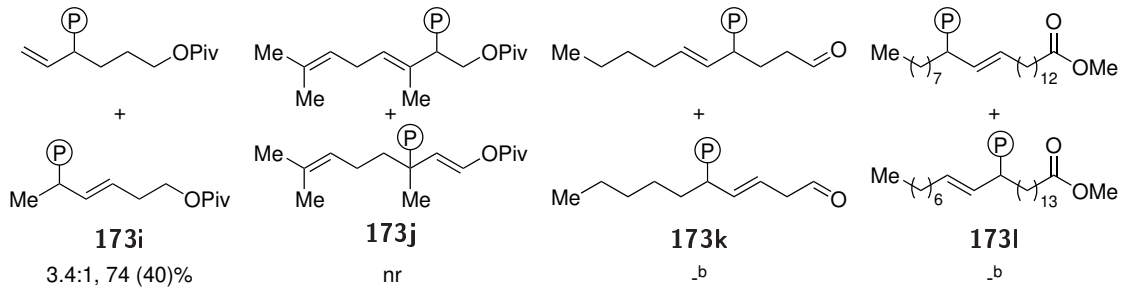


Figure 3.7: Selected H,C-HMBC (blue) and P,H-HMBC (red) couplings of product mixture **173g**.

During the phosphatation reactions of asymmetric alkenes **174h–k**, product formation was observed only with hexenol derivative **174h**. The inseparable mixture (3.4:1) of allylic phosphates **173i** was obtained in 74% yield. The major product was the terminal alkene, the minor product had an internal double bond. Their ratio was determined *via* the integrals of the double bond protons in ^{1}H NMR. The signals of the terminal alkene were a doublet of doublets of doublets at 5.82 ppm (J = 17.2, 10.4, 6.9 Hz), a doublet of triplets at 5.32 ppm (J = 17.2, 1.2 Hz) and a doublet of triplets at 5.22 ppm (J = 10.4, 1.1 Hz) with couplings to each other and the carbinol proton at 4.77 ppm. The internal alkene had two double bond signals at 5.70 ppm (dt, J = 15.5, 6.5 Hz) and 5.60 ppm (ddt, J = 15.5, 6.6, 1.2 Hz) that coupled with each other and the carbinol proton or the CH_2 group next to the double bond. The signal of the carbinol proton was a sextet at 4.88 ppm. The high multiplicity could be explained by the coupling to one of the double bond protons, the three protons of the methyl group and the coupling to the phosphorus atom. With geraniol derivative **174i**, only the starting material was observed after 8 h. A possible reason could be the trisubstitution of the double bonds, which could hinder the formation of the seleniranium ion. The attempted phosphatation of aldehyde **174j** did not occur, but the aldehyde was consumed in an unknown side reaction, which was visible by the disappearance of the aldehyde signal at 9.77 ppm in NMR. The functionalization of fatty acid ester **174k** was observed in ^{31}P NMR by the appearance of two singlets at −1.44 and −1.51 ppm which were attributed to two formed isomers. In ^{1}H NMR, a doublet of triplets at 5.61 ppm (J = 14.1, 6.6 Hz) and a quintet at 4.57 ppm (J = 7.0 Hz) indicated the formation of a product with an allylic functionalization. Unfortunately, only an allylic alcohol was isolated in 16% yield. For the pure compound, no signal appeared in ^{31}P NMR and in ^{1}H NMR, the signal of the carbinol proton was shifted to higher field and appeared as a quartet at 4.03 ppm, which is reminiscent of

Table 3.24: Phosphatation reactions of asymmetric alkenes **174**.[a][159]





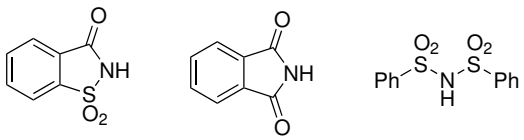
[a] NMR yield, standard: TMB, (isolated yields). [b] Decomposition.

the shift of the carbinol proton in allylic ethers **149**, which was typically between 3.5 and 4.5 ppm. The change of the multiplicity could be explained by phosphorus as the coupling partner in the phosphate and therefore one less coupling partner in the alcohol. The signals of the double bond did not suffer from a shift and appeared at 5.62 and 5.44 ppm. The formation of the alcohol was further confirmed with ESI mass spectrometry.

3.4 Investigations toward the selenium-catalyzed amination of olefins

3.4.1 Intermolecular light-driven amination

As the oxidative functionalization of alkenes with several exogenous oxygen nucleophiles was realized by our group using photo-aerobic selenium-π-acid catalysis, the application of this method in the functionalization of alkenes with exogenous nitrogen nucleophiles was examined.[91,134,144,159] In previous works, only the use of *N*-halogenated oxidants led to the formation of aminated products. However, the intermolecular nucleophiles in these reactions originated from the oxidant (with one exception; cf. Subsection 1.2.1).[63–67,69] Therefore, experiments on the light-driven amination of alkenes were conducted, using *cis*-cyclooctene (**181**) as a simple, unfunctionalized substrate. Saccharin (**182**) and phthalimide (**183**) were chosen as nucleophiles due to their easy availability and the potential transformation of the corresponding amidation products into amines (Figure 3.8). Furthermore, dibenzenesulfonimide (**184**) was used because the imidation with the corresponding *N*-fluorinated compound as an oxidant and nucleophile source worked well.[63]



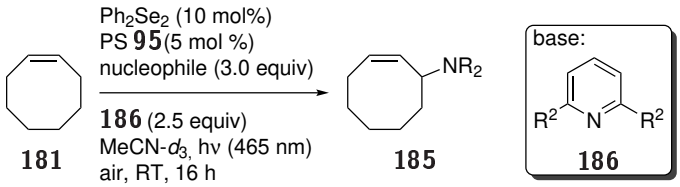
182 **183** **184**

Figure 3.8: Nucleophiles for the amination of olefins.

The reactions were carried out using 3.0 equiv of the respective nucleophile, 10 mol% of Ph_2Se_2 and 5 mol% of photocatalyst **95** in acetonitrile-d_3 (Table 3.25). In order to increase the nucleophilicity of the used amines, 2.5 equiv of pyridine derivatives **186** were used as a base. Under these conditions, only saccharin showed reactivity and the presumed amination product was isolated in 42% yield with pyridine as the base, in 32 and 15% yield when 2,6-dimethylpyridine or 2,6-di-*tert*-butylpyridine were used (Table 3.25, entries 1-3).

Further analysis of the isolated product of the reactions with saccharin showed that not only one, but two products had been formed. In mass spectrometry, both products contained the signals of the mass of the desired product, which led to the conclusion that the products were constitutional isomers. The ^{1}H NMR spectra of both isomers had two signals for the double bond protons at approx. 6.0 and 5.8 ppm and a signal with a shift for a proton in α-position to a heteroatom. These α-protons and the corresponding carbon atoms of the two products differed strongly in their chemical shift and the signals were at 5.21 ppm (^{1}H) and 52.2 ppm (^{13}C) for compound **185a** and at 5.64 ppm (^{1}H) and 81.2 ppm (^{13}C) for compound **185b** (Figure 3.9). Therefore, it was concluded that in both products, cyclooctene had been substituted in the allylic position by saccharin, but one of the products was the desired amination product, whereas the other was the result of the nucleophilic attack with the oxygen of the carbonyl moiety. It was assumed that the

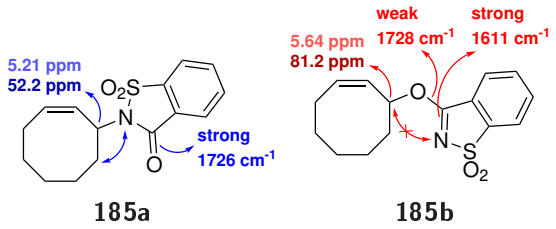
Table 3.25: Amination of cyclooctene (**181**) with different nucleophiles and bases.



181 **185** **186**

entry	Nu	R^2	yield
1	**182**	H	42%
2	**182**	Me	32%
3	**182**	*t*Bu	15%
4	**183**	H	nr
5	**183**	Me	nr
6	**183**	*t*Bu	nr
7	**184**	H	nr
8	**184**	Me	nr
9	**184**	*t*Bu	nr

product **185a** with the lower shift of the allylic proton was the desired amination product. To further support this hypothesis, an N,H-HMBC experiment was conducted for both products, which would show couplings between the nitrogen atom and protons over three bonds. In the nitrogen-substituted product, couplings are possible to one of the double bond protons and the CH_2 group in the homoallylic position. In the oxygen-substituted molecule, the protons are too far away for a coupling. Indeed, the spectrum of alkene **185a** showed a coupling between the nitrogen atom and the mentioned methylene group, whereas for alkene **185b**, no couplings were observed. The IR spectrum served as a final evidence. A strong signal at 1726 cm^{-1} for compound **185a** indicated a C=O bond, whereas for compound **185b**, only a weak signal at 1728 cm^{-1} was observed. Instead, a strong signal at 1611 cm^{-1} indicated an imine bond.



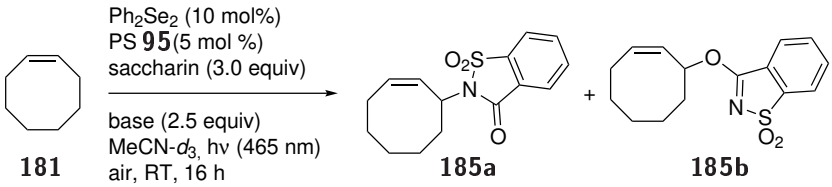
185a **185b**

Figure 3.9: Spectroscopic data used for the assignment of the structures of compounds **185a** and **185b**.

As saccharin was the only nucleophile that showed reactivity in the first experiments, the influence of different bases on the yield and selectivity of this reaction was examined. With most carbonate bases, no reaction occurred and the fluorescence of the photocatalyst was quenched (Table 3.26, entries 2-4). Only with $NaHCO_3$ products **185** were formed in 14% combined yield in a ratio of 1:1 (Table 3.26, entry 1). With fluoride bases KF, CsF and CaF_2, the products were obtained

in 5, 19 and 43% combined yield (Table 3.26, entries 5-7). While with KF and CsF, more of the oxygen-substitution product **185b** was formed, the ratio was 1:1 with CaF_2. Except for the reaction with CaF_2, the extinction of the fluorescence was observed. This observation was also made in similar experiments and was explained with the probable nucleophilic attack of fluoride ions on the photocatalyst **95**.[127] With phosphate bases, combined yields between 23 and 59% were obtained (Table 3.26, entries 8-11). Only with K_3PO_4, no product formation was observed and the fluorescence was quenched (Table 3.26, entry 12). The product ratios were all approx. 1:1, the highest yield was obtained with KH_2PO_4 as the base.

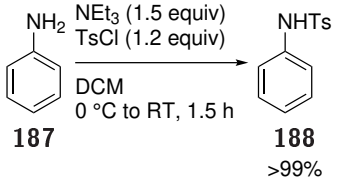
Table 3.26: Amination of cyclooctene (**181**) with saccharin and different bases.



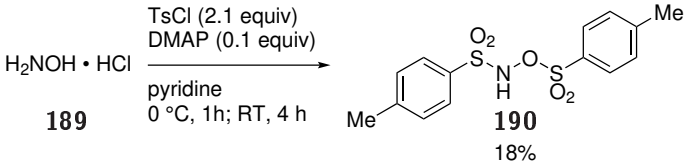
entry	base	% **185a** + **185b**[a]
1	$NaHCO_3$	7 + 7
2	$KHCO_3$	nr
3	Na_2CO_3	nr
4	K_2CO_3	nr
5	KF	0 + 5
6	CsF	3 + 16[b]
7	CaF_2	22 + 21[b]
8	NaH_2PO_4	13 + 9
9	Na_2HPO_4	12 + 11
10	KH_2PO_4	32 + 27
11	K_2HPO_4	14 + 13
12	K_3PO_4	nr
13	pyridine	27 + 15

[a] NMR yield, standard: DMB. [b] Isolated yield.

Because the formation of the oxygen-linked side product **185b** could not be avoided during the reactions with saccharin, more experiments were conducted with other nucleophiles. For this purpose, sulfonamide derivatives were synthesized. Tosylanilide (**188**) was synthesized according to literature in quantitative yield from aniline using 1.2 equiv *p*-toluenesulfonylchoride and 1.5 equiv NEt_3 (Equation 3.22).[163] In order to increase the nucleophilicity of the nitrogen, sulfonamide **190** with an additional tosyloxy moiety was synthesized from hydroxylamine hydrochloride (**189**) in 18% yield using *p*-toluenesulfonylchoride (2.1 equiv) and DMAP (0.1 equiv) (Equation 3.23).[164]



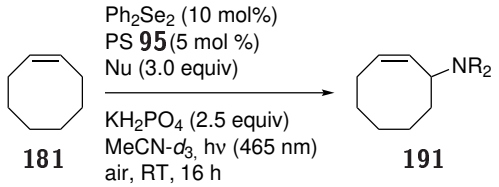
(3.22)



(3.23)

As the use of KH_2PO_4 was beneficial in the reaction with saccharin, it was used as the base in the following experiments. Under the altered conditions, the use of phthalimide **183** and electron-poor chloro- and nitro-substituted phthalimide derivatives did not lead to product formation (Table 3.27, entries 1-4). With dibenzenesulfonimide (**184**), traces of the desired product were obtained and identified by the ^{1}H NMR signals of the double bond and the proton in α position to the nitrogen at 5.98 ppm (dd, J = 10.6, 8.5 Hz), 5.62 ppm (dt, J = 10.2, 8.8 Hz) and 5.11 ppm (ddd, J = 12.1, 8.5, 3.9 Hz), respectively (Table 3.27, entry 5). In order to make the reagent more nucleophilic, the sodium salt of dibenzenesulfonimide was formed and used in the reaction without an additional base (Table 3.27, entry 6).[165] Unfortunately, the reactivity of the salt was comparable to the amine and the product was obtained in 3% yield. As a similar

Table 3.27: Attempted amination of cyclooctene (**181**) with different nucleophiles.

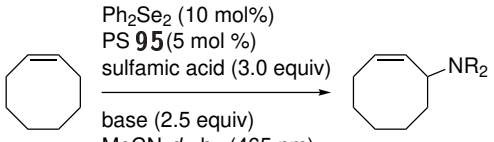


entry	nucleophile	yield
1	phthalimide **183**	-[a]
2	4,5-dichlorophthalimide	-[a]
3	tetrachlorophthalimide	-[a]
4	4-chloro-5-nitrophthalimide	-[a]
5	dibenzensulfonimide **184**	traces
6[b]	$(PhSO_2)_2NNa$	3%[c]
7	1,2-benzenedisulfonimide	traces
8	tosyl anilide (**188**)	-[a]
9	TsNHOTs (**190**)	-[a]
10	$TsNHCO_2tBu$	-[a]
11	NH_3	nr

[a] Decomposition. [b] No base used. [c] Isolated yield.

nucleophile, 1,2-benzenedisulfonimide was used and indeed, product formation was observed in mass spectrometry (Table 3.27, entry 7). In ^{1}H NMR, a doublet of doublets of doublets at 5.14 ppm with coupling constants 12.4, 8.3 and 5.2 Hz (comparable to the signal at 5.21 ppm in the spectrum of amine **185a**) and two multiplets at 6.04 and 5.89 ppm (presumably the protons at the double bond) hinted at product formation. Unfortunately, the assumed product could not be isolated and the formation was not quantified. When tosylanilide (**188**) and sulfonamide **190** were used, only decomposition of the starting material was observed (Table 3.27, entries 8 and 9). Inspired by the type of nucleophile used by White *et al.*, *tert*-butyl tosylcarbamate was applied in the reaction, but also did not lead to product formation (Table 3.27, entry 10).[166] When simple ammonia was used for the direct formation of an allylic amine, the decomposition of the photocatalyst was observed and no reaction occurred (Table 3.27, entry 11).
In order to further examine the use of ammonia, but avoid the reaction with the photocatalyst, sulfamic acid was used. This reagent was first used by Carreira *et al.* as an ammonia equivalent in the iridium-catalyzed formation of allylic amines from allylic alcohols.[167] When sulfamic acid was used without an added base, only the decomposition of the starting material was observed (Table 3.28, entry 1). The same observation was made with KH_2PO_4, CaF_2 and pyridine as base additives (Table 3.28, entries 2-4). In the reaction of Carreira, DMF as the solvent was needed to form an adduct with sulfamic acid and liberate ammonia. Unfortunately, when 5.0 equiv of DMF were added to the reaction, in one case along with KH_2PO_4 as the base, no reaction was observed (Table 3.28, entries 5 and 6).

Table 3.28: Attempted functionalization of cyclooctene (**181**) with sulfamic acid.



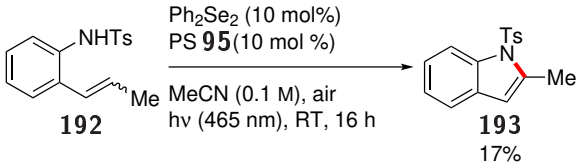
181 **191**

entry	base/additive	observation
1	-	decomposition
2	KH_2PO_4	decomposition
3	CaF_2	decomposition
4	pyridine	decomposition
5	KH_2PO_4; DMF (5.0 equiv)	nr
6	DMF (5.0 equiv)	nr

3.4.2 Intramolecular light-driven amination

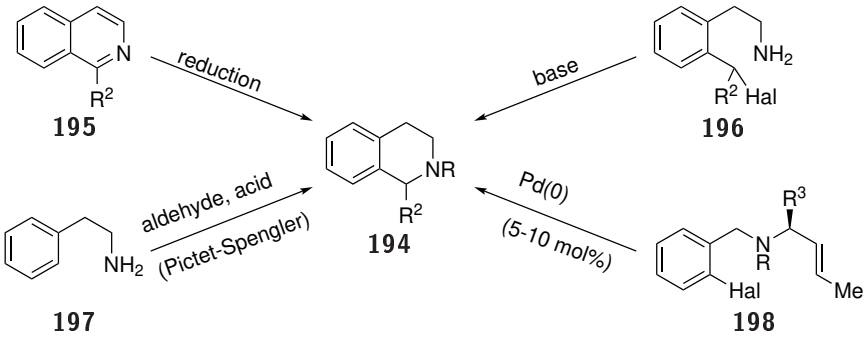
As the intermolecular light-driven amination reaction proved to be challenging due to low reactivity of the used nucleophiles or decomposition of the starting material under photoconditions, the use of photo-aerobic selenium-π-acid catalysis in the intramolecular amination of alkenes was

investigated. Our group has already reported the intramolecular amination of alkenes for the formation of (aza-)indoles with NFSI as the terminal oxidant.[65,127] Therefore, tosyl amid **192**[1] was subjected to photoconditions using diphenyl diselenide (10 mol%) and *p*-MeO-TPT (10 mol%) in MeCN under air and irradiation with blue light (Equation 3.24). Gratifyingly, indole **193** was formed in 17% yield.



(3.24)

Motivated by these findings, the formation of tetrahydroisoquinolines **194** under photo-aerobic selenium-π-acid catalysis was examined. Conventional methods for the synthesis of this class of natural products are the reduction of isoquinolines **195**, the nucleophilic substitution of a halide by nitrogen (compound **196**) and the PICTET-SPENGLER reaction (Scheme 3.3).[168–171] Furthermore, it was shown by TIETZE *et al.* that the HECK reaction can be used for the formation of diastereo-enriched tetrahydroisoquinolines from halides **198**.[172,173]

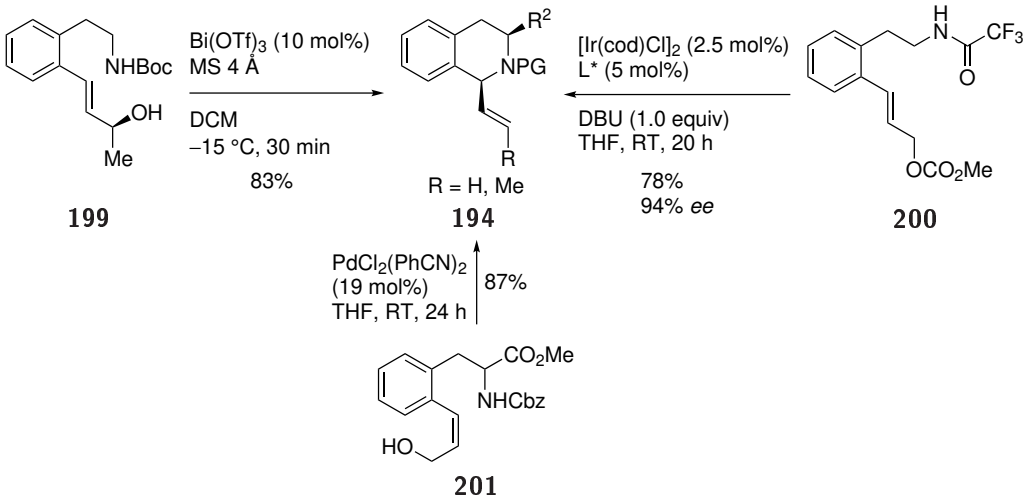


Scheme 3.3: Previous methods for the synthesis of tetrahydroisoquinolines (**194**).

In order to make the formation of tetrahydroisoquinolines more efficient, catalytic methods for the direct allylic C–H amination were developed by the groups of KAWAI, FERINGA, EUSTACHE and YAMAMOTO. The reactions proceeded with bismuth, iridium or palladium catalysts in high yields between 78 and 87% (Scheme 3.4).[174–177] With bismuth, the reaction proceeded stereospecifically due to the 1,3-chirality transfer in the reaction of alcohol **199**. The use of an iridium catalyst and a chiral ligand in the stereoselective reaction of carbonate **200** yielded the desired product in 94% *ee*.

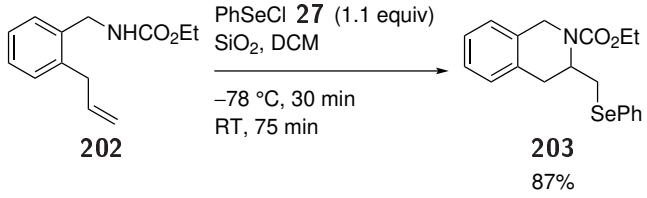
As the presented reactions all proceed *via* an S_N2' reaction and thus need prefunctionalized starting materials with a leaving group in the allylic position, selenium-catalysis could be a useful alternative to improve the redox economy in these regimes.[178] This suggestion is supported by

[1] Tosyl amid **192** was synthesized by Dr. S. Ortgies.[127]



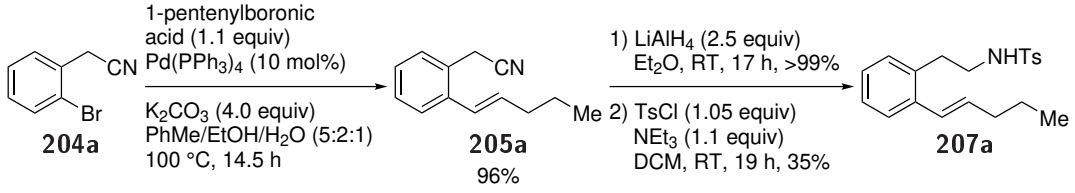
Scheme 3.4: Synthesis of tetrahydroisoquinolines (**194**) *via* direct allylic C–H amination.

the work of Clive and coworkers who have reported the formation of selenated tetrahydroisoquinoline **203** from compound **202** in 87% yield (Equation 3.25).[179]



(3.25)

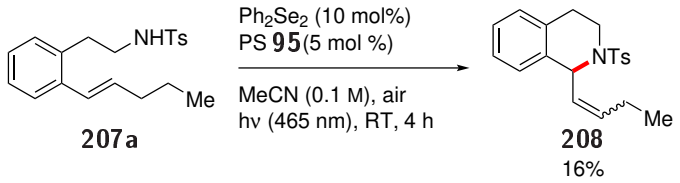
For the experiments on the photo-aerobic selenium-π-acid catalyzed formation of tetrahydroisoquinolines, tosyl amide **207a** was synthesized in three steps starting from bromide **204a** (Scheme 3.5). The Suzuki coupling with 1-pentenylboronic acid (1.1 equiv) afforded nitrile **205a** in 96% yield.[180] The following reduction of the nitrile to amine **206a** with 2.5 equiv $LiAlH_4$ proceeded with quantitative yield and the product was then .transformed into tosyl amide **207a** with 1.05 equiv TsCl and 1.1 equiv NEt_3 in 35% yield, following a procedure by Zhou *et al.*[181]



Scheme 3.5: Synthesis of tosyl amide **207a**.[180,181]

With the starting material in hand, the cyclization was attempted using 10 mol% diphenyl diselenide, 5 mol% *p*-MeO-TPT in MeCN under air and irradiation with blue light (Equation 3.26). Gratifyingly, tetrahydroisoquinoline **208** was obtained in 16% yield. A first hint for the desired

product formation was given by the HR-ESI mass spectrum and the IR spectrum, where the N−H vibration at 3271 cm^{-1} disappeared. The structure of the product was verified by NMR spectroscopy. In $CDCl_3$, the ^1H NMR signals of the double bond and another proton overlapped between 5.37-5.60 ppm and did not allow further analysis of the coupling constants, but the agreement of the data with data of similar structures supported the suggested structure.[174] For further analysis, 1D and 2D NMR spectra were measured in benzene-d_6, where the signal separated into a multiplet between 5.47 and 5.45 ppm for the vinylic protons and a doublet at 5.75 ppm, most likely the signal of proton **d** at the stereogenic center (Figure 3.10). Starting from the triplet of the methyl group **m** at 0.72 ppm, the structure of the side chain was determined by the COSY couplings and it was confirmed that proton **d** was vicinal to the double bond. More evidence for the formation of tetrahydroisoquinoline **208** was supplied by the signals of the methylene groups adjacent to the nitrogen atom. Their splitting into two signals for each CH_2 moiety and their chemical shifts of 3.85, 3.13, 2.57 and 2.14 ppm together with high coupling constants of 13 or 17 Hz for the geminal couplings and up to 11 Hz for the vicinal couplings suggested the formation of a cyclic structure containing a stereocenter.



(3.26)

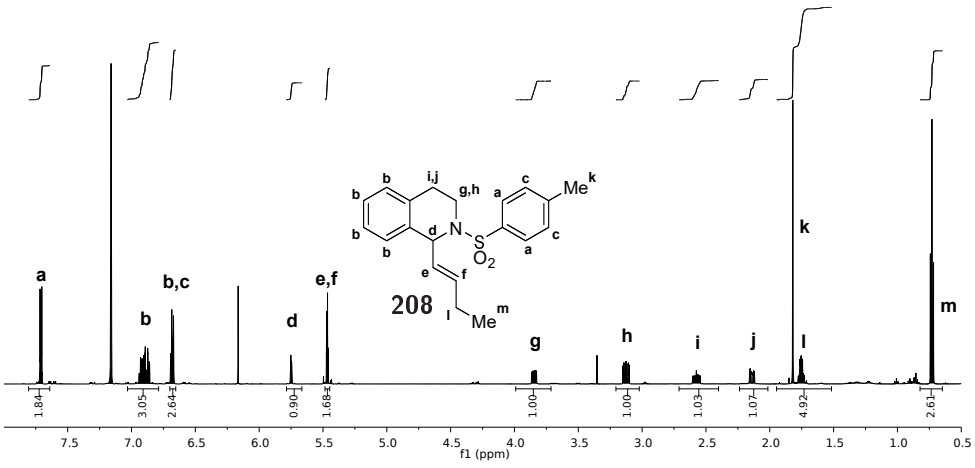
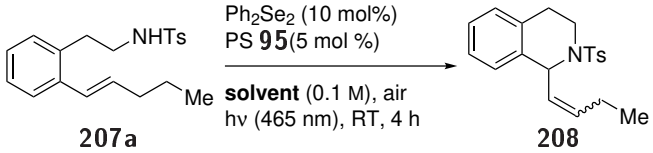


Figure 3.10: Assignment of the ^1H NMR signals of tetrahydroisoquinoline **208**.

In order to improve the yield of the reaction, the influence of different solvents was examined. When acetone was used instead of acetonitrile, the product was formed in 11% yield (Table 3.29, entry 2). Ethereal solvents, like THF and 1,4-dioxane, led to yields of 11 and 7%, respectively (Table 3.29, entries 3 and 4). With nitromethane, product **208** was obtained in 9% yield (Table 3.29, entry 5). The use of both DCE and toluene resulted in only trace amounts of the

product (Table 3.29, entries 6 and 7). As the yield of the first experiment in MeCN, 16%, could not be improved, the following experiments were also conducted in this solvent.

Table 3.29: Optimization of used solvents in the intramolecular amination.

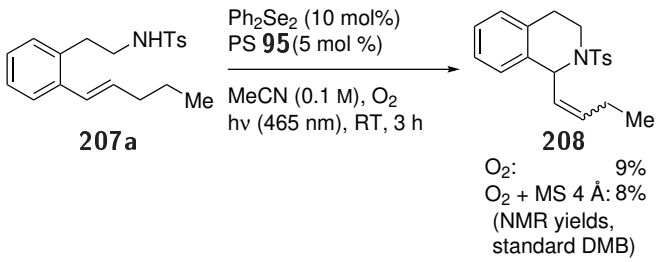


entry	solvent	NMR yield[a]
1	MeCN	16%
2	acetone	11%
3	THF	11%
4	1,4-dioxane	7%
5	nitromethane	9%
6	DCE	4%
7	toluene	5%

[a] Standard: DMB.

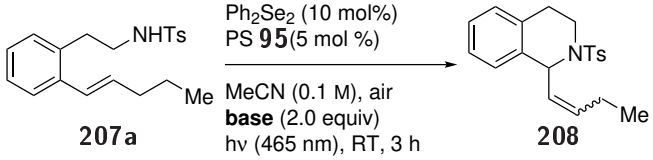
Subsequently, it was investigated if the yield of tetrahydroisoquinoline **208** could be improved by adding bases. Due to the experience that some bases, e.g. K_3PO_4, KF and CsF, led to decomposition of the photocatalyst and stagnation of the reaction, these bases were not considered (cf. Table 3.5 and Table 3.26). Phosphate bases gave the best results: using NaH_2PO_4 and KH_2PO_4 resulted in 13% yield, respectively, and with Na_2HPO_4, the product was obtained in 10% yield (Table 3.30, entries 2-4). The use of K_2HPO_4 led to decomposition of the photocatalyst and no reaction occurred (Table 3.30, entry 5). With $NaHCO_3$ and CaF_2, the product was afforded in 7 and 10% yield, respectively (Table 3.30, entries 6 and 7). The formation of the product did not occur with NaOAc as the base and decomposition of the photocatalyst was observed (Table 3.30, entry 8).

As the addition of the discussed bases did not improve the yield of product **208**, the question came up if the use of oxygen instead of air, which was used in the previous experiments, was beneficial. Consequently, two reactions with oxygen were conducted (Equation 3.27). Using only oxygen led to a yield of 9%, additional use of molecular sieves did influence the yield and the product was obtained in 8%.



(3.27)

Table 3.30: Optimization of used bases in the intramolecular amination.



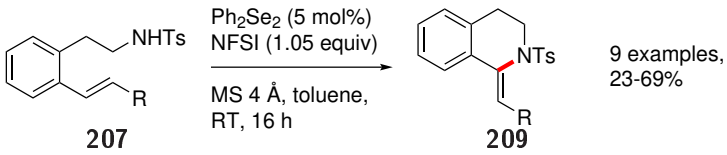
entry	base	yield (NMR yield)[a]
1	-	16%
2	NaH_2PO_4	13%
3	Na_2HPO_4	10%
4	KH_2PO_4	14%
5	K_2HPO_4	nr
6	$NaHCO_3$	7%
7	CaF_2	10%
8	NaOAc	nr

[a] Standard: DMB.

As the yield in the formation of tetrahydroisoquinoline **208** under photoconditions could not be increased with different solvents or bases, but full conversion of the starting material to unidentified side products was observed, it was assumed that it was decomposed under the reaction conditions. Oxidative decomposition could be induced by the used photocatalyst, which has a redox potential of the excited state $E^*_{red} = 1.84$ V vs. SCE.[129,182] As the redox potential of tosyl amides was reported as $E_{ox} = 2.38$ V vs. SCE, it was assumed that the observed decomposition was not an oxidation of the amide moiety.[183] However, the oxidation of the styrenic double bond seemed more probable, as Nicewicz and colleagues reported the oxidation potentials of different styrene derivatives as $E_{ox} = 1.2$-1.7 V vs. SCE.[184] To avoid this side reaction, the oxidation potential of the double bond could be increased by introducing electron-withdrawing substituents at the aromatic ring. A second possibility to avoid overoxidation is to use a photocatalyst with a lower reduction potential than *p*-MeO-TPT (**95**), like acridinium salt **131** ($E^*_{red} = 1.65$ V vs. SCE) or ruthenium complex **132** ($E^*_{red} = 1.45$ V vs. SCE), which were also tested in the intramolecular etherification reaction.[128,130] Furthermore, changing the protecting group at the nitrogen atom and thereby the pK_a of the N−H unit could influence the turnover of the desired reaction, as was also observed in the selenium-catalyzed formation of indoles.[65] An interesting protecting group could be a carbamate moiety, like it was used in the reaction of Clive *et al.*[179]

In order to evaluate if the formation of tetrahydroisoquinolines **209** was more efficient under non-photochemical conditions, the cyclization of tosyl amides **207** under selenium-catalysis with NFSI as the oxidant was investigated by C. Schlawis.[185] He was able to optimize the conditions for the formation of products **209** to the use of 5 mol% diphenyl diselenide, 1.05 equiv NFSI and 4 Å molecular sieves in toluene at room temperature and obtained the desired products in good yields of up to 69% (Equation 3.28). Surprisingly, the change of the oxidant also led to a change

in the structure of the product. Instead of the formation of a stereogenic center in the benzylic position, the formation of an isomer with a double bond conjugated to the aromatic system was observed. This was indicated by the ^{1}H NMR signals of the vinylic proton, a triplet at 6.24 ppm, and the methylene groups in the ring, which did not split into separate signals for the geminal protons. Their signals appeared as a multiplet at 2.41-2.55 ppm, which overlapped with the signal of the CH_2 group next to the double bond, and as a broad singlet at 3.83 ppm.[185]

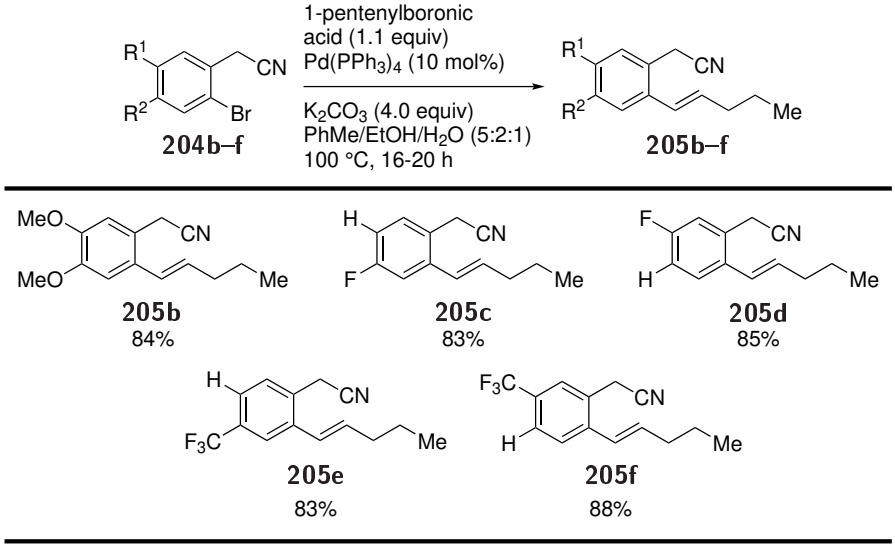


(3.28)

3.4.3 Synthesis and cyclization of *ortho*-vinyl homobenzylamides

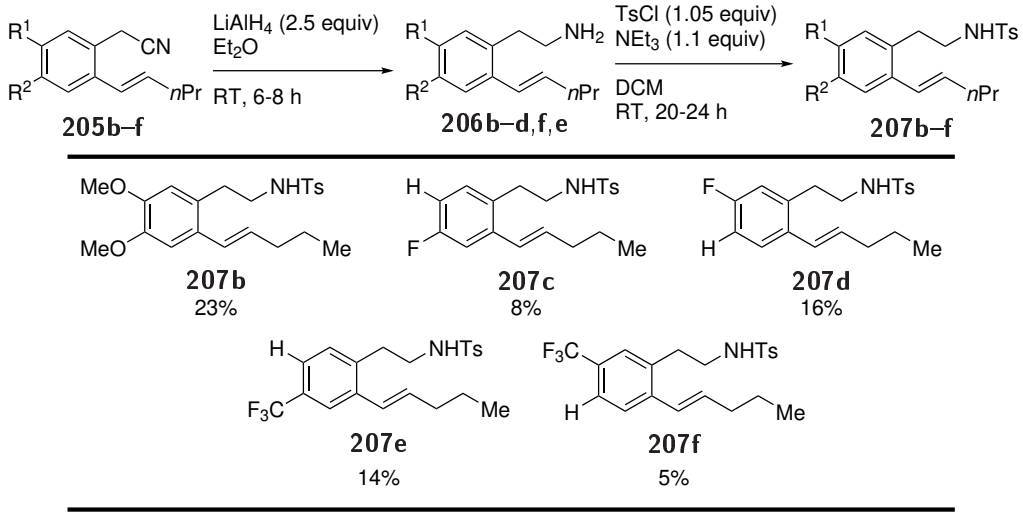
The formation of tetrahyroisoquinolines **209** with different substituents in the side chain was examined by C. Schlawis.[185] It was further interesting to evaluate the influence of different substituents on the aromatic ring. Therefore, several *ortho*-vinyl homobenzylamide derivatives **207** were synthesized using different synthetic strategies. In the first synthetic path, the desired compounds were synthesized in an analogous manner to the synthesis of amide **207a** (cf. Scheme 3.5). Starting from bromophenylacetonitriles **204**, the SUZUKI coupling to 1-pentenylboronic acid afforded nitriles **205b–f** in good yields between 83 and 88% (Table 3.31).[180]

Table 3.31: SUZUKI reaction of bromophenylacetonitriles **204** to nitriles **205**.[180]



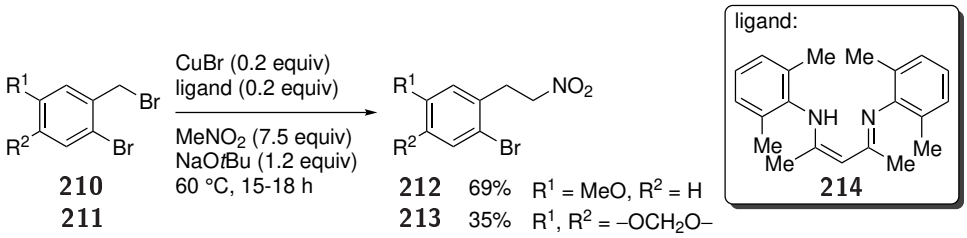
In the next step, the nitrile function was reduced to the amine with lithium aluminum hydride (Table 3.32). The products **206b–f** were used without further purification in the following reaction with toluenesulfonic acid chloride to provide tosyl amides **207b–f** in overall yields between 5 and 23%.

Table 3.32: Reduction of nitriles **205** to amines **206** and subsequent reaction to tosyl amides **207**.[a][181]



[a] Isolated yield respective to nitriles **205** (two steps).

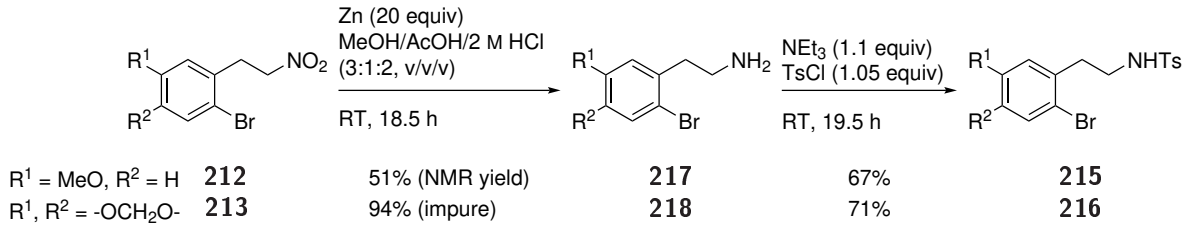
The synthesis of a mono methoxy substituted and a benzo[*d*][1,3]dioxole derived *ortho*-vinyl homobenzylamide started from 1-bromo-2-(bromomethyl)-4-methoxybenzene (**210**) and 5-bromo-6-(bromomethyl)benzo[*d*][1,3]dioxole (**211**) with a nitromethylation, following a procedure by Watson and coworkers.[186] The reaction with nitromethane (7.5 equiv) and sodium *tert*-butoxide (1.2 equiv) was catalyzed by copper(I)bromide (0.2 equiv) with *m*-xylyl-nacnac (**214**) (0.2 equiv) as the ligand. It afforded the methoxy-subtituted product **212** in 69% yield and the benzodioxole derivative **213** in 35% yield (Equation 3.29).



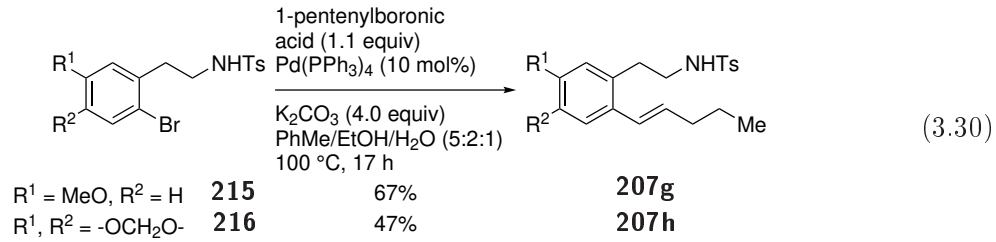
(3.29)

Nitro compounds **212** and **213** were then reduced in a Clemmensen-type reduction following a procedure by Gong and coworkers.[187] The reaction with zinc (20 equiv) in a solvent mixture of methanol/acetic acid/2 M HCl (3:1:2, v/v/v) afforded the desired amines **217** and **218** in 51 and 94% yield. The amine groups were subsequently converted into tosyl amide groups using the previously applied method (cf. Scheme 3.5 and Table 3.32) to obtain tosyl amides **215** and **216** in 67 and 71% yield (Scheme 3.6).[181]

In the last step, tosyl amides **215** and **216** were reacted with 1-pentenylboronic acid in a Suzuki coupling using the established conditions (cf. Table 3.31) to afford *ortho*-vinyl homobenzylamides **207g** and **207h** in 67 and 47% yield (Equation 3.30).[180]

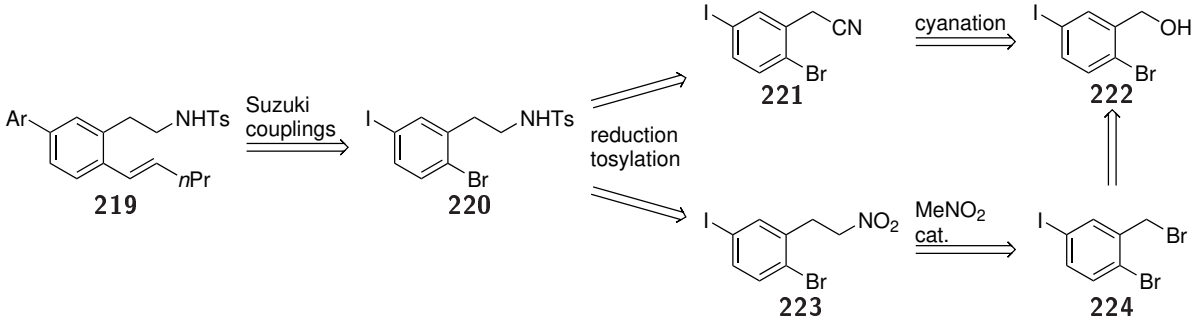


Scheme 3.6: Reduction and following tosyl amide protection of nitro compounds **212** and **213**.[181,187]



(3.30)

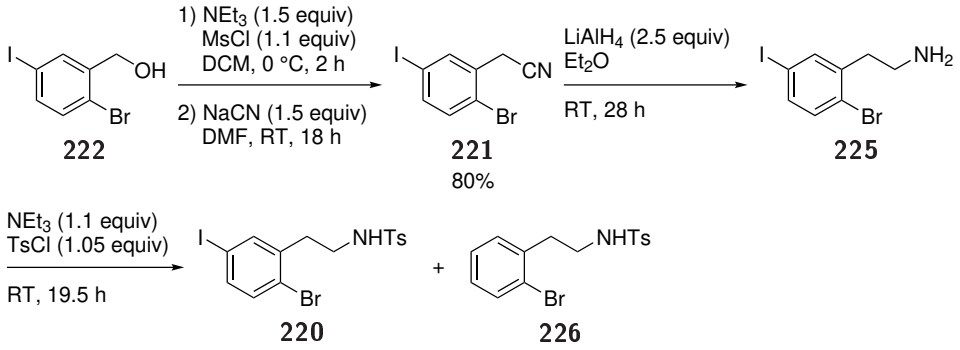
In addition to tosyl amides **207b**–**h**, arylated derivatives were to be synthesized. For this purpose, a synthetic path was developed which allowed for the introduction of different aryl moieties in the penultimate step (Scheme 3.7). Consequently, compounds **219** could be obtained from dihalide **220** *via* two subsequent Suzuki reactions. The introduction of the tosylated side chain could be achieved in the established synthetic path from either nitrile **221** or benzyl bromide **224**, which could both be obtained from benzyl alcohol **222**.



Scheme 3.7: Retrosynthetic considerations for the synthesis of arylated *ortho*-vinyl homobenzylamides **219**.

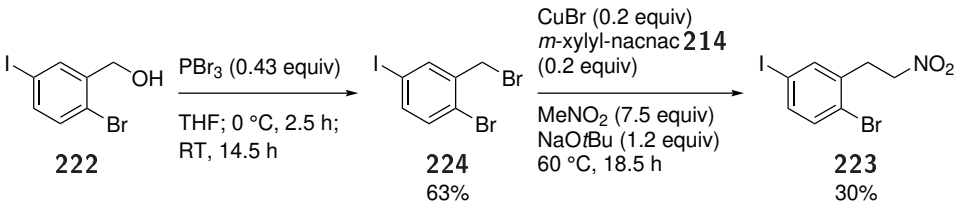
First, the synthesis *via* nitrile **221** was attempted using a procedure by Hu and Zuo.[188] The cyanation of 2-bromo-5-iodobenzylalcohol (**222**) was conducted by transferring it into the mesylalcohol with triethylamine (1.5 equiv) and methanesulfonyl chloride (1.1 equiv) and then substituting the mesyl alcohol with sodium cyanate (1.5 equiv) (Scheme 3.8). Nitrile **221** was obtained in 80% yield. The reduction of nitrile **221** and the following tosyl amide protection were conducted under the established conditions.[181] Unfortunately, the desired product **220** was ob-

tained in an inseparable mixture with protodeiodinated side product **226** and other unidentified side products.



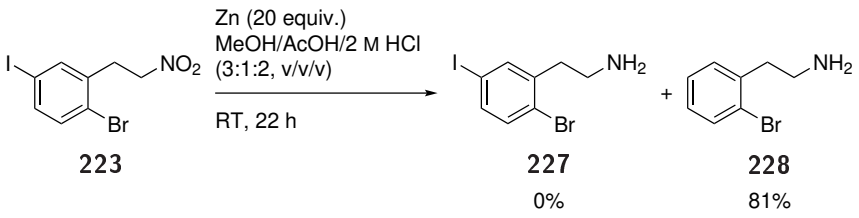
Scheme 3.8: Cyanation and attempted reduction and following tosyl amide protection of benzyl alcohol **221**.

In order to avoid this problem, the alternative synthesis *via* the nitro compound was attempted. The synthesis started with the substitution of the hydroxyl group of 2-bromo-5-iodobenzylalcohol (**222**) by a bromide. Using PBr_3 (0.43 equiv) in THF afforded 1-bromo-2-(bromomethyl)-4-iodobenzene (**224**) in a yield of 63% (Scheme 3.9). With benzyl bromide **224** in hand, the nitromethylation was conducted according to previous experiments (cf. Equation 3.29) and afforded the nitro compound **223** in 30% yield.[186]



Scheme 3.9: Bromination and following nitromethylation of benzyl alcohol **222**.

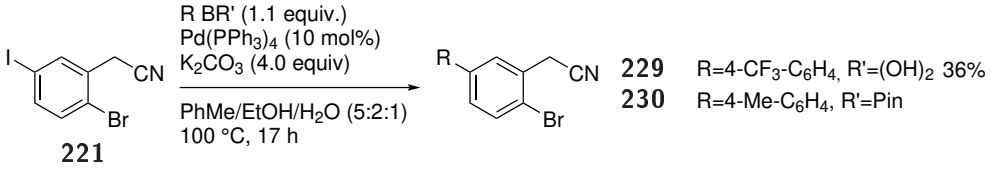
Unfortunately, the reduction of nitro compound **223** to amine **227** analogous to previous reactions (cf. Scheme 3.6) afforded the protodeiodinated amine **228** in 81% (Equation 3.31). The formation of this side product was determined from the combined integral of the aromatic region of 4.



(3.31)

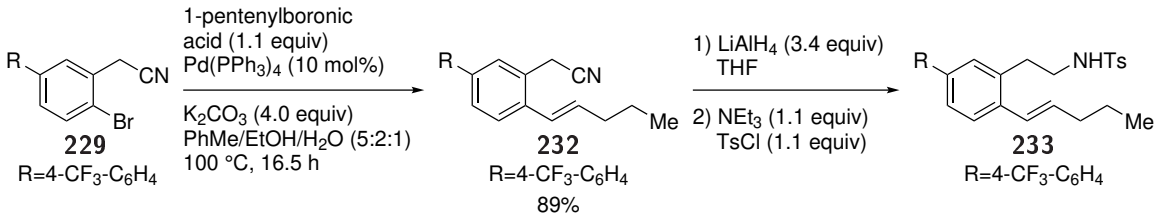
As the hydrogenation of both the nitrile or the nitro function led to cleavage of the iodide, it was attempted to perform the Suzuki couplings before the reduction reactions. The reaction of nitrile **221** with either 4-(trifluoromethyl)phenylboronic acid or 4-methylphenylboronic acid pincacol

ester under the established conditions afforded product **229** (trifluoromethyl substituent) in 36% yield. Product **230** (methyl substituent) could only be obtained in a mixture with an unidentified side product (Equation 3.32).[180] Product **229** was identified by the signals of the benzyl group at 3.92 ppm (singlet, integral 2) and the aromatic protons at 7.80-7.60 ppm (multiplet, integral 6) and 7.42 ppm (doublet of doublets, integral 1). In the spectrum of product **230**, there were two singlets at 3.89 (integral 2) and 3.90 ppm (integral 1.2), presumably the benzyl group, and two singlets at 2.40 (integral 3) and 2.42 ppm (integral 1.5), presumably the methyl group. Together with the high integral of 33 of the aromatic region between 7.2 and 7.8 ppm, this led to the conclusion that the impureness could be a protodehalogenated side product.



(3.32)

Aryl substituted nitrile **229** was then coupled to 1-pentenylboronic acid in another Suzuki reaction to obtain nitrile **232** in 89% yield (Scheme 3.10).[180] The following reduction and tosylation of nitrile **232** under the established conditions afforded an inseparable mixture of the desired tosyl amide **233** and an unidentified side product.[181] The formation of the amine was indicated by the appearance of two multiplets at 2.89 and 2.93 ppm for the amine side chain and confirmed *via* ESI mass spectrometry. The successful reaction of the amine to the amide was indicated by several ^{1}H NMR signals, such as a doublet and a doublet of triplets for the protons at the double bond at 6.61 and 6.09 ppm, a multiplet at 4.44 ppm that was assigned to the proton at the nitrogen, and signals of the *n*-propyl moiety (0.98, 1.51, and 2.22 ppm) as well as the ethylene moiety (3.15 and 3.36 ppm). The signals in the aromatic region showed an integral that was too high (16 instead of expected 11) and additional signals like a doublet at 1.26 ppm with the integral 3 and a doublet at 2.43 ppm (integral 0.75) belonged to an unidentified side product which could not be separated.

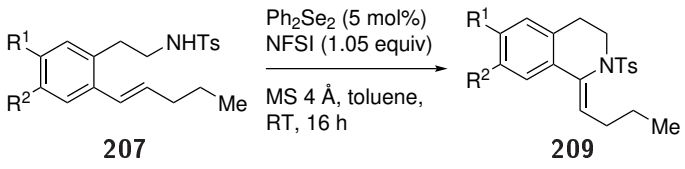


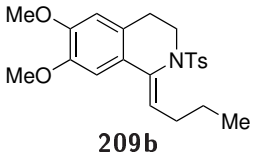
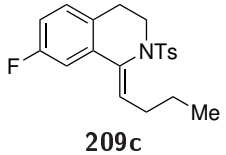
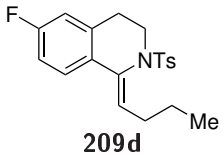
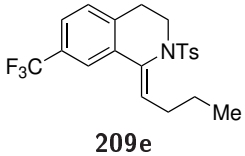
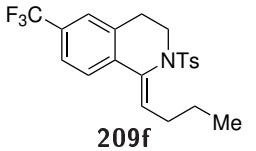
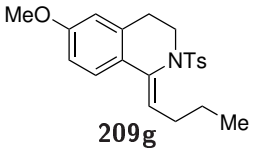
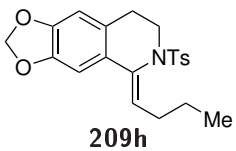
Scheme 3.10: SUZUKI reaction and attempted tosylation of aryl bromide **229**.

Since the attempted syntheses of arylated *ortho*-vinyl homobenzylamides led to the formation of various side products, the catalytic cyclization of synthesized compounds **207** was conducted under the previously established conditions with 5 mol% diphenyl diselenide, 1.05 equiv NFSI and 4 Å molecular sieves in toluene at room temperature (Table 3.33).[185] Tetrahydroisoquinolines

209c–h were obtained in 21-57% yield. In the attempted formation of tetrahydroisoquinoline **209b**, only the decomposition of the starting material was observed. The products were identified in ^{1}H NMR by the triplet of the vinylic proton between 6.1 and 6.3 ppm and the broad singlet at approx. 3.8 ppm that was assigned to the methylene group α to the nitrogen. The position and nature of the substituents seemed to have a great influence on the yield. Products with electron-withdrawing substituents in *meta*-position to the double bond were obtained in higher yields (products **209c** and **209e**) than the analogous products with the substituent in *para*-position (products **209d** and **209f**). Electron-donating moieties led to higher yields than electron-withdrawing groups, also when they were attached in *para*-position to the double bond (products **209g** and **209h**).

Table 3.33: Cyclization of tosyl amides **207**.[a]



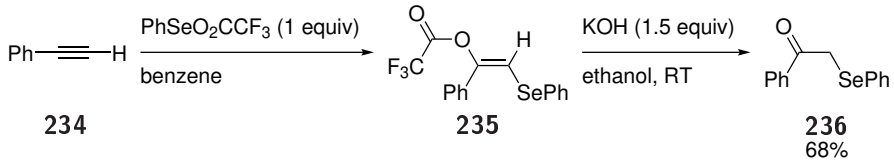
			
209b	**209c**	**209d**	**209e**
-[b]	47%	21%	26%
			
209f	**209g**	**209h**	
23%	48%	57%	

[a] Isolated yield. [b] Decomposition.

3.5 Selenium-π-acid catalyzed synthesis of allenylamides

3.5.1 Preliminary investigations and optimization of reaction conditions

After the examination of reactions with challenging nucleophiles such as alcohols and amines, the question occurred if it was possible to also conduct the reactions with substrates with different π-bonds; and alkynes attracted our attention. The π-acid activation of the triple bond by selenium followed by a nucleophilic attack would lead to a vinylic selenofunctionalization product. In the context of a selenium-catalyzed reaction, it is interesting to find out if oxidative elimination of the selenium species is possible and which product is formed. Previously, only few selenium-mediated reactions with alkynes as substrates have been reported. Although the formation of a thiirenium ion followed by thiofunctionalization was reported by KHARASCH and ASSONY already in 1953,[189] the respective selenium-variant was not disclosed until 1974. In the course of his investigations into the addition of phenylselenyl trifluoroacetate to alkenes, REICH also demonstrated its addition to phenyl acetylene (**234**) (Scheme 3.11).[190]

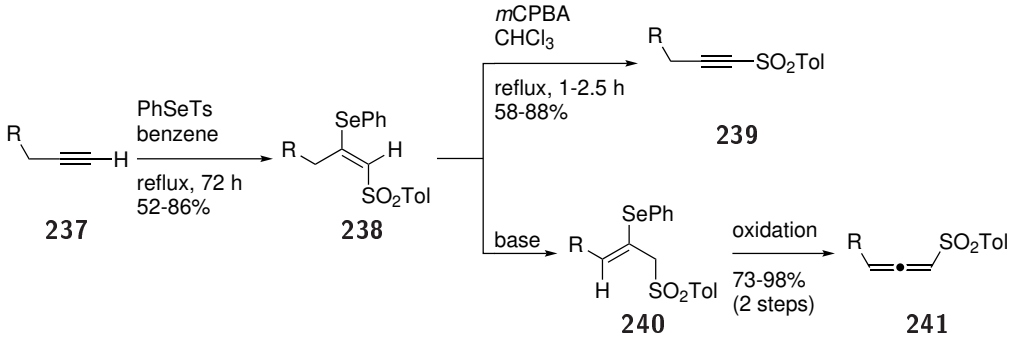


Scheme 3.11: Addition of phenylselenyl trifluoroacetate to phenyl acetylene (**234**) and the following hydrolysis.

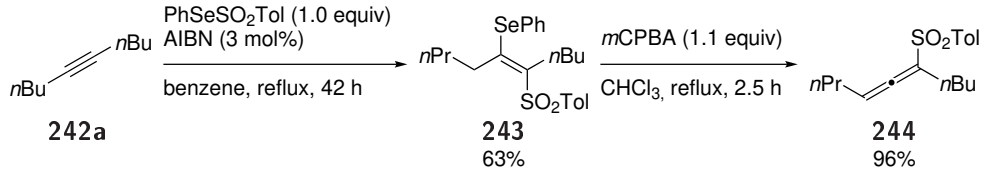
However, REICH did not conduct the oxidative elimination of the selenium species, but hydrolized the acetate, which led to the formation of β-phenylselenyl ketone **236**. The elimination was first examined by BACK and colleagues in 1981.[191] They demonstrated the addition of *Se*-phenyl *p*-toluneselenosulfonate to terminal alkynes **237** and the following elimination of the selenium moiety by oxidation with *m*CPBA to acetylenic sulfone **239** in up to 88% yield (Scheme 3.12). When they subjected alkenes **238** first to basic conditions to induce isomerization of the double bond and then oxidized the resulting vinylic selenides **240**, they were able to obtain allenic sulfones **241** in up to 98% yield instead.[192,193]

The formation of functionalized allenes from internal alkynes was realized by the same group under similar conditions to the formation of acetylenic sulfones **239**. The addition of *Se*-phenyl *p*-toluneselenosulfonate (1.0 equiv) to 5-decyne (**242a**) proceeded in 63% yield and the elimination was initiated by oxidation with *m*CPBA (1.1 equiv) and heating (Scheme 3.13).[194] As vinyl selenide **243** has a tetrasubstituted double bond, the elimination of a vinylic hydrogen, like in the case of vinyl selenides **238**, is not possible and an allylic hydrogen is eliminated instead, leading to the formation of allene **244** in 96% yield.

The first procedure for the oxidative functionalization of alkynes that used a substoichiometric amount of a selenium species was the propargylic oxidation of alkynes by the group of ZHAO.[195] They were able to form ynones **246** from propargylphosphonates and -esters **245** in yields between

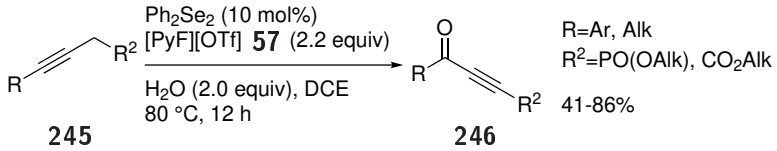


Scheme 3.12: Addition of Se-phenyl *p*-tolueneselenosulfonate to alkynes **237** and the following reactions to alkynes **239** or allenes **241**.



Scheme 3.13: Addition of *Se*-phenyl *p*-tolueneselenosulfonate to 5-decyne (**242a**) and the following elimination to allene **244**.

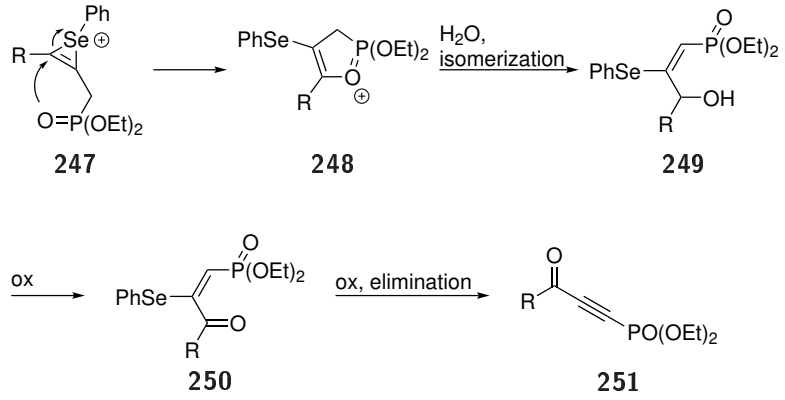
41 and 86% using 10 mol% of diphenyl diselenide, 2.2 equiv of [PyF][OTf] (**57**) as the oxidant and 2.0 equiv H_2O (Equation 3.33). Though they were able to use substrates with aromatic and aliphatic alkynes, a drawback of their method is that they need substrates with an oxygen-containing group R^2 in the propargylic position.



(3.33)

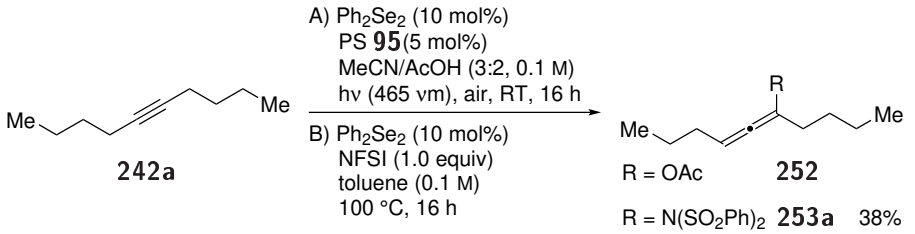
The required nature of the substrates is explained in the proposed mechanism, as the oxygen of the phosphonate or ester group is needed to open selenirenium ion **247** (Scheme 3.14). Oxaphosphole **248** is opened by H_2O and subsequent isomerization of the double bond yields allyl alcohol **249**, which is oxidized to ketone **250**. In the last step, oxidation of the selenium moiety leads to elimination and formation of ynone **251**.

In order to avoid prefunctionalized substrates and to introduce external nucleophiles, our group performed experiments on the oxidative functionalization of 5-decyne (**242a**). In the experiments of Dr. S. Ortgies under the conditions of the photo-aerobic selenium-π-acid catalysis[91] with acetic acid as an exogenous nucleophile, the isolated product could not be separated from leftover solvent due to its volatility (Equation 3.34, conditions A).[127] As the ^{1}H NMR contained a signal at 4.36 ppm, which would fit the vinylic proton, the product was assumed to be allene **252**. Unfortunately, the aliphatic signals overlapped with solvent signals and the product could not



Scheme 3.14: Proposed mechanism of the propargylic oxidation by Zhao *et al.*

be definitely identified.[127] Therefore, the reaction was carried out using conditions based on the selenium-catalyzed formation of indoles with NFSI as the oxidant and nucleophile (Equation 3.34, conditions B).[65,127] The reaction with diphenyl diselenide (10 mol%) and NFSI (1.0 equiv) in toluene at 100 °C led to the formation of allene **253a** in 38% yield (along with 8% of the selenofunctionalized intermediate).

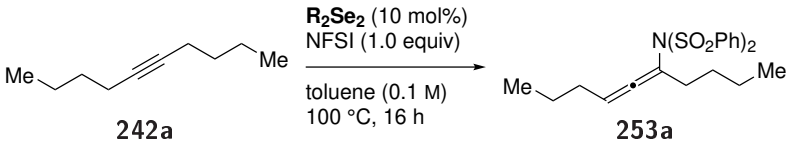


(3.34)

Based on these findings, the conditions for the allene formation were examined further during this work. First, the performance of different diselenide catalysts was compared. In addition to diphenyl diselenide, the performance of $(2\text{-anisyl})_2Se_2$, which had been successfully applied in the intramolecular etherification, was evaluated. The reactions were carried out with 10 mol% of the respective diselenide and 1.0 equiv NFSI in toluene at 100 °C for 16 h (Table 3.34, entries 1 and 2).[196] Product **253a** was obtained in 36% with diphenyl diselenide, confirming the result of the original experiment. With more electron-rich $(2\text{-anisyl})_2Se_2$, it was obtained in 45%. Therefore, further experiments were conducted using this catalyst. To assure that the reaction was indeed catalyzed by the diselenide, a control reaction was conducted. When only the alkyne and NFSI were used, no reaction occurred, leading to the conclusion that the diselenide catalyst was needed for the reaction (Table 3.34, entry 3).

Next, the influence of the temperature and different solvents was examined. In order to avoid the formation of side products by residual water in the reaction mixture, molecular sieves was added to the reactions. As lowering the temperature to 50 °C decreased the yield to 7% (Table 3.35, entry 2), the reaction was conducted in different solvents at 100 °C by R. Rieger.[196]

Table 3.34: Experiments on the used catalyst in the allenylation. Grayed reaction by R. Rieger.[196]



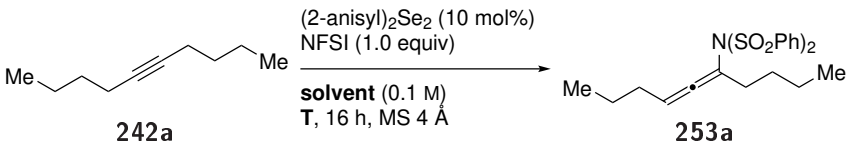
242a 253a

entry	R_2Se_2	yield[a]
1	Ph_2Se_2	36%
2	$(2\text{-anisyl})_2Se_2$	45%
3	no catalyst	-

[a] NMR yield, standard: TMB.

When chlorinated solvents, like 1,1,2,2-tetrachloroethane and 1,2-dichloroethane, were used, allene **253a** was obtained in 19 and 9% yield, respectively (Table 3.35, entries 3 and 4). The use of propionitrile resulted in 17% yield (Table 3.35, entry 5). With nitromethane, the product was only obtained in 8% yield (Table 3.35, entry 6). Ethereal solvents led to yields that were comparable to the one achieved with toluene. With 1,4-dioxane, the product was obtained in 36% yield, with THF in 40% yield (Table 3.35, entries 7 and 8). This result matches the results of the amination of alkenes by Breder *et al.*, where ethereal solvents gave the best results.[63]

Table 3.35: Experiments on temperature and used solvents in the allenylation. Grayed reactions by R. Rieger.[196]



242a 253a

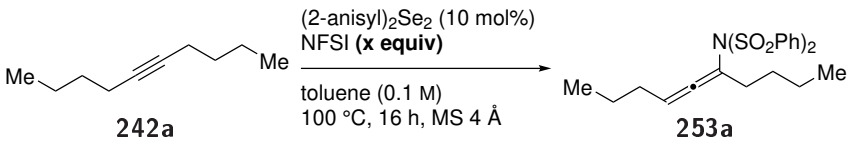
entry	solvent	temperature	yield[a]
1	toluene	100 °C	45%
2	toluene	50 °C	7%
3	TCE	100 °C	19%
4[b]	DCE	100 °C	9%
5	propionitrile	100 °C	17%
6	$MeNO_2$	100 °C	8%
7	1,4-dioxane	100 °C	36%
8[b]	THF	100 °C	40%

[a] NMR yield, standard: TMB. [b] Reaction conducted in a pressure tube.

After toluene was identified as the best solvent, it was examined if changing the ratio between starting material and oxidant would increase the yield of the reaction. In the first experiments, 5-decyne (**242a**) was used in an excess of 1.5, 3.0 and 5.0 equiv and product **253a** was obtained in 50, 36 and 36% yield, respectively (Table 3.36, entries 1-3). In the experiments with the higher decyne loading, the decomposition of NFSI was observed. Therefore, the ratio of the reagents

was reversed to avoid the stagnation of the reaction due to missing nucleophile. With 1.2 equiv NFSI, allene **253a** was obtained in 53% yield, with 3 equiv NFSI it was still obtained in 41% yield (Table 3.36, entries 4 and 5).

Table 3.36: Optimization of reagent amounts in the allenylation. Grayed reactions by R. Rieger.[196]



242a **253a**

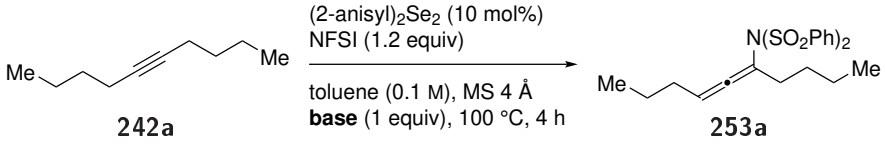
entry	amount of **242a**	amount of NFSI	yield[a]
1	1.5 equiv	1.0 equiv	50%
2	3.0 equiv	1.0 equiv	36%
3	5.0 equiv	1.0 equiv	36%
4	1.0 equiv	1.2 equiv	53%
5	1.0 equiv	3.0 equiv	41%

[a] NMR yield, standard: TMB.

Having determined that a slight excess of NFSI results in higher yields, the effect of different bases on the reaction was investigated. NFSI was added gradually as a solution in toluene to further prevent its decomposition. As complete conversion of the alkyne was observed as soon as the addition of NFSI was complete, the reaction time was shortened to 4 h. The addition of NaH_2PO_4, Na_2HPO_4 or Na_3PO_4 led to yields of 38, 56 or 65%, respectively (Table 3.37, entries 1-3; grayed reaction conducted by R. Rieger).[196] With potassium phosphates KH_2PO_4 and K_2HPO_4, allene **253a** was also obtained in good yields of 52 and 65% (Table 3.37, entries 4 and 5). Only K_3PO_4 led to a low yield of 11% (Table 3.37, entry 6). The addition of carbonate bases to the reaction had a beneficial effect in most cases. With sodium carbonates $NaHCO_3$ and Na_2CO_3, the desired product was obtained in 57 and 64% yield (Table 3.37, entries 7 and 8), lithium carbonate and calcium carbonate afforded the product in the highest yields of 68 and 66% (Table 3.37, entries 11 and 13). The addition of potassium carbonates $KHCO_3$ and K_2CO_3 or caesium carbonate led to moderate yields of 27, 29 or 32% yield (Table 3.37, entries 9, 10 and 12). With NaOAc and KOAc, the product was obtained in only 9 and 16% yield (Table 3.37, entries 14 and 15).

In many of the previous reactions, the formation of a side product was observed after the full conversion of the alkyne. A first clue to this side product being the selenofunctionalized compound **254** gave the appearance of additional signals in the aromatic region of the ^{1}H NMR spectrum. In addition to the signals at 6.75-7.08 ppm (integral 2), 7.31 ppm (integral 1) and approx. 7.49 ppm (overlap with signal of desired product; integral approx. 1), a singlet at 3.90 ppm (integral 3, probably the methoxy group) was observed (Figure 3.11, signals marked in red). When the side product was isolated, its identity was further hinted at by the missing signals of the carbon atoms of the allene moiety at 99.0, 106.8 and 206 ppm in ^{13}C NMR. Instead, two signals for the vinylic

Table 3.37: Optimization of bases used in the allenylation. Grayed reaction by R. Rieger.[196]



242a **253a**

entry	base	yield[a]	entry	base	yield[a]
1	NaH_2PO_4	38%	9	$KHCO_3$	27%
2	Na_2HPO_4	56%	10	K_2CO_3	29%
3	Na_3PO_4	65%	11	Li_2CO_3	68%
4	KH_2PO_4	52%	12	Cs_2CO_3	32%
5	K_2HPO_4	65%	13	$CaCO_3$	66%
6	K_3PO_4	11%	14	NaOAc	9%
7	$NaHCO_3$	57%	15	KOAc	16%
8	Na_2CO_3	64%			

[a] NMR yield, standard: TMB. NFSI added gradually in THF.

carbon atoms at 133.5 and 146.7 ppm were observed. Additionally, a signal in the ^{77}Se NMR spectrum at 314.1 ppm and mass spectrometric analysis supported the identification of the side product as selenofunctionalized compound **254**.

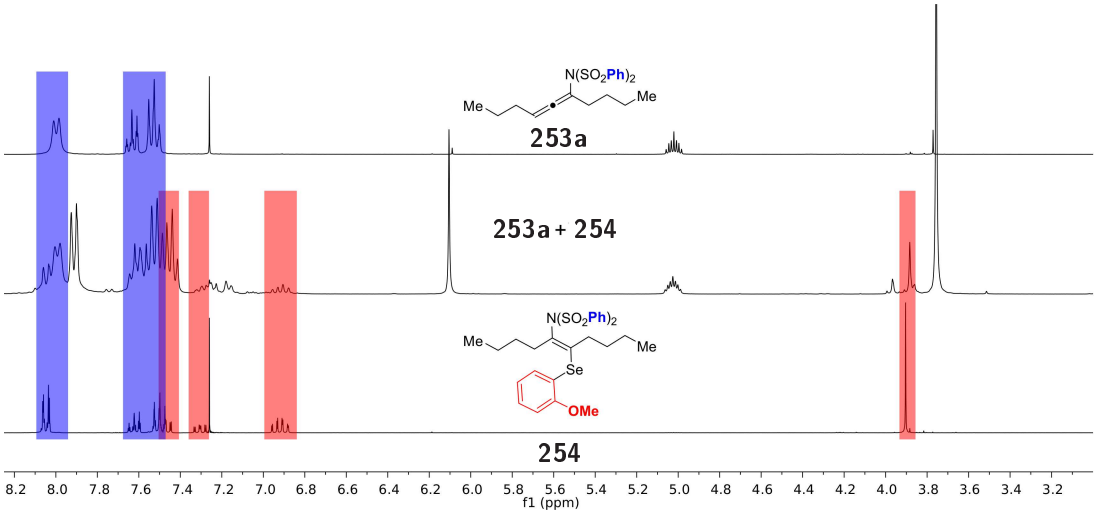
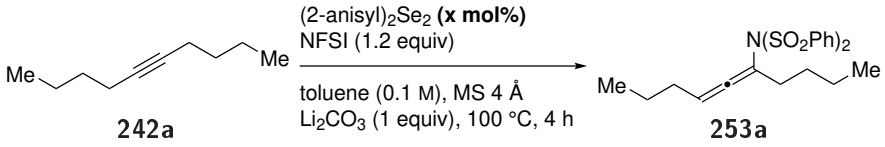


Figure 3.11: Extract from ^{1}H NMR spectra of allene **253a** (top), the crude reaction mixture (middle) and selenofunctionalized compound **254** (bottom).

As the maximum amount of formed selenofunctionalized compound is twice the amount of applied catalyst, it appeared reasonable to decrease the catalyst loading. The stepwise decrease of the used amount of $(2\text{-anisyl})_2Se_2$ from 10 to 5 and 2.5 mol% increased the yield from 68% to 74 and 77% (Table 3.38, entries 1-3). Lowering the catalyst loading to 1 mol% led to only 10% yield (Table 3.38, entry 4).

Table 3.38: Optimization of catalyst loading in the allenylation.

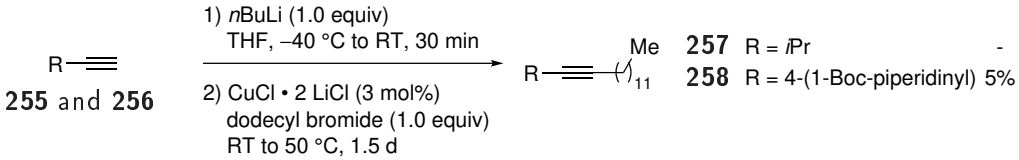


entry	x	yield[a]
1	10	68%
2	5	74%
3	2.5	77%
4	1	10%

[a] NMR yield, standard: TMB.

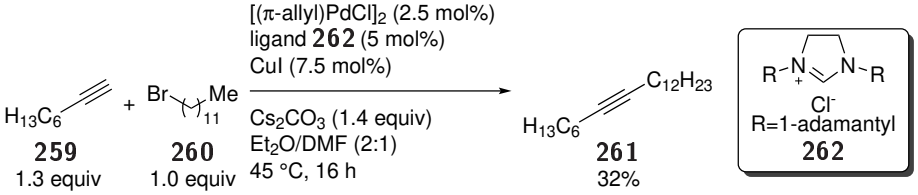
3.5.2 Synthesis of alkynes and allenylamides

With the optimized reaction conditions in hand, the synthesis of unsymmetrically and symmetrically substituted aliphatic alkynes was investigated. The first synthetic route was the nucleophilic substitution of dodecyl bromide with a lithiated terminal alkyne. Following a procedure by PÁPAI and REPO, the reaction was conducted using 3-methyl-1-butyne (**255**) or 1-Boc-4-ethynylpiperidine (**256**), 1.0 equiv of *n*-butyl lithium and 3 mol% of CuCl · 2 LiCl (Equation 3.35).[197] Unfortunately, the reactions did not show complete conversion. Alkyne **257** could not be separated from equally unpolar starting materials and side products by column chromatography. Alkyne **258** was isolated in only 5% yield.



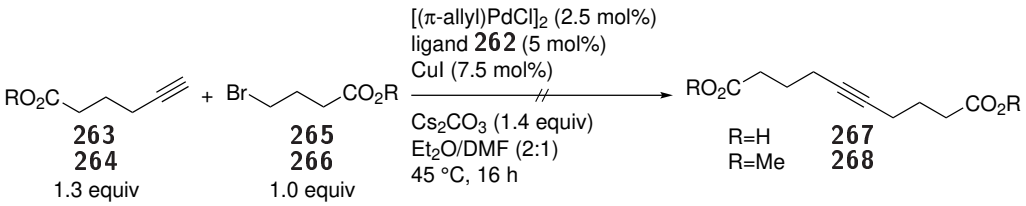
(3.35)

Instead of by a nucleophilic substitution, a terminal alkyne and a bromide could also be connected by a cross coupling reaction, e.g. a SONOGASHIRA reaction.[198] Therefore, the reaction of 1-octyne (**259**) and dodecyl bromide (**260**) was conducted using conditions by FU and colleagues with 2.5 mol% of $[(\pi\text{-allyl})PdCl]_2$, 5 mol% of NHC ligand **262**, 7.5 mol% of CuI and 1.4 equiv of Cs_2CO_3 as the base (Equation 3.36).[199] Alkyne **261** was obtained in 32% yield.



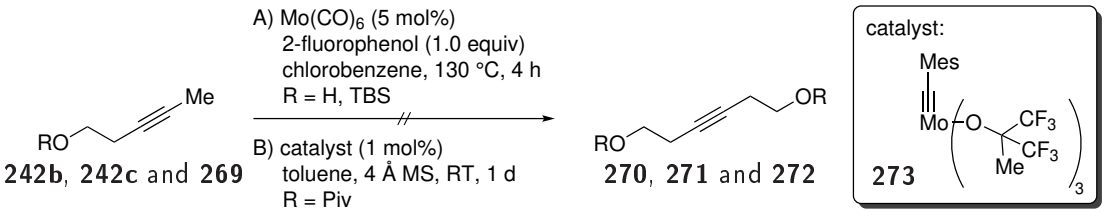
(3.36)

As the performance of a simple alkyne in the allenylation reaction had already been examined during the optimization, the substrate syntheses targeted molecules with different functional groups. In order to obtain alkynes with acid-derived side chains using the previously described cross coupling reaction, acids **263** and **265** were transferred into the respective methoxy esters **264** and **266** in 79 and 78% yield, respectively. The following SONOGASHIRA reaction was attempted with both the unprotected and the protected acid derivatives (Equation 3.37).[199] In the reaction of the free acids, the side reaction of bromide **265** to γ-butyrolactone was predominant. In case of the protected acid derivatives, the signals of the starting materials disappeared, but the absence of new signals between 2 and 2.5 ppm which matched the singlet at 3.68 ppm of the methoxy groups led to the conclusion that acid derivatives were not suitable substrates for this reaction.



(3.37)

As an alternative synthetic route towards the formation of symmetric alkynes, their direct formation *via* alkyne metathesis was examined. For this purpose, 3-pentyne-1-ol (**269**) was transformed into TBS ether **242b** and pivalic acid ester **242c**[2]. The homodimerization of 3-pentyne-1-ol (**269**) and TBS ether **242b** was attempted with $Mo(CO)_6$ (5 mol%) and 2-fluorophenol (1.0 equiv), using a procedure by GRELA *et al.* (Equation 3.38, conditions A).[201] Unfortunately, no reaction occurred and only the starting material was observed. Therefore, an alternative procedure by the group of TAMM was examined, which needed a substrate with a different protecting group to be compatible with the catalyst. The homodimerization of pivalic acid ester **242c** was attempted using 1 mol% of molybdenum catalyst **273**[3] (Equation 3.38, conditions B).[202,203] Unfortunately, again only the starting material was observed.

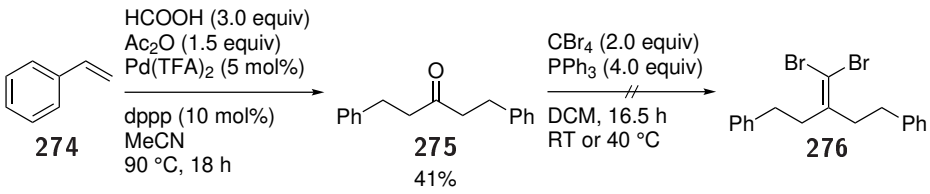


(3.38)

For the synthesis of an alkyne *via* COREY-FUCHS reaction, ketone **275** was synthesized by a palladium-catalyzed carbonylation of styrene (**274**).[204] The reaction with 3.0 equiv formic acid,

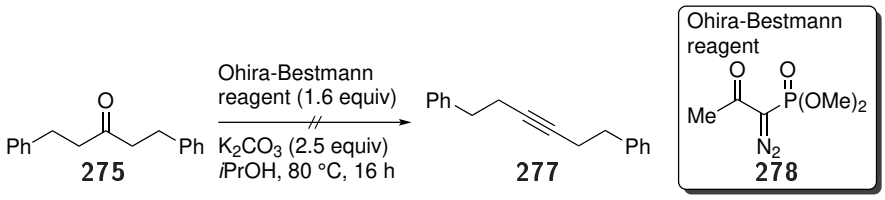
[2]Pivalic acid ester **242c** was synthesized by F. Krätzschmar.[200]
[3]Catalyst **273** was provided by Ò. Àrias, TU Braunschweig.

1.5 equiv acetic anhydride, 5 mol% $Pd(TFA)_2$ as the catalyst and 10 mol% 1,3-bis(diphenylphosphino)propane (dppp) as the ligand afforded ketone **275** in 41% yield (Scheme 3.15). Consequently, the formation of dibromide **276** was attempted with a procedure by MAK.[205] Unfortunately, the use of carbon tetrabromide (2.0 equiv) and triphenylphosphine (4.0 equiv) at room temperature or 40 °C did not lead to the formation of dibromoalkene **276** (Scheme 3.15). A slight upfield shift of the NMR signals of the methylene groups and the observation of a new unpolar species in the TLC hinted at the possible product formation, but only 64% of the starting material was isolated. In mass spectrometric analysis, the mass and isotopic pattern of the desired product could not be observed.



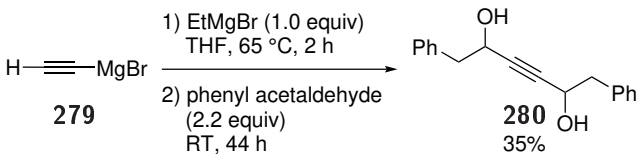
Scheme 3.15: Synthesis of ketone **275** and attempted COREY-FUCHS reacion.

As the SEYFERTH-GILBERT homologation also uses carbonyl compounds as starting material, the reaction of ketone **275** with the OHIRA-BESTMANN reagent (**278**, 1.6 equiv) and K_2CO_3 (2.5 equiv) was examined (Equation 3.39).[206] The analysis of the reaction mixture by ^1H and ^{13}C NMR only showed the starting material. In ^{31}P NMR, the shift of the signal of phosphonate **278** from 14.2 ppm to 22.3 ppm indicated its possible transformation into the reactive anionic intermediate.



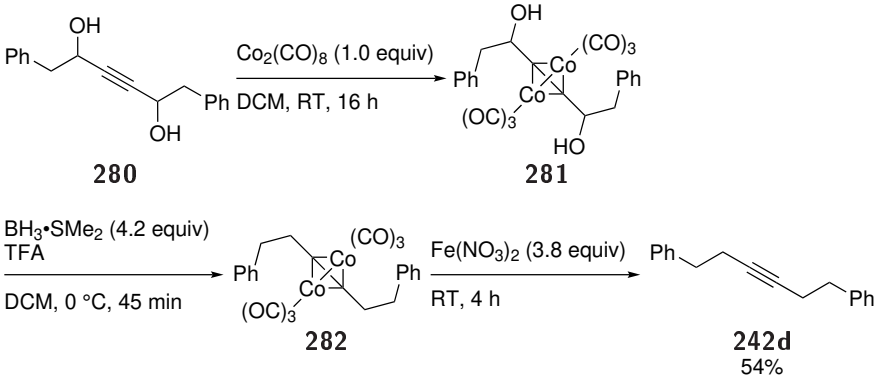
(3.39)

Due to the transformation of a carbonyl group into a triple bond not being successful, the introduction of the triple bond as a whole was considered. The groups of BROADBENT and ZHOU used acetylene bismagnesium bromide for the synthesis of symmetric alkynes.[207,208] Based on their work, the synthesis of propargylic diol **280** was conducted by first forming the bis-GRIGNARD reagent from ethinyl magnesium bromide and ethyl magnesium bromide and then adding phenyl acetaldehyde (2.2 equiv) (Equation 3.40). Compound **280** was obtained in 35% yield.



(3.40)

In order to reduce diol **280**, the triple bond was protected as dicobalt complex **281** using 1.0 equiv $Co_2(CO)_8$.[209] The reduction was conducted with 4.2 equiv of borane dimethylsulfide complex and the final deprotection of complex **282** with 3.8 equiv $Fe(NO_3)_2$ afforded alkyne **242d** in 54% yield (Scheme 3.16).[209]

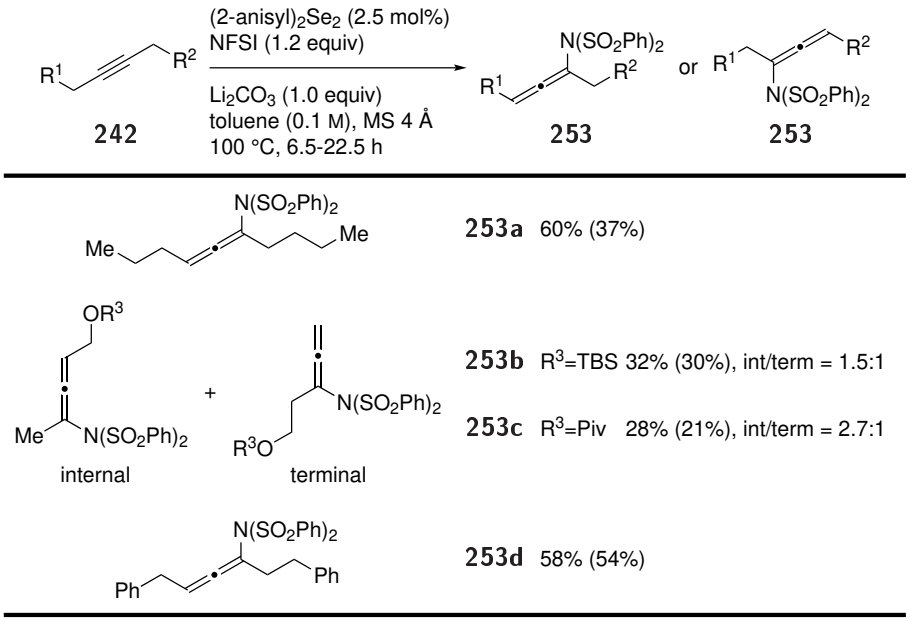


Scheme 3.16: Protection of alkyne **280** as dicobalt complex **281** and subsequent reduction and deprotection.[209]

The allenylation of the obtained alkynes **242** was conducted under optimized conditions with 2.5 mol% $(2\text{-anisyl})_2Se_2$, 1.2 equiv NFSI, 1.0 equiv Li_2CO_3 and molecular sieves in toluene at 100 °C (Table 3.39). Allenes **253** were obtained in moderate to good yields. Alkynes **242a** and **242d**, that contained simple alkyl or aryl moieties, gave similarly high yields of 60 and 58%, respectively. With TBS ether **242b** and pivalic acid ester **242c**, two products, the internal allene and the terminal allene, were formed in combined yields of 32 and 28%, respectively. The internal allenes have a signal for the vinylic proton at 5.18 or 5.12 ppm, respectively, which is similar to the shift of 5.02 ppm of the respective signal in allene **253a**. The signal of the allylic methylene group splits into two doublets of doublets at approx. 4.2 ppm due to the axial chirality of the molecule. In comparison, in the spectrum of the terminal allene, two triplets at 4.7 and 3.7-4.2 ppm were observed for the vinylic protons and the carbinol protons (Figure 3.12). The ratio of the two products was 1.5:1 (TBS ether) or 2.7:1 (pivalic acid ester) in favor of the internal allene.

As the allenylation uses an endogenous nucleophile originating from NFSI, the question came up if the use of $[TMPyF][BF_4]$ (**65**) as a bulky oxidant would allow for the use of external nucleophiles, like it was conducted by Zhao *et al.* in their pyridination reaction.[69] The following reactions of 5-decyne (**242a**) with 1.2 equiv of $[TMPyF][BF_4]$ (**65**) as the oxidant and 1.0 equiv of either $HN(SO_2Ph)_2$ or $KN(SO_2Ph)_2$ as the nucleophile did not yield the desired product, but in both cases, traces of the selenofunctionalized product **254** were observed (Equation 3.41).

Table 3.39: Synthesis of allenylamides **253**.[a]



[a] NMR yield, standard: TMB, isolated yield in brackets.

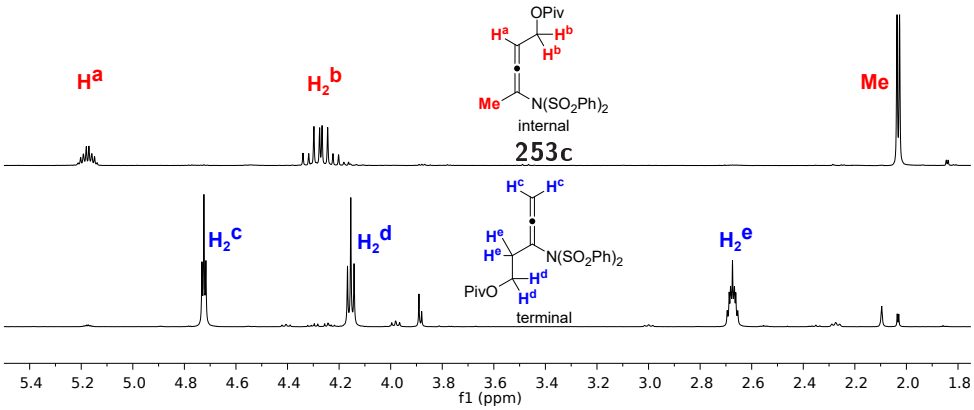
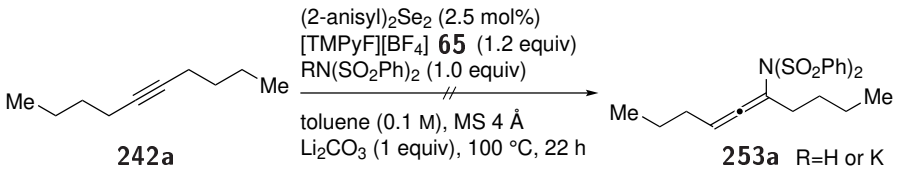


Figure 3.12: Comparison of relevant regions of the ^{1}H NMR spectra of the internal and terminal allene **253c**.



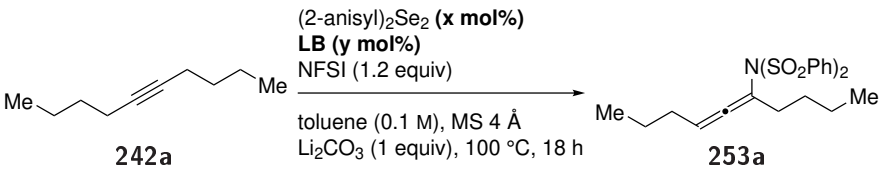
(3.41)

3.5.3 Mechanistic investigations

As was previously explained (cf. Subsection 1.1.1), selenium can act as a π-acid to activate the alkyne, but it could also activate the nucleophile by a Lewis basic interaction. In order to find

out if the reaction relied on a LEWIS basic activation, the reaction was carried out using different LEWIS bases instead of (2-anisyl)$_2$Se$_2$. When 5 mol% of Se=PPh$_3$ were used, product **253a** was formed in 10% yield (Table 3.40, entry 1). With 10 mol% of DMF, no product formation was observed (Table 3.40, entry 2). From these results, it was concluded that LEWIS base activation played only a small role in the catalytic allenylation. To examine if the addition of a LEWIS base to the reaction under otherwise unchanged conditions would lead to an increased yield, 5 mol% of Se=PPh$_3$ were added to the reaction along with 2.5 mol% of (2-anisyl)$_2$Se$_2$ (Table 3.40, entry 3). The formation of allene **253a** was observed in 56%, which was a small decrease compared to the optimized reaction conditions.

Table 3.40: Allenylation of 5-decyne **242a** using LEWIS base.



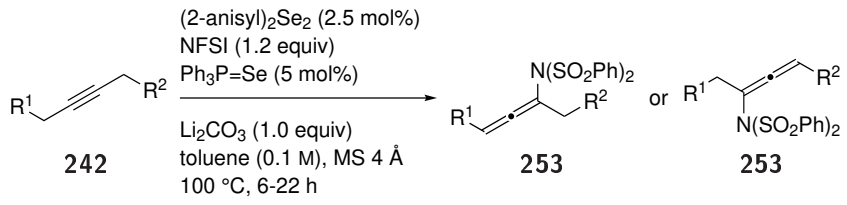
242a **253a**

entry	amount R_2Se_2	LB (amount)	yield[a]
1	-	Se=PPh$_3$ (5 mol%)	10%
2	-	DMF (10 mol%)	-
3	2.5 mol%	Se=PPh$_3$ (5 mol%)	56%

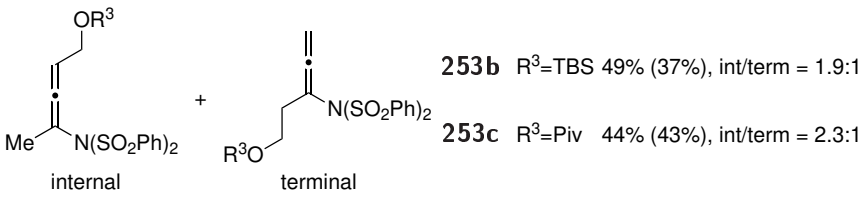
[a] NMR yield, standard: TMB, isolated yield in brackets.

As the allenylation of alkynes **242b** and **242c** resulted in moderate yields, it was attempted to increase the yield by adding 5 mol% Se=PPh$_3$. Indeed, allenes **253b** and **253c** were obtained in improved yields of 49 and 44% (Table 3.41). Again, the formation of the internal allenes was preferred with ratios of 1.9:1 (TBS ether) or 2.3:1 (pivalic acid ester).

Table 3.41: Amidoallenylation of alkynes **242b** and **242c** using additional LEWIS base.[a]

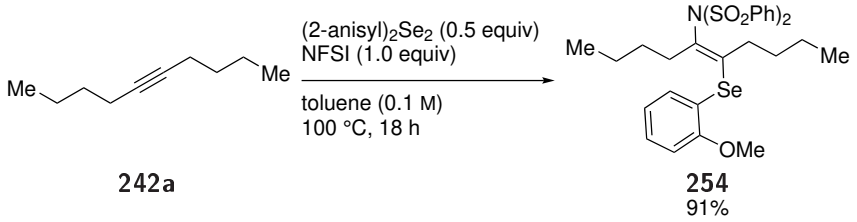


242 **253** **253**



[a] NMR yield, standard: TMB, isolated yield in brackets.

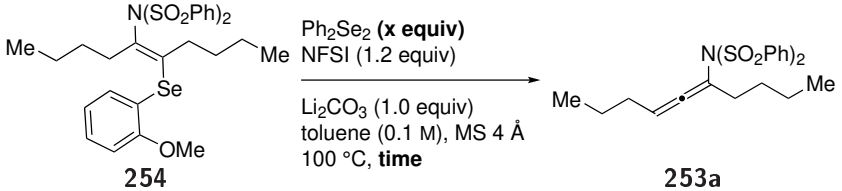
During the optimization of the reaction conditions, the formation of the selenofunctionalized compound **254** was observed in many cases, which is consistent with the isolation of such a species by REICH and BACK.[190–193] As BACK was able to transfer the selenium adduct into the respective allene by oxidizing the selenium moiety (cf. Scheme 3.13), it was assumed that compound **254** was an intermediate in the selenium-catalyzed allenylation and its oxidation would lead to the elimination of the selenium species and formation of allenes **253**. In order to verify this assumption by further experiments, compound **254** was synthesized from 5-decyne (**242a**) with 0.5 equiv of (2-anisyl)$_2$Se$_2$ and 1.0 equiv of NFSI in 91% (Equation 3.42).



242a **254** 91% (3.42)

In the first experiments, selenofunctionalized product **254** was subjected to the optimized reaction conditions, but the diselenide catalyst was left out. The formation of product **253a** was only observed in traces, leading to the conclusion that the oxidation of the selenium moiety by NFSI was not enough to initiate its elimination (Table 3.42, entries 1 and 2). During the mechanistic investigations of the photo-aerobic selenium-π-acid catalyzed lactonization, the formation of trimeric selenonium ions from diphenyl diselenide was observed.[144] It was proposed that these trimers transfer a phenylselenium moiety onto the substrate. The hypothetical transfer of such a moiety onto selenofunctionalized product **254** could facilitate the elimination of the selenium moiety. Therefore the question arose, if the addition of diphenyl diselenide to the intermediate would lead to the formation of product **253a**. Consequently, the reaction was repeated and 0.5 equiv Ph_2Se_2 were added (Table 3.42, entry 3). Unfortunately, no product formation was observed.

Table 3.42: Experiments on the formation of allene **253a** from compound **254**.

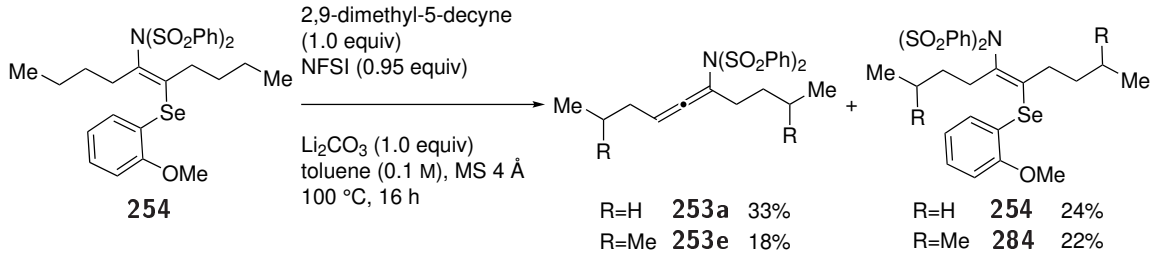


254 **253a**

entry	Ph_2Se_2	time	yield[a]
1	-	3 h	2%
2	-	18.5 h	8%
3	0.5 equiv	18.5 h	-

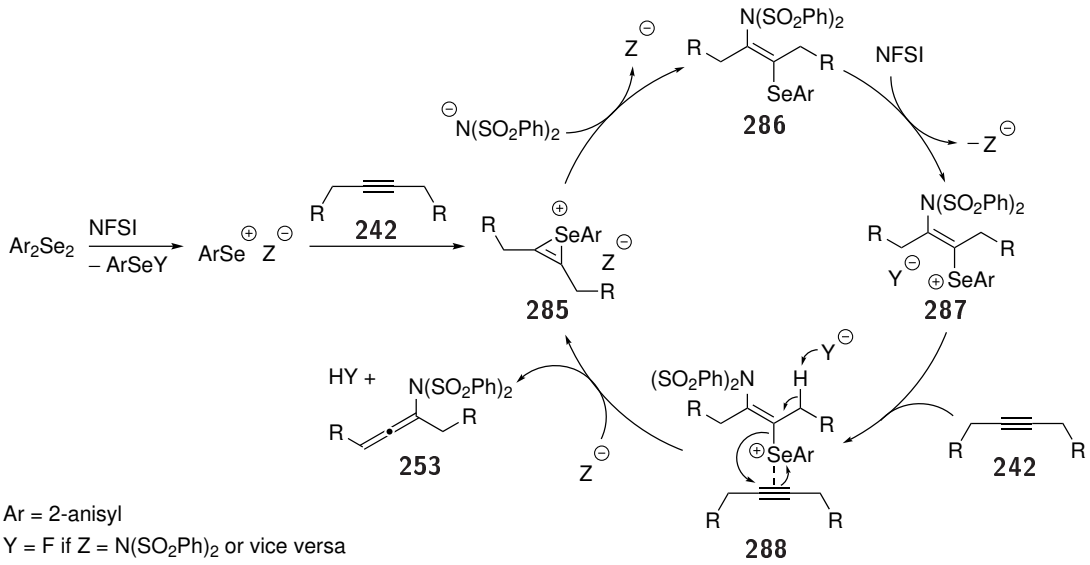
[a] NMR yield, standard: TMB.

As the product formation from compound **254** could not be initiated with an excess of NFSI or the addition of diphenyl diselenide, it came to mind that the transfer of the oxidized selenium moiety to an unreacted alkyne molecule could lead to product formation and propagate the reaction. Such a mechanism is remotely reminiscent of the transfer of chalcogenium groups between olefins which was reported by DENMARK (cf. Subsection 1.2.4) and would explain the observation of leftover selenofunctionalized intermediate after full conversion of the alkyne starting material.[109,110] To examine if the investigated reaction followed this mechanism, selenofunctionalized compound **254** was reacted with 1.0 equiv 2,9-dimethyl-5-decyne and 0.95 equiv NFSI to avoid the decomposition of the alkyne by an excess of oxidant (Equation 3.43). Indeed, the formation of allenes **253a** and **253e** in 33 and 18% yield, the formation of the selenofunctionalization product **284** from the added alkyne in 22% yield and the formation of (2-anisyl)$_2$Se$_2$ in 9% were observed.



(3.43)

Based on these findings, a mechanism for the reaction was proposed (Scheme 3.17). In the initial phase, the diselenide catalyst is oxidized by NFSI and selenirenium ion **285** is formed from $ArSe^+$ and alkyne **242**. Opening of the ion by $N(SO_2Ph)_2^-$ and subsequent oxidation by another entity of NFSI leads to the formation of oxidized selenofunctionalized intermediate **287**. The elimination of the selenium moiety is facilitated by the coordination of alkyne **242** (intermediate **288**) and product **253** is released with simultaneous reformation of selenirenium ion **285** from the selenium moiety and the coordinated alkyne.



Scheme 3.17: Proposed catalytic cycle for the selenium-π-acid catalyzed synthesis of allenylamides.

3.6 Synthesis and application of chiral diselenide catalysts

As was already explained (cf. Subsection 1.2.4, Section 2), the synthesis of sterically demanding diselenides was to be examined and binaphthyl derivatives appeared as suitable structural motifs. The first of two designs of chiral binaphthyl-derived diselenides, compound **121**, is based on the chiral phosphoric acids **290** used by Akiyama, Terada and List.[120–123] An important aspect in the design of phosphoric acids **290** was the attachment of substituted aryl moieties *ortho* to the oxygen atoms, as using an unsubstituted phenyl ring led to low selectivity, but substitution with bulky 2,4,6-triisopropylphenyl moieties resulted in high selectivity.[123] Therefore, diselenide **121** should also feature this kind of substitution (Figure 3.13, left side). The second design of chiral binaphthyl diselenides is based on a work by Tomoda and Iwaoka, who used diselenide **291** in an asymmetric ring-opening reaction and achieved *ee*'s up to 50%.[210] In order to improve the selectivity, envisioned catalyst **122** contains additional aryl moieties in proximity to selenium (Figure 3.13, right side).

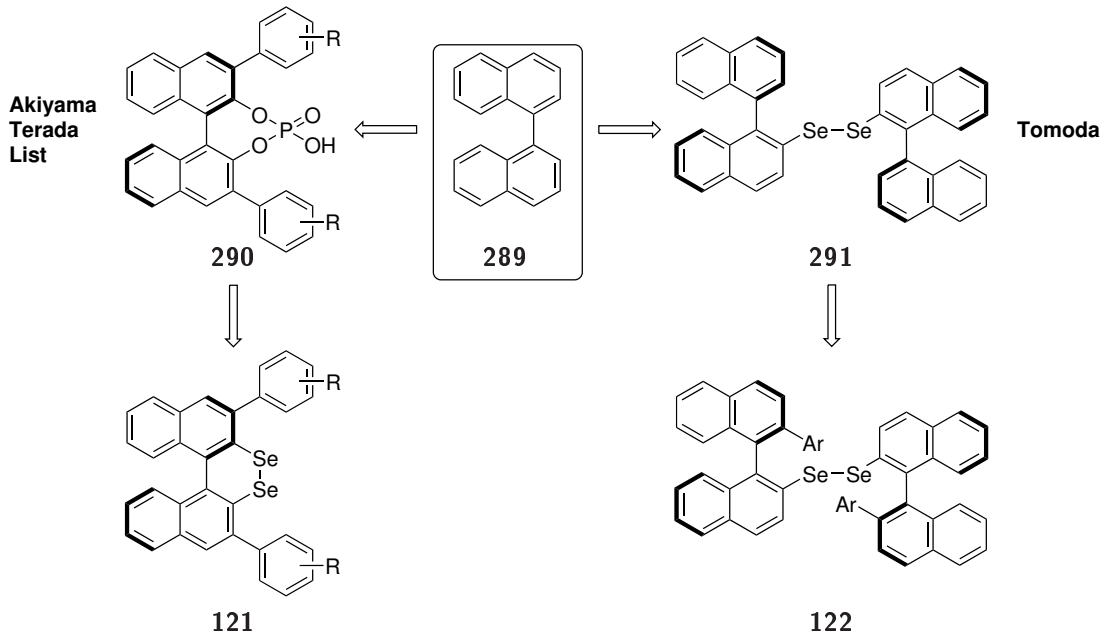
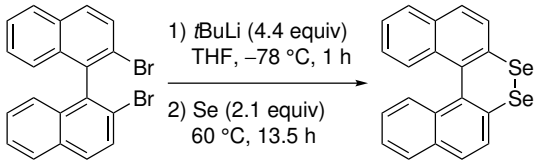


Figure 3.13: Binaphthyl (**289**) and derived chiral catalysts.

3.6.1 Examination of selenation methods

As the selenation step is crucial in the synthesis of diselenide catalysts, preliminary investigations on different methods for the introduction of the diselenide bridge in binaphthyl derivatives were carried out. A common method for diselenation is the metalation of an aryl halide and subsequent selenation with selenium powder.[114,211] The reaction of racemic binaphthyl dibromide **292** with *tert*-butyl lithium (4.4 equiv) at −78 °C, subsequent addition of selenium powder (2.1 equiv) and heating at 60 °C afforded the diselenide **293** in 12% yield (Equation 3.44).



292 **293** 12%

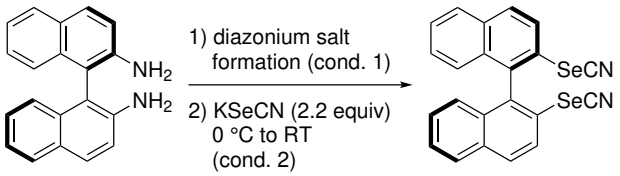
(3.44)

As an alternative method, the reduction of selenocyanates was examined. Selenocyanates are easily reduced or hydrolized to diselenides in reactions with hydrides, hydroxides or alkoxides.[212–214] As they can be obtained in a SANDMEYER-type reaction from amines, the preparation of binaphthyl diselenide from binaphthyl diamine would only take two steps. The first attempt of the synthesis of (*R*)-2,2′-diselenocyanato-1,1′-binaphthalene (**295**) followed the synthesis of an aryl selenocyanate by NAKAMURA and coworkers.[215] The diazonium compound was prepared from (*R*)-BINAM (**294**) by addition of 6 N HCl (12 equiv) and $NaNO_2$ (3.0 equiv) at 0 °C. The selenocyanate source (KSeCN, 2.2 equiv) was added as an aqueous solution (Table 3.43, entry 1). The formation of the product was not observed, instead two side products were isolated. ^{1}H NMR analysis of the side products showed only signals in the aromatic region. In both cases, the integrals indicated symmetrically substituted products. The amount of signals in the ^{13}C NMR spectrum supported this assumption. Furthermore, as in both cases only 10 signals were observed, functionalization with a carbon-containing unit can be excluded. In both products, one proton was shifted to low field (8.62 ppm and 9.37 ppm, respectively) compared to the signals in (*R*)-BINAM (**294**), which are between 7 and 8 ppm, so an electron-withdrawing substituent seems probable.[216] Since TOMODA had reported an indicative signal at 100.7 ppm for the SeCN moiety, which was not observed in either of the products, and the correct mass was not found in mass spectrometric analysis, it was concluded that the desired product had not been formed.[210] As a consequence, the conditions for the diazonium salt formation as well as the conditions for the addition of the nucleophile were changed. The diazonium salt was formed with 7.0 equiv *tert*-butyl nitrite and 8.0 equiv boron trifluoride diethyl etherate at −30 °C and −5 °C. It was isolated by filtration and added to a solution of 2.2 equiv KSeCN in acetonitrile at 0 °C (Table 3.43, entry 2). The new conditions led to the formation of the product in 5% yield. The analytical data matched those reported by TOMODA *et al.*[210]

In order to increase the yield, several variations for the addition of the nucleophile were tested. The diazonium salt was prepared with *tert*-butyl nitrite as described above, but the filtration of the diazonium salt was avoided in order not to lose too much of the compound in the filter. First, a one-pot synthesis was attempted. The diazonium salt was kept in THF and KSeCN was added in THF. As the solubility in THF of both the salt and KSeCN were low, the desired product was not formed (Table 3.43, entry 3). In the next reaction, the solvent was removed by a syringe and KSeCN was added in acetonitrile. The product was obtained in 14% yield (Table 3.43, entry 4). In order to increase the nucleophilicity of the selenocyanate, 2.2 equiv 18-crown-6 were added to

the solution of KSeCN in acetonitrile, which was then added to the diazonium salt. The previous results could not be improved and the yield in this reaction was 12% (Table 3.43, entry 5). As the yield was still quite low, no further attempts to synthesize the desired product were made.

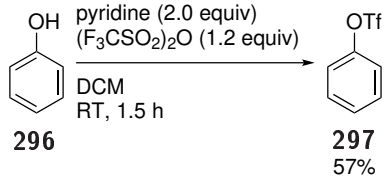
Table 3.43: Tested conditions for the synthesis of (*R*)-2,2′-diselenocyanato-1,1′-binaphthalene (**295**).



294 **295**

entry	conditions 1	conditions 2	yield
1	$NaNO_2$, 6 N HCl, 0 °C	H_2O	-
2	tBuNO$_2$, $BF_3 \cdot OEt_2$	MeCN	5%
3	tBuNO$_2$, $BF_3 \cdot OEt_2$	one-pot; THF	-
4	tBuNO$_2$, $BF_3 \cdot OEt_2$	remove solvent by syringe; MeCN	14%
5	tBuNO$_2$, $BF_3 \cdot OEt_2$	remove solvent by syringe; 18-crown-6 in MeCN	12%

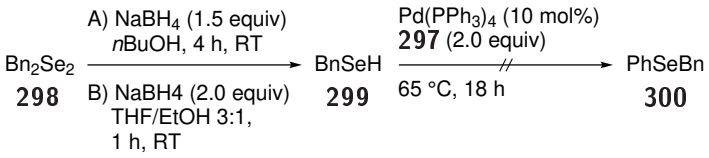
Another possible way for the selenation could be the synthesis of an aryl alkyl selenide, followed by cleavage of the alkyl residue. The attempted synthesis of the selenide was carried out using a triflate and dibenzyl diselenide. For this purpose, phenyl trifluoromethanesulfonate (**297**) was prepared from phenol (**296**) in 57% yield, using pyridine (2.0 equiv) and trifluoromethanesulfonic anhydride (1.2 equiv) following a procedure by HUFFMAN and colleagues (Equation 3.45).[217]



296 **297** 57%

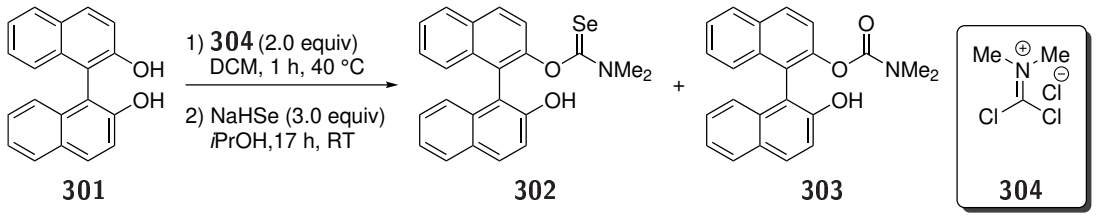
(3.45)

In order to synthesize phenyl benzyl selenide (**300**), the preparation of benzylselenol (**299**) was attempted using two different methods.[218,219] In the first method, 1.5 equiv sodium borohydride were added to a solution of dibenzyl diselenide (**298**) in *n*-butanol and stirred for 4 h at room temperature. In the second method, 2.0 equiv sodium borohydride were added to a solution of dibenzyl diselenide (**298**) in a mixture of THF and ethanol (3:1) and stirred for 1 h at room temperature. The decoloration of the formerly yellow solutions indicated the reduction of the diselenide to the selenolate. To both solutions, $Pd(PPh_3)_4$ (10 mol%) and phenyl triflate (**297**, 2.0 equiv) were added and heated at 65 °C for 18 h (Equation 3.46).[220,221] In both cases, the desired product could not be isolated, but dibenzyl diselenide was reisolated. A possible reason for this is the recombination reaction of benzylselenol to dibenzyl diselenide being faster than the reaction with phenyl triflate.



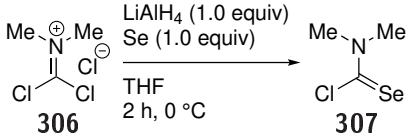
(3.46)

The NEWMAN-KWART rearrangement is a way of obtaining thiophenols from phenols. This is accomplished by a rearrangement of thiocarbamates that can be either thermally induced[222,223] or palladium-catalyzed.[224] In 2013, PITTELKOW and coworkers presented a variation of this reaction that allowed to make selenophenols from phenols by using a thermally induced rearrangement similar to the NEWMAN-KWART rearrangement.[225] They used *O*-aryl selenocarbamates that undergo a thermally induced rearrangement to *Se*-aryl selenocarbamates. In order to apply this protocol to the synthesis of binaphthyl diselenides, binaphthyl di(*O*-aryl selenocarbamate) could be used for the rearrangement, and the carbamate moieties cleaved to obtain the diselenol, which could in turn be oxidized to the diselenide. The synthesis of *O*-aryl selenocarbamate **302** was performed according to PITTELKOW *et al.*[225] Racemic BINOL (**301**) was heated with 2.0 equiv of *N*-(dichloromethylene)-*N*-methylmethanaminium chloride (**304**) for 1 h and the solution was added to a freshly prepared NaHSe solution (Equation 3.47). Unfortunately, the desired disubstituted product was not formed and instead, two monosubstituted products were isolated in traces. The shifts of the ^{1}H NMR signals in the aromatic region differed only slightly, but the two singlets of the NMe_2 moiety were observed at 3.30 and 2.59 ppm for product **302** and at 2.74 and 2.43 ppm for product **303**. By comparison with literature and mass spectrometric analysis, the compounds were identified as the mono-selenocarbamate (compound **302**) and the mono-carbamate (compound **303**).[226]



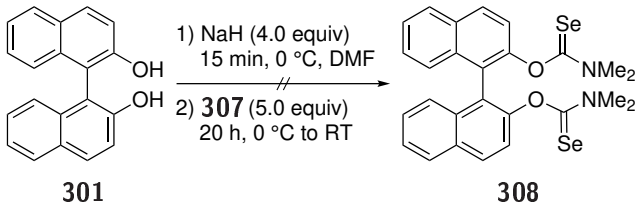
(3.47)

As for the synthesis of thiocarbamates, *N,N*-dimethylthiocarbamoyl chloride is used, the use of its selenium analogue **307** was attempted.[227] *N,N*-dimethylselenocarbamoyl chloride (**307**) was prepared from dichloromethylene-dimethyliminium chloride (**306**), 1.0 equiv lithium aluminum hydride and 1.0 equiv selenium according to a synthesis of IMAKUBO (Equation 3.48).[228]



(3.48)

The prepared reagent was then used without further purification in a reaction with the freshly prepared sodium alcoholate of racemic BINOL (**301**) (Equation 3.49). Unfortunately, the desired product was not formed and BINOL (**301**) was completely reisolated.

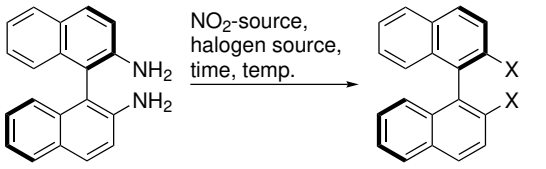


301 **308** (3.49)

3.6.2 Synthesis of di(binaphthyl) diselenides

The synthesis of di(binaphthyl)diselenides **122** began with the formation of binaphthyl dihalides **309**, **310** and **311** from (*R*)-BINAM (**294**) *via* SANDMEYER-type reactions.[229–232] The formation of the diazonium salt was achieved with *tert*-butyl nitrite or sodium nitrite and the corresponding copper(I) or potassium salts as halogen source (Table 3.44). For the bromination and iodination, 48% HBr and PTSA were used as additives. The best yield of 58% was obtained in the iodination reaction, the chlorination had a similar yield (56%) and the bromination provided the product in 50% yield.

Table 3.44: Halogenation of (*R*)-BINAM (**294**) in SANDMEYER-type reactions.

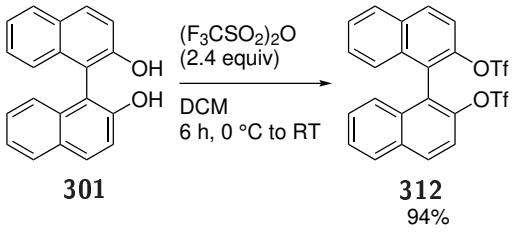


294

X = Cl **309** 56%
Br **310** 50%
I **311** 58%

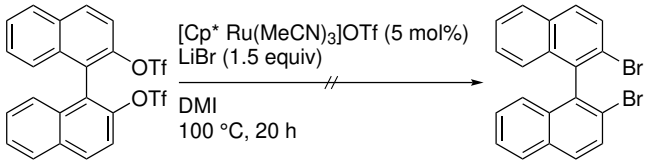
product	NO_2-source (equiv)	halogen source (equiv)	additive (equiv)	time, temp.	yield
309	tBuNO$_2$ (4.2)	$CuCl_2$ (2.6 equiv)	-	65 °C, 16 h	56%
310	$NaNO_2$ (3.0)	CuBr (2.5 equiv)	HBr	0 °C, 30 min; RT, 16.5 h	50%
311	$NaNO_2$ (4.0)	KI (5.0 equiv)	PTSA (6.0)	10 °C, 10 min; RT, 2 h	58%

As the yields in the halogenation reactions were moderate, a method by HAYASHI and SHIRAKAWA for the formation of dibromide **310** from the respective bis(triflate) **312** was examined.[233] Binaphthyl bis(trifluoromethanesulfonate) (**312**) was prepared from BINOL (**301**) in 94% yield using 2.4 equiv trifluoromethanesulfonic anhydride (Equation 3.50).[217]



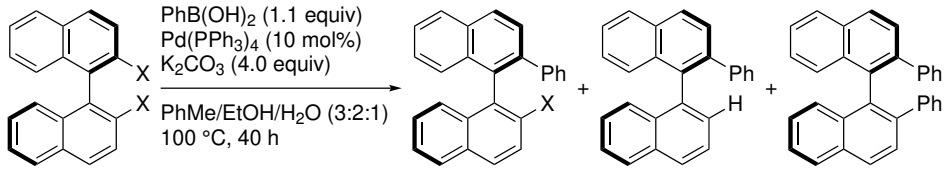
301 312 94% (3.50)

The reaction of triflate **312** with [Cp*Ru(MeCN)$_3$]OTf (5 mol%) and lithium bromide (1.5 equiv) in DMI did not afford the desired product (Equation 3.51).[233] Instead, the entire starting material was reisolated.



312 310 (3.51)

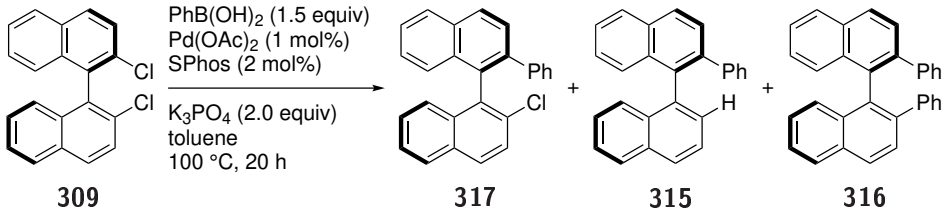
The monoarylation of binaphthyl dihalogenides **309**, **310** and **311** was first examined by conducting a Suzuki coupling with phenyl boronic acid. The couplings of dibromide **310** and diiodide **311** were conducted with 10 mol% Pd(PPh$_3$)$_4$, 1.1 equiv boronic acid and 4.0 equiv potassium carbonate as the base (Equation 3.52).[180] Unfortunately, only a mixture of products was observed, which could not be separated by column chromatography. In the mass spectra, evidence of the desired products **313** and **314** was found, as well as a hydrogenated product **315** with a phenyl ring in 2-position and hydrogen instead of halogen in 2′-position. The diarylated product **316** was also present in the mixture. Due to the similarity of the products with only aromatic hydrogen atoms, the ratio of the products could not be determined in NMR spectroscopy. In the reaction with diiodide **311**, 7% of the starting material were reisolated.



X = Br **310**, X = I **311** — X = Br **313**, X = I **314**, **315**, **316** (3.52)

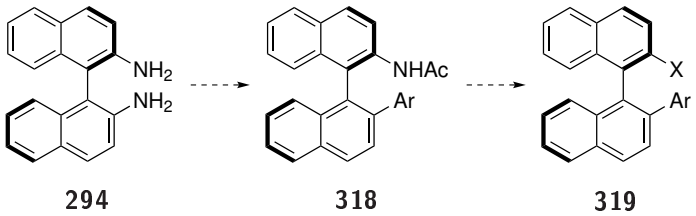
The conditions used for the dibromide and diiodide were applied in a Suzuki reaction of dichloride **309**, but no conversion was observed and the starting material was recovered completely. Therefore, conditions used by Chatani and Tobisu were applied instead and the reaction of dichloride **309** with palladium acetate (1 mol%), SPhos (2 mol%), phenyl boronic acid (1.5 equiv) and potassium phosphate (2.0 equiv) showed conversion (Equation 3.53).[234] A similar mixture of the desired, the hydrogenated and the diarylated product, like in the reactions of the dibro-

mide and diiodide, was obtained, but could not be separated. 39% of the starting material were reisolated.



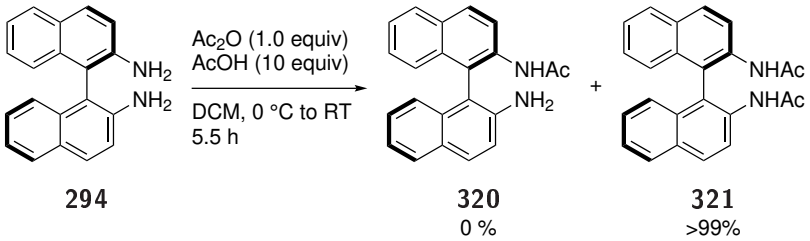
(3.53)

An alternative for this synthesis is the monoacetylation of BINAM, followed by a SANDMEYER-type transformation of the unprotected amino group into a halogen. In a cross-coupling reaction, this halogen atom could be substituted by an aryl residue. After deprotection and another SANDMEYER-type halogenation, the precursor for the selenation would be obtained (Scheme 3.18).



Scheme 3.18: Possible synthesis of monoarylated binaphthyl halogenide **319**.

The monoacetylation reaction was attempted with a procedure by SHI and colleagues using 1.0 equiv acetic acid anhydride and 10.0 equiv acetic acid in DCM (Equation 3.54).[235] Unfortunately, all material was converted to the diacetylated product, which can be seen the ^{1}H NMR spectrum, where the symmetric substitution is indicated by a single set of aromatic protons between 7.0 and 8.5 ppm and two matching singlets at 6.91 (NH) and 1.83 ppm (methyl at acetyl moiety) (Figure 3.14). This assumption was confirmed by a comparison with spectra available for the monoacetylated product.[236]



(3.54)

3.6.3 Synthesis of arylated binaphthyl diselenides

As the attempts in the synthesis of di(binapthyl) diselenides did not afford the desired products, the work was focussed on the synthesis of binaphthyl diselenides. In order to synthesize sterically demanding catalysts, the arylation of binaphthyl derivatives in 3- and 3′-position was

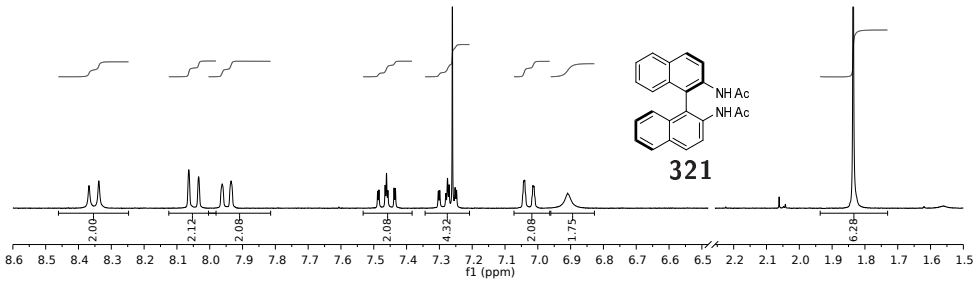
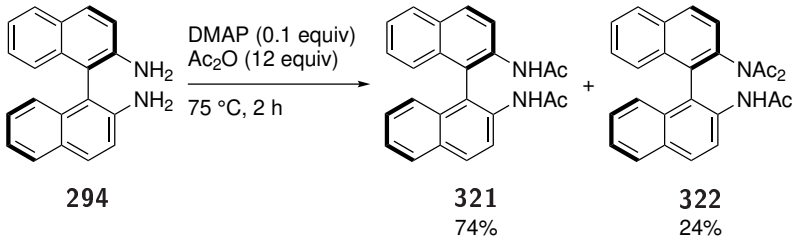


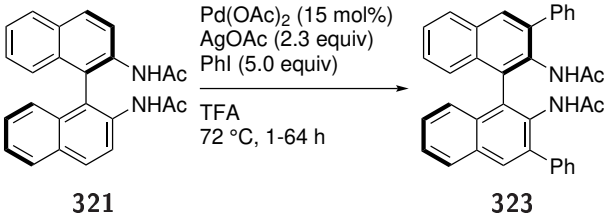
Figure 3.14: ^{1}H NMR spectrum of the product of the attempted monoacetylation.

attempted. One way of achieving this is the protection of the amino functions of BINAM (**294**) with acetyl moieties, followed by arylation *via* Daugulis-Zaitsev coupling. The acetylation of the amino groups was conducted with DMAP (0.1 equiv) and acetic acid anhydride as the solvent (12.0 equiv) (Equation 3.55).[237] The desired product **321** was obtained in a good yield of 74%, but side product **322** was isolated in 24% yield. This side product contains one additional acetyl moiety at one of the nitrogen atoms, which was determined from the three singlets at 2.28, 1.96 and 1.80 ppm with a respective integral of 3 (3×Ac) and the signals in the range between 6.8 and 8.5 ppm with a combined integral of 13 (aromatic system and NH). As in the previously attempted monoacetylation (Equation 3.54), the diacetylated product was obtained in quantitative yield without a side product, that approach was preferred for future syntheses of diacetylated BINAM (**321**).



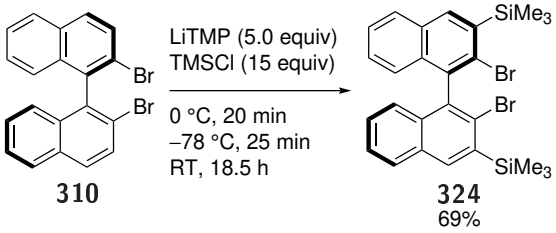
(3.55)

The arylation of the protected binaphthyl diamine **321** was carried out as described by Stahl *et al.* with a Daugulis-Zaitsev coupling.[237] Bisamide **321** was heated to 72 °C with palladium acetate (0.15 equiv), silver acetate (2.3 equiv) and iodobenzene (5.0 equiv) in trifluoroacetic acid (Equation 3.56). The reaction afforded a mixture of products that could not be separated. The formation of the desired product could be determined by mass spectrometry, but the isolation of the product was not successful.



(3.56)

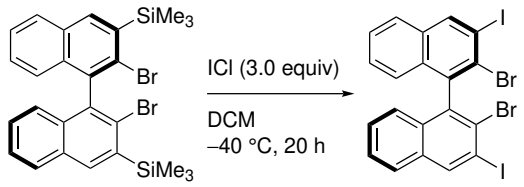
As an alternative route to 3,3′-arylated binaphthyl derivatives, a strategy based on works of WIDHALM[238] and MATTSON[239] was carried out. The synthesis started from (*R*)-2,2′-dibromo-1,1′-binaphthalene (**310**) with a disilylation in 3 and 3′ position. The reaction with LiTMP (5.0 equiv) and TMSCl (15 equiv) afforded the disilylated product **324** in 69% yield (Equation 3.57). The successful reaction was indicated by the appearance of the signals of the trimethylsilyl groups at 0.53 ppm and the disappearance of the signals of two protons in the aromatic region. Additionally, the analytical data matched the reported data by Widhalm *et al.*[238] As a side product, the monosilylated product was isolated in 2%.



310 **324** 69%

(3.57)

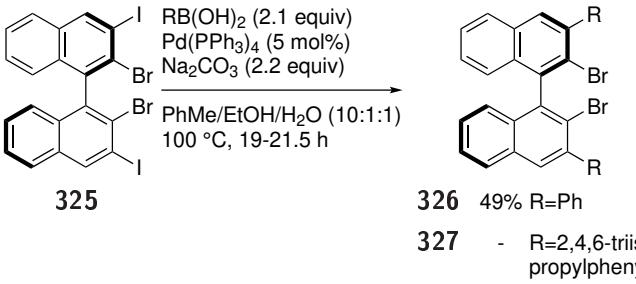
In order to facilitate a selective cross-coupling reaction, the trimethylsilyl moieties were replaced by iodides in the reaction with iodine monochloride (3.0 equiv). Dibromodiiodobinaphthalene **325** was obtained in 89% yield (Equation 3.58). In the ^{1}H NMR spectrum, the protons *ortho* to the iodides were shifted to lower field (singlet at 8.61 ppm instead of 8.09 ppm in the starting material) and the signals of the trimethylsilyl groups disappeared. The data was in agreement with the one reported by Widhalm *et al.*[238]



324 **325** 89 %

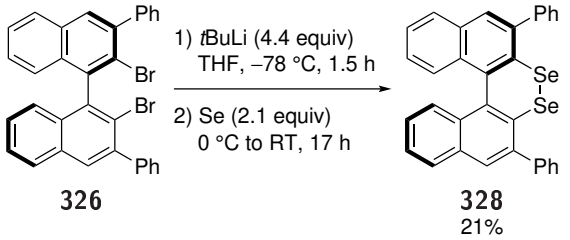
(3.58)

The SUZUKI coupling of compound **325** with 2.1 equiv phenyl boronic acid to biarylated dibromide **326** was achieved in 49% yield with 5 mol% $Pd(PPh_3)_4$ as the catalyst and 2.2 equiv of sodium carbonate as the base (Equation 3.59).[238] The reaction was chemoselective and only the iodine atoms were replaced by phenyl moieties. The formation of the product was confirmed by mass spectrometry and comparison of NMR data with literature data.[238] 7% of the starting material was reisolated, as well as 22% of the monoarylated product. The reaction with 2,4,6-triisopropylphenylboronic acid under the same conditions did not afford the desired product **327**, but 62% of the starting material **325** were reisolated.



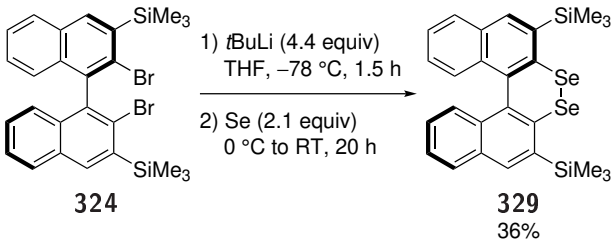
(3.59)

To obtain a diselenide, the diarylated binaphthyl derivative **326** was then treated with *tert*-butyl lithium (4.4 equiv) and selenium powder (2.1 equiv). Diselenide **328** was obtained in 21% yield (Equation 3.60), which was confirmed by mass spectrometry with the help of its isotope pattern.



(3.60)

To see if trimethylsilyl groups were also useful as steric bulk, compound **324** was also selenated in order to examine its potential as a catalyst. The procedure corresponded to the one used for the arylated binaphthyl derivative **326** and the silylated diselenide **329** was obtained in 36% yield (Equation 3.61). Its formation was also confirmed *via* mass spectrometry.

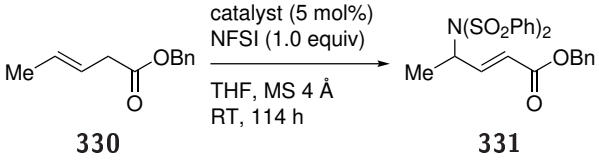


(3.61)

3.6.4 Application of diselenide catalysts

With the two binaphthyldiselenide catalysts **328** and **329** in hand, the amination of pentenoic acid ester **330** under the previously established conditions by Breder *et al.* was performed (Table 3.45).[63] With catalyst **328**, product **331** was obtained in 5% yield after 114 h. However, the enantiomeric excess was 53%. This finding is in agreement with results by Breder and Maruoka, who also found that a rigid catalyst structure leads to stereoinduction.[119,240] The reaction with catalyst **329** did not afford the desired product.

Table 3.45: Amination of pentenoic acid ester **330** with chiral catalysts **328** and **329**.

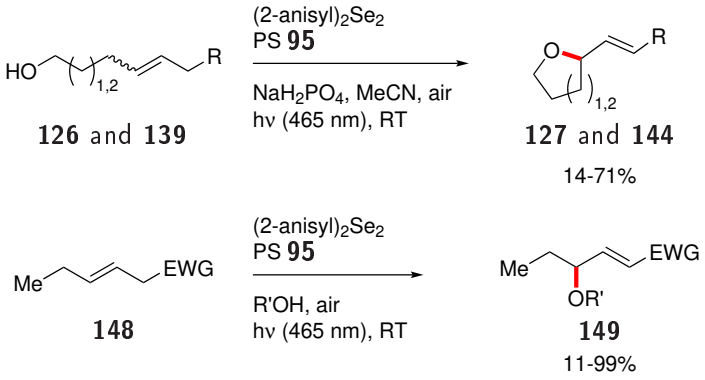


330 **331**

entry	catalyst	yield	*ee*
1	**328**	5%	53%
2	**329**	-	-

4 Conclusion and Outlook

Based on the recently disclosed work on photo-aerobic selenium-π-acid catalyzed acyloxylation of simple alkenes by BREDER *et al.*,[91] this methodology was successfully expanded to the use of alcohols as exogenous nucleophiles.[134] Both the intramolecular and intermolecular reaction proceeded in good yields with $(2\text{-anisyl})_2Se_2$ as the diselenide catalyst and *p*-MeO-TPT (**95**) as the photosensitizer (Scheme 4.1). In the formation of tetrahydrofurans **127** and tetrahydropyrans **144**, various functional groups were tolerated. The functionalization of electron-poor alkenes **148** was most efficient with electron-poor alcohols. However, due to the weak nucleophilicity of the used alcohols, the intermolecular reaction needed higher catalyst loadings and longer reaction times which in some cases led to the decomposition of the starting material.

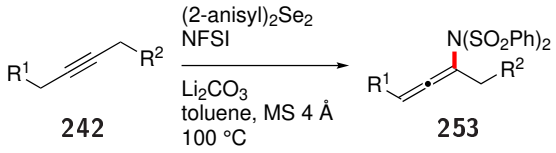


Scheme 4.1: Intra- and intermolecular etherification of alkenes **126**, **139** and **148**.[134]

Following these results, the scope of other photo-aerobic selenium-π-acid catalyzed transformations were examined after preliminary studies by C. Depken and R. Rieger.[137,142,158] In the formation of 5-membered and 6-membered ring lactones **77** and **170** from unsaturated acids **34** and **137**, substrates containing carbonyl moieties, alcohols, protected amines, substituted aryls, sterically demanding branched groups and additional double bonds were tolerated and the products were afforded in good to excellent yields.[144] Moreover, the 5-*exo*-cyclization of 4-alkenoic acid as well as the 7-*exo*-cyclization of a 6-alkenoic acid showed the regioselectivity of the reaction. In the investigation of the phosphatation of alkenes, phosphates **173** were obtained in moderate to good yields, but many substrates turned out to be problematic.[159] Nevertheless, these reactions demonstrate the versatility and further potential of photo-aerobic selenium-π-acid catalysis for the functionalization of alkenes with exogenous nucleophiles.

Aside from exogenous oxygen nucleophiles, the use of exogenous nitrogen nucleophiles was examined. Unfortunately, most of the used nitrogen compounds turned out to be unsuitable for the reaction. Only with saccharin, a moderate reactivity was observed, but two constitutional isomers were formed. Therefore, it was suspected that the use of intramolecular nucleophiles would lead to better results. The formation of indole **193** in 17% yield confirmed this assumption and initiated the investigation of the formation of tetrahydroisoquinolines. Under the conditions of

photo-aerobic selenium-π-acid catalysis, the desired product was obtained in up to 16% yield after full conversion in several optimization experiments. As this decomposition was attributed to the photocatalyst, the reaction was attempted using NFSI as the oxidant, which led to improved results.[185] Hence, the scope of this reaction concerning the substitution of the aromatic core was examined and tetrahydroisoquinolines **209** were obtained in moderate to good yields.
As in previous examples for selenium-π-acid catalysis, olefins served as substrates, another topic of this work was the use of alkynes. Following preliminary experiments,[127] the conditions for the selenium-catalyzed transformation of alkynes **242** into imidoallenes **253** using $(2\text{-anisyl})_2Se_2$ as the catalyst and NFSI as the oxidant and nucleophile were optimized (Equation 4.1). Subsequently, different syntheses of alkynes were examined and allenes **253** were obtained in good yields. In order to understand the reaction mechanism, experiments with the selenofunctionalized reaction intermediate were conducted, which led to the conclusion that the transfer of the selenium moiety to another alkyne molecule plays an important role for the propagation of the reaction.



(4.1)

During the last part of this work, the synthesis of a binaphthyl-derived diselenide catalyst was realized and it was applied in the imidation of pentenoic acid ester **330**. The product was obtained with an *ee* of 53%, which suggested that the rigid character of the catalyst was beneficial for stereoinduction. In contrast, the yield of the reaction was very low, presumably due to the reactive center being blocked by the large phenyl moieties. Therefore, future catalyst designs should feature rigidity with simultaneous accessibility of the catalytic center.
Based on the results of this thesis, the expansion of photo-aerobic selenium-π-acid catalysis to further classes of nucleophiles, like halogens or cyanides, should be the focus of future investigations. For the application of nitrogen nucleophiles, further investigation into the oxidation potentials of the nucleophiles and formed intermediates, e.g. by CV measurements, could help to find suitable catalyst combinations and prevent decomposition of the starting materials. This methodology was already successfully applied in the investigations on the mechanism of the photo-aerobic selenium-π-acid catalyzed lactonization.[126,127] Furthermore, the functionalization of alkynes provides many possibilities for further studies. Especially additional mechanistic investigations in the presented allenylation could help to develop strategies for the application of air as the terminal oxidant in cognate functionalizations with different nucleophiles.

5 Experimental Section

5.1 General Methods

5.1.1 Preparative Methods

If not indicated otherwise, all reactions were performed in heat-dried glassware under an argon atmosphere. Dry solvents were distilled from a suitable drying agent and stored over molecular sieves under argon or taken from an *MBraun* SPS (THF, toluene, DCM, Et_2O and DMF). Commercially available substances were used directly without further purification. For reactions at low temperatures, common freezing mixtures (liquid nitrogen/acetone, liquid nitrogen/isopropanol) or a cryostate TC100E-F from *Huber* or CORIO CD-601F from *Julabo* were used. For reactions with a syringe pump, an LA-100 from *Landgraf Laborsysteme HLL* was used. Irradiation experiments were performed at λ=465 nm using commercially available blue LED strips (2835 super bright SMD-LEDs, 100 diodes/m, 400 lm/m, 24 V, 12 W).

5.1.2 Chromatographic Methods

Thin Layer Chromatography (TLC): Analytical thin layer chromatography was performed on TLC plates Silica gel 60 F_{254} from *Merck*. Reported are the R_f values (substance level/solvent front level). Visualization was performed by fluorescence quenching at 254 nm and staining with solutions of potassium permanganate, ninhydrin or *p*-anisaldehyde.

Column chromatography: Column chromatographic separations were performed under increased pressure on silica gel 60 (0.063–0.200 mm, 70–230 mesh ASTM) from *Merck*.

5.1.3 Instrumental Analysis

IR spectra: IR spectra were measured on a *Bruker* FT-IR Alpha ATR or a *Jasco* FT/IR-4600LE spectrometer.

NMR spectra: NMR spectra were recorded at 300 MHz (^{1}H) and 76 MHz (^{13}C) with *Varian* Unity-300, AMX 300, and *Bruker* Avance 300; at 400 MHz (^{1}H), 101 MHz (^{13}C), 162 MHz (^{31}P), 376 MHz (^{19}F) and 76 MHz (^{77}Se) with *Varian* Inova 400 and 500 MHz (^{1}H), 126 MHz (^{13}C), 203 MHz (^{31}P) and 95 MHz (^{77}Se) with *Varian* Inova 500. Chemical shifts are reported as δ-values in ppm relative to the residual peak of the deuterated solvent or its carbon atom. For characterization of the multiplicities, the following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), hept (heptet), m (multiplet), dd (doublet of doublet), td (triplet of doublet), and analogues. The coupling constants J are reported in Hertz (Hz).

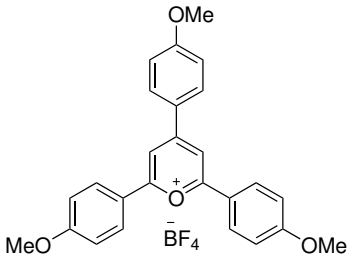
Mass spectra: ESI and ESI-HRMS spectra were measured on a micrOTOF and a maXis mass spectrometer (both *Bruker Daltonik*). EI and EI-HRMS spectra were measured on a *Joel* AccuTOF.

Melting points: Melting points were measured on a *Büchi* 540 apparatus or a *Krüss* M5000. The values were not corrected.

High Performance Liquid Chromatography: HPLC analyses were performed on an *Agilent* 1260 Infinity. The signals were detected on a diode array detector (DAD). The enantiomers were separated on a Chiralpak IA or Chiralcel OD column from *Daicel*. As solvent, a mixture of isopropanol and *n*-hexane was used.

5.2 Synthesis of diaryl diselenides and photosensitizer 95

2,4,6-Tris(4-methoxyphenyl)pyrylium tetrafluoroborate (95)[182]

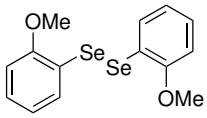


95

To a solution of 4′-methoxyacetophenone (15.0 g, 100 mmol, 2.0 equiv) and freshly distilled 4-methoxybenzaldehyde (6.08 mL, 6.81 g, 50.0 mmol, 1.0 equiv) in dry toluene (5 mL) under an argon atmosphere, $BF_3 \cdot Et_2O$ (14.8 mL, 17.0 g, 120 mmol, 2.4 equiv) was slowly added and the mixture was stirred at 100 °C for 2 h. The formed Et_2O was removed under reduced pressure and the residue was dissolved in acetone. Et_2O was added and the formed precipitate was filtered off and recrystallized from acetone. The title compound was obtained as a red solid (5.53 g, 11.4 mmol, 23%).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2941, 2841, 1585, 1482, 1457, 1434, 1258, 1235, 1174, 1016, 829, 562, 518; **^{1}H NMR** (300 MHz, DMSO-d_6): δ [ppm] = 8.54 (s, 2 H), 8.50-8.34 (m, 2 H), 8.34-8.18 (m, 4 H), 7.28-7.00 (m, 6 H), 3.94 (s, 3 H), 3.91 (s, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6): δ [ppm] = 167.5, 165.2, 164.4, 161.5, 132.3, 130.4, 124.2, 121.1, 115.2, 115.2, 110.3, 56.0, 55.9; **HR-ESI-MS m/z**: calcd. $C_{26}H_{23}O_4$ [M-BF_4^-]$^+$: 399.1591, found: 399.1587.

1,2-Bis(2-methoxyphenyl)diselane (129)



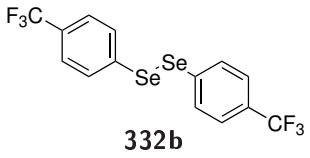
332a

2-Bromoanisole (3.78 g, 20.2 mmol, 1.0 equiv) was dissolved in THF (70 mL) and the solution was cooled to −78 °C. *Tert*-butyl lithium (1.7 M in pentane, 25 mL, 42.5 mmol, 2.1 equiv) was added dropwise over 15 min, the solution was stirred for 15 min at −78 °C and for 45 min at 0 °C. Selenium powder (1.76 g, 22.3 mmol, 1.1 equiv) was added in one portion and the suspension was stirred for 15 min at 0 °C and for 18 h at room temperature. The reaction was quenched by the addition of 1 M aq. HCl (14 mL), the solution was diluted with H_2O (70 mL), the aq. phase was extracted with Et_2O (3 × 70 mL), the combined org. phases were washed with sat. aq. NaCl solution (70 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in Et_2O (35 mL), NaOH (2 pellets) was added and stirred for 2 h at room temperature under air. Removal of the solvent in vacuum and purification by column

chromatography (50:1 *n*-pentane:EtOAc) afforded the product as an orange oil. Recrystallization (9:1 hexane:DCM) afforded the product as yellow crystals (1.89 g, 5.09 mmol, 50%).

R_f = 0.20 (*n*-pentane:Et_2O, 40:1); **m.p.** = 80 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3057, 3001, 2962, 2939, 2835, 1573, 1465, 1430, 1303, 1266, 1234, 1182, 1159, 1122, 1051, 1016, 786, 747, 711, 653, 569, 539, 486, 433; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.56 (ddd, J = 7.8, 1.6, 0.3 Hz, 2 H), 7.21 (ddd, J = 8.1, 7.4, 1.6 Hz, 2 H), 6.88 (ddd, J = 7.4, 1.2 Hz, 2 H), 6.82 (dd, J = 8.1, 1.2 Hz, 2 H), 3.91 (s, 6 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 157.0, 130.8, 128.3, 122.0, 118.9, 110.3, 56.1; **^{77}Se NMR** (76 MHz, $CDCl_3$): δ [ppm] = 332.8; **HR-ESI-MS m/z**: calcd. $C_{14}H_{14}O_2Se_2Na$ $[M+Na]^+$: 396.9219, found: 396.9212.

1,2-Bis(4-(trifluoromethyl)phenyl)diselane (130)



332b

4-Bromobenzotrifluoride (4.56 g, 20.2 mmol, 1.0 equiv) was dissolved in THF (70 mL) and the solution was cooled to −78 °C. *Tert*-butyl lithium (1.7 M in pentane, 25 mL, 42.5 mmol, 2.1 equiv) was added dropwise over 15 min, the solution was stirred for 15 min at −78 °C and for 45 min at 0 °C. Selenium powder (1.76 g, 22.3 mmol, 1.1 equiv) was added in one portion and the suspension was stirred for 15 min at 0 °C and for 18 h at room temperature. The reaction was quenched by the addition of 1 M aq. HCl (14 mL), the solution was diluted with H_2O (70 mL), the aq. phase was extracted with Et_2O (3 × 70 mL), the combined org. phases were washed with sat. aq. NaCl solution (70 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in EtOH (35 mL), NaOH (2 pellets) was added and stirred for 2 h at room temperature under air. Removal of the solvent in vacuo and purification by column chromatography (*n*-pentane) afforded the product as an orange oil. Recrystallization (9:1 hexane:DCM) afforded the product as a yellow solid (1.98 g, 4.41 mmol, 44%).

R_f = 0.34 (*n*-pentane); **m.p.** = 58 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 1597, 1495, 1398, 1321, 1162, 1101, 1068, 1008, 948, 841, 820, 772, 719, 684, 587, 489, 426, 407; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.77–7.66 (m, 4 H), 7.57–7.47 (m, 4 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 135.1–134.7 (m), 130.9, 130.1 (q, ^2J = 32.7 Hz), 126.3 (q, ^3J = 3.8 Hz), 124.0 (q, ^1J = 272.2 Hz); **^{77}Se NMR** (76 MHz, $CDCl_3$): δ [ppm] = 453.1; **^{19}F NMR** (376 MHz, $CDCl_3$): δ [ppm] = −62.7; **HR-EI-MS m/z**: calcd. $C_{14}H_8F_6Se_2$ $[M]^+$: 449.8863, found: 449.8847.

5.3 Intramolecular etherification *via* photo-aerobic selenium-π-acid catalysis

5.3.1 Synthesis of unsaturated alcohols 126 and 139

General procedure A: Wittig reaction

Under an atmosphere of argon, the carboxyalkyl triphenyl phosphonium bromide (2.0 equiv) is dissolved in anhydrous THF (0.6 M). The suspension is cooled to 0 °C and KO*t*Bu (powder or 1 M solution in THF; 4.0 equiv) is added dropwise. After 30 min of stirring at room temperature, a solution of the aldehyde (1.0 equiv) in anhydrous THF (2 M) is added dropwise at 0 °C. The reaction is stirred at room temperature and after the aldehyde is consumed, the mixture is quenched with 1 M aq. HCl solution or sat. aq. NH_4Cl, extracted with Et_2O (3×) and washed with H_2O (2×). The combined organic layers are washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent is removed under reduced pressure. The residue is purified on silica gel to yield the title compound.

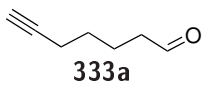
General procedure B: reduction with $LiAlH_4$

A solution of acid **34** or **137** (1.0 equiv) in anhydrous THF (7 mL) is added dropwise with stirring to a suspension of $LiAlH_4$ (2.4 M in THF; 1.5 equiv) in anhydrous THF (3 mL) at 0 °C. After stirring at RT, the reaction mixture is cooled to 0 °C, diluted with Et_2O (15 mL), quenched with sodium sulfate decahydrate, and filtered. The filter cake is washed with a sat. aq. solution of potassium sodium tartrate (Rochelle salt) and extracted with Et_2O (5 × 10 mL). The combined org. layers are washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent is removed under reduced pressure. The product is used without further purification.

General procedure C: cross metathesis reaction

Under an atmosphere of argon, 4-penten-1-ol (3 equiv) and the respective alkene (1.0 equiv) are dissolved in degassed, dry DCM (0.5 M). 2nd generation Grubbs catalyst (0.05 equiv) is added and the reaction mixture is stirred at 40 °C. The solvent is removed under reduced pressure and the residue is purified on silica gel to yield the title compound.

Hept-6-ynal (333a)



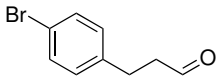
333a

A solution of Dess-Martin periodinane (5.09 g, 12.0 mmol, 2.0 equiv) in dry DCM (27 mL) was cooled to 0 °C, 6-heptyn-1-ol (673 mg, 6.00 mmol, 1.0 equiv) in DCM (3 mL) was added and the mixture was stirred at RT for 5 h. DCM (5 mL) was added, the mixture was washed with sat. aq. $Na_2S_2O_3$ sol. (30 mL), 1 M NaOH (30 mL), and sat. aq. NaCl (30 mL). The aq. phase was extracted with DCM (90 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified on silica

gel (*n*-pentane:Et_2O, 9:1) to yield the title compound as a colorless oil (337 mg, 3.06 mmol, 51%).

R_f = 0.29 (*n*-pentane:Et_2O, 9:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3296, 2942, 2869, 2116, 1706, 1414, 1289, 1234, 1146, 1038, 934; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 9.77 (t, J = 1.7 Hz, 1 H), 2.46 (td, J = 7.3, 1.7 Hz, 2 H), 2.22 (td, J = 7.0, 2.7 Hz, 2 H), 1.95 (t, J = 2.7 Hz, 1 H), 1.83-1.66 (m, 2 H), 1.65-1.42 (m, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 202.3, 83.9, 68.9, 43.4, 27.9, 21.2, 18.3.

3-(4-Bromophenyl)propanal (333b)

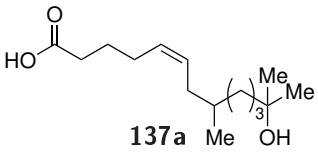


333b

A solution of Dess-Martin periodinane (5.09 g, 12.0 mmol, 2.0 equiv) in dry DCM (27 mL) was cooled to 0 °C, 3-(4-bromophenyl)propanol (1.29 g, 6.00 mmol, 1.0 equiv) in DCM (3 mL) was added and the mixture was stirred at RT for 3 h. DCM (5 mL) was added, the mixture was washed with sat. aq. $Na_2S_2O_3$ sol. (30 mL), 1 M NaOH (30 mL), and sat. aq. NaCl (30 mL). The aq. phase was extracted with DCM (90 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified on silica gel (*n*-pentane:EtOAc, 10:1) to yield the title compound as a colorless oil (614 mg, 2.88 mmol, 48%).

R_f = 0.38 (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2928, 2823, 2725, 2359, 2341, 1721, 1488, 1444, 1405, 1389, 1358, 1201, 1106, 1071, 1011, 861, 801, 713; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 9.80 (t, J = 1.3 Hz, 1 H), 7.55-7.34 (m, 2 H), 7.14-6.86 (m, 2 H), 3.01-2.85 (m, 2 H), 2.85-2.63 (m, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 201.1, 139.5, 131.8, 130.2, 120.2, 45.2, 27.6; **HR-EI-MS m/z**: calcd. C_9H_9BrO $[M]^+$: 211.9837, found: 211.9839.

(*Z*)-12-Hydroxy-8,12-dimethyltridec-5-enoic acid (137a)

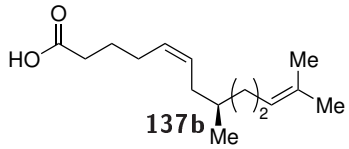


137a

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (3.1 g, 7.0 mmol, 2.0 equiv) in THF (11 mL), potassium *tert*-butoxide (1.57 g, 14.0 mmol, 4.0 equiv), 7-hydroxycitronellal (0.60 g, 3.5 mmol, 1.0 equiv) in THF (1 mL); reaction time 17 h; eluting with Et_2O; colorless oil; 709 mg, 2.77 mmol, 79%.

R_f = 0.20 (Et_2O); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2935, 2869, 1707, 1459, 1377, 1198, 1158, 934, 906, 763, 699, 495; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 6.40 (s, 2 H), 5.59-5.17 (m, 2 H), 2.34 (t, J = 7.3 Hz, 2 H), 2.19-1.97 (m, 3 H), 1.81 (m, 1 H), 1.68 (quint, J = 7.1 Hz, 2 H), 1.57-1.24 (m, 6 H), 1.21 (s, 6 H), 1.14 (m, 1 H), 0.87 (d, J = 6.7 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 178.9, 129.8, 129.3, 71.6, 44.1, 37.2, 34.3, 33.6, 33.5, 29.3, 29.2, 26.7, 24.8, 21.8, 19.9; **HR-ESI-MS m/z**: calcd. $C_{15}H_{28}NaO_3$ $[M+Na]^+$: 279.1931, found: 279.1929.

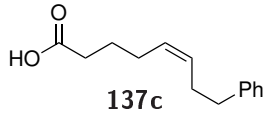
(*S*,*Z*)-8,12-Dimethyltrideca-5,11-dienoic acid (137b)



Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (1.8 g, 4.0 mmol, 2.0 equiv) in THF (7 mL), potassium *tert*-butoxide (0.90 g, 8.0 mmol, 4.0 equiv), (*S*)-citronellal (0.31 g, 2.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 1:1; yellow oil; 377 mg, 1.58 mmol, 79%.

R_f = 0.36 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954, 2913, 2870, 1707, 1437, 1377, 1267, 1240, 1205, 929, 692, 490; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.51–5.29 (m, 2 H), 5.10 (tdq, J = 7.1, 2.9, 1.4 Hz, 1 H), 2.36 (t, J = 7.5 Hz, 2 H), 2.17-2.01 (m, 2 H), 1.99 (tdd, J = 8.0, 4.3, 1.7 Hz, 2 H), 1.96–1.78 (m, 2 H), 1.79–1.62 (m, 5 H), 1.61 (d, J = 1.4 Hz, 3 H), 1.47 (m, 1 H), 1.35 (m, 1 H), 1.15 (m, 1 H), 0.87 (d, J = 6.6 Hz, 2 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 179.7, 131.2, 129.9, 129.1, 124.9, 37.0, 34.7, 33.6, 33.2, 26.8, 25.9, 25.9, 24.8, 19.7, 17.9; **HR-ESI-MS m/z**: calcd. $C_{15}H_{25}O_2$ $[M-H]^-$: 237.1860, found: 237.1862.

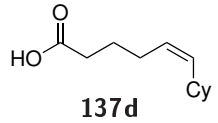
(*Z*)-8-Phenyloct-5-enoic acid (137c)



Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (3.1 g, 7.0 mmol, 2.0 equiv) in THF (11 mL), potassium *tert*-butoxide (1.57 g, 14.0 mmol, 4.0 equiv), 3-phenylpropionaldehyde (0.47 g, 3.5 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 4:1 to 0:1; colorless oil; 629 mg, 2.88 mmol, 82%.

R_f = 0.13 (*n*-pentane:Et_2O, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3062, 3026, 2929, 2857, 1703, 1603, 1496, 1453, 1411, 1239, 1090, 1030, 931, 749, 725, 697, 584, 484; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.33-7.25 (m, 2 H), 7.22-7.14 (m, 2 H), 5.46 (m, 1 H), 5.35 (m, 1 H), 2.72-2.59 (m, 2 H), 2.39-2.32 (m, 2 H), 2.34-2.24 (m, 2 H), 2.09-1.98 (m, 2 H), 1.63 (quint, J = 7.5 Hz, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 179.7, 142.1, 130.2, 129.2, 128.6, 128.4, 126.0, 36.0, 33.4, 29.3, 26.6, 24.6; **HR-ESI-MS m/z**: calcd. $C_{14}H_{18}O_2Na$ $[M+Na]^+$: 241.1199, found: 241.1206.

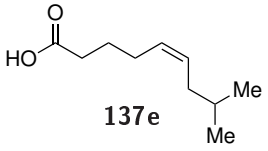
(*Z*)-6-Cyclohexylhex-5-enoic acid (137d)



Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (1.8 g, 4.0 mmol, 2.0 equiv) in THF (7 mL), potassium *tert*-butoxide (0.90 g, 8.0 mmol, 4.0 equiv), cyclohexanecarboxaldehyde (0.22 g, 2.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 1:1; colorless oil; 290 mg, 1.48 mmol, 74%.

R_f = 0.36 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2999, 2922, 2849, 1704, 1447, 1411, 1289, 1241, 1203, 1164, 930, 889, 732, 487; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.30–5.16 (m, 2 H), 2.37 (t, J = 7.5 Hz, 2 H), 2.22 (m, 1 H), 2.16–2.07 (m, 2 H), 1.76-1.65 (m, 5 H), 1.63–1.54 (m, 2 H), 1.39–1.12 (m, 3 H), 1.11–0.99 (m, 2 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 180.2, 137.5, 126.4, 36.5, 33.6, 33.5, 26.8, 26.2, 26.1, 24.9; **HR-ESI-MS m/z**: calcd. $C_{12}H_{19}O_2$ $[M-H]^-$: 195.1391, found: 195.1394.

(*Z*)-8-Methylnon-5-enoic acid (137e)

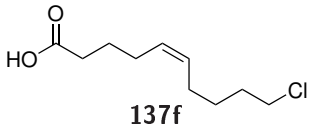


137e

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (1.8 g, 4.0 mmol, 2.0 equiv) in THF (7 mL), potassium *tert*-butoxide (0.90 g, 8.0 mmol, 4.0 equiv), isovaleraldehyde (0.17 g, 2.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 3:1 to 1:1; colorless oil; 204 mg, 1.20 mmol, 60%.

R_f = 0.5 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3008, 2954, 2870, 1706, 1461, 1412, 1384, 1366, 1314, 1241, 1167, 1122, 928, 826, 703, 481; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.54–5.24 (m, 2 H), 2.37 (t, J = 7.5 Hz, 2 H), 2.17–2.01 (m, 2 H), 1.95-1.87 (m, 2 H), 1.77–1.53 (m, 3 H), 0.89 (d, J = 6.6 Hz, 6 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 179.9, 130.1, 128.9, 36.6, 33.7, 28.9, 26.8, 24.8, 22.6; **HR-ESI-MS m/z**: calcd. $C_{10}H_{17}O_2$ $[M-H]^-$: 169.1234, found: 169.1234.

(*Z*)-10-Chlorodec-5-enoic acid (137f)

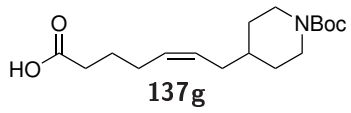


137f

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (3.6 g, 8.0 mmol, 2.0 equiv) in THF (10 mL), potassium *tert*-butoxide (1.80 g, 16.0 mmol, 4.0 equiv), 5-chloropentanal (0.48 g, 4.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 3 h; eluting with *n*-pentane/Et_2O, 5:1 to 0:1; colorless oil; 491 mg, 2.40 mmol, 60%.

R_f = 0.07 (*n*-pentane:Et_2O, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3007, 2934, 2863, 1704, 1412, 1239, 1204, 917, 716, 651, 485; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.56-5.23 (m, 2 H), 3.53 (t, J = 6.7 Hz, 2 H), 2.36 (t, J = 7.5 Hz, 2 H), 2.22-1.91 (m, 4 H), 1.91-1.59 (m, 4 H), 1.58-1.35 (m, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 179.8, 130.5, 129.1, 45.1, 33.5, 32.3, 27.0, 26.6, 26.6, 24.7; **HR-ESI-MS m/z**: calcd. $C_{10}H_{17}O_2ClNa$ $[M+Na]^+$: 227.0809, found: 227.0814.

(*Z*)-7-(1-(*tert*-butoxycarbonyl)piperidin-4-yl)hept-5-enoic acid (137g)

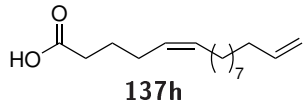


137g

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (1.8 g, 4.0 mmol, 2.0 equiv) in THF (7 mL), potassium *tert*-butoxide (0.90 g, 8.0 mmol, 4.0 equiv), *N*-Boc-4-piperidineacetaldehyde (0.47 g, 2.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 3:1; yellow oil; 257 mg, 0.83 mmol, 42%.

$\mathbf{R_f} = 0.30$ (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2922, 2851, 1736, 1696, 1422, 1366, 1278, 1243, 1160, 1127, 1084, 966, 947, 909, 863, 769, 733; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.48–5.33 (m, 2 H), 4.13-3.98 (m, 2 H), 2.66 (t, J = 12.8 Hz, 2 H), 2.35 (t, J = 7.5 Hz, 2 H), 2.13–2.03 (m, 2 H), 1.97 (dd, J = 6.7, 5.6 Hz, 2 H), 1.76–1.56 (m, 3 H), 1.45 (s, 9 H), 1.09 (qd, J = 12.6, 4.3 Hz, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 178.8, 154.9, 129.7, 128.5, 79.3, 36.5, 34.0, 33.3, 32.0, 28.5, 26.5, 24.6; **HR-ESI-MS m/z**: calcd. $C_{17}H_{28}NO_4$ $[M\text{-}H]^-$: 310.2024, found: 310.2023.

(*Z*)-Hexadeca-5,15-dienoic acid (137h)

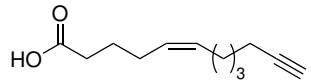


137h

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (3.55 g, 8.00 mmol, 2.00 equiv), potassium *tert*-butoxide (1 M in THF; 16 mL, 16.0 mmol, 4.00 equiv), 10-undecenal (673 mg, 4.00 mmol, 1.00 equiv), THF (6 mL); reaction time 17 h; eluting with *n*-pentane:Et_2O, 3:1; yield: 733 mg, 2.90 mmol, 73%, colorless oil.

$\mathbf{R_f} = 0.25$ (*n*-pentane:Et_2O, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3005, 2924, 2853, 2359, 2341, 1707, 1640, 1413, 1240, 1205, 1170, 992, 908, 721, 687; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1 H), 5.59-5.17 (m, 2 H), 4.99 (ddt, J = 17.1, 2.3, 1.6 Hz, 1 H), 4.93 (ddt, J = 10.2, 2.3, 1.2 Hz, 1 H), 2.36 (td, J = 7.6, 4.3 Hz, 2 H), 2.15-1.86 (m, 6 H), 1.85-1.58 (m, 2 H), 1.49-1.10 (m, 12 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 179.6, 139.3, 131.4, 128.2, 114.2, 34.0, 33.6, 29.9, 29.7, 29.7, 29.5, 29.4, 29.2, 27.5, 26.7, 24.8; **HR-ESI-MS m/z**: calcd. $C_{16}H_{29}O_2$ $[M+H]^+$: 253.2162, found: 253.2154.

(*Z*)-Dodec-5-en-11-ynoic acid (137i)

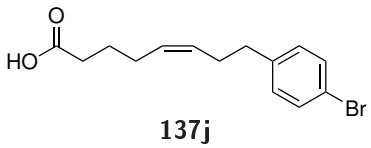


137i

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (2.66 g, 6.00 mmol, 2.00 equiv), potassium *tert*-butoxide (1 M in THF; 12 mL, 12.0 mmol, 4.00 equiv), hept-6-ynal (300 mg, 3.00 mmol, 1.00 equiv), THF (5 mL); reaction time 17 h; eluting with *n*-pentane:Et_2O, 3:1; yield: 317 mg, 1.63 mmol, 54%, yellow oil. Contains allene (10%).

R_f = 0.14 (*n*-pentane:Et_2O, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3303, 3006, 2935, 2860, 1705, 1457, 1432, 1412, 1267, 1239, 1206, 1098, 1040, 932; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 9.25 (s, 1 H), 5.47-5.29 (m, 2 H), 2.37 (t, J = 7.4 Hz, 2 H), 2.19 (td, J = 6.9, 2.7 Hz, 2 H), 2.15-2.00 (m, 4 H), 1.94 (t, J = 2.7 Hz, 1 H), 1.70 (quint, J = 7.4 Hz, 2 H), 1.60-1.36 (m, 4 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 179.8, 130.8, 128.8, 84.7, 68.4, 33.6, 28.8, 28.2, 26.8, 26.6, 24.7, 18.4; **HR-ESI-MS m/z**: calcd. $C_{12}H_{18}O_2Na$ $[M+Na]^+$: 217.1199, found: 217.1198.

(*Z*)-8-(4-Bromophenyl)oct-5-enoic acid (137j)

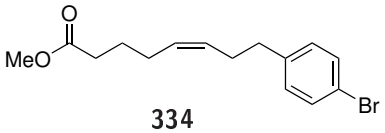


137j

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (3.55 g, 8.00 mmol, 2.00 equiv), potassium *tert*-butoxide (1 M in THF; 16 mL, 16.0 mmol, 4.00 equiv), 3-(4-bromophenyl)propanal (864 mg, 4.00 mmol, 1.00 equiv), THF (6 mL); reaction time 17 h; eluting with *n*-pentane:Et_2O, 4:1; yield: 976 mg, 3.28 mmol, 81%, yellow oil.

R_f = 0.06 (*n*-pentane:Et_2O, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3006, 2928, 2858, 1899, 1703, 1487, 1405, 1239, 1202, 1103, 1072, 1011, 934, 829, 813, 773, 714; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.45-7.30 (m, 2 H), 7.12-6.94 (m, 2 H), 5.52-5.25 (m, 2 H), 2.61 (dd, J = 8.5, 6.7 Hz, 2 H), 2.39-2.22 (m, 4 H), 2.08-1.90 (m, 2 H), 1.73-1.51 (m, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 179.6, 140.9, 131.4, 130.3, 129.6, 129.4, 119.6, 35.5, 33.5, 29.2, 26.6, 24.6; **HR-ESI-MS m/z**: calcd. $C_{14}H_{17}O_2BrNa$ $[M+Na]^+$: 319.0304, found: 319.0309.

Methyl (*Z*)-8-(4-bromophenyl)oct-5-enoate (334)

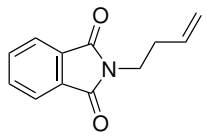


334

Acid **137j** (446 mg, 1.5 mmol, 1.0 equiv) and conc. HCl (0.1 mL) were dissolved in MeOH (67 mL) and stirred at RT for 15.5 h. Washing of the mixture with H_2O (70 mL), sat. aq. NaCl (70 mL) and extracting of the comb. aq. phases with EtOAc (150 mL) afforded the product as a colorless oil (275 mg, 884 µmol, 59%).

R_f = 0.21 (*n*-pentane:Et_2O, 2:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3006, 2948, 2859, 1736, 1488, 1435, 1404, 1366, 1313, 1242, 1197, 1170, 1072, 1011, 814, 773, 715; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.51-7.32 (m, 2 H), 7.15-6.85 (m, 2 H), 5.58-5.18 (m, 2 H), 3.66 (s, 3 H), 2.61 (t, J = 7.6 Hz, 2 H), 2.47-2.14 (m, 4 H), 2.00 (td, J = 7.5, 6.2 Hz, 2 H), 1.75-1.48 (m, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 174.0, 140.9, 131.4, 130.3, 129.6, 129.4, 119.6, 51.7, 35.5, 33.6, 29.1, 26.8, 24.9; **HR-ESI-MS m/z**: calcd. $C_{15}H_{20}BrO_2$ $[M+H]^+$: 311.0641, found: 311.0643.

2-(But-3-en-1-yl)isoindoline-1,3-dione (335)

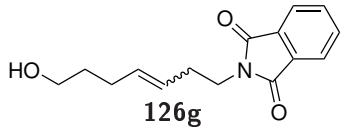


335

4-Bromo-1-butene (743 mg, 5.50 mmol, 1.1 equiv), phthalimide (736 mg, 5.01 mmol, 1.0 equiv) and Cs_2CO_3 (1.79 g, 5.49 mmol, 1.1 equiv) were dissolved in DMF (3.5 mL) and the solution was stirred at 70 °C for 4 h. The mixture was poured in H_2O and filtered. The resulting precipitate was washed with water and dried. The desired compound was obtained as a white solid (740 mg, 3.68 mmol, 74%).

R_f = 0.48 (*n*-pentane:Et_2O, 2:1); **m.p.** = 50 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2942, 1769, 1694, 1641, 1612, 1450, 1396, 1361, 1332, 1188, 1055, 1015, 983, 867, 798, 721, 712, 651, 611, 530; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.96-7.77 (m, 2 H), 7.76-7.63 (m, 2 H), 5.79 (ddt, J = 17.1, 10.1, 6.9 Hz, 1 H), 5.1-4.97 (m, 2 H), 3.77 (t, J = 7.1 Hz, 2 H), 2.45 (qt, J = 7.0, 1.3 Hz, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 168.3, 134.5, 133.9, 132.2, 123.3, 117.6, 37.5, 33.0; **HR-ESI-MS m/z**: calcd. $C_{12}H_{11}NO_2Na$ $[M+Na]^+$: 224.0682, found: 224.0684.

2-(7-Hydroxyhept-3-en-1-yl)isoindoline-1,3-dione (126g)

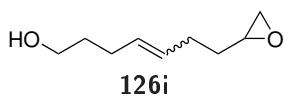


126g

Following general procedure **C**: 4-pentene-1-ol (904 mg, 10.5 mmol, 3.0 equiv), 2-(but-3-en-1-yl)isoindoline-1,3-dione (**335**) (704 mg, 3.50 mmol, 1.0 equiv), DCM (7 mL), 2nd gen. Grubbs catalyst (149 mg, 175 µmol, 0.05 equiv); reaction time 20 h; eluting with *n*-pentane/Et_2O, 2:1; colorless liquid; 408 mg, 1.57 mmol, 45%.

R_f = 0.25 (*n*-pentane:EtOAc, 2:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2935, 2864, 1771, 1700, 1614, 1467, 1436, 1393, 1359, 1187, 1130, 1057, 1015, 971, 870, 794, 718, 624, 530; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.85-7.81 (m, 2 H), 7.72-7.68 (m, 2 H), 5.48-5.37 (m, 2 H), 3.73 (t, J = 7.0 Hz, 2 H), 3.53 (t, J = 6.5 Hz, 2 H), 2.43-2.31 (m, 2 H), 2.15-1.94 (m, 3 H), 1.66-1.40 (m, 2 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = major isomer: 168.4, 133.9, 132.8, 132.2, 126.7, 123.2, 62.3, 38.0, 32.3, 31.9, 28.9; **HR-ESI-MS m/z**: calcd. $C_{15}H_{18}NO_3$ $[M+H]^+$: 260.1281, found: 260.1284.

7-(Oxiran-2-yl)hept-4-en-1-ol (126i)



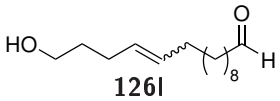
126i

Following general procedure **C**: 4-pentene-1-ol (904 mg, 10.5 mmol, 3.0 equiv), 1,2-epoxy-5-hexene (343 mg, 3.50 mmol, 1.0 equiv), DCM (7 mL), 2nd gen. Grubbs catalyst (149 mg, 175 µmol, 0.05 equiv); reaction time 22.5 h; eluting with *n*-pentane/EtOAc, 5:1 to 0:1; brown liquid; 254 mg, 1.63 mmol, 47%.

R_f = 0.19 (*n*-pentane:EtOAc, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3407, 2928, 2859, 1723, 1441, 1410, 1260, 1050, 970, 915, 833, 514, 439, 419, 402; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.76-5.14

(m, 2 H), 3.64 (t, J = 6.4 Hz, 2 H), 2.92 (dddd, J = 10.1, 5.2, 2.8, 1.2 Hz, 1 H), 2.75 (dd, J = 5.0, 4.0 Hz, 1 H), 2.47 (dt, J = 5.1, 2.9 Hz, 1 H), 2.40-1.85 (m, 4 H), 1.74-1.42 (m, 5 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 133.4, 130.5, 129.8, 126.7, 62.6, 62.2, 52.4, 52.1, 47.3, 47.3, 36.2, 32.5, 32.1, 29.3, 29.1, 26.0; **HR-ESI-MS m/z**: calcd. $C_9H_{16}O_2Na$ $[M+Na]^+$: 179.1043, found: 179.1041.

14-Hydroxytetradec-10-enal (126l)

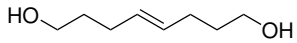


126l

Following general procedure **C**: 4-pentene-1-ol (904 mg, 10.5 mmol, 3.0 equiv), 10-undecenal (589 mg, 3.50 mmol, 1.0 equiv), DCM (7 mL), 2nd gen. Grubbs catalyst (149 mg, 175 µmol, 0.05 equiv); reaction time 22 h; eluting with *n*-pentane/EtOAc, 9:1; brown solid; 178 mg, 786 µmol, 22%.

R_f = 0.09 (*n*-pentane:EtOAc, 9:1); **m.p.** = 46.2 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3419, 2923, 2853, 2717, 1723, 1461, 1409, 1391, 1051, 967, 723, 517; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 9.76 (t, J = 1.9 Hz, 1 H), 5.63-5.24 (m, 2 H), 3.64 (td, J = 6.6, 3.7 Hz, 2 H), 2.41 (td, J = 7.3, 1.9 Hz, 2 H), 2.35-1.89 (m, 4 H), 1.69-1.52 (m, 4 H), 1.49-1.19 (m, 11 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 203.1, 131.3, 130.9, 130.1, 129.6, 63.1, 62.7, 44.1, 32.7, 32.6, 29.6, 29.4, 29.4, 29.3, 29.3, 29.2, 29.1, 29.0, 22.2, 22.2; **HR-ESI-MS m/z**: calcd. $C_{14}H_{27}O_2$ $[M+H]^+$: 227.2006, found: 227.2015.

Oct-4-ene-1,8-diol (126m)

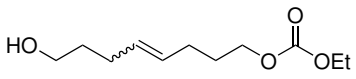


126m

4-Pentene-1-ol (5.00 g, 58.1 mmol, 1.0 equiv) was dissolved in degassed DCM (200 mL). Grubbs catalyst 2nd generation (50 mg, 59 µmol, 0.1 mol%) was added and the reaction was stirred for 22 h at room temperature. After 3 h, another portion of Grubbs catalyst 2nd generation (50 mg, 59 µmol, 0.1 mol%) was added, after 3 more hours, another portion (50 mg, 59 µmol, 0.1 mol%) was added. After 3 more hours, Grubbs catalyst 2nd generation (100 mg, 118 µmol, 0.2 mol%) in DCM (6 mL) was added via syringe pump over 6 h. The solvent was removed in vacuum and the product afforded *via* column chromatography (*n*-pentane/EtOAc, 3:1 to 0:1) as a brown liquid (1.88 g, 13.0 mmol, 45%).

R_f = 0.07 (*n*-pentane:EtOAc, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3316, 2931, 2865, 1440, 1375, 1351, 1051, 966, 915, 631; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.75–5.20 (m, 2 H), 3.72–3.46 (m, 4 H), 2.86-1.89 (m, 6 H), 1.74–1.27 (m, 4 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 130.2, 62.4, 32.5, 29.0; **HR-ESI-MS m/z**: calcd. $C_8H_{16}O_2Na$ $[M+Na]^+$: 167.1043, found: 167.1043.

Ethyl (8-hydroxyoct-4-en-1-yl) carbonate (126n)

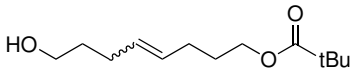


126n

Oct-4-ene-1,8-diol **126m** (216 mg, 1.50 mmol, 1.0 equiv) and DMAP (4.6 mg, 38 µmol, 0.025 equiv) were dissolved in dry DCM (2 mL) and cooled to 0 °C. Pyridine (237 mg, 3.0 mmol, 2.0 equiv) was added dropwise, then ethyl chloroformate (163 mg, 1.50 mmol, 1.5 equiv) was added dropwise and the reaction was allowed to warm up to room temperature. The solution was stirred for 23 h, subsequently washed with H_2O (5 × 2 mL) and the comb. aq. phases were extracted with DCM (10 mL). The comb. org. phases were dried over Na_2SO_4, the solvent was removed in vacuum and the product was afforded *via* column chromatography (*n*-pentane/EtOAc, 4:1) as a colorless oil (113 mg, 520 µmol, 35%).

R_f = 0.21 (*n*-pentane:EtOAc, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2983, 2934, 2874, 1742, 1467, 1448, 1403, 1386, 1368, 1251, 1054, 1010, 969, 863, 791; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.69-5.29 (m, 2 H), 4.18 (q, J = 7.1 Hz, 2 H), 4.14-4.07 (m, 2 H), 3.64 (t, J = 6.5 Hz, 2 H), 2.23-1.98 (m, 4 H), 1.83-1.67 (m, 2 H), 1.67-1.56 (m, 2 H), 1.51 (m, 1 H), 1.31 (t, J = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 155.3, 130.8, 129.4, 67.4, 64.0, 62.6, 32.6, 29.0, 28.8, 28.7, 14.5; **HR-ESI-MS m/z**: calcd. $C_{11}H_{20}O_4Na$ $[M+Na]^+$: 239.1254, found: 239.1256.

8-Hydroxyoct-4-en-1-yl pivalate (126o)

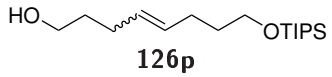


126o

Oct-4-ene-1,8-diol **126m** (216 mg, 1.50 mmol, 1.0 equiv) and DMAP (202 mg, 1.65 mmol, 1.1 equiv) were dissolved in DCM (5 mL) and pivalic acid chloride (199 mg, 1.65 mmol, 1.1 equiv) was added dropwise. The solution was stirred for 23 h at room temperature, subsequently washed with aq. sat. Na_2CO_3 solution (5 mL) and aq. 1 M HCl (5 mL) and the comb. aq. phases were extracted with DCM (10 mL). The comb. org. phases were dried over Na_2SO_4, the solvent was removed in vacuo and the product was afforded *via* column chromatography (*n*-pentane/EtOAc, 4:1) as a colorless oil (113 mg, 520 µmol, 35%).

R_f = 0.29 (*n*-pentane:EtOAc, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958, 2934, 2872, 1727, 1480, 1460, 1398, 1366, 1284, 1153, 1055, 1036, 968, 892, 772; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.83-5.22 (m, 2 H), 4.04 (t, J = 6.5 Hz, 2 H), 3.64 (t, J = 6.5 Hz, 2 H), 2.20-1.90 (m, 4 H), 1.87-1.50 (m, 4 H), 1.41 (s, 1 H), 1.20 (d, J = 1.1 Hz, 9 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 178.6, 130.6, 129.6, 63.9, 62.6, 39.0, 32.6, 29.1, 28.7, 27.4; **HR-ESI-MS m/z**: calcd. $C_{13}H_{24}O_3Na$ $[M+Na]^+$: 251.1618, found: 251.1624.

8-((Triisopropylsilyl)oxy)oct-4-en-1-ol (126p)

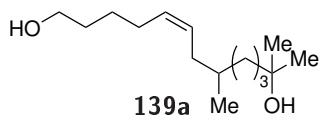


126p

Oct-4-ene-1,8-diol **126m** (216 mg, 1.50 mmol, 1.0 equiv) was dissolved in dry DCM (1.3 mL), imidazole (123 mg, 1.80 mmol, 1.2 equiv) and TIPSCl (318 mg, 1.65 mmol, 1.1 equiv) were added and the solution stirred at room temperature for 17 h. Subsequently, it was washed with aq. sat. NaCl (2 × 1 mL) and the aq. phase was extracted with DCM (2 × 3 mL). The comb. org. phases were dried over Na_2SO_4, the solvent was removed in vacuo and the product was afforded *via* column chromatography (*n*-pentane/EtOAc, 4:1) as a colorless oil (167 mg, 556 µmol, 37%).

R_f = 0.43 (*n*-pentane:EtOAc, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2940, 2865, 2047, 1968, 1463, 1383, 1246, 1104, 1064, 1013, 995, 967, 919, 882, 788, 724, 679, 658, 507, 460, 419, 395; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.77-5.20 (m, 2 H), 3.81-3.57 (m, 4 H), 2.43-1.92 (m, 4 H), 1.69-1.49 (m, 4 H), 1.25 (m, 1 H), 1.18-0.92 (m, 21 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 130.8, 129.9, 62.9, 62.7, 33.0, 32.6, 29.1, 29.0, 18.2, 12.2; **HR-ESI-MS m/z**: calcd. $C_{17}H_{37}O_2Si$ $[M+H]^+$: 301.2557, found: 301.2554.

(*E*/*Z*)-8,12-Dimethyltridec-5-ene-1,12-diol (139a)

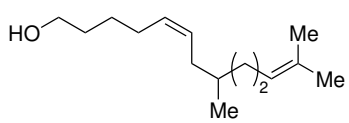


139a

Following general procedure **B**: acid **137a** (710 mg, 2.77 mmol, 1.0 equiv), $LiAlH_4$ (2.4 M in THF; 1.73 mL, 4.16 mmol, 1.5 equiv), THF (9 mL); reaction time 4.5 h; yield: 404 mg, 1.89 mmol, 68%; mixture of *E*/*Z* isomers, colorless liquid.

R_f = 0.21 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3327, 2933, 2866, 1459, 1377, 1198, 1160, 1065, 937, 907, 688; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.61-5.20 (m, 2 H), 3.63 (td, J = 6.5, 0.6 Hz, 2 H), 2.03 (dtd, J = 13.5, 6.4, 5.4, 4.0 Hz, 3 H), 1.86 (m, 1 H), 1.67 (d, J = 0.8 Hz, 2 H), 1.63-1.24 (m, 11 H), 1.20 (d, J = 0.5 Hz, 6 H), 0.87 (dd, J = 6.6, 0.5 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = major isomer: 130.3, 128.8, 71.2, 63.0, 44.4, 37.3, 34.6, 33.6, 32.6, 29.5, 29.4, 27.2, 26.0, 22.0, 19.9; minor isomer: 131.3, 129.3, 63.0, 40.2, 37.2, 33.3, 32.5, 32.4, 25.9, 22.0, 19.8; **HR-ESI-MS m/z**: calcd. $C_{15}H_{30}NaO_2$ $[M+Na]^+$: 265.2138, found: 265.2139.

(*E*/*Z*)-8,12-Dimethyltrideca-5,11-dien-1-ol (139b)



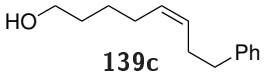
139b

Following general procedure **B**: acid **137b** (663 mg, 2.78 mmol, 1.0 equiv), $LiAlH_4$ (2.4 M in THF; 1.74 mL, 4.17 mmol, 1.5 equiv), THF (9 mL); reaction time 17.5 h; yield: 471 mg, 2.11 mmol, 76%; mixture of *E*/*Z* isomers, colorless liquid.

R_f = 0.21 (*n*-pentane:Et_2O, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3333, 2924, 2858, 2042, 2016, 1966, 1653, 1454, 1376, 1341, 1063, 985, 824, 699; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.56-5.23 (m,

2 H), 5.10 (tdt, J = 7.1, 2.9, 1.5 Hz, 1 H), 3.65 (t, J = 6.5 Hz, 2 H), 2.15-1.80 (m, 6 H), 1.68 (q, J = 1.3 Hz, 3 H), 1.64-1.52 (m, 5 H), 1.52-1.28 (m, 4 H), 1.25 (s, 1 H), 1.15 (m, 1 H), 0.88 (d, J = 6.5 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 131.2, 130.2, 128.9, 125.0, 63.1, 37.0, 34.7, 33.3, 32.7, 27.3, 26.1, 25.9, 25.9, 19.8, 17.9; **HR-ESI-MS m/z**: calcd. $C_{15}H_{29}O$ $[M+H]^+$: 225.2213, found: 225.2211.

(*Z*)-8-Phenyloct-5-en-1-ol (139c)

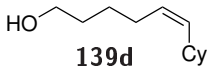


139c

Following general procedure **B**: acid **137c** (610 mg, 2.79 mmol, 1.0 equiv), $LiAlH_4$ (2.4 M in THF; 1.78 mL, 4.27 mmol, 1.50 equiv), THF (9 mL); reaction time 4 h; yield: 293 mg, 1.43 mmol, 51%, colorless liquid.

R_f = 0.11 (*n*-pentane:Et_2O, 9:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3332, 3026, 3005, 2930, 2857, 1495, 1453, 1059, 1031, 746, 722, 696, 583, 489; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.32-7.20 (m, 2 H), 7.17 (d, J = 7.0 Hz, 3 H), 5.62-5.01 (m, 2 H), 3.59 (t, J = 6.5 Hz, 1 H), 2.64 (dd, J = 8.7, 6.7 Hz, 2 H), 2.48-2.14 (m, 2 H), 2.07-1.83 (m, 2 H), 1.63-1.38 (m, 2 H), 1.32 (dddd, J = 14.7, 11.0, 6.2, 2.2 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 142.2, 130.3, 129.2, 128.6, 128.4, 125.9, 63.0, 36.1, 32.5, 29.4, 27.0, 25.8; **HR-ESI-MS m/z**: calcd. $C_{14}H_{20}ONa$ $[M+Na]^+$: 227.1406, found: 227.1408.

(*Z*)-6-Cyclohexylhex-5-en-1-ol (139d)

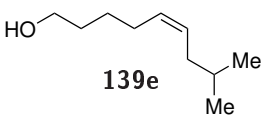


139d

Following general procedure **B**: acid **137d** (530 mg, 2.70 mmol, 1.0 equiv), $LiAlH_4$ (2.4 M in THF; 1.7 mL, 4.0 mmol, 1.5 equiv), THF (9 mL); reaction time 17.5 h; yield: 451 mg, 2.47 mmol, 91%, colorless liquid.

R_f = 0.15 (*n*-pentane:Et_2O, 7:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3328, 2999, 2921, 2849, 1447, 1059, 993, 889, 729; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.53-4.73 (m, 2 H), 3.65 (t, J = 6.6 Hz, 2 H), 2.23 (tdq, J = 11.1, 7.8, 3.8 Hz, 1 H), 2.14-2.01 (m, 2 H), 1.82-1.64 (m, 2 H), 1.64-1.49 (m, 5 H), 1.49-1.37 (m, 2 H), 1.35-1.12 (m, 4 H), 1.10-0.97 (m, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 136.6, 127.6, 63.1, 36.5, 33.5, 32.5, 27.3, 26.2, 26.1; **GC-MS (EI) m/z**: calcd. $C_{12}H_{22}O$ $[M]^+$: 182.2, found: 182.3.

(*Z*)-8-Methylnon-5-en-1-ol (139e)



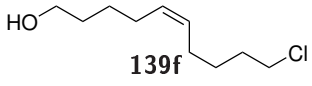
139e

Following general procedure **B**: acid **137e** (500 mg, 2.94 mmol, 1.0 equiv), $LiAlH_4$ (2.4 M in THF; 1.8 mL, 4.4 mmol, 1.5 equiv), THF (9 mL); reaction time 4 h; yield: 334 mg, 2.14 mmol, 71%, colorless liquid.

R_f = 0.22 (*n*-pentane:Et_2O, 9:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3318, 3006, 2953, 2931, 2868, 1464, 1383, 1366, 1336, 1064, 989, 968, 937, 828, 707, 580; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.53-5.04 (m, 2 H), 3.61 (t, J = 6.5 Hz, 2 H), 2.04 (dddd, J = 7.9, 6.5, 4.9,

0.6 Hz, 2 H), 1.95-1.76 (m, 3 H), 1.67-1.48 (m, 3 H), 1.48-1.22 (m, 2 H), 0.87 (d, J = 6.6 Hz, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 130.1, 129.0, 62.9, 36.6, 32.6, 28.8, 27.2, 26.0, 22.6; **GC-MS EI m/z**: calcd. $C_{10}H_{20}O$ $[M]^+$: 156.2, found: 156.2.

(*E*/*Z*)-10-Chlorodec-5-en-1-ol (139f)

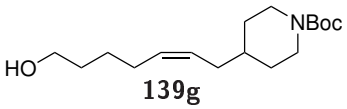


139f

Following general procedure **B**: acid **137f** (477 mg, 2.34 mmol, 1.0 equiv), $LiAlH_4$ (2.4 M in THF; 1.46 mL, 3.51 mmol, 1.5 equiv), THF (8 mL); reaction time 17.5 h; yield: 161 mg, 842 µmol, 36%; mixture of E/Z isomers, colorless liquid.

R_f = 0.29 (n-pentane:Et_2O, 3:2); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3342, 3004, 2933, 2859, 1455, 1363, 1311, 1058, 715, 651; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.57.-5.19 (m, 2 H), 3.65 (t, J = 6.5 Hz, 2 H), 3.54 (t, J = 6.7 Hz, 2 H), 2.26-1.94 (m, 4 H), 1.94-1.69 (m, 2 H), 1.69-1.34 (m, 6 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = major isomer: 130.2, 129.4, 63.1, 45.2, 32.6, 32.4, 27.2, 27.1, 26.6, 26.0; minor isomer: 130.7, 130.0, 32.5, 32.3, 31.9, 27.8, 25.9; **GC-MS (EI) m/z**: calcd. $C_{10}H_{17}Cl$ $[M\text{-}H_2O]^+$: 172.1, found: 172.2.

tert-Butyl (*Z*)-4-(7-hydroxyhept-2-en-1-yl)piperidine-1-carboxylate (139g)

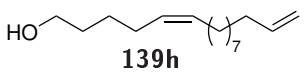


139g

Following general procedure **B**: acid **137g** (829 mg, 2.66 mmol, 1.0 equiv), $LiAlH_4$ (2.4 M in THF; 1.7 mL, 4.0 mmol, 1.5 equiv), THF (9 mL); reaction time 4.5 h; yield: 480 mg, 1.61 mmol, 61%, colorless liquid.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3447, 2927, 2854, 1693, 1422, 1365, 1277, 1243, 1161, 970, 864, 767; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.64-5.21 (m, 2 H), 4.06 (d, J = 13.1 Hz, 2,H), 3.64 (td, J = 6.5, 1.5 Hz, 2 H), 2.66 (t, J = 12.8 Hz, 2 H), 2.25 (s, 1 H), 2.05 (q, J = 6.8 Hz, 2 H), 1.97 (t, J = 6.6 Hz, 2 H), 1.83-1.45 (m, 5 H), 1.51-1.33 (m, 11 H), 1.19-0.97 (m, 2 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 154.9, 130.9, 127.7, 79.3, 63.0, 56.2, 46.6, 36.8, 34.3, 32.6, 28.7, 27.3, 26.0; **HR-ESI-MS m/z**: calcd. $C_{17}H_{31}NO_3Na$ $[M+Na]^+$: 320.2196, found: 320.2197.

(*Z*)-Hexadeca-5,15-dien-1-ol (139h)



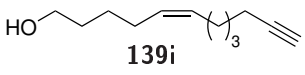
139h

Following general procedure **B**: acid **137h** (719 mg, 2.85 mmol, 1.00 equiv), $LiAlH_4$ (2.4 M in THF; 1.78 mL, 4.27 mmol, 1.50 equiv), THF (9 mL); reaction time 5.5 h; yield: 578 mg, 2.42 mmol, 85%, colorless liquid.

R_f = 0.36 (n-pentane:Et_2O, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3697, 3322, 3076, 3004, 2923, 2853, 2360, 2341, 1726, 1640, 1460, 136, 1060, 991, 908, 721; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1 H), 5.55-5.26 (m, 2 H), 4.99 (ddt, J = 17.1, 2.1, 1.7 Hz, 1 H), 4.93

(ddt, J = 10.2, 2.4, 1.2 Hz, 1 H), 3.65 (t, J = 6.6 Hz, 2 H), 2.26-1.91 (m, 6 H), 1.71-1.52 (m, 2 H), 1.48-1.12 (m, 15 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 139.4, 130.5, 129.4, 114.2, 63.1, 34.0, 32.5, 29.9, 29.6, 29.6, 29.4, 29.3, 29.1, 27.4, 27.1, 26.0; **HR-ESI-MS m/z**: calcd. $C_{16}H_{31}O$ $[M+H]^+$: 239.2369, found: 239.2368.

(*Z*)-Dodec-5-en-11-yn-1-ol (139i)

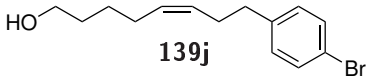


139i

Following general procedure **B**: acid **137i** (310 mg, 1.60 mmol, 1.00 equiv), $LiAlH_4$ (2.4 M in THF; 1.00 mL, 2.40 mmol, 1.50 equiv), THF (8 mL); reaction time 4 h; yield: 262 mg, 1.45 mmol, 91%, colorless liquid. Contains allene (10%).

$\mathbf{R_f}$ = 0.22 (*n*-pentane:Et_2O, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3304, 3005, 2931, 2858, 2117, 1955, 1653, 1456, 1433, 1327, 1057, 972, 939, 843; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.54-5.28 (m, 2 H), 3.65 (t, J = 6.5 Hz, 2 H), 2.27-2.14 (m, 2 H), 2.14-1.97 (m, 4 H), 1.94 (t, J = 2.7 Hz, 1 H), 1.67-1.35 (m, 9 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 129.9, 129.8, 84.7, 68.4, 63.1, 32.6, 28.9, 28.3, 27.2, 26.9, 26.1, 18.5; **HR-ESI-MS m/z**: calcd. $C_{12}H_{20}ONa$ $[M+Na]^+$: 203.1406, found: 203.1401.

(*Z*)-8-(4-Bromophenyl)oct-5-en-1-ol (139j)



139j

Following general procedure **B**: acid **137j** (650 mg, 2.19 mmol, 1.00 equiv), $LiAlH_4$ (2.4 M in THF; 1.37 mL, 3.28 mmol, 1.50 equiv), THF (9 mL); reaction time 4 h; yield: 303 mg, 1.07 mmol, 49% (1:0.4 inseparable mixture with debrominated product **139c**), colorless liquid.

$\mathbf{R_f}$ = 0.11 (*n*-pentane:Et_2O, 9:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3324, 3005, 2929, 2857, 1487, 1453, 1403, 1070, 1011, 813, 772, 698; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.54-7.34 (m, 2 H), 7.11-6.94 (m, 2 H), 5.42-5.31 (m, 2 H), 3.61 (t, J = 6.5 Hz, 2 H), 2.61 (t, J = 7.6 Hz, 2 H), 2.33 (dddd, J = 8.6, 7.6, 5.1, 1.3 Hz, 2 H), 2.03-1.90 (m, 2 H), 1.55-1.46 (m, 2 H), 1.39-1.29 (m, 2 H), 1.24 (s, 1 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 141.0, 131.3, 130.6, 130.4, 128.6, 119.6, 63.0, 35.5, 32.5, 29.2, 27.2, 25.9; **HR-ESI-MS m/z**: calcd. $C_{14}H_{20}OBr$ $[M+H]^+$: 283.0692, found: 283.0690.

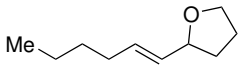
5.3.2 Synthesis of tetrahydrofurans and tetrahydropyrans 127 and 144

General procedure D: intramolecular etherification

To a solution of alcohol **126** or **139** (1.00 mmol, 1.0 equiv) in MeCN (0.2 M) are added (2-anisyl)$_2$Se$_2$ (18.6 mg, 50.0 µmol, 0.05 equiv), *p*-MeO-TPT (**95**) (14.6 mg, 30.0 µmol, 0.03 equiv)

and NaH_2PO_4 (96 mg, 0.8 mmol, 0.8 equiv). The mixture is stirred vigorously at room temperature under ambient air and irradiation at $\lambda = 465$ nm until complete conversion (monitored by TLC/NMR). Removal of the solvent in vacuo, followed by column chromatography afford products **127** or **144**.

(E)-2-(Hex-1-en-1-yl)tetrahydrofuran (127a)

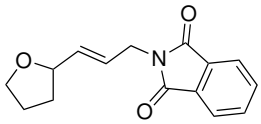


127a

Following general procedure **D**: alcohol **126a**; reaction time: 7 h; eluting with *n*-pentane:Et_2O (9:1); yield: 49 mg, 0.32 mmol, 32%; colorless liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 65%.

R_f = 0.31 (*n*-pentane:Et_2O, 9:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2957, 2926, 2857, 1459, 1377, 1153, 1054, 966, 731; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.67 (dtd, J = 15.2, 6.7, 0.9 Hz, 1 H), 5.44 (ddt, J = 15.3, 7.2, 1.4 Hz, 1 H), 4.22 (q, J = 7.1 Hz, 1 H), 3.89 (ddd, J = 8.3, 7.3, 6.3 Hz, 1 H), 3.75 (td, J = 7.9, 6.1 Hz, 1 H), 2.08-1.98 (m, 3 H), 1.97-1.79 (m, 2 H), 1.65-1.51 (m, 2 H), 1.33 (tddd, J = 10.0, 8.7, 7.0, 4.3 Hz, 3 H), 0.88 (t, J = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 133.0, 130.7, 80.2, 68.0, 32.4, 32.0, 31.4, 26.1, 22.4, 14.1; **HR-ESI-MS m/z**: calcd. $C_{10}H_{19}O$ $[M+H]^+$: 155.1430, found: 155.1433. The analytical data was in agreement with literature.[125]

(*E*)-2-(3-(Tetrahydrofuran-2-yl)allyl)isoindoline-1,3-dione (127g)

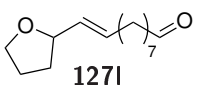


127g

Following general procedure **D**: alcohol **126g**; reaction time: 7.5 h; eluting with *n*-pentane:EtOAc (4:1); yield: 85 mg, 0.33 mmol, 37%; yellow liquid; ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard: 45%.

R_f = 0.19 (*n*-pentane:EtOAc, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2972, 2868, 1770, 1705, 1613, 1467, 1428, 1391, 1188, 1112, 1087, 1050, 939, 854, 794, 718, 614, 529, 444; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.87-7.81 (m, 2 H), 7.76-7.66 (m, 2 H),5.84-5.62 (m, 2 H), 4.39-4.13 (m, 3 H), 3.87 (ddd, J = 8.3, 7.1, 6.4 Hz, 1 H), 3.80-3.69 (m, 1 H), 2.08-1.96 (m, 1 H), 1.95-1.78 (m, 2 H), 1.63-1.51 (m, 1 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 167.9, 135.1, 134.0, 132.2, 124.2, 123.3, 78.7, 68.2, 39.2, 32.2, 25.9; **HR-ESI-MS m/z**: calcd. $C_{15}H_{16}NO_3$ $[M+H]^+$: 258.1125, found: 258.1124.

(*E*)-10-(Tetrahydrofuran-2-yl)dec-9-enal (127l)



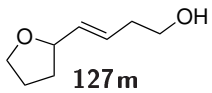
127l

Following general procedure **D**: alcohol **126l** (170 mg, 751 µmol, 1.0 equiv), (2-anisyl)$_2$)Se_2 (14 mg, 0.038 mmol, 0.05 equiv), photosensitizer **95** (11 mg, 0.023 mmol, 0.03 equiv) and NaH_2PO_4 (72 mg, 0.60 mmol, 0.8 equiv); reaction

time: 16.5 h; eluting with *n*-pentane:EtOAc (20:1); yield: 12 mg, 0.55 mmol, 7%; colorless liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 24%.

R_f = 0.21 (*n*-pentane:EtOAc, 20:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2926, 2854, 2716, 2168, 2015, 1723, 1461, 1410, 1371, 1179, 1051, 967, 920, 869, 726, 520, 401; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 9.75 (t, J = 1.9 Hz, 1 H), 5.65 (dtd, J = 15.3, 6.6, 0.9 Hz, 1 H), 5.44 (ddt, J = 15.3, 7.1, 1.4 Hz, 1 H), 4.21 (q, J = 7.1 Hz, 1 H), 3.89 (m, 1 H), 3.75 (td, J = 7.8, 6.1 Hz, 1 H), 2.41 (td, J = 7.4, 1.9 Hz, 2 H), 2.11-1.77 (m, 6 H), 1.69-1.48 (m, 2 H), 1.45-1.16 (m, 8 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 202.8, 132.7, 130.8, 80.1, 68.0, 44.1, 32.5, 32.4, 29.4, 29.3, 29.2, 29.1, 26.2, 22.3; **HR-ESI-MS m/z**: calcd. $C_{14}H_{25}O_2$ [M+H]$^+$: 225.1849, found: 225.1847.

(*E*)-4-(Tetrahydrofuran-2-yl)but-3-en-1-ol (127m)

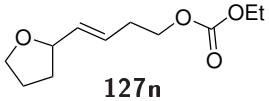


127m

Following general procedure **D**: alcohol **126m**; reaction time: 7 h; eluting with *n*-pentane/Et_2O (9:1); yield: 49 mg, 0.32 mmol, 32%; colorless liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 65%.

R_f = 0.31 (*n*-pentane:Et_2O, 9:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2957, 2926, 2857, 1459, 1377, 1153, 1054, 966, 731; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.67 (dtd, J = 15.2, 6.7, 0.9 Hz, 1 H), 5.44 (ddt, J = 15.3, 7.2, 1.4 Hz, 1 H), 4.22 (q, J = 7.1 Hz, 1 H), 3.89 (ddd, J = 8.3, 7.3, 6.3 Hz, 1 H), 3.75 (td, J = 7.9, 6.1 Hz, 1 H), 2.08-1.98 (m, 3 H), 1.97-1.79 (m, 2 H), 1.65-1.51 (m, 2 H), 1.33 (tddd, J = 10.0, 8.7, 7.0, 4.3 Hz, 3 H), 0.88 (t, J = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 133.0, 130.7, 80.2, 68.0, 32.4, 32.0, 31.4, 26.1, 22.4, 14.1; **HR-ESI-MS m/z**: calcd. $C_{10}H_{19}O$ [M+H]$^+$: 155.1430, found: 155.1433.

(*E*)-Ethyl (4-(tetrahydrofuran-2-yl)but-3-en-1-yl) carbonate (127n)

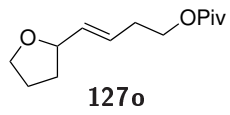


127n

Following general procedure **D**: alcohol **126n** (113 mg, 524 µmol, 1.0 equiv), (2-anisyl)$_2Se_2$ (10 mg, 0.026 mmol, 0.05 equiv), photosensitizer **95** (7.6 mg, 0.016 mmol, 0.03 equiv) and NaH_2PO_4 (50 mg, 0.42 mmol, 0.8 equiv); reaction time: 7 h; eluting with *n*-pentane/EtOAc (7:1); yield: 31 mg, 0.14 mmol, 28%; colorless liquid; ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard: 47%.

R_f = 0.23 (*n*-pentane:EtOAc, 7:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2978, 2868, 1741, 1464, 1384, 1366, 1247, 1091, 1051, 1007, 968, 873, 791; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.64 (m, 1 H), 5.58 (m, 1 H), 4.22 (m, 1 H), 4.20-4.11 (m, 4 H), 3.88 (m, 1 H), 3.76 (m, 1 H), 2.51-2.30 (m, 2 H), 2.14-1.76 (m, 3 H), 1.59 (m, 1 H), 1.30 (t, J = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 155.1, 134.1, 126.6, 79.6, 68.1, 67.1, 64.0, 32.3, 31.8, 26.1, 14.5; **HR-ESI-MS m/z**: calcd. $C_{11}H_{19}O_4$ [M+H]$^+$: 215.1278, found: 215.1281.

(*E*)-4-(Tetrahydrofuran-2-yl)but-3-en-1-yl pivalate (127o)

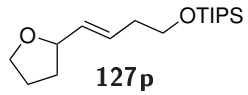


127o

Following general procedure **D**: alcohol **126o** (134 mg, 586 µmol, 1.0 equiv), $(2\text{-anisyl})_2Se_2$ (11 mg, 0.029 mmol, 0.05 equiv), photosensitizer **95** (8.5 mg, 0.018 mmol, 0.03 equiv) and NaH_2PO_4 (58 mg, 0.47 mmol, 0.8 equiv); reaction time: 11 h; eluting with *n*-pentane/EtOAc (7:1); yield: 33 mg, 0.15 mmol, 25%; colorless liquid; ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard: 44%.

$\mathbf{R_f} = 0.29$ (*n*-pentane:EtOAc, 7:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2970, 2872, 1726, 1480, 1460, 1398, 1366, 1283, 1150, 1052, 967, 869, 770; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.64 (m, 1 H), 5.55 (m, 1 H), 4.24 (m, 1 H), 4.09 (t, J = 6.7 Hz, 2 H), 3.88 (ddd, J = 8.0, 7.1, 6.3 Hz, 1 H), 3.76 (m, 1 H), 2.59-2.16 (m, 2 H), 2.01 (m, 1 H), 1.90 (m, 2 H), 1.58 (m, 1 H), 1.18 (s, 9 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 178.4, 133.7, 127.3, 79.6, 68.1, 63.5, 38.9, 32.4, 31.9, 27.4, 26.1; **HR-ESI-MS m/z**: calcd. $C_{13}H_{23}O_3$ $[M+H]^+$: 227.1642, found: 227.1643.

(*E*)-Triisopropyl((4-(tetrahydrofuran-2-yl)but-3-en-1-yl)oxy)silane (127p)

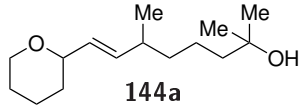


127p

Following general procedure **D**: alcohol **126p** (163 mg, 541 µmol, 1.0 equiv), $(2\text{-anisyl})_2Se_2$ (10 mg, 0.027 mmol, 0.05 equiv), photosensitizer **95** (7.9 mg, 0.016 mmol, 0.03 equiv) and NaH_2PO_4 (52 mg, 0.43 mmol, 0.8 equiv); reaction time: 25 h; eluting with *n*-pentane/EtOAc (75:1); yield: 37 mg, 0.13 mmol, 23%; colorless liquid; ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard: 29%.

$\mathbf{R_f} = 0.33$ (*n*-pentane:EtOAc, 75:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2942, 2892, 2865, 1463, 1382, 1101, 1055, 1013, 995, 966, 919, 881, 783, 737, 679, 657, 445; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.70 (dtd, J = 15.4, 6.8, 0.9 Hz, 1 H), 5.52 (ddt, J = 15.3, 7.0, 1.3 Hz, 1 H), 4.23 (m, 1 H), 3.88 (m, 1 H), 3.81-3.63 (m, 3 H), 2.35-2.23 (m, 2 H), 2.09-1.76 (m, 3 H), 1.58 (m, 1 H), 1.18-0.88 (m, 21 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 132.7, 129.0, 80.0, 68.1, 63.3, 36.3, 32.4, 26.2, 18.3, 12.3; **HR-ESI-MS m/z**: calcd. $C_{17}H_{35}O_2Si$ $[M+H]^+$: 299.2401, found: 299.2402.

(*E*)-2,6-Dimethyl-8-(tetrahydro-2*H*-pyran-2-yl)oct-7-en-2-ol (144a)



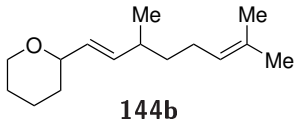
144a

Following general procedure **D**: alcohol **139a**; reaction time: 7 h; eluting with *n*-pentane/Et_2O (1:1); yield: 172 mg, 717 µmol, 71%; yellow liquid; mixture of diastereomers; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 72%.

$\mathbf{R_f} = 0.19$ (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3437, 2934, 2845, 1463, 1374, 1203, 1175, 1083, 1049, 1033, 968, 938, 895, 754; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.53 (dddd,

J = 15.7, 8.4, 7.4, 1.0 Hz, 1 H), 5.42 (dddd, J = 15.6, 6.2, 2.3, 0.9 Hz, 1 H), 4.00 (ddt, J = 11.6, 4.0, 1.6 Hz, 1 H), 3.74 (m, 1 H), 3.47 (m, 1 H), 2.12 (m, 1 H), 1.82 (m, 1 H), 1.72-1.22 (m, 12 H), 1.19 (s, 6 H), 0.98 (dd, J = 6.7, 3.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 137.4, 137.3, 129.9, 129.7, 78.5, 78.3, 71.2, 71.1, 68.5, 44.10, 44.08, 37.4, 37.3, 36.52, 36.46, 32.6, 32.5, 29.41, 29.38, 29.36, 26.03, 26.01, 23.6, 22.1, 22.0, 20.6, 20.4; **HR-ESI-MS m/z**: calcd. $C_{15}H_{29}O_2$ $[M+H]^+$: 241.2162, found: 241.2160.

(*E*)-2-(3,7-Dimethylocta-1,6-dien-1-yl)tetrahydro-2*H*-pyran (144b)

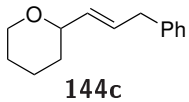


144b

Following general procedure **D**: alcohol **139b**; reaction time: 10 h; eluting with *n*-pentane/Et_2O (5:1); yield: 43 mg, 0.19 mmol, 19%; colorless liquid; mixture of diastereomers; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 25%.

R_f = 0.71 (*n*-pentane:Et_2O, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2929, 2848, 1452, 1375, 1266, 1204, 1175, 1085, 1051, 1035, 968, 897, 847, 543, 442, 419; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.54 (dddd, J = 15.5, 12.7, 7.3, 1.0 Hz, 1 H), 5.42 (dddd, J = 15.5, 5.7, 4.5, 0.9 Hz, 1 H), 5.08 (dddd, J = 7.2, 5.8, 2.7, 1.3 Hz, 1 H), 4.00 (ddt, J = 11.5, 3.5, 1.6 Hz, 1 H), 3.74 (ddt, J = 10.8, 5.6, 1.4 Hz, 1 H), 3.47 (tdd, J = 11.5, 2.6, 1.0 Hz, 1 H), 2.10 (dq, J = 13.6, 6.7 Hz, 1 H), 1.94 (quint, J = 7.1 Hz, 2 H), 1.83 (m, 1 H), 1.67 (t, J = 1.2 Hz, 3 H), 1.65-1.44 (m, 6 H), 1.45-1.16 (m, 4 H), 0.98 (dd, J = 6.7, 2.7 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 137.6, 137.2, 131.4, 130.0, 129.8, 124.8, 124.8, 78.6, 78.4, 68.5, 68.5, 37.1, 37.1, 36.2, 36.0, 32.6, 32.5, 26.1, 26.0, 25.9, 25.9, 25.9, 23.6, 23.6, 20.6, 20.4, 17.9; **HR-ESI-MS m/z**: calcd. $C_{15}H_{27}O$ $[M+H]^+$: 223.2056, found: 223.2058.

(*E*)-2-(3-Phenylprop-1-en-1-yl)tetrahydro-2*H*-pyran (144c)

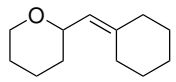


144c

Following general procedure **D**: alcohol **139c**; reaction time: 7 h; eluting with *n*-pentane/DCM (1:9); yield: 90 mg, 0.44 mmol, 44%; yellow liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 54%.

R_f = 0.43 (*n*-pentane:DCM, 1:9); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2933, 2841, 1495, 1453, 1438, 1204, 1175, 1083, 1048, 1033, 967, 894, 745, 697, 580, 543, 497, 456; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.38-7.24 (m, 2 H), 7.24-7.03 (m, 3 H), 5.83 (dtd, J = 15.4, 6.7, 1.2 Hz, 1 H), 5.54 (ddt, J = 15.4, 6.1, 1.5 Hz, 1 H), 4.01 (m, 1 H), 3.79 (m, 1 H), 3.47 (m, 1 H), 3.41-3.24 (m, 2 H), 1.84 (m, 1 H), 1.74-1.30 (m, 5 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 140.2, 132.8, 130.2, 128.7, 128.4, 126.1, 78.1, 68.5, 39.0, 32.4, 26.1, 23.6; **HR-ESI-MS m/z**: calcd. $C_{14}H_{19}O$ $[M+H]^+$: 203.1430, found: 203.1434.

2-(Cyclohexylidenemethyl)tetrahydro-2*H*-pyran (144d)

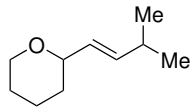


144d

Following general procedure **D**: alcohol **139d**; reaction time: 17 h; eluting with *n*-pentane/DCM (1:9); yield: 62 mg, 0.35 mmol, 35%; colorless liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 53%.

$\mathbf{R_f} = 0.43$ (*n*-pentane:DCM, 1:9); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2926, 2851, 1446, 1204, 1174, 1084, 1051, 1033, 992, 901, 846; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.11 (dquint, J = 8.0, 1.2 Hz, 1 H), 4.29-3.87 (m, 2 H), 3.47 (td, J = 11.4, 2.5 Hz, 1 H), 2.35-1.94 (m, 5 H), 1.83 (m, 1 H), 1.69-1.26 (m, 10 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 142.7, 123.3, 74.3, 68.4, 37.1, 32.9, 29.7, 28.6, 28.1, 26.9, 26.1, 23.8; **HR-ESI-MS m/z**: calcd. $C_{12}H_{21}O$ $[M+H]^+$: 181.1587, found: 181.1588.

(*E*)-2-(3-Methylbut-1-en-1-yl)tetrahydro-2*H*-pyran (144e)

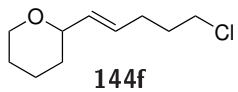


144e

Following general procedure **D**: alcohol **139e**; reaction time: 7 h; eluting with *n*-pentane/Et_2O (9:1); yield: 58 mg, 0.38 mmol, 38%; colorless liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 52%.

$\mathbf{R_f} = 0.43$ (*n*-pentane:Et_2O, 9:1);**IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2955, 2934, 2841, 1464, 1362, 1263, 1204, 1176, 1085, 1051, 1035, 968, 896, 847; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.64 (ddd, J = 15.6, 6.4, 1.1 Hz, 1 H), 5.41 (ddd, J = 15.6, 6.2, 1.4 Hz, 1 H), 4.01 (m, 1 H), 3.73 (dddd, J = 10.8, 6.2, 2.1, 1.1 Hz, 1 H), 3.47 (m, 1 H), 2.26 (m, 1 H), 1.83 (m, 1 H), 1.70-1.29 (m, 5 H), 0.98 (dd, J = 6.7, 0.9 Hz, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 138.8, 128.4, 78.5, 68.5, 32.5, 30.9, 26.1, 23.7, 22.5; **HR-ESI-MS m/z**: calcd. $C_{10}H_{19}O$ $[M+H]^+$: 155.1430, found: 155.1436.

(*E*)-2-(5-Chloropent-1-en-1-yl)tetrahydro-2*H*-pyran (144f)

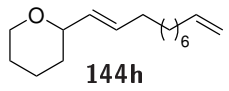


144f

Following general procedure **D**: alcohol **139f** (156 mg, 818 µmol), 1.0 equiv), $(2\text{-aisyl})_2Se_2$ (15 mg, 0.041 mmol, 0.05 equiv), photosensitizer **95** (12 mg, 0.025 mmol, 0.03 equiv) and NaH_2PO_4 (79 mg, 0.65 mmol, 0.8 equiv); reaction time: 7 h; eluting with *n*-pentane/DCM (1:9); yield: 88 mg, 0.47 mmol, 47%; yellow liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 62%.

$\mathbf{R_f} = 0.44$ (*n*-pentane:DCM, 1:9); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2934, 2844, 1440, 1265, 1204, 1083, 1049, 1034, 968, 895, 726, 653; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.64 (dtd, J = 15.5, 6.3, 0.8 Hz, 1 H), 5.52 (ddt, J = 15.5, 5.8, 1.0 Hz, 1 H), 4.00 (m, 1 H), 3.75 (m,1 H), 3.53 (t, J = 6.6 Hz, 2 H), 2.18 (dddd, J = 8.0, 7.0, 6.0, 0.8 Hz, 2 H), 2.03-1.74 (m, 3 H), 1.73-1.23 (m, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 132.8, 129.4, 78.1, 68.5, 44.6, 32.4, 32.1, 29.6, 26.1, 23.6; **HR-ESI-MS m/z**: calcd. $C_{10}H_{17}ClONa$ $[M+Na]^+$: 211.0860, found: 211.0865.

(*E*)-2-(Undeca-1,10-dien-1-yl)tetrahydro-2*H*-pyran (144h)

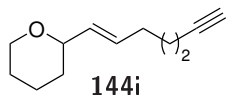


144h

Following general procedure **D**: alcohol **139h**; reaction time: 17 h; eluting with *n*-pentane:Et_2O (20:1); yield: 86 mg, 0.37 mmol, 37%; colorless liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 55%.

R_f = 0.23 (*n*-pentane:Et_2O, 20:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2924, 2852, 1727, 1640, 1463, 1439, 1371, 1263, 1203, 1175, 1085, 1035, 966, 907, 861, 843, 810, 723; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1 H), 5.66 (dtd, J = 15.5, 6.6, 1.1 Hz, 1 H), 5.45 (ddt, J = 15.5, 6.2, 1.4 Hz, 1 H), 5.04-4.88 (m, 2 H), 4.00 (ddt, J = 11.6, 4.1, 1.8 Hz, 1 H), 3.73 (ddd, J = 9.2, 4.5, 1.9 Hz, 1 H), 3.47 (m, 1 H), 2.02 (qdd, J = 6.9, 5.4, 1.2 Hz, 4 H), 1.84 (m, 1 H), 1.70-1.19 (m, 15 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 139.3, 131.9, 131.3, 114.2, 78.4, 68.5, 34.0, 32.5, 32.4, 29.5, 29.4, 29.31, 29.28, 29.1, 26.1, 23.7; **HR-ESI-MS m/z**: calcd. $C_{16}H_{28}ONa$ $[M+Na]^+$: 259.2032, found: 259.2034.

(*E*)-2-(Hept-1-en-6-yn-1-yl)tetrahydro-2*H*-pyran (144i)



144i

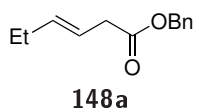
Following general procedure **D**: alcohol **139i**; reaction time: 14.5 h; eluting with *n*-pentane:Et_2O (30:1); yield: 54 mg, 0.31 mmol, 31%; colorless liquid; ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard: 37%.

R_f = 0.11 (*n*-pentane:Et_2O, 30:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3304, 2933, 2843, 1439, 1344, 1263, 1203, 1175, 1083, 1049, 1034, 967, 896, 842, 810; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.64 (dtd, J = 15.5, 6.5, 0.9 Hz, 1 H), 5.50 (ddt, J = 15.5, 6.0, 1.2 Hz, 1 H), 4.00 (m, 1 H), 3.74 (m, 1 H), 3.47 (m, 1 H), 2.37-2.04 (m, 4 H), 1.93 (t, J = 2.6 Hz, 1 H), 1.83 (m, 1 H), 1.68-1.23 (m, 7 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 132.3, 130.3, 84.4, 78.2, 68.52, 68.49, 32.4, 31.4, 28.1, 26.1, 23.6, 18.1; **HR-ESI-MS m/z**: calcd. $C_{12}H_{19}O$ $[M+H]^+$: 179.1430, found: 179.1429.

5.4 Intermolecular etherification *via* photo-aerobic selenium-π-acid catalysis

5.4.1 Synthesis of alkenes 148

Benzyl (*E*)-hex-3-enoate (148a)



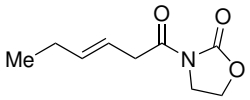
148a

A solution of (*E*)-hex-3-enoic acid (3.00 g, 26.3 mmol, 1.00 equiv), benzyl alcohol (5.68 g, 52.6 mmol, 2.00 equiv) and *p*-toluenesulfonic acid (350 mg, 1.31 mmol, 0.05 equiv) in toluene (25 mL) was stirred for 5 h at 150 °C. After cooling down to room temperature, the solution was diluted with EtOAc (50 mL) and washed with sat. aq. $NaHCO_3$ sol. (3 × 50 mL) and sat. aq. NaCl sol. (50 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Column

chromatography (*n*-pentane/EtOAc, 20:1) afforded the product as a yellow oil (4.62 g, 22.7 mmol, 86%).

R_f = 0.65 (*n*-pentane:EtOAc, 20:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2963, 1735, 1498, 1455, 1377, 1317, 1234, 1152, 966, 734, 696, 580, 481, 465; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.45-7.28 (m, 5 H), 5.78-5.39 (m, 2 H), 5.13 (s, 2 H), 3.12-2.88 (m, 2 H), 2.19-1.94 (m, 2 H), 0.99 (t, J = 7.5 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 172.2, 136.6, 136.1, 128.7, 128.3, 128.3, 120.6, 66.4, 38.2, 25.6, 13.6; **HR-ESI-MS m/z**: calcd. $C_{13}H_{16}O_2Na$ $[M+Na]^+$: 227.1048, found: 227.1047.

(*E*)-3-(Hex-3-enoyl)oxazolidin-2-one (148b)

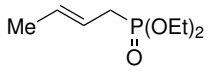


148b

To a solution of 2-oxazolidinone (435 mg, 5.00 mmol, 1.0 equiv) and DMAP (79 mg, 0.65 mmol, 0.13 equiv) in DCM (6.6 mL), (*E*)-3-hexenoic acid (741 mg, 6.50 mmol, 1.3 equiv) was added and the solution was cooled to 0 °C. DCC (1.35 g, 6.55 mmol, 1.31 equiv) was added, the solution was stirred for 10 min at 0 °C and 17.5 h at room temperature. The mixture was filtered, the precipitate was washed with DCM (2×), the comb. org. phases were washed with sat. aq. $NaHCO_3$ sol. (2×) and dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 2:1) afforded the product as a yellow oil (292 mg, 1.59 mmol, 32%).

R_f = 0.36 (*n*-pentane:EtOAc, 2:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2965, 2925, 2876, 2851, 1711, 1695, 1479, 1385, 1362, 1328, 1290, 1218, 1189, 1104, 1035, 1017, 1005, 960, 757, 694; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.65 (m, 1 H), 5.57 (m, 1 H), 4.41 (t, J = 8.2 Hz, 2 H), 4.04-3.99 (m, 2 H), 3.64 (dq, J = 6.3, 1.0 Hz, 2 H), 2.06 (qdq, J = 7.4, 6.1, 1.2 Hz, 2 H), 0.99 (t, J = 7.5 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 172.1, 153.6, 137.2, 120.1, 62.2, 42.7, 38.9, 25.7, 13.6; **HR-ESI-MS m/z**: calcd. $C_9H_{14}NO_3$ $[M+H]^+$: 184.0968, found: 184.0971.

Diethyl (*E*)-but-2-en-1-ylphosphonate (148c)



148c

Diethyl phosphite (9.05 g, 66.0 mmol, 1.10 equiv) was dissolved in dry THF (200 mL) and cooled to −10 °C. *n*-BuLi (2.5 M in hexane; 26.4 mL, 66.0 mmol, 1.1 equiv) was added dropwise and the mixture was stirred for 5 min. A solution of (*E*)-crotyl bromide (8.10 g, 60.0 mmol, 1.00 equiv) in dry THF (24 mL) was added dropwise, the solution was stirred for 15 min at −10 °C, allowed to warm up to 23 °C and stirred for 18 h. The reaction was quenched by the addition of sat. aq. NH_4Cl-sol. (25 mL), the aq. phase was extracted with Et_2O (3 × 25 mL), the comb. org. phases were washed with sat. aq. NaCl sol. (3 × 40 mL) and dried over Na_2SO_4. Removal

of the solvent in vacuo and vacuum distillation afforded the product as a colorless oil (7.06 g, 36.7 mmol, 61%).

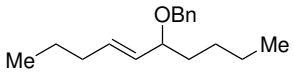
R_f = 0.32 (*n*-pentane:EtOAc, 1:2); **b.p.** = 115 °C (19 mbar); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2980, 2935, 2908, 1444, 1392, 1251, 1166, 1096, 1020, 956, 849, 831, 806, 776, 707, 683; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.61 (dddt, J = 15.2, 6.5, 5.1, 1.3 Hz, 1 H), 5.41 (m, 1 H), 4.08 (dqd, J = 7.8, 7.1, 3.9 Hz, 4 H), 2.52 (ddt, J = 21.4, 7.3, 1.2 Hz, 2 H), 1.69 (dddd, J = 6.5, 4.5, 1.7, 1.2 Hz, 3 H), 1.39-0.90 (m, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 130.8 (d, J_{CP} = 14.7 Hz), 119.7 (d, J_{CP} = 11.4 Hz), 61.9 (d, J_{CP} = 6.8 Hz), 30.6 (d, J_{CP} = 140.0 Hz), 18.2 (d, J_{CP} = 2.6 Hz), 16.6 (d, J_{CP} = 6.0 Hz); **^{31}P{^{1}H} NMR** (203 MHz, $CDCl_3$): δ [ppm] = 28.1; **HR-ESI-MS m/z**: calcd. $C_8H_{18}O_3P$ $[M+H]^+$: 193.0988, found: 193.0992.

5.4.2 Synthesis of allylic ethers 149

General Procedure E: intermolecular etherification

Alkene **148** (1.0 mmol), $(2\text{-anisyl})_2Se_2$ (36 mg, 0.10 mmol, 0.1 equiv) and *p*-MeO-TPT (**95**) (24 mg, 0.050 mmol, 0.05 equiv) are dissolved in the respective alcohol (0.2 M; 5 mL) and the solution is stirred vigorously at room temperature under an atmosphere of air and irradiation at λ = 465 nm until completion, which is determined by NMR or TLC. After removal of the solvent, the product is afforded *via* column chromatography.

(*E*)-((Dec-6-en-5-yloxy)methyl)benzene (151)

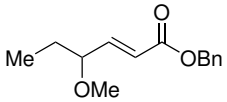


151

Isolated from a combination of three reaction mixtures, yield 12 mg, 48 µmol, yellow oil.

R_f = 0.29 (*n*-pentane:EtOAc, 75:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958, 2928, 2861, 1362, 2340, 1722, 1456, 1263, 1090, 1067, 1028, 970, 801, 746, 734, 697, 672; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.45-7.27 (m, 5 H), 5.59 (dt, J = 15.4, 6.7 Hz, 1 H), 5.33 (ddt, J = 15.4, 8.3, 1.4 Hz, 1 H), 4.58 (d, J = 12.0 Hz, 1 H), 4.33 (d, J = 12.0 Hz, 1 H), 3.66 (dt, J = 8.2, 6.5 Hz, 1 H), 2.21-1.96 (m, 2 H), 1.81-1.07 (m, 8 H), 1.02-0.71 (m, 6 H); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ [ppm] = 139.3, 134.2, 131.2, 128.4, 127.9, 127.4, 80.4, 69.7, 35.7, 34.5, 27.9, 22.8, 22.6, 14.2, 13.8. No HRMS could be obtained.

Benzyl (*E*)-4-methoxyhex-2-enoate (149a)

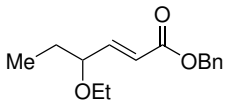


149a

Following general procedure **E**: alkene **148a** (102 mg, 500 µmol, 1.0 equiv), MeOH (2.5 mL), $(2\text{-anisyl})_2Se_2$ (18 mg, 50 µmol, 0.1 equiv) and *p*-MeO-TPT **95** (12.0 mg, 0.025 mmol, 0.05 equiv); reaction time 70.5 h; eluting with *n*-pentane:EtOAc (250:1); yield: 32 mg, 0.14 mmol, 27%; colorless liquid; ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard: 32%.

R_f = 0.43 (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2968, 2933, 2878, 2824, 1717, 1657, 1455, 1377, 1355, 1266, 1198, 1159, 1127, 1087, 981, 846, 737, 696; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.47-7.30 (m, 5 H), 6.85 (dd, J = 15.8, 6.4 Hz, 1 H), 6.04 (dd, J = 15.8, 1.3 Hz, 1 H), 5.20 (s, 2 H), 3.67 (qd, J = 6.3, 1.3 Hz, 1 H), 3.31 (s, 3 H), 1.89-1.36 (m, 2 H), 0.92 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 166.2, 148.9, 136.0, 128.7, 128.4, 128.4, 121.9, 81.9, 66.4, 57.2, 27.7, 9.6; **HR-ESI-MS m/z**: calcd. $C_{14}H_{18}O_3Na$ $[M+Na]^+$: 257.1148, found: 257.1146.

Benzyl (*E*)-4-ethoxyhex-2-enoate (149b)

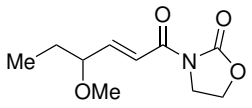


149b

Following general procedure **E**: alkene **148a** (204 mg, 1.00 mmol, 1.0 equiv), EtOH (5 mL); reaction time 92 h; eluting with *n*-pentane:EtOAc (50:1); yield: 48 mg, 0.19 mmol, 19%; colorless liquid; ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard: 31%.

R_f = 0.31 (*n*-pentane:EtOAc, 50:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2972, 2932, 2875, 1719, 1658, 1456, 1377, 1338, 1268, 1164, 1126, 1092, 983, 748, 697; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.47-7.30 (m, 5 H), 6.87 (dd, J = 15.8, 6.2 Hz, 1 H), 6.03 (dd, J = 15.8, 1.3 Hz, 1 H), 5.19 (d, J = 0.5 Hz, 2 H), 3.77 (qd, J = 6.2, 1.4 Hz, 1 H), 3.53 (dq, J = 9.3, 7.0 Hz, 1 H), 3.38 (dqd, J = 9.2, 7.0, 0.9 Hz, 1 H), 1.69-1.49 (m, 2 H), 1.20 (t, J = 7.0 Hz, 3 H), 1.08-0.79 (m, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 166.2, 149.5, 136.1, 128.6, 128.32, 128.30, 121.3, 80.1, 66.4, 64.9, 28.1, 15.6, 9.8; **HR-ESI-MS m/z**: calcd. $C_{15}H_{20}O_3Na$ $[M+Na]^+$: 271.1305, found: 271.1303.

(*E*)-3-(4-Methoxyhex-2-enoyl)oxazolidin-2-one (149e)

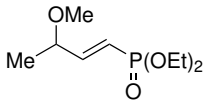


149e

Following general procedure **E**: alkene **148b** (183 mg, 1.00 mmol, 1.0 equiv), MeOH (5 mL); reaction time 95 h; eluting with *n*-pentane:EtOAc (3:1); yield: 22 mg, 0.10 mmol, 10%; yellow liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 11%.

R_f = 0.14 (*n*-pentane:EtOAc, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2965, 2930, 2881, 2826, 1769, 1683, 1640, 1476, 1462, 1440, 1385, 1362, 1335, 1194, 1105, 1088, 1033, 984, 972, 853, 759, 700; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.36 (dd, J = 15.6, 1.1 Hz, 1 H), 6.96 (dd, J = 15.6, 6.8 Hz, 1 H), 4.55-4.27 (m, 2 H), 4.17-3.99 (m, 2 H), 3.75 (m, 1 H), 3.32 (s, 3 H), 1.79-1.49 (m, 2 H), 0.92 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 164.8, 153.4, 150.0, 121.0, 82.2, 62.2, 57.2, 42.9, 27.9, 9.7; **HR-ESI-MS m/z**: calcd. $C_{10}H_{15}NO_4Na$ $[M+Na]^+$: 236.0893, found: 236.0897.

Diethyl (*E*)-(3-methoxybut-1-en-1-yl)phosphonate (149f)

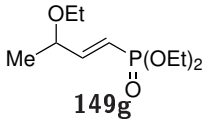


149f

Following general procedure **E**: alkene **148c** (192 mg, 1.00 mmol, 1.0 equiv), MeOH (5 mL); reaction time 8 d; eluting with DCM:acetone (20:1) + 1% AcOH; yield: 81 mg, 0.36 mmol, 36%; yellow liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: >99%.

$\mathbf{R_f}$ = 0.07 (DCM:acetone, 20:1 + 1% AcOH); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2980, 2933, 2905, 2871, 2826, 1744, 1722, 1635, 1444, 1392, 1369, 1337, 1248, 1216, 1112, 1049, 1020, 956, 858, 826, 789, 746; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 6.66 (ddd, J = 22.4, 17.2, 5.3 Hz, 1 H), 5.85 (ddd, J = 20.5, 17.2, 1.4 Hz, 1 H), 4.08 (dqt, J = 8.4, 7.1, 1.1 Hz, 4 H), 3.87 (qddd, J = 6.6, 5.3, 2.4, 1.4 Hz, 1 H), 3.31 (s, 3 H), 1.32 (t, J = 7.1 Hz, 6 H), 1.26 (d, J = 6.6 Hz, 3 H) **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 153.5 (d, J_{CP} = 4.3 Hz), 116.9 (d, J_{CP} = 187.8 Hz), 77.4, 61.9 (dd, J_{CP} = 5.6, 2.1 Hz), 56.9, 20.3 (d, J_{CP} = 1.9 Hz), 16.5 (d, J_{CP} = 6.2 Hz); **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ [ppm] = 18.3; **HR-ESI-MS m/z**: calcd. $C_9H_{20}O_4P$ $[M+H]^+$: 223.1094, found: 223.1095.

Diethyl (*E*)-(3-ethoxybut-1-en-1-yl)phosphonate (149g)

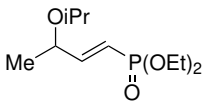


149g

Following general procedure **E**: alkene **148c** (192 mg, 1.00 mmol, 1.0 equiv), ethanol (5 mL); reaction time 8.5 d; eluting with DCM:acetone (30:1) + 1% AcOH; yield: 73 mg, 0.31 mmol, 31%; yellow liquid; ^{1}H NMR yield using phthalide as the internal standard: 50%.

$\mathbf{R_f}$ = 0.10 (DCM:acetone, 30:1 + 1% AcOH); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2978, 2934, 2904, 2872, 1721, 1634, 1444, 1392, 1369, 1336, 1245, 1206, 1163, 1094, 1050, 1020, 957, 855, 828, 749; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 6.68 (ddd, J = 22.4, 17.2, 5.2 Hz, 1 H), 5.85 (ddd, J = 20.8, 17.2, 1.4 Hz, 1 H), 4.16-4.02 (m, 4 H), 3.98 (dddd, J = 6.6, 5.2, 2.5, 1.4 Hz, 1 H), 3.46 (dqd, J = 9.2, 7.0, 2.1 Hz, 2 H), 1.32 (tt, J = 7.1, 0.3 Hz, 6 H), 1.26 (d, J = 6.6 Hz, 3 H), 1.20 (t, J = 7.0 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 154.2 (d, J_{CP} = 4.4 Hz), 116.4 (d, J_{CP} = 188.1 Hz), 75.5 (d, J_{CP} = 21.9 Hz), 64.6, 61.9 (dd, J_{CP} = 5.6, 2.5 Hz), 20.7 (d, J_{CP} = 2.1 Hz), 16.5 (d, J_{CP} = 6.4 Hz), 15.5; **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ [ppm] = 18.5; **HR-ESI-MS m/z**: calcd. $C_{10}H_{22}O_4P$ $[M+H]^+$: 237.1250, found: 237.1257.

Diethyl (*E*)-(3-isopropoxybut-1-en-1-yl)phosphonate (149h)

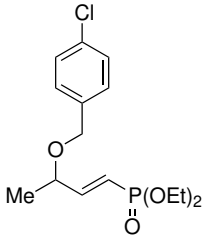


149h

Following general procedure **E**: alkene **148c** (192 mg, 1.00 mmol, 1.0 equiv), isopropanol (5 mL); reaction time 12 d; eluting with DCM:acetone (30:1) + 1% AcOH; yield: 101 mg, 402 µmol, 40%; yellow liquid; ^{1}H NMR yield using benzaldehyde as the internal standard: 43%.

$\mathbf{R_f}$ = 0.10 (DCM:acetone, 30:1 + 1% AcOH); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2975, 2934, 2909, 2872, 1722, 1633, 1445, 1369, 1247, 1121, 1020, 958, 851, 802, 751; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 6.70 (ddd, J = 22.2, 17.2, 4.9 Hz, 1 H), 5.86 (ddd, J = 21.1, 17.2, 1.5 Hz, 1 H), 4.14-4.01 (m, 5 H), 3.60 (quint, J = 6.1 Hz, 1 H), 1.32 (td, J = 7.1, 0.5 Hz, 6 H), 1.23 (d, J = 6.6 Hz, 3 H), 1.14 (dd, J = 6.1, 3.2 Hz, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 155.1 (d, J_{CP} = 4.5 Hz), 115.8 (d, J_{CP} = 188.3 Hz), 72.8 (d, J_{CP} = 21.7 Hz), 70.1, 62.0 (dd, J_{CP} = 5.6, 3.0 Hz), 23.1, 22.1, 21.3 (d, J_{CP} = 2.1 Hz), 16.5 (d, J_{CP} = 6.4 Hz); **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ [ppm] = 18.8; **HR-ESI-MS m/z**: calcd. $C_{11}H_{24}O_4P$ $[M+H]^+$: 251.1407, found: 251.1400.

Diethyl (*E*)-(3-((4-chlorobenzyl)oxy)but-1-en-1-yl)phosphonate (149k)

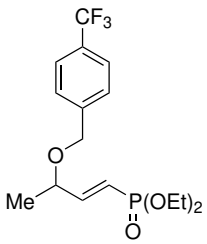


149k

Following general procedure **E**: alkene **148c** (192 mg, 1.00 mmol, 1.0 equiv), 4-chlorobenzyl alcohol (214 mg, 1.50 mmol, 1.5 equiv), MeCN (2.5 mL); reaction time 95 h; DCM:acetone (30:1) + 1% AcOH; yield: 68 mg, 204 µmol, 20%; yellow liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 27%.

$\mathbf{R_f}$ = 0.19 (DCM:acetone, 30:1 + 1% AcOH); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2979, 2929, 2904, 2867, 1722, 1633, 1492, 1391, 1244, 1164, 1088, 1015, 958, 807, 750, 668; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.34-7.28 (m, 2 H), 7.28-7.23 (m, 2 H), 6.70 (ddd, J = 22.4, 17.2, 5.4 Hz, 1 H), 5.90 (ddd, J = 20.4, 17.2, 1.4 Hz, 1 H), 4.51 (d, J = 12.0 Hz, 1 H), 4.41 (d, J = 12.0 Hz, 1 H), 4.21-3.98 (m, 5 H), 1.35-1.29 (m, 9 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 153.4 (d, J_{CP} = 4.5 Hz), 136.7, 133.6, 129.0, 128.7, 117.1 (d, J_{CP} = 188.1 Hz), 75.2 (d, J_{CP} = 22.1 Hz), 70.2, 62.02 (d, J_{CP} = 2.2 Hz), 61.98 (d, J_{CP} = 2.3 Hz), 20.6 (d, J_{CP} = 1.9 Hz), 16.5 (d, J_{CP} = 6.3 Hz); **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ [ppm] = 18.1; **HR-ESI-MS m/z**: calcd. $C_{15}H_{23}O_4PCl$ $[M+H]^+$: 333.1017, found: 333.1019.

Diethyl (*E*)-(3-((4-(trifluoromethyl)benzyl)oxy)but-1-en-1-yl)phosphonate (149l)



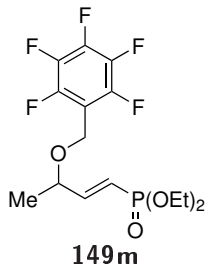
149l

Following general procedure **E**: alkene **148b** (134 mg, 700 µmol, 1.0 equiv), 4-trifluoromethylbenzyl alcohol (3.5 mL), diphenyl diselenide (22 mg, 70 µmol, 0.1 equiv) and *p*-MeO-TPT **95** (17 mg, 35 µmol, 0.05 equiv); reaction time 73 h; eluting with DCM:acetone (30:1) + 1% AcOH; yield: 123 mg, 0.34 mmol, 48%; brown liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 68%.

$\mathbf{R_f}$ = 0.21 (DCM:acetone, 30:1 + 1% AcOH); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2987, 2935, 2871, 1623, 1444, 1424, 1392, 1369, 1325, 1248, 1161, 1121, 1066, 1051, 1017, 956, 823; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.70-7.53 (m, 2 H), 7.55-7.40 (m, 2 H), 6.72 (ddd, J = 22.4, 17.2, 5.4 Hz, 1 H), 5.92 (ddd, J = 20.2, 17.2, 1.4 Hz, 1 H), 4.61 (d, J = 12.5 Hz, 1 H),

4.51 (d, J = 12.5 Hz, 1 H), 4.26-3.87 (m, 5 H), 1.37-1.30 (m, 9 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 153.0 (d, J_{CP} = 4.5 Hz), 142.4, 130.0 (d, J_{CF} = 32.3 Hz), 127.6, 125.6 (q, J_{CF} = 271.8 Hz), 125.5 (q, J_{CF} = 3.8 Hz), 117.4 (d, J_{CP} = 188.1 Hz), 75.6 (d, J_{CP} = 22.1 Hz), 70.2, 61.7-62.4 (m), 20.6 (d, J_{CP} = 1.9 Hz), 16.5 (d, J_{CP} = 6.2 Hz); **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ [ppm] = −62.5; **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ [ppm] = 17.9; **HR-ESI-MS m/z**: calcd. $C_{16}H_{23}F_3O_4P$ $[M+H]^+$: 367.1281, found: 367.1283.

Diethyl (*E*)-(3-((perfluorophenyl)methoxy)but-1-en-1-yl)phosphonate (149m)

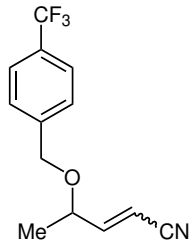


149m

Following general procedure **E**: alkene **148c** (192 mg, 1.00 mmol, 1.0 equiv), pentafluorobenzyl alcohol (5 mL); reaction time 1.5 d; DCM:acetone (30:1) + 1% AcOH; yield: 148 mg, 381 µmol, 38%; yellow liquid; ^{1}H NMR yield using benzaldehyde as the internal standard: 81%.

R_f = 0.25 (DCM:acetone, 30:1 + 1% AcOH); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2983, 2936, 2909, 2875, 1750, 1722, 1656, 1636, 1522, 1504, 1393, 1305, 1248, 1123, 1046, 1022, 957, 936, 848, 821, 787, 753, 673; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 6.67 (ddd, J = 22.4, 17.2, 5.4 Hz, 1 H), 5.90 (ddd, J = 20.0, 17.2, 1.4 Hz, 1 H), 4.60 (dt, J = 11.0, 1.9 Hz, 1 H), 4.52 (dt, J = 11.2, 1.9 Hz, 1 H), 4.26-3.96 (m, 5 H), 1.33 (td, J = 7.1, 1.3 Hz, 6 H), 1.29 (d, J = 6.5 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 152.4 (d, J_{CP} = 4.8 Hz), 145.7 (dddt, J_{CF} = 249.3, 11.9, 8.2, 3.9 Hz), 141.6 (dtt, J_{CF} = 255.0, 13.4, 5.3 Hz), 137.6 (m), 117.6 (d, J_{CP} = 188.0 Hz), 111.3 (td, J_{CF} = 18.0, 3.8 Hz), 76.3 (d, J_{CP} = 22.3 Hz), 62.1 (dd, J_{CP} = 5.6, 2.1 Hz), 58.0 (d, J_{CP} = 2.9 Hz), 20.7 (d, J_{CP} = 2.0 Hz), 16.5 (d, J_{CP} = 6.3 Hz); **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ [ppm] = −143.0 (m), −153.5 (m), −161.8 (m); **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ [ppm] = 17.7; **HR-ESI-MS m/z**: calcd. $C_{15}H_{19}F_5O_4P$ $[M+H]^+$: 389.0936, found: 389.0933.

(*E*/*Z*)-4-((4-(Trifluoromethyl)benzyl)oxy)pent-2-enenitrile (149n)



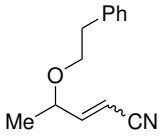
149n

Following general procedure **E**: 3-pentenenitrile (81 mg, 1.0 mmol, 1.0 equiv), 4-trifluoromethylbenzyl alcohol (5 mL); reaction time 1 d; eluting with *n*-pentane:EtOAc (30:1); yield: 63 mg, 0.25 mmol, 25% (*E*/*Z* = 2:1); yellow liquid; ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard: 54% (*E*/*Z* = 2:1).

R_f = 0.10 (*n*-pentane:EtOAc, 30:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = *E* isomer: 2982, 2936, 2869, 2360, 2341, 2226, 1729, 1621, 1421, 1325, 1163, 1121, 1065, 1018, 965, 824; *Z* isomer: 2984, 2934, 2872, 2360, 2341, 1326, 1163, 1122, 1066, 1019, 824; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] (*E* isomer) = 7.74-7.55 (m, 2 H), 7.47-7.35 (m, 2 H), 6.70 (dd, J = 16.3, 5.2 Hz, 1 H), 5.63 (dd, J = 16.4, 1.6 Hz, 1 H), 4.59 (d, J = 12.4 Hz, 1 H), 4.54 (d, J = 12.5 Hz, 1 H), 4.12 (qdd, J = 6.6, 5.2, 1.6 Hz, 1 H), 1.35 (d, J = 6.5 Hz, 3 H); δ [ppm]

(*Z* isomer) = 7.66-7.55 (m, 2 H), 7.49-7.44 (m, 2 H), 6.45 (dd, J = 11.1, 8.6 Hz, 1 H), 5.48 (dd, J = 11.1, 0.9 Hz, 1 H), 4.59 (d, J = 12.2 Hz, 1 H), 4.52 (d, J = 12.0 Hz, 1 H), 4.50 (m, 1 H), 1.39 (d, J = 6.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] (*E* isomer) = 155.5, 141.8, 130.3 (q, J_{CF} = 32.4 Hz), 127.6, 125.6 (q, J_{CF} = 3.8 Hz), 124.2 (q, J_{CF} = 272.0 Hz), 117.0, 100.0, 74.4, 70.3, 20.3; δ [ppm] (*Z* isomer) = 155.4, 141.9, 130.2 (d, J_{CF} = 32.4 Hz), 127.8, 125.6 (q, J_{CF} = 3.9 Hz), 125.3 (m), 115.2, 100.9, 74.2, 70.6, 20.7; **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ [ppm] (both isomers) = −62.6; **HR-ESI-MS m/z**: calcd. $C_{13}H_{13}F_3NO$ $[M+H]^+$: 256.0944, found: 256.0938.

(*E*/*Z*)-4-Phenethoxypent-2-enenitrile (149o)

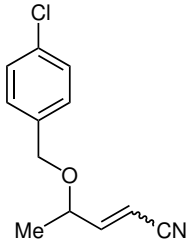


149o

Following general procedure **E**: 3-pentenenitrile (81 mg, 1.0 mmol, 1.0 equiv), 2-phenyl ethanol (183 mg, 1.5 mmol, 1.5 equiv), MeCN (2.5 mL); reaction time 1 d; eluting with *n*-pentane:EtOAc (20:1); yield: 29 mg, 145 µmol, 15% (*E*/*Z* = 6.5:1); yellow liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 18% (*E*/*Z* = 12:1).

R_f = 0.22 (*n*-pentane:EtOAc, 20:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3087, 3062, 3028, 2979, 2932, 2866, 2224, 1635, 1604, 1496, 1454, 1370, 1342, 1248, 1148, 1093, 1030, 963, 749, 699; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] (*E* isomer) = 7.34-7.27 (m, 2 H), 7.25-7.19 (m, 3 H), 6.60 (dd, J = 16.3, 4.8 Hz, 1 H), 5.41 (dd, J = 16.3, 1.7 Hz, 1 H), 3.98 (qdd, J = 6.6, 4.8, 1.7 Hz, 1 H), 3.65 (t, J = 6.8 Hz, 1 H), 3.61 (t, J = 7.1 Hz, 1 H), 2.88 (t, J = 6.9 Hz, 2 H), 1.25 (d, J = 6.6 Hz, 3 H); δ [ppm] (*Z* isomer) = 7.36-7.27 (m, 2 H), 7.25-7.14 (m, 3 H), 6.35 (dd, J = 11.2, 8.6 Hz, 1 H), 5.40 (m, 1 H), 4.39 (dqd, J = 8.6, 6.4, 1.0 Hz, 1 H), 3.67 (t, J = 6.8 Hz, 1 H), 3.59 (t, J = 7.1 Hz, 1 H), 2.88 (t, J = 6.9 Hz, 2 H), 1.31 (d, J = 6.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] (*E* isomer) = 156.0, 138.7, 129.0, 128.5, 126.6, 117.3, 99.3, 74.7, 70.4, 36.6, 20.2; δ [ppm] (*Z* isomer) = 156.2, 138.7, 129.0, 128.5, 126.6, 117.3, 100.2, 74.2, 70.4, 36.5, 20.6; **HR-ESI-MS m/z**: calcd. $C_{13}H_{16}NO$ $[M+H]^+$: 202.1226, found: 202.1226.

(*E*/*Z*)-4-((4-Chlorobenzyl)oxy)pent-2-enenitrile (149p)



149p

Following general procedure **E**: 3-pentenenitrile (81 mg, 1.0 mmol, 1.0 equiv), 4-chlorobenzyl alcohol (214 mg, 1.5 mmol, 1.5 equiv), MeCN (2.5 mL); reaction time 1 d; eluting with *n*-pentane:EtOAc (15:1); yield: 6.9 mg, 31 µmol, 31% (*E*/*Z* = 3.5:1); yellow liquid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 18% (*E*/*Z* = 4.3:1).

R_f = 0.19 (*n*-pentane:EtOAc, 15:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2979, 2931, 2868, 2225, 1599, 1493, 1468, 1443, 1410, 1371, 1345, 1254, 1205, 1148, 1087, 1015, 965, 809, 761; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = δ [ppm] (*E* isomer) = 7.41-7.16 (m, 4 H), 6.68 (dd, J = 16.3, 5.2 Hz, 1 H), 5.61 (dd, J = 16.3, 1.6 Hz, 1 H), 4.50 (d, J = 11.9 Hz, 1 H),

4.44 (d, J = 11.9 Hz, 1 H), 4.09 (qdd, J = 6.6, 5.2, 1.6 Hz, 1 H), 1.32 (d, J = 6.6 Hz, 3 H); δ [ppm] (Z isomer) = 7.41-7.16 (m, 4 H), 6.44 (ddd, J = 11.2, 8.7, 0.5 Hz, 1 H), 5.46 (dd, J = 11.1, 0.9 Hz, 1 H), 4.55-4.40 (m, 1 H), 4.50 (d, J = 11.9 Hz, 1 H), 4.43 (d, J = 11.9 Hz, 1 H), 1.36 (d, J = 6.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] (E isomer) = 155.6, 136.1, 133.8, 128.9, 128.8, 117.0, 99.9, 74.1, 70.4, 20.4; δ [ppm] (Z isomer) = 155.5, 136.3, 133.7, 129.2, 128.7, 117.0, 100.6, 73.9, 70.7, 20.8; **HR-ESI-MS m/z**: calcd. $C_{12}H_{13}ClNO$ $[M+H]^+$: 222.0680, found: 222.0682.

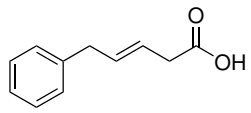
5.5 Synthesis and lactonization of unsaturated acids *via* photo-aerobic selenium-π-acid catalysis

5.5.1 Synthesis of unsaturated carboxylic acids 34, 137 and 167

General Procedure F: Knoevenagel reaction

Malonic acid (2.2 equiv) is dissolved in DMSO (0.6 M), a solution of piperidine 0.02 equiv) and acetic acid (0.02 equiv) in DMSO (0.04 M for piperidine) is added dropwise. The solution is heated to 65 °C, the respective aldehyde (1.0 equiv) is added dropwise and the solution is stirred at 65 °C. The reaction is quenched by the addition of water, extracted with Et_2O (3 ×), washed with water (3 ×), extracted with sat. aq. Na_2CO_3 (3 ×), to the aq. phase, conc. HCl is added until pH=1 and it is extracted with Et_2O (2 ×). The org. phase is dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography afford the product.

(*E*)-5-Phenylpent-3-enoic acid (34b)

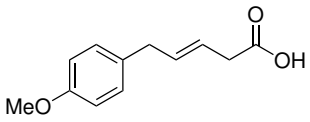


34b

Following general procedure **F**: Malonic acid (2.56 g, 24.6 mmol, 2.2 equiv), piperidine (19.0 mg, 220 µmol, 0.02 equiv), acetic acid (13.4 mg, 220 µmol, 0.02 equiv) 3-phenylpropanal (1.50 g, 11.2 mmol, 1.0 equiv); reaction time 3 h; eluting with n-pentane/Et_2O, 3:1; colorless liquid; yield: 550 mg, 3.12 mmol, 28%.

R_f = 0.20 (n-pentane:Et_2O, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3027, 2901, 1704, 1494, 1417, 1286, 1220, 1156, 968, 932, 745, 698, 490; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 10.5 (s, 1 H), 7.39-7.15 (m, 5 H), 5.90-5.54 (m, 2 H), 3.41 (d, J = 6.5 Hz, 2 H), 3.14 (dd, J = 6.7, 1.0 Hz, 2 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 178.6, 140.0, 133.9, 128.7, 128.6, 126.3, 122.5, 39.0, 37.8; **HR-ESI-MS m/z**: calcd. $C_{11}H_{11}O_2$ $[M-H]^-$: 175.0765, found: 175.0766.

(*E*)-5-(4-Methoxyphenyl)pent-3-enoic acid (34c)

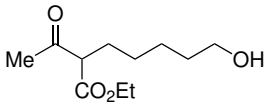


34c

Following general procedure **F**: Malonic acid (697 mg, 6.70 mmol, 2.2 equiv), piperidine (6.0 µL, 5.2 mg, 61 µmol, 0.02 equiv), acetic acid (3.5 µL, 3.7 mg, 61 µmol, 0.02 equiv), 3-(4-methoxyphenyl)propionaldehyde (500 mg, 3.05 mmol, 1.0 equiv); reaction time 10 h; eluting with *n*-pentane/Et_2O, 5:1; white solid; yield: 133 mg, 0.645 mmol, 43%.

R_f = 0.07 (*n*-pentane:Et_2O, 5:1); **m.p.** = 58 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3033, 3001, 2953, 2932, 2906, 2836, 1704, 1610, 1584, 1510, 1464, 1418, 1299, 1176, 1108, 1034, 969, 937, 813, 557, 521; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.20–7.02 (m, 2 H), 6.91–6.65 (m, 2 H), 5.75 (m, 1 H), 5.62 (m, 1 H), 3.80 (s, 3 H), 3.35 (d, J = 6.5 Hz, 3 H), 3.13 (dd, J = 6.7, 1.1 Hz, 2 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 178.4, 158.0, 134.3, 132.0, 129.5, 122.0, 114.0, 55.4, 38.2, 37.8; **HR-ESI-MS m/z**: calcd. $C_{12}H_{14}O_3Na$ $[M+Na]^+$: 229.0835, found: 229.0834.

Ethyl 2-acetyl-7-hydroxyheptanoate (159)

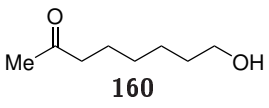


159

Sodium (344 mg, 15.0 mmol, 1.0 equiv) was dissolved in dry ethanol (9.0 mL) and ethyl acetoacetate (1.95 g, 15.0 mmol, 1.0 equiv) was added. The solution was stirred for 1 h at 80 °C. 5-Bromo-1-pentanol (2.5 g, 15 mmol, 1.0 equiv) was added and stirring continued for 3 h at 80 °C. The solvent was removed in vacuo, the residue dissolved in EtOAc, filtered and concentrated in vacuo. Column chromatography (DCM/EtOAc, 2:1) afforded the product as a colorless liquid (1.31 g, 6.07 mmol, 40%).

R_f = 0.29 (DCM/EtOAc, 2:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3419, 2935, 2862, 1735, 1710, 1463, 1360, 1242, 1196, 1149, 1053, 1025; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 4.19 (q, J = 7.1 Hz, 2 H), 3.62 (t, J = 6.4 Hz, 2 H), 3.39 (t, J = 7.3 Hz, 1 H), 2.21 (s, 3 H), 1.85 (tdd, J = 8.2, 6.5, 4.1 Hz, 2 H), 1.65–1.49 (m, 2 H), 1.45–1.17 (m, 7 H); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ [ppm] = 203.4, 170.0, 62.8, 61.5, 59.9, 32.5, 28.9, 28.2, 27.3, 25.6, 14.2; **HR-ESI-MS m/z**: calcd. $C_{11}H_{20}O_4Na$ $[M+Na]^+$: 239.1254, found: 239.1259.

8-Hydroxyoctan-2-one (160)

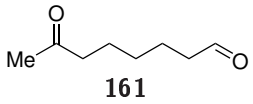


160

Ethyl 2-acetyl-7-hydroxyheptanoate (159) (1.30 g, 6.01 mmol, 1.0 equiv) was added to a solution of NaOH (601 mg, 15.0 mmol, 2.5 equiv) in H_2O (30 mL). When everything was dissolved, a solution of H_2SO_4 (0.65 mL, 12.0 mmol, 2.0 equiv) in H_2O (60 mL) was added and stirred at 50 °C for 1 h. The solution was extracted with EtOAc (2 × 30 mL), washed with sat. aq. NaCl solution (15 mL) and dried over Na_2SO_4. The product was obtained as a colorless oil (814 mg, 5.65 mmol, 94%).

R_f = 0.21 (DCM:EtOAc, 9:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3399, 2932, 2859, 1707, 1410, 1360, 1165, 1056, 597, 522; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 3.59 (t, J = 6.5 Hz, 2 H), 2.53–2.30 (m, 2 H), 2.10 (t, J = 0.4 Hz, 3 H), 2.03 (s, 1 H), 1.73–1.44 (m, 4 H), 1.44–1.00 (m, 4 H); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ [ppm] = 209.3, 62.8, 43.8, 32.7, 30.0, 29.1, 25.7, 23.9; **HR-ESI-MS m/z**: calcd. $C_8H_{16}O_2Na$ [M+Na]$^+$: 167.1043, found: 167.1045.

7-Oxooctanal (161)

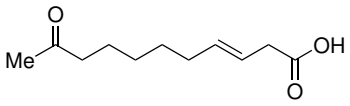


161

DMP (4.56 g, 10.7 mmol, 2.0 equiv) was dissolved in DCM (22 mL) and cooled to 0 °C. 8-Hydroxyoctan-2-one (160) (775 mg, 5.37 mmol, 1.0 equiv) in DCM (5 mL) was added and the solution was stirred at rt for 3.5 h. DCM was added, the mixture washed with sat. aq. $Na_2S_2O_3$, 1 M aq. NaOH and sat. aq. NaCl. Extraction with DCM, drying over Na_2SO_4, removal of the solvent in vacuo, followed by column chromatography (DCM/EtOAc, 9:1) afforded the product as a colorless liquid (210 mg, 1.48 mmol, 28%).

R_f = 0.57 (DCM:EtOAc, 9:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 9.75 (t, J = 1.7 Hz, 1 H), 2.43 (td, J = 7.3, 1.4 Hz, 4 H), 2.12 (t, J = 0.5 Hz, 3 H), 1.74–1.48 (m, 4 H), 1.44–1.15 (m, 2 H).

(*E*)-10-Oxoundec-3-enoic acid (34e)

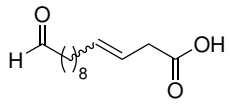


34e

DMAP (17 mg, 0.14 mmol, 0.1 equiv) was dissolved in DMF (3.5 mL), malonic acid (147 mg, 1.41 mmol, 1.0 equiv) and **161** (200 mg, 1.41 mmol, 1.0 equiv) were added and the solution was stirred at rt for 66 h. Et_2O was added, the org. phase was washed with NH_4Cl, H_2O, $NaHCO_3$ and again water. The aq. phase was extracted with Et_2O and dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/Et_2O, 1:1 to Et_2O, pure) afforded the product as a colorless liquid (1:1.5 mixture of α,βand β,γunsaturated product; 61 mg, 0.33 mmol, 23%).

R_f = 0.43 (Et_2O); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2930, 2859, 1703, 1654, 1410, 1361, 1282, 1222, 1171, 971; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.04 (dt, J = 15.6, 7.0 Hz, 1 H), 5.80 (dt, J = 15.6, 1.5 Hz, 1 H), 5.68–5.34 (m, 2.9 H), 3.09–2.98 (m, 3 H), 2.42 (ddt, J = 9.6, 4.5, 2.2 Hz, 6 H), 2.34 (t, J = 7.4 Hz, 1 H), 2.28–2.15 (m, 2 H), 2.12 (d, J = 1.2 Hz, 8 H), 2.10–1.97 (m, 3 H), 1.74–1.17 (m, 20 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 209.3, 209.1, 179.4, 177.8, 171.6, 152.0, 134.7, 121.4, 120.8, 43.7, 43.7, 43.6, 37.9, 34.0, 32.3, 32.2, 30.1, 30.0, 28.8, 28.7, 28.7, 27.9, 24.6, 23.6, 23.5, 23.5; **HR-ESI-MS m/z**: calcd. $C_{10}H_{16}O_3Na$ [M+Na]$^+$: 207.0992, found: 207.0994.

(*E*/*Z*)-13-Oxotridec-3-enoic acid (34f)

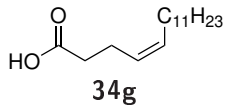


34f

To a degassed solution of 4-butenoic acid (0.26 g, 3.0 mmol, 1.0 equiv) and 10-undecenyl aldehyde (1.5 g, 9.0 mmol, 3.0 equiv) in DCM (6.0 mL), HOVEYDA-GRUBBS catalyst 2nd gen. (94 mg, 0.15 mmol, 0.05 equiv) was added. The solution was heated to 40 °C for 13.5 h. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 3:1) afforded the product as a brown liquid (389 mg, 1.72 mmol, 57%).

R_f = 0.21 (*n*-pentane:EtOAc, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2925, 2854, 1708, 1463, 1410, 1290, 1220, 1167, 968, 935; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 9.76 (t, J = 1.9 Hz, 1 H), 5.70–5.43 (m, 2 H), 3.23–2.96 (m, 2 H), 2.42 (td, J = 7.4, 1.9 Hz, 2 H), 2.03 (q, J = 6.6 Hz, 2 H), 1.62 (quint, J = 7.2 Hz, 2 H), 1.45–1.18 (m, 11 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 203.2, 178.2, 135.6, 120.9, 44.0, 37.9, 32.5, 29.4, 29.3, 29.3, 29.2, 29.1, 22.2; **HR-ESI-MS m/z**: calcd. $C_{13}H_{2103}$ [M-H]$^-$: 225.1496, found: 225.1496.

(*Z*)-Hexadec-4-enoic acid (34g)

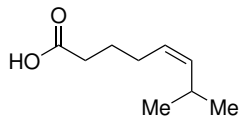


34g

Following general procedure **A**: (3-carboxypropyl)triphenylphosphonium bromide (2.6 g, 6.0 mmol, 2.0 equiv) in THF (9 mL), potassium *tert*-butoxide (1.4 g, 12.0 mmol, 4.0 equiv), dodecanal (0.55 g, 3.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 3:1; white solid; in vacuo, followed by column chromatography (*n*-pentane/Et_2O, 3:1) afforded the product as a white solid (282 mg, 1.11 mmol, 37%).

R_f = 0.50 (*n*-pentane:Et_2O, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2953, 2915, 2849, 1710, 1469, 1432, 1299, 1215, 890, 718, 678; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 11.48 (s, 1 H), 5.55–5.21 (m, 2 H), 2.49–2.33 (m, 4 H), 2.04 (qd, J = 7.2, 1.5 Hz, 2 H), 1.44–1.16 (m, 18 H), 0.88 (t, J = 6.9 Hz, 3 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 179.5, 132.1, 127.0, 34.3, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 27.4, 22.9, 22.7, 14.3; **HR-ESI-MS m/z**: calcd. $C_{16}H_{29}O_2$ [M-H]$^-$: 253.2173, found: 253.2173.

(*Z*)-7-Methyloct-5-enoic acid (137l)



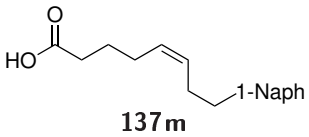
137l

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (1.8 g, 4.0 mmol, 2.0 equiv) in THF (7 mL), potassium *tert*-butoxide (0.90 g, 8.0 mmol, 4.0 equiv), isobutyraldehyde (0.14 g, 2.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 2:1; colorless oil; 221 mg, 1.41 mmol, 71%.

R_f = 0.50 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3001, 2956, 2869, 1705, 1459, 1412, 1361, 1297, 1239, 1205, 1165, 1102, 927, 740, 486; **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 5.32–5.11

(m, 2 H), 2.57 (dhept, J = 9.1, 6.6 Hz, 1 H), 2.37 (t, J = 7.5 Hz, 2 H), 2.11 (dddd, J = 8.4, 7.5, 6.7, 0.9 Hz, 2 H), 1.70 (quintd, J = 7.3, 0.7 Hz, 2 H), 0.94 (d, J = 6.6 Hz, 6 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 179.9, 138.9, 125.8, 33.6, 26.8, 26.7, 25.0, 23.4; **HR-ESI-MS m/z**: calcd. $C_9H_{15}O_2$ $[M\text{-}H]^-$: 155.1078, found: 155.1083.

(*Z*)-8-(Naphthalen-1-yl)oct-5-enoic acid (137m)

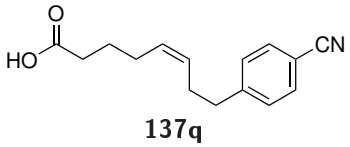


137m

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (1.8 g, 4.0 mmol, 2.0 equiv) in THF (7 mL), potassium *tert*-butoxide (0.90 g, 8.0 mmol, 4.0 equiv), 3-(naphthalen-1-yl)propanal (0.37 g, 2.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 4:1; yellow oil; 249 mg, 930 µmol, 47%.

R_f = 0.07 (*n*-pentane:Et_2O, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3043, 3006, 2921, 2850, 1703, 1596, 1510, 1457, 1434, 1410, 1239, 1205, 937, 859, 796, 774, 732, 481, 423; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.05 (m, 1 H), 7.85 (m, 1 H), 7.72 (d, J = 8.2 Hz, 1 H), 7.52 (ddd, J = 8.5, 6.7, 1.7 Hz, 2 H), 7.48 (m, 1 H), 7.40 (dd, J = 8.2, 7.0 Hz, 1 H), 7.33 (m, 1 H), 5.57 (m, 1 H), 5.38 (m, 1 H), 3.16-3.10 (m, 2 H), 2.67–2.44 (m, 2 H), 2.22 (t, J = 7.5 Hz, 2 H), 2.04–1.90 (m, 2 H), 1.58 (quint, J = 7.5 Hz, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 179.8, 138.0, 134.0, 132.0, 130.2, 129.3, 128.9, 126.8, 126.2, 125.9, 125.6, 125.5, 123.8, 33.4, 33.1, 28.6, 26.6, 24.6; **HR-ESI-MS m/z**: calcd. $C_{18}H_{19}O_2$ $[M\text{-}H]^-$: 267.1391, found: 267.1391.

(*Z*)-8-(4-Cyanophenyl)oct-5-enoic acid (137q)

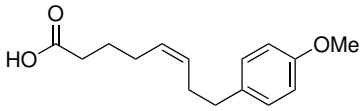


137q

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (1.5 g, 3.4 mmol, 2.0 equiv) in THF (6 mL), potassium *tert*-butoxide (0.76 mg, 6.8 mmol, 4.0 equiv), 3-(4-cyanophenyl)propanal (0.27 g, 1.7 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 1:1; yellow oil; 210 mg, 863 µmol, 51%.

R_f = 0.21 (*n*-pentane/Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3007, 2932, 2861, 2227, 1703, 1607, 1505, 1412, 1239, 1177, 936, 841, 823, 554; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.66–7.52 (m, 2 H), 7.31–7.26 (m, 2 H), 5.50–5.29 (m, 2 H), 2.72 (dd, J = 8.2, 7.0 Hz, 2 H), 2.39–2.32 (m, 2 H), 2.29 (t, J = 7.4 Hz, 2 H), 2.07–1.96 (m, 2 H), 1.65–1.56 (m, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 179.6, 147.7, 132.3, 130.0, 129.5, 129.1, 119.2, 109.9, 36.1, 33.3, 28.7, 26.5, 24.5; **HR-ESI-MS m/z**: calcd. $C_{15}H_{17}NO_2$ $[M\text{-}H]^-$: 242.1187, found: 242.1185.

(*Z*)-8-(4-Methoxyphenyl)oct-5-enoic acid (137r)

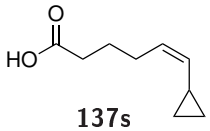


137r

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (2.2 g, 5.0 mmol, 2.0 equiv) in THF (6 mL), potassium *tert*-butoxide (1.12 g, 10.0 mmol,, 4.0 equiv), 3-(4-methoxyphenyl)propanal (0.41 g, 2.5 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 0:1; yellow oil; 468 mg, 1.88 mmol, 75%.

R_f = 0.56 (Et_2O); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3005, 2932, 2835, 1704, 1611, 1584, 1510, 1440, 1299, 1241, 1176, 1109, 1036, 938, 823, 694, 516; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.17–7.04 (m, 2 H), 6.92–6.77 (m, 2 H), 5.45 (m, 1 H), 5.35 (m, 1 H), 3.78 (s, 3 H), 2.60 (dd, J = 8.5, 6.8 Hz, 2 H), 2.38–2.18 (m, 4 H), 2.11–1.93 (m, 2 H), 1.63 (quint, J = 7.5 Hz, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 179.6, 157.9, 134.2, 130.3, 129.5, 129.1, 113.8, 55.4, 35.1, 33.4, 29.6, 26.6, 24.6; **HR-ESI-MS m/z**: calcd. $C_{15}H_{20}O_3Na$ $[M+Na]^+$: 271.1305, found: 271.1308.

6-Cyclopropylhex-5-enoic acid (137s)

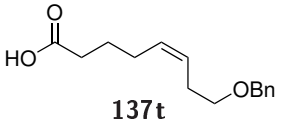


137s

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (1.8 g, 4.0 mmol, 2.0 equiv) in THF (7 mL), potassium *tert*-butoxide (0.90 g, 8.0 mmol, 4.0 equiv), cyclopropanecarboxaldehyde (0.14 g, 2.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 1:1; colorless oil; mixture of *Z*/*E* 7:1; 169 mg, 1.09 mmol, 55%.

R_f = 0.28 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3082, 2005, 2934, 2868, 1703, 1412, 1240, 1205, 1046, 1020, 933, 5, 810, 731, 601, 489; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] (*Z* isomer) = 5.26 (dtd, J = 10.7, 7.4, 0.9 Hz, 1 H), 4.79 (ddt, J = 11.1, 9.9, 1.5 Hz, 1 H), 2.40 (t, J = 7.5 Hz, 2 H), 2.23 (qd, J = 7.4, 1.5 Hz, 2 H), 1.75 (quint, J = 7.7 Hz, 2 H), 1.51 (m, 1 H), 0.78–0.68 (m, 2 H), 0.38–0.27 (m, 2 H); δ [ppm] (*E* isomer) = 5.45 (dt, J = 15.3, 6.9 Hz, 1 H), 4.99 (ddt, J = 15.2, 8.5, 1.4 Hz, 1 H), 2.37–2.31 (m, 2 H), 2.12–1.97 (m, 2 H), 1.71 (d, J = 7.5 Hz, 2 H), 1.42–1.28 (m, 1 H), 0.69–0.59 (m, 2 H), 0.38–0.27 (m, 2 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 180.3, 135.3, 135.2, 126.6, 33.6, 33.6, 31.9, 27.0, 24.9, 24.7, 13.7, 9.8, 7.1, 6.6; **HR-ESI-MS m/z**: calcd. $C_9H_{14}O_2Na$ $[M+Na]^+$: 177.0886, found: 177.0878.

(*Z*)-8-(Benzyloxy)oct-5-enoic acid (137t)

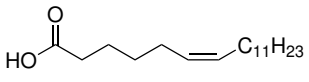


137t

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (1.8 g, 4.0 mmol, 2.0 equiv) in THF (7 mL), potassium *tert*-butoxide (0.90 g, 8.0 mmol, 4.0 equiv), 3-benzyloxypropionaldehyde (0.33 g, 2.0 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 1:1; colorless oil; 60 mg, 0.24 mmol, 12%.

R_f = 0.36 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3087, 3063, 3030, 3010, 2931, 2865, 1705, 1496, 1454, 1410, 1238, 1206, 1095, 1001, 904, 734, 697, 652, 595, 464; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.58–7.23 (m, 10 H), 6.62 (dddd, J = 16.8, 11.2, 10.2, 1.1 Hz, 1 H), 6.06 (dddd, J = 11.8, 10.1, 1.5, 0.8 Hz, 1 H), 5.52–5.36 (m, 3 H), 5.21 (ddt, J = 17.0, 1.6, 0.8 Hz, 1 H), 5.12 (dddd, J = 10.2, 2.2, 1.4, 0.8 Hz, 2 H), 4.69 (s, 2 H), 4.53 (s, 2 H), 3.49 (t, J = 6.9 Hz, 2 H), 2.46–2.31 (m, 8 H), 2.26 (qd, J = 7.5, 1.6 Hz, 3 H), 2.19–2.03 (m, 3 H), 1.82–1.60 (m, 6 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 179.4, 179.3, 140.7, 138.4, 137.0, 133.6, 132.0, 131.1, 130.4, 130.4, 128.6, 128.4, 127.7, 127.7, 127.6, 127.1, 126.9, 117.6, 115.4, 73.0, 70.0, 65.4, 33.6, 33.5, 31.9, 28.1, 27.1, 26.7, 24.7, 24.5, 24.3; **HR-ESI-MS m/z**: calcd. $C_{15}H_{19}O_3$ [M-H]$^-$: 247.1340, found: 247.1342.

(*Z*)-Octadec-6-enoic acid (167)



167

Following general procedure **A**: (4-carboxybutyl)triphenylphosphonium bromide (2.3 g, 5.0 mmol, 2.0 equiv) in THF (6 mL), potassium *tert*-butoxide (1.12 g, 10.0 mmol, 4.0 equiv), dodecanal (0.46 g, 2.5 mmol, 1.0 equiv) in THF (1 mL); reaction time 2 h; eluting with *n*-pentane/Et_2O, 1:1; white solid; 582 mg, 2.06 mmol, 82%.

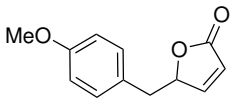
R_f = 0.29 (*n*-pentane/Et_2O, 1:1); **m.p.** = 35 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2922, 2853, 1708, 1461, 1412, 1288, 1234, 934, 721; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.45–5.26 (m, 2 H), 2.42–2.28 (m, 2 H), 2.20–1.90 (m, 4 H), 1.73–1.56 (m, 2 H), 1.49–1.35 (m, 2 H), 1.26 (s_{br}, 18 H), 0.93–0.71 (m, 3 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 179.8, 130.7, 129.1, 34.0, 32.1, 29.9, 29.8, 29.8, 29.7, 29.5, 29.5, 29.3, 27.4, 26.9, 24.4, 22.9, 14.3; **HR-ESI-MS m/z**: calcd. $C_{18}H_{33}O_2$ [M-H]$^-$: 281.2486, found: 281.2487.

5.5.2 Synthesis of lactones 77, 170 and 171

General procedure G: catalytic lactonization

The respective acid **34** or **137** (1.0 mmol, 1.0 equiv), diphenyl diselenide (16 mg, 50 µmol, 0.05 equiv) and *p*-MeO-TPT (**95**) (24 mg, 50 µmol, 0.05 equiv) are dissolved in acetonitrile (10 mL) and stirred vigorously under air and irradiation at λ = 465 nm at room temperature until complete conversion. The solvent is removed in vacuo and the product **77** or **170** afforded *via* column chromatography.

5-(4-Methoxybenzyl)furan-2(5*H*)-one (77c)



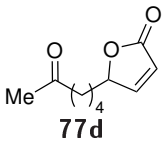
77c

Following general procedure **G**: acid **34c**, 23 h; yellow oil (106 mg, 0.519 mmol, 52%); *n*-pentane/Et_2O, 2:1.

R_f = 0.19 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2916, 2837, 1743, 1612, 1584, 1511, 1464, 1337, 1300, 1244, 1178, 1159, 1097, 1071, 1025,

981, 916, 902, 857, 843, 811, 782, 748, 695, 668, 615, 557, 532; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.39 (dd, J = 5.7, 1.5 Hz, 1 H), 7.18–7.05 (m, 2 H), 6.91–6.75 (m, 2 H), 6.06 (ddt, J = 5.7, 2.0, 0.4 Hz, 1 H), 5.19 (dddd, J = 7.0, 6.2, 2.0, 1.5 Hz, 1 H), 3.79 (s, 3 H), 3.10 (dd, J = 14.0, 6.2 Hz, 1 H), 2.91 (dd, J = 14.0, 7.0 Hz, 1 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 172.8, 158.8, 155.6, 130.5, 126.8, 122.1, 114.2, 83.7, 55.4, 38.9; **HR-ESI-MS m/z**: calcd. $C_{12}H_{13}O_3$ $[M+H]^+$: 205.0859, found: 205.0861.

5-(6-Oxoheptyl)furan-2(5*H*)-one (77d)

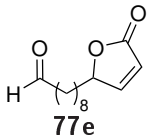


77d

Following general procedure **G**: Acid **34e** (35 mg, 0.19 mmol, 1.0 equiv), diphenyl diselenide (3.0 mg, 9.5 µmol, 0.05 equiv) and *p*-MeO-TPT (4.6 mg, 9.5 µmol, 0.05 equiv), acetonitrile (2 mL) 19 h; yellow oil (15 mg, 81 µmol, 43%); *n*-pentane/Et_2O, 0:1.

R_f = 0.21 (Et_2O); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2930, 2866, 1745, 1709, 1358, 1163, 1102, 1012, 900, 818; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.44 (dd, J = 5.7, 1.5 Hz, 1 H), 6.09 (dd, J = 5.7, 2.0 Hz, 1 H), 5.03 (ddt, J = 7.6, 5.1, 1.8 Hz, 1 H), 2.44 (t, J = 7.1 Hz, 2 H), 2.12 (s, 3 H), 1.86–1.36 (m, 6 H); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ [ppm] = 208.6, 173.2, 156.2, 121.8, 83.2, 43.3, 33.1, 30.1, 24.6, 23.3; **HR-ESI-MS m/z**: calcd. $C_{10}H_{15}O_3$ $[M+H]^+$: 183.1016, found: 183.1019.

9-(5-Oxo-2,5-dihydrofuran-2-yl)nonanal (77e)

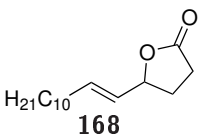


77e

Following general procedure **G**: acid **34f**, 48 h; yellow oil (78 mg, 0.35 mmol, 35%); *n*-pentane/Et_2O, 3:1.

R_f = 0.17 (*n*-pentane:EtOAc, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2927, 2855, 1749, 1720, 1602, 1464, 1162, 1100, 1011, 898, 816, 706, 669, 511; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 9.76 (t, J = 1.8 Hz, 1 H), 7.44 (dd, J = 5.7, 1.5 Hz, 1 H), 6.10 (dd, J = 5.7, 2.0 Hz, 1 H), 5.03 (ddt, J = 7.2, 5.3, 1.8 Hz, 1 H), 2.42 (td, J = 7.3, 1.8 Hz, 2 H), 1.84–1.17 (m, 14 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 202.7, 173.1, 156.2, 121.7, 83.5, 44.1, 33.4, 29.4, 29.4, 29.3, 29.3, 25.2, 22.2; **HR-ESI-MS m/z**: calcd. $C_{13}H_{21}O_3$ $[M+H]^+$: 225.1485, found: 225.1492.

(*E*)-5-(Dodec-1-en-1-yl)dihydrofuran-2(3*H*)-one (168)



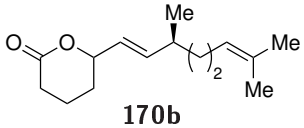
168

Following general procedure **G**: acid **166**; 16 h; white solid (161 mg, 637 µmol, 64%); *n*-pentane/Et_2O 3:1.

R_f = 0.43 (*n*-pentane:Et_2O, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2923, 2853, 1773, 1459, 1326, 1173, 968, 914, 756; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.80 (dtd, J = 15.3, 6.6, 1.0 Hz, 1 H), 5.48 (ddt, J = 15.3, 7.1, 1.5 Hz, 1 H), 4.89 (m, 1 H), 2.54

(dd, J = 9.2, 1.1 Hz, 1 H), 2.52 (dd, J = 9.2, 2.2 Hz, 1 H), 2.36 (ddt, J = 13.0, 7.5, 6.4 Hz, 1 H), 2.18–1.88 (m, 3 H), 1.49-1.15 (m, 16 H), 0.91–0.84 (m, 3 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 177.0, 135.8, 127.4, 81.3, 32.3, 32.1, 29.8, 29.8, 29.7, 29.5, 29.3, 29.1, 29.0, 29.0, 22.9, 14.3; **HR-ESI-MS m/z**: calcd. $C_{16}H_{29}O_2$ $[M+H]^+$: 253.2162, found: 253.2163.

6-((*S*,*E*)-3,7-Dimethylocta-1,6-dien-1-yl)tetrahydro-2*H*-pyran-2-one (170b)

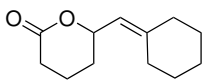


170b

Following general procedure **G**: acid **137b**; 40 h; orange oil (29 mg, 0.12 mmol, 12%); *n*-pentane/EtOAc 5:1.

R$_f$ = 0.33 (*n*-pentane:EtOAc, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2959, 2913, 1872, 1733, 1441, 1376, 1341, 1233, 1161, 1034, 971, 928, 741, 465; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.62 (dddd, J = 15.5, 7.7, 5.1, 1.0 Hz, 1 H), 5.43 (m, 1 H), 5.05 (tdquint, J = 7.2, 2.9, 1.4 Hz, 1 H), 4.75 (m, 1 H), 2.74–2.27 (m, 2 H), 2.12 (ddt, J = 13.7, 9.7, 6.8 Hz, 1 H), 2.02–1.74 (m, 6 H), 1.65 (s, 3 H), 1.56 (m, 3 H), 1.39–1.19 (m, 2 H), 0.96 (dd, J = 6.7, 2.0 Hz, 3 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 171.4, 140.0, 131.5, 126.5, 124.4, 80.8, 36.9, 36.1, 29.7, 28.7, 25.9, 25.9, 20.4, 18.5, 17.9; **HR-ESI-MS m/z**: calcd. $C_{15}H_{25}O_2$ $[M+H]^+$: 237.1849, found: 237.1853.

6-(Cyclohexylidenemethyl)tetrahydro-2*H*-pyran-2-one (170d)

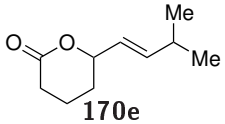


170d

Following general procedure **G**: acid **137d**; 16 h; light yellow oil (56 mg, 0.29 mmol, 29%); *n*-pentane/Et_2O, 2:1.

R$_f$ = 0.21 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2926, 2853, 1727, 1672, 1446, 1344, 1227, 1182, 1157, 1028, 987, 926, 831, 639, 469; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.18 (dt, J = 8.6, 1.2 Hz, 1 H), 5.07 (ddd, J = 10.1, 8.6, 3.1 Hz, 1 H), 2.58 (m, 1 H), 2.46 (m, 1 H), 2.29–2.04 (m, 4 H), 1.99–1.78 (m, 3 H), 1.76–1.37 (m, 7 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 171.8, 145.9, 120.0, 37.1, 29.7, 29.6, 29.1, 28.5, 27.9, 26.7, 18.8; **HR-ESI-MS m/z**: calcd. $C_{12}H_{19}O_2$ $[M+H]^+$: 195.1380, found: 195.1382.

(*E*)-6-(3-Methylbut-1-en-1-yl)tetrahydro-2*H*-pyran-2-one (170e)



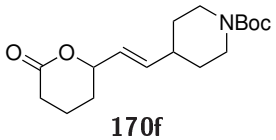
170e

Following general procedure **G**: acid **137e**; 14.5 h; yellow oil (116 mg, 689 µmol, 69%); *n*-pentane/Et_2O 1:1.

R$_f$ = 0.29 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2957, 2870, 1729, 1464, 1339, 1231, 1160, 1032, 971, 927, 657, 570, 466; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.73 (ddd, J = 15.5, 6.6, 1.2 Hz, 1 H), 5.43 (ddd, J = 15.5, 6.6, 1.4 Hz, 1 H), 4.75 (dddt, J = 10.2, 6.7, 3.5, 0.8 Hz, 1 H), 2.57 (dddd, J = 17.7, 6.8, 5.4, 1.3 Hz, 1 H), 2.46 (ddd, J = 17.7, 8.3, 6.8 Hz, 1 H), 2.30 (ddtd, J = 13.4, 7.4, 6.7, 1.7 Hz, 1 H), 1.99–1.78 (m, 3 H), 1.65 (m, 1 H), 0.99 (dd, J = 6.8, 1.4 Hz, 6 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 171.6,

141.4, 125.2, 81.0, 30.8, 29.6, 28.6, 22.1, 18.4; **HR-ESI-MS m/z**: calcd. $C_{10}H_{16}O_2Na$ $[M+Na]^+$: 191.1043, found: 191.1139.

tert-butyl(*E*)-4-(2-(6-Oxotetrahydro-2*H*-pyran-2-yl)vinyl)piperidine-1-carboxylate (170f)

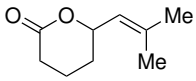


170f

Following general procedure **G**: Acid **137g** (257 mg, 0.83 mmol, 1.0 equiv), diphenyl diselenide (13 mg, 42 µmol, 0.05 equiv) and *p*-MeO-TPT (20 mg, 42 µmol, 0.05 equiv), acetonitrile (8.3 mL); 16 h; light yellow oil (201 mg, 0.65 mmol, 78%) *n*-pentane/Et_2O 1:1.

$\mathbf{R_f} = 0.10$ (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2974, 2930, 2851, 1733, 1684, 1421, 1365, 1274, 1231, 1160, 1092, 1033, 968, 929, 867, 753, 665, 461; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.70 (ddd, J = 15.6, 6.5, 1.1 Hz, 1 H), 5.47 (ddd, J = 15.6, 6.3, 1.2 Hz, 1 H), 4.74 (ddt, J = 9.8, 6.8, 2.5 Hz, 1 H), 4.07 (d, J = 13.4 Hz, 2 H), 2.70 (t, J = 12.7 Hz, 2 H), 2.63–2.35 (m, 2 H), 2.12 (m, 1 H), 2.01–1.74 (m, 3 H), 1.70–1.54 (m, 3 H), 1.43 (s, 9 H), 1.36–1.10 (m, 2 H); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ [ppm] = 171.4, 154.9, 137.8, 126.9, 80.6, 79.5, 43.7, 38.6, 31.5, 29.6, 28.6, 28.5, 18.4; **HR-ESI-MS m/z**: calcd. $C_{17}H_{27}NO_4$ $[M+Na]^+$: 332.1832, found: 332.1835.

6-(2-Methylprop-1-en-1-yl)tetrahydro-2*H*-pyran-2-one (170g)

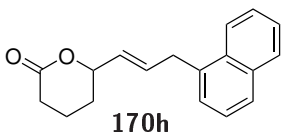


170g

Following general procedure **G**: acid **137l**; 14.5 h; yellow oil (51 mg, 0.33 mmol, 33%); *n*-pentane/Et_2O, 1:1.

$\mathbf{R_f} = 0.29$ (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2934, 2880, 1725, 1442, 1377, 1341, 1233, 1181, 1027, 925, 869, 820, 659, 571, 454; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.23 (ddt, J = 8.6, 2.6, 1.2 Hz, 1 H), 5.01 (ddd, J = 10.3, 8.6, 3.1 Hz, 1 H), 2.58 (m, 1 H), 2.45 (ddd, J = 17.7, 8.6, 7.1 Hz, 1 H), 2.04–1.77 (m, 3 H), 1.74 (d, J = 1.5 Hz, 3 H), 1.70 (d, J = 1.5 Hz, 3 H), 1.62 (m, 1 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 171.8, 138.5, 123.3, 77.6, 29.6, 28.6, 25.8, 18.7, 18.5; **HR-EI-MS m/z**: calcd. $C_9H_{14}O_2Na$ $[M+Na]^+$: 177.0886, found: 177.0879.

(*E*)-6-(3-(Naphthalen-1-yl)prop-1-en-1-yl)tetrahydro-2*H*-pyran-2-one (170h)



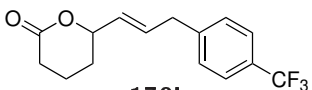
170h

Following general procedure **G**: acid **137m** (249 mg, 0.93 mmol, 1.0 equiv), diphenyl diselenide (15 mg, 47 µmol, 0.05 equiv) and *p*-MeO-TPT (23 mg, 47 µmol, 0.05 equiv), (9.3 mL); 16 h; yellow oil (141 mg, 530 µmol, 57%); *n*-pentane/Et_2O 1:1.

$\mathbf{R_f} = 0.17$ (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3048, 3011, 2952, 2882, 1727, 1596, 1509, 1440, 1394, 1340, 1232, 1161, 1089, 1032, 969, 926, 777, 750, 665, 554, 466, 425, 407; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.98 (m, 1 H), 7.86 (m, 1 H), 7.75

(dt, J = 8.0, 1.0 Hz, 1 H), 7.56–7.45 (m, 2 H), 7.41 (dd, J = 8.2, 7.0 Hz, 1 H), 7.33 (m, 1 H), 6.08 (dtd, J = 15.5, 6.3, 1.2 Hz, 1 H), 5.55 (ddt, J = 15.5, 6.2, 1.7 Hz, 1 H), 4.78 (dddd, J = 10.9, 6.2, 2.8, 1.1 Hz, 1 H), 3.85 (dd, J = 6.4, 1.6 Hz, 2 H), 2.55 (m, 1 H), 2.44 (ddd, J = 17.6, 8.2, 6.8 Hz, 1 H), 1.97–1.73 (m, 4 H), 1.61 (m, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 171.3, 135.6, 134.0, 132.4, 132.0, 129.8, 128.9, 127.3, 126.6, 126.1, 125.7, 124.0, 80.4, 35.7, 29.6, 28.4, 18.3; **HR-EI-MS m/z**: calcd. $C_{18}H_{18}O_2$ $[M]^+$: 266.1307, found: 266.1308.

(*E*)-6-(3-(4-(Trifluoromethyl)phenyl)prop-1-en-1-yl)tetrahydro-2*H*-pyran-2-one (170j)

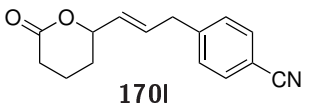


170j

Following general procedure **G**: acid **137o**; 16 h; yellow oil (208 mg, 732 µmol, 73%); *n*-pentane/Et_2O 2:1.

R_f = 0.21 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954, 1731, 1618, 1418, 1322, 1234, 1159, 1107, 1065, 1034, 1018, 971, 927, 848, 822, 733, 594; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.61–7.45 (m, 2 H), 7.33–7.23 (m, 2 H), 5.92 (dtd, J = 15.4, 6.7, 1.2 Hz, 1 H), 5.57 (ddt, J = 15.4, 6.2, 1.5 Hz, 1 H), 4.80 (m, 1 H), 3.44 (d, J = 6.7 Hz, 2 H), 2.70–2.30 (m, 2 H), 2.07–1.74 (m, 3 H), 1.65 (m, 1 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 171.1, 143.5 (d, J = 1.6 Hz), 131.5, 130.2, 129.0, 128.7 (q, J = 32.4 Hz), 125.5 (q, J = 3.9 Hz), 124.3 (q, J = 271.3 Hz), 80.2, 38.4, 29.7, 28.5, 18.4; **^{19}F NMR** (282 MHz, $CDCl_3$): δ [ppm] = −62.4 (s); **HR-ESI-MS m/z**: calcd. $C_{15}H_{15}F_3O_2Na$ $[M+Na]^+$: 307.0916, found: 307.0918.

(*E*)-4-(3-(6-Oxotetrahydro-2*H*-pyran-2-yl)allyl)benzonitrile (170l)

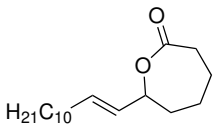


170l

Following general procedure **G**: acid **137q**; 16 h; yellow oil (152 mg, 629 µmol, 81%); *n*-pentane/Et_2O 1:1.

R_f = 0.07 (*n*-pentane:Et_2O, 1:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2952, 2226, 1726, 1606, 1504, 1338, 1232, 1176, 1088, 1034, 972, 927, 847, 821, 550; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.70–7.54 (m, 2 H), 7.29–7.26 (m, 2 H), 5.90 (dtd, J = 15.5, 6.7, 1.2 Hz, 1 H), 5.58 (ddt, J = 15.4, 6.2, 1.5 Hz, 1 H), 4.80 (m, 1 H), 3.48–3.40 (m, 2 H), 2.58 (m, 1 H), 2.47 (ddd, J = 17.7, 8.4, 6.8 Hz, 1 H), 2.08–1.76 (m, 3 H), 1.64 (m, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 171.1, 145.1, 132.5, 130.9, 130.8, 129.5, 119.0, 110.5, 80.1, 38.6, 29.6, 28.4, 18.4; **HR-ESI-MS m/z**: calcd. $C_{15}H_{15}NO_2Na$ $[M+Na]^+$: 264.0995, found: 264.0995.

(*E*)-7-(Dodec-1-en-1-yl)oxepan-2-one (171)



171

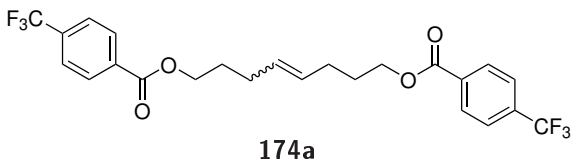
Following general procedure **G**: acid **167**; 21.5 h; colorless oil (13 mg, 46 µmol, 5%); *n*-pentane/Et_2O 3:1.

$\mathbf{R_f} = 0.43$ (*n*-pentane:Et_2O, 3:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2923, 2853, 1730, 1457, 1347, 1328, 1277, 1251, 1226, 1175, 1039, 1009, 967, 847, 699, 564; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.74 (dtd, J = 15.0, 6.8, 1.1 Hz, 1 H), 5.53 (ddt, J = 15.4, 6.8, 1.5 Hz, 1 H), 4.70 (dd, J = 9.4, 6.7 Hz, 1 H), 2.73–2.57 (m, 2 H), 2.06–1.88 (m, 4 H), 1.80–1.51 (m, 3 H), 1.41–1.18 (m, 17 H), 0.88 (t, J = 6.9 Hz, 3 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 175.4, 133.5, 128.8, 81.1, 35.6, 35.2, 32.36, 32.1, 29.86, 29.7, 29.6, 29.5, 29.3, 29.1, 28.3, 23.0, 22.8, 14.3; **HR-ESI-MS m/z**: calcd. $C_{18}H_{32}O_2Na$ $[M+Na]^+$: 303.2295, found: 303.2297.

5.6 Synthesis and phosphatation of alkenes

5.6.1 Synthesis of alkenes 174

Oct-4-ene-1,8-diyl bis(4-(trifluoromethyl)benzoate) (174a)

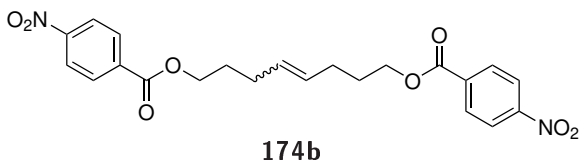


174a

Diol **126m** (216 mg, 1.50 mmol, 1.0 equiv), 4-(trifluoromethyl)benzoylchloride (688 mg, 3.30 mmol, 2.2 equiv) and 4-(dimethylamino)pyridine (403 mg, 3.30 mmol, 2.2 equiv) were dissolved in DCM (5 mL) and stirred for 17 h at room temperature. The reaction was quenched by addition of conc. sat. Na_2CO_3 solution (5 mL), the org. phase was washed with sat. aq. NaCl solution (5 mL) and 1 M aq. HCl solution (5 mL). The aq. phase was extracted with DCM (10 mL) and the org. phase was dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 10:1) afforded the product as a colorless liquid (653 mg, 1.34 mmol, 89%).

$\mathbf{R_f} = 0.57$ (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2957, 2922, 2873, 2854, 1721, 1412, 1323, 1270, 1163, 1097, 1065, 1017, 968, 862, 774, 703, 492; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.36–8.00 (m, 4 H), 7.78–7.55 (m, 4 H), 5.72–5.32 (m, 2 H), 4.52–4.11 (m, 4 H), 2.37–2.06 (m, 4 H), 1.98–1.69 (m, 4 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 165.4, 134.5 (q, J = 32.6 Hz), 133.7, 130.0, 129.5, 125.47 (q, J = 3.8 Hz), 123.73 (q, J = 272.2 Hz), 65.1, 29.1, 28.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ [ppm] = −63.1 (s); **HR-ESI-MS m/z**: calcd. $C_{24}H_{23}F_6O_4$ $[M+H]^+$: 489.1495, found: 489.1498.

Oct-4-ene-1,8-diyl bis(4-nitrobenzoate) (174b)

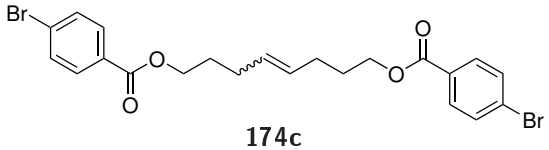


174b

Diol **126m** (216 mg, 1.50 mmol, 1.0 equiv), 4-nitrobenzoylchloride (612 mg, 3.30 mmol, 2.2 equiv) and 4-(dimethylamino)pyridine (403 mg, 3.30 mmol, 2.2 equiv) were dissolved in DCM (5 mL) and stirred for 17 h at room temperature. The reaction was quenched by addition of conc. sat. Na_2CO_3 solution (5 mL), the org. phase was washed with sat. aq. NaCl solution (5 mL) and 1 M aq. HCl solution (5 mL). The aq. phase was extracted with DCM (10 mL) and the org. phase was dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 10:1 to 5:1) afforded the product as a white solid (589 mg, 1.33 mmol, 89%).

$\mathbf{R_f} = 0.14$ (*n*-pentane:EtOAc, 10:1); **m.p.** = 114.8 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3147, 2955, 2937, 2854, 1713, 1599, 1522, 1462, 1346, 1321, 1270, 1167, 1123, 1102, 1010, 975, 911, 870, 857, 834, 787, 712, 505, 409; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.29–8.20 (m, 4 H), 8.20–8.11 (m, 4 H), 5.75–5.41 (m, 2 H), 4.33 (td, J = 6.6, 5.1 Hz, 4 H), 2.28–2.00 (m, 4 H), 1.84 (dq, J = 8.4, 6.6 Hz, 4 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 164.6, 150.5, 135.8, 130.7, 129.9, 123.5, 65.4, 29.0, 28.5; **HR-ESI-MS m/z**: calcd. $C_{22}H_{22}N_2O_8Na$ $[M+Na]^+$: 465.1268, found: 465.1279.

Oct-4-ene-1,8-diyl bis(4-bromobenzoate) (174c)

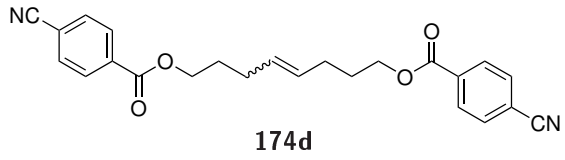


174c

Diol **126m** (216 mg, 1.50 mmol, 1.0 equiv), 4-bromobenzoylchloride (724 mg, 3.30 mmol, 2.2 equiv) and 4-(dimethylamino)pyridine (403 mg, 3.30 mmol, 2.2 equiv) were dissolved in DCM (5 mL) and stirred for 17 h. The reaction was quenched by addition of conc. sat. Na_2CO_3 solution (5 mL), the org. phase was washed with sat. aq. NaCl solution (5 mL) and 1 M aq. HCl solution (5 mL). The aq. phase was extracted with DCM (10 mL) and the org. phase was dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 10:1) afforded the product as a white solid (725 mg, 1.42 mmol, 94%).

$\mathbf{R_f} = 0.50$ (*n*-pentane:EtOAc, 10:1); **m.p.** = 55.7 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2959, 2935, 2893, 2847, 1714, 1589, 1472, 1396, 1267, 1173, 1102, 1066, 1008, 963, 848, 751, 708, 682, 469; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.00–7.75 (m, 4 H), 7.70–7.39 (m, 4 H), 5.71–5.23 (m, 2 H), 4.40–4.08 (m, 4 H), 2.29–1.95 (m, 4 H), 1.82 (quint, J = 6.7 Hz, 4 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 165.9, 131.7, 131.1, 130.0, 129.4, 128.0, 64.8, 29.2, 28.7; **HR-ESI-MS m/z**: calcd. $C_{22}H_{23}Br_2O_4$ $[M+H]^+$: 510.9939, found: 510.9945.

Oct-4-ene-1,8-diyl bis(4-cyanobenzoate) (174d)

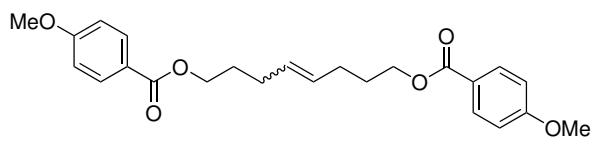


174d

Diol **126m** (216 mg, 1.50 mmol, 1.0 equiv), 4-cyanobenzoylchloride (546 mg, 3.30 mmol, 2.2 equiv) and 4-(dimethylamino)pyridine (403 mg, 3.30 mmol, 2.2 equiv) were dissolved in DCM (5 mL) and stirred for 17 h at room temperature. The reaction was quenched by addition of conc. sat. Na_2CO_3 solution (5 mL), the org. phase was washed with sat. aq. NaCl solution (5 mL) and 1 M aq. HCl solution (5 mL). The aq. phase was extracted with DCM (10 mL) and the org. phase was dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 5:1) afforded the product as a white solid (488 mg, 1.20 mmol, 81%).

R_f = 0.25 (*n*-pentane:EtOAc, 5:1); **m.p.** = 85.6 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2969, 2951, 2873, 2847, 2230, 1716, 1406, 1270, 1177, 1108, 1017, 957, 862, 766, 690, 546, 503; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.35–7.99 (m, 4 H), 7.92–7.50 (m, 4 H), 5.69–5.09 (m, 2 H), 4.62–3.79 (m, 4 H), 2.33–1.97 (m, 4 H), 1.98–1.70 (m, 4 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 164.9, 134.3, 132.3, 130.1, 130.0, 118.0, 116.5, 65.3, 29.1, 28.6; **HR-ESI-MS m/z**: calcd. $C_{24}H_{22}N_2O_4Na$ $[M+Na]^+$: 425.1472, found: 425.1474.

Oct-4-ene-1,8-diyl bis(4-methoxybenzoate) (174e)

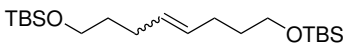


174e

Diol **126m** (649 mg, 4.50 mmol, 1.0 equiv), 4-methoxybenzoylchloride (1.7 g, 9.9 mmol, 2.2 equiv) and 4-(dimethylamino)pyridine (1.21 g, 9.90 mmol, 2.2 equiv) were dissolved in DCM (15 mL) and stirred for 18 h at room temperature. The reaction was quenched by addition of conc. sat. Na_2CO_3 solution (15 mL), the org. phase was washed with sat. aq. NaCl solution (15 mL) and 1 M aq. HCl solution (15 mL). The aq. phase was extracted with DCM (30 mL) and the org. phase was dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 3:1) afforded the product as a white solid (1.68 g, 4.08 mmol, 91%).

R_f = 0.43 (*n*-pentane:EtOAc, 3:1); **m.p.** = 57.8 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3004, 2958, 2839, 1700, 1604, 1580, 1509, 1455, 1418, 1386, 1315, 1273, 1249, 1167, 1117, 1101, 1028, 971, 958, 850, 787, 770, 754, 695, 637, 613, 508; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.11–7.85 (m, 4 H), 6.99–6.66 (m, 4 H), 5.62–5.40 (m, 2 H), 4.28 (t, J = 6.6 Hz, 4 H), 3.85 (d, J = 4.3 Hz, 6 H), 2.15 (tdd, J = 7.6, 3.9, 2.0 Hz, 4 H), 1.88–1.71 (m, 4 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 166.5, 163.4, 131.7, 130.1, 123.0, 113.7, 64.3, 55.5, 29.2, 28.7; **HR-ESI-MS m/z**: calcd. $C_{24}H_{28}O_6Na$ $[M+Na]^+$: 435.1778, found: 435.1778.

1,8-Bis(*tert*-butyldimethylsilyloxy)oct-4-ene (174f)

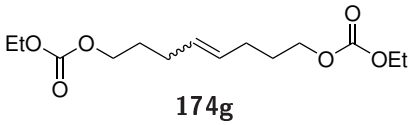


174f

Diol **126m** (577 mg, 4.00 mmol, 1.0 equiv) was dissolved in DCM (3.5 mL), TBSCl (1.33 g, 8.80 mmol, 2.2 equiv) and imidazole (654 mg, 9.60 mmol, 2.4 equiv) were added sequentially and the solution was stirred at room temperature for 17 h. The reaction mixture was washed with sat. aq. NaCl solution (2 × 4 mL), the aq. phase was extracted with DCM (2 × 8 mL) and the comb. org. phase was dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 4:1) afforded the product as a colorless liquid (1.39 g, 3.72 mmol, 93%).

R_f = 0.93 (*n*-pentane:EtOAc, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2953, 2929, 2893, 2857, 1472, 1387, 1361, 1253, 1098, 1006, 966, 938, 832 772, 716, 662; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.67–5.15 (m, 2 H), 3.60 (td, J = 6.6, 1.6 Hz, 4 H), 2.51–1.91 (m, 4 H), 1.73–1.44 (m, 4 H), 1.05–0.80 (m, 18 H), 0.14–(−0.02) (m, 12 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 130.2, 62.8, 32.9, 29.0, 26.2, 18.6, −5.0; **HR-ESI-MS m/z**: calcd. $C_{14}H_{45}O_2Si_2$ $[M+H]^+$: 373.2953, found: 373.2949.

Diethyl oct-4-ene-1,8-diyl bis(carbonate) (174g)

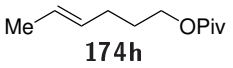


174g

Diol **126m** (577 mg, 4.00 mmol, 1.0 equiv) and DMAP (12 mg, 0.10 mmol, 0.025 equiv) were dissolved in DCM (6.0 mL) and cooled to 0 °C. Pyridine (633 mg, 8.00 mmol, 2.0 equiv) and ethylchloroformate (434 mg, 4.00 mmol, 1.0 equiv) were added dropwise sequentially. The solution was allowed to warm to room temperature and stirred for 13 h. Pyridine (633 mg, 8.00 mmol, 2.0 equiv), ethylchloroformate (434 mg, 4.00 mmol, 1.0 equiv) and DMAP (12 mg, 0.10 mmol, 0.025 equiv) were added and stirred for 24 h. After stirring at 40 °C for 19 h, the reaction was stopped, the solution was washed with H_2O (3 × 6 mL). Drying of the org. phase over Na_2SO_4, removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 2:1) afforded the product as a yellow liquid (881 mg, 3.05 mmol, 76%).

R_f = 0.86 (*n*-pentane:EtOAc, 2:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2983, 2962, 2939, 2912, 1739, 1467, 1402, 1367, 1244, 1091, 1007, 971, 864, 790; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.67–5.29 (m, 2 H), 4.18 (qd, J = 7.1, 0.9 Hz, 4 H), 4.12 (td, J = 6.7, 1.4 Hz, 4 H), 2.45–2.00 (m, 4 H), 1.72 (dq, J = 8.3, 6.6 Hz, 4 H), 1.30 (t, J = 7.1 Hz, 6 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 155.4, 130.0, 67.4, 64.0, 28.7, 28.6, 14.4; **HR-ESI-MS m/z**: calcd. $C_{14}H_{25}O_6$ $[M+H]^+$: 289.1646, found: 289.1641.

(*E*)-Hex-4-en-1-yl pivalate (174h)

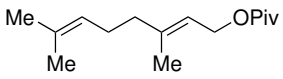


174h

DMAP (202 mg, 1.65 mmol, 1.1 equiv) and 4-hexene-1-ol (150 mg, 1.50 mmol, 1.0 equiv) were dissolved in DCM (5 mL) and pivaloyl chloride (199 mg, 1.65 mmol, 1.1 equiv) was added dropwise. The solution was stirred at room temperature for 5 h, washed with sat. aq. Na_2CO_3, sat. aq. NaCl and 1 M aq. HCl solution. The comb. aq. phases were extracted with DCM and the comb. org. phases were dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 20:1) afforded the product as a colorless liquid (207 mg, 1.12 mmol, 75%).

R_f = 0.71 (*n*-pentane:EtOAc, 20:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3015, 2970, 2872, 1728, 1480, 1459, 1398, 1366, 1283, 1150, 1150, 1034, 771, 699; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.56–5.43 (m, 1 H), 5.43–5.29 (m, 1 H), 4.05 (t, J = 6.5 Hz, 2 H), 2.32–1.97 (m, 2 H), 1.78-1.63 (m, 2 H), 1.60 (ddt, J = 6.6, 1.7, 0.8 Hz, 3 H), 1.20 (d, J = 0.4 Hz, 9 H); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ [ppm] = 178.7, 129.3, 125.0, 63.9, 38.9, 28.6, 27.4, 27.4, 23.3, 12.8; **HR-ESI-MS m/z**: calcd. $C_{11}H_{20}O_2Na$ [M+Na]$^+$: 207.1356, found: 207.1363.

(*E*)-3,7-Dimethylocta-2,6-dien-1-yl pivalate (174i)

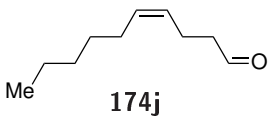


174i

DMAP (605 mg, 4.95 mmol, 1.1 equiv) and geraniol (694 mg, 4.50 mmol, 1.0 equiv) were dissolved in DCM (15 mL) and pivaloyl chloride (597 mg, 4.95 mmol, 1.1 equiv) was added dropwise. The solution was stirred at room temperature for 17 h, washed with sat. aq. Na_2CO_3, sat. aq. NaCl and 1 M aq. HCl solution. The comb. aq. phases were extracted with DCM and the comb. org. phases were dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 50:1) afforded the product as a colorless liquid (861 mg, 3.61 mmol, 80%).

R_f = 0.50 (*n*-pentane:EtOAc, 50:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2969, 2931, 2873, 1727, 1480, 1455, 1377, 1281, 1146, 1032, 951, 860, 830, 771; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 5.32 (tq, J = 6.9, 1.3 Hz, 1 H), 5.08 (dddd, J = 8.2, 6.8, 2.9, 1.4 Hz, 1 H), 4.57 (dq, J = 6.9, 0.7 Hz, 2H), 2.16–1.86 (m, 4 H), 1.80–1.64 (m, 6 H), 1.60 (d, J = 0.5 Hz, 3 H), 1.20 (s, 9 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 178.6, 141.7, 131.8, 123.9, 118.9, 61.5, 39.7, 39.0, 27.5, 26.5, 25.9, 17.9, 16.7; **HR-ESI-MS m/z**: calcd. $C_{15}H_{26}O_2Na$ [M+Na]$^+$: 261.1825, found: 261.1838.

(*Z*)-Dec-4-enal (174j)



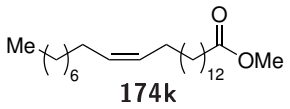
174j

Dess-Martin-periodinane (4.24 g, 10.0 mmol, 2.0 equiv) was dissolved in DCM (20 mL) and cooled to 0 °C. A solution of (*Z*)-4-decen-1-ol (782 mg, 5.00 mmol, 1.0 equiv) in DCM (5 mL) was added dropwise and the mixture was stirred at room temperature for 5 h. After diluting the solution with DCM (10 mL), it was washed with sat. aq. $Na_2S_2O_3$, 1 M aq. NaOH and sat.

aq. NaCl solution. The comb. aq. phases were extracted with DCM and the comb. org. phases were dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/Et_2O, 20:1) afforded the product as a colorless liquid (581 mg, 3.77 mmol, 75%).

R_f = 0.36 (*n*-pentane:Et_2O, 20:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3009, 2956, 2925, 2856, 2717, 1725, 1459, 1409, 1389, 1055, 857, 757, 725, 575, 503; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 9.77 (t, J = 1.7 Hz, 1 H), 5.43 (dtt, J = 10.9, 7.1, 1.4 Hz, 1 H), 5.32 (m, 1 H), 2.78–2.42 (m, 2 H), 2.42–2.13 (m, 2 H), 2.14–1.90 (m, 2 H), 1.46–1.06 (m, 6 H), 0.96–0.70 (m, 3 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 202.4, 131.9, 127.2, 44.0, 31.6, 29.4, 27.3, 22.7, 20.2, 14.2; **HR-ESI-MS m/z**: calcd. $C_{10}H_{18}O$ [M-H]$^+$: 153.1285, found: 153.1274.

Methyl (*Z*)-tetracos-15-enoate (174k)



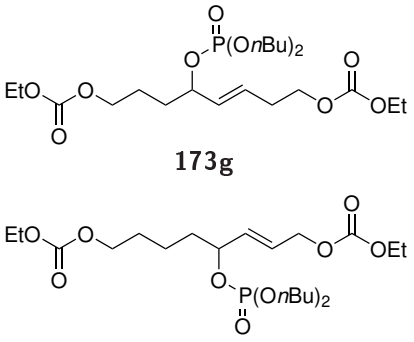
174k

(*Z*)-15-Tetracosenoic acid (1.29 g, 3.52 mmol, 1.0 equiv) and PTSA (33 mg, 0.18 mmol, 0.05 equiv) were dissolved in MeOH (35 mL) and stirred at 65 °C for 4 h. The solvent was removed in vacuo, the residue was dissolved in EtOAc and washed with H_2O, sat. aq. $NaHCO_3$ solution and again H_2O. Reextraction of the aq. phase with EtOAc, drying over Na_2SO_4 and removal of the solvent in vacuo afforded the product as a yellow liquid (1.26 g, 3.32 mmol, 94%).

R_f = 0.86 (DCM:EtOAc, 75:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2922, 2853, 1743, 1463, 1436, 1363, 1195, 1169, 721; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 5.35 (ddd, J = 5.6, 4.4, 1.1 Hz, 2 H), 3.66 (s, 3 H), 2.30 (t, J = 7.6 Hz, 2 H), 2.18–1.87 (m, 4 H), 1.61 (quint, J = 7.3 Hz, 2 H), 1.44–1.02 (m, 32 H), 0.92–0.83 (m, 3 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 174.8, 130.1, 51.6, 34.3, 32.1, 30.0, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 27.4, 25.1, 22.8, 14.3; **HR-ESI-MS m/z**: calcd. $C_{25}H_{49}O_2$ [M+H]$^+$: 381.3727, found: 381.3737.

5.6.2 Synthesis of phosphates 173

(*E*)-5-((Dibutoxyphosphoryl)oxy)oct-3-ene-1,8-diyl diethyl bis(carbonate) (173g)

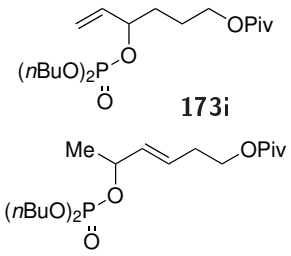


Alkene **174g** (865 mg, 3.00 mmol, 3.0 equiv), dibutyl phosphate (210 mg, 1.00 mmol, 1.0 equiv), Na_2HPO_4 (114 mg, 800 µmol, 0.8 equiv), *p*-MeO-TPT (**95**) (49 mg, 0.10 mmol, 0.1 equiv), diphenyl diselenide (31 mg, 0.10 mmol, 0.1 equiv) and 4 Å molecular sieves (30 mg) were dissolved in DCE (10 mL) and stirred under oxygen and irradiation with blue light at room temperature for 7.5 h. The solvent was removed, the residue was dissolved in a mixture of Et_2O and H_2O (1:1) and the aq. phase was extracted with Et_2O (3 ×). The comb. org. phases were washed

with H_2O and dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (DCM→*n*-pentane/EtOAc, 5:1) afforded the product as a yellow liquid as a mixture of products with different double bond positions (3-alkene:2-alkene, 6.6:1; 96.6 mg, 195 µmol, 20%). ^{31}P NMR yield 42% (6:1 major/minor) with triphenylphosphine (117 mg, 447 µmol) as a standard.

R_f = 0.14 (*n*-pentane:EtOAc, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2961, 2936, 2875, 1741, 1466, 1403, 1384, 1367, 1249, 976, 910, 868, 791, 736, 542; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = major product: 5.74 (dt, J = 15.4, 6.8 Hz, 1 H), 5.57 (ddt, J = 15.5, 7.4, 1.4 Hz, 1 H), 4.73 (quint, J = 6.6 Hz, 1 H), 4.18 (q, J = 7.2 Hz, 4 H), 4.15-4.11 (m, 4 H), 4.04-3.94 (m, 4 H), 2.42 (qd, J = 6.7, 1.3 Hz, 2 H), 1.84-1.67 (m, 4 H), 1.63 (sext, J = 6.8 Hz, 4 H), 1.44-1.34 (m, 4 H), 1.30 (t, J = 7.1 Hz, 6 H), 1.02-0.86 (m, 6 H); minor product: 5.87 (dt, J = 15.6, 5.5 Hz, 1 H), 5.79 (m, 1 H), 4.83 (m, 1 H), 4.61 (d, J = 5.5 Hz, 2 H), 4.18 (q, J = 7.2 Hz, 4 H), 4.15-4.11 (m, 2 H), 4.04-3.94 (m, 4 H), 1.90-1.83 (m, 2 H), 1.84-1.67 (m, 4 H), 1.63 (sext, J = 6.8 Hz, 4 H), 1.44-1.33 (m, 4 H), 1.30 (t, J = 7.1 Hz, 6 H), 1.02-0.86 (m, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = major product: 155.3, 155.2, 131.7 (d, J_{CP} = 3.3 Hz), 129.3, 78.7 (d, J_{CP} = 5.7 Hz), 67.5, 67.4, 66.6, 64.0, 32.4, 32.4 (d, J_{CP} = 2.3 Hz), 31.7, 24.4, 18.8, 14.4, 13.7; minor product: 155.3, 155.2, 132.8 (d, J_{CP} = 3.6 Hz), 126.8, 77.7 (d, J_{CP} = 5.6 Hz), 67.4, 67.3, 67.0, 64.1, 64.0, 32.4, 29.1 (d, J_{CP} = 5.5 Hz), 24.3, 24.2, 18.8, 14.4, 13.7; **^{31}P{^{1}H} NMR** (203 MHz, $CDCl_3$): δ [ppm] = major product: −1.46; minor product: −1.24; **HR-ESI-MS m/z**: calcd. $C_{22}H_{42}O_{10}P$ $[M+H]^+$: 497.2510, found: 497.2509.

4-((Dibutoxyphosphoryl)oxy)hex-5-en-1-yl pivalate (173i)



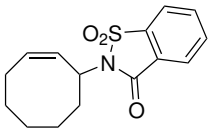
Alkene **174i** (553 mg, 3.00 mmol, 3.0 equiv), dibutyl phosphate (210 mg, 1.00 mmol, 1.0 equiv), Na_2HPO_4 (114 mg, 800 µmol, 0.8 equiv), *p*-MeO-TPT (**95**) (49 mg, 0.10 mmol, 0.1 equiv), diphenyl diselenide (31 mg, 0.10 mmol, 0.1 equiv) and 4 Å molecular sieves (30 mg) were dissolved in DCE (10 mL) and stirred under oxygen and irradiation with blue light at room temperature for 6.5 h. After 3 h, more *p*-MeO-TPT (25 mg, 0.05 mmol, 0.05 equiv) was added. The solvent was removed, the residue was dissolved in a mixture of Et_2O and H_2O (1:1) and the aq. phase was extracted with Et_2O (3 ×). The comb. org. phases were washed with H_2O and dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (DCM→*n*-pentane/EtOAc, 25:1 to 10:1) afforded the product as a yellow liquid (mixture of the terminal alkene and the internal alkene 3.4:1; 156 mg, 397 mmol, 40%). ^{1}H NMR yield 74% (1:1 internal/terminal) with 1,3,5-trimethoxybenzene (69.6 mg, 414 µmol) as a standard.

R_f = 0.13 (*n*-pentane:EtOAc, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2962, 2936, 2874, 1725, 1480, 1460, 1398, 1365, 1283, 1152, 989, 771, 755, 553; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = major

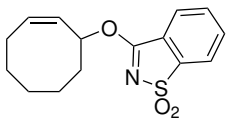
product: 5.82 (ddd, J = 17.2, 10.4, 6.9 Hz, 1 H), 5.32 (dt, J = 17.2, 1.2 Hz, 1 H), 5.22 (dt, J = 10.4, 1.1 Hz, 1 H), 4.77 (m, 1 H), 4.11-4.04 (m, 2 H), 4.04-3.96 (m, 4 H), 2.01-1.69 (m, 4 H), 1.66-1.58 (m, 4 H), 1.46-1.34 (m, 4 H), 1.18 (s, 9 H), 0.98-0.88 (m, 6 H); minor product: 5.70 (dt, J = 15.5, 6.5 Hz, 1 H), 5.60 (ddt, J = 15.5, 6.6, 1.2 Hz, 1 H), 4.88 (sext, J = 6.5 Hz, 1 H), 4.11-4.04 (m, 2 H), 4.04-3.96 (m, 4 H), 1.66-1.58 (m, 4 H), 1.46-1.34 (m, 7 H), 1.18 (s, 9 H), 0.98-0.88 (m, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = major product: 178.6, 136.7 (d, J_{CP} = 3.6 Hz), 117.6, 79.2 (d, J_{CP} = 5.8 Hz), 67.5 (d, J_{CP} = 1.8 Hz), 67.5 (d, J_{CP} = 1.6 Hz), 64.0, 38.9, 32.5, 32.4 (d, J_{CP} = 2.7 Hz), 32.4 (d, J_{CP} = 2.2 Hz), 27.3, 24.2, 18.8 (d, J_{CP} = 0.7 Hz), 13.7; minor product: 178.6, 133.0 (d, J_{CP} = 5.3 Hz), 128.3, 75.5 (d, J_{CP} = 5.5 Hz), 67.5 (d, J_{CP} = 1.8 Hz), 67.5 (d, J_{CP} = 1.6 Hz), 63.2, 38.9, 32.4 (d, J_{CP} = 2.7 Hz), 32.4 (d, J_{CP} = 2.2 Hz), 31.6, 27.3, 22.4 (d, J_{CP} = 4.8 Hz), 18.8 (d, J_{CP} = 0.7 Hz), 13.7; **^{31}P{^{1}H} NMR** (203 MHz, $CDCl_3$): δ [ppm] = major product: −1.42; minor product: −1.53; **HR-ESI-MS m/z**: calcd. $C_{19}H_{38}O_6P$ $[M+H]^+$: 393.2401, found: 393.2400.

5.7 Light-driven intermolecular amination

(*Z*)-2-(Cyclooct-2-en-1-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (185a) and (*Z*)-3-(Cyclooct-2-en-1-yloxy)benzo[*d*]isothiazole 1,1-dioxide (185b)



185a



185b

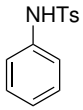
Cyclooctene (55.0 mg, 500 µmol, 1.0 equiv), saccharin (275 mg, 1.50 mmol, 3.0 equiv), CaF_2 (98.0 mg, 1.25 mmol, 2.5 equiv), diphenyl diselenide (16 mg, 50 µmol, 0.1 equiv) and *p*-MeO-TPT (12 mg, 25 µmol, 0.05 equiv) were dissolved in acetonitrile-d_3 (5 mL) and stirred under air and irradiation with blue light at room temperature for 16 h. The solvent was removed in vacuo and the products afforded *via* column chromatography (*n*-pentane/EtOAc, 7:1; **185a**: white solid, 32 mg, 0.11 mmol, 22%; **185b**: white solid, 29 mg, 0.10 mmol, 20%).

185a: **R_f** = 0.54 (*n*-pentane:EtOAc, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2928, 2856, 1726, 1461, 1333, 1292, 1252, 1179, 1126, 1061, 1049, 785, 750, 719, 676, 589, 575, 537, 508, 385; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.04 (m, 1 H), 7.98–7.65 (m, 3 H), 6.04 (ddd, J = 10.6, 8.4, 1.4 Hz, 1 H), 5.84 (dddd, J = 10.5, 9.0, 7.4, 1.4 Hz, 1 H), 5.21 (dddd, J = 12.7, 8.4, 4.2, 1.4 Hz, 1H), 2.52 (m, 1 H), 2.37 (dddd, J = 20.5, 7.4, 5.7, 3.9 Hz, 2 H), 2.19 (dddd, J = 13.5, 7.0, 4.7, 3.6 Hz, 1 H), 2.02 (ddt, J = 13.3, 8.8, 4.4 Hz, 1 H), 1.84–1.32 (m, 5 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 158.6, 137.7, 135.3, 134.6, 134.1, 131.7, 126.8, 124.9, 120.6, 52.5, 33.6, 29.1, 26.1, 26.0, 24.8.; **HR-ESI-MS m/z**: calcd. $C_{15}H_{17}NO_3SNa$ $[M+Na]^+$: 314.0821, found: 314.0818.

185b: **R_f** = 0.50 (*n*-pentane:EtOAc, 5:1); **m.p.** = 150 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2928, 2856, 1728, 1611, 1548, 1455, 1390, 1327, 1257, 1167, 1053, 1007, 920, 887, 868, 847, 785, 769, 750, 714, 701, 673, 651, 612, 575, 537, 453, 397; **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 7.87 (m, 1 H), 7.78–7.67 (m, 3 H), 6.05 (m, 1 H), 5.79 (dddd, J = 10.9, 9.0, 7.3, 1.6 Hz, 1 H), 5.64 (ddd,

J = 10.9, 7.0, 1.3 Hz, 1 H), 2.33–2.10 (m, 3 H), 1.77–1.52 (m, 7 H), 1.43 (m, 1 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 168.4, 143.5, 134.0, 133.4, 131.6, 128.4, 127.5, 123.4, 121.8, 81.2, 34.8, 28.8, 26.7, 25.9, 23.4; **HR-ESI-MS m/z**: calcd. $C_{15}H_{17}NO_3SNa$ $[M+Na]^+$: 314.0821, found: 314.0820.

4-Methyl-*N*-phenylbenzenesulfonamide (188)[163]

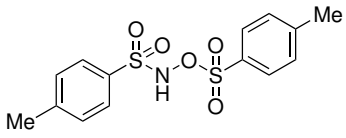


188

Aniline (373 mg, 4.00 mmol, 1.0 equiv) and triethyl amine (607 mg, 6.00 mmol, 1.5 equiv) were dissolved in DCM (11 mL) and cooled to 0 °C. Tosyl chloride (915 mg, 4.80 mmol, 1.2 equiv) was added portionwise and the solution stirred for 1 h at room temperature. The reaction was quenched by addition of 1 M aq. HCl solution (10 mL), the aq. phase was extracted with DCM (2 × 10 mL), the comb. org. phases were dried over Na_2SO_4 and the solvent was removed under vacuum. Column chromatography (*n*-pentane/EtOAc, 5:1) afforded the product as a white solid (989 mg, 4.00 mmol, >99%).

R_f = 0.26 (*n*-pentane:EtOAc, 5:1); **m.p.** = 96 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3248, 1597, 1482, 1415, 1337, 1319, 1289, 1154, 1122, 1089, 911, 823, 810, 755, 694, 659, 630, 562, 539, 506, 483; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.68 (d, J = 8.3 Hz, 2 H), 7.24–7.14 (m, 4 H), 7.11–6.99 (m, 3 H), 2.37 (s, 3 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 143.9, 136.6, 136.1, 129.7, 129.3, 127.3, 125.3, 121.6, 21.7; **HR-ESI-MS m/z**: calcd. $C_{13}H_{14}NO_2S$ $[M+H]^+$: 248.0740, found: 248.0740. The data were in agreement with literature.[163]

4-Methyl-*N*-(tosyloxy)benzenesulfonamide (190)[164]

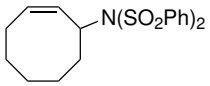


190

Hydroxylamine hydrochloride (347 mg, 5.00 mmol, 1.0 equiv) was dissolved in pyridine (5 mL) and cooled to 0 °C. DMAP (61 mg, 0.50 mmol, 0.1 equiv) was added and tosyl chloride (2.00 g, 10.5 mmol, 2.1 equiv) was added portionwise. The reaction mixture was stirred at room temperature for 5 h, EtOAc (5 mL) and aq. 1 M HCl solution (5 mL) were added. The org. phase was washed with aq. 1 M HCl solution (4 × 7 mL), the aq. phase was extracted with EtOAc (2 × 15 mL) and the org. phase was dried over Na_2SO_4. Removal of the solvent in vacuo, followed by column chromatography (DCM/EtOAc, 50:1) afforded the product as a white solid (304 mg, 890 µmol, 18%).

R_f = 0.21 (DCM:EtOAc, 50:1); **m.p.** = 155 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3194, 1597, 1374, 1294, 1267, 1194, 1169, 1121, 1088, 1019, 975, 910, 812, 776, 732, 681, 661, 574, 530, 469; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.88–7.78 (m, 2 H), 7.76–7.67 (m, 2 H), 7.54 (s, 1 H), 7.44–7.28 (m, 4 H), 2.46 (d, J = 5.1 Hz, 6 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ [ppm] = 146.5, 146.1, 132.3, 130.1, 129.9, 129.9, 129.0, 22.0, 21.9; **HR-ESI-MS m/z**: calcd. $C_{14}H_{15}NO_5S_2Na$ $[M+Na]^+$: 364.0284, found: 364.0295. The data were in agreement with literature.[164]

(*Z*)-*N*-(Cyclooct-2-en-1-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (336)

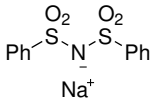


336

Cyclooctene (55.0 mg, 500 µmol, 1.0 equiv), dibenzensulfonimide (446 mg, 1.50 mmol, 3.0 equiv), CaF_2 (98.0 mg, 1.25 mmol, 2.5 equiv), diphenyl diselenide (16 mg, 50 µmol, 0.1 equiv) and *p*-MeO-TPT (**95**) (12 mg, 25 µmol, 0.05 equiv) were dissolved in acetonitrile-d_3 (5 mL) and stirred under air and irradiation with blue light at room temperature for 16 h. The solvent was removed in vacuo and the product afforded *via* column chromatography as a white solid (7.5 mg, 18 µmol, 4%).

$\mathbf{R_f} = 0.43$ (*n*-pentane:EtOAc, 7:1); **m.p.** = 124 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2922, 2855, 1711, 1446, 1377, 1349, 1289, 1157, 1081, 1021, 1001, 981, 898, 847, 833, 797, 756, 743, 720, 684, 614, 583, 548, 475, 388; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.31–7.91 (m, 4 H), 7.79–7.40 (m, 6 H), 5.98 (dd, J = 10.6, 8.5 Hz, 1 H), 5.62 (dt, J = 10.2, 8.8 Hz, 1 H), 5.11 (ddd, J = 12.1, 8.5, 3.9 Hz, 1 H), 2.38 (td, J = 12.3, 6.0 Hz, 1 H), 2.24–1.98 (m, 2 H), 1.84–1.02 (m, 7 H); **HR-ESI-MS m/z**: calcd. $C_{20}H_{23}NO_4S_2Na$ $[M+Na]^+$: 428.0961, found: 428.0952. The data were in agreement with literature.[241]

Sodium bis(phenylsulfonyl)amide (337)[165]

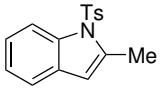


337

Dibenzene sulfonimide (500 mg, 1.7 mmol, 1.0 equiv) and NaOH (67 mg, 1.68 mmol, 1.0 equiv) were dissolved in a mixture of acetone and H_2O (1:1; 2 mL) and stirred for 16 h at room temperature. Removal of the solvent in vacuo afforded the product as a white solid (526 mg, 1.65 mmol, 98%),

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3061, 1447, 1366, 1269, 1159, 1134, 1082, 998, 874, 791, 751, 721, 686, 625, 575, 553; **^{1}H NMR** (300 MHz, D_2O): δ [ppm] = 7.64–7.54 (m, 4 H), 7.54–7.42 (m, 2 H), 7.43–7.29 (m, 4 H); **HR-ESI-MS m/z**: calcd. $C_{12}H_{10}NO_4Na_2S_2$ $[M+Na]^+$: 341.9841, found: 341.9843. The data were in agreement with literature.[165]

2-Methyl-1-tosyl-1*H*-indole (193)



193

4-Methyl-*N*-(2-(prop-1-en-1-yl)phenyl)benzenesulfonamide (72 mg, 0.25 mmol, 1.0 equiv), diphenyl diselenide (7.8 mg, 25 µmol, 0.1 equiv) and *p*-MeO-TPT (**95**) (12 mg, 25 µmol, 0.1 equiv) were dissolved in MeCN (2.5 mL) and stirred under air and irradiation with blue light at room temperature for 16 h. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 20:1) afforded the product as a white solid (12 mg, 43 µmol, 17%).

$\mathbf{R_f} = 0.43$ (*n*-pentane:EtOAc, 10:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.18 (m, 1 H), 7.82–7.58 (m, 3 H), 7.40 (dd, J = 7.7, 1.5 Hz, 1 H), 7.25–7.00 (m, 7 H), 6.34 (m, 1 H), 2.60 (d, J = 1.1 Hz, 3 H), 2.34 (s, 3 H). The analytical data was in agreement with literature.[65]

5.8 Synthesis of tetrahydroisoquinolines

General procedure H: Suzuki reaction[180]

Under an atmosphere of argon, the aryl halide (1.0 equiv), the respective boronic acid (1.1 equiv) and potassium carbonate (4.0 equiv) are added to a mixture of toluene, ethanol and water (0.08 M, 5:2:1) and the suspension is degassed with argon for 30 min. Tetrakis[triphenylphosphine]palladium(0) (0.1 equiv) is added and the mixture is heated to 100 °C. After completion of the reaction, detected by NMR and TLC, the mixture is allowed to cool down to room temperature, EtOAc is added and the org. phase is washed with H_2O and sat. aq. NaCl solution. The aq. phase is extracted with EtOAc, the combined org. phases are dried over Na_2SO_4 and the solvent is removed under reduced pressure. The residue is purified on silica gel to yield the title compound.

General procedure I: nitrile reduction

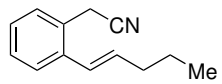
A solution of lithium aluminum hydride (2.5 equiv) in diethyl ether (0.35 M) is cooled to 0 °C and a solution of the respective nitrile (1.0 equiv) in diethyl ether (0.4 M) is added dropwise. The solution is allowed to warm to room temperature and stirred until completion is detected *via* NMR and TLC. The reaction is quenched by addition of sodium sulfate decahydrate, filtered over celite and the residue is washed with EtOAc. Removal of the solvent affords the product, which is used without further purification.

General procedure J: tosyl protection of amines[181]

The amine (1.0 equiv) and NEt_3 (1.1 equiv) are dissolved in DCM (0.5 M for the amine). Tosyl chloride (1.05 equiv) in DCM (1.05 M) is added and the solution is stirred at room temperature until completion is detected *via* NMR and TLC. The reaction is quenched by the addition of NH_4Cl, the phases are separated and the org. phase is washed with sat. aq. NaCl solution. The combined aq. phases are reextracted with DCM, the combined org. phases were dried over Na_2SO_4 and the solvent is removed under reduced pressure. The residue is purified on silica gel to yield the title compound.

5.8.1 Synthesis of *ortho*-vinyl homobenzylamides 207

(*E*)-2-(2-(Pent-1-en-1-yl)phenyl)acetonitrile (205a)

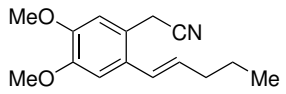


205a

Following general procedure **H**: 2-bromophenylacetonitrile (1.96 g, 10.0 mmol, 1.0 equiv), 1-pentenylboronic acid (1.25 g, 11.0 mmol, 1.1 equiv), potassium carbonate (5.53 g, 40.0 mmol, 4.0 equiv), toluene (77.5 mL), ethanol (31 mL), water (15.5 mL), tetrakis[triphenylphosphine]palladium(0) (1.2 g, 1.0 mmol, 0.1 equiv); reaction time 14.5 h; eluting with *n*-pentane/EtOAc, 20:1; yellow oil; 1.78 g, 9.58 mmol, 96%.

R_f = 0.29 (*n*-pentane:EtOAc, 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.45 (dd, J = 7.6, 1.7 Hz, 1 H), 7.39-7.17 (m, 3 H), 6.48 (dt, J = 15.6, 1.6 Hz, 1H), 6.14 (dt, J = 15.5, 6.9 Hz, 1 H), 3.74 (s, 2 H), 2.24 (qd, J = 7.2, 1.5 Hz, 2 H), 1.53 (sext, J = 7.3 Hz, 2 H), 0.98 (t, J = 7.4 Hz, 3 H). The analytical data are in agreement with literature.[185]

(*E*)-2-(4,5-Dimethoxy-2-(pent-1-en-1-yl)phenyl)acetonitrile (205b)

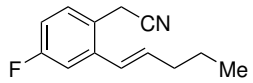


205b

Following general procedure **H**: 2-(2-bromo-4,5-dimethoxyphenyl)acetonitrile (250 mg, 976 µmol, 1.0 equiv), 1-pentenylboronic acid (122 mg, 1.07 mmol, 1.1 equiv), potassium carbonate (540 mg, 3.90 mmol, 4.0 equiv), toluene (7.5 mL), ethanol (3.0 mL), water (1.5 mL), tetrakis[triphenylphosphine]palladium(0) (113 mg, 97.8 µmol, 0.1 equiv); reaction time 16.5 h; eluting with *n*-pentane/EtOAc, 5:1; yellow oil; 202 mg, 823 µmol, 84%.

R_f = 0.29 (*n*-pentane:EtOAc, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3001, 2958, 2932, 2870, 2834, 2249, 1607, 1514, 1463, 1270, 1202, 1181, 1097, 1000, 962, 861, 751; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 6.93 (s, 1 H), 6.83 (s, 1 H), 6.40 (dt, J = 15.5, 1.5 Hz, 1 H), 6.04 (dt, J = 15.5, 6.9 Hz, 1 H), 3.90 (s, 1 H), 3.90 (s, 1 H), 3.69 (s, 2 H), 2.27-2.16 (m, 2 H), 1.62-1.42 (m, 2 H), 0.97 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 149.1, 148.6, 133.9, 129.8, 125.8, 118.9, 118.2, 111.9, 109.8, 56.2, 56.1, 35.5, 22.7, 21.4, 13.9; **HR-ESI-MS m/z**: calcd. $C_{14}H_{19}NO_2Na$ $[M+Na]^+$: 268.1308, found: 268.1310.

(*E*)-2-(4-Fluoro-2-(pent-1-en-1-yl)phenyl)acetonitrile (205c)

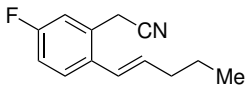


205c

Following general procedure **H**: 2-(2-bromo-4-fluorophenyl)acetonitrile (300 mg, 1.40 mmol, 1.0 equiv), 1-pentenylboronic acid (176 mg, 1.54 mmol, 1.1 equiv), potassium carbonate (775 mg, 5.61 mmol, 4.0 equiv), toluene (10 mL), ethanol (4.0 mL), water (2 mL), tetrakis[triphenylphosphine]palladium(0) (162 mg, 140 µmol, 0.1 equiv); reaction time 16.5 h; eluting with *n*-pentane/EtOAc, 30:1; yellow oil; 235 mg, 1.16 mmol, 83%.

R_f = 0.29 (*n*-pentane:EtOAc, 20:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2961, 2931, 2872, 2250, 1612, 1584, 1491, 1423, 1273, 1242, 1171, 1159, 962, 872, 806, 407; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.31 (dd, J = 8.5, 5.6 Hz, 1 H), 7.15 (dd, J = 9.9, 2.7 Hz, 1 H), 6.94 (td, J = 8.2, 2.7 Hz, 1 H), 6.43 (dq, J = 15.5, 1.5 Hz, 1 H), 6.17 (dt, J = 15.4, 6.9 Hz, 1 H), 3.69 (s, 2 H), 2.24 (qd, J = 7.1, 1.5 Hz, 2 H), 1.52 (sext, J = 7.4 Hz, 2 H), 0.97 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 162.9 (d, $^1J_{CF}$ = 246.7 Hz), 139.4 (d, $^3J_{CF}$ = 8.0 Hz), 136.9, 130.6 (d, $^3J_{CF}$ = 8.7 Hz), 125.2 (d, $^4J_{CF}$ = 2.2 Hz), 122.5 (d, $^4J_{CF}$ = 3.0 Hz), 117.7, 114.4 (d, $^2J_{CF}$ = 21.9 Hz), 113.6 (d, $^2J_{CF}$ = 22.4 Hz), 35.4, 22.4, 21.4, 13.9; **HR-ESI-MS m/z**: calcd. $C_{13}H_{15}FN$ $[M+H]^+$: 204.1183, found: 204.1175.

(*E*)-2-(5-Fluoro-2-(pent-1-en-1-yl)phenyl)acetonitrile (205d)

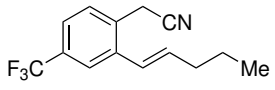


205d

Following general procedure **H**: 2-(2-bromo-5-fluorophenyl)acetonitrile (300 mg, 1.40 mmol, 1.0 equiv), 1-pentenylboronic acid (176 mg, 1.54 mmol, 1.1 equiv), potassium carbonate (775 mg, 5.61 mmol, 4.0 equiv), toluene (10 mL), ethanol (4.0 mL), water (2 mL), tetrakis[triphenylphosphine]palladium(0) (162 mg, 140 µmol, 0.1 equiv); reaction time 16.5 h; eluting with *n*-pentane/EtOAc, 30:1; yellow oil; 242 mg, 1.19 mmol, 85%.

R$_f$ = 0.26 (*n*-pentane:EtOAc, 30:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960, 2931, 2873, 2251, 1610, 1586, 1492, 1463, 1426, 1250, 1186, 1150, 965, 861, 832, 801, 731, 449; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.40 (dd, J = 8.6, 5.7 Hz, 1 H), 7.11 (dd, J = 9.2, 2.7 Hz, 1 H), 7.00 (dddd, J = 8.7, 8.1, 2.7, 0.5 Hz, 1 H), 6.39 (dd, J = 15.5, 0.7 Hz, 1 H), 6.07 (dt, J = 15.5, 6.9 Hz, 1 H), 3.72 (s, 2 H), 2.22 (qd, J = 7.1, 1.5 Hz, 2 H), 1.51 (sext, J = 7.4 Hz, 2 H), 0.97 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 162.0 (d, $^1J_{CF}$ = 247.5 Hz), 135.8 (d, $^4J_{CF}$ = 1.8 Hz), 133.46 (d, $^4J_{CF}$ = 3.5 Hz), 128.8 (d, $^3J_{CF}$ = 8.0 Hz), 128.6 (d, $^3J_{CF}$ = 7.6 Hz), 125.04, 117.25, 115.8 (d, $^2J_{CF}$ = 23.1 Hz), 115.6 (d, $^2J_{CF}$ = 21.0 Hz), 35.44, 22.53, 21.95 (d, $^4J_{CF}$ = 1.7 Hz), 13.83; **HR-ESI-MS m/z**: calcd. $C_{13}H_{14}FNNa$ $[M+Na]^+$: 226.1002, found: 226.1006.

(*E*)-2-(2-(Pent-1-en-1-yl)-4-(trifluoromethyl)phenyl)acetonitrile (205e)

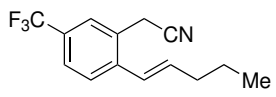


205e

Following general procedure **H**: 2-(2-bromo-4-trifluoromethylphenyl)acetonitrile (300 mg, 1.14 mmol, 1.0 equiv), 1-pentenylboronic acid (142 mg, 1.25 mmol, 1.1 equiv), potassium carbonate (628 mg, 4.54 mmol, 4.0 equiv), toluene (8.75 mL), ethanol (3.5 mL), water (1.75 mL), tetrakis[triphenylphosphine]palladium(0) (131 mg, 114 µmol, 0.1 equiv); reaction time 16.5 h; eluting with *n*-pentane/EtOAc, 30:1; light yellow oil; 240 mg, 946 µmol, 83%.

R$_f$ = 0.14 (*n*-pentane:EtOAc, 30:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2962, 2933, 2874, 2253, 1650, 1617, 1424, 1330, 1273, 1218, 1163, 1121, 1075, 965, 824, 747, 660, 454; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.68 (s, 1 H), 7.50 (d, J = 1.3 Hz, 2 H), 6.47 (dtd, J = 15.5, 1.5, 0.6 Hz, 1 H), 6.23 (dt, J = 15.5, 6.9 Hz, 1 H), 3.78 (s, 2 H), 2.36–2.09 (m, 2 H), 1.54 (sext, J = 7.3 Hz, 2 H), 0.98 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): 138.1, 137.7, 131.1 (q, $^2J_{CF}$ = 32.6 Hz), 130.5, 129.3, 124.9, 124.2 (q, $^3J_{CF}$ = 3.7 Hz), 124.0 (q, $^1J_{CF}$ = 272.4 Hz), 123.8 (q, $^3J_{CF}$ = 3.8 Hz), 117.0, 35.5, 22.4, 22.0, 13.8; **HR-ESI-MS m/z**: calcd. $C_{14}H_{14}F_3NNa$ $[M+Na]^+$: 276.0971, found: 276.0964.

(*E*)-2-(2-(Pent-1-en-1-yl)-5-(trifluoromethyl)phenyl)acetonitrile (205f)

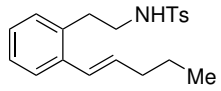


205f

Following general procedure **H**: 2-(2-bromo-5-trifluoromethylphenyl)acetonitrile (300 mg, 1.14 mmol, 1.0 equiv), 1-pentenylboronic acid (142 mg, 1.25 mmol, 1.1 equiv), potassium carbonate (628 mg, 4.54 mmol, 4.0 equiv), toluene (8.75 mL), ethanol (3.5.0 mL), water (1.75 mL), tetrakis[triphenylphosphine]palladium(0) (131 mg, 114 µmol, 0.1 equiv); reaction time 16.5 h; eluting with *n*-pentane/EtOAc, 30:1; light yellow oil; 255 mg, 1.01 mmol, 88%.

$\mathbf{R_f} = 0.29$ (*n*-pentane:EtOAc, 20:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2962, 2933, 2875, 2251, 1650, 1620, 1422, 1330, 1285, 1264, 1161, 1119, 1098, 1081, 966, 882, 843; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.61 (s, 1 H), 7.56 (s, 2 H), 6.49 (dt, J = 15.5, 1.5 Hz, 1 H), 6.25 (dt, J = 15.5, 6.9 Hz, 1 H), 3.78 (s, 2 H), 2.27 (qd, J = 7.3, 1.5 Hz, 2 H), 1.61-1.45 (m, 2 H), 0.98 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 140.9, 138.3, 129.7 (q, $^2J_{CF}$ = 32.8 Hz), 127.5, 127.4, 125.9 (q, $^3J_{CF}$ = 3.9 Hz), 125.6 (q, $^3J_{CF}$ = 3.7 Hz), 124.9, 123.9 (q, $^1J_{CF}$ = 272.1 Hz), 117.0, 35.6, 22.4, 22.0, 13.9; **HR-ESI-MS m/z**: calcd. $C_{14}H_{14}F_3NNa$ [M+Na]$^+$: 276.0971, found: 276.0975.

(*E*)-4-Methyl-*N*-(2-(pent-1-en-1-yl)phenethyl)benzenesulfonamide (207a)

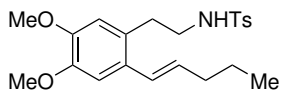


207a

Following general procedure **I**: lithium aluminum hydride (1.06 g, 28.0 mmol, 2.5 equiv) in diethyl ether (78 mL), nitrile **205a** (2.08 g, 11.2 mmol, 1.0 equiv) in diethyl ether (27 mL); reaction time 17 h; yellow oil. Following general procedure **J**: amine (1.42 g, 7.50 mmol, 1.0 equiv), NEt_3 (835 mg, 8.25 mmol, 1.1 equiv), DCM (16 mL), tosyl chloride (1.50 g, 7.88 mmol, 1.05 equiv) in DCM (8 mL); reaction time 17 h; eluting with *n*-pentane/EtOAc, 7:1; yellow oil; 1.86 g, 5.41 mmol, 72%.

$\mathbf{R_f} = 0.21$ (*n*-pentane:EtOAc, 7:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.73-7.61 (m, 2 H), 7.38 (dd, J = 7.5, 1.6 Hz, 1 H), 7.31-7.23 (m, 2 H), 7.23-7.08 (m, 2 H), 7.01 (dd, J = 7.4, 1.7 Hz, 1 H), 6.47 (d, J = 15.4 Hz, 1 H), 6.02 (dt, J = 15.5, 6.9 Hz, 1 H), 4.35 (t, J = 6.2 Hz, 1 H), 3.16 (q, J = 6.9 Hz, 2 H), 2.85 (t, J = 7.1 Hz, 2 H), 2.42 (s, 3 H), 2.16 (qd, J = 7.1, 1.5 Hz, 2 H), 1.46 (sext, J = 7.4 Hz, 2 H), 0.94 (t, J = 7.3 Hz, 3 H). The analytical data are in agreement with literature.[185]

(*E*)-*N*-(4,5-Dimethoxy-2-(pent-1-en-1-yl)phenethyl)-4-methylbenzenesulfonamide (207b)



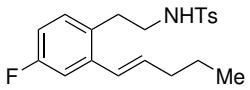
207b

Following general procedure **I**: lithium aluminum hydride (70 mg, 1.8 mmol, 2.5 equiv) in diethyl ether (5 mL), nitrile **205b** (180 mg, 734 µmol, 1.0 equiv) in diethyl ether (1.7 mL); reaction time 6 h; colorless oil. Following general procedure **J**: amine (150 mg, 602 µmol, 1.0 equiv), NEt_3 (67 mg, 0.66 mmol, 1.1 equiv), DCM (1.2 mL), tosyl chloride (120 mg, 632 µmol,

1.05 equiv) in DCM (0.6 mL); reaction time 20 h; eluting with *n*-pentane/EtOAc, 5:1; brown liquid; 68 mg, 0.17 mmol, 23% from nitrile.

$\mathbf{R_f} = 0.07$ (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3282, 2957, 2932, 2870, 2834, 1603, 1509, 1463, 1327, 1266, 1203, 1183, 1156, 1093, 1041, 1002, 964, 862, 814, 814, 752, 733, 707, 661, 549, 501, 471; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.66 (d, J = 8.3 Hz, 2 H), 7.26 (d, J = 7.9 Hz, 2 H), 6.89 (s, 1 H), 6.50 (s, 1 H), 6.41 (dt, J = 15.5, 1.5 Hz, 1 H), 5.94 (dt, J = 15.5, 7.0 Hz, 1 H), 4.39 (t, J = 6.2 Hz, 1 H), 3.88 (s, 3 H), 3.82 (s, 3 H), 3.13 (q, J = 6.9 Hz, 2 H), 2.80 (t, J = 7.1 Hz, 2 H), 2.41 (s, 3 H), 2.15 (qd, J = 7.2, 1.5 Hz, 2 H), 1.46 (sext, J = 7.4 Hz, 2 H), 0.93 (t, J = 7.4 Hz, 4 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 148.3, 148.1, 143.5, 137.0, 132.0, 129.8, 129.6, 127.2, 126.9, 126.6, 113.0, 109.3, 56.1, 56.0, 43.9, 35.5, 33.0, 22.8, 21.6, 13.9; **HR-ESI-MS m/z**: calcd. $C_{22}H_{29}NO_4SNa$ [M+Na]$^+$: 426.1710, found: 426.1710.

(*E*)-*N*-(4-Fluoro-2-(pent-1-en-1-yl)phenethyl)-4-methylbenzenesulfonamide (207c)

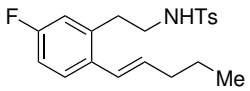


207c

Following general procedure **I**: lithium aluminum hydride (107 mg, 2.83 mmol, 2.5 equiv) in diethyl ether (8 mL), nitrile **205c** (230 mg, 1.13 mmol, 1.0 equiv) in diethyl ether (2.7 mL); reaction time 5 h; yellow oil. Following general procedure **J**: amine (200 mg, 965 µmol, 1.0 equiv), NEt_3 (108 mg, 1.06 mmol, 1.1 equiv), DCM (2 mL), tosyl chloride (193 mg,1.01 mmol, 1.05 equiv) in DCM (1 mL); reaction time 18 h; eluting with *n*-pentane/EtOAc, 10:1; yellow oil; 31 mg, 86 µmol, 8% from nitrile.

$\mathbf{R_f} = 0.13$ (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3281, 2959, 2929, 2872, 1609, 1582, 1490, 1456, 1420, 1323, 1269, 1154, 1092, 1072, 964, 870, 812, 755, 735, 706, 659, 549, 489, 467; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.83-7.59 (m, 2 H), 7.43-7.18 (m, 2 H), 7.06 (dd, J = 10.3, 2.8 Hz, 1 H), 6.96 (dd, J = 8.4, 5.9 Hz, 1 H), 6.79 (td, J = 8.3, 2.7 Hz, 1 H), 6.42 (dq, J = 15.5, 1.6 Hz, 1 H), 6.04 (dt, J = 15.5, 7.0 Hz, 1 H), 4.66 (t, J = 6.2 Hz, 1 H), 3.11 (q, J = 6.9 Hz, 2 H), 2.80 (t, J = 7.3 Hz, 2 H), 2.41 (s, 3 H), 2.16 (qd, J = 7.1, 1.5 Hz, 2 H), 1.46 (sext, J = Hz, 2 H), 0.93 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 162.1 (d, $^1J_{CF}$ = 244.4 Hz), 143.5, 139.1 (d, $^3J_{CF}$ = 7.6 Hz), 137.0, 135.0, 131.6 (d, $^3J_{CF}$ = 8.2 Hz), 130.3 (d, $^4J_{CF}$ = 3.0 Hz), 129.8, 127.1, 126.1 (d, $^4J_{CF}$ = 2.3 Hz), 113.9 (d, $^2J_{CF}$ = 21.3 Hz), 112.8 (d, $^3J_{CF}$ = 21.8 Hz), 43.6, 35.3, 33.0, 22.5, 21.6, 13.9; **HR-ESI-MS m/z**: calcd. $C_{20}H_{24}NO_2SFNa$ [M+Na]$^+$: 384.1404, found: 384.1412.

(*E*)-*N*-(5-Fluoro-2-(pent-1-en-1-yl)phenethyl)-4-methylbenzenesulfonamide (207d)



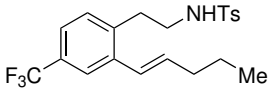
207d

Following general procedure **I**: lithium aluminum hydride (107 mg, 2.83 mmol, 2.5 equiv) in diethyl ether (8 mL), nitrile **205d** (230 mg, 1.13 mmol, 1.0 equiv) in diethyl ether (2.7 mL); reaction time 23 h; yellow oil. Following general procedure **J**: amine (200 mg, 966 µmol, 1.0 equiv),

NEt_3 (108 mg, 1.06 mmol, 1.1 equiv), DCM (2 mL), tosyl chloride (193 mg,1.01 mmol, 1.05 equiv) in DCM (1 mL); reaction time 17.5 h; eluting with *n*-pentane/DCM, 5:1; light yellow oil; 65 mg, 0.18 mmol, 16% from nitrile.

R_f = 0.07 (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3277, 2958, 2929, 2871, 1600, 1584, 1491, 1324, 1248, 1153, 1091, 965, 871, 813, 706, 660, 548, 494; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.71-7.65 (m, 2 H), 7.33 (dd, J = 8.6, 5.8 Hz, 1 H), 7.31–7.25 (m, 2 H), 6.86 (td, J = 8.4, 2.7 Hz, 1 H), 6.68 (dd, J = 9.4, 2.7 Hz, 1 H), 6.41 (dt, J = 15.5, 1.6 Hz, 1 H), 5.96 (dt, J = 15.5, 6.9 Hz, 1 H), 4.43 (t, J = 6.3 Hz, 1 H), 3.16 (td, J = 7.3, 6.3 Hz, 2 H), 2.81 (t, J = 7.2 Hz, 2 H), 2.42 (s, 3 H), 2.16 (qd, J = 7.1, 1.5 Hz, 2 H), 1.46 (sext, J = 7.4 Hz, 2 H), 0.94 (t, J = 7.4 Hz, 3 H);**^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 161.9 (d, $^1J_{CF}$ = 246.4 Hz), 143.6, 137.0, 136.6 (d, $^3J_{CF}$ = 7.0 Hz), 133.9 (d, $^4J_{CF}$ = 1.7 Hz), 133.5 (d, $^4J_{CF}$ = 3.2 Hz), 129.9, 128.2 (d, $^3J_{CF}$ = 7.9 Hz), 127.2, 126.0, 116.4 (d, $^2J_{CF}$ = 21.1 Hz), 114.2 (d, $^2J_{CF}$ = 21.0 Hz), 43.3, 35.4, 33.6 (d, $^4J_{CF}$ = 1.5 Hz), 22.7, 21.7, 13.9; **HR-ESI-MS m/z**: calcd. $C_{20}H_{25}NO_2SF$ $[M+H]^+$: 362.1585, found: 362.1581.

(*E*)-4-Methyl-*N*-(2-(pent-1-en-1-yl)-4-(trifluoromethyl)phenethyl)benzenesulfonamide (207e)

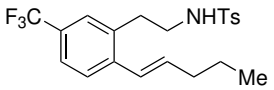


207e

Following general procedure **I**: lithium aluminum hydride (81 mg, 2.1 mmol, 2.5 equiv) in diethyl ether (6 mL), nitrile **205e** (215 mg, 849 µmol, 1.0 equiv) in diethyl ether (2 mL); reaction time 23 h; red liquid. Following general procedure **J**: amine (170 mg, 661 µmol, 1.0 equiv), NEt_3 (74 mg, 0.73 mmol, 1.1 equiv), DCM (1.3 mL), tosyl chloride (132 mg, 695 µmol, 1.05 equiv) in DCM (0.6 mL); reaction time 65 h; eluting with *n*-pentane/EtOAc, 5:1; yellow oil; 50.0 mg, 121 µmol, 14% from nitrile.

R_f = 0.19 (*n*-pentane:EtOAc, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3302, 2959, 2932, 2873, 1650, 1616, 1598, 1578, 1422, 1325, 1275, 1156, 1118, 1092, 1076, 966, 925, 903, 830, 815, 662, 550; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.79-7.62 (m, 2 H), 7.59 (d, J = 1.9 Hz, 1 H), 7.35 (dd, J = 8.0, 1.9 Hz, 1 H), 7.30-7.21 (m, 2 H), 7.13 (d, J = 7.9 Hz, 1 H), 6.48 (dt, J = 15.6, 1.6 Hz, 1 H), 6.10 (dt, J = 15.5, 7.0 Hz, 1 H), 4.50 (t, J = 6.3 Hz, 1 H), 3.16 (q, J = 6.9 Hz, 2 H), 2.90 (t, J = 7.2 Hz, 2 H), 2.41 (s, 3 H), 2.19 (qd, J = 7.1, 1.5 Hz, 2 H), 1.49 (q, J = 7.4 Hz, 2 H), 0.95 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 143.6, 138.4 (d,$^4J_{CF}$ = 1.6 Hz), 138.0, 136.9, 135.8, 130.5, 129.8, 129.6 (q, $^2J_{CF}$ = 32.4 Hz), 127.2, 125.9, 124.3 (q, $^1J_{CF}$ = 272.1 Hz), 123.6 (d, $^3J_{CF}$ = 3.8 Hz), 123.3 (d, $^3J_{CF}$ = 3.8 Hz), 43.2, 35.5, 33.7, 22.5, 21.6, 13.9; **HR-ESI-MS m/z**: calcd. $C_{21}H_{24}NO_2SF_3Na$ $[M+Na]^+$: 434.1372, found: 434.1369.

(*E*)-4-Methyl-*N*-(2-(pent-1-en-1-yl)-5-(trifluoromethyl)phenethyl)benzenesulfonamide (207f)

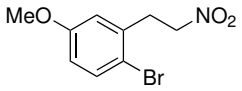


207f

Following general procedure **I**: lithium aluminum hydride (90.0 mg, 2.37 mmol, 2.5 equiv) in diethyl ether (6.6 mL), nitrile **205f** (240 mg, 948 µmol, 1.0 equiv) in diethyl ether (2.3 mL); reaction time 41 h; yellow oil. Following general procedure **J**: amine (195 mg, 758 µmol, 1.0 equiv), NEt_3 (84 mg, 0.83 mmol, 1.1 equiv), DCM (1.5 mL), tosyl chloride (152 mg, 796 µmol, 1.05 equiv) in DCM (0.75 mL); reaction time 22.5 h; eluting with *n*-pentane/DCM, 3:1; light yellow oil; 21 mg, 51 µmol, 5% from nitrile.

$\mathbf{R_f} = 0.13$ (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3282, 2960, 2930, 2873, 1648, 1616, 1599, 1459, 1419, 1327, 1286, 1155, 1118, 1083, 968, 896, 841, 813, 746, 735, 706, 664, 549, 500; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.79-7.58 (m, 2 H), 7.47 (d, J = 8.2 Hz, 1 H), 7.40 (dd, J = 8.2, 2.0 Hz, 1 H), 7.30-7.23 (m, 2 H), 7.20 (d, J = 1.9 Hz, 1 H), 6.52 (dt, J = 15.7, 1.6 Hz, 1 H), 6.14 (dt, J = 15.5, 7.0 Hz, 1 H), 4.64 (t, J = 6.3 Hz, 1 H), 3.18 (td, J = 7.3, 6.2 Hz, 2 H), 2.88 (dd, J = 8.1, 6.6 Hz, 2 H), 2.42 (s, 3 H), 2.21 (qd, J = 7.1, 1.5 Hz, 2 H), 1.50 (sext, J = 7.4 Hz, 2 H), 0.96 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 143.7, 140.9, 137.1, 136.4, 135.3, 129.9, 129.0 (q, $^2J_{CF}$ = 32.4 Hz), 127.1, 126.8, 126.7 (q, $^3J_{CF}$ = 3.8 Hz), 126.0, 124.2 (q, $^1J_{CF}$ = 271.9 Hz), 124.0 (q, $^3J_{CF}$ = 3.8 Hz), 43.4, 35.5, 33.7, 22.5, 21.6, 13.9; **HR-ESI-MS m/z**: calcd. $C_{21}H_{24}NO_2SF_3Na$ $[M+Na]^+$: 434.1372, found: 434.1375.

1-Bromo-4-methoxy-2-(2-nitroethyl)benzene (212)

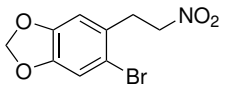


212

Copper(I)bromide (31 mg, 0.21 mmol, 0.2 equiv), *N*-((2*Z*,4*E*)-4-((2,6-Dimethylphenyl)imino)pent-2-en-2-yl)-2,6-dimethylaniline (66 mg, 0.21 mmol, 0.2 equiv) and sodium *tert*-butoxide (124 mg, 1.29 mmol, 1.2 equiv) were dissolved in 1,4-dioxane (6 mL). Nitromethane (430 µL, 491 mg, 8.04 mmol, 7.5 equiv) and 1-bromo-2-(bromomethyl)-4-methoxybenzene (300 mg, 1.07 mmol, 1.0 equiv) were added and the solution was heated to 60 °C for 15 h. Sat. aq. NH_4Cl (10 mL) was added, the aq. phase was extracted with Et_2O (10 mL), the combined org. phases were washed with sat. aq. NaCl (20 mL) and dried over Na_2SO_4. Removal of the solvent in vacuum and purification by column chromatography (12:1 *n*-pentane:EtOAc) afforded the product as a brown oil (192 mg, 740 µmol, 69%).

$\mathbf{R_f} = 0.25$ (*n*-pentane:EtOAc, 12:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.45 (d, J = 8.8 Hz, 1 H), 6.80 (d, J = 3.0 Hz, 1 H), 6.72 (dd, J = 8.8, 3.0 Hz, 1 H), 4.67-4.60 (m, 2 H), 3.78 (s, 3 H), 3.41 (t, J = 7.3 Hz, 2 H).

5-Bromo-6-(2-nitroethyl)benzo[*d*][1,3]dioxole (213)

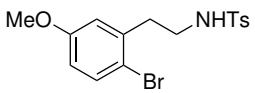


213

Copper(I)bromide (98 mg, 0.68 mmol, 0.2 equiv), *N*-((2*Z*,4*E*)-4-((2,6-Dimethylphenyl)imino)pent-2-en-2-yl)-2,6-dimethylaniline (209 mg, 680 µmol, 0.2 equiv) and sodium *tert*-butoxide (392 mg, 4.08 mmol, 1.2 equiv) were dissolved in 1,4-dioxane (20 mL). Nitromethane (1.37 mL, 1.56 g, 25.5 mmol, 7.5 equiv) and 5-bromo-6-(bromomethyl)benzo[*d*][1,3]dioxole (1.0 g, 3.4 mmol, 1.0 equiv) were added and the solution was heated to 60 °C for 19 h. Sat. aq. NH_4Cl (20 mL) was added, the aq. phase was extracted with Et_2O (15 mL), the combined org. phases were washed with water (20 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo, purification by column chromatography (30:1 *n*-pentane:EtOAc) and recrystallization from *n*-hexane/MeOH afforded the product as a white solid (330 mg, 1.20 mmol, 35%).

R_f = 0.14 (*n*-pentane:EtOAc, 30:1); **m.p.** = 58-60 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3111,3093, 3055, 3008, 2975, 2913, 1542, 1501, 1476, 1421, 1408, 1377, 1359, 1331, 1232, 1162, 1118, 1032, 990, 922, 877, 855, 826, 744, 654, 592, 536, 500, 428; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.01 (s, 1 H), 6.73 (s, 1 H), 5.97 (s, 2 H), 4.59 (t, J = 7.2 Hz, 2 H), 3.35 (t, J = 7.2 Hz, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 148.2, 147.8, 127.9, 114.8, 113.2, 110.8, 102.1, 74.7, 33.9; **HR-ESI-MS m/z**: calcd. $C_9H_7BrNO_4$ $[M\text{-}H]^-$: 271.9564, found: 271.9564.

N-(2-Bromo-5-methoxybenzyl)-4-methylbenzenesulfonamide (215)



215

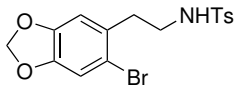
Nitroethyl compound **212** (700 mg, 2.69 mmol, 1.0 equiv) and zinc (3.5 g, 54 mmol, 20 equiv) were added to a mixture of methanol (27 mL), conc. acetic acid (9 mL) and 2 M aq. HCl (18 mL) and the mixture was stirred at room temperature for 6.5 h. The mixture was filtered over celite, methanol was removed in vacuo and the pH value of the aq. solution was adjusted to 10 with sat. aq. Na_2CO_3 solution. The aq. phase was extracted with DCM (4 × 25 mL) and the combined org. phases were dried over Na_2SO_4. Removal of the solvent afforded the amine, which was used without further purification.

The amine (200 mg, 869 µmol, 1.0 equiv) was dissolved in DCM (2 mL) and triethylamine (97 mg, 0.96 mmol, 1.1 equiv) was added. *p*-Toluenesulfonyl chloride (174 mg, 912 µmol, 1.05 equiv) in DCM (1 mL) was added dropwise and the mixture was stirred at room temperature for 19.5 h. The reaction was quenched by the addition of NH_4Cl (3 mL) and the phases were separated. The aq. phase was extracted with DCM (3 mL) and the combined organic phases were washed with sat. aq. NaCl solution (6 mL) and dried over Na_2SO_4. Purification by column chromatography (5:1 *n*-pentane/EtOAc) afforded the product as a yellow oil (226 mg, 588 µmol, 67%).

R_f = 0.36 (*n*-pentane:EtOAc, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3278, 2936, 2837, 1596, 1572, 1473, 1416, 1321, 1241, 1153, 1092, 1058, 1010, 811, 660, 548; **^{1}H NMR** (400 MHz, $CDCl_3$): δ[ppm] = 7.76–7.64 (m, 2 H), 7.36 (d, J = 8.7 Hz, 1 H), 7.30-7.26 (m, 2 H), 6.69 (d, J = 3.0 Hz,

1 H), 6.64 (dd, J = 8.7, 3.1 Hz, 1 H), 4.50 (t, J = 6.3 Hz, 1 H), 3.76 (s, 3 H), 3.30–3.14 (m, 2 H), 2.87 (t, J = 7.0 Hz, 2 H), 2.42 (s, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 159.2, 143.6, 138.2, 137.1, 133.7, 129.9, 127.2, 116.8, 114.8, 114.4, 55.6, 42.7, 36.7, 21.7; **HR-ESI-MS m/z**: calcd. $C_{16}H_{17}NO_3BrS$ $[M\text{-}H]^+$: 382.0118, found: 382.0110.

N-(2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)ethyl)-4-methylbenzenesulfonamide (216)



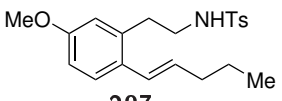
216

Nitroethyl compound **213** (330 mg, 1.20 mmol, 1.0 equiv) and zinc (1.57 g, 24.1 mmol, 20 equiv) were added to a mixture of methanol (12 mL), conc. acetic acid (4 mL) and 2 M aq. HCl (8 mL) and the mixture was stirred at room temperature for 20 h. The mixture was filtered over celite, methanol was removed in vacuo and the pH value of the aq. solution was adjusted to 10 with sat. aq. Na_2CO_3 solution. The aq. phase was extracted with DCM (4 × 10 mL) and the combined org. phases were dried over Na_2SO_4. Removal of the solvent afforded the amine, which was used without further purification.

The amine (275 mg, 1.13 mmol, 1.0 equiv) was dissolved in DCM (2.3 mL) and triethylamine (125 mg, 1.24 mmol, 1.1 equiv) was added. *p*-Toluenesulfonyl chloride (236 mg, 1.24 mmol, 1.05 equiv) in DCM (1.2 mL) was added dropwise and the mixture was stirred at room temperature for 20 h. The reaction was quenched by the addition of NH_4Cl (3 mL) and the phases were separated. The aq. phase was extracted with DCM (3 mL) and the combined organic phases were washed with sat. aq. NaCl solution (6 mL) and dried over Na_2SO_4. Purification by column chromatography (4:1 *n*-pentane/EtOAc) afforded the product as a yellow solid (321 mg, 805 µmol, 71%).

R_f = 0.14 (*n*-pentane:EtOAc, 4:1); **m.p.** = 103 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3301, 3287, 3276, 2924, 2904, 2881, 1598, 1504, 1478, 1410, 1324, 1243, 1158, 1116, 1093, 1041, 932, 814, 662, 551, 407; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.79–7.66 (m, 2 H), 7.28 (dd, J = 8.0, 0.7 Hz, 1 H), 6.93 (s, 1 H), 6.61 (s, 1 H), 5.95 (s, 2 H), 4.46 (t, J = 6.1 Hz, 1 H), 3.19 (q, J = 6.8 Hz, 2 H), 2.81 (t, J = 7.0 Hz, 2 H), 2.42 (s, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 147.5, 147.4, 143.5, 137.0, 130.1, 129.7, 127.2, 114.6, 113.0, 110.7, 101.9, 43.0, 36.4, 21.7; **HR-ESI-MS m/z**: calcd. $C_{16}H_{16}BrNO_4S$ $[M+H]^+$: 398.0056, found: 398.0046.

(*E*)-*N*-(5-Methoxy-2-(pent-1-en-1-yl)phenethyl)-4-methylbenzenesulfonamide (207g)

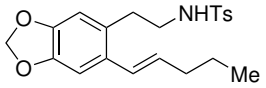


207g

Following general procedure **H**: toluenesulfonic acid amide **215** (200 mg, 520 µmol, 1.0 equiv), 1-pentenylboronic acid (65 mg, 0.57 mmol, 1.1 equiv), potassium carbonate (288 mg, 2.08 mmol, 4.0 equiv), toluene (3.75 mL), ethanol (1.5 mL), water (0.75 mL), tetrakis[triphenylphosphine]palladium(0) (60 mg, 52 µmol, 0.1 equiv); reaction time 16.5 h; eluting with *n*-pentane/EtOAc, 6:1; yellow oil; 129 mg, 346 µmol, 67%.

R_f = 0.5 (*n*-pentane:EtOAc, 2:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3279, 2957, 2929, 2871, 2836, 1606, 1494, 1463, 1324, 1254, 1155, 1092, 966, 872, 813, 661, 549, 501; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.73-7.60 (m, 2 H), 7.36-7.21 (m, 3 H), 6.72 (dd, J = 8.6 Hz, J = 2.7 Hz, 1 H), 6.56 (d, J = 2.7 Hz, 1 H), 6.39 (m, 1 H), 5.91 (dt, J = 15.5, 7.0 Hz, 1 H), 4.69 (t, J = 6.1 Hz, 1 H), 3.76 (s, 3 H), 3.15 (ddd, J = 7.3, 6.7, 5.9 Hz, 2 H), 2.81 (t, J = 7.2 Hz, 2 H), 2.41 (s, 3 H), 2.27-2.05 (m, 2 H), 1.45 (sext, J = 7.3 Hz, 2 H), 0.93 (t, J = 7.3 Hz, 3 H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ [ppm] = 158.9, 143.4, 136.0, 132.1, 130.1, 129.8, 127.8, 127.2, 126.6, 126.6, 115.3, 113.0, 55.4, 43.6, 35.4, 33.8, 22.8, 21.5, 13.8; **HR-ESI-MS m/z**: calcd. $C_{21}H_{28}NO_3S$ $[M+H]^+$: 374.1784, found: 374.1781.

(*E*)-4-Methyl-*N*-(2-(6-(pent-1-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)ethyl)benzenesulfonamide (207h)

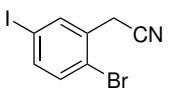


207h

Following general procedure **H**: toluenesulfonic acid amide **216** (310 mg, 778 µmol, 1.0 equiv), 1-pentenylboronic acid (98 mg, 0.86 mmol, 1.1 equiv), potassium carbonate (430 mg, 3.11 mmol, 4.0 equiv), toluene (6.25 mL), ethanol (2.5 mL), water (1.25 mL), tetrakis[triphenylphosphine]palladium(0) (90 mg, 78 µmol, 0.1 equiv); reaction time 25 h; eluting with *n*-pentane/EtOAc, 8:1; yellow solid; 143 mg, 368 µmol, 47%.

R_f = 0.29 (*n*-pentane:EtOAc, 4:1); **m.p.** = 84 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3256, 2955, 2926, 2872, 1596, 1503, 1479, 1421, 1373, 1316, 1255, 1159, 1092, 1073, 1039, 963, 939, 879, 856, 814, 665, 571, 551, 495, 469, 400; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.68 (d, J = 8.3 Hz, 2 H), 7.31–7.22 (m, 2 H), 6.87 (s, 1 H), 6.47 (s, 1 H), 6.38 (dt, J = 15.4, 1.5 Hz, 1 H), 6.05–5.73 (m, 3 H), 4.41 (t, J = 6.2 Hz, 1 H), 3.10 (td, J = 7.1, 6.1 Hz, 2 H), 2.75 (t, J = 7.1 Hz, 2 H), 2.42 (s, 3 H), 2.13 (qd, J = 7.1, 1.5 Hz, 2 H), 1.45 (sext, J = 7.4 Hz, 2 H), 0.92 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 147.0, 146.8, 143.5, 137.0, 132.3, 130.9, 129.8, 128.1, 127.2, 126.6, 109.9, 106.3, 101.1, 43.8, 35.4, 33.4, 22.8, 21.7, 13.9; **HR-ESI-MS m/z**: calcd. $C_{21}H_{26}NO_4S$ $[M+H]^+$: 388.1577, found: 388.1570.

2-(2-Bromo-5-iodophenyl)acetonitrile (221)



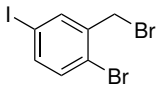
221

2-Bromo-5-iodobenzyl alcohol (1.0 g, 3.2 mmol, 1.0 equiv) was dissolved in DCM (10 mL), NEt_3 (485 mg, 4.79 mmol, 1.5 equiv) was added and the solution was cooled to 0 °C. A solution of methanesulfonyl chloride (403 mg, 3.52 mmol, 1.1 equiv) in DCM (6 mL) was added and the mixture was stirred at room temperature for 3 h. Sat. aq. $NaHCO_3$ solution (15 mL) was added, the aq. phase was extracted with DCM (3 × 15 mL), the combined org. phases were washed with H_2O (30 mL) and sat. aq. NaCl solution (30 mL) and dried over Na_2SO_4. After removal of the solvent in vacuo, the crude product was used without further purification. It was dissolved in DMF (6 mL) and added to a solution of NaCN (235 mg, 4.79 mmol, 1.5 equiv) in DMF (4 mL). The solution

was stirred at room temperature for 18.5 h, H_2O (10 mL) was added, the aq. phase was extracted with Et_2O (3 × 10 mL) and the combined org. phases were dried over Na_2SO_4. Removal of the solvent in vacuo and purification by column chromatography (5:1 *n*-pentane:DCM) afforded the product as a white solid (829 mg, 2.57 mmol, 80%).

R_f = 0.13 (*n*-pentane:DCM, 5:1); **m.p.** = 82 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2963, 2929, 2909, 2243, 1458, 1397, 1377, 1259, 1078, 1018, 878, 794, 683, 426; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.84 (d, J = 2.0 Hz, 1 H), 7.54 (dd, J = 8.5 Hz, J = 2.1 Hz, 1 H), 7.32 (d, J = 8.4 Hz, 1 H), 3.79 (s, 2 H); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ [ppm] = 139.1, 138.5, 134.7, 132.2, 123.5, 116.4, 93.0, 24.6; **HR-ESI-MS m/z**: calcd. C_8H_4BrIN [M-H]$^-$: 319.8577, found: 319.8562.

1-Bromo-2-(bromomethyl)-4-iodobenzene (224)

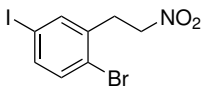


224

To a solution of 2-bromo-5-iodobenzyl alcohol (300 mg, 957 µmol, 1.0 equiv) in THF (7.0 mL), PBr_3 (112 mg, 414 µmol, 0.43 equiv) was added dropwise at 0 °C. The solution was stirred at 0 °C for 2.5 h and at room temperature for 14.5 h. Removal of the solvent in vacuo and purification by column chromatography (5:1 *n*-pentane:DCM) afforded the product as a white solid (226 mg, 601 µmol, 63%).

R_f = 0.64 (*n*-pentane:DCM, 5:1); **m.p.** = 110-113 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3068, 3045, 1901, 1886, 1762, 1630, 1547, 1460, 1431, 1373, 1273, 1213, 1074, 1024, 886, 872, 814, 718, 677, 615, 566, 501, 444, 430; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.77 (d, J = 2.2 Hz, 1 H), 7.47 (dd, J = 8.4 Hz, J = 2.2 Hz, 1 H), 7.29 (d, J = 8.4 Hz, 1 H), 4.50 (s, 2 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 139.9, 139.2, 139.0, 134.9, 124.3, 92.6, 32.2; **HR-EI-MS m/z**: calcd. $C_7H_5Br_2I$ [M]$^+$: 373.7803, found: 373.7810.

1-Bromo-4-iodo-2-(2-nitroethyl)benzene (223)



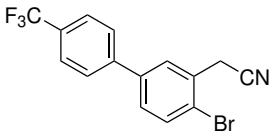
223

Copper(I)bromide (76 mg, 0.53 mmol, 0.2 equiv), *N*-((2*Z*,4*E*)-4-((2,6-dimethylphenyl)imino)pent-2-en-2-yl)-2,6-dimethylaniline (163 mg, 532 µmol, 0.2 equiv) and sodium *tert*-butoxide (307 mg, 3.19 mmol, 1.2 equiv) were dissolved in 1,4-dioxane (16 mL). Nitromethane (1.10 mL, 1.22 g, 20.0 mmol, 7.5 equiv) and 1-bromo-2-(bromomethyl)-4-iodobenzene (1.0 g, 2.7 mmol, 1.0 equiv) were added and the solution was heated to 60 °C for 18.5 h. Sat. aq. NH_4Cl (16 mL) was added, the aq. phase was extracted with Et_2O (16 mL), the combined org. phases were washed with water (16 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo, purification by column chromatography (5:1 *n*-pentane:DCM) and afforded the product as a light yellow solid (279 mg, 0.784 mmol, 30%).

R_f = 0.11 (*n*-pentane:DCM, 5:1); **m.p.** = 65 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 1548, 1535, 1456, 1432, 1374, 1323, 1274, 1215, 1173, 1131, 1080, 1041, 1022, 973, 950, 888, 862, 807, 717, 605, 526, 480,

454; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.59 (d, J = 2.2 Hz, 1 H), 7.47 (dd, J = 8.4 Hz, J = 2.2 Hz, 1 H), 7.29 (d, J = 8.4 Hz, 1 H), 4.63 (t, J = 7.3 Hz, 2 H), 3.39 (t, J = 7.3 Hz, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 139.9, 138.5, 137.4, 134.9, 124.3, 93.0, 74.0, 33.5; **HR-ESI-MS m/z**: calcd. $C_8H_7BrINO_2$ $[M]^+$: 354.8705, found: 354.8710.

2-(4-Bromo-4′-(trifluoromethyl)-[1,1′-biphenyl]-3-yl)acetonitrile (229)

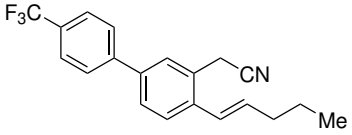


229

Following general procedure **H**: 2-(2-bromo-5-iodophenyl)acetonitrile (300 mg, 932 µmol, 1.0 equiv), 4-(trifluoromethyl)phenylboronic acid (195 mg, 1.03 mmol, 1.1 equiv), potassium carbonate (515 mg, 3.73 mmol, 4.0 equiv), toluene (7.5 mL), ethanol (3.0 mL), water (1.5 mL), tetrakis[triphenylphosphine]palladium(0) (108 mg, 93.2 µmol, 0.1 equiv); reaction time 65 h; eluting with *n*-pentane/EtOAc, 75:1; white solid; 113 mg, 332 µmol, 36%.

R_f = 0.07 (*n*-pentane:EtOAc, 75:1); **m.p.** = 105 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2934, 2910, 2248, 1616, 1472, 1398, 1388, 1322, 1164, 1103, 1072, 1014, 956, 928, 849, 817, 745, 715, 669, 607, 518, 442, 410; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.80-7.60 (m, 6 H), 7.44 (dd, J = 8.3, 2.3 Hz, 1 H), 3.92 (s, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 142.7, 140.1, 133.7, 132.3, 130.7, 130.3 (q, $^2J_{CF}$ = 32.7 Hz), 128.6, 128.4, 127.4, 126.1 (q, $^3J_{CF}$ = 3.7 Hz), 124.1 (q, $^1J_{CF}$ = 271.6), 123.6, 116.8, 25.2; **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$): δ [ppm] = −62.6; **HR-EI-MS m/z**: calcd. $C_{15}H_9BrF_3N$ $[M]^+$: 338.9870, found: 338.9866.

(*E*)-2-(4-(Pent-1-en-1-yl)-4′-(trifluoromethyl)-[1,1′-biphenyl]-3-yl)acetonitrile (232)



232

Following general procedure **H**: 2-(4-bromo-4′-(trifluoromethyl)-[1,1′-biphenyl]-3-yl)acetonitrile (100 mg, 294 µmol, 1.0 equiv), 1-pentenylboronic acid (61 mg, 0.32 mmol, 1.1 equiv), potassium carbonate (163 mg, 1.18 mmol, 4.0 equiv), toluene (2.5 mL), ethanol (1.0 mL), water (0.5 mL), tetrakis[triphenylphosphine]palladium(0) (34 mg, 29 µmol, 0.1 equiv); reaction time 16.5 h; eluting with *n*-pentane/DCM, 5:1; white solid; 87 mg, 0.26 mmol, 89%.

R_f = 0.09 (*n*-pentane:DCM, 5:1); **m.p.** = 75 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960, 2931, 2866, 2838, 2246, 1614, 1493, 1427, 1395, 1319, 1170, 1128, 1112, 1070, 1015, 968, 893, 836, 812, 741, 707, 601; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 7.70 (s, 4 H), 7.60 (d, J = 1.3 Hz, 1 H), 7.56 (d, J = 8.0 Hz, 1 H), 7.53 (dd, J = 8.1, 1.8 Hz, 1 H), 6.50 (dt, J = 15.4, 1.5 Hz, 1 H), 6.23 (dt, J = 15.5, 7.0 Hz, 1 H), 3.82 (s, 2 H), 2.27 (qd, J = 7.1, 1.5 Hz, 2 H), 1.55 (sext, J = 7.4 Hz, 2 H), 0.99 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 143.6, 139.0, 137.1, 136.4, 129.8 (q, $^2J_{CF}$ = 32.4 Hz), 127.7, 127.6, 127.5, 127.4, 127.3, 126.0 (q, $^3J_{CF}$ = 3.8 Hz),

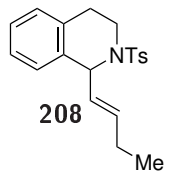
125.3, 124.4 (q, $^{1}J_{CF}$ = 271.9 Hz), 117.7, 35.6, 22.5, 22.1, 13.9; **HR-ESI-MS m/z**: calcd. $C_{20}H_{18}NF_3Na$ $[M+Na]^+$: 352.1284, found: 352.1273.

5.8.2 Synthesis of tetrahydroisoquinolines 209

General procedure K: Synthesis of tetrahydroisoquinolines

Tosyl amide **207** (1.0 equiv), NFSI (1.05 equiv), diphenyl diselenide (10 M in toluene, 0.05 equiv) and activated molecular sieves 4 Å (spatula tip) are dissolved in toluene (0.1 M) and stirred at room temperature until completion, detected by NMR and TLC. The solvent is removed in vacuo and the residue purified on silica gel to yield the title compound.

(*E*)-1-(But-1-en-1-yl)-2-tosyl-1,2,3,4-tetrahydroisoquinoline (208)

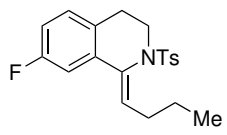


208

Tosyl amide **207a** (86 mg, 0.25 mmol, 1.0 equiv), diphenyl diselenide (7.8 mg, 25 µmol, 0.1 equiv) and *p*-MeO-TPT (**95**) (6.0 mg, 12.5 µmol, 0.05 equiv) were dissolved in MeCN (2.5 mL) and stirred under air and irradiation with blue light at room temperature for 4 h. Removal of the solvent in vacuo, followed by column chromatography (*n*-pentane/EtOAc, 7:1) afforded the product as a yellow oil (12 mg, 34 µmol, 13%).

$\mathbf{R_f}$ = 0.43 (*n*-pentane:EtOAc, 7:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2961, 2928, 2872, 1598, 1493, 1453, 1334, 1275, 1158, 1091, 1015, 964, 923, 813, 762, 713, 663, 569, 545; **^{1}H NMR** (600 MHz, C_6D_6): δ [ppm] = 7.78–7.65 (m, 2 H), 6.96–6.76 (m, 3 H), 6.72–6.62 (m, 3 H), 5.75 (d, J = 3.6 Hz, 1 H), 5.47-5.45 (m, 2 H), 3.85 (dddd, J = 13.4, 6.3, 2.4, 1.1 Hz, 1 H), 3.13 (ddd, J = 13.4, 11.6, 4.3 Hz, 1 H), 2.57 (ddd, J = 17.3, 11.6, 6.3 Hz, 1 H), 2.14 (ddd, J = 16.4, 4.3, 2.3 Hz, 1 H), 1.82 (s, 3 H), 1.80–1.63 (m, 1 H), 0.72 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (125 MHz, C_6D_6): δ [ppm] = 142.4, 139.5, 135.6, 135.4, 133.9, 129.4, 129.2, 129.1, 128.4, 127.7, 126.9, 126.2, 58.3, 39.6, 28.2, 25.6, 21.2, 13.4; **HR-ESI-MS m/z**: calcd. $C_{20}H_{24}NO_2S$ $[M+H]^+$: 342.1522, found: 342.1528.

(*Z*)-1-Butylidene-7-fluoro-2-tosyl-1,2,3,4-tetrahydroisoquinoline (209c)



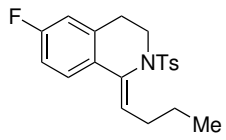
209c

Following general procedure **K**: tosyl amide **207c** (30 mg, 83 µmol, 1.0 equiv), NFSI (28 mg, 0.87 mmol, 1.05 equiv), diphenyl diselenide (10 M in toluene, 0.13 mL, 1.3 mg, 4.2 µmol, 0.05 equiv), activated molecular sieves 4 Å (spatula tip), toluene (0.8 mL); reaction time 17 h; eluting with *n*-pentane/EtOAc, 20:1; yellow oil; 13 mg, 36 µmol, 44%.

$\mathbf{R_f}$ = 0.29 (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958, 2929, 2871, 1613, 1597, 1583, 1491, 1455, 1429, 1346, 1268, 1184, 1159, 1133, 1090, 1063, 1020, 934, 889, 866, 811, 777, 722, 708, 685, 657, 573, 544, 502, 487, 470; **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 7.52 (d, J = 8.2 Hz,

2 H), 7.10 (dd, J = 10.1, 2.6 Hz, 1 H), 7.00 (d, J = 8.1 Hz, 2 H), 6.71 (td, J = 8.3, 2.6 Hz, 1 H), 6.66 (dd, J = 8.5, 5.8 Hz, 1 H), 6.21 (t, J = 7.3 Hz, 1 H), 3.80 (s, 2 H), 2.55-2.40 (m, 4 H), 2.27 (s, 3 H), 1.49 (q, J = 7.4 Hz, 2 H), 0.96 (t, J = 7.3 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 161.2 (d, $^{1}J_{CF}$ = 243.6 Hz), 143.4, 137.3, 134.7 (d, $^{3}J_{CF}$ = 7.1 Hz), 132.6, 132.5 (d, $^{4}J_{CF}$ = 3.0 Hz), 130.2 (d, $^{3}J_{CF}$ = 8.0 Hz), 129.0, 128.0 (d, $^{4}J_{CF}$ = 2.8 Hz), 127.6, 114.4 (d, $^{2}J_{CF}$ = 21.7 Hz), 110.4 (d, $^{2}J_{CF}$ = 22.5 Hz), 46.0, 31.2, 25.3, 22.5, 21.6, 14.2; **HR-ESI-MS m/z**: calcd. $C_{20}H_{23}FNO_2S$ $[M+H]^+$: 350.1428, found: 360.1428.

(*Z*)-1-Butylidene-6-fluoro-2-tosyl-1,2,3,4-tetrahydroisoquinoline (209d)

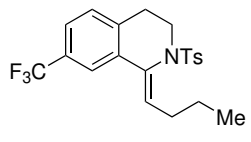


209d

Following general procedure **K**: tosyl amide **207d** (50 mg, 0.14 mmol, 1.0 equiv), NFSI (46 mg, 0.15 mmol, 1.05 equiv), diphenyl diselenide (10 M in toluene, 0.2 mL, 2.0 mg, 6.9 µmol, 0.05 equiv), activated molecular sieves 4 Å (spatula tip), toluene (1.4 mL); reaction time 16 h; eluting with *n*-pentane/EtOAc, 10:1; yellow oil; 10 mg, 28 µmol, 21%.

R_f = 0.43 (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958, 2929, 2871, 1611, 1597, 1492, 1454, 1345, 1305, 1247, 1227, 1160, 1107, 1089, 1063, 1019, 967, 888, 863, 813, 708, 688, 663, 636, 608, 587, 567, 547, 507; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.55-7.46 (m, 2 H), 7.38 (dd, J = 8.7, 5.6 Hz, 1 H), 7.04-6.96 (m, 2 H), 6.80 (td, J = 8.6, 2.7 Hz, 1 H), 6.41 (dd, J = 9.3, 2.6 Hz, 1 H), 6.15 (t, J = 7.3 Hz, 1 H), 3.82 (s, 2 H), 2.47 (t, J = 6.9 Hz, 4 H), 2.29 (s, 3 H), 1.49 (q, J = 7.4 Hz, 2 H), 0.96 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 161.9 (d, $^{1}J_{CF}$ = 247.1 Hz), 143.5, 137.5, 134.7 (d, $^{3}J_{CF}$ = 7.7 Hz), 132.5, 131.4 (d, $^{4}J_{CF}$ = 1.7 Hz), 129.5 (d, $^{4}J_{CF}$ = 3.1 Hz), 129.1, 127.7, 126.0 (d, $^{3}J_{CF}$ = 8.2 Hz), 114.9 (d, $^{2}J_{CF}$ = 21.1 Hz), 113.8 (d, $^{2}J_{CF}$ = 21.9 Hz), 45.6, 31.1, 25.2, 22.5, 21.6, 14.1; **HR-ESI-MS m/z**: calcd. $C_{20}H_{23}FNO_2S$ $[M+H]^+$: 360.1428, found: 360.1426.

(*Z*)-1-Butylidene-2-tosyl-7-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline (209e)



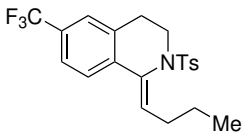
209e

Following general procedure **K**: tosyl amide **207e** (50 mg, 0.12 mmol, 1.0 equiv), NFSI (40 mg, 1.3 mmol, 1.05 equiv), diphenyl diselenide (10 M in toluene, 0.20 mL, 1.9 mg, 6.1 µmol, 0.05 equiv), activated molecular sieves 4 Å (spatula tip), toluene (0.8 mL); reaction time 16 h; eluting with *n*-pentane/EtOAc, 15:1; yellow oil; 13 mg, 32 µmol, 26%.

R_f = 0.19 (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2959, 2931, 2874, 1722, 1692, 1652, 1620, 1597, 1496, 1457, 1430, 1331, 1310, 1285, 1241, 1159, 1119, 1080, 893, 813, 678; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.59 (d, J = 1.8 Hz, 1 H), 7.51 (d, J = 8.3 Hz, 2 H), 7.23 (m, 1 H), 7.09-6.91 (m, 2 H), 6.84 (d, J = 8.0 Hz, 1 H), 6.29 (t, J = 7.3 Hz, 1 H), 3.86 (s, 2 H), 2.59 (t, J = 6.7 Hz, 2 H), 2.51 (q, J = 7.3 Hz, 2 H), 2.25 (s, 3 H), 1.51 (q, J = 7.4 Hz, 2 H), 0.97 (t, J = 7.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 143.7, 137.0, 136.5, 134.1,

133.4, 132.4, 129.3, 129.1, 128.9 (q, $^{2}J_{CF}$ = 32.4 Hz), 127.8, 124.2 (q, $^{1}J_{CF}$ = 272.1 Hz), 123.5 (q, $^{3}J_{CF}$ = 3.7 Hz), 121.3 (q, $^{3}J_{CF}$ = 4.0 Hz), 45.8, 31.1, 26.0, 22.4, 21.4, 14.1; **HR-ESI-MS m/z**: calcd. $C_{21}H_{23}NO_2SF_3$ $[M+H]^+$: 410.1396, found: 410.1395 .

(*Z*)-1-Butylidene-2-tosyl-6-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline (209f)

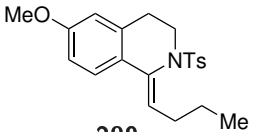


209f

Following general procedure **K**: tosyl amide **207f** (20 mg, 49 µmol, 1.0 equiv), NFSI (16 mg, 51 µmol, 1.05 equiv), diphenyl diselenide (10 M in toluene, 76 µL, 0.76 mg, 2.4 µmol, 0.05 equiv), activated molecular sieves 4 Å (spatula tip), toluene (0.5 mL); reaction time 16 h; eluting with *n*-pentane/EtOAc, 15:1; yellow oil; 4.7 mg, 12 µmol, 23%.

R_f = 0.36 (*n*-pentane:EtOAc, 15:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.64 (d, J = 8.0 Hz, 1 H), 7.60-7.42 (m, 2 H), 7.32 (d, J = 8.2 Hz, 1 H), 7.17 (t, J = 8.3 Hz, 1 H), 7.07-6.85 (m, 2 H), 6.34 (t, J = 7.3 Hz, 1 H), 3.87 (s, 2 H), 2.54 (dt, J = 15.1, 7.1 Hz, 4 H), 2.25 (s, 3 H), 1.79-1.39 (m, 2 H), 0.97 (t, J = 7.4 Hz, 3 H); **HR-ESI-MS m/z**: calcd. $C_{21}H_{22}NO_2SF_3Na$ $[M+Na]^+$: 432.1216, found: 432.1215.

(*Z*)-1-Butylidene-6-methoxy-2-tosyl-1,2,3,4-tetrahydroisoquinoline (209g)

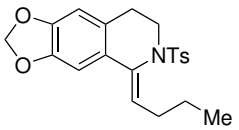


209g

Following general procedure **K**: tosyl amide **207g** (50 mg, 0.13 mmol, 1.0 equiv), NFSI (44 mg, 0.14 mmol, 1.05 equiv), diphenyl diselenide (10 M in toluene, 0.2 mL, 2.0 mg, 6.7 µmol, 0.05 equiv), activated molecular sieves 4 Å (spatula tip), toluene (1.4 mL); reaction time 16 h; eluting with *n*-pentane/EtOAc, 6:1; yellow oil; 23 mg, 62 µmol, 48%.

R_f = 0.71 (*n*-pentane:EtOAc, 6:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.56-7.46 (m, 2 H), 7.35 (d, J = 8.7 Hz, 1 H), 7.06-6.87 (m, 2 H), 6.67 (dd, J = 8.7, 2.7 Hz, 1 H), 6.21 (d, J = 2.7 Hz, 1 H), 6.10 (t, J = 7.3 Hz, 1 H), 3.90-3.73 (m, 2 H), 3.70 (d, J = 0.7 Hz, 3 H), 2.45 (q, J = 6.6 Hz, 4 H), 2.28 (s, 3 H), 1.48 (q, J = 7.4 Hz, 2 H), 0.95 (t, J = 7.4 Hz, 3 H); **HR-ESI-MS m/z**: calcd. $C_{21}H_{26}NO_3S$ $[M+H]^+$: 372.1628, found: 372.1625.

(*Z*)-5-Butylidene-6-tosyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-*g*]isoquinoline (209h)



209h

Following general procedure **K**: tosyl amide **207h** (50 mg, 0.13 mmol, 1.0 equiv), NFSI (43 mg, 0.14 mmol, 1.05 equiv), diphenyl diselenide (10 M in toluene, 0.20 mL, 2.0 mg, 6.5 µmol, 0.05 equiv), activated molecular sieves 4 Å (spatula tip), toluene (0.8 mL); reaction time 21 h; eluting with *n*-pentane/EtOAc, 20:1; yellow oil; 28 mg, 74 µmol, 57%.

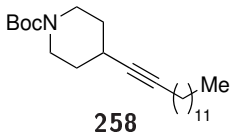
R_f = 0.50 (*n*-pentane:EtOAc, 5:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2956, 2923, 2872, 1502, 1483, 1382, 1346, 1222, 1159, 1091, 1039, 964, 939, 862, 841, 810, 785, 707, 682, 640, 603, 572, 552, 421; **^{1}H**

NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.64-7.38 (m, 2 H), 7.11-6.93 (m, 2 H), 6.88 (s, 1 H), 6.15 (s, 1 H), 6.04 (t, J = 7.3 Hz, 1 H), 5.87 (s, 2 H), 4.00-3.52 (m, 2 H), 2.46 (q, J = 7.4 Hz, 2 H), 2.40-2.32 (m, 2 H), 2.30 (s, 3 H), 1.47 (sext, J = 7.3 Hz, 2 H), 0.94 (t, J = 7.3 Hz, 3 H).

5.9 Synthesis of allenylamides

5.9.1 Synthesis of alkynes 242

tert-Butyl 4-(tetradec-1-yn-1-yl)piperidine-1-carboxylate (258)

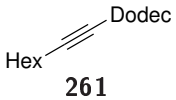


258

1-Boc-4-ethynylpiperidine (500 mg, 2.39 mmol, 1.0 equiv) was dissolved in dry THF (5 mL) and cooled to −40 °C. *n*-BuLi (2.5 M in hexane; 0.96 mL, 2.39 mmol, 1.0 equiv) was added dropwise and the solution was allowed to warm to room temperature. CuCl (7.0 mg, 72 µmol, 0.03 equiv), LiCl (6.0 mg, 0.14 mmol, 0.06 equiv) and dodecyl bromide (595 mg, 2.39 mmol, 1.0 equiv) were added and the mixture was stirred at RT for 22 h and at 50 °C for 13.5 h. The reaction was quenched by addition of aq. HCl (1 M, 3 mL), the solvent was removed in vacuo, *n*-pentane (5 mL) was added and the org. phase washed with aq. HCl (1 M, 5 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo and purification on silica gel (*n*-pentane:EtOAc, 20:1) yielded the title compound as a yellow oil (49 mg, 0.13 mmol, 5%).

R_f = 0.57 (*n*-pentane:EtOAc, 20:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2923, 2853, 1696, 1465, 1417, 1364, 1317, 1297, 1271, 1230, 1168, 1119, 1099, 1014, 933, 869, 810, 768, 722; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 3.66 (ddd, J = 13.3, 6.9, 3.9 Hz, 2 H), 3.18 (ddd, J = 13.4, 8.3, 3.4 Hz, 2 H), 2.53 (dddquint, J = 8.1, 6.1, 4.0, 2.0 Hz, 1 H), 2.14 (td, J = 7.1, 2.2 Hz, 2 H), 1.73 (ddt, J = 13.9, 7.2, 3.8 Hz, 2 H), 1.58-1.41 (m, 13 H), 1.41-1.17 (m, 18 H), 1.00-0.69 (m, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 154.9, 82.3, 82.0, 79.5, 42.4, 32.1, 32.1, 29.9, 29.9, 29.9, 29.8, 29.6, 29.4, 29.3, 29.1, 28.7, 27.3, 22.9, 18.9, 14.4; **HR-ESI-MS m/z**: calcd. $C_{24}H_{43}NO_2Na$ $[M+Na]^+$: 400.3186, found: 400.3186.

Icos-7-yne (261)



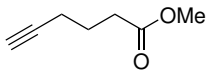
261

1,3-Bis(1-adamantyl)imidazolium chloride (19 mg, 50 µmol, 0.05 equiv), CuI (14 mg, 75 µmol, 0.075 equiv), allylpalladium(II) chloride dimer (9.0 mg, 25 µmol, 0.025 equiv) and $CsCO_3$ (456 mg, 1.40 mmol, 1.4 equiv) were dissolved in a mixture of dry Et_2O and dry DMF (2:1 v/v, 2 mL), 1-octyne (143 mg, 1.30 mmol, 1.3 equiv) and dodecyl bromide (249 mg, 1.0 mmol, 1.0 equiv) were added and the mixture was stirred at 45 °C for 15 h. Removal of the solvent in vacuo and purification on silica gel (*n*-pentane) afforded the title compound as a yellow oil (88 mg, 0.32 mmol, 32%).

R_f = 0.57 (*n*-pentane); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2921, 2853, 1465, 1378, 1332, 722; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 2.19-2.10 (m, 4 H), 1.56-1.20 (m, 28 H), 0.98-0.82 (m, 6 H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ [ppm] = 80.40, 80.39, 32.1, 31.6, 29.8, 29.8, 29.8, 29.7, 29.5, 29.3, 29.3, 29.0, 28.7, 22.9, 22.7, 18.9, 14.3, 14.2; **HR-EI-MS m/z**: calcd. $C_{20}H_{38}$ $[M]^+$: 278.2973, found: 278.2970.

Methyl hex-5-ynoate (264)

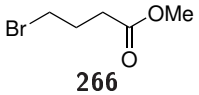


264

5-Hexynoic acid (561 mg, 5.0 mmol, 1.0 equiv), PTSA (43 mg, 0.25 mmol, 0.05 equiv), MeOH (0.41 mL, 320 mg, 10 mmol, 2.0 equiv) and Na_2SO_4 (300 mg) were added to toluene (5 mL) and the mixture was stirred at 120 °C for 4 h. The mixture was allowed to cool down, EtOAc (5 mL) was added, the org. phase was washed with sat. aq. $NaHCO_3$ (3 × 10 mL) and sat. aq. NaCl (10 mL). The comb. aq. phases were extracted with EtOAc (30 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo afforded the product as a brown liquid (491 mg, 3.89 mmol, 78%).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3293, 2952, 2362, 1732, 1436, 1369, 1317, 1215, 1157, 1058, 1015, 993, 898, 867, 773; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 3.68 (s, 3 H), 2.46 (t, J = 7.4 Hz, 2 H), 2.27 (td, J = 6.9, 2.6 Hz, 2 H), 1.97 (t, J = 2.7 Hz, 1 H), 1.85 (quintd, J = 7.2, 0.5 Hz, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 173.6, 83.4, 69.2, 51.7, 32.8, 23.8, 18.0; **HR-ESI-MS m/z**: calcd. $C_7H_{11}O_2$ $[M+H]^+$: 127.0754, found: 127.0745.

Methyl 4-bromobutanoate (266)

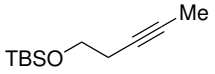


266

4-Bromobutyric acid (835 mg, 5.0 mmol, 1.0 equiv), PTSA (43 mg, 0.25 mmol, 0.05 equiv), MeOH (0.41 mL, 320 mg, 10 mmol, 2.0 equiv) and Na_2SO_4 (300 mg) were added to toluene (5 mL) and the mixture was stirred at 120 °C for 2.5 h. The mixture was allowed to cool down, EtOAc (5 mL) was added, the org. phase was washed with sat. aq. $NaHCO_3$ (3 × 10 mL) and sat. aq. NaCl (10 mL). The comb. aq. phases were extracted with EtOAc (30 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo afforded the product as a brown liquid (718 mg, 3.96 mmol, 79%).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2952, 1732, 1436, 1366, 1312, 1251, 1205, 1171, 1130, 1061, 1026, 993, 874, 779; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 3.69 (s, 3 H), 3.47 (t, J = 6.4 Hz, 2 H), 2.51 (t, J = 7.2 Hz, 2 H), 2.26-1.98 (m, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 173.1, 51.9, 32.8, 32.4, 27.9; **HR-EI-MS m/z**: calcd. $C_5H_9BrO_2$ $[M]^+$: 179.9786, found: 179.9777.

tert-Butyldimethyl(pent-3-yn-1-yloxy)silane (242b)



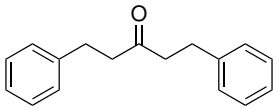
242b

3-Pentyne-1-ol (2.52 g, 30.0 mmol, 1.0 equiv) was dissolved in dry DCM (25 mL), TBSCl (4.97 g, 33.0 mmol, 1.1 equiv) and imidazole (2.45 g, 36.0 mmol, 1.2 equiv) were added subsequently and the solution was stirred at RT for 18 h. The reaction mixture was washed with sat. aq. NaCl (2 × 25 mL), the comb. aq. phases were extracted with DCM (2 × 25 mL) and the comb. org.

phases were dried over Na_2SO_4. Removal of the solvent in vacuo and purification on silica gel (*n*-pentane:EtOAc, 9:1) afforded the product as a colorless oil (5.72 g, 28.8 mmol, 96%).

R_f = 0.86 (*n*-pentane:EtOAc, 9:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954, 2928, 2857, 1471, 1387, 1362, 1335, 1254, 1145, 1098, 1058, 1006, 938, 913, 833, 773, 716, 661; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 3.69 (t, J = 7.3 Hz, 2 H), 2.34 (tq, J = 7.3, 2.5 Hz, 2 H), 1.77 (t, J = 2.5 Hz, 3 H), 0.90 (s, 9 H), 0.07 (s, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 76.8, 76.2, 62.5, 26.1, 23.4, 18.6, 3.7, −5.0; **HR-ESI-MS m/z**: calcd. $C_{11}H_{23}OSi$ $[M+H]^+$: 199.1513, found: 199.1514.

1,5-Diphenylpentan-3-one (275)



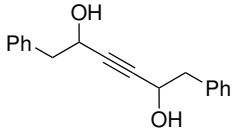
275

Styrene (1.04 g, 10.0 mmol, 1.0 equiv), freshly distilled formic acid (1.38 g, 30.0 mmol, 3.0 equiv) and freshly distilled acetic acid anhydride (1.53 g, 15.0 mmol, 1.5 equiv) were dissolved in dry MeCN (0.5 mL) and the solution was degassed (freeze-pump-thaw, 3 ×). Palladium(II) trifluoroacetate (166 mg, 500 µmol, 0.05 equiv) and 1,3-bis(diphenylphosphino)propane (412 mg, 1.0 mmol, 0.1 equiv) were added and the mixture was stirred at 90 °C for 18.5 h. Removal of the solvent in vacuo and purification on silica gel (*n*-pentane:EtOAc, 50:1) afforded the product as a yellow oil (492 mg, 2.06 mmol, 41%).[204]

Alternative procedure: 1,5,-diphenylpenta-1,4-dien-3-one (2.34 g, 10.0 mmol, 1.0 equiv), bis(pinacolato)diboron (10.1 g, 40.0 mmol, 4.0 equiv), CuBr (143 mg, 1.00 mmol, 0.1 equiv) and Cs_2CO_3 (9.8 g, 30 mmol, 3.0 equiv) were dissolved in a mixture of THF (40 mL) and toluene (200 mL) and the mixture was stirred at 90 °C under air for 19.5 h before being allowed to cool to RT. Filtration over celite and purification on silica gel (*n*-pentane:EtOAc, 20:1) afforded the product as a yellow oil (237 mg, 1.0 mmol, 10%).[242]

R_f = 0.29 (*n*-pentane:EtOAc, 50:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3083, 3060, 3026, 2925, 2896, 2860, 1711, 1603, 1495, 1452, 1405, 1368, 1179, 1143, 1092, 1076, 1030, 979, 909, 857, 746, 696; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.35-7.24 (m, 4 H), 7.24-7.11 (m, 6 H), 2.89 (t, J = 7.6 Hz, 4 H), 2.80-2.65 (m, 4 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 209.2, 141.1, 128.6, 128.4, 126.2, 44.6, 29.9; **HR-ESI-MS m/z**: calcd. $C_{17}H_{19}O$ $[M+H]^+$: 239.1430, found: 239.1435.

1,6-Diphenylhex-3-yne-2,5-diol (280)



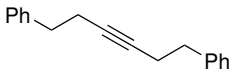
280

At RT, a solution of ethinylmagnesium bromide (0.5 M in THF; 3.3 mL, 3.0 mmol, 1.0 equiv) was added dropwise to a solution of ethylmagnesium bromide (0.9 M in THF; 6.0 mL, 3.0 mmol, 1.0 equiv) and the mixture was stirred at 65 °C for 2 h before being allowed to cool down to RT. A solution of phenylacetaldehyde (0.79 g, 6.6 mmol, 2.2 equiv) in dry THF (15 mL)

was added dropwise and the solution was stirred at RT for 44 h. The reaction was quenched by addition of sat. aq. NH_4Cl (15 mL), the aq. phase was extracted with Et_2O (2 × 15 mL), the comb. org. phases were washed with sat. aq. $NaHCO_3$ and dried over Na_2SO_4. Removal of the solvent in vacuo and purification on silica gel (*n*-pentane:EtOAc, 4:1) afforded the product as a white solid (283 mg, 1.06 mmol, 35%).

R_f = 0.50 (*n*-pentane:EtOAc, 4:1); **m.p.** = 80.1 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3312, 3060, 3028, 2923, 1708, 1603, 1495, 1453, 1335, 1260, 1123, 1077, 1029, 909, 854, 826, 734, 696; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.34-7.26 (m, 6 H), 7.24-7.17 (m, 4 H), 4.68-4.48 (m, 2 H), 2.97 (dd, J = 6.4, 1.5 Hz, 4 H), 1.91 (s, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 136.5, 136.5, 129.9, 128.6, 127.1, 86.3, 63.2, 63.2, 44.0, 44.0; **HR-ESI-MS m/z**: calcd. $C_{18}H_{18}O_2Na$ $[M+Na]^+$: 289.1199, found: 289.1204.

1,6-Diphenylhex-3-yne (242d)



242d

Diol **280** (100 mg, 375 µmol, 1.0 equiv) was dissolved in dry DCM (1.6 mL), $Co_2(CO)_8$ (129 mg, 375 µmol, 1.0 equiv) was added portionwise and the mixture was stirred at RT for 16 h. It was cooled to 0 °C, $BH_3 \cdot SMe_2$ (120 mg, 1.58 mmol, 4.2 equiv) was added dropwise, then TFA (0.75 mL) was added dropwise. The mixture was stirred at 0 °C for 30 min, poured into ice water and stirred for 15 min. The phases were separated, the org. phase was washed with H_2O (2 mL) and $Fe(NO_3) \cdot 9\,H_2O$ (576 mg, 1.43 mmol, 3.8 equiv) was added portionwise while stirring the mixture vigorously. After 4 h, the org. phase was decanted, the solvent removed under vacuum and the residue was purified on silica gel (*n*-pentane:EtOAc, 50:1). The product was afforded as a yellow oil (47 mg, 0.20 mmol, 54%).

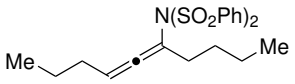
R_f = 0.15 (*n*-pentane:EtOAc, 50:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3085, 3061, 3026, 2925, 2858, 1738, 1603, 1495, 1453, 1430, 1341, 1219, 1154, 1076, 1030, 906, 745, 695; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.35-7.27 (m, 4 H), 7.25-7.18 (m, 6 H), 2.80 (t, J = 7.5 Hz, 4 H), 2.60-2.30 (m, 4 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 141.1, 128.6, 128.4, 126.3, 80.4, 35.6, 21.1; **EI-MS m/z**: calcd. $C_{18}H_{18}$ $[M]^+$: 234.1, found: 234.1.

5.9.2 Synthesis of imidoallenes 253

General Procedure L: allenylation

Alkyne **242** (1.00 mmol, 1.0 equiv), Li_2CO_3 (74 mg, 1.0 mmol, 1.0 equiv), $(2\text{-anisyl})_2Se_2$ (9.0 mg, 25 µmol, 0.025 equiv) and MS powder (4 Å, 30 mg) are dissolved in dry toluene (4 mL) and heated to 100 °C. NFSI (378 mg, 1.20 mmol, 1.2 equiv) is dissolved in dry toluene (6 mL) and added over the course of 3.5 h to the heated mixture using a syringe pump (1.7 mL/h). The reaction is stirred at 100 °C until complete conversion of the alkyne is determined by NMR or TLC. After removal of the solvent, the product is afforded *via* column chromatography.

N-(Deca-5,6-dien-5-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (253a)

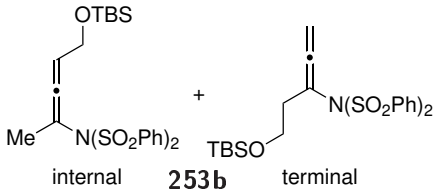


253a

Following general procedure **L**: 5-decyne **242a** (138 mg, 1.00 mmol, 1.0 equiv); reaction time 28 h; eluting with *n*-pentane:EtOAc, 10:1; yield: 161 mg, 371 µmol, 37%, yellow oil; ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard: 60%.

$\mathbf{R_f} = 0.43$ (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3066, 2957, 2930, 2871, 1585, 1478, 1448, 1407, 1372, 1356, 1312, 1291, 1254, 1165, 1121, 1084, 1024, 1000, 937, 894, 782, 752, 718, 684; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.00 (d, J = 7.7 Hz, 4 H), 7.63 (ddt, J = 8.3, 6.6, 1.3 Hz, 2 H), 7.58-7.45 (m, 4 H), 5.02 (tt, J = 7.4, 3.9 Hz, 1 H), 2.34-2.22 (m, 2 H), 1.86-1.74 (m, 2 H), 1.44-1.12 (m, 6 H), 0.95-0.85 (m, 3 H), 0.81 (t, J = 7.3 Hz, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 206.0, 133.7, 128.9, 128.6, 106.8, 99.0, 33.4, 30.6, 29.1, 22.4, 22.2, 14.2, 13.8; **HR-ESI-MS m/z**: calcd. $C_{22}H_{28}NO_4S_2$ [M+H]$^+$: 434.1454, found: 434.1447.

N-(5-((*tert*-Butyldimethylsilyl)oxy)penta-2,3-dien-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide and *N*-(5-((*tert*-butyldimethylsilyl)oxy)penta-1,2-dien-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (253b)



253b

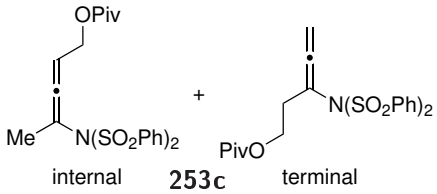
Following general procedure **L**: alkyne **242b** (198 mg, 1.00 mmol, 1.0 equiv), additional triphenylphosphine-selenide (17 mg, 50 µmol, 0.05 equiv); reaction time 5.5 h; eluting with *n*-pentane:Et_2O, 15:1; yield: 184 mg, 372 µmol, 37% (mixture of internal and terminal allene 1.7:1), white solid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 31% (internal allene), 18% (terminal allene).

Internal allene: $\mathbf{R_f} = 0.14$ (*n*-pentane:Et_2O, 15:1); **m.p.** = 95.2 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2952, 2927, 2887, 2854, 1471, 1447, 1400, 1363, 1360, 1309, 1294, 1255, 1167, 1151, 1085, 1051, 1002, 973, 902, 875, 835, 774, 754, 719, 687; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.12-7.75 (m, 4 H), 7.73-7.59 (m, 2 H), 7.59-7.45 (m, 4 H), 5.12 (tq, J = 6.6, 6.0, 3.1 Hz, 1 H), 3.98 (dd, J = 12.9, 6.7 Hz, 1 H), 3.91 (dd, J = 12.9, 5.9 Hz, 1 H), 2.02 (d, J = 3.0 Hz, 3 H), 0.87 (s, 9 H), 0.03 (s, 3 H), 0.02 (s, 3 H).; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 205.6, 139.6, 133.8, 128.9, 128.6, 103.7, 97.3, 60.3, 26.0, 21.0, 18.5, −4.9, −5.0; **HR-ESI-MS m/z**: calcd. $C_{23}H_{32}NO_5S_2Si$ [M+H]$^+$: 494.1486, found: 494.1486.

Terminal allene: $\mathbf{R_f} = 0.1$ (*n*-pentane:Et_2O, 15:1); **m.p.** = 94.3 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2952, 2926, 2894, 2853, 1472, 1448, 1427, 1365, 1351, 1309, 1295, 1254, 1164, 1085, 1059, 1007, 902, 871, 856, 835, 772, 755, 719, 686; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.15-7.88 (m, 4 H), 7.76-7.59 (m, 2 H), 7.59-7.42 (m, 4 H), 4.69 (t, J = 3.8 Hz, 2 H), 3.70 (t, J = 7.0 Hz, 2 H), 2.54

(tt, J = 7.2, 3.8 Hz, 2 H), 0.90 (s, 9 H), 0.05 (s, 6 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 211.1, 139.4, 134.0, 129.0, 128.8, 104.4, 82.1, 60.3, 36.5, 26.0, 18.4, −5.2; **HR-ESI-MS m/z**: calcd. $C_{23}H_{32}NO_5S_2Si$ $[M+H]^+$: 494.1486, found: 494.1482.

4-(*N*-(Phenylsulfonyl)phenylsulfonamido)penta-2,3-dien-1-yl pivalate and 3-(*N*-(phenylsulfonyl)phenylsulfonamido)penta-3,4-dien-1-yl pivalate (253c)

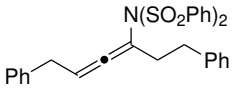


253c

Following general procedure **L**: alkyne **242c** (168 mg, 1.00 mmol, 1.0 equiv), additional triphenylphosphineselenide (17 mg, 50 µmol, 0.05 equiv); reaction time 22 h; eluting with *n*-pentane:Et_2O, 4:1; yield: 199 mg, 428 µmol, 43% (mixture of internal and terminal allene 2.3:1), yellow oil (internal), white solid (terminal); ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 25% (internal allene), 11% (terminal allene).

Internal allene: $\mathbf{R_f}$ = 0.25 (*n*-pentane:Et_2O, 4:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3067, 2971, 2932, 2873, 1726, 1584, 1479, 1448, 1377, 1359, 1313, 1281, 1167, 1140, 1084, 1033, 1000, 970, 932, 891, 796, 752, 720, 685; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.20-7.95 (m, 4 H), 7.76-7.61 (m, 2 H), 7.61-7.40 (m, 4 H), 5.18 (tq, J = 6.6, 3.0 Hz, 1 H), 4.31 (dd, J = 12.7, 6.7 Hz, 1 H), 4.23 (dd, J = 12.7, 6.5 Hz, 1 H), 2.03 (d, J = 3.0 Hz, 3 H), 1.19 (s, 9 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 207.5, 178.0, 139.5, 133.9, 129.0, 128.5, 104.6, 92.6, 60.5, 38.9, 27.3, 21.0; **HR-ESI-MS m/z**: calcd. $C_{22}H_{26}NO_6S_2$ $[M+H]^+$: 464.1196, found: 464.1199.
Terminal allene: $\mathbf{R_f}$ = 0.19 (*n*-pentane:Et_2O, 4:1); **m.p.** = 79.8 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3067, 2971, 2934, 2872, 2359, 1725, 1479, 1449, 1376, 1285, 1167, 1085, 1036, 895, 754, 720, 686; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 8.15-7.90 (m, 4 H), 7.72-7.60 (m, 2 H), 7.60-7.45 (m, 4 H), 4.72 (t, J = 3.8 Hz, 2 H), 4.15 (t, J = 6.4 Hz, 2 H), 2.67 (tt, J = 6.4, 3.8 Hz, 2 H), 1.21 (s, 9 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 210.7, 178.5, 139.2, 134.1, 129.1, 128.8, 104.0, 82.8, 61.0, 38.8, 32.6, 27.3; **HR-ESI-MS m/z**: calcd. $C_{22}H_{26}NO_6S_2$ $[M+H]^+$: 464.1196, found: 464.1201.

N-(1,6-Diphenylhexa-3,4-dien-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (253d)



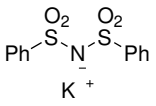
253d

Following general procedure **L**: alkyne **242d** (234 mg, 1.0 mmol, 1.0 equiv); reaction time 6.5 h; eluting with *n*-pentane:EtOAc, 50:1 to 10:1; yield: 288 mg, 544 µmol, 54%, light yellow solid; ^{1}H NMR yield using 1,3,5-trimethoxybenzene as the internal standard: 58%.

$\mathbf{R_f}$ = 0.29 (*n*-pentane:EtOAc, 10:1); **m.p.** = 99.5 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3084, 3059, 3029, 2921, 2851, 1602, 1582, 1495, 1476, 1447, 1406, 1372, 1357, 1312, 1184, 1164, 1120, 1084, 1025, 1000, 934, 895, 858, 753, 728, 684; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.07-7.83 (m, 4 H), 7.65-7.51 (m, 2 H), 7.51-7.36 (m, 4 H), 7.33-7.27 (m, 2 H), 7.26-7.17 (m, 6 H), 7.02-6.92 (m,

2 H), 5.12 (tt, J = 7.3, 3.6 Hz, 1 H), 3.15-3.11 (m, 2 H), 2.78-2.71 (m, 2 H), 2.71-2.64 (m, 2 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ [ppm] = 207.0, 140.8, 138.7, 133.9, 129.0, 128.7, 128.6, 128.5, 128.4, 126.6, 126.2, 106.6, 98.6, 34.7, 34.6, 32.9; **HR-ESI-MS m/z**: calcd. $C_{30}H_{28}NO_4S_2$ $[M+H]^+$: 530.1454, found: 530.1455.

Potassium bis(phenylsulfonyl)amide (338)



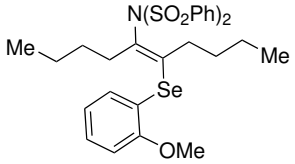
338

Dibenzenesulfonimide (500 mg, 1.68 mmol, 1.0 equiv) and KOH (94 mg, 1.7 mmol, 1.0 equiv) were dissolved in a mixture of acetone and H_2O (1:1 v/v, 2 mL) and stirred at RT for 16 h. Removal of the solvent in vacuo afforded the product as a white solid.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2359, 1737, 1445, 1265, 1148, 1088, 746, 718, 683; **^{1}H NMR** (400 MHz, D_2O): δ [ppm] = 7.64-7.59 (m, 4 H), 7.56-7.51 (m, 2 H), 7.44-7.38 (m, 4 H); **^{13}C{^{1}H} NMR** (101 MHz, D_2O): δ [ppm] = 140.9, 132.3, 128.8, 126.0; **HR-ESI-MS m/z**: calcd. $C_{12}H_{10}NO_4S_2$ $[M-K]^-$: 296.0057, found: 296.0057.

Mechanistic investigations

(*E*)-*N*-(6-((2-Methoxyphenyl)selanyl)dec-5-en-5-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (254)

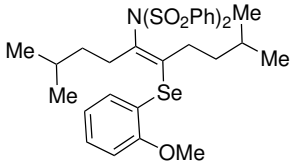


254

5-Decyne (553 mg, 4.00 mmol, 1.0 equiv), (2-anisyl)$_2$Se$_2$ (744 mg, 2.00 mmol, 0.5 equiv) and NFSI (1.26 g, 4.00 mmol, 1.0 equiv) were dissolved in dry toluene (40 mL) and stirred at 100 °C for 18 h. Removal of the solvent in vacuo and purification on silica gel (*n*-pentane:EtOAc, 10:1) afforded the product as a yellow oil (2.25 g, 3.63 mmol, 91%).

R_f = 0.29 (*n*-pentane:EtOAc, 10:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3064, 2955, 2930, 2871, 2261, 2035, 1902, 1725, 1579, 1474, 1447, 1432, 1373, 1356, 1312, 1290, 1272, 1244, 1166, 1123, 1083, 1058, 1023, 1000, 983, 930, 866, 792, 750, 718, 684; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.10-8.00 (m, 4 H), 7.66-7.59 (m, 2 H), 7.54-7.42 (m, 5 H), 7.31 (ddd, J = 8.2, 7.4, 1.7 Hz, 1 H), 7.08-6.75 (m, 2 H), 3.90 (s, 3 H), 2.66-2.48 (m, 2 H), 1.68-1.49 (m, 4 H), 1.33-1.16 (m, 4 H), 0.91-0.72 (m, 5 H), 0.61-0.49 (m, 3 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 158.5, 146.7, 140.0, 135.3, 133.8, 133.5, 129.4, 129.0, 128.9, 121.4, 118.2, 110.8, 56.1, 38.2, 34.1, 31.5, 31.3, 23.2, 22.7, 14.0, 13.6; **^{77}Se NMR** (76 MHz, $CDCl_3$): δ [ppm] = 314.1; **HR-ESI-MS m/z**: calcd. $C_{29}H_{35}NO_5SeS_2Na$ $[M+Na]^+$: 644.1015, found: 644.1011.

(*E*)-*N*-(6-((2-Methoxyphenyl)selanyl)-2,9-dimethyldec-5-en-5-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (284)



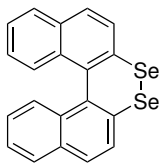
284

2,9-Dimethyl-5-decyne (83 mg, 0.5 mmol, 1.0 equiv), alkene **254** (311 mg, 500 µmol, 1.0 equiv), Li_2CO_3 (37 mg, 0.5 mmol, 1.0 equiv) and MS powder (4 Å, 30 mg) were dissolved in dry toluene (6 mL) and heated to 100 °C. NFSI (150 mg, 475 µmol, 0.95 equiv) was dissolved in dry toluene (4 mL) and added over the course of 2.5 h to the heated mixture *via* syringe pump (1.7 mL/h). The reaction was stirred at 100 °C for 16 h. Removal of the solvent in vacuo and purification on silica gel (*n*-pentane:EtOAc, 15:1) afforded the title compound as a yellow oil (70 mg, 0.11 mmol, 22%). Furthermore, diselenide **129** (8 mg, 22 µmol, 9%), starting material **254** (75 mg, 0.12 mmol, 24%) and a mixture of allenes **253a** and **253e** (1.8:1; 114 mg, 257 µmol) were isolated.

$\mathbf{R_f} = 0.29$ (*n*-pentane:EtOAc, 15:1); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3065, 2953, 2929, 2868, 1580, 1474, 1448, 1433, 1374, 1291, 1272, 1245, 1166, 1124, 1084, 1058, 1023, 984, 880, 793, 749, 730, 686; **^{1}H NMR** (500 MHz, $CDCl_3$): δ [ppm] = 8.09-7.99 (m, 4 H), 7.67-7.57 (m, 2 H), 7.57-7.40 (m, 5 H), 7.32 (ddd, J = 8.2, 7.4, 1.7 Hz, 1 H), 7.02-6.83 (m, 2 H), 3.91 (s, 3 H), 2.68-2.51 (m, 2 H), 1.59-1.47 (m, 3 H), 1.47-1.37 (m, 2 H), 1.22 (ddd, J = 12.1, 9.7, 6.4 Hz, 2 H), 0.96 (hept, J = 6.7 Hz, 1 H), 0.84 (d, J = 6.5 Hz, 6 H), 0.46 (d, J = 6.6 Hz, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 159.0, 147.4, 140.0, 136.4, 133.9, 132.5, 130.0, 129.1, 128.9, 121.3, 117.7, 110.9, 56.1, 38.0, 37.7, 36.6, 32.0, 28.8, 28.2, 22.5, 22.0; **^{77}Se NMR** (76 MHz, $CDCl_3$): δ [ppm] = 315.9; **HR-ESI-MS m/z**: calcd. $C_{31}H_{43}N_2O_5S_2Se$ $[M+NH_4]^+$: 667.1774, found: 667.1772.

5.10 Syntheses towards binaphthyl diselenides and catalysis

Dinaphtho[2,1-c:1′,2′-e][1,2]diselenine (293)



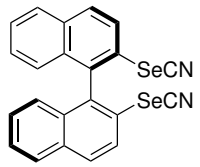
293

tert-Butyllithium (1.7 M in pentane; 0.63 mL, 1.1 mmol, 4.4 equiv) was cooled to −78 °C. 2,2′-dibromo-1,1′-binaphthalene (100 mg, 243 µmol, 1.0 equiv) in THF (0.4 mL) was addred dropwise. The solution was stirred for 2 h while being allowed to warm to room temperature. Selenium powder (40 mg, 0.51 mmol, 2.1 equiv) was added and stirred at 60 °C for 13.5 h. The reaction was quenched by the addition of H_2O (4 mL) and filtered over celite. The phases were separated, the aq. phase washed with EtOAc (4 mL), the combined org. phases were dried over Na_2SO_4 and the solvent removed in vacuo. Purification by column chromatography (40:1 PE:DCM) afforded the product as an orange solid (12 mg, 28 µmol, 12%).

$\mathbf{R_f} = 0.14$ (PE:DCM, 20:1); **m.p.** = 170-175 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2920, 2852, 1498, 1461, 1255, 904, 806, 771, 727, 687, 669, 453, 407; **^{1}H NMR** (600 MHz, $CDCl_3$): δ [ppm] = 8.17 (d,

J = 8.5 Hz, 2 H), 7.96 (dd, J = 8.6, 0.8 Hz, 2 H), 7.94 (d, J = 8.2 Hz, 2 H), 7.50 (ddd, J = 8.2, 6.8, 1.2 Hz, 2 H), 7.30 (ddd, J = 8.4, 6.8, 1.3 Hz, 2 H), 6.99 (dd, J = 8.5, 1.1 Hz, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 146.0, 134.2, 133.4, 133.1, 130.4, 129.7, 128.3, 127.7, 127.6, 127.3.; **HR-EI-MS m/z**: calcd. $C_{20}H_{12}Se_2$ $[M]^+$: 411.9, found: 411.9.

(*R*)-2,2′-diselenocyanato-1,1′-binaphthalene (295)

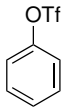


295

Boron trifluoride diethyl etherate (200 mg, 1.41 mmol, 8.0 equiv) was cooled to −30 °C. A solution of (*R*)-2,2′-diamino-1,1′-binaphthalene (50 mg, 0.18 mmol, 1.0 equiv) in THF (0.8 mL) and a solution of *tert*-butyl nitrite (127 mg, 1.23 mmol, 7.0 equiv) in THF (1.2 mL) were added dropwise and the mixture was stirred at −5 °C for 2.5 h. Diethyl ether (1.0 mL) was added and stirred at −5 °C for 15 min, then the supernatant was removed with a syringe. Potassium selenocyanate (56 mg, 0.39 mmol, 2.2 equiv) in acetonitrile (1.8 mL) was added dropwise at 0 °C. The solution was stirred for 2 h and allowed to warm to room temperature. It was washed with water (2 mL) and sat. aq. NaCl solution (2 mL), dried over Na_2SO_4 and the solvent removed in vacuo. Purification by column chromatography (8:1 PE:EtOAc) afforded the product as a brown solid (12 mg, 27 µmol, 15%).

R_f = 0.36 (PE:EtOAc, 5:1); **m.p.** = 146-150 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3055, 2923, 2151, 1577, 1500, 1312, 811, 784, 772, 747, 689, 524, 460; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.12 (d, J = 9.0 Hz, 2 H), 8.06-7.89 (m, 4 H), 7.60 (ddd, J = 8.2, 6.9, 1.2 Hz, 2 H), 7.41 (ddd, J = 8.3, 6.9, 1.3 Hz, 2 H), 7.05 (dd, J = 8.4, 1.0 Hz, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 134.1, 133.4, 132.5, 132.1, 129.0, 128.8, 127.9, 127.2, 124.8, 124.8, 101.1; **EI-MS m/z**: calcd. $C_{22}H_{12}N_2Se_2$ $[M]^+$: 463.9, found: 463.9. The analytical data was in agreement with literature.[210]

Phenyl trifluoromethanesulfonate (297)



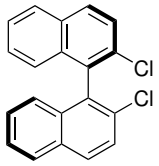
297

Phenol (98 mg, 1.0 mmol, 1.0 equiv) was dissolved in DCM (3 mL). Pyridine (168 mg, 2.13 mmol, 2.0 equiv) was added and the mixture cooled to 0 °C. Trifluoromethanesulfonic anhydride (360 mg, 1.28 mmol, 1.2 equiv) was added dropwise, the solution was allowed to warm to room temperature and stirred for 1.5 h. 1 M HCl solution (3 mL) was added and the phases separated. The org. phase was washed with sat. aq. $NaHCO_3$ solution (2 × 3 mL) and sat. aq. NaCl solution (3 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo and purification by column chromatography (8:1 PE:EtOAc) afforded the product as a yellow liquid (134 mg, 592 µmol, 57%).

R_f = 0.57 (PE:EtOAc, 8:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.51-7.36 (m, 3 H), 7.32-7.24 (m, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 149.8, 130.4, 128.5, 121.5, 118.9

(q, $^1J_{CF} = 318.8$ Hz); **^{19}F NMR** (282 MHz, $CDCl_3$): δ [ppm] = −72.9; **HR-EI-MS m/z**: calcd. $C_7H_5F_3O_3S$ $[M]^+$: 225.9912, found: 225.9920. The analytical data was in agreement with literature.[243]

(*R*)-2,2′-dichloro-1,1′-binaphthalene (309)

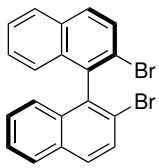


309

$CuCl_2$ (123 mg, 914 µmol, 2.6 equiv) and *t*$BuNO_2$ (152 mg, 1.48 mmol, 4.2 equiv) were dissolved in acetonitrile (2 mL). A suspension of (*R*)-2,2′-diamino-1,1′-binaphthalene (100 mg, 352 µmol, 1.0 equiv) in acetonitrile (2 mL) was added dropwise and the mixture was stirred at 65 °C for 16 h. Aq. 1 N HCl (4 mL) was added and the phases were separated. The org. phase was washed with H_2O (4 mL) and sat. aq. NaCl solution (4 mL), the aq. phase was extracted with DCM (8 mL) and the combined org. phases were dried over Na_2SO_4. Removal of the solvent in vacuo and purification by column chromatography (30:1 PE:DCM) afforded the product as a yellow solid (63 mg, 0.19 mmol, 56%).

R_f = 0.28 (PE:DCM, 30:1); **m.p.** = 134-138 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3054, 2923, 1581, 1502, 1128, 1117, 857, 845, 808, 771, 741, 612, 555, 458, 412; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.95 (dd, J = 8.4, 3.5 Hz, 4 H), 7.67 (d, J = 8.8 Hz, 2 H), 7.49 (ddd, J = 8.2, 6.8, 1.2 Hz, 2 H), 7.33 (ddd, J = 8.3, 6.9, 1.3 Hz, 2 H), 7.10 (d, J = 8.5 Hz, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 133.3, 133.1, 132.4, 132.2, 129.9, 128.4, 127.5, 127.4, 126.3, 125.7; **HR-EI-MS m/z**: calcd. $C_{20}H_{12}Cl_2$ $[M]^+$: 322.0316, found: 322.0310.

(*R*)-2,2′-dibromo-1,1′-binaphthalene (310)



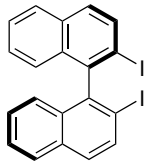
310

(*R*)-2,2′-diamino-1,1′-binaphthalene (100 mg, 0.352 mmol, 1.0 equiv) was dissolved in HBr (48%, 0.6 mL) and cooled to 0 °C. $NaNO_2$ (73.0 mg, 1.06 mmol, 3.0 equiv) was dissolved in H_2O (0.4 mL) and added to the first solution. The mixture was stirred at 0 °C for 30 min and a solution of CuBr (126 mg, 878 µmol, 2.5 equiv) in HBr (48%, 0.8 mL) was added. Subsequently, the mixture was allowed to warm to room temperature and stirred for 16.5 h. The reaction was quenched by the addition of ammonia solution (2 mL) and extracted with DCM. The organic phase was washed with sat. aq. NaCl solution, dried over Na_2SO_4 and the solvent removed in vacuo. Purification by column chromatography (20:1 PE:DCM) afforded the product as a yellow solid (73 mg, 0.18 mmol, 50%).

R_f = 0.31 (*n*-pentane:DCM, 20:1); **m.p.** = 152-158 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3057, 1579, 1501, 1110, 838, 808, 773, 747, 551, 453, 410; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.94 (d, J = 8.3 Hz, 2 H), 7.88 (d, J = 8.9 Hz, 2 H), 7.82 (d, J = 8.9 Hz, 2 H), 7.50 (ddd, J = 8.3, 6.8, 1.3 Hz, 2 H), 7.31 (ddd, J = 8.4, 6.8, 1.3 Hz, 2 H), 7.09 (dd, J = 8.4, 1.3 Hz, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 137.2, 133.4, 132.5, 130.1, 129.9, 128.4, 127.5, 126.5,

126.0, 122.9; **HR-EI-MS m/z**: calc. $C_{20}H_{12}Br_2$ $[M]^+$: 409.9306, found: 409.9315; **HPLC:** 13.387 min, 15.369 min (Daicel Chiralcel OD; solvents: *n*-hexane/isopropanol, 99.5/0.5, v/v; flow rate: 0.6 mL/min). The analytical data was in agreement with literature.[244]

(*R*)-2,2′-diiodo-1,1′-binaphthalene (311)[232]

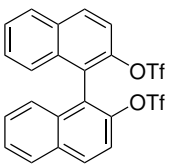


311

A suspension of (*R*)-2,2′-diamino-1,1′-binaphthalene (100 mg, 0.352 mmol, 1.0 equiv) and *para*-toluenesulfonic acid monohydrate (401 mg, 2.11 mmol, 6.0 Äq.) in MeCN (5 mL) was cooled to 10 °C. A solution of KI (292 mg, 1.76 mmol, 5.0 Äq.) and $NaNO_2$ (97.3 mg, 1.41 mmol, 4.0 Äq.) in H_2O (0.5 mL) was added dropwise and the solution stirred for 10 min at 10 °C. The solution was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by the addition of H_2O (10 mL), sat. aq. $NaHCO_3$ solution (6 mL), 10% $Na_2S_2O_3$ solution (2.5 mL). The aq. phase was extracted with DCM (3 × 10 mL), the combined org. phases were dried over Na_2SO_4 and the solvent removed in vacuo. Purification by column chromatography (20:1 PE:DCM) afforded the product as a white solid (104 mg, 0.205 mmol, 58%).

$\mathbf{R_f} = 0.37$ (PE:DCM, 20:1); ^{1}**H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.06 (d, $J = 8.7$ Hz, 2 H), 7.93 (m, 2 H), 7.72 (d, $J = 8.6$ Hz, 2 H), 7.51 (ddd, $J = 8.1$, 6.8, 1.2 Hz, 2 H), 7.29 (ddd, $J = 8.3$, 6.8, 1.3 Hz, 2 H), 7.07 (m, 2 H). The analytical data was in agreement with literature.[232]

[1,1′-binaphthalene]-2,2′-diyl bis(trifluoromethanesulfonate) (312)



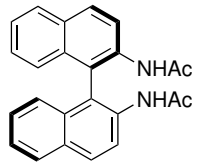
312

BINOL (200 mg, 0.699 mmol, 1.0 equiv) was dissolved in DCM (2 mL) and cooled to 0 °C. Trifluoromethanesulfonic anhydride (473 mg, 1.68 mmol, 2.4 equiv) was added dropwise, the reaction was allowed to warm to room temperature and stirred for 6 h. The reaction was quenched by the addition of aq. 1 M HCl solution (2 mL), the org. phase was washed with sat. aq. $NaHCO_3$ solution (2 mL) and sat. aq. NaCl solution (2 mL) and the aq. phase was extracted with DCM (6 mL). The combined org. phases were dried over Na_2SO_4 and the solvent removed in vacuo. Purification by column chromatography (8:1 PE:EtOAc) afforded the product as a white solid (362 mg, 0.658 mmol, 94%).

$\mathbf{R_f} = 0.57$ (PE:EtOAc, 8:1); **m.p.** = 118-123 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 1417, 1207, 1173, 1136, 954, 934, 829, 814, 750, 685, 629, 616, 494; ^{1}**H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.15 (dd, $J = 9.2$, 0.8 Hz, 2 H), 8.02 (dd, $J = 8.3$, 1.0 Hz, 2 H), 7.68-7.54 (m, 4 H), 7.42 (ddd, $J = 8.3$, 6.8, 1.2 Hz, 2 H), 7.26 (dt, $J = 8.6$, 0.9 Hz, 2 H); ^{13}**C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 145.5, 133.3, 132.5, 132.1, 128.5, 128.1, 127.5, 126.9, 123.6, 119.5, 118.3 (q, $J_{CF} = 320.2$ Hz); ^{19}**F NMR** (282 MHz, $CDCl_3$): δ [ppm] = −74.6; **HR-ESI-MS m/z**: calcd.

$C_{22}H_{13}F_6O_6S_2$ $[M+H]^+$: 551.0052, found: 551.0058. The analytical data was in agreement with literature.[245]

(*R*)-2,2′-Di[acetylamino]-1,1′-binaphthalene (321)



321

Procedure A:

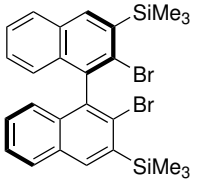
(*R*)-2,2′-diamino-1,1′-binaphthalene (100 mg, 352 µmol, 1.0 equiv) and DMAP (4.0 mg, 35 µmol, 1.0 equiv) were dissolved in acetic anhydride (399 µL, 430 mg, 4.22 mmol, 12.0 equiv) and stirred at 75 °C for 2 h. The solution was allowed to cool to room temperature, slowly added to 0.2 M aq. HCl-solution (3.5 mL) and stirred for 20 min. The phases were separated, the aq. phase was extracted with DCM (2 × 4 mL), the organic phase was dried over Na_2SO_4 and the solvent removed in vacuo. Purification by column chromatography (1:1 PE:EtOAc) afforded the product as a yellow solid (96 mg, 0.26 mmol, 74%).

Procedure B:

(*R*)-2,2′-diamino-1,1′-binaphthalene (100 mg, 352 µmol, 1.0 equiv) and acetic acid (211 mg, 3.52 mmol, 10.0 equiv) were dissolved in DCM (3.5 mL) and cooled to 0 °C. Acetic acid anhydride (36 mg, 0.35 mmol, 1.0 equiv) was added dropwise, the cooling bath was removed and stirred at room temperature for 4.5 h. Addition of 2.5 N aq. NaOH until pH = 7, extraction of the aq. phase with DCM (2 × 2 mL), washing of the combined org. phases with sat. aq. NaCl solution (5 mL), drying over Na_2SO_4 and removal of the solvent in vacuo afforded the product as a yellow solid (114 mg, 349 µmol, >99%).

R_f = 0.07 (PE:EtOAc, 1:1); **m.p.** = 94-96 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3400, 3236, 1686, 1630, 1598, 1494, 1425, 1278, 820, 773, 752, 729, 700, 573, 498; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.31 (d, J = 9.0 Hz, 2 H), 8.04 (dd, J = 8.8 Hz, 2 H), 7.94 (d, J = 8.2 Hz, 2 H), 7.45 (ddd, J = 8.1, 6.8, 1.2 Hz, 2 H), 7.26 (ddd, J = 8.2, 6.8, 1.3 Hz, 2 H), 7.07-6.89 (m, 2 H), 1.82 (s, 6 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 169.5, 135.0, 132.6, 131.6, 130.0, 128.5, 127.4, 125.8, 125.4, 122.6, 121.7, 24.3; **HR-ESI-MS m/z**: calcd. $C_{24}H_{21}N_2O_2$ $[M+H]^+$: 369.1598, found: 369.1600.

2,2′-Dibromo-3,3′-bis(trimethylsilyl)-1,1′-binaphthyl (324)



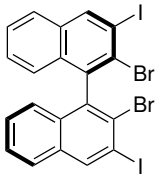
324

Tetramethylpiperidine (850 mg, 6.02 mmmol, 4.96 equiv) was dissolved in THF (10 mL) and cooled to 0 °C. *n*-Butyl lithium (2.5 M in hexane, 2.0 mL, 6.02 mmol, 4.96 equiv) was added dropwise, the solution was stirred at 0 °C for 20 min and cooled to −78 °C. TMSCl (1.96 g, 18.1 mmol, 14.9 equiv) was added dropwise and the mixture was stirred for 25 min at −78 °C. A solution of binaphthyl dibromide **310** (500 mg, 1.21 mmol, 1.0 equiv) in THF (5.0 mL) was cooled to −78 °C and added to the reaction mixture which was then allowed to warm to room temperature and stirred for 18.5 h. After addition of 1 M aq. HCl (2.5 mL), the aq. phase was extracted with DCM (2 × 10 mL), the combined org. phases were washed with

sat. aq. NaCl solution (2 × 10 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo and purification by column chromatography (*n*-pentane) afforded the product as a white solid (465 mg, 0.84 mmol, 69%).

R_f = 0.33 (PE); **m.p.** = 160-163 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2952, 1246, 1116, 972, 901, 878, 835, 788, 753, 688, 627, 561; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.09 (s, 2 H), 7.92 (d, J = 8.0 Hz, 2 H), 7.48 (ddd, J = 8.1, 6.8, 1.2 Hz, 2 H), 7.29 (ddd, J = 8.3, 6.8, 1.3 Hz, 2 H), 7.02 (d, J = 8.7 Hz, 2 H), 0.53 (s, 36 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 140.0, 137.9, 137.0, 133.9, 131.9, 129.8, 128.5, 127.8, 126.3, 125.8, 0.3; **HR-EI-MS m/z**: calcd. $C_{26}H_{28}Br_2Si_2$ $[M]^+$: 554.0096, found: 554.0100; **HPLC:** 6.123 min, 6.488 min (Daicel Chiralpak IA; solvents: *n*-hexane/isopropanol, 99.8/0.2, v/v; flow rate: 0.6 mL/min). The analytical data was in agreement with literature.[238]

2,2′-Dibromo-3,3′-diiodo-1,1′-binaphthalene (325)

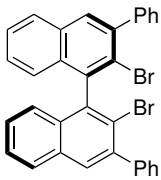


325

Dibromide **324** (230 mg, 413 µmol, 1.0 equiv) was dissolved in DCM (6 mL) and cooled to −40 °C. Iodine monochloride (1 M in DCM, 1.24 mL, 1.24 mmol, 3.0 equiv) was added dropwise and the mixture was stirred at −40 °C for 20 h. The reaction was quenched by the addition of 10% aq. $NaHSO_3$ (4.3 mL) and allowed to warm to room temperature. The mixture was washed with sat. aq. NaCl solution (4 mL), the aq. phase extracted with DCM (4 mL) and the combined org. phases were dried over Na_2SO_4. Removal of the solvent in vacuo and purification by column chromatography (PE) afforded the product as a white solid (242 mg, 364 µmol, 89%).

R_f = 0.57 (PE:EtOAc, 4:1); **m.p.** = 190-194 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3057, 2919, 1546, 1486, 1366, 1297, 1112, 947, 891, 858, 780, 746, 732, 554; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.61 (s, 2 H), 7.81 (d, J = 8.2 Hz, 2 H), 7.51 (ddd, J = 8.1, 6.8, 1.2 Hz, 2 H), 7.32 (ddd, J = 8.3, 6.9, 1.3 Hz, 2 H), 6.98 (dd, J = 8.5, 1.0 Hz, 2 H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ [ppm] = 140.2, 139.7, 133.8, 132.1, 128.6, 128.2, 127.4, 127.3, 126.0, 99.1; **HR-EI-MS m/z**: calcd. $C_{20}H_{10}Br_2I_2$ $[M]^+$: 661.7239, found: 661.7249; **HPLC:** 16.513 min, 17.996 min (Daicel Chiralpak IA; solvents: *n*-hexane/isopropanol, 99.8/0.2, v/v; flow rate: 0.6 mL/min). The analytical data was in agreement with literature.[238]

2,2′-Dibromo-3,3′-diphenyl-1,1′-binaphthalene (326)



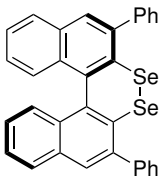
326

Phenylboronic acid (93 mg, 0.76 mmol, 2.1 equiv), Na_2CO_3 (84 mg, 0.80 mmol, 2.2 equiv) and tetrakis[triphenylphosphine]palladium(0) (21 mg, 18 µmol, 0.05 equiv) were dissolved in a mixture of ethanol (0.3 mL) and H_2O (0.45 mL) and the solution was degassed (30 min). 2,2′-Dibromo-3,3′-diiodo-1,1′-binaphthalene **325** (240 mg, 0.36 mmol, 1.0 equiv) was dissolved in toluene (4.5 mL) and added dropwise to the other solution. The reaction mixture was

heated at 100 °C for 19 h. H_2O (4 mL) was added, the phases were separated and the org. phase was washed with sat. aq. NaCl solution (4 mL). The combined aq. phases were extracted with DCM (5 mL) and the combined org. phases were dried over Na_2SO_4. Removal of the solvent in vacuo and purification by column chromatography (40:1 PE:DCM) afforded the product as a white solid (100 mg, 177 µmol, 49%).

R_f = 0.07 (PE:DCM, 40:1); **m.p.** = 205-208 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3054, 2922, 2852, 1494, 1089, 1029, 891, 873, 778, 761, 746, 697, 584, 521, 464; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.97 (s, 2 H), 7.94 (d, J = 8.2 Hz, 2 H), 7.63-7.57 (m, 4 H), 7.57-7.39 (m, 8 H), 7.35 (ddd, J = 8.3, 6.8, 1.3 Hz, 2 H), 7.18 (d, 8.5 Hz, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 141.7, 140.9, 139.1, 132.5, 130.1, 130.0, 128.4, 128.0, 127.8, 127.5, 126.9, 126.1, 124.0; **HR-EI-MS m/z**: calcd. $C_{32}H_{20}Br_2$ $[M]^+$: 561.9932, found: 561.9934. The analytical data was in agreement with literature.[238]

(*R*)-2,5-Diphenyldinaphtho[2,1-*c*:1′,2′-*e*][1,2]diselenine (328)

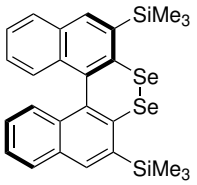


328

(*R*)-2,2′-Dibromo-3,3′-diphenyl-1,1′-binaphthalene **326** (33 mg, 58 µmol, 1.0 equiv) was dissolved in THF (0.1 mL), cooled to −78 °C and *tert*-butyl lithium (1.7 M in pentane, 0.15 mL, 0.26 mmol, 4.4 equiv) was added dropwise. The solution was stirred for 1.5 h at −78 °C and then allowed to warm to 0 °C. Selenium powder (10 mg, 0.12 mmol, 2.1 equiv) was added and the solution was stirred for 17 h while allowed to warm to room temperature. The reaction was quenched by addition of H_2O (1 mL), the phases were separated, the aq. phase was extracted with EtOAc (2 mL) and the combined org. phases were dried over Na_2SO_4. The residue was dissolved in ethanol (2 mL), sodium hydroxide (1 pellet) was added and stirred for 30 min. The solution was neutralized by addition of 1 M aq. HCl solution. Removal of the solvent in vacuo and purification by column chromatography (40:1 PE:DCM) afforded the product as a yellow solid (8.0 mg, 13 µmol, 21%).

R_f = 0.07 (PE:DCM, 20:1); **m.p.** = 215-220 °C; **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2921, 2852, 1728, 1579, 1492, 1446, 1260, 1074, 1026, 890, 793, 748, 699, 582, 511; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.00-7.92 (m, 4 H), 7.60-7.39 (m, 12 H), 7.19 (ddd, J = 8.3, 6.8, 1.3 Hz, 2 H), 7.04 (d, J = 8.5 Hz, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 142.4, 142.0, 141.6, 139.9, 132.7, 132.4, 128.9, 128.9, 128.4, 128.3, 128.0, 127.4, 126.6, 126.3; **EI-MS m/z**: calcd. $C_{32}H_{20}Se_2$ $[M]^+$: 564.0, found: 563.9.

(*R*)-2,5-Bis(trimethylsilyl)dinaphtho[2,1-*c*:1′,2′-*e*][1,2]diselenine (329)

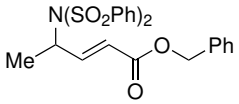


329

(*R*)-2,2′-dibromo-3,3′-bis(trimethylsilyl)-1,1′-binaphthyl **324** (55 mg, 99 µmol, 1.0 equiv) was dissolved in THF (0.2 mL) and cooled to −78 °C. *tert*-Butyl lithium (1.7 M in pentane, 0.26 mL, 0.43 mmol, 4.4 equiv) was added dropwise, the solution was stirred for 1.5 h at −78 °C and was allowed to warm to 0 °C. Selenium powder (16 mg, 0.21 mmol, 2.1 equiv) was added and the solution was stirred for 2 h at 0 °C and 17.5 h at room temperature. The reaction was quenched by addition of H_2O (1 mL) and filtered over celite. The phases were separated, the aq. phase was extracted with EtOAc (2 mL) and the combined org. phases were dried over Na_2SO_4. Removal of the solvent in vacuo and purification by column chromatography (PE) afforded the product as an orange solid (20 mg, 36 µmol, 36%).

R_f = 0.21 (PE); **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2953, 2924, 1248, 1163, 1119, 906, 868, 836, 751, 734; **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.94 (s, 2 H), 7.86 (d, J = 8.5 Hz, 2 H), 7.37 (ddd, J = 8.1, 6.8, 1.2 Hz, 2 H), 7.10 (ddd, J = 8.3, 6.8, 1.4 Hz, 2 H), 6.85 (d, J = 8.4 Hz, 1 H), 0.52 (s, 18 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ [ppm] = 144.5, 140.3, 139.6, 134.2, 133.5, 132.5, 128.3, 127.8, 126.8, 125.9, 0.4; **EI-MS m/z**: calcd. $C_{26}H_{28}Se_2Si_2$ $[M]^+$: 556.0, found: 556.0.

(*E*)-Benzyl-4-*N*-di(phenylsulfonyl)imido pent-2-enoate (331)



331

(*E*)-Benzyl pent-3-enoate (50 mg, 0.26 mmol, 1.0 equiv), NFSI (83 mg, 0.26 mmol, 1.0 equiv), diselenide **328** (7.5 mg, 13 µmol, 0.05 equiv) and molecular sieves (4 Å powder, spatula tip) were added to THF (1.5 mL) and the suspension was stirred at room temperature for 114 h. Removal of the solvent in vacuo and purification by column chromatography (10:1 PE:Et_2O) afforded the product as a colorless oil (4.5 mg, 9.3 mmol, 4%).

R_f = 0.11 (PE:Et_2O, 10:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 8.04-7.99 (m, 4 H), 7.65-7.58 (m, 2 H), 7.54-7.49 (m, 4 H), 7.40-7.34 (m, 5 H), 7.00 (dd, J = 15.9, 5.6 Hz, 1 H), 5.79 (dd, J = 15.9, 1.8 Hz, 1 H), 5.17 (s, 2 H), 4.91 (m, 1 H), 1.54 (d, J = 7.0 Hz, 3 H). The analytical data was in agreement with literature.[63]

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List of Abbreviations

Ac	acetyl
Alk	alkyl
approx.	approximately
aq.	aqueous
Ar	aryl
ATP	adenosine triphosphate
BINAM	1,1′-binaphthalene-2,2′-diamine
BINOL	1,1′-binaphthalene-2,2′-diol
Bn	benzyl
Boc	*tert*-butyloxycarbonyl
b.p.	boiling point
bpz	2,2′-bipyrazine
calc.	calculated
Cbz	carboxybenzyl, benzyloxycarbonyl
Ch	chalcogen
conc.	concentrated
COSY	correlation spectroscopy
CV	cyclic voltammetry
Cy	cyclohexyl
DAD	diode array detector
DB	double bond
DCC	*N*,*N*′-dicyclohexylcarbodiimide
DCE	1,2-dichloroethane
DCM	dichloromethane
DCN	1,4-dicyanonaphthalene
de	diastereomeric excess
DIBAL-H	diisobutylaluminum hydride
DMAP	4-(*N*,*N*-dimethylamino)pyridin
DMB	1,4-dimethoxybenzene
DMF	*N*,*N*-dimethylformamide
DMI	1,3-dimethyl-2-imidazolidinone
DMP	Dess-Martin periodinane
DMSO	dimethylsulfoxide
DMTA	10-(3,5-dimethoxyphenyl)-9-mesityl-1,3,6,8-tetramethoxyacridinium tetrafluoroborate **131**
DNA	deoxyribonucleic acid
Dodec	dodecyl

dppf	[1,1′-bis(diphenylphosphino)ferrocene]
dppp	1,3-bis(diphenylphosphino)propane
E	electrophile
ee	enantiomeric excess
EI	electron ionization
E_{ox}	oxidation potential
equiv	equivalents
E_{red}	reduction potential
ESI	electrospray ionization
Et_2O	diethyl ether
Et	ethyl
EtOAc	ethyl acetate
EtOH	ethanol
EWG	electron withdrawing group
GC	gas chromatography
gen.	generation
Hal	halide
Hex	hexyl
HPLC	high-performance liquid chromatography
HR-MS	high resolution mass spectrometry
*i*Bu	isobutyl
*i*Pr	isopropyl
IR	infrared
LB	Lewis base
LED	light-emitting diodes
m.p.	melting point
M	molar
*m*CPBA	*meta*-chloroperbenzoic acid
MeCN	acetonitrile
Me	methyl
MeOH	methanol
Mes	mesityl
m	mass
MS	mass spectrometry or molecular sieves
Ms	mesyl, methanesulfonyl
N	normal
Naph	naphthyl
NBS	*N*-bromosuccinimid
*n*Bu	*n*-butyl

NCS	*N*-chlorosuccinimide (**22**)
NFSI	*N*-fluorobenzenesulfonimide
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser enhancement spectroscopy
NPSS	*N*-phenylselenosuccinimide (**26**)
nr	no reaction
Nu	nucleophile
ox	oxidant
p-MeO-TPT	2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (**95**)
PE	petroleum ether
PG	protecting group
Ph	phenyl
PIDA	phenyliodine(III) diacetate, (diacetoxyiodo)benzene
PIFA	phenyliodine(III) bis(trifluoroacetate), (bis(trifluoroacetoxy)iodo)benzene
Pin	pinacolyl
Piv	pivaloyl
PMB	*para*-methoxybenzyl
PS	photosensitizer
PTSA	*para*-toluenesulfonic acid
[PyF]	*N*-fluoropyridinium
rac	racemic
RT	room temperature, 23 °C
sat.	saturated
SCE	saturated calomel electrode
SET	single electron transfer
SPhos	2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl
SPS	solvent purification system
TBS	*tert*-butyldimethylsilyl
*t*Bu	*tert*-butyl
TCE	1,1,2,2-tetrachloroethane
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxyl
temp.	temperature
TFAA	trifluoroacetic acid anhydride
TFA	trifluoroacetic acid
Tf	triflate, trifluoromethanesulfonate
THF	tetrahydrofurane
TIPS	triisopropyl silyl
TLC	thin layer chromatography
TMB	1,3,5-trimethoxybenzene

TMP	2,2,6,6-tetramethylpiperidine
[TMPyF]	*N*-fluoro-2,4,6-trimethylpyridinium
TMS	trimethylsilyl
Tol	*p*-tolyl
Ts	tosyl, *p*-toluenesulfonyl
z	charge

List of Figures

List of Schemes

List of Tables

Acknowledgements

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I would also like to thank all further members of the examination board: Dr. H. Frauendorf, Prof. Dr. K. Koszinowski, Prof. Dr. I. Siewert and Prof. Dr. D. Stalke.

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A big thank you goes to my former and current lab colleagues, bachelor students and lab rotation students. I'm especially grateful to: Christian Depken for Rocket Beans, for being such a laid-back/northern-German-style relaxed person, for bringing new music of different genres and for reminding me of old music; Felix "Harry" Krätzschmar for sharing your competence in lab techniques and devices as well as for entertainment and craziness (but also being down-to-earth when needed). Thank you for being the best writing buddy I could wish for, helping me by sharing the motivation/demotivation periods, discussing questions, papers and topics that confused or annoyed me and posing me occasional chemistry challenges; Stefan Ortgies for all your competence, for starting to train me in chemistry with the Kürti-Czakó-challenge, for leaving your Clayden in the lab when I was too lazy to bring mine, for answering questions about my thesis long after your time in the group, for being the nicest person in the world when in a good mood, for sharing some music moments and for being unexpectedly and enjoyably nerdy; Martina Palomba for Italian flair and contributing a lot to my project; Poorva Ramadas Narasimhamurthy for making me more active (for example with swimming dates), for becoming my scientific language tandem partner and for becoming a friend right from the start; and Rene Rieger for reliably making me laugh by his constant and generous contributions to the Phrasenschwein. All of you, I would like to thank for the good working atmosphere in the lab, the good teamwork, your help with problems, the discussions about chemistry and more, for being totally crazy and for making me

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(... und gut, dass wir uns darin einig waren: “Immer erst mal pöbeln!”)

To my friends, I am grateful that you care about me. Thank you for advice, comfort and all the things we do together, like trips in Germany and trips abroad, trips to the lake, many cooking evenings, board games, video games, pen and paper, going out, movie nights, ...
Thank you to the Friday Lunch Group for sticking together since the first semester and bringing diversion and different topics into my workday.

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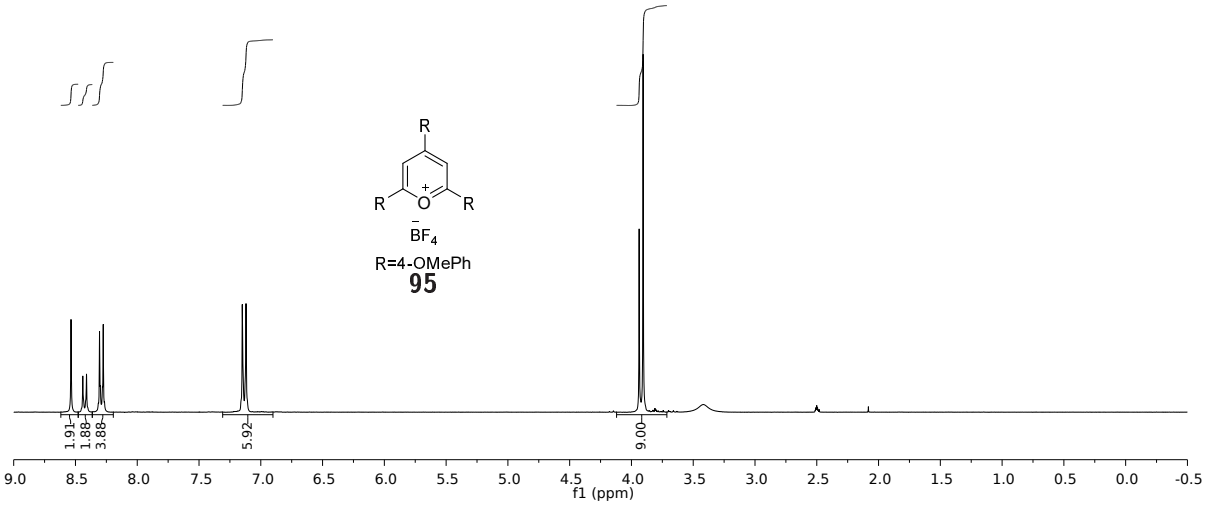
Eventually, I would like to thank my parents and my brother for their unconditional and constant interest, caring and support during these years. I would not be where I am without you.

Spectra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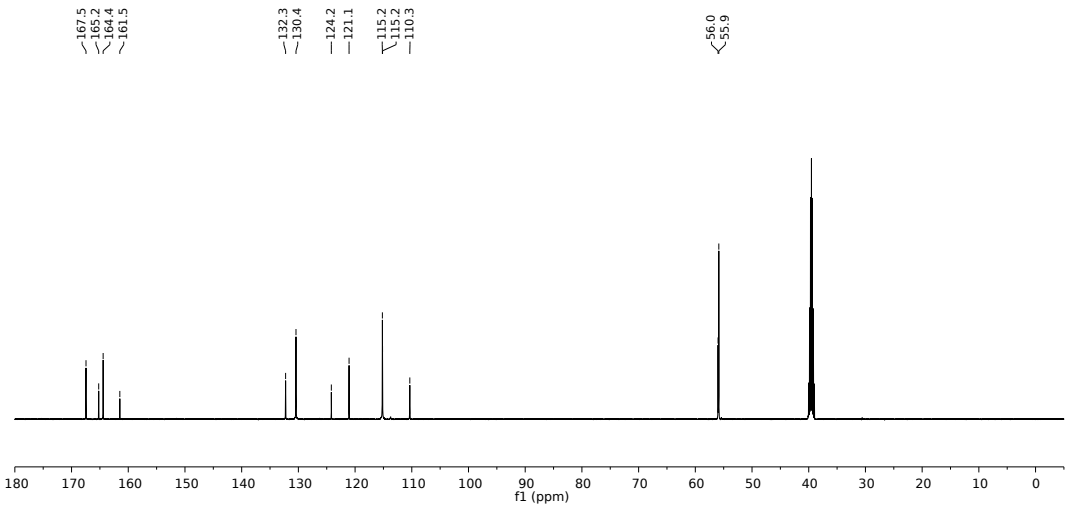
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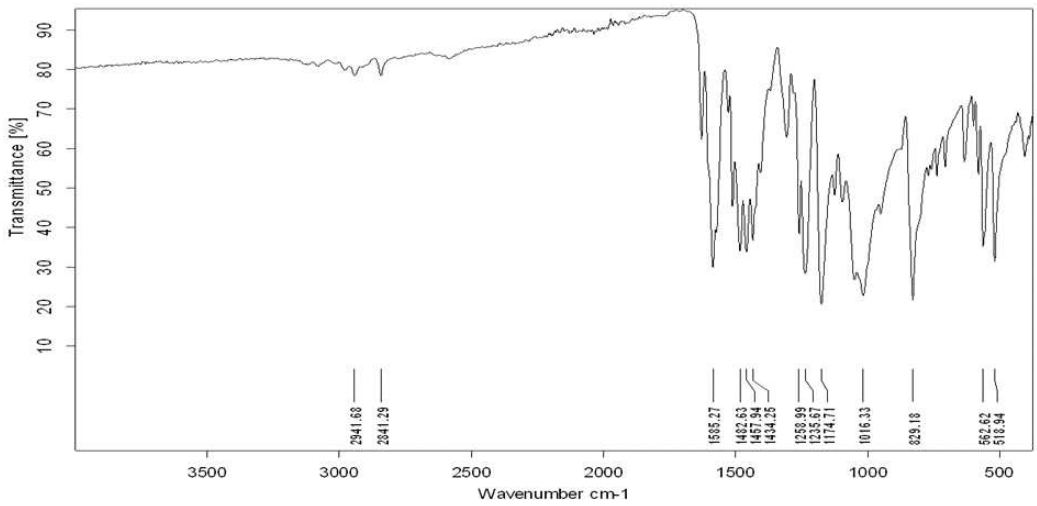
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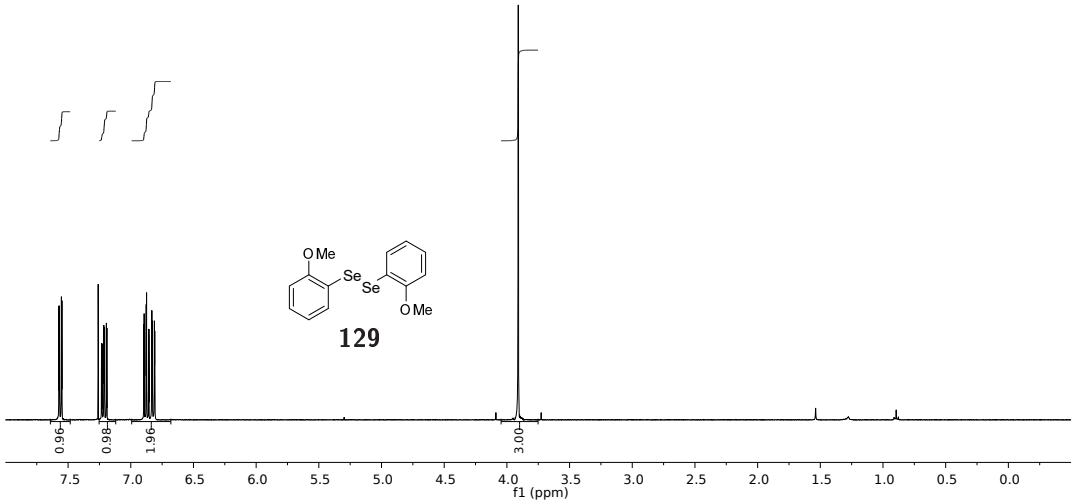
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Se
Se
OMe
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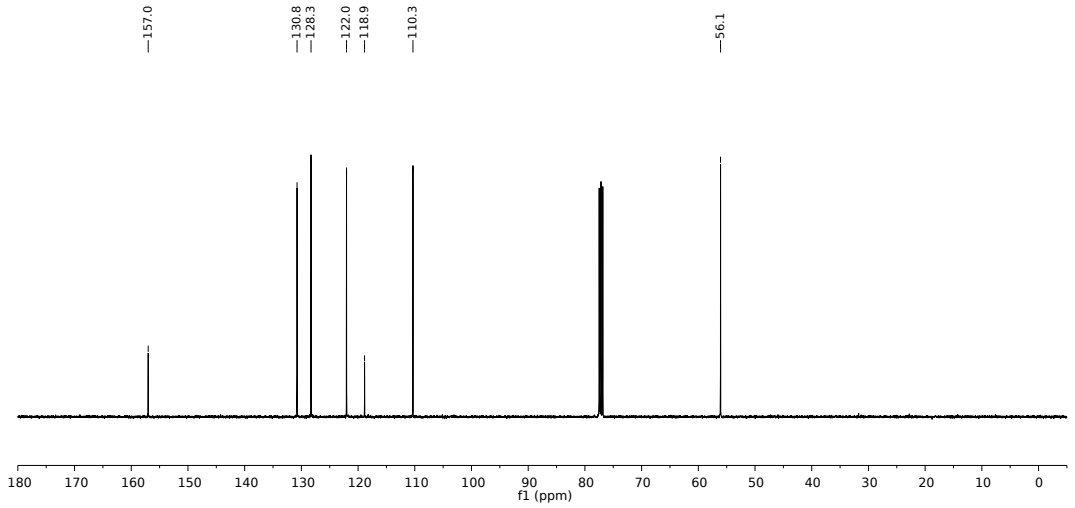
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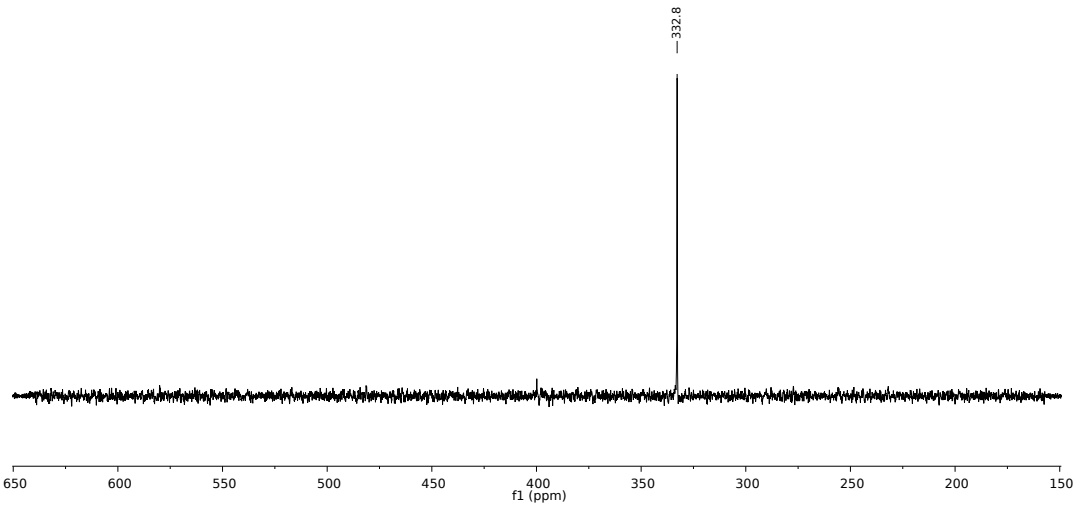
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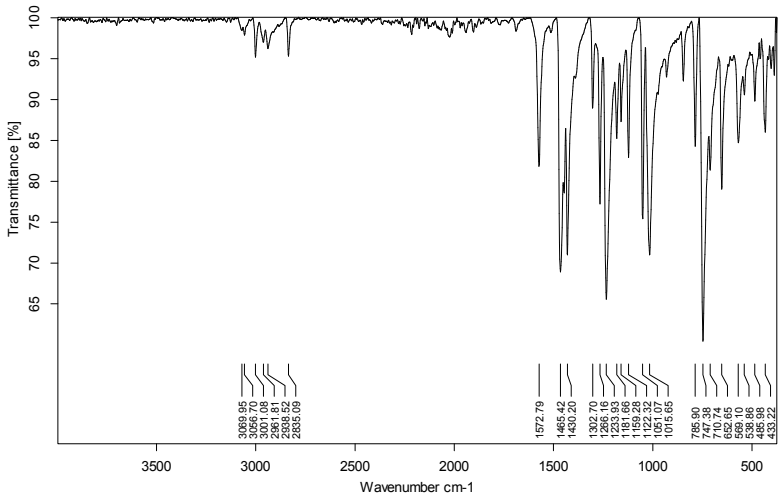
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1233.93
1181.66
1159.28
1122.32
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785.90
747.38
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1000
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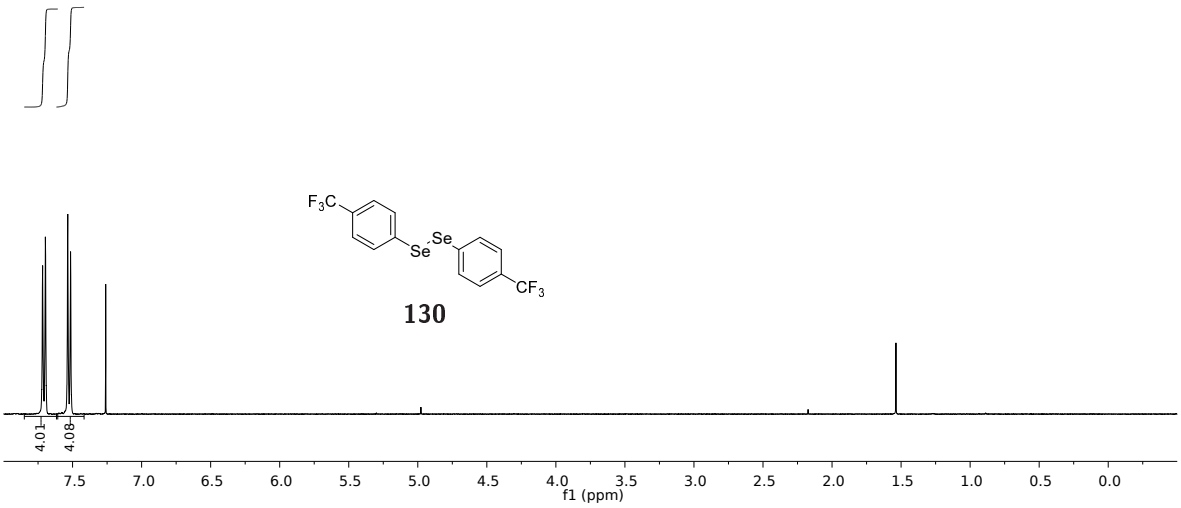
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Se
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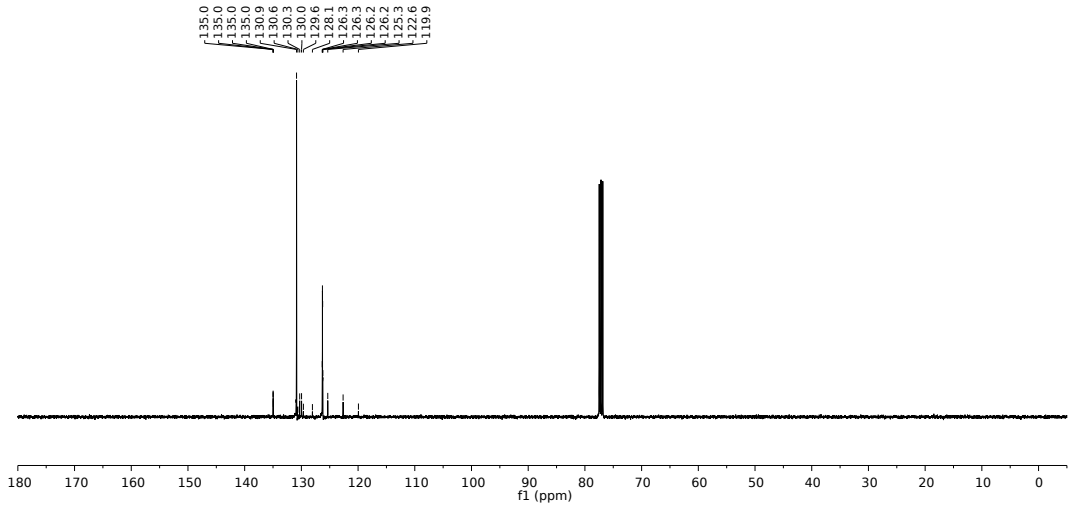
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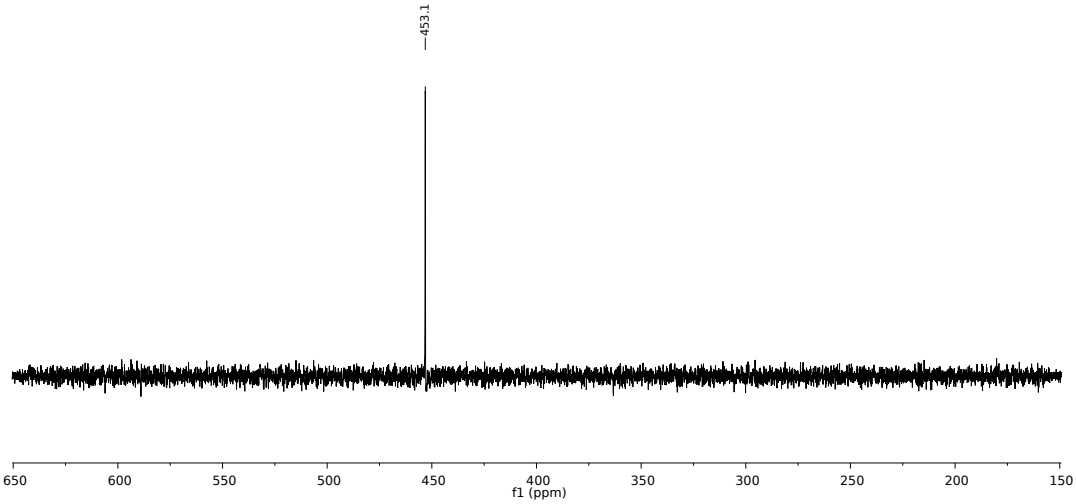
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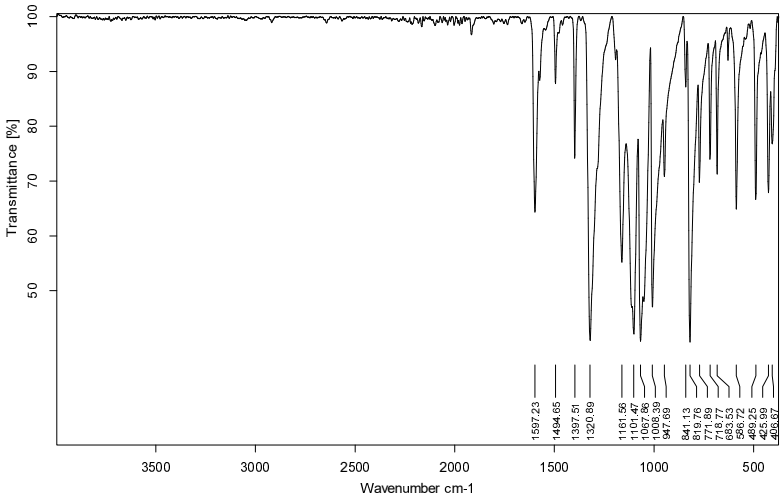
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1500
1000
500
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1320.69
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1101.47
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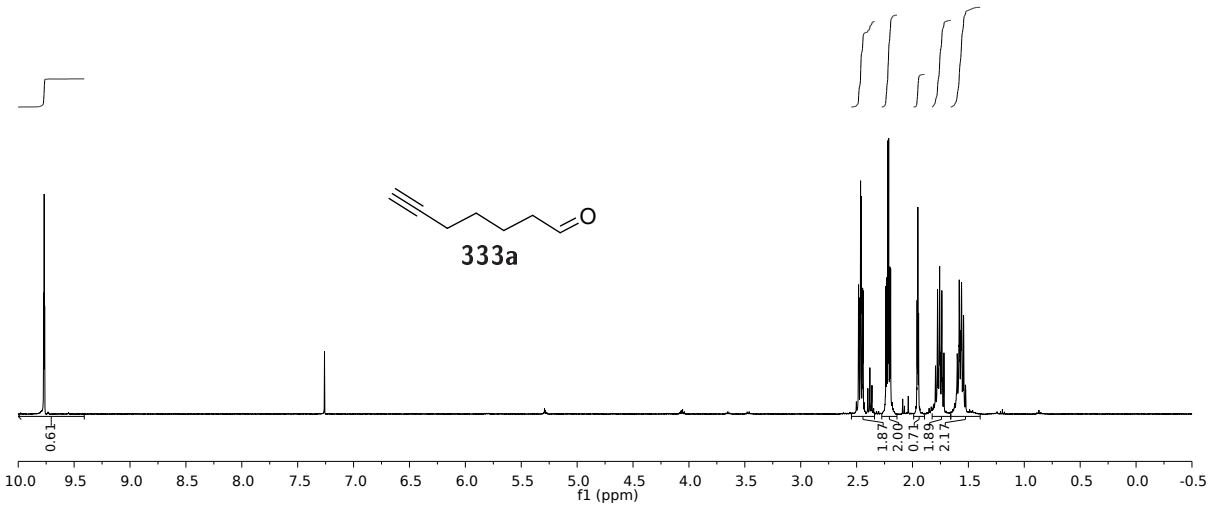
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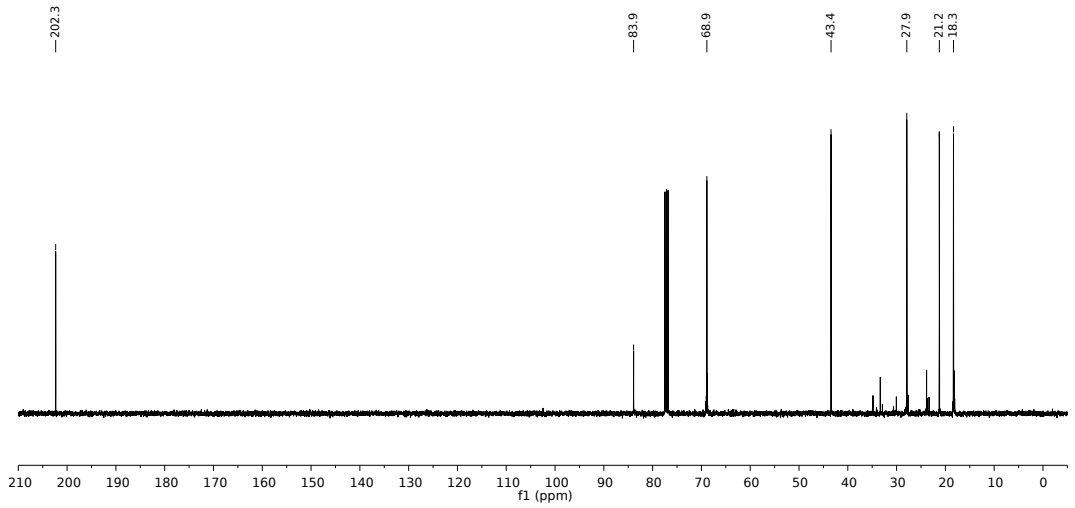
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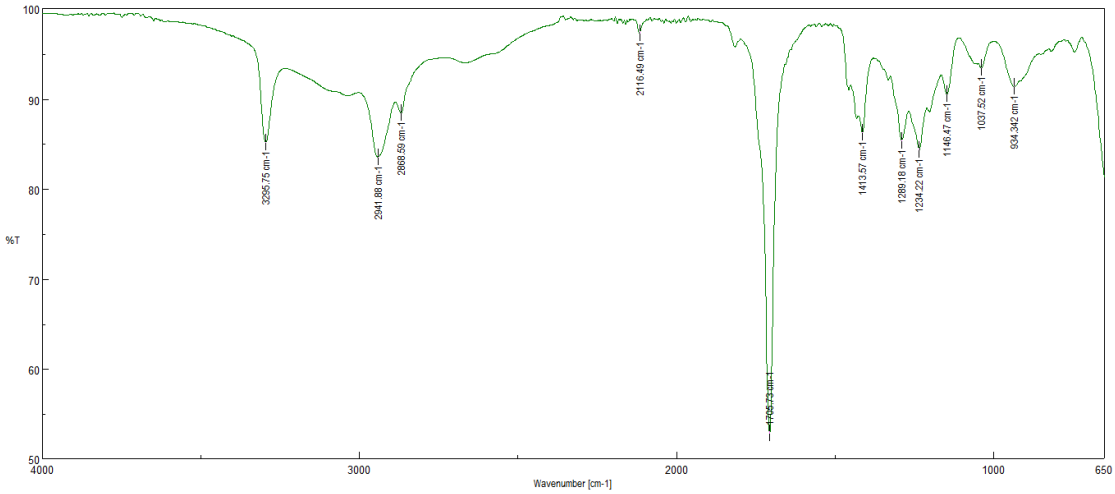
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2868.59 cm-1
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1234.22 cm-1
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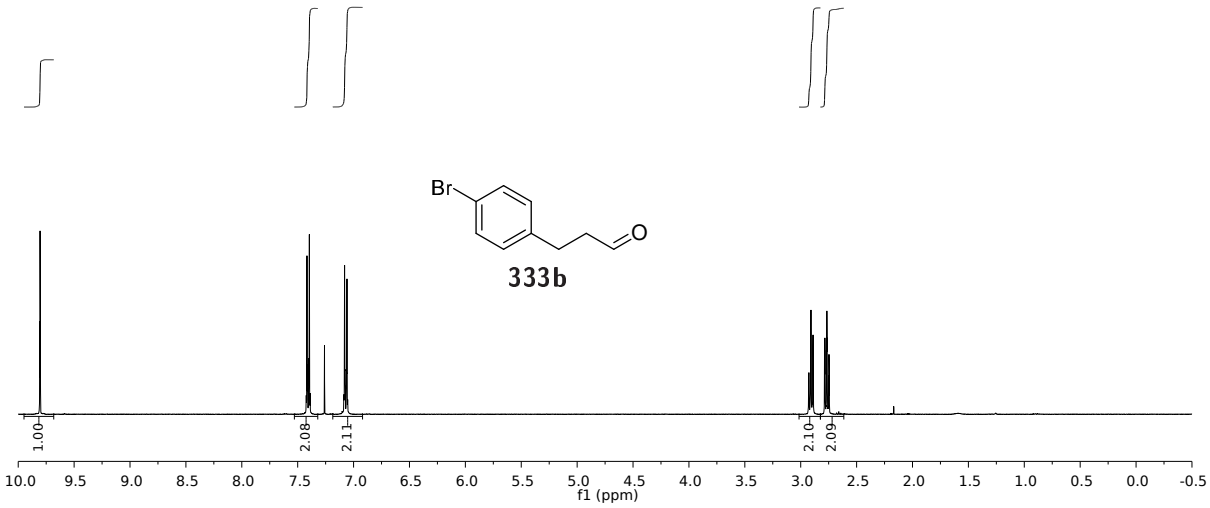
Wavenumber [cm-1]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O
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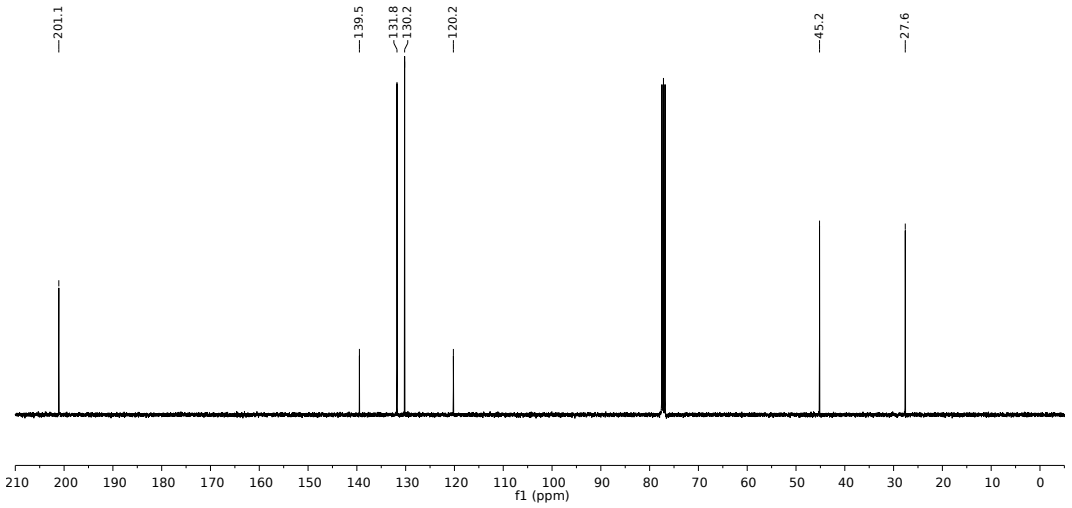
2.09
f1 (ppm)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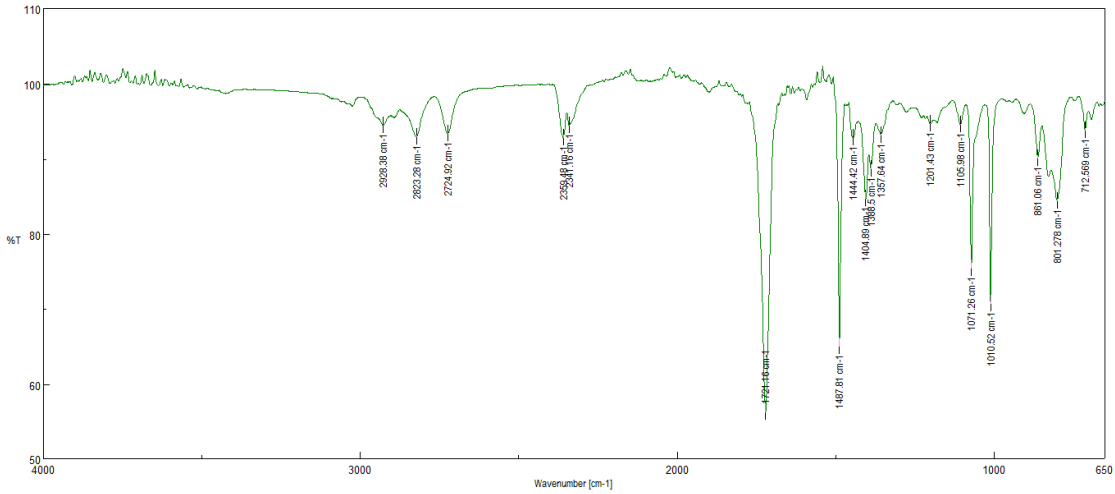
f1 (ppm)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1404.89 cm-1
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1357.04 cm-1
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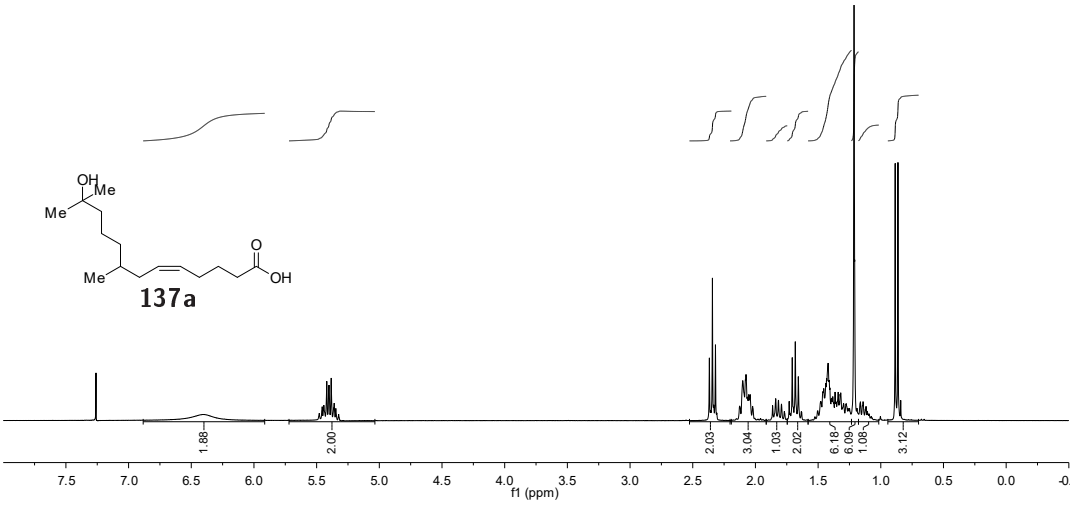
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Me
Me
O
OH
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6.09
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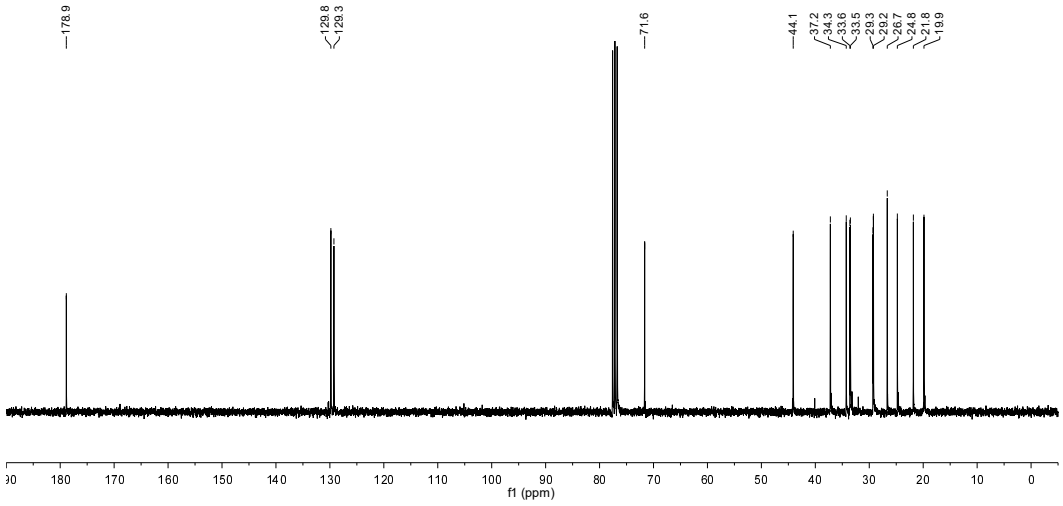
f1 (ppm)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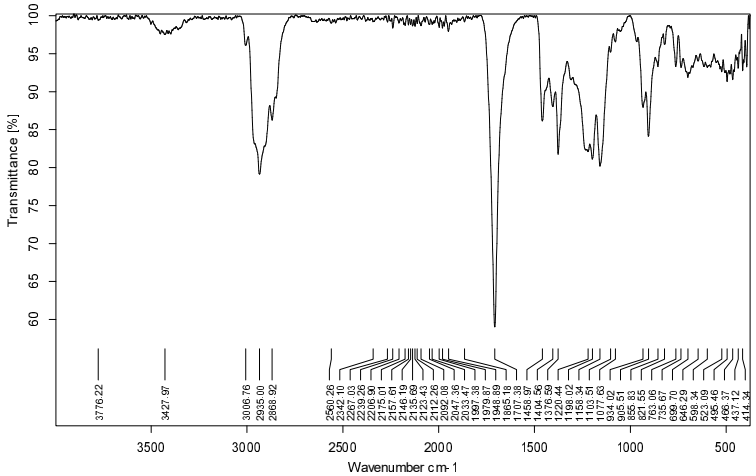
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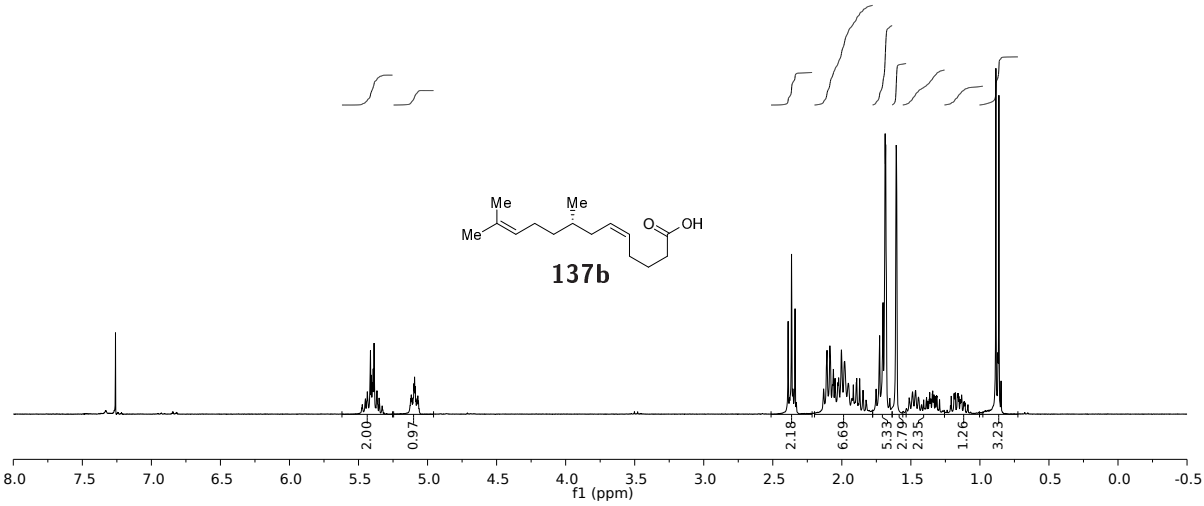
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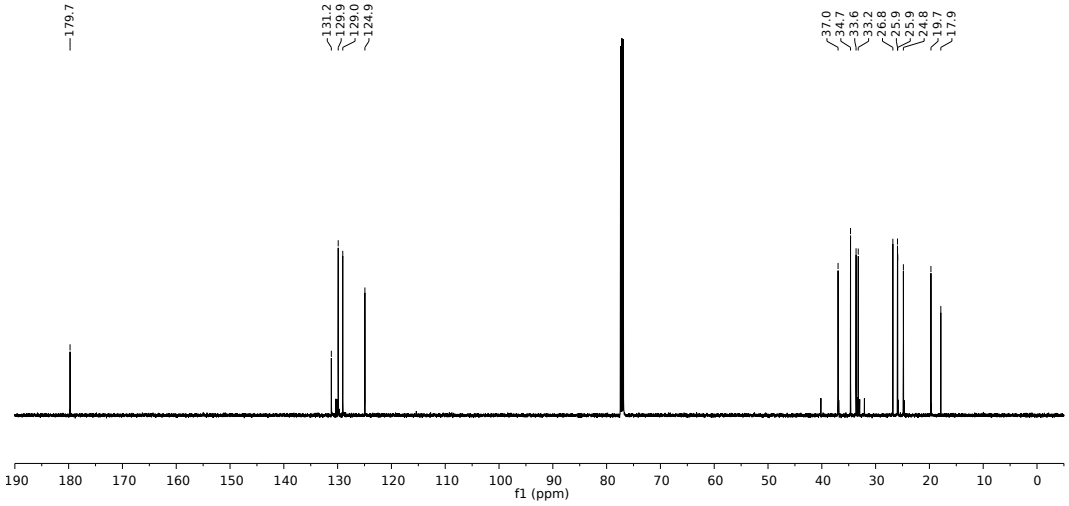
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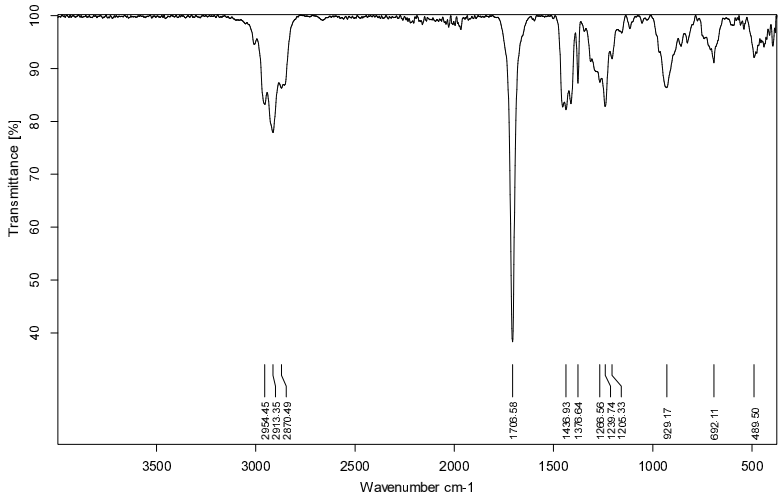
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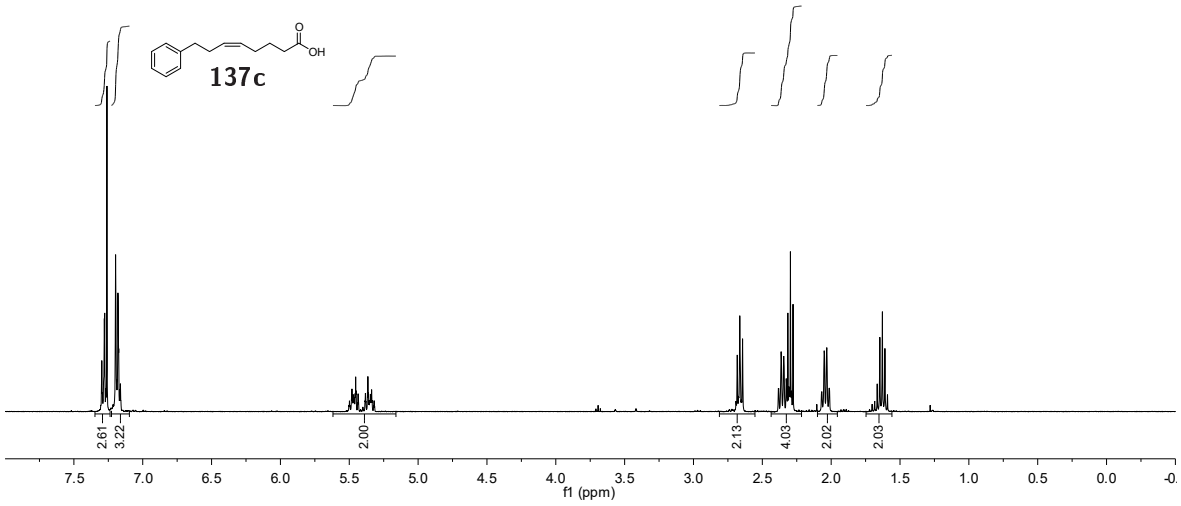
Wavenumber cm-1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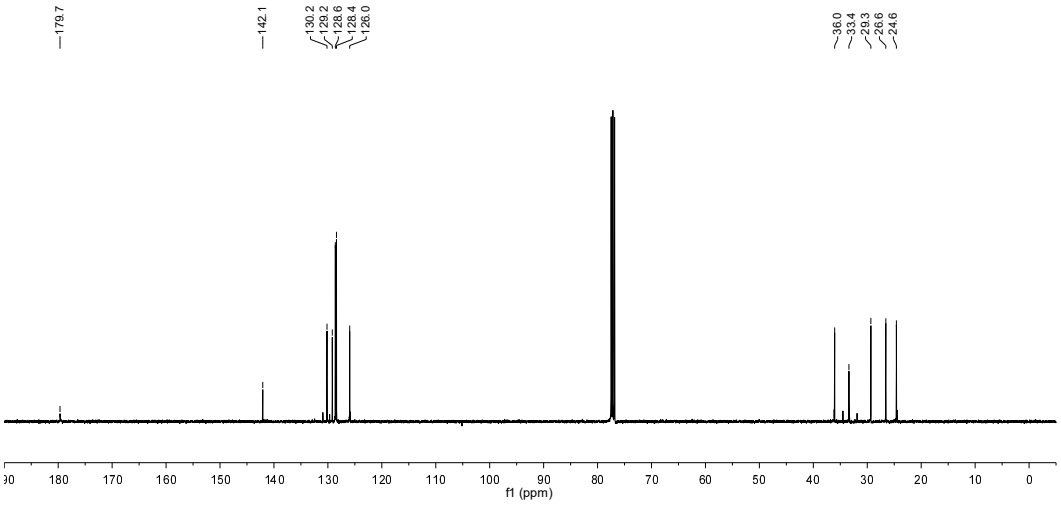
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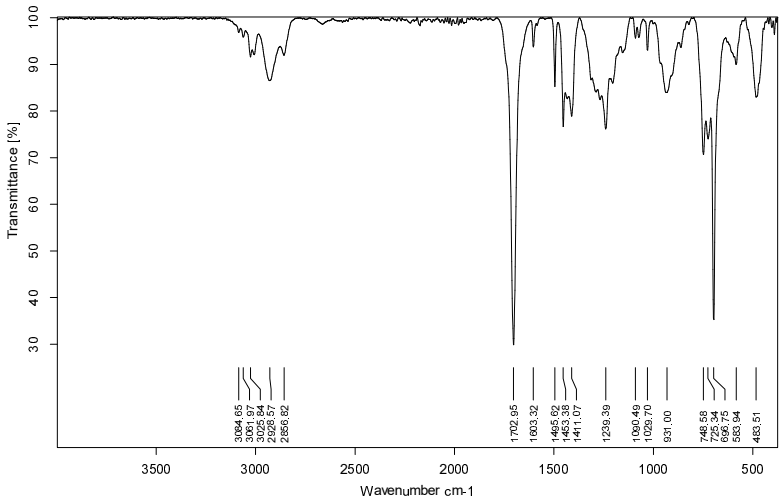
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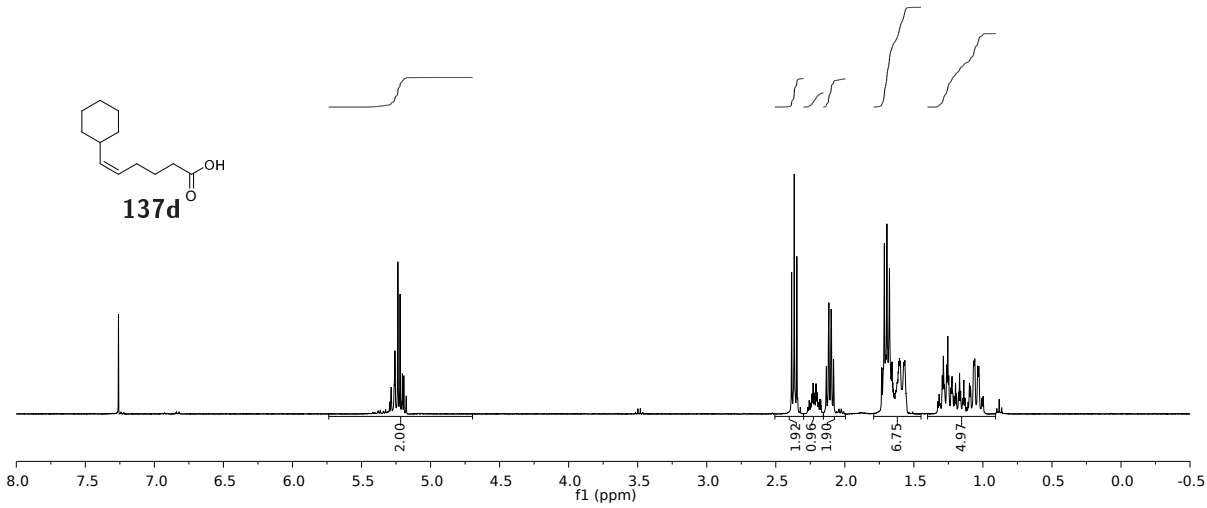
Wavenumber cm-1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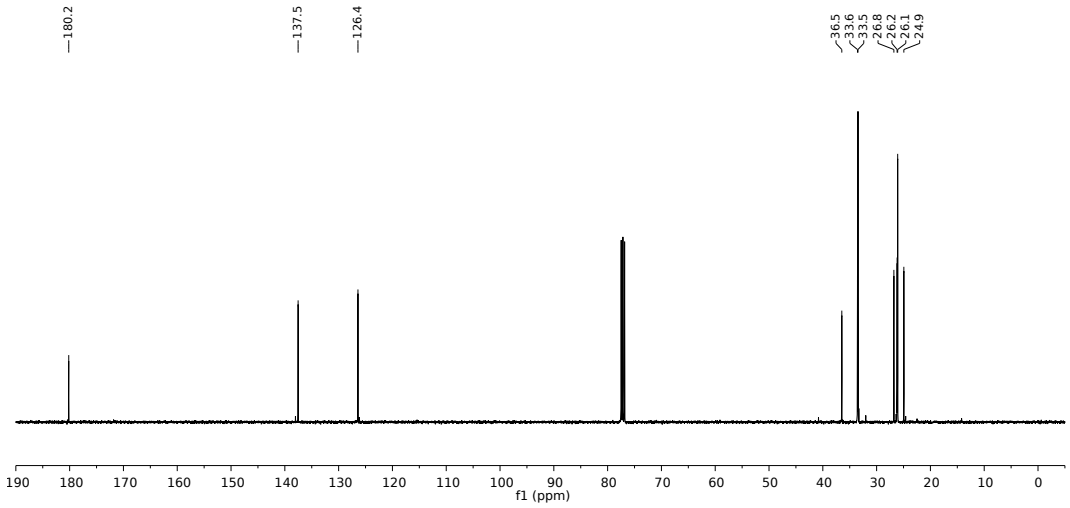
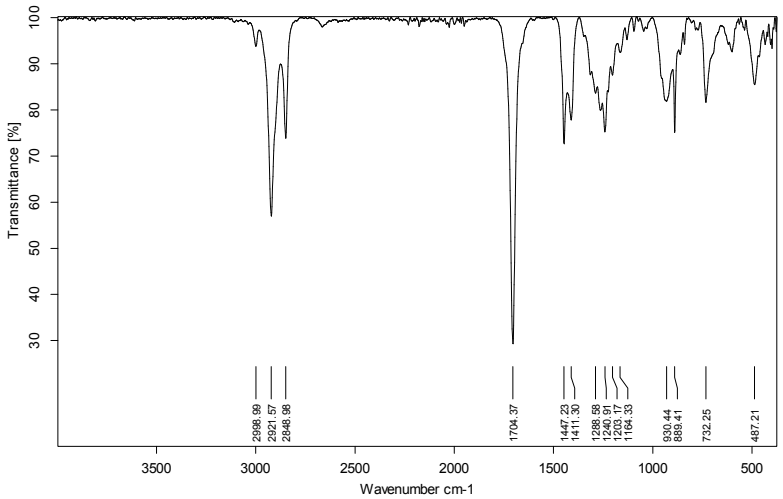
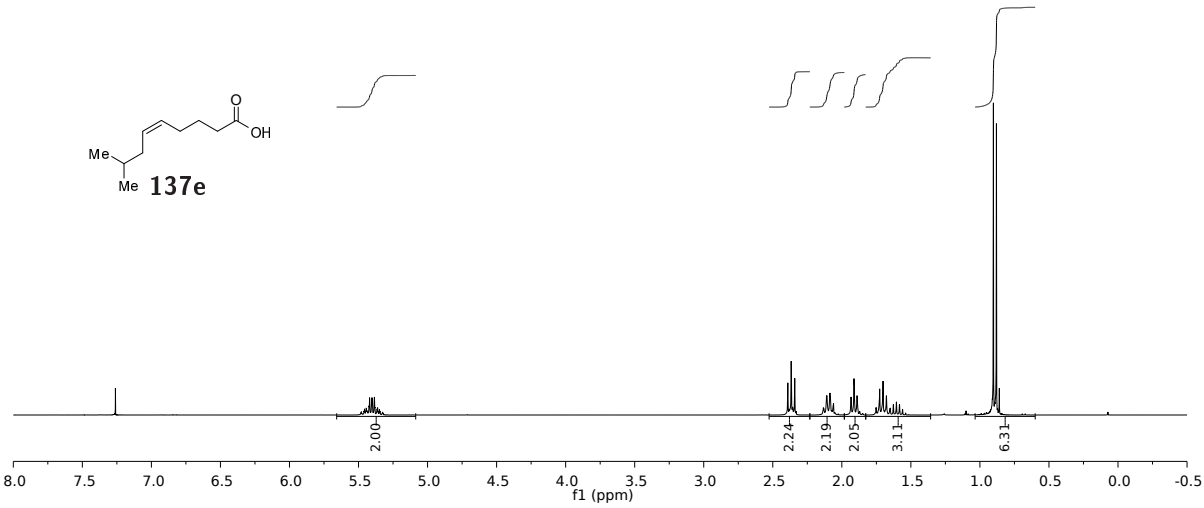
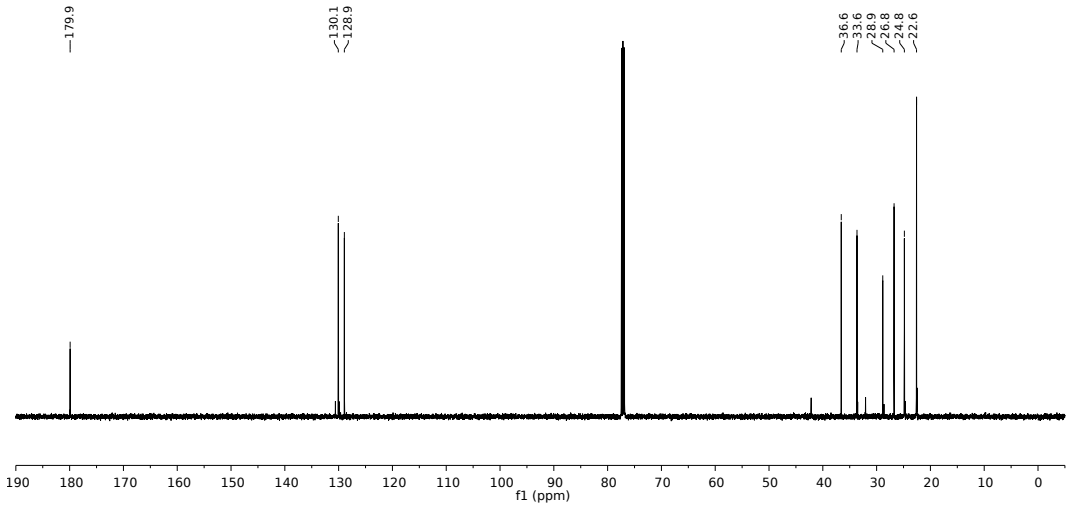
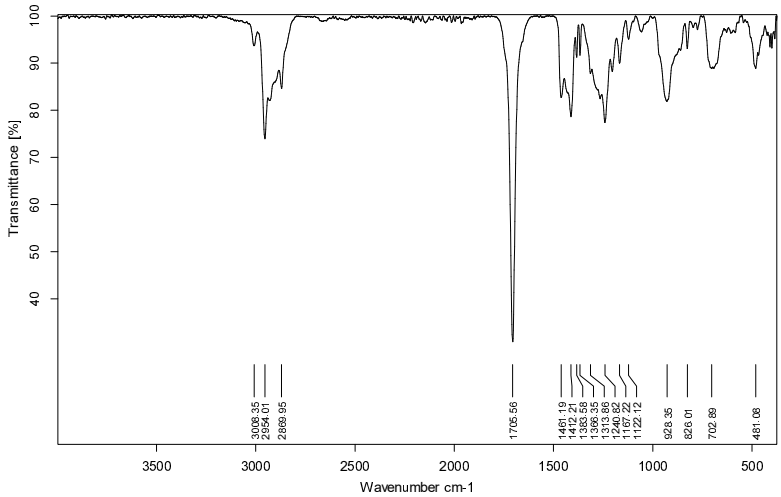
f1 (ppm)

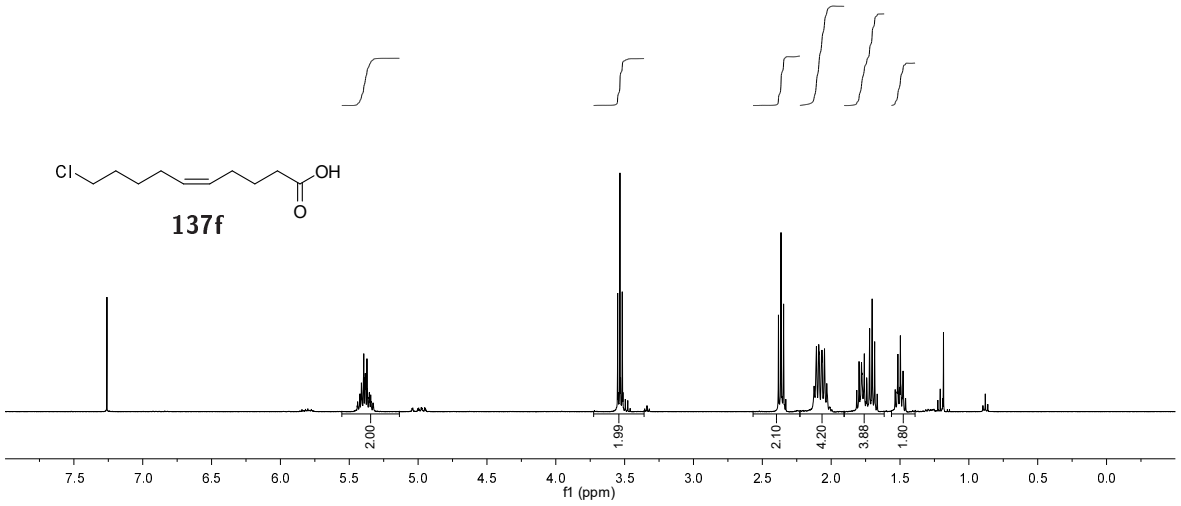

180.2
137.5
126.4
36.5
33.6
33.5
26.8
26.2
26.1
24.9
f1 (ppm)

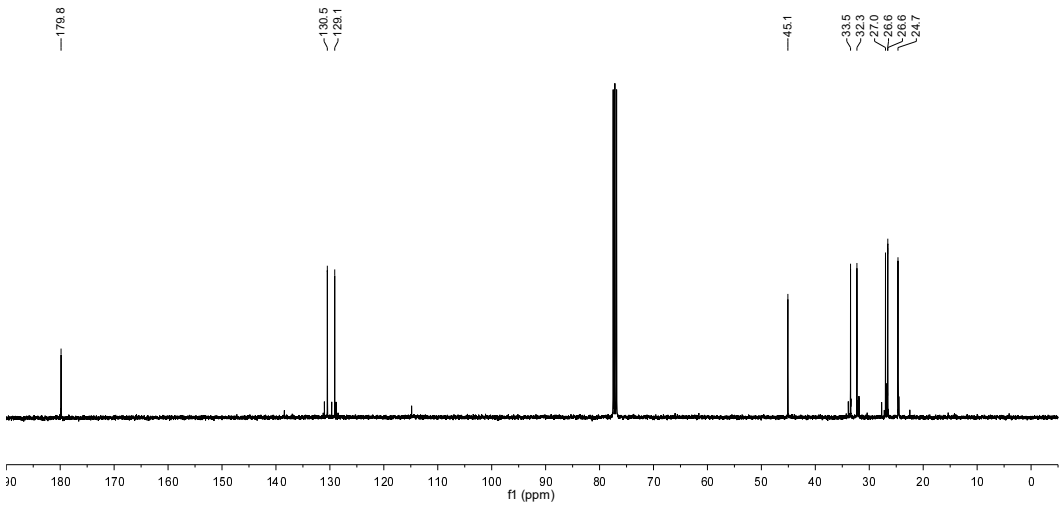

Transmittance [%]
2998.99
2921.57
2848.98
1704.37
1447.23
1411.30
1288.89
1240.91
1203.17
1164.33
930.44
889.41
732.25
487.21
Wavenumber cm-1

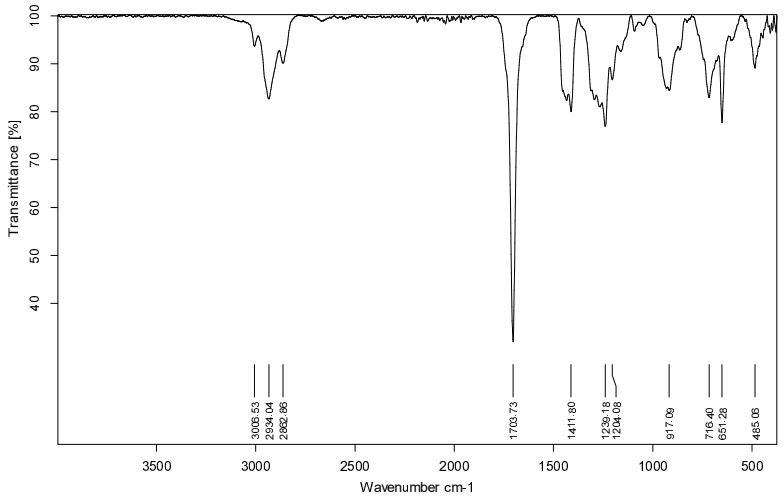

O
OH
Me
Me
137e
2.00
2.24
2.19
2.05
3.11
6.31
f1 (ppm)

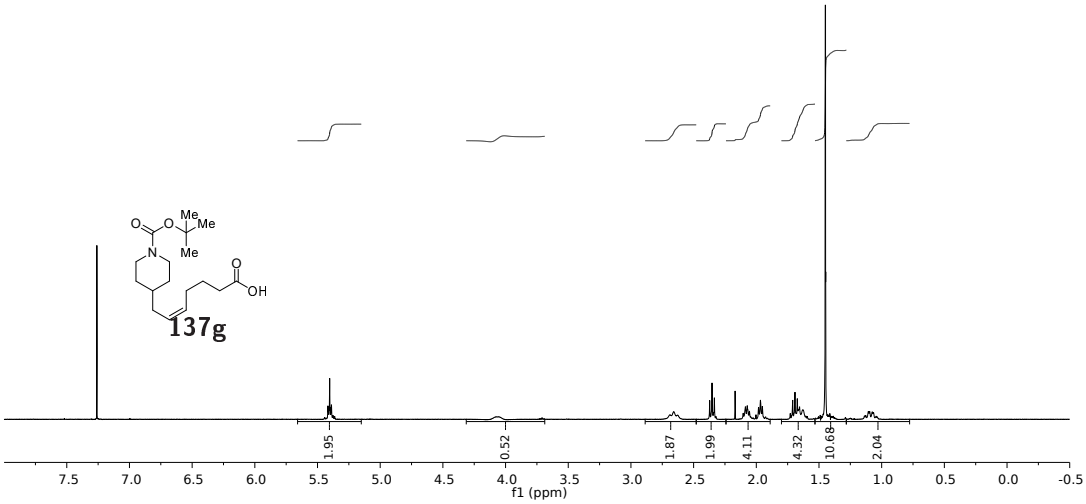

179.9
130.1
128.9
36.6
33.6
28.9
26.8
24.8
22.6
f1 (ppm)

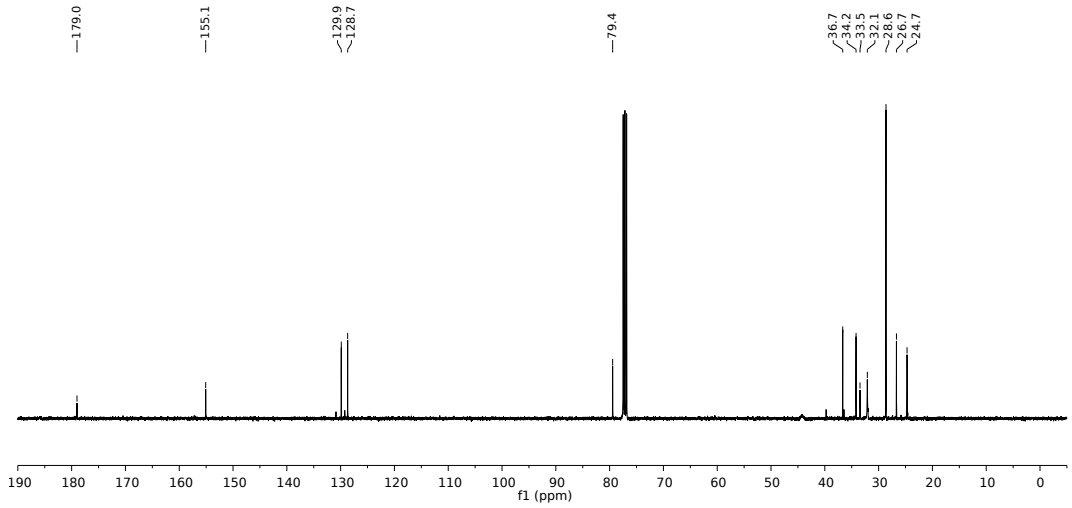

Transmittance [%]
3008.35
2954.01
2869.95
1705.56
1461.19
1412.21
1383.58
1366.35
1313.86
1240.82
1167.22
1122.12
928.35
826.01
702.89
481.08
Wavenumber cm-1

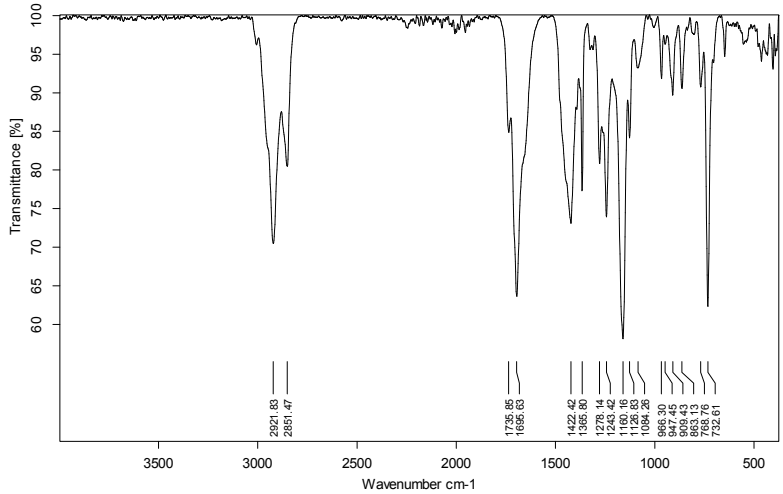

Cl
OH
O
137f
2.00
1.99
2.10
4.20
3.88
1.80
f1 (ppm)

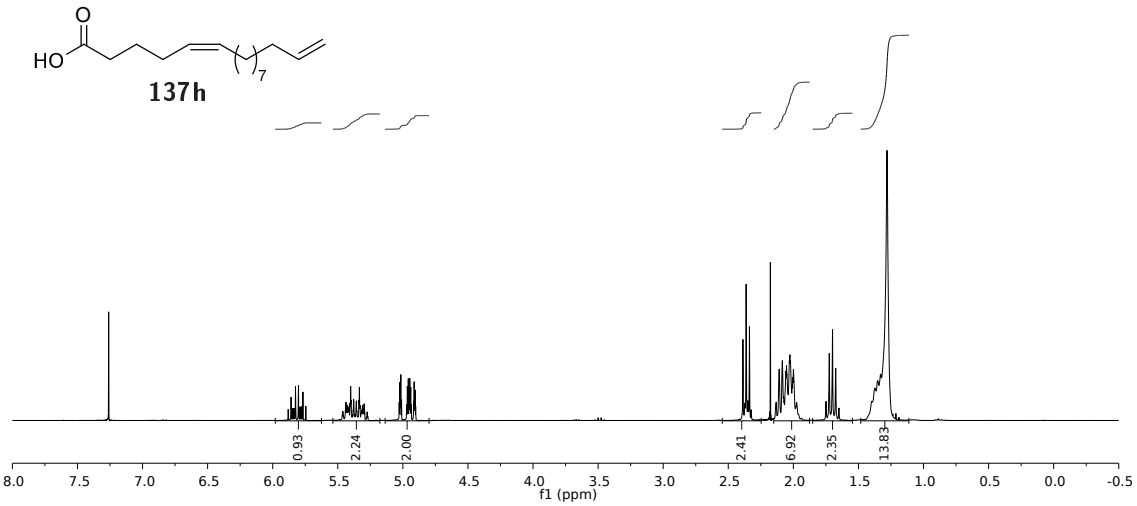

179.8
130.5
129.1
45.1
33.5
32.3
27.0
26.6
26.6
24.7
f1 (ppm)

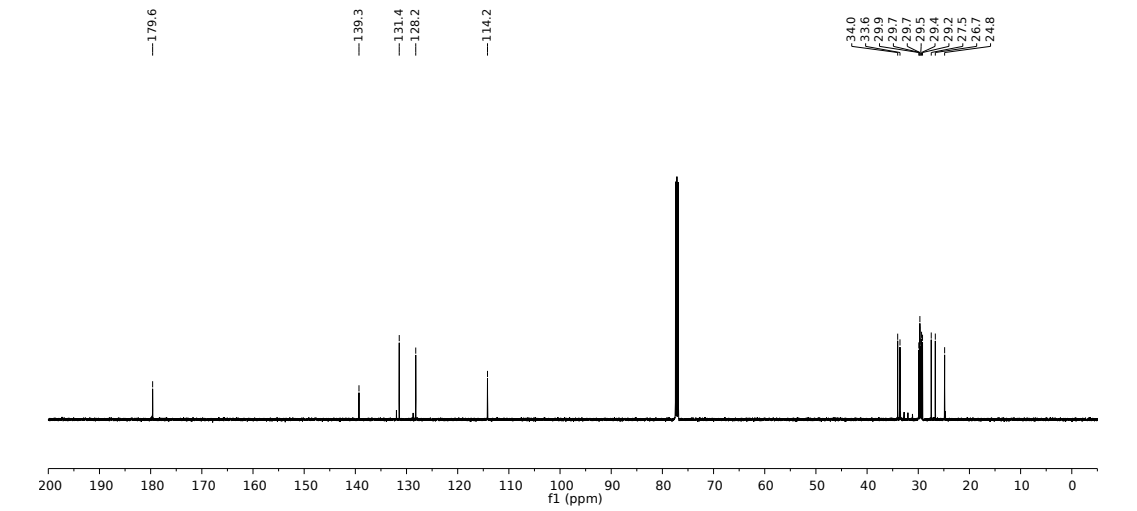

Transmittance [%]
3005.53
2934.04
2862.98
1703.73
1411.80
1239.18
1204.08
917.09
716.40
651.28
485.06
Wavenumber cm-1

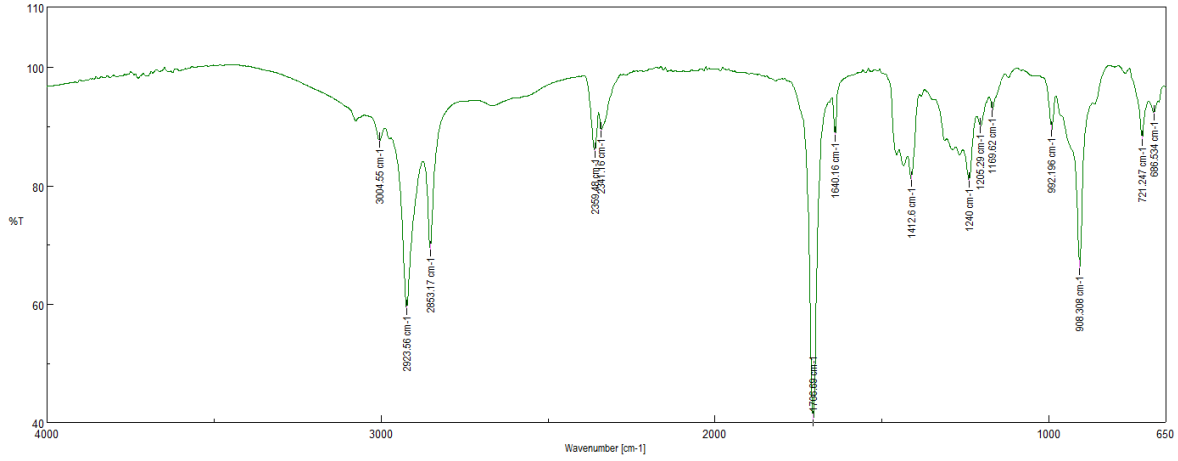

Me
Me
Me
O
O
N
O
OH
137g
1.95
0.52
1.87
1.99
4.11
4.32
10.68
2.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

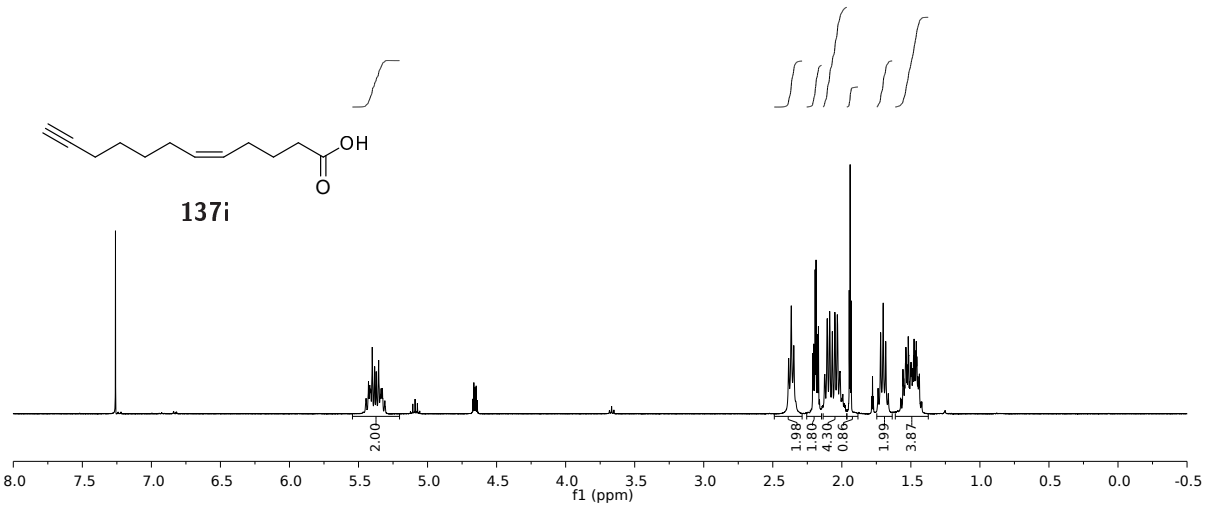

179.0
155.1
129.9
128.7
79.4
36.7
34.2
33.5
32.1
28.6
26.7
24.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

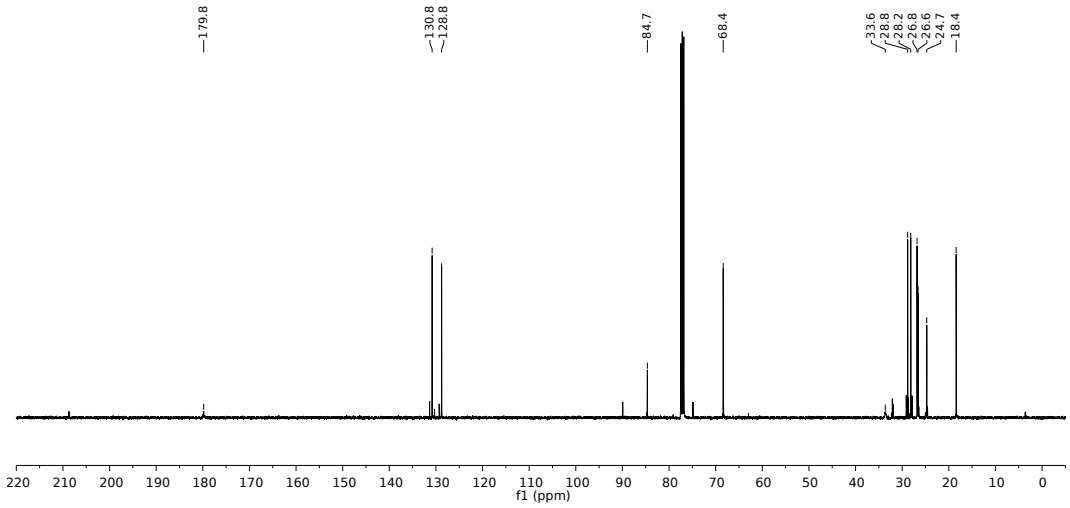

Transmittance [%]
100 95 90 85 80 75 70 65 60
2921.83
2851.47
1735.85
1685.63
1422.42
1365.80
1278.14
1243.42
1160.16
1135.88
1084.28
966.30
947.45
909.43
863.13
783.76
732.61
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

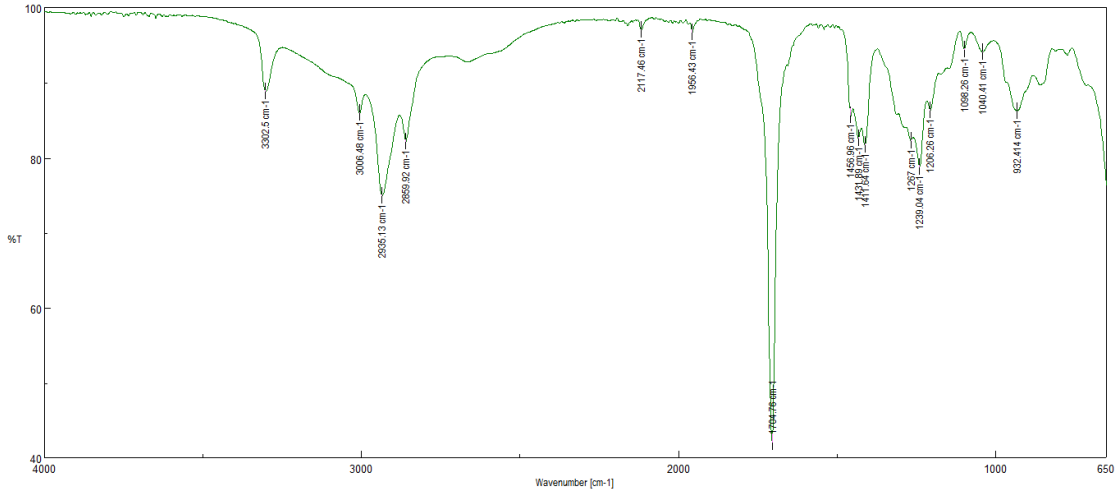

O
HO
7
137h
0.93
2.24
2.00
2.41
6.92
2.35
13.83
f1 (ppm)

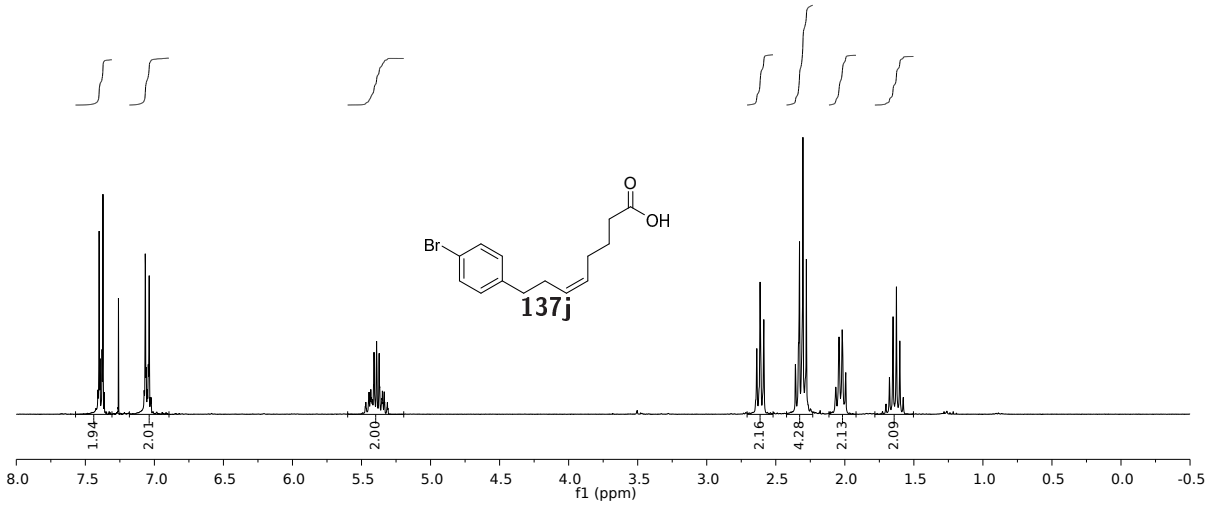

179.6
139.3
131.4
128.2
114.2
34.0
33.6
29.9
29.7
29.7
29.5
29.4
29.2
27.5
26.7
24.8
f1 (ppm)

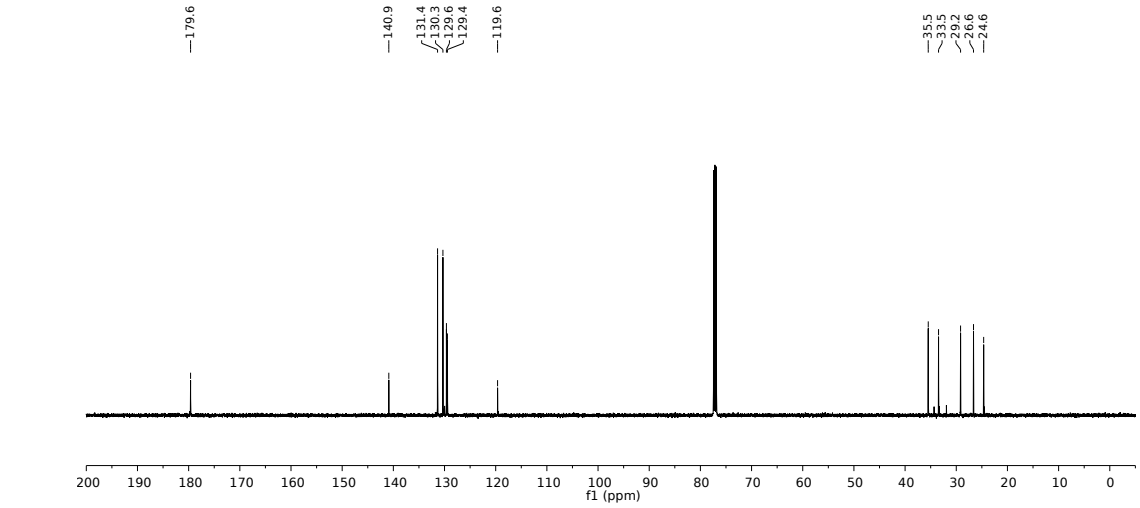

%T
3004.55 cm-1
2923.56 cm-1
2853.17 cm-1
2369.48 cm-1
2341.19 cm-1
1640.16 cm-1
1412.6 cm-1
1240 cm-1
1205.29 cm-1
1169.62 cm-1
992.196 cm-1
908.308 cm-1
721.247 cm-1
686.534 cm-1
Wavenumber [cm-1]

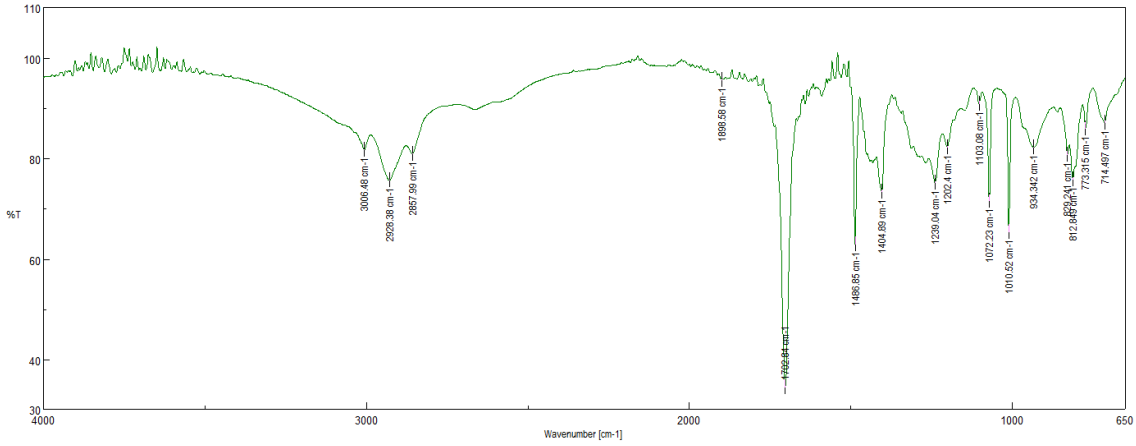

OH
O
137i
2.00
1.98
1.80
4.30
0.86
1.99
3.87
f1 (ppm)

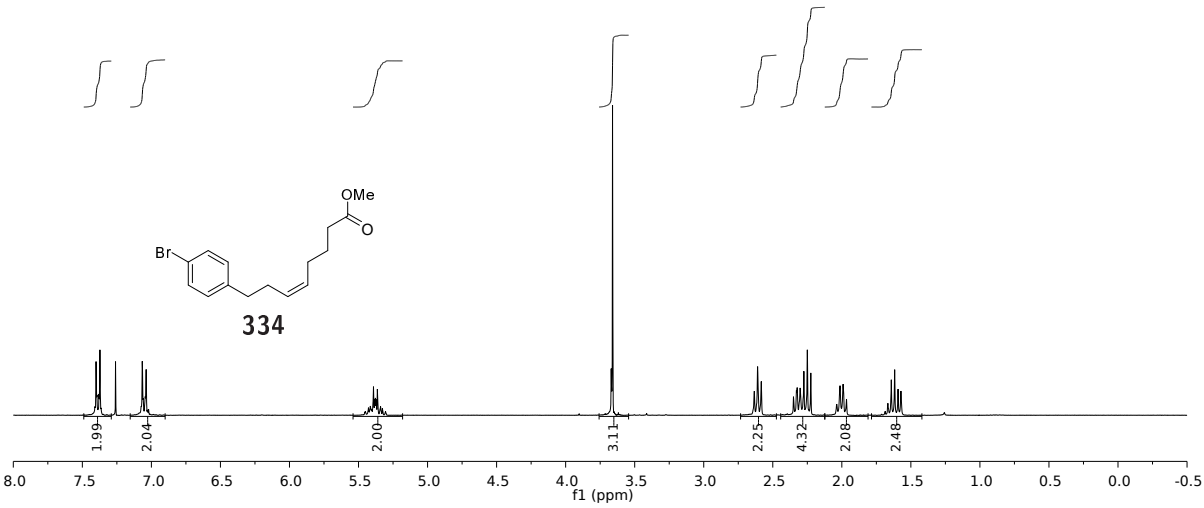

179.8
130.8
128.8
84.7
68.4
33.6
28.8
28.2
26.8
26.6
24.7
18.4
f1 (ppm)

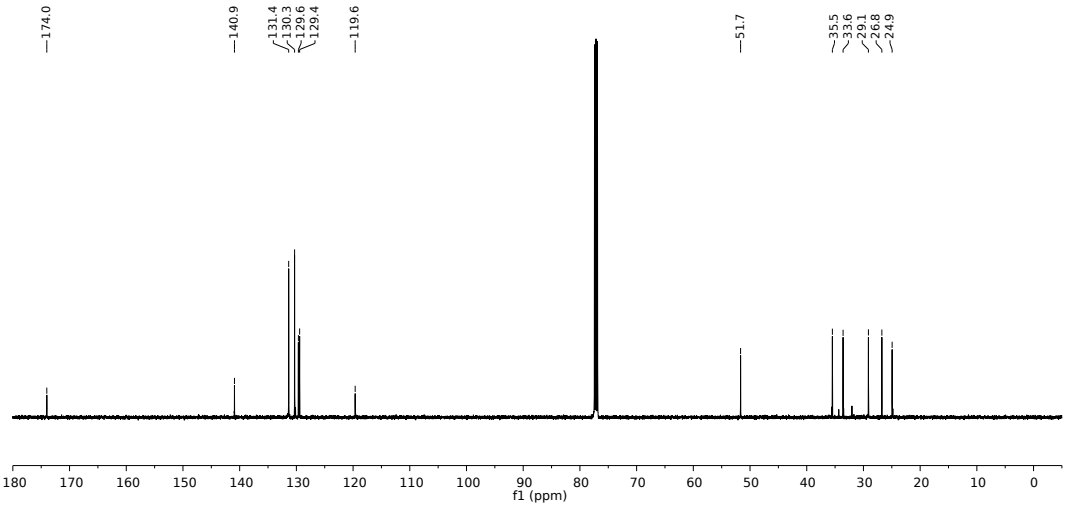

%T
3302.5 cm-1
3006.48 cm-1
2926.13 cm-1
2859.92 cm-1
2117.46 cm-1
1956.43 cm-1
1704.76 cm-1
1456.96 cm-1
1267 cm-1
1239.04 cm-1
1206.26 cm-1
1098.28 cm-1
1040.41 cm-1
932.414 cm-1
Wavenumber [cm-1]

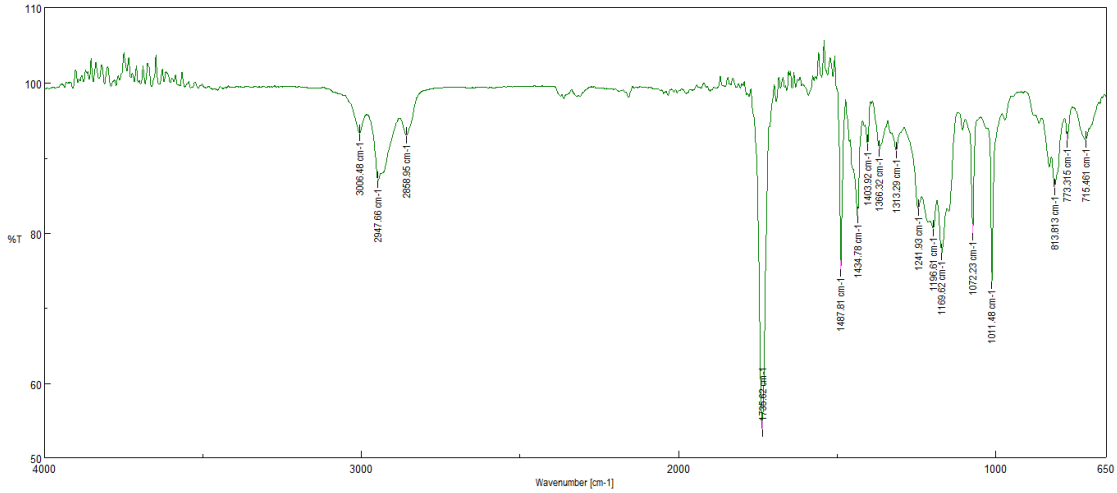

O
OH
Br
137j
1.94
2.01
2.00
2.16
4.28
2.13
2.09
f1 (ppm)

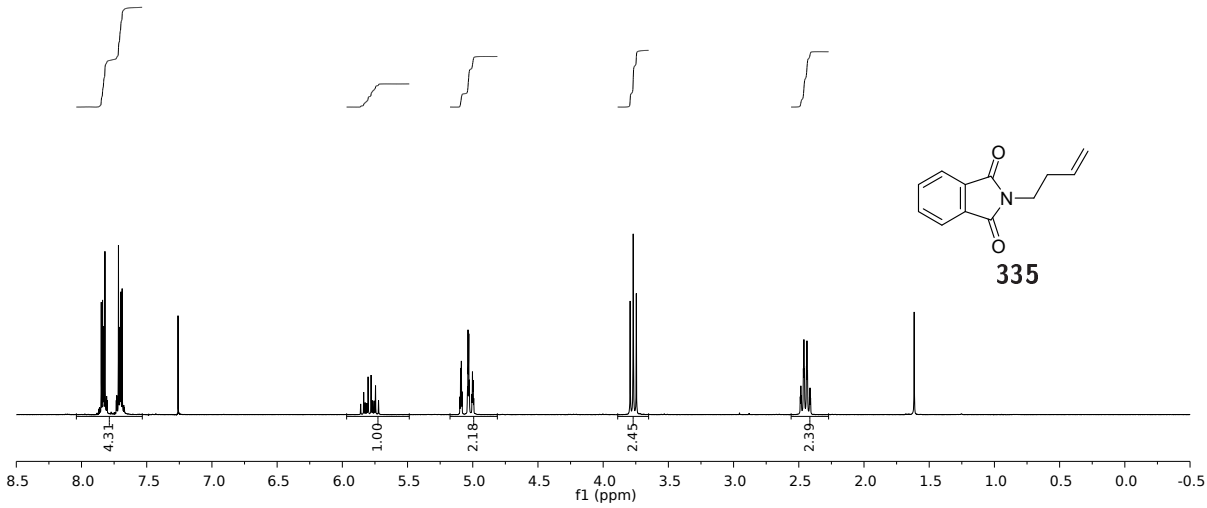

179.6
140.9
131.4
130.3
129.6
129.4
119.6
35.5
33.5
29.2
26.6
24.6
f1 (ppm)

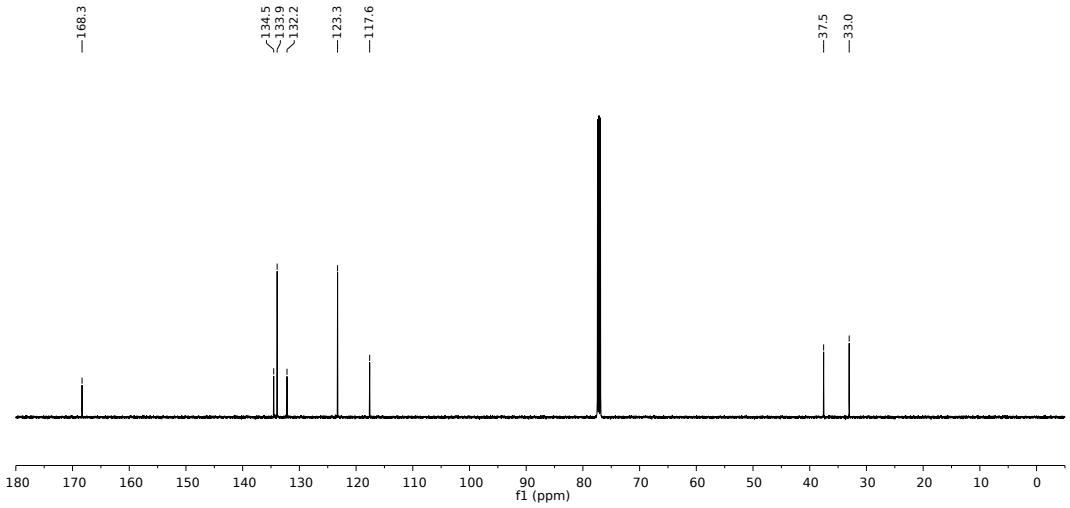

%T
3006.48 cm-1
2929.38 cm-1
2857.99 cm-1
1898.59 cm-1
1722.91 cm-1
1466.85 cm-1
1404.69 cm-1
1239.04 cm-1
1202.4 cm-1
1103.08 cm-1
1072.23 cm-1
1010.52 cm-1
934.342 cm-1
812.885 cm-1
773.315 cm-1
714.497 cm-1
Wavenumber [cm-1]

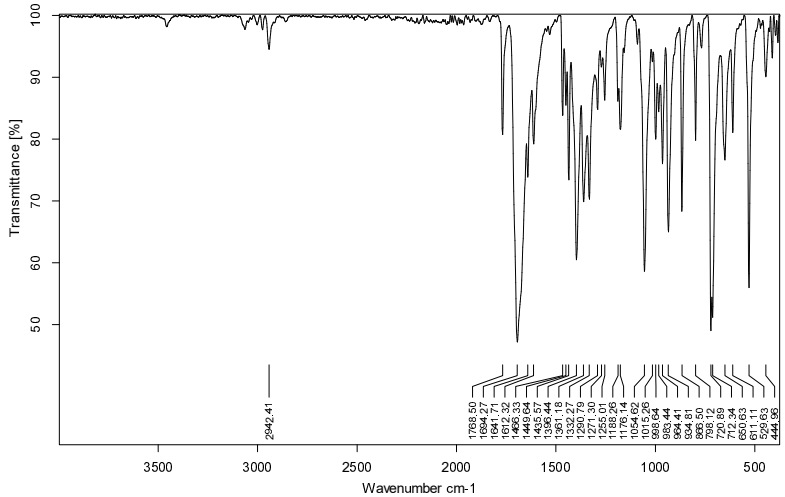

OMe
O
Br
334
1.99
2.04
2.00
3.11
2.25
4.32
2.08
2.48
f1 (ppm)

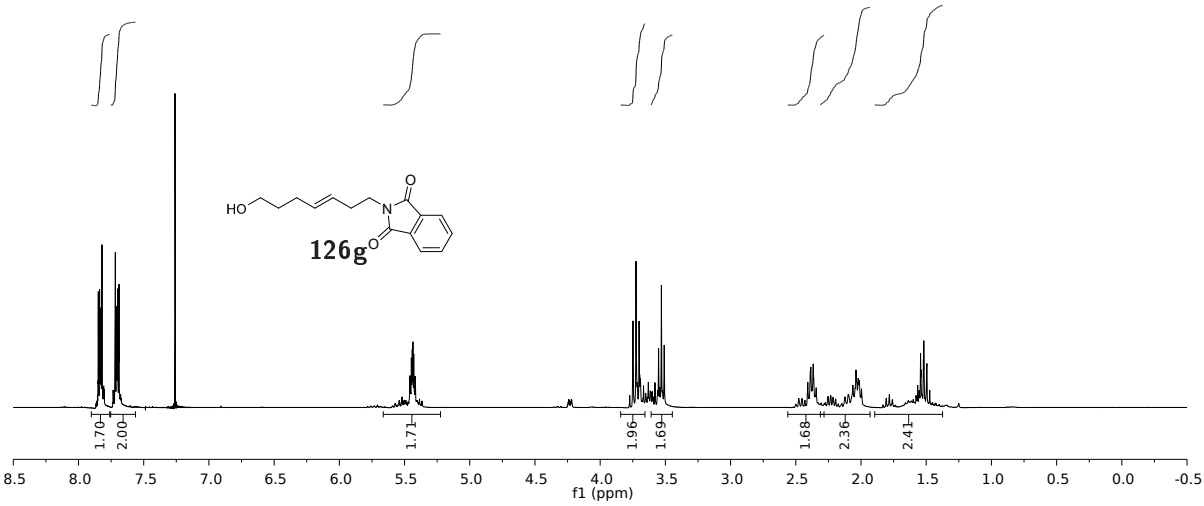

174.0
140.9
131.4
130.3
129.6
129.4
119.6
51.7
35.5
33.6
29.1
26.8
24.9
f1 (ppm)

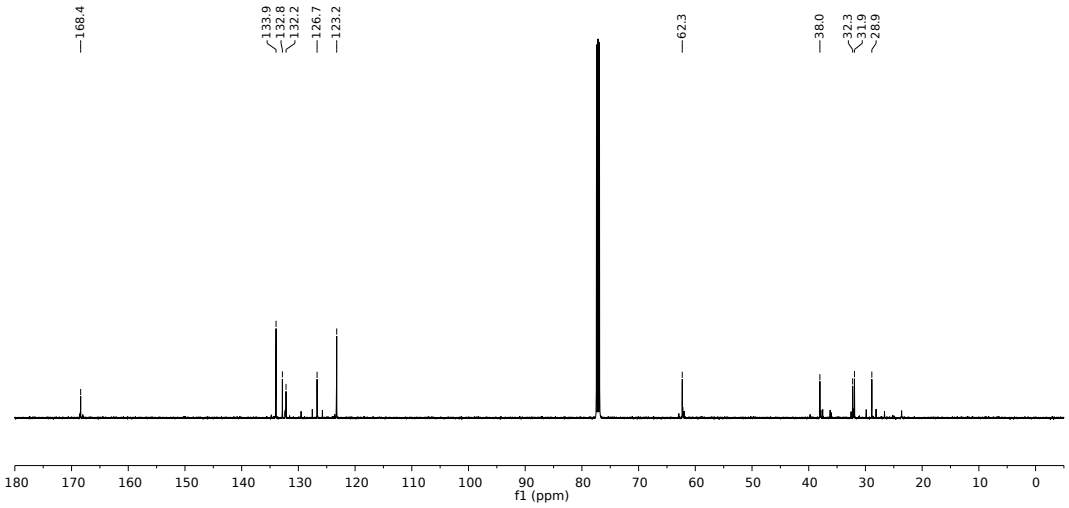

%T
3066.48 cm-1
2947.66 cm-1
2858.95 cm-1
1487.81 cm-1
1434.78 cm-1
1403.92 cm-1
1366.32 cm-1
1313.29 cm-1
1241.93 cm-1
1196.61 cm-1
1169.62 cm-1
1072.23 cm-1
1011.48 cm-1
813.813 cm-1
773.215 cm-1
715.461 cm-1
Wavenumber [cm-1]

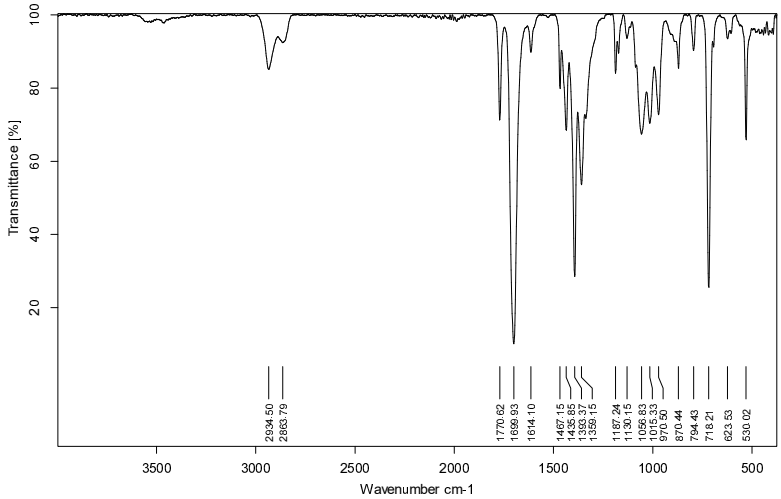

335
4.31
1.00
2.18
2.45
2.39
f1 (ppm)

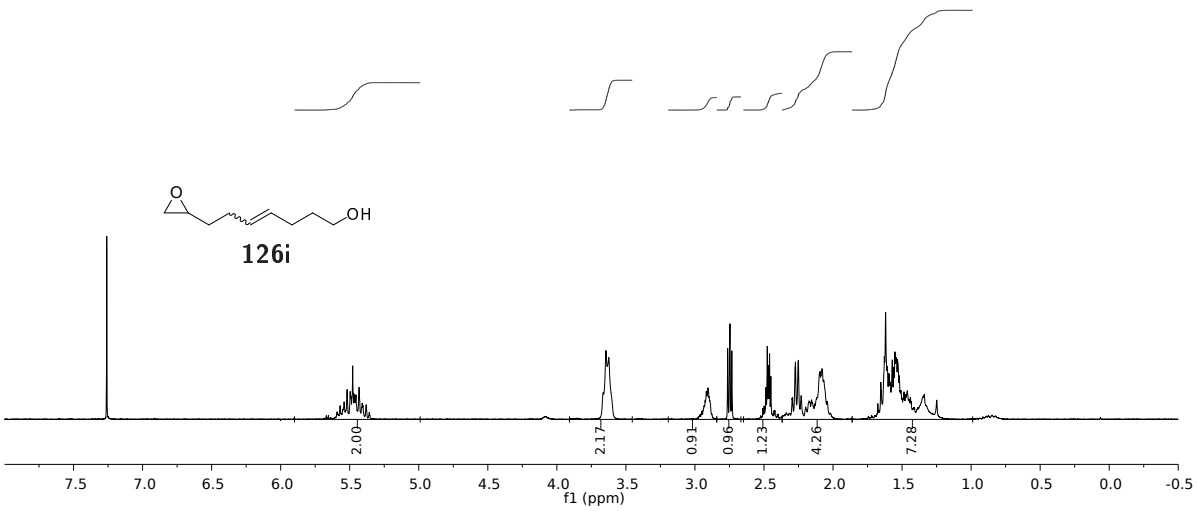

168.3
134.5
133.9
132.2
123.3
117.6
37.5
33.0
f1 (ppm)

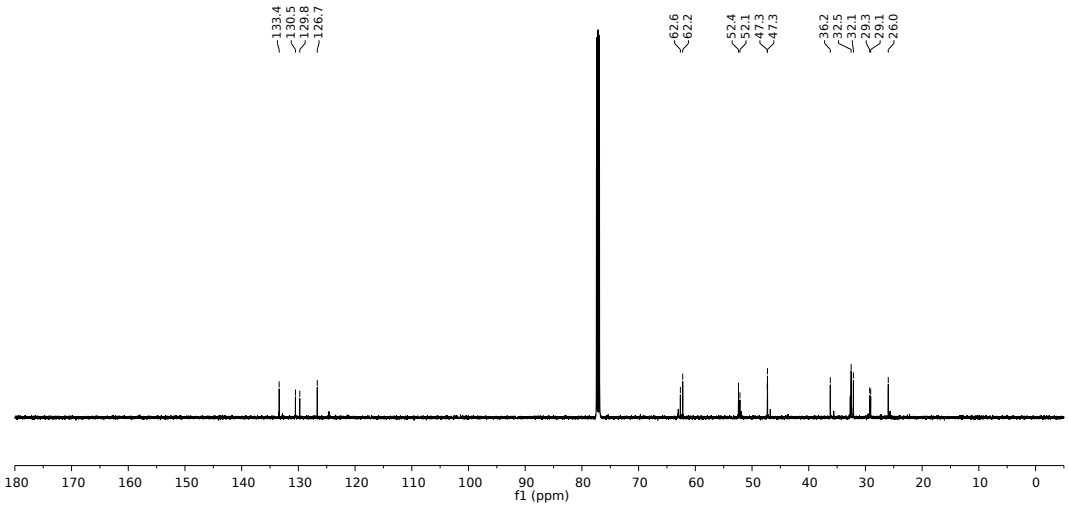

Transmittance [%]
Wavenumber cm-1
2942.41

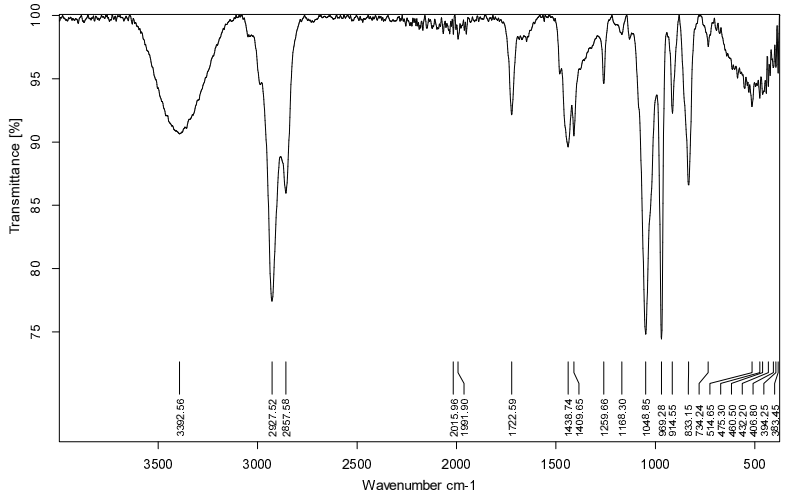

HO
N
O
O
126g
1.70
2.00
1.71
1.96
1.69
1.68
2.36
2.41
f1 (ppm)

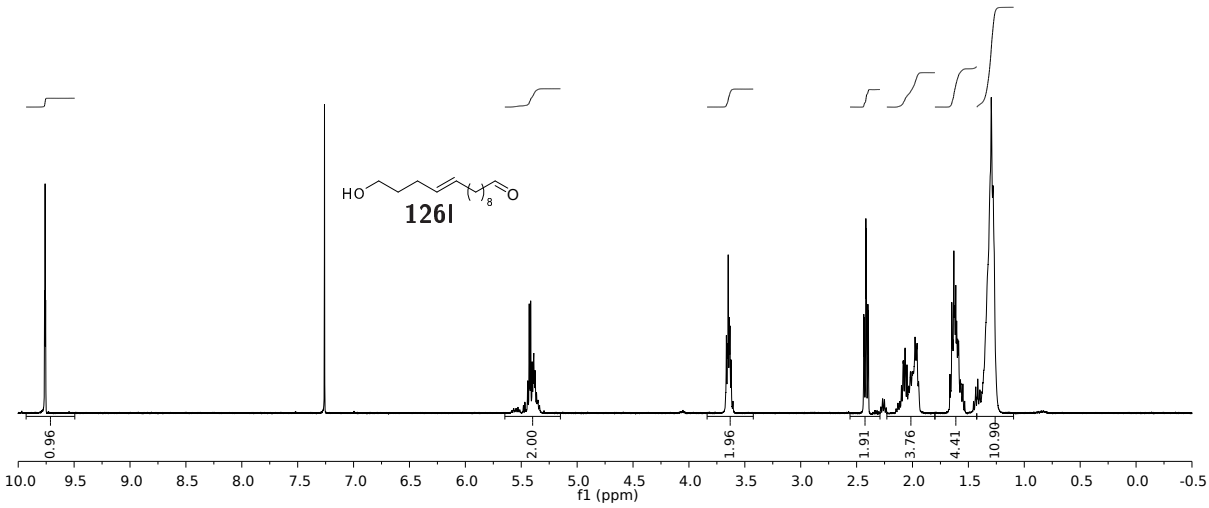

168.4
133.9
132.8
132.2
126.7
123.2
62.3
38.0
32.3
31.9
28.9
f1 (ppm)

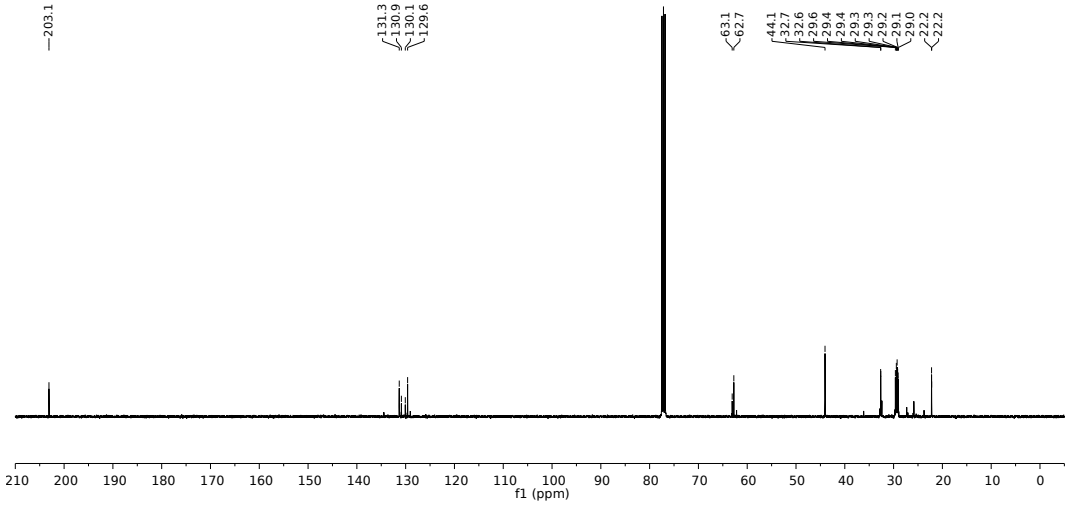

Transmittance [%]
2934.50
2863.79
1770.62
1699.93
1614.10
1467.15
1435.85
1393.37
1359.15
1167.24
1130.15
1056.83
1015.33
970.50
870.44
794.43
718.21
623.53
530.02
Wavenumber cm-1

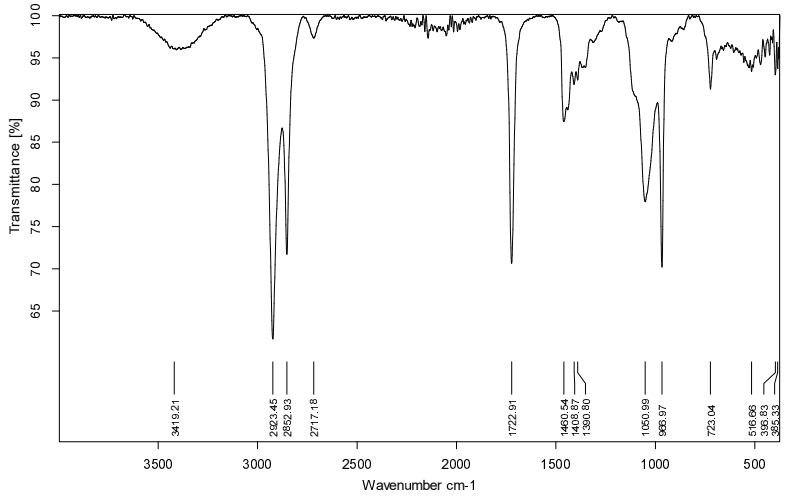

O
OH
126i
2.00
2.17
0.91
0.96
1.23
4.26
7.28
f1 (ppm)

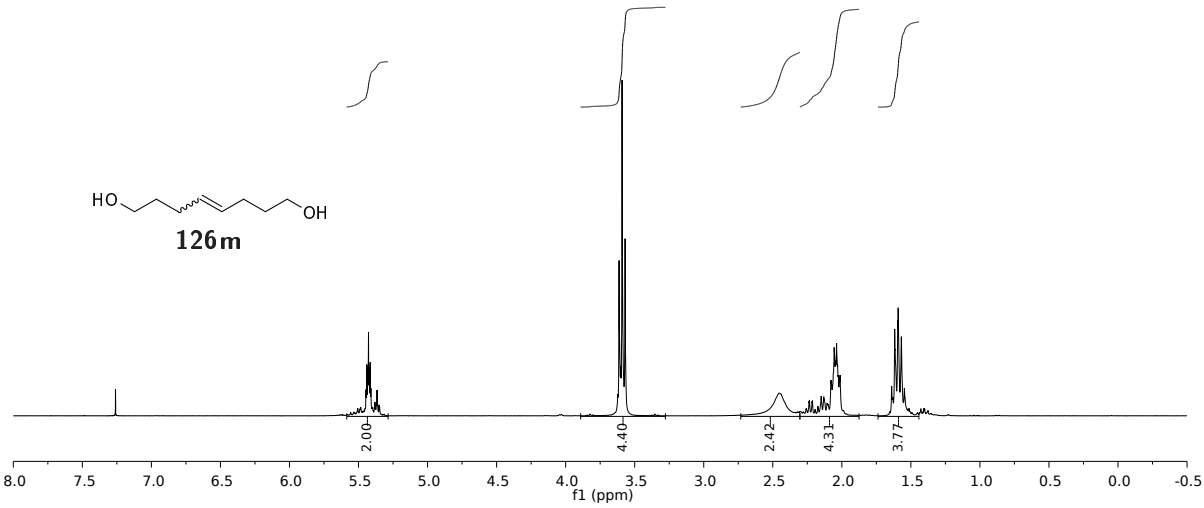

133.4
130.5
129.8
126.7
62.6
62.2
52.4
52.1
47.3
47.3
36.2
32.5
32.1
29.3
29.1
26.0
f1 (ppm)

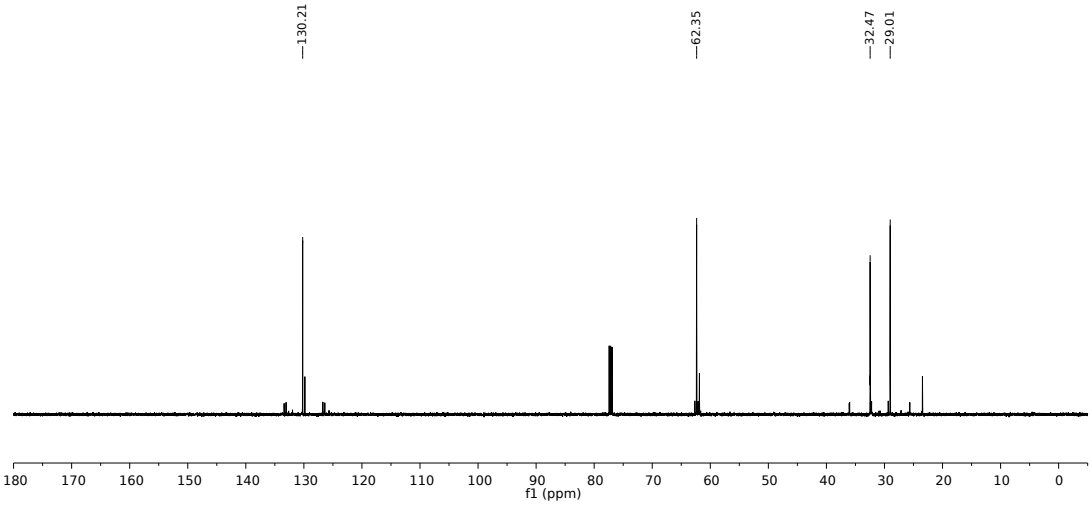

Transmittance [%]
3392.56
2927.52
2857.58
2015.96
1981.80
1722.59
1438.74
1409.65
1259.66
1168.30
1048.85
990.28
914.55
833.15
734.24
514.65
475.30
460.50
432.20
406.80
394.25
383.45
Wavenumber cm-1

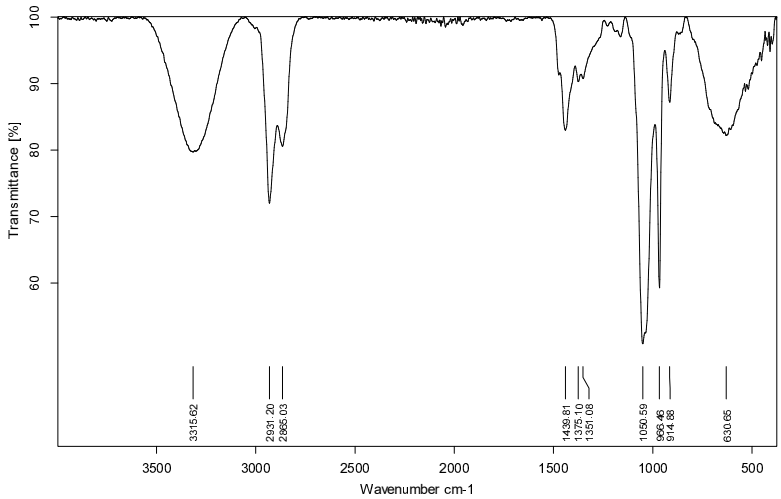

HO
8
O
126l
0.96
2.00
1.96
1.91
3.76
4.41
10.90
f1 (ppm)

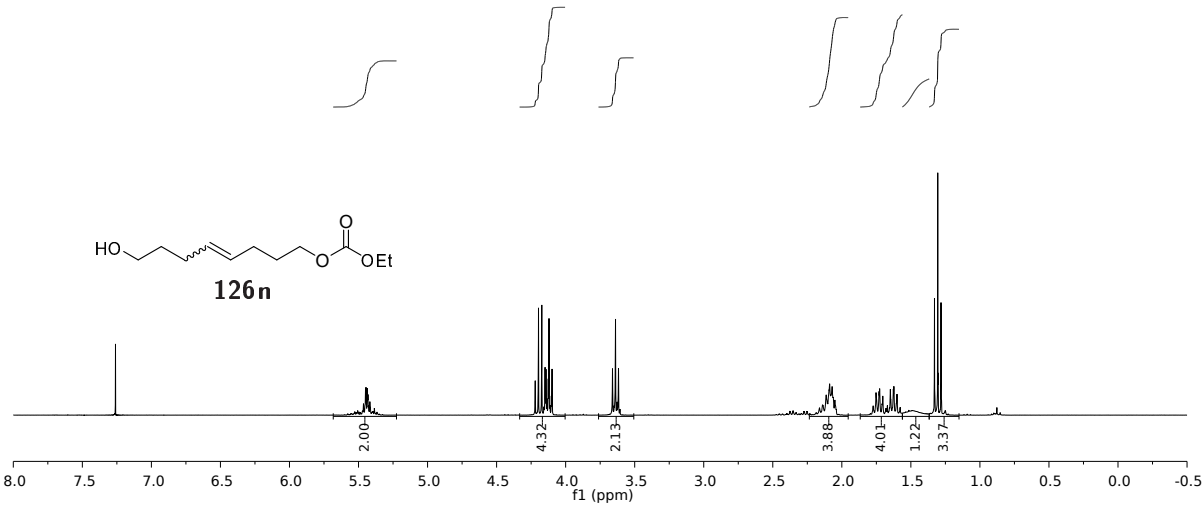

203.1
131.3
130.9
130.1
129.6
63.1
62.7
44.1
32.7
32.6
29.6
29.4
29.4
29.3
29.3
29.2
29.1
29.0
22.2
22.2
f1 (ppm)

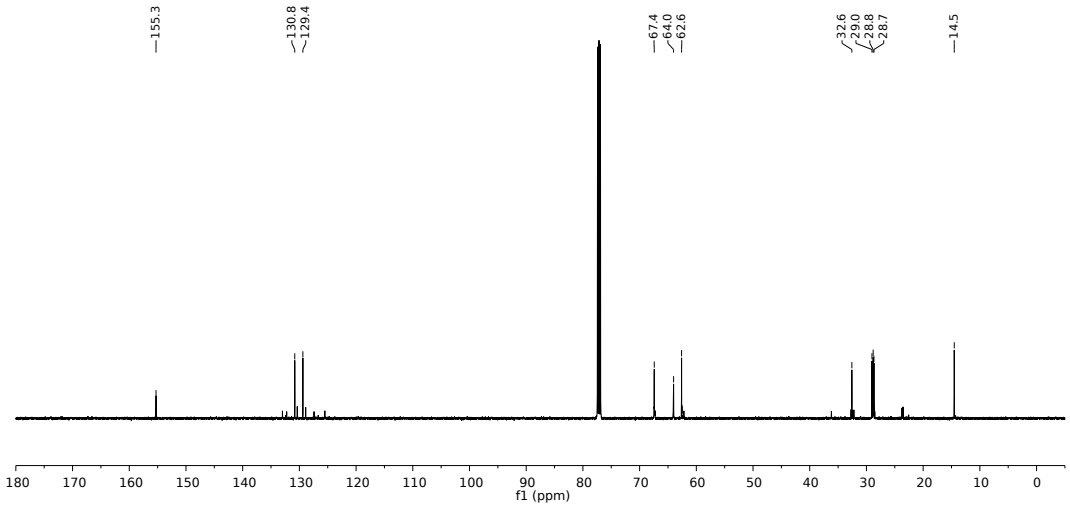

Transmittance [%]
3419.21
2923.45
2852.93
2717.18
1722.91
1460.54
1408.97
1390.80
1050.99
966.97
723.04
516.66
395.83
355.33
Wavenumber cm-1

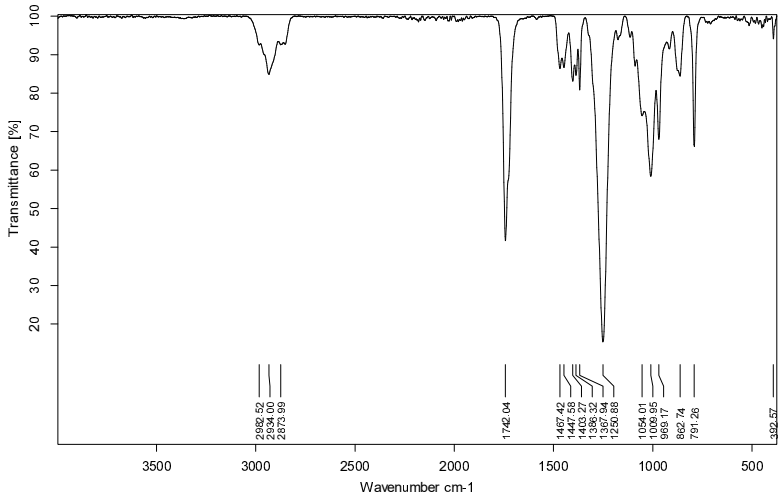

HO
OH
126m
2.00
4.40
2.42
4.31
3.77
f1 (ppm)

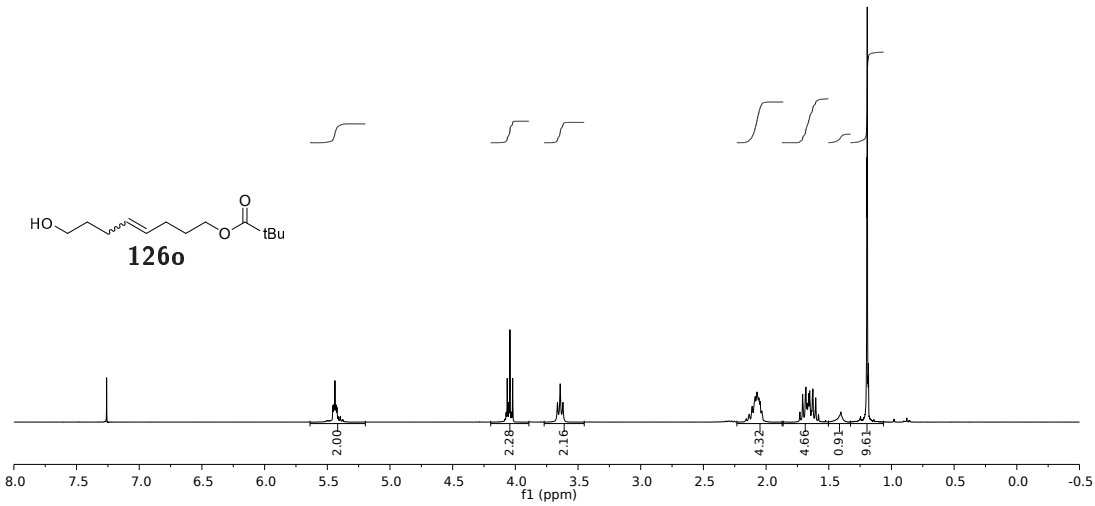

130.21
62.35
32.47
29.01
f1 (ppm)

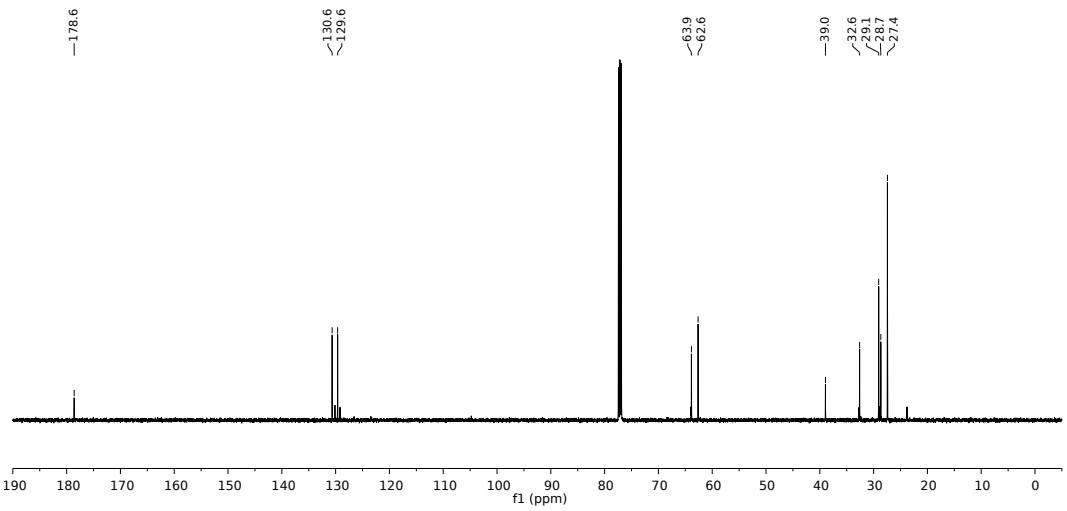

Transmittance [%]
3315.62
2931.20
2865.03
1439.81
1375.10
1351.08
1050.59
966.46
914.88
630.65
Wavenumber cm-1

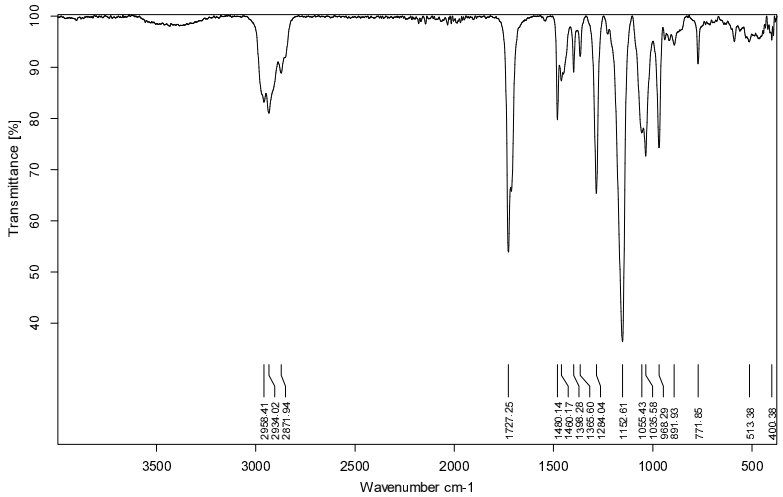

HO
O
O
OEt
126n
2.00
4.32
2.13
3.88
4.01
1.22
3.37
f1 (ppm)

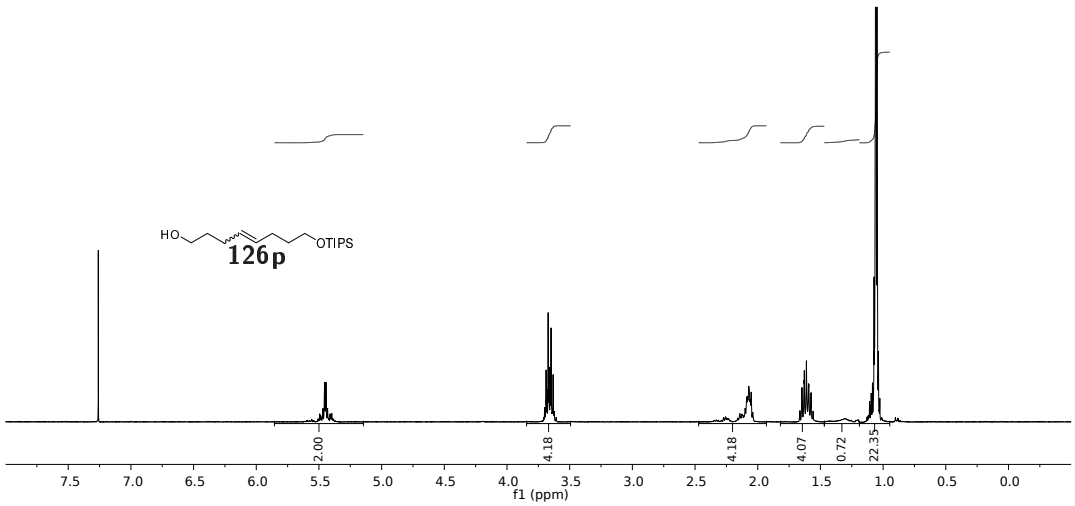

155.3
130.8
129.4
67.4
64.0
62.6
32.6
29.0
28.8
28.7
14.5
f1 (ppm)

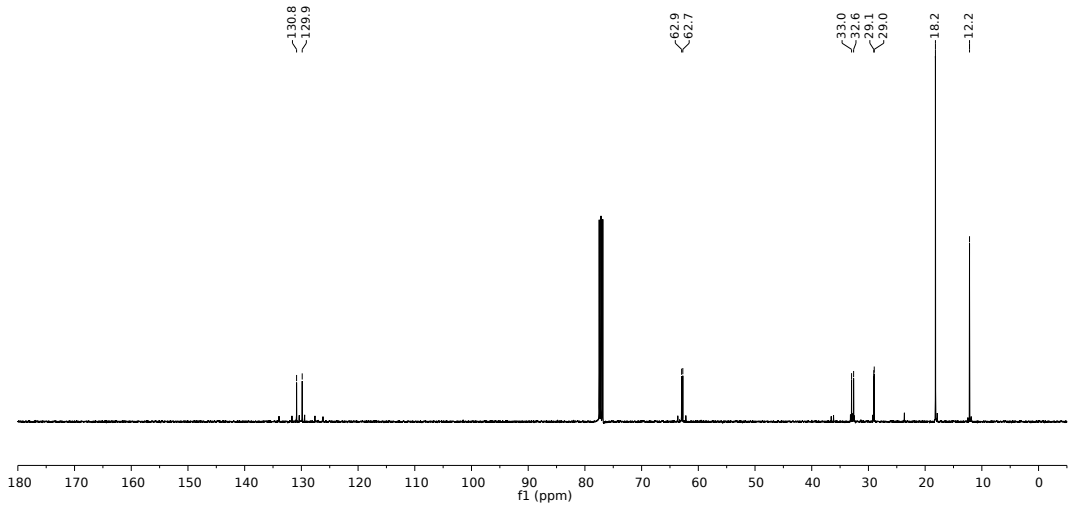

Transmittance [%]
2982.52
2934.00
2873.99
1742.04
1467.42
1447.58
1403.27
1386.32
1367.04
1250.88
1054.01
1009.95
968.17
862.74
791.26
592.57
Wavenumber cm-1

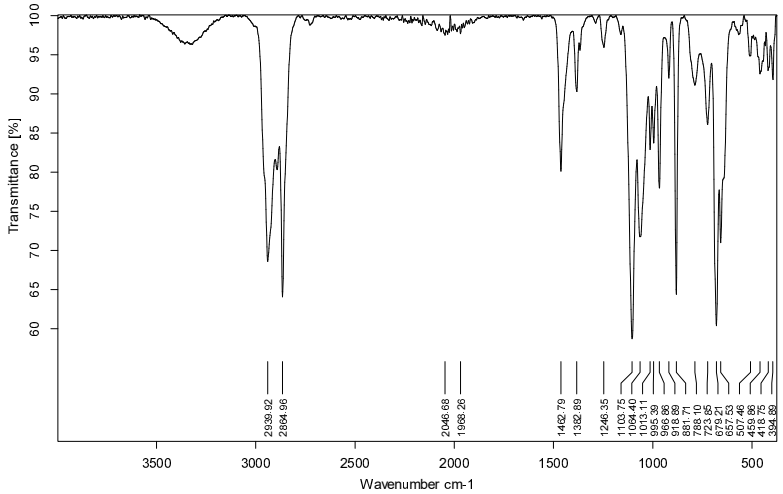

HO
O
O
tBu
126o
2.00
2.28
2.16
4.32
4.66
0.91
9.61
f1 (ppm)

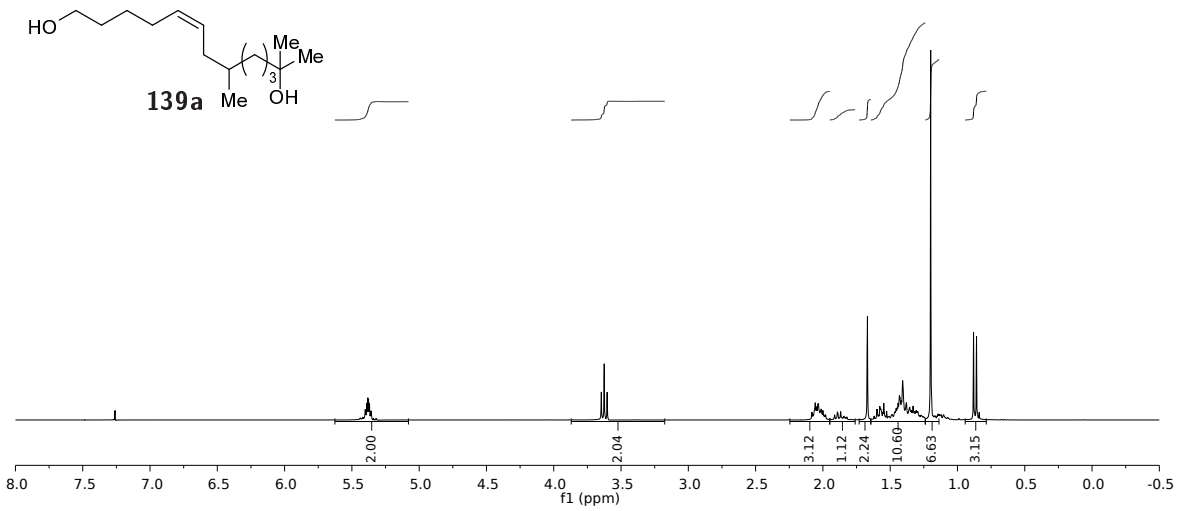

178.6
130.6
129.6
63.9
62.6
39.0
32.6
29.1
28.7
27.4
f1 (ppm)

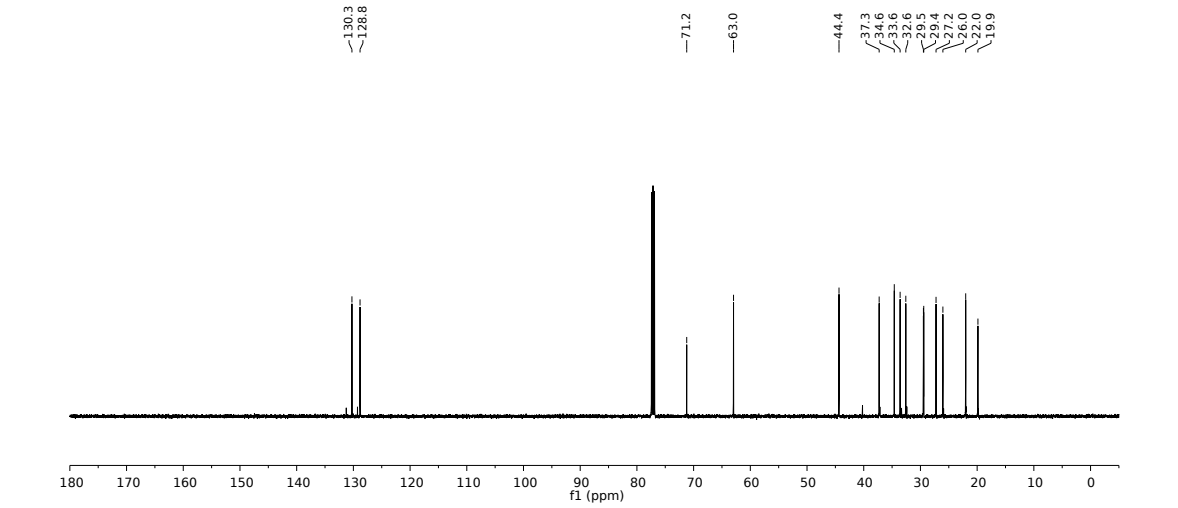

Transmittance [%]
2958.41
2934.02
2871.94
1727.25
1490.14
1460.17
1388.28
1365.00
1284.04
1152.61
1055.43
1035.58
968.29
891.93
771.85
513.38
400.38
Wavenumber cm-1

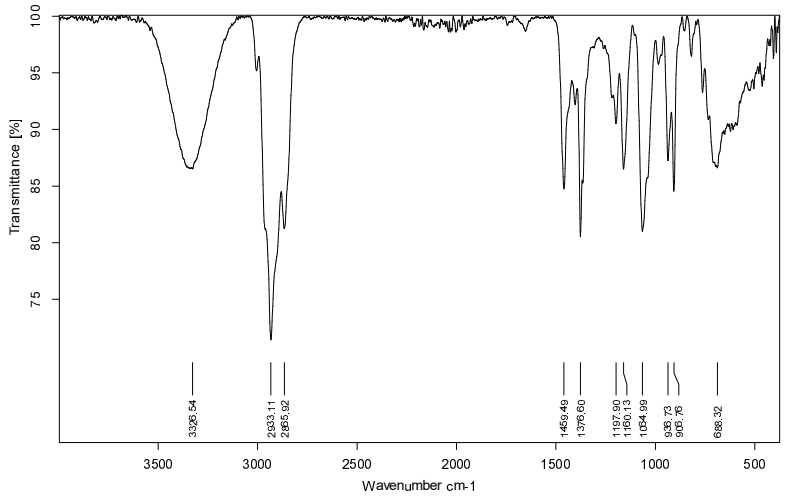

HO
OTIPS
126p
2.00
4.18
4.18
4.07
0.72
22.35
f1 (ppm)

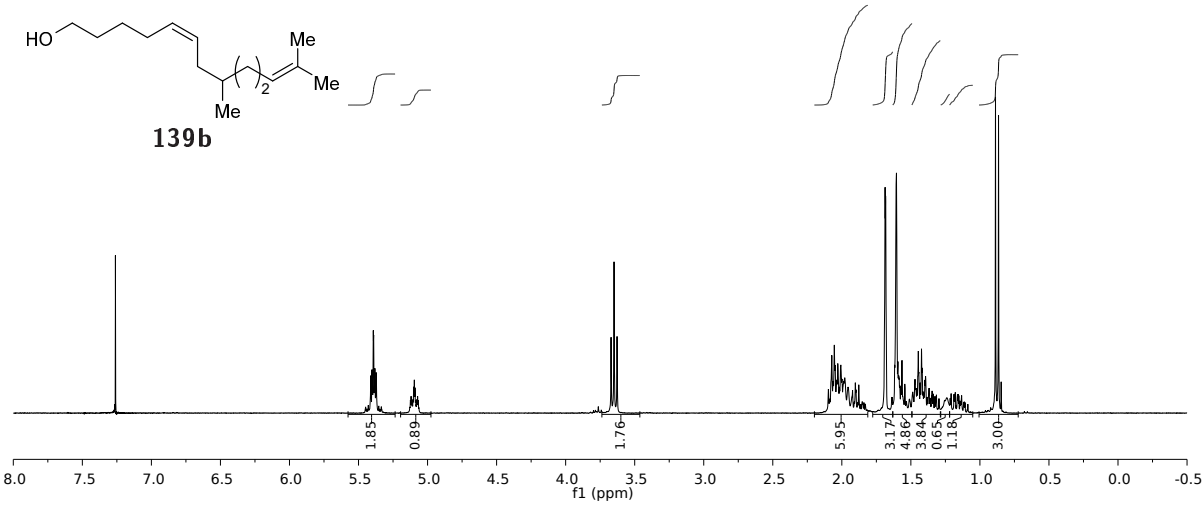

130.8
129.9
62.9
62.7
33.0
32.6
29.1
29.0
18.2
12.2
f1 (ppm)

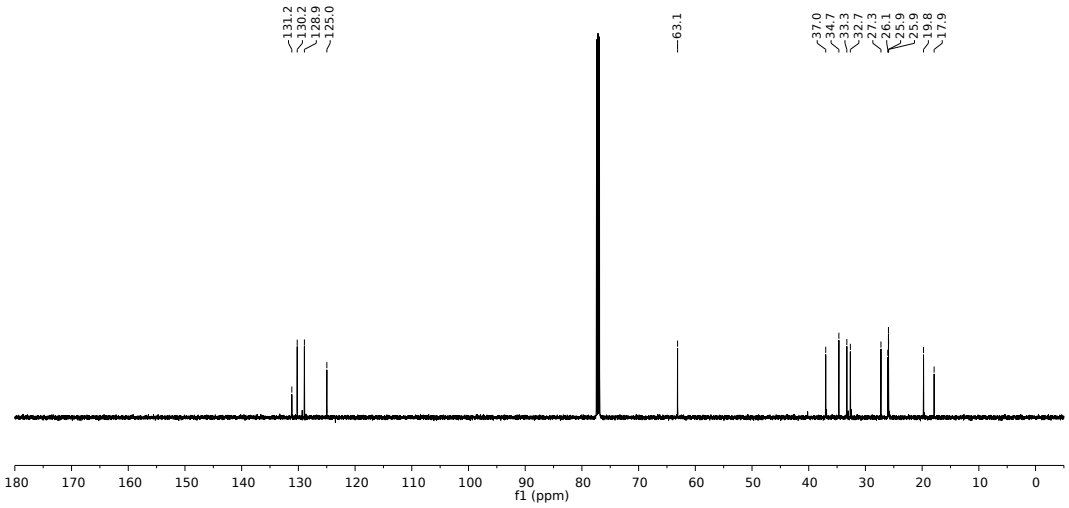

Transmittance [%]
2939.92
2864.96
2046.68
1968.26
1462.79
1382.89
1246.35
1103.75
1064.40
1013.11
995.39
966.86
918.89
881.77
788.10
723.85
679.21
657.53
507.46
459.86
418.75
384.89
Wavenumber cm-1

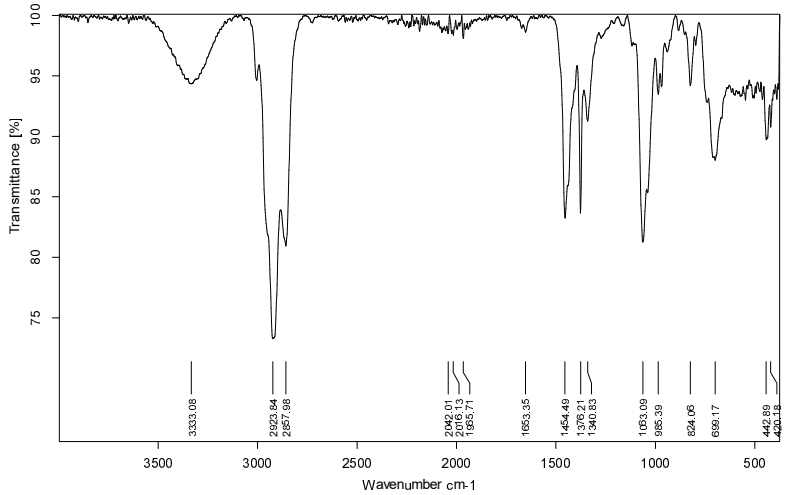

HO
Me
Me
3
Me
OH
139a
2.00
2.04
3.12
1.12
2.24
10.60
6.63
3.15
f1 (ppm)

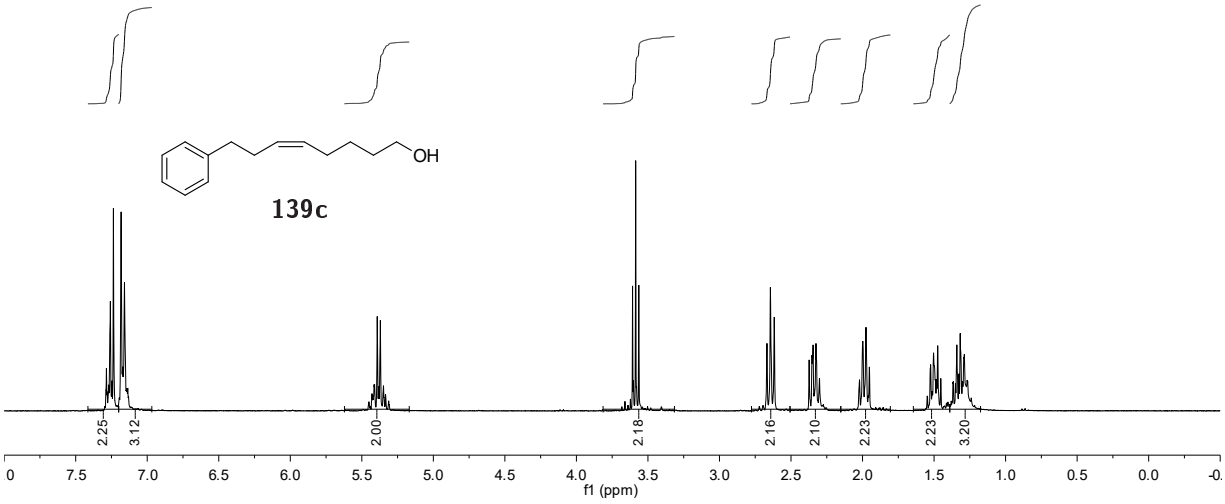

130.3
128.8
71.2
63.0
44.4
37.3
34.6
33.6
32.6
29.5
29.4
27.2
26.0
22.0
19.9
f1 (ppm)

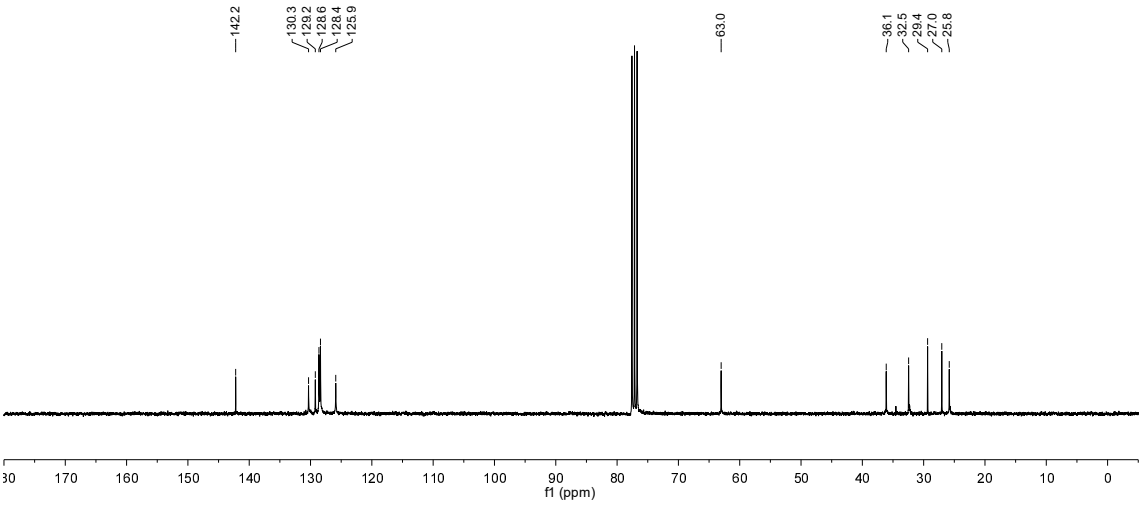

Transmittance [%]
3326.54
2933.11
2865.92
1459.49
1376.60
1197.90
1160.13
1054.99
995.73
965.76
688.32
Wavenumber cm-1

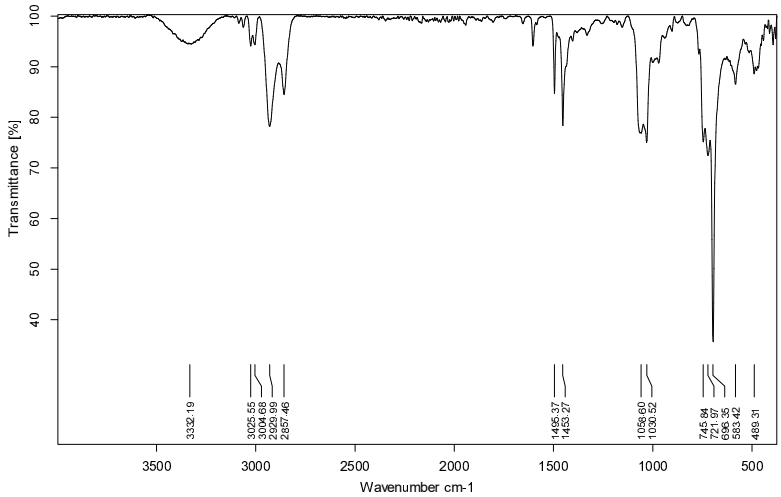

HO
Me
Me
Me
2
139b
1.85
0.89
1.76
5.95
3.17
4.86
3.84
0.65
1.18
3.00
f1 (ppm)

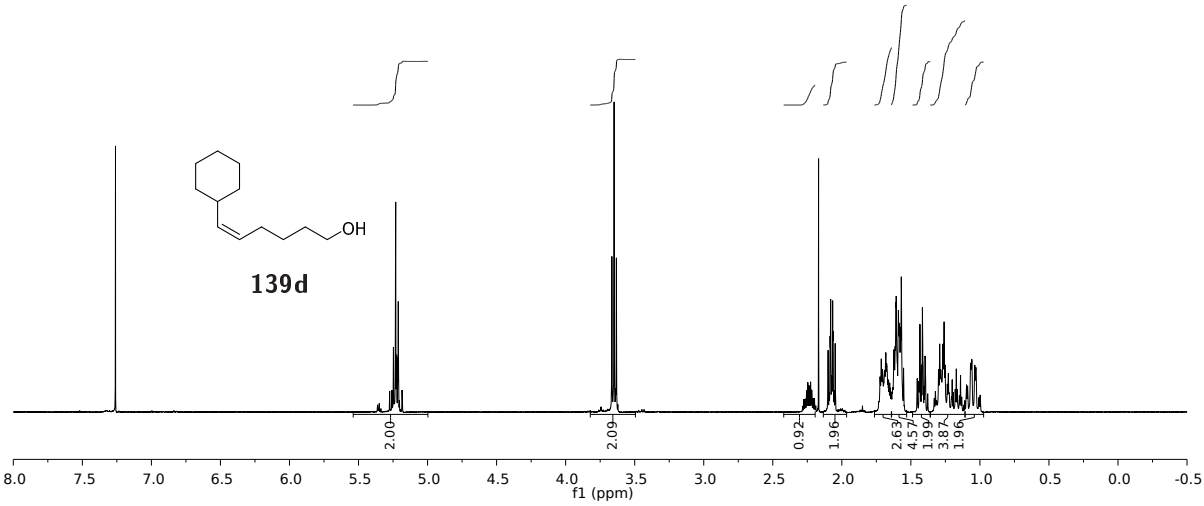

131.2
130.2
128.9
125.0
63.1
37.0
34.7
33.3
32.7
27.3
26.1
25.9
25.9
19.8
17.9
f1 (ppm)

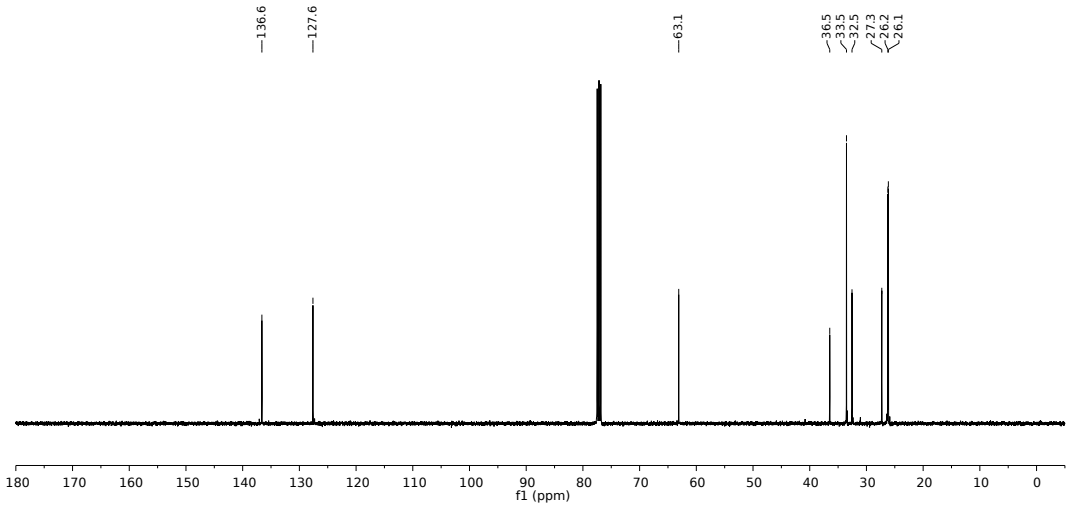

Transmittance [%]
3333.08
2923.84
2857.98
2042.01
2016.13
1955.71
1653.35
1454.49
1376.21
1340.83
1053.09
985.39
824.06
698.17
442.89
420.18
Wavenumber cm-1

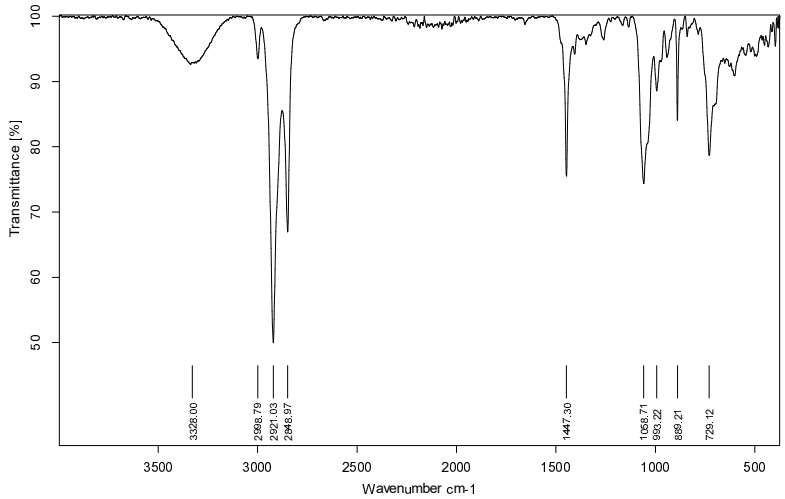

OH
139c
2.25
3.12
2.00
2.18
2.16
2.10
2.23
2.23
3.20
f1 (ppm)

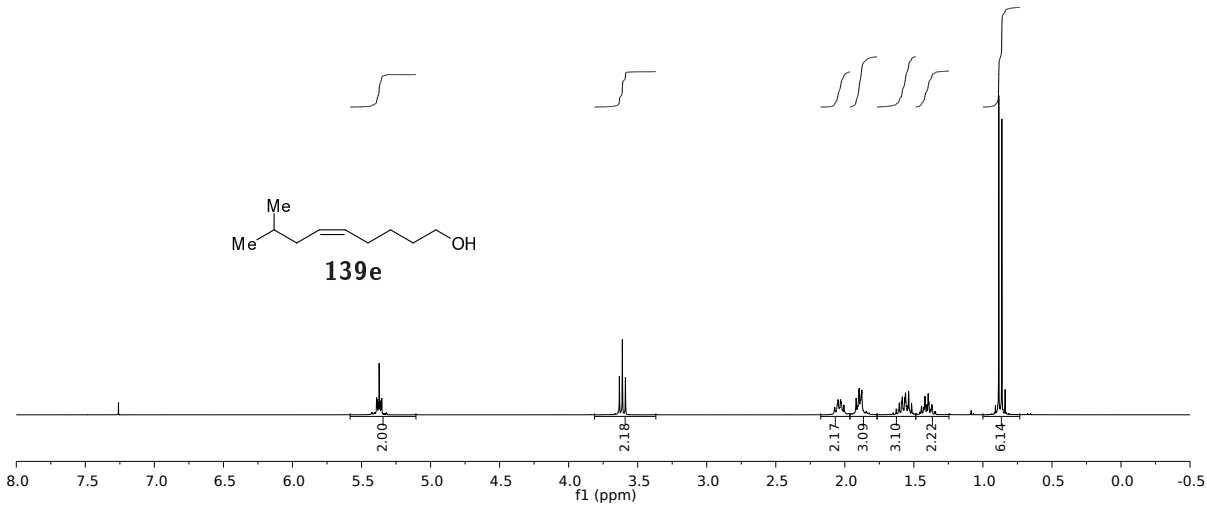

142.2
130.3
129.2
128.6
128.4
125.9
63.0
36.1
32.5
29.4
27.0
25.8
f1 (ppm)

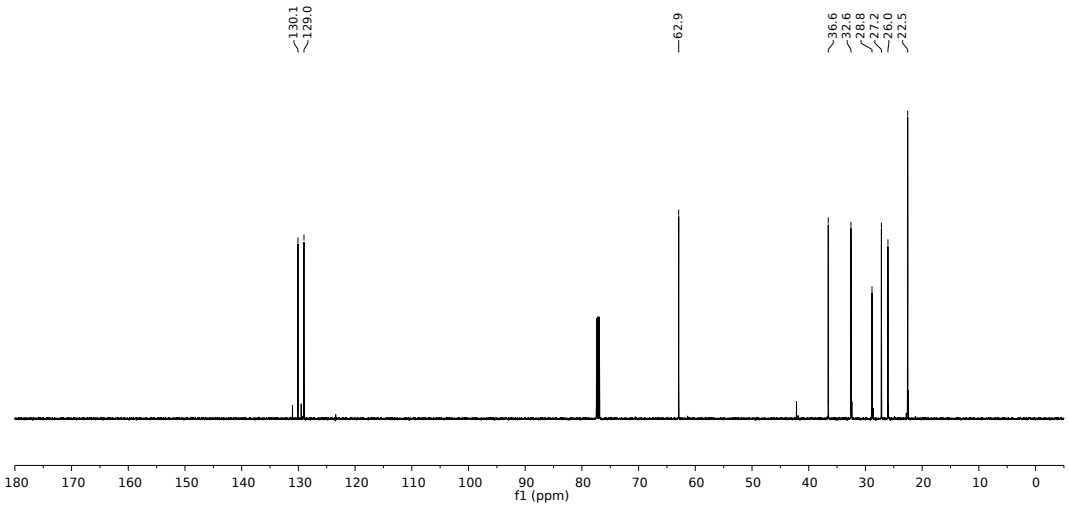

Transmittance [%]
3332.19
3025.55
3004.68
2929.99
2857.46
1495.37
1453.27
1058.60
1030.52
745.84
707.97
696.35
583.42
489.31
Wavenumber cm-1

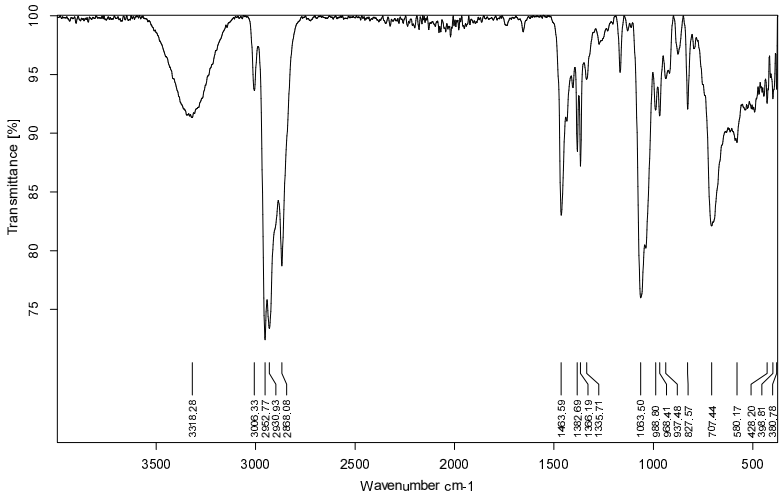

OH
139d
2.00
2.09
0.92
1.96
2.63
4.57
1.99
3.87
1.96
f1 (ppm)

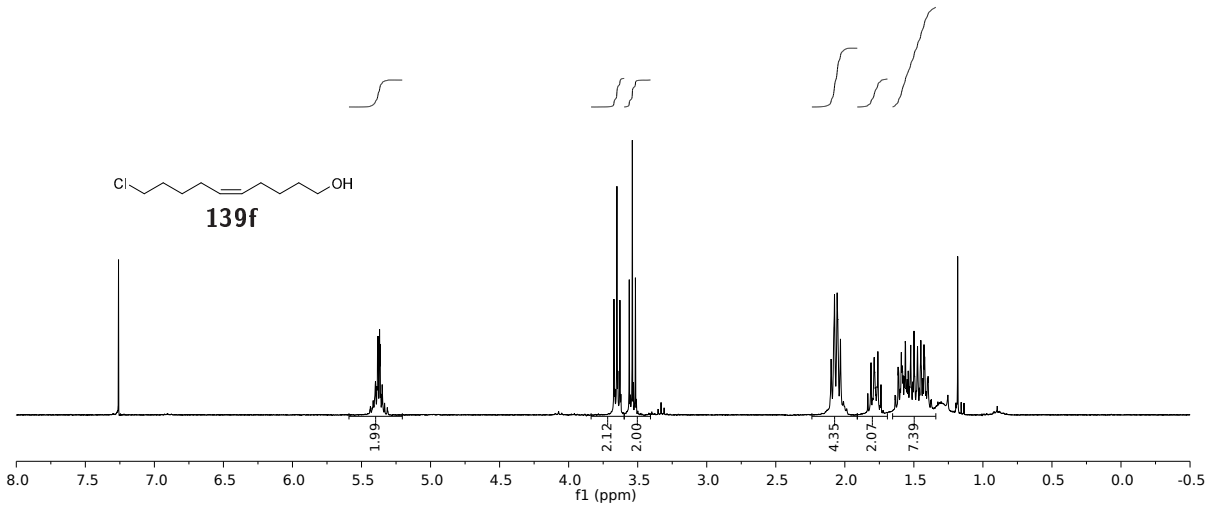

136.6
127.6
63.1
36.5
33.5
32.5
27.3
26.2
26.1
f1 (ppm)

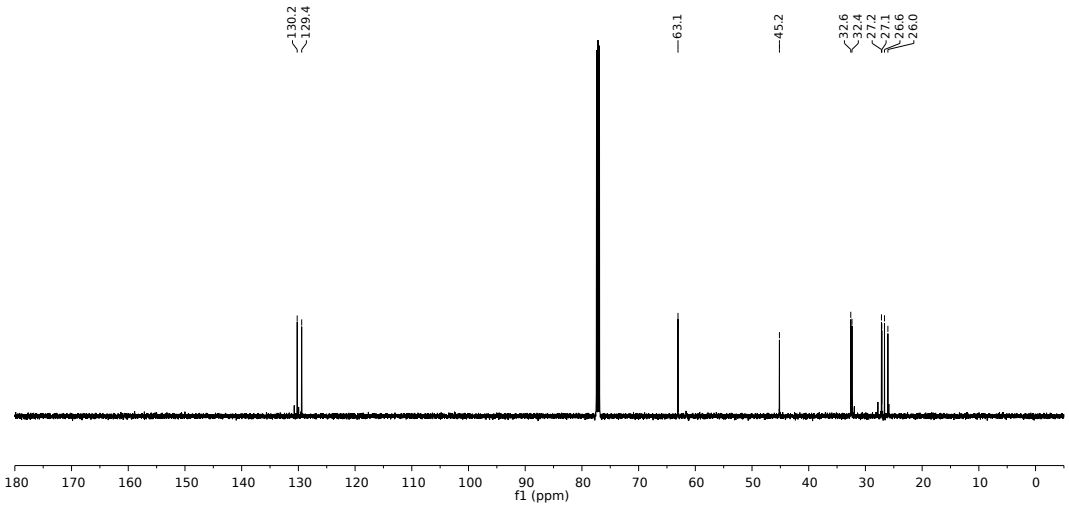

Transmittance [%]
3328.00
2868.79
2921.03
2848.97
1447.30
1058.71
993.22
889.21
729.12
Wavenumber cm-1

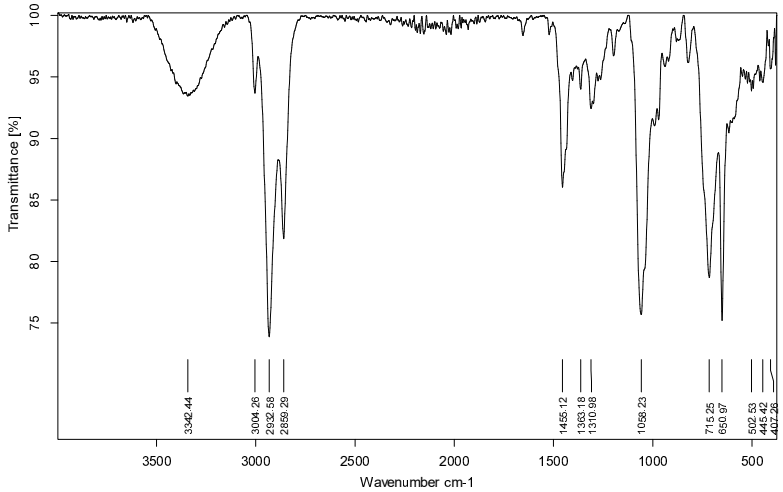

Me
Me
OH
139e
2.00
2.18
2.17
3.09
3.10
2.22
6.14
f1 (ppm)

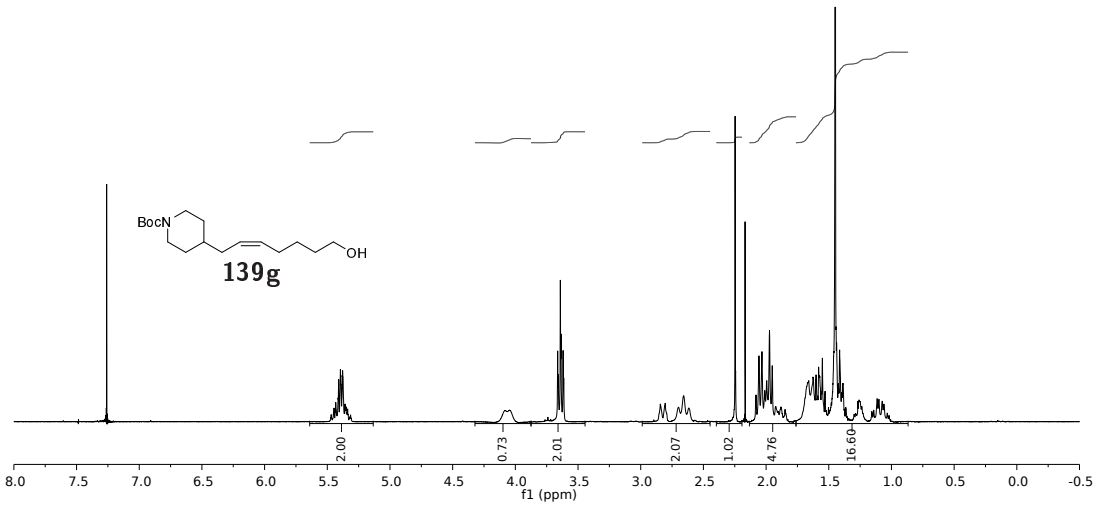

130.1
129.0
62.9
36.6
32.6
28.8
27.2
26.0
22.5
f1 (ppm)

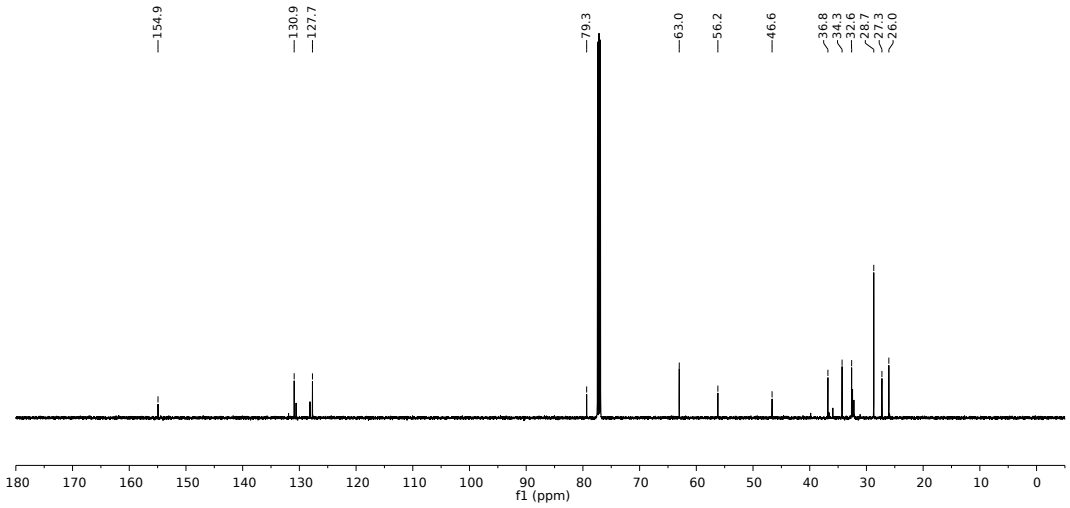

Transmittance [%]
3318.28
3006.33
2952.77
2930.93
2858.08
1463.59
1382.69
1365.19
1335.71
1053.50
988.80
968.41
937.48
827.57
707.44
580.17
428.20
398.81
380.78
Wavenumber cm-1

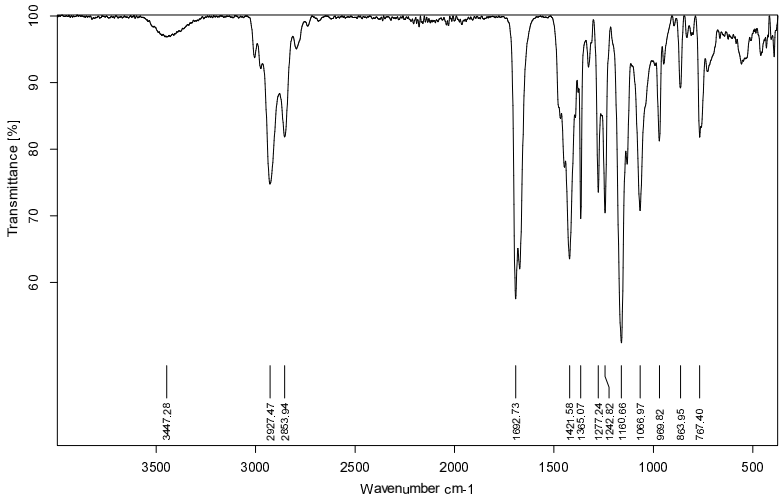

Cl
OH
139f
1.99
2.12
2.00
4.35
2.07
7.39
f1 (ppm)

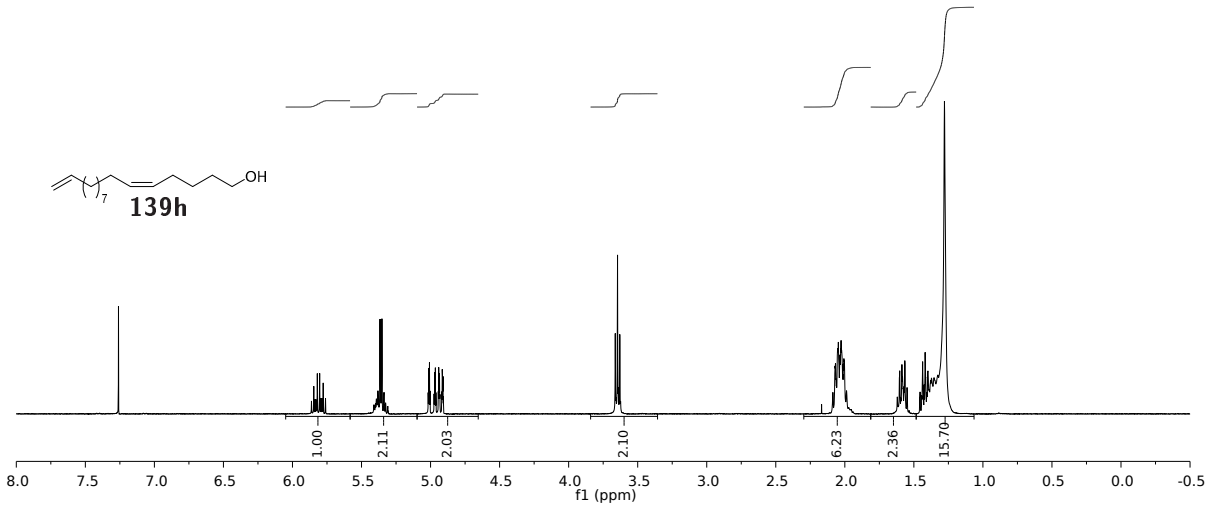

130.2
129.4
63.1
45.2
32.6
32.4
27.2
27.1
26.6
26.0
f1 (ppm)

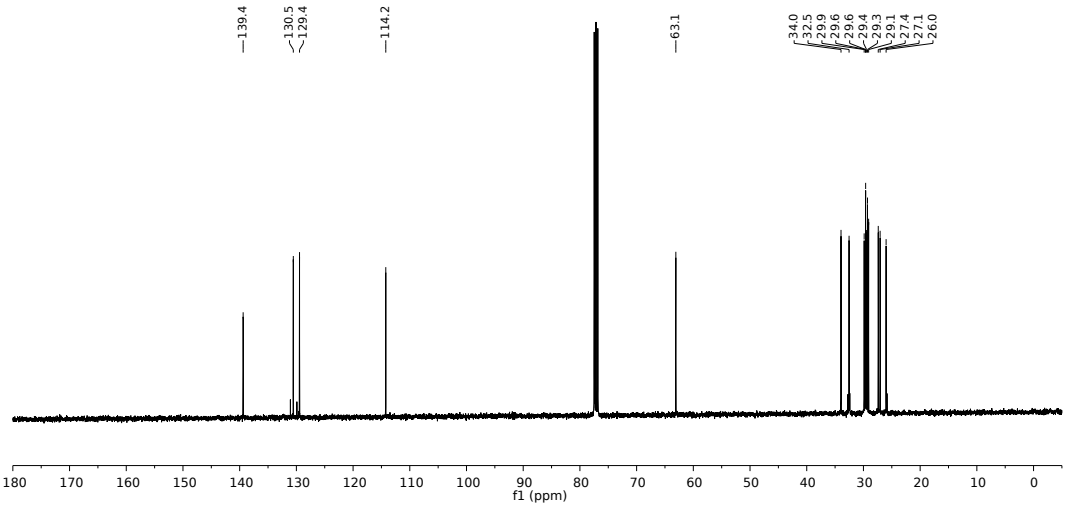

Transmittance [%]
3342.44
3004.26
2932.58
2859.29
1455.12
1383.18
1310.98
1058.23
715.25
650.97
502.53
445.42
407.26
Wavenumber cm-1

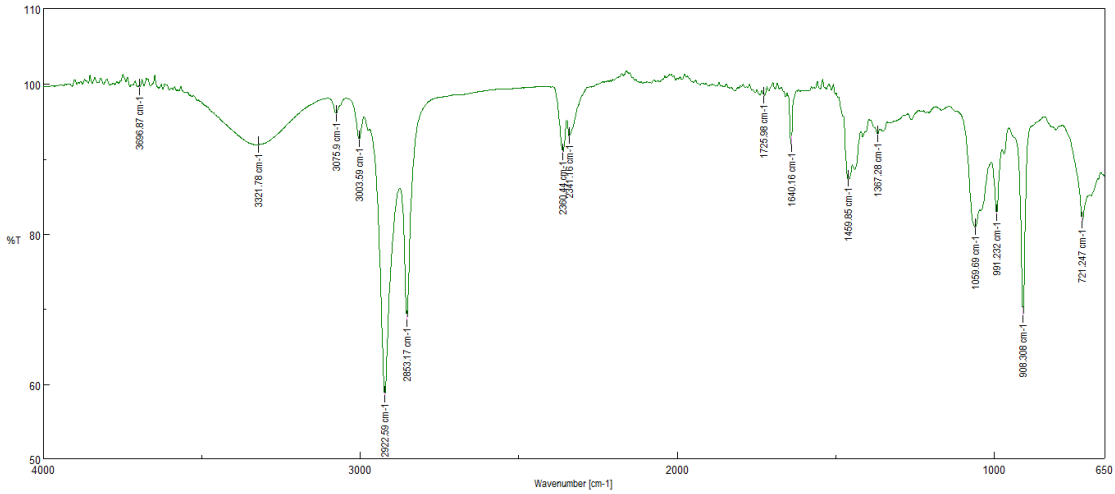

BocN
OH
139g
2.00
0.73
2.01
2.07
1.02
4.76
16.60
f1 (ppm)

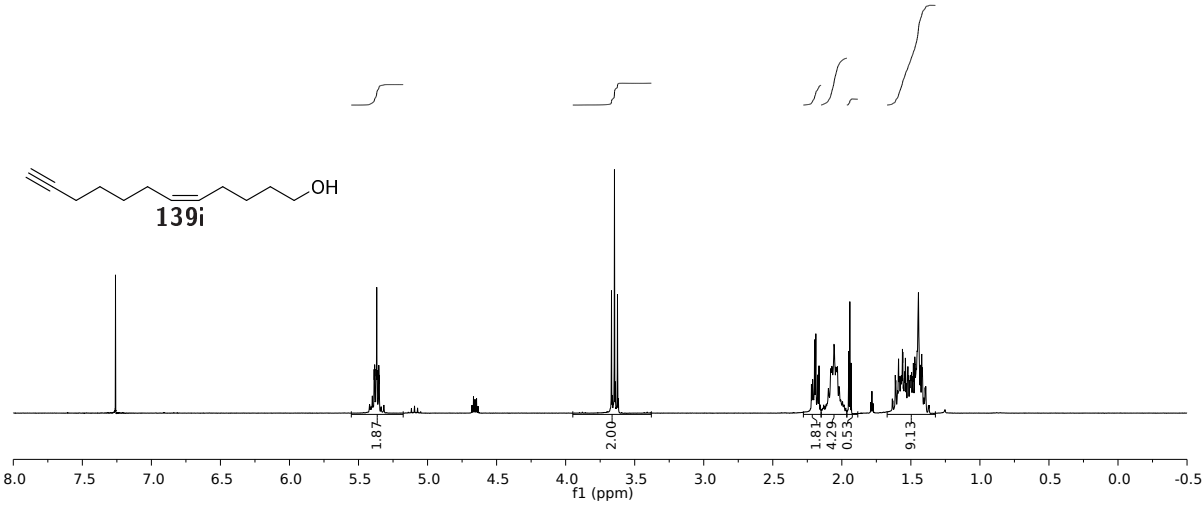

154.9
130.9
127.7
79.3
63.0
56.2
46.6
36.8
34.3
32.6
28.7
27.3
26.0
f1 (ppm)

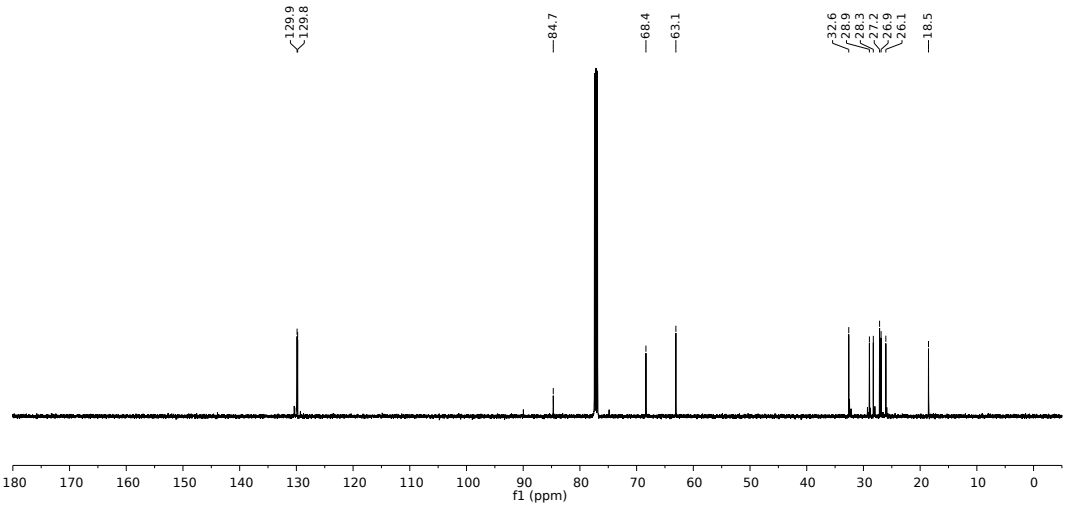

Transmittance [%]
3447.28
2927.47
2853.94
1692.73
1421.58
1365.07
1277.24
1242.82
1160.66
1066.97
980.82
863.95
767.40
Wavenumber cm-1

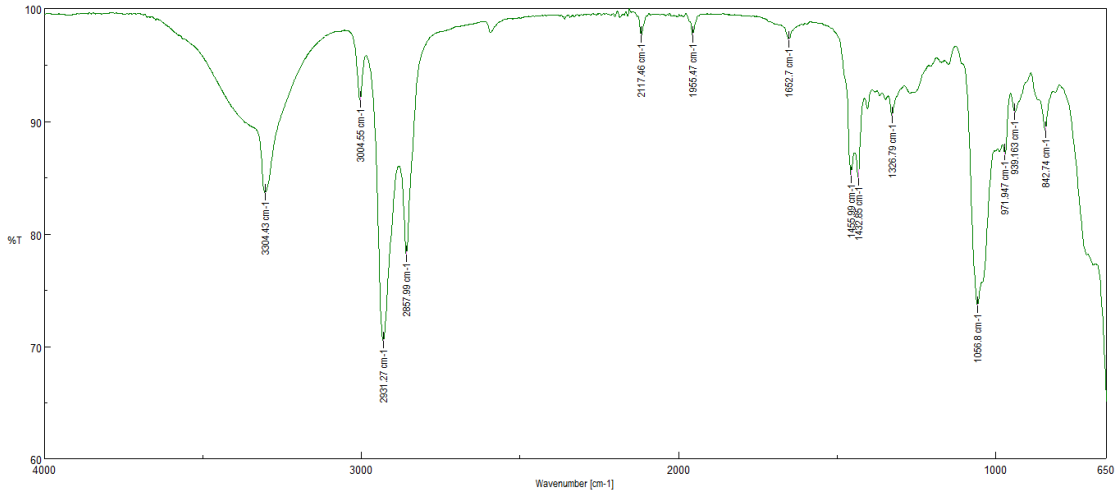

OH
7
139h
1.00
2.11
2.03
2.10
6.23
2.36
15.70
f1 (ppm)

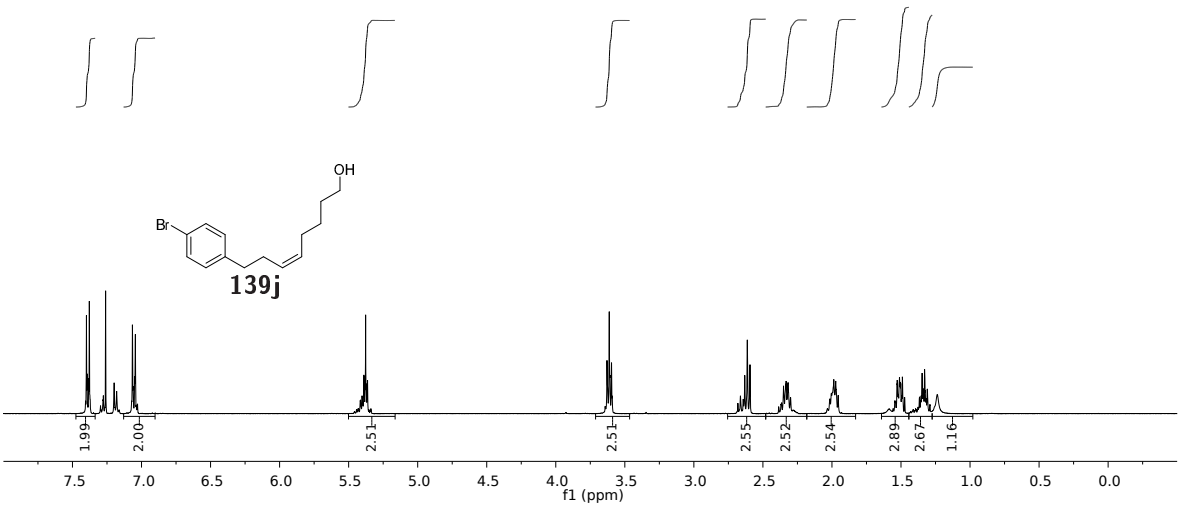

139.4
130.5
129.4
114.2
63.1
34.0
32.5
29.9
29.6
29.6
29.4
29.3
29.1
27.4
27.1
26.0
f1 (ppm)

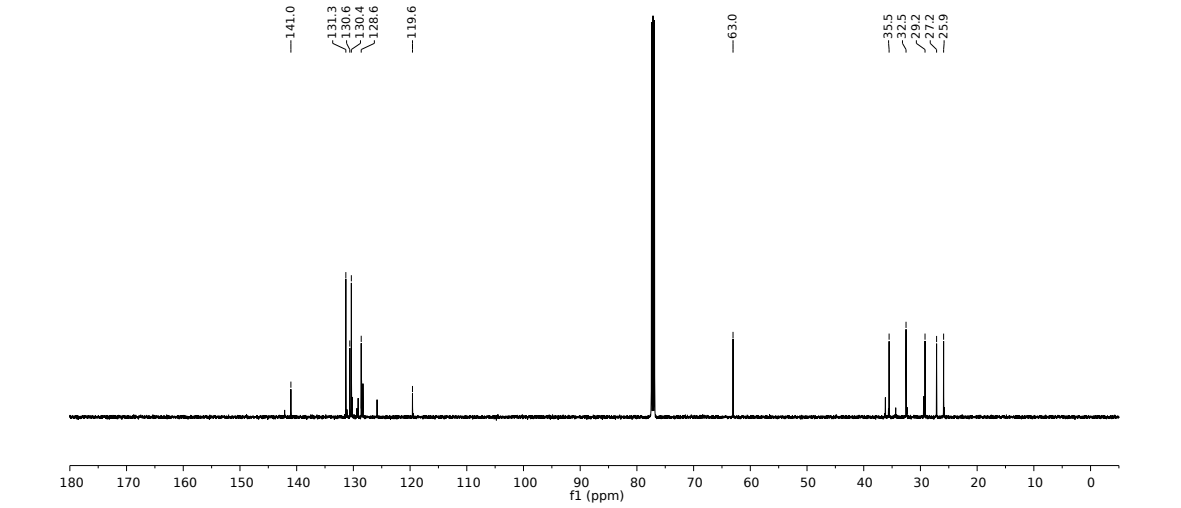

%T
3696.87 cm-1
3321.78 cm-1
3075.9 cm-1
3003.59 cm-1
2922.59 cm-1
2853.17 cm-1
2360.41 cm-1
2341.16 cm-1
1725.98 cm-1
1640.16 cm-1
1459.85 cm-1
1367.28 cm-1
1059.69 cm-1
991.232 cm-1
908.308 cm-1
721.247 cm-1
Wavenumber [cm-1]

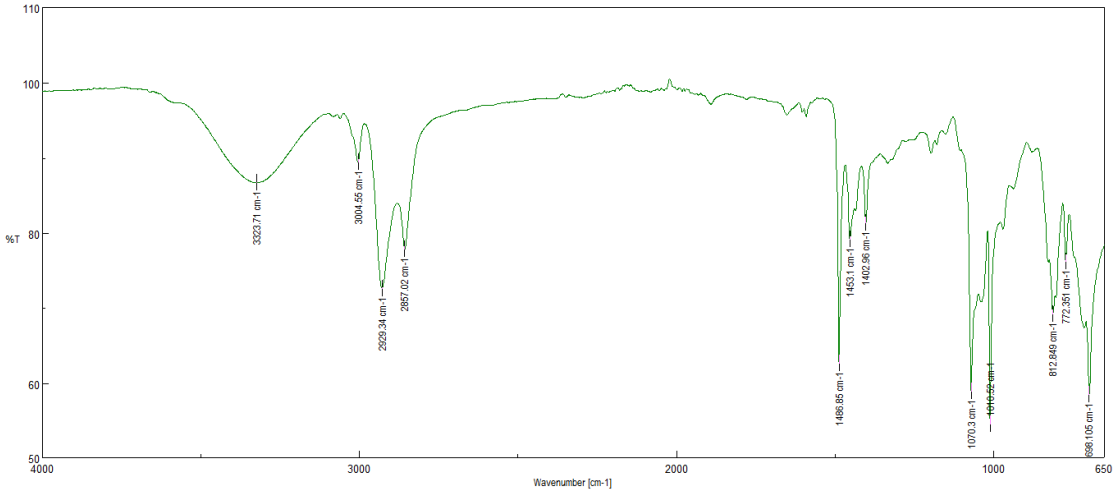

OH
139i
1.87
2.00
1.81
4.29
0.53
9.13
f1 (ppm)

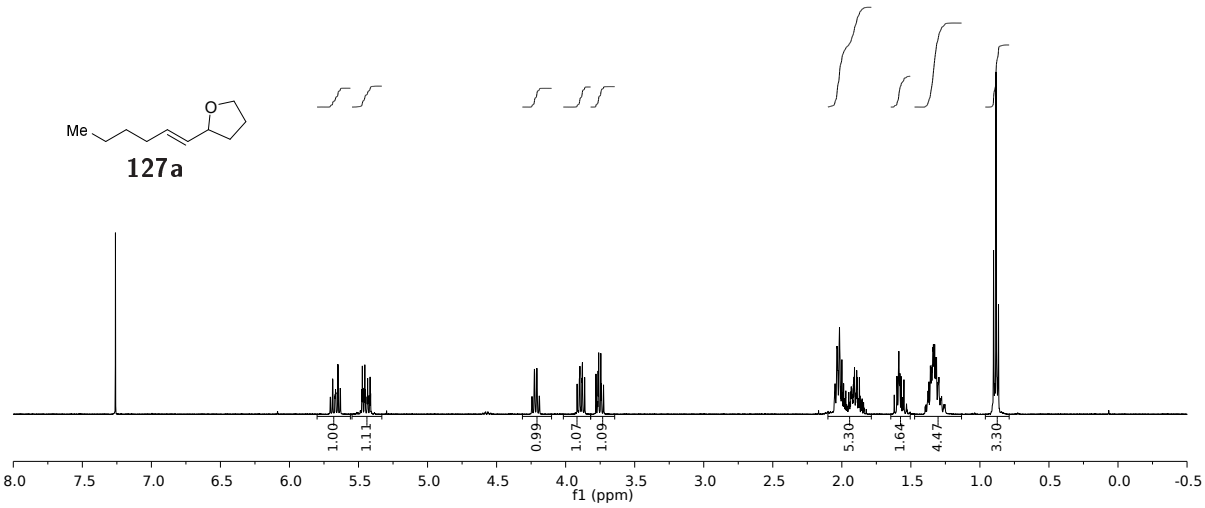

129.9
129.8
84.7
68.4
63.1
32.6
28.9
28.3
27.2
27.9
26.1
18.5
f1 (ppm)

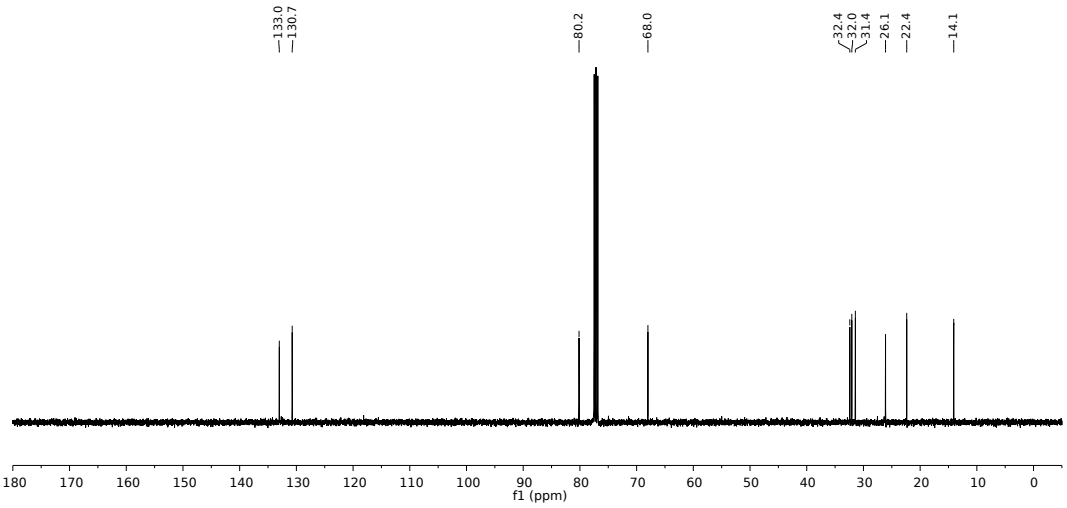

%T
3304.43 cm-1
3004.55 cm-1
2931.27 cm-1
2857.99 cm-1
2117.46 cm-1
1955.47 cm-1
1652.7 cm-1
1456.69 cm-1
1432.86 cm-1
1326.79 cm-1
1056.8 cm-1
971.947 cm-1
939.163 cm-1
842.74 cm-1
Wavenumber [cm-1]

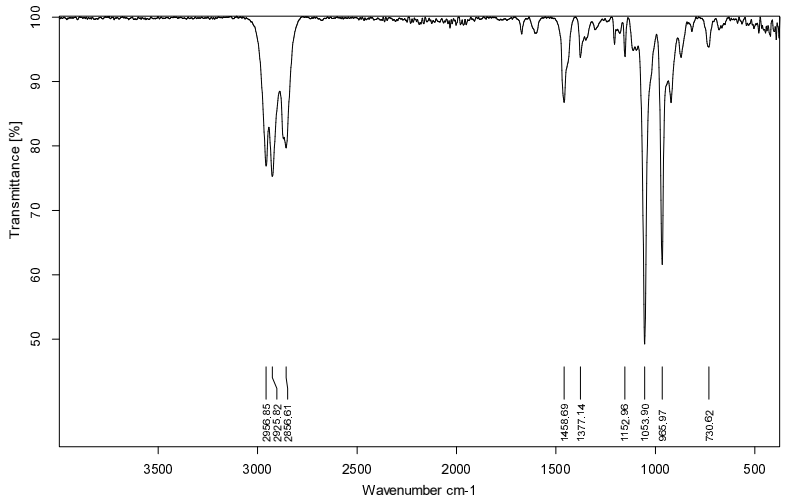

OH
Br
139j
1.99
2.00
2.51
2.51
2.55
2.52
2.54
2.89
2.67
1.16
f1 (ppm)

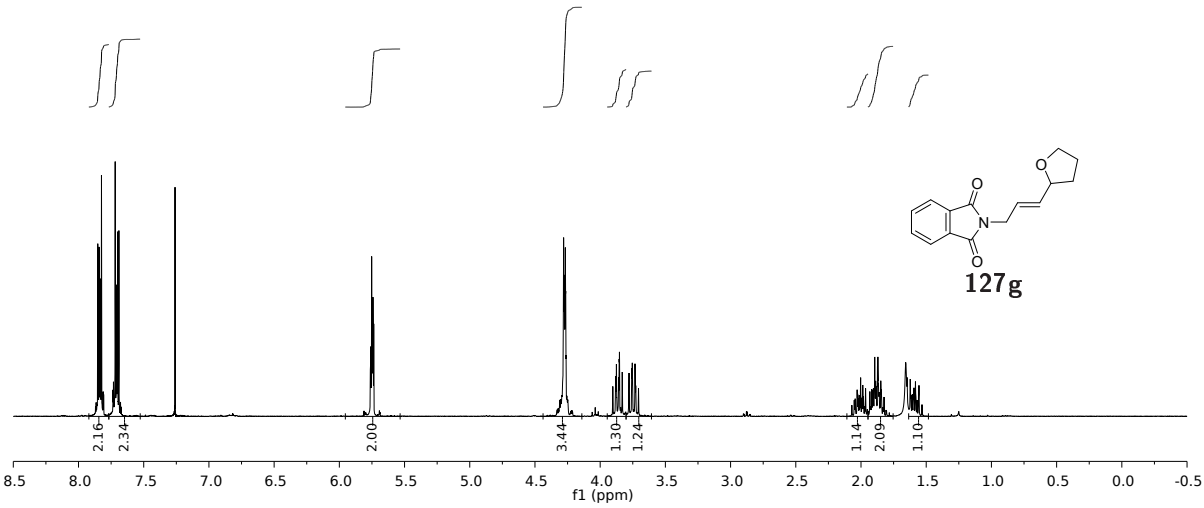

141.0
131.3
130.6
130.4
128.6
119.6
63.0
35.5
32.5
29.2
27.2
25.9
f1 (ppm)

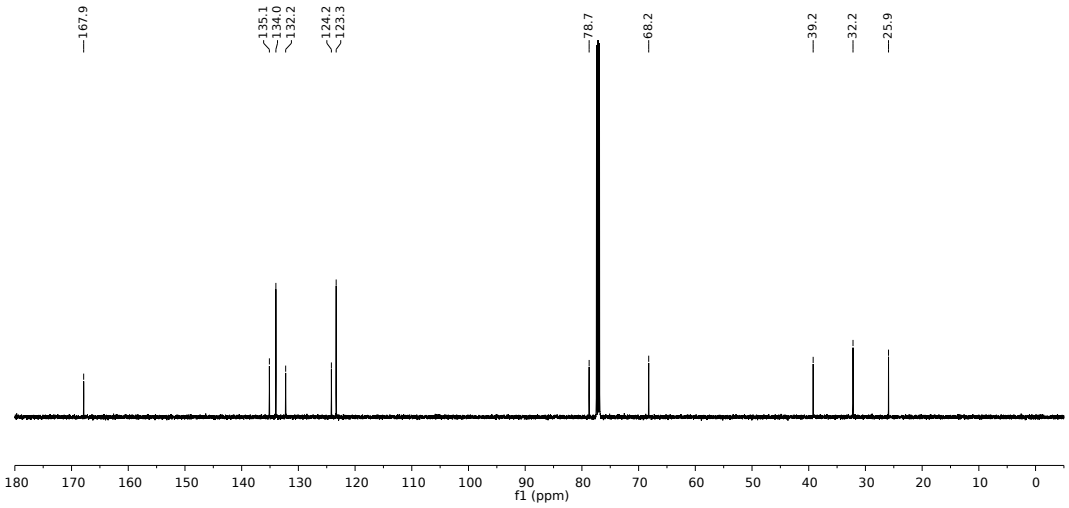

%T
3323.71 cm-1
3004.55 cm-1
2929.34 cm-1
2857.02 cm-1
1486.85 cm-1
1453.1 cm-1
1402.96 cm-1
1070.3 cm-1
1016.52 cm-1
812.849 cm-1
772.351 cm-1
698.105 cm-1
Wavenumber [cm-1]

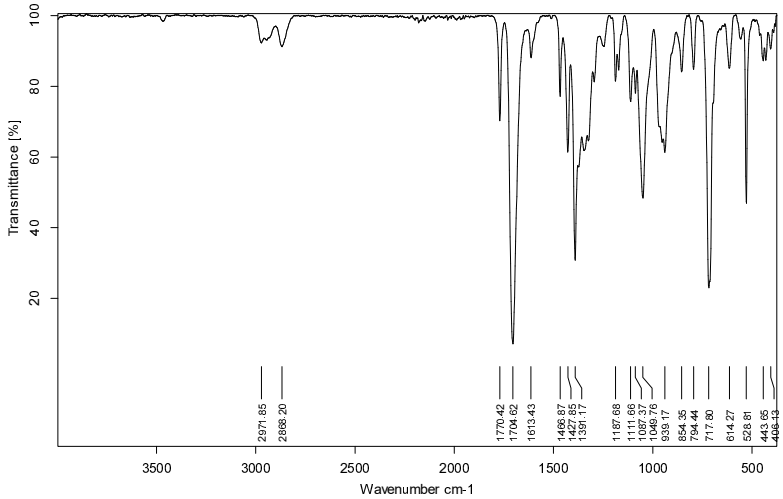

Me
O
127a
1.00
1.11
0.99
1.07
1.09
5.30
1.64
4.47
3.30
f1 (ppm)

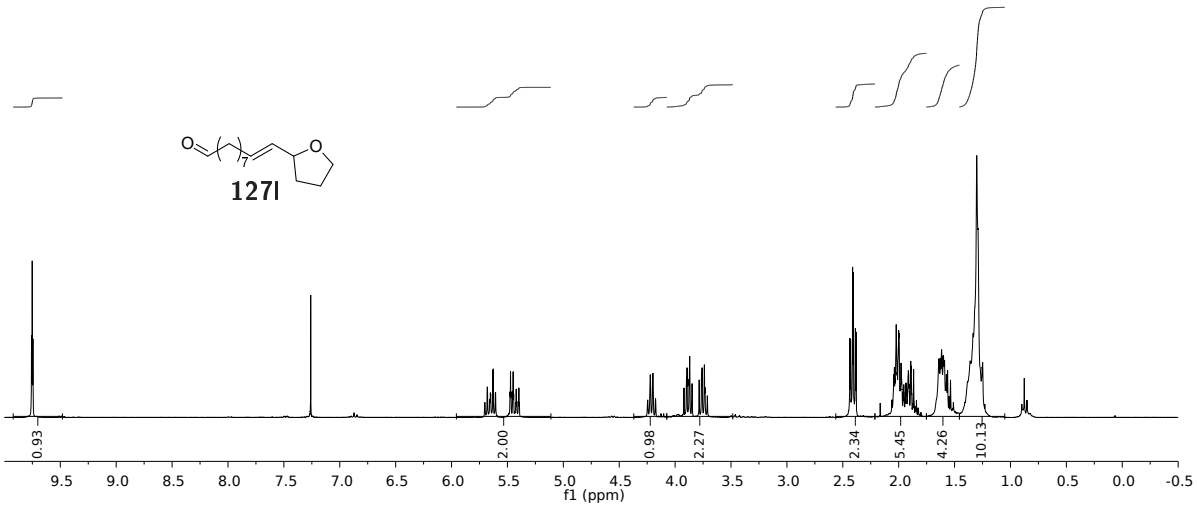

133.0
130.7
80.2
68.0
32.4
32.0
31.4
26.1
22.4
14.1
f1 (ppm)

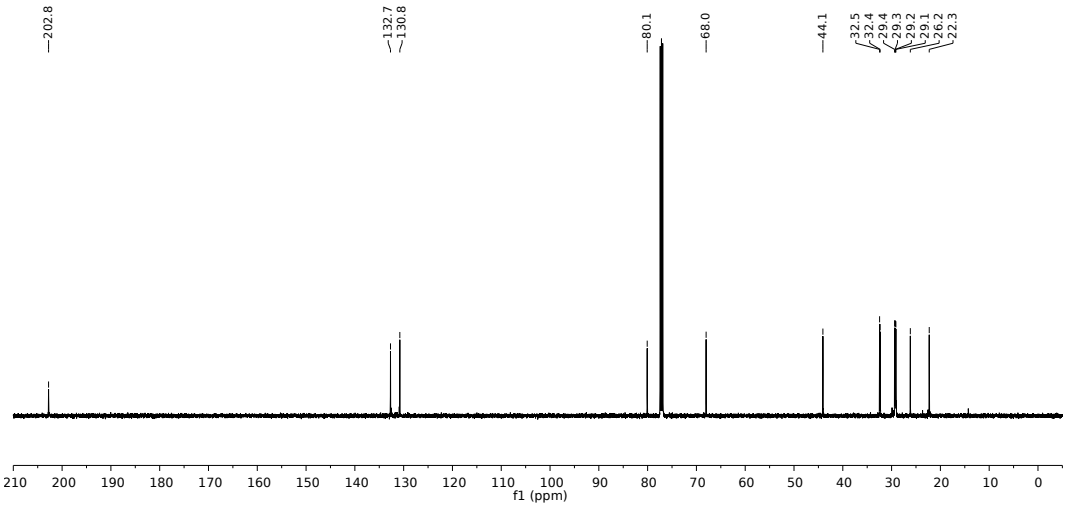

Transmittance [%]
2956.85
2925.82
2856.81
1458.69
1377.14
1152.96
1053.90
966.97
730.62
Wavenumber cm-1

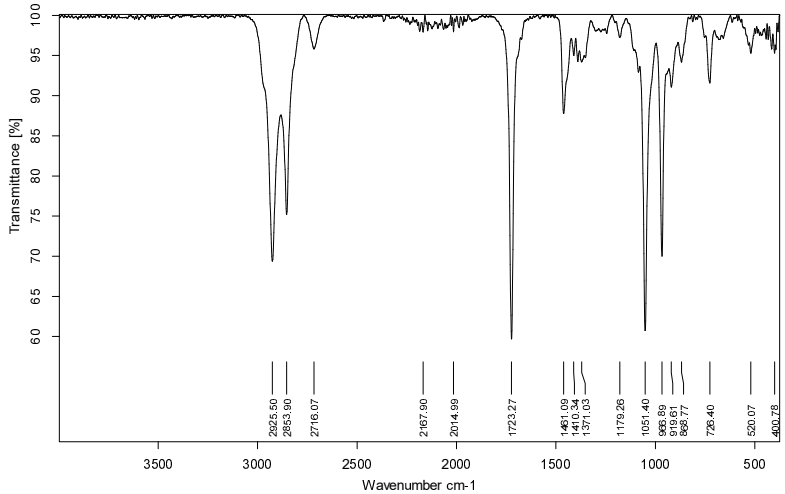

127g
2.16
2.34
2.00
3.44
1.30
1.24
1.14
2.09
1.10
f1 (ppm)

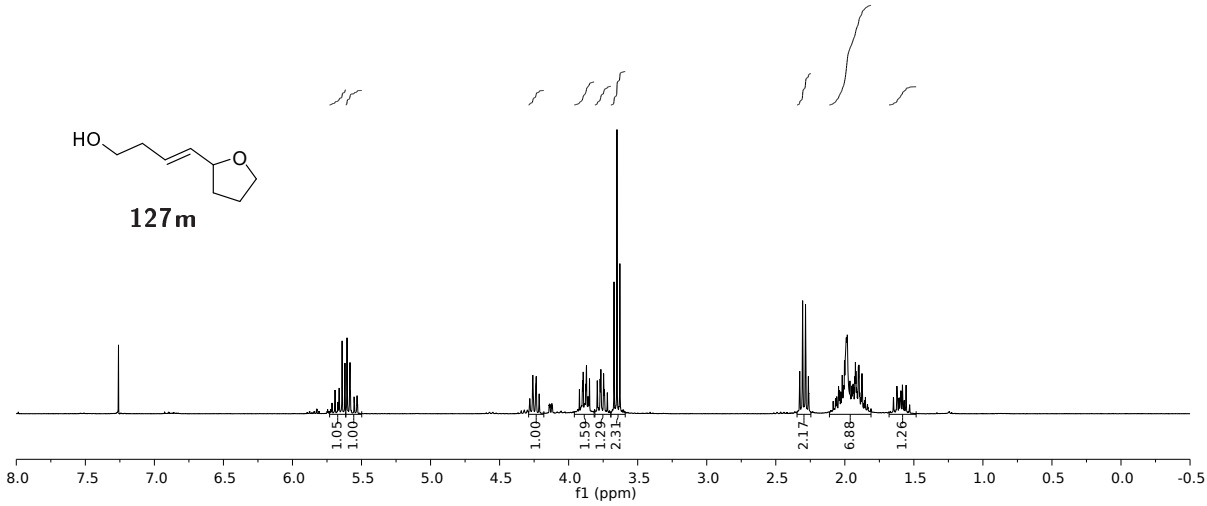

167.9
135.1
134.0
132.2
124.2
123.3
78.7
68.2
39.2
32.2
25.9
f1 (ppm)

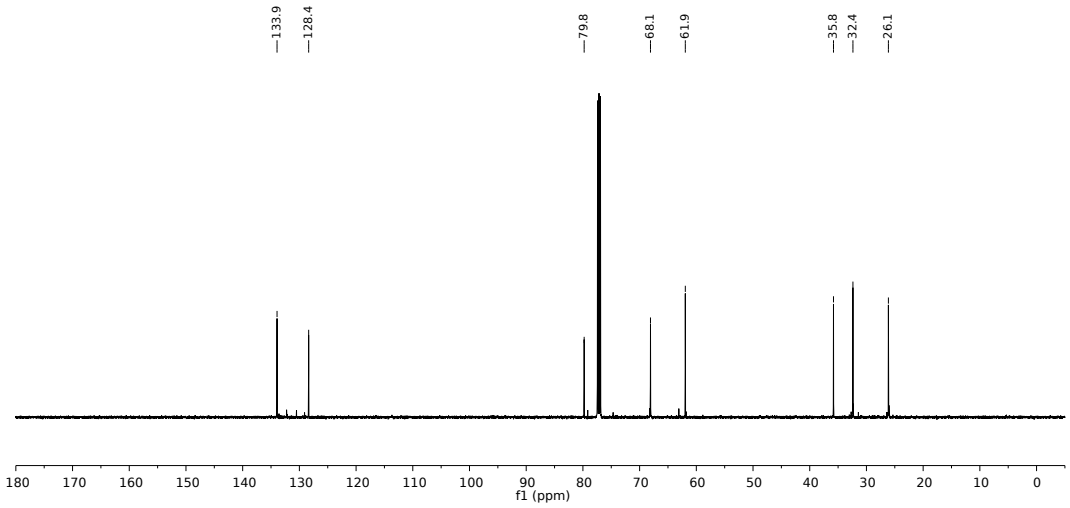

Transmittance [%]
2971.85
2868.20
1770.42
1704.62
1613.43
1466.87
1427.85
1391.17
1157.68
1111.66
1087.37
1049.76
933.17
854.35
794.44
717.80
614.27
528.81
443.65
408.13
Wavenumber cm-1

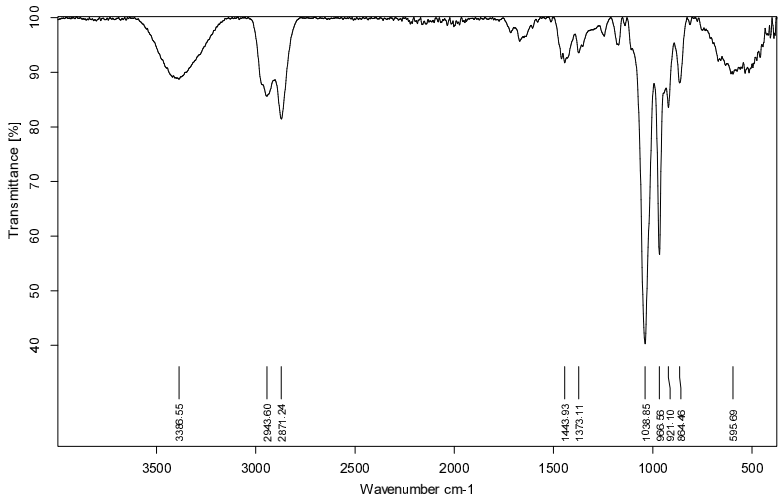

127l
0.93
2.00
0.98
2.27
2.34
5.45
4.26
10.13
f1 (ppm)

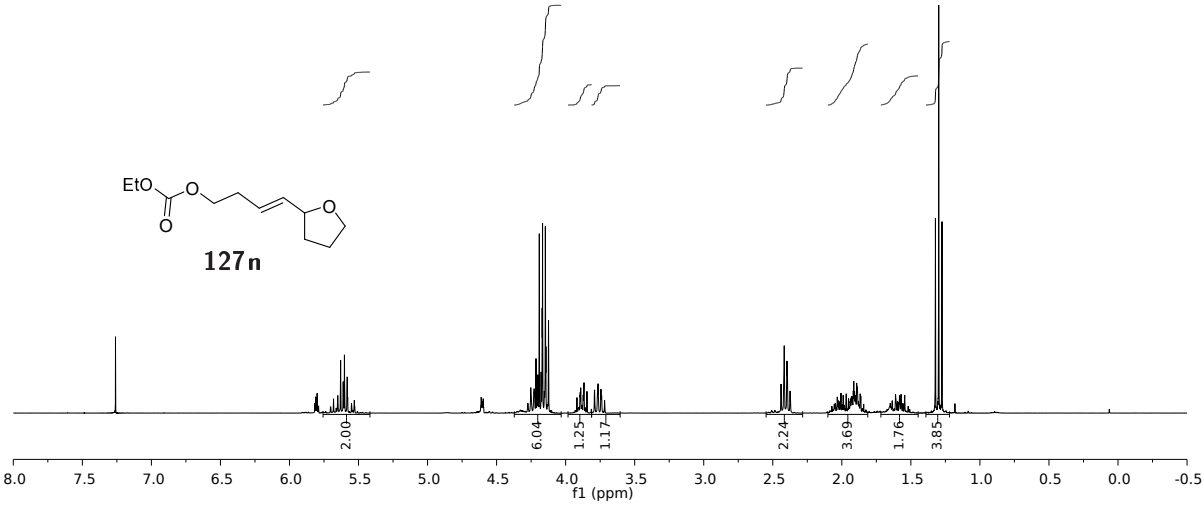

202.8
132.7
130.8
80.1
68.0
44.1
32.5
32.4
29.4
29.3
29.2
29.1
26.2
22.3
f1 (ppm)

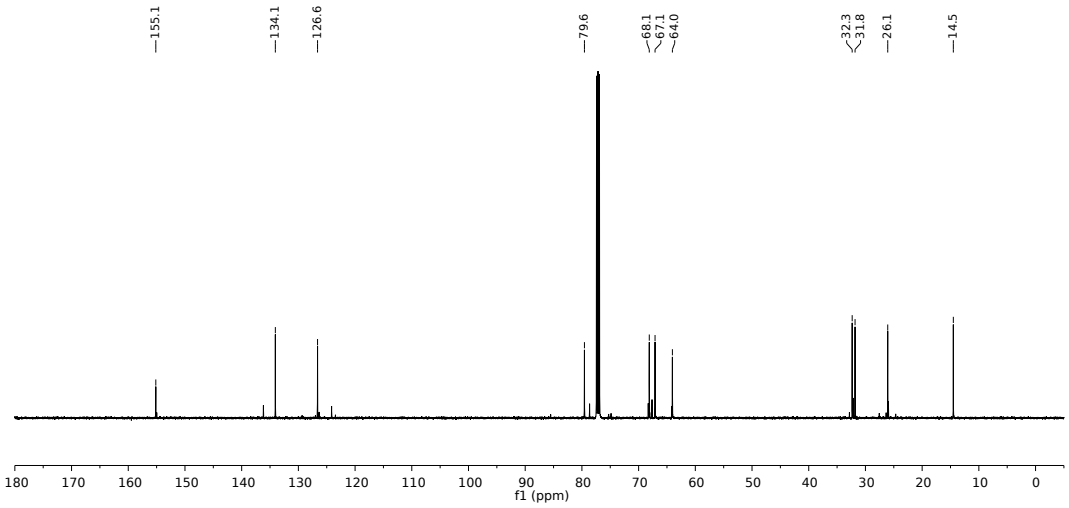

Transmittance [%]
2925.50
2853.90
2716.07
2167.90
2014.99
1723.27
1461.09
1410.34
1371.03
1179.26
1051.40
966.89
915.61
868.77
726.40
520.07
460.78
Wavenumber cm-1

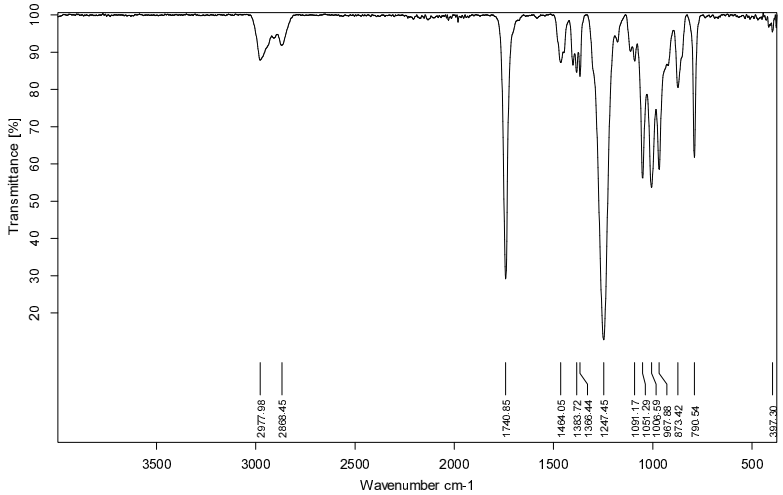

HO
O
127m
1.05
1.00
1.00
1.59
1.29
2.31
2.17
6.88
1.26
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

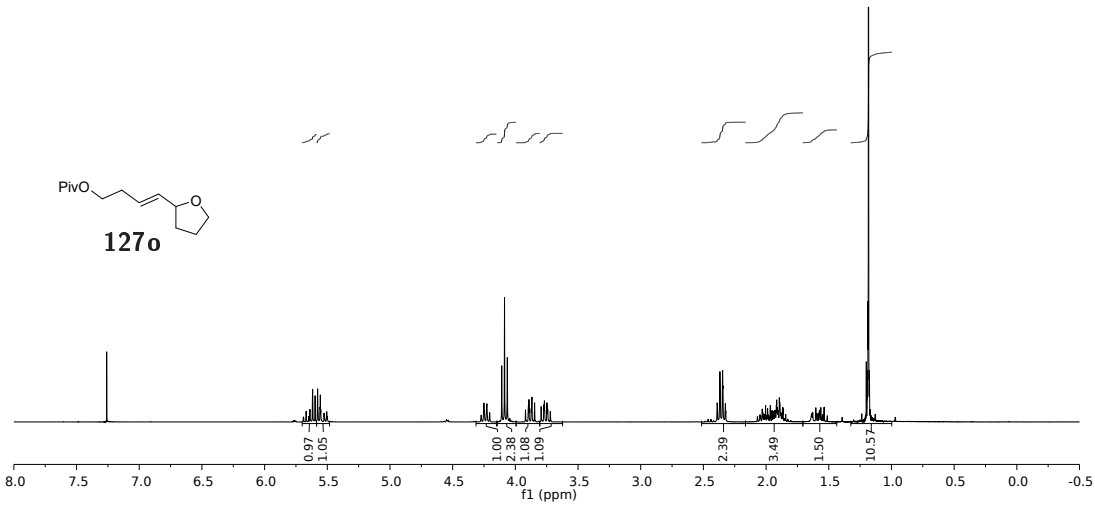

133.9
128.4
79.8
68.1
61.9
35.8
32.4
26.1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

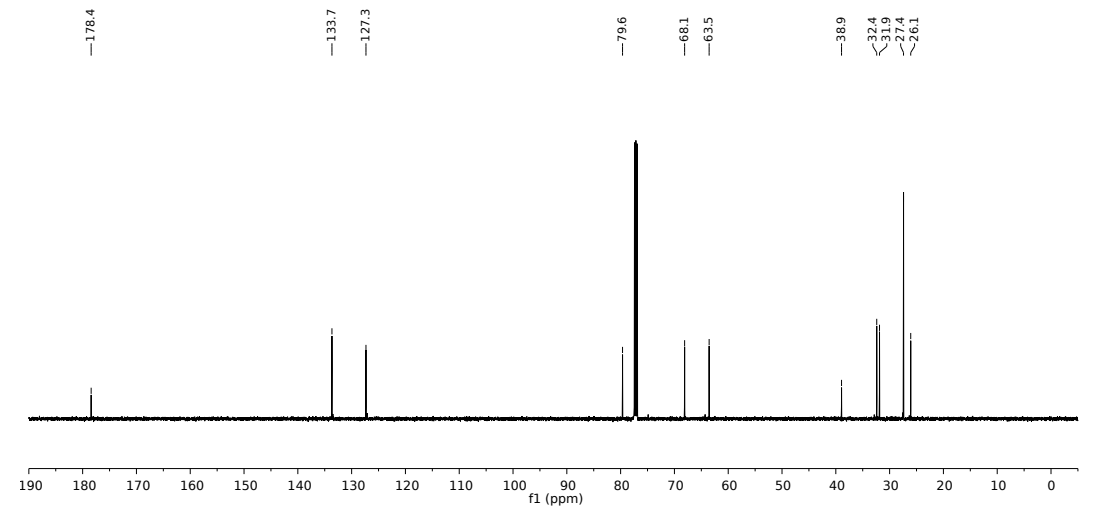

Transmittance [%]
100 90 80 70 60 50 40
3386.55
2943.60
2871.24
1443.93
1373.11
1038.85
996.85
921.10
864.46
595.69
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

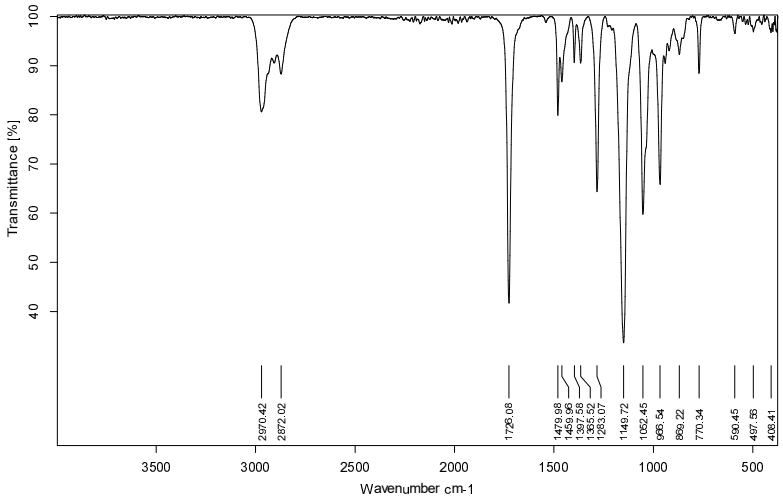

EtO
O
O
O
127n
2.00
6.04
1.25
1.17
2.24
3.69
1.76
3.85
f1 (ppm)

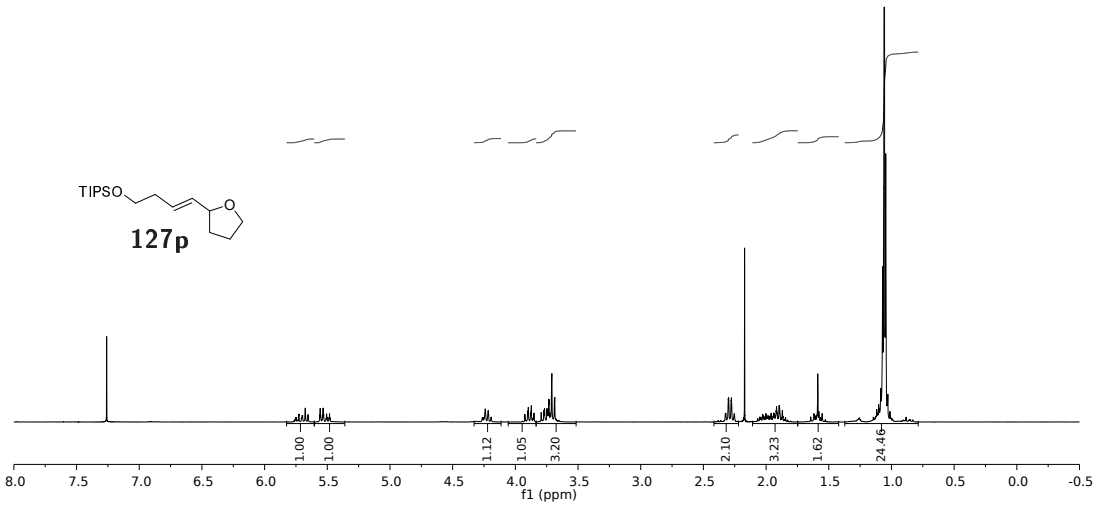

155.1
134.1
126.6
79.6
68.1
67.1
64.0
32.3
31.8
26.1
14.5
f1 (ppm)

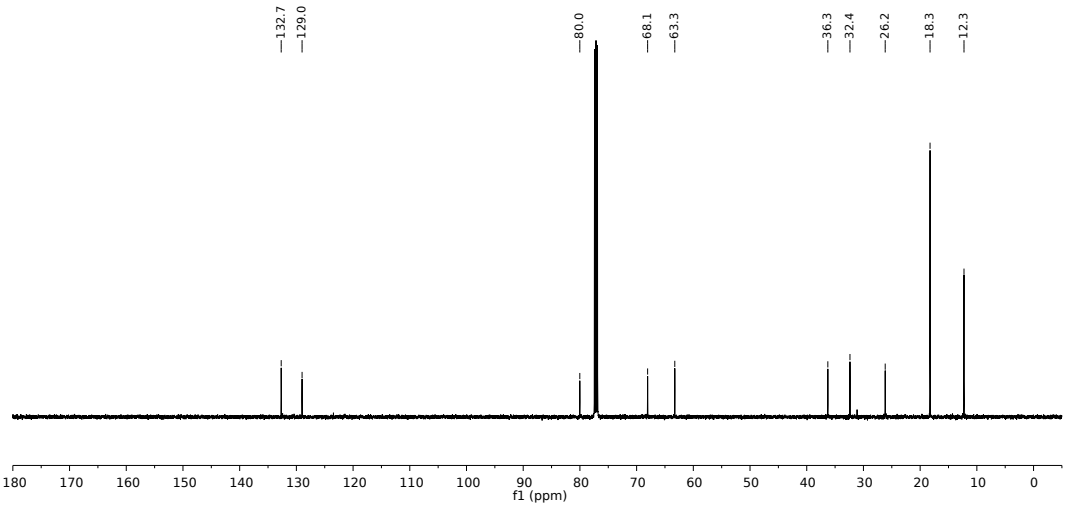

Transmittance [%]
2977.98
2868.45
1740.85
1464.05
1383.72
1366.44
1247.45
1091.17
1057.29
1006.59
967.88
873.42
790.54
597.30
Wavenumber cm-1

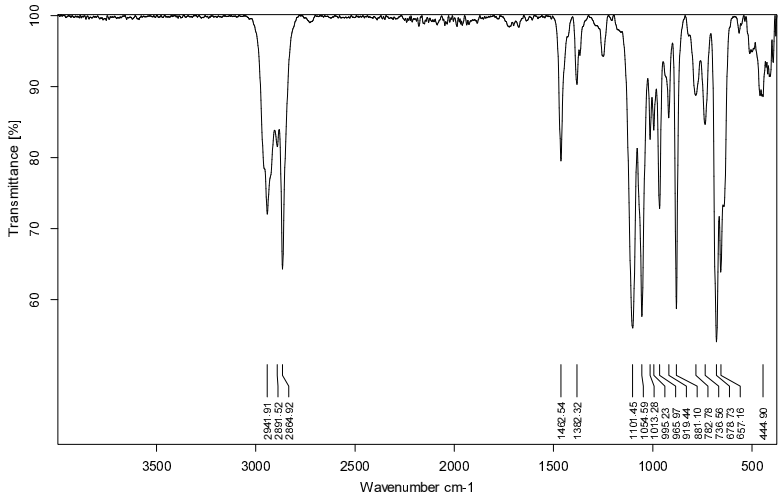

PivO
O
127o
0.97
1.05
1.00
2.38
1.08
1.09
2.39
3.49
1.50
10.57
f1 (ppm)

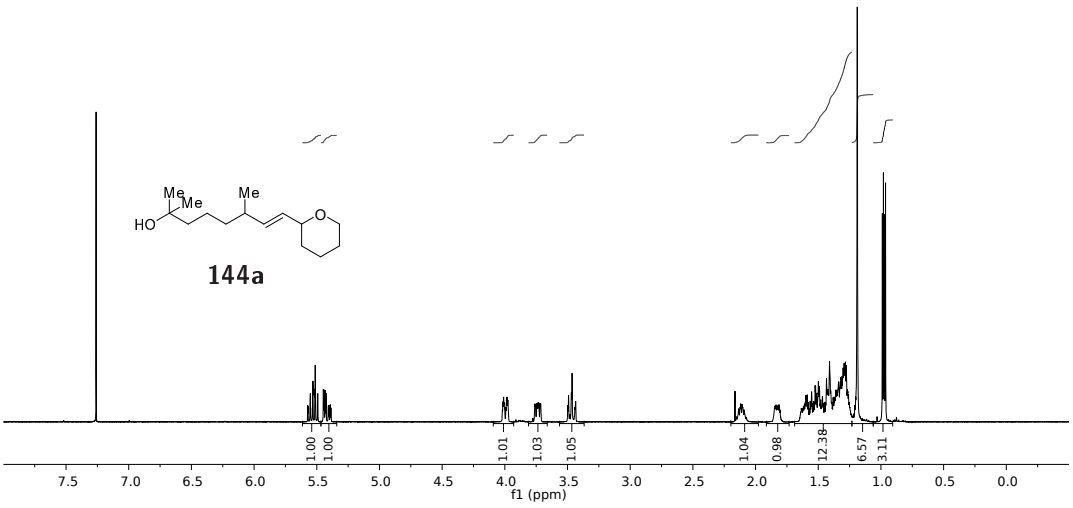

178.4
133.7
127.3
79.6
68.1
63.5
38.9
32.4
31.9
27.4
26.1
f1 (ppm)

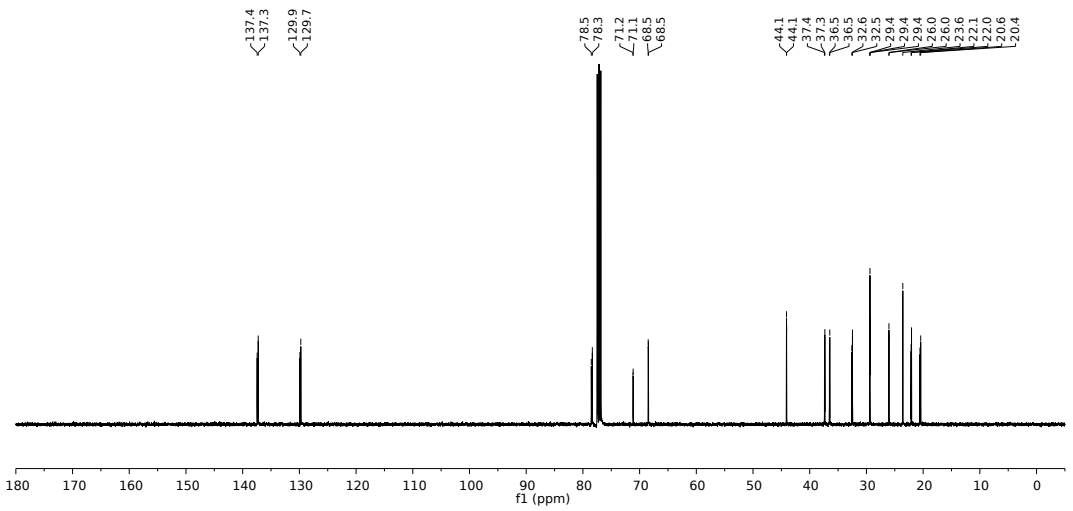

Transmittance [%]
2970.42
2872.02
1726.08
1479.98
1459.93
1387.58
1365.02
1283.07
1149.72
1052.45
965.54
889.22
770.34
590.45
497.66
408.41
Wavenumber cm-1

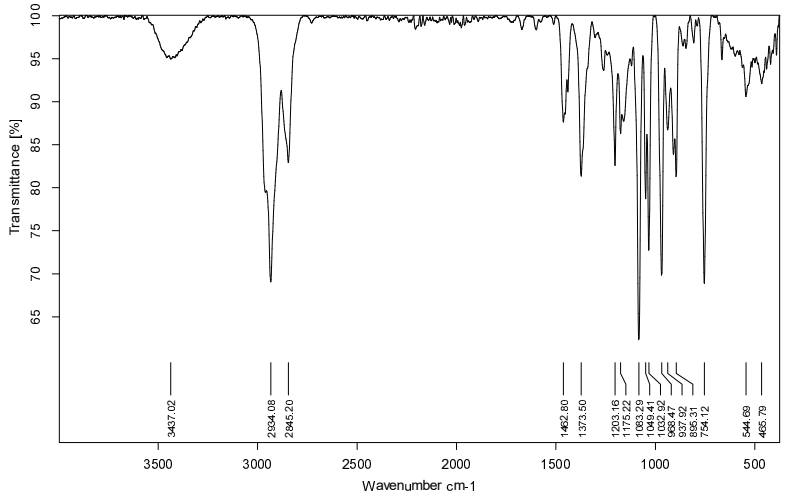

TIPSO
O
127p
1.00
1.00
1.12
1.05
3.20
2.10
3.23
1.62
24.46
f1 (ppm)

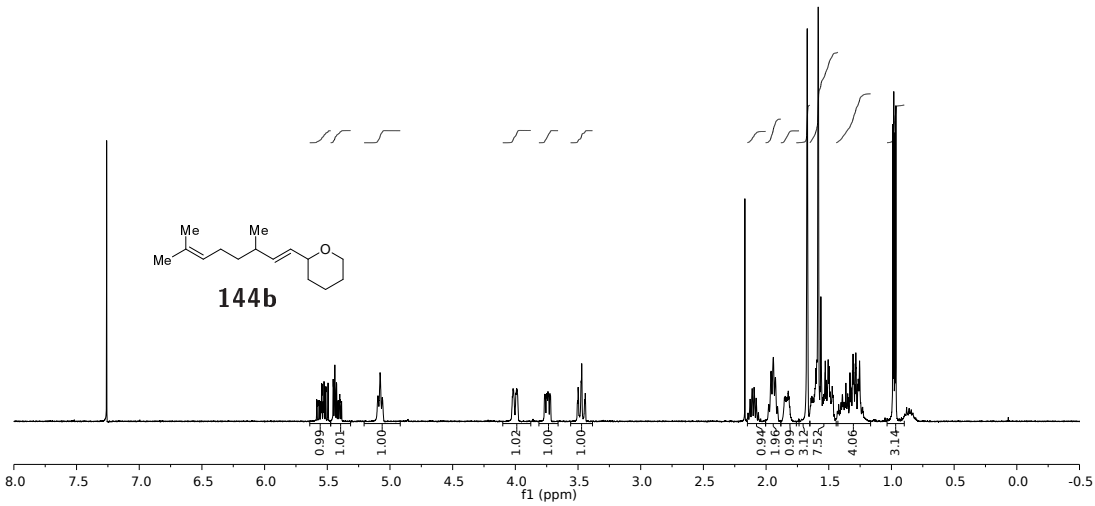

132.7
129.0
80.0
68.1
63.3
36.3
32.4
26.2
18.3
12.3
f1 (ppm)

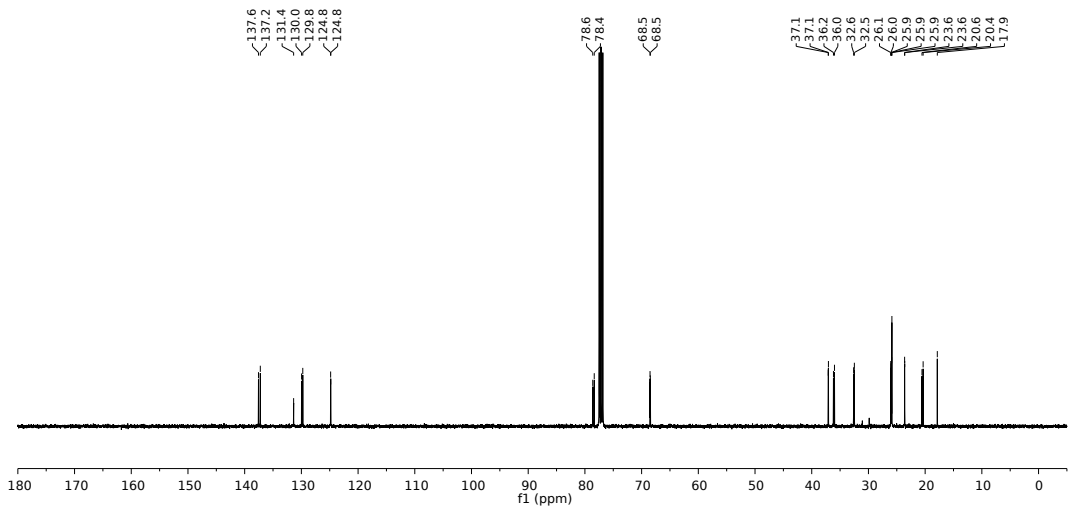

Transmittance [%]
2941.91
2891.52
2864.92
1462.54
1382.32
1101.45
1054.59
1013.28
995.23
965.97
918.44
881.10
782.78
736.56
673.73
615.16
444.90
Wavenumber cm-1

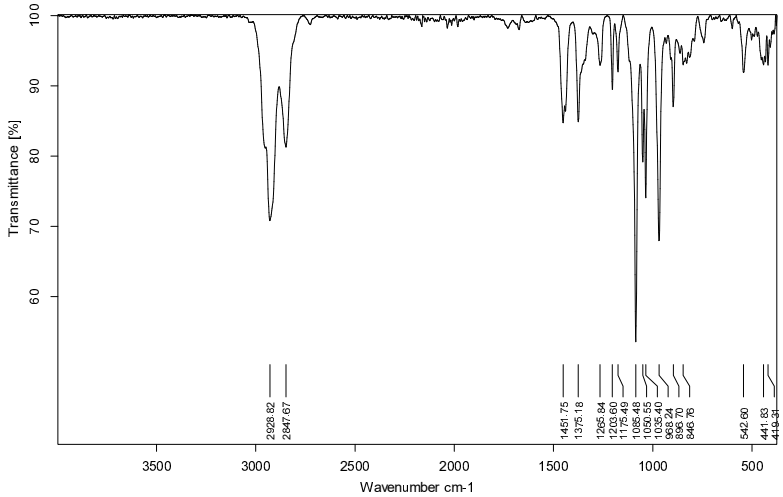

Me
Me
Me
HO
O
144a
1.00
1.00
1.01
1.03
1.05
1.04
0.98
12.38
6.57
3.11
f1 (ppm)

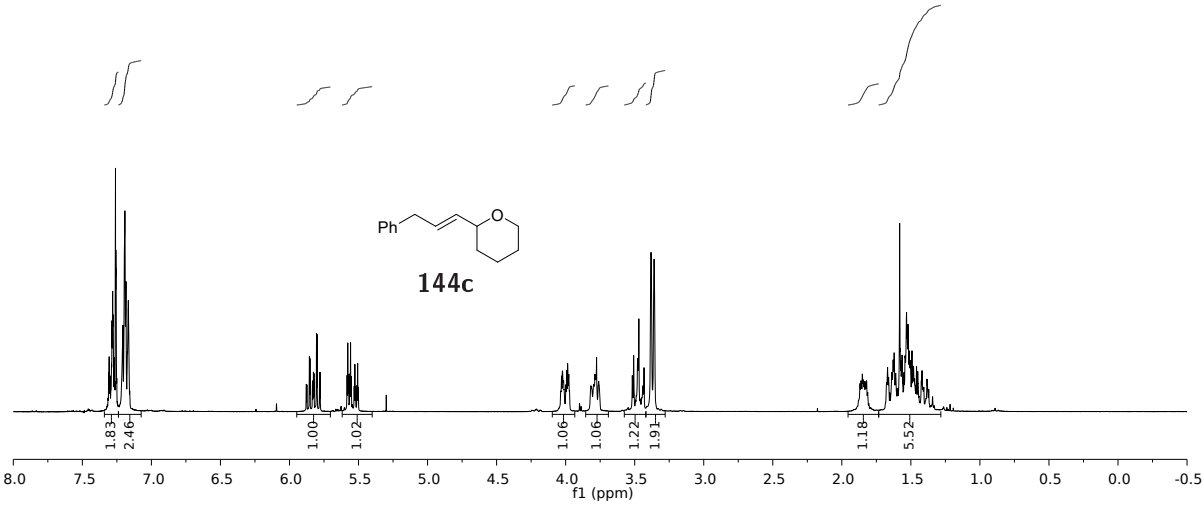

137.4
137.3
129.9
129.7
78.5
78.3
71.2
71.1
68.5
68.5
44.1
44.1
37.4
37.3
36.5
36.5
32.6
32.5
29.4
29.4
29.4
26.0
26.0
23.6
22.1
22.0
20.6
20.4
f1 (ppm)

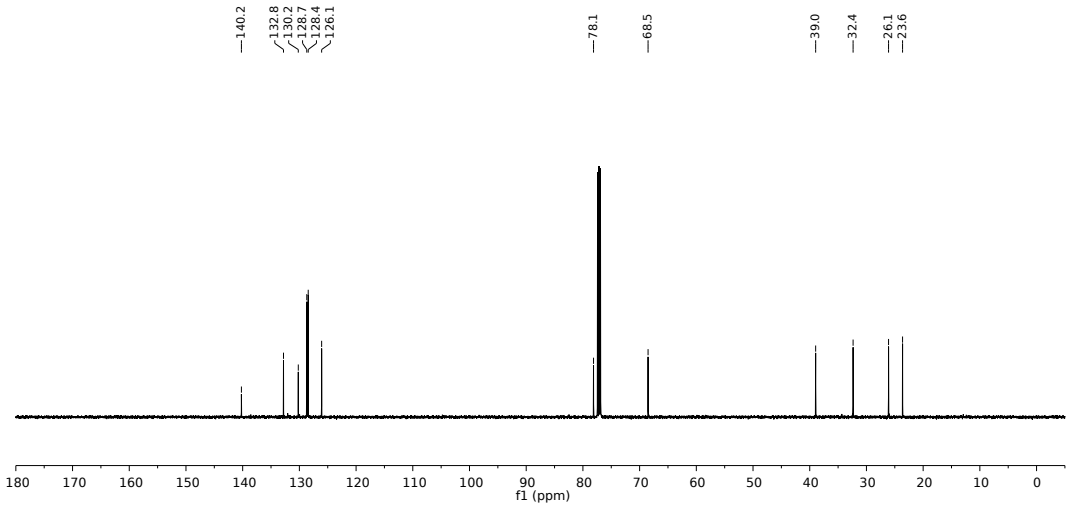

Transmittance [%]
3437.02
2934.08
2845.20
1462.80
1373.50
1203.16
1175.22
1063.29
1049.41
1003.02
968.47
937.92
895.31
754.12
544.69
465.79
Wavenumber cm-1

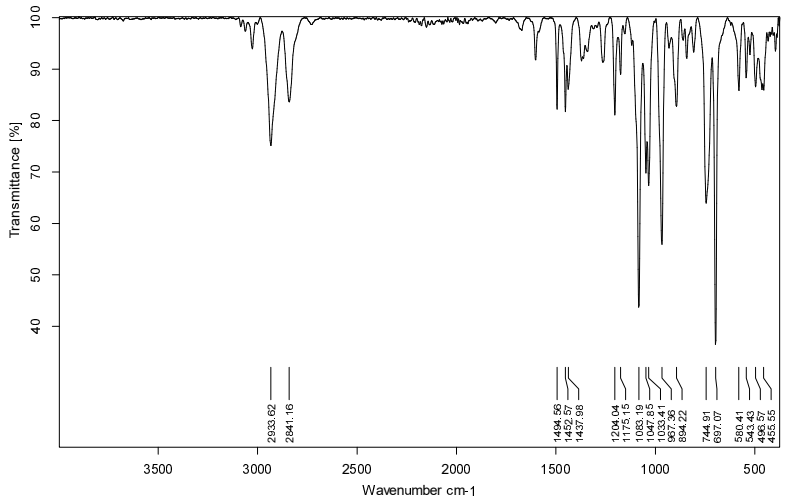

Me
Me
Me
O
144b
0.99
1.01
1.00
1.02
1.00
1.00
0.94
1.96
0.99
3.12
7.52
4.06
3.14
f1 (ppm)

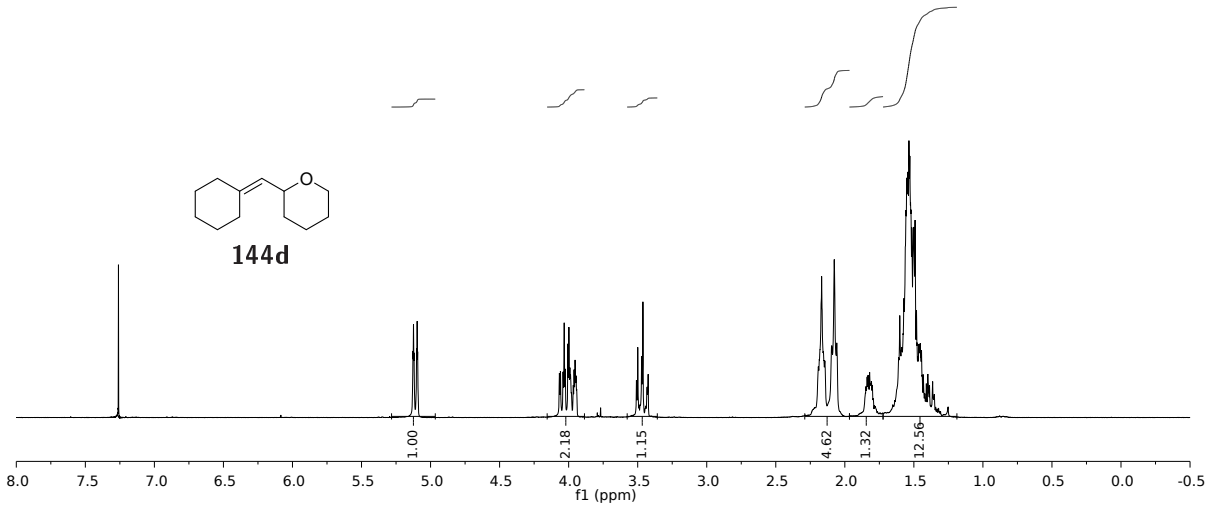

137.6
137.2
131.4
130.0
129.8
124.8
124.8
78.6
78.4
68.5
68.5
37.1
37.1
36.2
36.0
32.6
32.5
26.1
26.0
25.9
25.9
23.6
20.6
20.4
17.9
f1 (ppm)

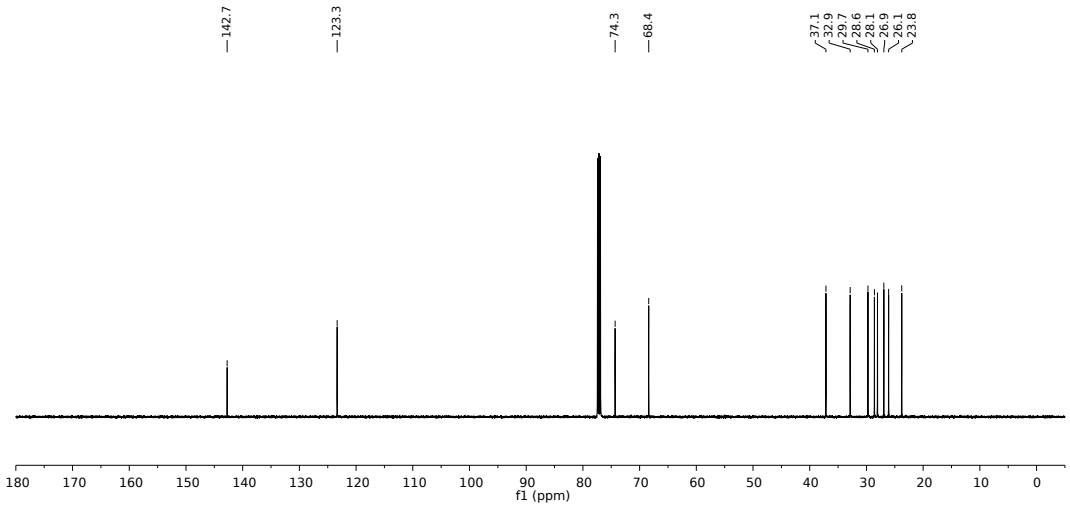

Transmittance [%]
2928.82
2847.67
1451.75
1375.18
1265.84
1203.60
1175.49
1085.48
1052.55
1036.40
968.24
898.70
848.76
542.60
441.83
418.31
Wavenumber cm-1

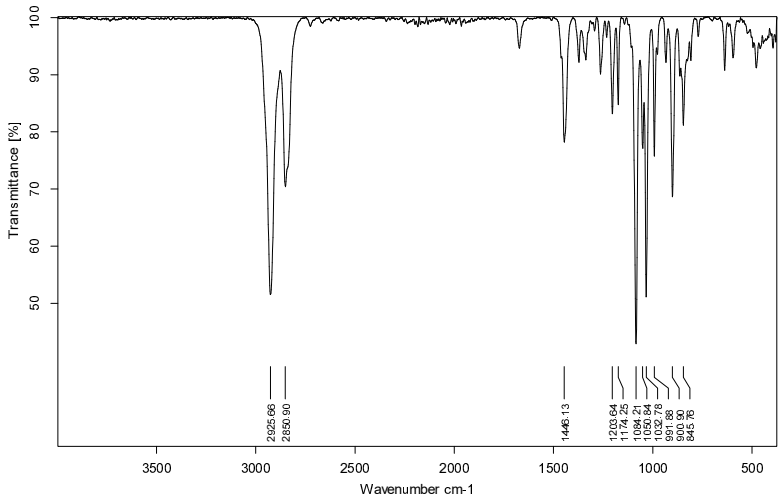

Ph
O
144c
1.83
2.46
1.00
1.02
1.06
1.06
1.22
1.91
1.18
5.52
f1 (ppm)

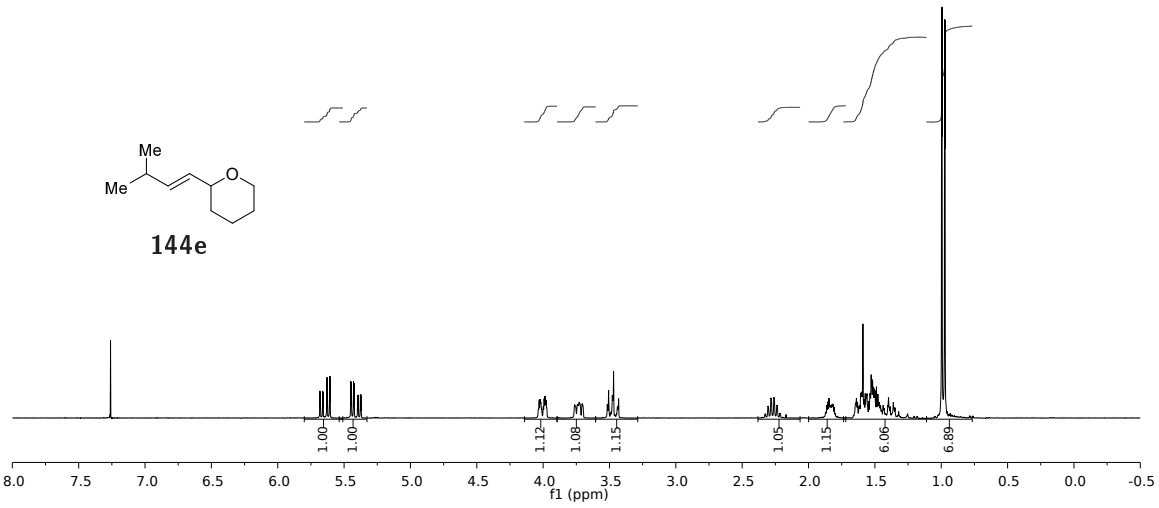

140.2
132.8
130.2
128.7
128.4
126.1
78.1
68.5
39.0
32.4
26.1
23.6
f1 (ppm)

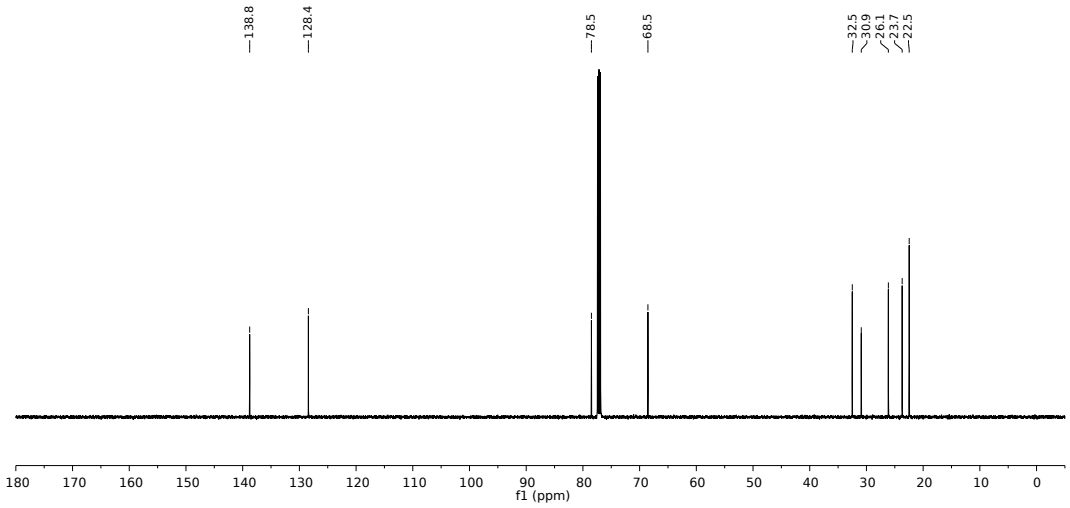

Transmittance [%]
2933.62
2841.16
1494.56
1452.57
1437.98
1204.04
1175.15
1083.19
1047.85
1024.41
987.36
894.22
744.91
697.07
560.41
543.43
495.27
455.55
Wavenumber cm-1

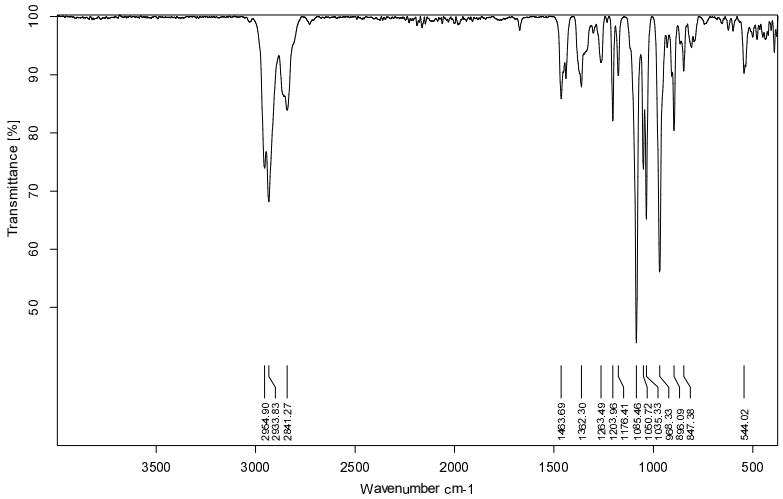

144d
1.00
2.18
1.15
4.62
1.32
12.56
f1 (ppm)

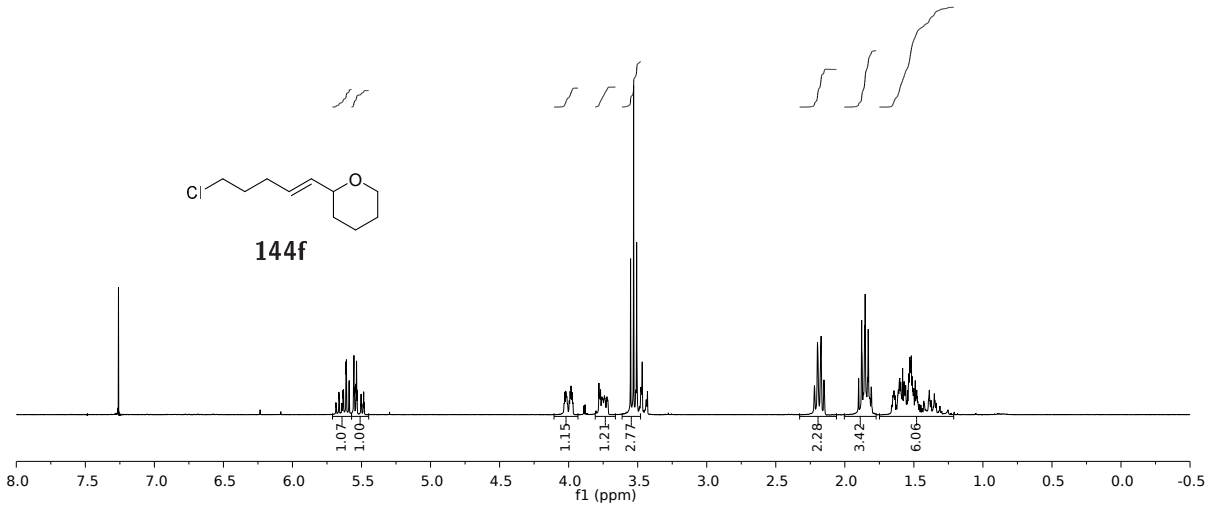

142.7
123.3
74.3
68.4
37.1
32.9
29.7
28.6
28.1
26.9
26.1
23.8
f1 (ppm)

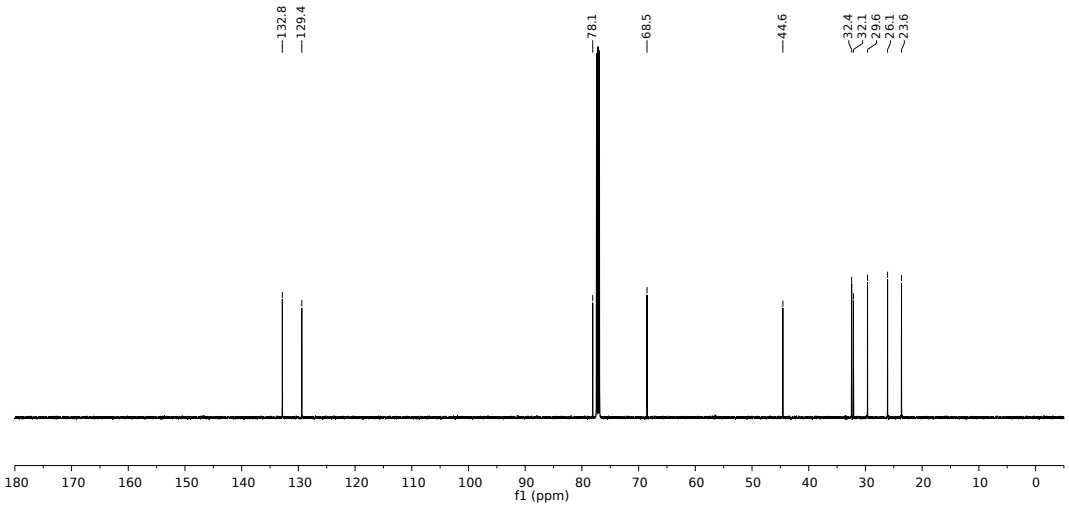

Transmittance [%]
2925.66
2850.90
1446.13
1203.64
1174.25
1084.21
1052.84
1032.13
991.88
900.90
845.76
Wavenumber cm-1

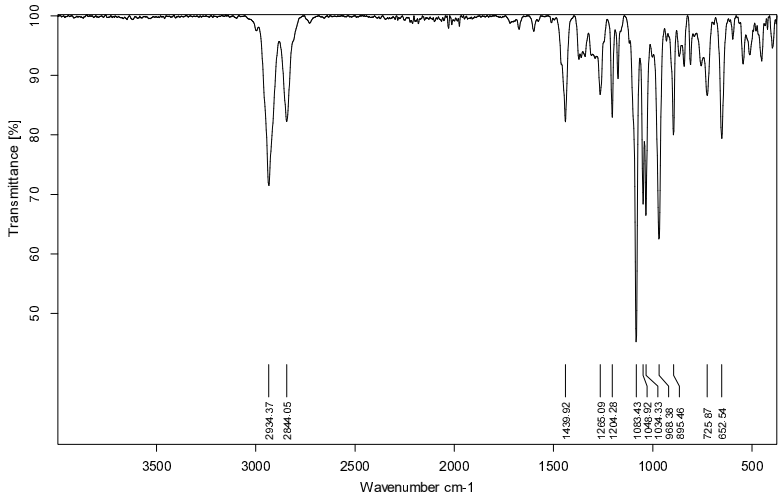

Me
Me
O
144e
1.00
1.00
1.12
1.08
1.15
1.05
1.15
6.06
6.89
f1 (ppm)

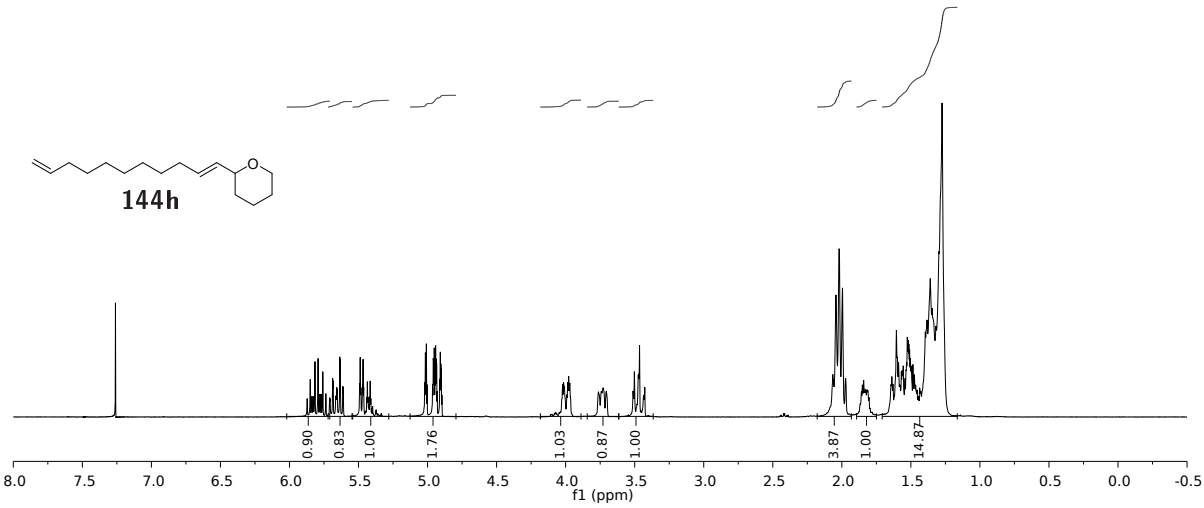

138.8
128.4
78.5
68.5
32.5
30.9
26.1
23.7
22.5
f1 (ppm)

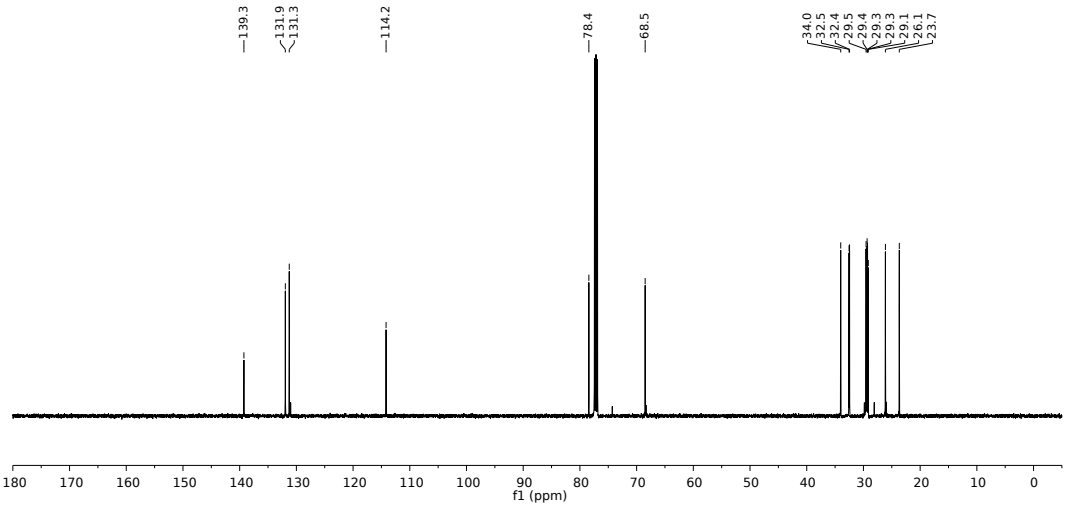

Transmittance [%]
2954.90
2933.83
2841.27
1463.69
1352.30
1263.49
1203.95
1176.41
1085.46
1050.72
1003.13
968.33
895.09
847.38
544.02
Wavenumber cm-1

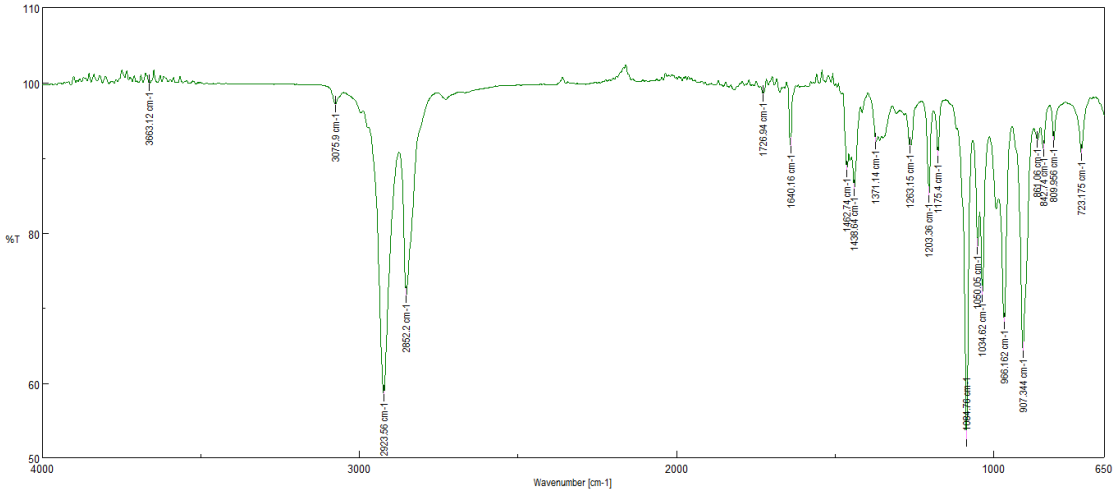

Cl
O
144f
1.07
1.00
1.15
1.21
2.77
2.28
3.42
6.06
f1 (ppm)

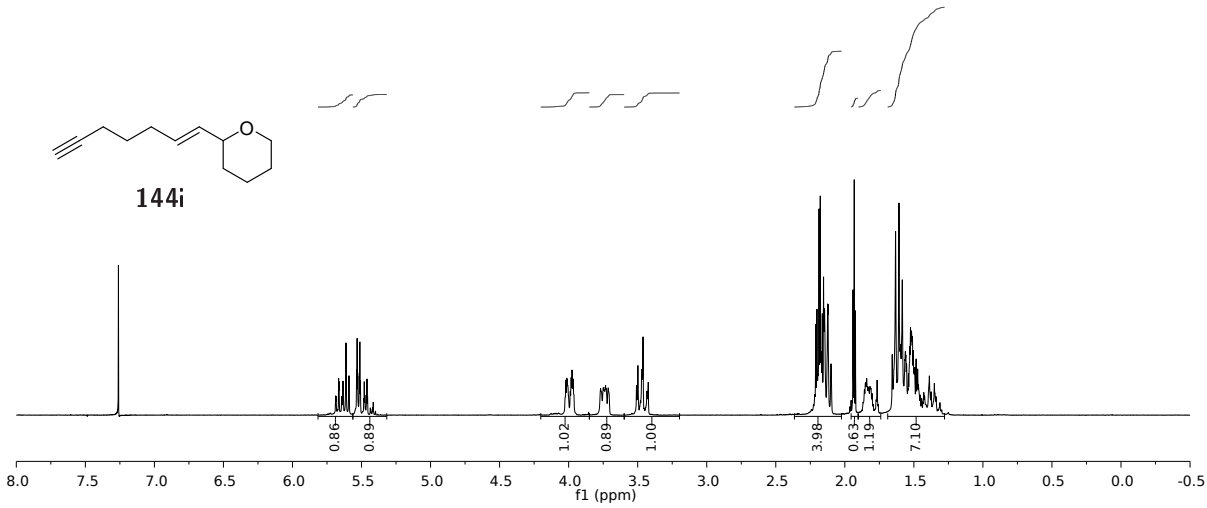

132.8
129.4
78.1
68.5
44.6
32.4
32.1
29.6
26.1
23.6
f1 (ppm)

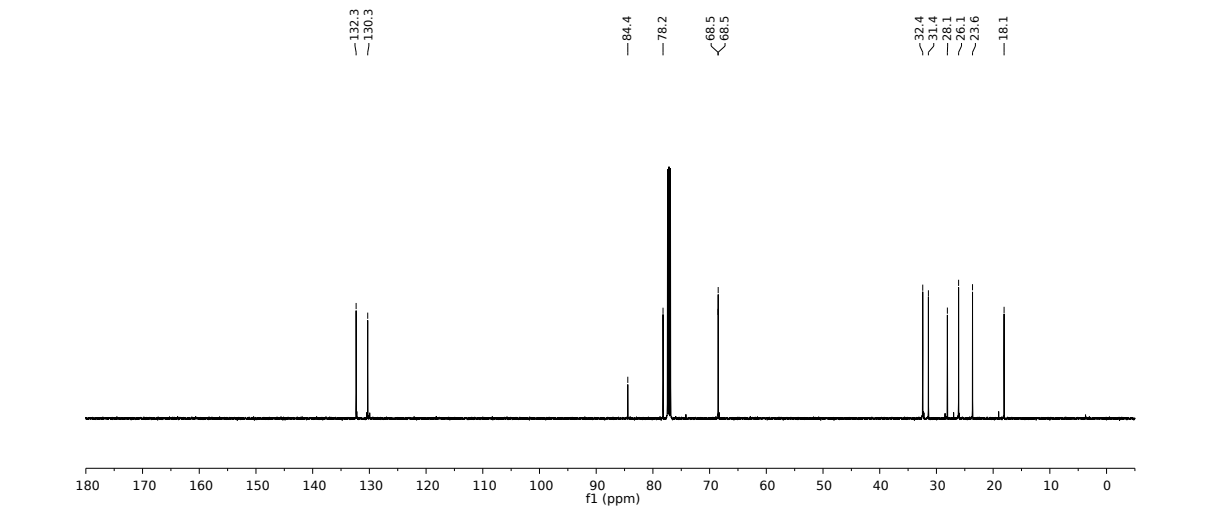

Transmittance [%]
2934.37
2844.05
1439.92
1265.09
1204.28
1083.43
1048.32
1004.33
968.38
895.46
725.87
652.54
Wavenumber cm-1

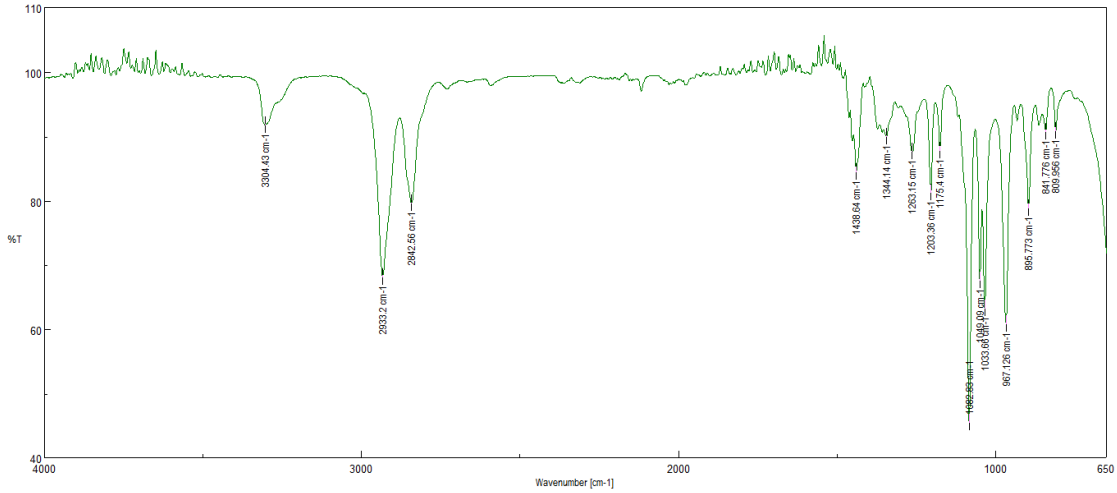

144h
O
0.90
0.83
1.00
1.76
1.03
0.87
1.00
3.87
1.00
14.87
f1 (ppm)

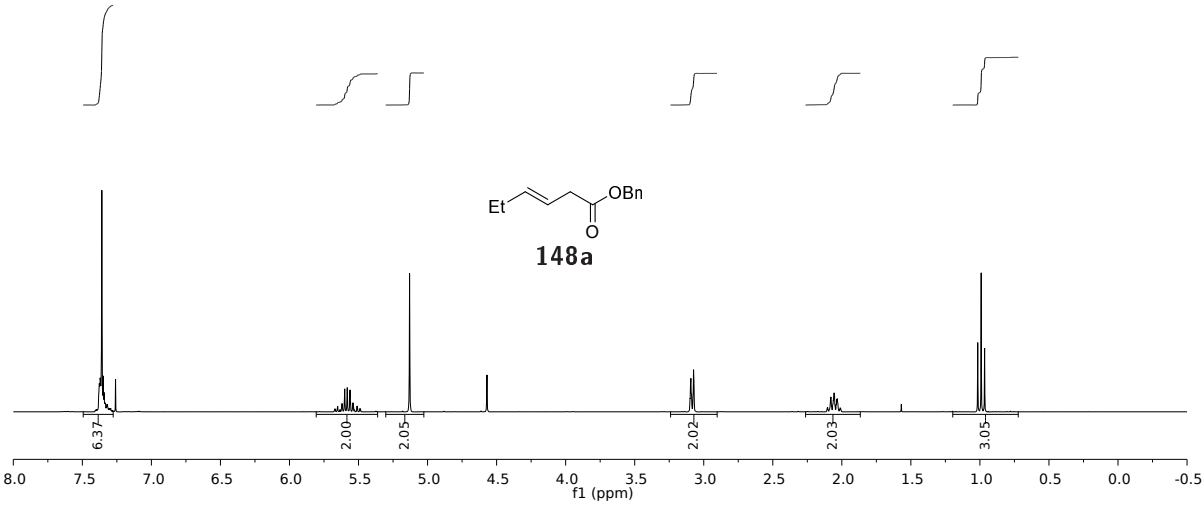

139.3
131.9
131.3
114.2
78.4
68.5
34.0
32.5
32.4
29.5
29.4
29.3
29.3
29.1
26.1
23.7
f1 (ppm)

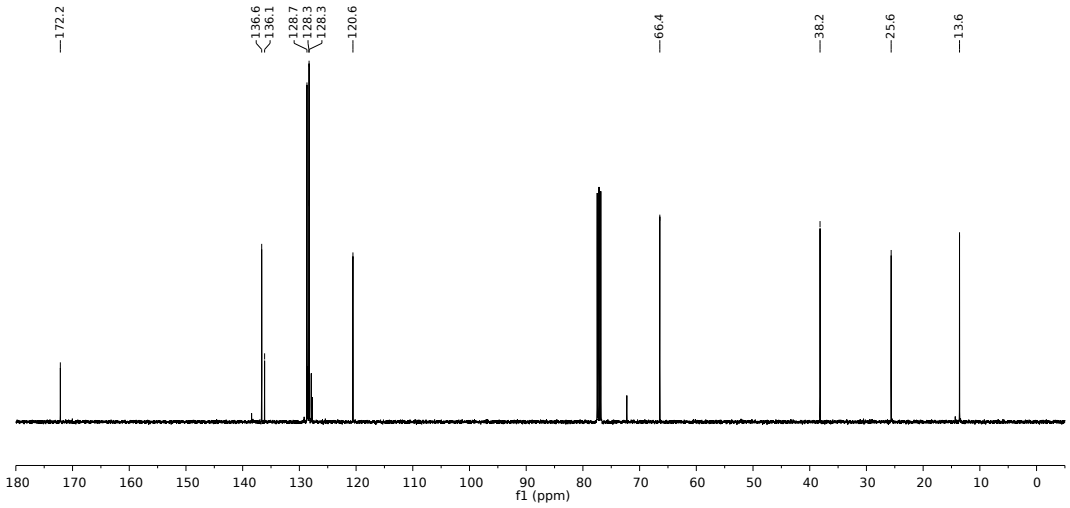

%T
3663.12 cm-1
3075.9 cm-1
2923.56 cm-1
2852.2 cm-1
1726.94 cm-1
1640.16 cm-1
1462.74 cm-1
1438.64 cm-1
1371.14 cm-1
1263.15 cm-1
1203.36 cm-1
1175.4 cm-1
1084.76 cm-1
1050.05 cm-1
1034.62 cm-1
966.162 cm-1
907.344 cm-1
861.06 cm-1
842.74 cm-1
809.956 cm-1
723.175 cm-1
Wavenumber [cm-1]

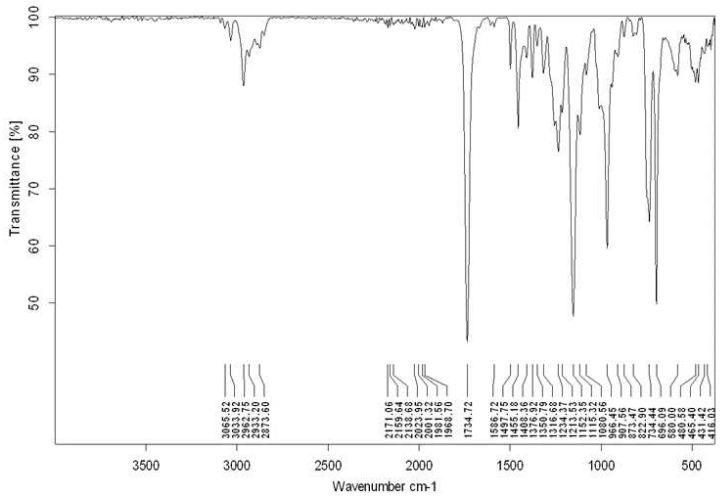

144i
0.86
0.89
1.02
0.89
1.00
3.98
0.63
1.19
7.10
f1 (ppm)

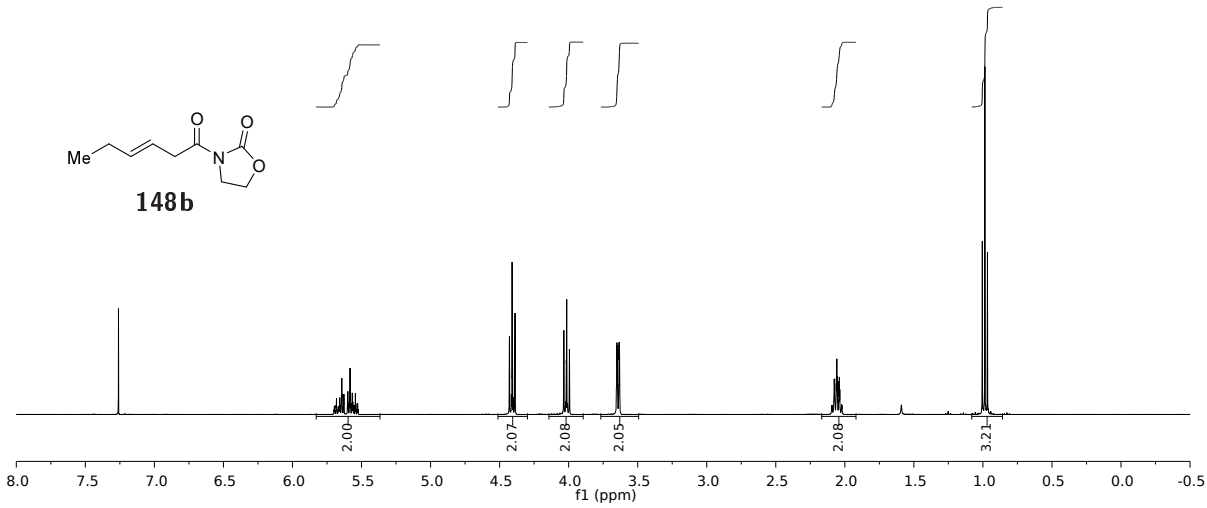

132.3
130.3
84.4
78.2
68.5
68.5
32.4
31.4
28.1
26.1
23.6
18.1
f1 (ppm)

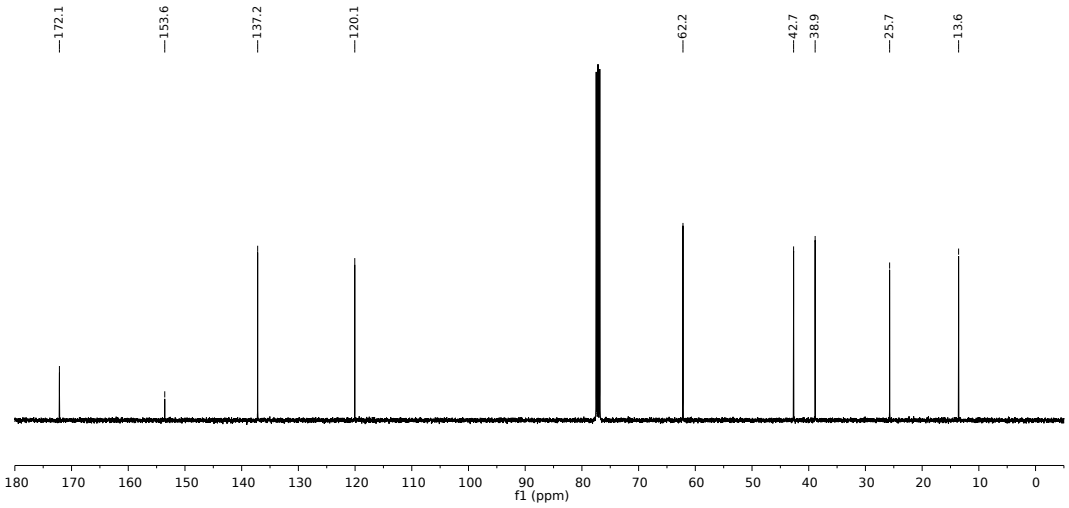

%T
3304.43 cm-1
2933.2 cm-1
2842.56 cm-1
1438.64 cm-1
1344.14 cm-1
1263.15 cm-1
1203.36 cm-1
1176.4 cm-1
1049.09 cm-1
1033.66 cm-1
967.126 cm-1
895.773 cm-1
841.776 cm-1
809.996 cm-1
Wavenumber [cm-1]

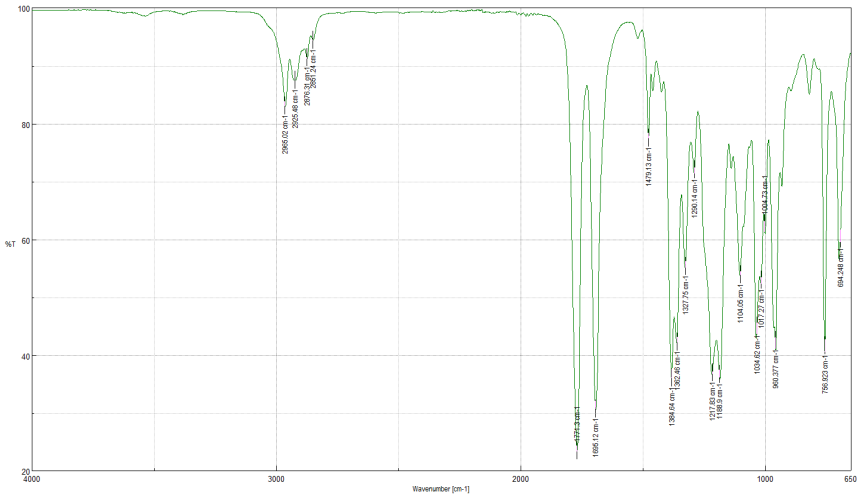

Et
OBn
O
148a
6.37
2.00
2.05
2.02
2.03
3.05
f1 (ppm)

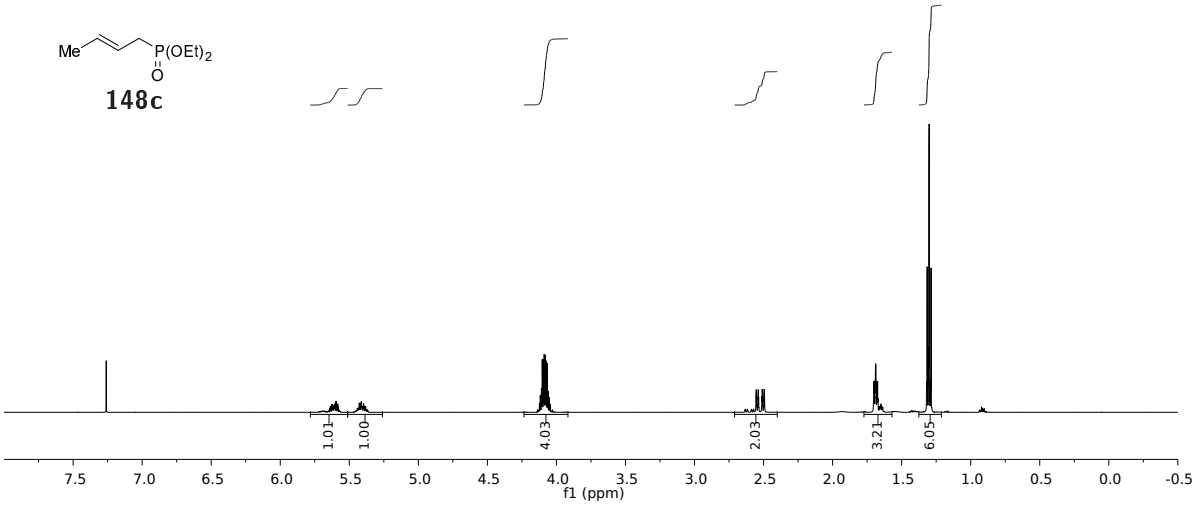

172.2
136.6
136.1
128.7
128.3
128.3
120.6
66.4
38.2
25.6
13.6
f1 (ppm)

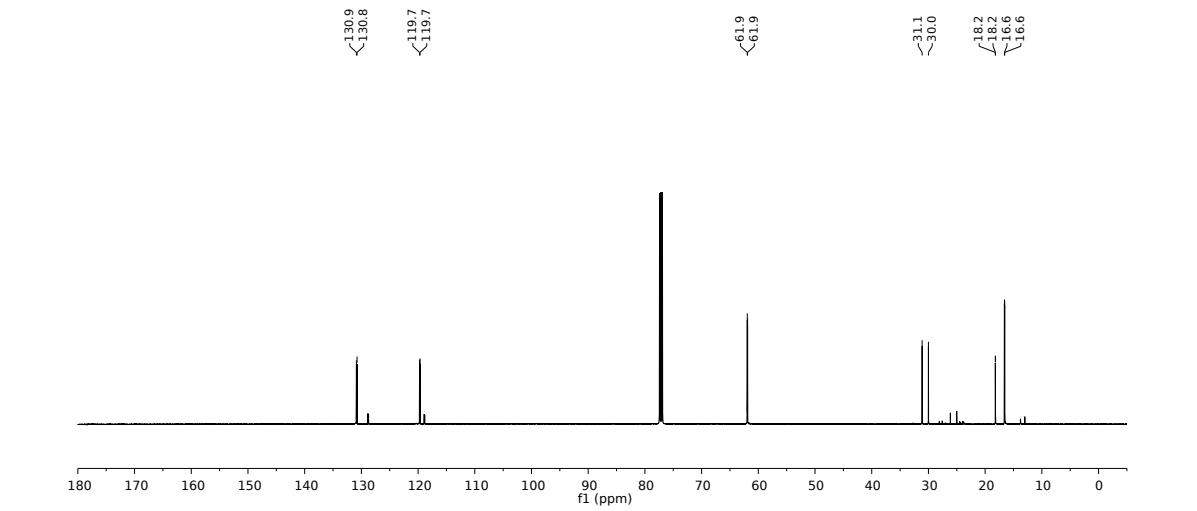

Transmittance [%]
Wavenumber cm-1

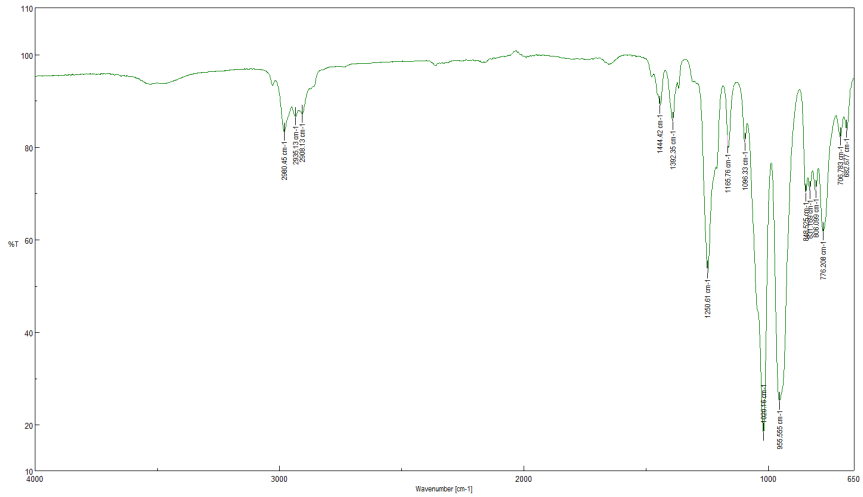

Me
148b
2.00
2.07
2.08
2.05
2.08
3.21
f1 (ppm)

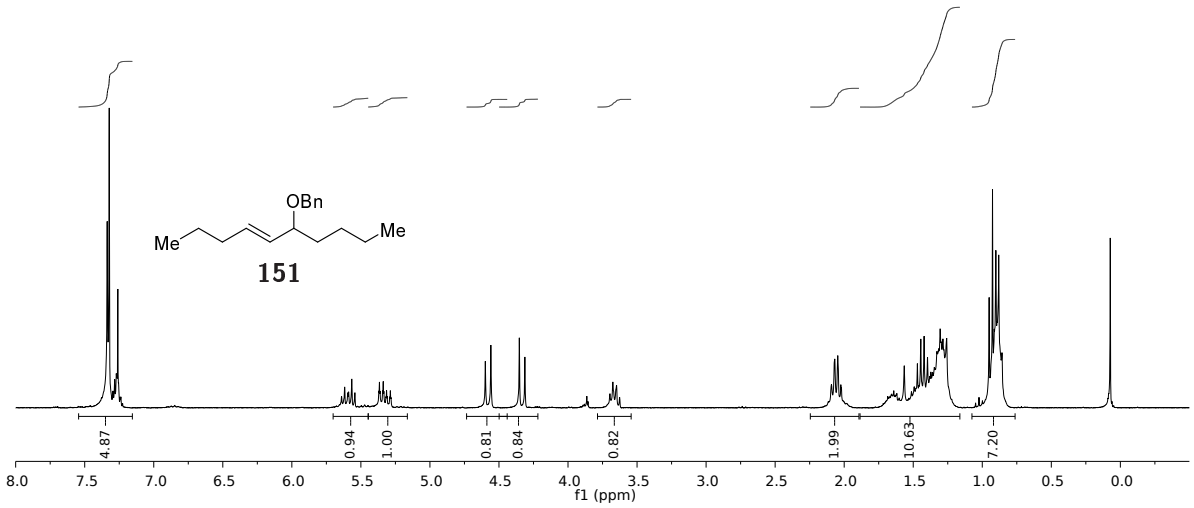

172.1
153.6
137.2
120.1
62.2
42.7
38.9
25.7
13.6
f1 (ppm)

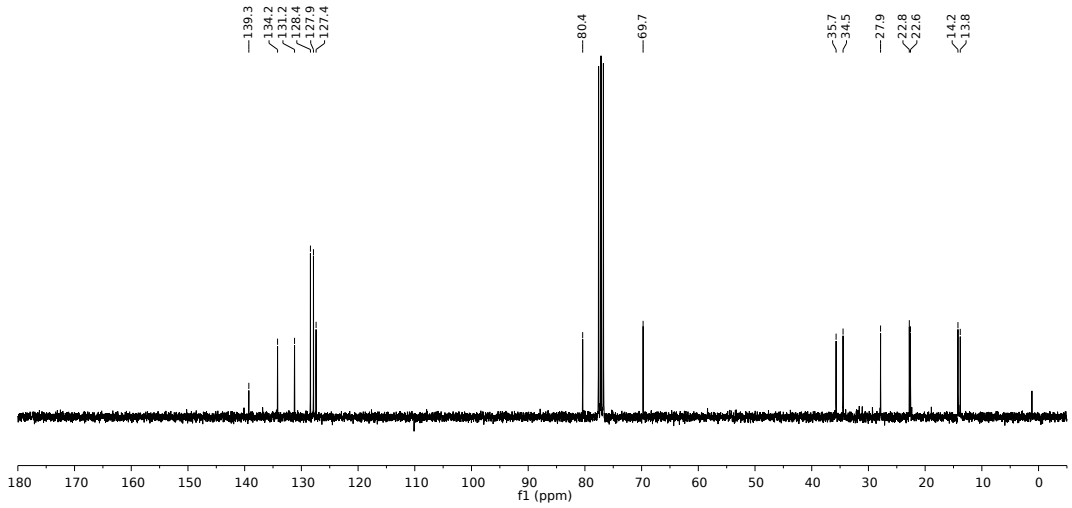

%T
Wavenumber [cm-1]

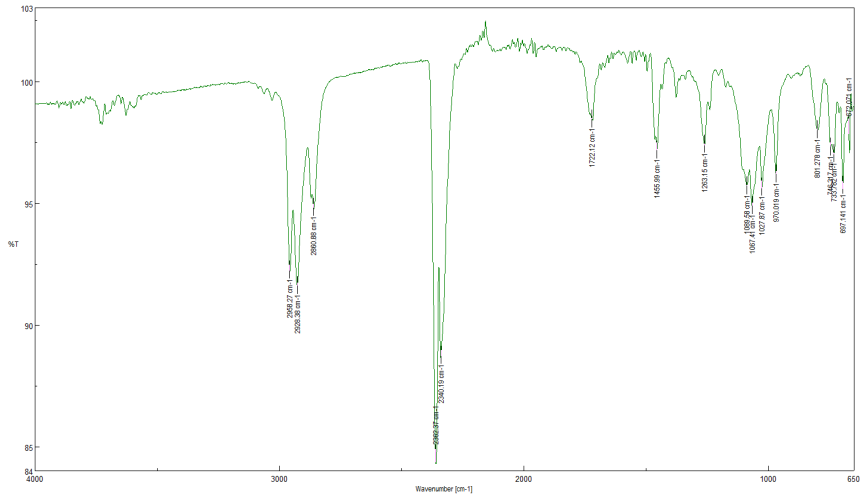

Me
P(OEt)2
O
148c
1.01
1.00
4.03
2.03
3.21
6.05
f1 (ppm)

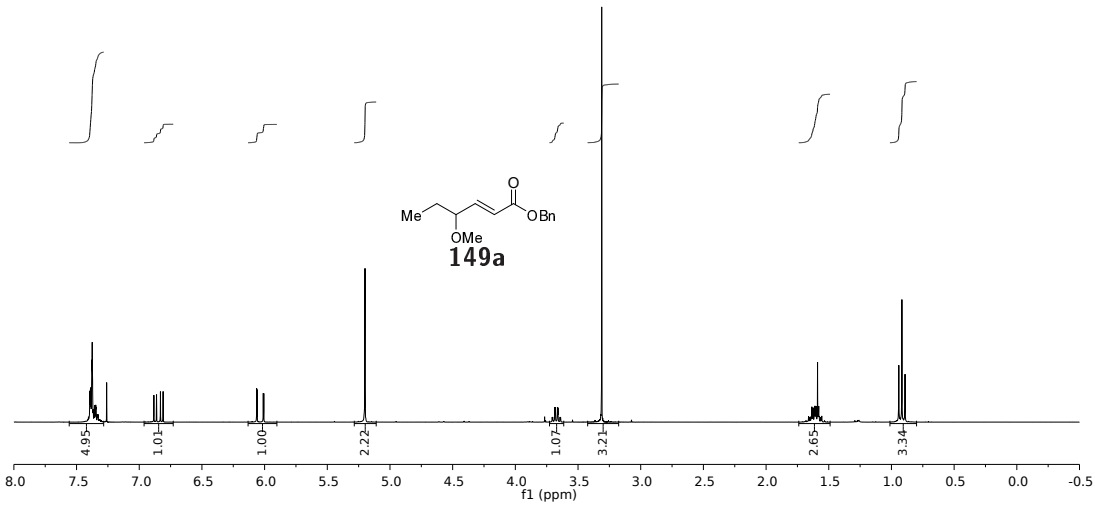

130.9
130.8
119.7
119.7
61.9
61.9
31.1
30.0
18.2
18.2
16.6
16.6
f1 (ppm)

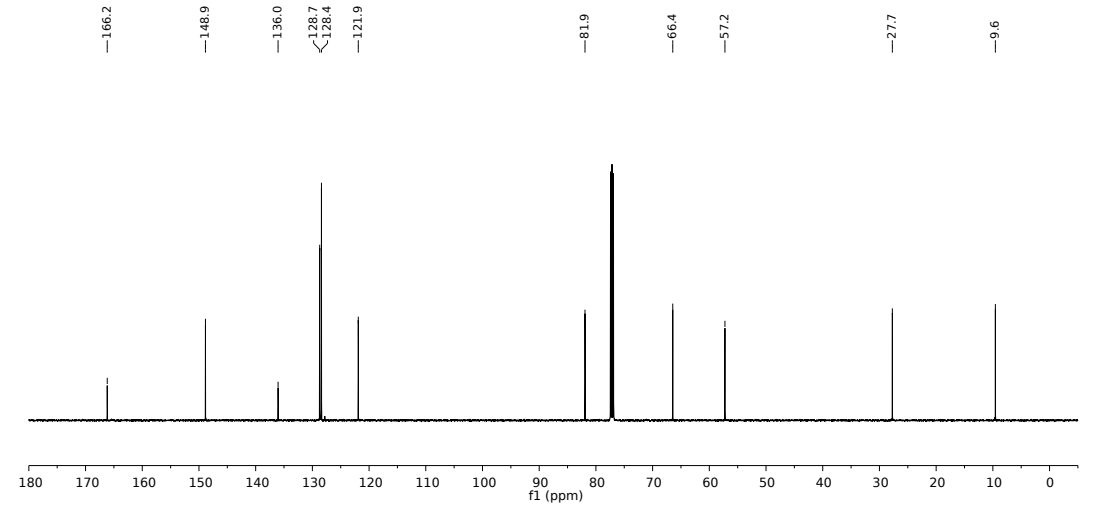

%T
Wavenumber [cm-1]

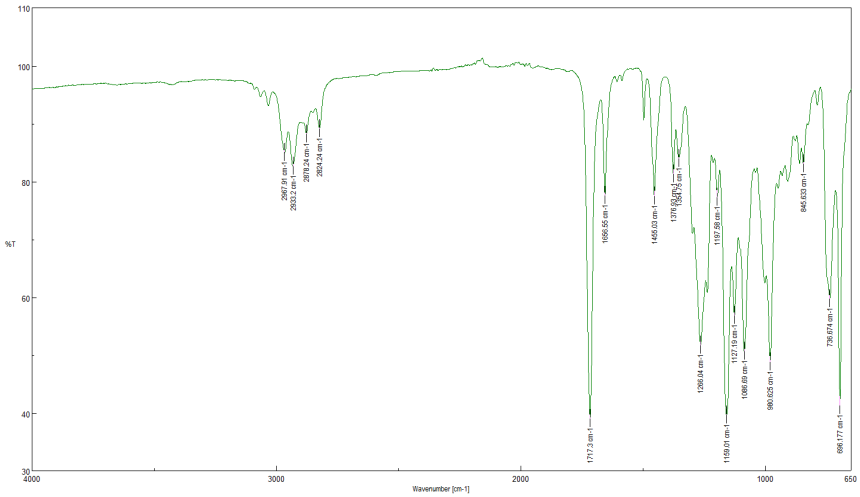

OBn
Me
Me
151
4.87
0.94
1.00
0.81
0.84
0.82
1.99
10.63
7.20
f1 (ppm)

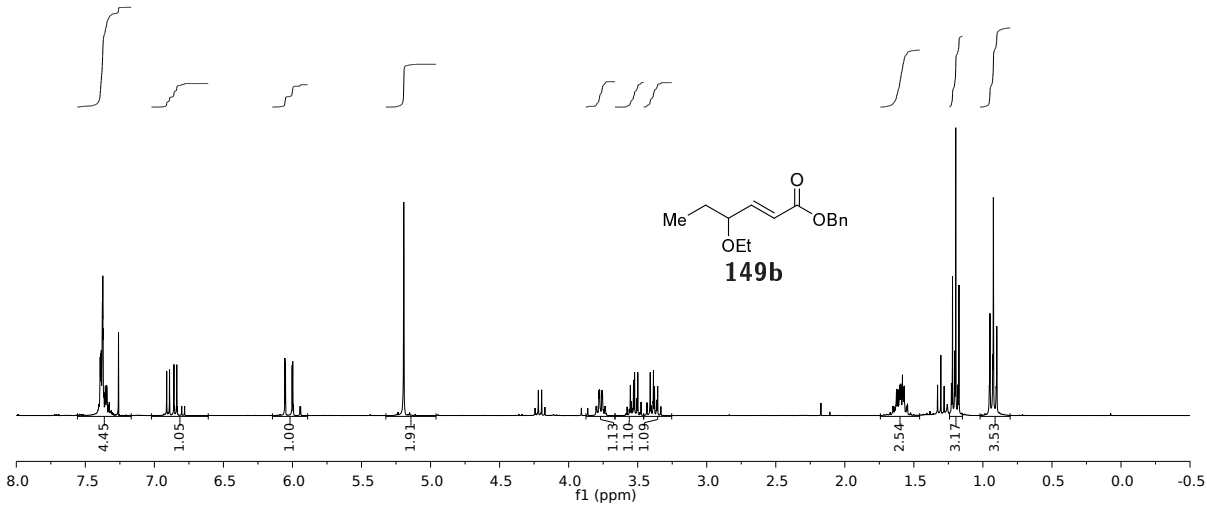

139.3
134.2
131.2
128.4
127.9
127.4
80.4
69.7
35.7
34.5
27.9
22.8
22.6
14.2
13.8
f1 (ppm)

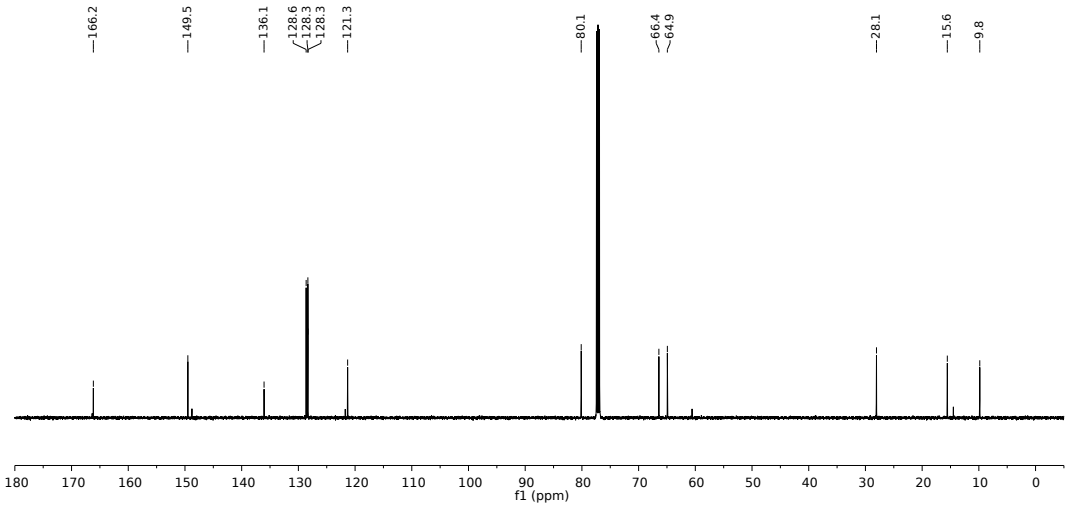

%T
Wavenumber [cm-1]

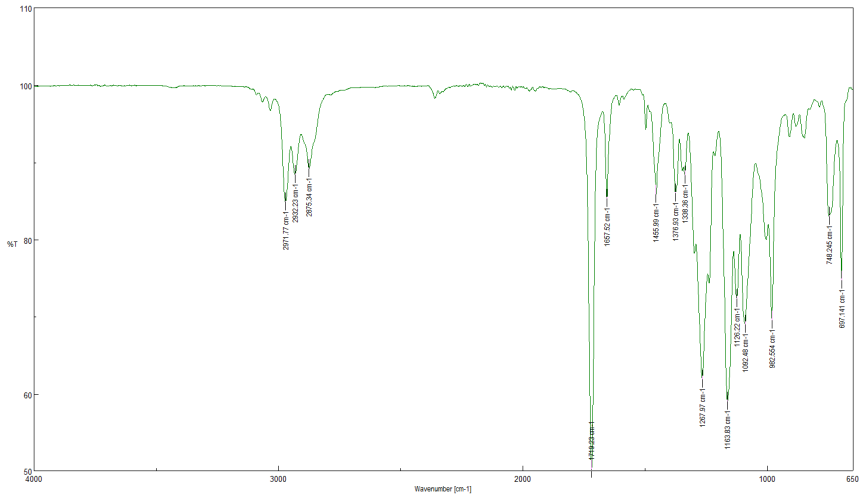

Me
OMe
O
OBn
149a
4.95
1.01
1.00
2.22
1.07
3.21
2.65
3.34
f1 (ppm)

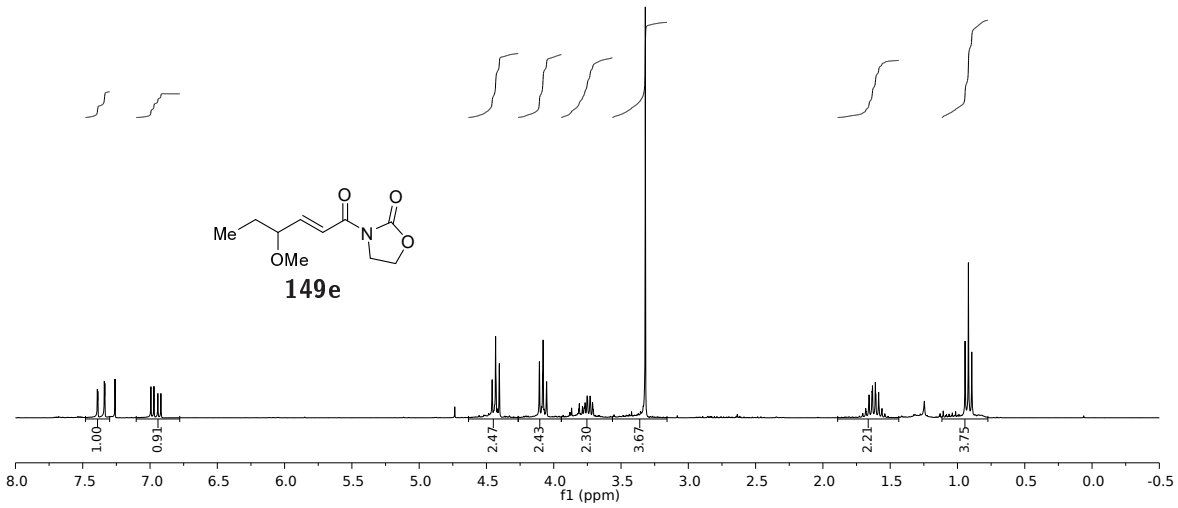

166.2
148.9
136.0
128.7
128.4
121.9
81.9
66.4
57.2
27.7
9.6
f1 (ppm)

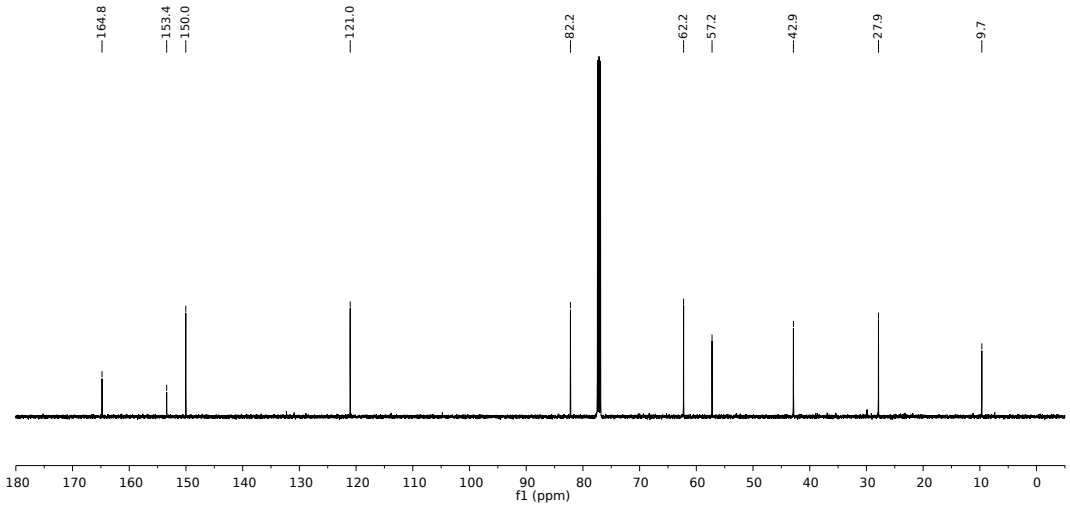

%T
Wavenumber [cm-1]

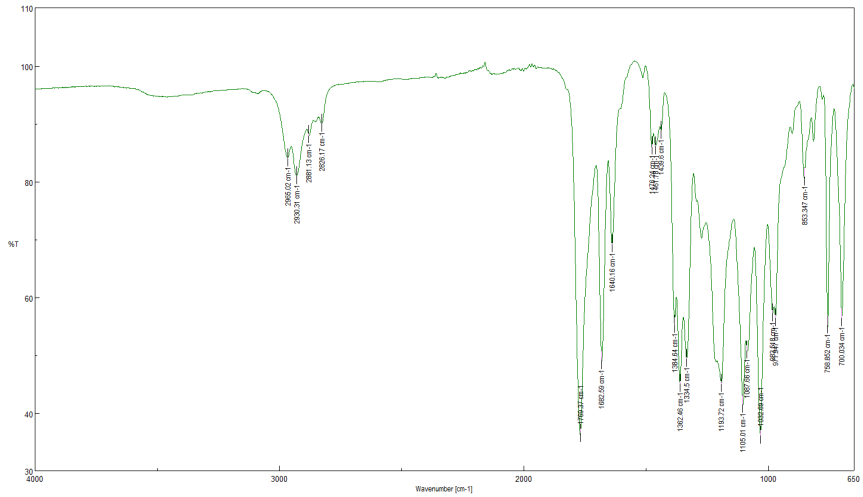

Me
OEt
O
OBn
149b
4.45
1.05
1.00
1.91
1.13
1.10
1.09
2.54
3.17
3.53
f1 (ppm)

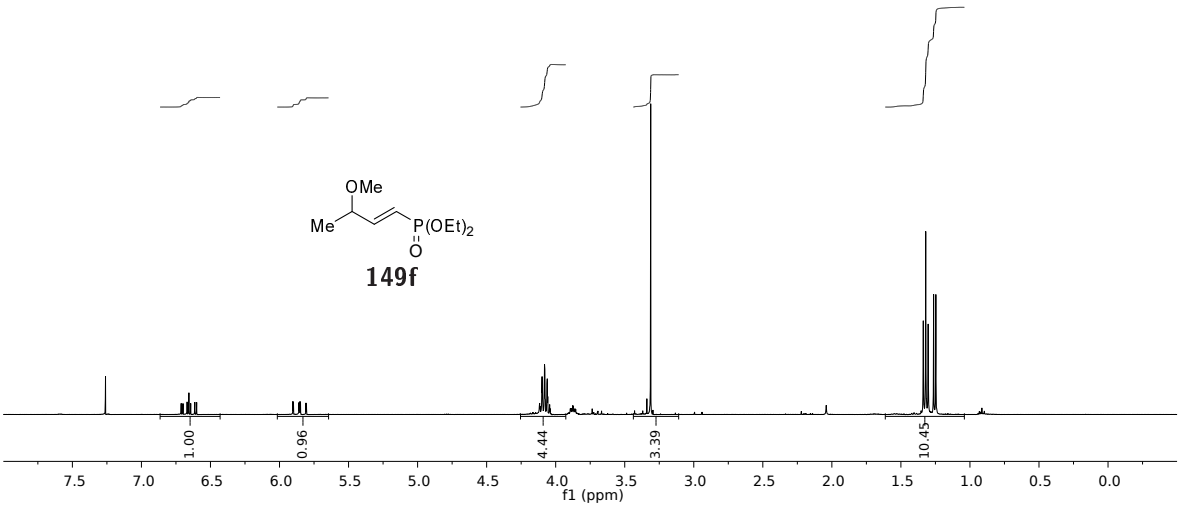

166.2
149.5
136.1
128.6
128.3
128.3
121.3
80.1
66.4
64.9
28.1
15.6
9.8
f1 (ppm)

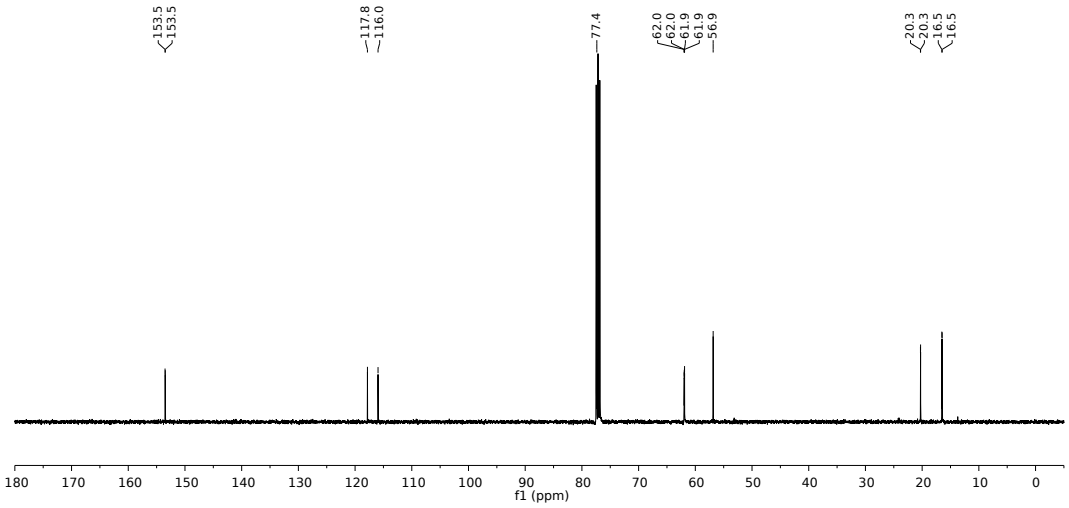

%T
Wavenumber [cm-1]

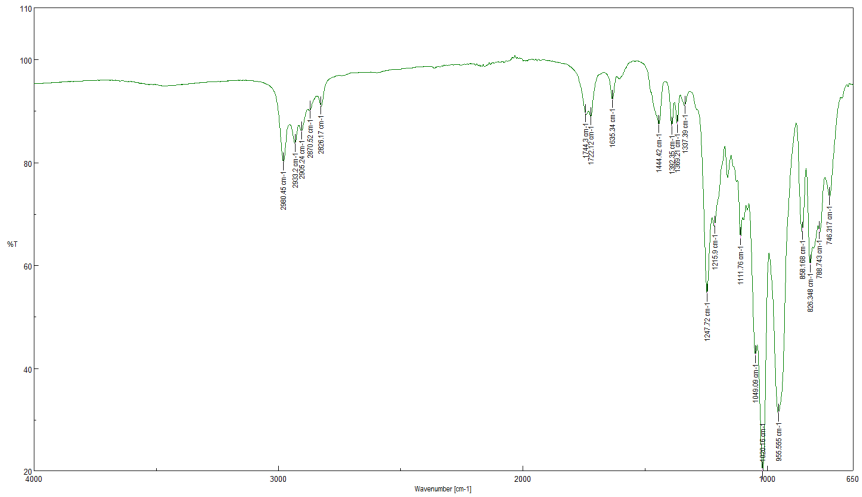

Me
OMe
O
O
N
O
149e
1.00
0.91
2.47
2.43
2.30
3.67
2.21
3.75
f1 (ppm)

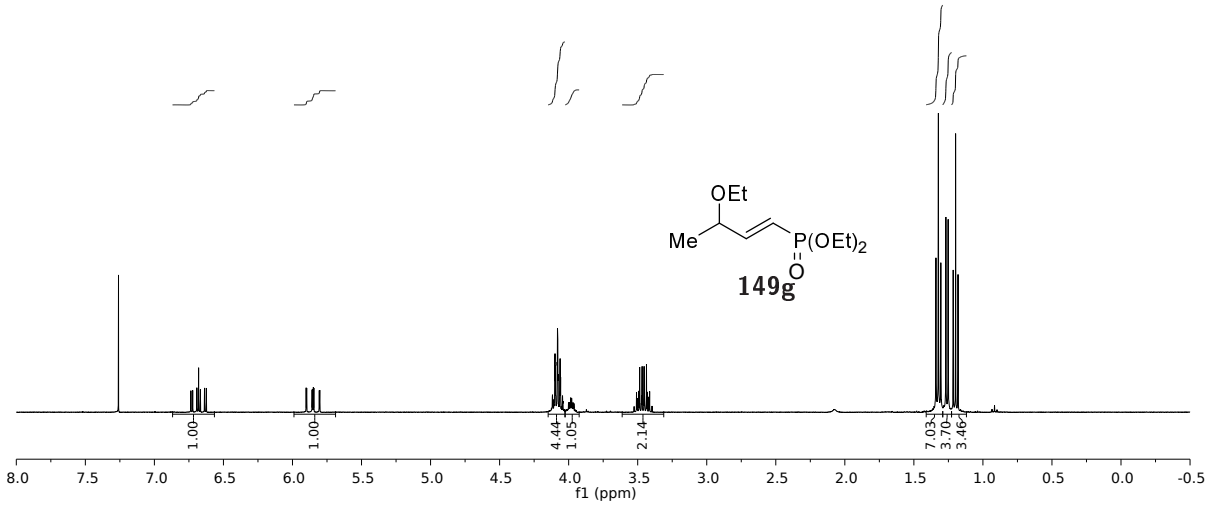

164.8
153.4
150.0
121.0
82.2
62.2
57.2
42.9
27.9
9.7
f1 (ppm)

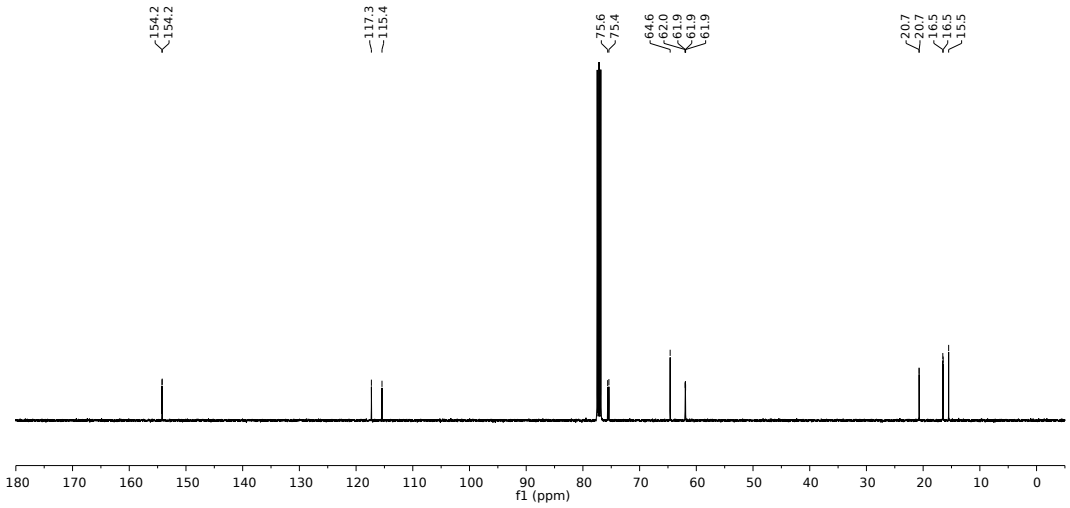

%T
Wavenumber [cm-1]

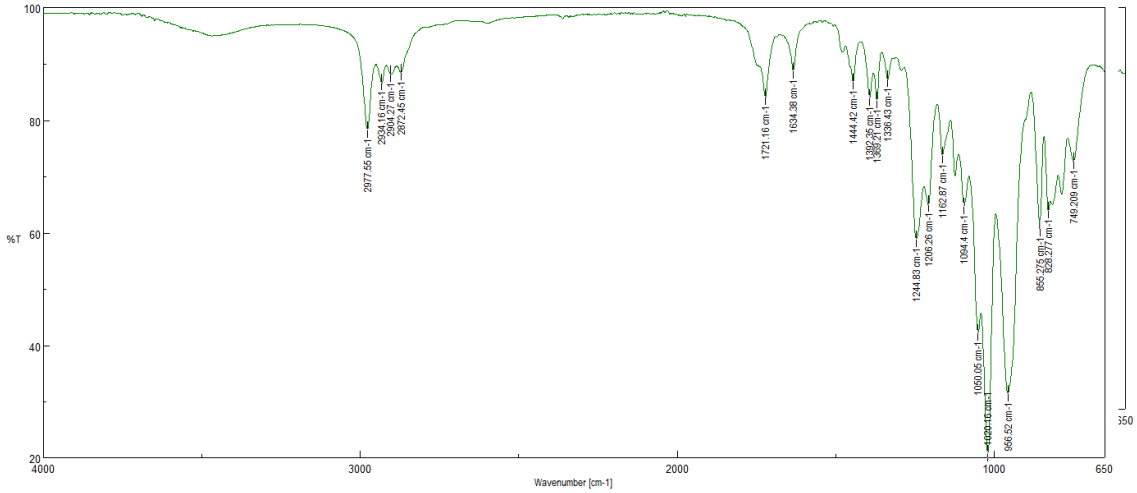

OMe
Me
P(OEt)2
O
149f
1.00
0.96
4.44
3.39
10.45
f1 (ppm)

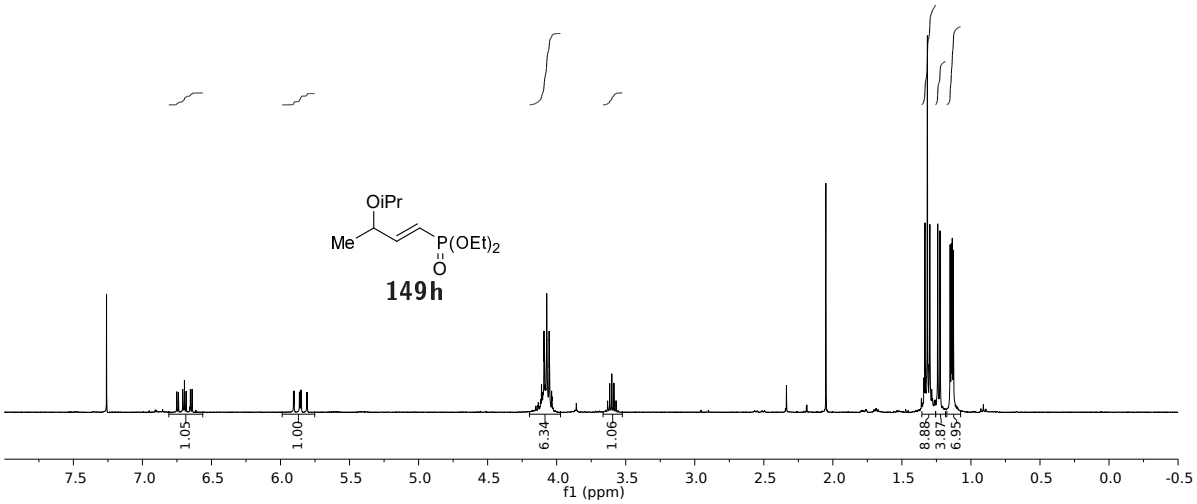

153.5
153.5
117.8
116.0
77.4
62.0
62.0
61.9
61.9
56.9
20.3
20.3
16.5
16.5
f1 (ppm)

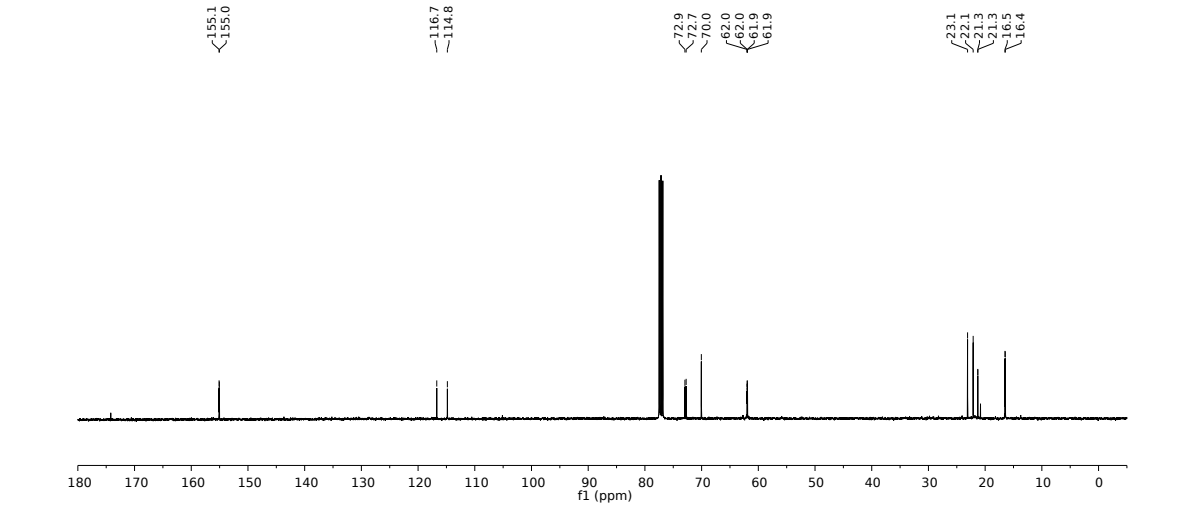

%T
Wavenumber [cm-1]

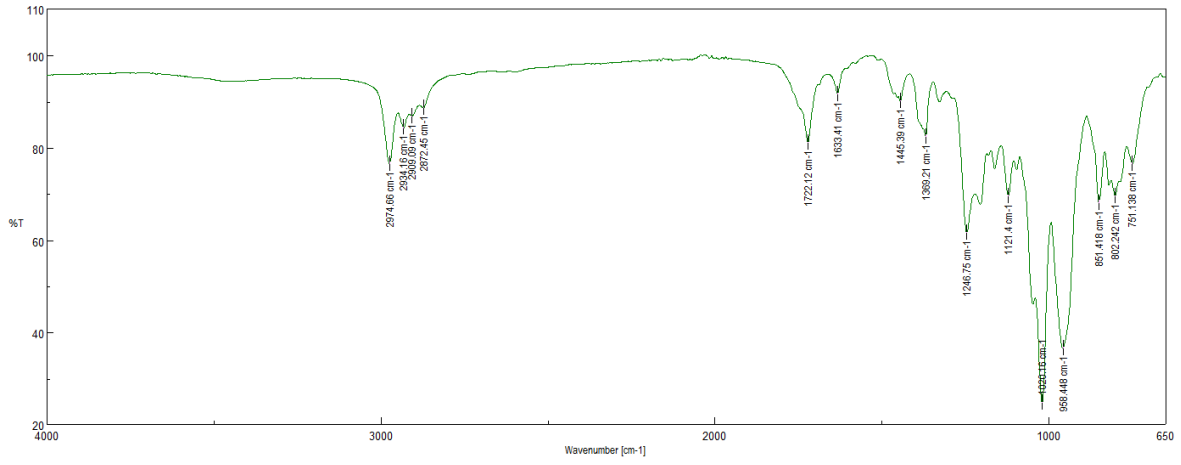

OEt
Me
P(OEt)2
O
149g
1.00
1.00
4.44
1.05
2.14
7.03
3.70
3.46
f1 (ppm)

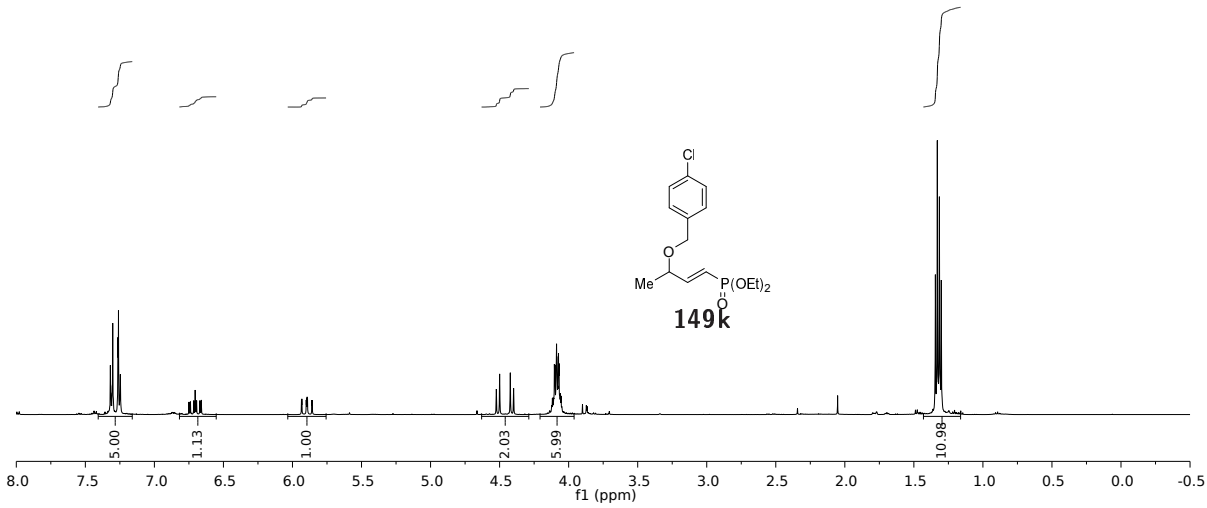

154.2
154.2
117.3
115.4
75.6
75.4
64.6
62.0
61.9
61.9
61.9
20.7
20.7
16.5
16.5
15.5
f1 (ppm)

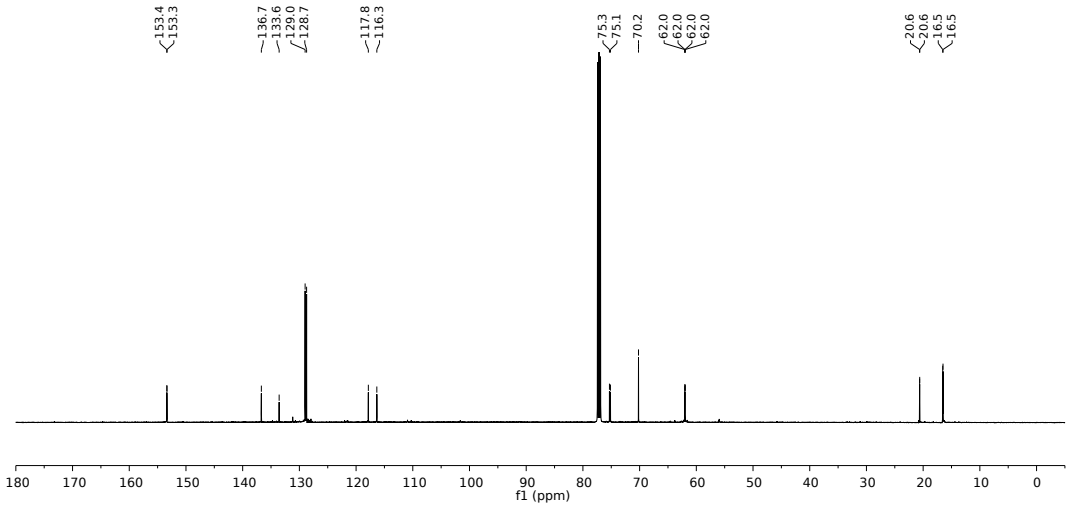

%T
2977.55 cm-1
2934.16 cm-1
2904.27 cm-1
2872.45 cm-1
1721.16 cm-1
1634.38 cm-1
1444.42 cm-1
1392.35 cm-1
1336.43 cm-1
1244.83 cm-1
1206.26 cm-1
1162.87 cm-1
1094.4 cm-1
1060.06 cm-1
966.52 cm-1
865.275 cm-1
828.277 cm-1
749.209 cm-1
Wavenumber [cm-1]

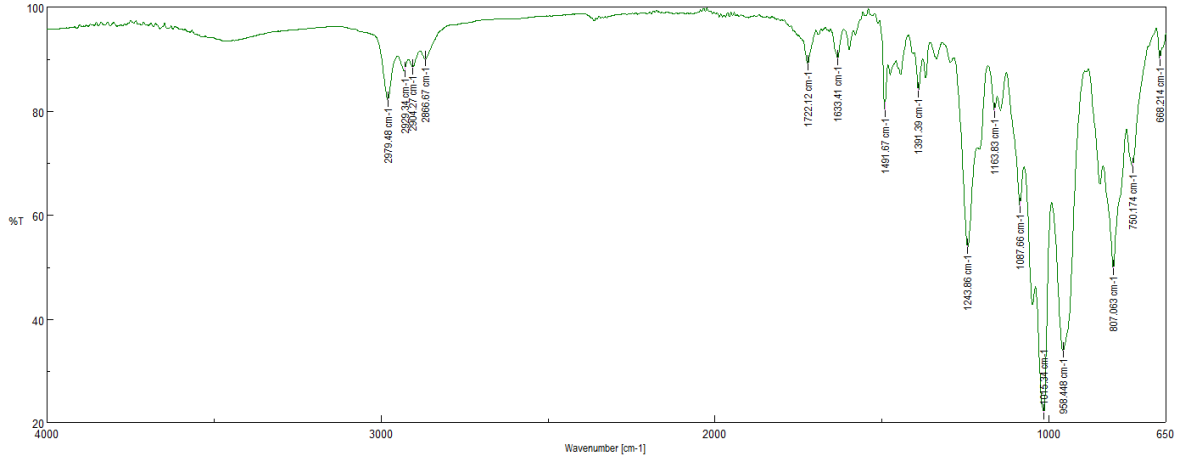

OiPr
Me
P(OEt)2
O
149h
1.05
1.00
6.34
1.06
8.88
3.87
6.95
f1 (ppm)

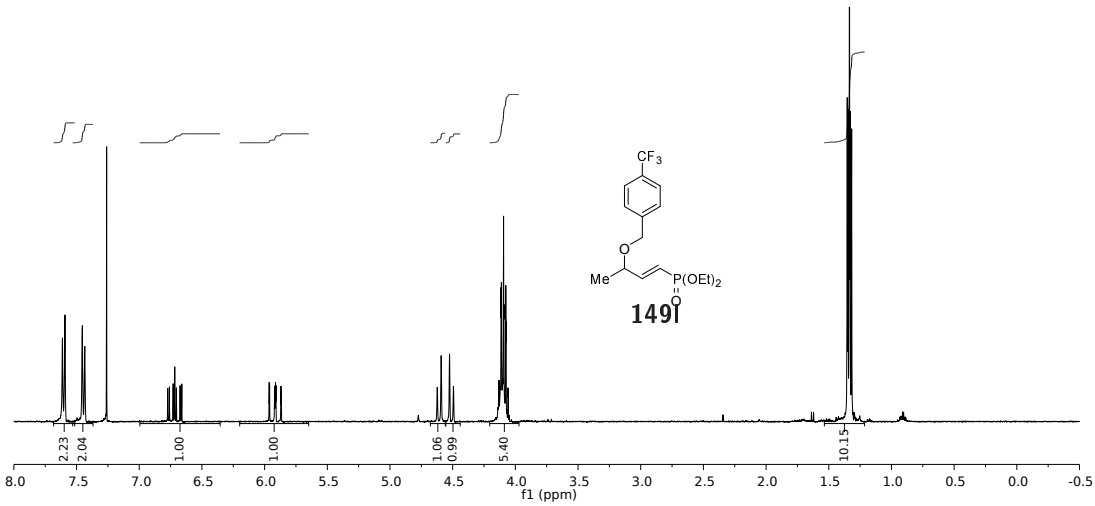

155.1
155.0
116.7
114.8
72.9
72.7
70.0
62.0
62.0
61.9
61.9
23.1
22.1
21.3
21.3
16.5
16.4
f1 (ppm)

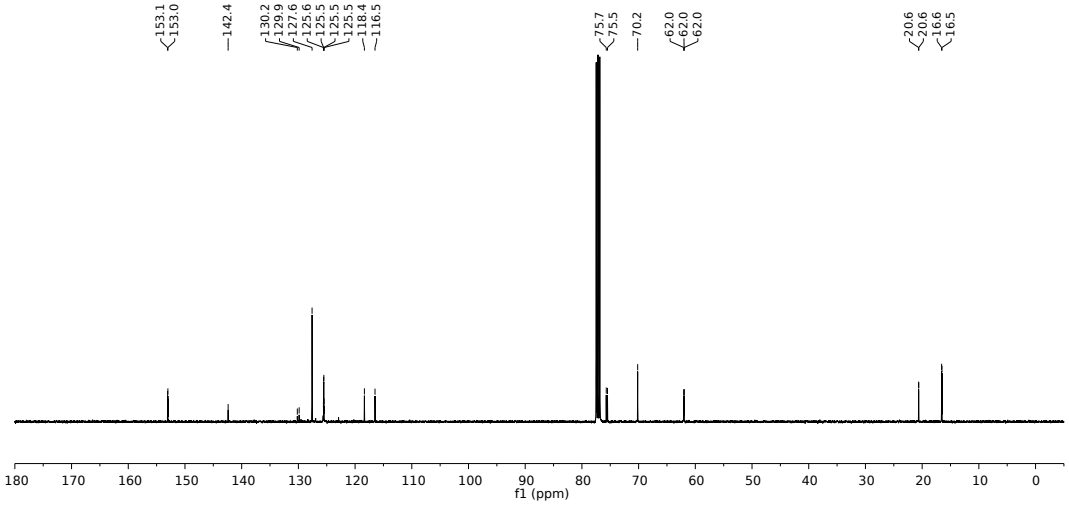

%T
2974.66 cm-1
2934.16 cm-1
2909.09 cm-1
2872.45 cm-1
1722.12 cm-1
1633.41 cm-1
1445.39 cm-1
1369.21 cm-1
1246.75 cm-1
1121.4 cm-1
1020.15 cm-1
958.448 cm-1
851.418 cm-1
802.242 cm-1
751.138 cm-1
Wavenumber [cm-1]

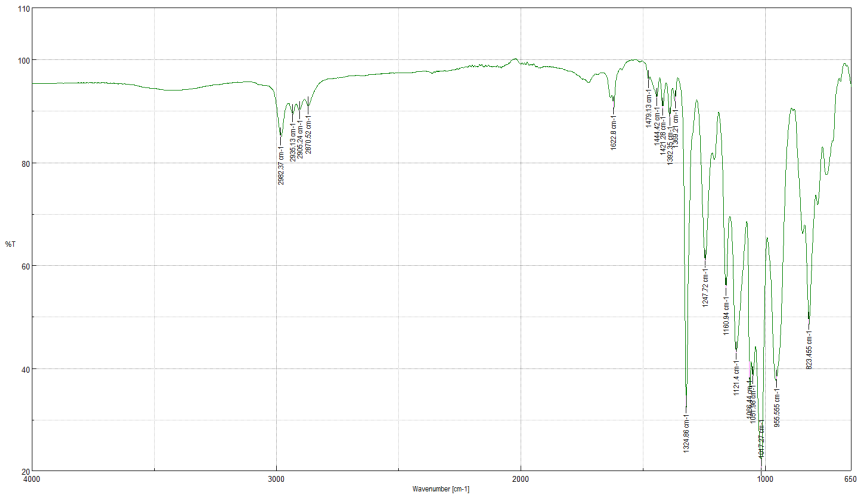

Cl
O
Me
P(OEt)2
O
H
149k
5.00
1.13
1.00
2.03
5.99
10.98
f1 (ppm)

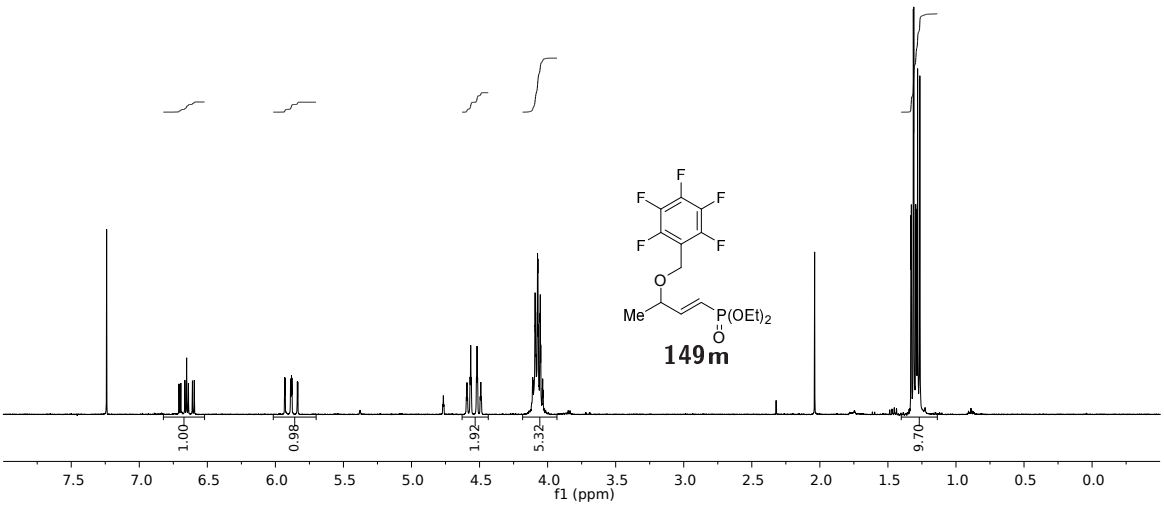

153.4
153.3
136.7
133.6
129.0
128.7
117.8
116.3
75.3
75.1
70.2
62.0
62.0
62.0
62.0
20.6
20.6
16.5
16.5
f1 (ppm)

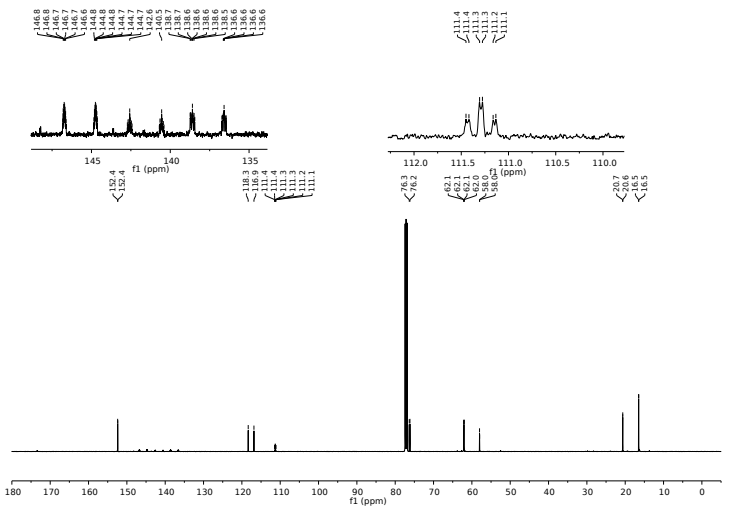

%T
2979.48 cm-1
2933.34 cm-1
2904.37 cm-1
2866.67 cm-1
1722.12 cm-1
1633.41 cm-1
1491.67 cm-1
1391.39 cm-1
1243.86 cm-1
1163.83 cm-1
1087.66 cm-1
1015.31 cm-1
958.448 cm-1
807.063 cm-1
750.174 cm-1
698.214 cm-1
Wavenumber [cm-1]


CF3
O
Me
P(OEt)2
O
1491
2.23
2.04
1.00
1.00
1.06
0.99
5.40
10.15
f1 (ppm)

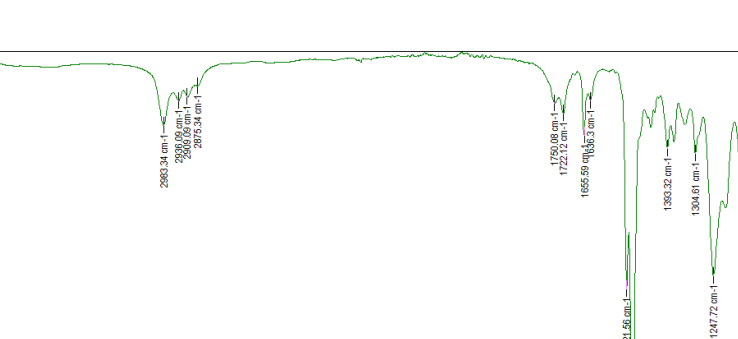

153.1
153.0
142.4
130.2
129.9
127.6
125.6
125.5
125.5
125.5
118.4
116.5
75.7
75.5
70.2
62.0
62.0
62.0
20.6
20.6
16.6
16.5
f1 (ppm)


%T
Wavenumber [cm-1]

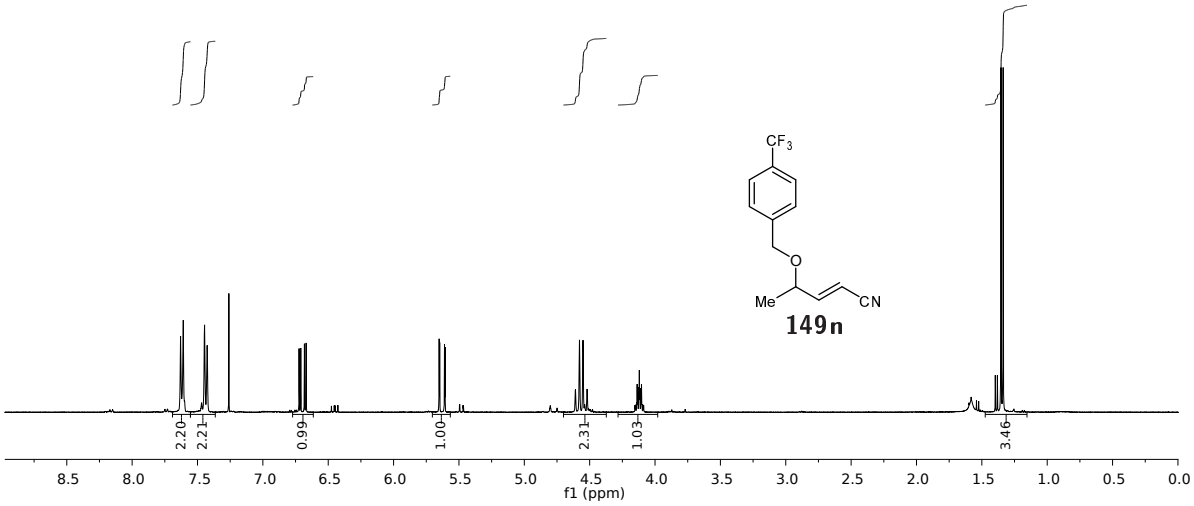

F
F
F
F
F
O
Me
P(OEt)2
O
149m
1.00
0.98
1.92
5.32
9.70
f1 (ppm)

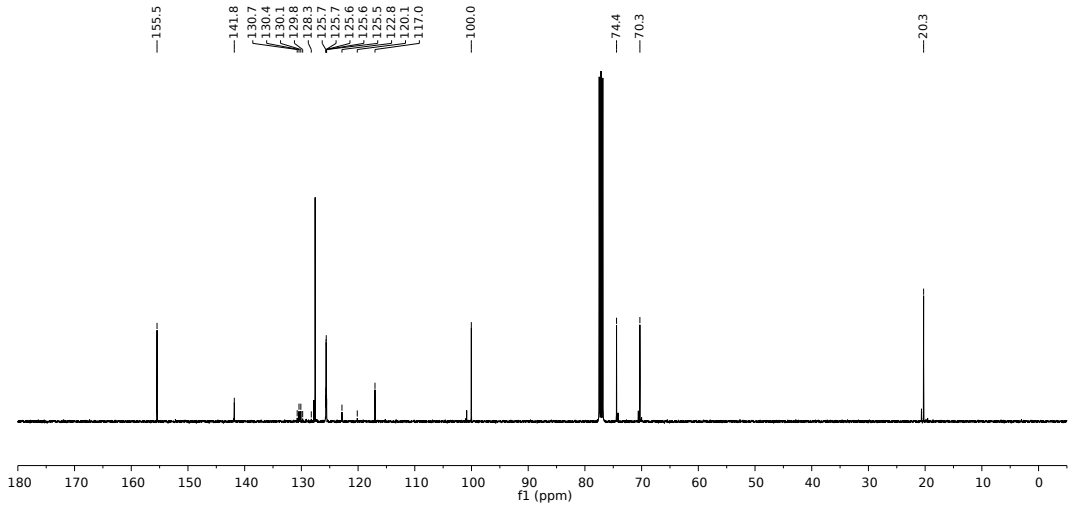

f1 (ppm)

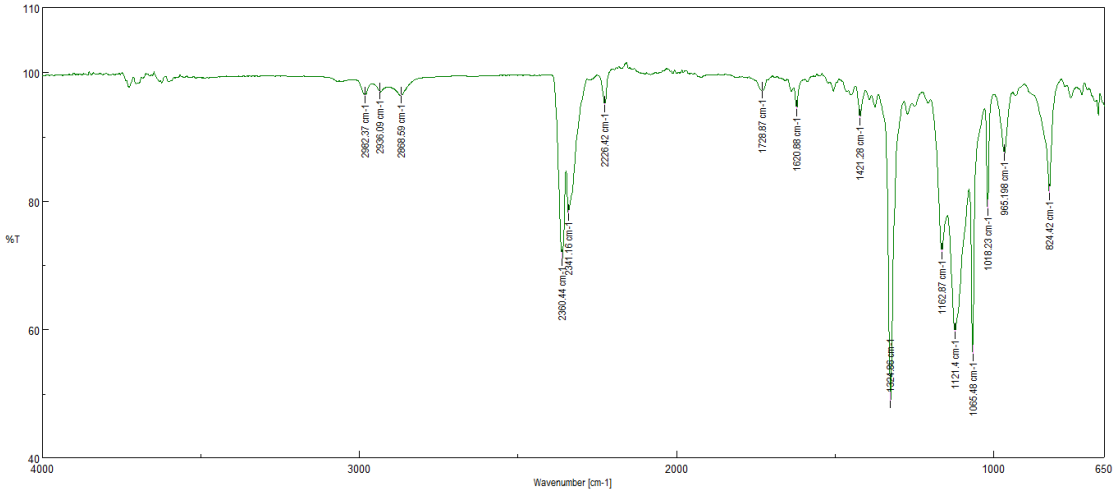
f1 (ppm)

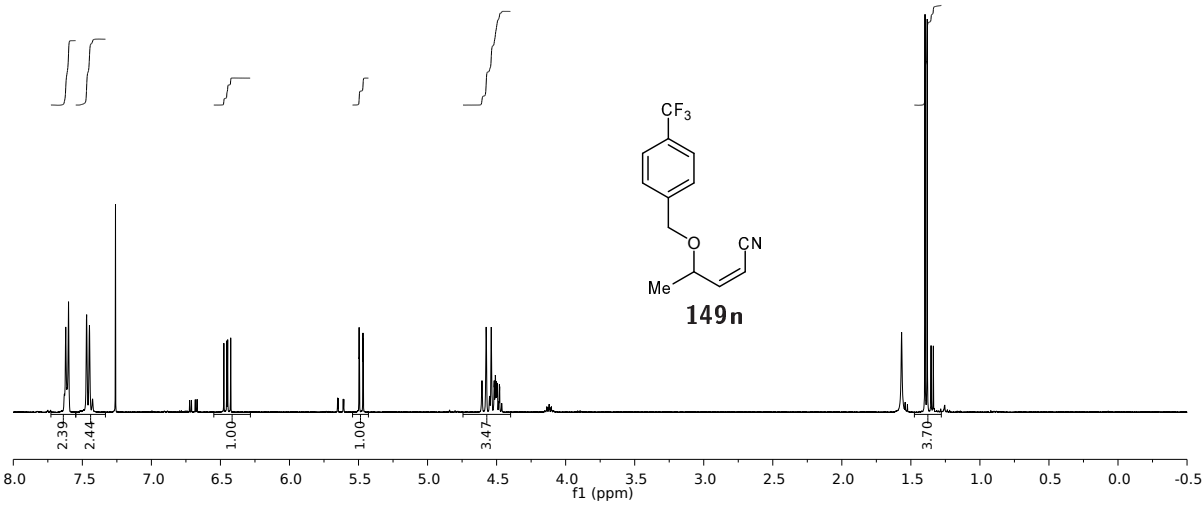

f1 (ppm)

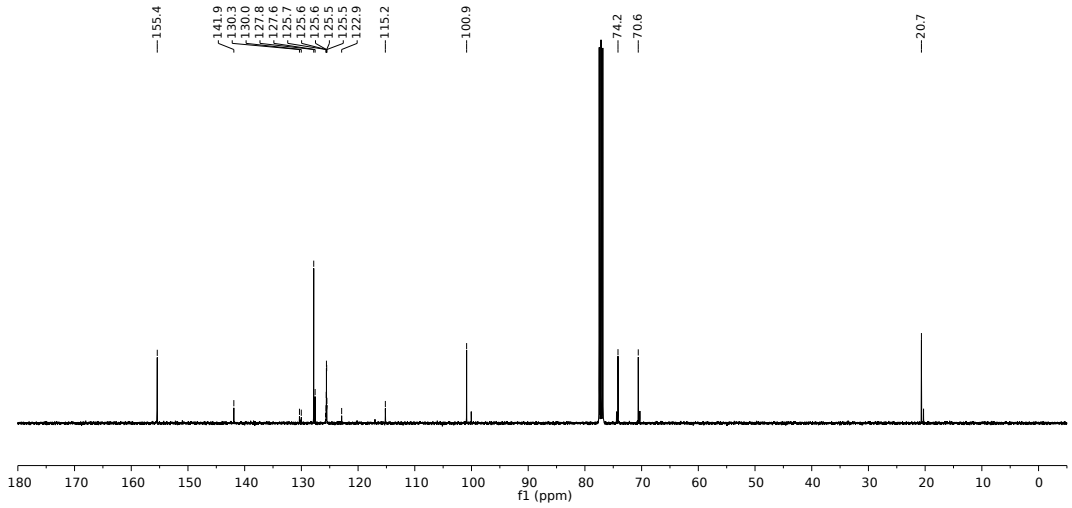
%T
Wavenumber [cm-1]
2963.34 cm-1
2926.09 cm-1
2855.60 cm-1
2875.34 cm-1
1750.08 cm-1
1722.12 cm-1
1656.3 cm-1
1665.59 cm-1
1521.66 cm-1
1604.2 cm-1
1393.32 cm-1
1304.61 cm-1
1247.72 cm-1
1123.33 cm-1
1046.10 cm-1
957.484 cm-1
847.561 cm-1
820.563 cm-1
796.45 cm-1
753.096 cm-1
673.036 cm-1

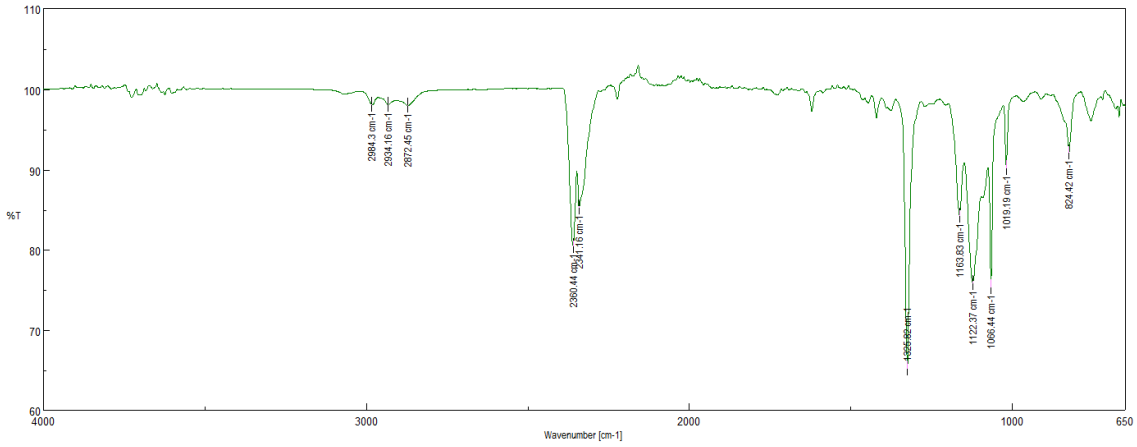

CF3
O
Me
CN
149n
2.20
2.21
0.99
1.00
2.31
1.03
3.46
f1 (ppm)

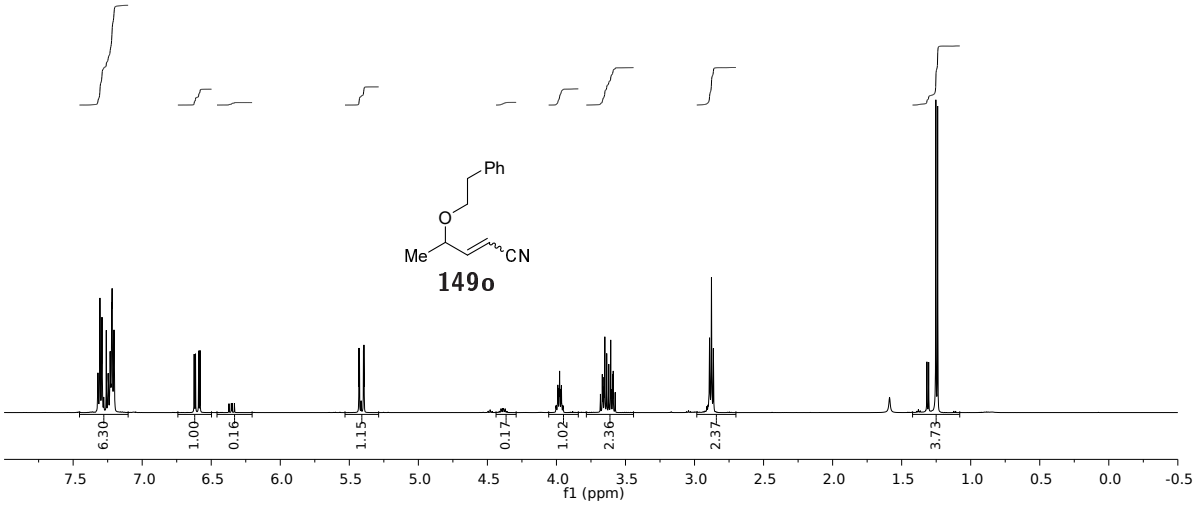

155.5
141.8
130.7
130.4
130.1
129.8
128.3
125.7
125.7
125.6
125.6
125.5
122.8
120.1
117.0
100.0
74.4
70.3
20.3
f1 (ppm)

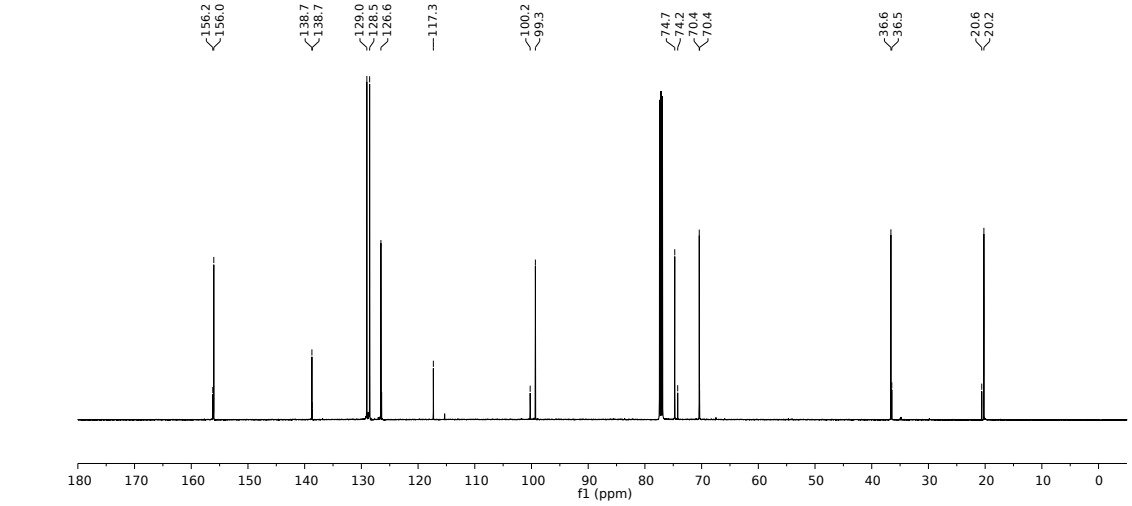

%T
2982.37 cm-1
2936.09 cm-1
2868.59 cm-1
2360.44 cm-1
2341.16 cm-1
2226.42 cm-1
1738.87 cm-1
1620.88 cm-1
1421.28 cm-1
1162.87 cm-1
1121.4 cm-1
1065.48 cm-1
1018.23 cm-1
965.198 cm-1
824.42 cm-1
Wavenumber [cm-1]

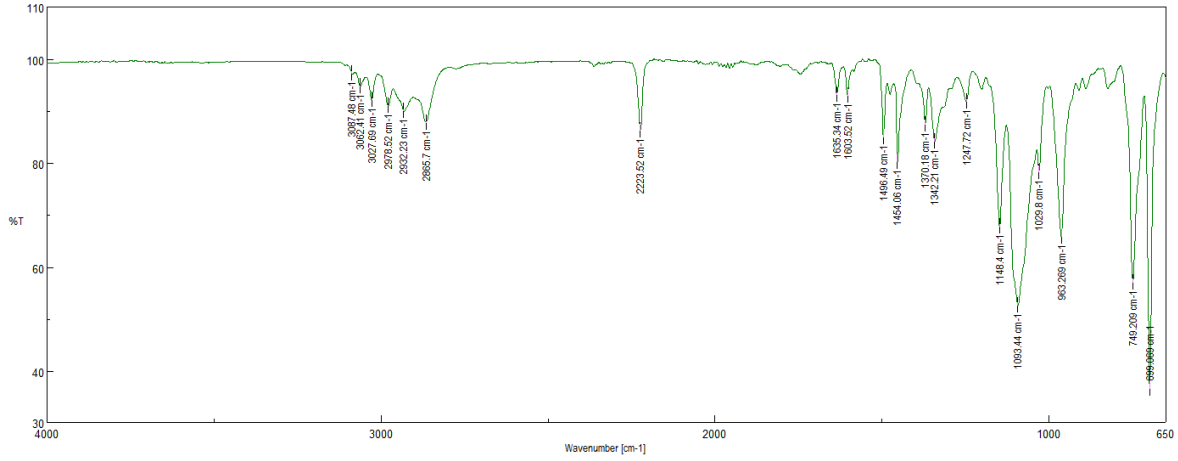

CF3
O
CN
Me
149n
2.39
2.44
1.00
1.00
3.47
3.70
f1 (ppm)

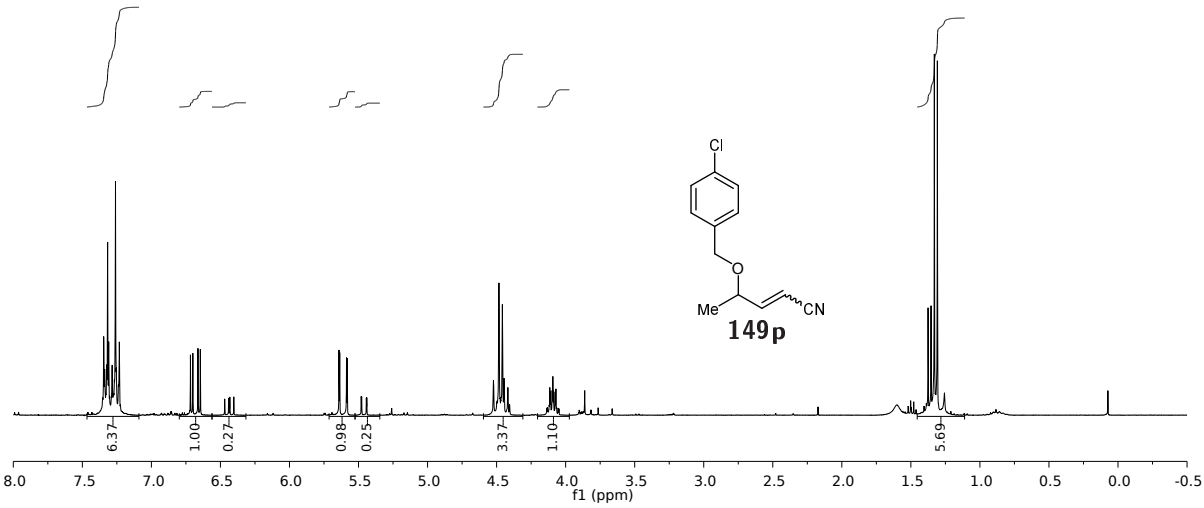

155.4
141.9
130.3
130.0
127.8
127.6
125.7
125.6
125.6
125.5
125.5
122.9
115.2
100.9
74.2
70.6
20.7
f1 (ppm)

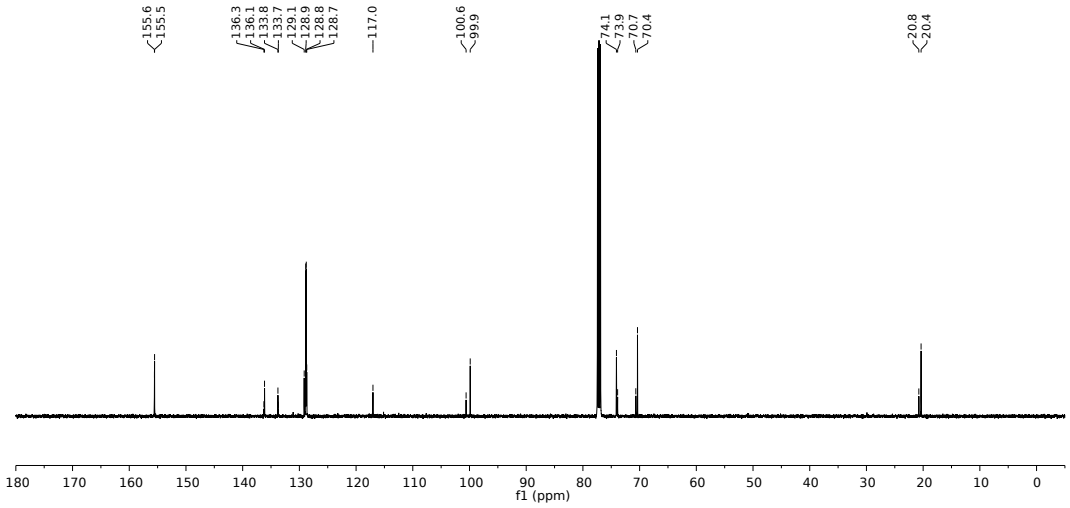

%T
2984.3 cm-1
2934.16 cm-1
2872.45 cm-1
2360.44 cm-1
2341.18 cm-1
1163.83 cm-1
1122.37 cm-1
1066.44 cm-1
1015.19 cm-1
824.42 cm-1
Wavenumber [cm-1]

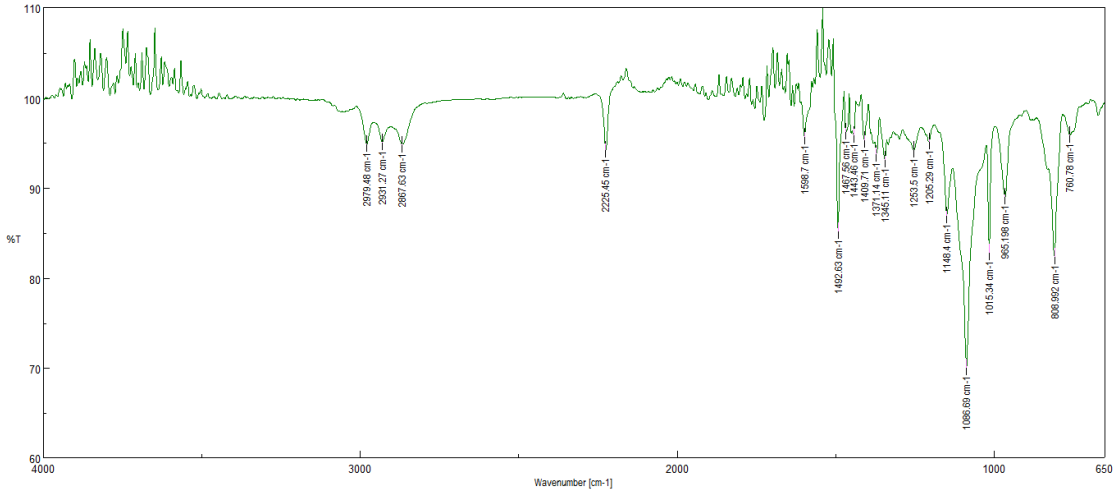

Ph
O
Me
CN
149o
6.30
1.00
0.16
1.15
0.17
1.02
2.36
2.37
3.73
f1 (ppm)

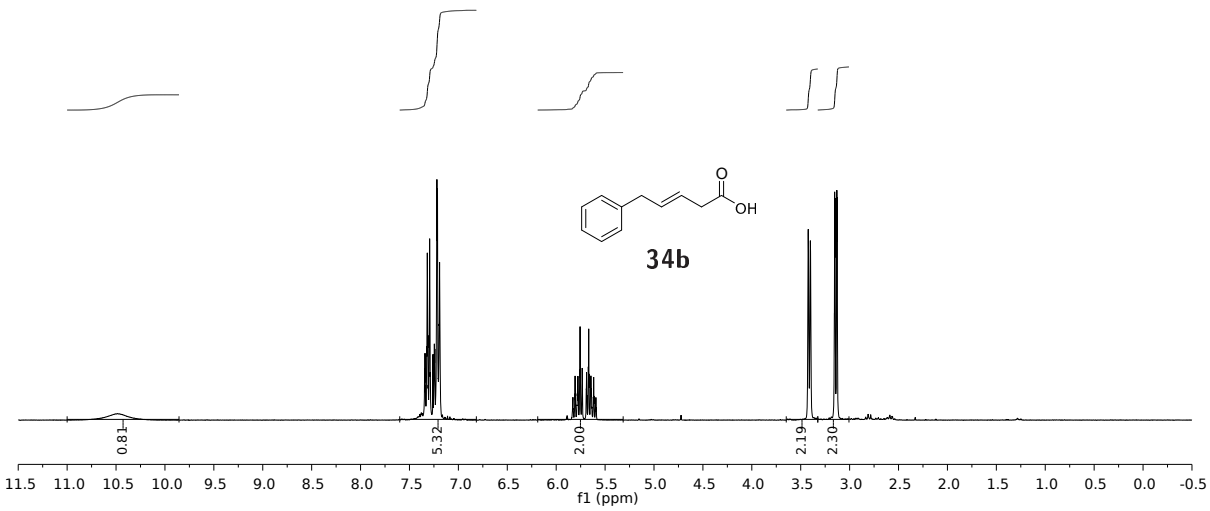

156.2
156.0
138.7
138.7
129.0
128.5
126.6
117.3
100.2
99.3
74.7
74.2
70.4
70.4
36.6
36.5
20.6
20.2
f1 (ppm)

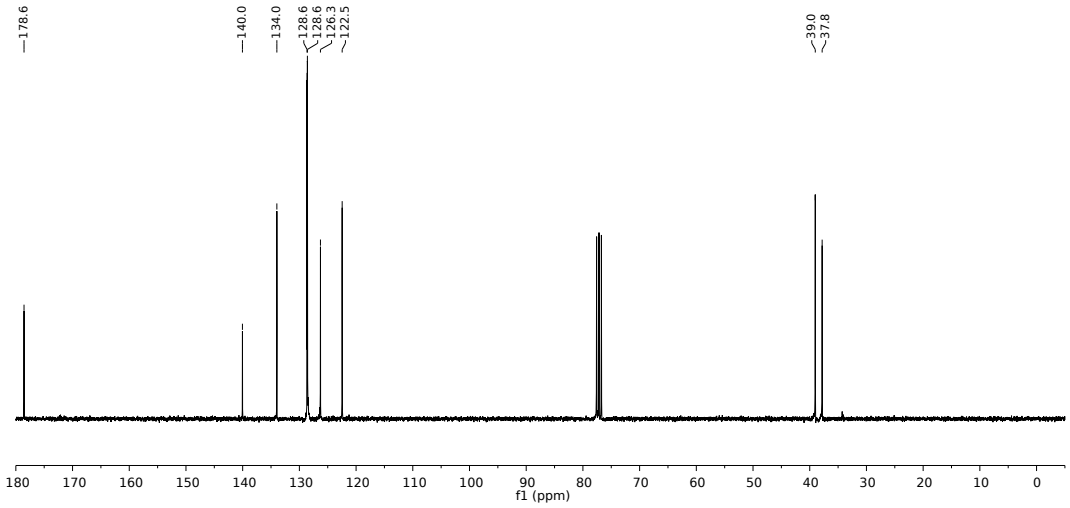

%T
3087.48 cm-1
3062.41 cm-1
3027.69 cm-1
2978.52 cm-1
2922.23 cm-1
2865.7 cm-1
2223.52 cm-1
1638.34 cm-1
1603.52 cm-1
1496.49 cm-1
1454.06 cm-1
1370.18 cm-1
1342.21 cm-1
1247.72 cm-1
1148.4 cm-1
1093.44 cm-1
1029.8 cm-1
963.269 cm-1
749.209 cm-1
699.069 cm-1
Wavenumber [cm-1]

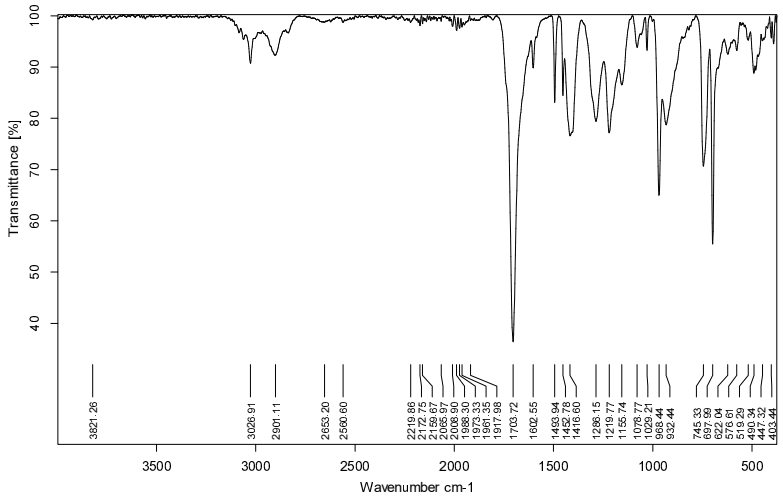

Cl
O
Me
CN
149p
6.37
1.00
0.27
0.98
0.25
3.37
1.10
5.69
f1 (ppm)

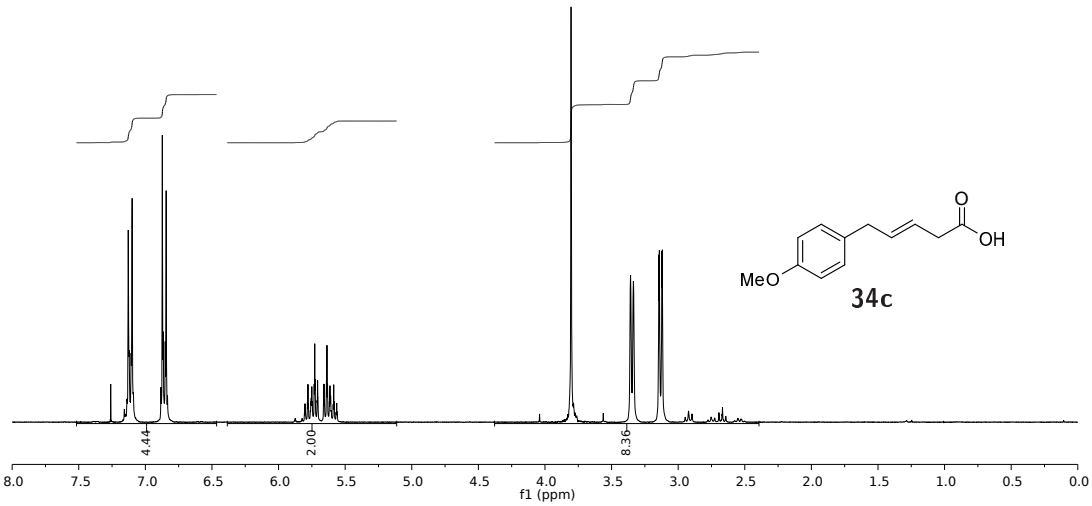

155.6
155.5
136.3
136.1
133.8
133.7
129.1
128.9
128.8
128.7
117.0
100.6
99.9
74.1
73.9
70.7
70.4
20.8
20.4
f1 (ppm)

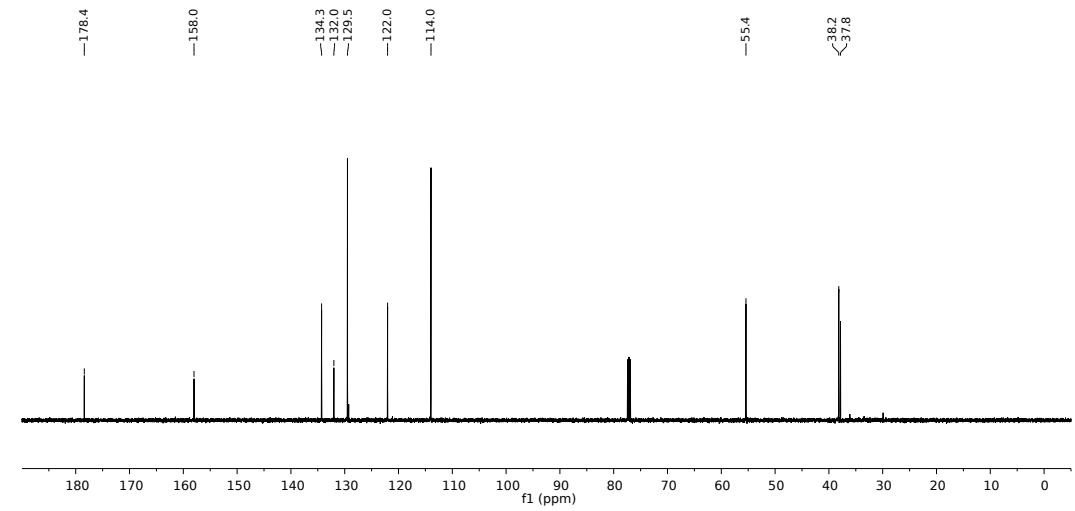

%T
2979.48 cm-1
2931.27 cm-1
2867.63 cm-1
2226.45 cm-1
1598.7 cm-1
1492.63 cm-1
1447.26 cm-1
1371.14 cm-1
1345.11 cm-1
1253.5 cm-1
1205.29 cm-1
1148.4 cm-1
1086.69 cm-1
1015.34 cm-1
965.198 cm-1
808.992 cm-1
760.79 cm-1
Wavenumber [cm-1]

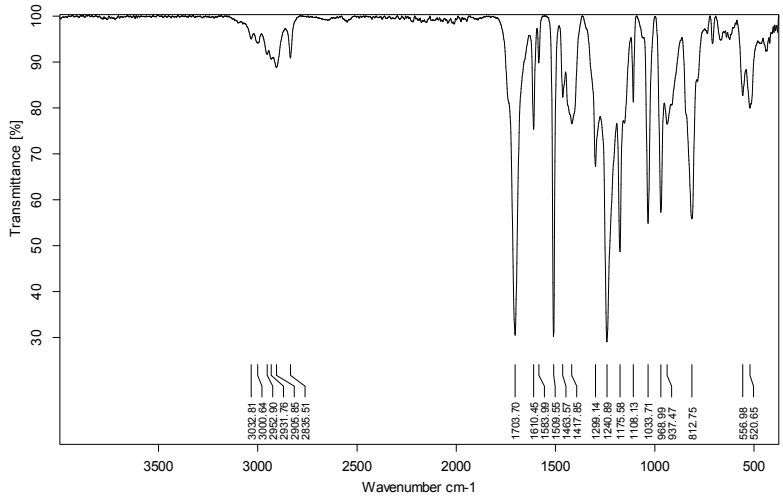

O
OH
34b
0.81
5.32
2.00
2.19
2.30
f1 (ppm)

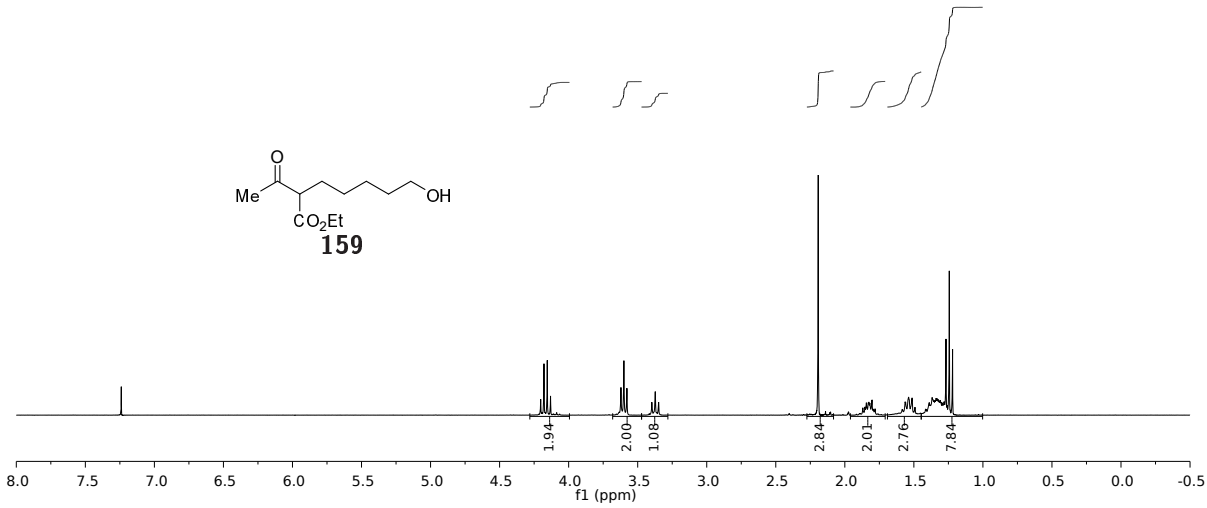

178.6
140.0
134.0
128.6
128.6
126.3
122.5
39.0
37.8
f1 (ppm)

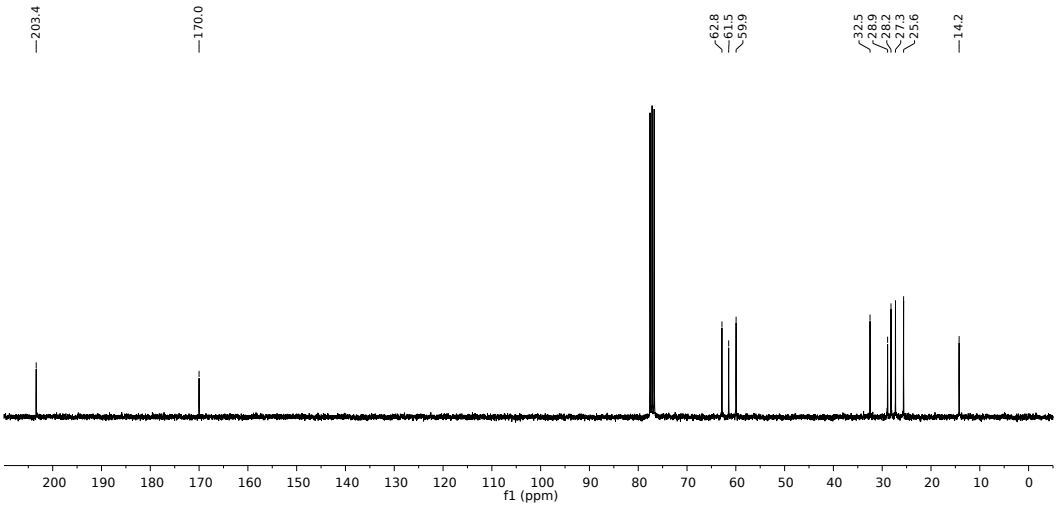

Transmittance [%]
Wavenumber cm-1
3821.26
3026.91
2901.11
2653.20
2560.60
1703.72
1602.55
1493.94
1452.78
1416.60
1286.15
1219.77
1155.74
1078.77
1029.21
966.44
932.44
745.33
697.99
622.64
575.65
519.29
490.34
447.32
403.44

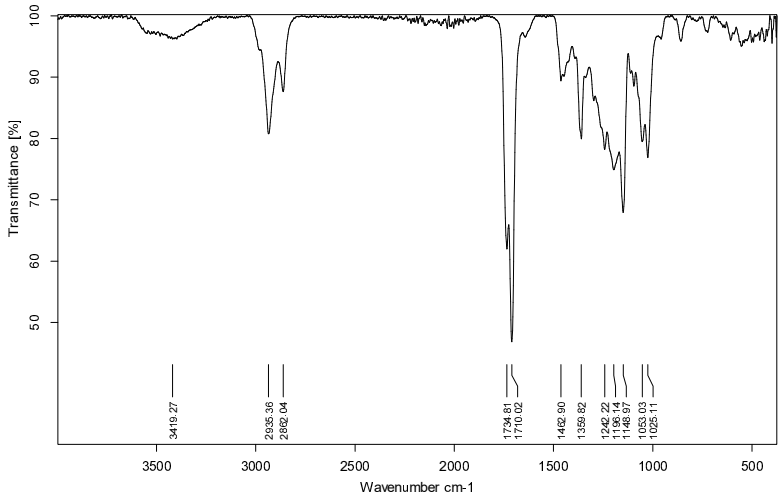

4.44
2.00
8.36
f1 (ppm)
MeO
OH
O
34c

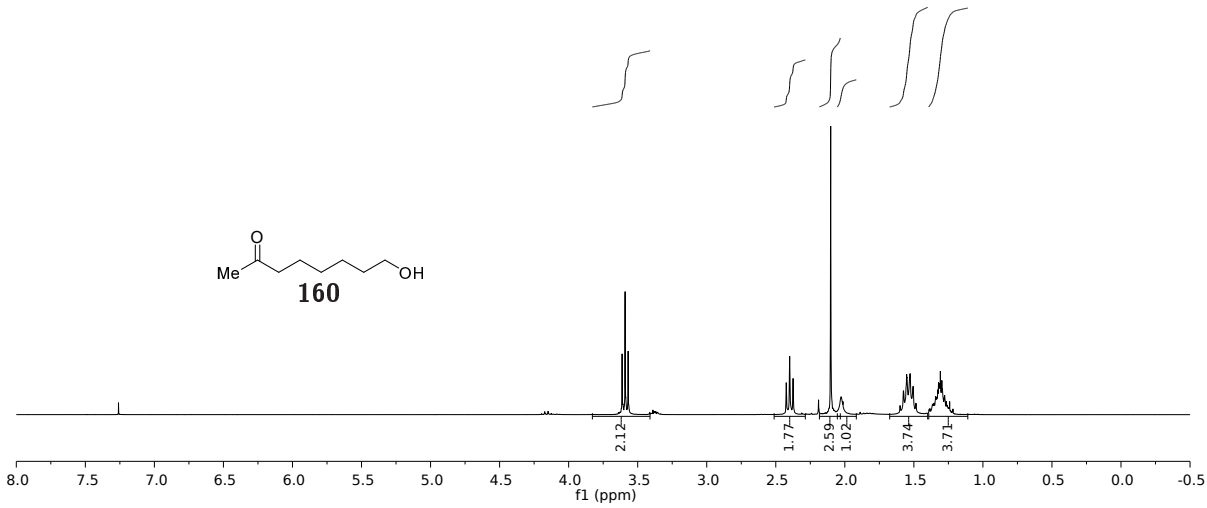

178.4
158.0
134.3
132.0
129.5
122.0
114.0
55.4
38.2
37.8
f1 (ppm)

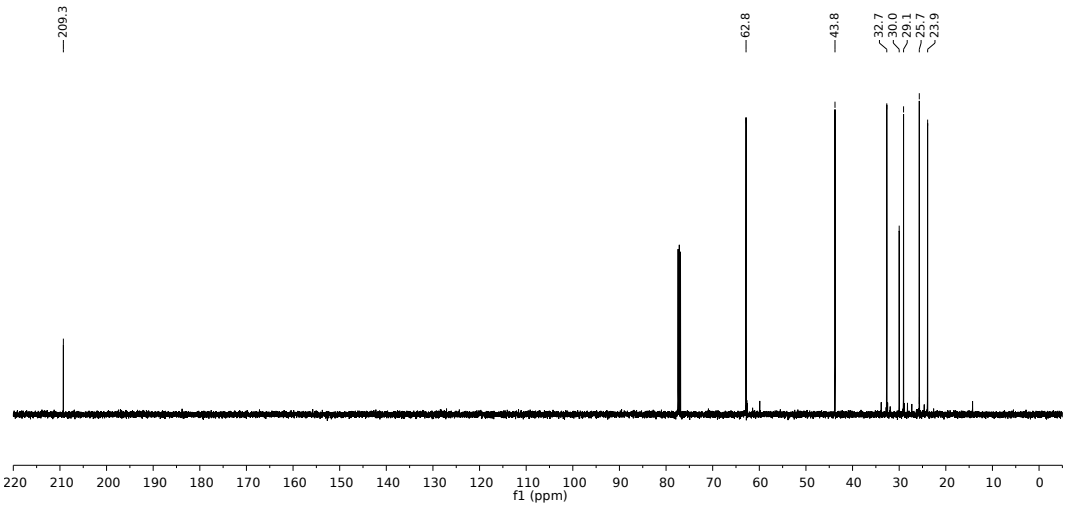

Transmittance [%]
3032.81
3000.64
2952.90
2931.76
2905.85
2835.51
1703.70
1610.45
1583.99
1509.55
1463.57
1417.85
1299.14
1240.89
1175.38
1108.13
1033.71
969.97
937.47
812.75
556.98
520.65
Wavenumber cm-1

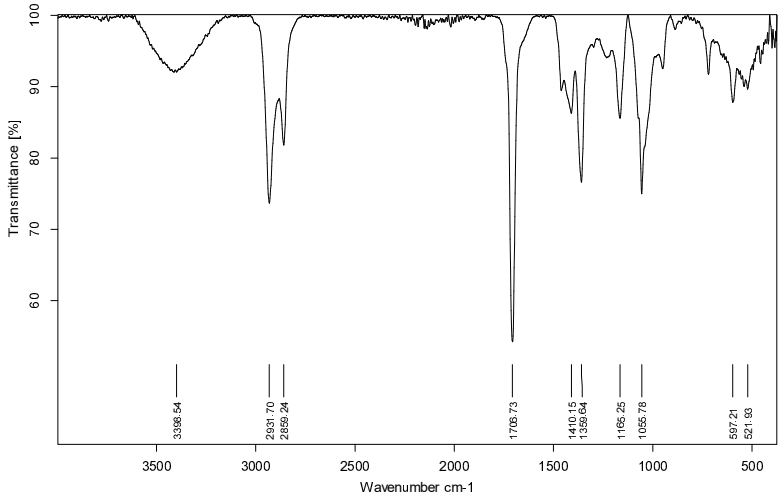

O
Me
OH
CO2Et
159
1.94
2.00
1.08
2.84
2.01
2.76
7.84
f1 (ppm)

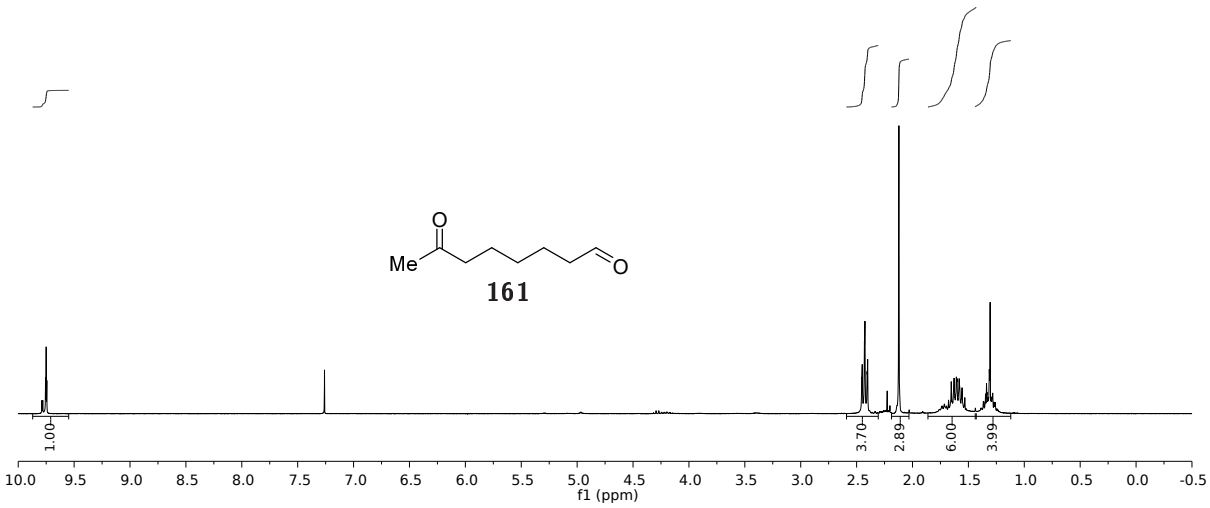

203.4
170.0
62.8
61.5
59.9
32.5
28.9
28.2
27.3
25.6
14.2
f1 (ppm)

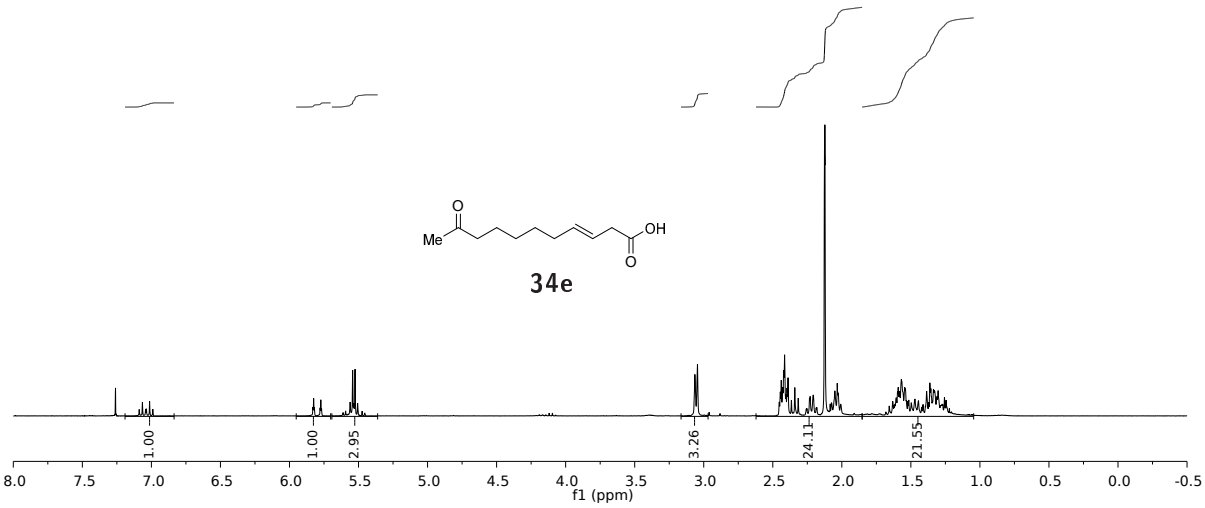

Transmittance [%]
3419.27
2935.36
2862.04
1734.61
1710.02
1462.90
1359.82
1240.22
1196.14
1148.97
1053.03
1025.11
Wavenumber cm-1

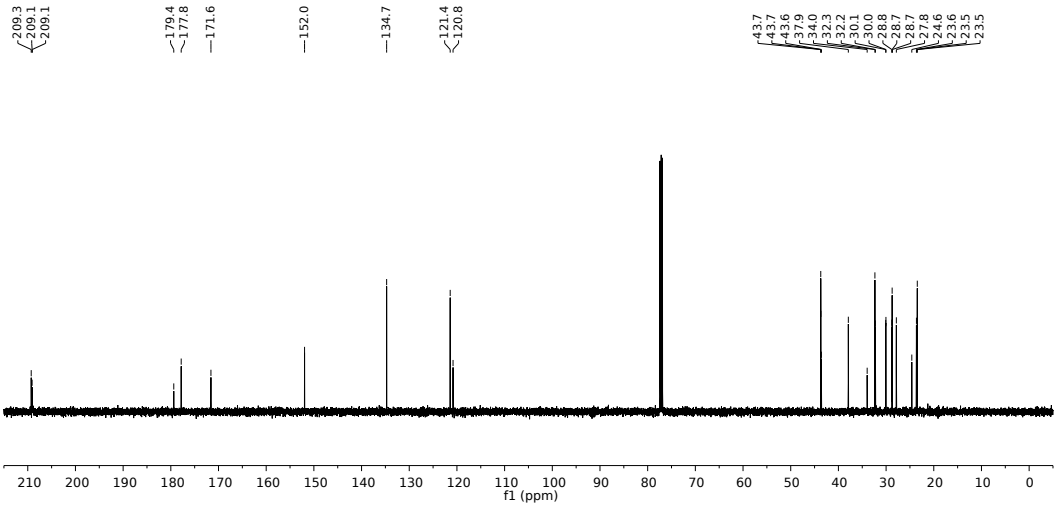

O
Me
OH
160
2.12
1.77
2.59
1.02
3.74
3.71
f1 (ppm)

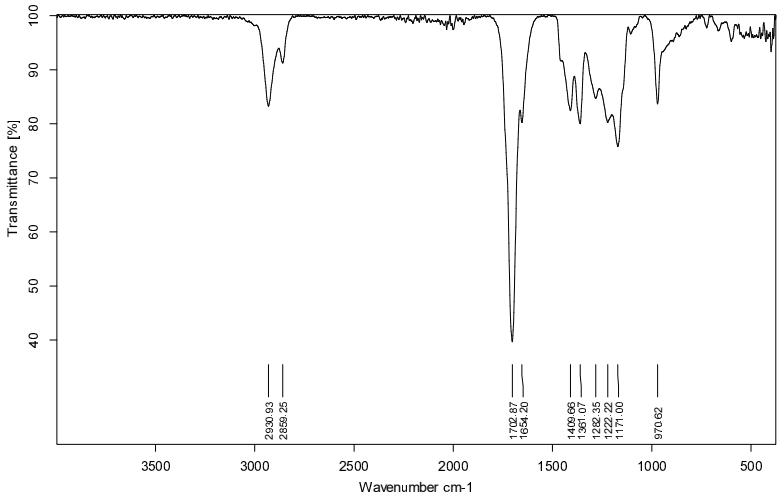

209.3
62.8
43.8
32.7
30.0
29.1
25.7
23.9
f1 (ppm)

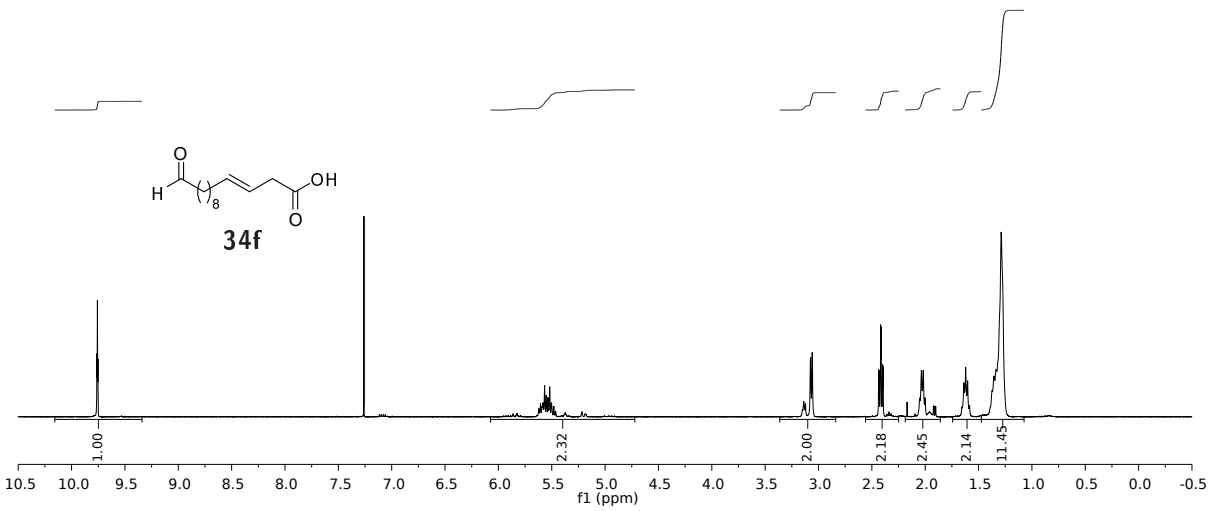

Transmittance [%]
3336.54
2931.70
2859.24
1705.73
1410.15
1359.64
1165.25
1055.78
597.21
521.93
Wavenumber cm-1

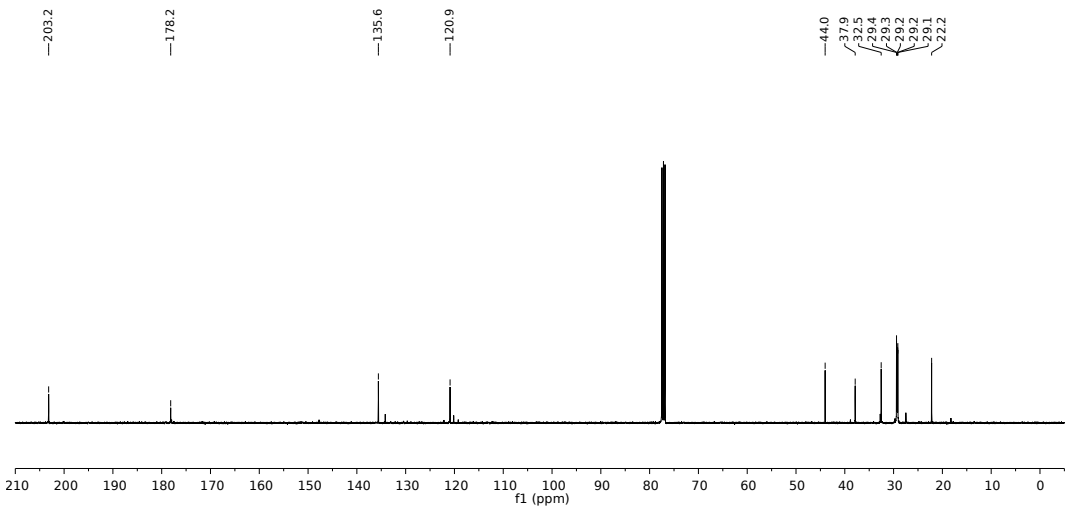

O
Me
O
161
1.00
3.70
2.89
6.00
3.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

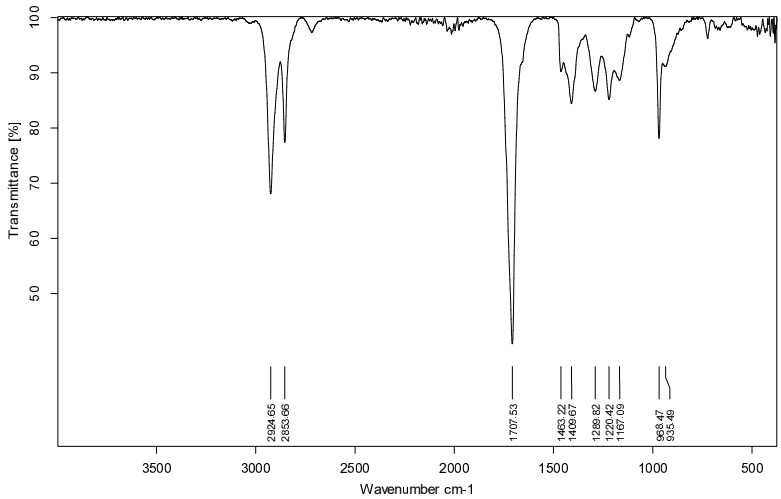

O
Me
OH
O
34e
1.00
1.00
2.95
3.26
24.11
21.55
f1 (ppm)

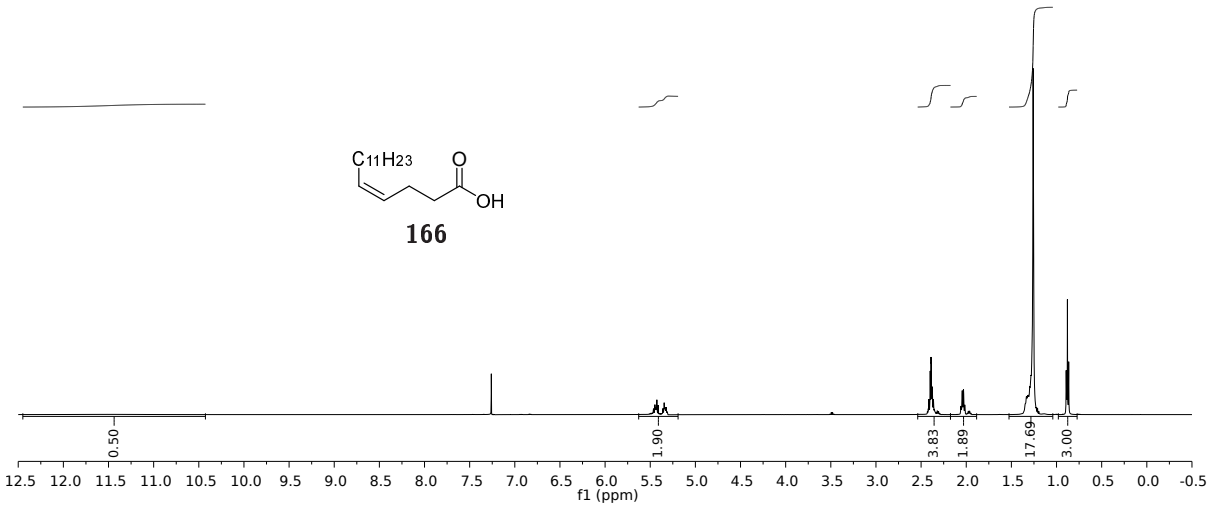

209.3
209.1
209.1
179.4
177.8
171.6
152.0
134.7
121.4
120.8
f1 (ppm)

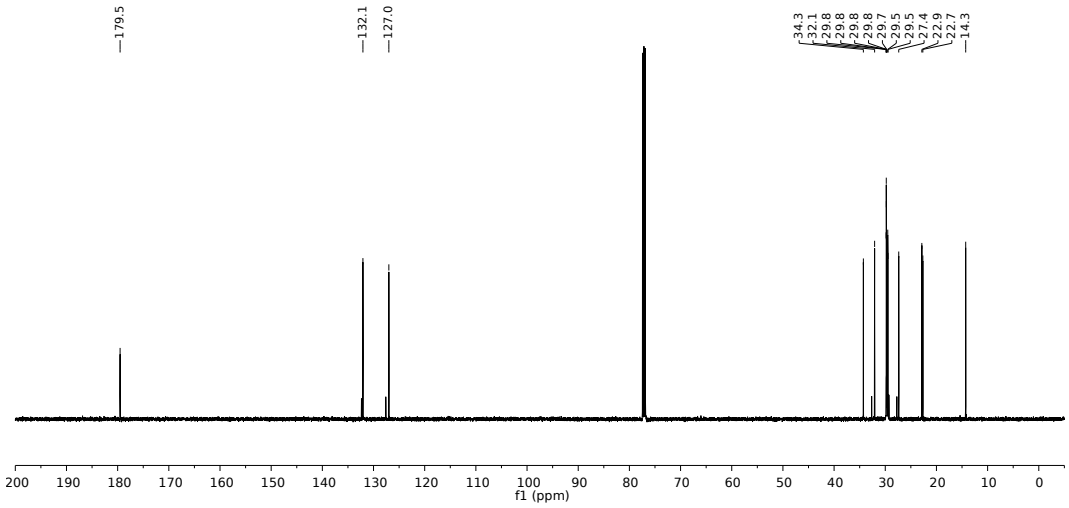

Transmittance [%]
2930.93
2859.25
1702.87
1654.20
1409.66
1361.07
1282.35
1222.22
1171.00
970.62
Wavenumber cm-1

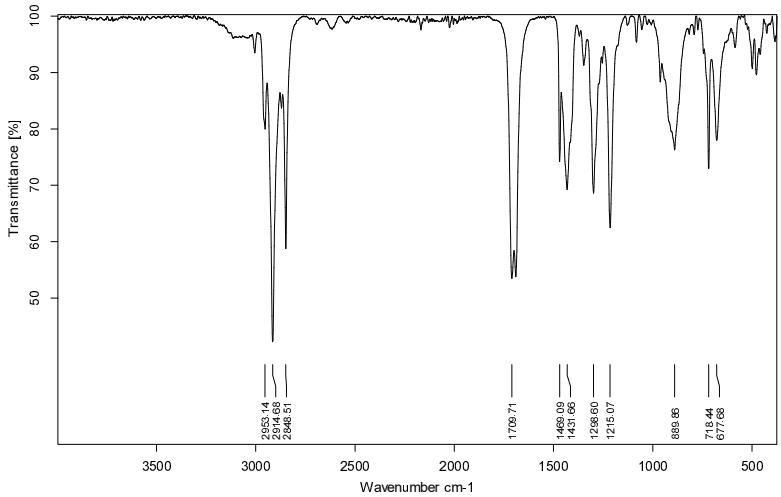

34f
1.00
2.32
2.00
2.18
2.45
2.14
11.45
f1 (ppm)

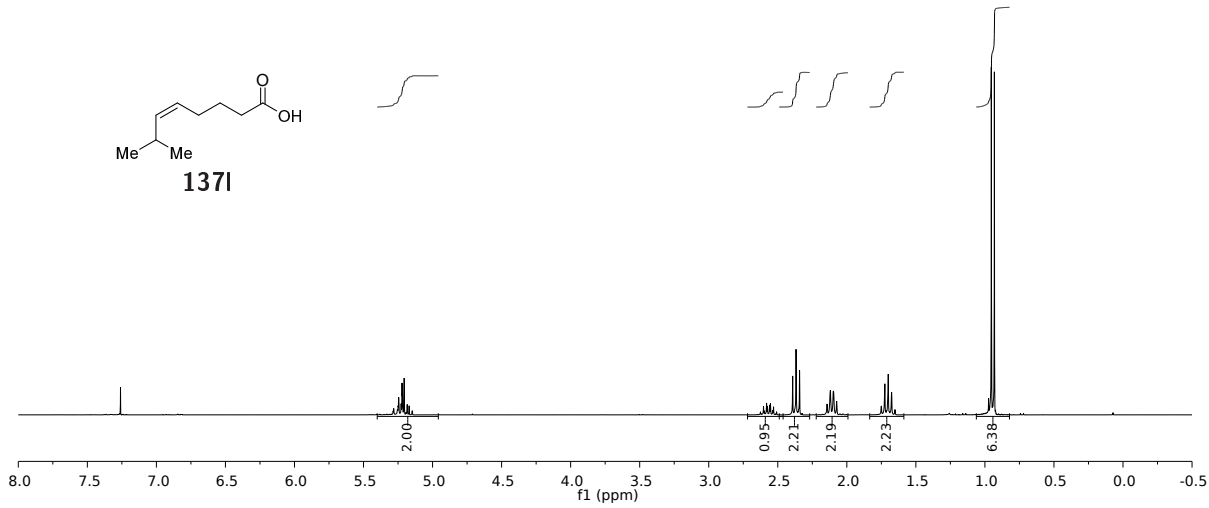

203.2
178.2
135.6
120.9
44.0
37.9
32.5
29.4
29.3
29.2
29.2
29.2
29.1
22.2
f1 (ppm)

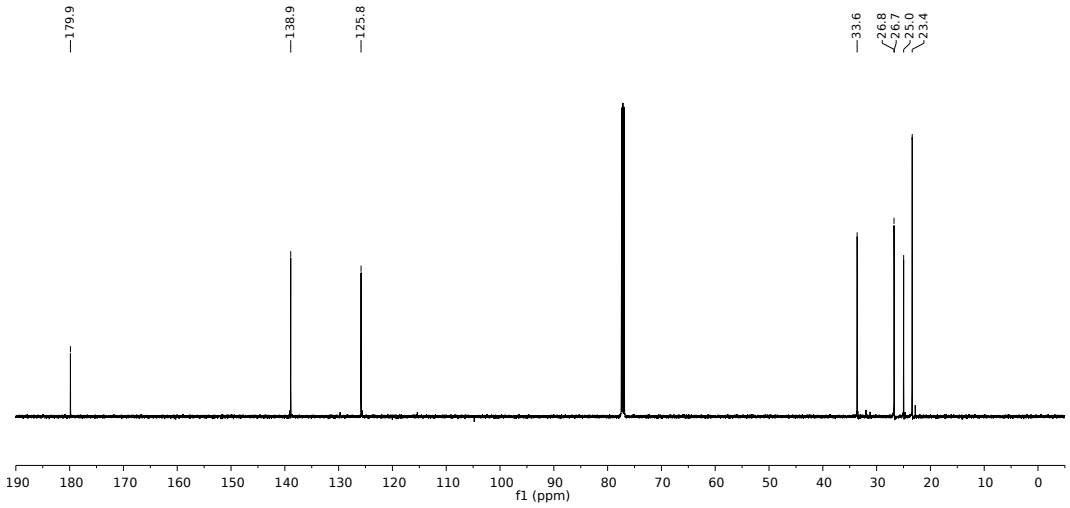

Transmittance [%]
2924.65
2853.66
1707.53
1463.22
1409.67
1288.82
1220.42
1167.09
968.47
935.49
Wavenumber cm-1

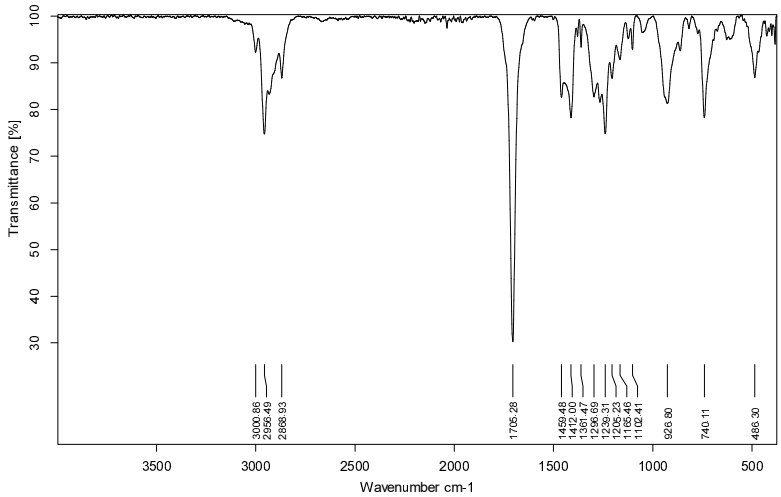

C11H23
O
OH
166
0.50
1.90
3.83
1.89
17.69
3.00
f1 (ppm)

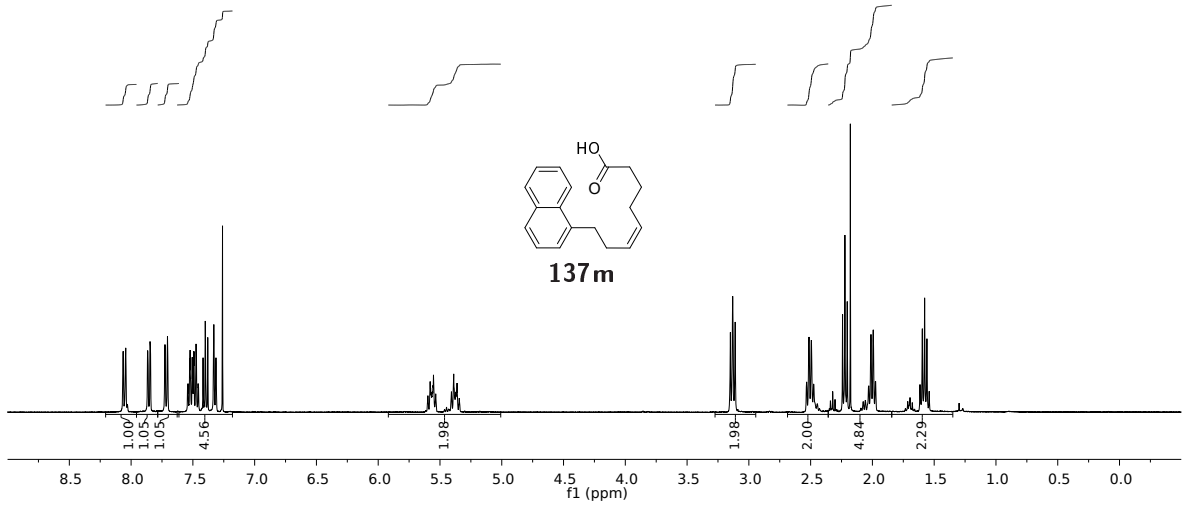

179.5
132.1
127.0
34.3
32.1
29.8
29.8
29.8
29.8
29.7
29.5
29.5
27.4
22.9
22.7
14.3
f1 (ppm)

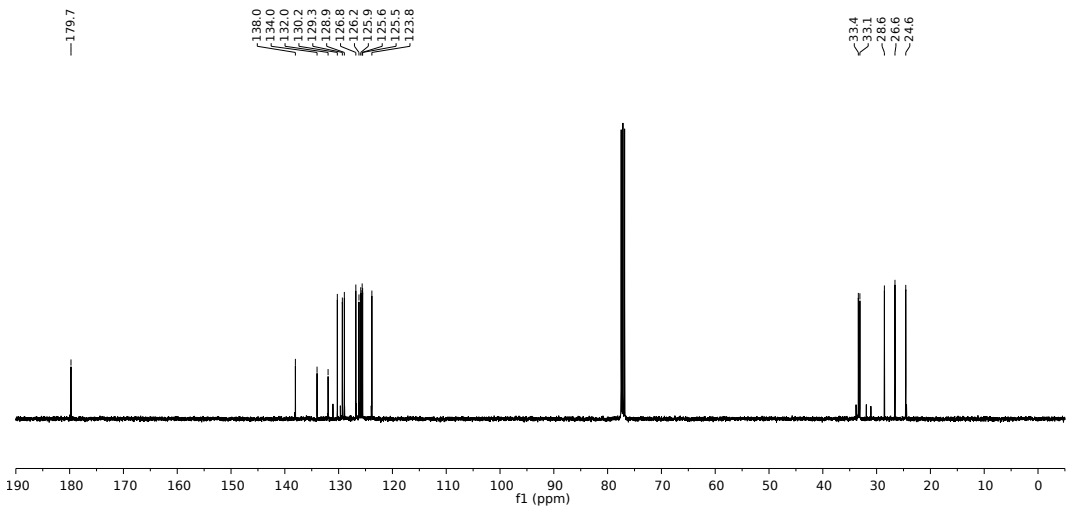

Transmittance [%]
2953.14
2914.68
2848.51
1709.71
1469.09
1431.66
1298.60
1215.07
889.85
718.44
677.68
Wavenumber cm-1

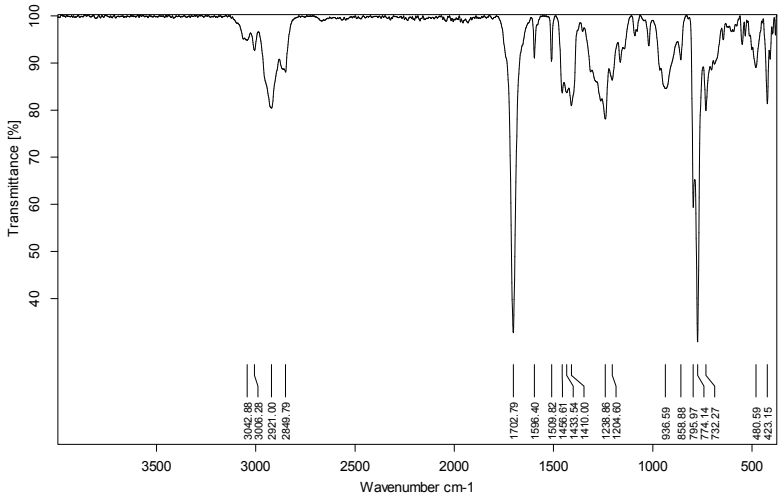

O
OH
Me
Me
137l
2.00
0.95
2.21
2.19
2.23
6.38
f1 (ppm)

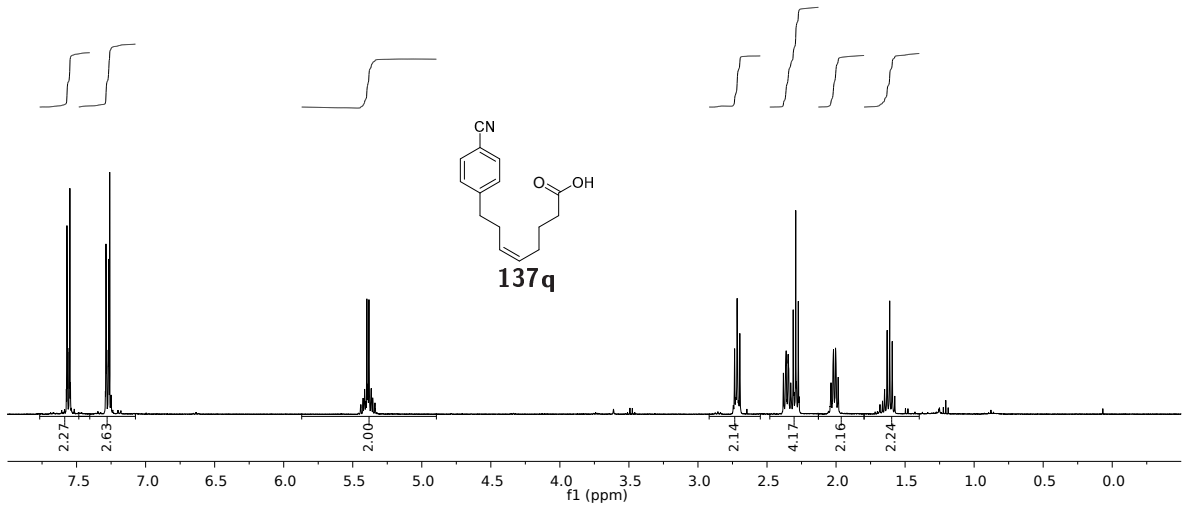

179.9
138.9
125.8
33.6
26.8
26.7
25.0
23.4
f1 (ppm)

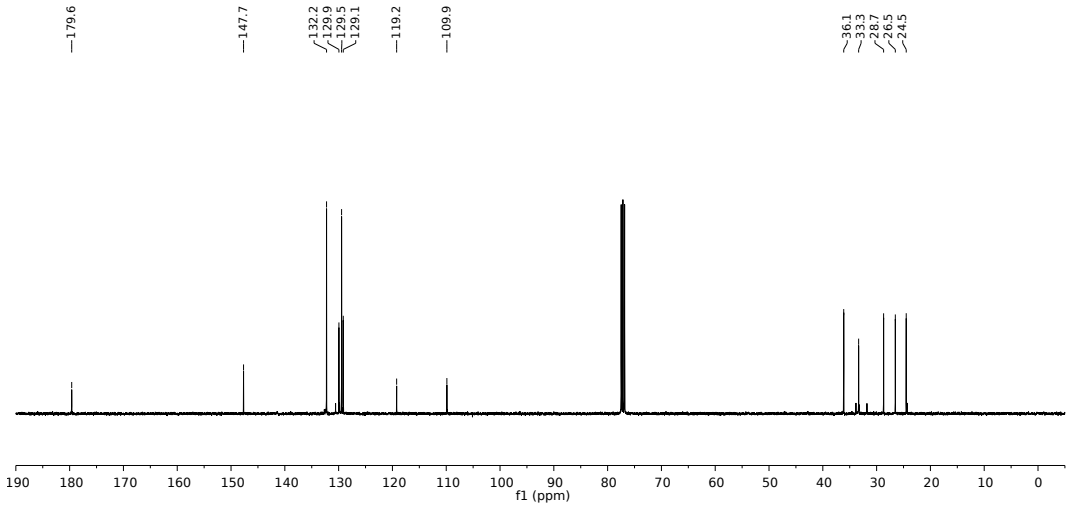

Transmittance [%]
3000.86
2956.49
2868.93
1705.28
1459.48
1412.00
1361.47
1296.69
1239.31
1205.23
1165.46
1102.41
926.80
740.11
486.30
Wavenumber cm-1

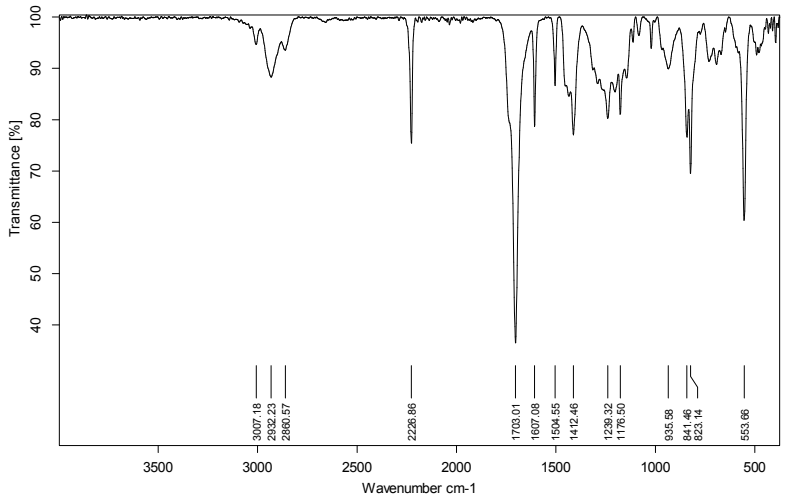

HO
O
137m
1.00
1.05
1.05
4.56
1.98
1.98
2.00
4.84
2.29
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

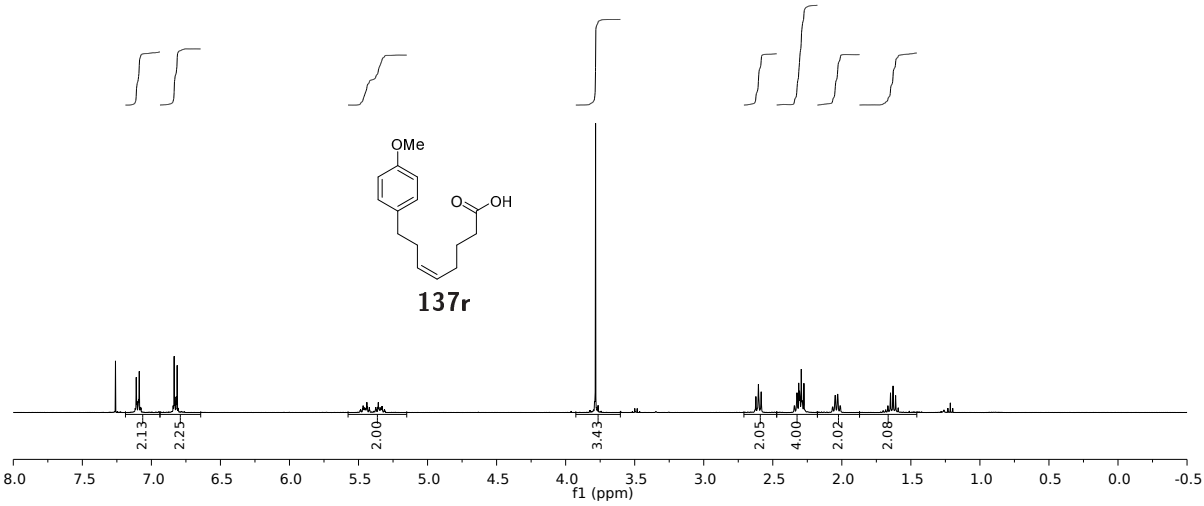

179.7
138.0
134.0
132.0
130.2
129.3
128.9
126.8
126.2
125.9
125.6
125.5
123.8
33.4
33.1
28.6
26.6
24.6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

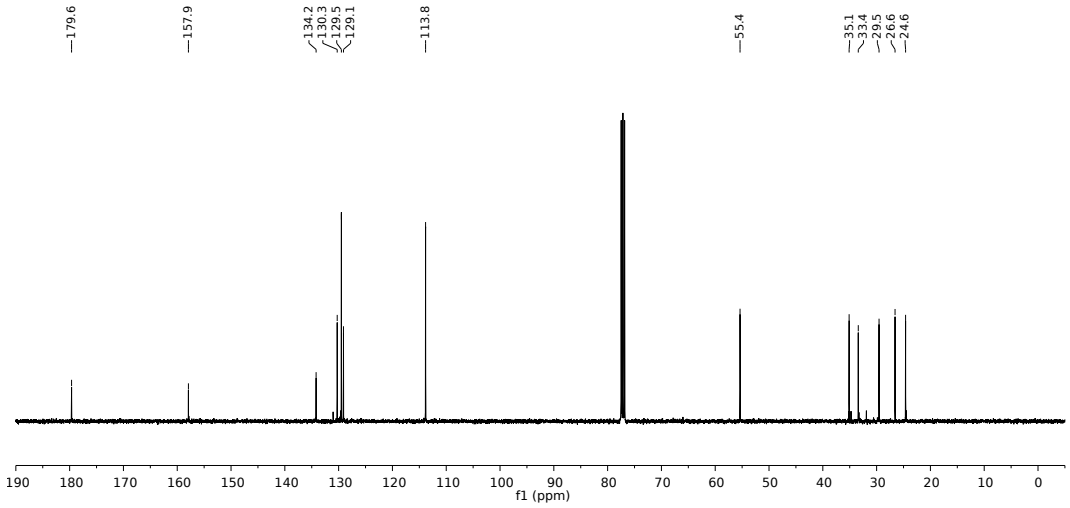

Transmittance [%]
100 90 80 70 60 50 40
3042.88
3006.28
2921.00
2849.79
1702.79
1596.40
1509.82
1468.61
1445.54
1410.00
1238.86
1204.60
936.59
858.88
795.97
774.14
732.27
480.59
423.15
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

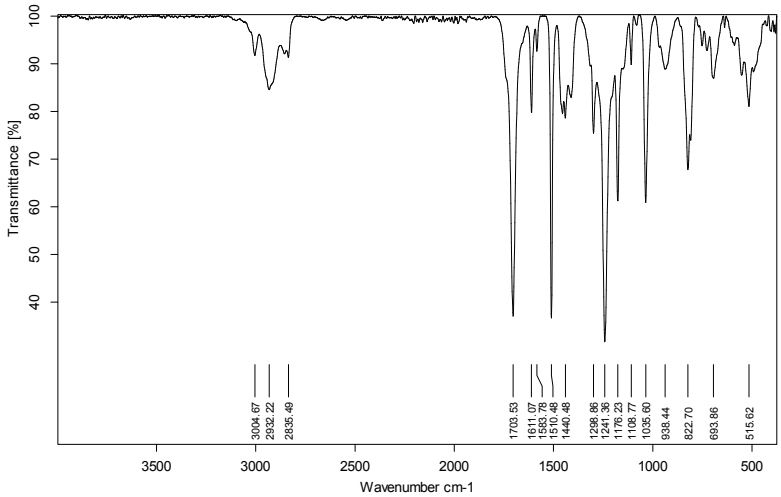

CN
O
OH
137q
2.27
2.63
2.00
2.14
4.17
2.16
2.24
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

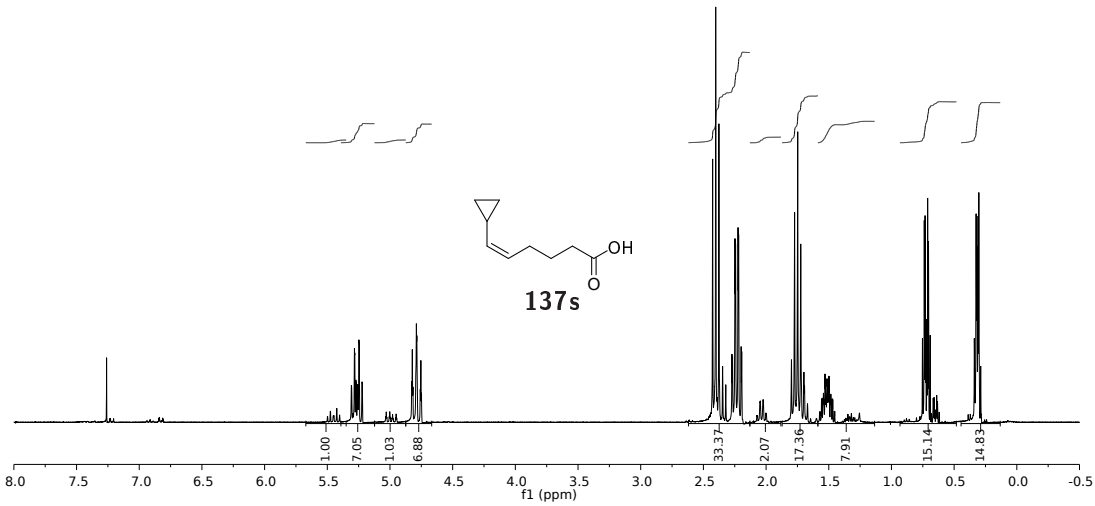

179.6
147.7
132.2
129.9
129.5
129.1
119.2
109.9
36.1
33.3
28.7
26.5
24.5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

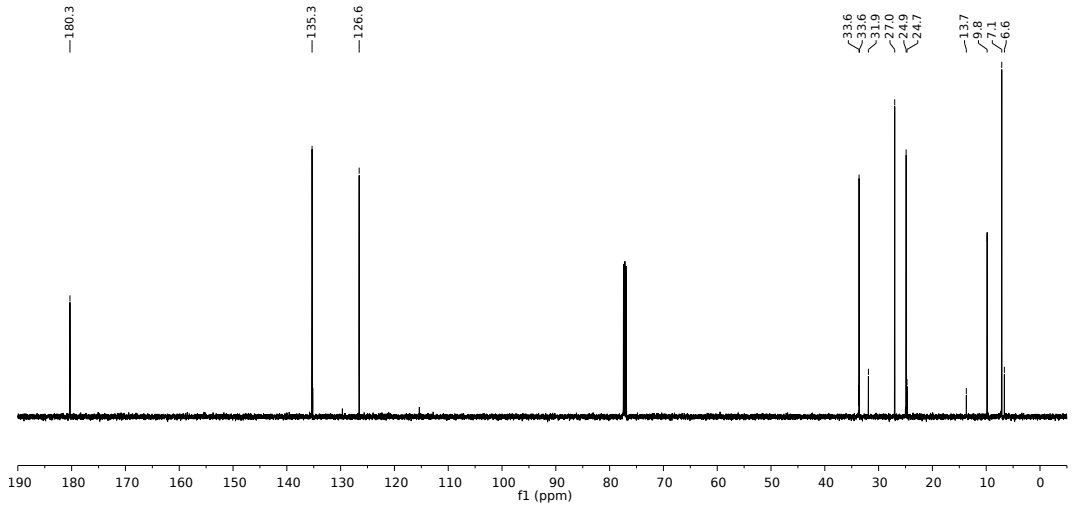

Transmittance [%]
100 90 80 70 60 50 40
3007.18
2932.23
2860.57
2228.86
1703.01
1607.08
1504.55
1412.46
1239.32
1176.50
935.98
841.46
823.14
553.66
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

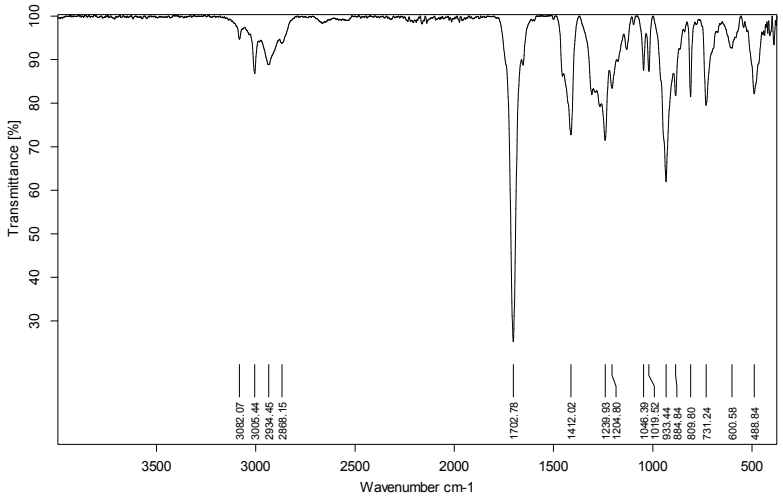

OMe
O
OH
137r
2.13
2.25
2.00
3.43
2.05
4.00
2.02
2.08
f1 (ppm)

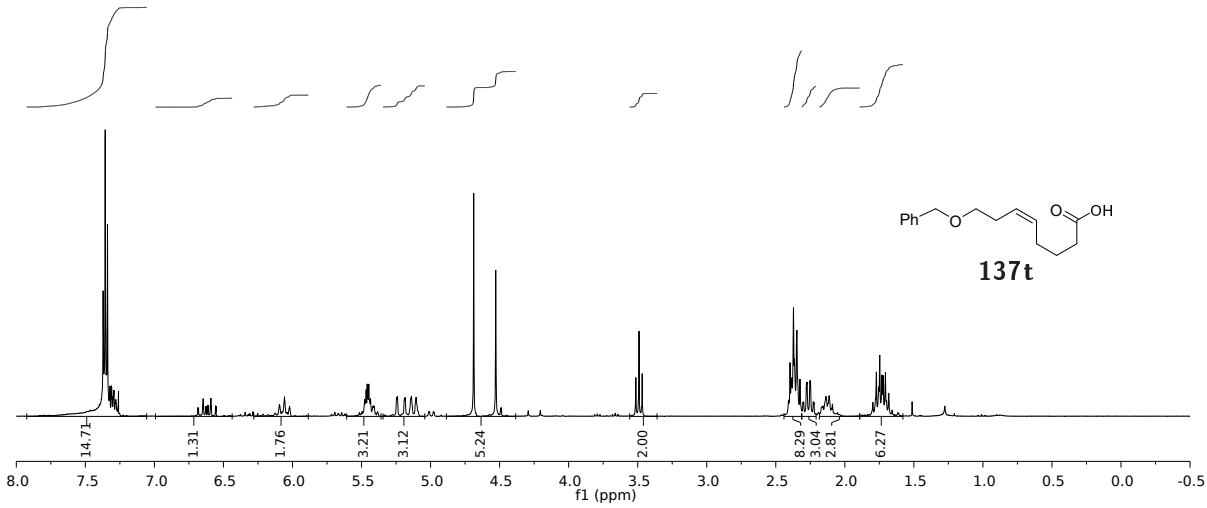

179.6
157.9
134.2
130.3
129.5
129.1
113.8
55.4
35.1
33.4
29.5
26.6
24.6
f1 (ppm)

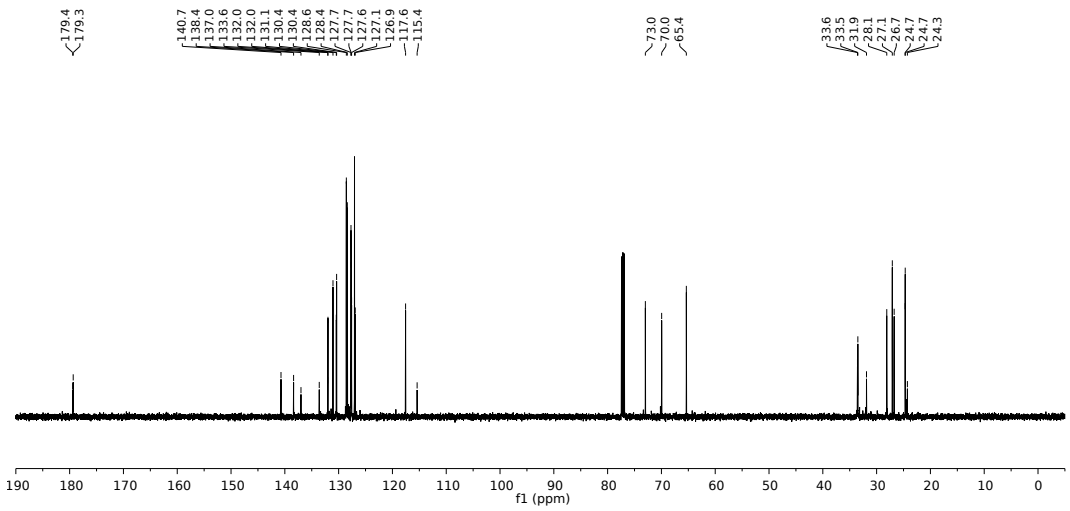

Transmittance [%]
3004.67
2932.22
2835.49
1703.53
1611.07
1583.78
1510.48
1440.48
1298.86
1241.36
1176.23
1108.77
1035.60
938.44
822.70
693.86
515.62
Wavenumber cm-1

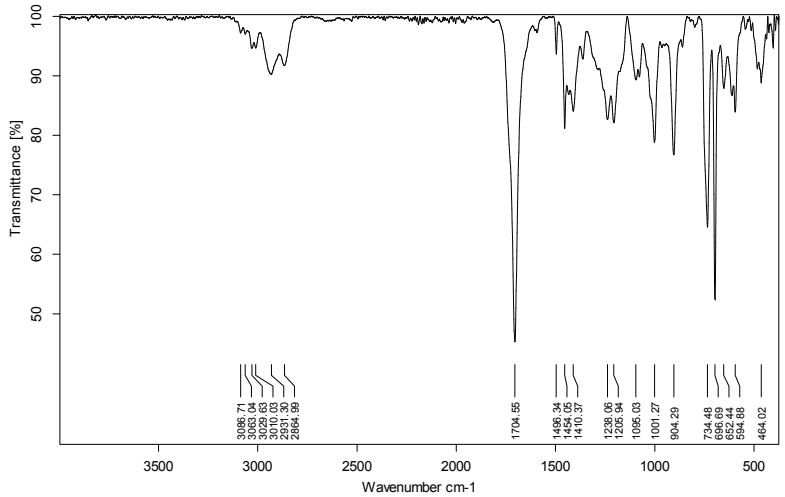

OH
O
137s
1.00
7.05
1.03
6.88
33.37
2.07
17.36
7.91
15.14
14.83
f1 (ppm)

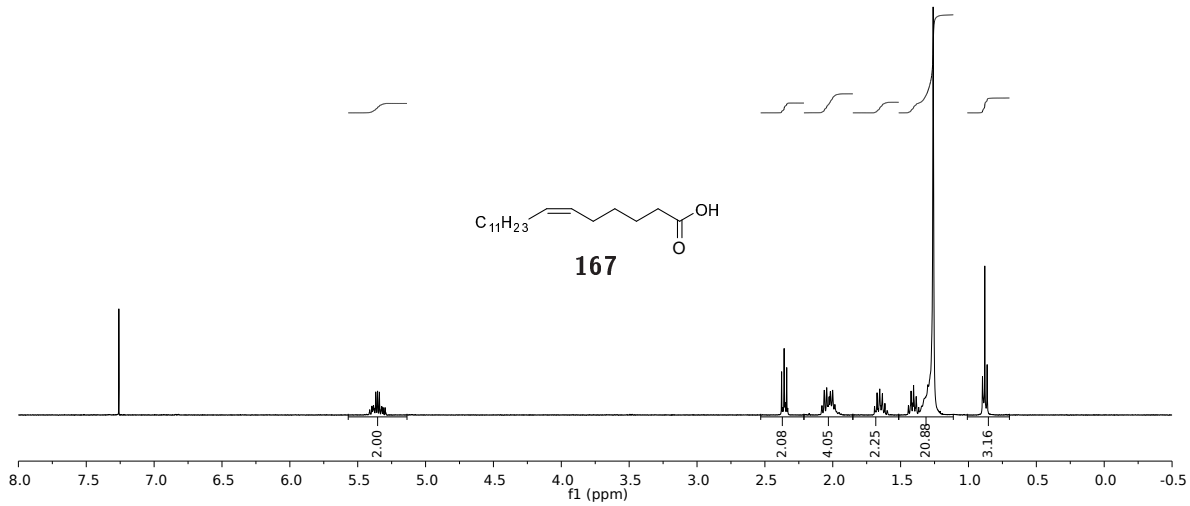

180.3
135.3
126.6
33.6
33.6
31.9
27.0
24.9
24.7
13.7
9.8
7.1
6.6
f1 (ppm)

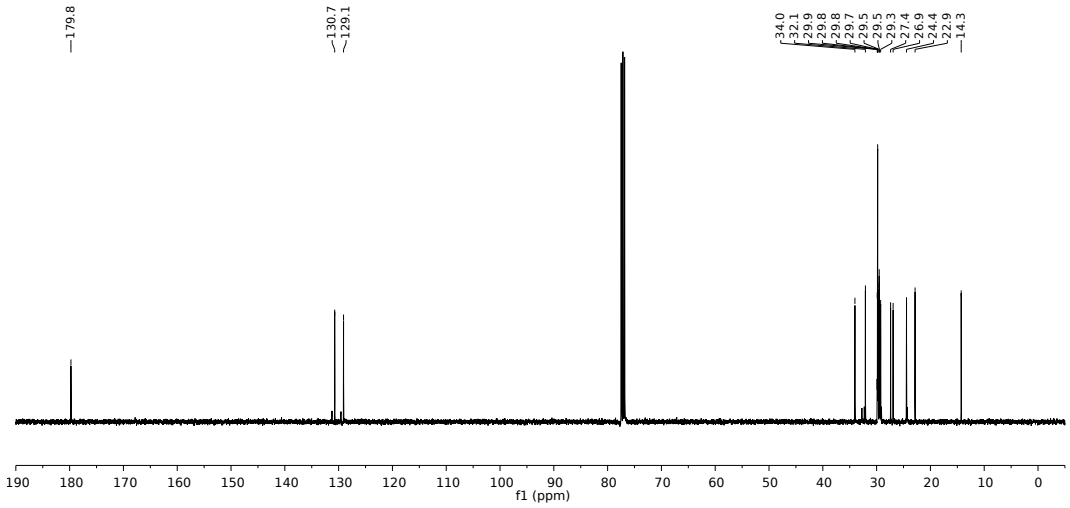

Transmittance [%]
3082.07
3005.44
2934.45
2888.15
1702.78
1412.02
1239.93
1204.80
1046.39
1019.92
933.44
884.84
809.80
731.24
600.58
488.84
Wavenumber cm-1

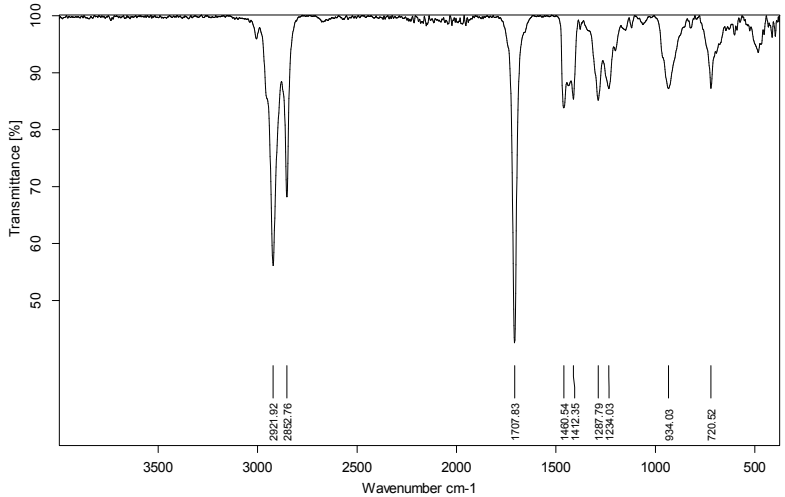

Ph
O
O
OH
137t
14.71
1.31
1.76
3.21
3.12
5.24
2.00
8.29
3.04
2.81
6.27
f1 (ppm)

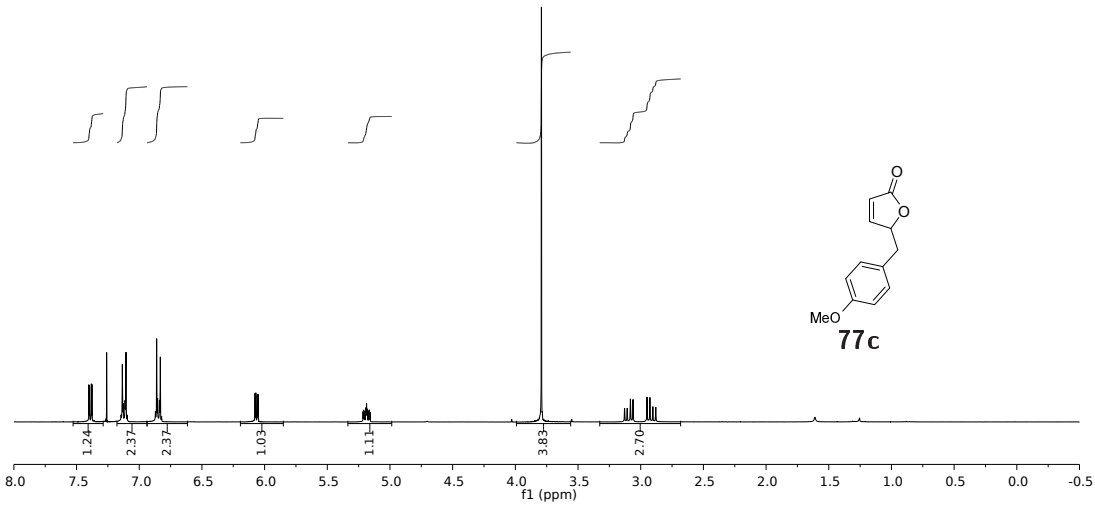

179.4
179.3
140.7
138.4
137.0
133.6
132.0
132.0
131.1
130.4
130.4
128.6
128.4
127.7
127.7
127.6
127.1
126.9
117.6
115.4
73.0
70.0
65.4
33.6
33.5
31.9
28.1
27.1
26.7
24.7
24.7
24.3
f1 (ppm)

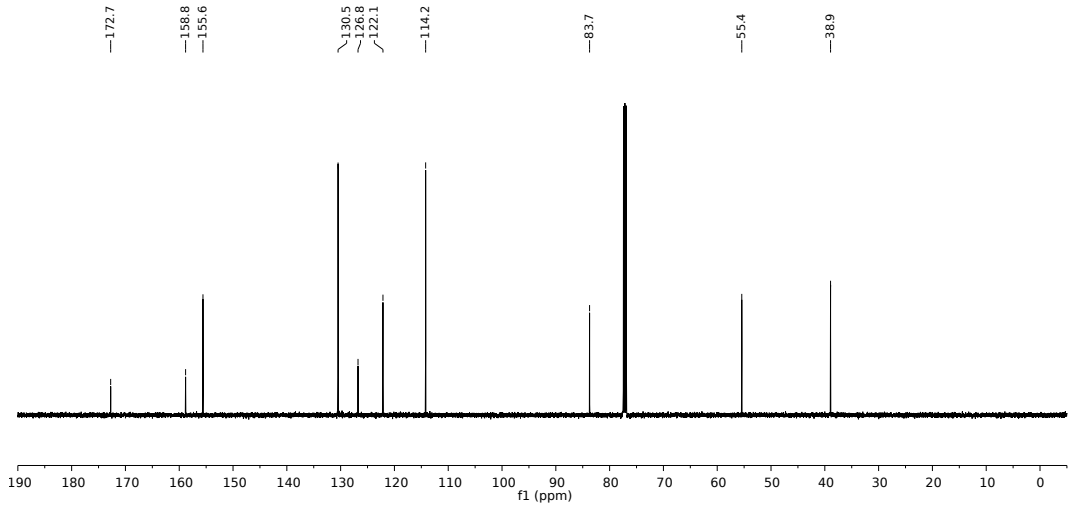

Transmittance [%]
3086.71
3063.04
3029.63
3010.03
2931.30
2864.99
1704.55
1496.34
1454.05
1410.37
1238.08
1205.94
1095.03
1001.27
904.29
734.48
695.69
650.44
594.88
464.02
Wavenumber cm-1

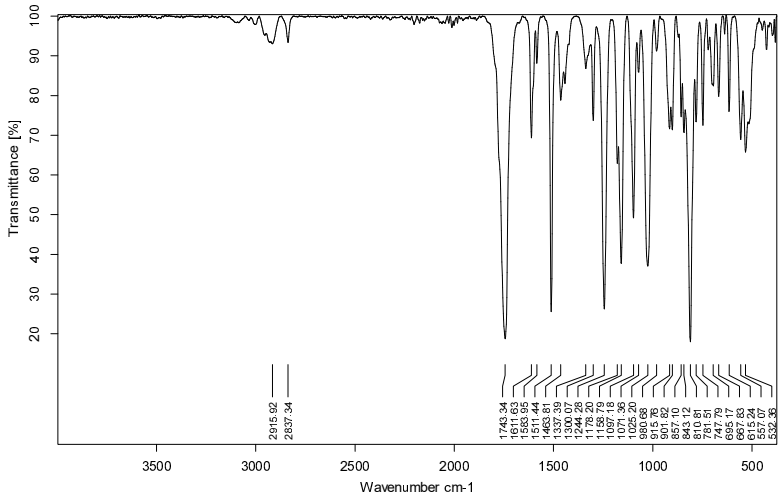

C11H23
OH
O
167
2.00
2.08
4.05
2.25
20.88
3.16
f1 (ppm)

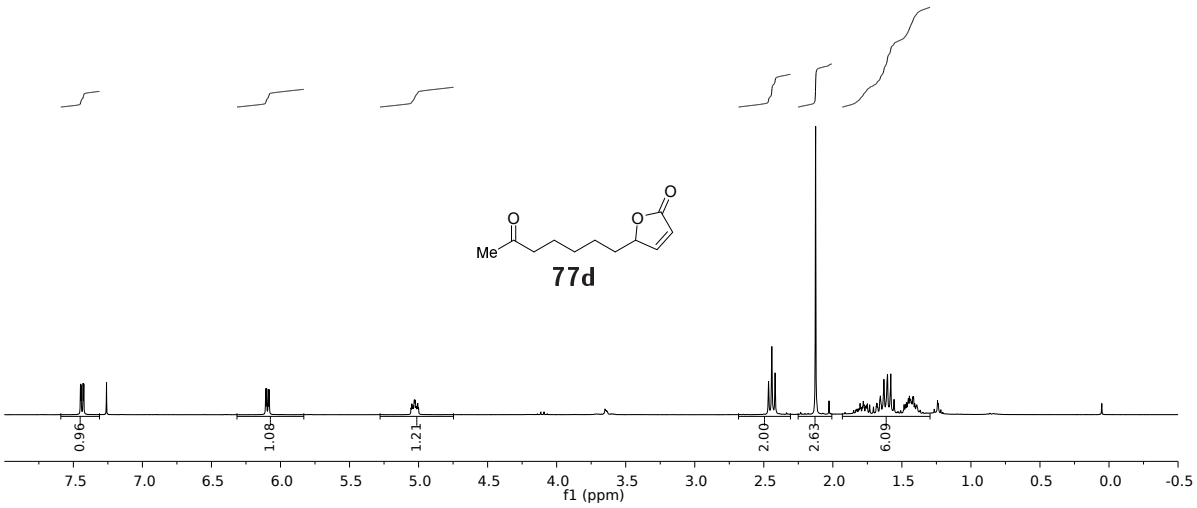

179.8
130.7
129.1
34.0
32.1
29.9
29.8
29.8
29.7
29.5
29.5
29.3
27.4
26.9
24.4
22.9
14.3
f1 (ppm)

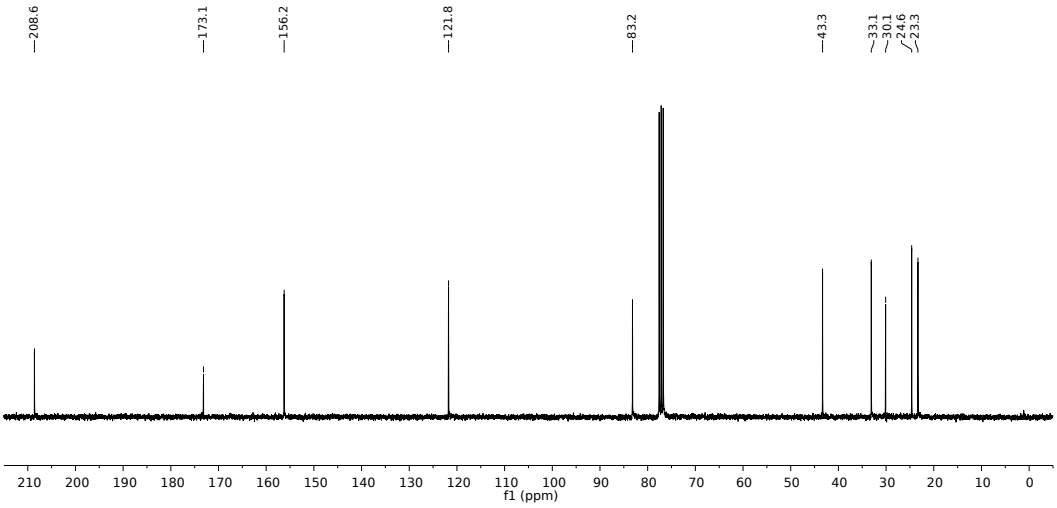

Transmittance [%]
2921.92
2852.76
1707.83
1460.54
1412.35
1287.79
1234.03
934.03
720.52
Wavenumber cm-1

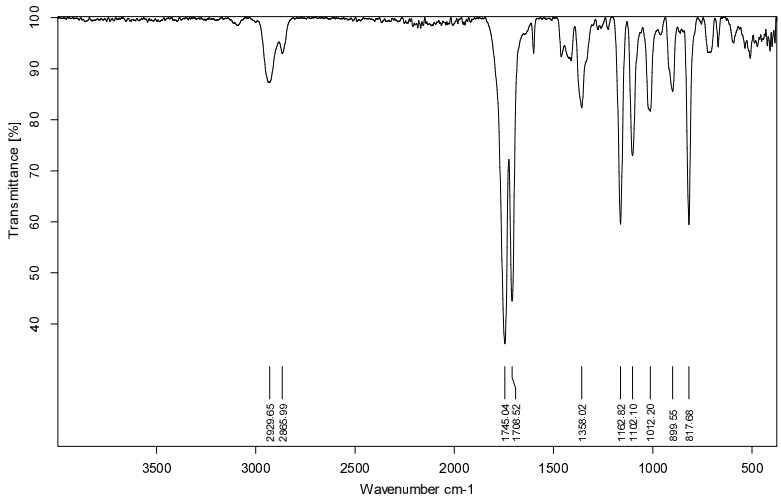

MeO
77c
1.24
2.37
2.37
1.03
1.11
3.83
2.70
f1 (ppm)

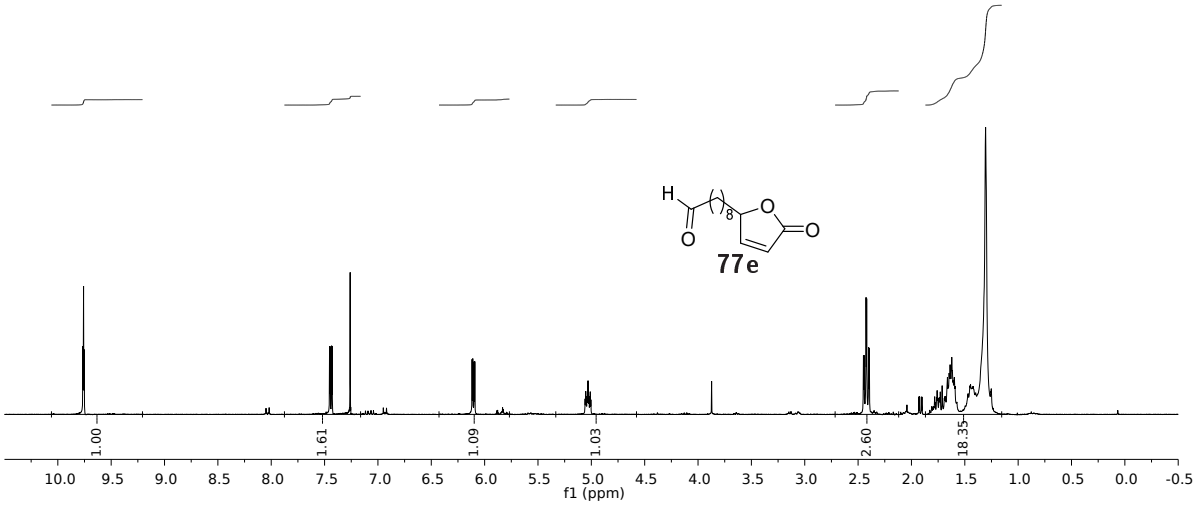

172.7
158.8
155.6
130.5
126.8
122.1
114.2
83.7
55.4
38.9
f1 (ppm)

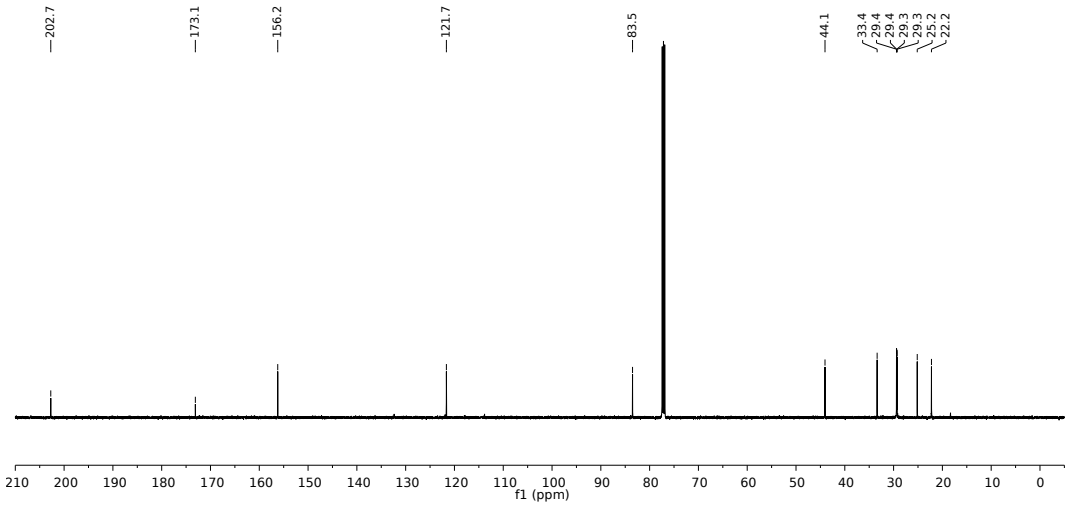

Transmittance [%]
2915.92
2837.34
Wavenumber cm-1

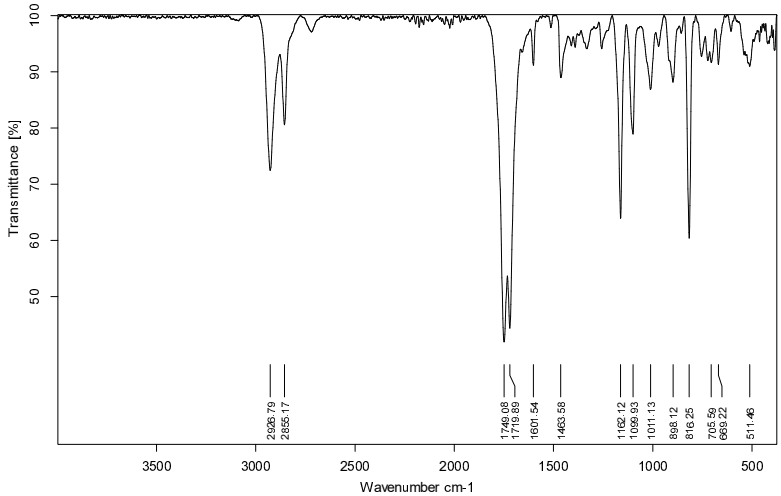

Me
77d
0.96
1.08
1.21
2.00
2.63
6.09
f1 (ppm)

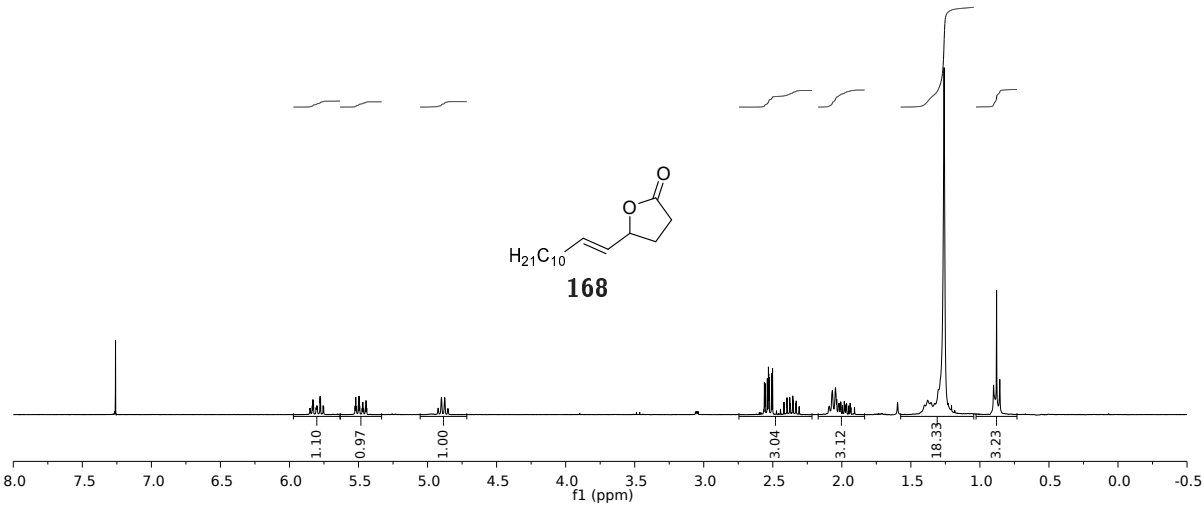

208.6
173.1
156.2
121.8
83.2
43.3
33.1
30.1
24.6
23.3
f1 (ppm)

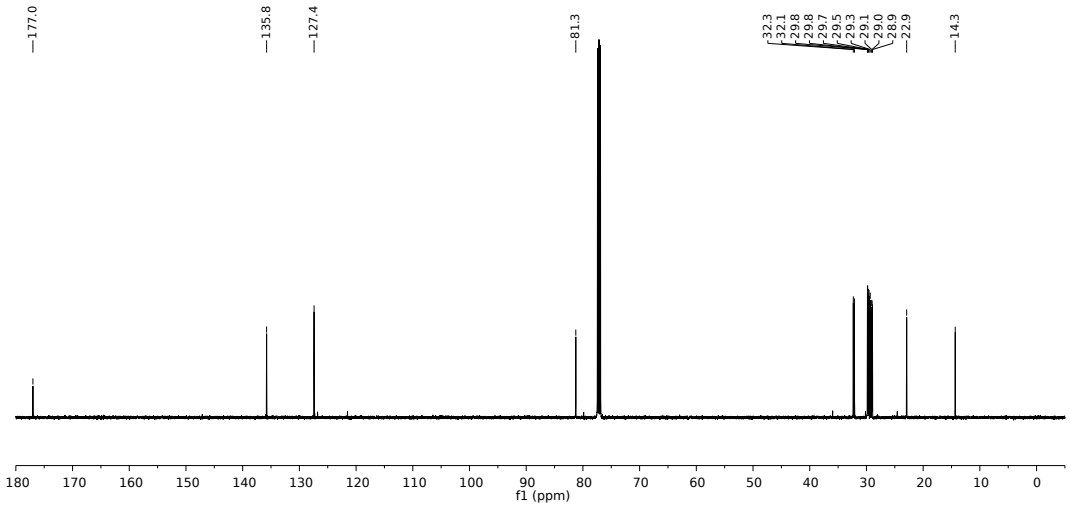

Transmittance [%]
2929.65
2865.99
1745.04
1708.52
1358.02
1162.82
1102.10
1012.20
899.55
817.68
Wavenumber cm-1

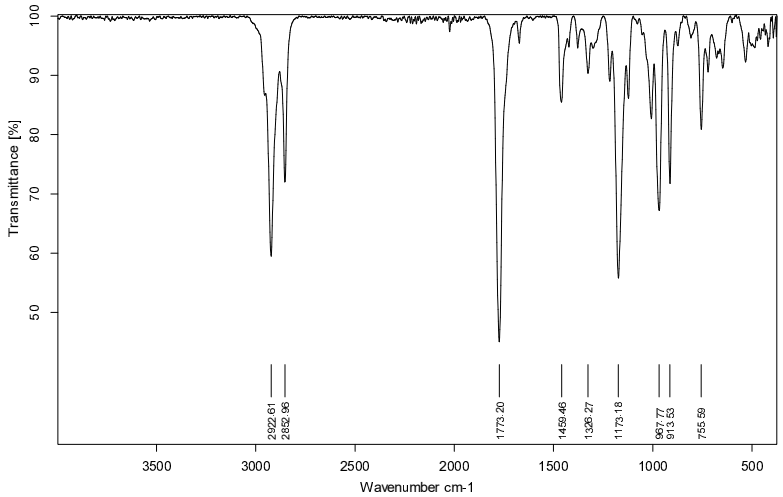

H
O
O
O
8
O
77e
1.00
1.61
1.09
1.03
2.60
18.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

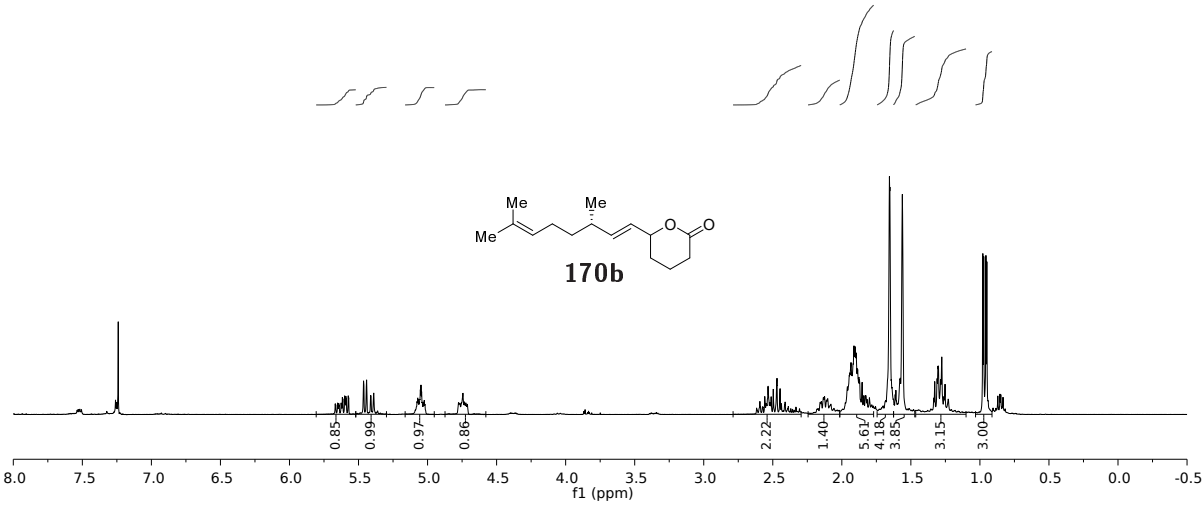

202.7
173.1
156.2
121.7
83.5
44.1
33.4
29.4
29.4
29.3
29.3
25.2
22.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

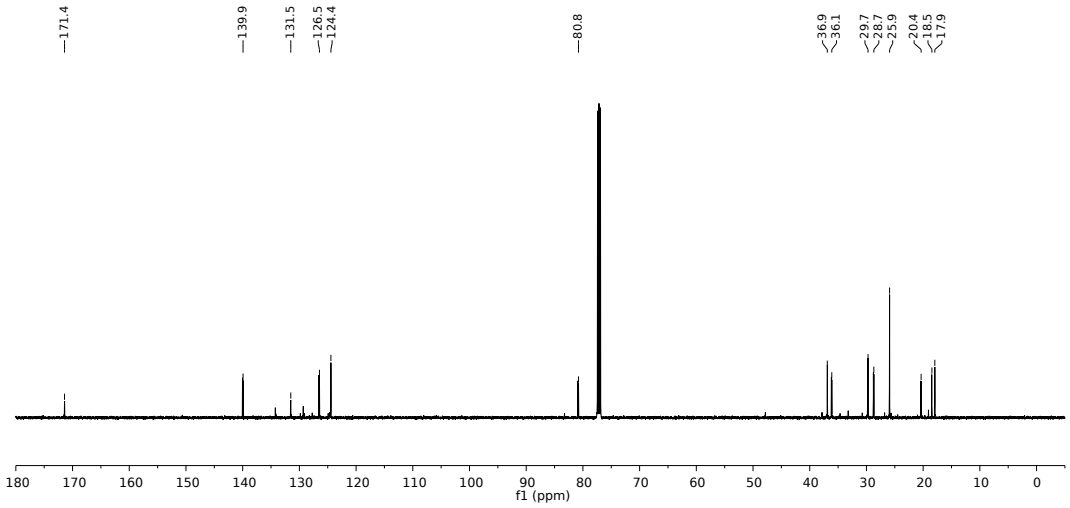

Transmittance [%]
100
90
80
70
60
50
2926.79
2855.17
1749.08
1719.89
1601.54
1463.58
1162.12
1099.93
1011.13
868.12
816.25
705.59
669.22
511.46
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

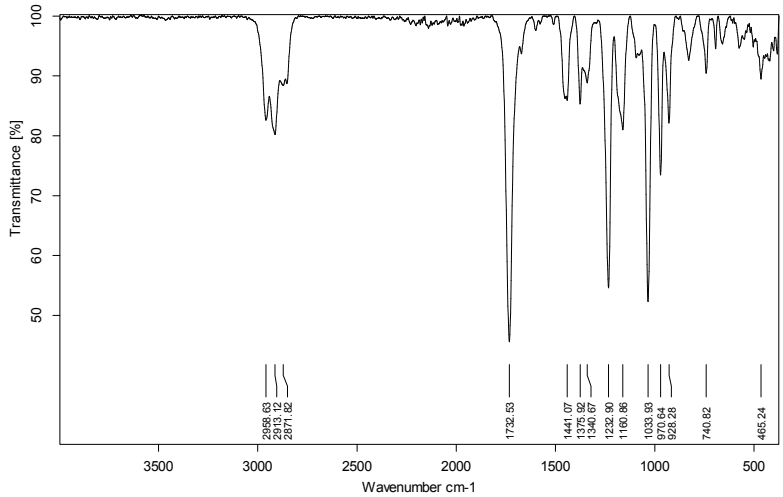

O
O
$H_{21}C_{10}$
168
1.10
0.97
1.00
3.04
3.12
18.33
3.23
f1 (ppm)

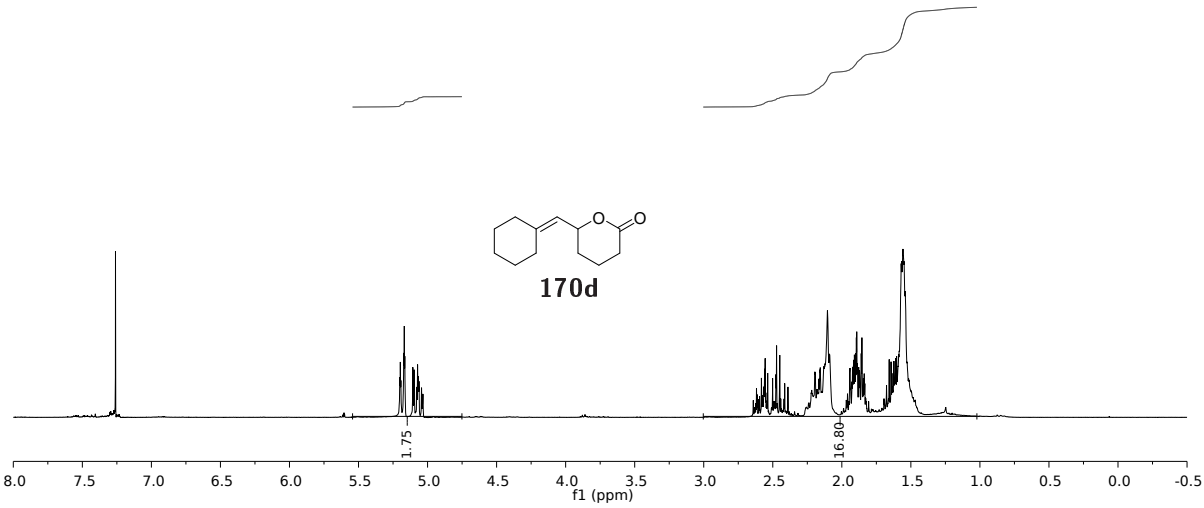

177.0
135.8
127.4
81.3
32.3
32.1
29.8
29.8
29.7
29.5
29.3
29.1
29.0
28.9
22.9
14.3
f1 (ppm)

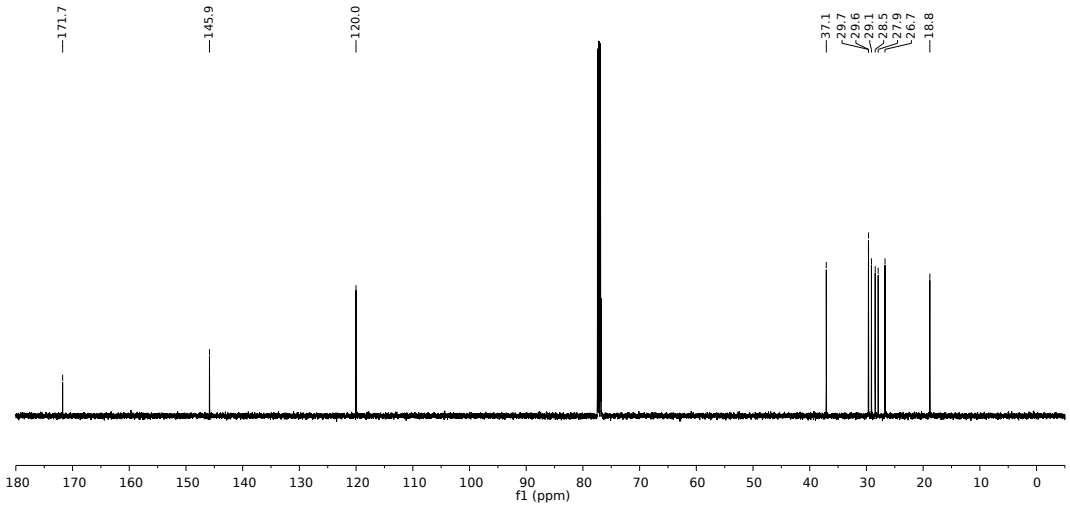

Transmittance [%]
2922.61
2852.96
1773.20
1459.46
1386.27
1173.18
967.77
913.53
755.59
Wavenumber cm-1

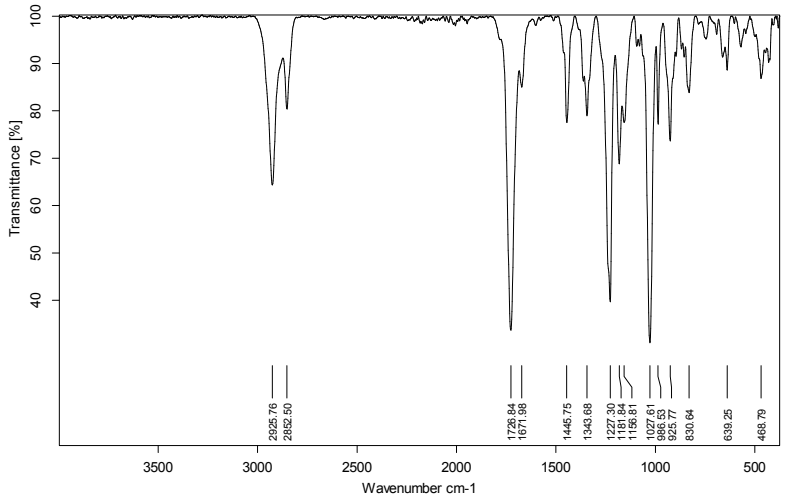

Me
Me
Me
O
O
170b
0.85
0.99
0.97
0.86
2.22
1.40
5.61
4.18
3.85
3.15
3.00
f1 (ppm)

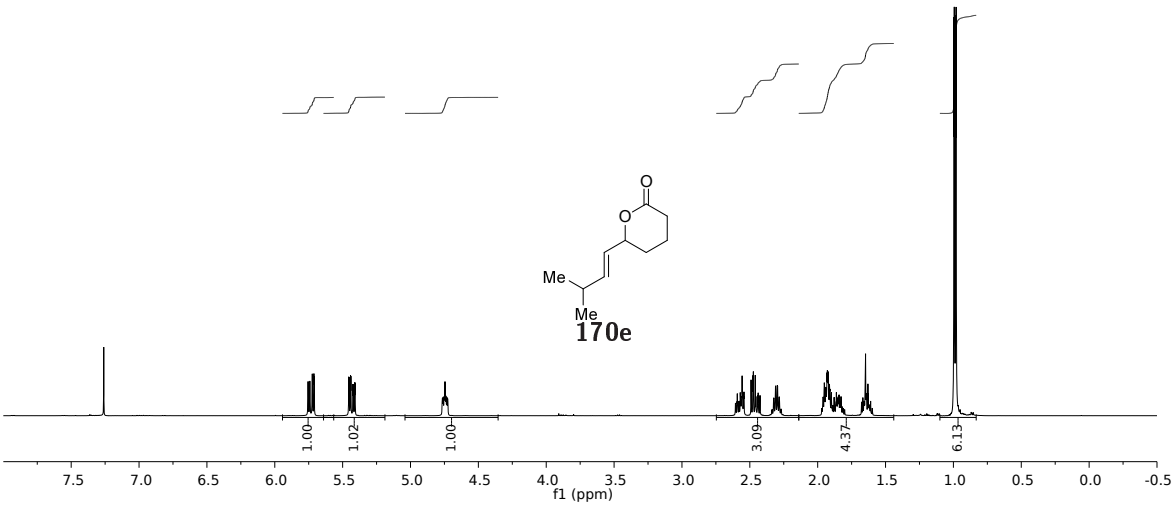

171.4
139.9
131.5
126.5
124.4
80.8
36.9
36.1
29.7
28.7
25.9
20.4
18.5
17.9
f1 (ppm)

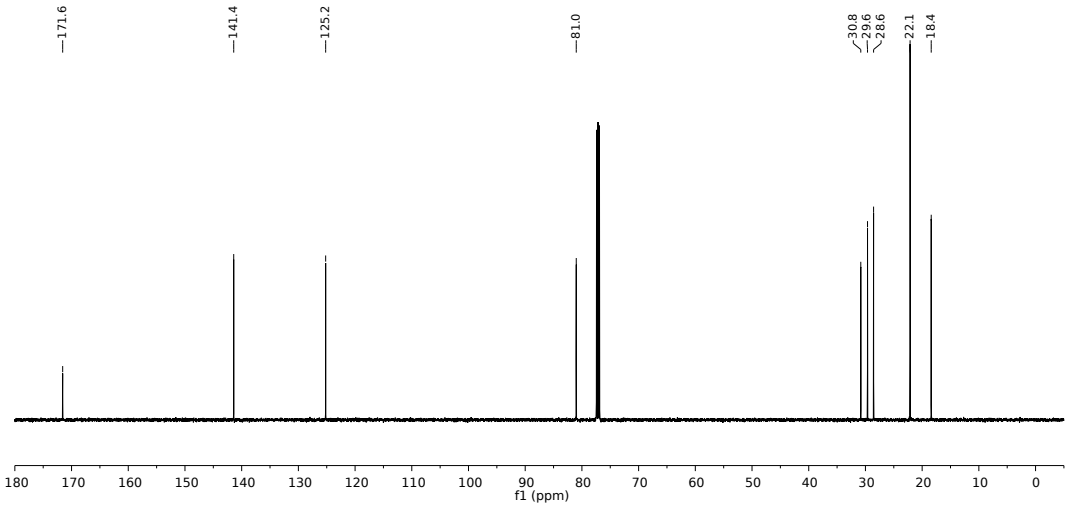

Transmittance [%]
2958.63
2913.12
2871.82
1732.53
1441.07
1375.92
1340.07
1232.90
1160.86
1033.93
970.64
928.28
740.82
465.24
Wavenumber cm-1

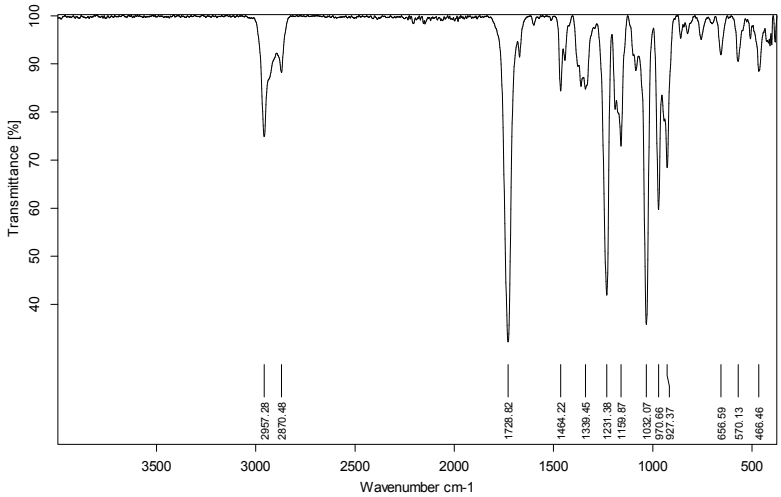

170d
1.75
16.80
f1 (ppm)

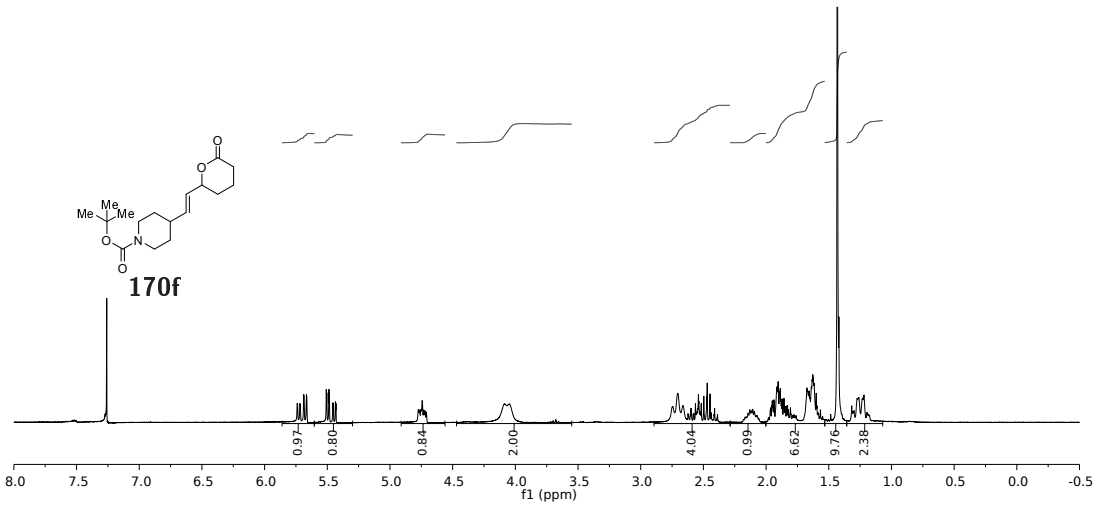

171.7
145.9
120.0
37.1
29.7
29.6
29.1
28.5
27.9
26.7
18.8
f1 (ppm)

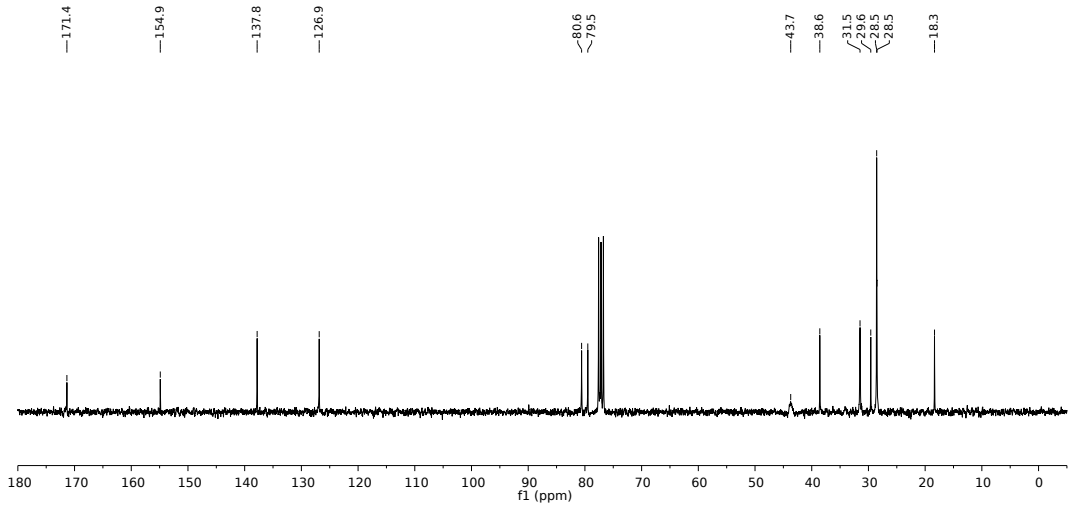

Transmittance [%]
2925.76
2852.60
1728.84
1671.98
1445.75
1343.68
1227.30
1161.84
1156.81
1027.61
986.52
925.77
830.64
639.25
468.79
Wavenumber cm-1

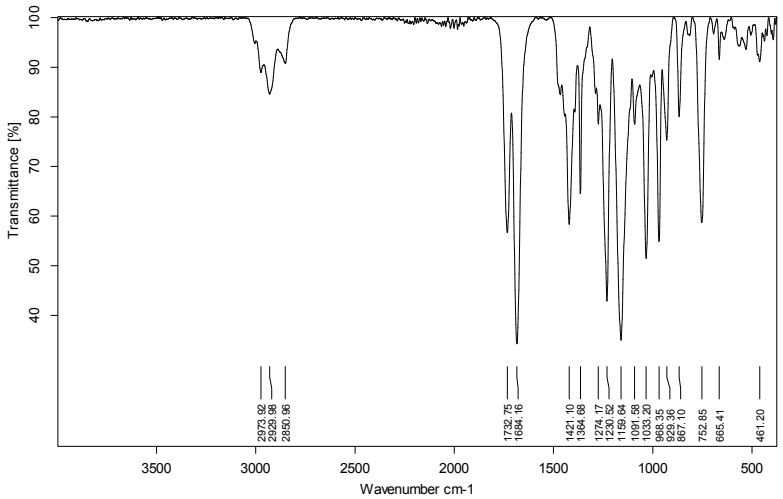

O
O
Me
Me
170e
1.00
1.02
1.00
3.09
4.37
6.13
f1 (ppm)

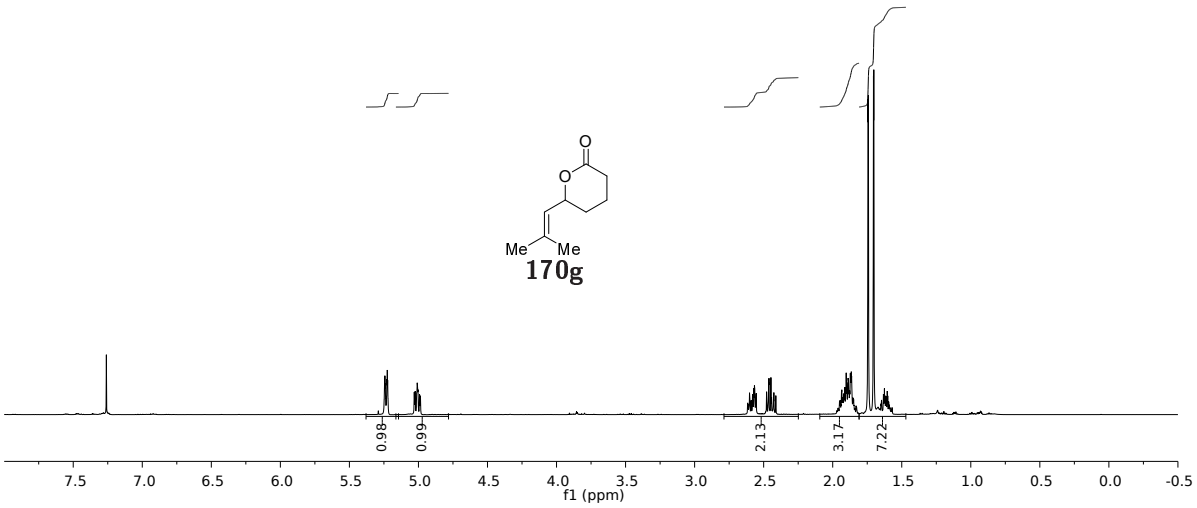

171.6
141.4
125.2
81.0
30.8
29.6
28.6
22.1
18.4
f1 (ppm)

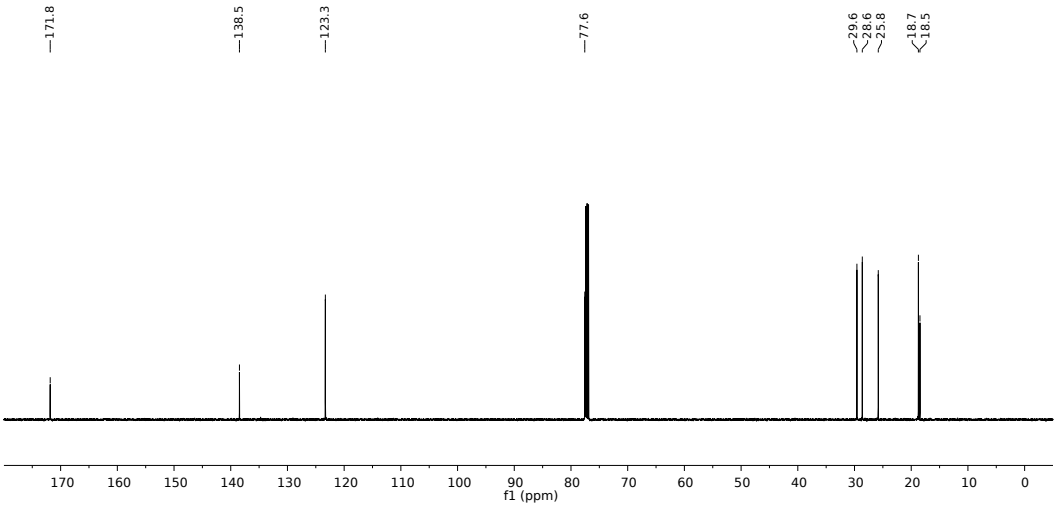

Transmittance [%]
2957.28
2870.48
1728.82
1464.22
1339.45
1231.38
1159.87
1032.07
970.66
927.37
656.59
570.13
466.46
Wavenumber cm-1

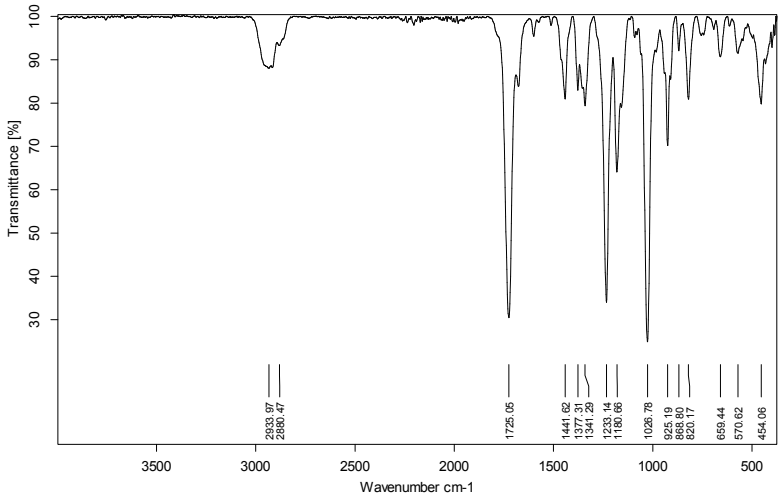

170f
0.97
0.80
0.84
2.00
4.04
0.99
6.62
9.76
2.38
f1 (ppm)

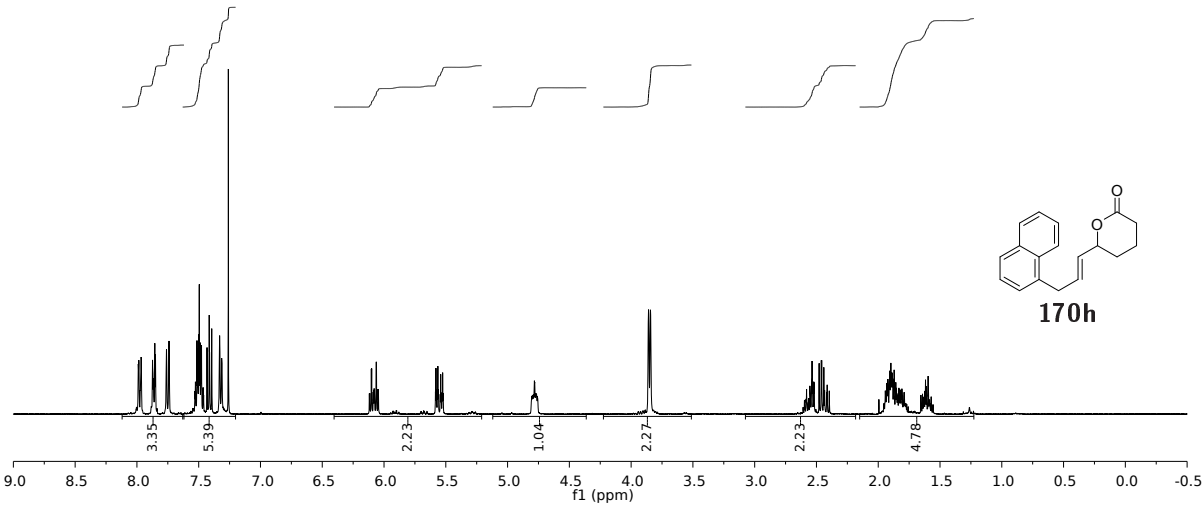

171.4
154.9
137.8
126.9
80.6
79.5
43.7
38.6
31.5
29.6
28.5
28.5
18.3
f1 (ppm)


Transmittance [%]
2973.92
2929.98
2850.96
1732.75
1684.16
1421.10
1364.68
1274.17
1230.52
1159.64
1091.58
1033.20
968.25
929.36
867.10
752.85
666.41
461.20
Wavenumber cm-1

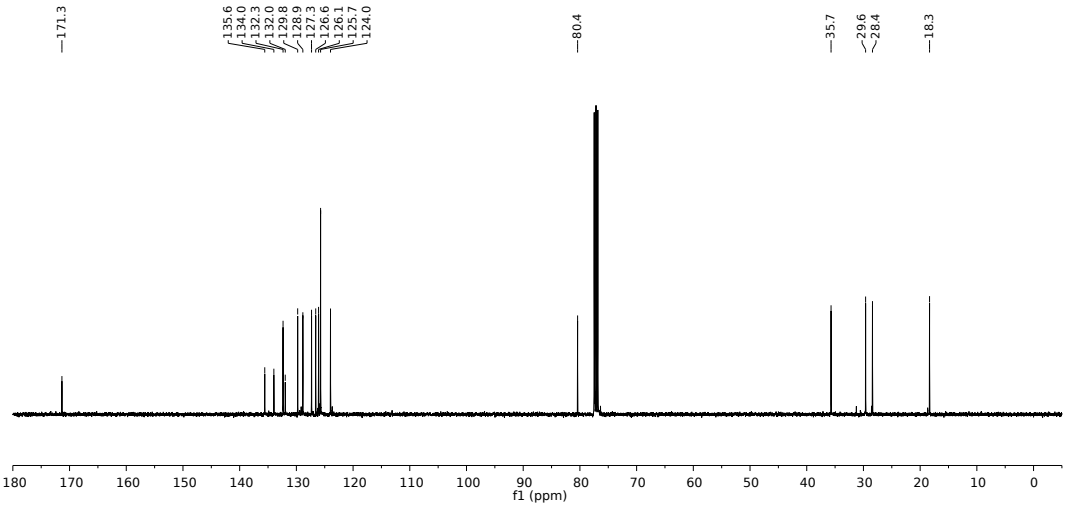

O
O
Me
Me
170g
0.98
0.99
2.13
3.17
7.22
f1 (ppm)

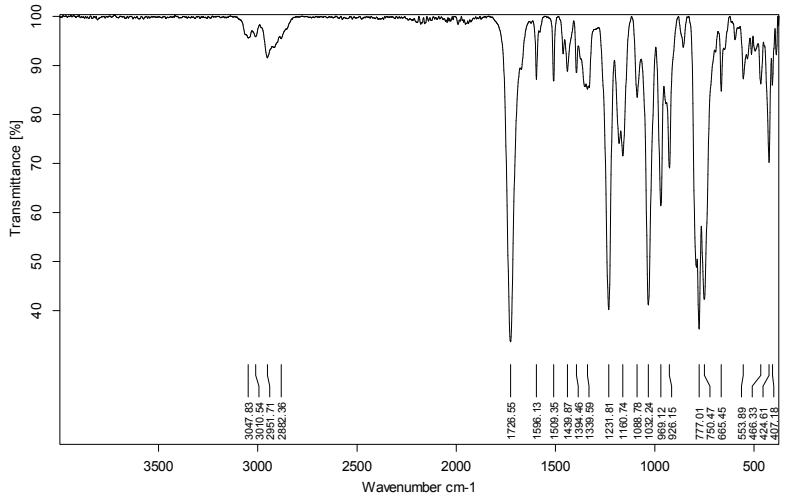

171.8
138.5
123.3
77.6
29.6
28.6
25.8
18.7
18.5
f1 (ppm)

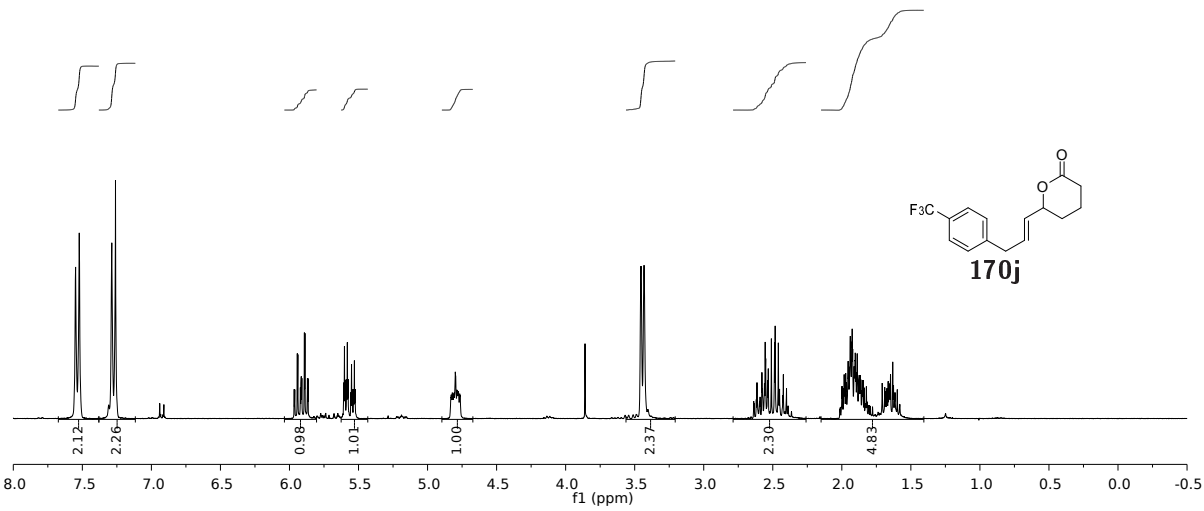

Transmittance [%]
2933.97
2880.47
1725.05
1441.62
1377.31
1341.29
1233.14
1160.66
1026.78
925.19
868.80
820.17
659.44
570.62
454.06
Wavenumber cm-1

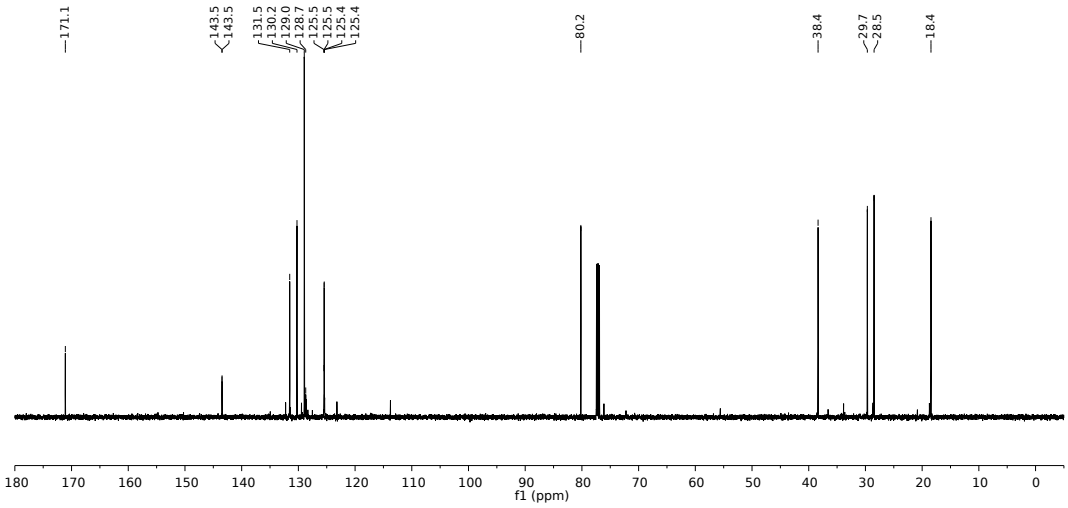

3.35
5.39
2.23
1.04
2.27
2.23
4.78
f1 (ppm)

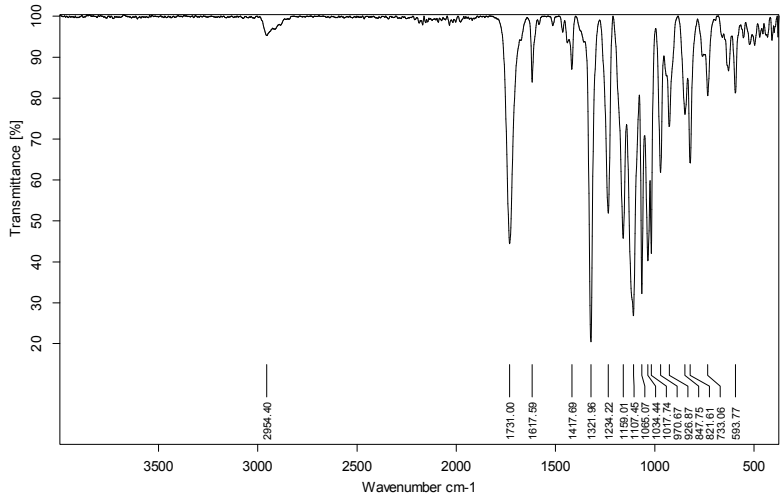
170h

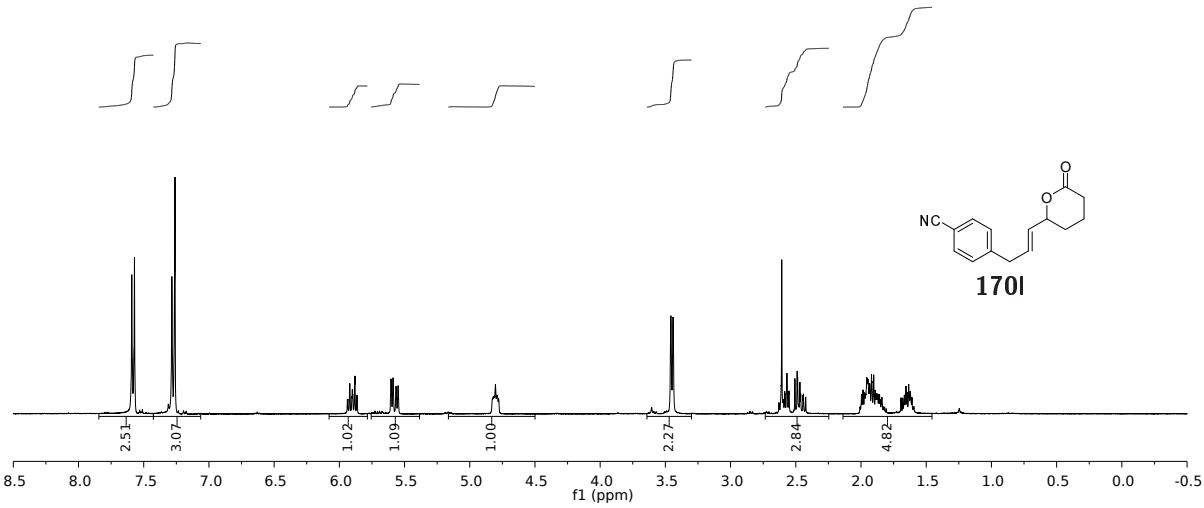

171.3
135.6
134.0
132.3
132.0
129.8
128.9
127.3
126.6
126.1
125.7
124.0
80.4
35.7
29.6
28.4
18.3
f1 (ppm)


Transmittance [%]
3047.83
3010.54
2951.71
2882.36
1726.55
1596.13
1509.35
1439.87
1394.46
1339.59
1231.81
1160.74
1088.78
1032.24
968.12
928.15
777.01
750.47
666.45
553.89
466.33
424.61
407.18
Wavenumber cm-1

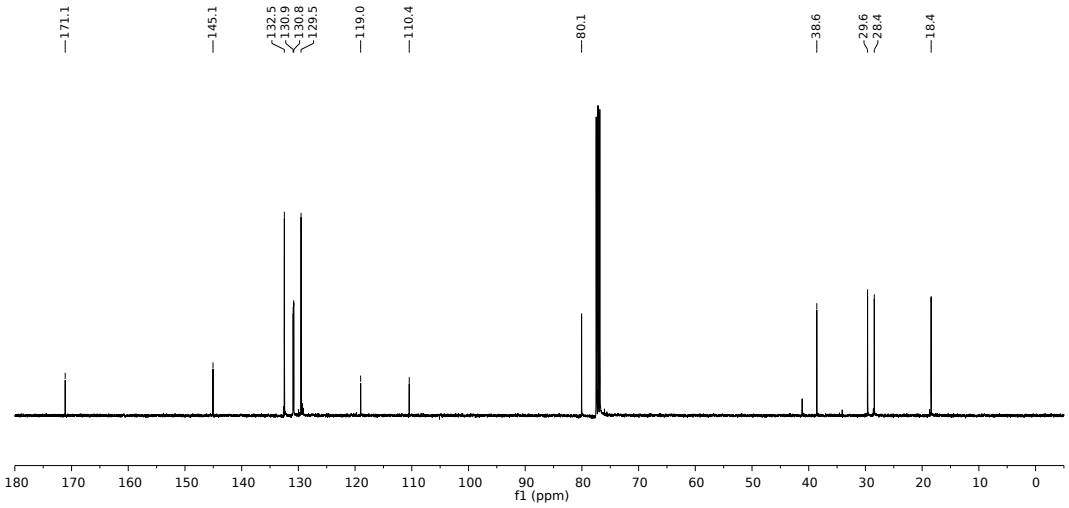

F3C
O
O
170j
2.12
2.26
0.98
1.01
1.00
2.37
2.30
4.83
f1 (ppm)

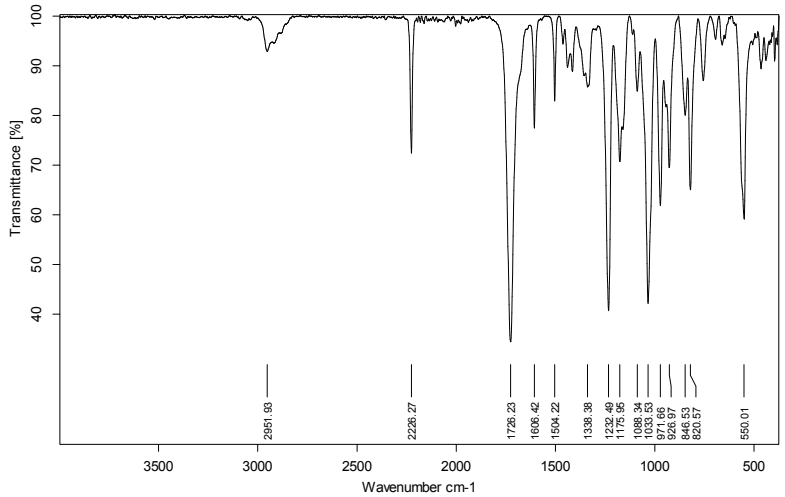

171.1
143.5
143.5
131.5
130.2
129.0
128.7
125.5
125.5
125.4
125.4
80.2
38.4
29.7
28.5
18.4
f1 (ppm)

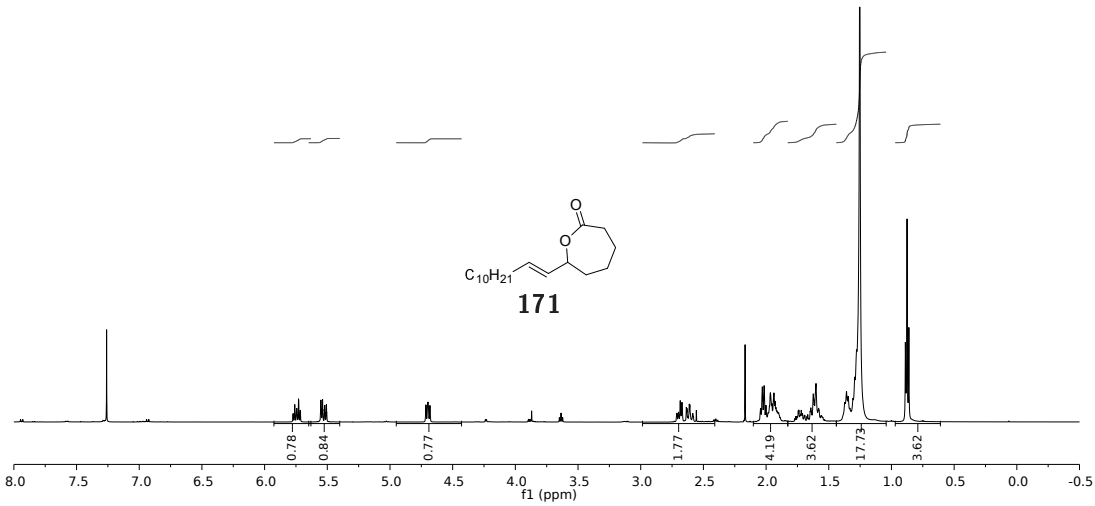

Transmittance [%]
2954.40
1731.00
1617.59
1417.89
1321.96
1234.22
1159.01
1117.45
1065.07
1034.44
1017.74
976.87
908.87
847.75
821.61
733.06
593.77
Wavenumber cm-1

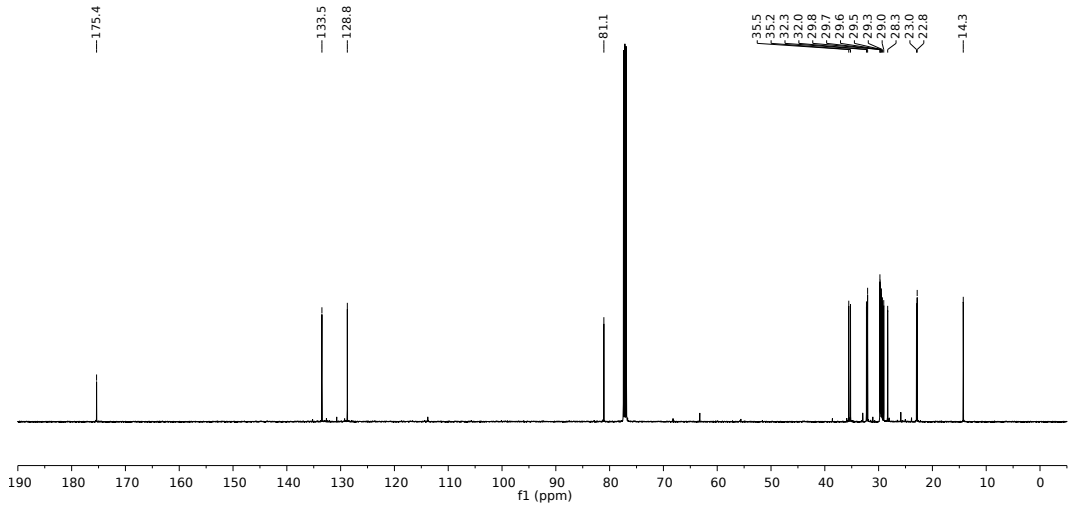

NC
O
O
2.51
3.07
1.02
1.09
1.00
2.27
2.84
4.82
f1 (ppm)

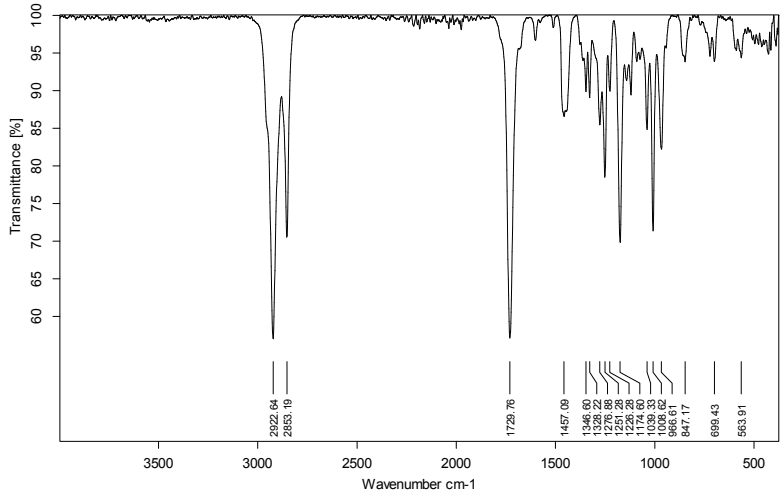
170l

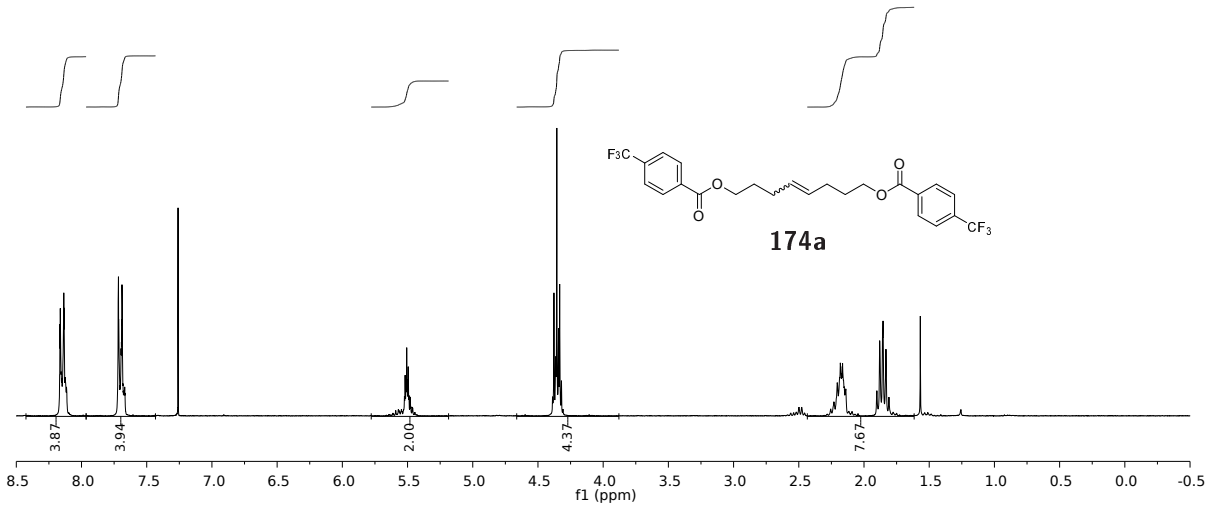

171.1
145.1
132.5
130.9
130.8
129.5
119.0
110.4
80.1
38.6
29.6
28.4
18.4
f1 (ppm)

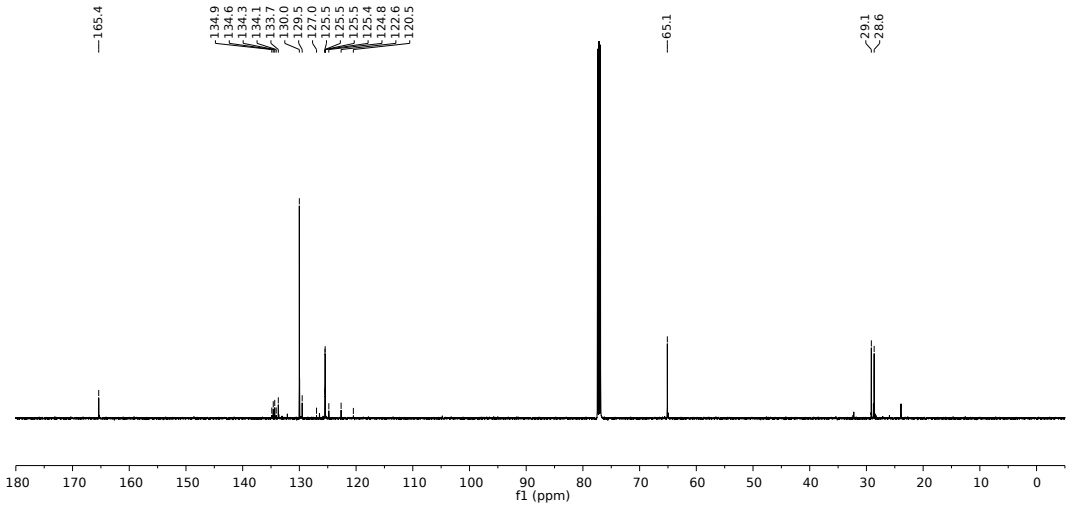

Transmittance [%]
2951.93
2226.27
1726.23
1606.42
1504.22
1338.38
1232.49
1175.95
1088.34
1033.63
977.66
926.97
846.53
820.57
550.01
Wavenumber cm-1

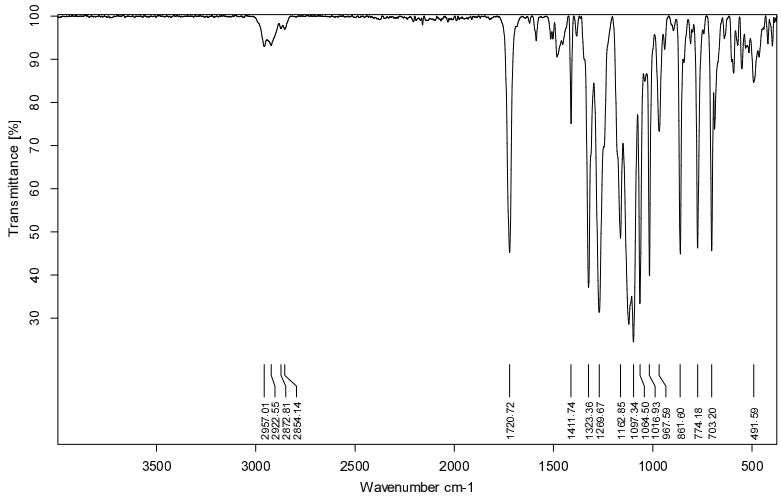

O
O
$C_{10}H_{21}$
171
0.78
0.84
0.77
1.77
4.19
3.62
17.73
3.62
f1 (ppm)

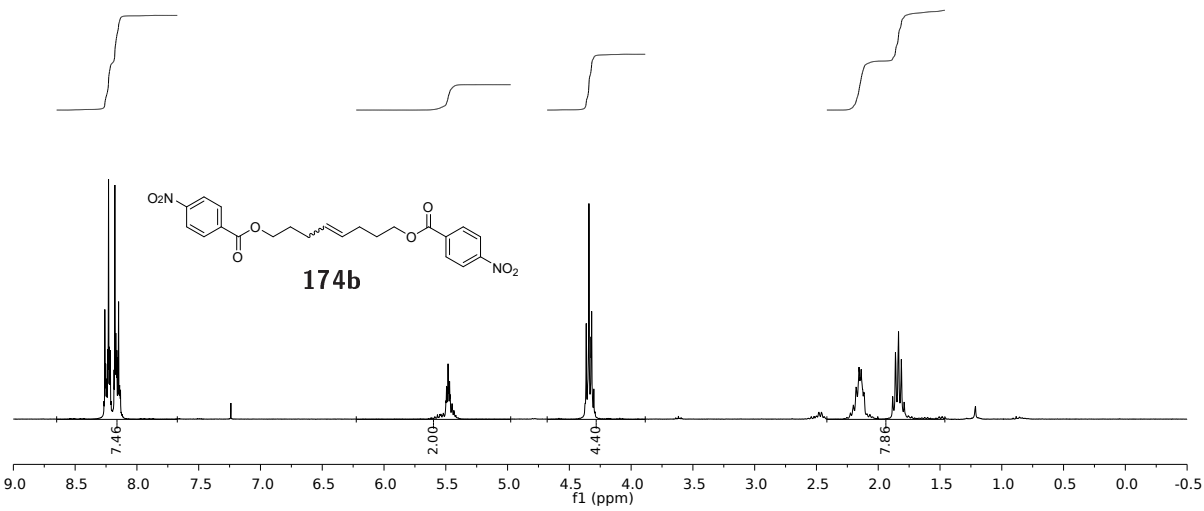

175.4
133.5
128.8
81.1
35.5
35.2
32.3
32.0
29.8
29.7
29.6
29.5
29.3
29.0
28.3
23.0
22.8
14.3
f1 (ppm)

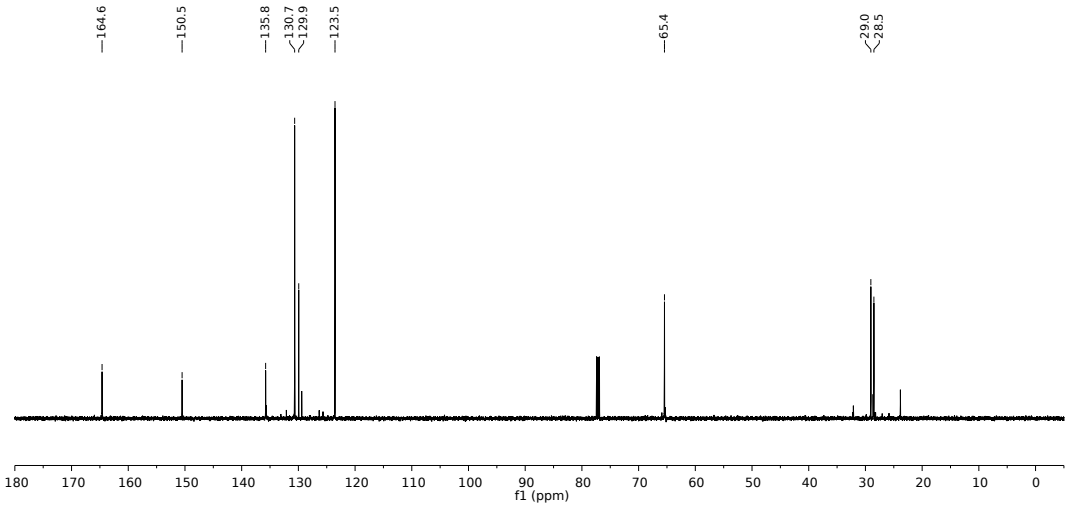

Transmittance [%]
2922.64
2853.19
1729.76
1457.09
1346.60
1328.22
1276.88
1251.51
1226.28
1174.60
1039.33
1008.62
966.61
847.17
699.43
563.91
Wavenumber cm-1

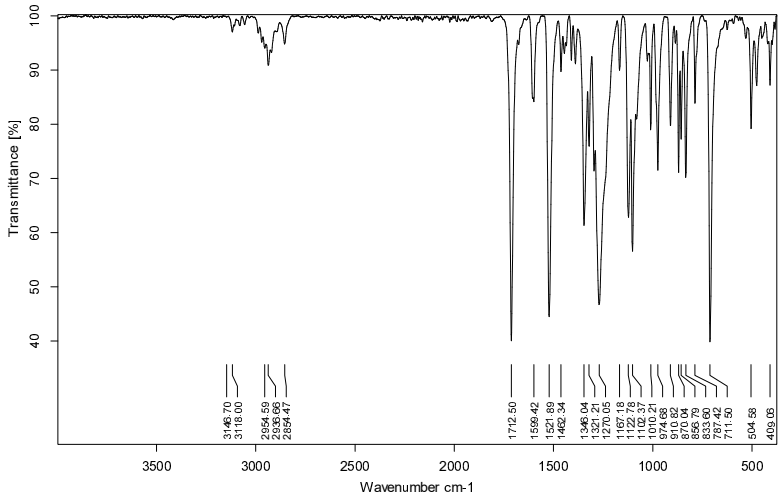

F3C
O
O
O
O
CF3
174a
3.87
3.94
2.00
4.37
7.67
f1 (ppm)

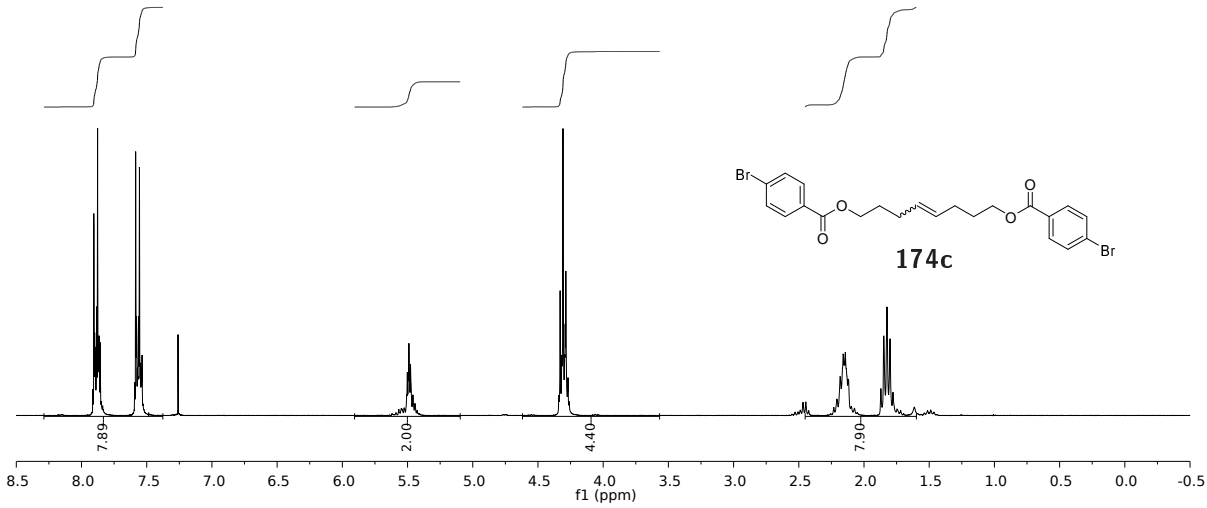

165.4
134.9
134.6
134.3
134.1
133.7
130.0
129.5
127.0
125.5
125.5
125.5
125.4
124.8
122.6
120.5
65.1
29.1
28.6
f1 (ppm)

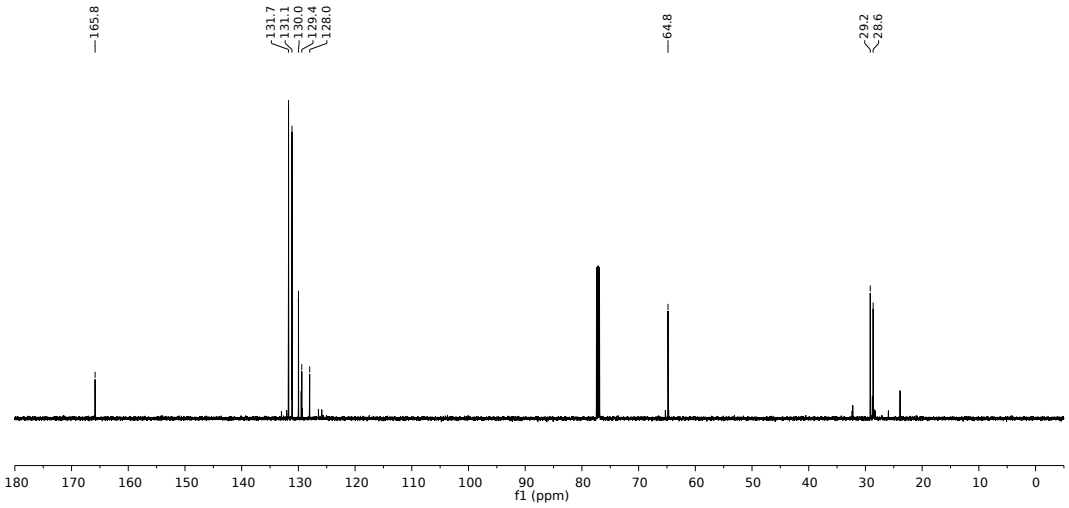

Transmittance [%]
2957.01
2922.55
2872.81
2854.14
1720.72
1411.74
1323.36
1269.67
1162.85
1097.34
1064.03
1016.93
967.59
861.60
774.18
703.20
491.59
Wavenumber cm-1

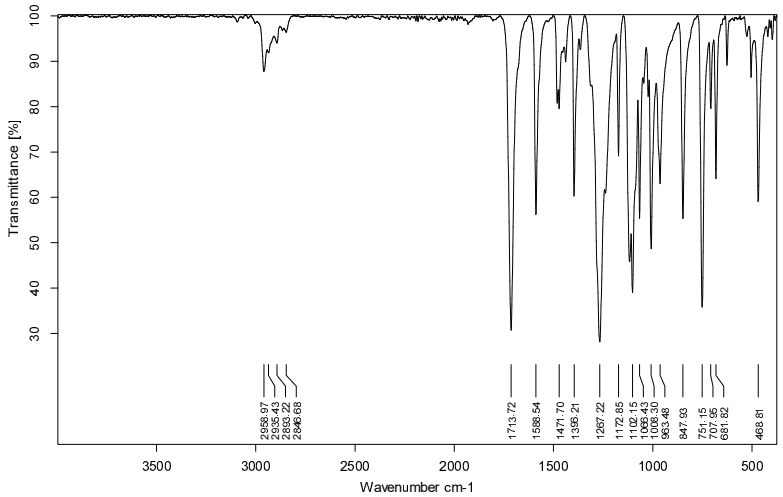

O2N
NO2
174b
7.46
2.00
4.40
7.86
f1 (ppm)

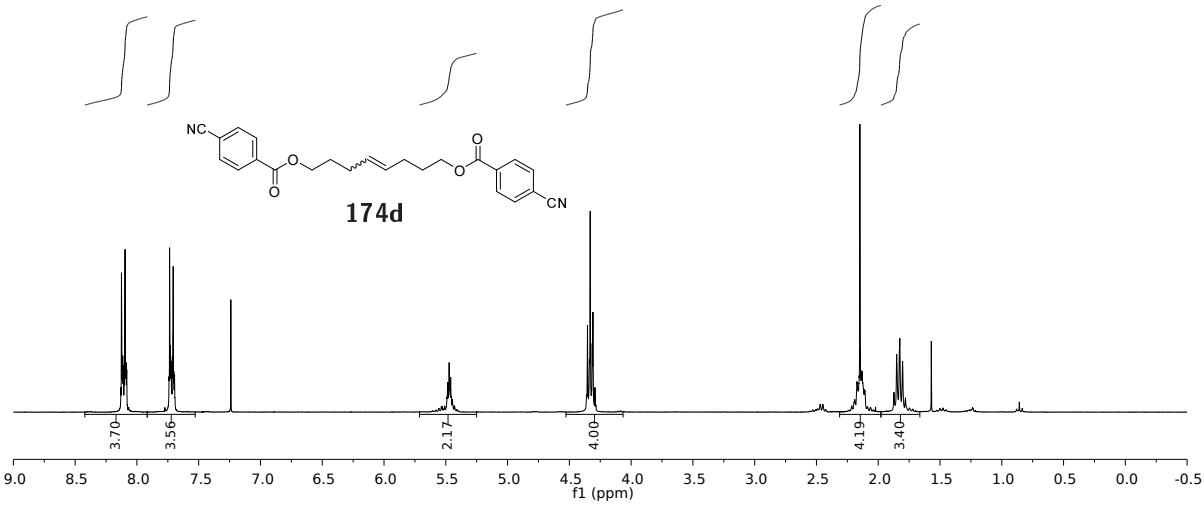

164.6
150.5
135.8
130.7
129.9
123.5
65.4
29.0
28.5
f1 (ppm)

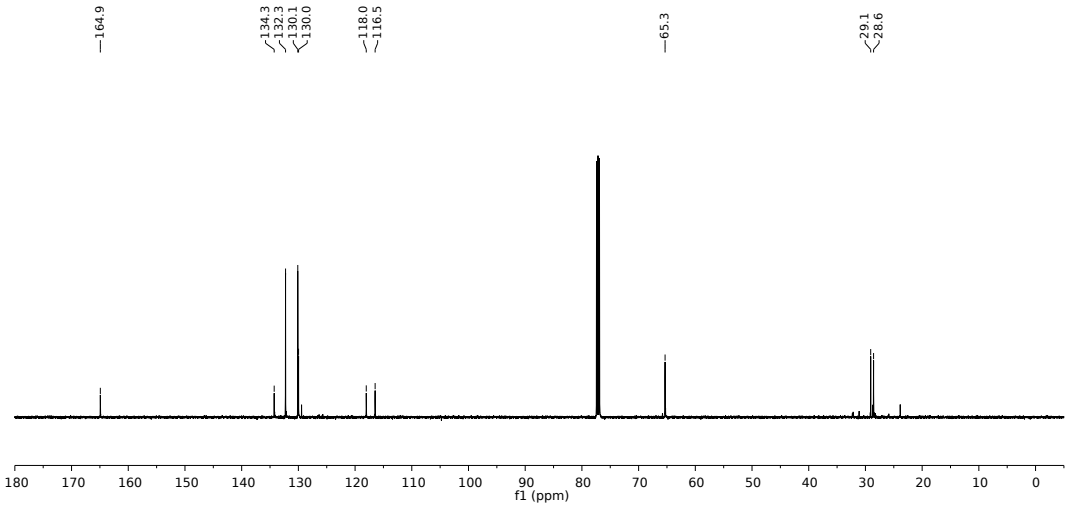

Transmittance [%]
Wavenumber cm-1

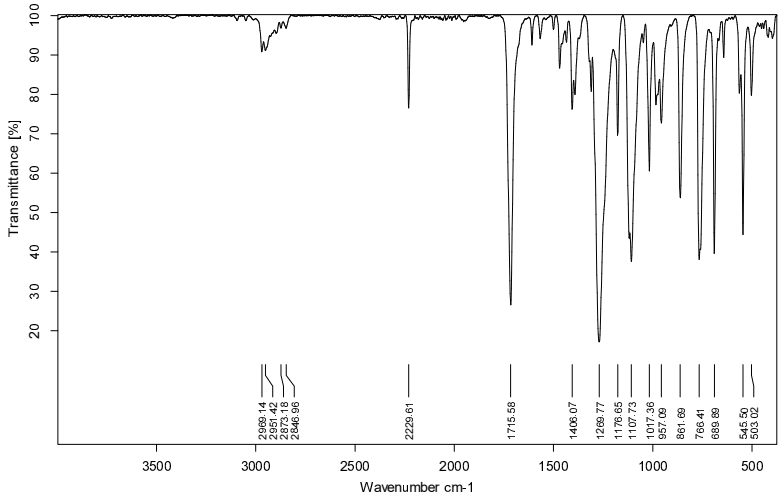

Br
O
O
O
O
Br
174c
7.89
2.00
4.40
7.90
f1 (ppm)

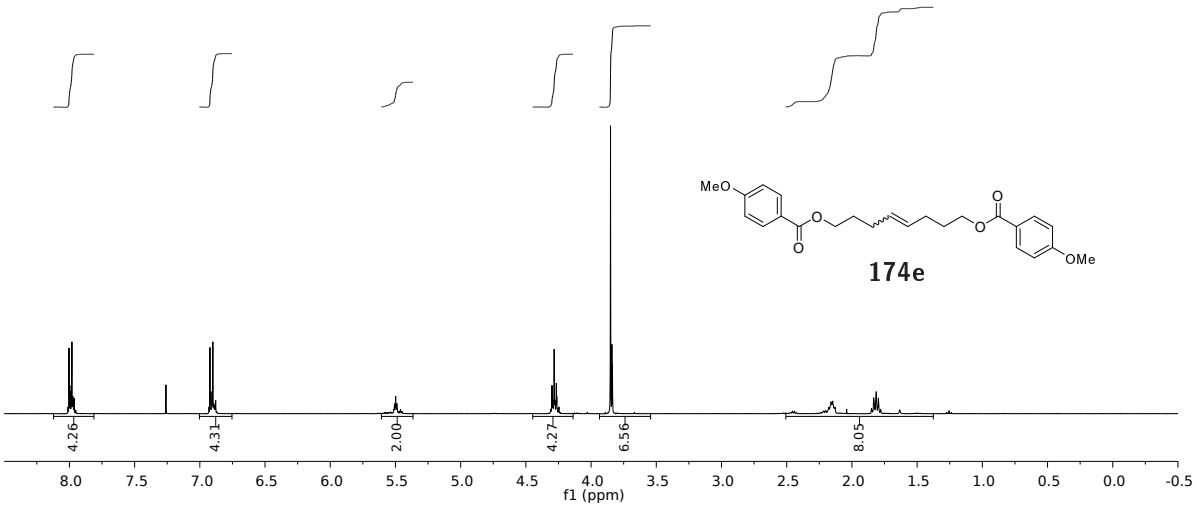

165.8
131.7
131.1
130.0
129.4
128.0
64.8
29.2
28.6
f1 (ppm)

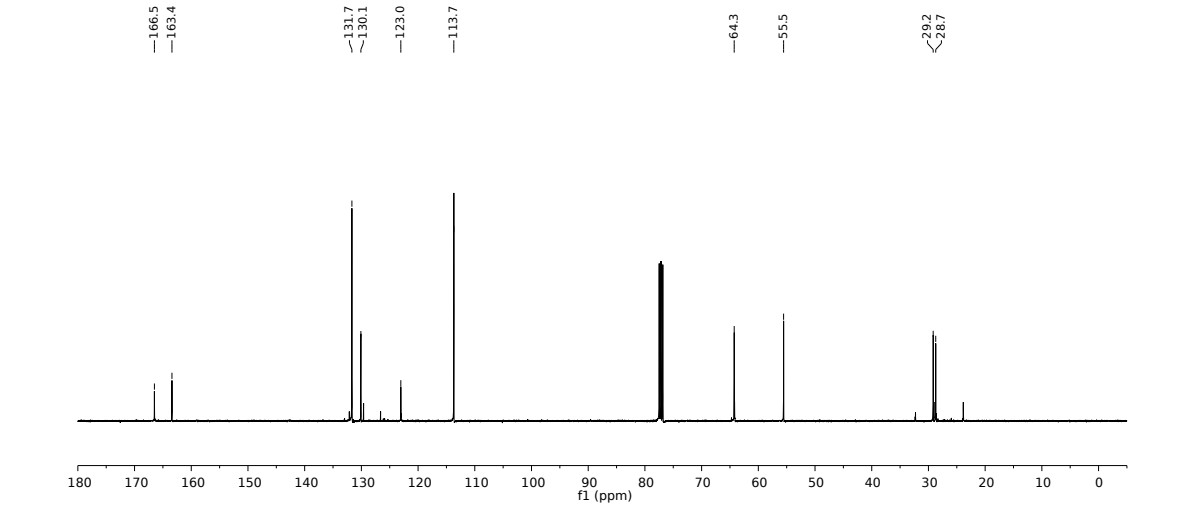

Transmittance [%]
2958.97
2935.43
2893.22
1713.72
1588.54
1471.70
1395.21
1267.22
1172.85
1102.15
1068.43
1008.30
963.48
847.93
751.15
707.95
681.82
468.81
Wavenumber cm-1

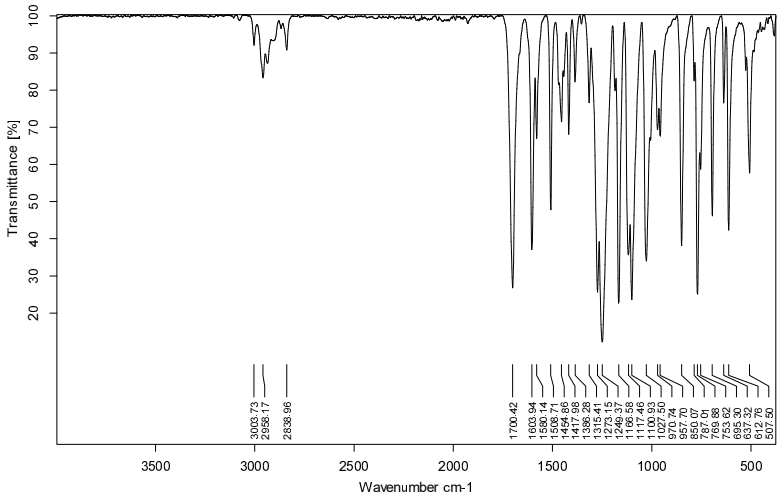

NC
O
O
O
O
CN
174d
3.70
3.56
2.17
4.00
4.19
3.40
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

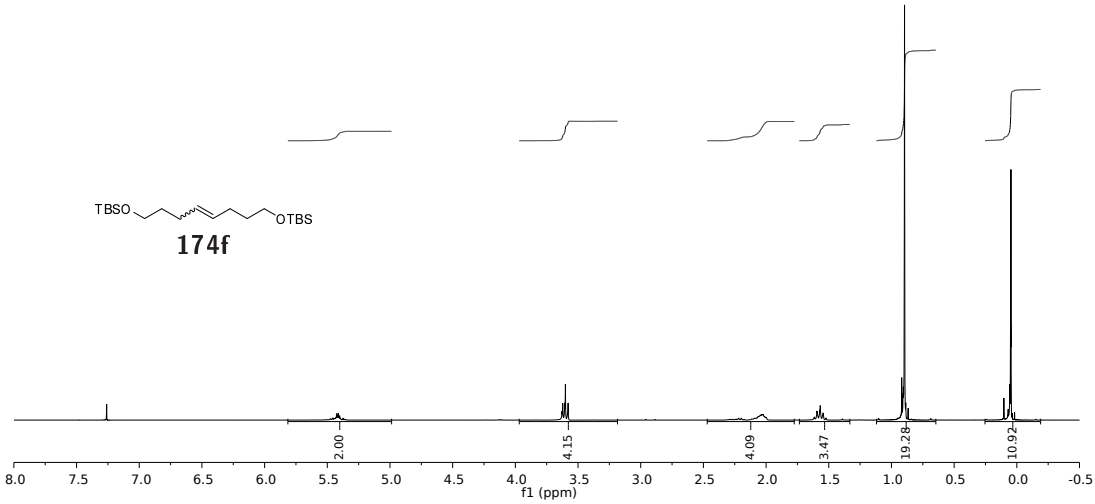

164.9
134.3
132.3
130.1
130.0
118.0
116.5
65.3
29.1
28.6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

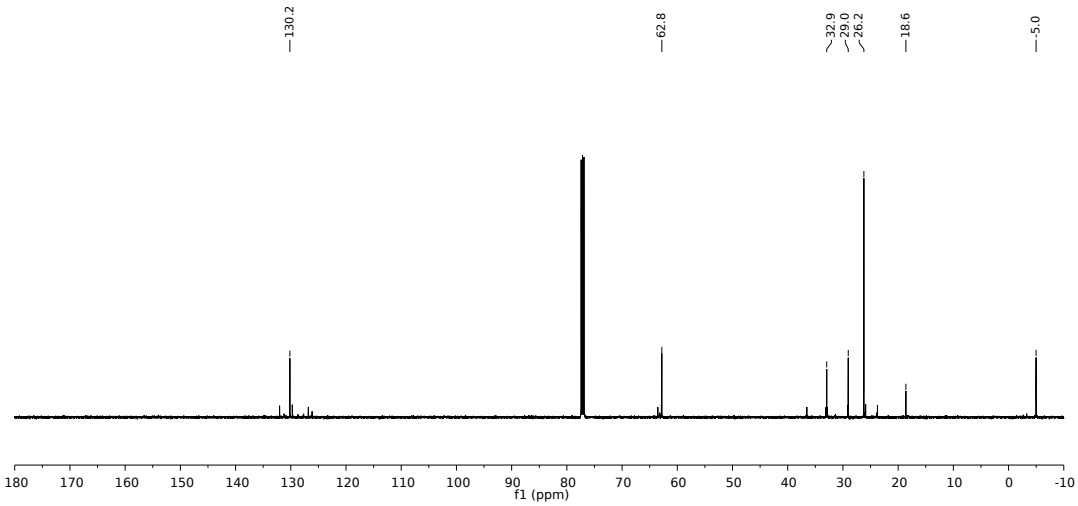

Transmittance [%]
100 90 80 70 60 50 40 30 20
2969.14
2951.42
2873.18
2846.96
2229.61
1715.58
1406.07
1269.77
1176.65
1107.73
1017.36
957.09
861.69
768.41
688.89
545.50
503.02
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

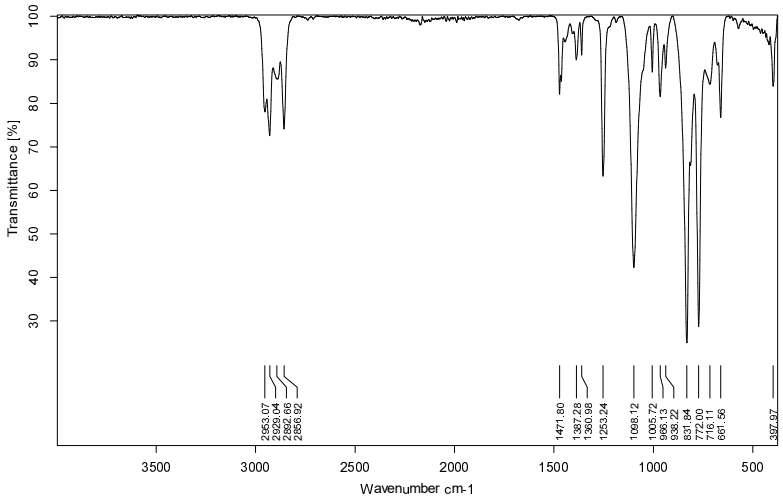

MeO
O
O
O
O
OMe
174e
4.26
4.31
2.00
4.27
6.56
8.05
f1 (ppm)

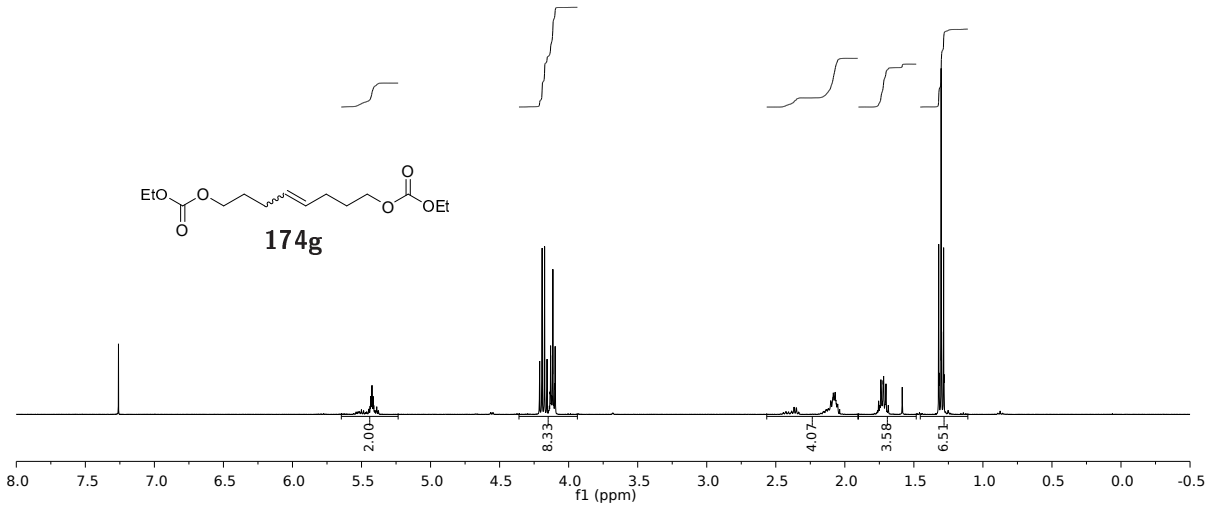

166.5
163.4
131.7
130.1
123.0
113.7
64.3
55.5
29.2
28.7
f1 (ppm)

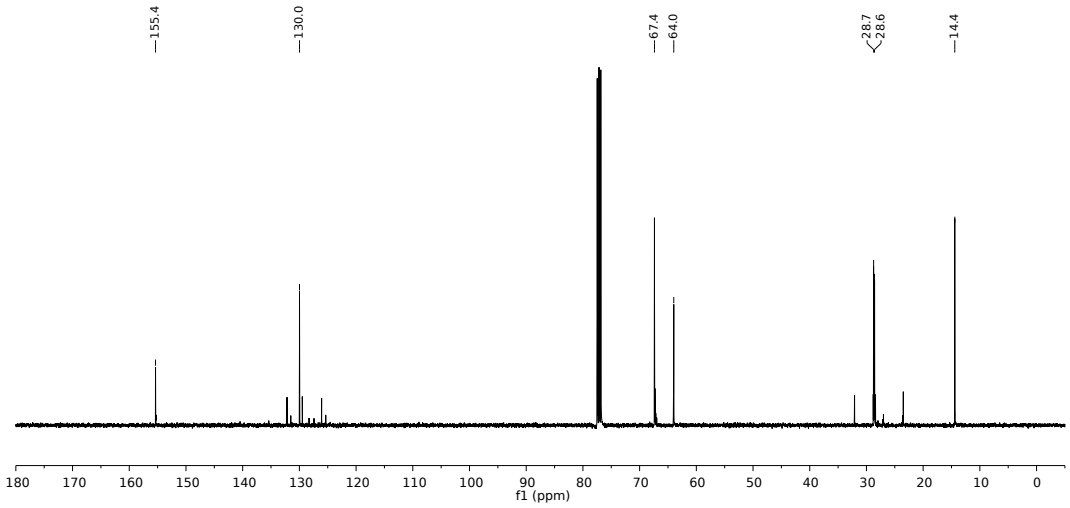

Transmittance [%]
3003.73
2938.17
2838.96
1700.42
1603.94
1580.14
1508.71
1454.66
1447.28
1396.20
1315.41
1273.15
1249.37
1176.68
1117.46
1100.93
1027.50
957.70
850.07
787.01
766.88
753.62
695.30
637.32
612.76
587.50
Wavenumber cm-1

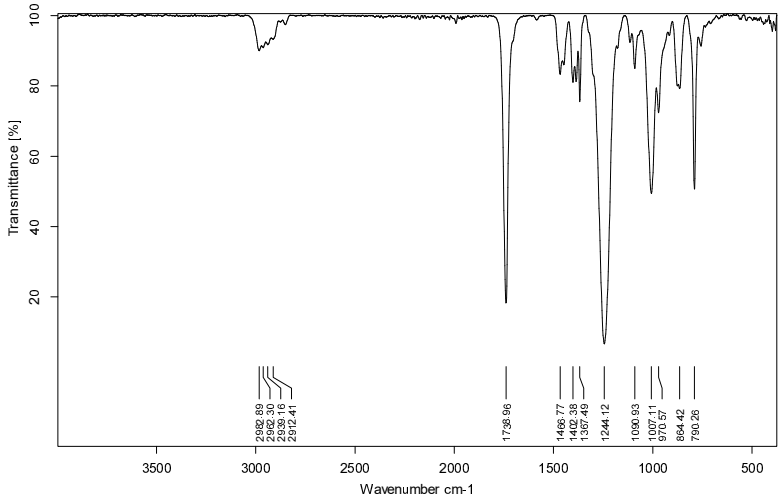

TBSO
OTBS
174f
2.00
4.15
4.09
3.47
19.28
10.92
f1 (ppm)

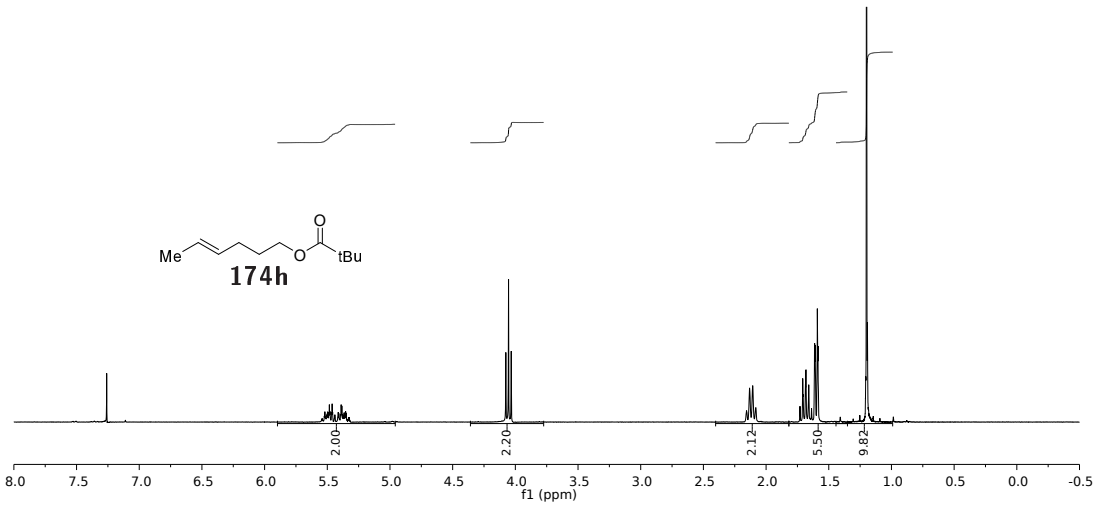

130.2
62.8
32.9
29.0
26.2
18.6
-5.0
f1 (ppm)

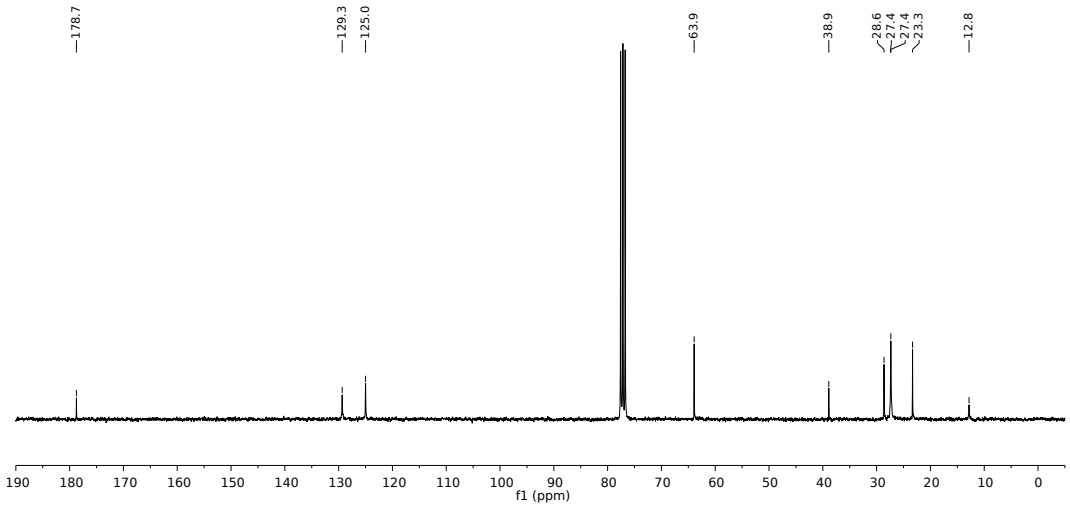

Transmittance [%]
2953.07
2929.04
2892.66
2856.92
1471.80
1387.28
1360.68
1253.24
1008.12
1005.72
966.13
938.22
857.64
772.00
716.11
661.56
397.97
Wavenumber cm-1

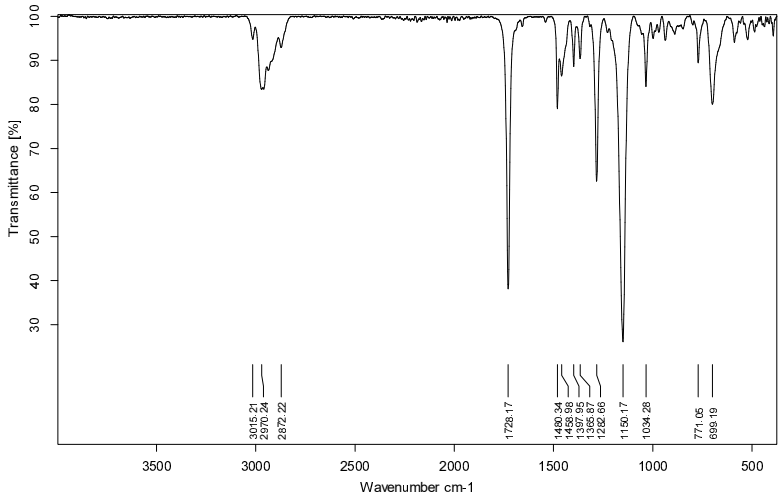

EtO
O
O
O
O
OEt
174g
2.00
8.33
4.07
3.58
6.51
f1 (ppm)

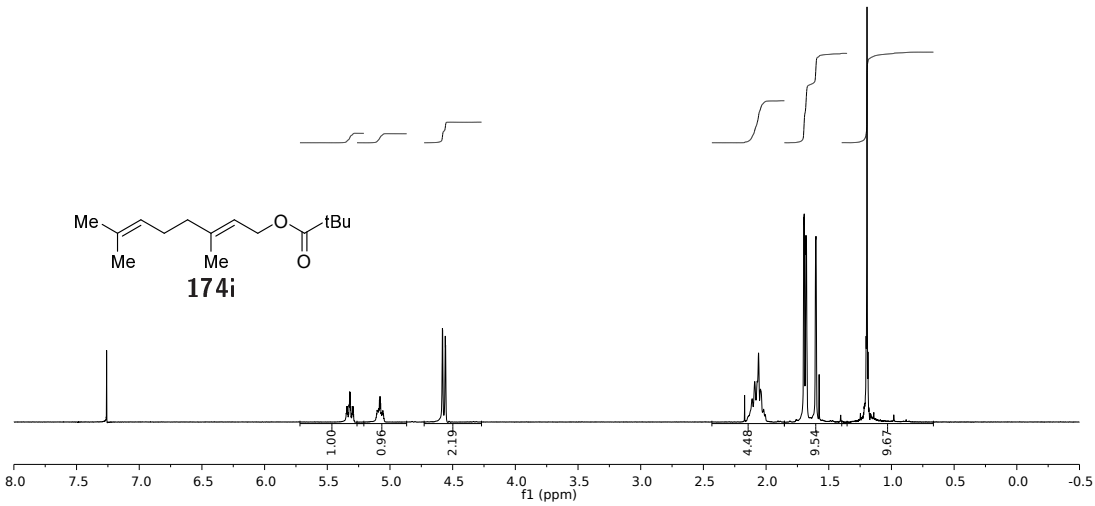

155.4
130.0
67.4
64.0
28.7
28.6
14.4
f1 (ppm)

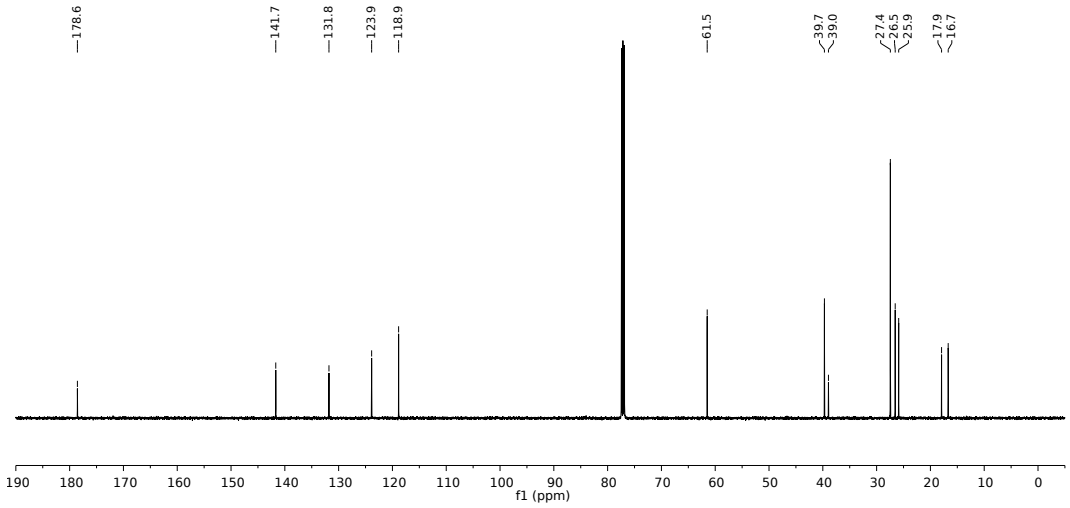

Transmittance [%]
2982.89
2932.30
2908.15
2912.41
1738.96
1466.77
1402.38
1367.49
1244.12
1090.93
1007.11
970.57
864.42
790.26
Wavenumber cm-1

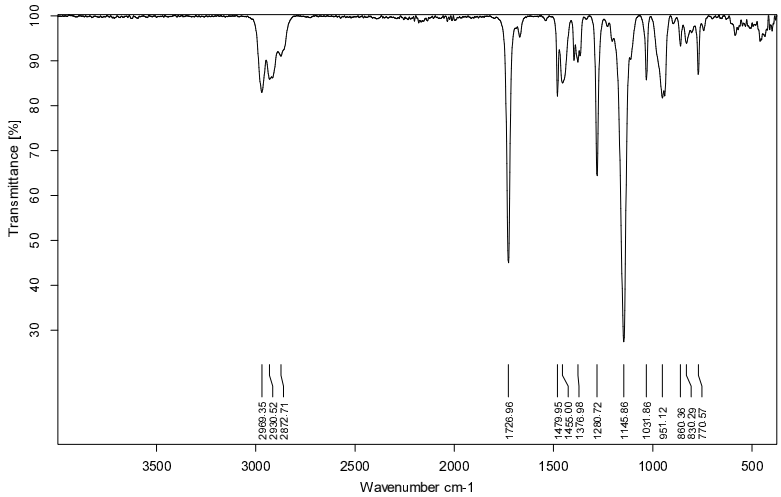

Me
O
O
tBu
174h
2.00
2.20
2.12
5.50
9.82
f1 (ppm)

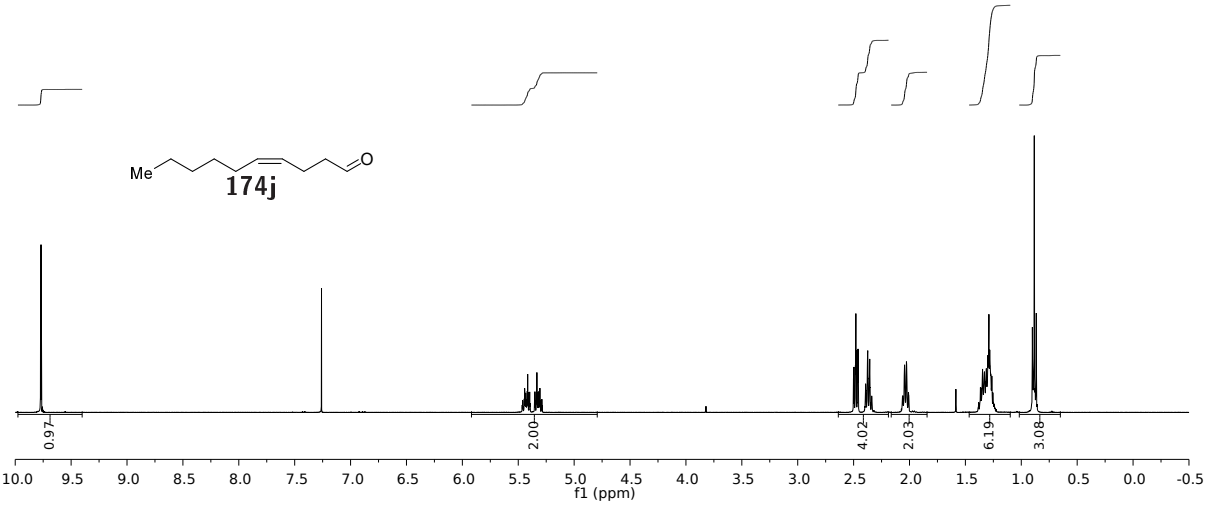

178.7
129.3
125.0
63.9
38.9
28.6
27.4
27.4
23.3
12.8
f1 (ppm)

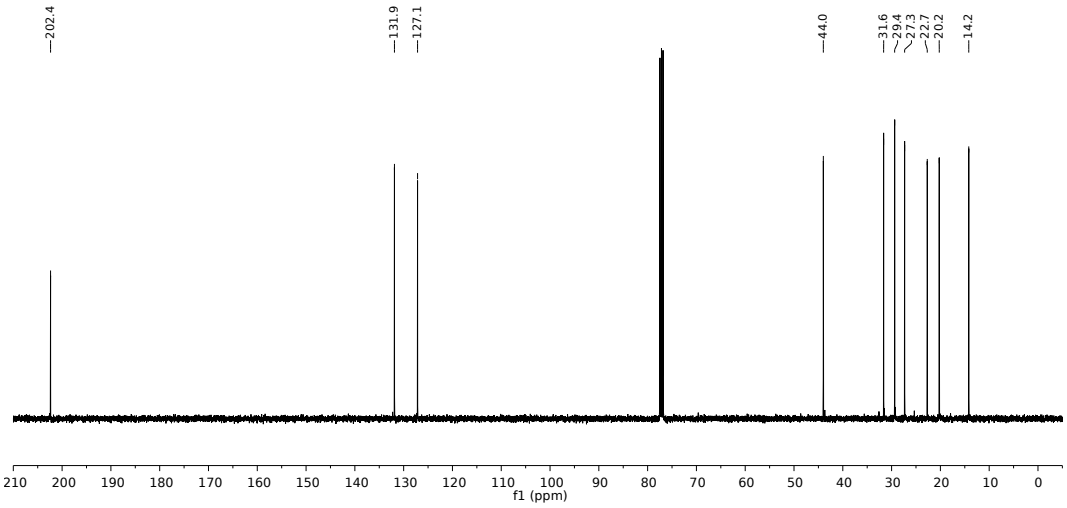

Transmittance [%]
3015.21
2970.24
2872.22
1728.17
1490.34
1458.98
1397.95
1365.37
1282.66
1150.17
1034.28
771.05
699.19
Wavenumber cm-1

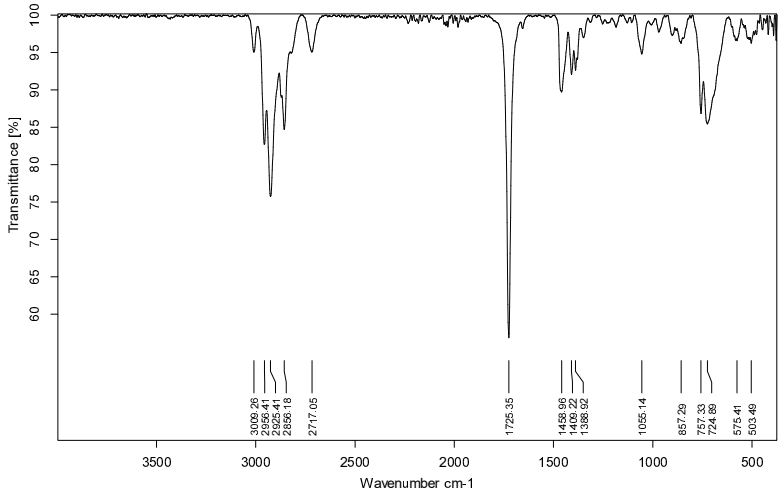

Me
Me
Me
O
O
tBu
174i
1.00
0.96
2.19
4.48
9.54
9.67
f1 (ppm)

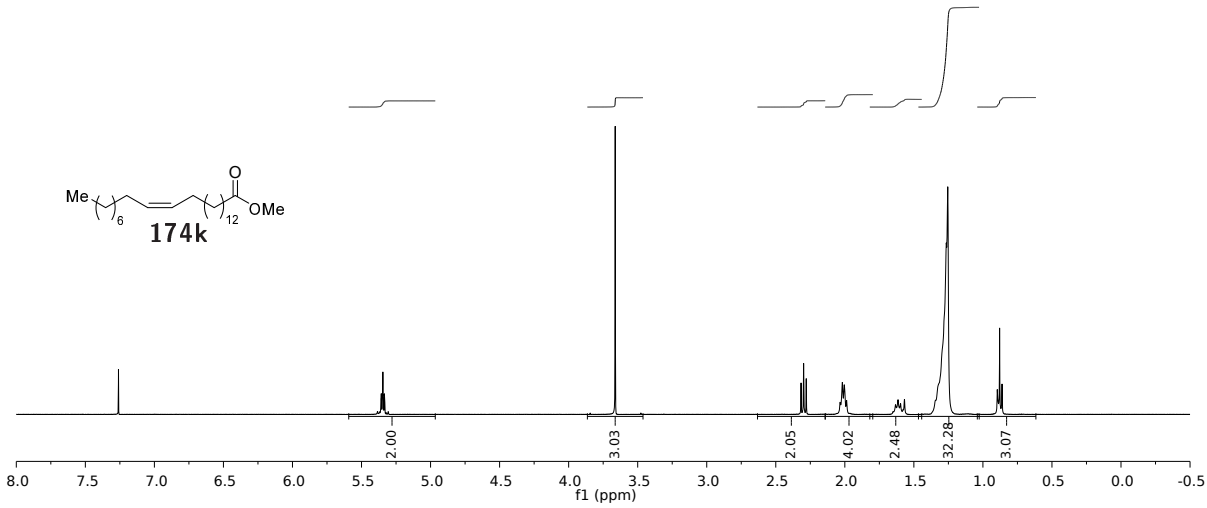

178.6
141.7
131.8
123.9
118.9
61.5
39.7
39.0
27.4
26.5
25.9
17.9
16.7
f1 (ppm)

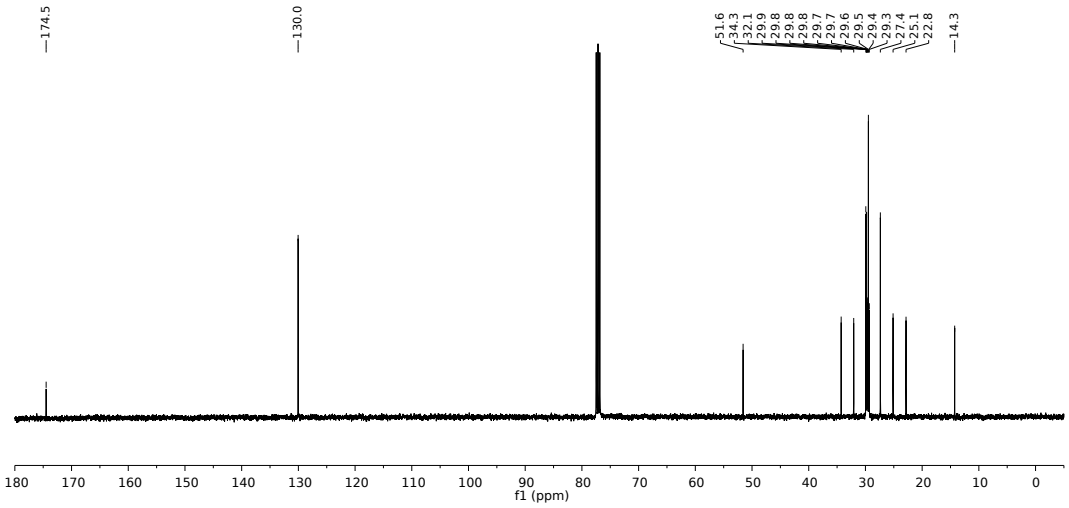

Transmittance [%]
2969.35
2930.52
2872.71
1726.96
1479.95
1455.00
1376.98
1280.72
1145.86
1031.86
951.12
860.36
830.29
770.57
Wavenumber cm-1

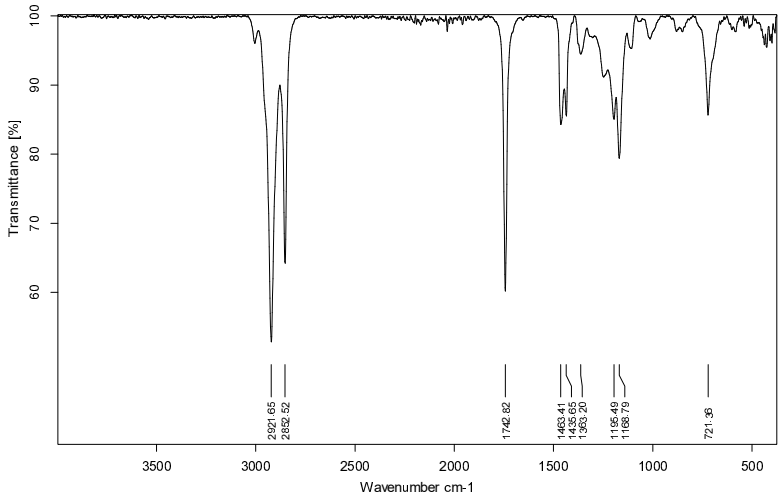

Me
O
174j
0.97
2.00
4.02
2.03
6.19
3.08
f1 (ppm)

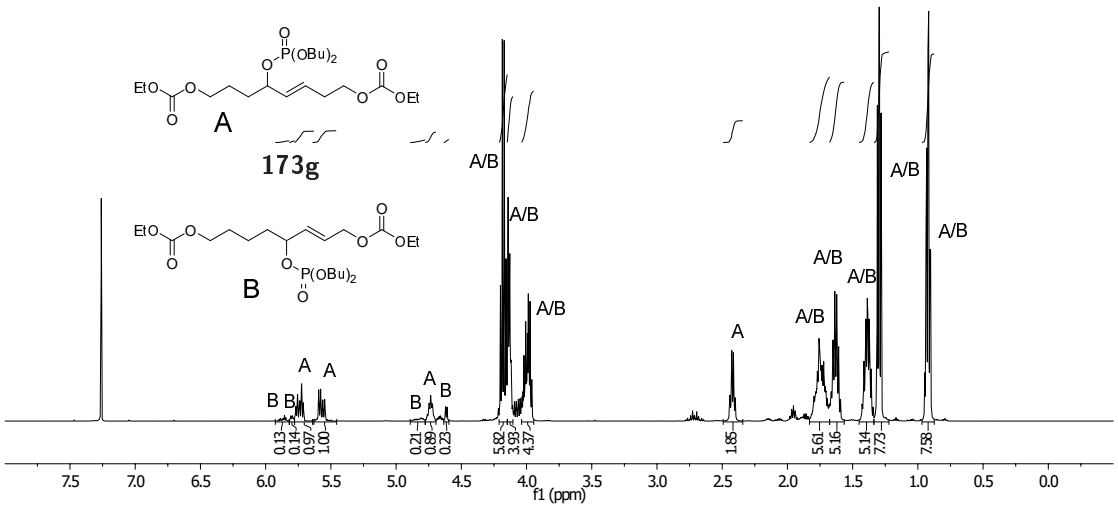

202.4
131.9
127.1
44.0
31.6
29.4
27.3
22.7
20.2
14.2
f1 (ppm)

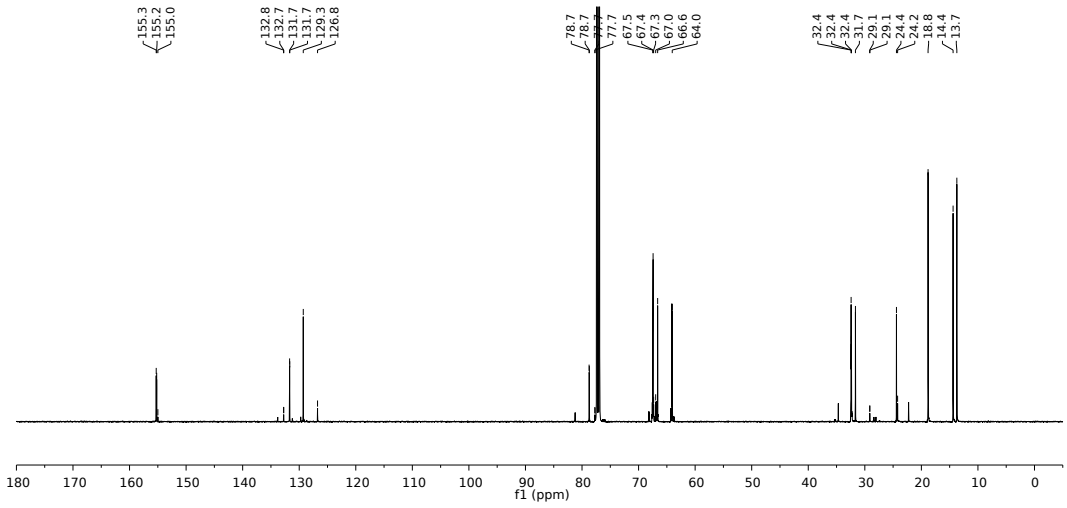

Transmittance [%]
3009.26
2956.41
2925.41
2856.18
2717.05
1725.35
1458.96
1409.22
1388.92
1055.14
857.29
757.33
724.89
575.41
503.49
Wavenumber cm-1

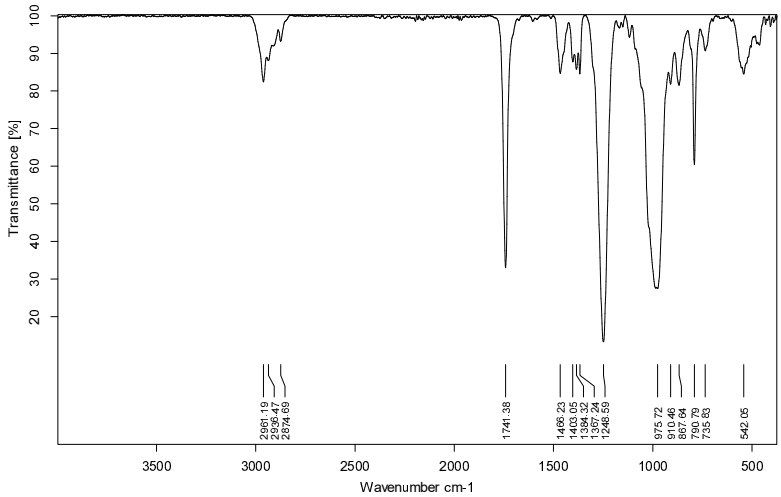

Me
6
12
OMe
O
174k
2.00
3.03
2.05
4.02
2.48
32.28
3.07
f1 (ppm)

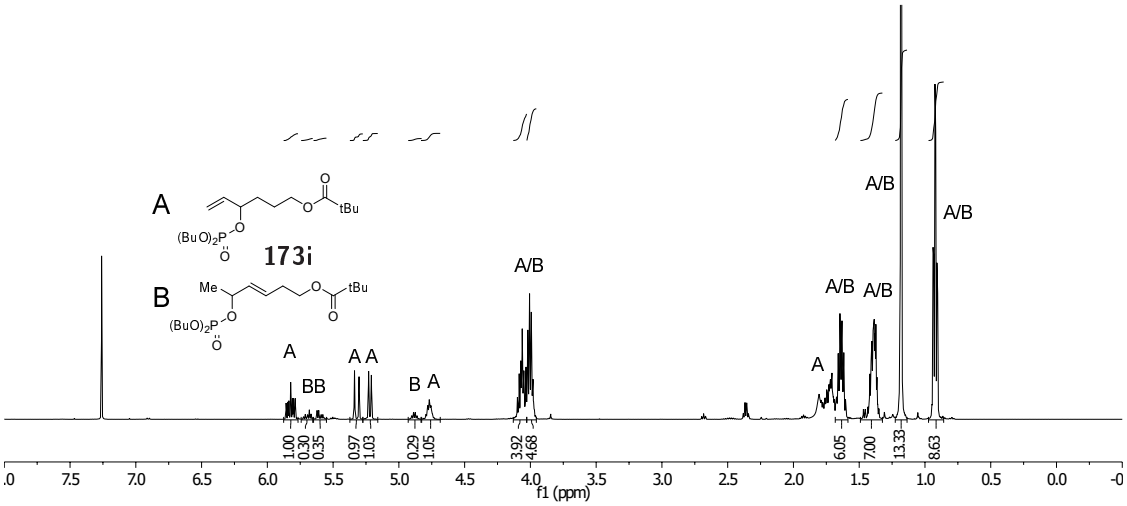

174.5
130.0
51.6
34.3
32.1
29.9
29.8
29.8
29.8
29.7
29.7
29.6
29.5
29.4
29.3
27.4
25.1
22.8
14.3
f1 (ppm)

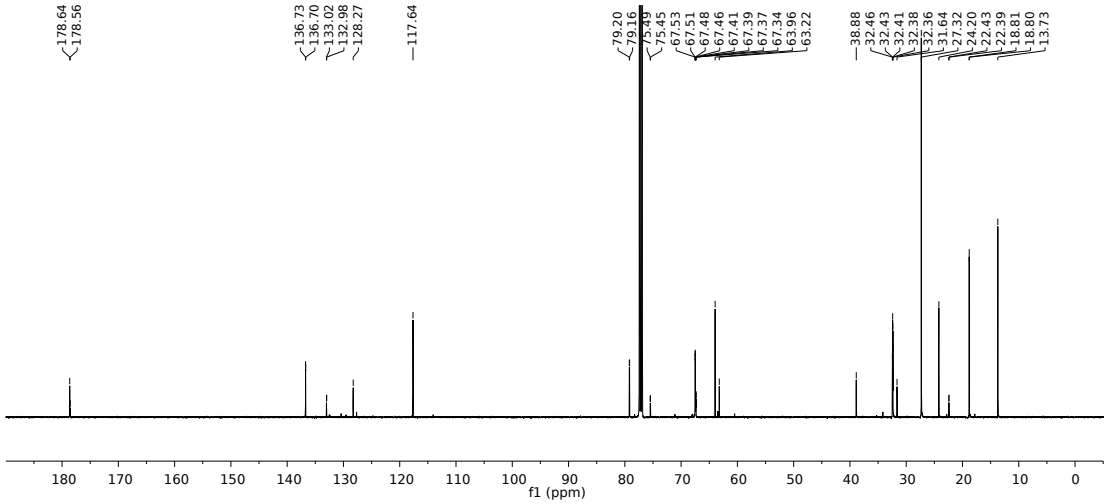

Transmittance [%]
2921.65
2852.52
1742.82
1463.41
1435.65
1393.20
1195.49
1168.79
721.35
Wavenumber cm-1

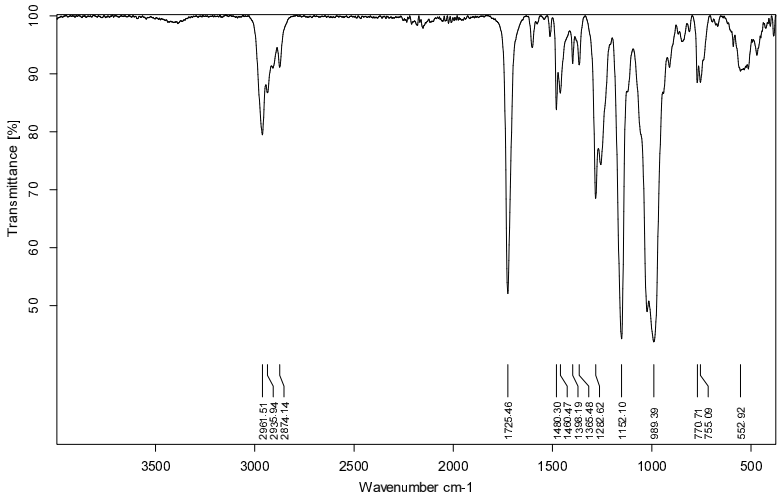

A
173g
B
A/B
f1 (ppm)

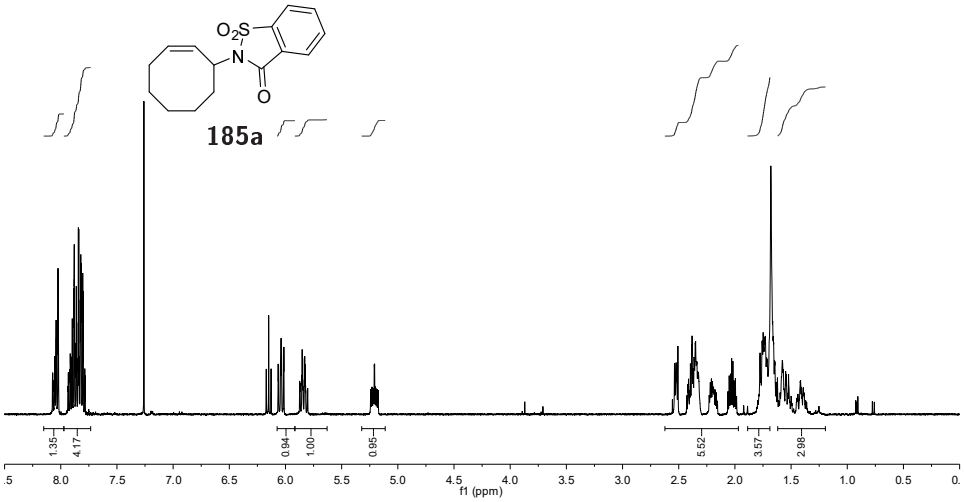

f1 (ppm)

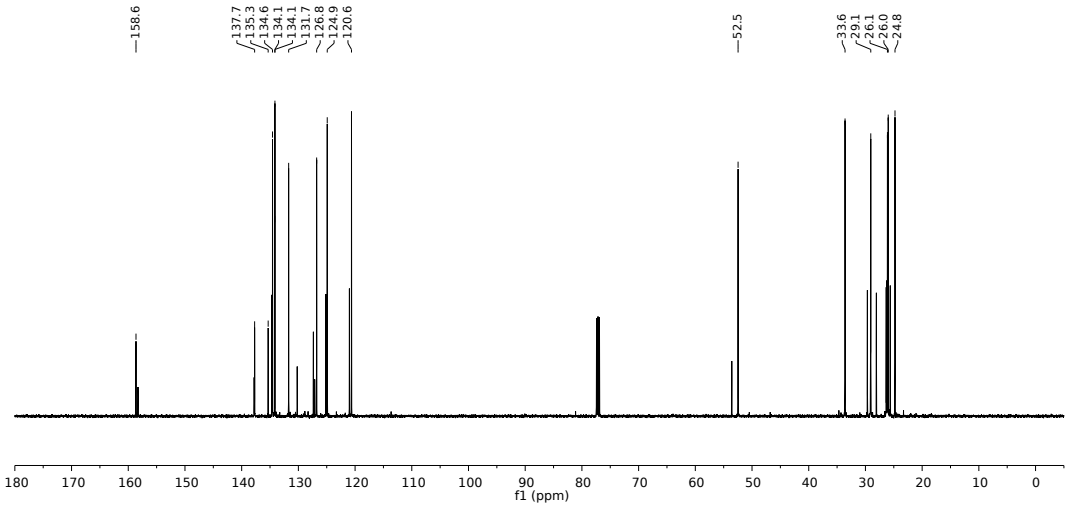

Transmittance [%]
Wavenumber cm-1

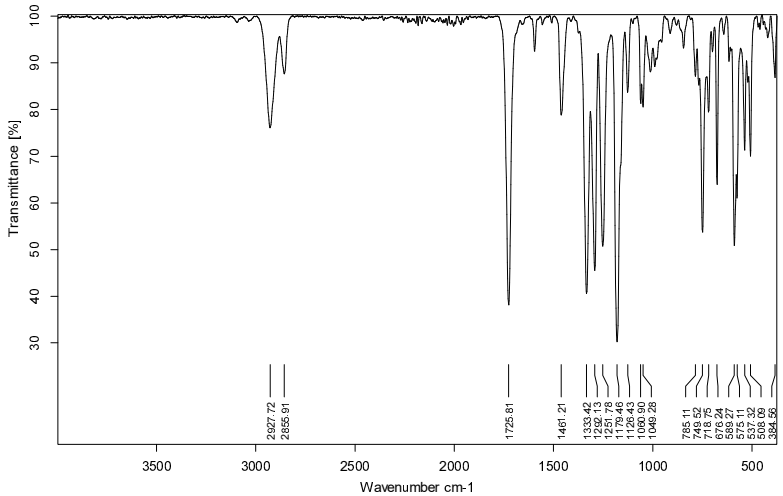

A
(BuO)2P
O
tBu
173i
B
Me
A
BB
A A
B A
A/B
A
A/B A/B
A/B
A/B
1.00
0.30
0.35
0.97
1.03
0.29
1.05
3.92
4.68
6.05
7.00
13.33
8.63
f1 (ppm)

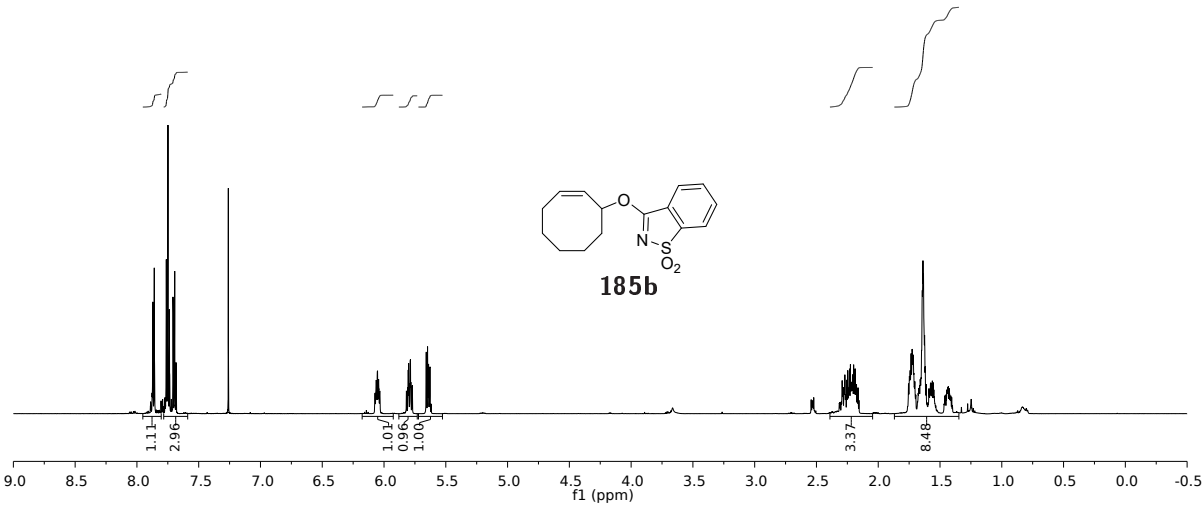

178.64
178.56
136.73
136.70
133.02
132.98
128.27
117.64
79.20
79.16
75.49
75.45
67.53
67.51
67.48
67.46
67.41
67.39
67.37
67.34
63.96
63.22
38.88
32.46
32.43
32.41
32.38
32.36
31.64
27.32
24.20
22.43
22.39
18.81
18.80
13.73
f1 (ppm)

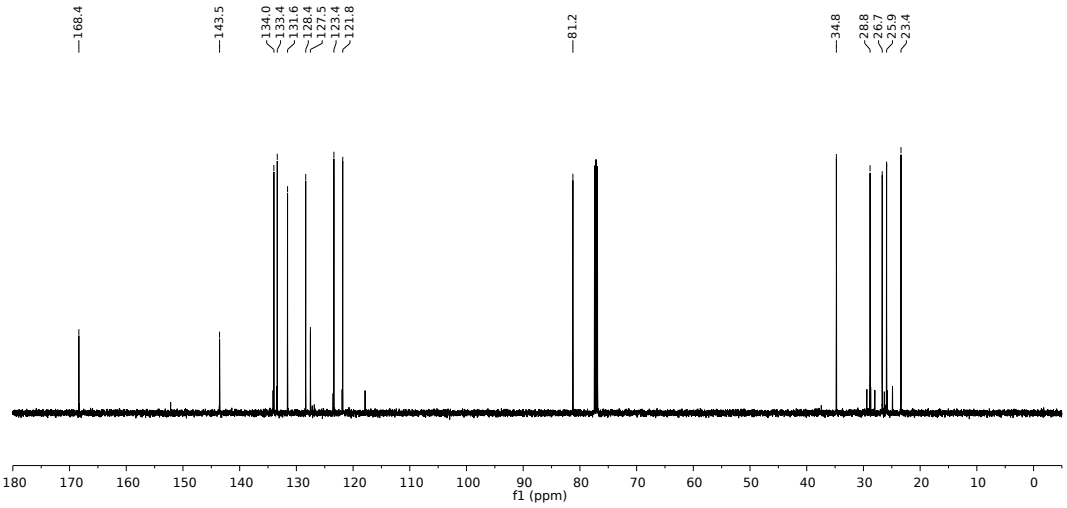

Transmittance [%]
2961.51
2935.84
2874.14
1725.46
1490.30
1460.47
1388.19
1365.48
1252.82
1152.10
989.39
770.71
755.09
552.92
Wavenumber cm-1

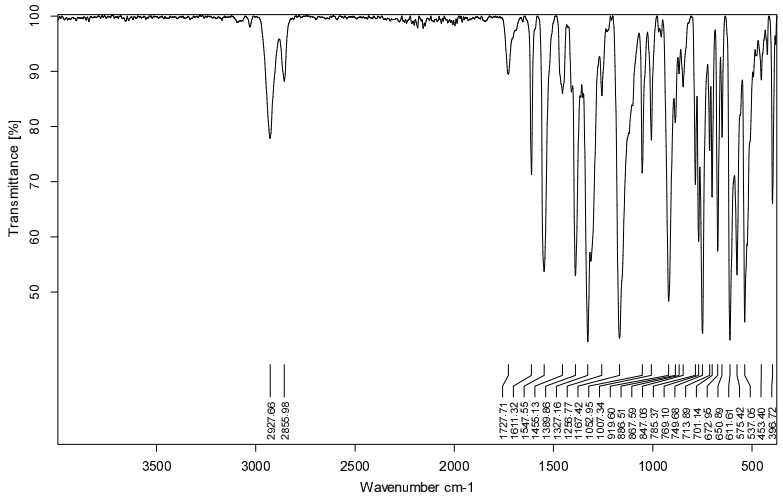

185a
1.35
4.17
0.94
1.00
0.95
5.62
3.57
2.98
f1 (ppm)

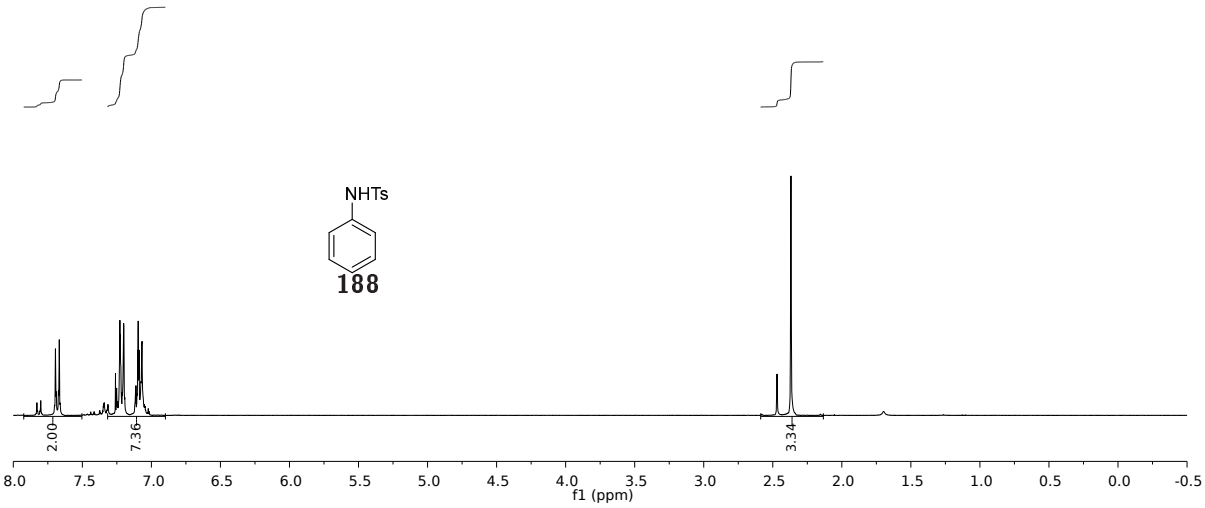

158.6
137.7
135.3
134.6
134.1
131.7
126.8
124.9
120.6
52.5
33.6
29.1
26.1
26.0
24.8
f1 (ppm)

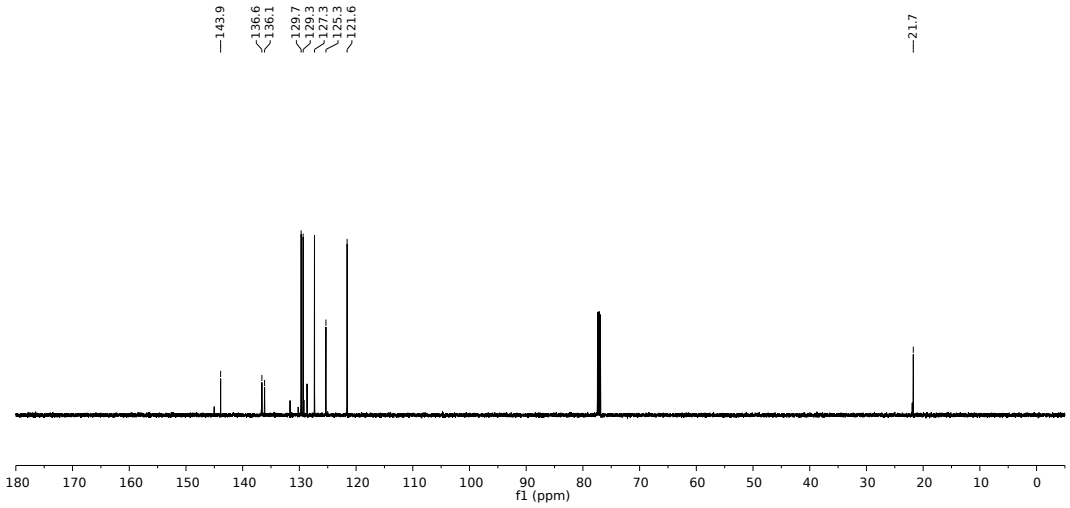

Transmittance [%]
2927.72
2855.91
1725.81
1461.21
1333.42
1292.13
1251.78
1178.46
1136.43
1060.90
1049.28
785.11
749.52
718.75
676.24
637.27
575.11
537.32
508.09
Wavenumber cm-1

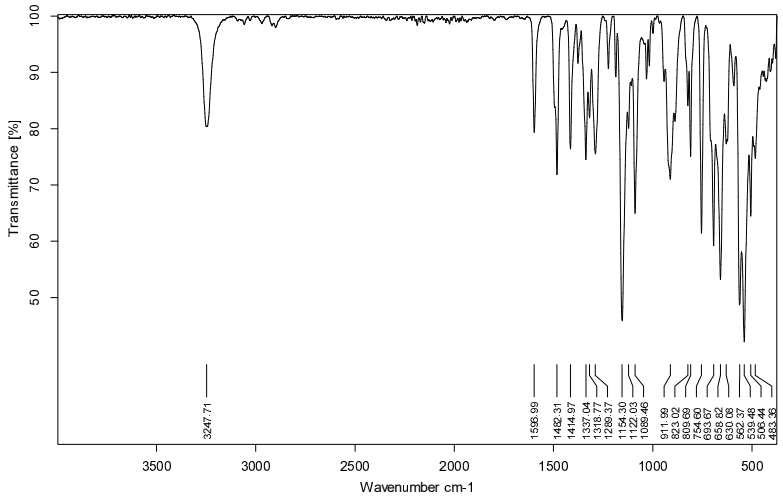

185b
1.11
2.96
1.01
0.96
1.00
3.37
8.48
f1 (ppm)

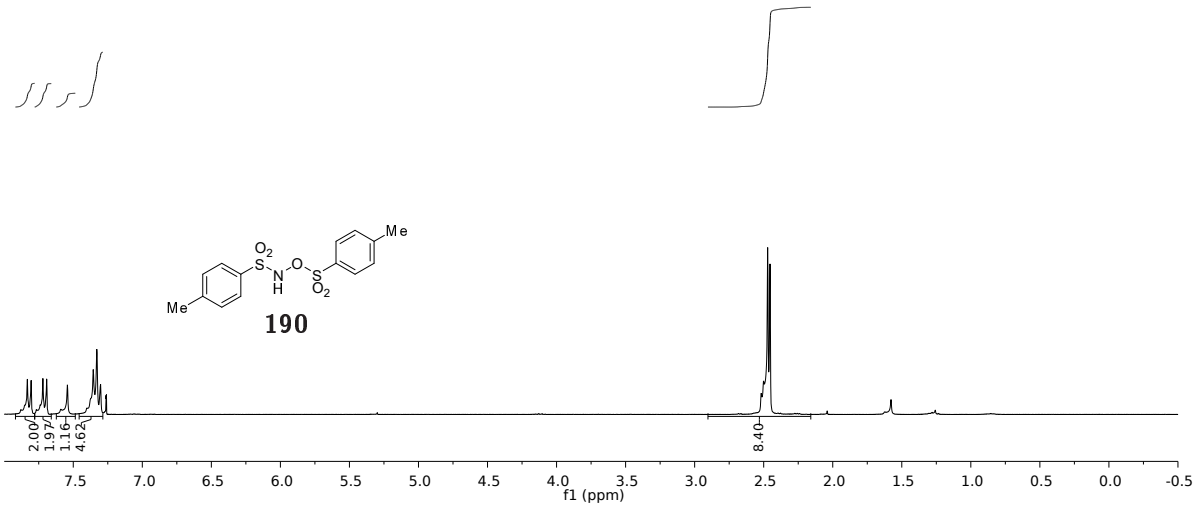

168.4
143.5
134.0
133.4
131.6
128.4
127.5
123.4
121.8
81.2
34.8
28.8
26.7
25.9
23.4
f1 (ppm)

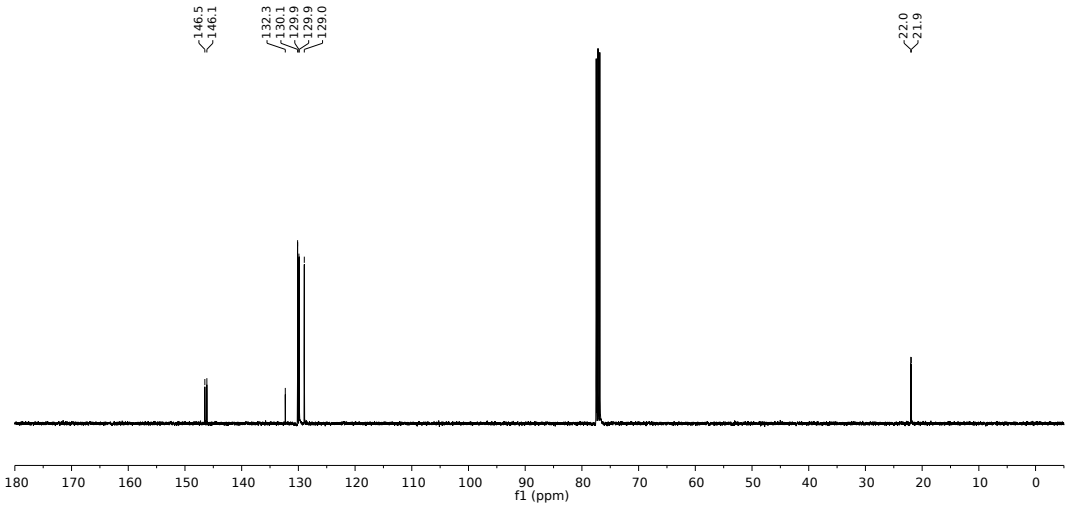

Transmittance [%]
2927.66
2855.98
Wavenumber cm-1

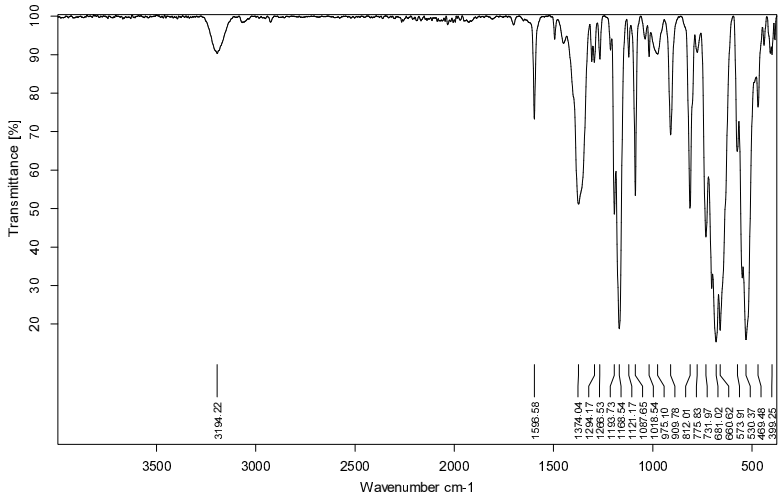

NHTs
188
2.00
7.36
3.34
f1 (ppm)

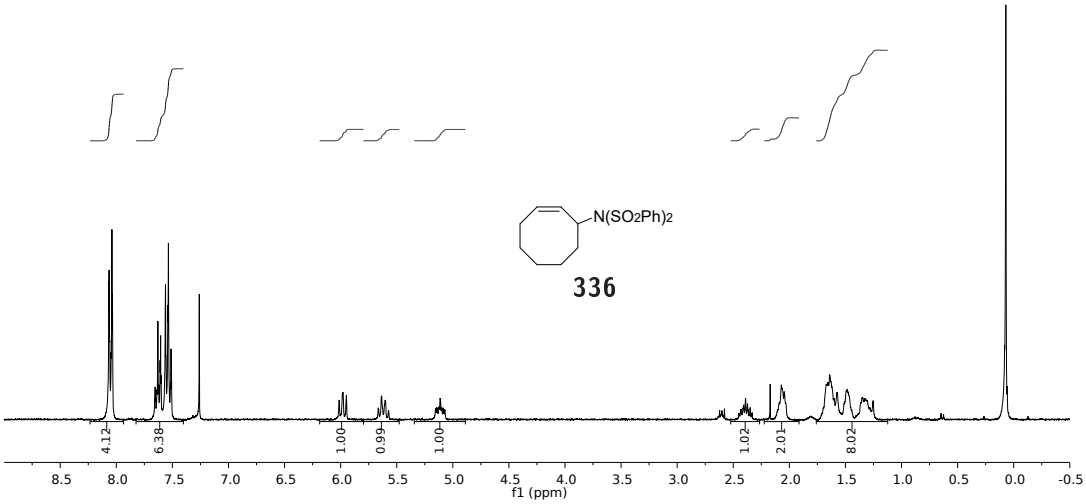

143.9
136.6
136.1
129.7
129.3
127.3
125.3
121.6
21.7
f1 (ppm)

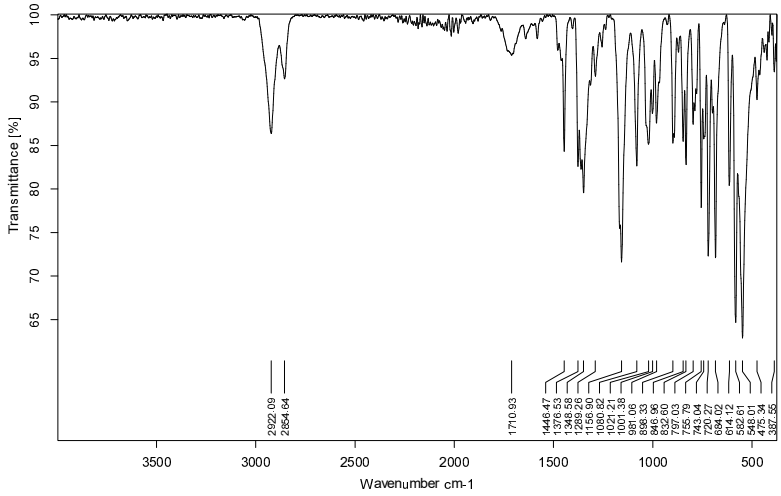

Transmittance [%]
3247.71
1586.99
1482.31
1414.97
1337.04
1318.77
1289.37
1154.30
1122.03
1088.46
911.99
823.02
800.69
754.60
693.67
658.82
640.08
562.37
539.48
508.44
483.33
Wavenumber cm-1

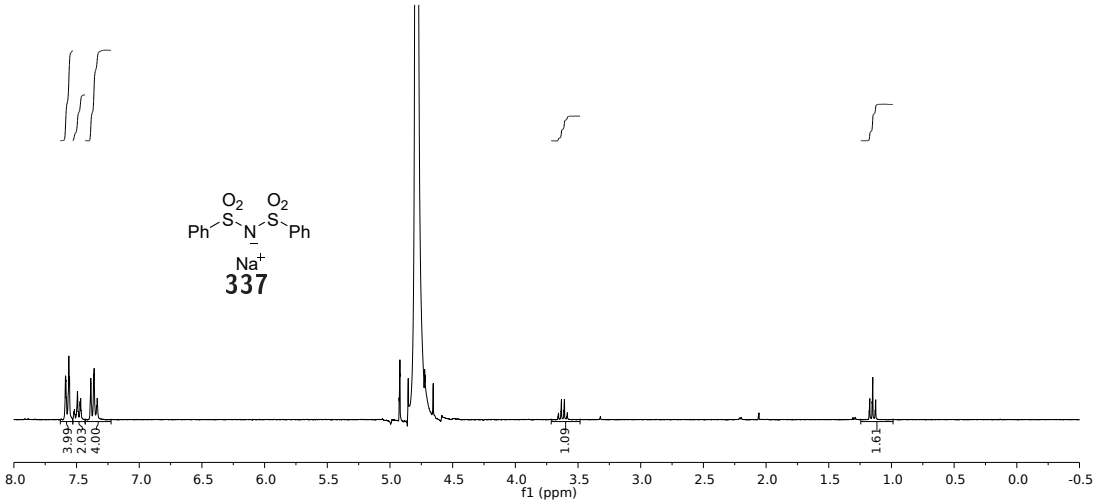

Me
O2
S
N
H
O
S
O2
Me
190
2.00
1.97
1.16
4.62
8.40
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

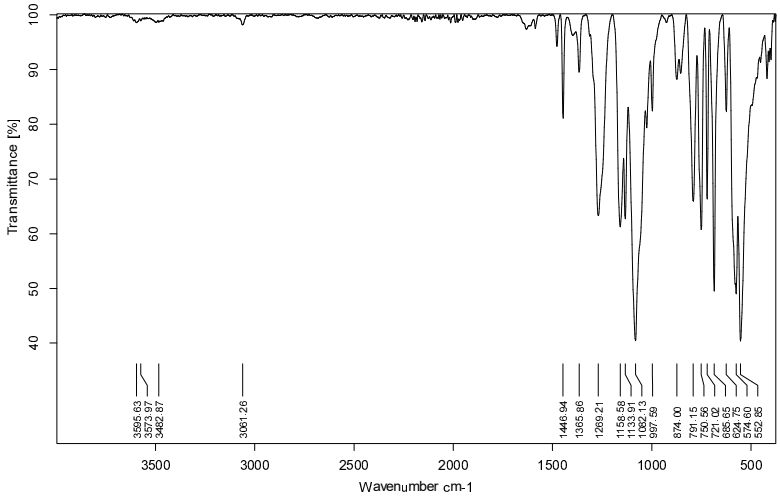

146.5
146.1
132.3
130.1
129.9
129.9
129.0
22.0
21.9
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

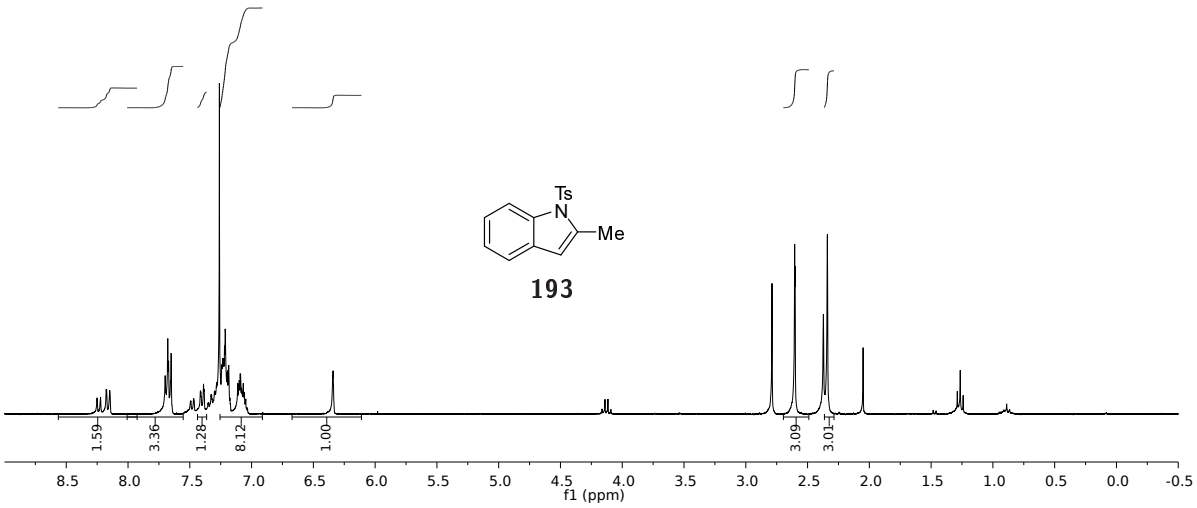

Transmittance [%]
100 90 80 70 60 50 40 30 20
3194.22
1586.58
1374.04
1234.77
1206.53
1193.73
1168.54
1157.17
1057.65
1018.54
975.10
909.78
872.01
775.83
731.97
681.02
660.62
573.97
530.37
468.48
393.25
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

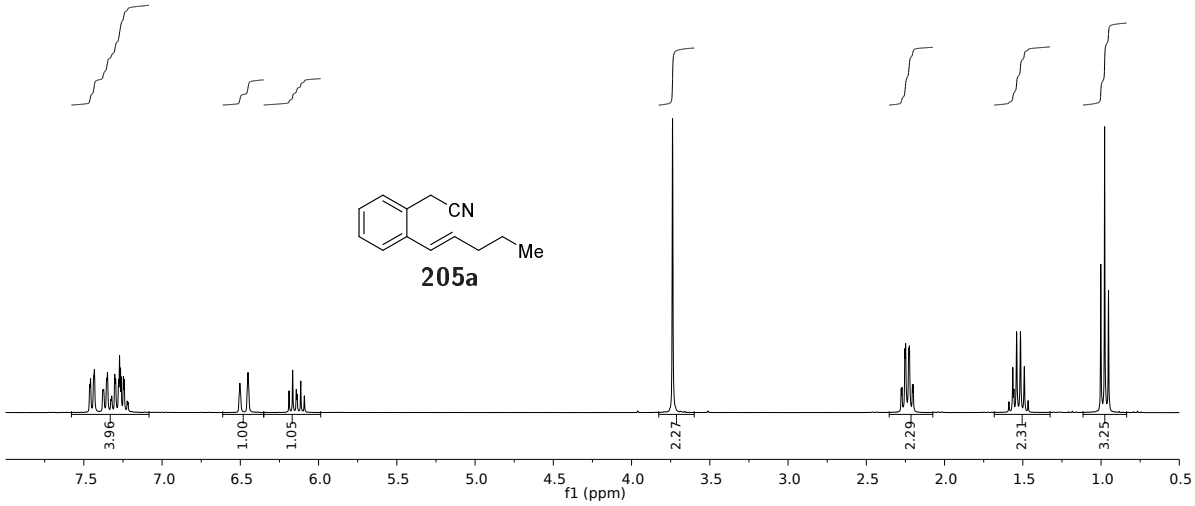

N(SO2Ph)2
336
4.12
6.38
1.00
0.99
1.00
1.02
2.01
8.02
f1 (ppm)

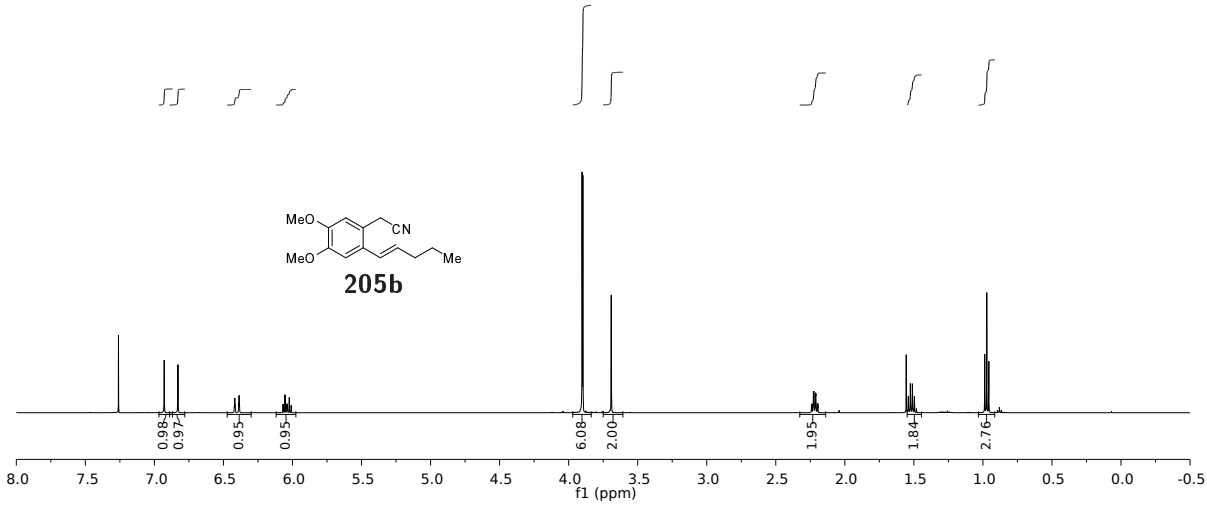

Transmittance [%]
Wavenumber cm-1
2922.09
2854.64
1710.93
1446.47
1376.53
1348.58
1289.26
1155.60
1080.82
1021.21
1001.38
898.53
846.96
832.60
797.03
755.79
743.04
720.27
694.02
654.42
582.61
548.01
475.34
387.85

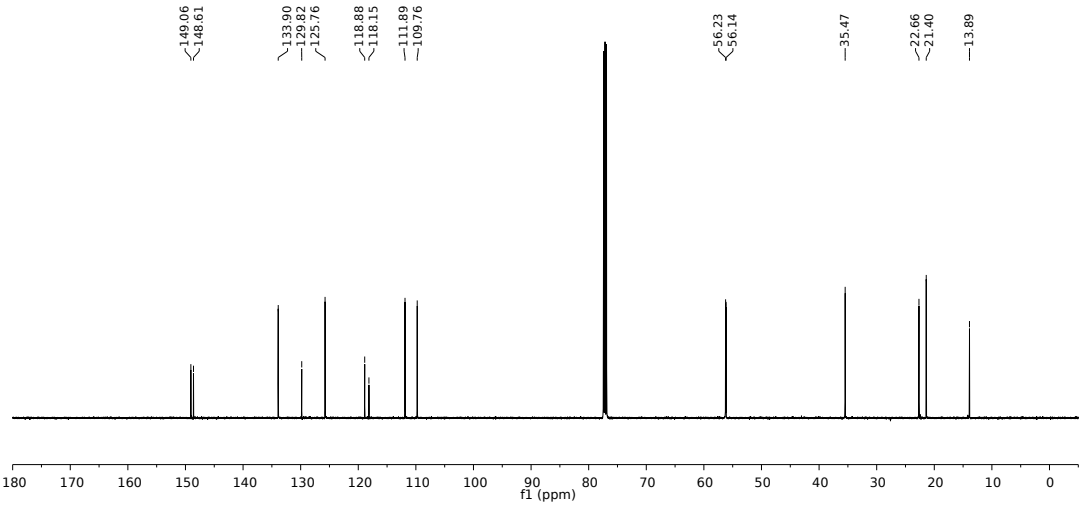

O2 O2
Ph S N S Ph
Na+
337
3.99
2.03
4.00
1.09
1.61
f1 (ppm)

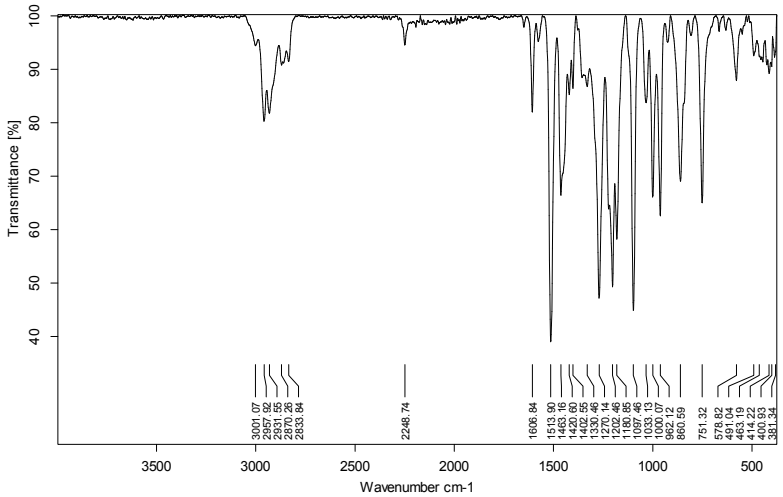

Transmittance [%]
3595.63
3573.97
3482.87
3061.26
1446.94
1365.86
1269.21
1158.58
1131.15
1082.13
997.59
874.00
791.15
750.56
727.51
685.05
624.75
574.60
552.85
Wavenumber cm-1

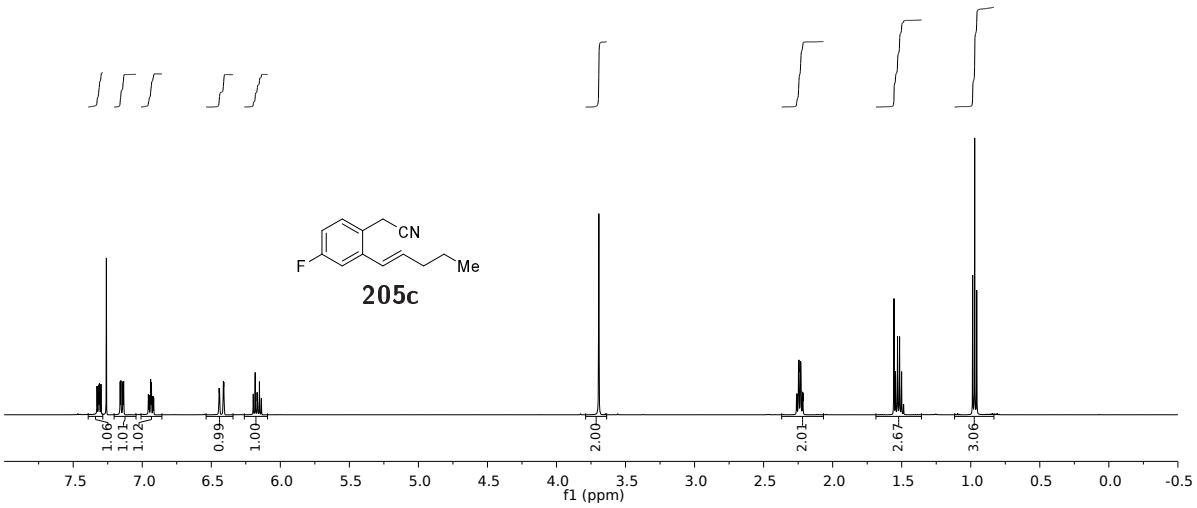

Ts
N
Me
193
1.59
3.36
1.28
8.12
1.00
3.09
3.01
f1 (ppm)

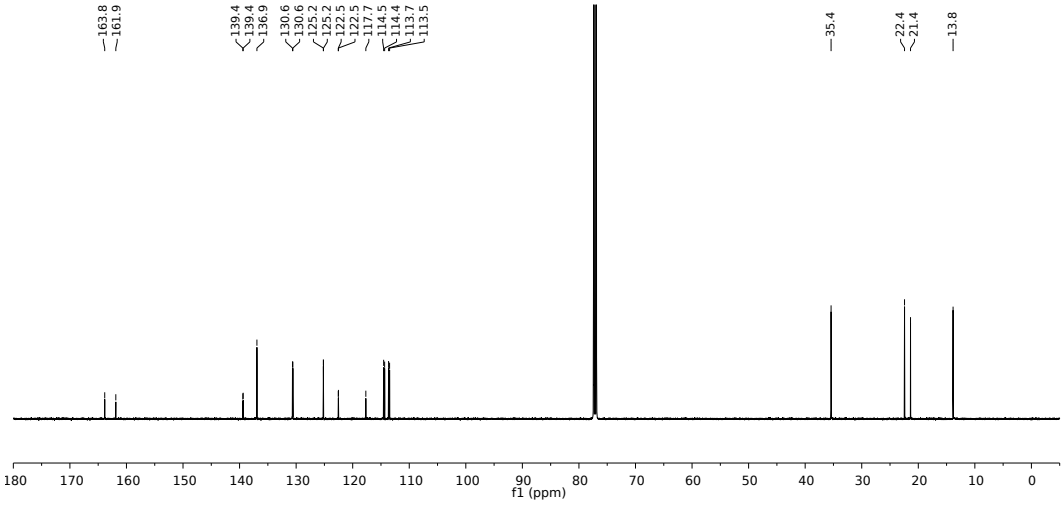

CN
Me
205a
3.96
1.00
1.05
2.27
2.29
2.31
3.25
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

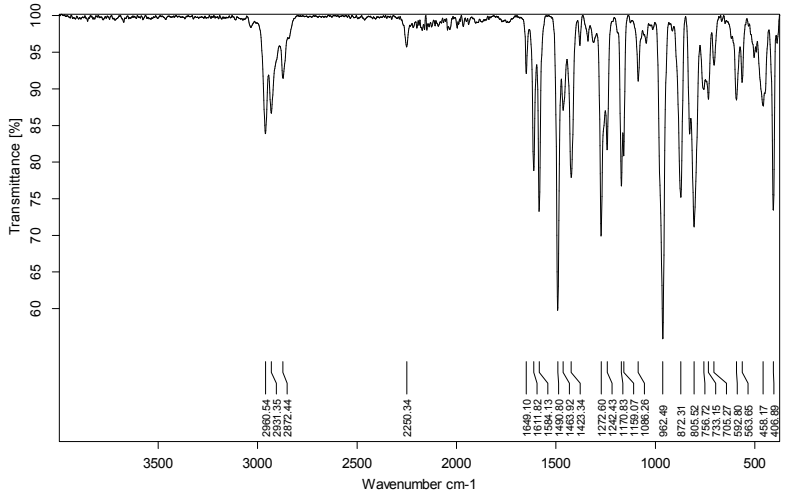

MeO
MeO
CN
Me
205b
0.98
0.97
0.95
0.95
6.08
2.00
1.95
1.84
2.76
f1 (ppm)

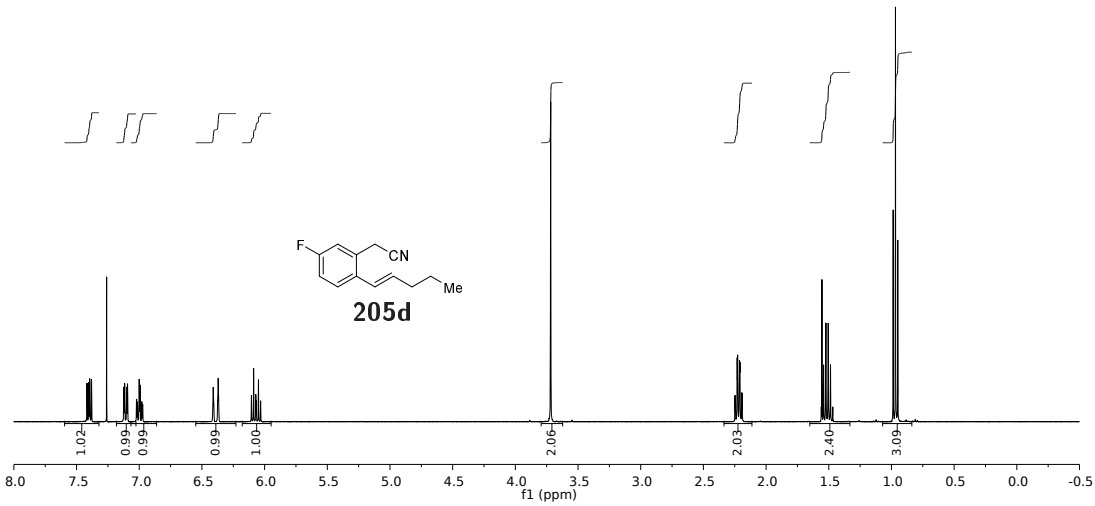

149.06
148.61
133.90
129.82
125.76
118.88
118.15
111.89
109.76
56.23
56.14
35.47
22.66
21.40
13.89
f1 (ppm)

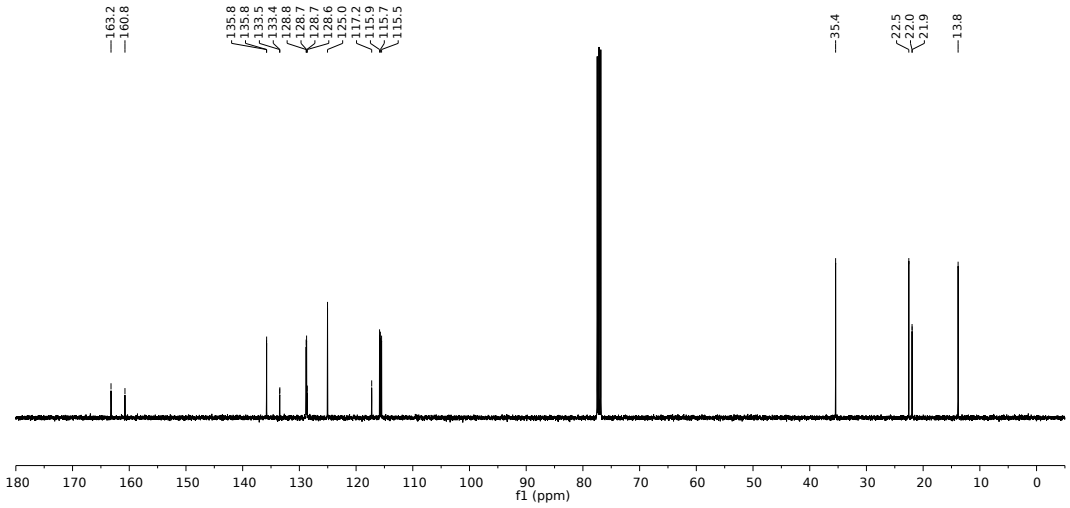

Transmittance [%]
3001.07
2957.92
2931.55
2870.26
2833.84
2248.74
1606.84
1513.90
1463.15
1420.60
1402.55
1330.46
1270.14
1222.46
1180.85
1097.46
1033.13
1000.07
962.12
860.59
751.32
578.82
540.04
463.19
414.22
400.93
381.34
Wavenumber cm-1

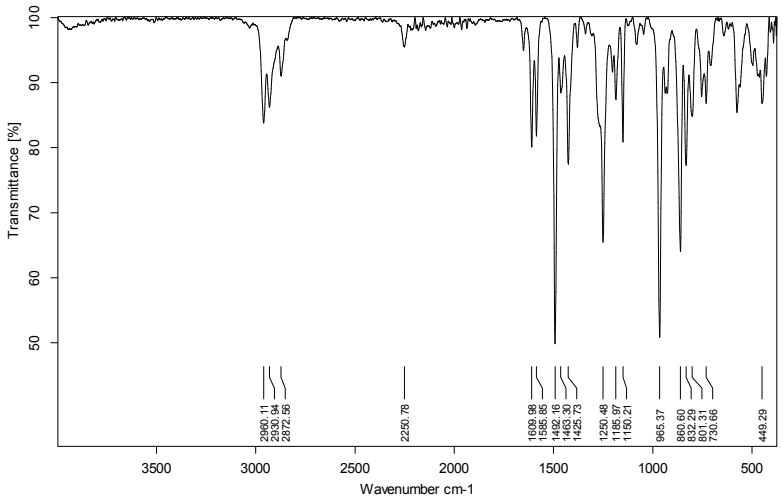

CN
F
Me
205c
1.06
1.01
1.02
0.99
1.00
2.00
2.01
2.67
3.06
f1 (ppm)

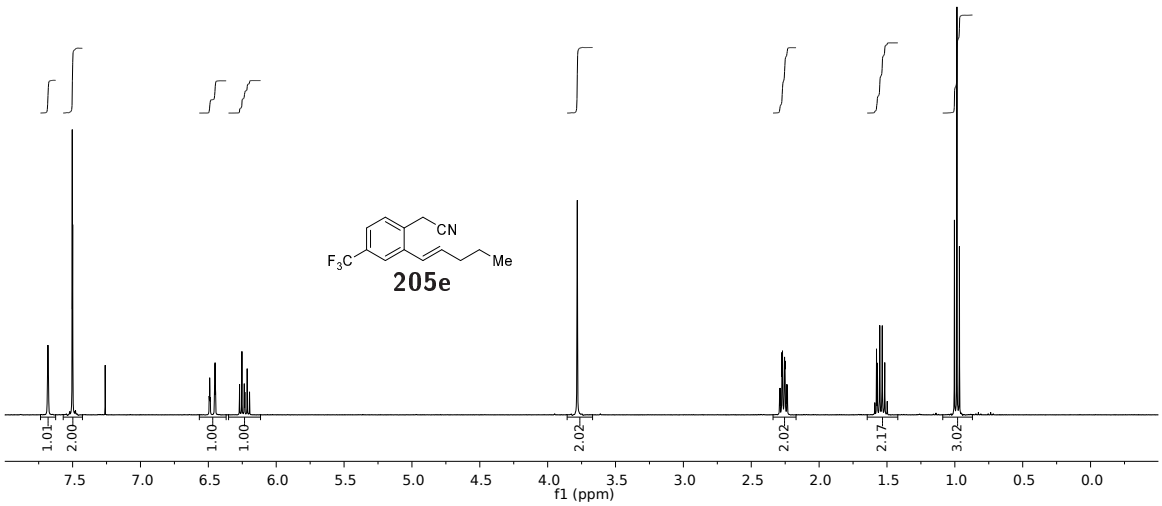

163.8
161.9
139.4
139.4
136.9
130.6
130.6
125.2
122.5
122.5
117.7
114.5
114.4
113.7
113.5
35.4
22.4
21.4
13.8
f1 (ppm)

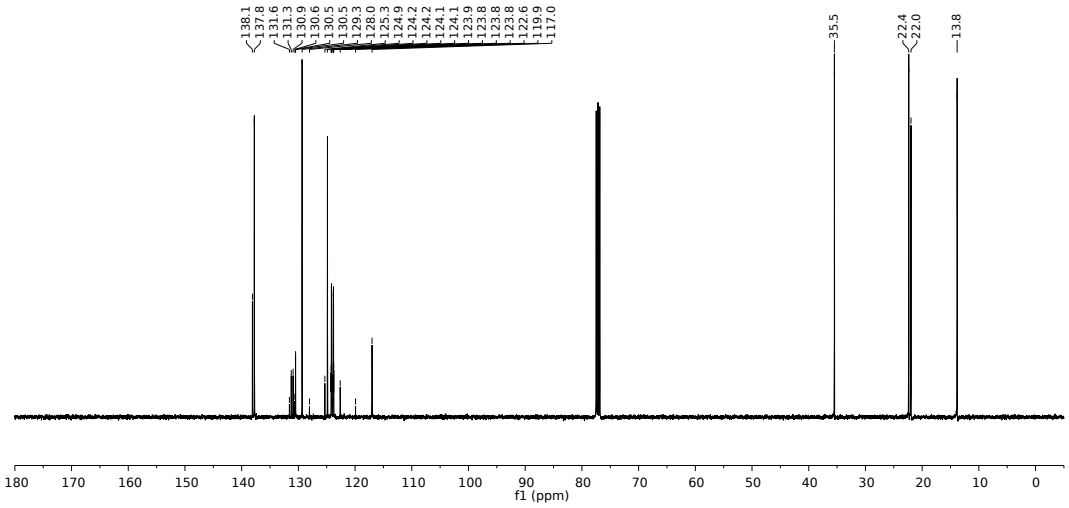

Transmittance [%]
2960.54
2931.35
2872.44
2250.34
1649.10
1611.62
1584.13
1490.80
1463.92
1423.34
1272.60
1242.43
1170.83
1140.07
1086.26
962.49
872.31
805.52
756.12
733.15
705.27
592.80
563.65
458.17
406.89
Wavenumber cm-1

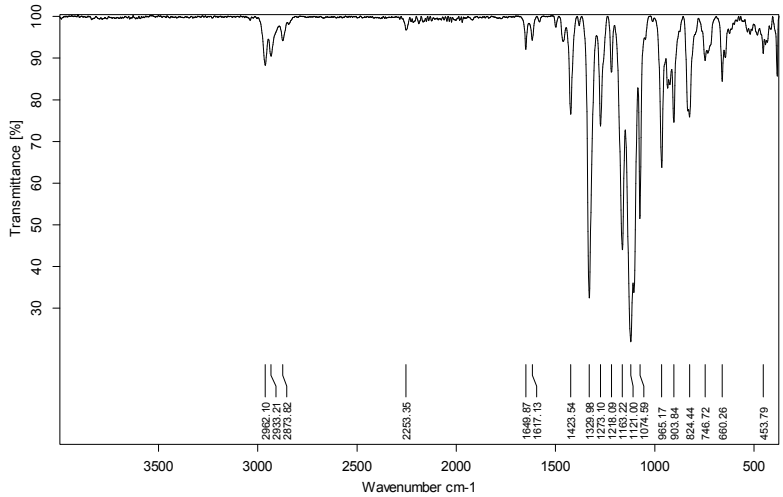

F
CN
Me
205d
1.02
0.99
0.99
0.99
1.00
2.06
2.03
2.40
3.09
f1 (ppm)

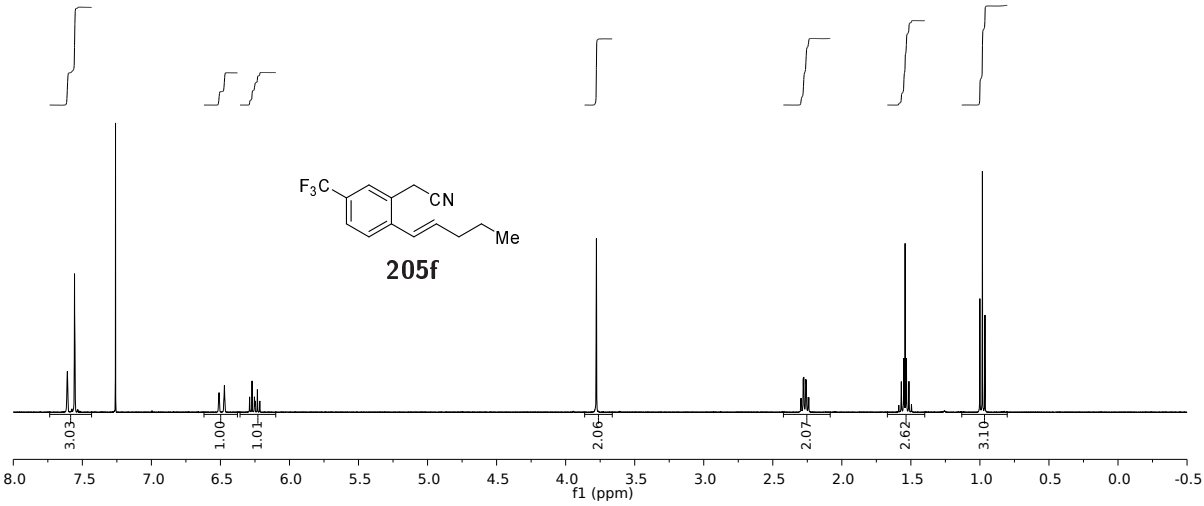

163.2
160.8
135.8
135.8
133.5
133.4
128.8
128.7
128.7
128.6
125.0
117.2
115.9
115.7
115.5
35.4
22.5
22.0
21.9
13.8
f1 (ppm)

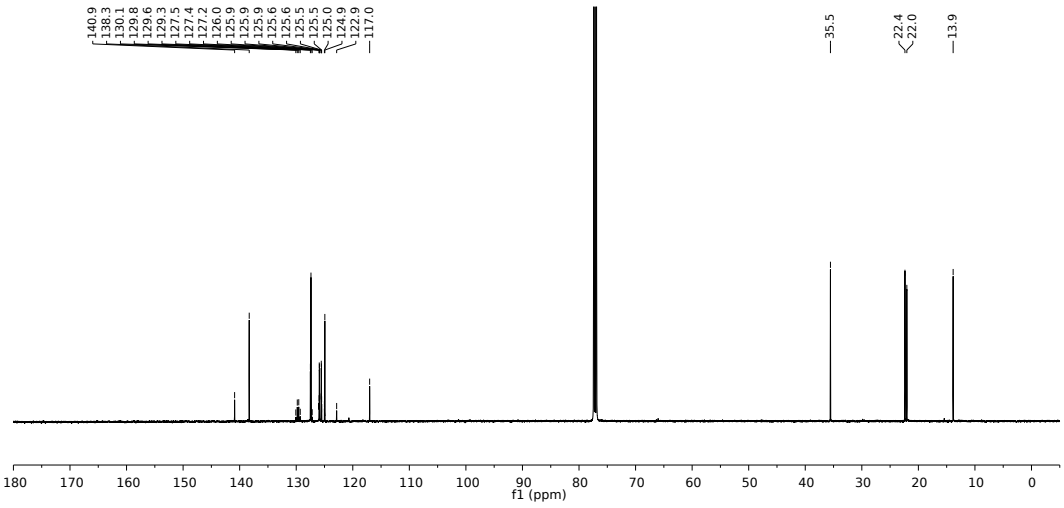

Transmittance [%]
2960.11
2930.94
2872.56
2250.78
1609.98
1585.85
1492.16
1463.30
1425.73
1250.48
1195.97
1150.21
965.37
860.60
832.29
802.31
730.65
449.29
Wavenumber cm-1

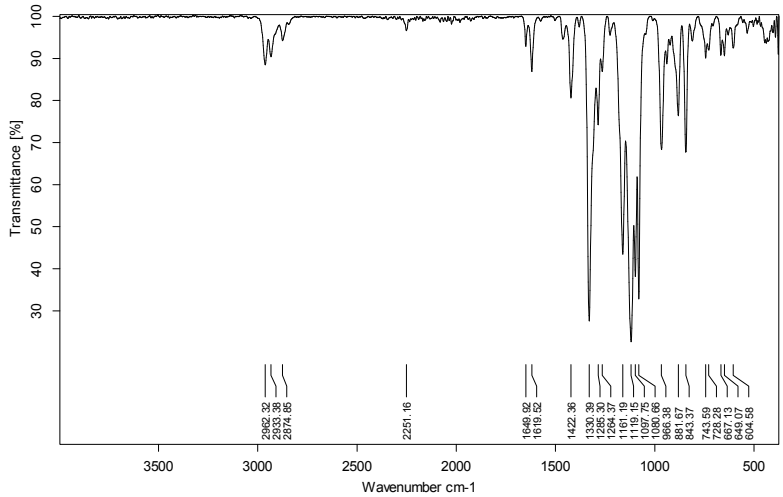

CN
F3C
Me
205e
1.01
2.00
1.00
1.00
2.02
2.02
2.17
3.02
f1 (ppm)

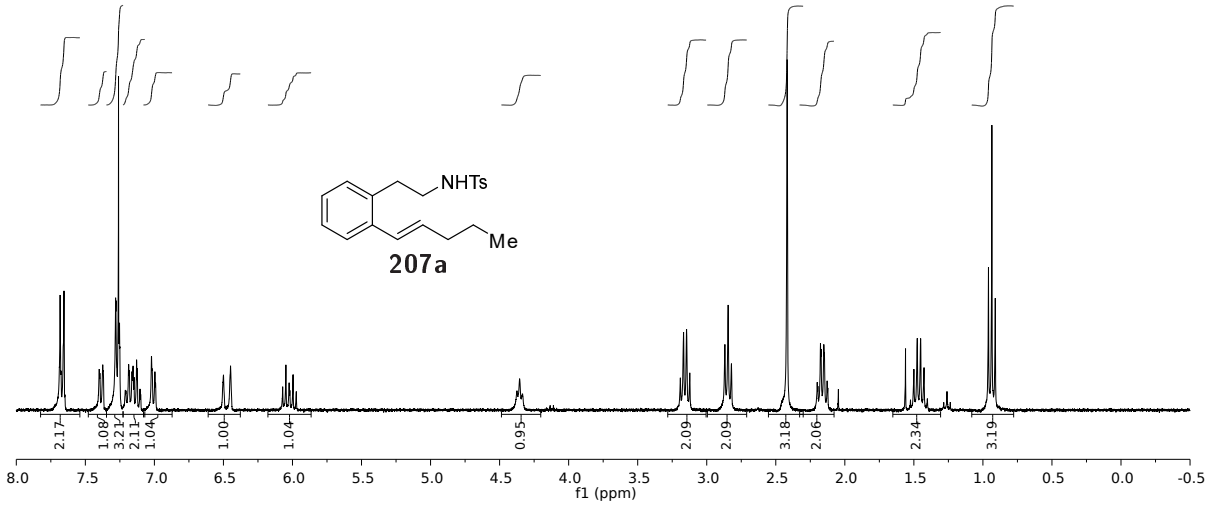

138.1
137.8
131.6
131.3
130.9
130.6
130.5
130.5
129.3
128.0
125.3
124.9
124.2
124.2
124.1
124.1
123.9
123.8
123.8
123.8
122.6
119.9
117.0
35.5
22.4
22.0
13.8
f1 (ppm)

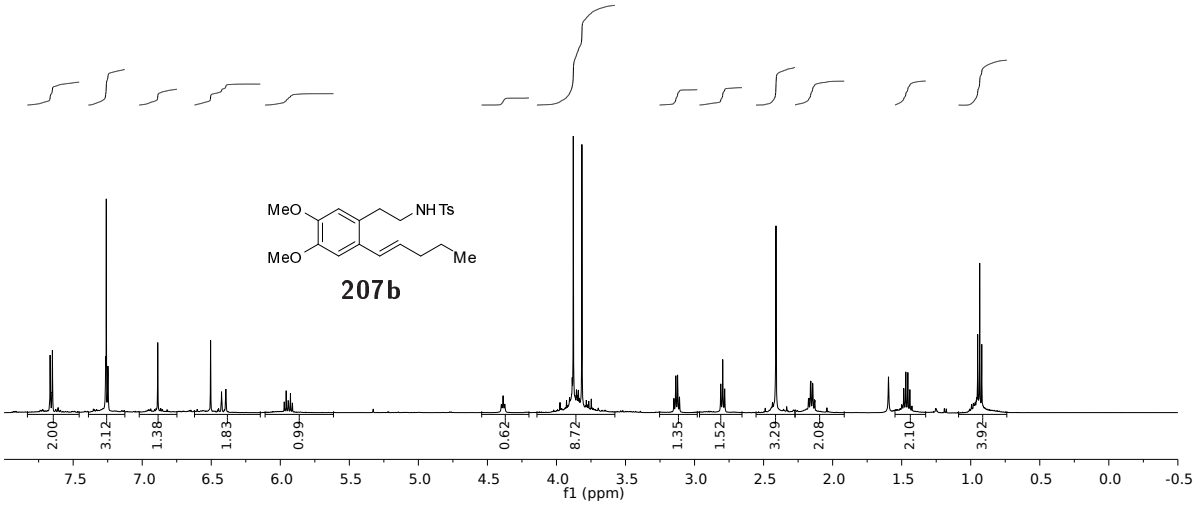

Transmittance [%]
2962.10
2933.21
2873.82
2253.35
1649.87
1617.13
1423.54
1329.98
1273.10
1218.09
1183.22
1157.00
1074.99
965.17
903.84
824.44
746.72
660.26
453.79
Wavenumber cm-1

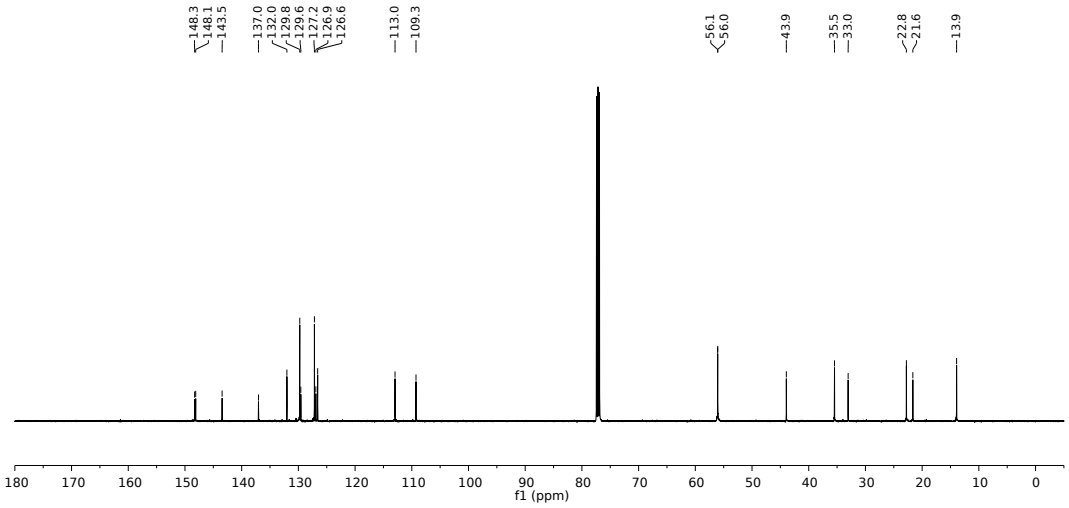

F3C
CN
Me
205f
3.03
1.00
1.01
2.06
2.07
2.62
3.10
f1 (ppm)

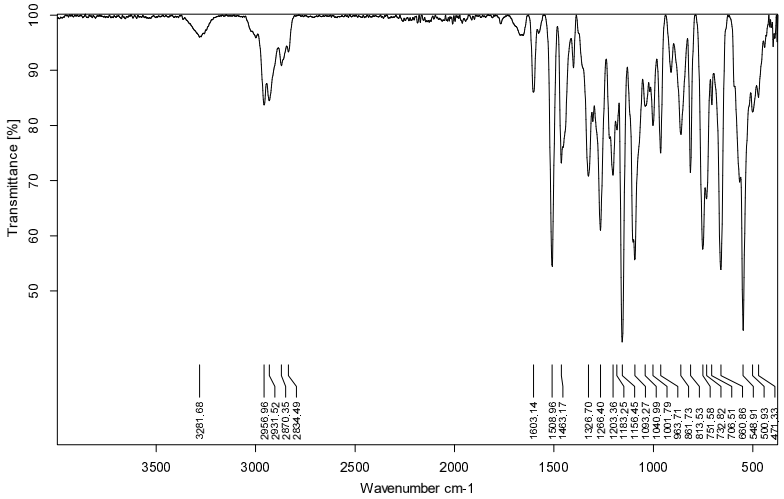

140.9
138.3
130.1
129.8
129.6
129.3
127.5
127.4
127.2
126.0
125.9
125.9
125.9
125.6
125.6
125.5
125.5
125.0
124.9
122.9
117.0
35.5
22.4
22.0
13.9
f1 (ppm)

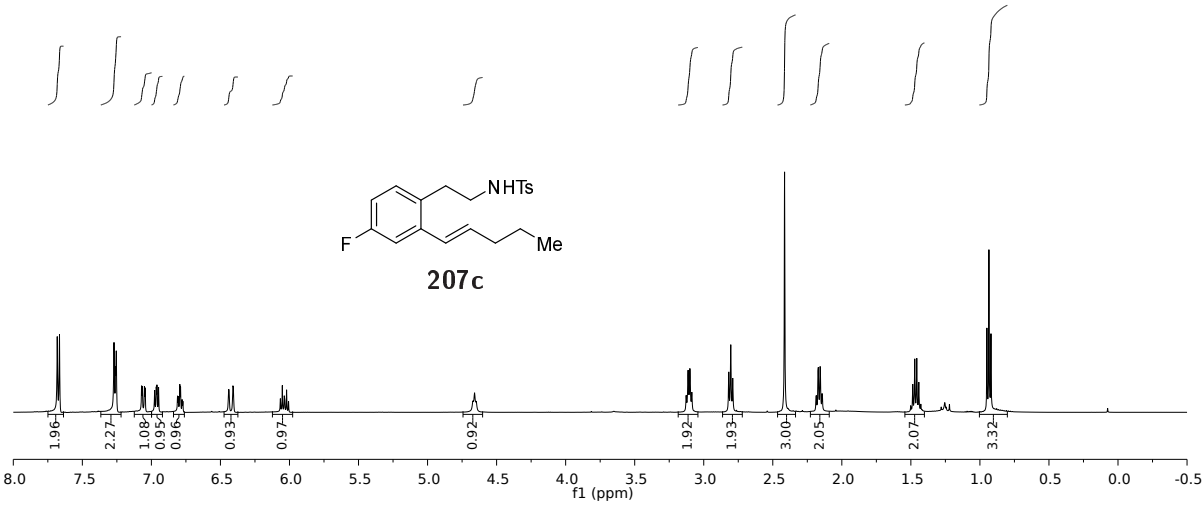

Transmittance [%]
2962.32
2933.38
2874.85
2251.16
1649.92
1619.52
1422.36
1330.39
1285.30
1264.37
1161.19
1119.15
1097.75
1080.66
966.38
881.67
843.37
743.59
729.28
667.13
649.07
604.58
Wavenumber cm-1

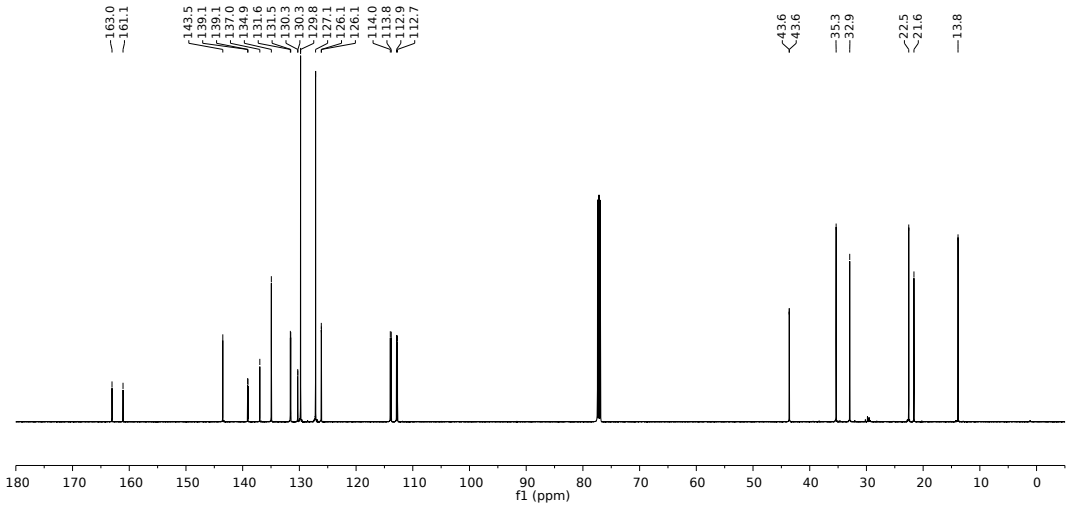

NHTs
Me
207a
2.17
1.08
3.21
2.11
1.04
1.00
1.04
0.95
2.09
2.09
3.18
2.06
2.34
3.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

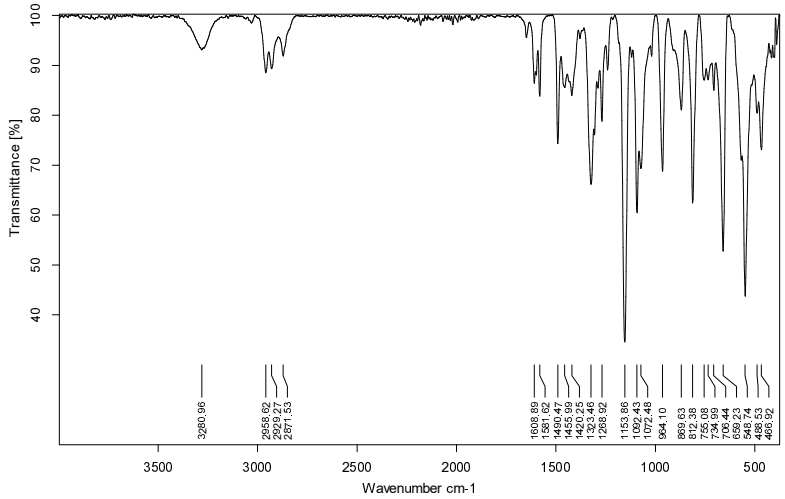

MeO
MeO
NH Ts
Me
207b
2.00
3.12
1.38
1.83
0.99
0.62
8.72
1.35
1.52
3.29
2.08
2.10
3.92
f1 (ppm)

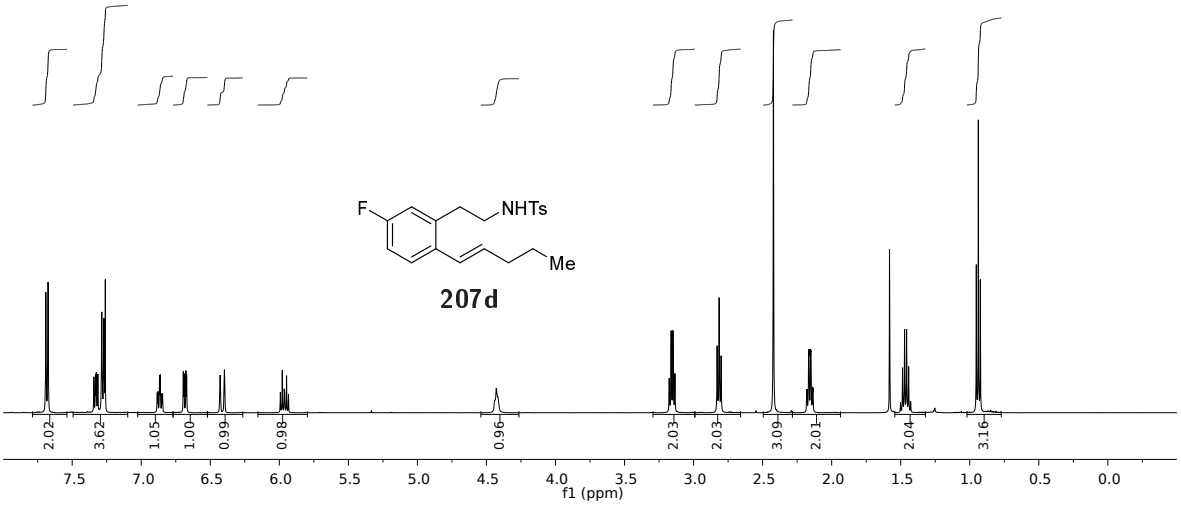

148.3
148.1
143.5
137.0
132.0
129.8
129.6
127.2
126.9
126.6
113.0
109.3
56.1
56.0
43.9
35.5
33.0
22.8
21.6
13.9
f1 (ppm)

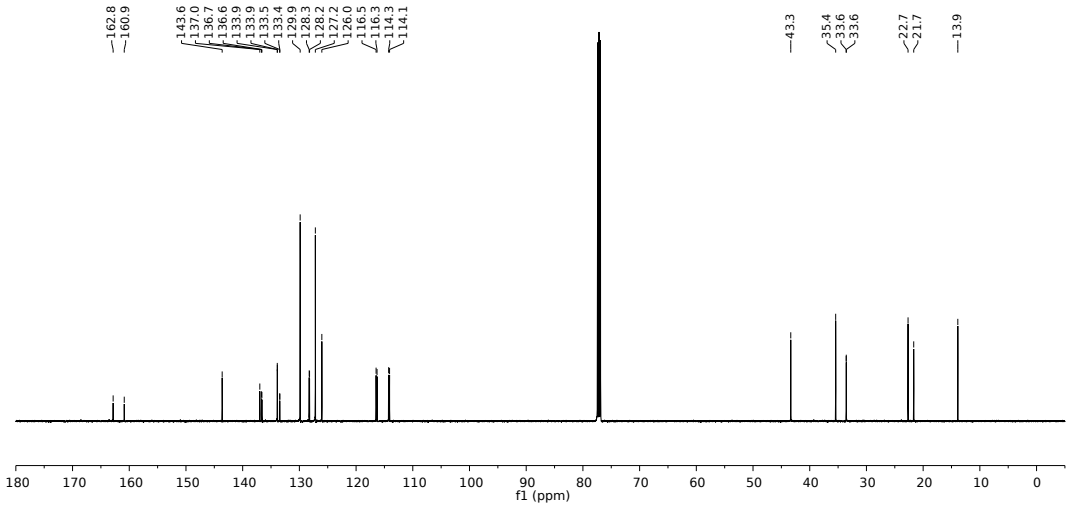

Transmittance [%]
3281.68
2956.96
2931.52
2870.35
2834.49
1603.14
1508.96
1463.17
1326.70
1266.40
1203.36
1183.25
1156.45
1093.27
1040.99
1001.79
963.71
897.73
851.53
751.58
732.82
700.61
660.61
548.91
500.93
471.33
Wavenumber cm-1

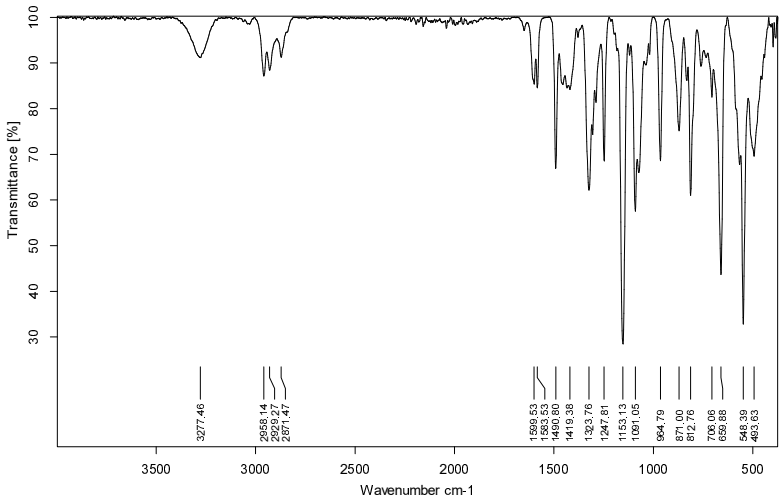

NHTs
F
Me
207c
1.96
2.27
1.08
0.95
0.96
0.93
0.97
0.92
1.92
1.93
3.00
2.05
2.07
3.32
f1 (ppm)

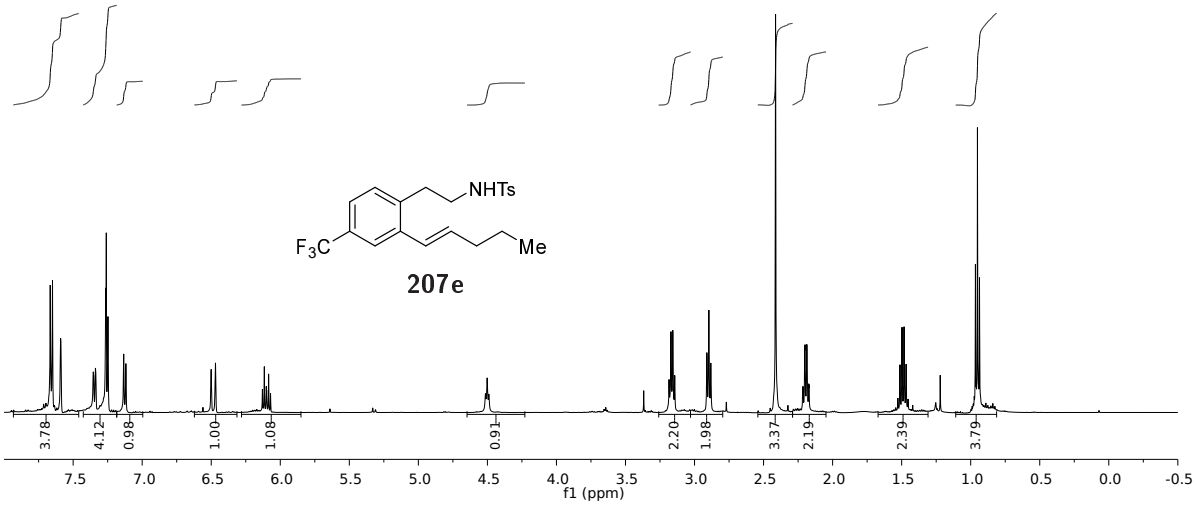

163.0
161.1
143.5
139.1
139.1
137.0
134.9
131.6
131.5
130.3
130.3
129.8
127.1
126.1
126.1
114.0
113.8
112.9
112.7
43.6
43.6
35.3
32.9
22.5
21.6
13.8
f1 (ppm)

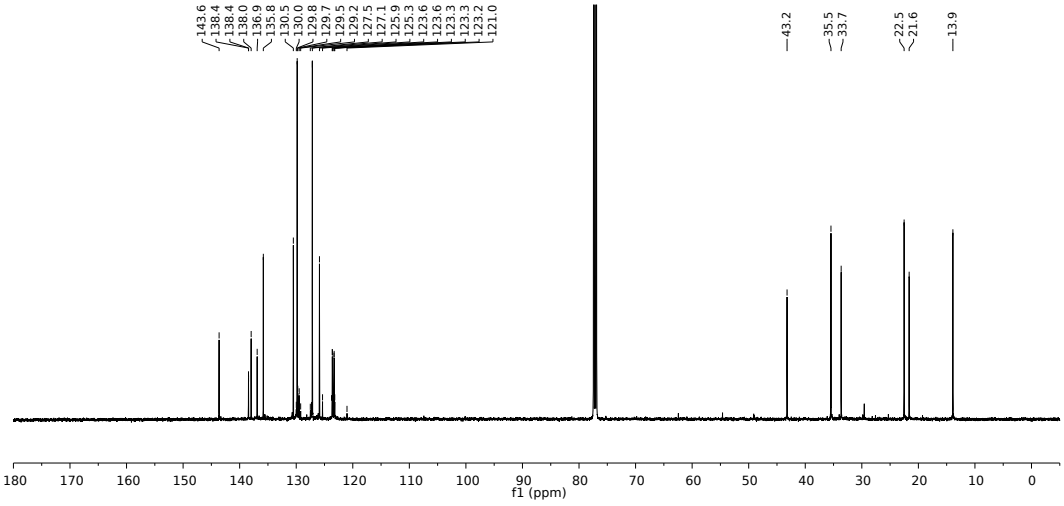

Transmittance [%]
3260.96
2958.62
2929.27
2871.53
1608.89
1581.62
1490.47
1455.99
1420.25
1332.46
1268.92
1153.86
1092.43
1072.48
964.10
869.63
812.38
755.08
734.99
706.44
688.23
648.74
498.53
466.92
Wavenumber cm-1

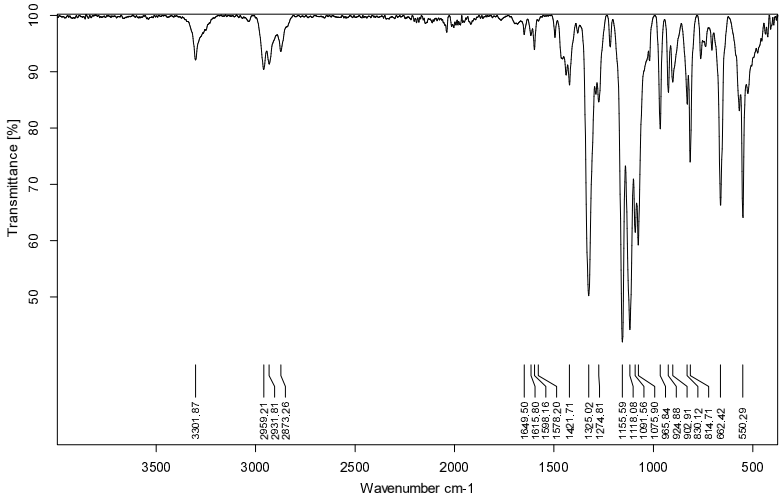

F
NHTs
Me
207d
2.02
3.62
1.05
1.00
0.99
0.98
0.96
2.03
2.03
3.09
2.01
2.04
3.16
f1 (ppm)

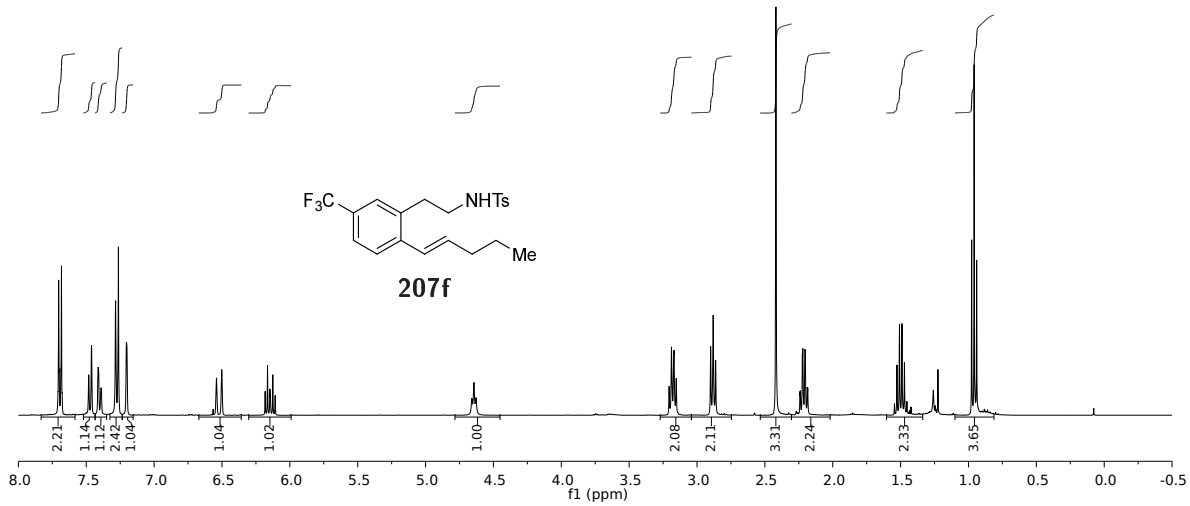

162.8
160.9
143.6
137.0
136.7
136.6
133.9
133.9
133.5
133.4
129.9
128.3
128.2
127.2
126.0
116.5
116.3
114.3
114.1
43.3
35.4
33.6
33.6
22.7
21.7
13.9
f1 (ppm)

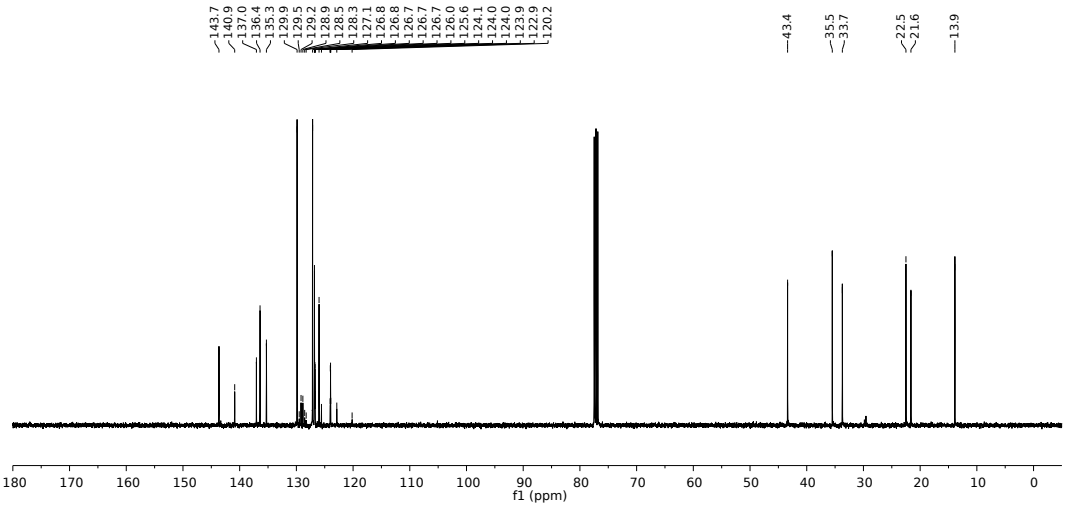

Transmittance [%]
3277.46
2958.14
2929.27
2871.47
1599.53
1583.53
1490.80
1419.38
1323.76
1247.81
1153.13
1091.05
964.79
871.00
812.76
706.06
659.88
548.39
463.63
Wavenumber cm-1

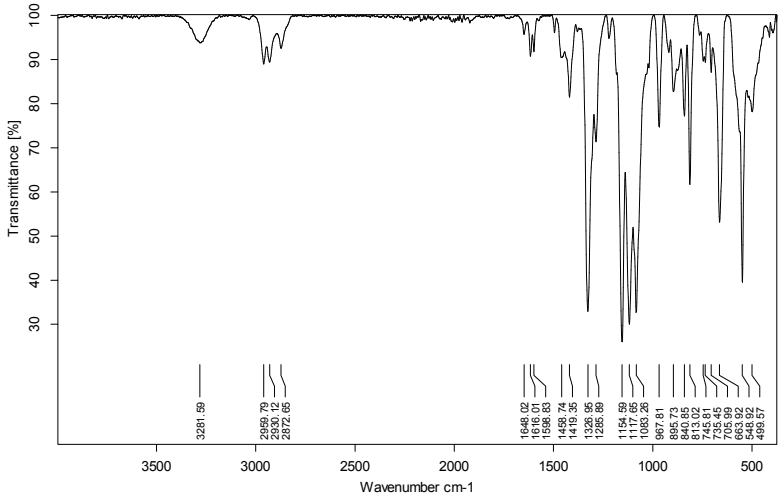

NHTs
F3C
Me
207e
3.78
4.12
0.98
1.00
1.08
0.91
2.20
1.98
3.37
2.19
2.39
3.79
f1 (ppm)

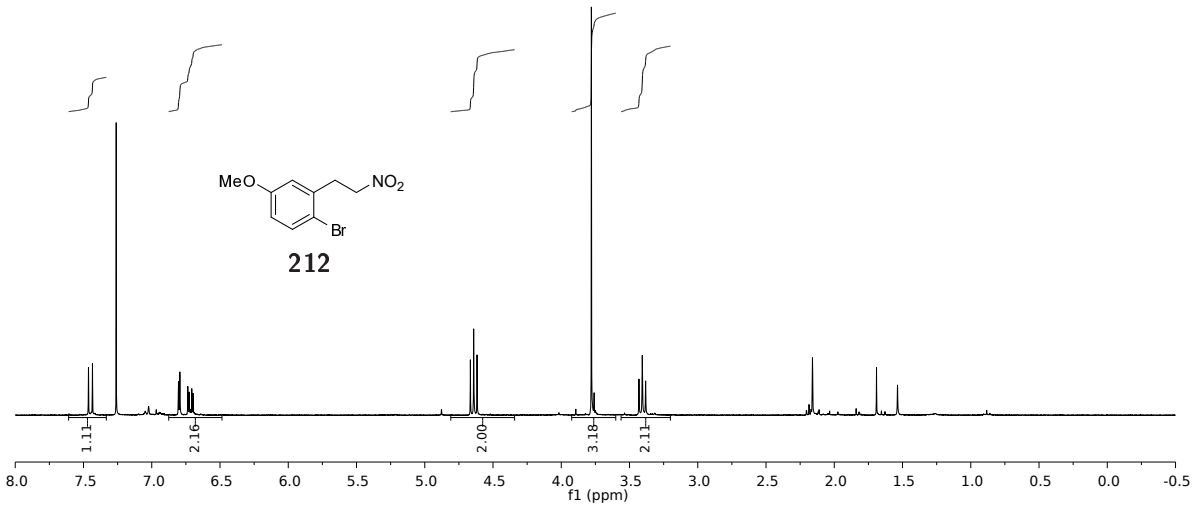

143.6
138.4
138.4
138.0
136.9
135.8
130.5
130.0
129.8
129.7
129.5
129.2
127.5
127.1
125.9
125.3
123.6
123.6
123.3
123.3
123.2
121.0
43.2
35.5
33.7
22.5
21.6
13.9
f1 (ppm)

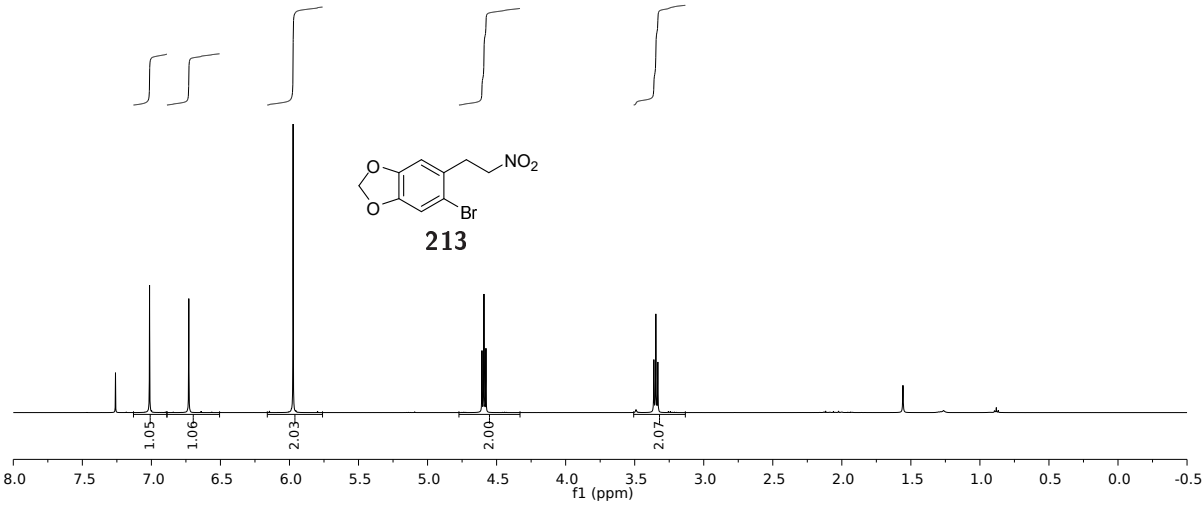

Transmittance [%]
3301.87
2959.21
2931.81
2873.26
1649.50
1615.60
1598.10
1578.20
1421.71
1325.02
1274.81
1155.59
1118.08
1101.65
1075.90
965.84
924.88
900.51
830.12
814.71
692.42
550.29
Wavenumber cm-1

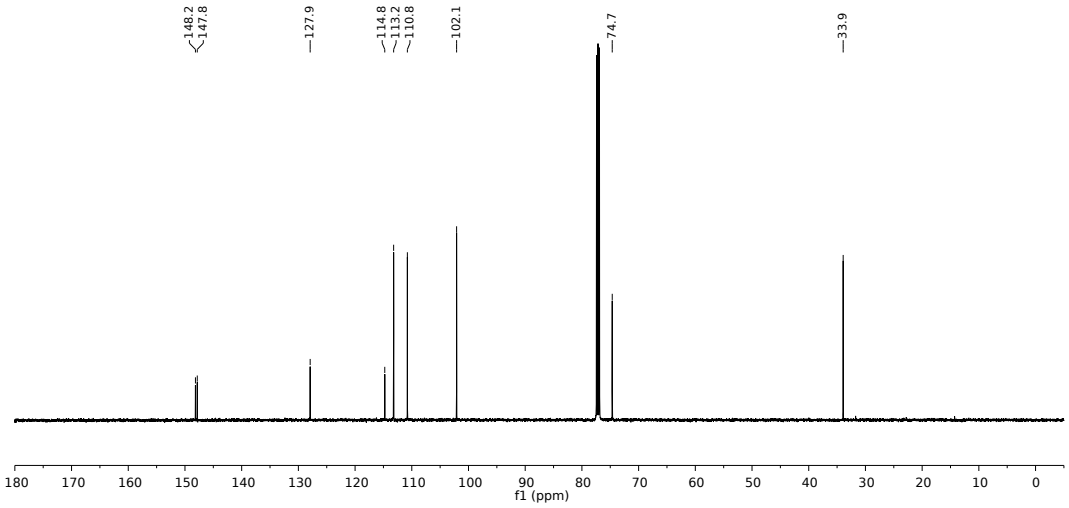

F3C
NHTs
Me
207f
2.21
1.14
1.12
2.42
1.04
1.04
1.02
1.00
2.08
2.11
3.31
2.24
2.33
3.65
f1 (ppm)

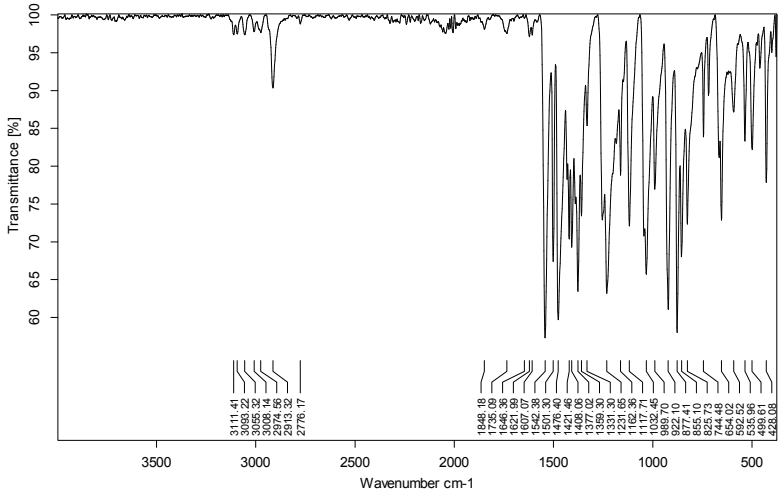

143.7
140.9
137.0
136.4
135.3
129.9
129.5
129.2
128.9
128.5
128.3
127.1
126.8
126.8
126.7
126.7
126.7
126.0
125.6
124.1
124.0
124.0
123.9
122.9
120.2
43.4
35.5
33.7
22.5
21.6
13.9
f1 (ppm)

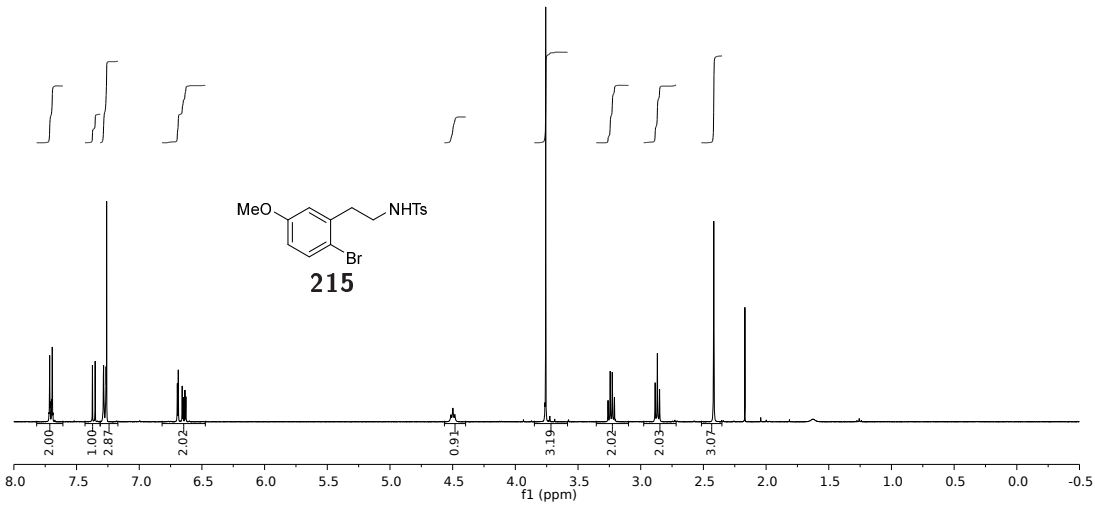

Transmittance [%]
3281.59
2959.79
2930.12
2872.65
1648.02
1616.01
1598.73
1498.74
1419.35
1326.95
1285.89
1154.69
1117.65
1053.26
967.81
896.73
840.85
813.02
745.81
705.45
705.09
663.92
548.92
499.57
Wavenumber cm-1

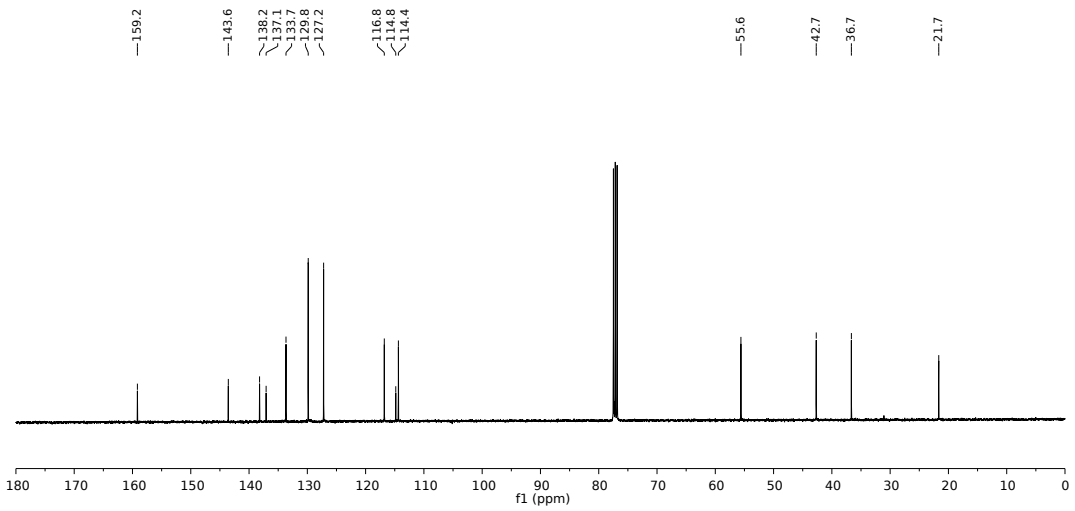

MeO
NO2
Br
212
1.11
2.16
2.00
3.18
2.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

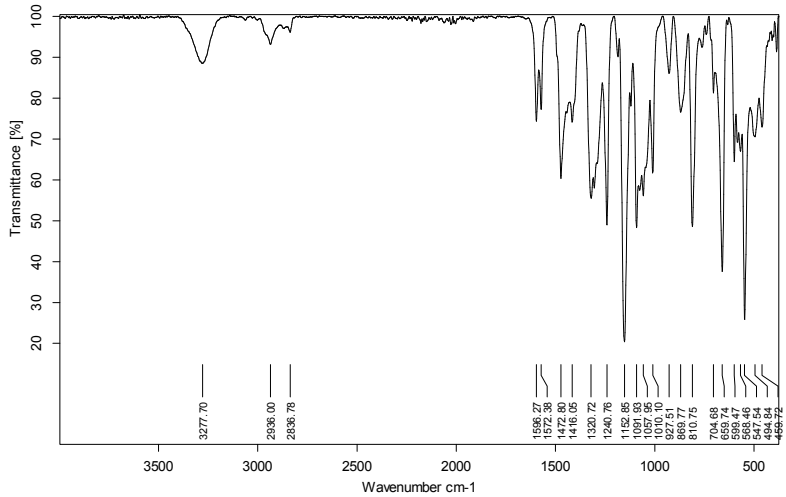

O
O
NO2
Br
213
1.05
1.06
2.03
2.00
2.07
f1 (ppm)

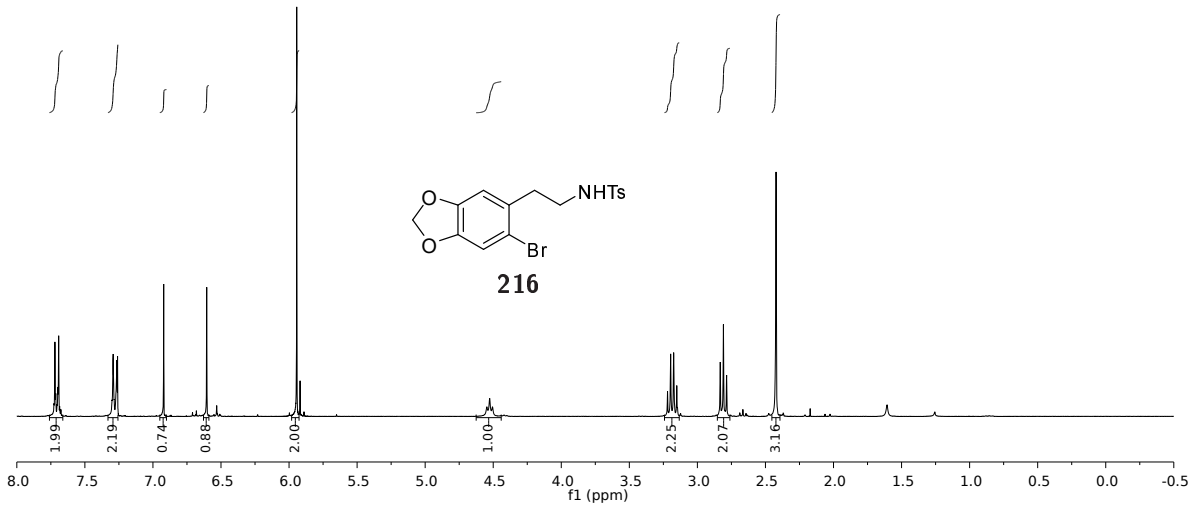

148.2
147.8
127.9
114.8
113.2
110.8
102.1
74.7
33.9
f1 (ppm)

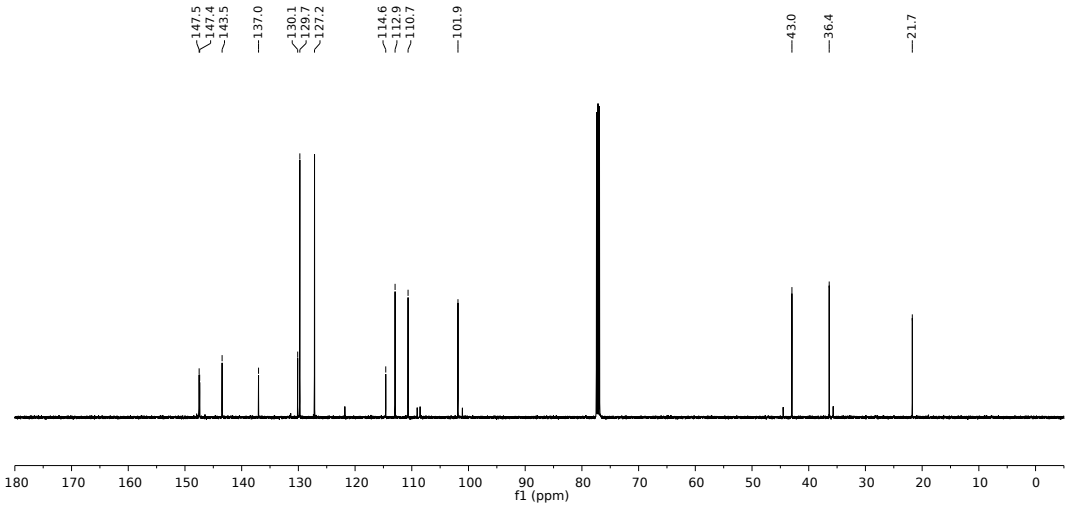

Transmittance [%]
Wavenumber cm-1

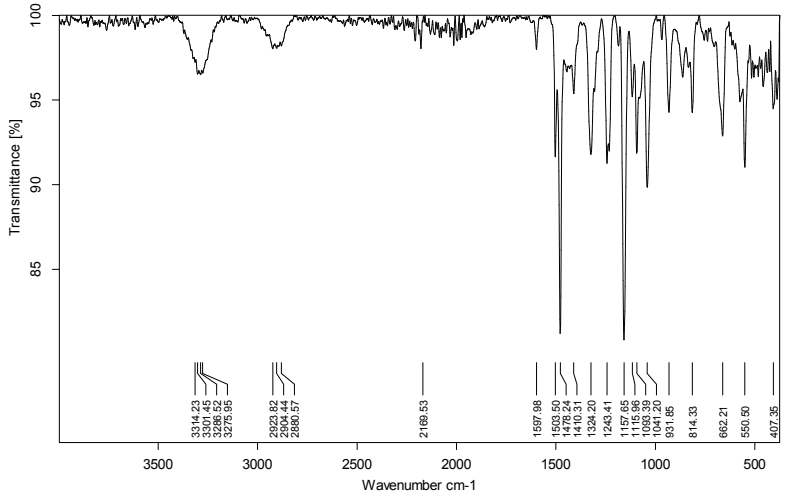

MeO
NHTs
Br
215
2.00
1.00
2.87
2.02
0.91
3.19
2.02
2.03
3.07
f1 (ppm)

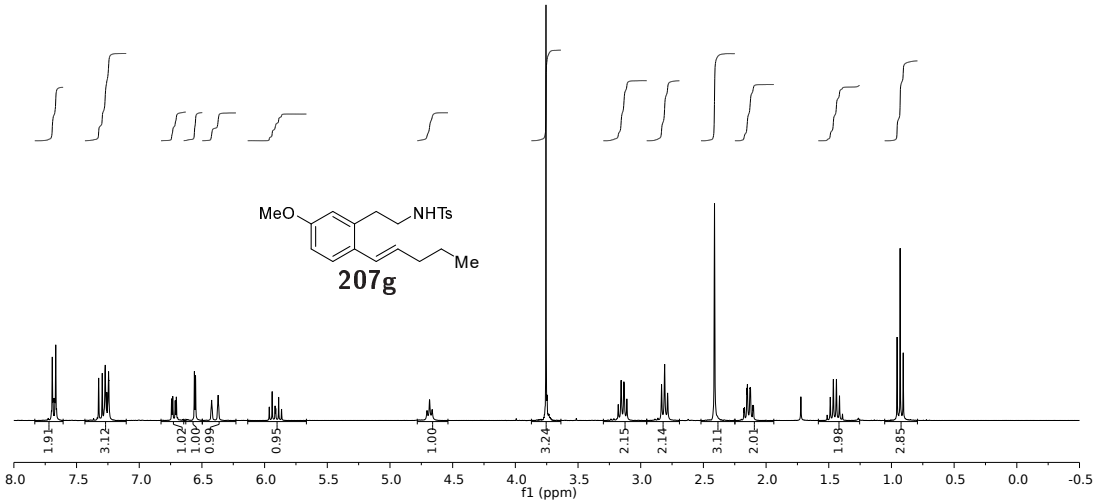

159.2
143.6
138.2
137.1
133.7
129.8
127.2
116.8
114.8
114.4
55.6
42.7
36.7
21.7
f1 (ppm)

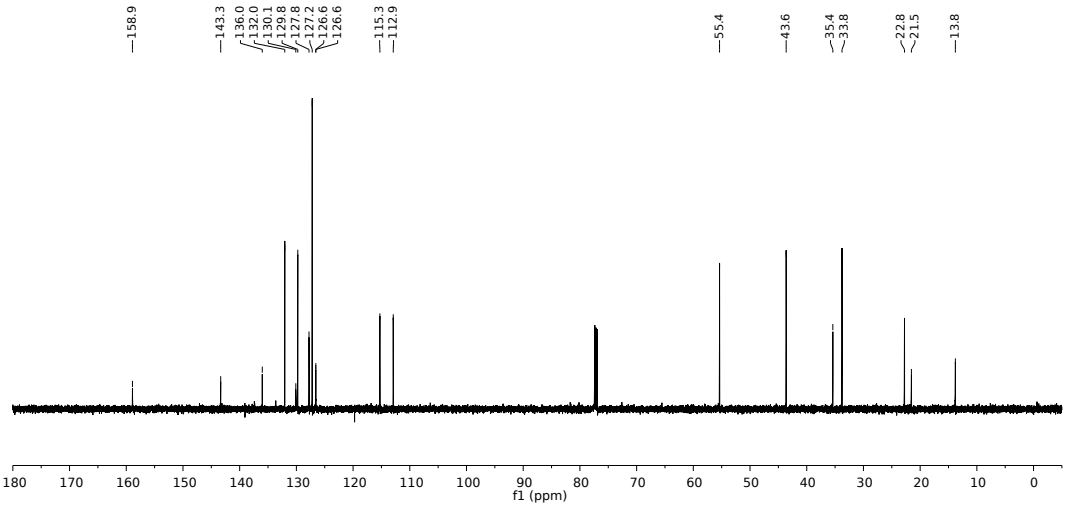

Transmittance [%]
3277.70
2936.00
2836.78
1596.27
1572.58
1472.80
1416.05
1320.72
1240.76
1152.85
1091.93
1057.05
1010.10
927.51
869.77
810.75
704.68
659.74
599.47
564.46
547.54
494.84
468.72
Wavenumber cm-1

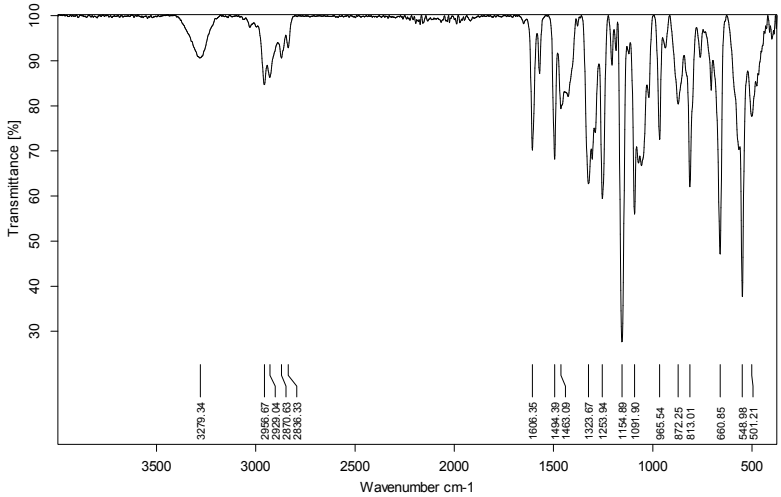

NHTs
O
O
Br
216
1.99
2.19
0.74
0.88
2.00
1.00
2.25
2.07
3.16
f1 (ppm)

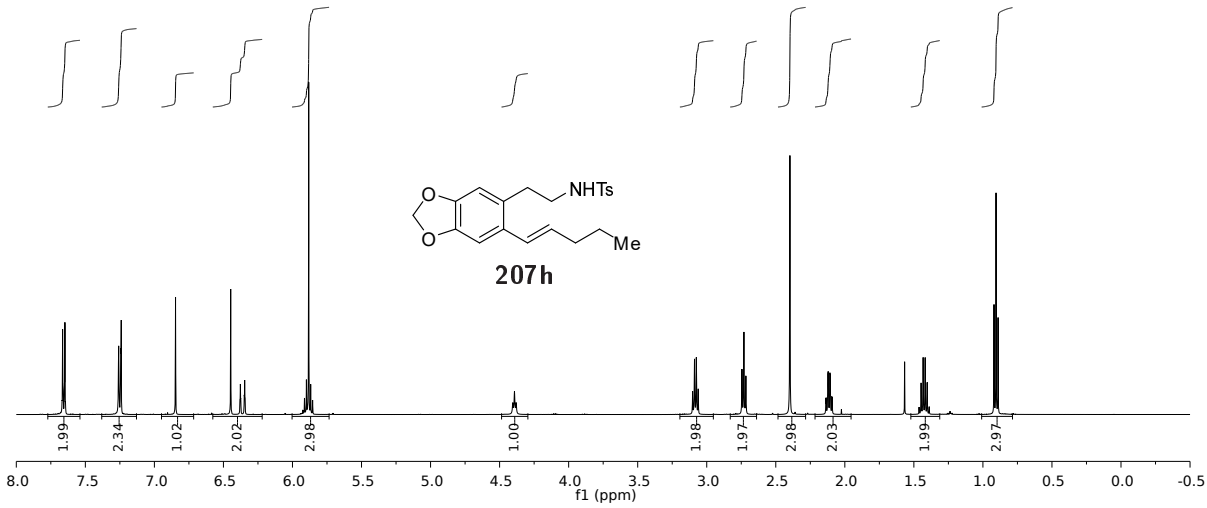

147.5
147.4
143.5
137.0
130.1
129.7
127.2
114.6
112.9
110.7
101.9
43.0
36.4
21.7
f1 (ppm)

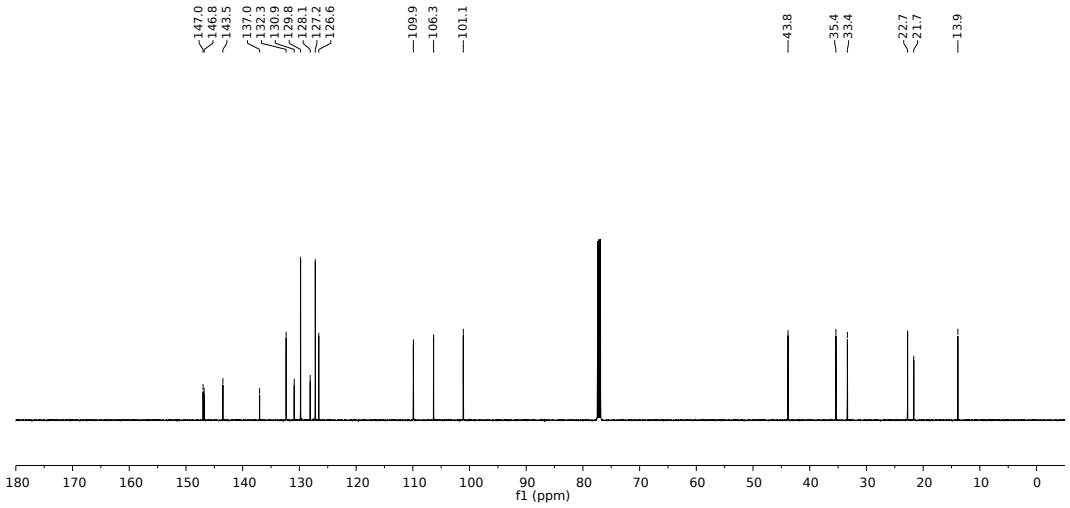

Transmittance [%]
100
95
90
85
3314.23
3301.45
3286.52
3275.95
2923.82
2894.44
2886.57
2169.53
1597.98
1503.50
1478.24
1440.31
1324.20
1243.41
1157.65
1119.96
1093.38
1041.20
931.85
814.33
662.21
550.50
407.35
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

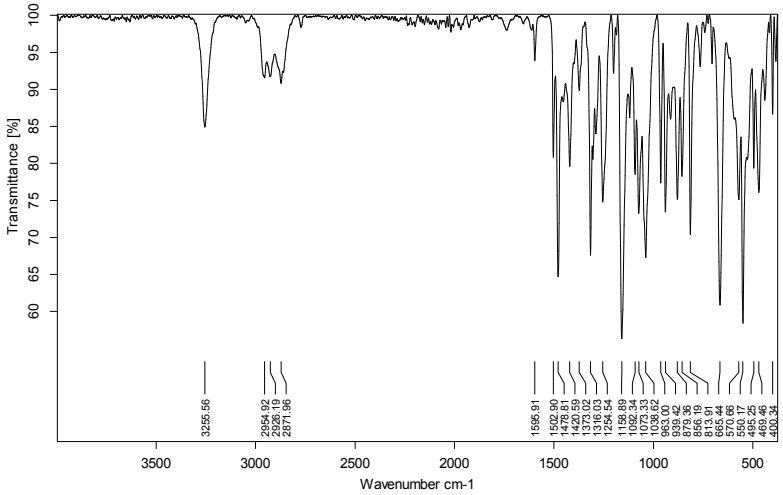

MeO
NHTs
Me
207g
1.91
3.12
1.02
1.00
0.99
0.95
1.00
3.24
2.15
2.14
3.11
2.01
1.98
2.85
f1 (ppm)

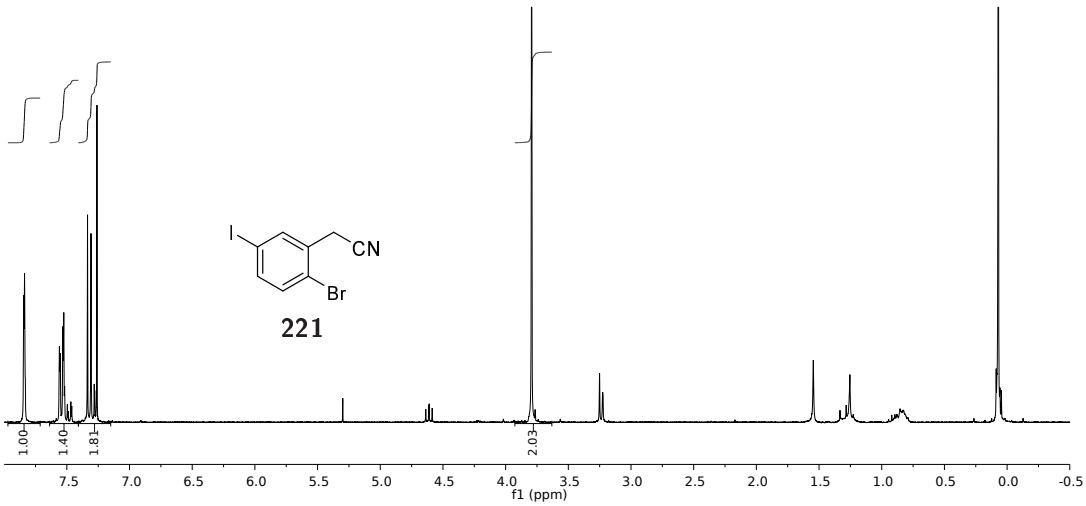

158.9
143.3
136.0
132.0
130.1
129.8
127.8
127.2
126.6
126.6
115.3
112.9
55.4
43.6
35.4
33.8
22.8
21.5
13.8
f1 (ppm)

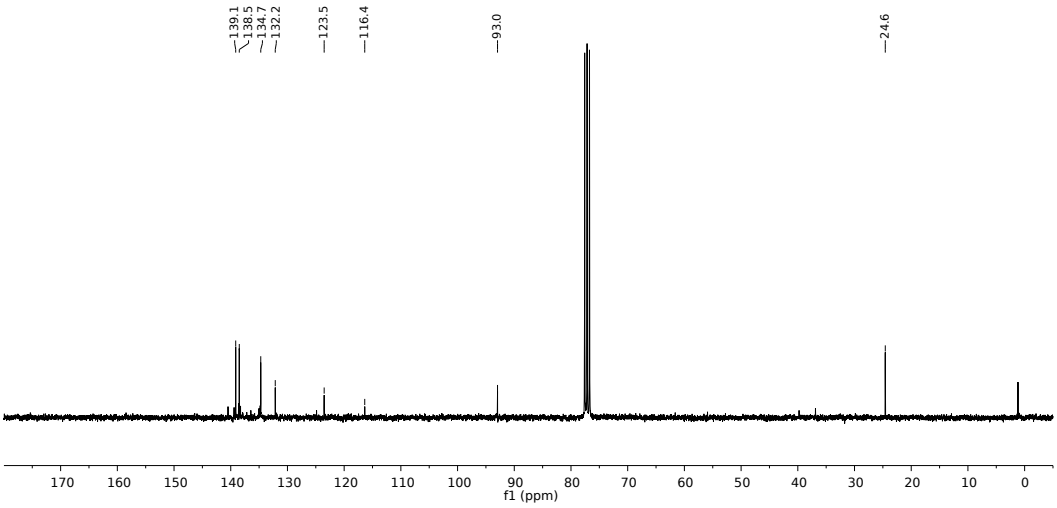

Transmittance [%]
3279.34
2956.67
2929.04
2870.63
2836.33
1606.35
1494.39
1463.09
1323.67
1253.94
1154.89
1091.90
965.54
872.25
813.01
660.85
548.98
501.21
Wavenumber cm-1

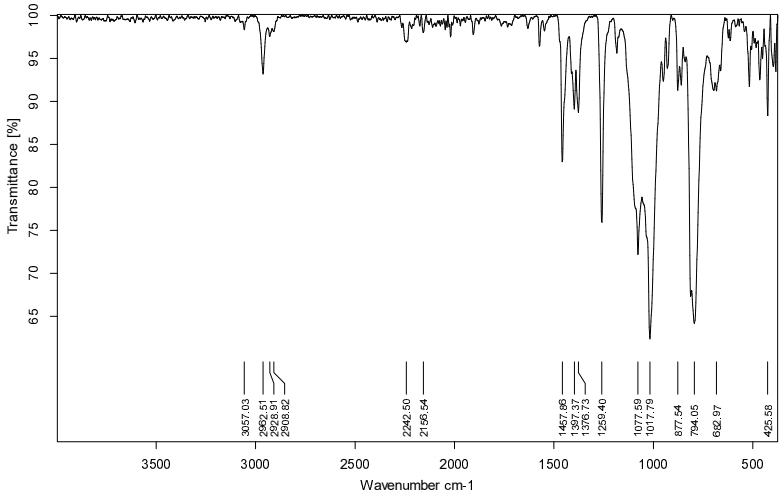

NHTs
Me
O
O
207h
1.99
2.34
1.02
2.02
2.98
1.00
1.98
1.97
2.98
2.03
1.99
2.97
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

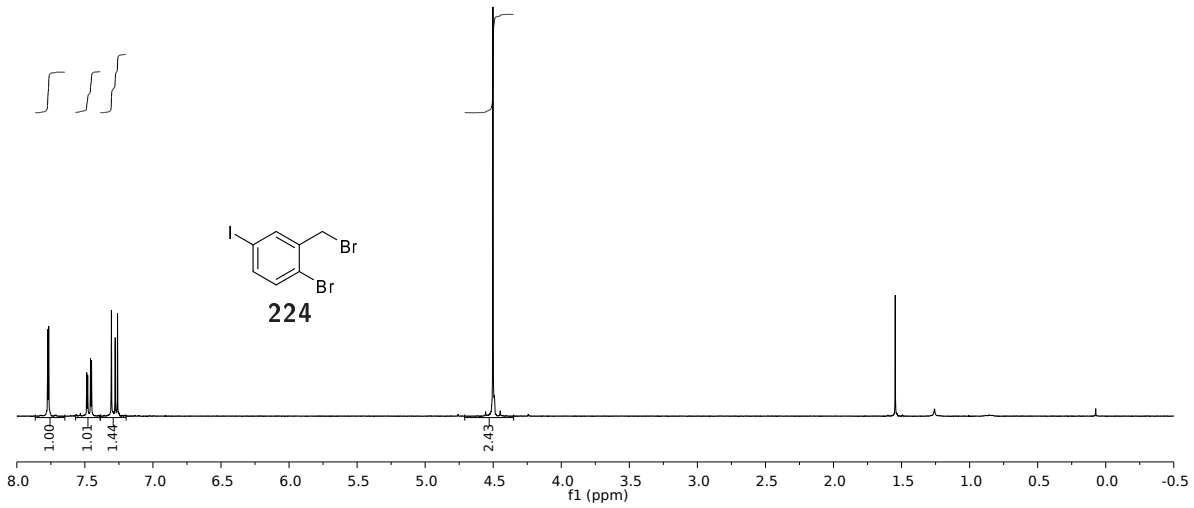

147.0
146.8
143.5
137.0
132.3
130.9
129.8
128.1
127.2
126.6
109.9
106.3
101.1
43.8
35.4
33.4
22.7
21.7
13.9
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

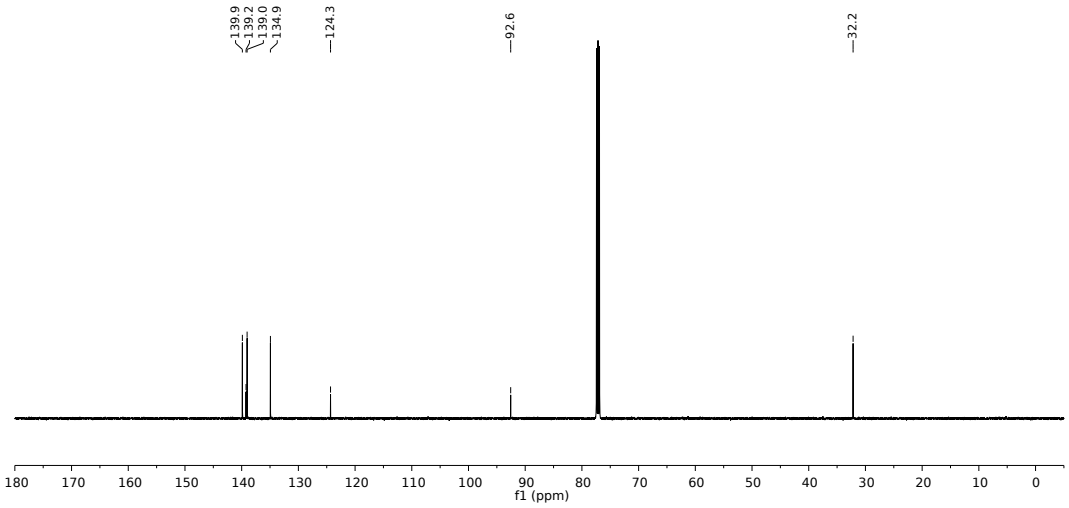

Transmittance [%]
100 95 90 85 80 75 70 65 60
3255.56
2954.92
2928.19
2871.96
1595.91
1502.90
1478.81
1447.89
1373.02
1316.03
1254.54
1188.89
1092.34
1072.33
1038.62
963.00
939.42
918.35
866.19
813.91
665.44
570.66
550.17
495.25
469.46
460.34
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

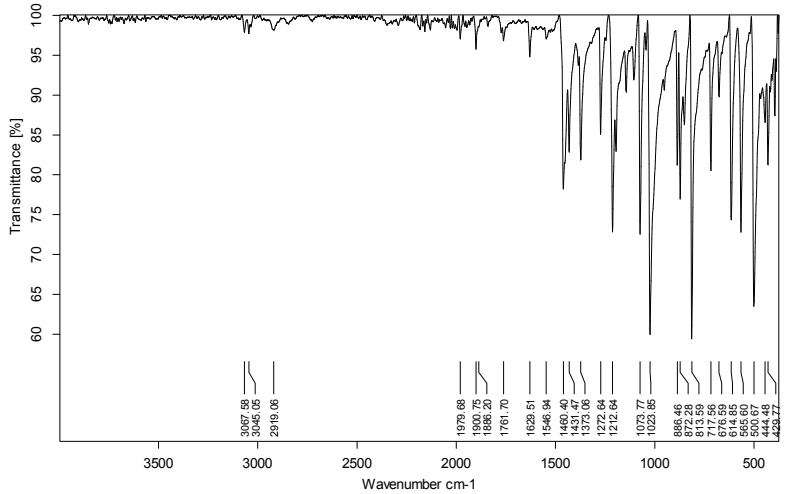

I
CN
Br
221
1.00
1.40
1.81
2.03
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

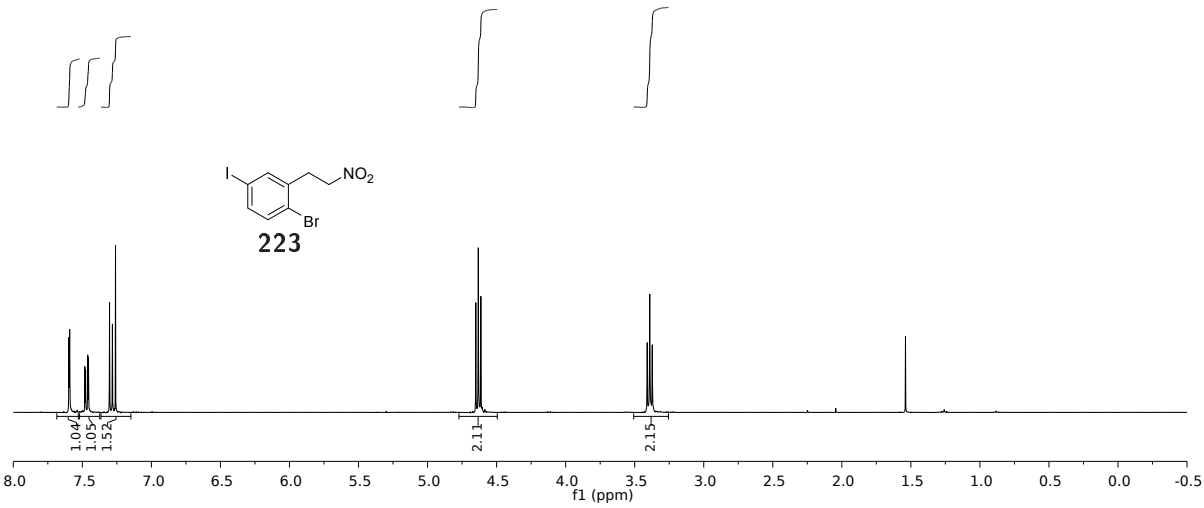

139.1
138.5
134.7
132.2
123.5
116.4
93.0
24.6
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

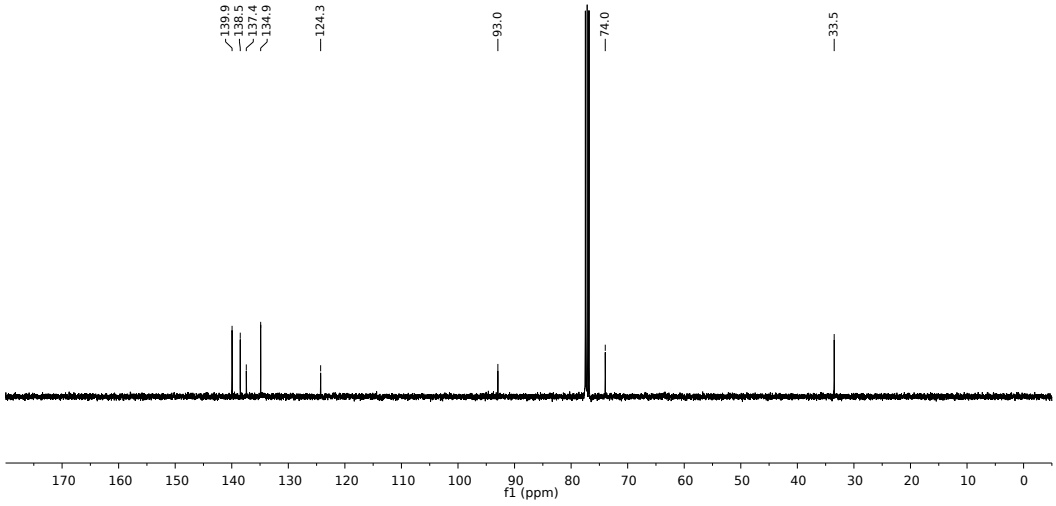

Transmittance [%]
100 95 90 85 80 75 70 65
3057.03
2952.51
2928.91
2908.82
2242.50
2198.54
1467.66
1447.27
1376.73
1269.40
1077.59
1017.79
877.54
794.05
682.97
425.58
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

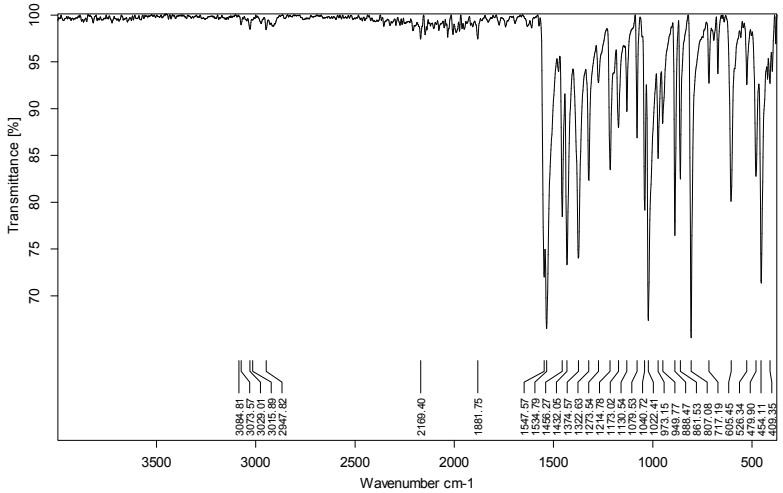

I
Br
Br
224
1.00
1.01
1.44
2.43
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

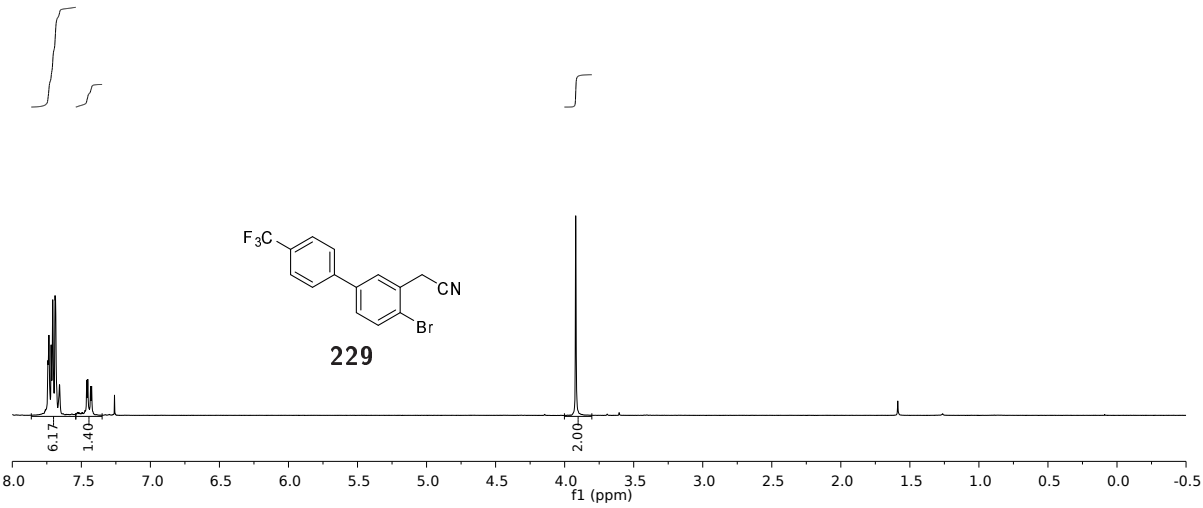

139.9
139.2
139.0
134.9
124.3
92.6
32.2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

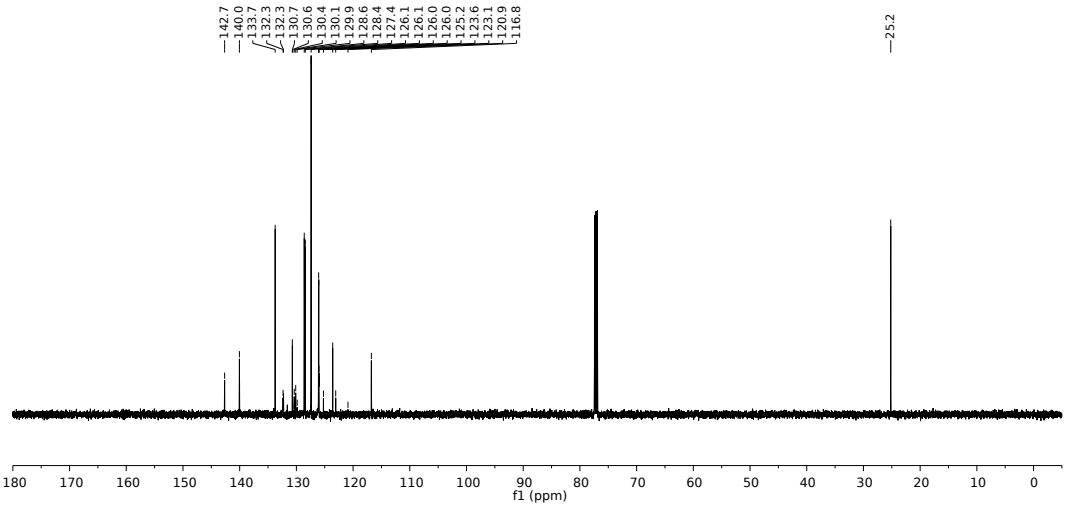

Transmittance [%]
100 95 90 85 80 75 70 65 60
3067.58
3045.05
2919.06
1979.88
1900.75
1886.20
1761.70
1629.51
1546.94
1460.40
1431.47
1373.06
1272.64
1212.64
1073.77
1023.86
886.46
872.23
813.59
717.56
676.59
614.85
565.60
500.67
444.48
428.77
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

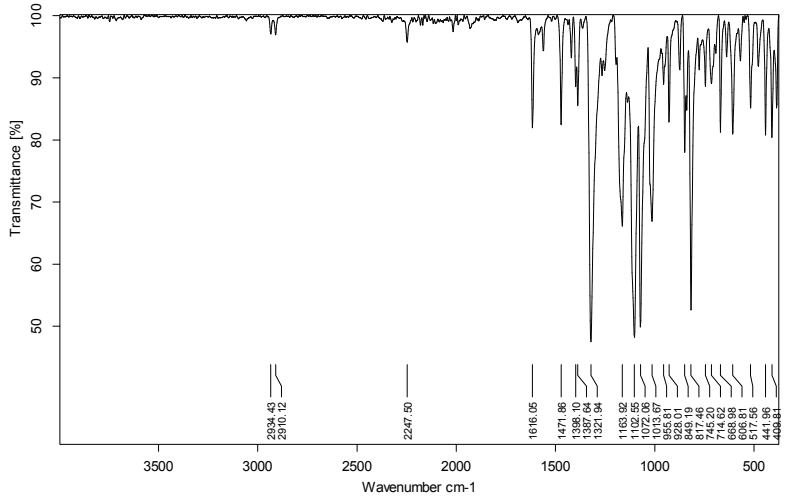

I
NO2
Br
223
1.04
1.05
1.52
2.11
2.15
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

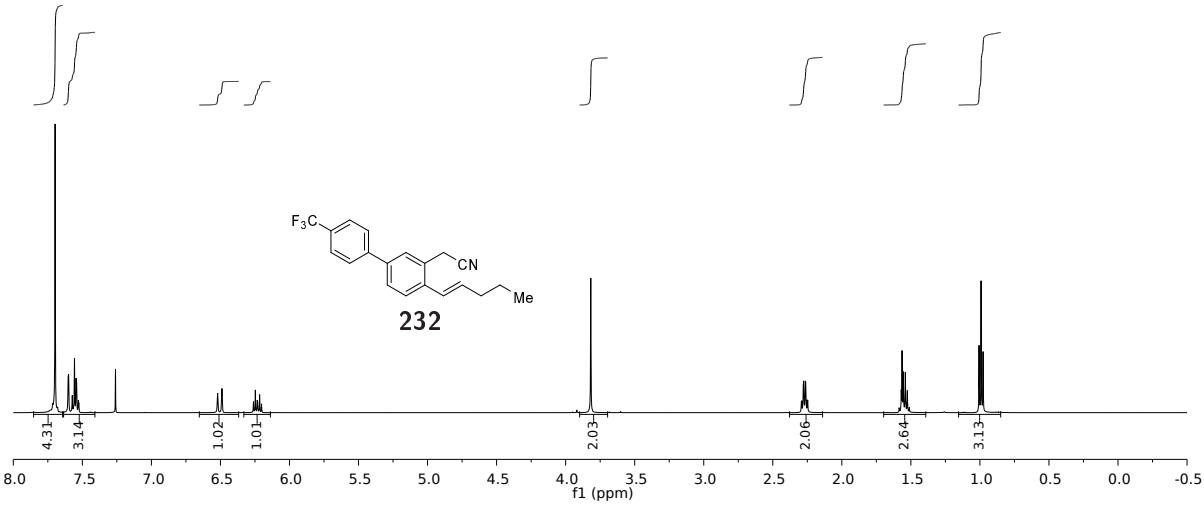

139.9
138.5
137.4
134.9
124.3
93.0
74.0
33.5
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

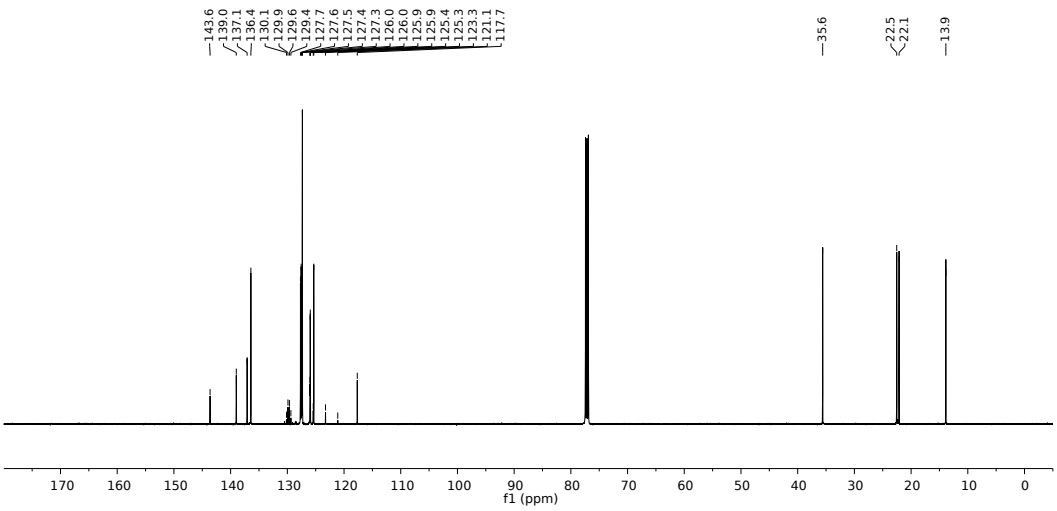

Transmittance [%]
100 95 90 85 80 75 70
3094.81
3073.57
3029.01
3015.89
2947.02
2169.40
1881.75
1547.57
1494.79
1446.27
1432.05
1374.57
1322.63
1273.34
1214.78
1173.02
1130.54
1078.52
1046.72
1022.41
973.15
948.77
898.47
861.53
807.08
717.19
686.45
526.34
479.90
454.11
409.35
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

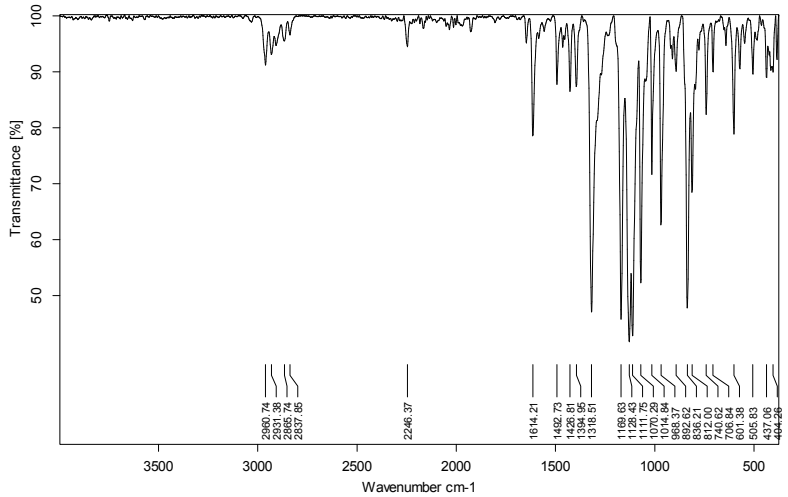

F3C
CN
Br
229
6.17
1.40
2.00
f1 (ppm)

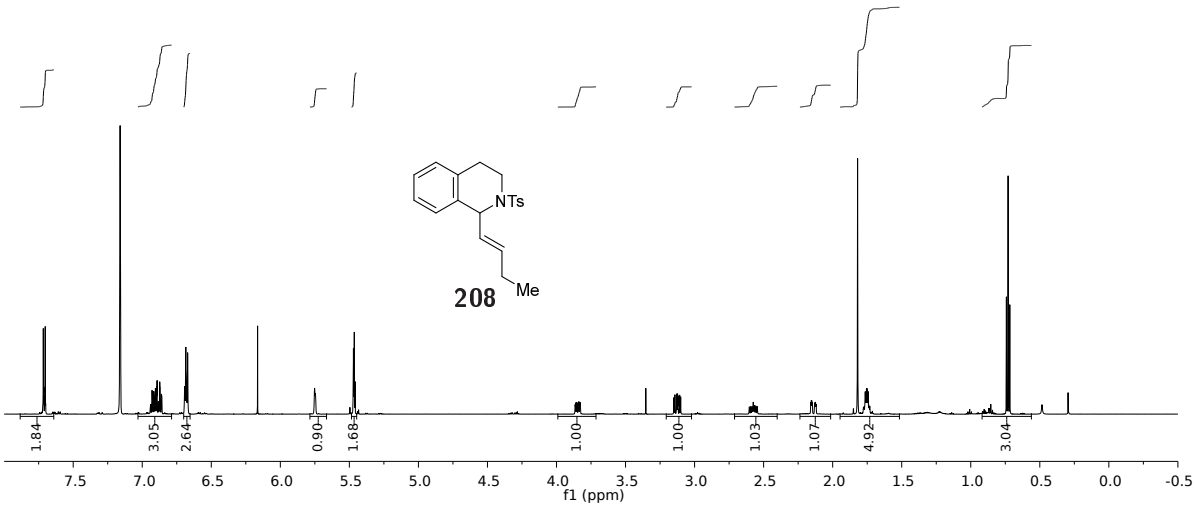

142.7
140.0
133.7
132.3
132.3
130.7
130.6
130.4
130.1
129.9
128.6
128.4
127.4
126.1
126.1
126.0
126.0
125.2
123.6
123.1
120.9
116.8
25.2
f1 (ppm)

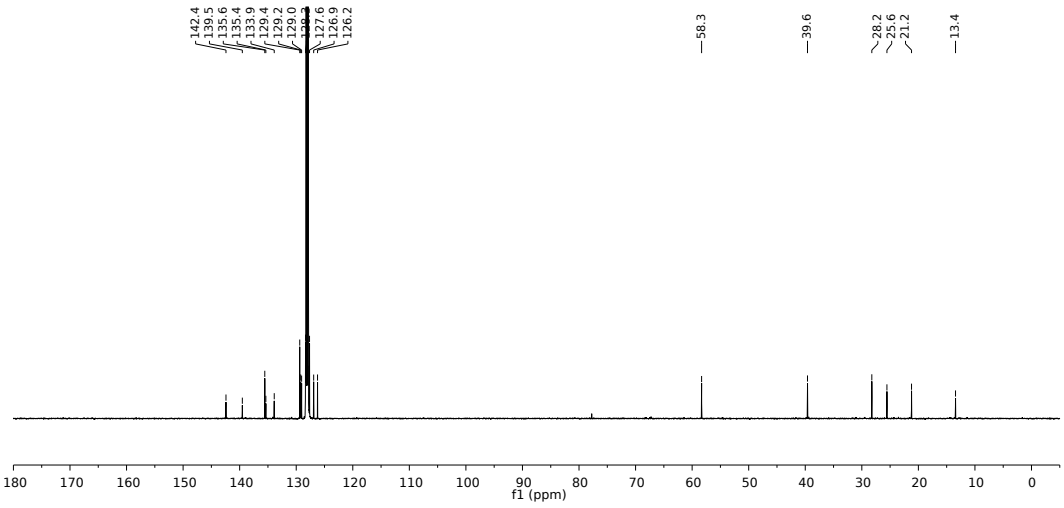

Transmittance [%]
2934.43
2910.12
2247.50
1616.05
1471.86
1398.10
1387.64
1321.94
1183.92
1155.05
1072.55
1013.67
955.81
928.01
868.19
817.46
745.20
714.62
688.91
606.81
517.56
441.96
400.84
Wavenumber cm-1

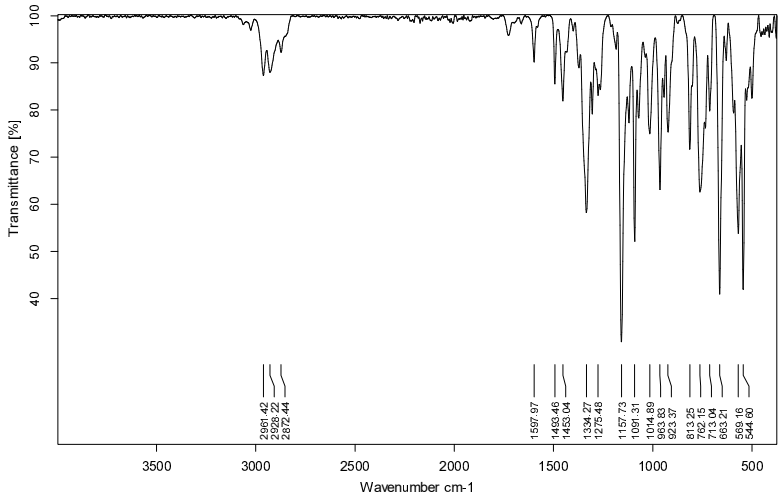

F3C
CN
Me
232
4.31
3.14
1.02
1.01
2.03
2.06
2.64
3.13
f1 (ppm)

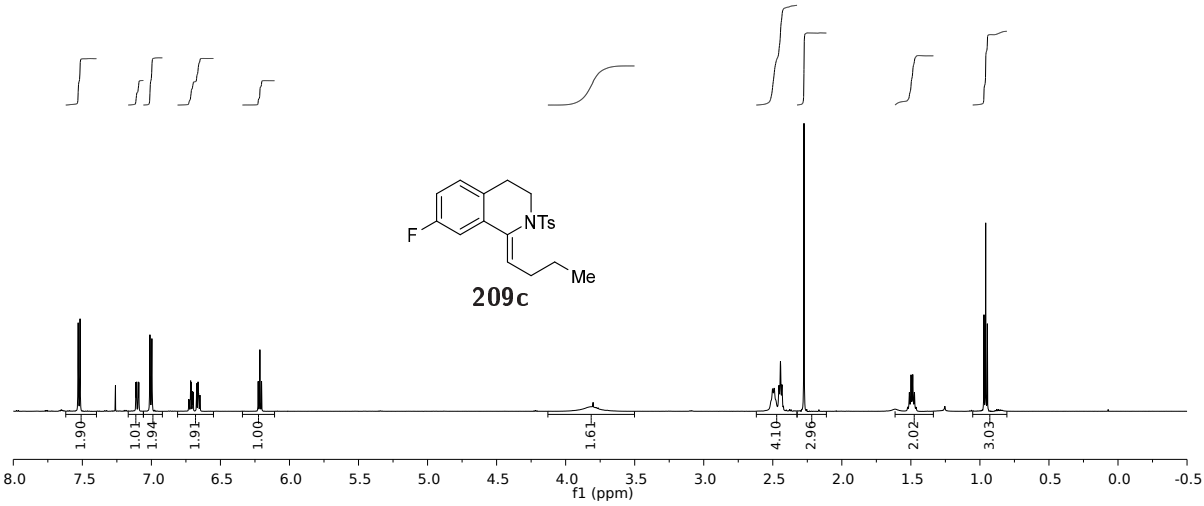

143.6
139.0
137.1
136.4
130.1
129.9
129.6
129.4
127.7
127.6
127.5
127.4
127.3
126.0
126.0
125.9
125.9
125.4
125.3
123.3
121.1
117.7
35.6
22.5
22.1
13.9
f1 (ppm)

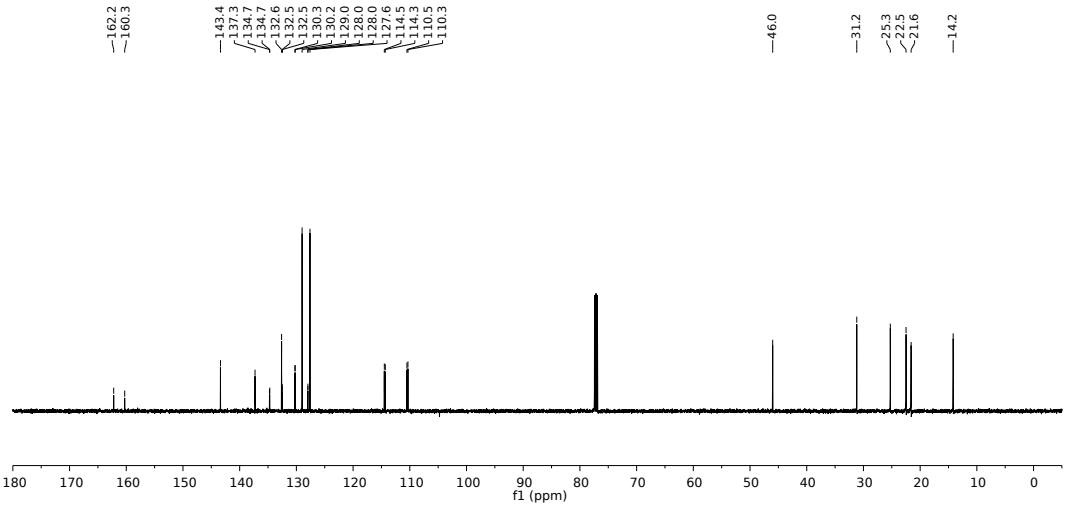

Transmittance [%]
2960.74
2931.38
2865.74
2837.85
2246.37
1614.21
1492.73
1426.81
1394.95
1318.51
1169.63
1128.45
1111.75
1070.29
1014.84
968.37
892.62
836.21
812.00
747.62
706.84
601.38
505.83
437.06
404.26
Wavenumber cm-1

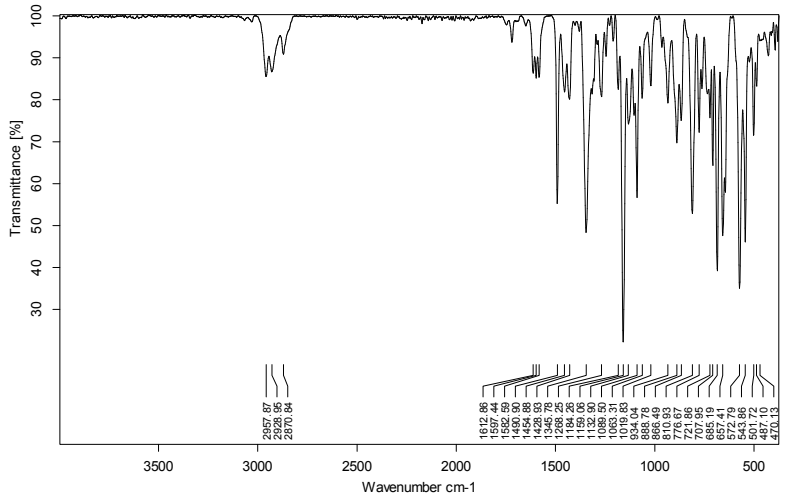

NTs
Me
208
1.84
3.05
2.64
0.90
1.68
1.00
1.00
1.03
1.07
4.92
3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

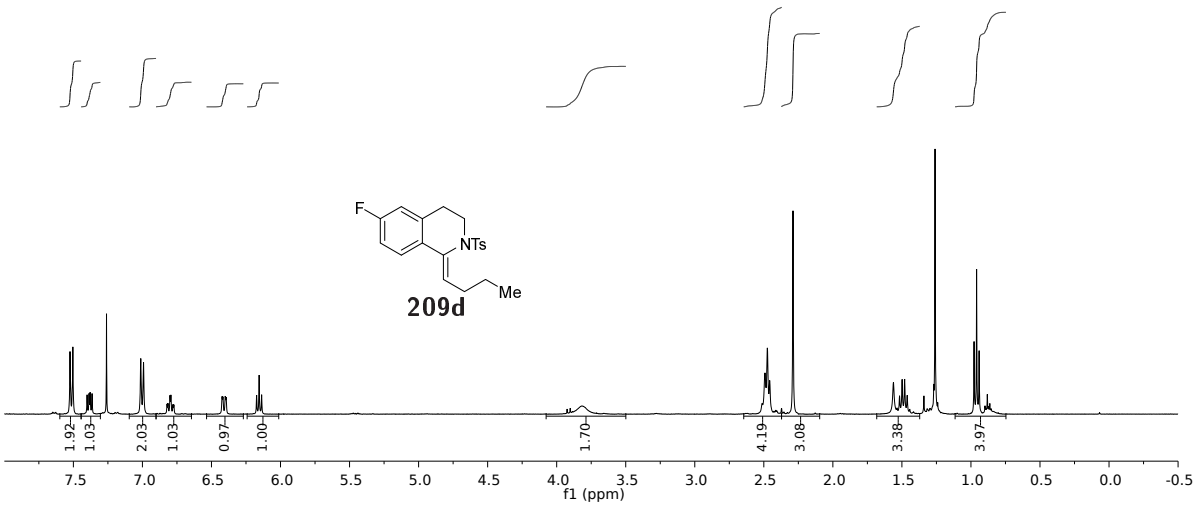

142.4
139.5
135.6
135.4
133.9
129.4
129.2
129.0
127.6
126.9
126.2
58.3
39.6
28.2
25.6
21.2
13.4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

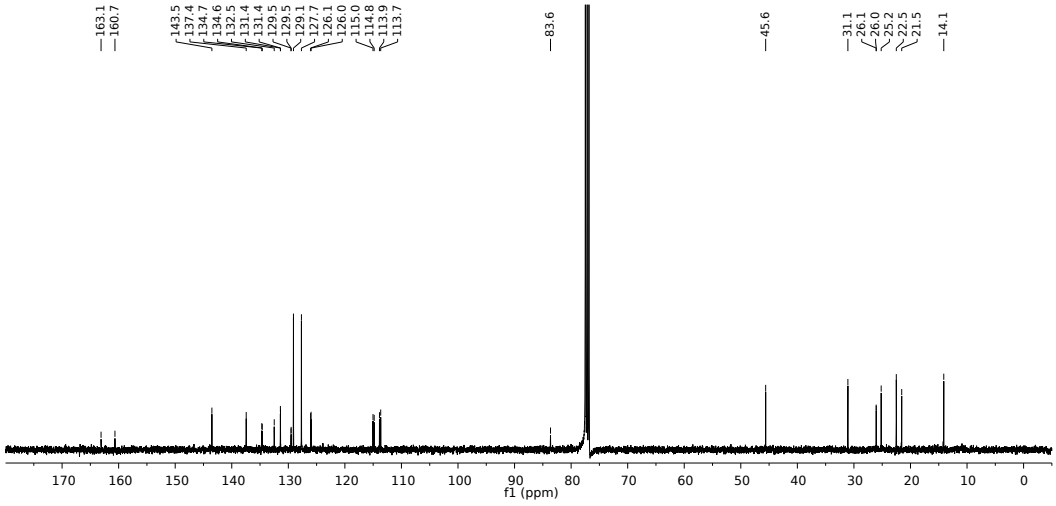

Transmittance [%]
100 90 80 70 60 50 40
2961.42
2928.22
2872.44
1597.97
1493.46
1453.04
1334.27
1275.48
1157.73
1091.31
1014.89
963.83
923.37
813.25
757.15
713.04
663.21
569.16
544.60
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

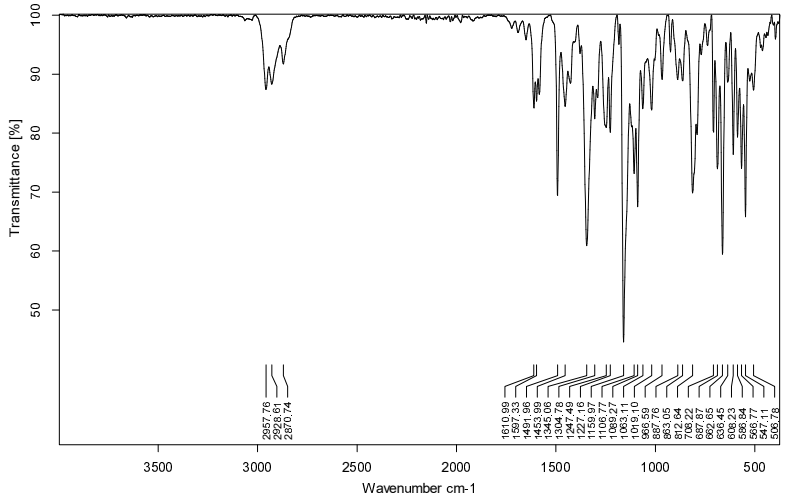

F
NTs
Me
209c
1.90
1.01
1.94
1.91
1.00
1.61
4.10
2.96
2.02
3.03
f1 (ppm)

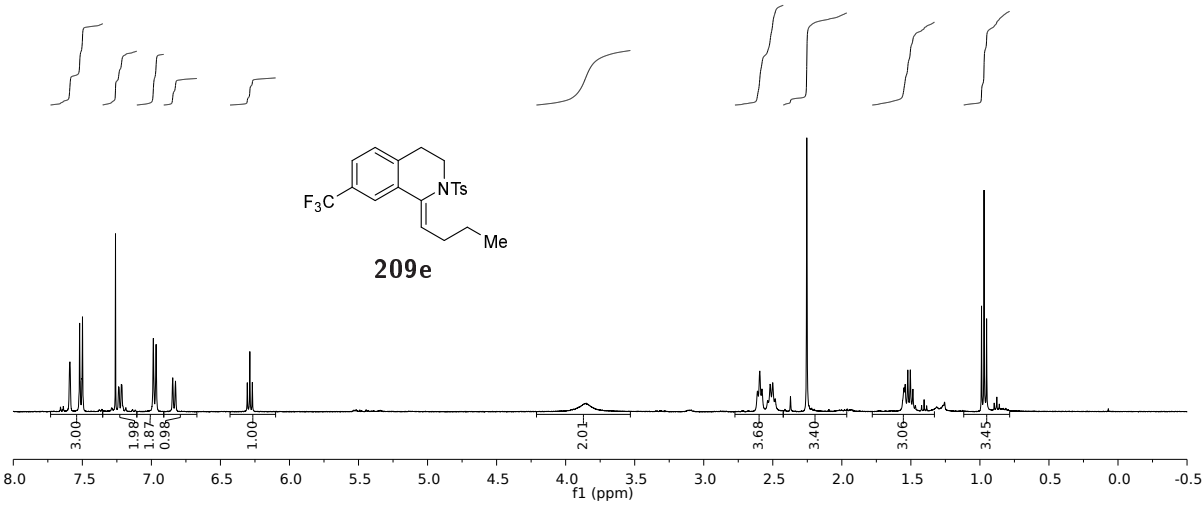

162.2
160.3
143.4
137.3
134.7
134.7
132.6
132.5
132.5
130.3
130.2
129.0
128.0
128.0
127.6
114.5
114.3
110.5
110.3
46.0
31.2
25.3
22.5
21.6
14.2
f1 (ppm)

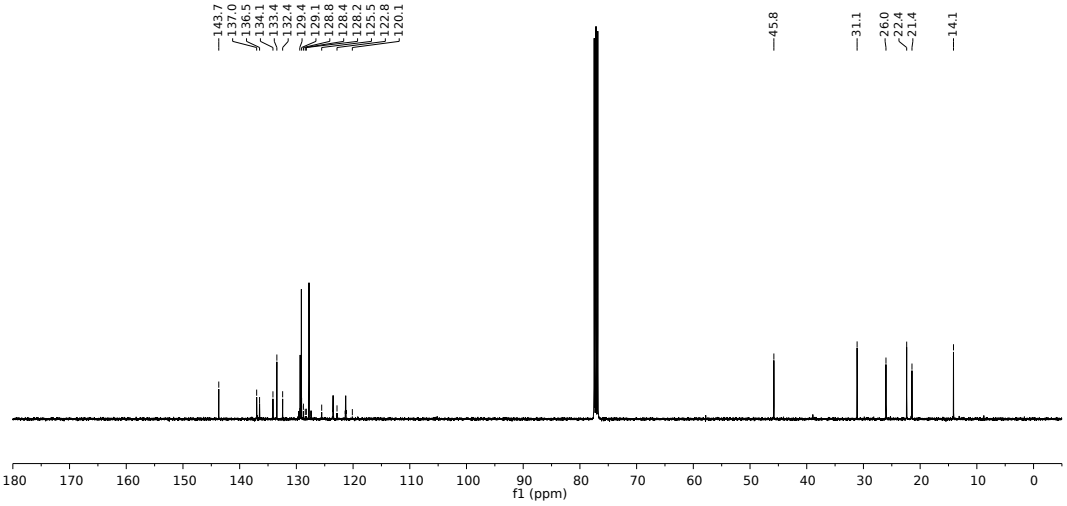

Transmittance [%]
2957.87
2928.95
2870.84
1612.86
1597.44
1582.09
1490.90
1454.88
1428.18
1345.70
1288.25
1184.26
1159.06
1113.00
1089.90
1063.31
1019.83
994.04
938.74
866.49
810.93
776.67
727.66
707.95
685.19
657.41
627.73
543.86
501.72
487.10
470.13
Wavenumber cm-1

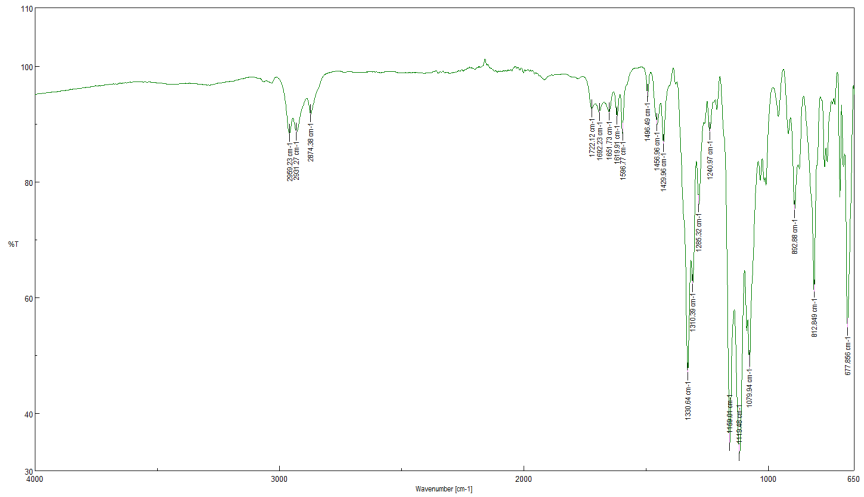

F
NTs
Me
209d
1.92
1.03
2.03
1.03
0.97
1.00
1.70
4.19
3.08
3.38
3.97
f1 (ppm)

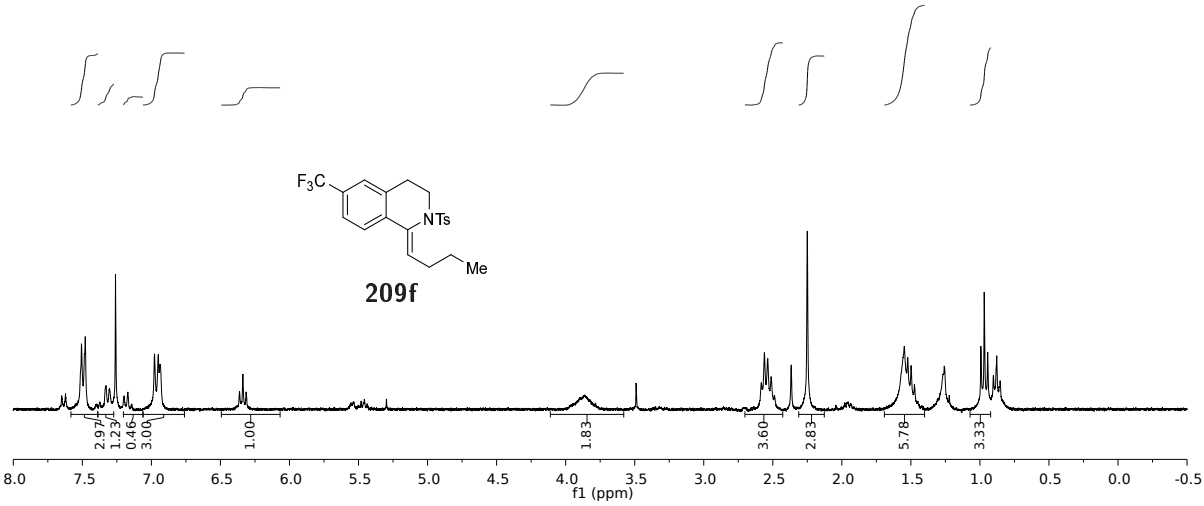

163.1
160.7
143.5
137.4
134.7
134.6
132.5
131.4
131.4
129.5
129.5
129.1
127.7
126.1
126.0
115.0
114.8
113.9
113.7
83.6
45.6
31.1
26.1
26.0
25.2
22.5
21.5
14.1
f1 (ppm)

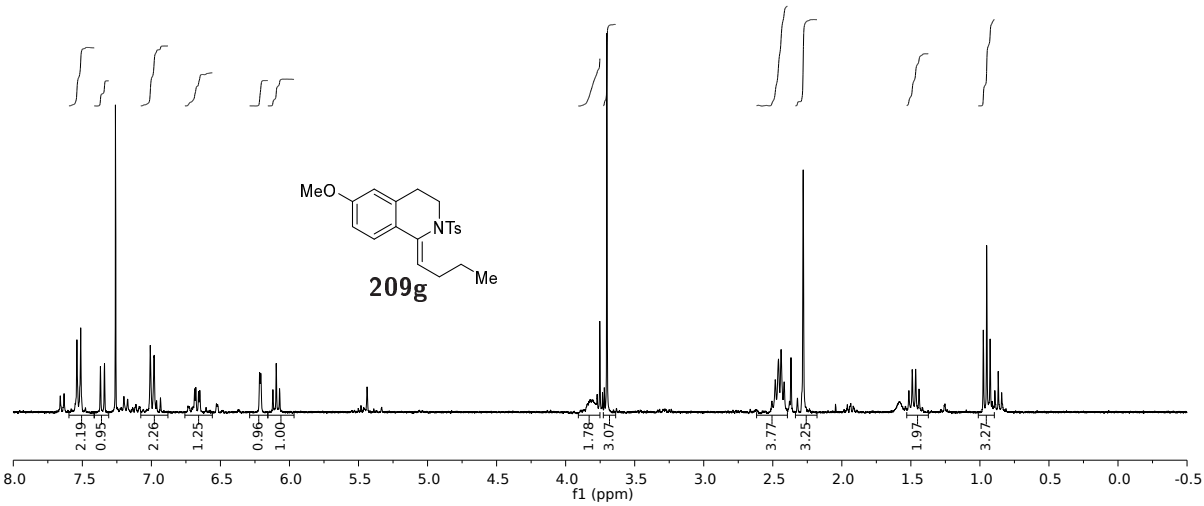

Transmittance [%]
2957.76
2928.61
2870.74
1610.99
1597.33
1491.96
1453.09
1345.10
1304.78
1247.49
1227.18
1159.07
1106.77
1089.27
1063.11
1019.10
969.59
887.76
863.05
812.64
760.22
687.87
662.65
636.45
606.23
586.84
566.77
547.11
500.78
Wavenumber cm-1

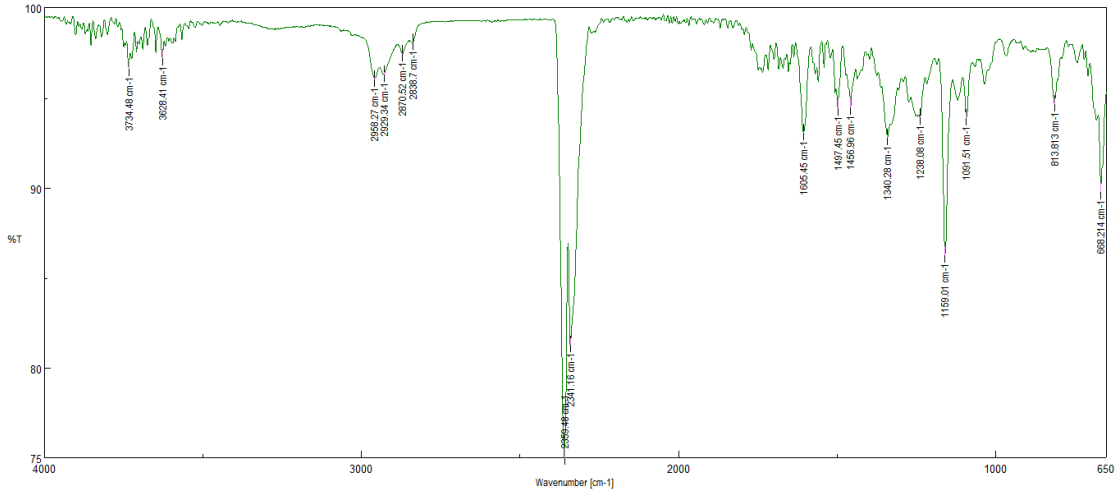

F3C
NTs
Me
209e
3.00
1.98
1.87
0.98
1.00
2.01
3.68
3.40
3.06
3.45
f1 (ppm)

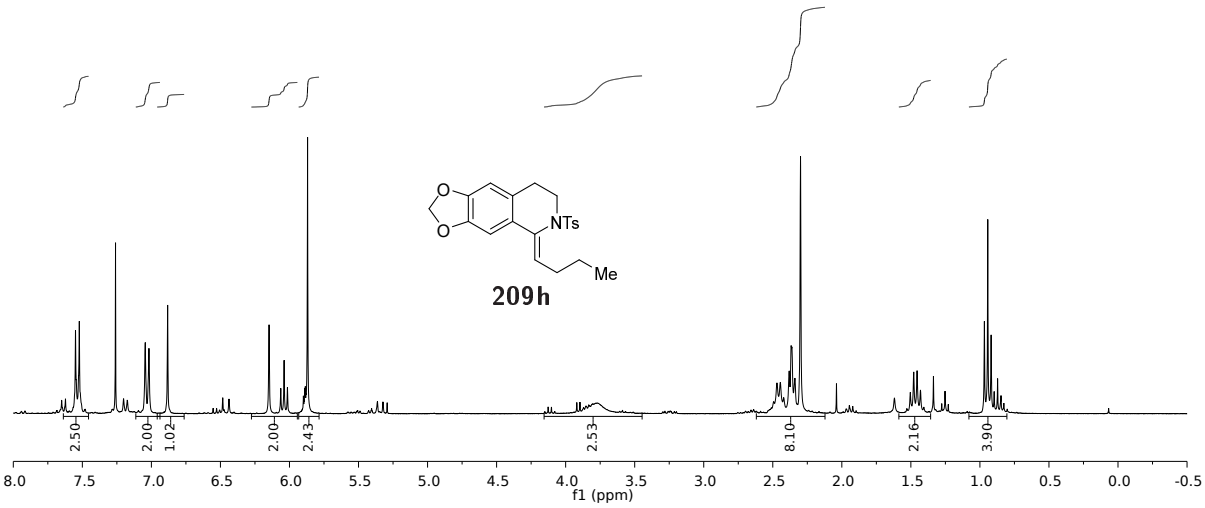

143.7
137.0
136.5
134.1
133.4
132.4
129.4
129.1
128.8
128.4
128.2
125.5
122.8
120.1
45.8
31.1
26.0
22.4
21.4
14.1
f1 (ppm)

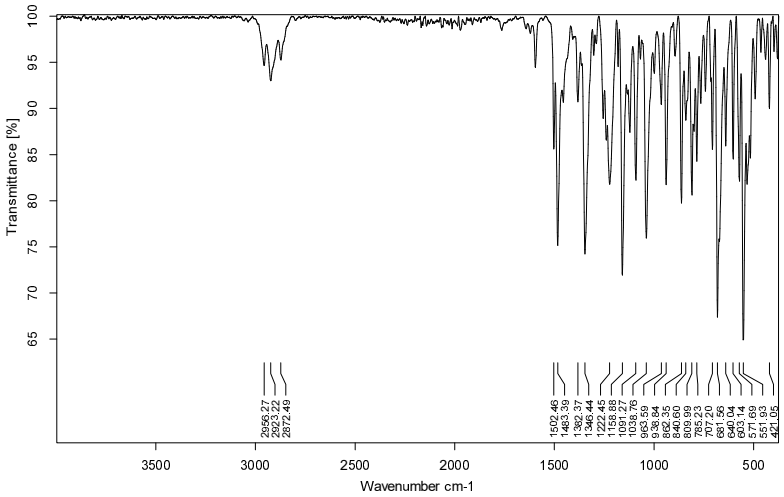

%T
Wavenumber [cm-1]

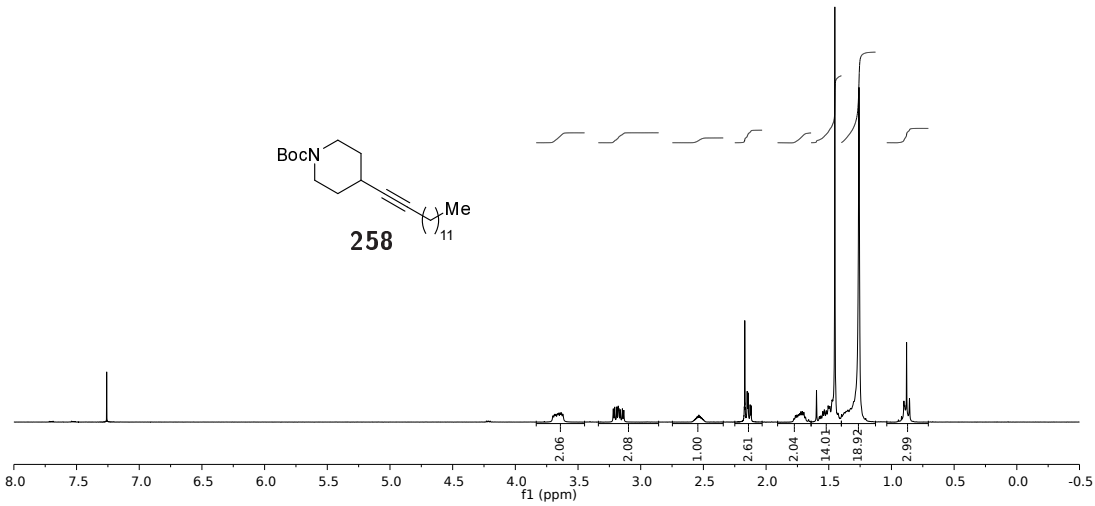

F3C
NTs
Me
209f
2.97
1.23
0.46
3.00
1.00
1.83
3.60
2.83
5.78
3.33
f1 (ppm)

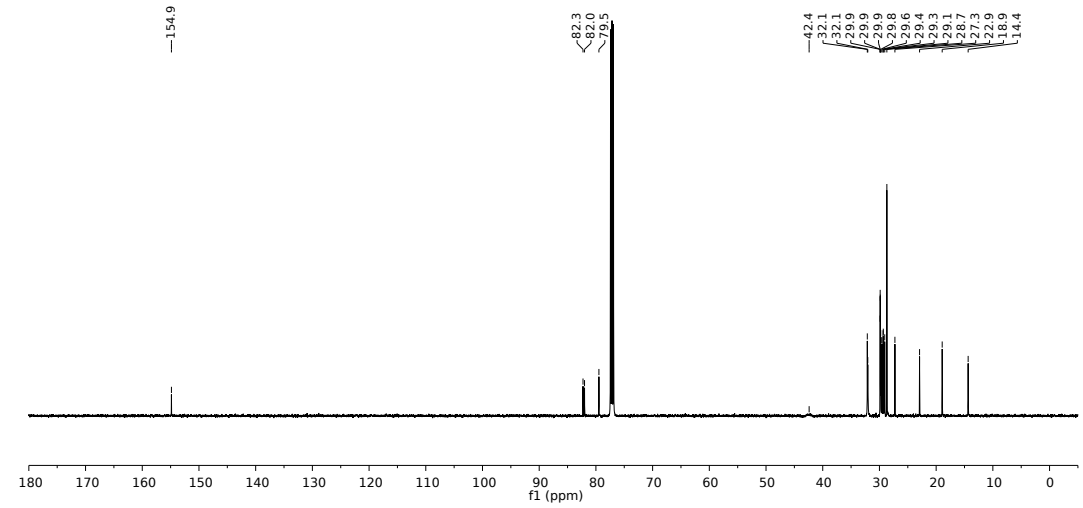

MeO
NTs
Me
209g
2.19
0.95
2.26
1.25
0.96
1.00
1.78
3.07
3.77
3.25
1.97
3.27
f1 (ppm)

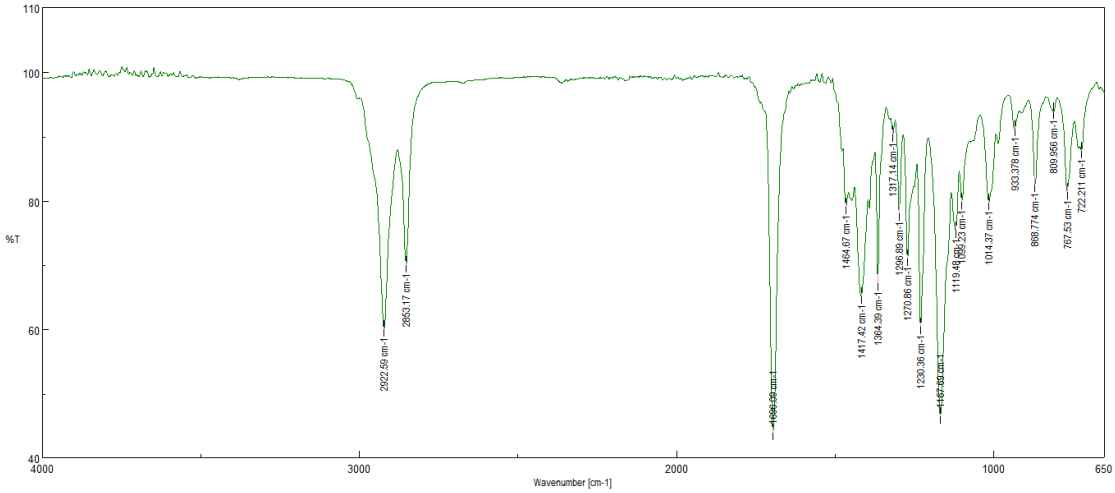

%T
Wavenumber [cm-1]
3734.48 cm-1
3628.41 cm-1
2958.27 cm-1
2929.34 cm-1
2870.52 cm-1
2838.7 cm-1
2341.16 cm-1
1606.45 cm-1
1497.45 cm-1
1456.96 cm-1
1340.28 cm-1
1238.08 cm-1
1189.01 cm-1
1091.51 cm-1
813.913 cm-1
668.214 cm-1

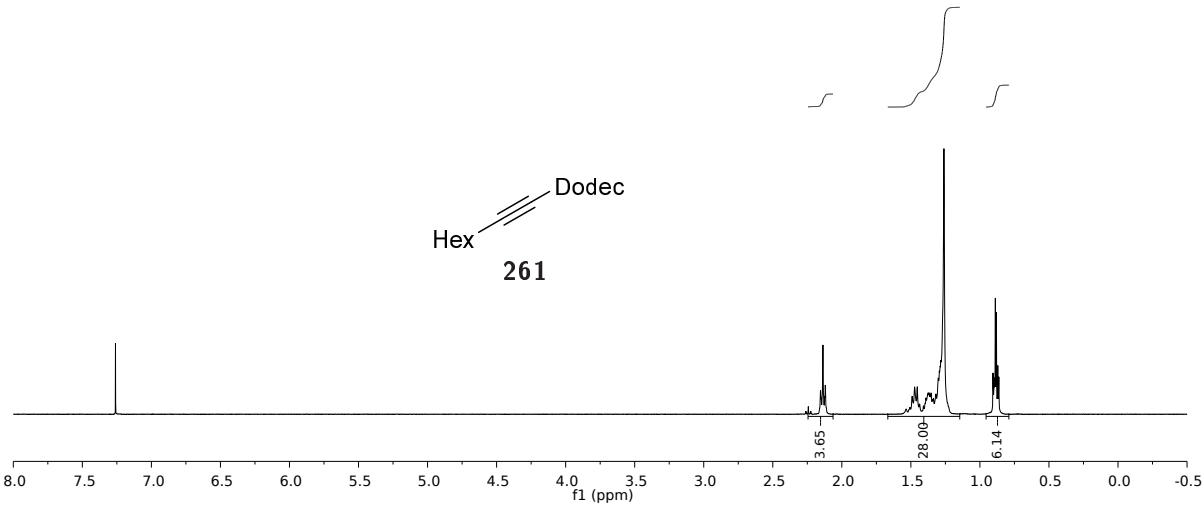

O
O
NTs
Me
209h
2.50
2.00
1.02
2.00
2.43
2.53
8.10
2.16
3.90
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

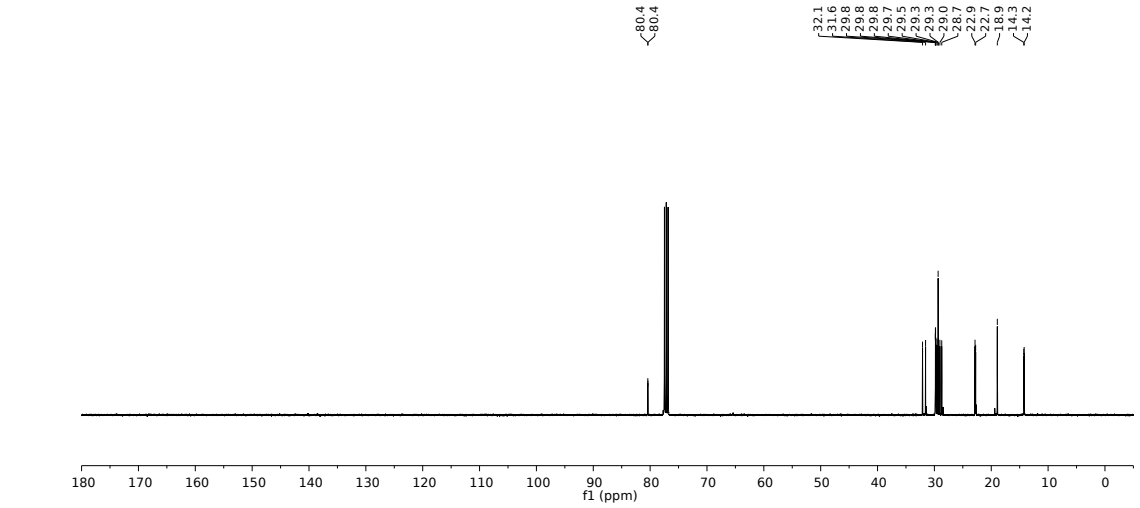

Transmittance [%]
100 95 90 85 80 75 70 65
2956.27
2923.22
2872.49
1502.46
1483.39
1382.37
1346.44
1222.45
1158.88
1091.27
1053.76
963.59
938.84
862.35
840.60
809.69
785.23
707.20
681.56
643.04
620.13
571.69
551.93
421.05
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

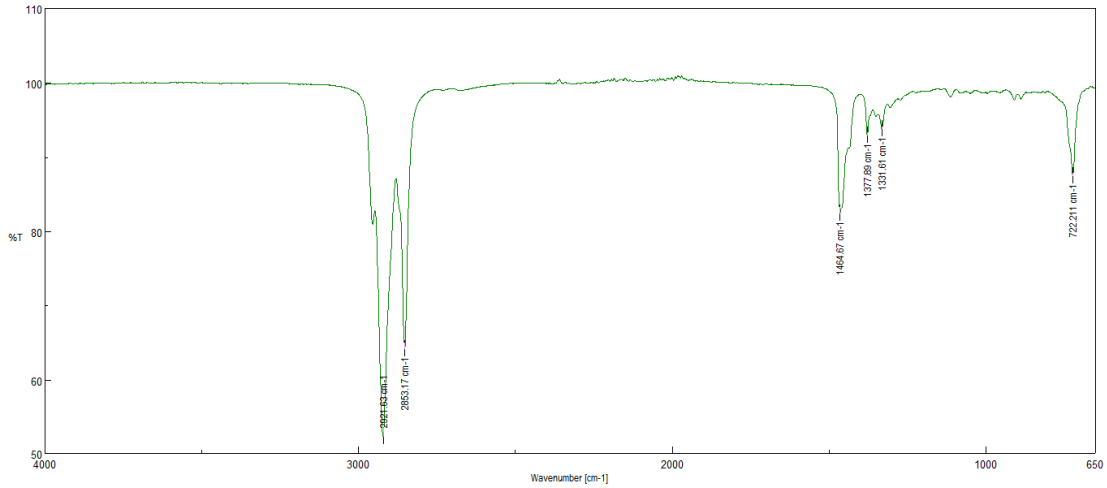

BocN
Me
11
258
2.06
2.08
1.00
2.61
2.04
14.01
18.92
2.99
f1 (ppm)

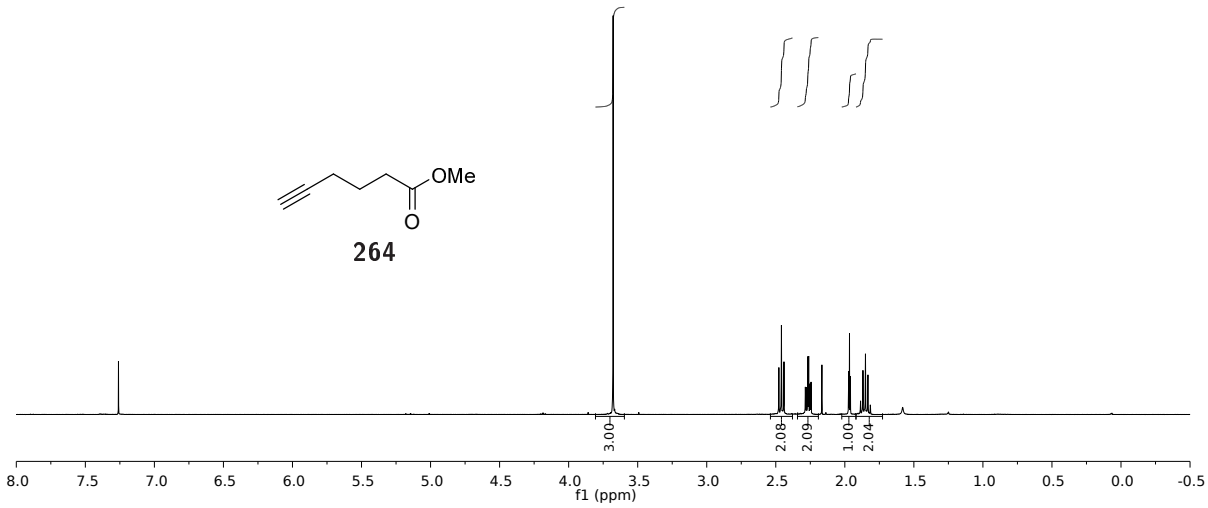

154.9
82.3
82.0
79.5
42.4
32.1
32.1
29.9
29.9
29.9
29.8
29.6
29.4
29.3
29.1
28.7
27.3
22.9
18.9
14.4
f1 (ppm)

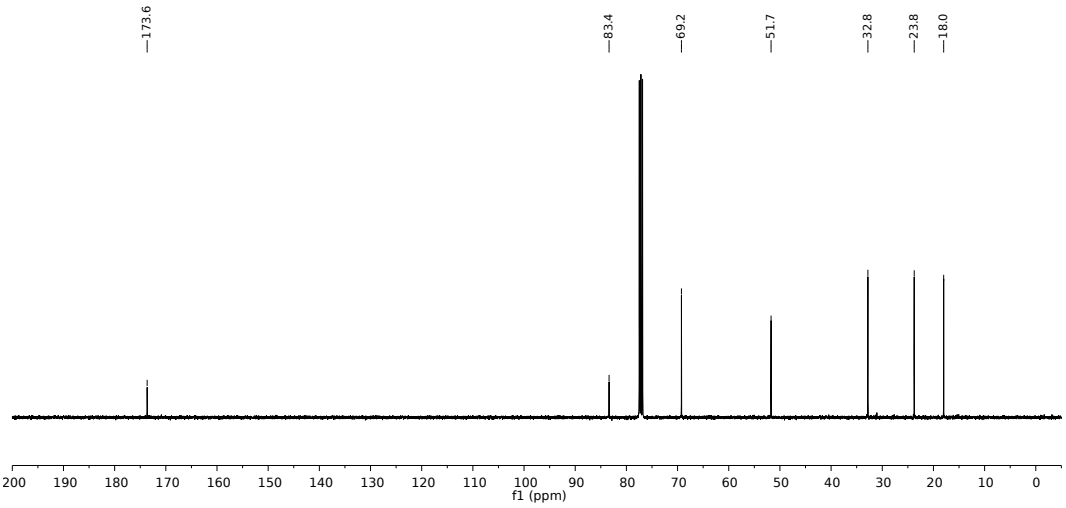

%T
2922.59 cm-1
2853.17 cm-1
1464.87 cm-1
1417.42 cm-1
1364.39 cm-1
1317.14 cm-1
1270.86 cm-1
1230.36 cm-1
1014.37 cm-1
933.378 cm-1
868.774 cm-1
809.956 cm-1
767.53 cm-1
722.211 cm-1
Wavenumber [cm-1]

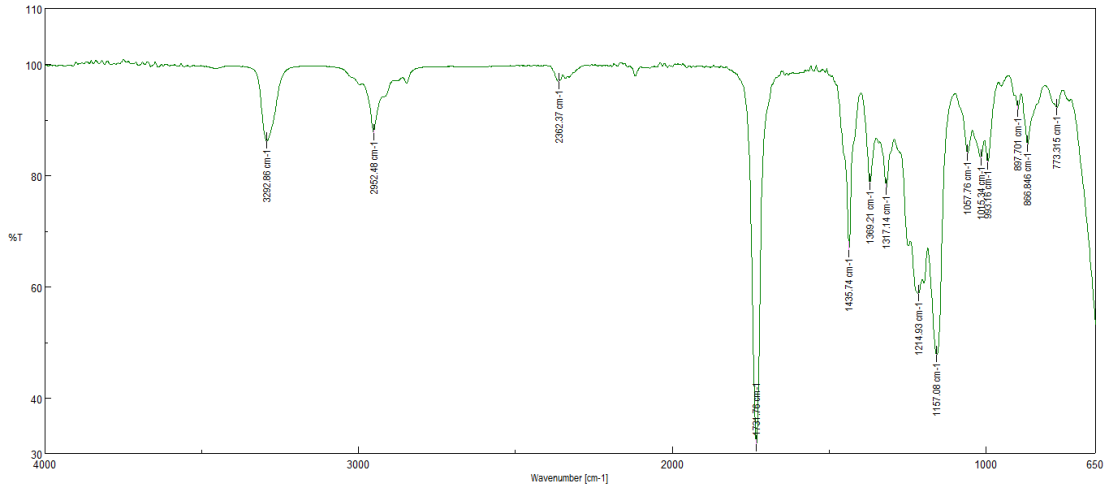

Dodec
Hex
261
3.65
28.00
6.14
f1 (ppm)

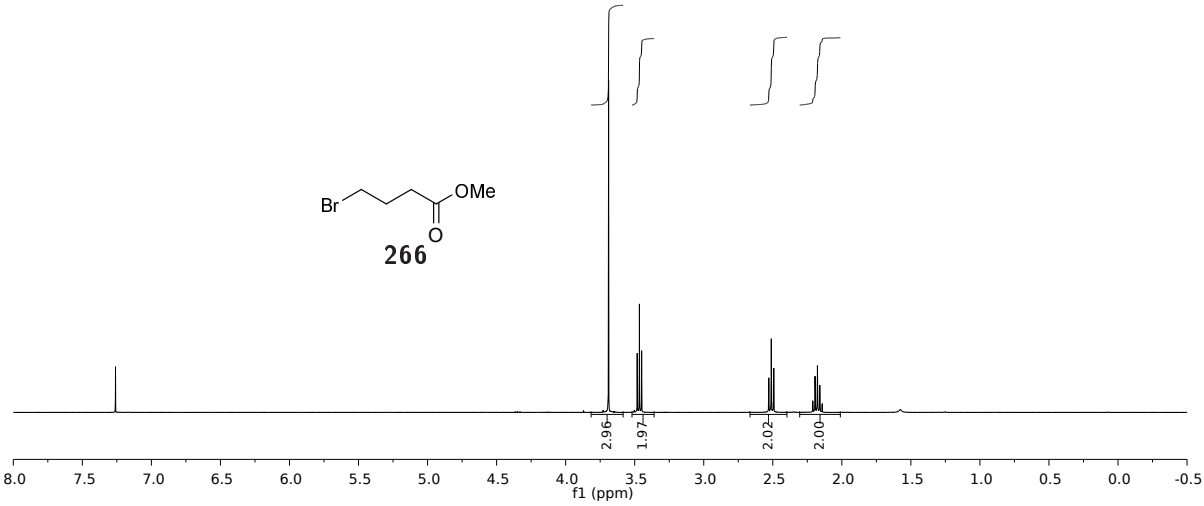

80.4
80.4
32.1
31.6
29.8
29.8
29.8
29.7
29.5
29.3
29.3
29.0
28.7
22.9
22.7
18.9
14.3
14.2
f1 (ppm)

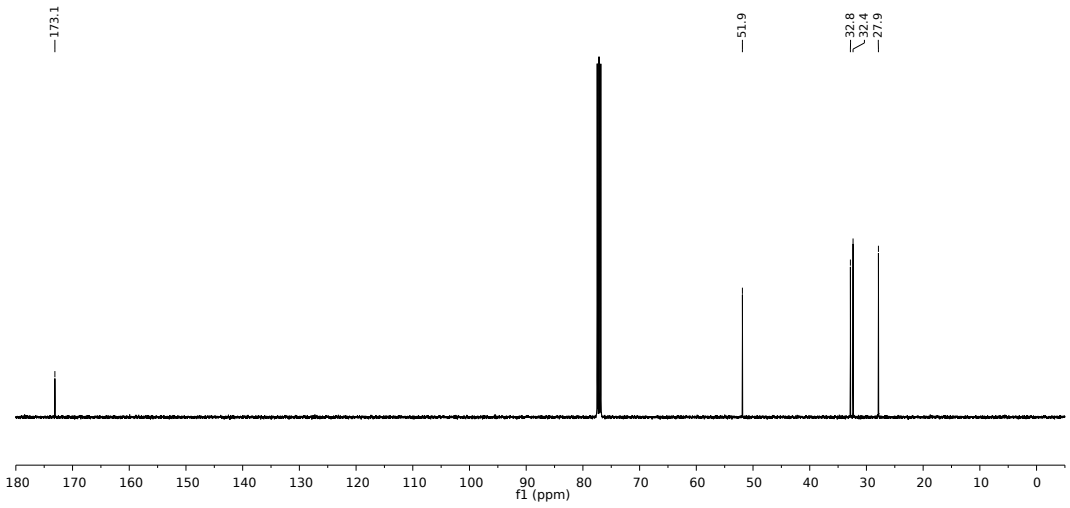

%T
2921.63 cm-1
2853.17 cm-1
1464.67 cm-1
1377.89 cm-1
1331.61 cm-1
722.211 cm-1
Wavenumber [cm-1]

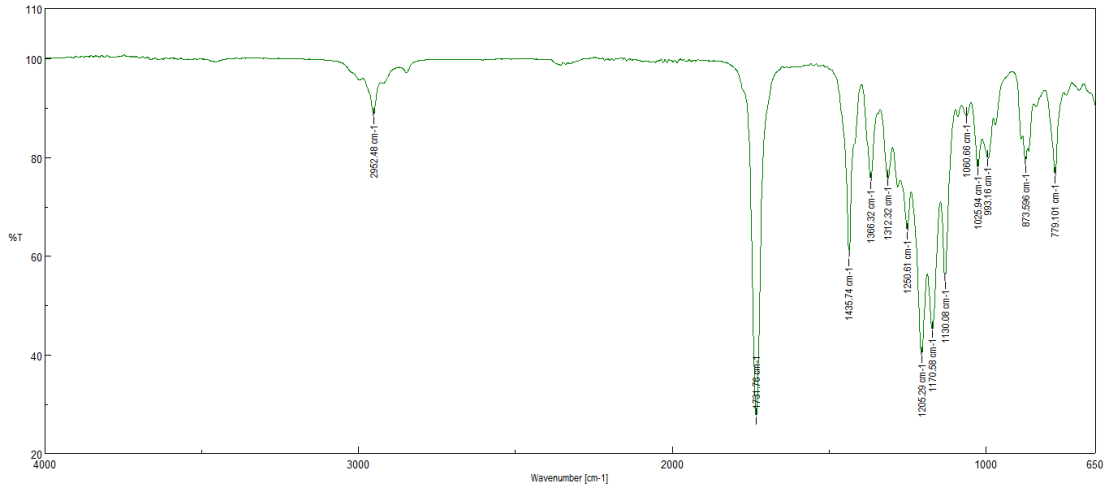

OMe
O
264
3.00
2.08
2.09
1.00
2.04
f1 (ppm)

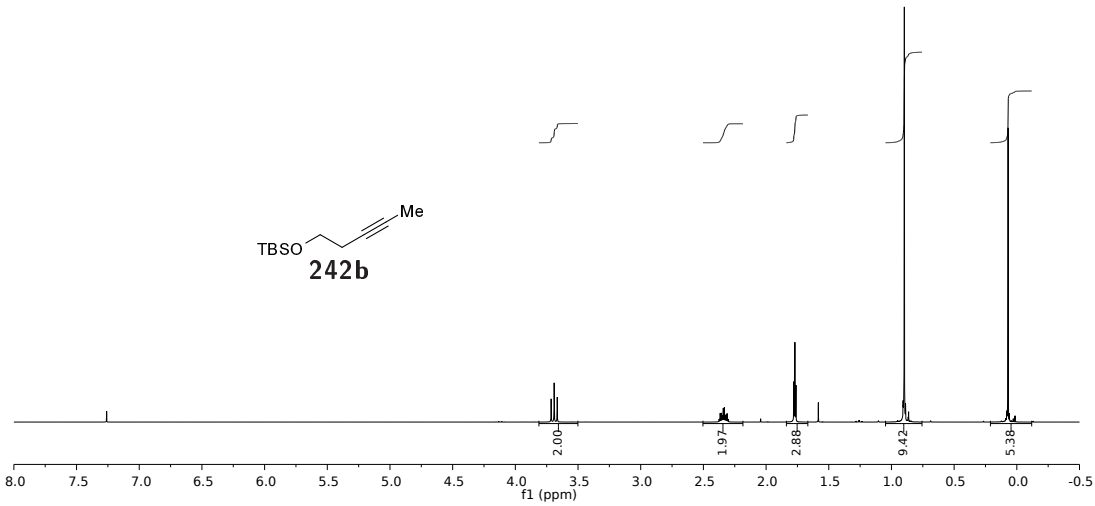

173.6
83.4
69.2
51.7
32.8
23.8
18.0
f1 (ppm)

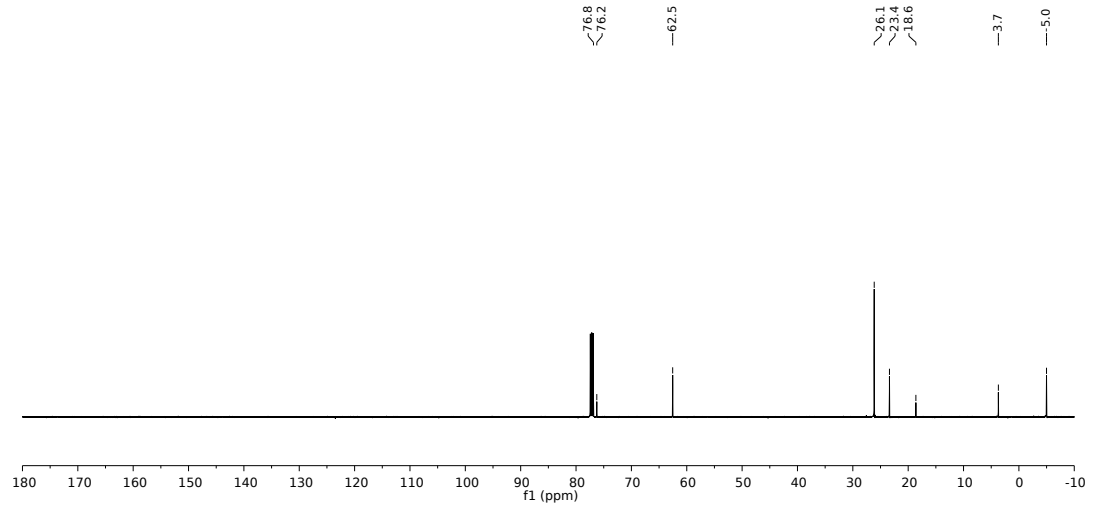

%T
Wavenumber [cm-1]
3292.86 cm-1
2952.48 cm-1
2362.37 cm-1
1435.74 cm-1
1369.21 cm-1
1317.14 cm-1
1214.93 cm-1
1157.08 cm-1
1057.76 cm-1
897.701 cm-1
866.846 cm-1
773.315 cm-1

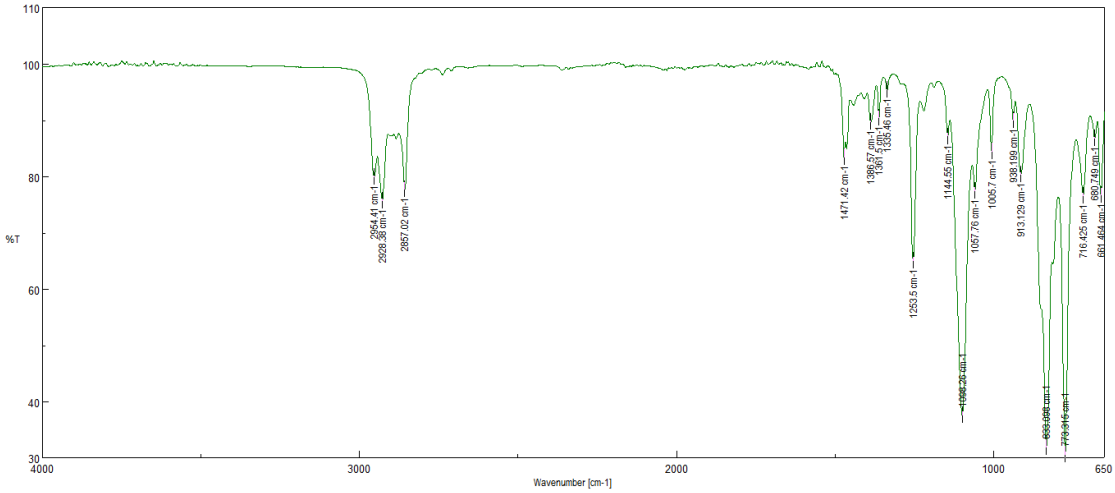

Br
OMe
O
266
2.96
1.97
2.02
2.00
f1 (ppm)

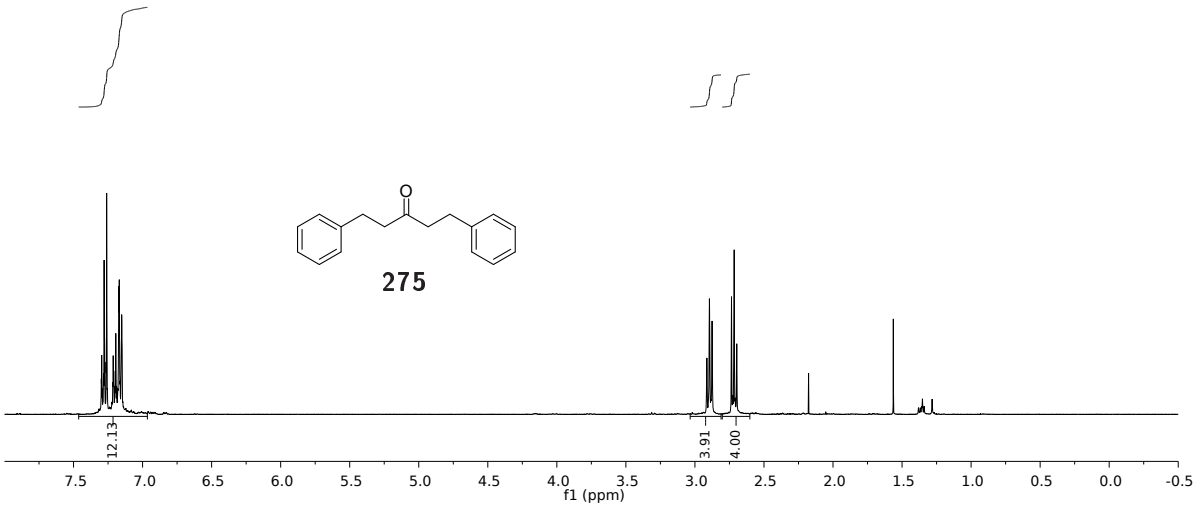

173.1
51.9
32.8
32.4
27.9
f1 (ppm)

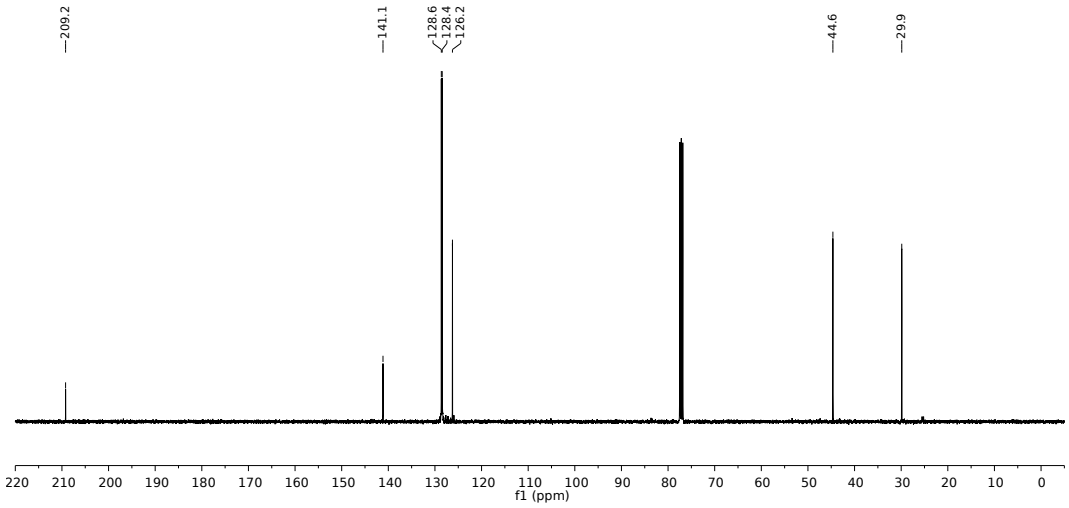

%T
2952.48 cm-1
1435.74 cm-1
1366.32 cm-1
1312.32 cm-1
1260.61 cm-1
1205.29 cm-1
1170.89 cm-1
1130.08 cm-1
1060.66 cm-1
1025.94 cm-1
993.16 cm-1
873.598 cm-1
779.101 cm-1
Wavenumber [cm-1]

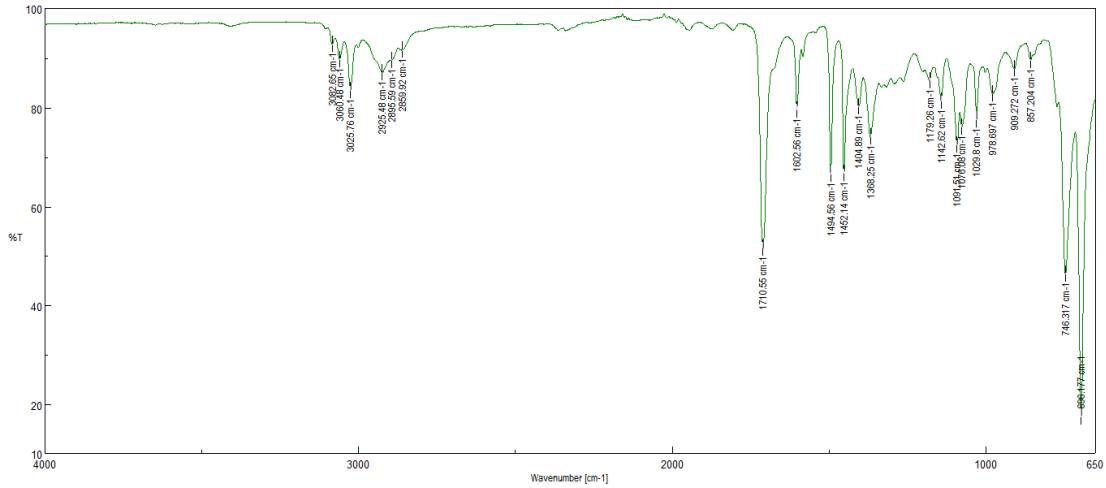

Me
TBSO
242b
2.00
1.97
2.88
9.42
5.38
f1 (ppm)

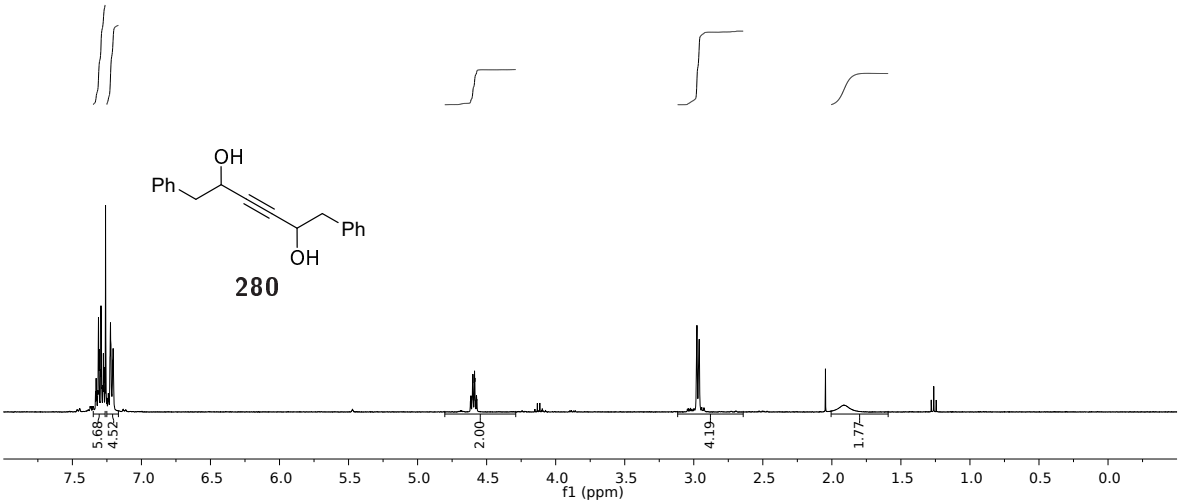

76.8
76.2
62.5
26.1
23.4
18.6
3.7
-5.0
f1 (ppm)

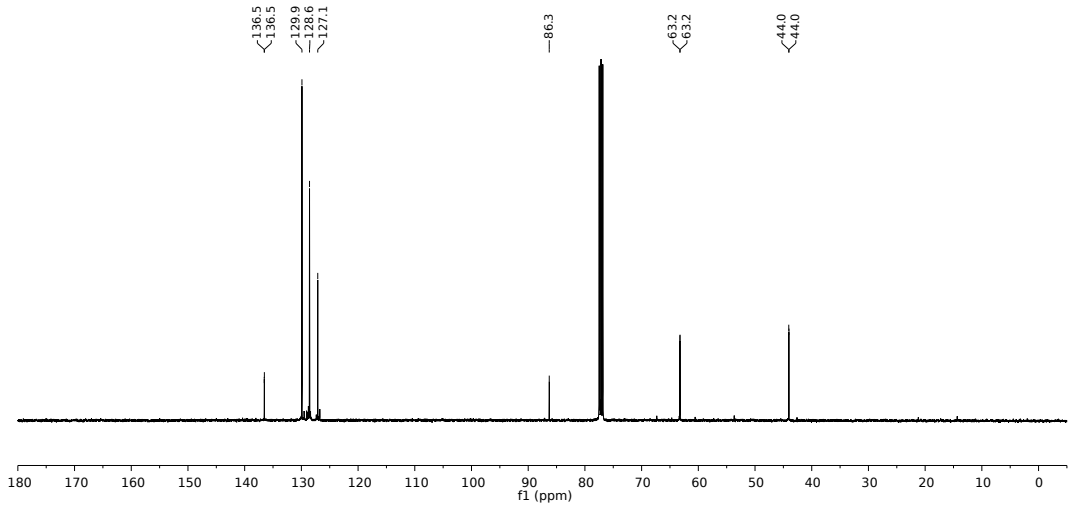

%T
2954.41 cm-1
2928.36 cm-1
2857.02 cm-1
1471.42 cm-1
1386.67 cm-1
1361.5 cm-1
1335.46 cm-1
1253.5 cm-1
1144.55 cm-1
1057.76 cm-1
1005.7 cm-1
913.129 cm-1
838.199 cm-1
716.425 cm-1
Wavenumber [cm-1]

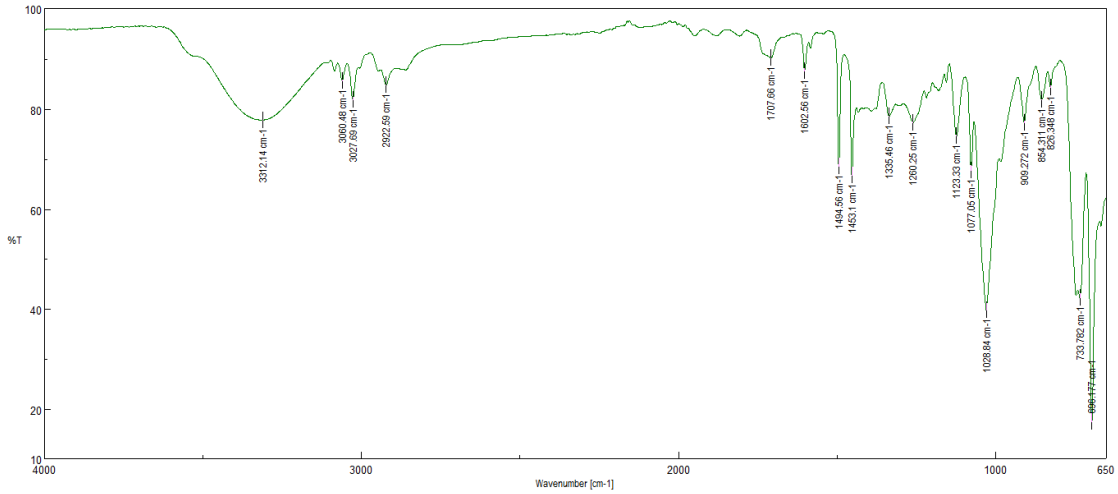

275
12.13
3.91
4.00
f1 (ppm)

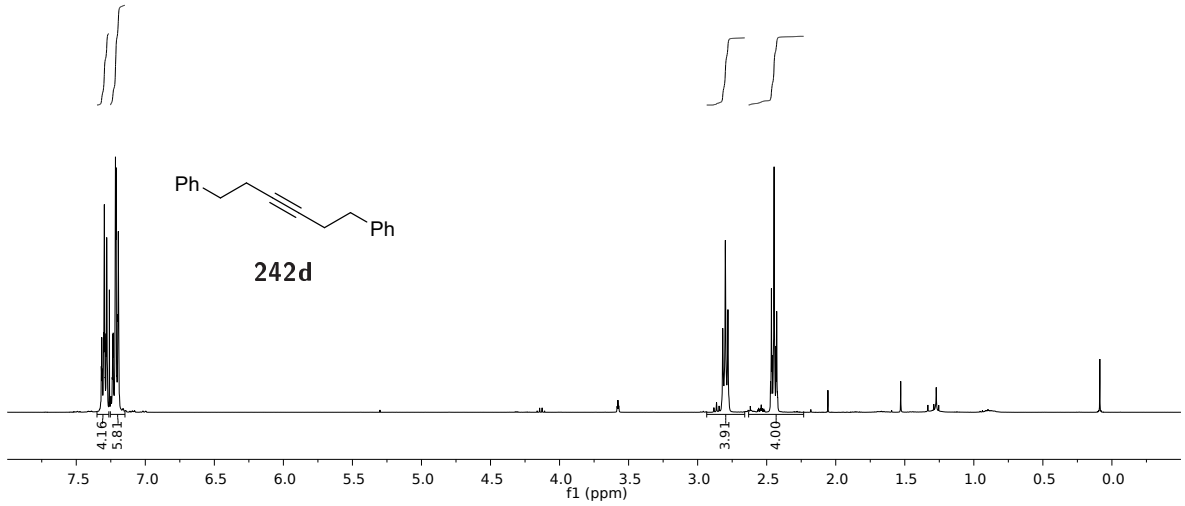

209.2
141.1
128.6
128.4
126.2
44.6
29.9
f1 (ppm)

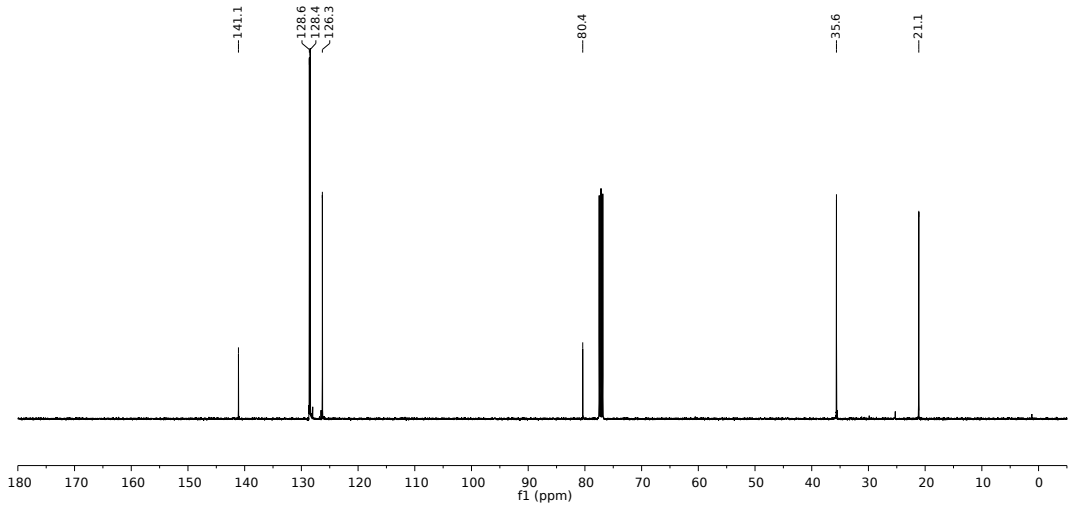

%T
Wavenumber [cm-1]
1710.55 cm-1
1602.56 cm-1
1494.56 cm-1
1452.14 cm-1
1404.89 cm-1
1368.25 cm-1
1179.26 cm-1
1142.62 cm-1
1029.8 cm-1
978.697 cm-1
909.272 cm-1
857.204 cm-1
746.317 cm-1

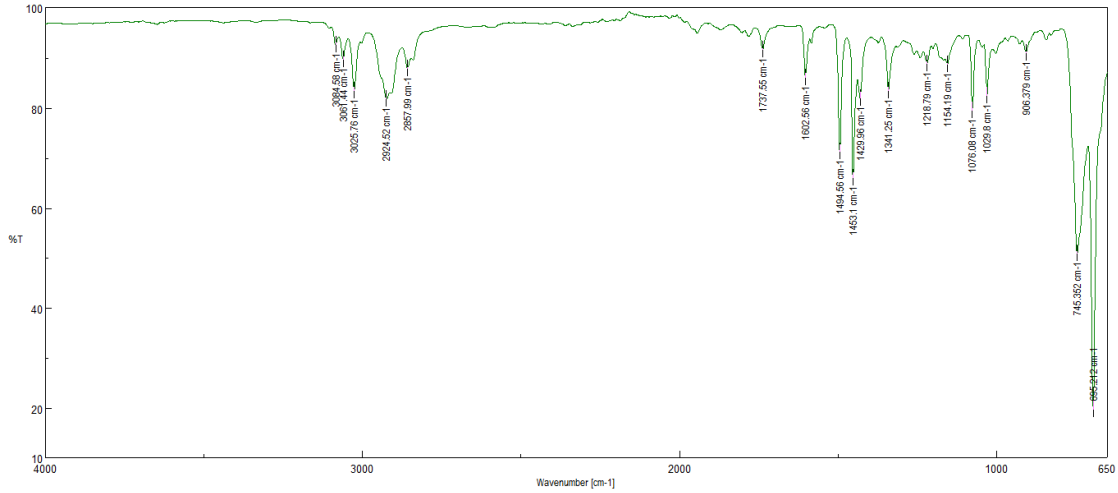

OH
Ph
Ph
OH
280
5.68
4.52
2.00
4.19
1.77
f1 (ppm)

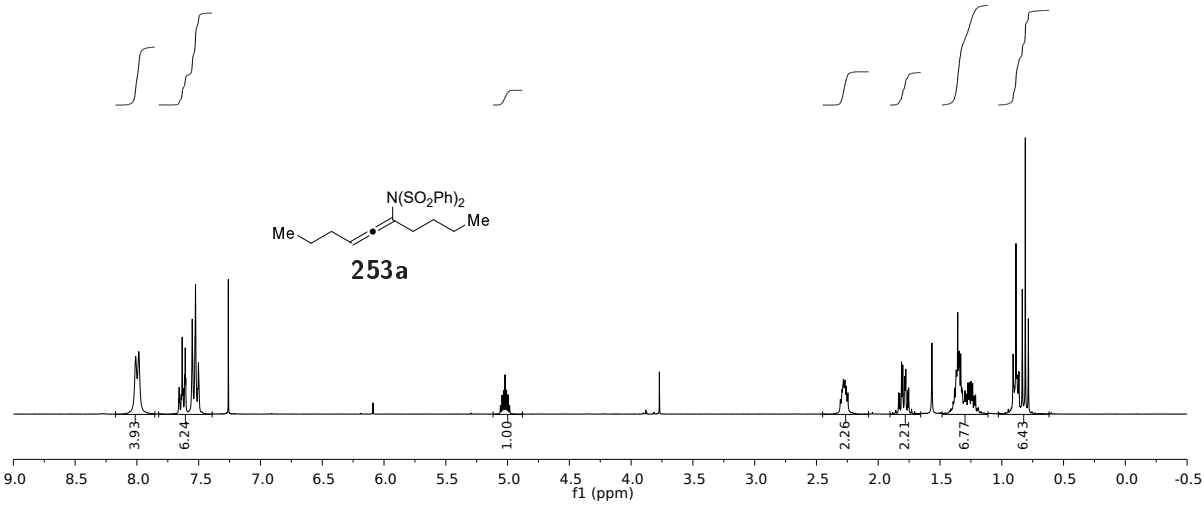

136.5
136.5
129.9
128.6
127.1
86.3
63.2
63.2
44.0
44.0
f1 (ppm)

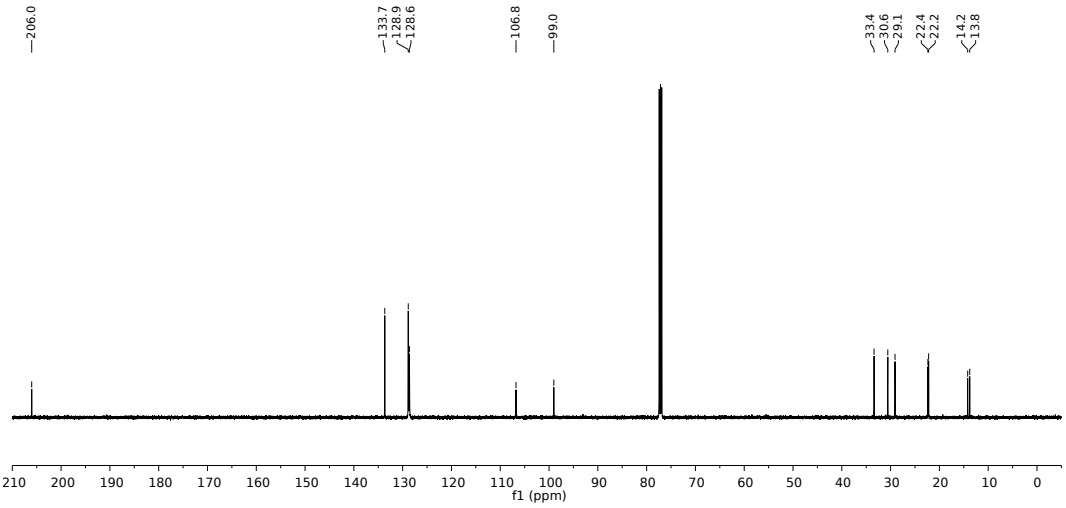

%T
3312.14 cm-1
3060.48 cm-1
3027.69 cm-1
2922.59 cm-1
1707.66 cm-1
1602.56 cm-1
1494.56 cm-1
1453.1 cm-1
1335.46 cm-1
1260.25 cm-1
1123.33 cm-1
1077.05 cm-1
1028.84 cm-1
909.272 cm-1
864.911 cm-1
826.346 cm-1
733.782 cm-1
690.117 cm-1
Wavenumber [cm-1]

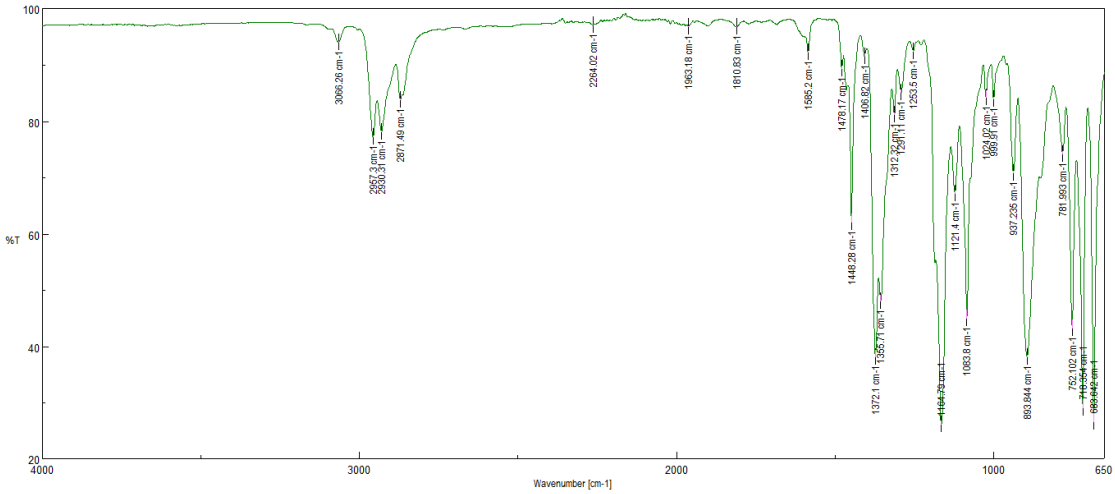

Ph
Ph
242d
4.16
5.81
3.91
4.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

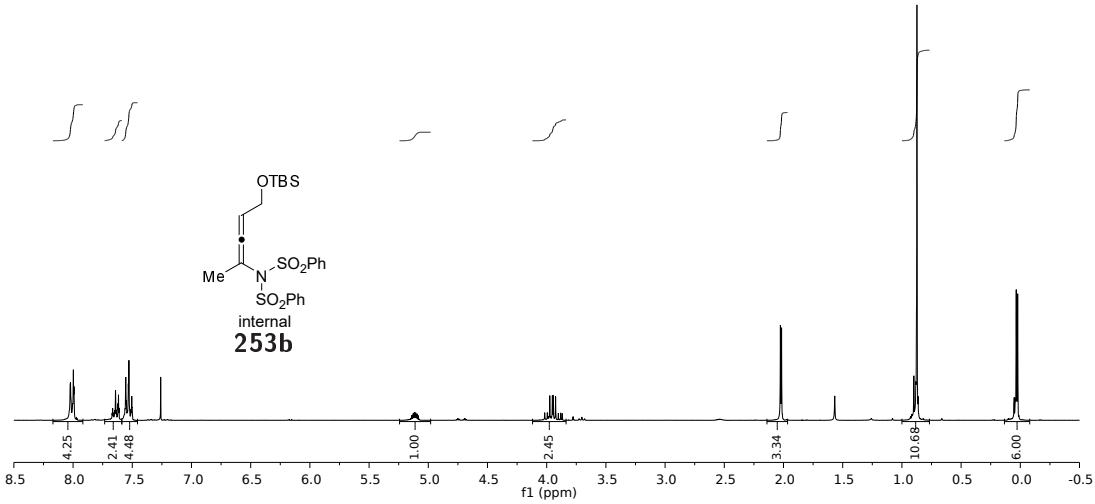

141.1
128.6
128.4
126.3
80.4
35.6
21.1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

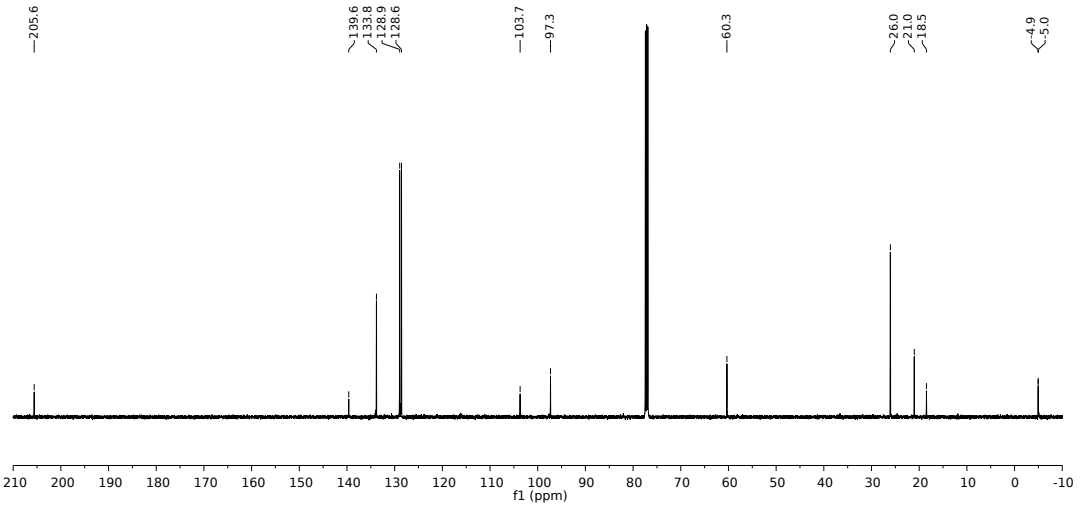

%T
100
80
60
40
20
10
4000
3000
2000
1000
650
Wavenumber [cm-1]
3084.58 cm-1
3061.44 cm-1
3025.76 cm-1
2924.52 cm-1
2857.99 cm-1
1737.55 cm-1
1602.58 cm-1
1494.56 cm-1
1453.1 cm-1
1429.96 cm-1
1341.25 cm-1
1218.79 cm-1
1154.19 cm-1
1076.08 cm-1
1029.6 cm-1
906.379 cm-1
745.352 cm-1
695.212 cm-1

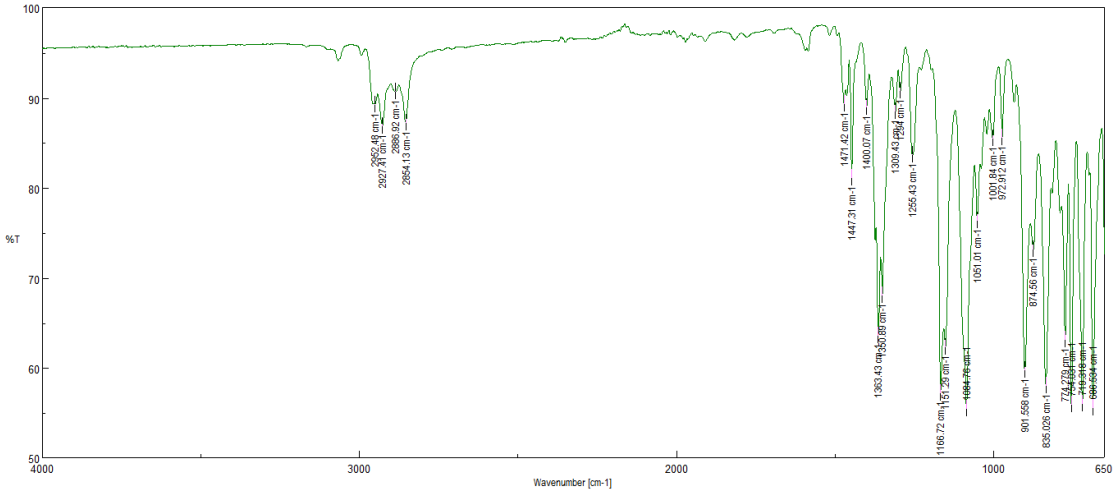

N(SO2Ph)2
Me
Me
253a
3.93
6.24
1.00
2.26
2.21
6.77
6.43
f1 (ppm)

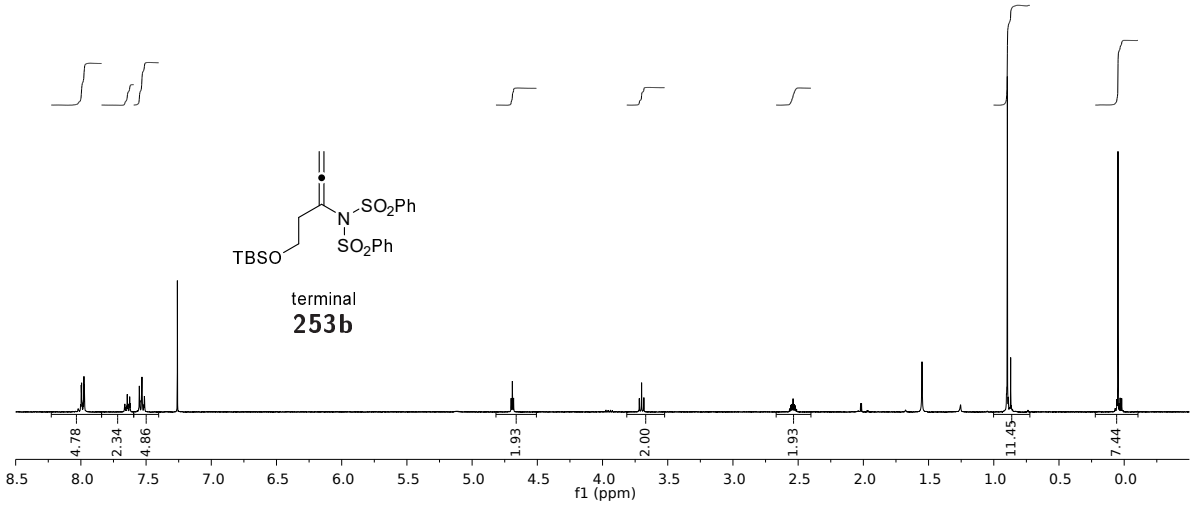

206.0
133.7
128.9
128.6
106.8
99.0
33.4
30.6
29.1
22.4
22.2
14.2
13.8
f1 (ppm)

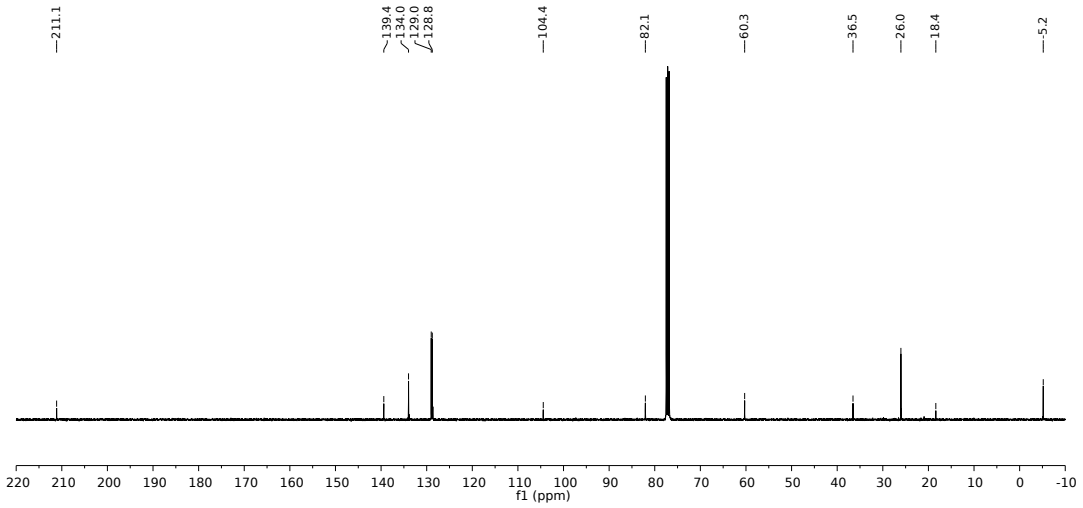

%T
Wavenumber [cm-1]
3066.26 cm-1
2957.3 cm-1
2930.31 cm-1
2871.49 cm-1
2264.02 cm-1
1963.18 cm-1
1810.83 cm-1
1585.2 cm-1
1478.17 cm-1
1448.28 cm-1
1406.82 cm-1
1372.1 cm-1
1312.32 cm-1
1253.5 cm-1
1121.4 cm-1
1083.8 cm-1
937.235 cm-1
893.844 cm-1
781.993 cm-1
752.102 cm-1

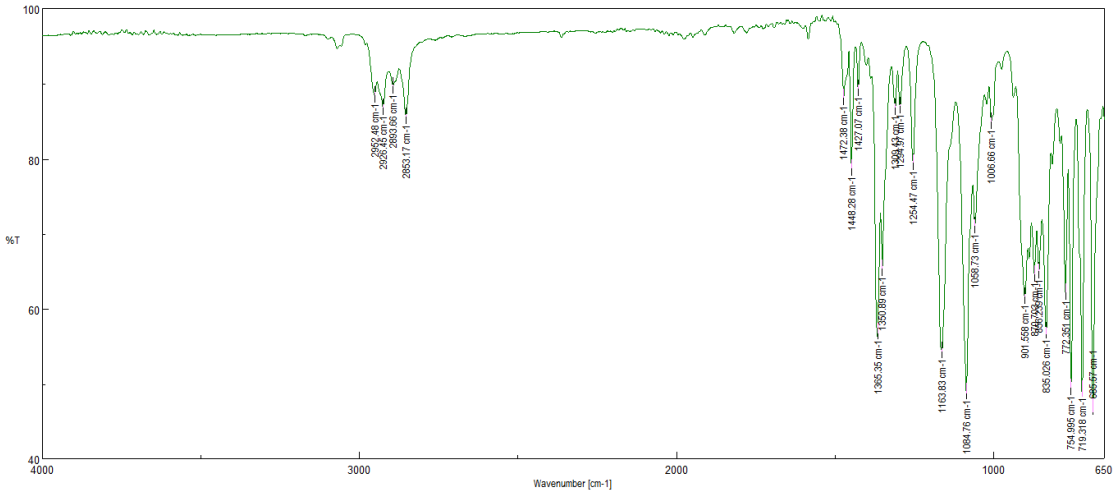

OTBS
Me
N
SO2Ph
SO2Ph
internal
253b
4.25
2.41
4.48
1.00
2.45
3.34
10.68
6.00
f1 (ppm)

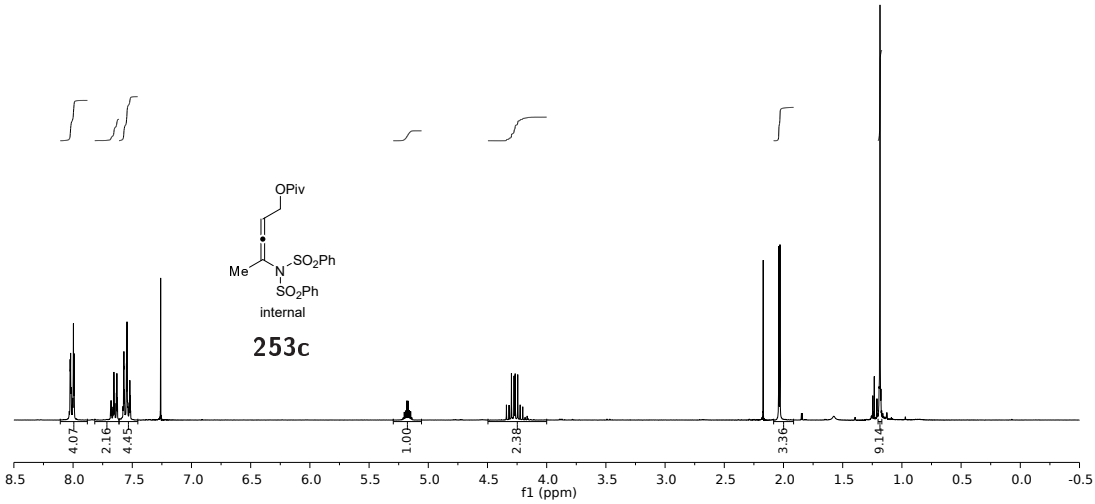

205.6
139.6
133.8
128.9
128.6
103.7
97.3
60.3
26.0
21.0
18.5
4.9
5.0
f1 (ppm)

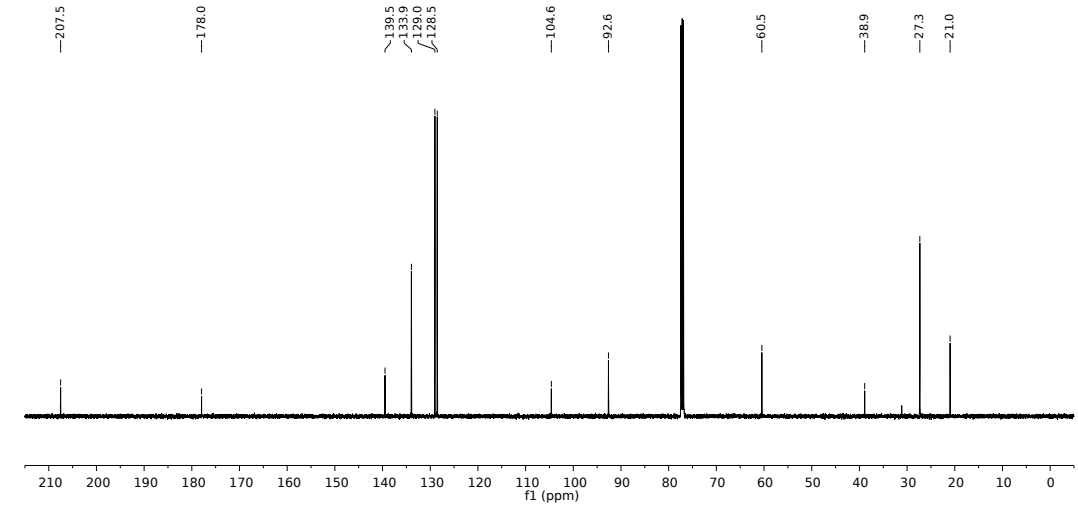

%T
2952.49 cm-1
2927.41 cm-1
2888.92 cm-1
2854.13 cm-1
1471.42 cm-1
1447.31 cm-1
1400.07 cm-1
1363.43 cm-1
1300.43 cm-1
1255.43 cm-1
1166.72 cm-1
1151.29 cm-1
1051.01 cm-1
1001.84 cm-1
972.912 cm-1
901.568 cm-1
874.56 cm-1
835.026 cm-1
774.279 cm-1
Wavenumber [cm-1]

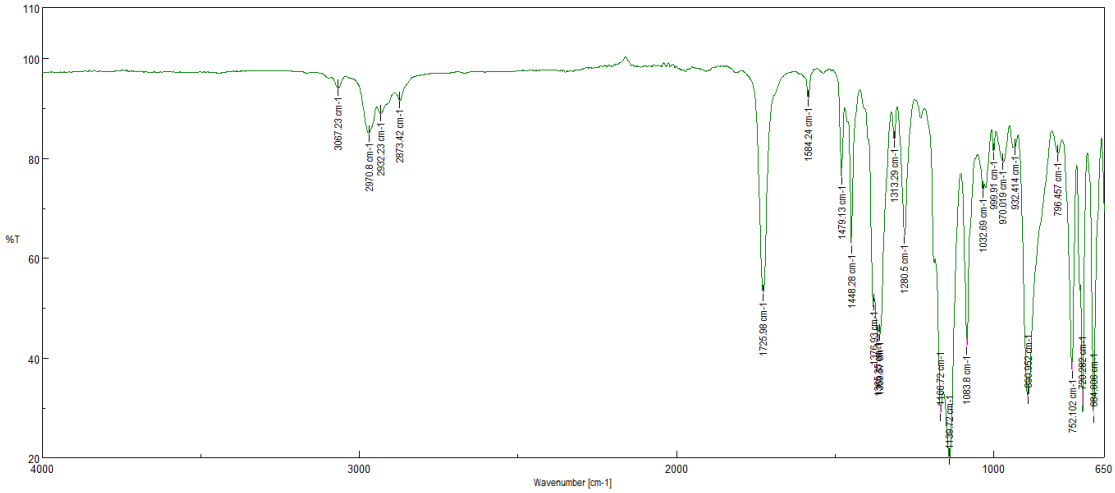

SO2Ph
N
SO2Ph
TBSO
terminal
253b
4.78
2.34
4.86
1.93
2.00
1.93
11.45
7.44
f1 (ppm)

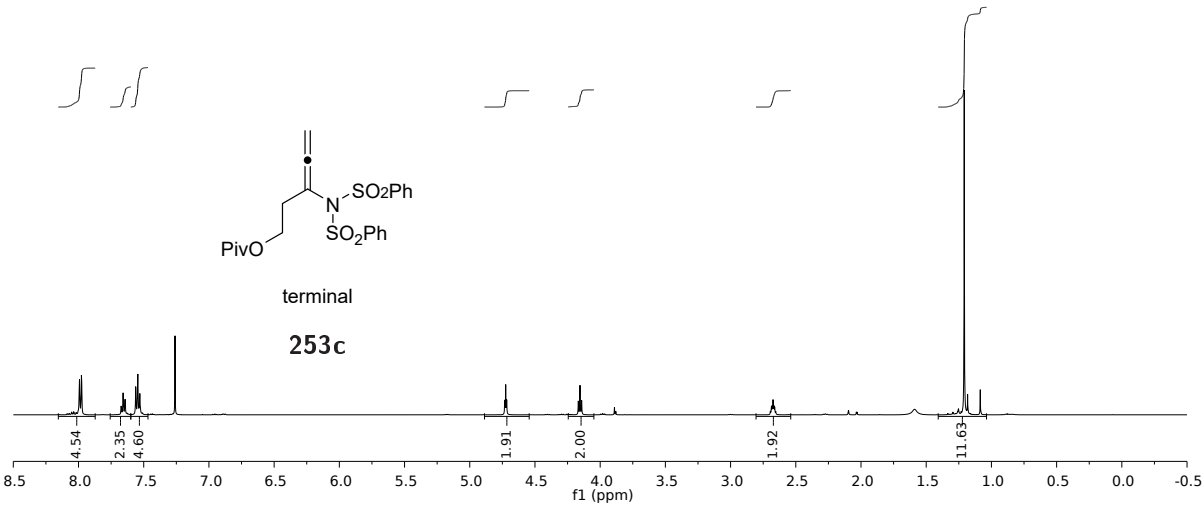

211.1
139.4
134.0
129.0
128.8
104.4
82.1
60.3
36.5
26.0
18.4
5.2
f1 (ppm)

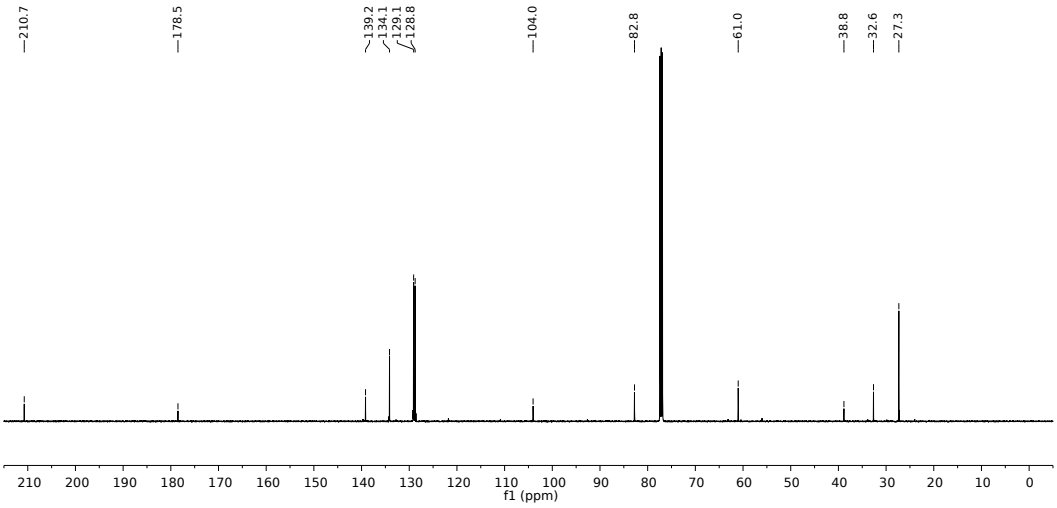

%T
Wavenumber [cm-1]

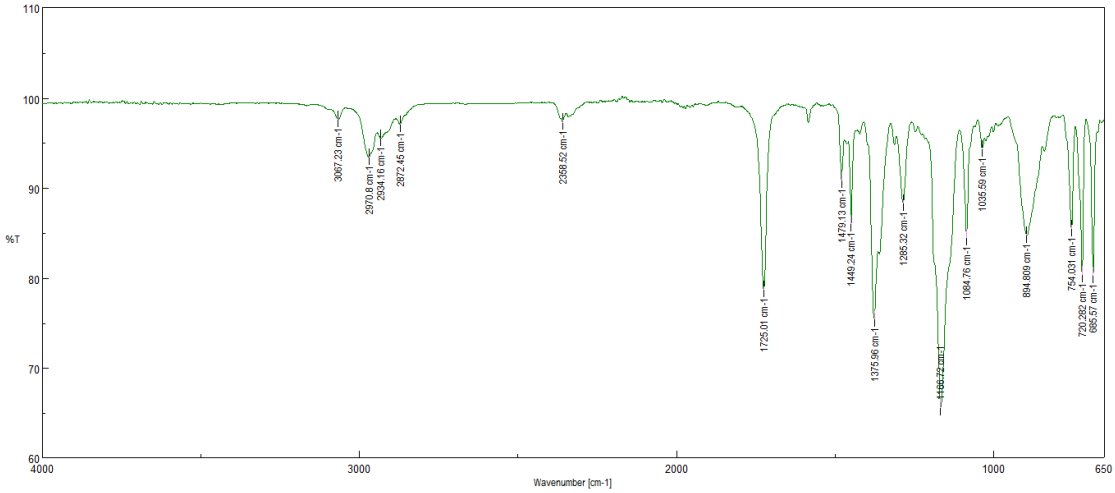

OPiv
Me
N
SO2Ph
SO2Ph
internal
253c
4.07
2.16
4.45
1.00
2.38
3.36
9.14
f1 (ppm)

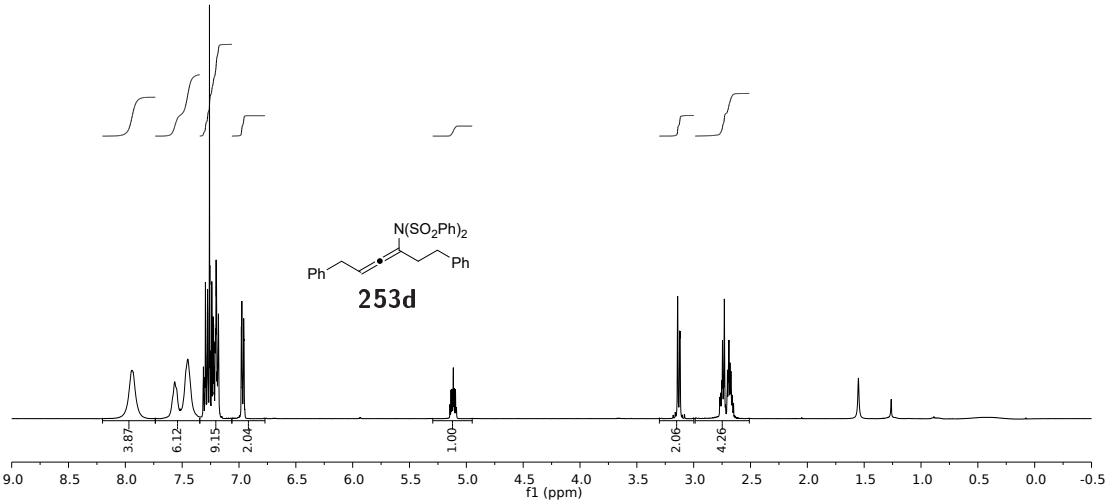

207.5
178.0
139.5
133.9
129.0
128.5
104.6
92.6
60.5
38.9
27.3
21.0
f1 (ppm)

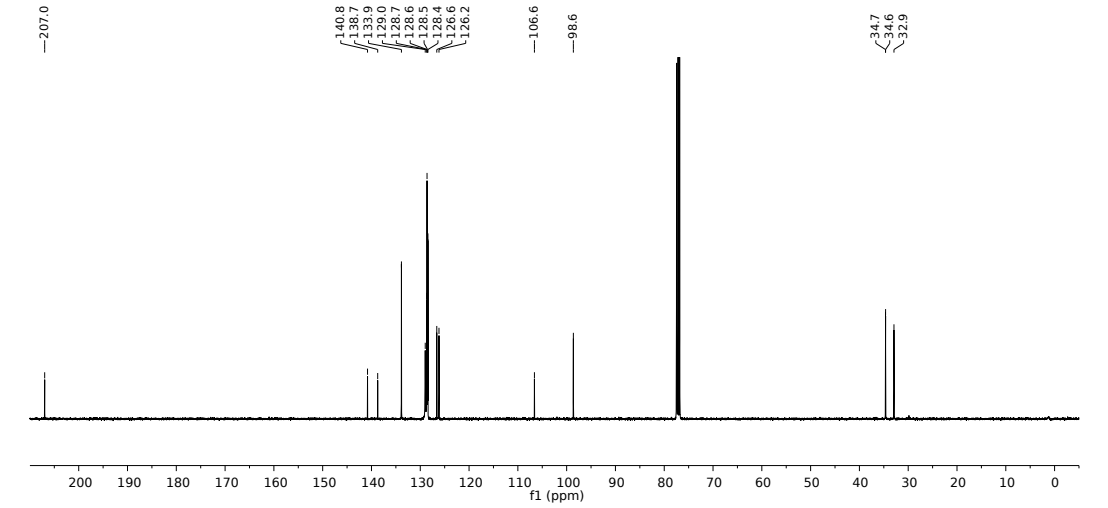

%T
3067.23 cm-1
2970.8 cm-1
2932.23 cm-1
2873.42 cm-1
1725.98 cm-1
1584.24 cm-1
1479.13 cm-1
1448.28 cm-1
1313.29 cm-1
1280.5 cm-1
1083.8 cm-1
1032.69 cm-1
995.91 cm-1
970.019 cm-1
932.414 cm-1
796.457 cm-1
752.102 cm-1
Wavenumber [cm-1]

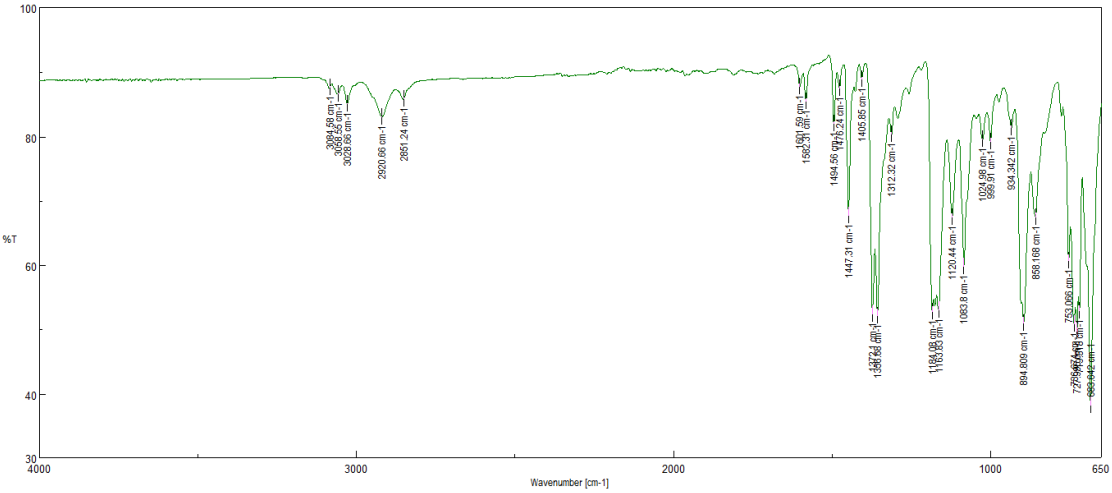

SO2Ph
N
SO2Ph
PivO
terminal
253c
4.54
2.35
4.60
1.91
2.00
1.92
11.63
f1 (ppm)

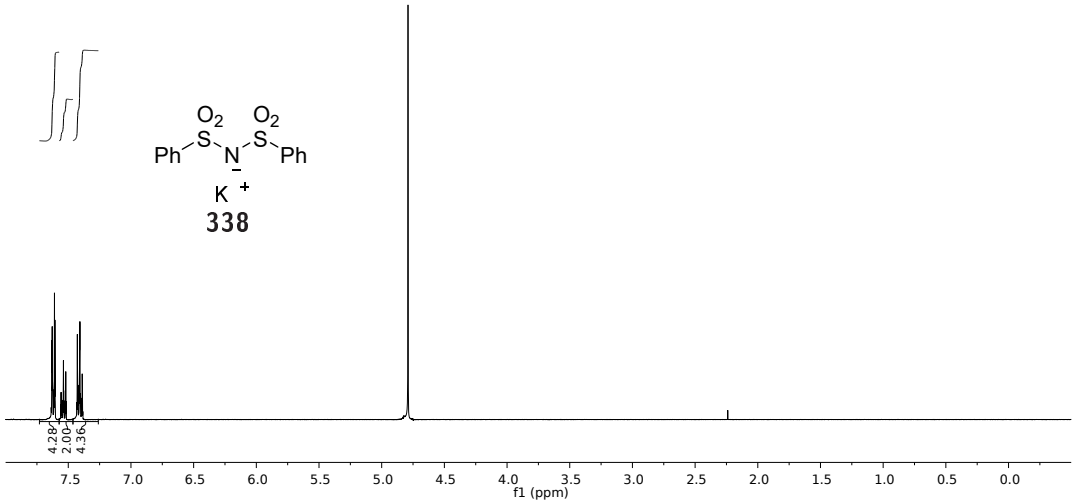

210.7
178.5
139.2
134.1
129.1
128.8
104.0
82.8
61.0
38.8
32.6
27.3
f1 (ppm)

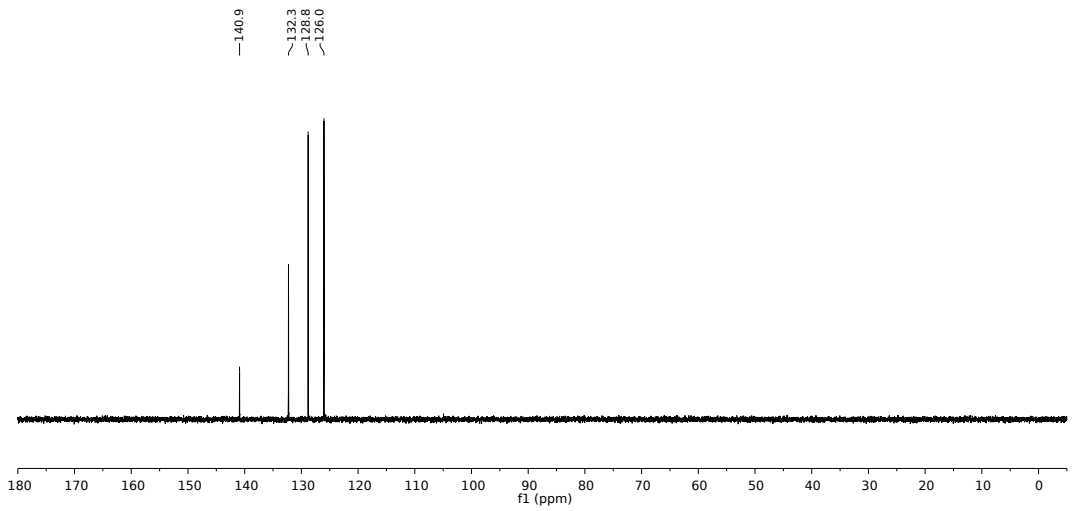

%T
3067.23 cm-1
2970.8 cm-1
2934.16 cm-1
2872.45 cm-1
2368.52 cm-1
1725.01 cm-1
1479.13 cm-1
1449.24 cm-1
1375.96 cm-1
1285.32 cm-1
1084.76 cm-1
1035.59 cm-1
894.869 cm-1
754.031 cm-1
720.282 cm-1
695.57 cm-1
Wavenumber [cm-1]

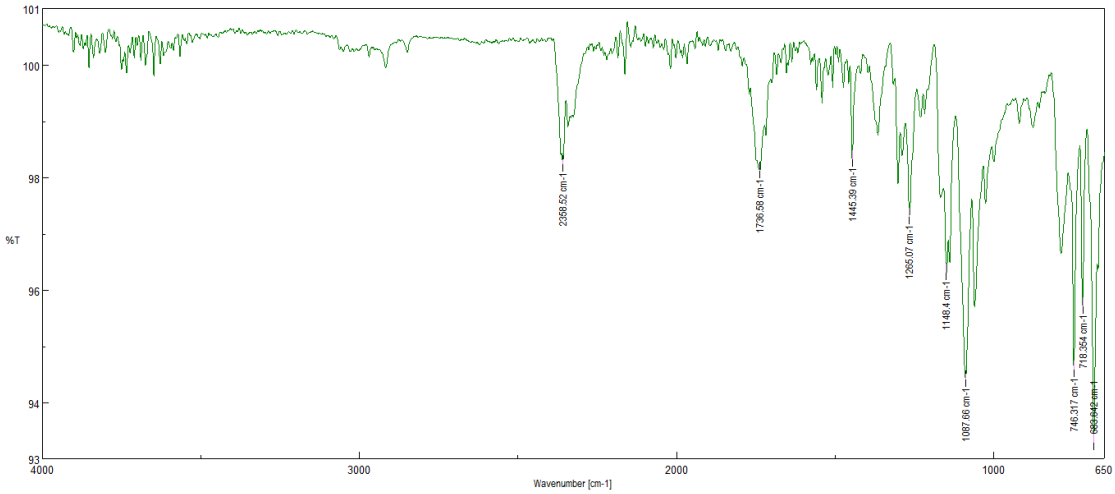

N(SO2Ph)2
Ph
Ph
253d
3.87
6.12
9.15
2.04
1.00
2.06
4.26
f1 (ppm)

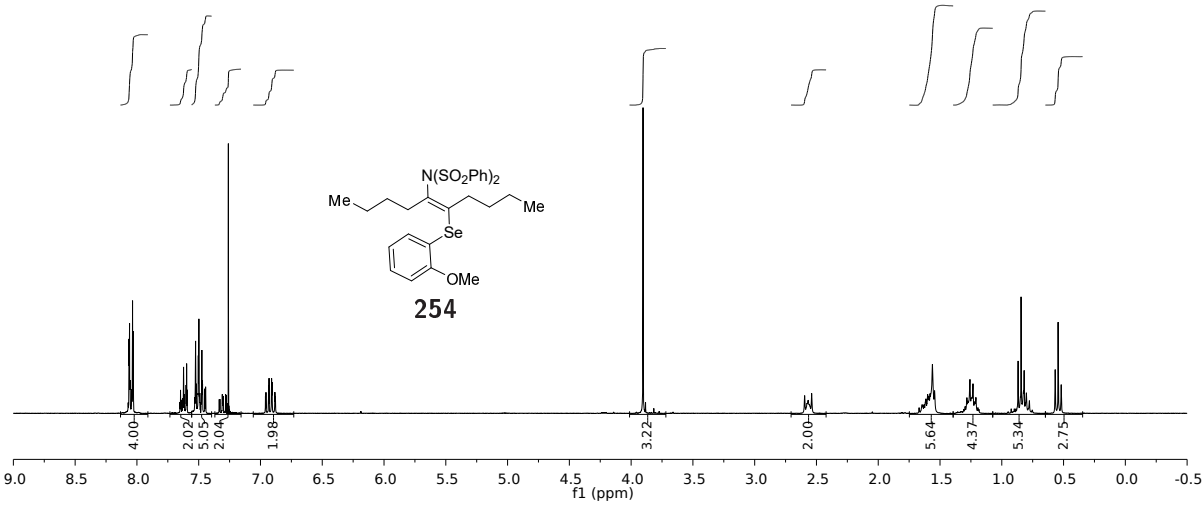

207.0
140.8
138.7
133.9
129.0
128.7
128.6
128.5
128.4
126.6
126.2
106.6
98.6
34.7
34.6
32.9
f1 (ppm)

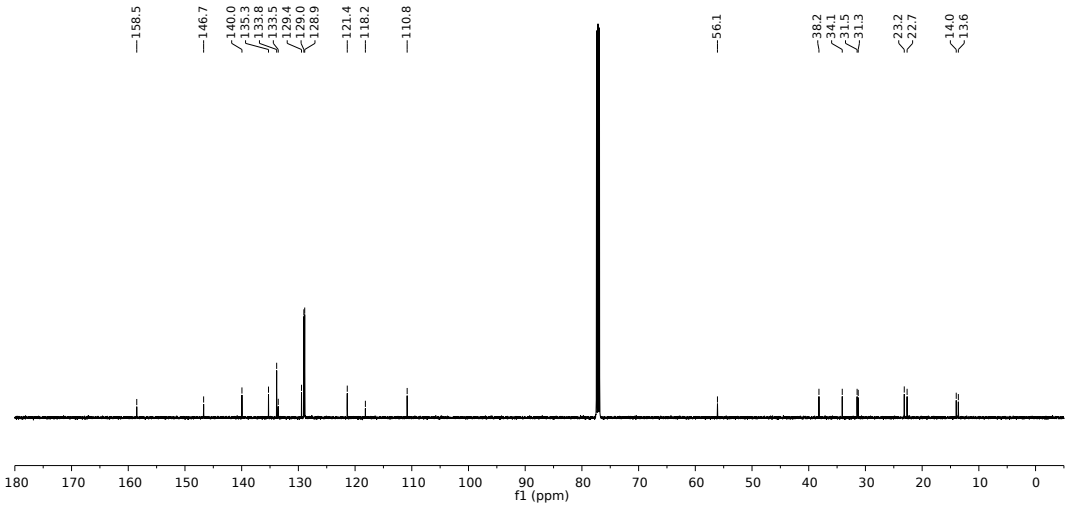

%T
3084.58 cm-1
3060.55 cm-1
3028.86 cm-1
2920.66 cm-1
2851.24 cm-1
1601.69 cm-1
1582.33 cm-1
1494.56 cm-1
1476.24 cm-1
1447.31 cm-1
1405.85 cm-1
1312.32 cm-1
1184.08 cm-1
1163.83 cm-1
1120.44 cm-1
1063.8 cm-1
1024.98 cm-1
999.01 cm-1
934.342 cm-1
894.809 cm-1
858.168 cm-1
753.005 cm-1
Wavenumber [cm-1]

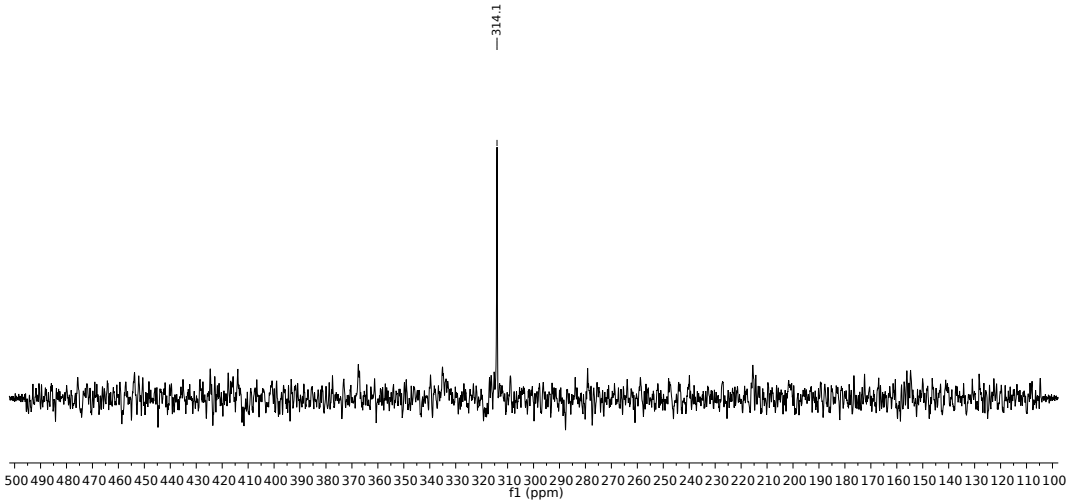

O2
O2
S
S
N
Ph
Ph
K +
338
4.29
2.00
4.36
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

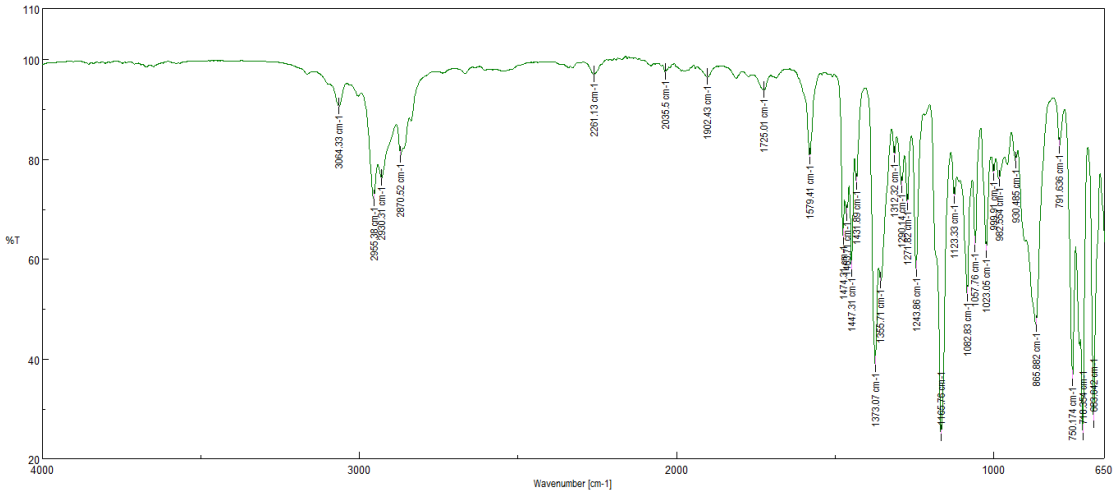

140.9
132.3
128.8
126.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

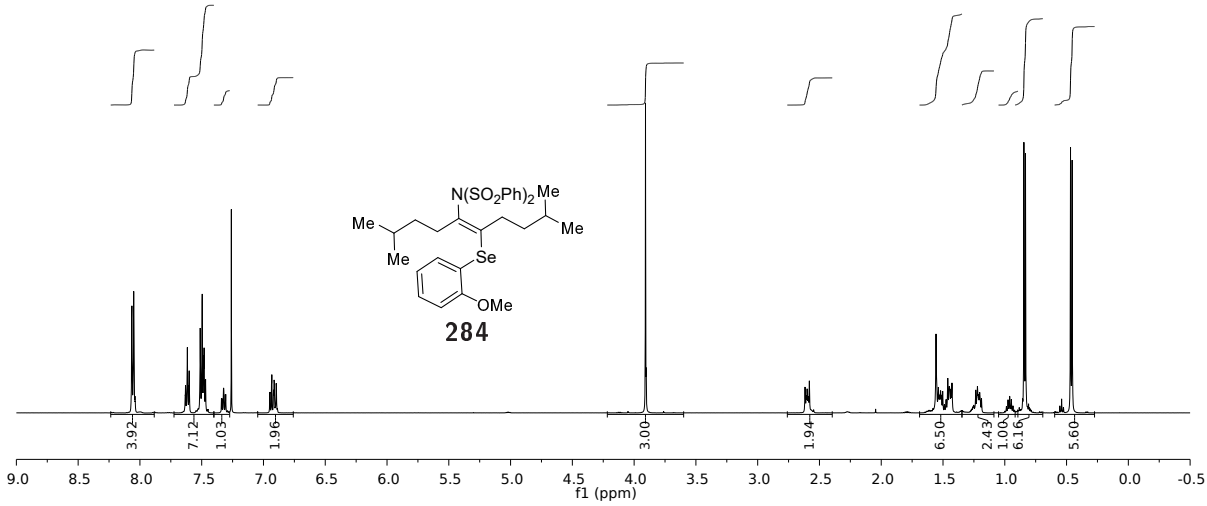

101
100
98
96
94
93
%T
2358.52 cm-1
1736.58 cm-1
1445.39 cm-1
1265.07 cm-1
1148.4 cm-1
1087.66 cm-1
746.317 cm-1
718.354 cm-1
4000
3000
2000
1000
650
Wavenumber [cm-1]

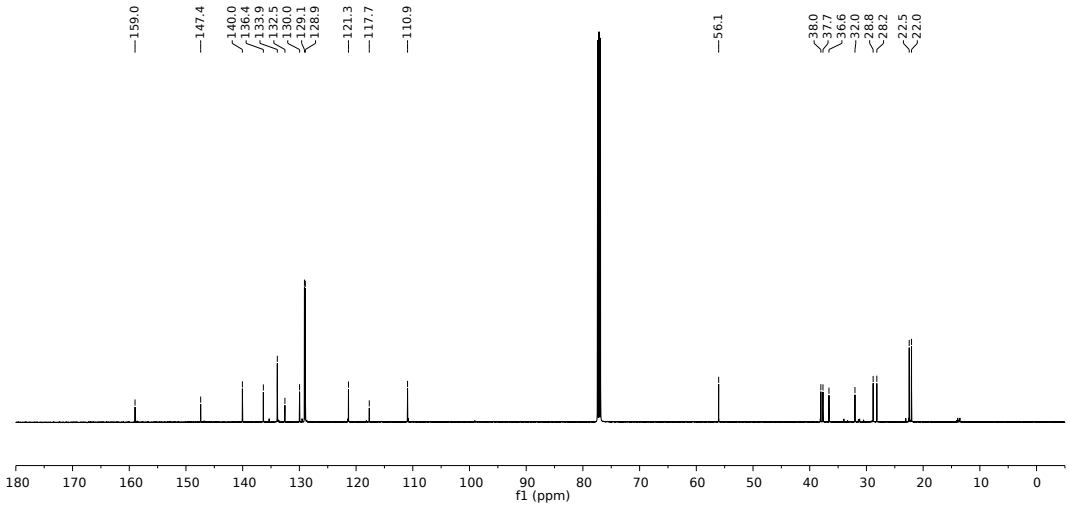

N(SO2Ph)2
Me
Me
Se
OMe
254
4.00
2.02
5.05
2.04
1.98
3.22
2.00
5.64
4.37
5.34
2.75
f1 (ppm)

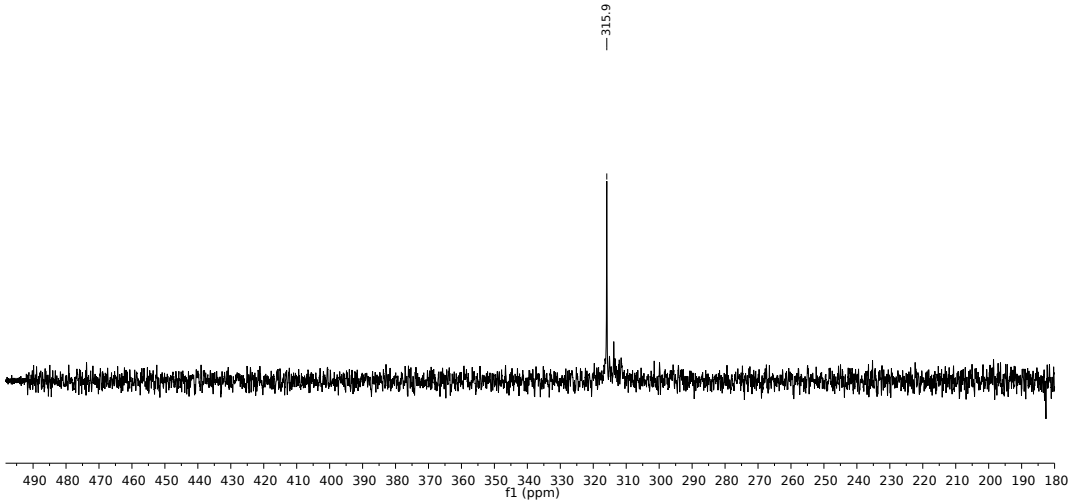

158.5
146.7
140.0
135.3
133.8
133.5
129.4
129.0
128.9
121.4
118.2
110.8
56.1
38.2
34.1
31.5
31.3
23.2
22.7
14.0
13.6
f1 (ppm)

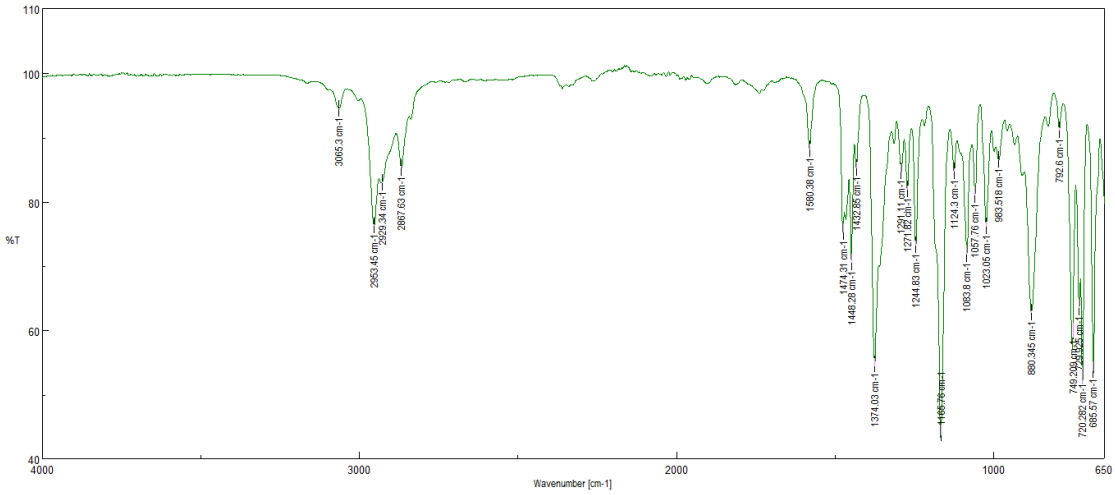

314.1
f1 (ppm)

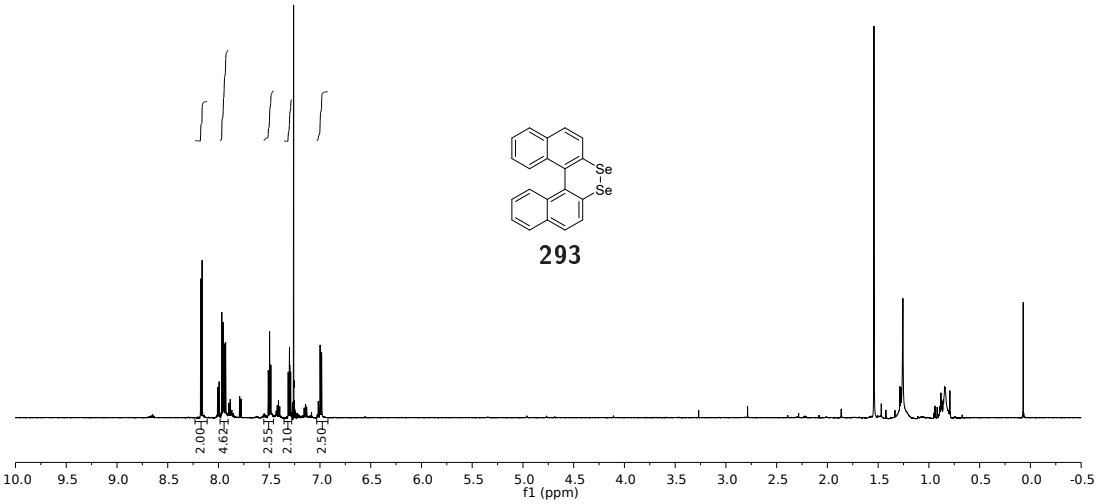

%T
Wavenumber [cm-1]
3004.33 cm-1
2955.88 cm-1
2930.31 cm-1
2870.52 cm-1
2291.13 cm-1
2035.5 cm-1
1902.43 cm-1
1725.01 cm-1
1579.41 cm-1
1447.31 cm-1
1437.89 cm-1
1373.07 cm-1
1355.71 cm-1
1312.22 cm-1
1243.86 cm-1
1123.33 cm-1
1082.83 cm-1
1057.76 cm-1
1023.05 cm-1
998.91 cm-1
962.954 cm-1
930.485 cm-1
865.882 cm-1
791.636 cm-1
750.174 cm-1

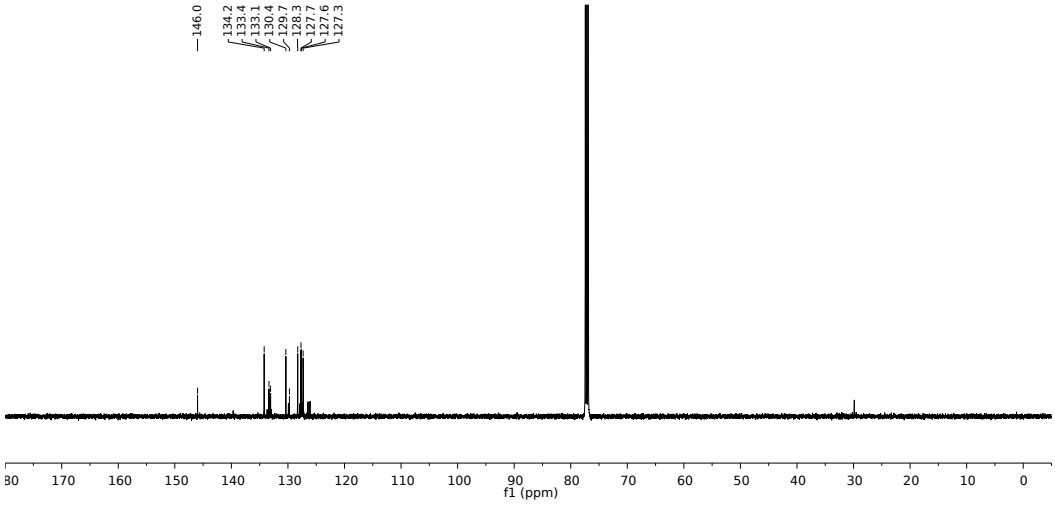

N(SO2Ph)2
Me
Me
Me
Me
Se
OMe
284
3.92
7.12
1.03
1.96
3.00
1.94
6.50
2.43
1.00
6.16
5.60
f1 (ppm)

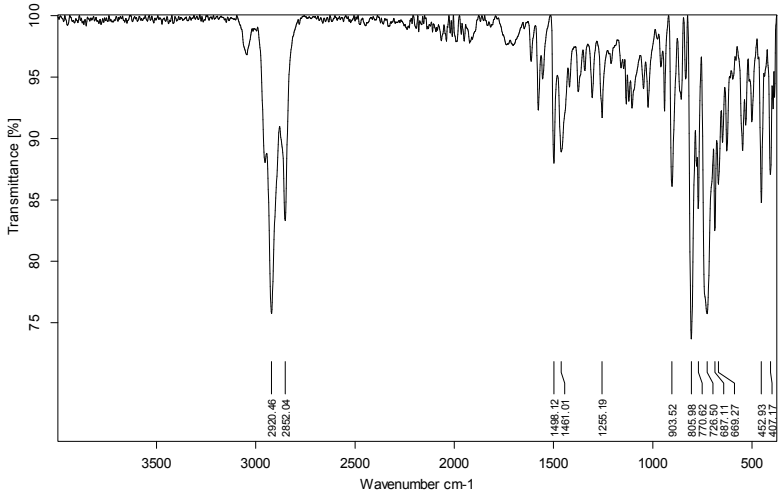

159.0
147.4
140.0
136.4
133.9
132.5
130.0
129.1
128.9
121.3
117.7
110.9
56.1
38.0
37.7
36.6
32.0
28.8
28.2
22.5
22.0
f1 (ppm)

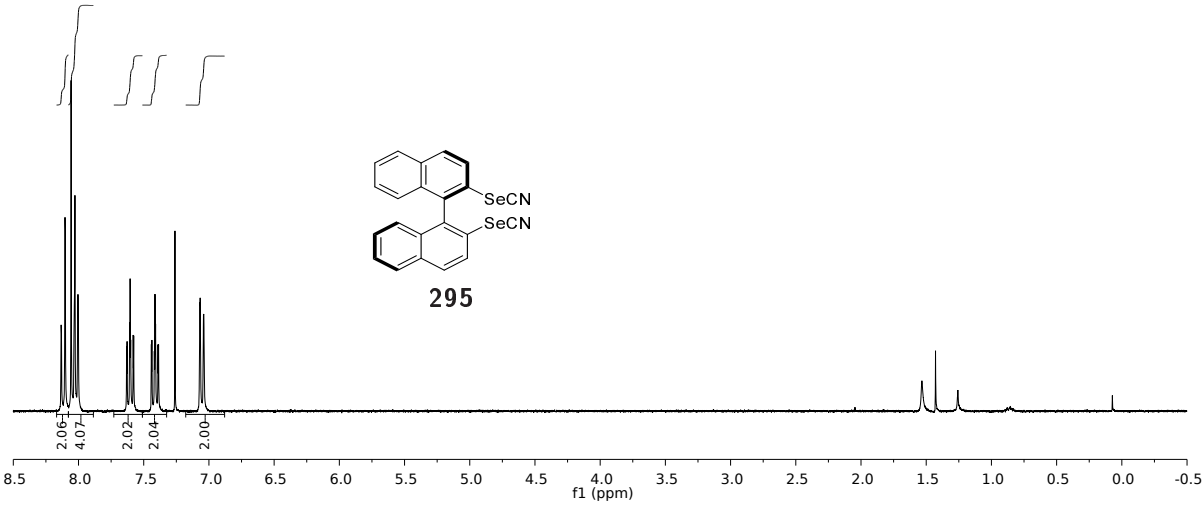

315.9
f1 (ppm)

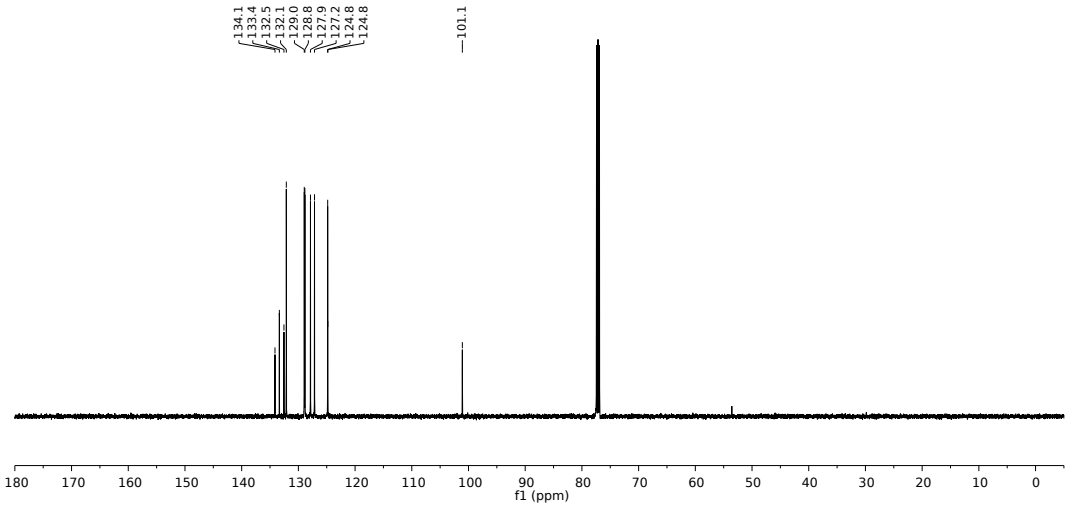

110
100
80
60
40
%T
4000
3000
2000
1000
650
Wavenumber [cm-1]
3065.3 cm-1
2953.45 cm-1
2929.34 cm-1
2867.63 cm-1
1580.38 cm-1
1474.31 cm-1
1448.28 cm-1
1432.85 cm-1
1374.03 cm-1
1271.1 cm-1
1244.83 cm-1
1124.3 cm-1
1083.8 cm-1
1057.76 cm-1
1023.05 cm-1
983.918 cm-1
880.345 cm-1
792.6 cm-1
749.209 cm-1
720.282 cm-1
685.57 cm-1

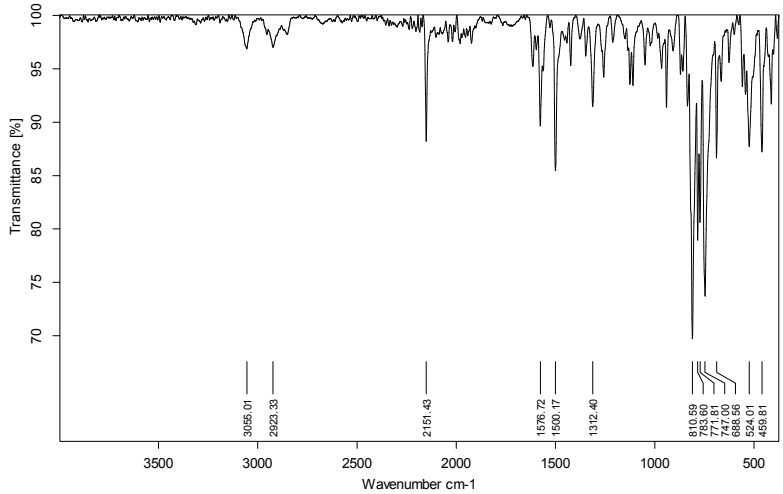

Se
Se
293
2.00
4.62
2.55
2.10
2.50
f1 (ppm)

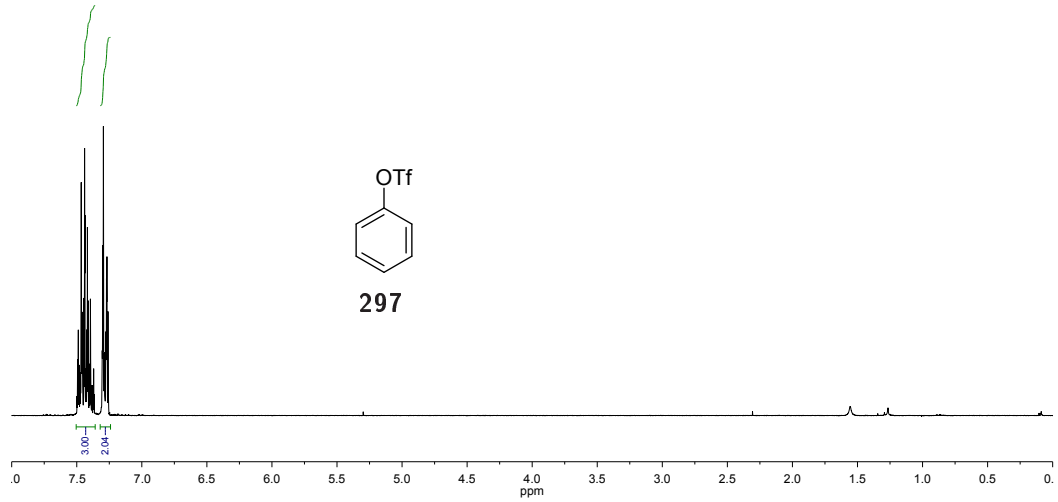

146.0
134.2
133.4
133.1
130.4
129.7
128.3
127.7
127.6
127.3
f1 (ppm)

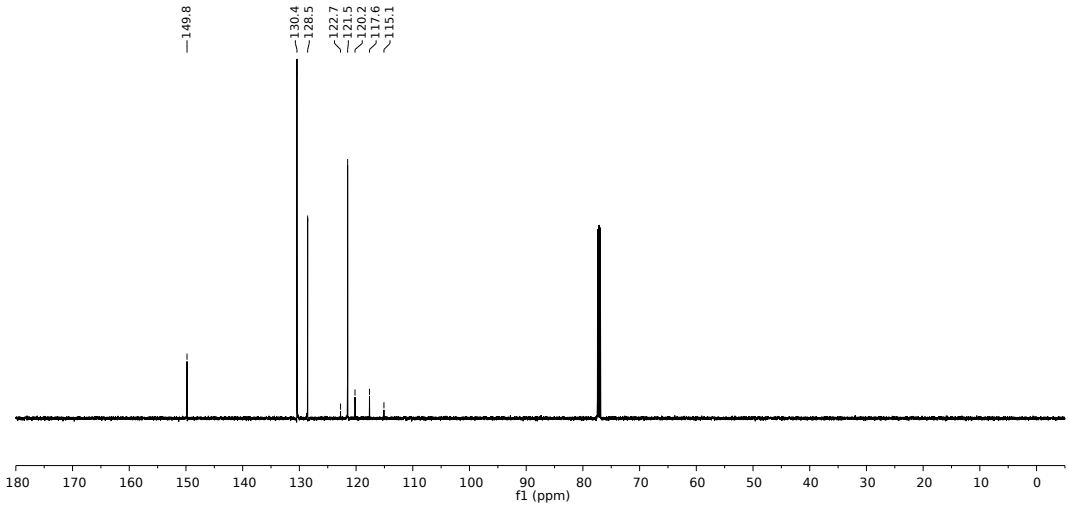

Transmittance [%]
2920.46
2852.04
1498.12
1461.01
1255.19
903.52
805.98
772.62
726.50
687.11
669.27
452.93
407.17
Wavenumber cm-1

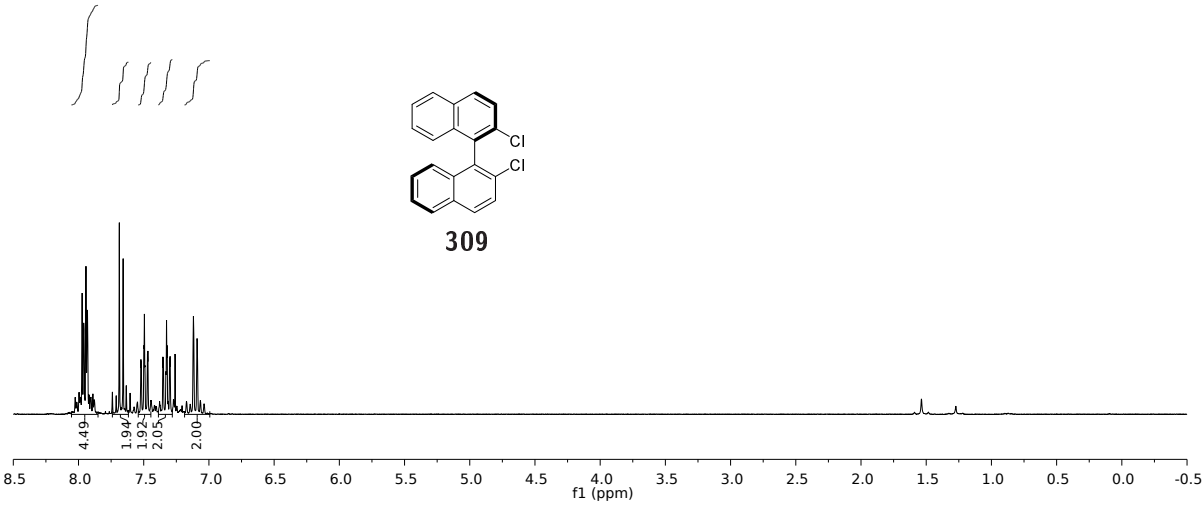

SeCN
SeCN
295
2.06
4.07
2.02
2.04
2.00
f1 (ppm)

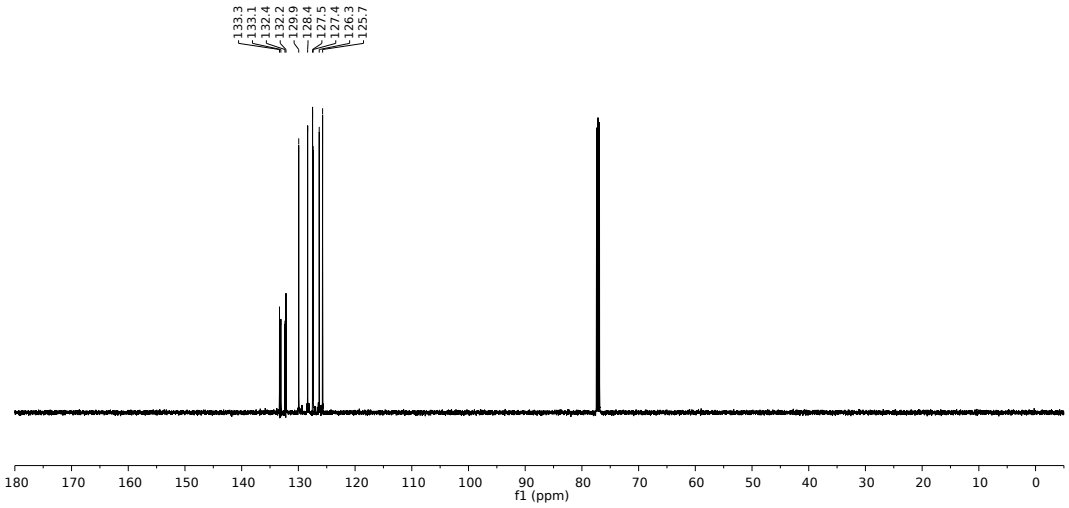

134.1
133.4
132.5
132.1
129.0
128.8
127.9
127.2
124.8
124.8
101.1
f1 (ppm)

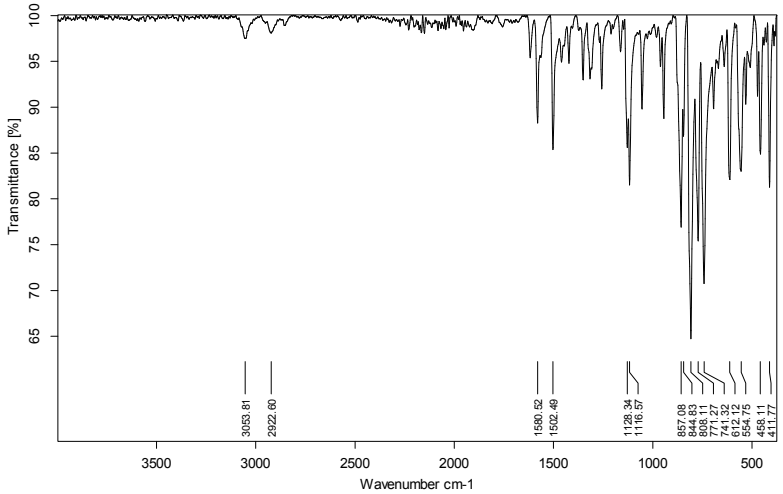

Transmittance [%]
3055.01
2923.33
2151.43
1576.72
1500.17
1312.40
810.69
747.00
688.56
524.01
459.81
Wavenumber cm-1

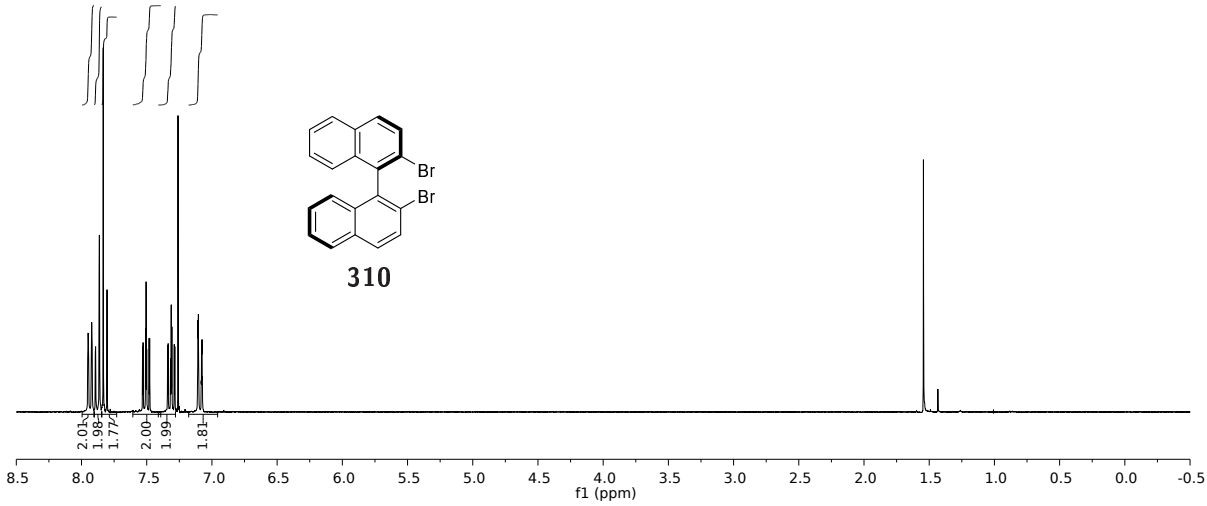

OTf
297
3.00
2.04
ppm

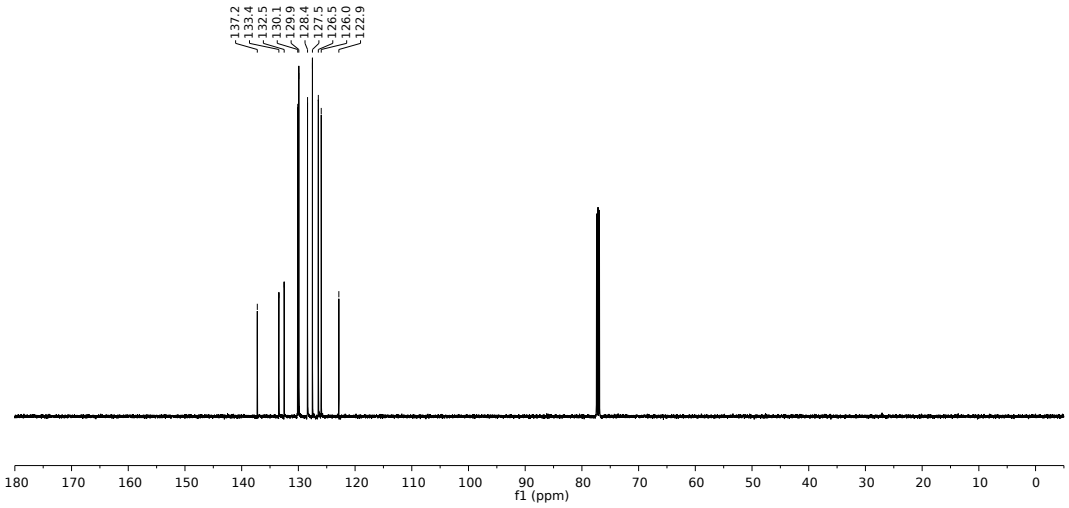

149.8
130.4
128.5
122.7
121.5
120.2
117.6
115.1
f1 (ppm)

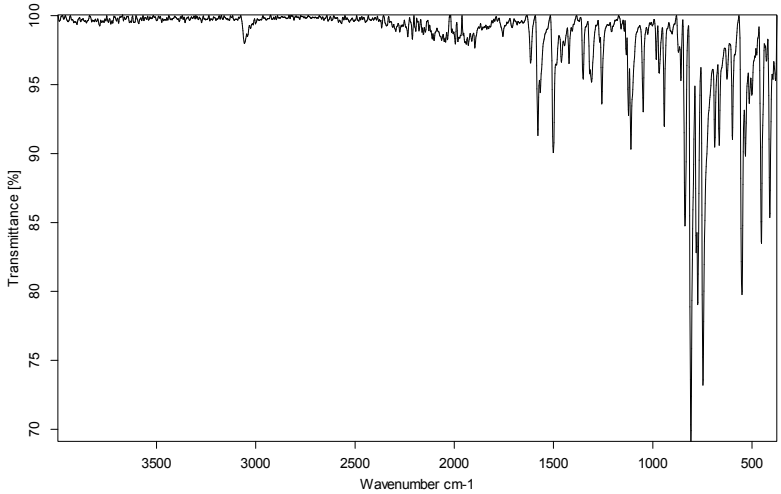

Cl
Cl
309
4.49
1.94
1.92
2.05
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


133.3
133.1
132.4
132.2
129.9
128.4
127.5
127.4
126.3
125.7
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

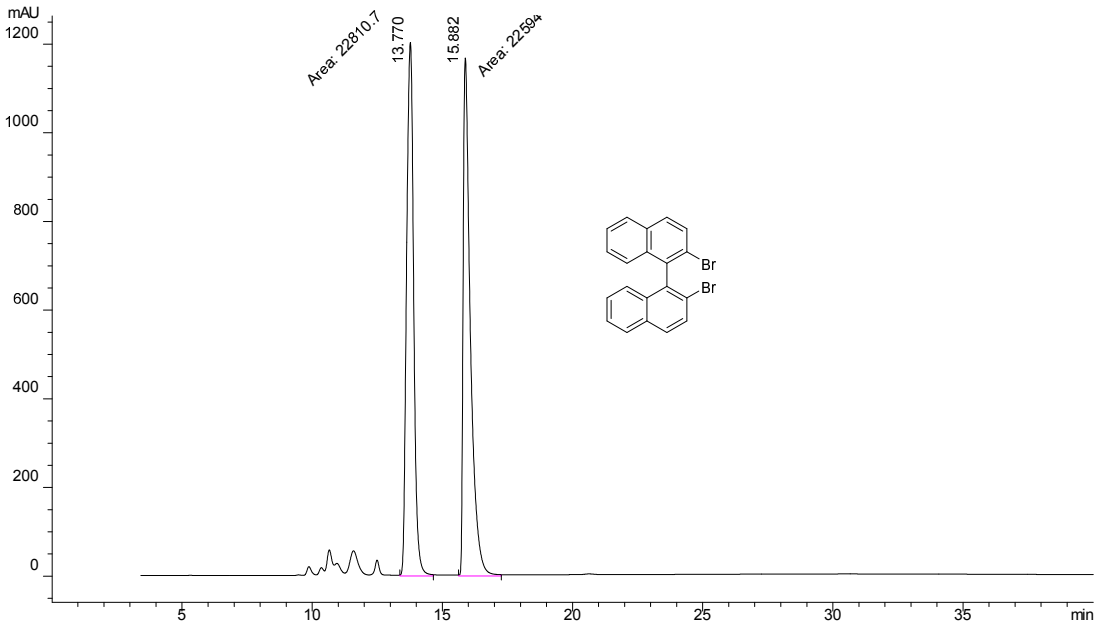

Transmittance [%]
100 95 90 85 80 75 70 65
3053.81
2922.60
1580.52
1502.49
1128.34
1116.57
857.08
844.83
808.11
777.27
741.32
612.12
554.75
458.11
411.77
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

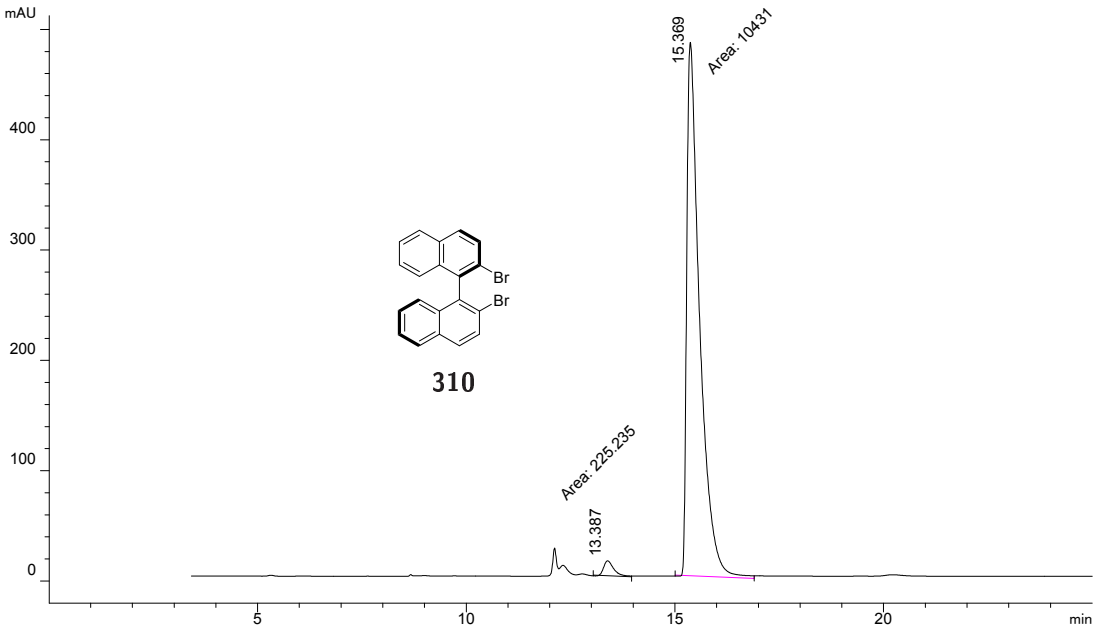

Br
Br
310
2.01
1.98
1.77
2.00
1.99
1.81
f1 (ppm)


137.2
133.4
132.5
130.1
129.9
128.4
127.5
126.5
126.0
122.9
f1 (ppm)

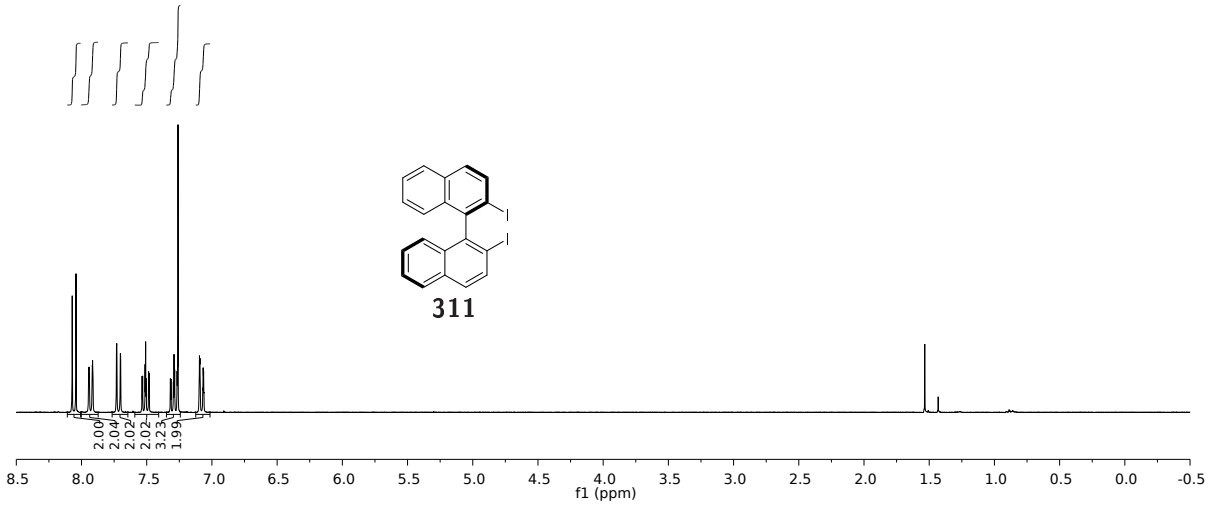

Transmittance [%]
Wavenumber cm-1

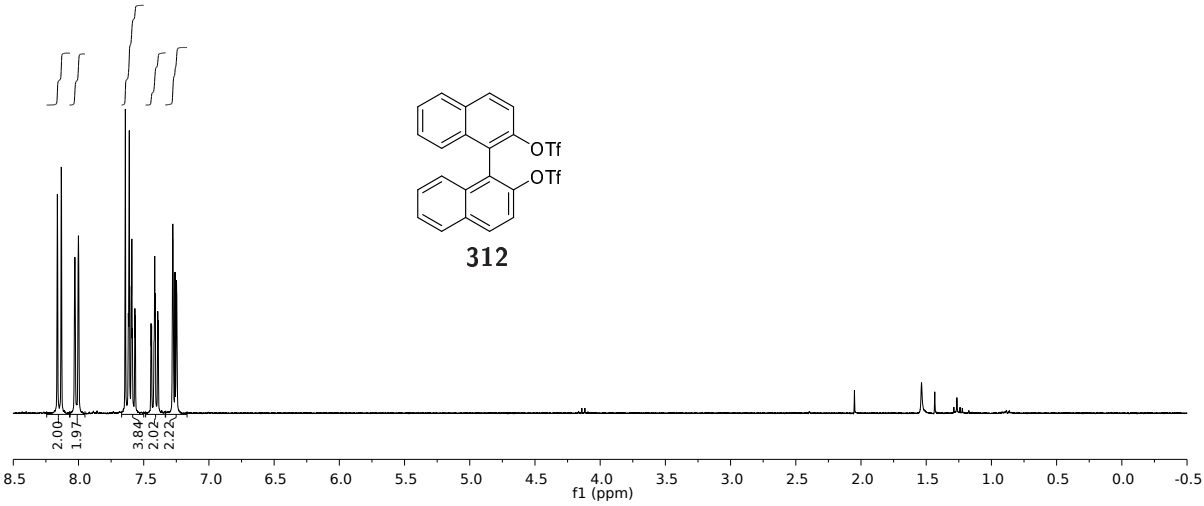
Column: Chiralcel OD
Eluent: *n*-hexane/*i*PrOH (99.5/0.5)
Flow rate: 0.6 mL/min
Detection: UV 250.4 nm



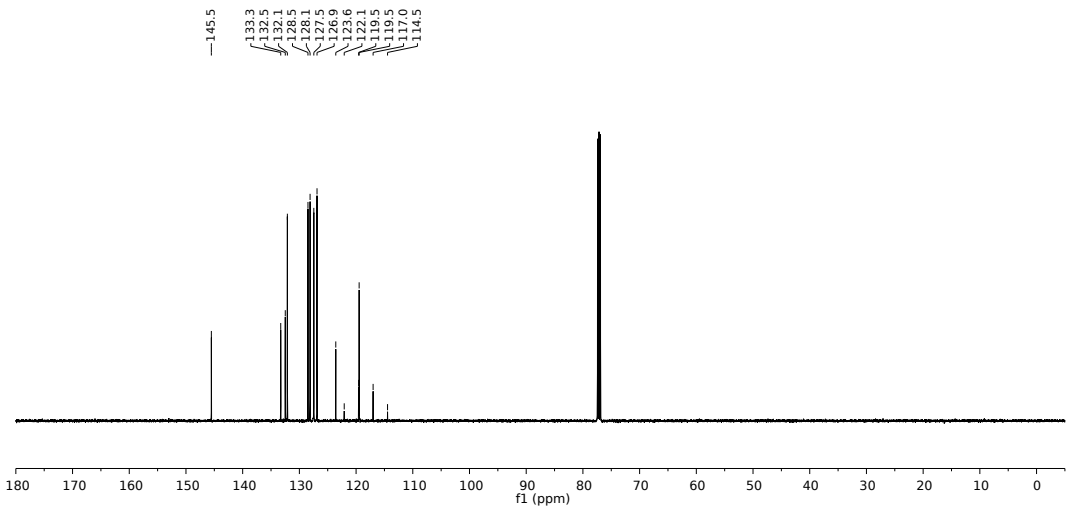


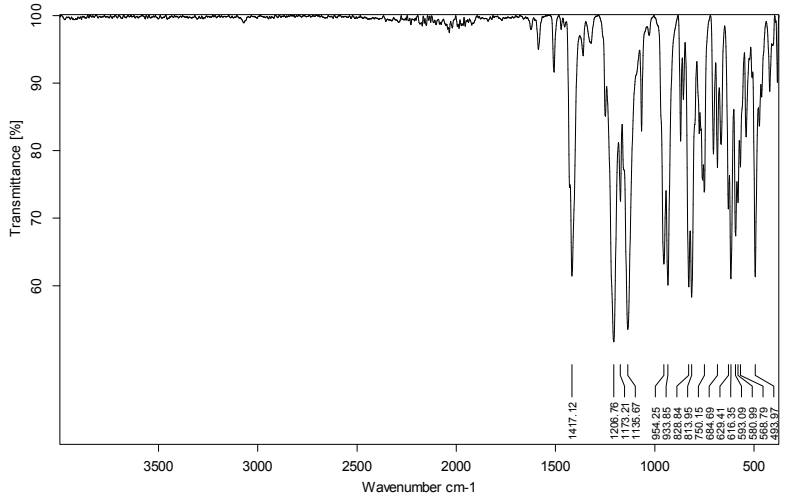
310

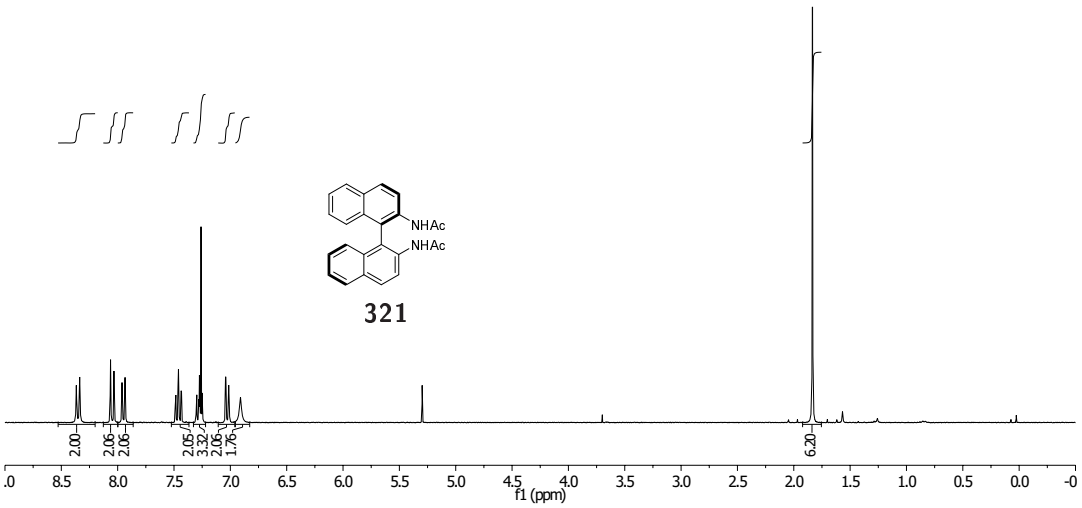

311
2.00
2.04
2.02
2.02
3.23
1.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

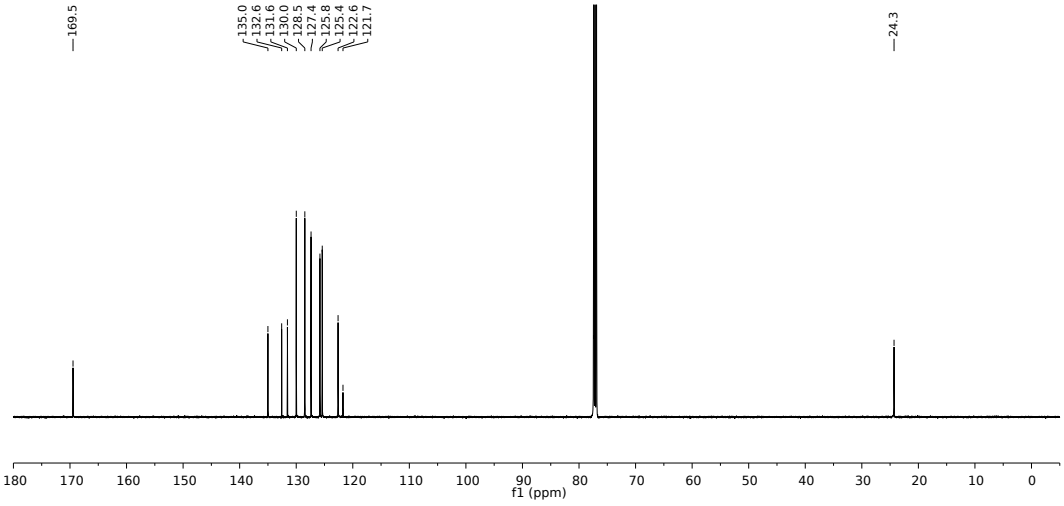

OTf
OTf
2.00
1.97
3.84
2.02
2.22
f1 (ppm)

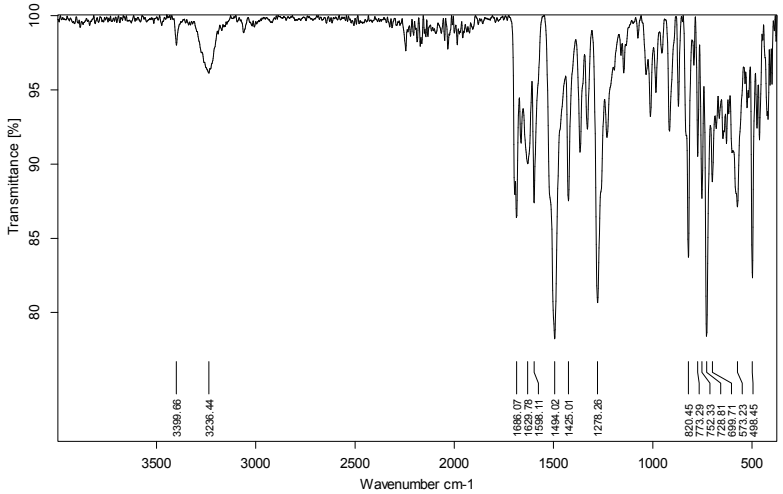
312

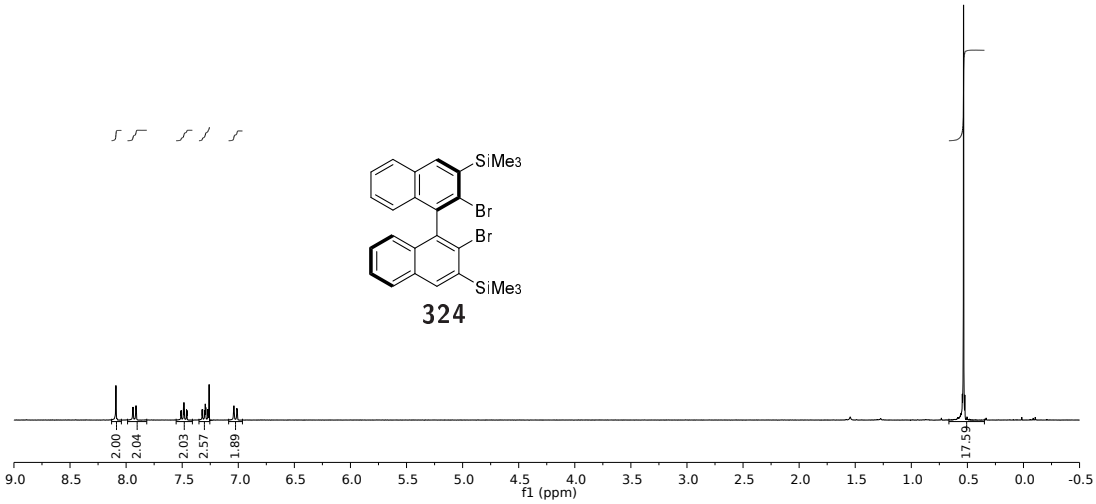

145.5
133.3
132.5
132.1
128.5
128.1
127.5
126.9
123.6
122.1
119.5
119.5
117.0
114.5
f1 (ppm)


Transmittance [%]
1417.12
1206.76
1173.21
1135.67
954.25
933.85
828.84
811.95
750.15
684.69
626.41
615.45
593.09
580.99
568.79
493.97
Wavenumber cm-1

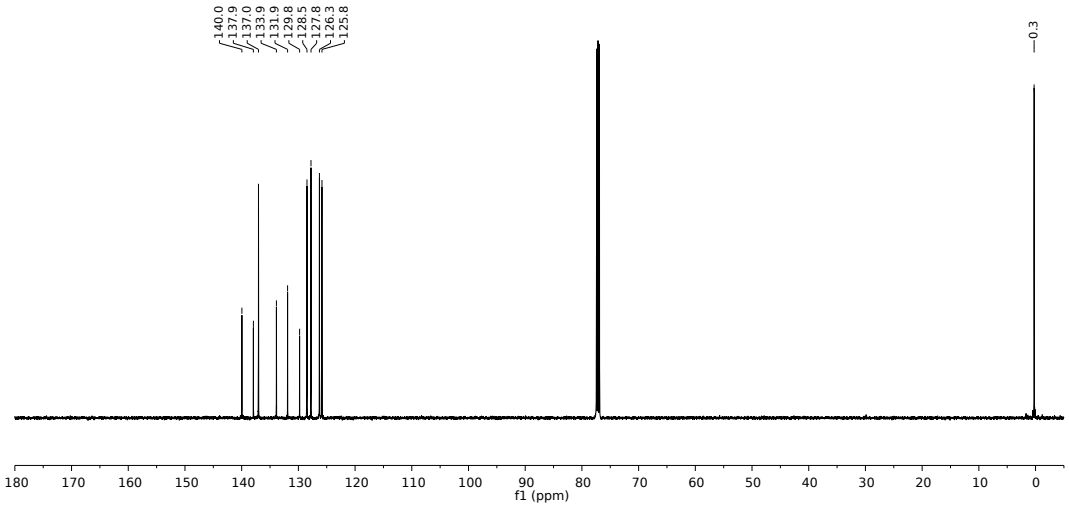

NHAc
NHAc
321
2.00
2.06
2.06
2.05
3.32
2.06
1.76
6.20
f1 (ppm)

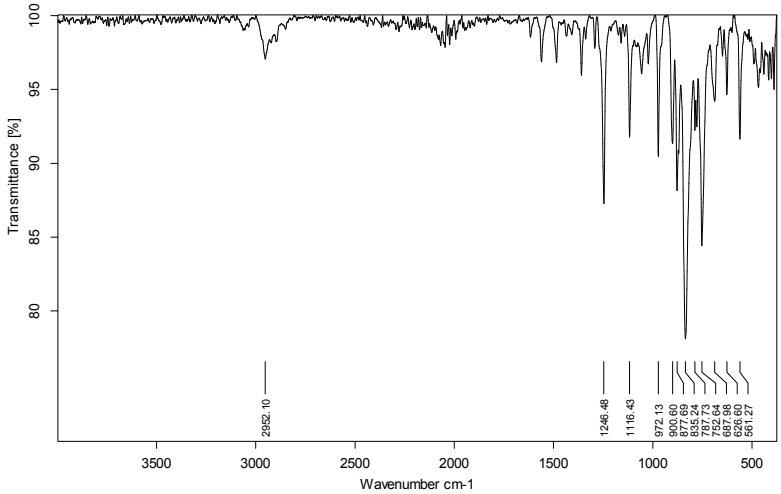

169.5
135.0
132.6
131.6
130.0
128.5
127.4
125.8
125.4
122.6
121.7
24.3
f1 (ppm)


Transmittance [%]
3399.66
3236.44
1686.07
1629.78
1598.11
1494.02
1425.01
1278.26
820.45
772.29
752.33
728.81
699.71
677.23
498.45
Wavenumber cm-1

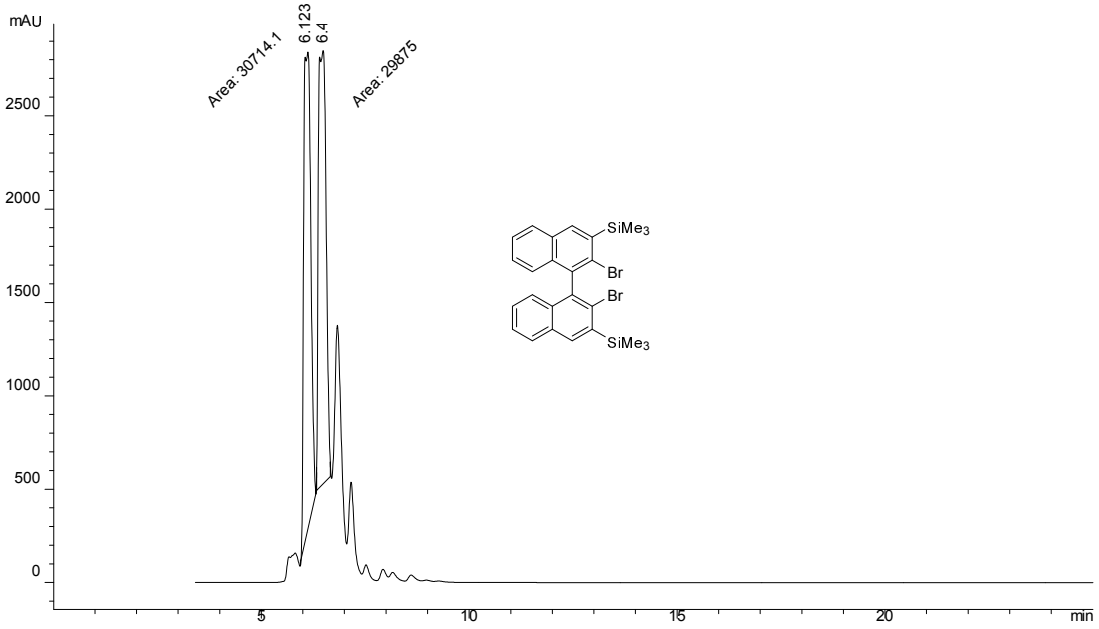

SiMe3
Br
Br
SiMe3
2.00
2.04
2.03
2.57
1.89
17.59
f1 (ppm)

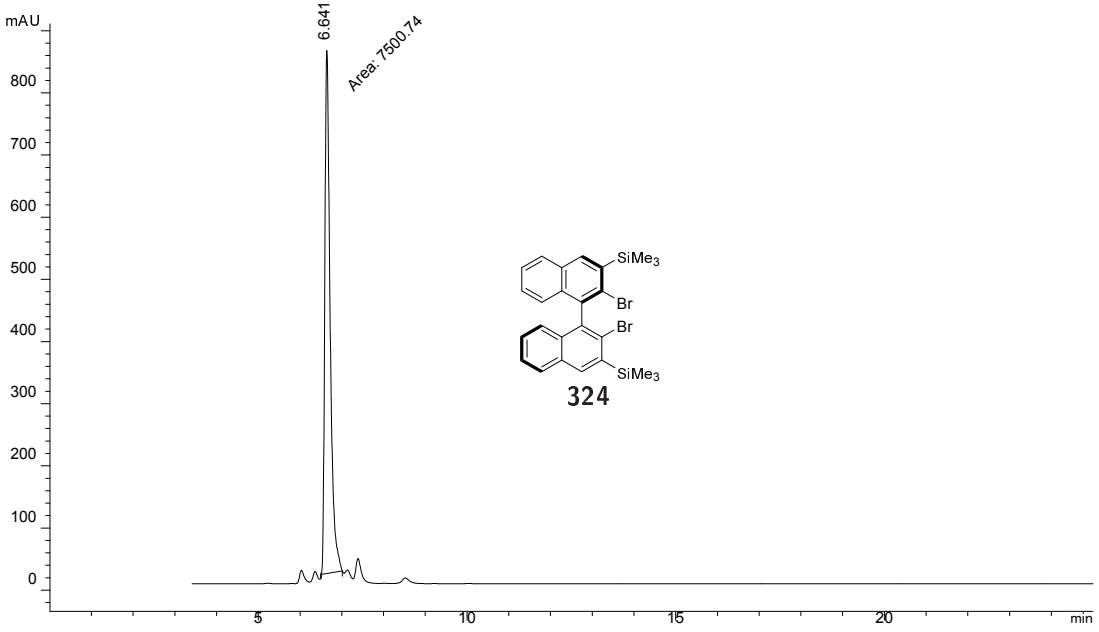
324


140.0
137.9
137.0
133.9
131.9
129.8
128.5
127.8
126.3
125.8
0.3
f1 (ppm)

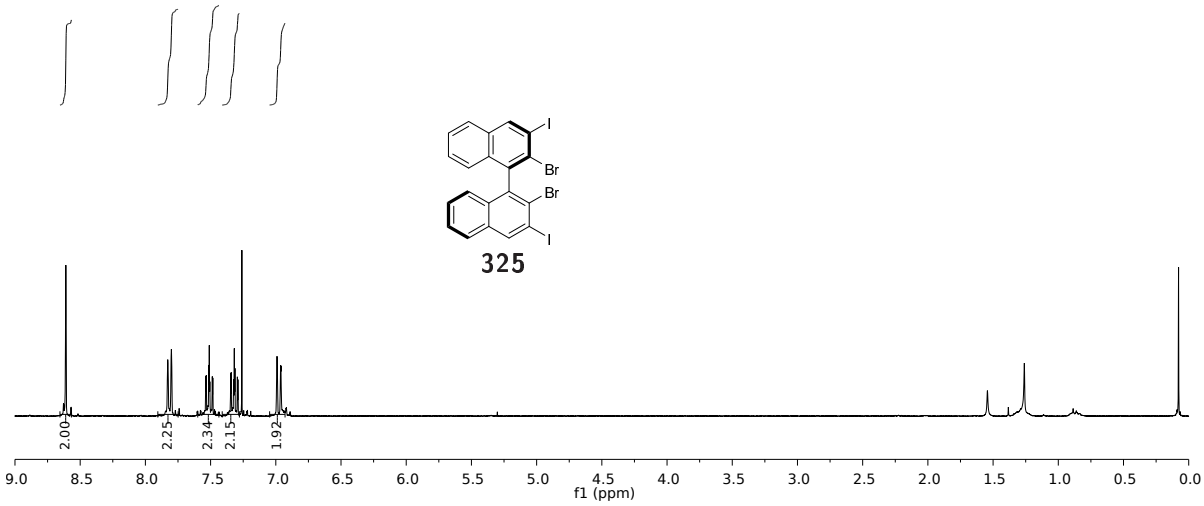

Transmittance [%]
2962.10
1246.48
1116.43
972.13
900.60
877.69
835.24
787.73
757.64
687.98
626.60
561.27
Wavenumber cm-1

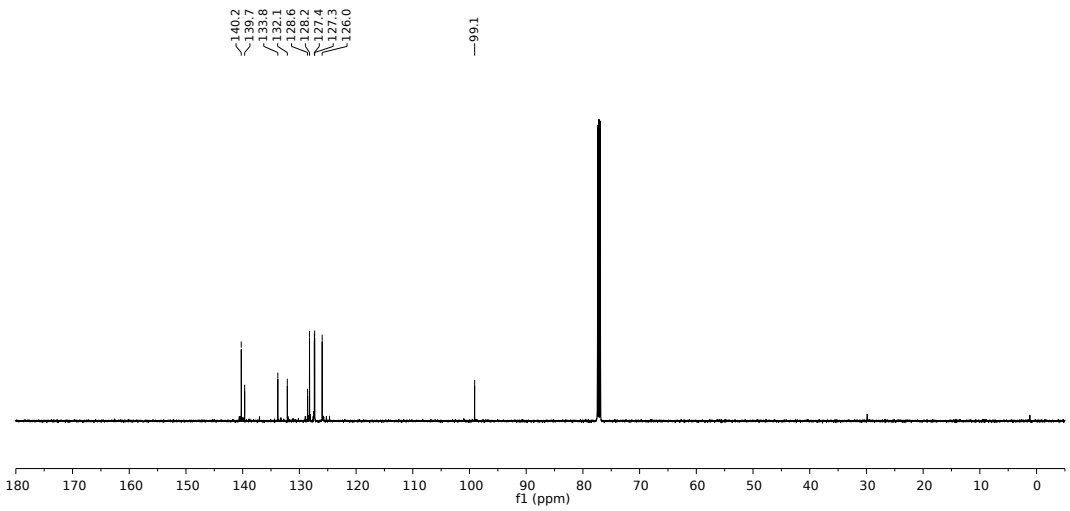
Column: Chiralpak IA
Eluent: *n*-hexane/*i*PrOH (99.8/0.2)
Flow rate: 0.6 mL/min
Detection: UV 250.4 nm

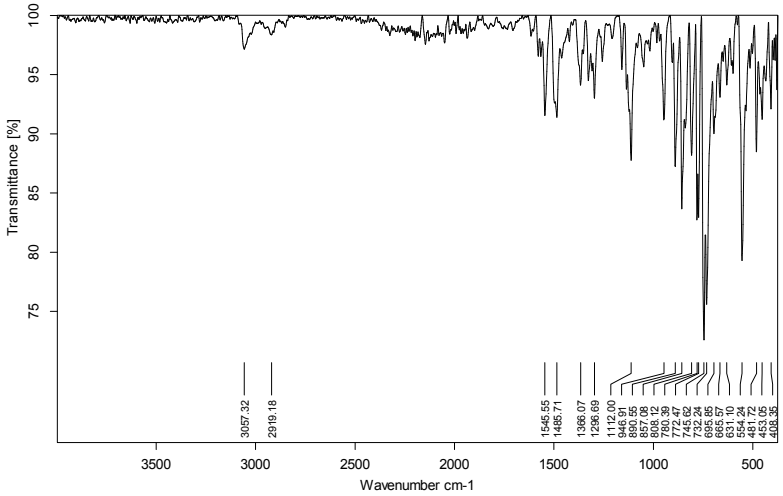




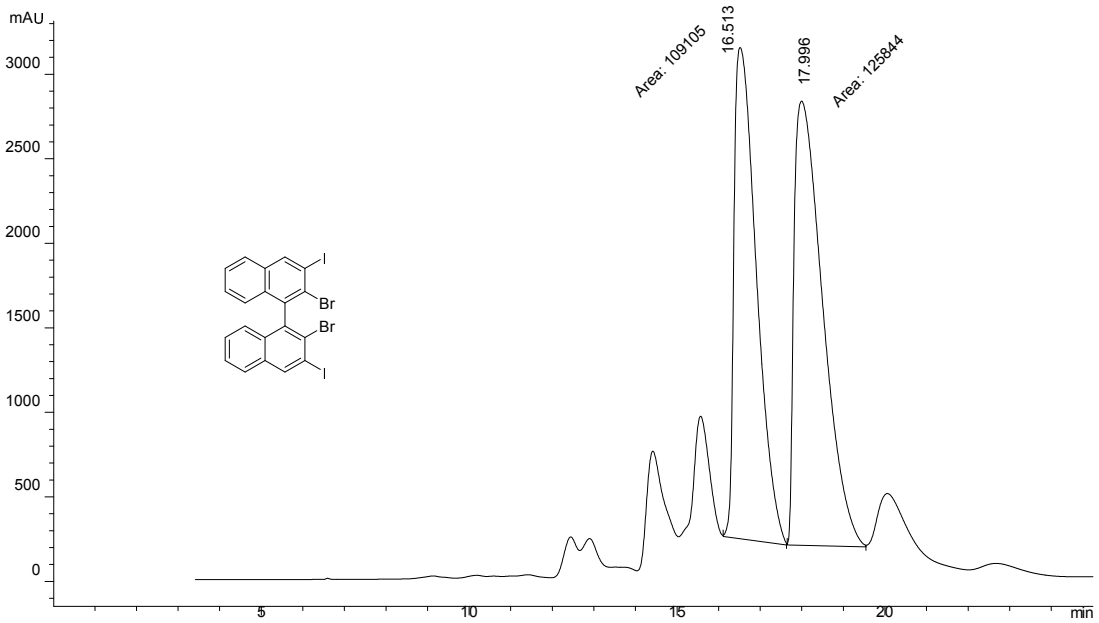
324

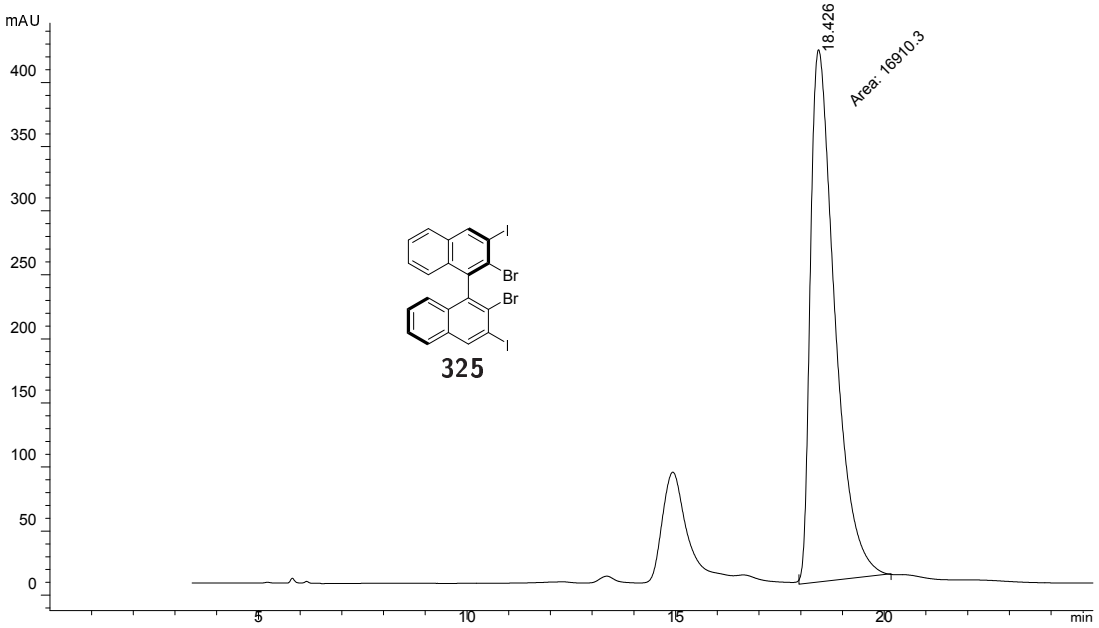

I
Br
Br
I
325
2.00
2.25
2.34
2.15
1.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

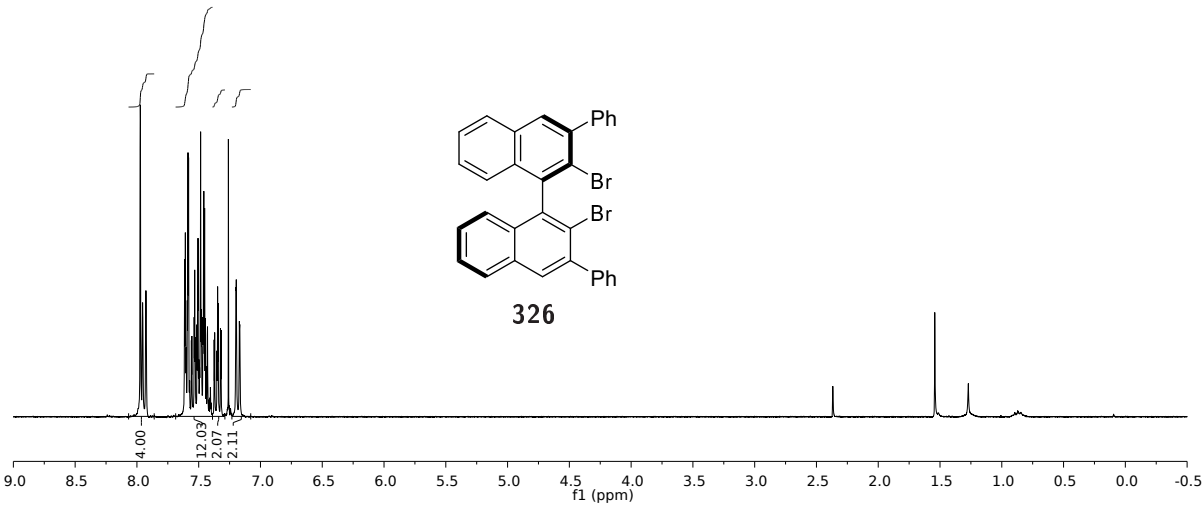

140.2
139.7
133.8
132.1
128.6
128.2
127.4
127.3
126.0
99.1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

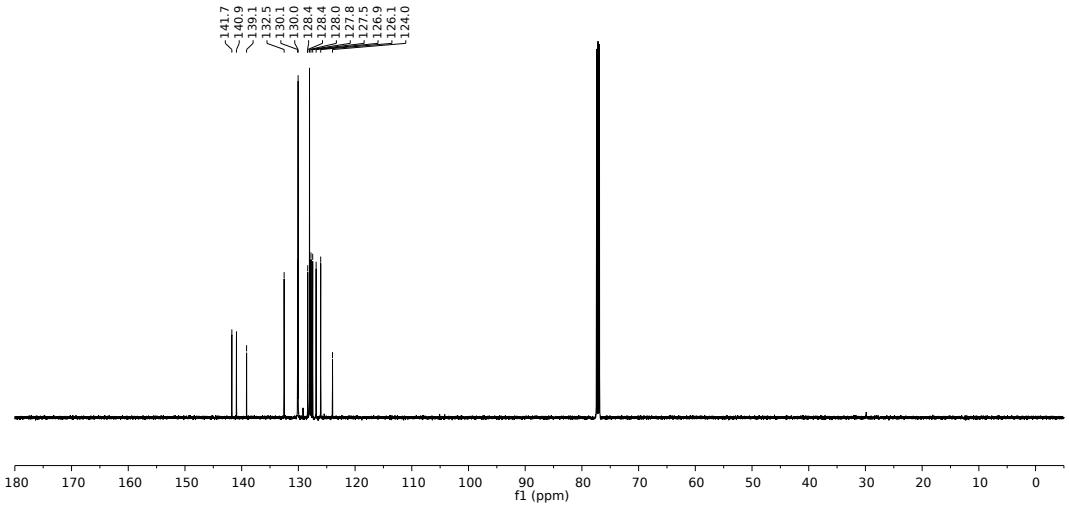

Transmittance [%]
100
95
90
85
80
75
3057.32
2919.18
1545.55
1485.71
1366.07
1296.69
1112.00
946.91
890.85
857.98
808.12
780.39
772.47
745.62
732.24
695.85
665.57
651.10
554.24
481.72
453.05
408.35
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

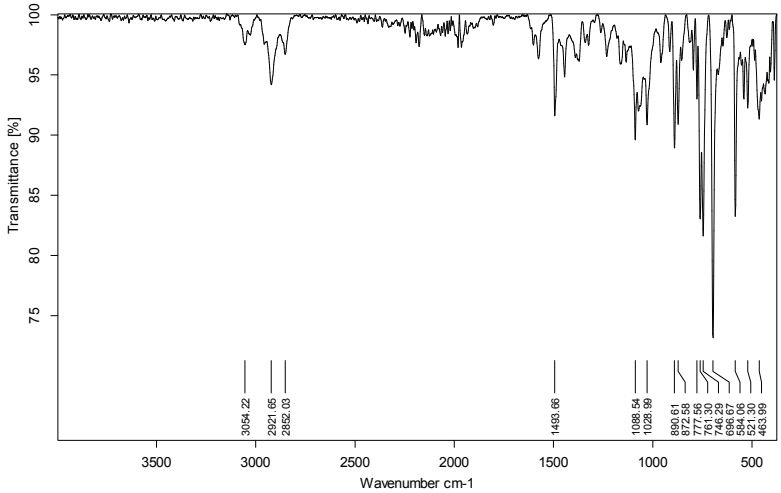
Column: Chiralpak IA
Eluent: *n*-hexane/*i*PrOH (99.8/0.2)
Flow rate: 0.6 mL/min
Detection: UV 250.4 nm

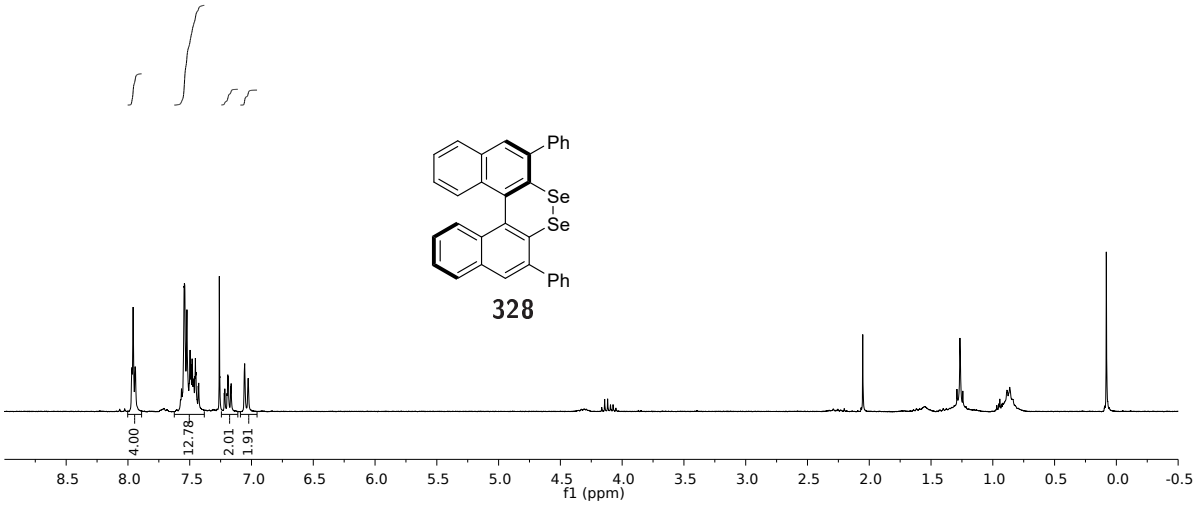


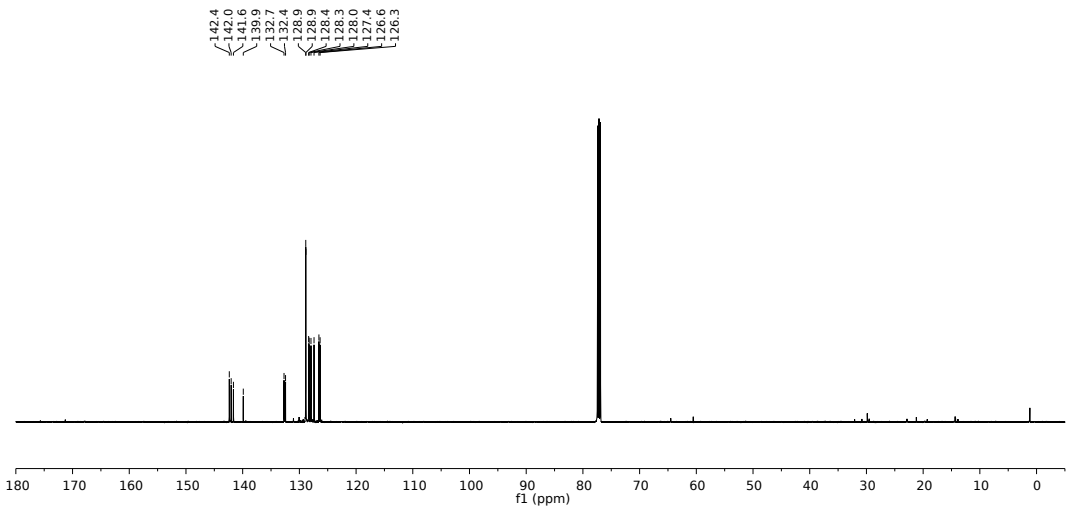


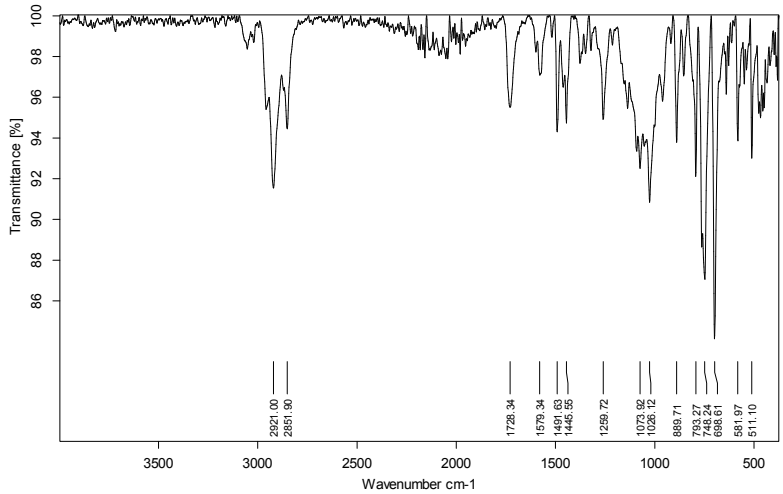

Ph
Br
Br
Ph
326
4.00
12.03
2.07
2.11
f1 (ppm)

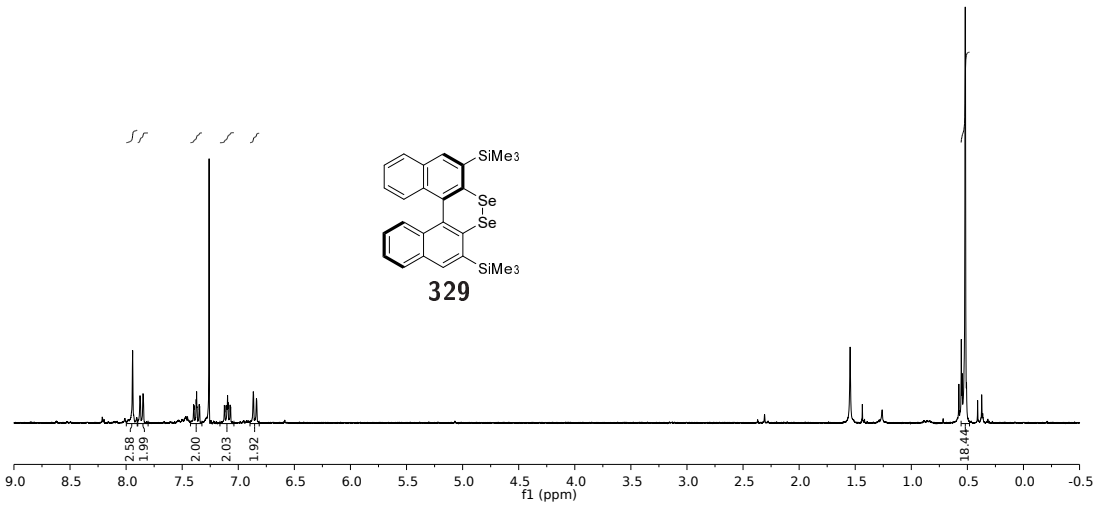

141.7
140.9
139.1
132.5
130.1
130.0
128.4
128.4
128.0
127.8
127.5
126.9
126.1
124.0
f1 (ppm)

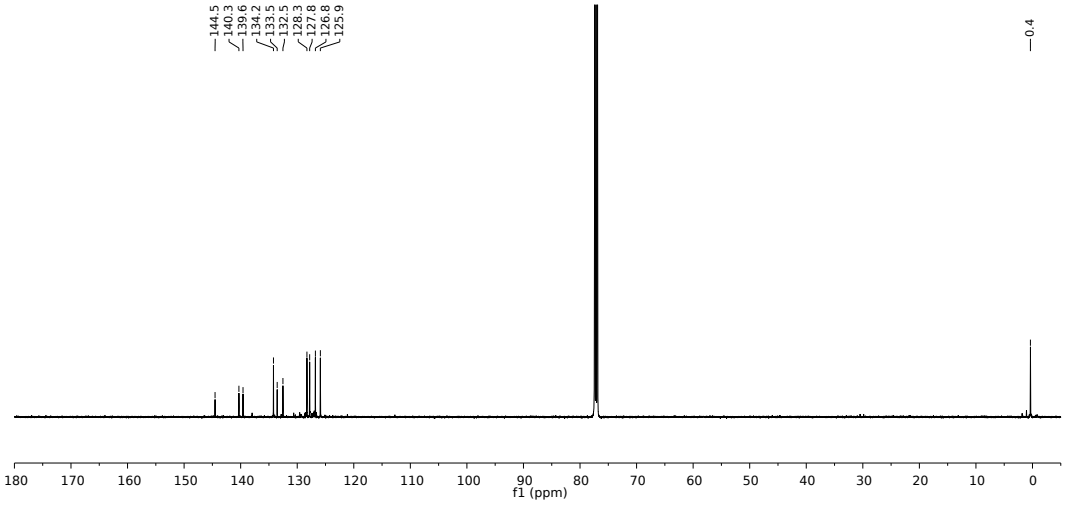

Transmittance [%]
3054.22
2921.65
2852.03
1493.66
1088.54
1028.99
890.61
872.58
777.56
761.30
746.29
698.67
584.06
521.30
463.99
Wavenumber cm-1

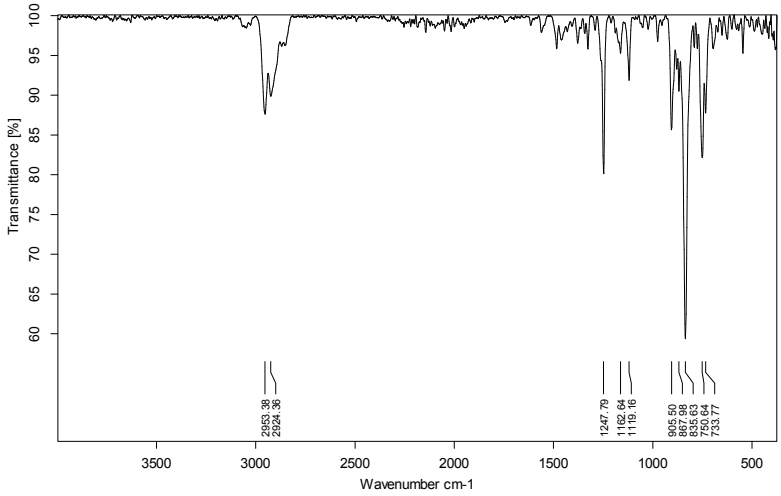

Ph
Se
Se
Ph
328
4.00
12.78
2.01
1.91
f1 (ppm)

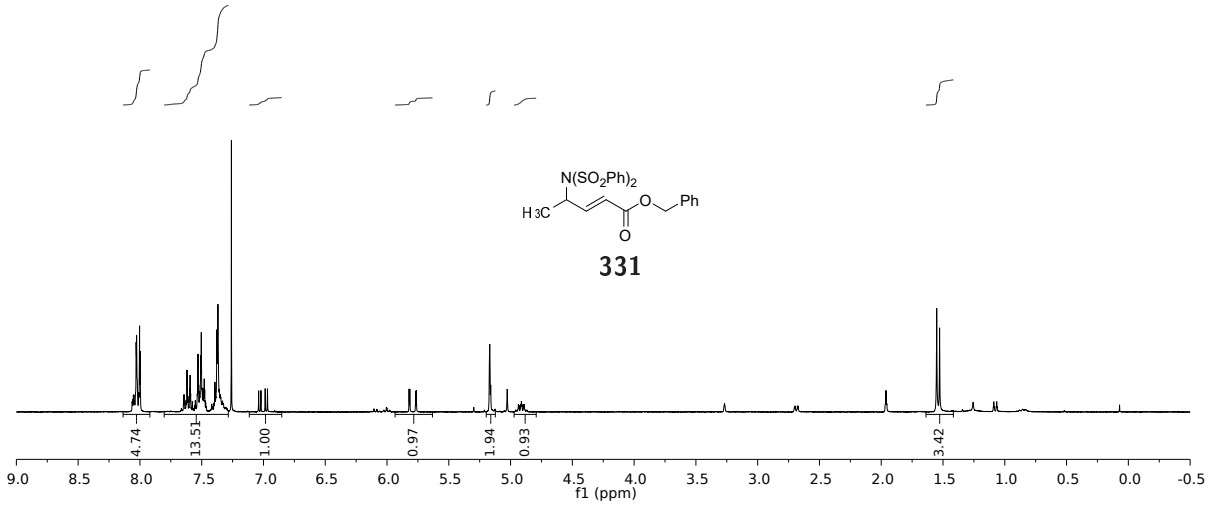

142.4
142.0
141.6
139.9
132.7
132.4
128.9
128.9
128.4
128.3
128.0
127.4
126.6
126.3
f1 (ppm)


Transmittance [%]
2921.00
2851.90
1728.34
1579.34
1491.63
1445.55
1259.72
1073.92
1026.12
889.71
793.27
748.24
698.61
581.97
511.10
Wavenumber cm-1


SiMe3
Se
Se
SiMe3
329
2.58
1.99
2.00
2.03
1.92
18.44
f1 (ppm)


144.5
140.3
139.6
134.2
133.5
132.5
128.3
127.8
126.8
125.9
0.4
f1 (ppm)


Transmittance [%]
2953.38
2924.36
1247.79
1162.64
1119.16
905.50
867.98
835.63
750.64
733.77
Wavenumber cm-1


N(SO2Ph)2
H3C
O
O
Ph
331
4.74
13.51
1.00
0.97
1.94
0.93
3.42
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)