WITTIG REARRANGEMENTS OF SILYL ALLYLIC CYCLIC ETHERS AND [1,2] CARBON TO CARBON SILYL MIGRATION OF α-HYDROXY ALLYL SILANES

By

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ABSTRACT

The [1,2]- and [1,4]-Wittig rearrangements of cyclic α/γ-silyl allyl ethers have been studied. These rearrangements are based on the ability of the silicon atom to stabilize an α-anion. Treatment of diastereomeric 2-silyl-6-aryl-5,6-dihydro-*2H*-pyrans with *n*-butyllithium (*sec*-butyllithium for *cis* diastereomer) result in stereoconvergent ring contraction to corresponding *α*-silylcyclopentenols and/or (*β*-cyclopropyl)acylsilanes via [1,2]- and [1,4]-Wittig rearrangements respectively. Studies on expanded ring size, 2-silyl-7-aryl-2,5,6,7-tetrahydrooxepins, led to the formation of *α*-silylcyclohexenols and (*β*-cyclobutyl)acylsilanes. On the other hand, moving the silyl group to the 4-position of the dihydropyran moiety led predominantly to [1,4]-Wittig rearrangement.

Concurrently, 2-silyl-3-hydroxy-5-arylcyclopentan-1-one and 2-silyl-3-hydrox-6-arylcycloyhexan-1-one can be accessed by subjecting 1-silyl-5-arylcyclopent-2-en-1-ol and 1-silyl-6-arylcyclohex-2-en-1-ol, respectively, to *m*-CPBA and $NaHCO_3$. In this transformation epoxidation triggers a [1,2]-carbon-to-carbon silyl migration. The stereochemical orientation of the resulting product is such that the α-silyl and β-hydroxy groups are *trans* to one another. Furthermore, the hydroxy group in the starting silane directs the epoxide formation, which in turn dictates the stereochemical outcome of the resulting β-hydroxy making this reaction stereospecific in nature. Lastly, the synthesis of 2-alkyl-2-silylalkanals can be achieved by conditions that effect spontaneous [1,2]-carbon-to-carbon silyl migration in 1-silyl-2-alkyl-2-alken-1-ols. These conditions are independent of the substituents on silicon but require an alkyl substituent at the olefin position next to the sp^3 carbon bearing the silyl group.

To my family: My dad Syverio; my mom Evalyne (Monica); my wife Harriet; my daughter Trixie; and my siblings; Andrew, Hildah, and Simon
Thank you for your patience and all the support

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LIST OF SYMBOLS AND ABBREVIATIONS

APCI	atmospheric-pressure chemical ionization
Ar	aromatic
BF_3•OEt_2	boron trifluoride diethyl ether
Bn	benzyl
Bz	benzoyl
CI	chemical ionization
d	doublet
DBU	1,8-diazabicycloundec-7-ene
DCM	dichloromethane
DMAP	4-diaminopyridine
DMF	N,N-dimethylformamide
DMP	Dess-Martin periodinane
DMSO	Dimethyl sulfoxide
dr	Diastereomeric ratio
ee	enantiomeric excess
EI	electron ionization
ESI	electrospray ionization
Et_3N	triethylamine
Et_2O	diethyl ether
EtOAc	ethyl acetate
equiv	equivalents
g	gram(s)
GC/MS	gas chromatography / mass spectrometry

h	hour(s)
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectrometry
Hz	hertz
i-Pr	isopropyl
IR	infrared
J	NMR coupling constant
m	multiplet
m-CPBA	3-chloroperbenzoic acid
min	minute
mg	milligram
mL	milliliter
mp	melting point
MHz	megahertz
M	molar
Me	methyl
MeO	methoxy
m/z	mass to charge ratio
n-BuLi	*n*-butyllithium
n-Pr	*n*-propyl
NaOH	sodium hydroxide
NMR	Nuclear Magnetic Resonance
NOE	nuclear Overhauser effect

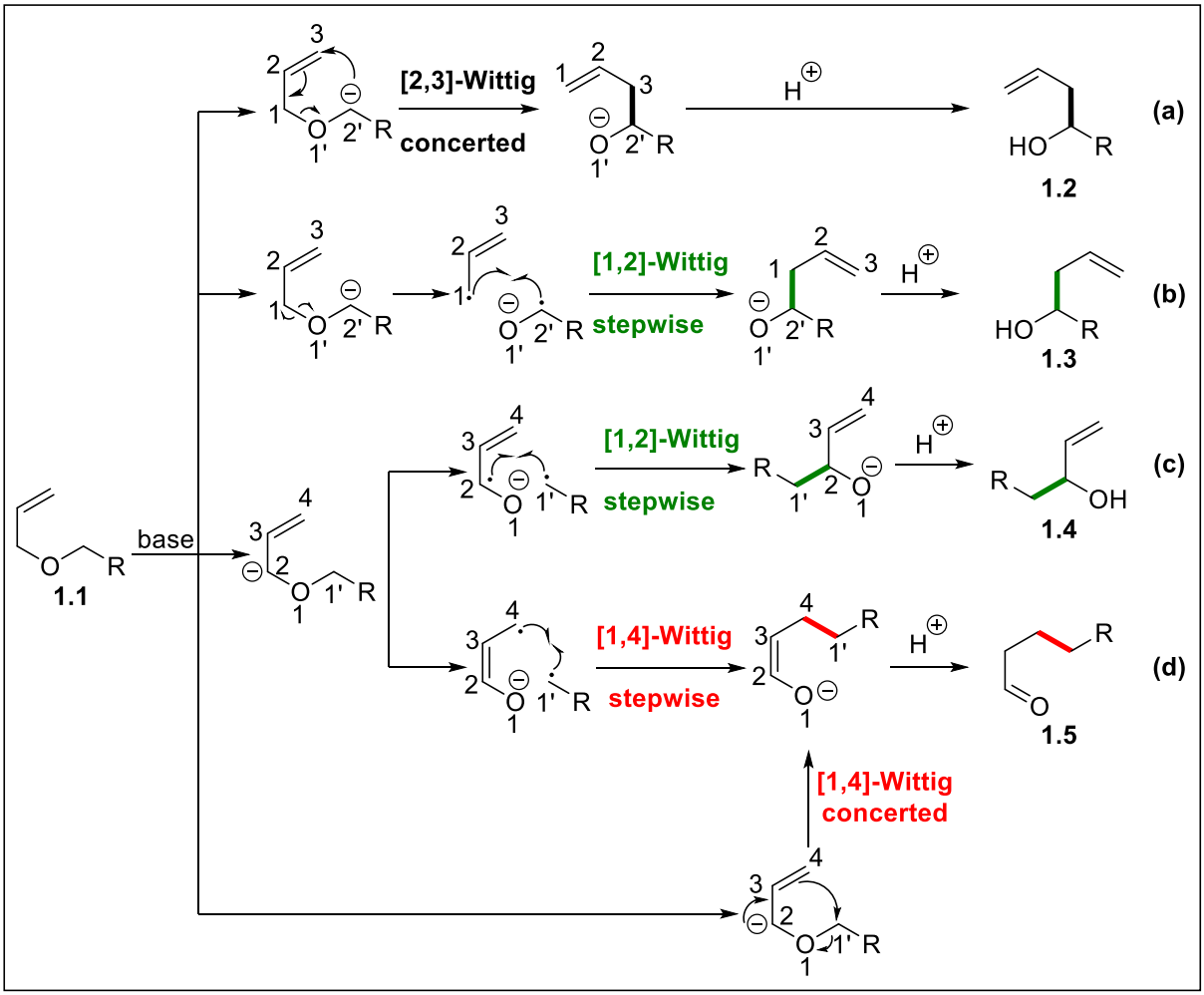
Ph	phenyl
q	quartet
RCM	ring-closing metathesis
s	singlet
sat	saturated
sec-BuLi	*sec*-butyllithium
$SiEt_3$	triethylsilyl
$SiMe_2Ph$	phenyldimethylsilyl
$SiPh_2Me$	diphenylmethylsilyl
S_N2	bimolecular nucleophilic substitution
rt	room temperature
t	triplet
t-BuLi	*tert*-butyllithium
t-BuONa	sodium *tert*-butoxide
TBAF	tetrabutylammonium fluoride
TBDPS	*tert*-butyldiphenylsilyl
TBS	*t*-butyldimethylsilyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
TMSCl	trimethylsilylchloride
TMSOTf	trimethylsilyl trifluoromethane sulfonate

CHAPTER 1.

INTRODUCTION

1.1. Background of Wittig rearrangements

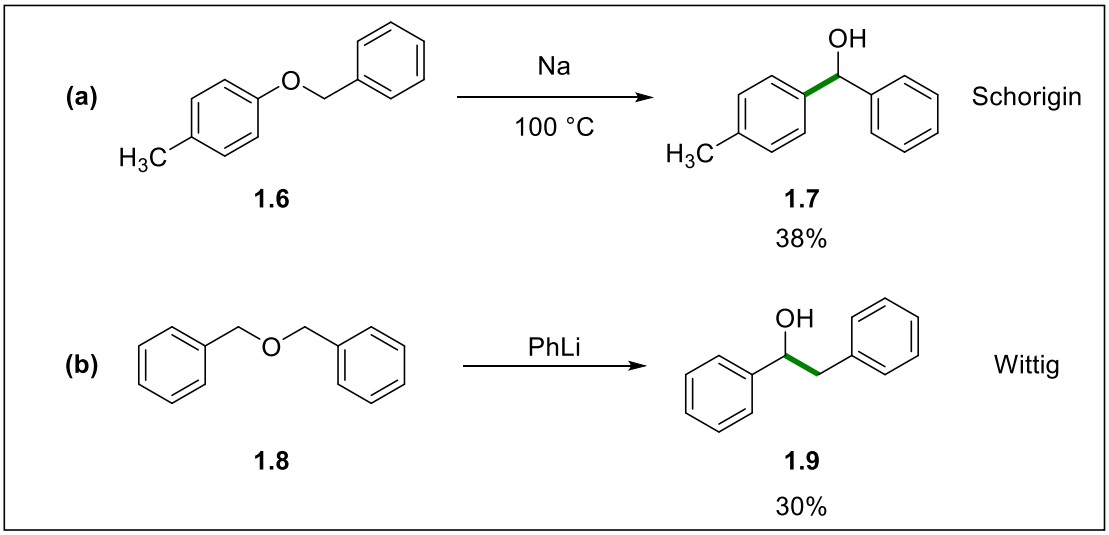
Wittig rearrangements entail restructuring of bonds of carbanionic ethers (usually allylic or benzylic) leading to structural isomers. The products resulting from Wittig rearrangements are of interest since they possess functional groups which can further be exploited during organic synthesis. Multiple rearrangements are possible depending on the substrate's nature (Scheme 1.1).



Scheme 1.1: Wittig rearrangements with proposed reaction mechanisms

1.2. First examples of Wittig rearrangements

The very first example of a [1,2]-alkyl shift was reported by Schorigin in 1924.[1] Schorigin conducted further experiments on this unusual rearrangement and reported the findings a year later.[2] Treatment of 1-(benzyloxy)-4-methylbenzene (**1.6**) with sodium at 100 °C led to the formation of phenyl(*p*-tolyl)methanol (**1.7**) (Scheme 1.2a). Later on in 1942, Wittig and Löhmann reported [1,2]-alkyl shifts of benzyl ethers to the corresponding alcohols triggered by deprotonation at the benzylic position.[2] An example from their work was the rearrangement of (oxybis(methylene))dibenzene (**1.8**) to 1,2-diphenylethan-1-ol (**1.9**) on treatment with phenyllithium (Scheme 1.2b). This discovery led to what is currently known as Wittig rearrangements.

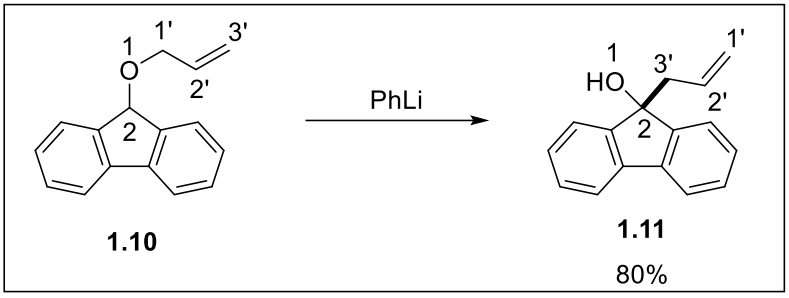


Scheme 1.2: First examples of [1,2]-Wittig rearrangements

1.3. The [2,3]-Wittig rearrangement

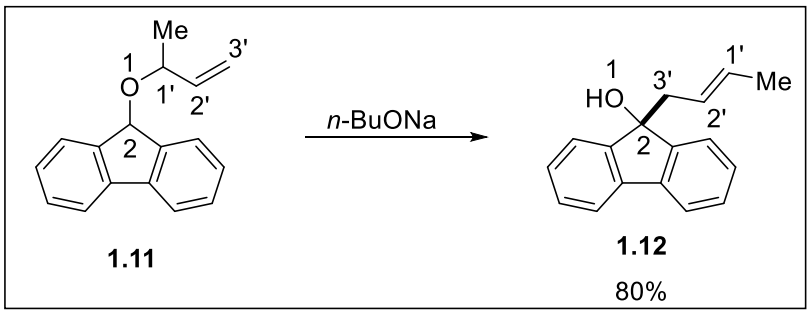
Of all the Wittig rearrangements, the [2,3]-Wittig has received the most attention from both synthetic and mechanistic standpoint. As the products of this rearrangement are homoallylic alcohols, the [2,3]-Wittig ranks highly among the known techniques for the synthesis of these alcohols in a stereoselective fashion.[4-7] The first [2,3]-Wittig rearrangement was reported by Wittig in 1949[8] where the rearrangement of allyl fluorenyl ether (**1.10**) led to the formation of 9-allyl-*9H*-

fluoren-9-ol (**1.11**) (Scheme 1.3).



Scheme 1.3: The [2,3]-Wittig rearrangement of 9-(allyloxy)-*9H*-fluorene

At first, the reaction mechanism of the formation of alcohol **1.11** was not clear since the above reaction could proceed by either [1,2]- or [2,3]-Wittig rearrangement. In 1960, Cast and Stevens subjected allyl fluorenyl ether **1.12** with a methyl group at carbon 1′ to Wittig rearrangement conditions leading to alcohol **1.13** (Scheme 1.4).[9] This was the first unambiguous scenario of [2,3]-shift that could be distinguished from the [1,2]-Wittig rearrangement.

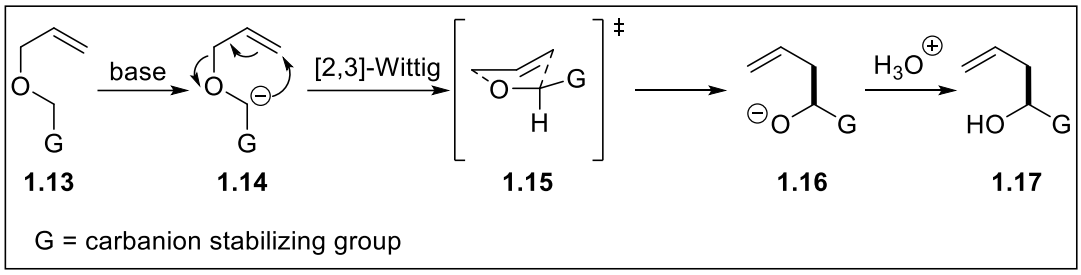


Scheme 1.4: Wittig rearrangement of 9-(but-3-en-2-yloxy)-*9H*-fluorene

1.3.1. Mechanism and stereochemistry of the [2,3]-Wittig rearrangement

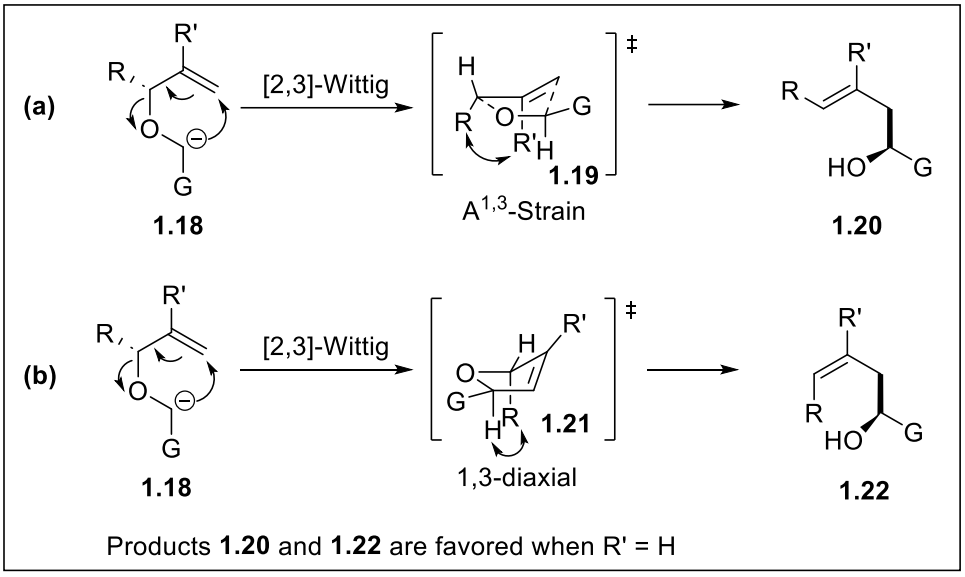
In most cases, [2,3]-Wittig rearrangements are carried out on allylic ether substrates that bear groups such as alkenes, aryl and alkynes that serve the purpose of stabilizing carbanions. Also used to stabilize the carbanion involved in this rearrangement are electron-deficient amides and esters. For example, a model substrate **1.13**, proceeds by initial metalation of the substrate leading to intermediate stabilized carbanion **1.14** (Scheme 1.5). This carbanion then undergoes [2,3]-Wittig rearrangement in a concerted fashion through an envelope-like five-membered transition state **1.15**

resulting in the formation of the homoallylic alkoxide **1.16**. The homoallylic alcohol product **1.17** is formed after the resulting alkoxide **1.16** is protonated during aqueous workup.[10]



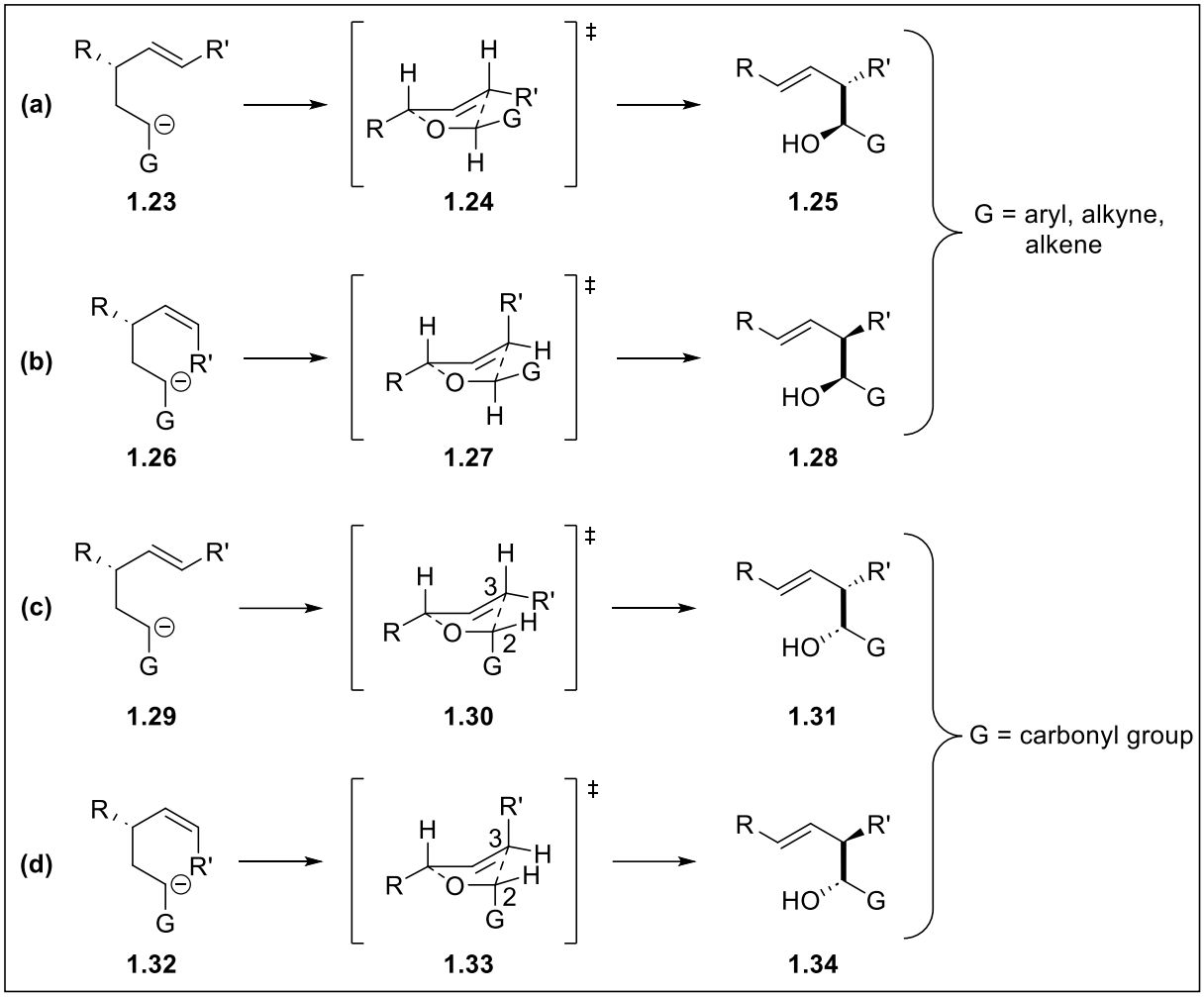
Scheme 1.5: Proposed mechanism of the [2,3]-Wittig rearrangement

Most [2,3]-Wittig rearrangements are stereoselective, that is, they result in the formation of one alkene stereoisomer.[4] This is attributed to the concerted mechanism shown in Scheme 5. For example, Wittig rearrangement of model substrate **1.18** leads to the formation of *E*-alkene **1.20** through transition state **1.19** where 1,3-diaxial interactions are minimized (Scheme 1.6a). Occasionally selectivity towards the *Z*-alkenes is observed when interactions between R and R′ become significant in transition state **1.19**. In these cases, the low energy route yields *Z*-alkene products **1.22** via the transition state **1.21** (Scheme 1.6b). The G-group in transition states **1.19** and **1.21** prefers an equatorial orientation, hence, chirality transfer is usually quite effective. As a result, optically active substrates such as **1.18** are converted to corresponding homoallylic alcohols **1.20** and **1.22** without losing optical purity.



Scheme 1.6: Chirality transfer and alkene stereochemistry in [2,3]-Wittig rearrangement

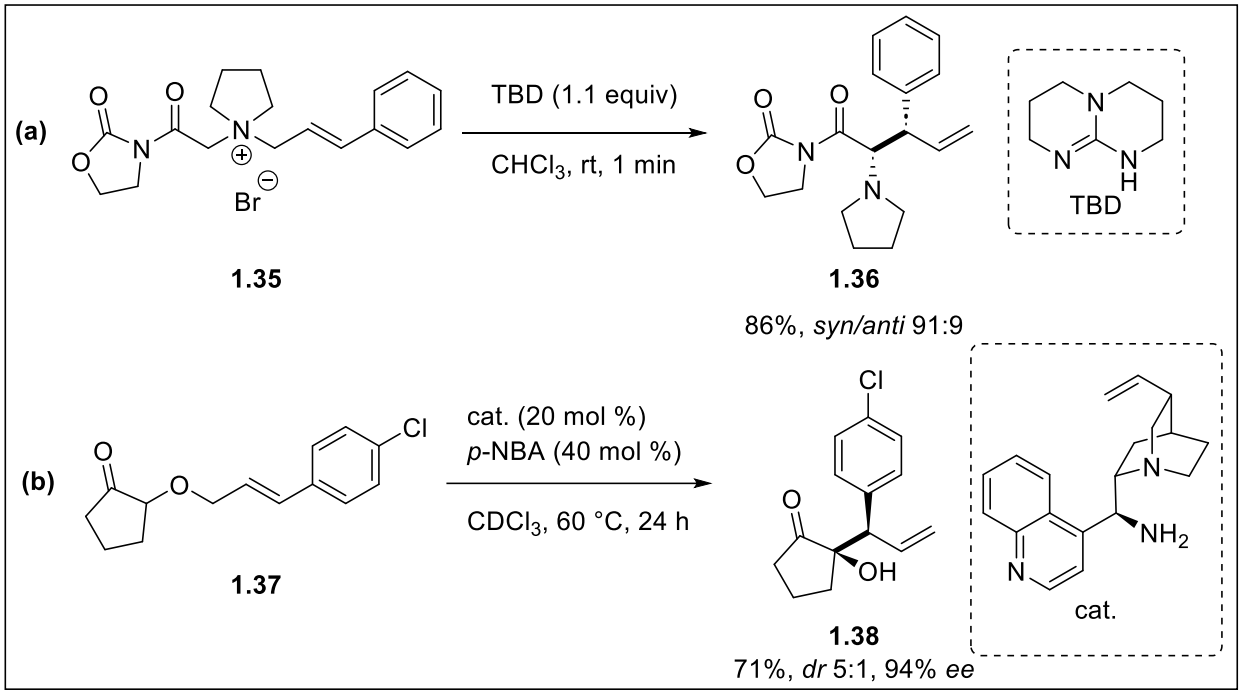
For internal alkenes, model allyl ethers **1.23** and **1.26** undergo diastereoselective [2,3]-Wittig rearrangement to the corresponding homoallylic alcohols **1.25** and **1.28** respectively when G = aryl, alkenyl or alkynyl (Scheme 1.7a, b).[10,11] However, switching the carbanion stabilizing group to a carbonyl-containing electron withdrawing groups such as an amide or an ester (G = $CONR_2$ (**1.29**) or G = COOR (**1.32**)) reverses the stereoselectivity (Scheme 1.7c, d). The [2,3]-Wittig rearrangements of **1.29** and **1.32** proceed via transition states **1.30** and **1.33** leading to homoallylic alcohols **1.31** and **1.34** respectively. The pseudoaxial orientation of the carbonyls in transition states **1.30** and **1.33** lead to the stabilization of the developing negative charge at C3.[10]



Scheme 1.7: [2,3]-Wittig transition state models for reactions of internal alkene substrates

1.3.2. Selected application of the [2,3]-Wittig rearrangements

As mentioned earlier, the [2,3]-Wittig rearrangement is the most utilized Wittig rearrangement from a synthetic perspective. Recent examples of this rearrangement include, but are not limited to, diastereoselective rearrangement of *N*-allyl ammonium ylides (Scheme 1.8a).[12] This is an example of the *aza*-Wittig rearrangement since the ethereal oxygen has been replaced by nitrogen. Use of organocatalysts to control stereochemical outcomes of [2,3]-Wittig rearrangement has also been reported recently. For instance, Kanger *et al.* developed a formal asymmetric [2,3]-Wittig rearrangement using *Cinchona*-derived amine organocatalyst α-branched ketones (Scheme 1.8b).[13]



Scheme 1.8: Recent report on [2,3]-Wittig rearrangement
TBD = 1,5,7-triazabicyclo[4.4.0]dec-5-ene. *p*-NBA = *para*-Nitrobenzoic acid

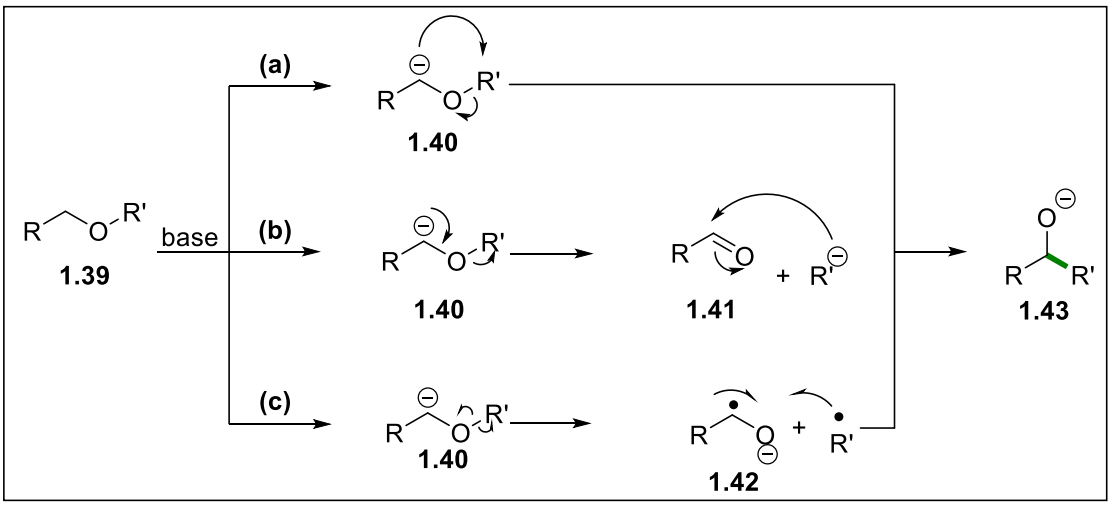
1.4. The [1,2]-Wittig rearrangement

The [1,2]-Wittig rearrangement is a sigmatropic shift resulting from benzyl or allyl carbanions, leading to the formation of allyl alcohol or homoallylic alcohol depending on the site of deprotonation (Scheme 1). It was the first type of Wittig rearrangement to be reported in the literature (Scheme 1.2).[1-3] The [1,2]-Wittig rearrangement's synthetic utility is usually constrained by the need for harsh reaction conditions employing strong bases that are at times not compatible with some functional groups present. Additionally, intramolecular elimination processes tend to compete with [1,2]-Wittig resulting in low yields. Despite this, construction of complex molecules in a stereoselective fashion has been achieved recently via [1,2]-Wittig rearrangements of specific classes of ethers.

1.4.1. Mechanism of the [1,2]-Wittig rearrangement

To carry out reactions that are expected to trigger [1,2]-Wittig rearrangements, it is important to understand the mechanism that leads to this rearrangement. This is helpful in designing

substrates that would eliminate or suppress other Wittig rearrangements in favor of the [1,2] shift. After its discovery, three different mechanistic pathways were proposed for the [1,2]-Wittig rearrangement (Scheme 1.9).

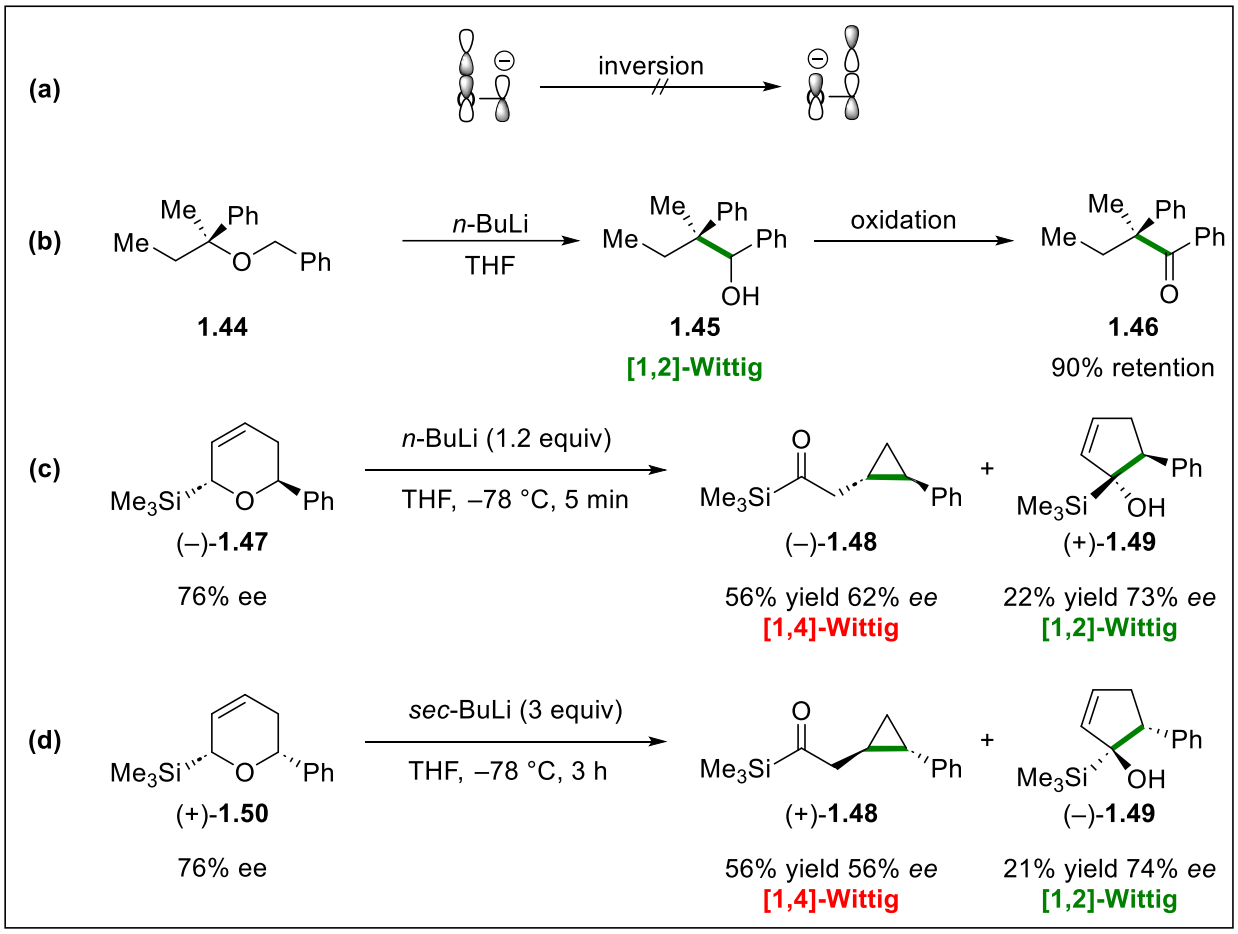


Scheme 1.9: Proposed pathways for the [1,2]-Wittig rearrangement reaction mechanisms

1.4.1.1. The concerted mechanism (Scheme 1.9, route a)

The rearrangement of carbanion **1.40 (**resulting from deprotonation of **1.39**) to form benzylic alkoxide **1.43** was proposed to undergo a concerted mechanism by Hauser and Kantor.[14] They argued for an intramolecular isomerization involving the 1,2-shift of an alkyl group presumably without its bonding pair of electrons to directly produce alkoxide **1.43** (Scheme 1.9, route **a**)**.** The concerted mechanism was thought to be the pathway until Woodward and Hoffman developed orbital symmetry rules,[15] which implied that such [1,2]-*antarafacial* migration was not possible geometrically. Furthermore, Fukui's frontier orbital theory[16,17] ruled out the first mechanism since if it were to occur this way then there would be inversion of stereochemistry at the migrating carbon center (Scheme 1.10a), which would not be in agreement with the results from the experiments carried out by Schöllkopf on optically active ethers. The [1,2]-Wittig rearrangements resulting from these ethers showed stereochemical retention of high degree at the migrating carbon center (Scheme 1.10b).[18-20] Recent studies by Mori and Maleczka on optically

active dihydropyrans also showed excellent retention of stereochemistry during the [1,2]-Wittig rearrangement (Scheme 1.10c, d).[21,22]

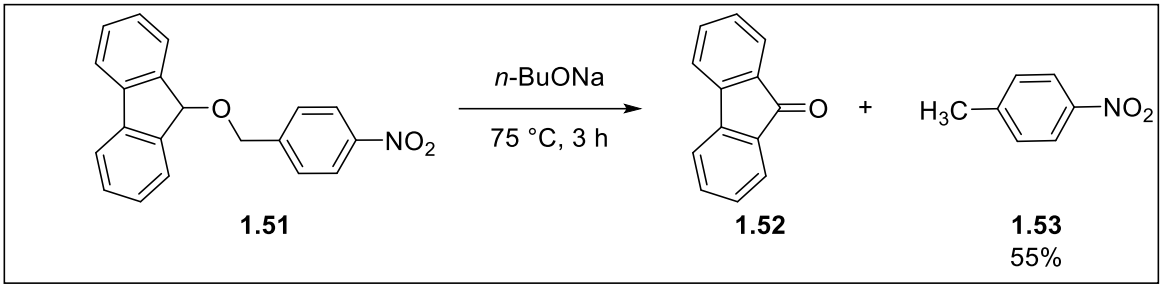


Scheme 1.10: Geometrically impossible [1,2]-antarafacial migration and retention of stereochemistry

1.4.1.2. Stepwise mechanism via carbanion and carbonyl intermediates (Scheme 9, b)

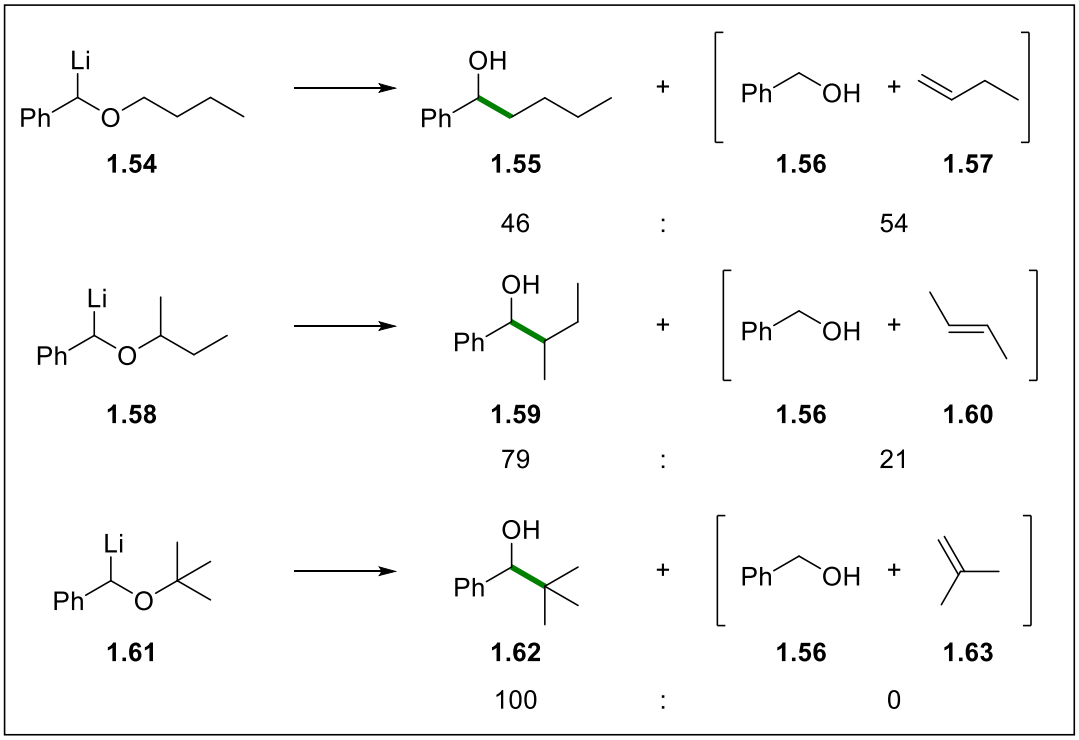
Following the above observation, a stepwise mechanism (Scheme 1.9, route **b**) involving elimination leading to a carbanion and carbonyl intermediate **1.41** was proposed. This carbanion then attacks the newly formed carbonyl **1.41** leading to the alkoxide **1.43**.[18,19,23] This agreed with the observed stereochemichal retention during the rearrangement. The isolation of *p*-nitrotoluene by Holmes when *p*-nitrobenzyl ethers underwent rearrangement was also considered as evidence to support this mechanism (Scheme 1.11a).[24] Recently, Sanz and Faza *et al.* have shown evidence

supporting the ionic character of [1,2]-Wittig rearrangement.[25]



Scheme 1.11: Evidence for stepwise mechanism via carbanion and carbonyl intermediates

However, there was a drawback to this mechanism (Scheme 1.9, route b). It was observed that tertiary alkyl groups migrated easily followed by secondary then primary ones, hence, ruling out stepwise mechanism involving heterolytic cleavage.[26] Furthermore, significant β-hydride elimination was observed during [1,2]-Wittig rearrangements of benzyl alkyl ethers with primary alkyl groups containing protons α to the migrating carbon (Scheme 1.12).[3, 26-28]

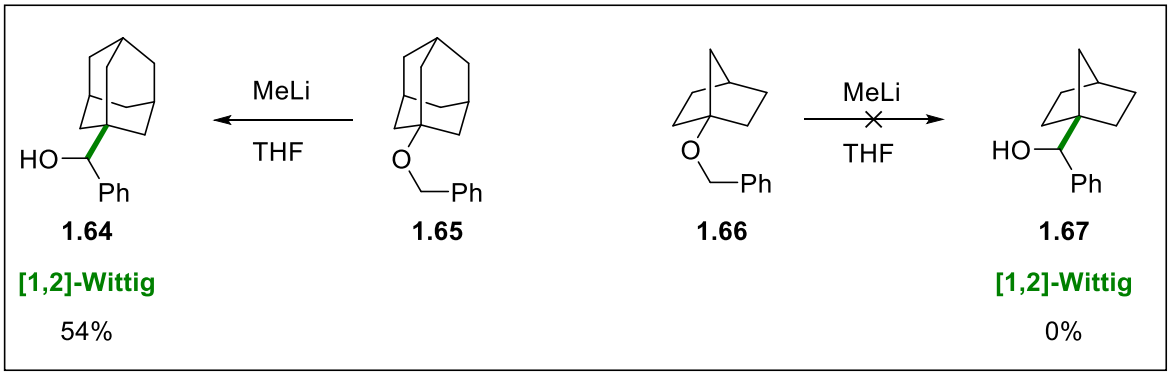


Scheme 1.12: β-hydride elimination during [1,2]-Wittig rearrangements of benzyl butyl ethers

1.4.1.3. Stepwise mechanism via radical / radical anion intermediates (Scheme 9, route c)

The above trend suggested presence of radicals as intermediates during the migration. Therefore, Lansbury, Pattison, Sidler and Bieber proposed a stepwise mechanism where following deprotonation, homolytic cleavage of the C–O bond occurs. The carbon radical and the carbon-centered radical anion recombine. The driving force here is the transfer of the formal negative charge from carbon to the electronegative oxygen atom (Scheme 1.9, route c).[26]

In favor of the homolytic cleavage stepwise mechanism (Scheme 1.9, route c) and against the heterolytic cleavage stepwise mechanism (Scheme 1.9, route b) was the following observation: 1-(Benzyloxy)adamantane (**1.65**) was found to undergo [1,2]-Wittig rearrangement to form adamantan-1-yl(phenyl)methanol (**1.64**) but 1-(benzyloxy)norbonane (**1.66**) did not (Scheme 1.13).[26, 29] This follows from the reasoning that the 1-norbornyl radical bears more strain and is thus less stable than the 1-adamantyl radical,[30] and the opposite is true for the corresponding anions.[31] This was in agreement with the stepwise mechanism involving radical / radical anion intermediates.

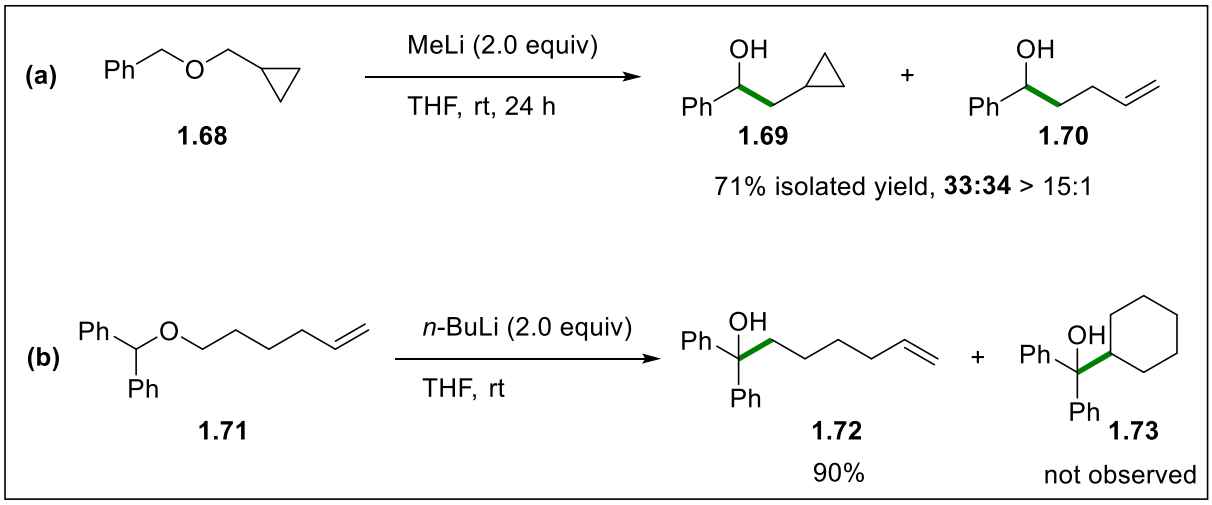


Scheme 1.13: Radical versus anion stability with respect to [1,2]-Wittig rearrangement

1.4.2. Rationale behind Retention of Stereochemistry after [1,2]-Wittig Rearrangement

The stereochemistry retention during [1,2]-Wittig rearrangement[18-20] (Scheme 1.10) suggests that the radical /radical anion pair recombines at a rate that is faster than rate of

racemization of that center. This has been explained as being due to the Wittig rearrangement occurring within a "solvent cage". Radical clock experiments have been used to gather evidence for a fleeting life of the migrating radical species: The cyclopropylmethyl group in ((cyclopropylmethoxy)methyl)benzene (**1.68**) experienced negligible isomerization after [1,2]-Wittig rearrangement (Scheme 1.14a).[23] From this observation it can be inferred that the recombination between the radical and radical anion is faster than 9.4×10^7 s^{-1}, which is the time it takes for the cyclopropyl ring to open.[32] Further rationalization involves inverse approach experiments: The expected [1,2]-Wittig rearrangement product **1.72** was exclusively formed from the rearrangement of ((hex-5-en-1-yloxy)methylene)dibenzene (**1.71**). Isomerization of the 5-hexenyl radical to form product **1.73** was not observed (Scheme 1.14b).[33,34] This is in agreement with the faster rate of rearrangement and, hence, the reason behind observed retention of stereochemistry.

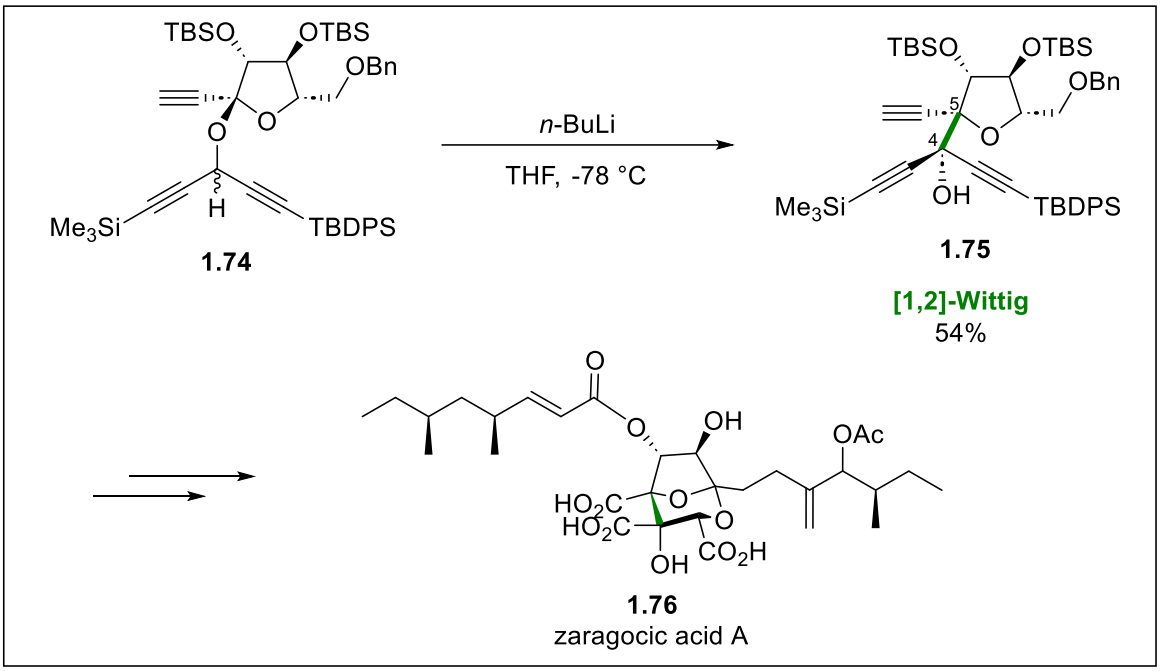


Scheme 1.14: Radical clock experiment during [1,2]-Wittig rearrangements

1.4.3. Representative applications of [1,2]-Wittig rearrangements in total synthesis

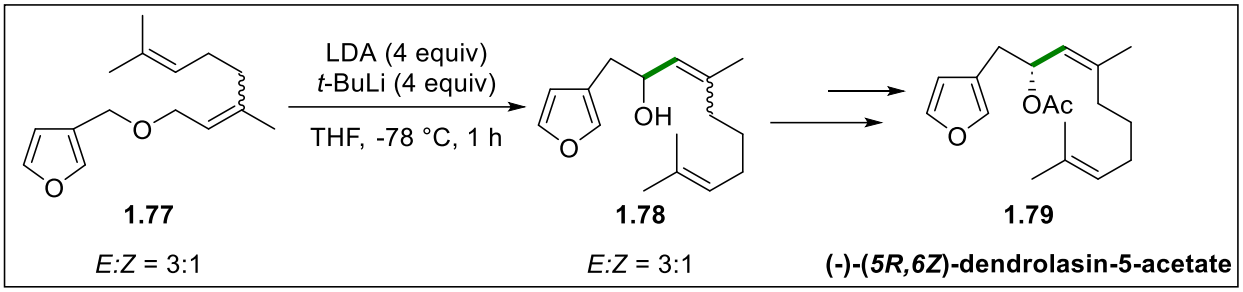
Unlike the [2,3]-Wittig rearrangement, the requirements to tune substrates in order to stabilize the radical of the migrating fragments has made the application of the [1,2]-Wittig

rearrangement limited.[35] Furthermore, generating an α-carbanionic ether by use of strong bases that do not always tolerate the functional groups that may be present has also limited the use of the [1,2]-Wittig rearrangement in total synthesis. However, Nakai took advantage of the chirality present in carbohydrates to develop a stereocontrolled acetal systems [1,2]-Wittig rearrangement.[36-38] He further utilized this technology[37] in one of the steps towards the total synthesis of zaragozic acid A (**1.76**) (Scheme 1.15).[38]



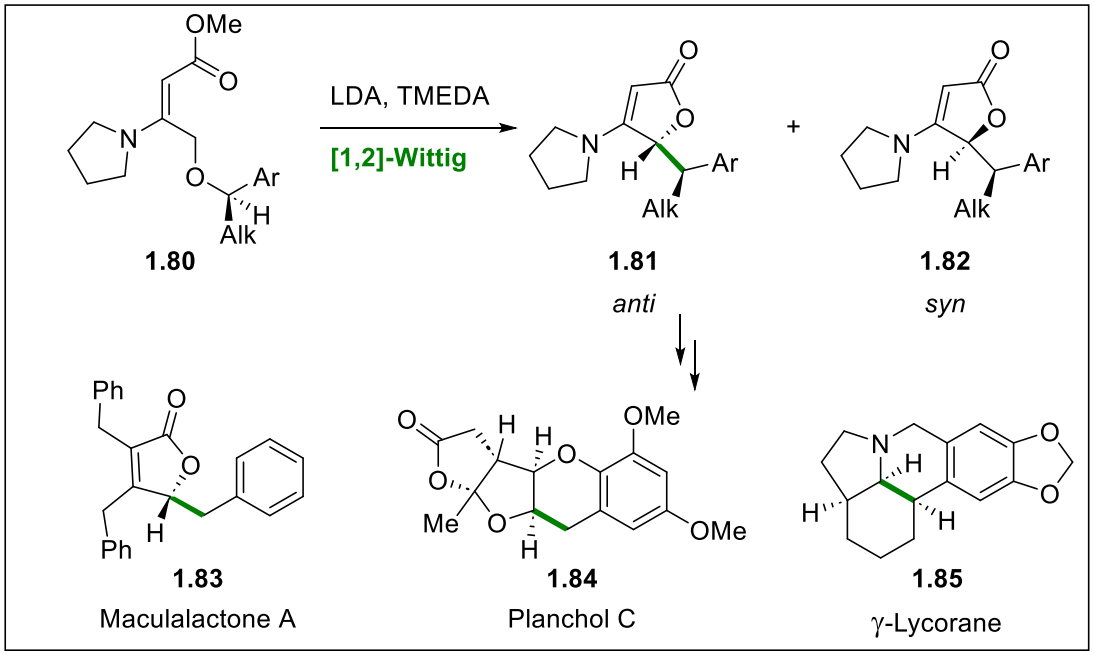
Scheme 1.15: Application of [1,2]-Wittig rearrangement to total synthesis of zaragozic acid A

Garson *et al*. reported the isolation and total synthesis of (−)-(5*R*,6*Z*)-dendrolasin-5-acetate in five steps.[39-42] The key step employed involved a [1,2]-Wittig rearrangement of geranyl 3-furylmethyl ether (**1.77**) to produce alcohol **1.78**, followed by acetylation and resolution to obtain target molecule **1.79** (Scheme 1.16).



Scheme 1.16: Application of [1,2]-Wittig rearrangement to total synthesis of dendrolasin-5-acetate

Recently, Ho and Li developed a practical method to functionalize γ-benzyloxy vinylogous urethanes into γ-benzyl butenolides through tandem [1,2]-Wittig rearrangement/lactonization. As a proof of concept, they applied this development in the total synthesis of maculalactone A, planchol C and γ-lycorane (Scheme 1.17).[43]



Scheme 1.17: Application of [1,2]-Wittig rearrangement to total synthesis of Maculalactone A, Planchol C and γ-Lycorane

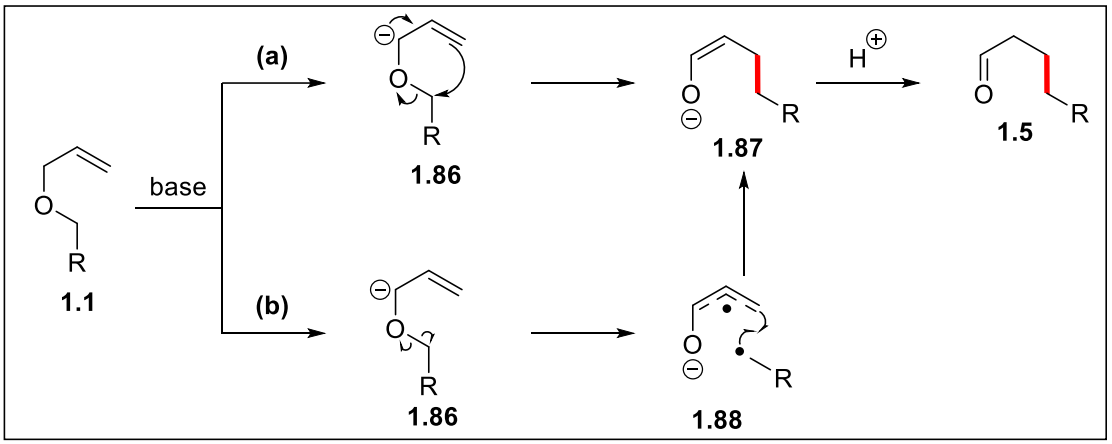
1.5. The [1,4]-Wittig rearrangement

Transformations via [1,4]-Wittig rearrangement are rare due to the competing [1,2]-Wittig (Scheme 1.1). First reported by Falkin and Tambute in 1969,[44] the [1,4]-Wittig rearrangement results in the formation of enolate which is transformed into carbonyl after protonation. The enolate

can also be trapped by various electrophiles.

1.5.1. Mechanism of the [1,4]-Wittig rearrangement

There are two different proposed mechanistic pathways for the [1,4]-Wittig rearrangement: An orbital symmetry allowed concerted pathway (Scheme 1.18, route a) or a stepwise mechanism like the [1,2]- case involving radical / radical anion intermediates (Scheme 1.18, route b).



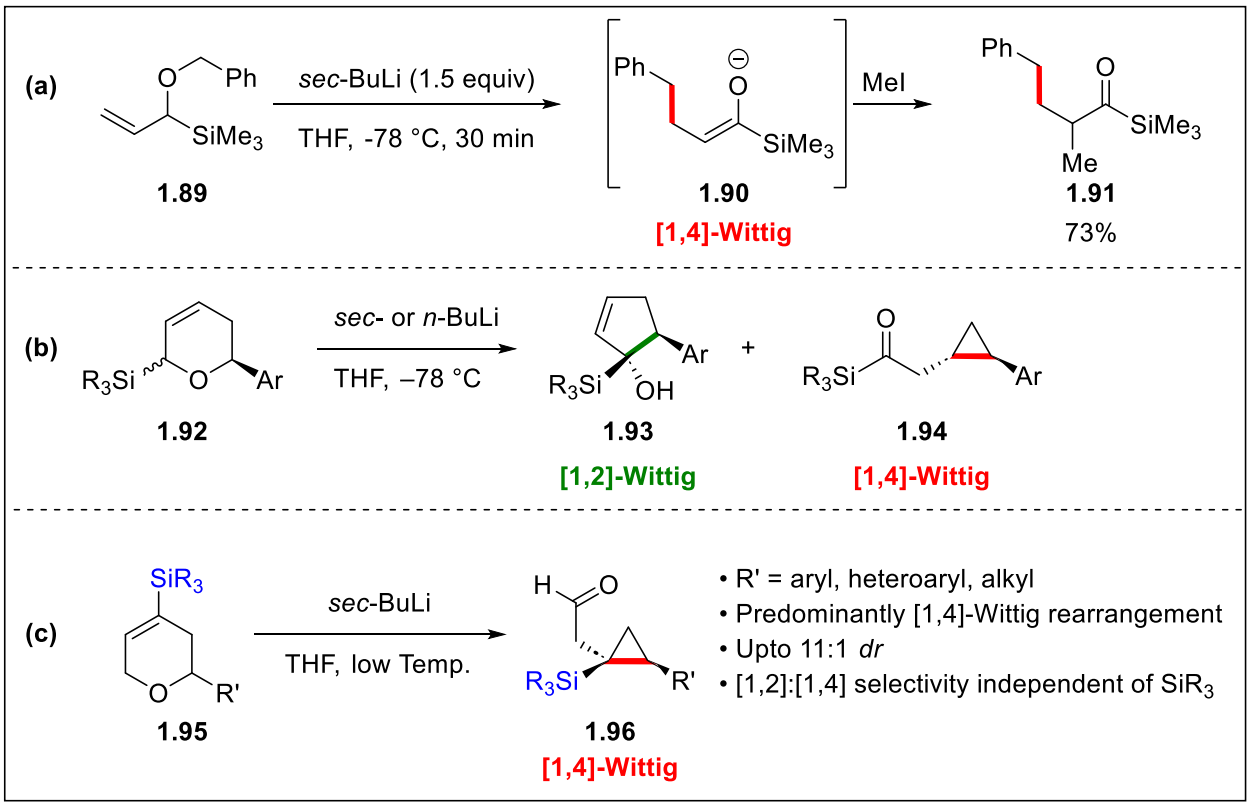
Scheme 1.18: Proposed mechanistic pathways for [1,4]-Wittig rearrangement

Experimental evidence in support of both approaches have been reported in the literature.[21,22,45] In addition, a DFT study carried out recently by Joshi *et al.* on dihydrofuran systems indicated that the reaction followed a stepwise mechanism during the [1,4]-Wittig rearrangement.[22]

1.5.2. Application of [1,4]-Wittig rearrangement

The [1,4]-Wittig rearrangement has been observed during [1,2]-Wittig rearrangements.[37,46-48] Although the bases used to initiate Wittig rearrangements play a role in the selectivity between [1,2]- and [1,4]-Wittig rearrangements, the cause of the reaction is highly substrate-dependent. Generally, low temperatures tend to favor [1,4]-Wittig. There have been recent reports on high-yielding reactions that proceed via the [1,4]-Wittig rearrangement. Extensive studies on the [1,4]-Wittig rearrangement have been conducted by the Maleczka group. A highly selective [1,4]-Wittig rearrangement of α-benzyloxyallylsilane (**1.89**) has been reported by Onyeozili and

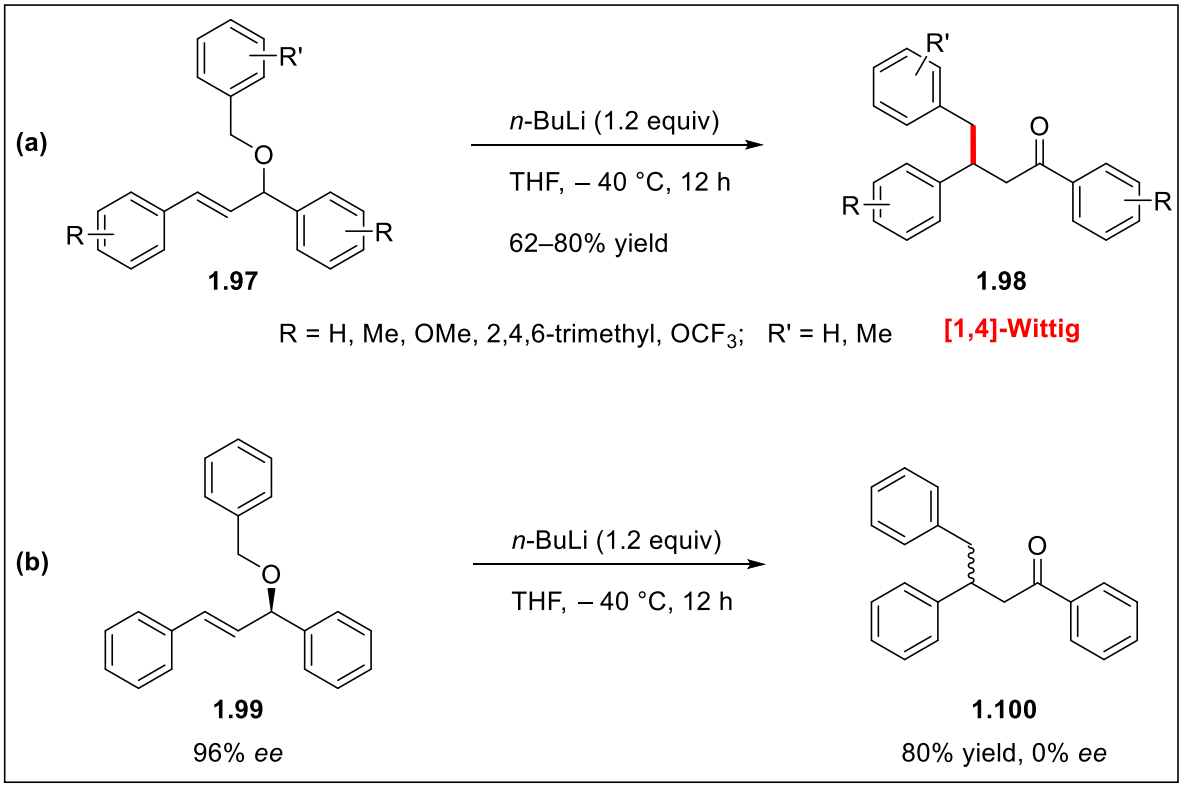
Maleczka (Scheme 1.19a).[48] The enolate product **1.90** from this rearrangement could be trapped with various electrophiles leading to acylsilanes **1.91** substituted at the α-position. In 2015, Maleczka and Mori were able to tune the dihydropyrans in favor of either [1,2]- or [1,4]-Wittig rearrangement. For instance, the [1,2]-Wittig rearrangement was achieved when they employed electron-deficient aromatic groups and/or small groups on silicon. The compliment was also true (Scheme 19b).[21] Surprisingly, when the silyl group was moved to form 4-silyl-6-aryl/alkyldihydropyrans, [1,4]-Wittig rearrangement was to the corresponding silylcyclopropane acetaldehydes predominated (Scheme 1.19c),[49] (Chapter 3).



Scheme 1.19: Selective [1,4]-Wittig rearrangement examples from Maleczka group

In 2015, Xu reported that chalcone-derived allylic ethers **1.97** undergo [1,4]-Wittig rearrangement resulting in the formation of benzyl ketones **1.98**, which are disubstituted at the β-position (Scheme 1.20a).[50] Not surprisingly, the [1,4]-Wittig rearrangement of optically active (*R*,*E*)-(3-(benzyloxy)prop-1-ene-1,3-diyl)dibenzene (**1.99**) led to racemic 1,3,4-triphenylbutan-1-

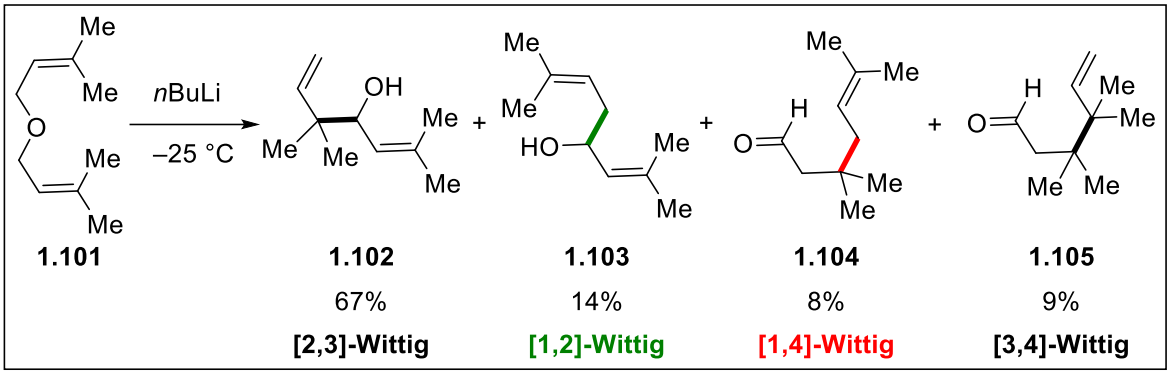
one (**1.100**). This could be attributed to the change of hybridization to sp^2 at the stereogenic carbon during the reaction (Scheme 1.20b).



Scheme 1.20: [1,4]-Wittig rearrangement of (*E*)-(3-(benzyloxy)prop-1-ene-1,3-diyl)dibenzenes

1.6. Control of regioselectivity during Wittig rearrangements

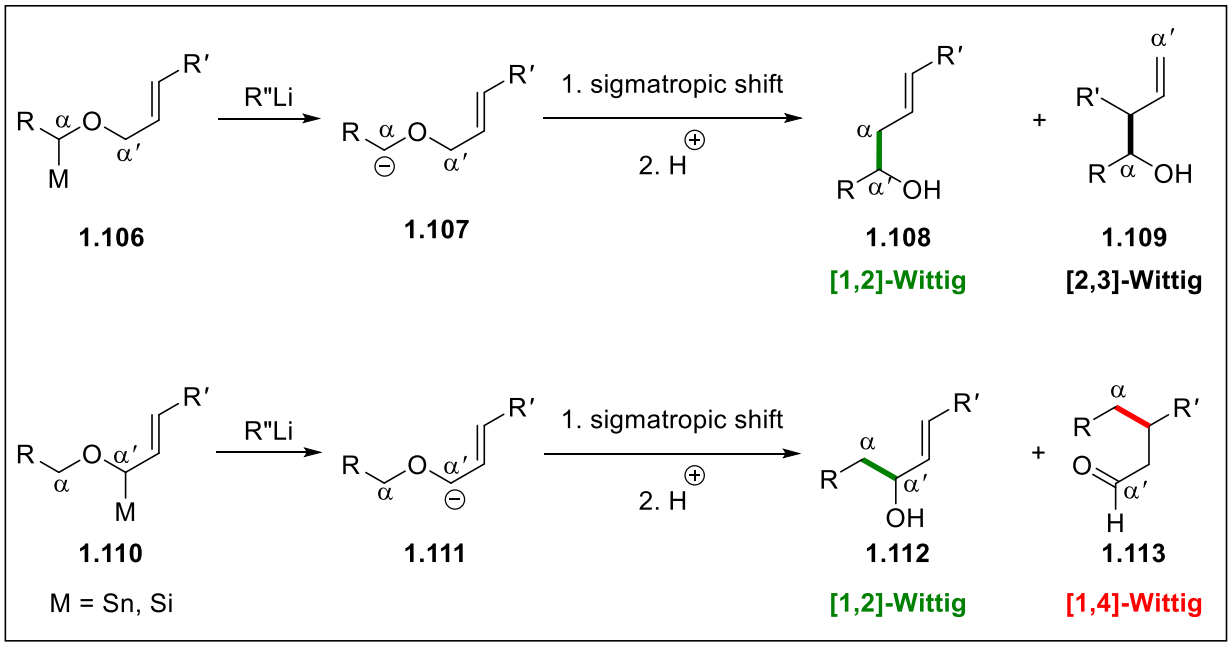
As illustrated in scheme 1.1 and throughout the previous discussion, the [1,2]-Wittig rearrangements tend to compete with [2,3]-Wittig, whereas the [1,4]-Wittig competes with the [1,2]-Wittig. For instance, Rautenstrauch observed [2,3]-, [1,2]-, [1,4]- and [3,4]-Wittig rearrangements when 3-methyl-1-((3-methylbut-2-en-1-yl)oxy)but-2-ene (**1.101**) was treated with a base, leading to formation of products **1.102**, **1.103**, **1.104** and **1.105** respectively (Scheme 1.21).[51]



Scheme 1.21: All possible Wittig rearrangements

1.6.1. Control of regioselectivity via metal/lithium exchange

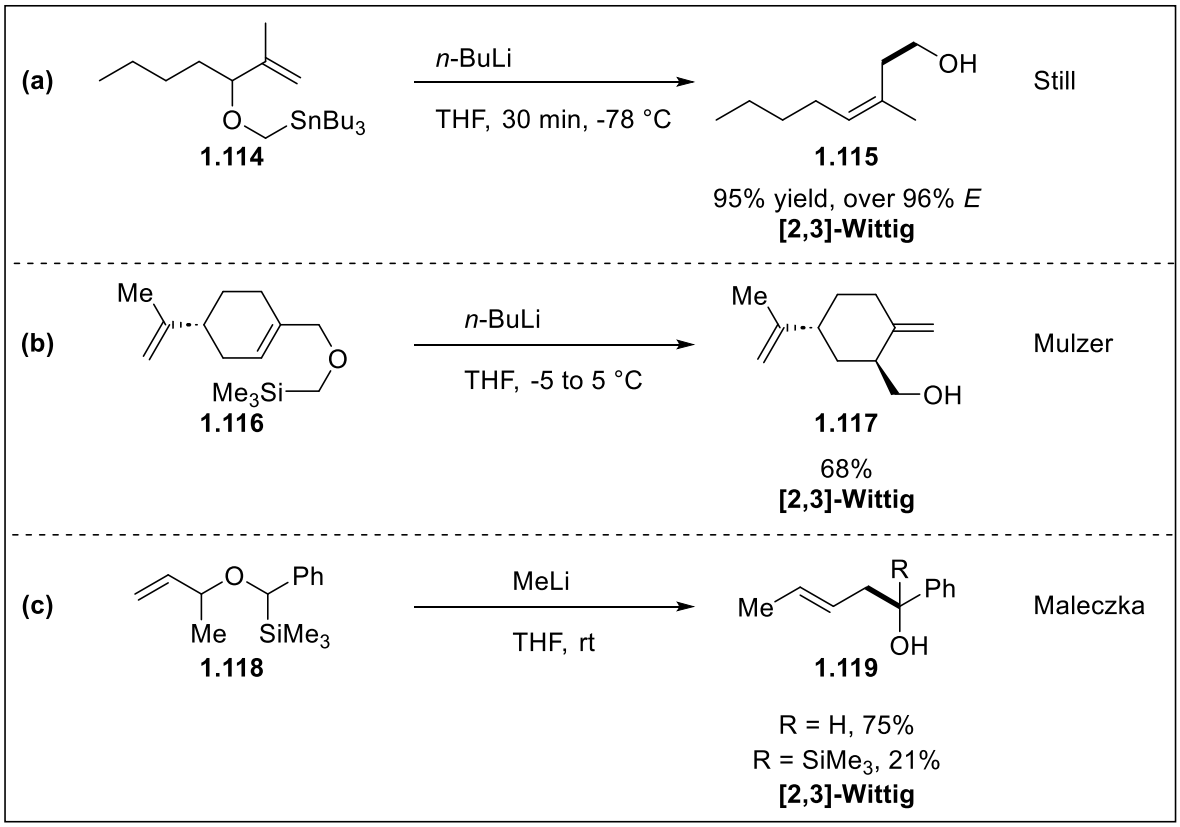
For ethers that are substituted unsymmetrically, regioselective Wittig rearrangement becomes a challenge. The ability to generate the anion can be controlled by installing a displaceable group M at either the α or α' positions. This group can then be displaced to generate an anion, which will determine the type of Wittig rearrangement the substrate will undergo, overcoming the regioselectivity challenge (Scheme 1.22).



Scheme 1.22: Control of regioselectivity via group M-directed carbanion generation

The above idea led to the discovery of what is currently known as the Wittig-Still

rearrangement (Scheme 1.23a).[52] The M-group in this case is tributyl tin. The tin-lithium exchange generates unstable carbanions, which can then isomerize via Wittig rearrangements.[53] The Wittig-Still rearrangement is a powerful synthetic tool[54] that has been applied widely in the total synthesis of natural product,[55-59] however, toxicity of organotin[60-62] led to a search for approaches involving non-toxic materials. Mulzer and List's pioneer work on use of silicon in place of tin (Scheme 1.23b)[63] motivated Maleczka and Geng to carry out regioselective Wittig rearrangement of α-alkoxy silanes via silicon/lithium exchange (Scheme 1.23c).[64]

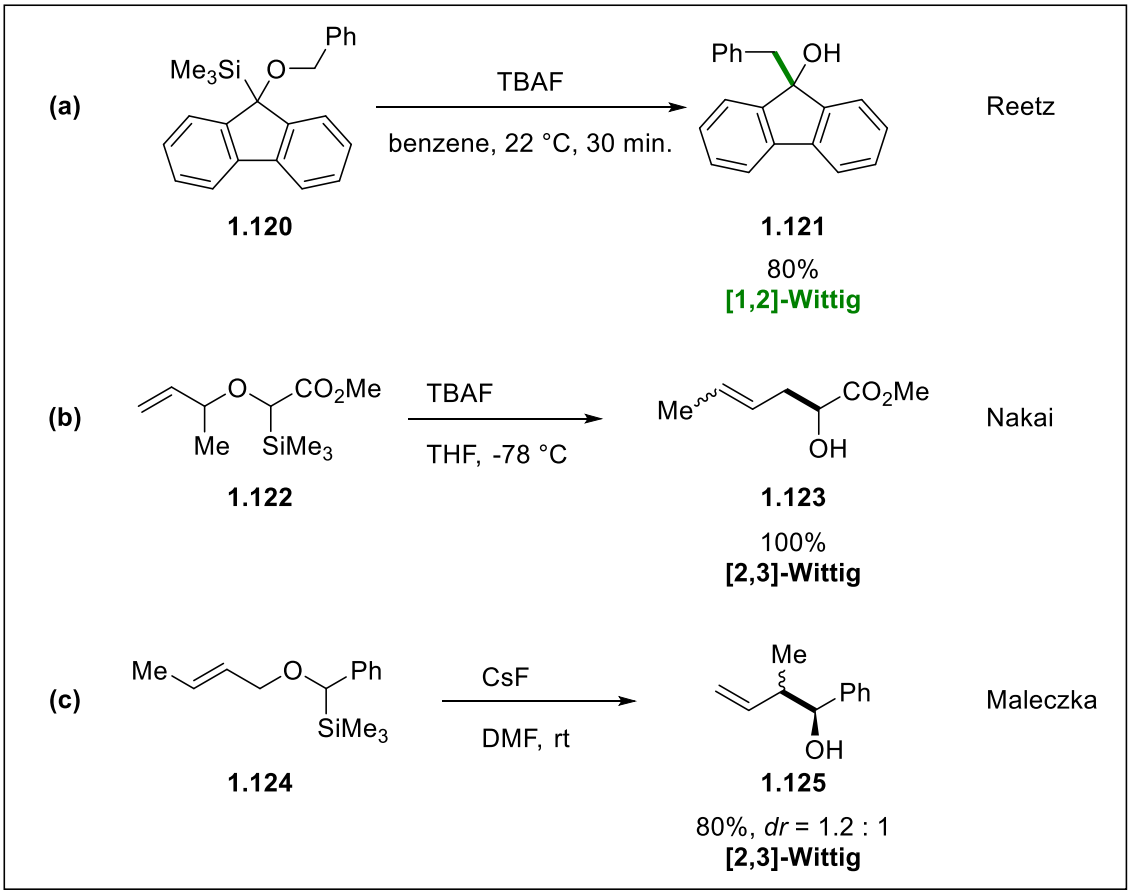


Scheme 1.23: Examples involving silicon-lithium exchange / Wittig rearrangements

The absence of groups that could stabilize the resulting anion in Mulzer's examples enabled efficient Si/Li exchange and subsequent Wittig rearrangement. In prior work by the Maleczka group, however, the trimethylsilyl group's carbanion-stabilizing effect together with phenyl and olefin groups present in these molecules caused competition between deprotonation / rearrangement

and Si/Li exchange.

Replacement of tin with silicon solved the toxicity problem. However, use of strong bases limits the substrate scope due to incompatibility of these bases with many functional groups. To solve this problem, the generation of carbanions by use of fluoride anions has been studied by Nakai,[35] Reetz[65] and Maleczka.[66] The resulting carbanions then undergo Wittig rearrangements. In this case silyl groups are thought to be carbanion masks. Displacement of these groups generates carbanions, which then undergo Wittig rearrangements (Scheme 1.24).

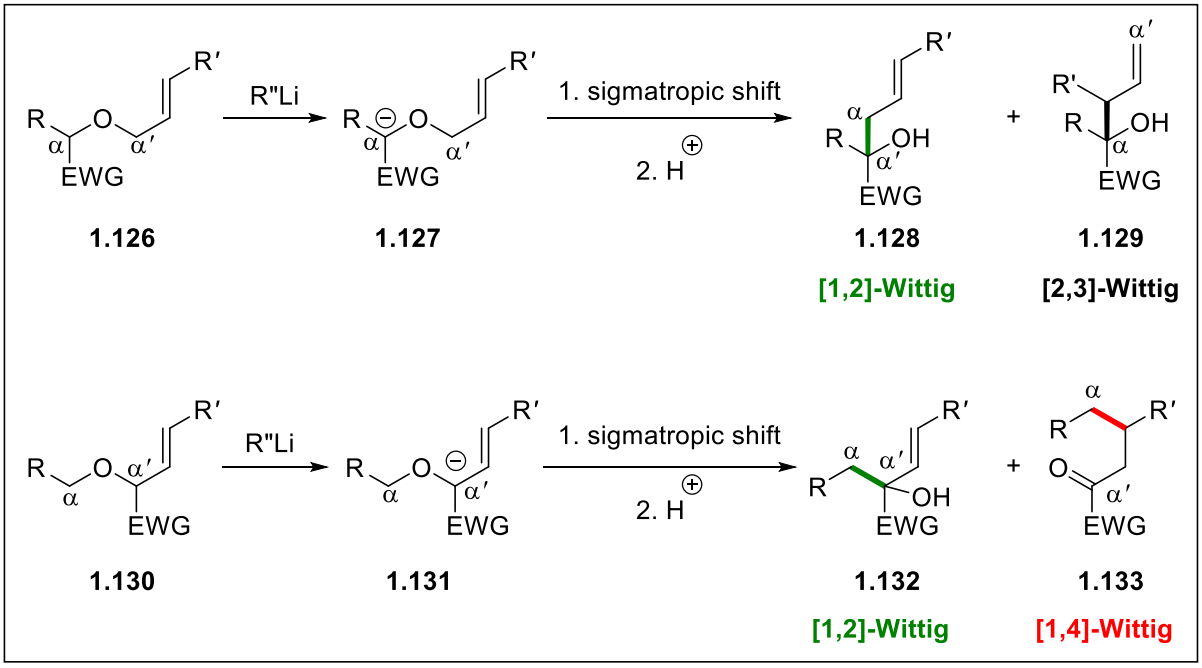


Scheme 1.24: Fluoride-promoted Wittig rearrangements

1.6.2. Control of regioselectivity via EWG-directed deprotonation

Another way of controlling the regioselectivity of unsymmetrically substituted ethers is by modifying the *p*Ka of the protons at the α and α' position. This in turn determines the deprotonation

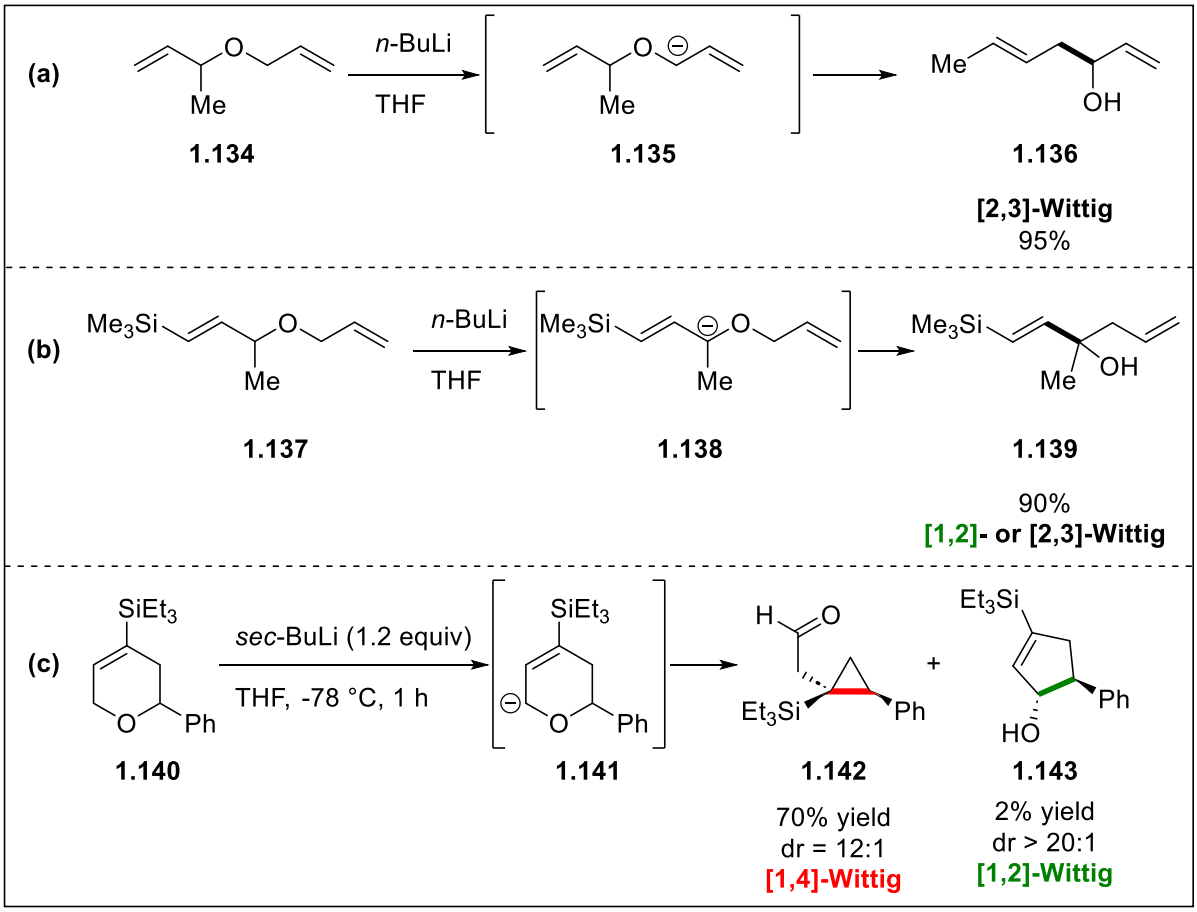
site and therefore the possible Wittig rearrangements. For instance, placing an EWG group at the α (or α′) position can act as an anion stabilizing group and therefore make deprotonation and Wittig rearrangement regioselective (Scheme 25). Groups such as phenyl, alkynes, carbonyls (esters, amides, ketones, aldehydes), sulfonyl, silyl, and cyano can act to stabilize the anion and are therefore good substituents (EWG) at promoting Wittig rearrangements.[67,68]



Scheme 1.25: Control of regioselectivity via group EWG-directed deprotonation

Of particular interest are the silyl groups since they have the ability to delocalize the negative charge of adjacent carbanions through silicon's d orbitals and, thereby stabilizing the charge.[69,70] Even though this ability has been attributed to hyperconjugation,[71,72] the silyl group makes the α-proton more acidic by reducing the conjugated acid's *p*Ka. Therefore, the presence of silicon in a molecule can change the regioselective outcome of the Wittig rearrangement. For example, silicon-free bisallylic ethers were found to undergo selective deprotonation at the less substituted α′ position (Scheme 1.26a),[31] however, selective deprotonation at the α position occurred after introduction of the silyl group at the γ position. This was followed by Wittig

rearrangement (most substituted position) (Scheme 1.26b).[52] In this case, vinyl trialkylsilyl group was used as the G-group. The Wittig rearrangements of 6-aryl-4-silyl-5,6-dihydro-(*2H*)-pyrans has also been studied. The vinyl silyl group led to exclusive deprotonation at the allylic position. The resulting carbanions underwent [1,2]- and [1,4]-Wittig rearrangements. Surprisingly, the major products isolated were mostly the result of [1,4]-Wittig rearrangement (Scheme 1.26c).[49]



Scheme 1.26: Silicon-directed deprotonation at the allylic position

With regard to the earlier observation on competitive deprotonation vs Li/Si exchange (Scheme 1.19a),[62] placing the silane group at the α' position resulted in exclusive deprotonation and avoided the Si/Li exchange as reported by Maleczka and Onyeozili.[48] The α-benzyloxyallylsilanes were able to undergo [1,4]-Wittig rearrangement in a very efficient manner. The resulting enolate intermediates were trapped with various electrophiles. This provided a new

synthetic approach to substituted acylsilanes (Scheme 19a).[48] Cyclic versions of the above have also been studied by the Maleczka group.[21,49] Wittig rearrangements of diastereomeric 2-silyl-5,6-dihydro-6-aryl-(*2H*)-pyrans resulted in regiodivergent ring contractions to the corresponding *α*-silylcyclopentenols and/or (*α*-cyclopropyl)acylsilanes. The [1,4]-Wittig was found to predominate when the aryl substituent on starting pyrans contained electron donating and/or by sterics emanating from the substituents on silicon. The [1,2]-Wittig was achieved with electron withdrawing groups and smaller silyl groups. Substituting the olefin part of the dihydropyran proximal to the silyl group led to exclusive [1,2]-Wittig rearrangements. Furthermore, the *cis* and *trans* diastereomers rearranged in a convergent manner leading to the corresponding α-silylcyclopentenols and cyclopropyl acyl silanes as a single diastereomer (Scheme 19b).

Regarding the relative stereochemistry of 2-silyl-6-aryl dihydropyrans, *trans* diastereomers are more reactive than the *cis* isomers. Mori hypothesized that these reactivity differences were "presumably because an optimal conformation suitable for allylic deprotonation is easily attainable" in the *trans* isomer and prevented by sterics in the *cis*. Mori's hypothesis is consistent with conformational analysis and the fact that increased sterics about the silyl groups or aryl rings did not change the reactivity of the *trans* isomers, while the *cis* cyclic ethers become less reactive. Computational studies recently done by Joshi *et al.* confirmed this.[22]

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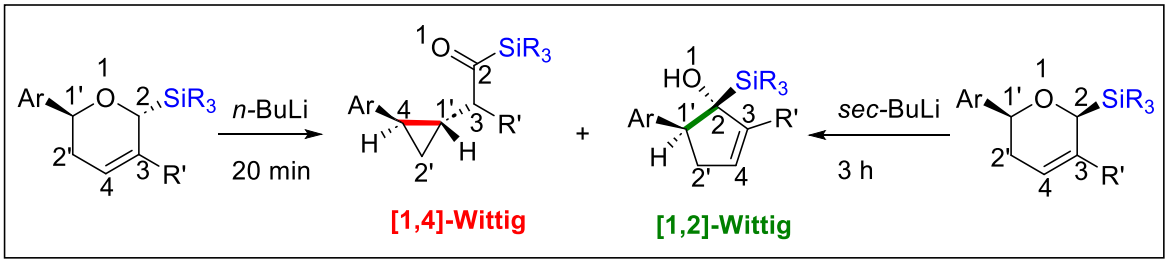
CHAPTER 2.

THE [1,2]- AND [1,4]-WITTIG REARRANGEMENTS OF 2-SILYL-7-ARYL-2,5,6,7-TETRAHYDROOXEPINS

2.1. Introduction

The first reported Wittig rearrangement reaction was the [1,2]-Wittig.[1] Despite this fact, the [1,2]-Wittig rearrangement has fewer synthetic applications compared to its [2,3]- counterpart. This is partly attributed to competition observed between the [1,2]- and the [2,3]-Wittig rearrangement. Furthermore, the [1,2]-Wittig rearrangement experiences narrower substrate scope and relatively lower yields restricting its synthetic applicability.[2-11] In addition, the [1,4]-Wittig rearrangement, which was first observed by Felkin and Tambute in 1969 also competes with the [1,2]-Wittig rearrangement.[7, 12-14]

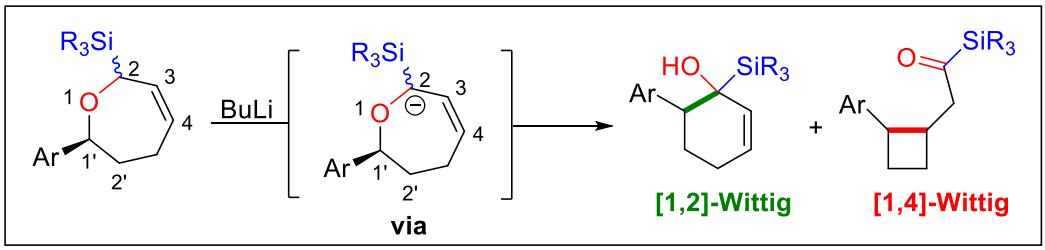
In 2015, Mori and Maleczka reported that diastereomeric 2-silyl-5,6-dihydro-6-aryl-(*2H*)-pyrans undergo stereoconvergent [1,2]- and/or [1,4]-Wittig rearrangements to afford α-silylcyclopentenols and/or (α-cyclopropyl)acylsilanes respectively (Scheme 1.1).[15] Although there is usually a competition between the [1,2]- and [1,4]-Wittig pathways, they have shown that the isomerization can be selective towards the [1,2]- or [1,4]-Wittig rearrangements. For instance, the [1,2]-Wittig pathway predominated with electron-deficient aryl groups and smaller alkyl/aryl substituents on silicon. The opposite was true for the [1,4]-Wittig rearrangement. Furthermore, *cis* and *trans* dihydropyrans exhibited different reactivities, but converged to single diastereomeric Wittig products (Scheme 2.1). The [1,2]- and [1,4]-Wittig rearrangements are proposed to follow stepwise mechanism. This proposal has been supported by recent computational studies.[16]



Scheme 2.1: [1,2]- and [1,4]-Wittig rearrangements of 2-silyl-6-aryl-5,6-dihydropyrans[15]

2.2. Expected products of [1,2]- and [1,4]-Wittig rearrangements of 2-silyl-7-aryl-2,5,6,7-tetrahydrooxepins

From the above results, we hypothesized that increasing the ring size of the starting material from 2-silyl-6-aryl-5,6-dihydropyrans to 2-silyl-7-aryl-2,5,6,7-tetrahydrooxepins would enable access to 1-silyl-6-arylcyclohex-2-en-1-ols and/or (α-cyclobutyl)acylsilanes via [1,2]- and/or [1,4]-Wittig rearrangement (Scheme 2.2). To the best of our knowledge, the ring contraction of tetrahydrooxepins by Wittig rearrangements has not been previously reported.

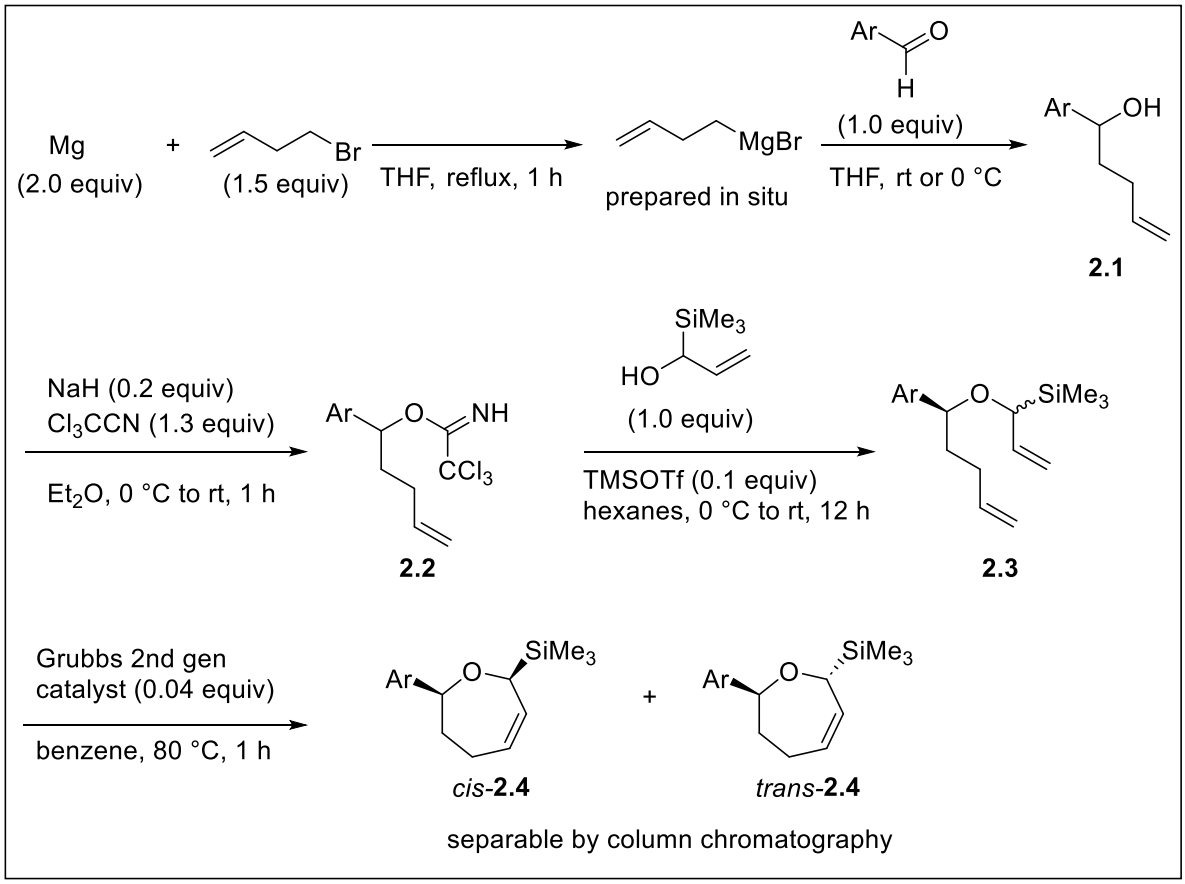


Scheme 2.2: Proposed [1,2]- and [1,4]-Wittig rearrangements of 2-silyl-7-aryl-2,5,6,7-tetrahydrooxepins

2.3. Synthesis of 2-silyl-7-aryl-2,5,6,7-tetrahydrooxepins

To test the above hypothesis, we first synthesized the starting material by homoallylation of benzaldehydes followed by conversion of the resulting alcohols **2.1** to trichloroacetimidates **2.2**. The trichloroacetimidates were then coupled with 1-(trimethylsilyl)prop-2-en-1-ol in the presence of catalytic amount of a Lewis acid (BF_3•OEt_2 or TMSOTf) to form diastereomeric dienes **2.3**. The assignment of relative stereochemistry of these dienes was done after the ring closing metathesis by Grubbs 2nd generation catalyst. In some instances, the diastereomeric dienes were separable by column chromatography. In these cases, the dienes were subjected to ring closing metathesis as

single diastereomers. In cases where the diastereomeric dienes **2.3** were subjected to ring closing metathesis as a mixture of diastereomers (*syn*:*anti*), the resulting diastereomers of 2-silyl-2,5,6,7-tetrahydro-7-aryl-oxepins (**2.4**) were separable by column chromatography and their relative stereochemistry assigned by ^{1}H NMR NOESY experiments (Scheme 2.3). Typically, the *anti* dienes underwent ring closing metathesis to the corresponding *cis* oxepins whereas the *syn* dienes led to *trans* oxepins.

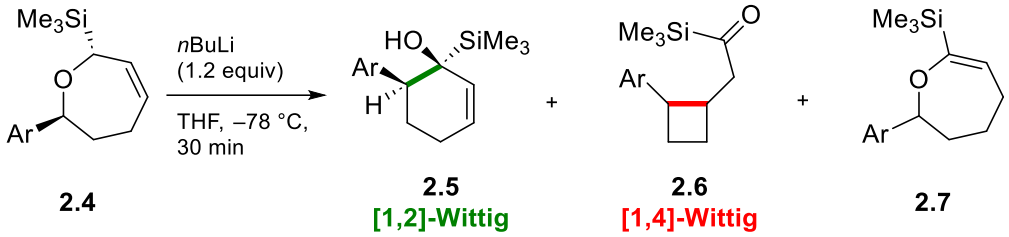


Scheme 2.3: Synthesis of *cis/trans* -silyl-2,5,6,7-tetrahydro-7-aryl-oxepins

2.4. Wittig rearrangements of 2-trimethylsilyl-2,5,6,7-tetrahydro-7-aryl-oxepins

With the starting materials at hand, we subjected them to Wittig rearrangement conditions. Exposure of (*trans*)-2-trimethylsilyl-2,5,6,7-tetrahydro-7-aryl-oxepins (**2.4**) to *n*-butyllithium led to formation of compounds **2.5**, **2.6**, and **2.7** in varying yields (Table 1).

Table 2.1[a]: Wittig rearrangement of 2-trimethylsilyl-2,5,6,7-tetrahydro-7-aryl-oxepins



2.4 **2.5** [1,2]-Wittig **2.6** [1,4]-Wittig **2.7**

Entry	Substrate	Ar	% (**2.5**)	*dr* (**2.5**)	% (**2.6**)	*dr* (**2.6**)	% (**2.7**)
1	**2.4a**	C_6H_5	25	5:1	n.d	-	51
2	**2.4b**	4-Cl-C_6H_4	72	5:1	n.d	-	22
3	*trans*-**2.4c**	4-OMe-C_6H_4	13	1.5:1	3	2:1	58
4	*cis*-**2.4c**[b]	4-OMe-C_6H_4	24	12:1	16	1:1	n.d[c]
5	**2.4d**	2-Naph	48	4:1	26	1:1	n.d[d]

[a]Diastereomeric ratio determined by ^{1}H NMR spectroscopy of the crude reaction mixture. The relative stereochemistry was determined by 1D and 2D NMR NOESY analysis. [b]Reaction performed with *sec*-butyllithium (3.0 equiv.) at –10 °C for 5 hours then quenched with deuterium oxide. n.d = not detected. [c]48% of *ortho* deuterated starting material recovered. [d]Approximately 10% of desilylated cyclohexanone **2.8c** was formed instead (see experimental section)

Unlike the dihydropyrans, the *cis* diastereomers were resistant to rearrangement even after employing the conditions successfully used earlier on their *cis* dihydropyrans counterpart, that is, *sec*-butyllithium at –78 °C for 3 hours.[1] Increasing the temperature to –10 °C led to Wittig rearrangement in case of *cis*-**2.4c** (see experimental section). Compound **2.7** was formed as a resultant of deprotonated *trans*-tetrahydrooxepins reluctance to rearrange. Subjecting compound

2.7 to butyllithium results in the formation of 2-arylcyclohexanone **2.8** with a concomitant loss of the silyl group (See experimental section).

2.5. Conclusion

In summary, we report the first ring contraction of 2-trimethylsilyl-2,5,6,7-tetrahydro-7-aryl-oxepins by Wittig rearrangements, which proceeds with modest diastereoselectivities via [1,2]- and [1,4]-Wittig pathways to produce silyl cyclohexenols and cyclobutyl acyl silanes, respectively. An unexpected product resulting from alkene migration was also observed. Treatment of this unexpected product with butyllithium did not yield Wittig rearrangement products but resulted in the formation of 2-arylcyclohexan-1-one with a loss of the silyl group. Finally, unlike the *cis* dihydropyrans, the *cis* oxepins could only undergo rearrangement after increasing the reaction temperature.

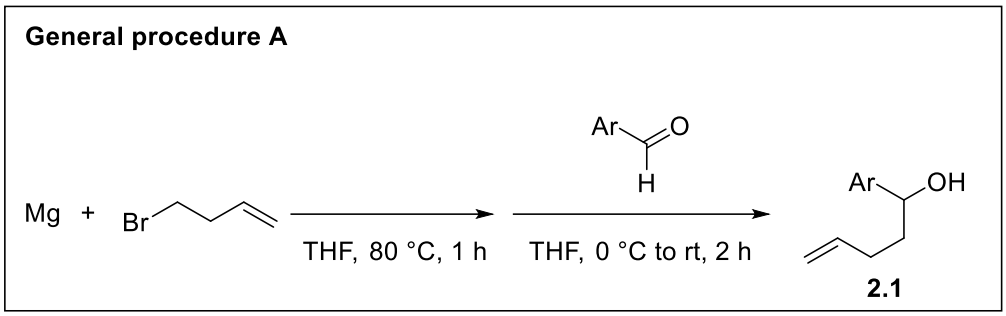
2.6. Experimental section

2.6.1. General Information

Unless otherwise noted, all reactions were run under a positive atmosphere of nitrogen in oven-dried or flame-dried round-bottomed flasks or conical vials or disposable drum vials capped with rubber septa. Solvents were removed by rotary evaporation under reduced pressure at temperatures lower than 45 ºC. Column chromatography was run on 230–400 mesh silica gel. Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone ketyl; dichloromethane, benzene, trimethylsilyl chloride were distilled from calcium hydride. Trimethylsilyltrifluoromethane sulfonate (TMSOTf) was redistilled and stored under nitrogen at –10 °C before the reaction. *tert*-butyllithium (1.7 M in pentane) and $BF_3.OEt_2$ were used as received. *n*-Butyllithum (2.5 M in hexanes) and *sec*-butyllithium (1.4 M in cyclohexane) were purchased from Aldrich and their concentration calculated by titration with diphenylacetic acid (average of

three runs). ^{1}H NMR spectra was collected in 500 MHz Varian instruments using $CDCl_3$ as solvent, which was referenced at 7.26 ppm (residual chloroform proton) and ^{13}C NMR spectra was collected in $CDCl_3$ at 126 MHz and referenced at 77.0 ppm. High-resolution mass spectrometric analysis was run in TOF instruments.

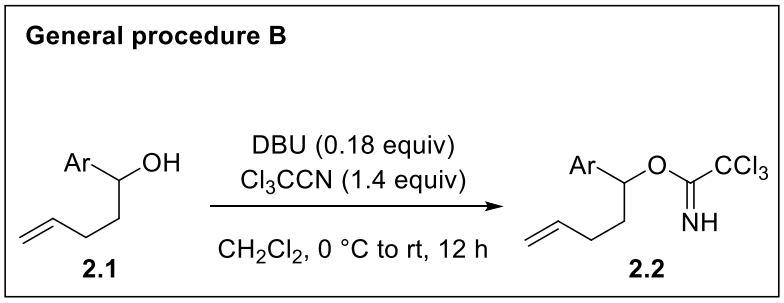
2.6.2. Preparation of 1-arylpent-4-en-1-ols (2.1a – 2.1c) – general procedure A



To a 250 mL 3-neck round-bottomed flask fitted with a magnetic stir bar was weighed 2.2 g of magnesium powder (90 mmol, 3.0 equiv.) and 2 crystals of iodine. The side necks of the flask were sealed by two rubber septa and a reflux condenser attached to the middle neck then purged with nitrogen. An oil bath was placed underneath the flask. This was followed by addition of 60 mL dry THF and the resulting brown suspension was vigorously stirred. Homoallylic bromide (7.6 mL, 10.13 g, 75 mmol, 2.5 equiv.) was then added slowly. After complete addition of the bromide, the temperature of the oil bath had risen to 40 °C. The mixture was then further heated on an oil bath to 80 °C (reflux) for 1 hour. The oil bath was removed, and the mixture was allowed to cool down to room temperature. The mixture was cooled down further to 0 °C by placing an ice bath underneath the flask. This was followed by dropwise addition of appropriate aryl aldehyde (30 mmol, 1.0 equiv.) as a solution in 20 mL dry THF. The resulting mixture was stirred at 0 °C to room temperature over a period of 2 hours. The mixture was then cooled to 0 °C and quenched by slow addition of 20 mL saturated aqueous ammonium chloride solution. The mixture was diluted with 40 mL of diethyl ether and 20 mL of saturated aqueous ammonium chloride solution. The

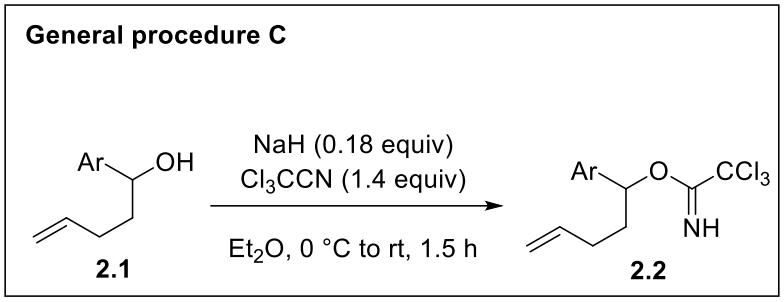
resulting mixture was transferred into a 1000 mL separating funnel and the layers were separated. The aqueous layer was extracted with diethyl ether (50 mL x 3). The combined organic layers were washed with saturated aqueous ammonium chloride solution (50 mL), water (50 mL x 2) and brine (50 mL) respectively and then dried over anhydrous magnesium sulfate. This was followed by filtration and the filtrate was concentrated on the rotorvap under reduced pressure affording 1-arylpent-4-en-1-ol **2.1** which was used in the next step without need for further purification.

2.6.3. Preparation of trichloroacetimidates 2.2 – general procedure B



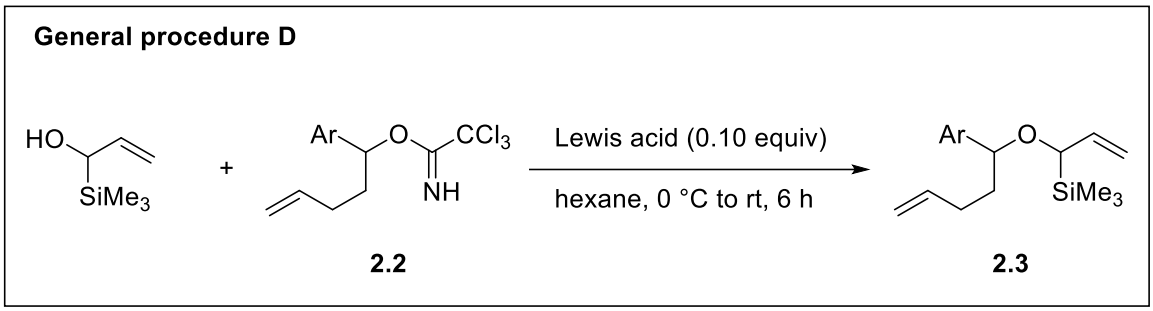
Following our reported procedure with a slight modification,[1] to a dry 250 mL round-bottomed flask fitted with a magnetic stir bar and sealed with a rubber septum was added 60 mL of dry dichloromethane under nitrogen. The desired 1-arylpent-4-en-1-ol **2.1** (20 mmol, 1.00 equiv) in dichloromethane (20 mL) was then transferred into the flask. This was followed by addition of 0.54 mL of 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) (0.55 g, 3.6 mmol, 0.18 equiv.). After stirring for 5 minutes, the solution was cooled to 0 °C on an ice bath. This was followed by dropwise addition of 2.8 mL of tricchloroacetonitrile (4.04 g, 28 mmol, 1.40 equiv.). After 12 hours, the resulting dark brown mixture was filtered through a plug of silica (5 cm thick) to remove the dark residue. The filtrate was concentrated, and the crude mixture subjected to column chromatography (EtOAc/hexanes) to afford the desired trichloroacetimidate **2.2**.

2.6.4. Alternative preparation of trichloroacetimidates 2.2 – general procedure C[15]



Following our reported procedure,[15] 240 mg of sodium hydride 60% w/w dispersion in mineral oil (6 mmol, 0.18 equiv) was weighed into a dry 100 mL round-bottomed flask fitted with a magnetic stir bar and 20 mL of freshly distilled diethyl ether was added into the flask. The flask was sealed with a rubber septum and purged with nitrogen. The resulting grey suspension was cooled on an ice bath and the desired 1-arylpent-4-en-1-ol **2.1** (30 mmol, 1.00 equiv) in dry diethyl ether (20 mL) was then transferred into the flask slowly resulting in a fizzy reaction. The mixture was stirred at 0 °C for 10 minutes. This was followed by dropwise addition of 4.2 mL of trichloroacetonitrile (6.06 g, 42 mmol, 1.40 equiv.). The mixture turned dark brown after complete addition of the trichloroacetonitrile. The mixture was stirred at 0 °C for 20 minutes and then the ice bath was removed, and the mixture stirred at room temperature for 1 hour. The diethyl ether was then removed by rotorvap and methanol (0.25 mL, 6.0 mmol, 0.18 equiv.) in 15 mL pentane was added to the crude mixture. The mixture was further diluted with 40 mL pentane and filtered through a plug of celite (5 cm thick). The filtrate was concentrated, and the crude mixture subjected to column chromatography (EtOAc/hexanes) to afford the desired trichloroacetimidate **2.2**.

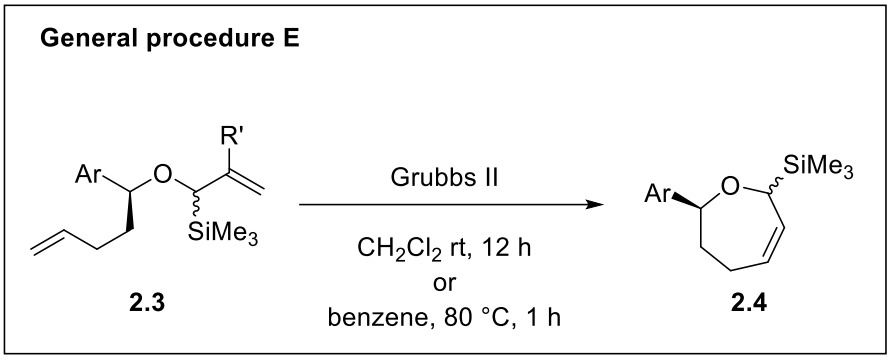
2.6.5. Preparation of diastereomeric dienes 2.3 – general procedure D[15]



A dry 250 mL round-bottomed flask with a magnetic stir bar was sealed with a rubber septum and purged with nitrogen. A solution of 1-(trimethylsilyl)prop-2-en-1-ol (10 mmol, 1 equiv) in 20 mL hexanes was transferred into the flask followed by a solution of the corresponding trichloroacetimidate **2.2** (15 mmol, 1.5 equiv.) in 20 mL hexanes. Additional 40 mL of hexanes was then added into the flask and the resulting mixture was cooled on ice bath to 0 °C while stirring. To the cold solution was added appropriate Lewis acid: BF_3•OEt_2 (0.12 mL, 1 mmol, 0.1 equiv.) or TMSOTf (0.18 mL, 1 mmol, 0.1 equiv.). After complete addition, a thick precipitate was formed. The mixture was stirred at 0 °C to room temperature for 6 hours and filtered through a plug of celite (5 cm thick) and the filtrate was transferred into a separating funnel. The filtrate was then washed with saturated solution of aqueous sodium bicarbonate (50 mL x 3), water (50 mL x 2) and brine (50 mL) respectively. The organic layer was dried over anhydrous sodium sulfate and then filtered. The filtrate was concentrated under reduced pressure to afford diene **2.3** as a mixture of diastereomers. The resulting crude reaction mixture was purified by column chromatography (dichloromethane/hexanes). It is important to note that some diastereomers were separable by column chromatography and hence only one of them (*syn*) was taken to the next step (RCM). The diastereomers that could not be separated by column chromatography were taken to the next step as a mixture. The stereochemistry of these diastereomers were determined after the RCM reaction: *syn* diastereomers underwent RCM to form *cis* dihydropyrans or tetrahyrooxepins and vice versa.

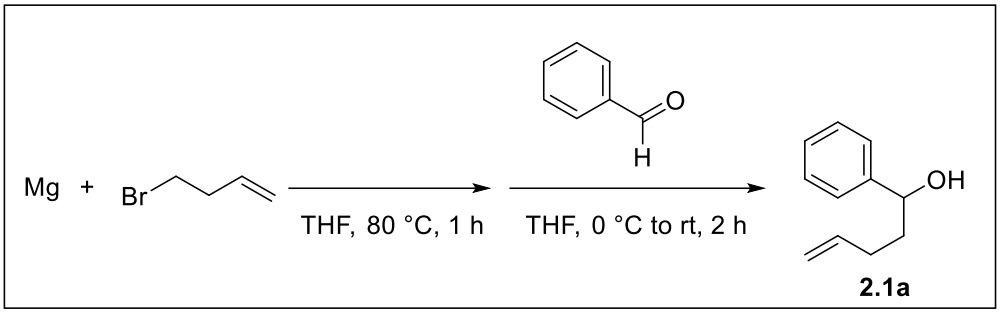
It is also worth noting that for most of the compounds reported herein, the *syn* diastereomer exhibited lower R_f value than its *anti* counterpart (dichloromethane/hexanes).

2.6.6. Preparation of tetrahydrooxepins 2.4 via ring closing metathesis (RCM) – general procedure E[15]



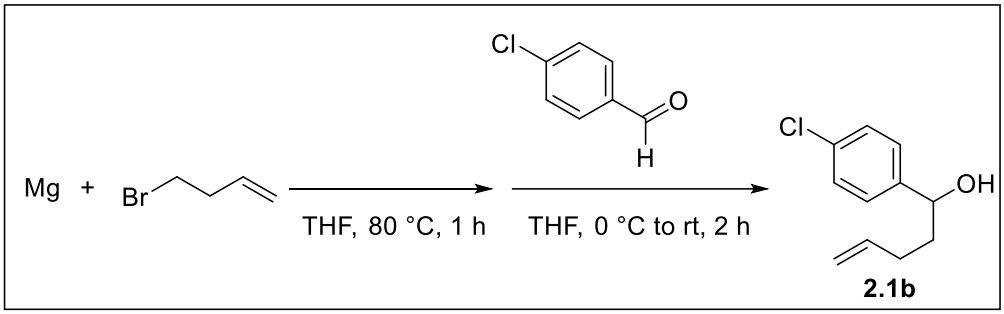
To a dry 250 mL round-bottomed flask with a magnetic stir bar was weighed 170 mg of Grubbs catalyst 2nd generation (0.2 mmol, 0.04 equiv.) and the flask was sealed with a rubber septum and purged with nitrogen. This was followed by addition of 80 mL of dry dichloromethane and corresponding diene **2.3** (5 mmol, 1.0 equiv) as a solution in 20 mL dry dichloromethane as a single diastereomer (*syn*) or as a mixture of diastereomers (*syn:anti* = 1:1). The resulting mixture was stirred at room temperature for 12 hours. The mixture was concentrated under reduced pressure to afford tetrahydrooxepins **2.4**. The resulting crude reaction mixture was purified by column chromatography (dichloromethane/hexanes). The *cis* and *trans* diastereomers were separable by column chromatography. The stereochemistry of these diastereomers were determined by 1D NOESY experiment and confirmed with X-ray crystallography (*trans*-**2.4d**). It is also worth noting that for most of the compounds reported here the *trans* diastereomer has lower R_f value than its *cis* counterpart (dichloromethane/hexanes).

Synthesis of 1-phenylpent-4-en-1-ol (2.1a)



Applying general procedure A to magnesium powder (2.9 g, 120 mmol, 1.2 equiv), homoallylic bromide (12.2 mL, 120 mmol, 1.2 equiv), benzaldehyde (9.65 mL, 100 mmol, 1.0 equiv), and THF (200 mL) afforded 15.8 g, 97.4 mmol (97% isolated yield) of compound **2.1a** as a yellow oil after column chromatography, R_f = 0.5 (20% ethyl acetate in hexanes): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.29 (dtd, *J* = 7.0, 5.7, 2.5 Hz, 1H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.00 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 4.68 (dd, *J* = 7.7, 5.5 Hz, 1H), 2.24 – 2.01 (m, 3H), 1.90 (dddd, *J* = 13.7, 8.8, 7.7, 6.0 Hz, 1H), 1.80 (dddd, *J* = 13.6, 9.2, 6.4, 5.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 138.1, 128.4, 127.5, 125.9, 114.9, 73.9, 38.0, 30.0. IR (FTIR, film, cm^{-1}) 3389, 2935, 1640, 1451, 909, 800. **2.1a** is a known compound and spectroscopic data are in agreement with those reported in literature.[17]

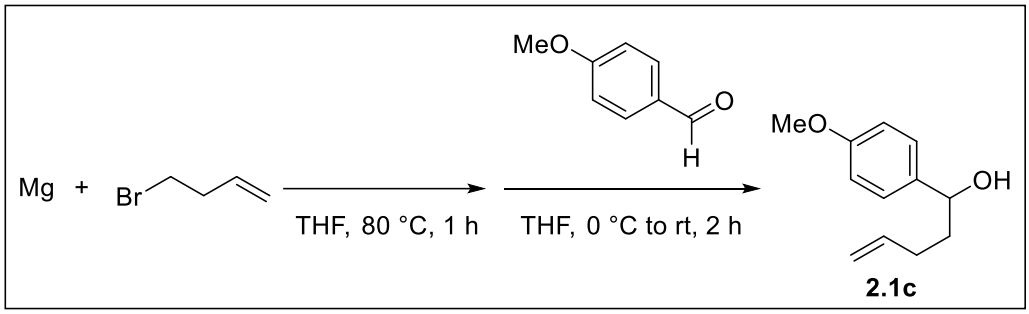
Synthesis of 1-(4-chlorophenyl)pent-4-en-1-ol (2.1b)



Following general procedure A, magnesium powder (2.9 g, 120 mmol, 1.2 equiv), 4-bromobut-1-ene (12.2 mL, 120 mmol, 1.2 equiv), 4-chlorobenzaldehyde (14.6 g, 100 mmol, 1.0

equiv.) and THF (220 mL) afforded 18.81 g, 95.6 mmol (96% isolated yield) of 1-(4-chlorophenyl)pent-4-en-1-ol **2.1b** as a yellow oil after column chromatography, R_f = 0.4 (20% ethyl acetate in hexanes). ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.99 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.66 (dd, *J* = 7.7, 5.5 Hz, 1H), 2.19 – 2.01 (m, 3H), 1.90 – 1.81 (m, 1H), 1.75 (dddd, *J* = 13.9, 9.0, 6.5, 5.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.0, 137.9, 133.1, 128.5, 127.2, 115.2, 73.3, 38.0, 29.9. IR (FTIR, film, cm^{-1}) ṽ = 3326, 2935, 1640, 1491, 1090, 1012, 911, 828. **2.1b** is a known compound and spectroscopic data are in agreement with those reported in literature.[17]

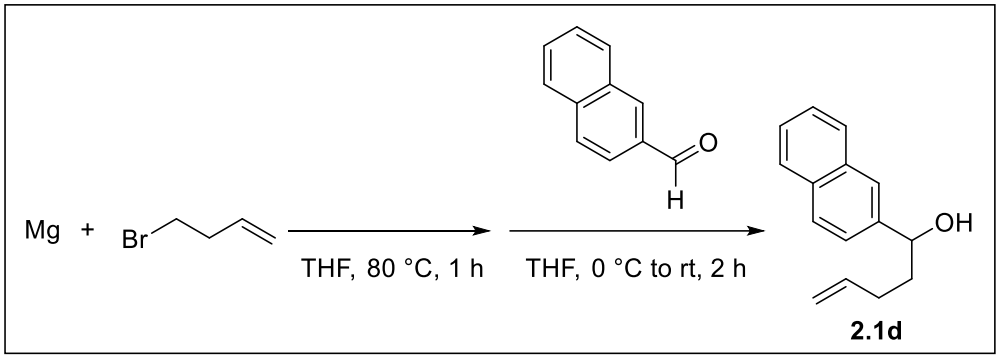
Synthesis of 1-(4-methoxyphenyl)pent-4-en-1-ol (2.1c)



Following general procedure A, magnesium powder (2.2 g, 90 mmol, 3.0 equiv), 4-bromobut-1-ene (7.6 mL, 75 mmol, 2.5 equiv), 3.65 mL of *p*-anisaldehyde (4.08 g, 30 mmol, 1.0 equiv.) and THF (120 mL) afforded 7.35 g, 38 mmol (quantitative crude yield) of 1-(4-methoxyphenyl)pent-4-en-1-ol **2.1c** as a yellow oil in THF. The product was taken to the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 7.26 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.98 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 4.63 (dd, *J* = 7.5, 5.8 Hz, 1H), 3.80 (s, 3H), 2.19 – 2.01 (m, 3H), 1.89 (dddd, *J* = 13.7, 8.9, 7.5, 6.1 Hz, 1H), 1.77 (ddt, *J* = 13.6, 9.3, 6.1 Hz, 1H). ^{13}C{^{1}H}-NMR (126

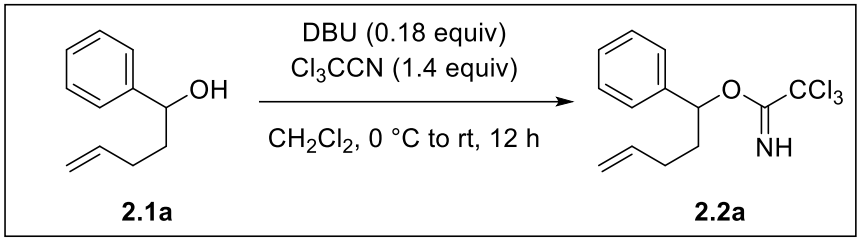
MHz, $CDCl_3$, ppm) δ = 159.0, 138.2, 136.7, 127.1, 114.8, 113.8, 73.5, 55.2, 37.9, 30.1. **2.1c** is a known compound and spectroscopic data are in agreement with those reported in literature.[18]

Synthesis of 1-(naphthalen-2-yl)pent-4-en-1-ol (2.1d)



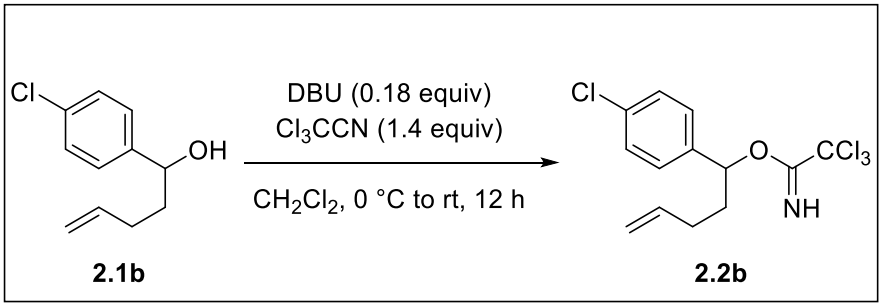
Following general procedure A, magnesium powder (2.33 g, 96 mmol, 1.2 equiv), 4-bromobut-1-ene (9.8 mL, 96 mmol, 1.2 equiv), 2-naphthaldehyde (12.96 g, 80 mmol, 1.0 equiv.) and THF (150 mL) afforded 16.8 g, 79 mmol (99% crude yield) of 1-(naphthalen-2-yl)pent-4-en-1-ol **2.2d** as a yellow oil in THF. The product was taken to the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.88 – 7.81 (m, 3H), 7.78 (s, 1H), 7.48 (qd, *J* = 5.2, 4.2, 2.6 Hz, 3H), 5.87 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.01 (dq, *J* = 10.2, 1.5 Hz, 1H), 4.91 – 4.82 (m, 1H), 2.26 – 2.04 (m, 3H), 2.04 – 1.95 (m, 1H), 1.90 (ddt, *J* = 13.5, 9.1, 6.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.9, 138.1, 133.2, 132.9, 128.3, 127.9, 127.7, 126.1, 125.8, 124.6, 124.0, 115.0, 74.1, 37.9, 30.0. IR (FTIR, film, cm^{-1}) ṽ = 3324, 3055, 2919, 1638, 1507, 1270, 1017, 817, 745. **2.2d** is a known compound and spectroscopic data are in agreement with those reported in literature.[18]

Synthesis of 1-phenylpent-4-en-1-yl 2,2,2-trichloroacetimidate (2.2a)



Applying general procedure B to 1-phenylpent-4-en-1-ol **2.1a** (15.74 g, 97 mmol, 1 equiv), DBU (2.6 mL, 17.5 mmol, 0.18 equiv), and trichloroacetonitrile (13.6 mL, 135.8 mmol, 1.4 equiv), in CH_2Cl_2 (180 mL) afforded 27.5 g, 89.7 mmol (92% crude yield) of compound **2.2a** as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.43 – 7.39 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 5.90 – 5.78 (m, 2H), 5.06 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.02 (dt, *J* = 10.1, 1.6 Hz, 1H), 2.30 – 2.12 (m, 3H), 2.00 – 1.89 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 140.2, 137.4, 128.4, 127.9, 126.1, 115.5, 91.7, 80.1, 36.1, 29.6. IR (FTIR, film, cm^{-1}) 3341, 3065, 2943, 1661, 1284, 1071, 792.

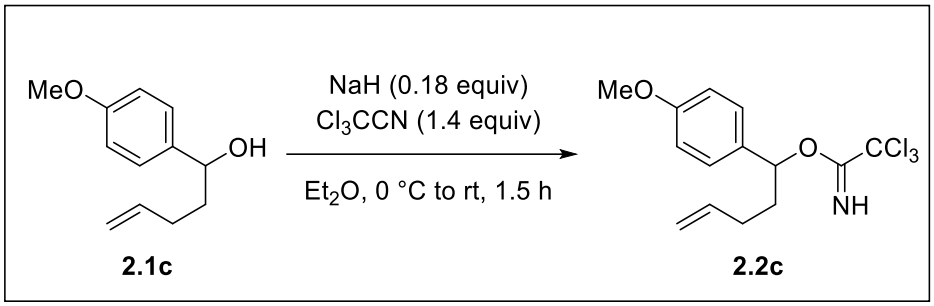
Synthesis of 1-(4-chlorophenyl)pent-4-en-1-yl 2,2,2-trichloroacetimidate (2.2b)



Following general procedure B, 1-(4-chlorophenyl)pent-4-en-1-ol **2.1b** (15.74 g, 80 mmol, 1.0 equiv), DBU (2.2 mL, 14.4 mmol, 0.18 equiv), trichloroacetonitrile (11.2 mL, 112 mmol, 1.4 equiv.) and dichloromethane (200 mL), 27.6 g, 80.9 mmol (>99% isolated yield) of 1-(4-chlorophenyl)pent-4-en-1-yl 2,2,2-trichloroacetimidate **2.2b** was obtained as a yellow oil after column chromatography, R_f = 0.4 (10% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.27

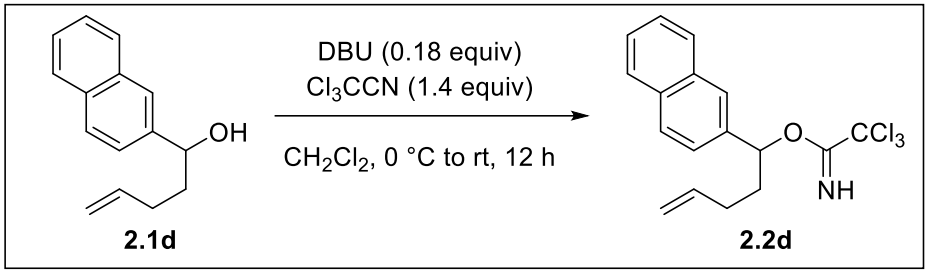
(s, 1H), 7.33 (s, 4H), 5.88 – 5.76 (m, 2H), 5.09 – 4.98 (m, 2H), 2.28 – 2.08 (m, 3H), 1.96 – 1.85 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.4, 138.7, 137.1, 133.7, 128.6, 127.6, 115.7, 91.5, 79.3, 36.0, 29.5. IR (FTIR, film, cm^{-1}) ṽ = 3340, 2943, 1662, 1282, 1069, 791. HRMS (ESI), *m/z* [M–$Cl_3CONH]^+$ calcd for $C_{11}H_{12}Cl$: 179.0628; found: 179.0603.

Synthesis of 1-(4-methoxyphenyl)pent-4-en-1-yl 2,2,2-trichloroacetimidate (2.2c)



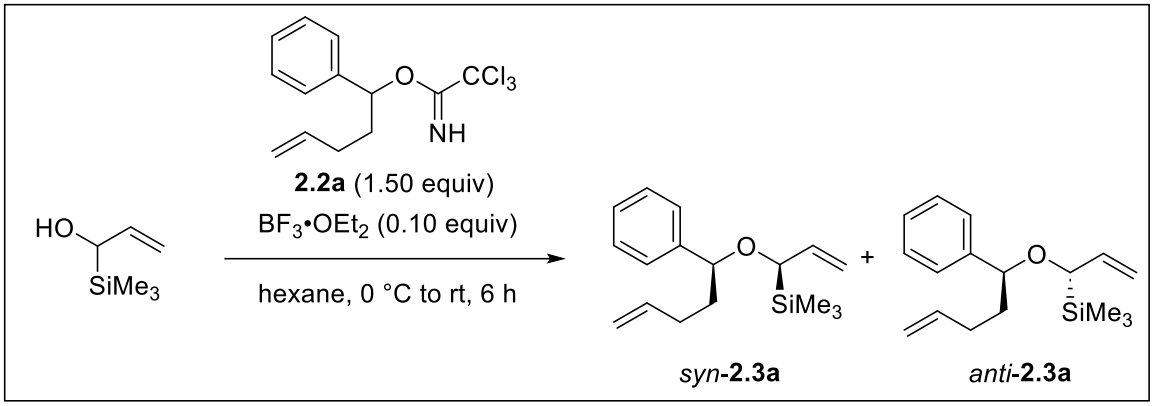
Following general procedure C, 1-(4-methoxyphenyl)pent-4-en-1-ol **2.1c** (5.77 g, 30 mmol, 1.0 equiv), NaH 60% w/w dispersion in mineral oil (240 mg, 6 mmol, 0.20 equiv), trichloroacetonitrile (4.2 mL, 42 mmol, 1.4 equiv.) and diethyl ether (15 mL), 10.67 g, 31.7 mmol (quantitative crude yield) of 1-(4-methoxyphenyl)pent-4-en-1-yl 2,2,2-trichloroacetimidate **2.2c** which was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.25 (s, 1H), 7.34 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.91 – 5.76 (m, 2H), 5.09 – 4.99 (m, 2H), 3.81 (s, 3H), 2.28 – 2.12 (m, 3H), 1.97 – 1.86 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.5, 159.3, 137.5, 127.6, 115.4, 113.8, 91.8, 80.0, 55.2, 36.0, 29.7. IR (FTIR, cm^{-1}) ṽ = 3362, 3239, 3177, 1690, 1609, 1381, 1108, 829 MS (GC/MS): *m*/z (%) = 175 (100) [M – $Cl_3CCONH]^+$, 121 (80). HRMS (ESI), *m/z* [M + H]$^+$ calcd for $C_{14}H_{17}Cl_3NO_2$: 336.0325; found: 336.0333.

Synthesis of 1-(naphthalen-2-yl)pent-4-en-1-yl 2,2,2-trichloroacetimidate (2.2d)



Following general procedure B, 1-(naphthalen-2-yl)pent-4-en-1-ol **2.1d** (14.86 g, 70 mmol, 1.0 equiv), DBU (1.89 mL, 12.6 mmol, 0.18 equiv), trichloroacetonitrile (9.83 mL, 98 mmol, 1.4 equiv.) and dichloromethane (200 mL), 25.89 g, 72.58 mmol (quantitative crude yield) of 1-(naphthalen-2-yl)pent-4-en-1-yl 2,2,2-trichloroacetimidate **2.2d** was obtained as a dark brown oil in dichloromethane. The product was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.30 (s, 1H), 7.96 – 7.80 (m, 4H), 7.56 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.50 (qt, *J* = 7.2, 3.9 Hz, 2H), 6.03 (dd, *J* = 7.9, 5.0 Hz, 1H), 5.89 (ddt, *J* = 16.4, 10.0, 6.2 Hz, 1H), 5.14 – 5.00 (m, 2H), 2.36 – 2.19 (m, 3H), 2.05 (tdd, *J* = 10.9, 7.4, 3.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 161.5, 137.5, 137.3, 133.1, 128.3, 128.0, 127.7, 126.2, 126.0, 125.4, 123.9, 115.5, 91.7, 80.2, 36.0, 29.7. IR (FTIR, cm^{-1}) $\tilde{\nu}$ = 3337, 3057, 2941, 1661, 1284, 1071, 986, 791 MS (GC/MS): *m*/z (%) = 355 (0.1) [M^+], 301 (15), 184 (70), 156 (45), 141 (100), 115 (48). HRMS (ESI), *m/z* [M + H]$^+$ calcd for $C_{17}H_{17}Cl_3NO$: 356.0376; found: 356.0370.

Synthesis of *syn/anti*-(1-((1-phenylpent-4-en-1-yl)oxy)allyl)trimethylsilane (*syn/anti*-2.3a)



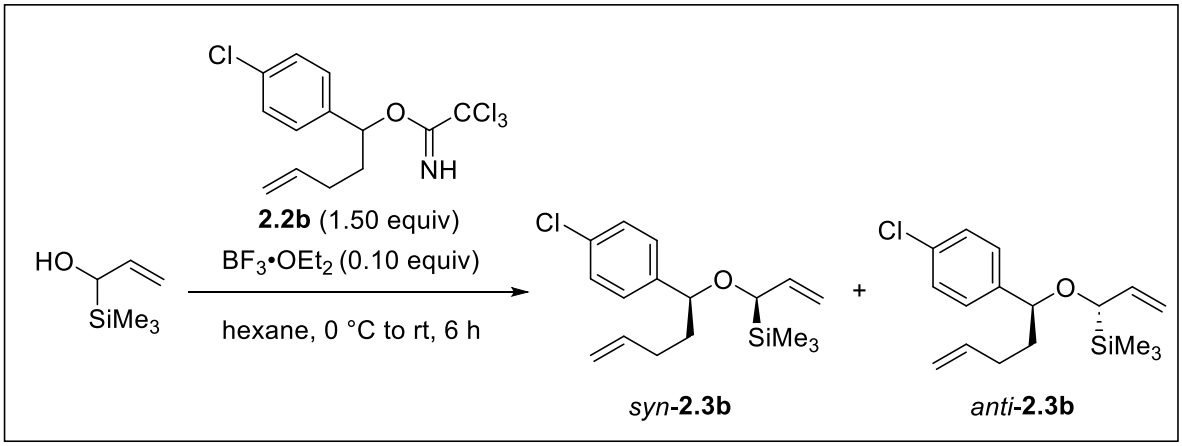
Applying general procedure D to 1-(trimethylsilyl)prop-2-en-1-ol (5.2 g, 40 mmol, 1.0 equiv), trichloroacetimidate **2.2a** (17.7 g, 60 mmol, 1.5 equiv), and boron trifluoro diethyl etherate (0.5 mL, 4.0 mmol, 0.1 equiv) in hexane (200 mL) afforded after column chromatography (5% CH_2Cl_2 in hexanes) a total of 8.04 g, 29.3 mmol (73% isolated yield) of *syn*/*anti*-**2.3a** (1:1) as a colorless oil. Compounds *syn*-**2.3a** and *anti*-**2.3a** were partially separable by column chromatography.

Spectroscopic data for *syn*-**2.3a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.25 (ddd, *J* = 8.7, 5.0, 3.8 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.67 (ddd, *J* = 17.4, 10.6, 7.1 Hz, 1H), 5.00 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.98 – 4.89 (m, 2H), 4.83 (dt, *J* = 10.6, 1.8 Hz, 1H), 4.36 (t, *J* = 6.0 Hz, 1H), 3.78 (dt, *J* = 7.2, 1.5 Hz, 1H), 2.09 – 1.97 (m, 2H), 1.88 (ddt, *J* = 12.8, 9.3, 6.2 Hz, 1H), 1.80 – 1.71 (m, 1H), 0.09 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 143.9, 138.7, 138.0, 127.9, 126.8, 126.6, 114.4, 111.7, 80.9, 75.7, 36.2, 29.3, -3.7.

Spectroscopic data for *anti*-**2.3a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 3H), 7.30 – 7.26 (m, 2H), 5.85 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.77 (ddd, *J* = 17.4, 10.6, 7.7 Hz, 1H), 5.11 – 5.03 (m, 2H), 5.01 – 4.94 (m, 2H), 4.43 (dd, *J* = 8.2, 5.3 Hz, 1H), 3.43 (dt, *J* = 7.7, 1.3 Hz, 1H), 2.21 (dddt, *J* = 10.2, 5.1, 2.2, 1.2 Hz, 1H), 2.08 (dddd, *J* = 16.4, 8.3, 4.9, 2.0 Hz, 1H), 1.93 – 1.85

(m, 1H), 1.68 (dddd, J = 13.6, 9.6, 6.1, 5.3 Hz, 1H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 143.0, 138.8, 137.8, 128.4, 128.1, 127.3, 114.3, 113.0, 78.8, 72.9, 37.7, 30.3, -4.0.

Synthesis of *syn/anti*-(1-((1-(4-chlorophenyl)pent-4-en-1-yl)oxy)allyl)trimethylsilane (*syn/anti*-2.3b)



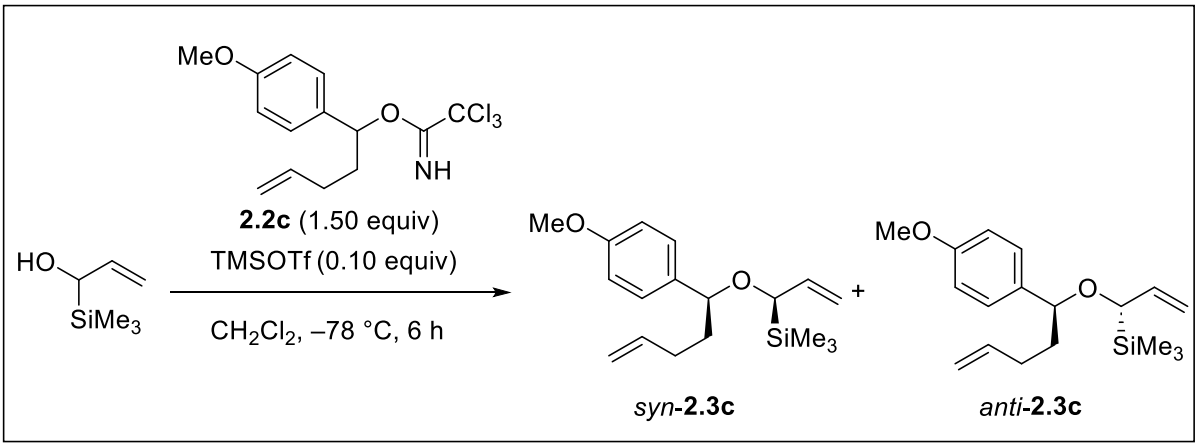
Compound **2.3b** was prepared following general procedure D, a solution of 2-(trimethylsilyl)prop-2-en-1-ol (3.91 g, 30 mmol, 1 equiv.) and 1-(4-chlorophenyl)pent-4-en-1-yl 2,2,2-trichloroacetimidate **2.2b** (15.35 g, 45 mmol, 1.5 equiv.), BF_3•OEt_2 (0.37 mL, 3.0 mmol, 0.1 equiv.) and hexanes (165 mL) for 12 hours followed by workup, concentration and column chromatography, R_f for *anti*-**2.3b** = 0.6 and R_f for *syn*-**2.3b** = 0.4 (2% DCM in hexanes) afforded a total of 5.40 g, 17.5 mmol (58% isolated yield) partially separable mixture of diastereomers of compound **2.3** as colorless liquid.

Spectroscopic data for *syn*-**2.3b:** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.27 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 5.78 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.62 (ddd, J = 17.6, 10.5, 7.2 Hz, 1H), 5.01 – 4.92 (m, 2H), 4.88 (dt, J = 17.2, 1.8 Hz, 1H), 4.82 (dt, J = 10.5, 1.6 Hz, 1H), 4.31 (t, J = 6.1 Hz, 1H), 3.74 (dt, J = 7.3, 1.5 Hz, 1H), 2.06 – 1.94 (m, 2H), 1.83 (ddt, J = 13.6, 9.6, 6.0 Hz, 1H), 1.70 (ddt, J = 13.7, 9.6, 6.1 Hz, 1H), 0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.5, 138.4, 137.8, 132.4, 128.1, 127.9, 114.6, 111.9, 80.3, 76.1, 36.1, 29.2, -3.8. IR (FTIR, cm^{-1}) $\tilde{\nu}$ =

3078, 2954, 2926, 1640, 1627, 1490, 1246, 839. MS (GC/MS): *m*/z (%) = 179 (17.5) [M – $C_6H_{13}OSi]^+$, 125 (100).

Spectroscopic data for *anti*-**2.3b:** ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.30 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 5.85 – 5.78 (m, 1H), 5.78 – 5.70 (m, 1H), 5.06 – 4.98 (m, 2H), 4.98 – 4.92 (m, 2H), 4.39 (dd, *J* = 8.1, 5.4 Hz, 1H), 3.37 (dt, *J* = 7.8, 1.3 Hz, 1H), 2.22 – 2.12 (m, 1H), 2.09 – 2.00 (m, 1H), 1.90 – 1.79 (m, 2H), 1.63 (ddt, *J* = 13.5, 9.5, 5.8 Hz, 1H), -0.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 141.5, 138.5, 137.5, 128.6, 128.3, 127.2, 114.5, 113.2, 78.1, 73.1, 37.6, 30.1, -4.0. IR (FTIR, cm^{-1}) ṽ = 3105, 2949, 1641, 1592, 1490, 1089, 1013, 822. HRMS (APCI), *m/z* $[M + H]^+$ calcd for $C_{17}H_{26}ClOSi$: 309.1441; found: 309.1428.

Synthesis of *syn/anti*-(1-((1-(4-methoxyphenyl)pent-4-en-1-yl)oxy)allyl)trimethylsilane (*syn/anti*-2.3c)



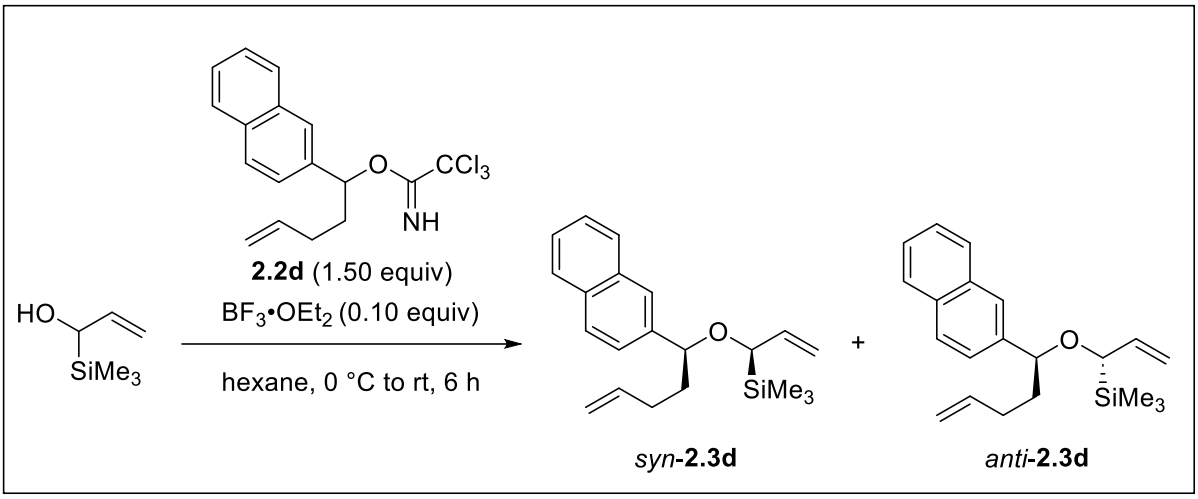
Compound **2.3c** was prepared following general procedure D with slight modification to minimize formation of the side product as a result of elimination. A solution of 1-(trimethylsilyl)prop-2-en-1-ol (1.95 g, 15 mmol, 1 equiv.) and 1-(4-methoxyphenyl)pent-4-en-1-yl 2,2,2-trichloroacetimidate **2.2c** (5.05 g, 15 mmol, 1 equiv.) in dichloromethane (120 mL) was cooled to −78 °C. TMSOTf (0.27 mL, 1.5 mmol, 0.1 equiv.) was added dropwise and the mixture stirred at –78 °C for 6 hours. The rubber septum was removed, and 7 g of sodium bicarbonate was

poured into the flask. The dry ice-acetone bath was removed, and the mixture was allowed to warm up to room temperature. The mixture was filtered and concentrated under reduced pressure to remove dichloromethane. Hexanes was then added to the resulting mixture resulting in the formation of white precipitate. Subsequent filtration and concentration furnished a residue which was purified by column chromatography, R_f for *anti*-**2.3c** = 0.5 and R_f for *syn*-**2.3c** = 0.3 (10% DCM in hexanes) to afford a total of 3.02 g, 9.9 mmol (66% isolated yield) partially separable mixture of diastereomers of compound **2.3c** (*syn:anti* = 1:1) as colorless liquid.

Spectroscopic data for *syn*-**2.3c:** ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.21 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.80 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.65 (ddd, *J* = 17.4, 10.5, 7.0 Hz, 1H), 4.98 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.96 – 4.87 (m, 2H), 4.81 (ddd, *J* = 10.6, 2.1, 1.5 Hz, 1H), 4.28 (t, *J* = 6.2 Hz, 1H), 3.80 (s, 3H), 3.74 (dt, *J* = 7.1, 1.6 Hz, 1H), 2.05 – 1.96 (m, 2H), 1.91 – 1.81 (m, 1H), 1.76 – 1.66 (m, 1H), 0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.5, 138.7, 138.1, 136.0, 127.7, 114.3, 113.2, 111.4, 80.6, 75.5, 55.2, 36.2, 29.4, -3.7. HRMS (ESI), *m/z* $[M - H]^-$ calcd for $C_{18}H_{27}O_2Si$: 303.1780; found: 303.1789.

Spectroscopic data for *anti*-**2.3c:** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.75 (ddd, *J* = 17.2, 10.5, 7.6 Hz, 1H), 5.06 – 4.91 (m, 4H), 4.36 (dd, *J* = 8.0, 5.5 Hz, 1H), 3.82 (s, 3H), 3.41 (dt, *J* = 7.6, 1.4 Hz, 1H), 2.23 – 2.13 (m, 1H), 2.10 – 2.00 (m, 1H), 1.88 (dddd, *J* = 13.5, 9.3, 8.0, 5.6 Hz, 1H), 1.65 (ddt, *J* = 13.5, 9.6, 5.8 Hz, 1H), -0.02 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.8, 138.8, 137.9, 135.0, 128.4, 114.3, 113.5, 112.8, 78.3, 72.5, 55.2, 37.7, 30.3, -4.0. HRMS (APCI), *m/z* $[M + H]^+$ calcd for $C_{18}H_{29}O_2Si$: 305.1937; found: 305.1928.

Synthesis of *syn/anti*-trimethyl(1-((1-(naphthalen-2-yl)pent-4-en-1-yl)oxy)allyl)silane (*syn/anti*-2.3d)



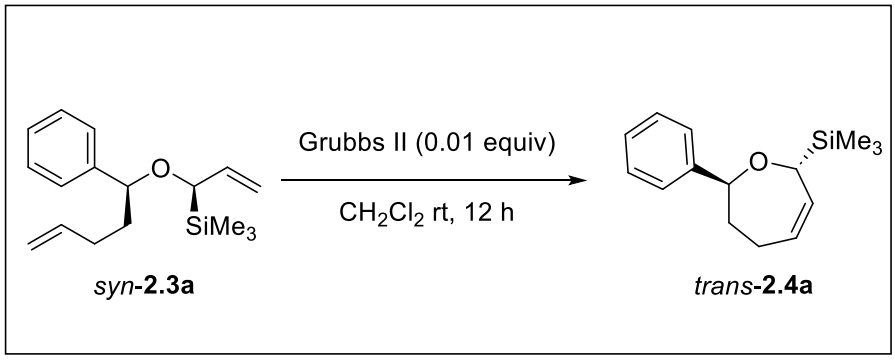
Compound **2.3d** was prepared following general procedure D, a solution of 1-(trimethylsilyl)prop-2-en-1-ol (1.30 g, 10 mmol, 1 equiv.) and 1-(naphthalen-2-yl)pent-4-en-1-yl 2,2,2-trichloroacetimidate **2.2d** (5.36 g, 15 mmol, 1.5 equiv.), BF_3•OEt_2 (0.13 mL, 1.0 mmol, 0.1 equiv.) and hexanes (80 mL) for 12 hour followed by workup, concentration and column chromatography, R_f for *anti/syn*-**2.3d** = 0.5 (10% DCM in hexanes) afforded a total of 2.19 g, 6.8 mmol (68% isolated yield) partially separable mixture of diastereomers of compound **2.3d** as colorless liquid.

Spectroscopic data for *syn/anti*-**2.3d:** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 – 7.80 (m, 6H), 7.75 (s, 1H), 7.70 (s, 1H), 7.54 – 7.45 (m, 6H), 5.93 – 5.78 (m, 3H), 5.69 (ddd, *J* = 17.5, 10.5, 7.1 Hz, 1H), 5.10 (ddd, *J* = 10.6, 2.0, 1.2 Hz, 1H), 5.08 – 4.93 (m, 6H), 4.82 (ddd, *J* = 10.6, 2.1, 1.5 Hz, 1H), 4.62 (dd, *J* = 8.0, 5.5 Hz, 1H), 4.54 (t, *J* = 6.1 Hz, 1H), 3.86 (dt, *J* = 7.1, 1.5 Hz, 1H), 3.49 (dt, *J* = 7.6, 1.4 Hz, 1H), 2.30 – 2.20 (m, 1H), 2.17 – 2.06 (m, 3H), 2.06 – 1.95 (m, 2H), 1.90 – 1.82 (m, 1H), 1.79 (ddt, *J* = 11.6, 9.6, 3.8 Hz, 1H), 0.13 (s, 9H), 0.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.4, 140.4, 138.7, 138.0, 137.8, 133.1, 133.0, 132.8, 128.1, 127.9, 127.8, 127.7, 127.6, 126.4, 125.9, 125.8, 125.6, 125.4, 125.3, 125.1, 124.9, 114.5, 114.4, 113.0, 111.7, 81.2, 79.0, 76.0, 72.9,

37.5, 36.2, 30.3, 29.4, -3.7, -4.0.

Spectroscopic data for *syn*-**2.3d** only**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86 – 7.78 (m, 3H), 7.73 (s, 1H), 7.51 – 7.43 (m, 3H), 5.83 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H), 5.67 (ddd, *J* = 17.4, 10.5, 7.1 Hz, 1H), 5.00 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.98 – 4.90 (m, 2H), 4.80 (dt, *J* = 10.6, 1.8 Hz, 1H), 4.52 (t, *J* = 6.1 Hz, 1H), 3.83 (dt, *J* = 7.1, 1.5 Hz, 1H), 2.11 – 2.02 (m, 2H), 1.96 (ddt, *J* = 12.7, 9.1, 6.2 Hz, 1H), 1.83 (ddt, *J* = 13.4, 9.2, 6.3 Hz, 1H), 0.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 141.4, 138.6, 138.0, 133.1, 132.8, 127.9, 127.63, 127.62, 125.8, 125.4, 125.3, 124.9, 114.5, 111.7, 81.2, 76.0, 36.2, 29.4, -3.7. HRMS (ESI), *m/z* $[M + H]^+$ calcd for $C_{21}H_{29}OSi$: 325.1988; found: 325.2025.

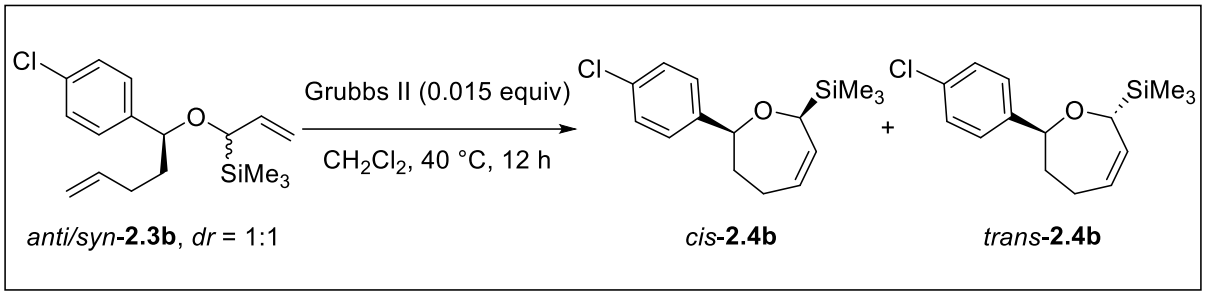
Synthesis of *trans*-(7-phenyl-2,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane (*trans*-2.4a)



syn-**2.3a** *trans*-**2.4a**

Applying general procedure E to *syn*-**2.3a** (4.1 g, 15 mmol, 1 equiv) and second-generation Grubbs catalyst (127 mg, 0.15 mmol, 0.01 equiv) in CH_2Cl_2 (200 mL) afforded after column chromatography (40% CH_2Cl_2 in hexanes) 3.41 g, 13.8 mmol (92% isolated yield) of *trans*-**2.4a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.25 (m, 1H), 5.78 – 5.72 (m, 1H), 5.60 (dt, *J* = 11.3, 2.8 Hz, 1H), 4.87 (dd, *J* = 10.9, 4.3 Hz, 1H), 4.04 (dtd, *J* = 4.5, 3.1, 1.8 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.41 – 2.28 (m, 2H), 2.18 – 2.10 (m, 1H), -0.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 130.8, 128.6, 128.0, 127.2, 127.0, 80.3, 68.6, 33.6, 26.5, -3.1.

Synthesis of *cis/trans*- (7-(4-chlorophenyl)-2,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane (*cis/trans*-2.4b)



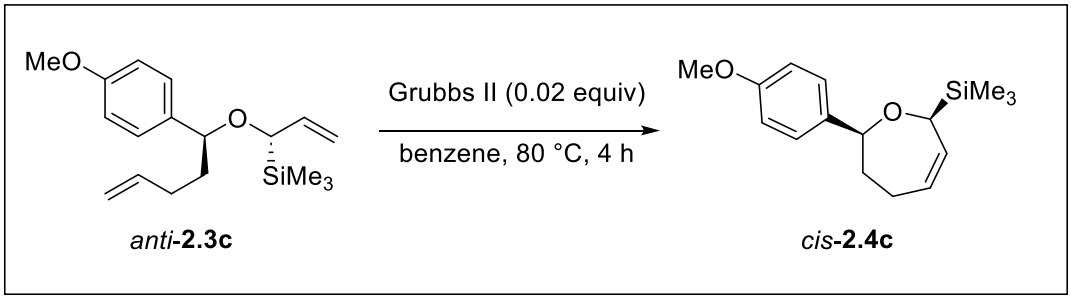
Compound **2.4b** was prepared following general procedure E: Grubbs catalyst 2nd generation (191 mg, 0.225 mmol, 0.015 equiv.) and *syn/anti*-(1-((1-(4-chlorophenyl)pent-4-en-1-yl)oxy)allyl)trimethylsilane, *syn:anti* = 1:1, **2.4b** (4.64 g, 15 mmol, 1 equiv.) and dichloromethane (120 mL) at 40 °C for 12 hours followed by concentration and column chromatography, R_f for *cis*-**2.4b** = 0.7 and R_f for *trans*-**2.4b** = 0.4 (20% DCM in hexanes) afforded a total of 3.09 g, 11 mmol (73% isolated yield) fully separable mixture of diastereomers of compound **2.4b** as colorless liquid.

Spectroscopic data for *cis*-**2.4b:** ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.28 (s, 4H), 5.69 (dddd, *J* = 11.9, 7.3, 4.7, 2.5 Hz, 1H), 5.54 (dt, *J* = 11.2, 2.6 Hz, 1H), 4.73 (dd, *J* = 8.4, 5.4 Hz, 1H), 4.05 (dt, *J* = 4.4, 3.3 Hz, 1H), 2.62 (dddd, *J* = 16.2, 8.1, 3.7, 1.4 Hz, 1H), 2.32 (ddt, *J* = 13.7, 10.5, 5.2 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.83 (ddt, *J* = 13.6, 8.4, 5.1 Hz, 1H), 0.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.7, 132.0, 130.6, 128.1, 126.6, 126.1, 80.8, 77.3, 37.4, 23.5, -3.7. IR (FTIR, film, cm^{-1}) ṽ = 3014, 2932, 2780, 1719, 1490, 1246, 1089, 937. MS (GC/MS): *m*/z (%) = 280 (0.2) $[M]^+$, 245 (0.5), 142 (95), 127 (30), 73 (100). HRMS (ESI), *m/z* $[M - H^-]^+$ calcd for $C_{15}H_{20}ClOSi$: 279.0972; found: 279.0959.

Spectroscopic data for *trans*-**2.4b:** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 5.73 (ddt, *J* = 10.1, 7.3, 2.4 Hz, 1H), 5.58 (dt, *J* = 11.2, 2.8 Hz, 1H), 4.82 (dd, *J* = 11.0, 4.4 Hz, 1H), 3.98 (dtd, *J* = 4.4, 2.8, 1.6 Hz, 1H), 2.50 (dddt, *J* = 16.2, 9.3, 4.0, 2.5 Hz,

1H), 2.35 – 2.24 (m, 2H), 2.10 (ddt, *J* = 13.2, 6.5, 2.9 Hz, 1H), -0.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.2, 132.9, 130.7, 128.5, 128.4, 128.2, 79.6, 68.7, 33.7, 26.4, -3.1. HRMS (ESI), *m/z* $[M + H]^+$ calcd for $C_{15}H_{22}ClOSi$: 281.1129; found: 281.1107.

Synthesis of *cis*-(7-(4-methoxyphenyl)-2,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane (*cis*-2.4c)

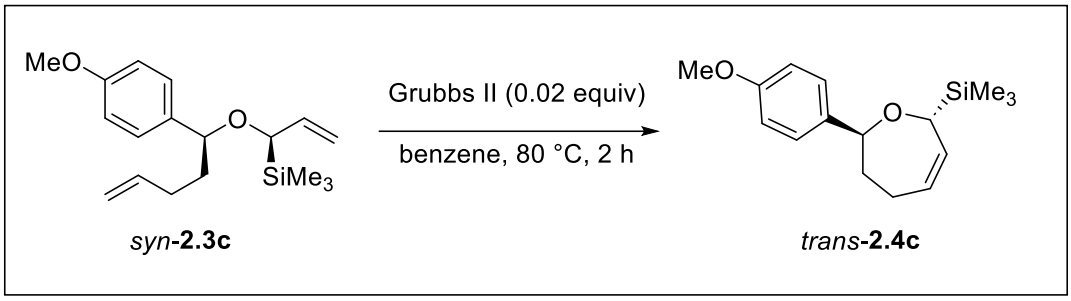


anti-**2.3c** *cis*-**2.4c**

Compound *cis*-**2.4c** was prepared following general procedure E: Grubbs catalyst 2nd generation (119 mg, 0.14 mmol, 0.02 equiv.) and *anti*-(1-((1-(4-methoxyphenyl)pent-4-en-1-yl)oxy)allyl)trimethylsilane *anti*-**2.3c** (2132 mg, 7.0 mmol, 1 equiv.) and benzene (100 mL) at 80 °C for 4 hours followed by concentration and column chromatography, R_f for *cis*-**2.4c** = 0.6 (40% DCM in hexanes) afforded a total of 1786 mg, 6.5 mmol (92% isolated yield) of compound *cis*-**2.4c** as a colorless liquid.

Spectroscopic data for *cis*-**2.4c:** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.71 (dddd, *J* = 11.3, 7.2, 4.7, 2.5 Hz, 1H), 5.56 (ddd, *J* = 11.2, 3.2, 2.1 Hz, 1H), 4.74 (dd, *J* = 8.4, 5.3 Hz, 1H), 4.07 (qd, *J* = 3.3, 1.2 Hz, 1H), 3.81 (s, 3H), 2.72 – 2.60 (m, 1H), 2.33 (ddt, *J* = 13.7, 10.4, 5.1 Hz, 1H), 2.00 (ddtd, *J* = 15.3, 7.4, 4.9, 1.2 Hz, 1H), 1.89 (ddt, *J* = 13.6, 8.4, 5.1 Hz, 1H), 0.13 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.2, 137.5, 130.7, 126.3, 126.2, 113.4, 81.2, 77.1, 55.2, 37.4, 23.6, -3.7. HRMS (ESI), *m/z* $[M – OH]^+$ calcd for $C_{16}H_{23}OSi$: 259.1518; found: 259.1513.

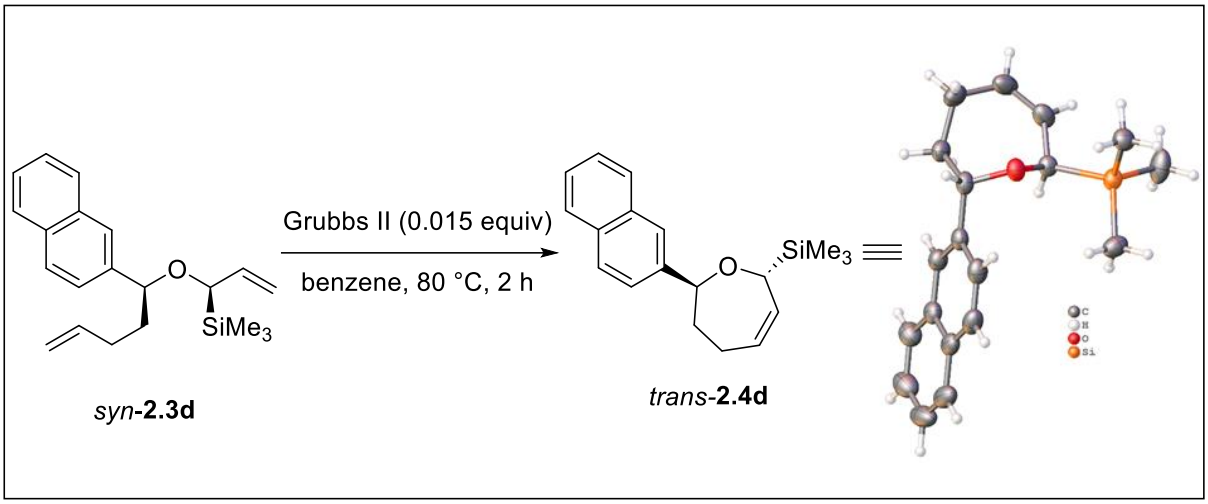
Synthesis of *trans*-(7-(4-methoxyphenyl)-2,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane (*trans*-2.4c)



syn-**2.3c** *trans*-**2.4c**

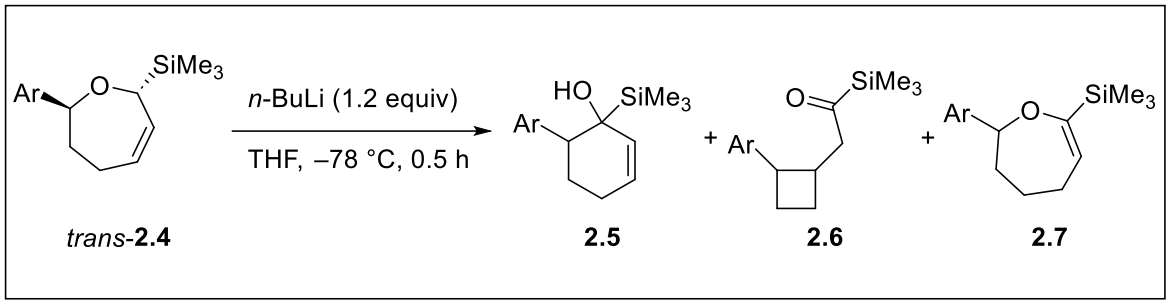
Compound *trans*-**2.4c** was prepared following general procedure E: Grubbs catalyst 2nd generation (81 mg, 0.095 mmol, 0.02 equiv.) and *syn*-(1-((1-(4-methoxyphenyl)pent-4-en-1-yl)oxy)allyl)trimethylsilane *syn*-**2.4c** (1.45 g, 4.75 mmol, 1 equiv.) and benzene (80 mL) at 80 °C for 2 hours followed by concentration and column chromatography, R_f for *trans*-**2.4c** = 0.4 (40% DCM in hexanes) afforded 943 mg, 3.4 mmol (72% isolated yield) of compound *trans*-**2.4c** as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.74 (ddt, *J* = 13.6, 6.0, 3.8 Hz, 1H), 5.57 (dt, *J* = 11.1, 2.8 Hz, 1H), 4.84 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.97 (dtd, *J* = 4.1, 2.8, 1.4 Hz, 1H), 3.81 (s, 3H), 2.52 (dddq, *J* = 16.7, 9.3, 5.2, 2.5 Hz, 1H), 2.40 – 2.24 (m, 2H), 2.13 – 2.05 (m, 1H), -0.02 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 158.8, 134.7, 130.9, 128.7, 128.4, 113.3, 79.8, 67.9, 55.2, 33.4, 26.4, -3.2. IR (FTIR, cm^{-1}) $\tilde{\nu}$ = 3010, 2952, 1511, 1242, 1032, 825. HRMS (ESI), *m/z* $[M + H]^+$ calcd for $C_{16}H_{25}O_2Si$: 277.1624; found: 277.1624.

Synthesis of *trans*-trimethyl(7-(naphthalen-2-yl)-2,5,6,7-tetrahydrooxepin-2-yl)silane (*trans*-2.4d)



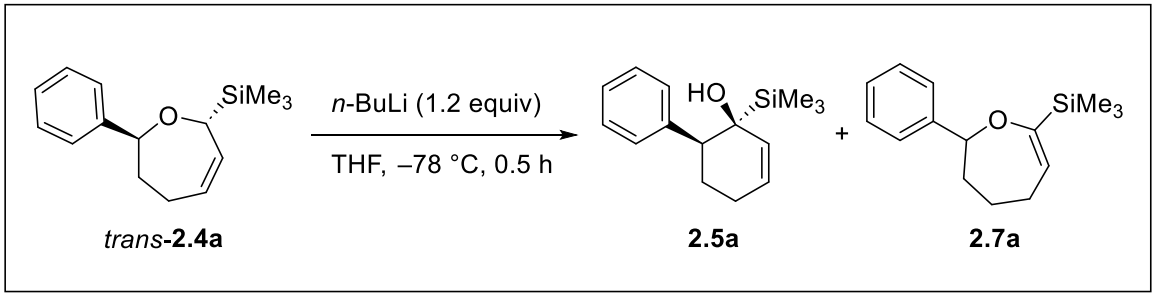
Compound *trans*-**2.4d** was prepared following general procedure E: Grubbs catalyst 2nd generation (76 mg, 0.1 mmol, 0.015 equiv.) and *syn*-(1-((1-(4-chlorophenyl)pent-4-en-1-yl)oxy)allyl)trimethylsilane, **2.3d** (2.12 g, 6 mmol, 1 equiv.) and benzene (80 mL) at 80 °C for 2 hours followed by concentration and column chromatography, R_f for *trans*-**2.4d** = 0.5 (30% DCM in hexanes) afforded a total of 1.493 g, 5 mmol (84% isolated yield) of *trans*-**2.4d** as a light yellow crystalline solid (mp 30–32 °C). The crystal structure of compound *trans*-**2.4d** was solved by X-ray crystallography and the results deposited to the Cambridge Crystallographic Data Centre and assigned CCDC 1902771. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 – 7.78 (m, 4H), 7.57 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.52 – 7.44 (m, 2H), 5.78 (ddt, *J* = 10.3, 6.7, 2.7 Hz, 1H), 5.61 (dt, *J* = 11.2, 2.8 Hz, 1H), 5.04 (dd, *J* = 10.9, 4.4 Hz, 1H), 4.05 (td, *J* = 4.3, 2.7 Hz, 1H), 2.59 (dddq, *J* = 16.4, 11.7, 4.6, 2.5 Hz, 1H), 2.48 (dtd, *J* = 13.6, 11.3, 1.8 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.26 (dt, *J* = 13.8, 4.4 Hz, 1H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 140.0, 133.0, 132.8, 130.9, 128.6, 128.0, 127.7, 127.6, 126.3, 125.9, 125.7, 124.9, 80.2, 68.6, 33.6, 26.4, -3.1. IR (FTIR, film, cm^{-1}) $\tilde{\nu}$ = 3052, 2948, 2773, 1600, 1245, 1097, 829. HRMS (ESI), *m/z* $[M + H]^+$ calcd for $C_{19}H_{25}OSi$: 297.1675; found: 297.1663.

2.6.7. General procedure F: Wittig rearrangement of *trans*-2-trimethylsilyl-2,5,6,7-tetrahydro-7-aryl-oxepins



Following a reported procedure,[15] freshly prepared and purified *trans*-2-trimethylsilyl-2,5,6,7-tetrahydro-7-aryl-oxepin was dissolved in THF under nitrogen (concentration 0.08 M, unless otherwise noted) and the solution cooled at −78 °C (dry ice/acetone bath), *n*-butyllithium (1.2 equiv, 1.6 M or 2.5 M in hexanes) was added dropwise (1 drop/s) to give a colored solution. The reaction was quenched after the indicated time (10−30 min) by adding saturated $NH_4Cl_{(aq)}$ and diluted with H_2O and diethyl ether. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with saturated $NH_4Cl_{(aq)}$, H_2O, and brine. The solution was dried over magnesium sulfate, filtered, quickly concentrated in a rotovap at temperatures lower than 45 °C. Column chromatography with EtOAc in hexanes afforded cyclohexenols. Other products including the ones resulting from [1,4]-Wittig rearrangement were also observed (see individual substrate).

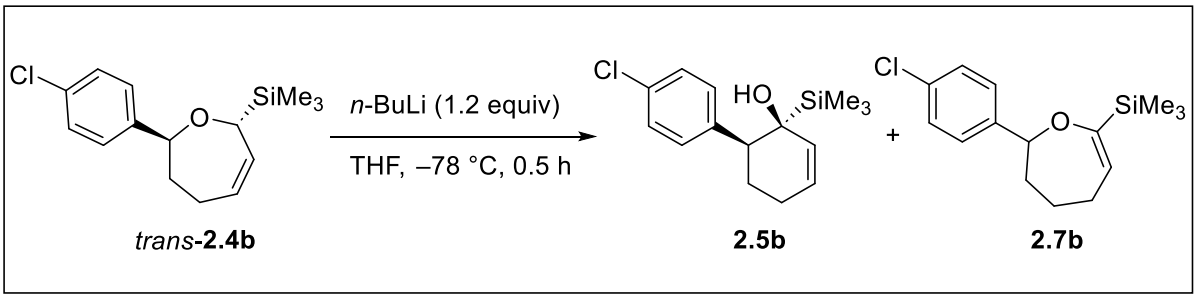
Synthesis of 2-(trimethylsilyl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-2-ol (2.5a) and 7-phenyl-4,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane (2.7a)



Applying general procedure F to *trans*-trimethyl(-7- phenyl-2,5,6,7-tetrahydrooxepin-2-yl)silane **2.4a** (1.6g, 6.5 mmol, 1.0 equiv), *n*-butyllithium (2.3 M in hexanes, 3.4 mL, 7.8 mmol, 1.2 equiv), and THF (70mL) afforded after column chromatography (5-10% EtOAc in hexanes) 404 mg, 1.64 mmol (25%) of compound **2.5a** and 819 mg, 3.3 mmol (51% isolated yield) of **2.7a** as colorless oils.

Spectroscopic data for **2.5a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 5.96 (ddd, *J* = 10.0, 4.8, 2.6 Hz, 1H), 5.88 (dt, *J* = 10.0, 1.9 Hz, 1H), 2.91 (dd, *J* = 10.9, 3.0 Hz, 1H), 2.20 (dtdd, *J* = 18.2, 5.1, 3.5, 1.6 Hz, 1H), 2.16 – 2.06 (m, 1H), 2.00 (dddd, *J* = 13.0, 10.9, 9.6, 5.4 Hz, 1H), 1.68 (ddt, *J* = 12.8, 6.3, 3.4 Hz, 1H), 1.30 (s, 1H), -0.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 130.8, 130.4, 129.3, 128.2, 126.5, 66.2, 47.3, 25.7, 25.3, -3.4.

Synthesis of 4'-chloro-2-(trimethylsilyl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-2-ol (2.5b) and (7-(4-chlorophenyl)-4,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane (2.7b)



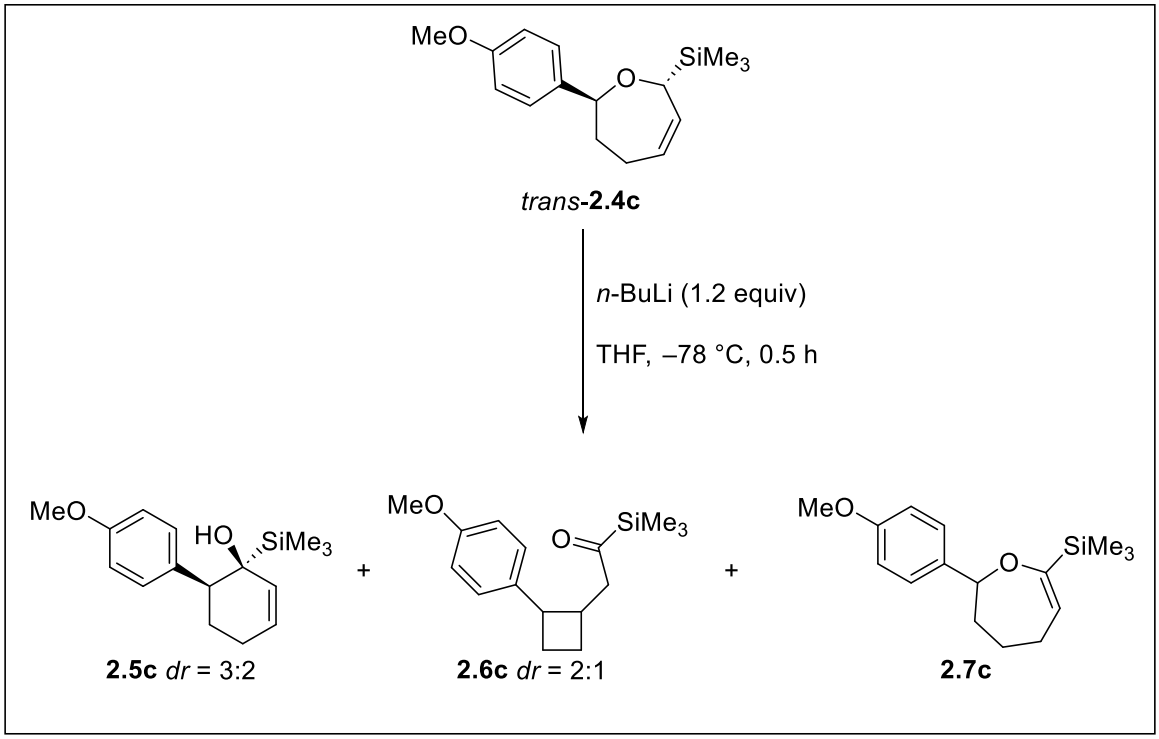
Applying general procedure F to *trans*-(7-(4-chlorophenyl)-2,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane *trans*-**2.4b** (2.4 g, 8.5 mmol, 1.0 equiv), *n*-butyllithium (2.5 M in hexanes, 5.6 mL, 6.0 mmol, 1.2 equiv), and THF (100mL) afforded after column chromatography, R_f for **2.7b** = 0.7 and R_f for **2.5b** = 0.3 (2% EtOAc in hexanes) 667 mg, 2.4 mmol (28% isolated yield) of compound **2.5b** and 515.8 mg, 1.84 mmol (21% isolated yield) of **2.7b** as colorless oils.

Spectroscopic data for **2.5b.** ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.34 (d, *J* = 8.5 Hz, 2H), 7.27

(d, J = 8.4 Hz, 2H), 5.97 (ddd, J = 10.0, 4.9, 2.6 Hz, 1H), 5.89 (dt, J = 10.0, 2.0 Hz, 1H), 2.87 (dd, J = 11.2, 2.9 Hz, 1H), 2.25 – 2.07 (m, 2H), 1.96 (dddd, J = 13.0, 11.1, 9.8, 5.6 Hz, 1H), 1.64 (ddt, J = 12.6, 6.6, 3.1 Hz, 1H), 1.24 (s, 1H), -0.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 142.6, 132.2, 130.8, 130.7, 130.5, 128.2, 66.0, 46.7, 25.7, 25.3, -3.4. HRMS (ESI): m/z $[M]^+$ calcd for $C_{15}H_{21}ClOSi$: 280.1050; found: 280.1015.

Spectroscopic data for **2.7b.** ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.20 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 5.03 (td, J = 4.0, 1.1 Hz, 1H), 3.28 (tq, J = 6.0, 1.7 Hz, 1H), 2.16 – 2.01 (m, 2H), 1.95 (dddd, J = 12.9, 9.5, 6.1, 3.3 Hz, 1H), 1.62 (dddd, J = 13.3, 10.9, 5.9, 3.0 Hz, 1H), 1.54 – 1.40 (m, 2H), 0.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 150.2, 142.9, 131.5, 129.7, 128.1, 106.1, 45.4, 32.7, 24.0, 19.2, 0.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{22}ClOSi$: 281.1129; found: 281.1147.

Synthesis of 4'-methoxy-2-(trimethylsilyl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-2-ol (2.5c), 2-(2-(4-methoxyphenyl)cyclobutyl)-1-(trimethylsilyl)ethan-1-one (2.6c) and (7-(4-methoxyphenyl)-4,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane (2.7c)



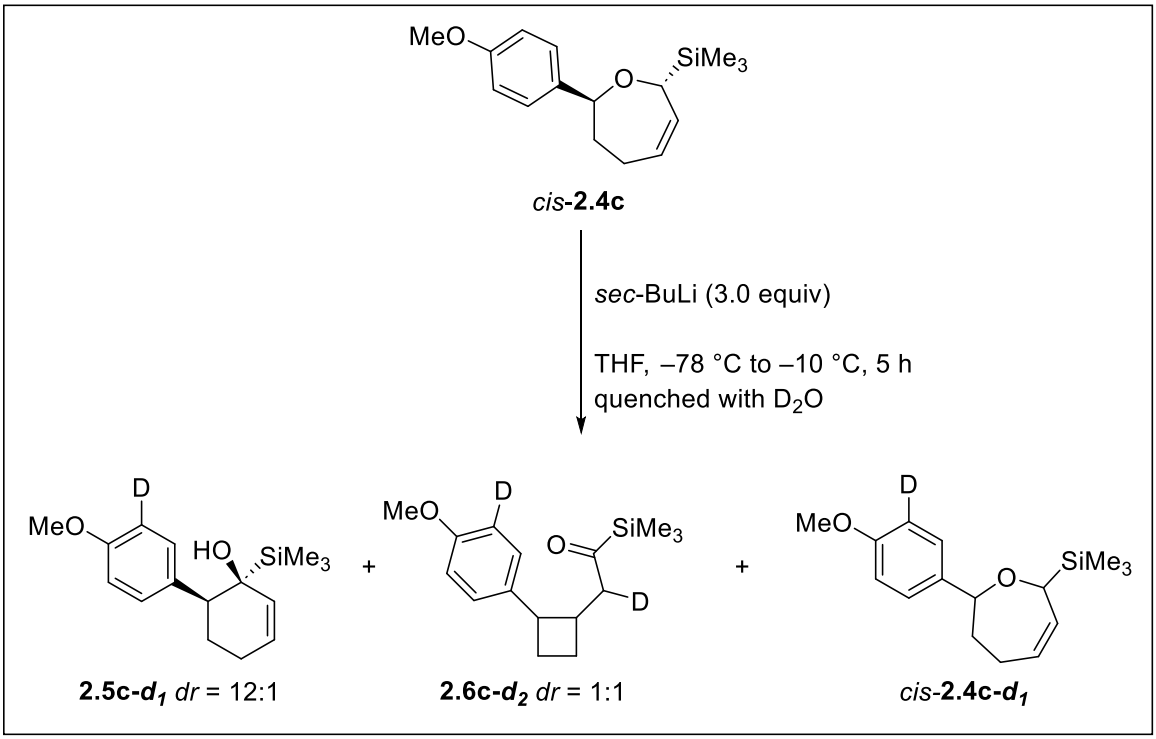
Applying general procedure F to *trans*-(7-(4-methoxyphenyl)-2,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane *trans*-**2.4c** (885 mg, 3.2 mmol, 1.0 equiv), *n*-butyllithium (2.5 M in hexanes, 5.6 mL, 6.0 mmol, 1.2 equiv), and THF (100mL) afforded after column chromatography, R_f for **2.6c** = 0.7, R_f for **2.7c** = 0.5 and R_f for **2.5c** = 0.3 (5% EtOAc in hexanes) 117 mg, 0.42 mmol (13% isolated yield) of compound **2.5c**, 28 mg, 0.1 mmol (3% isolated yield) of **2.6c** and 562 mg, 2 mmol, (64% isolated yield) of **2.7c** as colorless oils.

Spectroscopic data for **2.5c:** ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.30 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.95 (dddd, *J* = 10.0, 4.8, 2.6, 0.7 Hz, 1H), 5.87 (ddd, *J* = 10.0, 2.3, 1.6 Hz, 1H), 5.84 – 5.79 (m, 1H), 5.69 (ddd, *J* = 9.9, 2.5, 1.7 Hz, 1H), 3.82 (s, 2H), 3.81 (s, 3H), 2.92 – 2.85 (m, 2H), 2.31 – 2.05 (m, 5H), 2.01 – 1.91 (m, 2H), 1.69 – 1.62 (m, 2H), 1.52 (s, 1H), 1.28 (s, 1H), -0.10 (s, 9H), -0.21 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 158.4, 158.2, 135.9, 135.1, 132.8, 130.9, 130.3, 130.2, 129.4, 127.1, 113.54, 113.47, 72.0, 66.3, 55.3, 55.2, 50.3, 46.4, 25.7, 25.52, 250.5, 25.45, -2.4, -3.4. HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{25}O_2Si$: 277.1624; found: 277.1623.

Spectroscopic data for **2.6c** (*cis*:*trans* = 1:1): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.14 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.86 – 6.80 (m, 4H), 3.82 – 3.77 (m, 7H), 3.70 (q, *J* = 8.1 Hz, 1H), 3.20 (dtd, *J* = 14.6, 7.9, 7.3, 1.4 Hz, 1H), 3.01 (q, *J* = 8.8 Hz, 1H), 2.87 – 2.71 (m, 2H), 2.51 (dd, *J* = 17.6, 7.6 Hz, 1H), 2.32 – 2.23 (m, 3H), 2.23 – 2.16 (m, 2H), 2.16 – 2.05 (m, 1H), 1.98 (qd, *J* = 10.3, 8.6 Hz, 1H), 1.66 – 1.59 (m, 2H), 1.53 (tt, *J* = 10.3, 8.6 Hz, 1H), 0.13 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 248.1, 248.0, 158.0, 157.8, 136.4, 134.0, 128.8, 127.7, 113.7, 113.5, 55.3, 54.8, 50.1, 46.5, 41.6, 38.4, 33.5, 27.4, 25.6, 24.5, 23.5, -3.3, -3.4. IR (FTIR, cm^{-1}): ṽ = 2951, 2938, 2865, 2835, 1639, 1610, 1511, 1244, 1175, 1034, 827. HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{25}O_2Si$: 277.1624; found: 277.1625.

Spectroscopic data for **2.7c:** ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.31 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.40 (dd, *J* = 6.2, 5.1 Hz, 1H), 4.50 (dd, *J* = 10.9, 2.4 Hz, 1H), 3.81 (s, 3H), 2.36 – 2.19 (m, 2H), 2.17 – 2.08 (m, 1H), 1.96 (dddt, *J* = 15.5, 11.4, 7.1, 4.2 Hz, 2H), 1.52 (dtt, *J* = 11.6, 6.8, 2.2 Hz, 1H), 0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 166.2, 158.4, 136.4, 126.8, 122.9, 113.4, 83.2, 55.2, 39.4, 27.3, 25.5, -2.3. IR (FTIR, cm^{-1}): $\tilde{\nu}$ = 2952, 2927, 2835, 1613, 1512, 1244, 1100, 837. HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{25}O_2Si$: 277.1624; found: 277.1624.

Synthesis of 4'-methoxy-2-(trimethylsilyl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3'-*d*-2-ol (2.5c-*d*$_1$), 2-(2-(4-methoxyphenyl-3-*d*)cyclobutyl)-1-(trimethylsilyl)ethan-1-one-2-*d* (2.6c-*d*$_2$) and (7-(4-methoxyphenyl-3-*d*)-2,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane (*cis*-2.4c-*d*$_1$)



Compounds **2.5c-*d*$_1$**, **2.6c-*d*$_2$**, and *cis*-**2.4c-*d*$_1$** were prepared as follows: 1104 mg (4.0 mmol, 1.0 equiv) of freshly prepared and purified *cis*-(7-(4-methoxyphenyl)-2,5,6,7-tetrahydrooxepin-2-yl)trimethylsilane (*cis*-**2.4c**) was dissolved in 50 mL dry THF under nitrogen, and the resulting solution was cooled at −78 °C (dry ice/acetone bath), *sec*-butyllithium, 1.4 M in cyclohexane (8.6

mL, 12.0 mmol, 3.0 equiv) was added dropwise (1 drop/s) to give a dark brown solution. The reaction mixture was allowed to warm up slowly without removing the cooling bath to –10 °C. The mixture was stirred at this temperature for 5 hours then cooled back to –78 °C. The reaction was quenched at –78 °C with D_2O (5 mL), and the cooling bath was removed. After warming up to room temperature, the reaction mixture was diluted with 20 mL ether and loaded into a separating funnel. The layers were separated, and the aqueous phase was extracted with diethyl ether (20 mL x 3). Combined organic extracts were washed with brine (15 mL), and dried over anhydrous magnesium sulfate, filtered, quickly concentrated in a rotovap at temperatures lower than 45 °C. The crude material was purified by column chromatography, R_f for *cis*-**2.4c-*d*$_1$** = 0.6, R_f for **2.6c-*d*$_2$** = 0.4 and R_f for **2.5c-*d*$_1$** = 0.3 (10% EtOAc in hexanes) 259 mg, 0.93 mmol (23% isolated yield) of compound **2.5c-*d*$_1$**, 172 mg, 0.62 mmol (16% isolated yield) of **2.6c-*d*$_2$** and 503 mg, 1.8 mmol (45%) of recovered starting material *cis*-**2.4c-*d*$_1$** with deuterium incorporation in the aromatic ring as colorless oils.

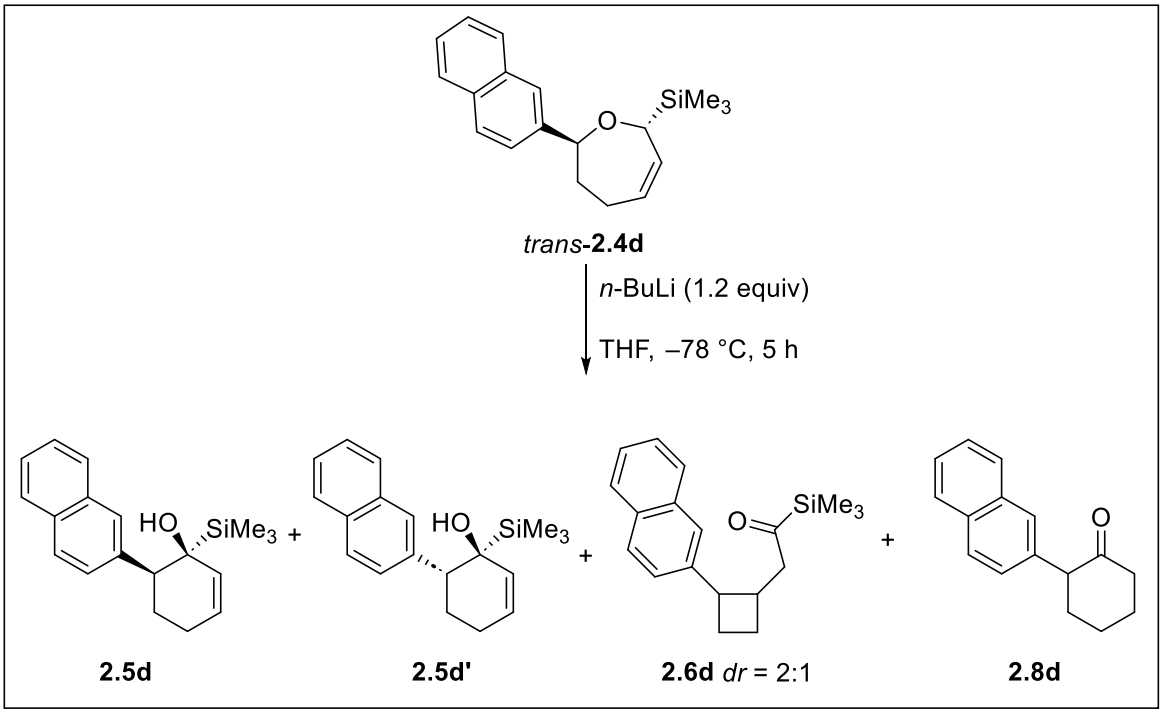
Spectroscopic data for **2.5c-*d*$_1$:** ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.29 (dq, *J* = 4.6, 2.3 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 1H), 5.94 (dddd, *J* = 10.0, 4.9, 2.6, 0.7 Hz, 1H), 5.86 (ddd, *J* = 10.0, 2.4, 1.7 Hz, 1H), 3.79 (s, 3H), 2.87 (dd, *J* = 10.9, 3.0 Hz, 1H), 2.18 (dtdd, *J* = 18.3, 5.3, 3.6, 1.6 Hz, 1H), 2.14 – 2.04 (m, 1H), 1.95 (dddd, *J* = 13.0, 10.9, 9.6, 5.5 Hz, 1H), 1.64 (ddt, *J* = 12.7, 6.3, 3.2 Hz, 1H), 1.28 (s, 1H), -0.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 158.2, 135.9, 130.9, 130.22, 130.20, 130.1, 113.6, 66.3, 55.1, 46.4, 25.7, 25.5, -3.4. ^{29}Si NMR (99 MHz, $CDCl_3$) δ = 5.03. HRMS (ESI): *m*/*z* $[M - H^-]^+$ calcd for $C_{16}H_{22}DO_2Si$: 276.1536; found: 276.1523.

Spectroscopic data for **2.6c-*d*$_2$** (*cis:trans* = 1:1): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.14 (dq, *J* = 4.1, 2.2 Hz, 2H), 7.04 (dq, *J* = 3.8, 2.2 Hz, 2H), 6.84 (d, *J* = 5.1 Hz, 1H), 6.82 (d, *J* = 5.1 Hz, 1H), 3.78 (s, 3H), 3.78 (s, 3H), 3.70 (q, *J* = 8.1 Hz, 1H), 3.19 (p, *J* = 7.9 Hz, 1H), 3.01 (q, *J* =

9.1 Hz, 1H), 2.85 – 2.67 (m, 2H), 2.47 (dt, *J* = 7.5, 2.5 Hz, 1H), 2.30 – 2.23 (m, 2H), 2.22 – 2.14 (m, 2H), 2.13 – 2.05 (m, 1H), 1.98 (qd, *J* = 10.3, 8.5 Hz, 1H), 1.66 – 1.58 (m, 1H), 1.58 – 1.48 (m, 1H), 0.13 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 248.2, 248.1, 157.9, 157.7, 136.3, 133.9, 128.8, 128.7, 127.7, 127.6, 113.7, 113.5, 55.2, 55.2, 54.4, 49.7, 46.4, 41.6, 38.3, 33.4, 27.4, 25.5, 24.4, 23.5, -3.3, -3.4. ^{29}Si NMR (99 MHz, $CDCl_3$) δ = -10.71, -10.89. HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{22}D_2O_2Si$: 279.1744; found: 279.1738.

Spectroscopic data for *cis*-**2.4c**-***d*$_1$**:** ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.34 – 7.27 (m, 2H), 6.89 (d, *J* = 9.1 Hz, 1H), 5.72 (dddd, *J* = 11.1, 7.2, 4.7, 2.5 Hz, 1H), 5.57 (ddd, *J* = 11.2, 3.1, 2.1 Hz, 1H), 4.74 (dd, *J* = 8.4, 5.3 Hz, 1H), 4.08 (qd, *J* = 3.3, 1.2 Hz, 1H), 3.81 (s, 3H), 2.71 – 2.61 (m, 1H), 2.33 (ddt, *J* = 13.6, 10.4, 5.0 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.89 (ddt, *J* = 13.6, 8.4, 5.2 Hz, 1H), 0.13 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 158.1, 137.4, 130.7, 126.3, 126.23, 126.18, 113.4, 81.2, 77.1, 55.2, 37.4, 23.6, -3.7. ^{29}Si NMR (99 MHz, $CDCl_3$) δ = -1.06. HRMS (ESI): *m*/*z* $[M – OH]^+$ calcd for $C_{16}H_{22}DOSi$: 260.1575; found: 260.1572.

Synthesis of 6-(naphthalen-2-yl)-1-(trimethylsilyl)cyclohex-2-en-1-ol (2.5d), 2-(2-(naphthalen-2-yl)cyclobutyl)-1-(trimethylsilyl)ethan-1-one (2.6d) and 2-(naphthalen-2-yl)cyclohexan-1-one (2.8d)



Applying general procedure F to *trans*-trimethyl(7-(naphthalen-2-yl)-2,5,6,7-tetrahydrooxepin-2-yl)silane *trans*-**2.4d** (593 mg, 2.0 mmol, 1.0 equiv), *n*-butyllithium (2.5 M in hexanes, 5.6 mL, 6.0 mmol, 1.2 equiv), and THF (100mL) afforded after column chromatography, R_f for **2.6d** = 0.7, R_f for **2.5d** = 0.5, R_f for **2.5d′** = 0.4 and R_f for **2.8d** = 0.3 (10% EtOAc in hexanes) 283 mg, 0.95 mmol (48% isolated yield) of compound **2.5d** and **2.5d′**, 156 mg, 0.53 mmol (26% isolated yield) of **2.6d** and 59 mg, 0.26 mmol (13% isolated yield) of **2.8d** as colorless oils.

Spectroscopic data for **2.5d** (silyl and naphthalenyl groups *cis* to one another): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.85 – 7.77 (m, 4H), 7.57 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.49 – 7.41 (m, 2H), 6.01 (ddd, *J* = 10.1, 5.0, 2.3 Hz, 1H), 5.93 (dt, *J* = 10.0, 1.9 Hz, 1H), 3.10 (dd, *J* = 10.6, 3.1 Hz, 1H), 2.28 – 2.05 (m, 3H), 1.78 – 1.69 (m, 1H), 1.38 (s, 1H), -0.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 141.5, 133.4, 132.3, 131.0, 130.4, 128.1, 127.73, 127.68, 127.6, 127.5, 125.8,

125.3, 66.4, 47.5, 25.7, 25.5, -3.3. HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{24}OSi$: 296.1596; found: 296.1592.

Spectroscopic data for **2.5d′** (silyl and naphthalenyl groups *trans* to one another): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.85 – 7.78 (m, 3H), 7.75 (s, 1H), 7.55 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.50 – 7.41 (m, 2H), 5.87 (dd, *J* = 10.0, 3.4 Hz, 1H), 5.74 (d, *J* = 10.3 Hz, 1H), 3.10 (dt, *J* = 12.8, 3.5 Hz, 1H), 2.32 – 2.26 (m, 2H), 2.10 (dp, *J* = 6.7, 5.1 Hz, 1H), 1.59 (s, 1H), -0.26 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ = 140.7, 133.3, 132.9, 132.3, 127.78, 127.76, 127.6, 127.5, 127.3, 126.7, 125.9, 125.4, 72.0, 51.3, 25.48, 25.46, -2.3. MS (GC/MS): *m*/z (%) = 296 (5) $[M]^+$, 279 (38), 165 (14), 73 (100). HRMS (ESI): *m*/*z* $[M - H^-]^+$ calcd for $C_{19}H_{23}OSi$: 295.1518; found: 295.1505.

Spectroscopic data for **2.6d:** ^{1}H NMR (500 MHz, $CDCl_3$, ppm) for *trans* diastereomer: δ =7.82 – 7.78 (m, 2H), 7.75 (d, J = 8.5 Hz, 1H), 7.58 (s, 1H), 7.48 – 7.41 (m, 2H), 7.27 – 7.22 (m, 1H), 3.93 (q, J = 8.2 Hz, 1H), 3.40 – 3.29 (m, 1H), 2.54 (dd, J = 17.7, 7.5 Hz, 1H), 2.51 – 2.44 (m, 1H), 2.42 – 2.36 (m, 1H), 2.36 – 2.25 (m, 2H), 1.72 (ddtd, J = 11.5, 9.4, 5.8, 0.9 Hz, 1H), -0.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) *trans* diastereomer: δ = 248.0, 139.4, 133.4, 132.0, 127.54, 127.48, 127.46, 127.0, 125.8, 125.7, 125.2, 50.0, 42.4, 33.6, 24.5, 23.1, -3.6. ^{13}C NMR (126 MHz, $CDCl_3$, ppm) *cis/trans* isomers: δ = 249.2, 248.0, 139.5, 135.7, 134.4, 133.2, 133.4, 132.0, 129.8, 127.54, 127.48, 127.47, 127.3, 127.04, 127.00, 126.4, 126.1, 125.8, 125.7, 125.5, 125.2, 125.0, 50.0, 45.7, 42.4, 41.4, 33.6, 27.1, 26.2, 24.6, 23.1, 21.7, -3.3, -3.5. HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{25}OSi$: 297.1675; found: 297.1661.

Spectroscopic data for **2.8d:** ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.63 (s, 1H), 7.53 – 7.41 (m, 2H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.80 (dd, *J* = 12.2, 5.5 Hz, 1H), 2.59 (dtd, *J* = 13.7, 4.0, 1.3 Hz, 1H), 2.51 (dddd, *J* = 13.7, 12.4, 5.9, 1.2 Hz, 1H), 2.35 (dddd, *J* = 15.2, 7.3, 3.4, 2.3 Hz, 1H), 2.24 – 2.12 (m, 2H), 2.05 (dddq, *J* = 10.5, 6.8, 4.5, 2.4, 2.0 Hz, 1H), 1.95 – 1.82 (m, 2H). ^{13}C

NMR (126 MHz, $CDCl_3$, ppm): δ = 210.4, 136.3, 133.4, 132.5, 127.72, 127.65, 127.6, 126.92, 126.90, 125.8, 125.5, 57.4, 42.2, 35.0, 27.7, 25.2. **2.8d** is a known compound, and the spectroscopic data are in agreement with those reported in the literature.[19]

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APPENDIX

X-ray data for compound 2.4d

Crystal structure confirms relative stereo chemistry, both enantiomers are present.

Crystal data and experimental

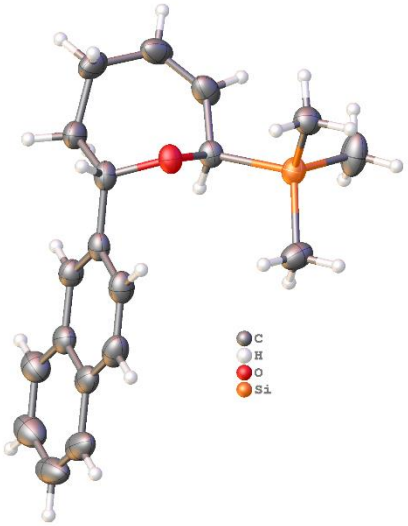


Figure 2.1: Crystal structure of compound **2.4d**

Experimental. Single yellow needle-shaped crystals of **2.4d** were used as received. A suitable crystal 0.43×0.12×0.05 mm^3 was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 173(2) K during data collection. The structure was solved with the ShelXT (Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov *et al*., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, Acta Cryst. A64 2008, 112-122) using Least Squares minimization.

Crystal data. $C_{19}H_{24}OSi$, M_r = 296.47, monoclinic, $C2/c$ (No. 15), a = 32.3150(4) Å, b = 6.20960(10) Å, c = 22.7493(3) Å, β = 132.1830(10)°, $\alpha = \gamma$ = 90°, V = 3382.64(9) $Å^3$, T = 173(2) K, Z = 8, Z' = 1, $\mu(CuK_\alpha)$ = 1.182, 25668 reflections measured, 3340 unique (R_{int} = 0.0417) which were used in all calculations. The final wR_2 was 0.1021 (all data) and R_1 was 0.0367 (I > 2(I)).

Table 2.2: Crystal data

Compound	**2.4d**
CCDC	1902771
Formula	$C_{19}H_{24}OSi$
$D_{calc.}$/ g cm^{-3}	1.164
μ/mm^{-1}	1.182
Formula Weight	296.47
Color	yellow
Shape	needle
Size/mm^3	0.43×0.12×0.05
T/K	173(2)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	32.3150(4)
b/Å	6.20960(10)
c/Å	22.7493(3)
α/°	90
β/°	132.1830(10)
γ/°	90
V/Å^3	3382.64(9)
Z	8
Z'	1
Wavelength/Å	1.541838
Radiation type	CuK$_\alpha$
Θ_{min}/°	3.692
Θ_{max}/°	72.149
Measured Refl.	25668
Independent Refl.	3340
Reflections with I > 2(I)	2924
R_{int}	0.0417
Parameters	193
Restraints	0
Largest Peak	0.293
Deepest Hole	-0.226
GooF	1.044
wR_2 (all data)	0.1021
wR_2	0.0975
R_1 (all data)	0.0425
R_1	0.0367

Reflections:	d min (Cu) 0.81	I/σ 40.6	Rint 4.17%	complete 100%
Refinement:	Shift 0.001	Max Peak 0.3	Min Peak -0.2	GooF 1.044

Figure 2.2: Structure quality indicators

A yellow needle-shaped crystal with dimensions 0.43×0.12×0.05 mm^3 was mounted on a nylon loop with paratone oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 173(2) K.

Data were measured using ω and ϕ of 1.00° per frame for 100.00 s using CuK_α radiation (sealed tube, 40 kV, 30 mA). The total number of runs and images was based on the strategy calculation from the program **COSMO** (BRUKER, V1.61, 2009). The actually achieved resolution was Θ = 72.149.

Cell parameters were retrieved using the **SAINT** (Bruker, V8.38A, after 2013) software and refined using **SAINT** (Bruker, V8.38A, after 2013) on 9911 reflections, 39 % of the observed reflections. Data reduction was performed using the **SAINT** (Bruker, V8.38A, after 2013) software which corrects for Lorentz polarization. The final completeness is 100.00 out to 72.149 in Θ **SADABS**-2016/2 (Bruker,2016/2) was used for absorption correction. wR_2(int) was 0.0735 before and 0.0532 after correction. The Ratio of minimum to maximum transmission is 0.8774. The $\lambda/2$ correction factor is Not present.

The structure was solved in the space group *C*2/*c* (# 15) by Intrinsic Phasing using the ShelXT (Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8) structure solution program. The structure was refined by Least Squares using version 2014/6 of **XL** (Sheldrick, 2008) incorporated in **Olex2** (Dolomanov *et al*., 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the hydrogen atom on the non-carbon atom(s) which was found by difference Fourier methods and refined isotropically.

CCDC 1902771 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

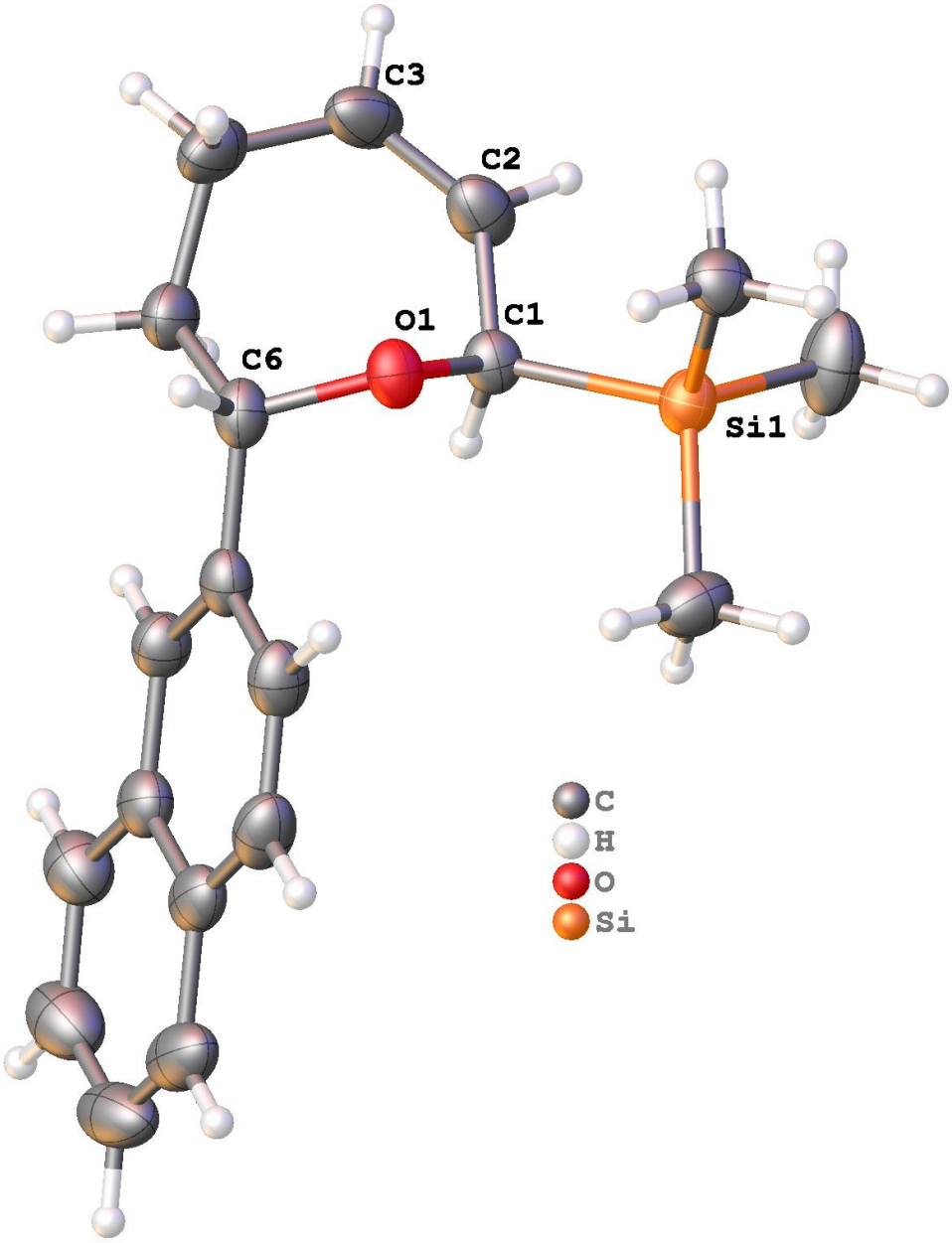


Figure 2.3: Model has Chirality at C1 (Centro SPGR) R Verify: Model has Chirality at C6 (Centro SPGR) S Verify. Being in a centrosymmetric space group means both enantiomers are present in the crystal

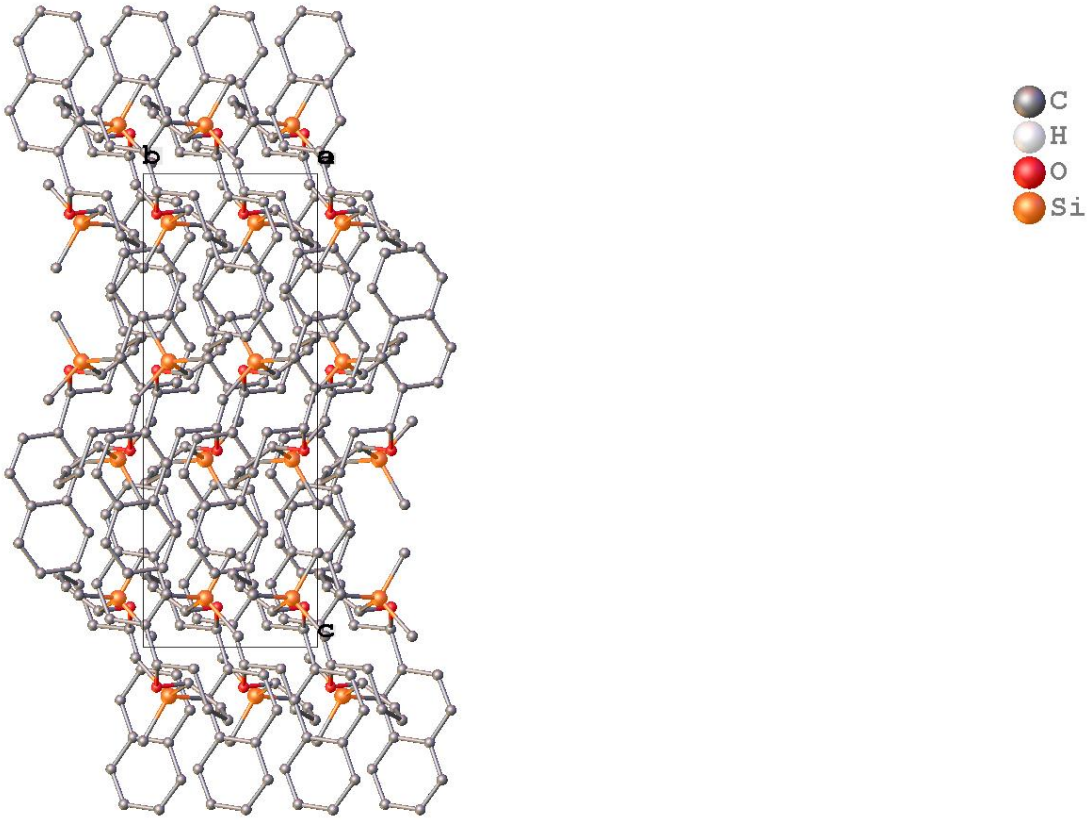


Figure 2.4: Packing diagram of **2.4d**

Data Plots: Diffraction data

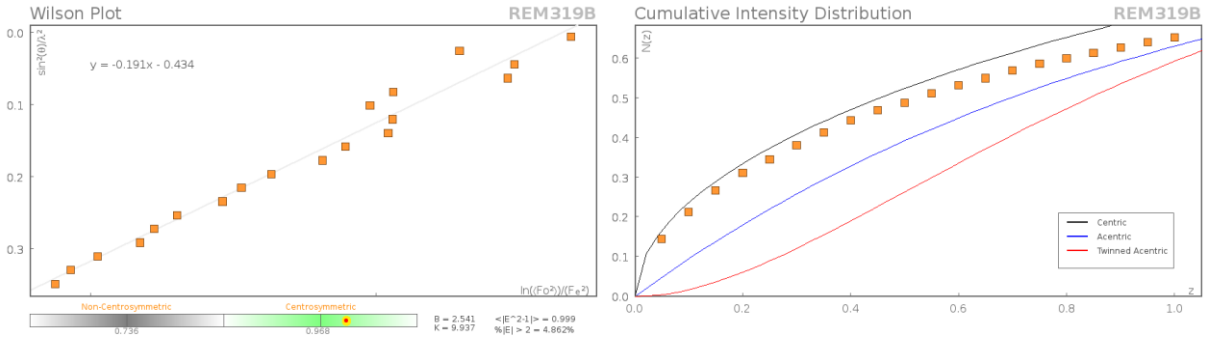
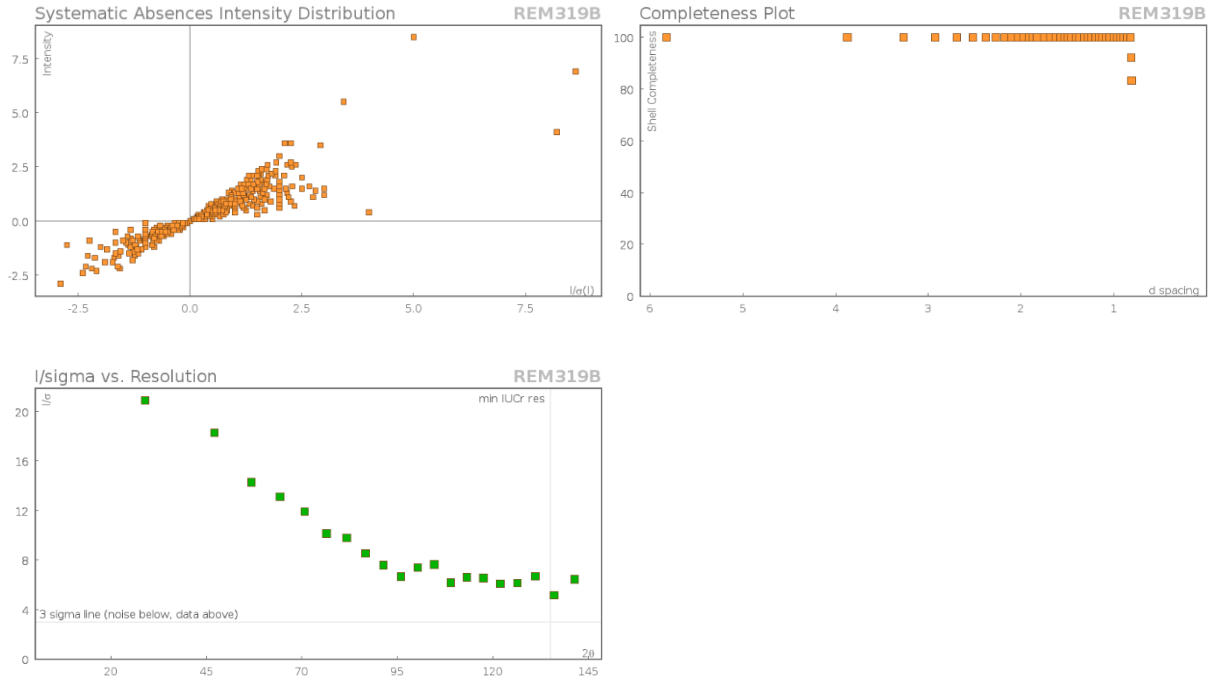


Figure 2.5: Data plots: Diffraction data

Figure 2.5 (cont'd)



Data Plots: Refinement and data

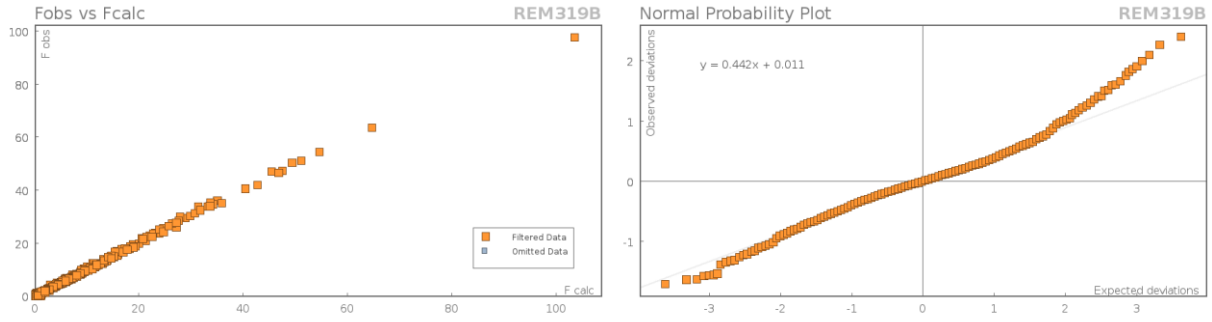


Figure 2.6: Data plots: Refinement and data

Table 2.3: Reflection statistics

Total reflections (after filtering)	26650	Unique reflections	3340
Completeness	0.998	Mean I/σ	25.28
hkl_{max} collected	(39, 7, 25)	hkl_{min} collected	(-39, -7, -28)
hkl_{max} used	(29, 7, 28)	hkl_{min} used	(-39, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	16.86	d_{min} used	0.81
Friedel pairs	3742	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.0417

Table 2.3 (cont'd)

R_{sigma}	0.0246	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(3206, 3053, 1800, 754, 476, 289, 284, 234, 92, 12)	Maximum multiplicity	24
Removed systematic absences	982	Filtered off (Shel/OMIT)	0

Images of the crystal on the diffractometer

Figure 2.7: Images of the crystal on the diffractometer

Table 2.4: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2.4d**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}

Atom	x	Y	z	U_{eq}
Si1	6251.6(2)	3547.1(6)	3967.8(2)	31.32(12)
O1	5536.0(4)	4241.9(14)	4154.0(5)	31.5(2)
C1	5847.6(6)	2421(2)	4236.2(8)	30.7(3)
C2	5474.3(7)	562(2)	3721.4(9)	41.6(3)
C3	4970.0(7)	142(3)	3455.3(9)	47.8(4)
C4	4691.5(7)	1294(3)	3685.7(9)	47.5(4)
C5	5109.8(6)	2106(2)	4539.5(8)	37.6(3)
C6	5385.3(6)	4203(2)	4622.3(8)	33.2(3)
C7	5877.6(6)	4880(2)	5471.9(8)	32.3(3)
C8	6123.5(7)	6915(2)	5592.9(10)	39.8(3)
C9	6551.7(7)	7674(2)	6334.7(10)	43.3(4)
C10	6773.1(6)	6447(2)	7018.7(9)	39.0(3)
C11	7224.5(7)	7161(3)	7804.0(11)	52.2(4)
C12	7420.5(7)	5904(3)	8436.9(11)	58.4(5)
C13	7180.1(8)	3889(3)	8325.1(10)	56.1(5)
C14	6746.8(7)	3149(3)	7578.3(9)	45.7(4)
C15	6533.2(6)	4401(2)	6907.3(9)	36.0(3)
C16	6084.0(6)	3673(2)	6122.1(8)	34.0(3)
C17	6598.9(9)	1286(3)	3899.5(14)	57.4(5)
C18	5762.6(6)	5013(2)	3011.0(9)	39.0(3)
C19	6787.4(6)	5447(3)	4770.3(9)	45.3(4)

Table 2.5: Anisotropic displacement parameters ($\times 10^4$) **2.4d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	32.8(2)	28.5(2)	37.4(2)	3.82(14)	25.53(18)	1.96(14)
O1	38.8(5)	27.6(4)	36.8(5)	5.9(4)	28.9(4)	4.1(4)
C1	35.8(7)	26.1(6)	34.8(7)	1.9(5)	25.6(6)	0.8(5)
C2	59.4(9)	31.0(7)	47.4(8)	-6.3(6)	41.2(8)	-8.4(7)
C3	58.3(10)	47.3(9)	39.0(8)	-11.6(7)	33.2(8)	-22.8(8)
C4	38.5(8)	61.0(10)	41.9(8)	-2.4(7)	26.5(7)	-16.8(7)
C5	38.6(7)	43.9(8)	38.8(7)	-0.2(6)	29.4(7)	-5.3(6)
C6	36.5(7)	33.8(7)	38.6(7)	5.0(6)	29.0(6)	4.4(6)
C7	37.1(7)	30.3(6)	41.0(7)	0.2(5)	30.9(6)	1.8(6)
C8	48.8(8)	32.7(7)	52.1(9)	2.7(6)	39.7(8)	0.7(6)
C9	47.9(9)	33.2(7)	63.4(10)	-8.0(7)	43.3(8)	-7.3(6)
C10	34.9(7)	39.8(8)	49.9(8)	-10.1(6)	31.7(7)	-0.3(6)
C11	37.3(8)	55.2(10)	62.7(11)	-22.6(9)	33.0(8)	-4.6(7)
C12	37.0(8)	76.2(12)	44.8(9)	-18.6(9)	20.4(8)	7.7(9)
C13	48.8(9)	71.1(12)	41.1(9)	2.1(8)	27.1(8)	17.5(9)
C14	45.1(9)	51.1(9)	41.5(8)	3.9(7)	29.2(7)	8.1(7)
C15	34.5(7)	39.2(7)	41.7(8)	-1.6(6)	28.6(7)	3.9(6)
C16	36.8(7)	30.6(7)	40.6(7)	-0.9(5)	28.5(6)	-2.1(6)
C17	67.0(11)	42.6(9)	94.9(14)	10.9(9)	67.5(12)	12.4(8)
C18	43.2(8)	40.1(7)	36.1(7)	2.3(6)	27.6(7)	-1.4(6)
C19	35.8(8)	48.4(9)	40.8(8)	2.5(7)	21.2(7)	-7.7(7)

Table 2.6: Bond Lengths in Å for **2.4d**

Atom	Atom	Length/Å
Si1	C1	1.9072(13)
Si1	C17	1.8680(16)
Si1	C18	1.8559(15)
Si1	C19	1.8649(16)
O1	C1	1.4402(15)
O1	C6	1.4382(15)
C1	C2	1.5044(19)
C2	C3	1.328(2)
C3	C4	1.493(2)
C4	C5	1.526(2)
C5	C6	1.5164(19)
C6	C7	1.521(2)
C7	C8	1.4180(19)
C7	C16	1.3674(19)
C8	C9	1.360(2)
C9	C10	1.421(2)
C10	C11	1.420(2)
C10	C15	1.420(2)
C11	C12	1.363(3)
C12	C13	1.403(3)
C13	C14	1.365(2)
C14	C15	1.413(2)
C15	C16	1.421(2)

Table 2.7: Bond Angles in ° for **2.4d**

Atom	Atom	Atom	Angle/°
C17	Si1	C1	109.25(7)
C18	Si1	C1	109.17(6)
C18	Si1	C17	110.94(8)
C18	Si1	C19	109.72(7)
C19	Si1	C1	107.68(7)
C19	Si1	C17	110.02(9)
C6	O1	C1	116.45(9)
O1	C1	Si1	103.89(8)
O1	C1	C2	112.10(11)
C2	C1	Si1	113.30(9)
C3	C2	C1	127.04(14)
C2	C3	C4	126.15(14)
C3	C4	C5	112.19(13)
C6	C5	C4	112.71(12)
O1	C6	C5	112.66(11)
O1	C6	C7	110.56(11)
C5	C6	C7	114.90(11)
C8	C7	C6	117.69(12)
C16	C7	C6	123.87(12)
C16	C7	C8	118.41(13)
C9	C8	C7	121.37(14)
C8	C9	C10	121.18(14)
C11	C10	C9	123.17(15)
C11	C10	C15	118.70(16)
C15	C10	C9	118.13(14)
C12	C11	C10	120.44(17)
C11	C12	C13	120.73(16)
C14	C13	C12	120.41(18)
C13	C14	C15	120.54(17)
C10	C15	C16	118.91(13)
C14	C15	C10	119.18(14)
C14	C15	C16	121.91(14)
C7	C16	C15	122.00(13)

Table 2.8: Torsion angles in ° for **2.4d**

Atom	Atom	Atom	Atom	Angle/°
Si1	C1	C2	C3	-142.51(15)
O1	C1	C2	C3	-25.3(2)
O1	C6	C7	C8	56.42(16)
O1	C6	C7	C16	-125.63(13)
C1	O1	C6	C5	-50.23(15)
C1	O1	C6	C7	79.84(14)
C1	C2	C3	C4	-7.4(3)
C2	C3	C4	C5	-31.9(2)
C3	C4	C5	C6	81.04(17)
C4	C5	C6	O1	-41.76(17)
C4	C5	C6	C7	-169.59(12)
C5	C6	C7	C8	-174.70(12)
C5	C6	C7	C16	3.25(19)
C6	O1	C1	Si1	-154.03(9)
C6	O1	C1	C2	83.27(14)
C6	C7	C8	C9	177.60(13)
C6	C7	C16	C15	-177.84(12)
C7	C8	C9	C10	0.5(2)
C8	C7	C16	C15	0.1(2)
C8	C9	C10	C11	179.14(14)
C8	C9	C10	C15	-0.2(2)
C9	C10	C11	C12	-179.65(15)
C9	C10	C15	C14	179.89(13)
C9	C10	C15	C16	-0.16(19)
C10	C11	C12	C13	-0.1(2)
C10	C15	C16	C7	0.2(2)
C11	C10	C15	C14	0.5(2)
C11	C10	C15	C16	-179.54(12)
C11	C12	C13	C14	0.4(3)
C12	C13	C14	C15	-0.1(2)
C13	C14	C15	C10	-0.3(2)
C13	C14	C15	C16	179.75(14)
C14	C15	C16	C7	-179.84(13)
C15	C10	C11	C12	-0.3(2)
C16	C7	C8	C9	-0.5(2)

Table 2.9: Hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2.4d**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}

Atom	x	Y	z	U_{eq}
H1	6117.96	1947.53	4803.17	37
H2	5614.28	-418.73	3570.24	50
H3	4767.49	-999.26	3083.29	57
H4A	4423.78	306.51	3623.63	57
H4B	4478.04	2530.58	3324.32	57
H5A	4915.08	2317.72	4733.37	45
H5B	5401.68	997.83	4877.39	45
H6	5095.22	5345.81	4396.99	40
H8	5986.08	7766.51	5146.42	48
H9	6705.7	9049.64	6396.69	52
H11	7391.04	8522.55	7889	63
H12	7723.27	6398	8959.48	70
H13	7319.7	3034.48	8771.89	67
H14	6587.52	1781.35	7509.17	55
H16	5922.26	2306.59	6046.79	41
H17A	6836.27	479.74	4399.32	86
H17B	6828.38	1867.19	3799.03	86
H17C	6314.09	323.48	3464.26	86
H18A	5471.27	4025.42	2595.97	58
H18B	5967.82	5584.8	2868.34	58
H18C	5590.34	6204.57	3063.59	58
H19A	6602.6	6597.83	4815.47	68
H19B	6997.22	6073.94	4642.44	68
H19C	7044.08	4668.02	5274.65	68

Citations

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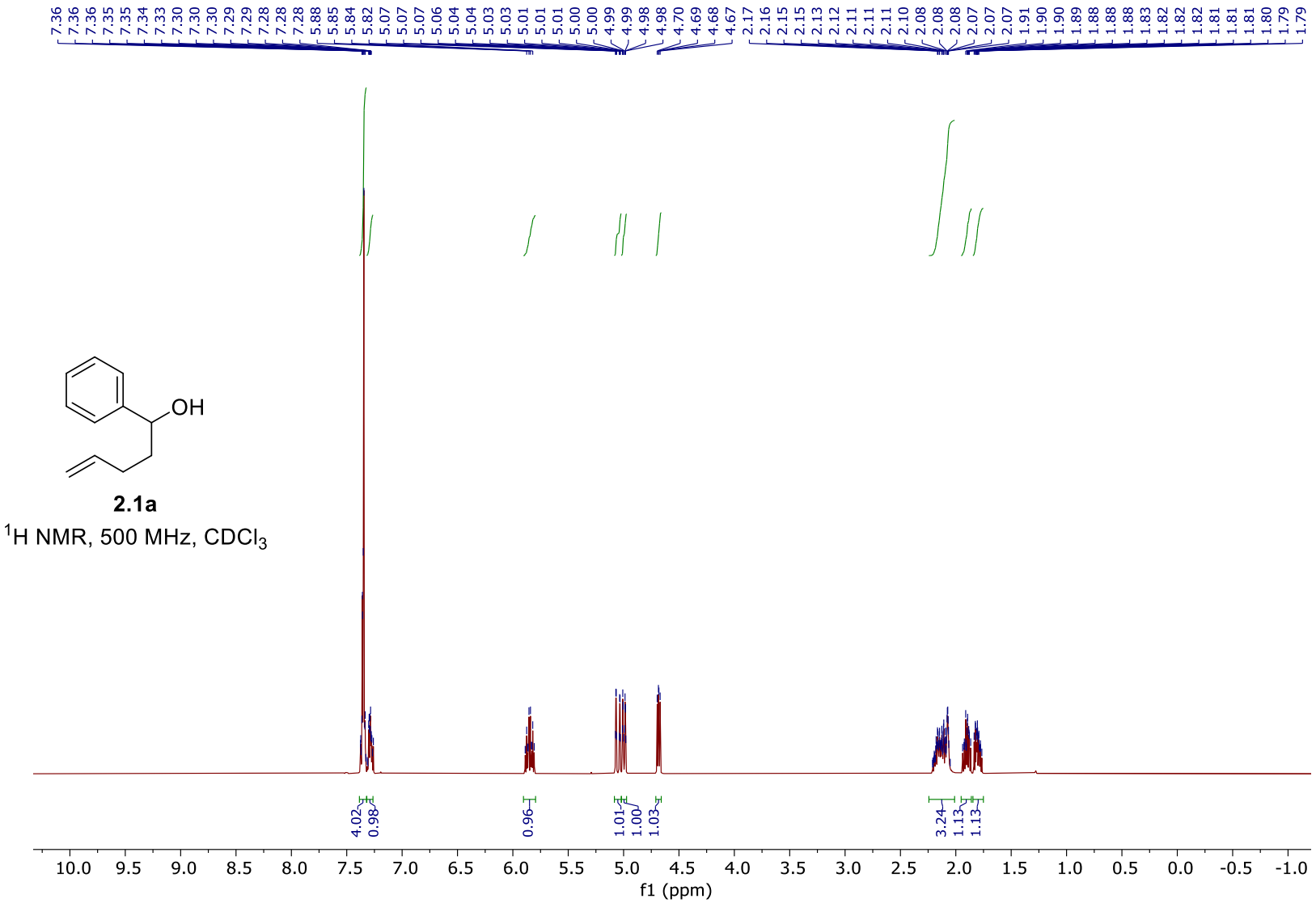
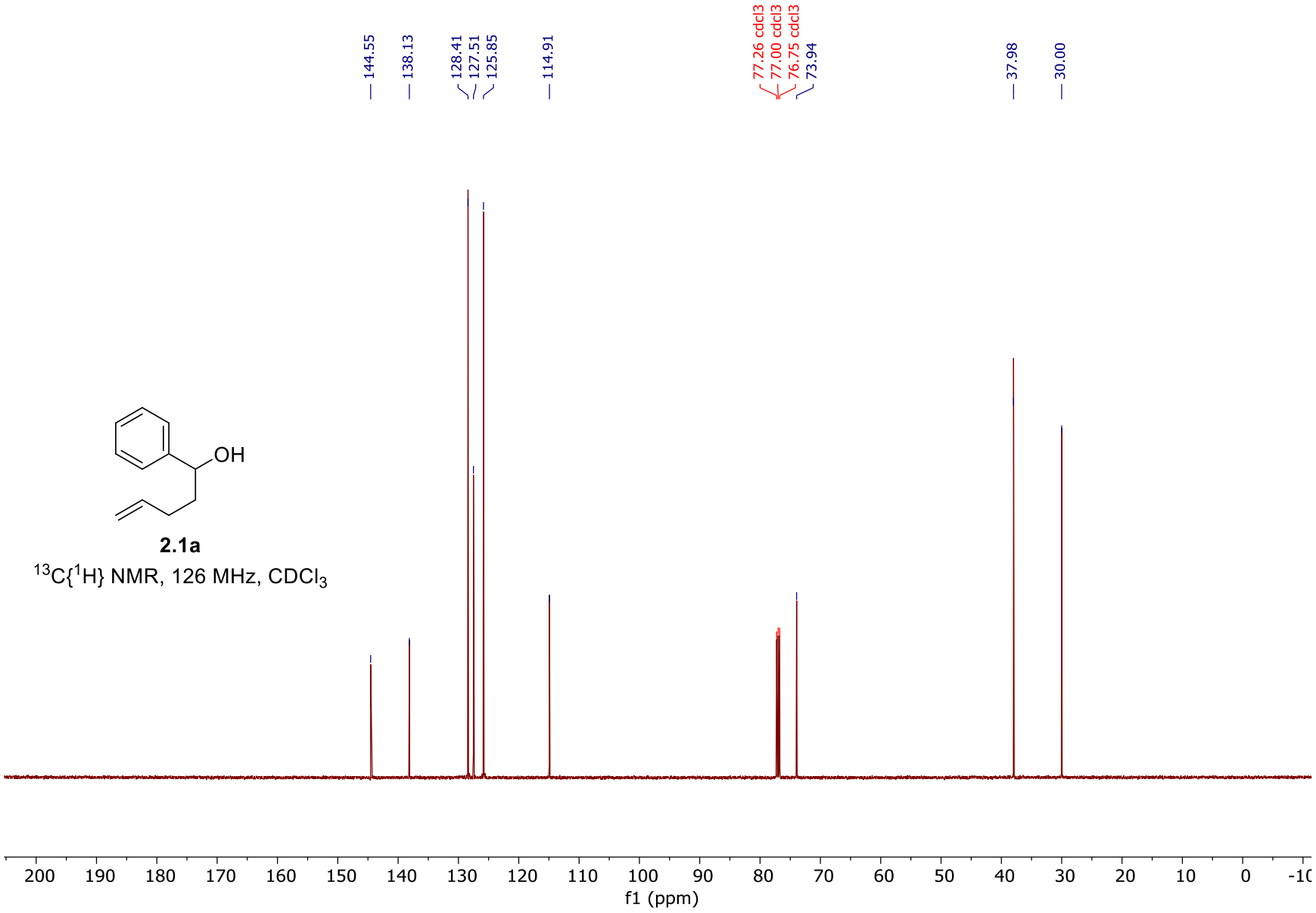
Copies of NMR Spectra

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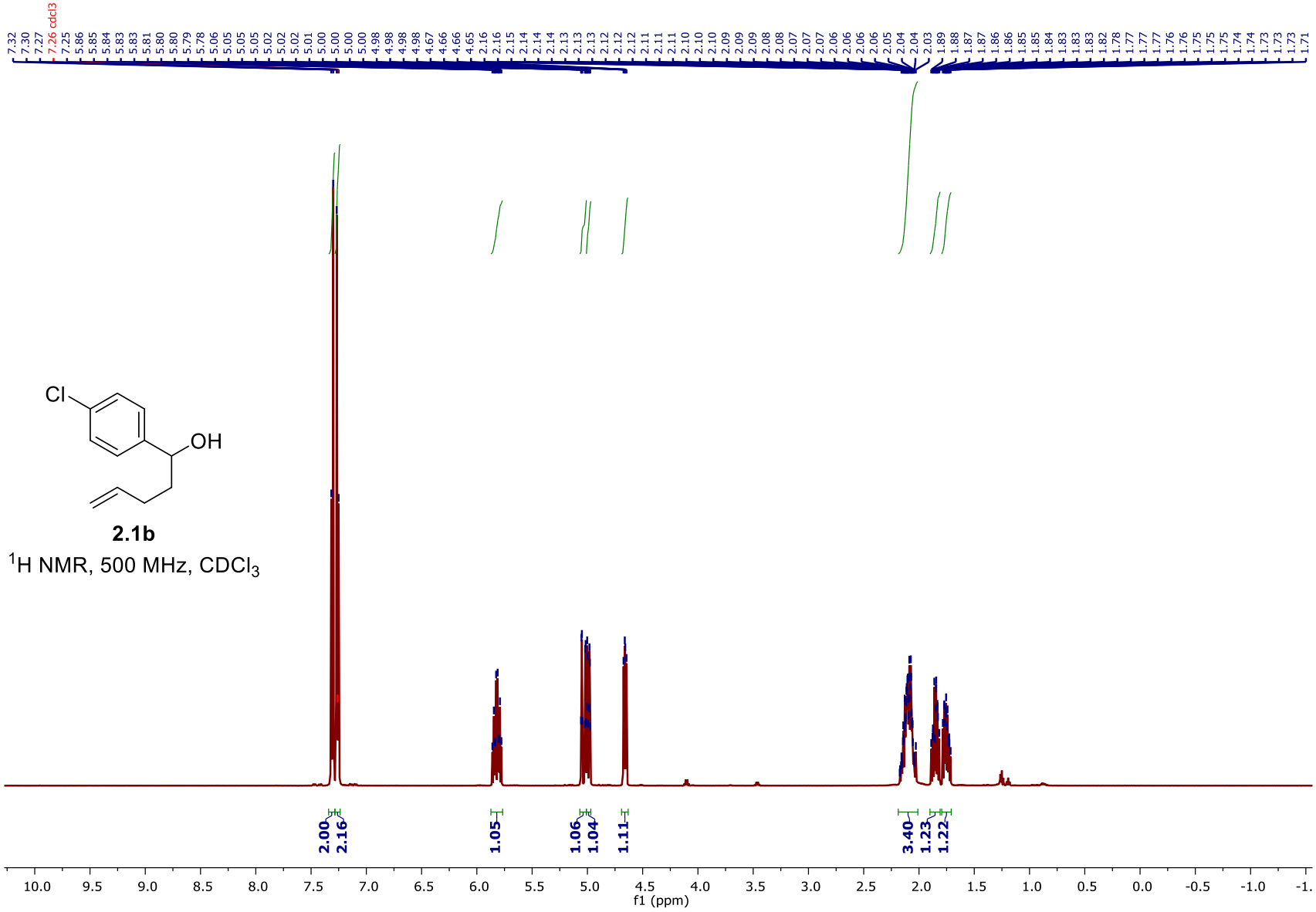
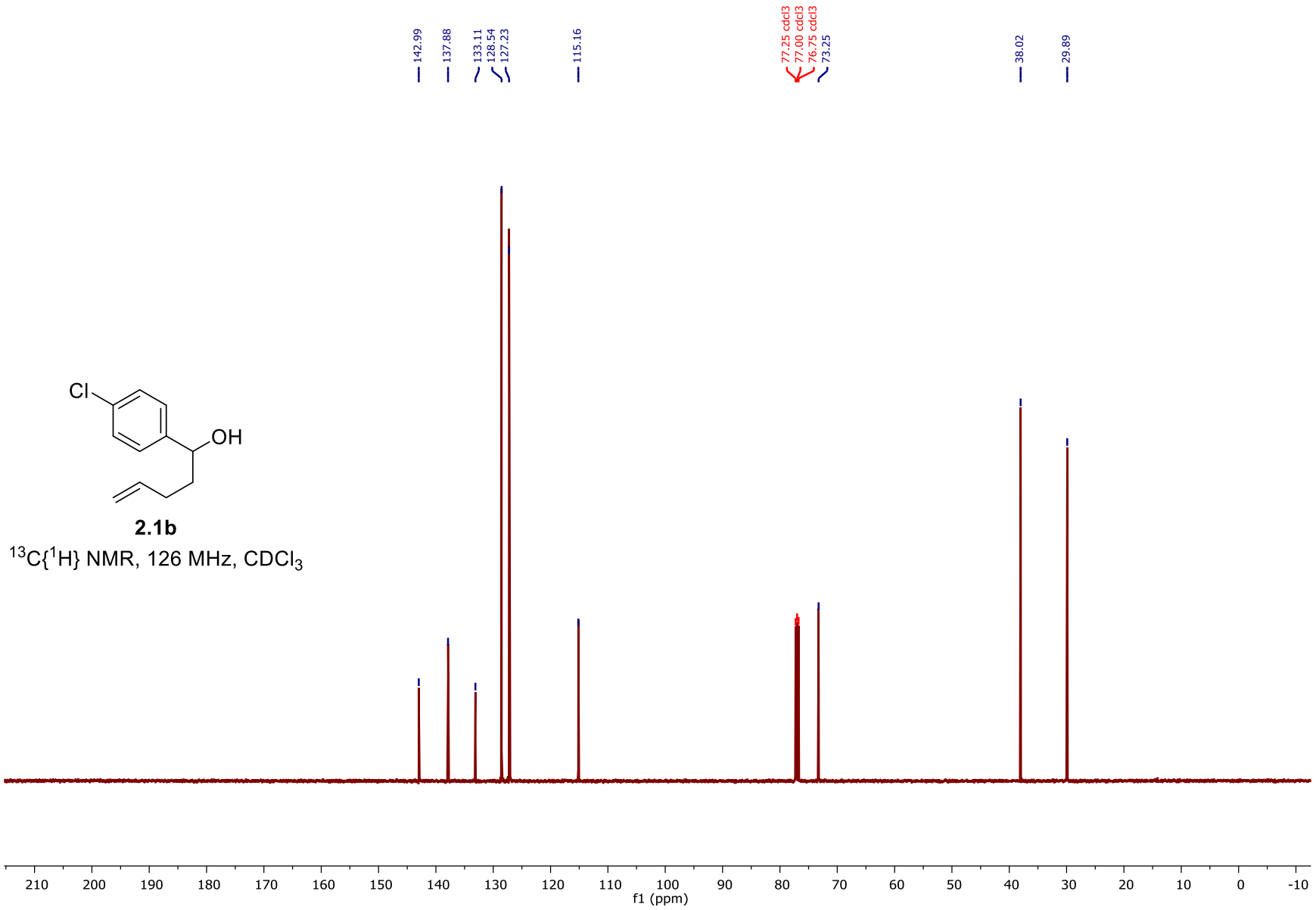
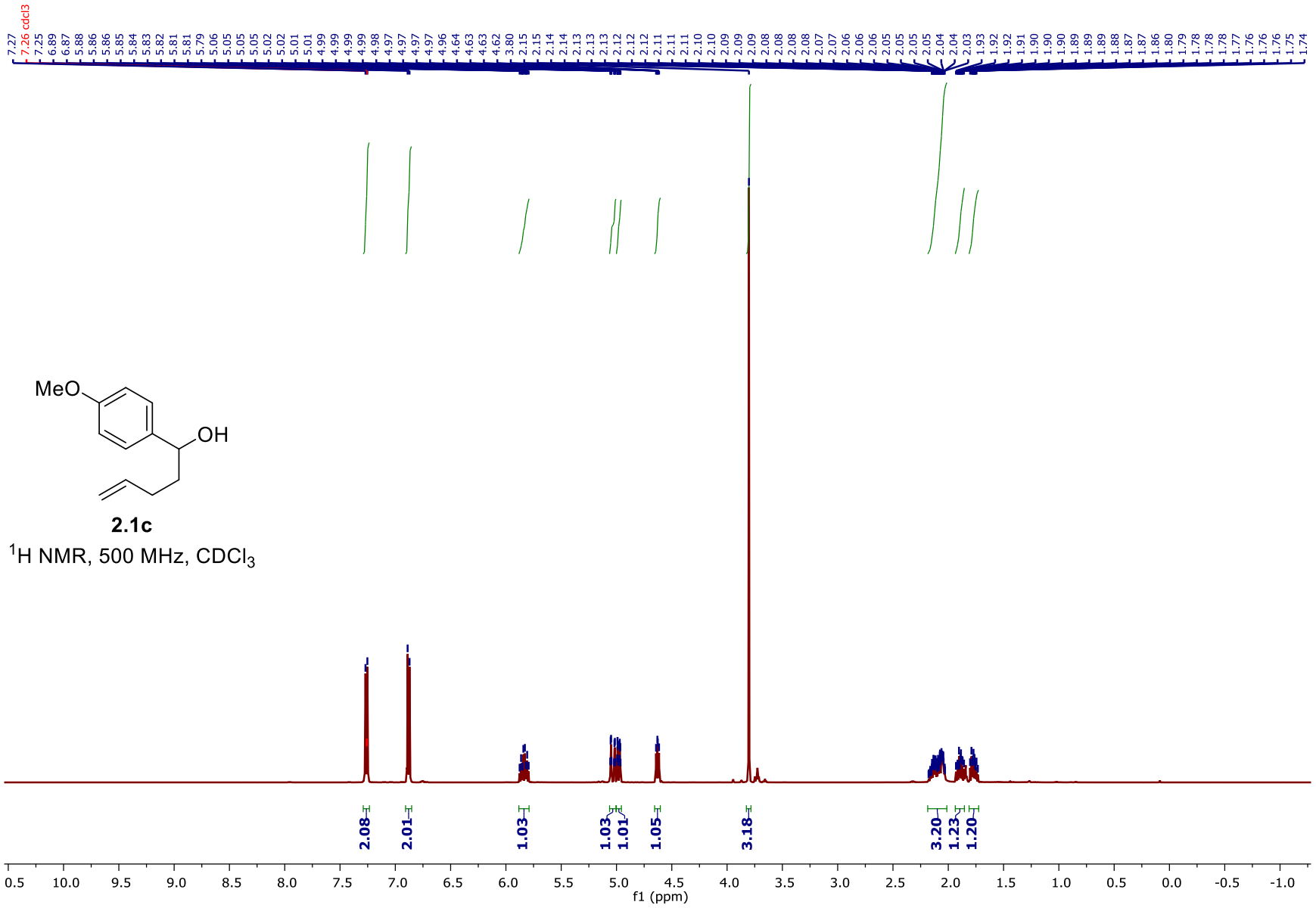
0
f1 (ppm)

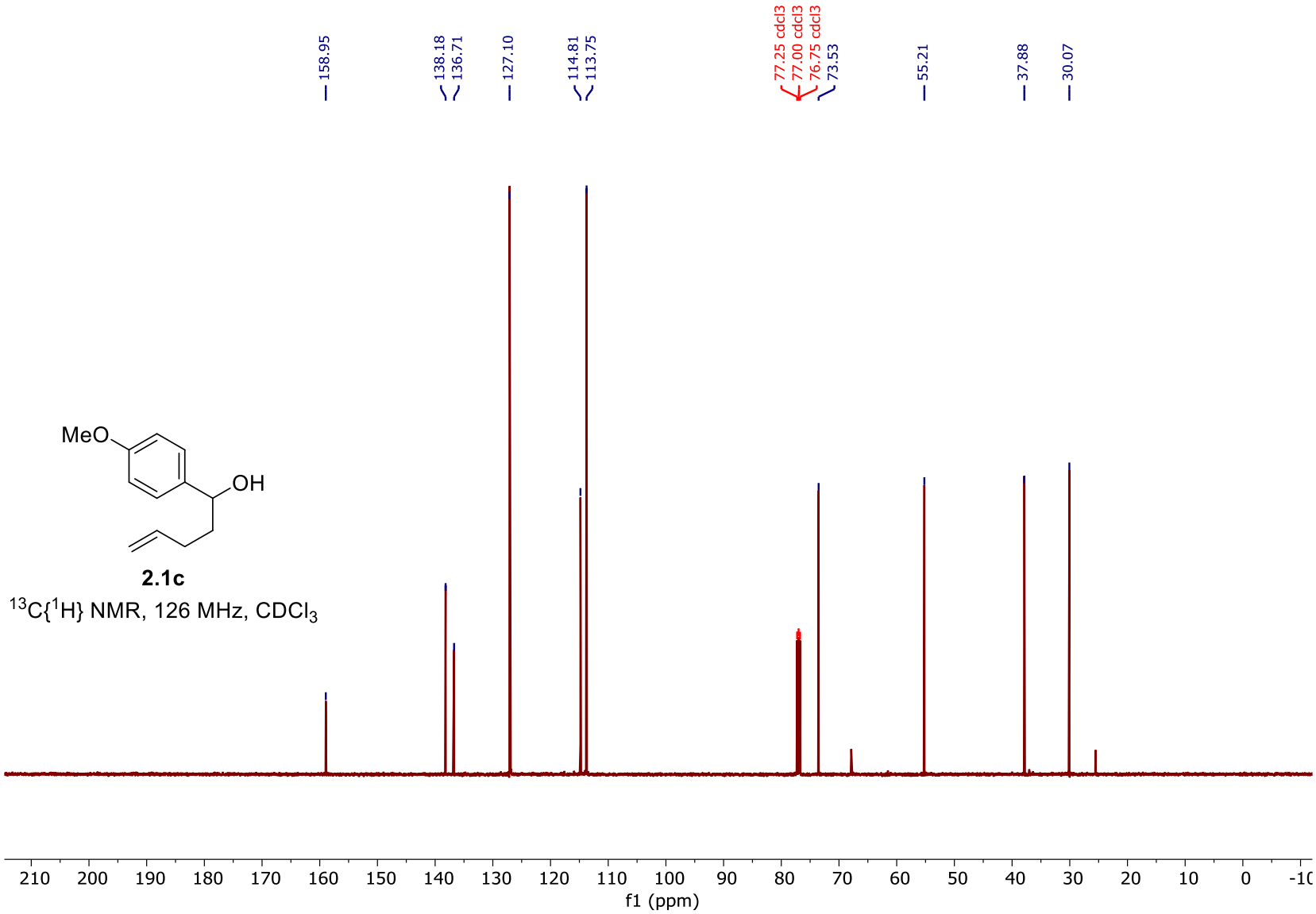

Cl
OH
2.1b
1H NMR, 500 MHz, CDCl3
7.26 cdcl3
2.00
2.16
1.05
1.06
1.04
1.11
3.40
1.23
1.22
f1 (ppm)

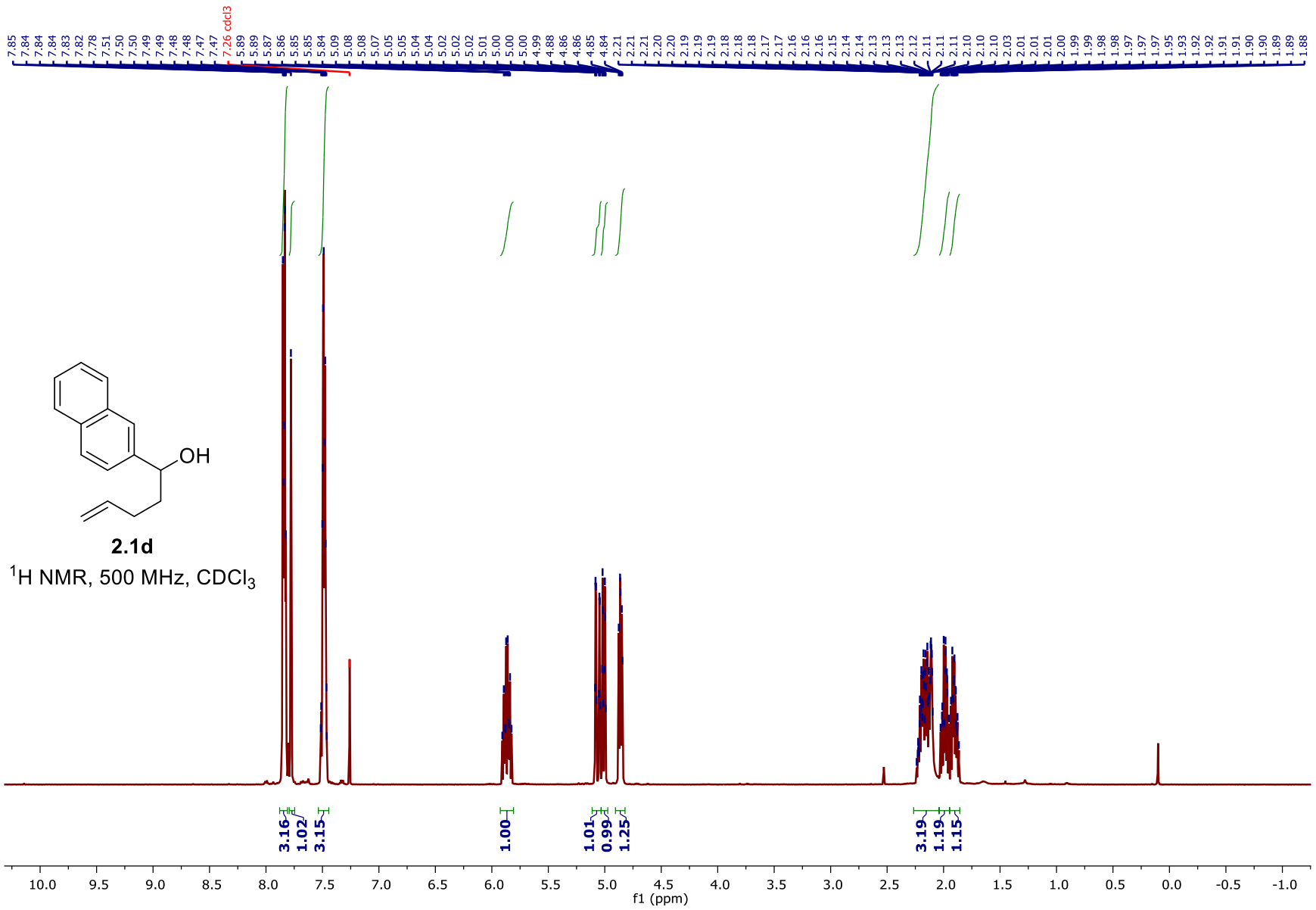

142.99
137.88
133.11
128.54
127.23
115.16
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
73.25
38.02
29.89
Cl
OH
2.1b
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

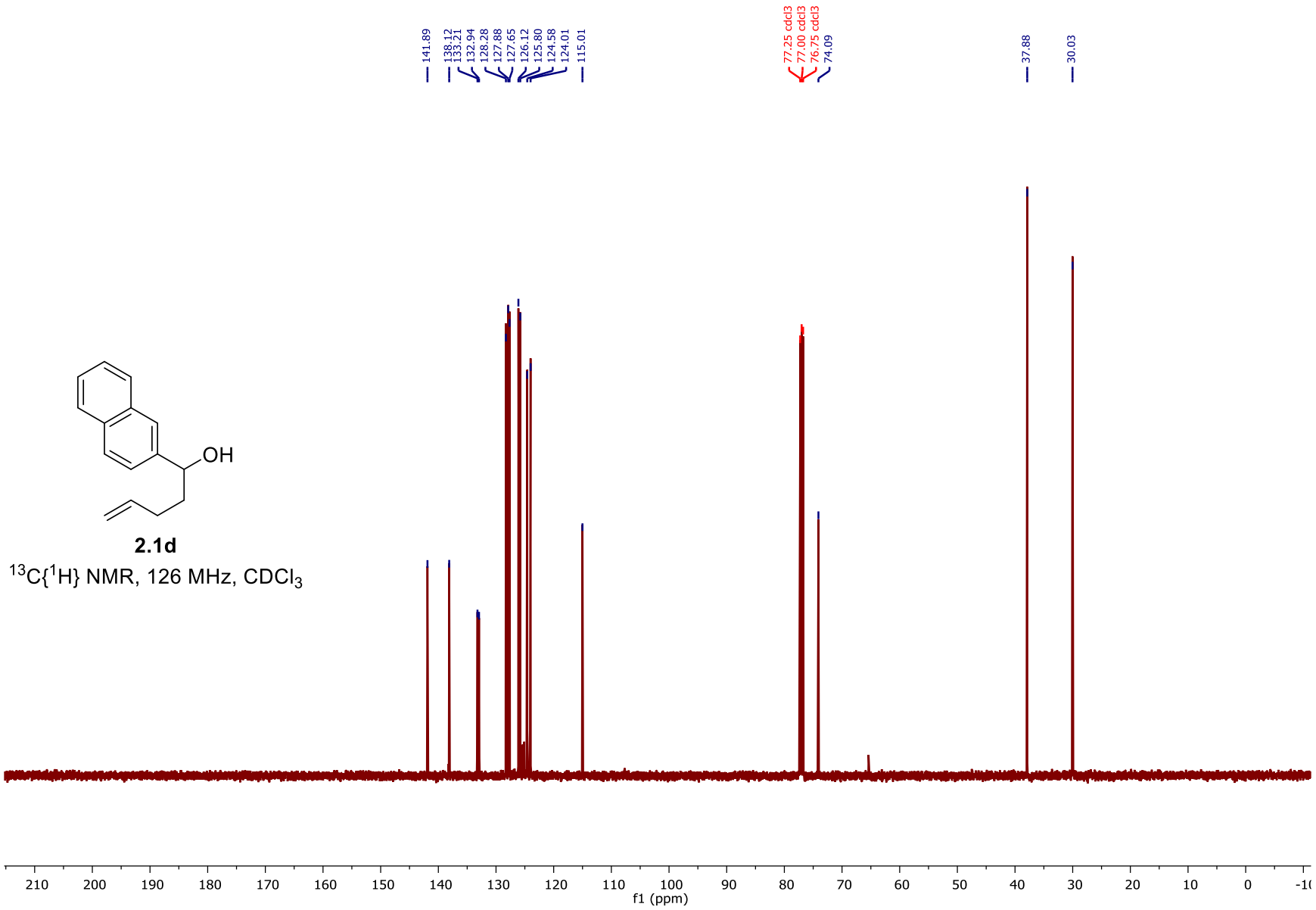


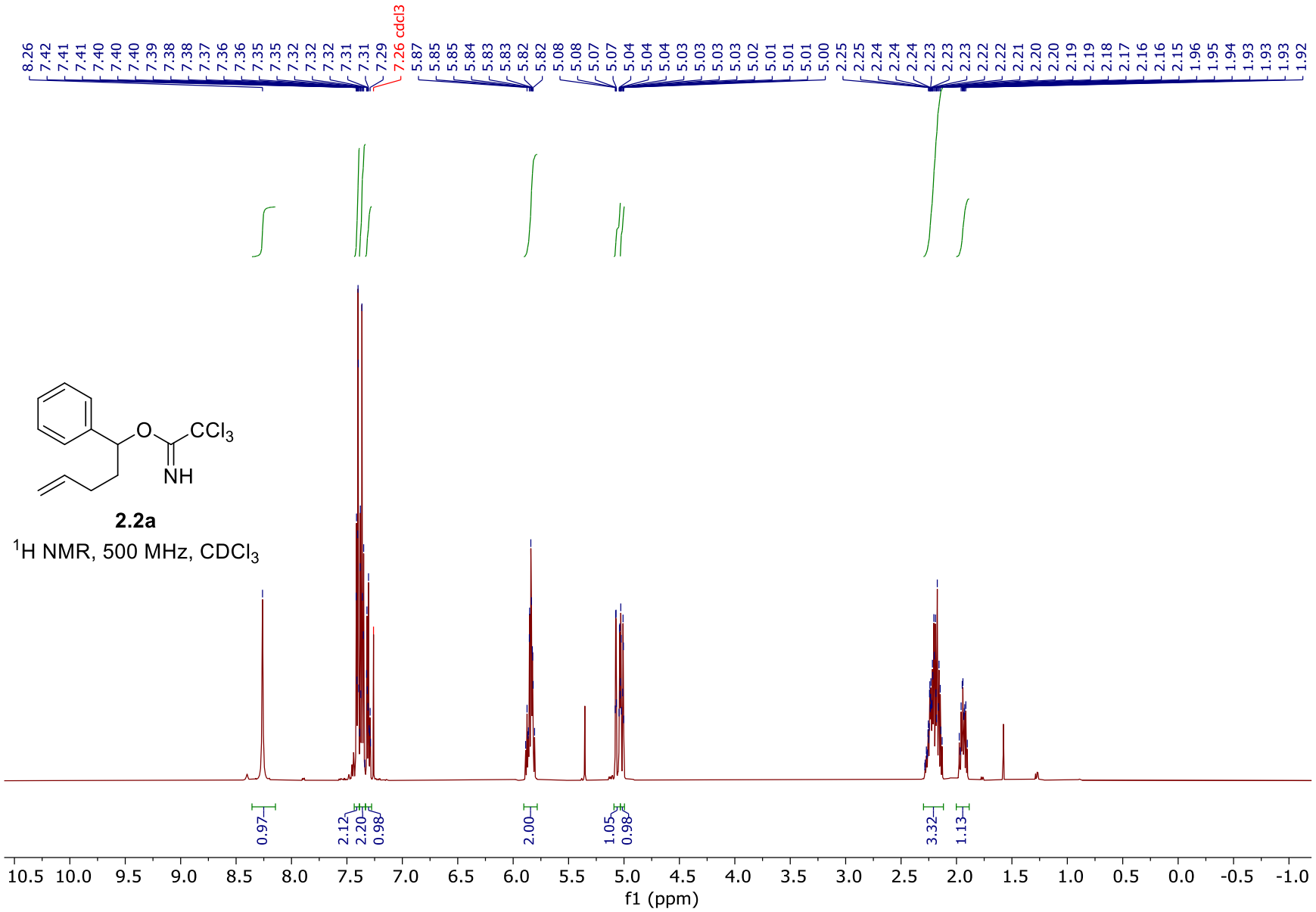
2.1c

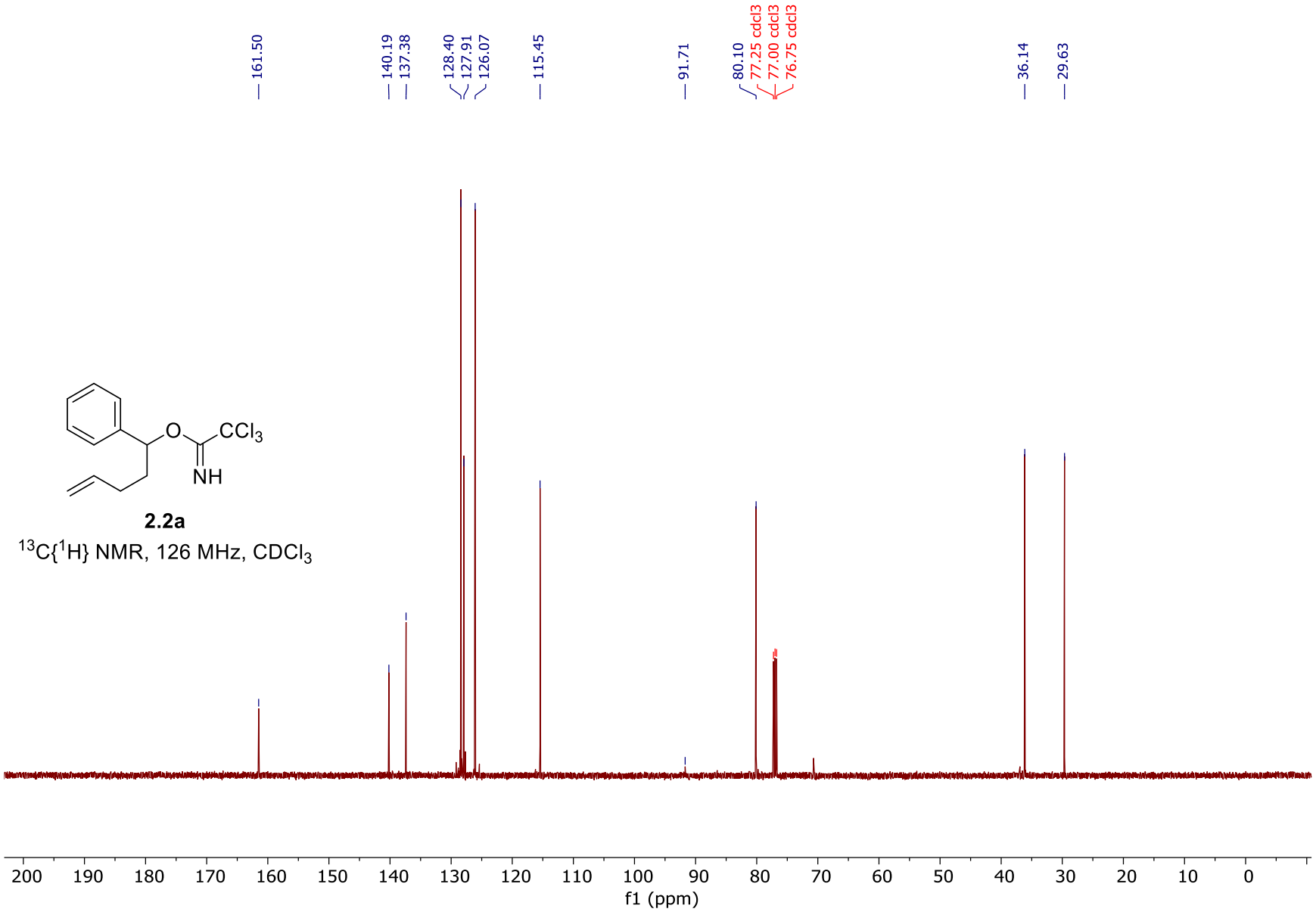
^{1}H NMR, 500 MHz, $CDCl_3$

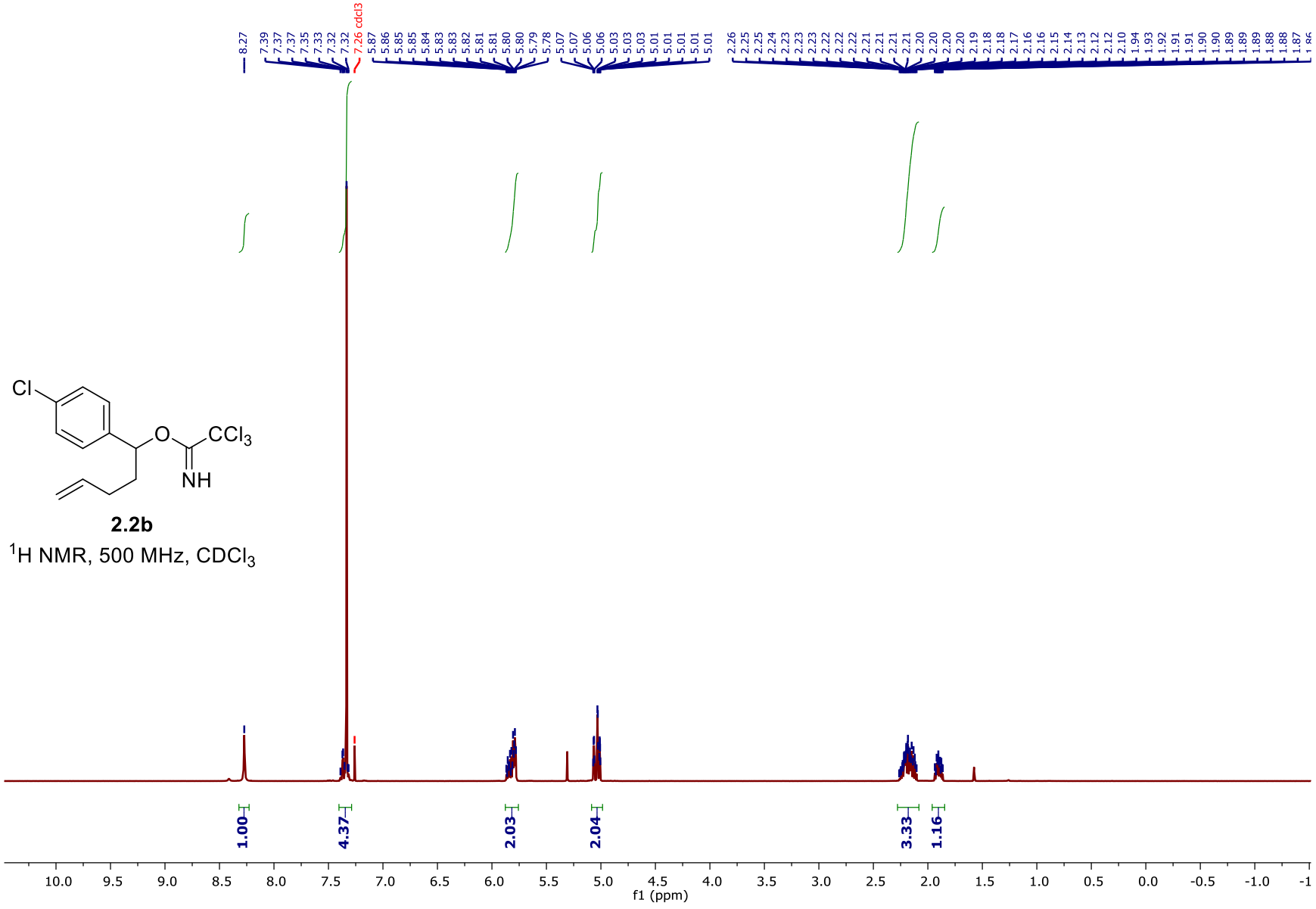

158.95
138.18
136.71
127.10
114.81
113.75
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
73.53
55.21
37.88
30.07
MeO
OH
2.1c
13C{1H} NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

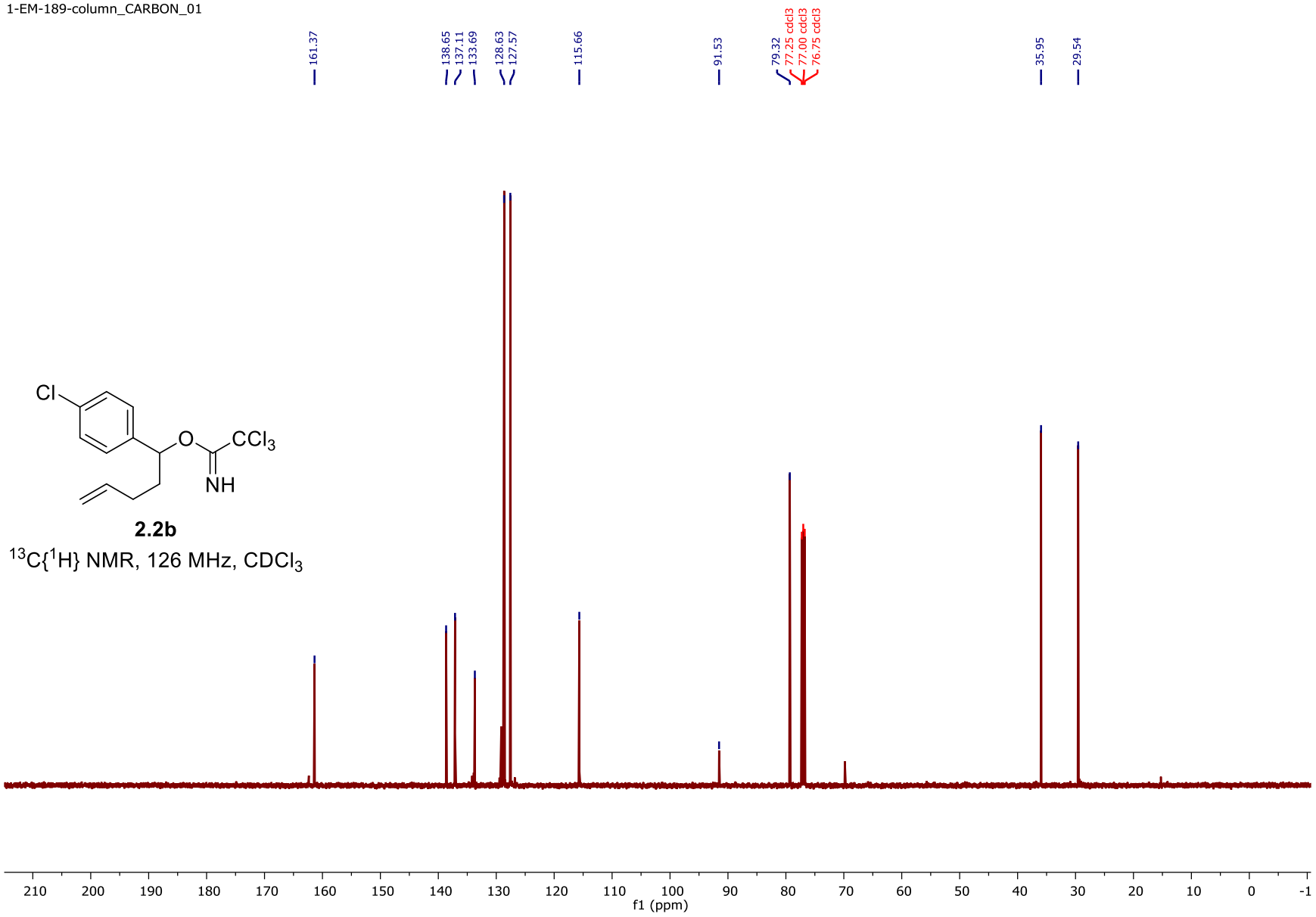

OH
2.1d
^{1}H NMR, 500 MHz, $CDCl_3$
7.26 cdcl3
3.16
1.02
3.15
1.00
1.01
0.99
1.25
3.19
1.19
1.15
f1 (ppm)

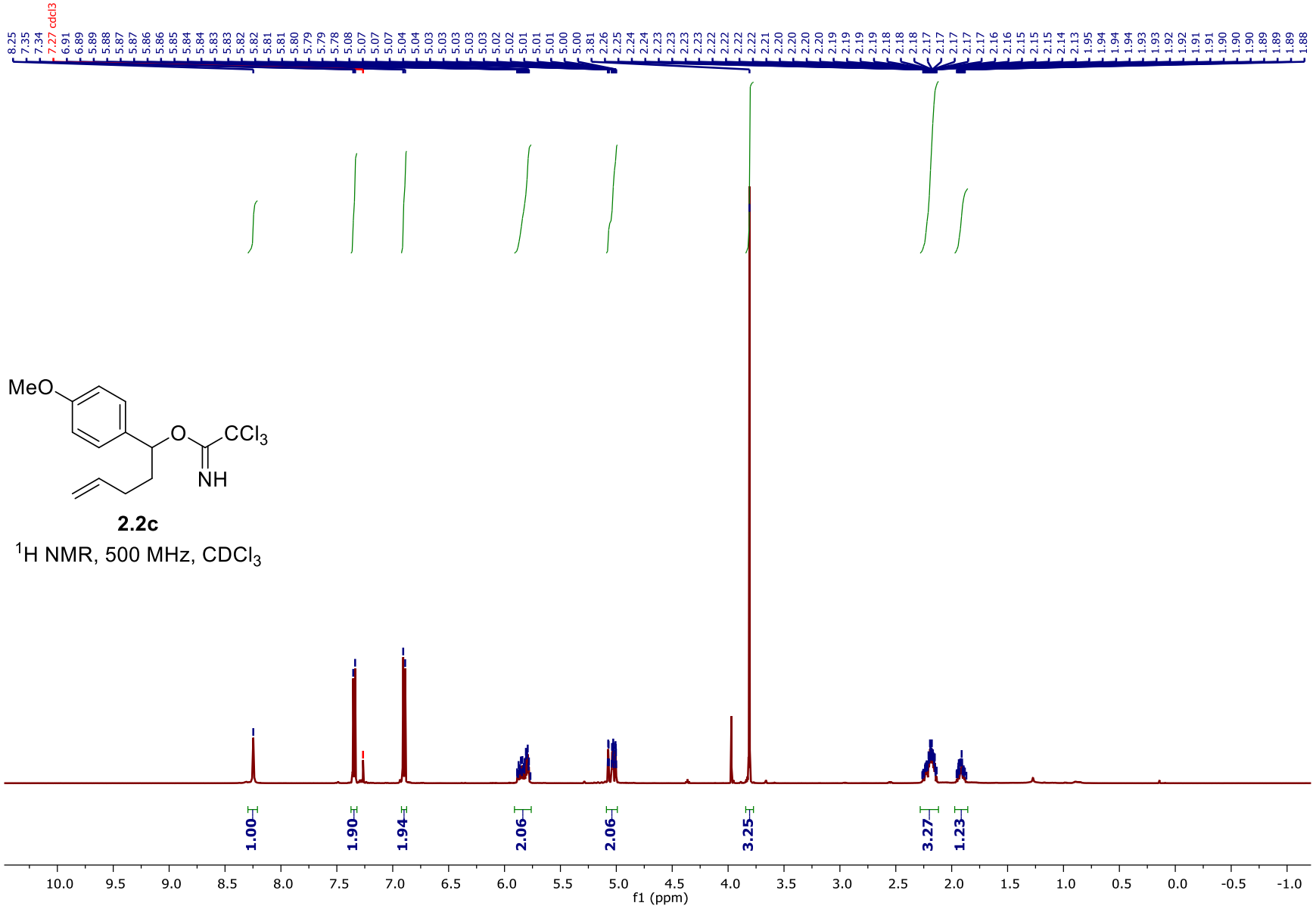

141.89
138.12
133.21
132.94
128.28
127.88
127.65
126.12
125.80
124.58
124.01
115.01
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
74.09
37.88
30.03
OH
2.1d
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1(
f1 (ppm)

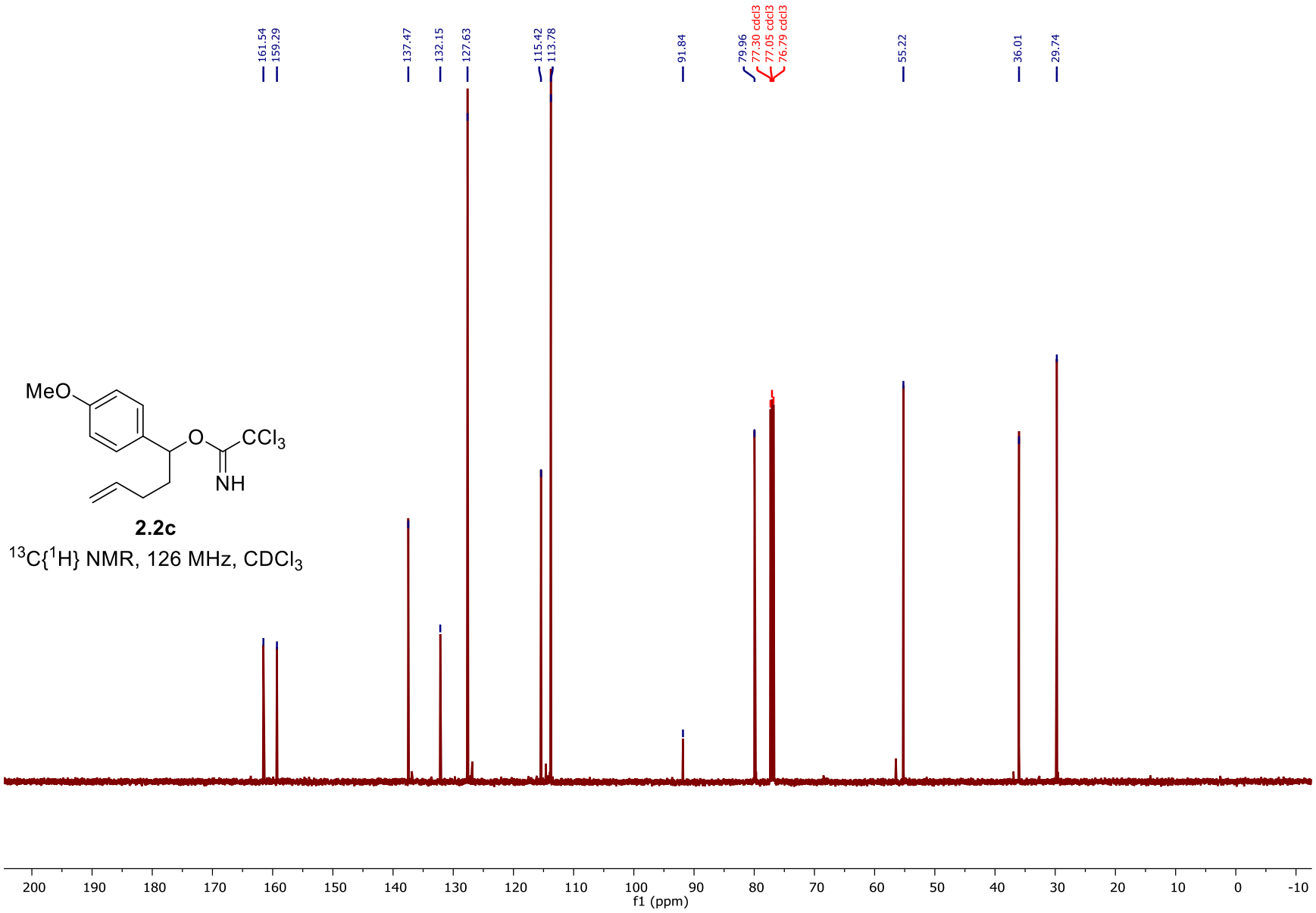

8.26 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.32 7.32 7.32 7.31 7.31 7.29 7.26 cdcl3
5.87 5.85 5.85 5.84 5.83 5.83 5.82 5.82 5.08 5.08 5.07 5.07 5.04 5.04 5.04 5.03 5.03 5.03 5.03 5.02 5.01 5.01 5.01 5.00
2.25 2.24 2.24 2.24 2.23 2.23 2.23 2.22 2.22 2.21 2.20 2.20 2.19 2.18 2.17 2.16 2.16 2.15 1.96 1.95 1.94 1.93 1.93 1.93 1.92
O
CCl3
NH
2.2a
1H NMR, 500 MHz, CDCl3
0.97 2.12 2.20 0.98 2.00 1.05 0.98 3.32 1.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

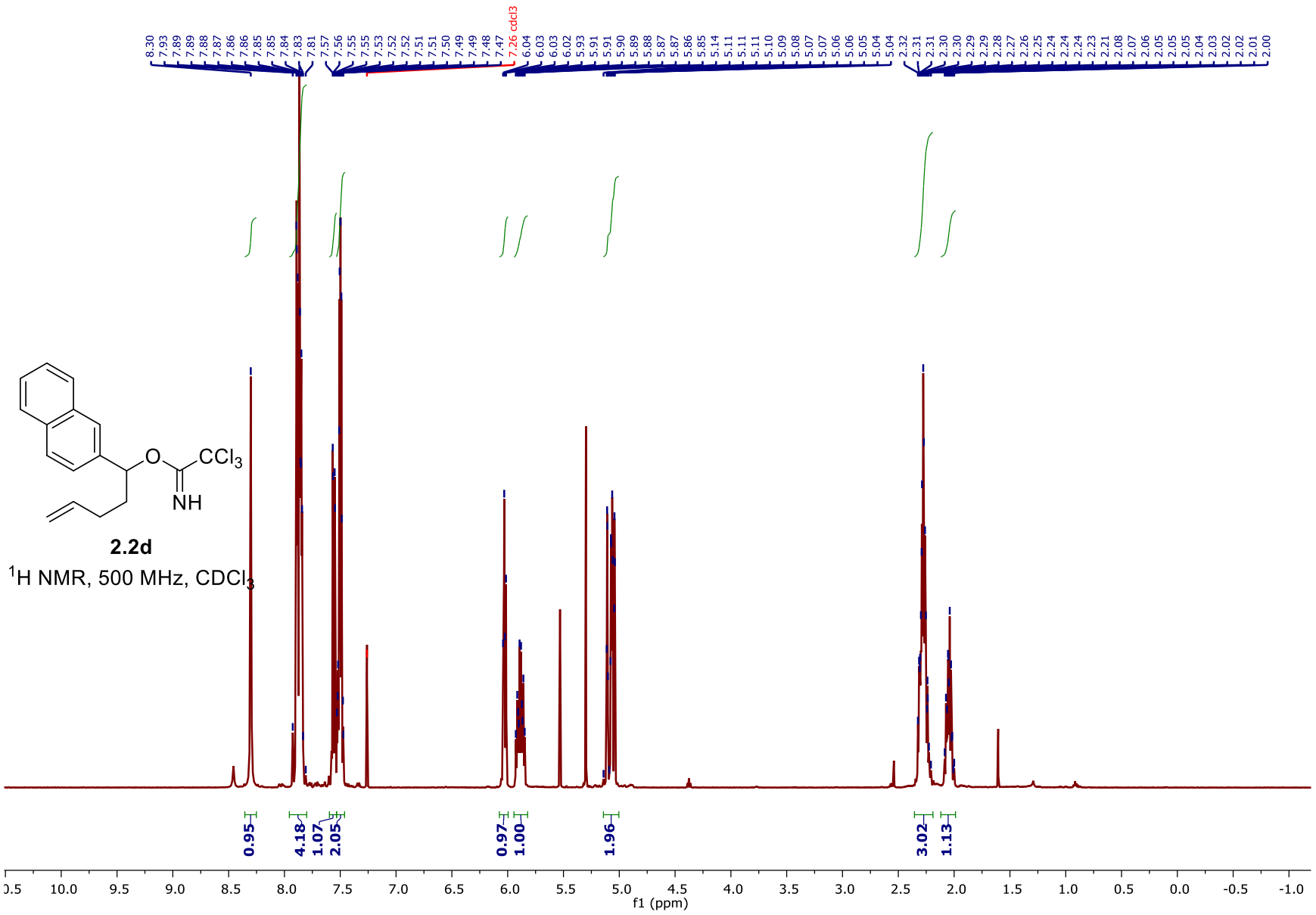

161.50
140.19
137.38
128.40
127.91
126.07
115.45
91.71
80.10
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
36.14
29.63
O
CCl3
NH
2.2a
13C{1H} NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

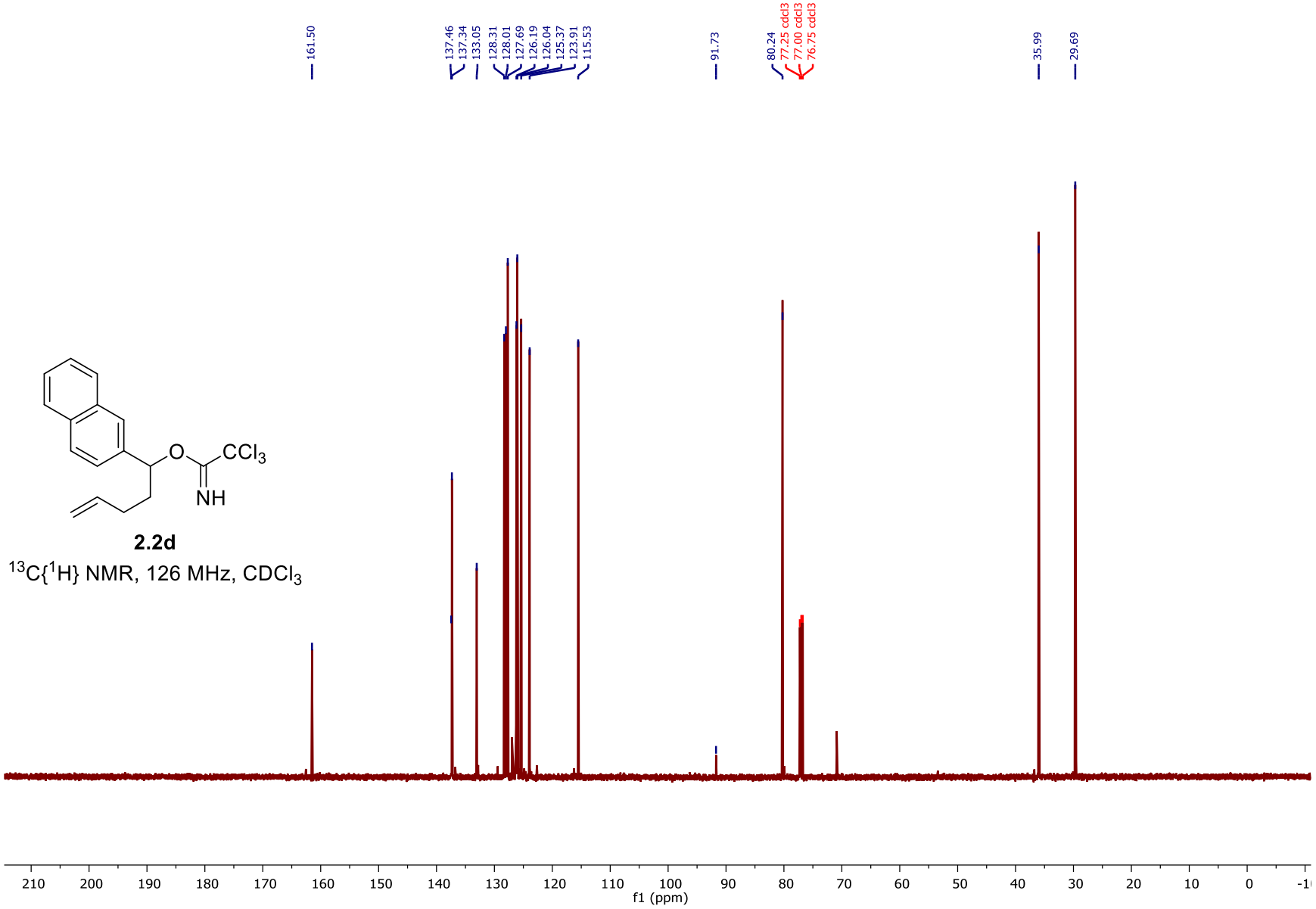

Cl
O
CCl3
NH
2.2b
1H NMR, 500 MHz, CDCl3
f1 (ppm)

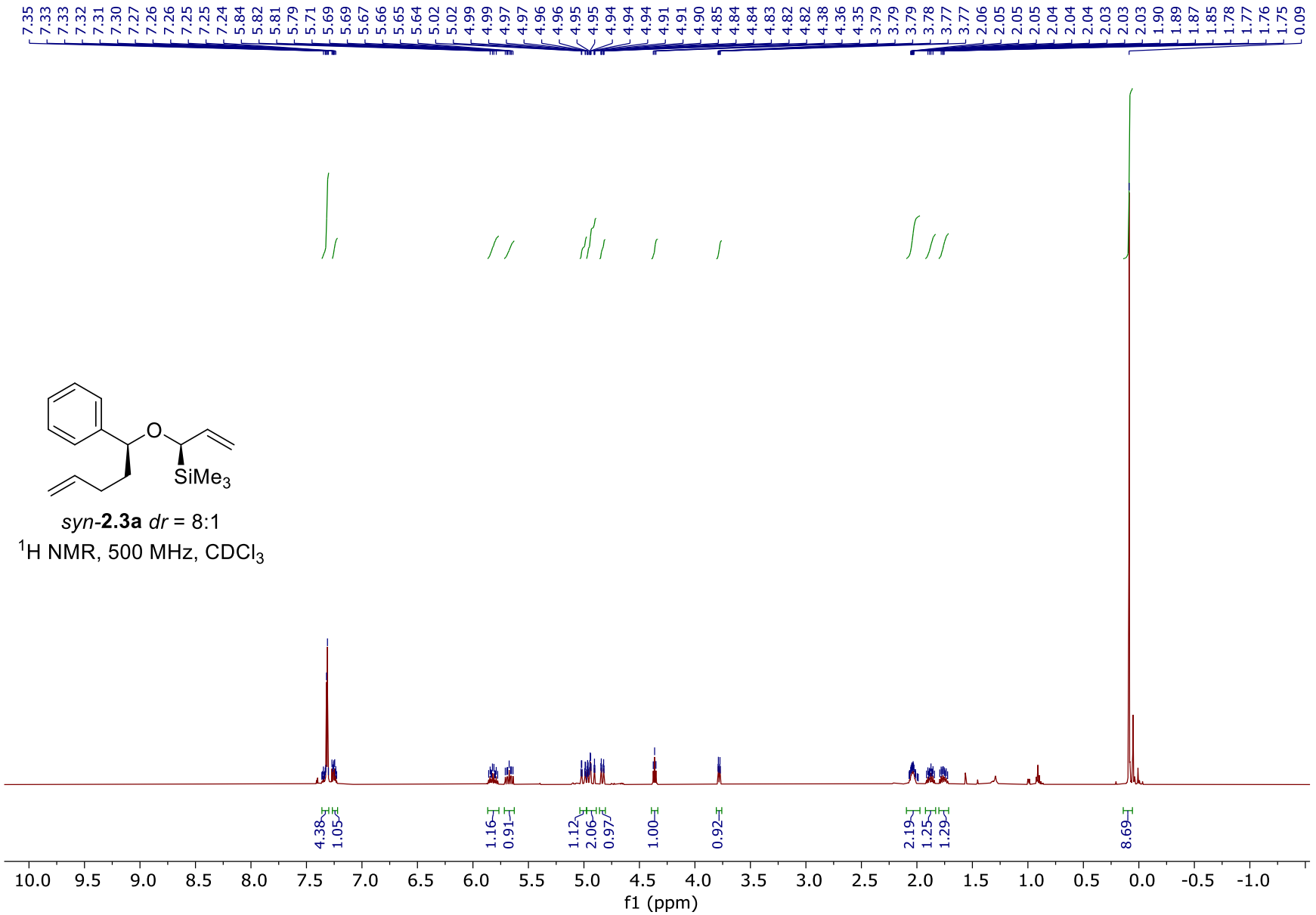

1-EM-189-column_CARBON_01
161.37
138.65
137.11
133.69
128.63
127.57
115.66
91.53
79.32
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
35.95
29.54
Cl
O
CCl3
NH
2.2b
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


MeO
O
CCl3
NH
2.2c
1H NMR, 500 MHz, CDCl3
1.00
1.90
1.94
2.06
2.06
3.25
3.27
1.23
f1 (ppm)


161.54
159.29
137.47
132.15
127.63
115.42
113.78
91.84
79.96
77.30 cdcl3
77.05 cdcl3
76.79 cdcl3
55.22
36.01
29.74
MeO
O
CCl3
NH
2.2c
13C{1H} NMR, 126 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

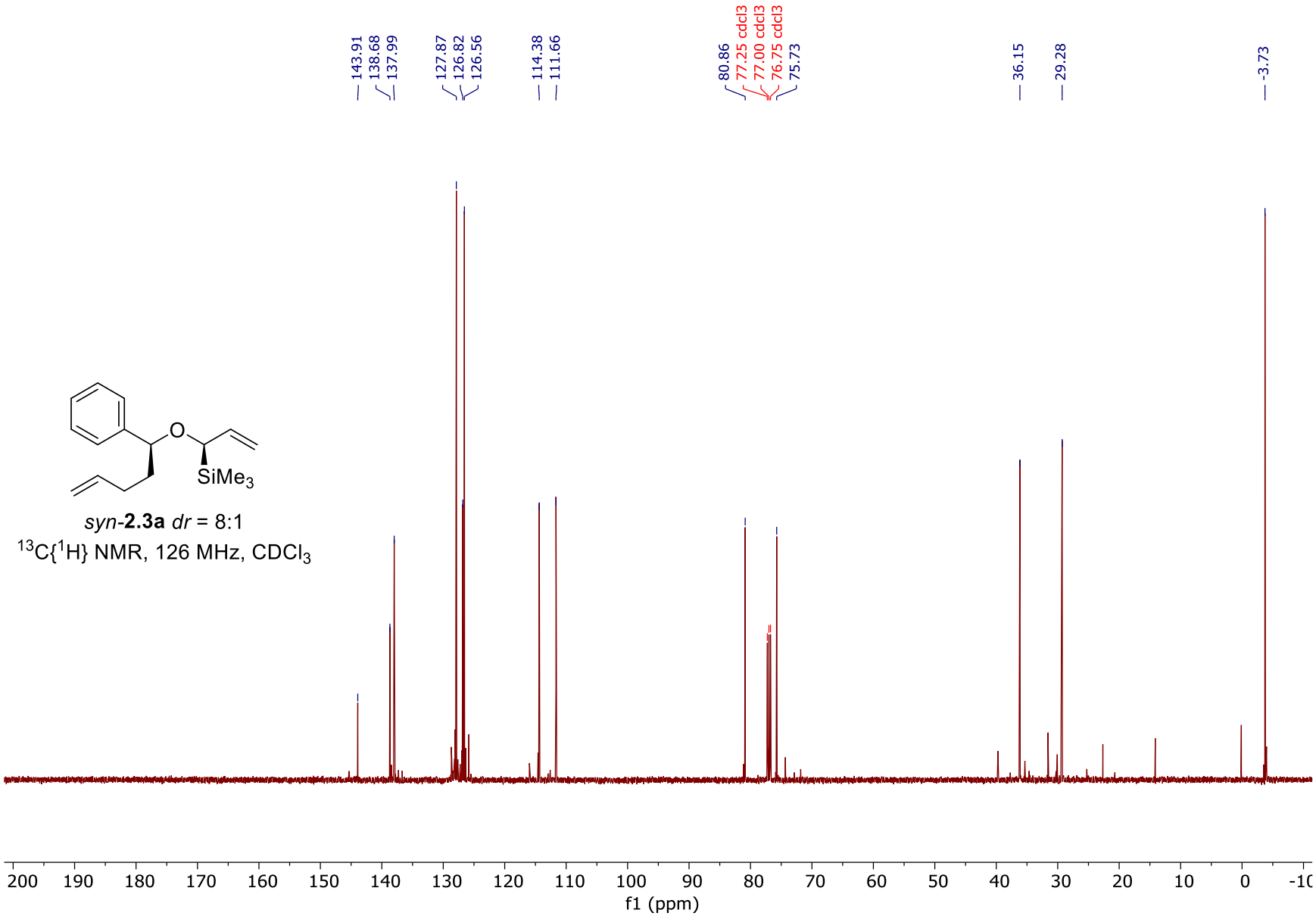

7.26 cdcl3
O
CCl3
NH
2.2d
1H NMR, 500 MHz, CDCl3
0.95
4.18
1.07
2.05
0.97
1.00
1.96
3.02
1.13
f1 (ppm)

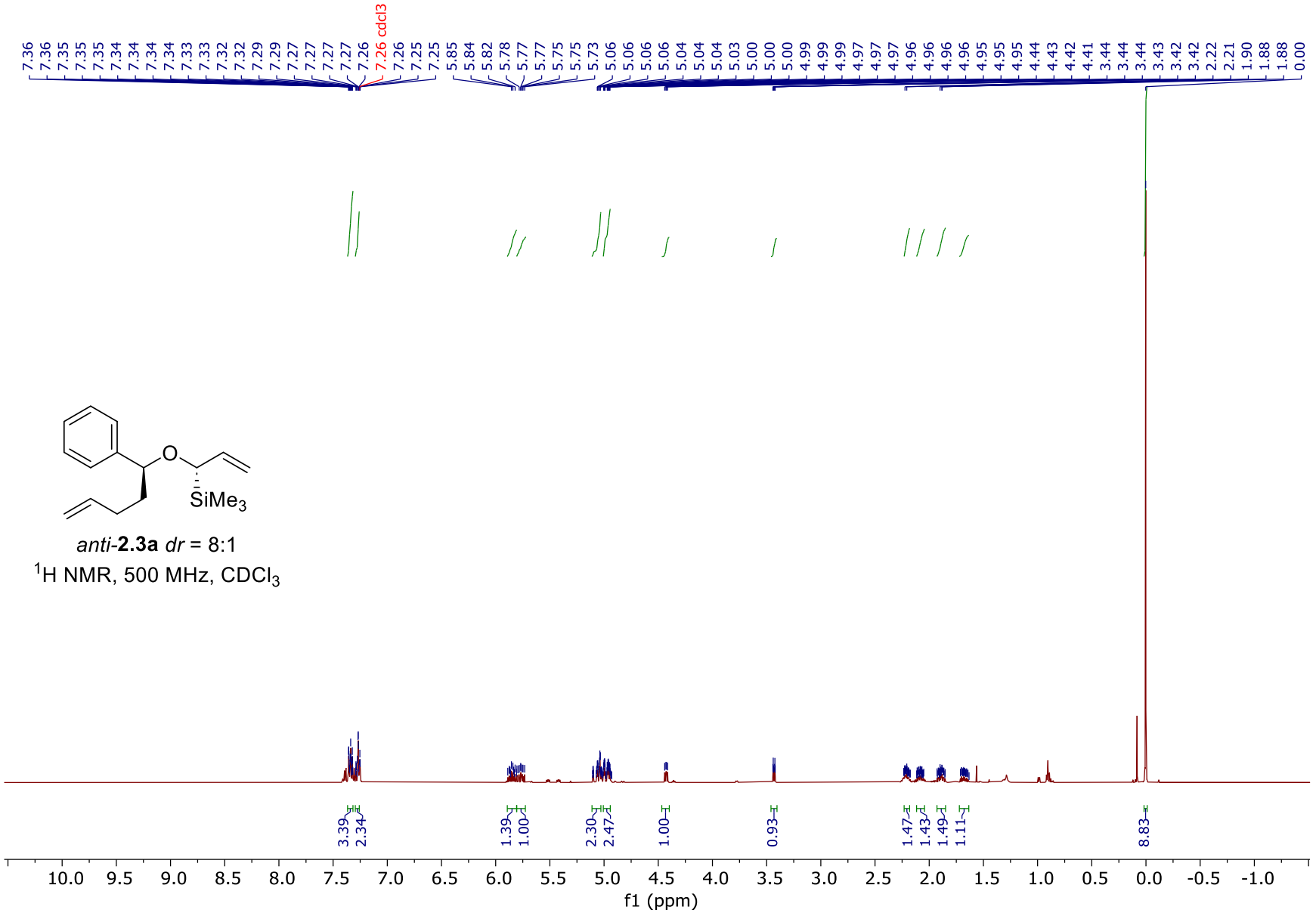

161.50
137.46
137.34
133.05
128.31
128.01
127.69
126.19
126.04
125.37
123.91
115.53
91.73
80.24
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
35.99
29.69
O
CCl3
NH
2.2d
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



syn-**2.3a** *dr* = 8:1

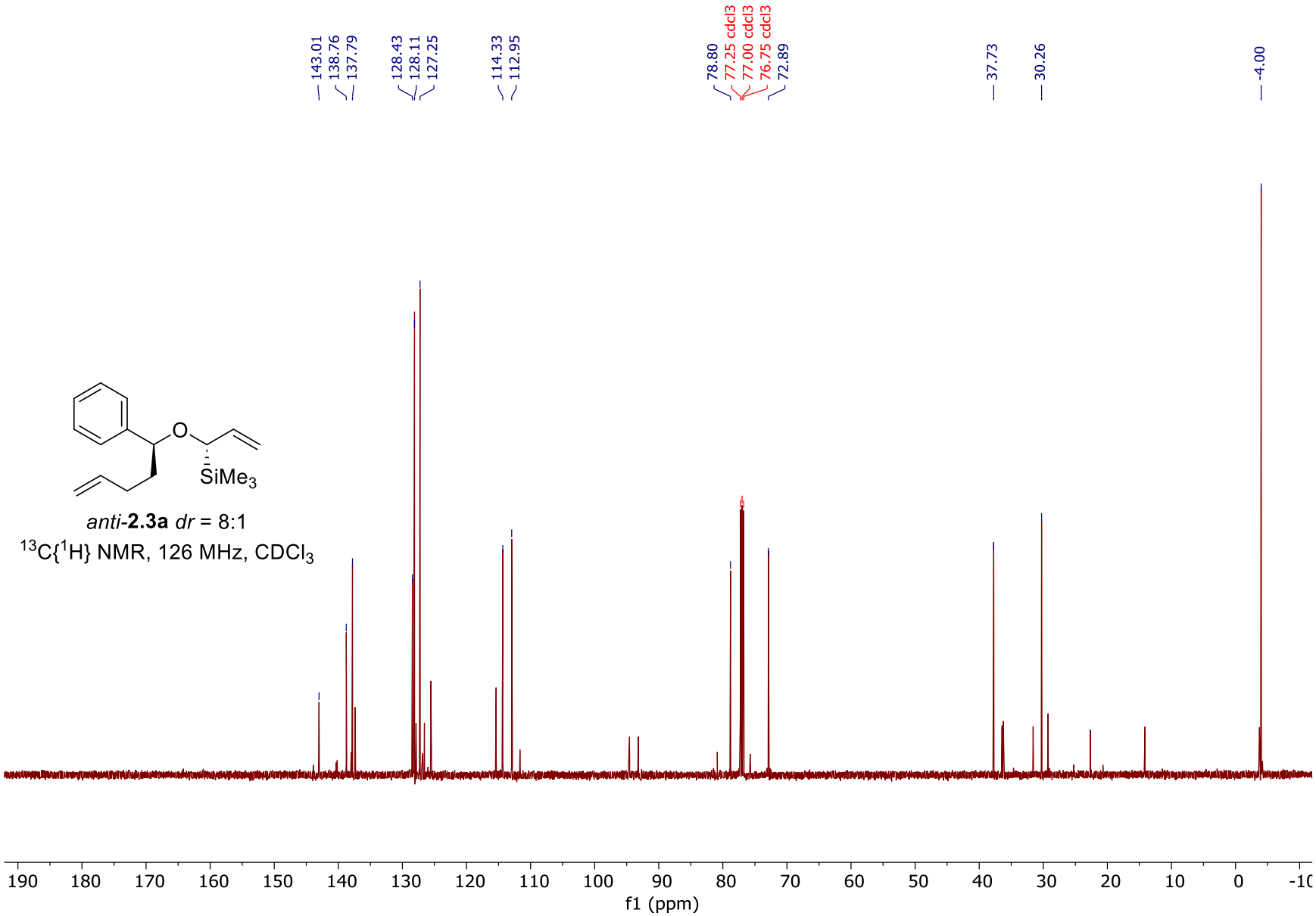
^{1}H NMR, 500 MHz, $CDCl_3$

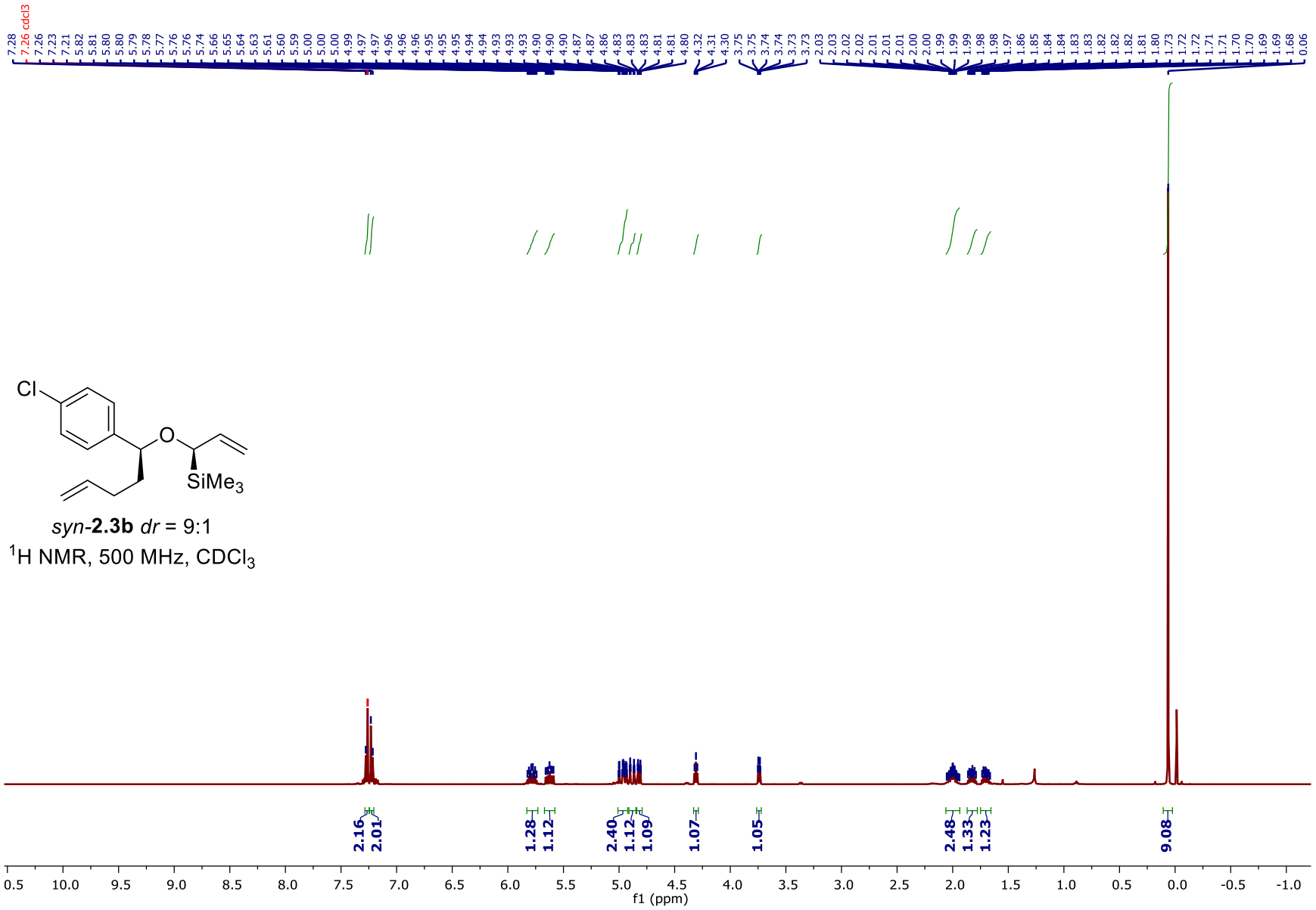

143.91
138.68
137.99
127.87
126.82
126.56
114.38
111.66
80.86
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
75.73
36.15
29.28
-3.73
O
SiMe3
syn-2.3a dr = 8:1
13C{1H} NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

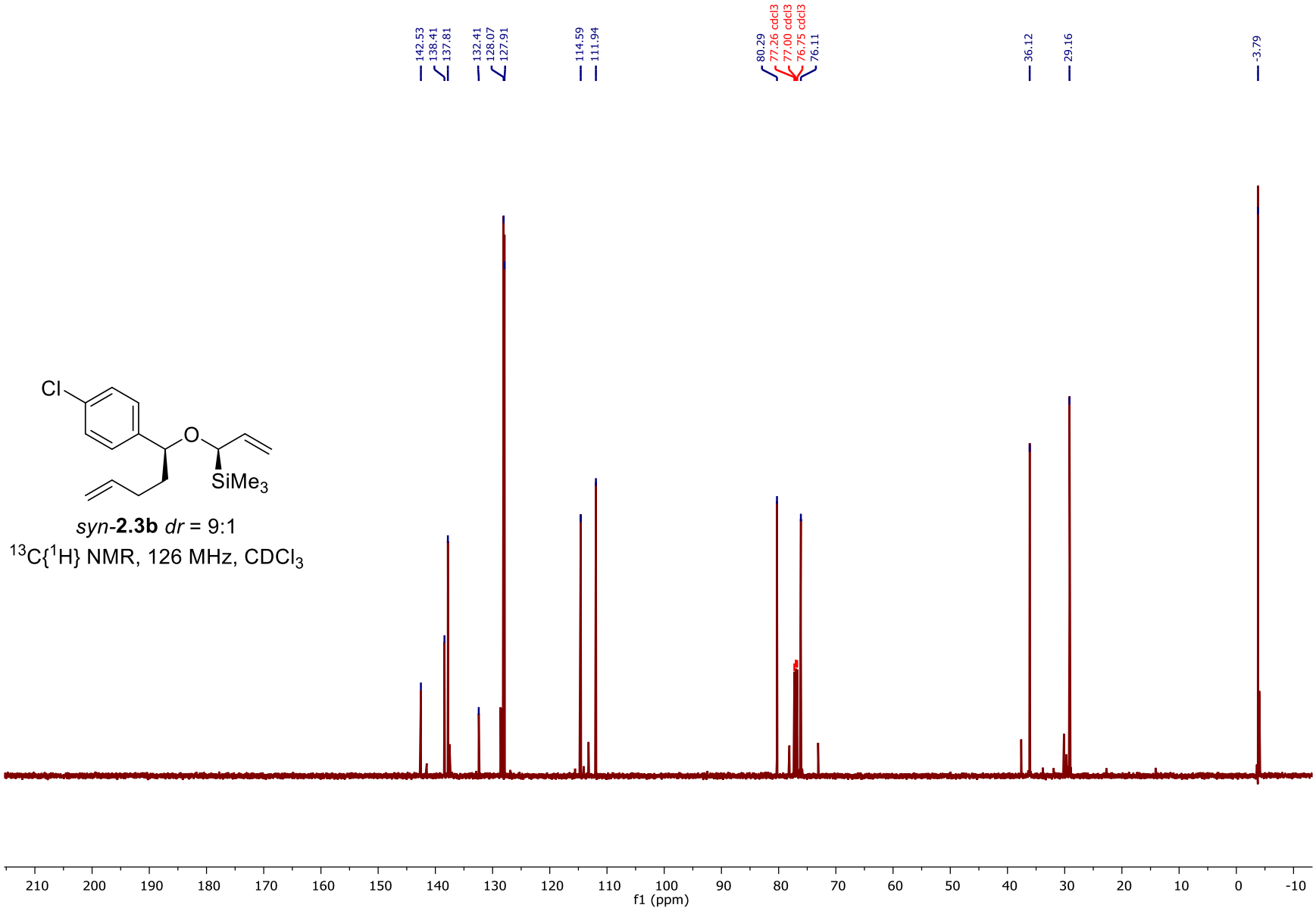


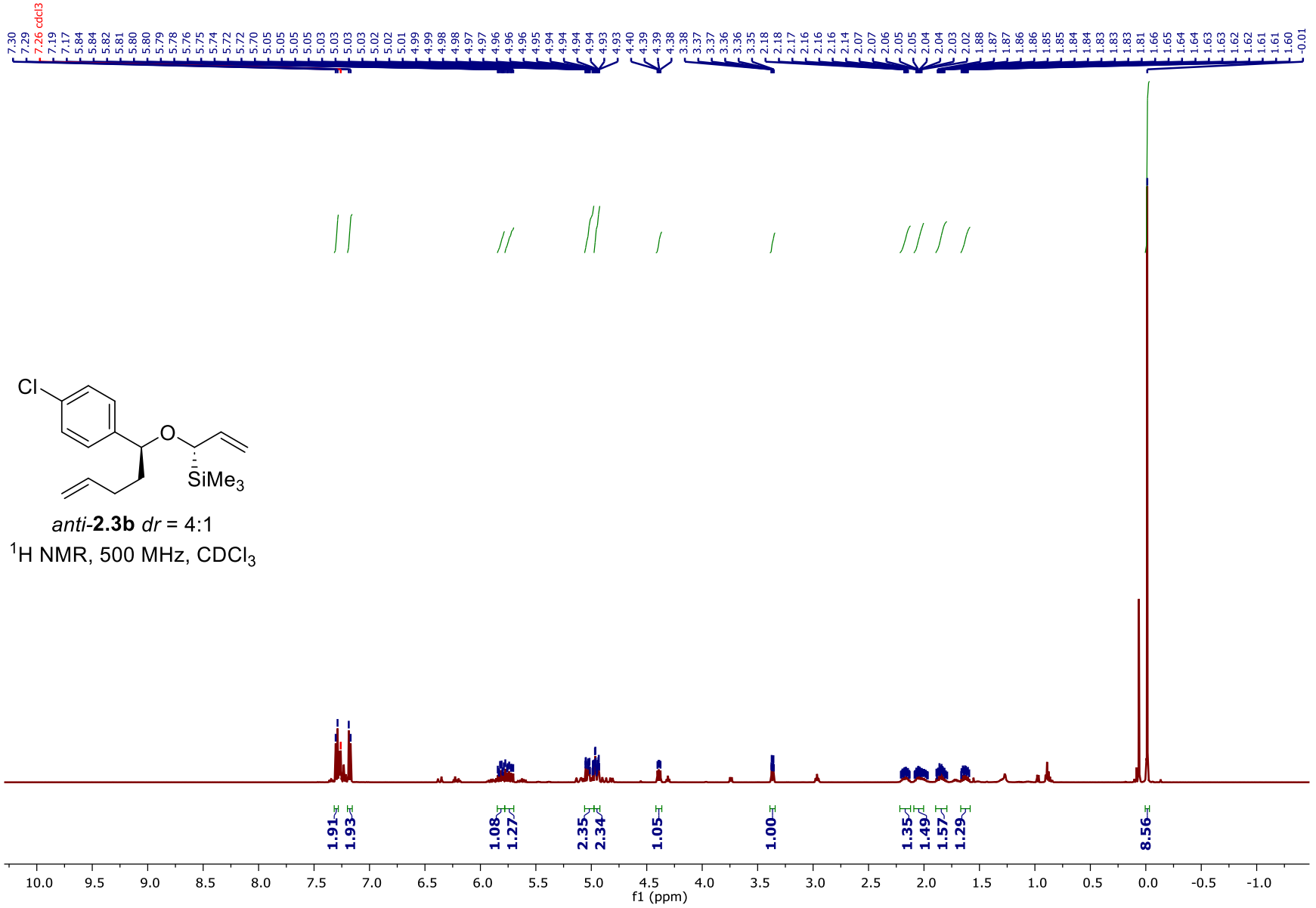
anti-**2.3a** *dr* = 8:1

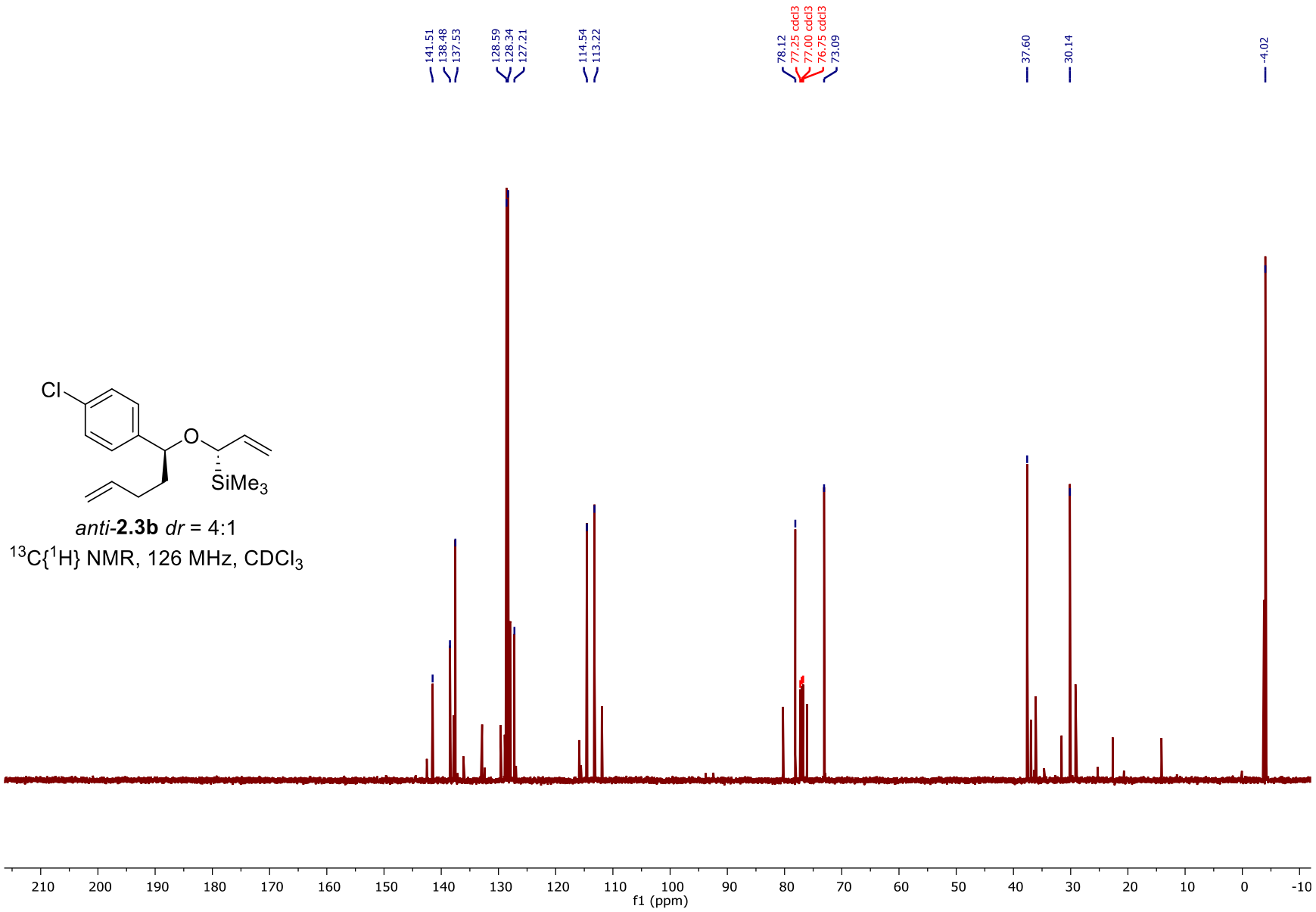
^{1}H NMR, 500 MHz, $CDCl_3$

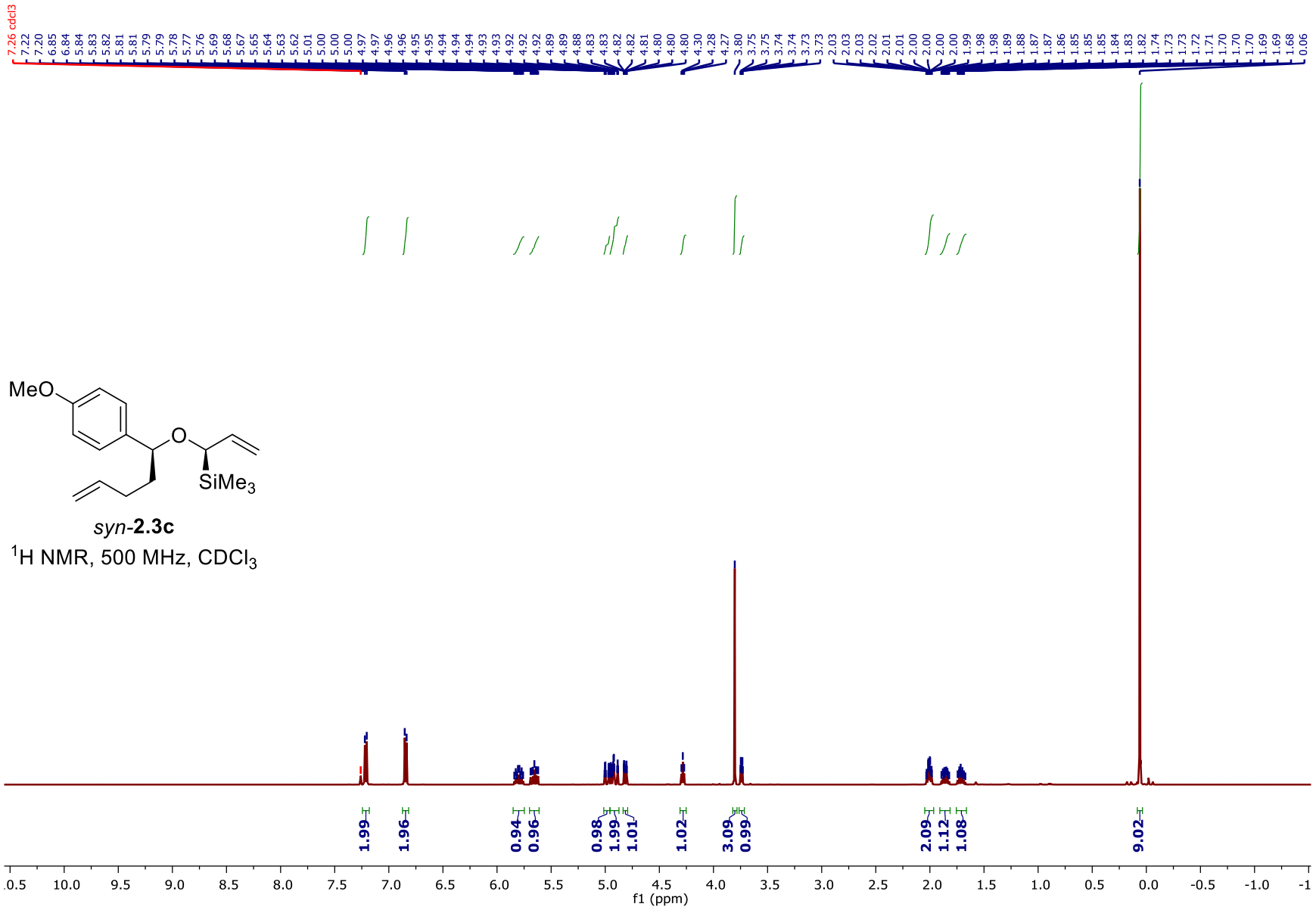

143.01
138.76
137.79
128.43
128.11
127.25
114.33
112.95
78.80
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
72.89
37.73
30.26
-4.00
O
SiMe3
anti-2.3a dr = 8:1
13C{1H} NMR, 126 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

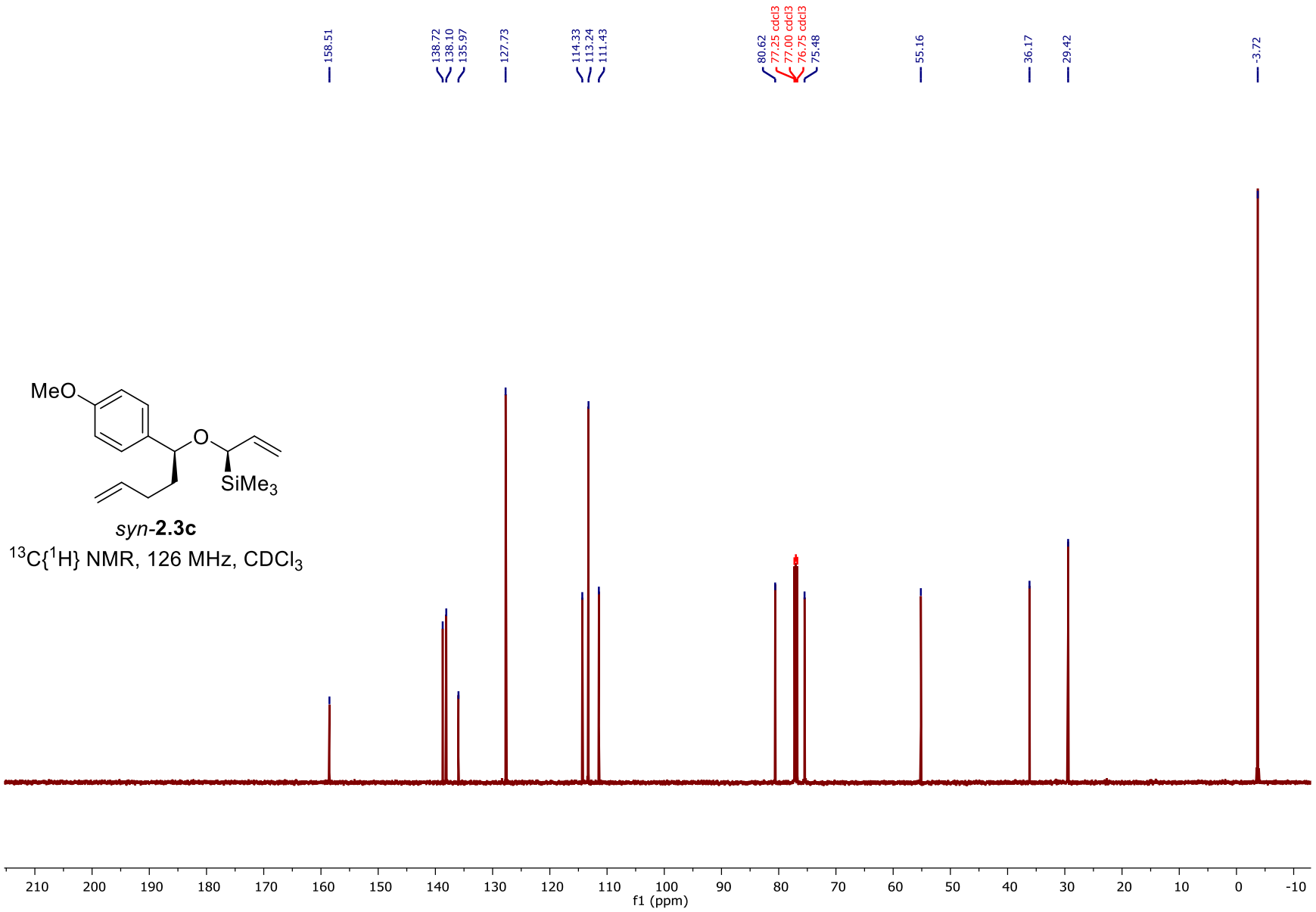

Cl
O
SiMe3
syn-2.3b dr = 9:1
1H NMR, 500 MHz, CDCl3
f1 (ppm)

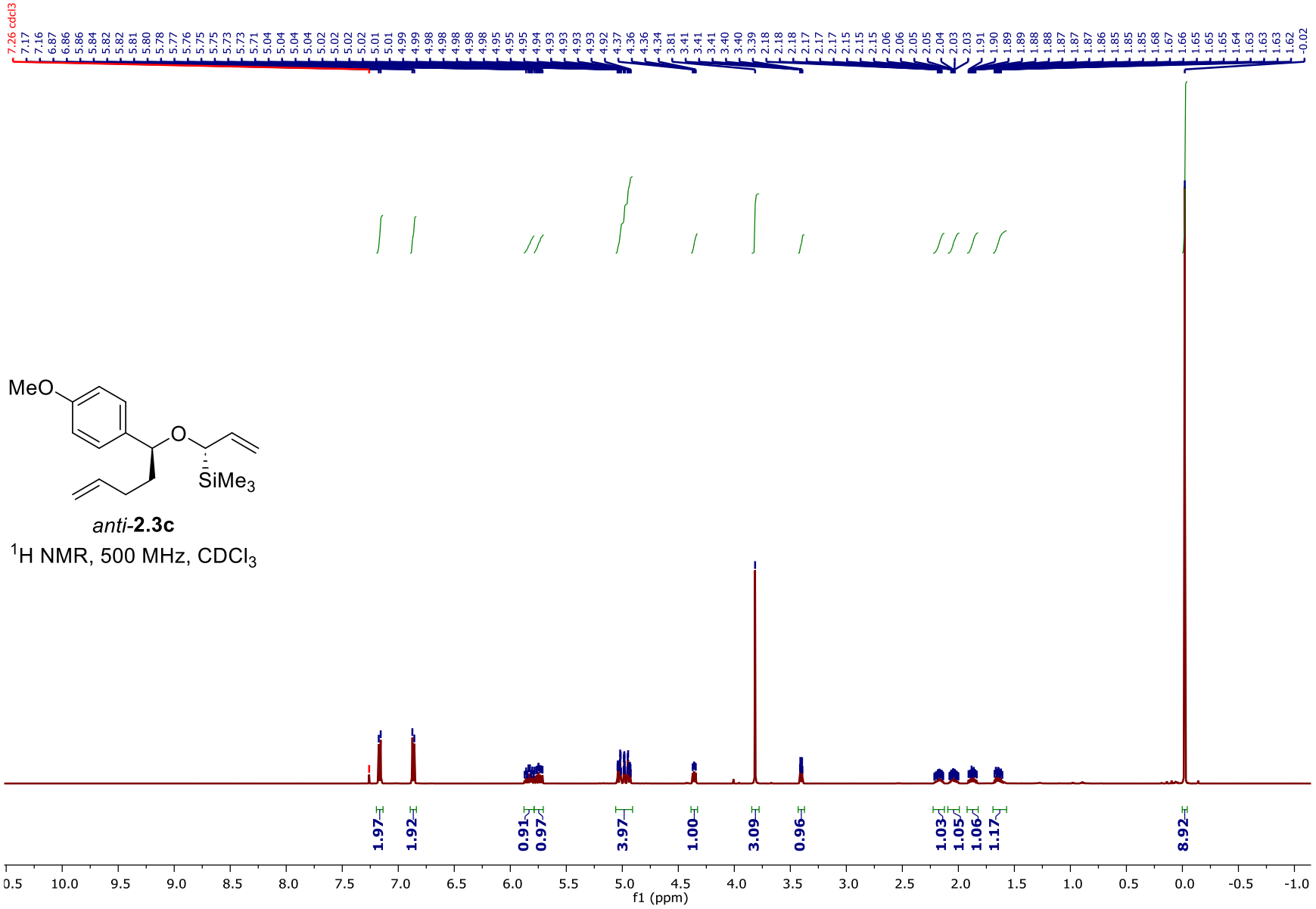

142.53
138.41
137.81
132.41
128.07
127.91
114.59
111.94
80.29
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
76.11
36.12
29.16
-3.79
Cl
O
SiMe3
syn-2.3b dr = 9:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

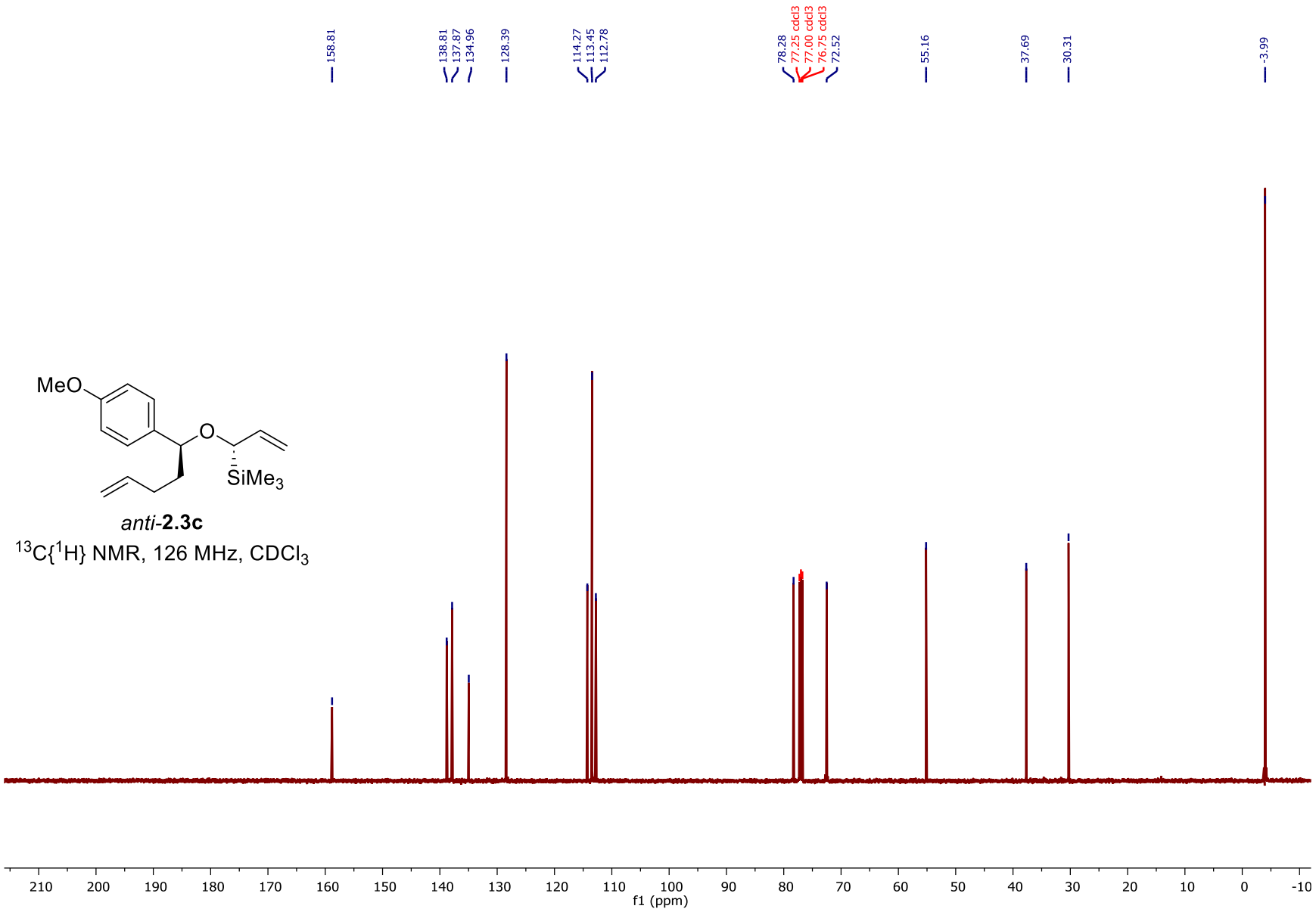

Cl
O
SiMe3
anti-2.3b dr = 4:1
1H NMR, 500 MHz, CDCl3
f1 (ppm)

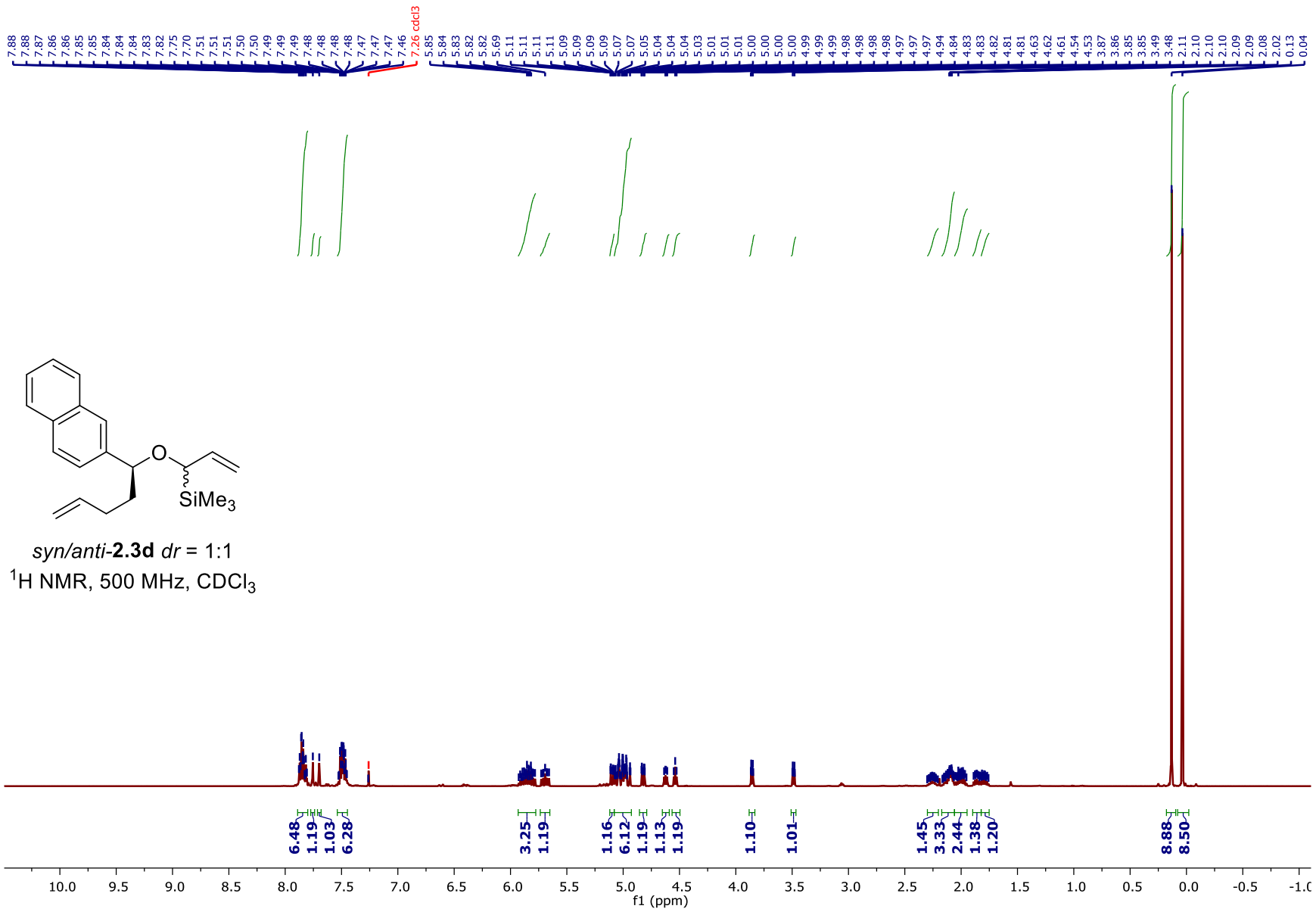

141.51
138.48
137.53
128.59
128.34
127.21
114.54
113.22
78.12
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
73.09
37.60
30.14
-4.02
Cl
O
SiMe3
anti-2.3b dr = 4:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
O
SiMe3
syn-2.3c
1H NMR, 500 MHz, CDCl3
f1 (ppm)


158.51
138.72
138.10
135.97
127.73
114.33
113.24
111.43
80.62
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
75.48
55.16
36.17
29.42
-3.72
MeO
O
SiMe3
syn-2.3c
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

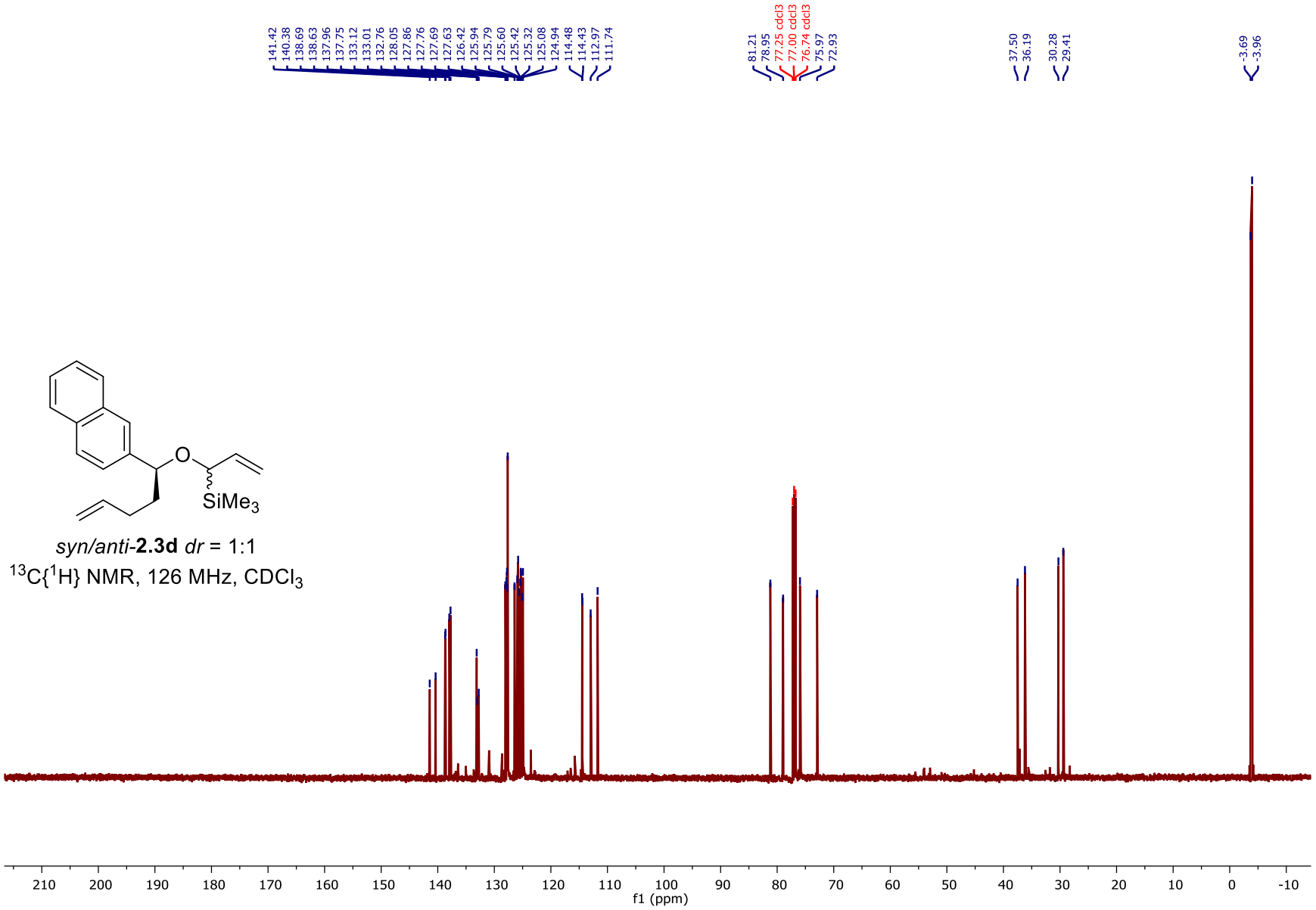

MeO
O
SiMe3
anti-2.3c
1H NMR, 500 MHz, CDCl3
f1 (ppm)

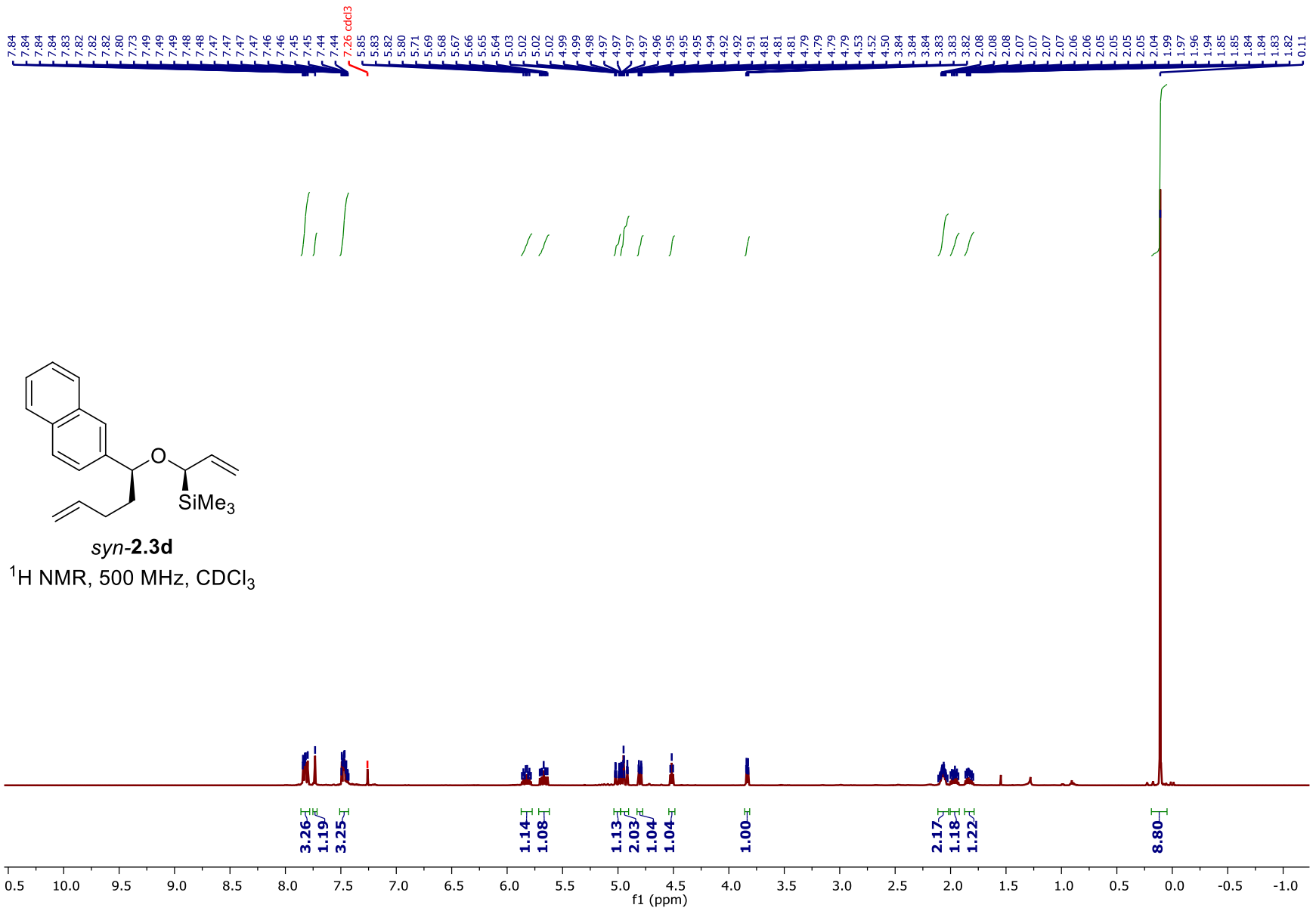

158.81
138.81
137.87
134.96
128.39
114.27
113.45
112.78
78.28
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
72.52
55.16
37.69
30.31
-3.99
MeO
O
SiMe3
anti-2.3c
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



syn/anti-**2.3d** *dr* = 1:1

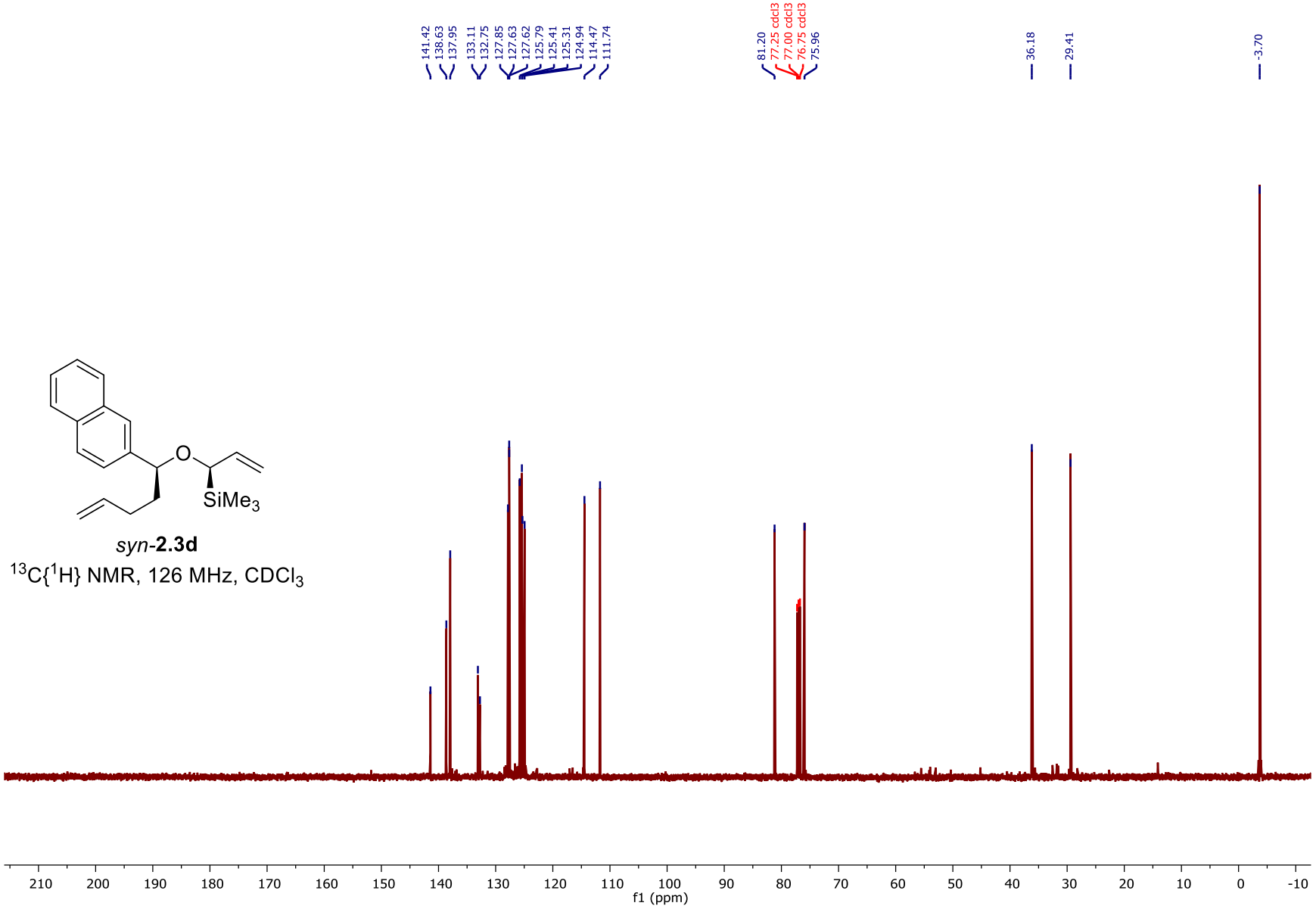
^{1}H NMR, 500 MHz, $CDCl_3$

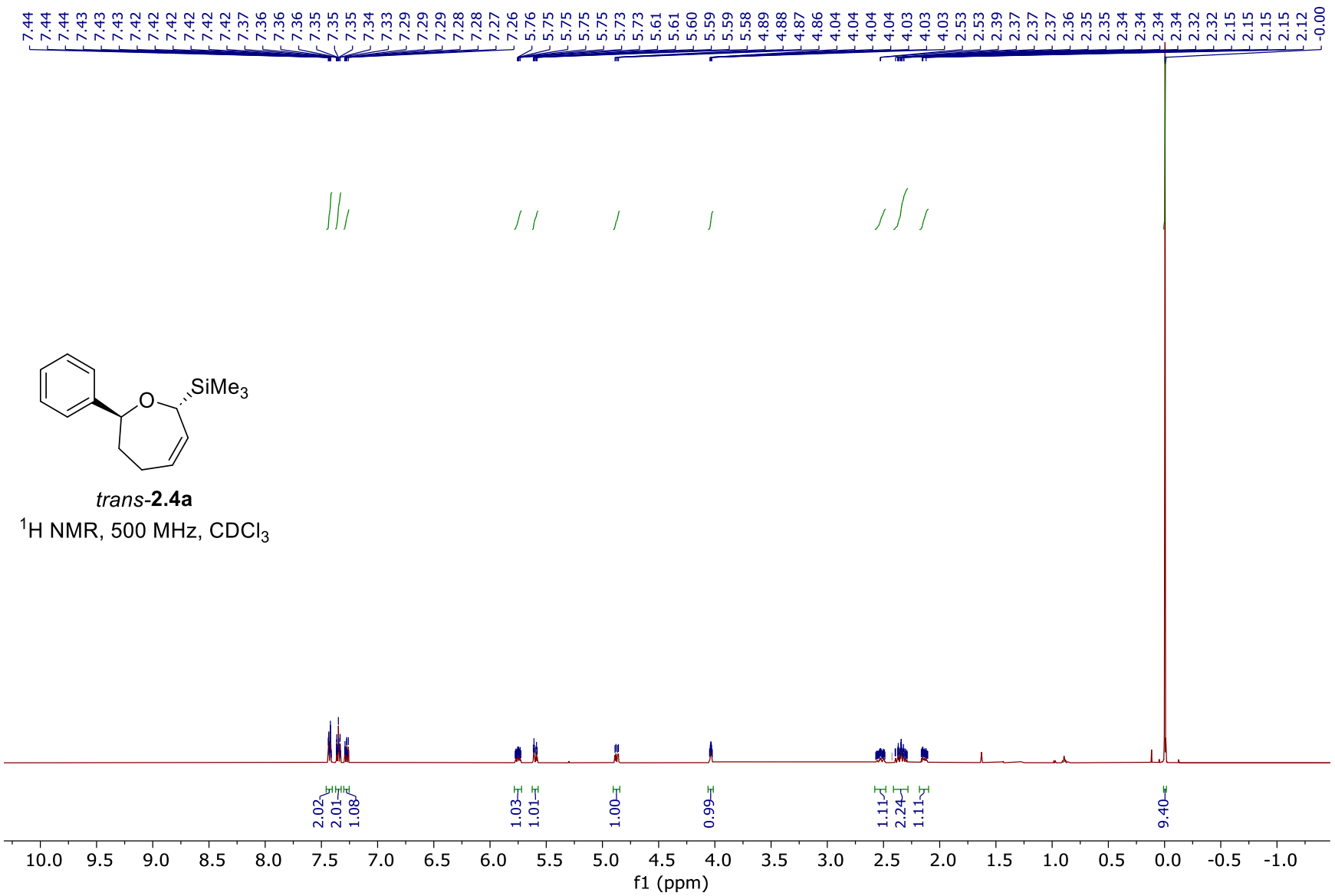

141.42
140.38
138.69
138.63
137.96
137.75
133.12
133.01
132.76
128.05
127.86
127.76
127.69
127.63
126.42
125.94
125.79
125.60
125.42
125.32
125.08
124.94
114.48
114.43
112.97
111.74
81.21
78.95
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
75.97
72.93
37.50
36.19
30.28
29.41
-3.69
-3.96
O
SiMe3
syn/anti-2.3d dr = 1:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



syn-**2.3d**

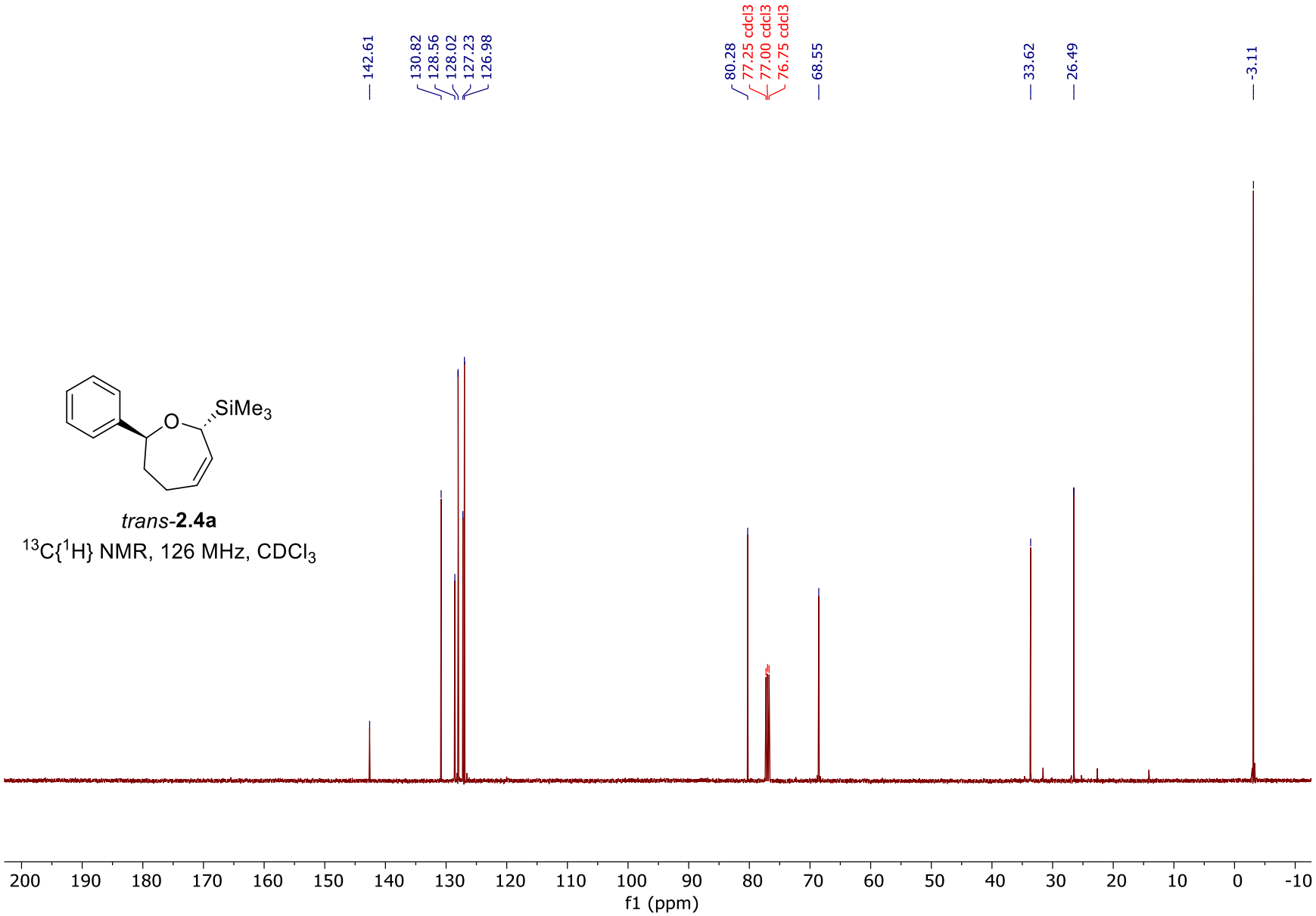
^{1}H NMR, 500 MHz, $CDCl_3$


141.42
138.63
137.95
133.11
132.75
127.85
127.63
127.62
125.79
125.41
125.31
124.94
114.47
111.74
81.20
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
75.96
36.18
29.41
-3.70
O
SiMe3
syn-2.3d
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



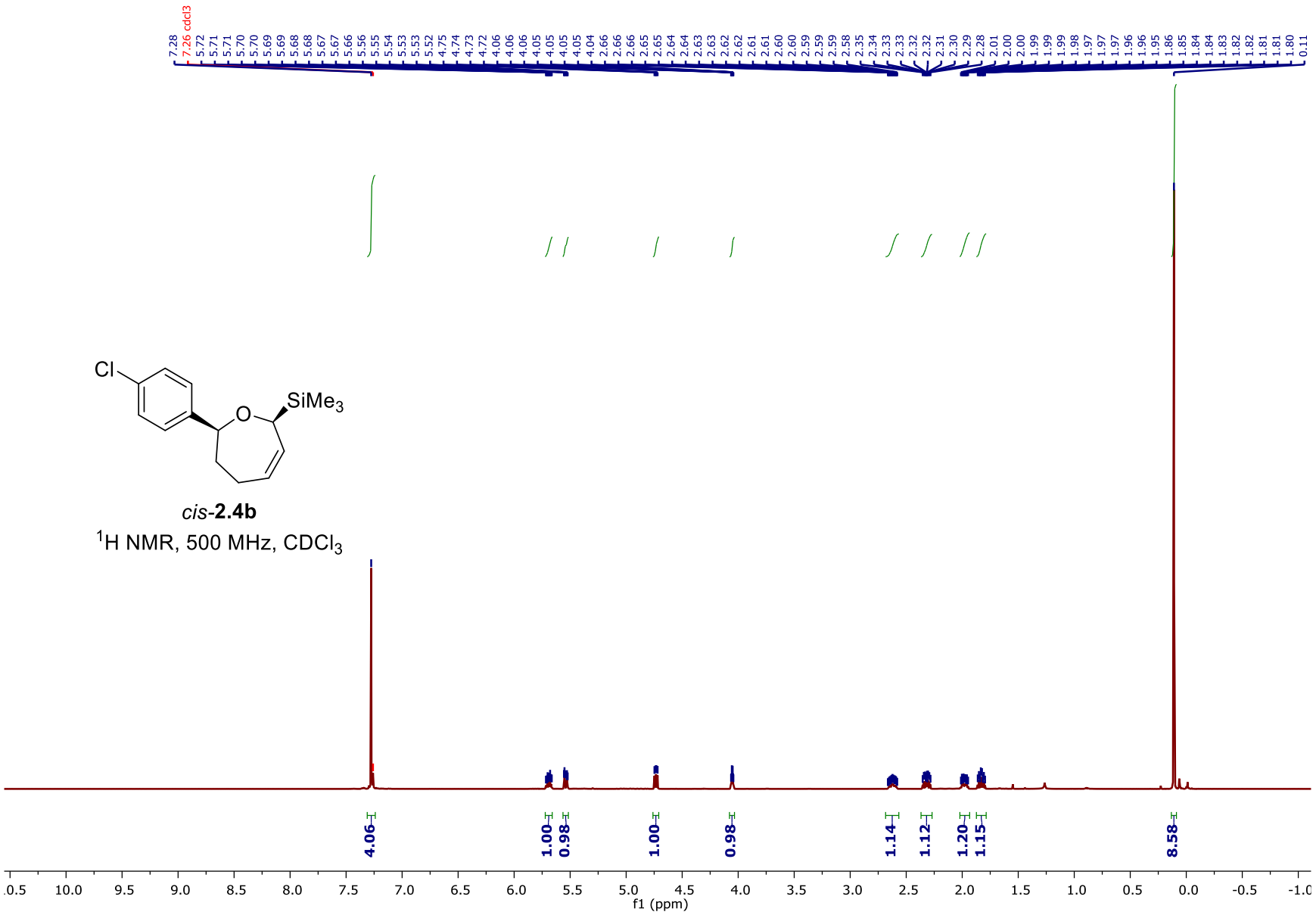
trans-**2.4a**

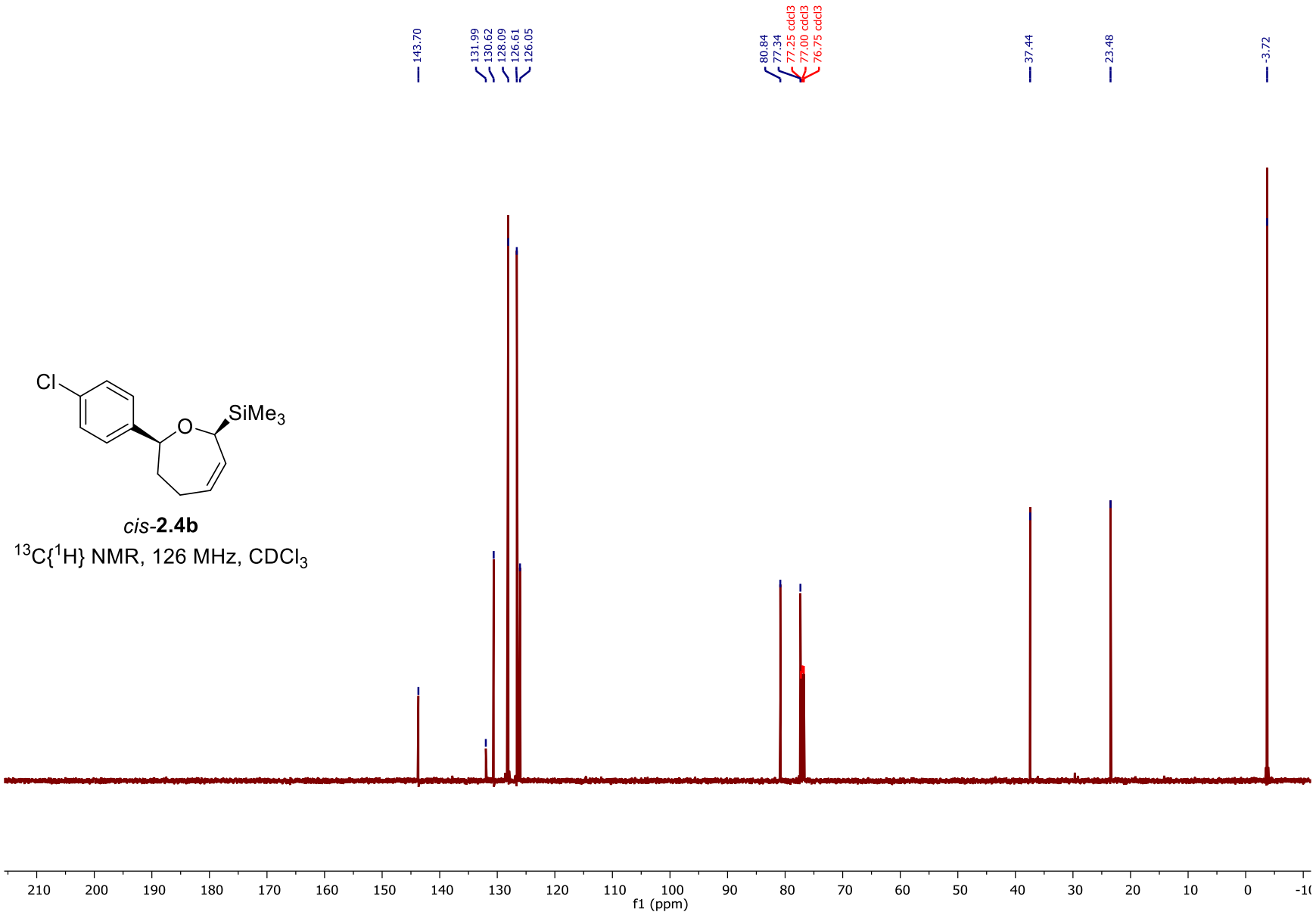
^{1}H NMR, 500 MHz, $CDCl_3$

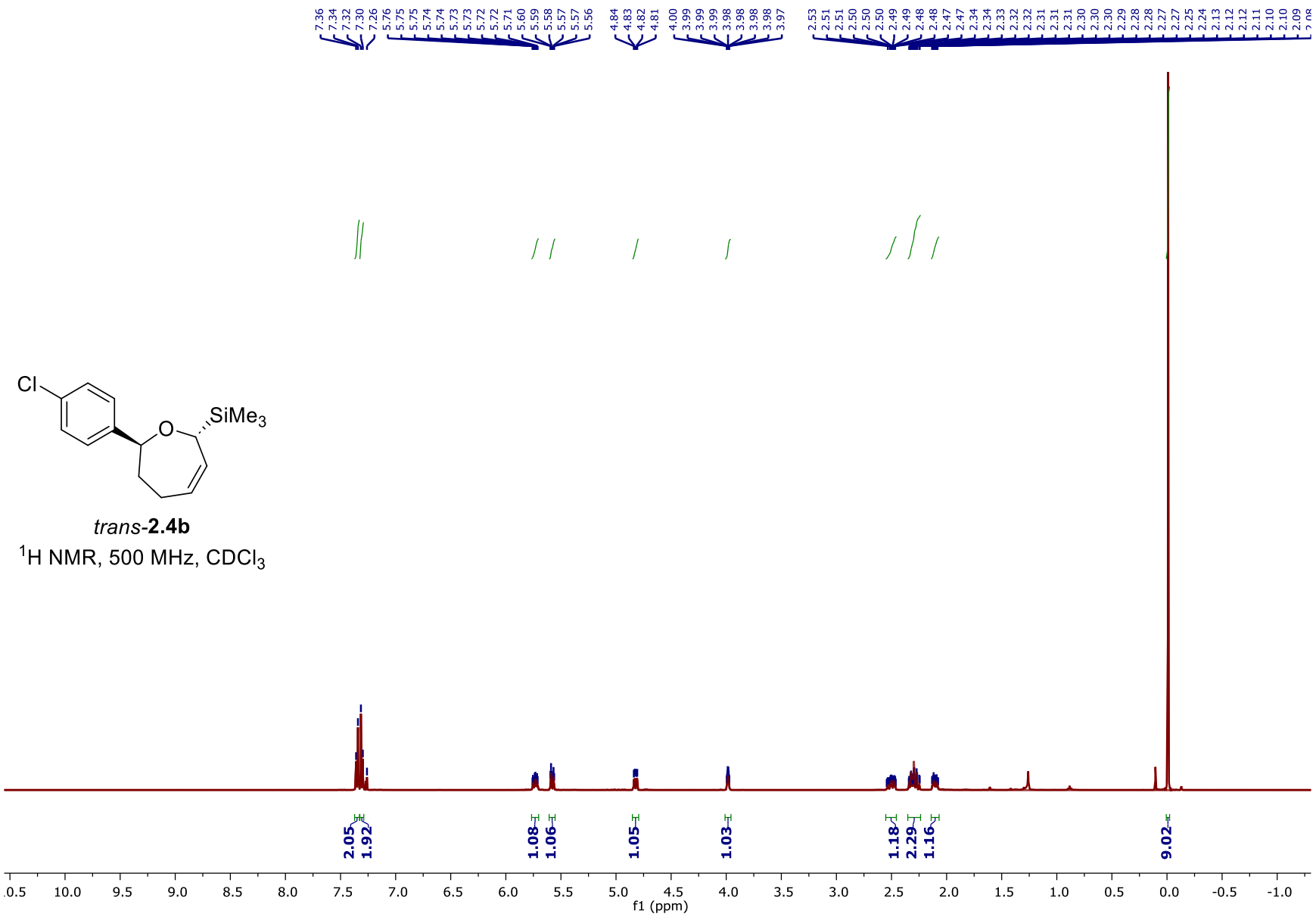


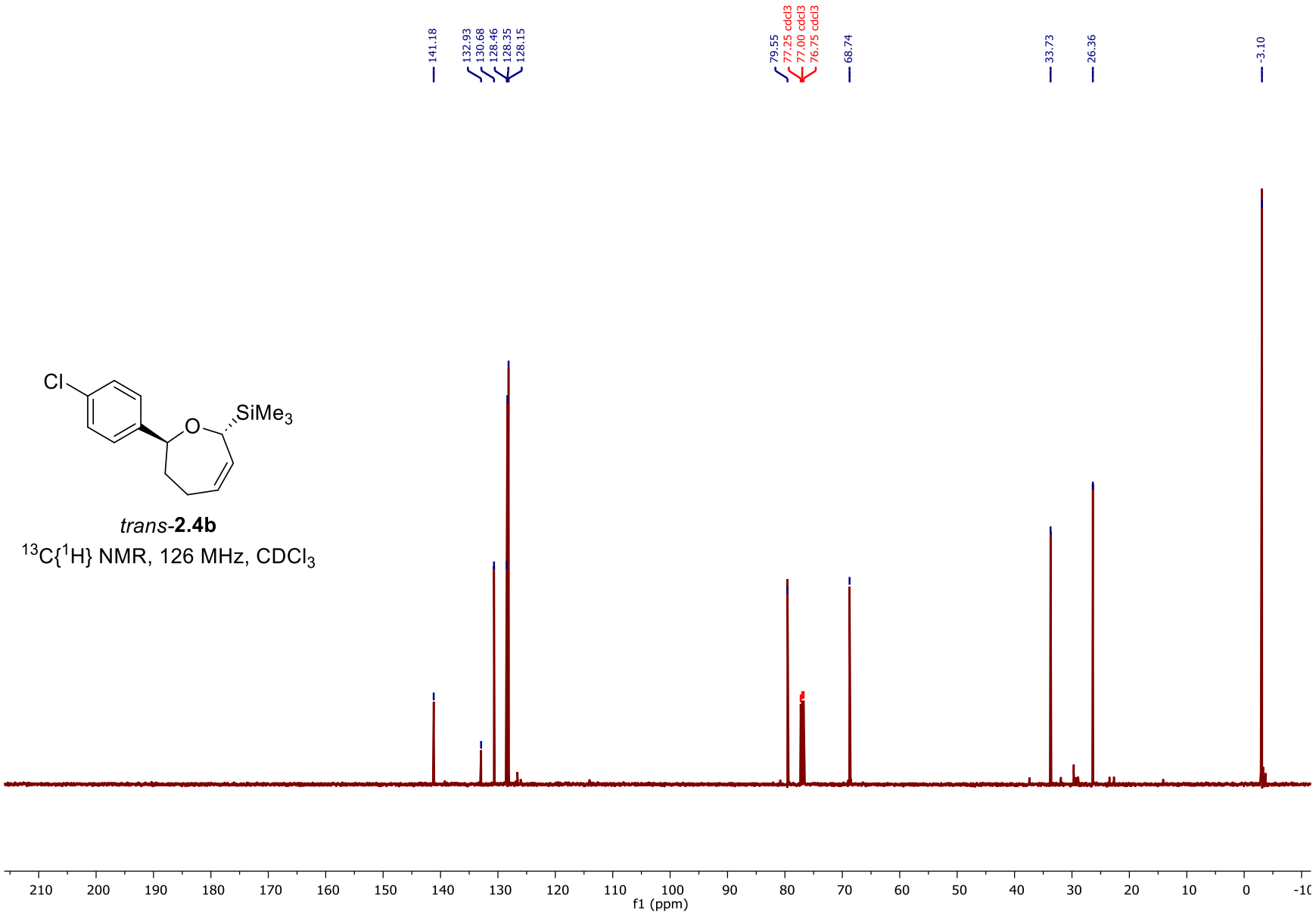
trans-**2.4a**

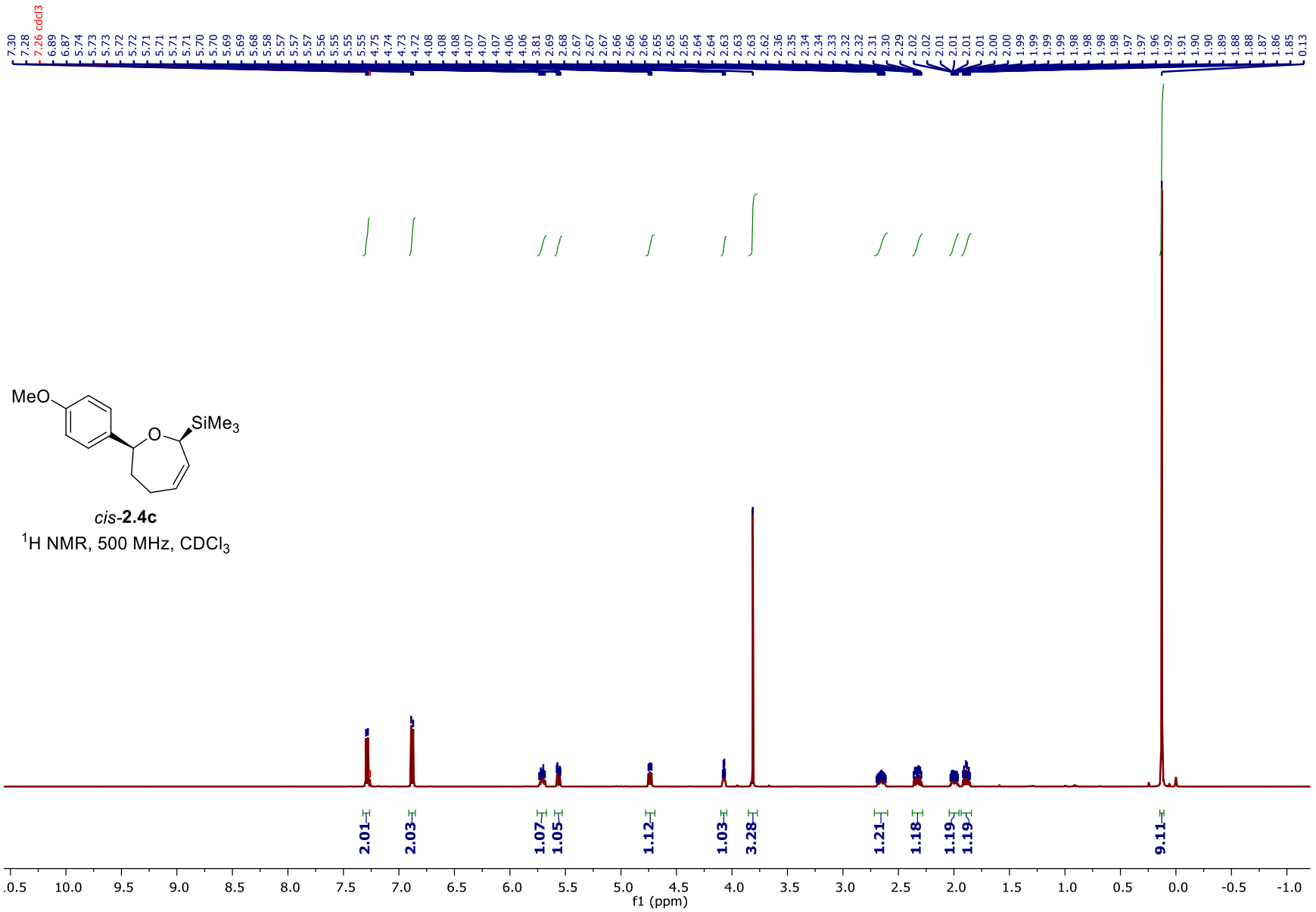
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

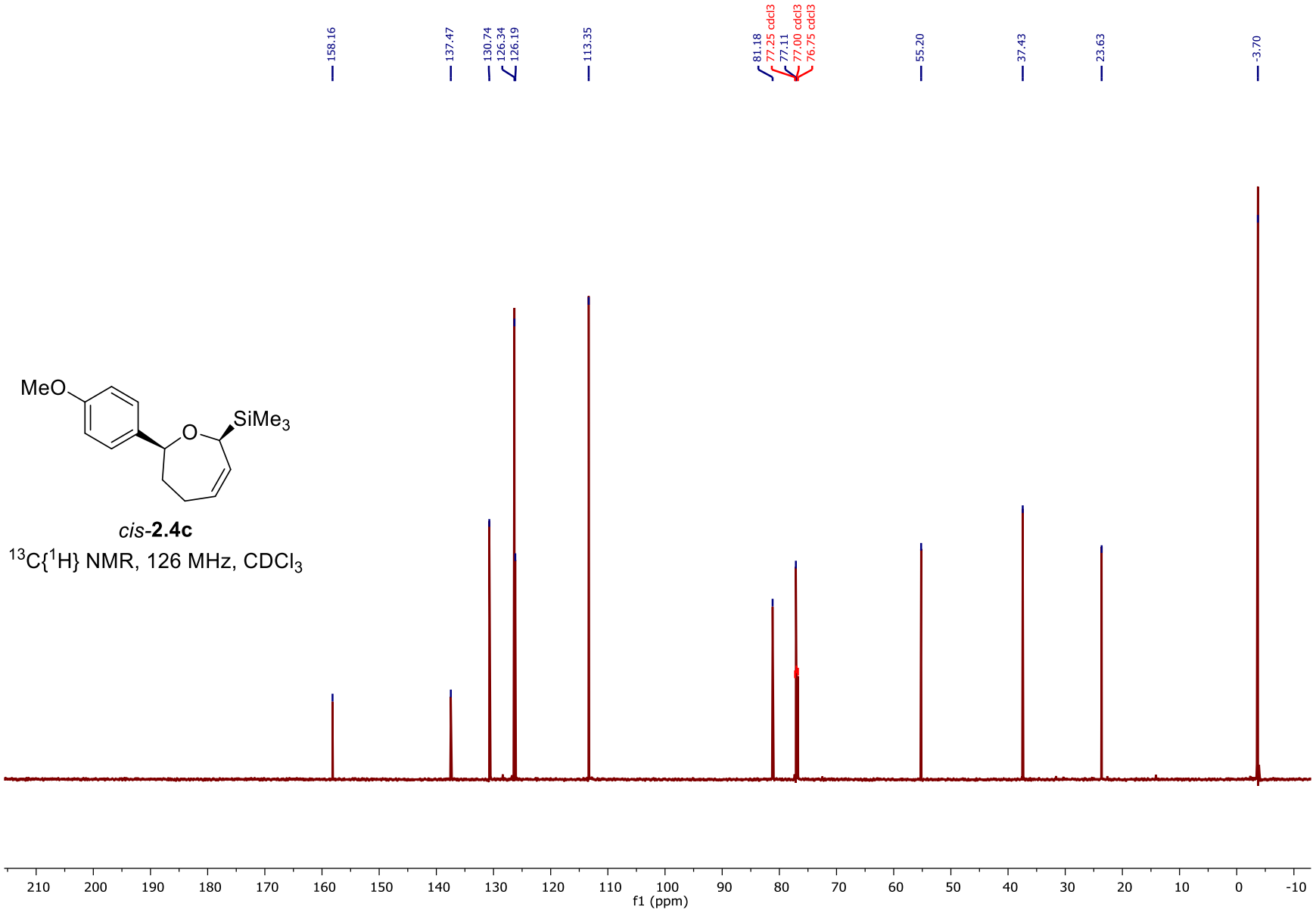

Cl
O
SiMe3
cis-2.4b
1H NMR, 500 MHz, CDCl3
4.06
1.00
0.98
1.00
0.98
1.14
1.12
1.20
1.15
8.58
f1 (ppm)

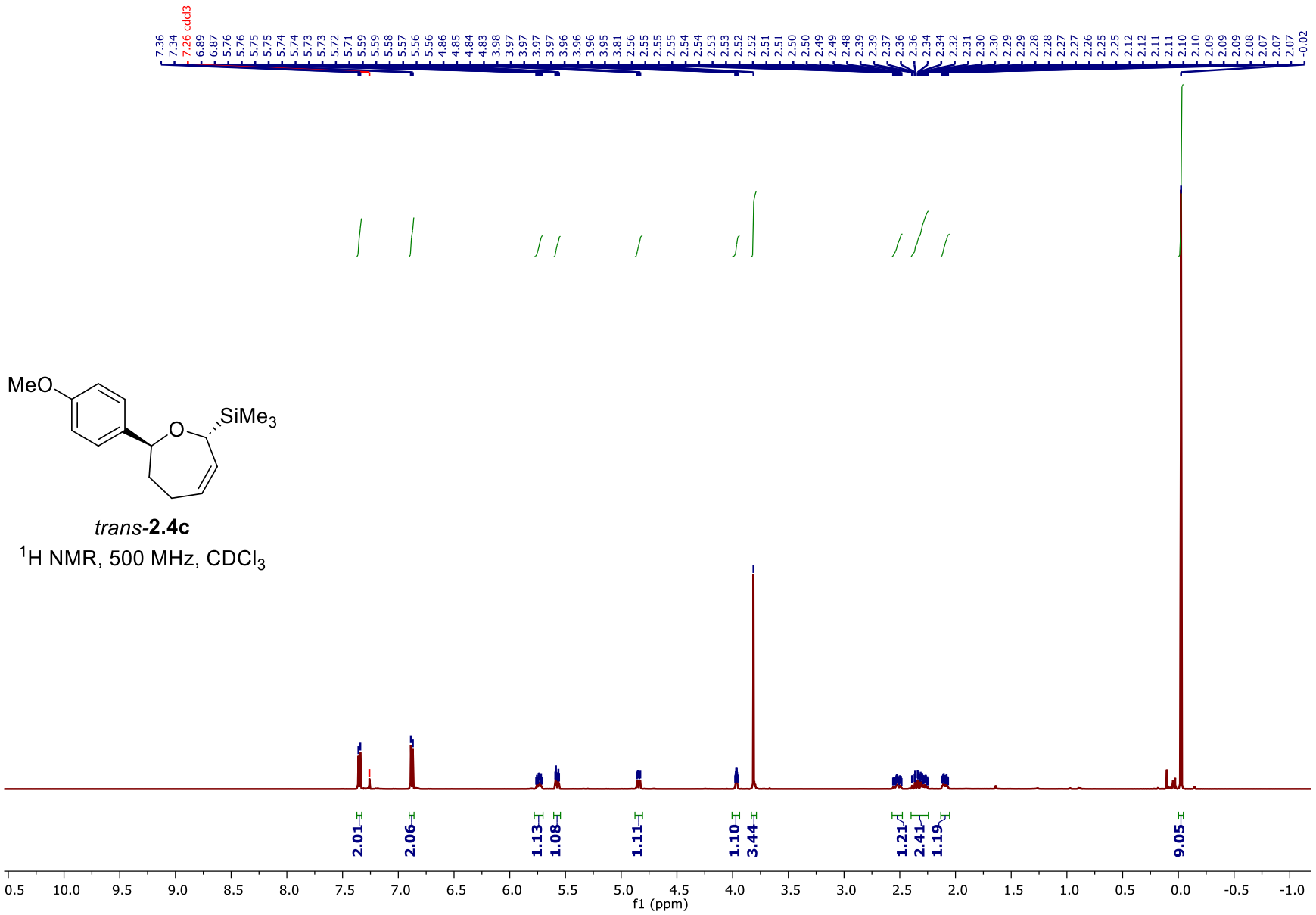

143.70
131.99
130.62
128.09
126.61
126.05
80.84
77.34
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
37.44
23.48
-3.72
Cl
O
SiMe3
cis-2.4b
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

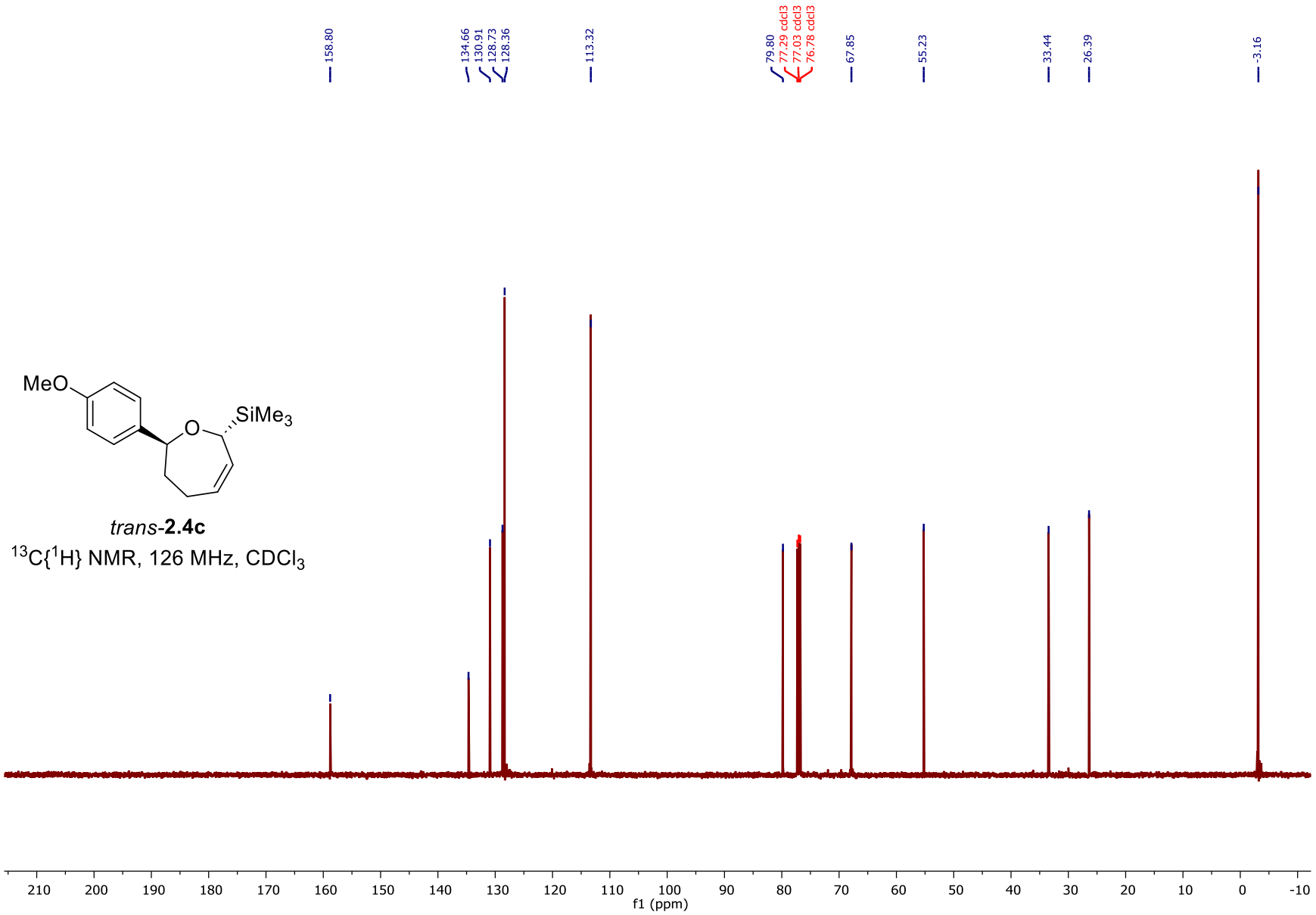

Cl
O
SiMe3
trans-2.4b
1H NMR, 500 MHz, CDCl3
7.36 7.34 7.32 7.30 7.26 5.76 5.75 5.75 5.74 5.74 5.73 5.73 5.72 5.72 5.71 5.60 5.59 5.58 5.57 5.57 5.56 4.84 4.83 4.82 4.81 4.00 3.99 3.99 3.99 3.98 3.98 3.98 3.98 3.97 2.53 2.51 2.51 2.50 2.50 2.50 2.49 2.49 2.48 2.48 2.47 2.47 2.34 2.34 2.33 2.32 2.32 2.31 2.31 2.31 2.30 2.30 2.30 2.29 2.28 2.28 2.27 2.27 2.25 2.24 2.13 2.12 2.12 2.11 2.10 2.10 2.09
2.05 1.92 1.08 1.06 1.05 1.03 1.18 2.29 1.16 9.02
f1 (ppm)

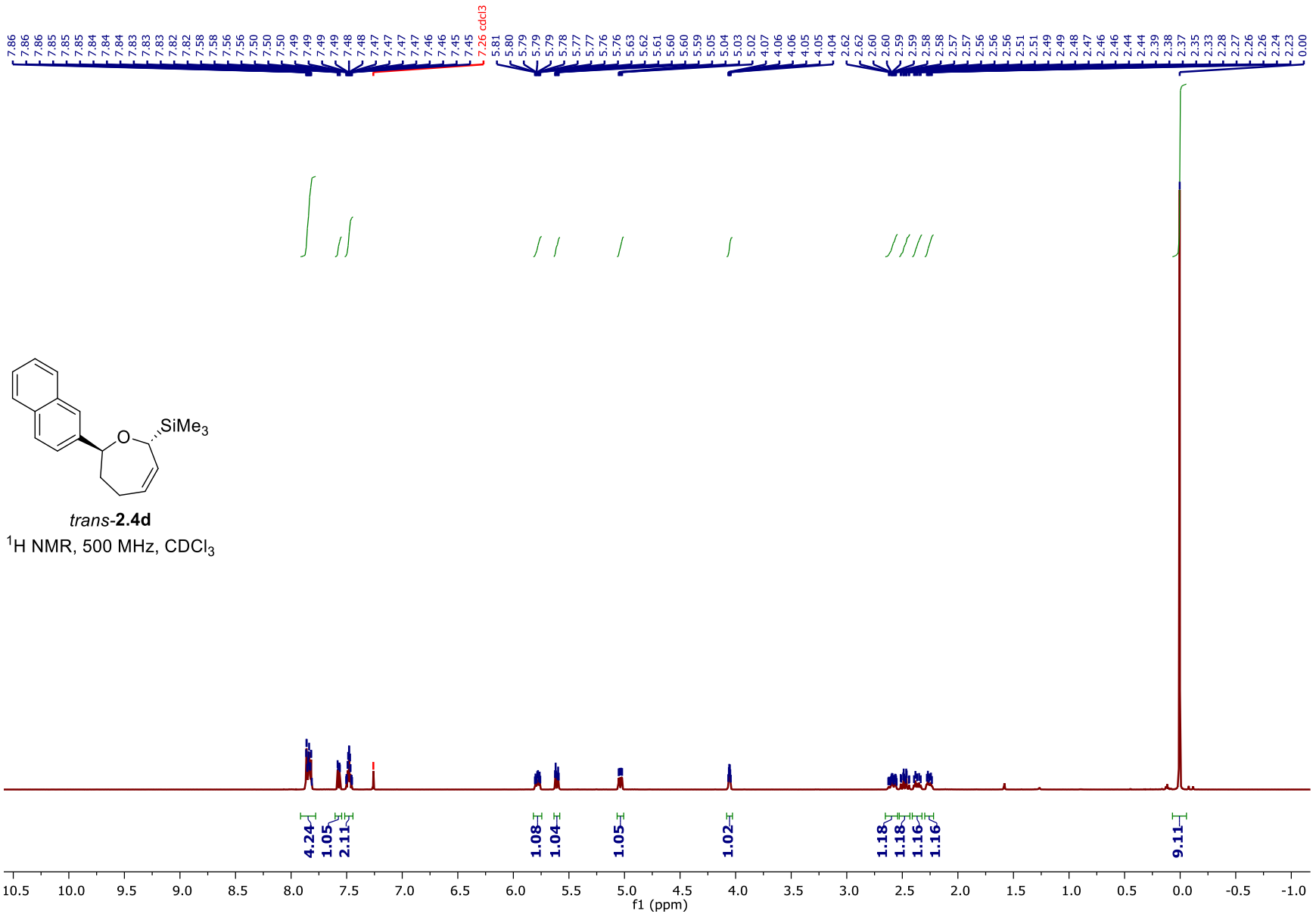

141.18
132.93
130.68
128.46
128.35
128.15
79.55
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
68.74
33.73
26.36
-3.10
Cl
O
SiMe3
trans-2.4b
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
SiMe3
O
cis-2.4c
1H NMR, 500 MHz, CDCl3
2.01
2.03
1.07
1.05
1.12
1.03
3.28
1.21
1.18
1.19
1.19
9.11
f1 (ppm)


158.16
137.47
130.74
126.34
126.19
113.35
81.18
77.25 cdcl3
77.11
77.00 cdcl3
76.75 cdcl3
55.20
37.43
23.63
-3.70
MeO
O
SiMe3
cis-2.4c
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

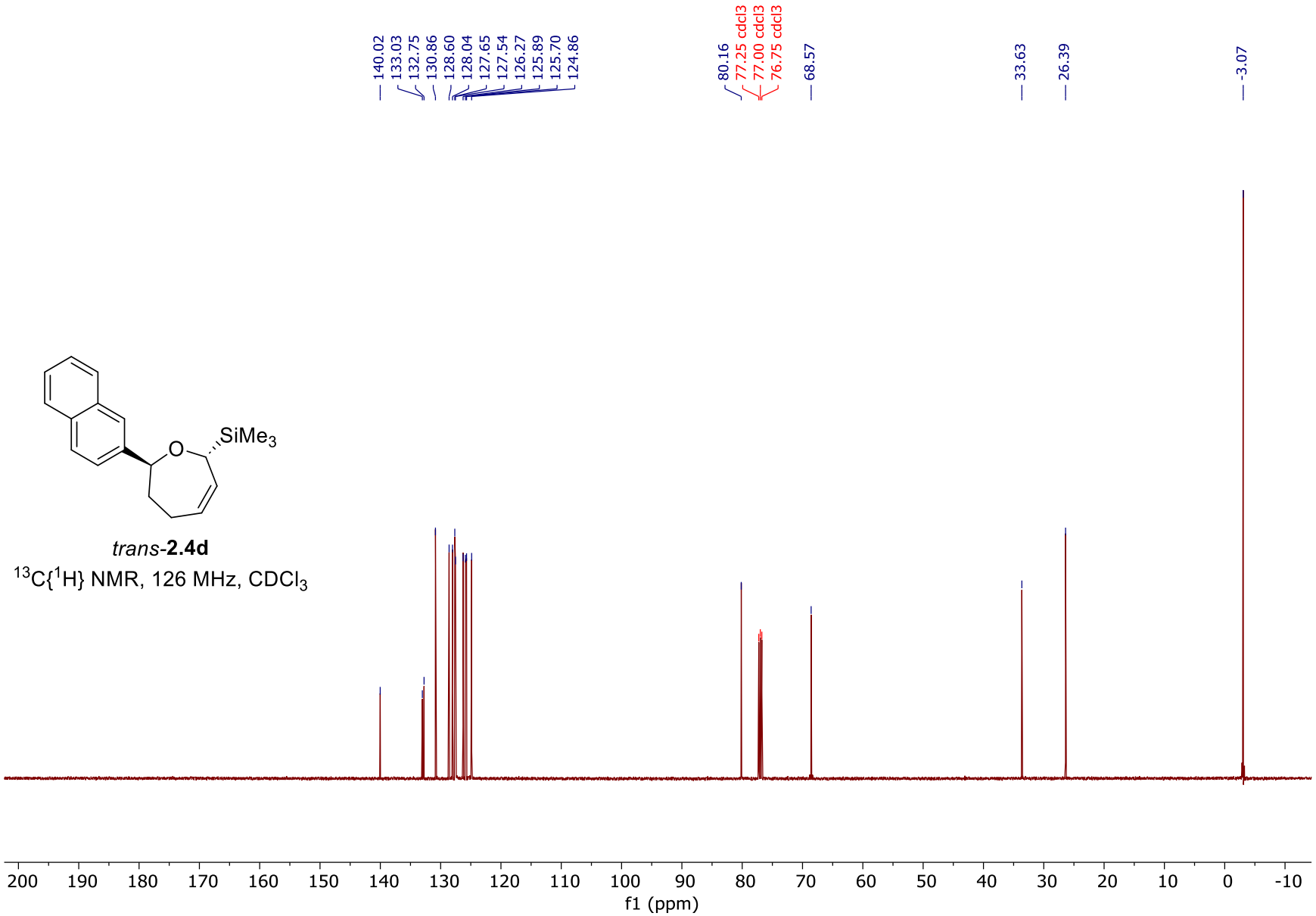

MeO
O
SiMe3
trans-2.4c
1H NMR, 500 MHz, CDCl3
f1 (ppm)


158.80
134.66
130.91
128.73
128.36
113.32
79.80
77.29 cdcl3
77.03 cdcl3
76.78 cdcl3
67.85
55.23
33.44
26.39
-3.16
MeO
O
SiMe3
trans-2.4c
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



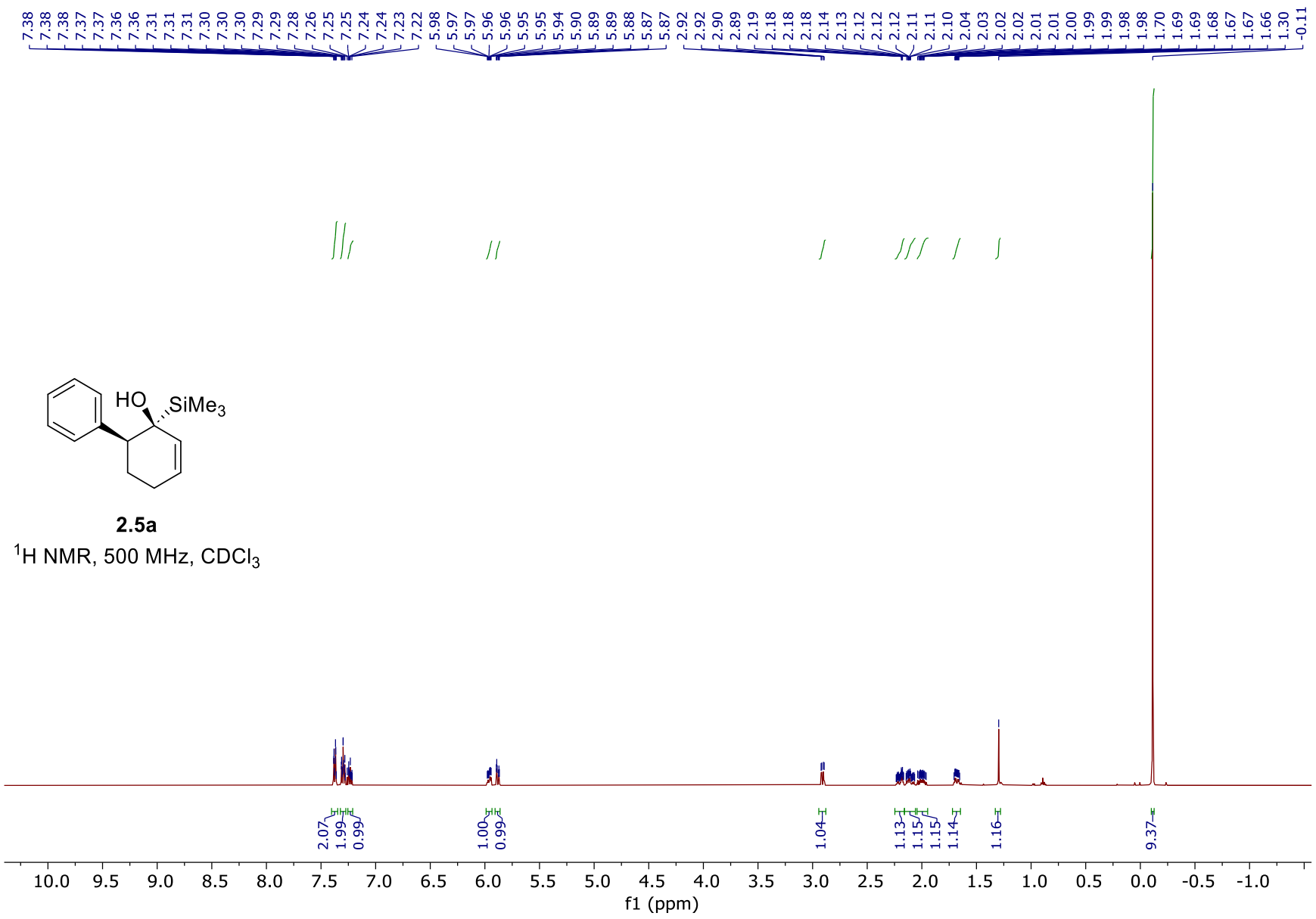
trans-**2.4d**

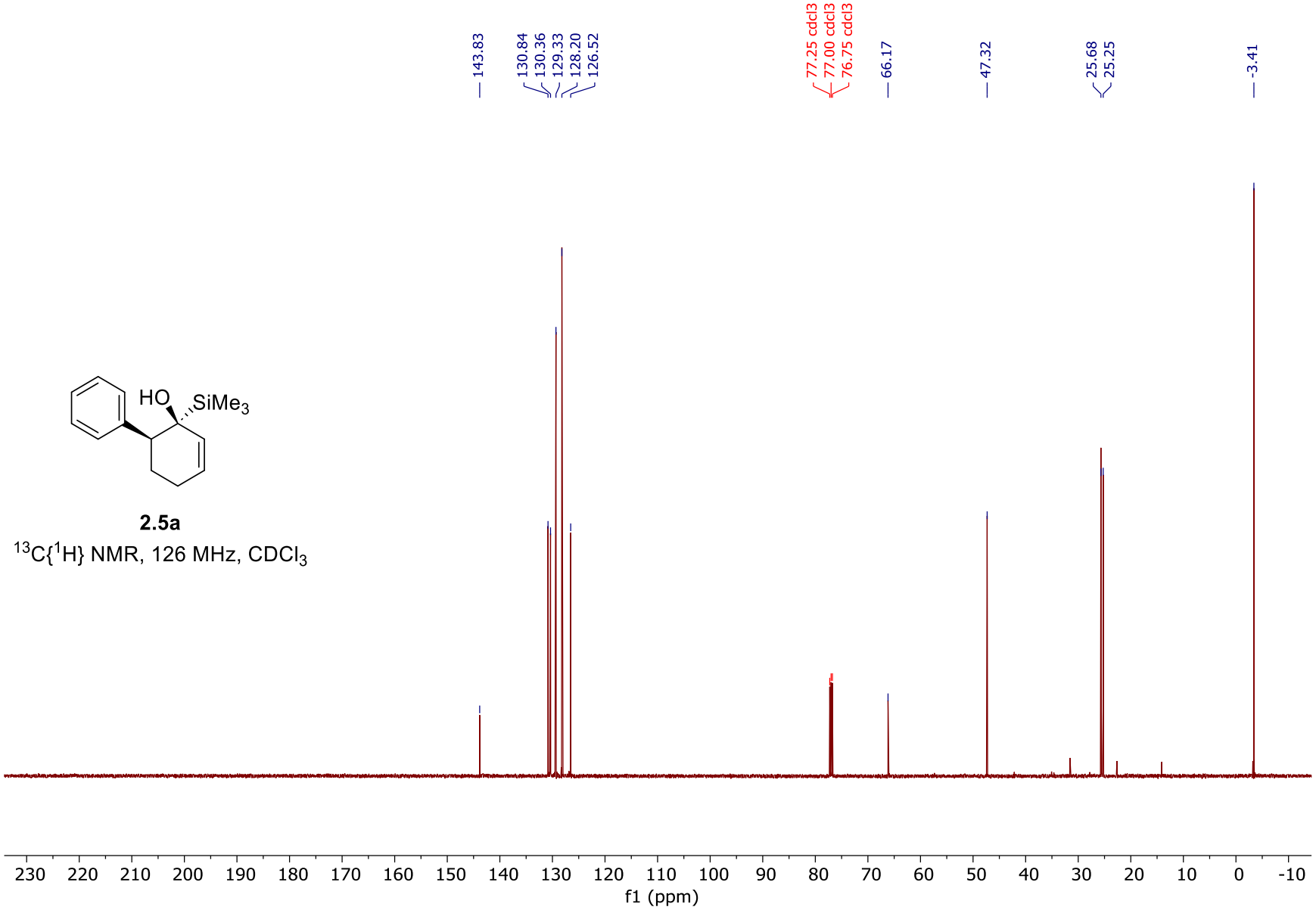
^{1}H NMR, 500 MHz, $CDCl_3$

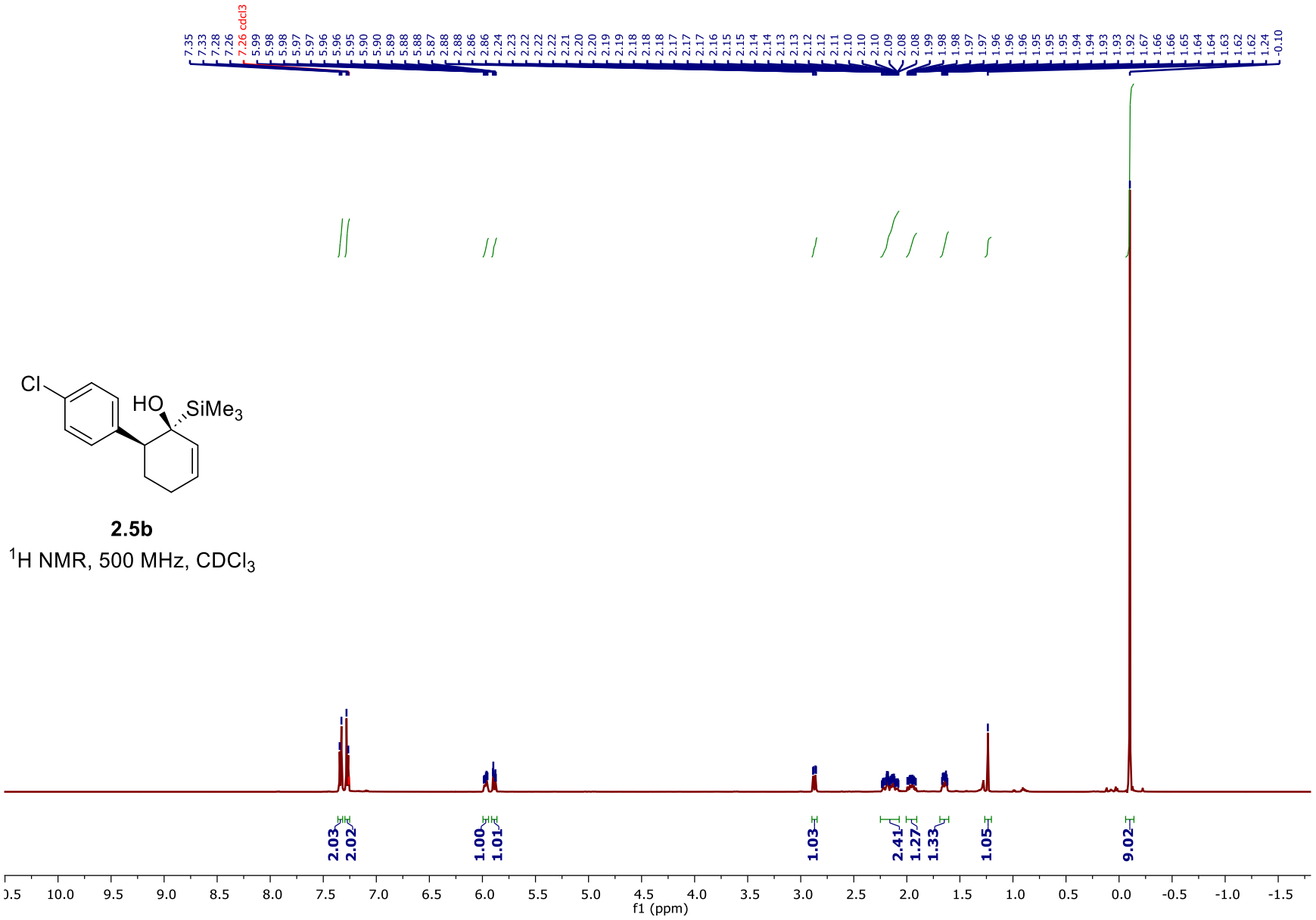


trans-**2.4d**

$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

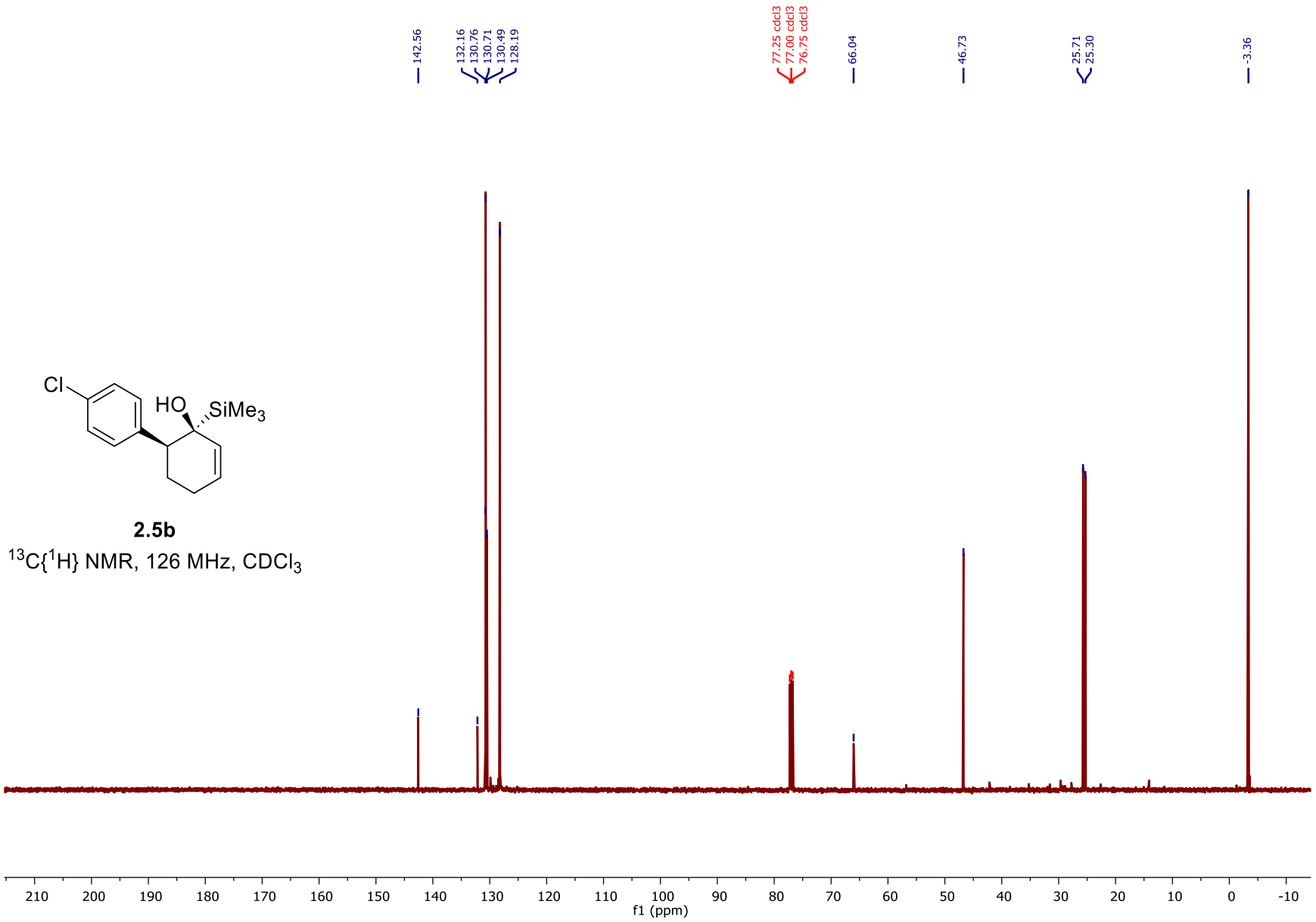

HO
SiMe3
2.5a
1H NMR, 500 MHz, CDCl3
f1 (ppm)

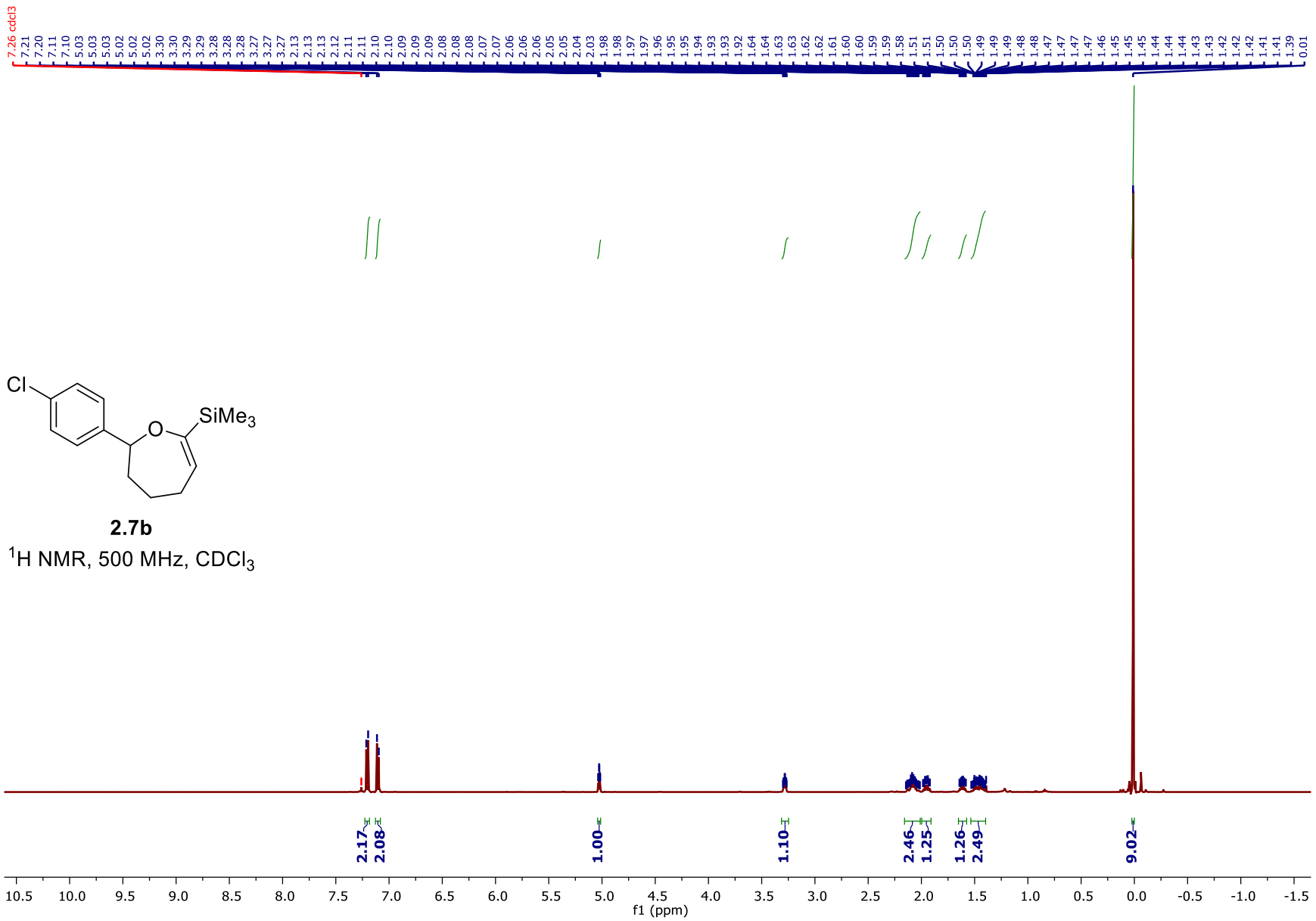

143.83
130.84
130.36
129.33
128.20
126.52
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
66.17
47.32
25.68
25.25
-3.41
HO
SiMe3
2.5a
13C{1H} NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



2.5b

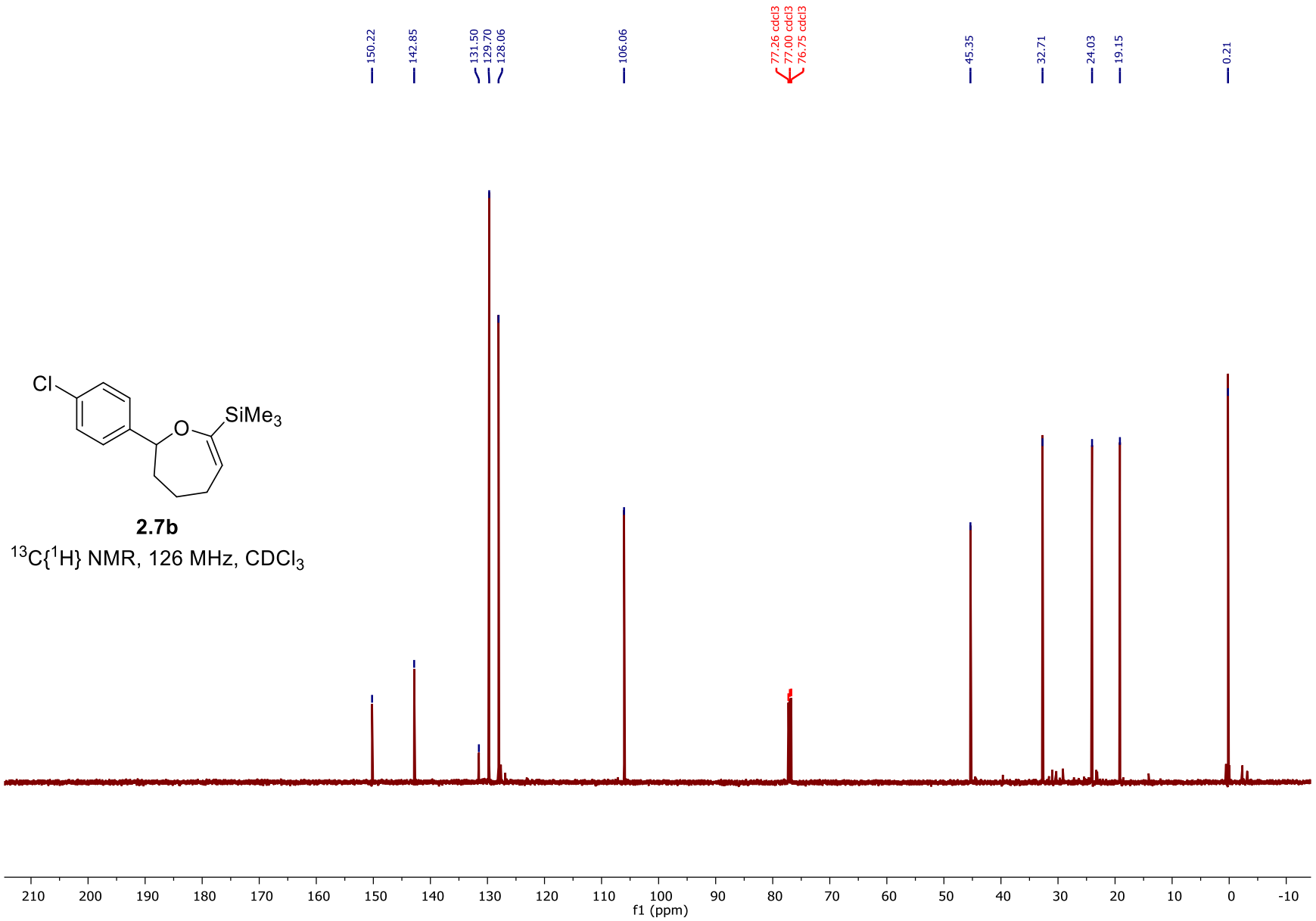
^{1}H NMR, 500 MHz, $CDCl_3$

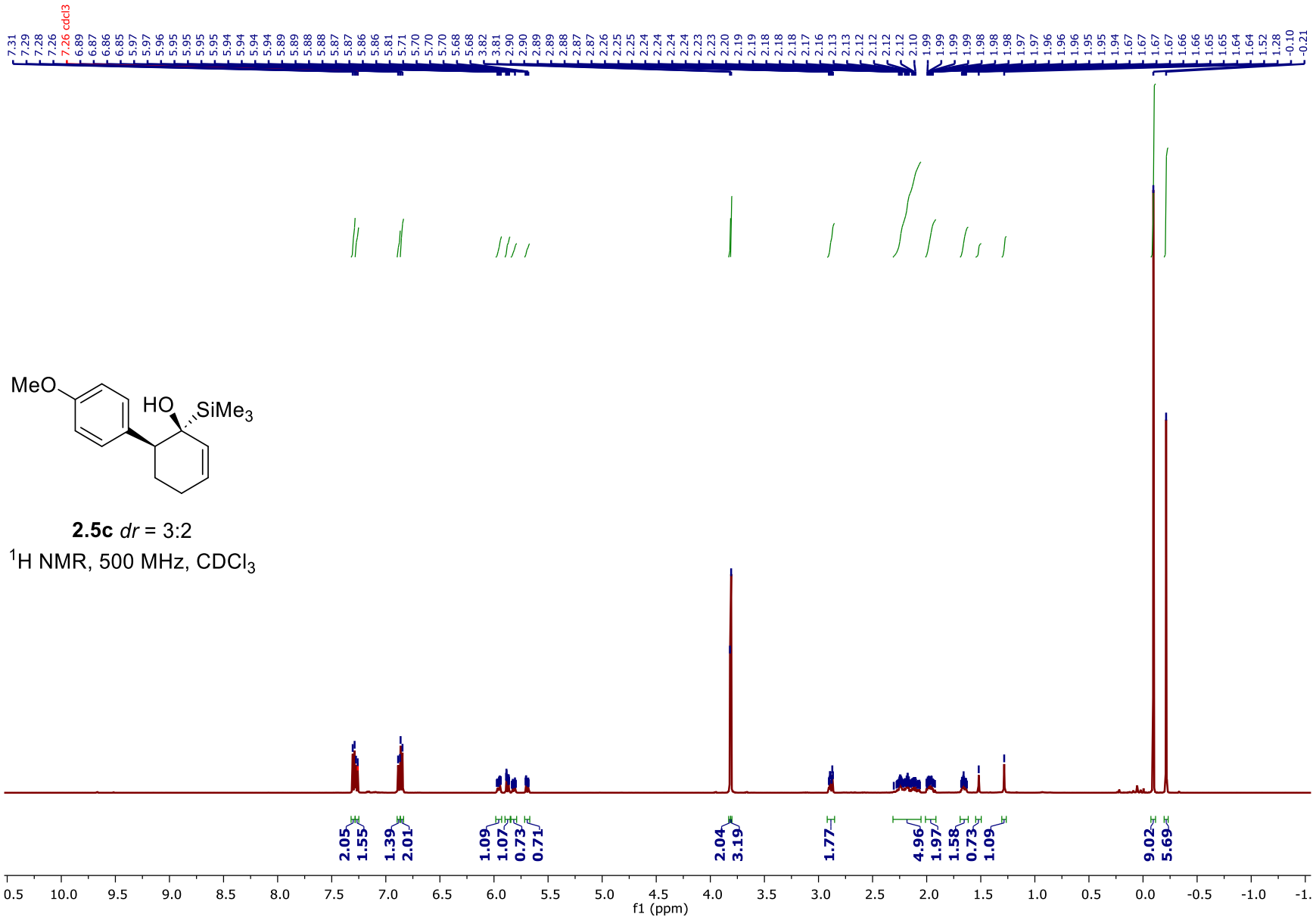

142.56
132.16
130.76
130.71
130.49
128.19
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
66.04
46.73
25.71
25.30
-3.36
Cl
HO
SiMe3
2.5b
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2.7b

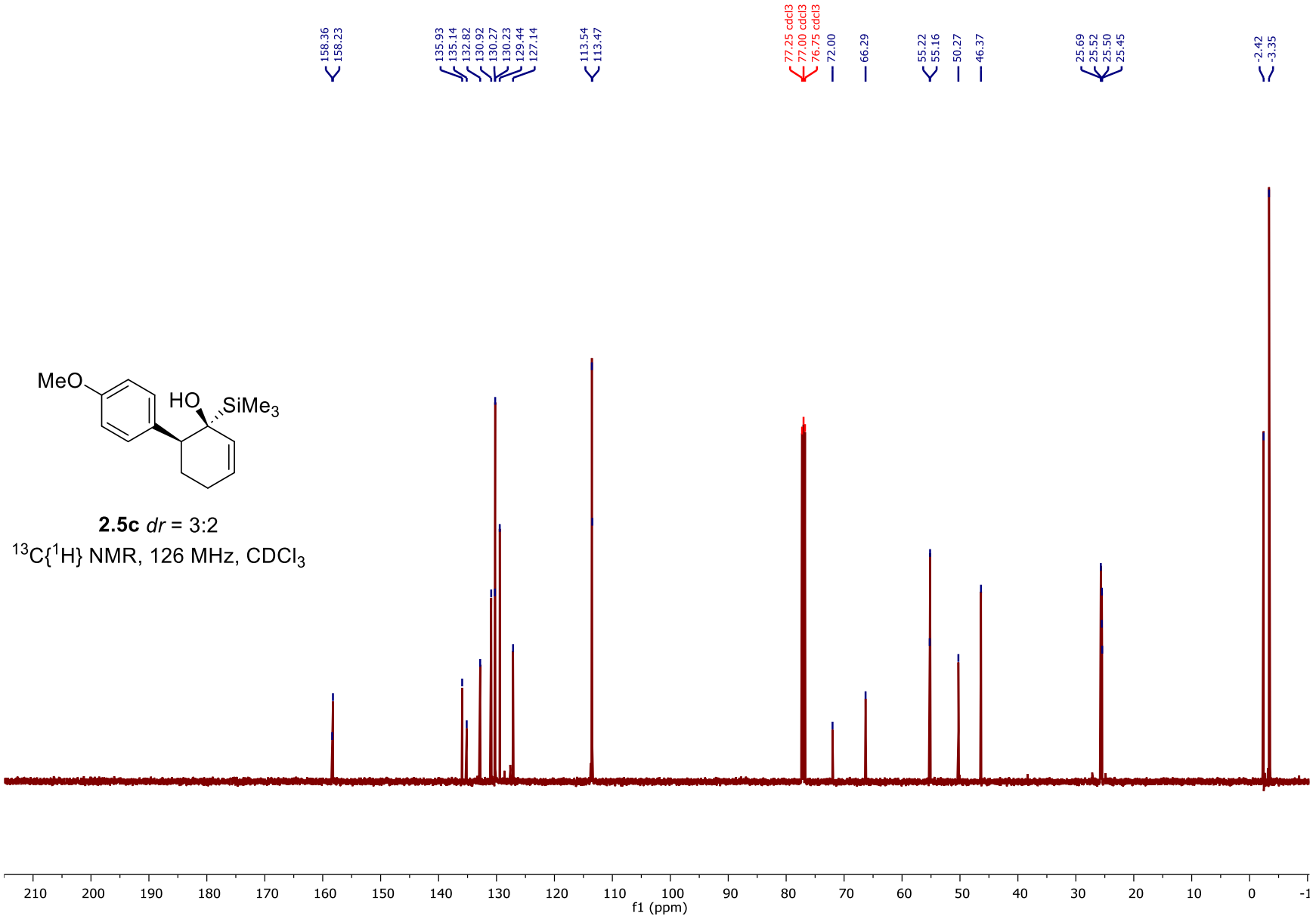
^{1}H NMR, 500 MHz, $CDCl_3$


150.22
142.85
131.50
129.70
128.06
106.06
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
45.35
32.71
24.03
19.15
0.21
Cl
O
SiMe3
2.7b
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



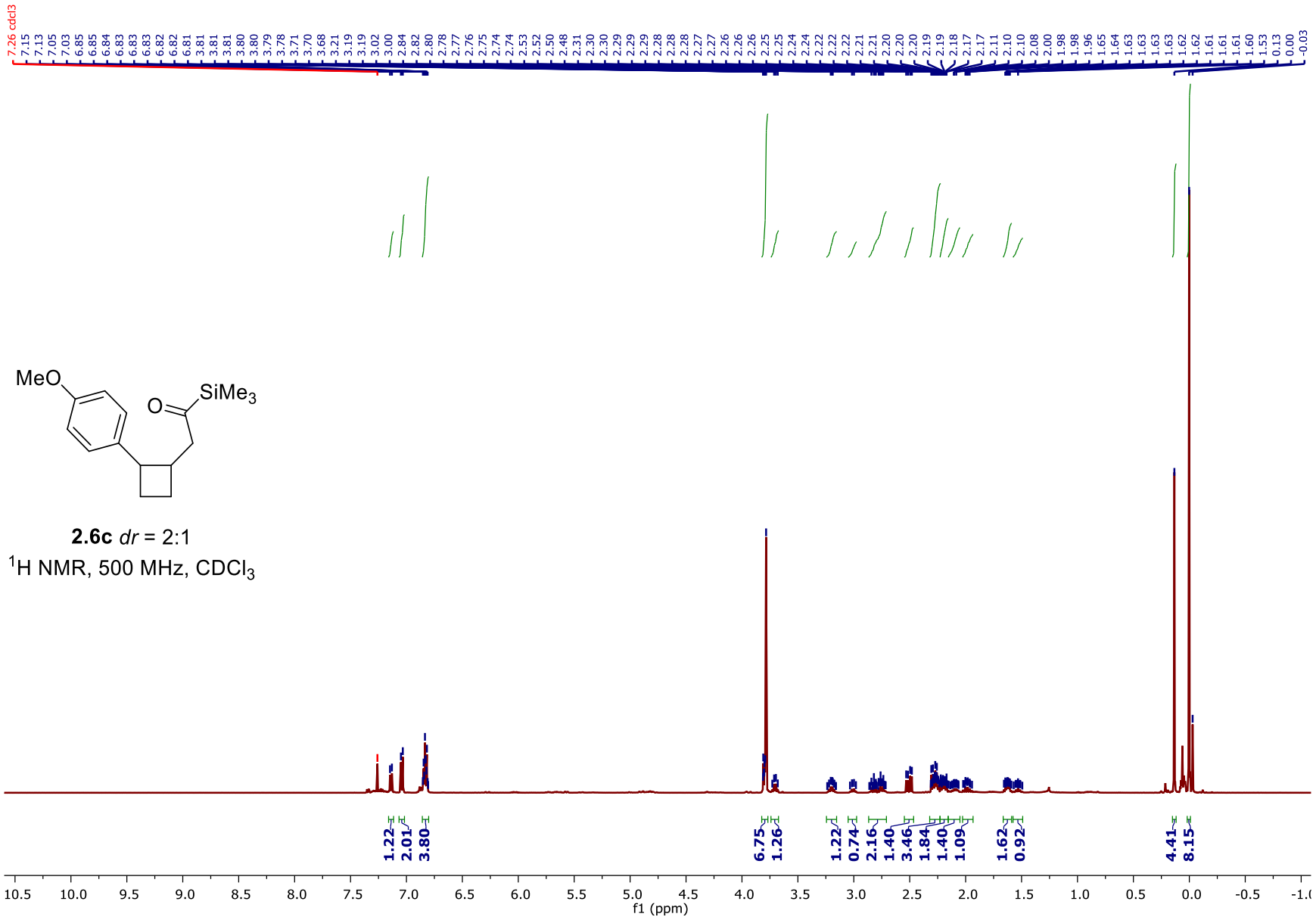
2.5c *dr* = 3:2

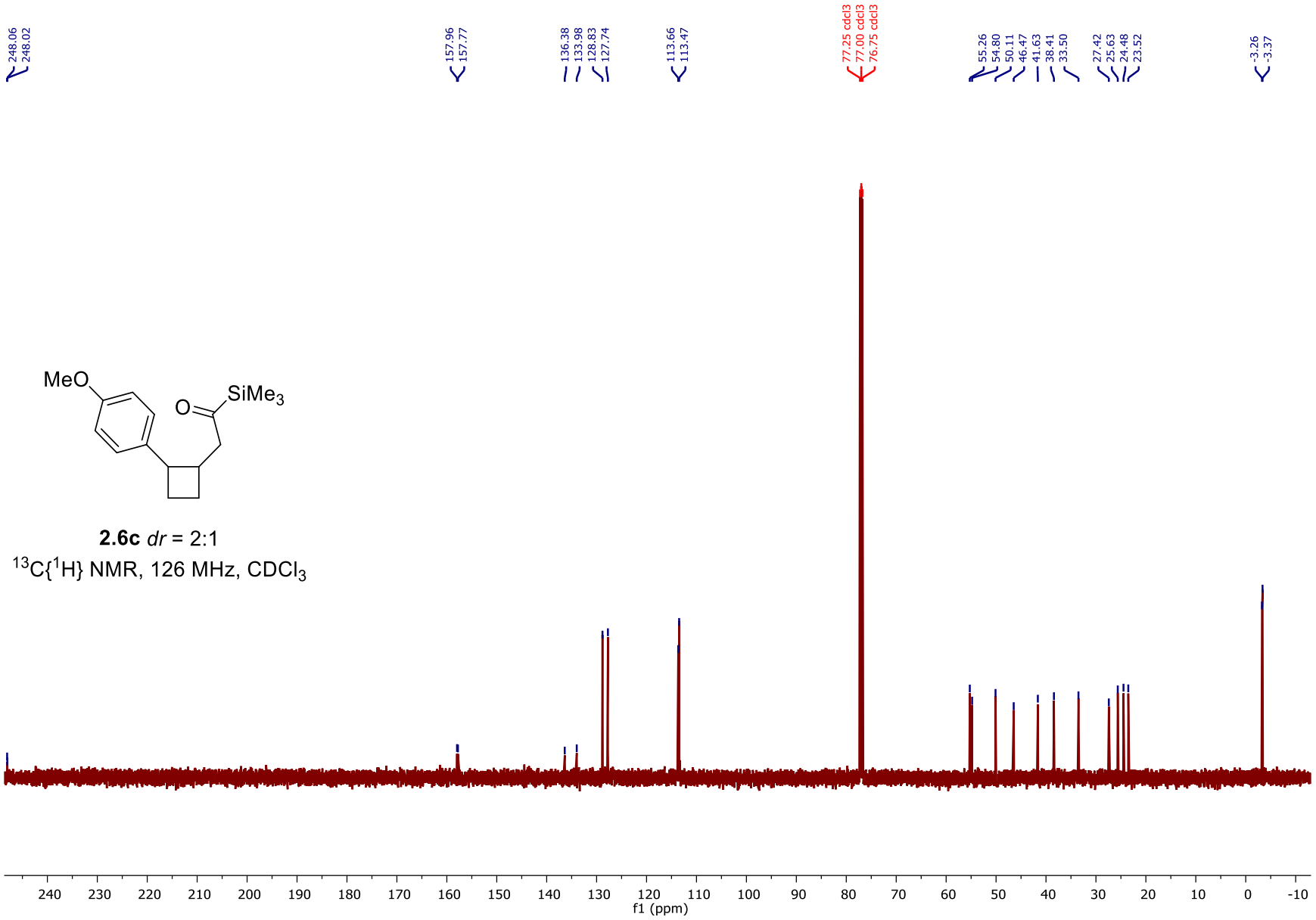
^{1}H NMR, 500 MHz, $CDCl_3$



2.5c *dr* = 3:2

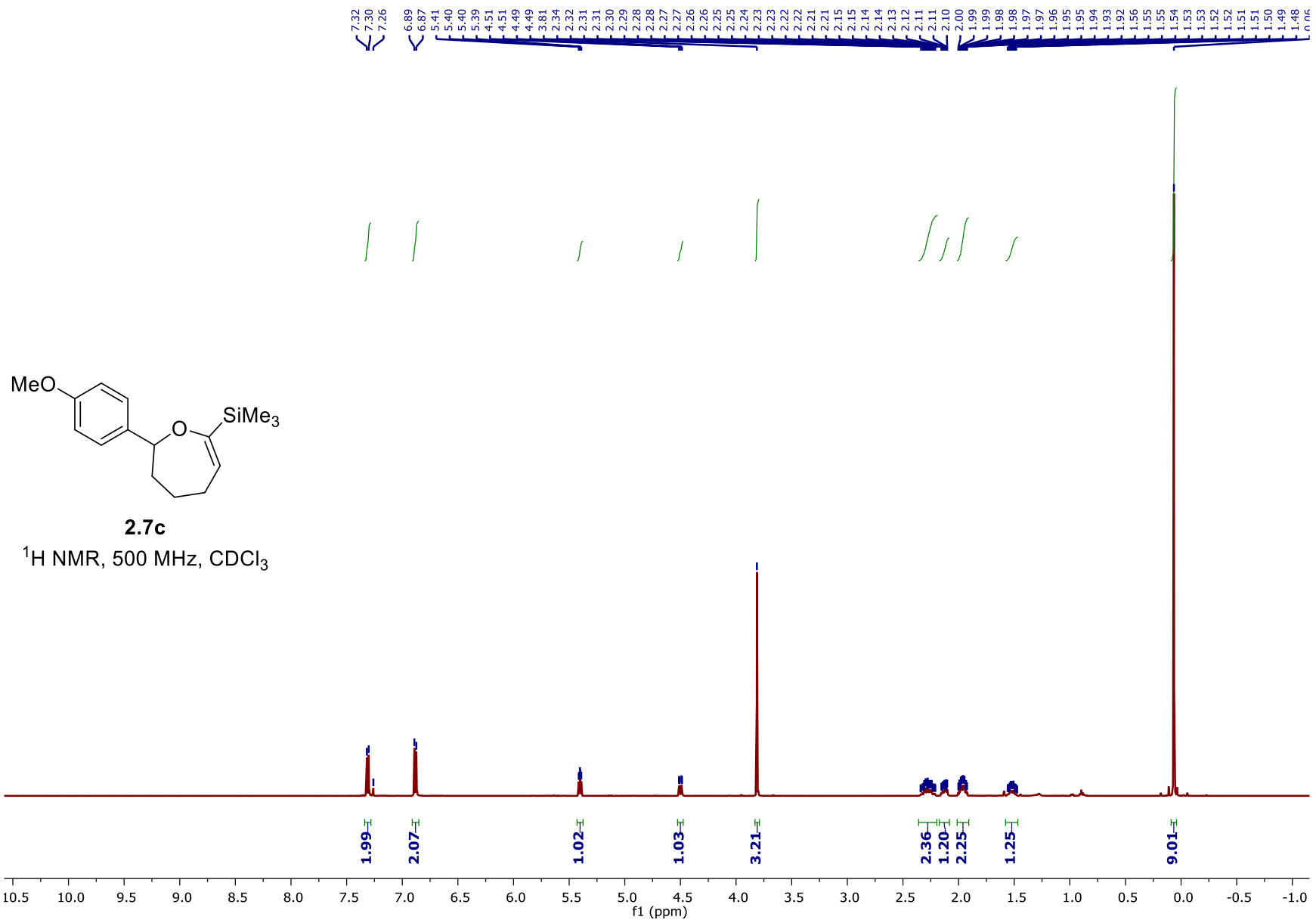
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

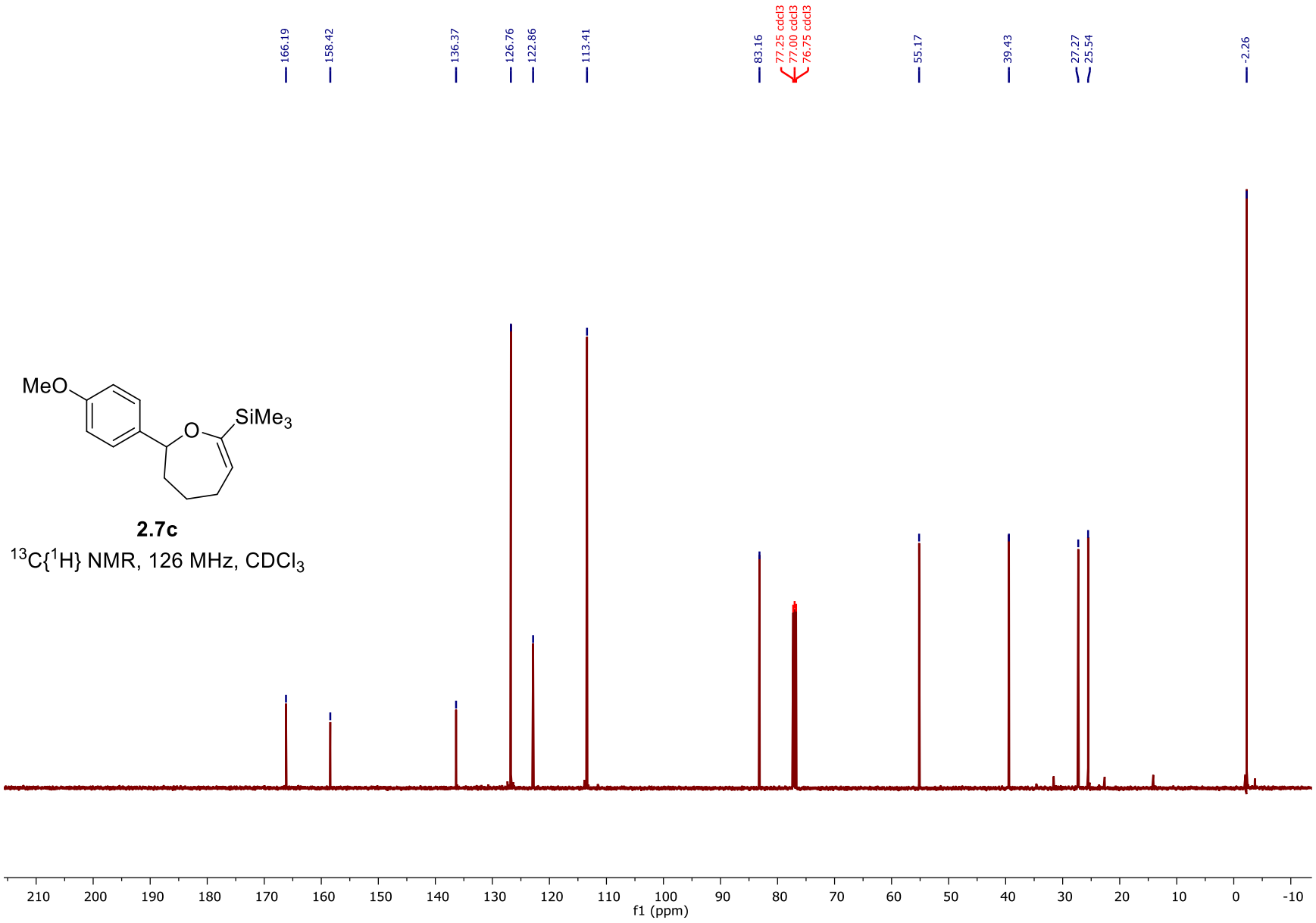

MeO
O
SiMe3
2.6c dr = 2:1
1H NMR, 500 MHz, CDCl3
f1 (ppm)

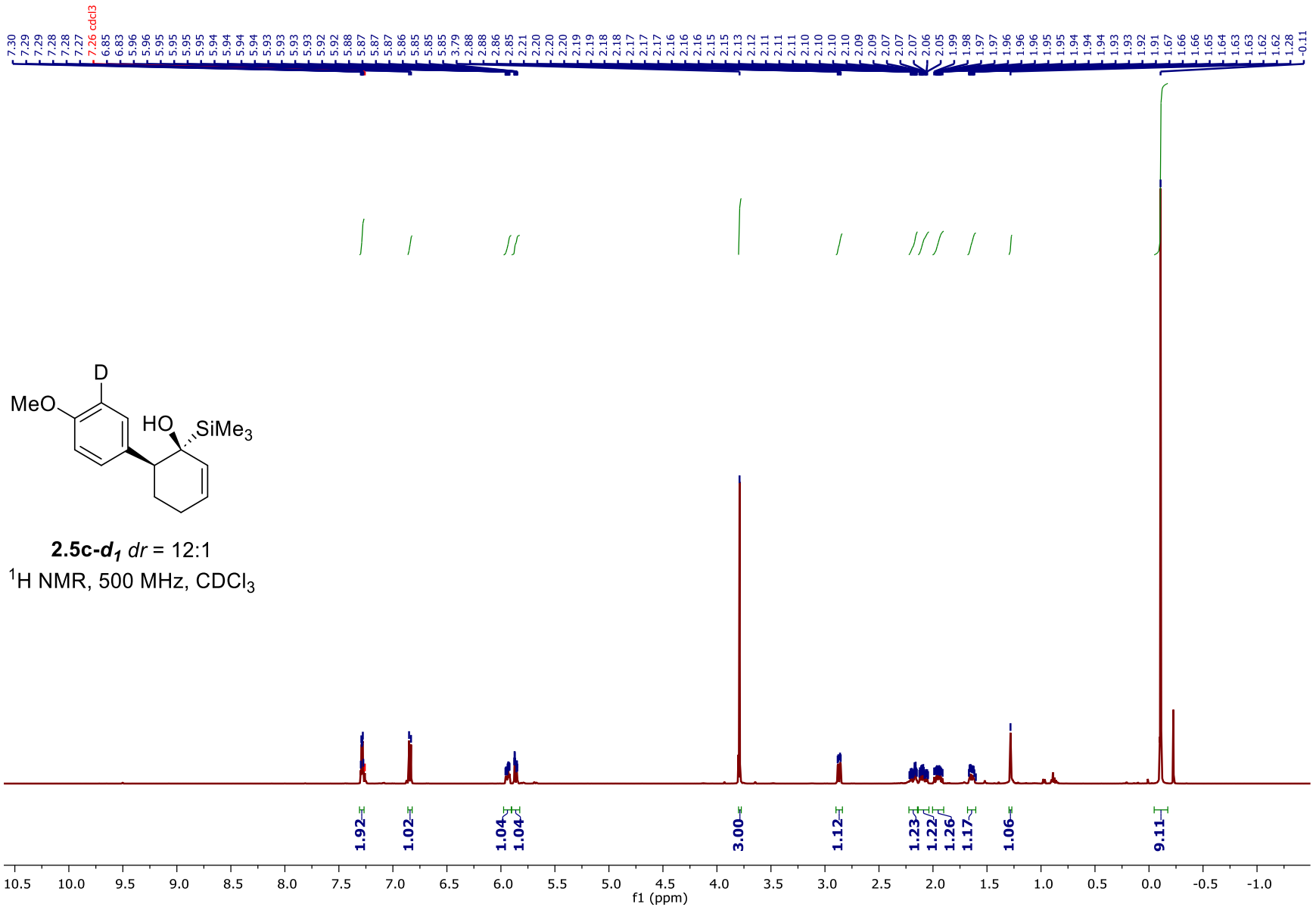


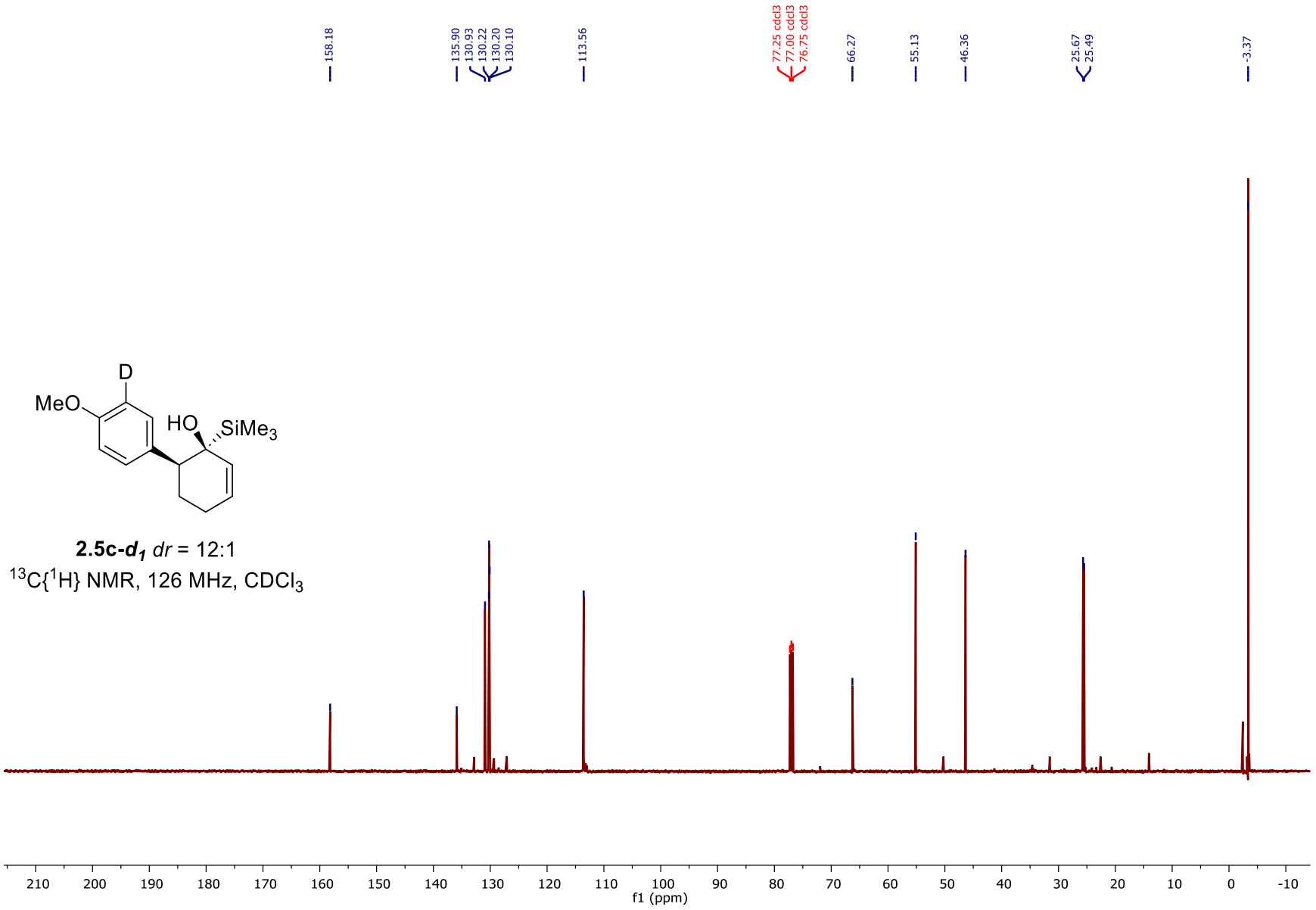
2.6c *dr* = 2:1

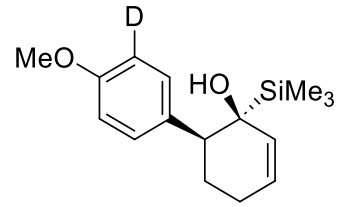
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$


MeO
O
SiMe3
2.7c
1H NMR, 500 MHz, CDCl3
1.99
2.07
1.02
1.03
3.21
2.36
1.20
2.25
1.25
9.01
f1 (ppm)


166.19
158.42
136.37
126.76
122.86
113.41
83.16
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
55.17
39.43
27.27
25.54
-2.26
MeO
O
SiMe3
2.7c
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)

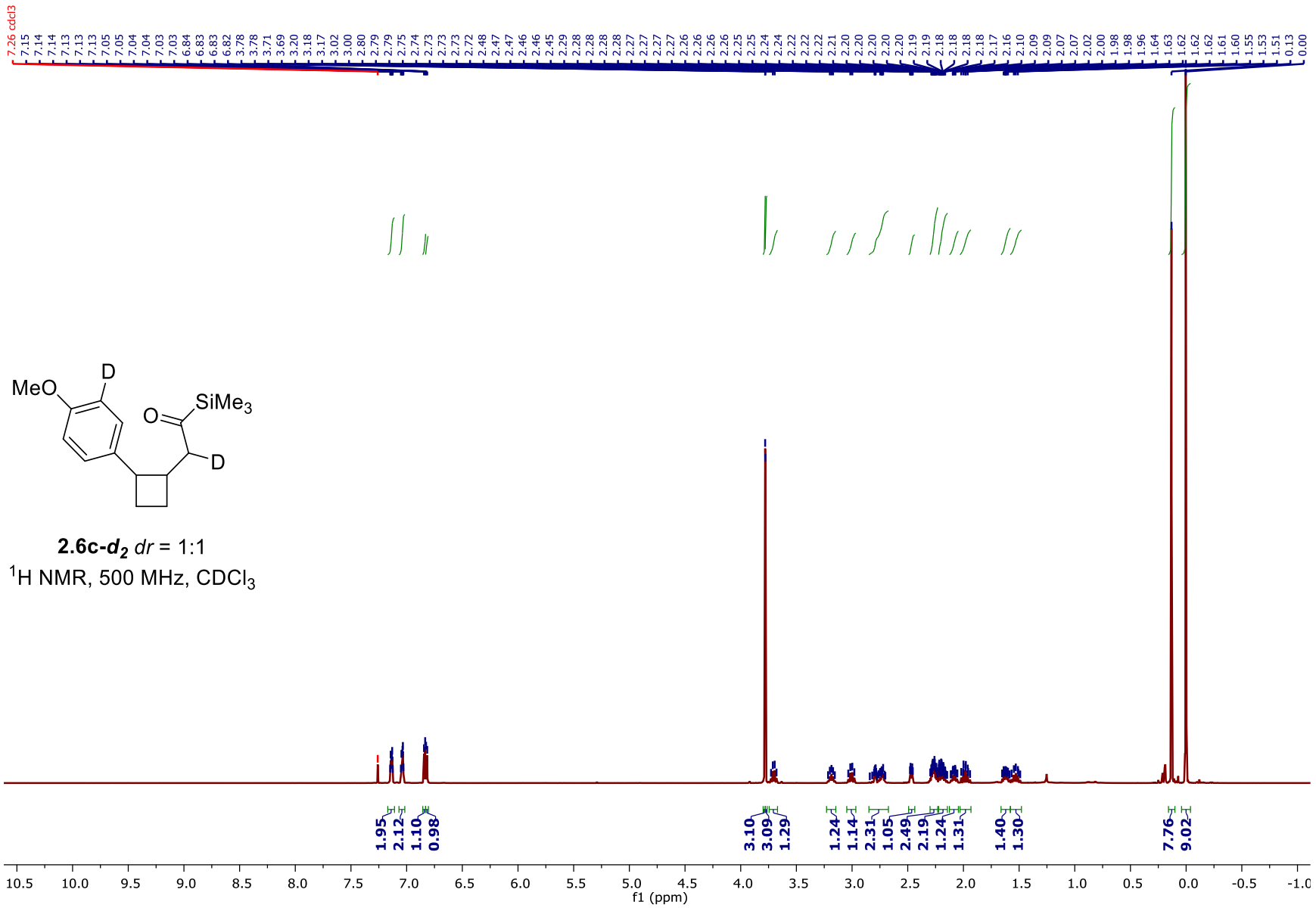

D
MeO
HO
SiMe3
2.5c-d1 dr = 12:1
1H NMR, 500 MHz, CDCl3
1.92
1.02
1.04
1.04
3.00
1.12
1.23
1.22
1.26
1.17
1.06
9.11
f1 (ppm)

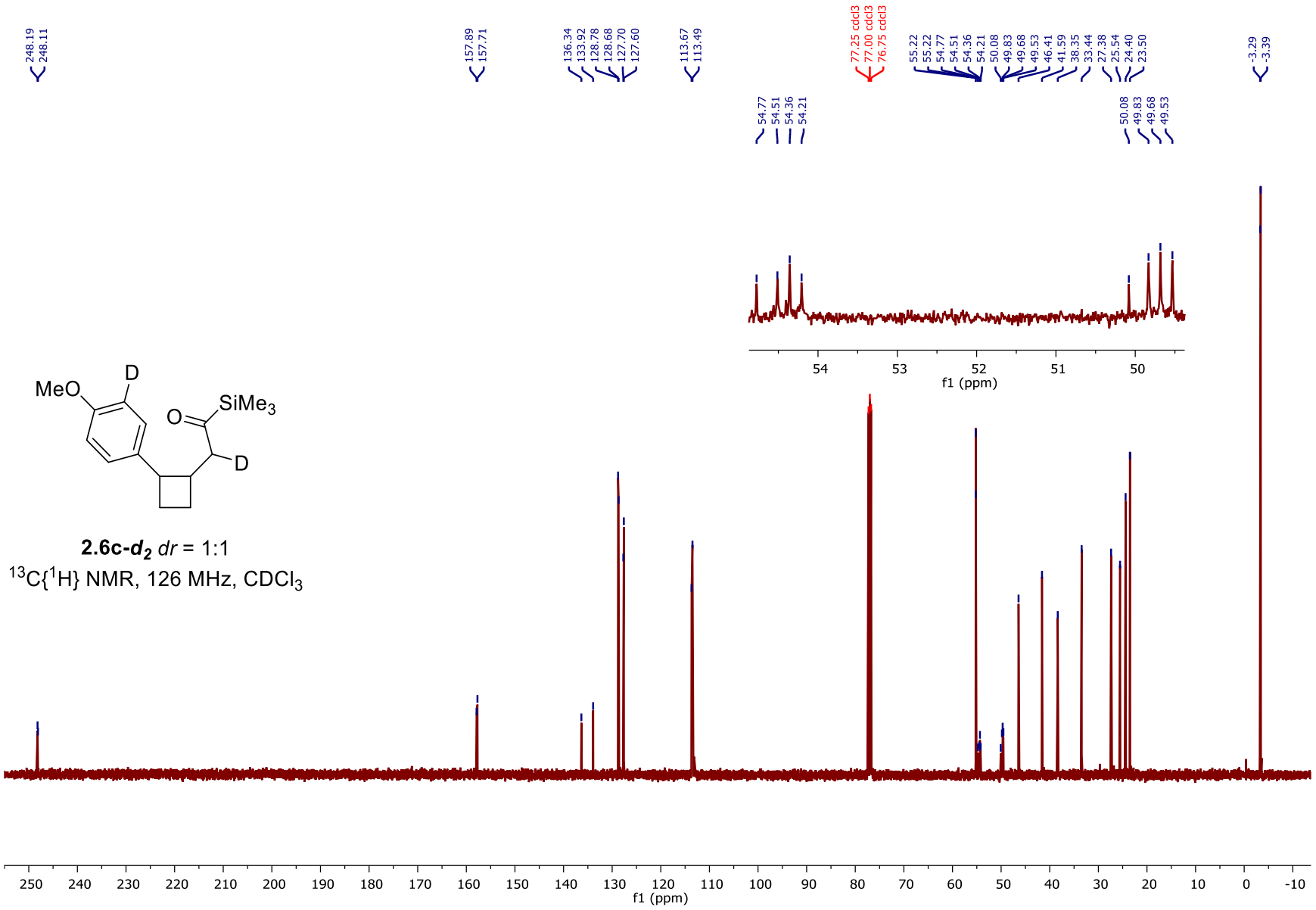

158.18
135.90
130.93
130.22
130.20
130.10
113.56
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
66.27
55.13
46.36
25.67
25.49
-3.37
D
MeO
HO
SiMe3
2.5c-d1 dr = 12:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2.5c-*d*$_1$ *dr* = 12:1

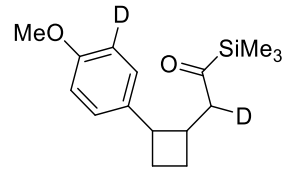
^{29}Si NMR, 99 MHz, $CDCl_3$


MeO
D
O
SiMe3
D
2.6c-d2 dr = 1:1
1H NMR, 500 MHz, CDCl3
f1 (ppm)



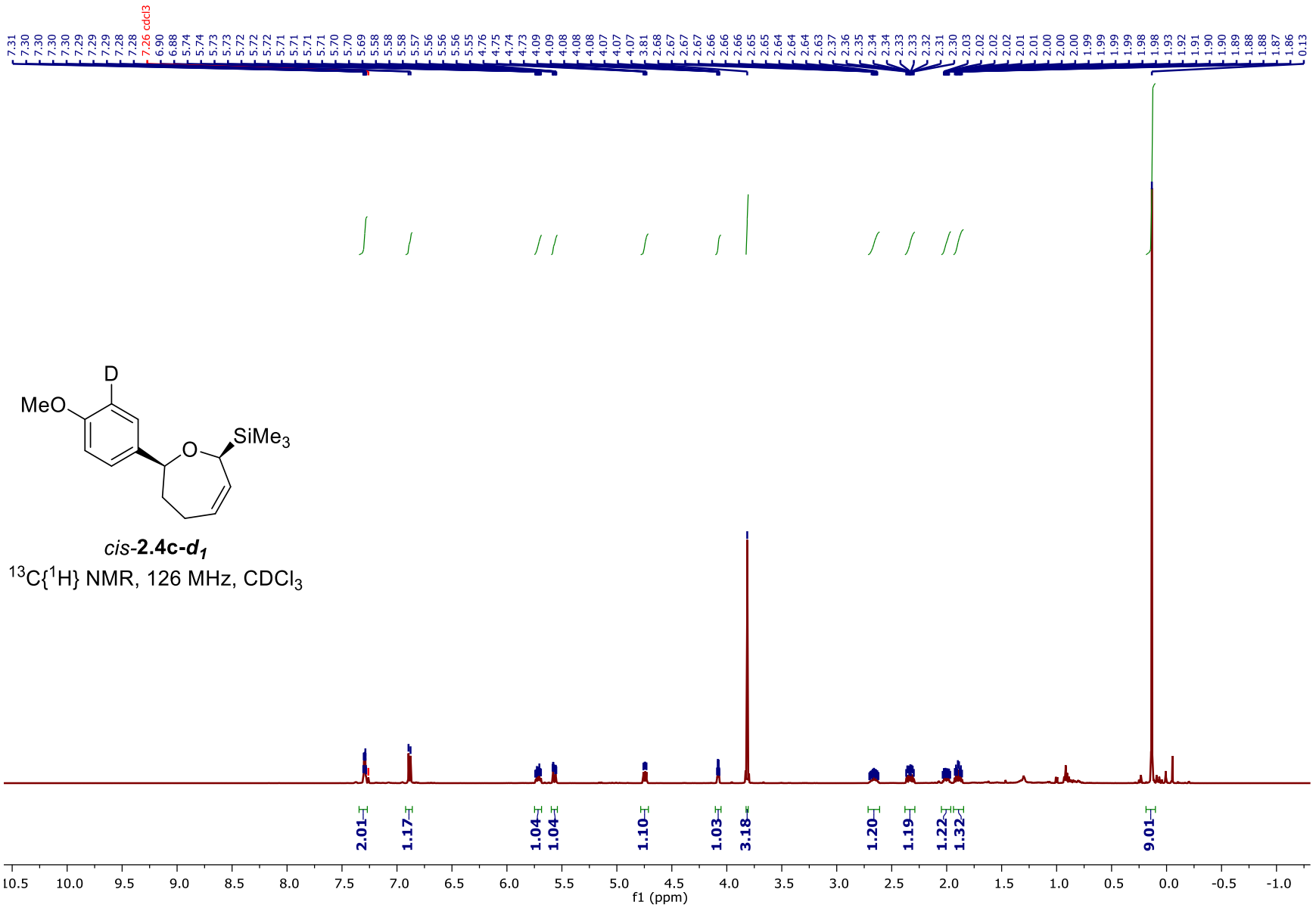
2.6c-d_2 *dr* = 1:1

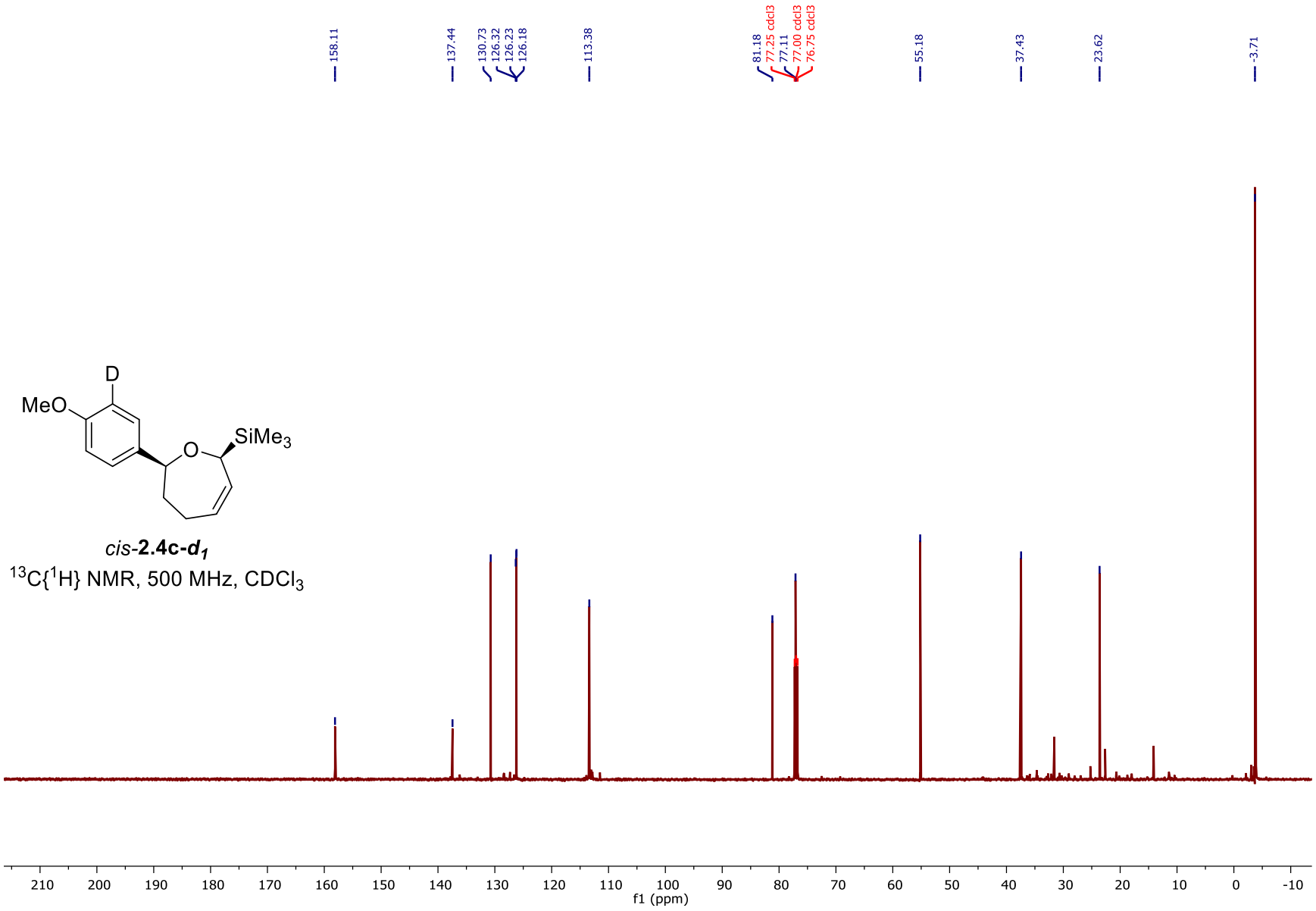
$^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$

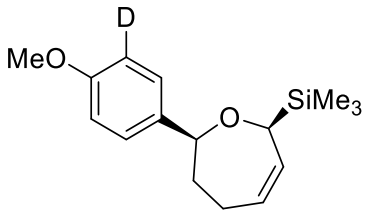


2.6c-d_2 *dr* = 1:1

^{29}Si NMR, 99 MHz, $CDCl_3$

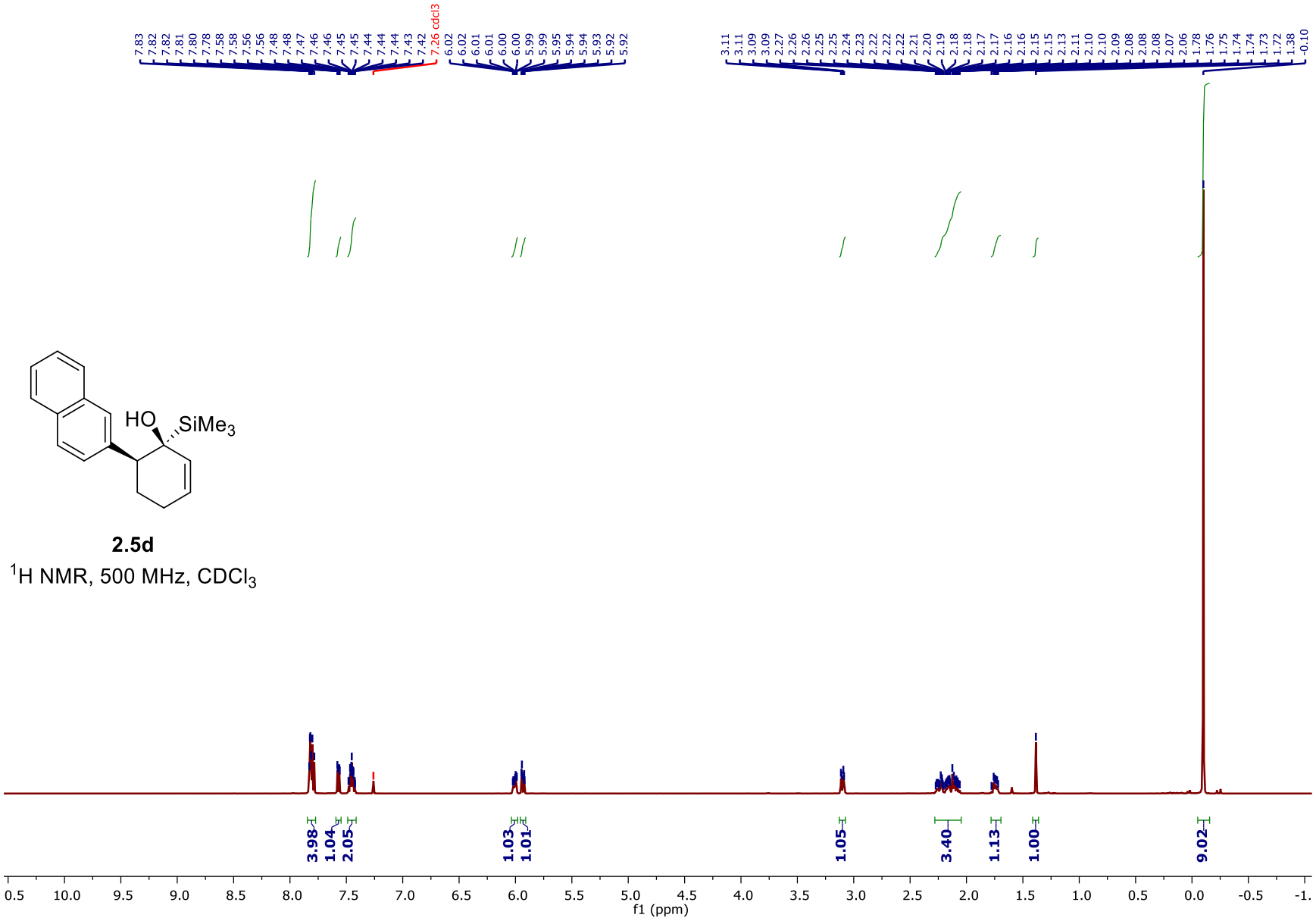

D
MeO
O
SiMe3
cis-2.4c-d1
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)


158.11
137.44
130.73
126.32
126.23
126.18
113.38
81.18
77.25 cdcl3
77.11
77.00 cdcl3
76.75 cdcl3
55.18
37.43
23.62
-3.71
D
MeO
O
SiMe3
cis-2.4c-d1
13C{1H} NMR, 500 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



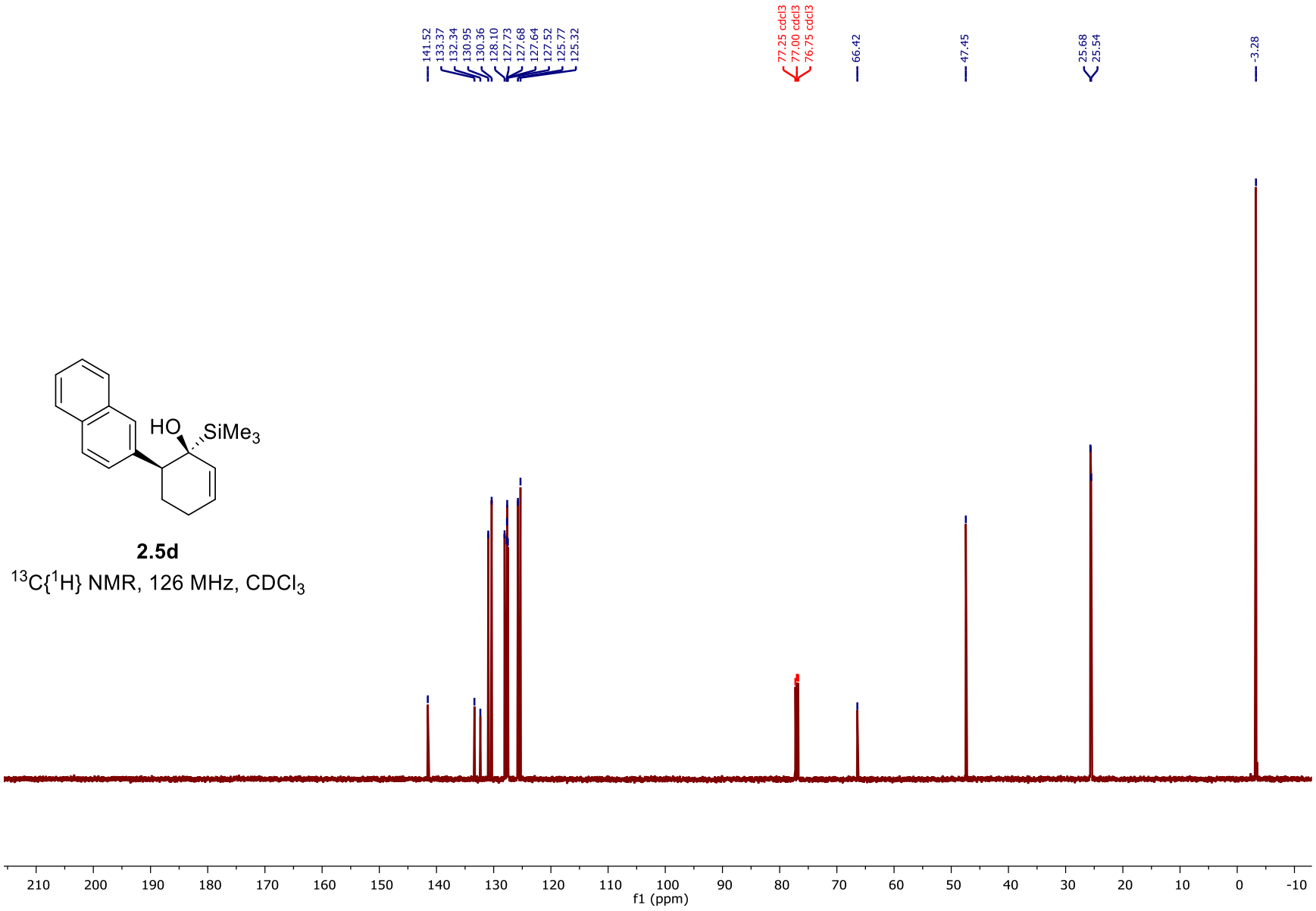
cis-**2.4c-*d*$_1$**

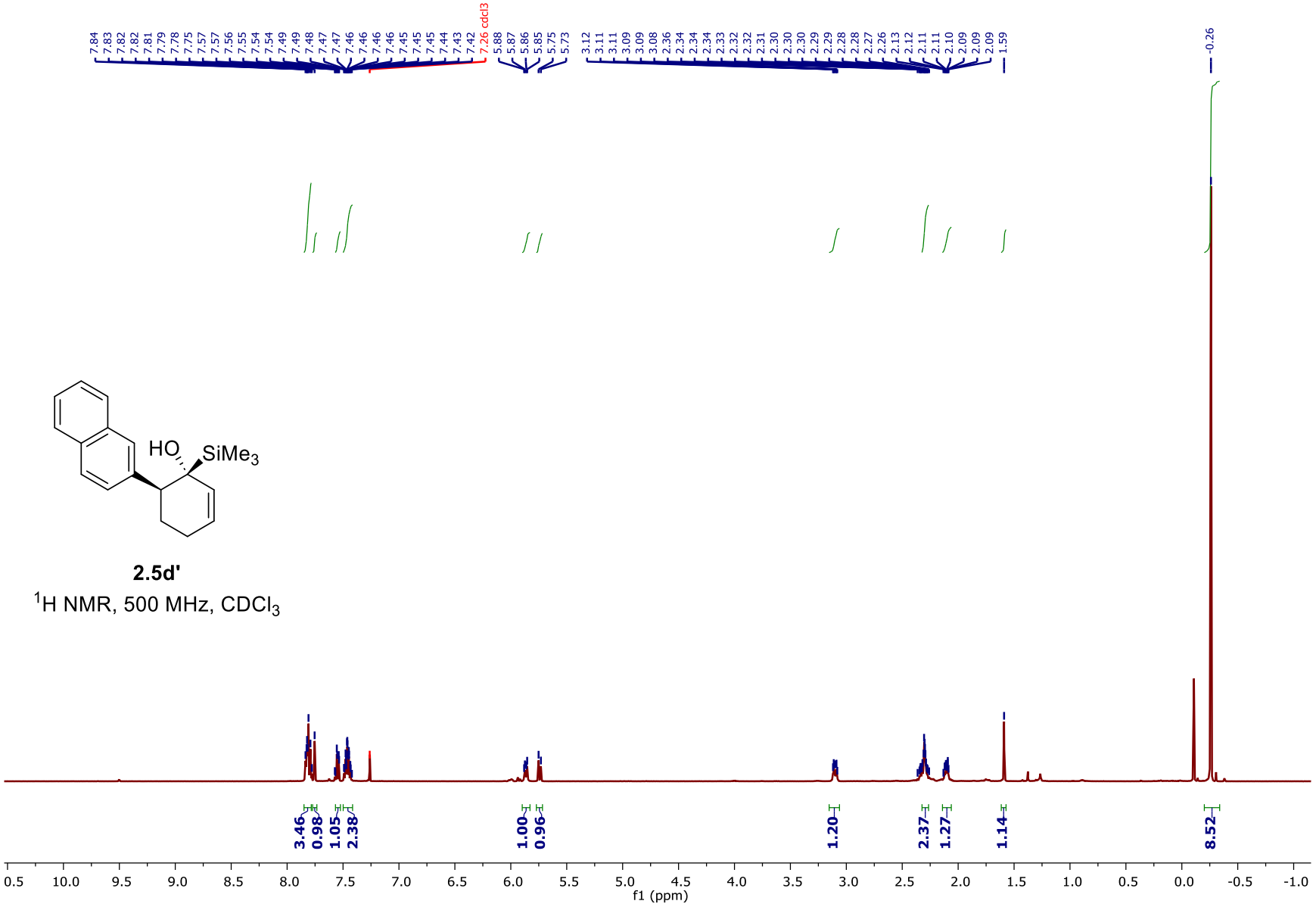
^{29}Si NMR, 99 MHz, $CDCl_3$

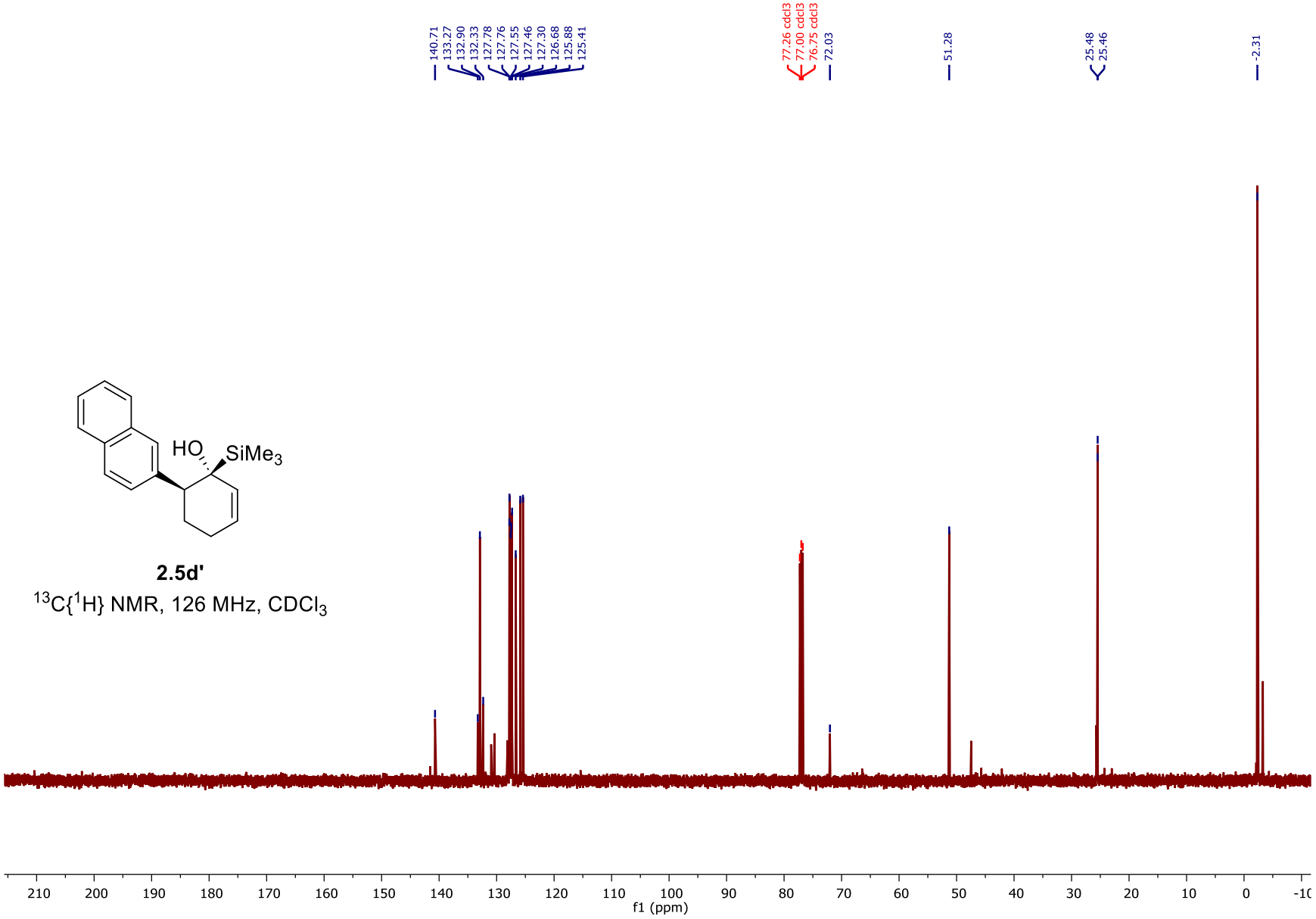


2.5d

^{1}H NMR, 500 MHz, $CDCl_3$


141.52
133.37
132.34
130.95
130.36
128.10
127.73
127.68
127.64
127.52
125.77
125.32
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
66.42
47.45
25.68
25.54
-3.28
HO
SiMe3
2.5d
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
SiMe3
2.5d'
1H NMR, 500 MHz, CDCl3
f1 (ppm)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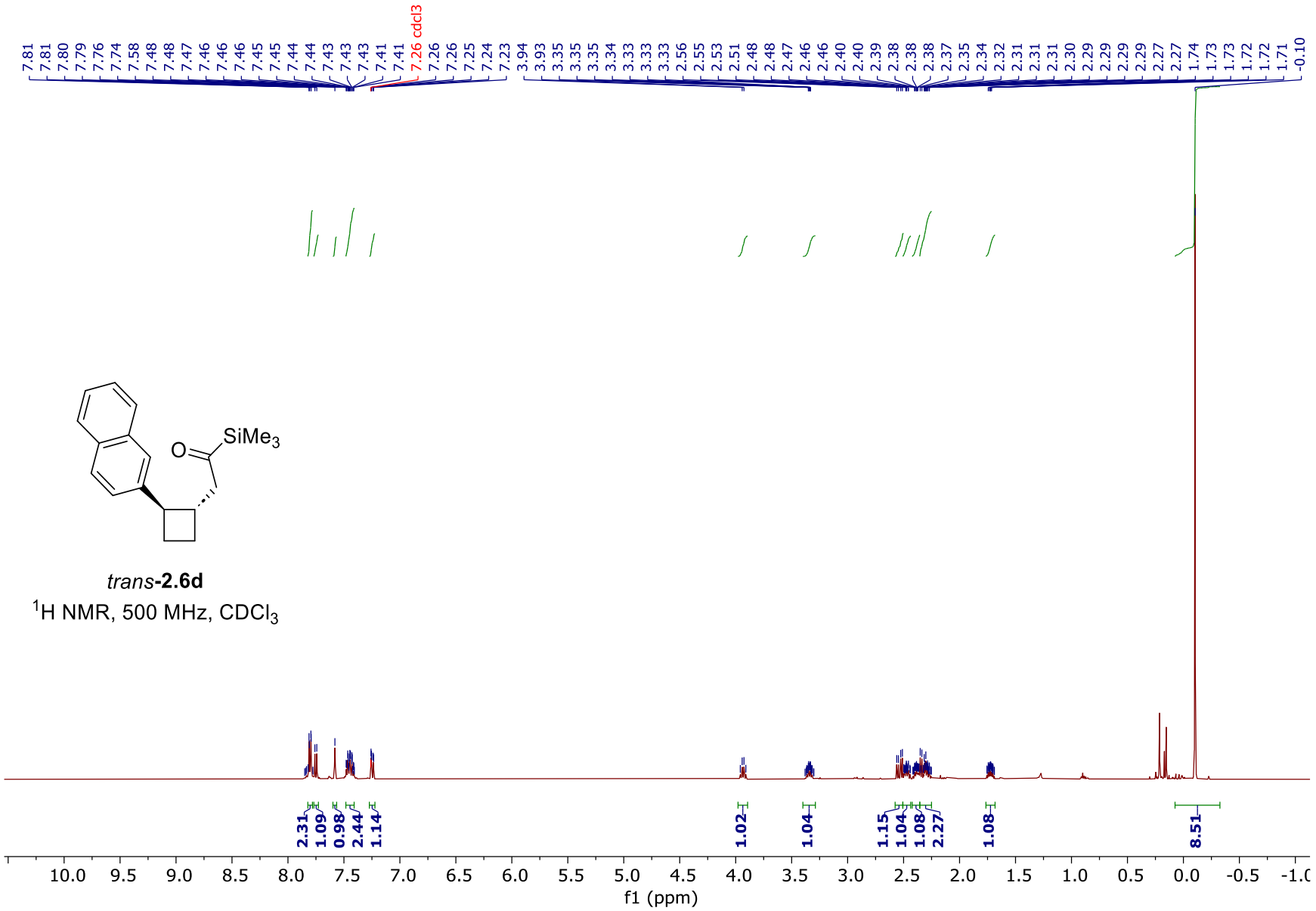
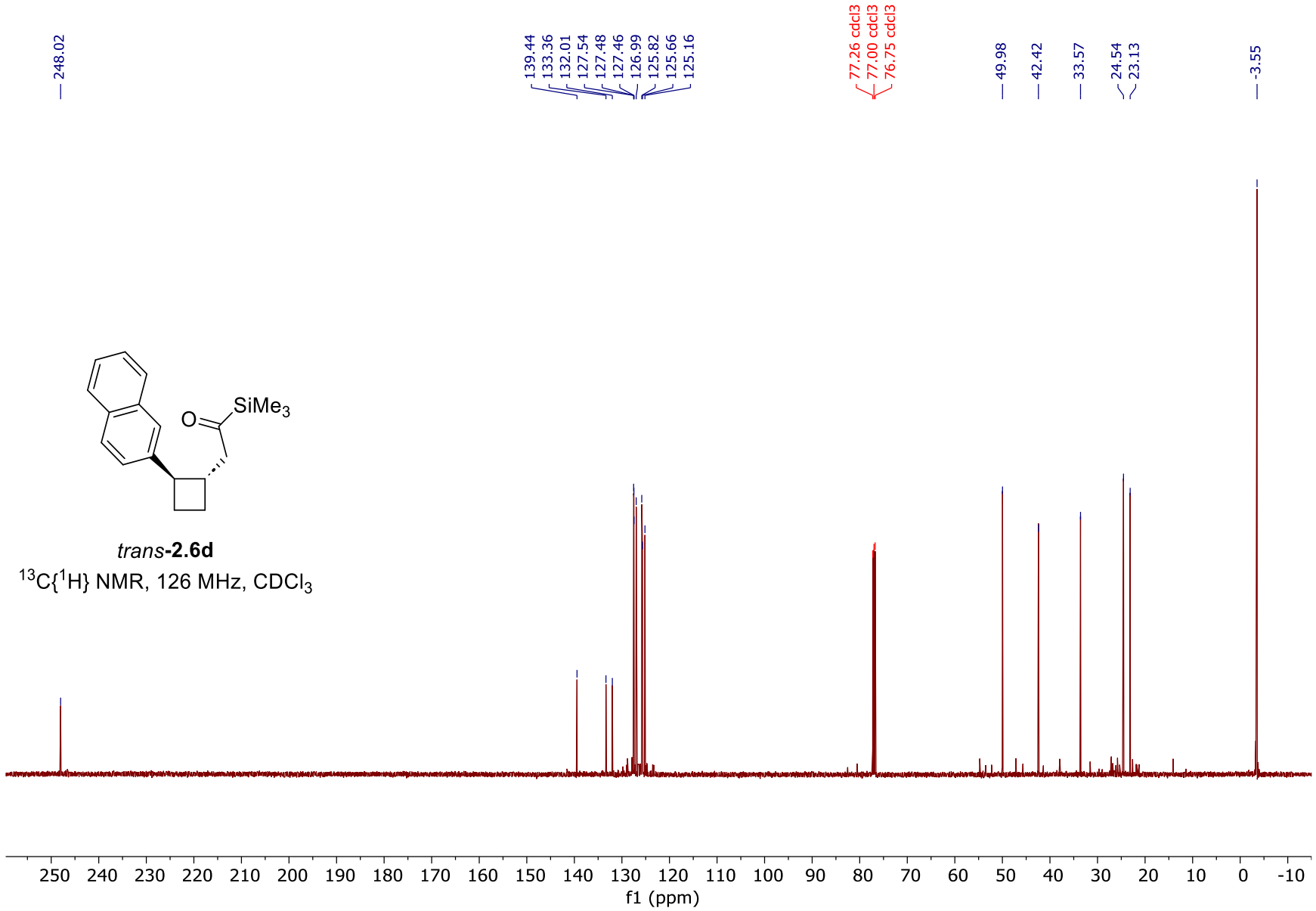
133.27
132.90
132.33
127.78
127.76
127.55
127.46
127.30
126.68
125.88
125.41
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
72.03
51.28
25.48
25.46
-2.31
HO
SiMe3
2.5d'
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



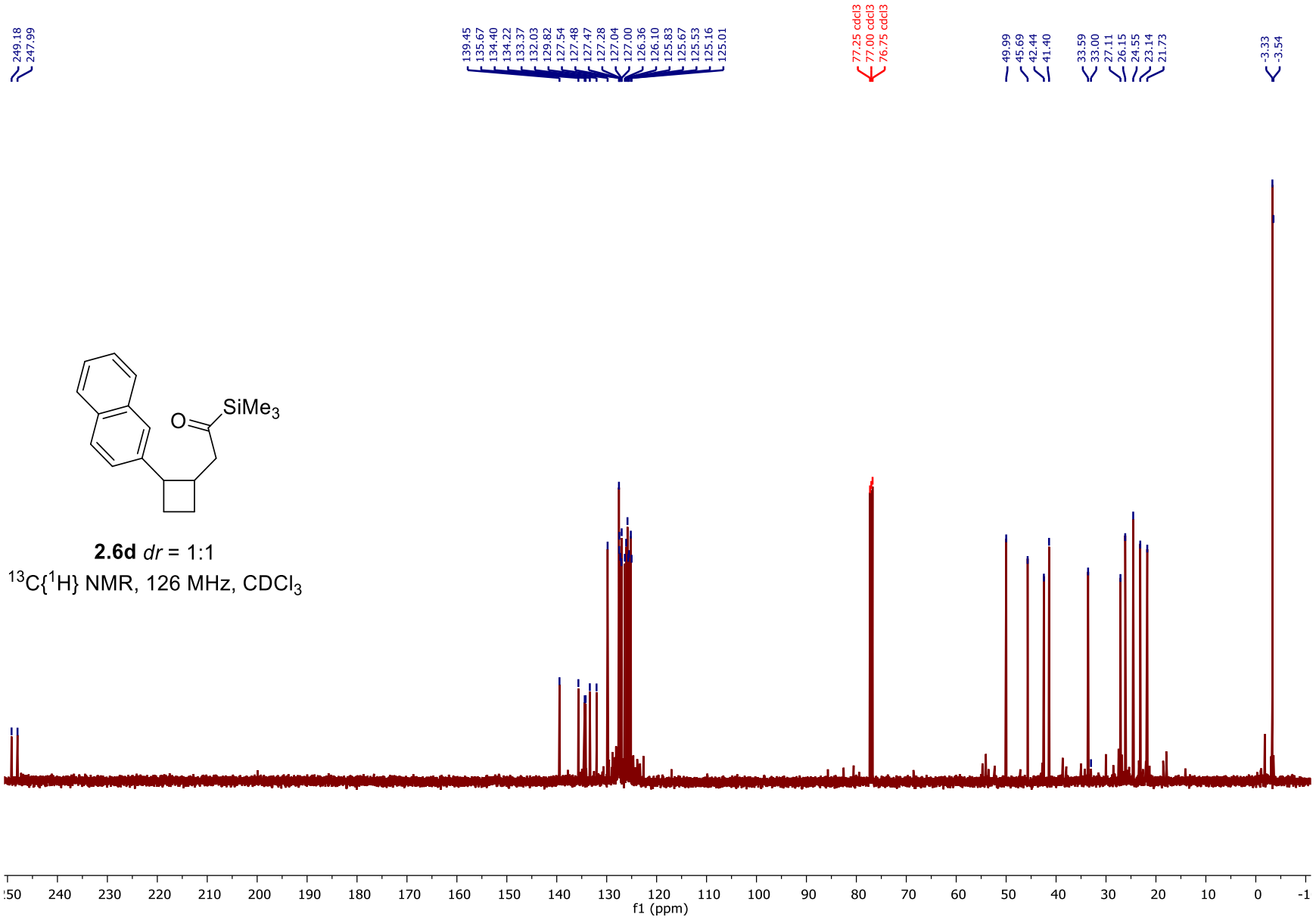
trans-**2.6d**

^{1}H NMR, 500 MHz, $CDCl_3$



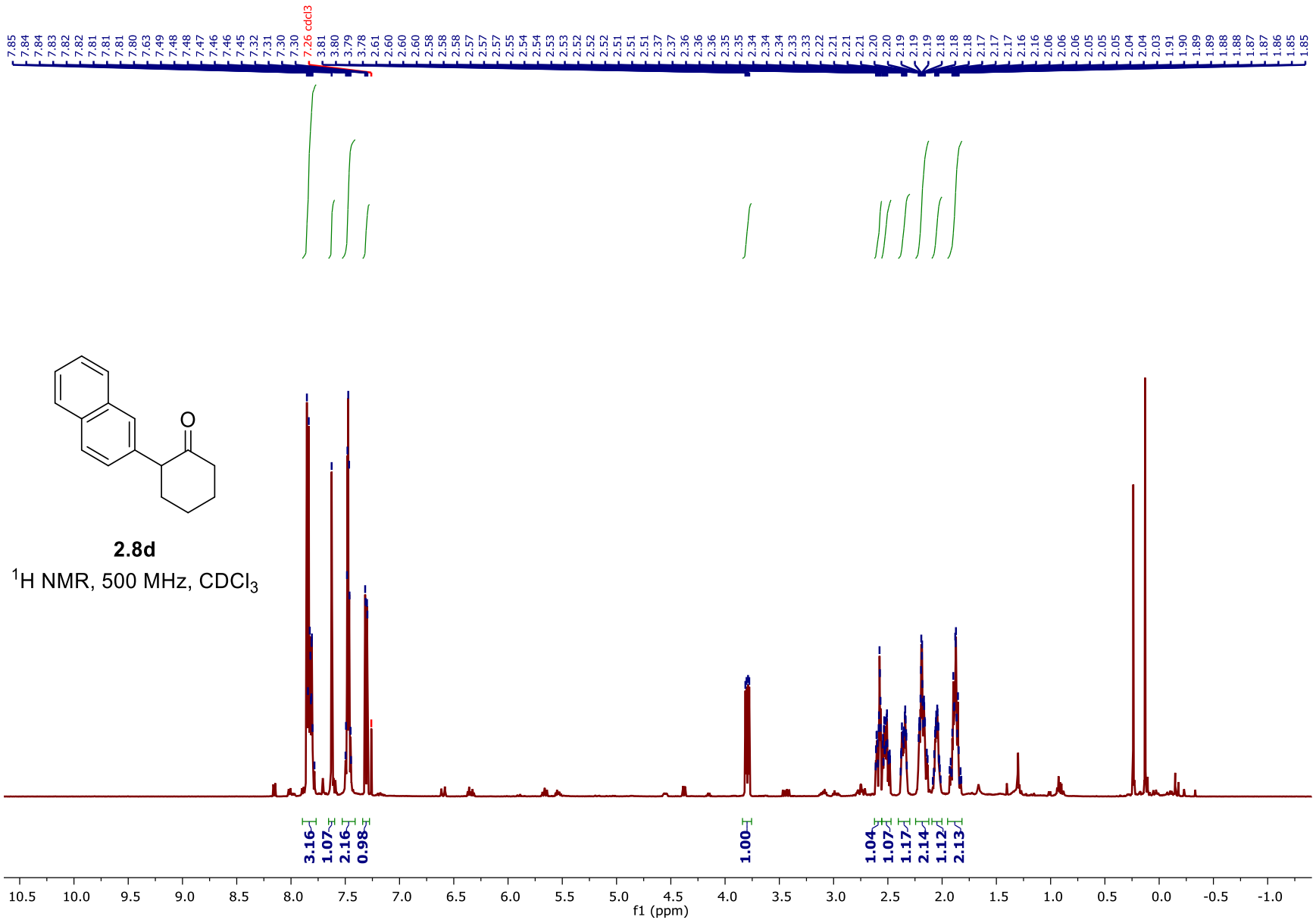
trans-**2.6d**

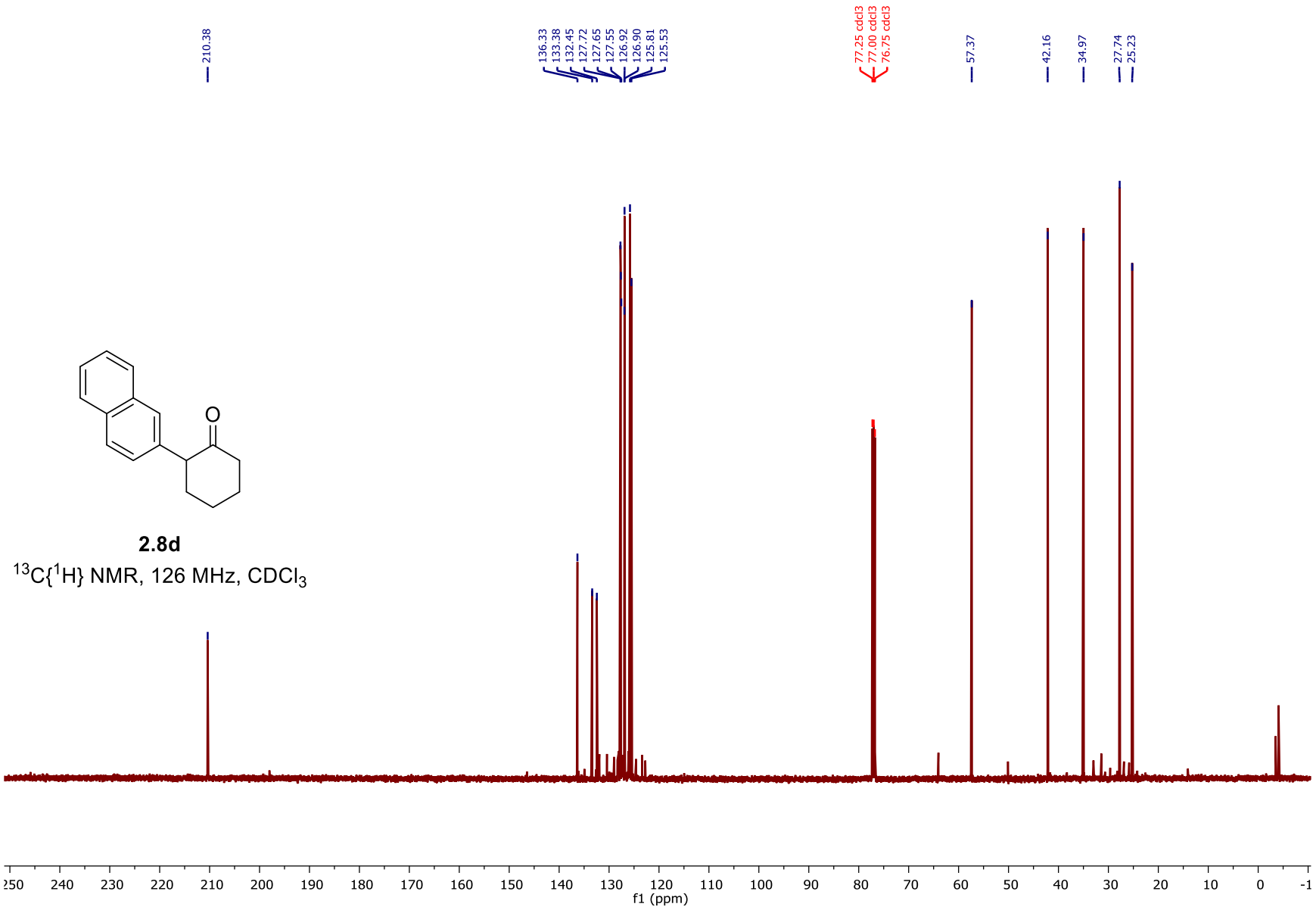
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$



2.6d *dr* = 1:1

$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$


O
2.8d
1H NMR, 500 MHz, CDCl3
7.26 cdcl3
3.16
1.07
2.16
0.98
1.00
1.04
1.07
1.17
2.14
1.12
2.13
f1 (ppm)


210.38
136.33
133.38
132.45
127.72
127.65
127.55
126.92
126.90
125.81
125.53
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
57.37
42.16
34.97
27.74
25.23
O
2.8d
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$
f1 (ppm)

CHAPTER 3.

SILYLCYCLOPROPANES BY SELECTIVE [1,4]-WITTIG REARRANGEMENT OF 4-SILYL-5,6-DIHYDROPYRANS

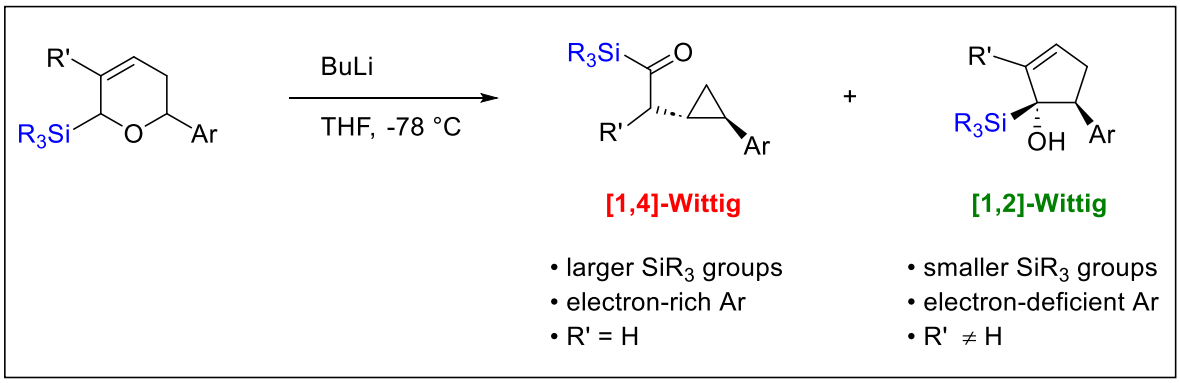
This work has been adapted with permission from: Mori-Quiroz, L. M.; Maloba, E. W.; Maleczka, R. E., Jr. Silylcyclopropanes by selective [1,4]-Wittig rearrangement of 4-silyl-5,6-dihydropyrans. *Org. Lett.* **2021**, *23*, 5724 – 5728. This work was done in collaboration with Dr. Luis Martin Mori-Quiroz. Dr. Mori worked on reaction design and optimization. I worked on additional substrate scope, comparative studies, and derivatization of compound **3.2c**.

3.1. Introduction

[1,4]-Wittig rearrangements of allyl ethers generate enolates, whereas the more common [2,3]- and [1,2]-pathways produce alkoxides.[1-6] In addition, the [1,4]-Wittig pathway is inherently interwoven with the [1,2]-manifold, which typically predominates. Despite its synthetic potential, the [1,4]-migration path is largely underdeveloped with selective and efficient [1,4]-Wittig pathways being relatively rare and of limited scope.[7-9]

In 2006, our research group found that (1-trimethylsilyl)allylbenzyl ether rearranged selectively through the [1,4]-pathway, forming the acylsilane product.[10] The apparent ability of the silyl group to allow (1) selective allylic deprotonation and (2) selective [1,4]-migration of the benzyl group led us to explore more complex acyclic analogues. These studies were hampered by lower reactivity of such higher analogues, which we speculated was due to sterics hindering access to conformations necessary for deprotonation.[11] In contrast, we found that related cyclic ethers rearrange efficiently to give α-cyclopropyl acylsilanes or α-silylcyclopentenols by [1,4]- and [1,2]-Wittig migrations, respectively.[12] We also learned that cis/trans diastereomers of these cyclic ethers exhibited very different rates of deprotonation, again presumably reflecting their different ability to

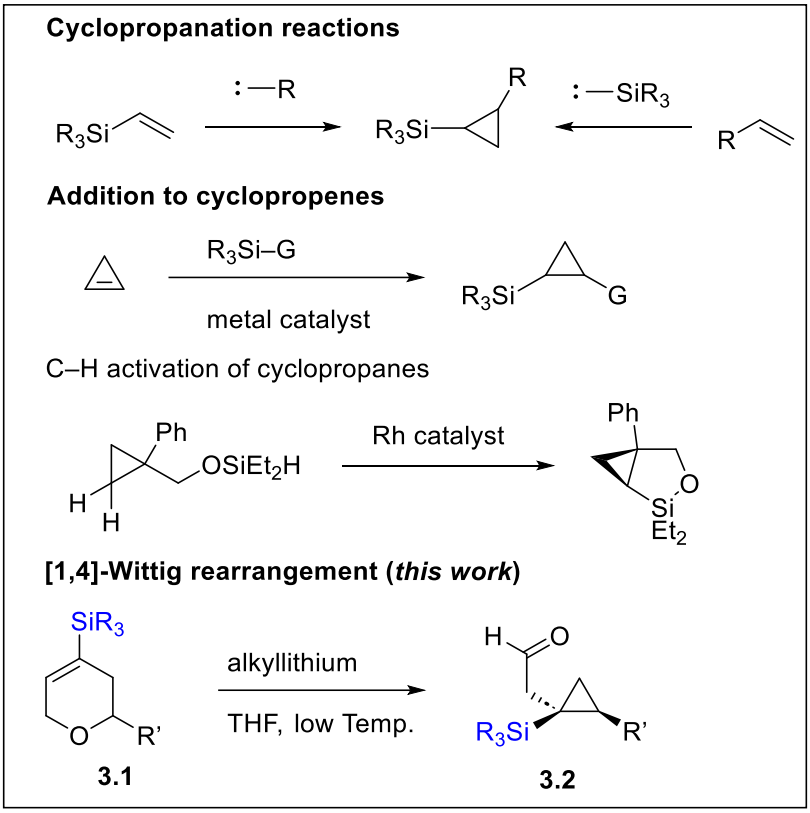
achieve the optimal conformation for deprotonation. Once deprotonated, [1,4]-migration and the competing [1,2]-pathway proceed in a stereoconvergent fashion, with [1,4]-/[1,2]- selectivity being highly sensitive to steric and electronic factors (Scheme 3.1).[12]



Scheme 3.1: Wittig rearrangements of 2-silyl-6-aryl-5,6-dihydropyrans

A question that arose from these studies was whether relocation of the silyl group to the 4-position of the dihydropyran scaffold would favor the [1,4]- or [1,2]-pathway. Herein, we report that 4-silyl-5,6-dihydropyrans undergo highly selective [1,4]-Wittig rearrangement to afford silylcyclopropyl acetaldehydes.

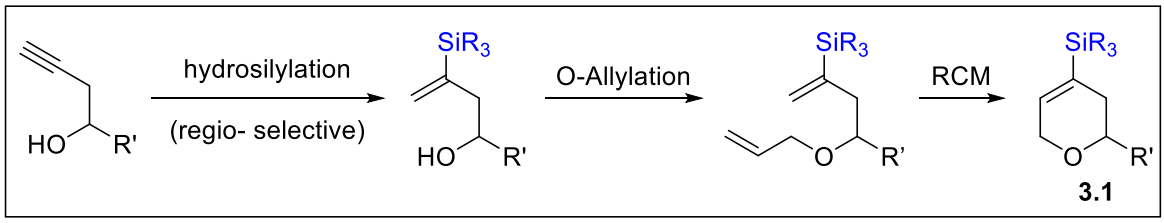
Silylcyclopropanes are versatile building blocks in organic synthesis.[13] For instance, they engage in reactions with both nucleophilic and electrophilic partners. Traditional synthetic approaches (Scheme 3.2) involve the cyclopropanation of vinylsilanes[14-24] and the addition of silyl carbenoids to olefins.[25-32] Other metal-catalyzed processes have been developed, such as the addition of silyl reagents to cyclopropenes,[33-37] intramolecular C–H silylation of cyclopropanes,[38] and annulation reactions.[39-43] To the best of our knowledge, the synthesis of silylcyclopropanes by means of ring contraction had not been reported.



Scheme 3.2: General approaches to silylcyclopropanes

3.2. Synthesis of 4-silyl-5,6-dihydro-*2H*-pyrans

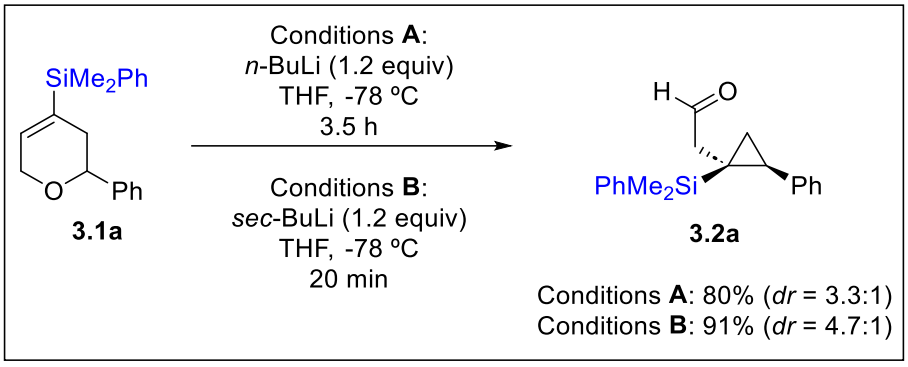
For our purpose, the 4-silyl-5,6-dihydropyrans were prepared from readily available homopropargylic alcohols in three steps involving regioselective alkyne hydrosilylation using Trost catalyst[44,45] or Tomooka's Pt-catalyzed method,[46] followed by O-allylation, and ring-closing metathesis (RCM) of the diene precursor using Grubbs' second-generation catalyst (Scheme 3.3).[47,48] A variety of substrates bearing different silyl groups were thus accessed.



Scheme 3.3: Synthetic route to dihydropyrans **3.1**

3.3. Optimization of reaction conditions for Wittig rearrangement

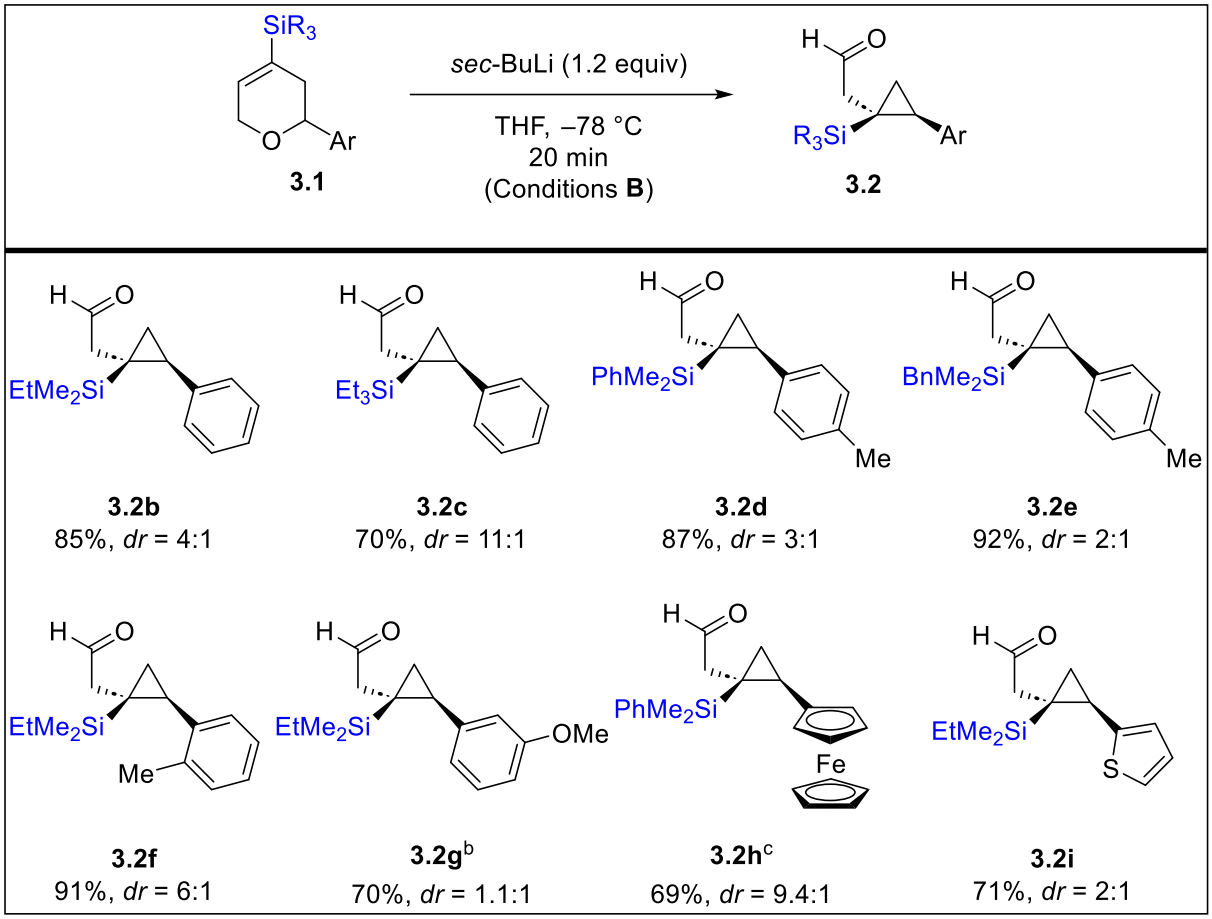
We started this study by evaluating dihydropyran **3.1a** under Wittig conditions used in our previous reports (Scheme 3.4). Treatment of **3.1a** with *n*-butyllithium in THF at −78 °C for 3.5 h (conditions A) afforded exclusively [1,4]-Wittig product **3.2a** in 80% yield with modest diastereoselectivity (3.3:1), together with a small amount of unreacted **3.1a** (7%). The use of the stronger *sec*-butyllithium (conditions B) resulted in complete deprotonation followed by rearrangement to afford **3.2a** in 91% yield after only 20 min. Slightly higher diastereoselectivity (4.7:1) was also realized. Under both reaction conditions, we were unable to detect any [1,2]-Wittig product by ^{1}H NMR analysis of the crude reaction mixtures.



Scheme 3.4: [1,4]-Wittig rearrangement of model substrate **3.1a**

3.4. Wittig rearrangements of 4-silyl-5,6-dihydro-*2H*-pyrans with aryl substituents at the migrating carbon

We next evaluated a variety of substrates bearing different silyl groups at the 4-position and aryl substituents at the migrating carbon (Scheme 3.5). The smaller $EtMe_2Si$ group afforded silylcyclopropylacetaldehyde **3.2b** in 85% yield and 3.3:1 diastereoselectivity, whereas the more sterically demanding Et_3Si group led to silylcyclopropane **3.2c** in a slightly lower yield (70%) but higher diastereoselectivity (11:1).



Scheme 3.5: Substrate scope of aryl-substituted dihydropyrans bearing different silyl groups[a]

[a]Diastereoselectivity determined by ^{1}H NMR of the crude reaction mixture
[b]Reaction run on a 2 mmol scale
[c]A small amount (<5%) of the presumed [1,2]-Wittig product within a complex mixture was observed but not fully characterized
[d]15% of unreacted dihydropyran **3.1h** was recovered
[e]2.2 equiv of *sec*-BuLi was used

Consistent with prior observations, electron-donating groups such as a 4-methyl on the phenyl group afforded exclusively silylcyclopropanes **3.2d** and **3.2e** bearing $PhMe_2Si$ and $BnMe_2Si$ groups in good yields and low diastereoselectivities. *o*-Methyl substitution at the aryl group was tolerated, leading to silylcyclopropane **3.2f** in 91% yield and 8.3:1 diastereoselectivity. *m*-Methoxy substitution of the aryl ring, which confers an electron-deficient character to the migrating (benzylic) carbon, afforded predominantly the [1,4]-Wittig product **3.2g** in 61% yield. This was in contrast with the observation in our previous work on 2-

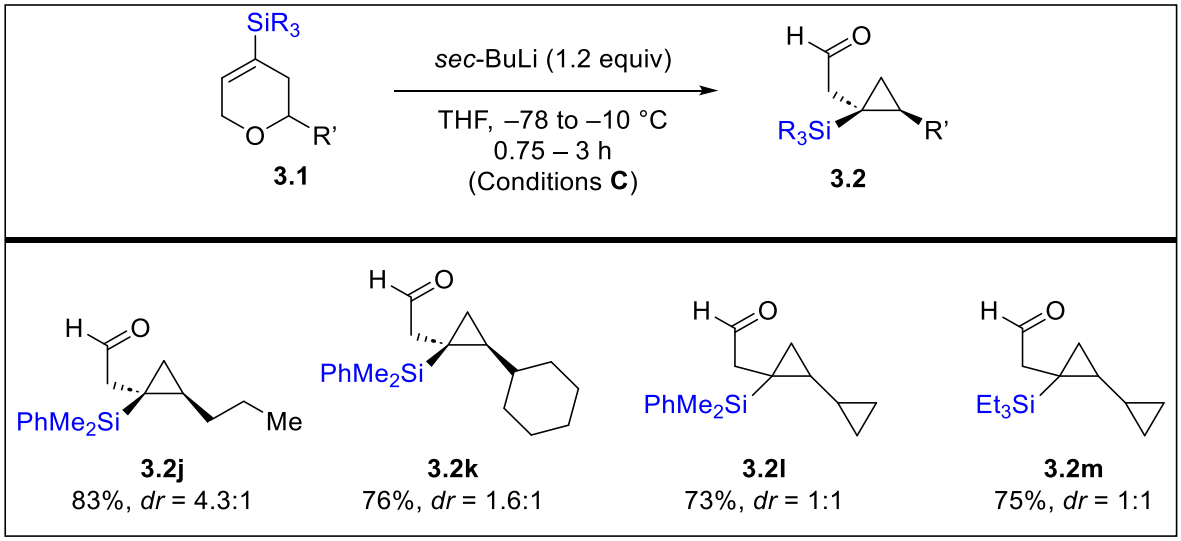
silyl-6-aryl-5,6-dihydropyrans, where a near equal mixture of [1,2], and [1,4] products was observed.[12] Other (hetero)aromatic substituents at the migrating center such as ferrocenyl and 2-thiophene-yl were tolerated, providing access to silylcyclopropyl acetaldehydes **3.2h** and **3.2i** in 69% and 71% yield, respectively. However, in contrast to all previous examples, the major diastereomer in **3.2i** was trans. This outcome is best explained by the fact that 2.2 equiv of *sec*-BuLi was used to ensure complete allylic deprotonation of **3.2i**. Such conditions were used because the 2-thiophenyl group undergoes competitive deprotonation at the 5 position, as previously observed.[12] Therefore, the actual species that undergoes rearrangement is likely the dianion **Li_2–3.1i** (Scheme 3.5, inset), whose unique electronic characteristics might be responsible for the observed stereochemistry of **3.2i**.

We determined the relative stereochemistry of the major diastereomer in **3.2a** by NOESY studies and assigned the relative stereochemistry of compounds **3.2b**–**3.2i** by comparison. Specifically, protons corresponding to the alkyl groups attached to silicon (Me, Et) appeared upfield in the NMR spectrum relative to those in the minor diastereomer, presumably due to shielding effects by the *cis*-oriented aromatic group. In addition, protons corresponding to methyl groups in dimethylsilyl products (i.e., **3.2b**, **3.2d**–**3.2h**) became inequivalent due to the expected slow rotation induced by the bulky aryl groups. We further confirmed the structure of compound **3.2c** by X-ray crystallographic analysis of its 2,4-dinitrophenylhydrazine derivative (see the experimental section).

3.5. Wittig rearrangements of 4-silyl-5,6-dihydro-*2H*-pyrans with alkyl substituents at the migrating carbon

We next evaluated dihydropyrans bearing alkyl substituents at the migrating carbon (Scheme 3.6). These substrates underwent slow deprotonation under conditions A and B (see Scheme 3.4). However, addition of *sec*-butyllithium at −78 °C and warming to −10 °C

(conditions C) allowed deprotonation and rearrangement with excellent [1,4]-selectivity. Dihydropyrans bearing $PhMe_2Si$ groups on the 4-position and *n*-propyl and cyclohexyl substituents at the migrating carbon led to the corresponding silylcyclopropanes **3.2j** and **3.2k** in 83% and 76% yields, respectively. The *n*-propyl-substituted dihydropyran (**3.2j**) rearranged with higher diastereoselectivity compared to the dihydropyrans bearing cycloalkyl groups (Scheme 3.6). Interestingly, cyclopropyl-substituted dihydropyrans **3.1l** and **3.1m** underwent rearrangement without observable formation of the ring-opened products.

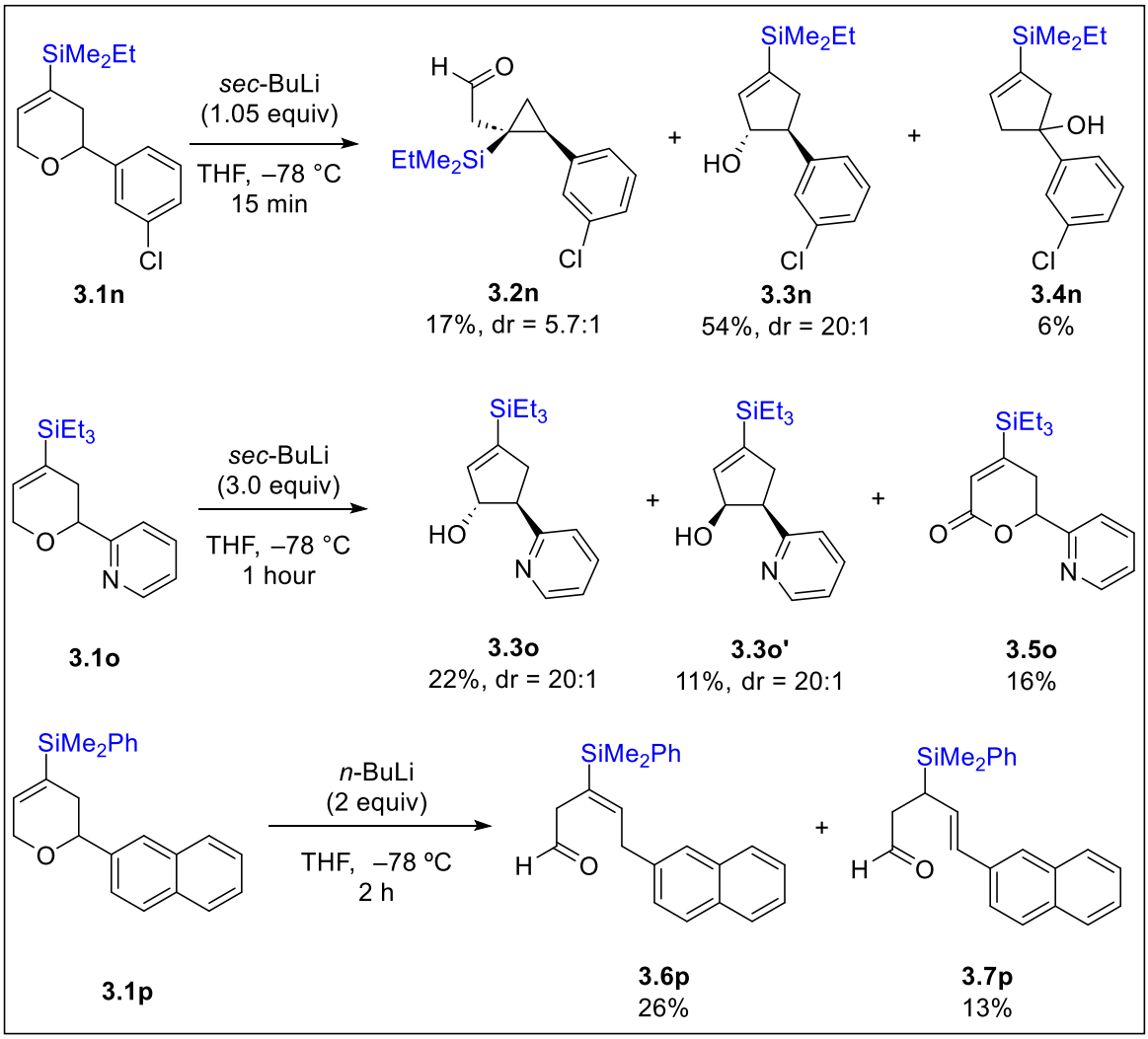


Scheme 3.6: Selective [1,4]-Wittig rearrangement of dihydropyrans **3.1** bearing alkyl groups at the migrating center[a]
[a]Diastereoselectivity determined by ^{1}HNMR of the crude reaction mixture

3.6. Rearrangement of substrates bearing electron-deficient aryl groups and 2-naphthyl derivative

Dihydropyrans with electron-deficient aryl groups such as **3.1n** underwent Wittig rearrangements with flipped [1,4]-/[1,2]-selectivity. Here, the predominant product was the [1,2]-Wittig alcohol **3.3n** (54%), followed by the [1,4]-silylcyclopropane **3.2n** (17%) and a small amount of an isomeric [1,2]-Wittig product **3.4n** (6%). Formation of **4n** indicates that benzylic deprotonation becomes competitive when electron-deficient aryl groups are present. Similarly, 2-pyridyl-substituted dihydropyran (**3.1o**) predominantly afforded diastereomeric [1,2]-Wittig

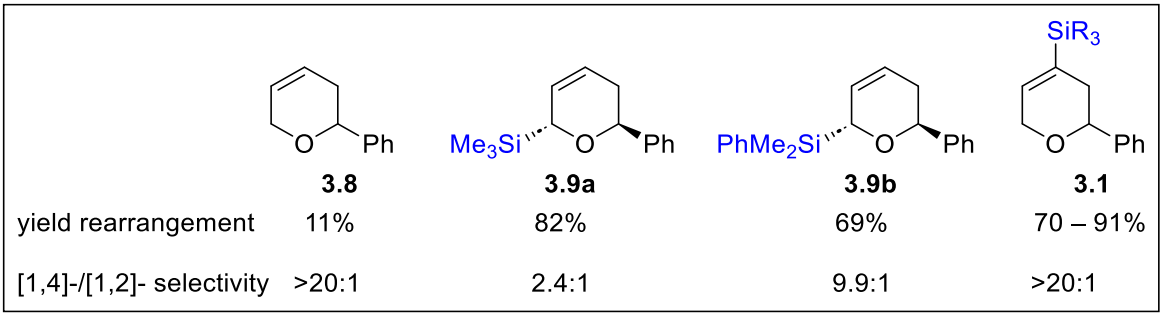
products **3.3o** and **3.3o′** (2:1 ratio), resulting from allylic deprotonation. Unreacted **3.1o** could not be isolated and instead underwent oxidation during workup and purification to give lactone **3.5o**.[49] Attempts to access the 4-pyridyl analogue using our established route (Scheme 3.3) were unsuccessful due to reluctance of the diene precursor to undergo ring-closing metathesis (see the experimental section). 2-Naphthyl-substituted dihydropyran (**3.1p**) failed to undergo Wittig rearrangement, and instead, ring-opened products **3.6p** and **3.7p** were observed (Scheme 3.7).



Scheme 3.7: Rearrangement of substrates bearing electron-deficient aryl groups and 2-naphthyl derivative

3.7. Comparative studies on Wittig rearrangements of dihydropyrans

On a last note, it is worth comparing the ability of silyldihydropyrans **3.1** and isomeric **3.9a/b**[12] to undergo clean rearrangements relative to the unsubstituted analogue **3.8** (Figure 3.1). While **3.1** and **3.9a/b** undergo Wittig rearrangements in good yields, dihydropyran **3.8** reacts sluggishly to give a low yield of [1,4]-Wittig product together with a complex mixture of undetermined byproducts. On the other hand, the exclusive [1,4]-selectivity of **3.1** is independent of the nature of the silyl groups, while those of **3.9a** or **3.9b** are very sensitive to the sterics of the silyl group.



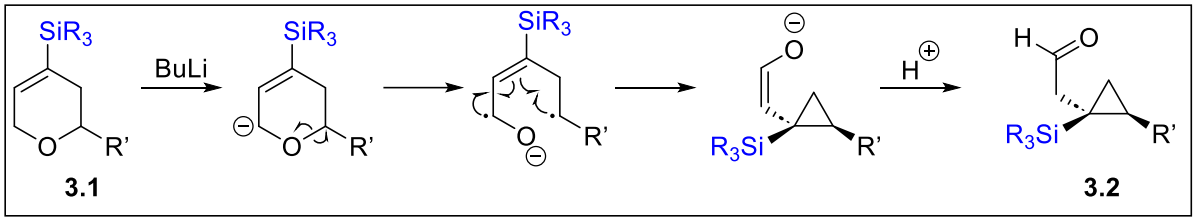
	3.8	**3.9a**	**3.9b**	**3.1**
yield rearrangement	11%	82%	69%	70 – 91%
[1,4]-/[1,2]- selectivity	>20:1	2.4:1	9.9:1	>20:1

Figure 3.1: Comparison of yields and [1,4]-/[1,2]-selectivities of **3.1** vs 2-silyl analogues **3.9a**/**3.9b** and desilylated analogue **3.8**

3.8. Proposed mechanism of the [1,4]-Wittig rearrangement of 4-silyl-6-aryl(alkyl)-5,6-dihydroprans

In line with our previously proposed mechanistic hypothesis, we maintain that the [1,4]-Wittig rearrangement of silyl dihydropyrans proceeds primarily by a stepwise process involving a homolytic C–O bond cleavage and intramolecular radical/radical anion recombination (Scheme 3.8),[12] a process that must be faster than $\sim 7 \times 10^7$ s^{-1} given that cyclopropyl-bearing substrates did not lead to ring opened products.[50] As previously reported,[12] the product distributions from **3.9a** or **3.9b** suggest that increasing the steric demand of the silyl group prevents [1,2]-recombination due to steric clash with the phenyl group. These observations, together with the exclusive [1,4]-selectivity displayed by **3.1** suggest that the [1,4]-/[1,2]-selectivity is determined

by the ability of the silyl group to transiently and locally stabilize the allylic radical,[51] guiding recombination toward the Si-bearing carbon.



Scheme 3.8: Proposed mechanism of the [1,4]-Wittig rearrangement of 4-silyl-6-aryl(alkyl)-5,6-dihydroprans

However, there remains the question as to why varying diastereoselectivities are observed with different silyl or aryl groups (Scheme 3.5). For instance, the diastereoselectivity increases nearly 3-fold from the relatively small $SiMe_2Et$ group (**3.2b**, *dr* = 3.3:1) to the more sterically demanding $SiEt_3$ group (**3.2c**, *dr* = 11:1). Similarly, the bulkier aryl group 2-methyl phenyl in **3.2f** affords a higher diastereoselectivity (8.3:1) relative to the phenyl analogue **3.2b** (Scheme 3.5). At this point, we conjecture that a concerted mechanism is operative to a certain extent and leads to the minor diastereomer (*trans*). In this scenario, bulkier silyl or aryl groups preclude such a competitive mechanism, indirectly leading to higher diastereoselectivity by the dominant, stepwise mechanism.

3.9. Conclusion

In conclusion, silylcyclopropane acetaldehydes with a variety of silyl groups can be accessed efficiently by selective [1,4]-Wittig rearrangement of 4-silyl-5,6-dihyropyrans. High selectivity is achievable with substrates whose migrating group has an electron-neutral or electron-rich character. In general, the diastereoselectivity of the [1,4]-migration is such that the bulkier groups (silyl and aryl/alkyl) end up in a *cis* relationship.

The rearrangement proceeds even when the substituent at the 6-position of the dihydropyran is alkyl. The [1,4]-Wittig selectivity is independent of the substituents on silicon,

but it is influenced by the electronic character of the migrating center.

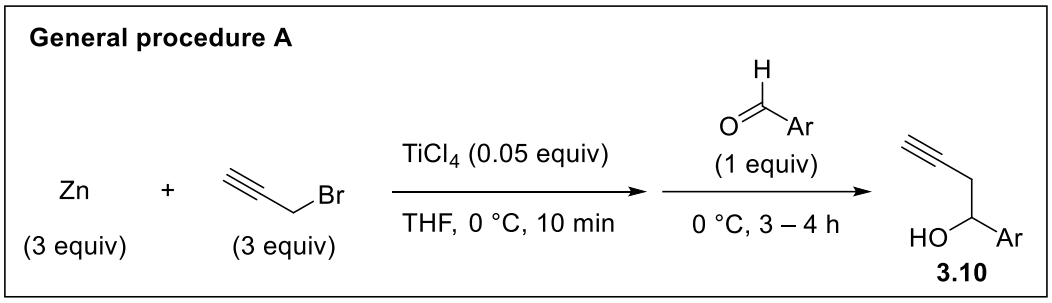
3.10. Experimental section

3.10.1. General Information

Unless otherwise noticed all reactions were run under a positive atmosphere of nitrogen in oven- dried (at least 4 hours) or flame-dried round bottom flasks or disposable drum vials capped with rubber septa. Solvents were removed by rotary evaporation at temperatures lower than 45 ºC. Column chromatography was run on 230–400 mesh silica gel. Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone ketyl; dichloromethane, benzene, trimethylsilyl chloride were distilled from calcium hydride. Acetone was distilled from drierite and used immediately. Triethylsilane, dimethylbenzylsilane, dimethylphenysilane, dimethylethylsilane, and vinyldimethylchlorosilane were used as received. *n*-Butyllithum (1.6 M in hexanes) and *sec*-butyllithium (1.4 M in cyclohexane) were purchased from Aldrich and their concentration calculated by titration with diphenylacetic acid (average of three runs). ^{1}H NMR spectra was collected in 500 MHz and 600 MHz Varian instruments using $CDCl_3$ as solvent, which was referenced at 7.24 ppm (residual chloroform proton) and ^{13}C NMR spectra was collected in $CDCl_3$ at 126 MHz or 151 MHz and referenced at 77.0 ppm. Other deuterated solvents used for NMR analysis were dimethyl sulfoxide (referenced at 2.50 for ^{1}HNMR and 39.51 for ^{13}CNMR) and benzene (referenced at 7.16 for ^{1}HNMR and 128.39 for ^{13}CNMR). High resolution mass spectrometric (HRMS) analysis was run in TOF instruments.

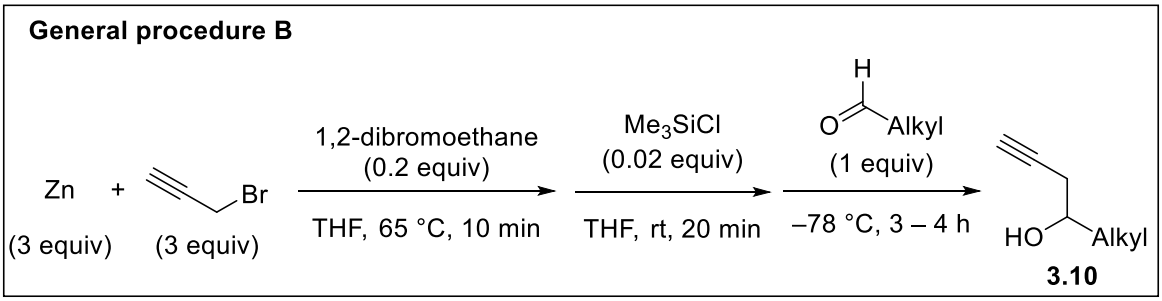
3.10.2. Synthesis of 4-silyl-5,6-dihydropyrans and precursors

3.10.2.1. Preparation of aryl homopropargylic alcohols 3.10 – general procedure A



Following a reported procedure,[52] to a vigorously stirred suspension of Zinz dust (5.3 g, 81 mmol, 3 equiv) in THF (200 mL) at 0 ºC was added propargyl bromide (80% w/w in toluene, 12 g, 81 mmol, 3 equiv) followed by $TiCl_4$ (1M in CH_2Cl_2, 1.35 mL, 1.35 mmol, 0.05 equiv). After 10 minutes, the desired aryl aldehyde (27 mmol, 1 equiv) in THF (60 mL) was adde via syringe slowly. The reaction was followed by TLC and was typically complete in 3-4 hours. The reaction was quenched by adding $NH_4Cl_{(sat)}$ (~150 mL) and slightly acidified with 1M HCl to remove the emulsion. The mixture was extracted with Et_2O (3 × 150 mL). Combined organic extracts were dried over $MgSO_4$ and concentrated. The product was purified by column chromatography.

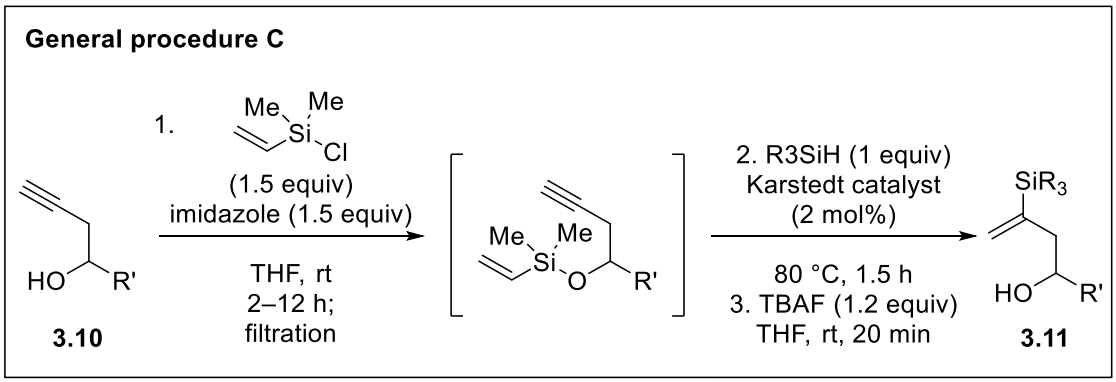
3.10.2.2. Preparation of alkyl homopropargylic alcohols 3.10 – general procedure B



Following a reported procedure slightly modified,[53] to a solution of 1,2-dibromoethane (0.15 mL, 1.783 mmol, 0.2 equiv) in THF (20 mL) was added Zn dust (1.17 g, 17.83 mmol, 2 equiv) with vigorous stirring. The mixture was heated at 65 ºC for 10 minutes and then cooled

down at room temperature. After 20 minutes trimethylsilyl chloride (23 μL, 0.178 mmol, 0.02 equiv) was added dropwise and 20 minutes later the reaction was cooled down at 0 ºC. Propargyl bromide (80% w/w in toluene, 2.65 g, 17.83 mmol, 2 equiv) was added slowly with vigorous stirring. After 1 hour the mixture was cooled down at –78 ºC and the desired alkyl aldehyde (8.915 mmol, 1 equiv) was slowly added as a solution in THF (10 mL). The temperature was slowly raised to 0 ºC. The reaction was monitored by TLC until completion. The reaction was quenched by adding $NH_4Cl_{(sat)}$ (10 mL) and extracted with Et_2O (3 × 15 mL). Combined organic extracts were dried over $MgSO_4$ and concentrated. The product was purified by column chromatography.

3.10.2.3. Preparation of 3-silyl homoallylic alcohols 3.11 – general procedure C

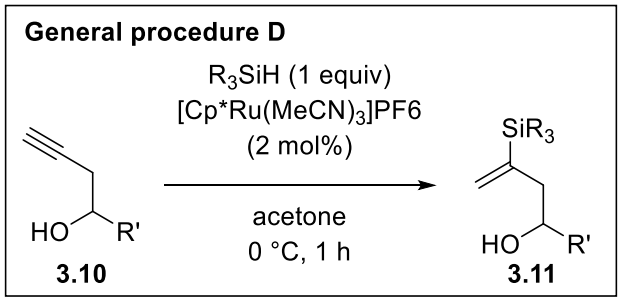


Following a reported procedure,[46] to a solution of the desired homopropargylic alcohol (1.286 mmol, 1 equiv) and dimethylvinylsilyl chloride (1.929 mmol, 1.5 equiv) in THF (5.6 mL) at room temperature was added imidazole (1.929 mmol, 1.5 equiv) in one portion and the mixture was stirred for 2-12 hours under nitrogen. The reaction was monitored by TLC until completion. The mixture was then filtered through a plug of celite, rinsing with hexanes, and the filtrate was concentrated and suspended in hexanes. Filtration through a plug of celite and concentration afforded the crude dimethylvinylsiloxy that was used in the next step without further purification. In some cases, it was necessary to repeat the treatment with hexanes to remove all insoluble material.

Alternatively, to an 8 mL conical vial fitted with a vane magnetic stir bar and sealed with a rubber septum, the desired homopropargylic alcohol (5.0 mmol, 1 equiv) and dimethylvinylsilyl chloride (6.0 mmol, 1.2 equiv) were dissolved in 5 mL of dry DMF (dried over molecular sieves) under nitrogen. Triethyl amine (1.7 mL, 12 mmol, 2.4 equiv) was added dropwise and the mixture stirred at room temperature for 5 minutes then on a pre-heated oil bath at 80 °C for 4 hours. The mixture was allowed to cool to room temperature filtered, and the filtrate was transferred to a separating funnel and a cold solution of saturated aqueous sodium hydrogen carbonate (5 mL) was added resulting in an exothermic reaction. The mixture was extracted with pentane (30 mL x 3) and the organic portion was washed with brine and dried over anhydrous magnesium sulfate. Filtration and concentration yielded the desired product which was used in the next step without further purification.

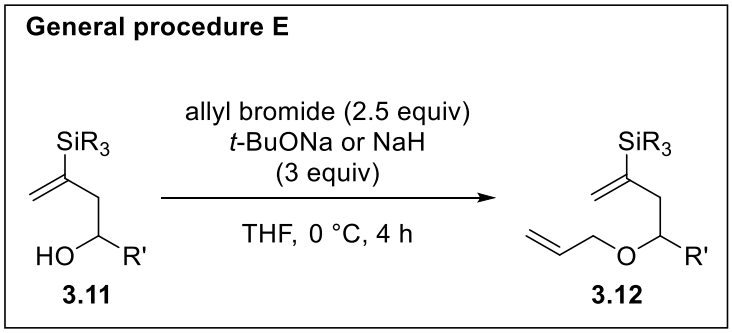
To a mixture of the above *O*-dimethylvinylsilyl homopropargylic alcohol (1.813 mmol, 1 equiv) and the corresponding silane (1.813 mmol, 1 equiv) was added Karstedt catalyst as a solution in xylenes (2% w/w in xylenes, 80.7 μL, 0.002 equiv) and the mixture was heated under nitrogen at 80 ºC for 1-1.5 hours. The reaction mixture was cooled down at room temperature and diluted with THF (18 mL) and TBAF (1M in THF, 2.18 mmol, 2.18 mL, 1.2 equiv) was added slowly. After 20 minutes the solution was concentrated and the residue subjected to column chromatography (EtOAc/hexanes) to afford the desired 3-silyl homoallylic alcohol **3.11**.

3.10.2.4. Preparation of 3-silyl homoallylic alcohols 3.11 – general procedure D



Following a literature procedure,[45] a solution of the desired homopropargylic alcohol (3.625 mmol, 1 equiv) and silane (4.35 mmol, 1.2 equiv) in dry dichloromethane was cooled down at 0 ºC and $[Cp^*Ru(MeCN)_3]PF_6$ (36.6 mg, 0.072 mmol, 0.02 equiv) was added quickly, the reaction was kept under nitrogen and the cold bath was removed. After about 1 hour the reaction mixture was concentrated and the product purified by column chromatography (EtOAc/hexanes).

3.10.2.5. Etherification of 3-silyl homoallylic alcohols 3.11 to RCM precursors 3.12 – general procedure E

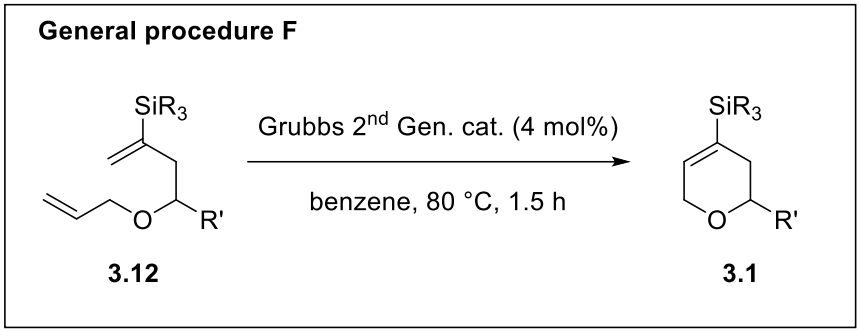


To a solution of 3-silyl homoallylic alcohol **3.11** (0.918 mmol, 1 equiv) and allyl bromide (194 μL, 2.296 mmol, 2.5 equiv) in THF (2 mL) at 0 ºC was added *t*-BuONa (265 mg, 2.75 mmol, 3 equiv) and the mixture was vigorously stirred at room temperature. After 4 hours the reaction was quenched with water (3 mL) and diluted with EtOAc (5 mL). The aqueous phase was extracted with EtOAc (3 × 5 mL). Combined organic extracts were washed with water (3 mL), brine, dried over $MgSO_4$ and concentrated. The diene product **3.12** was purified by short column chromatography.

Alternatively, sodium hydride, 60% w/w dispersion in mineral oil (345 mg, 9.0 mmol, 3.0 equiv) was weighed into a 100 mL dry round bottomed flask fitted with a magnetic stir bar. The flask was sealed and purged with nitrogen, then 20 mL THF was added followed by 0.52 mL of allyl bromide (726 mg, 6.0 mmol, 2.0 equiv) and the resulting suspension was cooled on an ice-bath at 0 °C. To the cold suspension, 3-silyl homoallylic alcohol **3.11** (3.0 mmol, 1 equiv) in THF

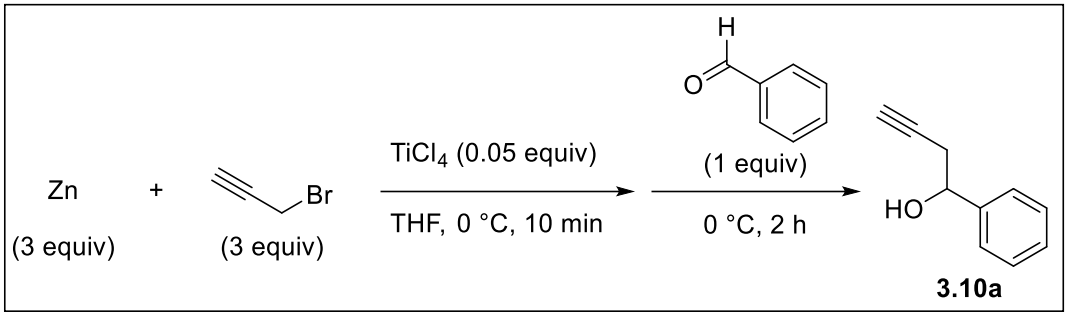
(10 mL) was added in a dropwise manner and the resulting mixture stirred at 0 °C to room temperature. After 4 hours, the reaction was quenched with saturated aqueous ammonium chloride (10 mL) and diluted with ether (20 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted with ether (20 mL x 3). The combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. This was followed by filtration and the filtrate was concentrated under reduced pressure on a rotorvap. The diene product **3.12** was purified by short column chromatography.

3.10.2.6. Preparation of 4-silyl dihydropyrans 3.1 via ring-closing metathesis of dienes 3.12 – general procedure F



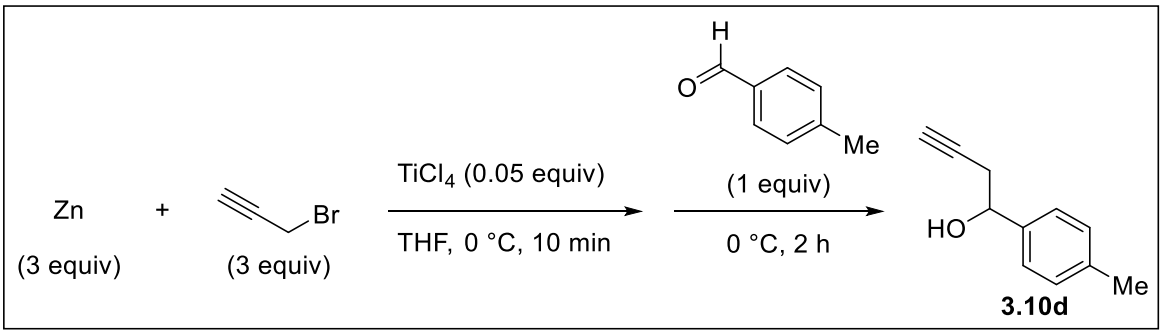
A round-bottom flask was charged with a magnetic stirred, diene **3.12** (100 mg, 0.31 mmol, 1 equiv) and benzene (6.2 mL), and then second-generation Grubbs catalyst (10.5 mg, 0.0124 mmol, 0.04 equiv) was added in one portion. A condenser was attached, and the system flushed with nitrogen. The reaction was heated in an oil bath at 80 ºC for 1-1.5 hours. The reaction was then cooled down at room temperature and concentrated. The residue was subjected to column chromatography (CH_2Cl_2 in hexanes) to afford the desired product **3.1** as a colorless oil.

Preparation of 1-phenyl-3-butyn-1-ol (3.10a)



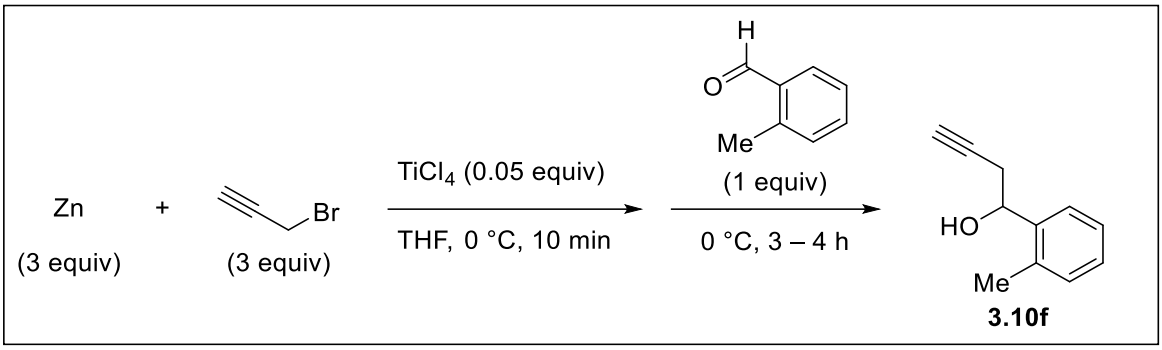
Following general procedure A, 1-Phenyl-3-butyn-1-ol (**3.10a**) was prepared in ~100% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 4.86 (t, *J* = 6.4 Hz, 1H), 2.64 (dd, *J* = 6.4, 2.7 Hz, 2H), 2.56 (s, 1H), 2.08 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 128.4, 127.9, 125.7, 80.6, 72.2, 70.9, 29.3. Spectral data are in accord with reported literature values.[54]

Preparation of 1-(4-methylphenyl)-3-butyn-1-ol (3.10d)



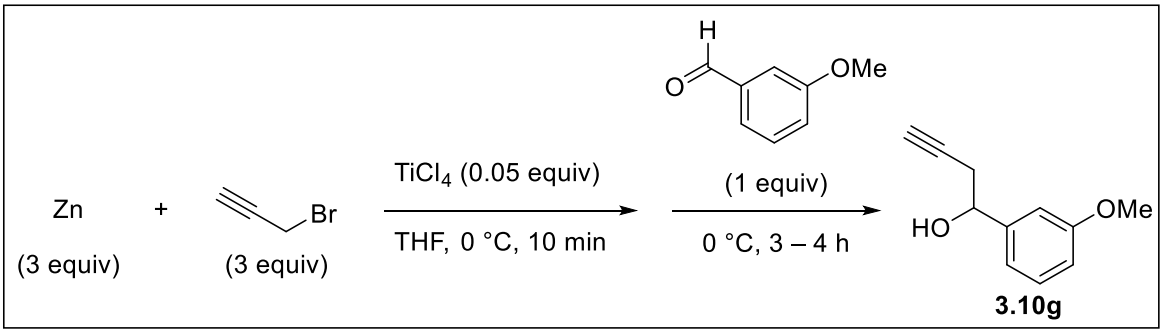
Following general procedure A, 1-(4-methylphenyl)-3-butyn-1-ol (**3.10d**) was prepared in 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.64 (dd, *J* = 6.4, 2.6 Hz, 2H), 2.35 (s, 3H), 2.31 (s, 1H), 2.07 (t, *J* = 2.6 Hz, 1H). Spectral data are in accord with reported literature values.[55]

Preparation of 1-(2-methylphenyl)-3-butyn-1-ol (3.10f)



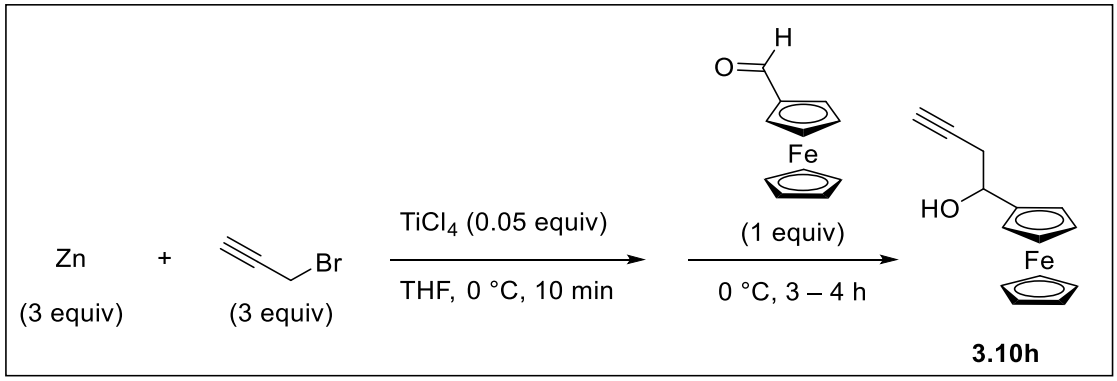
Following General Procedure A, 1-(2-methylphenyl)-3-butyn-1-ol (**3.10f**) was prepared in 90% yield. Spectral data are in accord with reported literature values.[56]

Preparation of 1-(3-methoxyphenyl)-3-butyn-1-ol (3.10g)



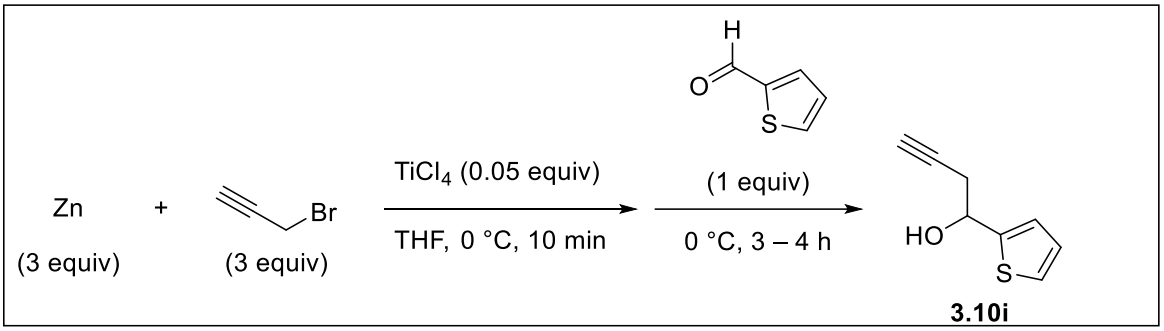
Following General Procedure A, 1-(3-methoxyphenyl)-3-butyn-1-ol (**3.10g**) was prepared in ~100% yield. Spectral data are in accord with reported literature values.[56]

Preparation of 1-(ferrocenyl)-3-butyn-1-ol (3.10h)



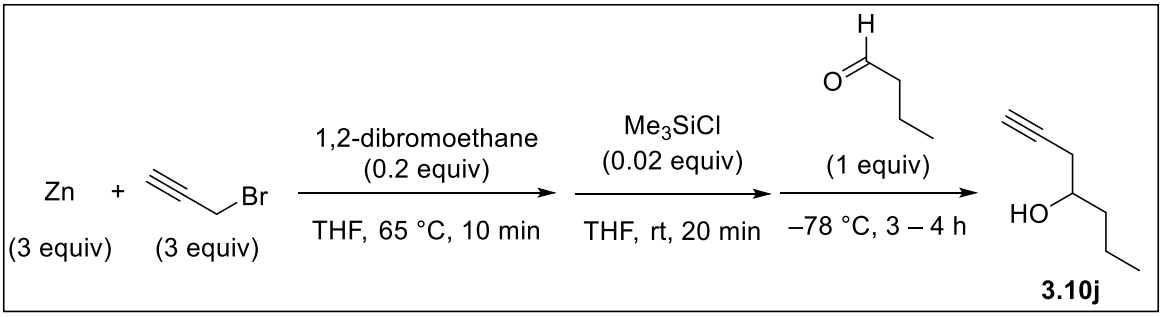
Following General Procedure A, 1-(ferrocenyl)-3-butyn-1-ol (**3.10h**) was prepared in 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.53 (td, *J* = 6.2, 4.0 Hz, 1H), 4.33 – 4.27 (m, 1H), 4.27 – 4.23 (m, 1H), 4.22 – 4.18 (m, 5H), 4.17 (dt, *J* = 2.4, 0.8 Hz, 2H), 2.69 – 2.49 (m, 2H), 2.24 (dd, *J* = 4.1, 0.5 Hz, 1H), 2.06 (td, *J* = 2.7, 0.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 91.82, 81.1, 70.61, 68.5, 68.2, 68.1, 68.0, 67.0, 65.8, 28.2. (This compound was used in the next step without further purification. See preparation of compound **3.11h**)

Preparation of 1-(2-thiophenyl)-3-butyn-1-ol (3.10i)



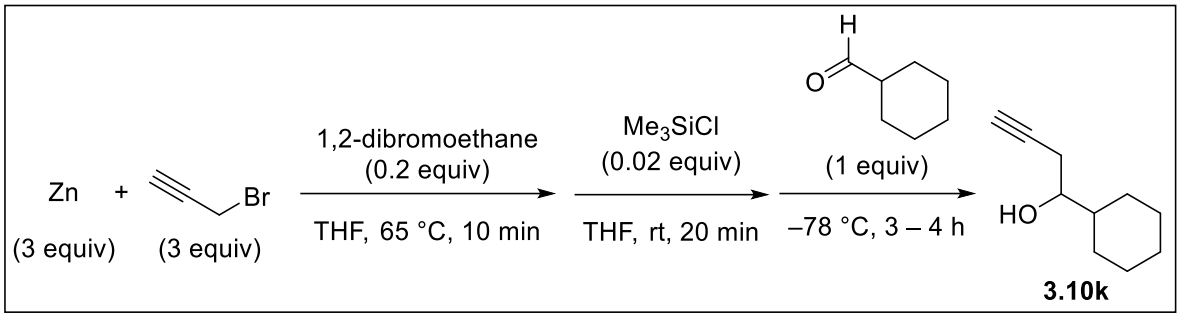
Following General Procedure A, 1-(2-thiophenyl)-3-butyn-1-ol (**3.10i**) was prepared in 91% yield. Spectral data are in accord with reported literature values.[57]

Preparation of 1-heptyn-4-ol (3.10j)



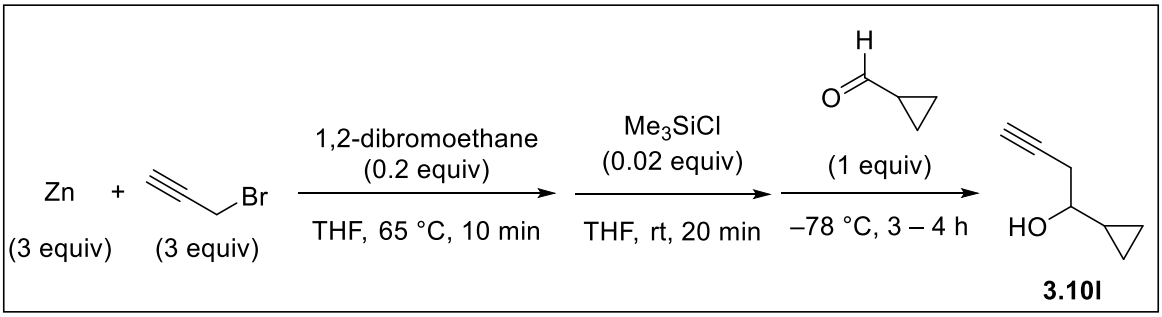
Following General Procedure B, 1-heptyn-4-ol (**3.10j**) was prepared in 84% yield. Spectral data are in accord with reported literature values.[58]

Preparation of 1-cyclohexylbut-3-yn-1-ol (3.10k)



Following general procedure B, 1-cyclohexylbut-3-yn-1-ol (**3.10k**) was prepared in 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.49 (dp, *J* = 7.2, 3.8 Hz, 1H), 2.45 (ddd, *J* = 16.7, 4.1, 2.7 Hz, 1H), 2.35 (ddd, *J* = 16.7, 7.5, 2.6 Hz, 1H), 2.05 (td, *J* = 2.7, 0.6 Hz, 1H), 1.97 – 1.86 (m, 2H), 1.75 (ddddd, *J* = 13.2, 6.4, 5.0, 3.3, 1.8 Hz, 2H), 1.66 (dddd, *J* = 13.6, 6.9, 3.3, 1.7 Hz, 2H), 1.46 (tdt, *J* = 11.7, 6.7, 3.4 Hz, 1H), 1.24 (dddd, *J* = 16.2, 9.0, 3.4, 1.9 Hz, 2H), 1.20 – 1.11 (m, 1H), 1.07 – 0.96 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 81.3, 74.0, 70.7, 42.5, 29.0, 28.1, 26.3, 26.1, 25.9, 24.6. Spectral data are in accord with reported literature values.[57]

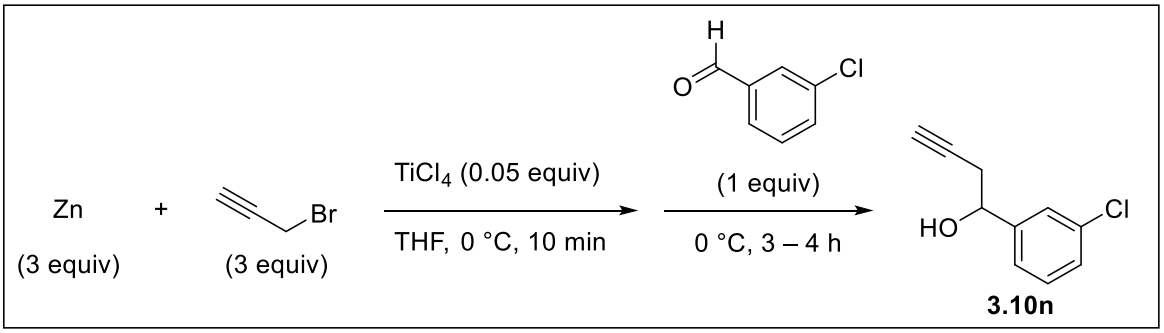
Preparation of 1-cyclopropylbut-3-yn-1-ol (3.10l)



Following General Procedure B, 1-cyclopropylbut-3-yn-1-ol (**3.10l**) was prepared in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.06 (ddd, *J* = 8.6, 6.8, 4.5 Hz, 1H), 2.56 (dddd, *J* = 16.7, 4.6, 2.6, 1.1 Hz, 1H), 2.47 (dddd, *J* = 16.9, 6.8, 2.7, 1.1 Hz, 1H), 2.06 (td, *J* = 2.6, 1.1 Hz, 1H), 2.02 (s, 1H), 1.09 – 0.99 (m, 1H), 0.59 – 0.51 (m, 2H), 0.37 (dddt, *J* = 8.8, 5.0, 2.5, 1.0 Hz, 1H), 0.26 (dddt, *J* = 10.5, 4.5, 2.3, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 81.0, 74.6, 70.5, 27.1, 16.8, 2.9,

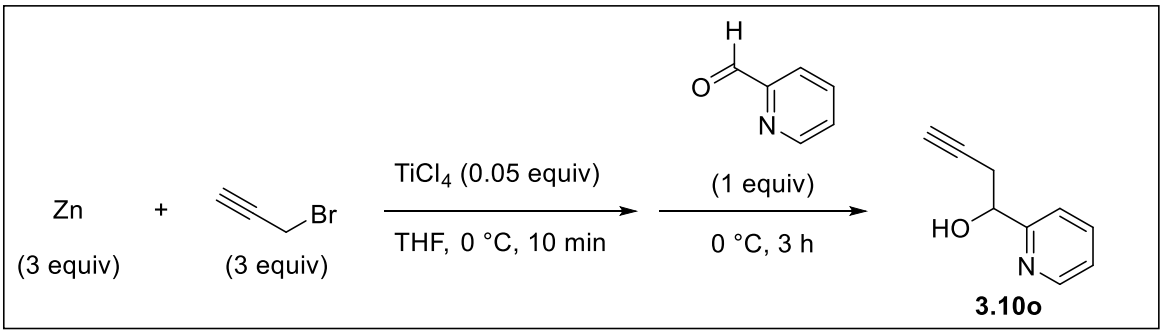
2.5.

Preparation of 1-(3-chlorophenyl)-3-butyn-1-ol (3.10n)



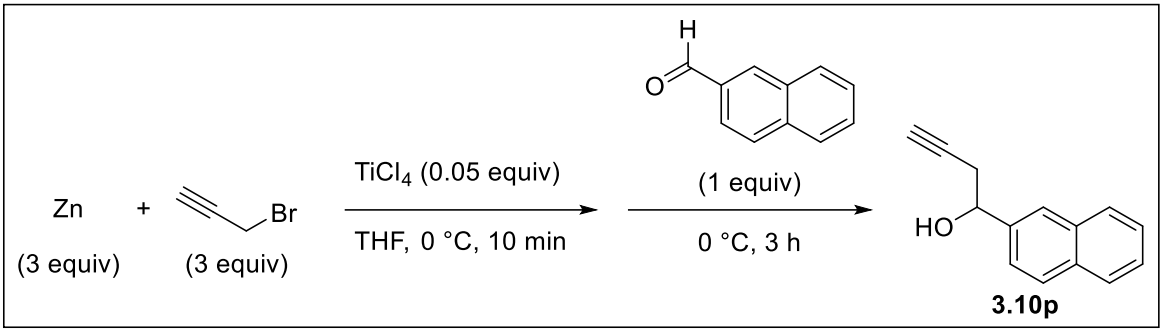
Following General Procedure A, 1-(3-chlorophenyl)-3-butyn-1-ol was prepared in ~100% yield. Spectral data are in accord with reported literature values.[59]

Preparation of 1-(pyridin-2-yl)but-3-yn-1-ol (3.10o)



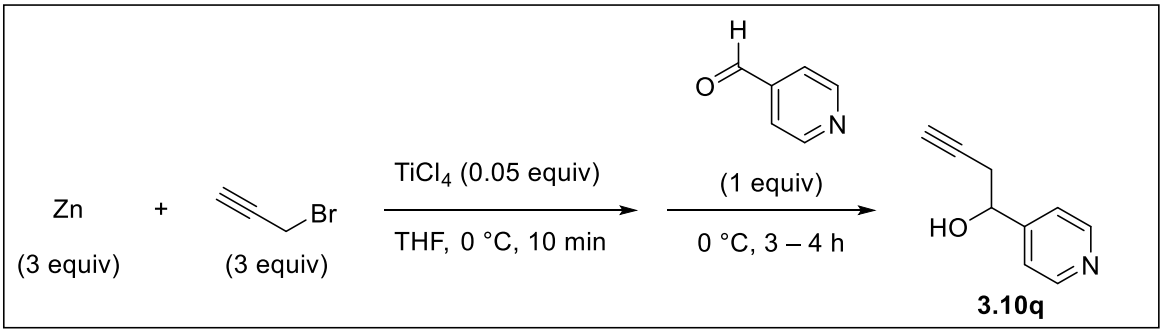
Following General Procedure A, 1-(pyridin-2-yl)but-3-yn-1-ol (**3.10o**) was prepared in ~100% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.9 Hz, 1H), 7.70 (td, *J* = 7.7, 1.8 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.23 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 4.89 (t, *J* = 6.1 Hz, 1H), 4.49 (s, 1H), 2.70 (ddd, *J* = 6.1, 2.7, 1.0 Hz, 2H), 2.01 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 148.3, 136.7, 122.8, 120.7, 80.4, 71.0, 70.8, 28.3. Spectral data are in accord with reported literature values.[57]

Preparation of 1-(naphthalen-2-yl)but-3-yn-1-ol (3.10p)



Following General Procedure A, 1-(naphthalen-2-yl)but-3-yn-1-ol (**3.10p**) was prepared in ~100% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 4H), 7.52 – 7.48 (m, 3H), 5.03 (t, *J* = 6.4 Hz, 1H), 2.74 (dd, *J* = 6.4, 2.6 Hz, 2H), 2.70 (s, 1H), 2.10 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7, 133.1, 133.0, 128.2, 128.0, 127.6, 126.2, 126.0, 124.6, 123.6, 80.6, 72.4, 71.0, 29.3. Spectral data are in accord with reported literature values.[57]

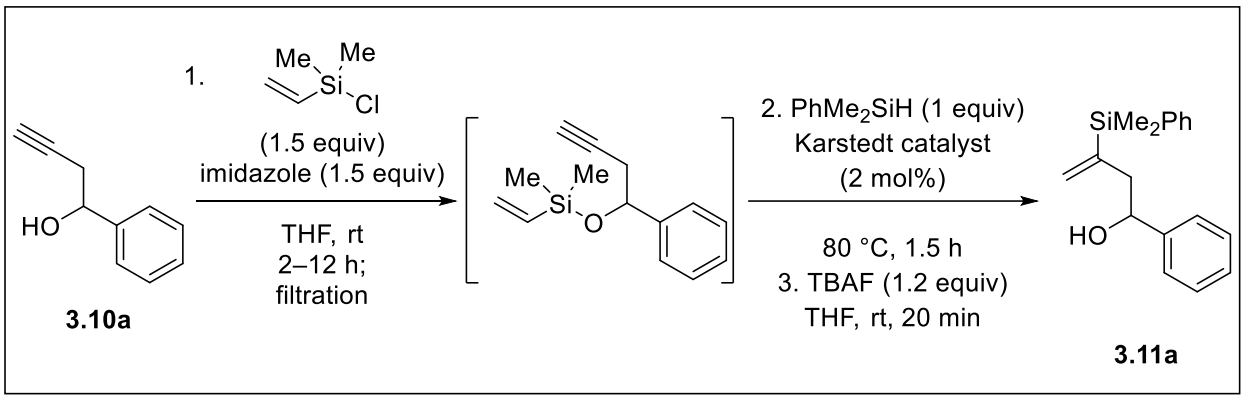
Preparation of 1-(pyridin-4-yl)but-3-yn-1-ol (3.10q)



Following General Procedure A, 1-(pyridin-4-yl)but-3-yn-1-ol (**3.10q**) was prepared in ~100% yield as white solid that was soluble in DMF and DMSO. The solid was insoluble in THF, diethyl ether, pentane, hexanes, cyclohexane, benzene, toluene, dichloromethane, and chloroform. Spectroscopic and melting point data for this compound: mp 136 to 137 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 (d, *J* = 6.2 Hz, 2H), 7.50 (d, *J* = 6.2 Hz, 2H), 5.84 (d, *J* = 4.5 Hz, 1H (OH)), 4.75 (q, *J* = 6.0 Hz, 1H), 2.75 (t, *J* = 2.6 Hz, 1H), 2.61 – 2.51 (m, 2H). ^{13}C NMR (126 MHz, DMSO-

d_6) δ 155.1, 149.1, 122.5, 81.4, 73.5, 69.9, 28.6. IR (neat) 3492, 3270, 3097, 1618, 1559, 1424, 1392, 1334, 1065, 1028, 845, 817 cm^{-1}.

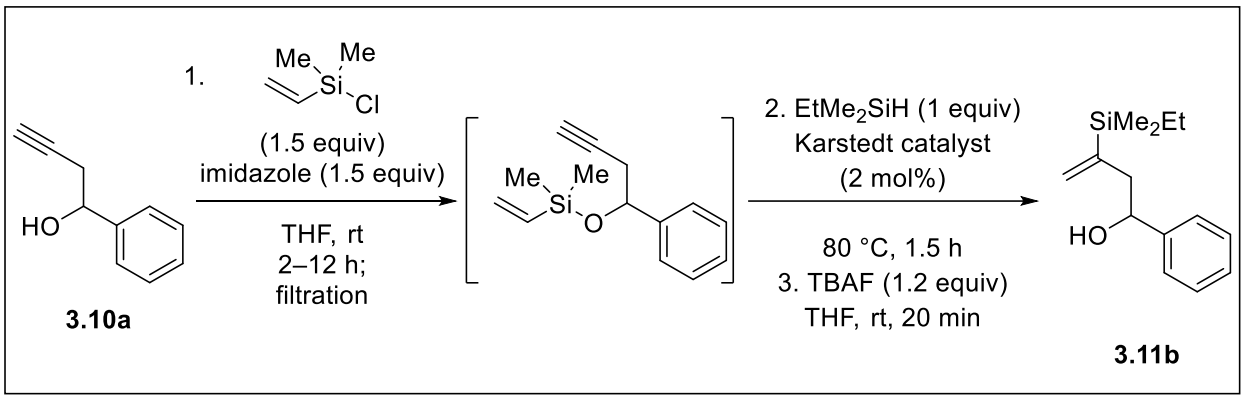
Preparation of 3-(dimethyl(phenyl)silyl)-1-phenylbut-3-en-1-ol (3.11a)



Following general procedure C, 1-phenylbut-3-yn-1-ol (**3.10a**) (1.68 g, 11.5 mmol, 1 equiv), dimethylvinylsilyl chloride (1.19 g, 17.5 mmol, 1.5 equiv), imidazole (2.08, 17.5 mmol, 1.5 equiv), in THF (50 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (1.22 g, 5.3 mmol, 1 equiv) was then treated with dimethylphenylsilane (0.72 g, 5.3 mmol, 1 equiv), and Karstedt catalyst solution (236 μL, 0.002 equiv) at 80 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution (6.3 mL, 6.3 mmol, 1.2 equiv), workup and purification by silica gel chromatography (12% EtOAc in hexanes) afforded **3.11a** as a colorless oil (507 mg, 1.8 mmol) and a mixture its regioisomer (278 mg, 1.0 mmol) in 53% overall yield. **3.11a** is a known compound and its spectral data are in accord with reported literature values.[60] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.36 (m, 3 H), 7.28 (m, 2 H), 7.21 (m, 3 H), 5.84 (m, 1 H), 5.62 (m, 1 H), 4.53 (dt, *J* = 3.0, 9.5 Hz, 1 H), 2.58 (A of ABX system, m, 1 H), 2.43 (B of ABX system, dd, *J* = 10.0, 14.0 Hz, 1 H), 1.94 (d, *J* = 2.5 Hz, 1 H), 0.43 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 144.1, 137.6, 133.9 (2 C), 130.0, 129.3, 128.3 (2 C), 128.0 (2

C), 127.3, 125.7 (2 C), 72.2, 47.0, -2.90, -2.99. IR (neat) 3420, 3067, 2957, 1427, 1250, 1111, 833 cm^{-1}.

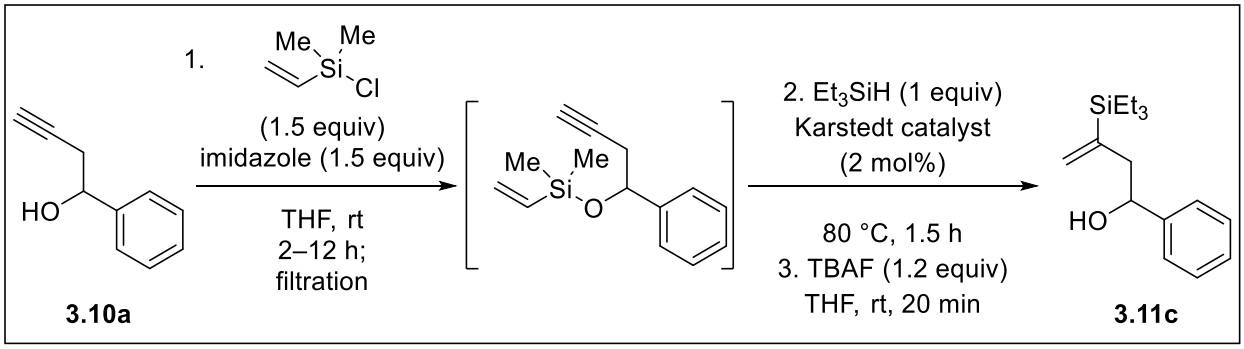
Preparation of 3-(ethyldimethylsilyl)-1-phenylbut-3-en-1-ol (3.11b)



Compound **3.11b** was prepared by a slight modification of General Procedure C. 1-phenylbut-3-yn-1-ol (0.77 g, 5.27 mmol, 1 equiv), dimethylvinylsilyl chloride (0.95 g, 7.9 mmol, 1.5 equiv), imidazole (538 mg, 7.9 mmol, 1.5 equiv), in THF (20 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield. The O-dimethylvinylsilyl intermediate (0.5 g, 2.17 mmol, 1 equiv) was then treated with ethyldimethylsilane (0.21 g, 2.39 mmol, 1.1 equiv), and Karstedt catalyst solution (97 μL, 0.002 equiv) at 45 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution (2.4 mL, 2.4 mmol, 1.1 equiv), workup and purification by silica gel chromatography (10% EtOAc in hexanes) afforded **3.11b** as a colorless oil (193 mg, 0.82 mmol) and a mixture of **3.11b** and its regioisomer (200 mg, 0.85 mmol) in 77% overall yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4 H), 7.26 (m, 1 H), 5.76 (m, 1 H), 5.53 (dt, *J* = 0.5, 8.0, Hz, 1 H), 4.73 (ddd, *J* = 2.0, 3.5, 10.0 Hz, 1 H), 2.62 (dddd, *J* = 0.5, 1.5, 3.5, 14.0 Hz, 1 H), 2.43 (dd, *J* = 9.5, 14.5 Hz, 1 H), 2.10 (m, 1 H), 0.93 (t, *J* = 8.0 Hz, 3 H), 0.61 (q, *J* = 8.0 Hz, 2 H), 0.11 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 128.7, 128.4 (2 C), 127.4, 125.8 (2 C), 72.2, 47.1, 7.3, 6.9, -3.6, -3.7. IR (film) 3389, 3031, 2955, 1248, 1049, 833 cm^{-1}. HRMS (EI) *m/z*

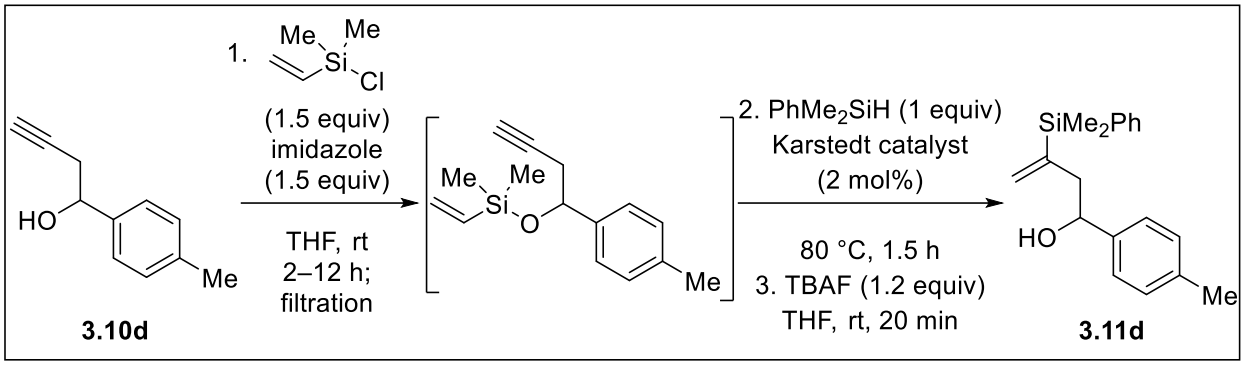
217.1401 [(M-HO)$^+$; calcd for $C_{14}H_{21}Si$, 217.1413].

Preparation of 1-phenyl-3-(triethylsilyl)but-3-en-1-ol (3.11c)



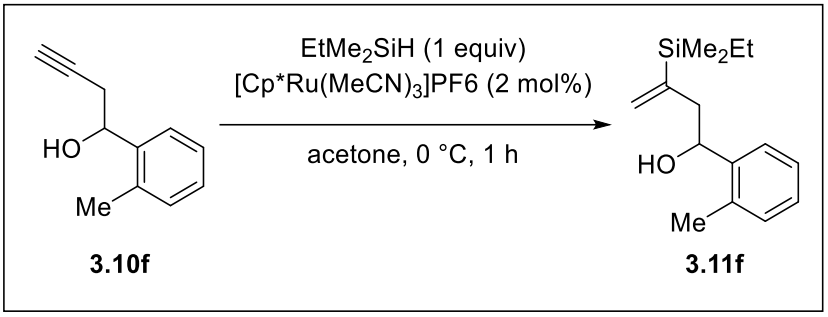
Following general procedure C, 1-phenylbut-3-yn-1-ol (**3.10a**) (1.5 g, 10.26 mmol, 1 equiv), dimethylvinylsilyl chloride (1.86 g, 15.39 mmol, 1.5 equiv), imidazole (1.05, 15.39 mmol, 1.5 equiv), in THF (45 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (1.4 g, 6.07 mmol, 1 equiv) was then treated with triethylsilane (0.7 g, 6.07 mmol, 1 equiv), and Karstedt catalyst solution (230 μL, 0.002 equiv) at 80 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution (6.1 mL, 6.1 mmol, 1 equiv), workup and purification by silica gel chromatography (9% EtOAc in hexanes) afforded **3.11c** as a colorless oil (1.08 g, 4.11 mmol) and a mixture of **3.11c** and its regioisomer (144 mg, 0.55 mmol) in 77% overall yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.32 (m, 4 H), 7.26 (m, 1 H), 5.82 (m, 1 H), 5.52 (d, *J* = 2.5 Hz, 1 H), 4.73 (dd, *J* = 2.5, 8.0 Hz, 1 H), 2.60 (m, 1 H), 2.40 (dd, *J* = 8.0, 11.5 Hz, 1 H), 2.13 (s, 1 H), 0.95 (t, *J* = 6.5 Hz, 9 H), 0.65 (dq, *J* = 1.5, 6.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 144.1, 129.5, 128.4 (2 C), 127.4, 125.8 (2 C), 72.0, 47.2, 7.3, 2.9. IR (film) 3406, 3032, 2953, 2876, 1456, 1008, 721 cm^{-1}. HRMS (EI) *m/z* 245.1712 [(M-OH)$^+$; calcd for $C_{16}H_{25}Si$, 245.1726].

Preparation of 3-(dimethyl(phenyl)silyl)-1-(*p*-tolyl)but-3-en-1-ol (3.11d)



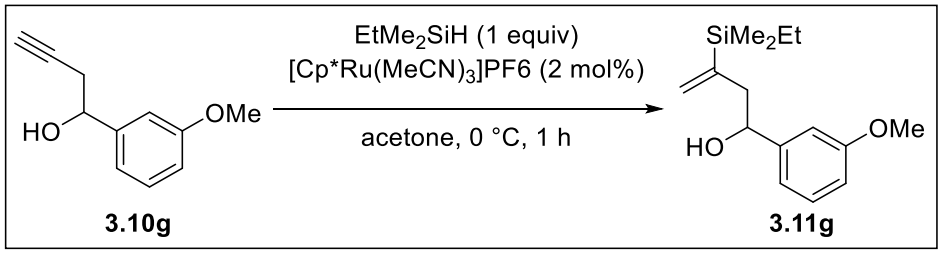
Following general procedure C, 1-(*p*-tolyl)but-3-yn-1-ol (**3.10d**) (1.1 g, 6.9 mmol, 1 equiv), dimethylvinylsilyl chloride (1.25 g, 10.35 mmol, 1.5 equiv), imidazole (0.7, 10.35 mmol, 1.5 equiv), in THF (30 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (957 mg, 3.92 mmol, 1 equiv) was then treated with phenyldimethylsilane (534 mg, 3.92 mmol, 1 equiv), and Karstedt catalyst solution (175 μL, 0.002 equiv) at 80 ºC for 1.1 h and cooled down to room temperature. Treatment with TBAF solution (4.7 mL, 4.7 mmol, 1.2 equiv), workup and purification by silica gel chromatography (12% EtOAc in hexanes) afforded **3.11d** as a colorless oil (233 mg, 0.79 mmol), and a mixture of **3.11d** and its regioisomer (506 mg, 1.71 mmol) in 77% overall yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.37 (m, 3 H), 7.11 (s, 4 H), 5.85 (m, 1 H), 5.62 (d, *J* = 2.5 Hz, 1 H), 4.53 (ddd, *J* = 2.5, 3.5, 9.5 Hz, 1 H), 2.57 (A of ABX system, m, 1 H), 2.44 (B of ABX system, dd, *J* = 10.0, 14.0 Hz, 1 H), 2.32 (s, 3 H), 1.92 (d, *J* = 2.0 Hz, 1 H), 0.438 (s, 3 H), 0.429 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 141.1, 137.7, 136.9, 133.9 (2 C), 129.8, 129.2, 128.9 (2 C), 127.9 (2 C), 125.6 (2 C), 72.0, 46.9, 21.1, -2.896, -2.977. IR (neat) 3422, 3047, 2955, 1427, 1248, 1111, 1047, 815 cm^{-1}. HRMS (EI) *m/z* 279.1568 [(M-OH)$^{+}$; calcd for $C_{19}H_{23}Si$, 279.1569].

Preparation of 3-(ethyldimethylsilyl)-1-(o-tolyl)but-3-en-1-ol (3.11f)



Following General Procedure D, 1-(*o*-tolyl)but-3-yn-1-ol (**3.10f**) (400 mg, 2.5 mmol, 1 equiv), ethyldimethylsilane (265 mg, 3 mmol, 1.2 equiv), dichloromethane (5 mL) and $[Cp^*Ru(MeCN)_3]PF_6$ (25.2 mg, 0.05 mmol, 0.02 equiv) at room temperature for 1 h, followed by silica gel chromatography (10% EtOAc in hexanes) afforded **3.11f** as colorless oil (435 mg, 1.75 mmol) and a mixture of **3.11f** and its regioisomer (110 mg, 0.44 mmol) in 88% overall yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 1.2, 7.2 Hz, 1 H), 7.23 (m, 1 H), 7.16 (dt, *J* = 1.8, 7.2 Hz, 1 H), 7.12 (dd, *J* = 0.6, 7.8 Hz, 1 H), 5.82 (m, 1 H), 5.58 (d, *J* = 3.0 Hz, 1 H), 4.96 (dd, *J* = 3.0, 9.6 Hz, 1 H), 2.59 (m, 1 H), 2.36 (dd, *J* = 10.2, 13.8 Hz, 1 H), 2.35 (s, 3 H), 2.05 (s, 1 H), 0.94 (t, *J* = 8.4 Hz, 3 H), 0.62 (q, *J* = 7.8 Hz, 2 H), 0.12 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 142.3, 134.2, 130.3, 128.8, 127.1, 126.3, 125.3, 68.4, 45.4, 19.2, 7.3, 6.9, -3.6, -3.7. IR (film) 3408, 3052, 2953, 1458, 1248, 1049, 819 cm^{-1}. HRMS (EI) *m/z* 231.1555 [$(M\text{-}OH)^+$; calcd for $C_{15}H_{23}Si$, 231.1569].

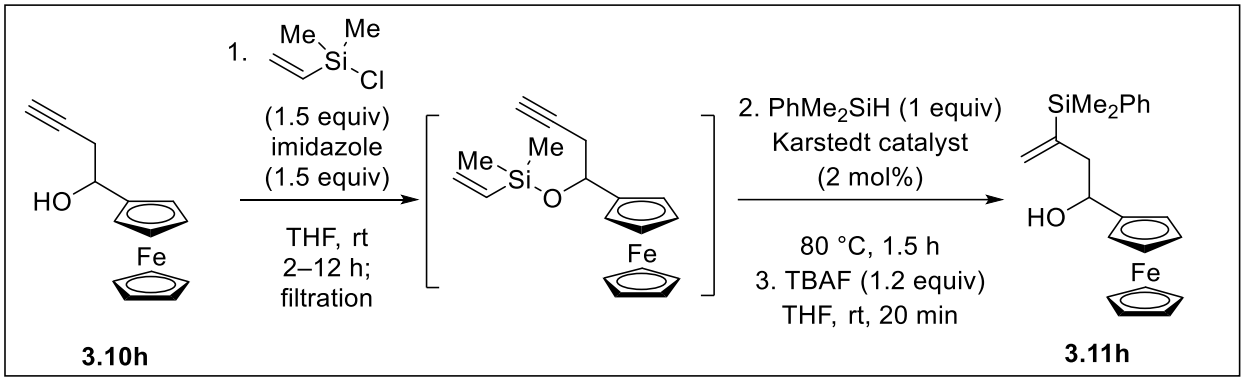
Preparation of 3-(ethyldimethylsilyl)-1-(3-methoxyphenyl)but-3-en-1-ol (3.11g)



Following General Procedure D, 1-(3-methoxyphenyl)but-3-yn-1-ol (**3.10g**) (400 mg, 2.27

mmol, 1 equiv), ethyldimethylsilane (240 mg, 2.72 mmol, 1.2 equiv), dichloromethane (4.5 mL) and [Cp*Ru(MeCN)$_3$]PF$_6$ (22.9 mg, 0.045 mmol, 0.02 equiv) at room temperature for 1.5 h, followed by silica gel chromatography (12–15% EtOAc in hexanes) afforded **3.11g** as colorless oil (305.8 mg, 1.16 mmol) and a mixture of **3.11g** and its regioisomer (28.5 mg, 0.12 mmol) in 53% overall yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.0 Hz, 1 H), 6.93 (m, 2 H), 6.80 (m, 1 H), 5.76 (m, 1 H), 5.53 (d, *J* = 2.5 Hz, 1 H), 4.70 (dt, *J* = 3.0, 4.5 Hz, 1 H), 3.81 (s, 3 H), 2.62 (m, 1 H), 2.41 (dd, *J* = 10.0, 14.0 Hz, 1 H), 2.08 (d, *J* = 2.0 Hz, 1 H), 0.93 (t, *J* = 8.0 Hz, 3 H), 0.60 (q, *J* = 8.0 Hz, 2 H), 0.10 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 148.2, 145.9, 129.4, 128.7, 118.1, 112.8, 111.3, 72.1, 55.2, 47.0, 7.3, 6.9, -3.6, -3.7. IR (film) 3049, 2955, 1603, 1255, 1045, 777 cm^{-1}. HRMS (EI) *m/z* 246.1441 [(M-H$_2$O)$^+$; calcd for $C_{15}H_{22}OSi$, 246.1440].

Preparation of 3-(dimethyl(phenyl)silyl)-1-(ferrocenyl)but-3-en-1-ol (3.11h)



Following general procedure C, 1-(ferrocenyl)but-3-yn-1-ol (**3.10h**) (1.6 g, 6.3 mmol, 1 equiv), dimethylvinylsilyl chloride (1.14 g, 9.4 mmol, 1.5 equiv), imidazole (642 mg, 9.4 mmol, 1.5 equiv), in THF (27 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (6.3 mmol, 1 equiv) was then treated with phenyldimethylsilane (858 mg, 6.3 mmol, 1 equiv), and Karstedt catalyst solution (281 μL, 0.013 mmol, 0.002 equiv) at 75 ºC for 2 h and cooled down to room temperature. Treatment with TBAF solution (7.6 mL, 7.6 mmol, 1.2 equiv),

workup and purification by silica gel chromatography (10% EtOAc in hexanes) afforded a mixture of **3.11h** and its regioisomer (1.0:0.2 ratio) as an orange oil (1.72 g, 4.47 mmol, 71% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.35 (m, 3 H), 5.79 (m, 1 H), 5.57 (d, *J* = 3.0 Hz, 1 H), 4.28 (dq, *J* = 4.0, 9.5 Hz, 1 H), 4.15 (q, *J* = 1.5 Hz, 1 H), 4.08 (t, *J* = 3.0 Hz, 2 H), 4.07 (s, 5 H), 4.01 (q, *J* = 3.0 Hz, 1 H), 2.51 (m, 1 H), 2.42 (dd, *J* = 9.0, 14.0 Hz, 1 H), 1.86 (d, *J* = 3.5 Hz, 1 H), 0.40 (s, 3 H), 0.39 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 138.0, 134.0 (2 C), 129.2, 129.1, 127.9 (2 C), 93.3, 68.3 (5 C), 68.1, 67.7, 67.6, 66.8, 65.7, 45.1, -2.8, -2.9. IR (film) 3412, 3097, 2955, 1427, 1248, 1107, 817 cm^{-1}. HRMS (ESI) *m/z* 373.1069 [(M-OH)$^{+}$; calcd for $C_{22}H_{25}FeSi$, 373.1075].

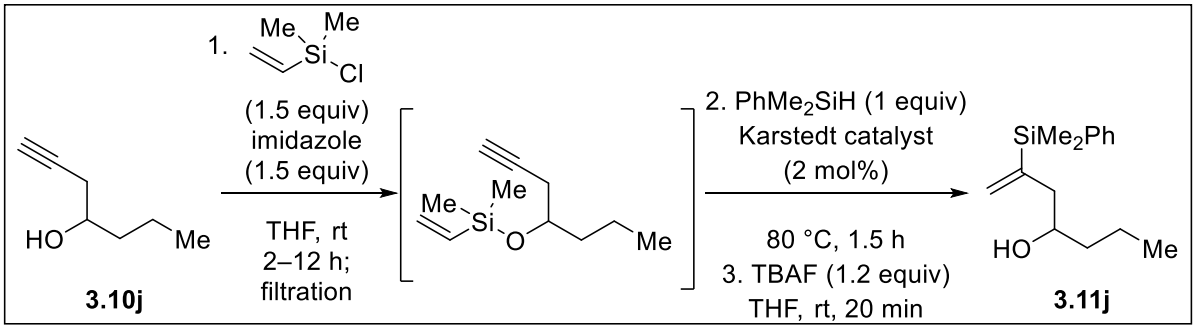
Preparation of 3-(ethyldimethylsilyl)-1-(thiophen-2-yl)but-3-en-1-ol (3.11i)

3.10i **3.11i**

Following General Procedure D, 1-(thiophen-2-yl)but-3-yn-1-ol (**3.10i**) (400 mg, 2.63 mmol, 1 equiv), ethyldimethylsilane (278 mg, 3.15 mmol, 1.2 equiv), dichloromethane (5.3 mL) and $[Cp^*Ru(MeCN)_3]PF_6$ (26.5 mg, 0.053 mmol, 0.02 equiv) at room temperature for 1.5 h, followed by silica gel chromatography (15% EtOAc in hexanes) afforded **3.11i** as colorless oil (178 mg, 0.61 mmol, 23% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 1.5, 5.0 Hz, 1 H), 6.96 (m, 2 H), 5.75 (m, 1 H), 5.53 (d, *J* = 2.5 Hz, 1 H), 4.99 (dt, *J* = 3.0, 9.5 Hz, 1 H), 2.73 (m, 1 H), 2.58 (dd, *J* = 9.5, 14.5 Hz, 1 H), 2.17 (d, *J* = 3.0 Hz, 1 H), 0.93 (t, *J* = 8.0 Hz, 3 H), 0.59 (q, *J* = 8.0 Hz, 2 H), 0.09 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 147.6, 128.9 126.5, 124.4, 123.5, 68.5, 46.8, 7.3, 6.8, -3.7, -3.8. IR (film) 3402, 2955, 1248, 1116, 833 cm^{-1}. HRMS (EI) *m/z*

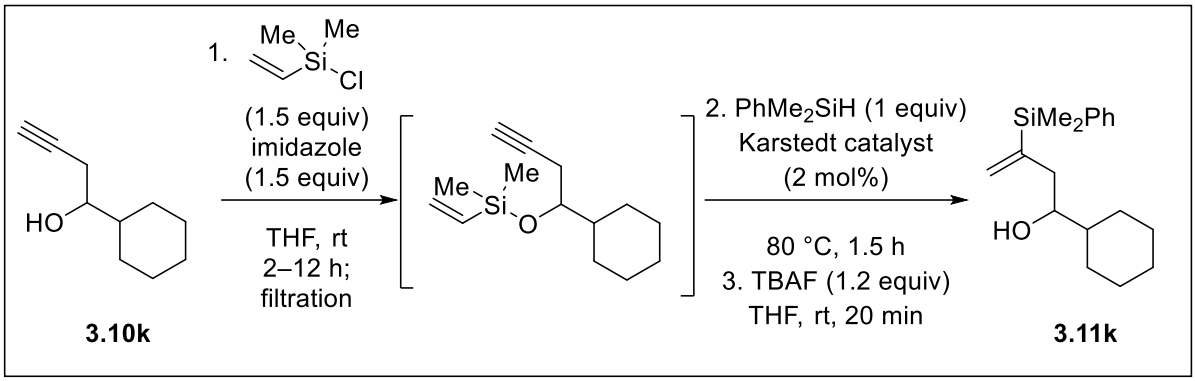
223.0975 [(M-OH)$^+$; calcd for $C_{12}H_{19}SSi$, 223.0977].

Preparation of 2-(dimethyl(phenyl)silyl)hept-1-en-4-ol (3.11j)



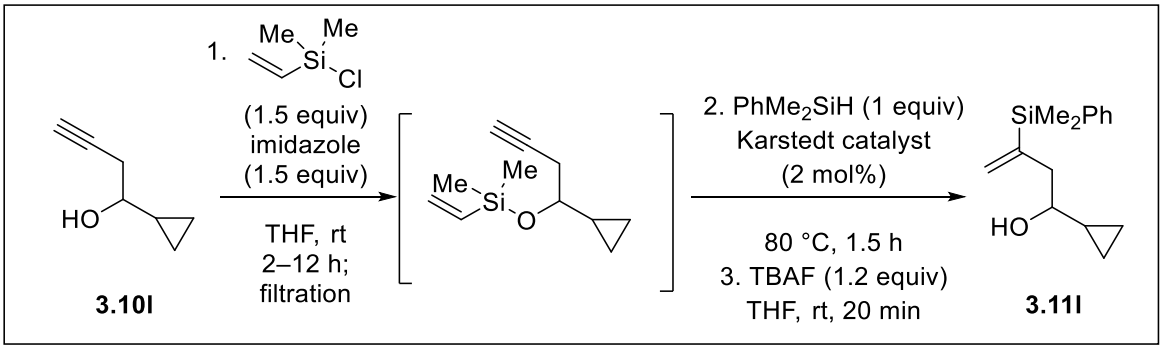
Following general procedure C, hept-1-yn-4-ol (**3.10j**) (1.1 g, 9.8 mmol, 1 equiv), dimethylvinylsilyl chloride (1.77 g, 14.7 mmol, 1.5 equiv), imidazole (1 g, 14.7 mmol, 1.5 equiv), in THF (43 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (1.9 g, 9.8 mmol, 1 equiv) was then treated with phenyldimethylsilane (1.3 g, 9.8 mmol, 1 equiv), and Karstedt catalyst solution (440 μL, 0.02 mmol, 0.002 equiv) at 80 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution (10.5 mL, 10.5 mmol, 1.2 equiv), in THF (100 mL), workup and purification by silica gel chromatography (15% EtOAc in hexanes) afforded **3.11j** as a colorless oil (845 mg, 3.40 mmol) and a mixture of **3.11j** and its regioisomer (929 mg, 3.74 mmol) in 73% overall yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.34 (m, 3 H), 5.78 (m, 1 H), 5.57 (d, *J* = 3.0 Hz, 1 H), 3.48 (m, 1 H), 2.37 (m, 1 H), 2.13 (dd, *J* = 9.0, 13.5 Hz, 1 H), 1.50 (s, 1 H), 1.35 (m, 3 H), 1.23 (m, 1 H), 0.84 (t, *J* = 6.5 Hz, 3 H), 0.39 (s, 3 H), 0.38 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 137.8, 133.8 (2 C), 129.4, 129.2, 127.9 (2 C), 69.3, 45.0, 39.1, 18.8, 14.0, -2.87, -2.93. IR (film) 3379, 3049, 2957, 2872, 1427, 1250, 1111, 817 cm^{-1}. HRMS (EI) *m/z* 230.1503 [(M-H_2O)$^+$; calcd for $C_{15}H_{22}Si$, 230.1491].

Preparation of 1-cyclohexyl-3-(dimethyl(phenyl)silyl)but-3-en-1-ol (3.11k)



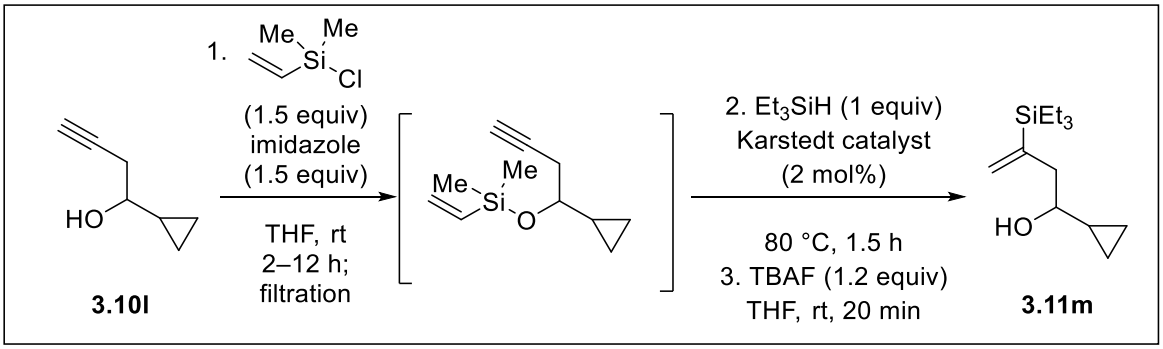
Following general procedure C, 1-cyclohexylbut-3-yn-1-ol (**3.10k**) (1.05 g, 6.9 mmol, 1 equiv), dimethylvinylsilyl chloride (1.25 g, 10.39 mmol, 1.5 equiv), imidazole (0.7 g, 10.39 mmol, 1.5 equiv), in THF (30 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (1.06 g, 4.46 mmol, 1 equiv) was then treated with phenyldimethylsilane (608 mg, 4.46 mmol, 1 equiv), and Karstedt catalyst solution (199 μL, 0.009 mmol, 0.002 equiv) at 75 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution (5.35 mL, 5.35 mmol, 1.2 equiv), in THF (50 mL), workup and purification by silica gel chromatography (10% EtOAc in hexanes) afforded a mixture of **3.11k** and its regioisomer (1.0:0.14 ratio) as a colorless oil (856 mg, 2.99 mmol, 67% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.34 (m, 3 H), 5.79 (quintet, 1 H), 5.57 (d, *J* = 3.0 Hz, 1 H), 3.24 (m, 1 H), 2.45 (A of ABX system, m, 1 H), 2.07 (B of ABX system, dd, *J* = 10.0, 13.5 Hz, 1 H), 1.75–1.67 (m, 3 H), 1.61 (m, 1 H), 1.55 (m, 1 H), 1.30–1.23 (m, 2 H), 1.22–1.08 (m, 3 H), 0.94 (m, 2 H), 0.39 (s, 3 H), 0.38 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 137.8, 133.8 (2 C), 129.5, 129.1, 127.9 (2 C), 73.4, 43.3, 41.7, 28.9, 28.1, 26.5, 26.3, 26.1, -2.77, -2.86. IR (neat) 3472, 3049, 2926, 2853, 1427, 1250, 1113, 817 cm^{-1}. HRMS (EI) *m/z* 288.1894 [$(M)^+$; calcd for $C_{18}H_{28}OSi$, 288.1909].

Preparation of 1-cyclopropyl-3-(dimethyl(phenyl)silyl)but-3-en-1-ol (3.11l)



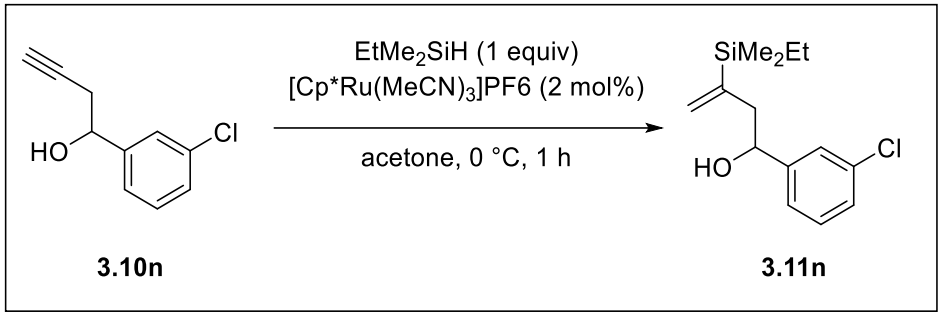
Following general procedure C, 1-cyclopropylbut-3-yn-1-ol (**3.10l**) (928 mg, 8.42 mmol, 1 equiv), dimethylvinylsilyl chloride (1.53 g, 12.64 mmol, 1.5 equiv), imidazole (861 mg, 12.64 mmol, 1.5 equiv), in THF (34 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (833 mg, 4.2 mmol, 1 equiv) was then treated with phenyldimethylsilane (572 mg, 4.2 mmol, 1 equiv), and Karstedt catalyst solution (187 μL, 0.008 mmol, 0.002 equiv) at 80 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution (4.2 mL, 4.2 mmol, 1.2 equiv), in THF (70 mL), workup and purification by silica gel chromatography (15% EtOAc in hexanes) afforded **3.11l** as a colorless oil (527 mg, 2.14 mmol, 51% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.34 (m, 3 H), 5.81 (m, 1 H), 5.56 (dd, *J* = 1.0, 3.0 Hz, 1 H), 2.76 (dt, *J* = 3.0, 9.0 Hz, 1 H), 2.52 (m, 1 H), 2.29 (dd, *J* = 4.5, 13.5 Hz, 1 H), 1.58 (s, 1 H), 0.80 (m, 1 H), 0.50–0.36 (m, 2 H), 0.38 (s, 6 H), 0.21 (m, 1 H), 0.00 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 137.8, 133.8 (2 C), 129.3, 129.1, 127.9 (2 C), 74.5, 44.3, 17.3, 2.9, 2.2, -2.8, -2.9. IR (film) 3408, 3069, 2957, 2909, 1427, 1250, 1111, 817 cm^{-1}. HRMS (EI) *m/z* 228.1331 [$(M-H_2O)^+$; calcd for $C_{15}H_{20}Si$, 228.1334].

Preparation of 1-cyclopropyl-3-(triethylsilyl)but-3-en-1-ol (3.11m)



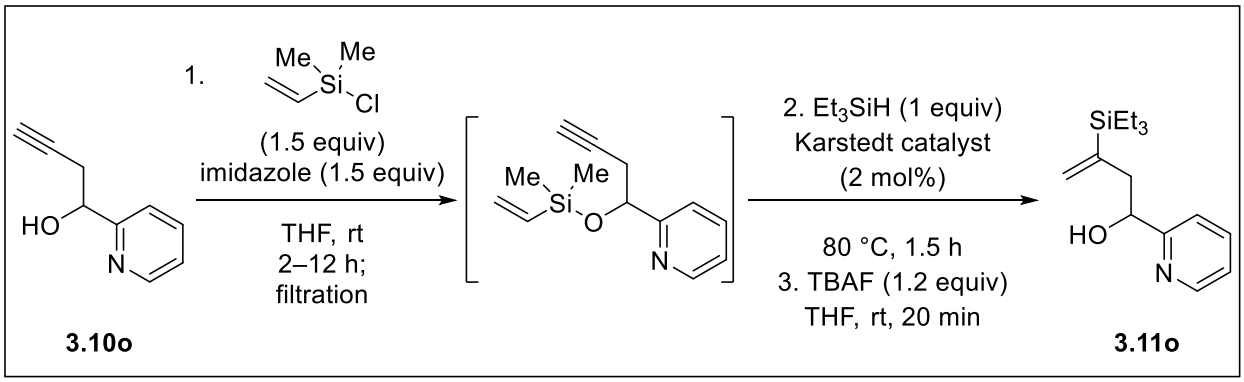
Following general procedure C, 1-cyclopropylbut-3-yn-1-ol (**3.10l**) (928 mg, 8.42 mmol, 1 equiv), dimethylvinylsilyl chloride (1.53 g, 12.64 mmol, 1.5 equiv), imidazole (861 mg, 12.64 mmol, 1.5 equiv), in THF (34 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (833 mg, 4.2 mmol, 1 equiv) was then treated with triethylsilane (488 mg, 4.2 mmol, 1 equiv), and Karstedt catalyst solution (187 μL, 0.008 mmol, 0.002 equiv) at 80 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution (4.2 mL, 4.2 mmol, 1.0 equiv), in THF (70 mL), workup and purification by silica gel chromatography (10% EtOAc in hexanes) afforded **3.11m** as a colorless oil (570 mg, 2.52 mmol, 60% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddd, *J* = 2.9, 1.6, 1.1 Hz, 1H), 5.46 (dt, *J* = 3.0, 0.7 Hz, 1H), 2.93 (ddd, *J* = 9.7, 8.1, 3.1 Hz, 1H), 2.53 (dddd, *J* = 14.1, 3.1, 1.6, 0.7 Hz, 1H), 2.26 (ddt, *J* = 13.9, 9.6, 0.8 Hz, 1H), 0.95 – 0.84 (m, 10H), 0.59 (qd, *J* = 7.9, 3.1 Hz, 6H), 0.55 – 0.45 (m, 2H), 0.38 – 0.30 (m, 1H), 0.22 – 0.14 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 128.8, 74.2, 44.6, 17.4, 7.3, 3.0, 2.2. HRMS (EI) *m/z* 206.1484 [$(M-H_2O)^+$; calcd for $C_{13}H_{24}Si$, 206.1491].

Preparation of 1-(3-chlorophenyl)-3-(ethyldimethylsilyl)but-3-en-1-ol (3.11n)



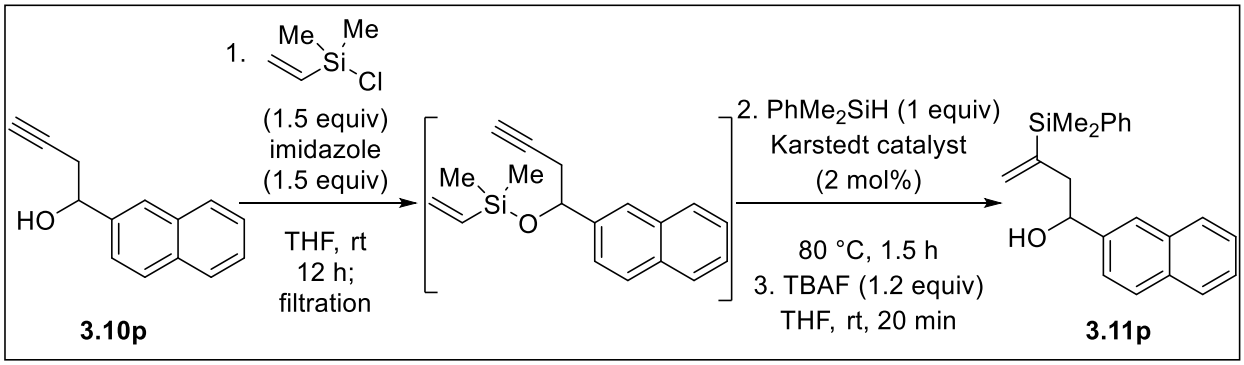
Following general procedure D, 1-(3-chlorophenyl)but-3-yn-1-ol (**3.10n**) (400 mg, 2.21 mmol, 1 equiv), ethyldimethylsilane (234 mg, 2.66 mmol, 1.2 equiv), dichloromethane (4.4 mL) and $[Cp^*Ru(MeCN)_3]PF_6$ (22.3 mg, 0.044 mmol, 0.02 equiv) at room temperature for 1.5 h, followed by silica gel chromatography (10% EtOAc in hexanes) afforded **3.11n** as colorless oil (438 mg, 1.63 mmol) and a mixture of its regioisomer (47 mg, 0.17 mmol) in 81% overall yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 2 H), 7.25–7.21 (m, 3 H), 5.76 (m, 1 H), 5.55 (dt, *J* = 1.0, 3.0 Hz, 1 H), 4.69 (dd, *J* = 3.5, 10.5 Hz, 1 H), 2.59 (m, 1 H), 2.36 (ddd, *J* = 0.5, 10.0, 14.0 Hz, 1 H), 2.14 (s, 1 H), 0.93 (t, *J* = 7.5 Hz, 3 H), 0.60 (q, *J* = 8.0 Hz, 2 H), 0.10 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 146.2, 134.3, 129.6, 129.1, 127.5, 126.0, 123.9, 71.5, 47.1, 7.3, 6.9, -3.6, -3.7. IR (film) 3402, 3051, 2955, 1431, 1248, 1055, 817 cm^{-1}. HRMS (EI) *m/z* 251.1014 [$(M\text{-}OH)^+$; calcd for $C_{14}H_{20}SiCl$, 251.1023].

Preparation of 1-(pyridin-2-yl)-3-(triethylsilyl)but-3-en-1-ol (3.11o)



Following general procedure C, 1-(pyridin-2-yl)but-3-yn-1-ol (**3.10o**) (2.21 g, 15.0 mmol, 1.0 equiv), dimethylvinylsilyl chloride (2.5 mL, 18.0 mmol, 1.2 equiv), triethyl amine (5.1 mL, 36.0 mmol, 2.4 equiv), in DMF (15 mL) afforded 3.08 g, 89% of O-dimethylvinylsilyl derivative, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (1.39 g, 6.0 mmol, 1.0 equiv) was then treated with triethylsilane (0.96 mL, 6.0 mmol, 1.0 equiv), and Karstedt catalyst solution (270 μL, 0.012 mmol, 0.002 equiv) at 80 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution 1.0 M in THF (7.2 mL, 7.2 mmol, 1.2 equiv), in THF (40 mL), workup and purification by silica gel chromatography (50% EtOAc in hexanes) afforded 350 mg, 1.32 mmol (22% isolated yield) of homoallylic alcohol **3.11o** as a colorless oil and about 75% of unreacted homopropargyl alcohol. Spectroscopic data for compound **3.11o**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (ddd, *J* = 4.9, 1.7, 1.0 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.18 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 5.80 (dt, *J* = 2.9, 1.4 Hz, 1H), 5.50 (dt, *J* = 2.8, 0.8 Hz, 1H), 4.83 (dd, *J* = 9.1, 4.1 Hz, 1H), 3.69 (s, 1H), 2.67 (dddd, *J* = 14.4, 4.2, 1.6, 0.8 Hz, 1H), 2.41 (ddt, *J* = 14.4, 9.0, 1.1 Hz, 1H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 148.4, 145.5, 136.5, 128.9, 122.2, 120.5, 71.9, 45.6, 7.3, 2.9. HRMS (ESI) *m/z* 264.1783 [(M + H)$^+$; calcd for $C_{15}H_{26}NOSi$, 264.1784].

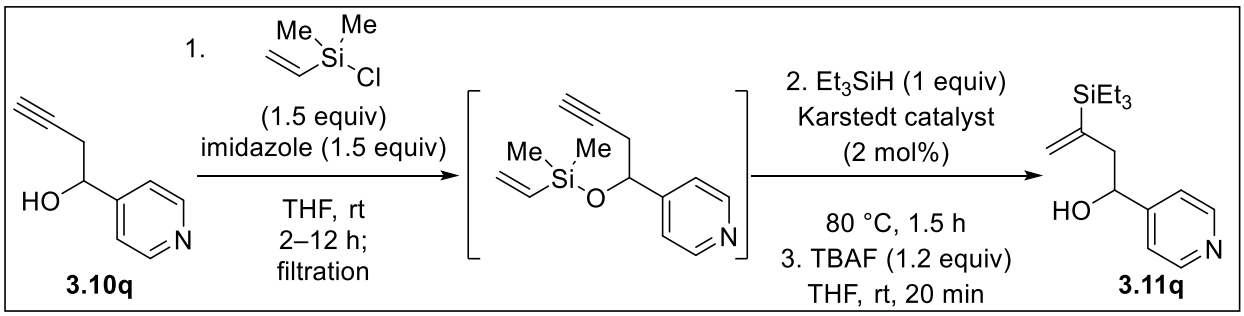
Preparation of 3-(dimethyl(phenyl)silyl)-1-(naphthalen-2-yl)but-3-en-1-ol (3.11p)



Following general procedure C, 1-(naphthalen-2-yl)but-3-yn-1-ol (**3.10p**) (2.65 g, 13.5

mmol, 1 equiv), dimethylvinylsilyl chloride (2.8 mL, 20.25 mmol, 1.5 equiv), imidazole (1.38 g, 20.25 mmol, 1.5 equiv), in THF (60 mL) afforded the O-dimethylvinylsilyl derivative in nearly quantitative yield, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (1.4 g, 5.0 mmol, 1 equiv) was then treated with dimethylphenylsilane (0.77 mL, 5.0 mmol, 1 equiv), and Karstedt catalyst solution (220 μL, 0.01 mmol, 0.002 equiv) at 80 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution (6.0 mL, 5.0 mmol, 1.2 equiv), in THF (70 mL), workup and purification by silica gel chromatography (15% EtOAc in hexanes) afforded **3.11p** as a colorless oil (1.26 g, 3.8 mmol, 76% isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 – 7.80 (m, 3H), 7.66 (s, 1H), 7.63 – 7.58 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.40 (m, 3H), 7.37 (dd, *J* = 8.5, 1.7 Hz, 1H), 5.91 (dt, *J* = 2.8, 1.3 Hz, 1H), 5.68 (d, *J* = 2.8 Hz, 1H), 4.74 (dd, *J* = 9.9, 3.7 Hz, 1H), 2.72 (dddd, *J* = 14.1, 3.8, 1.5, 0.6 Hz, 1H), 2.56 (ddt, *J* = 14.1, 9.6, 1.0 Hz, 1H), 2.15 (s, 1H), 0.51 (s, 3H), 0.49 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.3, 141.4, 137.6, 133.9, 133.2, 132.8, 130.0, 129.3, 127.99, 128.97, 127.87, 127.6, 126.0, 125.6, 124.3, 123.9, 72.3, 46.9, -2.90, -2.94. IR (neat) 3424, 3051, 2955, 1427, 1248, 1111, 815 cm^{-1}. HRMS (EI) m/z 315.1553 [(M-OH)$^{+}$; calcd for $C_{22}H_{23}Si$, 315.1569].

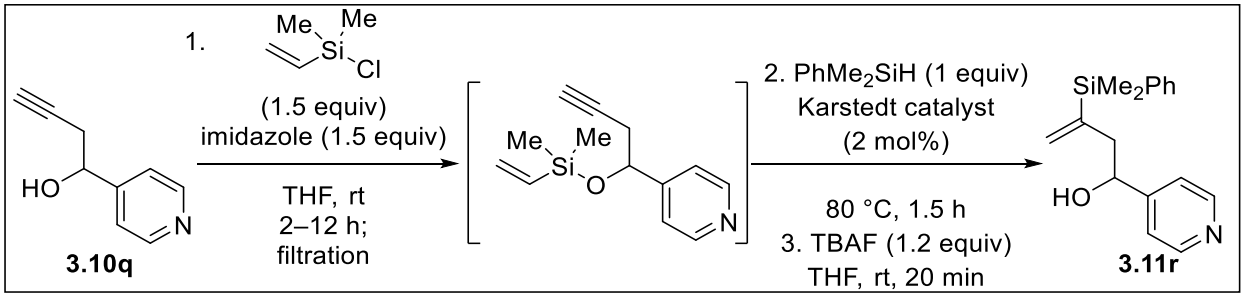
Preparation of 1-(pyridin-4-yl)-3-(triethylsilyl)but-3-en-1-ol (3.11q)



Following general procedure C, 1-(pyridin-4-yl)but-3-yn-1-ol (**3.10q**) (2.21 g, 15.0 mmol, 1.0 equiv), dimethylvinylsilyl chloride (2.5 mL, 18.0 mmol, 1.2 equiv), triethyl amine (5.1 mL,

36.0 mmol, 2.4 equiv), in DMF (15 mL) afforded 2.85 g, 82% of O-dimethylvinylsilyl derivative, which was used in the next step without further purification. The O-dimethylvinylsilyl intermediate (926 mg, 4.0 mmol, 1.0 equiv) was then treated with triethylsilane (0.64 mL, 4.0 mmol, 1.0 equiv), and Karstedt catalyst solution (180 μL, 0.008 mmol, 0.002 equiv) at 80 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution 1.0 M in THF (4.8 mL, 4.8 mmol, 1.2 equiv), in THF (40 mL), workup and purification by silica gel chromatography (60% EtOAc in hexanes) afforded 706 mg, 2.68 mmol (67% isolated yield) of homoallylic alcohol **3.11q** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 6.2 Hz, 2H), 7.28 (d, *J* = 6.1 Hz, 2H), 5.79 (dt, *J* = 2.7, 1.3 Hz, 1H), 5.53 (d, *J* = 2.7 Hz, 1H), 4.71 (dd, *J* = 9.8, 3.6 Hz, 1H), 3.21 (s, 1H), 2.56 (dd, *J* = 14.2, 3.6 Hz, 1H), 2.34 (dd, *J* = 14.2, 9.8 Hz, 1H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.64 (qd, *J* = 7.8, 2.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 149.5, 145.3, 129.9, 120.8, 70.6, 46.7, 7.3, 2.9. HRMS (ESI) *m/z* 264.1788 [$(M + H)^+$; calcd for $C_{15}H_{26}NOSi$, 264.1784].

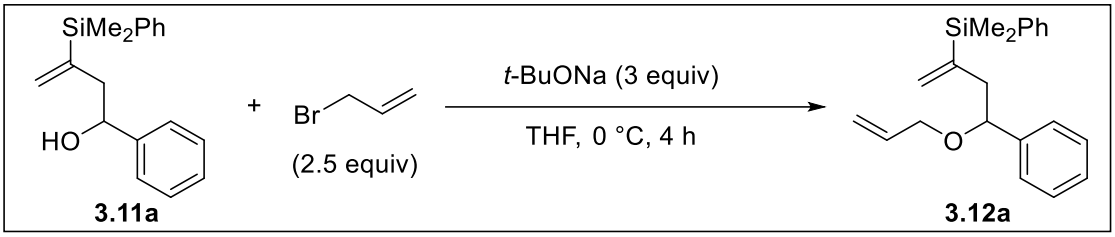
Preparation of 3-(dimethyl(phenyl)silyl)-1-(pyridin-4-yl)but-3-en-1-ol (3.11r)



The O-dimethylvinylsilyl of 1-(pyridin-4-yl)but-3-yn-1-ol (**3.10q**) intermediate (1273 mg, 5.5 mmol, 1.0 equiv) was treated with dimethylphenyl silane (0.84 mL, 5.5 mmol, 1.0 equiv), and Karstedt catalyst solution (250 μL, 0.008 mmol, 0.002 equiv) at 80 ºC for 1.5 h and cooled down to room temperature. Treatment with TBAF solution 1.0 M in THF (6.6 mL, 6.6 mmol, 1.2 equiv), in THF (40 mL), workup and purification by silica gel chromatography (20% EtOAc in hexanes)

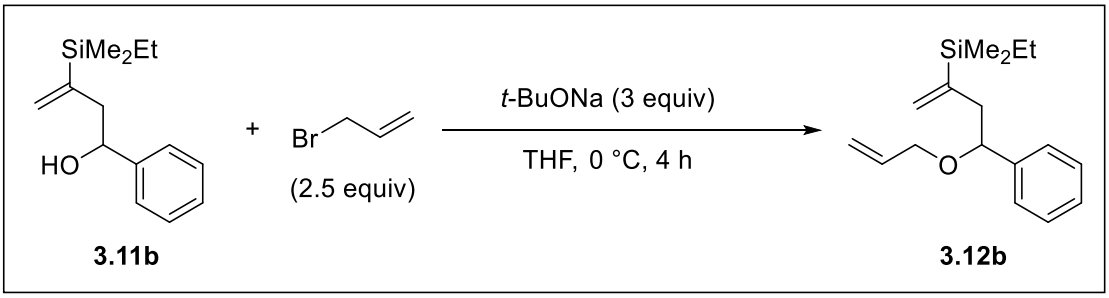
afforded 1175 mg, 4.13 mmol (75% isolated yield) of homoallylic alcohol **3.11r** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 6.1 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.41 – 7.34 (m, 3H), 7.08 (d, *J* = 6.1 Hz, 2H), 5.83 (dt, *J* = 2.6, 1.3 Hz, 1H), 5.65 (d, *J* = 2.7 Hz, 1H), 4.48 (dd, *J* = 9.7, 3.7 Hz, 1H), 3.01 (s, 1H), 2.55 (ddd, *J* = 13.9, 3.7, 1.4 Hz, 1H), 2.37 (dd, *J* = 14.1, 9.7 Hz, 1H), 0.44 (s, 3H), 0.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 149.4, 146.7, 137.4, 133.8, 130.4, 129.4, 128.0, 120.7, 70.7, 46.6, -3.0, -3.1. HRMS (ESI) *m/z* 284.1475 [$(M + H)^+$; calcd for $C_{17}H_{22}NOSi$, 284.1471].

Preparation of (4-(allyloxy)-4-phenylbut-1-en-2-yl)dimethyl(phenyl)silane (3.12a)



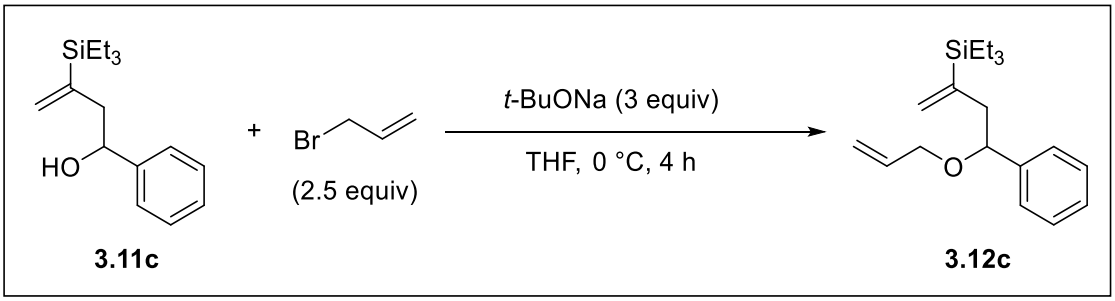
Following General Procedure E, alcohol **3.11a** (486 mg, 1.72 mmol, 1 equiv), allyl bromide (0.36 mL, 4.3 mmol, 2.5 equiv), THF (3.6 mL), and *t*-BuONa (496 mg, 5.16 mmol, 3 equiv) afforded, after silica gel chromatography (25% CH_2Cl_2 in hexanes), compound **3.12a** as a colorless oil (499 mg, 1.55 mmol, 90% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.33 (m, 3 H), 7.27 (t, *J* = 6.5 Hz, 2 H), 7.22 (m, 1 H), 7.13 (m, 2H), 5.77(m, 1 H), 5.69 (m, 1 H), 5.47 (d, *J* = 2.5 Hz, 1 H), 5.14 (m, 1 H), 5.07 (m, 1 H), 4.19 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.74 (A of ABX system, ddt, *J* = 1.5, 5.5, 13.0 Hz, 1 H), 3.52 (B of ABX system, ddt, *J* = 1.5, 6.0, 13.0 Hz, 1 H), 2.64 (A of ABX system, dd, *J* = 8.0, 14.5 Hz, 1 H), 2.39 (B of ABX system, dd, *J* = 5.5, 14.5 Hz, 1 H), 0.36 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 142.4, 138.3, 135.0, 134.0 (2 C), 129.2, 128.9, 128.2 (2 C), 127.7 (2 C), 127.4, 126.8 (2 C), 116.5, 80.7, 69.4, 44.7, -2.924, -2.917. IR (neat) 3067, 2955, 1427, 1248, 1111, 815 cm^{-1}. HRMS (EI) *m/z* 307.1504 [$(M-CH_3)^+$; calcd for $C_{20}H_{23}OSi$, 307.1518].

Preparation of (4-(allyloxy)-4-phenylbut-1-en-2-yl)(ethyl)dimethylsilane (3.12b)



Following general procedure E, alcohol **3.11b** (181 mg, 0.77 mmol, 1 equiv), allyl bromide (0.16 mL, 1.93 mmol, 2.5 equiv), THF (1.6 mL), and *t*-BuONa (223 mg, 2.32 mmol, 3 equiv) afforded, after silica gel chromatography (30% CH_2Cl_2 in hexanes), compound **3.12b** as a colorless oil (165.2 mg, 0.60 mmol, 78% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 2 H), 7.26 (m, 2 H), 7.24 (m, 1 H), 5.86 (m, 1 H), 5.58 (m, 1 H), 5.37 (dt, *J* = 0.5, 3.0 Hz, 1 H), 5.19 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.11 (m, 1 H), 4.36 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.85 (ddt, A of ABX system, *J* = 1.5, 5.0, 12.5, Hz, 1 H), 3.72 (ddt, B of ABX system, *J* = 1.5, 6.0, 12.5 Hz, 1 H), 2.64 (m, 1 H), 2.39 (m, 1 H), 0.89 (t, *J* = 8.0 Hz, 3 H), 0.54 (q, *J* = 8.0 Hz, 2 H), 0.04 (s, 3 H), 0.02 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 142.5, 135.0, 128.3 (2 C), 127.6, 127.4, 126.9 (2 C), 116.6, 81.1, 69.5, 44.5, 7.4, 6.8, -3.7, -3.8. IR (film) 3030, 2955, 2874, 1248, 1087, 819 cm^{-1}. HRMS (EI) *m/z* 274.1748 [(M)$^+$; calcd for $C_{17}H_{26}OSi$, 274.1753].

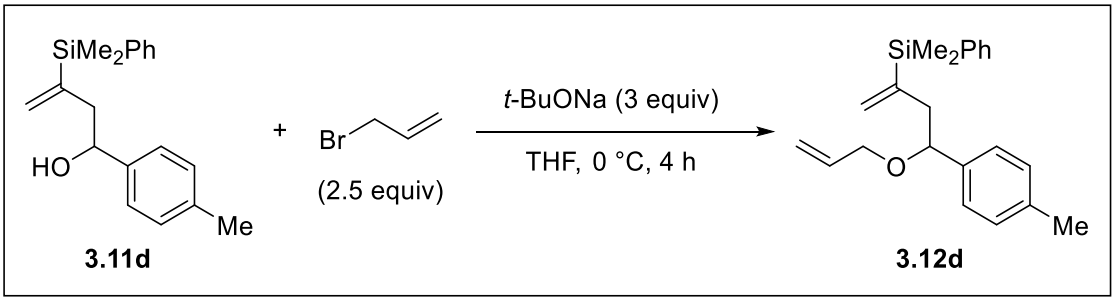
Preparation of (4-(allyloxy)-4-phenylbut-1-en-2-yl)triethylsilane (3.12c)



Following general procedure E, alcohol **3.11c** (402 mg, 1.53 mmol, 1 equiv), allyl bromide

(0.32 mL, 3.83 mmol, 2.5 equiv), THF (3.1 mL), and *t*-BuONa (442 mg, 4.59 mmol, 3 equiv) afforded, after silica gel chromatography (20% CH_2Cl_2 in hexanes), compound **3.12c** as a colorless oil (407 mg, 1.35 mmol, 88% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.23 (m, 5 H), 5.86 (m, 1 H), 5.64 (m, 1 H), 5.36 (d, *J* = 3.5 Hz, 1 H), 5.19 (dq, *J* = 2.0, 17.5 Hz, 1 H), 5.10 (m, 1 H), 4.37 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.85 (m, 1 H), 3.71 (m, 1 H), 2.62 (dd, A of ABX system, *J* = 8.0, 14.5 Hz, 1 H), 2.37 (dd, B of ABX system, *J* = 5.5, 14.5 Hz, 1 H), 0.90 (t, *J* = 8.0 Hz, 9 H), 0.58 (dq, *J* = 2.0, 8.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 142.6, 135.0, 128.38, 128., 127.4, 126.9, 116.6, 81.0, 69.5, 44.5, 7.3, 2.8. IR (film) 3030, 2953, 1454, 1086, 924, 700 cm^{-1}. HRMS (EI) *m/z* 302.2051 [(M)$^+$; calcd for $C_{19}H_{30}OSi$, 302.2066].

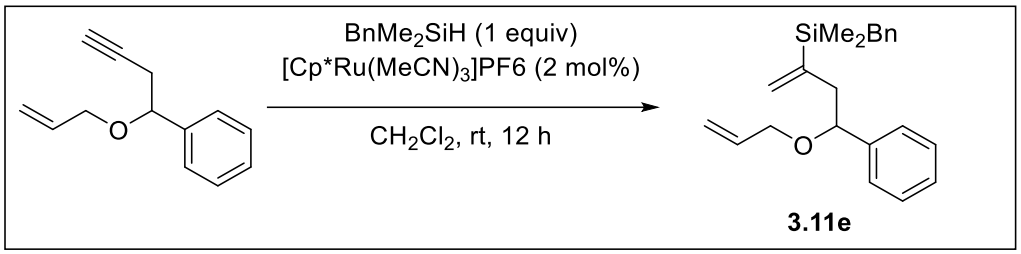
Preparation of (4-(allyloxy)-4-(p-tolyl)but-1-en-2-yl)dimethyl(phenyl)silane (3.12d)



Following general procedure E, alcohol **3.11d** (714 mg, 2.41 mmol, 1 equiv), allyl bromide (0.51 mL, 6.02 mmol, 2.5 equiv), THF (4.9 mL), and *t*-BuONa (694 mg, 7.2 mmol, 3 equiv) afforded, after silica gel chromatography (25% CH_2Cl_2 in hexanes), compound **3.12d** as a colorless oil (698 mg, 2.07 mmol, 86% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.34 (m, 3 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 5.78 (m, 1 H), 5.70 (m, 1 H), 5.47 (m, 1 H), 5.14 (m, 1 H), 5.07 (m, 1 H), 4.17 (dd, *J* = 5.0, 8.0 Hz, 1 H), 3.74 (A of ABX system, m, 1 H), 3.52 (B of ABX system, m, 1 H), 2.64(A of ABX system, ddd, *J* = 0.5, 8.0, 14.5 Hz, 1 H), 2.38 (B, of ABX system, ddd, *J* = 0.5, 5.0, 14.0 Hz, 1 H), 2.32 (s, 3 H), 0.364 (s, 3 H), 0.361 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 139.3, 138.3, 137.0, 135.1, 134.0 (2 C), 129.1, 128.9,

128.8 (2 C), 127.7 (2 C), 126.8 (2 C), 116.4, 80.4, 69.3, 44.7, 21.1, -2.89, -2.91. IR (neat) 3049, 2955, 2858, 1427, 1248, 1111, 815 cm^{-1}. HRMS (EI) *m/z* 321.1667 [$(M\text{-}CH_3)^+$; calcd for $C_{21}H_{25}OSi$, 321.1675].

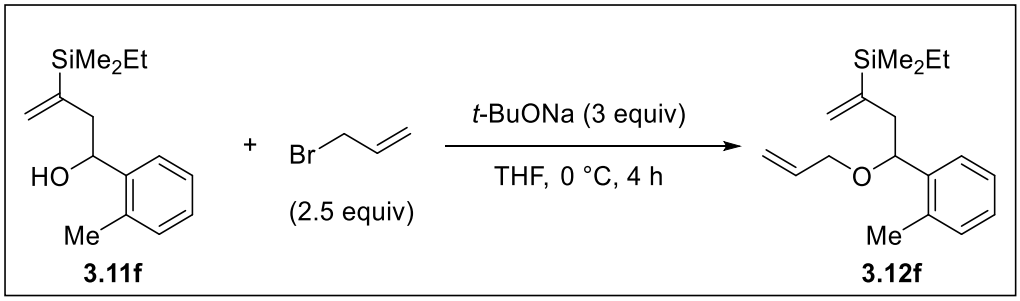
Preparation of (4-(allyloxy)-4-(p-tolyl)but-1-en-2-yl)(benzyl)dimethylsilane (3.12e)



Compound **3.12e** was prepared by a modification of General Procedure D. A 25 mL round bottom flask was charged with a magnetic stirrer, 1-(1-(allyloxy)but-3-yn-1-yl)-4-methylbenzene (500 mg, 2.5 mmol, 1 equiv), dichloromethane (5 mL), and benzydimethylsilane (451 mg, 3 mmol, 1.2 equiv). The flask was flushed with nitrogen and $[Cp^*Ru(MeCN)_3]PF_6$ (25.2 mg, 0.05 mmol, 0.02 equiv) was added quickly, the reaction was kept under nitrogen. The reaction was run overnight at room temperature. The reaction mixture was concentrated and the crude product purified by silica gel chromatography (30% CH_2Cl_2 in hexanes) to afford **3.12e** as a colorless oil (297 mg, 1.48 mmol, 59% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (m, 5 H), 7.05 (t, *J* = 7.0 Hz, 1 H), 6.96 (d, *J* = 7.5 Hz, 2 H), 5.86 (m, 1 H), 5.64 (s, 1 H), 5.38 (s, 1 H), 5.21 (d, *J* = 17.5 Hz, 1 H), 5.11 (d, *J* = 10.0 Hz, 1 H), 4.35 (m, 1 H), 3.86 (dd, A of ABX system, *J* = 4.5, 12.5 Hz, 1 H), 3.71 (dd, B of ABX system, *J* = 5.5, 12.5 Hz, 1 H), 2.65 (dd, C of CDX system, *J* = 8.0, 14.5 Hz, 1 H), 2.38 (dd, *J* = 5.0, 14.5 Hz, 1 H), 2.34 (s, 3 H), 2.13 (s, 2 H), 0.03 (s, 3 H), 0.01 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 140.0, 139.3, 137.1, 135.0, 129.0 (2 C), 128.3 (2 C), 128.2, 128.0 (2 C), 126.9 (2 C), 123.9, 116.6, 81.0, 69.4, 44.4, 25.4, 21.1, -3.5. IR (film) 3025, 2922, 1493, 1248, 1084, 815 cm^{-1}. HRMS (EI) *m/z* 350.2060 [(M^+); calcd for $C_{23}H_{30}OSi$,

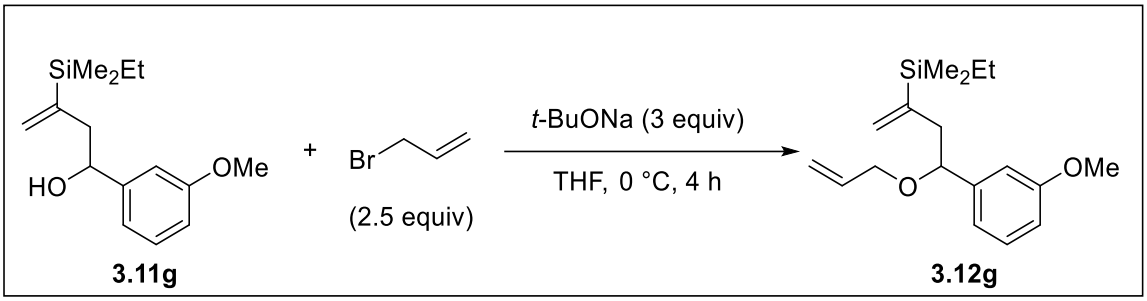
350.2066].

Preparation of (4-(allyloxy)-4-(o-tolyl)but-1-en-2-yl)(ethyl)dimethylsilane (3.12f)



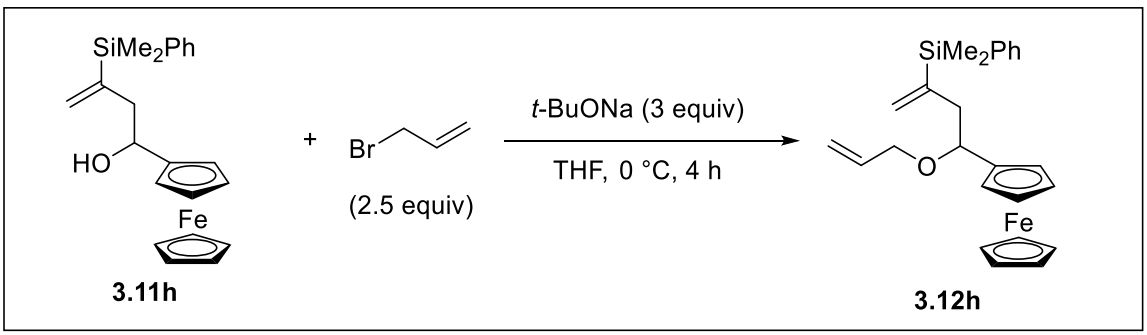
Following general procedure E, alcohol **3.11f** (412 mg, 1.66 mmol, 1 equiv), allyl bromide (0.35 mL, 4.15 mmol, 2.5 equiv), THF (3.3 mL), and *t*-BuONa (478 mg, 4.98 mmol, 3 equiv) afforded, after silica gel chromatography (30% CH_2Cl_2 in hexanes), compound **3.12f** as a colorless oil (439 mg, 1.53 mmol, 92% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 1.0, 7.5 Hz, 1 H), 7.20 (t, *J* = 7.5 Hz, 1 H), 7.15 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.10 (m, 1 H), 5.87 (m, 1 H), 5.67 (quintet, *J* = 1.5 Hz, 1 H), 5.41 (dt, *J* = 1.0, 3.0 Hz, 1 H), 5.19 (dq, *J* = 1.0, 17.5 Hz, 1 H), 5.11 (dq, *J* = 1.5, 10.5 Hz, 1 H), 4.64 (dd, *J* = 4.0, 9.0 Hz, 1 H), 3.85 (ddt, A of ABX system, *J* = 1.5, 5.0, 12.5 Hz, 1 H), 3.69 (ddt, B of ABX system, *J* =1.5, 6.0, 13.0 Hz, 1 H), 2.54 (m, 1 H), 2.34 (m, 1 H), 2.30 (s, 3 H), 0.90 (t, *J* = 8.0 Hz, 3 H), 0.56 (q, *J* = 8.0 Hz, 2 H), 0.05 (s, 3 H), 0.04 (s 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 140.8, 135.20, 135.18, 130.3, 127.1, 127.0, 126.22, 126.18, 116.5, 77.6, 69.4, 43.2, 19.3, 7.4, 6.8, -3.75, -3.78. IR (film) 3049, 2957, 1426, 1248, 1109, 815 cm^{-1}. HRMS (EI) *m*/*z* 230.1484 [$(M-OCH_2CHCH_2)^+$; calcd for $C_{15}H_{22}Si$, 230.1491].

Preparation of (4-(allyloxy)-4-(3-methoxyphenyl)but-1-en-2-yl)(ethyl)dimethylsilane (3.12g)



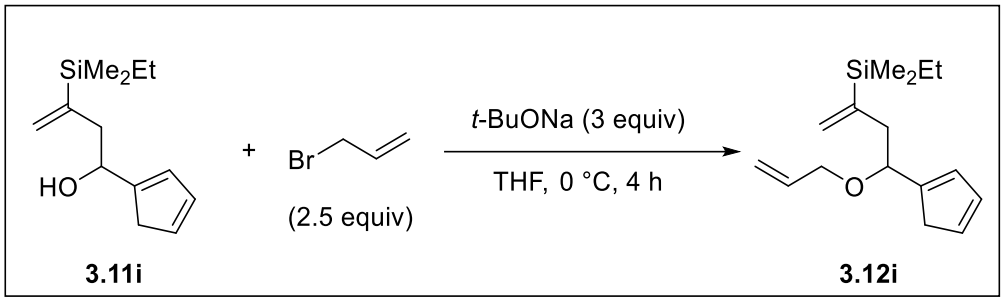
Following general procedure E, alcohol **3.11g** (289 mg, 1.09 mmol, 1 equiv), allyl bromide (0.23 mL, 2.73 mmol, 2.5 equiv), THF (2.2 mL), and *t*-BuONa (315 mg, 3.28 mmol, 3 equiv) afforded, after silica gel chromatography (30% CH_2Cl_2 in hexanes), compound **3.12g** as a colorless oil (283 mg, 0.93 mmol, 85% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.0 Hz, 1 H), 6.85 (m, 2 H), 6.79 (m, 1 H), 5.86 (m, 1 H), 5.60 (m, 1 H), 5.38 (d, *J* = 3.0 Hz, 1 H), 5.20 (dq, *J* = 1.5, 17.5 Hz, 1 H), 5.11 (dq, *J* = 1.5, 10.5 Hz, 1 H), 4.34 (dd, *J* = 5.0, 8.0 Hz, 1 H), 3.88 (ddt, A of ABX system, *J* = 1.5, 5.0, 12.5 Hz, 1 H), 3.80 (s, 3 H), 3.71 (ddt, B of ABX system, *J* = 1.5, 6.0, 12.5 Hz, 1 H), 2.62 (dd, C of CDX system, *J* = 8.0, 14.5 Hz, 1 H), 2.38 (dd, D of CDX system, *J* = 5.0, 14.5 Hz, 1 H), 0.89 (t, *J* = 8.0 Hz, 3 H), 0.54 (q, *J* = 8.0 Hz, 2 H), 0.04 (s, 3 H), 0.03 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 147.2, 144.3, 135.0, 129.2, 127.5, 119.4, 116.7, 112.9, 112.2, 81.0, 69.6, 55.2, 44.5, 7.4, 6.8, -3.71, -3.73. IR (film) 3049, 2953, 1601, 1257, 1045, 819, 779 cm^{-1}. HRMS (EI) *m*/*z* 246.1441 [(M-C_3H_6O)$^+$; calcd for $C_{15}H_{22}OSi$, 246.1440].

Preparation of (4-(allyloxy)-4-(ferrocenyl)but-1-en-2-yl)dimethyl(phenyl)silane (3.12h)



Following general procedure E, alcohol **3.11h** (1.72 g, 4.4 mmol, 1 equiv), allyl bromide (0.93 mL, 11 mmol, 2.5 equiv), THF (8.8 mL), and *t*-BuONa (1.27 g, 13.2 mmol, 3 equiv) afforded, after silica gel chromatography (25–35% CH_2Cl_2 in hexanes), compound **3.12h** as an orange oil (1.49 g, 3.43 mmol, 78% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 2 H), 7.36 (m, 3 H), 5.85 (m, 1 H), 5.78 (ddt, *J* = 5.5, 10.5, 17.5 Hz, 1 H), 5.56 (d, *J* = 2.5 Hz, 1 H), 5.18 (dq, *J* = 1.2, 17.0 Hz, 1 H), 5.06 (dq, *J* = 1.5, 10.5 Hz, 1 H), 4.12 (dd, *J* = 3.5, 9.0 Hz, 1 H), 4.08 (m, 4 H), 3.99 (s, 5 H), 3.89 (ddt, *J* = 1.5, 5.0, 12.5 Hz, 1 H), 3.69 (ddt, *J* = 1.5, 5.5, 12.5 Hz, 1 H), 2.72 (A of ABX system, m, 1 H), 2.65 (B of ABX system, dd, *J* = 4.5, 15.0 Hz, 1 H), 0.429 (s, 3 H), 0.421 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 138.3, 135.4, 134.0 (2 C), 129.1, 128.4, 127.8 (2 C), 89.3, 76.1, 69.2, 68.6 (5 C), 68.4, 67.8, 67.1, 66.1, 42.1, -2.69, -2.75. IR (neat) 3070, 2955, 1427, 1248, 1107, 815 cm^{-1}. HRMS (EI) *m*/*z* 430.1402 [(M)$^+$; calcd for $C_{25}H_{30}SiOFe$, 430.1415].

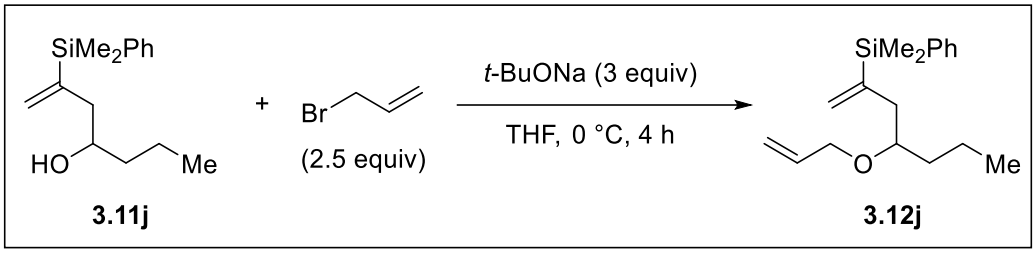
Preparation of (4-(allyloxy)-4-(thiophen-2-yl)but-1-en-2-yl)(ethyl)dimethylsilane (3.12i)



Following general procedure E, alcohol **3.11i** (169 mg, 0.7 mmol, 1 equiv), allyl bromide (0.15 mL, 1.76 mmol, 2.5 equiv), THF (1.5 mL), and *t*-BuONa (203 mg, 2.11 mmol, 3 equiv) afforded, after silica gel chromatography (20% CH_2Cl_2 in hexanes), compound **3.12i** as a colorless oil (166 mg, 0.59 mmol, 84% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 0.5, 5.0 Hz, 1 H), 6.92 (dd, *J* = 3.5, 5.0 Hz, 1 H), 6.89 (dd, *J* = 1.0, 3.0 Hz, 1 H), 5.86 (m, 1 H), 5.59 (dt, *J* = 1.5, 2.5 Hz, 1 H), 5.37 (d, *J* = 3.0 Hz, 1 H), 5.21 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.13 (dq, *J* = 1.5, 10.0 Hz, 1 H), 6.64 (t, *J* = 7.0 Hz, 1 H), 3.95 (ddt, A of ABX system, *J* = 1.5, 5.5, 12.5 Hz, 1 H),

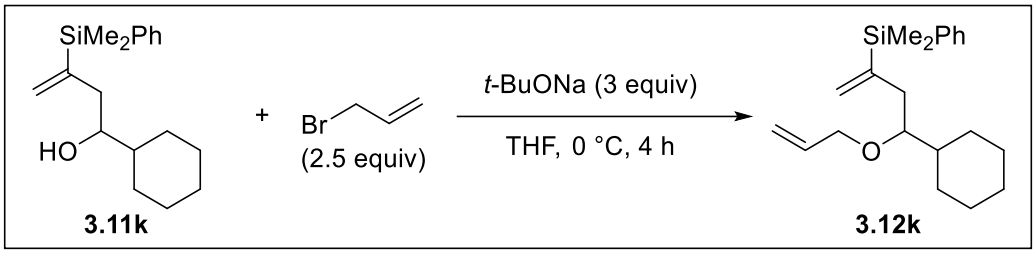
3.79 (ddt, B of ABX system, J = 1.5, 6.5, 12.5 Hz, 1 H), 2.76 (m, 1 H), 2.51 (m, 1 H), 0.89 (t, J = 8.0 Hz, 3 H), 0.54 (q, J = 8.0 Hz, 2 H), 0.04 (s, 3 H), 0.03 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 146.4, 134.8, 127.7, 126.2, 125.3, 124.7, 117.0, 76.3, 69.4, 44.8, 7.3, 6.8, -3.7, -3.8. HRMS (EI) *m*/*z* 280.1310 [$(M)^+$; calcd for $C_{15}H_{24}SiOS$, 280.1317].

Preparation of (4-(allyloxy)hept-1-en-2-yl)dimethyl(phenyl)silane (3.12j)



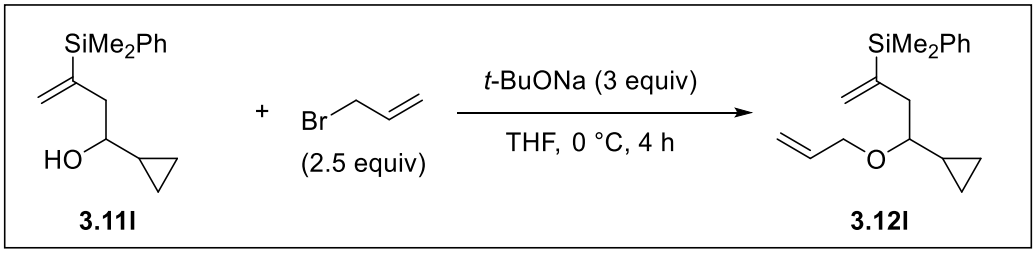
Following general procedure E, alcohol **3.11j** (828 mg, 3.33 mmol, 1 equiv), allyl bromide (0.7 mL, 8.33 mmol, 2.5 equiv), THF (6.7 mL), and *t*-BuONa (961 mg, 10 mmol, 3 equiv) afforded, after silica gel chromatography (20% CH_2Cl_2 in hexanes), compound **3.12j** as a colorless oil (864 mg, 3.0 mmol, 90% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.33 (m, 3 H), 5.81 (m, 1 H), 5.74 (m, 1 H), 5.49 (d, J = 3.0 Hz, 1 H), 5.16 (dq, J = 1.5, 17.0 Hz, 1 H), 5.08 (m, 1 H), 3.82 (ddt, A of ABX system, J = 1.5, 6.0, 13.0 Hz, 1 H), 3.76 (ddt, B of ABX system, J = 1.5, 6.0, 12.5 Hz, 1 H), 3.22 (m, 1 H), 2.44 (ddt, C of CDX system, J = 1.0, 5.5, 14.0 Hz, 1 H), 2.15 (dd, D of CDX system, J = 7.5, 14.0 Hz, 1 H), 1.35–1.25 (m, 3 H), 1.13 (m, 1 H), 0.79 (t, J = 7.0 Hz, 3 H), 0.38 (s, 3 H), 0.37 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 138.1, 135.5, 133.9 (2 C), 129.0, 128.9, 127.7 (2 C), 116.3, 77.9, 69.9, 41.4, 36.0, 18.5, 14.1, -2.7, -2.9. IR (neat) 3062, 2924, 2851, 1248, 1111, 816 cm^{-1}. HRMS (EI) *m/z* 273.1660 [$(M\text{-}CH_3)^+$; calcd for $C_{17}H_{25}OSi$, 273.1675].

Preparation of (4-(allyloxy)-4-cyclohexylbut-1-en-2-yl)dimethyl(phenyl)silane (3.12k)



Following general procedure E, alcohol **3.11k** (827 mg, 2.87 mmol, 1 equiv), allyl bromide (0.61 mL, 7.18 mmol, 2.5 equiv), THF (6 mL), and *t*-BuONa (827 mg, 8.6 mmol, 3 equiv) afforded, after silica gel chromatography (20–25% CH_2Cl_2 in hexanes), compound **3.12k** as a colorless oil (647 mg, 1.98 mmol, 69% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.33 (m, 3 H), 5.81 (m, 1 H), 5.77 (m, 1 H), 5.49 (d, *J* = 3.0 Hz, 1 H), 5.15 (dq, *J* = 2.0, 17.5 Hz, 1 H), 5.05 (dq, *J* = 1.5, 10.5 Hz, 1 H), 3.79 (A of ABX system, ddt, *J* = 1.5, 5.5, 12.5 Hz, 1 H), 3.74 (B of ABX system, ddt, *J* = 1.5, 6.0, 13.0 Hz, 1 H), 3.02 (m, 1 H), 2.28 (d, *J* = 6.5 Hz, 1 H), 1.67 (m, 2 H), 1.59 (m, 2 H), 1.39–1.29 (m, 2 H), 1.15–1.01 (m, 4 H), 0.97 (m, 1 H), 0.39 (s, 3 H), 0.37 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 138.3, 135.7, 133.9 (2 C), 128.9, 128.8, 127.7 (2 C), 116.0, 82.3, 71.1, 40.8, 38.0, 29.2, 27.4, 26.6, 26.5, 26.4, -2.71, -2.86. IR (neat) 3069, 2926, 2853, 1450, 1248, 1111, 817 cm^{-1}. HRMS (EI) *m/z* 328.2233 [$(M)^+$; calcd for $C_{21}H_{32}OSi$, 328.2222].

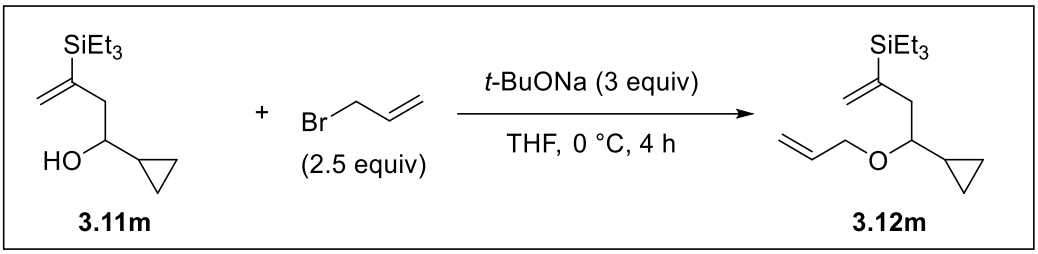
Preparation of (4-(allyloxy)-4-cyclopropylbut-1-en-2-yl)dimethyl(phenyl)silane (3.12l)



Following general procedure E, alcohol **3.11l** (312 mg, 1.27 mmol, 1 equiv), allyl bromide (0.27 mL, 3.17 mmol, 2.5 equiv), THF (2.5 mL), and *t*-BuONa (365 mg, 3.8 mmol, 3 equiv)

afforded, after silica gel chromatography (20–25% CH_2Cl_2 in hexanes), compound **3.12l** as a colorless oil (290 mg, 1.02 mmol, 80% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.32 (m, 3 H), 5.81 (m, 2 H), 5.48 (d, *J* = 2.5 Hz, 1 H), 5.18 (dq, *J* = 1.5, 14.5 Hz, 1 H), 5.07 (dq, *J* = 1.5, 9.0 Hz, 1 H), 4.04 (ddt, A of ABX system, *J* = 1.0, 4.5, 10.5 Hz, 1 H), 3.75 (ddt, B of ABX system, *J* = 1.5, 4.5, 10.5 Hz, 1 H), 2.60 (dt, *J* = 3.5, 6.5 Hz, 1 H), 2.45 (dd, C of CDX system, *J* = 6.5, 12.0 Hz, 1 H), 2.39 (dd, D of CDX system, *J* = 3.5, 12.0 Hz, 1 H), 0.73 (m, 1 H), 0.49 (m, 1 H), 0.36 (s, 6 H), 0.34 (m, 1 H), 0.25 (m, 1 H), -0.10 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.0, 138.4, 135.7, 134.0 (2 C), 128.9, 128.8, 127.7 (2 C), 116.0, 82.2, 69.7, 42.0, 15.1, 4.4, 1.3, -2.7, -2.8. IR (film) 3069, 3005, 2957, 2858, 1427, 1111, 815 cm^{-1}. HRMS (EI) *m/z* 286.1741 [$(M)^+$; calcd for $C_{18}H_{26}OSi$, 286.1753].

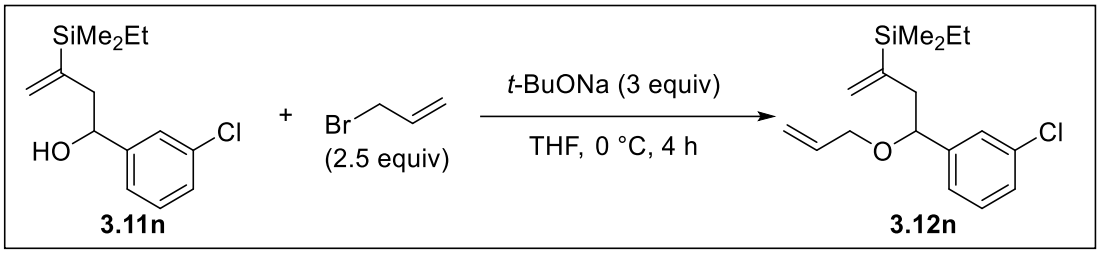
Preparation of (4-(allyloxy)-4-cyclopropylbut-1-en-2-yl)triethylsilane (3.12m)



Following general procedure E, alcohol **3.11m** (265 mg, 1.17 mmol, 1 equiv), allyl bromide (0.25 mL, 2.93 mmol, 2.5 equiv), THF (2.4 mL), and *t*-BuONa (337 mg, 3.5 mmol, 3 equiv) afforded, after silica gel chromatography (20–25% CH_2Cl_2 in hexanes), compound **3.12m** as a colorless oil (261 mg, 0.98 mmol, 84% isolated yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.88 (m, 1 H), 5.48 (dt, *J* = 1.8, 3.0 Hz, 1 H), 5.37 (d, *J* = 3.0 Hz, 1 H), 5.22 (dq, *J* = 1.8, 17.4 Hz, 1 H), 5.09 (dq, *J* = 1.8, 12.0 Hz, 1 H), 4.16 (ddt, A of ABX system, *J* = 1.8, 6.0, 13.2 Hz, 1 H), 3.93 (ddt, B of ABX system, *J* = 1.2, 5.4, 12.6 Hz, 1 H), 2.79 (dt, *J* = 4.8, 7.8 Hz, 1 H), 2.42 (dd, C of CDX system, *J* = 7.2, 14.4 Hz, 1 H), 2.35 (dd, D of CDX system, *J* = 4.8, 14.4 Hz, 1 H), 0.91 (t, *J* = 7.8

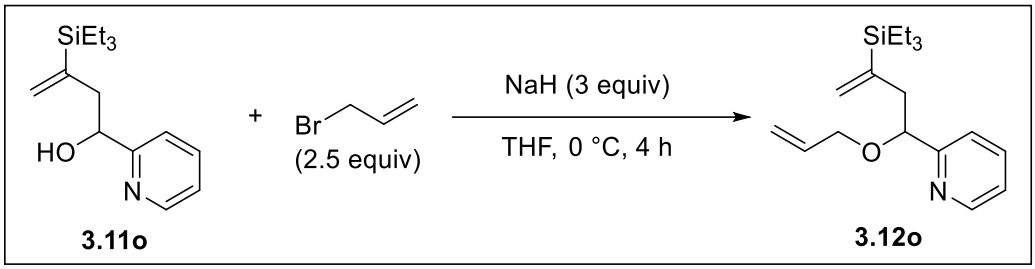
Hz, 9 H), 0.83 (m, 1 H), 0.59 (q, *J* = 7.8 Hz, 6 H), 0.55 (m, 1 H), 0.43 (m, 1 H), 0.36 (m, 1 H), 0.08 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 135.7, 128.0, 116.1, 82.3, 69.8, 41.9, 15.2, 7.4, 4.4, 3.0, 1.4. IR (film) 3070, 2957, 1427, 1113, 815 cm^{-1}. HRMS (EI) *m/z* 266.2062 [(M)$^+$; calcd for $C_{16}H_{30}OSi$, 266.2066].

Preparation of (4-(allyloxy)-4-(3-chlorophenyl)but-1-en-2-yl)(ethyl)dimethylsilane (3.12n)



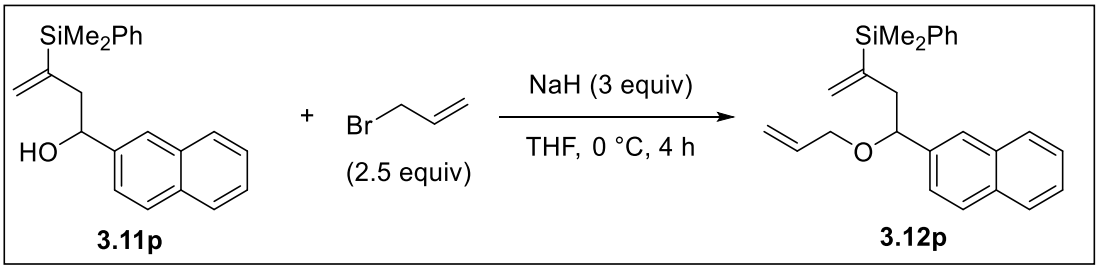
Following general procedure E, alcohol **3.11n** (423 mg, 1.57 mmol, 1 equiv), allyl bromide (0.33 mL, 3.93 mmol, 2.5 equiv), THF (3.2 mL), and *t*-BuONa (454 mg, 4.72 mmol, 3 equiv) afforded, after silica gel chromatography (30% CH_2Cl_2 in hexanes), compound **3.12n** as a colorless oil (442 mg, 1.43 mmol, 91% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (s, 1 H), 7.25–7.21 (m, 2 H), 7.15 (dt, *J* = 1.5, 6.5 Hz, 1 H), 5.85 (m, 1 H), 5.56 (m, 1 H), 5.38 (d, *J* = 2.5 Hz, 1 H), 5.20 (dq, *J* = 1.5, 17.0 Hz, 1 H), 5.13 (dq, *J* = 1.5. 10.5 Hz, 1 H), 4.33 (dd, *J* = 5.5, 8.0 Hz, 1 H), 3.86 (ddt, A of ABX system, *J* = 1.5, 5.5, 13.0 Hz, 1 H), 3.72 (ddt, B of ABX system, *J* = 1.5, 6.0, 13.0 Hz, 1 H), 2.61 (dd, C of CDX system, *J* = 8.0, 14.5 Hz, 1 H), 2.35 (dd, D of CDX system, *J* = 5.5, 15.0 Hz, 1 H), 0.89 (t, *J* = 7.5 Hz, 3 H), 0.53 (q, *J* = 7.5 Hz, 2 H), 0.04 (s, 3 H), 0.02 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 144.8, 134.7, 134.2, 129.6, 127.9, 127.6, 127.0, 125.1, 116.9, 80.5, 69.7, 44.4, 7.3, 6.8, -3.7, -3.8. IR (film) 3060, 2955, 1427, 1248, 1092, 815 cm^{-1}. HRMS (EI) *m*/*z* 308.1372 [(M^+); calcd for $C_{17}H_{25}OSiCl$, 308.1363].

Preparation of 2-(1-(allyloxy)-3-(triethylsilyl)but-3-en-1-yl)pyridine (3.12o)



Following alternative general procedure E, alcohol **3.11o** (356 mg, 1.35 mmol, 1 equiv), allyl bromide (0.24 mL, 2.70 mmol, 2.0 equiv), THF (30 mL), and sodium hydride, 60% w/w dispersion in mineral oil (155 mg, 4.05 mmol, 3 equiv) afforded, after silica gel chromatography (30% EtOAc in hexanes), compound **3.12o** as a colorless oil (391 mg, 1.28 mmol, 95% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.16 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 5.87 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.72 (dt, *J* = 2.8, 1.5 Hz, 1H), 5.37 (dd, *J* = 2.8, 1.0 Hz, 1H), 5.22 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.11 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.56 (dd, *J* = 7.4, 5.7 Hz, 1H), 3.90 (ddt, *J* = 12.7, 5.3, 1.5 Hz, 1H), 3.83 (ddt, *J* = 12.7, 5.8, 1.4 Hz, 1H), 2.55 (dq, *J* = 6.9, 1.2 Hz, 2H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.60 (qd, *J* = 7.9, 2.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 149.0, 144.7, 136.4, 134.7, 128.2, 122.3, 120.9, 116.7, 82.2, 70.1, 42.8, 7.3, 2.8. HRMS (ESI) *m/z* 304.2100 [(M + H)$^+$; calcd for $C_{18}H_{30}NOSi$, 304.2097].

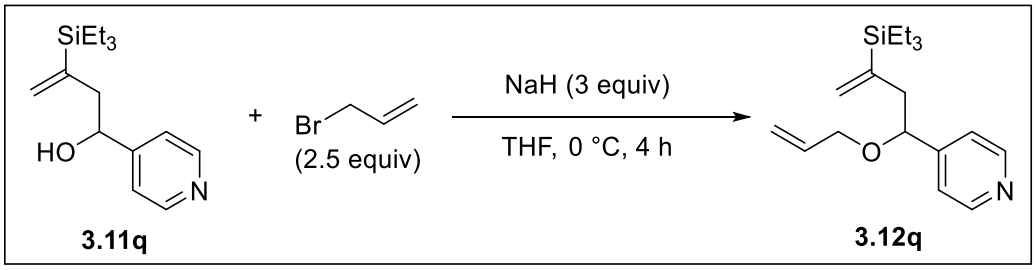
Preparation of (4-(allyloxy)-4-(naphthalen-2-yl)but-1-en-2-yl)dimethyl(phenyl)silane (3.12p)



Following alternative general procedure E, alcohol **3.11p** (998 mg, 3.0 mmol, 1 equiv),

allyl bromide (0.52 mL, 6.0 mmol, 2.0 equiv), THF (30 mL), and sodium hydride, 60% w/w dispersion in mineral oil (345 mg, 9.0 mmol, 3 equiv) afforded, after silica gel chromatography (30% CH_2Cl_2 in hexanes), compound **3.12p** as a colorless oil (1.07 g, 2.88 mmol, 96% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 3H), 7.59 – 7.54 (m, 2H), 7.52 – 7.47 (m, 3H), 7.44 – 7.36 (m, 4H), 5.84 (dddd, *J* = 17.2, 10.4, 6.0, 5.2 Hz, 1H), 5.74 (dt, *J* = 2.7, 1.3 Hz, 1H), 5.55 – 5.49 (m, 1H), 5.20 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.14 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.40 (dd, *J* = 7.8, 5.5 Hz, 1H), 3.82 (ddt, *J* = 12.7, 5.2, 1.5 Hz, 1H), 3.62 (ddt, *J* = 12.7, 6.1, 1.4 Hz, 1H), 2.80 (ddt, *J* = 14.3, 7.8, 1.1 Hz, 1H), 2.55 (ddt, *J* = 14.4, 5.5, 1.0 Hz, 1H), 0.43 (s, 3H), 0.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 139.7, 138.3, 134.9, 134.0, 133.1, 133.0, 129.3, 129.0, 128.1, 127.81, 127.76, 127.7, 126.0, 125.9, 125.7, 124.6, 116.7, 80.8, 69.4, 44.6, -2.9, -3.0. IR (neat) 3051, 2957, 2856, 1427, 1248, 1111, 1082, 817 cm^{-1}. HRMS (EI) m/z 372.1906 [$(M)^+$; calcd for $C_{25}H_{28}OSi$, 372.1909].

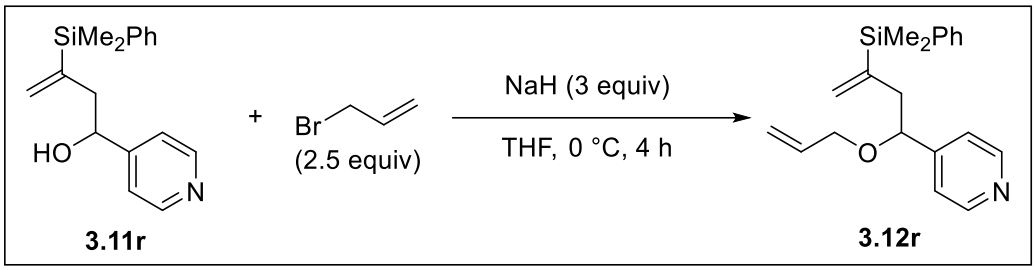
Preparation of 4-(1-(allyloxy)-3-(triethylsilyl)but-3-en-1-yl)pyridine (3.12q)



Following alternative general procedure E, alcohol **3.11q** (606 mg, 2.30 mmol, 1 equiv), allyl bromide (0.4 mL, 4.60 mmol, 2.0 equiv), THF (30 mL), and sodium hydride, 60% w/w dispersion in mineral oil (264.5 mg, 6.90 mmol, 3 equiv) afforded, after silica gel chromatography (25% EtOAc in hexanes), compound **3.12q** as a colorless oil (542 mg, 1.8 mmol, 78% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 6.0 Hz, 2H), 7.20 (d, *J* = 6.1 Hz, 2H), 5.85 (dddd, *J* = 17.2, 10.3, 6.0, 5.2 Hz, 1H), 5.63 (dt, *J* = 2.7, 1.4 Hz, 1H), 5.38 (d, *J* = 2.7 Hz, 1H),

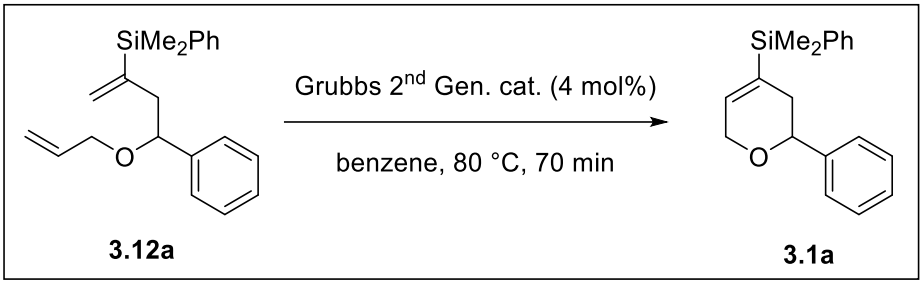
5.21 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.14 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.36 (dd, *J* = 7.8, 5.4 Hz, 1H), 3.87 (ddt, *J* = 12.6, 5.2, 1.5 Hz, 1H), 3.75 (ddt, *J* = 12.6, 6.0, 1.4 Hz, 1H), 2.58 (ddt, *J* = 14.4, 7.9, 1.1 Hz, 1H), 2.33 (ddt, *J* = 14.5, 5.4, 1.2 Hz, 1H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.58 (qd, *J* = 7.9, 1.7 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.5, 149.8, 144.1, 134.3, 129.0, 121.9, 117.1, 79.8, 70.0, 44.1, 7.3, 2.8. HRMS (ESI) *m*/*z* 304.2102 [(M + H)$^+$; calcd for $C_{18}H_{30}NOSi$, 304.2097].

Preparation of 4-(1-(allyloxy)-3-(dimethyl(phenyl)silyl)but-3-en-1-yl)pyridine (3.12r)



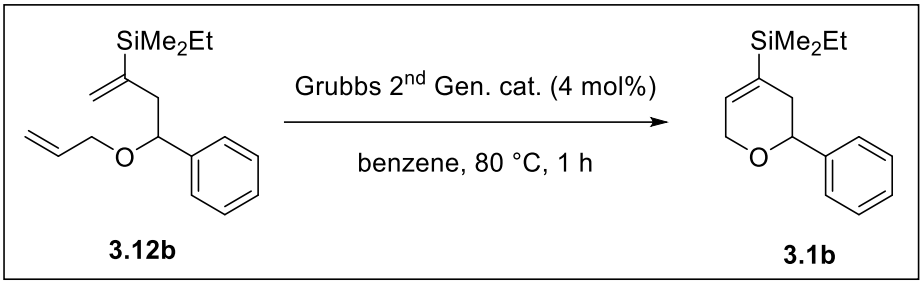
Following alternative general procedure E, alcohol **3.11r** (1077 mg, 3.8 mmol, 1 equiv), allyl bromide (0.66 mL, 7.60 mmol, 2.0 equiv), THF (30 mL), and sodium hydride, 60% w/w dispersion in mineral oil (437 mg, 11.40 mmol, 3 equiv) afforded, after silica gel chromatography (30% EtOAc in hexanes), compound **3.12r** as a colorless oil (1010 mg, 3.12 mmol, 82% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 6.0 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.40 – 7.31 (m, 3H), 7.02 (d, *J* = 6.2 Hz, 2H), 5.82 – 5.72 (m, 1H), 5.67 (dt, *J* = 2.7, 1.3 Hz, 1H), 5.52 (d, *J* = 2.7 Hz, 1H), 5.16 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.11 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.14 (dd, *J* = 7.9, 5.3 Hz, 1H), 3.75 (ddt, *J* = 12.7, 5.2, 1.5 Hz, 1H), 3.55 (ddt, *J* = 12.7, 6.0, 1.4 Hz, 1H), 2.61 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.35 (dd, *J* = 14.3, 5.3 Hz, 1H), 0.39 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (126 MHz, $_{CDCl3}$) δ 151.3, 149.7, 145.5, 137.9, 134.3, 133.9, 129.7, 129.1, 127.8, 121.7, 116.9, 79.4, 69.8, 44.3, -3.05, -3.08. HRMS (ESI) *m*/*z* 324.1803 [(M + H)$^+$; calcd for $C_{20}H_{26}NOSi$, 324.1784].

Preparation of dimethyl(phenyl)(2-phenyl-3,6-dihydro-*2H*-pyran-4-yl)silane (3.1a)



Following General Procedure F, diene **3.12a** (100 mg, 0.31 mmol, 1 equiv) in benzene (6.2 mL), and second-generation Grubbs catalyst (10.5 mg, 0.0124 mmol, 0.04 equiv) at 80 ºC for 70 minutes, followed by silica gel chromatography (1:1 CH_2Cl_2/hexanes) afforded dihydropyran **3.1a** as a colorless oil (89.9 mg, 0.30 mmol, 99% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.36–7.29 (m, 7 H), 7.25 (m, 1 H), 6.10 (m, 1 H), 4.47 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.40 (m, 2 H), 2.35–2.28 (m, 1 H), 2.26–2.21 (m, 1 H), 0.36 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 137.4, 136.1, 135.1, 134.0 (2 C), 129.1, 128.3 (2 C), 127.8 (2 C), 127.4, 125.8 (2 C), 75.6, 67.7, 34.5, -3.86, -3.98. IR (neat) 3067, 2955, 2901, 2818, 1427, 1248, 1115, 833, 819 cm^{-1}. HRMS (EI) *m/z* 294.1434 [(M)$^+$; calcd for $C_{19}H_{22}OSi$, 294.1440].

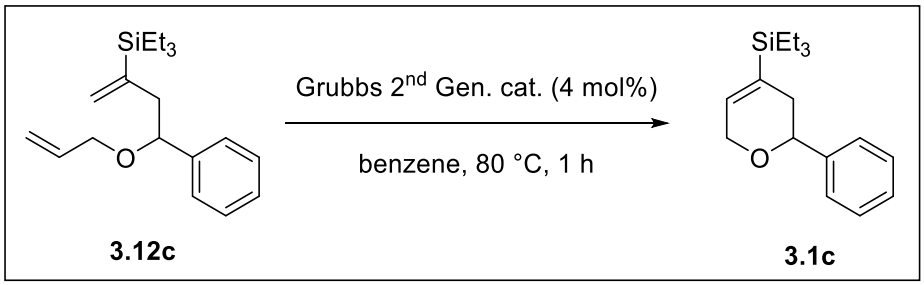
Preparation of ethyldimethyl(2-phenyl-3,6-dihydro-*2H*-pyran-4-yl)silane (3.1b)



Following General Procedure F, diene **3.12b** (69.6 mg, 0.254 mmol, 1 equiv) in benzene (5.1 mL), and second-generation Grubbs catalyst (8.6 mg, 0.01 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (1:1 CH_2Cl_2/hexanes) afforded dihydropyran **3.1b** as a

colorless oil (56.4 mg, 0.231 mmol, 91% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4 H), 7.26 (m, 1 H), 6.04 (m, 1 H), 4.48 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.39 (m, 2 H), 2.31 (m, 1 H), 2.24 (m, 1 H), 0.93 (t, *J* = 8.0 Hz, 3 H), 0.56 (q, *J* = 8.0 Hz, 2 H), 0.05 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 135.9, 134.6, 128.4 (2 C), 127.4, 125.8 (2 C), 75.7, 67.7, 34.8, 7.4, 6.1, -4.8. IR (film) 3032, 2953, 2816, 1246, 1124, 1026, 819 cm^{-1}. HRMS (EI) *m/z* 246.1426 [$(M)^+$; calcd for $C_{15}H_{22}OSi$, 246.1440].

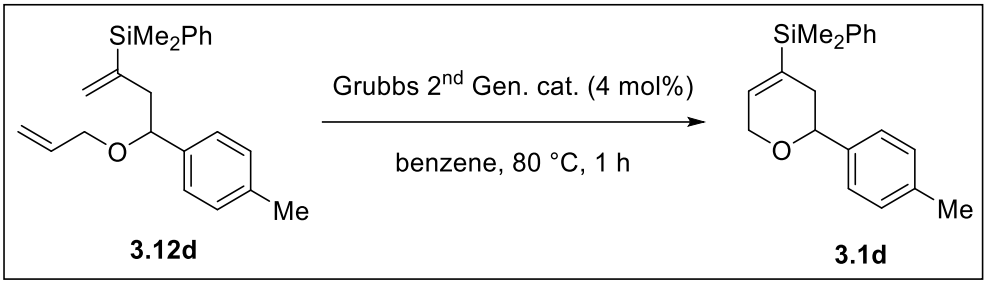
Preparation of triethyl(2-phenyl-3,6-dihydro-*2H*-pyran-4-yl)silane (3.1c)



3.12c **3.1c**

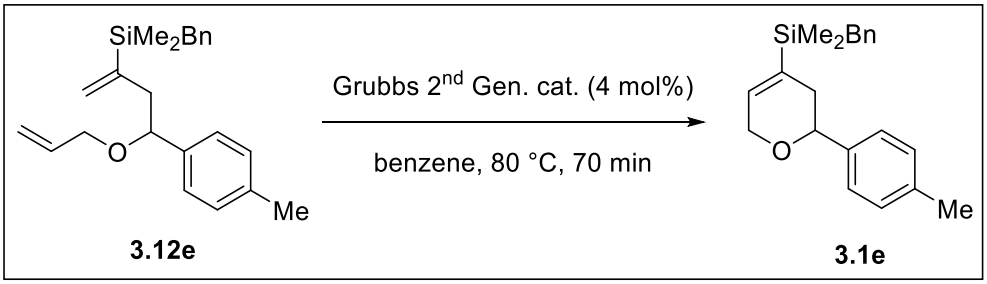
Following General Procedure F, diene **3.12c** (110 mg, 0.364 mmol, 1 equiv) in benzene (7.3 mL), and second-generation Grubbs catalyst (12.3 mg, 0.015 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (30% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1c** as a colorless oil (101 mg, 0.360 mmol, 99% isolated yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4 H), 7.26 (m, 1 H), 6.03 (m, 1 H), 4.47 (dd, *J* = 3.0, 10.0 Hz, 1 H), 4.40 (m, 2 H), 2.31 (m, 1 H), 2.22 (m, 1 H), 0.94 (t, *J* = 8.0 Hz, 9 H), 0.59 (q, *J* = 8.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 135.5, 133.9, 128.4 (2 C), 127.4, 125.9 (2 C), 75.7, 67.8, 35.3, 7.4, 2.3. IR (film) 3030, 2953, 2814, 1454, 1126, 1026, 698 cm^{-1}. HRMS (EI) *m/z* 274.1751 [$(M)^+$; calcd for $C_{17}H_{26}OSi$, 274.1753].

Preparation of dimethyl(phenyl)(2-(*p*-tolyl)-3,6-dihydro-*2H*-pyran-4-yl)silane (3.1d)



Following General Procedure F, diene **3.12d** (95 mg, 0.282 mmol, 1 equiv) in benzene (5.6 mL), and second-generation Grubbs catalyst (9.6 mg, 0.011 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (1:1 CH_2Cl_2/hexanes) afforded dihydropyran **3.1d** as a colorless oil (89 mg, 0.279 mmol, 99% isolated yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.34 (m, 3 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.09 (m, 1 H), 4.44 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.39 (m, 2 H), 2.35–2.27 (m, 1 H), 2.31 (s, 3 H), 2.22 (m, 1 H), 0.35 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 137.5, 137.0, 136.1, 135.2, 134.0 (2 C), 129.1, 129.0 (2 C), 127.8 (2 C), 125.8 (2 C), 75.5, 67.7, 34.5, 21.1, -3.85, -3.98. IR (neat) 3013, 2920, 2814, 1427, 1248, 1115, 817 cm^{-1}. HRMS (EI) *m*/*z* 308.1596 [(M^+); calcd for $C_{20}H_{24}OSi$, 308.1596].

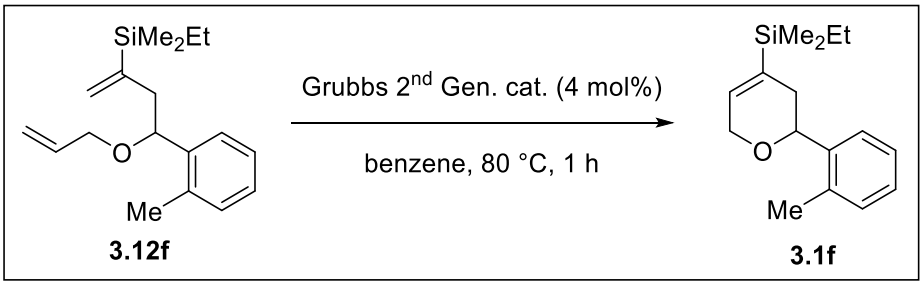
Preparation of benzyldimethyl(2-(*p*-tolyl)-3,6-dihydro-*2H*-pyran-4-yl)silane (3.1e)



Following General Procedure F, diene **3.12e** (113 mg, 0.322 mmol, 1 equiv) in benzene (4 mL), and second-generation Grubbs catalyst (10.9 mg, 0.013 mmol, 0.04 equiv) at 80 ºC for 70 minutes, followed by silica gel chromatography (30% CH_2Cl_2 in hexanes) afforded dihydropyran

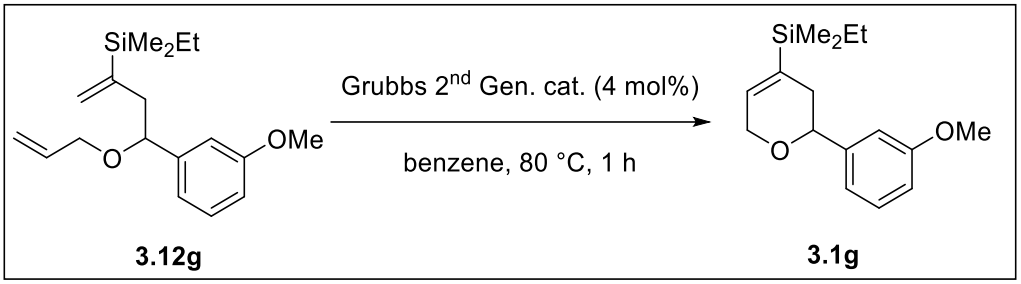
3.1e as a colorless oil (82 mg, 0.258 mmol, 80% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.18 (m, 4 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.98 (d, *J* = 7.5 Hz, 2 H), 6.01 (m, 1 H), 4.29 (dd, *J* = 3.5, 10.5 Hz, 1 H), 4.36 (m, 2 H), 2.33 (s, 3 H), 2.29–2.21 (m, 1 H), 2.14 (s, 2 H), 2.09 (m, 1 H), 0.05 (s, 3 H), 0.04 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 137.0, 135.5, 135.2, 129.0 (4 C), 128.2 (4 C), 125.7, 124.1, 75.5, 67.7, 34.9, 25.0, 21.1, -4.5, -4.6. IR (film) 3030, 2957, 1492, 1112, 833 cm^{-1}. HRMS (EI) *m*/*z* 322.1731 [(M^+); calcd for $C_{18}H_{22}OSi$, 322.1753].

Preparation of ethyldimethyl(2-(*o*-tolyl)-3,6-dihydro-*2H*-pyran-4-yl)silane (3.1f)



Following General Procedure F, diene **3.12f** (111 mg, 0.385 mmol, 1 equiv) in benzene (8.5 mL), and second-generation Grubbs catalyst (14.5 mg, 0.017 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (45% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1f** as a colorless oil (98.8 mg, 0.381 mmol, 99% isolated yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 1 H), 7.17 (t, *J* = 7.5 Hz, 1 H), 7.10 (m, 2 H), 5.99 (m, 1 H), 4.60 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.34 (m, 2 H), 2.29 (s, 3 H), 2.24 (m, 1 H), 2.17 (m, 1 H), 0.88 (t, *J* = 8.0 Hz, 3 H), 0.51 (q, *J* = 8.0 Hz, 2 H), 0.00 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 136.2, 134.55, 134.51, 130.2, 127.2, 126.3, 125.4, 72.7, 67.9, 33.2, 19.1, 7.4, 6.1, -4.7, -4.8. IR (film) 3370, 3009, 2953, 2814, 1460, 1246, 1124, 1032, 835 cm^{-1}. HRMS (EI) *m*/*z* 260.1582 [(M^+); calcd for $C_{16}H_{24}OSi$, 260.1596].

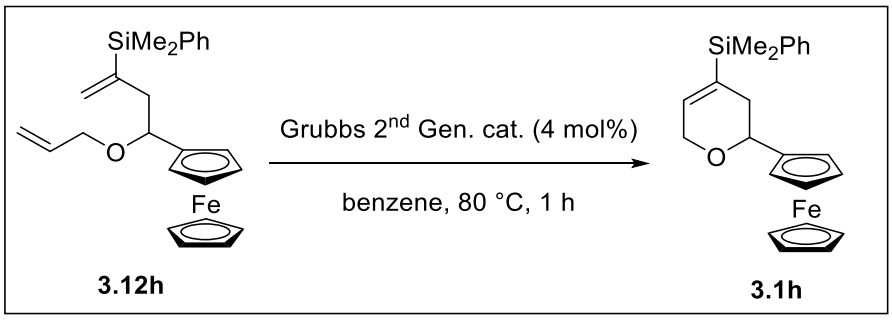
Preparation of ethyl(2-(3-methoxyphenyl)-3,6-dihydro-*2H*-pyran-4-yl)dimethylsilane (3.1g)



3.12g **3.1g**

Following General Procedure F, diene **3.12g** (100 mg, 0.328 mmol, 1 equiv) in benzene (5 mL), and second-generation Grubbs catalyst (11.1 mg, 0.013 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (1:1 CH_2Cl_2/hexanes) afforded dihydropyran **3.1g** as a colorless oil (78 mg, 0.282 mmol, 86% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.0 Hz, 1 H), 6.93 (m, 2 H), 6.80 (m, 1 H), 6.02 (m, 1 H), 4.45 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.38 (m, 2 H), 2.30 (m, 1 H), 2.23 (m, 1 H), 0.92 (t, *J* = 8.0 Hz, 3 H), 0.55 (q, *J* = 8.0 Hz, 2 H), 0.03 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 144.6, 135.9, 134.5, 129.4, 118.2, 113.1, 111.2, 75.6, 67.7, 55.2, 34.8, 7.4, 6.1, -4.8. IR (film) 3005, 2953, 1257, 1033, 775 cm^{-1}. HRMS (EI) *m*/*z* 276.1540 [(M)$^+$; calcd for $C_{16}H_{24}O_2Si$, 276.1546].

Preparation of dimethyl(phenyl)(2-(ferrocenyl)-3,6-dihydro-*2H*-pyran-4-yl)silane (3.1h)

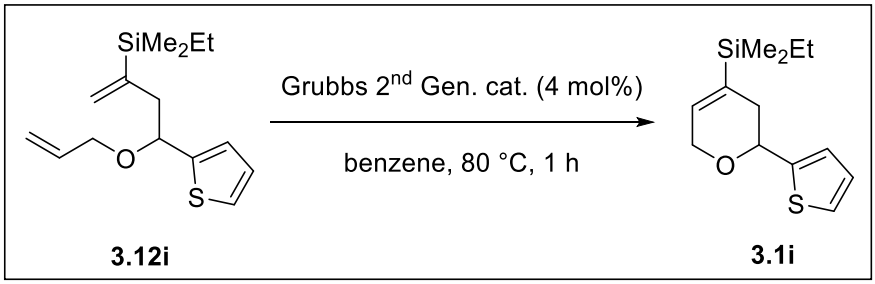


3.12h **3.1h**

Following General Procedure F, diene **3.12h** (180.3 mg, 0.419 mmol, 1 equiv) in benzene (8.4 mL), and second-generation Grubbs catalyst (14.2 mg, 0.0167 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (7:3 CH_2Cl_2/hexanes) afforded dihydropyran **3.1h** as

an orange oil (175.3 mg, 0.335 mmol, 70% isolated yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.37 (m, 3 H), 6.07 (m, 1 H), 4.32 (dd, *J* = 4.0, 7.0 Hz, 1 H), 4.29 (m, 1 H), 4.25 (m, 1 H), 4.21 (m, 1 H), 4.11 (m, 2 H), 4.08 (m, 1 H), 4.06 (s, 5 H), 2.34 (m, 2 H), 0.40 (s, 3 H), 0.39 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 136.1, 134.9, 133.9 (2 C), 129.1, 127.8 (2 C), 88.8, 71.7, 68.6 (5 C), 68.0, 67.6, 67.5, 66.8, 66.4, 32.4, -3.9, -4.0. IR (film) 3069, 2956, 1424, 1248, 1110, 815 cm^{-1}. HRMS (EI) *m/z* 402.1108 [$(M)^+$; calcd for $C_{23}H_{26}OSiFe$, 402.1102].

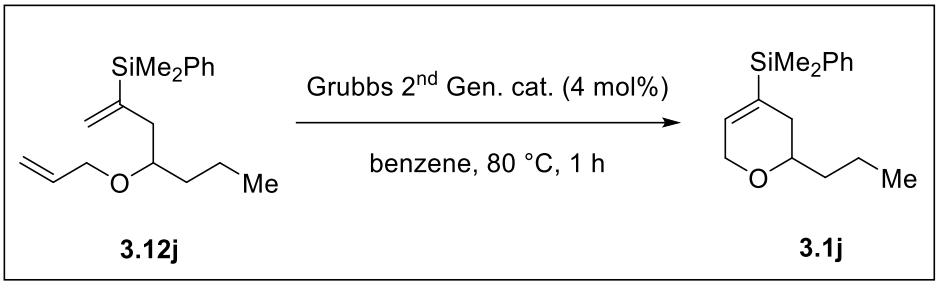
Preparation of ethyldimethyl(2-(thiophen-2-yl)-3,6-dihydro-*2H*-pyran-4-yl)silane (3.1i)



3.12i **3.1i**

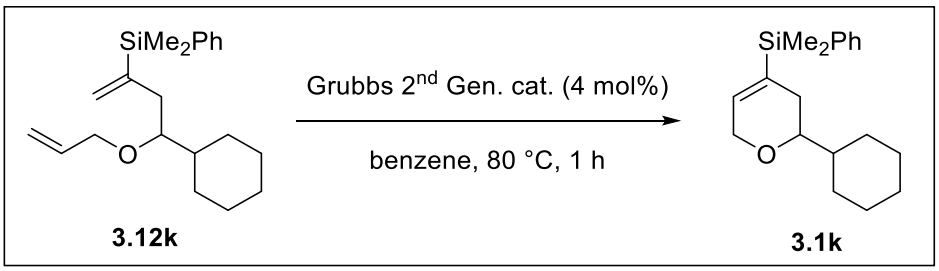
Following General Procedure F, diene **3.12i** (80 mg, 0.285 mmol, 1 equiv) in benzene (3.6 mL), and second-generation Grubbs catalyst (9.7 mg, 0.0114 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (20–25% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1i** as a colorless oil (43 mg, 0.171 mmol, 60% isolated yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 1 H), 6.99 (m, 1 H), 6.96 (dd, *J* = 3.5, 5.0 Hz, 1 H), 6.00 (m, 1 H), 4.77 (dd, *J* = 3.5, 9.5 Hz, 1 H), 4.39 (m, 1 H), 4.33 (m, 1 H), 2.47 (m, 1 H), 2.37 (m, 1 H), 0.92 (t, *J* = 8.0 Hz, 3 H), 0.56 (q, *J* = 8.0 Hz, 2 H), 0.05 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 135.3, 134.4, 126.5, 124.6, 123.7, 71.4, 67.3, 34.4, 7.4, 6.0, -4.8. IR (film) 2953, 1246, 1120, 833 cm^{-1}. HRMS (EI) *m/z* 252.0992 [$(M)^+$; calcd for $C_{13}H_{20}OSiS$, 252.1004].

Preparation of dimethyl(phenyl)(2-propyl-3,6-dihydro-*2H*-pyran-4-yl)silane (3.1j)



Following General Procedure F, diene **3.12j** (136 mg, 0.471 mmol, 1 equiv) in benzene (9 mL), and second-generation Grubbs catalyst (16 mg, 0.019 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (35% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1j** as a colorless oil (92 mg, 0.353 mmol, 0.75% isolated yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (m, 2 H), 7.34 (m, 3 H), 6.02 (m, 1 H), 4.21 (m, 2 H), 3.41 (m, 1 H), 1.96 (m, 2 H), 1.50 (m, 1 H), 1.46 –1.32 (m, 3 H), 0.89 (t, *J* = 7.2 Hz, 3 H), 0.33 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.7, 136.2, 134.7, 134.0 (2 C), 129.0, 127.8 (2 C), 73.3, 67.1, 38.1, 32.4, 18.7, 14.1, -3.9, -4.0. IR (film) 3069, 2957, 2812, 1427, 1248, 1130, 833 cm^{-1}. HRMS (EI) *m/z* 260.1596 [(M)$^+$; calcd for $C_{16}H_{24}OSi$, 260.1596].

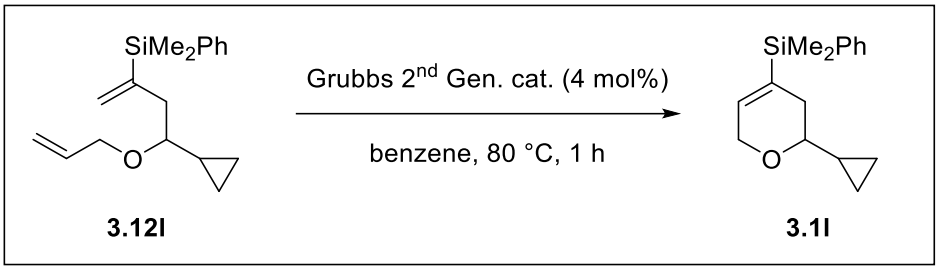
Preparation of (2-cyclohexyl-3,6-dihydro-2*H*-pyran-4-yl)dimethyl(phenyl)silane (3.1k)



Following General Procedure F, diene **3.12k** (87 mg, 0.265 mmol, 1 equiv) in benzene (5.3 mL), and second-generation Grubbs catalyst (9 mg, 0.011 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (35% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1k** as a colorless oil (82.3 mg, 0.262 mmol, 99% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (m,

2 H), 7.35 (m, 3 H), 6.01 (m, 1 H), 4.25–4.15 (m, 2 H), 3.14 (ddd, *J* = 3.5, 5.5, 10.0 Hz, 1 H), 2.03 (m, 1 H), 1.99–1.92 (m, 2 H), 1.70 (m, 2 H), 1.62 (m, 2 H), 1.33 (m, 1 H), 1.25–1.11 (m, 3 H), 0.96 (m, 2 H), 0.32 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 136.5, 134.7, 134.0 (2 C), 129.0, 127.8 (2 C), 77.9, 67.5, 42.8, 29.4, 29.0, 28.5, 26.6, 26.2, 26.1, -3.8, -3.9. IR (neat) 2924, 2853, 1427, 1246, 1126, 835 cm^{-1}. HRMS (EI) *m/z* 300.1893 [(M)$^+$; calcd for $C_{19}H_{28}OSi$, 300.1909].

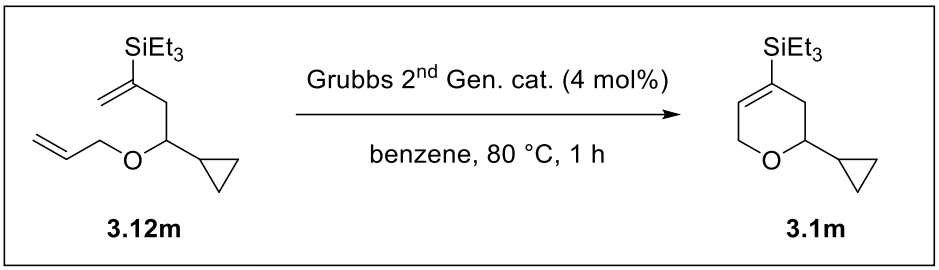
Preparation of (2-cyclopropyl-3,6-dihydro-*2H*-pyran-4-yl)dimethyl(phenyl)silane (3.1l)



3.12l **3.1l**

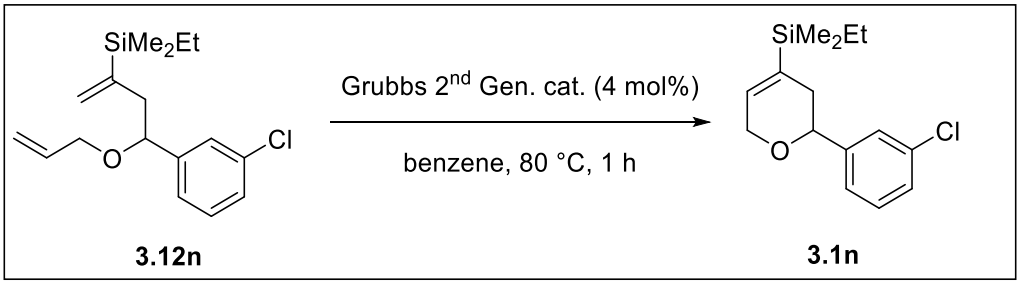
Following General Procedure F, diene **3.12l** (82 mg, 0.286 mmol, 1 equiv) in benzene (5.7 mL), and second-generation Grubbs catalyst (9.7 mg, 0.0114 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (20–25% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1l** as a colorless oil (63 mg, 0.243 mmol, 85% isolated yield).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.34 (m, 3 H), 5.99 (m, 1 H), 4.26 (m, 1 H), 4.18 (m, 1 H), 2.75 (ddd, *J* = 3.0, 7.8, 9.6 Hz, 1 H), 2.17–2.11 (m, 1 H), 2.09–2.05 (m, 1 H), 0.87 (m, 1 H), 0.51 (m, 1 H), 0.45 (m, 1 H), 0.33 (s, 6 H), 0.33 (overlapped) 0.17 (m, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6, 136.2, 134.6, 134.0 (2 C), 129.0, 127.8 (2 C), 77.9, 67.2, 31.9. 15.7, 2.8, 1.8, -3.8, -3.9. IR (neat) 3070, 3007, 2957, 1427, 1248, 1122, 817 cm^{-1}. HRMS (EI) *m/z* 258.1429 [(M)$^+$; calcd for $C_{16}H_{22}OSi$, 258.1440].

Preparation of (2-cyclopropyl-3,6-dihydro-2*H*-pyran-4-yl)triethylsilane (3.1m)



Following General Procedure F, diene **3.12m** (106 mg, 0.398 mmol, 1 equiv) in benzene (8 mL), and second-generation Grubbs catalyst (13.6 mg, 0.016 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (20–25% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1m** as a colorless oil (81.6 mg, 0.342 mmol, 86% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (m, 1 H), 4.25 (m, 1 H), 4.17 (m, 1 H), 2.74 (m, 1 H), 2.13 (m, 1 H), 2.04 (m, 1 H), 0.91 (t, *J* = 8.0 Hz, 9 H), 0.90 (m, heavily overlapped, 1 H), 0.57 (q, *J* = 8.0 Hz, 6 H), 0.53–0.48 (m, 2 H), 0.34 (m, 1 H), 0.20 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.4, 133.5, 78.0, 67.2, 32.6, 15.7, 7.4, 2.9, 2.3, 1.8. IR (film) 3082, 3007, 2953, 1124, 1018, 731 cm^{-1}. HRMS (EI) *m*/*z* 238.1763 [$(M)^+$; calcd for $C_{14}H_{26}OSi$, 238.1753].

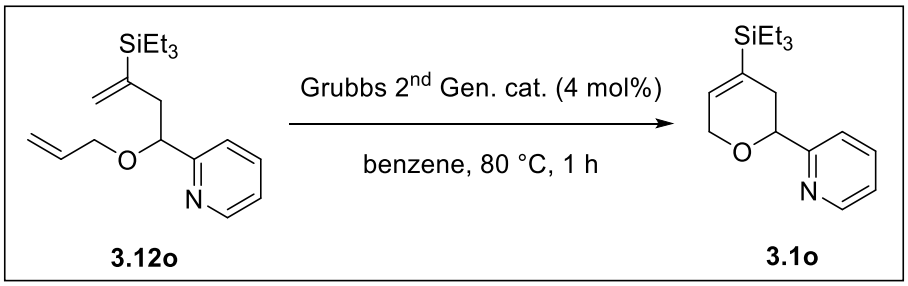
Preparation of (2-(3-chlorophenyl)-3,6-dihydro-2*H*-pyran-4-yl)(ethyl)dimethylsilane (3.1n)



Following General Procedure F, diene **3.12n** (123 mg, 0.398 mmol, 1 equiv) in benzene (8 mL), and second-generation Grubbs catalyst (13.5 mg, 0.016 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (30% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1n** as a colorless oil (93.8 mg, 0.334 mmol, 84% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J*

= 1.5 Hz, 1 H), 7.27–7.21 (m, 3 H), 6.01 (m, 1 H), 4.44 (dd, *J* = 5.5, 8.0 Hz, 1 H), 4.36 (q, *J* = 2.5 Hz, 2 H), 2.23 (m, 2 H), 0.91 (t, *J* = 8.0 Hz, 3 H), 0.54 (q, *J* = 8.0 Hz, 2 H), 0.03 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 135.6, 134.4, 134.3, 129.6, 127.4, 126.0, 123.9, 74.9, 67.6, 34.6, 7.4, 6.0, -4.8. IR (film) 3013, 2953, 2820, 1126, 835 cm^{-1}. HRMS (EI) *m*/*z* 280.1064 [(M^+); calcd for $C_{15}H_{21}OSiCl$, 280.1050].

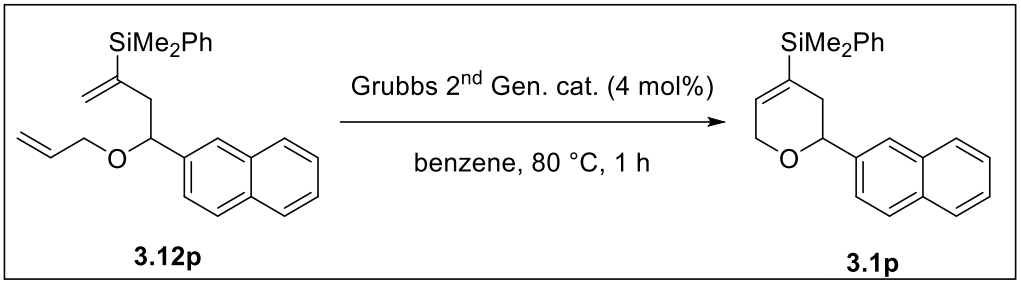
Preparation of 2-(4-(triethylsilyl)-3,6-dihydro-2*H*-pyran-2-yl)pyridine (3.1o)



3.12o **3.1o**

Following General Procedure F, diene **3.12o** (334 mg, 1.1 mmol, 1 equiv) in benzene (40 mL), and second-generation Grubbs catalyst (38 mg, 0.044 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (30% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1o** as a colorless oil (302 mg, 1.09 mmol, 99% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (ddd, *J* = 5.7, 1.8, 0.8 Hz, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.17 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.03 (q, *J* = 2.7 Hz, 1H), 4.61 (dd, *J* = 10.4, 3.3 Hz, 1H), 4.43 (dt, *J* = 4.6, 2.3 Hz, 2H), 2.44 (dq, *J* = 16.5, 2.2 Hz, 1H), 2.29 (ddq, *J* = 16.8, 9.8, 3.1 Hz, 1H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 148.8, 136.7, 135.2, 133.7, 122.2, 120.0, 76.3, 67.6, 33.6, 7.3, 2.2. HRMS (ESI) *m*/*z* 274.1627 [($M - H)^+$; calcd for $C_{16}H_{24}NOSi$, 274.1627].

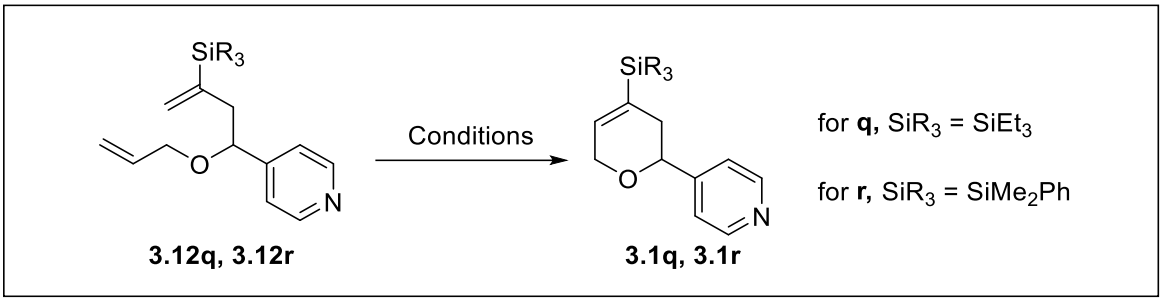
Synthesis of dimethyl(2-(naphthalen-2-yl)-3,6-dihydro-*2H*-pyran-4-yl)(phenyl)silane (3.1p)



3.12p **3.1p**

Following General Procedure F, diene **3.12p** (932 mg, 2.5 mmol, 1 equiv) in benzene (80 mL), and second-generation Grubbs catalyst (85 mg, 0.044 mmol, 0.04 equiv) at 80 ºC for 1 h, followed by silica gel chromatography (40% CH_2Cl_2 in hexanes) afforded dihydropyran **3.1p** as a colorless oil (492 mg, 1.40 mmol, 56% isolated yield). ^{1}H NMR (500 MHz, C_6D_6) δ 7.76 (s, 1H), 7.63 – 7.55 (m, 3H), 7.47 (dq, *J* = 5.4, 2.1 Hz, 2H), 7.44 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.25 – 7.13 (m, 5H), 5.91 (tt, *J* = 3.2, 1.5 Hz, 1H), 4.53 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.27 (dtd, *J* = 17.2, 3.1, 1.0 Hz, 1H), 4.19 (dddd, *J* = 17.2, 4.0, 3.2, 1.8 Hz, 1H), 2.43 (dddt, *J* = 16.7, 10.0, 3.9, 2.7 Hz, 1H), 2.30 (dtt, *J* = 17.1, 3.3, 1.2 Hz, 1H), 0.26 (s, 3H), 0.25 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 141.4, 138.0, 137.5, 135.4, 134.7, 134.3, 133.7, 129.9, 128.72, 128.66, 128.62, 128.4, 126.5, 126.2, 125.1, 125.0, 76.1, 68.0, 35.6, -3.4, -3.5. IR (neat) 3057, 2955, 2818, 1427, 1248, 1115, 815 cm^{-1}. HRMS (EI) m/z 344.1580 [$(M)^+$; calcd for $C_{23}H_{24}OSi$, 344.1596].

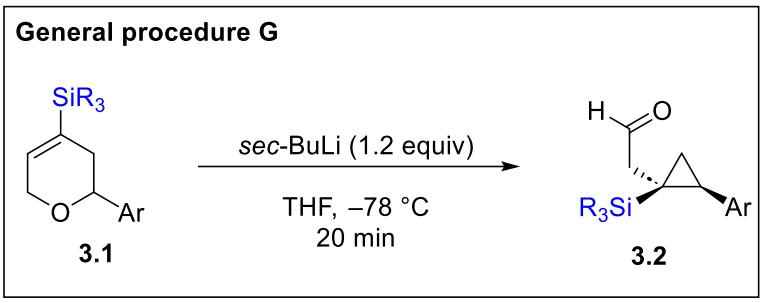
Table 3.1: Conditions for ring closing metathesis



Entry	S.M	Cat. (mol %)	Add.	Solvent	Temp (°C)	Time (h)	% Conv
1	**S2-q**	A (0.04)	None	benzene	80	1	0
2	**S2-q**	A (0.04)	None	benzene	80	12	0
3	**S2-q**	A (0.04)	None	toluene	110	12	0
4	**S2-q**	A (0.04)	None	DCM	25	24	0
5	**S2-q**	B (0.04)	None	toluene	60	12	0
6	**S2-r**	A (0.04)	None	benzene	80	1	5[a]
7	**S2-r**	A (0.04)	TMSCl	1,2-DCE	90 °C	4	20[a]

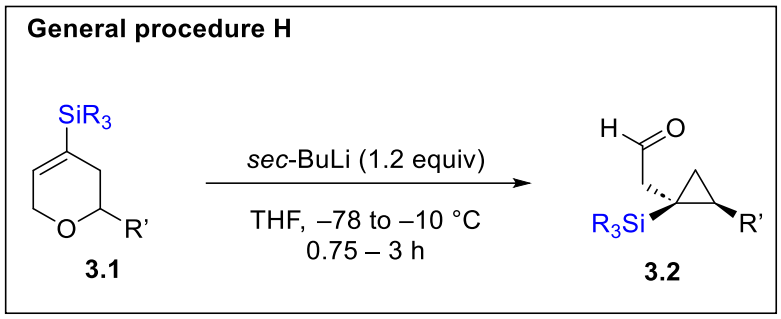
[a]The product was not isolated but analyzed as a mixture with the starting material. S.M. = starting material, Cat. = catalyst, Add. = additive. Cat. A = Grubbs II, cat. B = Hoveyda-Grubbs II. DCM = dichloromethane. TMSCl = chlorotrimethylsilane. 1,2-DCE = 1,2-dichloroethane

3.10.3. Wittig rearrangements of 4-silyl-6-aryl dihydropyrans 3.1 – general procedure G



Freshly prepared and purified dihydropyran **3.1** was dissolved in THF under nitrogen (concentration = 0.08 M, unless otherwise noticed) and the solution cooled down at –78 ºC (dry ice/acetone bath). *n*-Butyllithium (1.2 equiv, 1.6 M in hexanes) or *sec*-butyllithium (1.2 equiv, 1.4 M in cyclohexane) was added dropwise (1 drop/second) to give a colored solution. After the indicated time (~3 hours or ~10 minutes, respectively) the reaction was quenched by adding $NH_4Cl_{(sat)}$, diluted with water and diethyl ether. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with water, and brine. The solution was dried over $MgSO_4$, filtered, concentrated in a rotavap at room temperature (or lower) and the residue purified by column chromatography (5-10% EtOAc in hexanes) to afford the aldehyde and or alcohol as colorless oils.

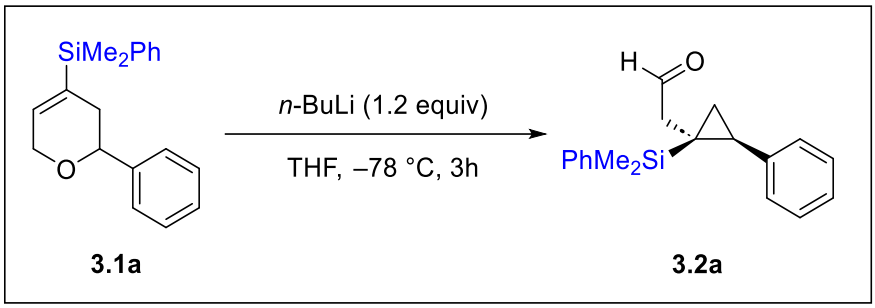
3.10.4. Wittig rearrangements of 4-silyl-6-alkyl dihydropyrans 3.1 – general procedure H



Freshly prepared and purified **3.1** was dissolved in THF under nitrogen (concentration = 0.08 M, unless otherwise noticed) and the solution cooled down at –78 ºC (dry ice/acetone bath).

n-Butyllithium (1.2 equiv, 1.6 M in hexanes) or *sec*-butyllithium (1.2 equiv, 1.4 M in cyclohexane) was added dropwise (1 drop/second) with stirring to give a colored solution. After ~25 minutes the temperature was raised to –10 ºC (unless otherwise indicated). After the indicated time (1.5-3 hours) the reaction was cooled down at –78 ºC and quenched by adding $NH_4Cl_{(sat)}$, diluted with water and diethyl ether. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with water, and brine. The solution was dried over $MgSO_4$, filtered, concentrated in a rotavap at room temperature (or lower) and the residue purified by column chromatography (4-5% EtOAc in hexanes) to afford the aldehyde as a colorless oil.

Preparation of 2-(1-(dimethyl(phenyl)silyl)-2-phenylcyclopropyl)acetaldehyde (3.2a)

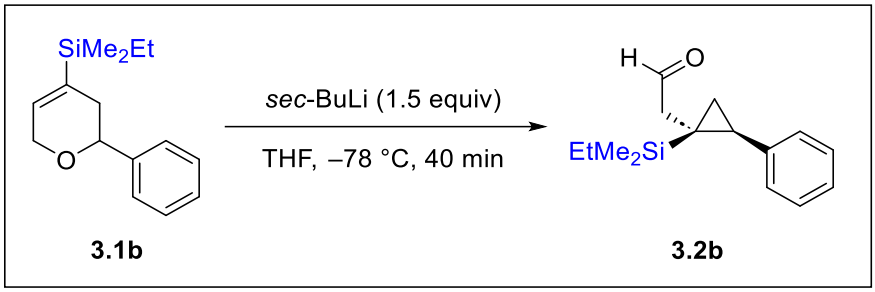


3.1a **3.2a**

Following General Procedure G, dihydropyran **3.1a** (89 mg, 0.302 mmol, 1 equiv) in THF (3.8 mL) and *n*-butyllithium (0.23 mL, 0.36 mmol, 1.2 equiv) at –78 ºC for 3 h, followed by workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2a** as a colorless oil (70.7 mg, 0.242 mmol, 80% isolated yield, *dr* = 1.0:0.3). ^{1}H NMR (500 MHz, $CDCl_3$) mixture of diastereomers (1.0:0.3 ratio) δ 9.67 (t, *J* = 2.0 Hz, 1 H), 9.33 (dd, *J* = 2.0, 2.5 Hz, 0.3 H), 7.55 (m, 0,6 H), 7.38 (m, 0,9 H), 7.33–7.17 (m, 10.9 H), 7.10 (m, 0.6 H), 2.66 (dd, *J* = 2.0, 17.0 Hz, 1 H), 2.25 (dd, *J* = 6.0, 8.0 Hz, 0.3 H, partially overlapped), 2.22 (dd, *J* = 6.0, 8.0 Hz, 1 H), 2.18 (dd, *J* = 3.0, 17.5 Hz, 0.3 H), 2.01 (dd, *J* = 2.0, 17.0 Hz, 1 H), 1.79 (dd, *J* = 2.0, 17.5 Hz, 0.3 H), 1.39 (dd, *J* = 4.5, 6.0 Hz, 1 H), 1.16 (dd, *J* = 5.5, 8.0 Hz, 0.3 H), 1.09 (t, *J* = 5.0 Hz, 0.3 H), 0.93 (dd, *J* = 4.5, 8.5 Hz, 1 H), 0.36 (s, 0.9 H), 0.35 (s, 0.9 H), 0.08 (s, 3 H), -0.23 (s, 3 H). ^{13}C

NMR (126 MHz, $CDCl_3$) major diastereomer δ 202.7, 139.1, 137.9, 134.0, 129.9, 129.0, 128.0, 127.7, 126.5, 53.2, 29.4, 15.7, -2.8, -3.4. Minor diastereomer (a substituted aromatic carbon could not be located) δ 203.2, 137.8, 134.1 (2 C), 129.5, 129.3 (2 C), 128.2 (2 C), 127.9 (2 C), 126.4, 45.1, 24.9, 10.3, -4.35, -4.43. IR (neat) 3063, 2956, 1722, 1496. 1427, 1250, 1111, 816 cm^{-1}. HRMS (EI) *m/z* 294.1430 [$(M)^+$; calcd for $C_{19}H_{22}OSi$, 294.1440].

Preparation of 2-(1-(ethyldimethylsilyl)-2-phenylcyclopropyl)acetaldehyde (3.2b)

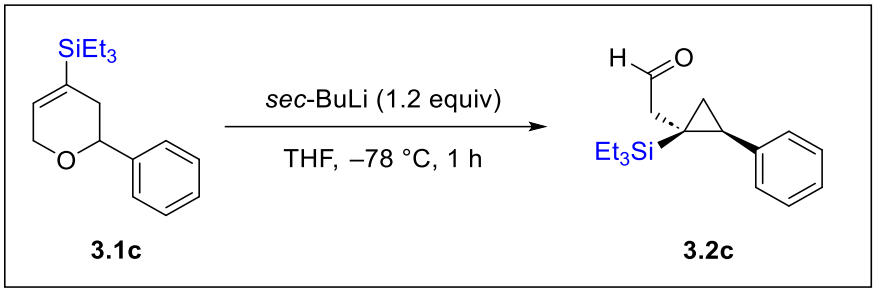


3.1b **3.2b**

Following General Procedure G, dihydropyran **3.1b** (38 mg, 0.154 mmol, 1 equiv) in THF (1.9 mL) and *sec*-butyllithium (0.16 mL, 0.23 mmol, 1.5 equiv) at –78 ºC for 40 minutes, followed by workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2b** as a colorless oil (70.7 mg, 0.123 mmol, 80% isolated yield, crude *dr* = 1.0:0.26, isolated *dr* = 1.0:0.3). Mixture of diastereomers (1.0:0.3 ratio) ^1H NMR 600 MHz, $CDCl_3$) δ 9.90 (dd, *J* = 1.8, 6.0 Hz, 1 H), 9.50 (dd, *J* = 2.4, 6.0 Hz, 0.3 H), 7.29 (m, 2 H), 7.24 (m, 2.6 H), 7.17 (m, 1.9 H), 2.74 (dd, *J* = 6.0, 16.8 Hz, 1 H), 2.19 (m, 1.6 H), 2.01 (dd, *J* = 1.8, 16.8 Hz, 1 H), 1.80 (dd, *J* = 2.4, 17.4 Hz, 0.3 H), 1.24 (dd, *J* = 4.8, 6.0 Hz, 1 H), 1.13 (dd, *J* = 5.4, 7.8 Hz, 0.3 H), 1.07 (t, *J* = 5.4 Hz, 0.3 H), 0.97 (t, *J* = 7.8 Hz, 0.9 H), 0.86 (dd, *J* = 4.8, 8.4 Hz, 1.3 H), 0.76 (t, *J* = 7.8 Hz, 3 H), 0.56 (q, *J* = 7.8 Hz, 0.6 H), 0.26 (m, 2 H), 0.00 (s, 1.8 H), -0.32 (s, 3 H), -0.42 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) Major diastereomer: δ 202.9, 139.4, 129.9 (2 C), 127.9 (2 C), 126.4, 53.4, 29.4, 15.3, 9.9, 7.3, 6.6, -3.8, -4.0. Minor diastereomer: δ 203.4, 138.1, 129.4 (2 C), 128.2 (2 C), 126.4, 45.4, 24.7, 13.7, 9.1, 7.4, 5.8, -5.0, -5.1. IR (film) 3059, 2955, 1724, 1454, 1250, 814

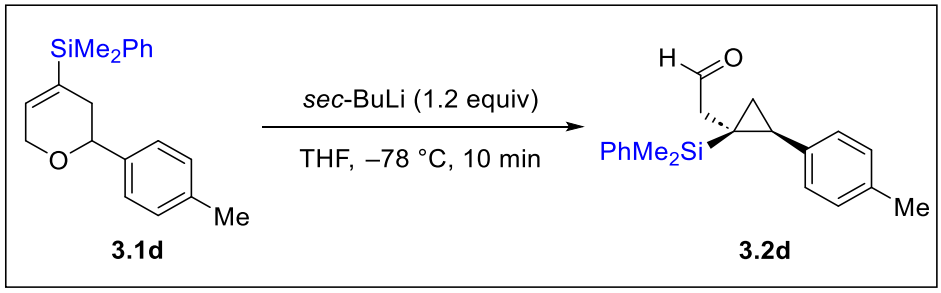
cm^{-1}. HRMS (EI) *m/z* 246.1431 [(M)$^+$; calcd for $C_{15}H_{22}OSi$, 246.1440].

Preparation of 2-(2-phenyl-1-(triethylsilyl)cyclopropyl)acetaldehyde (3.2c)



Following General Procedure G, dihydropyran **3.1c** (89 mg, 0.324 mmol, 1 equiv) in THF (4 mL) and *sec*-butyllithium (0.27 mL, 0.389 mmol, 1.2 equiv) at –78 ºC for 1 h, followed by workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2c** as a colorless oil (62 mg, 0.227 mmol, 70% isolated yield, crude *dr* = 11:1, isolated *dr* > 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (dd, *J* = 2.5, 3.0 Hz, 1 H), 7.30 (m, 2 H), 7.24 (m, 2 H), 7.18 (m, 1 H), 2.72 (dd, A of ABX system, *J* = 2.5, 17.0 Hz, 1 H), 2.14 (dd, *J* = 6.0, 8.0 Hz, 1 H), 2.04 (dd, B of ABX system, *J* = 2.0, 17.0 Hz, 1 H), 1.32 (dd, *J* = 4.5, 5.5 Hz, 1 H), 0.91 (dd, *J* = 4.5, 8.0 Hz, 1 H), 0.78 (t, *J* = 8.0 Hz, 9 H), 0.30 (m, 3 H), 0.15 (m, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.2, 139.4, 129.7 (2 C), 127.9 (2 C), 126.4, 53.6, 28.7, 15.7, 9.4, 7.5, 3.2. IR (film) 3060, 2956, 1725, 1450, 1250, 814 cm^{-1}. HRMS (EI) *m/z* 274.1747 [(M)$^+$; calcd for $C_{17}H_{26}OSi$, 274.1753].

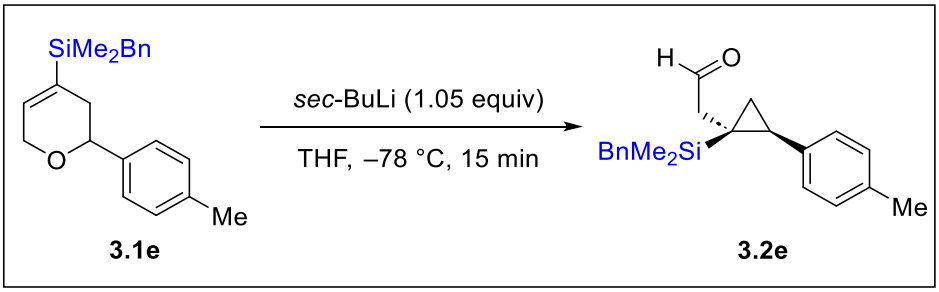
Preparation of 2-(1-(dimethyl(phenyl)silyl)-2-(*p*-tolyl)cyclopropyl)acetaldehyde (3.2d)



Following General Procedure G, dihydropyran **3.1d** (108 mg, 0.35 mmol, 1 equiv) in THF

(4.5 mL) and *sec*-butyllithium (0.3 mL, 0.42 mmol, 1.2 equiv) at –78 ºC for 10 minutes, followed by workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2d** as a colorless oil (93.7 mg, 0.305 mmol, 87% isolated yield, crude *dr* = 1.0:0.3, isolated *dr* = 1.0:0.4). Mixture of diastereomers (1:0.4 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (t, *J* = 2.0 Hz, 1 H), 9,34 (t, *J* = 2.0 Hz, 0.4 H), 7.55 (m, 0.8 H), 7.39–7.27 (m, 6.2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.05 (m, 2.8 H), 6.99 (d, *J* = 8.0 Hz, 0.8 H), 2.64 (dd, *J* = 2.0, 17.0 Hz, 1 H), 2.33 (s, 2 H), 2.30 (s, 0.8 H), 2.22–2.16 (m, 1.8 H), 1.99 (dd, *J* = 2.0, 17.5 Hz, 1 H), 1.81 (dd, *J* = 2.0, 17.5 Hz, 0.4 H), 1.38 (t, *J* = 4.5 Hz, 1 H), 1.14 (dd, *J* = 5.0, 8.0 Hz, 0.4 H), 1.07 (t, *J* = 5.5 Hz, 0.4 H), 0.92 (dd, *J* = 4.5, 8.0 Hz, 1 H), 0.36 (s, 1.2 H), 0.35 (s, 1.2 H), 0.10 (s, 3 H), -0.21 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) Major diastereomer: δ 202.6, 138.0, 135.97, 135.96, 134.1, 134.0 (2 C), 129.7 (2 C), 128.6 (2 C), 127.7 (2 C), 53.2, 29.0, 21.1, 15.7, 10.3, -2.7, -3.4. Minor diastereomer (one aromatic carbon could not be located): δ 203.2, 136.8, 135.94, 134.6, 129.4, 129.2 (2 C), 129.0 (2 C), 128.9 (2 C), 127.9 (2 C), 45.1, 24.5, 21.0, 13.9, 9.3, -4.2, -4.4. IR (film) 3033, 2954, 1719, 1490, 1250, 830 cm^{-1}. HRMS (EI) *m/z* 308.1591 [(M^+); calcd for $C_{20}H_{24}OSi$, 308.1596].

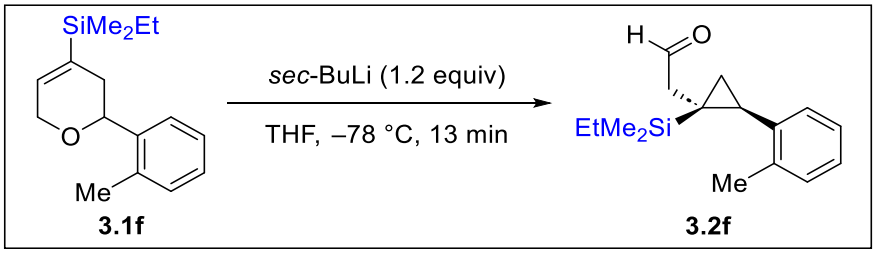
Preparation of 2-(1-(benzyldimethylsilyl)-2-(*p*-tolyl)cyclopropyl)acetaldehyde (3.2e)



Following General Procedure G, dihydropyran **3.1e** (78 mg, 0.242 mmol, 1 equiv) in THF (3 mL) and *sec*-butyllithium (0.18 mL, 0.254 mmol, 1.05 equiv) at –78 ºC for 15 minutes, followed by workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2e** as a colorless oil (71.7 mg, 0.223 mmol, 92% isolated yield, crude *dr* = 1.0:0.5, isolated *dr* =

1.0:0.24). Mixture of diastereomers (1.0:0.24 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (dd, *J* = 2.0, 2.5 Hz, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.12 (t, *J* = 7.5 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 7.00 (t, *J* = 7.5 Hz, 1 H), 6.78 (m, 2 H), 2.79 (dd, A of ABX system, *J* = 3.0, 17.5 Hz, 1 H), 2.32 (s, 3 H), 2.18 (m, 1 H), 2.04 (dd, B of ABX system, *J* = 2.5, 17.5 Hz, 1 H), 1.86 (d, C of CDX system, *J* = 13.5 Hz, 1 H), 1.80 (dd, D of CDX system, *J* = 13.5 Hz, 1 H), 1.22 (t, *J* = 5.5 Hz, 1 H), 0.86 (dd, *J* = 5.0, 8.5 Hz, 1 H), -0.32 (s, 3 H), -0.45 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer δ 202.8, 139.7, 136.2, 136.1, 129.8 (2 C), 128.7 (2 C), 128.2 (2 C), 128.0 (2 C), 124.0, 53.4, 29.3, 24.8, 21.1, 15.5, 9.8, -3.3, -3.6. IR (film) 3024, 2957, 2720, 1722, 1493, 1250, 827 cm^{-1}. HRMS (EI) *m*/*z* 231.1197 [(M-C_7H_7)$^+$; calcd for $C_{14}H_{19}OSi$, 231.1205]. The minor diastereomer was also partially purified as the major component. (1.0:0.2 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (dd, *J* = 2.0, 3.0 Hz, 1 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.07 (m, 3 H), 7.02 (m, 2 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 2.32 (s, 3 H), 2.18 (m, 4 H), 1.87 (dd, *J* = 2.0, 17.5 Hz, 1 H), 1.12 (dd, *J* = 5.5, 8.0 Hz, 1 H), 1.05 (t, *J* = 5.5 Hz, 1 H), -0.01 (s, 3 H), -0.02 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.3, 139.5, 136.0, 134.6, 129.3 (2 C), 128.9 (2 C), 128.3 (4 C), 124.2, 45.4, 24.6, 24.2, 21.0, 13.9, 8.9, -4.5, -4.7. IR (film) 3025, 2956, 2720, 1722, 1493, 1251, 827 cm^{-1}. HRMS (EI) *m*/*z* 231.1209 [(M-C_7H_7)$^+$; calcd for $C_{14}H_{19}OSi$, 231.1205].

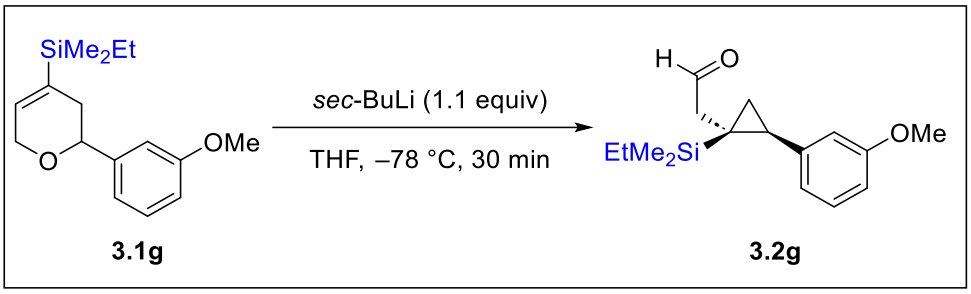
Preparation of 2-(1-(ethyldimethylsilyl)-2-(*o*-tolyl)cyclopropyl)acetaldehyde (3.2f)



Following General Procedure G, dihydropyran **1f** (95 mg, 0.365 mmol, 1 equiv) in THF (4.6 mL) and *sec*-butyllithium (0.3 mL, 0.438 mmol, 1.2 equiv) at –78 ºC for 13 minutes, followed

by workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **2f** as a colorless oil (86.5 mg, 0.332 mmol, 91% isolated yield, crude *dr* = 8.3:1.0, isolated *dr* = 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (t, *J* = 2.5 Hz, 1 H), 7.12–7.05 (m, 4 H), 2.56 (dd, *J* = 2.5, 16.5 Hz, 1 H), 2.37 (overlapped, dd, *J* = 3.0, 16.5 Hz, 1 H), 2.37 (s, 3 H), 1.95 (dd, *J* = 6.0, 8.0 Hz, 1 H), 1.37 (dd, *J* = 5.0, 6.0 Hz, 1 H), 0.97 (dd, *J* = 5.0, 8.5 Hz, 1 H), 0.76 (t, *J* = 8.0 Hz, 3 H), 0.26 (m, 2 H), -0.30 (s, 3 H), -0.39 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 138.8, 137.5, 129.7, 128.3, 126.6, 125.3, 53.5, 29.0, 20.1, 14.7, 10.3, 7.3, 6.8, -3.7, -3.9. IR (film) 3029, 2953, 1722, 1124, 830 cm^{-1}. HRMS (EI) *m/z* 260.1605 [(M^+); calcd for $C_{16}H_{24}OSi$, 260.1596].

Synthesis of 2-(1-(ethyldimethylsilyl)-2-(3-methoxyphenyl)cyclopropyl)acetaldehyde (3.2g)

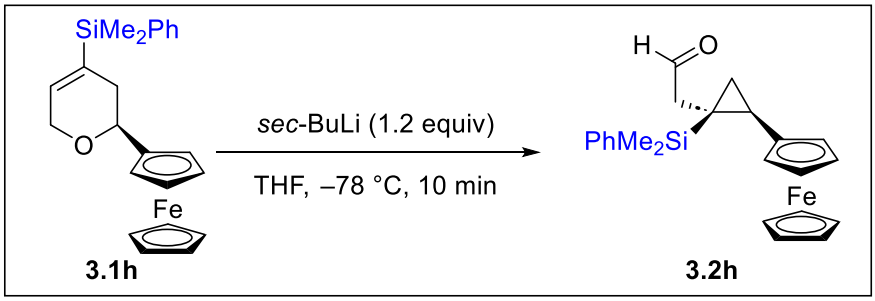


3.1g **3.2g**

Following General Procedure G, dihydropyran **3.1g** (68.9 mg, 0.249 mmol, 1 equiv) in THF (3.1 mL) and *sec*-butyllithium (0.2 mL, 0.274 mmol, 1.1 equiv) at –78 ºC for 30 minutes, followed by workup and silica gel chromatography (5-10% EtOAc in hexanes) afforded silylcyclopropane **3.1g** as a colorless oil (41.7 mg, 0.152 mmol, 61% isolated yield, crude *dr* = 2:1, isolated *dr* = 1.1:1.0). Mixture of diastereomers (*cis*/*trans* 1.1:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (t, *J* = 2.5 Hz, 1.1 H), 9.51 (dd, *J* = 2.0, 3.0 Hz, 1 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 7.15 (t, *J* = 8.0 Hz, 1.1 H), 6.87 (m, 2.1 H), 6.71 (m, 4.2 H), 3.78 (s, 3.3H), 3.77 (s, 3 H), 2.74 (dd, *J* = 3.0, 17.5 Hz, 1.1 H), 2.23–2.13 (m, 3.1 H), 2.01 (dd, t, *J* = 2.0, 17 Hz, 1.1 H), 1.83 (dd, t, *J* = 2.5, 17.5 Hz, 1 H), 1.22 (dd, *J* = 4.5, 5.5 Hz, 1.1 H), 1.12 (dd, *J* = 5.0, 8.0 Hz, 1 H), 1.05 (t, *J* = 5.5 Hz, 1 H), 0.97 (t, *J* = 8.0 Hz, 3 H), 0.86 (m, 1.1 H), 0.77 (t, *J* = 8.0 Hz, 3.3 H), 0.55 (q, *J* = 8.0 Hz, 2 H), 0.28

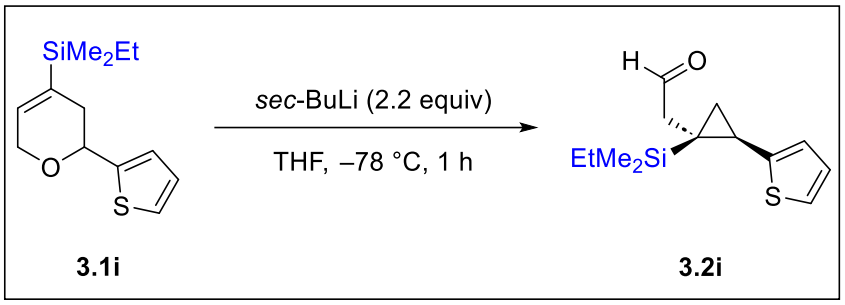
(m, 2.2 H), 0.00 (s, 6 H), -0.29 (s, 3.3 H), -0.39 (s, 3.3 H). ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer δ 202.9, 159.3, 141.1, 128.9, 121.8, 115.5, 112.0, 29.5, 15.5, 9.9, 7.3, 6.7, -4.0, -5.0. Minor diastereomer δ 203.5, 159.5, 139.8, 129.2, 122.3, 115.5, 111.4, 24.8, 13.9, 9.1, 7.4, 5.8, -3.7, -5.2. IR (film) 2955, 1722, 1601, 1255, 1045, 835 cm^{-1}. HRMS (EI) *m*/*z* 276.1550 [(M)$^+$; calcd for $C_{16}H_{24}O_2Si$, 276.1546]

Preparation of 2-(1-(dimethyl(phenyl)silyl)-2-ferrocenylcyclopropyl)acetaldehyde (3.2h)



Following General Procedure G, dihydropyran **3.1h** (117 mg, 0.291 mmol, 1 equiv) in THF (3.6 mL) and *sec*-butyllithium (0.25 mL, 0.349 mmol, 1.2 equiv) at –78 ºC for 10 minutes, followed by workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2h** as an orange oil (80.3 mg, 0.201 mmol, 69%, isolated yield, crude *dr* = 9.4:1, isolated *dr* = 1.0:0.1). Mixture of diastereomers (1.0:0.1 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer: δ 9.53 (t, *J* = 7.0 Hz, 1 H), 7.31 (m, 2 H), 7.28 (m, 3 H), 4.30 (m, 1 H), 4.09 (m, 1 H), 4.08 (s, 5 H), 3.92 (m, 1 H), 3.76 (m, 1 H), 2.42 (dd, A of ABX system, *J* = 2.0, 17.0 Hz, 1 H), 1.97 (dd, B of ABX system, *J* = 2.0, 17.0 Hz, 1 H), 1.93 (dd, *J* = 6.5, 9.0 Hz, 1 H), 1.03 (d, *J* = 4.5, 6.0 Hz, 1 H), 0.87 (dd, *J* = 5.0, 8.5 Hz, 1 H), 0.06 (s, 3 H), -0.04 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 138.1, 134.2 (2 C), 129.0, 127.6 (2 C), 86.5, 70.1, 69.3, 68.7 (5 C), 68.2, 66.0, 53.3, 24.9, 16.8, 11.2, -2.5, -2.9. IR (film) 3091, 2988, 1722, 1427, 1250, 1107, 816 cm^{-1}. HRMS (EI) *m*/*z* 402.1093 [(M$^+$); calcd for $C_{23}H_{26}OSiFe$, 402.1102].

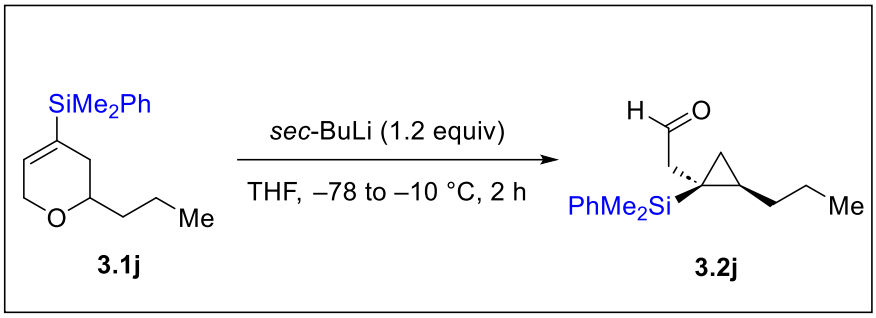
Preparation of 2-(1-(ethyldimethylsilyl)-2-(thiophen-2-yl)cyclopropyl)acetaldehyde (3.2i)



3.1i **3.2i**

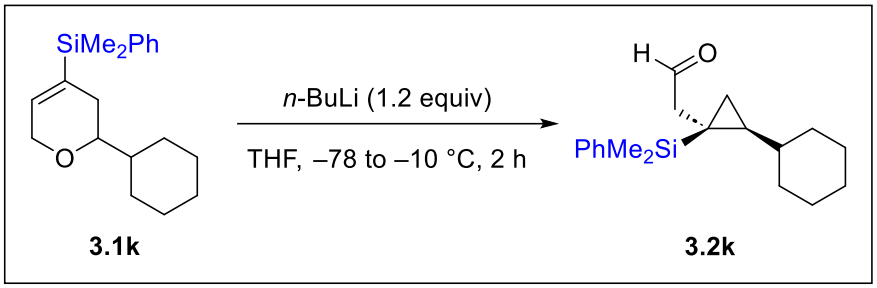
Following General Procedure G, dihydropyran **3.1i** (39.5 mg, 0.157 mmol, 1 equiv) in THF (2 mL) and *sec*-butyllithium (0.25 mL, 0.344 mmol, 2.2 equiv) at –78 ºC for 1 h, followed by workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2i** as a colorless oil (28 mg, 0.112 mmol, 71% isolated yield, crude *dr* = 1.0:0.5, isolated *dr* = 1.0:0.5). Mixture of diastereomers (*trans/cis* 1.0:0.5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (dd, *J* = 2.0, 3.0 Hz, 0.5 H), 9.57 (dd, *J* = 2.0, 3.0 Hz, 1 H), 7.10 (m, 1.5 H), 6.90 (dd, *J* = 3.5, 5.0 Hz, 1.0 H), 0.87 (dd, *J* = 3.5, 5.0 Hz, 0.5 H), 6.81 (dt, *J* = 1.5, 3.5 Hz, 0.5 H), 6.73 (dt, *J* = 1.5, 3.5 Hz, 1 H), 2.65 (dd, A of ABX system, *J* = 3.0, 17.5 Hz, 0.5 H), 2.30 (dd, C of CDX system, *J* = 3.0, 17.5 Hz, 1 H), 2.24 (dd, *J* = 5.5, 7.0 Hz, 1 H), 2.14 (dd, *J* = 6.0, 7.5 Hz, 0.5 H), 2.02 (dd, B of ABX system, *J* = 2.0, 17.0 Hz, 0.5 H), 1.95 (dd, D of CDX system, *J* = 2.0, 17.5 Hz, 1 H), 1.25 (m, 1.5 H), 1.01 (t, *J* = 5.0 Hz, 1 H), 1.00 (m, 0.5 H), 0.97 (t, *J* = 8.0 Hz, 3 H), 0.81 (t, *J* = 8.0 Hz, 1.5 H), 0.54 (q, *J* = 8.0 Hz, 2 H), 0.40–0.28 (m, 1 H), -0.01 (s, 3 H), 0.02 (s, 3 H), -0.21 (s, 1.5 H), -0.32 (s, 1.5 H). ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer: δ 203.2, 142.6, 126.9, 126.0, 124.1, 19.2, 16.4, 10.1, 7.4, 5.8, -5.0, -5.3. Minor diastereomer: δ 202.7, 144.1, 126.5, 126.2, 124.0, 23.3, 17.6, 11.2, 7.3, 6.4, -4.0, -4.3. IR (film) 2953, 1722, 1250, 833 cm^{-1}. HRMS (EI) *m/z* 252.1001 [$(M)^{+}$; calcd for $C_{13}H_{20}OSiS$, 252.1004].

Preparation of 2-(1-(dimethyl(phenyl)silyl)-2-propylcyclopropyl)acetaldehyde (3.2j)



Following general procedure H, dihydropyran **3.1j** (82.8 mg, 0.318, 1 equiv), in THF (4 mL) and *sec*-butyllithium (0.27 mL, 0.381 mmol, 1.2 equiv) at –78 ºC and warming to –10 ºC for 2 h, followed by aqueous workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2j** as a colorless oil (68.6 mg, 0.316 mmol, 83% isolated yield, crude *dr* = 4.3:1.0, isolated *dr* = 1.0:0.2). Mixture of diastereomers (*cis*/*trans* = 1.0:0.2 ratio). ^{1}H NMR (600 MHz, $CDCl_3$) major diastereomer (*cis*): δ 9.53 (t, *J* = 2.4 Hz, 1 H), 7.50 (m, 2 H), 7.34 (m, 3 H), 2.41 (dd, A of ABX system, *J* = 2.4, 16.8 Hz, 1 H), 1.80 (dd, B of ABX system, *J* = 2.4, 17.4 Hz, 1 H), 1.56 (m, 1 H), 1.38 (m, 2 H), 1.11 (m, 1 H), 0.88 (t, *J* = 7.2 Hz, 3 H), 0.81 (m, 1 H), 0,61 (dd, C of CDX system, *J* = 4.2, 8.4 Hz, 1 H), 0.56 (dd, D of CDX system, *J* = 4.2, 5.4 Hz, 1 H), 0.36 (s, 3 H), 0.32 (s, 3 H). Minor diastereomer (*trans*): δ 9.50 (t, *J* = 2.4 Hz, 1 H), 7.48 (m, 2 H), 2.38 (dd, A of ABX system, *J* = 3.0, 17.4 Hz, 1 H), 2.23 (dd, B of ABX system, *J* = 2.4, 17.4 Hz, 1 H), 0.24 (s, 6 H), all other protons are overlapped with major diastereomer, presumably at 7.34 (3 H), 1.38 (4 H), 0.92–079 (6 H). ^{13}C NMR (151 MHz, $CDCl_3$) mixture of diastereomers (*cis* / *trans* = 1.0:0.2 ratio), Major (*cis*) diastereomer: δ 203.3, 138.4, 134.1 (2 C), 129.1, 127.8 (2 C), 53.4, 33.5, 26.0, 23.3, 17.9, 13.9, 6.4, -1.4, -2.1. IR (neat) 3070, 2957, 2872, 1725, 1427, 1251, 1111, 816 cm^{-1}. HRMS (EI) *m/z* 260.1590 [$(M)^+$; calcd for $C_{16}H_{24}OSi$, 260.1596].

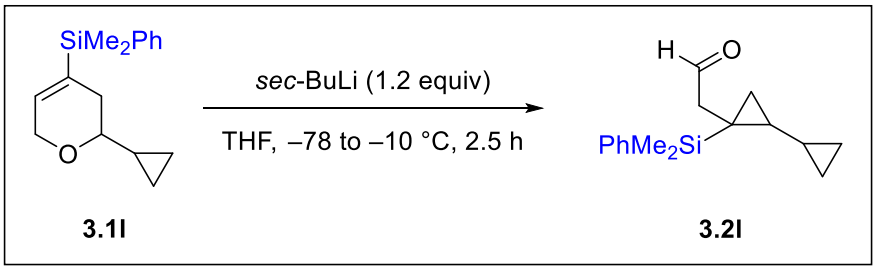
Preparation of 2-(2-cyclohexyl-1-(dimethyl(phenyl)silyl)cyclopropyl)acetaldehyde (3.2k)



3.1k **3.2k**

Following general procedure H, dihydropyran **3.1k** (67 mg, 0.223, 1 equiv), in THF (2.8 mL) and *n*-butyllithium (0.28 mL, 0.446 mmol, 2 equiv) at –78 ºC and warming to –10 ºC for 2 h, followed by aqueous workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2k** as a colorless oil (50.4 mg, 0.170 mmol, 76% isolated yield, crude *dr* = 1.6:1.0, isolated *dr* = 1.0:0.6). Mixture of diastereomers (~1:0.6 ratio). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (dd, *J* = 2.0, 3.0 Hz, 1 H), 9.47 (dd, *J* = 2.0, 3.0 Hz, 0.6 H), 7.49 (m, 3.2 H), 7.34 (m, 4.8 H), 2.54 (dd, *J* = 3.0, 17.0 Hz, 1 H), 2.50 (22, *J* = 3.5, 17.5 Hz, 0.6 H), 2.06 (dd, *J* = 2.0, 17.0 Hz, 0.6 H), 1.84 (m, 1 H), 1.75–1.56 (m, 8.80 H), 1.17–0.93 (m, 8.64 H), 0.89–0.80 (m, 2 H), 0.70 (m, 1 H), 0.63–0.52 (m, 3.2 H), 0.38 (s, 3 H), 0.31 (s, 3 H), -0.23 (d, 3.6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 203.7, 138.2, 137.1, 134.1, 134.0, 129.3, 129.1, 127.8, 127.7, 53.2, 44.5, 39.1, 37.6, 34.3, 33.43, 33.41, 33.38, 33.3, 26.6, 26.4, 26.33, 26.31, 26.30, 26.0, 25.9, 16.7, 14.1, 6.8, 5.3, -1.4, -2.2, -4.6, -4.7. HRMS (EI) *m/z* 300.1909 [$(M)^+$; calcd for $C_{19}H_{28}OSi$, 300.1909].

Preparation of 2-(2-(dimethyl(phenyl)silyl)-[1,1'-bi(cyclopropan)]-2-yl)acetaldehyde (3.2l)

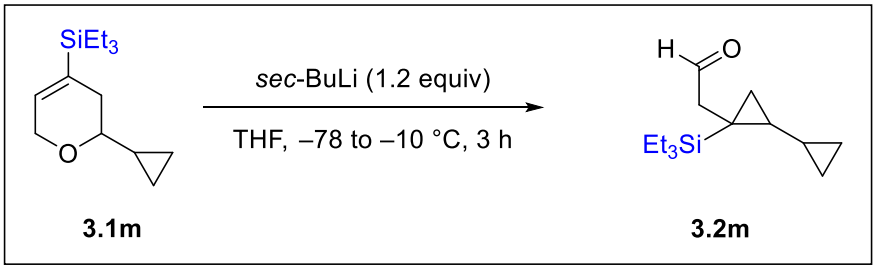


3.1l **3.2l**

Following general procedure H, dihydropyran **3.1l** (66.8 mg, 0.257, 1 equiv), in THF (3.2

mL) and *sec*-butyllithium (0.22 mL, 0.309 mmol, 1.2 equiv) at –78 ºC and warming to –10 ºC for 2.5 h, followed by aqueous workup and silica gel chromatography (5% EtOAc in hexanes) afforded silylcyclopropane **3.2l** as a colorless oil (51.6 mg, 0.188 mmol, 73% isolated yield, crude *dr* = 1:1, isolated *dr* = 1:1). Mixture of diastereomers (1:1 ratio) ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.58 (t, *J* = 3.0 Hz, 1 H), 9.49 (t, *J* = 2.4 Hz, 1 H), 7.54 (m, 2 H), 7.47 (m, 2 H), 7.34 (m, 6 H), 2.49 (dd, A of ABX system, *J* = 2.4, 17.4 Hz, 1 H), 2.40 (dd, B of ABX system, *J* = 2.4, 18.0 Hz, 1 H), 2.36 (dd, C of CDX system, *J* = 2.4, 16.8 Hz, 1 H), 1.81 (dd, D of CDX system, *J* = 2.4, 16.8 Hz, 1 H), 0.78–0.72 (m, 2 H), 0.71 (t, *J* = 4.8 Hz, 1 H), 0.61–0.57 (m, 2 H), 0.54–0.43 (m, 6 H), 0.40 (s, 3 H), 0.37 (m, 3 H), 0.31 (t, *J* = 4.8 Hz, 1 H), 0.26 (m, 1 H), 0.23 (s, 3 H), 0.22 (s, 3 H), 0.21 (m, overlapped with Me singlet at 0.22, 1 H), 0.17–0.12 (m, 2 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.0, 203.1, 138.3, 137.1, 134.2 (2 C), 134.0 (2 C), 129.3, 129.1, 127.83 (2 C), 127.80 (2 C), 53.1, 45.5, 29.8, 23.2, 17.3, 14.7, 11.9, 9.5, 7.3, 6.7, 6.1, 6.0, 5.3, 4.5, -1.9, -2.2, -4.52, -4.55. IR (neat) 3071, 3000, 2959, 2816, 1722, 1427, 1250, 1113, 815 cm^{-1}. HRMS (EI) *m/z* 258.1440 [(M)$^{+}$; calcd for $C_{16}H_{22}OSi$, 258.1440].

Preparation of 2-(2-(triethylsilyl)-[1,1'-bi(cyclopropan)]-2-yl)acetaldehyde (3.2m)

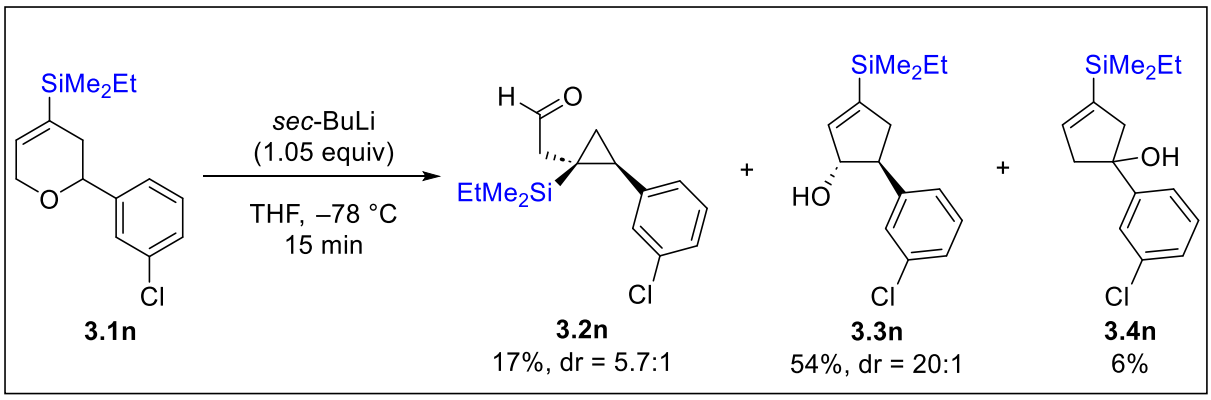


3.1m **3.2m**

Following general procedure H, dihydropyran **3.1m** (69.5 mg, 0.292, 1 equiv), in THF (3.6 mL) and *sec*-butyllithium (0.25 mL, 0.35 mmol, 1.2 equiv) at –78 ºC and warming to –10 ºC for 3 h, followed by aqueous workup and silica gel chromatography (3.5% EtOAc in hexanes) afforded silylcyclopropane **3.2m** as a colorless oil (52.4 mg, 0.219 mmol, 75% isolated yield, crude *dr* =

1.5:1.0, isolated *dr* = 1.0:0.7). Mixture of diastereomers (1:0.7 ratio, relative stereochemistry was not assigned) ^{1}H NMR (600 MHz, $CDCl_3$) (1:0.7 ratio) δ 9.79 (t, *J* = 2.5 Hz, 0.7 H), 9.68 (dd, *J* = 2.5, 3.5 Hz, 1 H), 2.49 (dd, A of ABX system, *J* = 2.5, 17.0 Hz, 0.7 H), 2.42 (dd, C of CDX system, *J* = 3.0, 16.5 Hz, 1 H), 2.40 (dd, B of ABX system, *J* = 2.5, 17.0 Hz, 0.7 H), 1.77 (dd, D of CDX system, *J* = 2.5, 17.0 Hz, 1 H), 0.97 (t, *J* = 8.0 Hz, 9 H), 0.92 (t, *J* = 8.0 Hz, 6.3 H), 0.74 (dd, *J* = 4.5, 8.0 Hz, 0.7 H), 0.69–0.60 (m, heavily overlapped with $SiCH_2$, not quantified), 0.60 (q, *J* = 8.0 Hz, 6 H), 0.52–0.47 (m, ~6 H), 0.46 (q, *J* = 8.0 Hz, 4.2 H), 0.37 (m, 1 H), 0.28–0.17 (m, ~4 H). ^{13}C NMR (126 MHz, $CDCl_3$) major diastereomer: δ 203.9, 53.5, 29.2, 17.4, 12.2, 7.6, 6.0, 5.3, 4.5, 3.7. Minor diastereomer: δ 204.5, 46.2, 22.8, 14.5, 9.6, 7.4, 6.5, 5.6, 4.3, 2.2. IR (film) 3078, 2999, 2953, 1724, 1458, 1018, 733 cm^{-1}. HRMS (EI) *m*/*z* 238.1756 [$(M)^+$; calcd for $C_{14}H_{26}OSi$, 238.1753].

Preparation of 2-(2-(3-chlorophenyl)-1-(ethyldimethylsilyl)cyclopropyl)acetaldehyde (2n), 5-(3-chlorophenyl)-3-(ethyldimethylsilyl)cyclopent-2-en-1-ol (3n), and 1-(3-chlorophenyl)-3-(ethyldimethylsilyl)cyclopent-3-en-1-ol (4n)



Following General Procedure G, dihydropyran **3.1n** (90 mg, 0.32 mmol, 1 equiv) in THF (4 mL) and *sec*-butyllithium (0.24 mL, 0.336 mmol, 1.05 equiv) at –78 ºC for 15 minutes, followed by workup and silica gel chromatography (6–15% EtOAc in hexanes) afforded silylcyclopropane **3.2n** (16.4 mg, 0.0544 mmol, 17% isolated yield, crude *dr* = 5.4:1, isolated *dr* = 1.0:0.12),

secondary alcohol **3.3n** (49.7 mg, 0.173 mmol, 54% isolated yield, *dr* = 20:1), and tertiary alcohol **3.4n** (6.3 mg, 0.0192 mmol, 6% isolated yield), all as colorless oils, together with unreacted **3.1n** (21.5 mg, 0.074 mmol, 23% recovery).

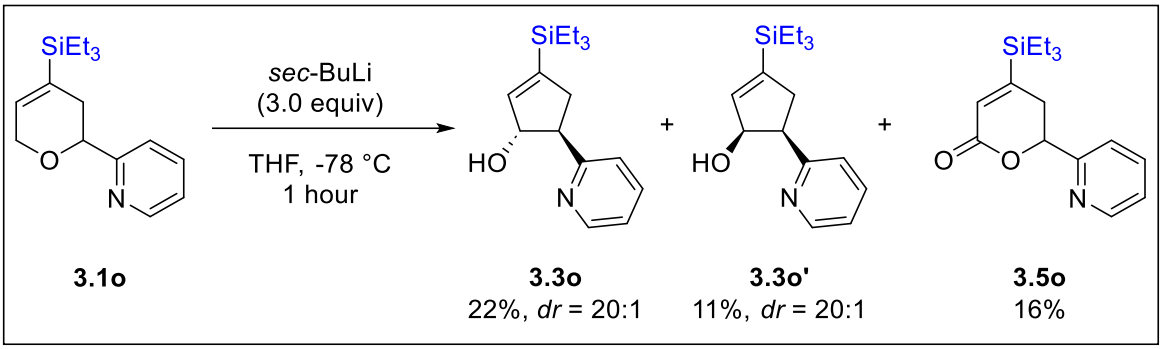
Spectroscopic data for **3.2n**: mixture of diastereomers (*cis* / *trans* = 1.0:0.12 ratio) ^{1}H NMR (600 MHz, $CDCl_3$) major (*cis*) diastereomer: δ 9.87 (dd, *J* = 1.8, 3.0 Hz, 1 H), 7.28 (m, 1 H), 7.21 (m, 1 H), 7.19–7.15 (m, 2 H), 2.78 (dd, *J* = 2.4, 17.4 Hz, 1 H), 2.12 (dd, *J* = 6.6, 8.4 Hz, 1 H), 2.00 (dd, *J* = 1.8, 17.4 Hz, 1 H), 1.20 (dd, *J* = 5.4, 6.0 Hz, 1 H), 0.87 (dd, *J* = 5.4, 8.4 Hz, 1 H), 0.77 (t, *J* = 7.8 Hz, 3 H), 0.26 (m, 2 H), -0.31 (s, 3 H), -0.41 (s, 3 H). Minor (*trans*) diastereomer: δ 9.51 (dd, *J* = 1.8, 3.0 Hz, 0.15 H), 7.20–7.14 (m, heavily overlapped with major diastereomer, 0.45 H), 7.03 (m, 0.15 H), 2.17 (m, 0.30 H), 1.79 (dd, *J* = 1.8, 17.4 Hz, 0.15 H), 1.14 (dd, *J* = 5.4, 7.8 Hz, 0.15 H), 1.03 (t, *J* = 5.4 Hz, 0.15 H), 0.96 (t, *J* = 7.8 Hz, 0.45 H), 0.55 (q, *J* = 7.8 Hz, 0.30 H), 0.01 (s, 0.9 H). ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer δ 202.4, 141.8, 133.8, 129.9, 129.2, 128.2, 126.6, 53.3, 29.0, 15.5, 10.2, 7.3, 6.7, -3.7, -3.9. IR (film) 3422, 3061, 2955, 2876, 1724, 1250, 814 cm^{-1}. HRMS (EI) *m/z* 228.1042 [$(M)^+$; calcd for $C_{15}H_{21}OSiCl$, 280.1050].

Spectroscopic data for **3.3n**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 1.8 Hz, 1 H), 7.20 (d, *J* = 7.2 Hz, 1 H), 7.17 (m, 1 H), 7.11 (m, 1 H), 5.99 (q, *J* = 1.8 Hz, 1 H), 4.83 (m, 1 H), 3.12 (m, 1 H), 2.95 (ddt, *J* = 1.8. 8.4, 16.8 Hz, 1 H), 2.41 (ddt, *J* = 1.8, 6.6, 16.8 Hz, 1 H), 1.80 (s, 1 H), 0.95 (t, *J* = 7.8 Hz, 3 H), 0.60 (q, *J* = 7.8 Hz, 2 H), 0.09 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 146.3, 141.8, 134.3, 129.8, 127.3, 126.4, 125.4, 86.4, 54.9, 43.0, 7.4, 6.6, -4.2, -4.3. IR (film) 3352, 2955, 1458, 1250, 1089, 837 cm^{-1}. HRMS (EI) *m/z* 263.1019 [$(M\text{-}OH)^+$; calcd for $C_{15}H_{20}SiCl$, 263.1023].

Spectroscopic data for **3.4n**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (t, *J* = 1.8 Hz, 1 H), 7.34 (ddd, *J* = 1.2, 1.8, 7.8 Hz, 1 H), 7.24 (m, 1 H), 7.20 (ddd, *J* = 1.2, 2.4, 7.8 Hz, 1 H), 6.01 (m, 1 H),

2.97 (dq, *J* = 1.8, 18.0 Hz, 1 H), 2.87 (m, 1 H), 2.80–2.75 (m, 2 H), 2.04 (s, 1 H), 0.94 (t, *J* = 7.8 Hz, 3 H), 0.58 (q, *J* = 7.8 Hz, 2 H), 0.08 (s, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.0, 142.3, 137.8, 134.1, 129.4, 126.8, 125.4, 123.1, 82.9, 53.9, 52.4, 7.4, 6.7, -4.11, -4.13. IR (film) 3397, 3031, 2955, 1253, 839 cm^{-1}. HRMS (EI) *m/z* 263.1009 [(M-OH)$^+$; calcd for $C_{15}H_{20}SiCl$, 263.1023].

Preparation of *trans*-5-(pyridin-2-yl)-3-(triethylsilyl)cyclopent-2-en-1-ol (3.3o), *cis*-5-(pyridin-2-yl)-3-(triethylsilyl)cyclopent-2-en-1-ol (3.3o'), and 6-(pyridin-2-yl)-4-(triethylsilyl)-5,6-dihydro-2H-pyran-2-one (3.5o)



Following General Procedure G, dihydropyran **3.1o** (248 mg, 0.90 mmol, 1 equiv) in THF (15 mL) and 1.4M *sec*-butyllithium (1.9 mL, 2.7 mmol, 3.0 equiv) at –78 ºC for 2 hours, followed by workup and silica gel chromatography (35% EtOAc in hexanes) afforded silylcyclopentenols **3.3o** (56 mg, 0.198 mmol, 22% isolated yield, *dr* = 20:1), **3.3o′** (29 mg, 0.099 mmol, 11% isolated yield, *dr* = 20:1), and lactone **3.5o** (40 mg, 0.144 mmol, 16% isolated), all as colorless oils.

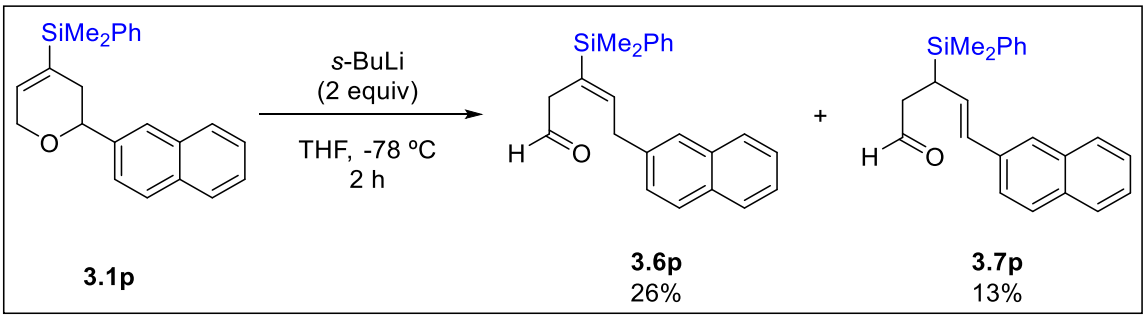
Spectroscopic data for **3.3o**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.62 (td, *J* = 7.7, 1.9 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.14 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 6.07 (dt, *J* = 2.7, 1.6 Hz, 1H), 5.14 (dq, *J* = 7.0, 1.9 Hz, 1H), 3.36 (td, *J* = 8.3, 6.9 Hz, 1H), 2.94 (ddt, *J* = 15.8, 8.3, 1.6 Hz, 1H), 2.59 (ddt, *J* = 15.8, 8.5, 2.3 Hz, 1H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 149.1, 143.8, 143.3, 136.5, 122.0, 121.4, 84.7, 57.0, 41.0, 7.4, 2.9. HRMS (ESI) *m/z* 274.1630 [(M – H)$^+$; calcd for $C_{16}H_{24}NOSi$, 274.1627].

Spectroscopic data for **3.3o′**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 4.9, 1.8, 0.9 Hz,

1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.20 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 6.09 (td, *J* = 2.8, 1.2 Hz, 1H), 5.54 (t, *J* = 2.1 Hz, 1H), 5.02 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.13 (s, 1H), 2.44 (ddd, *J* = 17.5, 3.2, 1.2 Hz, 1H), 2.25 (dddd, *J* = 17.5, 11.1, 2.8, 1.5 Hz, 1H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.63 (q, *J* = 8.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2, 149.0, 139.3, 136.8, 134.2, 122.4, 120.5, 89.6, 69.6, 33.2, 7.3, 2.2. HRMS (ESI) *m/z* 276.1787 [$(M + H)^+$; calcd for $C_{16}H_{26}NOSi$, 276.1784].

Spectroscopic data for **3.5o**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dt, *J* = 4.9, 1.3 Hz, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.22 (m, 1H), 6.27 (dd, *J* = 2.4, 1.1 Hz, 1H), 5.49 (dd, *J* = 10.6, 4.1 Hz, 1H), 2.88 (ddd, *J* = 18.1, 4.1, 1.1 Hz, 1H), 2.67 (ddd, *J* = 18.1, 10.7, 2.4 Hz, 1H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 160.9, 158.0, 149.0, 137.0, 128.1, 123.0, 120.5, 79.2, 32.5, 7.1, 1.8. HRMS (ESI) *m/z* 290.1579 [$(M + H)^+$; calcd for $C_{16}H_{24}NO_2Si$, 290.1576].

Preparation of (*E*)-3-(dimethyl(phenyl)silyl)-5-(naphthalen-2-yl)pent-3-enal (3.6p), and (*E*)-3-(dimethyl(phenyl)silyl)-5-(naphthalen-2-yl)pent-4-enal (3.7p)



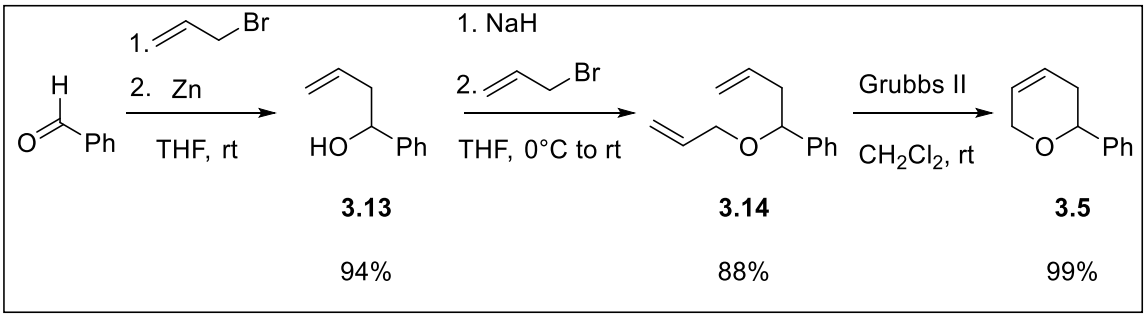
Following General Procedure G, dihydropyran **3.1p** (150 mg, 0.44 mmol, 1 equiv) in THF (15 mL) and 1.4M *sec*-butyllithium (0.63 mL, 0.88 mmol, 2.0 equiv) at –78 ºC for 2 hours, followed by workup and silica gel chromatography (5% EtOAc in hexanes) afforded aldehydes **3.6p** (39.2 mg, 0.114 mmol, 26% isolated yield), **3.7p** (20 mg, 0.057 mmol, 13% isolated yield) all as colorless oils.

Spectroscopic data for **3.6p**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (t, *J* = 2.2 Hz, 1H), 7.86 – 7.77 (m, 3H), 7.64 – 7.60 (m, 1H), 7.57 – 7.52 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.35 (m, 3H), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.42 (tt, *J* = 7.0, 1.1 Hz, 1H), 3.65 (d, *J* = 7.0 Hz, 2H), 3.37 (dd, *J* = 2.2, 1.0 Hz, 2H), 0.42 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 144.9, 137.2, 137.1, 134.0, 133.6, 132.1, 130.8, 129.3, 128.2, 127.9, 127.6, 127.5, 127.1, 126.5, 126.1, 125.4, 44.9, 35.7, -3.3. HRMS (ESI) *m/z* 344.1593 [$(M)^+$; calcd for $C_{23}H_{24}OSi$, 344.1596].

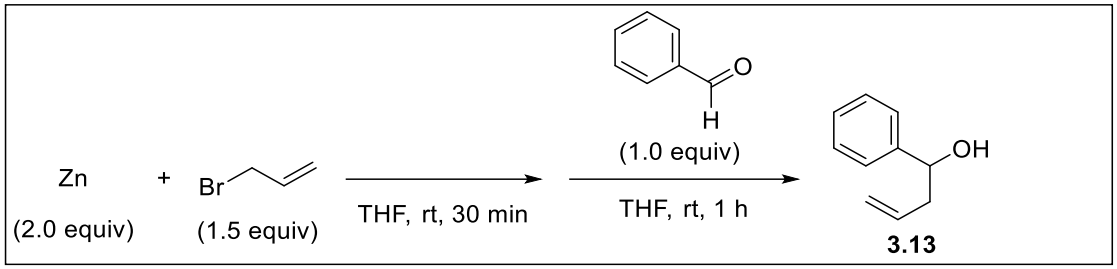
Spectroscopic data for **3.7p**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (t, *J* = 2.1 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.61 (s, 1H), 7.56 – 7.51 (m, 2H), 7.49 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.47 – 7.37 (m, 5H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 8.2 Hz, 1H), 2.65 – 2.43 (m, 3H), 0.39 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.9, 136.1, 135.0, 134.0, 133.6, 132.6, 130.3, 129.6, 128.9, 128.1, 128.0, 127.8, 127.6, 126.2, 125.5, 125.2, 123.3, 42.7, 27.7, -4.5, -5.3. HRMS (ESI) *m/z* 345.1676 [$(M + H)^+$; calcd for $C_{23}H_{25}OSi$, 345.1675].

3.10.5. Rearrangement of 6-phenyl-5,6-dihydropyran

The 6-phenyl-5,6-dihydropyran (**3.5**) was synthesized following three steps from benzaldehyde (see the scheme below):



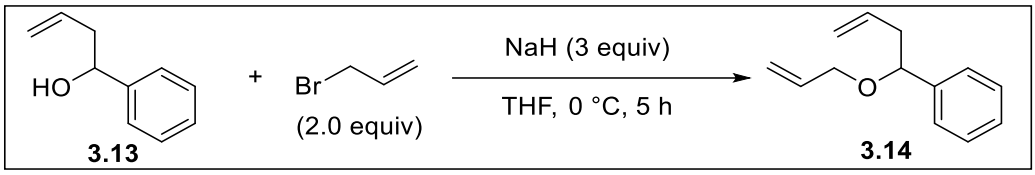
Preparation of 1-phenylbut-3-en-1-ol (3.13)



Following a reported procedure[61] with a slight modification, commercial zinc dust (3.92 g, 60 mmol, 2.0 equiv.) was weighed into a dry 250 mL round bottomed flask equipped with a magnetic stir bar. The flask was capped with a rubber septum and purged with nitrogen for approximately 5 minutes. Freshly distilled THF (80 mL) was added into the flask followed by 3.9 mL of allyl bromide (5.45g, 45 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 30 minutes after which 2.9 mL of benzaldehyde (3.18 g, 30 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred at room temperature for 1 h then quenched by addition of 10 mL of saturated aqueous ammonium chloride solution. The mixture was diluted with 20 mL of diethyl ether and 10 mL of water, respectively. The layers were separated, and the aqueous layer was extracted with diethyl ether (20 mL x 3). The combined organic layers were washed with 10 mL saturated aqueous ammonium chloride, (10 mL x 2) water and 10 mL of saturated aqueous sodium chloride solution then dried over anhydrous magnesium sulfate. Filtration and concentration under reduced pressure afforded homoallylic alcohol **3.13** as a yellow oil (4.17 g, 28.2 mmol, 94% crude yield) which was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 4.4 Hz, 4H), 7.29 (ddd, *J* = 8.8, 4.9, 3.9 Hz, 1H), 5.88 – 5.76 (m, 1H), 5.21 – 5.11 (m, 2H), 4.73 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.57 – 2.46 (m, 2H), 2.27 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 134.4, 128.3, 127.5, 125.8, 118.3, 73.3, 43.7. IR (neat) 3342, 3054, 1638, 1507, 1270, 1124, 1042, 817, 744 cm^{-1}. Spectroscopic data were

in agreement with those reported in literature.[62]

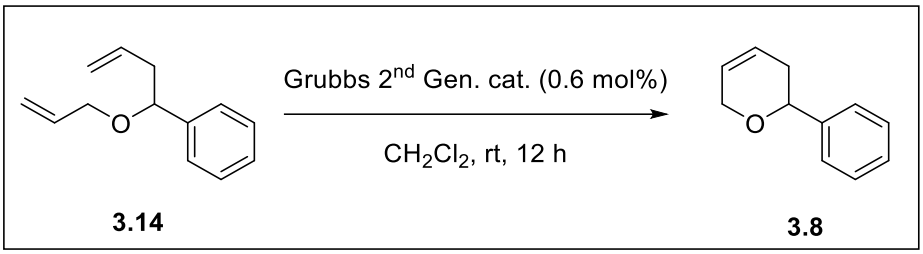
Preparation of (1-(allyloxy)but-3-en-1-yl)benzene (3.14)



To a dry 250 mL round bottomed flask fitted with a magnetic stir bar was weighed 1.73 g of sodium hydride (60% w/w suspension in mineral oil, 75 mmol, 3.0 equiv). The flask was sealed with a rubber septum and purged with nitrogen. Freshly distilled THF (40 mL) was then added to the flask via syringe. This was followed by addition of 4.3 mL of allyl bromide (6.05 g, 50 mmol, 2.0 equiv). The mixture was cooled to 0 °C using ice bath. To the cold suspension, 3.71 g of homoallylic **3.13** (25 mmol, 1.0 equiv) was added in a dropwise manner. After complete addition, the resulting mixtrure was allowed to warm up slowly to room temperature while stirring. The reaction was quenched after 5 hours by addition of 10 mL of saturated ammonium chloride solution. This was followed by addition of 20 mL of diethyl ether and 10 mL of water. The layers were separated, and the aqueous layer was extracted with diethyl ether (20 mL x 3). The combined organic layers were washed with 10 mL saturated ammonium chloride, (10 mL x 2) water and 10 mL of saturated sodium chloride solution then dried over anhydrous magnesium sulfate. Filtration and concentration under reduced pressure followed by a flash column chromatography purification (40% CH_2Cl_2 in hexanes) afforded 4.12 g, 22 mmol (88% isolated yield) of **3.14**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.34 – 7.27 (m, 3H), 5.91 (dddd, *J* = 17.3, 10.4, 6.0, 5.1 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.26 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.17 (dq, *J* = 10.4, 1.4 Hz, 1H), 5.10 – 5.00 (m, 2H), 4.35 (dd, *J* = 7.5, 5.9 Hz, 1H), 3.94 (ddt, *J* = 12.8, 5.1, 1.6 Hz, 1H), 3.79 (ddt, *J* = 12.8, 6.1, 1.4 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.44 (dddt, *J* = 14.3, 7.2, 5.9, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9, 134.9, 134.8, 128.3, 127.5, 126.7, 116.8, 116.7, 81.1,

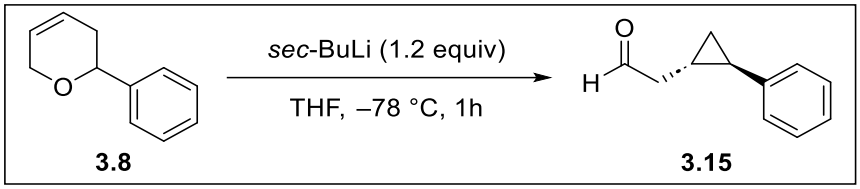
69.4, 42.6. Spectroscopic data were in agreement with those reported in literature.[63]

Preparation of 2-phenyl-3,6-dihydro-*2H*-pyran (3.8)



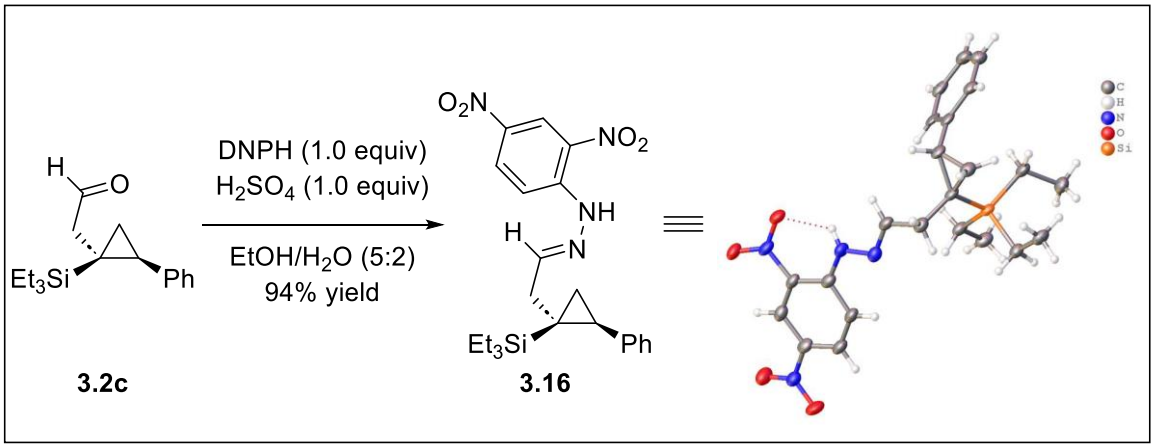
A dry 250 mL round bottomed flask fitted with a magnetic stir bar was sealed with a rubber septum and cooled under nitrogen. 136 mg (0.16 mmol, 0.008 equiv) of Grubbs catalyst 2nd generation was weighed into a vial and dissolved in dry dichloromethane (5 mL). The solution was transferred by means of syringe into the flask and additional 125 mL of dry dichloromethane added. This was followed by addition of 3.8 g (20 mmol, 1.0 equiv) of **3.14** in 20 mL dry dichloromethane. The resulting mixture was stirred under nitrogen for 12 hours after which the dichloromethane was removed by rotorvap under reduced pressure. The crude material was purified by flash column chromatography (40% CH_2Cl_2 in hexanes) to give 3.17 g, 19.8 mmol (99% isolated yield) of dihydropyran **3.8**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 4H), 7.33 – 7.27 (m, 1H), 5.95 (ddt, *J* = 9.9, 5.4, 2.2 Hz, 1H), 5.84 (dtt, *J* = 10.9, 3.1, 1.5 Hz, 1H), 4.58 (dd, *J* = 10.3, 3.5 Hz, 1H), 4.45 – 4.34 (m, 2H), 2.45 – 2.34 (m, 1H), 2.33 – 2.22 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 128.3, 127.4, 126.4, 125.8, 124.4, 75.6, 66.5, 32.8. HRMS (APCI) *m/z* 160.0836 [$(M)^+$; calcd for $C_{11}H_{12}O$, 160.0888].

Preparation of 2-(2-phenylcyclopropyl)acetaldehyde (3.15) by Wittig rearrangement of 6-phenyl-5,6-dihydro-*2H*-pyran (3.8)



Following General Procedure G, dihydropyran **3.8** (321 mg, 2.0 mmol, 1 equiv) in THF (40 mL) and *sec*-butyllithium (1.4 M in pentane) (1.7 mL, 2.4 mmol, 1.2 equiv) at –78 ºC for 1 hour, followed by workup and silica gel chromatography (5% EtOAc in hexanes) afforded cyclopropane **3.15** (34.5 mg, 0.22 mmol, 11% isolated yield, *dr* = 4:1) and 161 mg, 1.0 mmol (50% of recovered starting material) **3.8**. Spectroscopic data for compound **3.15:** ^{1}H NMR (500 MHz, C_6D_6) δ 9.28 (t, *J* = 1.9 Hz, 1H), 7.11 – 7.05 (m, 2H), 7.03 – 6.97 (m, 1H), 6.91 – 6.83 (m, 2H), 1.75 (ddd, *J* = 17.1, 6.9, 2.0 Hz, 1H), 1.67 (ddd, *J* = 17.0, 7.1, 2.0 Hz, 1H), 1.27 (dt, *J* = 9.1, 4.9 Hz, 1H), 0.93 – 0.85 (m, 1H), 0.66 (dt, *J* = 8.5, 5.1 Hz, 1H), 0.34 (dt, *J* = 8.6, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 200.2, 143.1, 128.9, 126.6, 126.3, 48.3, 23.1, 16.6, 15.6. HRMS (APCI) *m/z* 161.0948 [(M + H)$^+$; calcd for $C_{11}H_{13}O$, 161.0966].

3.10.6. Derivatization of 2-(2-phenyl-1-(triethylsilyl)cyclopropyl)acetaldehyde (3.2c)



Preparation of (*E*)-1-(2,4-dinitrophenyl)-2-(2-(2-phenyl-1-(triethylsilyl)cyclopropyl) ethylidene)hydrazine (3.16)

Compound **3.16** was prepared from aldehyde **3.2c** (*dr* > 20:1) utilizing the following procedure: To a 5 mL conical vial with a vane magnetic stir bar was weighed 50 mg (0.25 mmol, 1.0 equiv) of 2,4-dinitrophenylhydrazine (DNPH). A solution of ethanol/water (5:2), 2 mL was added to the vial followed by 13.4 μL of concentrated sulfuric acid (0.25 mmol, 1.0 equiv) and the resulting mixture stirred for about 5 minutes to make a homogeneous solution. Compound **3.2c** (68.7 mg, 0.25 mmol, 1.0 equiv) in 1 mL ethanol was added dropwise to the vial and the mixture stirred for additional 10 minutes resulting in the formation of a deep orange precipitate. The mixture was filtered, and the residue rinsed with 10 mL solution of ethanol/water (5:2). The residue was dried for 12 hours under high vacuum to give 107 mg, 0.235 mmol (94% crude yield) of **3.16** as a single diastereomer. This product was recrystallized in ethanol/dichloromethane (4:1) and its crystal structure solved by X-ray crystallography and the results deposited to the Cambridge Crystallographic Data Centre and assigned **CCDC 2031553.** Spectroscopic and melting point data for compound **3.16**: mp 115.5 to 117.0 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.52 (s, 1H), 8.86 (d, *J* = 2.7 Hz, 1H), 8.37 (dd, *J* = 9.7, 2.7 Hz, 1H), 8.29 (dd, *J* = 7.2, 4.6 Hz, 1H), 7.91 (d, *J* = 9.7 Hz, 1H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 2.74 (dd, *J* = 14.8, 7.3 Hz, 1H), 2.19 (t, *J* = 7.1 Hz, 1H), 2.04 (dd, *J* = 14.7, 4.7 Hz, 1H), 1.30 (dd, *J* = 5.9, 4.5 Hz, 1H), 0.97 (dt, *J* = 8.2, 4.8 Hz, 1H), 0.73 (t, *J* = 7.9 Hz, 9H), 0.30 (dq, *J* = 15.8, 7.9 Hz, 3H), 0.14 (dq, *J* = 15.7, 7.9 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.6, 144.8, 139.6, 136.6, 129.9, 129.6, 128.8, 127.8, 126.3, 123.2, 116.3, 42.2, 27.5, 15.3, 12.2, 7.5, 2.8. IR (neat) 3291, 3107, 2951, 2872, 1614, 1588, 1519, 1496, 1426, 1324, 1308, 1281, 1222, 1138, 1071 cm^{-1}. HRMS (ESI) *m/z* 455.2118 [(M + H)$^{+}$; calcd for $C_{23}H_{31}N_4O_4Si$, 455.2115].

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APPENDIX

Crystallographical information of compound 3.16

Crystal structure, Chirality not determined, but Regio-stereo chemistry is observed.

Crystal data and experimental

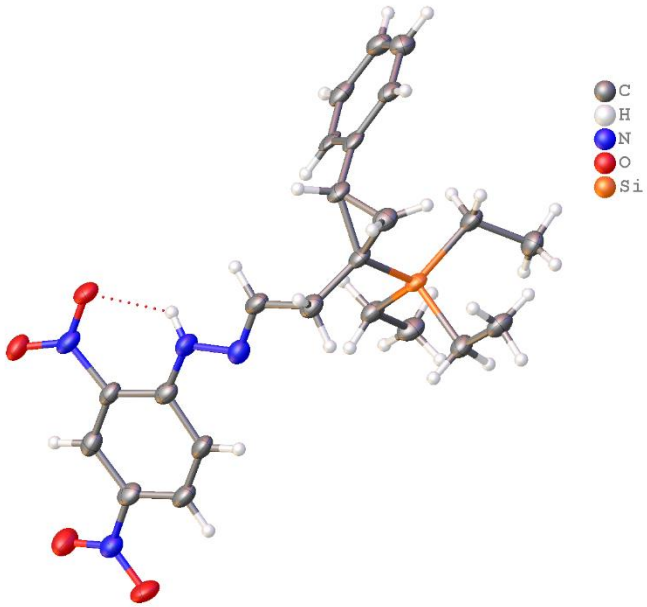


Figure 3.2: Crystal structure of compound **3.16**

Experimental. Single yellow needle crystals of **3.16** used as received. A suitable crystal with dimensions 0.21 × 0.05 × 0.03 mm^3 was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 100.00(10) K during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov *et al.*, 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal data. $C_{23}H_{30}N_4O_4Si$, M_r = 454.60, monoclinic, $P2_1/c$ (No. 14), a = 18.5519(12) Å, b = 7.2993(5) Å, c = 18.8084(12) Å, b = 114.662(8)°, a = g = 90°, V = 2314.6(3) Å^3, T = 100.00(10) K, Z = 4, Z' = 1, m(Cu K$_a$) = 1.204, 14074 reflections measured, 4597 unique (R_{int} = 0.0666) which were used in all calculations. The final wR_2 was 0.2855 (all data) and R_1 was 0.1072 (I≥2 s(I)).

Table 3.2: Crystal data

Compound	**3.16**
Formula	$C_{23}H_{30}N_4O_4Si$
CCDC	2031553
$D_{calc.}$/ g cm^{-3}	1.305
m/mm^{-1}	1.204
Formula Weight	454.60
Colour	yellow
Shape	needle
Size/mm^3	0.21×0.05×0.03
T/K	100.00(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	18.5519(12)
b/Å	7.2993(5)
c/Å	18.8084(12)
a/°	90
b/°	114.662(8)
g/°	90
V/Å^3	2314.6(3)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_a$
Q_{min}/°	4.725
Q_{max}/°	77.629
Measured Refl's.	14074
Indep't Refl's	4597
Refl's I≥2 s(I)	3836
R_{int}	0.0666
Parameters	296
Restraints	0
Largest Peak	0.802
Deepest Hole	-0.396
GooF	1.185
wR_2 (all data)	0.2855
wR_2	0.2802
R_1 (all data)	0.1193
R_1	0.1072

Structure quality indicators

Reflections:	d min (Cu) 0.79	I/σ(I) 15.6	Rint 6.66%	complete 99% (IUCr) 99%
Refinement:	Shift 0.000	Max Peak 0.8	Min Peak -0.4	GooF 1.185

Figure 3.3: Structure quality indicators

A yellow needle-shaped crystal with dimensions 0.21×0.05×0.03 mm^3 was mounted on a nylon loop with paratone oil. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 100.00(10) K.

Data were measured using *w* scans of 1.0° per frame for 4.3/17.4 s using Cu K_a radiation (micro-focus sealed X-ray tube, 50 kV, 1 mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.84a, 2020). The actually achieved resolution was Q = 77.629.

Cell parameters were retrieved using the CrysAlisPro (Rigaku, V1.171.40.84a, 2020) software and refined using CrysAlisPro (Rigaku, V1.171.40.84a, 2020) on 4376 reflections, 31 % of the observed reflections. Data reduction was performed using the CrysAlisPro (Rigaku, V1.171.40.84a, 2020) software which corrects for Lorentz polarization. The final completeness is 98.70 out to 77.629 in Q CrysAlisPro 1.171.40.84a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

The structure was solved in the space group $P2_1/c$ (# 14) by using dual methods using the ShelXT (Sheldrick, 2015) structure solution program. The structure was refined by Least Squares using version 2018/2 of XL (Sheldrick, 2008) incorporated in Olex2 (Dolomanov *et al.*, 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the hydrogen atom on the non-carbon atom(s) which were found by difference Fourier methods and refined isotropically when data permits.

CCDC 2031553 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Model has Chirality at C1 (Centro SPGR) R Verify. Model has Chirality at C2 (Centro SPGR) S Verify. In this centrosymmetric space group this means both, R,S and S,R confirmations are observed in the crystal studied.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

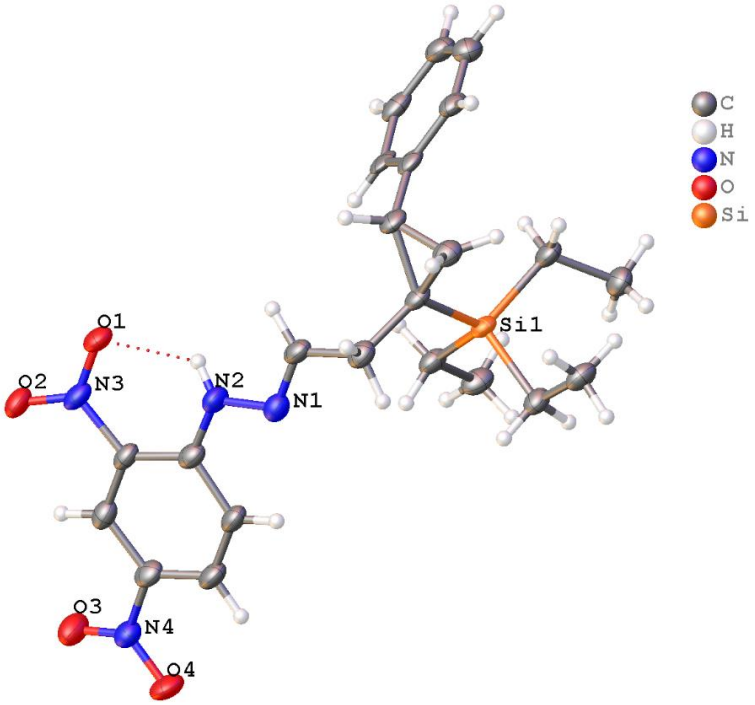


Figure 3.4: Crystal structure of **3.16** showing hydrogen bonding

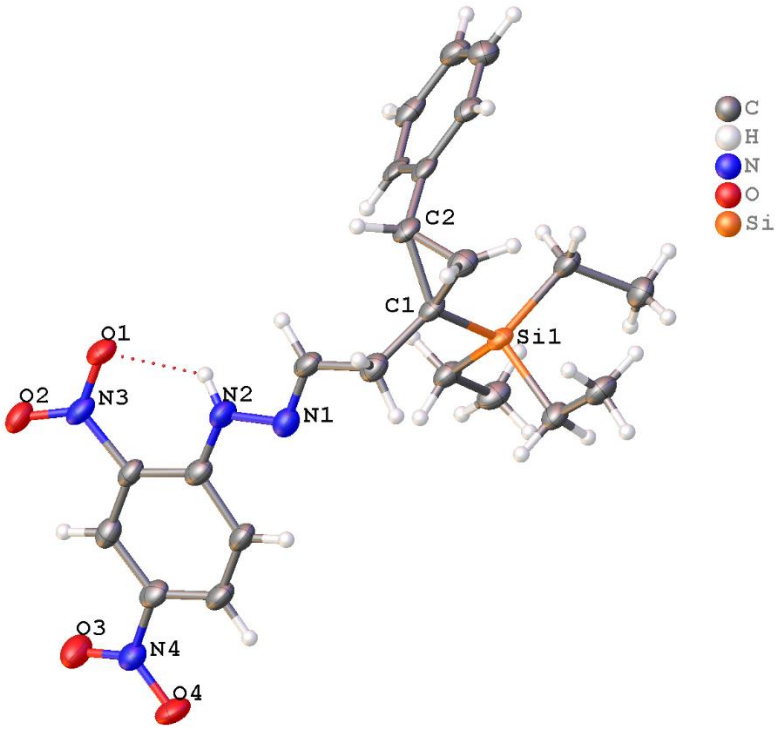


Figure 3.5: Model has Chirality at C1 (Centro SPGR) R Verify. Model has Chirality at C2 (Centro SPGR) S Verify. In this centrosymmetric space group this means both, R,S and S,R confirmations are observed in the crystal studied

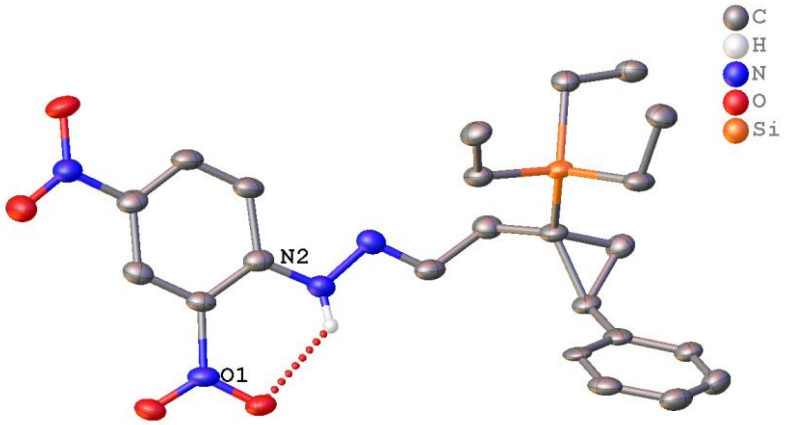


Figure 3.6: The following hydrogen bonding interactions with a maximum D-D distance of 2.9 Å and a minimum angle of 120 ˚ are present in **3.16**: N2–O1: 2.634 Å

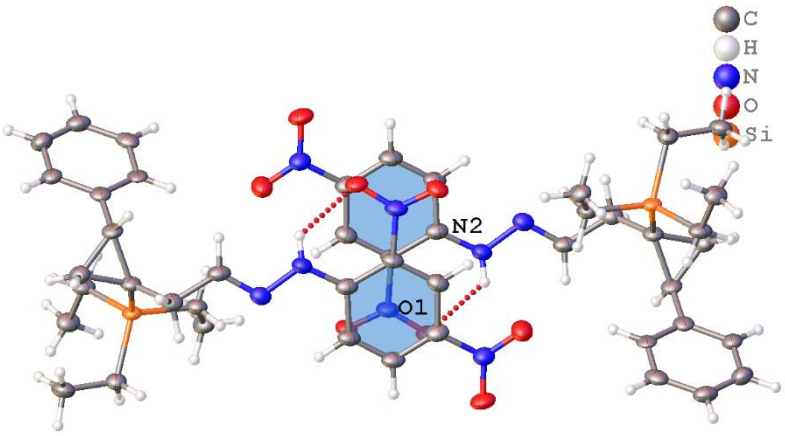


Figure 3.7: The *p-p* interactions of **3.16**. plane 2 *to* #2@3_676 (1-X,2-Y,1-Z): The angle between these two planes is 0.000 ˚, the centroid-centroid distance is 3.817 Å and the shift distance is 1.962 Å

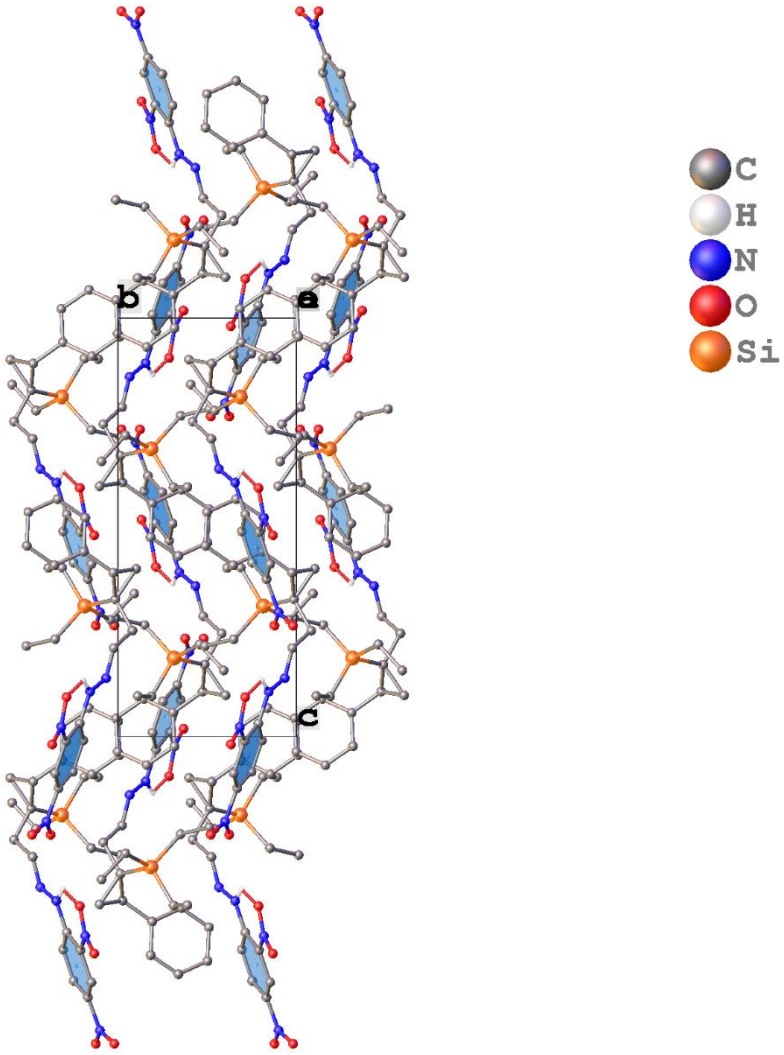


Figure 3.8: Packing diagram of **3.16**

Data Plots: Diffraction data

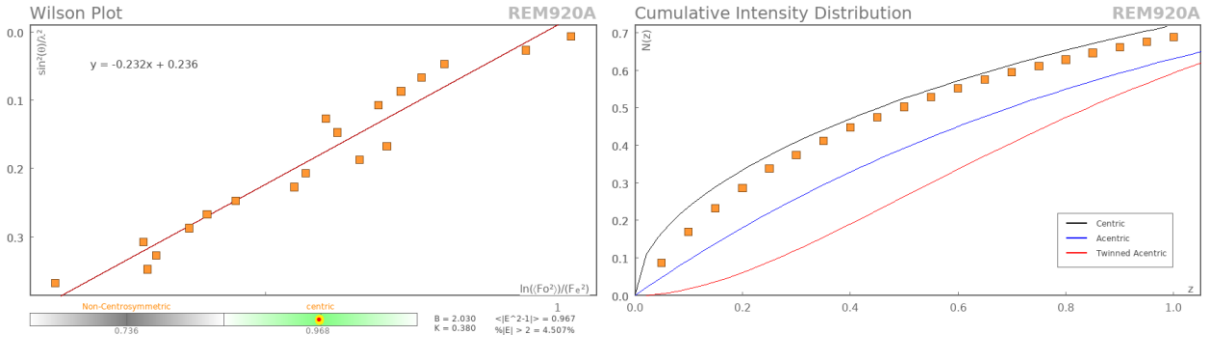
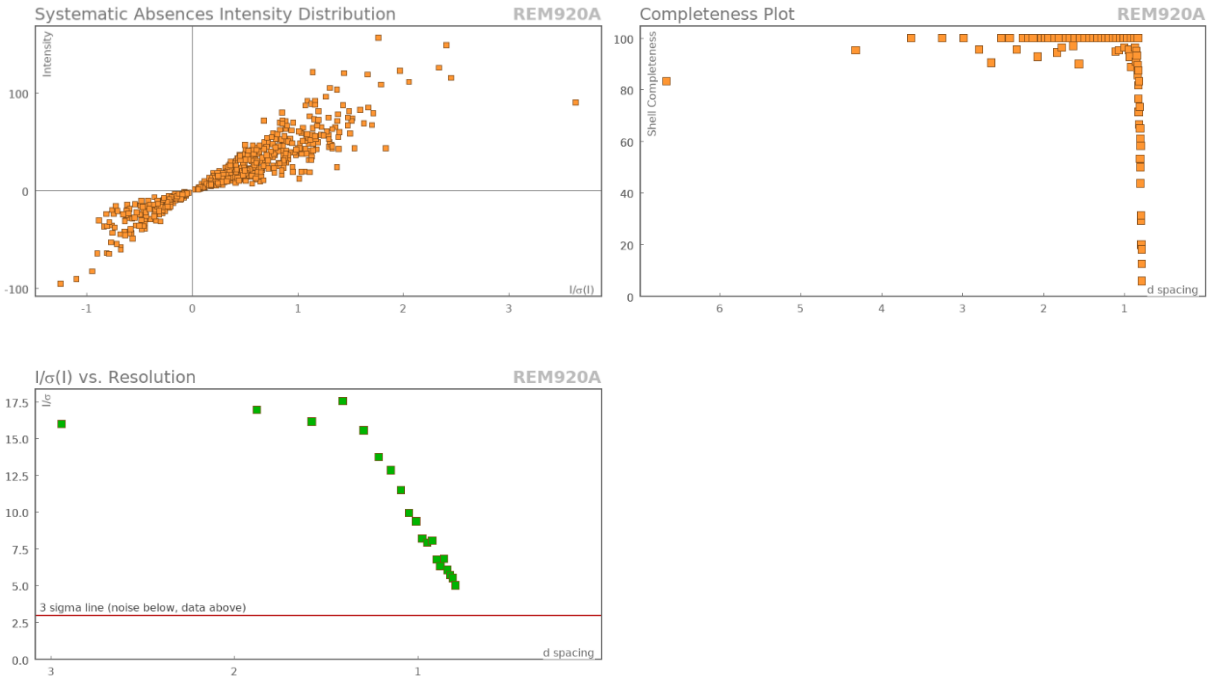


Figure 3.9: Data plots: Diffraction data

Figure 3.9 (cont'd)



Data Plots: Refinement and data

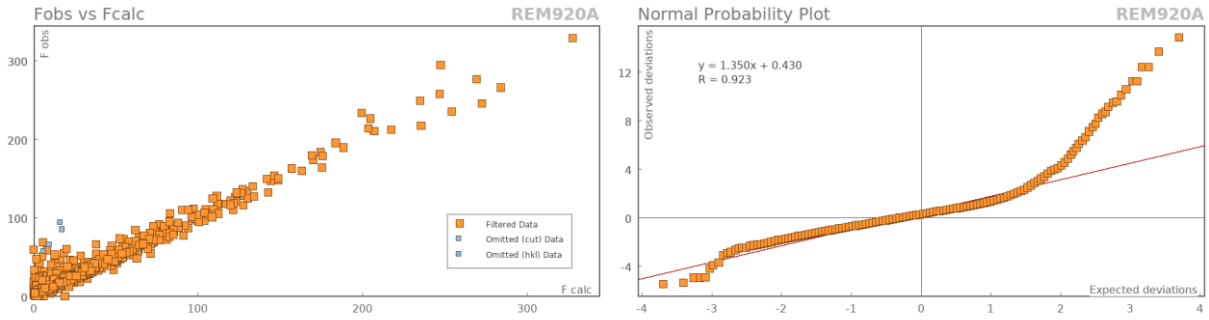


Figure 3.10: Data plots: Refinement and data

Table 3.3: Reflection statistics

Total reflections (after filtering)	14898	Unique reflections	4597
Completeness	0.933	Mean I/*s*	10.59
hkl_{max} collected	(22, 8, 23)	hkl_{min} collected	(-23, -9, -16)
hkl_{max} used	(21, 9, 23)	hkl_{min} used	(-23, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	17.09	d_{min} used	0.79
Friedel pairs	525	Friedel pairs merged	1
Inconsistent equivalents	29	R_{int}	0.0666
R_{sigma}	0.0642	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	12
Multiplicity	(4557, 2079, 970, 341, 210, 109, 27, 2)	Maximum multiplicity	13
Removed systematic absences	812	Filtered off (Shel/OMIT)	0

Table 3.4: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3.16**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}

Atom	x	y	z	U_{eq}
Si1	8542.1(8)	6859(2)	8121.6(8)	24.8(4)
O1	4210(2)	7872(7)	5945(2)	36.5(10)
O2	3309(2)	8675(7)	4812(2)	37.0(10)
O3	3938(3)	9804(8)	2654(3)	48.3(13)
O4	5030(3)	8764(8)	2654(3)	46.1(12)
N1	6295(3)	5659(7)	6397(3)	31.3(11)
N2	5580(3)	6558(8)	6070(3)	31.3(11)
N3	3985(3)	8173(7)	5231(3)	31.6(11)
N4	4574(3)	8999(8)	2970(3)	34.0(12)
C1	7861(3)	5142(8)	8281(3)	27.2(12)
C2	7564(3)	5259(9)	8922(3)	29.8(13)
C3	8222(3)	3977(9)	9013(3)	31.9(13)
C4	7281(3)	4185(9)	7533(3)	31.7(13)
C5	6530(3)	5230(9)	7122(3)	30.8(13)
C6	5309(3)	7133(8)	5315(3)	29.8(12)
C7	4551(3)	7906(8)	4893(3)	27.8(12)
C8	4302(3)	8517(9)	4124(4)	31.2(13)
C9	4816(3)	8320(9)	3766(3)	32.2(13)
C10	5557(3)	7522(9)	4157(4)	33.9(13)
C11	5800(3)	6939(9)	4907(3)	32.4(13)
C12	7683(3)	6914(9)	9425(3)	29.6(12)
C13	7321(3)	8549(9)	9101(3)	29.3(13)
C14	7407(3)	10100(9)	9561(4)	35.0(14)
C15	7883(4)	10015(10)	10365(4)	36.3(14)
C16	8242(4)	8385(10)	10681(4)	36.0(14)
C17	8146(3)	6835(9)	10229(3)	30.7(13)
C18	7928(3)	8512(9)	7331(3)	30.3(12)
C19	8372(4)	10119(9)	7168(4)	35.0(14)
C20	9204(3)	5423(9)	7794(3)	31.0(13)
C21	9739(4)	4081(9)	8418(4)	34.7(14)
C22	9201(3)	8121(9)	9039(4)	33.2(13)
C23	9973(3)	8892(10)	9031(4)	36.7(14)

Table 3.5: Anisotropic Displacement Parameters ($\times 10^4$) for **3.16**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	24.6(7)	30.9(8)	26.2(7)	-0.4(6)	17.9(6)	-0.6(6)
O1	32(2)	53(3)	35(2)	-1(2)	23.3(18)	0(2)
O2	26(2)	51(3)	42(2)	4(2)	21.0(18)	4.1(19)
O3	34(2)	75(4)	40(2)	11(2)	20(2)	10(2)
O4	44(2)	69(3)	39(2)	0(2)	31(2)	2(2)
N1	26(2)	35(3)	35(3)	-3(2)	16(2)	-1(2)
N2	25(2)	40(3)	33(3)	0(2)	16(2)	5(2)
N3	29(2)	36(3)	40(3)	-1(2)	25(2)	-1(2)
N4	29(2)	45(3)	33(3)	-1(2)	18(2)	-3(2)
C1	25(3)	33(3)	31(3)	1(2)	20(2)	-1(2)
C2	28(3)	40(3)	30(3)	2(2)	21(2)	-2(2)
C3	34(3)	36(3)	32(3)	4(3)	20(2)	0(3)
C4	29(3)	36(3)	36(3)	-1(3)	20(2)	-4(3)
C5	29(3)	37(3)	35(3)	-7(3)	22(2)	-6(2)
C6	29(3)	33(3)	35(3)	-5(2)	21(2)	-6(2)
C7	24(3)	30(3)	36(3)	-3(2)	20(2)	-2(2)
C8	25(3)	33(3)	40(3)	-2(3)	18(2)	-2(2)
C9	31(3)	37(3)	36(3)	-2(3)	22(2)	-8(3)
C10	29(3)	43(4)	40(3)	-5(3)	24(3)	-4(3)
C11	25(3)	41(4)	38(3)	-7(3)	20(2)	-4(3)
C12	24(3)	41(3)	33(3)	4(3)	22(2)	0(2)
C13	25(3)	45(4)	30(3)	6(3)	23(2)	3(2)
C14	32(3)	40(3)	47(3)	8(3)	30(3)	5(3)
C15	35(3)	45(4)	38(3)	-8(3)	25(3)	-5(3)
C16	36(3)	48(4)	30(3)	-3(3)	19(3)	-1(3)
C17	29(3)	43(4)	29(3)	4(3)	21(2)	1(3)
C18	29(3)	36(3)	34(3)	2(2)	21(2)	3(2)
C19	40(3)	39(4)	36(3)	6(3)	25(3)	2(3)
C20	26(3)	40(3)	33(3)	2(3)	18(2)	-1(2)
C21	34(3)	38(4)	41(3)	0(3)	25(3)	5(3)
C22	28(3)	43(4)	38(3)	-6(3)	23(2)	-5(3)
C23	28(3)	47(4)	40(3)	-5(3)	19(3)	-8(3)

Table 3.6: Bond Lengths in Å for **3.16**

Atom	Atom	Length/Å
Si1	C1	1.890(6)
Si1	C18	1.885(6)
Si1	C20	1.901(6)
Si1	C22	1.887(6)
O1	N3	1.249(6)
O2	N3	1.227(6)
O3	N4	1.227(7)
O4	N4	1.233(6)
N1	N2	1.374(7)
N1	C5	1.285(8)
N2	C6	1.361(8)
N3	C7	1.450(6)
N4	C9	1.458(8)
C1	C2	1.524(7)
C1	C3	1.516(8)
C1	C4	1.537(8)
C2	C3	1.491(8)
C2	C12	1.492(9)
C4	C5	1.490(8)
C6	C7	1.412(8)
C6	C11	1.422(7)
C7	C8	1.394(8)
C8	C9	1.385(8)
C9	C10	1.388(9)
C10	C11	1.358(9)
C12	C13	1.380(9)
C12	C17	1.396(8)
C13	C14	1.394(9)
C14	C15	1.398(9)
C15	C16	1.372(10)
C16	C17	1.381(9)
C18	C19	1.536(8)
C20	C21	1.533(8)
C22	C23	1.545(8)

Citations

CrysAlisPro (ROD), Rigaku Oxford Diffraction, Poland (?).

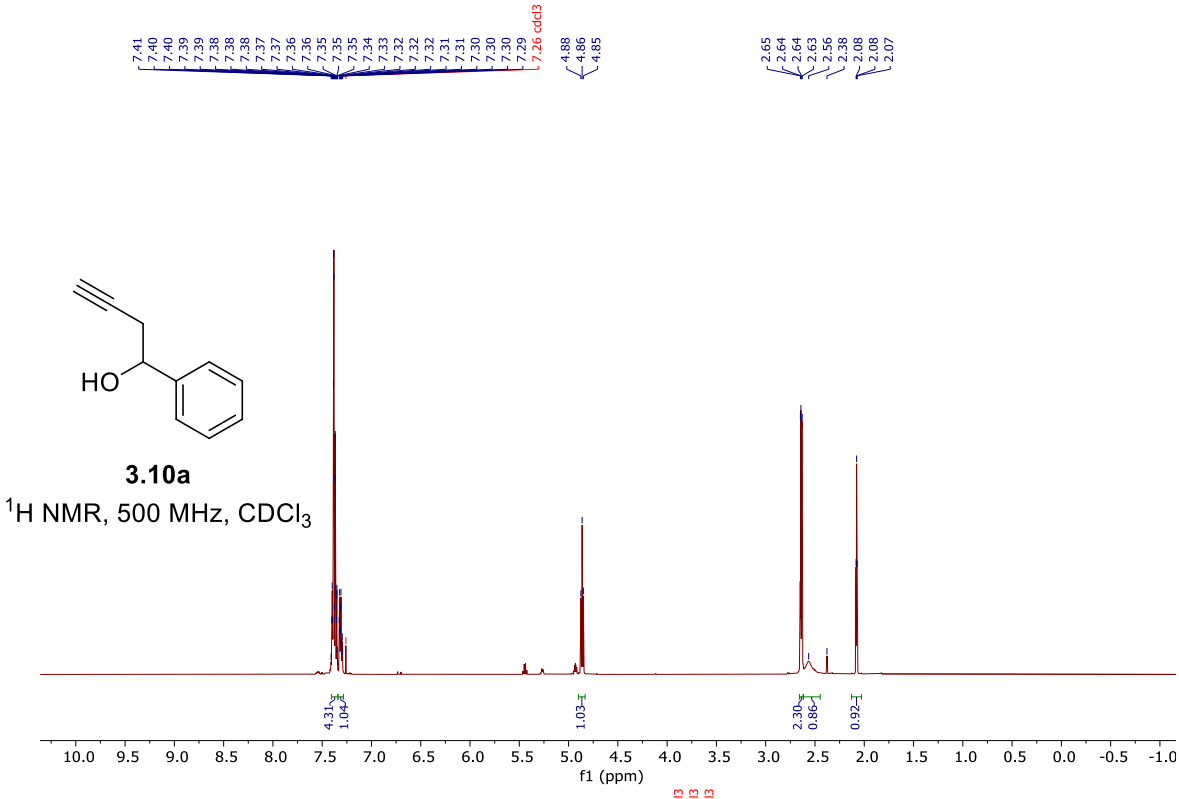
CrysAlisPro Software System, Rigaku Oxford Diffraction, (2020).

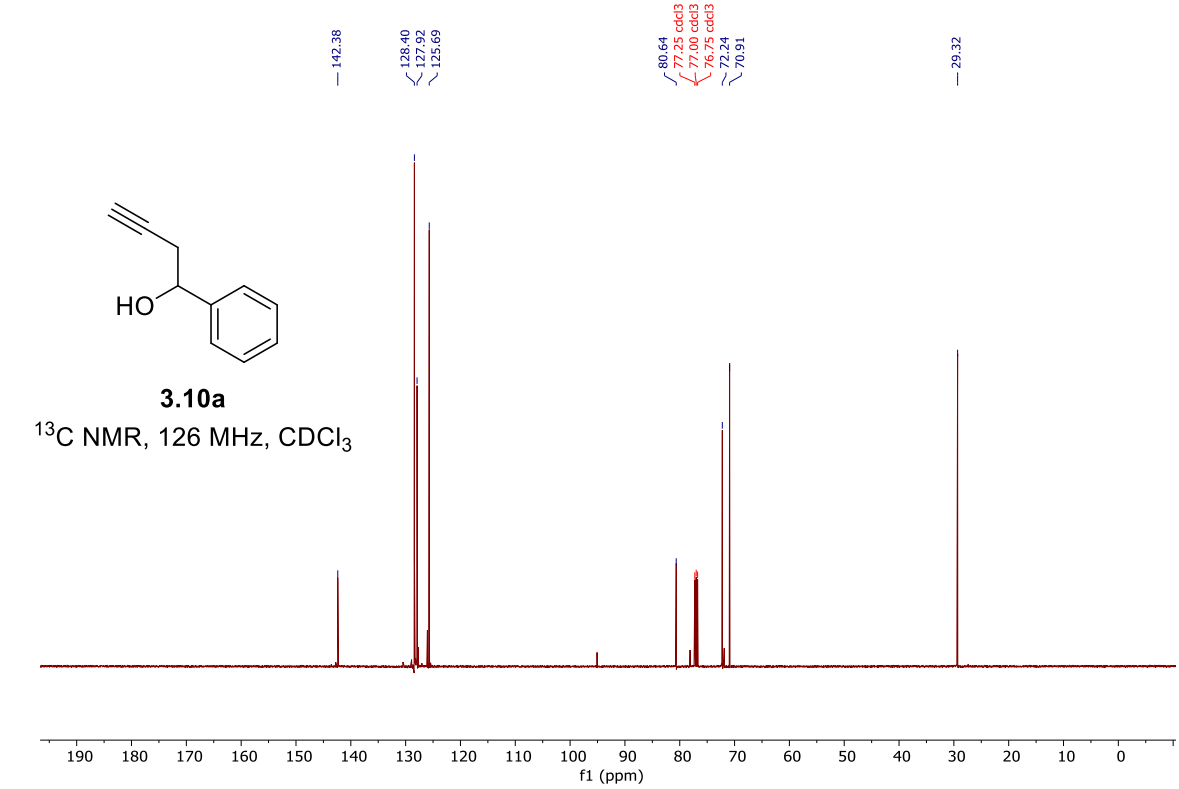
O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

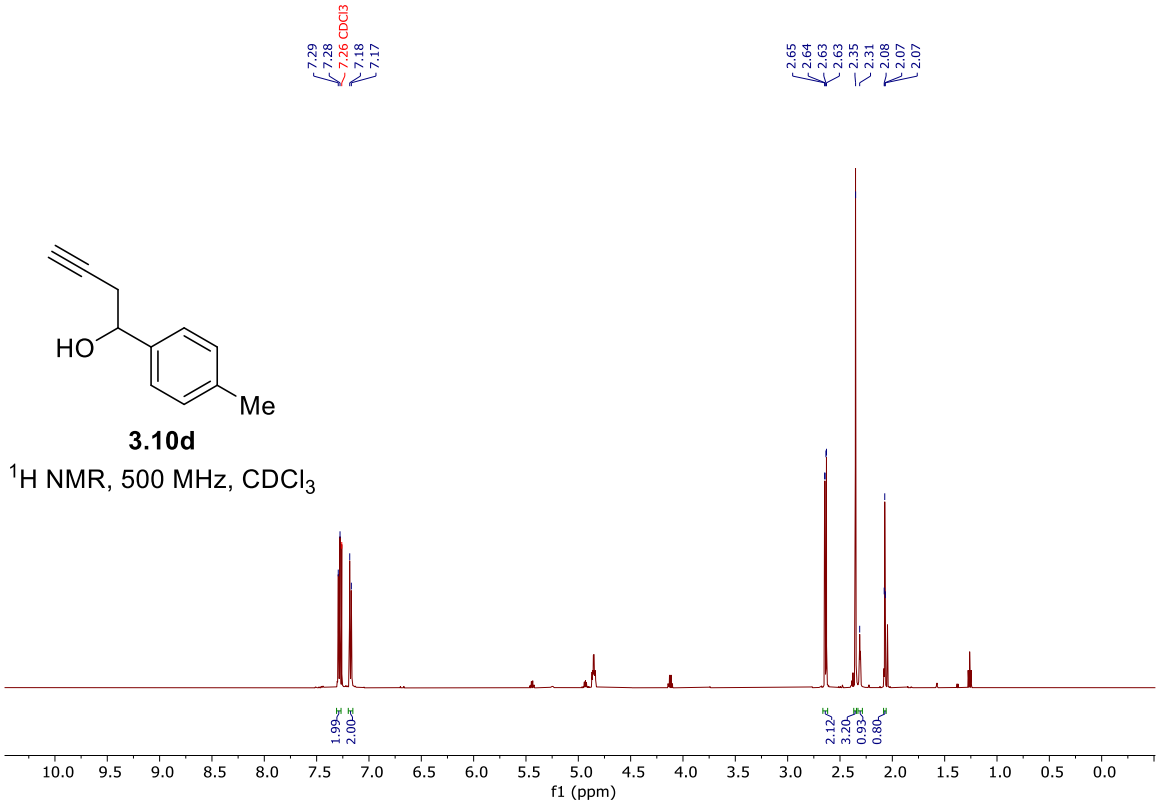
Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.

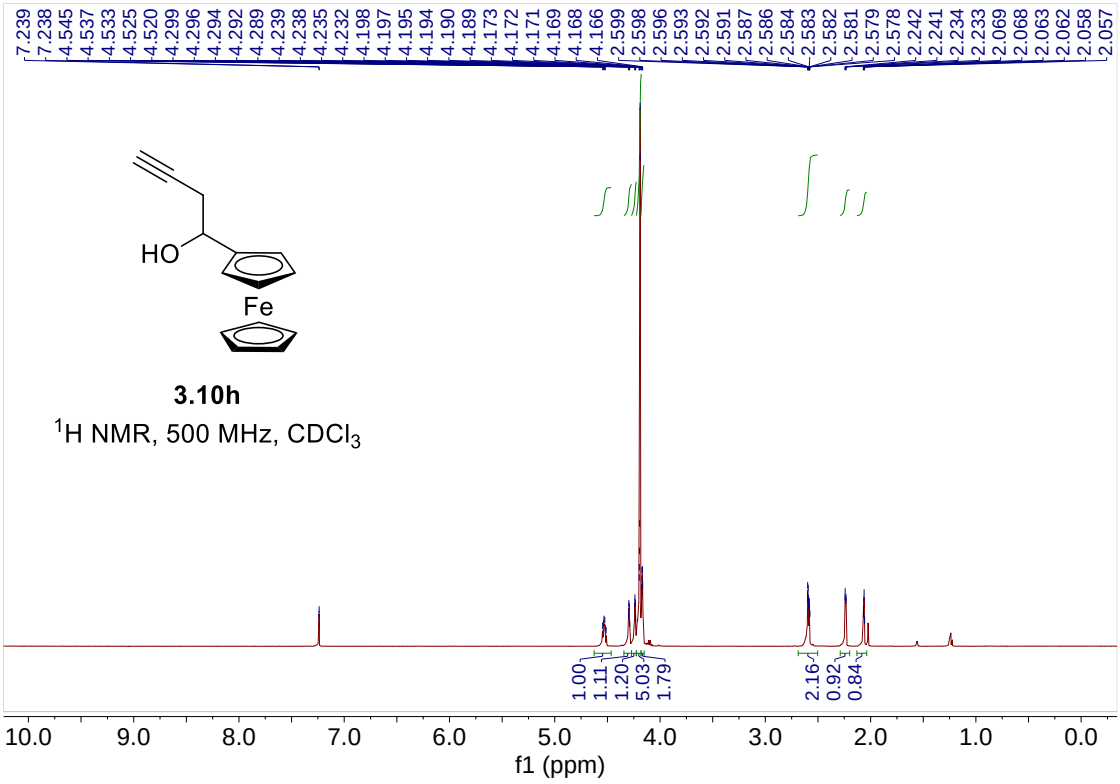
Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

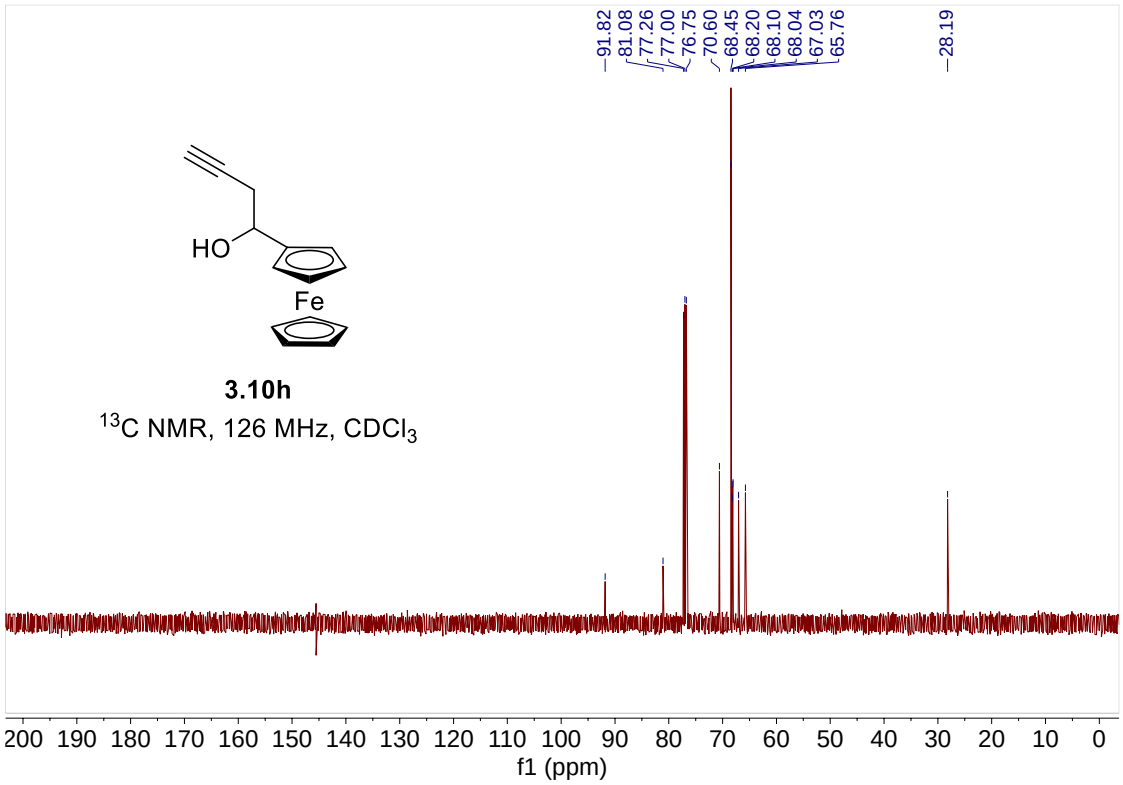
Copies of NMR spectra





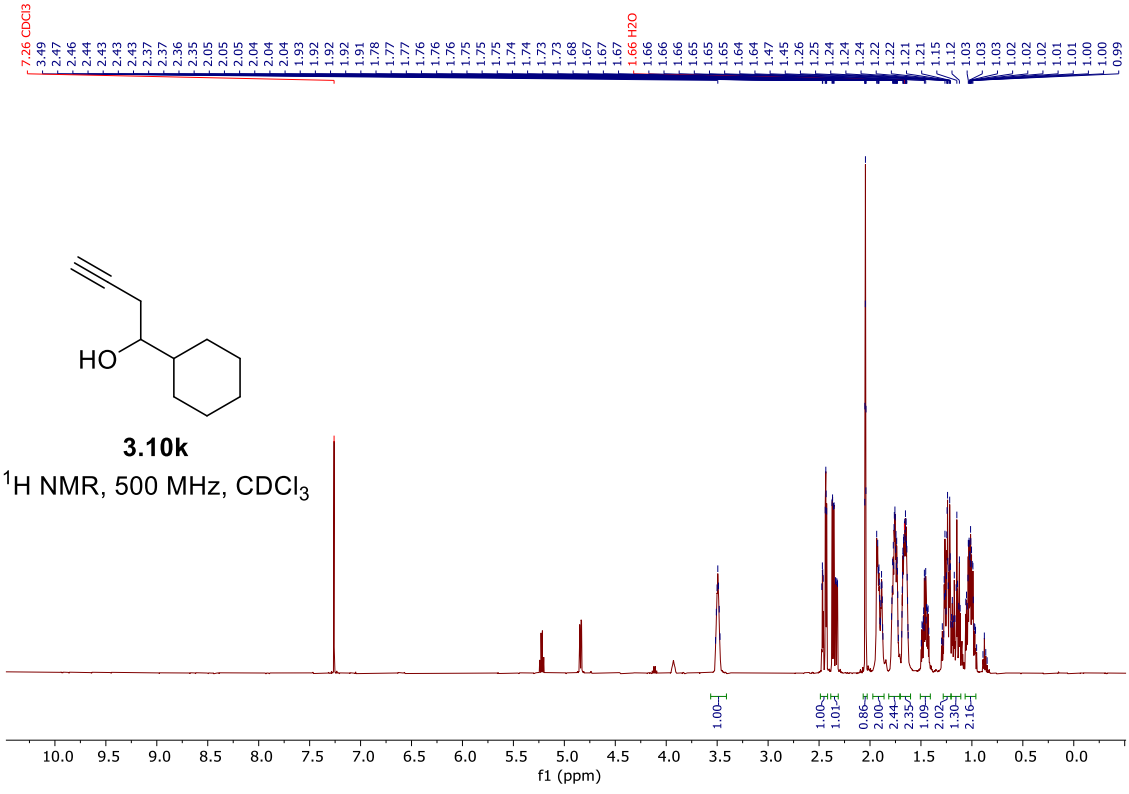

HO
Me
3.10d
1H NMR, 500 MHz, CDCl3
f1 (ppm)


HO
Fe
3.10h
1H NMR, 500 MHz, CDCl3
f1 (ppm)



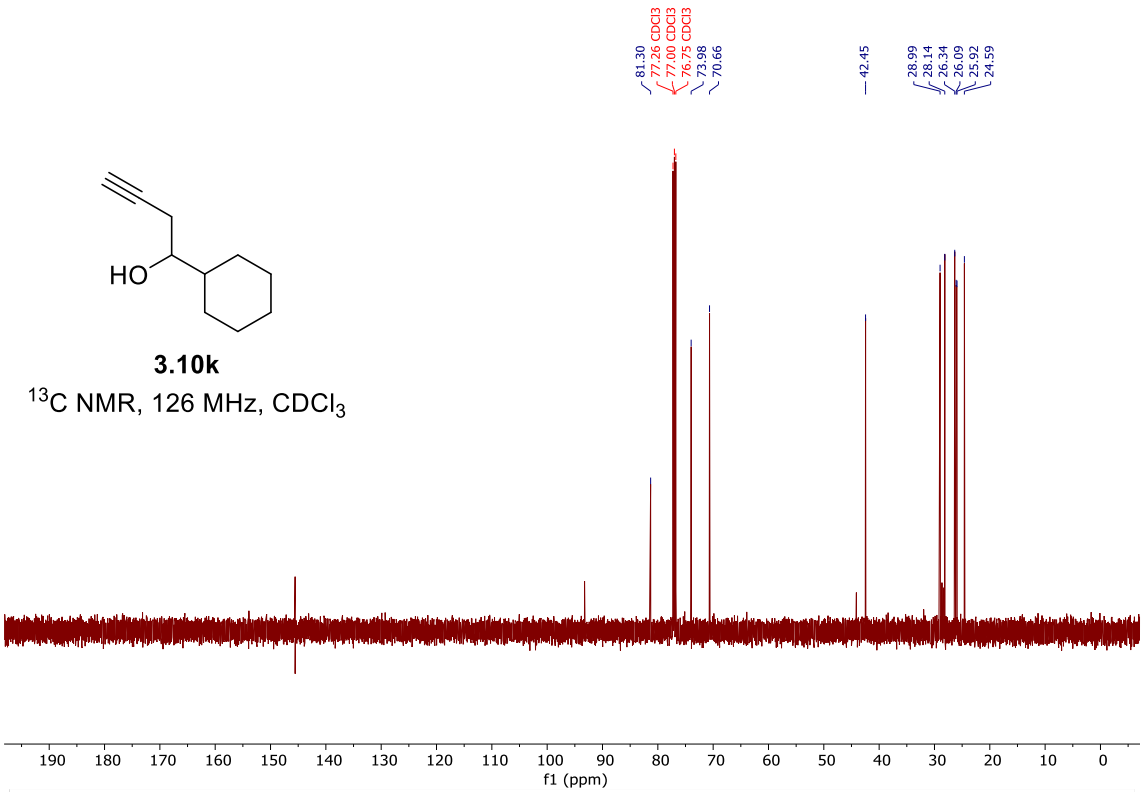
3.10h

^{13}C NMR, 126 MHz, $CDCl_3$



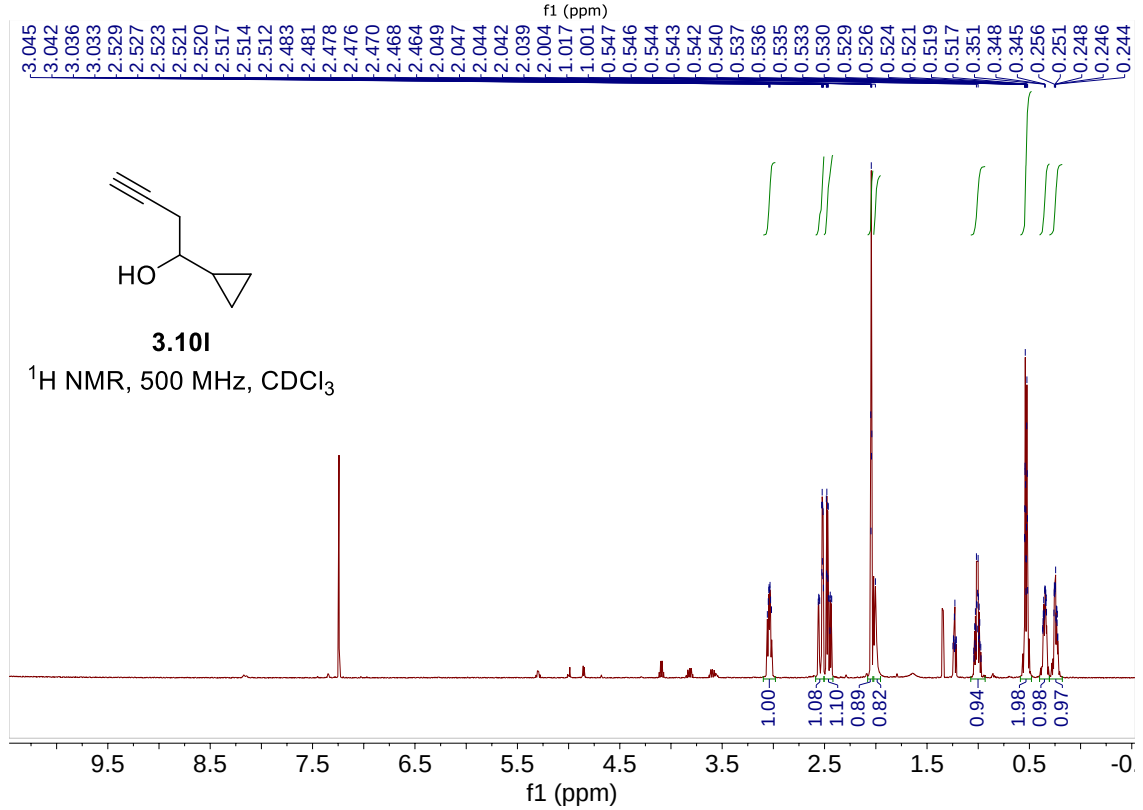
3.10k

^{1}H NMR, 500 MHz, $CDCl_3$



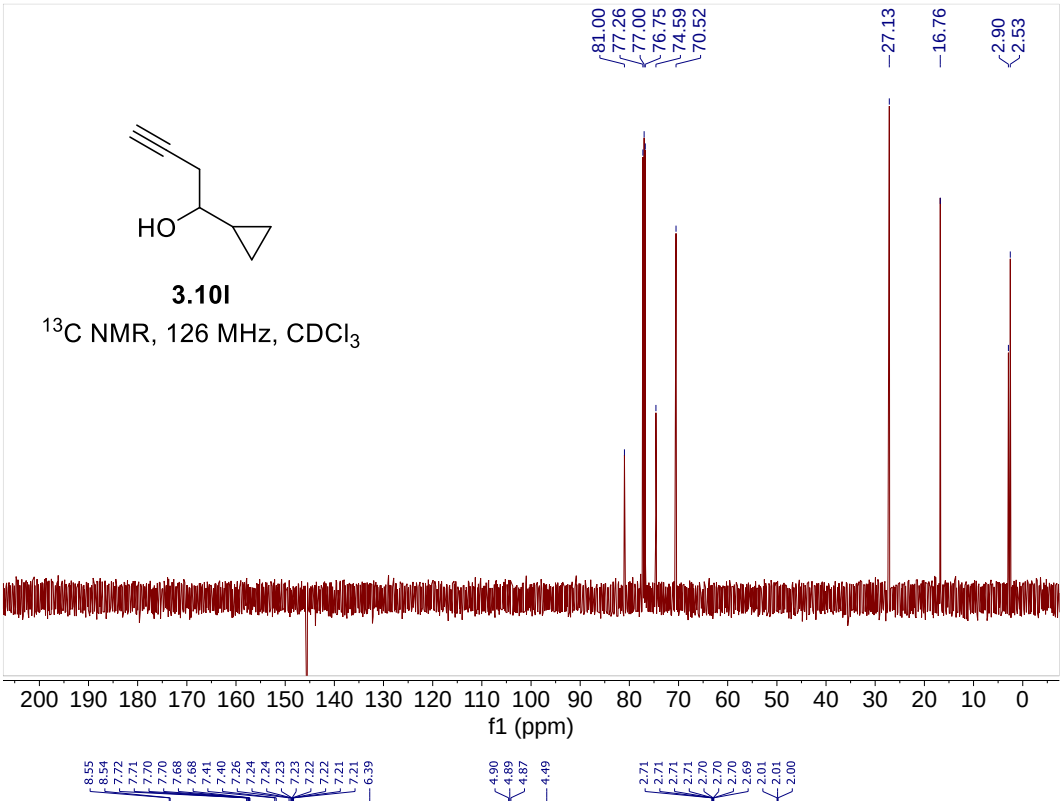
3.10k

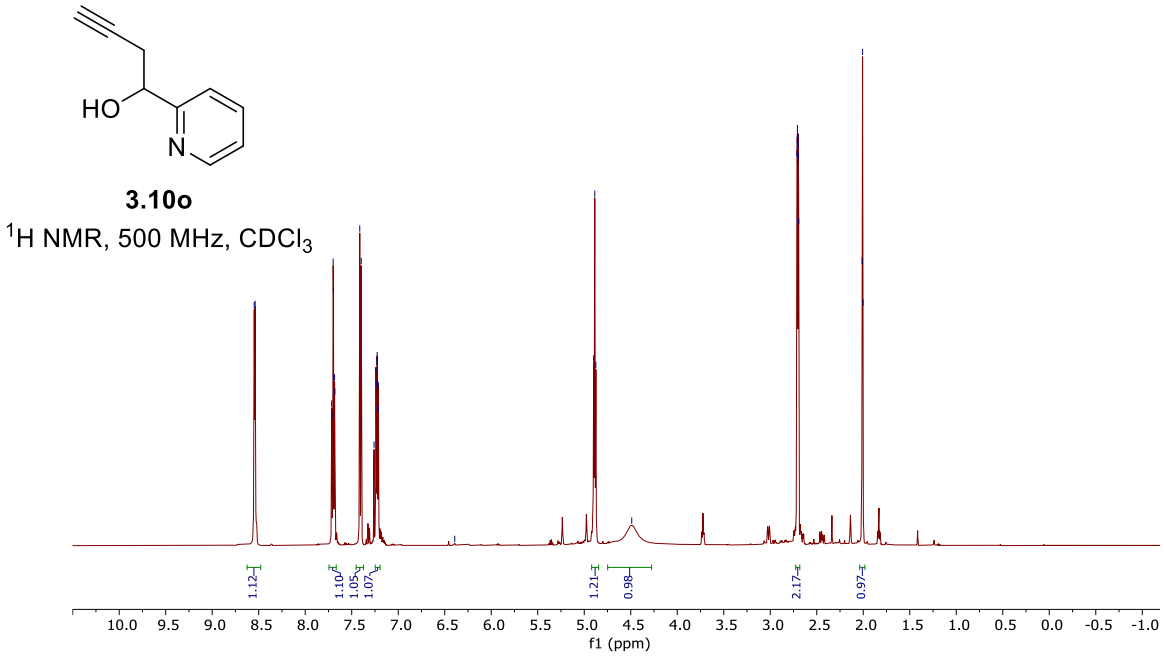
^{13}C NMR, 126 MHz, $CDCl_3$

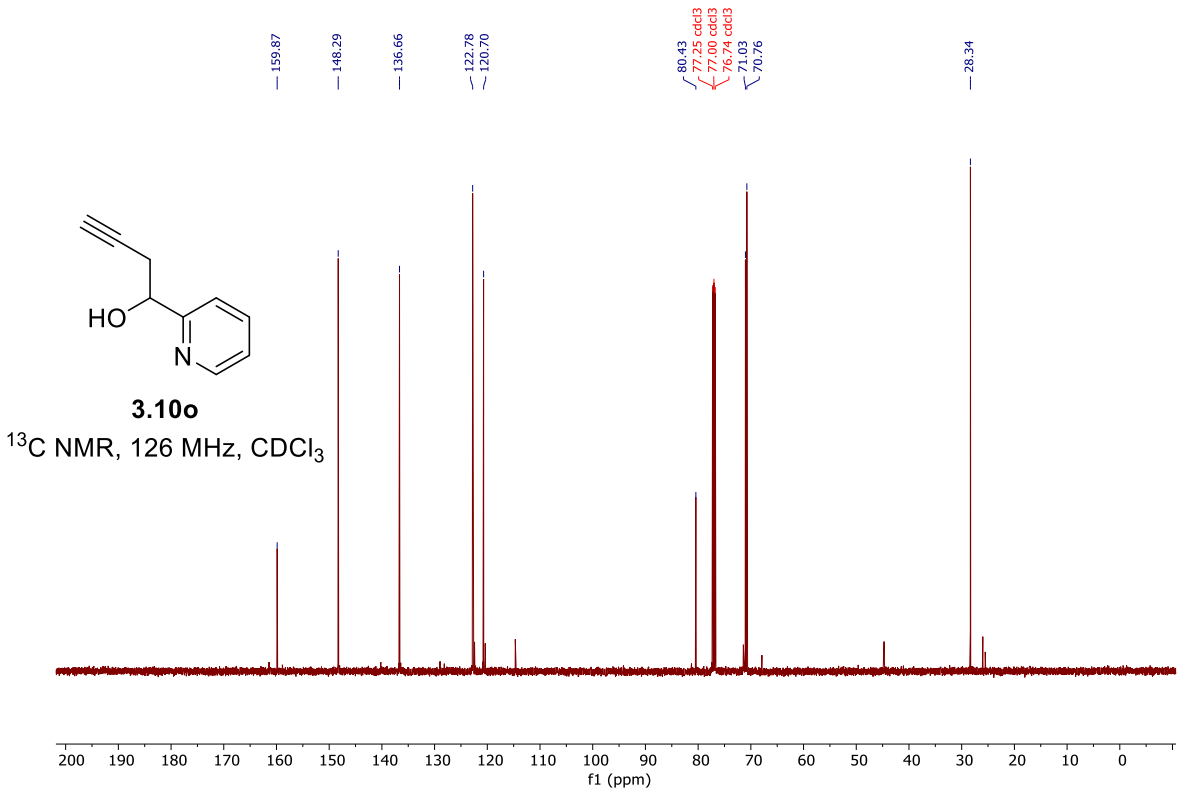


3.10l

^{1}H NMR, 500 MHz, $CDCl_3$

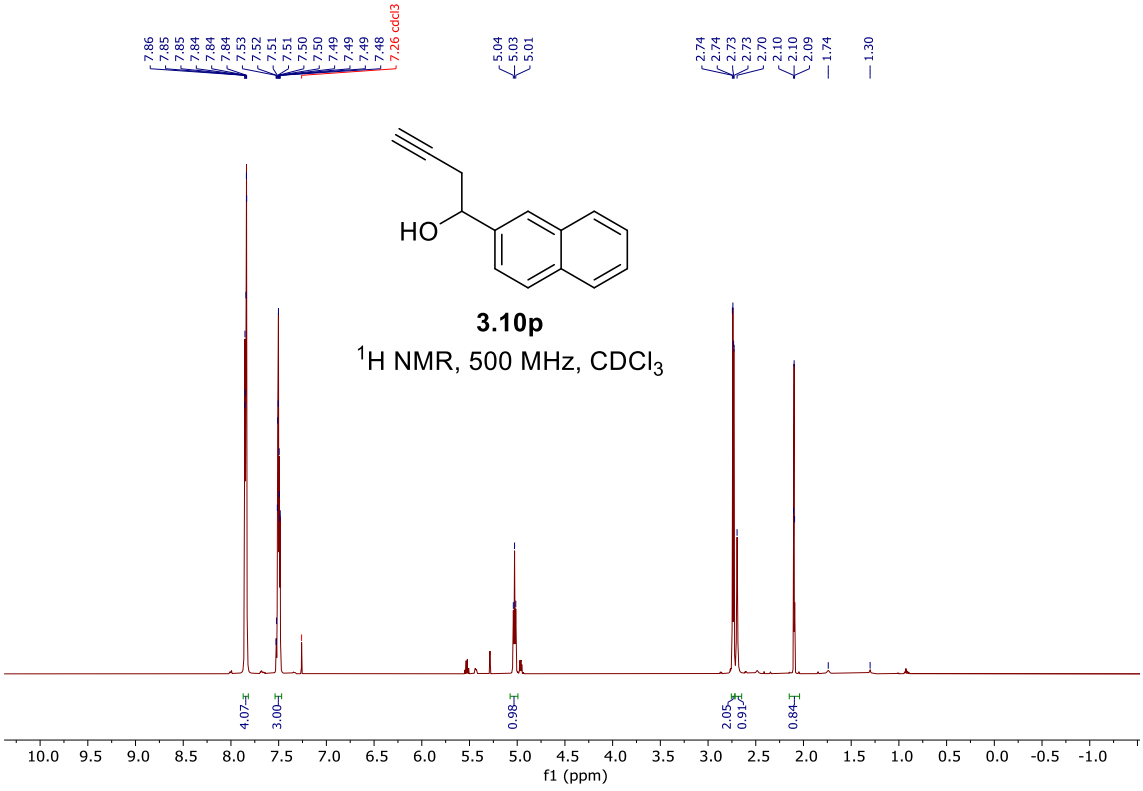

81.00
77.26
77.00
76.75
74.59
70.52
27.13
16.76
2.90
2.53
HO
3.10l
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


HO
N
3.10o
1H NMR, 500 MHz, CDCl3
1.12
1.10
1.05
1.07
1.21
0.98
2.17
0.97
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 -1.0
f1 (ppm)



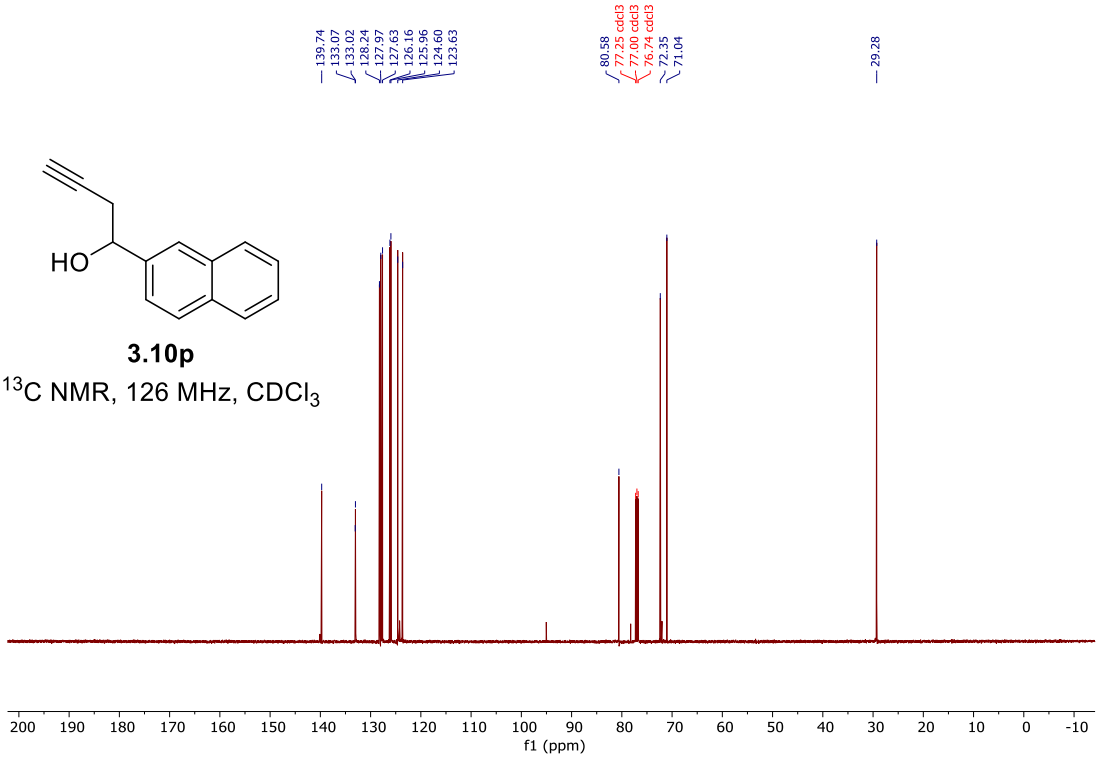
3.10o

^{13}C NMR, 126 MHz, $CDCl_3$



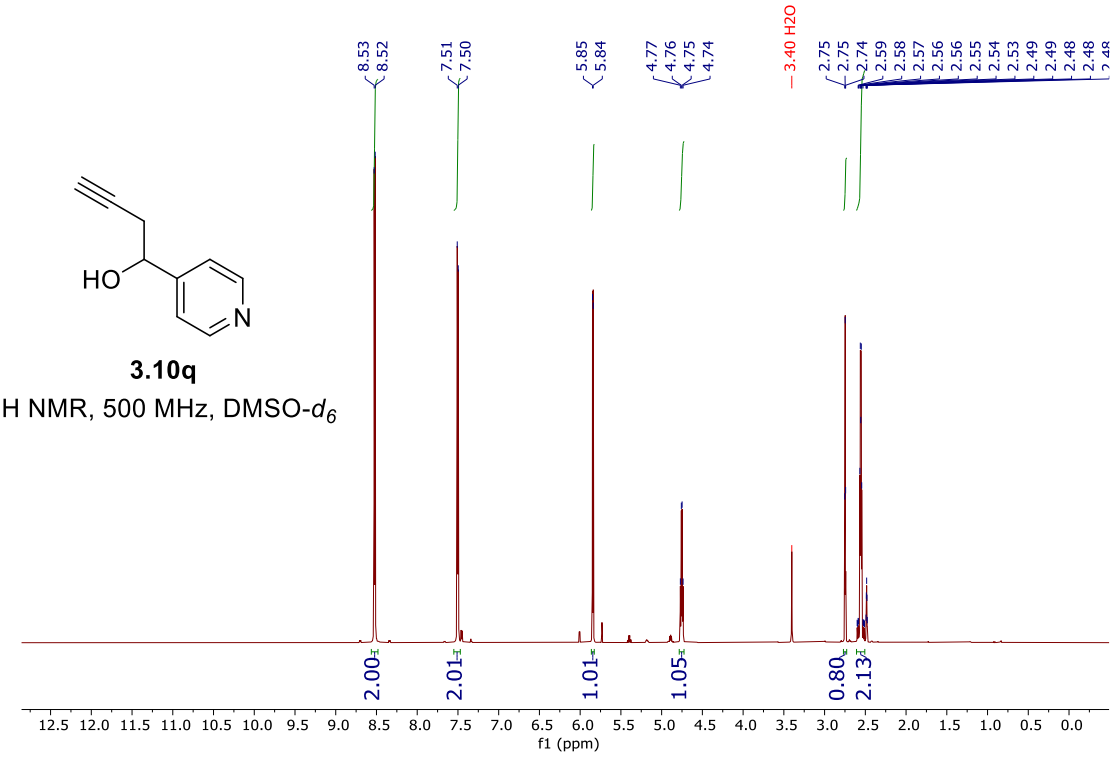
3.10p

^{1}H NMR, 500 MHz, $CDCl_3$



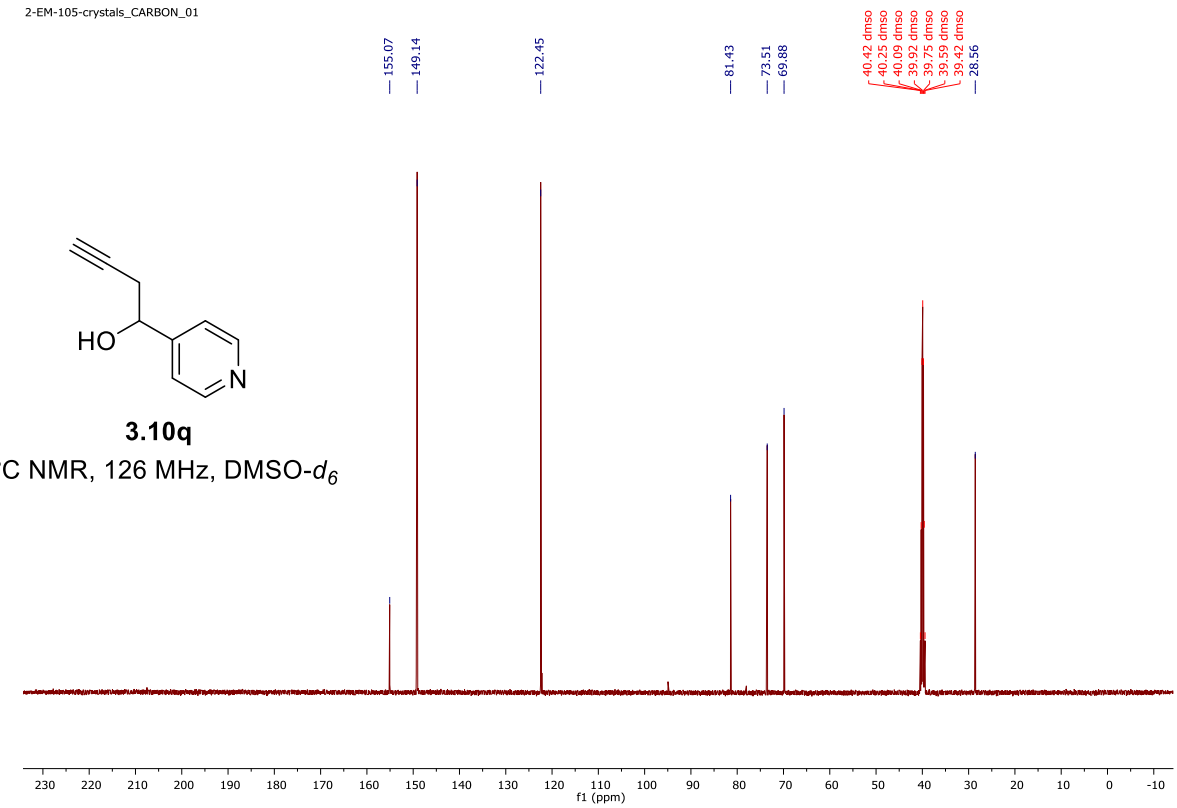
3.10p

^{13}C NMR, 126 MHz, $CDCl_3$



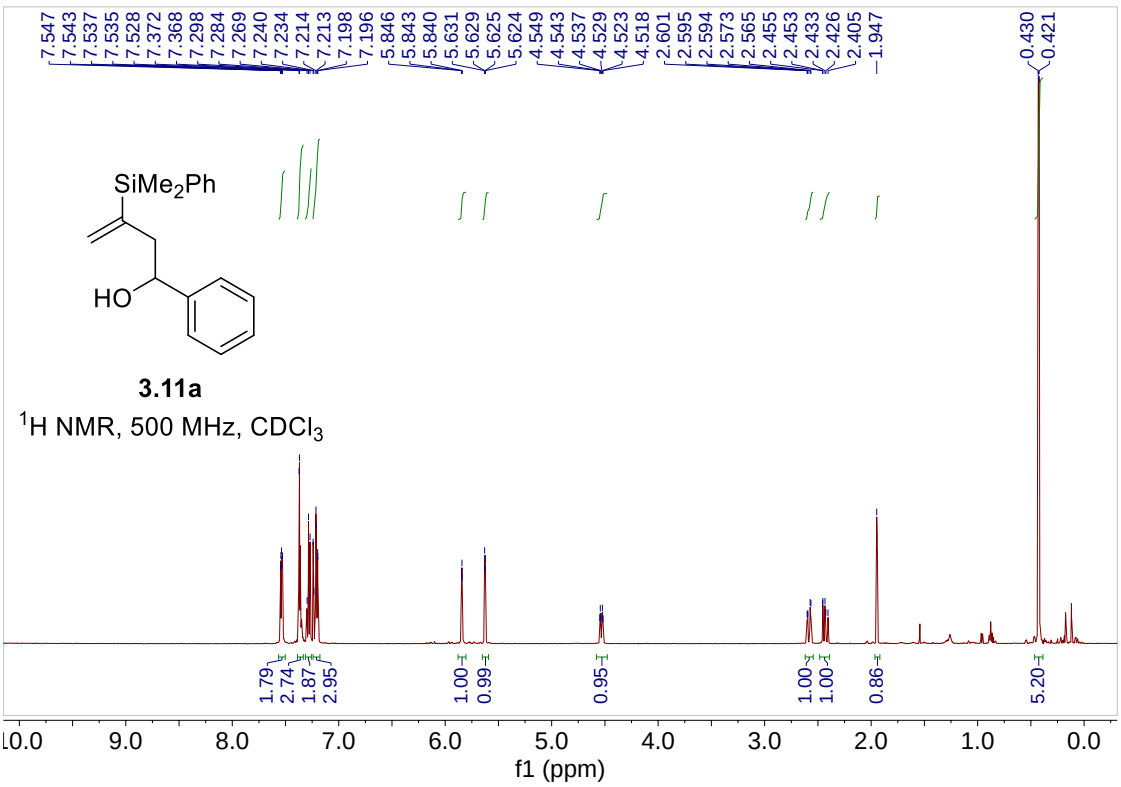
3.10q

^{1}H NMR, 500 MHz, DMSO-d_6



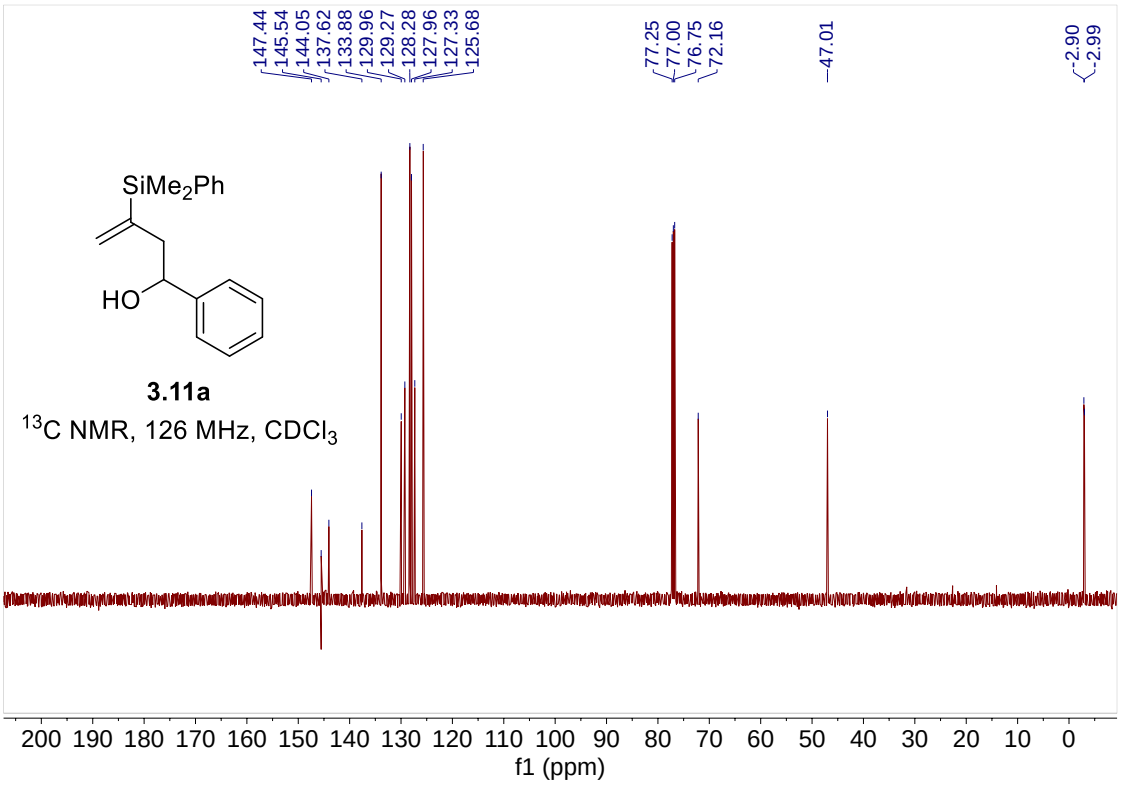
3.10q

^{13}C NMR, 126 MHz, DMSO-d_6



3.11a

^{1}H NMR, 500 MHz, $CDCl_3$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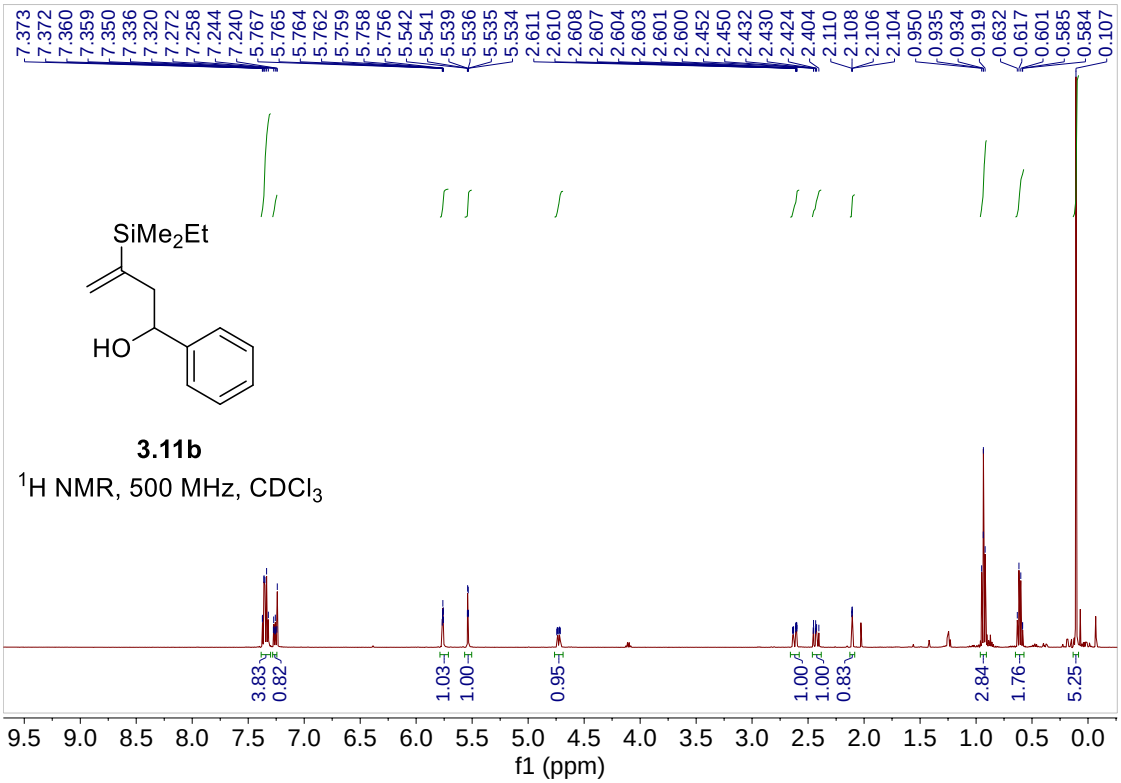
145.54
144.05
137.62
133.88
129.96
129.27
128.28
127.96
127.33
125.68
77.25
77.00
76.75
72.16
47.01
2.90
2.99
SiMe2Ph
HO
3.11a
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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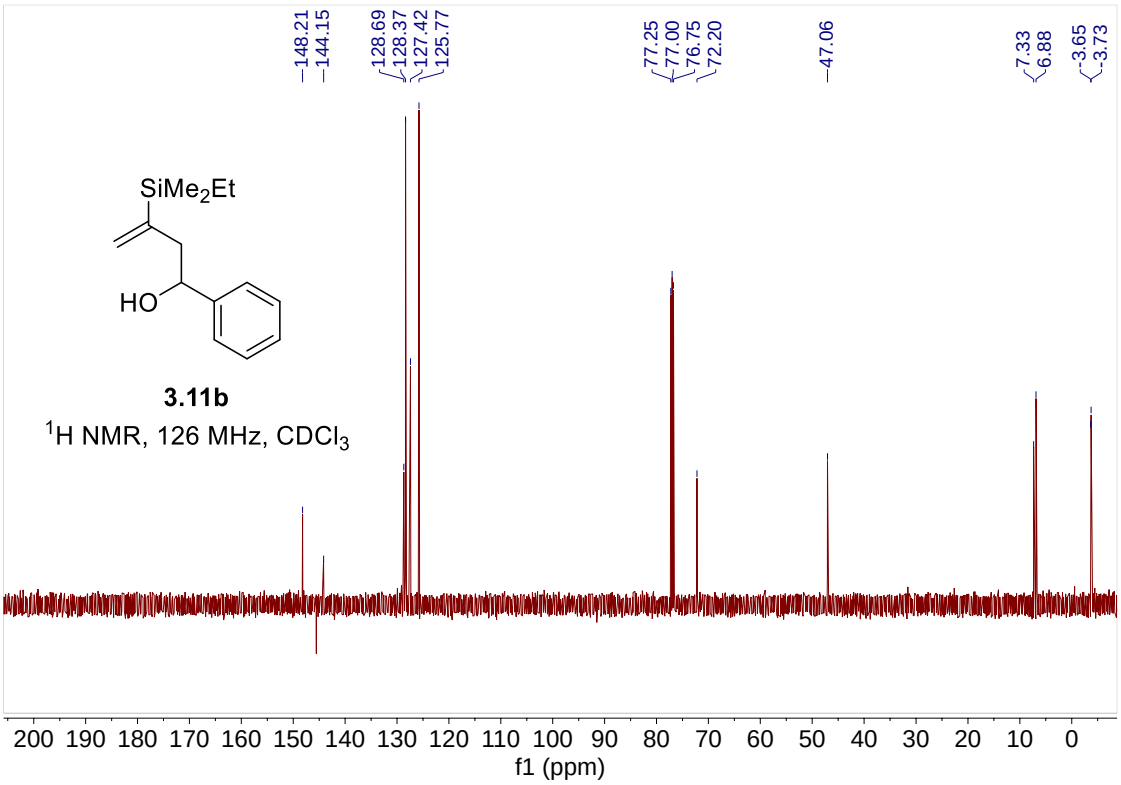
7.372
7.360
7.359
7.350
7.336
7.320
7.272
7.258
7.244
7.240
5.767
5.765
5.764
5.762
5.759
5.758
5.756
5.542
5.541
5.539
5.536
5.535
5.534
2.611
2.610
2.608
2.607
2.604
2.603
2.601
2.600
2.452
2.450
2.432
2.430
2.424
2.404
2.110
2.108
2.106
2.104
0.950
0.935
0.934
0.919
0.632
0.617
0.601
0.585
0.584
0.107
SiMe2Et
HO
3.11b
1H NMR, 500 MHz, CDCl3
3.83
0.82
1.03
1.00
0.95
1.00
1.00
0.83
2.84
1.76
5.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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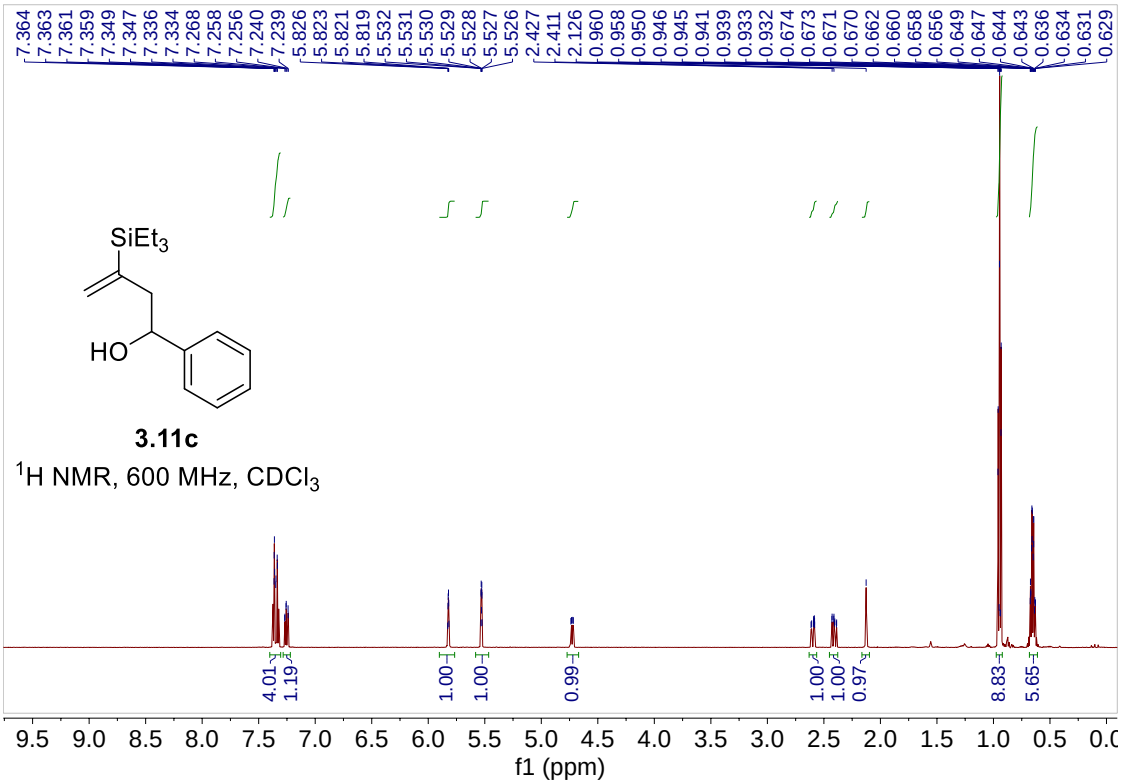
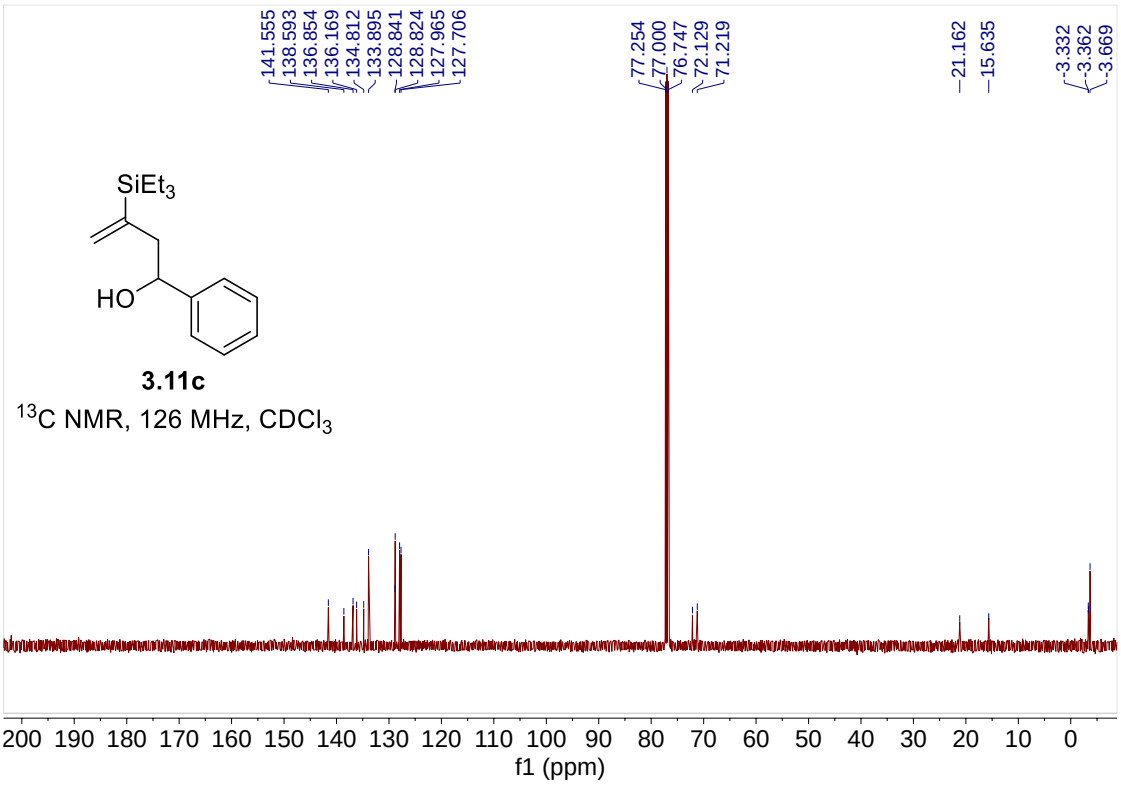
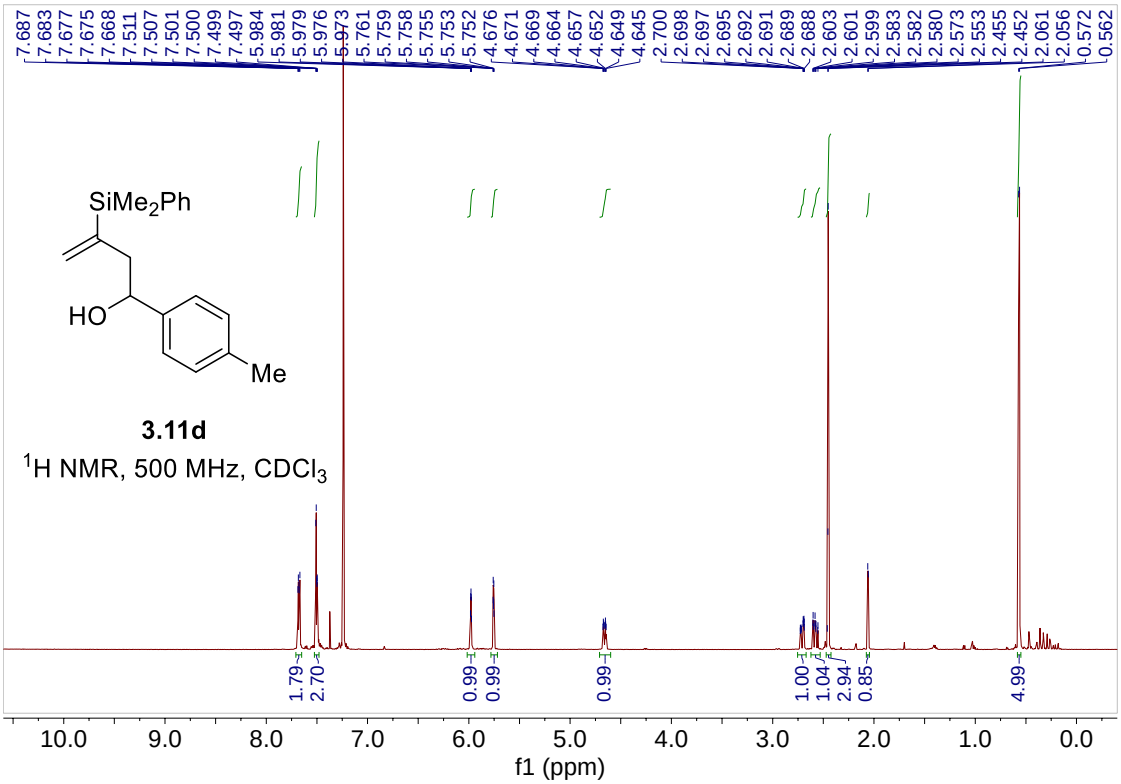
144.15
128.69
128.37
127.42
125.77
77.25
77.00
76.75
72.20
47.06
7.33
6.88
3.65
3.73
SiMe2Et
HO
3.11b
1H NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.364
7.363
7.361
7.359
7.349
7.347
7.336
7.334
7.268
7.258
7.256
7.240
7.239
5.826
5.823
5.821
5.819
5.532
5.531
5.530
5.529
5.528
5.527
5.526
2.427
2.411
2.126
0.960
0.958
0.950
0.946
0.945
0.941
0.939
0.933
0.932
0.674
0.673
0.671
0.670
0.662
0.660
0.658
0.656
0.649
0.647
0.644
0.643
0.636
0.634
0.631
0.629
SiEt3
HO
3.11c
1H NMR, 600 MHz, CDCl3
4.01
1.19
1.00
1.00
0.99
1.00
1.00
0.97
8.83
5.65
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



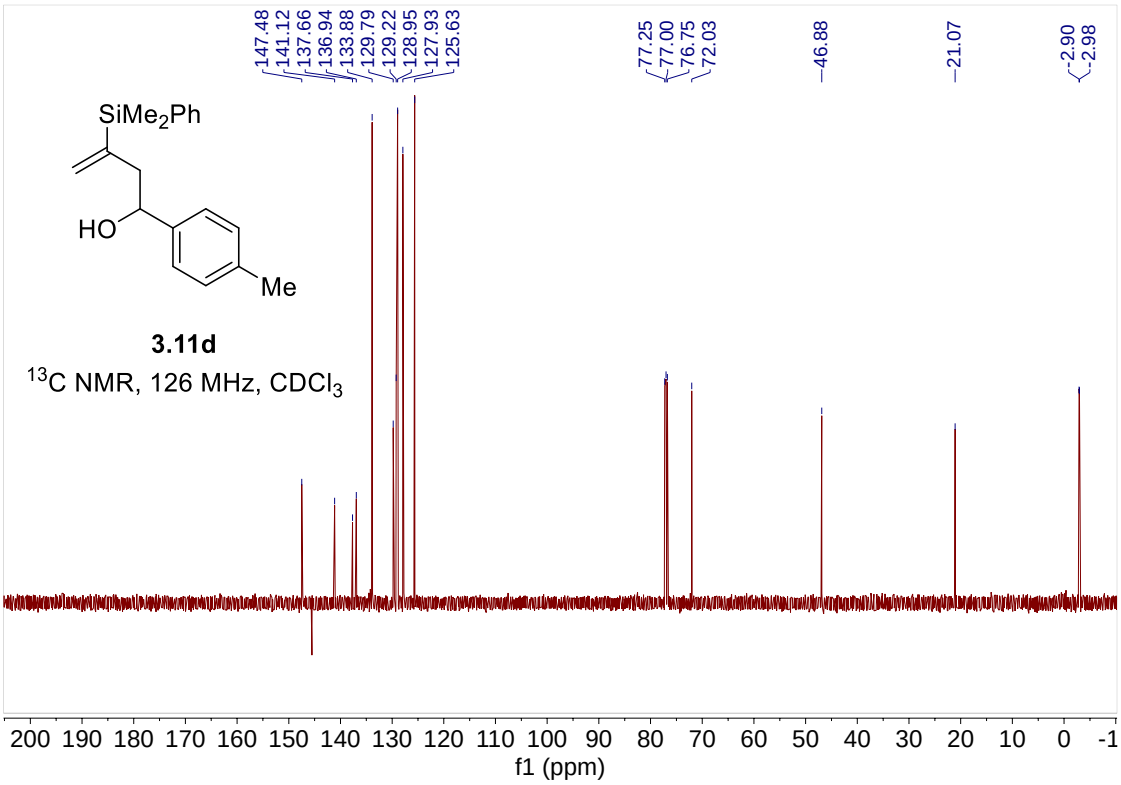
3.11c

^{13}C NMR, 126 MHz, $CDCl_3$



3.11d

^{1}H NMR, 500 MHz, $CDCl_3$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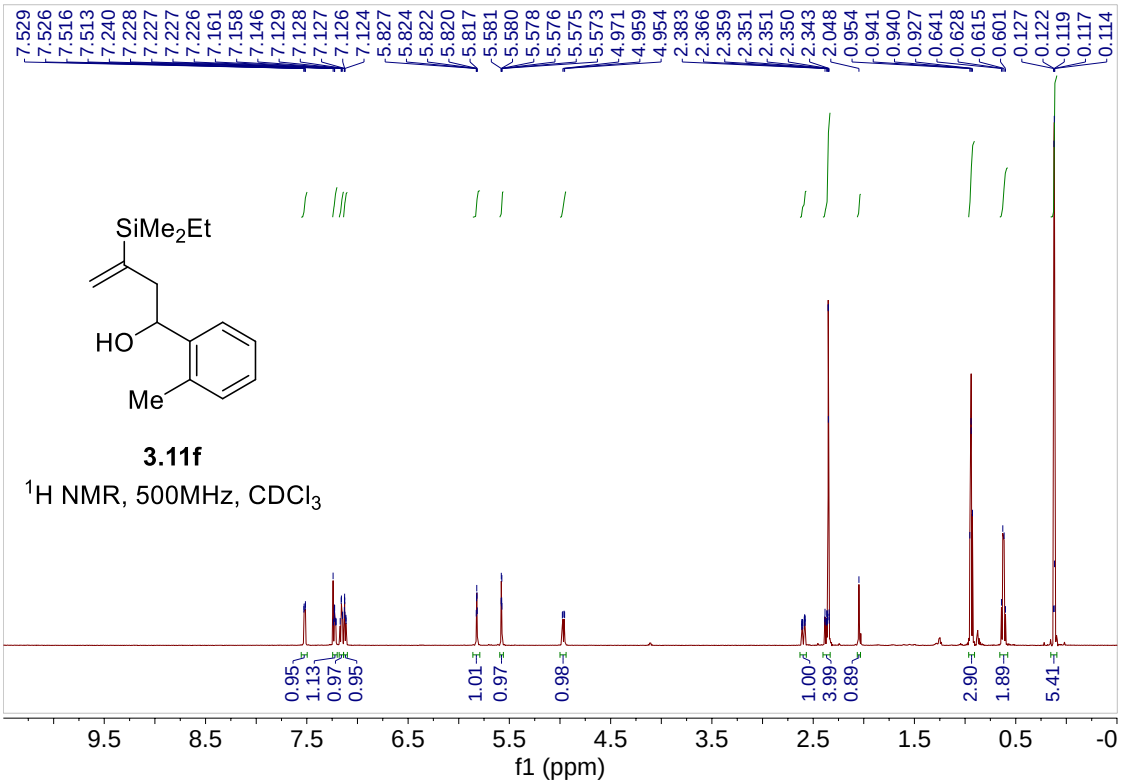
141.12
137.66
136.94
133.88
129.79
129.22
128.95
127.93
125.63
77.25
77.00
76.75
72.03
46.88
21.07
2.90
2.98
SiMe2Ph
HO
Me
3.11d
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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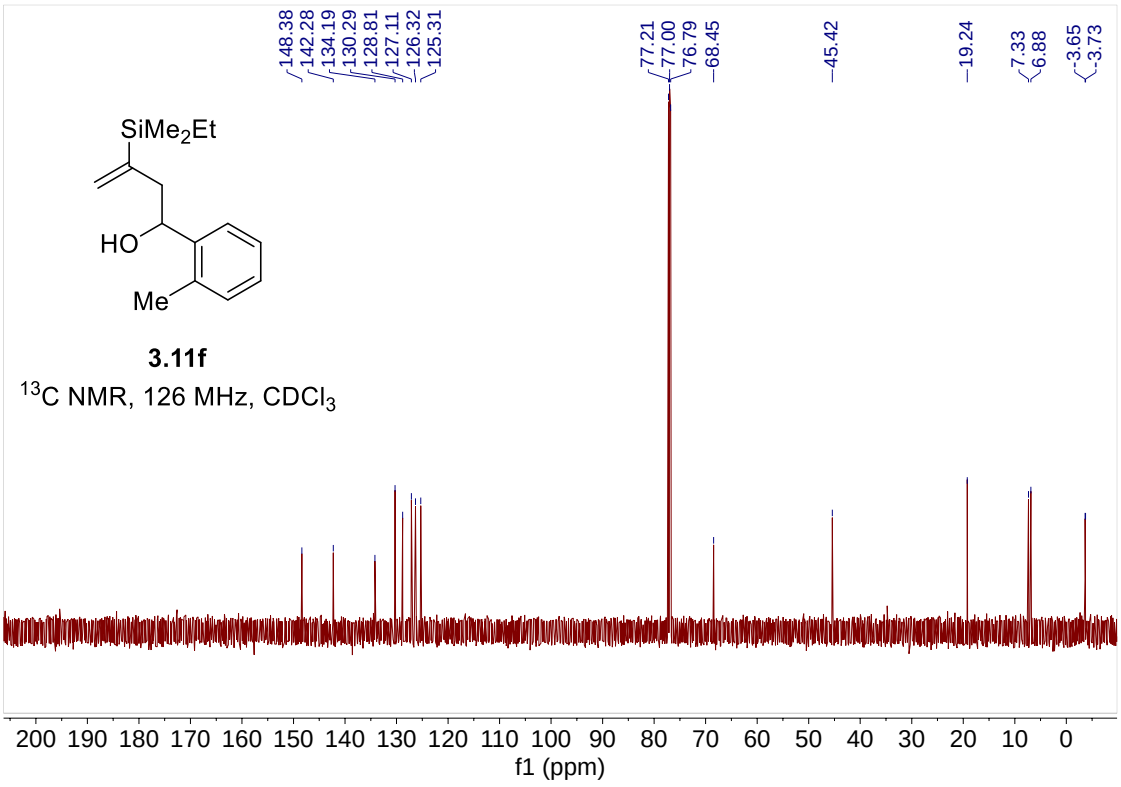
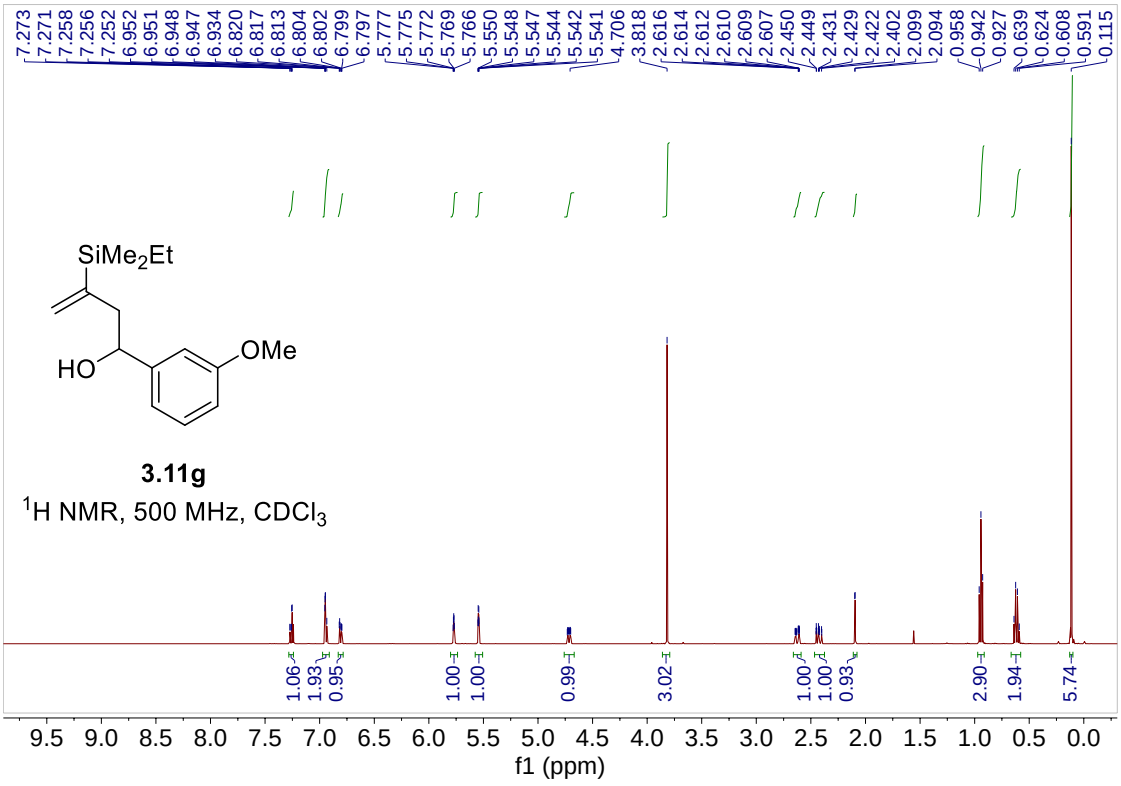
7.526
7.516
7.513
7.240
7.228
7.227
7.227
7.226
7.161
7.158
7.146
7.129
7.128
7.127
7.126
7.124
5.827
5.824
5.822
5.820
5.817
5.581
5.580
5.578
5.576
5.575
5.573
4.971
4.959
4.954
2.383
2.366
2.359
2.351
2.351
2.350
2.343
2.048
0.954
0.941
0.940
0.927
0.641
0.628
0.615
0.601
0.127
0.122
0.119
0.117
0.114
SiMe2Et
HO
Me
3.11f
1H NMR, 500MHz, CDCl3
0.95
1.13
0.97
0.95
1.01
0.97
0.98
1.00
3.99
0.89
2.90
1.89
5.41
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0
f1 (ppm)



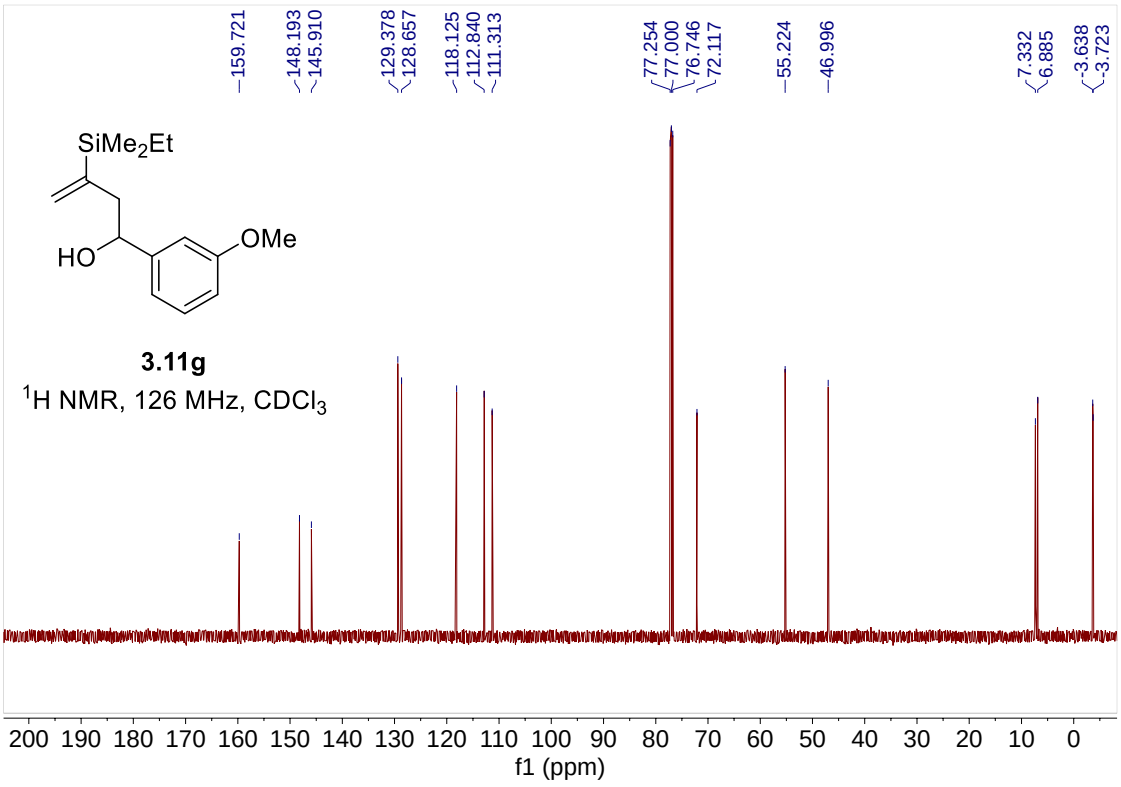
3.11f

^{13}C NMR, 126 MHz, $CDCl_3$



3.11g

^{1}H NMR, 500 MHz, $CDCl_3$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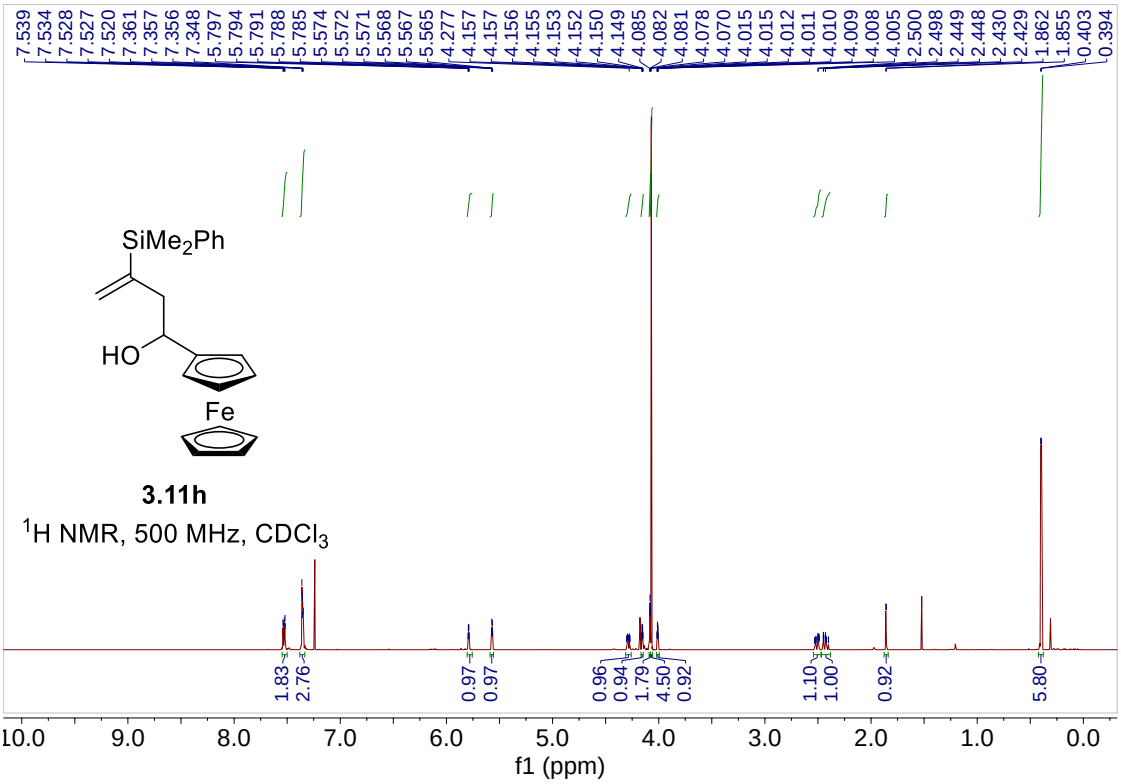
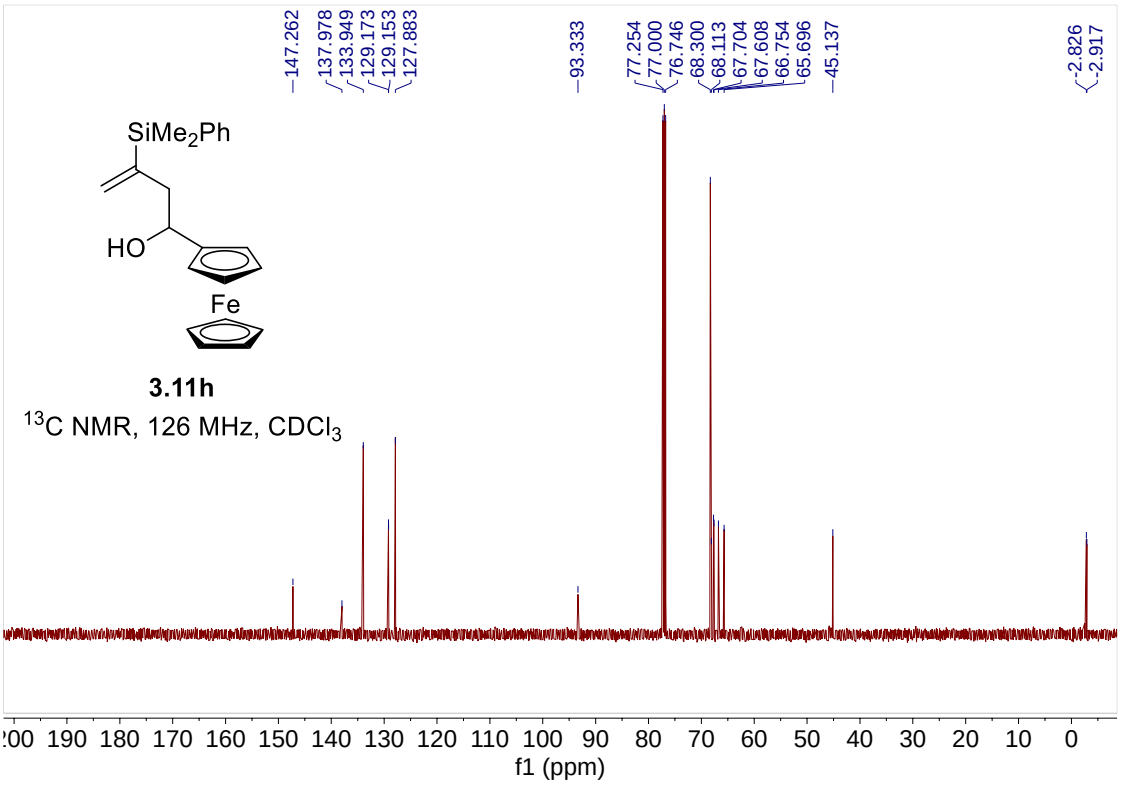
148.193
145.910
129.378
128.657
118.125
112.840
111.313
77.254
77.000
76.746
72.117
55.224
46.996
7.332
6.885
3.638
3.723
SiMe2Et
HO
OMe
3.11g
1H NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


SiMe2Ph
HO
Fe
3.11h
1H NMR, 500 MHz, CDCl3
1.83
2.76
0.97
0.97
0.96
0.94
1.79
4.50
0.92
1.10
1.00
0.92
5.80
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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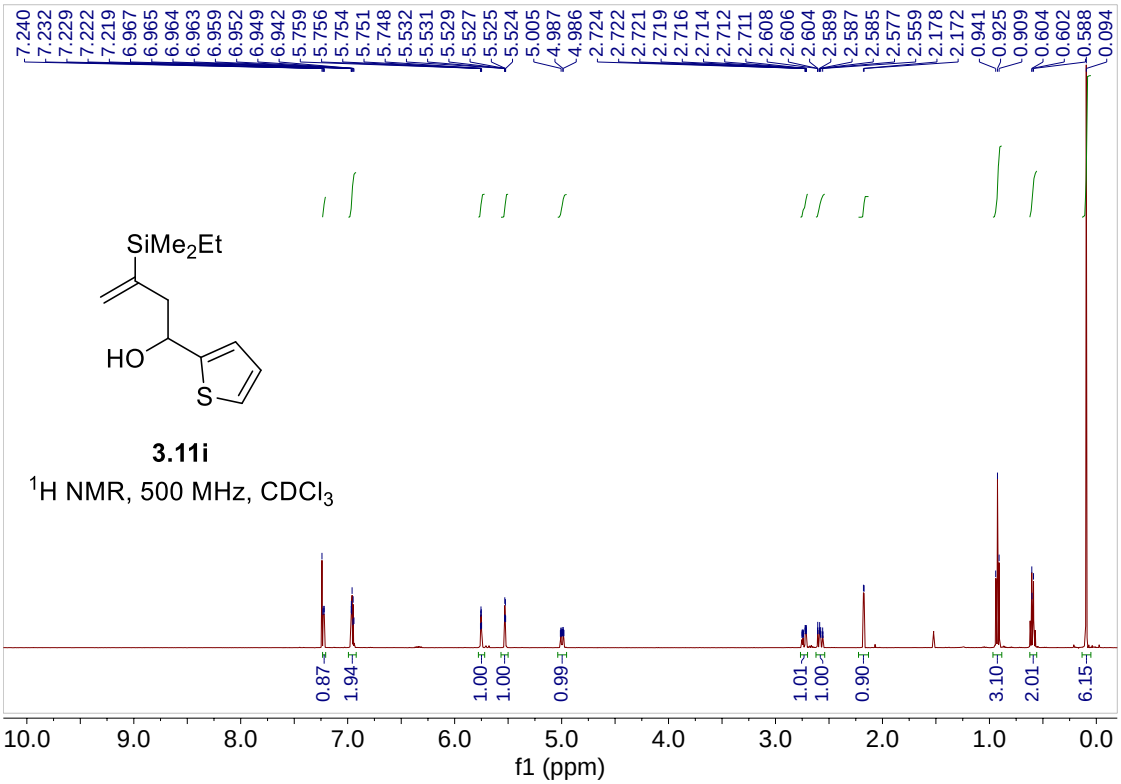
137.978
133.949
129.173
129.153
127.883
93.333
77.254
77.000
76.746
68.300
68.113
67.704
67.608
66.754
65.696
45.137
2.826
2.917
SiMe2Ph
HO
Fe
3.11h
13C NMR, 126 MHz, CDCl3
f1 (ppm)


7.240
7.232
7.229
7.222
7.219
6.967
6.965
6.964
6.963
6.959
6.952
6.949
6.942
5.759
5.756
5.754
5.751
5.748
5.532
5.531
5.529
5.527
5.525
5.524
5.005
4.987
4.986
2.724
2.722
2.721
2.719
2.716
2.714
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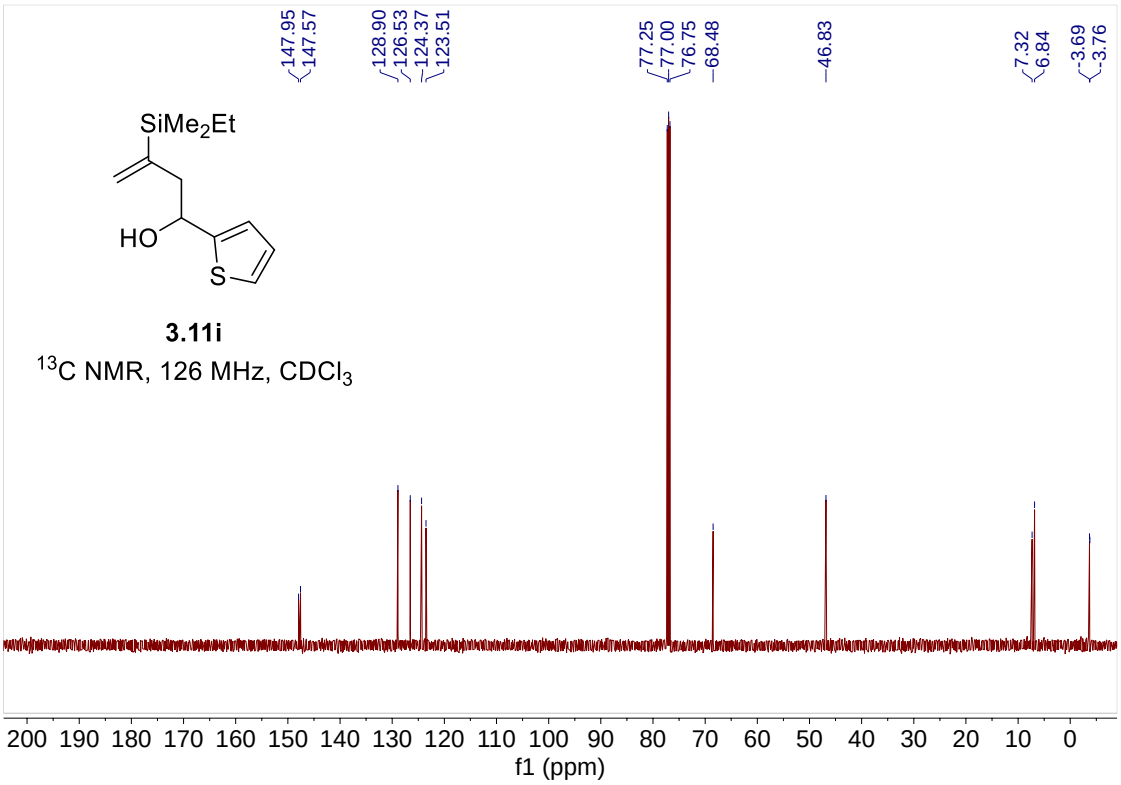
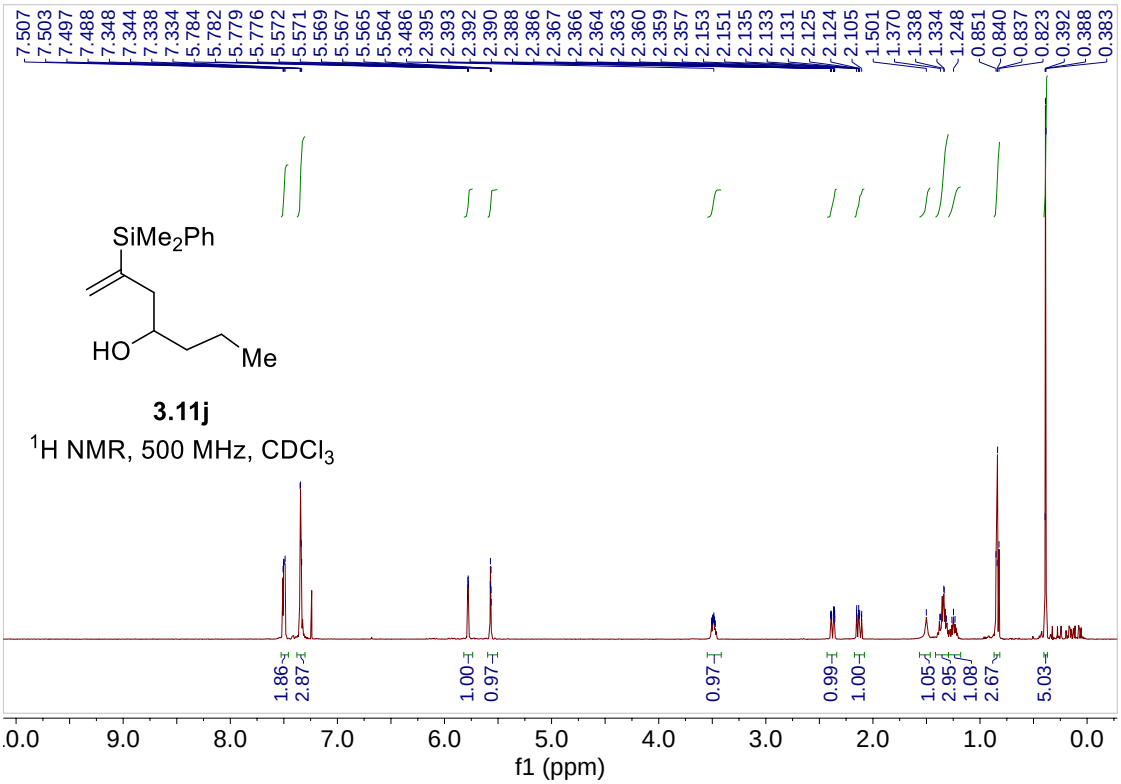
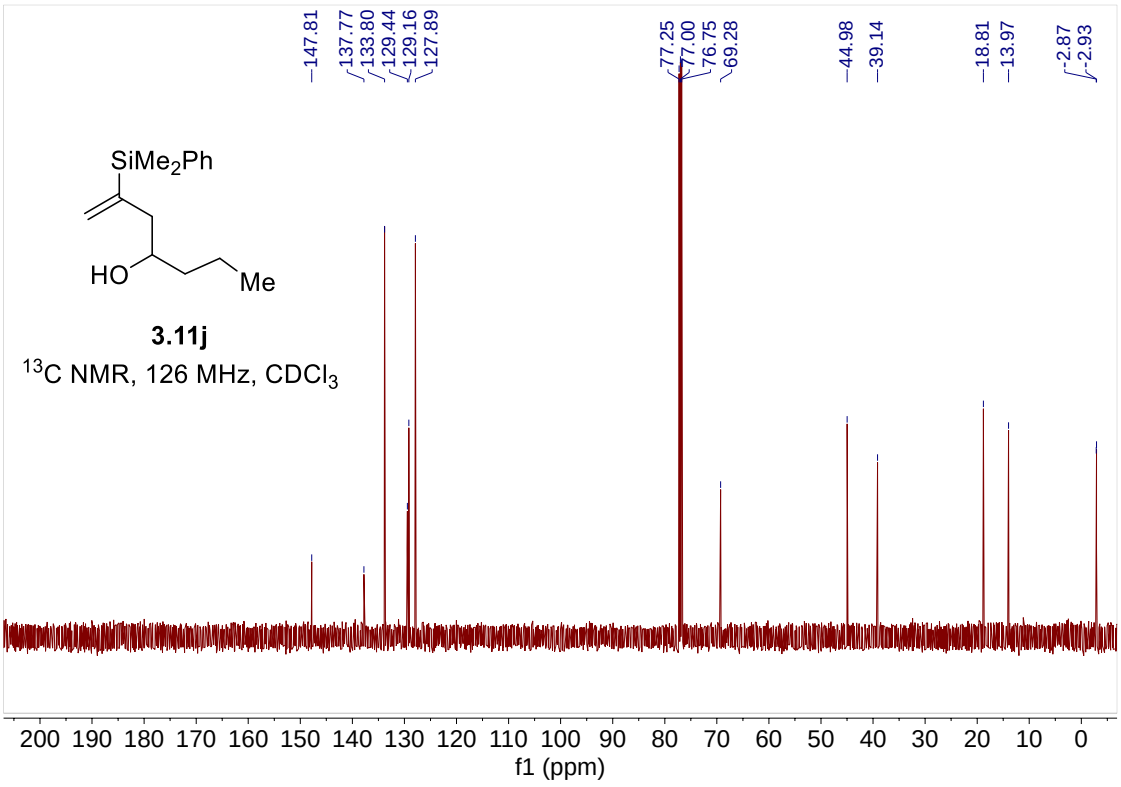
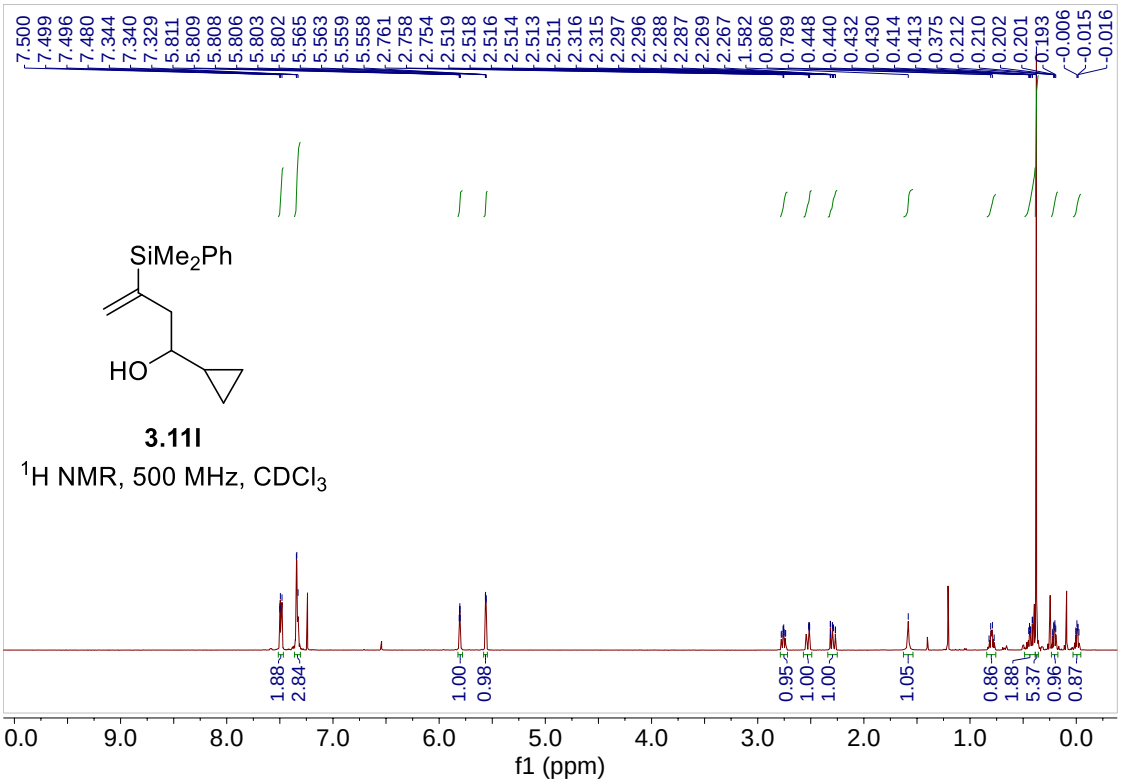
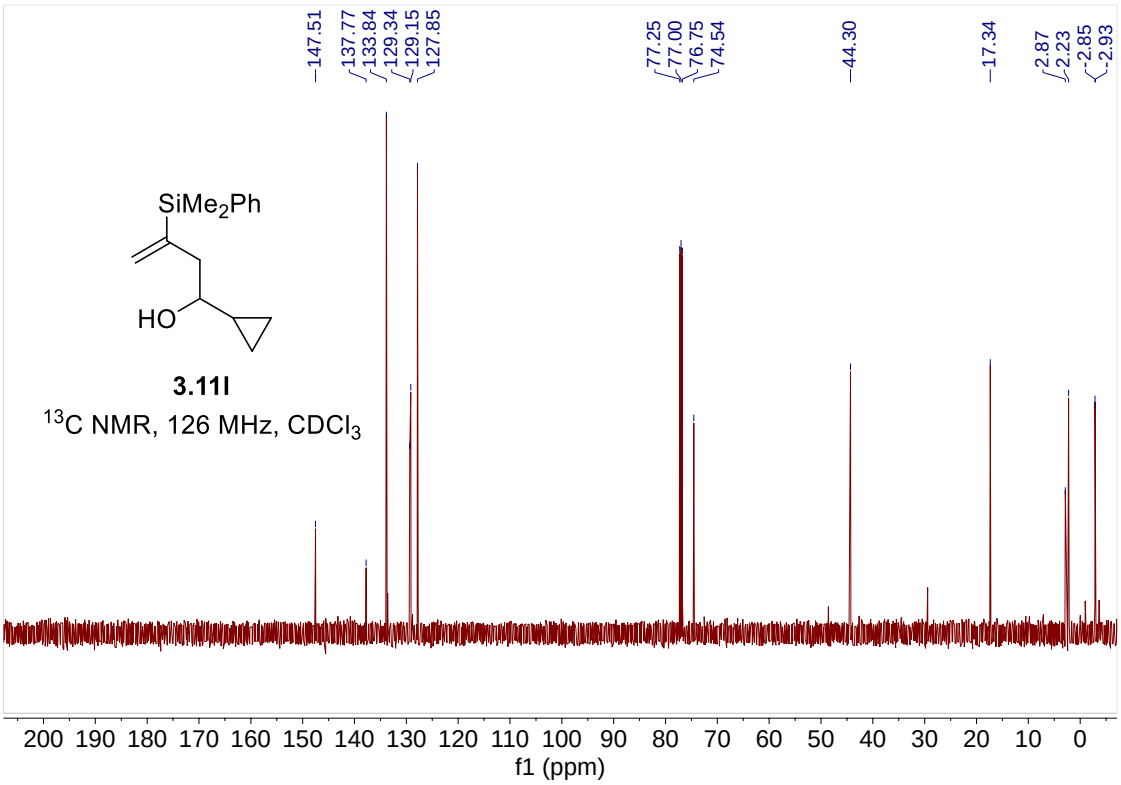
2.606
2.604
2.589
2.587
2.585
2.577
2.559
2.178
2.172
0.941
0.925
0.909
0.604
0.602
0.588
0.094
SiMe2Et
HO
S
3.11i
1H NMR, 500 MHz, CDCl3
0.87
1.94
1.00
1.00
0.99
1.01
1.00
0.90
3.10
2.01
6.15
f1 (ppm)

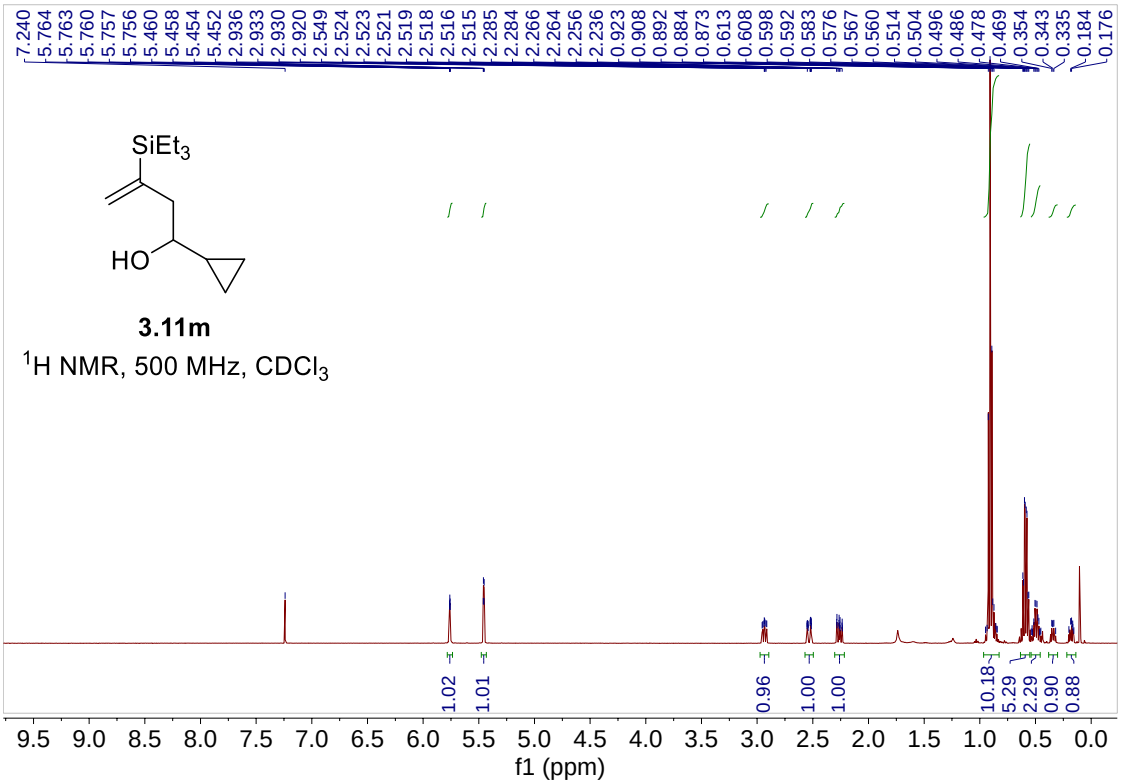

147.95
147.57
128.90
126.53
124.37
123.51
77.25
77.00
76.75
68.48
46.83
7.32
6.84
3.69
3.76
SiMe2Et
HO
S
3.11i
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

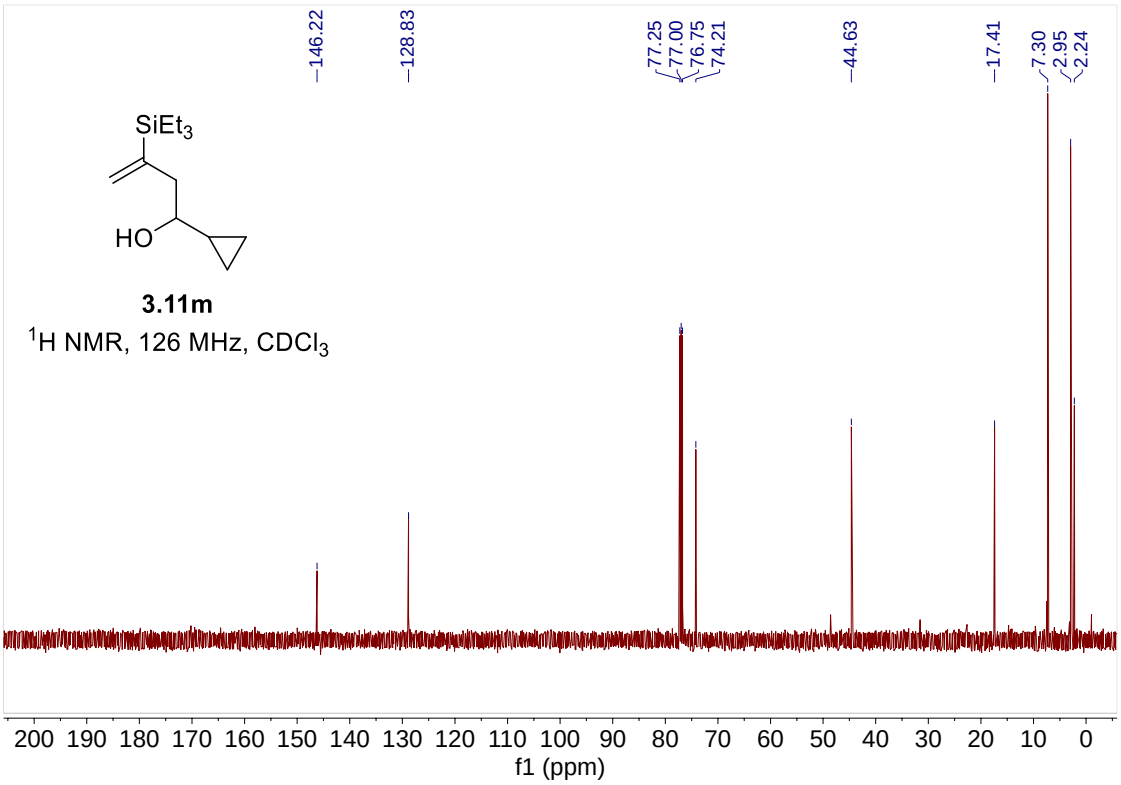

7.507
7.503
7.497
7.488
7.348
7.344
7.338
7.334
5.784
5.782
5.779
5.776
5.572
5.571
5.569
5.567
5.565
5.564
3.486
2.395
2.393
2.392
2.390
2.388
2.386
2.367
2.366
2.364
2.363
2.360
2.359
2.357
2.153
2.151
2.135
2.133
2.131
2.125
2.124
2.105
1.501
1.370
1.338
1.334
1.248
0.851
0.840
0.837
0.823
0.392
0.388
0.383
SiMe2Ph
HO
Me
3.11j
1H NMR, 500 MHz, CDCl3
1.86
2.87
1.00
0.97
0.97
0.99
1.00
1.05
2.95
1.08
2.67
5.03
.0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


147.81
137.77
133.80
129.44
129.16
127.89
77.25
77.00
76.75
69.28
44.98
39.14
18.81
13.97
2.87
2.93
SiMe2Ph
HO
Me
3.11j
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.500
7.499
7.496
7.480
7.344
7.340
7.329
5.811
5.809
5.808
5.806
5.803
5.802
5.565
5.563
5.559
5.558
2.761
2.758
2.754
2.519
2.518
2.516
2.514
2.513
2.511
2.316
2.315
2.297
2.296
2.288
2.287
2.269
2.267
1.582
0.806
0.789
0.448
0.440
0.432
0.430
0.414
0.413
0.375
0.212
0.210
0.202
0.201
0.193
-0.006
-0.015
-0.016
SiMe2Ph
HO
3.11l
1H NMR, 500 MHz, CDCl3
1.88
2.84
1.00
0.98
0.95
1.00
1.00
1.05
0.86
1.88
5.37
0.96
0.87
0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

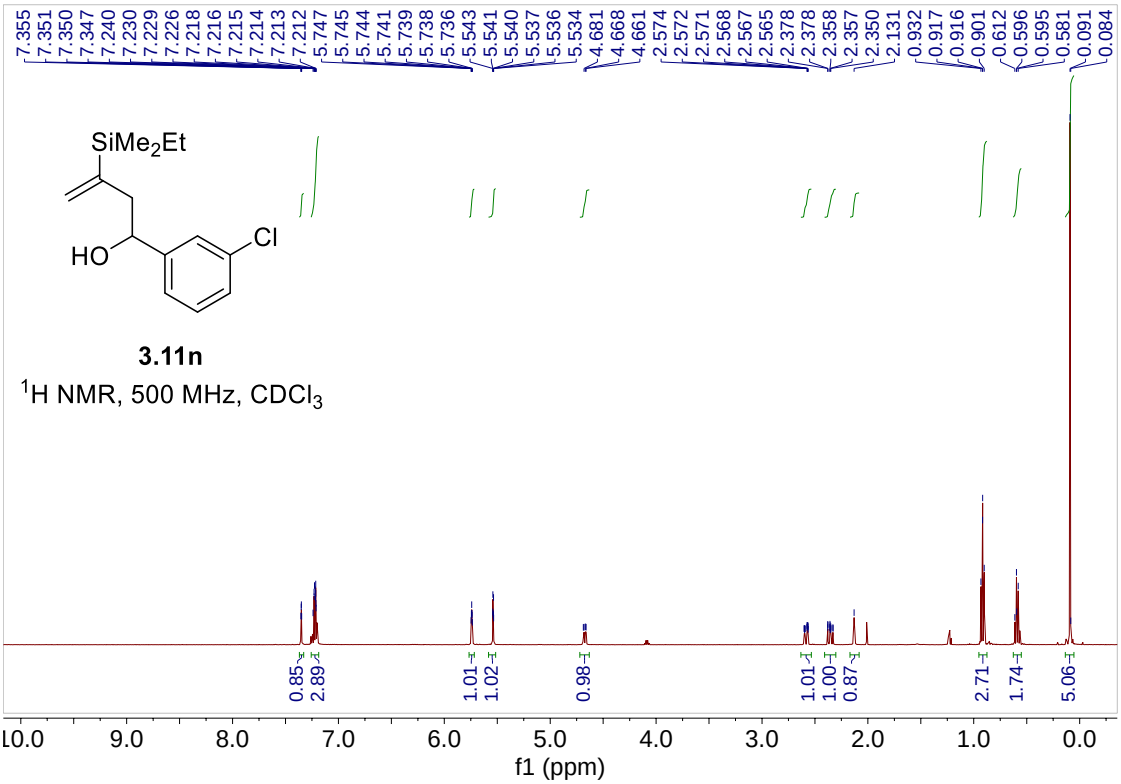

147.51
137.77
133.84
129.34
129.15
127.85
77.25
77.00
76.75
74.54
44.30
17.34
2.87
2.23
2.85
2.93
SiMe2Ph
HO
3.11l
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.240
5.764
5.763
5.760
5.757
5.756
5.460
5.458
5.454
5.452
2.936
2.933
2.930
2.920
2.549
2.524
2.523
2.521
2.519
2.518
2.516
2.515
2.285
2.284
2.266
2.264
2.256
2.236
0.923
0.908
0.892
0.884
0.873
0.613
0.608
0.598
0.592
0.583
0.576
0.567
0.560
0.514
0.504
0.496
0.486
0.478
0.469
0.354
0.343
0.335
0.184
0.176
SiEt3
HO
3.11m
1H NMR, 500 MHz, CDCl3
1.02
1.01
0.96
1.00
1.00
10.18
5.29
2.29
0.90
0.88
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



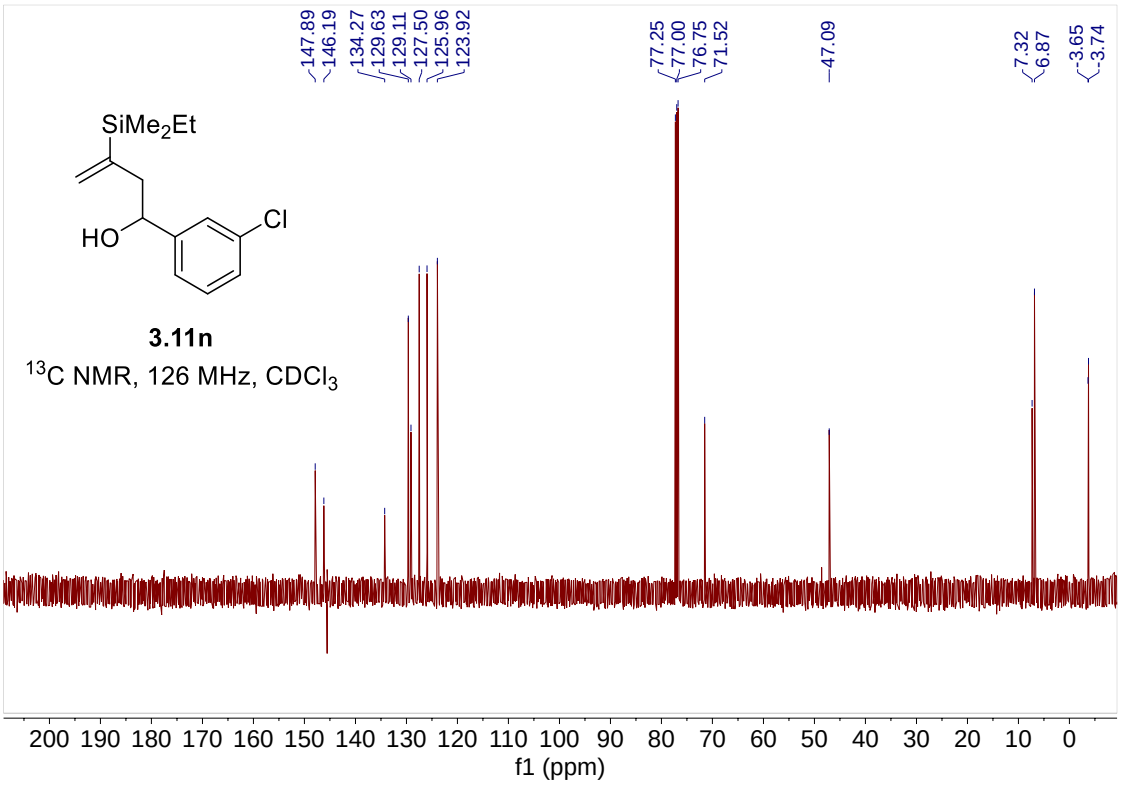
3.11m

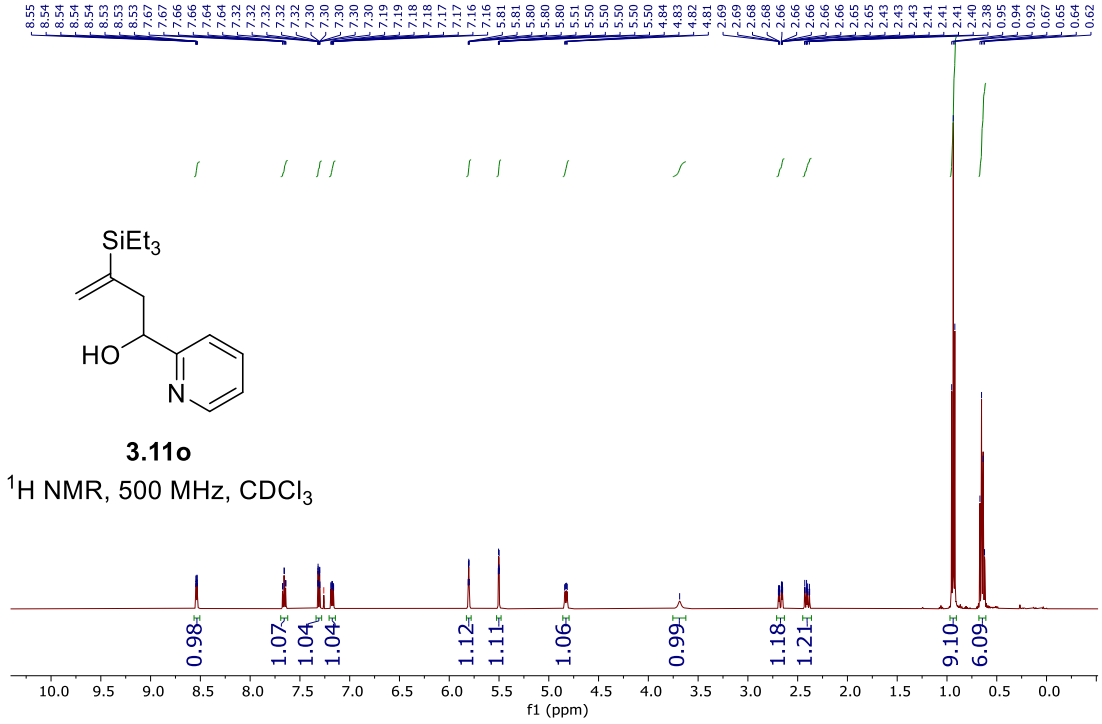
^{1}H NMR, 126 MHz, $CDCl_3$

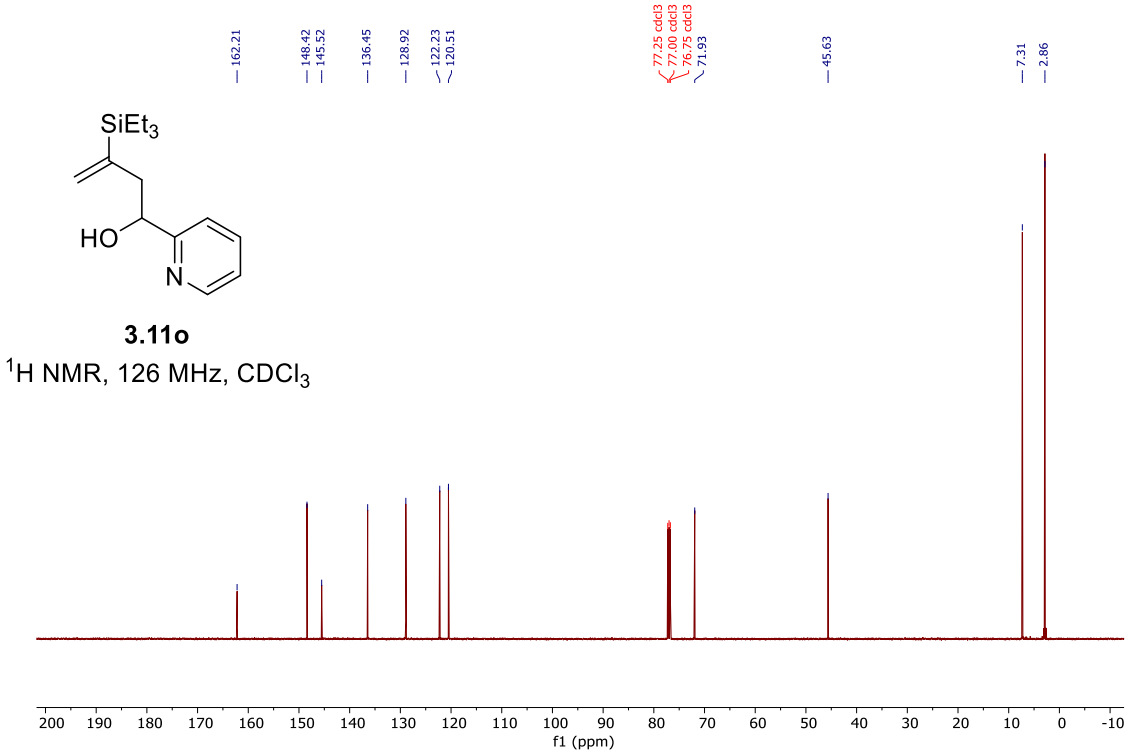


3.11n

^{1}H NMR, 500 MHz, $CDCl_3$

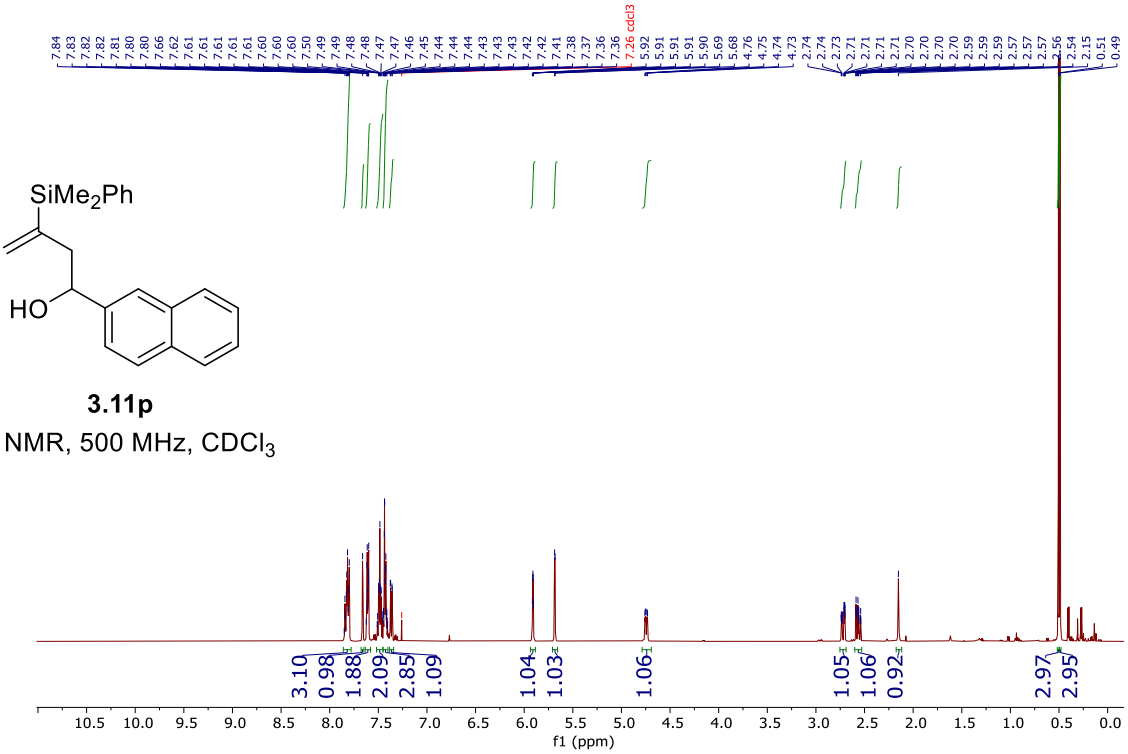

147.89
146.19
134.27
129.63
129.11
127.50
125.96
123.92
77.25
77.00
76.75
71.52
47.09
7.32
6.87
3.65
3.74
SiMe2Et
HO
Cl
3.11n
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


SiEt3
HO
N
3.11o
1H NMR, 500 MHz, CDCl3
0.98
1.07
1.04
1.04
1.12
1.11
1.06
0.99
1.18
1.21
9.10
6.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



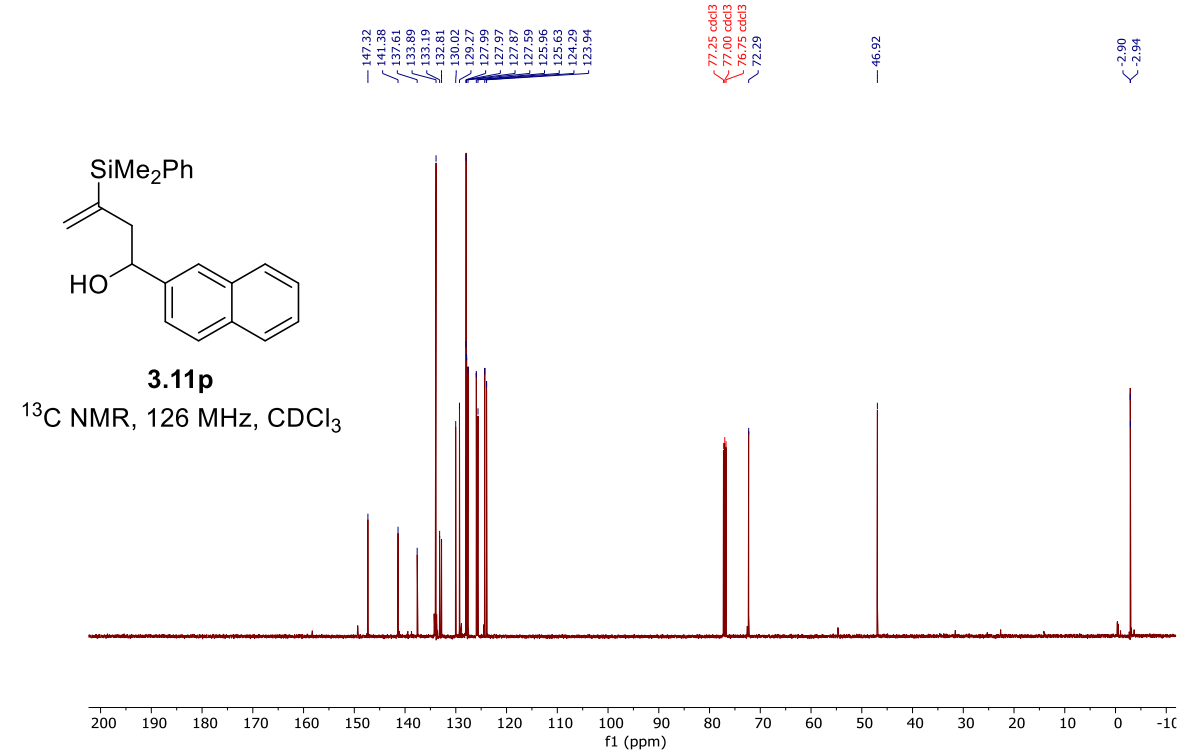
3.11o

^{1}H NMR, 126 MHz, $CDCl_3$



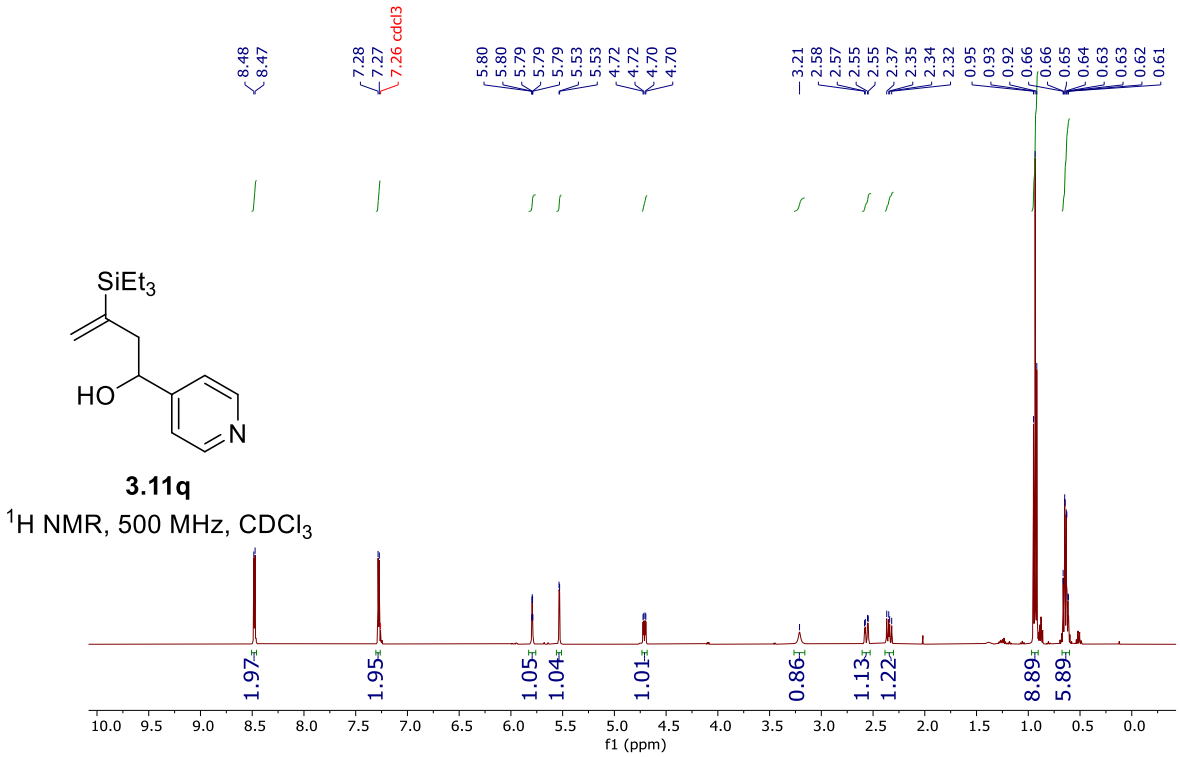
3.11p

^{1}H NMR, 500 MHz, $CDCl_3$



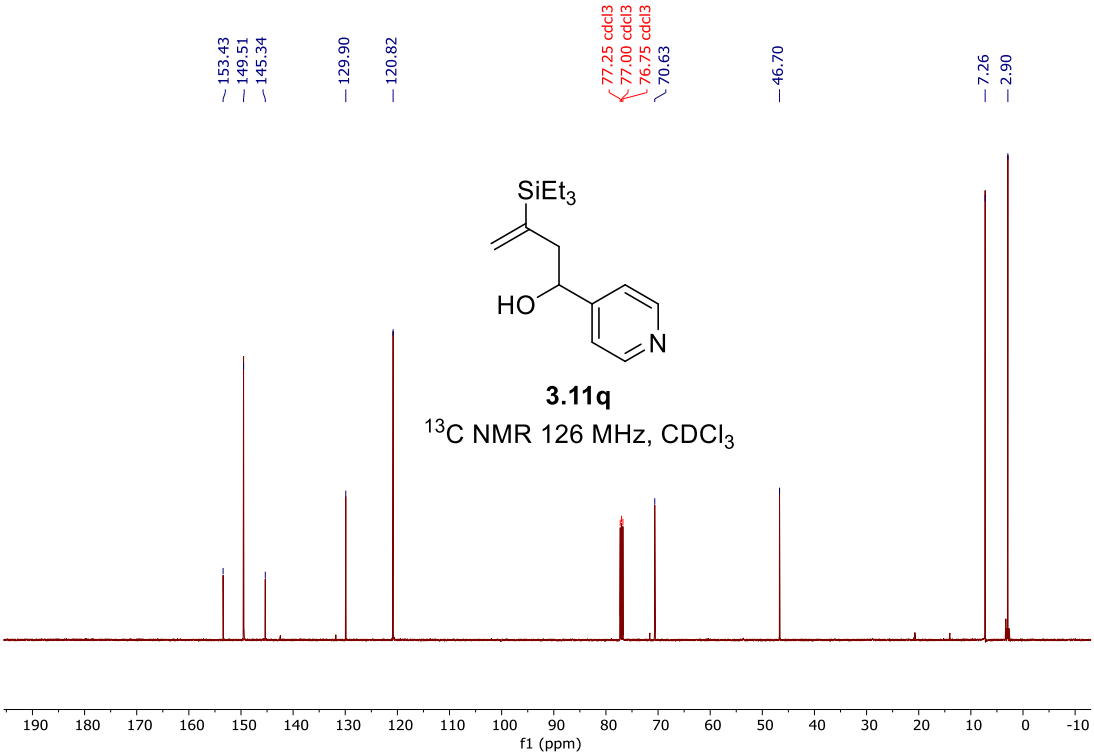
3.11p

^{13}C NMR, 126 MHz, $CDCl_3$



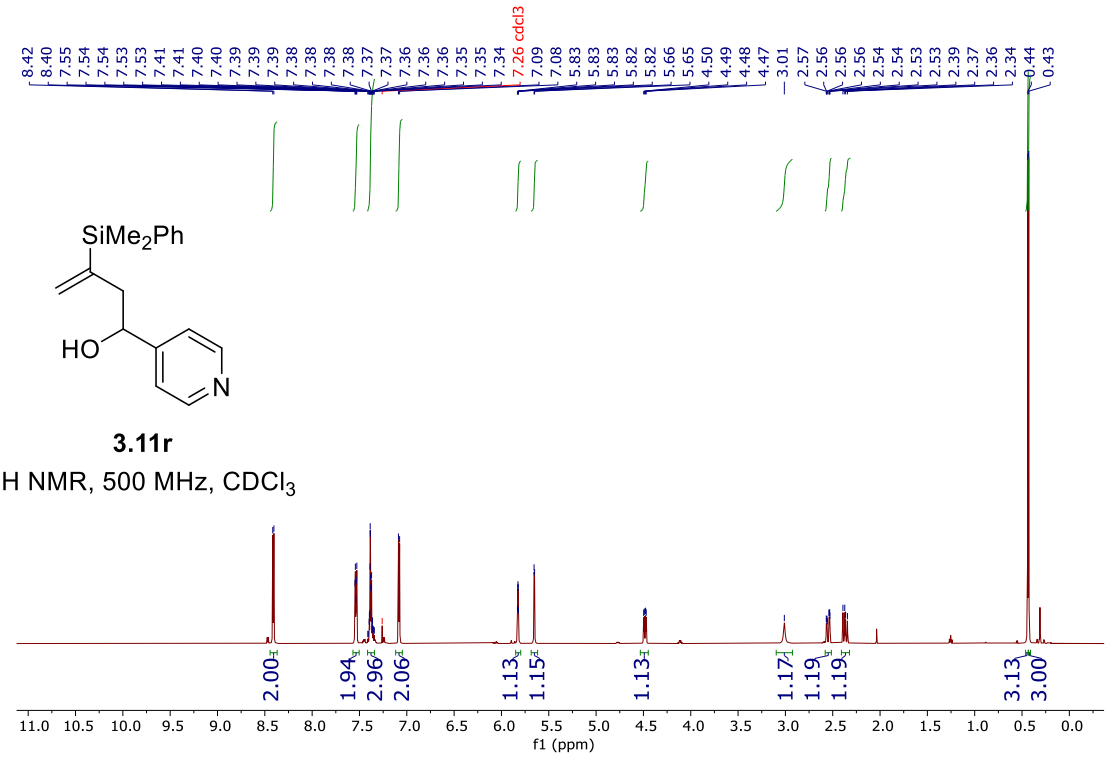
3.11q

^{1}H NMR, 500 MHz, $CDCl_3$



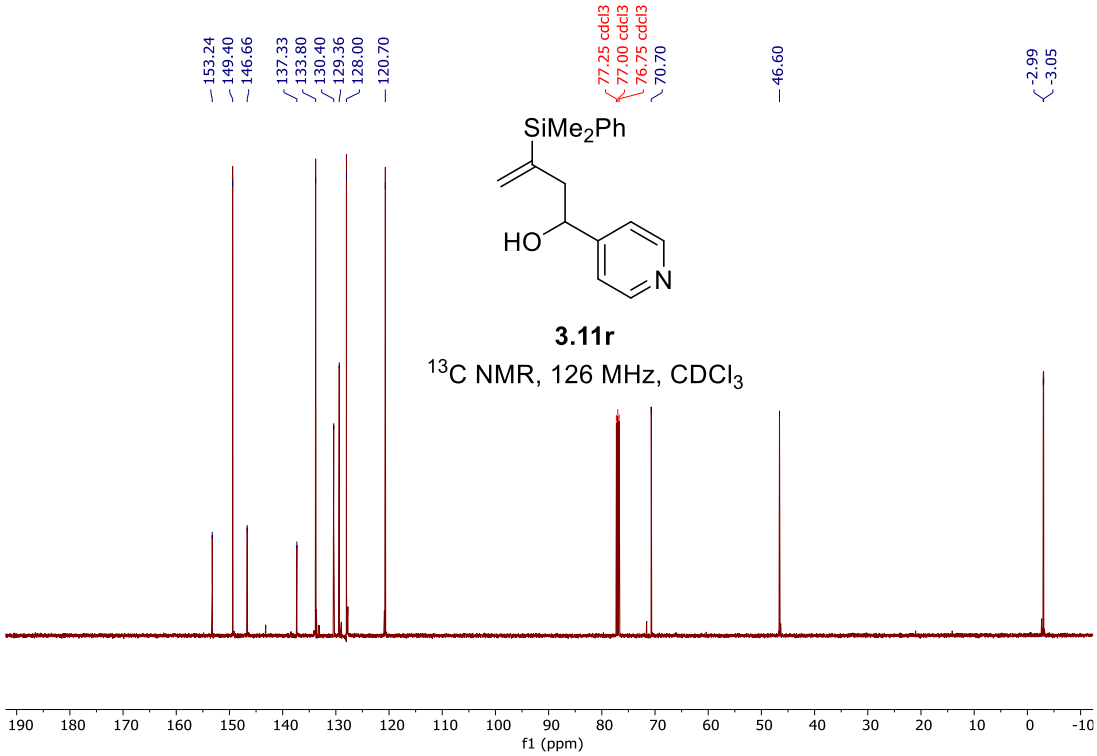
3.11q

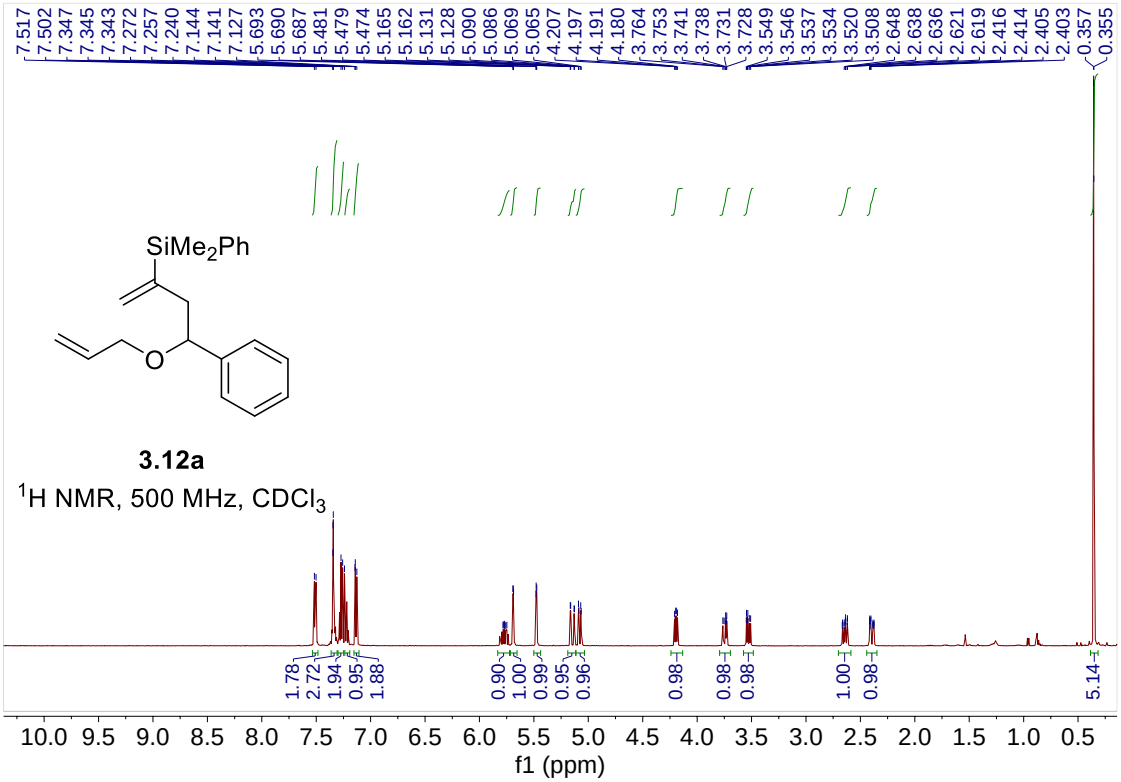
^{13}C NMR 126 MHz, $CDCl_3$

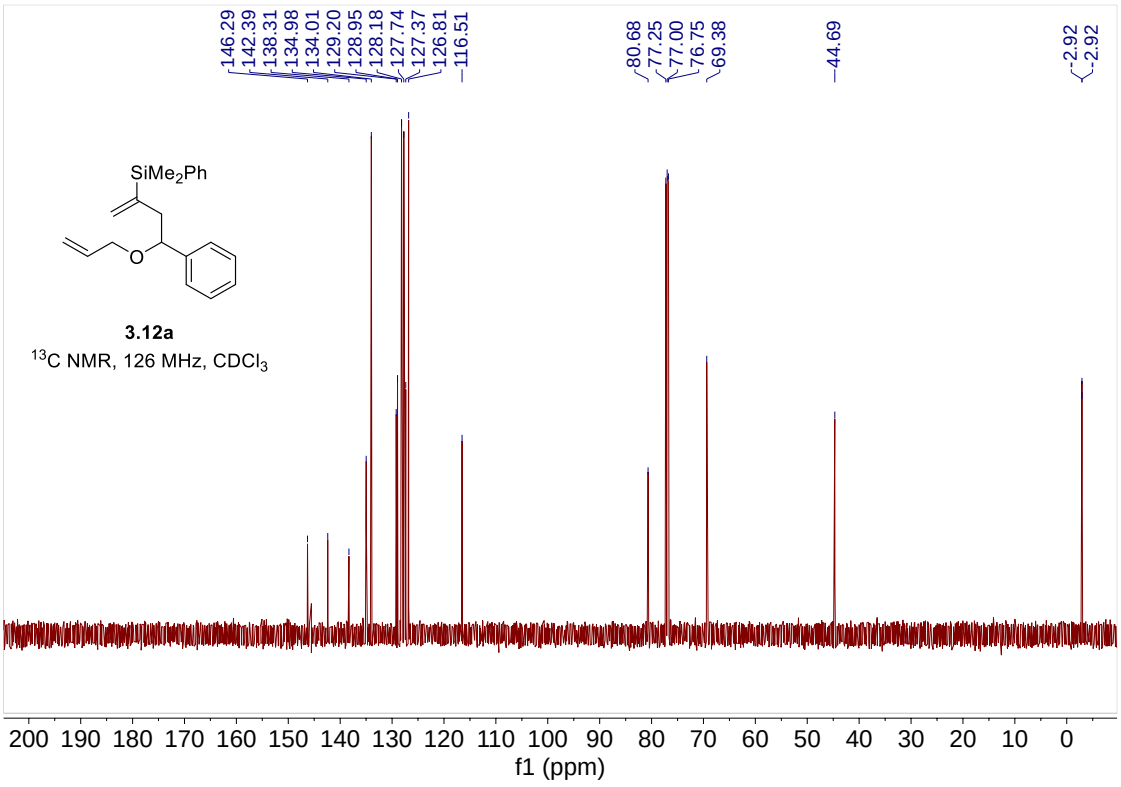


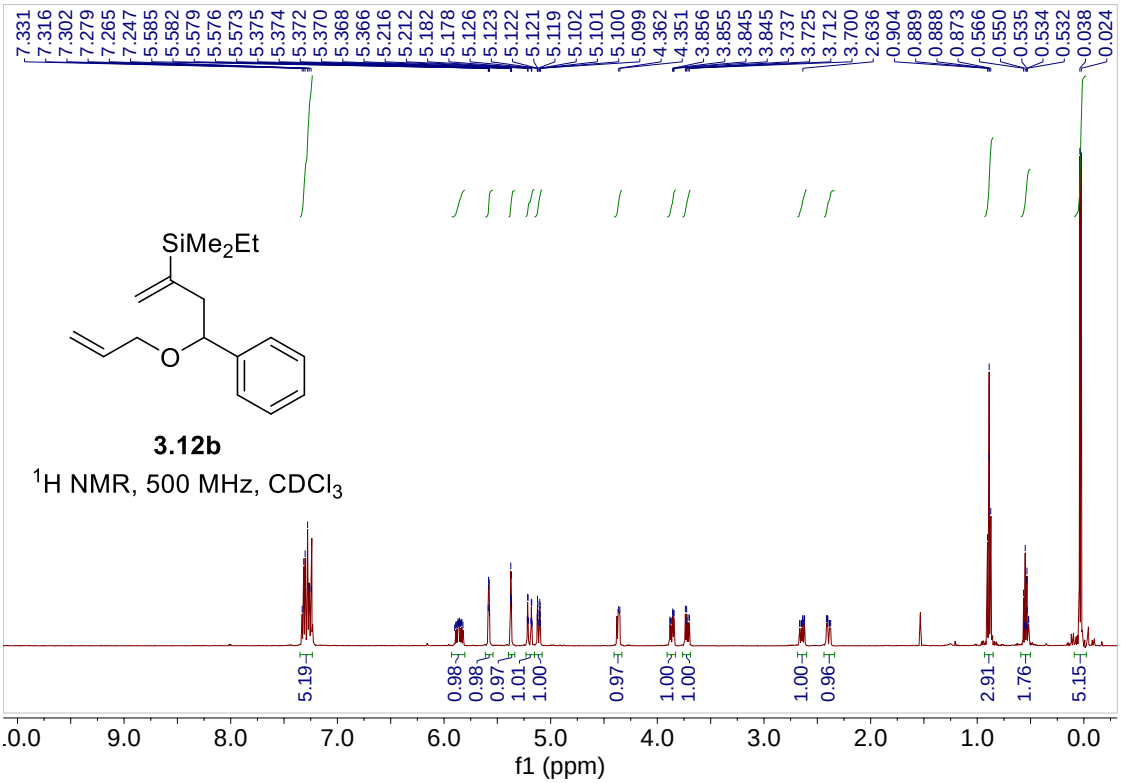
3.11r

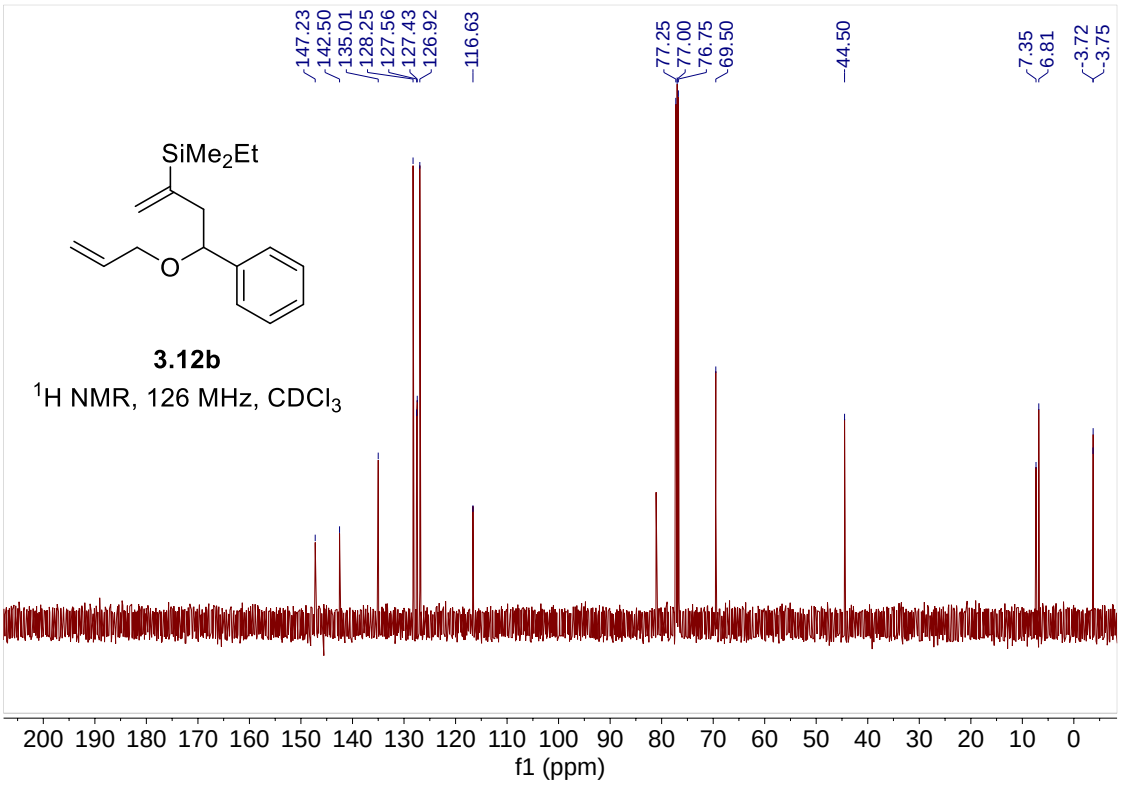
^{1}H NMR, 500 MHz, $CDCl_3$

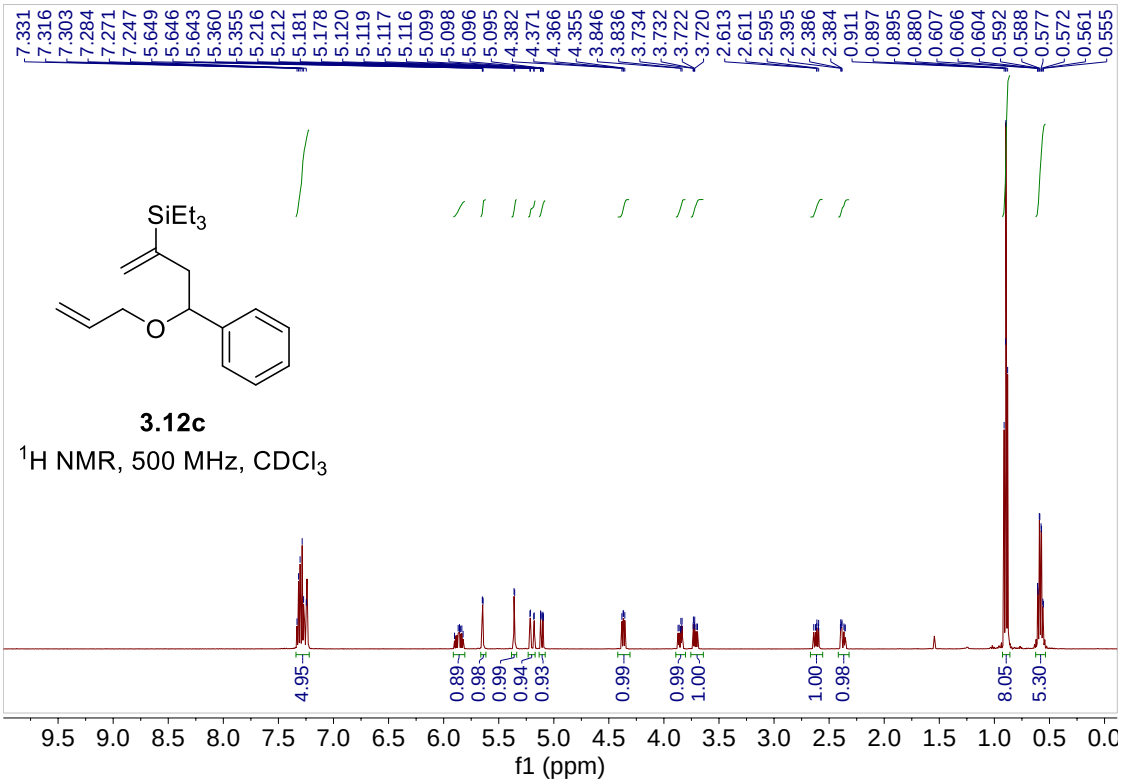

153.24
149.40
146.66
137.33
133.80
130.40
129.36
128.00
120.70
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.70
46.60
-2.99
-3.05
SiMe2Ph
HO
N
3.11r
13C NMR, 126 MHz, CDCl3
f1 (ppm)

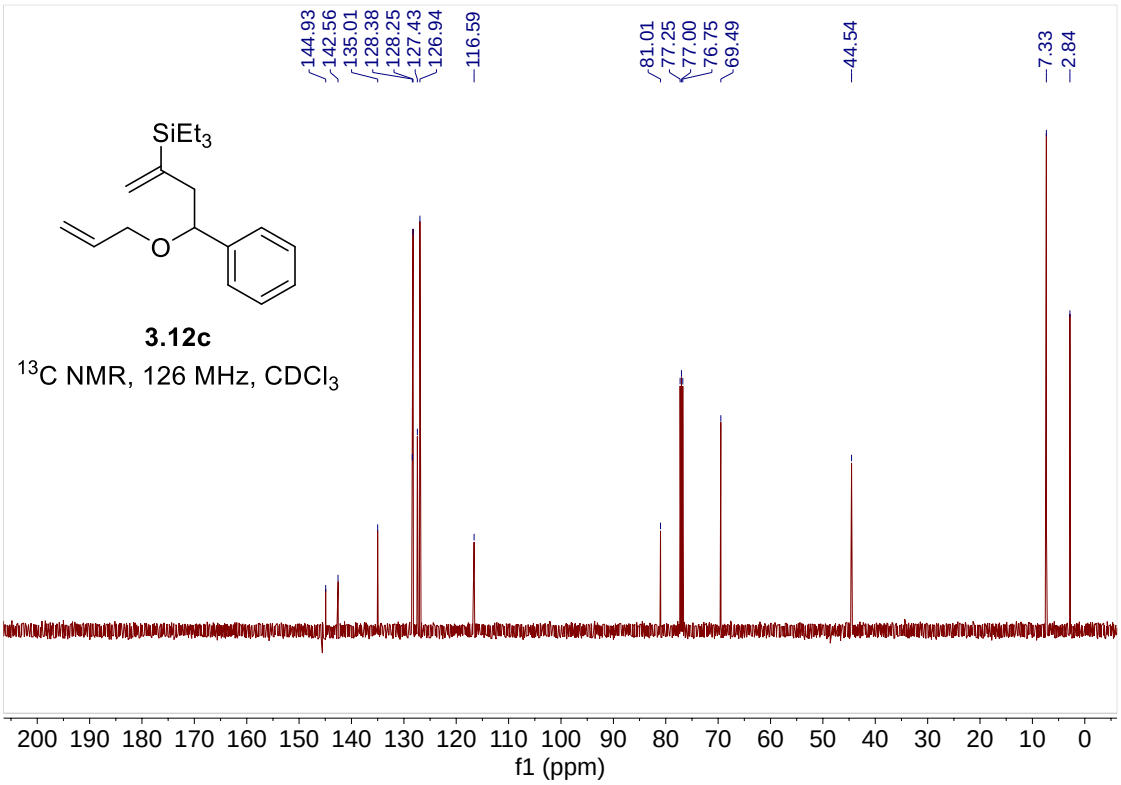

7.517
7.502
7.347
7.345
7.343
7.272
7.257
7.240
7.144
7.141
7.127
5.693
5.690
5.687
5.481
5.479
5.474
5.165
5.162
5.131
5.128
5.090
5.086
5.069
5.065
4.207
4.197
4.191
4.180
3.764
3.753
3.741
3.738
3.731
3.728
3.549
3.546
3.537
3.534
3.520
3.508
2.648
2.638
2.636
2.621
2.619
2.416
2.414
2.405
2.403
0.357
0.355
SiMe2Ph
O
3.12a
1H NMR, 500 MHz, CDCl3
1.78
2.72
1.94
0.95
1.88
0.90
1.00
0.99
0.95
0.96
0.98
0.98
0.98
1.00
0.98
5.14
f1 (ppm)

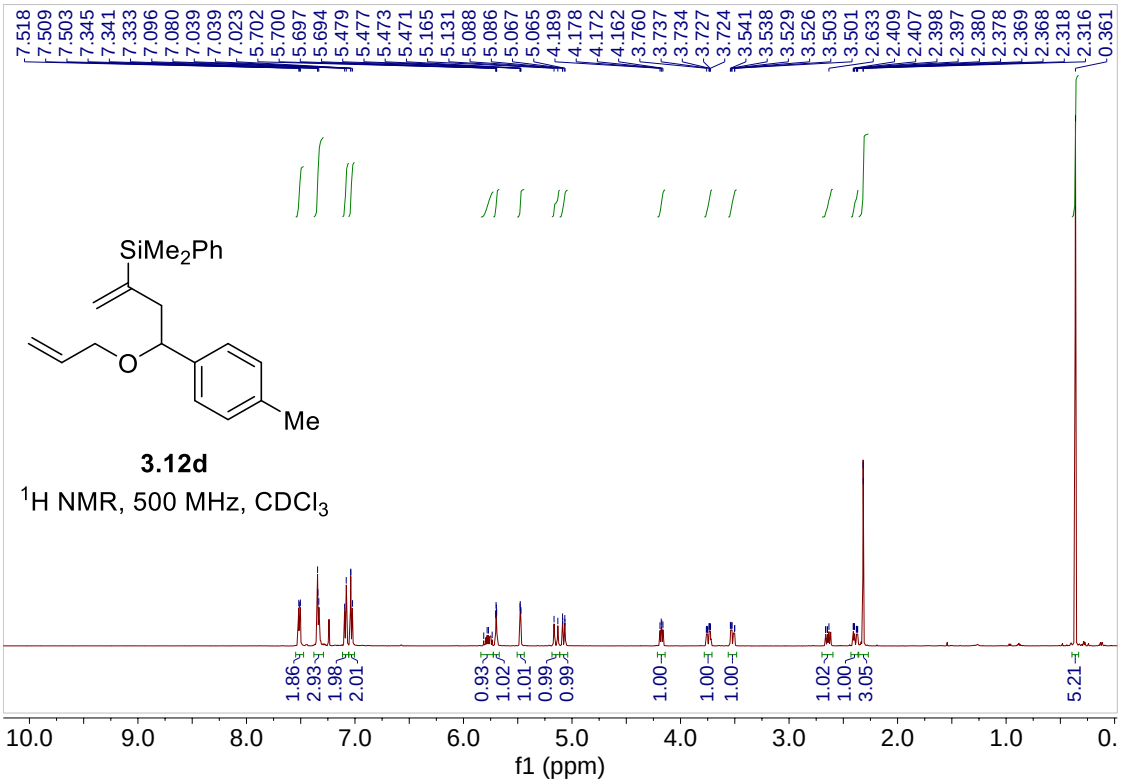

146.29
142.39
138.31
134.98
134.01
129.20
128.95
128.18
127.74
127.37
126.81
116.51
80.68
77.25
77.00
76.75
69.38
44.69
-2.92
-2.92
SiMe2Ph
O
3.12a
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

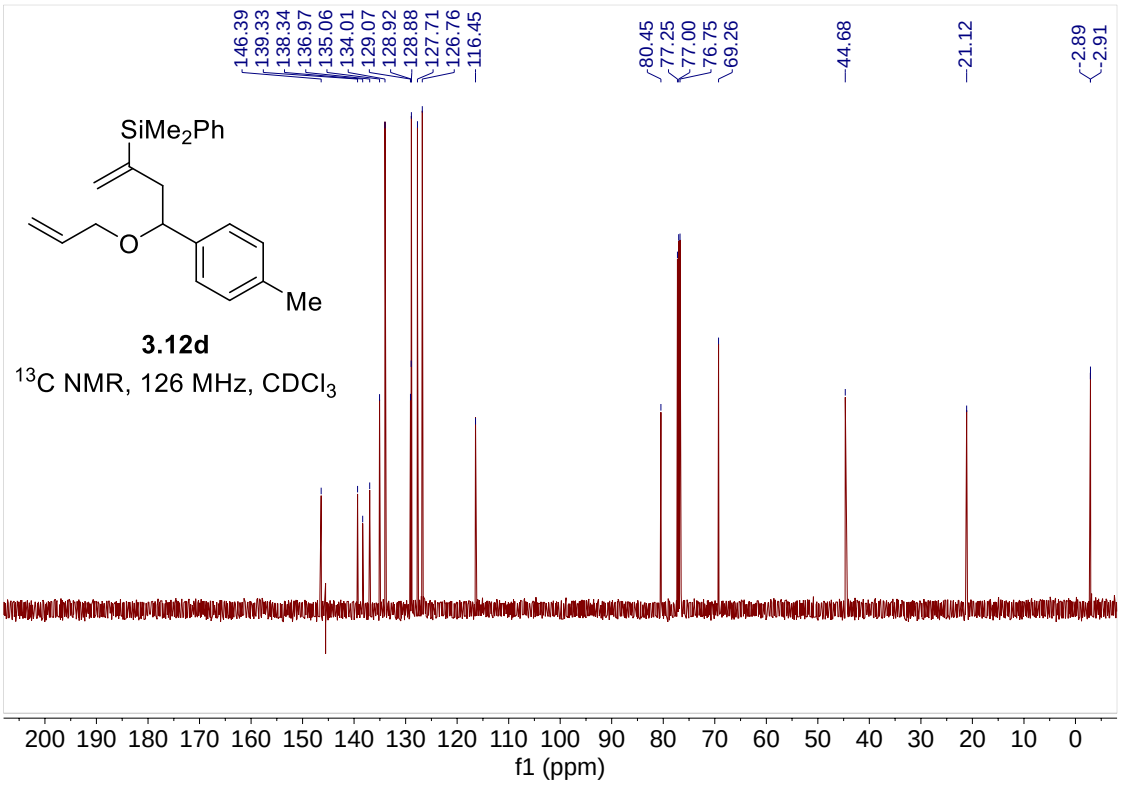

7.331
7.316
7.302
7.279
7.265
7.247
5.585
5.582
5.579
5.576
5.573
5.375
5.374
5.372
5.370
5.368
5.366
5.216
5.212
5.182
5.178
5.126
5.123
5.122
5.121
5.119
5.102
5.101
5.100
5.099
4.362
4.351
3.856
3.855
3.845
3.845
3.737
3.725
3.712
3.700
2.636
0.904
0.889
0.888
0.873
0.566
0.550
0.535
0.534
0.532
0.038
0.024
SiMe2Et
O
3.12b
1H NMR, 500 MHz, CDCl3
5.19
0.98
0.98
0.97
1.01
1.00
0.97
1.00
1.00
1.00
0.96
2.91
1.76
5.15
.0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

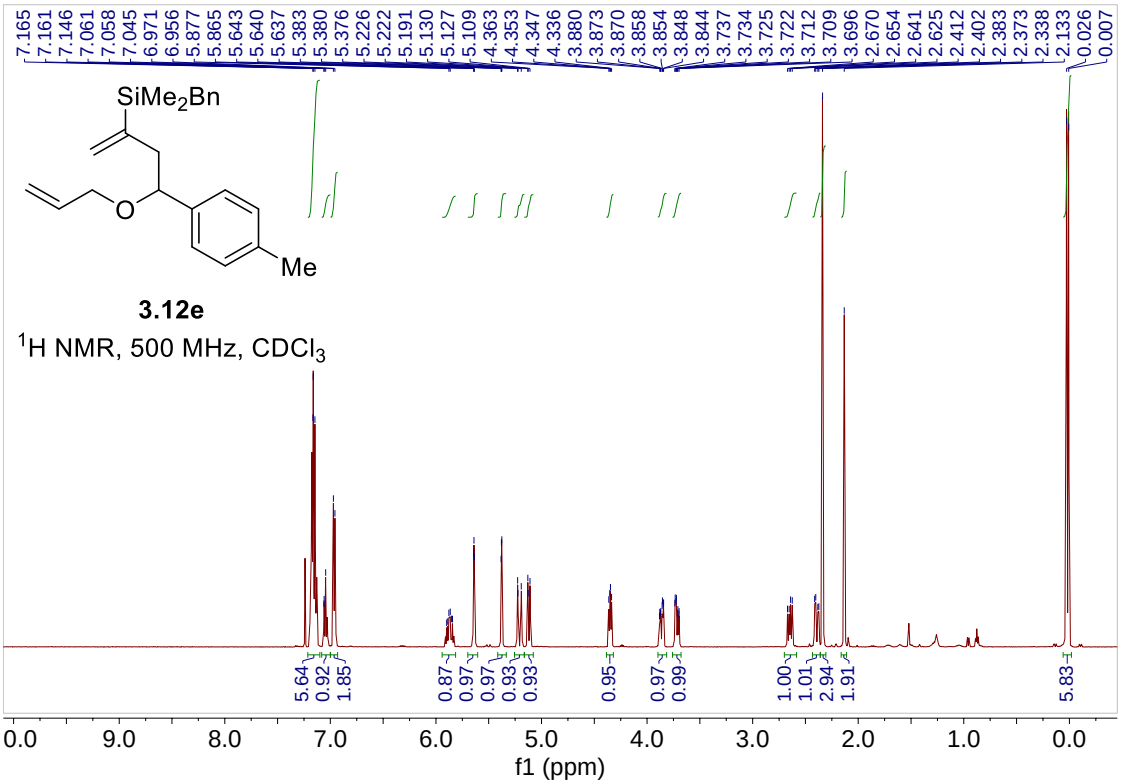

147.23
142.50
135.01
128.25
127.56
127.43
126.92
116.63
77.25
77.00
76.75
69.50
44.50
7.35
6.81
-3.72
-3.75
SiMe2Et
O
3.12b
1H NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.331
7.316
7.303
7.284
7.271
7.247
5.649
5.646
5.643
5.360
5.355
5.216
5.212
5.181
5.178
5.120
5.119
5.117
5.116
5.099
5.098
5.096
5.095
4.382
4.371
4.366
4.355
3.846
3.836
3.734
3.732
3.722
3.720
2.613
2.611
2.595
2.395
2.386
2.384
0.911
0.897
0.895
0.880
0.607
0.606
0.604
0.592
0.588
0.577
0.572
0.561
0.555
SiEt3
O
3.12c
1H NMR, 500 MHz, CDCl3
4.95
0.89
0.98
0.99
0.94
0.93
0.99
0.99
1.00
1.00
0.98
8.05
5.30
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.93
142.56
135.01
128.38
128.25
127.43
126.94
116.59
81.01
77.25
77.00
76.75
69.49
44.54
7.33
2.84
SiEt3
O
3.12c
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.518
7.509
7.503
7.345
7.341
7.333
7.096
7.080
7.039
7.039
7.023
5.702
5.700
5.697
5.694
5.479
5.477
5.473
5.471
5.165
5.131
5.088
5.086
5.067
5.065
4.189
4.178
4.172
4.162
3.760
3.737
3.734
3.727
3.724
3.541
3.538
3.529
3.526
3.503
3.501
2.633
2.409
2.407
2.398
2.397
2.380
2.378
2.369
2.368
2.318
2.316
0.361
SiMe2Ph
O
Me
3.12d
1H NMR, 500 MHz, CDCl3
1.86
2.93
1.98
2.01
0.93
1.02
1.01
0.99
0.99
1.00
1.00
1.00
1.02
1.00
3.05
5.21
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.
f1 (ppm)


146.39
139.33
138.34
136.97
135.06
134.01
129.07
128.92
128.88
127.71
126.76
116.45
80.45
77.25
77.00
76.75
69.26
44.68
21.12
2.89
2.91
SiMe2Ph
O
Me
3.12d
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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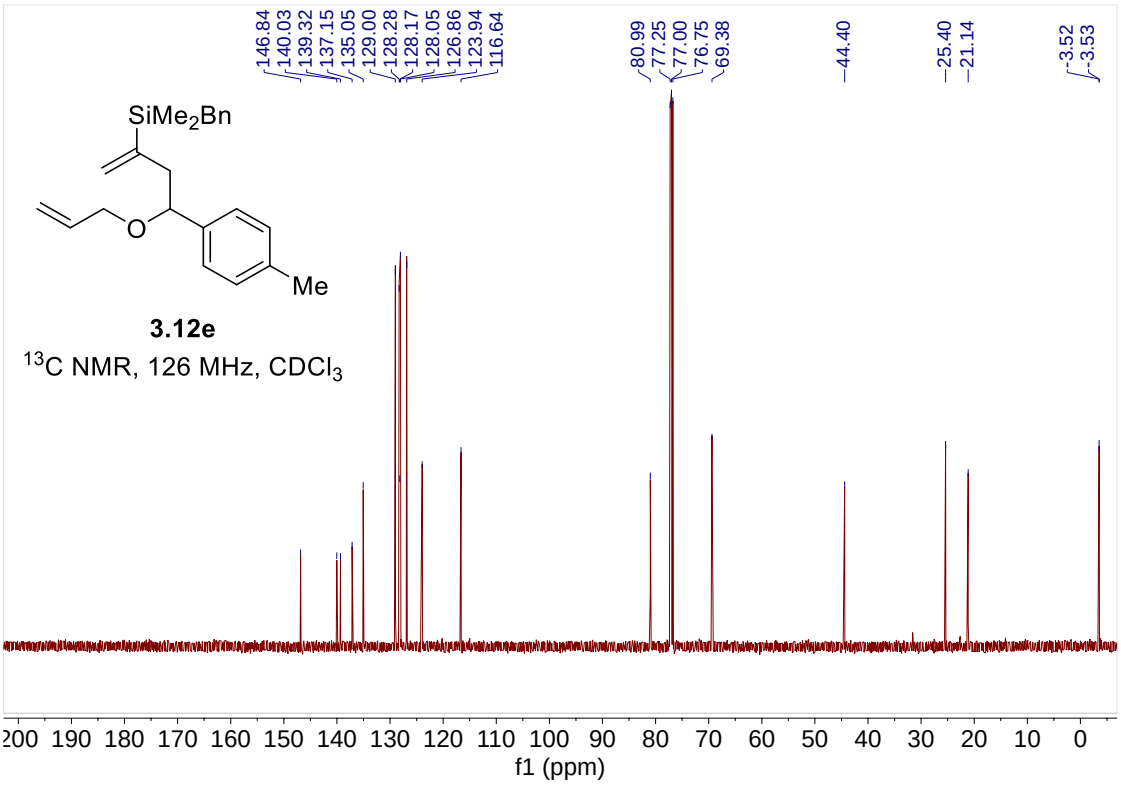
7.161
7.146
7.061
7.058
7.045
6.971
6.956
5.877
5.865
5.643
5.640
5.637
5.383
5.380
5.376
5.226
5.222
5.191
5.130
5.127
5.109
4.363
4.353
4.347
4.336
3.880
3.873
3.870
3.858
3.854
3.848
3.844
3.737
3.734
3.725
3.722
3.712
3.709
3.696
2.670
2.654
2.641
2.625
2.412
2.402
2.383
2.373
2.338
2.133
0.026
0.007
SiMe2Bn
O
Me
3.12e
1H NMR, 500 MHz, CDCl3
5.64
0.92
1.85
0.87
0.97
0.97
0.93
0.93
0.95
0.97
0.99
1.00
1.01
2.94
1.91
5.83
0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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140.03
139.32
137.15
135.05
129.00
128.28
128.17
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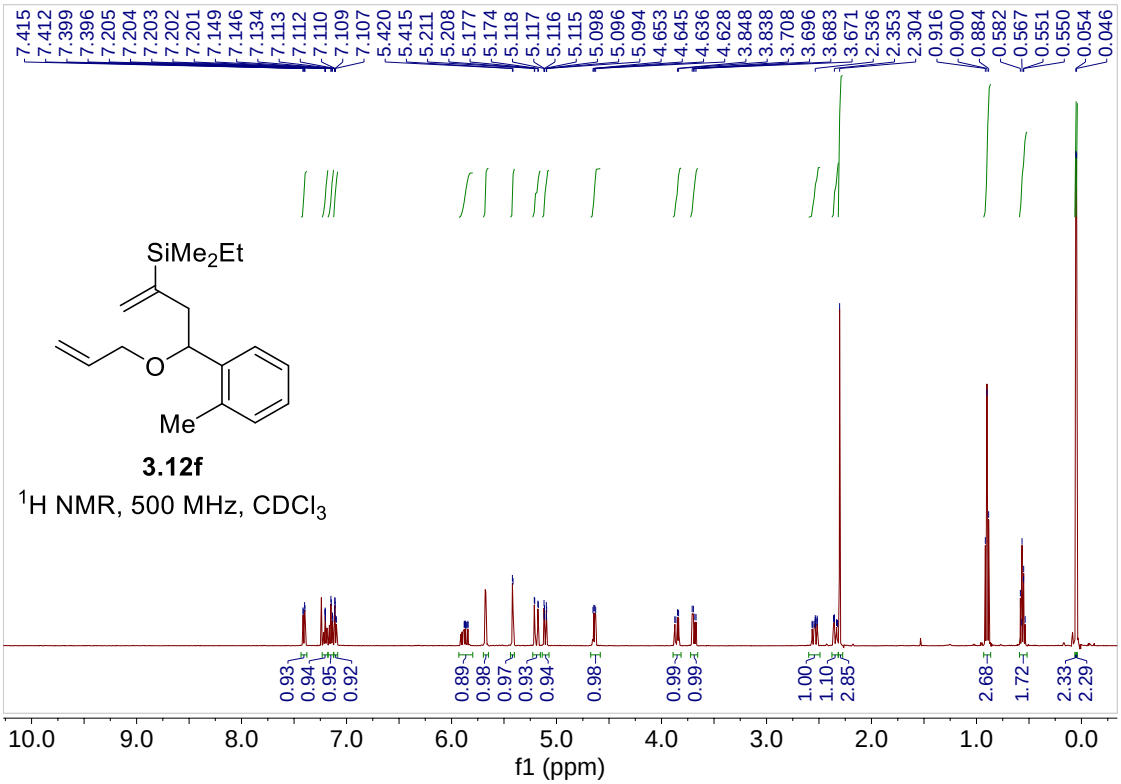
126.86
123.94
116.64
80.99
77.25
77.00
76.75
69.38
44.40
25.40
21.14
3.52
3.53
SiMe2Bn
O
Me
3.12e
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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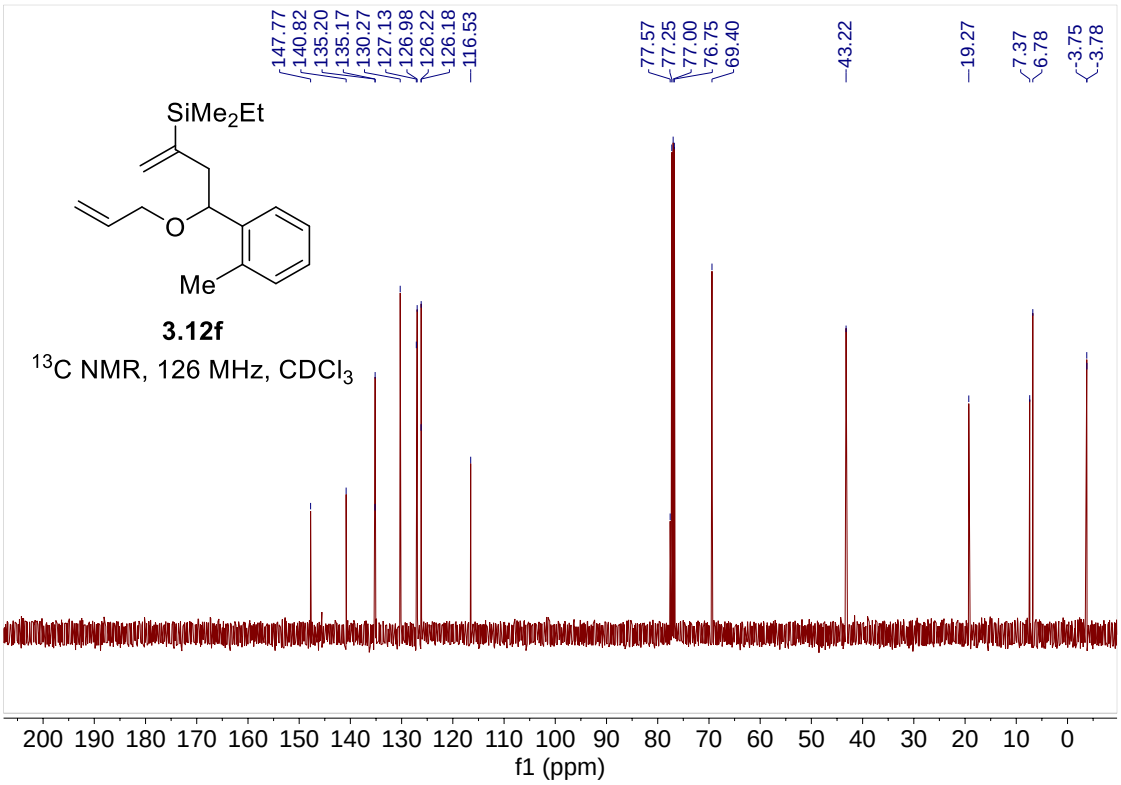
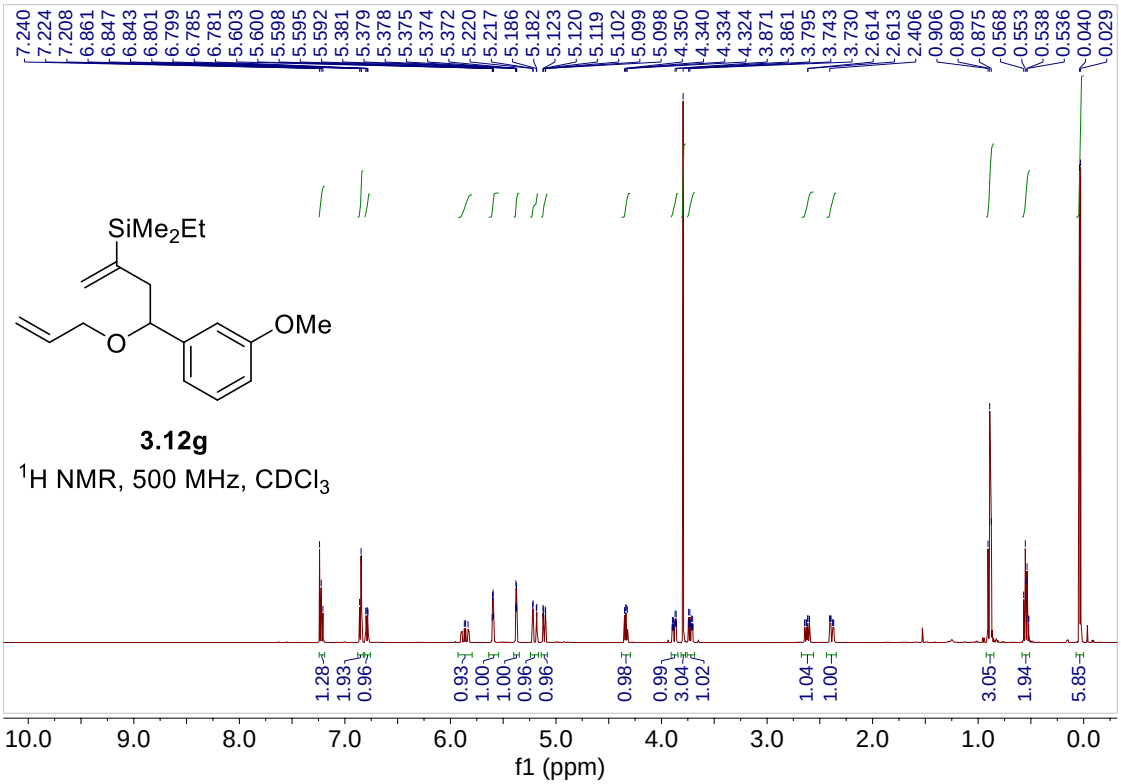
7.412
7.399
7.396
7.205
7.204
7.203
7.202
7.201
7.149
7.146
7.134
7.113
7.112
7.110
7.109
7.107
5.420
5.415
5.211
5.208
5.177
5.174
5.118
5.117
5.116
5.115
5.098
5.096
5.094
4.653
4.645
4.636
4.628
3.848
3.838
3.708
3.696
3.683
3.671
2.536
2.353
2.304
0.916
0.900
0.884
0.582
0.567
0.551
0.550
0.054
0.046
SiMe2Et
O
Me
3.12f
1H NMR, 500 MHz, CDCl3
0.93
0.94
0.95
0.92
0.89
0.98
0.97
0.93
0.94
0.98
0.99
0.99
1.00
1.10
2.85
2.68
1.72
2.33
2.29
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


147.77
140.82
135.20
135.17
130.27
127.13
126.98
126.22
126.18
116.53
77.57
77.25
77.00
76.75
69.40
43.22
19.27
7.37
6.78
3.75
3.78
SiMe2Et
O
Me
3.12f
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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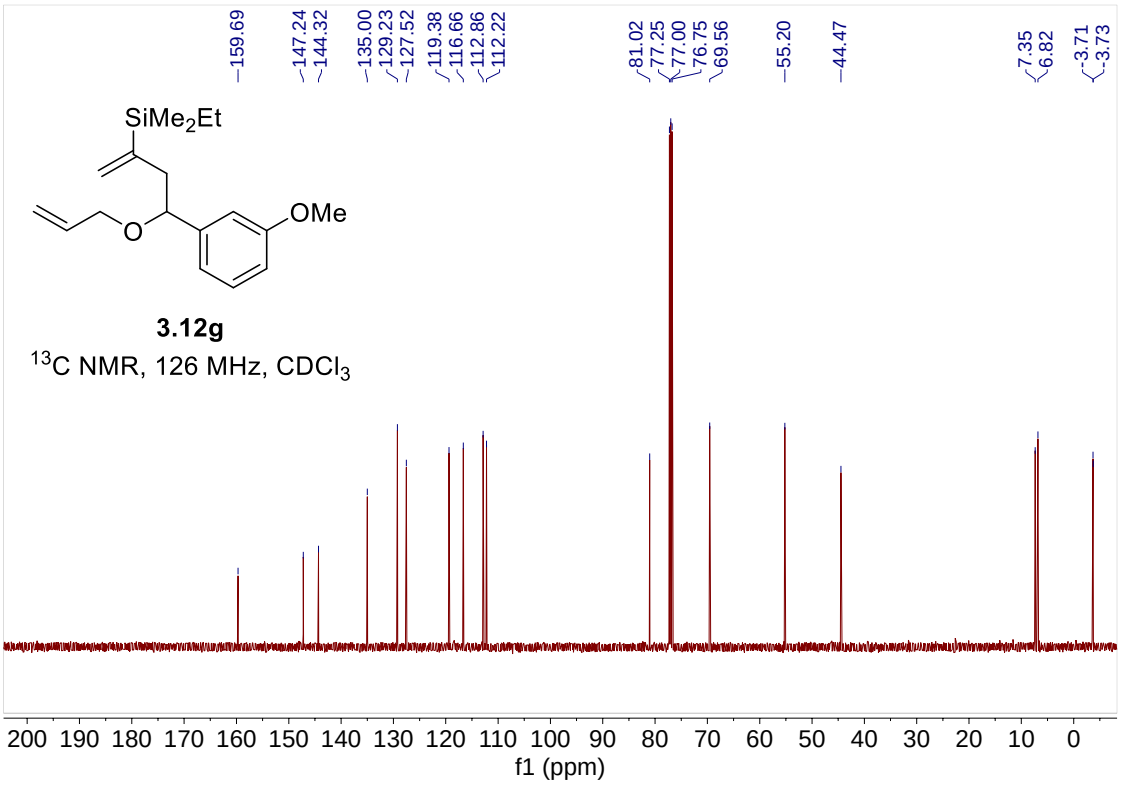
7.224
7.208
6.861
6.847
6.843
6.801
6.799
6.785
6.781
6.603
5.600
5.598
5.595
5.592
5.381
5.379
5.378
5.375
5.374
5.372
5.220
5.217
5.186
5.182
5.123
5.120
5.119
5.102
5.099
5.098
4.350
4.340
4.334
4.324
3.871
3.861
3.795
3.743
3.730
2.614
2.613
2.406
0.906
0.890
0.875
0.568
0.553
0.538
0.536
0.040
0.029
SiMe2Et
O
OMe
3.12g
1H NMR, 500 MHz, CDCl3
1.28
1.93
0.96
0.93
1.00
1.00
0.96
0.96
0.98
0.99
3.04
1.02
1.04
1.00
3.05
1.94
5.85
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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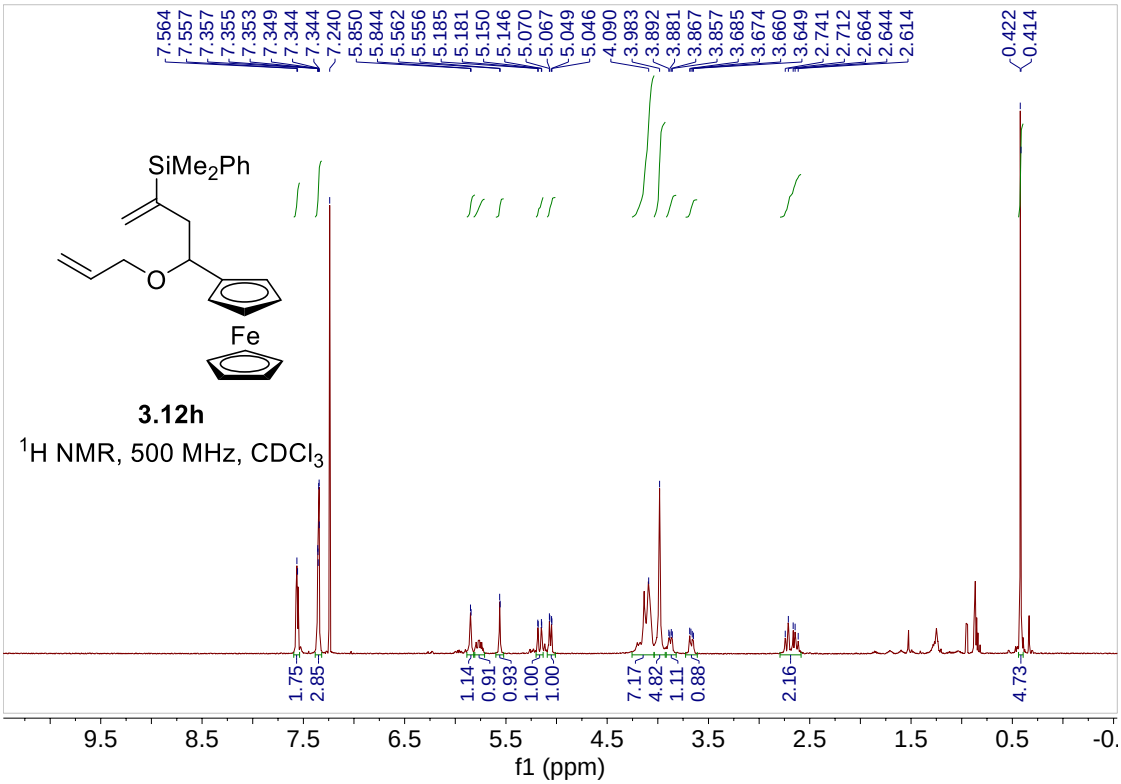
147.24
144.32
135.00
129.23
127.52
119.38
116.66
112.86
112.22
81.02
77.25
77.00
76.75
69.56
55.20
44.47
7.35
6.82
3.71
3.73
SiMe2Et
OMe
O
3.12g
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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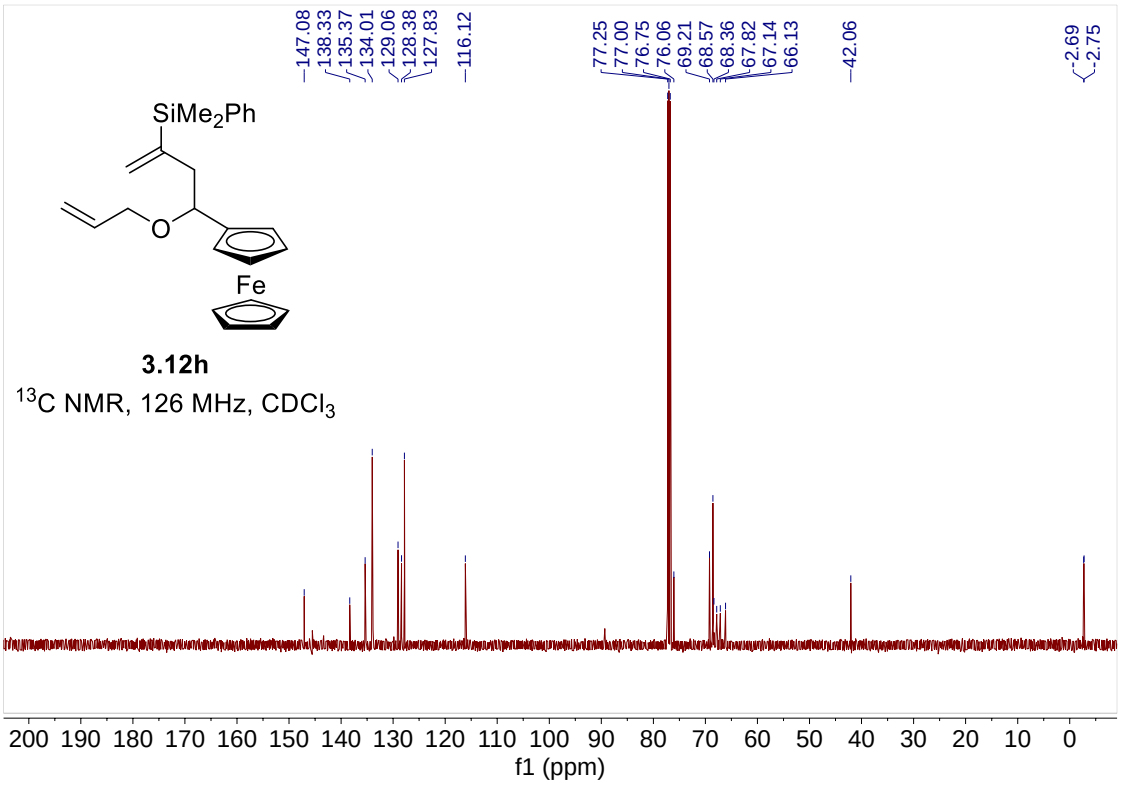
7.557
7.357
7.355
7.353
7.349
7.344
7.344
7.240
5.850
5.844
5.562
5.556
5.185
5.181
5.150
5.146
5.070
5.067
5.049
5.046
4.090
3.983
3.892
3.881
3.867
3.857
3.685
3.674
3.660
3.649
2.741
2.712
2.664
2.644
2.614
0.422
0.414
SiMe2Ph
O
Fe
3.12h
1H NMR, 500 MHz, CDCl3
1.75
2.85
1.14
0.91
0.93
1.00
1.00
7.17
4.82
1.11
0.88
2.16
4.73
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)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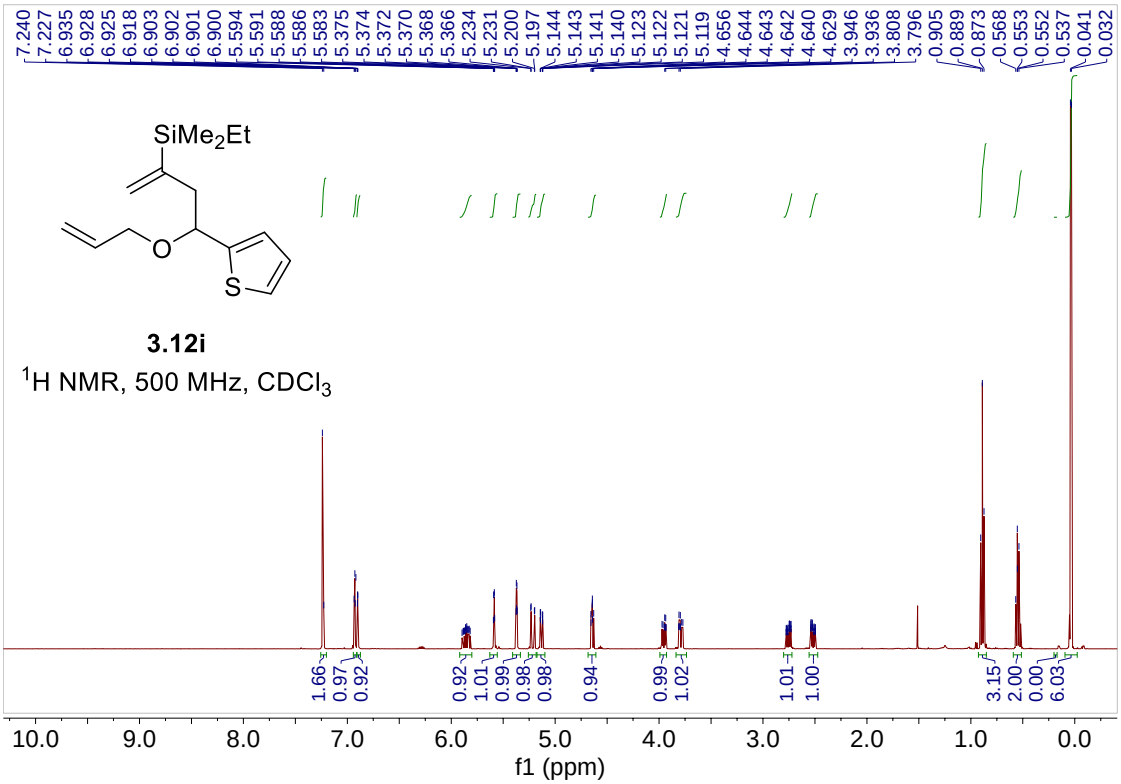
138.33
135.37
134.01
129.06
128.38
127.83
116.12
77.25
77.00
76.75
76.06
69.21
68.57
68.36
67.82
67.14
66.13
42.06
2.69
2.75
SiMe2Ph
O
Fe
3.12h
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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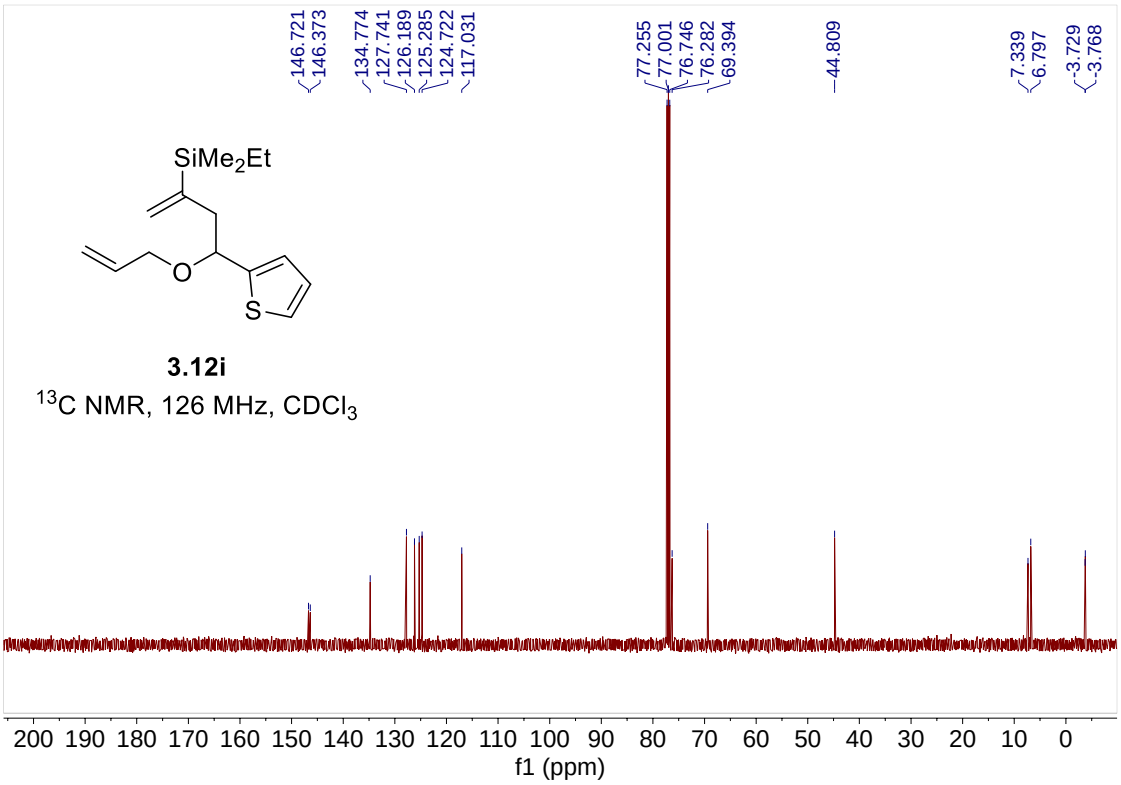
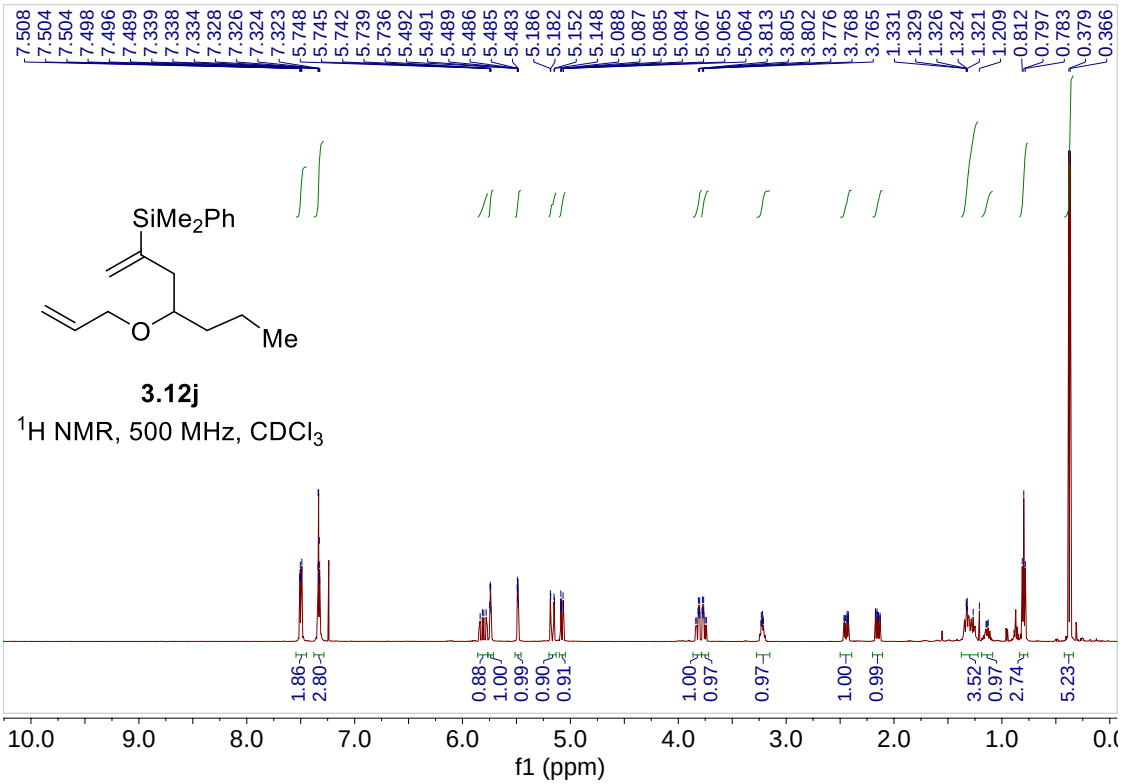
7.227
6.935
6.928
6.925
6.918
6.903
6.902
6.901
6.900
5.594
5.591
5.588
5.586
5.583
5.375
5.374
5.372
5.370
5.368
5.366
5.234
5.231
5.200
5.197
5.144
5.143
5.141
5.140
5.123
5.122
5.121
5.119
4.656
4.644
4.643
4.642
4.640
4.629
3.946
3.936
3.808
3.796
0.905
0.889
0.873
0.568
0.553
0.552
0.537
0.041
0.032
SiMe2Et
O
S
3.12i
1H NMR, 500 MHz, CDCl3
1.66
0.97
0.92
0.92
1.01
0.99
0.98
0.98
0.94
0.99
1.02
1.01
1.00
3.15
2.00
0.00
6.03
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)



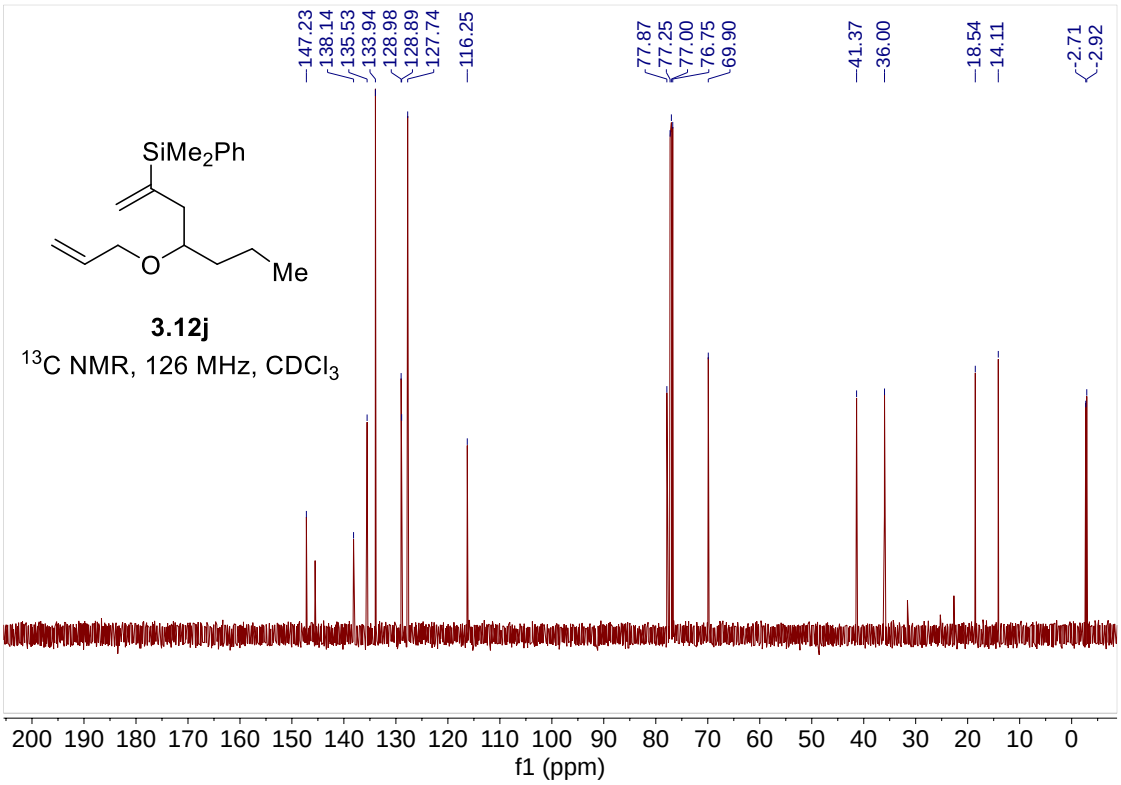
3.12i

^{13}C NMR, 126 MHz, $CDCl_3$



3.12j

^{1}H NMR, 500 MHz, $CDCl_3$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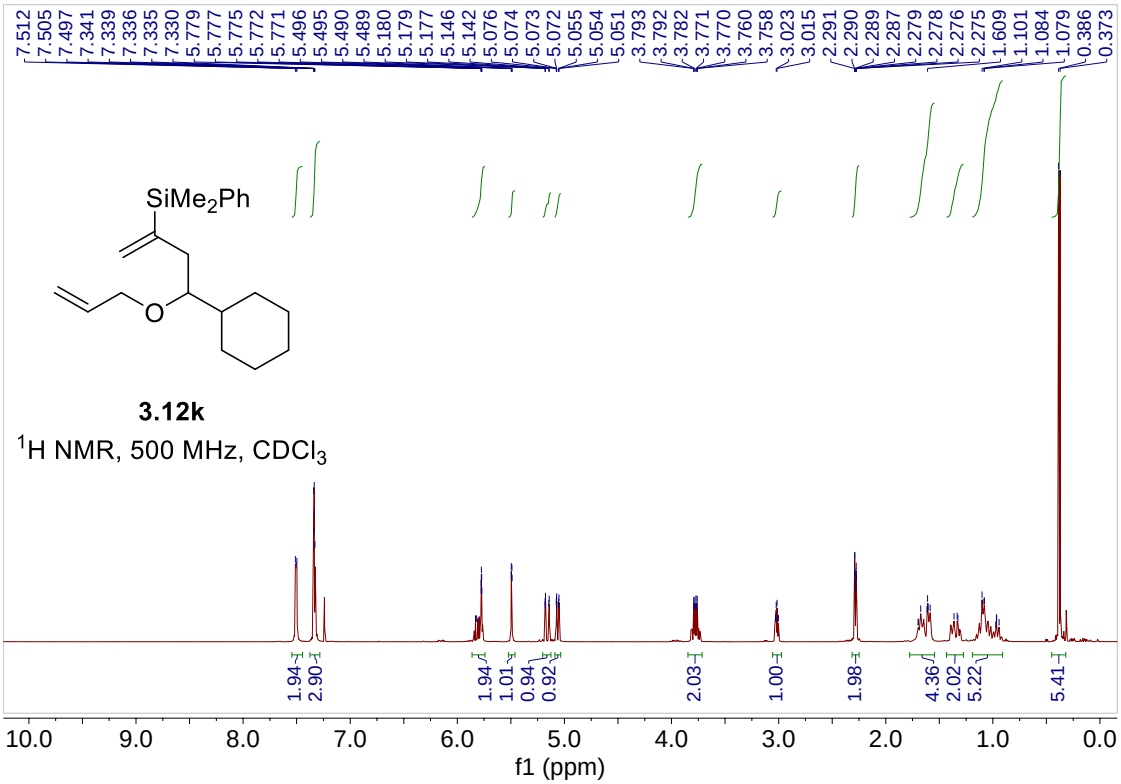
138.14
135.53
133.94
128.98
128.89
127.74
116.25
77.87
77.25
77.00
76.75
69.90
41.37
36.00
18.54
14.11
2.71
2.92
SiMe2Ph
O
Me
3.12j
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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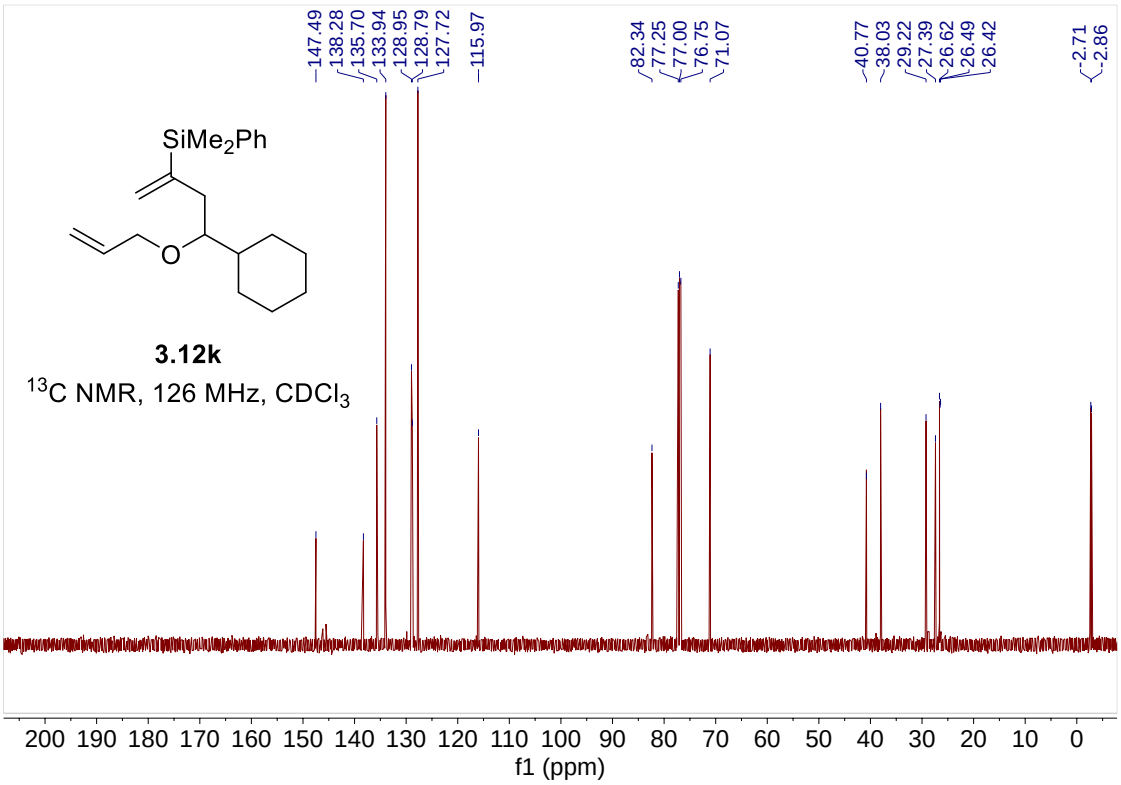
7.505
7.497
7.341
7.339
7.336
7.335
7.330
5.779
5.777
5.775
5.772
5.771
5.496
5.495
5.490
5.489
5.180
5.179
5.177
5.146
5.142
5.076
5.074
5.073
5.072
5.055
5.054
5.051
3.793
3.792
3.782
3.771
3.770
3.760
3.758
3.023
3.015
2.291
2.290
2.289
2.287
2.279
2.278
2.276
2.275
1.609
1.101
1.084
1.079
0.386
0.373
SiMe2Ph
O
3.12k
1H NMR, 500 MHz, CDCl3
1.94
2.90
1.94
1.01
0.94
0.92
2.03
1.00
1.98
4.36
2.02
5.22
5.41
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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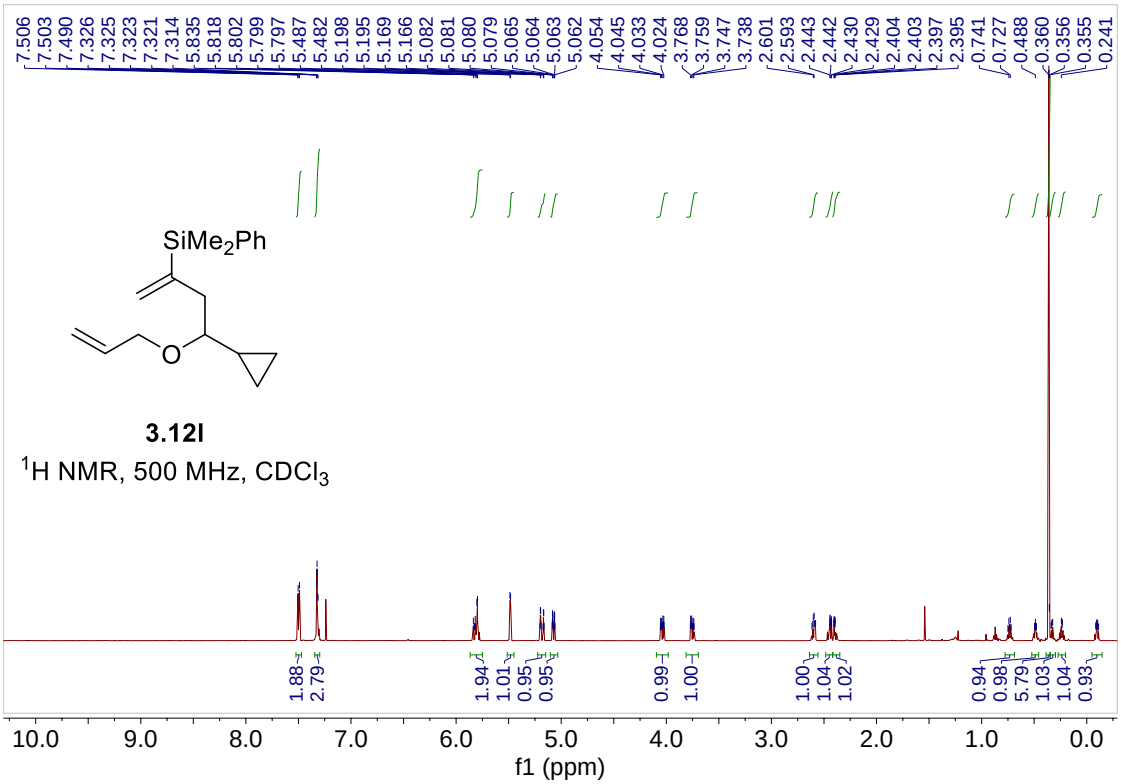
138.28
135.70
133.94
128.95
128.79
127.72
115.97
82.34
77.25
77.00
76.75
71.07
40.77
38.03
29.22
27.39
26.62
26.49
26.42
2.71
2.86
SiMe2Ph
O
3.12k
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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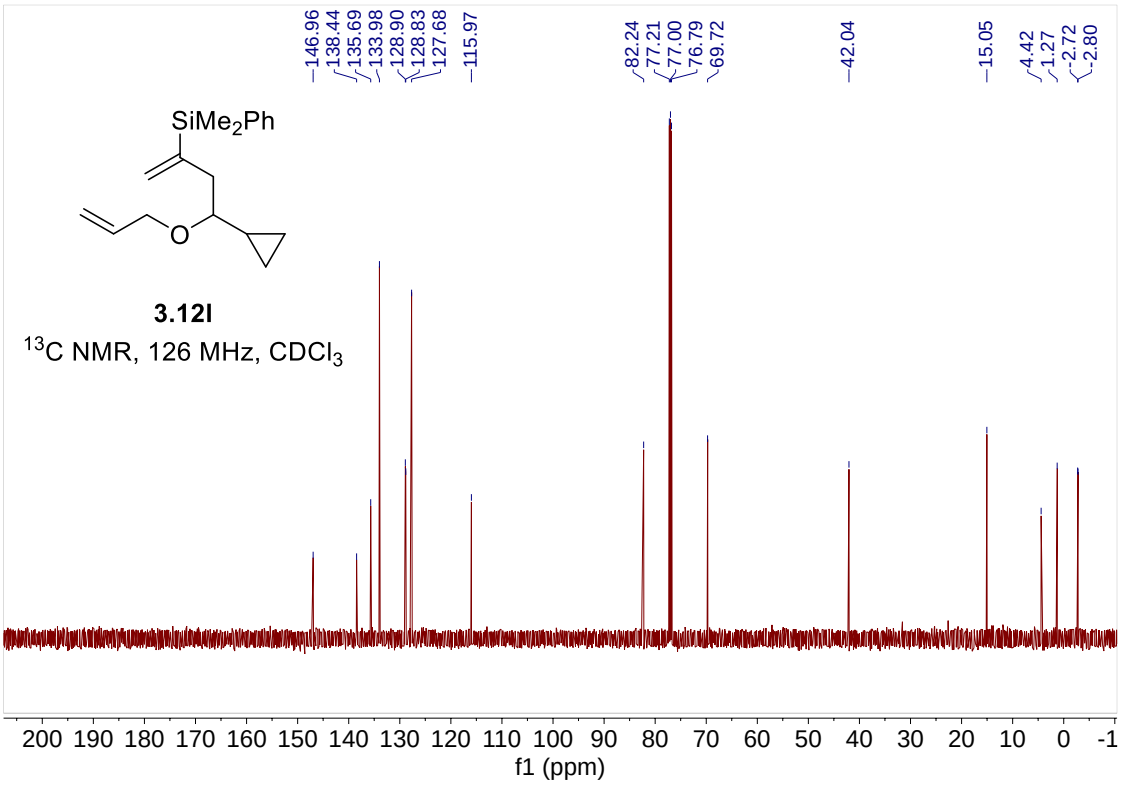
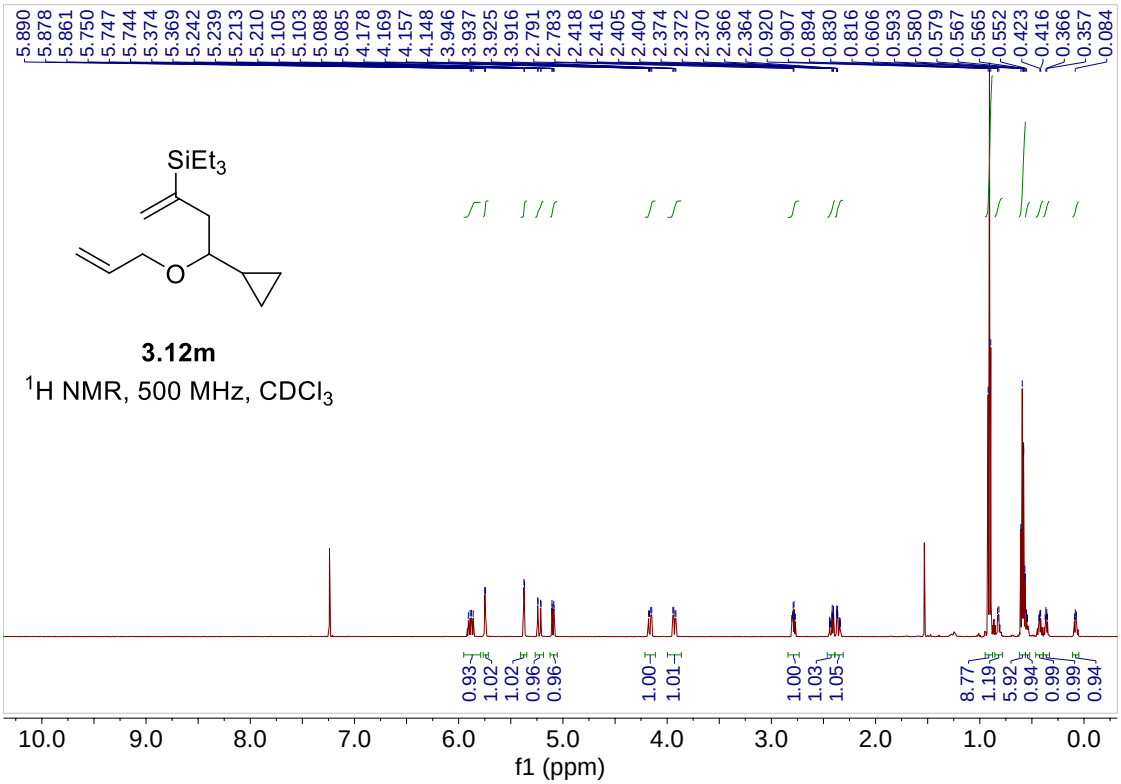
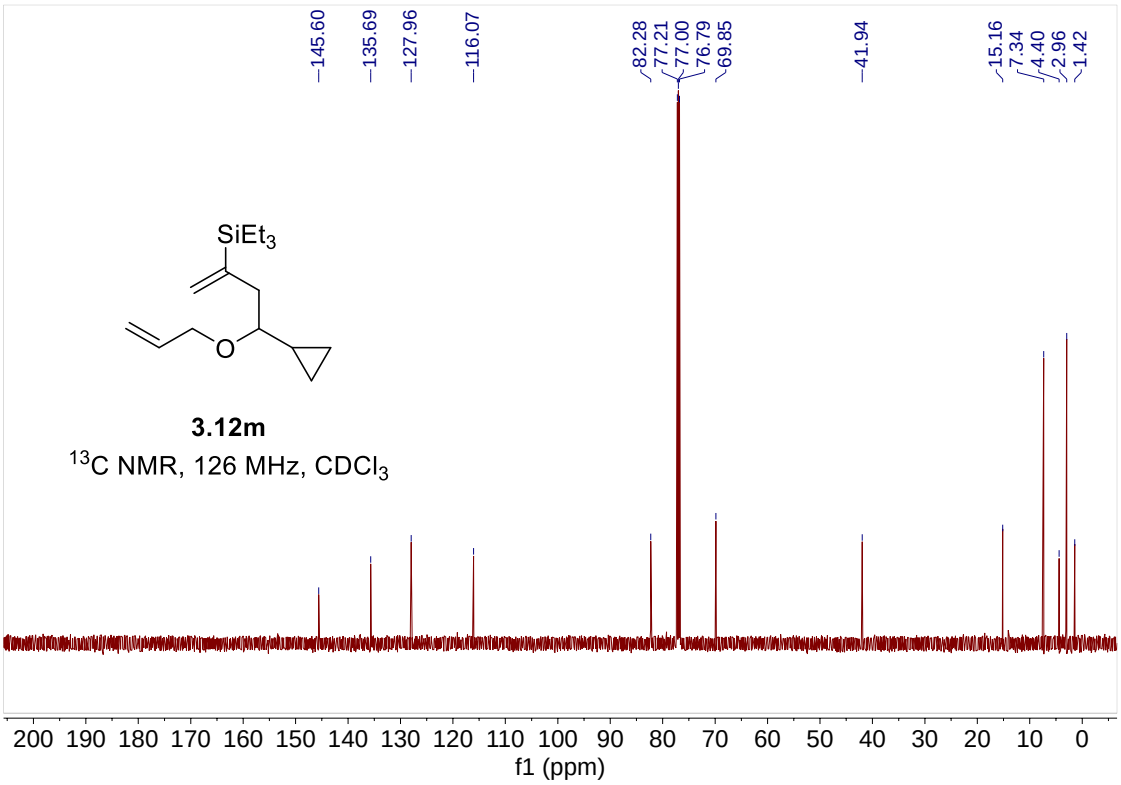
7.503
7.490
7.326
7.325
7.323
7.321
7.314
5.835
5.818
5.802
5.799
5.797
5.487
5.482
5.198
5.195
5.169
5.166
5.082
5.081
5.080
5.079
5.065
5.064
5.063
5.062
4.054
4.045
4.033
4.024
3.768
3.759
3.747
3.738
2.601
2.593
2.443
2.442
2.430
2.429
2.404
2.403
2.397
2.395
0.741
0.727
0.488
0.360
0.356
0.355
0.241
SiMe2Ph
O
3.12l
1H NMR, 500 MHz, CDCl3
1.88
2.79
1.94
1.01
0.95
0.95
0.99
1.00
1.00
1.04
1.02
0.94
0.98
5.79
1.03
1.04
0.93
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


SiMe2Ph
O
3.12l
13C NMR, 126 MHz, CDCl3
f1 (ppm)


SiEt3
O
3.12m
1H NMR, 500 MHz, CDCl3
f1 (ppm)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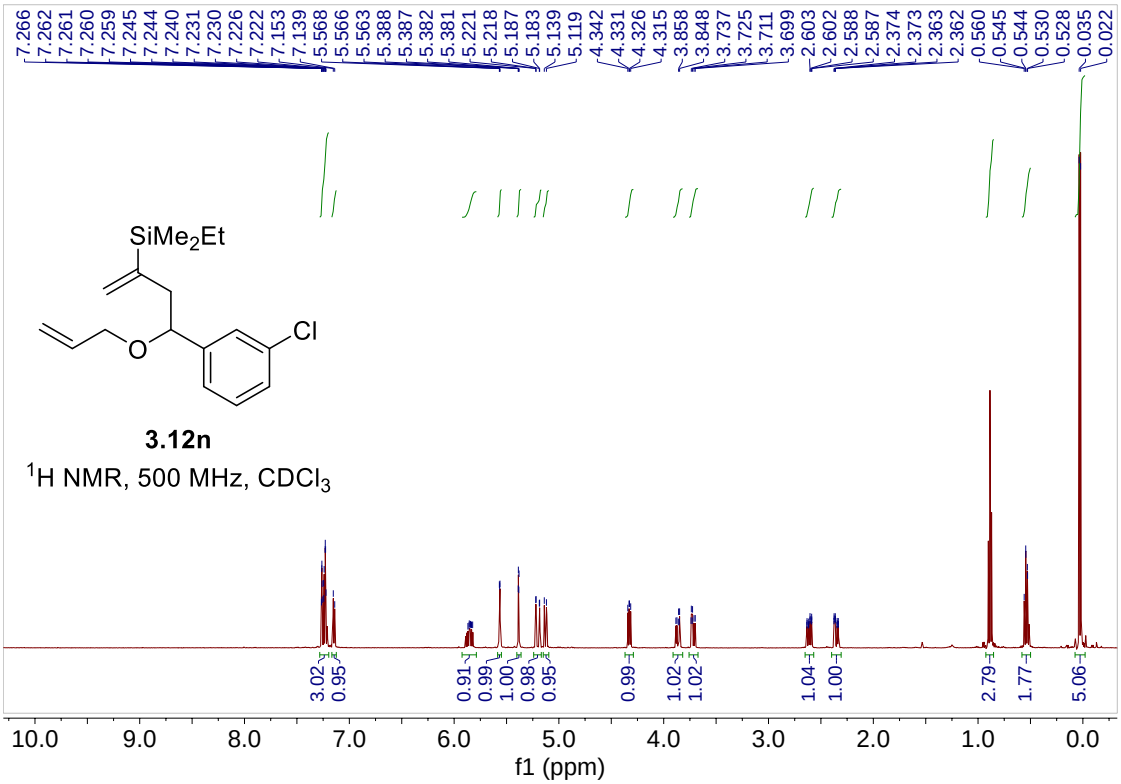
135.69
127.96
116.07
82.28
77.21
77.00
76.79
69.85
41.94
15.16
7.34
4.40
2.96
1.42
SiEt3
O
3.12m
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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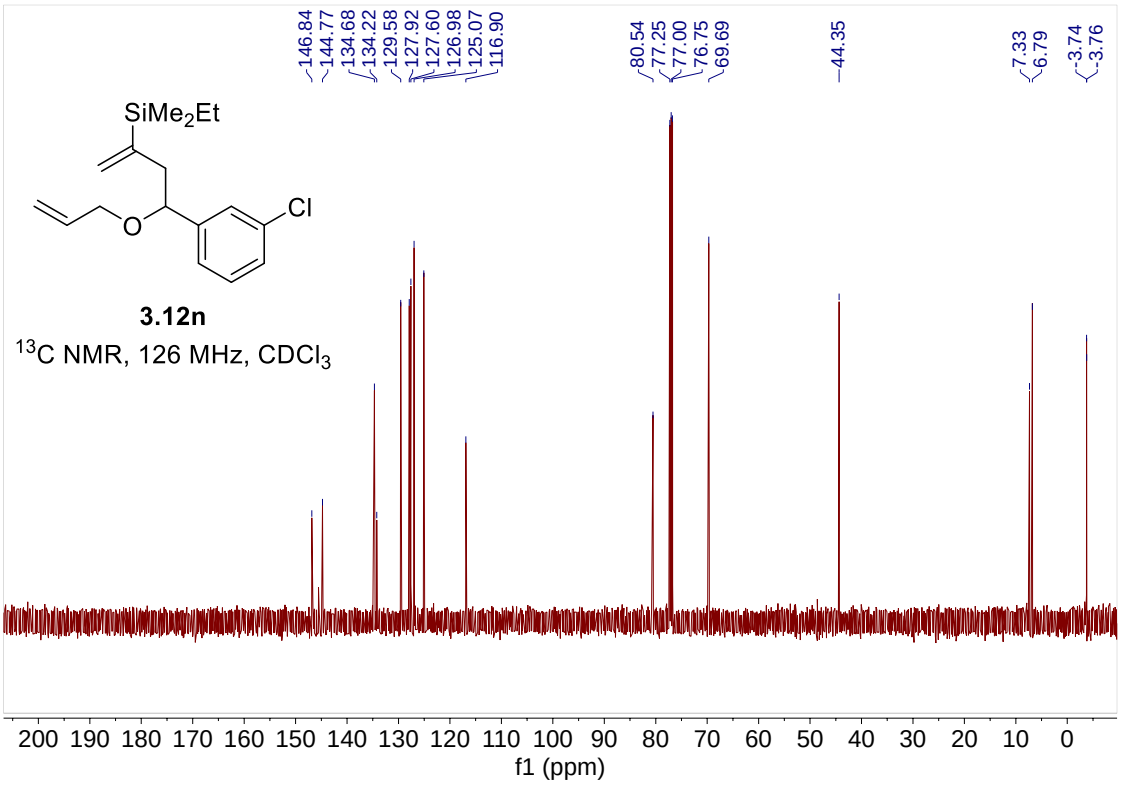
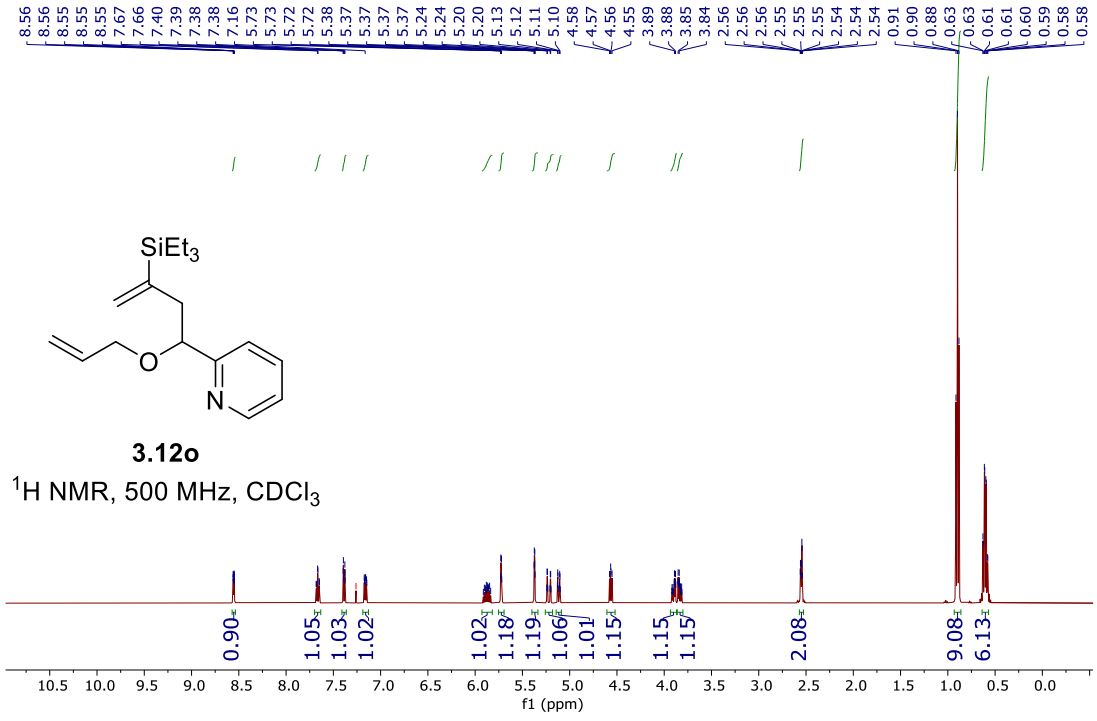
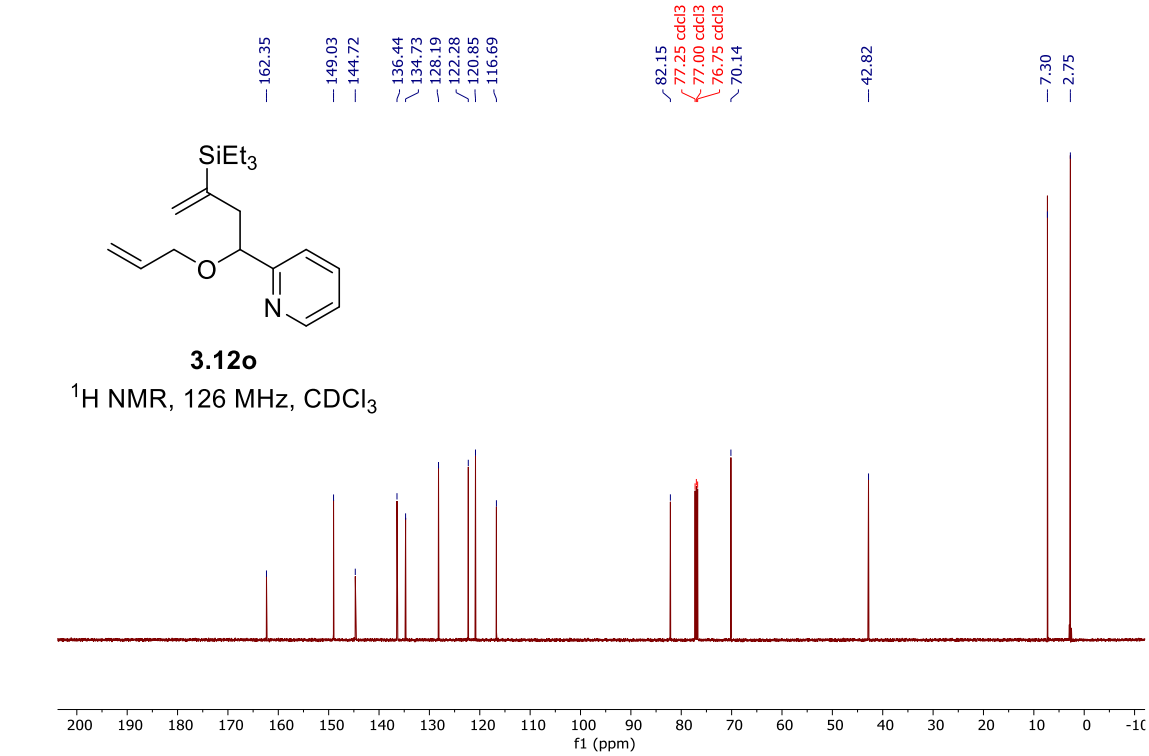
7.262
7.261
7.260
7.259
7.245
7.244
7.240
7.231
7.230
7.226
7.222
7.153
7.139
5.568
5.566
5.563
5.388
5.387
5.382
5.381
5.221
5.218
5.187
5.183
5.139
5.119
4.342
4.331
4.326
4.315
3.858
3.848
3.737
3.725
3.711
3.699
2.603
2.602
2.588
2.587
2.374
2.373
2.363
2.362
0.560
0.545
0.544
0.530
0.528
0.035
0.022
SiMe2Et
Cl
O
3.12n
1H NMR, 500 MHz, CDCl3
3.02
0.95
0.91
0.99
1.00
0.98
0.95
0.99
1.02
1.02
1.04
1.00
2.79
1.77
5.06
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

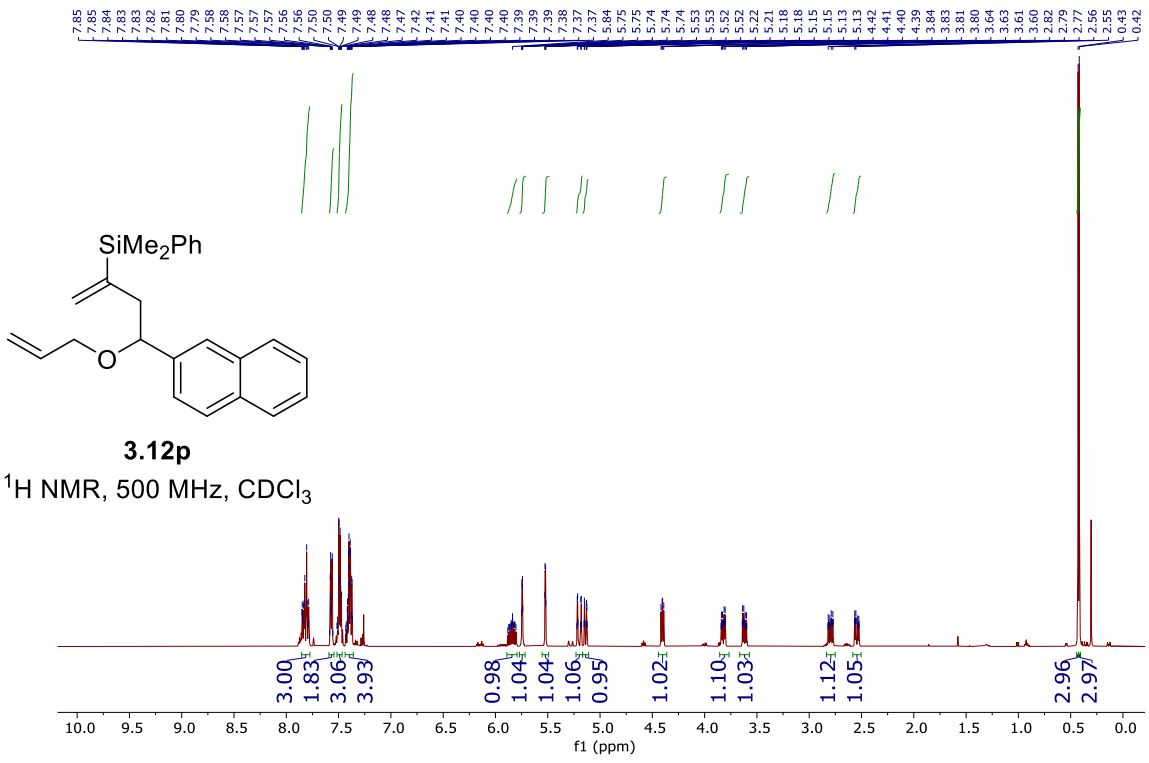

SiMe2Et
Cl
O
3.12n
13C NMR, 126 MHz, CDCl3
146.84
144.77
134.68
134.22
129.58
127.92
127.60
126.98
125.07
116.90
80.54
77.25
77.00
76.75
69.69
44.35
7.33
6.79
3.74
3.76
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


SiEt3
O
N
3.12o
1H NMR, 500 MHz, CDCl3
0.90
1.05
1.03
1.02
1.02
1.18
1.19
1.06
1.01
1.15
1.15
1.15
2.08
9.08
6.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



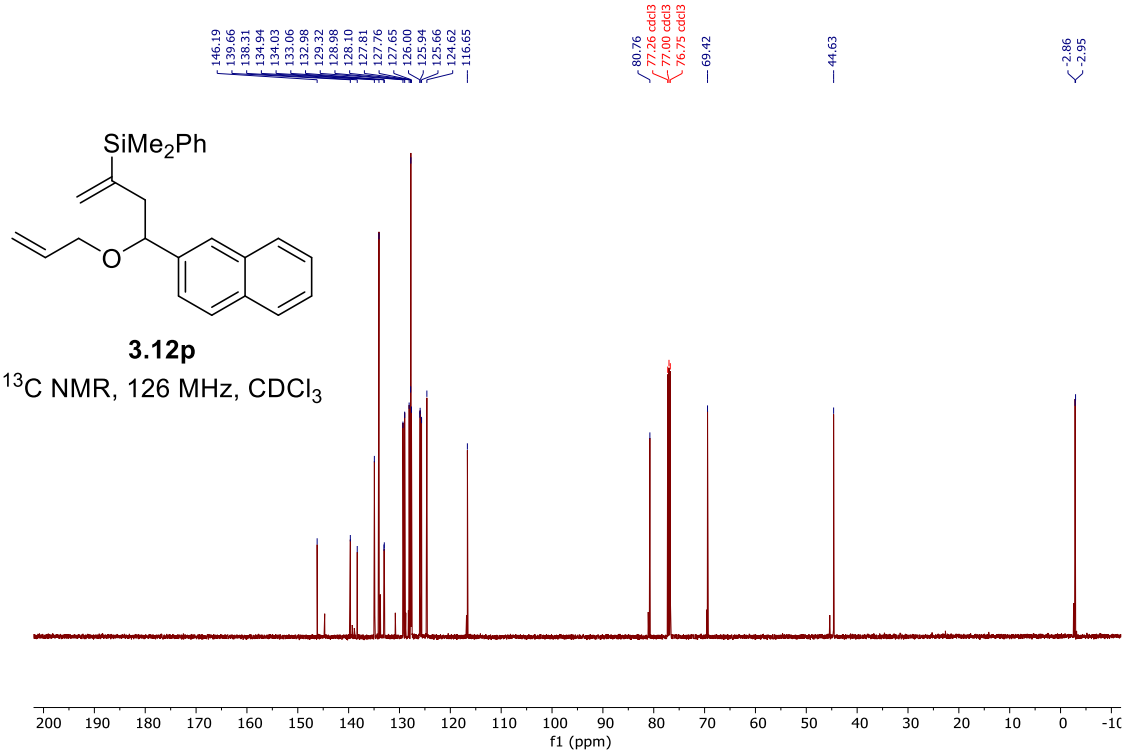
3.12o

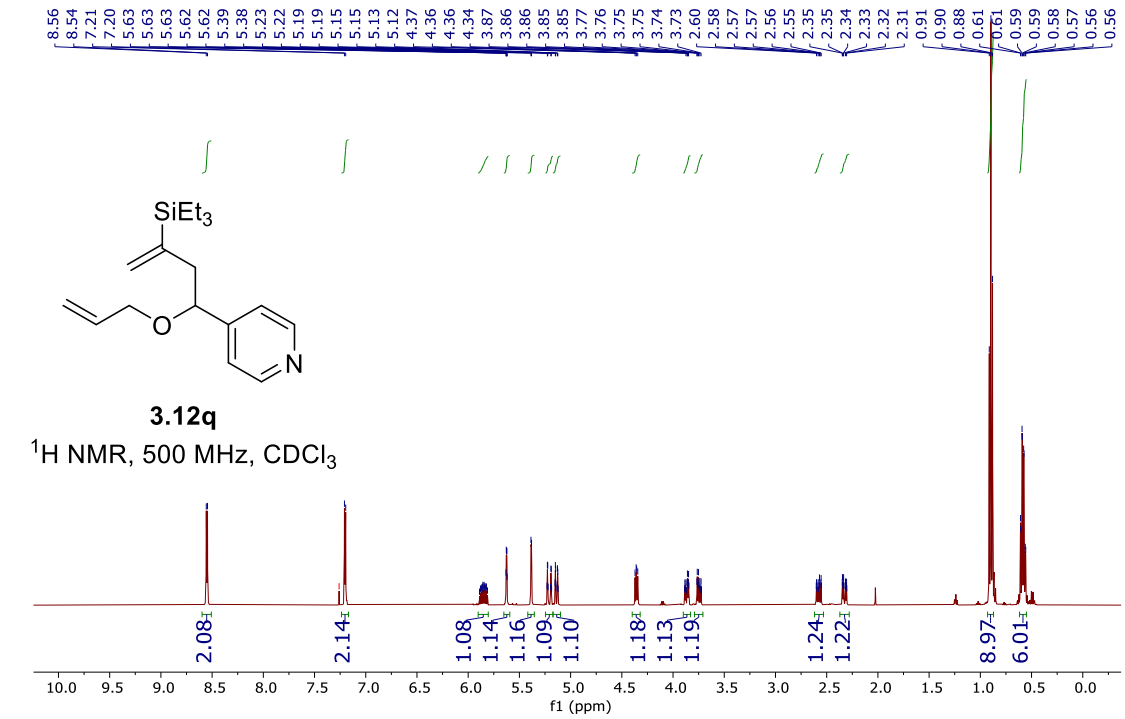
^{1}H NMR, 126 MHz, $CDCl_3$

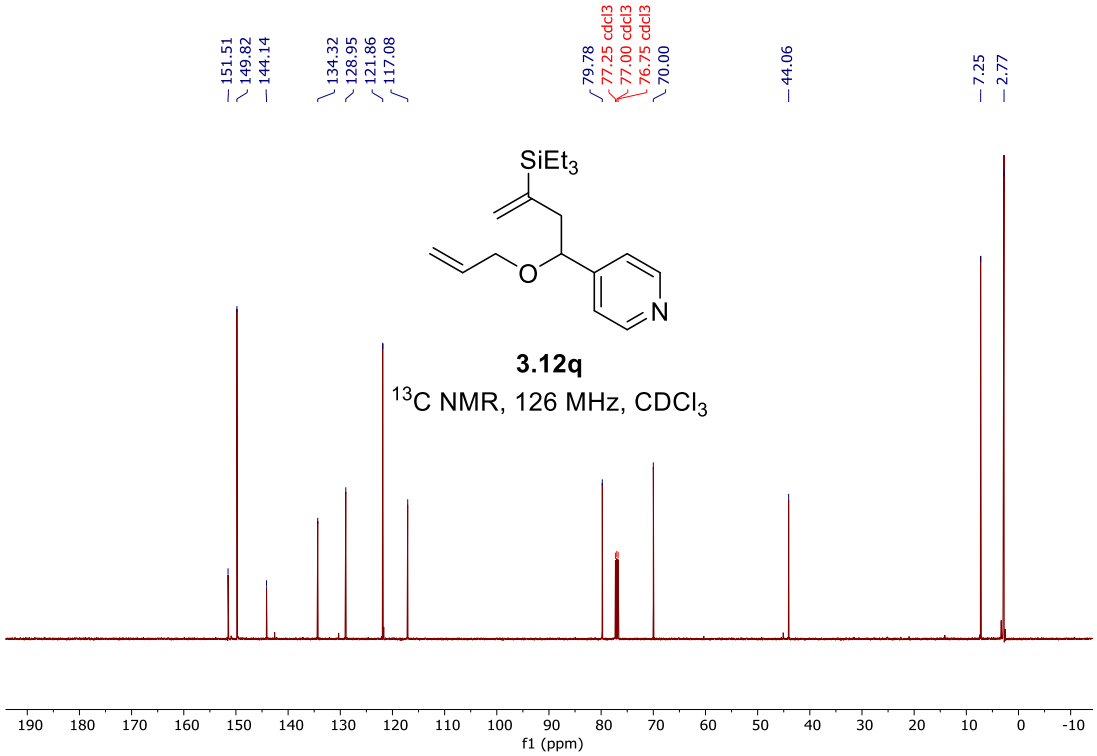


3.12p

^{1}H NMR, 500 MHz, $CDCl_3$

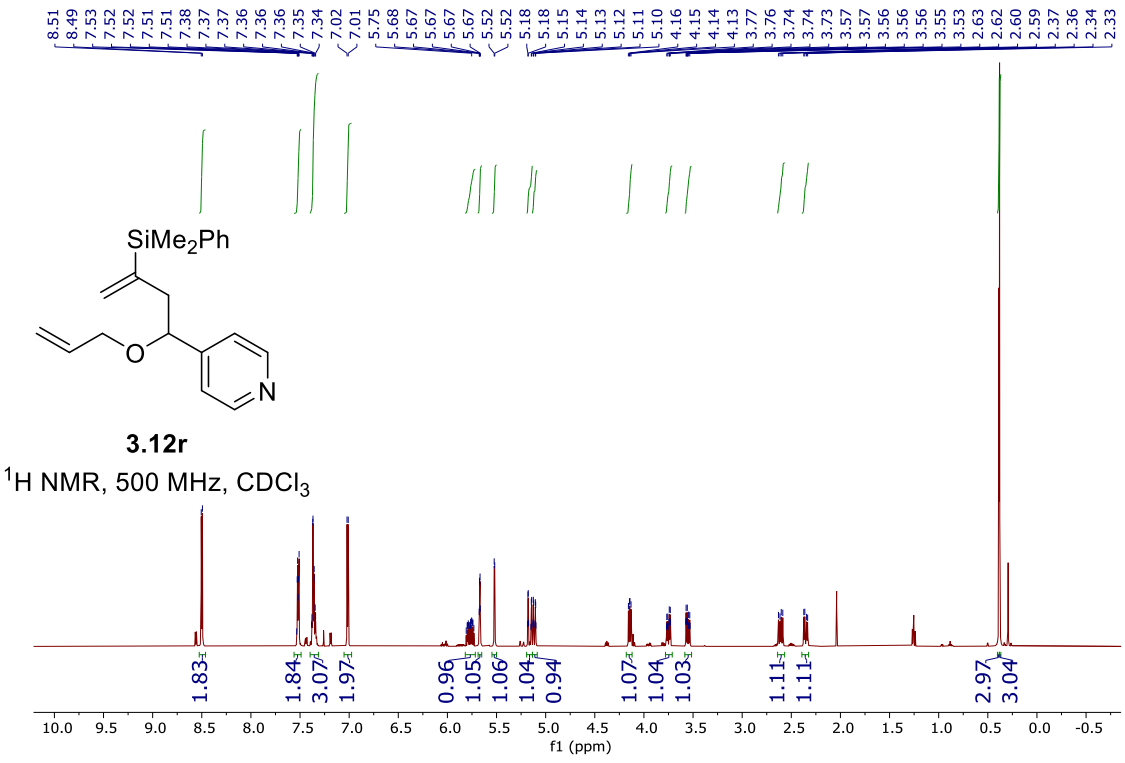

SiMe2Ph
O
3.12p
13C NMR, 126 MHz, CDCl3
f1 (ppm)


SiEt3
O
N
3.12q
1H NMR, 500 MHz, CDCl3
f1 (ppm)



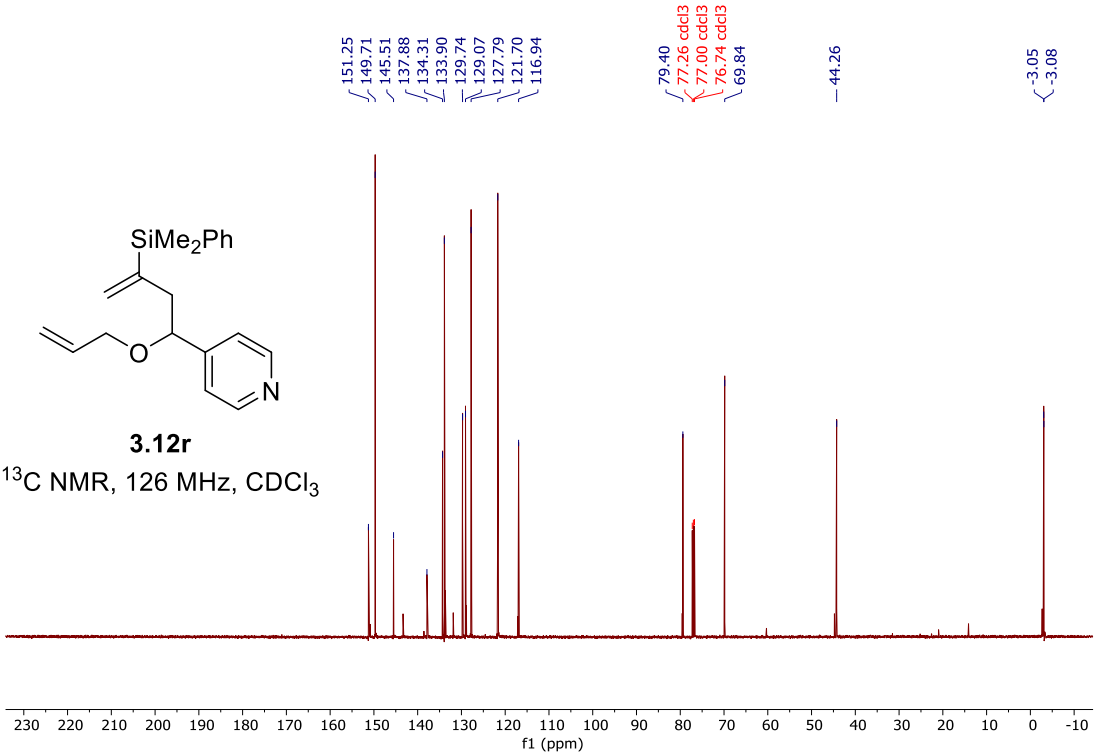
3.12q

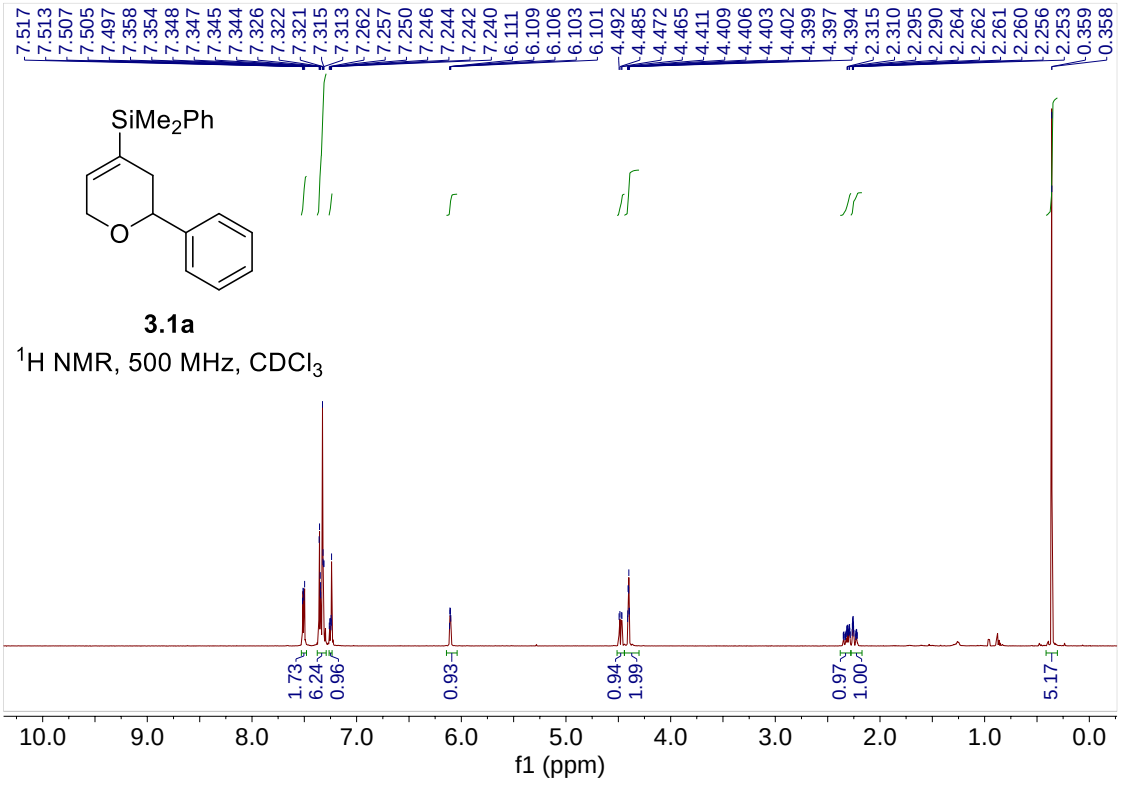
^{13}C NMR, 126 MHz, $CDCl_3$

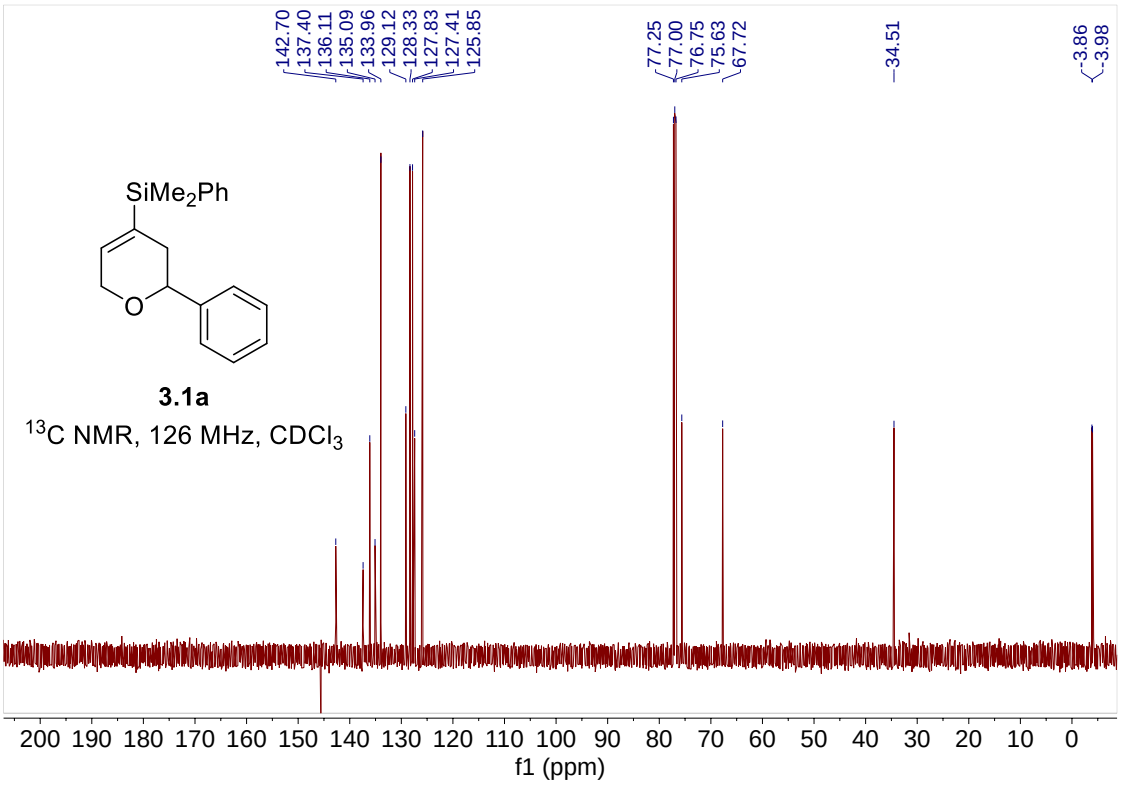


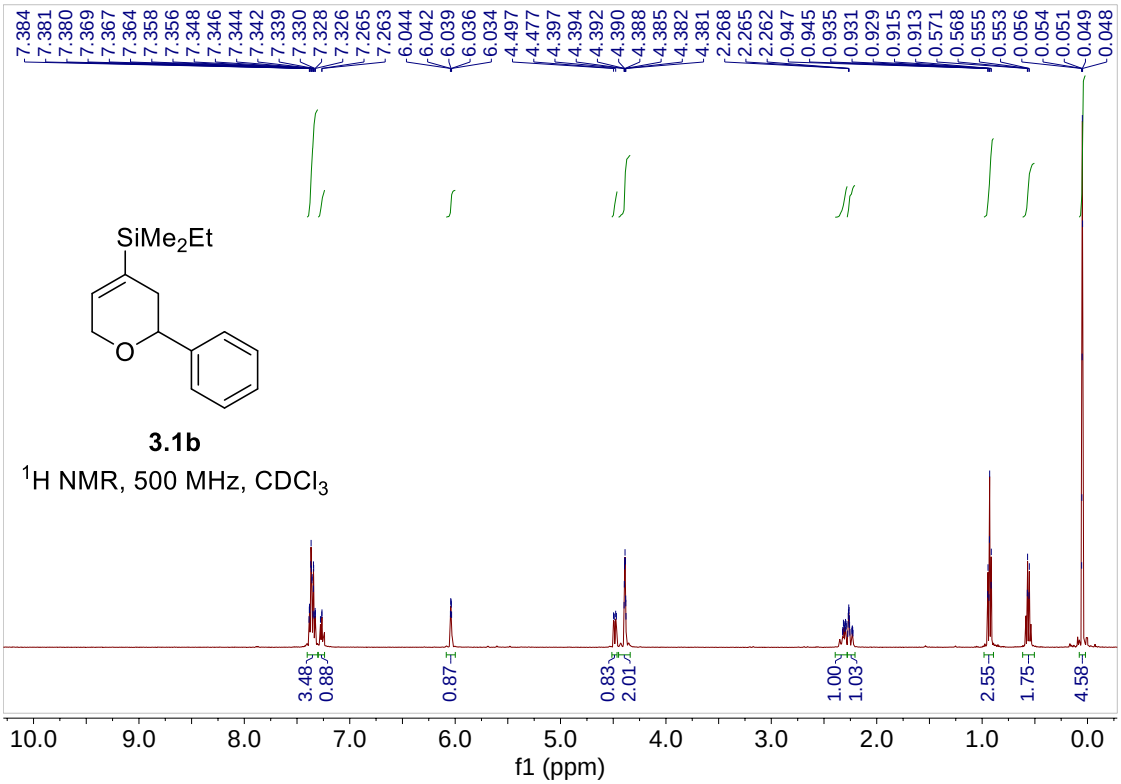
3.12r

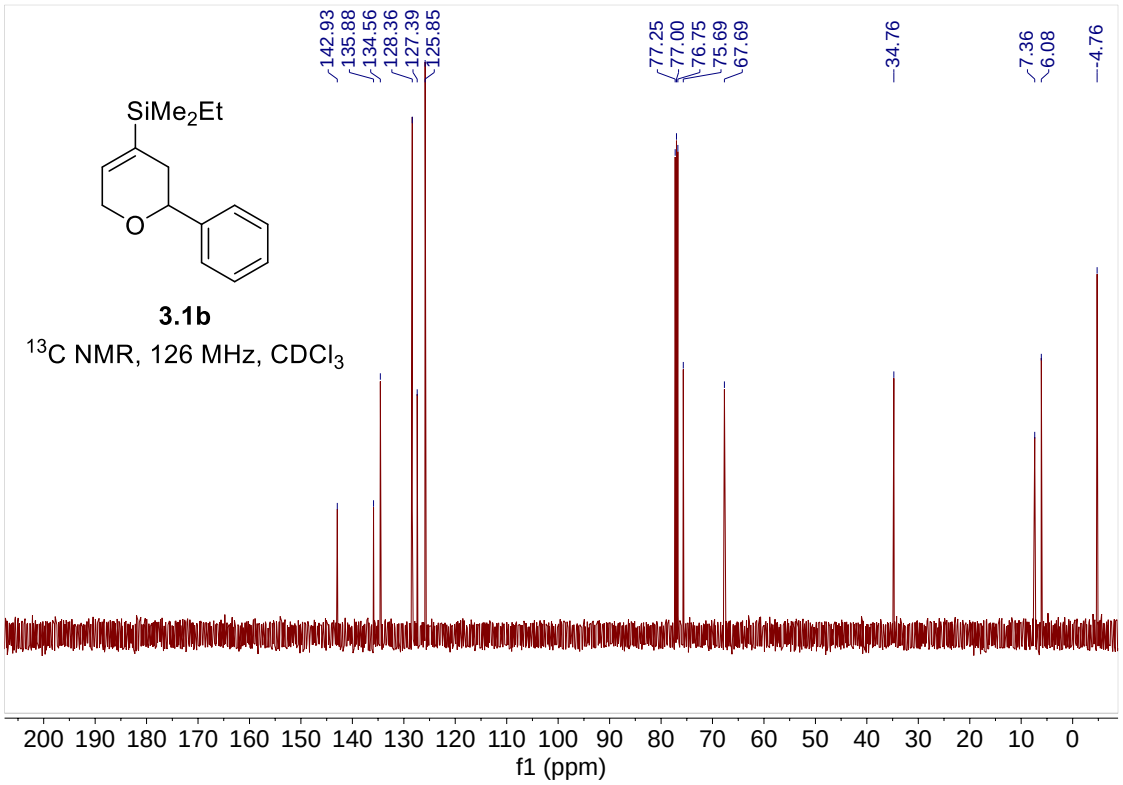
^{1}H NMR, 500 MHz, $CDCl_3$

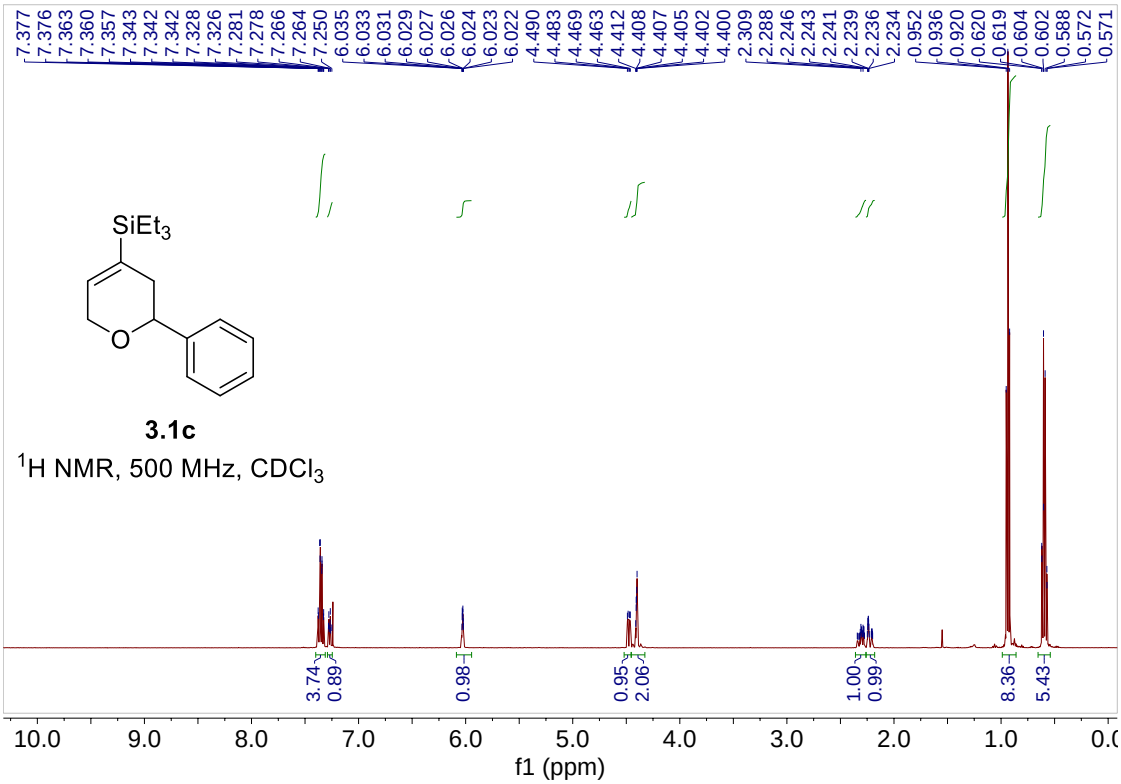

151.25
149.71
145.51
137.88
134.31
133.90
129.74
129.07
127.79
121.70
116.94
79.40
77.26 cdcl3
77.00 cdcl3
76.74 cdcl3
69.84
44.26
-3.05
-3.08
SiMe2Ph
O
N
3.12r
13C NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

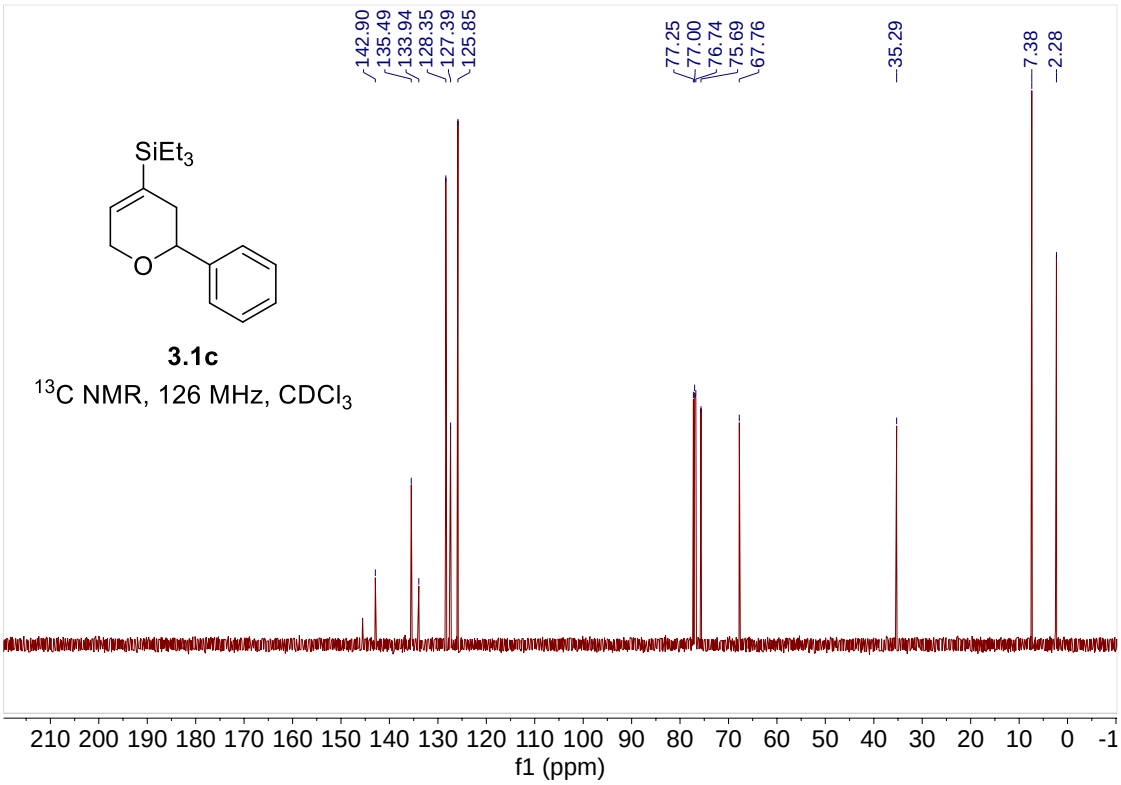

7.517
7.513
7.507
7.505
7.497
7.358
7.354
7.348
7.347
7.345
7.344
7.326
7.322
7.321
7.315
7.313
7.262
7.257
7.250
7.246
7.244
7.242
7.240
6.111
6.109
6.106
6.103
6.101
4.492
4.485
4.472
4.465
4.411
4.409
4.406
4.403
4.402
4.399
4.397
4.394
2.315
2.310
2.295
2.290
2.264
2.262
2.261
2.260
2.256
2.253
0.359
0.358
SiMe2Ph
O
3.1a
1H NMR, 500 MHz, CDCl3
1.73
6.24
0.96
0.93
0.94
1.99
0.97
1.00
5.17
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

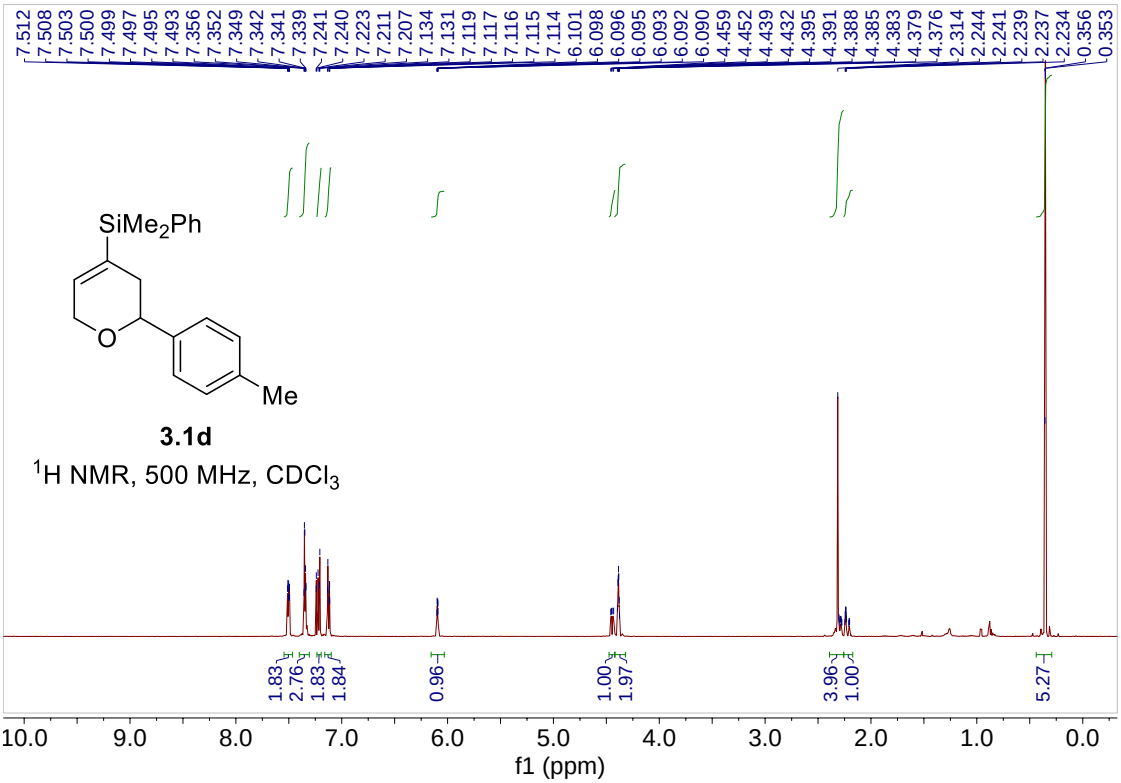

142.70
137.40
136.11
135.09
133.96
129.12
128.33
127.83
127.41
125.85
77.25
77.00
76.75
75.63
67.72
34.51
-3.86
-3.98
SiMe2Ph
O
3.1a
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

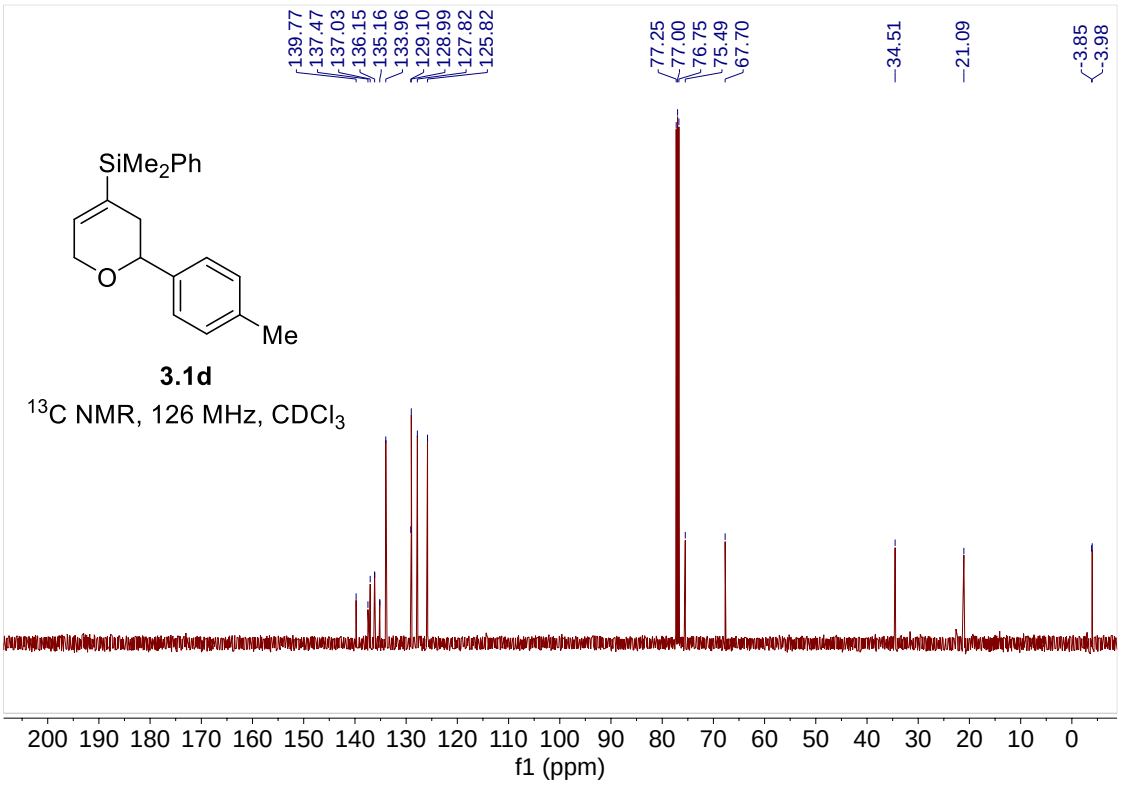

7.384
7.381
7.380
7.369
7.367
7.364
7.358
7.356
7.348
7.346
7.344
7.342
7.339
7.330
7.328
7.326
7.265
7.263
6.044
6.042
6.039
6.036
6.034
4.497
4.477
4.397
4.394
4.392
4.390
4.388
4.385
4.382
4.381
2.268
2.265
2.262
0.947
0.945
0.935
0.931
0.929
0.915
0.913
0.571
0.568
0.555
0.553
0.056
0.054
0.051
0.049
0.048
SiMe2Et
O
3.1b
1H NMR, 500 MHz, CDCl3
3.48
0.88
0.87
0.83
2.01
1.00
1.03
2.55
1.75
4.58
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

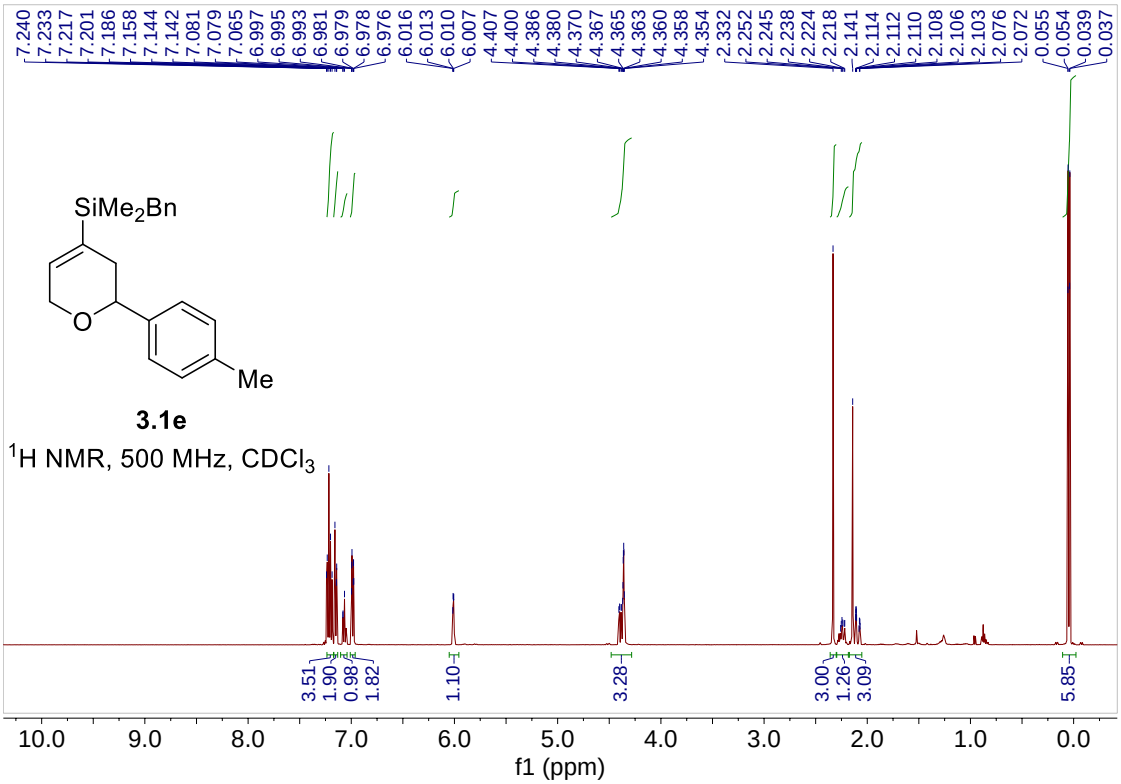

142.93
135.88
134.56
128.36
127.39
125.85
77.25
77.00
76.75
75.69
67.69
34.76
7.36
6.08
-4.76
SiMe2Et
O
3.1b
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

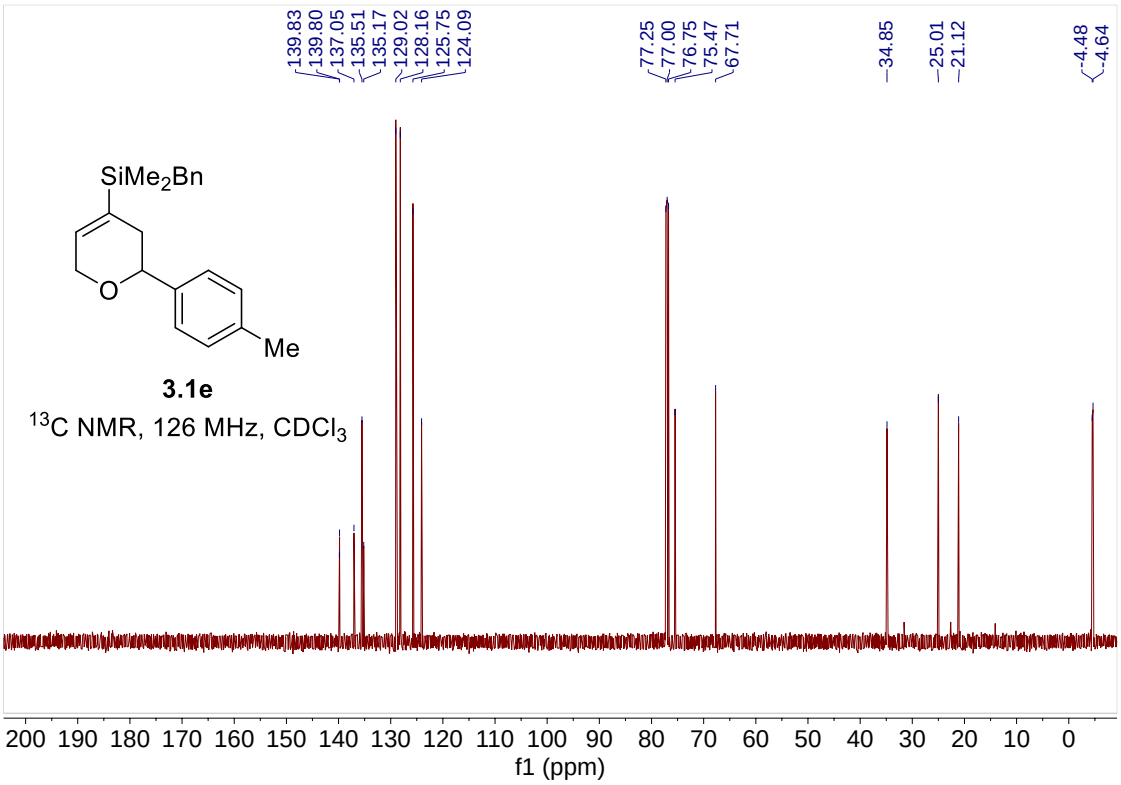

7.377
7.376
7.363
7.360
7.357
7.343
7.342
7.342
7.328
7.326
7.281
7.278
7.266
7.264
7.250
6.035
6.033
6.031
6.029
6.027
6.026
6.024
6.023
6.022
4.490
4.483
4.469
4.463
4.412
4.408
4.407
4.405
4.402
4.400
2.309
2.288
2.246
2.243
2.241
2.239
2.236
2.234
0.952
0.936
0.920
0.620
0.619
0.604
0.602
0.588
0.572
0.571
SiEt3
O
3.1c
1H NMR, 500 MHz, CDCl3
3.74
0.89
0.98
0.95
2.06
1.00
0.99
8.36
5.43
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


142.90
135.49
133.94
128.35
127.39
125.85
77.25
77.00
76.74
75.69
67.76
35.29
7.38
2.28
SiEt3
O
3.1c
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.512
7.508
7.503
7.500
7.499
7.497
7.495
7.493
7.356
7.352
7.349
7.342
7.341
7.339
7.241
7.240
7.223
7.211
7.207
7.134
7.131
7.119
7.117
7.116
7.115
7.114
6.101
6.098
6.096
6.095
6.093
6.092
6.090
4.459
4.452
4.439
4.432
4.395
4.391
4.388
4.385
4.383
4.379
4.376
2.314
2.244
2.241
2.239
2.237
2.234
0.356
0.353
SiMe2Ph
O
Me
3.1d
1H NMR, 500 MHz, CDCl3
1.83
2.76
1.83
1.84
0.96
1.00
1.97
3.96
1.00
5.27
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


139.77
137.47
137.03
136.15
135.16
133.96
129.10
128.99
127.82
125.82
77.25
77.00
76.75
75.49
67.70
34.51
21.09
3.85
3.98
SiMe2Ph
O
Me
3.1d
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.240
7.233
7.217
7.201
7.186
7.158
7.144
7.142
7.081
7.079
7.065
6.997
6.995
6.993
6.981
6.979
6.978
6.976
6.016
6.013
6.010
6.007
4.407
4.400
4.386
4.380
4.370
4.367
4.365
4.363
4.360
4.358
4.354
2.332
2.252
2.245
2.238
2.224
2.218
2.141
2.114
2.112
2.110
2.108
2.106
2.103
2.076
2.072
0.055
0.054
0.039
0.037
SiMe2Bn
O
Me
3.1e
1H NMR, 500 MHz, CDCl3
3.51
1.90
0.98
1.82
1.10
3.28
3.00
1.26
3.09
5.85
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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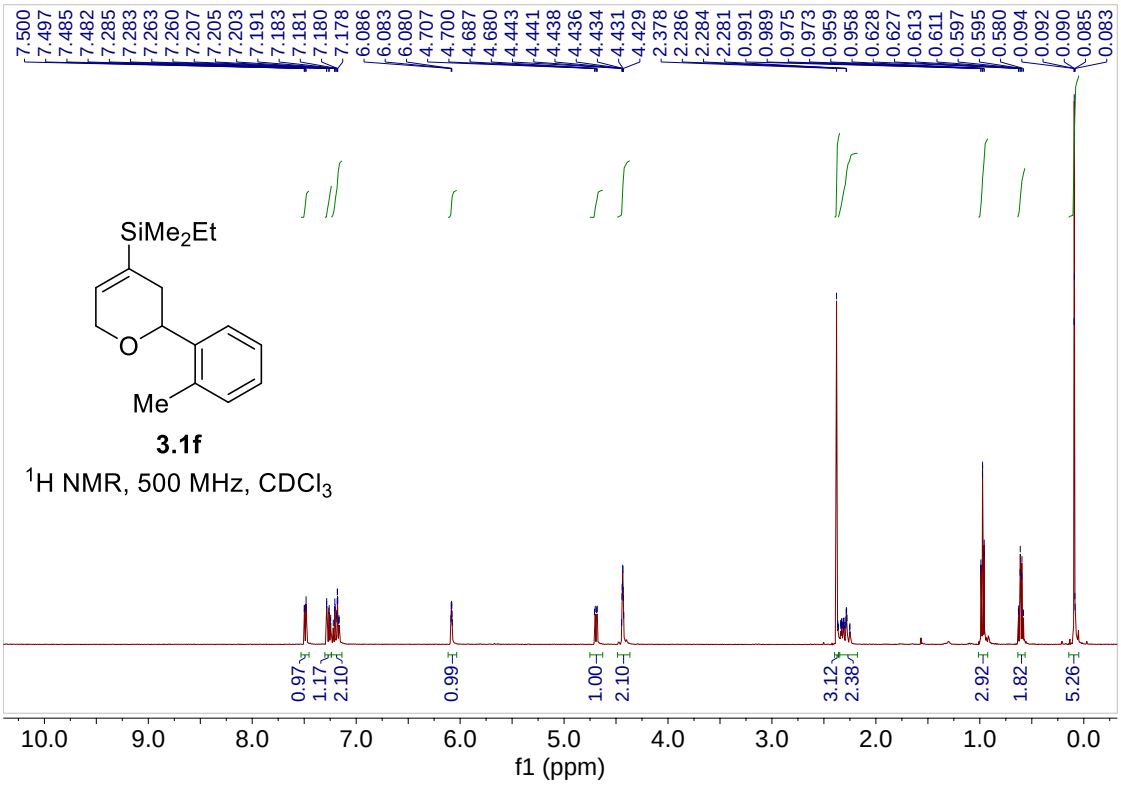
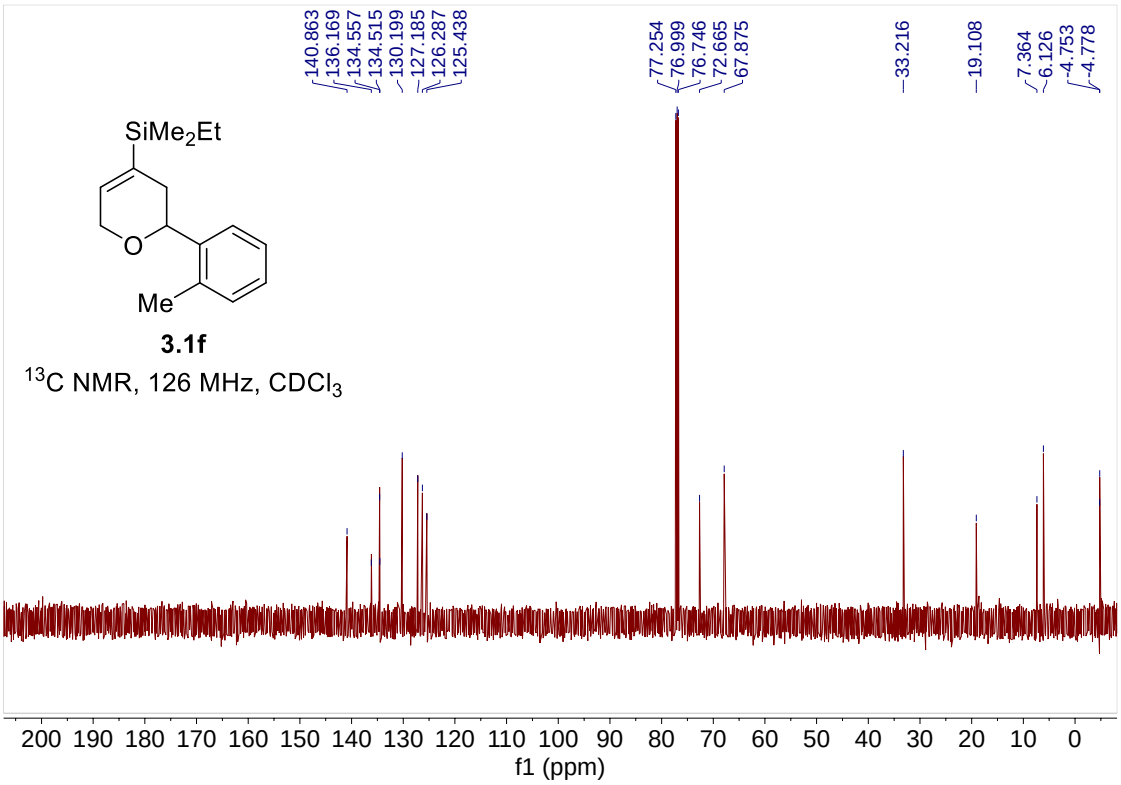
139.80
137.05
135.51
135.17
129.02
128.16
125.75
124.09
77.25
77.00
76.75
75.47
67.71
34.85
25.01
21.12
4.48
4.64
SiMe2Bn
O
Me
3.1e
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.500
7.497
7.485
7.482
7.285
7.283
7.263
7.260
7.207
7.205
7.203
7.191
7.183
7.181
7.180
7.178
6.086
6.083
6.080
4.707
4.700
4.687
4.680
4.443
4.441
4.438
4.436
4.434
4.431
4.429
2.378
2.286
2.284
2.281
0.991
0.989
0.975
0.973
0.959
0.958
0.628
0.627
0.613
0.611
0.597
0.595
0.580
0.094
0.092
0.090
0.085
0.083
SiMe2Et
O
Me
3.1f
1H NMR, 500 MHz, CDCl3
0.97
1.17
2.10
0.99
1.00
2.10
3.12
2.38
2.92
1.82
5.26
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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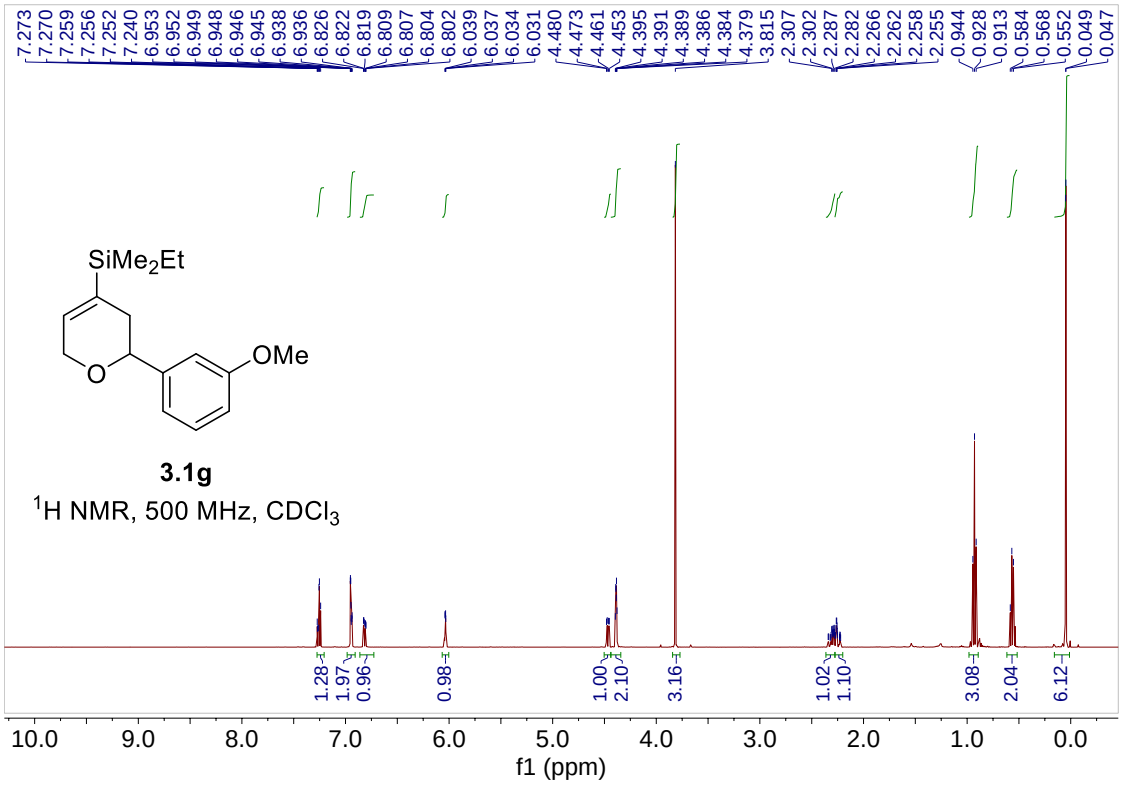
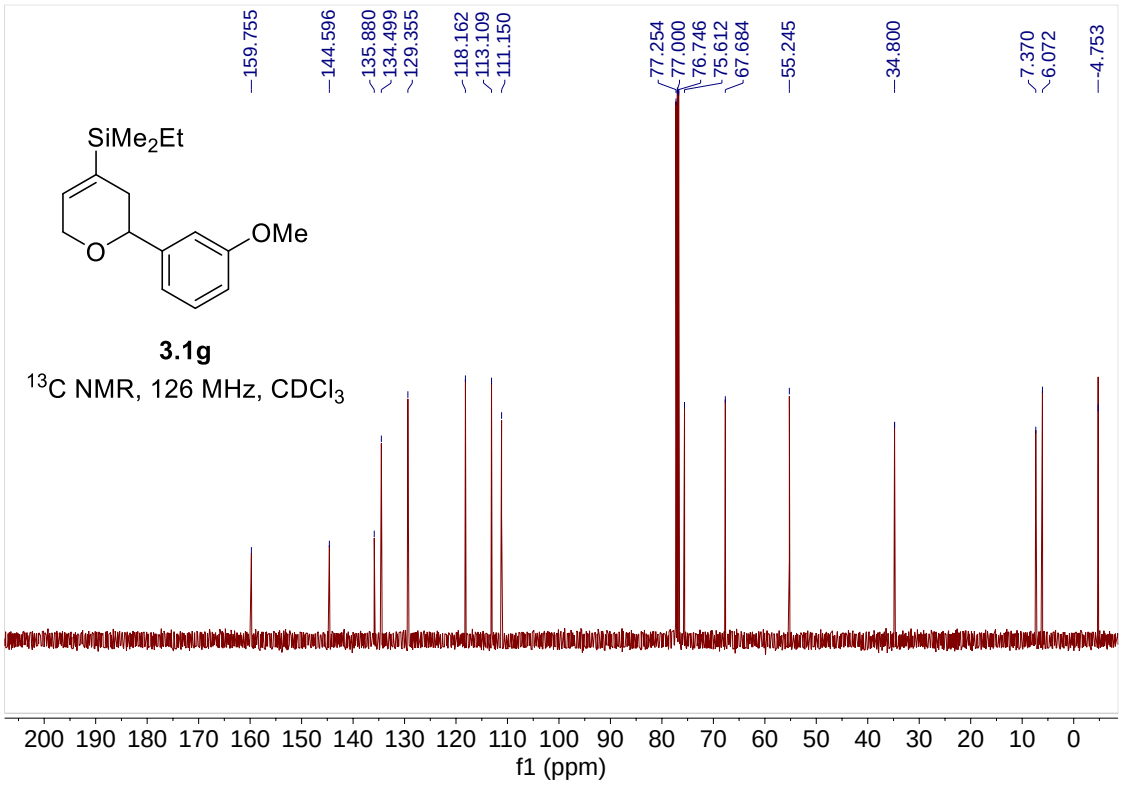
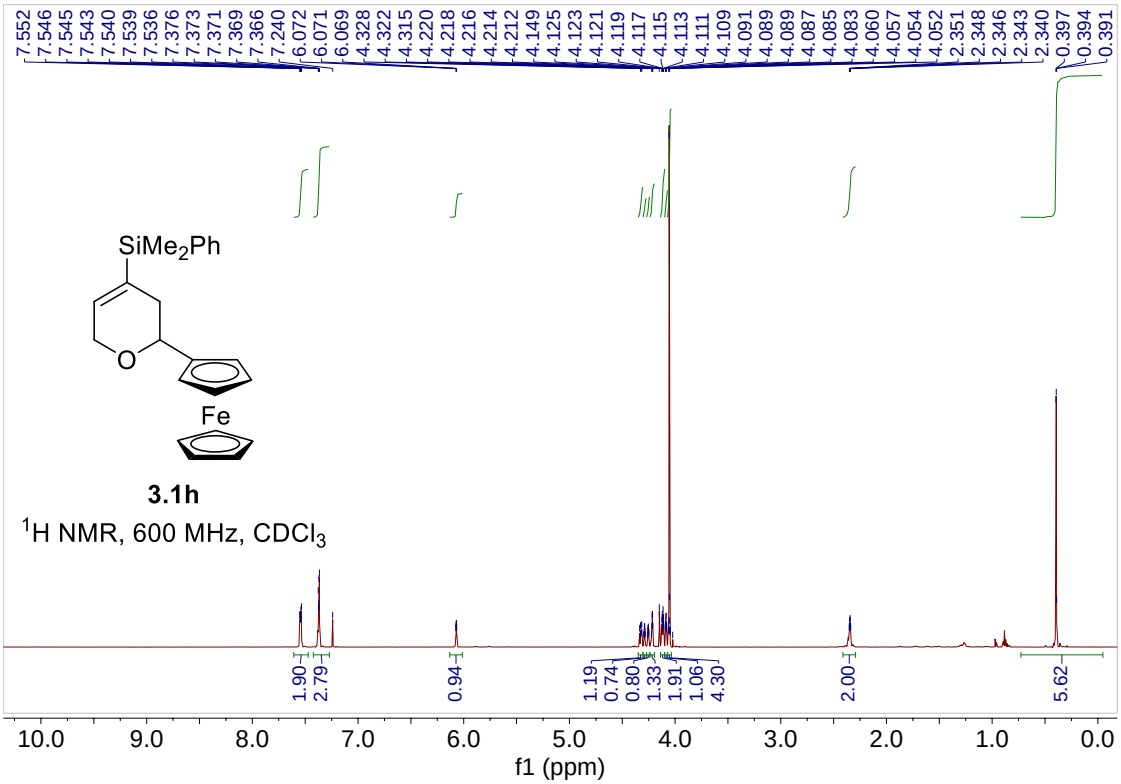
136.169
134.557
134.515
130.199
127.185
126.287
125.438
77.254
76.999
76.746
72.665
67.875
33.216
19.108
7.364
6.126
4.753
4.778
SiMe2Et
O
Me
3.1f
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.273
7.270
7.259
7.256
7.252
7.240
6.953
6.952
6.949
6.948
6.946
6.945
6.938
6.936
6.826
6.822
6.819
6.809
6.807
6.804
6.802
6.039
6.037
6.034
6.031
4.480
4.473
4.461
4.453
4.395
4.391
4.389
4.386
4.384
4.379
3.815
2.307
2.302
2.287
2.282
2.266
2.262
2.258
2.255
0.944
0.928
0.913
0.584
0.568
0.552
0.049
0.047
SiMe2Et
O
OMe
3.1g
1H NMR, 500 MHz, CDCl3
1.28
1.97
0.96
0.98
1.00
2.10
3.16
1.02
1.10
3.08
2.04
6.12
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


159.755
144.596
135.880
134.499
129.355
118.162
113.109
111.150
77.254
77.000
76.746
75.612
67.684
55.245
34.800
7.370
6.072
4.753
SiMe2Et
OMe
O
3.1g
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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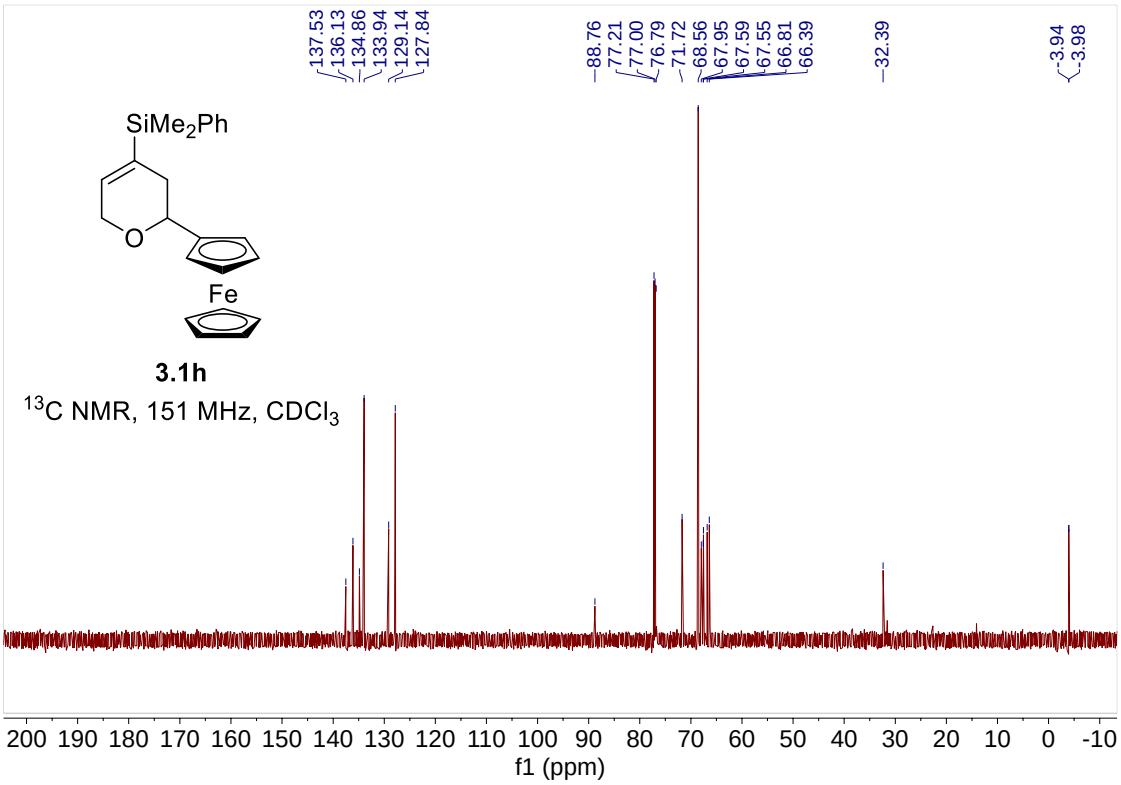
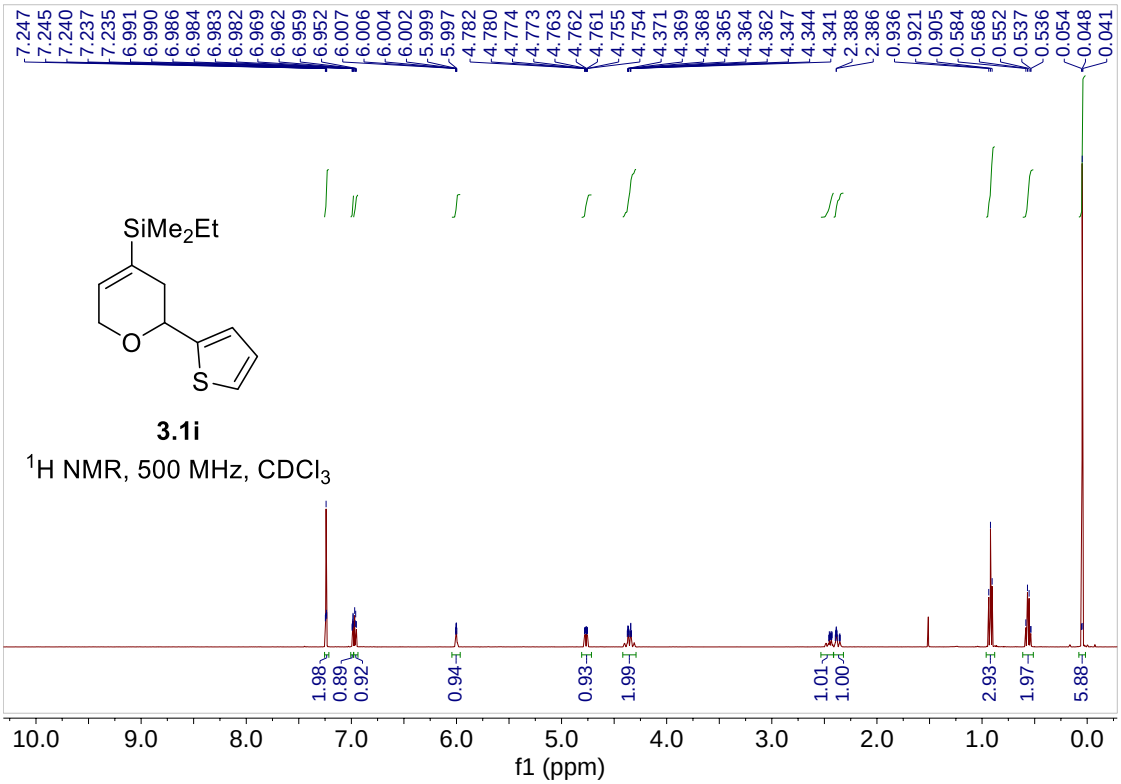
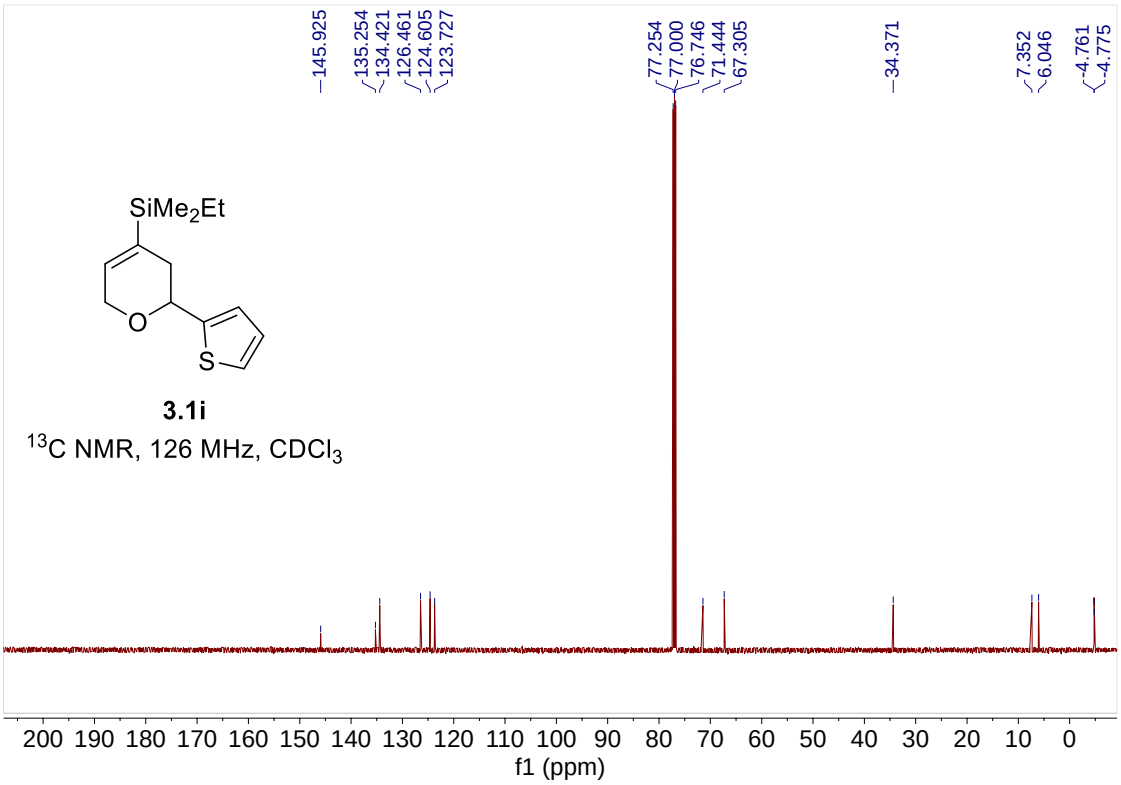
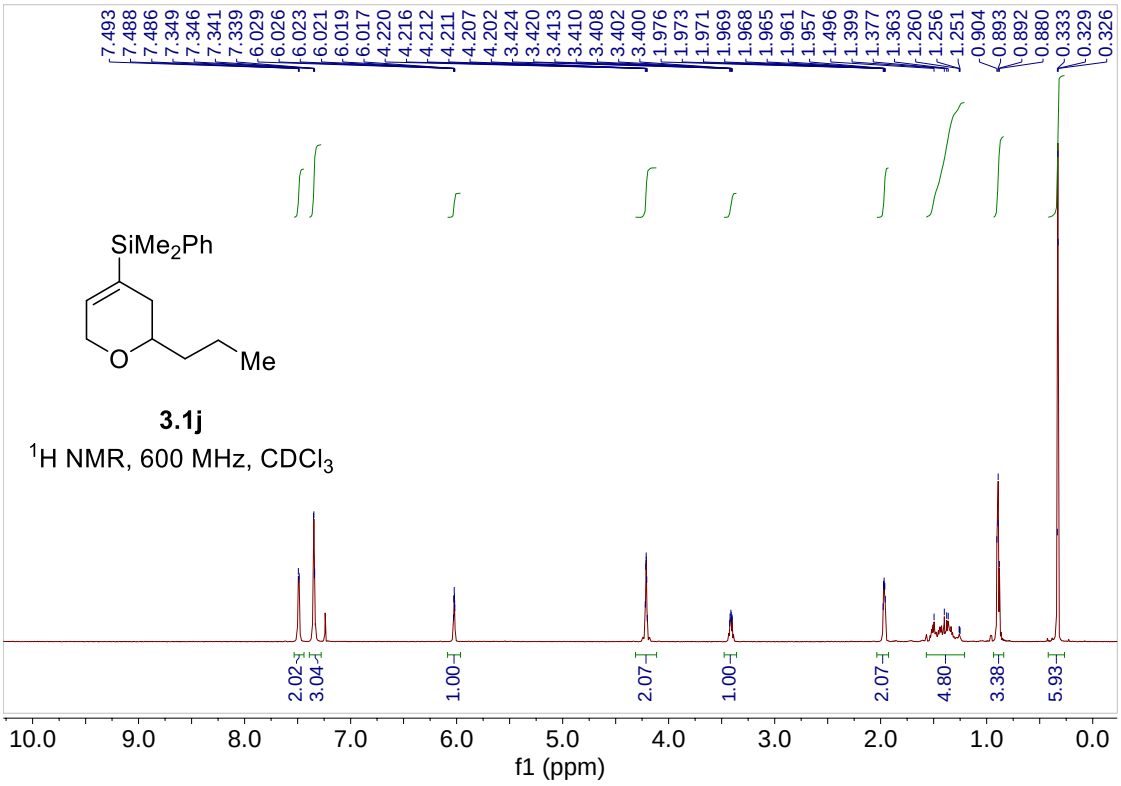
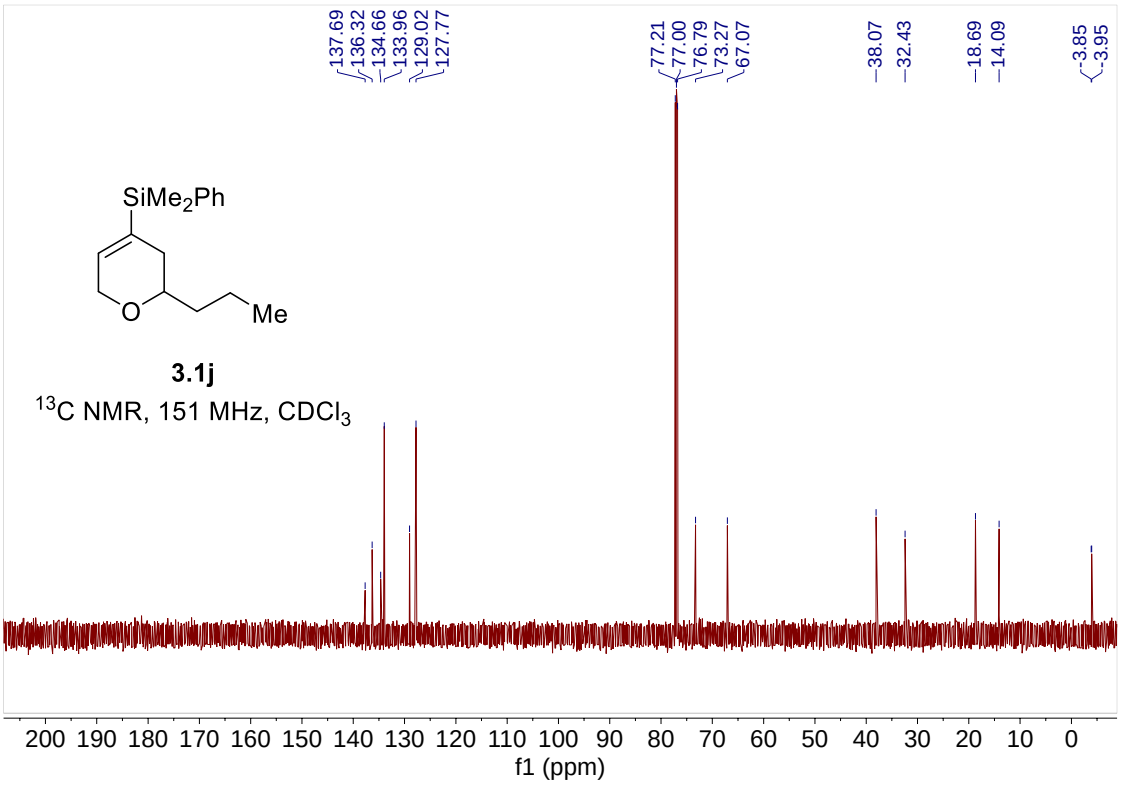
7.546
7.545
7.543
7.540
7.539
7.536
7.376
7.373
7.371
7.369
7.366
7.240
6.072
6.071
6.069
4.328
4.322
4.315
4.220
4.218
4.216
4.214
4.212
4.149
4.125
4.123
4.121
4.119
4.117
4.115
4.113
4.111
4.109
4.091
4.089
4.089
4.087
4.085
4.083
4.060
4.057
4.054
4.052
2.351
2.348
2.346
2.343
2.340
0.397
0.394
0.391
SiMe2Ph
O
Fe
3.1h
1H NMR, 600 MHz, CDCl3
1.90
2.79
0.94
1.19
0.74
0.80
1.33
1.91
1.06
4.30
2.00
5.62
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

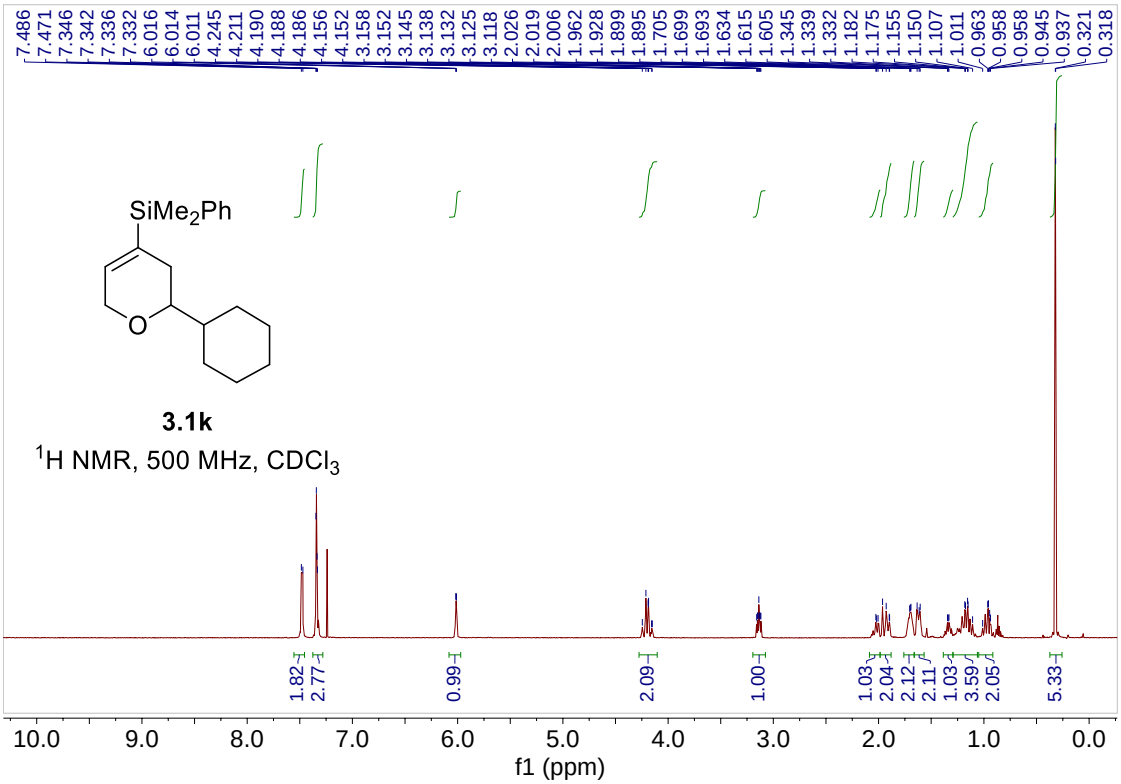

137.53
136.13
134.86
133.94
129.14
127.84
88.76
77.21
77.00
76.79
71.72
68.56
67.95
67.59
67.55
66.81
66.39
32.39
-3.94
-3.98
SiMe2Ph
O
Fe
3.1h
13C NMR, 151 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

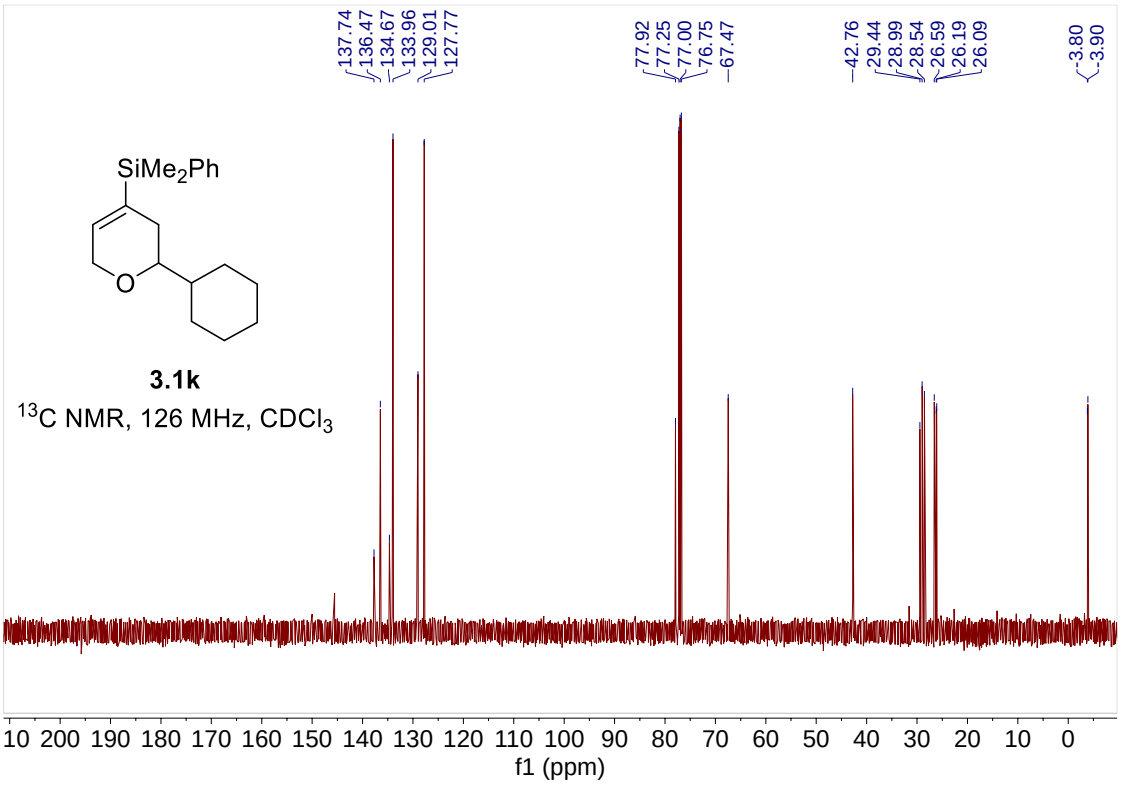

7.247
7.245
7.240
7.237
7.235
6.991
6.990
6.986
6.984
6.983
6.982
6.969
6.962
6.959
6.952
6.007
6.006
6.004
6.002
5.999
5.997
4.782
4.780
4.774
4.773
4.763
4.762
4.761
4.755
4.754
4.371
4.369
4.368
4.365
4.364
4.362
4.347
4.344
4.341
2.388
2.386
0.936
0.921
0.905
0.584
0.568
0.552
0.537
0.536
0.054
0.048
0.041
SiMe2Et
O
S
3.1i
1H NMR, 500 MHz, CDCl3
1.98
0.89
0.92
0.94
0.93
1.99
1.01
1.00
2.93
1.97
5.88
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

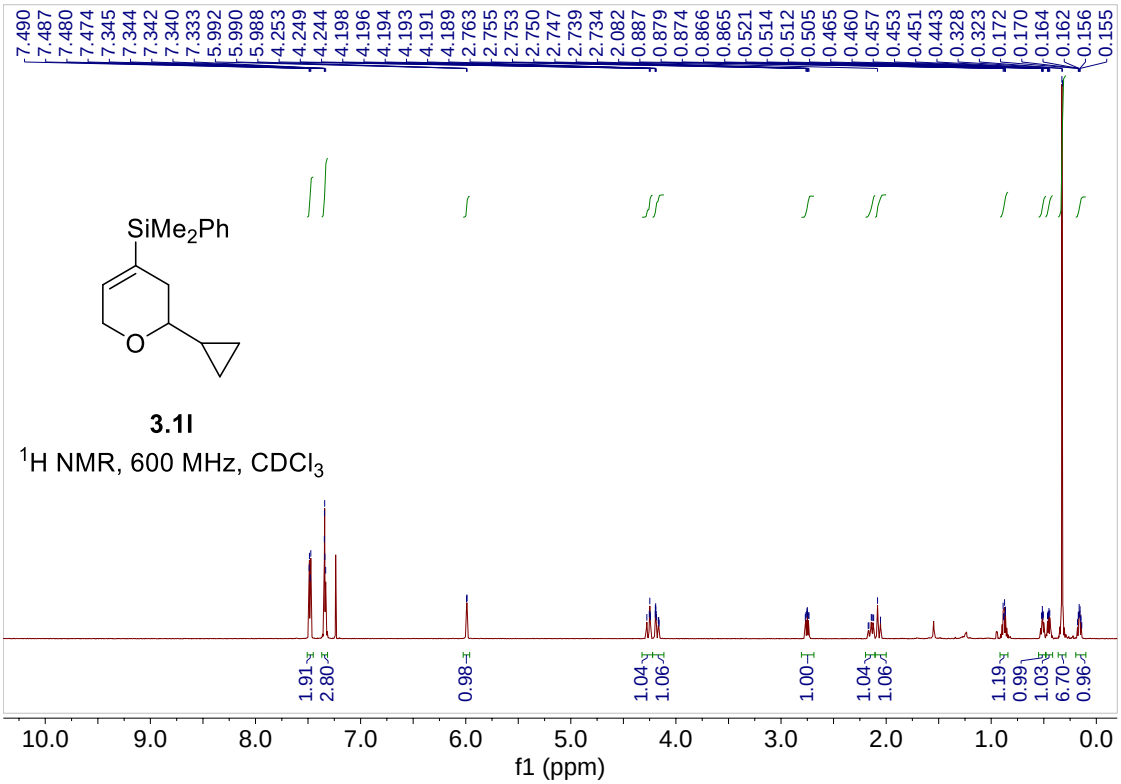

145.925
135.254
134.421
126.461
124.605
123.727
77.254
77.000
76.746
71.444
67.305
34.371
7.352
6.046
4.761
4.775
SiMe2Et
O
S
3.1i
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

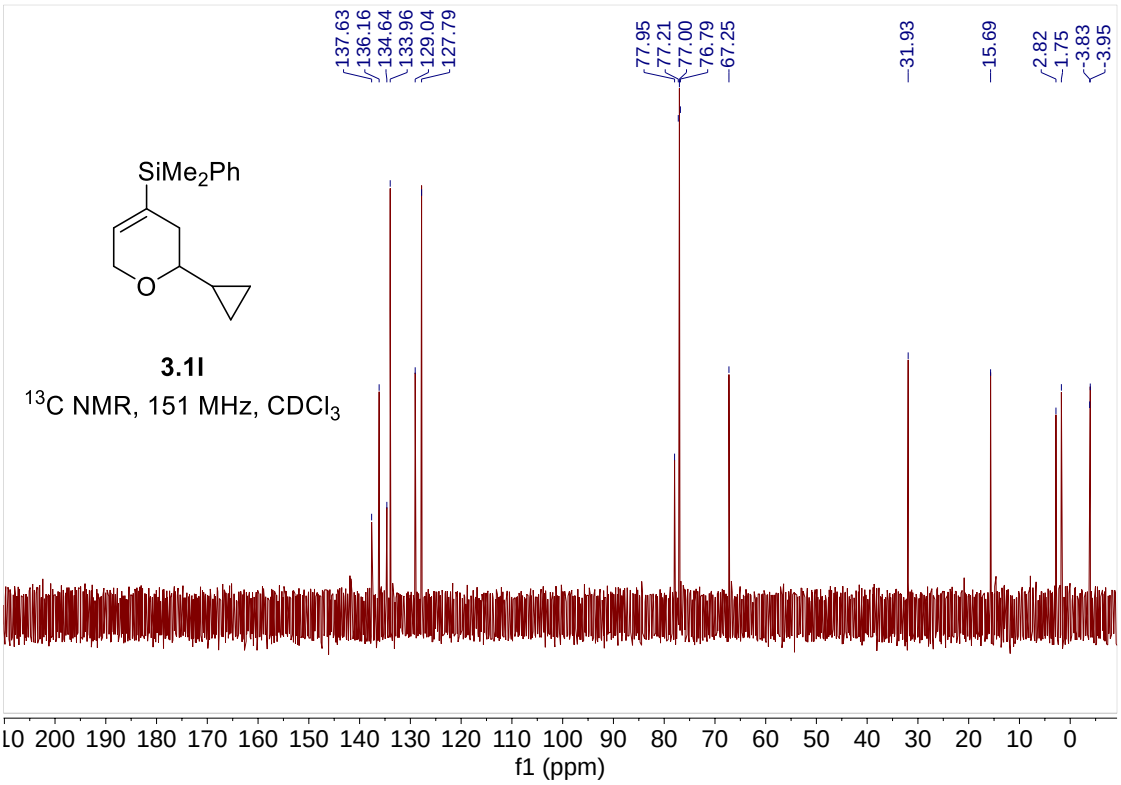

7.493
7.488
7.486
7.349
7.346
7.341
7.339
6.029
6.026
6.023
6.021
6.019
6.017
4.220
4.216
4.212
4.211
4.207
4.202
3.424
3.420
3.413
3.410
3.408
3.402
3.400
1.976
1.973
1.971
1.969
1.968
1.965
1.961
1.957
1.496
1.399
1.377
1.363
1.260
1.256
1.251
0.904
0.893
0.892
0.880
0.333
0.329
0.326
SiMe2Ph
O
Me
3.1j
1H NMR, 600 MHz, CDCl3
2.02
3.04
1.00
2.07
1.00
2.07
4.80
3.38
5.93
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

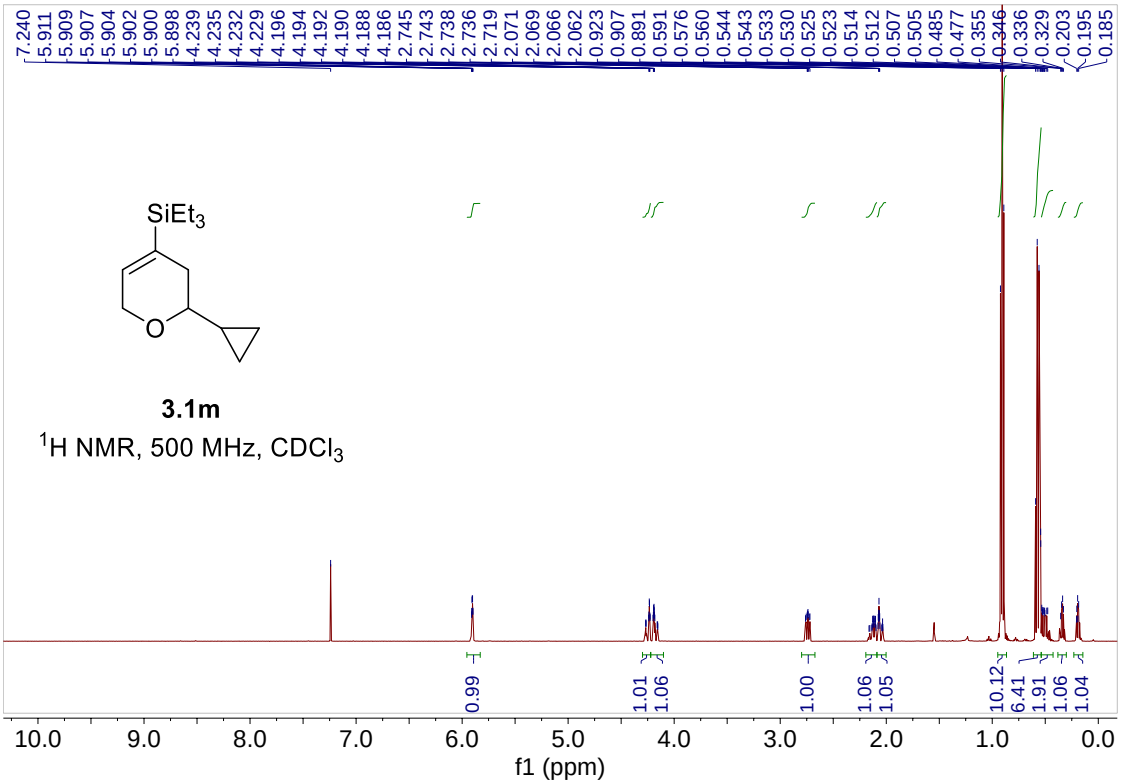

137.69
136.32
134.66
133.96
129.02
127.77
77.21
77.00
76.79
73.27
67.07
38.07
32.43
18.69
14.09
3.85
3.95
SiMe2Ph
O
Me
3.1j
13C NMR, 151 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

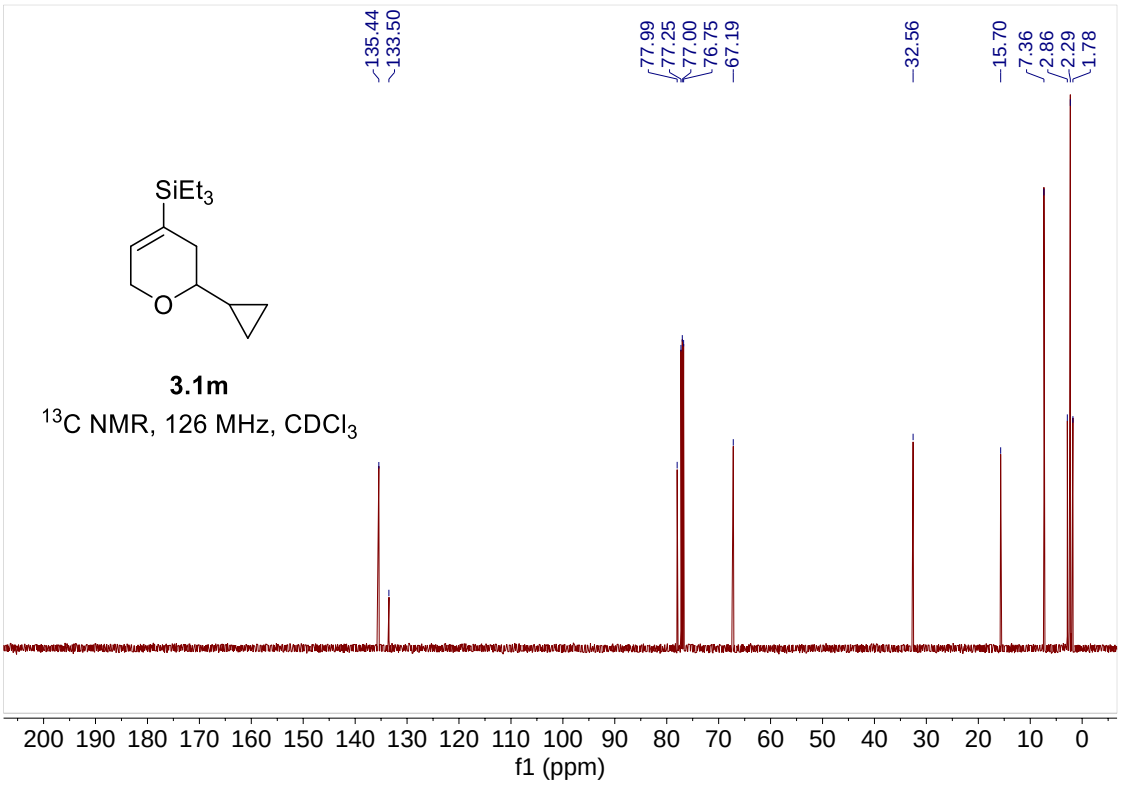

7.486
7.471
7.346
7.342
7.336
7.332
6.016
6.014
6.011
4.245
4.211
4.190
4.188
4.186
4.156
4.152
3.158
3.152
3.145
3.138
3.132
3.125
3.118
2.026
2.019
2.006
1.962
1.928
1.899
1.895
1.705
1.699
1.693
1.634
1.615
1.605
1.345
1.339
1.332
1.182
1.175
1.155
1.150
1.107
1.011
0.963
0.958
0.958
0.945
0.937
0.321
0.318
SiMe2Ph
O
3.1k
1H NMR, 500 MHz, CDCl3
1.82
2.77
0.99
2.09
1.00
1.03
2.04
2.12
2.11
1.03
3.59
2.05
5.33
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

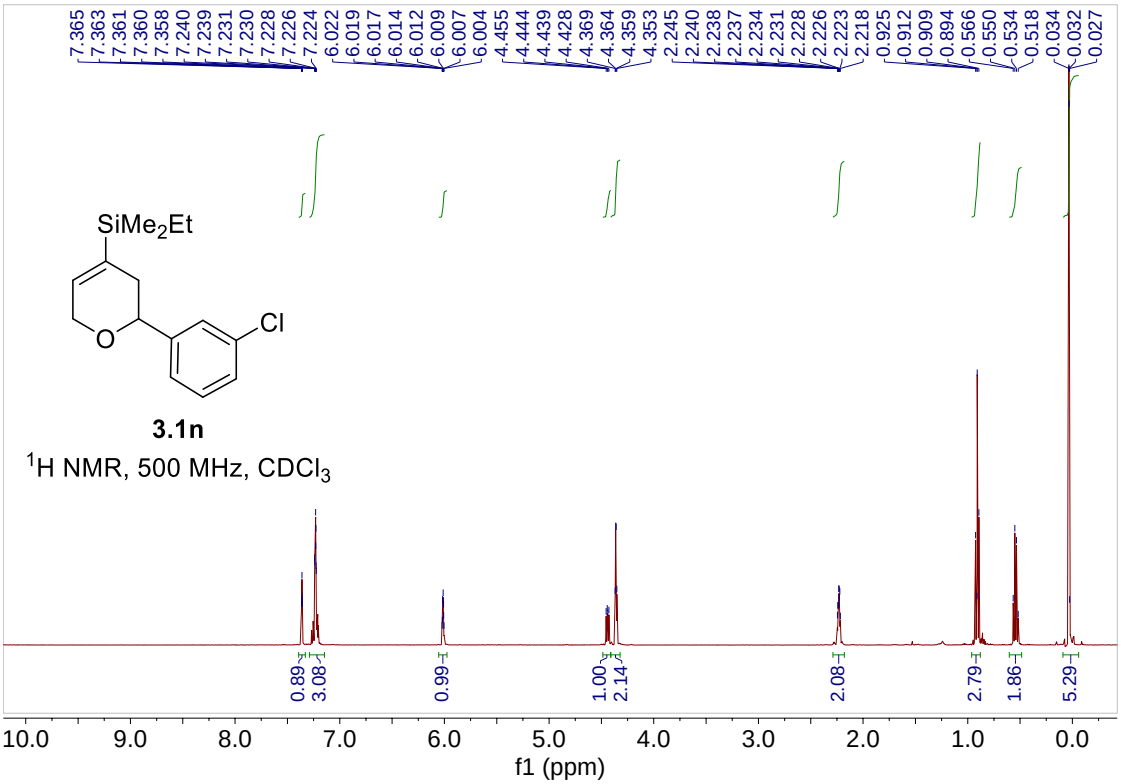

137.74
136.47
134.67
133.96
129.01
127.77
77.92
77.25
77.00
76.75
67.47
42.76
29.44
28.99
28.54
26.59
26.19
26.09
3.80
3.90
SiMe2Ph
O
3.1k
13C NMR, 126 MHz, CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

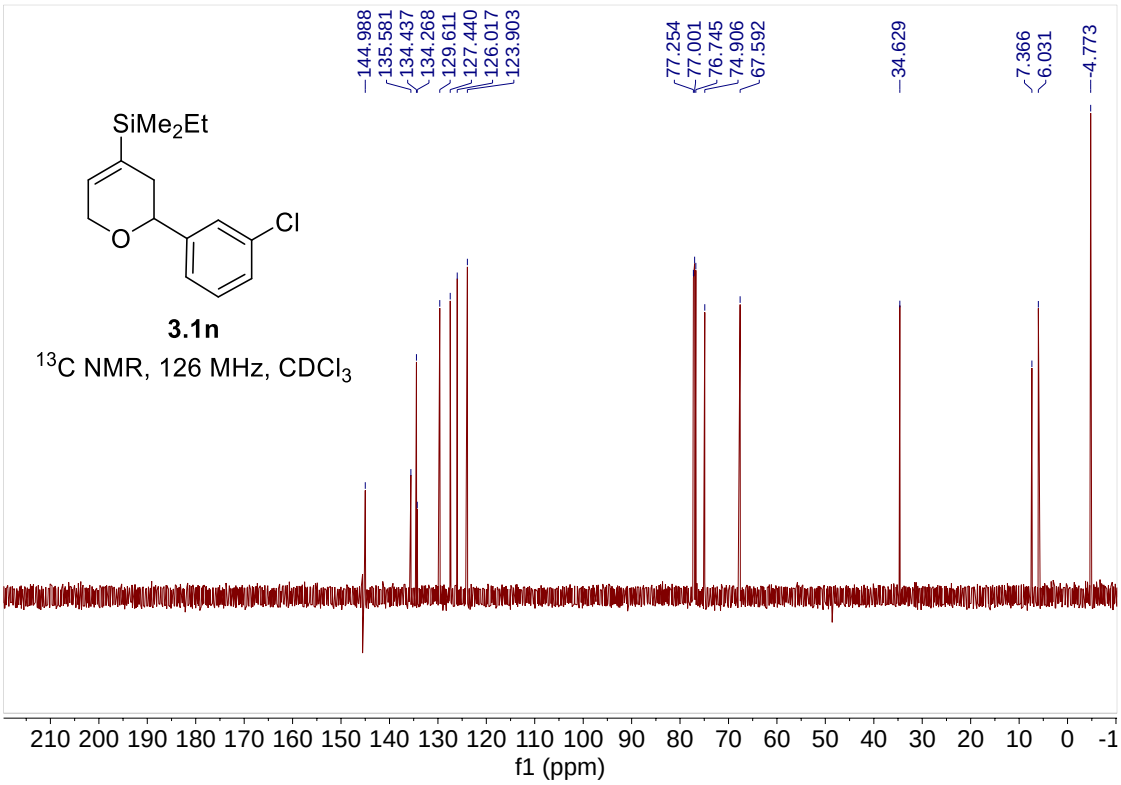

7.490
7.487
7.480
7.474
7.345
7.344
7.342
7.340
7.333
5.992
5.990
5.988
4.253
4.249
4.244
4.198
4.196
4.194
4.193
4.191
4.189
2.763
2.755
2.753
2.750
2.747
2.739
2.734
2.082
0.887
0.879
0.874
0.866
0.865
0.521
0.514
0.512
0.505
0.465
0.460
0.457
0.453
0.451
0.443
0.328
0.323
0.172
0.170
0.164
0.162
0.156
0.155
SiMe2Ph
O
3.1l
1H NMR, 600 MHz, CDCl3
1.91
2.80
0.98
1.04
1.06
1.00
1.04
1.06
1.19
0.99
1.03
6.70
0.96
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

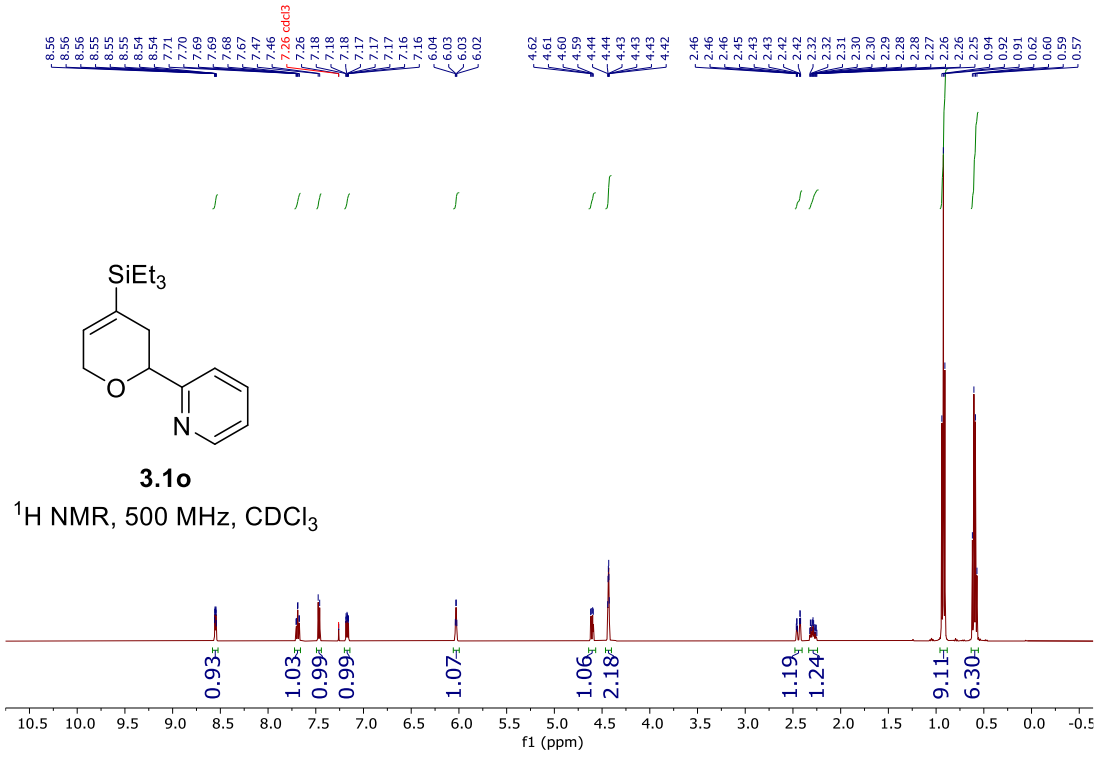

137.63
136.16
134.64
133.96
129.04
127.79
77.95
77.21
77.00
76.79
67.25
31.93
15.69
2.82
1.75
-3.83
-3.95
SiMe2Ph
O
3.1l
13C NMR, 151 MHz, CDCl3
f1 (ppm)

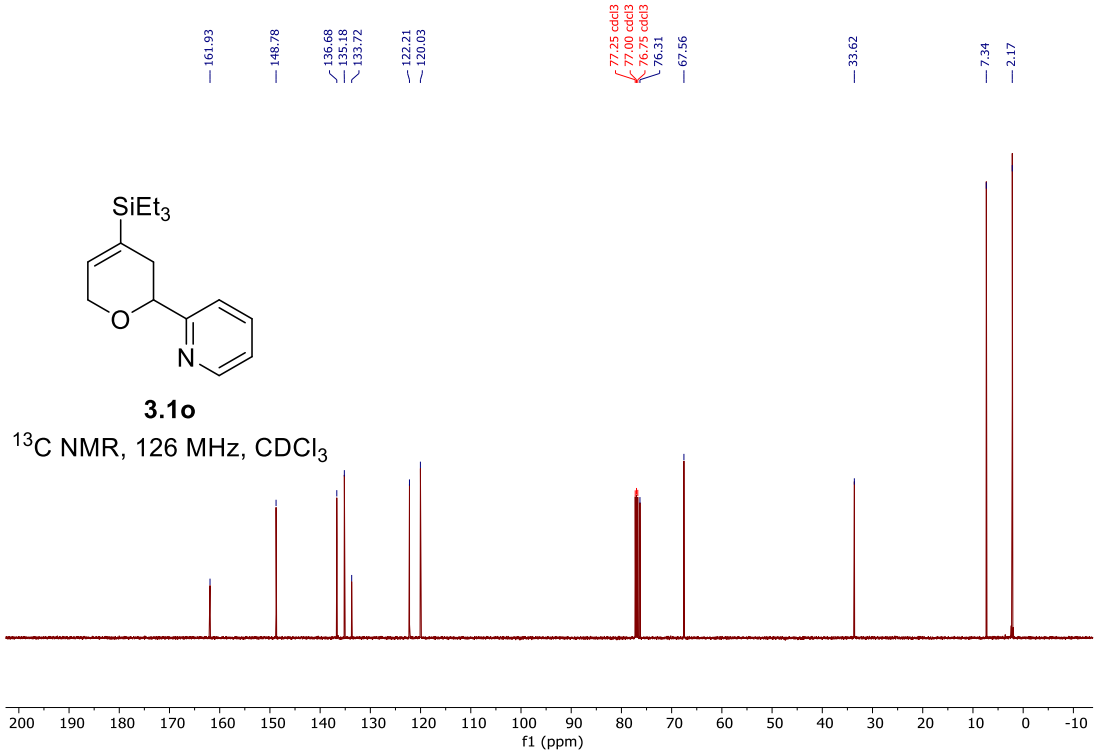

7.240
5.911
5.909
5.907
5.904
5.902
5.900
5.898
4.239
4.235
4.232
4.229
4.196
4.194
4.192
4.190
4.188
4.186
2.745
2.743
2.738
2.736
2.719
2.071
2.069
2.066
2.062
0.923
0.907
0.891
0.591
0.576
0.560
0.544
0.543
0.533
0.530
0.525
0.523
0.514
0.512
0.507
0.505
0.485
0.477
0.355
0.346
0.336
0.329
0.203
0.195
0.185
SiEt3
O
3.1m
1H NMR, 500 MHz, CDCl3
0.99
1.01
1.06
1.00
1.06
1.05
10.12
6.41
1.91
1.06
1.04
f1 (ppm)


135.44
133.50
77.99
77.25
77.00
76.75
67.19
32.56
15.70
7.36
2.86
2.29
1.78
SiEt3
O
3.1m
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.365
7.363
7.361
7.360
7.358
7.240
7.239
7.231
7.230
7.228
7.226
7.224
6.022
6.019
6.017
6.014
6.012
6.009
6.007
6.004
4.455
4.444
4.439
4.428
4.369
4.364
4.359
4.353
2.245
2.240
2.238
2.237
2.234
2.231
2.228
2.226
2.223
2.218
0.925
0.912
0.909
0.894
0.566
0.550
0.534
0.518
0.034
0.032
0.027
SiMe2Et
O
Cl
3.1n
1H NMR, 500 MHz, CDCl3
0.89
3.08
0.99
1.00
2.14
2.08
2.79
1.86
5.29
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

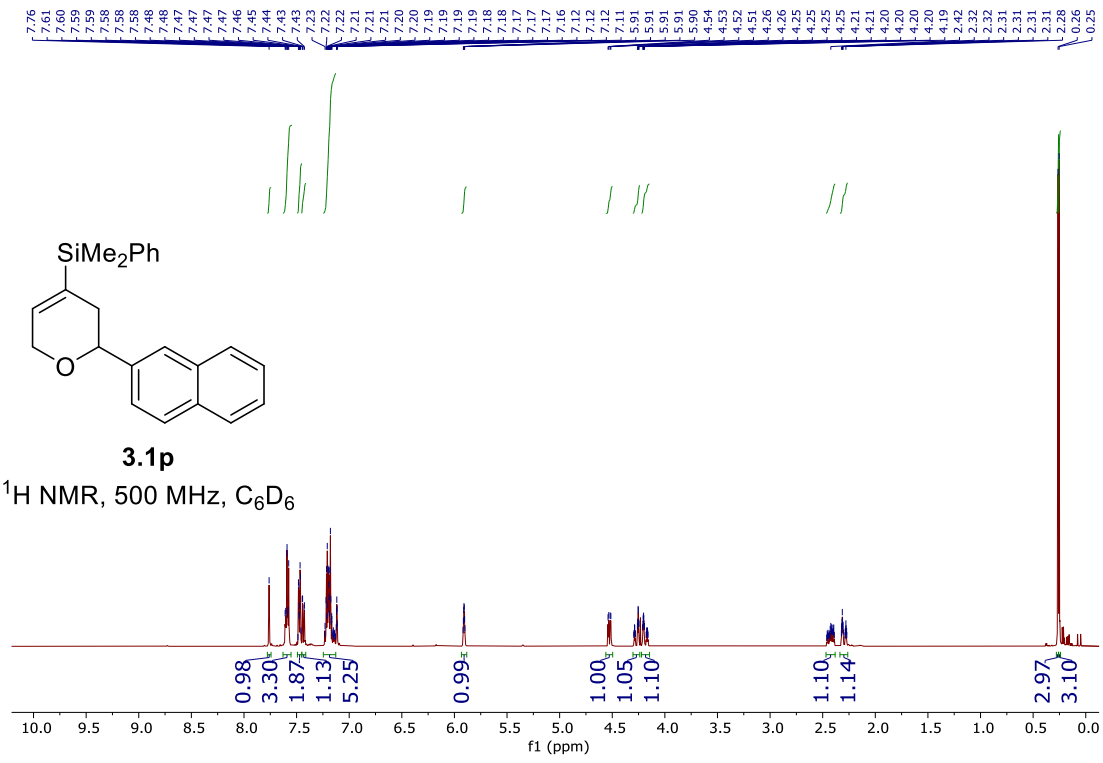

144.988
135.581
134.437
134.268
129.611
127.440
126.017
123.903
77.254
77.001
76.745
74.906
67.592
34.629
7.366
6.031
4.773
SiMe2Et
Cl
O
3.1n
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


SiEt3
O
N
3.1o
1H NMR, 500 MHz, CDCl3
0.93
1.03
0.99
0.99
1.07
1.06
2.18
1.19
1.24
9.11
6.30
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



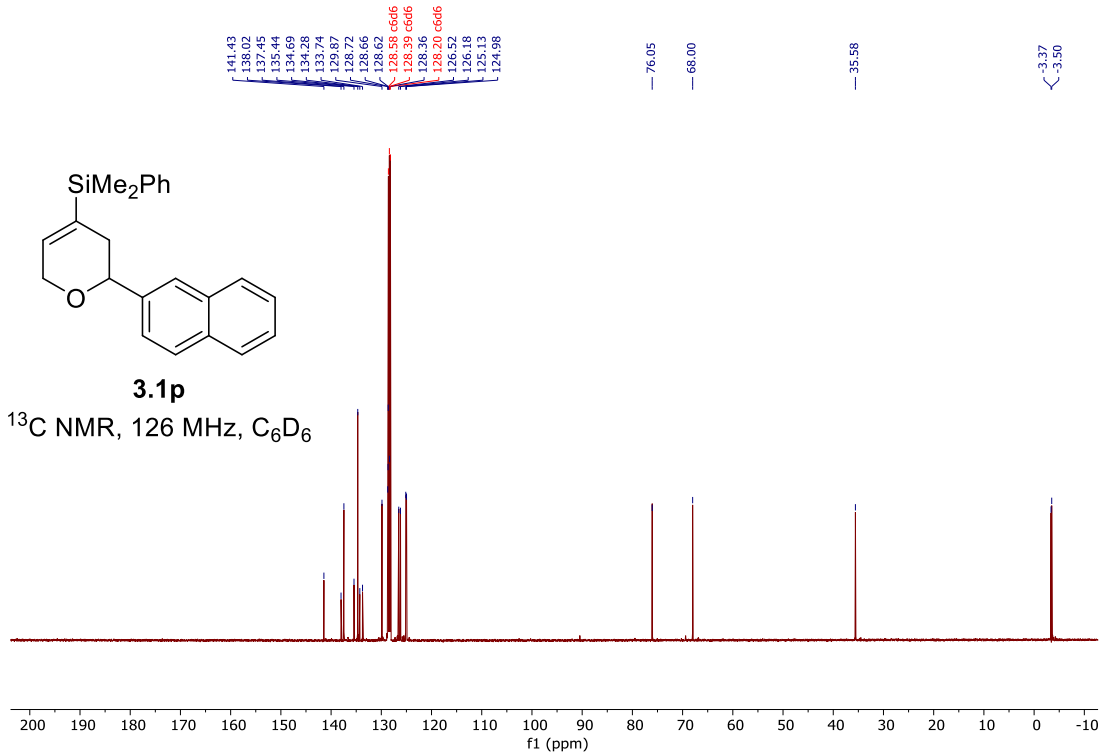
3.1o

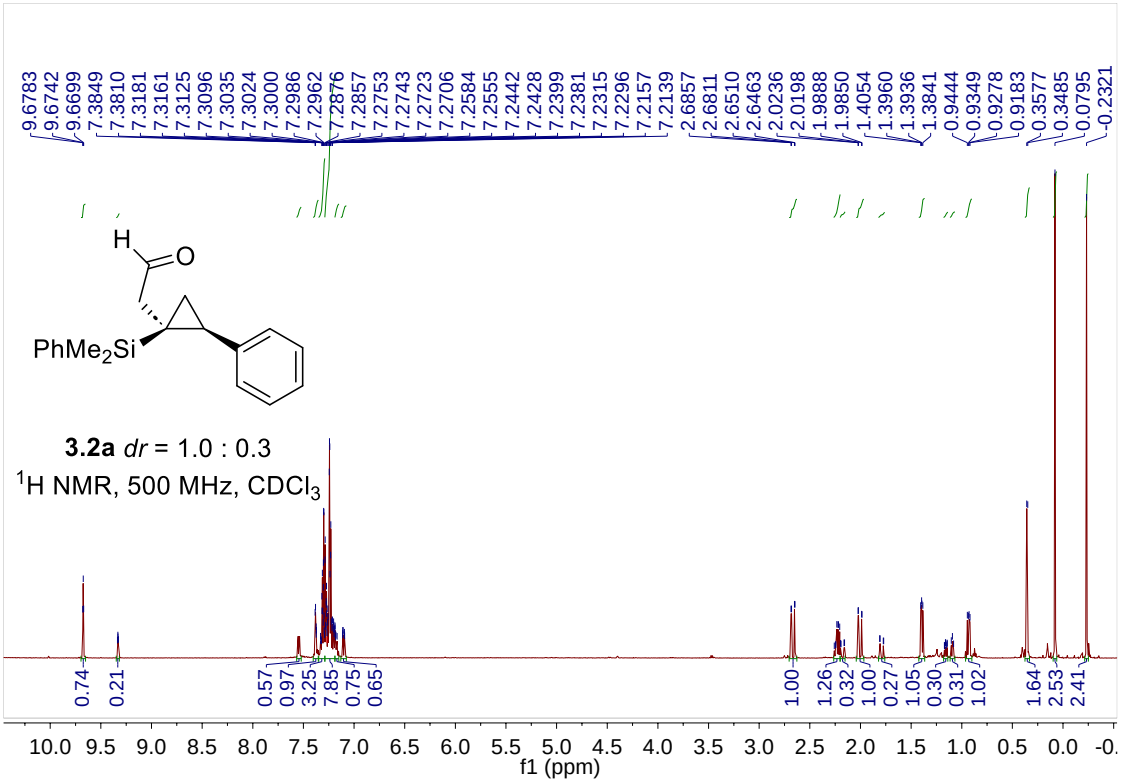
^{13}C NMR, 126 MHz, $CDCl_3$

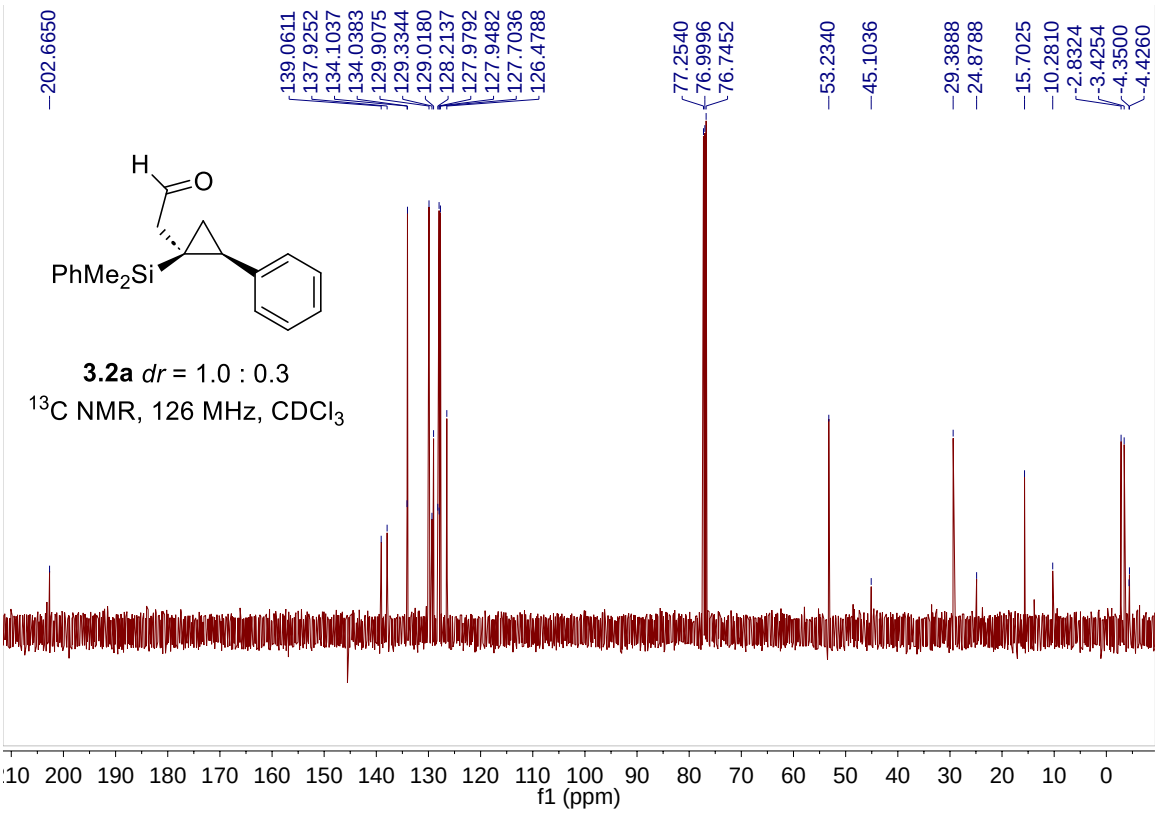


3.1p

^{1}H NMR, 500 MHz, C_6D_6


SiMe2Ph
O
3.1p
13C NMR, 126 MHz, C6D6
f1 (ppm)


H
O
PhMe2Si
3.2a dr = 1.0 : 0.3
1H NMR, 500 MHz, CDCl3
f1 (ppm)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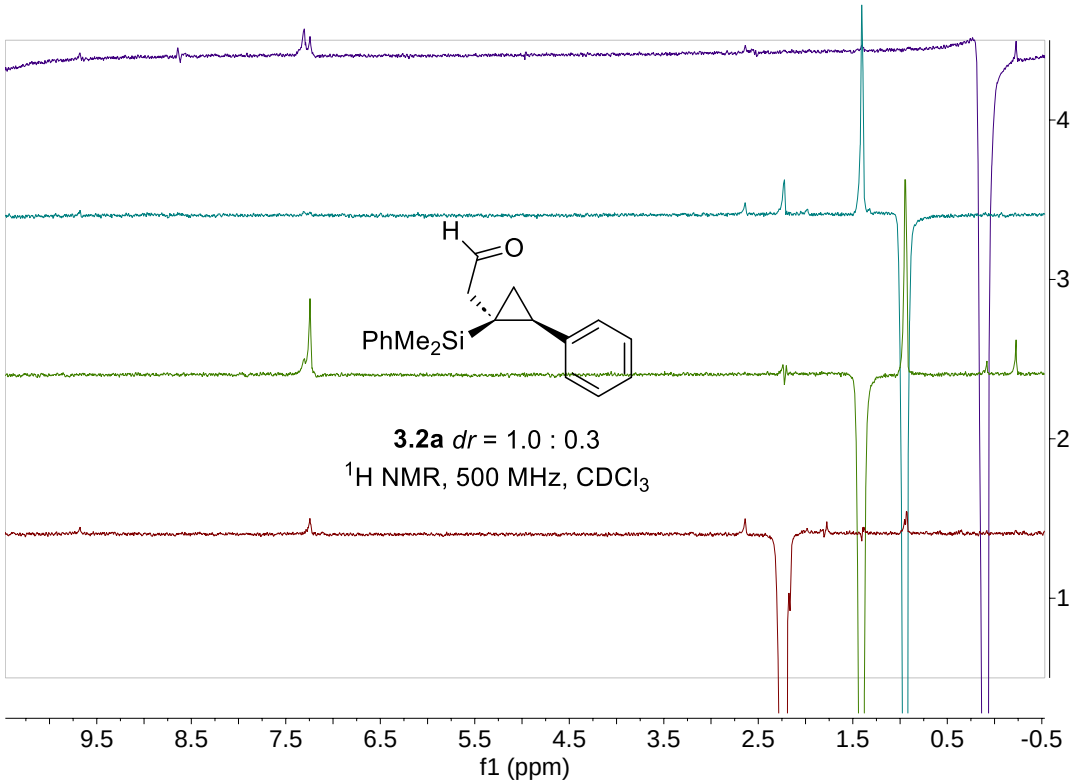
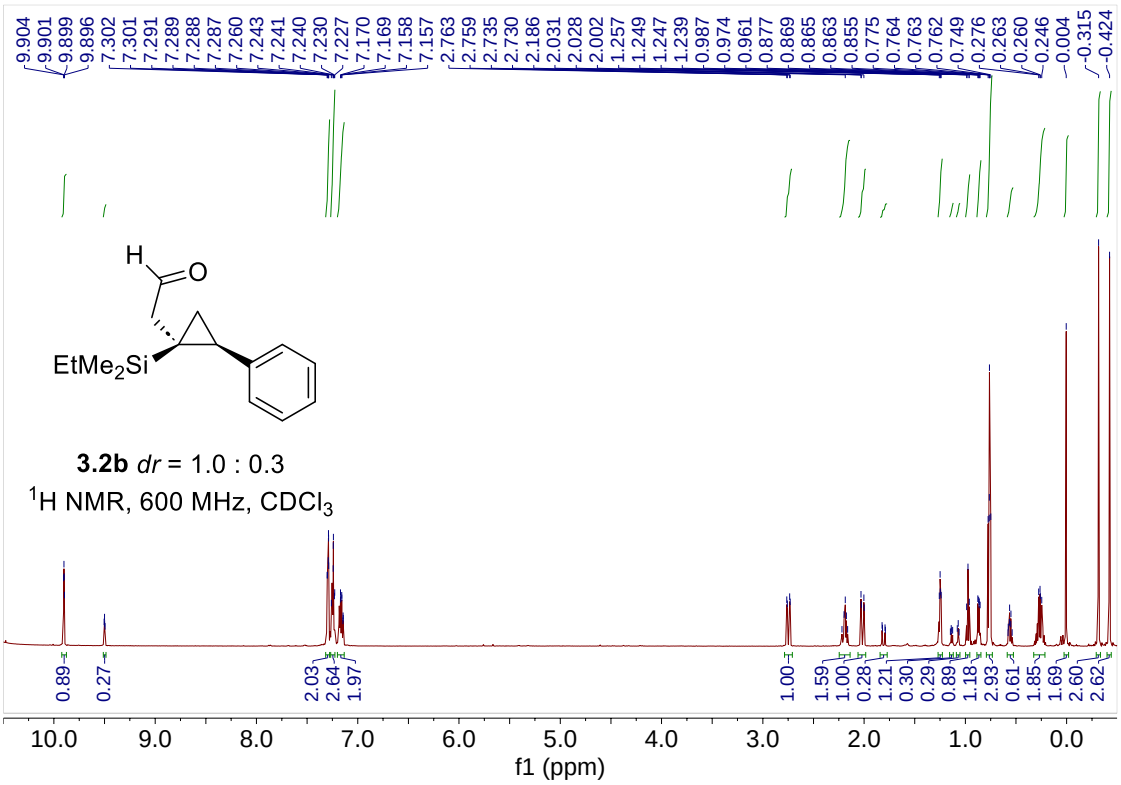
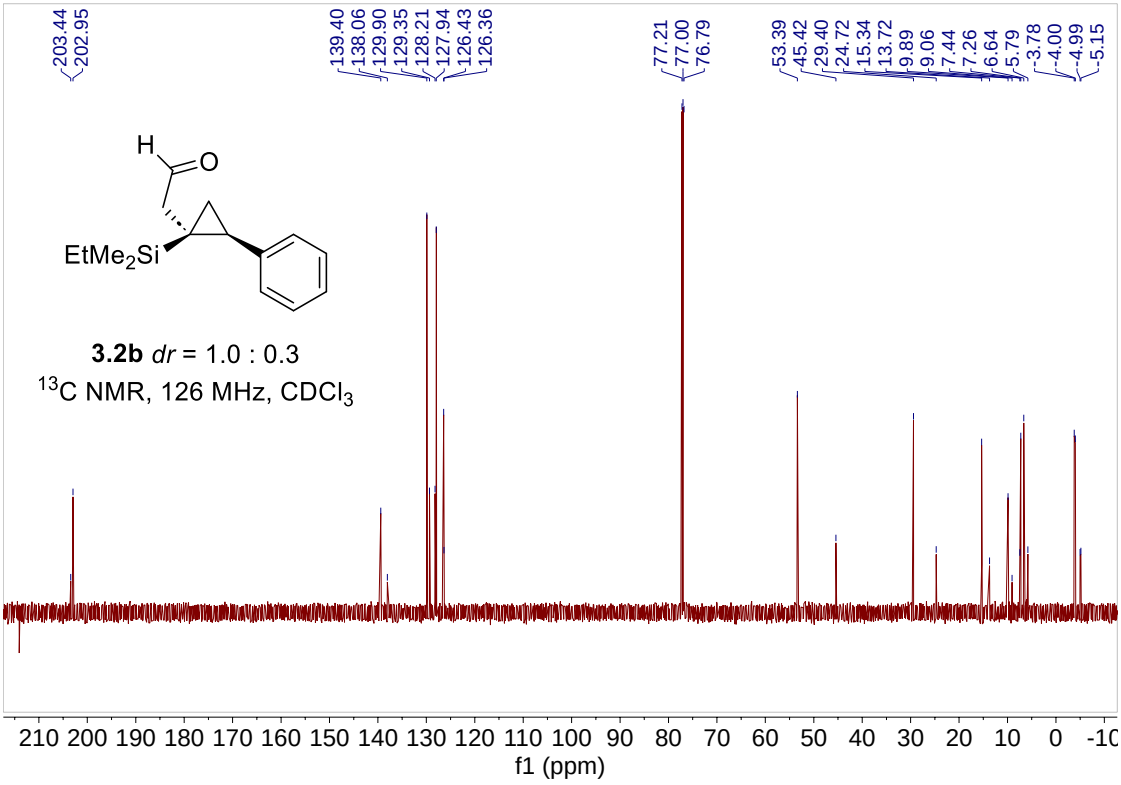
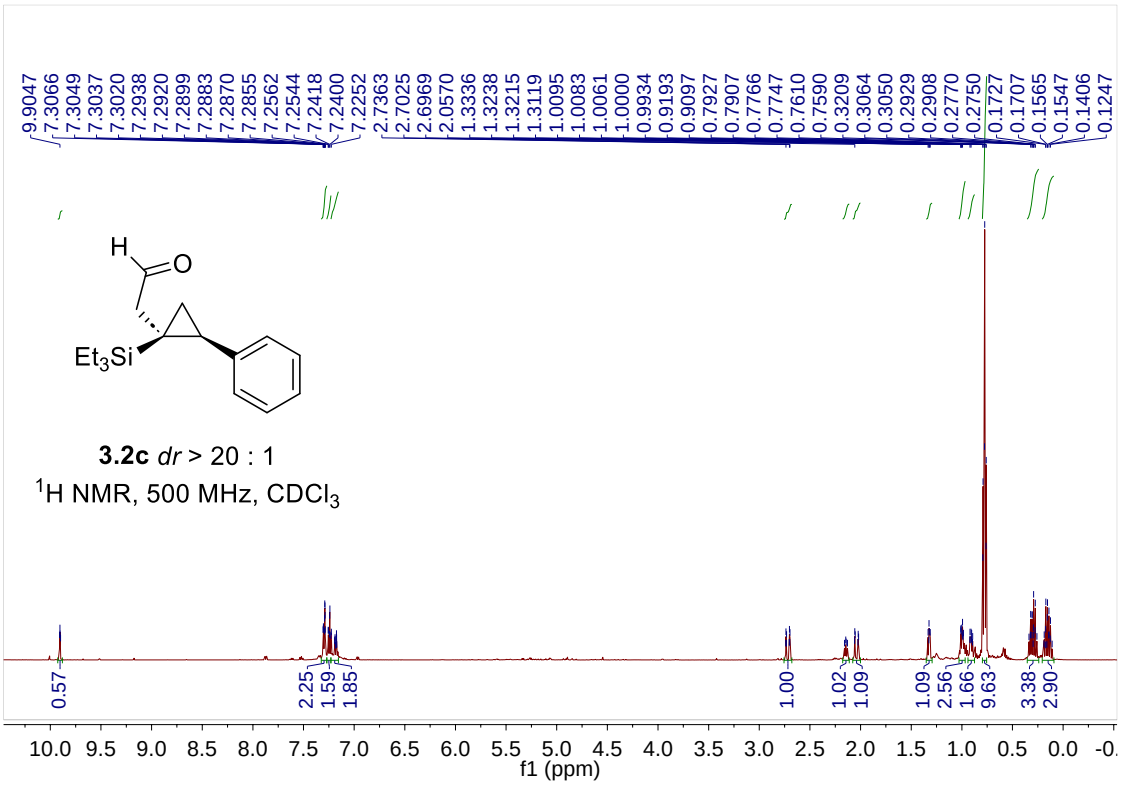
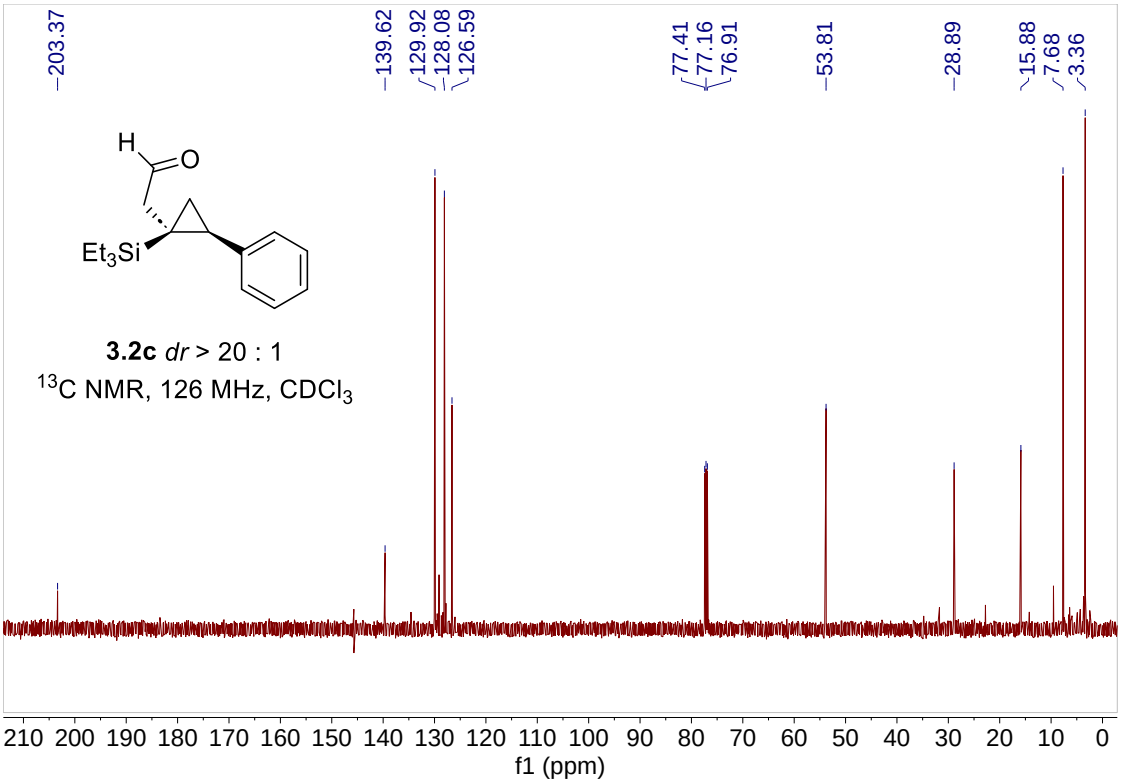
139.0611
137.9252
134.1037
134.0383
129.9075
129.3344
129.0180
128.2137
127.9792
127.9482
127.7036
126.4788
77.2540
76.9996
76.7452
53.2340
45.1036
29.3888
24.8788
15.7025
10.2810
-2.8324
-3.4254
-4.3500
-4.4260
H
O
PhMe2Si
3.2a dr = 1.0 : 0.3
13C NMR, 126 MHz, CDCl3
f1 (ppm)

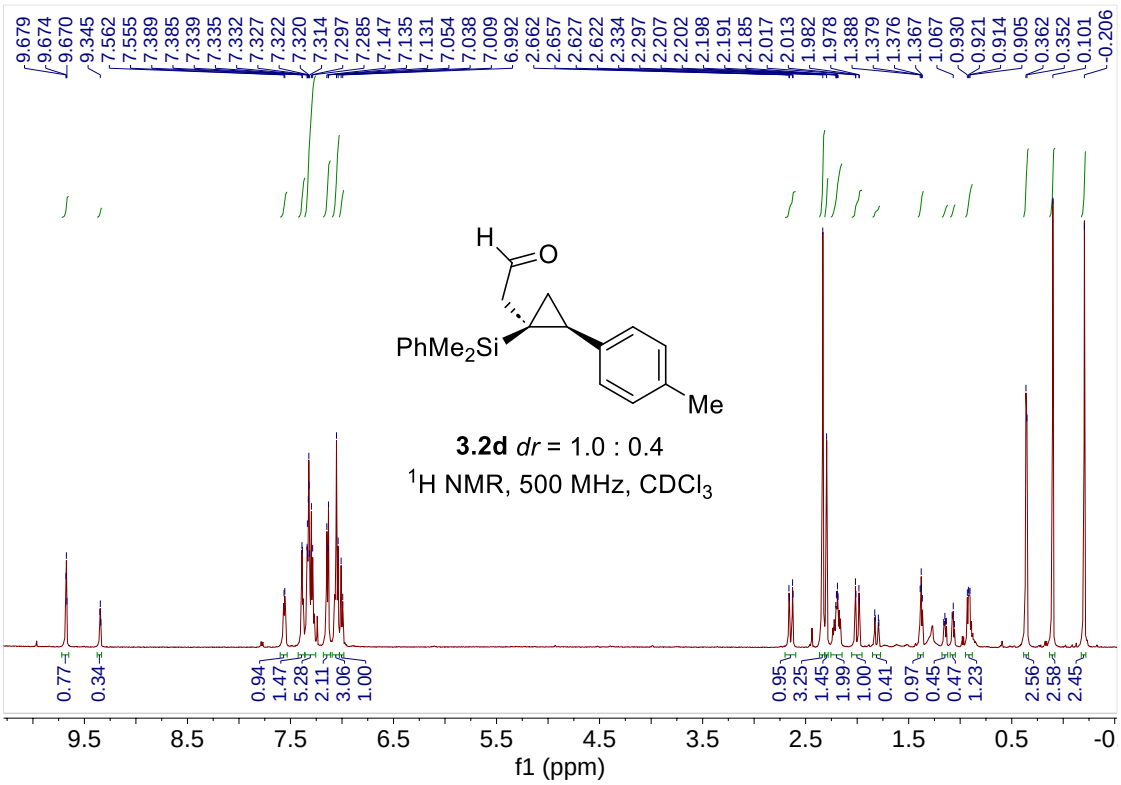

H
O
PhMe2Si
3.2a dr = 1.0 : 0.3
1H NMR, 500 MHz, CDCl3
f1 (ppm)

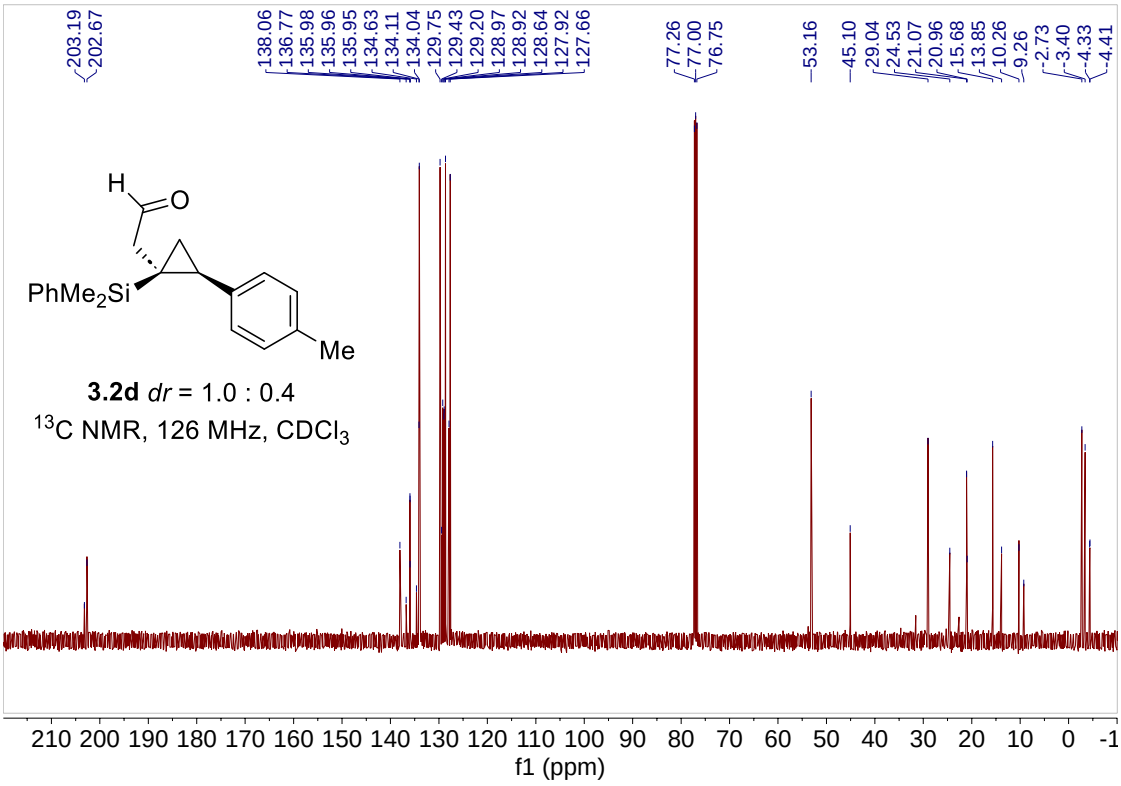

9.904
9.901
9.899
9.896
7.302
7.301
7.291
7.289
7.288
7.287
7.260
7.243
7.241
7.240
7.230
7.227
7.170
7.169
7.158
7.157
2.763
2.759
2.735
2.730
2.186
2.031
2.028
2.002
1.257
1.249
1.247
1.239
0.987
0.974
0.961
0.877
0.869
0.865
0.863
0.855
0.775
0.764
0.763
0.762
0.749
0.276
0.263
0.260
0.246
0.004
-0.315
-0.424
H
O
EtMe2Si
3.2b dr = 1.0 : 0.3
1H NMR, 600 MHz, CDCl3
0.89
0.27
2.03
2.64
1.97
1.00
1.59
1.00
0.28
1.21
0.30
0.29
0.89
1.18
2.93
0.61
1.85
1.69
2.60
2.62
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

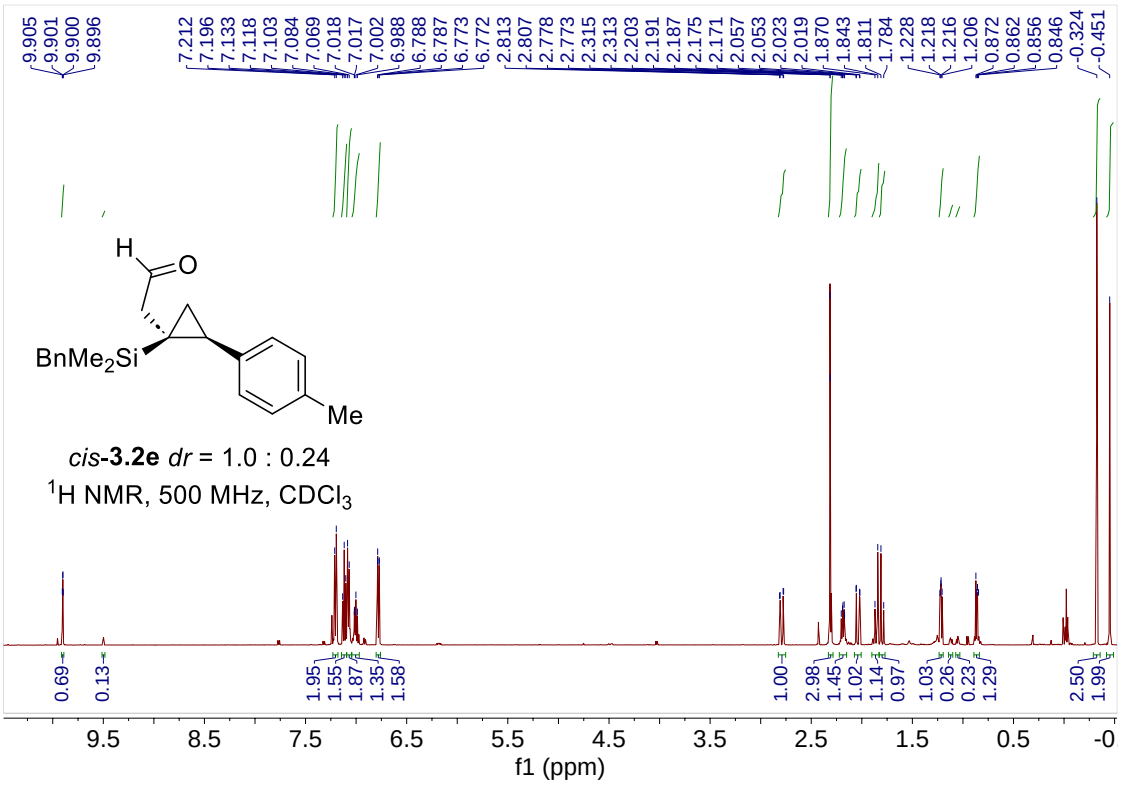

203.44
202.95
139.40
138.06
129.90
129.35
128.21
127.94
126.43
126.36
77.21
77.00
76.79
53.39
45.42
29.40
24.72
15.34
13.72
9.89
9.06
7.44
7.26
6.64
5.79
-3.78
-4.00
-4.99
-5.15
H
O
EtMe2Si
3.2b dr = 1.0 : 0.3
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

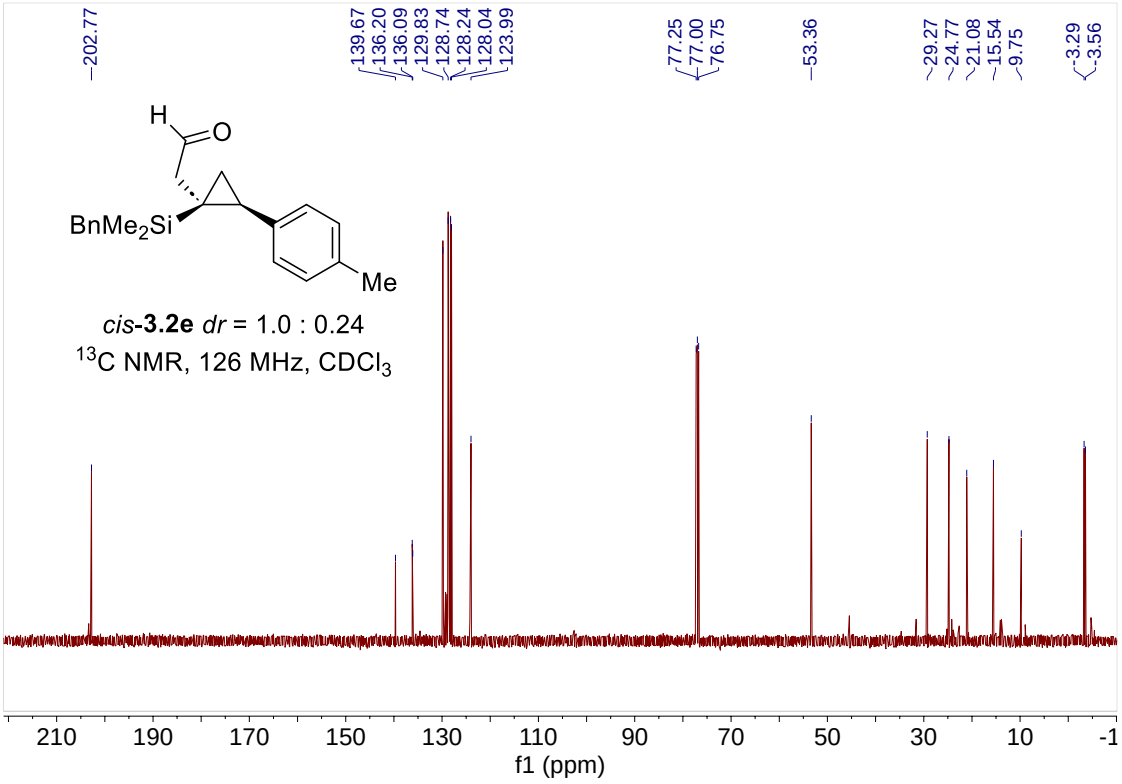

9.9047
7.3066
7.3049
7.3037
7.3020
7.2938
7.2920
7.2899
7.2883
7.2870
7.2855
7.2562
7.2544
7.2418
7.2400
7.2252
2.7363
2.7025
2.6969
2.0570
1.3336
1.3238
1.3215
1.3119
1.0095
1.0083
1.0061
1.0000
0.9934
0.9193
0.9097
0.7927
0.7907
0.7766
0.7747
0.7610
0.7590
0.3209
0.3064
0.3050
0.2929
0.2908
0.2770
0.2750
0.1727
0.1707
0.1565
0.1547
0.1406
0.1247
H
O
Et3Si
3.2c dr > 20 : 1
1H NMR, 500 MHz, CDCl3
0.57
2.25
1.59
1.85
1.00
1.02
1.09
1.09
2.56
1.66
9.63
3.38
2.90
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.
f1 (ppm)

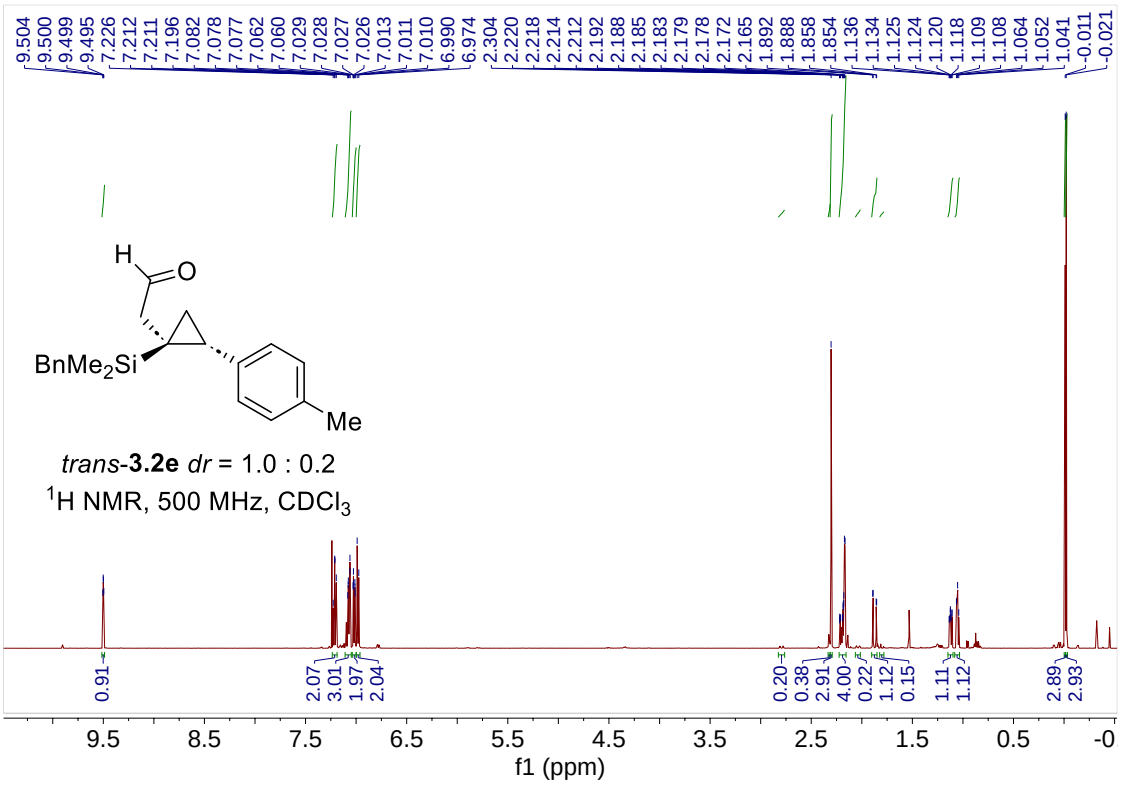

203.37
139.62
129.92
128.08
126.59
77.41
77.16
76.91
53.81
28.89
15.88
7.68
3.36
H
O
Et3Si
3.2c dr > 20 : 1
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

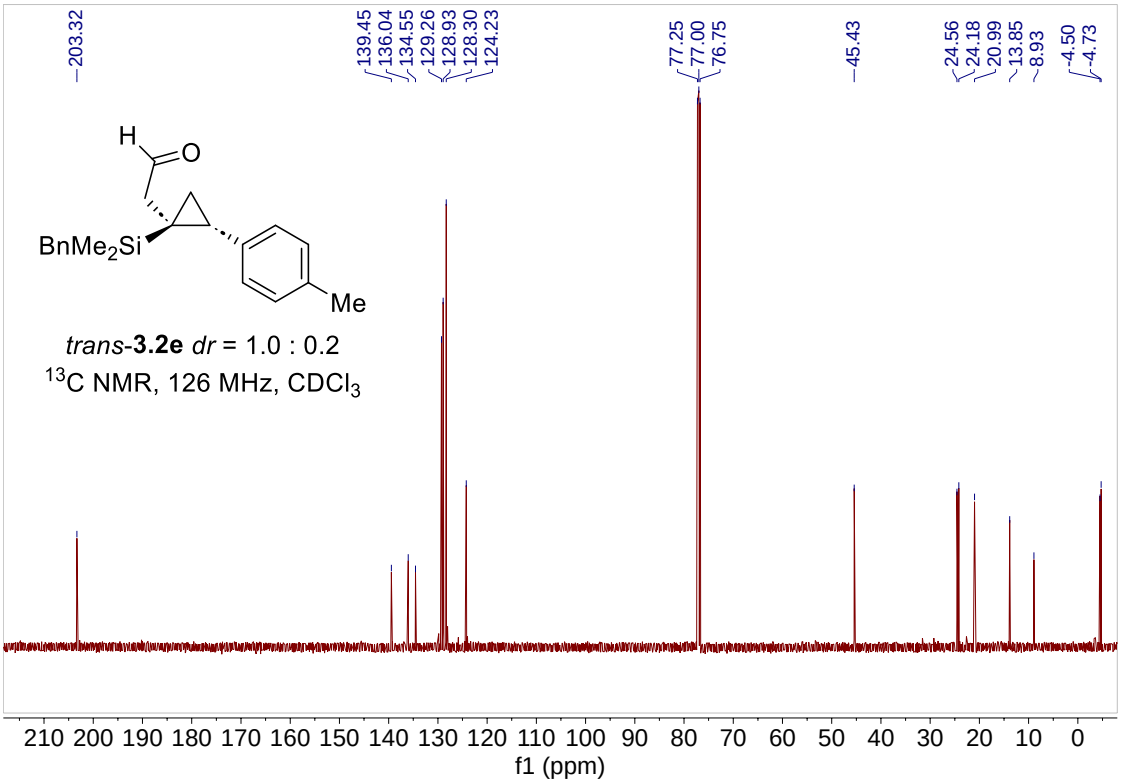

9.679
9.674
9.670
9.345
7.562
7.555
7.389
7.385
7.339
7.335
7.332
7.327
7.322
7.320
7.314
7.297
7.285
7.147
7.135
7.131
7.054
7.038
7.009
6.992
2.662
2.657
2.627
2.622
2.334
2.297
2.207
2.202
2.198
2.191
2.185
2.017
2.013
1.982
1.978
1.388
1.379
1.376
1.367
1.067
0.930
0.921
0.914
0.905
0.362
0.352
0.101
-0.206
0.77
0.34
0.94
1.47
5.28
2.11
3.06
1.00
0.95
3.25
1.45
1.99
1.00
0.41
0.97
0.45
0.47
1.23
2.56
2.58
2.45
H
O
PhMe2Si
Me
3.2d dr = 1.0 : 0.4
1H NMR, 500 MHz, CDCl3
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
f1 (ppm)

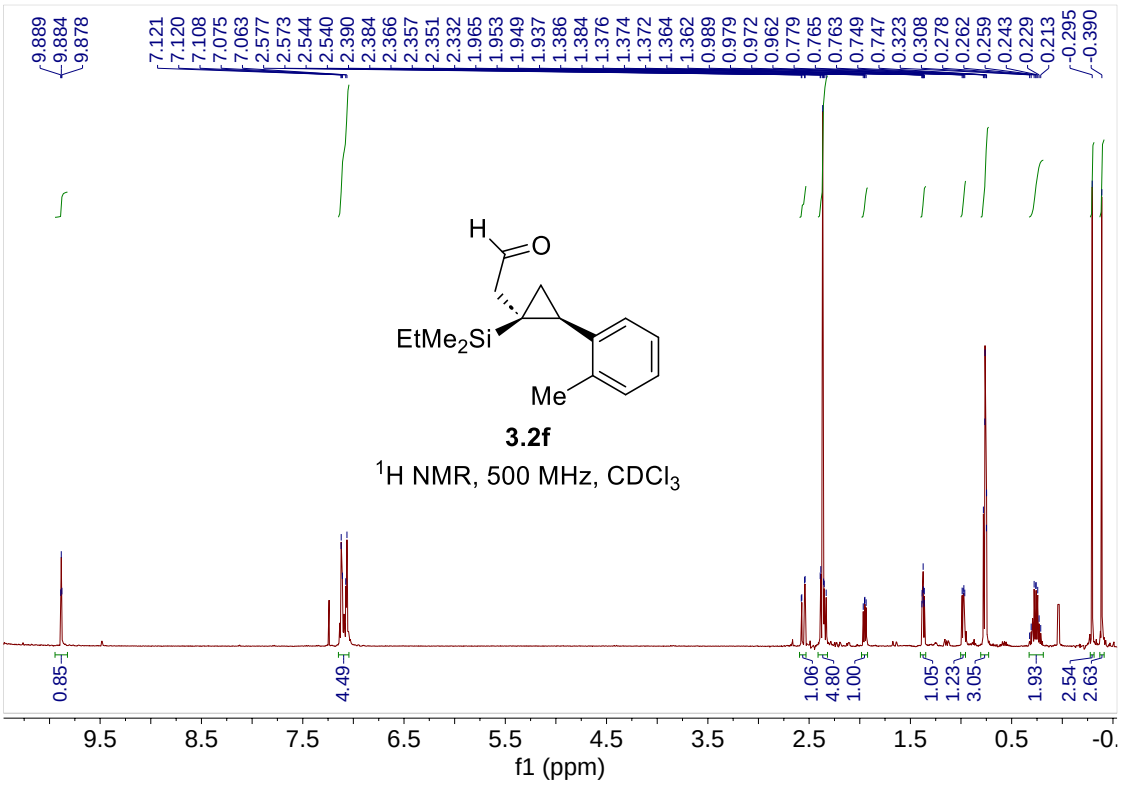

203.19
202.67
138.06
136.77
135.98
135.96
135.95
134.63
134.11
134.04
129.75
129.43
129.20
128.97
128.92
128.64
127.92
127.66
77.26
77.00
76.75
53.16
45.10
29.04
24.53
21.07
20.96
15.68
13.85
10.26
9.26
-2.73
-3.40
-4.33
-4.41
H
O
PhMe2Si
Me
3.2d dr = 1.0 : 0.4
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

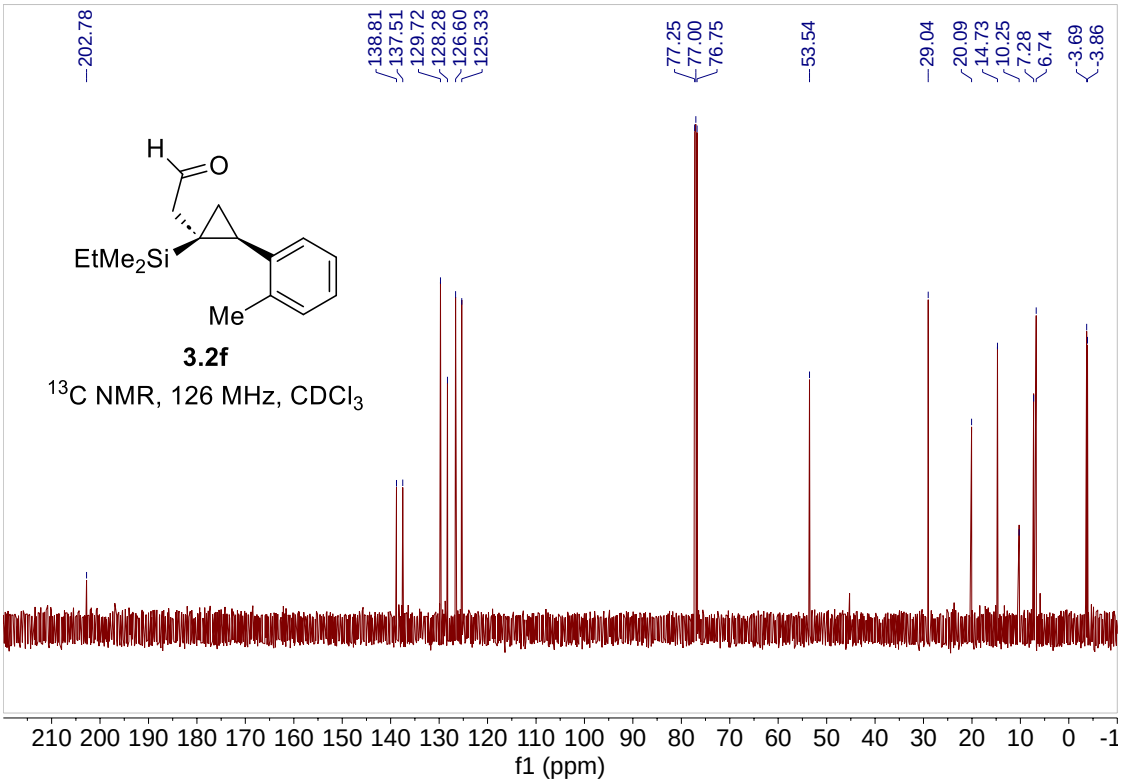

9.905
9.901
9.900
9.896
7.212
7.196
7.133
7.118
7.103
7.084
7.069
7.018
7.017
7.002
6.988
6.788
6.787
6.773
6.772
2.813
2.807
2.778
2.773
2.315
2.313
2.203
2.191
2.187
2.175
2.171
2.057
2.053
2.023
2.019
1.870
1.843
1.811
1.784
1.228
1.218
1.216
1.206
0.872
0.862
0.856
0.846
-0.324
-0.451
H
O
BnMe2Si
Me
cis-3.2e dr = 1.0 : 0.24
1H NMR, 500 MHz, CDCl3
0.69
0.13
1.95
1.55
1.87
1.35
1.58
1.00
2.98
1.45
1.02
1.14
0.97
1.03
0.26
0.23
1.29
2.50
1.99
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
f1 (ppm)

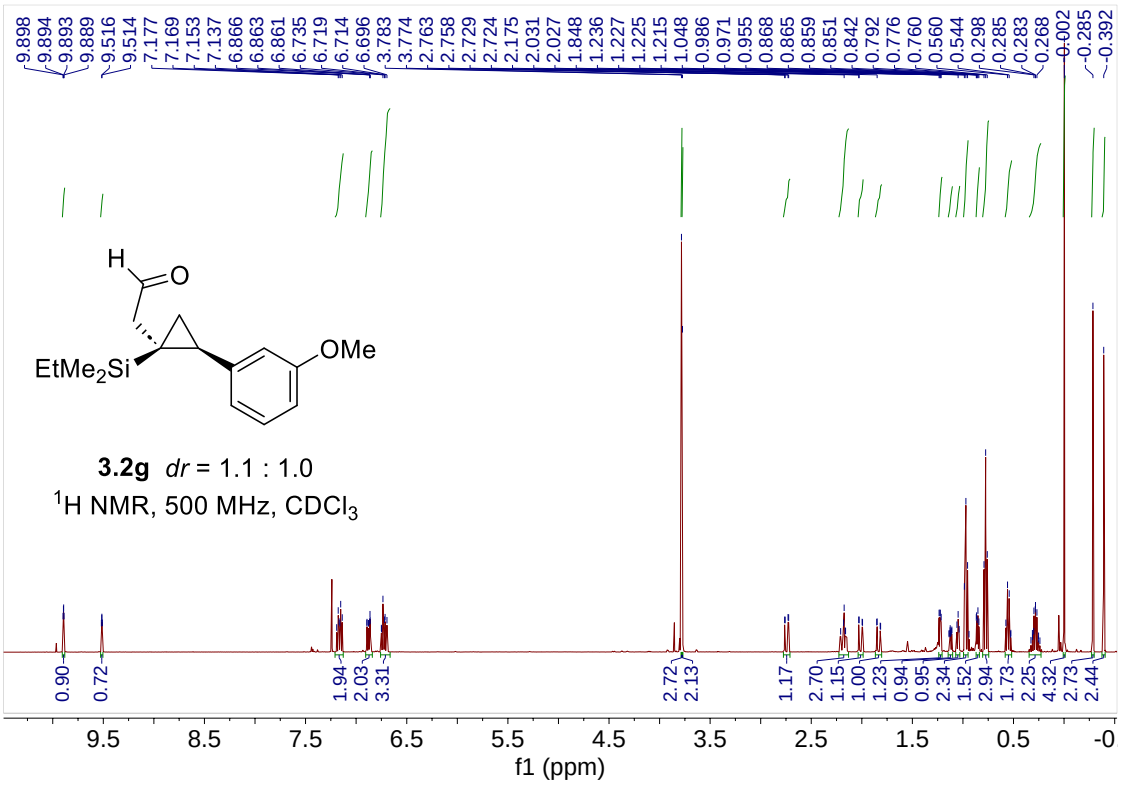

202.77
139.67
136.20
136.09
129.83
128.74
128.24
128.04
123.99
77.25
77.00
76.75
53.36
29.27
24.77
21.08
15.54
9.75
-3.29
-3.56
H
O
BnMe2Si
Me
cis-3.2e dr = 1.0 : 0.24
13C NMR, 126 MHz, CDCl3
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

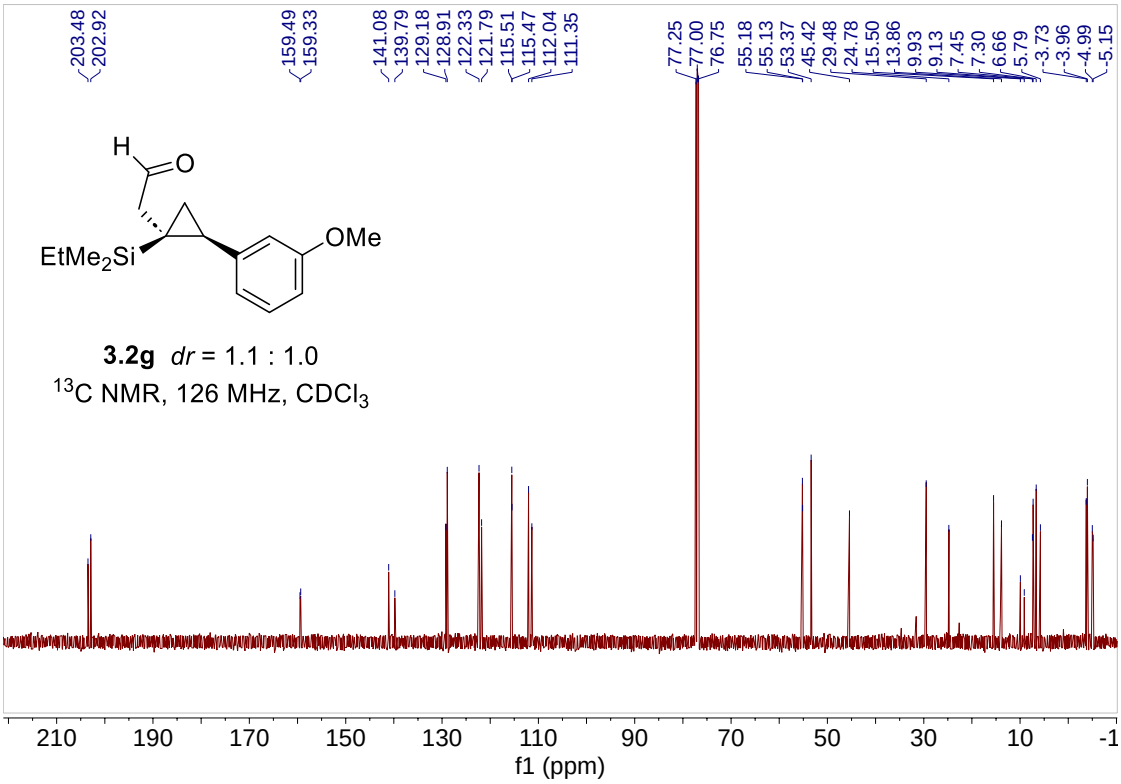

9.504
9.500
9.499
9.495
7.226
7.212
7.211
7.196
7.082
7.078
7.077
7.062
7.060
7.029
7.028
7.027
7.026
7.013
7.011
7.010
6.990
6.974
2.304
2.220
2.218
2.214
2.212
2.192
2.188
2.185
2.183
2.179
2.178
2.172
2.165
1.892
1.888
1.858
1.854
1.136
1.134
1.125
1.124
1.120
1.118
1.109
1.108
1.064
1.052
1.041
-0.011
-0.021
H
O
BnMe2Si
Me
trans-3.2e dr = 1.0 : 0.2
1H NMR, 500 MHz, CDCl3
0.91
2.07
3.01
1.97
2.04
0.20
0.38
2.91
4.00
0.22
1.12
0.15
1.11
1.12
2.89
2.93
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
f1 (ppm)

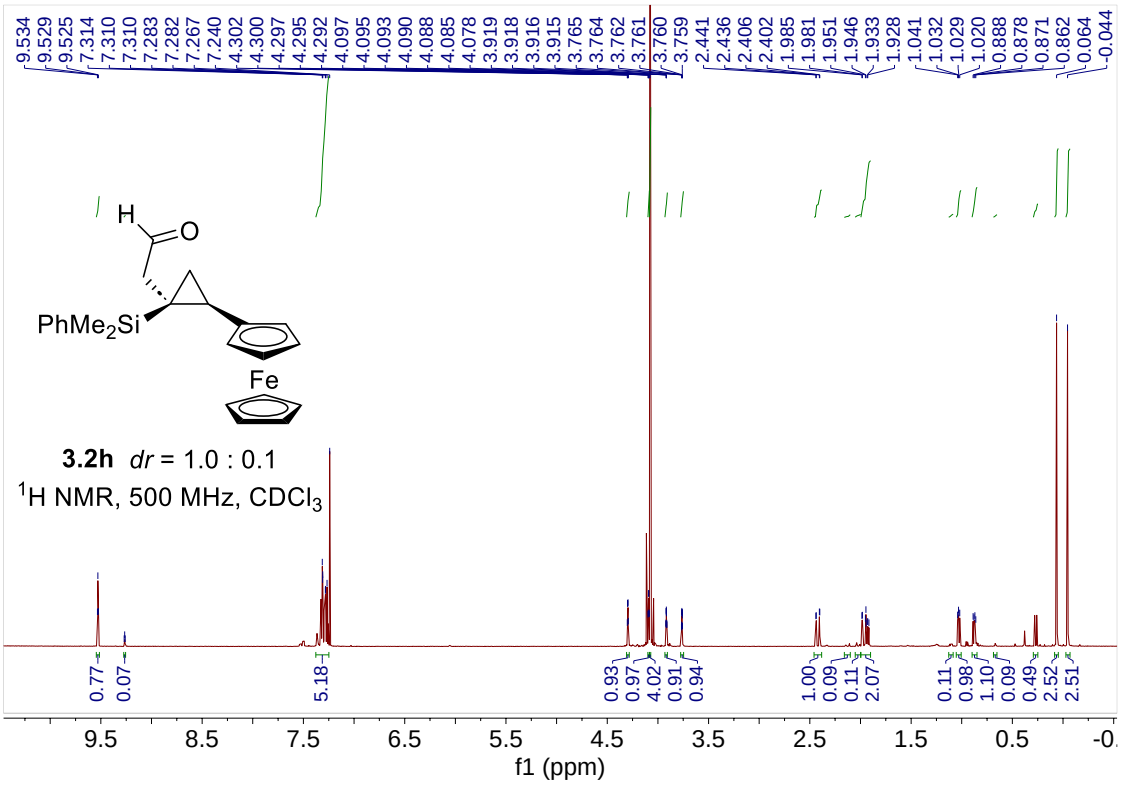

203.32
139.45
136.04
134.55
129.26
128.93
128.30
124.23
77.25
77.00
76.75
45.43
24.56
24.18
20.99
13.85
8.93
-4.50
-4.73
H
O
BnMe2Si
Me
trans-3.2e dr = 1.0 : 0.2
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

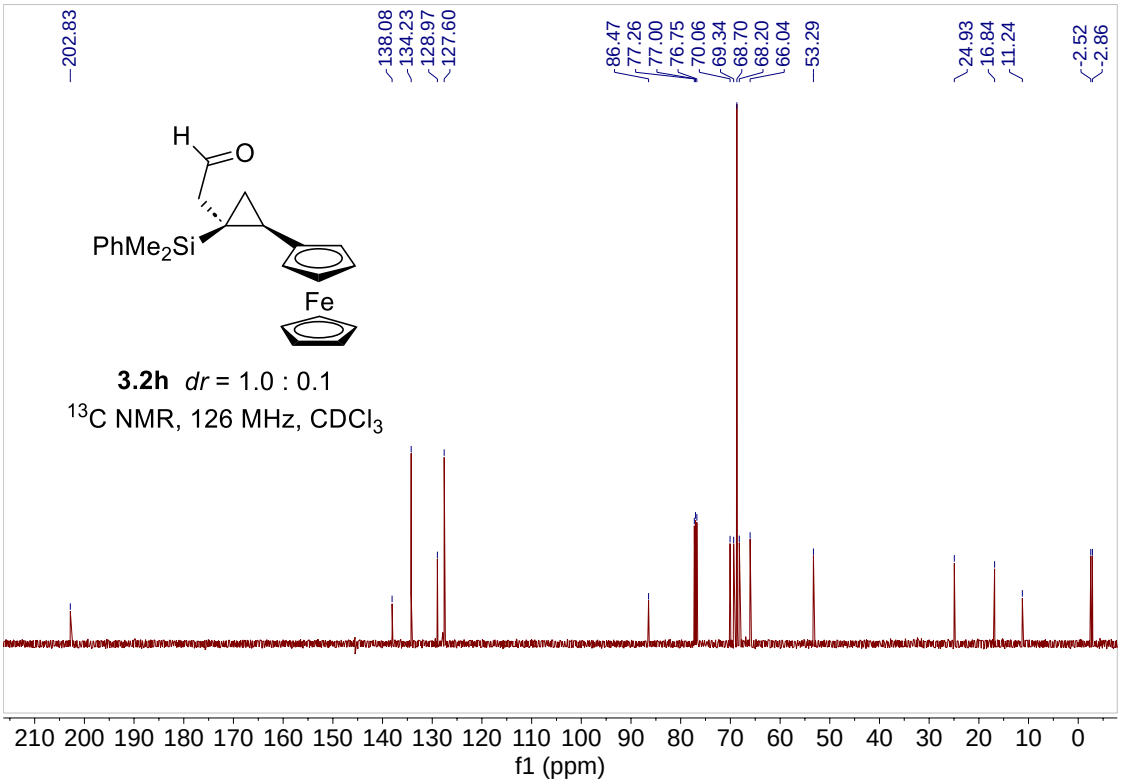

9.889
9.884
9.878
7.121
7.120
7.108
7.075
7.063
2.577
2.573
2.544
2.540
2.390
2.384
2.366
2.357
2.351
2.332
1.965
1.953
1.949
1.937
1.386
1.384
1.376
1.374
1.372
1.364
1.362
0.989
0.979
0.972
0.962
0.779
0.765
0.763
0.749
0.747
0.323
0.308
0.278
0.262
0.259
0.243
0.229
0.213
-0.295
-0.390
H
O
EtMe2Si
Me
3.2f
1H NMR, 500 MHz, CDCl3
0.85
4.49
1.06
4.80
1.00
1.05
1.23
3.05
1.93
2.54
2.63
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

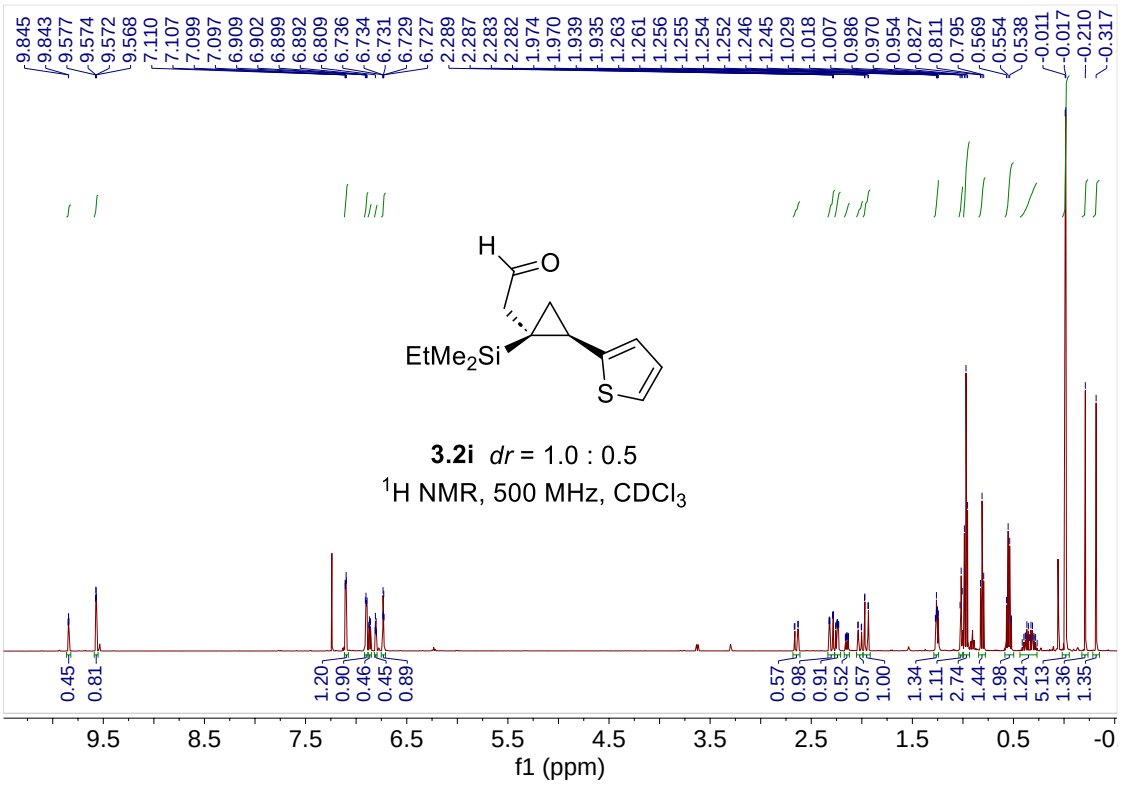

202.78
138.81
137.51
129.72
128.28
126.60
125.33
77.25
77.00
76.75
53.54
29.04
20.09
14.73
10.25
7.28
6.74
-3.69
-3.86
H
O
EtMe2Si
Me
3.2f
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

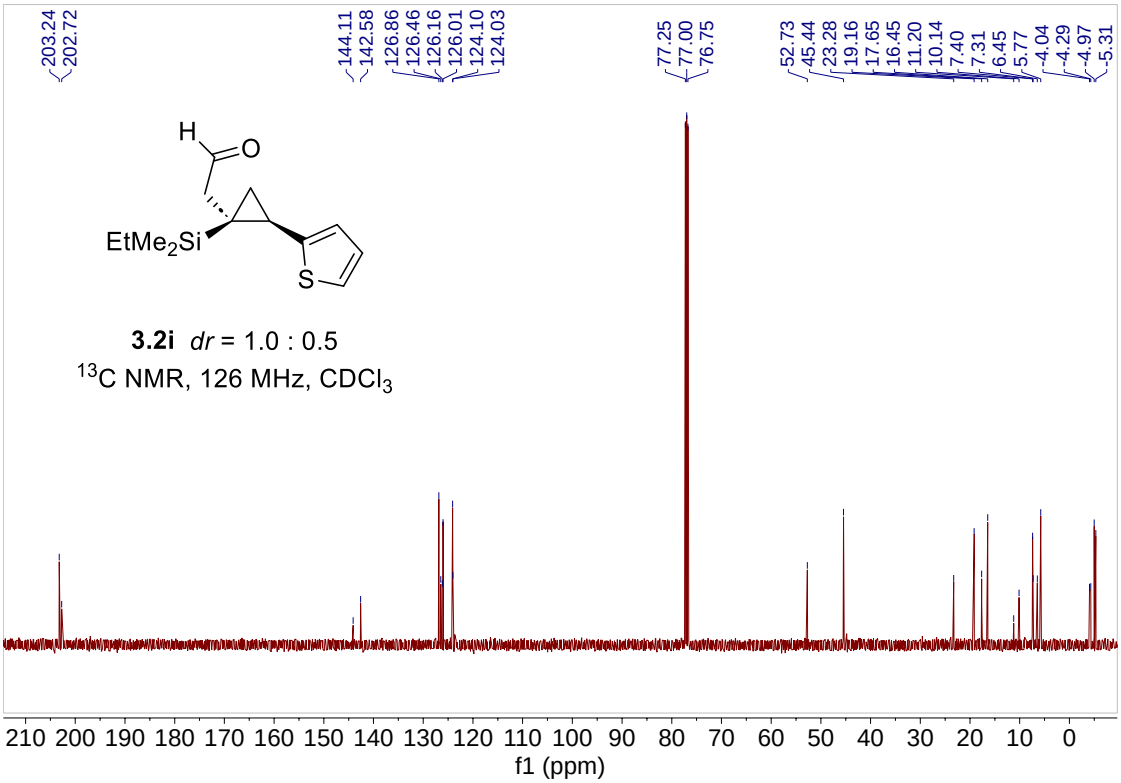

9.898
9.894
9.893
9.889
9.516
9.514
7.177
7.169
7.153
7.137
6.866
6.863
6.861
6.735
6.719
6.714
6.696
3.783
3.774
2.763
2.758
2.729
2.724
2.175
2.031
2.027
1.848
1.236
1.227
1.225
1.215
1.048
0.986
0.971
0.955
0.868
0.865
0.859
0.851
0.842
0.792
0.776
0.760
0.560
0.544
0.298
0.285
0.283
0.268
0.002
-0.285
-0.392
H
O
OMe
EtMe2Si
3.2g dr = 1.1 : 1.0
1H NMR, 500 MHz, CDCl3
0.90
0.72
1.94
2.03
3.31
2.72
2.13
1.17
2.70
1.15
1.00
1.23
0.94
0.95
2.34
1.52
2.94
1.73
2.25
4.32
2.73
2.44
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
f1 (ppm)

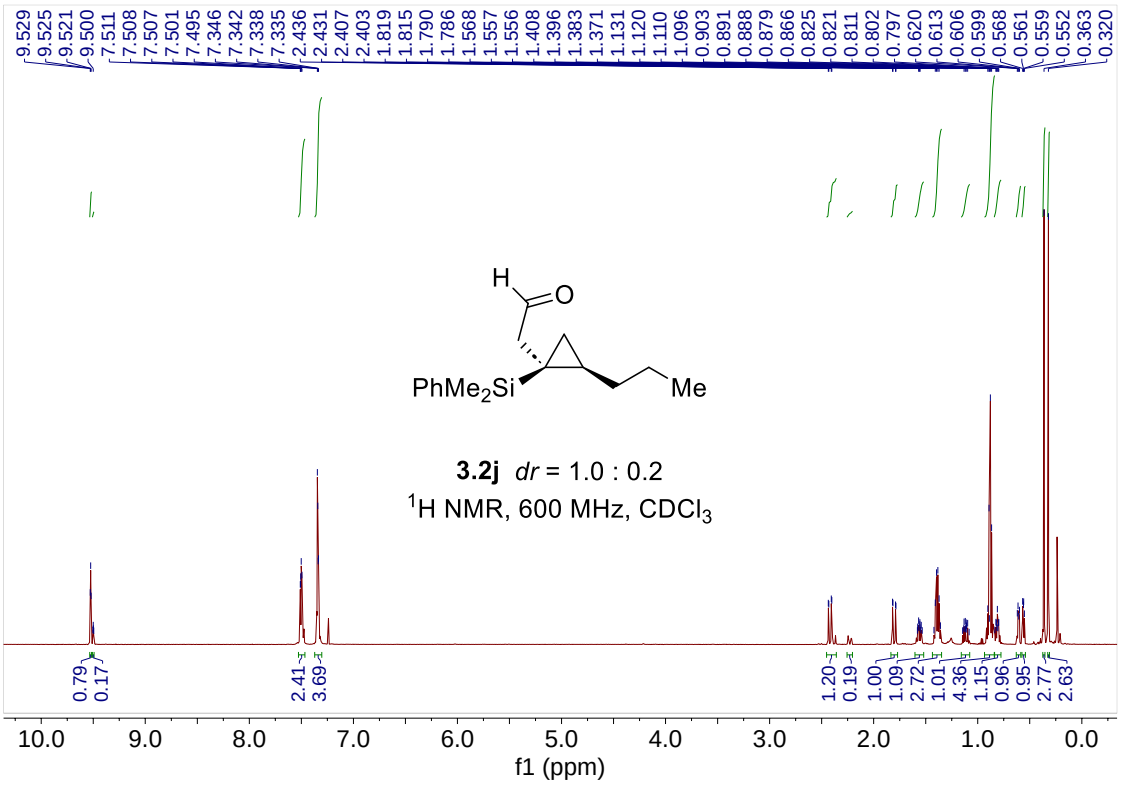

203.48
202.92
159.49
159.33
141.08
139.79
129.18
128.91
122.33
121.79
115.51
115.47
112.04
111.35
77.25
77.00
76.75
55.18
55.13
53.37
45.42
29.48
24.78
15.50
13.86
9.93
9.13
7.45
7.30
6.66
5.79
-3.73
-3.96
-4.99
-5.15
H
O
OMe
EtMe2Si
3.2g dr = 1.1 : 1.0
13C NMR, 126 MHz, CDCl3
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

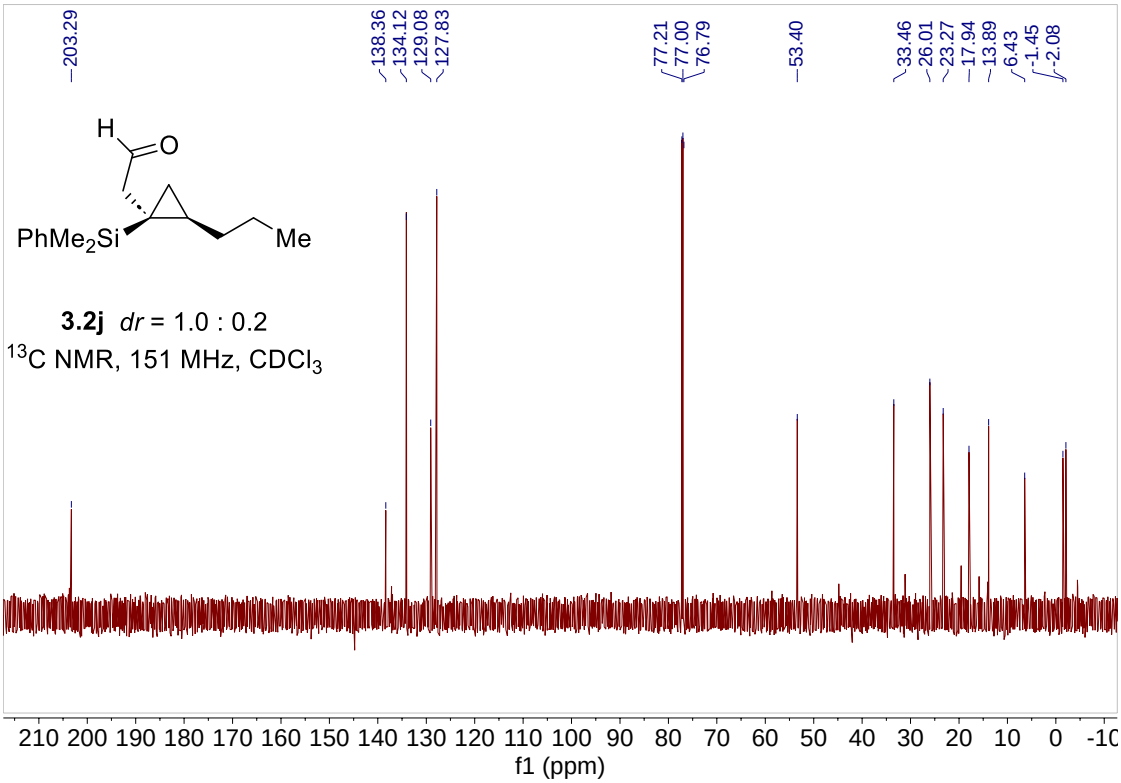

9.534
9.529
9.525
7.314
7.310
7.310
7.283
7.282
7.267
7.240
4.302
4.300
4.297
4.295
4.292
4.097
4.095
4.093
4.090
4.088
4.085
4.078
3.919
3.918
3.916
3.915
3.765
3.764
3.762
3.761
3.760
3.759
2.441
2.436
2.406
2.402
1.985
1.981
1.951
1.946
1.933
1.928
1.041
1.032
1.029
1.020
0.888
0.878
0.871
0.862
0.064
-0.044
H
O
PhMe2Si
Fe
3.2h dr = 1.0 : 0.1
1H NMR, 500 MHz, CDCl3
0.77
0.07
5.18
0.93
0.97
4.02
0.91
0.94
1.00
0.09
0.11
2.07
0.11
0.98
1.10
0.09
0.49
2.52
2.51
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

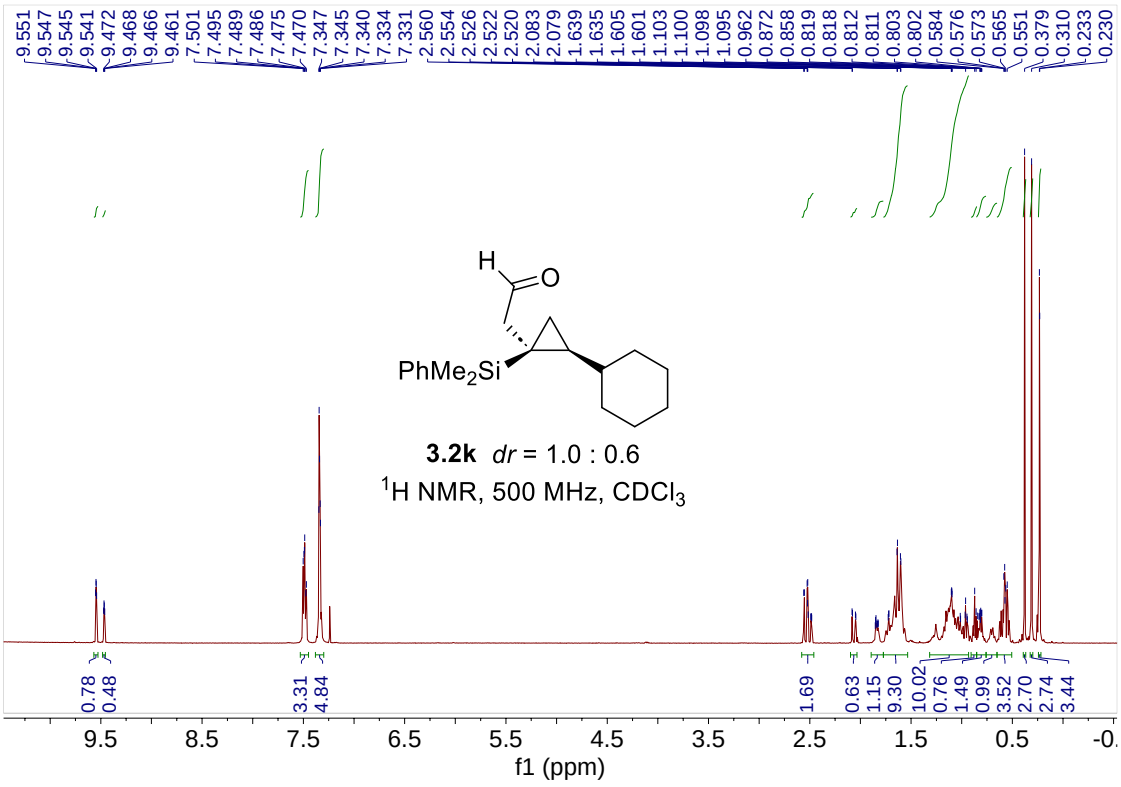

202.83
138.08
134.23
128.97
127.60
86.47
77.26
77.00
76.75
70.06
69.34
68.70
68.20
66.04
53.29
24.93
16.84
11.24
-2.52
-2.86
H
O
PhMe2Si
Fe
3.2h dr = 1.0 : 0.1
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

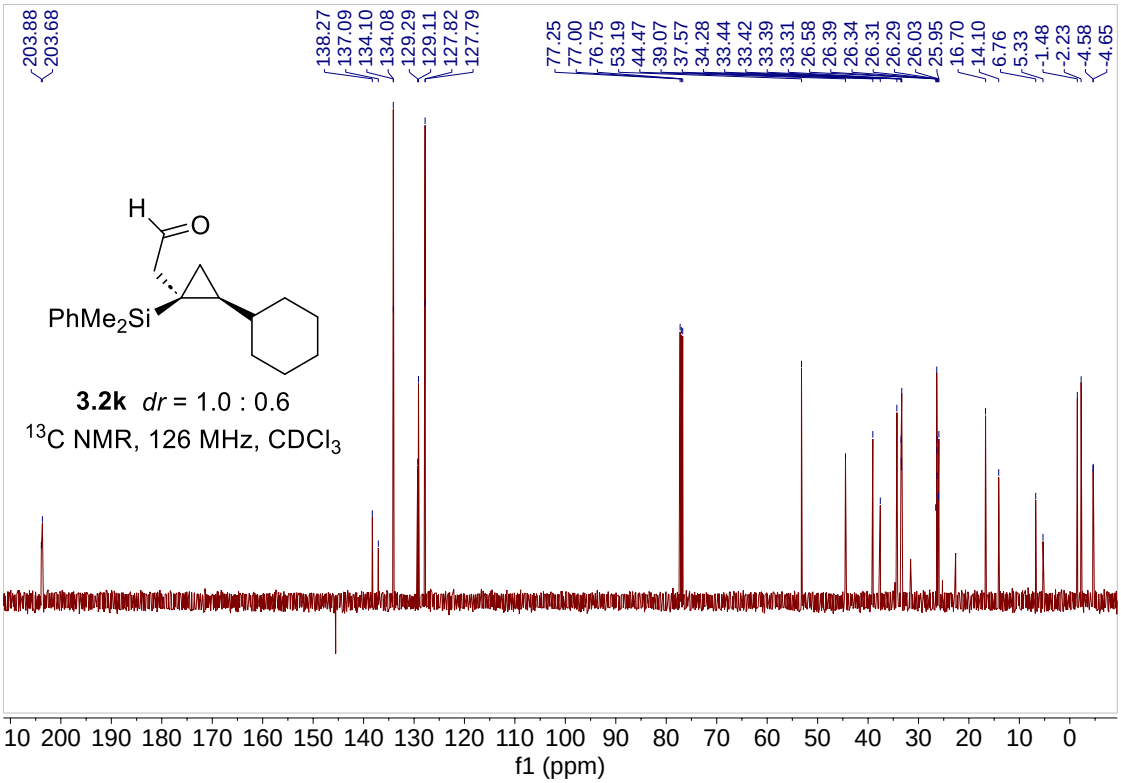

9.845 9.843 9.577 9.574 9.572 9.568 7.110 7.107 7.099 7.097 7.097 6.909 6.902 6.899 6.892 6.809 6.736 6.734 6.731 6.729 6.727 2.289 2.287 2.283 2.282 1.974 1.970 1.939 1.935 1.263 1.261 1.256 1.255 1.254 1.252 1.246 1.245 1.029 1.018 1.007 0.986 0.970 0.954 0.827 0.811 0.795 0.569 0.554 0.538 -0.011 -0.017 -0.210 -0.317
H
O
EtMe2Si
S
3.2i dr = 1.0 : 0.5
1H NMR, 500 MHz, CDCl3
0.45 0.81 1.20 0.90 0.46 0.45 0.89 0.57 0.98 0.91 0.52 0.57 1.00 1.34 1.11 2.74 1.44 1.98 1.24 5.13 1.36 1.35
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0
f1 (ppm)

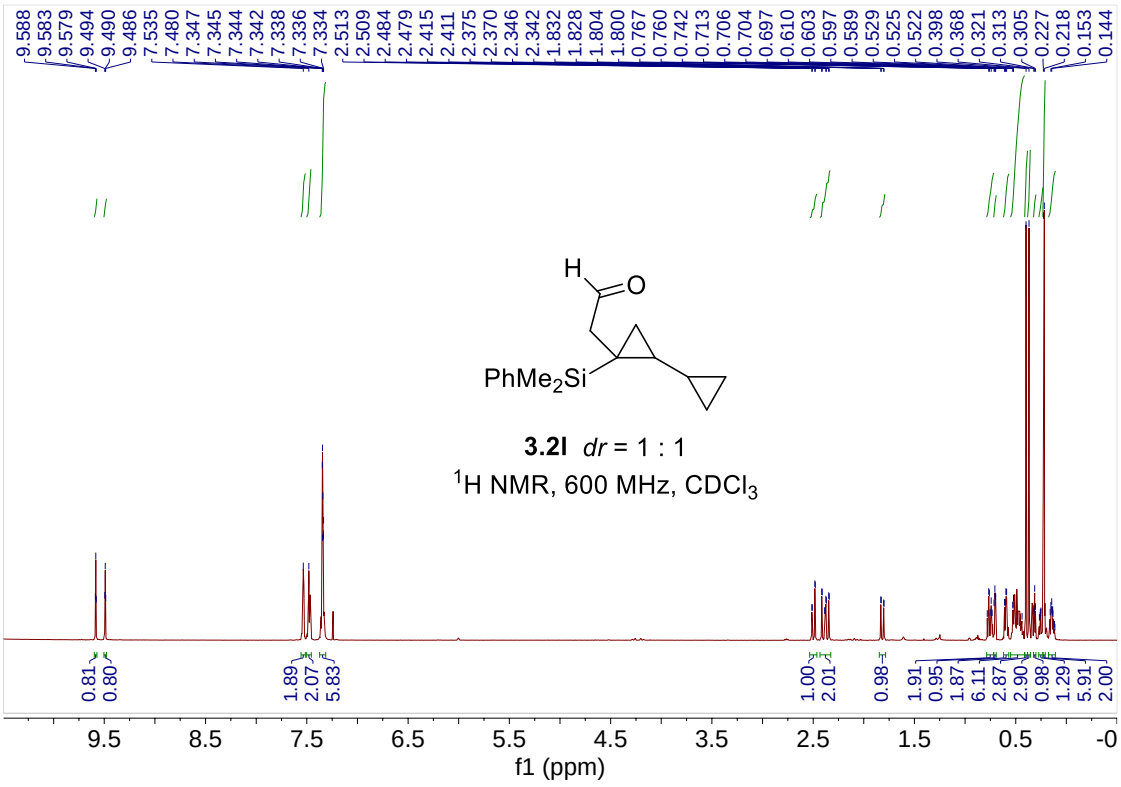

203.24 202.72 144.11 142.58 126.86 126.46 126.16 126.01 124.10 124.03 77.25 77.00 76.75 52.73 45.44 23.28 19.16 17.65 16.45 11.20 10.14 7.40 7.31 6.45 5.77 -4.04 -4.29 -4.97 -5.31
H
O
EtMe2Si
S
3.2i dr = 1.0 : 0.5
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

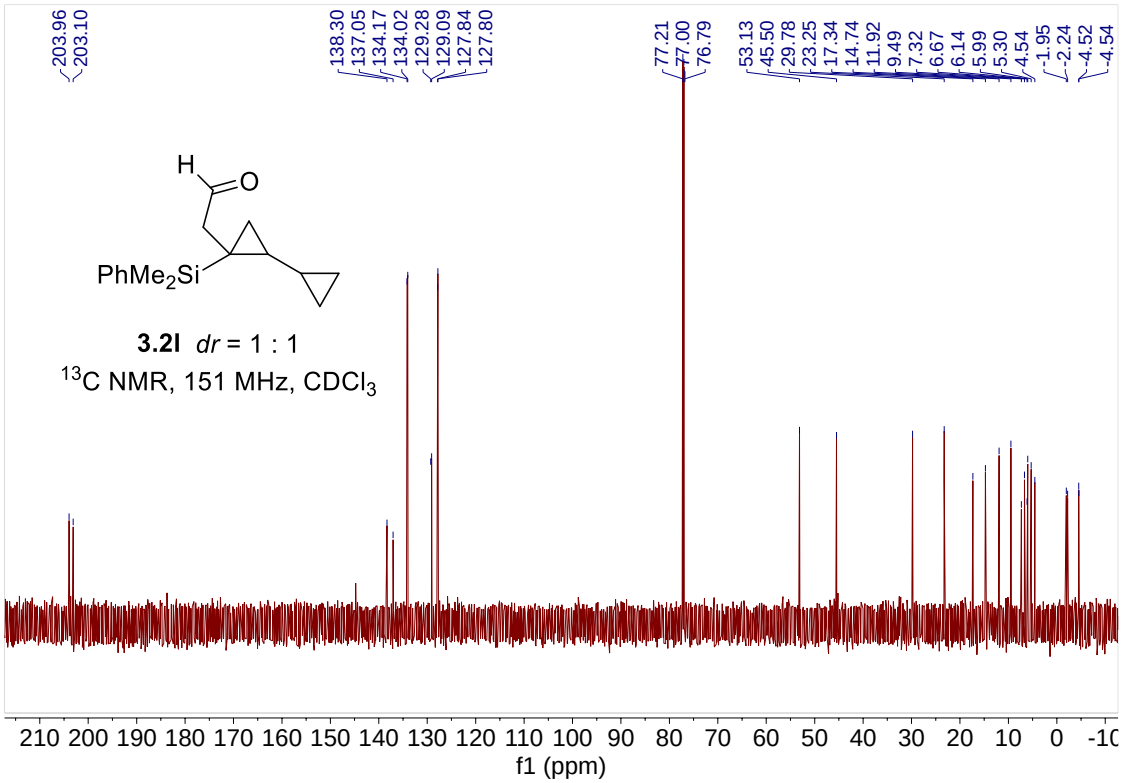

9.529
9.525
9.521
9.500
7.511
7.508
7.507
7.501
7.495
7.346
7.342
7.338
7.335
2.436
2.431
2.407
2.403
1.819
1.815
1.790
1.786
1.568
1.557
1.556
1.408
1.396
1.383
1.371
1.131
1.120
1.110
1.096
0.903
0.891
0.888
0.879
0.866
0.825
0.821
0.811
0.802
0.797
0.620
0.613
0.606
0.599
0.568
0.561
0.559
0.552
0.363
0.320
H
O
PhMe2Si
Me
3.2j dr = 1.0 : 0.2
1H NMR, 600 MHz, CDCl3
0.79
0.17
2.41
3.69
1.20
0.19
1.00
1.09
2.72
1.01
4.36
1.15
0.96
0.95
2.77
2.63
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

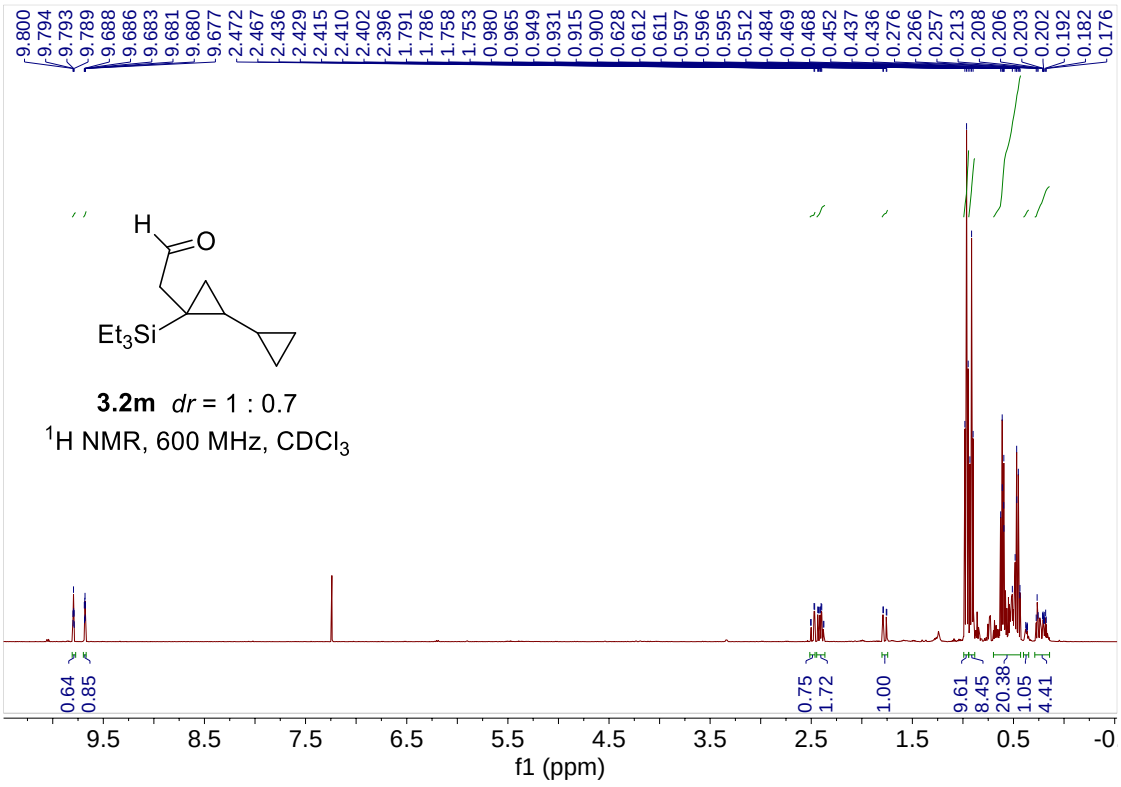

203.29
138.36
134.12
129.08
127.83
77.21
77.00
76.79
53.40
33.46
26.01
23.27
17.94
13.89
6.43
-1.45
-2.08
H
O
PhMe2Si
Me
3.2j dr = 1.0 : 0.2
13C NMR, 151 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

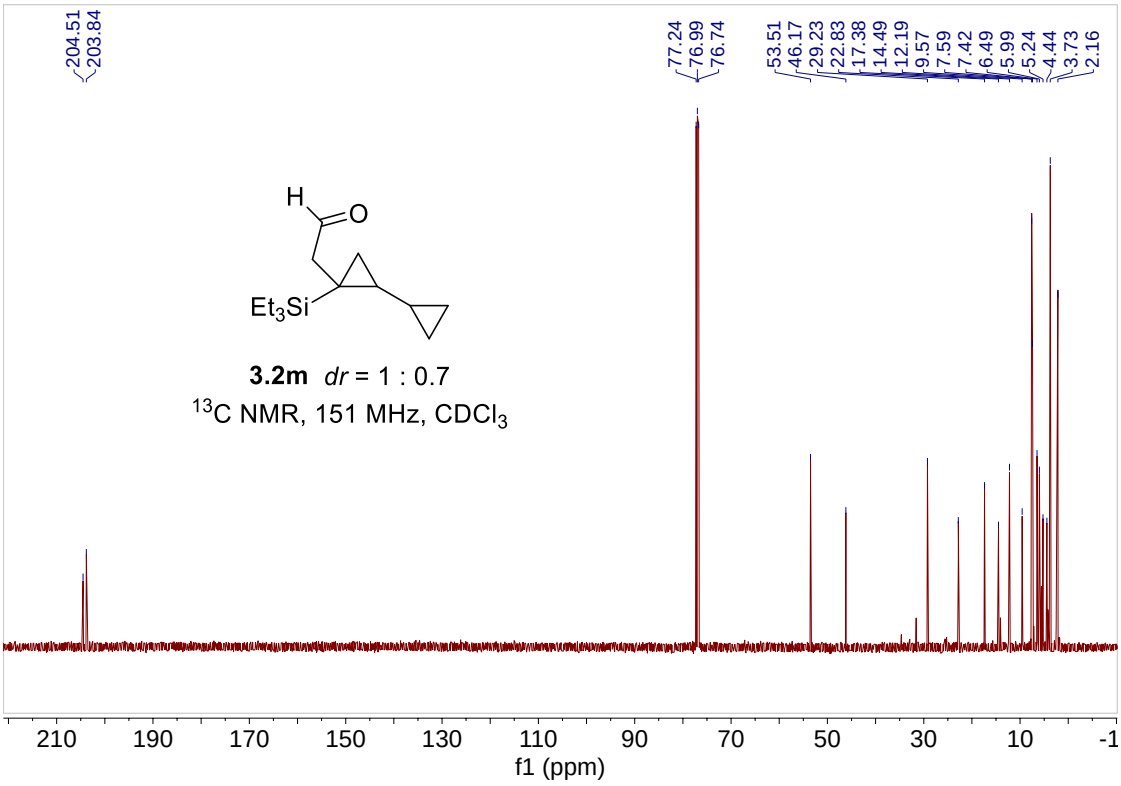

9.551
9.547
9.545
9.541
9.472
9.468
9.466
9.461
7.501
7.495
7.489
7.486
7.475
7.470
7.347
7.345
7.340
7.334
7.331
2.560
2.554
2.526
2.522
2.520
2.083
2.079
1.639
1.635
1.605
1.601
1.103
1.100
1.098
1.095
0.962
0.872
0.858
0.819
0.818
0.812
0.811
0.803
0.802
0.584
0.576
0.573
0.565
0.551
0.379
0.310
0.233
0.230
H
O
PhMe2Si
3.2k dr = 1.0 : 0.6
1H NMR, 500 MHz, CDCl3
0.78
0.48
3.31
4.84
1.69
0.63
1.15
9.30
10.02
0.76
1.49
0.99
3.52
2.70
2.74
3.44
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

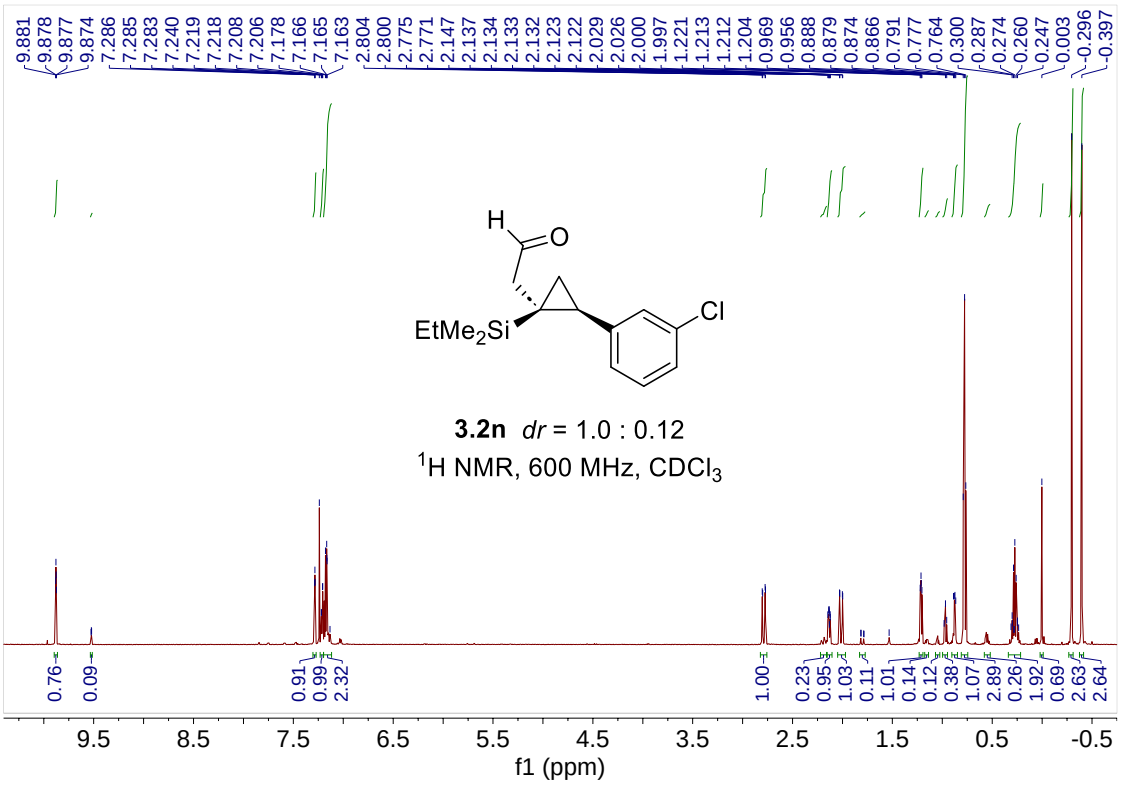

203.88
203.68
138.27
137.09
134.10
134.08
129.29
129.11
127.82
127.79
77.25
77.00
76.75
53.19
44.47
39.07
37.57
34.28
33.44
33.42
33.39
33.31
26.58
26.39
26.34
26.31
26.29
26.03
25.95
16.70
14.10
6.76
5.33
-1.48
-2.23
-4.58
-4.65
H
O
PhMe2Si
3.2k dr = 1.0 : 0.6
13C NMR, 126 MHz, CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

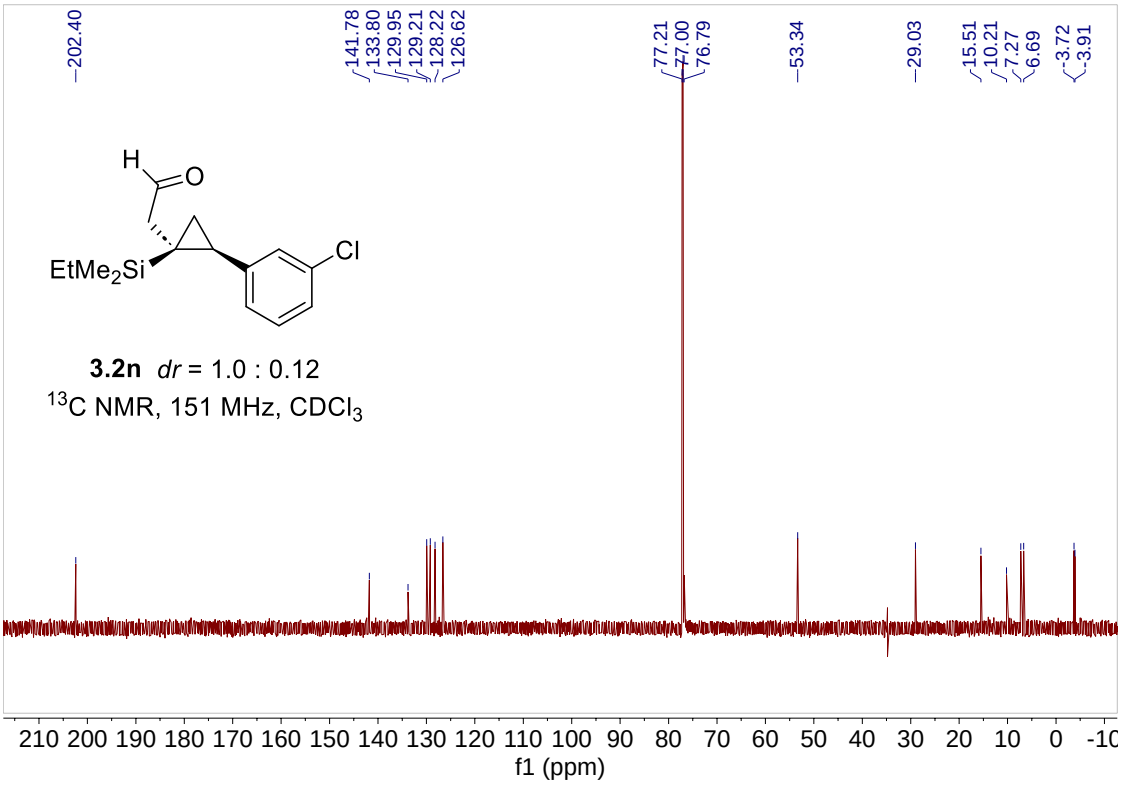

H
O
PhMe2Si
3.2l dr = 1 : 1
1H NMR, 600 MHz, CDCl3
f1 (ppm)

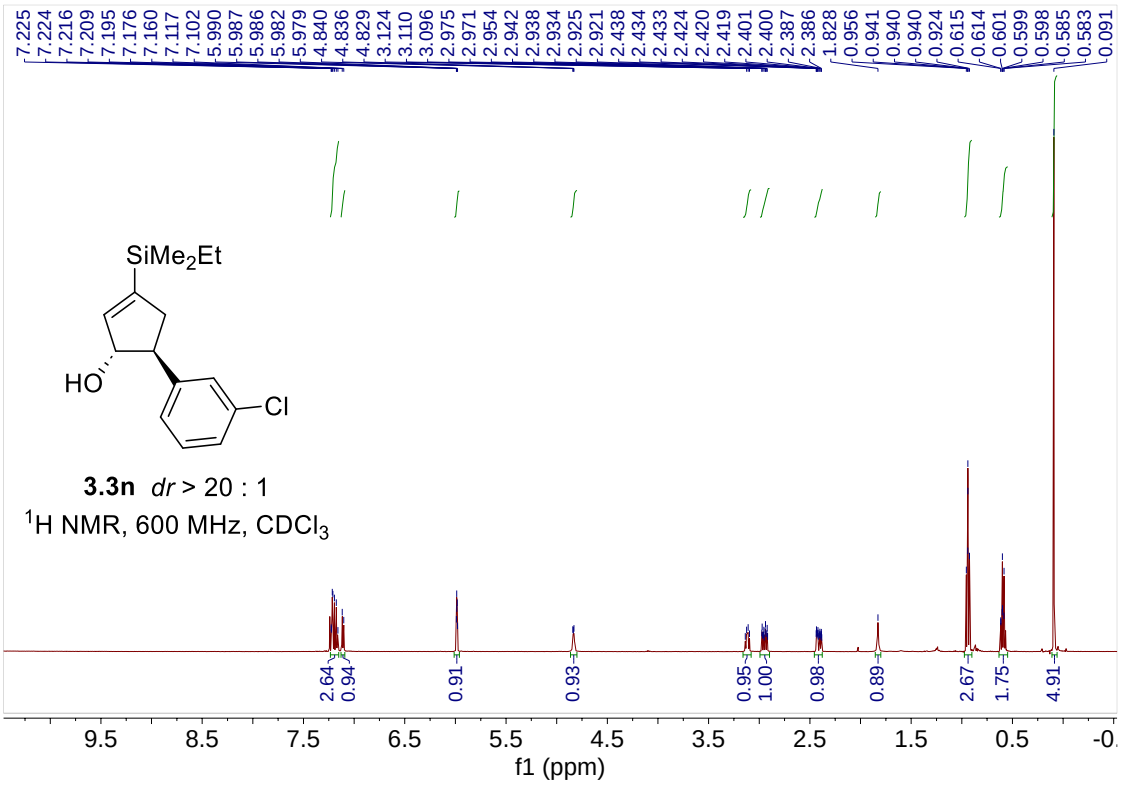

H
O
PhMe2Si
3.2l dr = 1 : 1
13C NMR, 151 MHz, CDCl3
f1 (ppm)

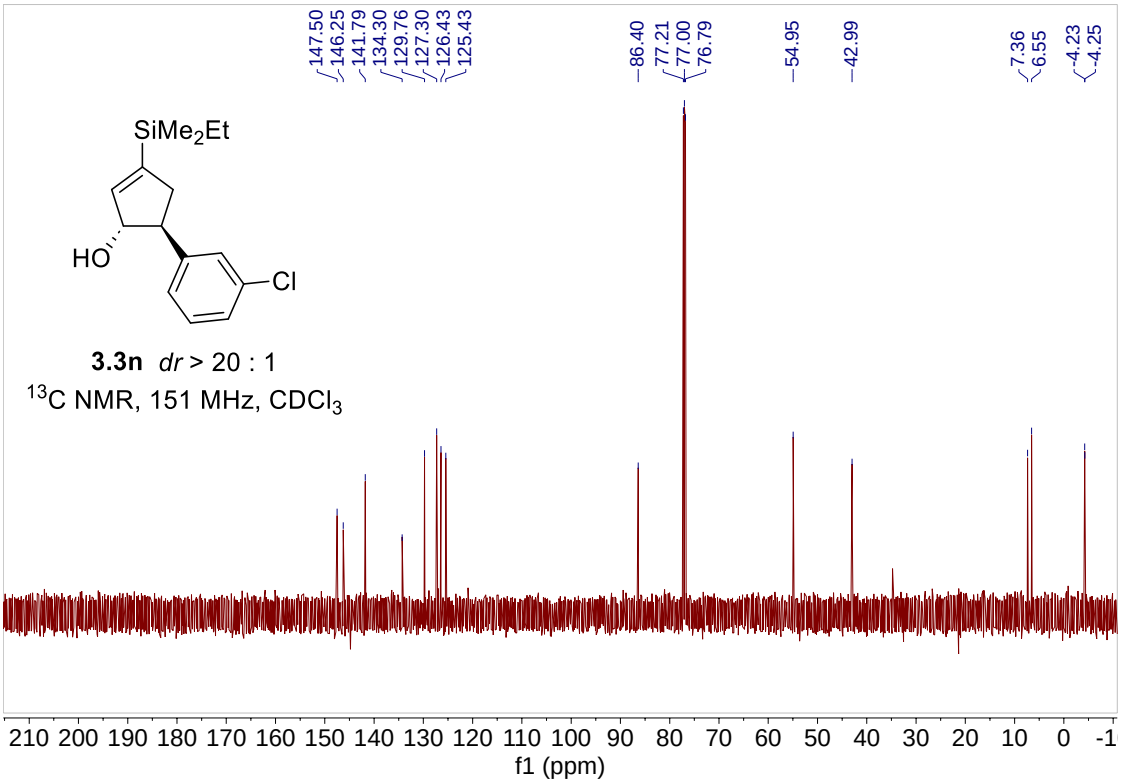

9.800
9.794
9.793
9.789
9.688
9.686
9.683
9.681
9.680
9.677
2.472
2.467
2.436
2.429
2.415
2.410
2.402
2.396
1.791
1.786
1.758
1.753
1.753
0.980
0.965
0.949
0.931
0.915
0.900
0.628
0.612
0.611
0.597
0.596
0.595
0.512
0.484
0.469
0.468
0.452
0.437
0.436
0.276
0.266
0.257
0.213
0.208
0.206
0.203
0.202
0.192
0.182
0.176
H
O
Et3Si
3.2m dr = 1 : 0.7
1H NMR, 600 MHz, CDCl3
0.64
0.85
0.75
1.72
1.00
9.61
8.45
20.38
1.05
4.41
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
f1 (ppm)

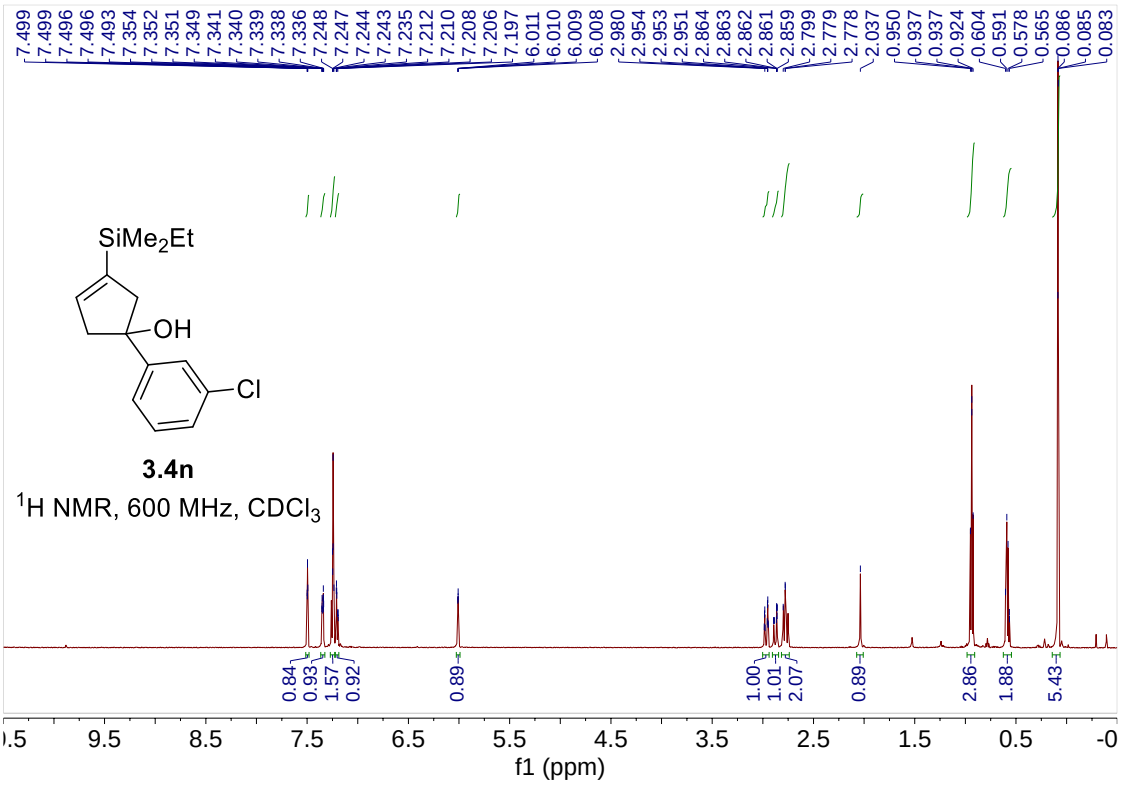

204.51
203.84
77.24
76.99
76.74
53.51
46.17
29.23
22.83
17.38
14.49
12.19
9.57
7.59
7.42
6.49
5.99
5.24
4.44
3.73
2.16
H
O
Et3Si
3.2m dr = 1 : 0.7
13C NMR, 151 MHz, CDCl3
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

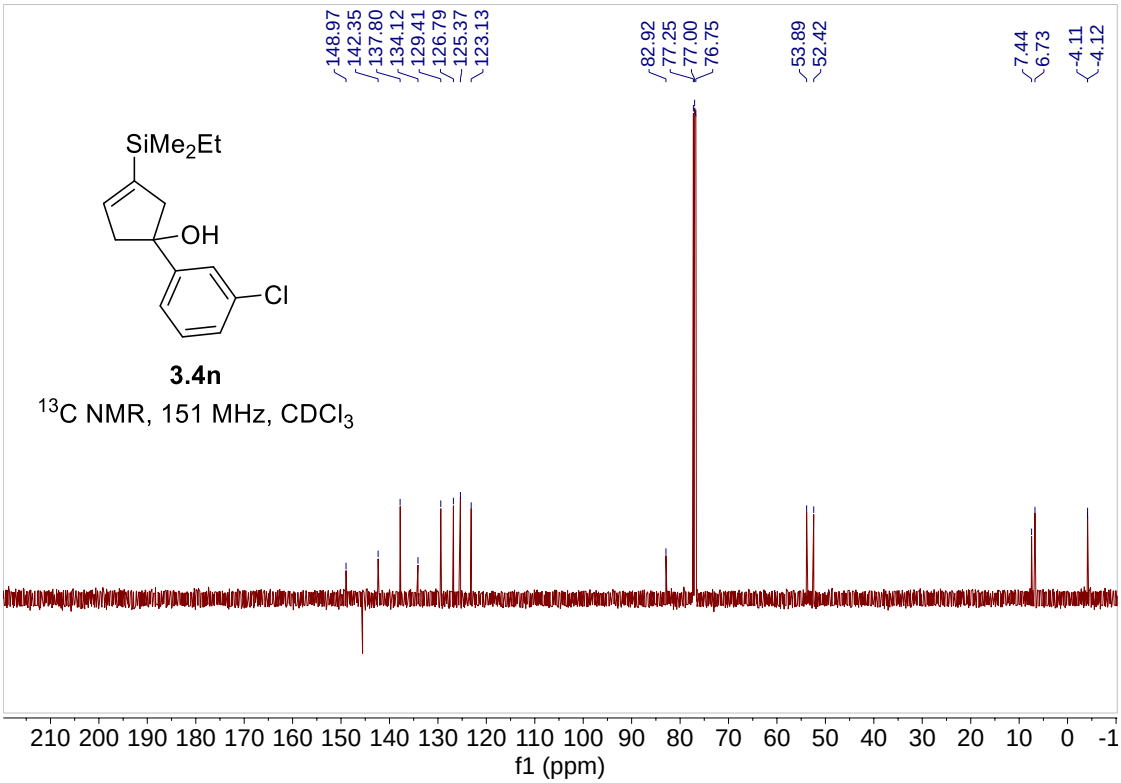

H
O
EtMe2Si
Cl
3.2n dr = 1.0 : 0.12
1H NMR, 600 MHz, CDCl3
f1 (ppm)

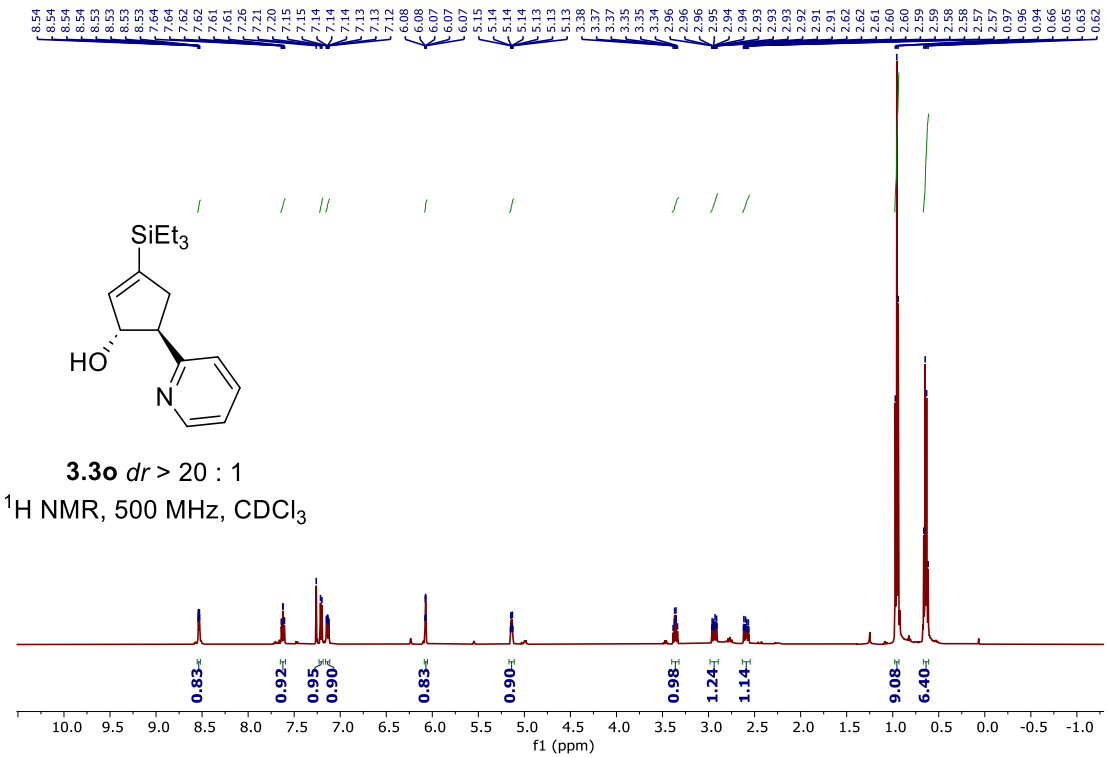

H
O
EtMe2Si
Cl
3.2n dr = 1.0 : 0.12
13C NMR, 151 MHz, CDCl3
f1 (ppm)


7.225
7.224
7.216
7.209
7.195
7.176
7.160
7.117
7.102
5.990
5.987
5.986
5.982
5.979
4.840
4.836
4.829
3.124
3.110
3.096
2.975
2.971
2.954
2.942
2.938
2.934
2.925
2.921
2.438
2.434
2.433
2.424
2.420
2.419
2.401
2.400
2.387
2.386
1.828
0.956
0.941
0.940
0.940
0.924
0.615
0.614
0.601
0.599
0.598
0.585
0.583
0.091
SiMe2Et
HO
Cl
3.3n dr > 20 : 1
1H NMR, 600 MHz, CDCl3
2.64
0.94
0.91
0.93
0.95
1.00
0.98
0.89
2.67
1.75
4.91
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


147.50
146.25
141.79
134.30
129.76
127.30
126.43
125.43
86.40
77.21
77.00
76.79
54.95
42.99
7.36
6.55
4.23
4.25
SiMe2Et
HO
Cl
3.3n dr > 20 : 1
13C NMR, 151 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

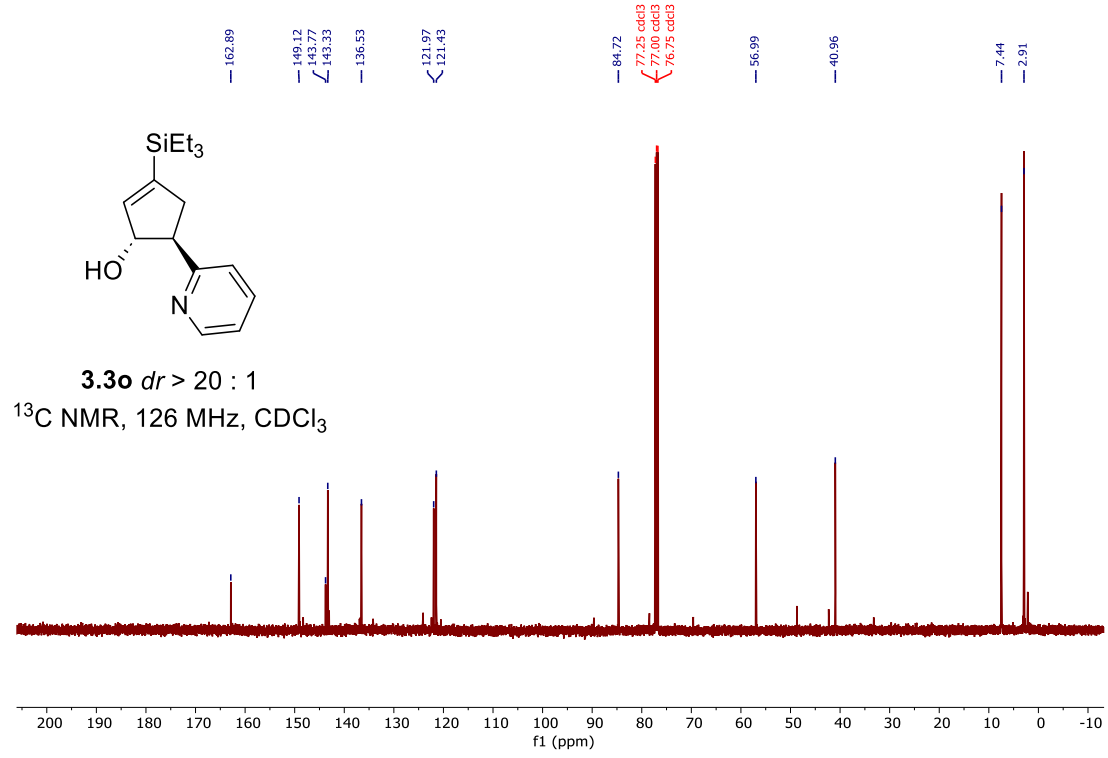

7.499
7.499
7.496
7.496
7.493
7.354
7.352
7.351
7.349
7.341
7.340
7.339
7.338
7.336
7.248
7.247
7.244
7.243
7.235
7.212
7.210
7.208
7.206
7.197
6.011
6.010
6.009
6.008
2.980
2.954
2.953
2.951
2.864
2.863
2.862
2.861
2.859
2.799
2.779
2.778
2.037
0.950
0.937
0.937
0.924
0.604
0.591
0.578
0.565
0.086
0.085
0.083
SiMe2Et
OH
Cl
3.4n
1H NMR, 600 MHz, CDCl3
0.84
0.93
1.57
0.92
0.89
1.00
1.01
2.07
0.89
2.86
1.88
5.43
f1 (ppm)


148.97
142.35
137.80
134.12
129.41
126.79
125.37
123.13
82.92
77.25
77.00
76.75
53.89
52.42
7.44
6.73
-4.11
-4.12
SiMe2Et
OH
Cl
3.4n
13C NMR, 151 MHz, CDCl3
f1 (ppm)



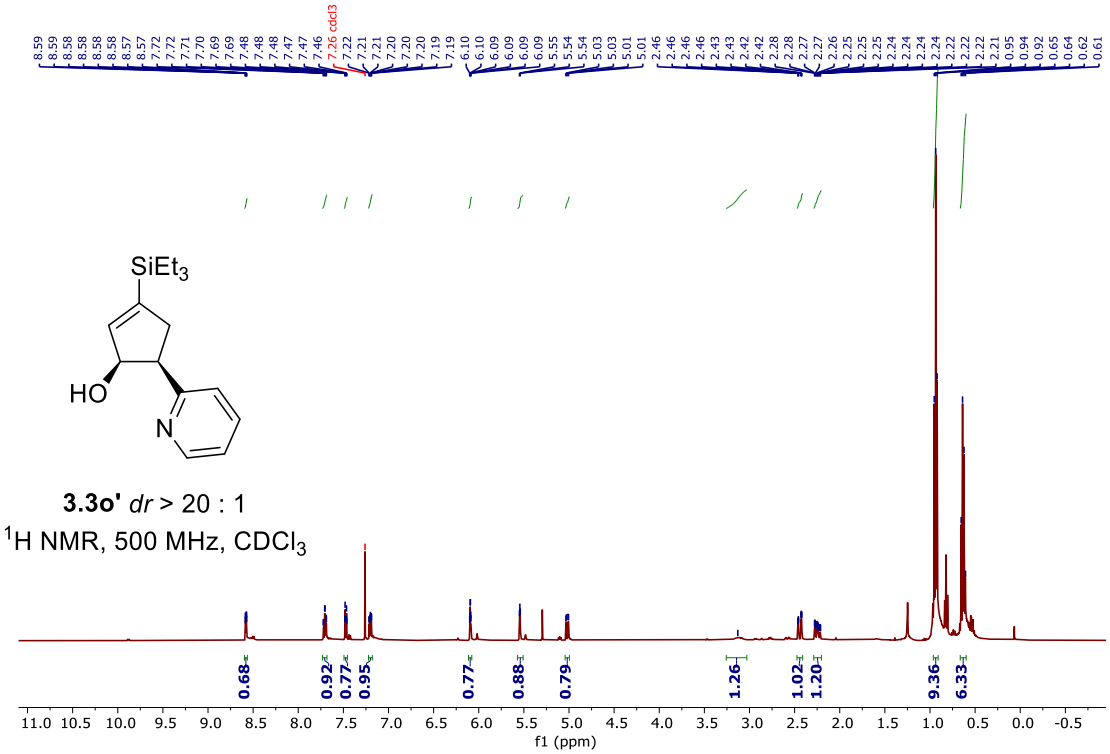
3.3o *dr* > 20 : 1

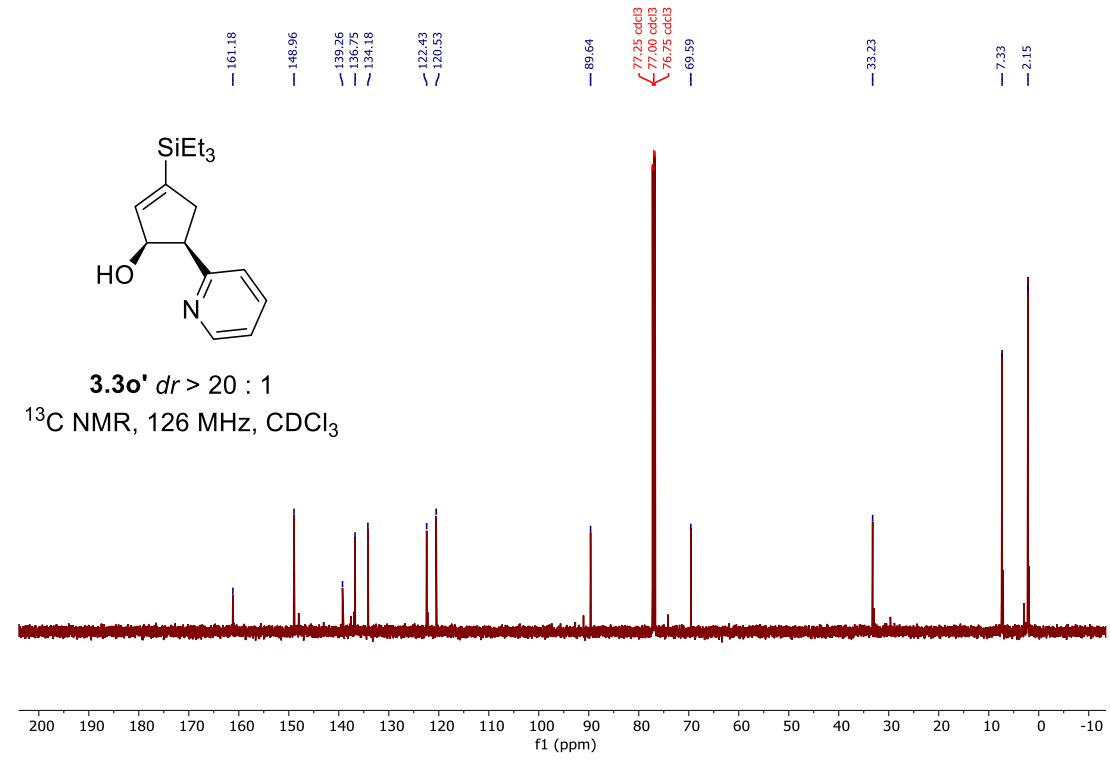
^{1}H NMR, 500 MHz, $CDCl_3$

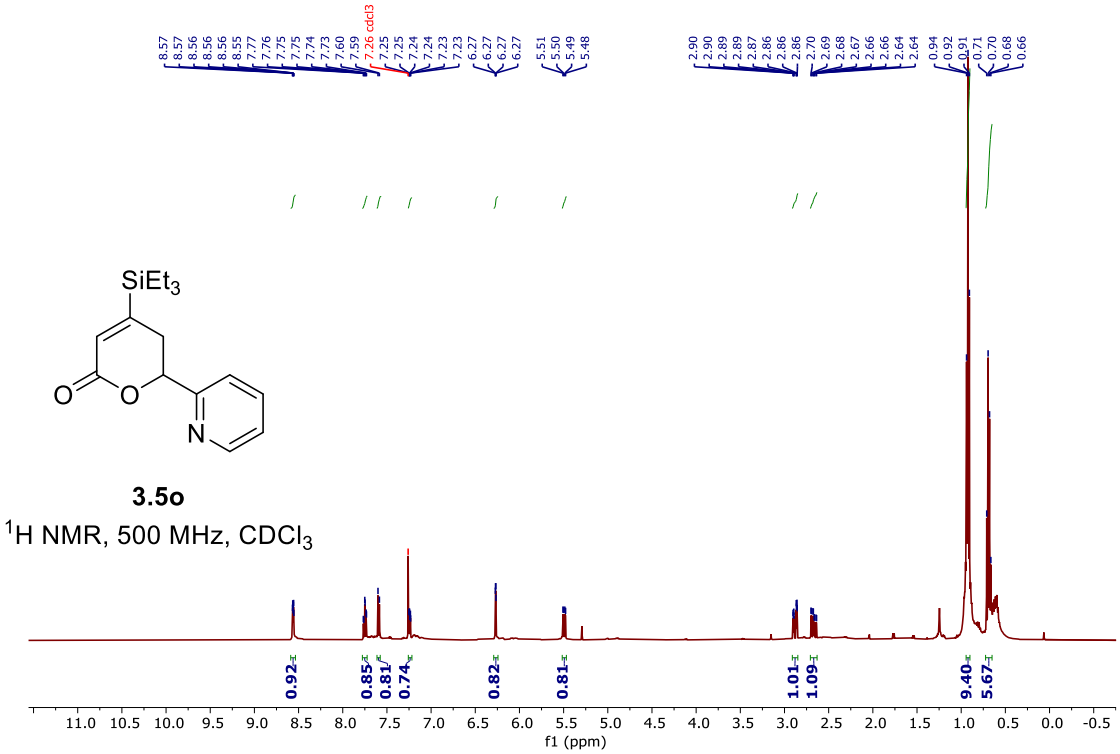


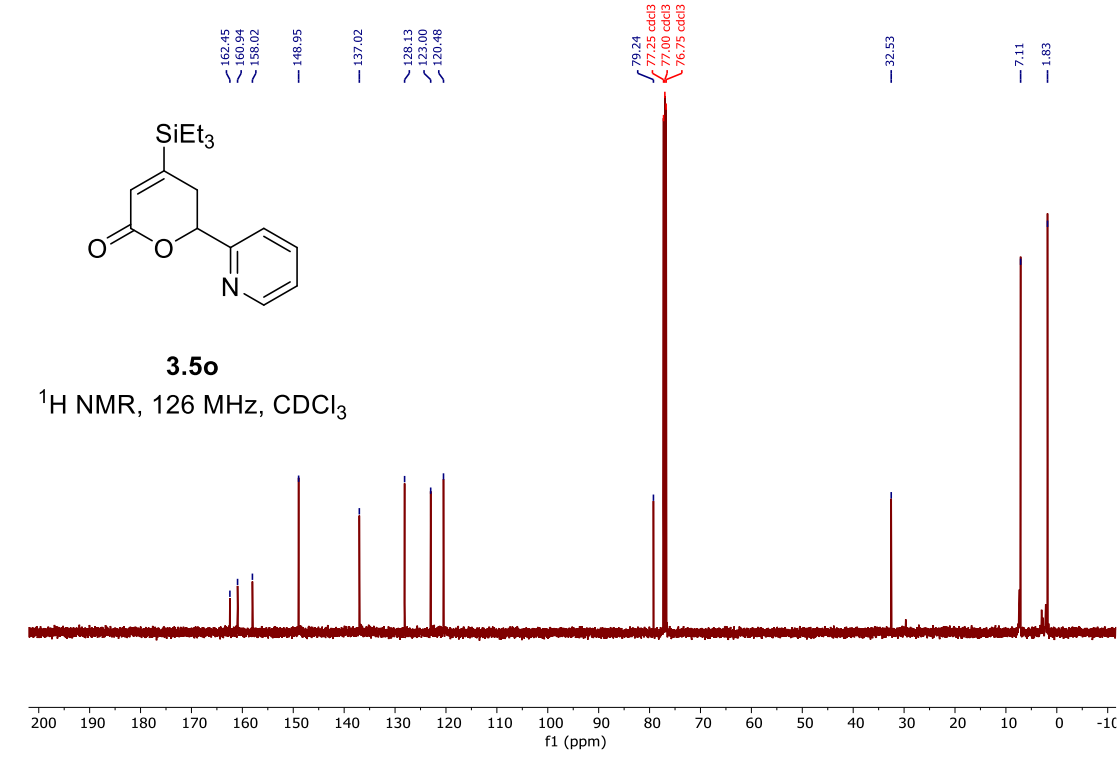
3.3o *dr* > 20 : 1

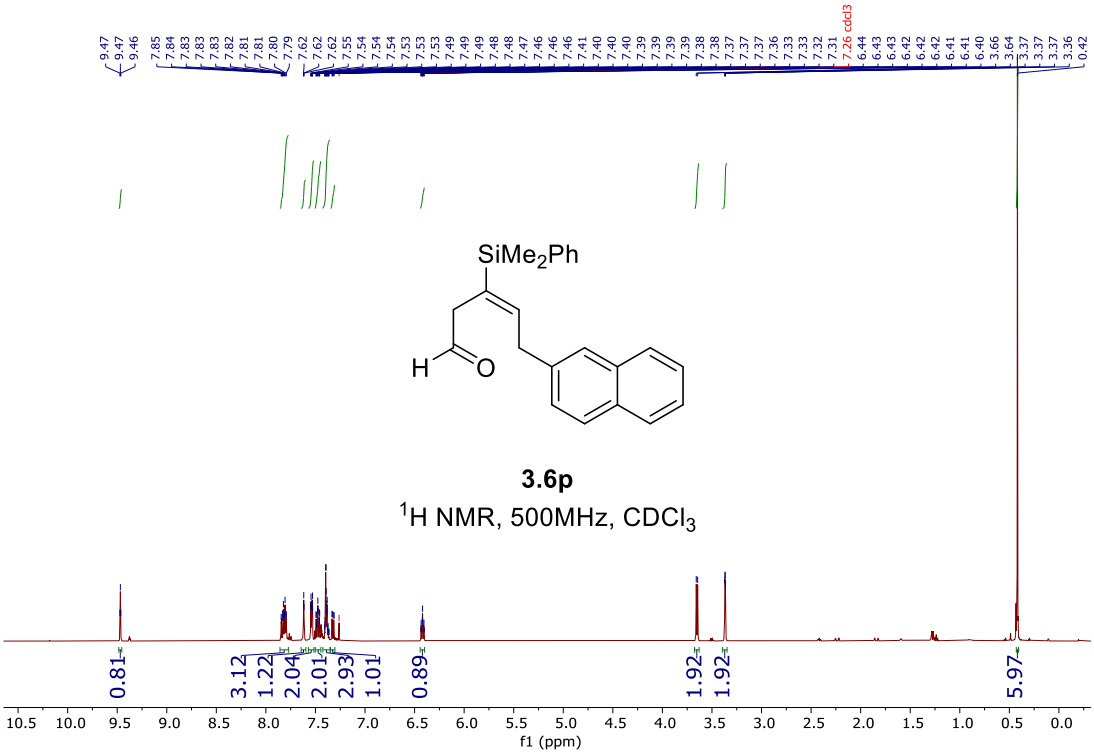
^{13}C NMR, 126 MHz, $CDCl_3$

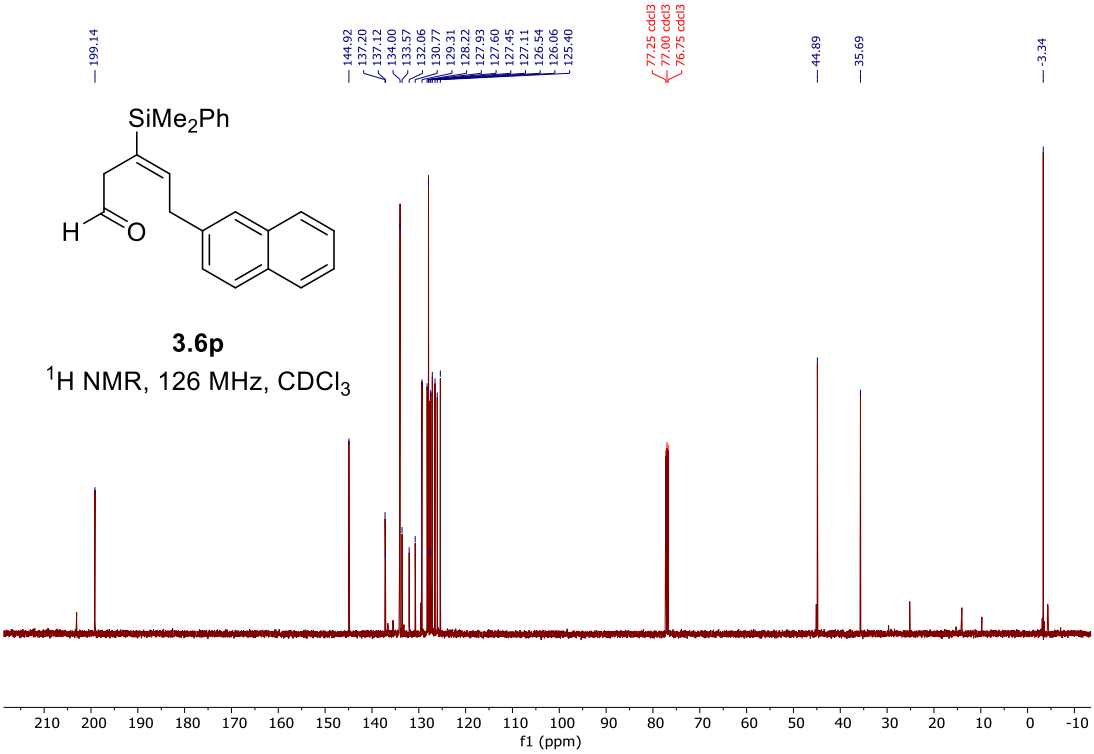

SiEt3
HO
N
3.3o' dr > 20 : 1
1H NMR, 500 MHz, CDCl3
0.68
0.92
0.77
0.95
0.77
0.88
0.79
1.26
1.02
1.20
9.36
6.33
f1 (ppm)

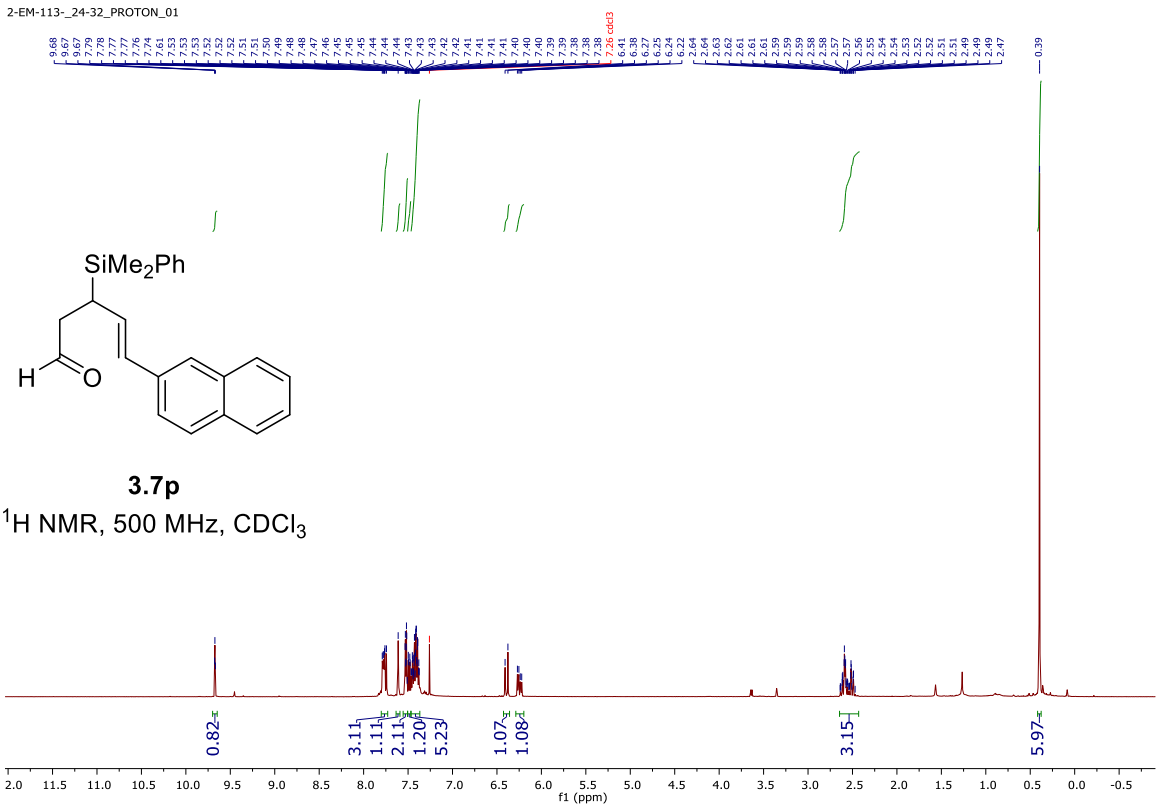

161.18
148.96
139.26
136.75
134.18
122.43
120.53
89.64
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
69.59
33.23
7.33
2.15
SiEt3
HO
N
3.3o' dr > 20 : 1
13C NMR, 126 MHz, CDCl3
f1 (ppm)


SiEt3
O
O
N
3.5o
1H NMR, 500 MHz, CDCl3
0.92
0.85
0.81
0.74
0.82
0.81
1.01
1.09
9.40
5.67
f1 (ppm)


SiEt3
O
O
N
3.5o
1H NMR, 126 MHz, CDCl3
162.45
160.94
158.02
148.95
137.02
128.13
123.00
120.48
79.24
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
32.53
7.11
1.83
f1 (ppm)

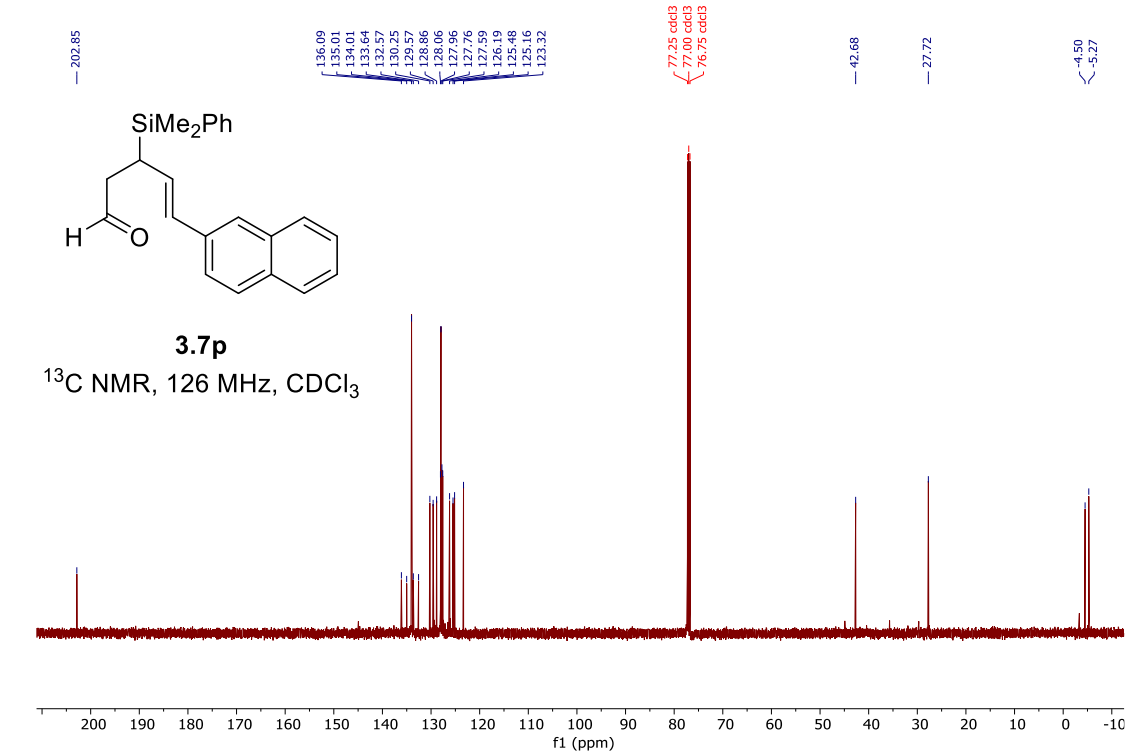

SiMe2Ph
H
O
3.6p
1H NMR, 500MHz, CDCl3
0.81
3.12
1.22
2.04
2.01
2.93
1.01
0.89
1.92
1.92
5.97
f1 (ppm)


SiMe2Ph
H
O
3.6p
1H NMR, 126 MHz, CDCl3
f1 (ppm)



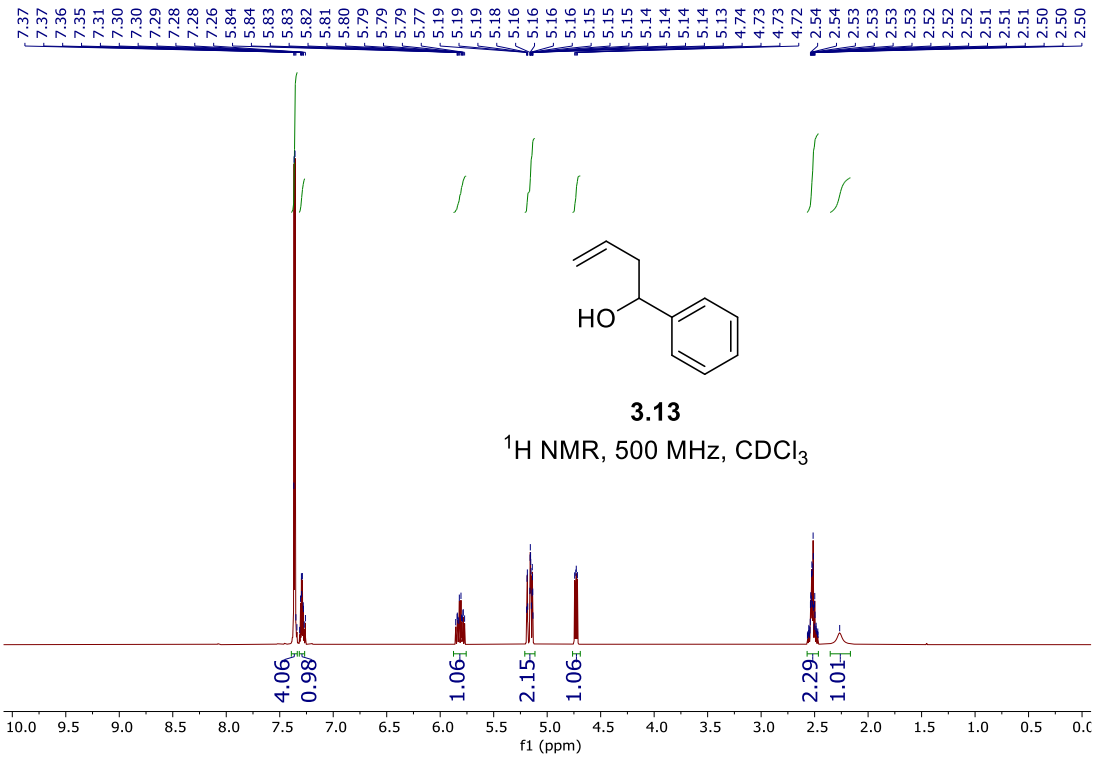
3.7p

^{1}H NMR, 500 MHz, $CDCl_3$



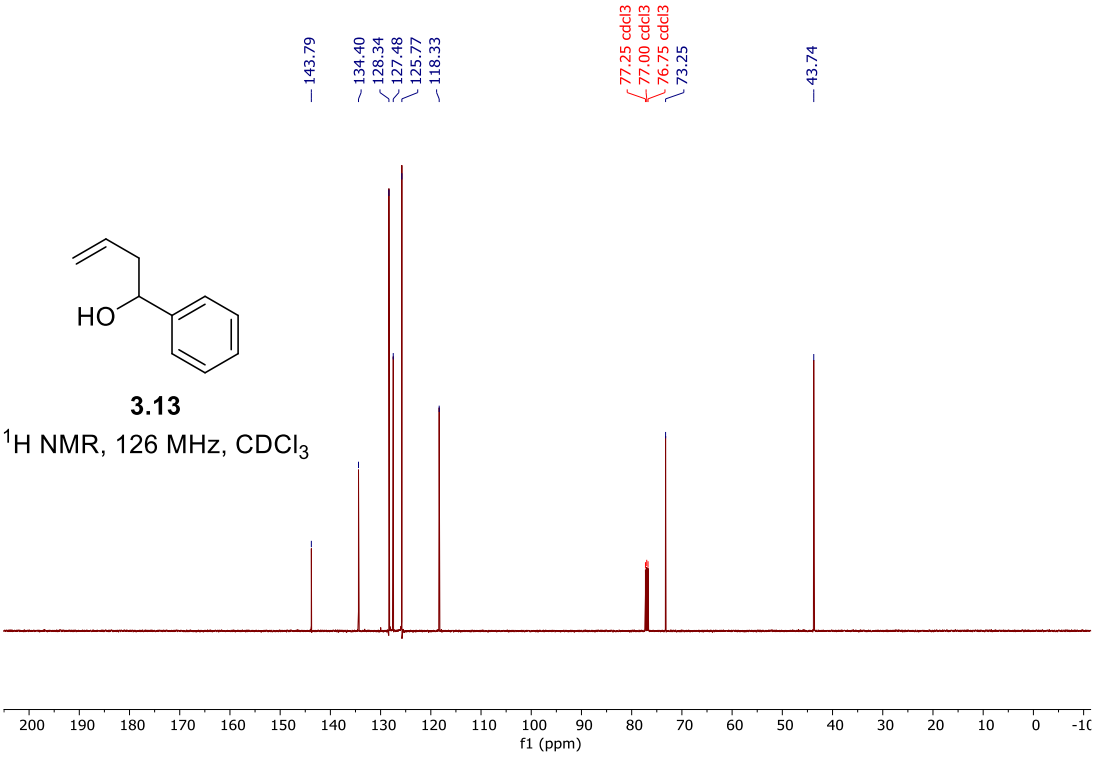
3.7p

^{13}C NMR, 126 MHz, $CDCl_3$



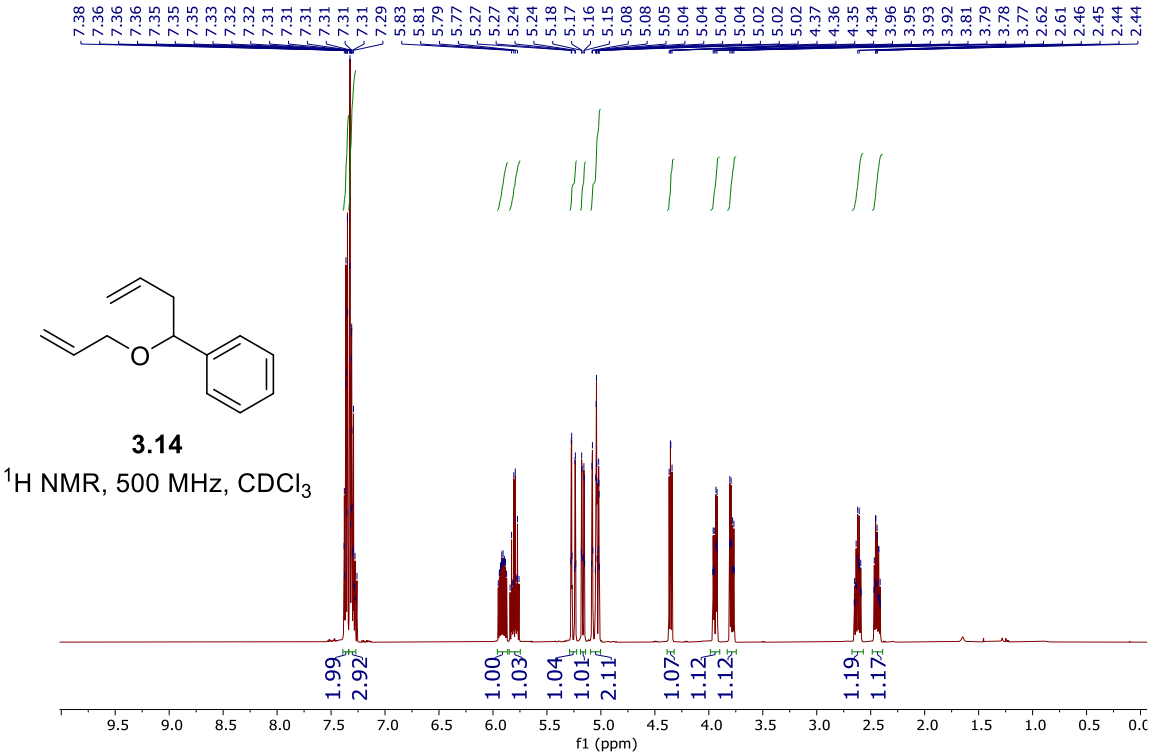
3.13

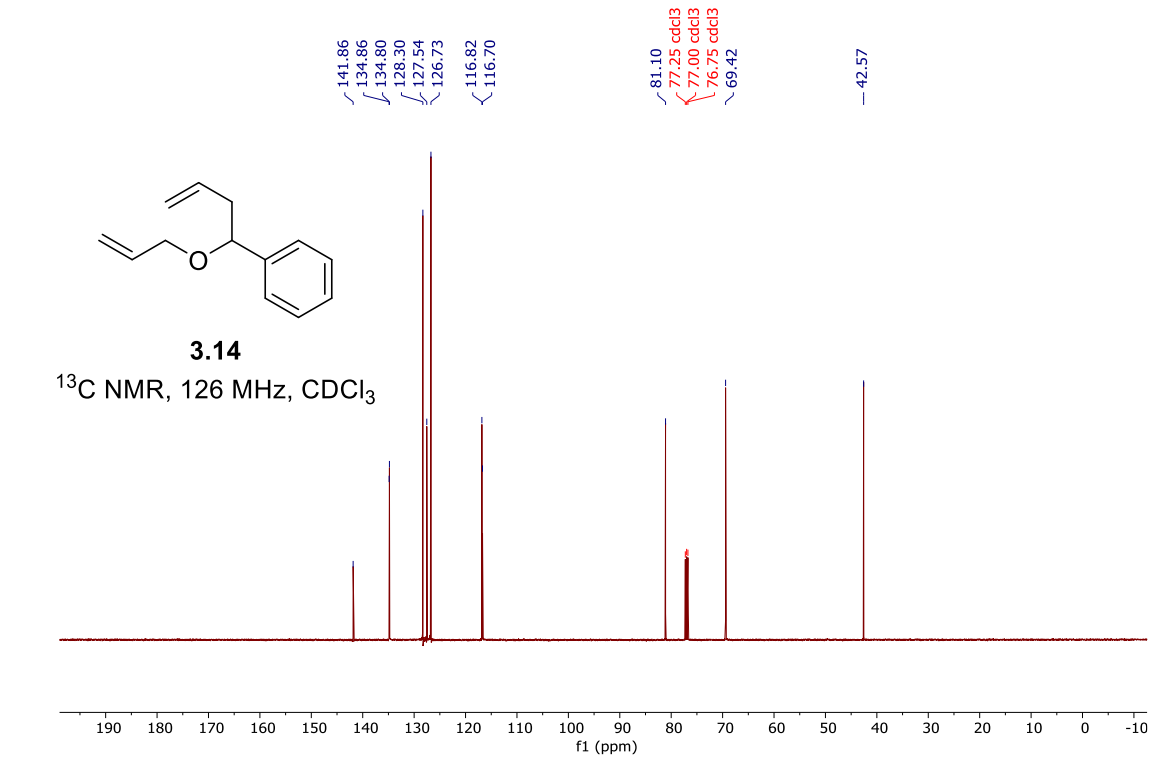
^{1}H NMR, 500 MHz, $CDCl_3$

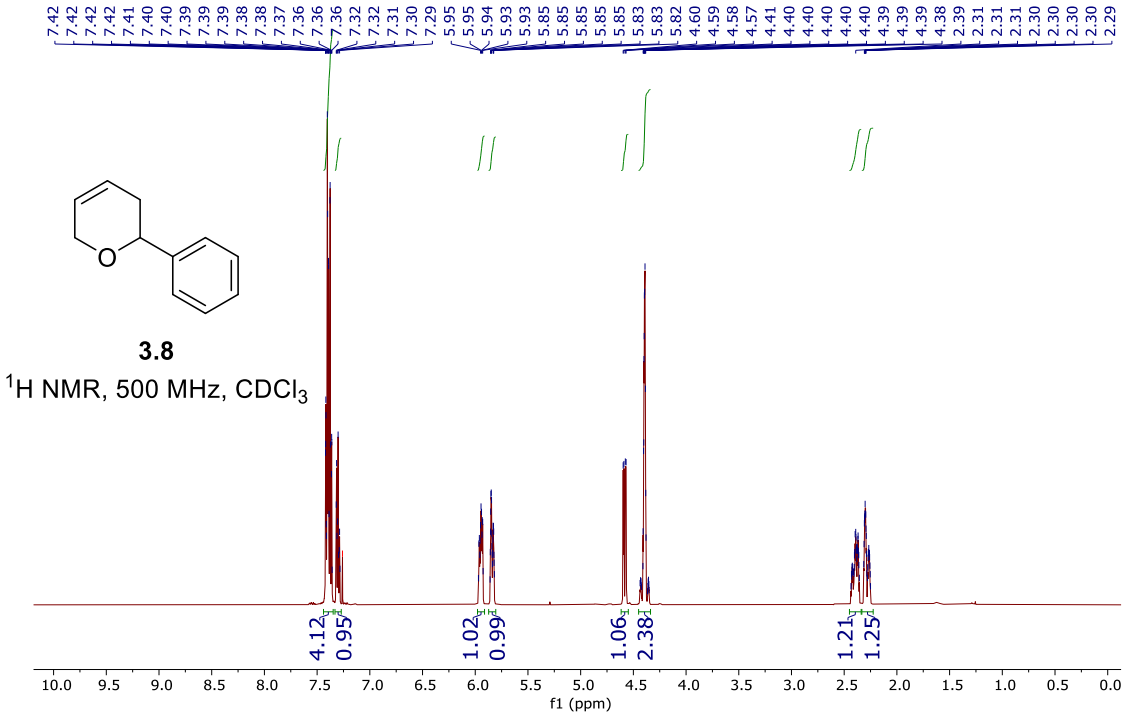


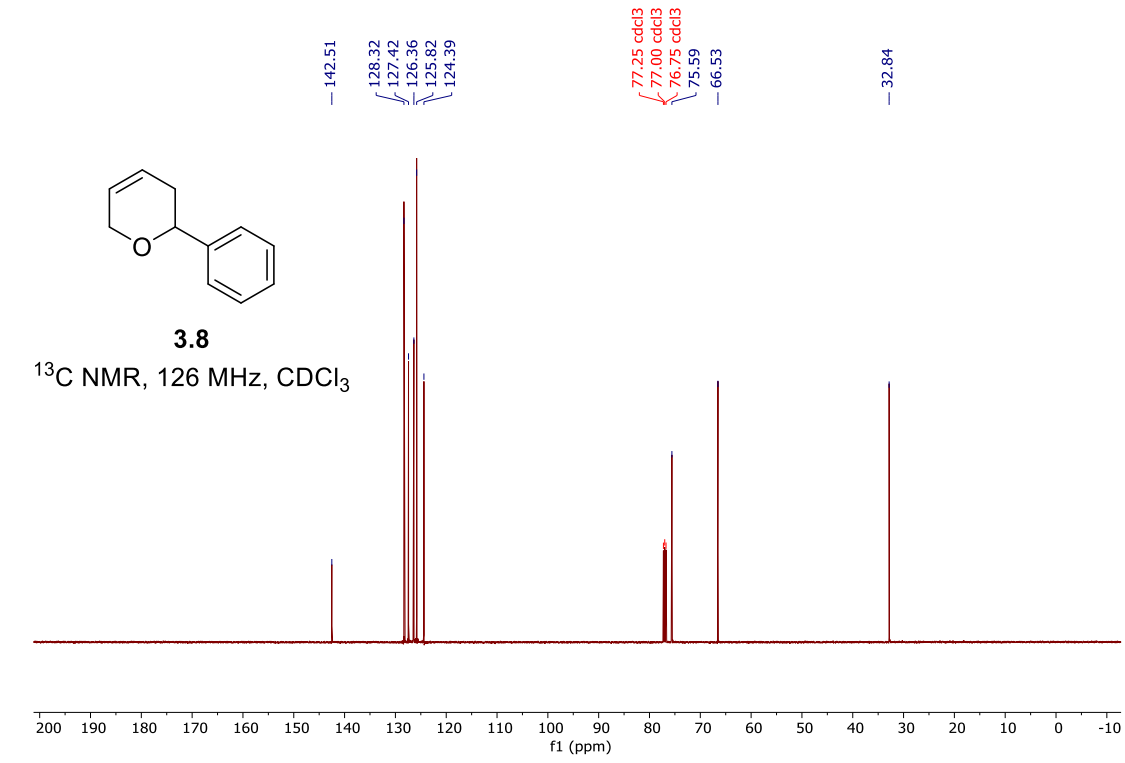
3.13

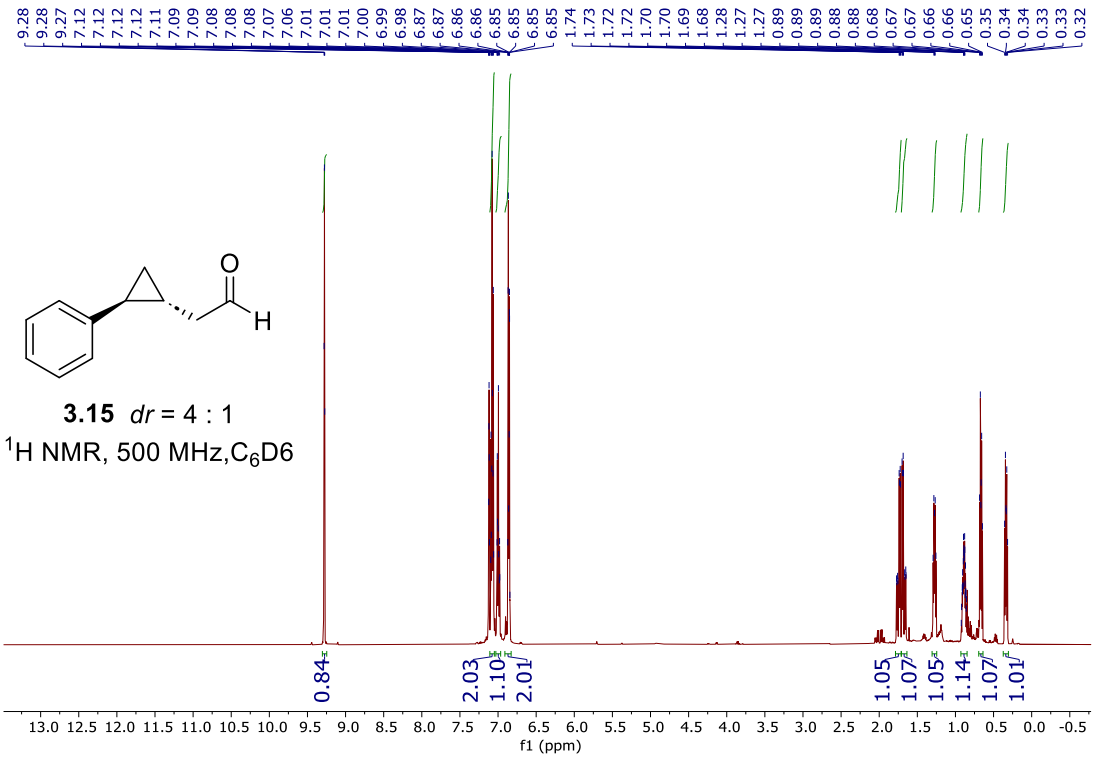
^{1}H NMR, 126 MHz, $CDCl_3$


7.38 7.36 7.36 7.36 7.35 7.35 7.35 7.33 7.32 7.32 7.31 7.31 7.31 7.31 7.31 7.29 5.83 5.81 5.79 5.77 5.27 5.24 5.24 5.18 5.17 5.16 5.15 5.08 5.08 5.05 5.04 5.04 5.04 5.04 5.02 5.02 5.02 4.37 4.36 4.35 4.34 3.96 3.95 3.93 3.92 3.81 3.79 3.78 3.77 2.62 2.61 2.46 2.45 2.44 2.44
O
3.14
1H NMR, 500 MHz, CDCl3
1.99 2.92 1.00 1.03 1.04 1.01 2.11 1.07 1.12 1.12 1.19 1.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


141.86 134.86 134.80 128.30 127.54 126.73 116.82 116.70 81.10 77.25 cdcl3 77.00 cdcl3 76.75 cdcl3 69.42 42.57
O
3.14
13C NMR, 126 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.42 7.42 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.32 7.32 7.31 7.30 7.29
5.95 5.95 5.94 5.93 5.93 5.85 5.85 5.85 5.85 5.85 5.83 5.83 5.82 4.60 4.59 4.58 4.57 4.41 4.40 4.40 4.40 4.40 4.40 4.39 4.39 4.39 4.38 2.39 2.31 2.31 2.31 2.30 2.30 2.30 2.30 2.29
O
3.8
1H NMR, 500 MHz, CDCl3
4.12
0.95
1.02
0.99
1.06
2.38
1.21
1.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.51
128.32
127.42
126.36
125.82
124.39
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
75.59
66.53
32.84
O
3.8
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
H
3.15 dr = 4 : 1
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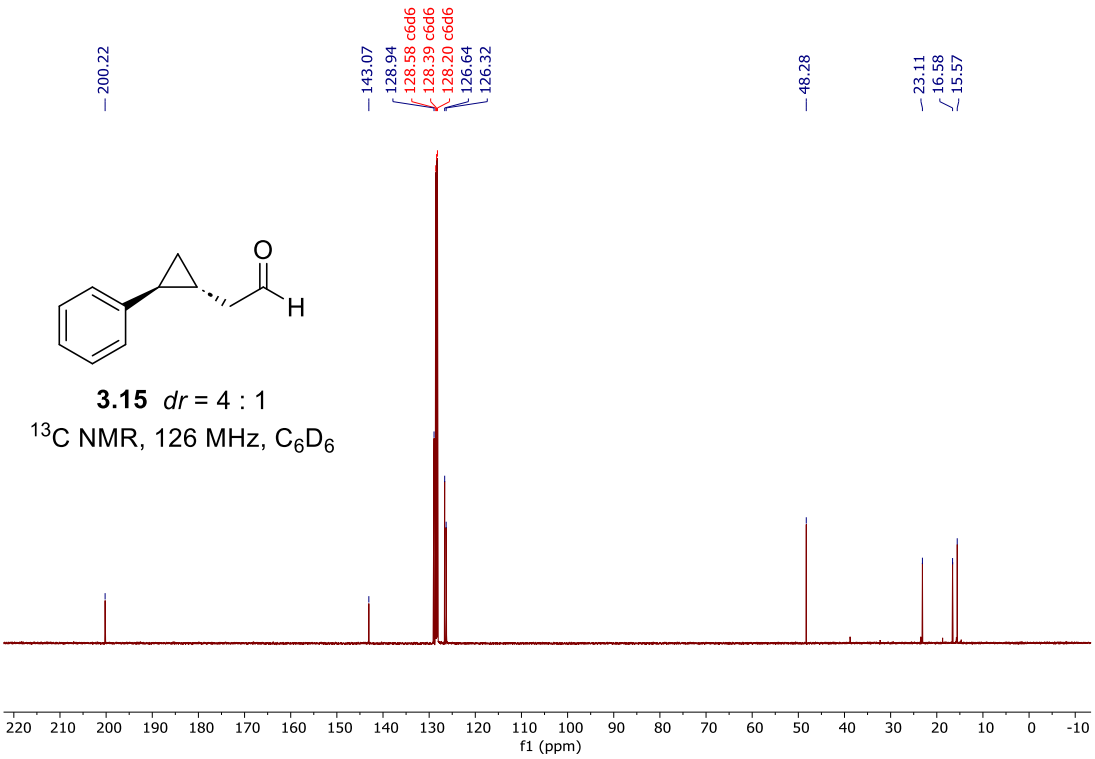
1.10
2.01
1.05
1.07
1.05
1.14
1.07
1.01
f1 (ppm)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143.07
128.94
128.58 c6d6
128.39 c6d6
128.20 c6d6
126.64
126.32
48.28
23.11
16.58
15.57
O
H
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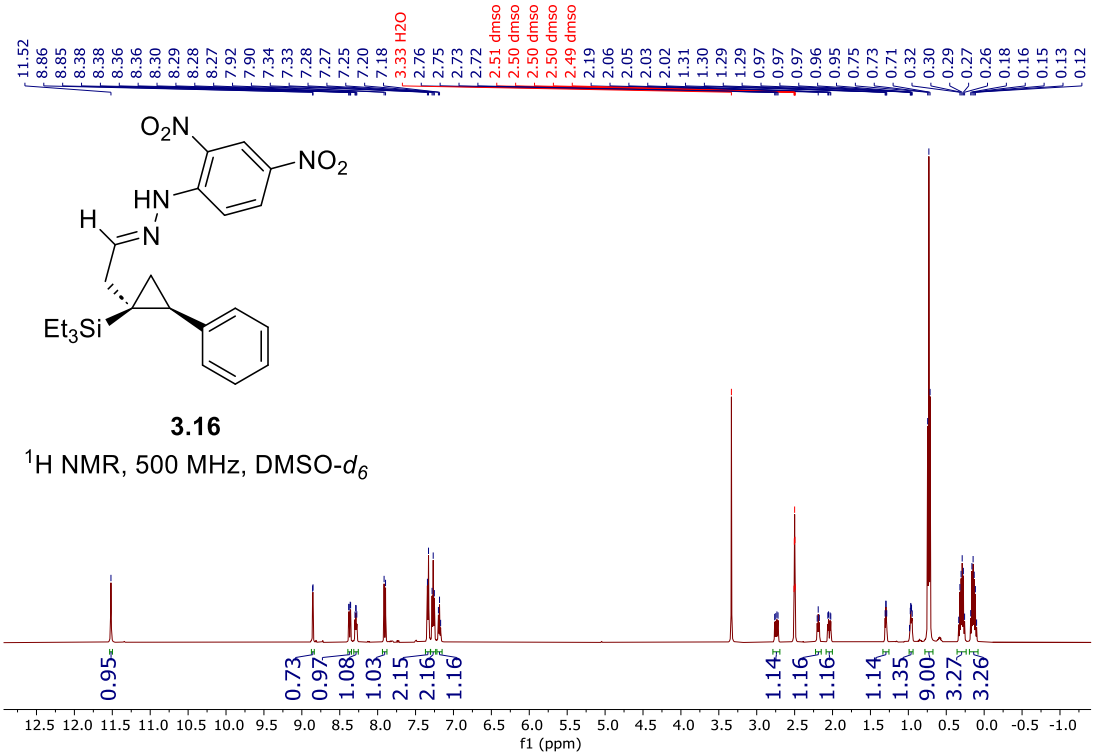
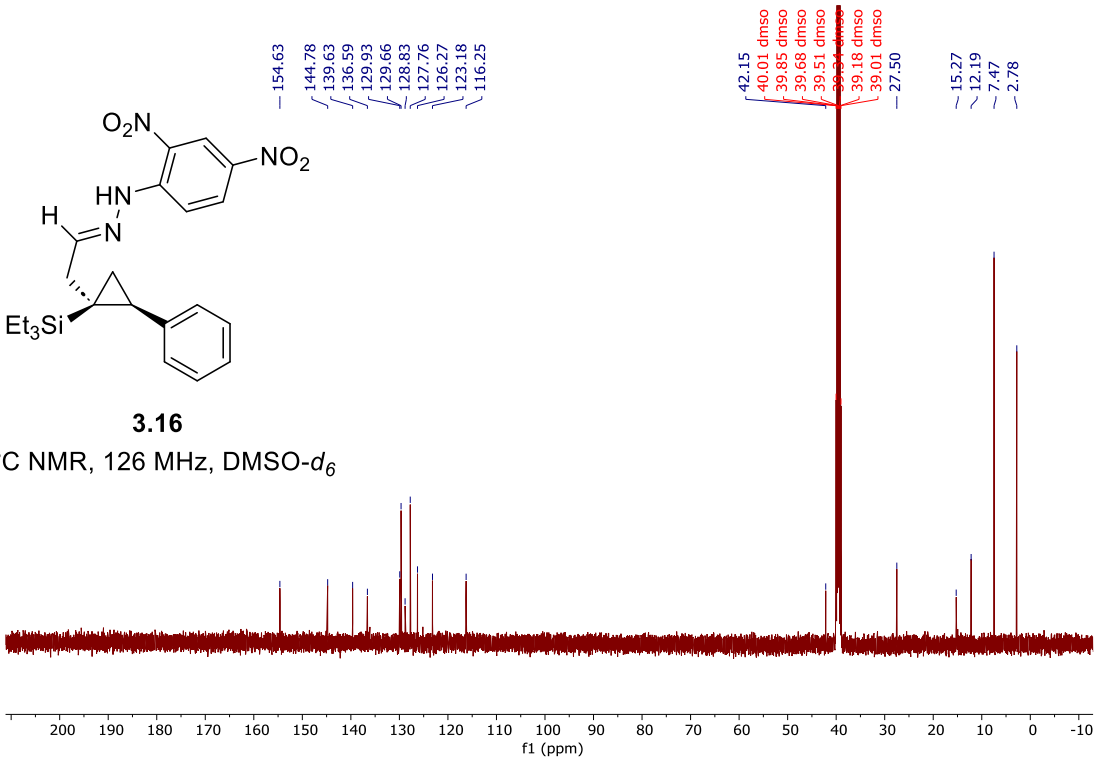
13C NMR, 126 MHz, C6D6
f1 (ppm)



3.16

^{1}H NMR, 500 MHz, DMSO-d_6



3.16

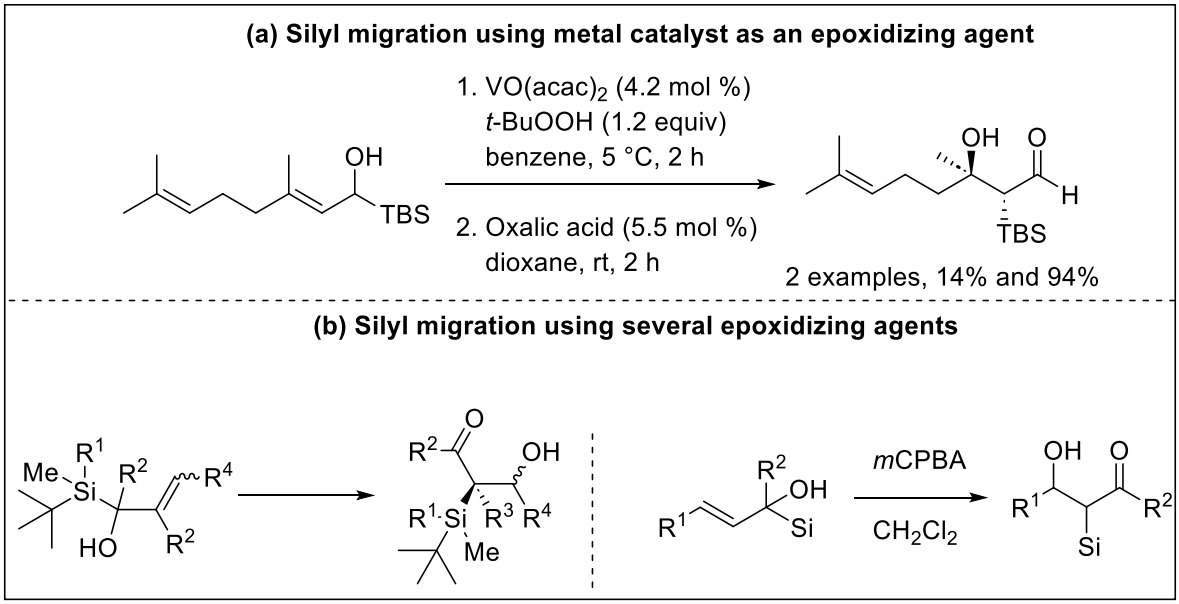
^{13}C NMR, 126 MHz, DMSO-d_6

CHAPTER 4.

A [1,2]-WITTIG / *m*-CPBA TRIGGERED [1,2]-CARBON-TO-CARBON SILYL MIGRATION APPROACH TO α-SILYL-β-HYDROXY CYCLOPENTANONES AND CYCLOHEXANONES

4.1. Introduction

The most explored [1,2]-silyl migrationinvolves the migration of the silicon group from carbon to oxygen (Brook rearrangement)[1-3] or its reverse reaction (retro-Brook rearrangement).[4-9] In contrast, the [1,2]-carbon-to-carbon silyl migration has remained largely unexplored. Reported examples of such [1,2]-carbon-to-carbon silyl migration involve the use of protic acids to trigger the migration.[10-16] Other examples involve alkynyl silanes or silyl propagylic systems that are catalyzed by Lewis acids[17,18] and/or transition metals.[19-25] With recent work from our lab on Wittig rearrangements of silyldihydropyrans,[26,27] we were looking to investigate the utility of the products formed. The [1,2]-silyl migration from carbon to carbon to generate α-silyl aldehydes (Scheme 4.1a)[28] and ketones (Scheme 4.1b)[29,30] has been previously reported and takes place via epoxide derivatives of acyclic α-silyl allylic alcohols.

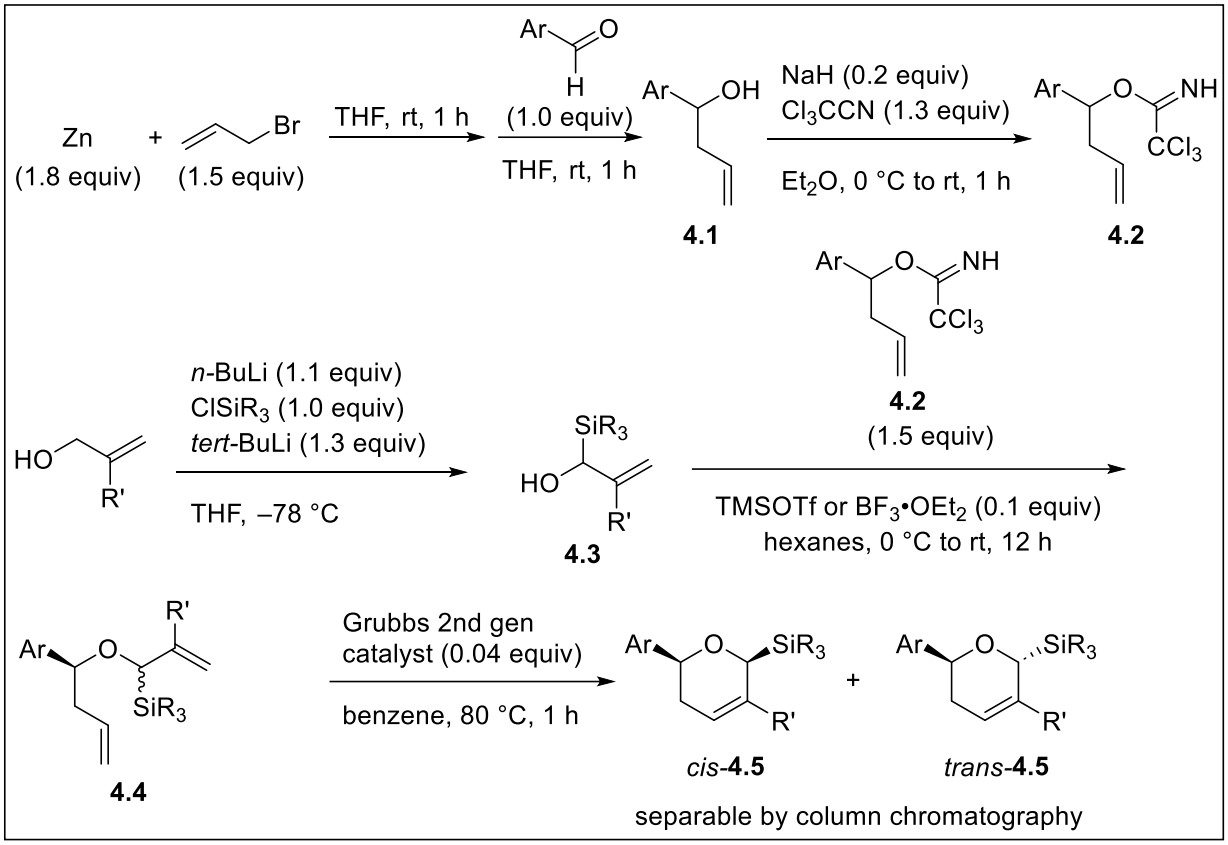


Scheme 4.1: [1,2]-carbon-to-carbon silyl migration triggered by epoxidation

In our quest to functionalize the olefin of the [1,2]-Wittig rearrangement products by epoxidation we saw an unexpected rearrangement involving a [1,2]-carbon-to-carbon silyl shift. We were interested to learn the generality of such migration in the context of the cyclic systems accessible by [1,2]-Wittig ring contraction of silyl cyclic ethers.

4.2. Synthesis of 2-silyl-6-aryl-5,6-dihydro-*2H*-pyrans

The 2-silyl-6-aryl-5,6-dihydro-*2H*-pyrans were synthesized following our earlier reported protocol.[26] The synthesis began by allylation of benzaldehydes followed by conversion of the resulting homoallylic alcohols **4.1** to trichloroacetimidates **4.2**. The trichloroacetimidates were then coupled with α-hydroxy allyl silanes **4.3** in the presence of catalytic amount of a Lewis acid to form diastereomeric dienes **4.4**. For most of the compounds reported herein, the *syn* diastereomer exhibited a lower R_f value than its *anti* counterpart (dichloromethane/hexanes). The *syn/anti* dienes were then subjected to ring closing metathesis using Grubbs 2nd generation catalyst leading to 2-silyl-6-aryl-5,6-dihydro-*2H*-pyrans **4.5**. The *cis/trans* diastereomers of pyrans **4.5** were separable by column chromatography. Generally, the *trans* diastereomer has lower R_f value than its *cis* counterpart (dichloromethane/hexanes). The relative stereochemistry of the dihydropyrans was determined by ^{1}H NMR NOESY experiments.

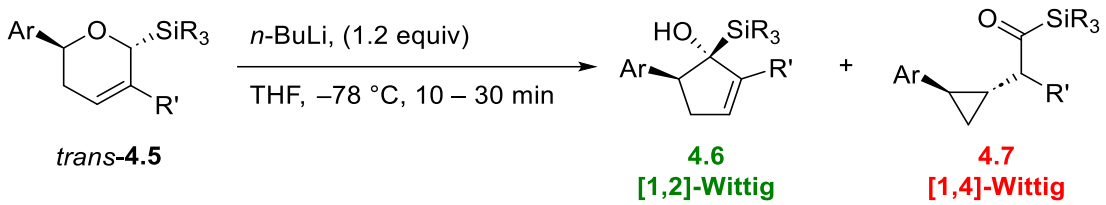


Scheme 4.2: Synthesis of 2-silyl-6-aryl-5,6-dihydro-*2H*-pyrans

4.3. Wittig rearrangements of 2-silyl-6-aryl-5,6-dihydro-*2H*-pyrans

Since the trans diastereomers have been shown to be more reactive,[26] they were subjected to Wittig rearrangement using *n*-butyllithium, whereas the *cis* diastereomers were reacted with *sec*-butyllithium resulting in the stereoconvergent [1,2]- and [1,4]-Wittig rearrangement products (Table 4.1).

Table 4.1: Wittig rearrangement of 2-silyl-6-aryl-5,6-dihydro-*2H*-pyrans



trans-**4.5**

4.6 **[1,2]-Wittig**

4.7 **[1,4]-Wittig**

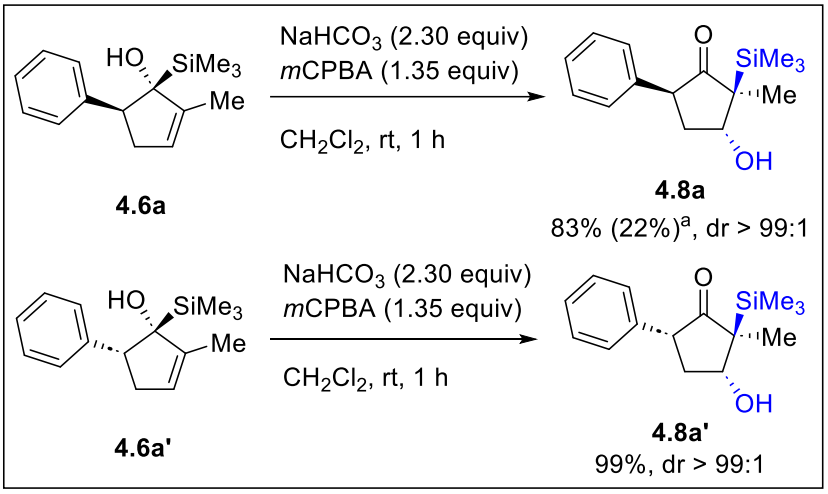
Entry	Substrate	Ar	SiR_3	R′	% (**4.6**)	% (**4.7**)
1	**4.5a**[a]	C_6H_5	$SiMe_3$	H	65[b]	n.d
2	**4.5b**	4-Cl-C_6H_4	$SiMe_3$	H	56	21
3	**4.5c**	4-CF_3-C_6H_4	$SiMe_3$	H	70	n.d.
4	**4.5d**	1-Naph	$SiMe_3$	H	81	n.d.
5	**4.5e**	4-Ph-C_6H_4	$SiMe_3$	H	75	n.d.
6	**4.5f**	2-Naph	$SiEt_3$	H	73	17
7	**4.5g**	4-Cl-C_6H_6	$SiMe_2Ph$	H	37	n.d.
8	**4.5h**	4-OMe-C_6H_6	$SiMe_3$	Me	85	n.d.
9	**4.5i**	4-Cl-C_6H_6	$SiMe_3$	Me	63	n.d.

[a]Reaction performed on a 1:1 mixture of diastereomers as follows: 0.6 equiv *n*-BuLi added at –78 °C and stirred at –78 °C for 15 minutes, then 0.5 equiv *sec*-BuLi was added at –78 °C and stirred at room temperature for 3 hours after the cold bath was removed. [b]**4.6a** and **4.6a′** were formed. n.d. Not detected. It is also worth noting that we were looking at the substrates that would favor [1,2]- over [1,4]-Wittig rearrangements

4.4. The [1,2]-carbon-to-carbon silyl migration in cyclic system triggered by epoxidation

4.4.1. [1,2]-carbon-to-carbon silyl migration of silylcyclopentenols 4.6a and 4.6a′

Having the starting materials in hand, we began by subjecting cyclopentenol **4.6a** to *m*-CPBA and $NaHCO_3$ leading to the formation of cyclopentanone **4.8a** as a single diastereomer in 83% yield. (Scheme 4.4, substrate **4.6a**). Given that we were unable to detect any epoxide intermediate in the reaction and determine the stereoselectivity of this step, we questioned whether epimerization of the benzylic position might have taken place. To test this, we subjected an epimer of **4.6a** (**4.6a′**), with aryl and hydroxy groups *cis* to each other, to our conditions that led to silyl migration with the resulting β-hydroxy and α-aryl in *cis* relationship (Scheme 4.4, substrate **4.6a′**).

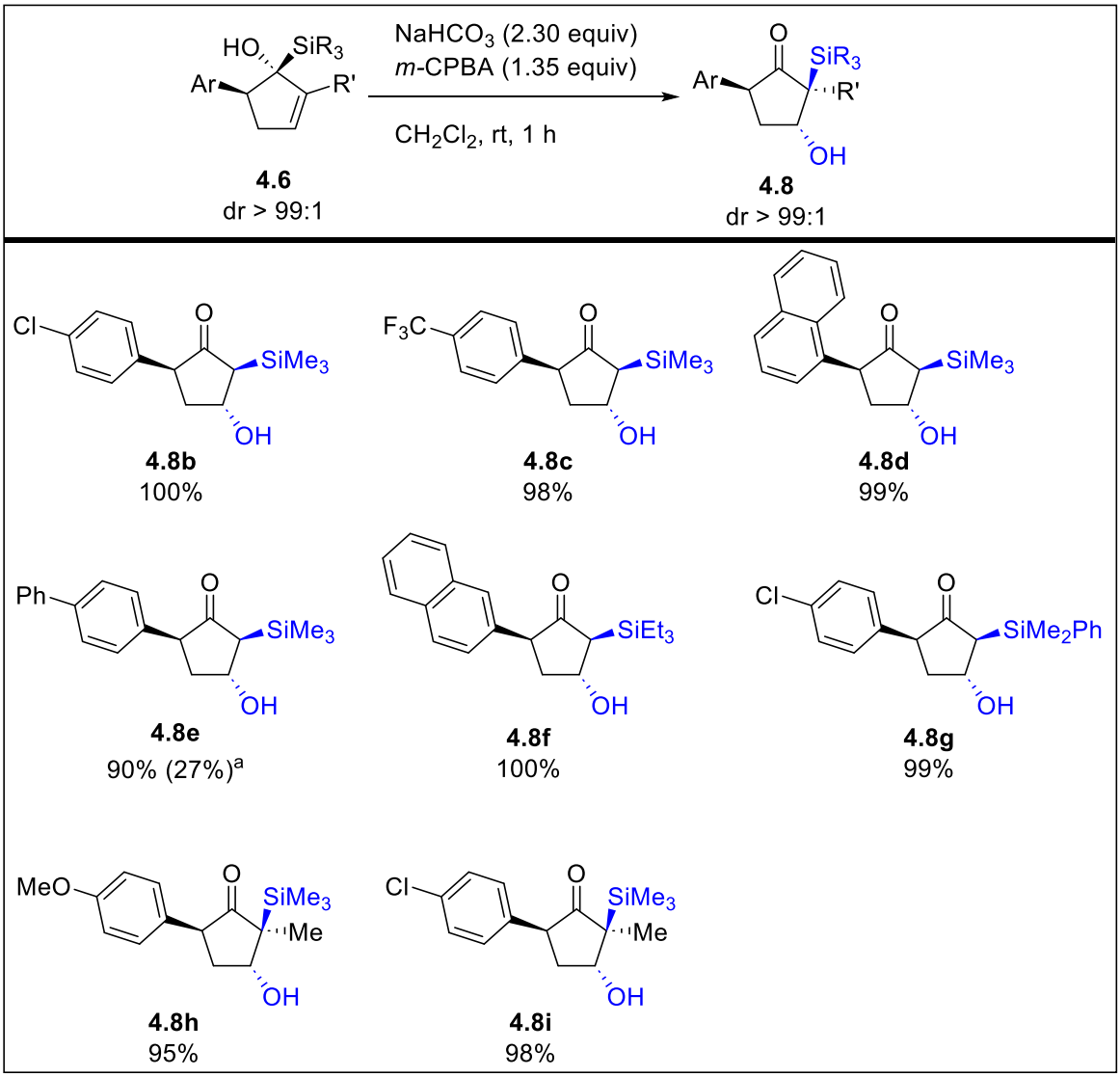


Scheme 4.3: [1,2]-carbon-to-carbon silyl migration of cyclopentenol **1a** and **1a′**
[a]Reaction conducted in absence of $NaHCO_3$

Although the substrates employed in Scheme 4.3 were racemic, the relative stereochemistry of the diastereomeric products suggests that the epoxidation step is stereoselective and takes place syn to the tertiary hydroxyl group. In addition, the [1,2]-silyl migration leading to epoxide ring opening appears to occur in a syn fashion, in such a way that the relative stereochemistry of the silyl and aryl groups is conserved.

4.4.2. Substrate scope for [1,2]-carbon-to-carbon silyl migration in silylcyclopentenols

We next explored the substrate scope of this transformation (Scheme 4.4). We started by modifying the substituents of the aromatic appendage. Incorporating electron withdrawing groups at the *para* position of the phenyl ring resulted in higher yields (>98%). Employing a sterically hindered aryl group (1-naphthyl) also led to higher yield (99%) of cyclopentanone **4.8d** as a single diastereomer.



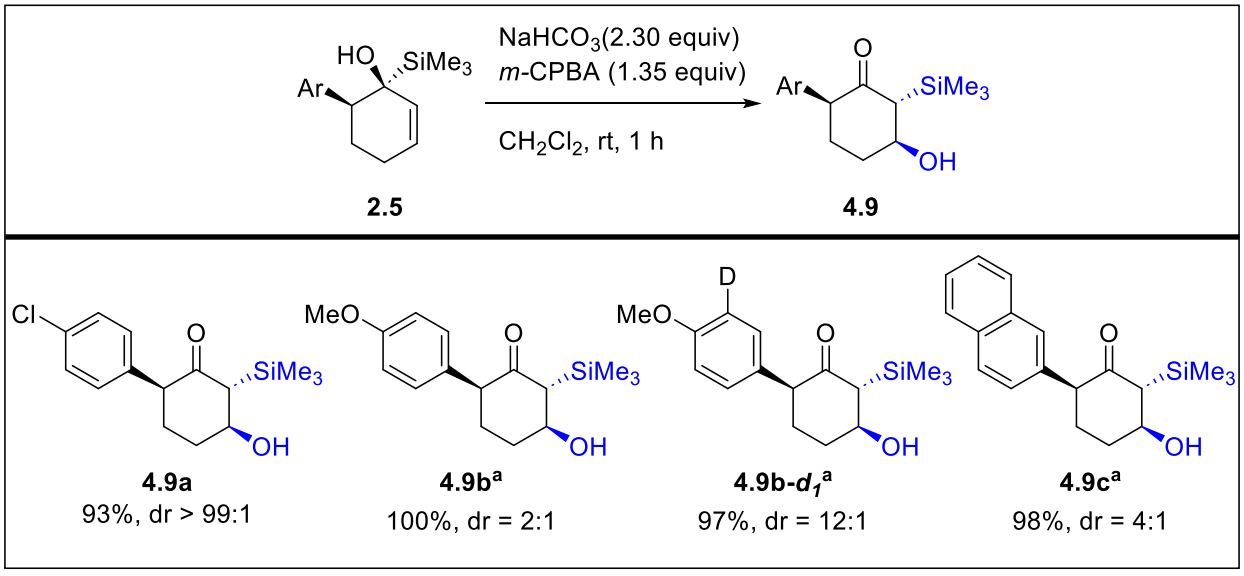
Scheme 4.4: Substrate scope for [1,2]-carbon-to-carbon silyl migration in silylcyclopentenols
[a]Reaction conducted in absence of $NaHCO_3$

Modifying the substituents on silicon to triethyl and dimethylphenyl groups respectively also

resulted in higher yields and greater diastereoselectivity (compounds **4.8e** and **4.8f**). We then explored the substrates with a methyl group at the olefin carbon proximal to silicon with varying aryl groups. All these resulted in high yields (compounds **4.8g**, **4.8h** and **4.8i**). It is worth noting that compounds **4.8b** through **4.8e** did not require further purification by column chromatography or crystallization.

4.4.3. Substrate scope for [1,2]-carbon-to-carbon silyl migration in silylcyclohexenols

Next, we evaluated the behavior of analogous silyl cyclohexenols that were synthesized through [1,2]-Wittig rearrangement of 2-trimethylsilyl-2,5,6,7-tetrahydro-7-aryl-oxepins (see Chapter 2). The 6-aryl-2-trimethylsilylcyclohex-2-en-1-ols were then exposed to the standard conditions for silyl migration (*m*-CPBA and $NaHCO_3$). This resulted in the formation of α-trimethylsilyl-β-hydroxy-6-arylcyclohexan-1-ones in high yields and high diastereoselectivities (Scheme 4.5).



Scheme 4.5: Substrate scope for [1,2]-carbon-to-carbon silyl migration in silylcyclohexenols
[a]Reaction performed on a mixture of diastereomers

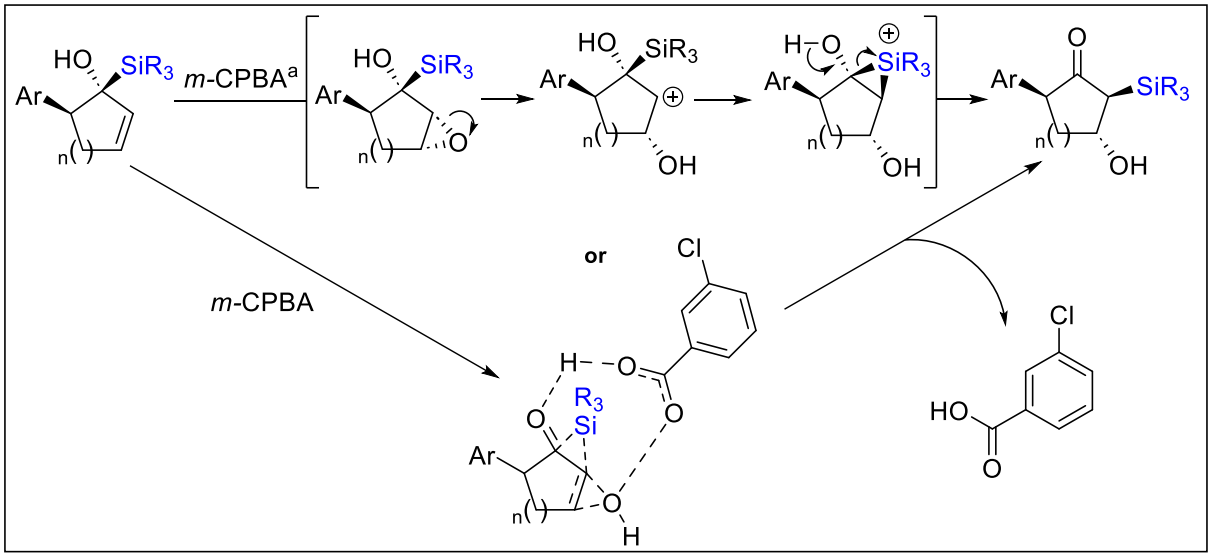
4.5. Proposed reaction mechanism for the silyl migration

Mechanistically, the stereoselective epoxidation of the double bond by *m*-CPBA could be

controlled by intramolecular hydrogen bond interactions with the tertiary allylic alcohol.[31-33] Furthermore, the epoxide opening may be triggered by the ring strain from a fused oxirane and the cyclopentane or cyclohexane skeleton. Since the same has also been seen in acyclic systems,[28-30] the ring opening could also be as a result of the ability of the silicon atom to stabilize the development of positive charge at a beta carbon atom, also known as the β-silicon effect or silicon hyperconjugation.[34-46] The silyl shift appears to be caused by a pinacol-type rearrangement,[47] resulting in carbonyl formation.[48-55]

We therefore propose that after stereoselective epoxidation, the epoxide opens up leading to the formation of a carbocation β to silyl group. This carbocation is then intramolecularly attacked by silicon through hyperconjugation resulting in silylium ion. Intramolecular proton abstraction from the alcohol by the resulting alkoxide followed by carbon oxygen double bond formation with concerted opening of the silyl heterocyclic ring furnishes the observed product.

We were unable to observe the epoxide intermediate in all the substrates herein. Thus, if this isomerization is a stepwise (epoxide formation and then ring opening to give a tertiary carbocation followed by silyl migration) or a concerted process (simultaneous epoxidation/silyl migration) is unknown at this point (Scheme 4.6).



Scheme 4.6: Proposed mechanistic pathways of the silyl shift
[a]Allylic alcohol directed epoxidation

4.6. Conclusion

In summary, a novel protocol to access α-silyl β-hydroxy cyclopentanones and cyclohexanones by [1,2]-Wittig rearrangement followed by [1,2]-carbon-to-carbon silyl migration has been developed. This transformation occurs with high yields and excellent diastereoselectivities and is independent of the substitution at the aromatic group and more importantly, alkyl substitution at the olefin is not a requirement.

The reaction proceeded with poor yields in the absence of sodium bicarbonate ($NaHCO_3$). The purity of *m*-CPBA also played an important role in the conversion of the starting material into the desired products. Column chromatography could not be used to purify the products which had epimerizable proton at the carbon bearing the silyl group. In such cases, recrystallization was helpful. Lastly, from the mechanistic standpoint, whether this transformation occurs in a concerted or stepwise version is unknown at the moment.

4.7. Experimental section

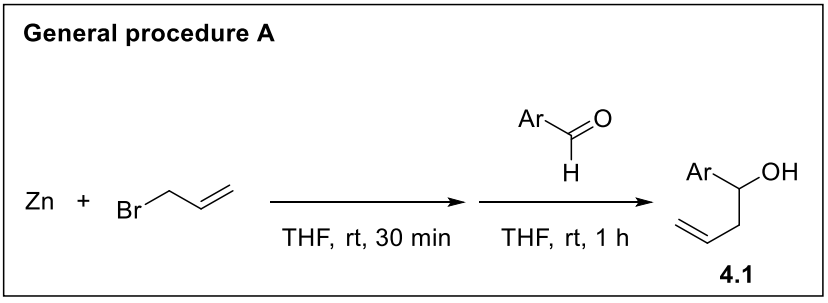
4.7.1. General information

Unless otherwise noted, all reactions were run under a positive atmosphere of nitrogen in oven-

dried or flame-dried round-bottomed flasks or conical vials or disposable drum vials capped with rubber septa. Solvents were removed by rotary evaporation under reduced pressure at temperatures lower than 45 ºC. Column chromatography was run on 230–400 mesh silica gel. Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone ketyl; dichloromethane, benzene, trimethylsilyl chloride were distilled from calcium hydride. Trimethylsilyltrifluoromethane sulfonate (TMSOTf) was redistilled and stored under nitrogen at –10 °C before the reaction. Triethylsily chloride, dimethylphenylsilyl chloride, *tert*-butyllithium (1.7 M in pentane) and BF_3•OEt_2 were used as received. *n*-Butyllithum (1.6 M or 2.5 M in hexanes) and *sec*-butyllithium (1.4 M in cyclohexane) were purchased from Aldrich and their concentration calculated by titration with diphenylacetic acid (average of three runs). ^{1}H NMR spectra was collected in 500 MHz and 600 MHz Varian instruments using $CDCl_3$ as solvent, which was referenced at 7.26 ppm (residual chloroform proton) and ^{13}C NMR spectra was collected in $CDCl_3$ at 126 MHz or 151 MHz and referenced at 77.0 ppm. High-resolution mass spectrometric analysis was run in TOF instruments.

4.7.2. Synthesis of 2-Silyl-5,6-Dihydropyrans

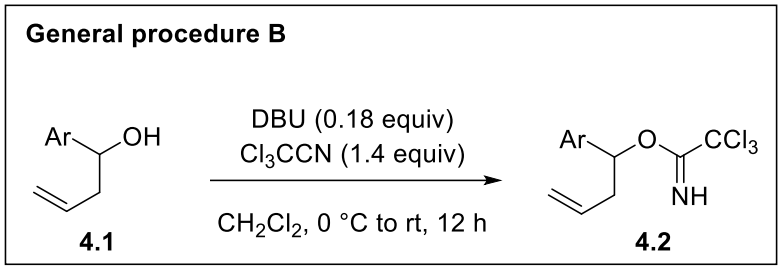
4.7.2.1. Preparation of aryl homoallylic alcohols 4.1 – peneral procedure A



Following a reported procedure[56] with a slight modification, commercial zinc dust (5.23 g, 80 mmol, 2.0 equiv.) was weighed into a dry 250 mL round-bottomed flask equipped with a magnetic stir bar. The flask was capped with a rubber septum and purged with nitrogen for approximately 5 minutes. Freshly distilled THF (100 mL) was added into the flask followed by 5.2 mL of allyl

bromide (7.26g, 60 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 30 minutes after which the desired aryl aldehyde (40 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred at room temperature for 1 h then quenched by addition of 20 mL of saturated aqueous ammonium chloride solution. The mixture was diluted with 40 mL of diethyl ether and 20 mL of water, respectively. The layers were separated, and the aqueous layer was extracted with diethyl ether (40 mL x 3). The combined organic layers were washed with 20 mL saturated aqueous ammonium chloride, (20 mL x 2) water and 20 mL of saturated aqueous sodium chloride solution then dried over anhydrous magnesium sulfate. Filtration and concentration under reduced pressure afforded aryl homoallylic alcohol **4.1** which was typically used in the next step without need for further purification.

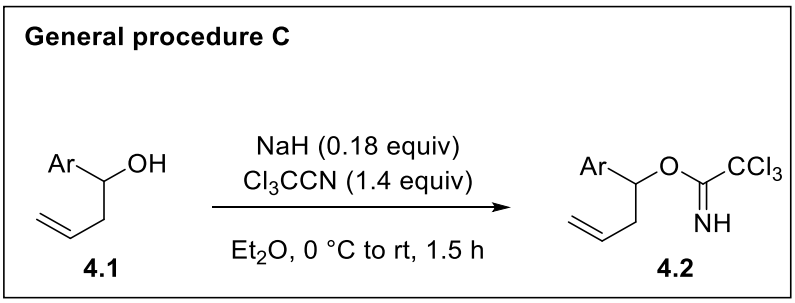
4.7.2.2. Preparation of trichloroacetimidates 4.2 – general procedure B



Following our reported procedure with a slight modification,[26] to a dry 250 mL round-bottomed flask fitted with a magnetic stir bar and sealed with a rubber septum was added 60 mL of dry dichloromethane under nitrogen. The desired homoallylic alcohol **4.1** (20 mmol, 1.00 equiv) in dichloromethane (20 mL) was then transferred into the flask. This was followed by addition of 0.54 mL of 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) (0.55 g, 3.6 mmol, 0.18 equiv.). After stirring for 5 minutes, the solution was cooled to 0 °C on an ice bath. This was followed by dropwise addition of 2.8 mL of tricchloroacetonitrile (4.04 g, 28 mmol, 1.40 equiv.). After 12 hours, the resulting dark brown mixture was filtered through a plug of silica (5 cm thick) to remove

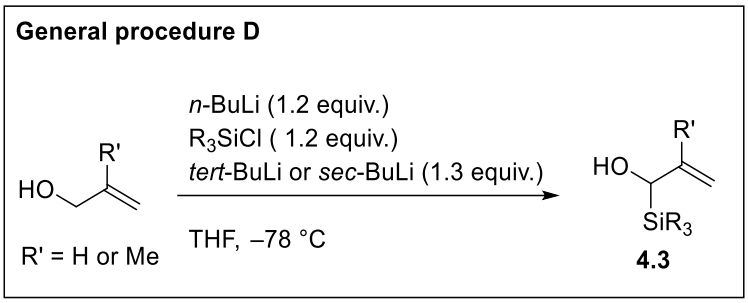
the dark residue. The filtrate was concentrated, and the crude mixture subjected to column chromatography (EtOAc/hexanes) to afford the desired trichloroacetimidate **4.2**.

4.7.2.3. Alternative preparation of trichloroacetimidates 4.2 – general procedure C[26]



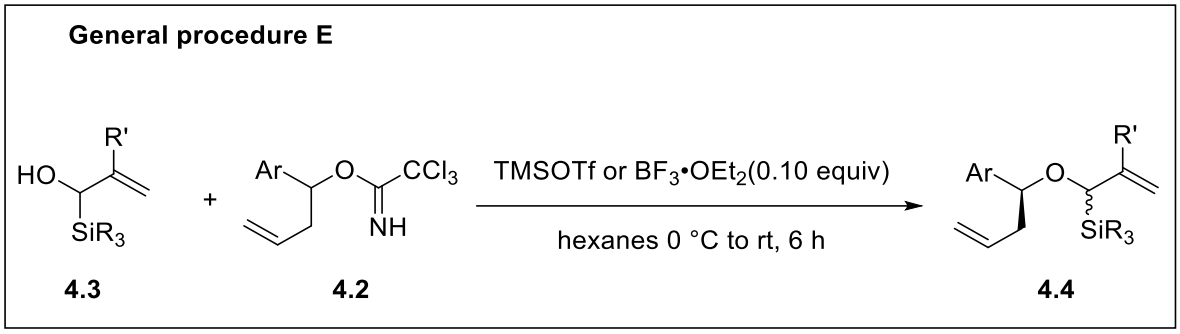
Following our reported procedure,[26] 240 mg of sodium hydride 60% w/w dispersion in mineral oil (6 mmol, 0.18 equiv) was weighed into a dry 100 mL round-bottomed flask fitted with a magnetic stir bar and 20 mL of freshly distilled diethyl ether was added into the flask. The flask was sealed with a rubber septum and purged with nitrogen. The resulting grey suspension was cooled on an ice bath and the desired homoallylic alcohol **4.1** (30 mmol, 1.00 equiv) in dry diethyl ether (20 mL) was then transferred into the flask slowly resulting in a fizzy reaction. The mixture was stirred at 0 °C for 10 minutes. This was followed by dropwise addition of 4.2 mL of trichloroacetonitrile (6.06 g, 42 mmol, 1.40 equiv.). The mixture turned dark brown after complete addition of the trichloroacetonitrile. The mixture was stirred at 0 °C for 20 minutes and then the ice bath was removed, and the mixture stirred at room temperature for 1 hour. The diethyl ether was then removed by rotorvap and methanol (0.25 mL, 6.0 mmol, 0.18 equiv.) in 15 mL pentane was added to the crude mixture. The mixture was further diluted with 40 mL pentane and filtered through a plug of celite (5 cm thick). The filtrate was concentrated, and the crude mixture subjected to column chromatography (EtOAc/hexanes) to afford the desired trichloroacetimidate **4.2**.

4.7.2.4. Preparation of α-hydroxy allyl silanes 4.3 – general procedure D[26]



A solution of the corresponding allylic alcohol in THF was cooled at −78 °C, and *n*-butyllithium (1.6 M or 2.5 M in hexanes) was added dropwise over 5 min. After 30 min the corresponding chlorosilane was added dropwise via syringe. After the resulting solution was stirred for a given amount of time (see individual compounds procedure below), *sec*-butyllithium or *tert*-butyllithium (see below for details) was added dropwise over 30−60 min, and then the reaction was kept at the indicated temperature.

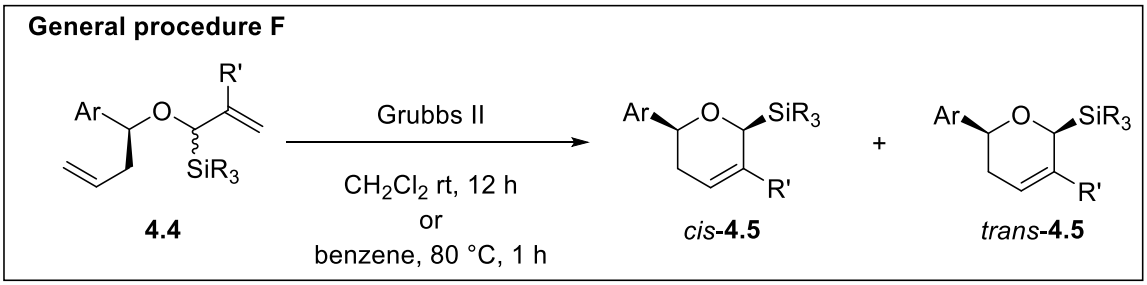
4.7.2.5. Preparation of diastereomeric dienes 4.4 – general procedure E[26]



A dry 250 mL round-bottomed flask with a magnetic stir bar was sealed with a rubber septum and purged with nitrogen. A solution of the corresponding allylic alcohol **4.3** (10 mmol, 1 equiv) in 20 mL hexanes was transferred into the flask followed by a solution of the corresponding trichloroacetimidate **4.2** (15 mmol, 1.5 equiv.) in 20 mL hexanes. An additional 40 mL of hexanes was then added into the flask and the resulting mixture was cooled on ice bath to 0 °C while stirring. To the cold solution was added appropriate Lewis acid: BF_3•OEt_2 (0.12 mL, 1 mmol, 0.1

equiv.) or TMSOTf (0.18 mL, 1 mmol, 0.1 equiv.). After complete addition, a thick precipitate was formed. The mixture was stirred at 0 °C to room temperature for 6 hours and filtered through a plug of celite (5 cm thick) and the filtrate was transferred into a separating funnel. The filtrate was then washed with saturated solution of aqueous sodium bicarbonate (50 mL x 3), water (50 mL x 2) and brine (50 mL) respectively. The organic layer was dried over anhydrous sodium sulfate and then filtered. The filtrate was concentrated under reduced pressure to afford diene **4.4** as a mixture of diastereomers. The resulting crude reaction mixture was purified by column chromatography (dichloromethane/hexanes). It is important to note that some diastereomers were separable by column chromatography and hence only one of them (*syn*) was taken to the next step (RCM). The diastereomers that could not be separated by column chromatography were taken to the next step as a mixture. The stereochemistry of these diastereomers were determined after the RCM reaction: *syn* diastereomers underwent RCM to form *cis* dihydropyrans or tetrahyrooxepins and vice versa. It is also worth noting that for most of the compounds reported herein, the *syn* diastereomer exhibited lower R_f value than its *anti* counterpart (dichloromethane/hexanes).

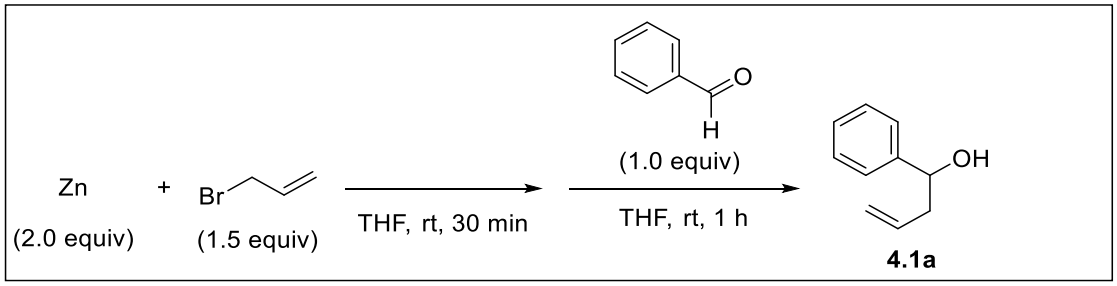
4.7.2.6. Preparation of dihydropyrans 4.5 and via RCM – general procedure F[26]



To a dry 250 mL round-bottomed flask with a magnetic stir bar was weighed 170 mg of Grubbs catalyst 2nd generation (0.2 mmol, 0.04 equiv.) and the flask was sealed with a rubber septum and purged with nitrogen. This was followed by addition of 80 mL of dry dichloromethane and corresponding diene (5 mmol, 1.0 equiv) as a solution in 20 mL dry dichloromethane as a single

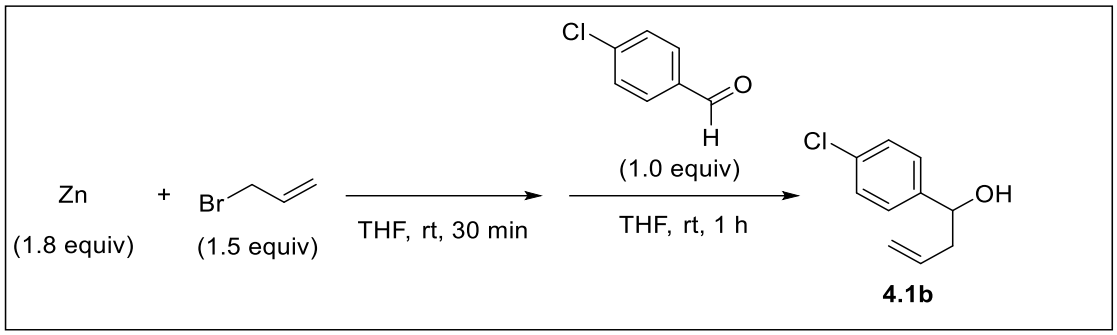
diastereomer (*syn*) or as a mixture of diastereomers (*syn:anti* = 1:1). The resulting mixture was stirred at room temperature for 12 hours. The mixture was concentrated under reduced pressure to afford dihydropyran **4.5**. The resulting crude reaction mixture was purified by column chromatography (dichloromethane/hexanes). The *cis* and *trans* diastereomers were separable by column chromatography. The stereochemistry of these diastereomers were determined by 1D NOESY experiment. It is also worth noting that for most of the compounds reported here the *trans* diastereomer has lower R_f value than its *cis* counterpart (dichloromethane/hexanes).

Synthesis of 1-phenylbut-3-en-1-ol (4.1a)



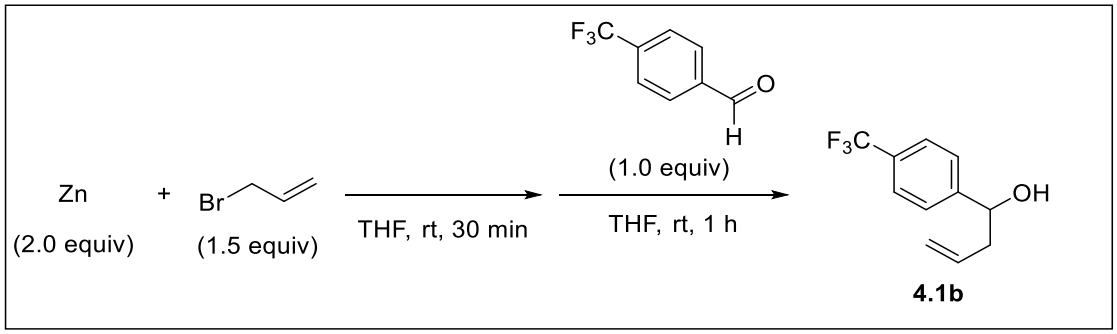
Following general procedure A, commercial zinc dust (3.92 g, 60 mmol, 2.0 equiv), allyl bromide (3.9 mL, 45 mmol, 1.5 equiv), benzaldehyde (3.18 g, 30 mmol, 1.0 equiv.) and THF (80 mL) homoallylic alcohol **4.1a** was obtained as a yellow oil (4.17 g, 94%) which was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 4.4 Hz, 4H), 7.29 (ddd, *J* = 8.8, 4.9, 3.9 Hz, 1H), 5.88 – 5.76 (m, 1H), 5.21 – 5.11 (m, 2H), 4.73 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.57 – 2.46 (m, 2H), 2.27 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.8, 134.4, 128.3, 127.5, 125.8, 118.3, 73.3, 43.7. IR (FTIR, film, cm^{-1}) $\tilde{\nu}$ = 3342, 3054, 1638, 1507, 1270, 1124, 1042, 817, 744. **4.1a** is a known compound and spectroscopic data are in agreement with those reported in literature.[57]

Synthesis of 1-(4-chlorophenyl)but-3-en-1-ol (4.1b)



Following general procedure A, commercial zinc dust (5.88 g, 90 mmol, 1.8 equiv), allyl bromide (6.5 mL, 75 mmol, 1.5 equiv), 4-chlorobenzaldehyde (7.02 g, 50 mmol, 1.0 equiv.) and THF (100 mL) homoallylic alcohol **4.1b** was obtained as a yellow oil in THF (13 g, ~100 %) which was used in the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 5.81 – 5.72 (m, 1H), 5.19 – 5.15 (m, 1H), 5.14 (q, *J* = 1.3 Hz, 1H), 4.70 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.60 (s, 1H), 2.53 – 2.48 (m, 1H), 2.48 – 2.42 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.0, 133.8, 133.1, 128.5, 127.2, 118.8, 72.6, 43.7. IR (FTIR, film, cm^{-1}) ṽ = 3348, 3077, 2905, 1640, 1492, 1090, 1012, 916, 824. **4.1b** is a known compound and spectroscopic data are in agreement with those reported in literature.[57]

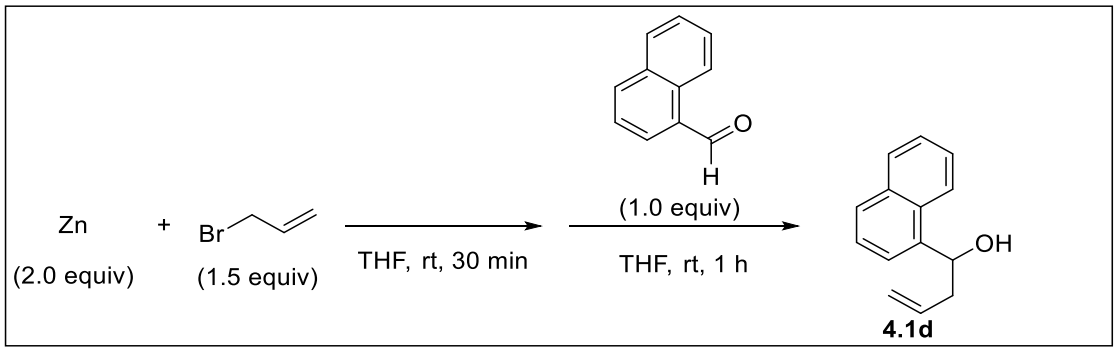
Synthesis of 1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol (4.1c)



Following general procedure A, commercial zinc dust (13.08 g, 200 mmol, 2.0 equiv), allyl bromide (13 mL, 150 mmol, 1.5 equiv), 4-trifluoromethylbenzaldehyde (17.41 g, 100 mmol, 1.0

equiv.) and THF (200 mL) homoallylic alcohol **4.1c** was obtained as a yellow oil in THF (27.84 g, quantitative yield) which was used in the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 5.83 – 5.73 (m, 1H), 5.19 (h, *J* = 1.8 Hz, 1H), 5.16 (tq, *J* = 3.2, 1.4 Hz, 1H), 4.79 (dd, *J* = 8.1, 4.7 Hz, 1H), 2.53 (dddt, *J* = 14.0, 6.2, 4.7, 1.3 Hz, 1H), 2.45 (dtt, *J* = 14.1, 7.9, 1.1 Hz, 1H), 2.32 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.7 (d, *J* = 1.4 Hz), 133.7, 129.7 (q, *J* = 32.4 Hz), 126.1, 125.3 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.9 Hz), 119.2, 72.5, 43.9. **4.1c** is a known compound and spectroscopic data are in agreement with those reported in literature.[57]

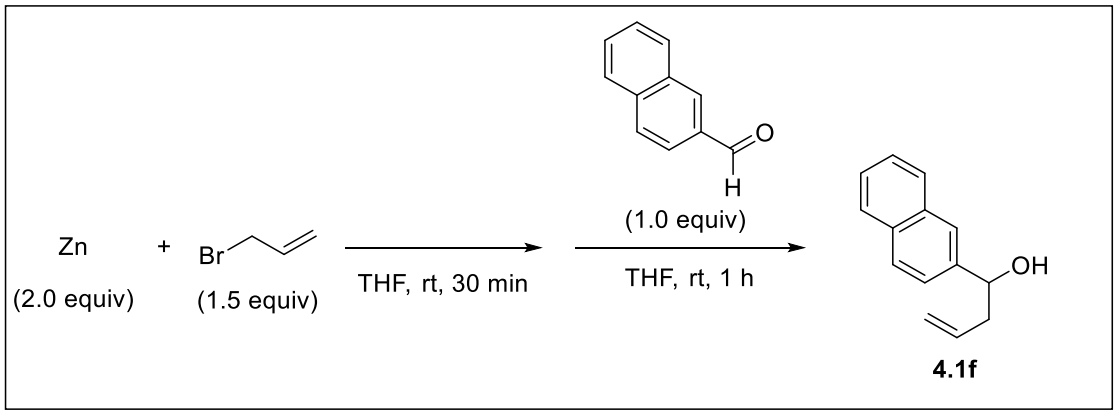
Synthesis of 1-(naphthalen-1-yl)but-3-en-1-ol (4.1d)



Following general procedure A, commercial zinc dust (11.77 g, 180 mmol, 2.0 equiv), allyl bromide (13 mL, 150 mmol, 1.5 equiv), 1-naphthaldehyde (15.62 g, 100 mmol, 1.0 equiv.) and THF (200 mL) homoallylic alcohol **4.1d** was obtained as a yellow oil in THF (39.11 g, quantitative yield) which was used in the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 8.11 – 8.04 (m, 1H), 7.90 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.80 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.67 (dt, *J* = 7.2, 1.0 Hz, 1H), 7.56 – 7.47 (m, 3H), 5.94 (dddd, *J* = 16.9, 10.2, 7.6, 6.5 Hz, 1H), 5.52 (dd, *J* = 8.4, 4.1 Hz, 1H), 5.27 – 5.17 (m, 2H), 2.77 (dddt, *J* = 14.3, 6.7, 4.1, 1.4 Hz, 1H), 2.62 (dtt, *J* = 14.3, 8.6, 1.1 Hz, 1H), 2.37 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.3, 134.7, 133.7, 130.2, 128.9, 127.9, 126.0, 125.5, 125.4, 122.9, 122.8, 118.3, 69.9, 42.8. **4.1d** is a known compound and

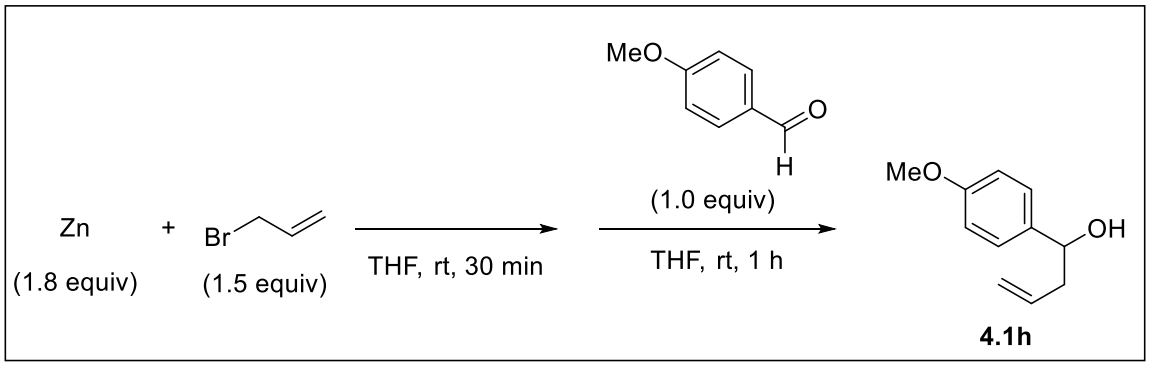
spectroscopic data are in agreement with those reported in literature.[58]

Synthesis of 1-(naphthalen-2-yl)but-3-en-1-ol (4.1f)



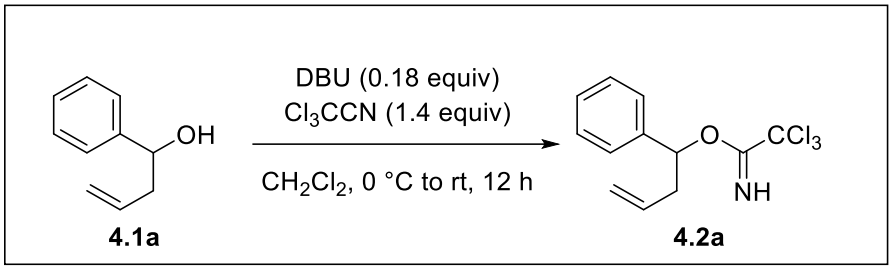
Following general procedure A, commercial zinc dust (5.23 g, 80 mmol, 2.0 equiv), allyl bromide (5.2 mL, 60 mmol, 1.5 equiv), 2-naphthaldehyde (6.25 g, 40 mmol, 1.0 equiv.) and THF (100 mL) homoallylic alcohol **4.1f** was obtained as a yellow oil in THF (9.64 g, quantitative yield) which was used in the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.87 – 7.82 (m, 3H), 7.81 (s, 1H), 7.54 – 7.45 (m, 3H), 5.84 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.25 – 5.13 (m, 2H), 4.91 (dd, *J* = 7.7, 5.2 Hz, 1H), 2.68 – 2.55 (m, 2H), 2.27 (s, 1H). ^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$) δ = 141.2, 134.3, 133.2, 132.9, 128.2, 127.9, 127.6, 126.1, 125.8, 124.5, 124.0, 118.5, 73.3, 43.7. IR (FTIR, cm^{-1}) $\tilde{\nu}$ = 3342, 3054, 1638, 1507, 1270, 1124, 1042, 817, 744. **S1-f** is a known compound and spectroscopic data are in agreement with those reported in literature.[57]

Synthesis of 1-(4-methoxyphenyl)but-3-en-1-ol (4.1h)



Following general procedure A, commercial zinc dust (5.88 g, 90 mmol, 1.8 equiv), allyl bromide (6.5 mL, 60 mmol, 1.5 equiv), 6.1 mL of *p*-anisaldehyde (6.81 g, 50 mmol, 1.0 equiv.) and THF (80 mL) homoallylic alcohol **4.1h** was obtained as a yellow oil in THF (13.44 g, quantitative yield) which was used in the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.78 (ddt, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.17 – 5.09 (m, 2H), 4.66 (t, *J* = 6.6 Hz, 1H), 3.79 (s, 3H), 2.53 – 2.44 (m, 2H), 2.23 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 158.9, 136.0, 134.6, 127.0, 118.1, 113.7, 72.9, 55.2, 43.6. IR (FTIR, cm^{-1}) ṽ = 3395, 2933, 2835, 1610, 1510, 1242, 1173, 1032, 829. **4.1h** is a known compound and spectroscopic data are in agreement with those reported in literature.[57]

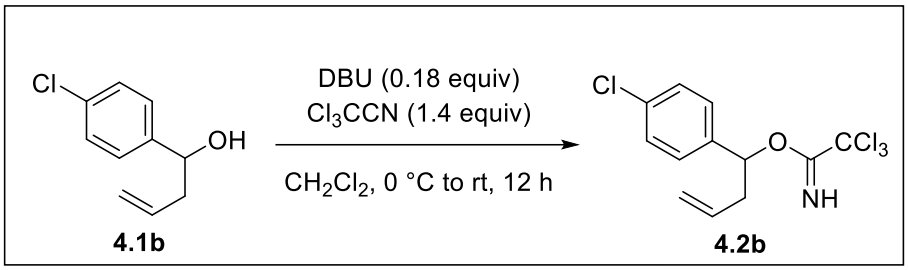
Synthesis of 1-phenylbut-3-en-1-yl 2,2,2-trichloroacetimidate (4.2a)



Following general procedure B, 1-phenylbut-3-en-1-ol **4.1-a** (2.23 g, 15 mmol, 1.0 equiv), DBU (0.4 mL, 2.7 mmol, 0.18 equiv), trichloroacetonitrile (2.1 mL, 21 mmol, 1.4 equiv.) and dichloromethane (40 mL), 1-phenylbut-3-en-1-yl 2,2,2-trichloroacetimidate **4.1a** was obtained as a dark brown oil in dichloromethane (4.5 g, ~100 %) which was used in the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 8.30 (s, 1H), 7.45 – 7.40 (m, 2H), 7.37 (ddd, *J* = 7.7, 6.7, 1.3 Hz, 2H), 7.34 – 7.29 (m, 1H), 5.90 (dd, *J* = 7.9, 5.4 Hz, 1H), 5.83 (ddt, *J* = 17.2, 10.2, 6.9 Hz, 1H), 5.14 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.10 (ddt, *J* = 10.2, 2.1, 1.1 Hz, 1H), 2.81 (dddt, *J* = 14.7, 8.0, 6.8, 1.3 Hz, 1H), 2.66 (dddd, *J* = 14.5, 6.9, 4.1, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.5, 139.6, 133.0, 128.4, 128.0, 126.2, 118.2, 91.6, 80.1, 41.0. **4.1a** is a known

compound and spectroscopic data are in agreement with those reported in literature.[59]

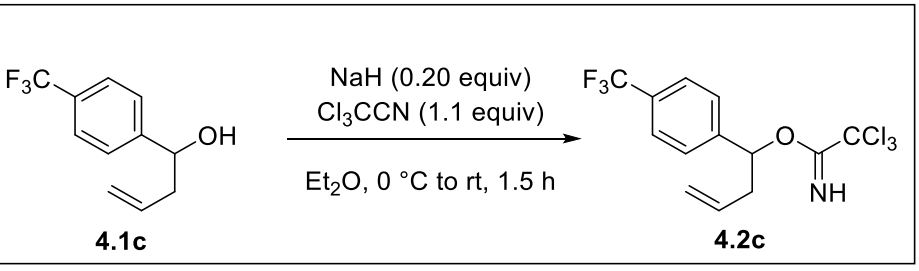
Synthesis of 1-(4-chlorophenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (4.2b)



4.1b **4.2b**

Following general procedure B, 1-(4-chlorophenyl)but-3-en-1-ol **4.1b** (14.61 g, 80 mmol, 1.0 equiv), DBU (2.15 mL, 14.4 mmol, 0.18 equiv), trichloroacetonitrile (11.2 mL, 112 mmol, 1.4 equiv.) and dichloromethane (200 mL), 1-(4-chlorophenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2b** was obtained as a dark brown oil in dichloromethane (29 g, quantitative yield) which was used in the next step without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 8.31 (s, 1H), 7.34 (s, 4H), 5.86 (dd, *J* = 7.8, 5.6 Hz, 1H), 5.79 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.17 – 5.06 (m, 2H), 2.78 (dddt, *J* = 14.6, 8.0, 6.8, 1.3 Hz, 1H), 2.62 (dddt, *J* = 14.2, 7.0, 5.6, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.3, 138.1, 133.7, 132.6, 128.6, 127.7, 118.6, 91.5, 79.3, 40.8. **4.2b** is a known compound and spectroscopic data are in agreement with those reported in literature.[59]

Synthesis of 1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (4.2c)

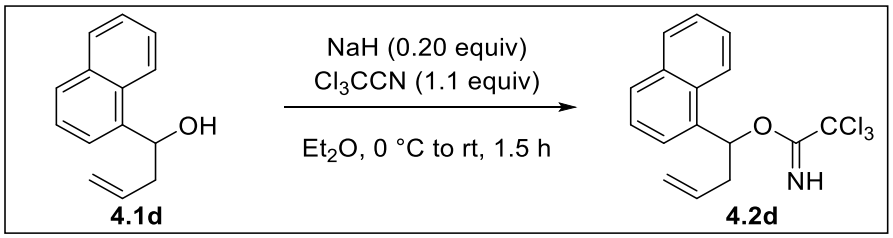


4.1c **4.2c**

Following general procedure C, 1-(4-trifluoromethylphenyl)but-3-en-1-ol **4.1c** (10.81 g, 50 mmol, 1.0 equiv), NaH 60% w/w dispersion in mineral oil (400 mg, 10 mmol, 0.20 equiv),

trichloroacetonitrile (5.51 mL, 55 mmol, 1.1 equiv.) and diethyl ether (15 mL), 18.5 g, 51 mmol (quantitative yield) of 1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2c** was obtained as a yellow oil after column chromatography, R_f = 0.3 (5% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.34 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 5.93 (dd, *J* = 7.7, 5.5 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.3, 7.0 Hz, 1H), 5.18 – 5.09 (m, 2H), 2.79 (dddt, *J* = 14.6, 8.0, 6.8, 1.3 Hz, 1H), 2.65 (dddt, *J* = 14.1, 6.9, 5.5, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ =161.4, 143.6 (d, *J* = 1.3 Hz), 132.4, 130.2 (q, *J* = 32.5 Hz), 126.5, 125.5 (q, *J* = 3.8 Hz) 124.0 (q, *J* = 272.2 Hz), 118.9, 91.4, 79.3, 40.8. **4.2c** is a known compound and spectroscopic data are in agreement with those reported in literature.[59]

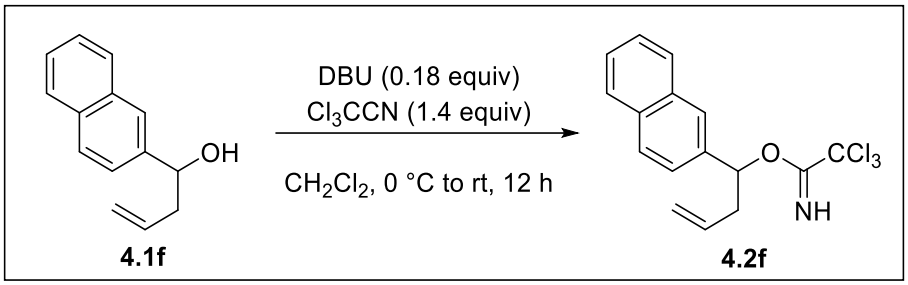
Synthesis of 1-(naphthalen-1-yl)but-3-en-1-yl 2,2,2-trichloroacetimidate (4.2d)



Following general procedure C, 1-(naphthalen-1-yl)but-3-en-1-ol **4.1d** (9.9 g, 50 mmol, 1.0 equiv), NaH 60% w/w dispersion in mineral oil (400 mg, 10 mmol, 0.20 equiv), trichloroacetonitrile (5.51 mL, 55 mmol, 1.1 equiv.) and diethyl ether (15 mL), 16.86 g, 49 mmol (98% isolated yield) of 1-(naphthalen-1-yl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2d** was obtained as a yellow oil after column chromatography, R_f = 0.4 (30% DCM in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.36 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.1 Hz, 1H), 7.60 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.57 – 7.48 (m, 2H), 6.73 (dd, *J* = 8.2, 4.8 Hz, 1H), 5.96 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.21 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.15 (dt, *J* = 10.3, 1.4 Hz, 1H), 2.97 (dddt, *J* = 15.0, 8.2, 6.8, 1.3 Hz, 1H), 2.89 (dddt, *J* =

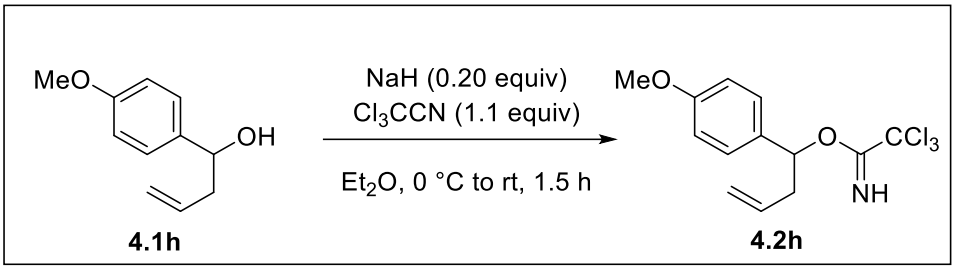
14.6, 7.3, 4.8, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.5, 135.5, 133.7, 133.4, 130.1, 128.9, 128.5, 126.3, 125.6, 125.3, 123.5, 123.0, 118.1, 91.7, 77.5, 40.5. MS (GC/MS): *m*/z (%) = 181 (12.5) $[M - Cl_3CCONH]^+$: $C_{14}H_{13}$ HRMS (ESI), *m/z* $[M + H]^+$ calcd for $C_{16}H_{15}Cl_3NO$: 342.0219 found: 342.0227.

Synthesis of 1-(naphthalen-2-yl)but-3-en-1-yl 2,2,2-trichloroacetimidate (4.2f)



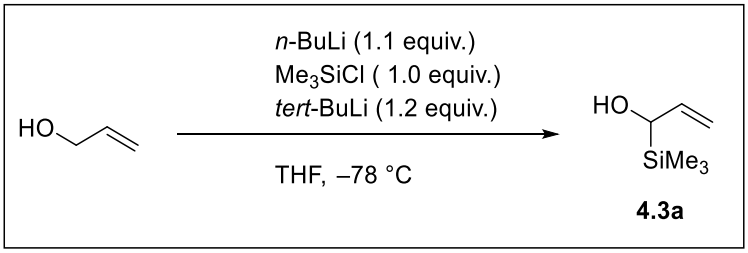
Following general procedure B, 1-(naphthalen-2-yl)but-3-en-1-ol **4.1f** (5.95 g, 30 mmol, 1.0 equiv), DBU (0.81 mL, 5.4 mmol, 0.18 equiv), trichloroacetonitrile (4.21 mL, 42 mmol, 1.4 equiv.) and dichloromethane (80 mL), 11.04 g, 32 mmol (quantitative yield) of 1-(naphthalen-2-yl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2f** was obtained as a yellow oil after column chromatography, R_f = 0.3 (4% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.33 (s, 1H), 7.90 (s, 1H), 7.89 – 7.83 (m, 3H), 7.56 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.54 – 7.46 (m, 2H), 6.08 (dd, *J* = 7.9, 5.5 Hz, 1H), 5.87 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.17 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.12 (ddt, *J* = 10.2, 2.0, 1.1 Hz, 1H), 2.92 (dddt, *J* = 14.7, 8.0, 6.8, 1.3 Hz, 1H), 2.76 (dddt, *J* = 14.2, 6.9, 5.6, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.5, 136.9, 133.1, 133.02, 133.00, 128.3, 128.1, 127.7, 126.2, 126.1, 125.5, 124.0, 118.3, 91.7, 80.2, 40.9. **4.2f** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of 1-(4-methoxyphenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (4.2h)



Following general procedure C, 1-(4-methoxyphenyl)but-3-en-1-ol **4.1h** (8.9 g, 50 mmol, 1.0 equiv), NaH 60% w/w dispersion in mineral oil (360 mg, 9 mmol, 0.18 equiv), trichloroacetonitrile (5.51 mL, 55 mmol, 1.1 equiv.) and diethyl ether (15 mL), 15.86 g, 49 mmol, (98% crude yield) of 1-(4-methoxyphenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2h** which was used in the next step without further purification. It is worth noting that compound **4.2h** is unstable on silica and it breaks down to the starting alcohol. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.27 (s, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.87 – 5.76 (m, 2H), 5.13 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.09 (ddt, *J* = 10.3, 2.1, 1.1 Hz, 1H), 3.81 (s, 3H), 2.80 (dddt, *J* = 14.7, 8.0, 6.8, 1.3 Hz, 1H), 2.62 (dddt, *J* = 14.2, 7.0, 5.7, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.5, 159.3, 133.2, 131.6, 127.7, 118.1, 113.7, 91.7, 79.9, 55.2, 40.9. **4.2h** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

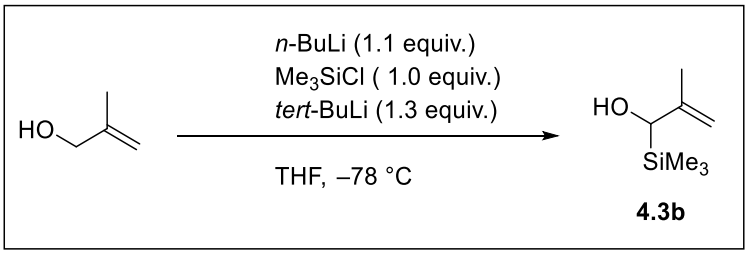
Synthesis of 1-(trimethylsilyl)prop-2-en-1-ol (4.3a)



Following general procedure D, a solution of allyl alcohol (3.49 g, 60 mmol, 1 equiv.) in THF (150 mL) was cooled to −78 °C. *n*-BuLi (2.5 M in hexanes, 26.4 mL, 66 mmol, 1.1 equiv.) was

added dropwise and the mixture stirred at –78 °C for 1 h. Freshly distilled chlorotrimethylsilane (7.6 mL, 60 mmol, 1 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –78 °C for 1.5 hours resulting in the formation of a white suspension. This was followed by addition of *tert*-BuLi (1.7 M in pentane, 43 mL, 72 mmol, 1.2 equiv.) dropwise via cannula and the reaction stirred for an additional 1.5 hours at –78 °C. The reaction was quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 50 mL). Then all the organic phases were combined, washed with H_2O (50 mL) and brine (50 mL) respectively, and dried over anhydrous $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography, R_f = 0.5 (30% Et_2O in pentane) to afford 5.17 g, 47.4 mmol, (79% isolated yield) of compound **4.3a** as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.03 (ddd, *J* = 17.1, 10.7, 5.3 Hz, 1H), 5.07 (ddd, *J* = 17.2, 2.1, 1.5 Hz, 1H), 4.99 (dt, *J* = 10.8, 1.8 Hz, 1H), 4.02 (dt, *J* = 5.3, 2.1 Hz, 1H), 1.42 (s, 1H), 0.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.9, 109.4, 69.0, -4.3. IR (FTIR, film, cm^{-1}) ṽ = 3405, 2956, 1632, 1247, 895. **4.3a** is a known compound and spectroscopic data are in agreement with those reported in literature.[60]

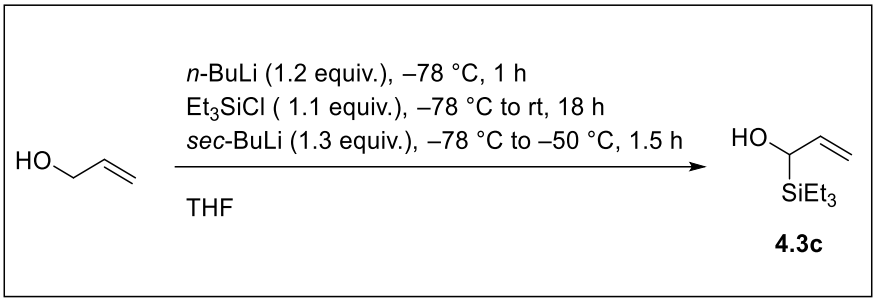
Synthesis of 2-methyl-1-(trimethylsilyl)prop-2-en-1-ol (4.3b)[61]



Following general procedure D, a solution of 2-methylprop-2-en-1-ol (4.33 g, 60 mmol, 1 equiv.) in THF (110 mL) was cooled to −78 °C. *n*-BuLi (2.5 M in hexanes, 26.4 mL, 66 mmol, 1.1 equiv.) was added dropwise and the mixture stirred at –78 °C for 1 h. Freshly distilled

chlorotrimethylsilane (7.6 mL, 60 mmol, 1 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –78 °C for 1.5 hours resulting in the formation of a white suspension. This was followed by addition of *tert*-BuLi (1.7 M in pentane, 45.9 mL, 78 mmol, 1.3 equiv.) dropwise via cannula and the reaction warmed up slowly to –35 °C and stirred at this temperature for an additional 3.5 hours. The reaction was cooled down to –78 °C and quenched by the addition of 4.5 mL acetic acid solution in 10 mL THF and the cold bath was removed. The reaction mixture was diluted with saturated aqueous $NaHCO_3$ (50 mL) solution and pentane (150 mL. After the layers were separated organic phase was washed with H_2O (50 mL x 3) and brine (50 mL) respectively and dried over anhydrous $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography, R_f = 0.4 (15% Et_2O in hexanes) to afford 5.37 g, 37.2 mmol, (62% isolated yield) of compound **4.3b** as a pale-yellow liquid. ^{1}H NMR (500 MHz, C_6D_6) δ = 4.85 (tq, *J* = 1.7, 0.8 Hz, 1H), 4.74 (h, *J* = 1.4 Hz, 1H), 3.63 (d, *J* = 1.4 Hz, 1H), 1.57 (dt, *J* = 1.5, 0.6 Hz, 3H), 1.00 (s, 1H), 0.08 (s, 9H). ^{13}C NMR (126 MHz, C_6D_6) δ = 148.6, 106.6, 71.4, 20.8, -3.3. **4.3b** is a known compound.[61]

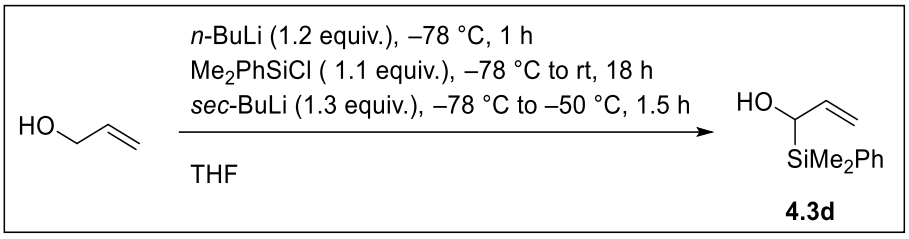
Synthesis of 1-(triethylsilyl)prop-2-en-1-ol (4.3c)



Following general procedure D, a solution of allyl alcohol (1.16 g, 20 mmol, 1 equiv.) in THF (35 mL) was cooled to −78 °C. *n*-BuLi (2.5 M in hexanes, 10 mL, 24 mmol, 1.2 equiv.) was added dropwise and the mixture stirred at –78 °C for 1 h. Chlorotriethylsilane (3.7 mL, 22 mmol, 1.1 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –78 °C to

room temperature for 18 hours resulting in the formation of a white suspension. The mixture was cooled back to –78 °C followed by dropwise addition of *sec*-butyllithium (1.4 M in cyclohexane, 18.6 mL, 26 mmol, 1.3 equiv.) and the reaction stirred for an additional 2 hours at –78 °C to –50 °C. The reaction mixture was cooled back to –78 °C and quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 20 mL). Then all the organic phases were combined, washed with H_2O (20 mL) and brine (20 mL) respectively, and dried over anhydrous $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography, R_f = 0.3 (15% Et_2O in hexanes) to afford 2.97 g, 17.2 mmol, (86% isolated yield) of compound **4.3c** as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.07 (ddd, *J* = 17.1, 10.7, 5.2 Hz, 1H), 5.09 (ddd, *J* = 17.2, 2.2, 1.6 Hz, 1H), 4.97 (ddd, *J* = 10.7, 2.1, 1.6 Hz, 1H), 4.18 (dt, *J* = 5.2, 2.1 Hz, 1H), 1.30 (s, 1H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.62 (qd, *J* = 8.0, 1.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 140.4, 109.0, 67.4, 7.4, 1.5. **4.3c** is a known compound and spectroscopic data are in agreement with those reported in literature.[60]

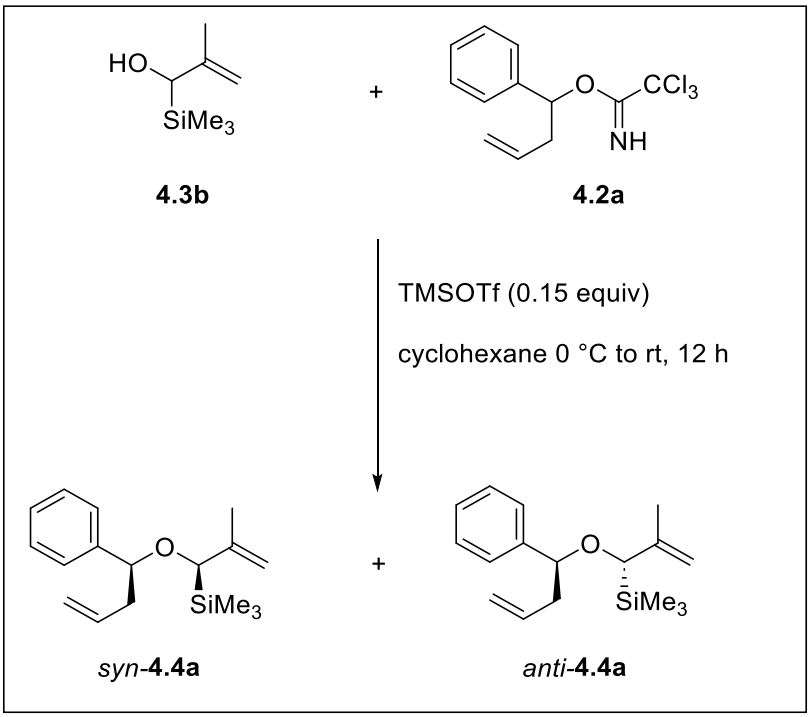
Synthesis of 1-(dimethyl(phenyl)silyl)prop-2-en-1-ol (4.3d)



Following general procedure D, a solution of allyl alcohol (1.16 g, 20 mmol, 1 equiv.) in THF (35 mL) was cooled to −78 °C. *n*-BuLi (2.5 M in hexanes, 10 mL, 24 mmol, 1.2 equiv.) was added dropwise and the mixture stirred at –78 °C for 1 h. chlorodimethyl(phenyl)silane (3.7 mL, 22 mmol, 1.1 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –

78 °C to room temperature for 18 hours resulting in the formation of a white suspension. The mixture was cooled back to –78 °C followed by dropwise addition of *sec*-butyllithium (1.4 M in cyclohexane, 18.6 mL, 26 mmol, 1.3 equiv.) and the reaction stirred for an additional 2 hours at –78 °C to –50 °C. The reaction mixture was cooled back to –78 °C and quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 20 mL). Then all the organic phases were combined, washed with H_2O (20 mL) and brine (20 mL) respectively, and dried over anhydrous $MgSO_4$. After filtration and concentration the residue was purified by column chromatography, R_f = 0.4 (15% Et_2O in hexanes) to afford 2.73 g, 14.2 mmol, (71% isolated yield) of compound **4.3d** as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.64 – 7.56 (m, 2H), 7.45 – 7.36 (m, 3H), 6.01 (ddd, *J* = 17.1, 10.7, 5.2 Hz, 1H), 5.08 (dt, *J* = 17.2, 1.8 Hz, 1H), 5.02 (dt, *J* = 10.7, 1.7 Hz, 1H), 4.23 (dt, *J* = 5.1, 2.0 Hz, 1H), 1.43 (s, 1H), 0.37 (s, 3H), 0.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.3, 136.0, 134.2, 129.5, 127.8, 110.0, 68.4, -5.8, -6.1. **4.3d** is a known compound and spectroscopic data are in agreement with those reported in literature.[62,63]

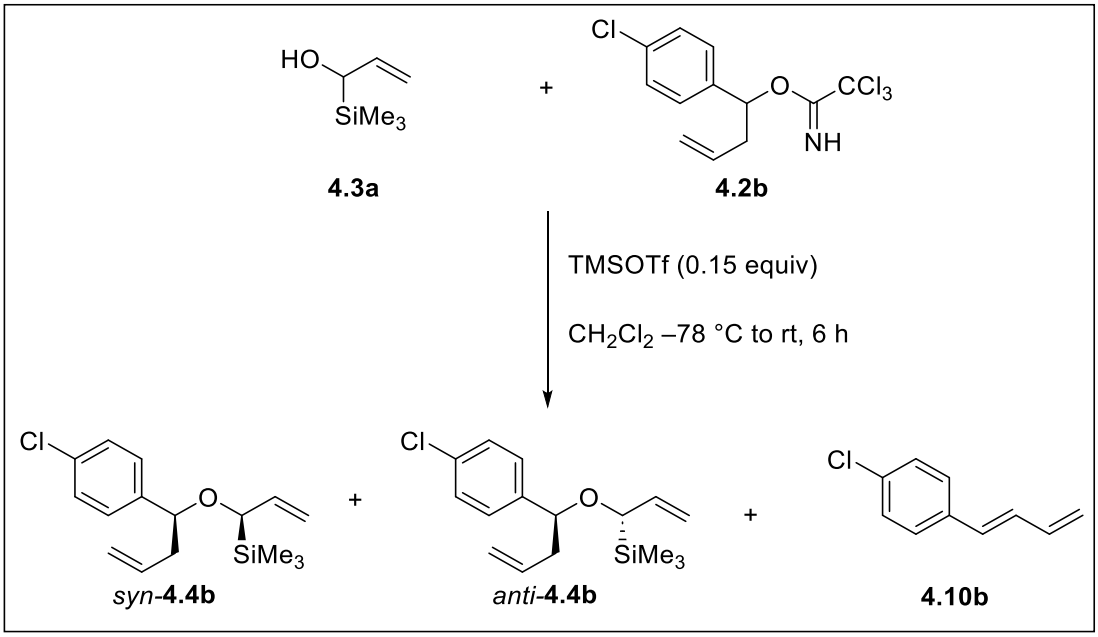
Synthesis of *syn/anti*-trimethyl(2-methyl-1-((1-phenylbut-3-en-1-yl)oxy)allyl)silane (*syn/anti*-4.4a)



Compound **4.4a** was prepared following general procedure E, a solution of 2-methyl-1-(trimethylsilyl)prop-2-en-1-ol **4.3b** (2.47 g, 17.1 mmol, 1 equiv.) and 1-phenylbut-3-en-1-yl 2,2,2-trichloroacetimidate **4.2a** (10.0 g, 34.18 mmol, 2.0 equiv.), TMSOTf (0.46 mL, 2.6 mmol, 0.15 equiv.) and cyclohehane (80 mL) for 12 hour followed by workup, concentration and column chromatography, R_f for *syn/anti*-**4.4d** = 0.6 (10% DCM in hexanes) afforded 1.64 g, 6 mmol (35% isolated yield) inseparable mixture of diastereomers of compound **4.4d** (*syn:anti* = 1:1) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35 – 7.26 (m, 8H), 7.26 – 7.20 (m, 2H), 5.81 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.74 – 5.63 (m, 1H), 5.03 – 4.95 (m, 4H), 4.87 – 4.81 (m, 1H), 4.69 (dddd, *J* = 6.6, 3.2, 1.8, 0.8 Hz, 3H), 4.34 (dd, *J* = 6.4, 5.4 Hz, 1H), 4.30 (dd, *J* = 7.7, 5.8 Hz, 1H), 3.79 (s, 1H), 3.33 (s, 1H), 2.59 – 2.52 (m, 2H), 2.52 – 2.45 (m, 1H), 2.40 – 2.33 (m, 1H), 1.70 – 1.63 (m, 3H), 1.53 (dd, *J* = 1.4, 0.8 Hz, 3H), 0.09 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 145.0, 144.4, 143.4, 142.3, 135.5, 134.6, 128.1, 127.8, 127.5, 127.4, 126.8, 126.6, 116.9, 116.4,

109.9, 109.5, 80.0, 79.1, 77.8, 75.4, 43.0, 40.5, 20.4, 20.3, -3.0, -3.2. ***Syn*-4.4b** and ***anti*-4.4b** are known compounds and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *syn/anti*-(1-((1-(4-chlorophenyl)but-3-en-1-yl)oxy)allyl)trimethylsilane (*syn/anti*-4.4b)



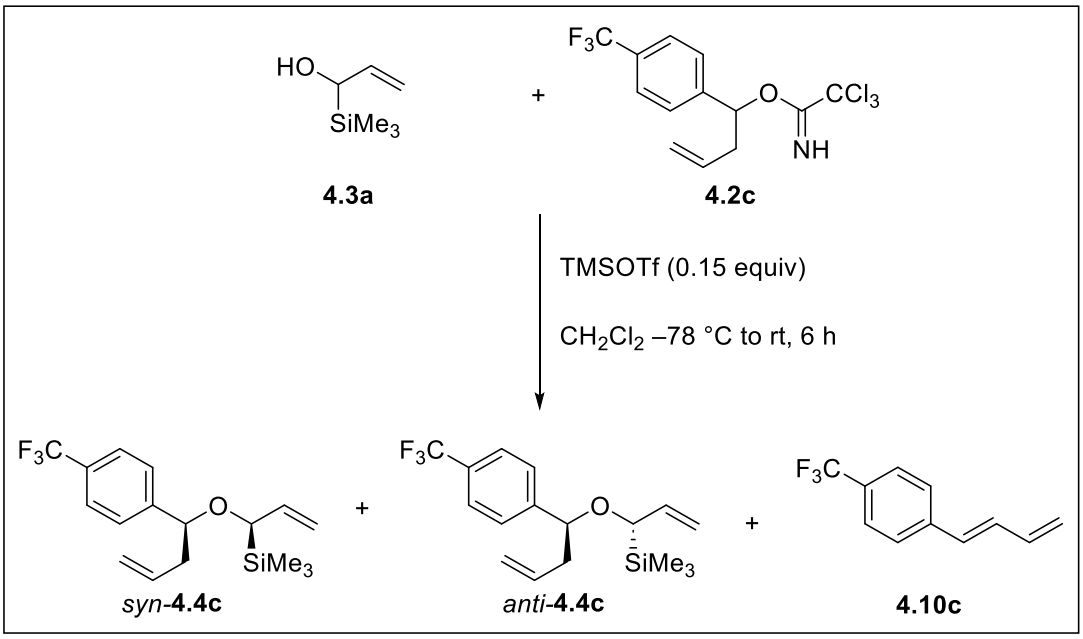
Compound **4.4b** was prepared following general procedure E with slight modification to minimize formation of the side product **4.10b** resulting from elimination. A solution of 1-(trimethylsilyl)prop-2-en-1-ol **4.3a** (1.96 g, 15 mmol, 1 equiv.) and 1-(4-chlorophenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2b** (4.91 g, 15 mmol, 1.0 equiv) in dichloromethane (100 mL) was cooled to −78 °C. TMSOTf (0.27 mL, 1.5 mmol, 0.1 equiv.) was added dropwise and the mixture stirred at –78 °C for 6 hours. The rubber septum was removed, and 5 g of sodium bicarbonate was poured into the flask. The dry ice-acetone bath was removed, and the mixture was allowed to warm up to room temperature. The mixture was filtered and concentrated under reduced pressure to remove dichloromethane. Hexanes was then added to the resulting mixture resulting in the formation of white precipitate. Subsequent filtration and concentration furnished a residue which was purified by column chromatography, R_f for **4.10b** = 0.8 and R_f for *syn/anti*-**4.4b** = 0.6 (5%

DCM in hexanes) to afford 2.15 g, 7.35 mmol, (49% isolated yield) inseparable mixture of diastereomers of compound **4.4b** (*syn:anti* = 1:1) as colorless liquid and 1.26 g, 7.65 mmol (51% isolated yield) elimination side product (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene **4.10b** (*E:Z* > 99:1).

Spectroscopic data for *syn:anti*-**4.4b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.82 – 5.60 (m, 4H), 5.06 – 4.95 (m, 6H), 4.90 (dt, *J* = 17.2, 1.7 Hz, 1H), 4.85 (dt, *J* = 10.6, 1.6 Hz, 1H), 4.42 (dd, *J* = 7.6, 5.9 Hz, 1H), 4.35 (t, *J* = 6.1 Hz, 1H), 3.80 (dt, *J* = 7.2, 1.5 Hz, 1H), 3.38 (dt, *J* = 7.5, 1.3 Hz, 1H), 2.56 – 2.46 (m, 2H), 2.40 (dddt, *J* = 14.3, 7.3, 6.2, 1.2 Hz, 1H), 2.36 – 2.28 (m, 1H), 0.06 (s, 9H), -0.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.1, 140.9, 137.6, 137.3, 134.9, 134.3, 133.0, 132.5, 128.7, 128.3, 128.0, 127.9, 117.2, 116.8, 113.1, 112.1, 80.3, 78.5, 75.9, 73.1, 42.9, 41.3, -3.8, -4.0. ***Syn*-4.4b** and ***anti*-4.4b** are known compounds and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for **4.10b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.76 (ddd, *J* = 15.2, 10.2, 0.9 Hz, 1H), 6.55 – 6.46 (m, 2H), 5.36 (dd, *J* = 16.4, 1.6 Hz, 1H), 5.24 – 5.19 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 136.8, 135.6, 133.1, 131.4, 130.1, 128.7, 127.5, 118.2. **4.10b** is a known compound and spectroscopic data are in agreement with those reported in literature.[64]

Synthesis of *syn/anti*-(1-((1-(4-trifluromethylphenyl)but-3-en-1-yl)oxy)allyl) trimethylsilane (*syn/anti*-4.4c)



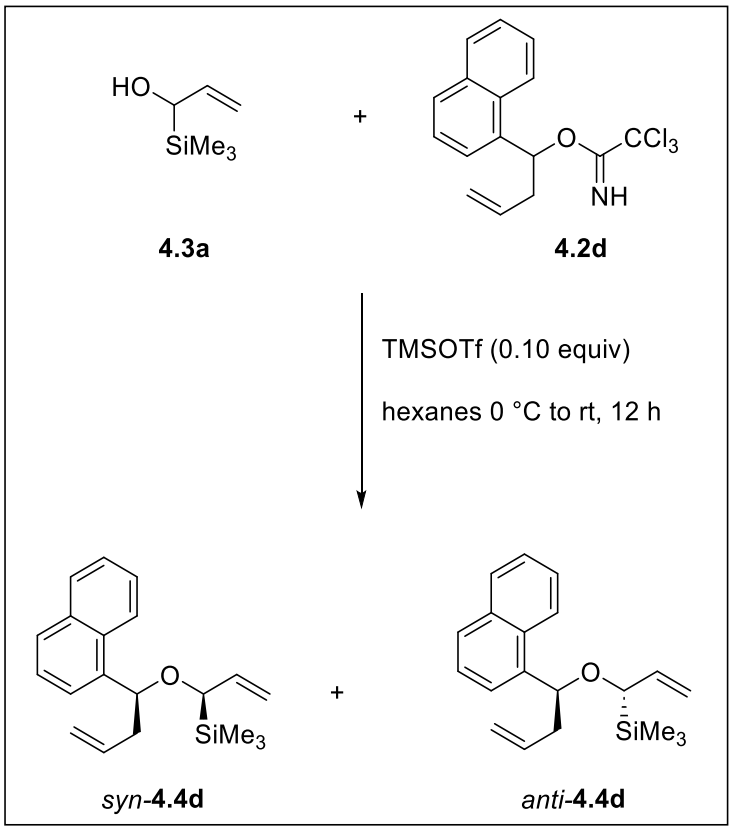
Compound **4.4c** was prepared following general procedure E with slight modification to minimize formation of the side product as a result of elimination. A solution of 1-(trimethylsilyl)prop-2-en-1-ol **4.3a** (2.61 g, 20 mmol, 1 equiv.) and 1-(4-trifluoromethylphenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2c** (10.1 g, 28 mmol, 1.4 equiv.) in dichloromethane (100 mL) was cooled to −78 °C. TMSOTf (0.36 mL, 2.0 mmol, 0.1 equiv.) was added dropwise and the mixture stirred at –78 °C for 6 hours. The rubber septum was removed and 7 g of sodium bicarbonate was poured into the flask. The dry ice-acetone bath was removed and the mixture was allowed to warm up to room temperature. The mixture was filtered and concentrated under reduced pressure to remove dichloromethane. Hexanes was then added to the resulting mixture resulting in the formation of white precipitate. Subsequent filtration and concentration furnished a residue which was purified by column chromatography, R_f for **4.10c** = 0.7 and R_f for *syn/anti*-**4.4c** = 0.5 (100% hexanes) to afford 2.2 g, 6.6 mmol (33% isolated yield) inseparable mixture of diastereomers of compound **4.4c** (*syn:anti* = 1:1) as colorless liquid and

1.72 g, 8.7 mmol (31% isolated yield based on the starting trichloroacetimidate) elimination side product (*E*)-1-(buta-1,3-dien-1-yl)-4-trifluoromethylbenzene **4.10c** (*E:Z* > 99:1).

Spectroscopic data for *syn:anti*-**4.4c:** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.59 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.83 – 5.61 (m, 4H), 5.06 (ddd, *J* = 10.6, 2.0, 1.2 Hz, 1H), 5.03 – 4.96 (m, 5H), 4.91 (dt, *J* = 17.2, 1.8 Hz, 1H), 4.87 (ddd, *J* = 10.6, 2.0, 1.4 Hz, 1H), 4.52 (dd, *J* = 7.6, 5.8 Hz, 1H), 4.45 (t, *J* = 6.0 Hz, 1H), 3.83 (dt, *J* = 7.3, 1.5 Hz, 1H), 3.39 (dt, *J* = 7.6, 1.3 Hz, 1H), 2.57 – 2.48 (m, 2H), 2.48 – 2.41 (m, 1H), 2.35 (dddt, *J* = 14.1, 7.1, 5.8, 1.2 Hz, 1H), 0.08 (s, 9H), 0.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.69 (d, *J* = 1.2 Hz), 146.65 (d, *J* = 1.2 Hz), 137.5, 137.2, 134.6, 134.0, 130.0 –128.7 (m, 2C), 127.7 –123.2 (m, 2C), 127.5, 126.7, 125.12 (q, *J* = 3.8 Hz), 124.85 (q, *J* = 3.8 Hz), 117.5, 117.0, 113.3, 112.4, 80.2, 78.7, 76.1, 73.5, 42.9, 41.2, –3.8, –4.0. ***Syn*-4.4c** and ***anti*-4.4c** are known compounds and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for **4.10c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 6.87 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.62 – 6.49 (m, 2H), 5.42 (d, *J* = 16.9 Hz, 1H), 5.28 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 140.58 (q, *J* = 1.3 Hz), 136.7, 132.0, 131.2, 129.25 (q, *J* = 32.4 Hz), 126.5, 125.55 (q, *J* = 3.9 Hz), 124.21 (q, *J* = 271.7 Hz), 119.4. **4.10c** is a known compound and spectroscopic data were in agreement with those reported in literature.[65]

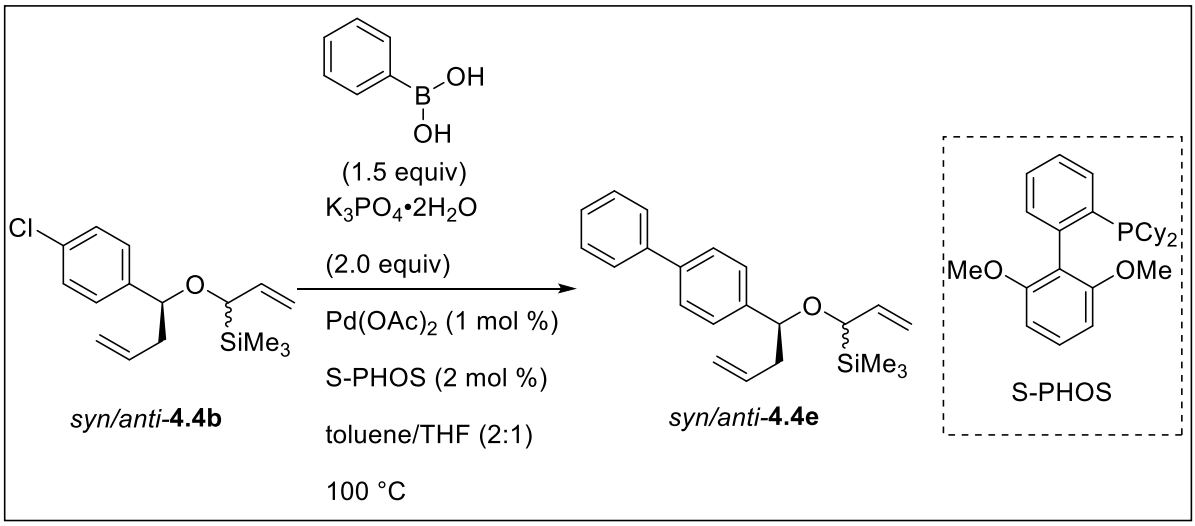
Synthesis of *syn/anti*-trimethyl(1-((1-(naphthalen-1-yl)but-3-en-1-yl)oxy)allyl)silane (*syn/anti*-4.4d)



Compound **4.4d** was prepared following general procedure E, a solution of 1-(trimethylsilyl)prop-2-en-1-ol **4.3a** (2.61 g, 20 mmol, 1 equiv.) and 1-(naphthalen-1-yl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2d** (9.6 g, 28 mmol, 1.4 equiv.), TMSOTf (0.36 mL, 2.0 mmol, 0.1 equiv.) and hexanes (50 mL) for 12 hour followed by workup, concentration and column chromatography, R_f for *syn/anti*-**4.4d** = 0.6 (10% DCM in hexanes) afforded 2.11 g, 6.8 mmol (34% isolated yield) inseparable mixture of diastereomers of compound **4.4d** (*syn:anti* = 1:1) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 6.8 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.57 – 7.46 (m, 7H), 5.94 (ddt, *J* = 17.4, 10.4, 7.2 Hz, 1H), 5.89 – 5.80 (m, 2H), 5.69 (ddd, *J* = 17.6, 10.5, 7.4 Hz, 1H), 5.31 – 5.23 (m, 1H), 5.14 (t, *J* = 6.0 Hz, 1H), 5.12 – 4.96 (m, 7H), 4.93

(dt, *J* = 17.2, 1.7 Hz, 1H), 4.80 (dt, *J* = 10.5, 1.6 Hz, 1H), 3.95 (dt, *J* = 7.4, 1.4 Hz, 1H), 3.52 (dt, *J* = 7.8, 1.3 Hz, 1H), 2.78 – 2.64 (m, 3H), 2.60 (dddt, *J* = 14.0, 7.4, 5.1, 1.2 Hz, 1H), 0.13 (s, 9H), 0.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.5, 137.8, 137.7, 135.7, 135.2, 133.8, 133.7, 131.5, 130.4, 128.8, 128.7, 127.7, 127.3, 125.6, 125.5, 125.4, 125.29, 125.28, 125.1, 124.3, 123.7, 116.7, 116.3, 113.6, 112.2, 78.8, 76.6, 73.4, 42.4, 41.3, -3.7, -3.9. IR (FTIR, cm^{-1}) $\tilde{\nu}$ = 3072, 3050, 2955, 2899, 1639, 1626, 1509, 1413, 1246, 909, 837, 775. HRMS (ESI), *m/z* $[M + H]^+$ calcd for $C_{20}H_{27}OSi$: 311.1826; found: 311.1837.

Synthesis of *syn/anti*-(1-((1-([1,1'-biphenyl]-4-yl)but-3-en-1-yl)oxy)allyl)trimethylsilane (*syn/anti*-4.4e)



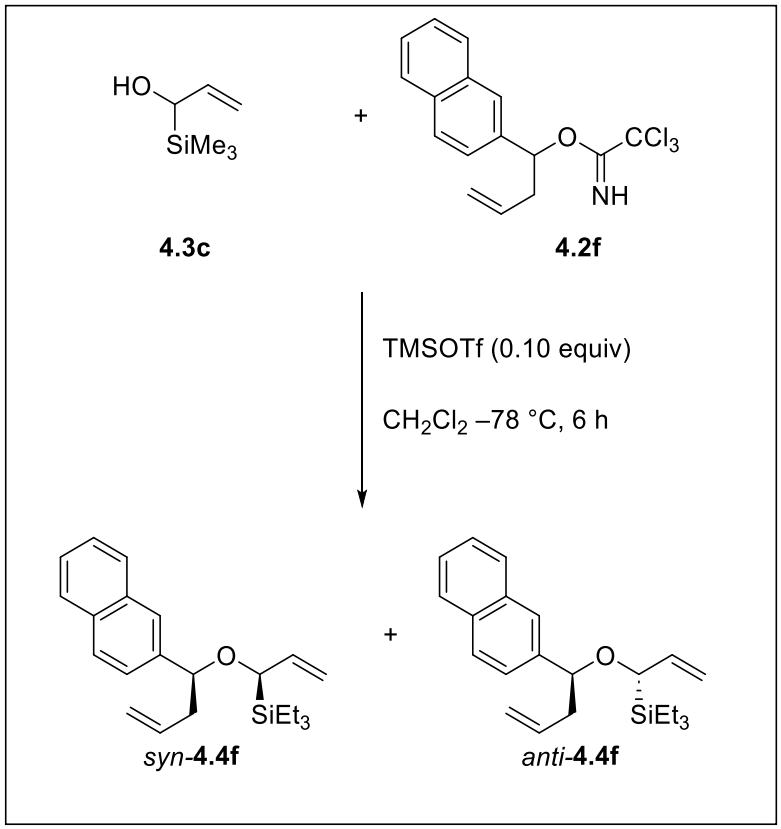
Compound **4.4e** was prepared as per the following procedure: A mixture of *syn/anti*-**4.4b** (*dr* = 1:1) (390 mg, 1.3 mmol, 1.0 equiv), phenylboronic acid (240 mg, 1.97 mmol, 1.5 equiv) and $K_3PO_4.2H_2O$ (652 mg, 2.6 mmol, 2.0 equiv) in toluene (2 mL) was degassed (3-freeze-pump-thaw actions) and then a solution of $Pd(OAc)_2$ (3 mg, 0.013 mmol, 0.01 equiv) and S-PHOS (10.8 mg, 0.026 mmol, 0.02 equiv) in THF (1 mL) was added resulting In formation of red solution. The resulting mixture was heated in an oil bath at 100 °C for 4.5 hours. The reaction mixture was concentrated and the residue subjected to column chromatography to give a total of 161 mg, 0.478

mmol (37% isolated yield) of partially separable mixture of diastereomers. R_f value for *syn*-**4.4e** = 0.36 and R_f value for *trans*-**4.4e** = 0.40.

Spectroscopic data for *syn*-**S4-e**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.62 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.33 (m, 1H), 5.84 – 5.69 (m, 2H), 5.09 – 5.01 (m, 2H), 4.98 (dt, *J* = 17.2, 1.8 Hz, 1H), 4.90 (dt, *J* = 10.6, 1.7 Hz, 1H), 4.47 (t, *J* = 6.1 Hz, 1H), 3.87 (dt, *J* = 7.1, 1.5 Hz, 1H), 2.62 – 2.55 (m, 1H), 2.55 – 2.47 (m, 1H), 0.11 (s, 9H). ^{13}C -NMR (151 MHz, $CDCl_3$) δ = 142.7, 141.1, 139.7, 137.9, 134.8, 128.7, 127.0, 127.0, 127.0, 126.6, 117.0, 112.0, 80.6, 75.7, 41.4, -3.7. *Syn*-**4.4e** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for *anti*-**4.4e**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.32 (m, 3H), 5.87 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.79 (ddd, *J* = 17.5, 10.6, 7.4 Hz, 1H), 5.10 – 5.00 (m, 4H), 4.52 (dd, *J* = 7.8, 5.7 Hz, 1H), 3.52 (d, *J* = 7.4 Hz, 1H), 2.63 – 2.56 (m, 1H), 2.45 – 2.38 (m, 1H), 0.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 141.6, 141.0, 140.2, 137.6, 135.4, 128.7, 127.7, 127.2, 127.0, 126.8, 116.5, 112.9, 78.9, 72.9, 43.07, -4.0. *Trans*-**S4-e** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *syn/anti*-triethyl(1-((1-(naphthalen-2-yl)but-3-en-1-yl)oxy)allyl)silane (*syn/anti*-4.4f)



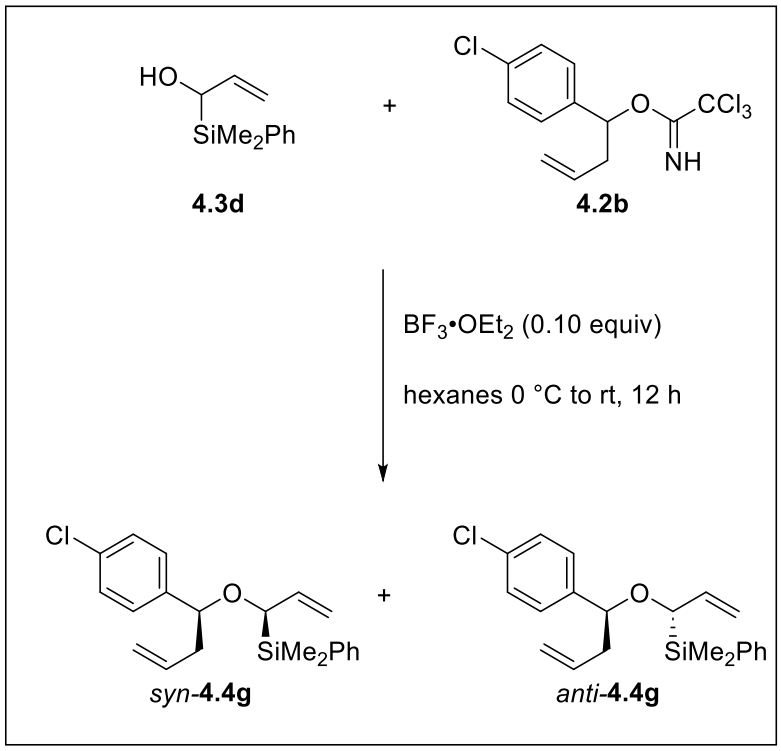
Compound **4.4f** was prepared following general procedure E with slight modification to minimize formation of the side product as a result of elimination. A solution of 1-(triethylsilyl)prop-2-en-1-ol **4.3c** (2.59 g, 15 mmol, 1 equiv.) and 1-(naphthalen-2-yl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2f** (6.17 g, 18 mmol, 1.2 equiv.) in dichloromethane (120 mL) was cooled to −78 °C. TMSOTf (0.28 mL, 1.5 mmol, 0.1 equiv.) was added dropwise and the mixture stirred at –78 °C for 6 hours. The rubber septum was removed and 7 g of sodium bicarbonate was poured into the flask. The dry ice-acetone bath was removed and the mixture was allowed to warm up to room temperature. The mixture was filtered and concentrated under reduced pressure to remove dichloromethane. Hexanes was then added to the resulting mixture resulting in the formation of white precipitate. Subsequent filtration and concentration furnished a residue which

was purified by column chromatography, R_f for *anti*-**4.4f** = 0.6 and R_f for *syn*-**4.4f** = 0.4 (10% DCM in hexanes) to afford a total of 2.48 g, 7.1 mmol (47% isolated yield) of partially separable mixture of diastereomers of compound **4.4f** (*syn:anti* = 1:1) as colorless liquid

Spectroscopic data for *syn*-**4.4f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86 – 7.79 (m, 3H), 7.74 (s, 1H), 7.51 – 7.43 (m, 3H), 5.80 – 5.68 (m, 2H), 5.05 – 4.93 (m, 3H), 4.82 (dt, *J* = 10.5, 1.6 Hz, 1H), 4.55 (t, *J* = 6.2 Hz, 1H), 4.08 (dt, *J* = 7.4, 1.5 Hz, 1H), 2.65 (dddt, *J* = 14.4, 7.3, 6.0, 1.3 Hz, 1H), 2.58 – 2.48 (m, 1H), 1.04 (t, *J* = 7.9 Hz, 9H), 0.68 (qd, *J* = 7.9, 2.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.2, 138.3, 134.7, 133.1, 132.7, 127.9, 127.6, 127.5, 125.7, 125.4, 125.3, 125.0, 116.9, 111.9, 81.2, 74.5, 41.4, 7.5, 1.8. *Syn*-**4.4f** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for *anti*-**4.4f**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.88 – 7.81 (m, 3H), 7.67 (s, 1H), 7.52 – 7.44 (m, 3H), 5.91 – 5.78 (m, 2H), 5.10 – 4.97 (m, 4H), 4.63 (dd, *J* = 7.8, 5.7 Hz, 1H), 3.62 (dt, *J* = 7.7, 1.4 Hz, 1H), 2.64 (dddt, *J* = 14.1, 8.0, 6.8, 1.3 Hz, 1H), 2.45 (dddt, *J* = 14.2, 7.1, 5.7, 1.2 Hz, 1H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.59 (qd, *J* = 7.9, 3.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.7, 137.9, 135.4, 133.10, 133.05, 128.0, 127.8, 127.7, 126.6, 125.9, 125.6, 125.1, 116.5, 112.9, 79.1, 71.5, 42.9, 7.4, 1.6. *Anti*-**4.4c** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *syn/anti*-(1-((1-(4-chlorophenyl)but-3-en-1-yl)oxy)allyl) dimethyl(phenyl)silane (*syn/anti*-S4-g)

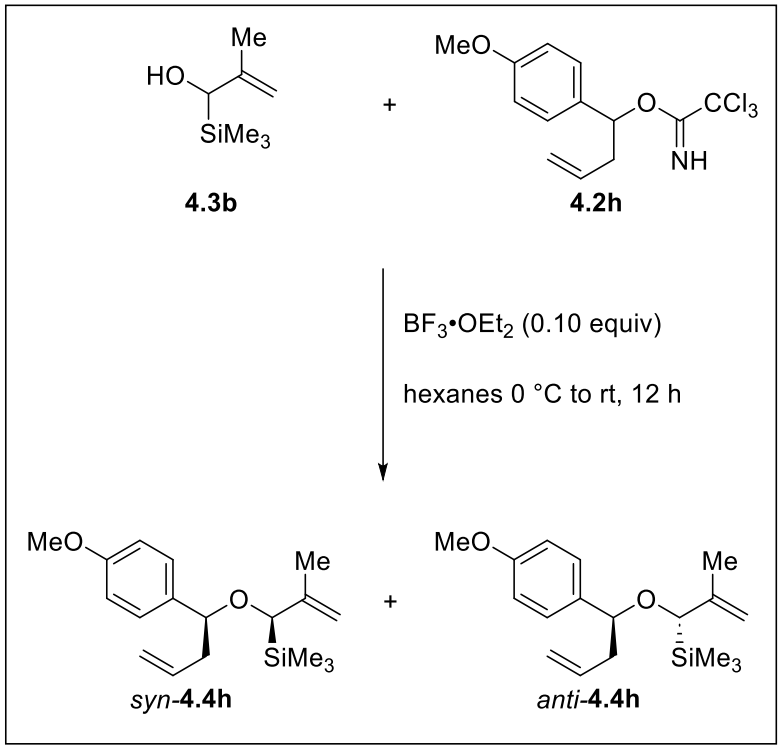


Compound **4.4c** was prepared following general procedure E, a solution of 1-(dimethyl(phenyl)silyl)prop-2-en-1-ol **4.3d** (2.40 g, 13.5 mmol, 1 equiv.) and 1-(4-chlorophenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2b** (6.18 g, 18.9 mmol, 1.4 equiv.), BF_3•OEt_2 (0.17 mL, 1.35 mmol, 0.1 equiv.) and hexanes (80 mL) for 12 hour followed by workup, concentration and column chromatography, R_f for *syn/anti*-**4.4g** = 0.6 (20% DCM in hexanes) afforded a total of 3.76 g, 10.5 mmol (78% isolated yield) inseparable mixture of diastereomers of compound **4.4g** (*syn:anti* = 1:1) as colorless liquid.

Spectroscopic data for *syn/anti*-**4.4g**: ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ = 7.64 – 7.58 (m, 2H), 7.53 (dt, *J* = 6.5, 1.6 Hz, 2H), 7.43 – 7.33 (m, 6H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.16 (m, 4H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.82 – 5.53 (m, 5H), 5.05 (dt, *J* = 10.6, 1.4 Hz, 1H), 5.03 – 4.88 (m, 6H), 4.86 (dt, *J* = 10.6, 1.7 Hz, 1H), 4.43 (dd, *J* = 7.6, 5.8 Hz, 1H), 4.28 (t, *J* = 6.1 Hz, 1H), 3.99

(dt, *J* = 7.0, 1.5 Hz, 1H), 3.58 (dt, *J* = 7.4, 1.3 Hz, 1H), 2.54 – 2.41 (m, 2H), 2.39 – 2.28 (m, 2H), 0.39 (s, 3H), 0.35 (s, 3H), 0.32 (s, 3H), 0.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.8, 140.5, 137.2, 136.8, 136.7, 136.6, 134.8, 134.4, 134.3, 134.2, 132.8, 132.5, 129.23, 129.15, 128.6, 128.21, 128.00, 127.95, 127.6, 127.5, 117.2, 116.8, 113.7, 112.6, 80.4, 78.5, 75.4, 72.7, 42.9, 41.3, -5.28, -5.31, -5.7, -6.3. **4.4g** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *syn/anti*-(1-((1-(4-methoxyphenyl)but-3-en-1-yl)oxy)-2-methylallyl)trimethyl silane (*syn/anti*-4.4h)



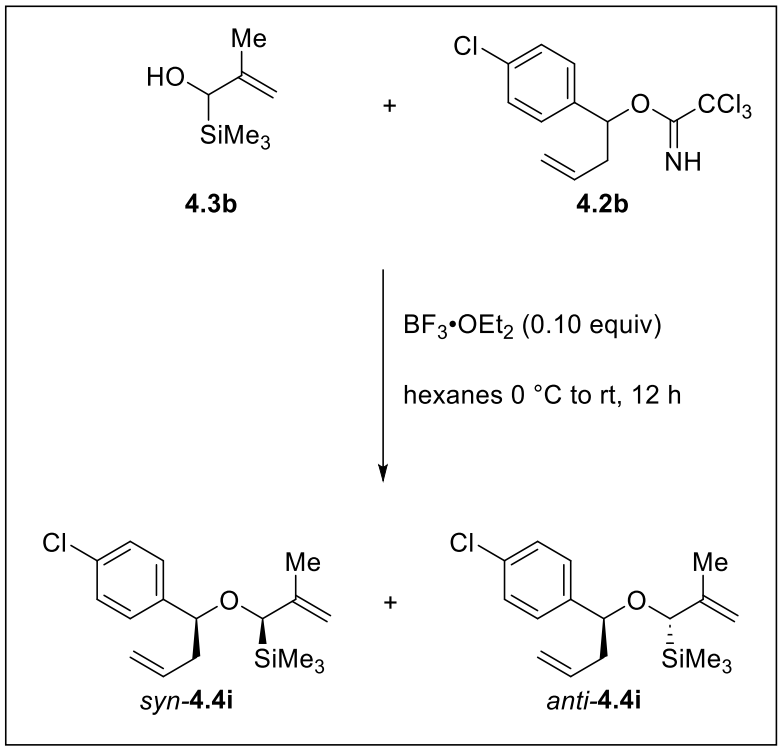
Compound **4.4h** was prepared following general procedure E, a solution of 2-methyl-1-(trimethylsilyl)prop-2-en-1-ol **4.3b** (1.44 g, 10 mmol, 1 equiv.) and 1-(4-methoxyphenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2h** (4.84 g, 15 mmol, 1.5 equiv.), BF_3•OEt_2 (0.12 mL, 1.0 mmol, 0.1 equiv.) and hexanes (80 mL) for 12 hour followed by workup, concentration and column chromatography, R_f for *anti*-**4.4h** = 0.7 and R_f for *syn*-**4.4h** = 0.6 (15% DCM in hexanes) afforded

a total of 1.15 g, 3.8 mmol (38% isolated yield) partially separable mixture of diastereomers of compound **4.4h** as colorless liquid.

Spectroscopic data for *syn*-**4.4h**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.68 (ddt, *J* = 17.3, 10.3, 7.0 Hz, 1H), 5.01 – 4.94 (m, 2H), 4.68 (ddt, *J* = 7.9, 2.2, 1.1 Hz, 2H), 4.28 (t, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 1H), 2.59 – 2.49 (m, 1H), 2.49 – 2.41 (m, 1H), 1.53 (t, *J* = 1.1 Hz, 3H), 0.08 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.4, 145.1, 135.5, 134.8, 127.7, 116.8, 113.1, 109.3, 79.7, 77.6, 55.1, 40.5, 20.3, -3.0. *Syn*-**4.4h** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for *anti*-**4.4h**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.80 (ddt, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.03 – 4.94 (m, 2H), 4.81 (dq, *J* = 2.8, 1.5 Hz, 1H), 4.68 (dt, *J* = 2.2, 1.0 Hz, 1H), 4.25 (dd, *J* = 7.7, 6.0 Hz, 1H), 3.82 (s, 3H), 3.31 (s, 1H), 2.54 (dddt, *J* = 13.8, 7.9, 6.8, 1.2 Hz, 1H), 2.34 (dddt, *J* = 13.7, 7.3, 6.1, 1.2 Hz, 1H), 1.68 – 1.61 (m, 3H), -0.01 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.9, 144.4, 135.7, 134.3, 128.6, 116.3, 113.4, 109.8, 78.4, 75.0, 55.1, 43.0, 20.4, -3.2. *Anti*-**4.4h** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

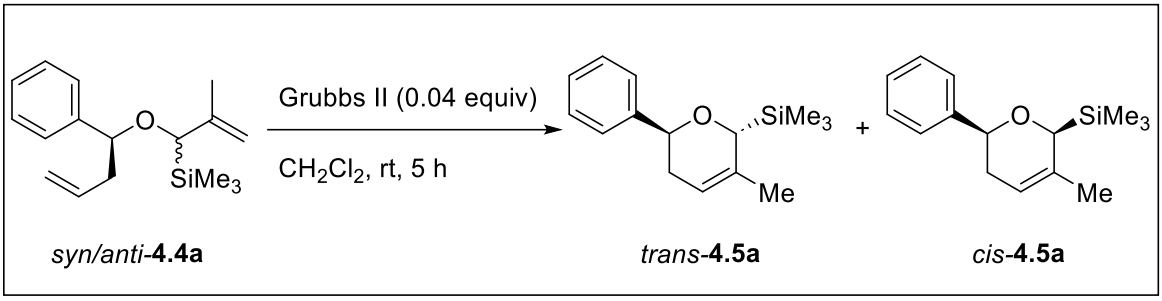
Synthesis of *syn/anti*-(1-((1-(4-chlorophenyl)but-3-en-1-yl)oxy)-2-methylallyl)trimethyl silane (*syn/anti*-S4-i)



Compound **4.4i** was prepared following general procedure E, a solution of 2-methyl-1-(trimethylsilyl)prop-2-en-1-ol **4.3b** (1.44 g, 10 mmol, 1 equiv.) and 1-(4-chlorophenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate **4.2b** (4.58 g, 14 mmol, 1.4 equiv.), BF_3•OEt_2 (0.12 mL, 1.0 mmol, 0.1 equiv.) and hexanes (60 mL) for 12 hour followed by workup, concentration and column chromatography, R_f for *anti*/*syn*-**4.4i** = 0.4 (100% hexanes) afforded a total of 1.80 g, 5.8 mmol (58% isolated yield) inseparable mixture of diastereomers of compound **4.4i** as colorless liquid. Spectroscopic data for *syn/anti*-**4.4i**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.79 (ddtd, *J* = 14.3, 10.6, 7.1, 2.4 Hz, 1H), 5.66 (ddt, *J* = 16.5, 10.7, 7.1 Hz, 1H), 5.19 – 5.12 (m, 1H), 5.03 – 4.95 (m, 4H), 4.84 (dq, *J* = 2.8, 1.5 Hz, 1H), 4.72 (qd, *J* = 1.6, 0.9 Hz, 1H), 4.68 (ddq, *J* = 4.2, 2.1, 0.9 Hz, 2H), 4.36 – 4.27 (m, 2H), 3.79 (s, 1H), 3.30 (s, 1H), 2.57 – 2.50 (m, 2H), 2.50 – 2.42 (m, 1H), 2.35

(dddt, J = 13.8, 7.3, 6.1, 1.2 Hz, 1H), 1.66 (s, 3H), 1.54 (s, 3H), 0.10 (s, 9H), 0.02 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 144.7, 144.1, 141.8, 140.8, 135.0, 134.0, 133.0, 132.4, 128.9, 128.3, 128.0, 127.9, 117.3, 116.8, 110.1, 109.7, 79.2, 78.3, 77.9, 75.6, 42.9, 40.3, 20.4, 20.3, -3.0, -3.2. MS (GC/MS): m/z (%) = 308 (0.02) $[M]^+$, 143 (33), 141 (100), 113 (25), 77 (65).

Synthesis of *cis/trans*-trimethyl(3-methyl-6-phenyl-5,6-dihydro-*2H*-pyran-2-yl)silane (*cis/trans*-4.5a)



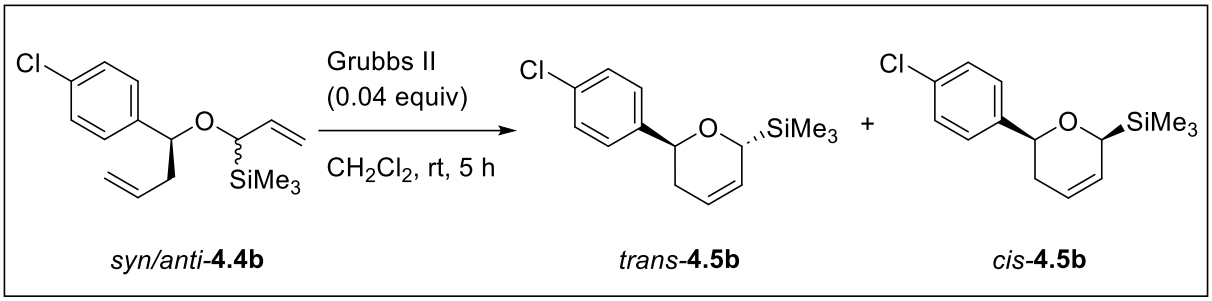
Compound **4.5a** was prepared following general procedure F: Grubbs catalyst 2nd generation (37 mg, 0.043 mmol, 0.04 equiv.) and *syn/anti*-trimethyl(2-methyl-1-((1-phenylbut-3-en-1-yl)oxy)allyl)silane, *syn:anti* = 1:2, **4.4a** (297 mg, 1.08 mmol, 1 equiv.) and dichloromethane (11 mL) for 5 hours followed by concentration and column chromatography, R_f for *cis*-**4.5a** = 0.7 and R_f for *trans*-**4.5b** = 0.4 (10% and 30% DCM in hexanes) afforded a total of 248 mg, 1.00 mmol (93% isolated yield) fully separable mixture of diastereomers of compound **4.5a** as colorless liquid.

Spectroscopic data for *cis*-**4.5a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.40 – 7.31 (m, 4H), 7.29 – 7.24 (m, 1H), 5.52 – 5.47 (m, 1H), 4.56 (dd, J = 8.0, 5.2 Hz, 1H), 4.06 – 4.01 (m, 1H), 2.40 – 2.27 (m, 2H), 1.66 (dt, J = 2.6, 1.3 Hz, 3H), 0.16 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 144.0, 135.3, 128.1, 126.8, 125.6, 117.0, 74.9, 74.3, 34.2, 20.0, -2.6. *Cis*-**4.5a** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for *trans*-**4.5a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 – 7.27 (m, 5H), 5.52 – 5.45 (m, 1H), 4.55 (dd, J = 8.0, 5.3 Hz, 1H), 4.03 (d, J = 2.8 Hz, 1H), 2.36 – 2.30 (m, 2H), 1.67

– 1.64 (m, 3H), 0.16 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.7, 135.4, 128.2, 127.2, 126.0, 115.8, 75.0, 72.9, 32.1, 20.4, -1.4. HRMS (ESI), *m/z* $[M - H^-]^+$ calcd for $C_{15}H_{21}OSi$: 245.1362; found: 245.1353.

Synthesis of *cis/trans*-(6-(4-chlorophenyl)-5,6-dihydro-*2H*-pyran-2-yl)trimethylsilane (*cis/trans*-4.5b)



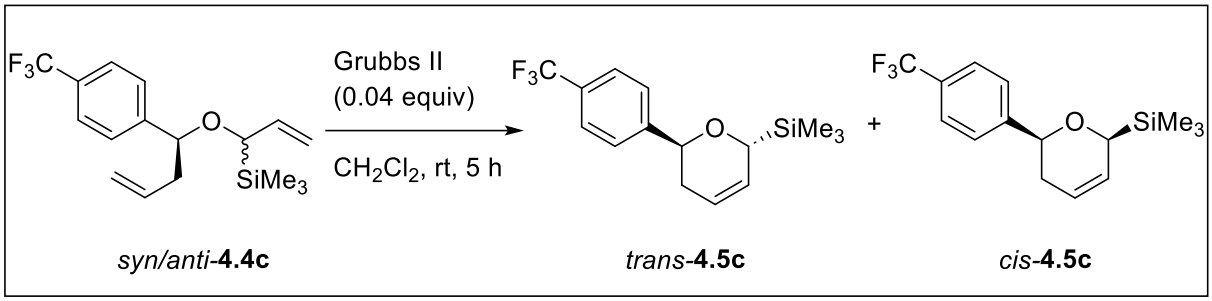
Compound **4.5b** was prepared following general procedure F: Grubbs catalyst 2nd generation (170 mg, 0.2 mmol, 0.04 equiv.) and *syn/anti*-(1-((1-(4-chlorophenyl)but-3-en-1-yl)oxy)allyl)trimethylsilane, *syn:anti* = 1:1, **4.4b** (1.47 g, 5 mmol, 1 equiv.) and dichloromethane (100 mL) for 12 hours followed by concentration and column chromatography, R_f for *cis*-**4.5b** = 0.7 and R_f for *trans*-**4.5b** = 0.4 (10% and 30% DCM in hexanes) afforded a total of 1.16 g, 4.35 mmol (87% isolated yield) fully separable mixture of diastereomers of compound **4.5b** as colorless liquid.

Spectroscopic data for *cis*-**4.5b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36 – 7.27 (m, 4H), 5.85 – 5.77 (m, 2H), 4.38 (dd, *J* = 10.1, 3.1 Hz, 1H), 4.18 (dddd, *J* = 5.0, 3.6, 2.2, 1.5 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.17 – 2.08 (m, 1H), 0.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$,) δ = 142.5, 132.6, 128.3, 128.1, 127.0, 120.4, 74.7, 71.7, 34.0, -4.0. *Cis*-**4.5b** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for *trans*-**4.5b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 – 7.29 (m, 4H), 5.85 – 5.76 (m, 2H), 4.72 (dd, *J* = 6.4, 4.5 Hz, 1H), 4.01 – 3.97 (m, 1H), 2.47 – 2.40 (m, 1H), 2.39 –

2.32 (m, 1H), 0.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 140.5, 132.9, 128.3, 128.2, 128.0, 119.7, 71.6, 69.7, 29.9, -3.1. *Trans*-**4.5b** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *cis/trans*-(6-(4-trifluoromethylphenyl)-5,6-dihydro-2H-pyran-2-yl)trimethyl silane (*cis/trans*-4.5c)

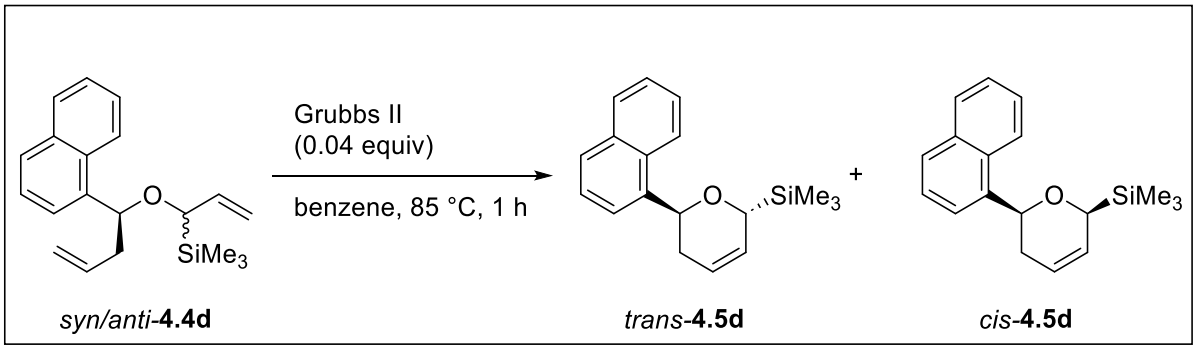


Compound **4.5c** was prepared following general procedure F: Grubbs catalyst 2nd generation (204 mg, 0.24 mmol, 0.04 equiv.) and *syn/anti*-(1-((1-(4-trifluorophenyl)but-3-en-1-yl)oxy)allyl)trimethylsilane, *syn:anti* = 1:1, **4.4c** (1.97 g, 6 mmol, 1 equiv.) and dichloromethane (100 mL) for 12 hours followed by concentration and column chromatography, R_f for *cis*-**4.5c** = 0.7 and R_f for *trans*-**4.5c** = 0.4 (10% and 30% DCM in hexanes) afforded a total of 1.74 g, 1.89 mmol (96% isolated yield) fully separable mixture of diastereomers of compound **4.5c** as colorless liquids. Spectroscopic data for *cis*-**4.5c**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 5.89 – 5.78 (m, 2H), 4.47 (dd, *J* = 10.3, 3.1 Hz, 1H), 4.20 (dddd, *J* = 5.0, 3.5, 2.3, 1.6 Hz, 1H), 2.31 – 2.24 (m, 1H), 2.19 – 2.11 (m, 1H), 0.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 148.0 (t, *J* = 1.4 Hz), 129.2 (q, *J* = 32.1 Hz), 128.1, 125.9, 125.1 (q, *J* = 3.8 Hz), 120.7,74.8, 71.7, 34.0, -4.0. *Cis*-**4.5c** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for *trans*-**4.5c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 5.87 – 5.78 (m, 2H), 4.80 (dd, *J* = 6.6, 4.5 Hz, 1H), 4.04 (dddd, *J* = 3.4,

2.6, 1.8, 0.6 Hz, 1H), 2.52 – 2.45 (m, 1H), 2.43 – 2.35 (m, 1H), 0.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.2 (d, *J* = 1.5 Hz), 129.4, (q, *J* = 32.2 Hz), 128.3, 126.8, 125.15 (q, *J* = 3.8 Hz), 119.6,71.7, 70.0, 30.1, -3.1. *Trans*-**4.5c** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *cis/trans*-trimethyl(6-(naphthalen-1-yl)-5,6-dihydro-*2H*-pyran-2-yl)silane (*cis/trans*-4.5d)



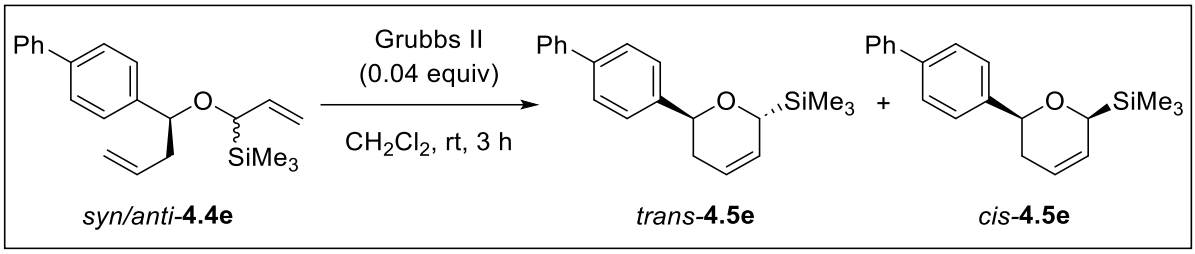
Compound **4.5d** was prepared following general procedure F: Grubbs catalyst 2nd generation (204 mg, 0.24 mmol, 0.04 equiv.) and *syn/anti*-trimethyl(1-((1-(naphthalen-1-yl)but-3-en-1-yl)oxy)allyl)silane, *syn:anti* = 1:1, **4.4d** (1.9 g, 6 mmol, 1 equiv.) and benzene (100 mL) at 85 °C for 1 hour followed by concentration and column chromatography, R_f for *cis*-**4.5d** = 0.7 and R_f for *trans*-**4.5d** = 0.4 (20% DCM in hexanes) afforded a total of 1.66 g, 5.88 mmol (98% isolated yield) fully separable mixture of diastereomers of compound **4.5d** as colorless liquid.

Spectroscopic data for *cis*-**4.5d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7 8.11 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 9.4 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.50 (tddd, *J* = 10.2, 8.4, 3.8, 2.3 Hz, 3H), 5.97 – 5.85 (m, 2H), 5.13 (dd, *J* = 9.9, 3.3 Hz, 1H), 4.33 (tdd, *J* = 4.0, 2.3, 1.2 Hz, 1H), 2.52 – 2.36 (m, 2H), 0.17 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.6, 133.6, 130.6, 128.7, 128.0, 127.5, 125.59, 125.56, 125.2, 123.7, 123.0, 121.5, 73.5, 72.0, 33.4, -3.9. IR (FTIR, cm^{-1}) ṽ = 3049, 3027, 2954, 2897, 1510, 1385, 1336, 1245, 1061, 837, 773. MS (GC/MS): *m*/z (%) = 282 (5) $[M]^+$, 281 (7.5) $[M - H]^+$, 192 (32), 191 (21), 141 (17.5), 73 (100). HRMS

(ESI), *m/z* $[M - H^-]^+$ calcd for $C_{18}H_{21}OSi$: 281.1362; found: 281.1360.

Spectroscopic data for *trans*-**4.5d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.33 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.48 – 7.43 (m, 1H), 5.95 (dq, *J* = 10.6, 3.8 Hz, 1H), 5.84 (dq, *J* = 10.3, 2.0 Hz, 1H), 5.55 (t, *J* = 5.1 Hz, 1H), 3.78 (p, *J* = 3.2 Hz, 1H), 2.72 (ddtd, *J* = 17.6, 5.3, 3.5, 1.9 Hz, 1H), 2.61 – 2.52 (m, 1H), 0.09 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 136.7, 133.9, 131.7, 128.6, 128.3, 128.1, 125.8, 125.4, 125.0, 124.5, 124.4, 120.4, 70.0, 68.3, 29.7, -3.3. IR (FTIR, cm^{-1}) ṽ = 3050, 3027, 2953, 2898, 1509, 1336, 1245, 1048, 838, 774. HRMS (ESI), *m/z* $[M + H]^+$ calcd for $C_{18}H_{23}OSi$: 283.1518; found: 283.1518.

Synthesis of *cis/trans*-(6-([1,1'-biphenyl]-4-yl)-5,6-dihydro-2H-pyran-2-yl)trimethylsilane (*cis/trans*-4.5e)



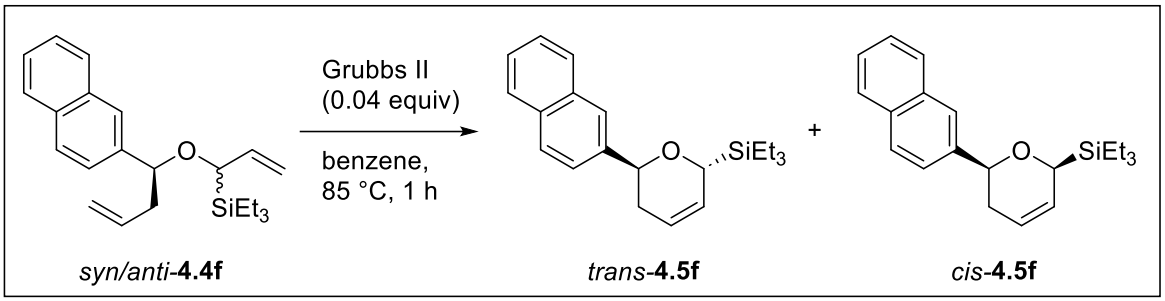
Compound **4.5e** was prepared following general procedure F: Grubbs catalyst 2nd generation (16 mg, 0.02 mmol, 0.04 equiv.) and *syn/anti*-(1-((1-([1,1'-biphenyl]-4-yl)but-3-en-1-yl)oxy)allyl)trimethylsilane, *syn:anti* = 2:1, **4.4e** (161 mg, 0.48 mmol, 1 equiv.) and CH_2Cl_2 (5 mL) at room temperature for 3 hours followed by concentration and column chromatography, R_f for *cis*-**4.5e** = 0.7 and R_f for *trans*-**4.5e** = 0.4 (25% DCM in hexanes) afforded a total of 92 mg, 0.30 mmol (63% isolated yield) fully separable mixture of diastereomers of compound **4.5e** as colorless liquid.

Spectroscopic data for *cis*-**4.5e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 – 7.58 (m, 4H), 7.50 – 7.43 (m, 4H), 7.39 – 7.34 (m, 1H), 5.94 – 5.80 (m, 2H), 4.49 (dd, *J* = 9.8, 3.4 Hz, 1H), 4.24 (tdd,

J = 3.9, 2.2, 1.2 Hz, 1H), 2.36 – 2.22 (m, 2H), 0.16 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.1, 141.2, 139.9, 128.7, 128.1, 127.1, 127.1, 126.9, 126.1, 121.1, 75.2, 71.7, 34.1, -4.0. *Cis*-**4.5e** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for *trans*-**4.5e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.62 – 7.57 (m, 4H), 7.49 – 7.46 (m, 2H), 7.44 (dddd, *J* = 7.4, 6.1, 1.3, 0.6 Hz, 2H), 7.37 – 7.32 (m, 1H), 5.89 – 5.79 (m, 2H), 4.81 (t, *J* = 5.6 Hz, 1H), 4.08 (q, *J* = 2.9 Hz, 1H), 2.54 – 2.42 (m, 2H), 0.14 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.2, 141.0, 140.1, 128.7, 128.2, 127.2, 127.09, 127.05, 127.0, 120.0, 72.1, 70.0, 30.2, -2.9. *Trans*-**4.5e** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *cis/trans*-triethyl(6-(naphthalen-2-yl)-5,6-dihydro-*2H*-pyran-2-yl)silane (*cis/trans*-4.5f)



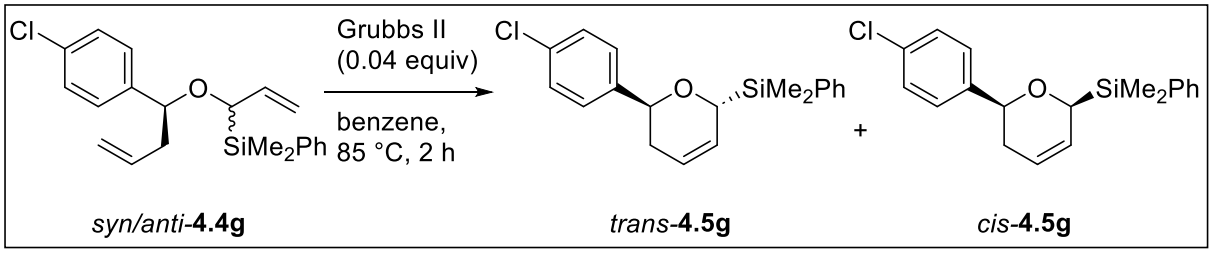
Compound **4.5f** was prepared following general procedure F: Grubbs catalyst 2nd generation (102 mg, 0.12 mmol, 0.04 equiv.) and *syn/anti*-triethyl(1-((1-(naphthalen-2-yl)but-3-en-1-yl)oxy)allyl)silane, *syn:anti* = 1:1, **4.4f** (1.06 g, 3 mmol, 1 equiv.) and benzene (100 mL) at 85 °C for 1 hour followed by concentration and column chromatography, R_f for *cis*-**4.5f** = 0.7 and R_f for *trans*-**4.5f** = 0.4 (10% and 20% DCM in hexanes) afforded a total of 883 mg, 2.52 mmol (84% isolated yield) fully separable mixture of diastereomers of compound **4.5f** as colorless liquid.

Spectroscopic data for *cis*-**4.5f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 – 7.82 (m, 3H), 7.81 (s,

1H), 7.51 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.49 – 7.42 (m, 2H), 5.94 – 5.87 (m, 1H), 5.82 (ddt, *J* = 10.4, 5.3, 2.6 Hz, 1H), 4.57 (dd, *J* = 9.0, 4.3 Hz, 1H), 4.41 (tdd, *J* = 4.3, 3.1, 2.2 Hz, 1H), 2.40 – 2.25 (m, 2H), 1.06 (t, *J* = 8.0 Hz, 9H), 0.72 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.5, 133.2, 132.7, 128.7, 128.0, 127.8, 127.6, 125.8, 125.5, 124.3, 124.1, 120.7, 75.9, 70.3, 34.0, 7.6, 1.9. *Cis*-**4.5f** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Spectroscopic data for *trans*-**4.5f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 – 7.83 (m, 3H), 7.82 (s, 1H), 7.56 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.51 – 7.44 (m, 2H), 5.88 – 5.79 (m, 2H), 4.94 (t, *J* = 5.3 Hz, 1H), 4.18 (td, *J* = 3.6, 1.8 Hz, 1H), 2.63 – 2.48 (m, 2H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.68 (qd, *J* = 8.0, 1.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.4, 133.2, 132.7, 129.0, 128.1, 127.8, 127.6, 125.8, 125.6, 125.3, 125.1, 119.4, 72.4, 67.6, 29.9, 7.5, 2.5. *Trans*-**4.5f** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *cis/trans*- (6-(4-chlorophenyl)-5,6-dihydro-*2H*-pyran-2-yl)dimethyl(phenyl) silane (*cis/trans*-4.5g)



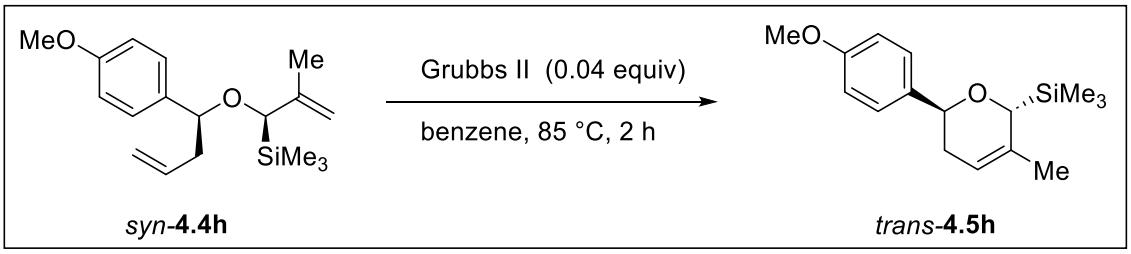
Compound **4.5g** was prepared following general procedure F: Grubbs catalyst 2nd generation (200 mg, 0.2 mmol, 0.026 equiv.) and *syn/anti*-(1-((1-(4-chlorophenyl)but-3-en-1-yl)oxy)allyl)dimethyl(phenyl)silane, *syn:anti* = 1:1, **4.4g** (3.21 g, 9 mmol, 1 equiv.) and benzene (200 mL) at 85 °C for 2 hours followed by concentration and column chromatography, R_f for *cis*-**4.5g** = 0.7 and R_f for *trans*-**4.5g** = 0.4 (30% DCM in hexanes) afforded a total of 2.96 g, 8.28 mmol (92% isolated yield) fully separable mixture of diastereomers of compound **4.5g** as colorless

liquids.

Spectroscopic data for *cis*-**4.5g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 – 7.61 (m, 2H), 7.44 – 7.36 (m, 3H), 7.36 – 7.32 (m, 2H), 7.32 – 7.29 (m, 2H), 5.81 (t, *J* = 1.9 Hz, 2H), 4.45 – 4.40 (m, 2H), 2.28 – 2.21 (m, 1H), 2.18 – 2.10 (m, 1H), 0.43 (s, 3H), 0.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.4, 136.5, 134.2, 132.6, 129.3, 128.3, 127.74, 127.71, 127.0, 121.3, 74.9, 71.3, 33.9, -5.2, -6.0. MS (GC/MS): *m*/z (%) = 328 (1.5) $[M]^+$, 250 (4), 135 (100), 107 (7), 75 (18). HRMS (ESI), *m/z* $[M - H^-]^+$ calcd for $C_{19}H_{20}ClOSi$: 327.0972; found: 327.0963.

Spectroscopic data for *trans*-**4.5g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.63 – 7.56 (m, 2H), 7.45 – 7.36 (m, 3H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.87 – 5.78 (m, 2H), 4.63 (t, *J* = 5.6 Hz, 1H), 4.30 – 4.24 (m, 1H), 2.42 – 2.29 (m, 2H), 0.44 (s, 3H), 0.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 140.4, 136.7, 134.1, 132.8, 129.3, 128.3, 128.0, 127.82, 127.80, 120.2, 71.5, 69.6, 30.0, -4.5, -4.7. *Trans*-**4.5g** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *trans*-(6-(4-methoxyphenyl)-3-methyl-5,6-dihydro-*2H*-pyran-2-yl)trimethyl silane (*trans*-4.5h)

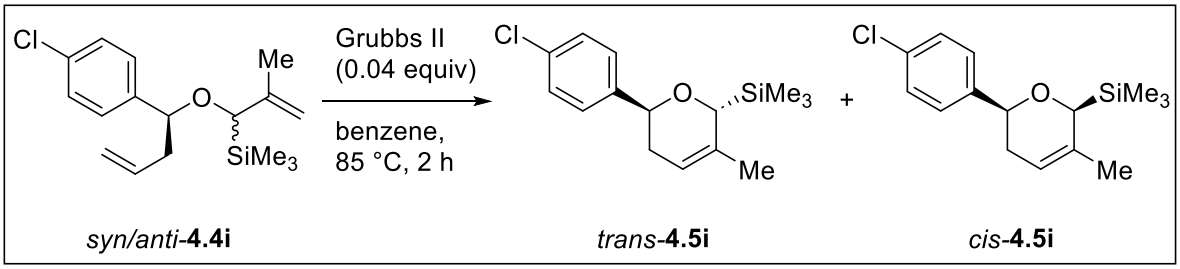


syn-**4.4h** *trans*-**4.5h**

Compound **4.5h** was prepared following general procedure F: Grubbs catalyst 2nd generation (51 mg, 0.06 mmol, 0.04 equiv.) and *syn*-(1-((1-(4-methoxyphenyl)but-3-en-1-yl)oxy)-2-methylallyl)trimethylsilane, *syn*-**4.4h** (457 mg, 1.5 mmol, 1 equiv.) and benzene (40 mL) at 85 °C for 2 hours followed by concentration and column chromatography, R_f for *trans*-**4.5h** = 0.5 (30% DCM in hexanes) afforded a total of 377 mg, 1.37 mmol (91% isolated yield) of compound *trans*-

4.5h as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.48 (ddq, *J* = 5.0, 3.4, 1.5 Hz, 1H), 4.50 (dd, *J* = 8.9, 4.2 Hz, 1H), 4.00 (s, 1H), 3.80 (s, 3H), 2.38 – 2.24 (m, 2H), 1.65 (s, 3H), 0.16 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.8, 135.4, 134.9, 127.3, 115.9, 113.6, 74.9, 72.6, 55.2, 32.0, 20.4, -1.4. *Trans*-**4.5h** is a known compound and spectroscopic data are in agreement with those reported in literature.[26]

Synthesis of *cis/trans*-(6-(4-chlorophenyl)-3-methyl-5,6-dihydro-*2H*-pyran-2-yl)trimethyl silane (*cis/trans*-4.5i)



syn/anti-**4.4i** *trans*-**4.5i** *cis*-**4.5i**

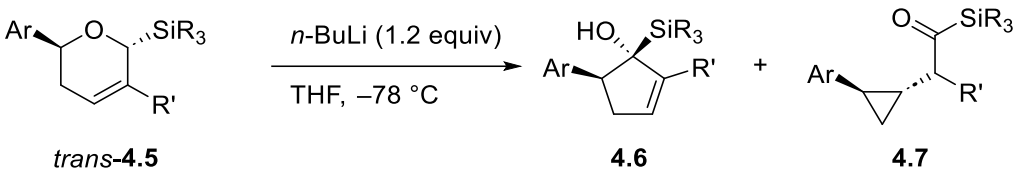
Compound **4.5i** was prepared following general procedure F: Grubbs catalyst 2nd generation (70.04 mg, 0.083 mmol, 0.03 equiv.) and *syn/anti*-(1-((1-(4-chlorophenyl)but-3-en-1-yl)oxy)-2-methylallyl)trimethylsilane, *syn:anti* = 1:1, **4.4i** (850 mg, 2.75 mmol, 1 equiv.) and dichloromethane (40 mL) at room temperature for 12 hours followed by concentration and column chromatography, R_f for *cis*-**4.5i** = 0.7 and R_f for *trans*-**4.5i** = 0.4 (20% DCM in hexanes) afforded a total of 763 mg, 2.70 mmol (98% isolated yield) fully separable mixture of diastereomers of compound **4.5i** as colorless liquid.

Spectroscopic data for *cis*-**4.5i**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 – 7.27 (m, 4H), 5.85 – 5.77 (m, 2H), 4.38 (dd, *J* = 10.1, 3.1 Hz, 1H), 4.18 (dtd, *J* = 5.0, 2.7, 1.5 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.13 (dddt, *J* = 14.8, 8.3, 2.7, 1.6 Hz, 1H), 0.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.5, 132.6, 128.2, 128.1, 127.0, 120.8, 74.7, 71.6, 34.0, -4.0. IR (FTIR, cm^{-1}) $\tilde{\nu}$ = 3057, 2953, 1492, 1380, 1243, 1012, 813. MS (GC/MS): *m*/z (%) = 280 (0.02) $[M]^+$, 208 (6), 68 (100).

Spectroscopic data for *trans*-**4.5i:** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35 – 7.29 (m, 4H), 5.84

– 5.76 (m, 2H), 4.72 (dd, *J* = 6.4, 4.5 Hz, 1H), 4.01 – 3.96 (m, 1H), 2.47 – 2.40 (m, 1H), 2.39 – 2.32 (m, 1H), 0.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 140.5, 132.9, 128.3, 128.2, 128.1, 119.7, 71.6, 69.8, 30.0, -3.0. IR (FTIR, cm^{-1}) ṽ = 3056, 2952, 1492, 1380, 1242, 1012, 812. MS (GC/MS): *m*/z (%) = 280 (0.015) $[M]^+$, 208 (5.8), 68 (100).

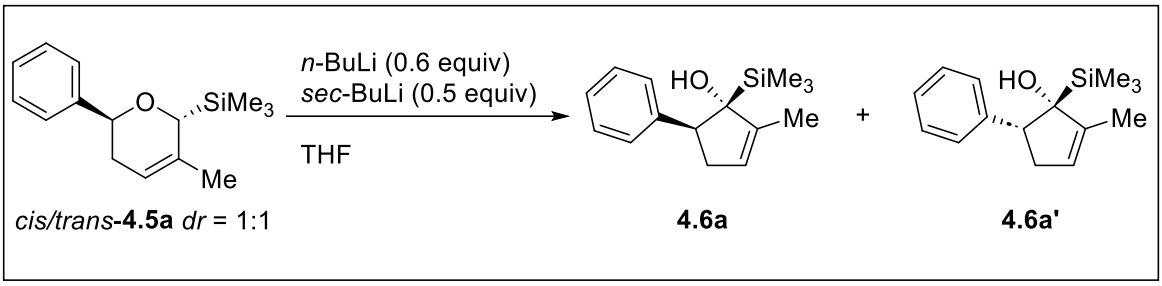
4.7.3. Wittig rearrangements of *trans*-2-silyl-5,6-dihydro-6-aryl-(*2H*)-pyrans *trans*-4.5: general procedure G



trans-**4.5** **4.6** **4.7**

Following our reported procedure,[8] freshly prepared and purified *trans*-2-silyl-5,6-dihydro-6-aryl-(*2H*)-pyran **4.5** was dissolved in THF under nitrogen (concentration 0.08 M, unless otherwise noted) and the solution cooled at −78 °C (dry ice/acetone bath), *n*-butyllithium (1.2 equiv, 1.6 M or 2.5 M in hexanes) was added dropwise (1 drop/s) to give a colored solution. The reaction was quenched after the indicated time (10−30 min) by adding saturated $NH_4Cl_{(aq)}$ and diluted with H_2O and diethyl ether. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with saturated $NH_4Cl_{(aq)}$, H_2O, and brine. The solution was dried over magnesium sulfate, filtered, quickly concentrated in a rotovap at temperatures lower than 45 °C. Column chromatography with EtOAc in hexanes afforded cyclopentenol **4.6**. Other products including the ones resulting from [1,4]-Wittig rearrangement (**4.7**) were also observed (see individual substrate).

Synthesis of 2-methyl-5-phenyl-1-(trimethylsilyl)cyclopent-2-en-1-ol (4.6a), –OH and phenyl *trans* to one another and (4.6a′), –OH and phenyl *cis*



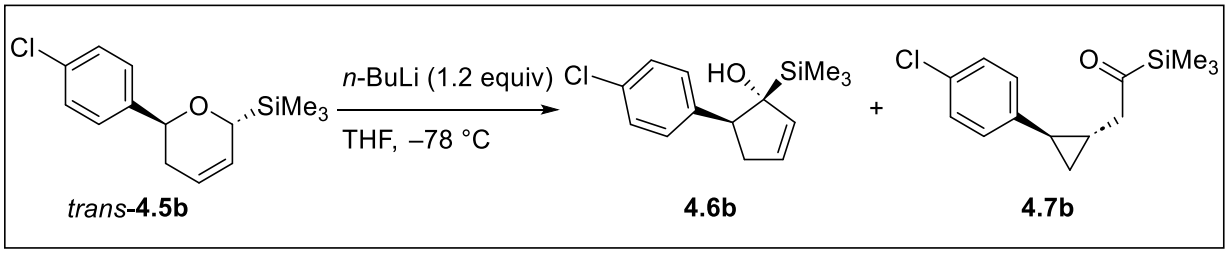
Following general procedure G with slight modification, 370 mg of *cis*-trimethyl(3-methyl-6-phenyl-5,6-dihydro-*2H*-pyran-2-yl)silane, *cis*-**4.5a** and 370 mg of *trans*-trimethyl(3-methyl-6-phenyl-5,6-dihydro-*2H*-pyran-2-yl)silane, *trans*-**4.5a** were weighed into a 20 mL vial respectively making a mixture of 1:1 *cis:trans* diastereomeric ratio (740 mg, 3.0 mmol, 1.0 equiv). This was dissolved in 20 mL dry THF and the resulting solution was transferred into a 100 mL round bottom flask via syringe. Additional 20 mL of THF was transferred into the flask and the resulting mixture was cooled to –78 °C on an acetone/dry-ice bath. This was followed by dropwise addition of 0.72 mL of *n*-butyllithium, 2.5 M in hexanes (1.8 mmol, 0.6 equiv.). The resulting mixture was stirred at –78 °C for 15 minutes (approximate time taken by the trans diastereomer to react), then 3.22 mL of *sec*-butyllithium, 1.4 M in cyclohexane (4.5 mmol, 1.5 equiv.) was added to the flask at –78 °C. The solution turned dark purple after complete addition of *sec*-butyllithium. The mixture was stirred at –78 °C for 1.5 hours after which the cold bath was removed, and the mixture allowed to warm up to room temperature. The mixture was stirred at room temperature for additional 3 hours and then cooled down to –78 °C and quenched by 10 mL water. The cold bath was removed again, and the mixture allowed to warm up to room temperature and diluted with diethyl ether. The resulting mixture was transferred into a separating funnel and the layers were separated. The aqueous layer was extracted with diethyl ether (25 mL x 3). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The mixture was filtered, and the filtrate was

concentrated on a rotavapor under reduced pressure to give crude reaction mixture. Further purification by column chromatography, R_f for **4.6a′** = 0.71 and R_f for **4.6a** = 0.44 (10% EtOAc in hexanes) furnished 287 mg, 1.2 mmol (40% isolated yield) of **4.6a** as a colorless liquid and 185 mg, 0.75 mmol (25% isolated yield) of **4.6a′** as a colorless liquid.

Spectroscopic data for **4.6a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 – 7.40 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H), 5.67 (dp, *J* = 3.2, 1.6 Hz, 1H), 3.44 (dd, *J* = 10.6, 7.6 Hz, 1H), 2.72 – 2.63 (m, 1H), 2.46 (dddt, *J* = 15.4, 7.7, 3.1, 1.5 Hz, 1H), 1.80 (dt, *J* = 2.9, 1.5 Hz, 3H), 1.47 (s, 1H), -0.27 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.6, 140.8, 128.6, 128.1, 126.7, 124.7, 84.8, 61.7, 32.8, 14.6, -2.2. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = 1.44. **4.6a** is a known compound and the spectroscopic data are in agreement with those reported in the literature.[26]

Spectroscopic data for **4.6a′**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 – 7.28 (m, 2H), 7.26 – 7.20 (m, 3H), 5.57 (dq, *J* = 3.2, 1.7 Hz, 1H), 3.71 (dt, *J* = 8.2, 1.6 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.54 (ddq, *J* = 16.8, 3.4, 1.7 Hz, 1H), 1.75 (dt, *J* = 3.0, 1.6 Hz, 3H), 0.82 (s, 1H), 0.15 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.2, 141.5, 128.6, 128.5, 126.8, 123.6, 81.6, 51.0, 38.6, 14.3, -3.2. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm): δ = 4.01. HRMS (ESI): *m*/*z* $[M - OH]^+$ calcd for $C_{15}H_{21}Si$: 229.1413; found: 229.1406.

Synthesis of 5-(4-chlorophenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (4.6b) and 2-(2-(4-chlorophenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (4.7b)



trans-**4.5b** **4.6b** **4.7b**

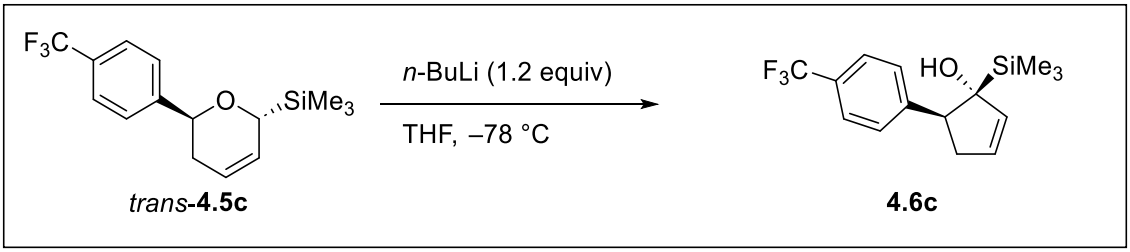
Following general procedure G, compounds **4.6b** and **4.7b** were prepared from *trans*-(6-(4-chlorophenyl)-5,6-dihydro-*2H*-pyran-2-yl)trimethylsilane, *trans*-**4.5b** (534 mg, 2.0 mmol, 1.0

equiv.), *n*-butyllithium 2.5 M in hexanes (1.0 mL, 2.4 mmol, 1.2 equiv.) and THF (25 mL) for 15 minutes. The reaction was quenched by adding water instead of saturated $NH_4Cl_{(aq)}$. Workup, concentration and column chromatography, R_f for **4.7b** = 0.7 and R_f for **4.6b** = 0.3 (10% EtOAc in hexanes) furnished 297 mg, 1.12 mmol (56% isolated yield) of **4.6b** as a yellow liquid and 111 mg, 0.42 mmol of **4.7b** (21% isolated yield) as a colorless liquid.

Spectroscopic data for **4.6b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 5.99 (ddd, *J* = 5.8, 2.9, 2.0 Hz, 1H), 5.77 (ddd, *J* = 5.8, 2.3, 1.4 Hz, 1H), 3.41 (dd, *J* = 10.2, 8.2 Hz, 1H), 2.72 – 2.59 (m, 2H), 1.52 (s, 1H), -0.27 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.0, 137.4, 132.3, 130.4, 129.8, 128.2, 84.2, 59.3, 35.3, -3.4. **4.6b** is a known compound and the spectroscopic data are in agreement with those reported in the literature.[26]

Spectroscopic data for **4.6b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 2.69 (dd, *J* = 6.7, 1.1 Hz, 2H), 1.60 (dt, *J* = 8.9, 4.9 Hz, 1H), 1.27 (dtdd, *J* = 8.6, 6.7, 5.7, 4.5 Hz, 1H), 0.94 (dt, *J* = 8.6, 5.2 Hz, 1H), 0.76 (dt, *J* = 8.6, 5.4 Hz, 1H), 0.20 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 247.1, 141.4, 131.0, 128.3, 127.4, 53.0, 22.2, 16.7, 15.5, -3.2. HRMS (APCI): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{20}ClOSi$: 267.0972; found: 267.0967.

Synthesis of 5-(4-trifluorophenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (4.6c)



trans-**4.5c** **4.6c**

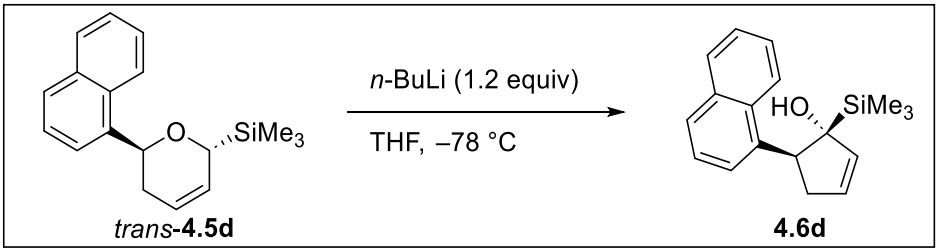
Following general procedure G, compound **4.6c** was prepared from *trans*-(6-(4-trifluorophenyl)-5,6-dihydro-*2H*-pyran-2-yl)trimethylsilane *trans*-**4.5c** (841 mg, 2.8 mmol, 1.0 equiv.), *n*-butyllithium 2.5 M in hexanes (1.4 mL, 3.36 mmol, 1.2 equiv.) and THF (40 mL) for 20 minutes. Workup, concentration and column chromatography, R_f = 0.5 (20% EtOAc in hexanes)

furnished 578 mg (70%) of **4.6c** as a yellow liquid. Compound **4.6c** is very unstable and upon storage at –15 °C slowly converts to 4-(4-(trifluoromethyl)phenyl)-3-(trimethylsilyl)cyclopent-2-en-1-one **4.11c.**

Spectroscopic data for **4.6c**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 6.01 (ddd, *J* = 5.8, 2.9, 1.9 Hz, 1H), 5.79 (ddd, *J* = 5.8, 2.3, 1.3 Hz, 1H), 3.50 (dd, *J* = 10.3, 8.0 Hz, 1H), 2.75 (ddt, *J* = 15.8, 10.3, 2.1 Hz, 1H), 2.66 (dddd, *J* = 15.9, 8.0, 2.9, 1.3 Hz, 1H), 1.56 (s, 1H), -0.29 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.75 (d, *J* = 1.4 Hz), 137.4, 130.4, 128.8, 129.02 (q, *J* = 32.4 Hz), 124.97 (q, *J* = 3.8 Hz), 124.28 (q, *J* = 271.8 Hz), 84.2, 59.7, 35.1, -3.5. **4.6c** is a known compound and the spectroscopic data are in agreement with those reported in the literature.[26]

Spectroscopic data for **4.11c** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 1.9 Hz, 1H), 4.26 (dt, *J* = 7.0, 2.1 Hz, 1H), 2.89 (dd, *J* = 19.2, 7.1 Hz, 1H), 2.28 (dd, *J* = 19.1, 2.3 Hz, 1H), -0.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 209.9, 185.0, 146.5 (d, *J* = 1.6 Hz), 142.3, 129.6 (q, *J* = 32.6 Hz), 128.0, 125.8 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.1 Hz), 50.3, 45.4, -1.8. ^{19}F NMR (470 MHz, $CDCl_3$, ppm): δ = -62.47.

Synthesis of 5-(naphthalen-1-yl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (4.6d)

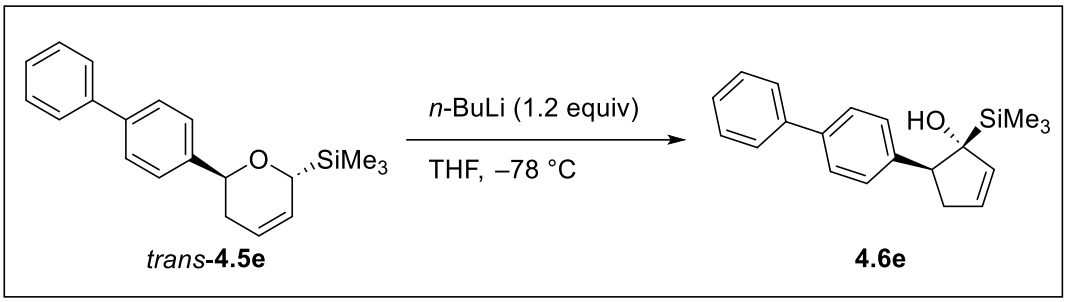


trans-**4.5d** **4.6d**

Following general procedure G, compound **4.6c** was prepared from *trans*-(6-naphthalen-1-yl)-5,6-dihydro-*2H*-pyran-2-yl)trimethylsilane *trans*-**4.5d** (701 mg, 2.48 mmol, 1.0 equiv.), *n*-butyllithium 2.5 M in hexanes (1.24 mL, 2.98 mmol, 1.2 equiv.) and THF (40 mL) for 20 minutes. Workup, concentration and column chromatography, R_f = 0.4 (10% EtOAc in hexanes) furnished

568 mg, 2.01 mmol (81% isolated yield) of **4.6d** as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.62 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.51 (dddd, *J* = 22.6, 8.0, 6.8, 1.3 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 6.10 (ddd, *J* = 5.7, 2.9, 1.9 Hz, 1H), 5.81 (ddd, *J* = 5.8, 2.4, 1.3 Hz, 1H), 4.47 (dd, *J* = 10.0, 8.1 Hz, 1H), 3.04 (ddt, *J* = 16.0, 10.0, 2.1 Hz, 1H), 2.81 (dddd, *J* = 16.2, 8.1, 2.8, 1.3 Hz, 1H), 1.72 (s, 1H), -0.43 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.4, 136.2, 134.0, 133.8, 130.8, 128.6, 127.4, 125.8, 125.5, 124.98, 124.97, 124.1, 86.0, 53.8, 37.4, -3.6. IR (FTIR, cm^{-1}): $\tilde{\nu}$ = 3423, 3046, 2952, 1508, 1396, 1244, 832, 777. MS (GC/MS): *m*/z (%) = 282 (20) $[M]^+$, 191 (25), 165 (18), 73 (100). HRMS (ESI): *m*/*z* $[M - H^-]^+$ calcd for $C_{18}H_{21}OSi$: 281.1362; found: 281.1353.

Synthesis of 5-([1,1'-biphenyl]-4-yl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (4.6e)

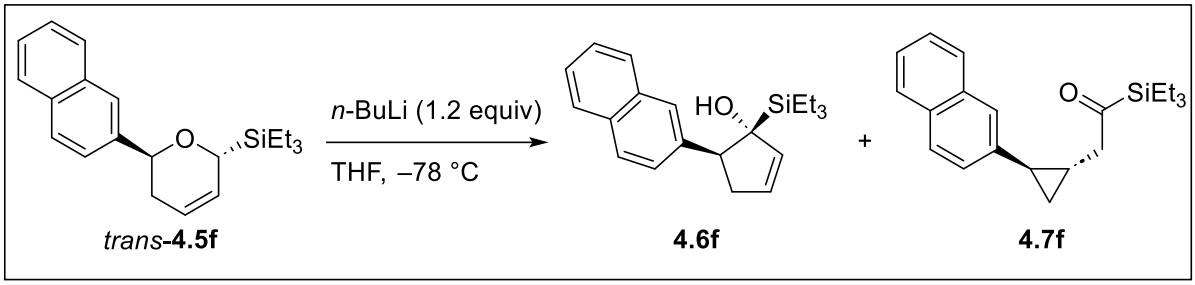


trans-**4.5e** **4.6e**

Following general procedure G, compound **4.6e** was prepared from *trans*-(6-([1,1'-biphenyl]-4-yl)-5,6-dihydro-2H-pyran-2-yl)trimethylsilane *trans*-**4.5e** (67 mg, 0.22 mmol, 1.0 equiv.), *sec*-butyllithium 1.4 M in cyclohexane (0.46 mL, 0.66 mmol, 3.0 equiv.) and THF (2.4 mL) for 3 hours. Workup, concentration and column chromatography, R_f = 0.4 (10% EtOAc in hexanes) furnished 51 mg, 0.165 mmol (75% isolated yield) of **4.6e** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 – 7.62 (m, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.38 – 7.33 (m, 1H), 6.04 (ddd, *J* = 5.8, 2.9, 1.9 Hz, 1H), 5.82 (ddd, *J* = 5.8, 2.3, 1.3 Hz, 1H), 3.52 (dd, *J* = 10.3, 7.9 Hz, 1H), 2.81 (ddt, *J* = 16.0, 10.3, 2.1 Hz, 1H), 2.70 (dddd, *J* = 16.0, 8.0, 2.9, 1.3 Hz, 1H), 1.58 (s, 1H), -0.23 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.9, 139.6,

137.3, 130.5, 128.9, 128.7, 127.1, 126.9, 126.8, 84.5, 59.7, 35.4, -3.4. **4.6e** is a known compound and the spectroscopic data are in agreement with those reported in the literature.[26]

Synthesis of 5-(naphthalen-2-yl)-1-(triethylsilyl)cyclopent-2-en-1-ol (4.6f) and 2-(2-(naphthalen-2-yl)cyclopropyl)-1-(triethylsilyl)ethan-1-one (4.7f)



trans-**4.5f** **4.6f** **4.7f**

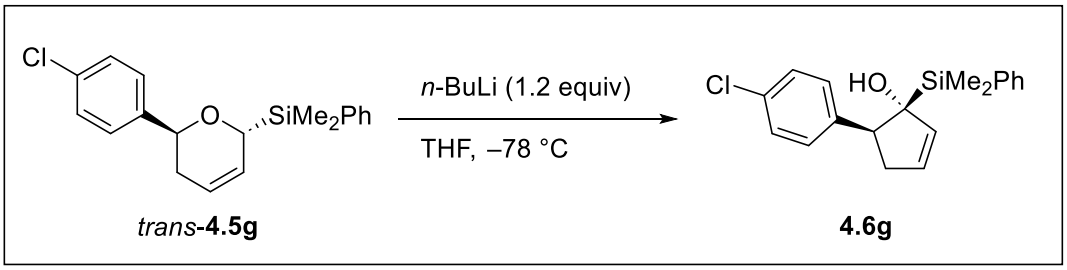
Following general procedure G, compounds **4.6f** and **4.7f** were prepared from *trans*-triethyl(6-(naphthalen-2-yl)-5,6-dihydro-2H-pyran-2-yl)silane *trans*-**4.5f** (650 mg, 2.0 mmol, 1.0 equiv.), *n*-butyllithium 2.5 M in hexanes (1.0 mL, 2.4 mmol, 1.2 equiv.) and THF (25 mL) for 15 minutes. The reaction was quenched by adding water instead of saturated $NH_4Cl_{(aq)}$. Workup, concentration and column chromatography, R_f for **4.7f** = 0.7 and R_f for **4.6f** = 0.3 (10% EtOAc in hexanes) furnished 473 mg, 1.46 mmol (73% isolated yield) of **4.6f** as a yellow liquid and 110 mg, 0.34 mmol of **4.7f** (17% isolated yield) as a colorless liquid.

Spectroscopic data for **4.6f**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 – 7.76 (m, 4H), 7.64 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.51 – 7.41 (m, 2H), 6.03 (ddd, *J* = 5.8, 2.9, 1.9 Hz, 1H), 5.91 (ddd, *J* = 5.8, 2.3, 1.3 Hz, 1H), 3.60 (dd, *J* = 10.0, 7.7 Hz, 1H), 2.90 (ddt, *J* = 16.0, 9.9, 2.1 Hz, 1H), 2.76 (dddd, *J* = 16.0, 7.8, 2.9, 1.3 Hz, 1H), 1.55 (s, 1H), 0.80 (t, *J* = 8.0 Hz, 9H), 0.28 (qd, *J* = 7.9, 1.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.5, 138.3, 133.3, 132.5, 130.5, 127.9, 127.7, 127.6, 127.4, 126.2, 125.8, 125.3, 85.9, 60.6, 35.8, 7.8, 2.3. **4.6f** is a known compound and the spectroscopic data are in agreement with those reported in the literature.[26]

Spectroscopic data for **4.7f**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 – 7.70 (m, 3H), 7.54 (s, 1H), 7.46 – 7.36 (m, 2H), 7.23 (dd, *J* = 8.6, 1.8 Hz, 1H), 2.80 (dd, *J* = 17.2, 6.2 Hz, 1H), 2.65 (dd,

J = 17.2, 7.0 Hz, 1H), 1.81 (dt, *J* = 9.2, 4.9 Hz, 1H), 1.51 – 1.44 (m, 1H), 1.12 (dt, *J* = 8.6, 5.1 Hz, 1H), 0.99 (t, *J* = 7.9 Hz, 8H), 0.83 (dt, *J* = 8.6, 5.3 Hz, 1H), 0.80 – 0.70 (m, 7H), 0.47 (qd, *J* = 8.3, 7.9, 3.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 247.1, 140.4, 133.5, 131.9, 127.8, 127.5, 127.2, 125.9, 124.91, 124.86, 123.9, 54.8, 22.8, 16.5, 15.7, 7.3, 2.1. **4.7f** is a known compound, and the spectroscopic data are in agreement with those reported in the literature.[26]

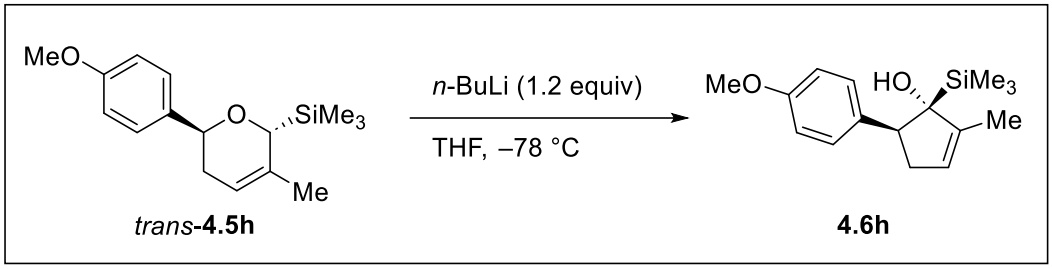
Synthesis of 5-(4-chlorophenyl)-1-(dimethyl(phenyl)silyl)cyclopent-2-en-1-ol (4.6g)



trans-**4.5g** **4.6g**

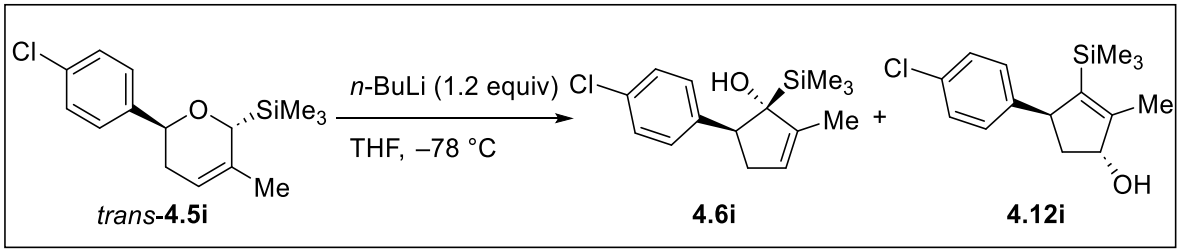
Following general procedure G, compound **4.6g** was prepared from *trans*- (6-(4-chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)dimethyl(phenyl)silane *trans*-**4.5g** (987 mg, 3.0 mmol, 1.0 equiv.), *n*-butyllithium 2.5 M in hexanes (1.5 mL, 3.6 mmol, 1.2 equiv.) and THF (10 mL) for 10 minutes. Workup, concentration and column chromatography, R_f = 0.4 (10% EtOAc in hexanes) furnished 362 mg, 1.11 mmol (37% isolated yield) of **4.6g** as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.37 – 7.32 (m, 1H), 7.32 – 7.25 (m, 4H), 7.21 – 7.14 (m, 4H), 6.01 (ddd, *J* = 5.7, 2.9, 1.9 Hz, 1H), 5.76 (ddd, *J* = 5.8, 2.4, 1.3 Hz, 1H), 3.42 (dd, *J* = 10.3, 7.8 Hz, 1H), 2.57 (dddd, *J* = 15.8, 7.8, 2.9, 1.3 Hz, 1H), 2.48 (ddt, *J* = 15.9, 10.4, 2.2 Hz, 1H), 1.63 (s, 1H), 0.07 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.5, 137.4, 136.5, 134.3, 132.3, 130.9, 129.9, 129.0, 127.9, 127.3, 84.2, 59.0, 35.3, -4.9, -5.2. **4.6g** is a known compound and the spectroscopic data are in agreement with those reported in the literature.[26]

Synthesis of 5-(4-methoxyphenyl)-2-methyl-1-(trimethylsilyl)cyclopent-2-en-1-ol (4.6h)



Following general procedure G, compound **4.6h** was prepared from *trans*-(6-(4-methoxyphenyl)-3-methyl-5,6-dihydro-2H-pyran-2-yl)trimethylsilane *trans*-**4.5h** (276 mg, 1.0 mmol, 1.0 equiv.), *n*-butyllithium 2.5 M in hexanes (0.5 mL, 1.2 mmol, 1.2 equiv.) and THF (10 mL) for 20 minutes. Workup, concentration and column chromatography, R_f = 0.4 (10% EtOAc in hexanes) furnished 236 mg, 0.85 mmol (85% isolated yield) of **4.6h** as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.65 (dp, *J* = 3.3, 1.6 Hz, 1H), 3.80 (s, 3H), 3.36 (dd, *J* = 10.6, 7.6 Hz, 1H), 2.60 (ddp, *J* = 15.6, 10.4, 2.5 Hz, 1H), 2.43 (dddt, *J* = 12.3, 6.1, 3.1, 1.5 Hz, 1H), 1.78 (dt, *J* = 2.8, 1.5 Hz, 3H), 1.41 (s, 1H), -0.27 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.5, 145.6, 132.9, 129.5, 124.7, 113.4, 84.8, 61.0, 55.2, 33.1, 14.6, -2.2. **4.6h** is a known compound and the spectroscopic data are in agreement with those reported in the literature.[26]

Synthesis of 5-(4-chlorophenyl)-2-methyl-1-(trimethylsilyl)cyclopent-2-en-1-ol (4.6i) and 4-(4-chlorophenyl)-2-methyl-3-(trimethylsilyl)cyclopent-2-en-1-ol (4.12i)



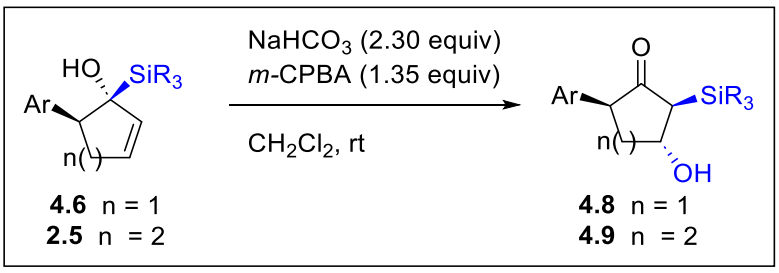
Following general procedure G, compounds **4.6i** and **4.12i** were prepared from *trans*-(6-(4-chlorophenyl)-3-methyl-5,6-dihydro-2H-pyran-2-yl)trimethylsilane, *trans*-**4.5i** (617 mg, 2.2

mmol, 1.0 equiv.), *n*-butyllithium 2.5 M in hexanes (1.06 mL, 2.64 mmol, 1.2 equiv.) and THF (30 mL) for 15 minutes. Workup, concentration and column chromatography, R_f for **4.6i** = 0.6 and R_f for **4.12i** = 0.3 (15% EtOAc in hexanes) furnished 388 mg, 1.386 mmol (63% isolated yield) of **4.6i** as a yellow liquid and 37 mg, 0.132 mmol of **4.12i** (6% isolated yield) as a colorless liquid. Compound **4.12i** might have been formed from **4.6i** during the workup.

Spectroscopic data for **4.6i**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 5.63 (dp, *J* = 3.3, 1.6 Hz, 1H), 3.36 (dd, *J* = 10.6, 7.6 Hz, 1H), 2.61 – 2.52 (m, 1H), 2.41 (dddt, *J* = 15.3, 7.6, 3.1, 1.5 Hz, 1H), 1.76 (dt, *J* = 2.9, 1.5 Hz, 3H), 1.45 (s, 1H), -0.29 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.7, 139.4, 132.3, 129.9, 128.1, 124.6, 84.7, 60.9, 32.8, 14.5, -2.1. IR (FTIR, cm^{-1}): $\tilde{\nu}$ = 3416, 3092, 3069, 2955, 1490, 1401, 1249, 1091, 1012, 822. MS (GC/MS): *m*/z (%) = 280 (15) $[M]^+$, 263 (15), 169 (35), 97 (15), 73 (100). HRMS (ESI): *m*/*z* $[M - OH]^+$ calcd for $C_{15}H_{20}ClSi$: 263.1023; found: 263.1010.

Spectroscopic data for **4.12i**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.82 (tdt, *J* = 7.2, 2.0, 1.0 Hz, 1H), 4.00 (ddt, *J* = 7.6, 3.7, 1.7 Hz, 1H), 2.09 (ddd, *J* = 6.8, 5.2, 2.2 Hz, 2H), 1.97 (dd, *J* = 1.7, 1.0 Hz, 3H), 1.70 (s, 1H), -0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 153.1, 145.1, 140.7, 131.5, 128.7, 128.4, 82.0, 53.6, 45.1, 14.3, -0.5. IR (FTIR, cm^{-1}): $\tilde{\nu}$ = 3400, 2957, 1489, 1249, 1090, 823. HRMS (ESI): *m*/*z* $[M - OH]^+$ calcd for $C_{15}H_{20}ClSi$: 263.1023; found: 263.1005.

4.7.4. The [1,2]-carbon-to-carbon silyl migration (1.0 mmol scale) – general procedure H

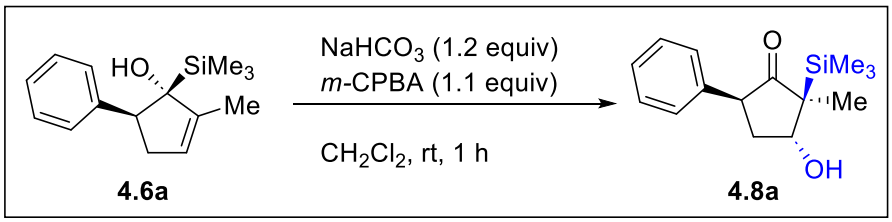


4.6 n = 1
2.5 n = 2

4.8 n = 1
4.9 n = 2

A dry 50 mL round-bottom flask fitted with a magnetic stir bar was charged with 193 mg (2.3 mmol, 2.3 equiv) of $NaHCO_3$. The flask was sealed with a rubber septum and kept under positive atmosphere of nitrogen gas. An amount corresponding to 1.0 mmol of alcohol from procedure I (starting material) was dissolved in 5 mL of dry CH_2Cl_2, and the solution transferred into the flask via syringe. An additional 5 mL of dry CH_2Cl_2 was added into the flask via syringe. Into a separate vial, 302.5 mg of 77% w/w *m*-CPBA (1.35 mmol, 1.35 equiv) was weighed and 5 mL dry CH_2Cl_2 transferred into the vial to dissolve the *m*-CPBA. The resulting solution was transferred into the flask via syringe. The resulting mixture (in the flask) was stirred for 1–3 hours monitoring by TLC. Typically, formation of a white suspension indicated the end of the reaction. The reaction mixture was transferred into a separating funnel and diluted with 50 mL CH_2Cl_2. The mixture was washed with 20 mL saturated $Na_2SO_{3(aq)}$, 20 mL saturated $NaHCO_{3(aq)}$ and 20 mL water respectively. The aqueous layers were combined and extracted with CH_2Cl_2 (30 mL X 2). All the organic layers were combined and washed with 20 mL saturated $NaCl_{(aq)}$ and dried over anhydrous Na_2SO_4. Filtration and concentration of the filtrate under reduced pressure afforded the desired product. In most cases, purification by column chromatography was not necessary.

Synthesis of 3-hydroxy-2-methyl-5-phenyl-2-(trimethylsilyl)cyclopentan-1-one (4.8a)

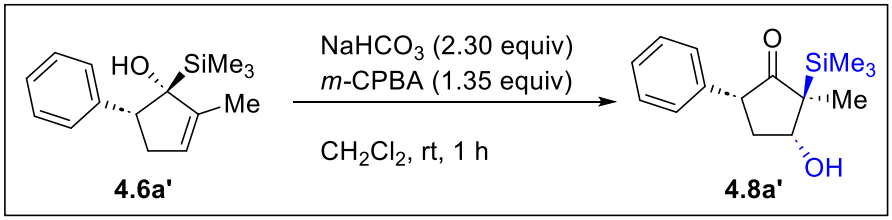


4.6a **4.8a**

Applying general procedure H to $NaHCO_3$, (6.5 mg, 0.09 mmol, 1.2 equiv.), 2-methyl-5-phenyl-1-(trimethylsilyl)cyclopent-2-en-1-ol **4.6a** (16 mg, 0.064 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 15.7 mg, 0.08 mmol, 1.1 equiv.), and DCM (2 mL) afforded 14 mg, 0.053 mmol (83% crude yield) of **4.8a** as a white solid. No further purification was necessary judging by the ^1H and ^{13}C

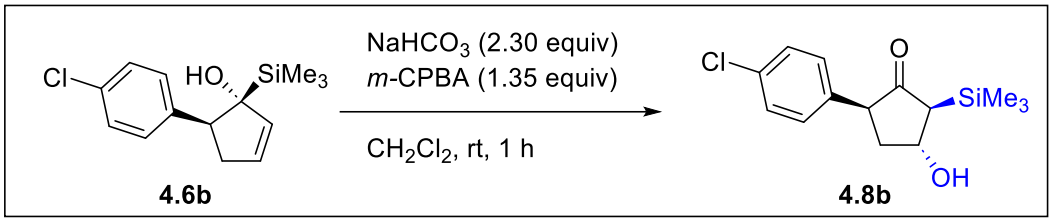
NMR analysis of the crude reaction mixture. The crystal structure of compound **4.8a** was solved by X-ray crystallography and the results deposited to the Cambridge Crystallographic Data Centre and assigned CCDC 2175610. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 – 7.31 (m, 2H), 7.31 – 7.28 (m, 2H), 7.25 – 7.22 (m, 1H), 4.57 (d, *J* = 4.1 Hz, 1H), 3.78 (dd, *J* = 12.6, 8.5 Hz, 1H), 2.52 (ddd, *J* = 13.6, 8.6, 1.3 Hz, 1H), 2.42 (ddd, *J* = 13.6, 12.5, 4.2 Hz, 1H), 1.75 (s, 1H), 1.30 (s, 3H), 0.06 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 218.1, 137.0, 128.4, 127.8, 126.7, 72.5, 50.7, 50.1, 36.7, 13.8, -2.3.

Synthesis of *epi*-3-hydroxy-2-methyl-5-phenyl-2-(trimethylsilyl)cyclopentan-1-one (4.8a′)



Applying general procedure H to $NaHCO_3$, (96.6 mg, 1.15 mmol, 2.30 equiv.), *epi*-2-methyl-5-phenyl-1-(trimethylsilyl)cyclopent-2-en-1-ol **4.6a′** (123.2 mg, 0.5 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 151.3 mg, 0.68 mmol, 1.35 equiv.), and DCM (8 mL) afforded after workup 130 mg, 0.495 mmol (99% crude yield) **4.8a′** as a white solid. The crystal structure of compound **4.8a′** was solved by X-ray crystallography and the results deposited to the Cambridge Crystallographic Data Centre and assigned CCDC 2158501. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 4.54 (dd, *J* = 5.7, 4.8 Hz, 1H), 3.39 (dd, *J* = 9.9, 8.2 Hz, 1H), 2.75 (ddd, *J* = 13.9, 9.9, 5.8 Hz, 1H), 2.19 (ddd, *J* = 13.9, 8.2, 4.8 Hz, 1H), 1.24 (s, 3H), 0.14 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 218.3, 139.2, 128.6, 128.4, 126.7, 72.7, 53.9, 49.8, 38.6, 12.2, -3.6. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = 6.79. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{22}NaO_2Si$: 285.1287; found: 285.1282.

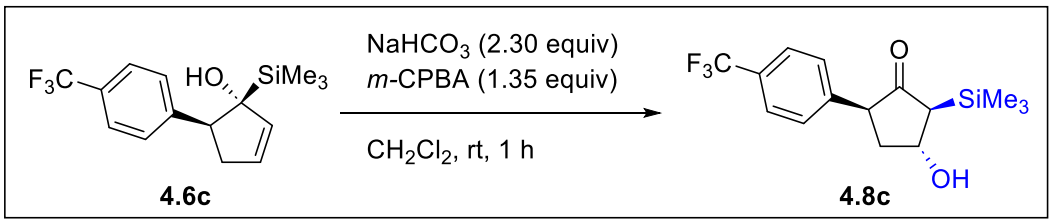
Synthesis of 5-(4-chlorophenyl)-3-hydroxy-2-(trimethylsilyl)cyclopentan-1-one (4.8b)



4.6b **4.8b**

Applying general procedure H to $NaHCO_3$, (116 mg, 1.38 mmol, 2.30 equiv.), 5-(4-chlorophenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol **4.6b** (160 mg, 0.6 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 182 mg, 0.81 mmol, 1.35 equiv.), and DCM (10 mL) afforded 170 mg, 0.6 mmol (100% crude yield) of **4.8b** as a white solid. No further purification was necessary judging by the ^{1}H and ^{13}C NMR analysis of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 4.68 (d, *J* = 3.9 Hz, 1H), 3.79 (dd, *J* = 12.5, 8.3 Hz, 1H), 2.49 (dddd, *J* = 13.6, 8.2, 3.0, 1.2 Hz, 1H), 2.30 (dd, *J* = 3.0, 1.6 Hz, 1H), 2.26 (ddd, *J* = 13.6, 12.7, 4.1 Hz, 1H), 2.03 (s, 1H), 0.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 215.5, 135.6, 132.7, 129.3, 128.6, 70.2, 54.0, 50.4, 38.9, -1.6. MS (GC/MS): *m*/z (%) = 282 (0.08) $[M]^+$, 192 (45), 157 (20), 129 (100).

Synthesis 5-(4-trifluoromethylphenyl)-3-hydroxy-2-(trimethylsilyl)cyclopentan-1-one (4.8c)

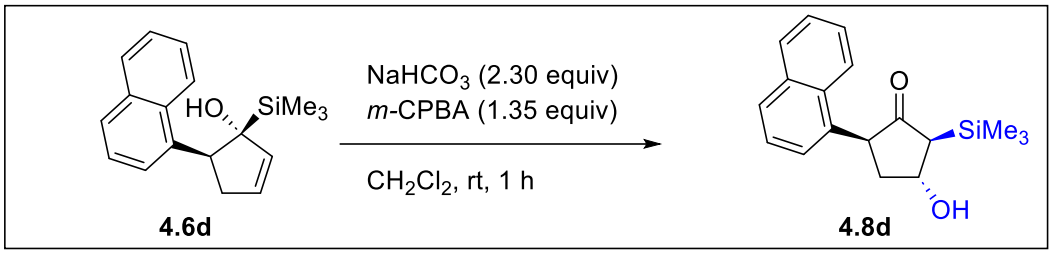


4.6c **4.8c**

Applying general procedure H to $NaHCO_3$, (193 mg, 2.3 mmol, 2.30 equiv.), 5-(4-trifluoromethylphenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol **4.6c** (301 mg, 1.0 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 303 mg, 1.35 mmol, 1.35 equiv.), and DCM (10 mL) afforded 309 mg, 0.98 mmol (98% crude yield) of **4.8c** as a white solid. No further purification was necessary judging by the ^{1}H and ^{13}C NMR analysis of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58

(d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.70 (d, *J* = 3.8 Hz, 1H), 3.89 (dd, *J* = 12.8, 8.2 Hz, 1H), 2.53 (dddd, *J* = 13.5, 8.2, 3.0, 1.1 Hz, 1H), 2.36 – 2.28 (m, 2H), 2.15 (s, 1H), 0.13 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 215.1, 141.2 (d, *J* = 1.5 Hz), 129.1 (q, *J* = 32.4 Hz), 128.3, 125.4 (q, *J* = 3.8 Hz), 70.2, 54.1, 50.9, 38.7, -1.6. MS (GC/MS): *m*/z (%) = 316 (0.12) $[M]^+$, 240 (35), 212 (100), 115 (35)

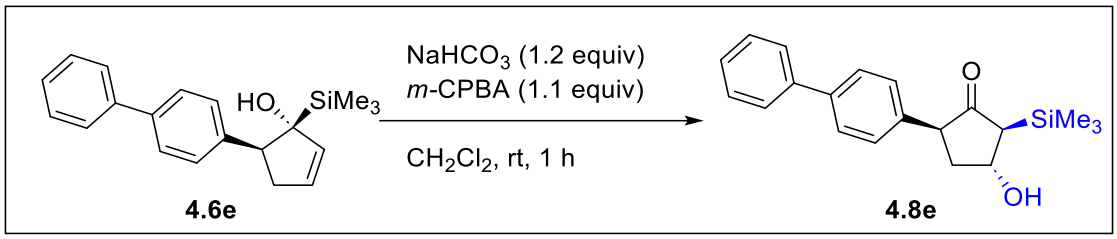
Synthesis of 3-hydroxy-5-(naphthalen-1-yl)-2-(trimethylsilyl)cyclopentan-1-one (4.8d)



4.6d **4.8d**

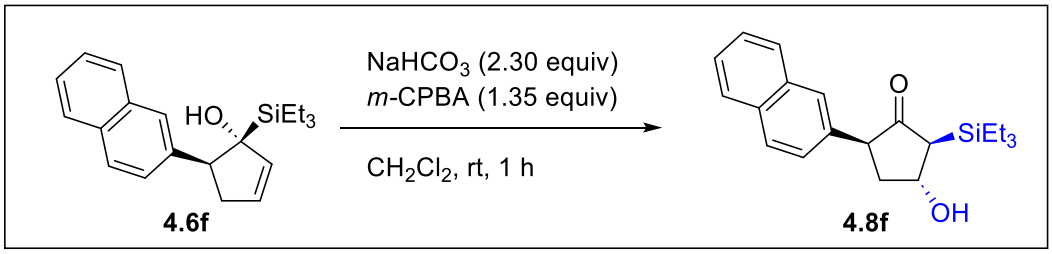
Applying general procedure H to $NaHCO_3$, (193 mg, 2.3 mmol, 2.30 equiv.), 5-(naphthalen-1-yl)-1-(trimethylsilyl)cyclopent-2-en-1-ol **4.6d** (283 mg, 1.0 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 300 mg, 1.34 mmol, 1.34 equiv.), and DCM (10 mL) afforded 285 mg, 0.96 mmol (96% crude yield) of **4.8d** as a white solid. No further purification was necessary judging by the ^{1}H and ^{13}C NMR analysis of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.5 Hz, 1H), 7.85 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.45 – 7.40 (m, 1H), 7.21 (d, *J* = 7.1 Hz, 1H), 4.71 – 4.62 (m, 2H), 2.63 (dddd, *J* = 13.6, 8.2, 3.0, 1.2 Hz, 1H), 2.40 (dd, *J* = 3.1, 1.6 Hz, 1H), 2.30 (td, *J* = 13.2, 4.1 Hz, 1H), 2.22 (s, 1H), 0.20 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 216.5, 134.4, 134.0, 132.7, 128.7, 127.5, 126.0, 125.7, 125.3, 123.9, 123.8, 70.5, 54.6, 47.8, 40.2, -1.5. MS (GC/MS): *m*/z (%) = 298 (0.03) $[M]^+$, 208 (100), 179 (80), 165 (70), 152 (45), 128 (20), 89 (30). HRMS (ESI): *m*/*z* $[M - OH]^+$ calcd for $C_{18}H_{21}OSi$: 281.1356; found: 281.1360.

Synthesis of 5-([1,1'-biphenyl]-4-yl)-3-hydroxy-2-(trimethylsilyl)cyclopentan-1-one (4.8e)



Applying general procedure H to $NaHCO_3$, (8.7 mg, 0.1 mmol, 1.2 equiv.), 5-([1,1'-biphenyl]-4-yl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4.6e**) (26.5 mg, 0.086 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 21.2 mg, 0.095 mmol, 1.1 equiv.), and DCM (10 mL) afforded 25.1 mg, 0.077 mmol (90% crude yield) of **4.8d** as a white solid. No further purification was necessary judging by the ^{1}H and ^{13}C NMR analysis of the crude reaction mixture. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 – 7.55 (m, 4H), 7.45 – 7.41 (m, 2H), 7.36 – 7.32 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.73 (d, *J* = 3.9 Hz, 1H), 3.89 (dd, *J* = 12.6, 8.2 Hz, 1H), 2.58 – 2.52 (m, 1H), 2.38 (td, *J* = 13.1, 4.1 Hz, 1H), 2.35 – 2.32 (m, 1H), 1.74 (s, 1H), 0.17 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 215.7, 140.9, 139.8, 136.4, 128.7, 128.4, 127.3, 127.2, 127.0, 70.5, 54.0, 51.0, 39.3, -1.5.

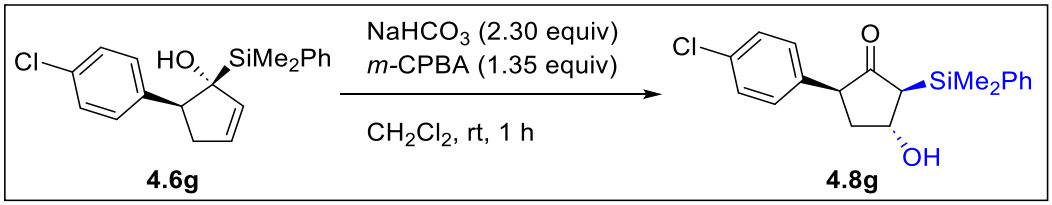
Synthesis of 3-hydroxy-5-(naphthalen-2-yl)-2-(triethylsilyl)cyclopentan-1-one (4.8f)



Applying general procedure H to $NaHCO_3$, (174 mg, 2.07 mmol, 2.30 equiv.), 5-(naphthalen-2-yl)-1-(triethylsilyl)cyclopent-2-en-1-ol **4.6f** (292 mg, 0.9 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 274 mg, 1.22 mmol, 1.35 equiv.), and DCM (10 mL) afforded 308 mg (quantitative yield) of **4.8f** as a white solid. No further purification was necessary judging by the ^{1}H and ^{13}C NMR analysis of the crude reaction mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.77 (m, 3H), 7.67 (s, 1H),

7.51 – 7.43 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 1H), 4.73 (d, *J* = 4.0 Hz, 1H), 4.00 (dd, *J* = 12.7, 8.2 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.49 – 2.41 (m, 2H), 2.14 – 1.98 (m, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 216.2, 134.8, 133.3, 132.4, 128.0, 127.7, 127.5, 126.5, 126.3, 125.9, 125.6, 70.3, 51.2, 50.7, 38.9, 7.3, 3.3. IR (FTIR, cm^{-1}): $\tilde{\nu}$ = 3463, 2952, 2933, 2899, 2873, 1697, 1415, 1242, 1115, 1011, 802, 740. HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{29}O_2Si$: 341.1937; found: 341.1934.

Synthesis of 5-(4-chlorophenyl)-2-(dimethyl(phenyl)silyl)-3-hydroxycyclopentan-1-one (4.8g)

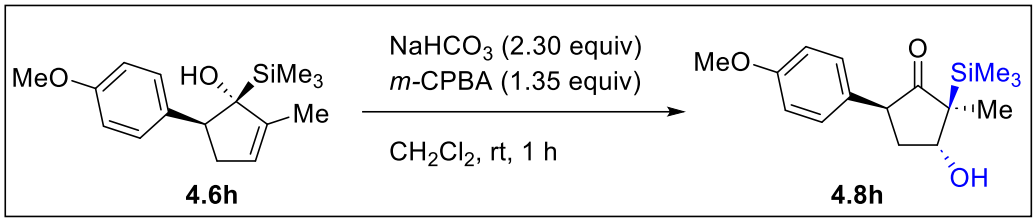


Applying general procedure H to $NaHCO_3$, (174 mg, 2.07 mmol, 2.30 equiv.), 5-(4-chlorophenyl)-1-(dimethyl(phenyl)silyl)cyclopent-2-en-1-ol **4.6g** (296 mg, 0.9 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 274 mg, 1.22 mmol, 1.35 equiv.), and DCM (10 mL) afforded 307 mg, 0.99 mmol (99% crude yield) of **4.8g** as a white solid. Attempted further purification by column chromatography, R_f = 0.6 (50% EtOAc in hexanes) led to some of the product to undergo epimerization at the carbon bearing the silyl group followed by subsequent Peterson olefination.

Spectroscopic data for **4.8g**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 – 7.40 (m, 3H), 7.38 – 7.32 (m, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 4.68 (d, *J* = 3.6 Hz, 1H), 3.70 (dd, *J* = 12.7, 8.1 Hz, 1H), 2.47 (dd, *J* = 3.0, 1.5 Hz, 1H), 2.29 (dddd, *J* = 13.5, 8.2, 3.0, 1.3 Hz, 1H), 1.95 (td, *J* = 13.1, 4.1 Hz, 1H), 1.55 (s, 1H), 0.49 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 215.1, 135.4, 135.3, 134.0, 132.5, 130.0, 129.3, 128.4, 128.3, 70.3, 53.6, 50.7, 38.3, -3.2, -3.6. IR (FTIR, cm^{-1}): $\tilde{\nu}$ = 3426, 2957, 1708, 1491, 1250, 1044, 789, 699. MS (GC/MS): *m*/z (%) = 344 (0.02) $[M]^+$,271 (100), 193 (90), 89 (35).

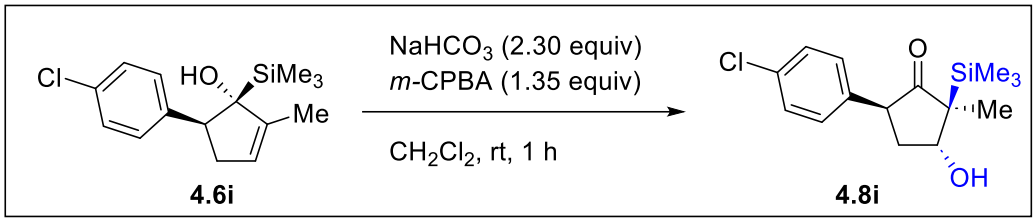
Spectroscopic data for **4.12g** (Peterson olefination product): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (dt, *J* = 5.6, 2.7 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.30 (dt, *J* = 5.7, 2.1 Hz, 1H), 3.53 (dd, *J* = 7.0, 2.6 Hz, 1H), 3.26 (ddt, *J* = 19.6, 7.1, 2.5 Hz, 1H), 2.78 (dq, *J* = 19.6, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 209.1, 164.1, 137.6, 133.4, 133.0, 132.8, 132.5, 50.1, 38.5. MS (GC/MS): *m*/z (%) = 192 (0.1) $[M]^+$, 178 (100), 115 (65), 75 (75).

Synthesis 3-hydroxy-5-(4-methoxyphenyl)-2-methyl-2-(trimethylsilyl)cyclopentan-1-one (4.8h)



Applying general procedure H to $NaHCO_3$, (135 mg, 1.61 mmol, 2.30 equiv.), 5-(4-methoxyphenyl)-2-methyl-1-(trimethylsilyl)cyclopent-2-en-1-ol **4.6h** (194 mg, 0.7 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 212 mg, 0.91 mmol, 1.35 equiv.), and DCM (10 mL) afforded after column chromatography, R_f = 0.5 (40% EtOAc in hexanes) 194 mg, 0.67 mmol (95% isolated yield) of **4.8h** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.21 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.55 (d, *J* = 3.9 Hz, 1H), 3.78 (s, 3H), 3.71 (dd, *J* = 12.6, 8.5 Hz, 1H), 2.48 (ddd, *J* = 13.7, 8.6, 1.3 Hz, 1H), 2.36 (ddd, *J* = 13.5, 12.6, 4.2 Hz, 1H), 1.93 (s, 1H), 1.29 (s, 3H), 0.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 218.6, 158.3, 129.1, 128.7, 113.8, 72.4, 55.2, 50.6, 49.4, 36.8, 13.8, -2.3. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{16}H_{25}O_3Si$: 293.1573; found: 293.1567.

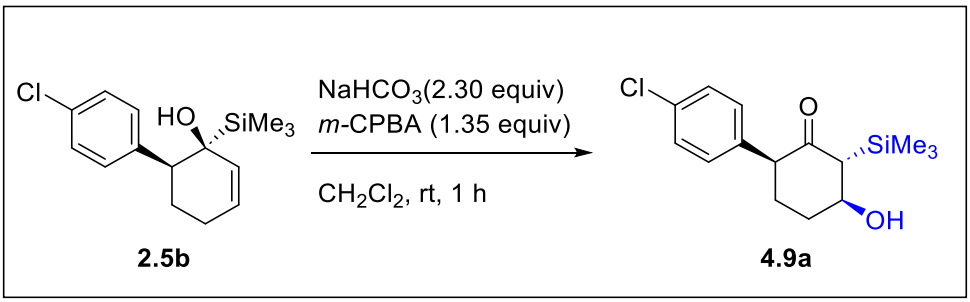
Synthesis of 5-(4-chlorophenyl)-3-hydroxy-2-methyl-2-(trimethylsilyl)cyclopentan-1-one (4.8i)



4.6i **4.8i**

Applying general procedure H to $NaHCO_3$, (212 mg, 2.53 mmol, 2.30 equiv.), 5-(4-chlorophenyl)-2-methyl-1-(trimethylsilyl)cyclopent-2-en-1-ol **4.6i** (309 mg, 1.1 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 333 mg, 1.49 mmol, 1.35 equiv.), and DCM (10 mL) afforded 321 mg, 1.08 mmol (98% crude yield) of **4.8i** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 4.56 (d, *J* = 3.9 Hz, 1H), 3.74 (dd, *J* = 12.6, 8.5 Hz, 1H), 2.51 (ddd, *J* = 13.6, 8.5, 1.2 Hz, 1H), 2.36 (ddd, *J* = 13.5, 12.6, 4.2 Hz, 1H), 1.78 (s, 1H), 1.29 (s, 3H), 0.04 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 217.6, 135.4, 132.5, 129.0, 128.5, 72.3, 50.9, 49.3, 36.4, 13.7, -2.3. IR (FTIR, cm^{-1}): $\tilde{\nu}$ = 3435, 2975, 2953, 2895, 1696, 1487, 1444, 1405, 1251, 1012, 836, 820. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{22}ClO_2Si$: 297.1078; found: 297.1077.

Synthesis of 6-(4-chlorophenyl)-3-hydroxy-2-(trimethylsilyl)cyclohexan-1-one (4.9a)

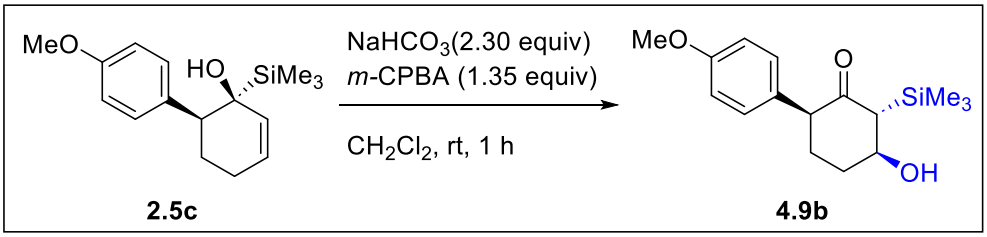


2.5b **4.9a**

Applying general procedure H to $NaHCO_3$, (193 mg, 2.3 mmol, 2.30 equiv.), 4'-chloro-2-(trimethylsilyl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-2-ol **2.5b** (281 mg, 1.0 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 303 mg, 1.35 mmol, 1.35 equiv.), and DCM (10 mL) afforded after workup and recrystallization (50% EtOAc in hexanes) 321 mg, 0.93 mmol (93% crude yield) of **4.9a** as white

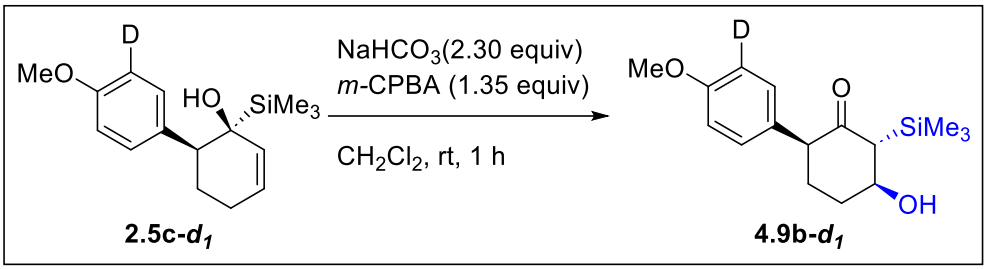
crystals. The crystal structure of compound **4.9a** was solved by X-ray crystallography and the results deposited to the Cambridge Crystallographic Data Centre and assigned CCDC 1890864. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.53 (dq, *J* = 3.3, 1.6 Hz, 1H), 3.32 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.62 (t, *J* = 2.0 Hz, 1H), 2.53 – 2.42 (m, 1H), 2.11 – 1.97 (m, 3H), 1.95 (s, 1H), 0.18 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 208.8, 137.8, 132.6, 130.1, 128.5, 70.3, 57.1, 56.6, 30.8, 28.0, -1.4.

Synthesis of 3-hydroxy-6-(4-methoxyphenyl)-2-(trimethylsilyl)cyclohexan-1-one (4.9b)



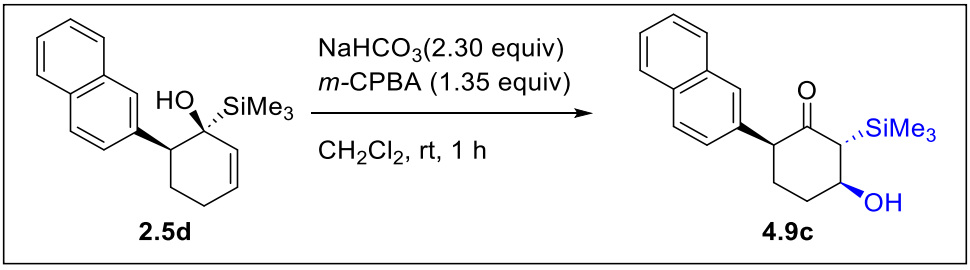
Applying general procedure H to $NaHCO_3$, (58 mg, 0.7 mmol, 2.30 equiv.), 6-(methoxyphenyl-2-yl)-1-(trimethylsilyl)cyclohex-2-en-1-ol (**2.5c**), *dr* = 2:1, (83 mg, 0.3 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 92 mg, 0.4 mmol, 1.35 equiv.), and DCM (5 mL) afforded after workup 89 mg (quantitative crude yield) of **4.9b** as a mixture of diastereomers (*dr* = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.90 – 6.83 (m, 4H), 4.53 (h, *J* = 1.5 Hz, 1H), 4.27 (dt, *J* = 5.8, 4.1 Hz, 1H), 3.79 (s, 3H), 3.79 (s, 3H), 3.67 (dd, *J* = 8.0, 6.3 Hz, 1H), 3.30 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.62 (t, *J* = 1.9 Hz, 1H), 2.52 – 2.43 (m, 1H), 2.38 (dt, *J* = 4.6, 1.4 Hz, 1H), 2.37 – 2.30 (m, 1H), 2.20 – 2.12 (m, 1H), 2.12 – 1.85 (m, 7H), 0.18 (s, 9H), -0.03 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 210.6, 209.5, 158.5, 158.4, 131.4, 129.9, 129.7, 129.1, 113.84, 113.77, 70.5, 70.2, 57.1, 56.4, 55.22, 55.20, 54.4, 52.9, 31.0, 30.6, 28.2, 24.3, -1.37, -1.4. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{16}H_{25}O_3Si$: 293.1573; found: 293.1571.

Synthesis of 3-hydroxy-6-(4-methoxyphenyl-3-*d*)-2-(trimethylsilyl)cyclohexan-1-one (4.9b-*d*$_1$)



Applying general procedure H to $NaHCO_3$, (135 mg, 1.6 mmol, 2.30 equiv.), 4'-methoxy-2-(trimethylsilyl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3'-*d*-2-ol (**2.5c-*d*$_1$**), *dr* = 12:1, (194 mg, 0.7 mmol, 1.0 equiv), *m*-CPBA (77% w/w, 212 mg, 0.95 mmol, 1.35 equiv.), and DCM (10 mL) afforded after workup 199 mg, 0.679 mmol (97% crude yield) of **4.9b-*d*$_1$**, *dr* = 12:1. A portion of the crude material was recrystallized in a mixture of hexanes and EtOAc (1:1) to give a single diastereomer of **4.9b-*d*$_1$**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.05 (dq, *J* = 4.4, 2.3 Hz, 2H), 6.87 (d, *J* = 9.1 Hz, 1H), 4.52 (dq, *J* = 3.3, 1.5 Hz, 1H), 3.79 (s, 3H), 3.30 (dd, *J* = 13.2, 5.3 Hz, 1H), 2.62 (t, *J* = 2.0 Hz, 1H), 2.55 – 2.41 (m, 1H), 2.23 – 1.93 (m, 4H), 0.18 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 209.6, 158.3, 131.4, 129.7, 129.6, 113.8, 70.4, 57.1, 56.4, 55.2, 30.9, 28.2, -1.4. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = 2.24. HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{24}DO_3Si$: 294.1630; found: 294.1628.

Synthesis of 3-hydroxy-6-(naphthalen-2-yl)-2-(trimethylsilyl)cyclohexan-1-one (4.9c)



Applying general procedure H to $NaHCO_3$, (155 mg, 1.84 mmol, 2.30 equiv.), 6-(naphthalen-2-yl)-1-(trimethylsilyl)cyclohex-2-en-1-ol (**2.5d**), *dr* = 4:1, (237 mg, 0.8 mmol, 1.0 equiv), *m*-

CPBA (77% w/w, 242 mg, 1.08 mmol, 1.35 equiv.), and DCM (10 mL) afforded after workup 242 mg, 0.784 mmol (98% crude yield) of **4.9c** as a mixture of diastereomers (*dr* = 4:1). A portion of the crude material was recrystallized in a mixture of ethyl acetate and hexanes (1:1). The resulting crystals were for the major diastereomer which crushed out as brown crystals of a single diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 – 7.75 (m, 3H), 7.59 (s, 1H), 7.49 – 7.41 (m, 2H), 7.28 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.57 (t, *J* = 2.2 Hz, 1H), 3.53 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.67 (d, *J* = 1.8 Hz, 1H), 2.62 (td, *J* = 12.9, 4.6 Hz, 1H), 2.18 – 2.02 (m, 3H), 1.88 (s, 1H), 0.22 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 209.1, 137.1, 133.5, 132.6, 127.8, 127.7, 127.6, 127.23, 127.19, 125.8, 125.5, 70.5, 57.4, 57.2, 30.9, 28.1, -1.3. IR (FTIR, cm^{-1}): $\tilde{\nu}$ = 3434, 3055, 3021, 2938, 2923, 2882, 2863, 1665, 1336, 1287, 1251, 1147, 1074, 956, 836, 740. HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{25}O_2Si$: 313.1624; found: 313.1623.

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APPENDIX

Crystallographic document of 4.8a′

Crystal structure of crystal provided hydrogen atom on the Oxygen atom was found and refined isotropically.

Crystal data and experimental

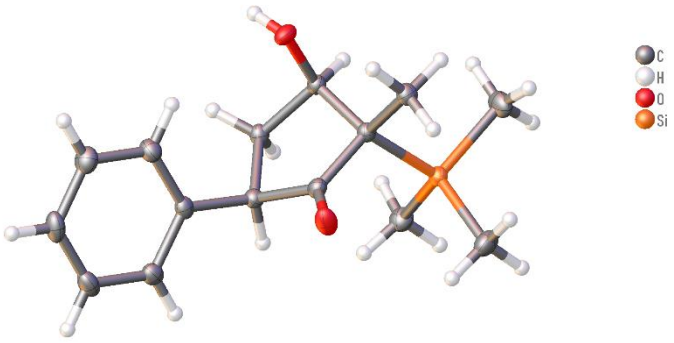


Figure 4.1: Crystal structure of compound **4.8a′**

Experimental. Single colourless block-shaped crystals of **4.8a′** used as received. A suitable crystal with dimensions 0.29 × 0.19 × 0.04 mm^3 was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 99.99(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov *et al.*, 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal data. $C_{15}H_{22}O_2Si$, M_r = 262.41, monoclinic, $P2_1/n$ (No. 14), a = 6.40749(6) Å, b = 23.6316(2) Å, c = 9.64907(10) Å, b = 93.6810(8)°, a = g = 90°, V = 1458.04(2) $Å^3$, T = 99.99(10) K, Z = 4, Z' = 1, m(Cu K_a) = 1.355, 14998 reflections measured, 2900 unique (R_{int} = 0.0328) which were used in all calculations. The final wR_2 was 0.0844 (all data) and R_1 was 0.0324 (I≥2 s(I)).

Table 4.2: Crystal data

Compound	**4.8a′**
Formula	$C_{15}H_{22}O_2Si$
CCDC	2158501
$D_{calc.}$/ g cm^{-3}	1.195
m/mm^{-1}	1.355
Formula Weight	262.41
Color	colourless
Shape	block-shaped
Size/mm^3	0.29×0.19×0.04
T/K	99.99(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	6.40749(6)
b/Å	23.6316(2)
c/Å	9.64907(10)
a/°	90
b/°	93.6810(8)
g/°	90
V/Å^3	1458.04(2)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_a$
Q_{min}/°	3.741
Q_{max}/°	77.169
Measured Refl's.	14998
Indep't Refl's	2900
Refl's I≥2 s(I)	2729
R_{int}	0.0328
Parameters	171
Restraints	0
Largest Peak	0.359
Deepest Hole	-0.263
GooF	1.054
wR_2 (all data)	0.0844
wR_2	0.0828
R_1 (all data)	0.0342
R_1	0.0324

Structure quality indicators

Reflections:	d min (Cu\a) 2Θ=154.3° 0.79	I/σ(I) 44.6	Rint 3.28%	Full 135.4° 94% to 154.3° 100
Refinement:	Shift 0.001	Max Peak 0.4	Min Peak -0.3	GooF 1.054

Figure 4.2: Structure quality indicators

A colourless block-shaped-shaped crystal with dimensions 0.29×0.19×0.04 mm^3 was mounted on a nylon loop with paratone oil. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 99.99(10) K.

MSU Data were measured using *w* scans using Cu K_a radiation (micro-focus sealed X-ray tube, 50 kV, 1 mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.41.123a (Rigaku OD, 2022). The achieved resolution was Q = 77.169.

Cell parameters were retrieved using the CrysAlisPro 1.171.41.123a (Rigaku OD, 2022) software and refined using CrysAlisPro 1.171.41.123a (Rigaku OD, 2022) on 9207 reflections, 61 % of the observed reflections. Data reduction was performed using the CrysAlisPro 1.171.41.123a (Rigaku OD, 2022) software which corrects for Lorentz polarization. The final completeness is 100.00 out to 77.169 in Q CrysAlisPro 1.171.41.123a (Rigaku Oxford Diffraction, 2022) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

The structure was solved in the space group $P2_1/n$ (# 14) by using dual methods using the ShelXT (Sheldrick, 2015) structure solution program. The structure was refined by Least Squares ShelXL incorporated in Olex2 software program. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the hydrogen atom on the non-carbon atom(s) which were found by difference Fourier methods and refined isotropically when data permits.

CCDC 2158501 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

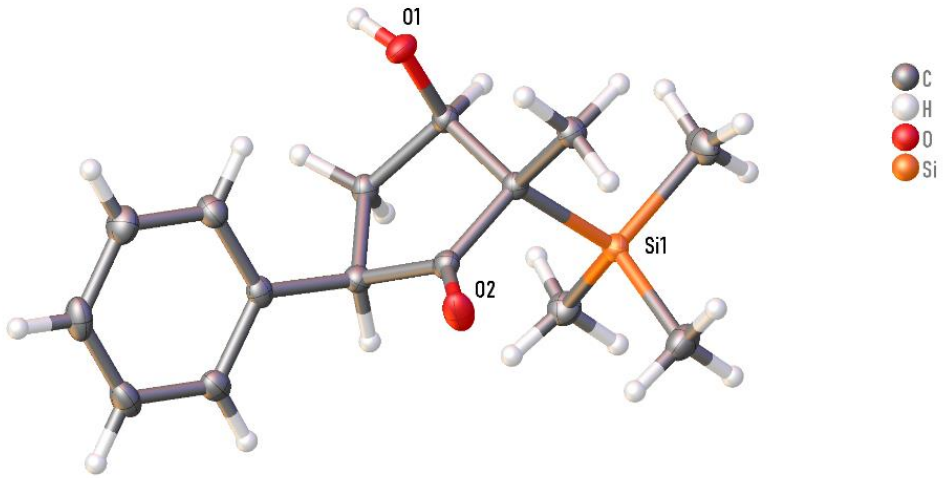


Figure 4.3: Drawing of molecule **4.8a′** with labeled heteroatoms

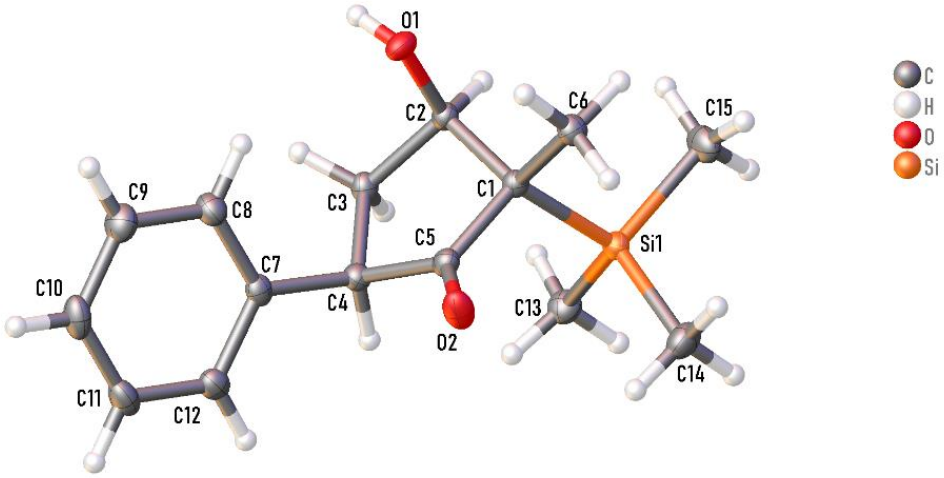


Figure 4.4: Drawing of molecule **4.8a′** with labeling scheme. although crystal is in the Centro-symmetric space group. Model has Chirality at C1 S, Model has Chirality at C2 (Centro SPGR) R; Model has Chirality at C4 (Centro SPGR) R Verify

Figure 4.5: The following hydrogen bonding interactions with a maximum D-D distance of 3.1 Å and a minimum angle of 110 ˚ are present in **4.8a′**: O1–O2_*1: 2.766 Å*

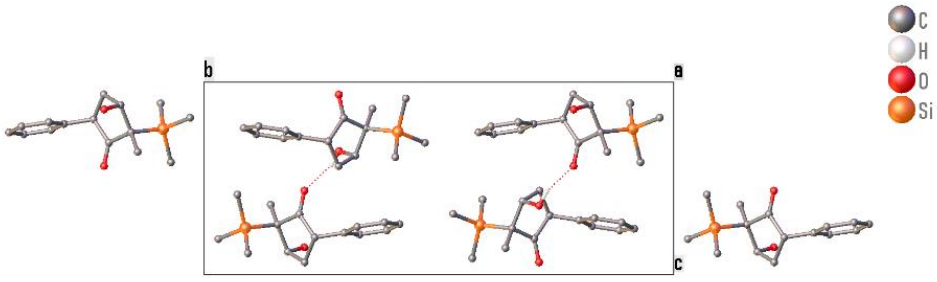


Figure 4.6: Packing diagram of **4.8a′**

Data Plots: Diffraction Data

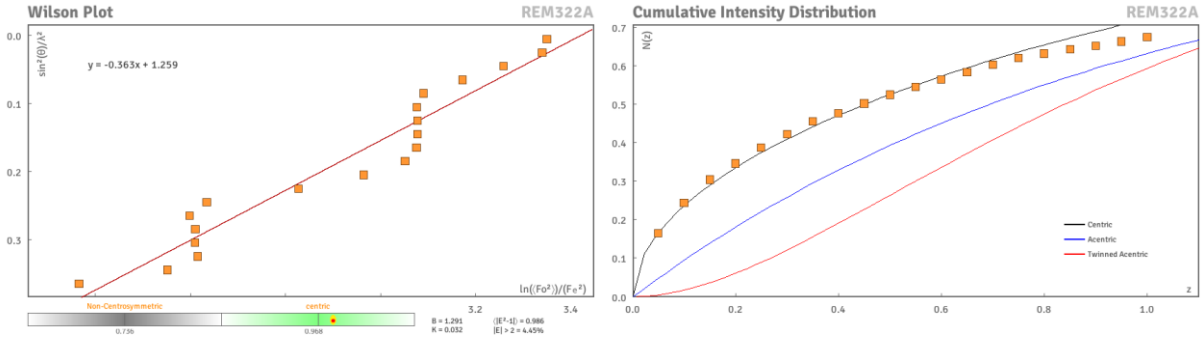
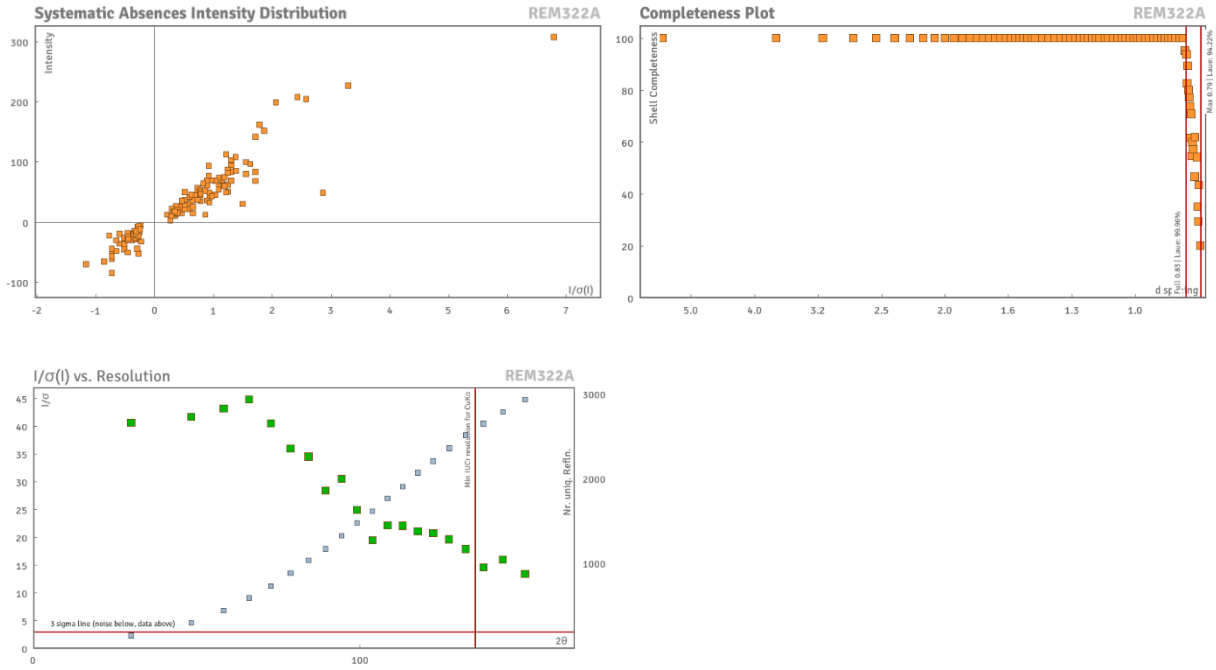


Figure 4.7: Data plots: Diffraction data

Figure 4.7 (cont'd)



Data plots: Refinement and data

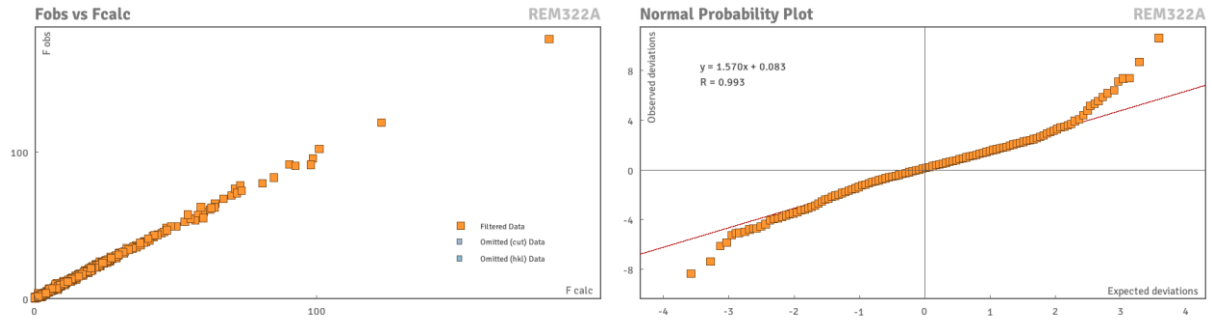


Figure 4.8: Data plots: Refinement and data

Table 4.3: Reflection statistics

Total reflections (after filtering)	15216	Unique reflections	2900
Completeness	0.942	Mean I/*s*	28.51
hkl_{max} collected	(3, 28, 12)	hkl_{min} collected	(-7, -28, -11)
hkl_{max} used	(7, 28, 12)	hkl_{min} used	(-7, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	11.82	d_{min} used	0.79
Friedel pairs	1065	Friedel pairs merged	1
Inconsistent equivalents	1	R_{int}	0.0328
R_{sigma}	0.0224	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(2746, 1774, 1016, 548, 292, 196, 88, 39, 12, 1)	Maximum multiplicity	17
Removed systematic absences	218	Filtered off (Shel/OMIT)	0

Selected crystal pictures

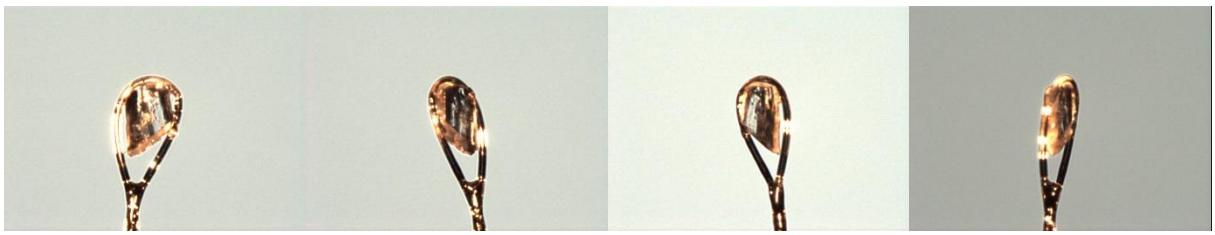


Figure 4.9: Selected crystal pictures

Table 4.4: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4.8a′**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}

Atom	x	y	z	U_{eq}
Si1	5412.1(5)	5875.8(2)	2579.5(3)	16.40(11)
O1	1373.5(13)	7131.8(4)	3587.1(10)	19.4(2)
O2	5249.2(15)	7133.1(4)	641.8(9)	25.0(2)
C1	3755.8(17)	6557.1(5)	2397.3(12)	14.4(2)
C2	3185.8(17)	6783.0(5)	3819.5(12)	15.0(2)
C3	5083.5(18)	7140.1(5)	4360.9(12)	16.3(2)
C4	6153.3(18)	7355.3(5)	3070.5(12)	16.2(2)
C5	5059.6(18)	7028.5(5)	1861.9(12)	16.2(2)
C6	1877.2(18)	6417.1(5)	1378.6(13)	18.2(3)
C7	6148.2(18)	7987.9(5)	2829.4(12)	16.5(2)
C8	4333.8(19)	8310.1(5)	2918.8(14)	21.1(3)
C9	4372(2)	8891.3(6)	2701.3(14)	24.4(3)
C10	6212(2)	9157.6(6)	2383.6(14)	25.2(3)
C11	8012(2)	8841.1(6)	2295.0(13)	23.7(3)
C12	7983.4(19)	8260.2(5)	2515.9(12)	19.3(3)
C13	7676(2)	5928.8(6)	3893.8(14)	22.7(3)
C14	6373(2)	5707.3(6)	841.9(14)	26.3(3)
C15	3645(2)	5300.8(6)	3150.7(16)	28.2(3)

Table 4.5: Anisotropic displacement parameters ($\times 10^4$) for **4.8a′**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	16.73(18)	13.66(18)	18.89(19)	-0.61(12)	1.90(12)	0.52(11)
O1	16.9(4)	21.6(5)	19.9(5)	-4.7(4)	2.3(3)	3.4(3)
O2	37.6(5)	21.8(5)	16.3(5)	0.0(4)	6.7(4)	-8.8(4)
C1	15.4(5)	14.1(6)	13.8(5)	0.3(4)	0.8(4)	-0.2(4)
C2	15.9(5)	14.0(6)	15.4(6)	-0.1(4)	1.7(4)	0.7(4)
C3	19.2(6)	14.7(6)	15.0(6)	-0.1(4)	-0.3(4)	-0.8(4)
C4	15.0(5)	15.9(6)	17.5(6)	-0.5(4)	0.9(4)	-0.5(4)
C5	17.6(5)	13.9(6)	17.2(6)	-0.1(4)	3.0(4)	1.2(4)
C6	18.6(6)	18.8(6)	16.9(6)	-0.8(5)	-0.9(4)	-1.2(4)
C7	20.1(6)	15.9(6)	13.2(5)	-1.1(4)	-1.0(4)	-2.3(4)
C8	19.7(6)	19.1(6)	24.2(6)	0.8(5)	-0.7(5)	-1.8(5)
C9	27.4(7)	19.7(7)	25.6(7)	0.8(5)	-1.6(5)	3.7(5)
C10	39.4(8)	15.0(6)	20.7(6)	0.9(5)	-1.4(5)	-4.2(5)
C11	29.5(7)	21.7(7)	20.2(6)	-0.4(5)	3.3(5)	-9.6(5)
C12	21.2(6)	21.2(6)	15.7(6)	-1.6(5)	2.2(4)	-3.0(5)
C13	21.2(6)	21.9(7)	24.8(7)	0.7(5)	-0.7(5)	3.9(5)
C14	26.8(7)	26.7(7)	25.4(7)	-6.6(5)	2.7(5)	4.9(5)
C15	26.7(7)	17.0(6)	41.1(8)	4.5(6)	2.8(6)	-1.1(5)

Table 4.6: Bond lengths in Å for **4.8a′**

Atom	Atom	Length/Å
Si1	C1	1.9302(12)
Si1	C13	1.8689(13)
Si1	C14	1.8659(14)
Si1	C15	1.8741(14)
O1	C2	1.4299(14)
O2	C5	1.2167(15)
C1	C2	1.5381(16)
C1	C5	1.5037(16)
C1	C6	1.5404(16)
C2	C3	1.5433(16)
C3	C4	1.5455(16)
C4	C5	1.5305(16)
C4	C7	1.5130(16)
C7	C8	1.3970(17)
C7	C12	1.3906(17)
C8	C9	1.3898(19)
C9	C10	1.388(2)
C10	C11	1.382(2)
C11	C12	1.3896(19)

Table 4.7: Bond angles in ° for **4.8a′**

Atom	Atom	Atom	Angle/°
C13	Si1	C1	113.84(5)
C13	Si1	C15	107.84(6)
C14	Si1	C1	107.91(6)
C14	Si1	C13	109.72(6)
C14	Si1	C15	110.49(7)
C15	Si1	C1	107.01(6)
C2	C1	Si1	111.65(8)
C2	C1	C6	115.04(9)
C5	C1	Si1	109.57(8)
C5	C1	C2	102.61(9)
C5	C1	C6	111.63(10)
C6	C1	Si1	106.34(8)
O1	C2	C1	107.29(9)
O1	C2	C3	110.62(9)
C1	C2	C3	105.35(9)
C2	C3	C4	106.72(9)
C5	C4	C3	104.05(9)
C7	C4	C3	116.90(10)
C7	C4	C5	112.64(10)
O2	C5	C1	125.11(11)
O2	C5	C4	124.44(11)
C1	C5	C4	110.44(10)
C8	C7	C4	121.51(11)
C12	C7	C4	119.81(11)
C12	C7	C8	118.68(12)
C9	C8	C7	120.43(12)
C10	C9	C8	120.33(13)
C11	C10	C9	119.50(12)
C10	C11	C12	120.38(12)
C11	C12	C7	120.68(12)

Table 4.8: Torsion angles in ° for **4.8a′**

Atom	Atom	Atom	Atom	Angle/°
Si1	C1	C2	O1	-157.81(7)
Si1	C1	C2	C3	84.30(9)
Si1	C1	C5	O2	88.25(13)
Si1	C1	C5	C4	-90.80(10)
O1	C2	C3	C4	-88.74(11)
C1	C2	C3	C4	26.88(12)
C2	C1	C5	O2	-153.01(12)
C2	C1	C5	C4	27.94(11)
C2	C3	C4	C5	-9.65(12)
C2	C3	C4	C7	115.23(11)
C3	C4	C5	O2	169.31(11)
C3	C4	C5	C1	-11.63(12)
C3	C4	C7	C8	-46.77(16)
C3	C4	C7	C12	132.98(11)
C4	C7	C8	C9	179.60(12)
C4	C7	C12	C11	-179.81(11)
C5	C1	C2	O1	84.93(10)
C5	C1	C2	C3	-32.97(11)
C5	C4	C7	C8	73.66(14)
C5	C4	C7	C12	-106.58(12)
C6	C1	C2	O1	-36.50(13)
C6	C1	C2	C3	-154.39(10)
C6	C1	C5	O2	-29.28(16)
C6	C1	C5	C4	151.67(10)
C7	C4	C5	O2	41.74(16)
C7	C4	C5	C1	-139.20(10)
C7	C8	C9	C10	0.4(2)
C8	C7	C12	C11	-0.04(18)
C8	C9	C10	C11	-0.5(2)
C9	C10	C11	C12	0.3(2)
C10	C11	C12	C7	-0.02(19)
C12	C7	C8	C9	-0.16(18)

Table 4.9: Hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4.8a′**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}

Atom	**x**	**y**	**z**	U_{eq}
H1	1160(30)	7293(8)	4300(20)	37(5)
H2	2918.1	6465.78	4470.56	18
H3A	6066.73	6906.39	4951.14	20
H3B	4620.53	7462.89	4918.67	20
H4	7644.54	7228.26	3159.86	19
H6A	2378.83	6319.69	470.41	27
H6B	950.92	6746.65	1282.43	27
H6C	1106.54	6095.74	1734.89	27
H8	3065.66	8130.8	3129.68	25
H9	3132.55	9107.3	2770.38	29
H10	6233.34	9554.51	2228.3	30
H11	9276.76	9021.76	2081.83	28
H12	9230.1	8046.79	2452.04	23
H13A	8530.96	5585.71	3860.43	34
H13B	7158.42	5969.13	4822.53	34
H13C	8526.92	6259.24	3687.77	34
H14A	7187.58	6027.02	520.06	39
H14B	5177.97	5637.08	178.99	39
H14C	7259.43	5369.18	914.01	39
H15A	4479.27	4966.18	3419.7	42
H15B	2630.72	5202.86	2384.79	42
H15C	2901.18	5432.54	3946.23	42

Table 4.10: Hydrogen bond information for **4.8a′**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	O2[1]	0.81(2)	1.99(2)	2.7659(13)	161.8(19)

[1]-1/2+x,3/2-y,1/2+z

Citations

CrysAlisPro (Rigaku, V1.171.41.123a, 2022)

CrysAlisPro (ROD), Rigaku Oxford Diffraction, Poland (?).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

Crystallographic document of 4.9a

Structure from thin plate, shows some disorder in the $SiMe_3$ portion, but the stereochemistry of the diastereomer is determined, both enantiomers are present in the crystal.

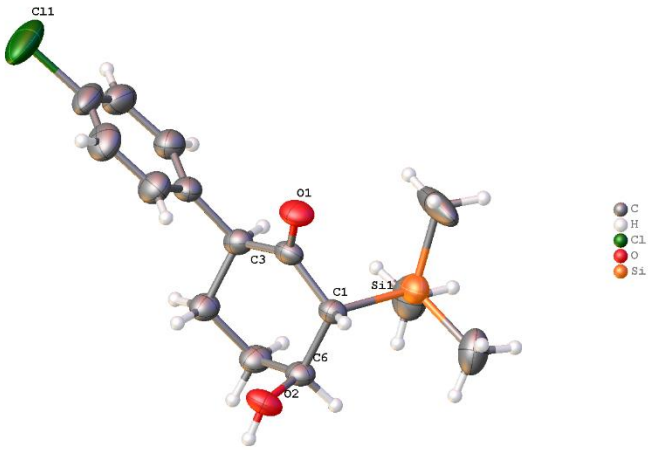


Figure 4.10: Crystal structure of compound **4.9a**

Experimental. Single colourless plate-shaped crystals of **4.9a** were used as received. A suitable crystal 0.34×0.20×0.02 mm^3 was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 173(2) K during data collection. The structure was solved with the XT (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov *et al*., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimization.

Crystal data. $C_{15}H_{21}ClO_2Si$, M_r = 296.86, monoclinic, $P2_1/n$ (No. 14), a = 6.4892(6) Å, b = 22.023(2) Å, c = 11.0546(11) Å, β = 94.8430(10)°, $\alpha = \gamma$ = 90°, V = 1574.2(3) $Å^3$, T = 173(2) K, Z = 4, Z' = 1, $\mu(MoK_\alpha)$ = 0.315, 12974 reflections measured, 2988 unique (R_{int} = 0.0378) which were used in all calculations. The final wR_2 was 0.1393 (all data) and R_1 was 0.0509 (I > 2(I)).

Table 4.11: Crystal data

Compound	**4.9a**
CCDC	1890864
Formula	$C_{15}H_{21}ClO_2Si$
$D_{calc.}$/ g cm^{-3}	1.253
μ/mm^{-1}	0.315
Formula Weight	296.86
Color	colourless
Shape	plate
Size/mm^3	0.34×0.20×0.02
T/K	173(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	6.4892(6)
b/Å	22.023(2)
c/Å	11.0546(11)
α/°	90
β/°	94.8430(10)
γ/°	90
V/Å^3	1574.2(3)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK□
Θ_{min}/°	1.849
Θ_{max}/°	25.703
Measured Refl.	12974
Independent Refl.	2988
Reflections with I > 2(I)	2231
R_{int}	0.0378
Parameters	201
Restraints	0
Largest Peak	0.503
Deepest Hole	-0.384
GooF	1.047
wR_2 (all data)	0.1393
wR_2	0.1267
R_1 (all data)	0.0691
R_1	0.0509

Structure iuality indicators

Reflections:	d min (Mo) 0.82	I/σ 31.4	Rint 3.78%	complete 100%
Refinement:	Shift 0.000	Max Peak 0.5	Min Peak -0.4	GooF 1.047

Figure 4.11: Structure quality indicators

A colourless plate-shaped crystal with dimensions 0.34×0.20×0.02 mm^3 was mounted on a nylon loop with paratone oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 173(2) K.

Data were measured using ϕ and ω scans of -0.50° per frame for 299.33 s using MoK□ radiation (sealed tube, 50 kV, 40 mA). The total number of runs and images was based on the strategy calculation from the program **COSMO** (BRUKER, V1.61, 2009). The actually achieved resolution was Θ = 25.703.

Cell parameters were retrieved using the **SAINT** (Bruker, V8.34A, after 2013) software and refined using **SAINT** (Bruker, V8.34A, after 2013) on 4999 reflections, 39 % of the observed reflections. Data reduction was performed using the **SAINT** (Bruker, V8.34A, after 2013) software which corrects for Lorentz polarization. The final completeness is 100.00 out to 25.703 in □ **SADABS**-2014/5 (Bruker,2014/5) was used for absorption correction. wR_2(int) was 0.0586 before and 0.0488 after correction. The Ratio of minimum to maximum transmission is 0.8603. The □/2 correction factor is 0.00150.

The structure was solved in the space group $P2_1/n$ (# 14) by Intrinsic Phasing using the XT (Sheldrick, 2015) structure solution program. The structure was refined by Least Squares using version 2018/3 of XL (Sheldrick, 2015) incorporated in **Olex2** (Dolomanov *et al.*, 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the Hydrogen atom on the nitrogen atom which was found by difference Fourier methods and refined isotropically.

β CCDC 1890864 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

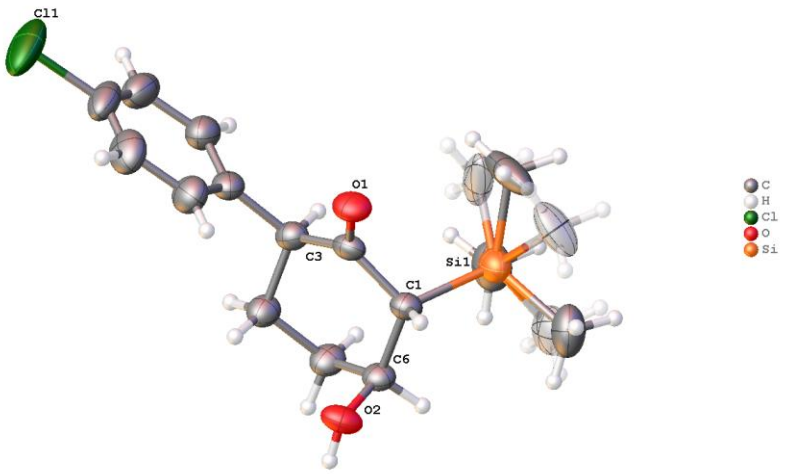


Figure 4.12: Drawing of **4.9a** with representative atoms

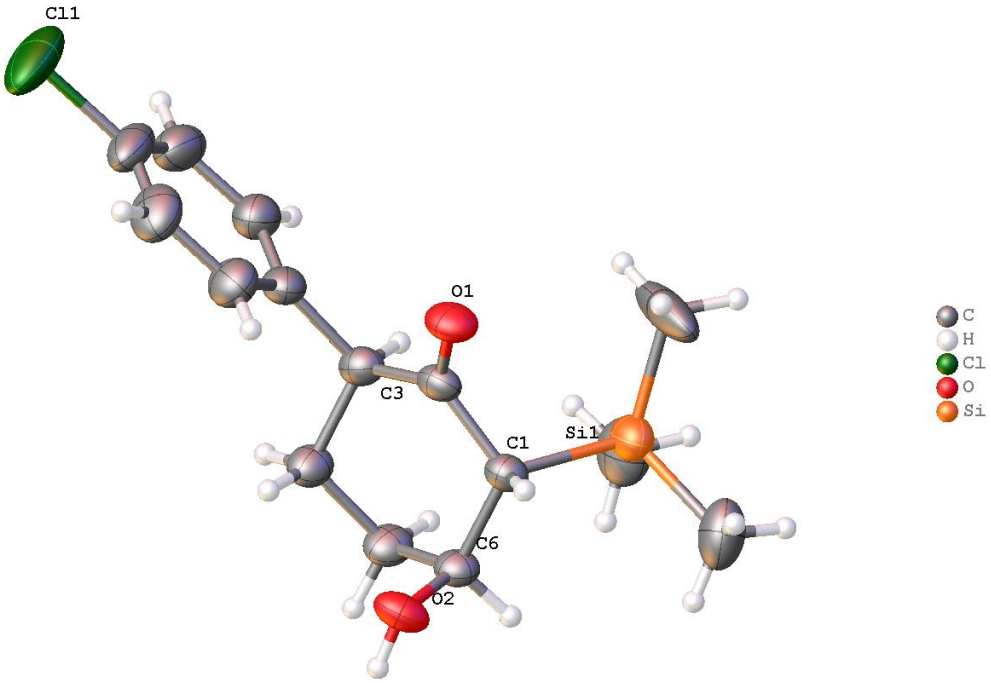


Figure 4.13: Model has Chirality at C1 (Centro SPGR) R Verify; Model has Chirality at C3 (Centro SPGR) S Verify; Model has Chirality at C6 (Centro SPGR) S Verify

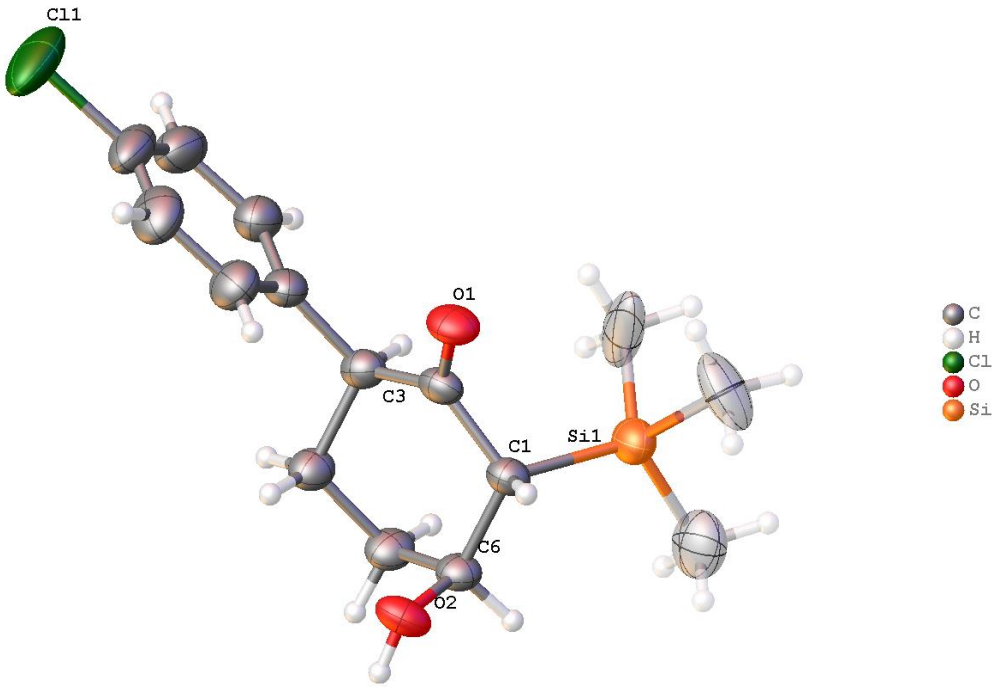


Figure 4.14: Drawing of **4.9a**

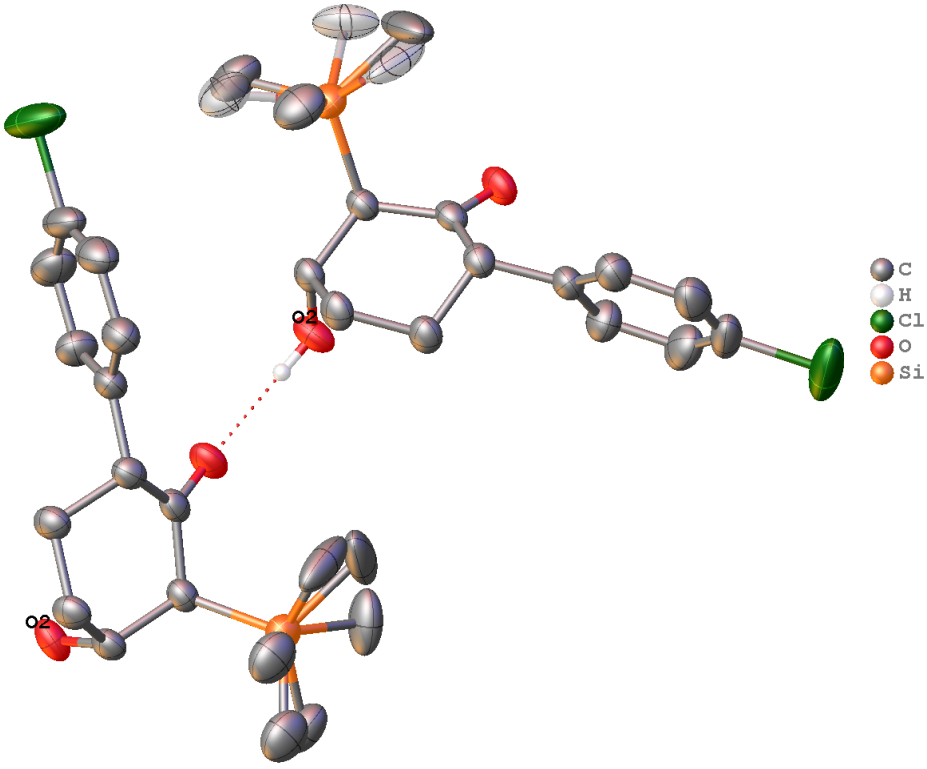


Figure 4.15: The following hydrogen bonding interactions with a maximum D-D distance of 2.9 Å and a minimum angle of 120 ˚ are present in **4.9a**: O2–O1_*1: 2.765 Å*

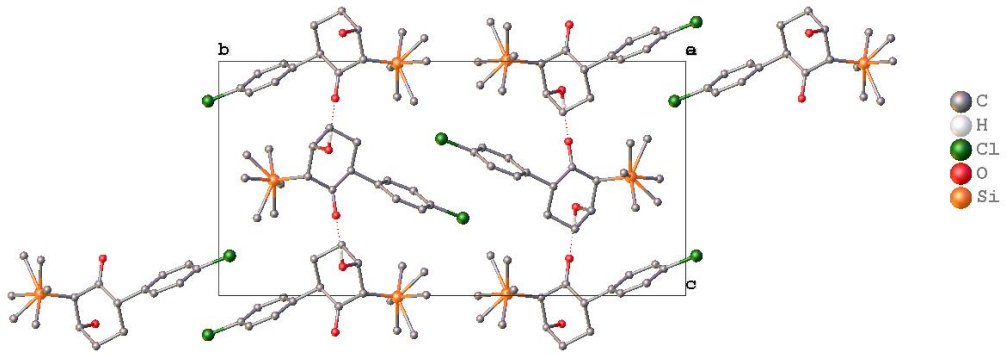


Figure 4.16: Packing diagram of **4.9a**

Data Plots: Diffraction Data

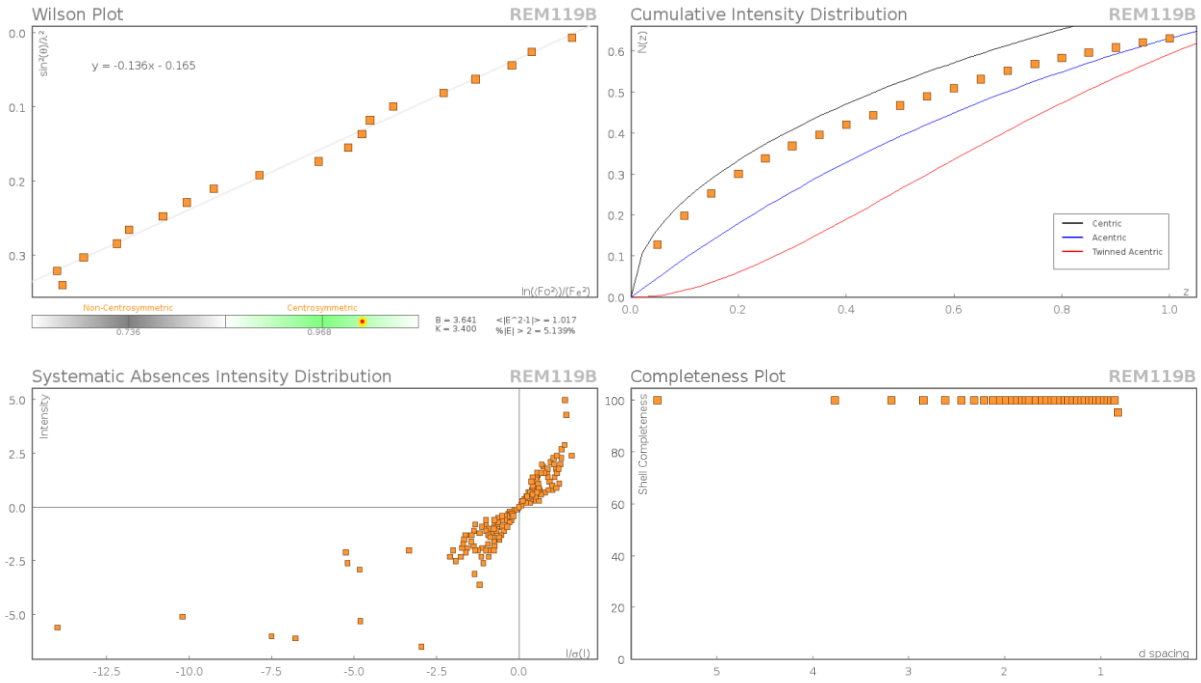


Figure 4.17: Data plots: Diffraction data

Data Plots: Refinement and Data

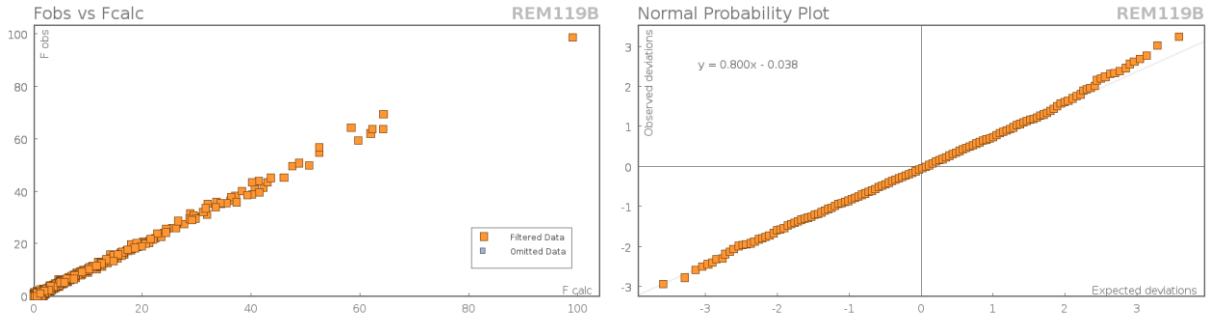


Figure 4.18: Data plots: Refinement and data

Table 4.12: Reflection statistics

Total reflections (after filtering)	13207	Unique reflections	2988
Completeness	1.0	Mean I/σ	15.77
hkl_{max} collected	(7, 26, 13)	hkl_{min} collected	(-7, -26, -13)
hkl_{max} used	(7, 26, 13)	hkl_{min} used	(-7, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	11.02	d_{min} used	0.82
Friedel pairs	5258	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.0378
R_{sigma}	0.0318	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(9289, 1854, 70)	Maximum multiplicity	10
Removed systematic absences	233	Filtered off (Shel/OMIT)	0

Images of the crystal on the diffractometer

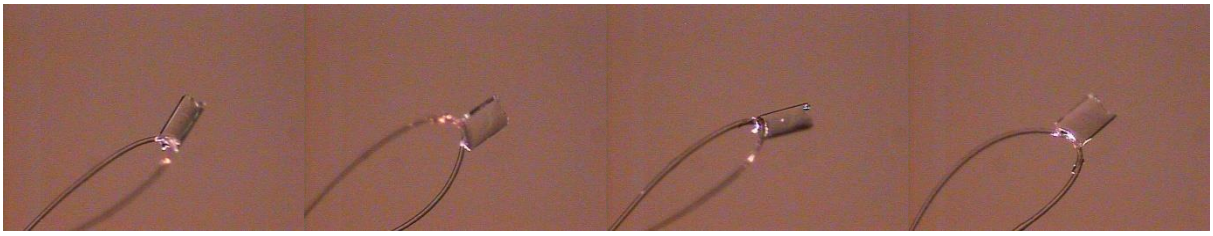


Figure 4.19: Images of the crystal on the diffractometer

Table 4.13: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4.9a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}

Atom	x	y	z	U_{eq}
Cl1	2851(2)	4768.2(4)	6691.2(8)	100.7(4)
Si1	6323.1(11)	8825.0(3)	5073.8(7)	45.7(2)
O1	7102(3)	7491.2(8)	6575.6(13)	43.3(4)
O2	10432(2)	7651.3(8)	3777.8(14)	44.1(4)
C1	7880(3)	8094.2(10)	4911.5(19)	33.5(5)
C2	6865(3)	7568.5(10)	5476.5(19)	33.6(5)
C3	5430(3)	7168.3(10)	4666(2)	35.7(5)
C4	6340(4)	7041.4(11)	3447(2)	39.9(6)
C5	6904(4)	7630.2(11)	2838.0(19)	40.2(6)
C6	8530(3)	7981.9(11)	3626.4(19)	35.3(5)
C7	4784(4)	6583.3(11)	5254(2)	40.3(6)
C8	2744(4)	6391.5(12)	5093(2)	49.2(6)
C9	2146(5)	5831.8(14)	5525(3)	60.2(8)
C10	3595(6)	5471.4(13)	6132(3)	62.5(8)
C11	5619(5)	5644.3(13)	6322(3)	64.0(8)
C12	6215(5)	6204.1(12)	5873(2)	51.8(7)
C13	4312(6)	8926.7(19)	3748(4)	70.7(12)
C13B	6760(20)	9400(6)	3999(15)	70.7(12)
C14	8236(7)	9442.7(18)	4983(4)	73.6(13)
C14B	7290(30)	9181(8)	6693(13)	78(5)
C15	5170(11)	8818(2)	6506(5)	111(3)
C15B	3560(20)	8679(6)	5240(20)	95(7)

Table 4.14: Anisotropic displacement parameters ($\times 10^4$) **4.9a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$\$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	186.6(12)	55.6(5)	61.4(5)	9.1(4)	18.8(6)	-49.9(6)
Si1	55.6(5)	36.3(4)	46.7(4)	3.8(3)	13.4(3)	6.0(3)
O1	50.8(10)	53.2(11)	27.1(8)	7.2(7)	10.3(7)	4.3(8)
O2	39.0(9)	63.8(11)	30.8(8)	-2.8(8)	10.3(7)	7.3(8)
C1	34.6(11)	38.4(12)	28.2(11)	0.5(9)	7.0(9)	1.9(10)
C2	32.7(12)	38.2(12)	31.1(11)	3.6(9)	10.0(9)	8.3(9)
C3	34.8(12)	37.7(13)	35.3(12)	5.0(9)	7.3(9)	2.0(10)
C4	48.4(14)	42.0(14)	29.6(12)	0.5(10)	5.0(10)	-5.6(11)
C5	48.0(14)	46.6(14)	26.0(11)	4.4(10)	3.2(10)	-3.5(11)
C6	40.3(12)	39.8(13)	26.8(11)	4.0(9)	7.8(9)	0.1(10)
C7	49.5(14)	38.4(13)	35.1(12)	1.4(10)	15.8(10)	-0.4(11)
C8	56.7(16)	46.4(15)	45.9(14)	-2.7(12)	13.5(12)	-6.0(12)
C9	72.7(19)	55.9(18)	54.7(17)	-6.2(14)	20.6(15)	-21.2(16)
C10	104(3)	40.7(16)	45.3(16)	-0.6(12)	24.0(16)	-22.8(16)
C11	95(2)	45.4(17)	51.6(17)	13.0(13)	9.1(16)	4.1(16)
C12	61.8(17)	42.7(15)	52.0(15)	10.1(12)	10.2(13)	2.2(12)
C13	67(2)	55(2)	88(3)	2(2)	-2(2)	15.3(19)
C13B	67(2)	55(2)	88(3)	2(2)	-2(2)	15.3(19)
C14	89(3)	42(2)	87(3)	-7(2)	-2(2)	0(2)
C14B	90(11)	83(11)	59(9)	-35(8)	-10(8)	30(9)
C15	187(7)	77(3)	83(4)	21(3)	84(4)	70(4)
C15B	48(8)	33(7)	210(20)	-17(10)	32(11)	2(6)

Table 4.15: Bond lengths in Å for **4.9a**

Atom	Atom	Length/Å
Cl1	C10	1.750(3)
Si1	C1	1.917(2)
Si1	C13	1.892(4)
Si1	C13B	1.776(15)
Si1	C14	1.850(4)
Si1	C14B	2.006(13)
Si1	C15	1.807(4)
Si1	C15B	1.847(13)
O1	C2	1.224(2)
O2	C6	1.431(3)
C1	C2	1.494(3)
C1	C6	1.536(3)
C2	C3	1.518(3)
C3	C4	1.541(3)
C3	C7	1.518(3)
C4	C5	1.520(3)
C5	C6	1.522(3)
C7	C8	1.387(4)
C7	C12	1.386(4)
C8	C9	1.389(4)
C9	C10	1.363(5)
C10	C11	1.366(4)
C11	C12	1.396(4)

Table 4.16: Bond angles in ° for **4.9a**

Atom	Atom	Atom	Angle/°
C1	Si1	C14B	106.5(4)
C13	Si1	C1	111.19(15)
C13B	Si1	C1	114.8(5)
C13B	Si1	C14B	105.2(8)
C13B	Si1	C15B	113.7(8)
C14	Si1	C1	104.54(16)
C14	Si1	C13	107.0(2)
C15	Si1	C1	109.55(16)
C15	Si1	C13	111.7(3)
C15	Si1	C14	112.6(3)
C15B	Si1	C1	112.8(4)
C15B	Si1	C14B	102.4(9)
C2	C1	Si1	110.93(14)
C2	C1	C6	115.28(18)
C6	C1	Si1	114.20(15)
O1	C2	C1	120.0(2)
O1	C2	C3	121.6(2)
C1	C2	C3	118.23(18)
C2	C3	C4	111.10(18)
C7	C3	C2	114.71(19)
C7	C3	C4	111.12(18)
C5	C4	C3	110.92(19)
C4	C5	C6	111.19(18)
O2	C6	C1	105.99(17)
O2	C6	C5	110.94(19)
C5	C6	C1	112.36(18)
C8	C7	C3	119.9(2)
C12	C7	C3	121.7(2)
C12	C7	C8	118.2(2)
C7	C8	C9	121.2(3)
C10	C9	C8	119.0(3)
C9	C10	Cl1	119.3(3)
C9	C10	C11	121.8(3)
C11	C10	Cl1	118.9(3)
C10	C11	C12	118.9(3)
C7	C12	C11	120.9(3)

Table 4.17: Hydrogen fractional atomic Coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4.9a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}

Atom	x	y	z	U_{eq}
H2	10915.64	7610.88	3101.1	66
H1	9203	8159.27	5426.81	40
H3	4136.26	7407.92	4470.65	43
H4A	7589.06	6784.64	3589.99	48
H4B	5314.99	6816.39	2904.89	48
H5A	5649.47	7883.61	2683.25	48
H5B	7441.42	7537.68	2046.5	48
H6	8779.35	8381.02	3232.94	42
H8	1737.16	6647.54	4680.66	59
H9	748.55	5702.08	5398.98	72
H11	6603.92	5387.82	6751.76	77
H12	7620.93	6326.8	5992.76	62
H13A	4992.41	8934.14	2989.88	106
H13B	3573.51	9309.95	3839.56	106
H13C	3327.57	8588.59	3728.08	106
H13D	8255.56	9458.59	3967.81	106
H13E	6132.1	9780.36	4239.55	106
H13F	6147.94	9277.1	3196.09	106
H14A	9210.09	9435.85	5710.1	110
H14B	7518.71	9834.57	4929.13	110
H14C	8992.71	9384.82	4260.84	110
H14D	6986.93	8898.16	7338.5	117
H14E	6576.98	9566.59	6803.47	117
H14F	8786.9	9252.73	6728.92	117
H15A	4045.06	8519.58	6470.27	167
H15B	4620.13	9221.41	6665.2	167
H15C	6220.55	8707.45	7158.11	167
H15D	2887.08	8536.91	4460.84	142
H15E	2892.3	9054.56	5477.09	142
H15F	3426.12	8367.89	5859.76	142

Table 4.18: Hydrogen bond information for **4.9a**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O2	H2	O1[1]	0.84	1.93	2.765(2)	178.2

[1]1/2+x,3/2-y,-1/2+z

Table 4.19: Atomic occupancies for all atoms that are not fully occupied in **4.9a**

Atom	Occupancy
C13	0.776(4)
H13A	0.776(4)
H13B	0.776(4)
H13C	0.776(4)
C13B	0.224(4)
H13D	0.224(4)
H13E	0.224(4)
H13F	0.224(4)
C14	0.776(4)
H14A	0.776(4)
H14B	0.776(4)
H14C	0.776(4)
C14B	0.224(4)
H14D	0.224(4)
H14E	0.224(4)
H14F	0.224(4)
C15	0.776(4)
H15A	0.776(4)
H15B	0.776(4)
H15C	0.776(4)
C15B	0.224(4)
H15D	0.224(4)
H15E	0.224(4)
H15F	0.224(4)

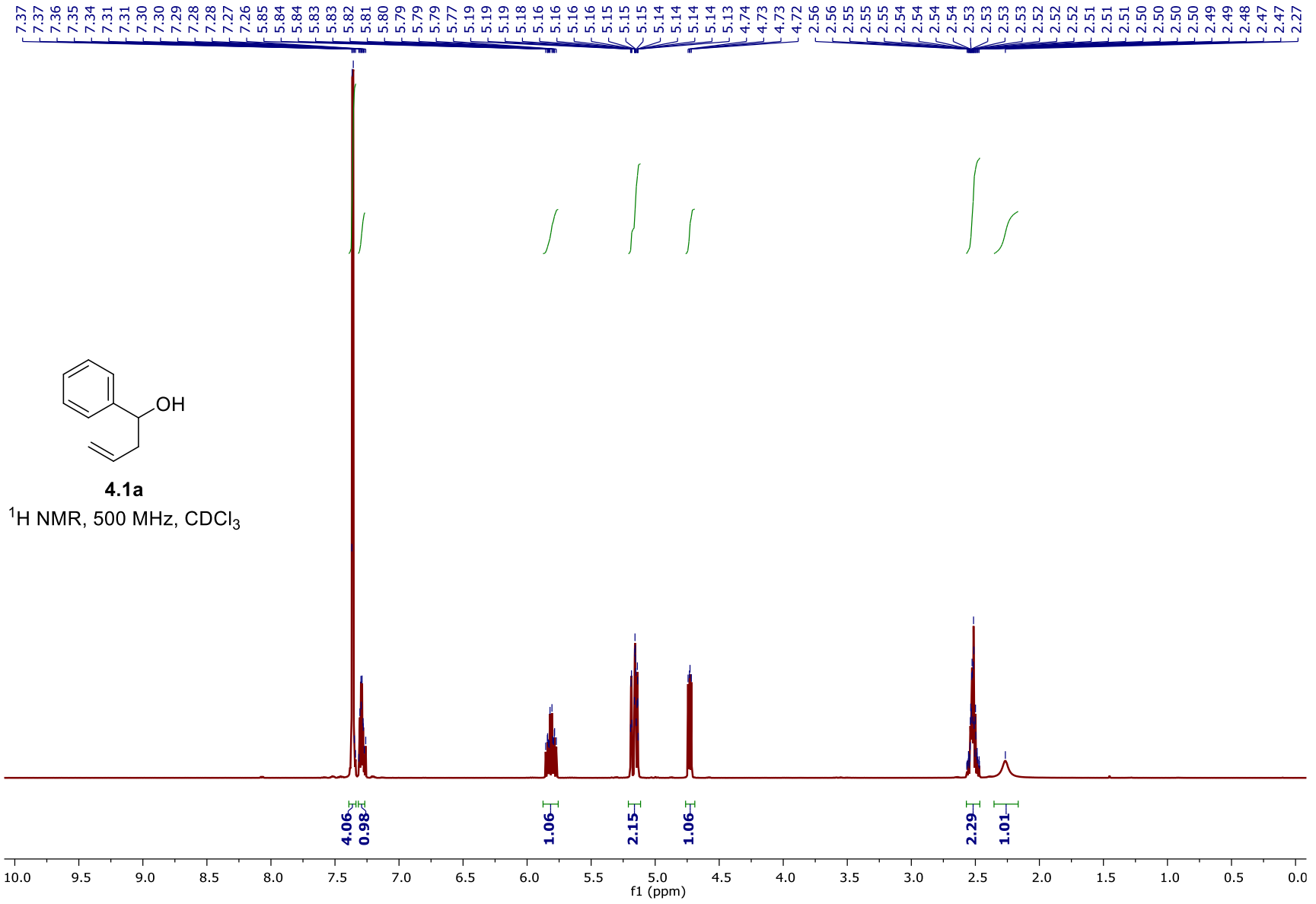
Citations

COSMO-V1.61 - Software for the CCD Detector Systems for Determining Data Collection Parameters, Bruker axs, Madison, WI (2000).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Bruker axs, Madison, WI (after 2013).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1.06
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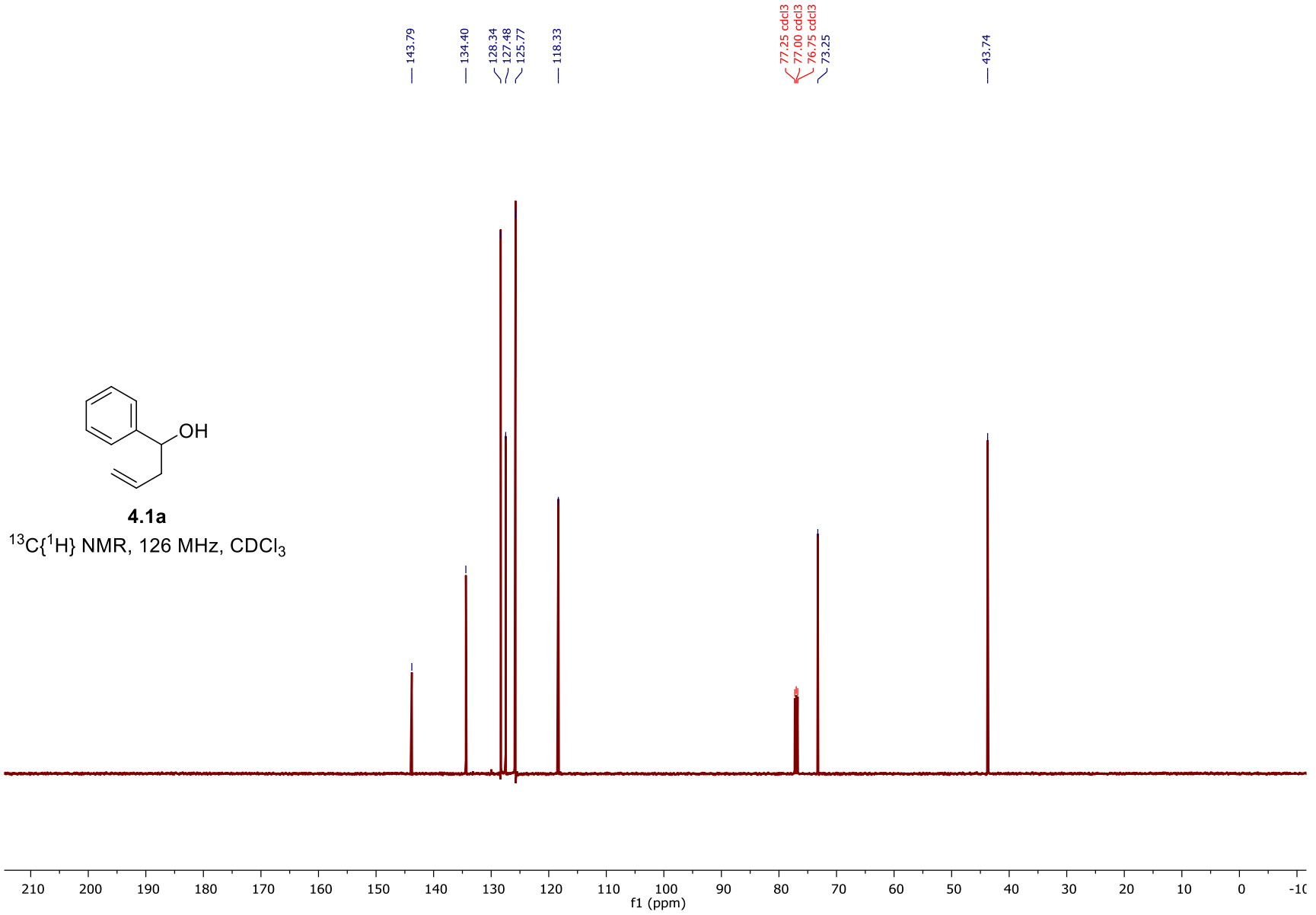
f1 (ppm)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128.34
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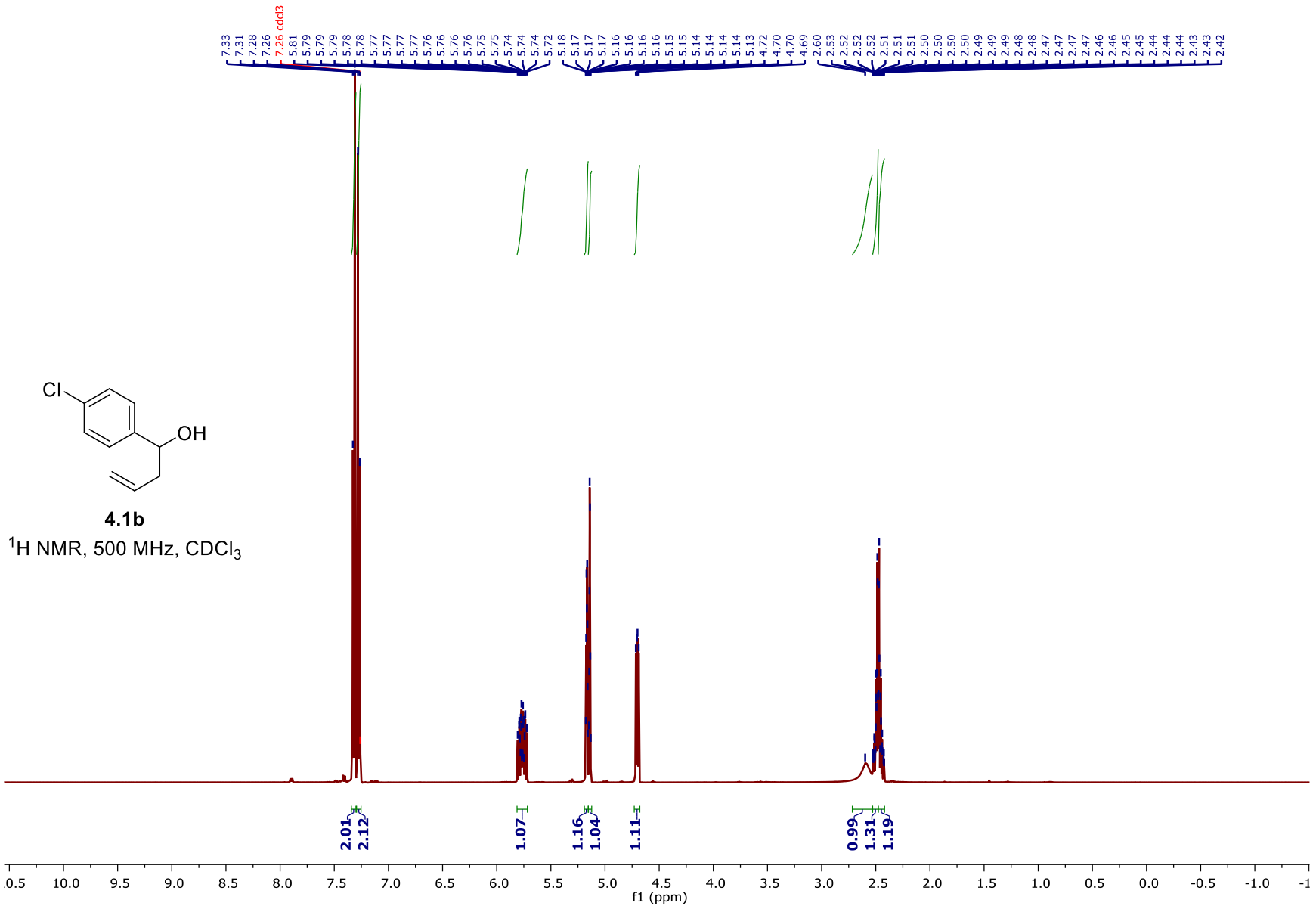
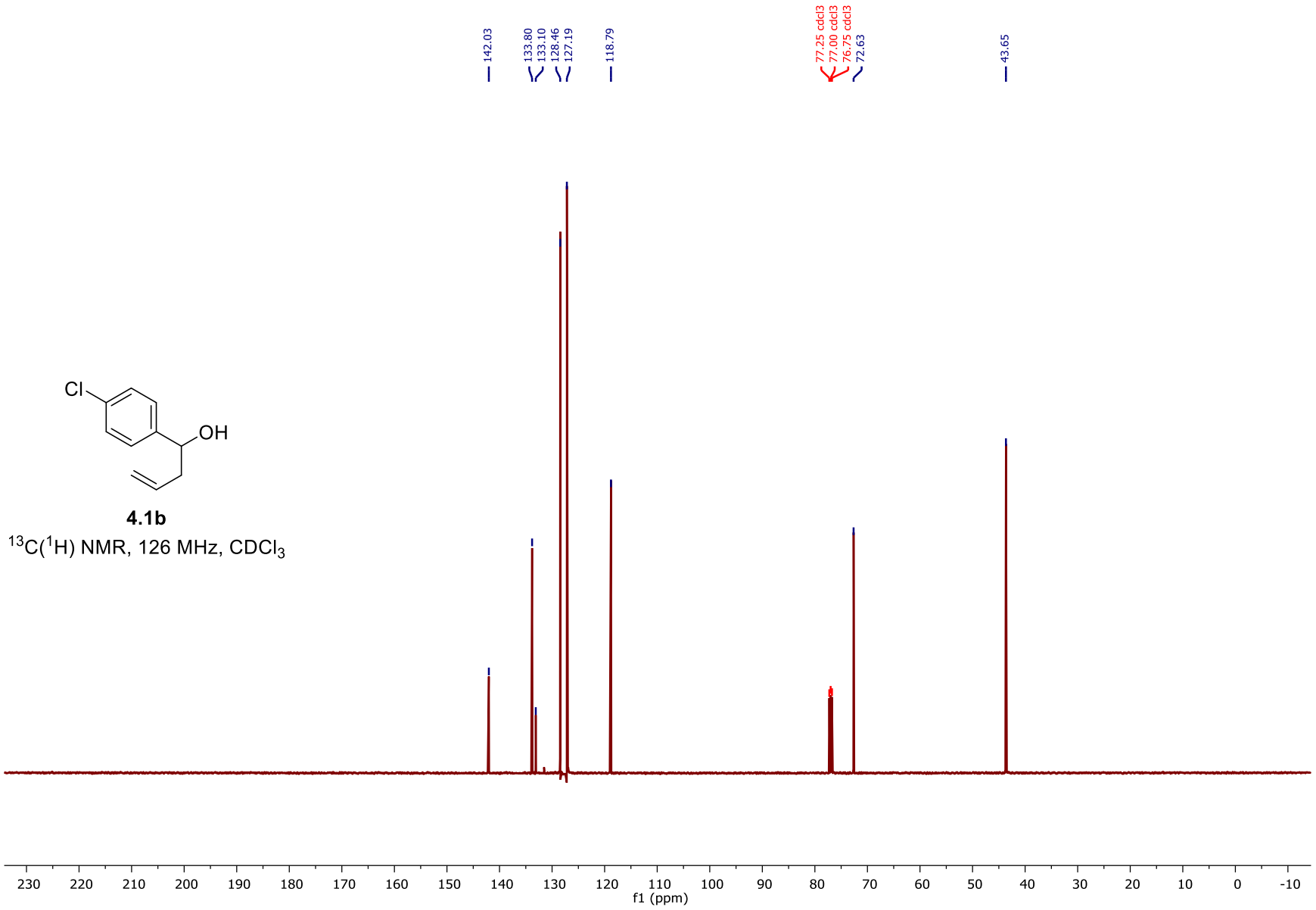
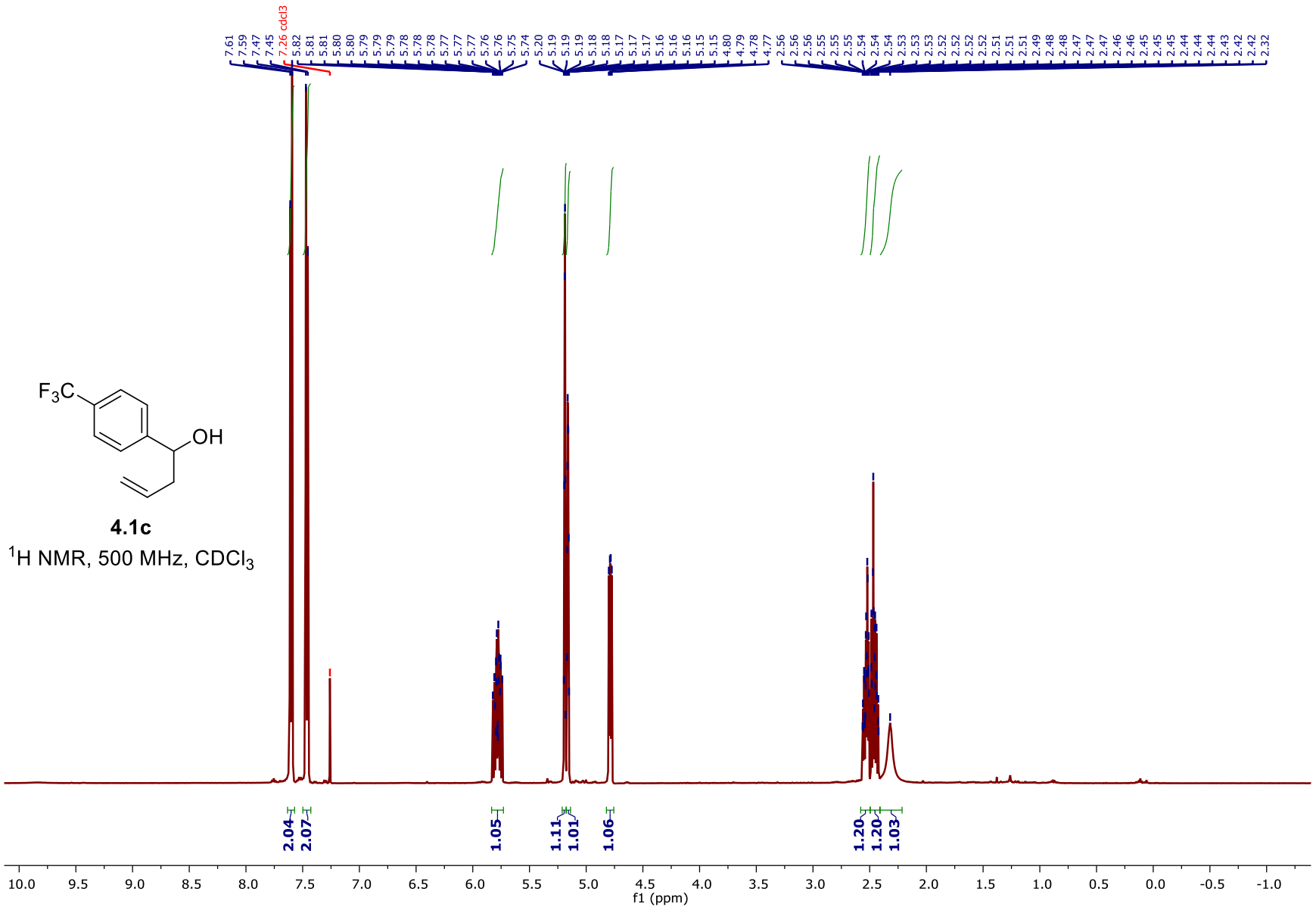
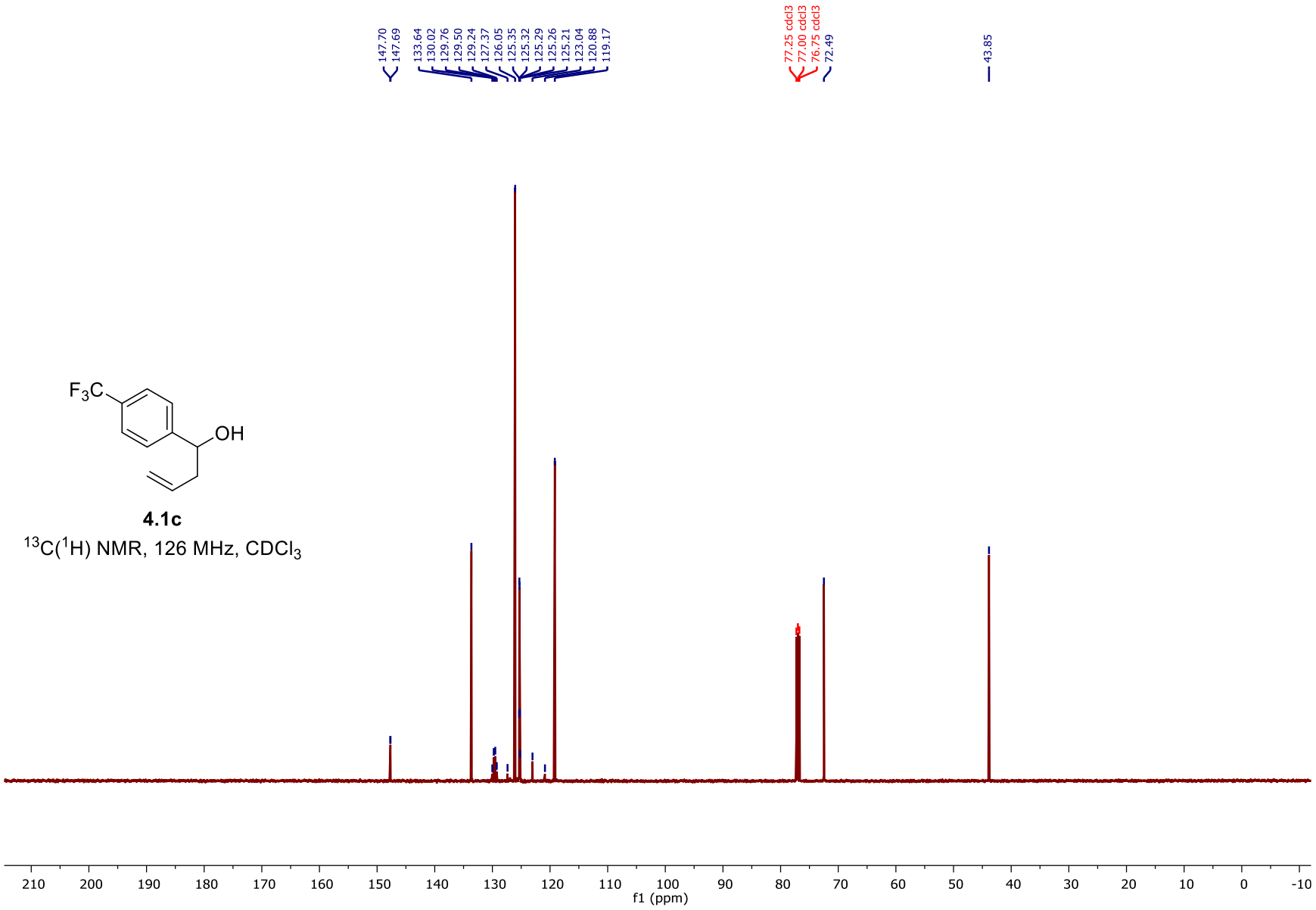
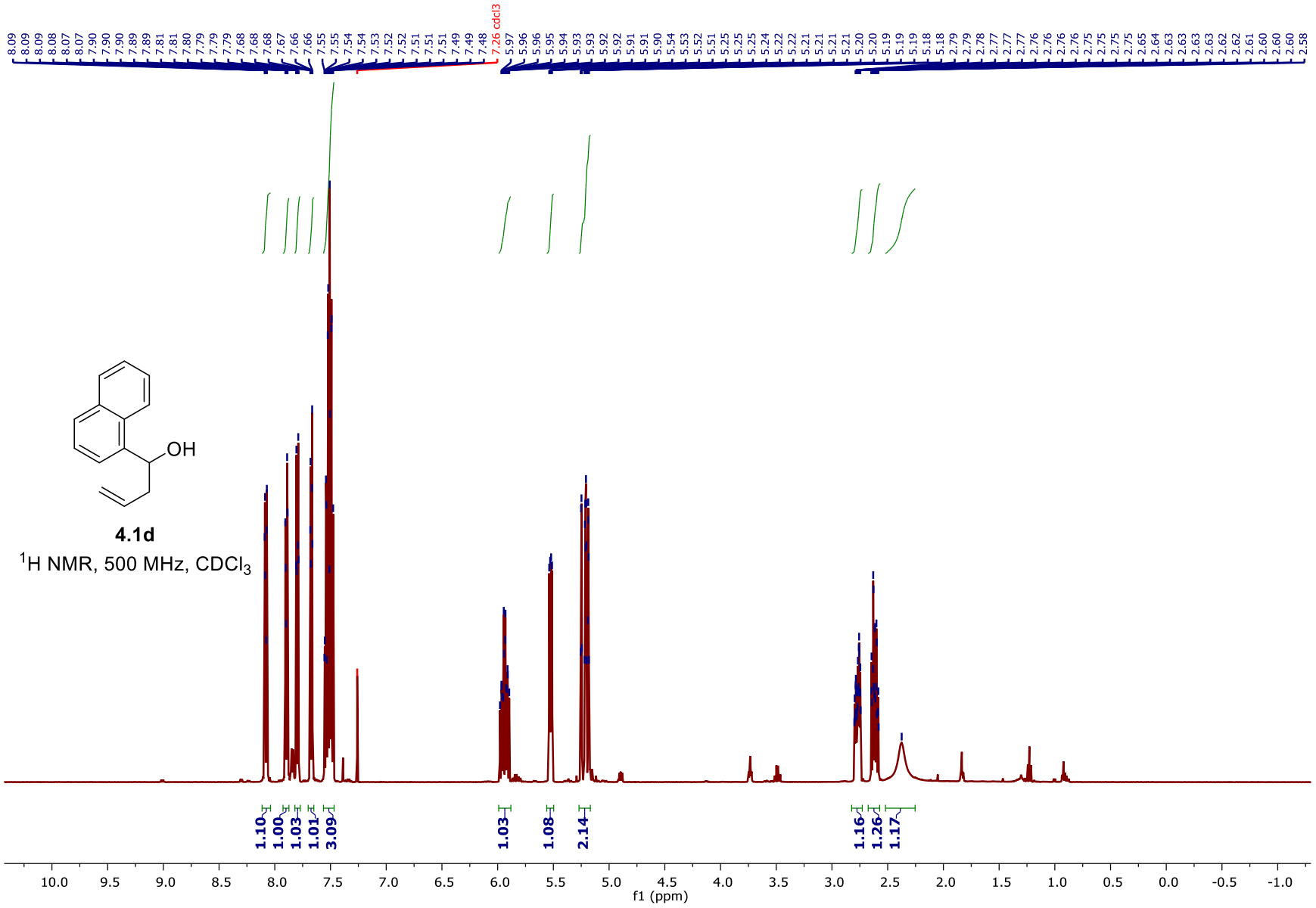
77.00 cdcl3
76.75 cdcl3
73.25
43.74
OH
4.1a
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$
f1 (ppm)

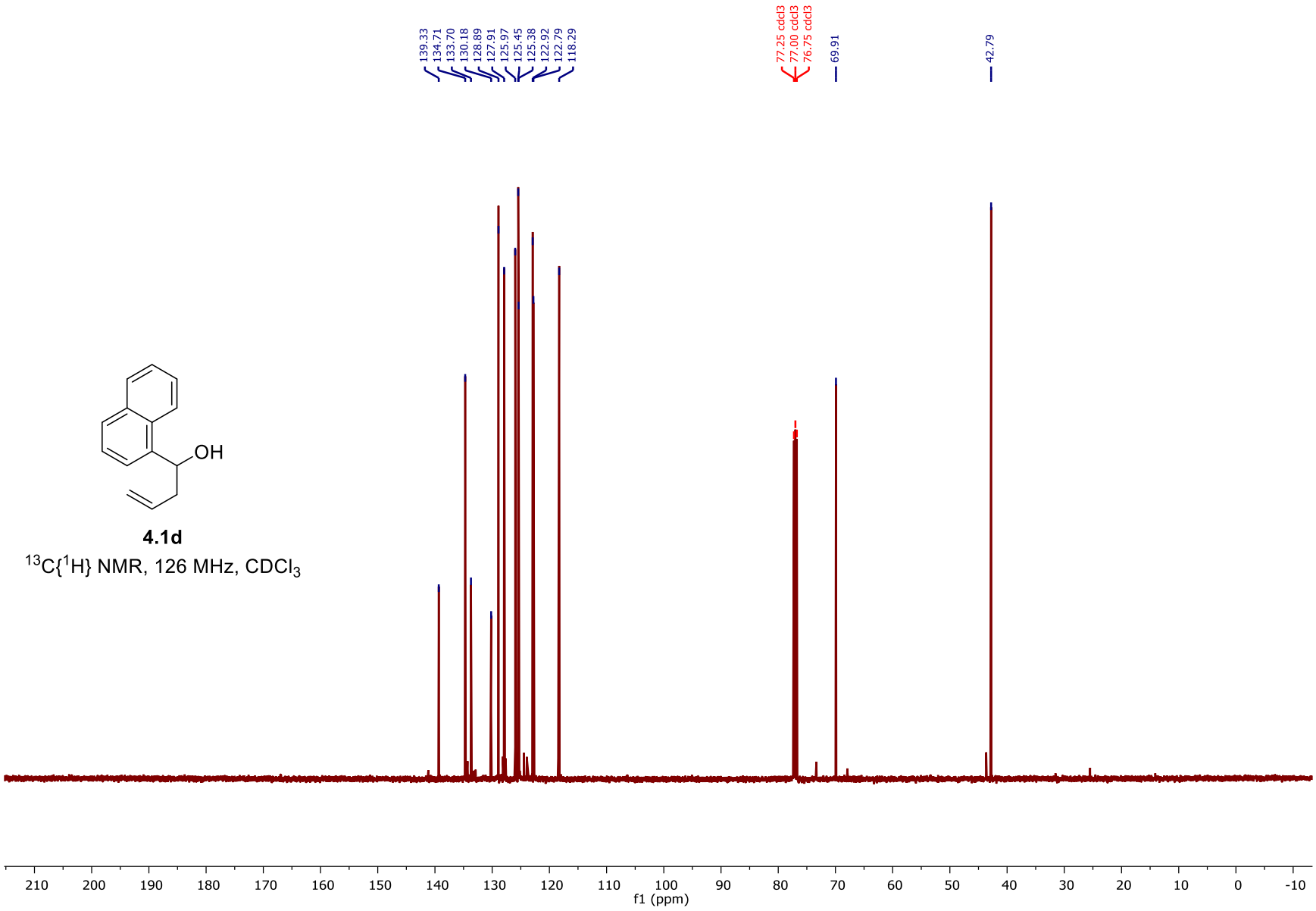

Cl
OH
4.1b
1H NMR, 500 MHz, CDCl3
7.26 cdcl3
2.01
2.12
1.07
1.16
1.04
1.11
0.99
1.31
1.19
f1 (ppm)


142.03
133.80
133.10
128.46
127.19
118.79
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
72.63
43.65
Cl
OH
4.1b
$^{13}C(^{1}H)$ NMR, 126 MHz, $CDCl_3$
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.61 7.59 7.47 7.45 7.26 cdcl3 5.82 5.81 5.81 5.80 5.80 5.79 5.79 5.78 5.78 5.77 5.77 5.77 5.76 5.76 5.75 5.74 5.20 5.19 5.19 5.19 5.18 5.18 5.17 5.17 5.17 5.16 5.16 5.16 5.15 5.15 4.80 4.79 4.78 4.77 2.56 2.56 2.56 2.55 2.55 2.55 2.54 2.54 2.54 2.53 2.53 2.53 2.52 2.52 2.52 2.52 2.51 2.51 2.51 2.49 2.48 2.48 2.47 2.47 2.47 2.46 2.46 2.45 2.45 2.45 2.44 2.44 2.44 2.43 2.42 2.42 2.32
F3C
OH
4.1c
1H NMR, 500 MHz, CDCl3
2.04 2.07 1.05 1.11 1.01 1.06 1.20 1.20 1.03
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 -1.0
f1 (ppm)

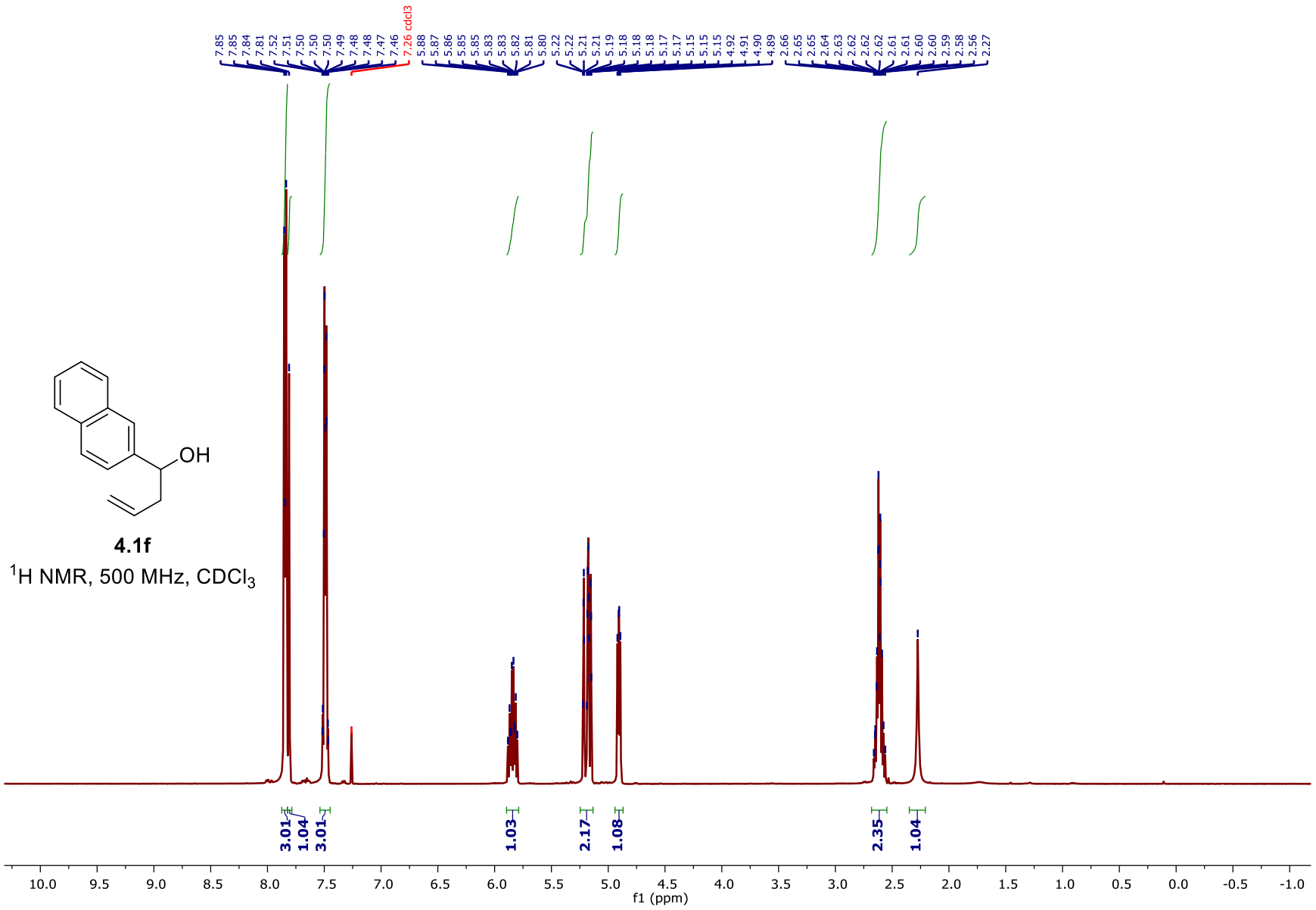

147.70
147.69
133.64
130.02
129.76
129.50
129.24
127.37
126.05
125.35
125.32
125.29
125.26
125.21
123.04
120.88
119.17
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
72.49
43.85
F3C
OH
4.1c
13C(1H) NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

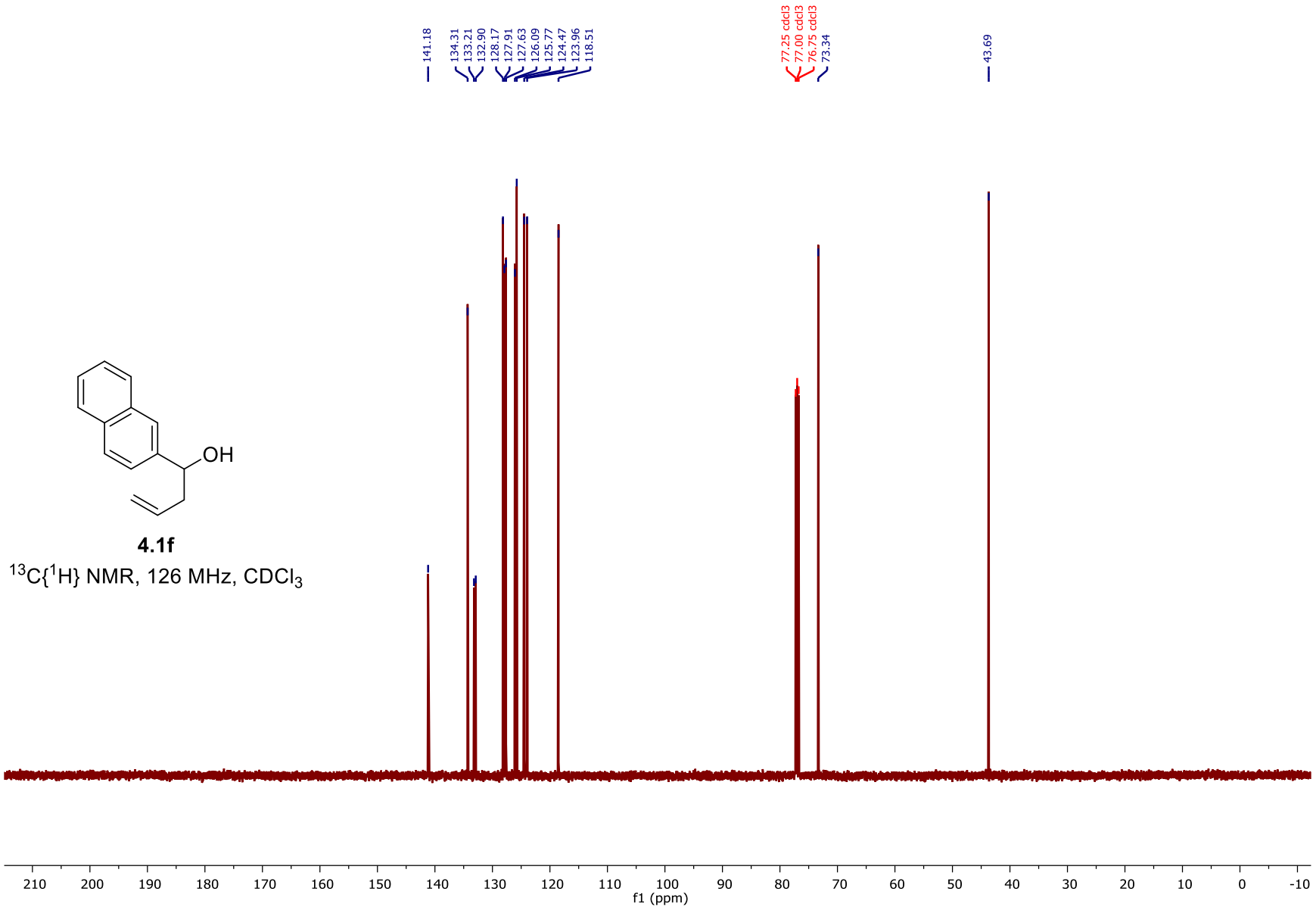

OH
4.1d
^{1}H NMR, 500 MHz, $CDCl_3$
7.26 cdcl3
1.10
1.00
1.03
1.01
3.09
1.03
1.08
2.14
1.16
1.26
1.17
f1 (ppm)

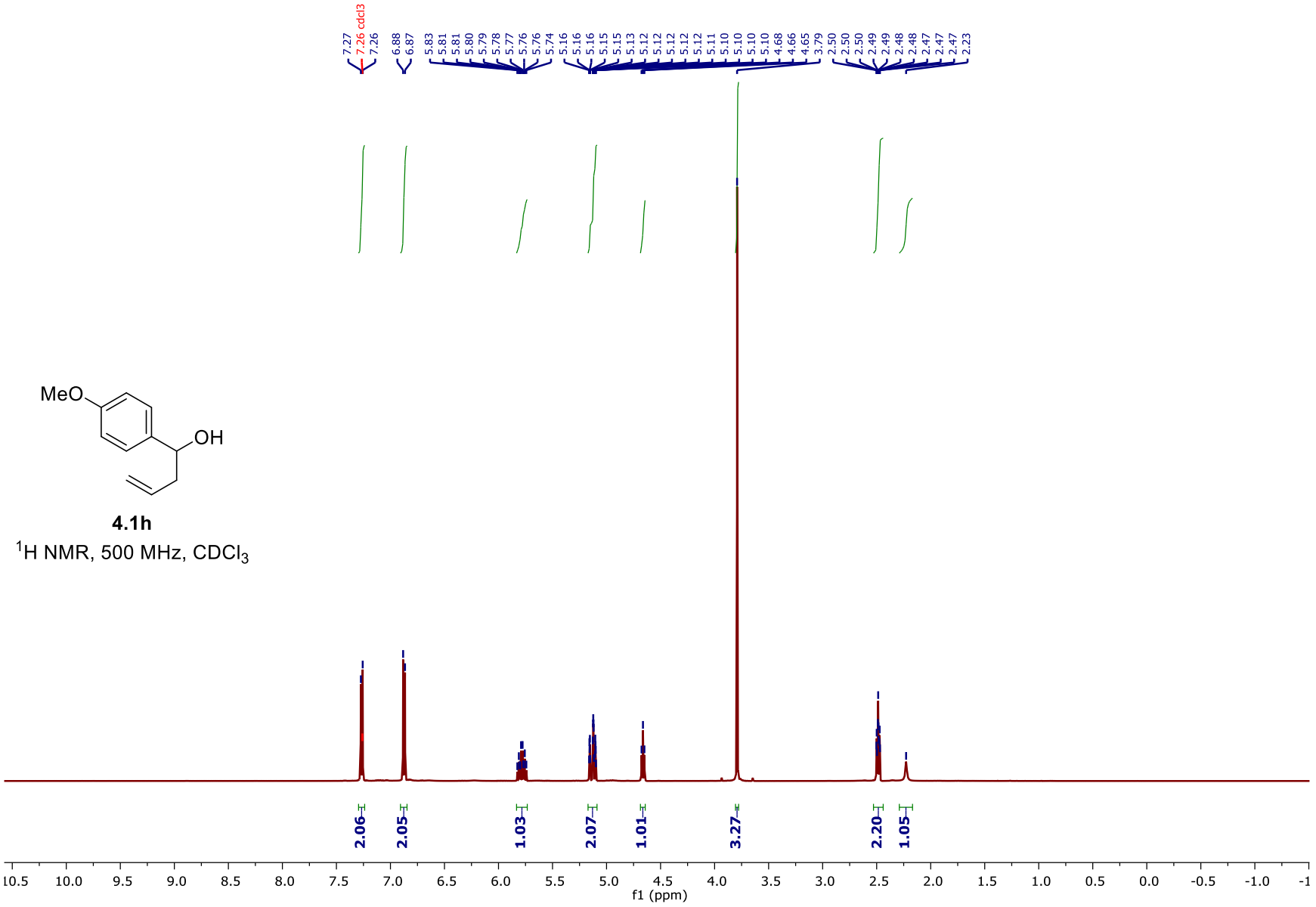


4.1d

$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

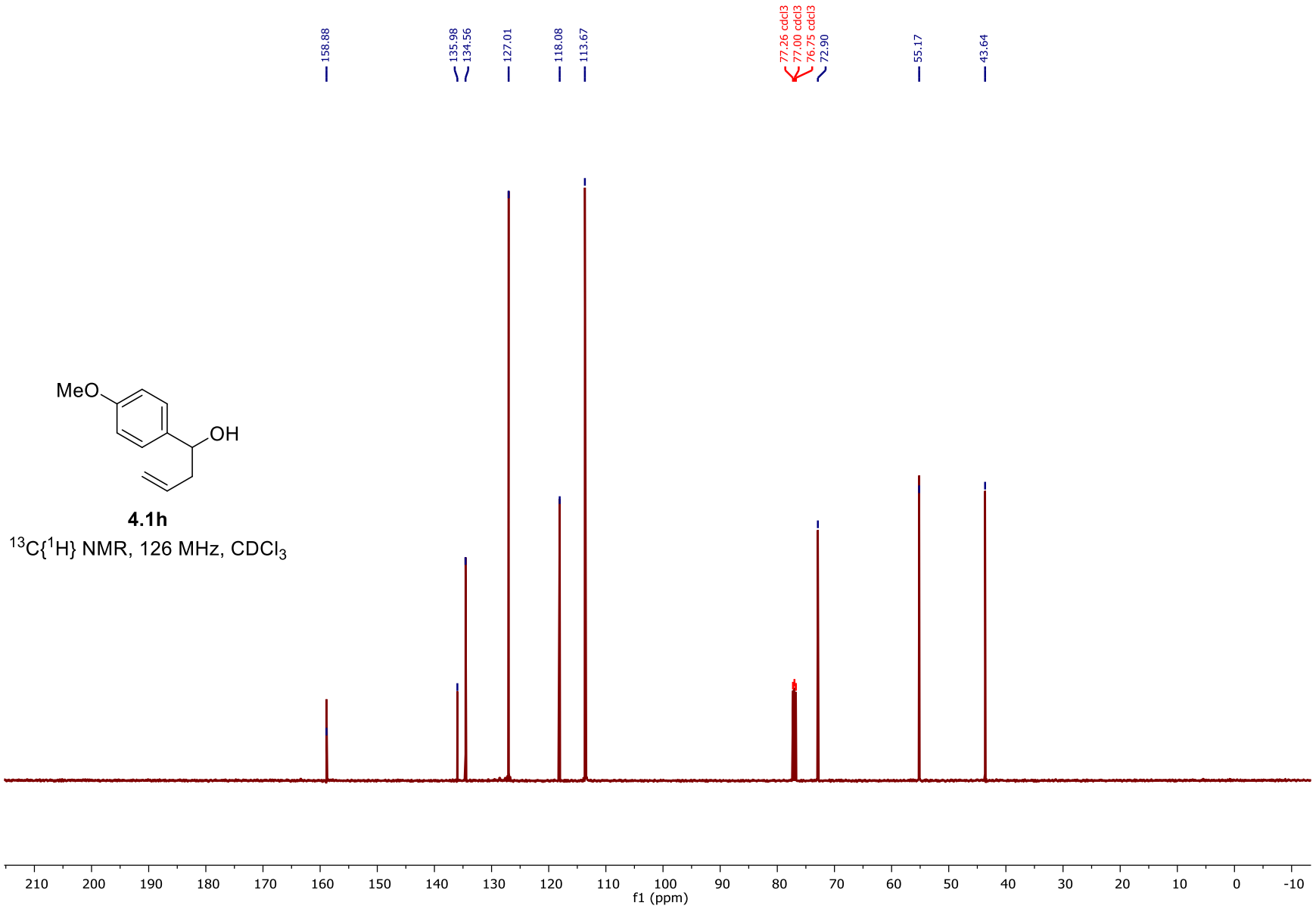

7.85 7.85 7.84 7.81 7.52 7.51 7.50 7.50 7.50 7.49 7.48 7.48 7.47 7.46 7.26 cdcl3
5.88 5.87 5.86 5.85 5.85 5.83 5.83 5.82 5.81 5.80 5.22 5.22 5.21 5.21 5.19 5.18 5.18 5.17 5.17 5.15 5.15 5.15 4.92 4.91 4.90 4.89
2.66 2.65 2.65 2.64 2.63 2.62 2.62 2.62 2.61 2.61 2.60 2.60 2.59 2.58 2.56 2.27
OH
4.1f
1H NMR, 500 MHz, CDCl3
3.01 1.04 3.01 1.03 2.17 1.08 2.35 1.04
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 -1.0
f1 (ppm)

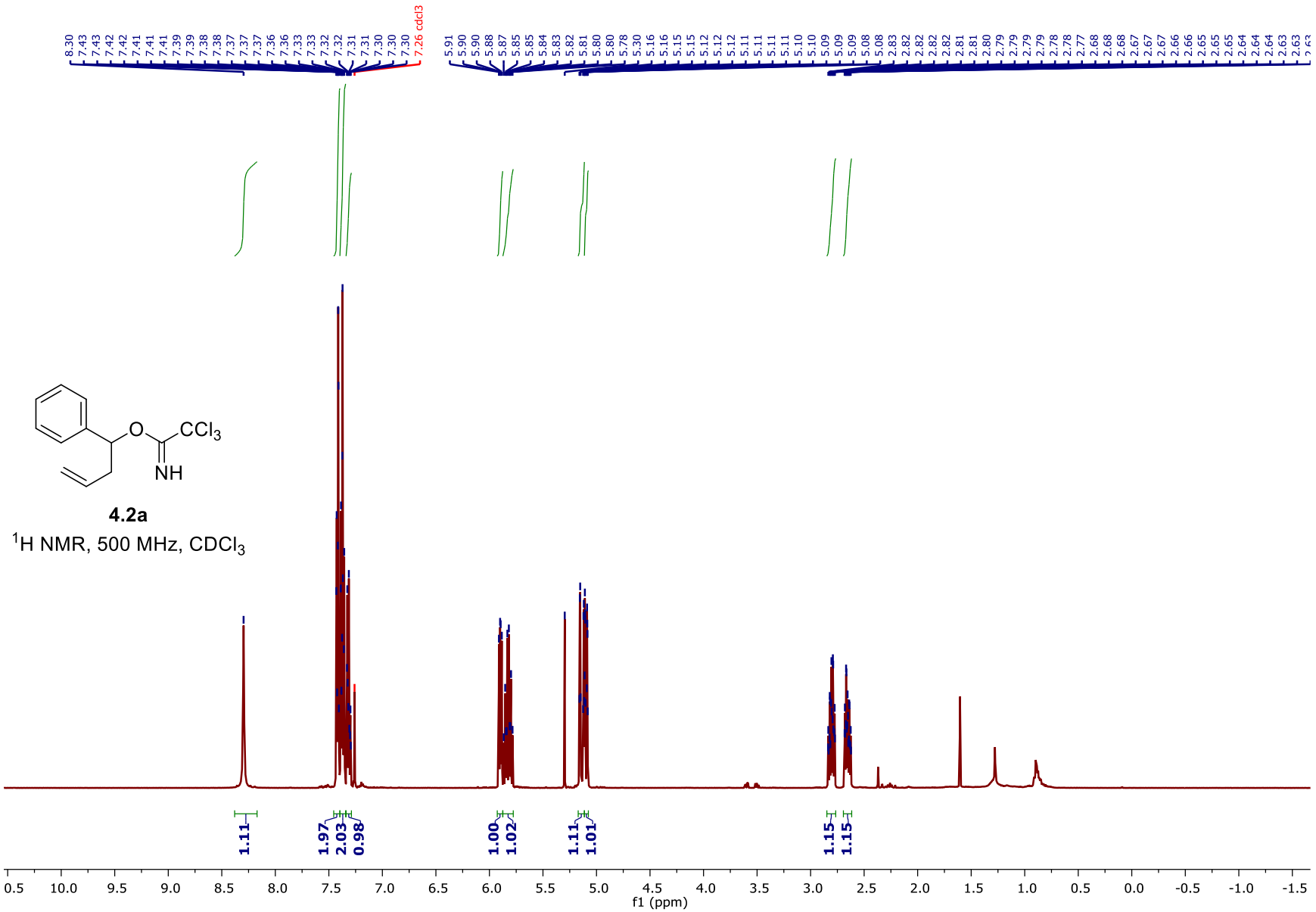

141.18
134.31
133.21
132.90
128.17
127.91
127.63
126.09
125.77
124.47
123.96
118.51
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
73.34
43.69
OH
4.1f
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

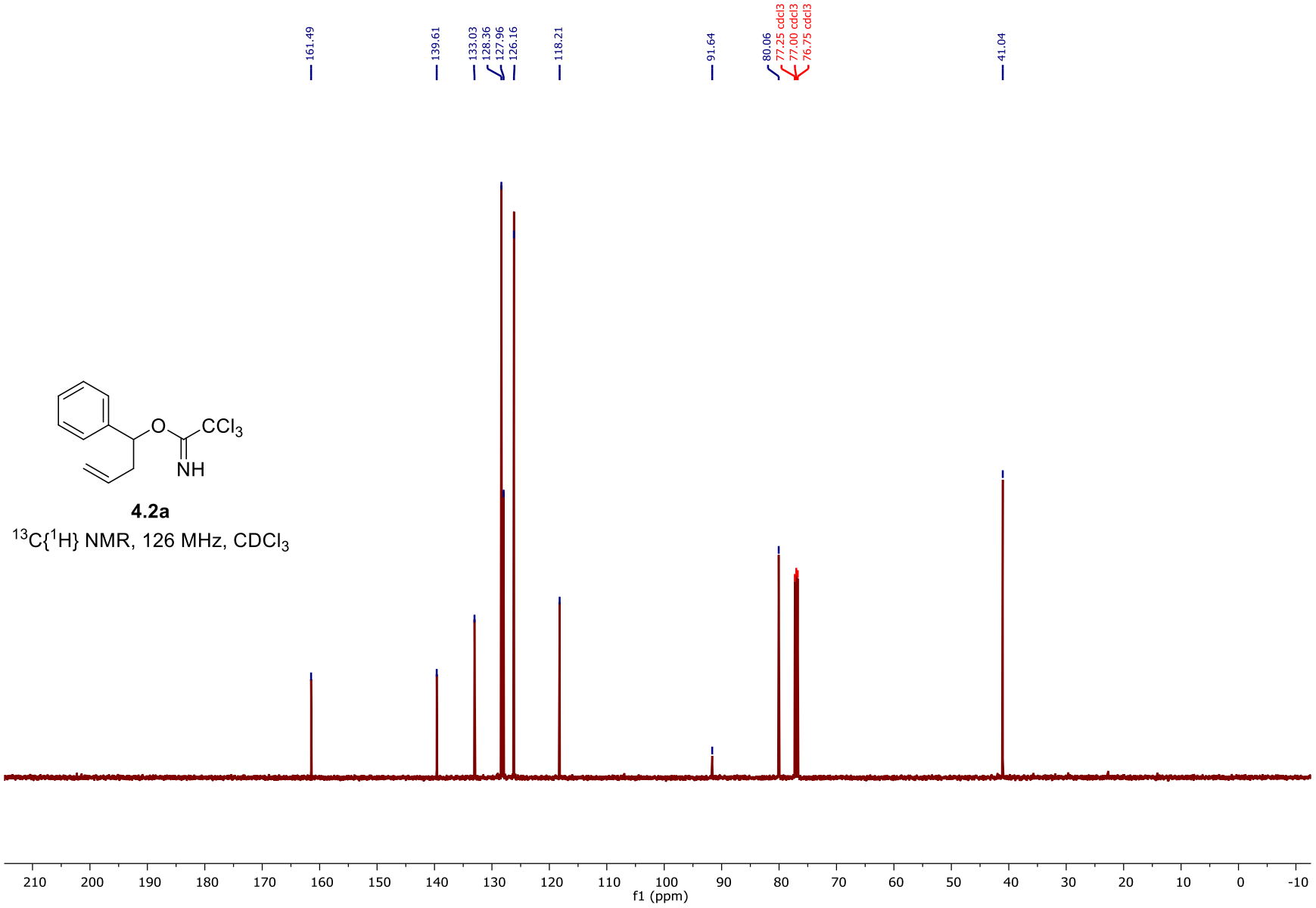


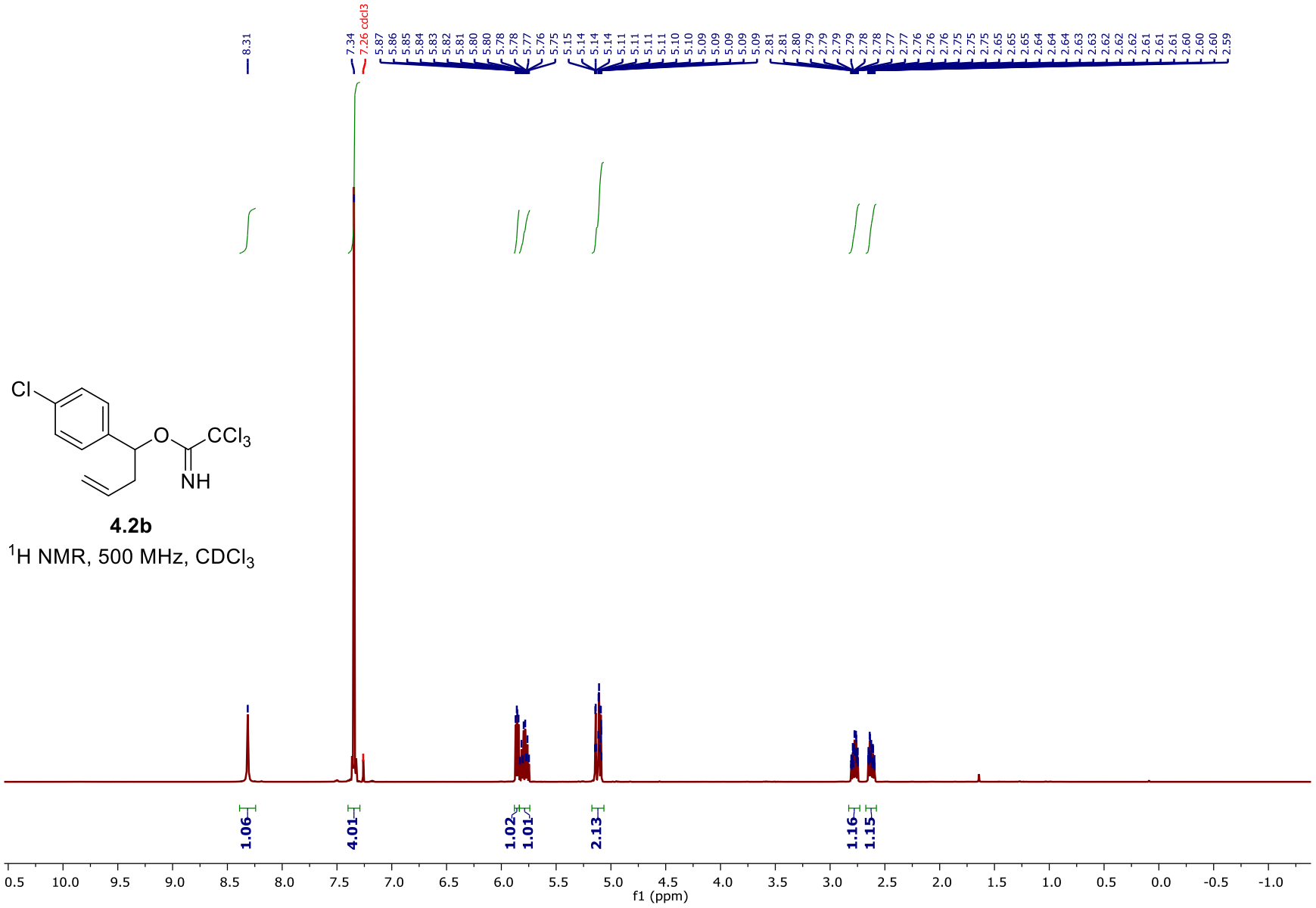
4.1h

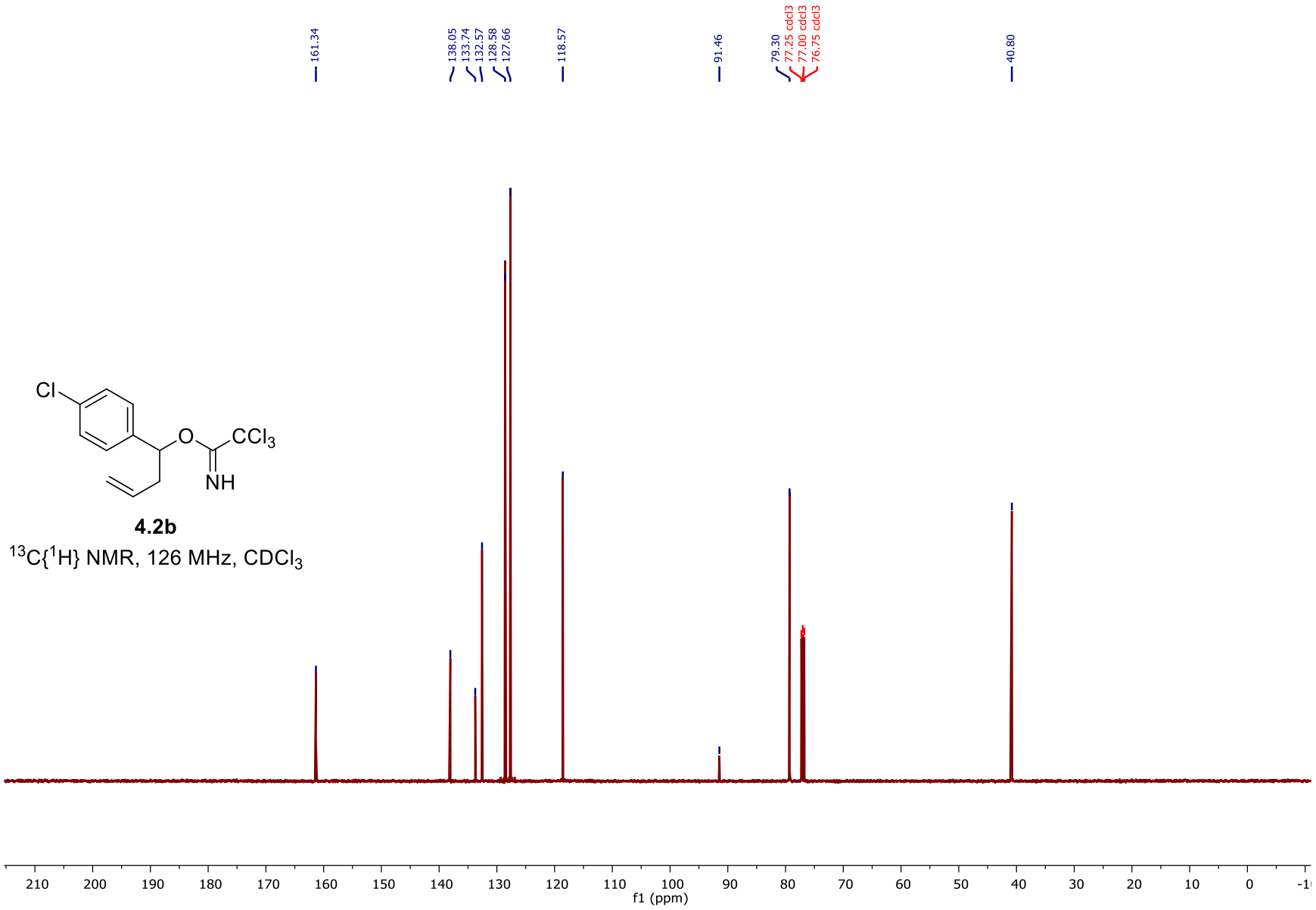
^{1}H NMR, 500 MHz, $CDCl_3$

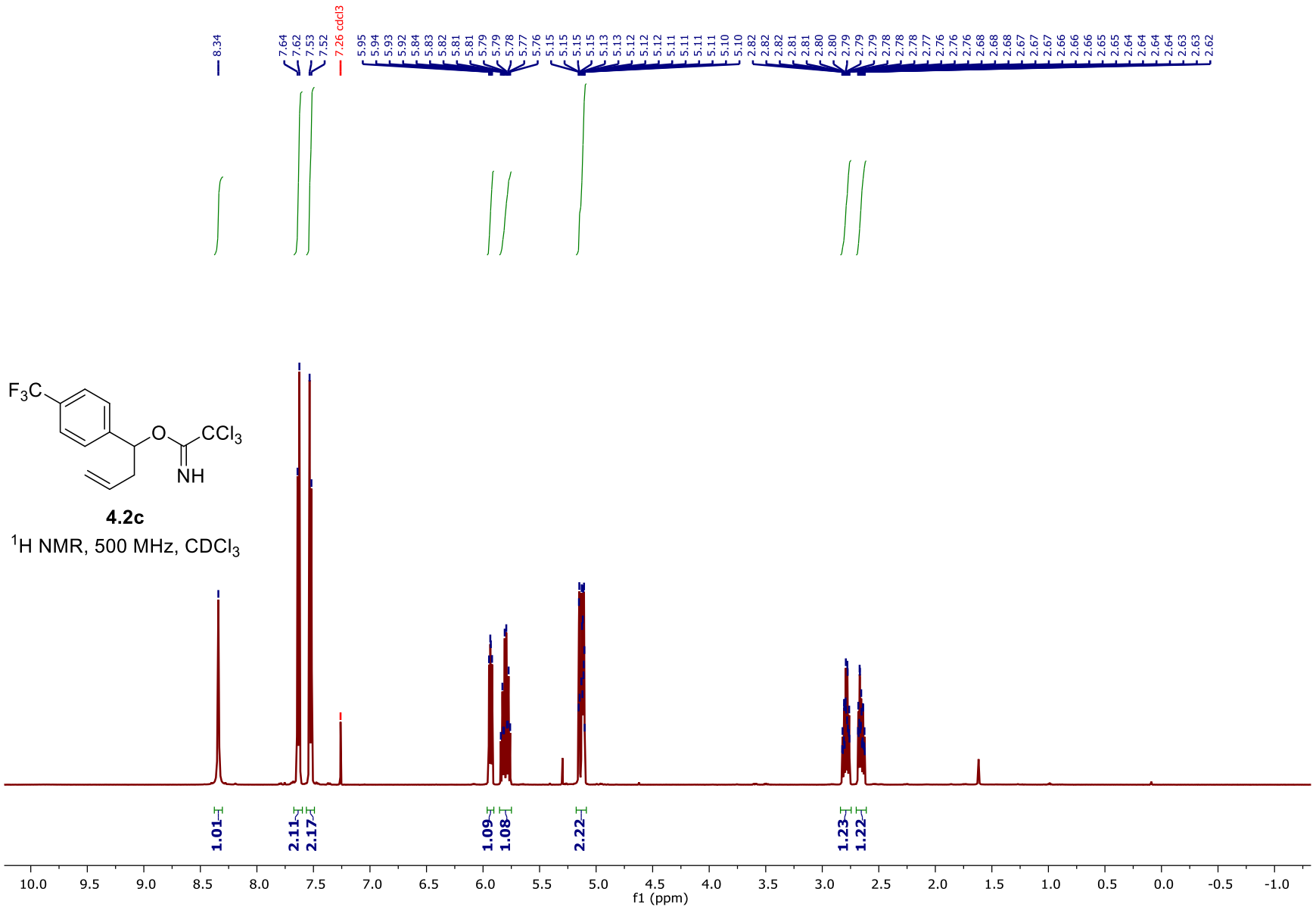

158.88
135.98
134.56
127.01
118.08
113.67
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
72.90
55.17
43.64
MeO
OH
4.1h
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

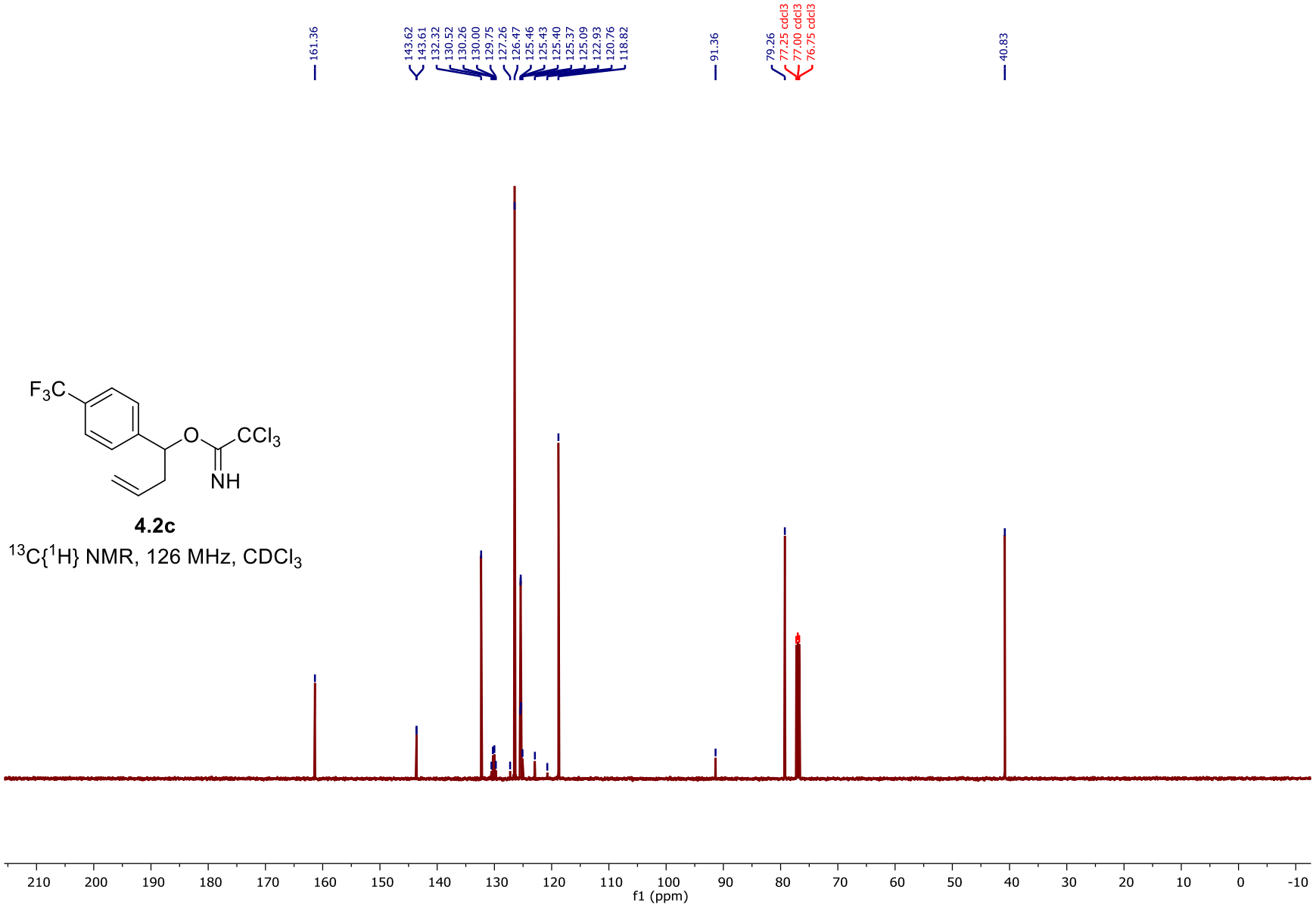

8.30 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.26 cdcl3
5.91 5.90 5.90 5.88 5.87 5.85 5.85 5.84 5.83 5.82 5.81 5.80 5.80 5.78 5.30 5.16 5.16 5.15 5.15 5.12 5.12 5.12 5.11 5.11 5.11 5.11 5.10 5.10 5.09 5.09 5.09 5.08 5.08 2.83 2.82 2.82 2.82 2.82 2.81 2.81 2.80 2.79 2.79 2.79 2.79 2.78 2.78 2.77 2.68 2.68 2.68 2.67 2.67 2.67 2.66 2.66 2.65 2.65 2.64 2.64 2.64 2.63 2.63
O
CCl3
NH
4.2a
1H NMR, 500 MHz, CDCl3
1.11
1.97
2.03
0.98
1.00
1.02
1.11
1.01
1.15
1.15
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

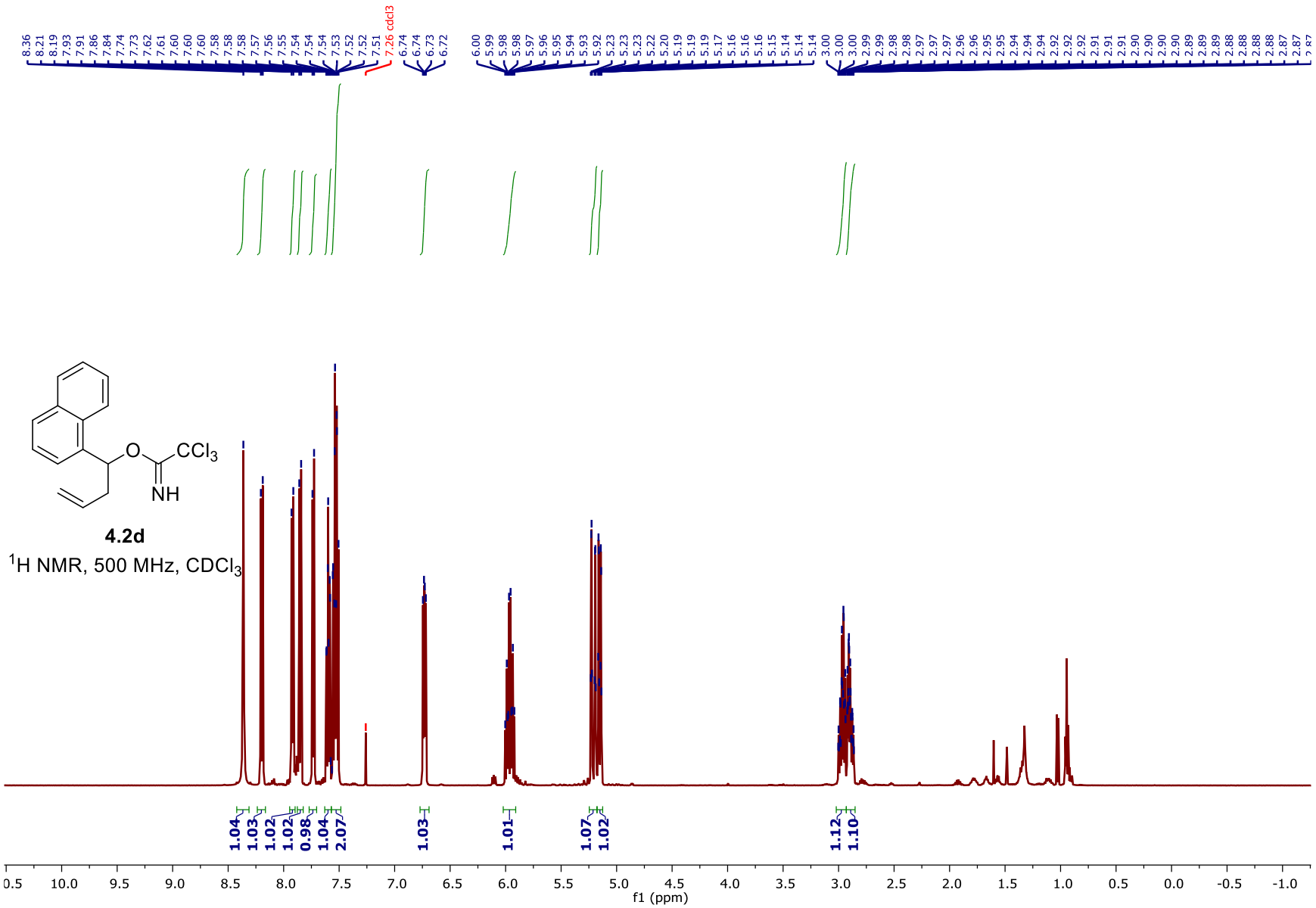

161.49
139.61
133.03
128.36
127.96
126.16
118.21
91.64
80.06
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
41.04
O
CCl3
NH
4.2a
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

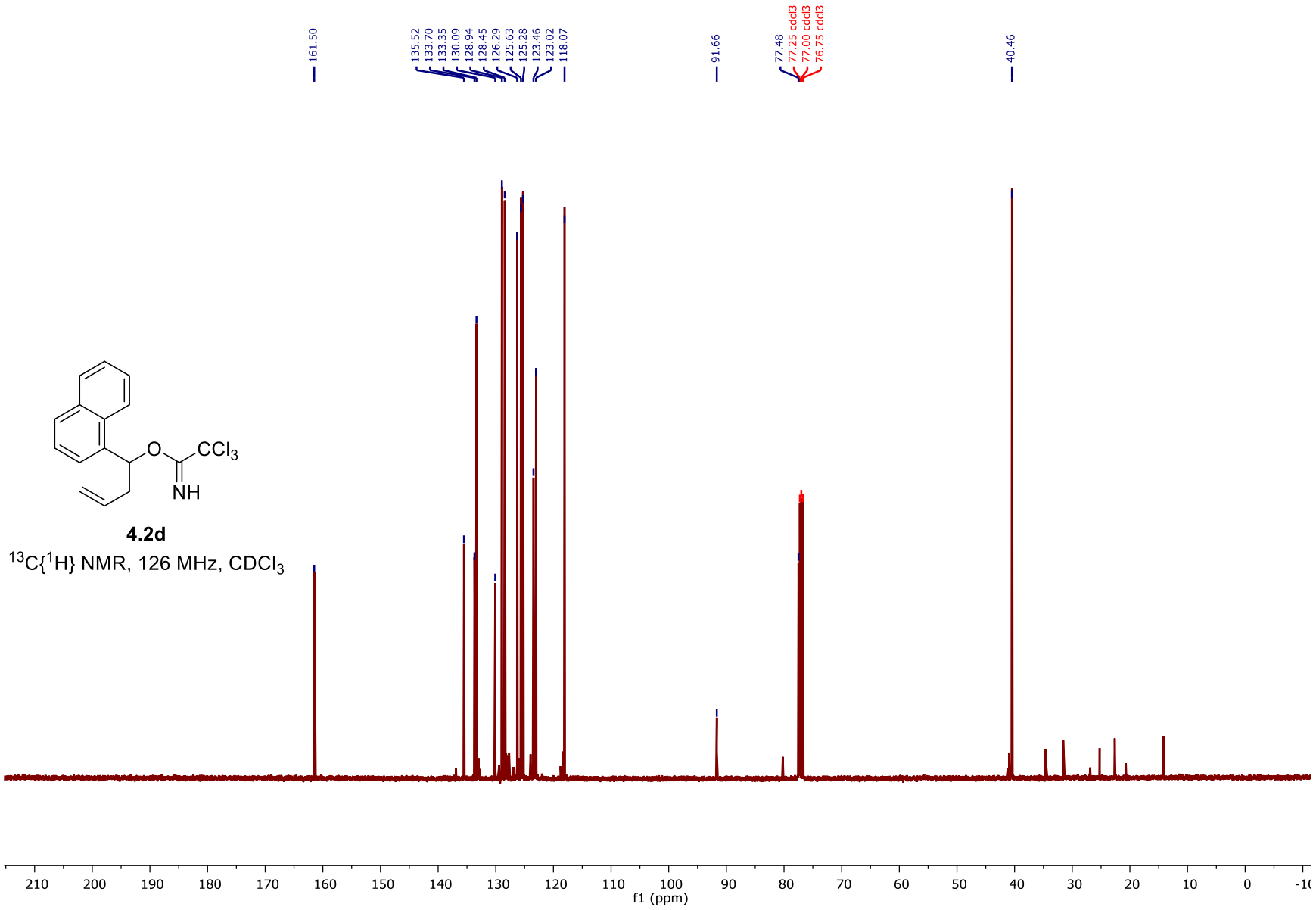

8.31
7.34
7.26 cdcl3
5.87
5.86
5.85
5.84
5.83
5.82
5.81
5.80
5.80
5.78
5.78
5.77
5.76
5.75
5.15
5.14
5.14
5.11
5.11
5.11
5.11
5.10
5.09
5.09
5.09
5.09
2.81
2.81
2.80
2.79
2.79
2.79
2.79
2.78
2.78
2.77
2.76
2.76
2.76
2.75
2.75
2.75
2.65
2.65
2.65
2.64
2.64
2.64
2.63
2.63
2.62
2.62
2.62
2.61
2.61
2.61
2.60
2.60
2.60
2.60
2.59
Cl
O
CCl3
NH
4.2b
1H NMR, 500 MHz, CDCl3
1.06
4.01
1.02
1.01
2.13
1.16
1.15
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

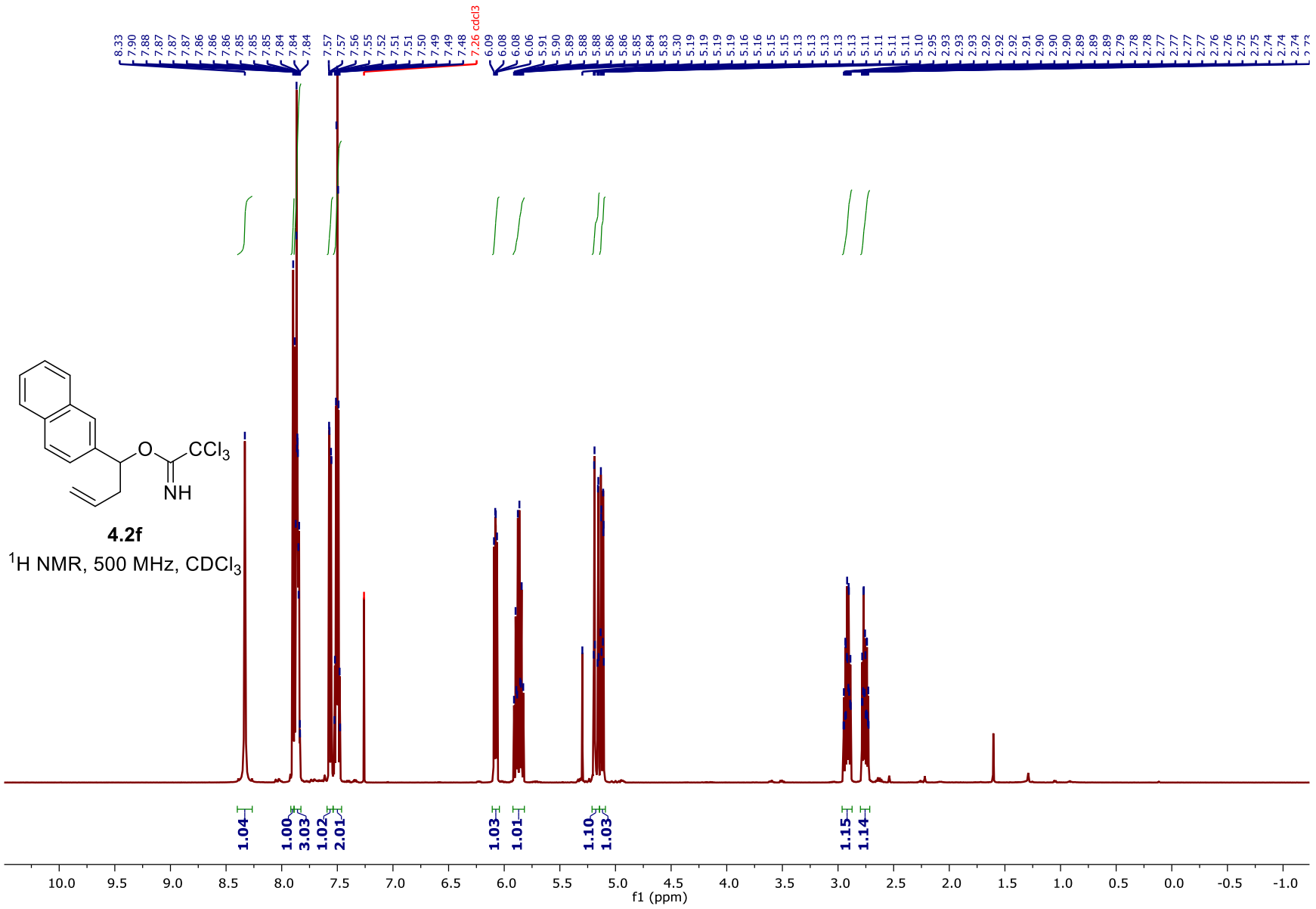

161.34
138.05
133.74
132.57
128.58
127.66
118.57
91.46
79.30
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
40.80
Cl
O
CCl3
NH
4.2b
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)

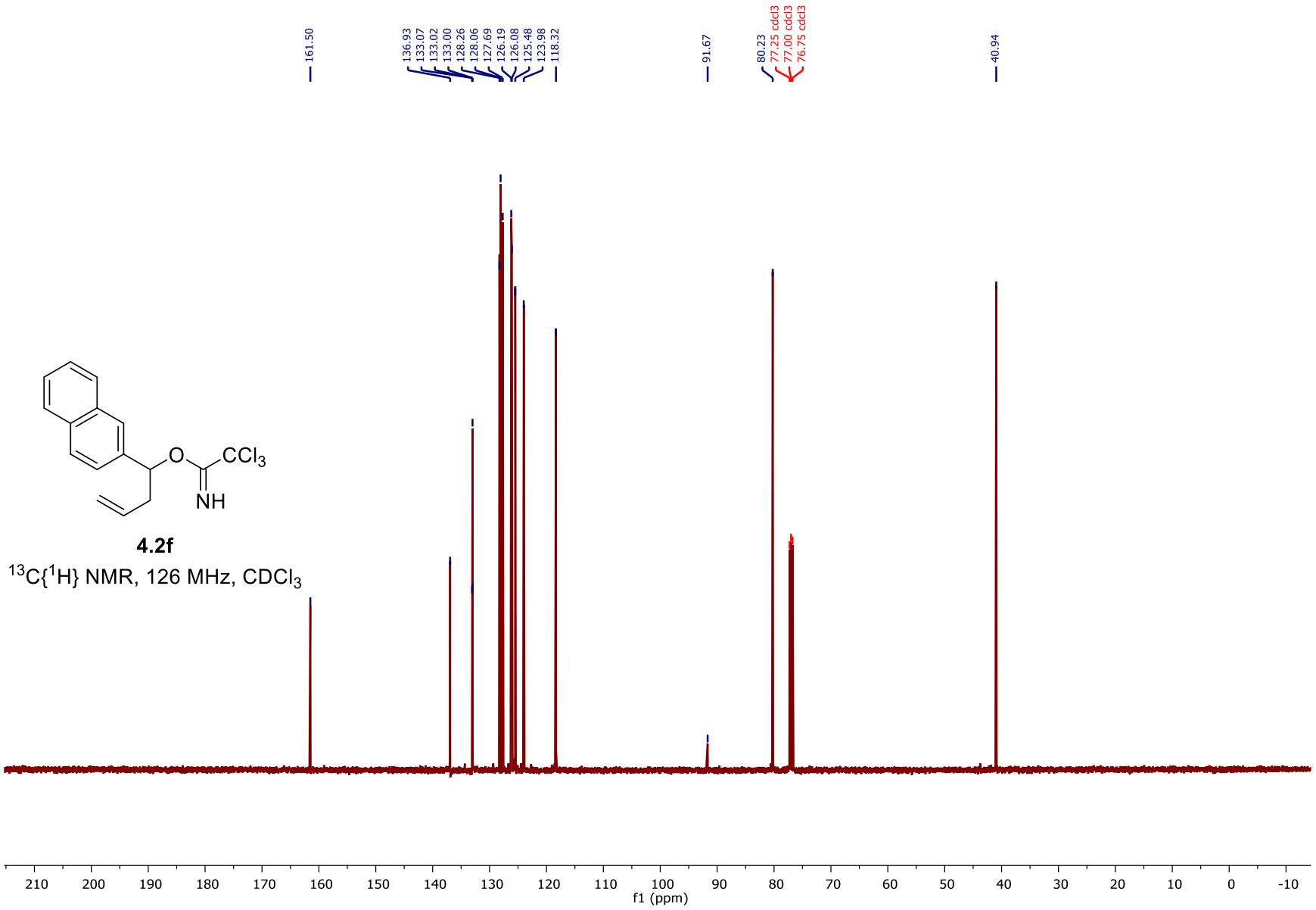

8.34
7.64
7.62
7.53
7.52
7.26 cdcl3
5.95
5.94
5.93
5.92
5.84
5.83
5.82
5.81
5.81
5.79
5.79
5.78
5.77
5.76
5.15
5.15
5.15
5.13
5.12
5.12
5.11
5.11
5.11
5.10
5.10
2.82
2.82
2.81
2.81
2.80
2.80
2.79
2.79
2.79
2.78
2.78
2.78
2.77
2.76
2.76
2.76
2.68
2.68
2.68
2.67
2.67
2.67
2.66
2.66
2.66
2.65
2.65
2.64
2.64
2.64
2.64
2.63
2.63
2.62
F3C
O
CCl3
NH
4.2c
1H NMR, 500 MHz, CDCl3
1.01
2.11
2.17
1.09
1.08
2.22
1.23
1.22
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
-1.0
f1 (ppm)

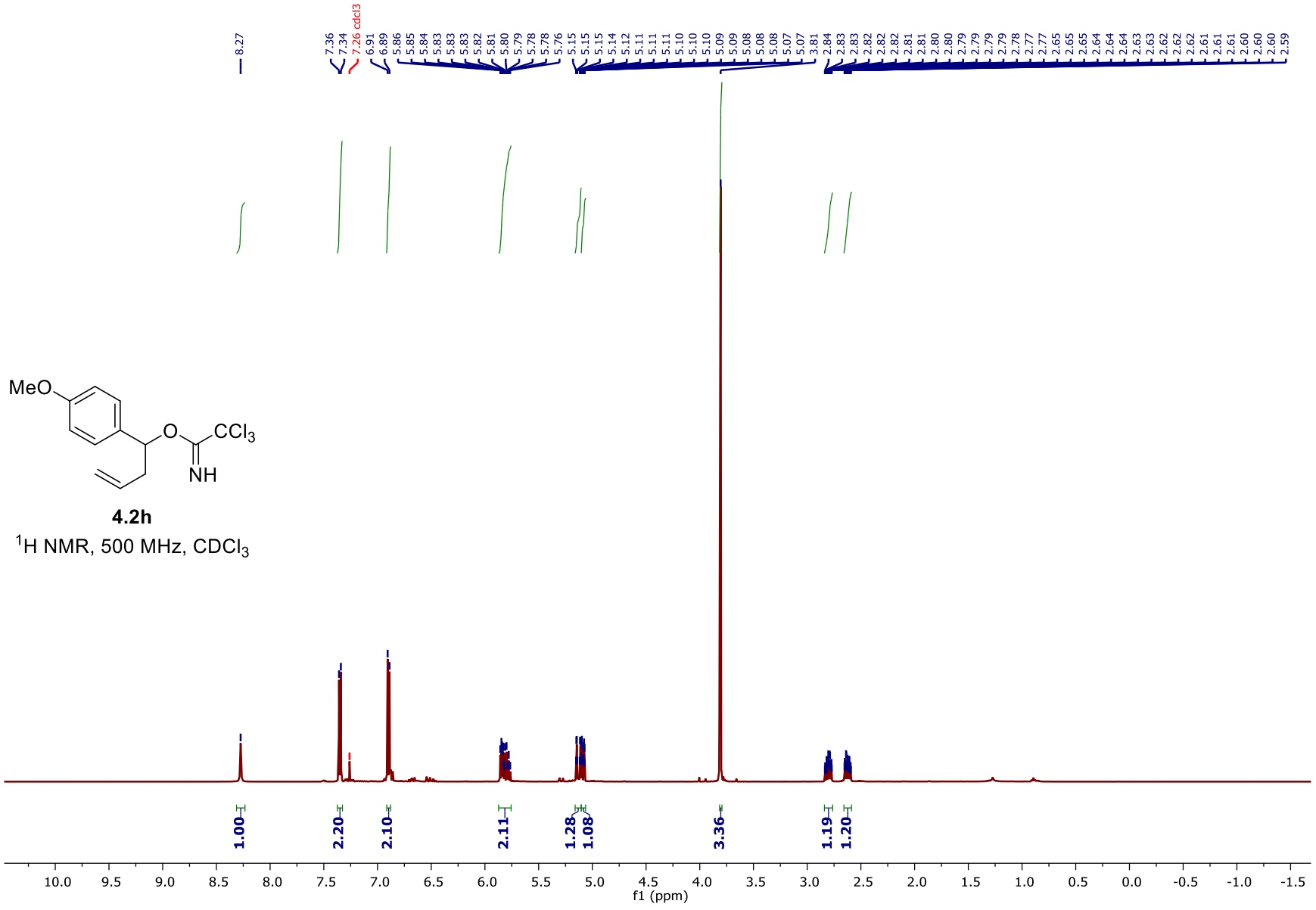

161.36
143.62
143.61
132.32
130.52
130.26
130.00
129.75
127.26
126.47
125.46
125.43
125.40
125.37
125.09
122.93
120.76
118.82
91.36
79.26
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
40.83
F3C
O
CCl3
NH
4.2c
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

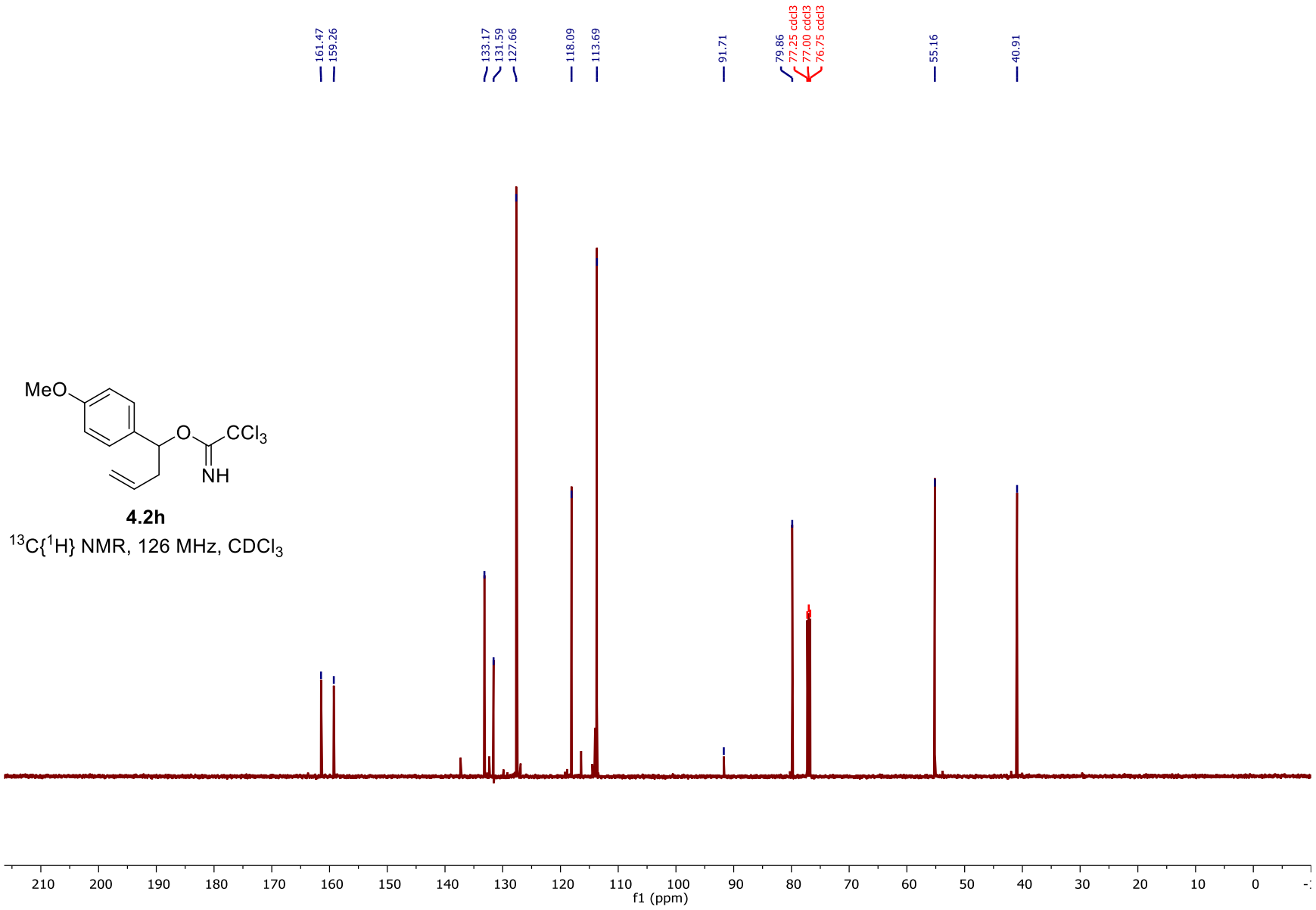

8.36 8.21 8.19 7.93 7.91 7.86 7.84 7.74 7.73 7.62 7.61 7.60 7.60 7.60 7.58 7.58 7.58 7.57 7.56 7.55 7.54 7.54 7.54 7.53 7.52 7.52 7.51 7.26 cdcl3 6.74 6.74 6.73 6.72
6.00 5.99 5.98 5.98 5.97 5.96 5.95 5.94 5.93 5.92 5.23 5.23 5.23 5.22 5.20 5.19 5.19 5.19 5.17 5.16 5.16 5.16 5.15 5.14 5.14 5.14
3.00 3.00 3.00 2.99 2.99 2.98 2.98 2.98 2.97 2.97 2.97 2.96 2.96 2.96 2.95 2.95 2.94 2.94 2.94 2.92 2.92 2.92 2.91 2.91 2.91 2.90 2.90 2.90 2.90 2.89 2.89 2.89 2.88 2.88 2.88 2.88 2.87 2.87 2.87
O
CCl3
NH
4.2d
1H NMR, 500 MHz, CDCl3
1.04 1.03 1.02 1.02 0.98 1.04 2.07 1.03 1.01 1.07 1.02 1.12 1.10
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

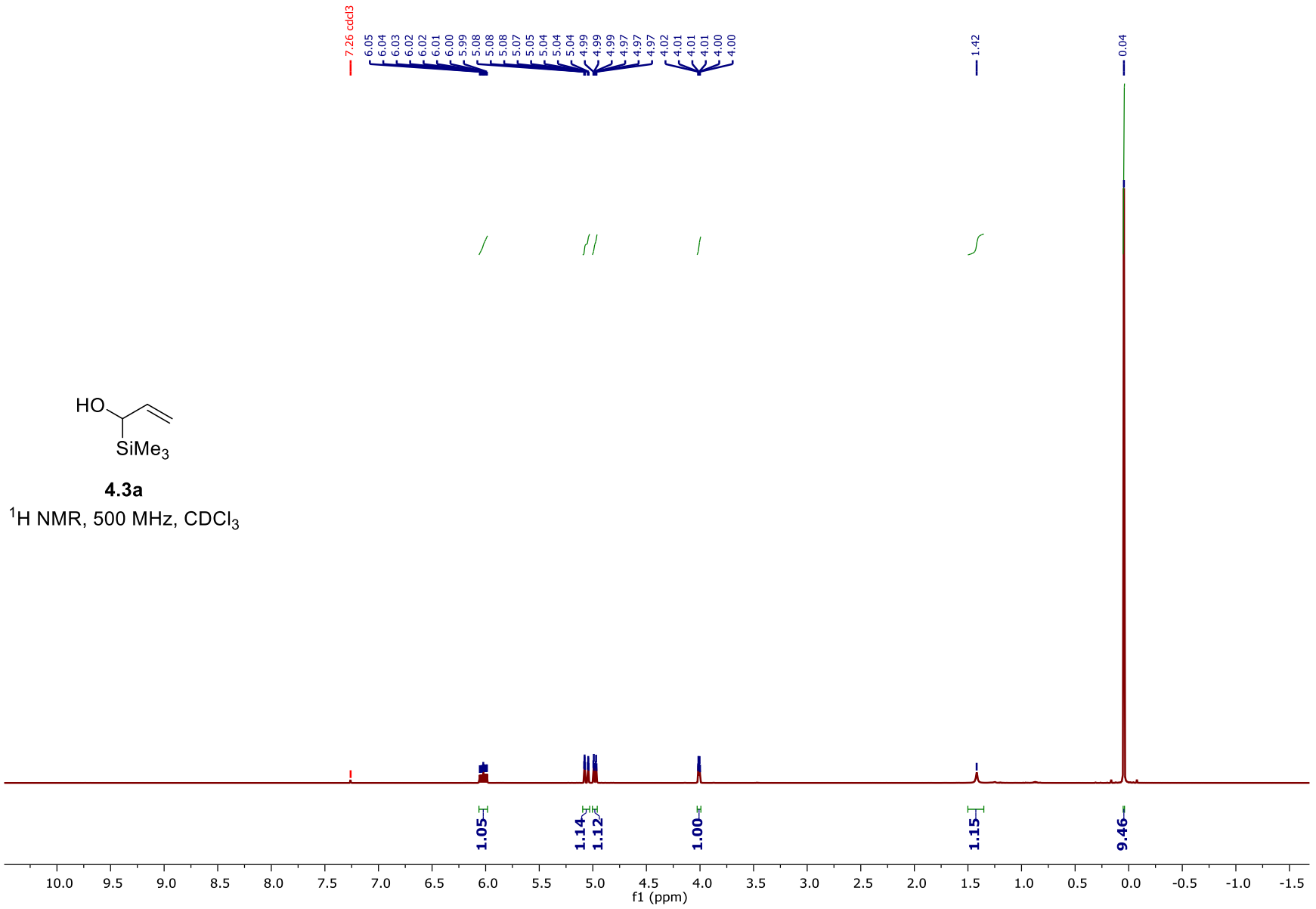

161.50
135.52
133.70
133.35
130.09
128.94
128.45
126.29
125.63
125.28
123.46
123.02
118.07
91.66
77.48
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
40.46
O
CCl3
NH
4.2d
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 cdcl3
O
CCl3
NH
4.2f
1H NMR, 500 MHz, CDCl3
1.04
1.00
3.03
1.02
2.01
1.03
1.01
1.10
1.03
1.15
1.14
f1 (ppm)


161.50
136.93
133.07
133.02
133.00
128.26
128.06
127.69
126.19
126.08
125.48
123.98
118.32
91.67
80.23
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
40.94
O
CCl3
NH
4.2f
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

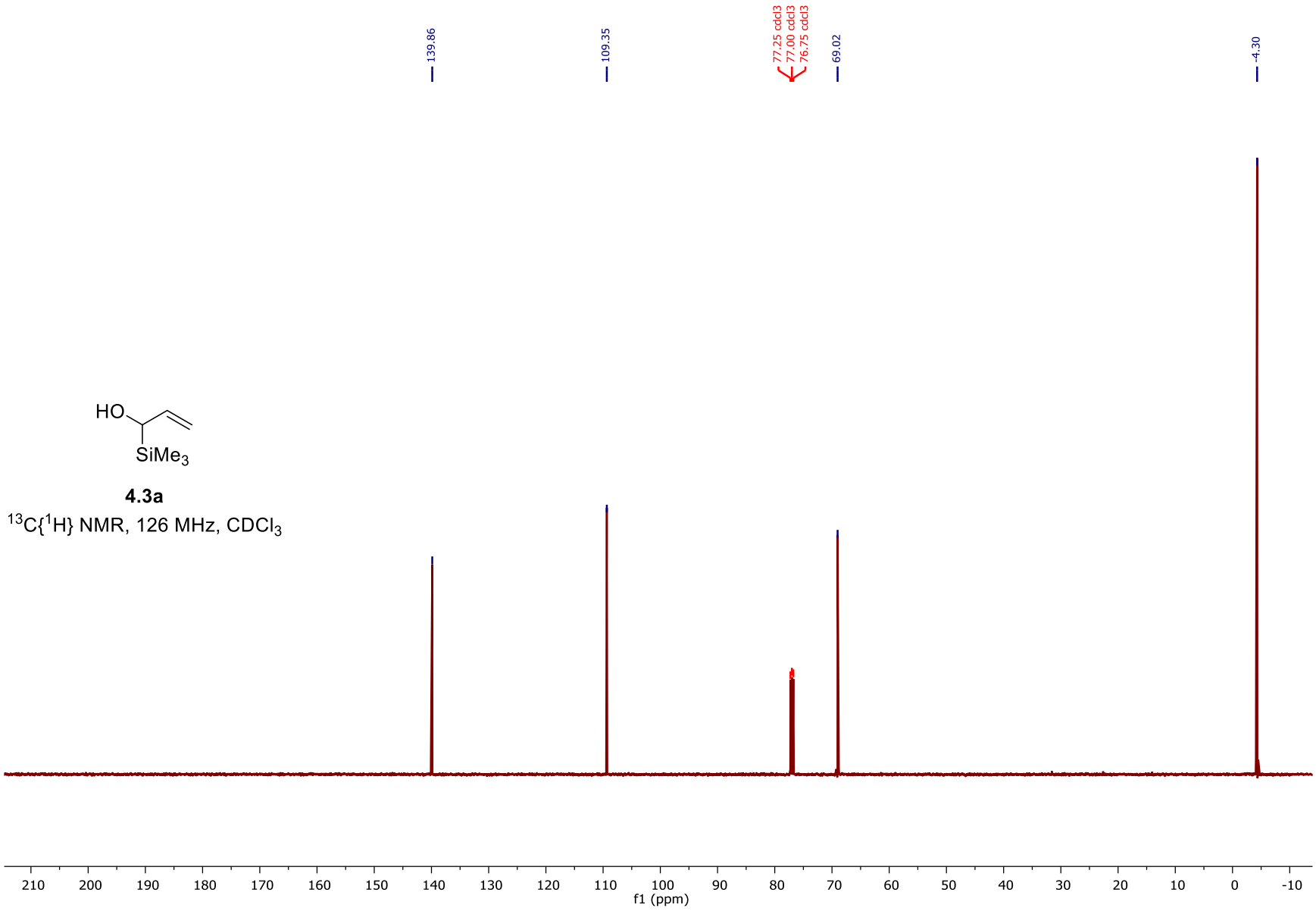

MeO
O
CCl3
NH
4.2h
1H NMR, 500 MHz, CDCl3
f1 (ppm)

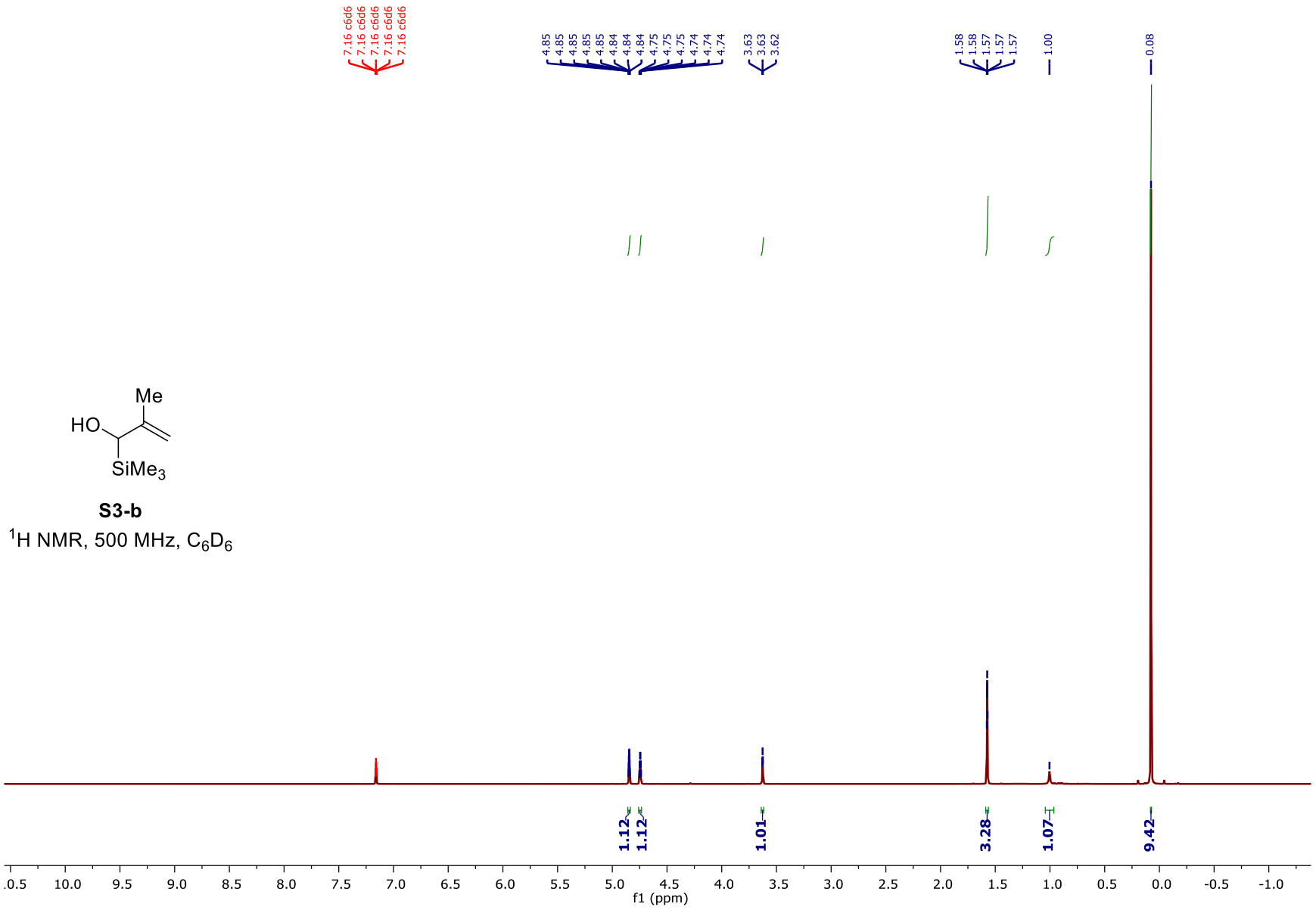

161.47
159.26
133.17
131.59
127.66
118.09
113.69
91.71
79.86
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
55.16
40.91
MeO
O
CCl3
NH
4.2h
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4.3a

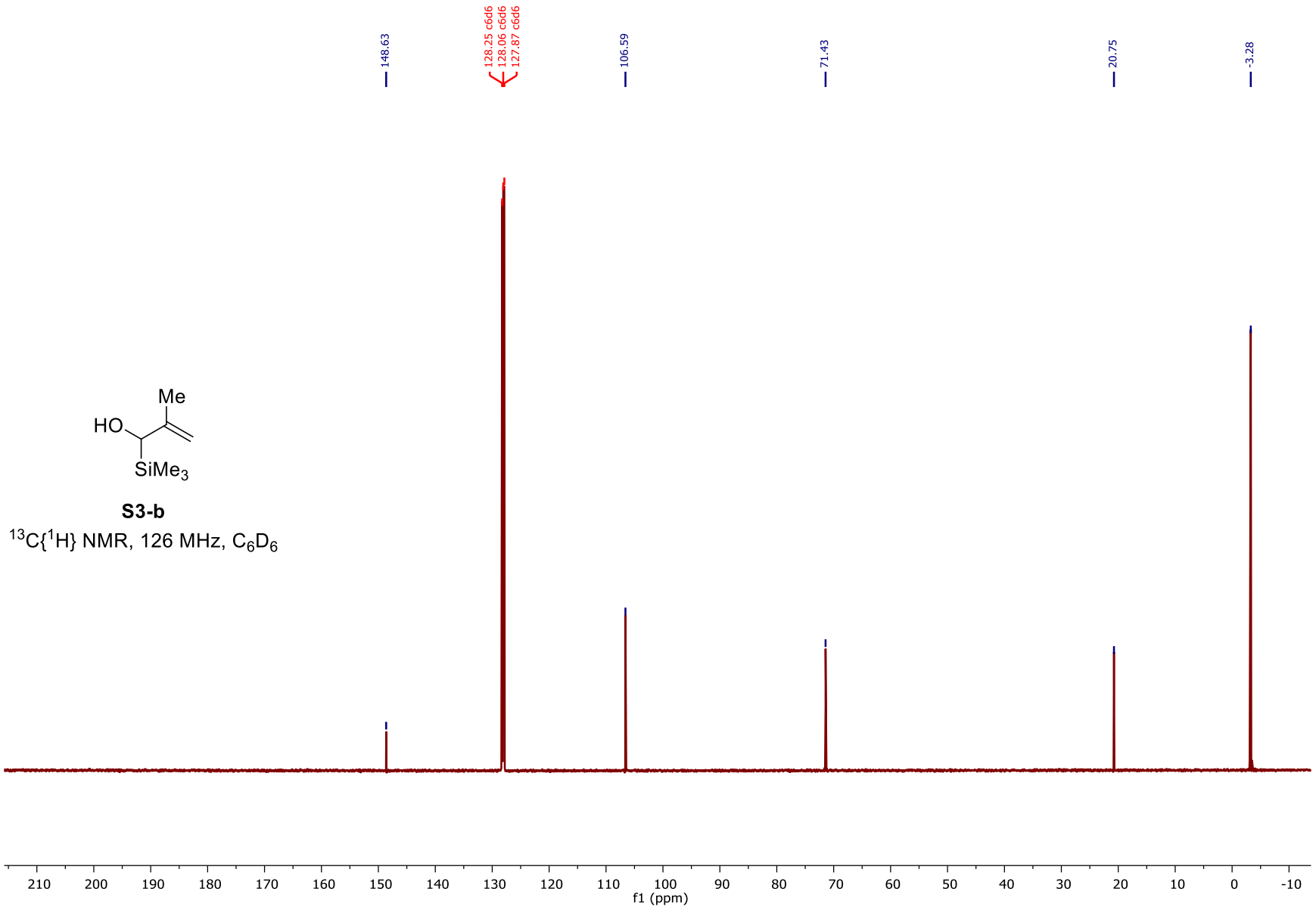
^{1}H NMR, 500 MHz, $CDCl_3$

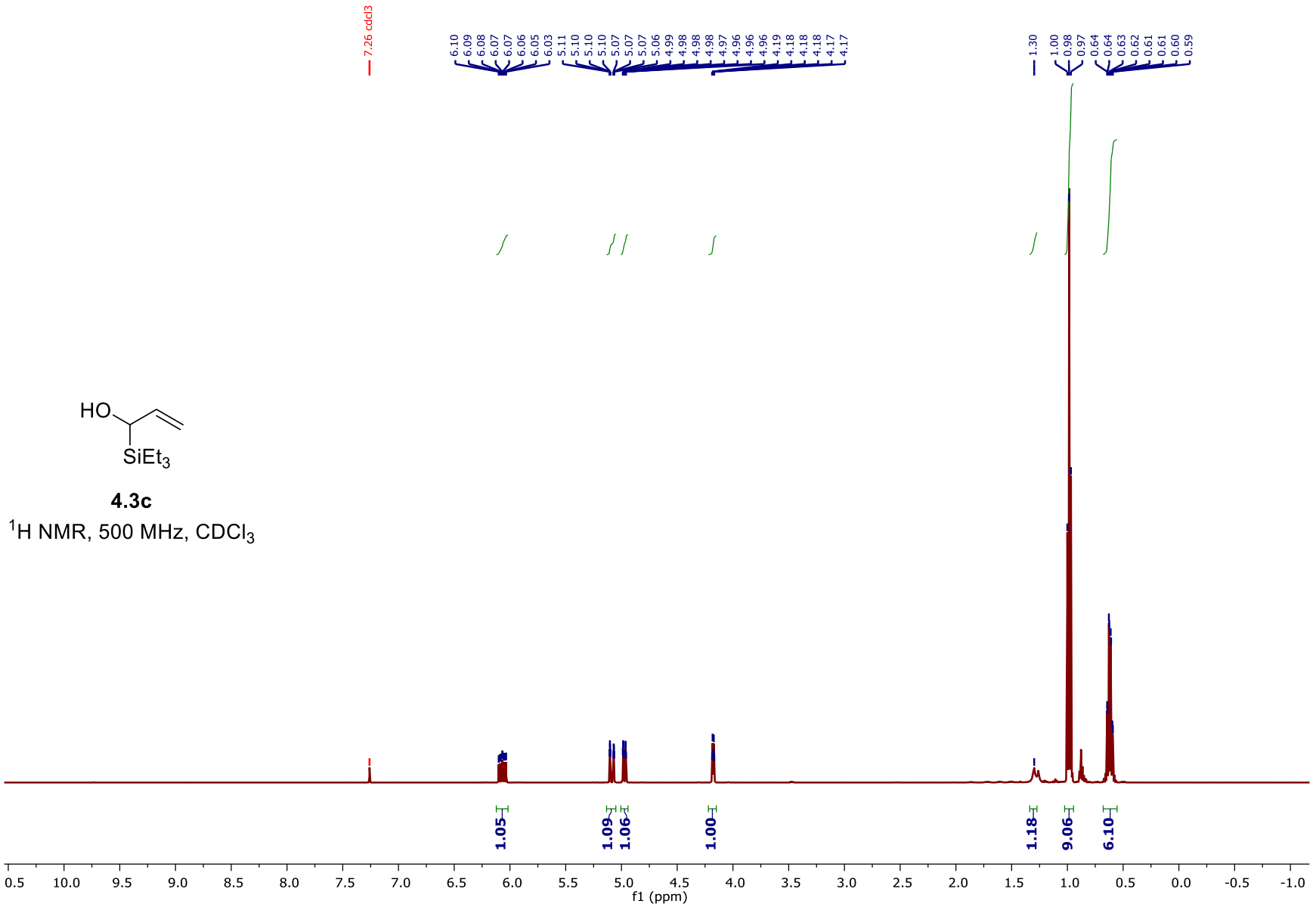

139.86
109.35
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
69.02
-4.30
HO
SiMe3
4.3a
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

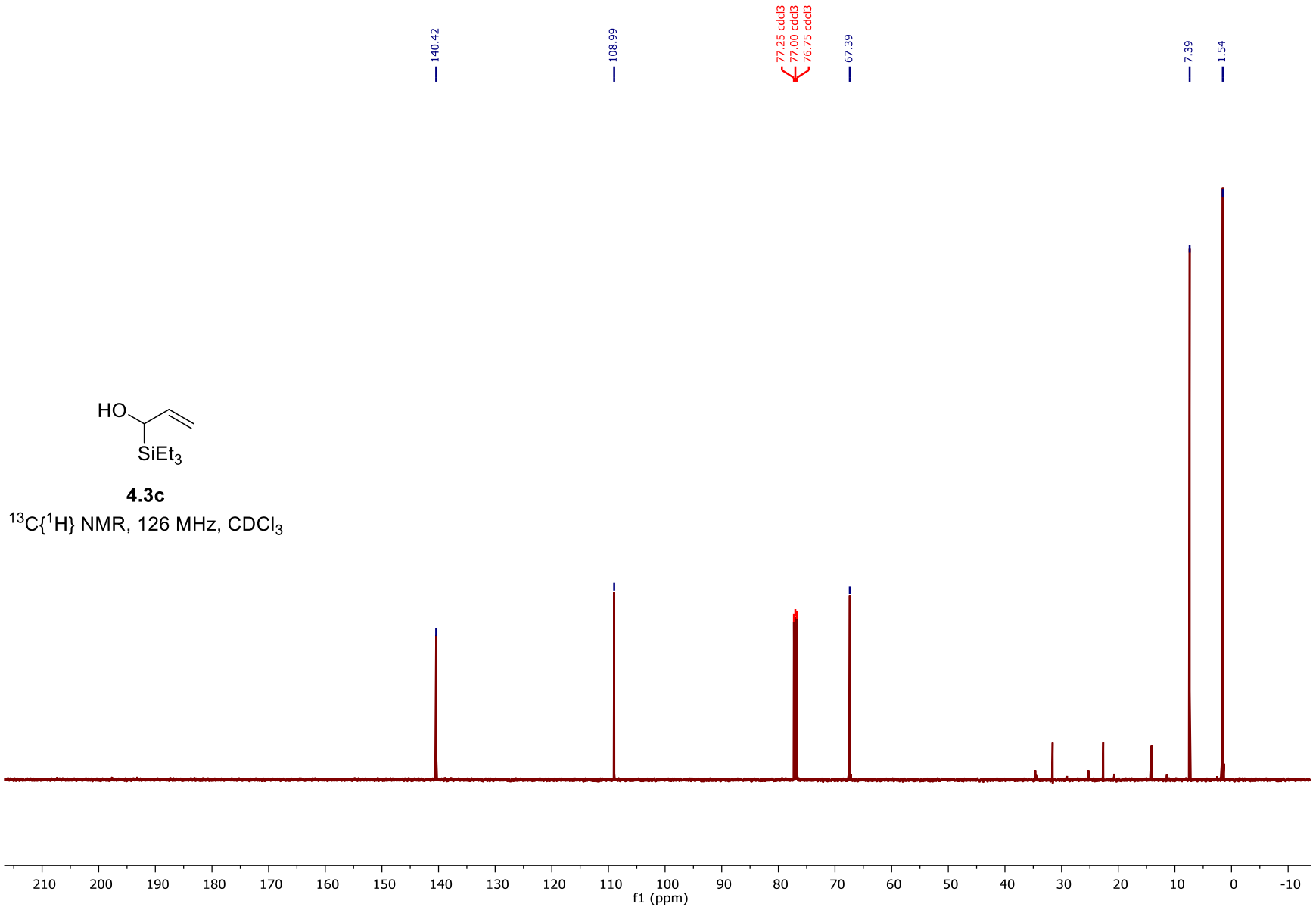


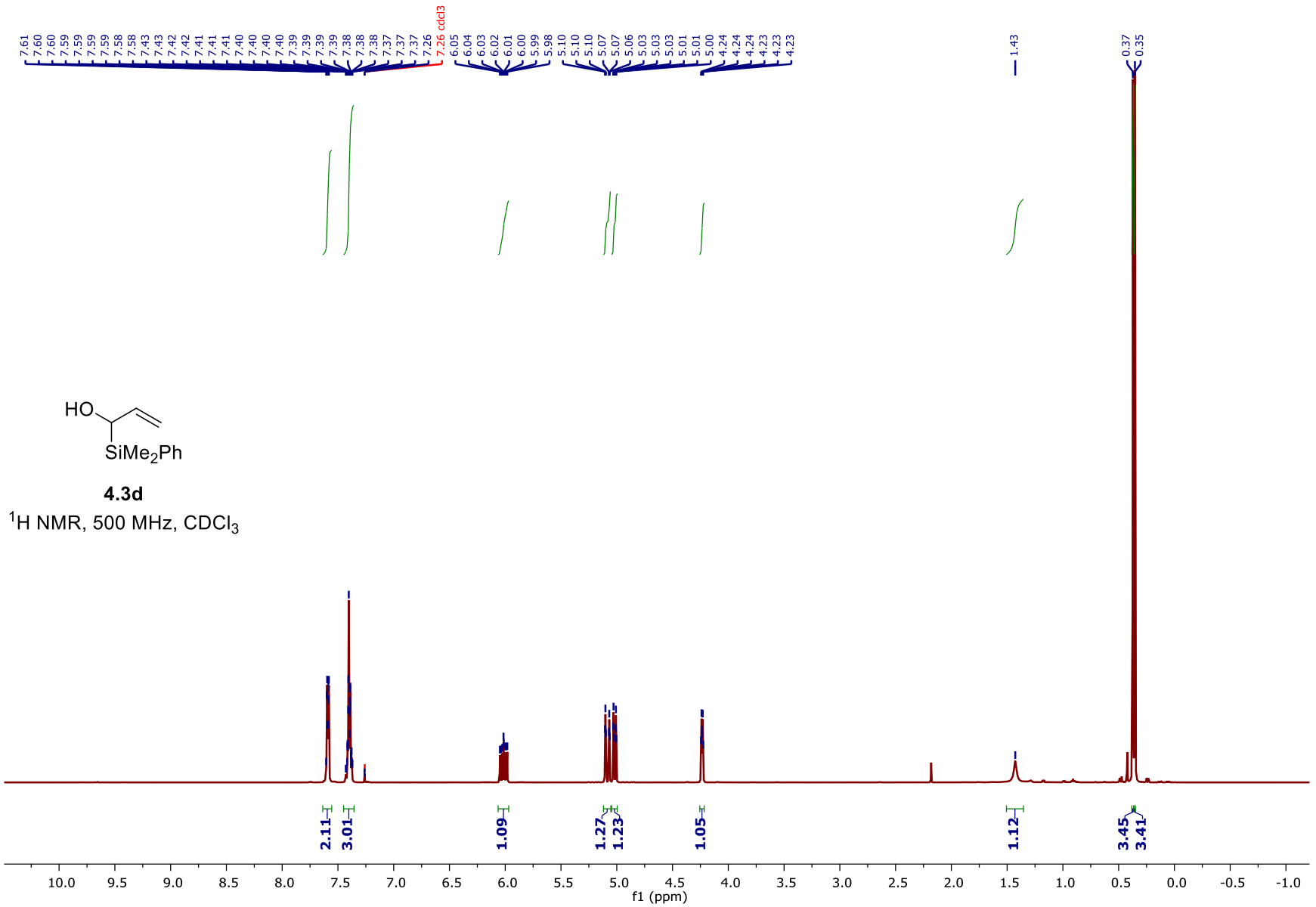
S3-b

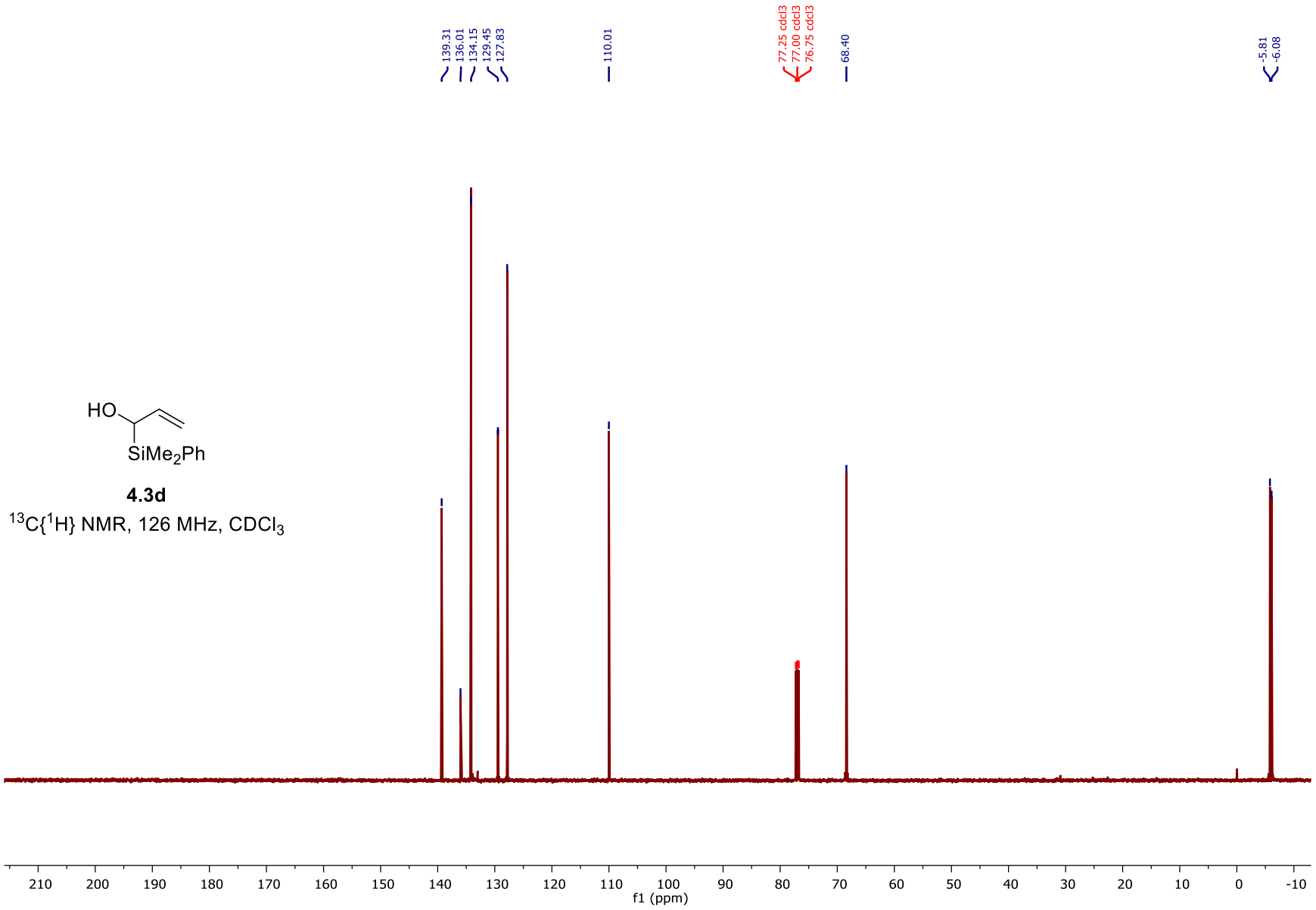
^{1}H NMR, 500 MHz, C_6D_6

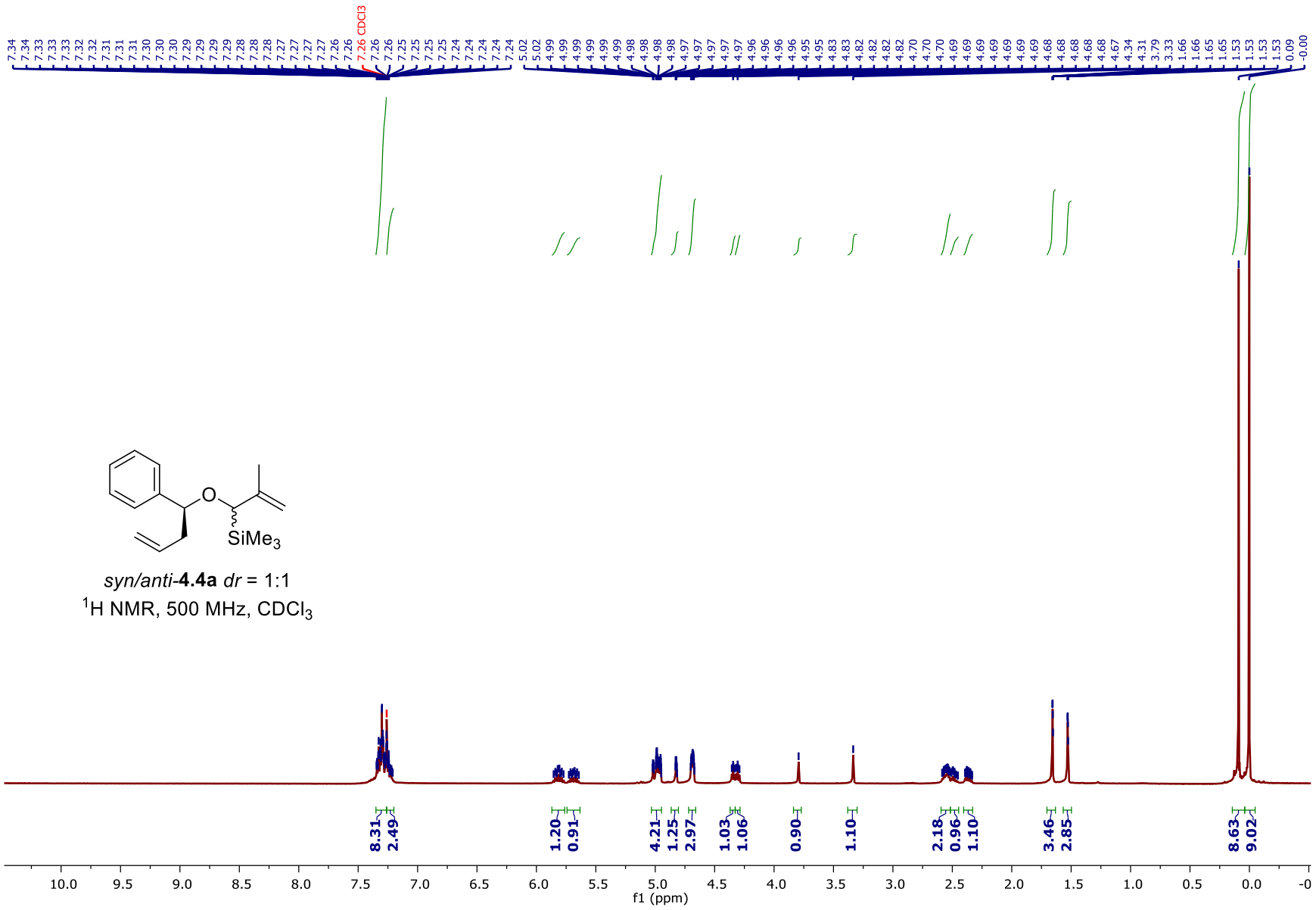

148.63
128.25 c6d6
128.06 c6d6
127.87 c6d6
106.59
71.43
20.75
-3.28
Me
HO
SiMe3
S3-b
13C{1H} NMR, 126 MHz, C6D6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 cdcl3
6.10 6.09 6.08 6.07 6.07 6.06 6.05 6.03
5.11 5.10 5.10 5.10 5.07 5.07 5.07 5.06 4.99 4.98 4.98 4.98 4.97 4.96 4.96 4.96 4.19 4.18 4.18 4.17 4.17
1.30
1.00 0.98 0.97 0.64 0.64 0.63 0.62 0.61 0.61 0.60 0.59
HO
SiEt3
4.3c
1H NMR, 500 MHz, CDCl3
1.05
1.09
1.06
1.00
1.18
9.06
6.10
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


140.42
108.99
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
67.39
7.39
1.54
HO
SiEt3
4.3c
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

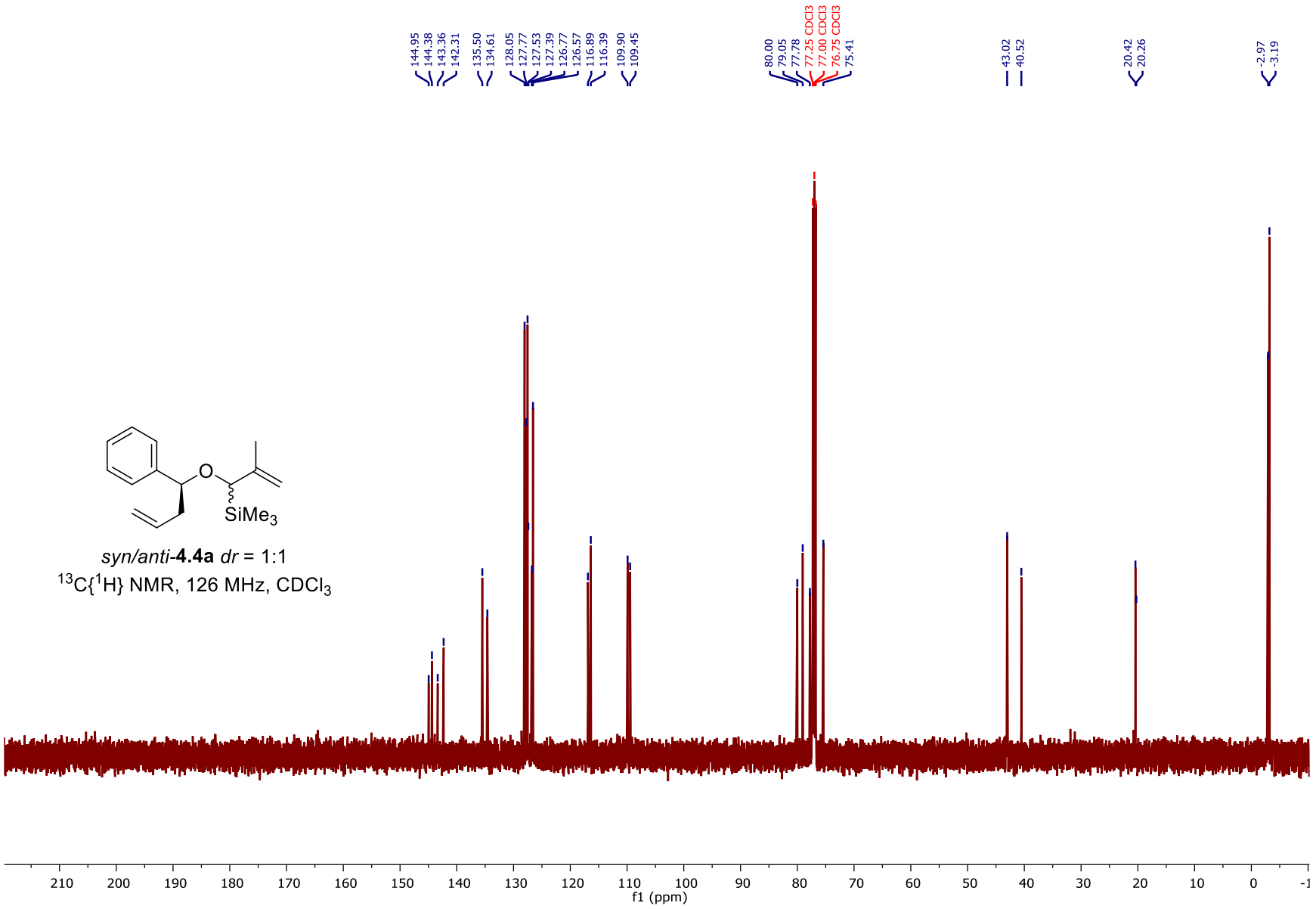

7.61 7.60 7.60 7.59 7.59 7.59 7.59 7.58 7.58 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.40 7.40 7.39 7.39 7.39 7.39 7.38 7.38 7.38 7.38 7.37 7.37 7.37 7.37 7.26 7.26 cdcl3
6.05 6.04 6.03 6.02 6.01 6.00 5.99 5.98
5.10 5.10 5.10 5.07 5.07 5.06 5.03 5.03 5.03 5.01 5.01 5.00
4.24 4.24 4.23 4.23 4.23
1.43
0.37 0.35
HO
SiMe2Ph
4.3d
1H NMR, 500 MHz, CDCl3
2.11 3.01 1.09 1.27 1.23 1.05 1.12 3.45 3.41
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 -1.0
f1 (ppm)

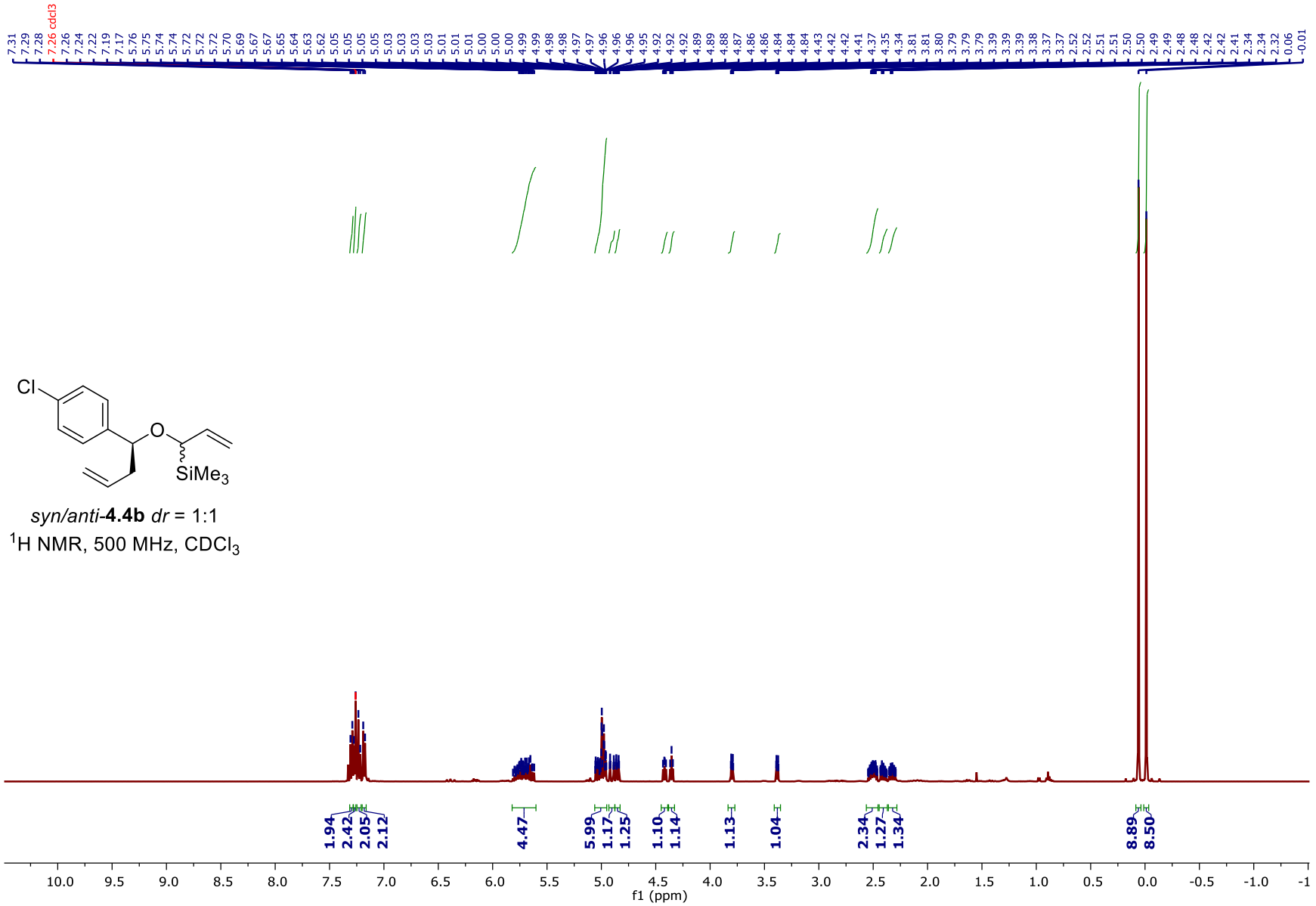

139.31
136.01
134.15
129.45
127.83
110.01
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
68.40
-5.81
-6.08
HO
SiMe2Ph
4.3d
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

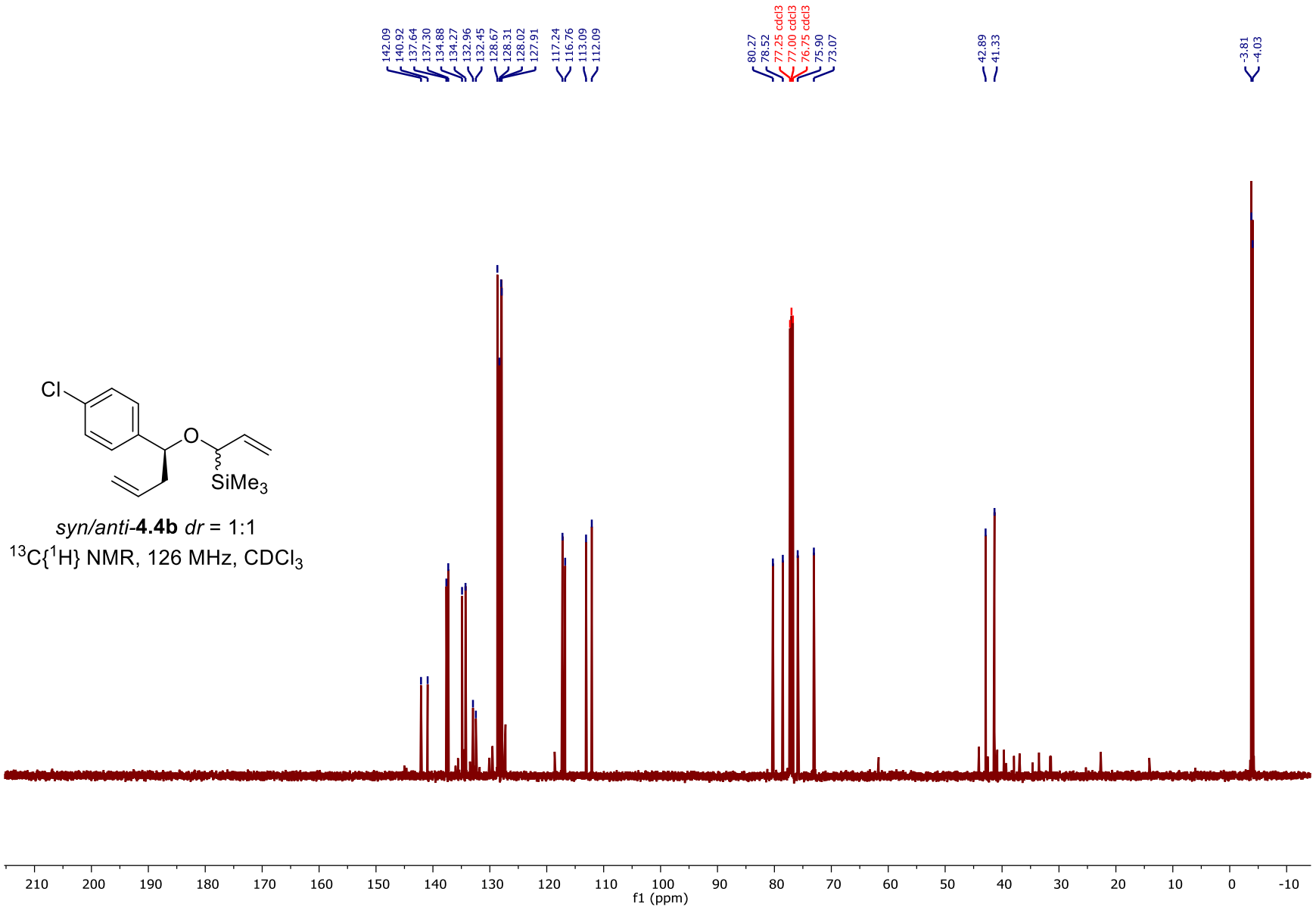


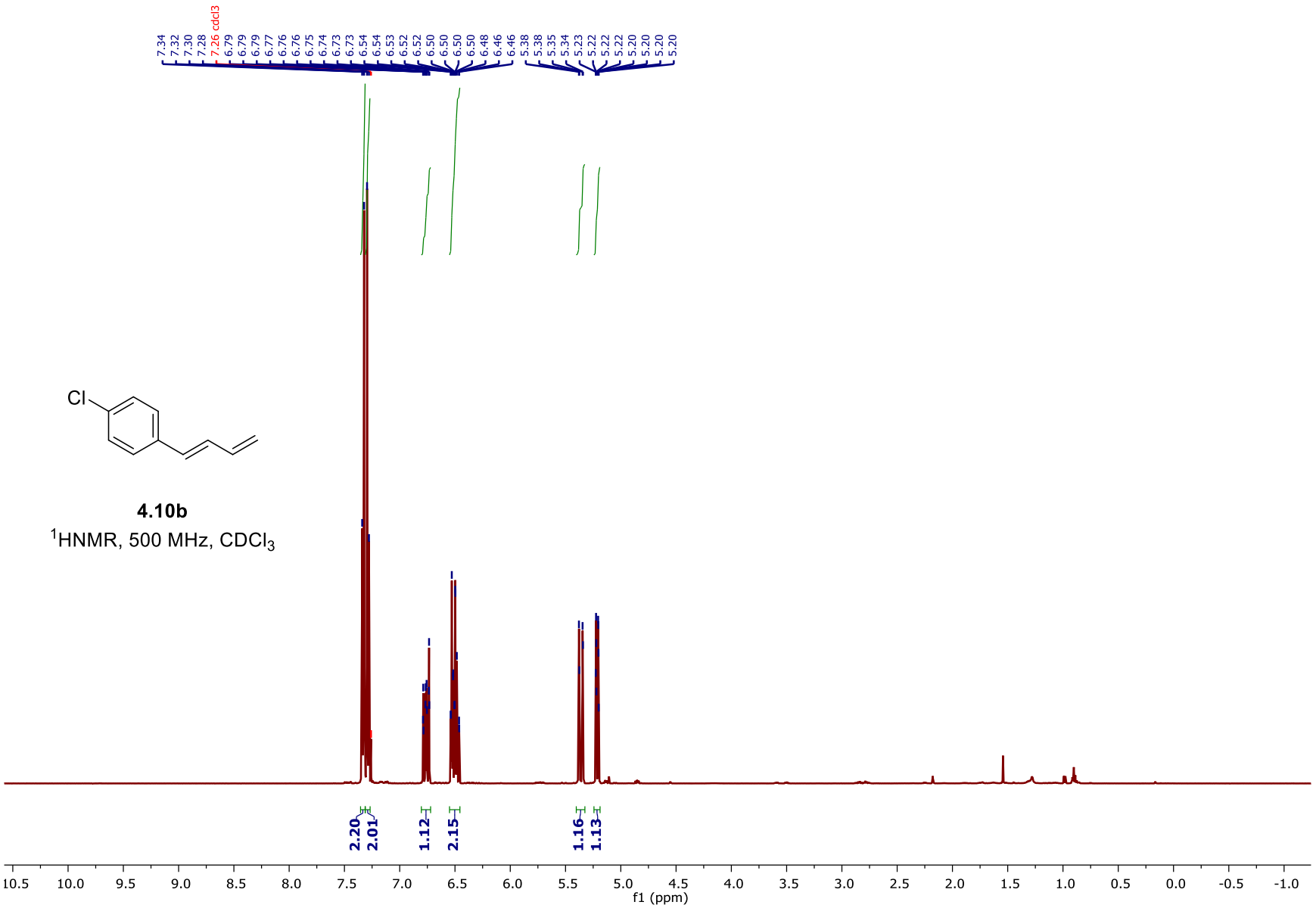
syn/anti-**4.4a** *dr* = 1:1

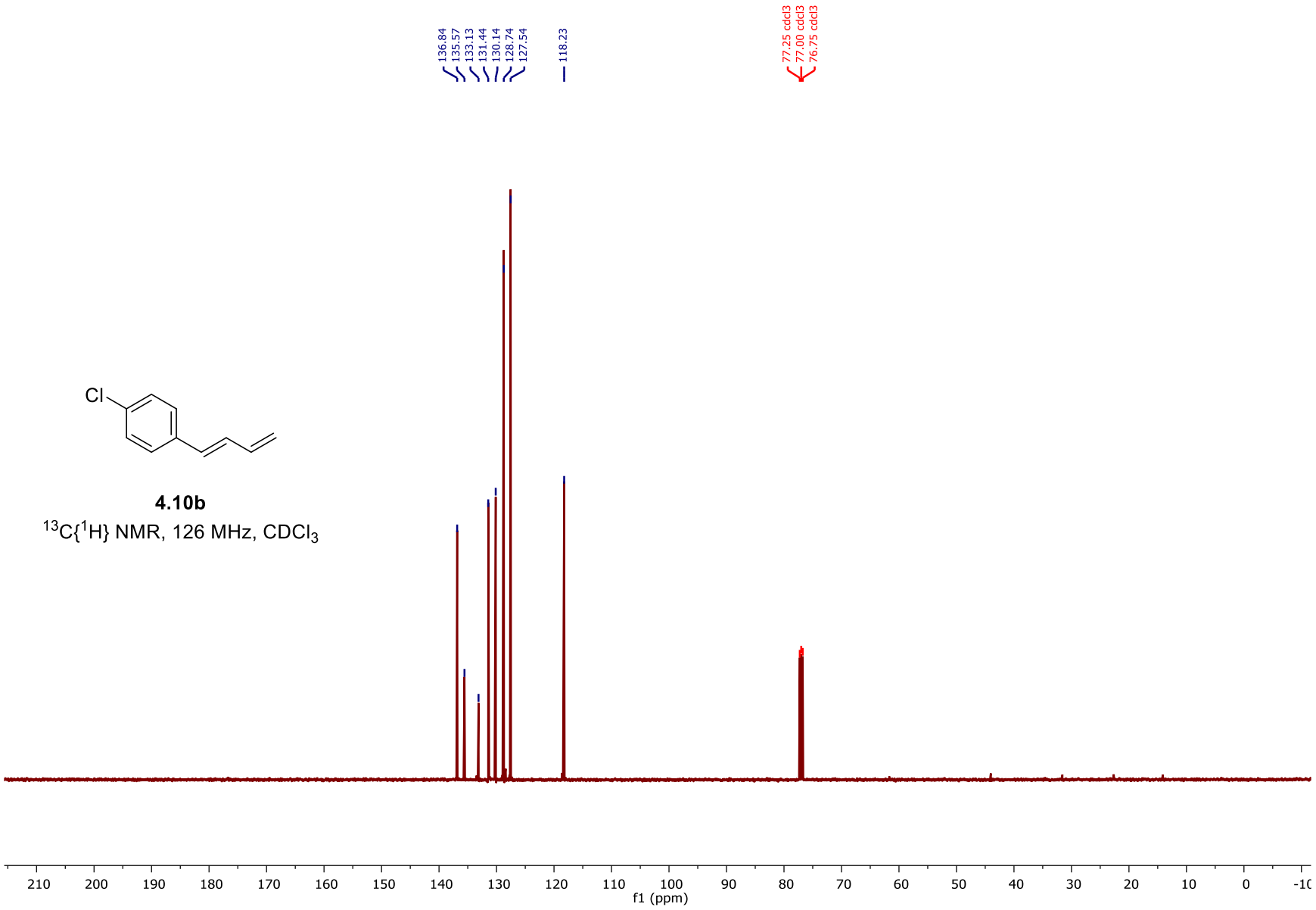
^{1}H NMR, 500 MHz, $CDCl_3$

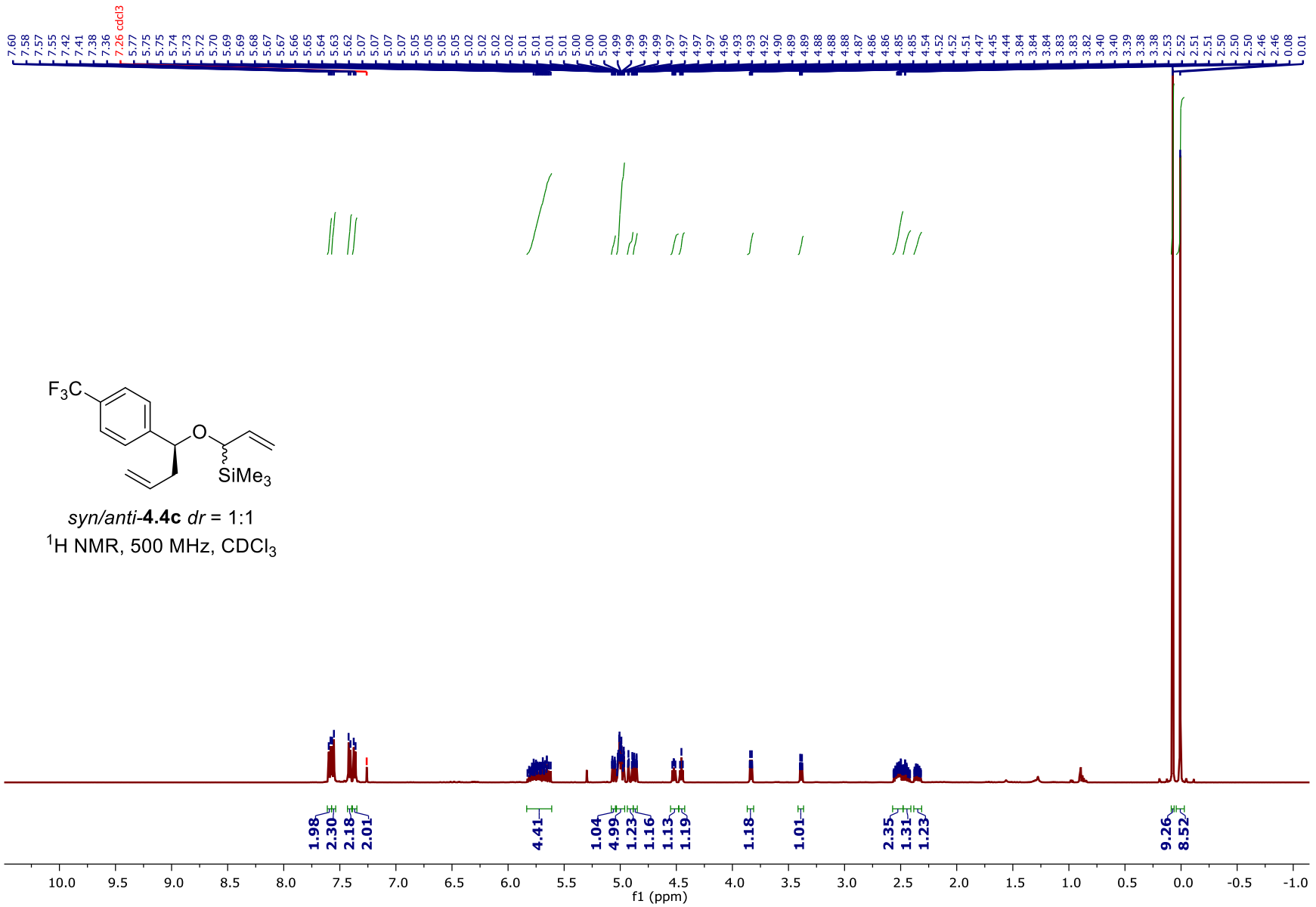

144.95
144.38
143.36
142.31
135.50
134.61
128.05
127.77
127.53
127.39
126.77
126.57
116.89
116.39
109.90
109.45
80.00
79.05
77.78
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
75.41
43.02
40.52
20.42
20.26
-2.97
-3.19
O
SiMe3
syn/anti-4.4a dr = 1:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

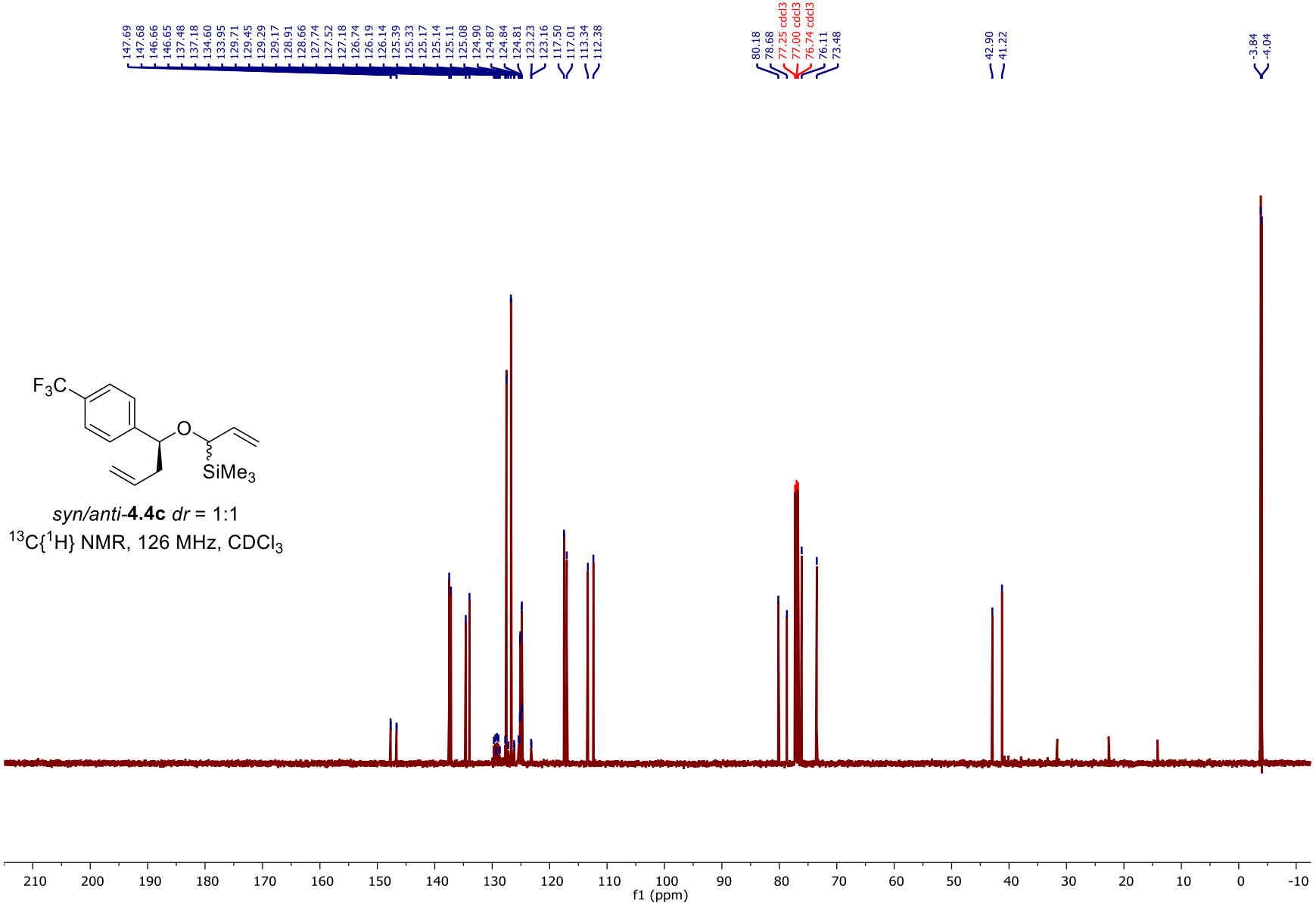

Cl
O
SiMe3
syn/anti-4.4b dr = 1:1
1H NMR, 500 MHz, CDCl3
1.94
2.42
2.05
2.12
4.47
5.99
1.17
1.25
1.10
1.14
1.13
1.04
2.34
1.27
1.34
8.89
8.50
f1 (ppm)

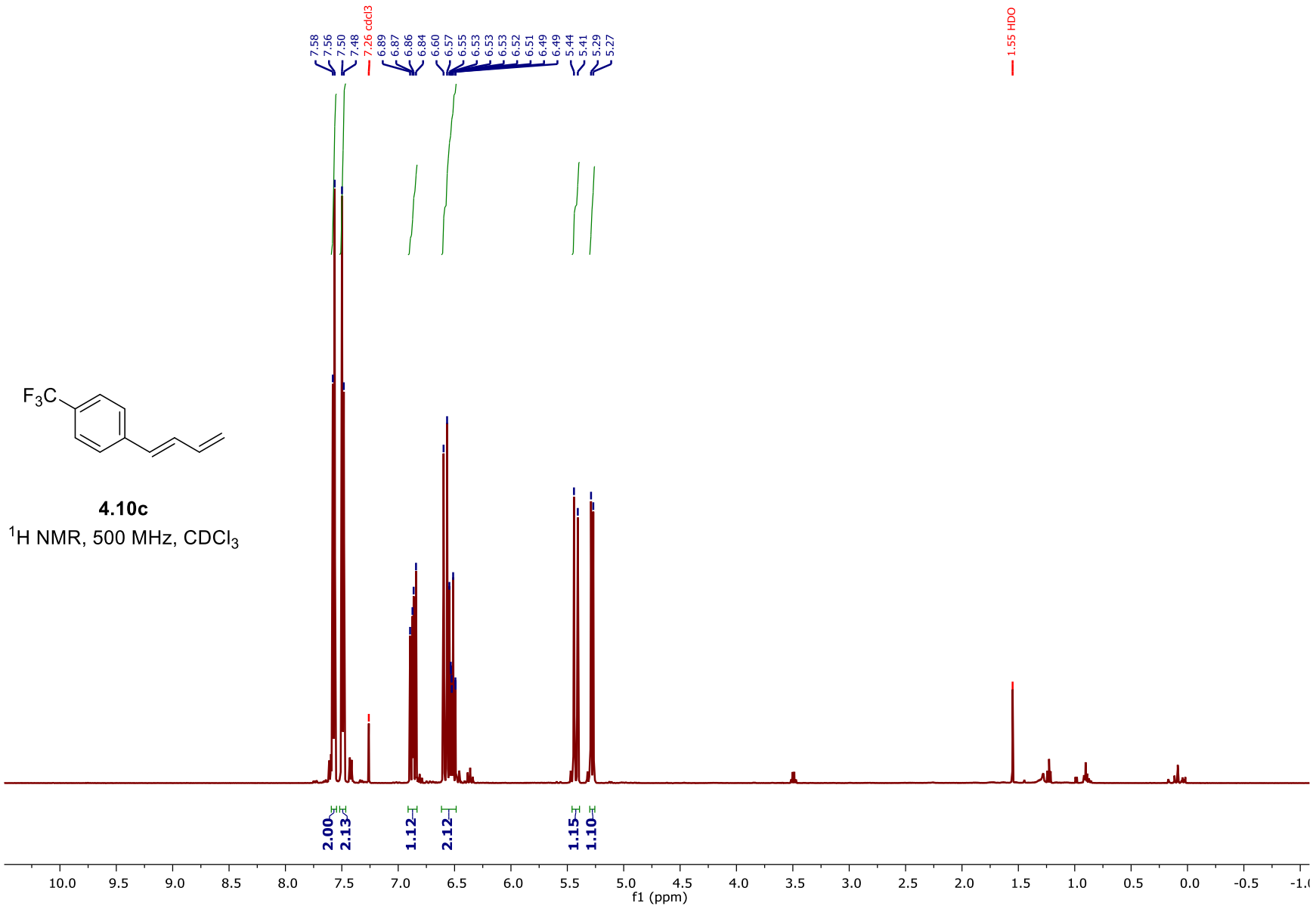

142.09
140.92
137.64
137.30
134.88
134.27
132.96
132.45
128.67
128.31
128.02
127.91
117.24
116.76
113.09
112.09
80.27
78.52
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
75.90
73.07
42.89
41.33
-3.81
-4.03
Cl
O
SiMe3
syn/anti-4.4b dr = 1:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

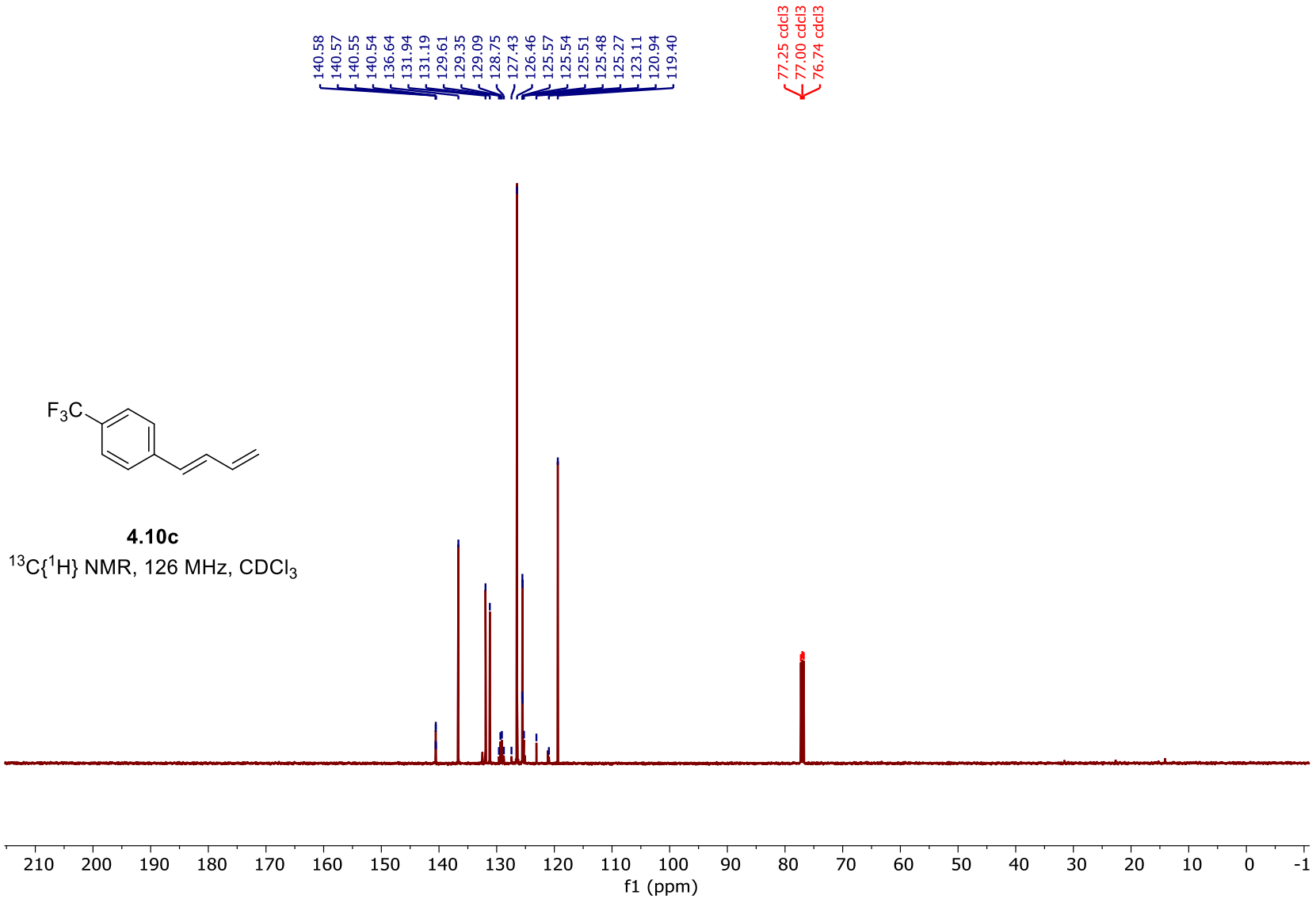

7.34
7.32
7.30
7.28
7.26 cdcl3
6.79
6.79
6.79
6.77
6.76
6.76
6.75
6.74
6.73
6.73
6.54
6.54
6.53
6.52
6.52
6.50
6.50
6.50
6.50
6.48
6.46
6.46
5.38
5.38
5.35
5.34
5.23
5.22
5.22
5.22
5.20
5.20
5.20
5.20
Cl
4.10b
1HNMR, 500 MHz, CDCl3
2.20
2.01
1.12
2.15
1.16
1.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

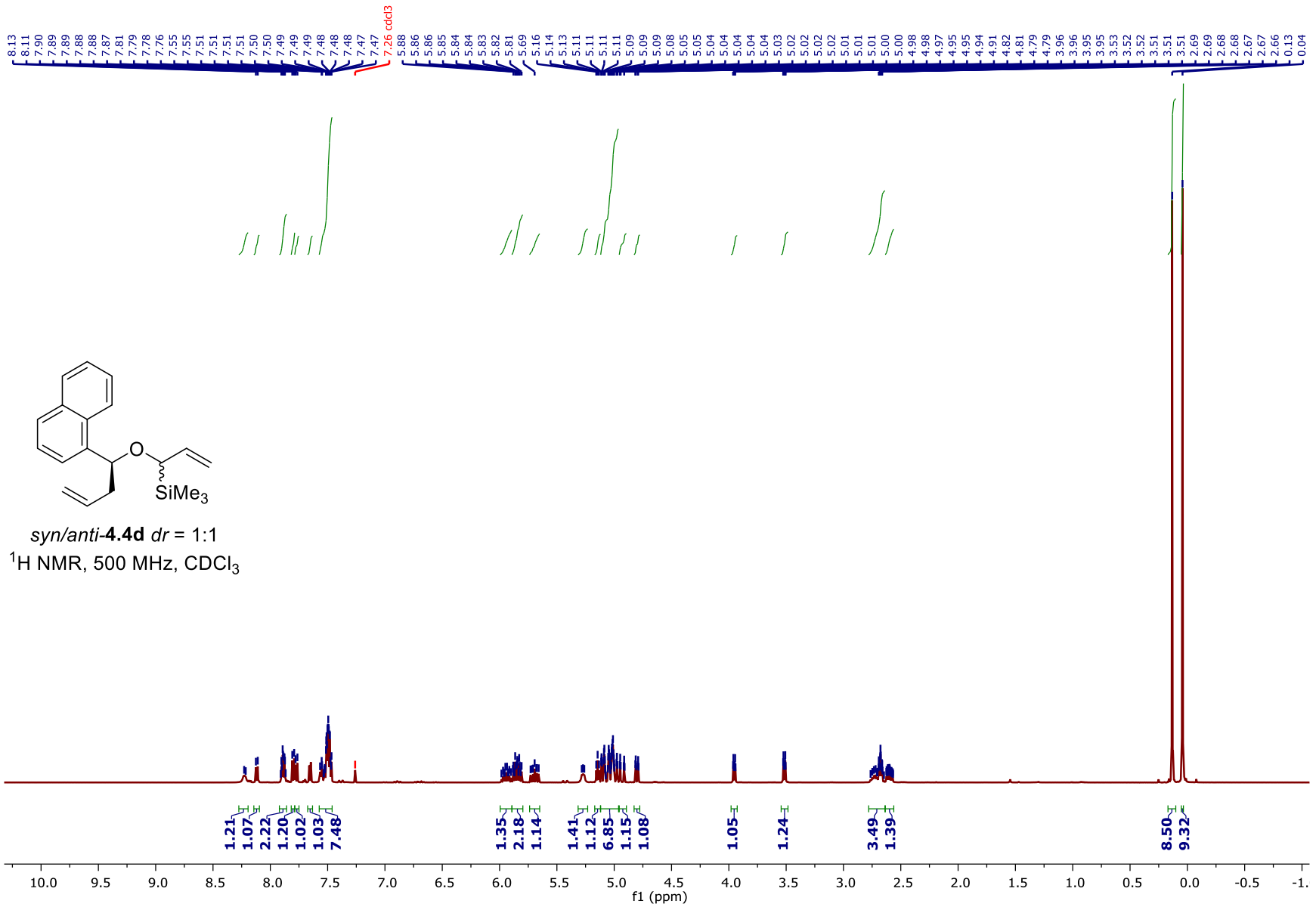

136.84
135.57
133.13
131.44
130.14
128.74
127.54
118.23
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
Cl
4.10b
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

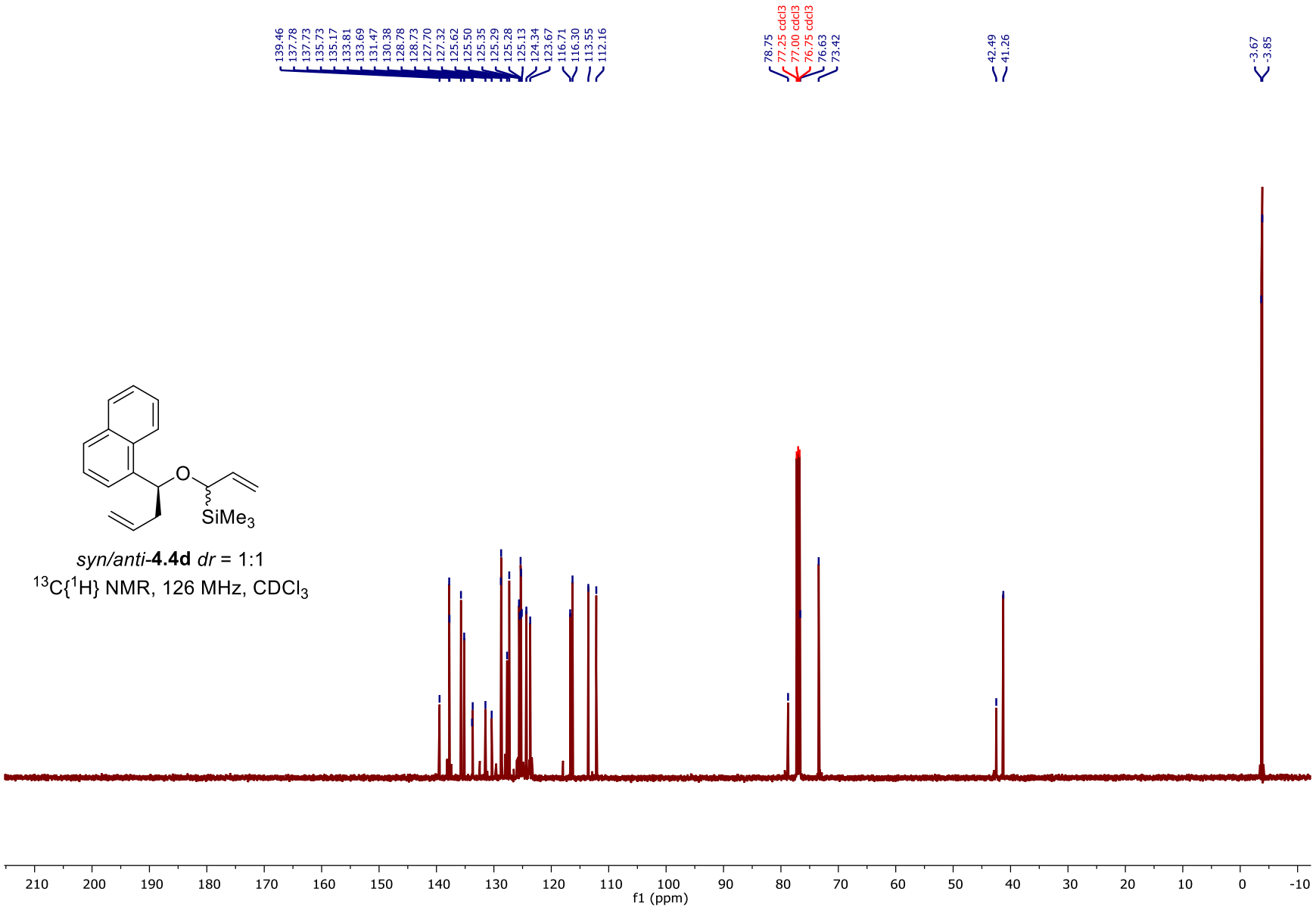

F3C
O
SiMe3
syn/anti-4.4c dr = 1:1
1H NMR, 500 MHz, CDCl3
f1 (ppm)

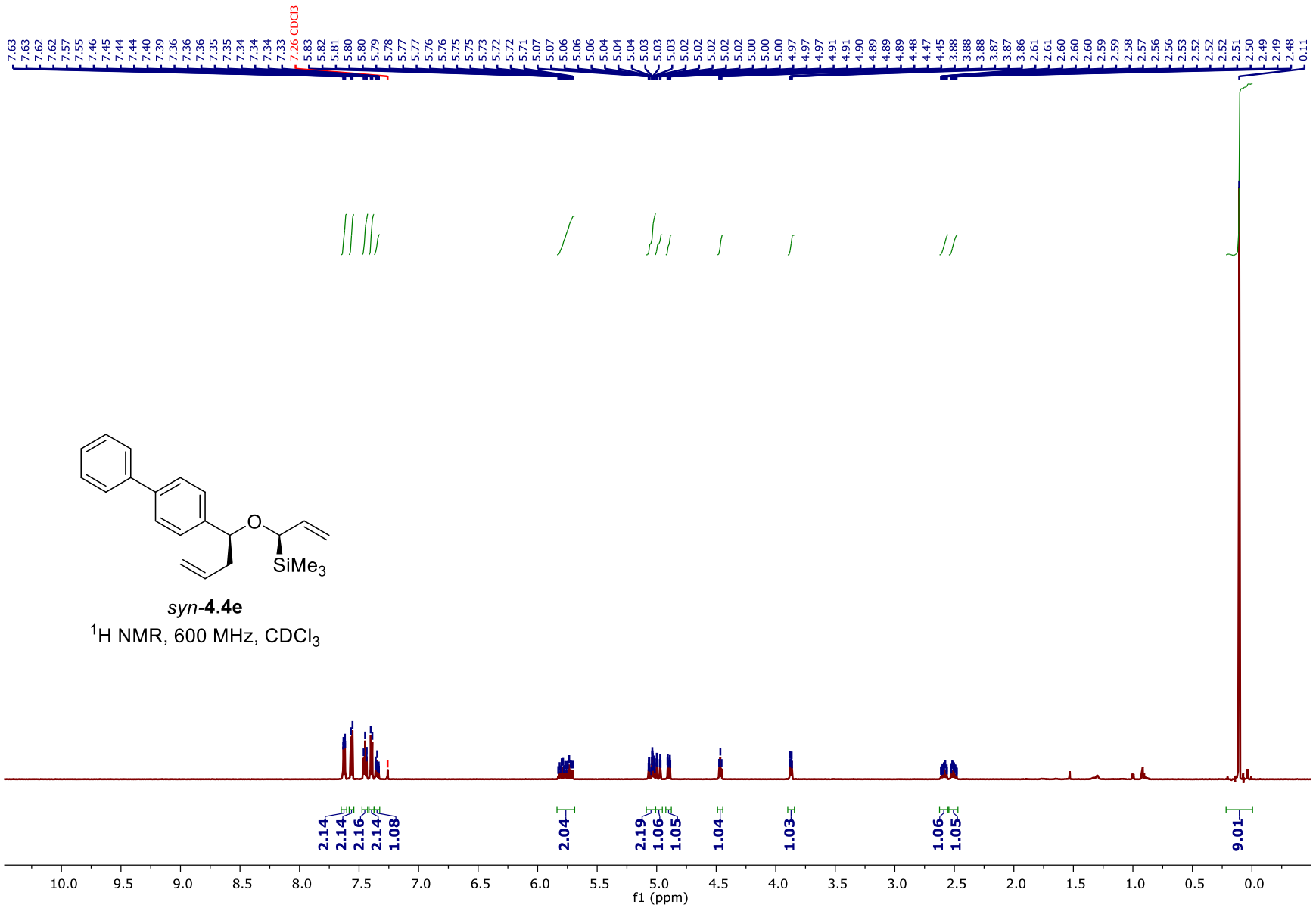

147.69
147.68
146.66
146.65
137.48
137.18
134.60
133.95
129.71
129.45
129.29
129.17
128.91
128.66
127.74
127.52
127.18
126.74
126.19
126.14
125.39
125.33
125.17
125.14
125.11
125.08
124.90
124.87
124.84
124.81
123.23
123.16
117.50
117.01
113.34
112.38
80.18
78.68
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
76.11
73.48
42.90
41.22
-3.84
-4.04
F3C
O
SiMe3
syn/anti-4.4c dr = 1:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.58
7.56
7.50
7.48
7.26 cdcl3
6.89
6.87
6.86
6.84
6.60
6.57
6.55
6.53
6.53
6.52
6.51
6.49
6.49
5.44
5.41
5.29
5.27
1.55 HDO
F3C
4.10c
1H NMR, 500 MHz, CDCl3
2.00
2.13
1.12
2.12
1.15
1.10
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)


140.58
140.57
140.55
140.54
136.64
131.94
131.19
129.61
129.35
129.09
128.75
127.43
126.46
125.57
125.54
125.51
125.48
125.27
123.11
120.94
119.40
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
F3C
4.10c
13C{1H} NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

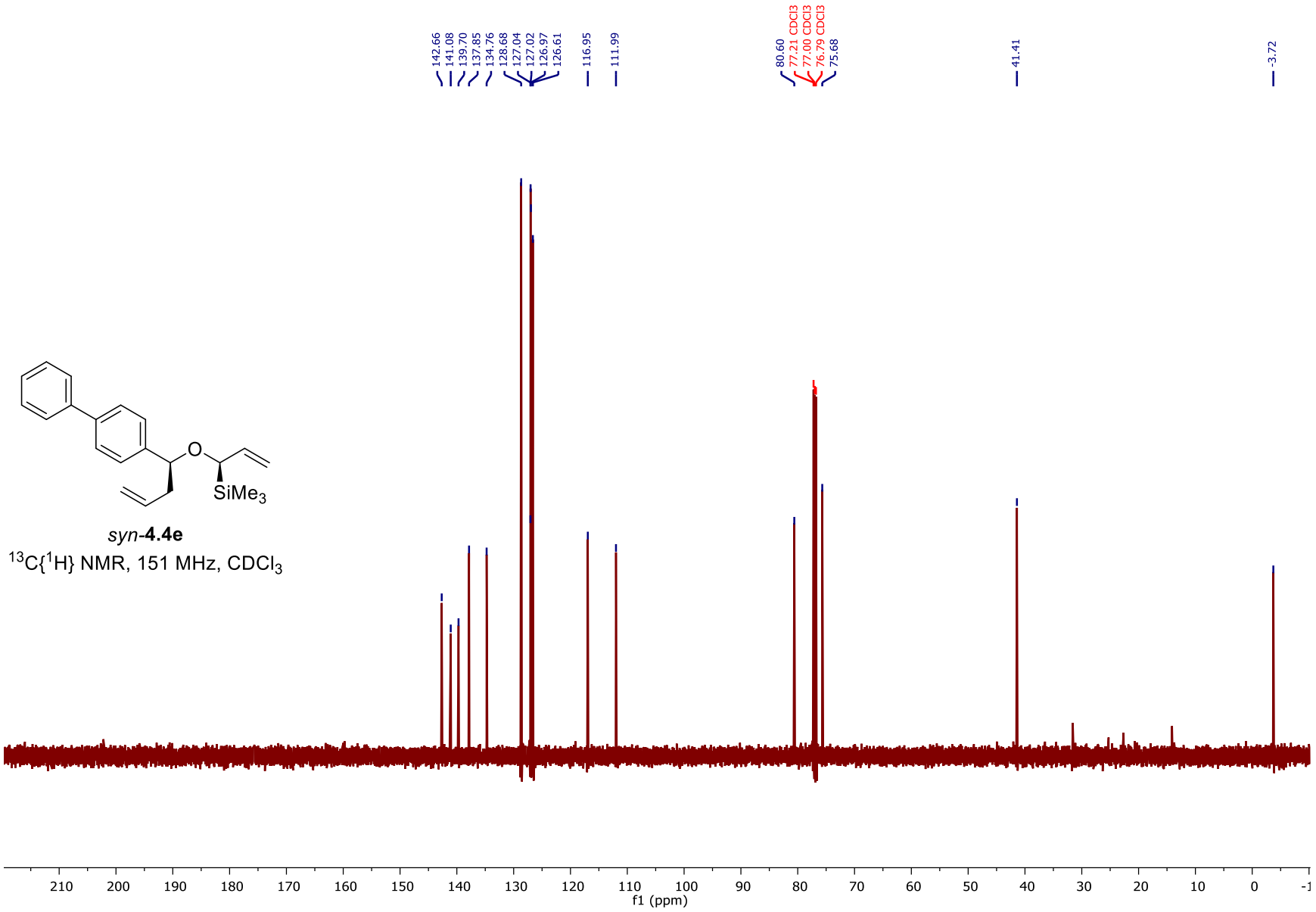

8.13 8.11 7.90 7.89 7.89 7.88 7.88 7.87 7.81 7.79 7.78 7.76 7.55 7.55 7.51 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.49 7.48 7.48 7.48 7.47 7.47 7.26 cdcl3
5.88 5.86 5.86 5.85 5.84 5.84 5.83 5.82 5.81 5.69 5.16 5.14 5.13 5.11 5.11 5.11 5.11 5.09 5.09 5.09 5.08 5.05 5.05 5.04 5.04 5.04 5.04 5.03 5.02 5.02 5.02 5.01 5.01 5.01 5.00 5.00 4.98 4.98 4.97 4.95 4.95 4.94 4.91 4.82 4.81 4.79 4.79 3.96 3.96 3.95 3.95 3.53 3.52 3.52 3.51 3.51 3.51 2.69 2.69 2.68 2.68 2.67 2.67 2.66 0.13 0.04
O
SiMe3
syn/anti-4.4d dr = 1:1
1H NMR, 500 MHz, CDCl3
1.21 1.07 2.22 1.20 1.02 1.03 7.48
1.35 2.18 1.14
1.41 1.12 6.85 1.15 1.08
1.05
1.24
3.49 1.39
8.50 9.32
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 -1.
f1 (ppm)


139.46
137.78
137.73
135.73
135.17
133.81
133.69
131.47
130.38
128.78
128.73
127.70
127.32
125.62
125.50
125.35
125.29
125.28
125.13
124.34
123.67
116.71
116.30
113.55
112.16
78.75
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
76.63
73.42
42.49
41.26
-3.67
-3.85
O
SiMe3
syn/anti-4.4d dr = 1:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



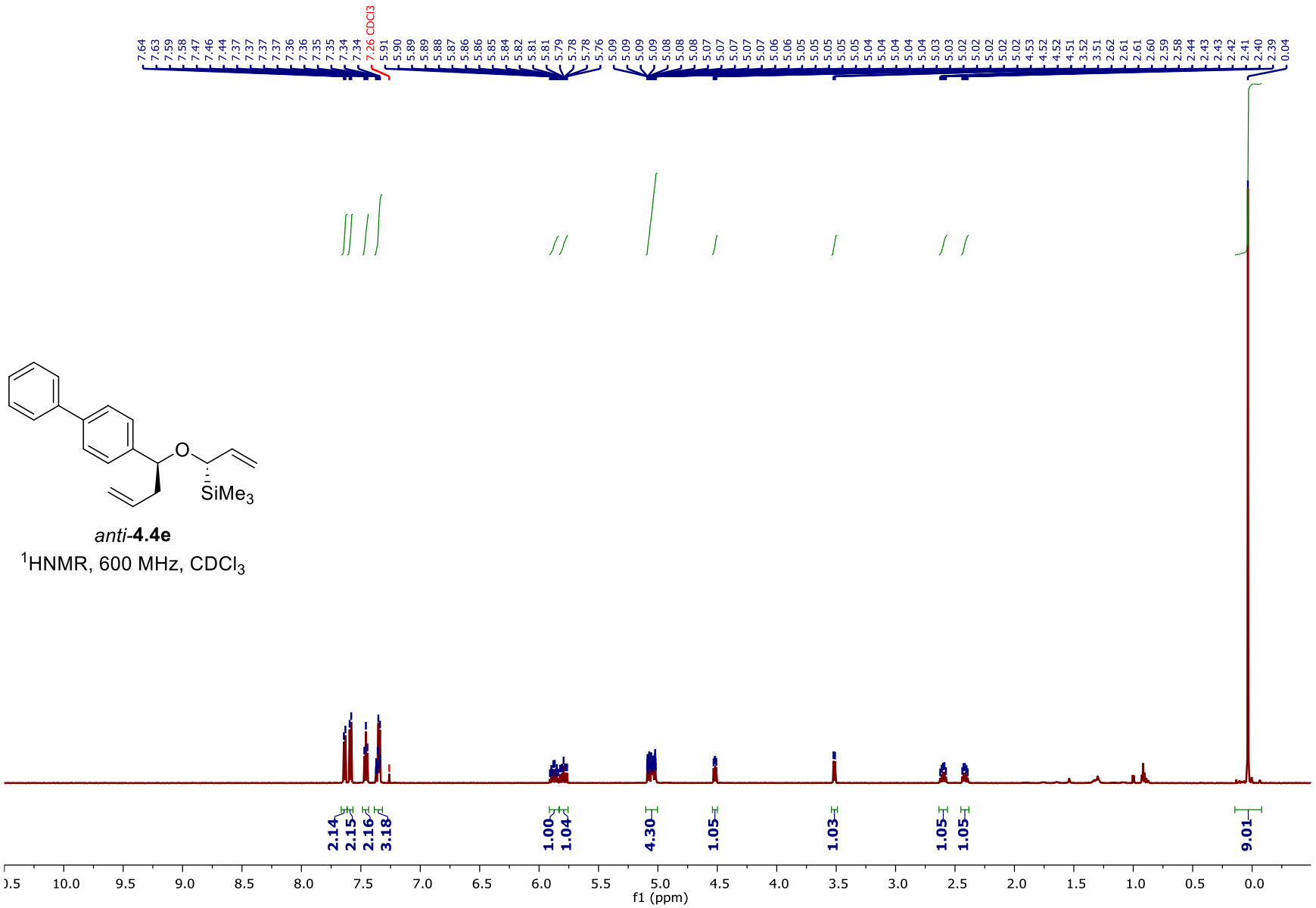
syn-**4.4e**

^{1}H NMR, 600 MHz, $CDCl_3$



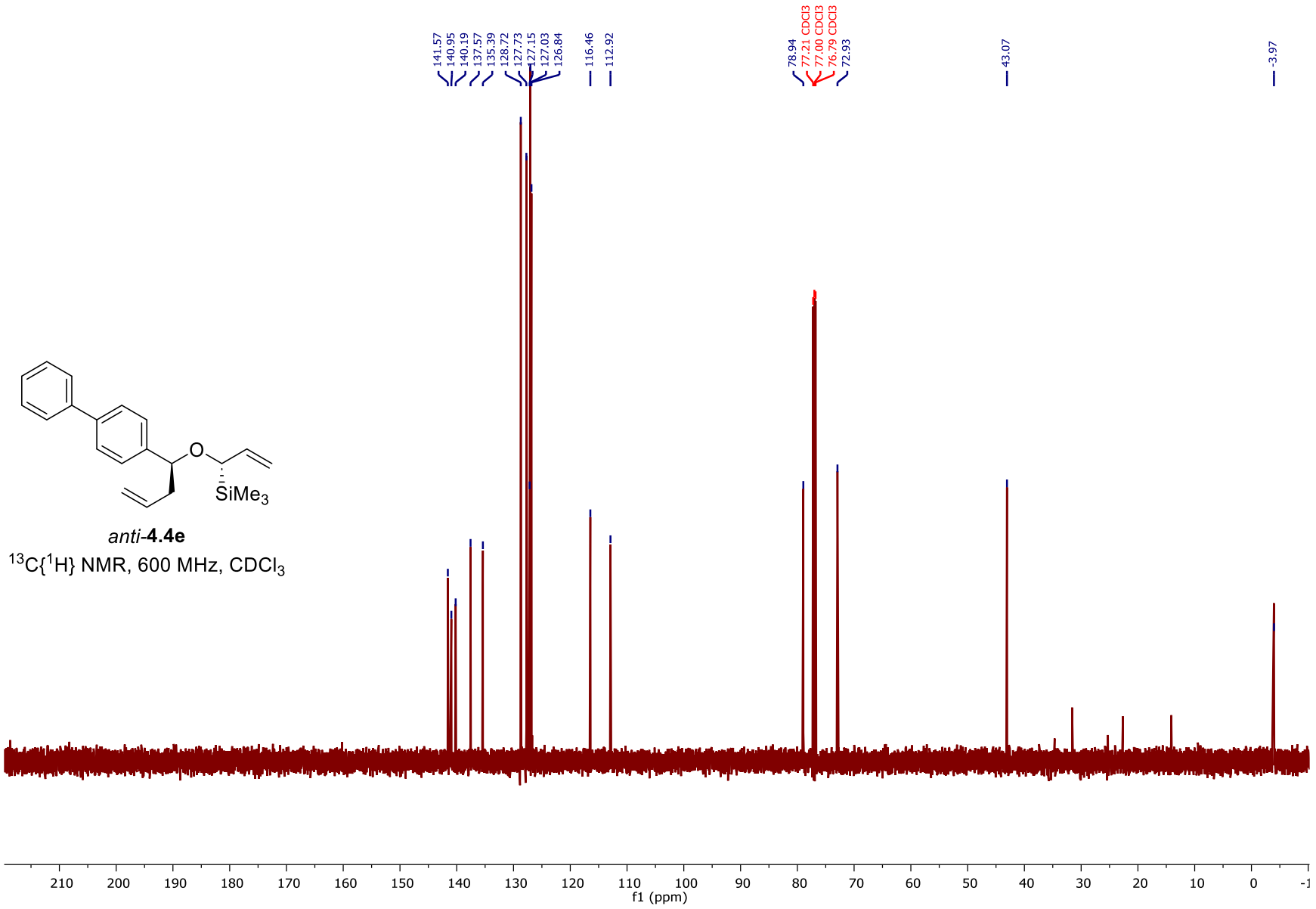
syn-**4.4e**

$^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$



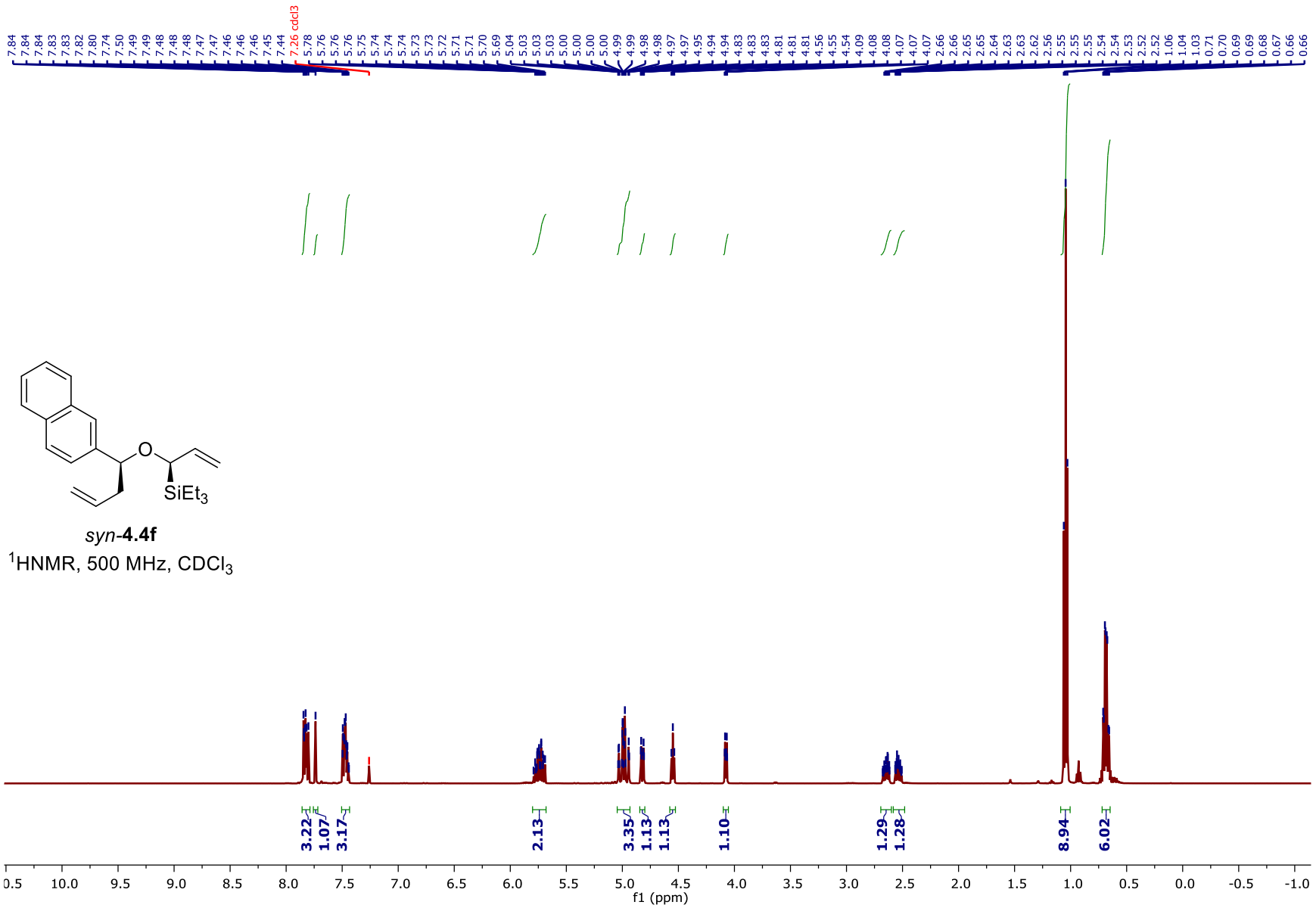
anti-**4.4e**

^{1}HNMR, 600 MHz, $CDCl_3$



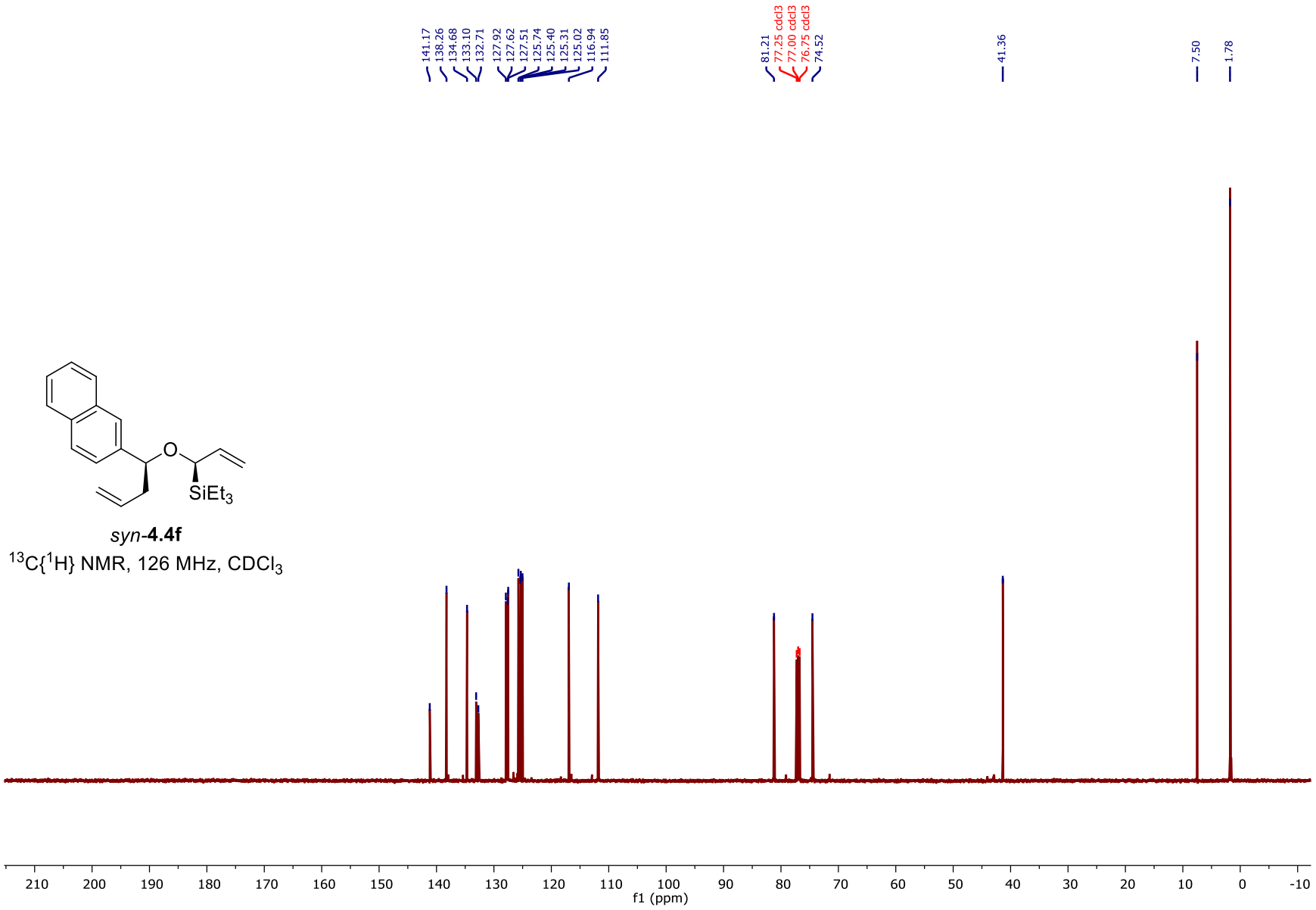
anti-**4.4e**

$^{13}C\{^{1}H\}$ NMR, 600 MHz, $CDCl_3$



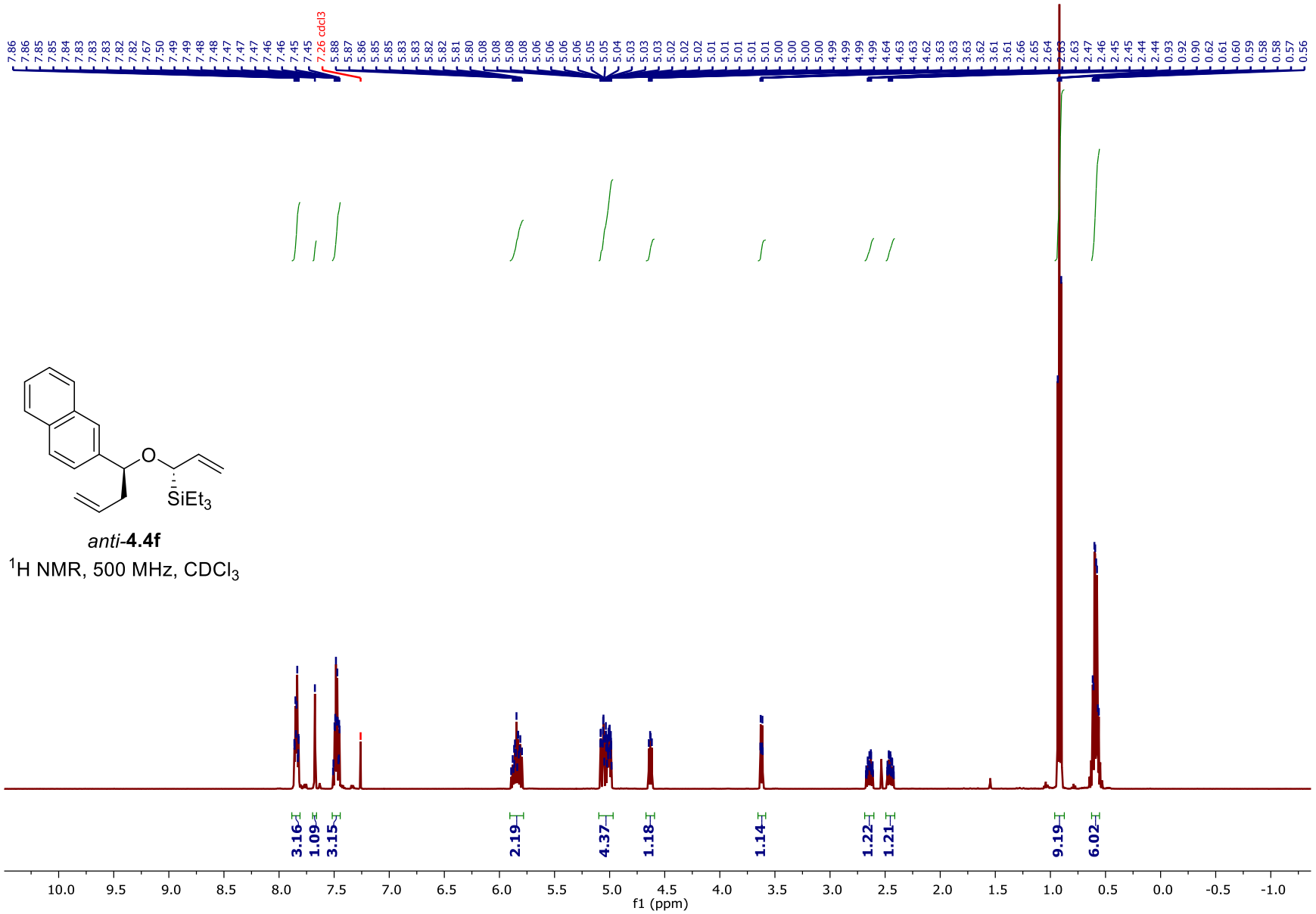
syn-**4.4f**

^{1}HNMR, 500 MHz, $CDCl_3$



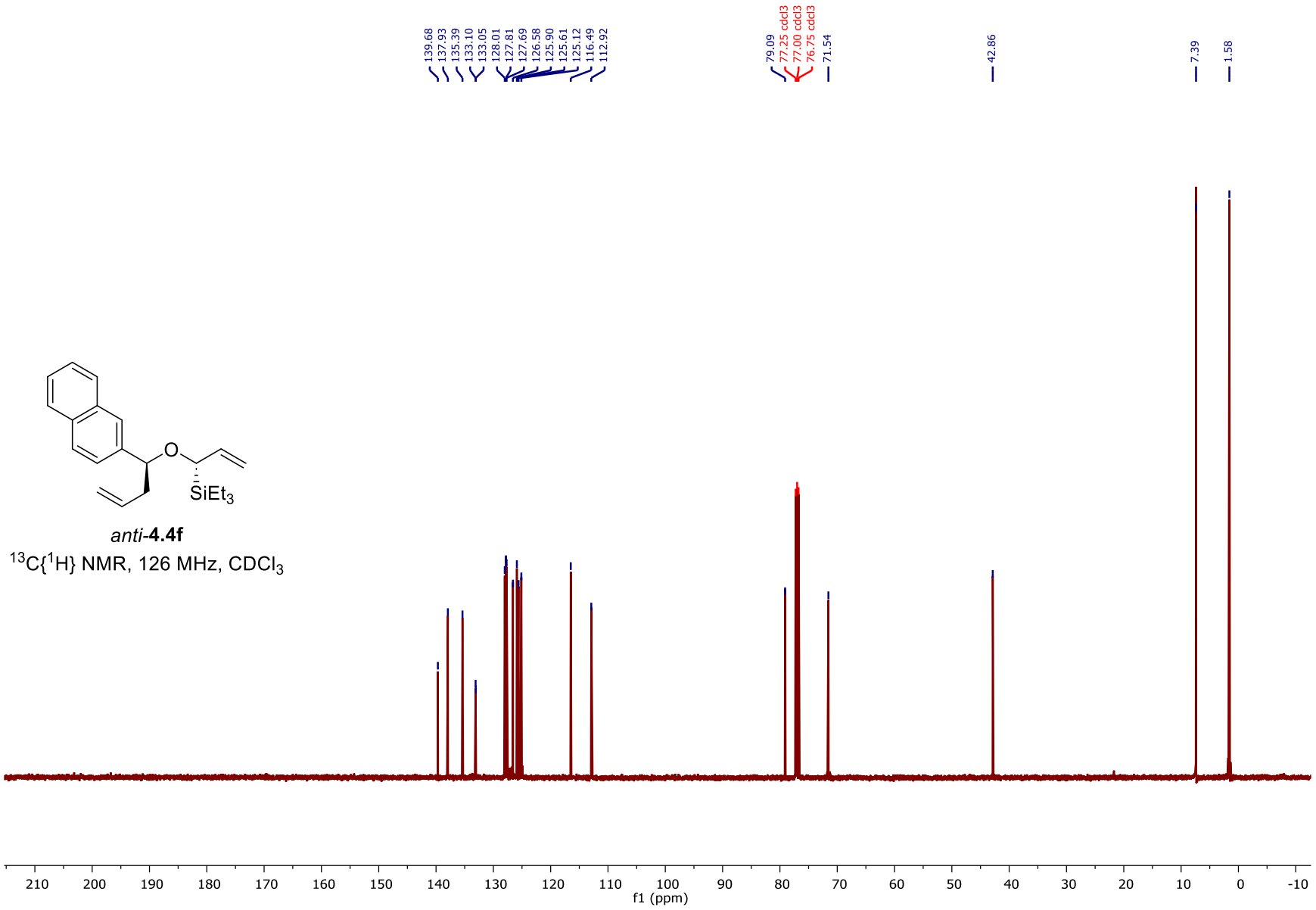
syn-**4.4f**

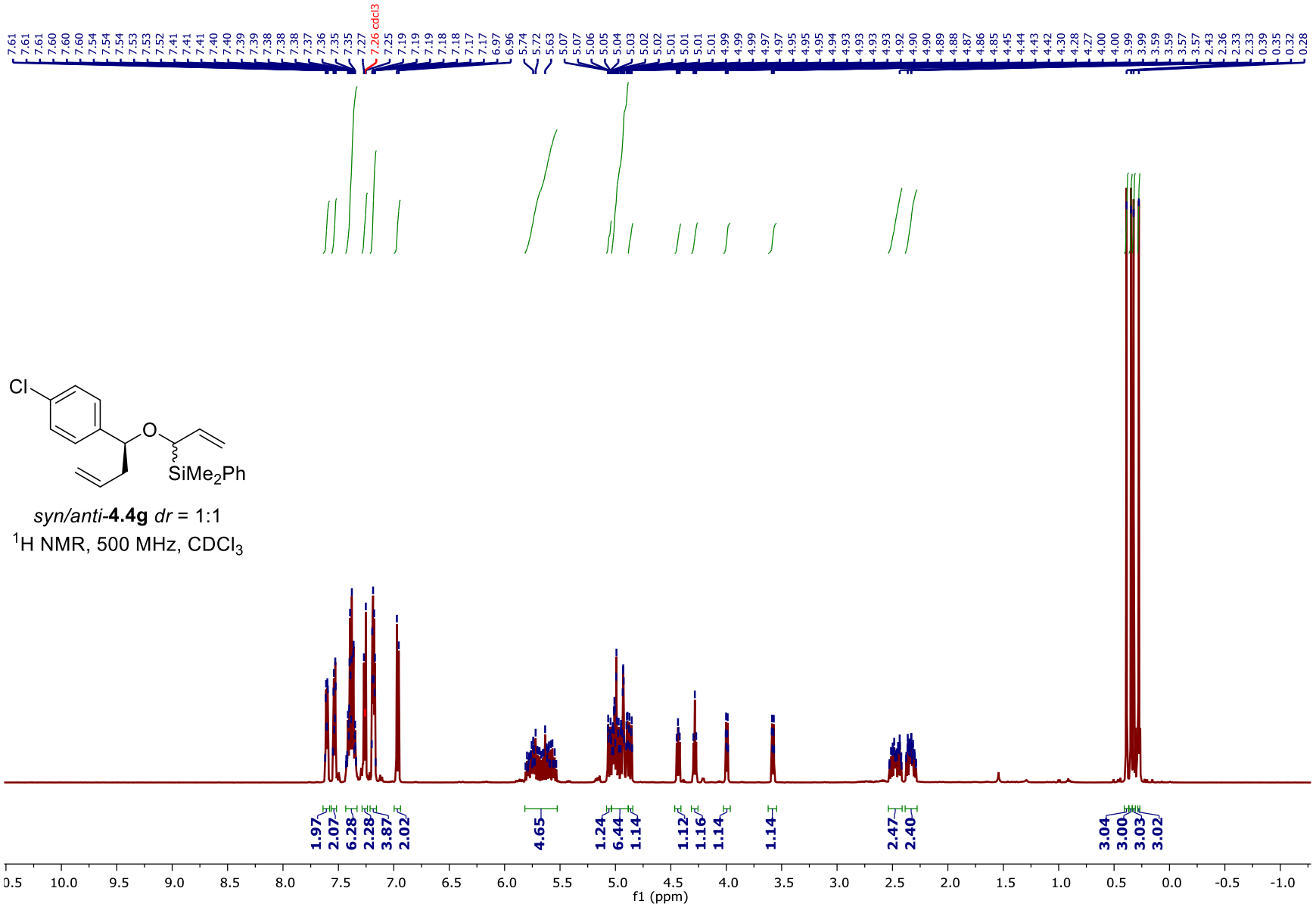
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

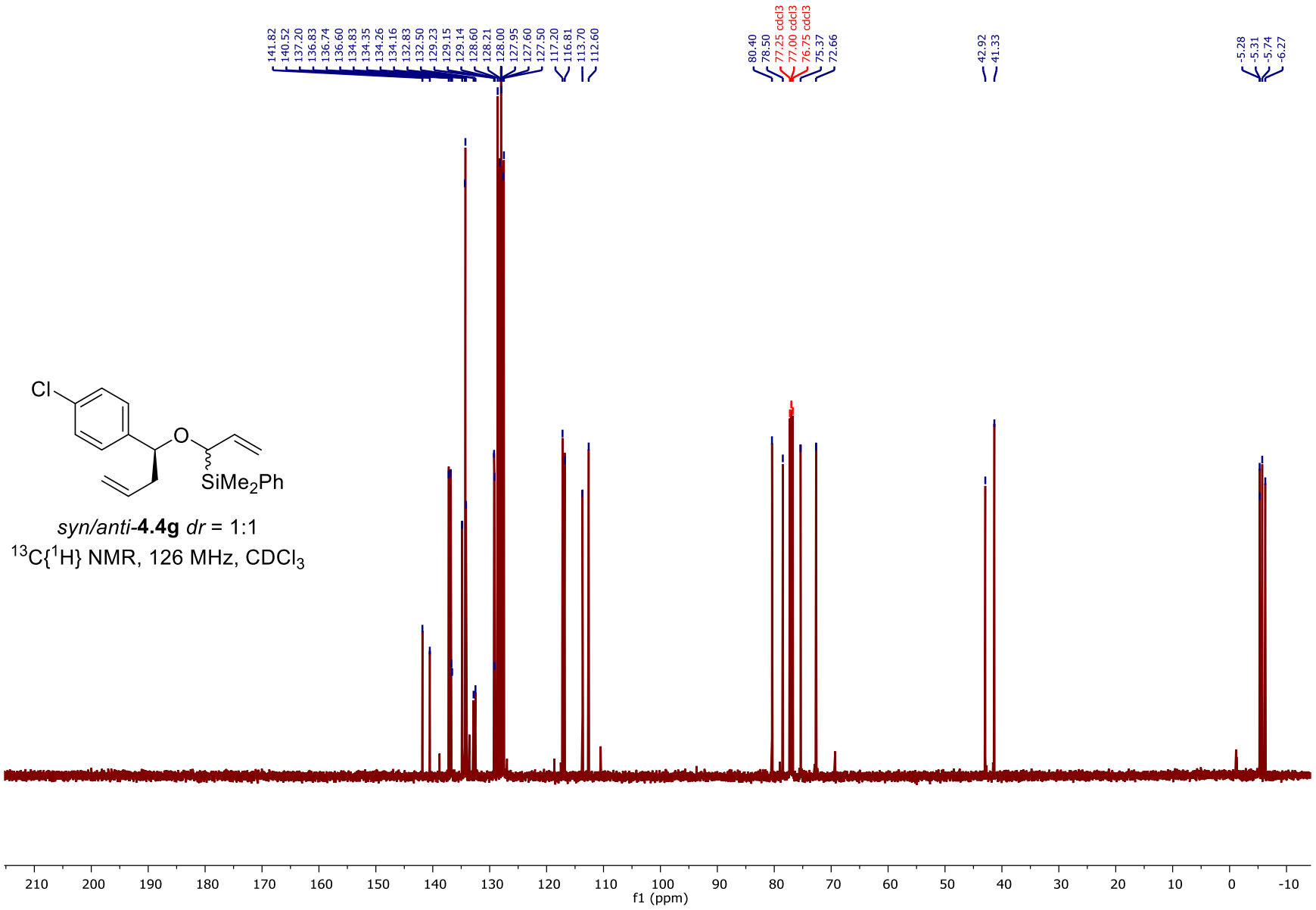


anti-**4.4f**

^{1}H NMR, 500 MHz, $CDCl_3$

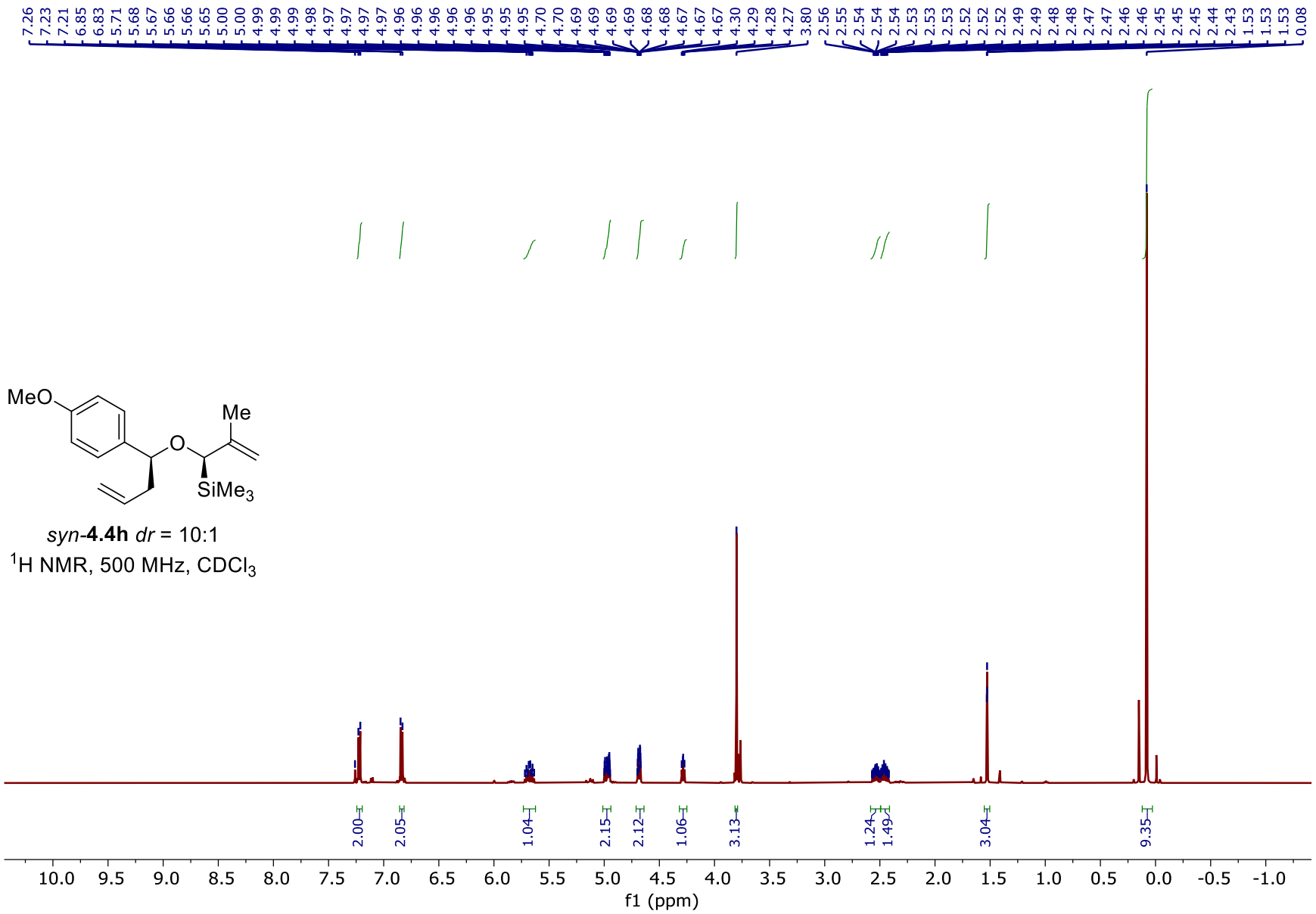

139.68
137.93
135.39
133.10
133.05
128.01
127.81
127.69
126.58
125.90
125.61
125.12
116.49
112.92
79.09
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
71.54
42.86
7.39
1.58
O
SiEt3
anti-4.4f
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
O
SiMe2Ph
syn/anti-4.4g dr = 1:1
1H NMR, 500 MHz, CDCl3
f1 (ppm)



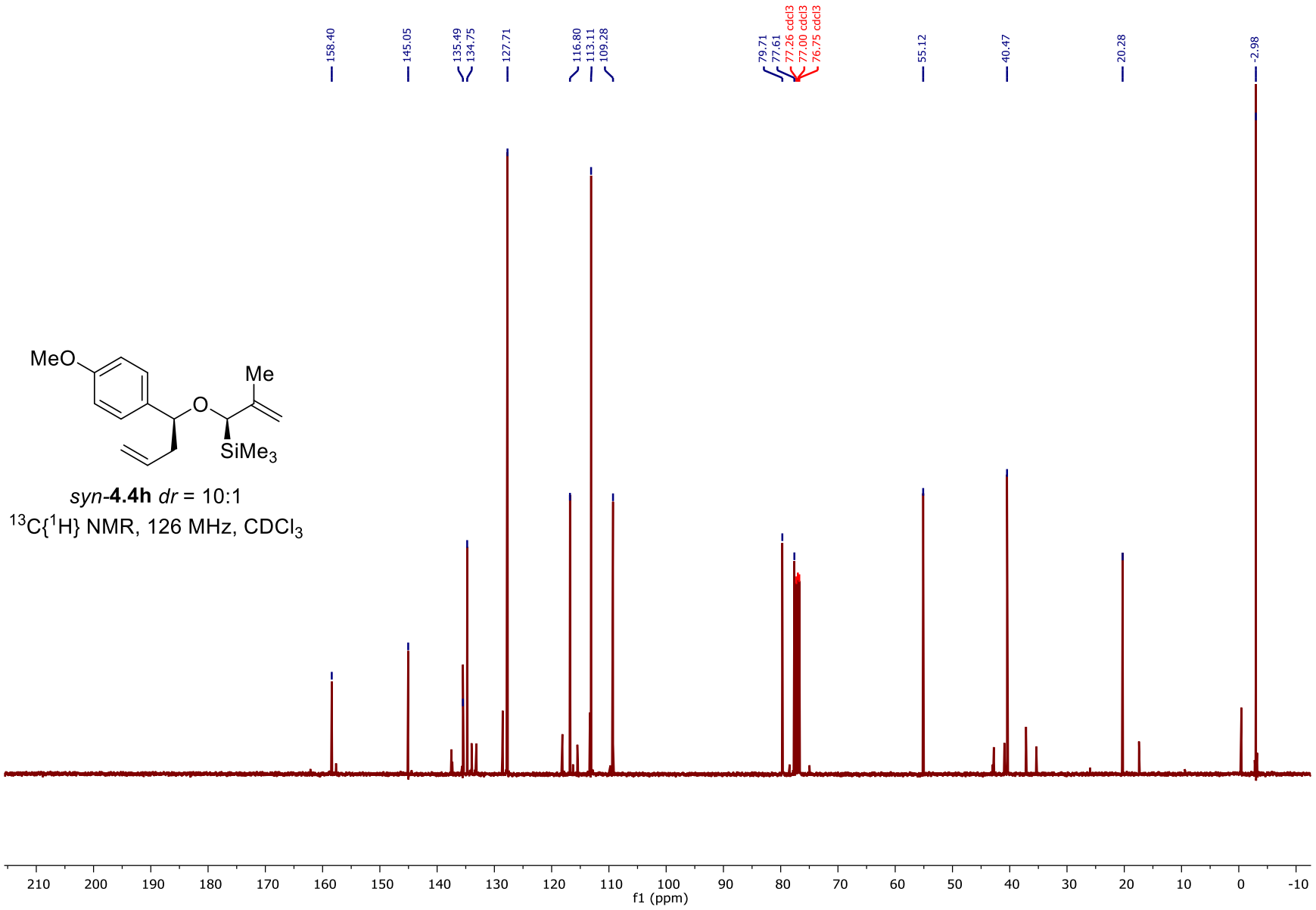
syn/anti-**4.4g** *dr* = 1:1

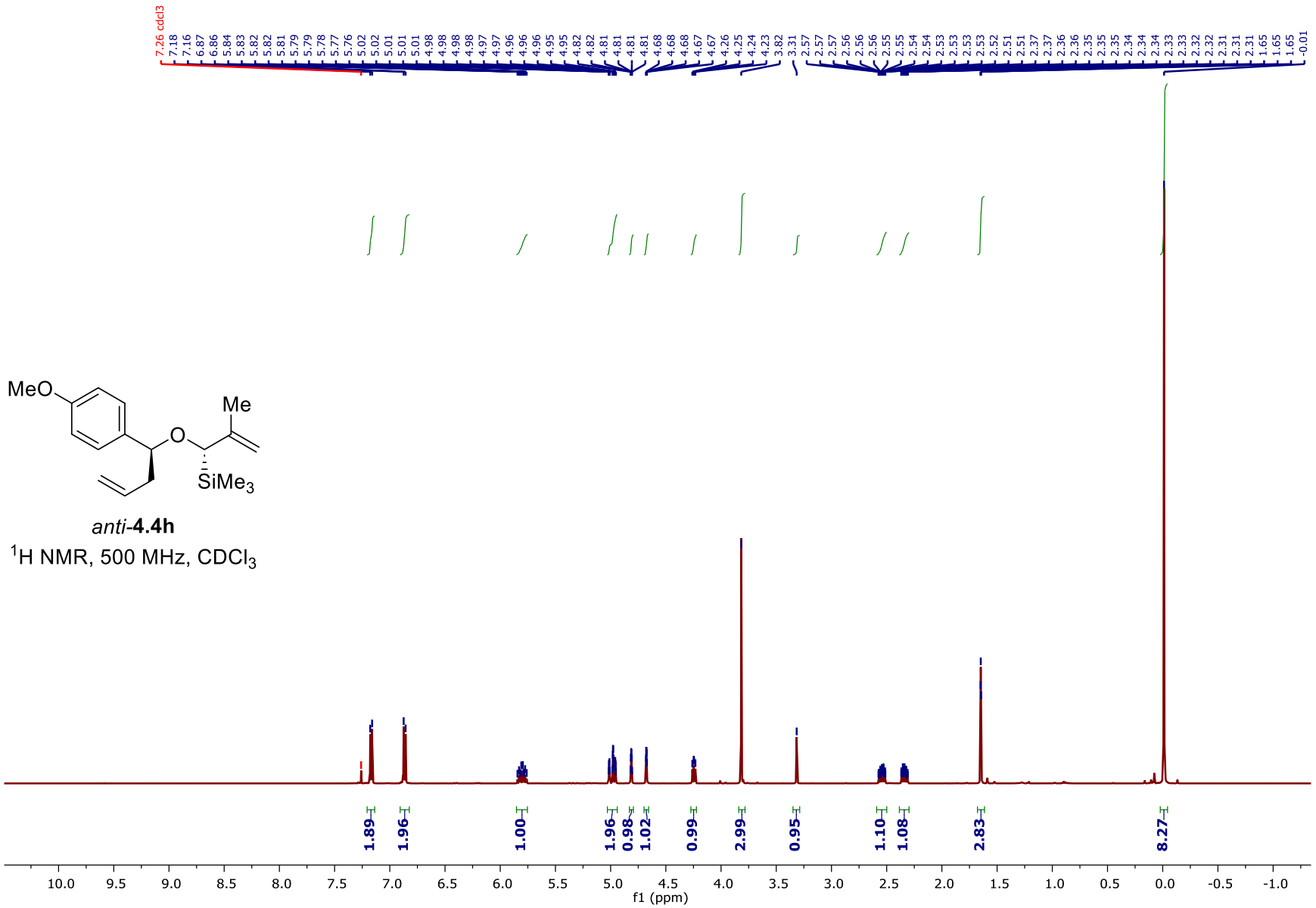
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$



syn-**4.4h** *dr* = 10:1

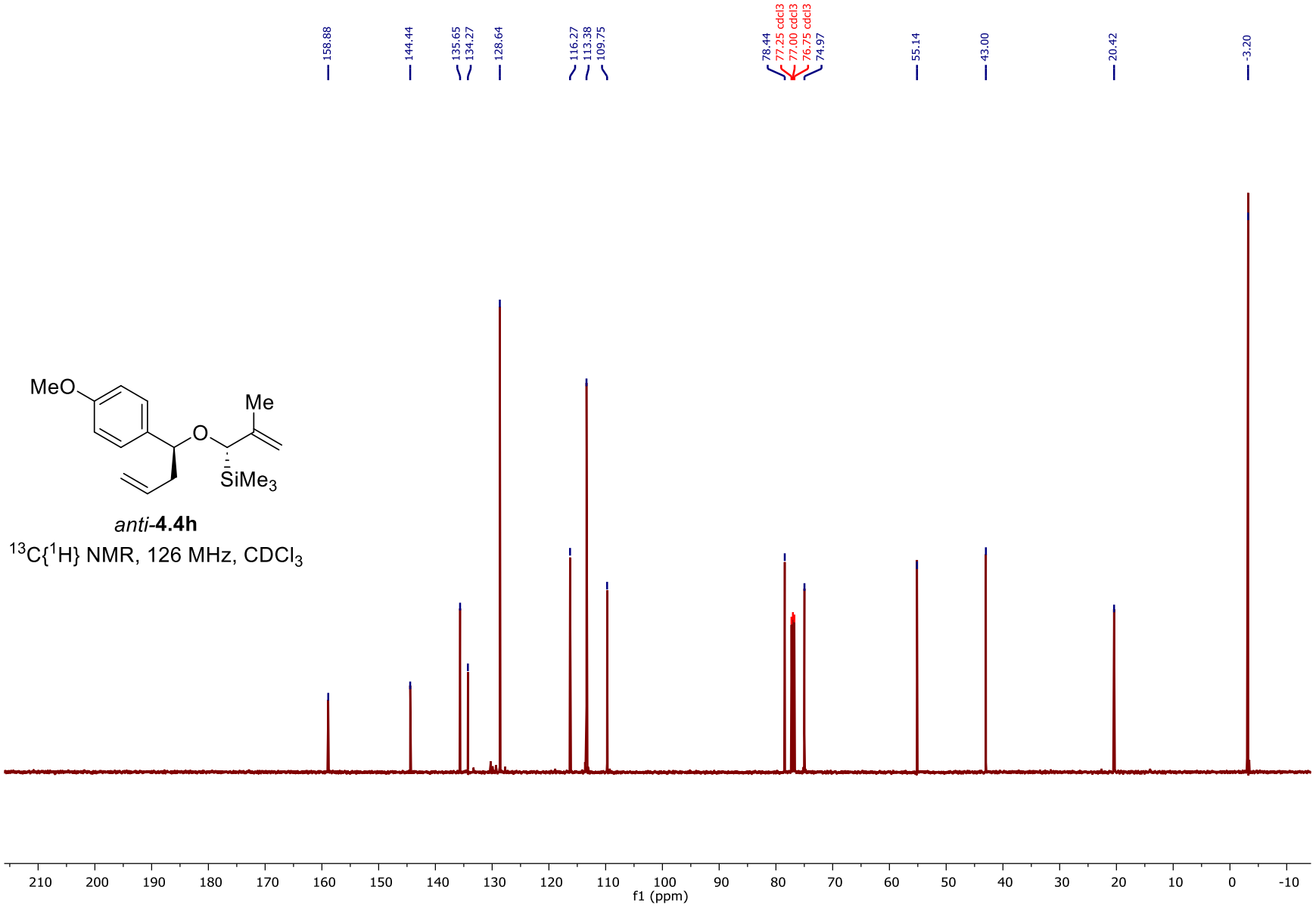
^{1}H NMR, 500 MHz, $CDCl_3$

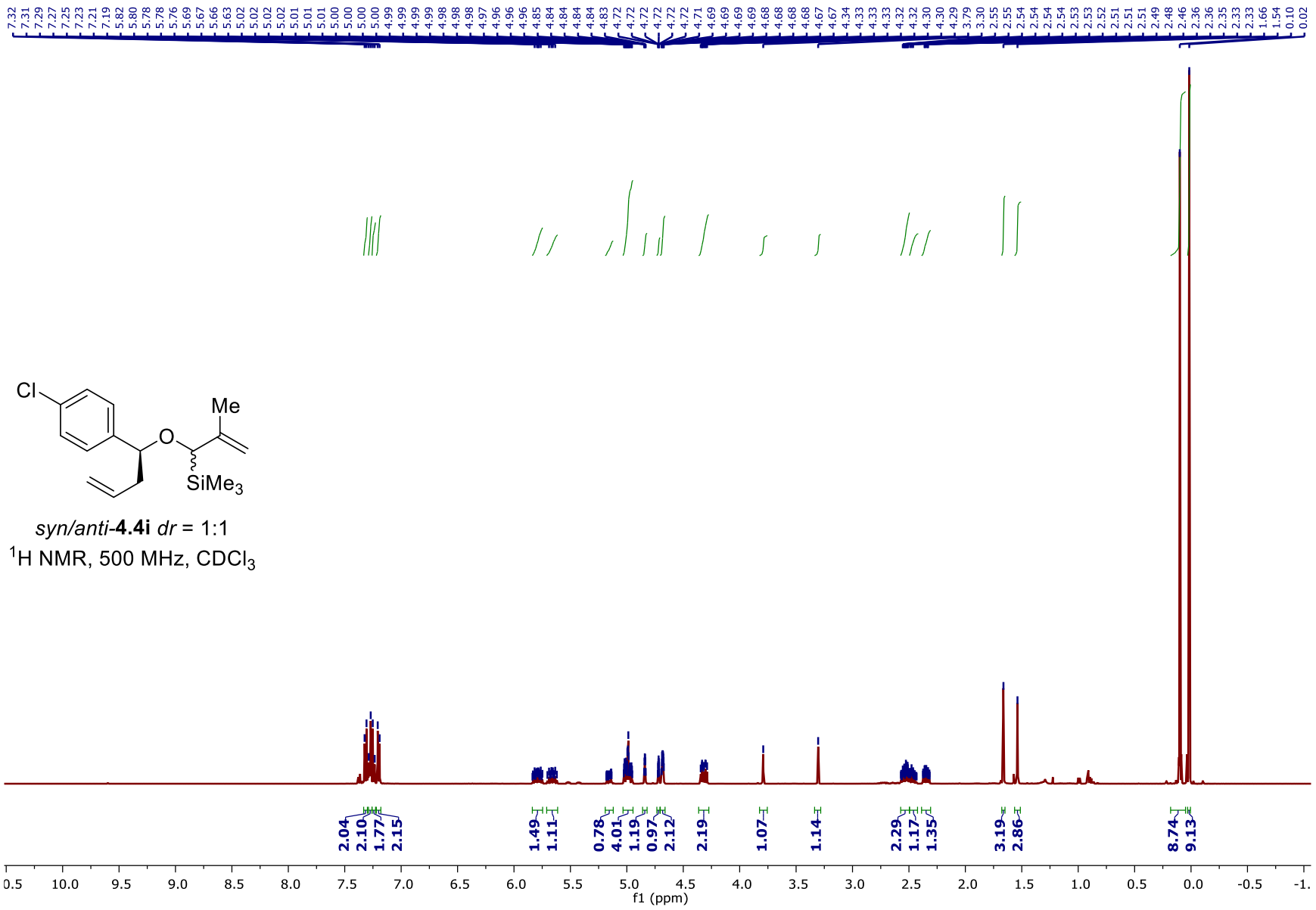

158.40
145.05
135.49
134.75
127.71
116.80
113.11
109.28
79.71
77.61
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
55.12
40.47
20.28
-2.98
MeO
Me
O
SiMe3
syn-4.4h dr = 10:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

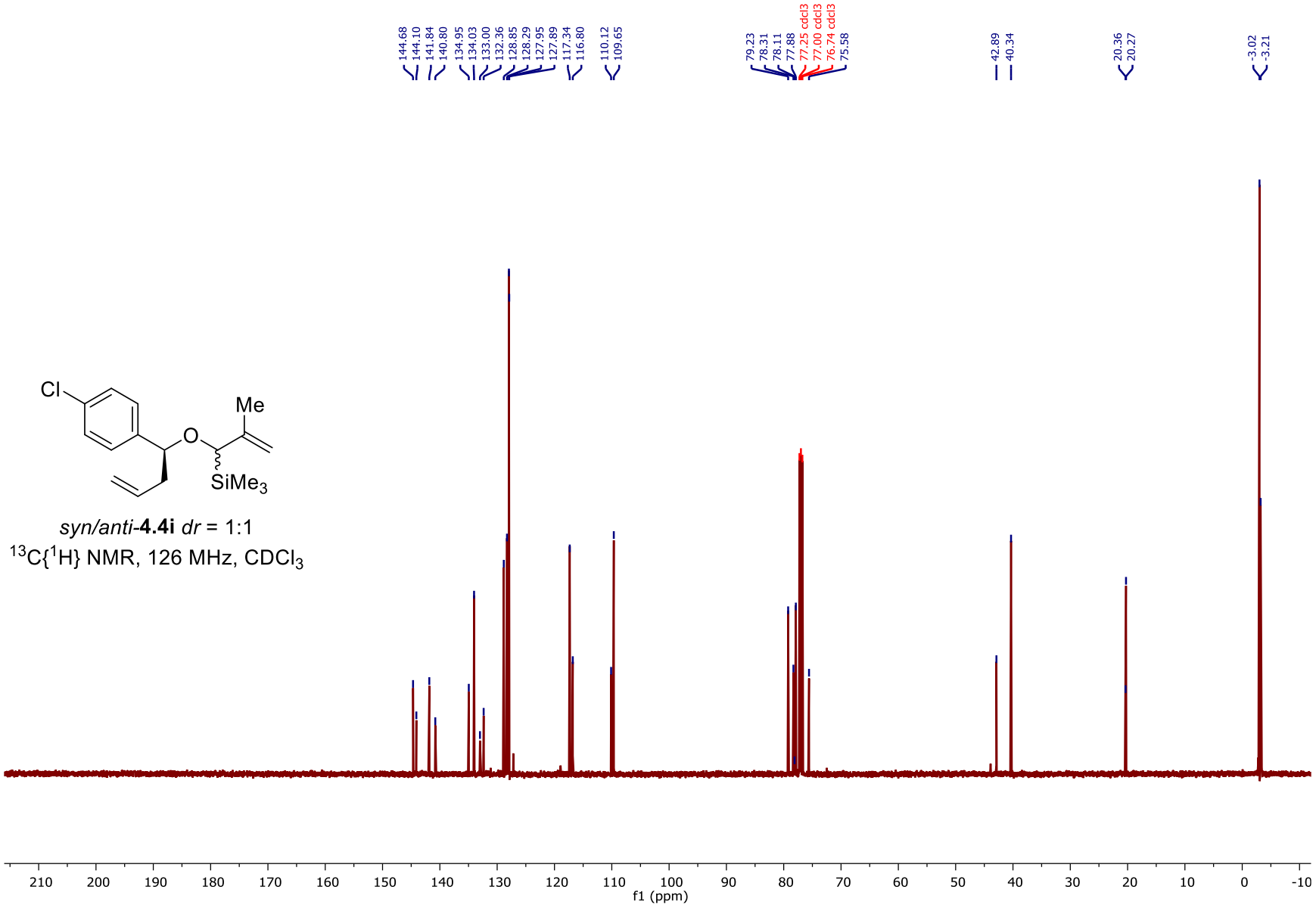


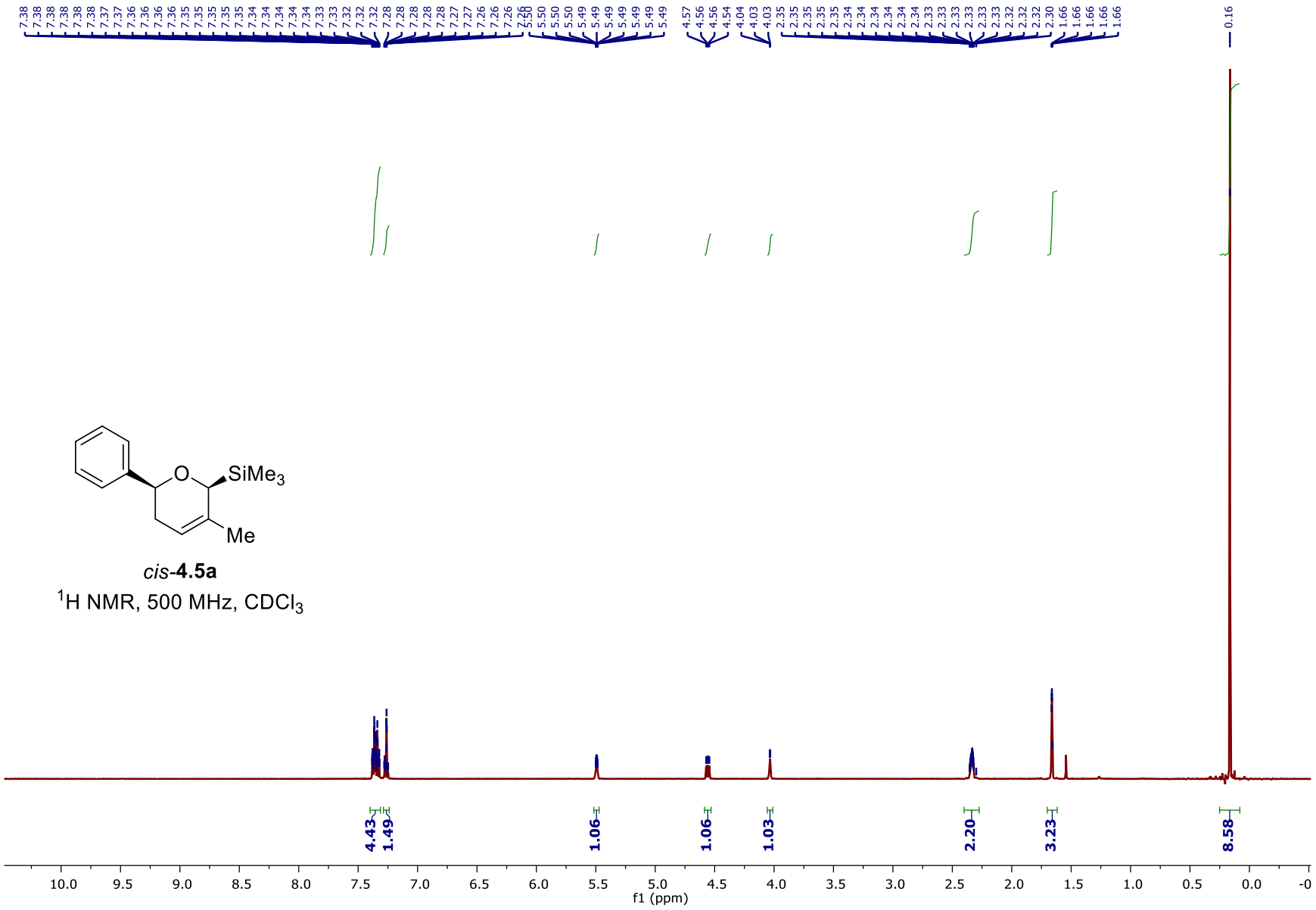
anti-**4.4h**

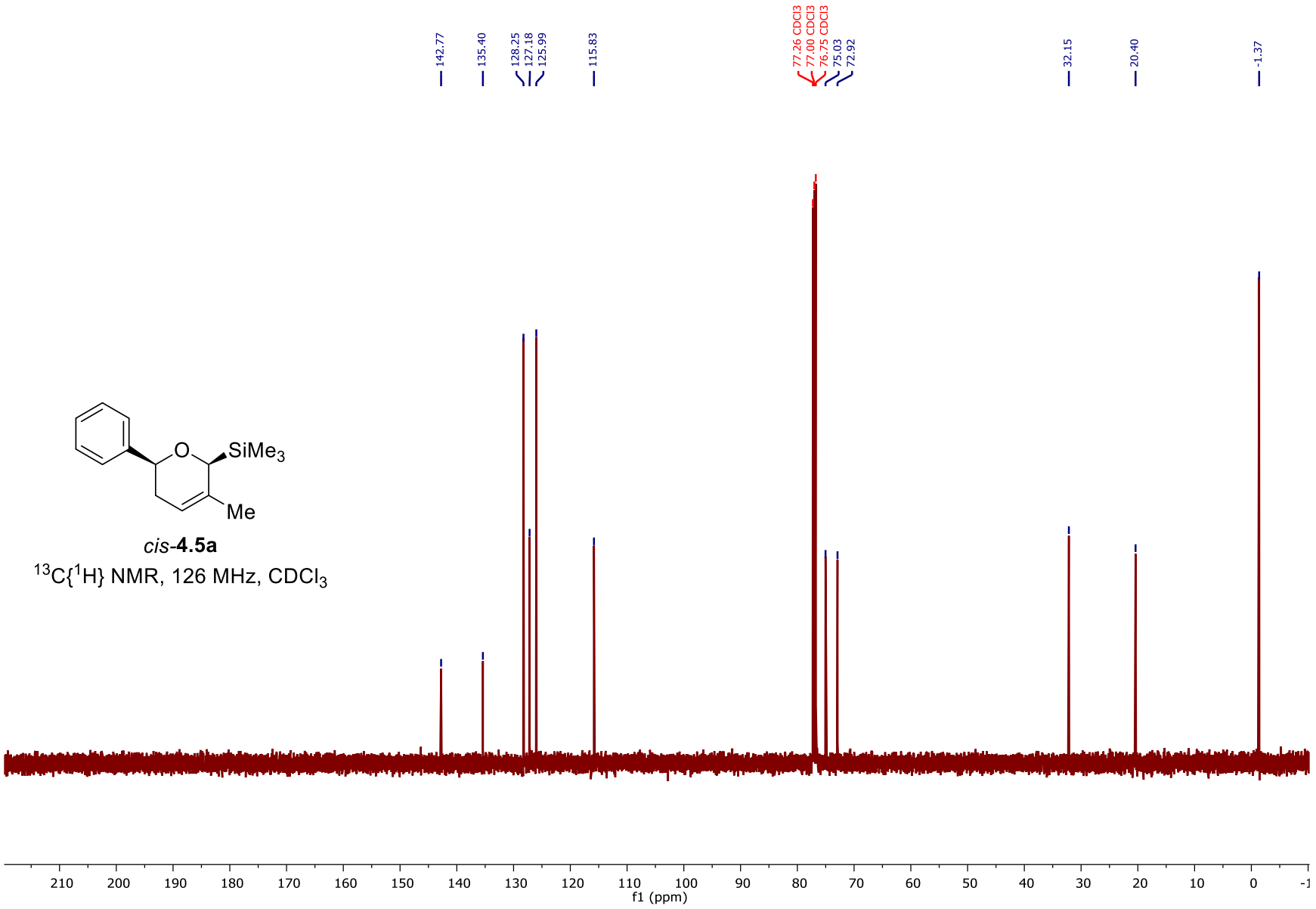
^{1}H NMR, 500 MHz, $CDCl_3$

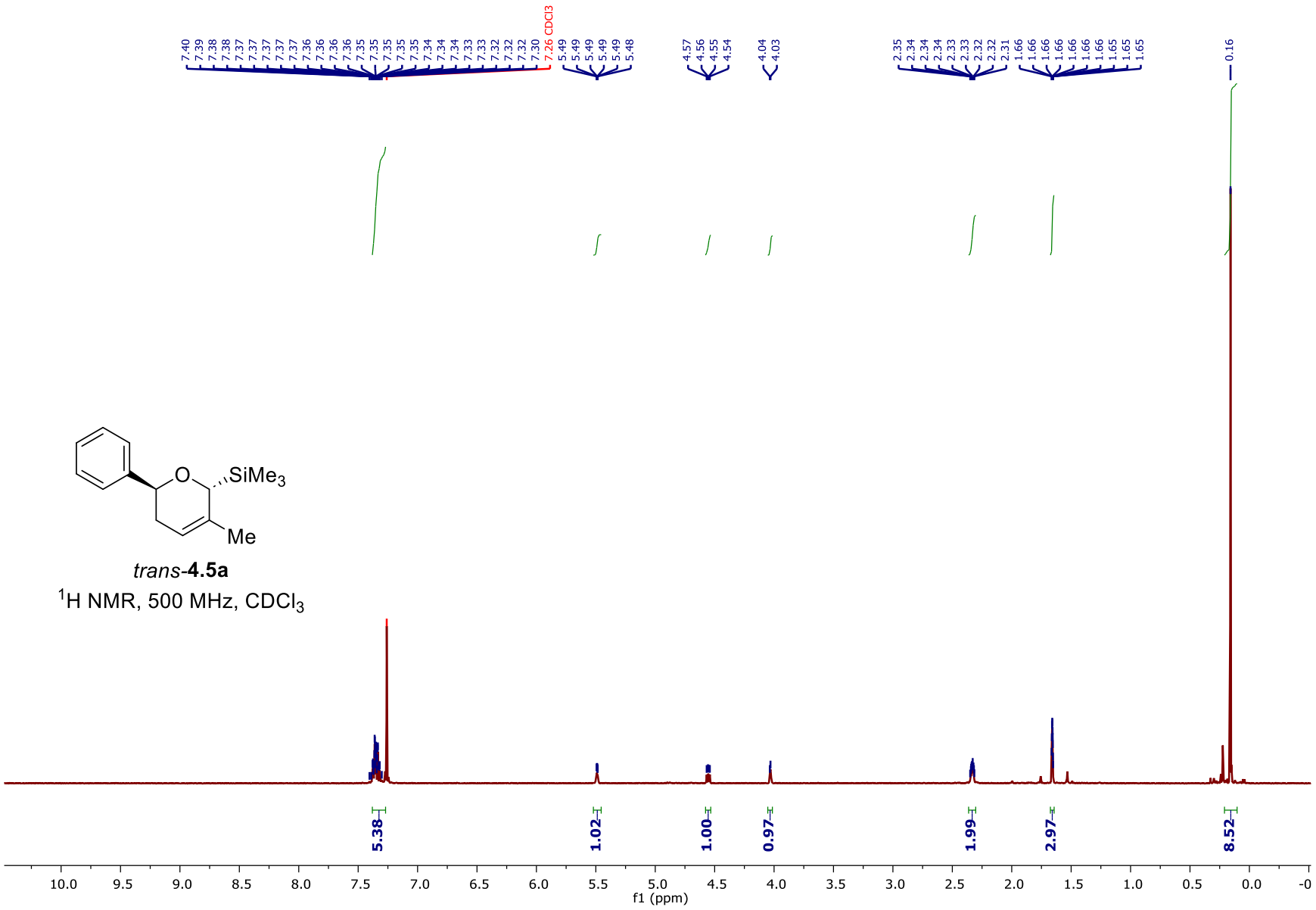

158.88
144.44
135.65
134.27
128.64
116.27
113.38
109.75
78.44
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
74.97
55.14
43.00
20.42
-3.20
MeO
Me
O
SiMe3
anti-4.4h
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

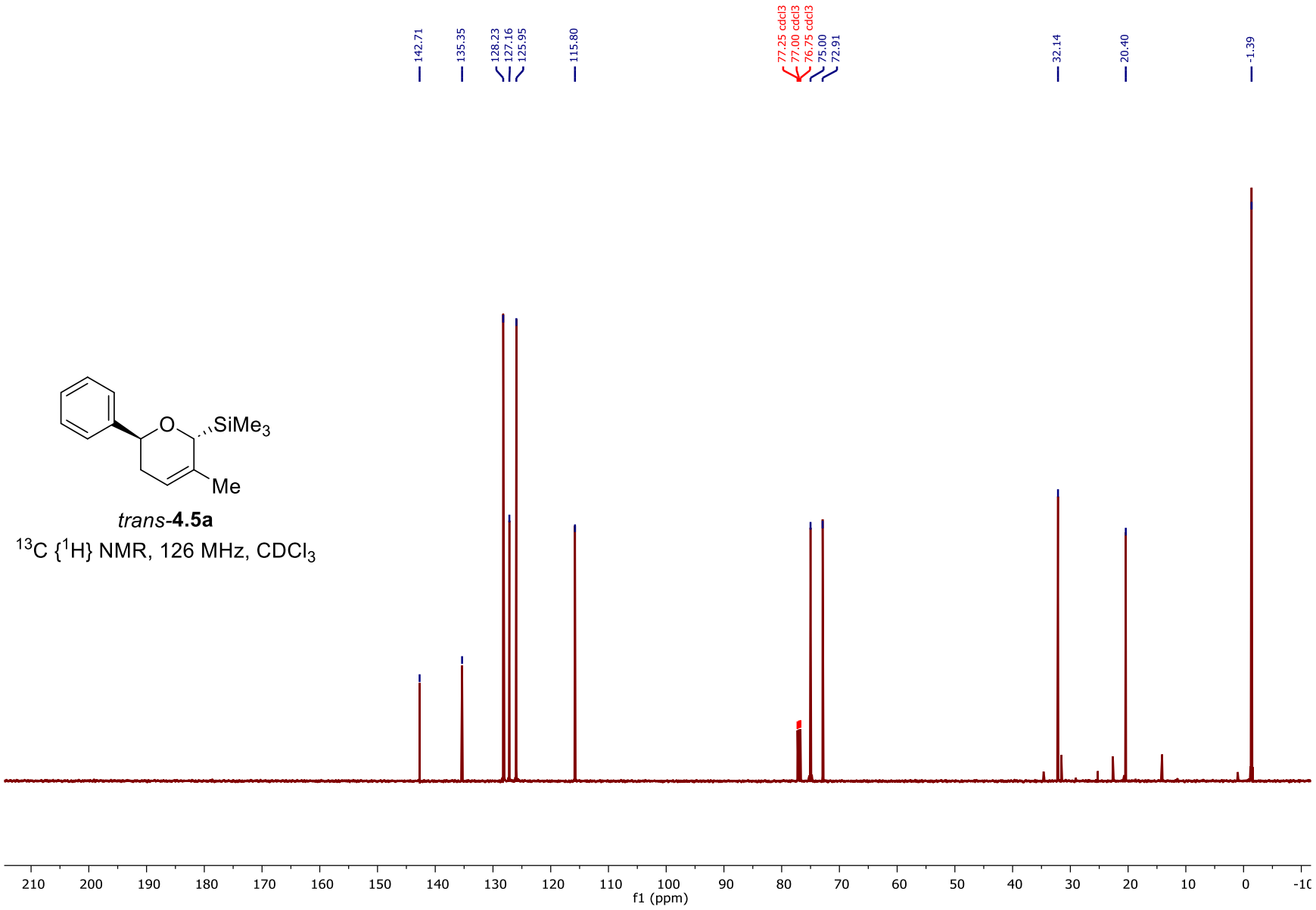

Cl
Me
O
SiMe3
syn/anti-4.4i dr = 1:1
1H NMR, 500 MHz, CDCl3
2.04
2.10
1.77
2.15
1.49
1.11
0.78
4.01
1.19
0.97
2.12
2.19
1.07
1.14
2.29
1.17
1.35
3.19
2.86
8.74
9.13
f1 (ppm)

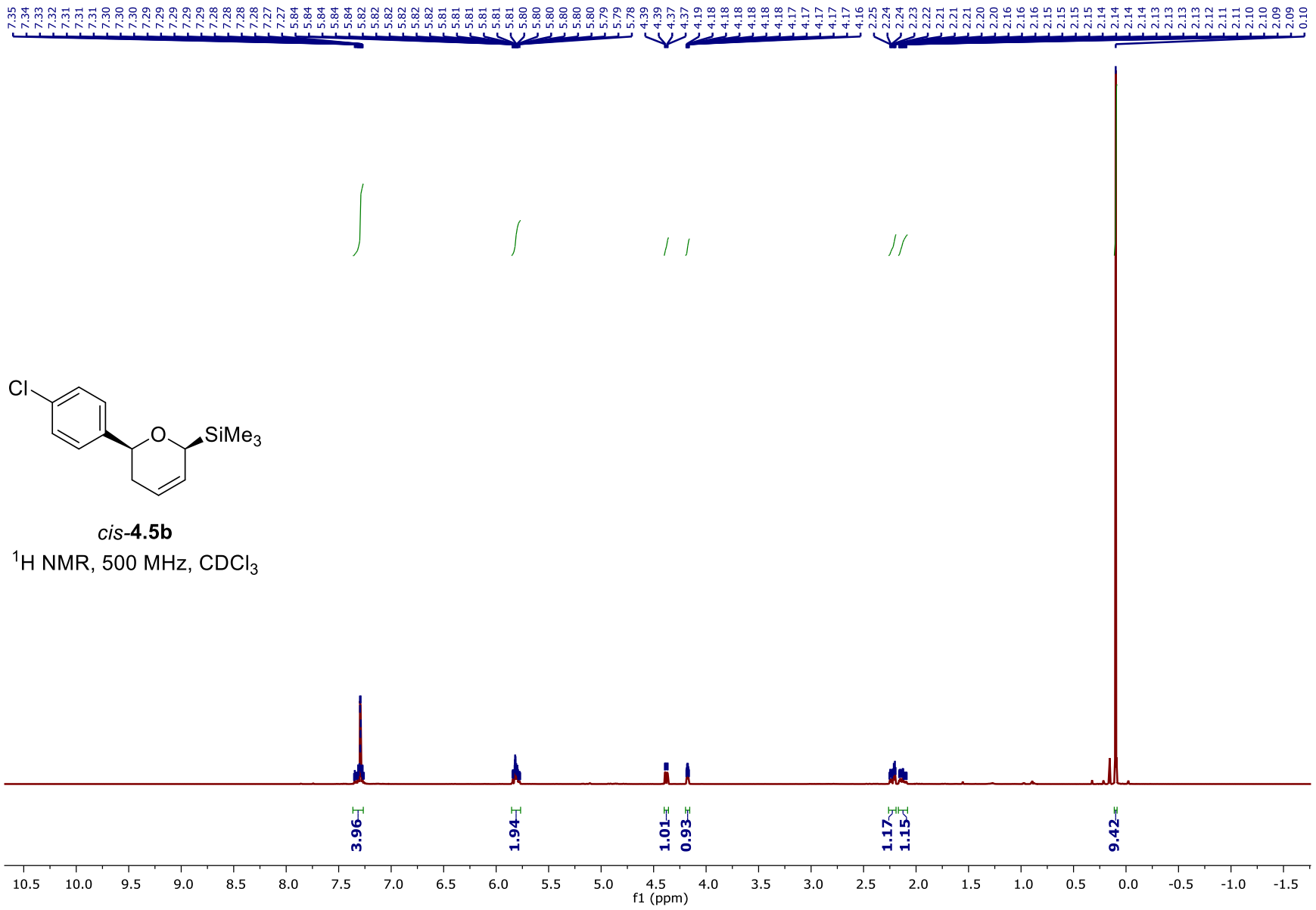

144.68
144.10
141.84
140.80
134.95
134.03
133.00
132.36
128.85
128.29
127.95
127.89
117.34
116.80
110.12
109.65
79.23
78.31
78.11
77.88
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
75.58
42.89
40.34
20.36
20.27
-3.02
-3.21
Cl
Me
O
SiMe3
syn/anti-4.4i dr = 1:1
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

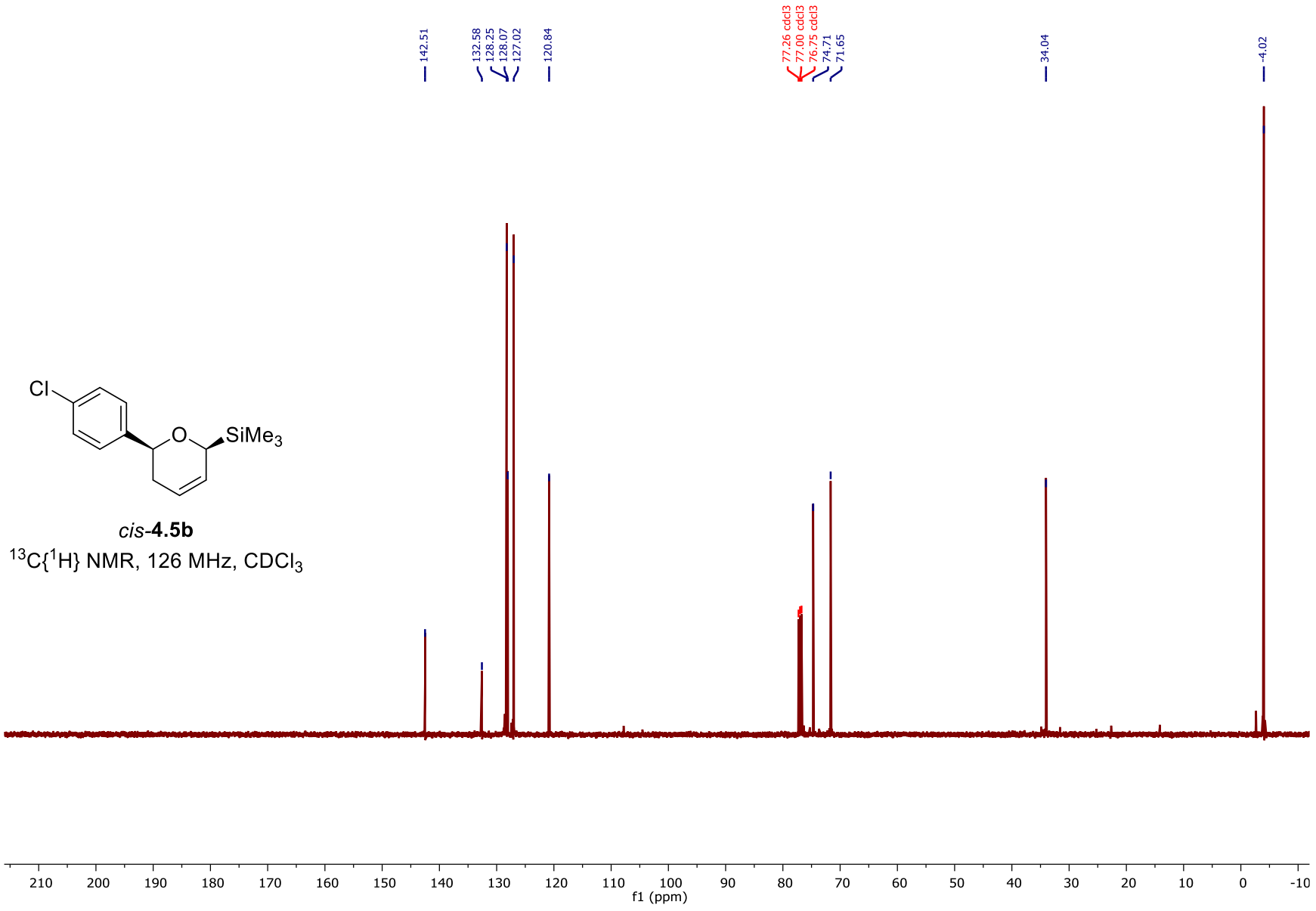

O
SiMe3
Me
cis-4.5a
1H NMR, 500 MHz, CDCl3
4.43
1.49
1.06
1.06
1.03
2.20
3.23
8.58
f1 (ppm)

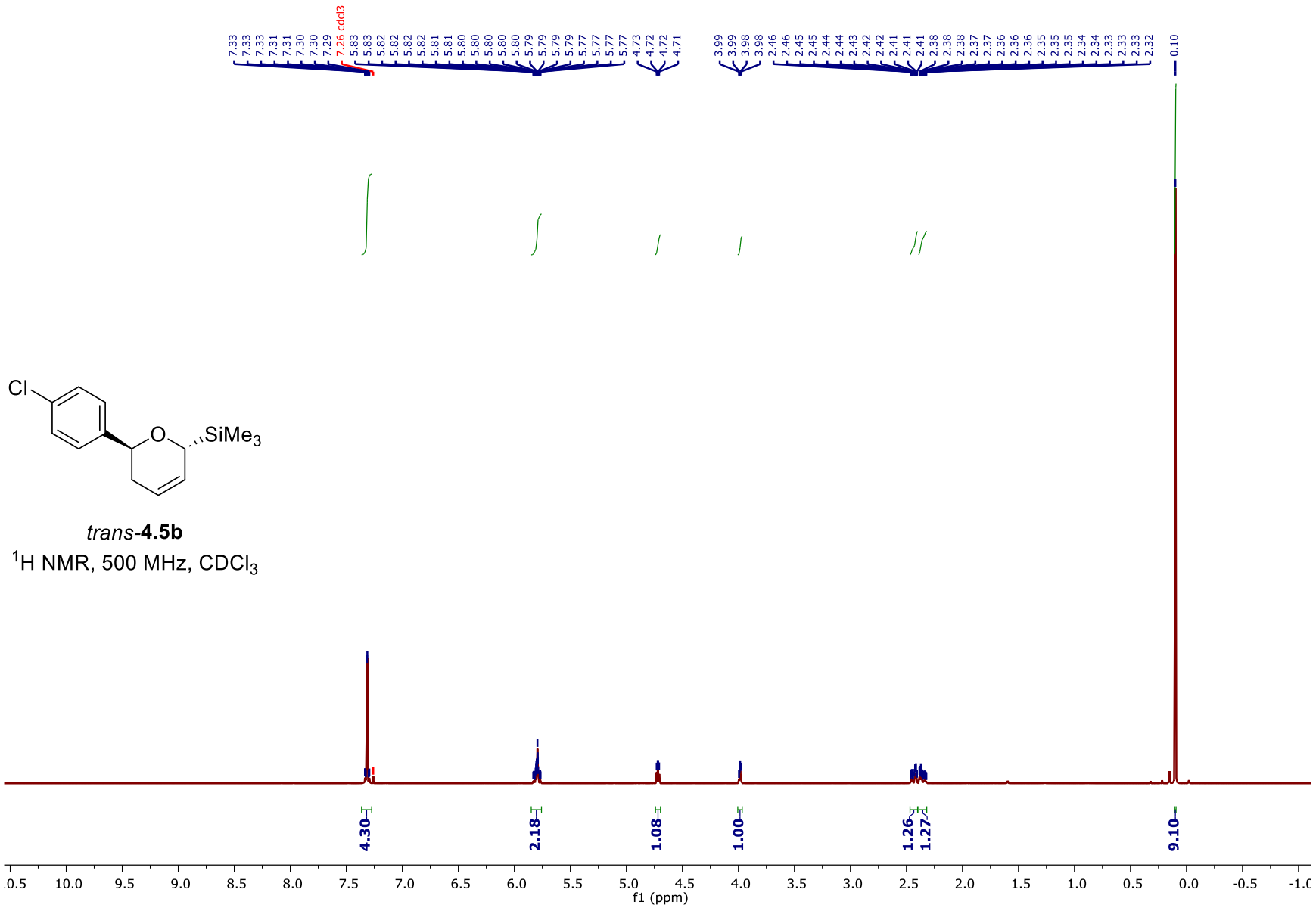

142.77
135.40
128.25
127.18
125.99
115.83
77.26 CDCl3
77.00 CDCl3
76.75 CDCl3
75.03
72.92
32.15
20.40
-1.37
O
SiMe3
Me
cis-4.5a
13C{1H} NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

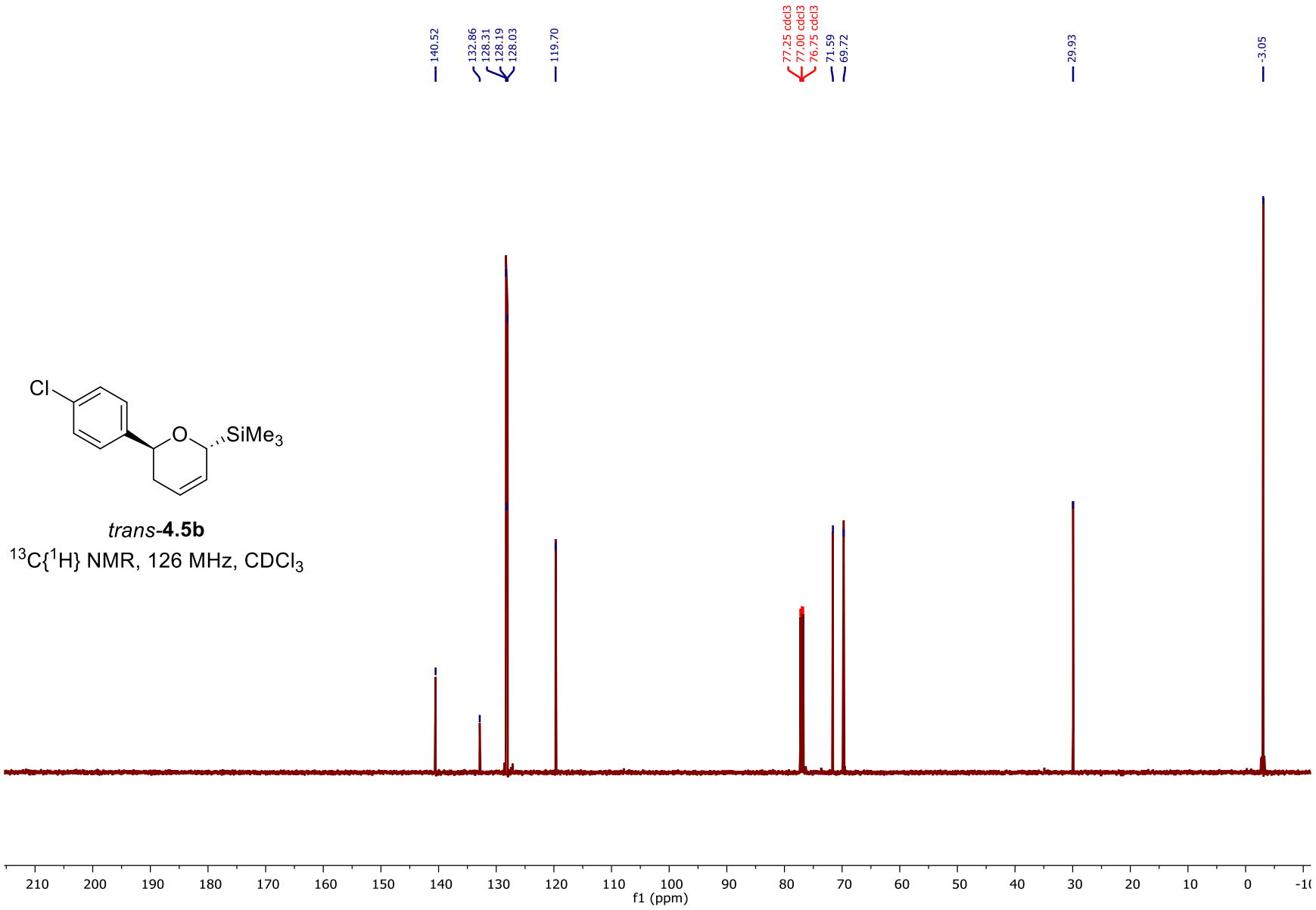

7.40 7.39 7.38 7.38 7.37 7.37 7.37 7.37 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.30 7.26 CDCl3
5.49 5.49 5.49 5.49 5.49 5.48
4.57 4.56 4.55 4.54
4.04 4.03
2.35 2.34 2.34 2.34 2.33 2.33 2.32 2.32 2.31
1.66 1.66 1.66 1.66 1.66 1.66 1.65 1.65 1.65
0.16
O
SiMe3
Me
trans-4.5a
1H NMR, 500 MHz, CDCl3
5.38
1.02
1.00
0.97
1.99
2.97
8.52
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

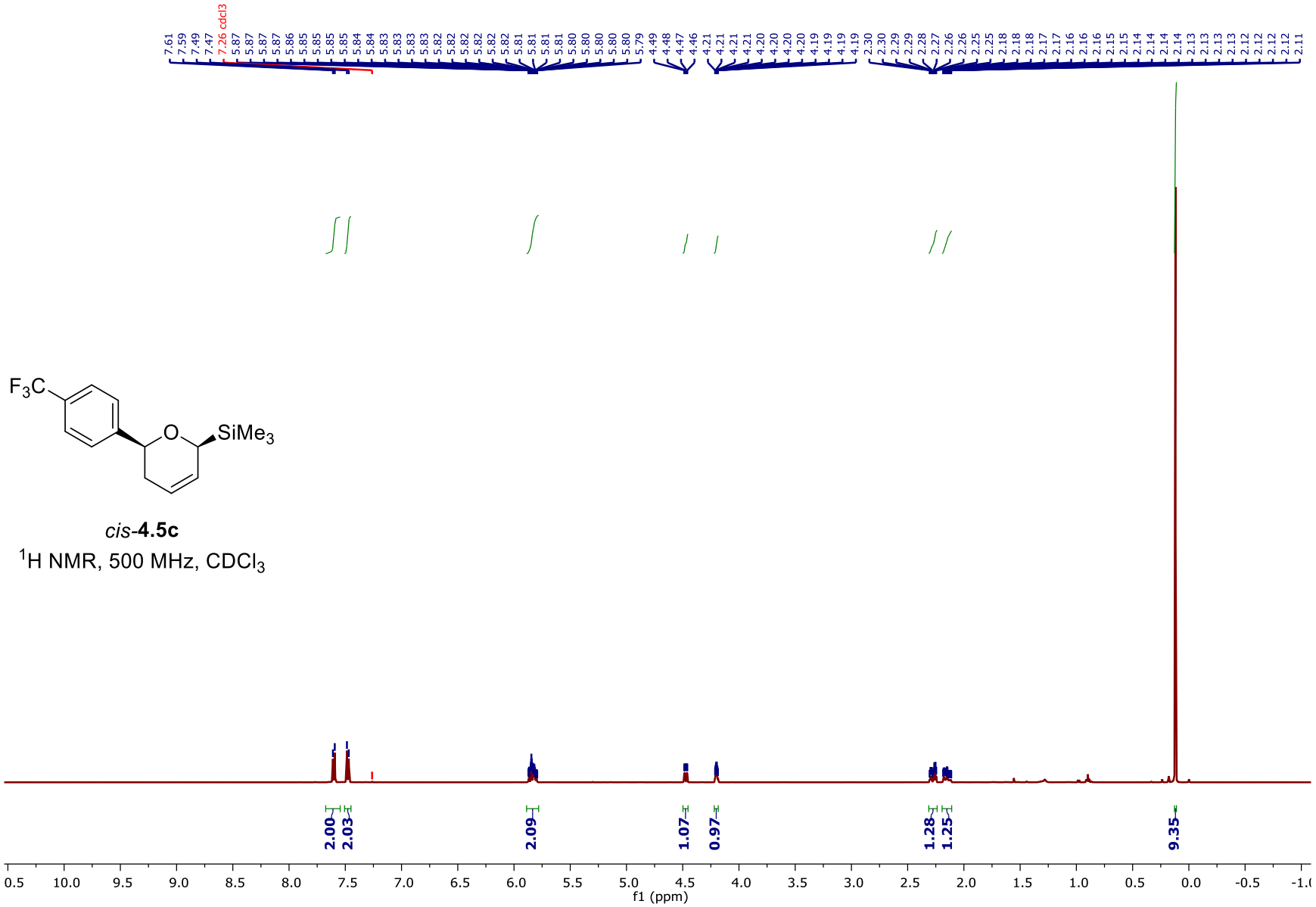

142.71
135.35
128.23
127.16
125.95
115.80
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
75.00
72.91
32.14
20.40
-1.39
O
SiMe3
Me
trans-4.5a
13C {1H} NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
O
SiMe3
cis-4.5b
1H NMR, 500 MHz, CDCl3
3.96
1.94
1.01
0.93
1.17
1.15
9.42
f1 (ppm)


142.51
132.58
128.25
128.07
127.02
120.84
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
74.71
71.65
34.04
-4.02
Cl
O
SiMe3
cis-4.5b
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

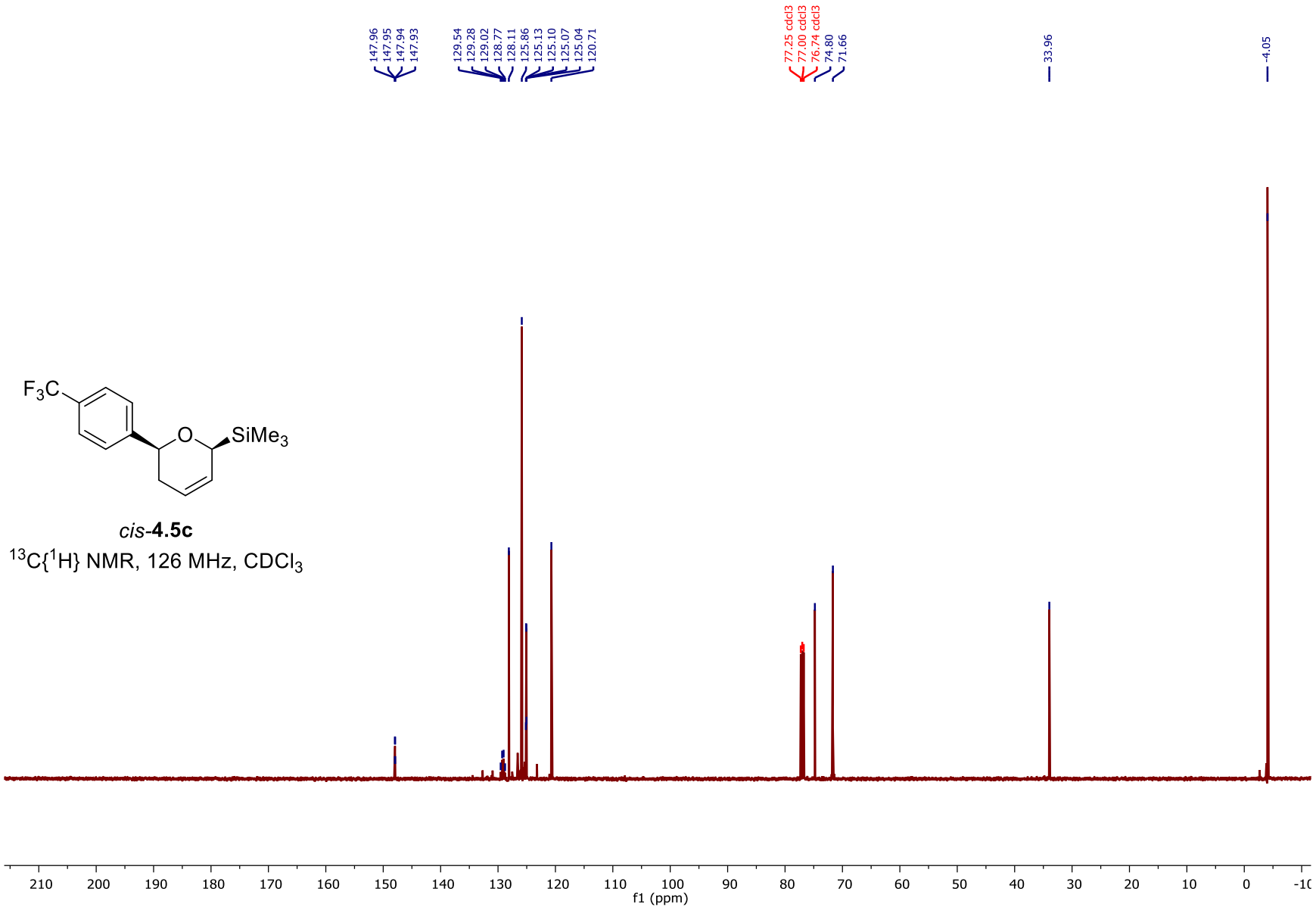

7.33 7.33 7.33 7.31 7.31 7.30 7.30 7.29 7.26 cdcl3 5.83 5.83 5.82 5.82 5.82 5.82 5.81 5.81 5.80 5.80 5.80 5.80 5.80 5.79 5.79 5.79 5.77 5.77 5.77 5.77 4.73 4.72 4.72 4.71 3.99 3.99 3.98 3.98 2.46 2.46 2.45 2.45 2.44 2.44 2.43 2.42 2.42 2.41 2.41 2.41 2.38 2.38 2.38 2.37 2.37 2.36 2.36 2.36 2.35 2.35 2.35 2.34 2.34 2.33 2.33 2.33 2.32 0.10
Cl
O
SiMe3
trans-4.5b
1H NMR, 500 MHz, CDCl3
4.30
2.18
1.08
1.00
1.26
1.27
9.10
f1 (ppm)

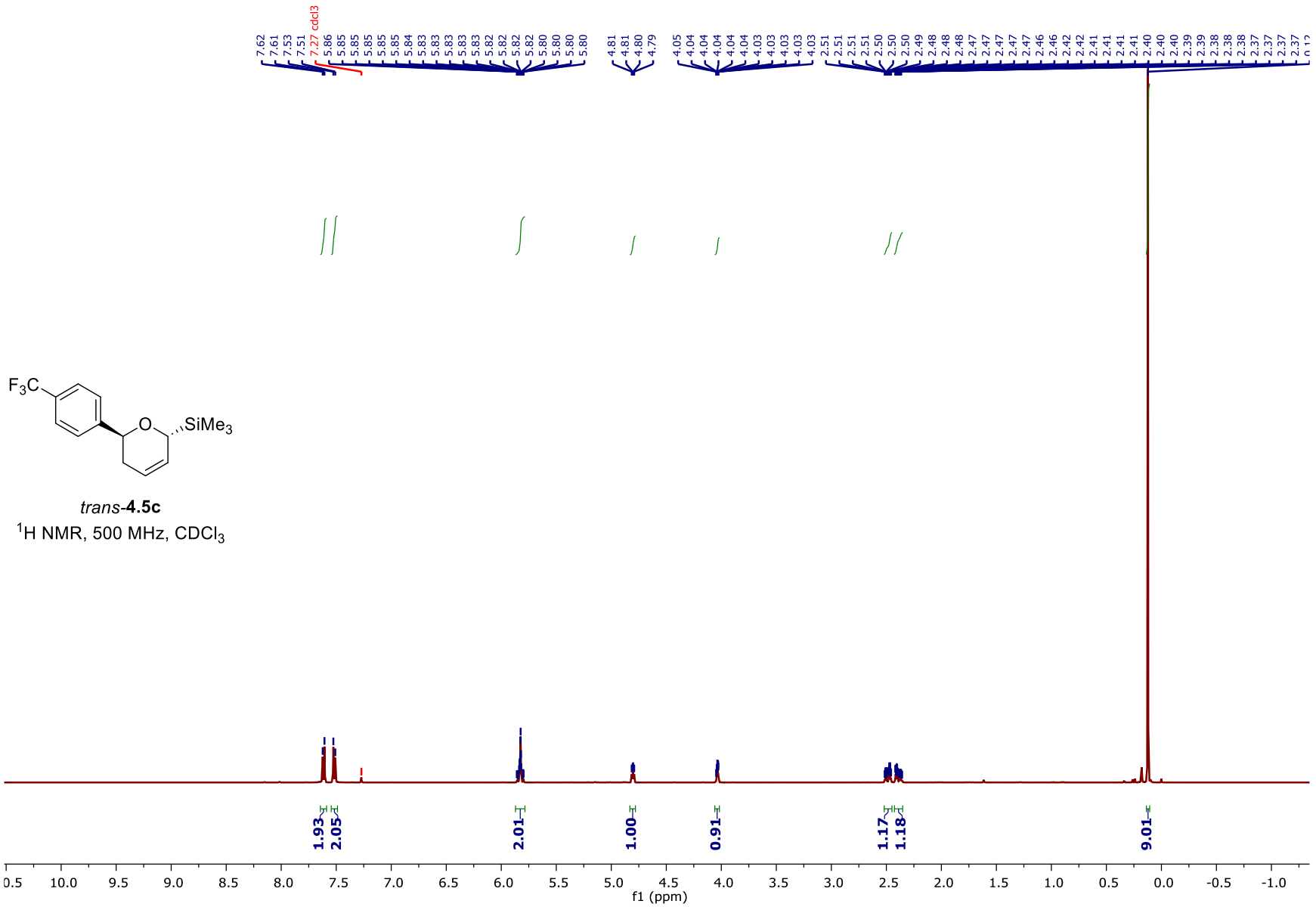

140.52
132.86
128.31
128.19
128.03
119.70
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
71.59
69.72
29.93
-3.05
Cl
O
SiMe3
trans-4.5b
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)

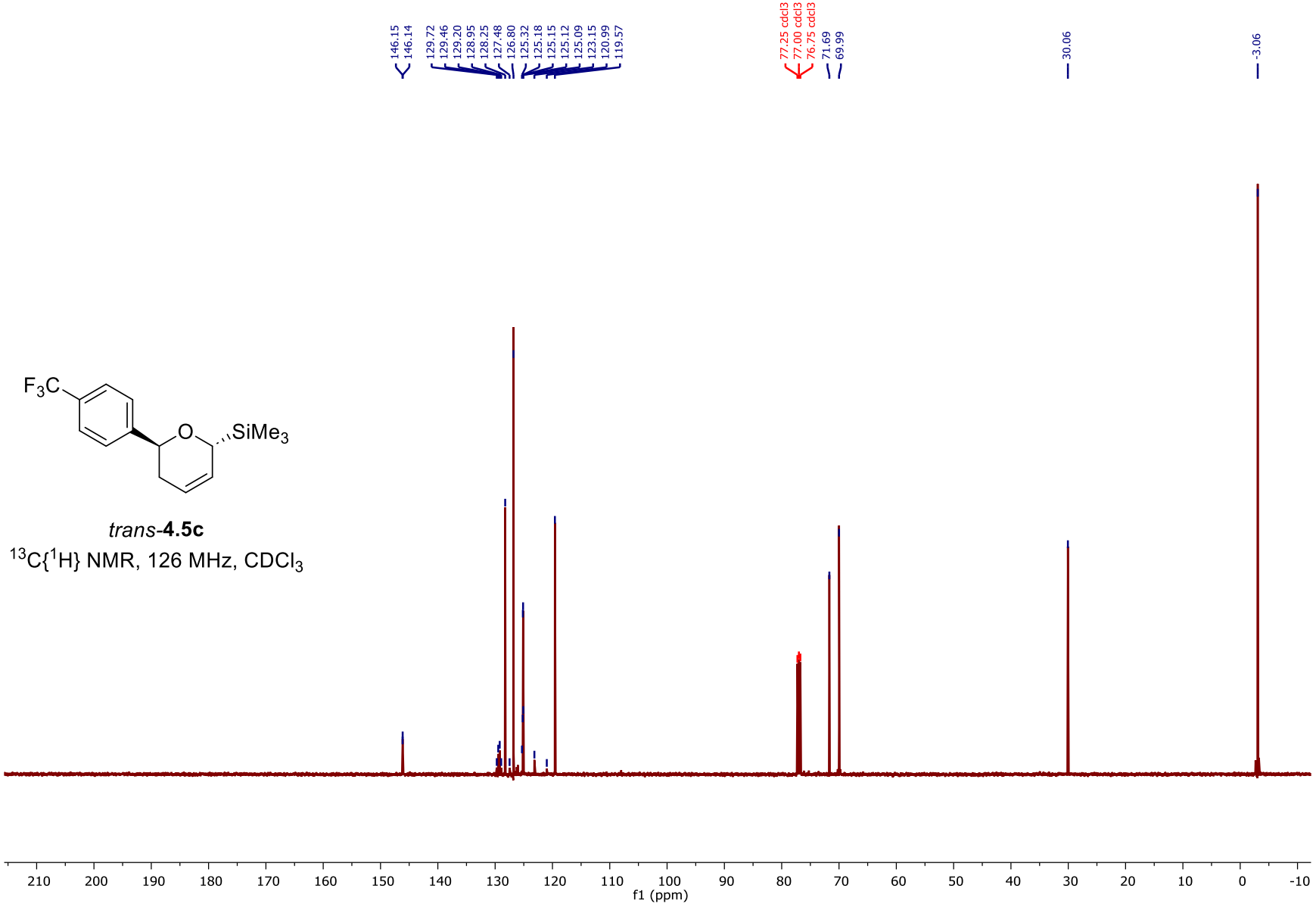


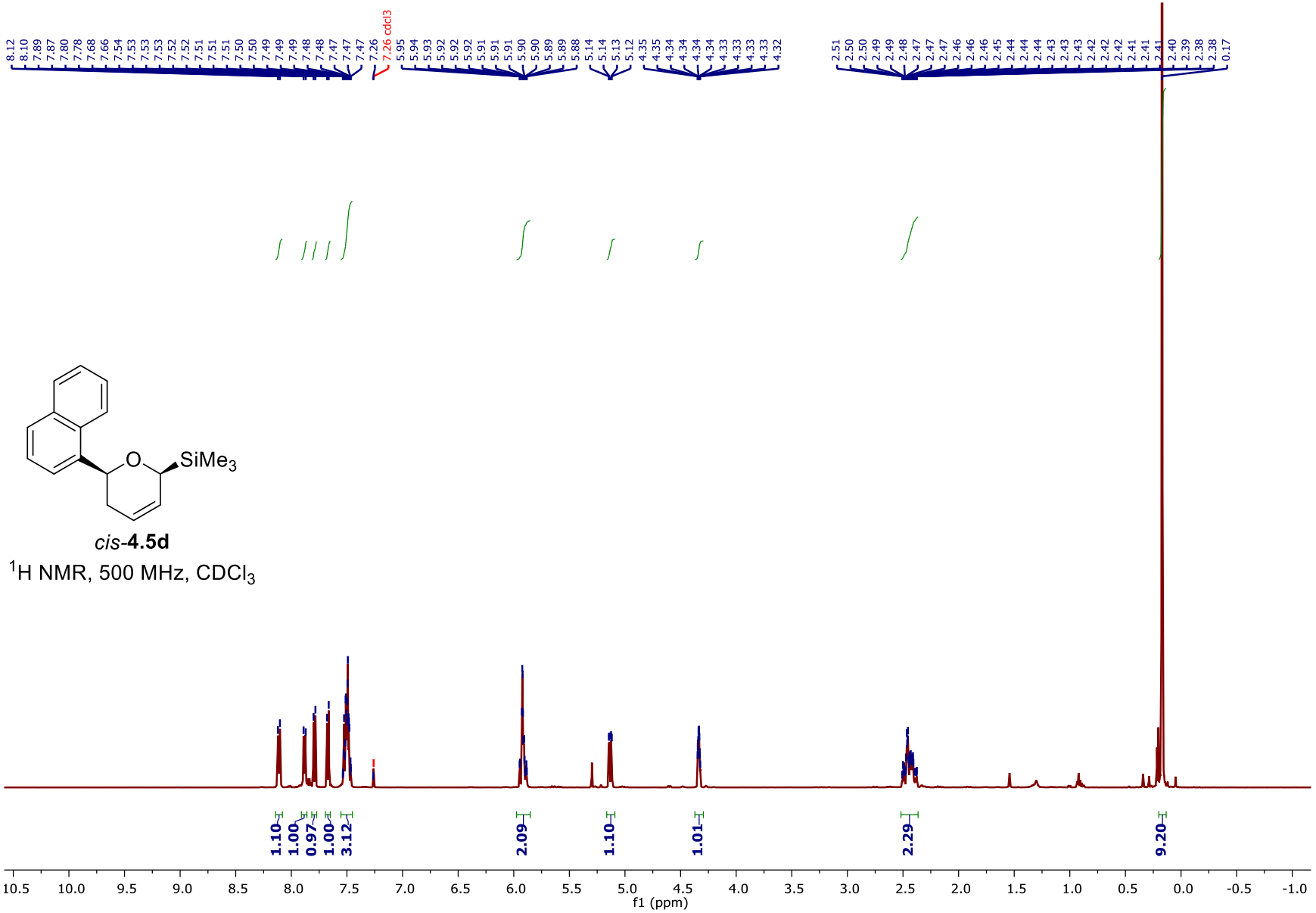
cis-**4.5c**

^{1}H NMR, 500 MHz, $CDCl_3$


147.96
147.95
147.94
147.93
129.54
129.28
129.02
128.77
128.11
125.86
125.13
125.10
125.07
125.04
120.71
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
74.80
71.66
33.96
-4.05
F3C
O
SiMe3
cis-4.5c
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)

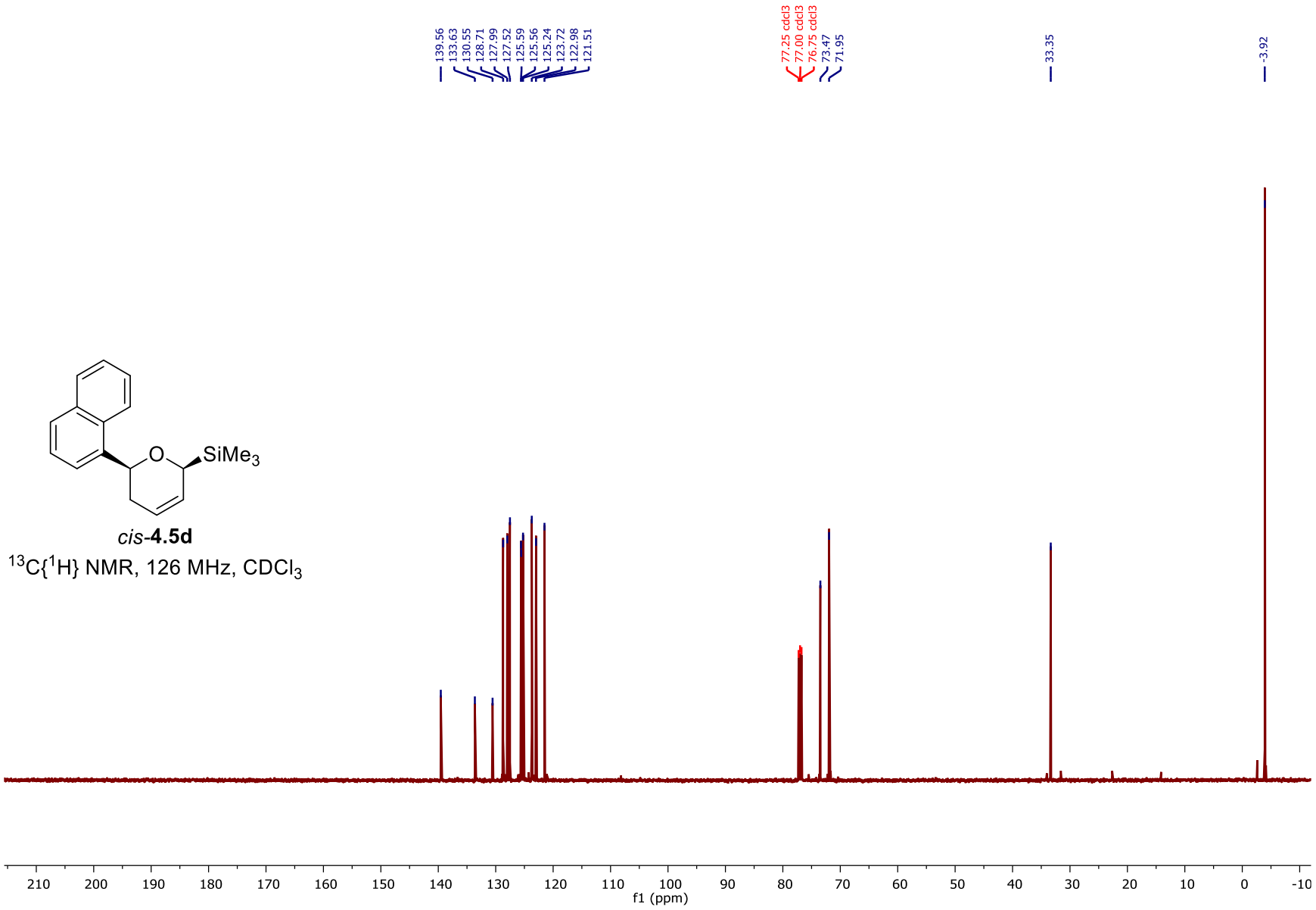

F3C
O
SiMe3
trans-4.5c
1H NMR, 500 MHz, CDCl3
7.27 cdcl3
1.93
2.05
2.01
1.00
0.91
1.17
1.18
9.01
f1 (ppm)

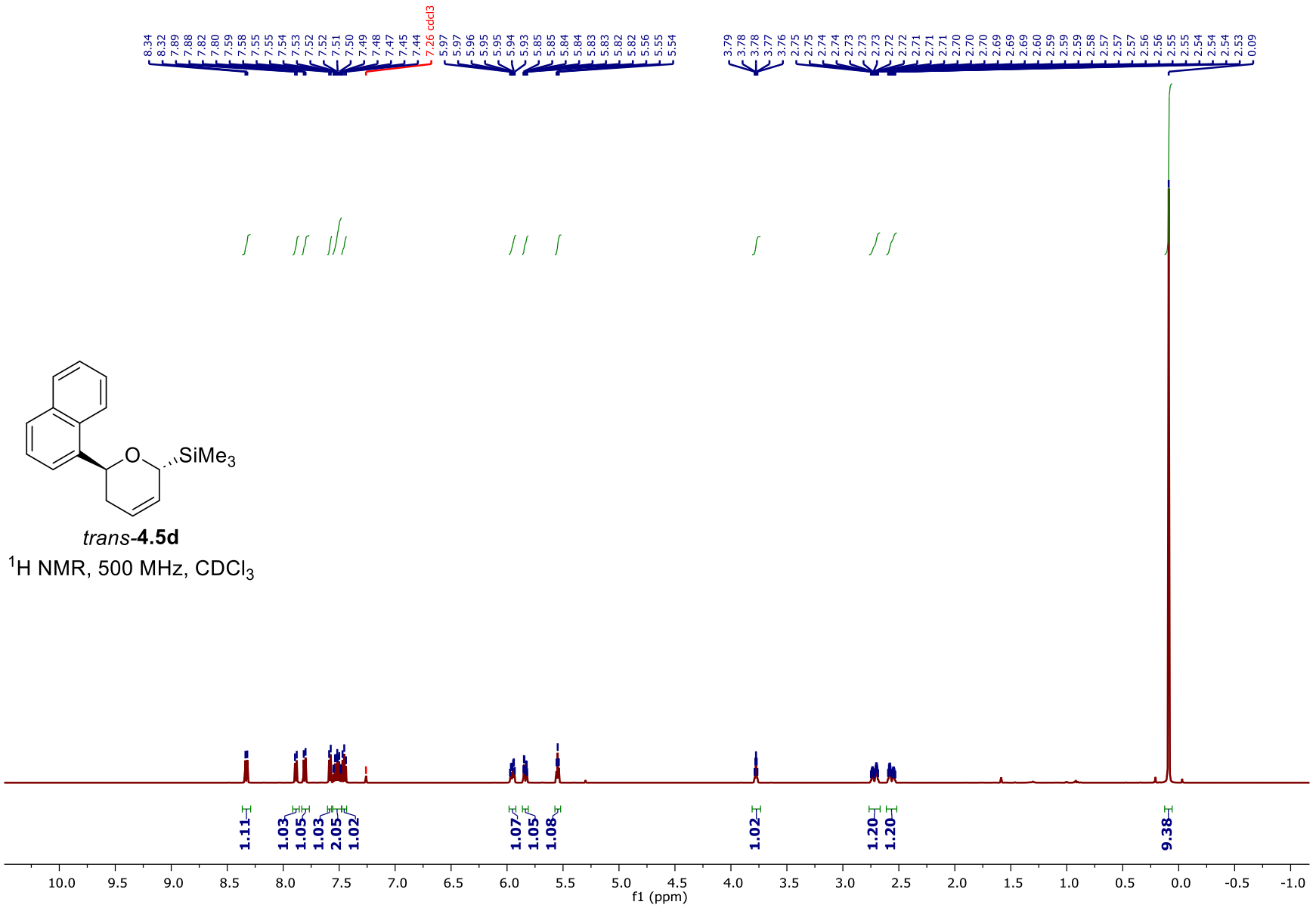

146.15
146.14
129.72
129.46
129.20
128.95
128.25
127.48
126.80
125.32
125.18
125.15
125.12
125.09
123.15
120.99
119.57
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
71.69
69.99
30.06
-3.06
F3C
O
SiMe3
trans-4.5c
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



cis-**4.5d**

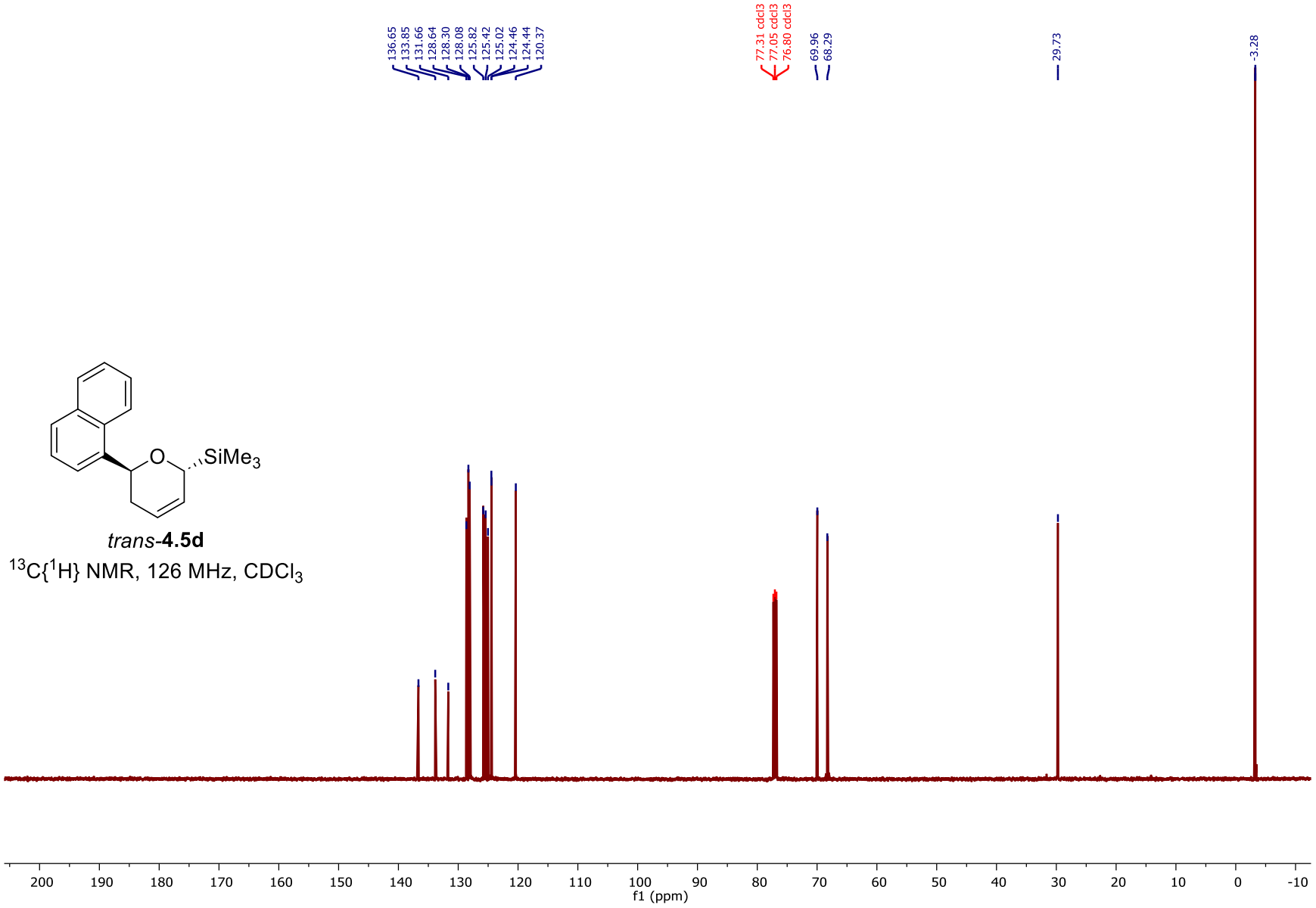
^{1}H NMR, 500 MHz, $CDCl_3$


139.56
133.63
130.55
128.71
127.99
127.52
125.59
125.56
125.24
123.72
122.98
121.51
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
73.47
71.95
33.35
-3.92
O
SiMe3
cis-4.5d
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



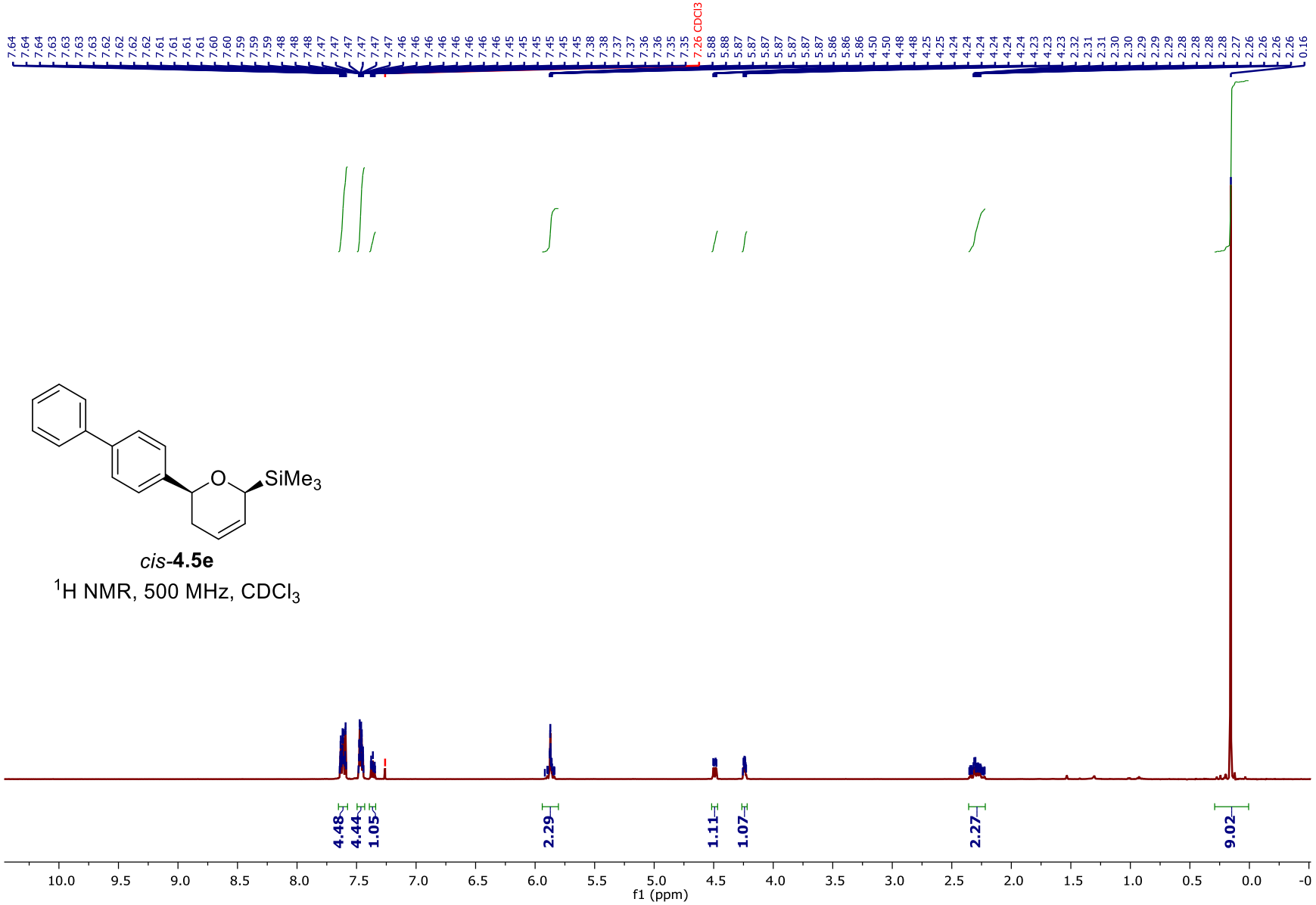
trans-**4.5d**

^{1}H NMR, 500 MHz, $CDCl_3$



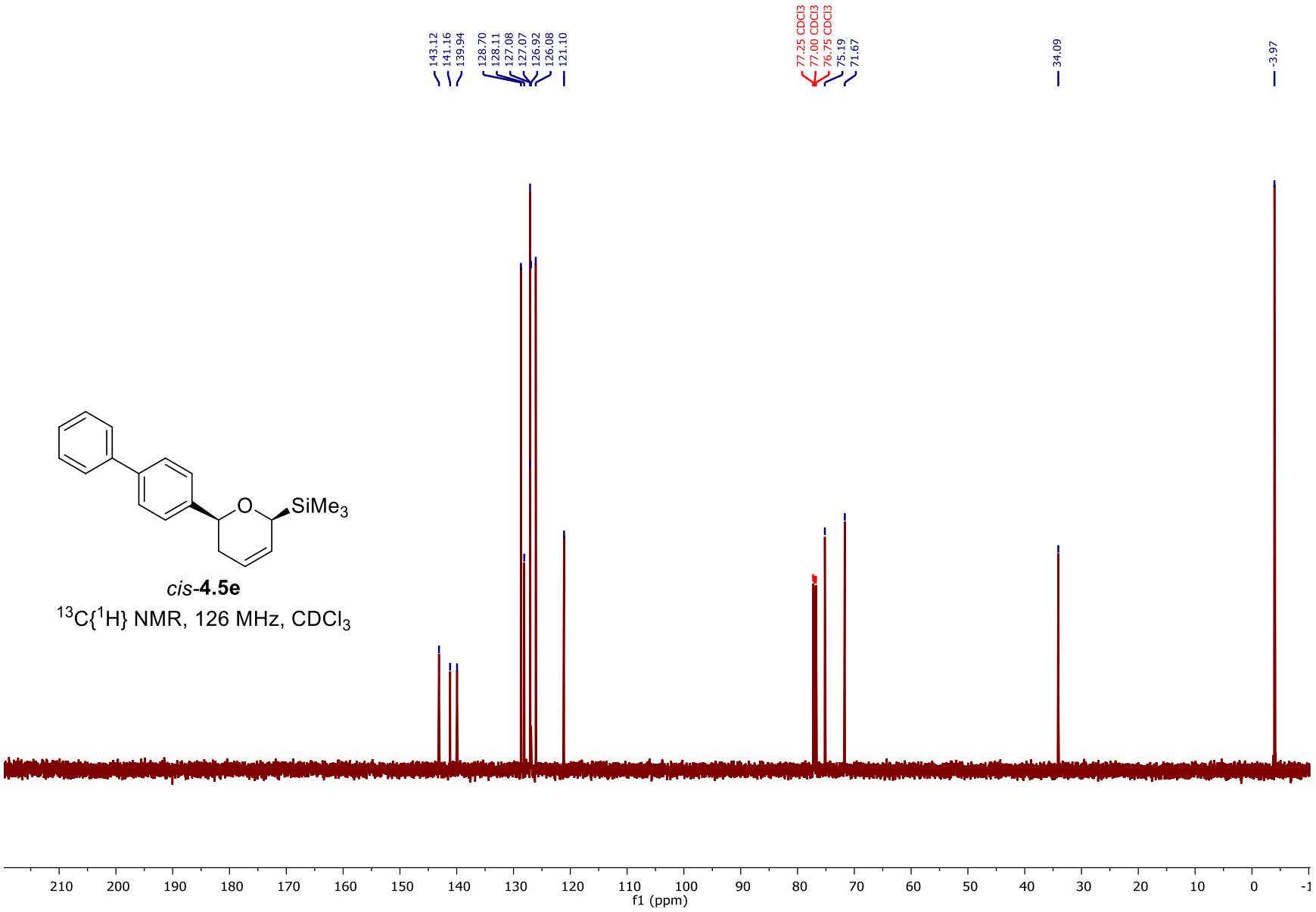
trans-**4.5d**

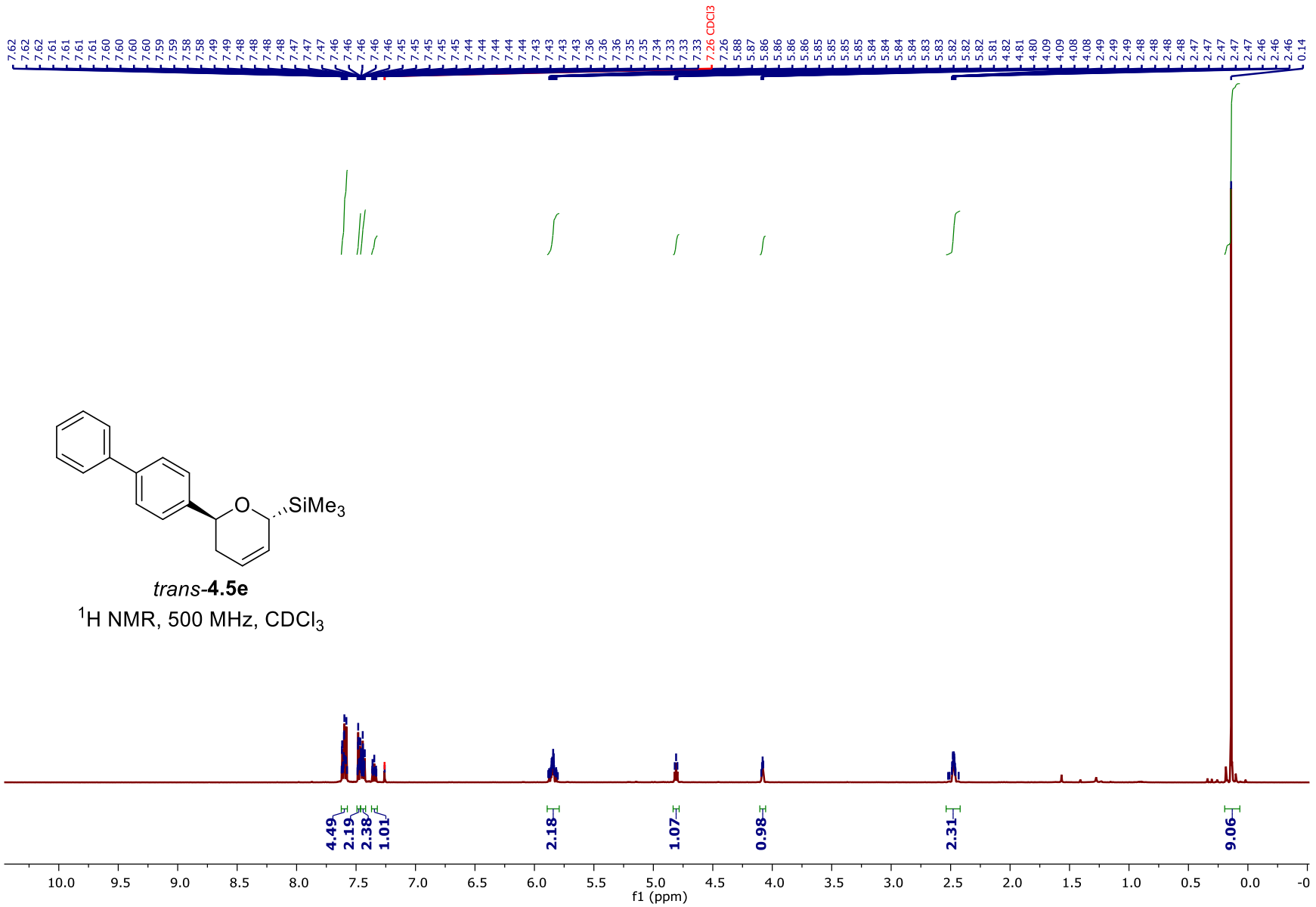
$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$



cis-**4.5e**

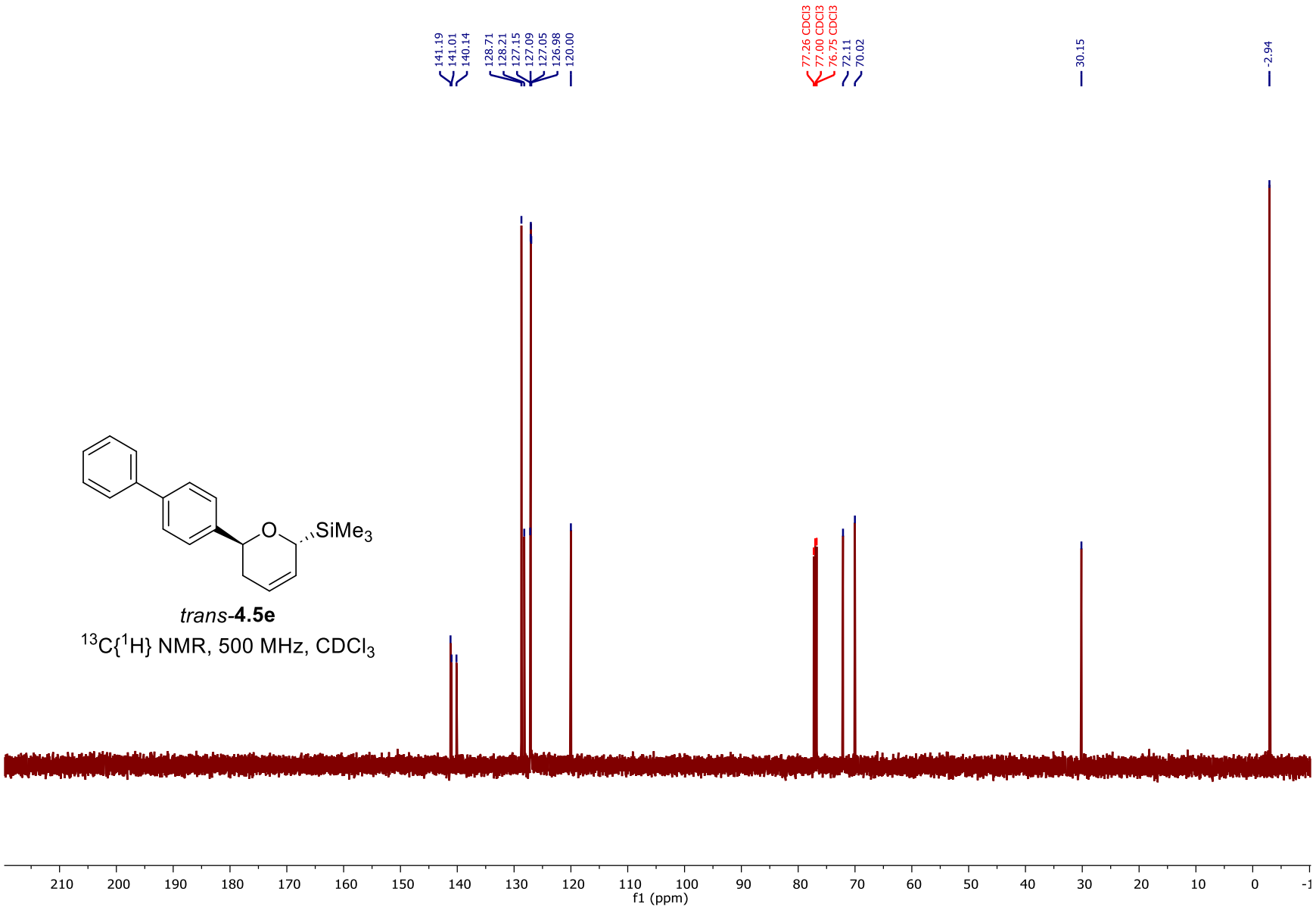
^{1}H NMR, 500 MHz, $CDCl_3$

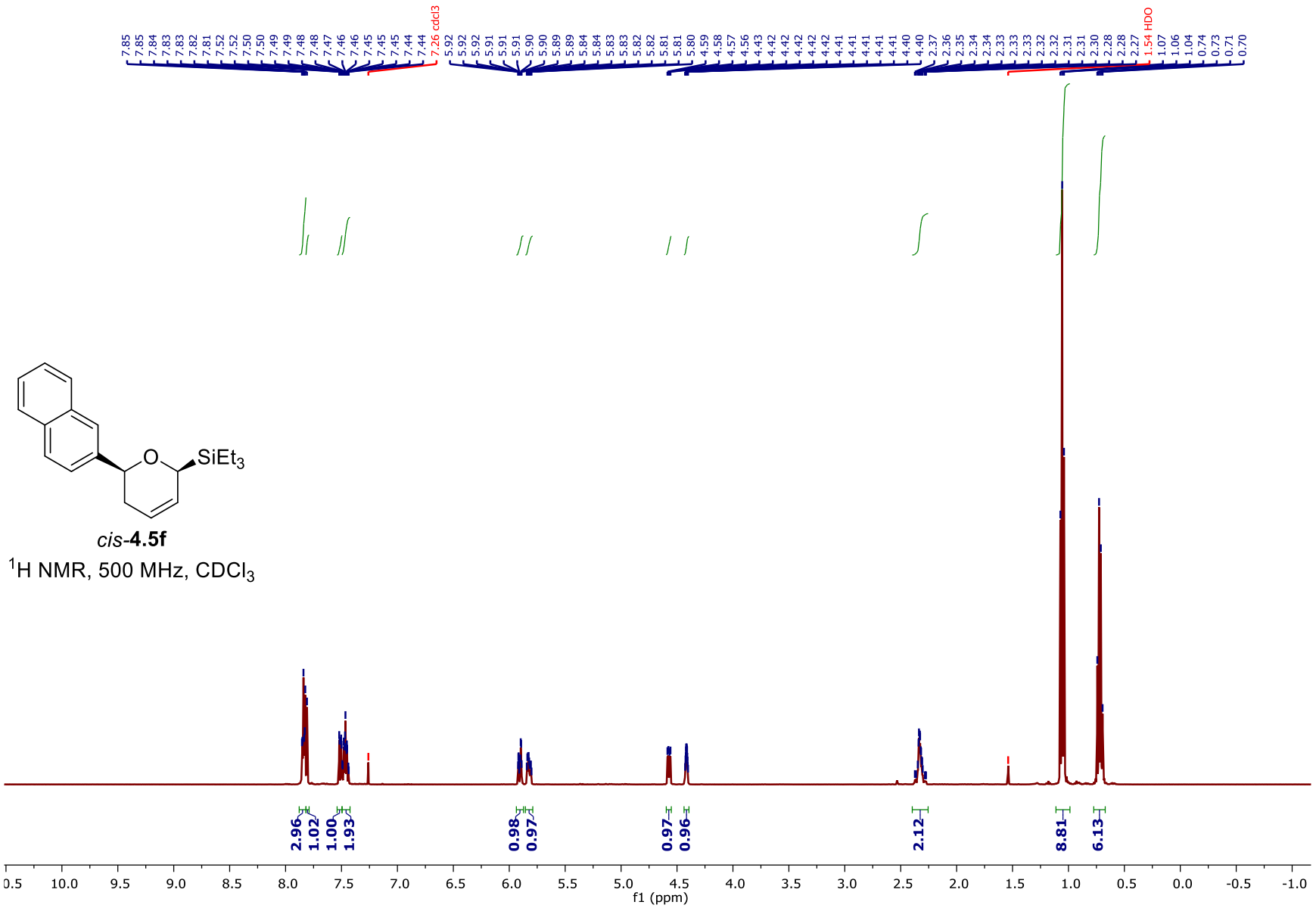

143.12
141.16
139.94
128.70
128.11
127.08
127.07
126.92
126.08
121.10
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
75.19
71.67
34.09
-3.97
O
SiMe3
cis-4.5e
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



trans-**4.5e**

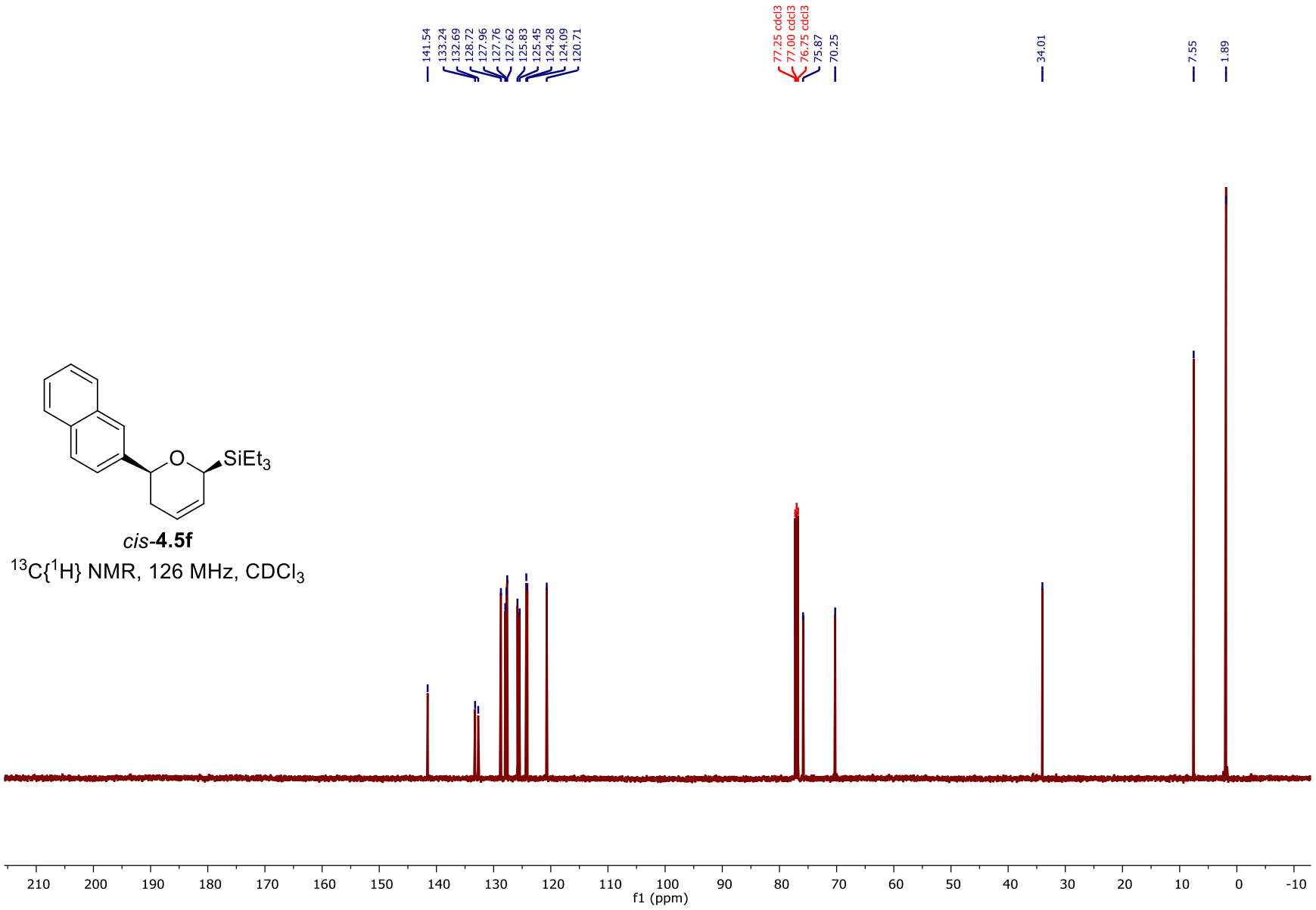
^{1}H NMR, 500 MHz, $CDCl_3$

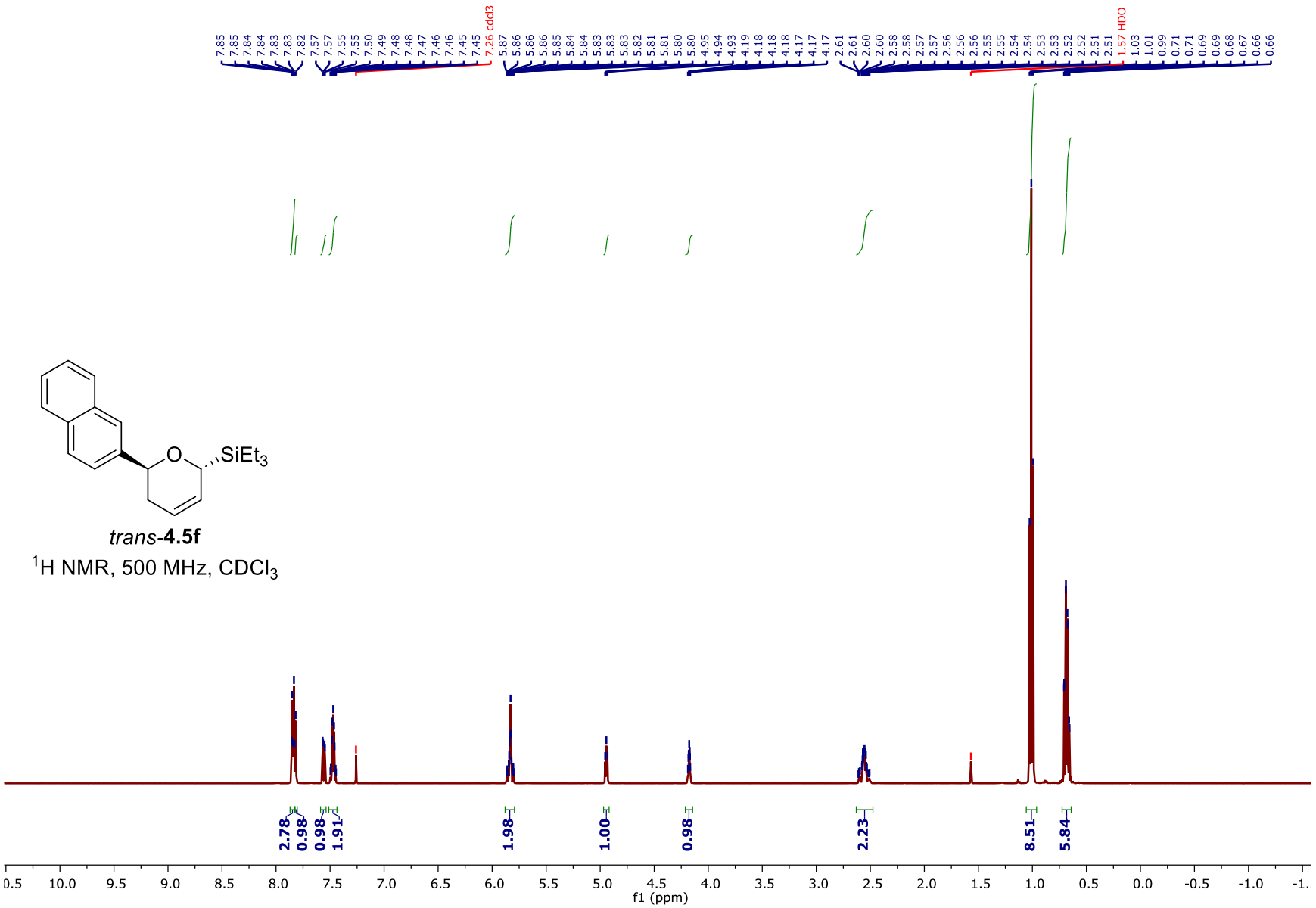

141.19
141.01
140.14
128.71
128.21
127.15
127.09
127.05
126.98
120.00
77.26 CDCl3
77.00 CDCl3
76.75 CDCl3
72.11
70.02
30.15
-2.94
O
SiMe3
trans-4.5e
13C{1H} NMR, 500 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



cis-**4.5f**

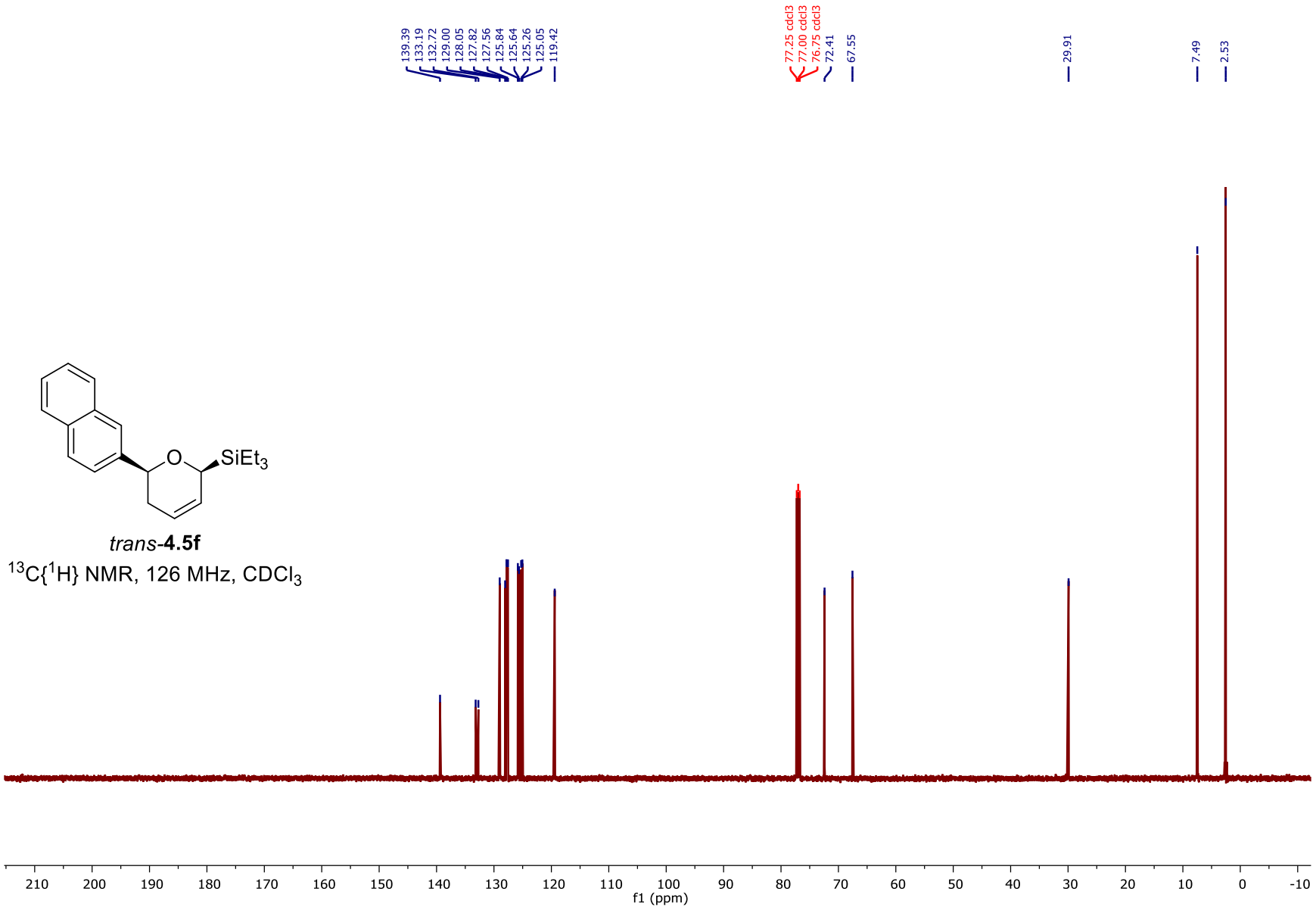
^{1}H NMR, 500 MHz, $CDCl_3$

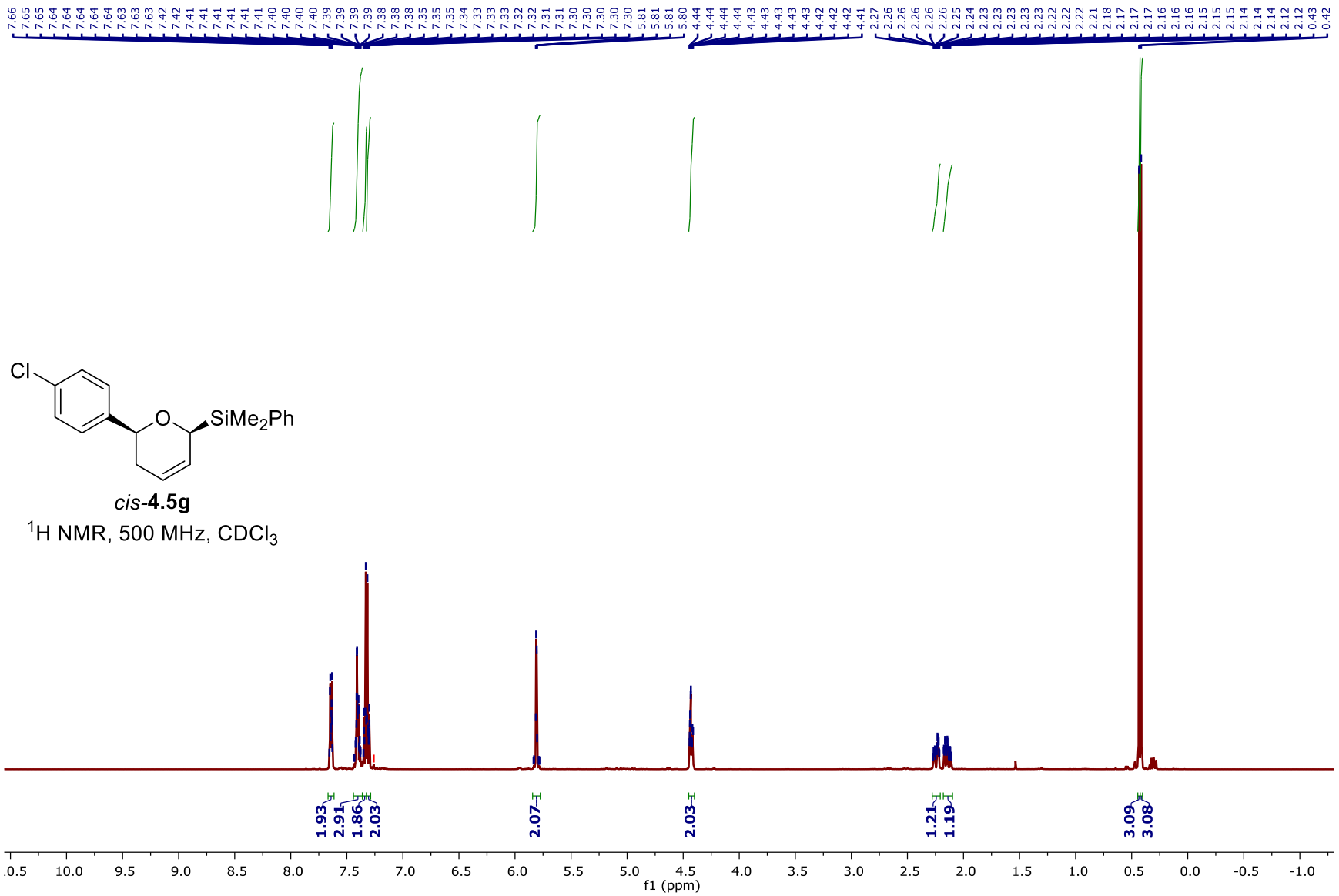

141.54
133.24
132.69
128.72
127.96
127.76
127.62
125.83
125.45
124.28
124.09
120.71
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
75.87
70.25
34.01
7.55
1.89
O
SiEt3
cis-4.5f
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

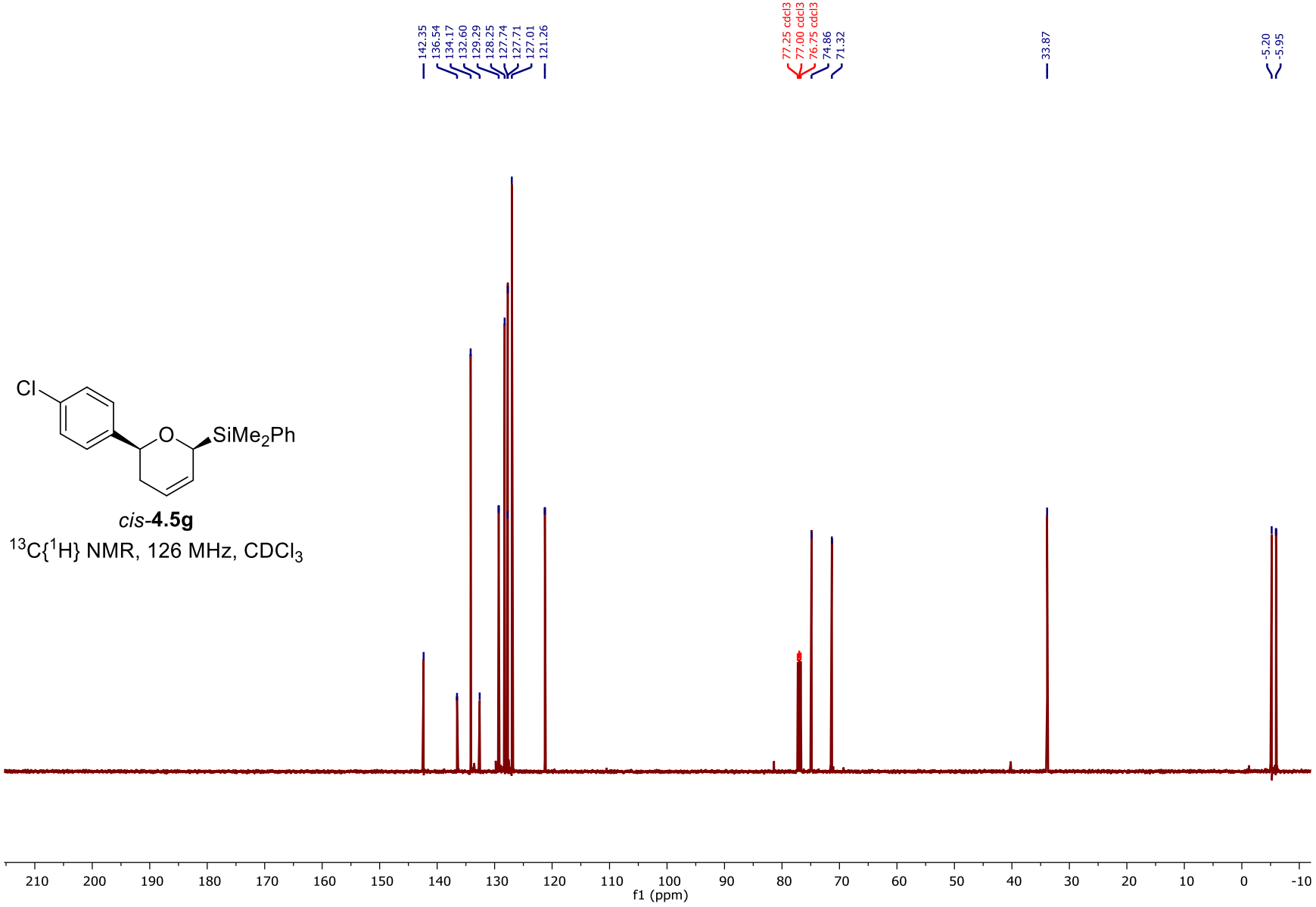


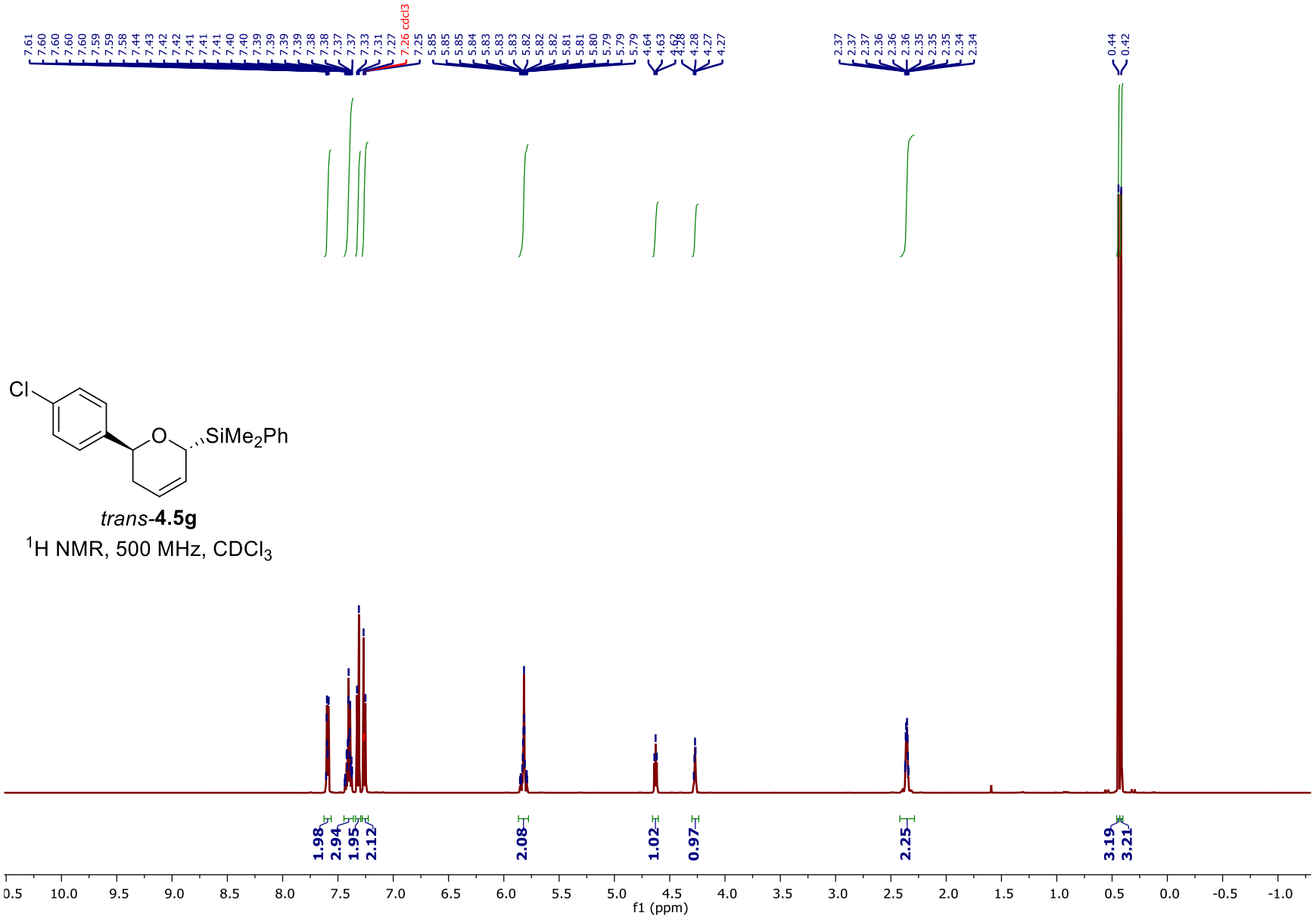
trans-**4.5f**

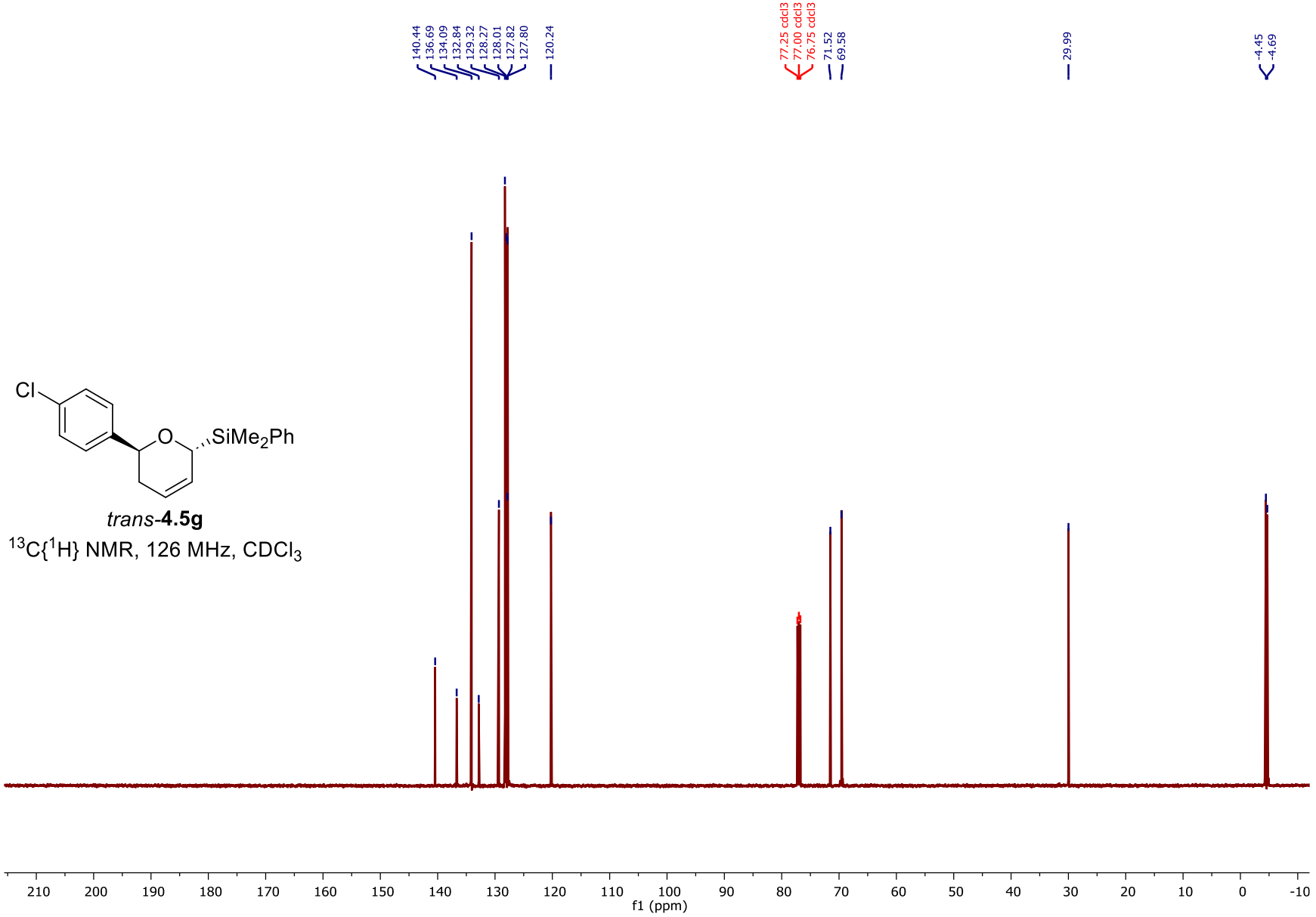
^{1}H NMR, 500 MHz, $CDCl_3$

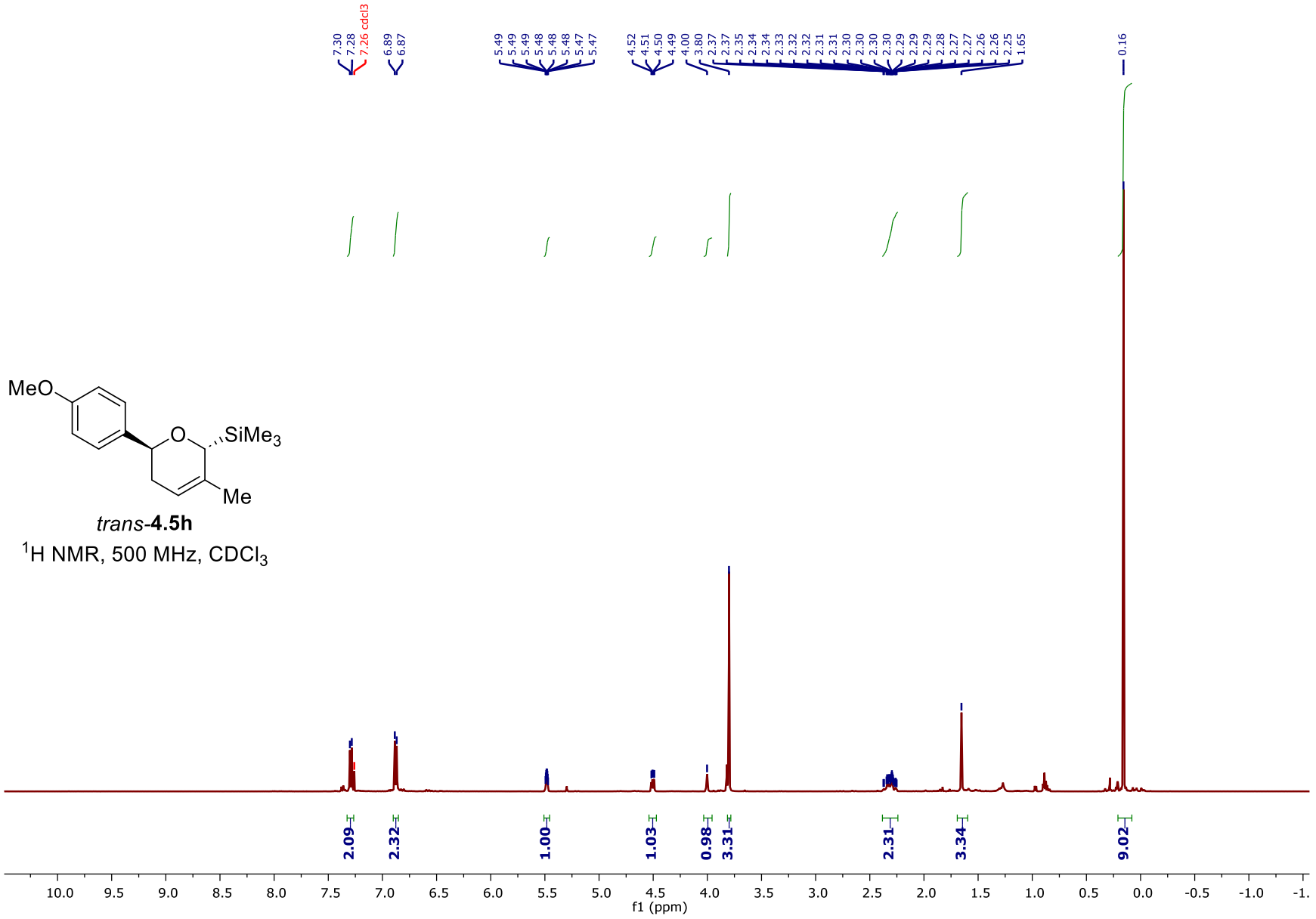

139.39
133.19
132.72
129.00
128.05
127.82
127.56
125.84
125.64
125.26
125.05
119.42
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
72.41
67.55
29.91
7.49
2.53
O
SiEt3
trans-4.5f
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

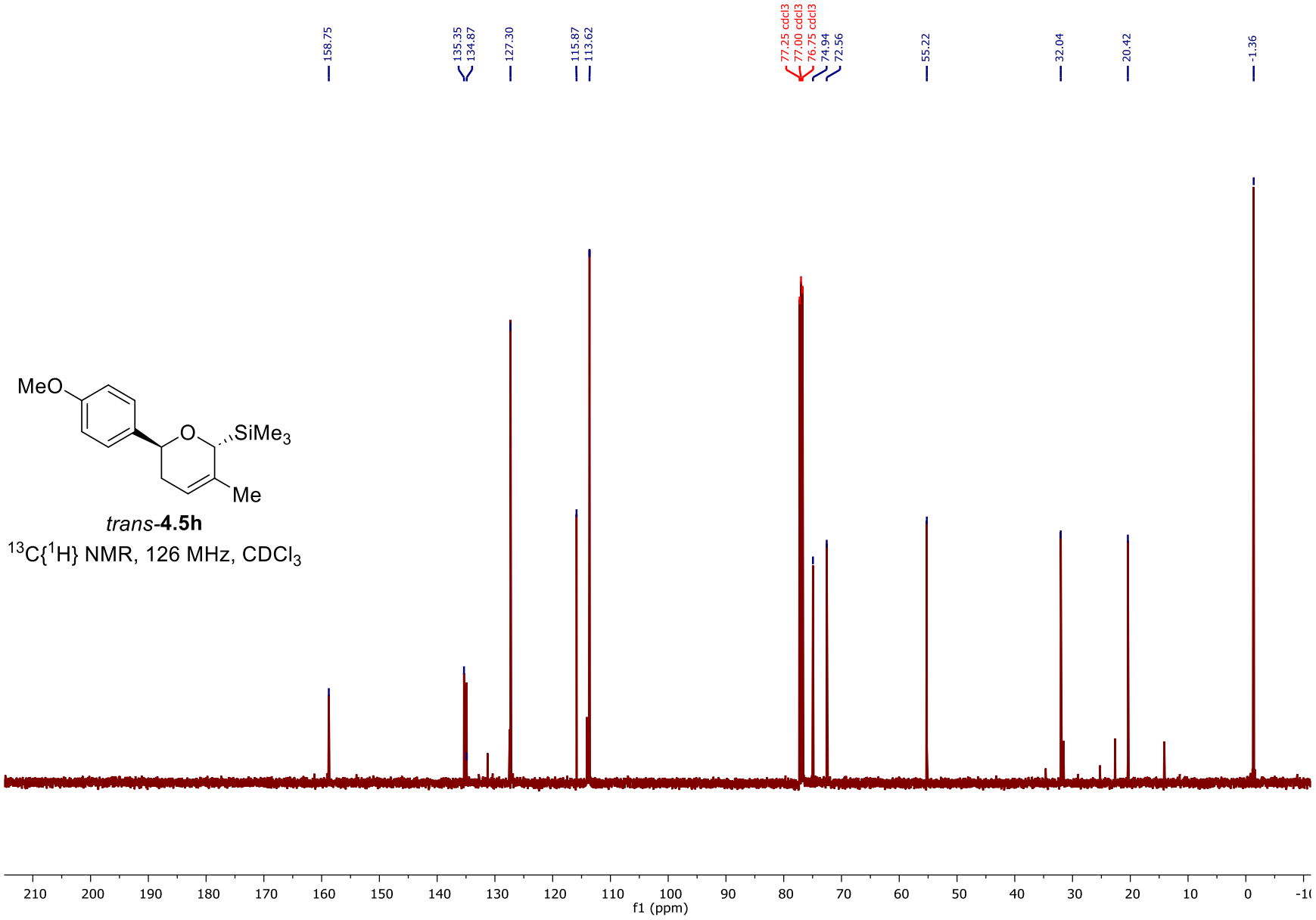

Cl
O
SiMe2Ph
cis-4.5g
1H NMR, 500 MHz, CDCl3
1.93
2.91
1.86
2.03
2.07
2.03
1.21
1.19
3.09
3.08
f1 (ppm)

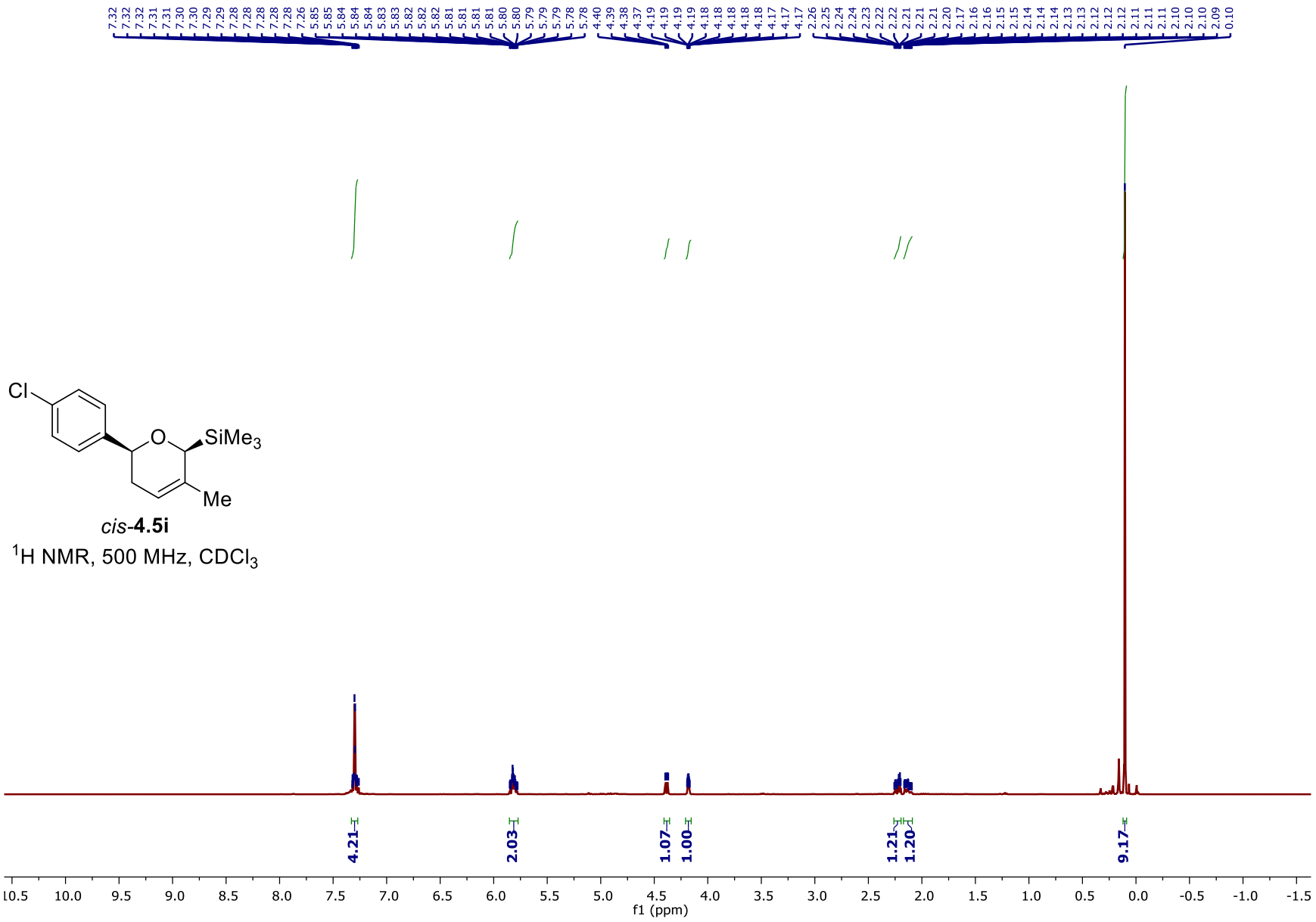

142.35
136.54
134.17
132.60
129.29
128.25
127.74
127.71
127.01
121.26
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
74.86
71.32
33.87
-5.20
-5.95
Cl
O
SiMe2Ph
cis-4.5g
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

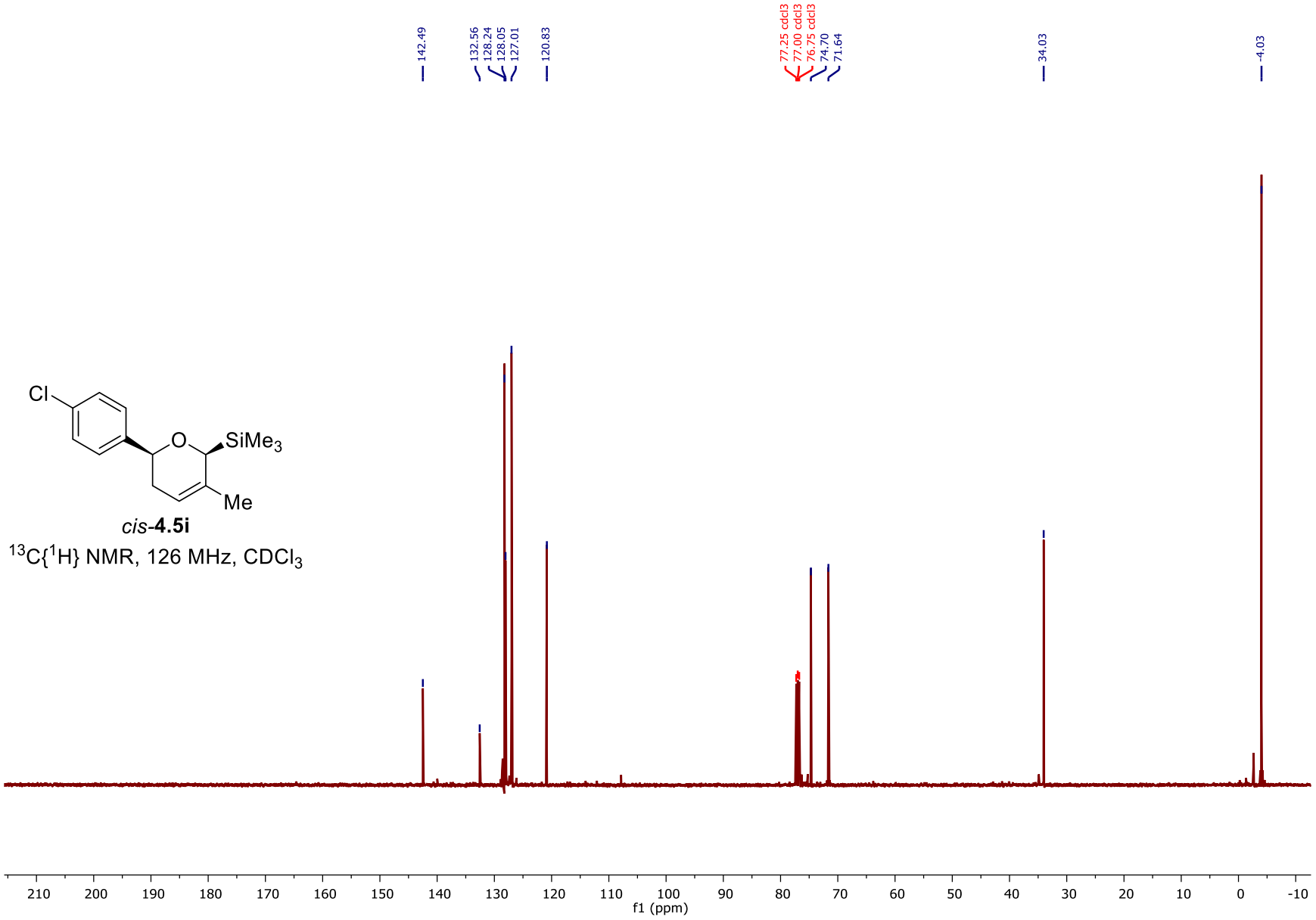

Cl
O
SiMe2Ph
trans-4.5g
1H NMR, 500 MHz, CDCl3
7.26 cdcl3
1.98
2.94
1.95
2.12
2.08
1.02
0.97
2.25
3.19
3.21
f1 (ppm)

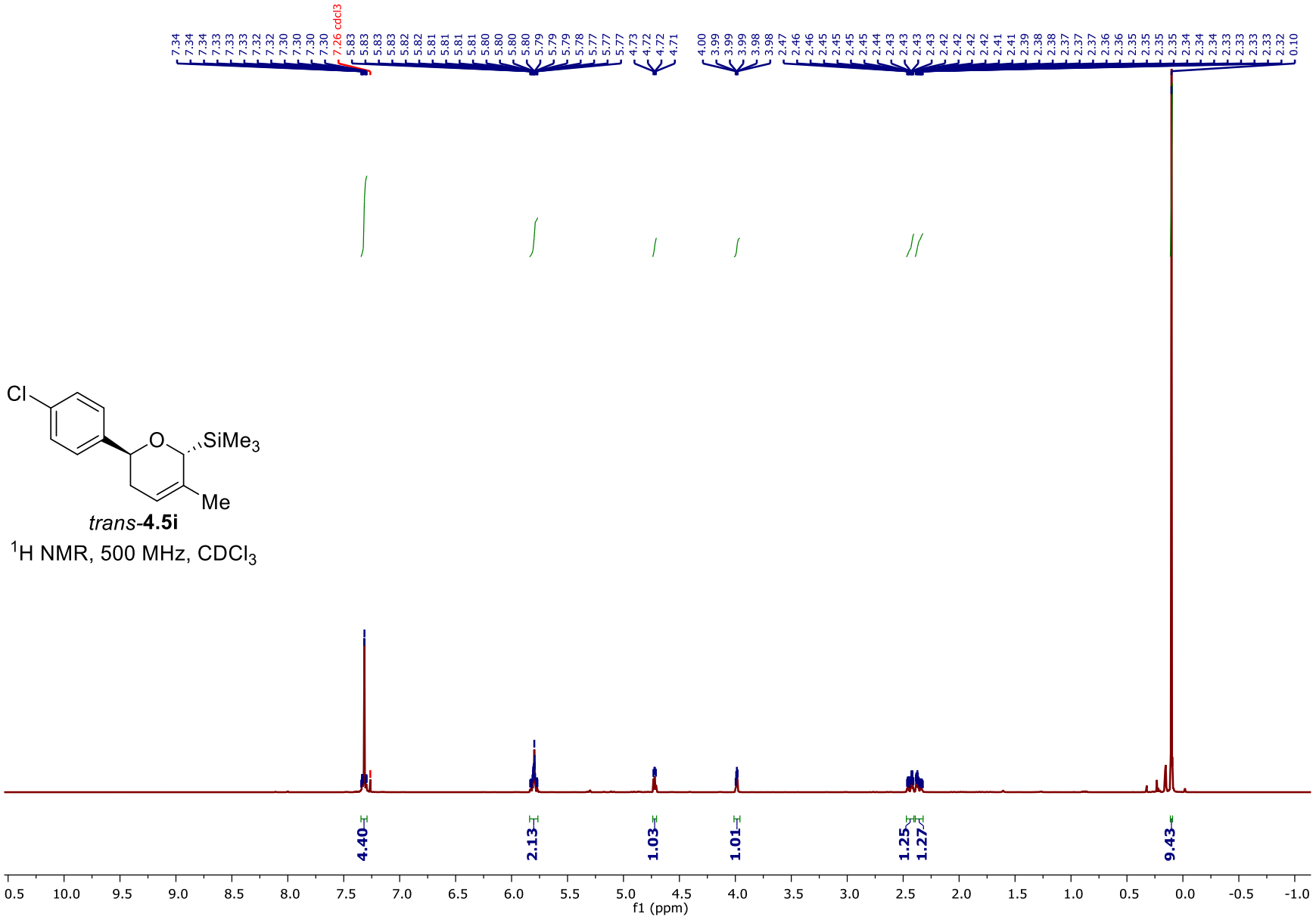

140.44
136.69
134.09
132.84
129.32
128.27
128.01
127.82
127.80
120.24
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
71.52
69.58
29.99
-4.45
-4.69
Cl
O
SiMe2Ph
trans-4.5g
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

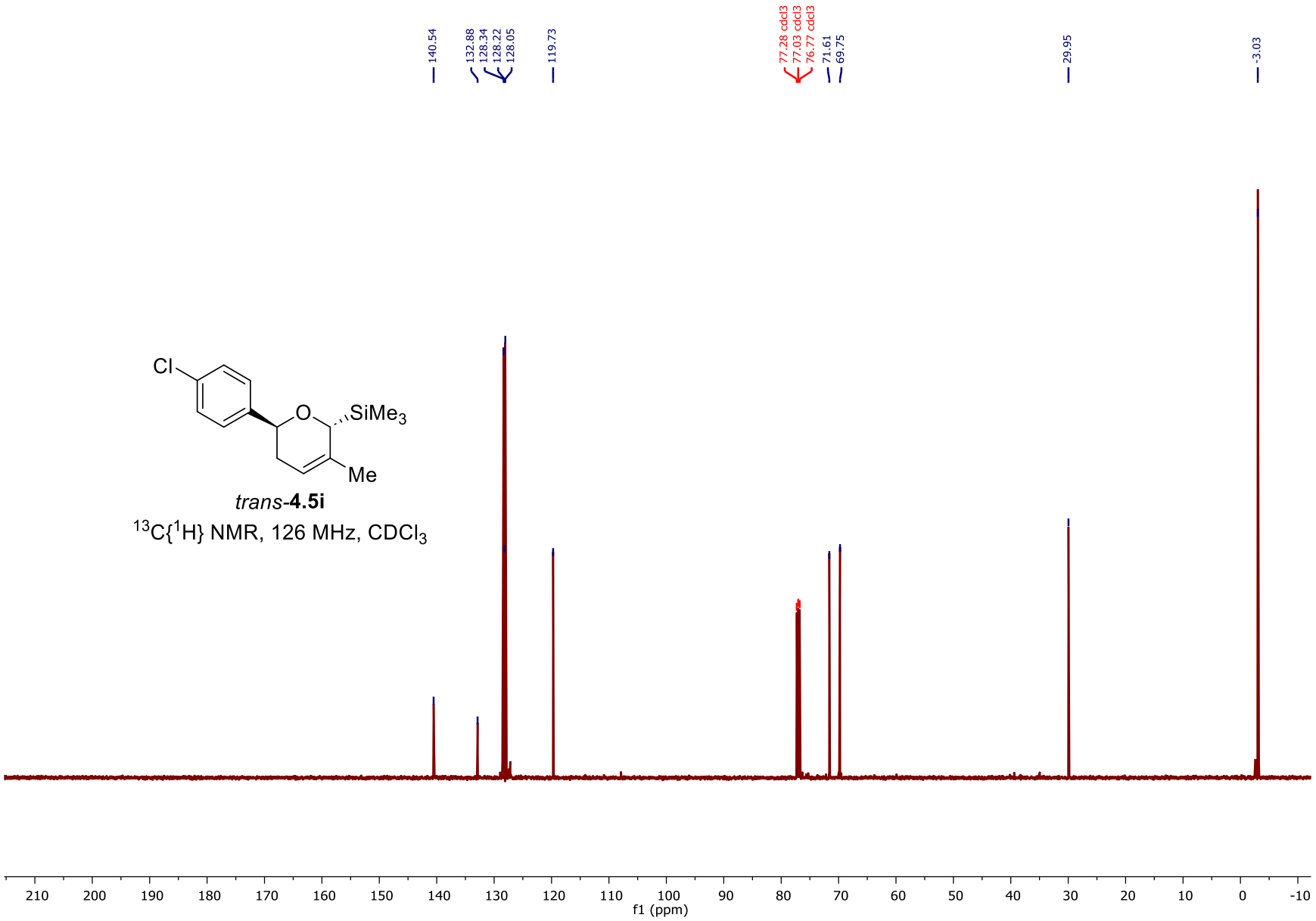

7.30
7.28
7.26 cdcl3
6.89
6.87
5.49
5.49
5.49
5.48
5.48
5.48
5.47
5.47
4.52
4.51
4.50
4.49
4.00
3.80
2.37
2.37
2.35
2.34
2.34
2.33
2.32
2.32
2.31
2.31
2.30
2.30
2.30
2.30
2.29
2.29
2.29
2.28
2.27
2.27
2.26
2.26
2.25
1.65
0.16
MeO
O
SiMe3
Me
trans-4.5h
1H NMR, 500 MHz, CDCl3
2.09
2.32
1.00
1.03
0.98
3.31
2.31
3.34
9.02
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
-1.0
f1 (ppm)

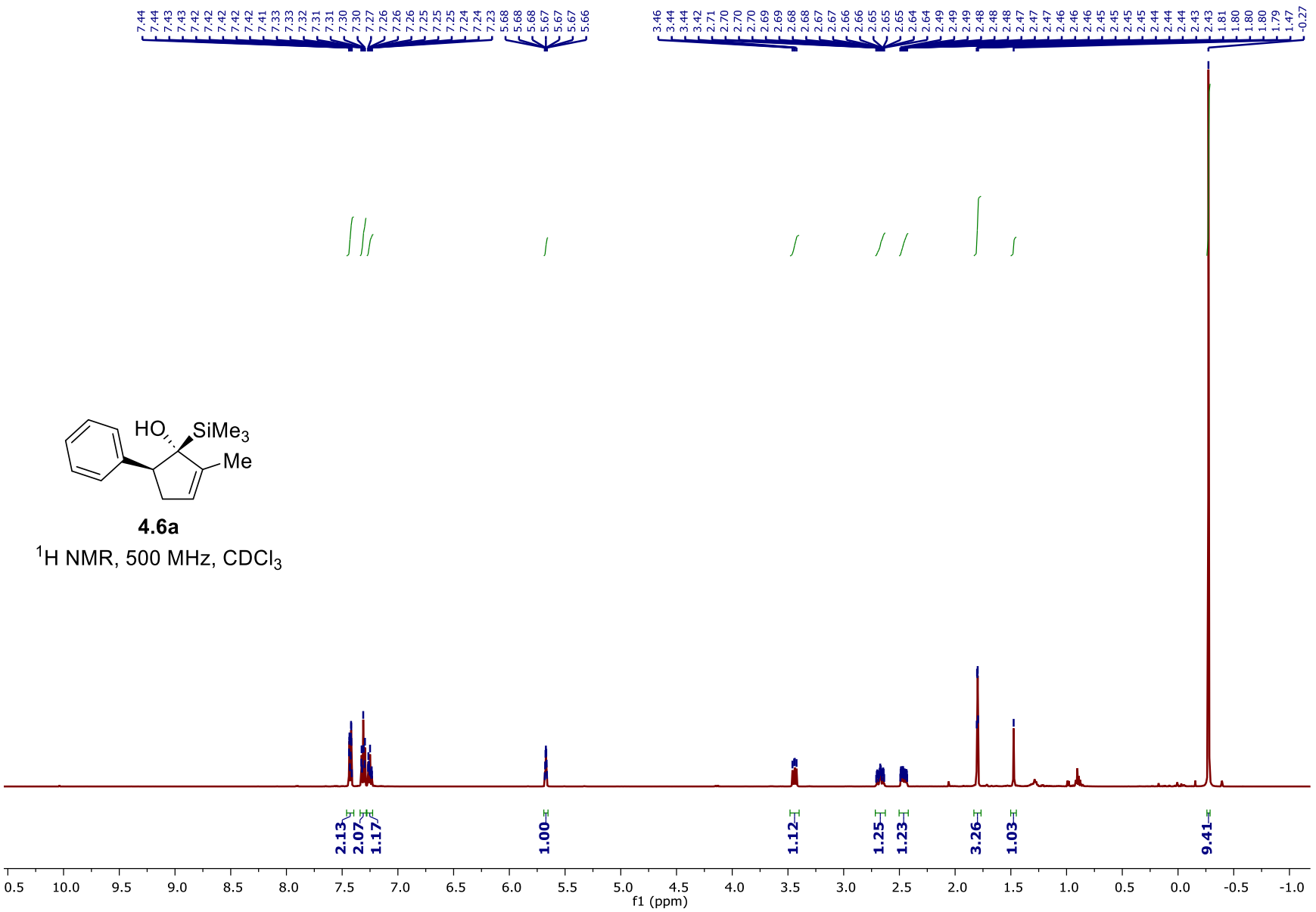

158.75
135.35
134.87
127.30
115.87
113.62
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
74.94
72.56
55.22
32.04
20.42
-1.36
MeO
O
SiMe3
Me
trans-4.5h
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)

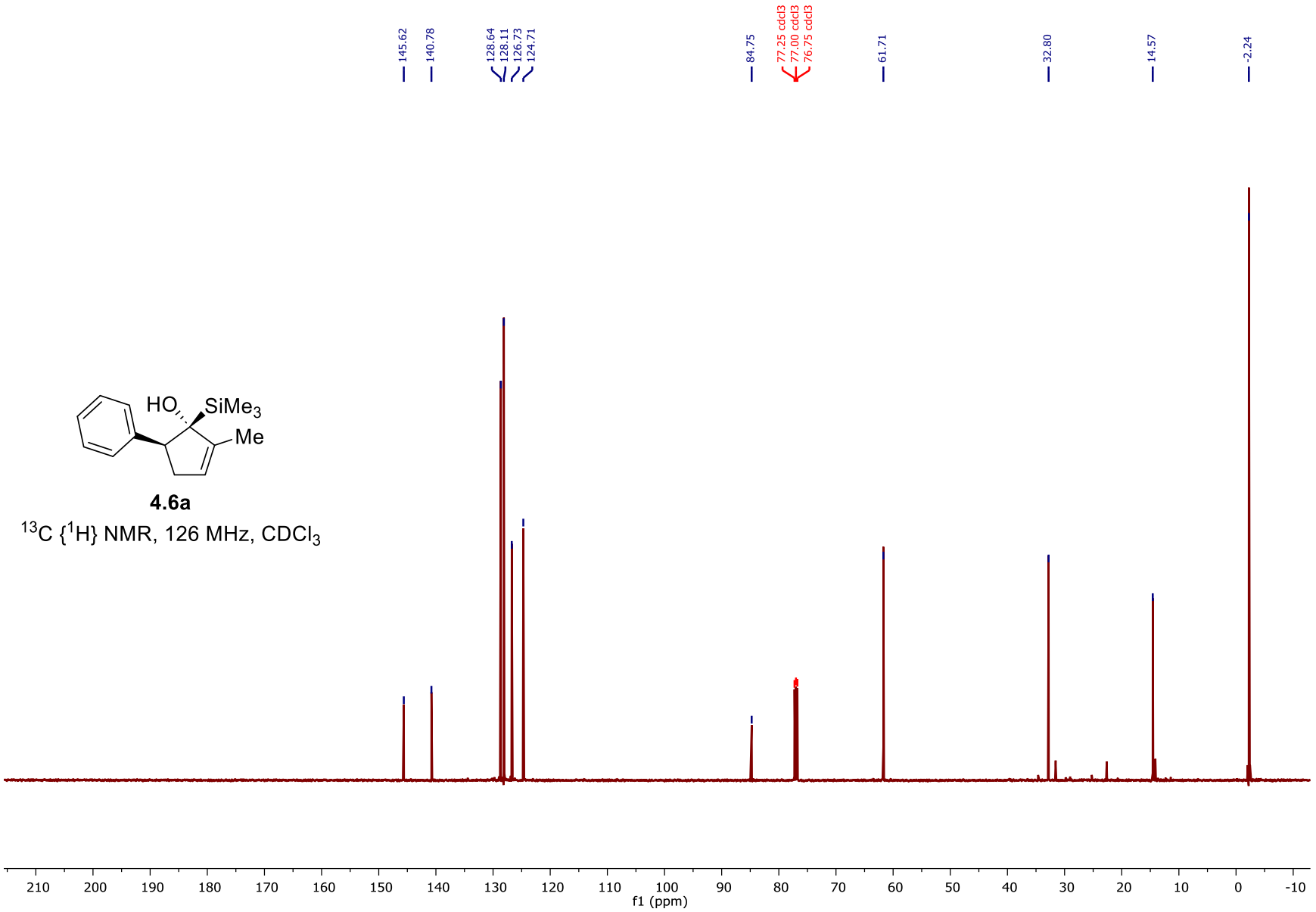

Cl
O
SiMe3
Me
cis-4.5i
1H NMR, 500 MHz, CDCl3
4.21
2.03
1.07
1.00
1.21
1.20
9.17
f1 (ppm)

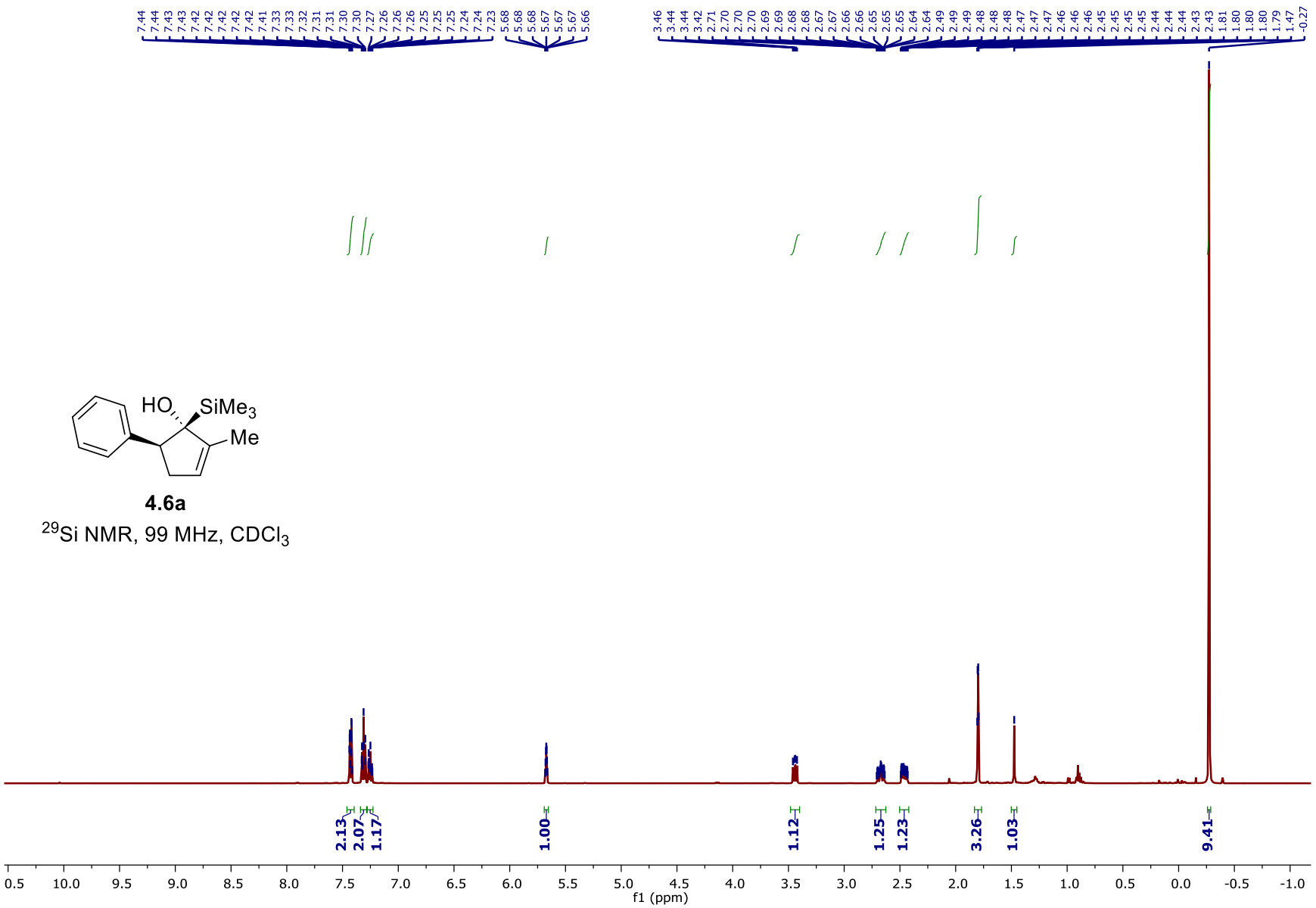

142.49
132.56
128.24
128.05
127.01
120.83
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
74.70
71.64
34.03
-4.03
Cl
O
SiMe3
Me
cis-4.5i
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

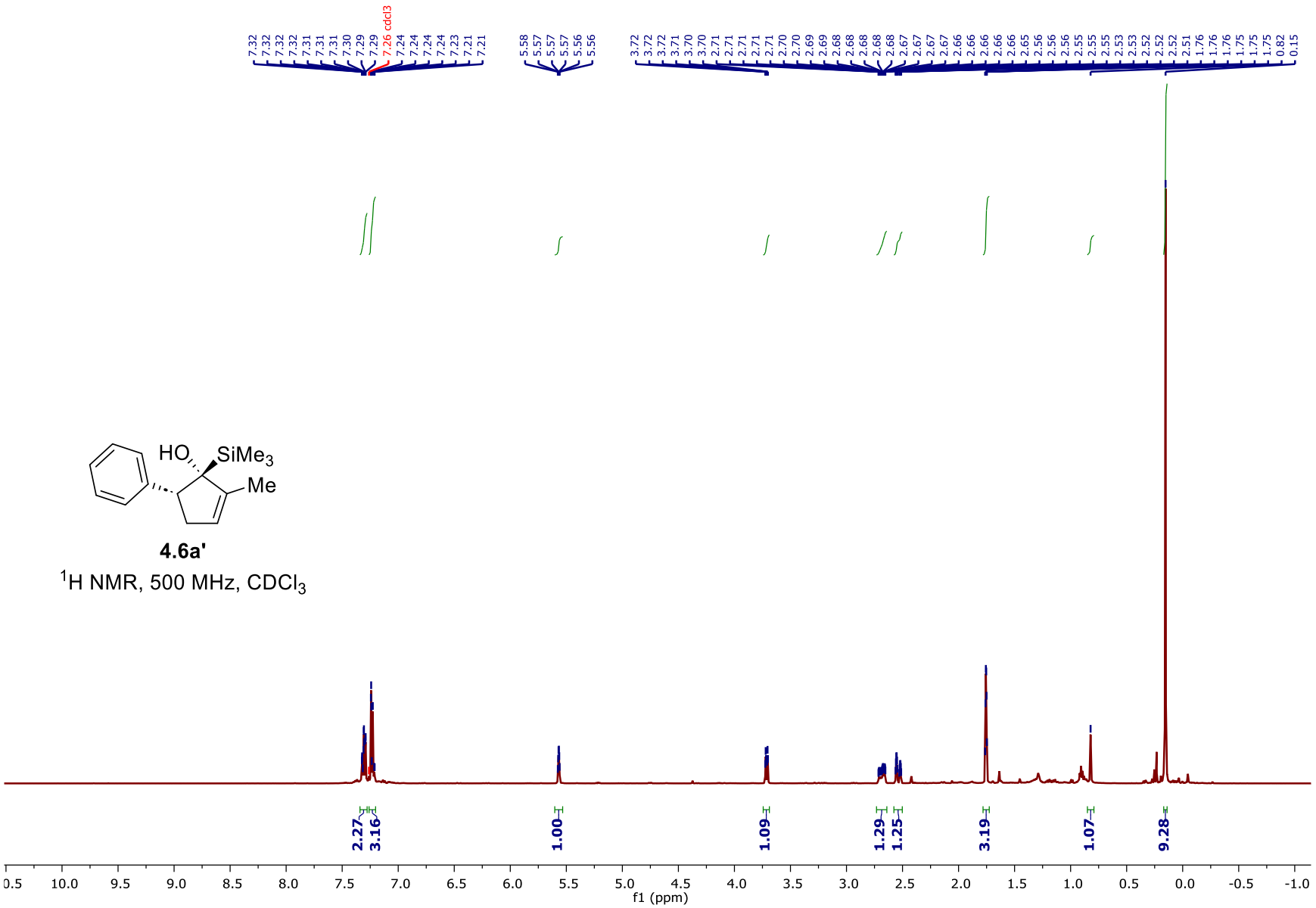

Cl
O
SiMe3
Me
trans-4.5i
1H NMR, 500 MHz, CDCl3
7.26 cdcl3
4.40
2.13
1.03
1.01
1.25
1.27
9.43
f1 (ppm)

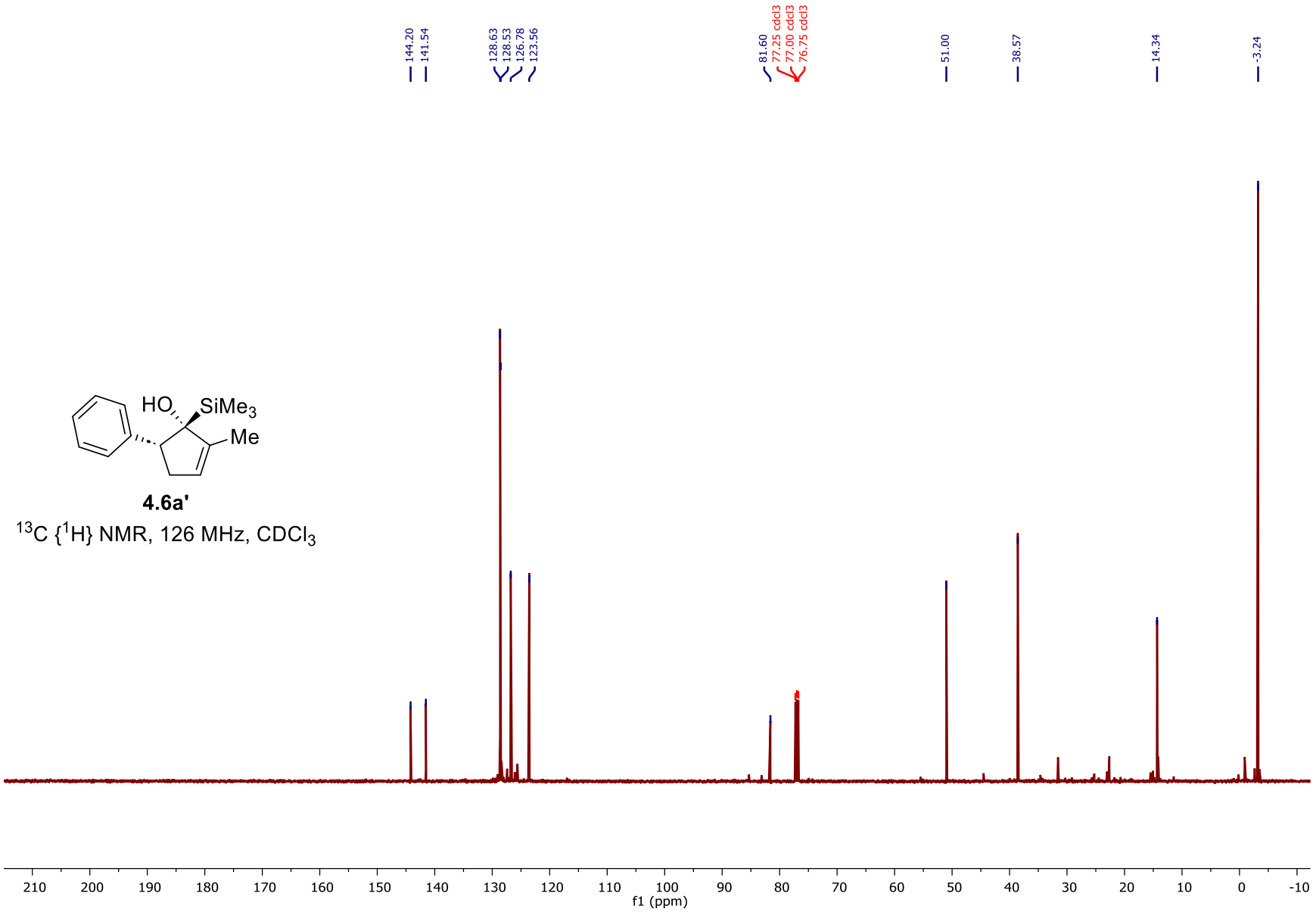

140.54
132.88
128.34
128.22
128.05
119.73
77.28 cdcl3
77.03 cdcl3
76.77 cdcl3
71.61
69.75
29.95
-3.03
Cl
O
SiMe3
Me
trans-4.5i
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

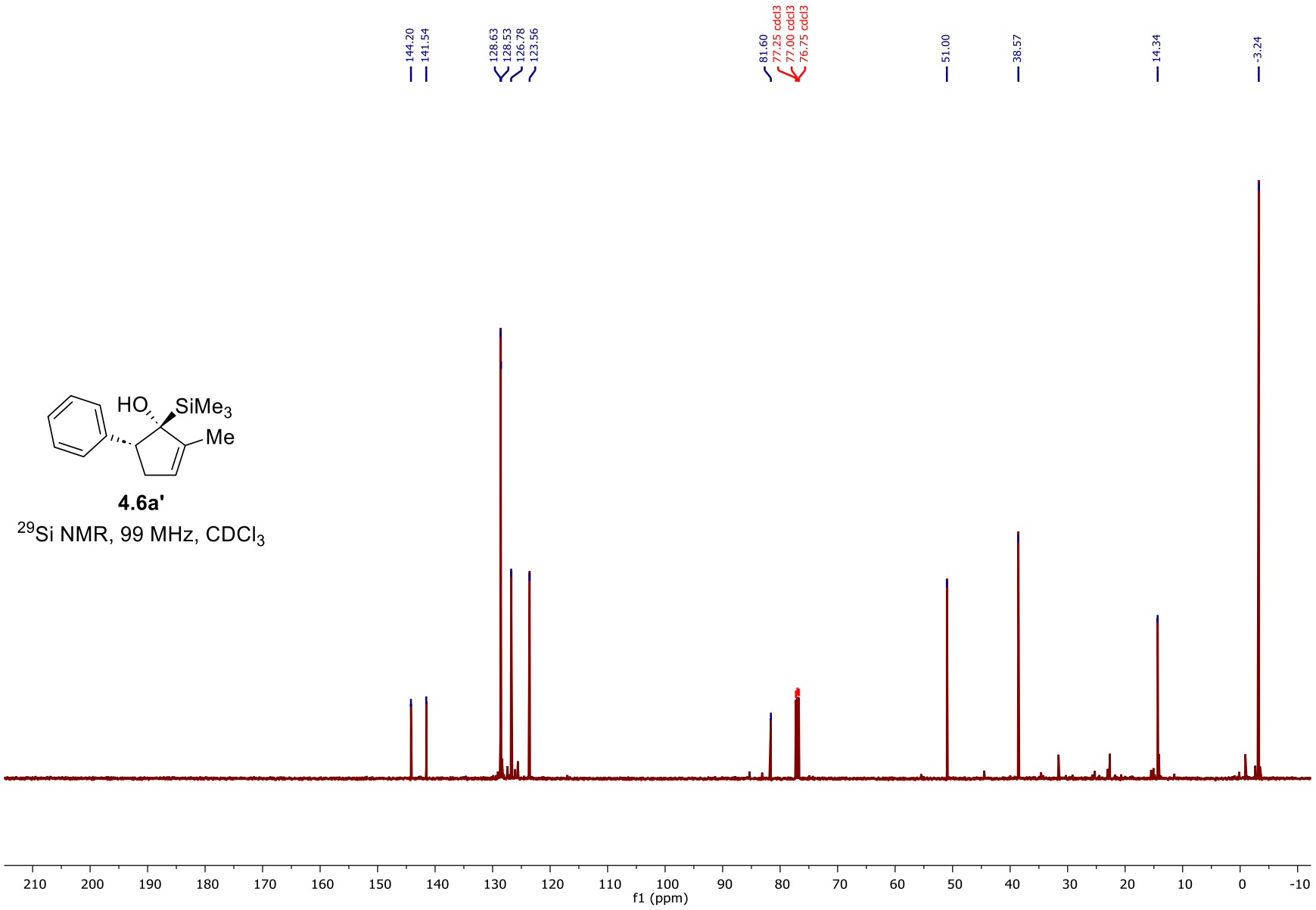

HO
SiMe3
Me
4.6a
1H NMR, 500 MHz, CDCl3
2.13
2.07
1.17
1.00
1.12
1.25
1.23
3.26
1.03
9.41
f1 (ppm)

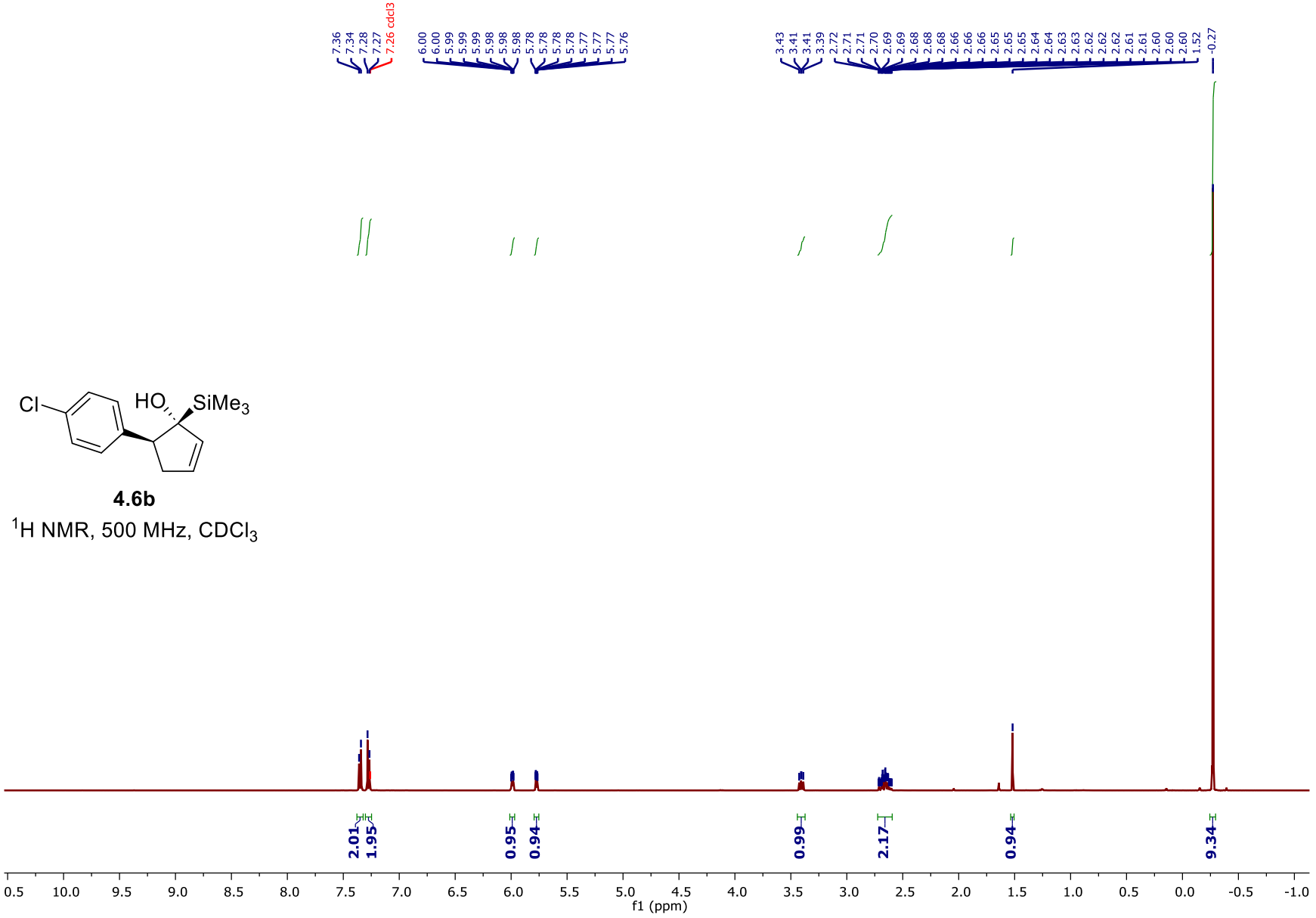

145.62
140.78
128.64
128.11
126.73
124.71
84.75
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
61.71
32.80
14.57
-2.24
HO
SiMe3
Me
4.6a
13C {1H} NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


HO
SiMe3
Me
4.6a
29Si NMR, 99 MHz, CDCl3
2.13
2.07
1.17
1.00
1.12
1.25
1.23
3.26
1.03
9.41
f1 (ppm)


HO
SiMe3
Me
4.6a'
1H NMR, 500 MHz, CDCl3
7.26 cdcl3
2.27
3.16
1.00
1.09
1.29
1.25
3.19
1.07
9.28
f1 (ppm)

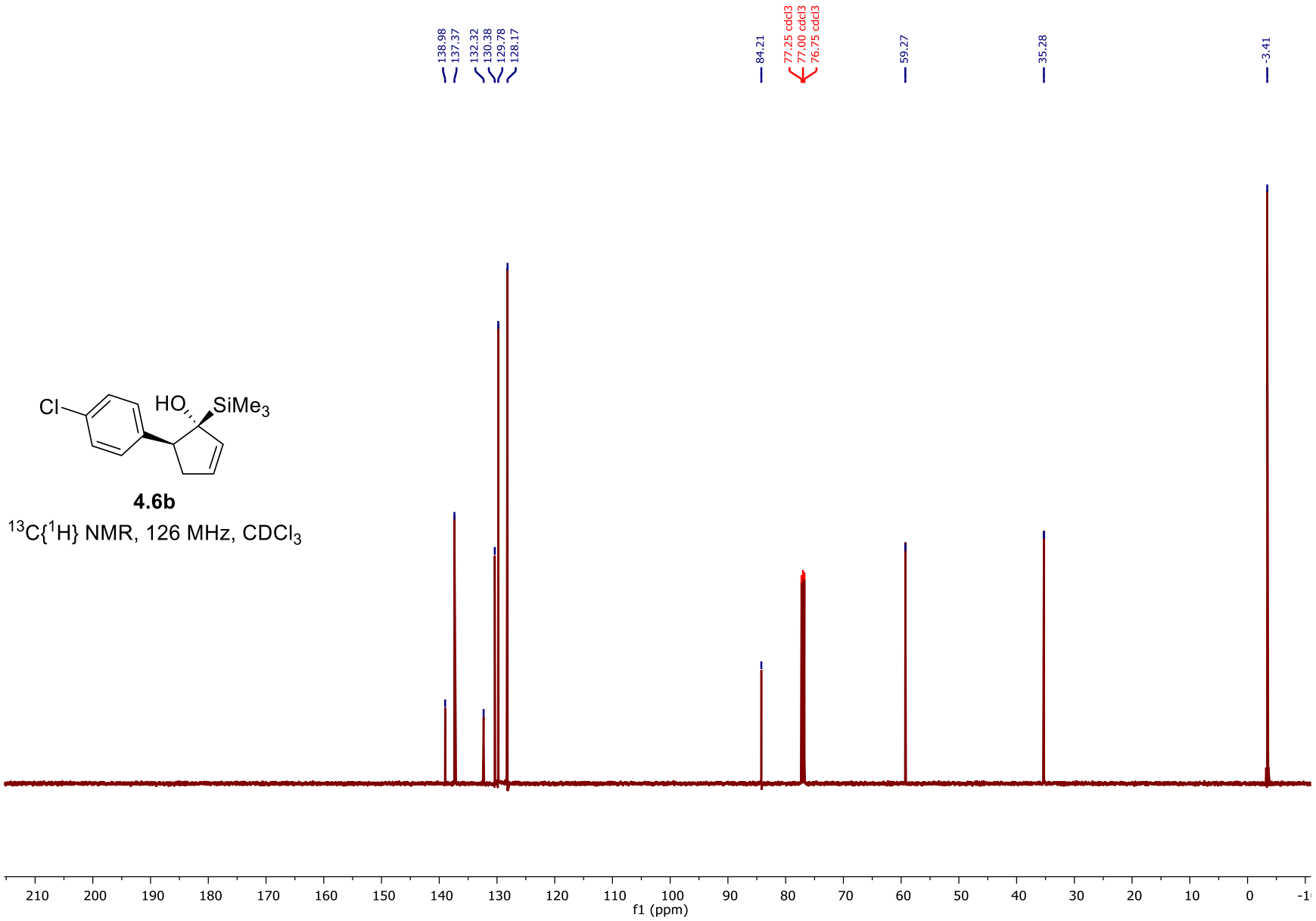

144.20
141.54
128.63
128.53
126.78
123.56
81.60
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
51.00
38.57
14.34
-3.24
HO
SiMe3
Me
4.6a'
13C {1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

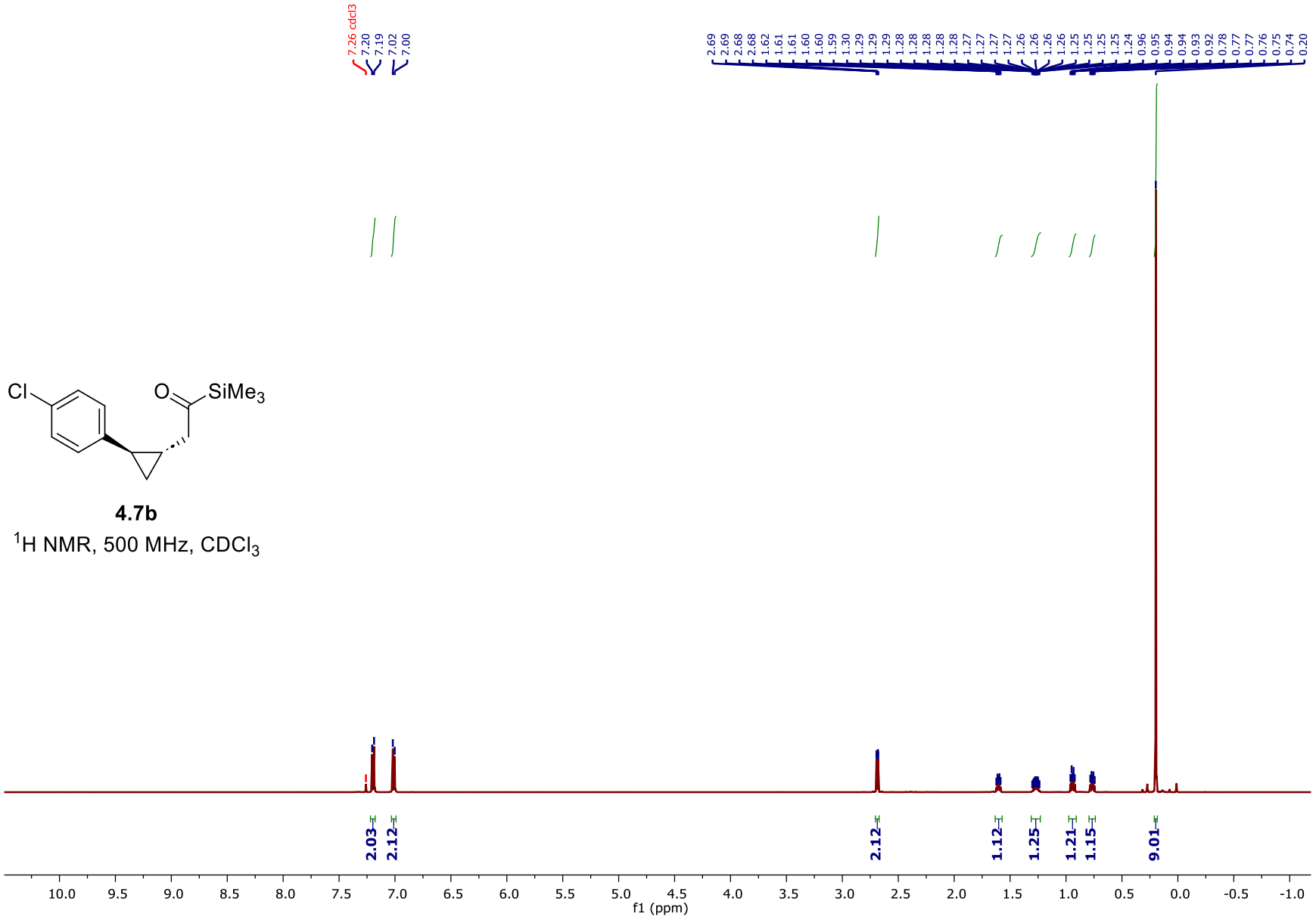

144.20
141.54
128.63
128.53
126.78
123.56
81.60
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
51.00
38.57
14.34
-3.24
HO
SiMe3
Me
4.6a'
29Si NMR, 99 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



4.6b

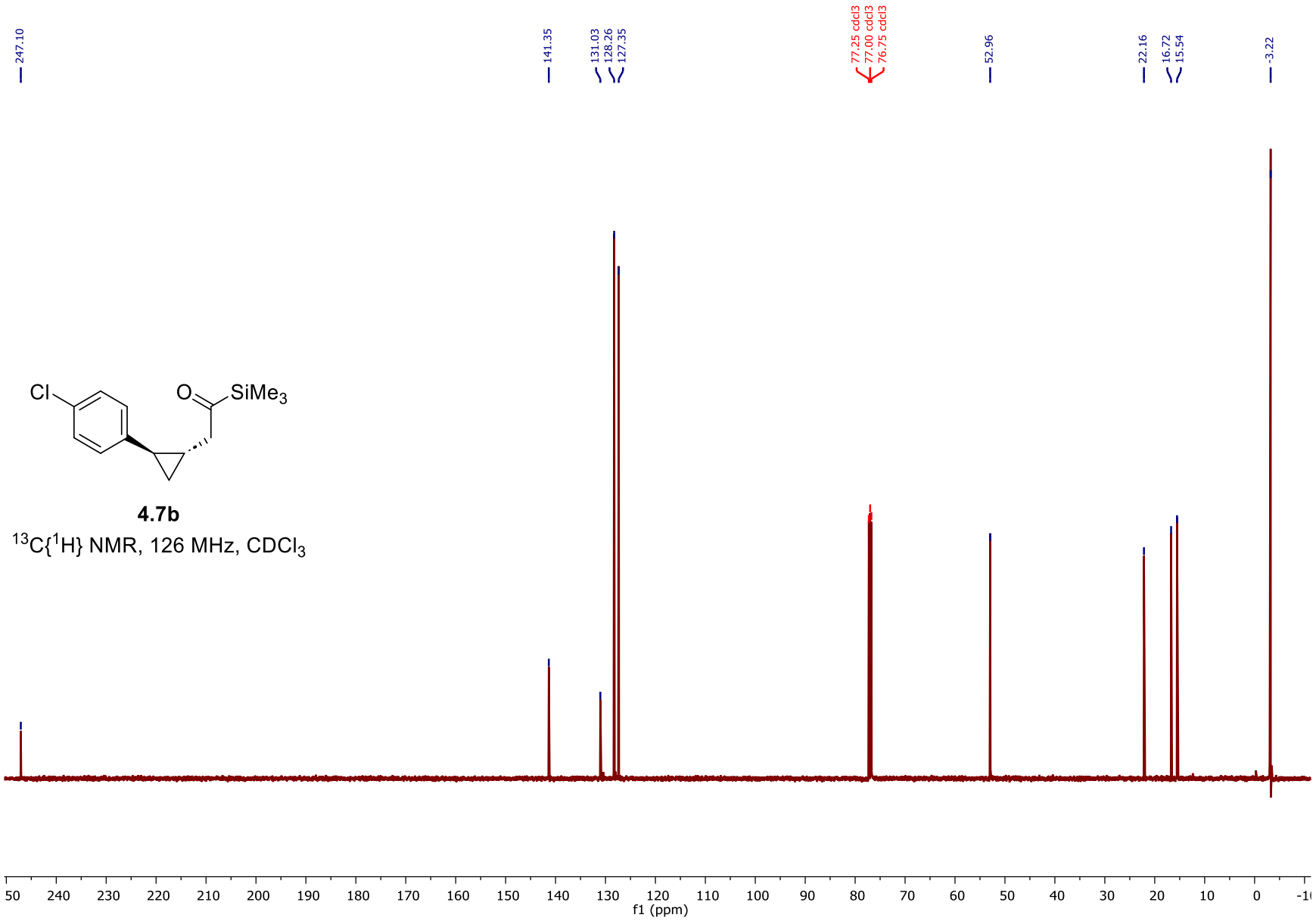
^{1}H NMR, 500 MHz, $CDCl_3$

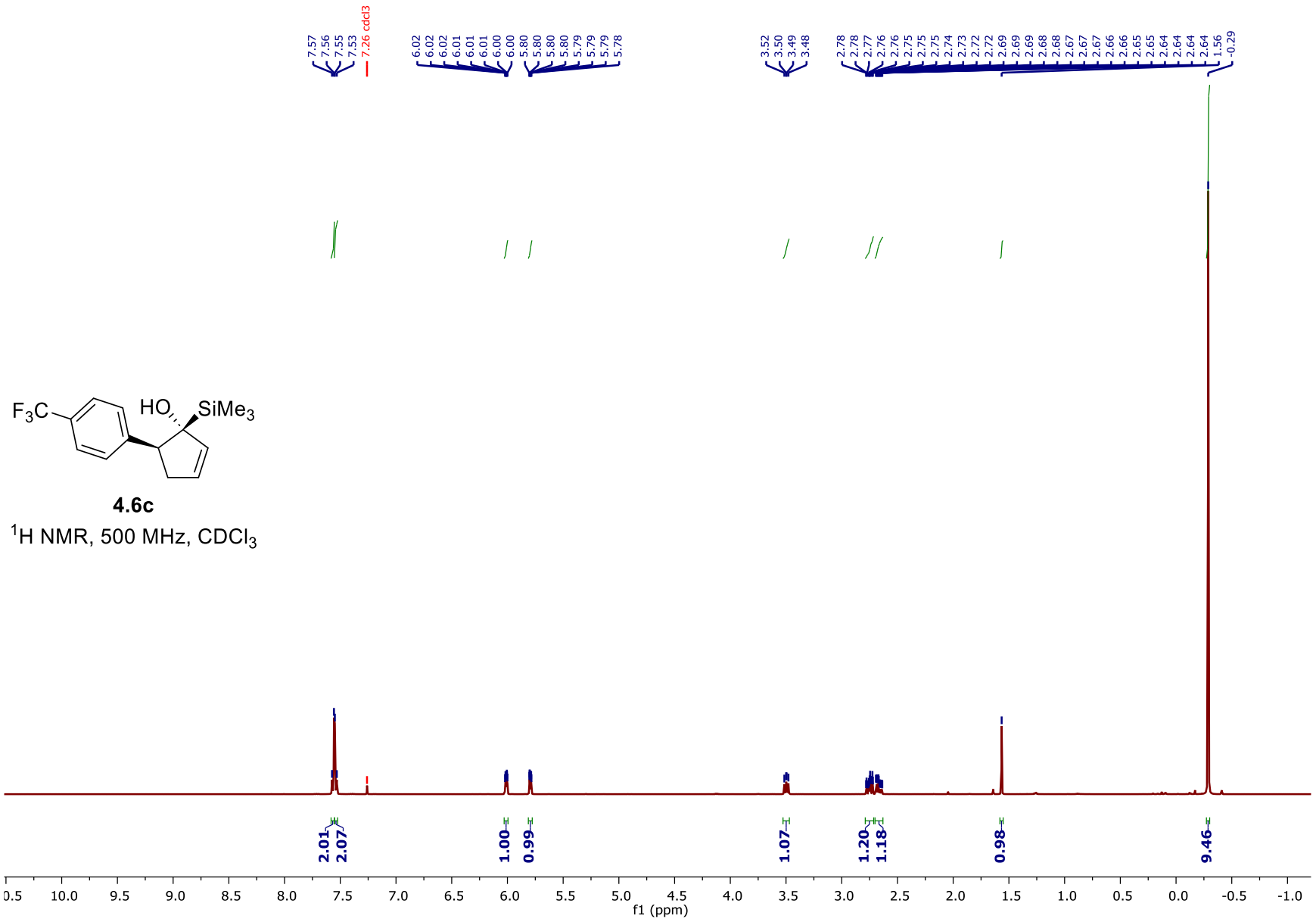

138.98
137.37
132.32
130.38
129.78
128.17
84.21
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
59.27
35.28
-3.41
Cl
HO
SiMe3
4.6b
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4.7b

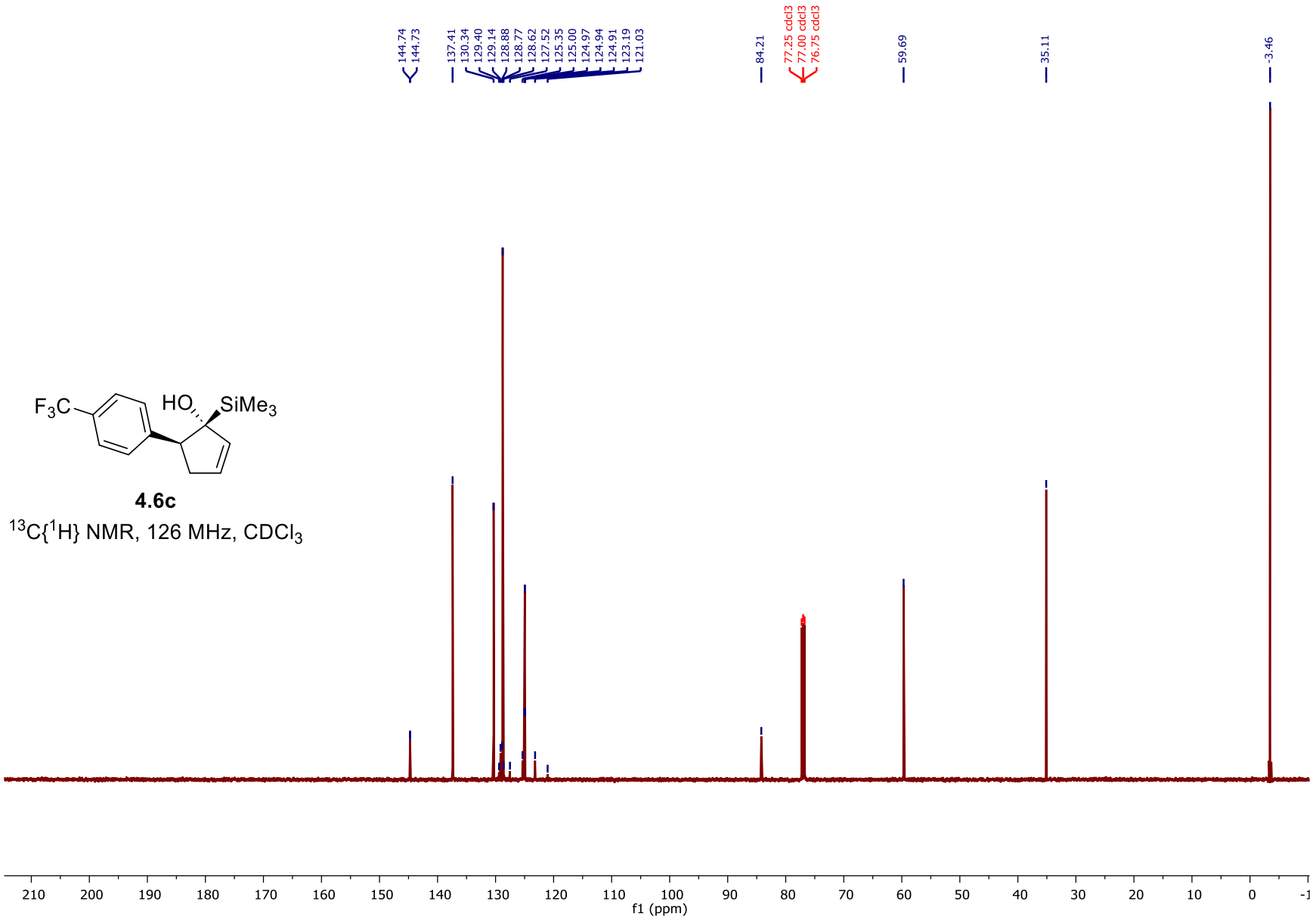
^{1}H NMR, 500 MHz, $CDCl_3$

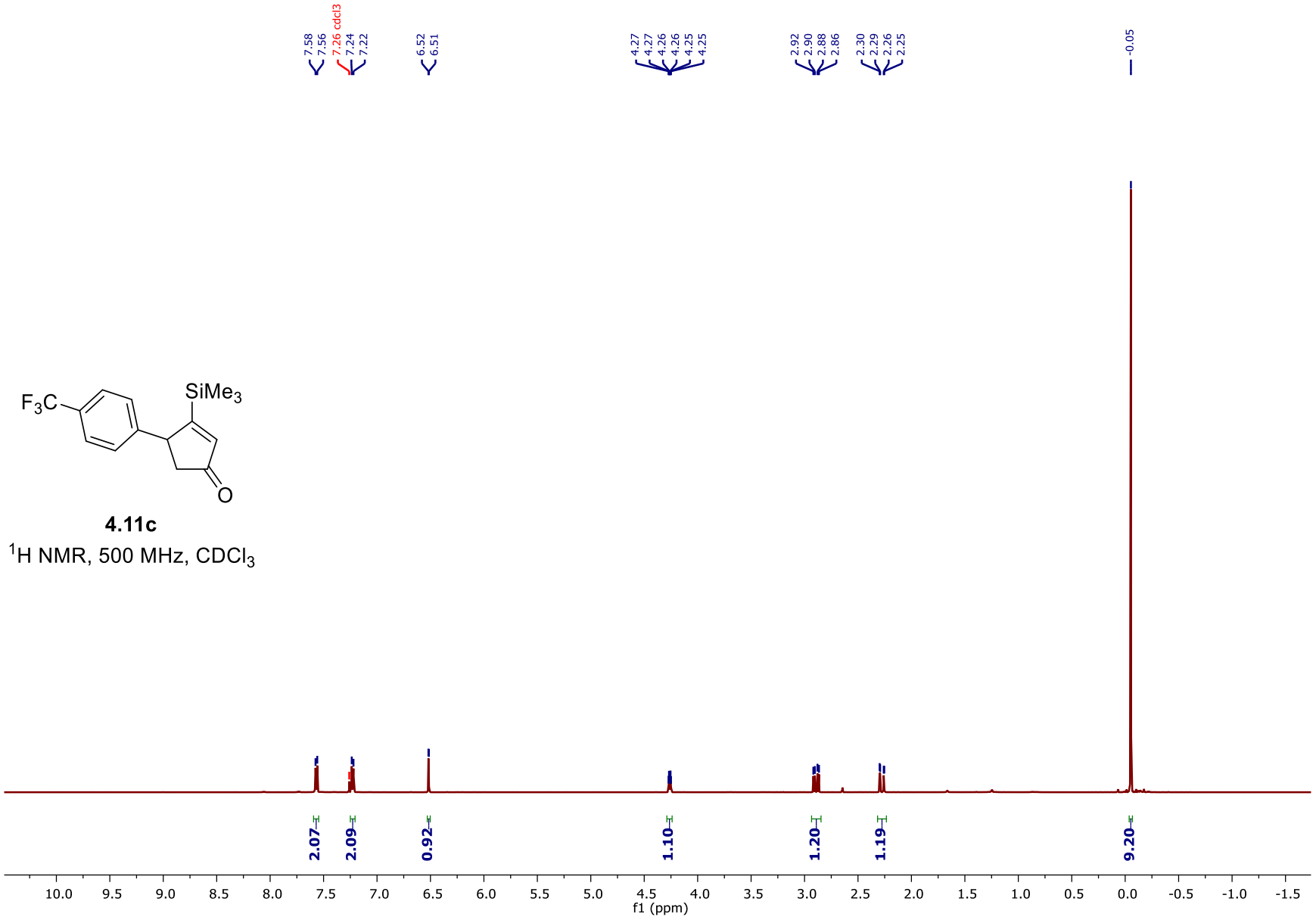

247.10
141.35
131.03
128.26
127.35
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
52.96
22.16
16.72
15.54
-3.22
Cl
O
SiMe3
4.7b
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)



4.6c

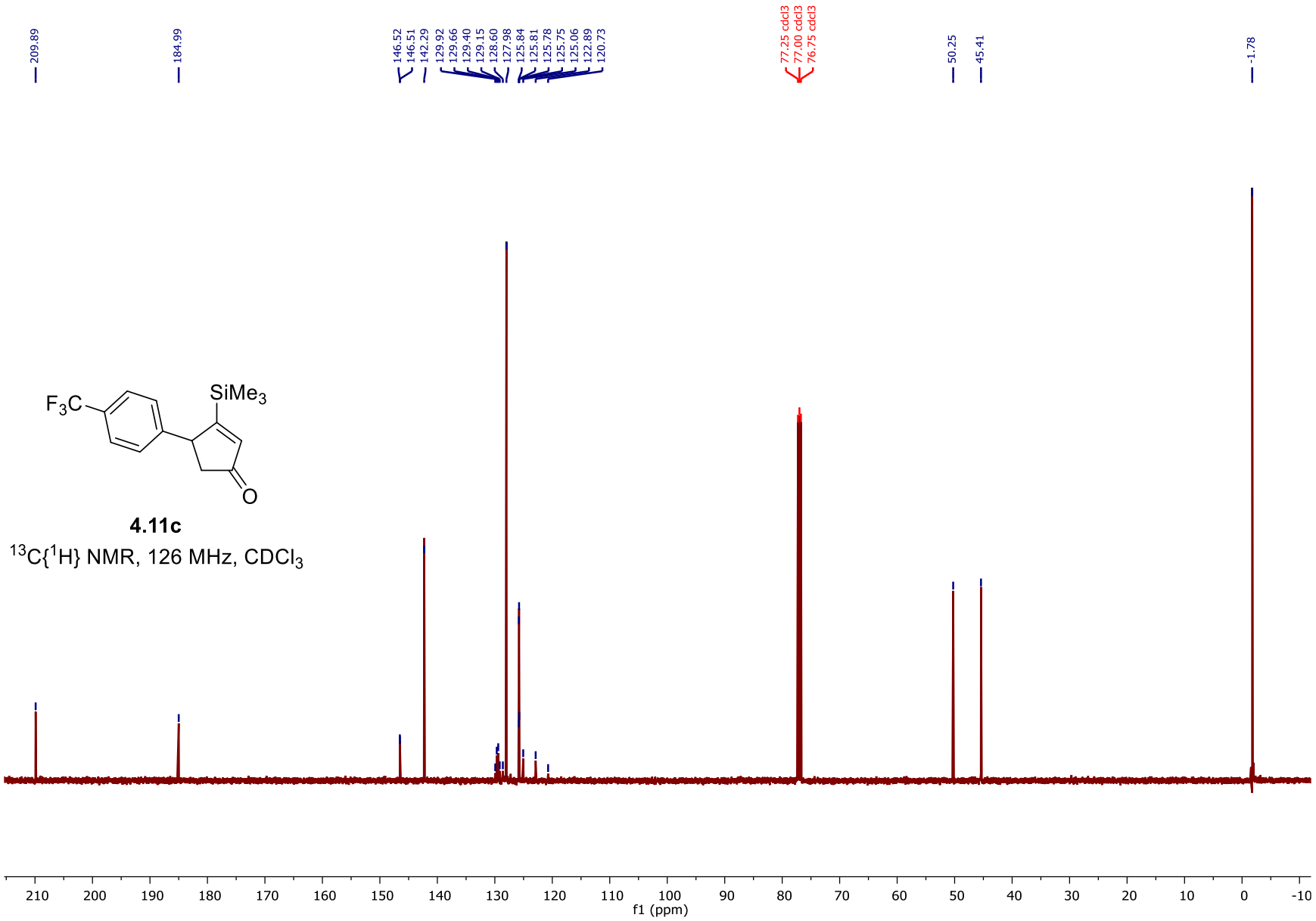
^{1}H NMR, 500 MHz, $CDCl_3$

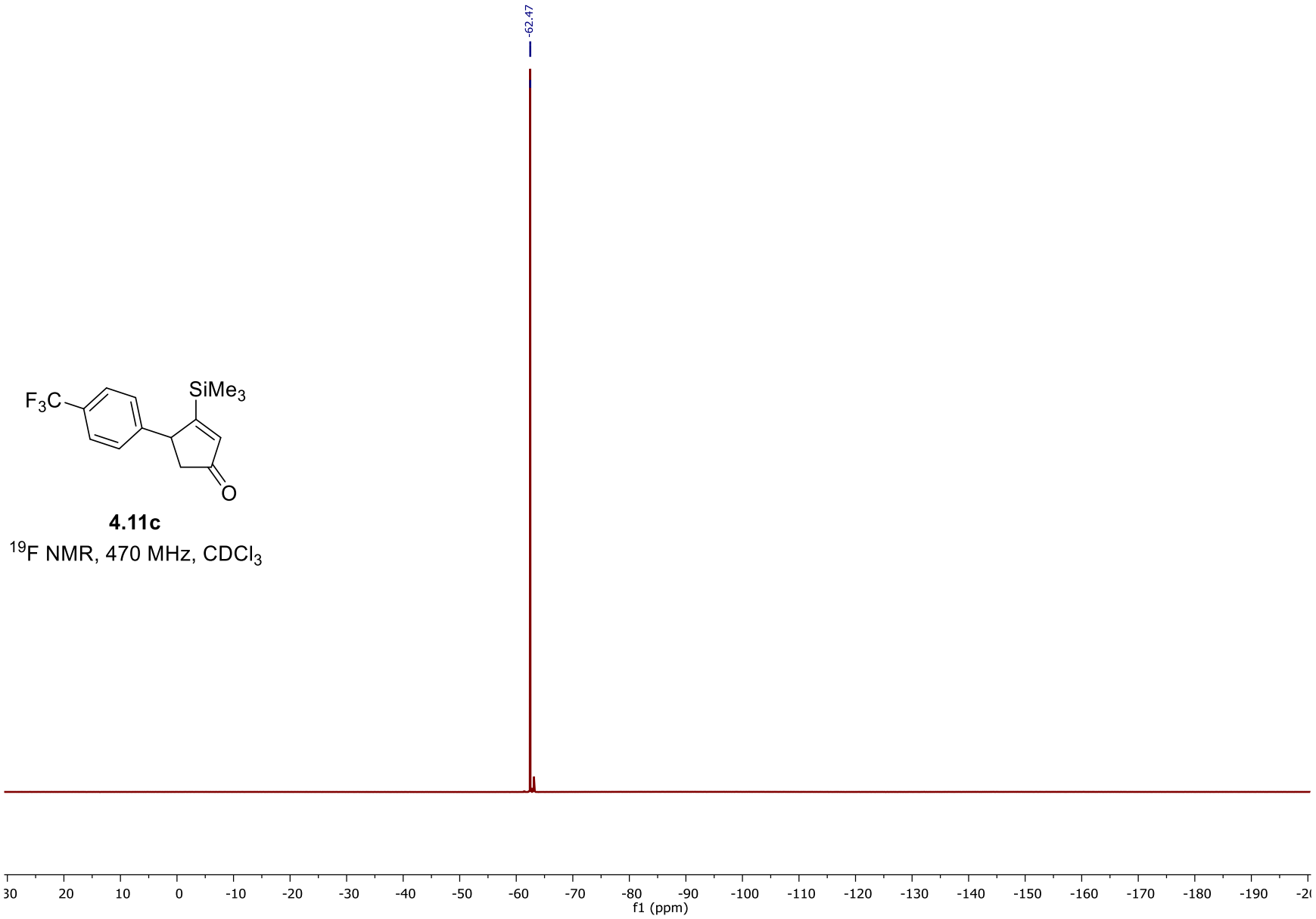

144.74
144.73
137.41
130.34
129.40
129.14
128.88
128.77
128.62
127.52
125.35
125.00
124.97
124.94
124.91
123.19
121.03
84.21
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
59.69
35.11
-3.46
F3C
HO
SiMe3
4.6c
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



4.11c

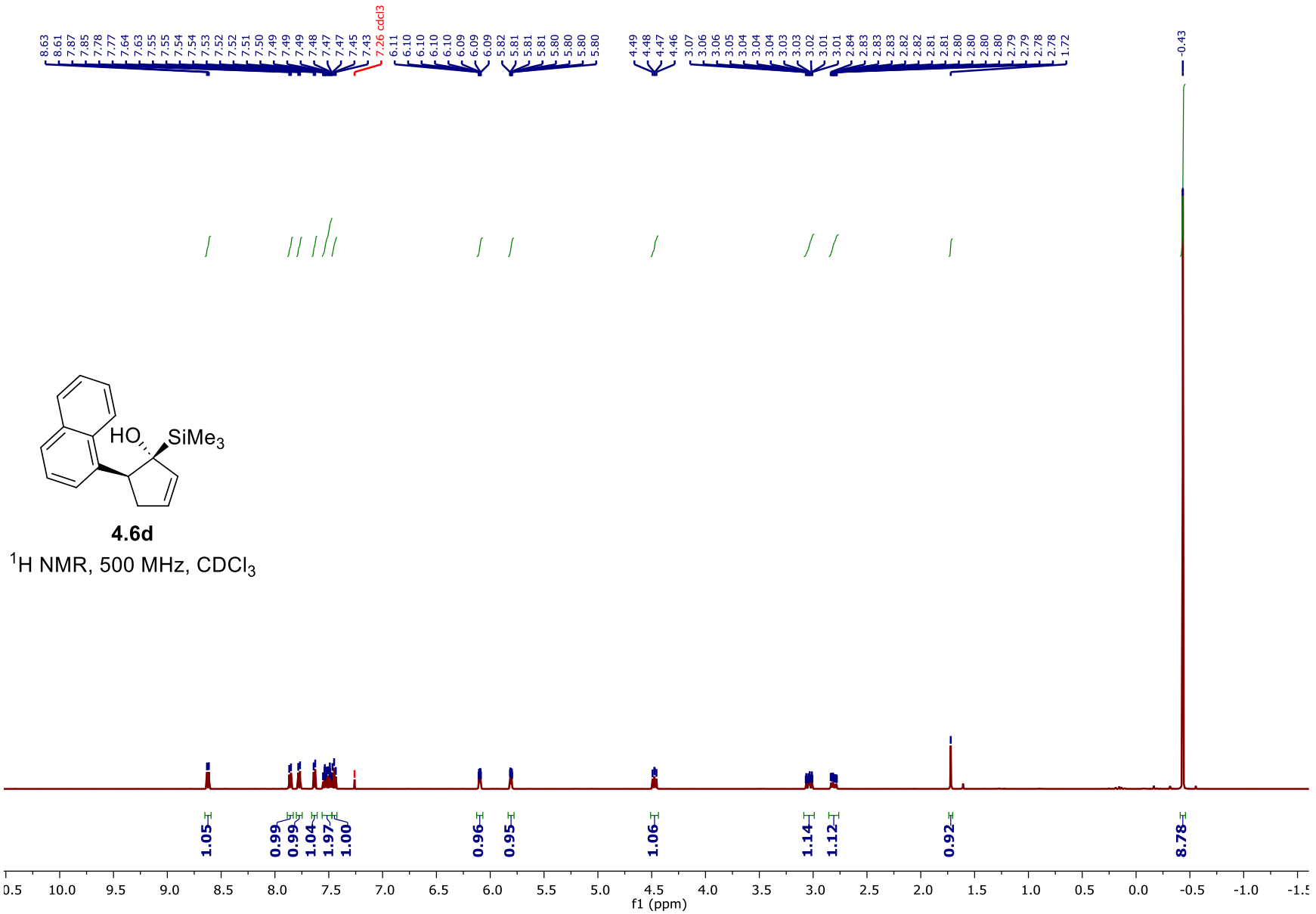
^{1}H NMR, 500 MHz, $CDCl_3$

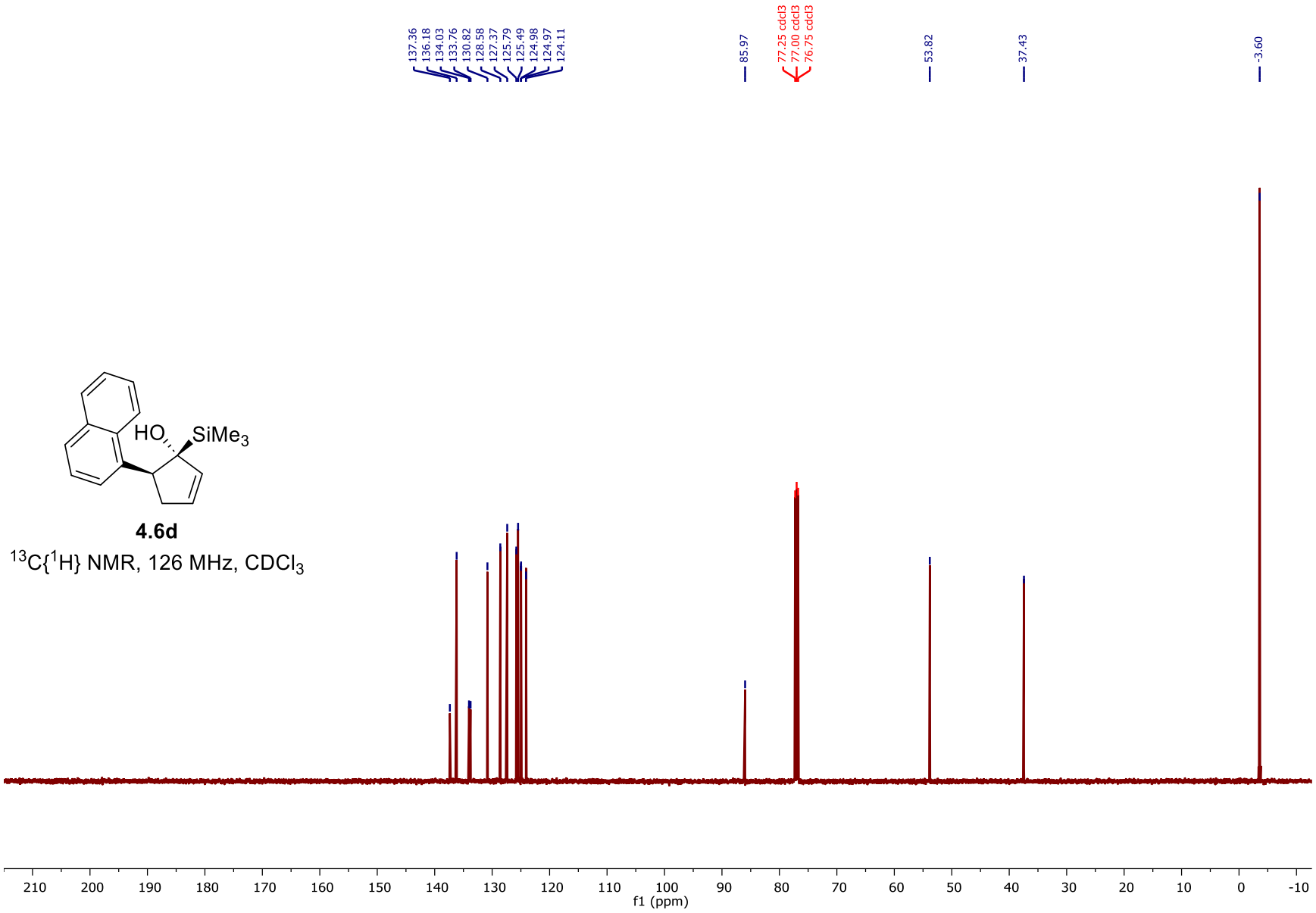

209.89
184.99
146.52
146.51
142.29
129.92
129.66
129.40
129.15
128.60
127.98
125.84
125.81
125.78
125.75
125.06
122.89
120.73
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
50.25
45.41
-1.78
F3C
SiMe3
O
4.11c
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

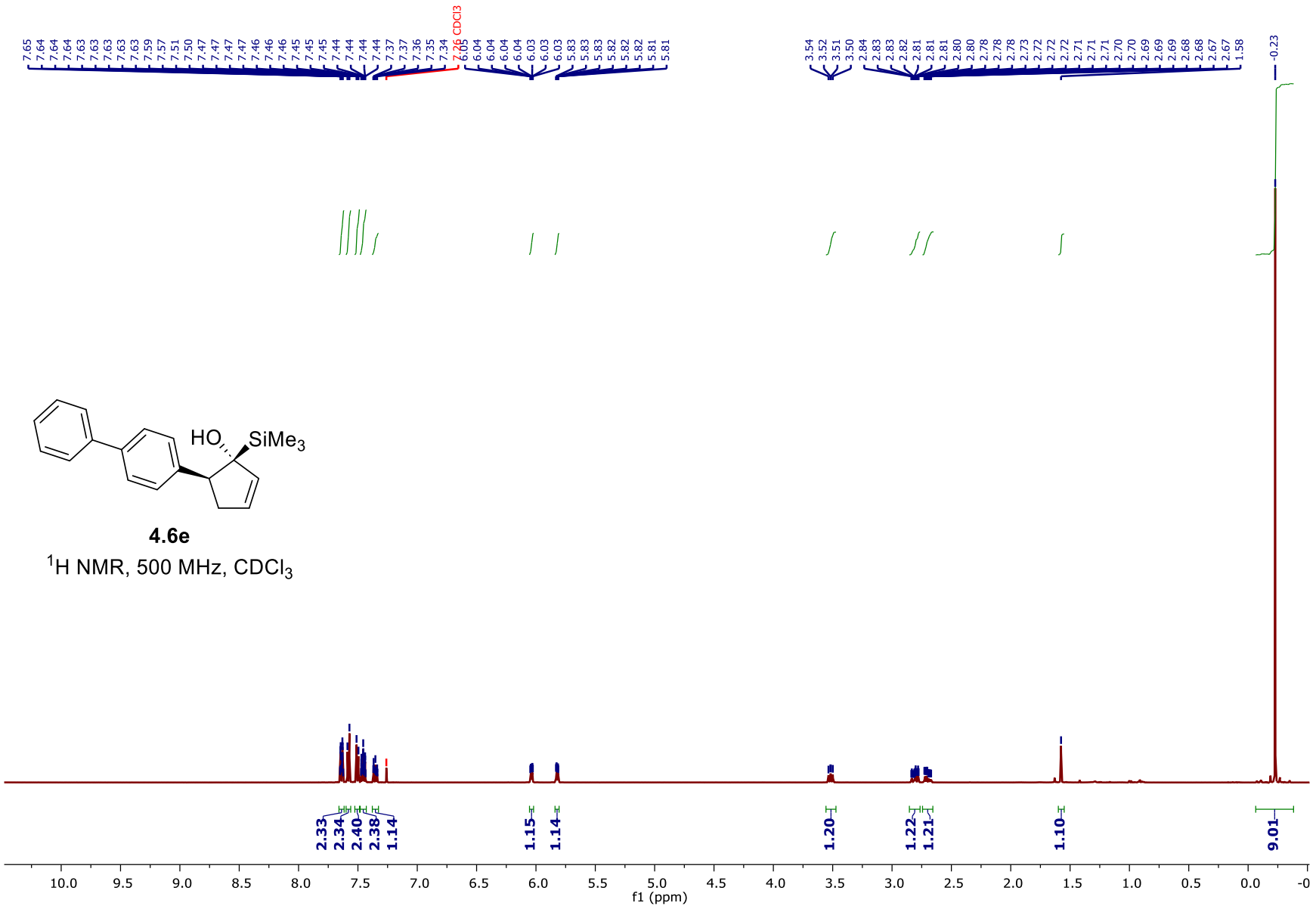


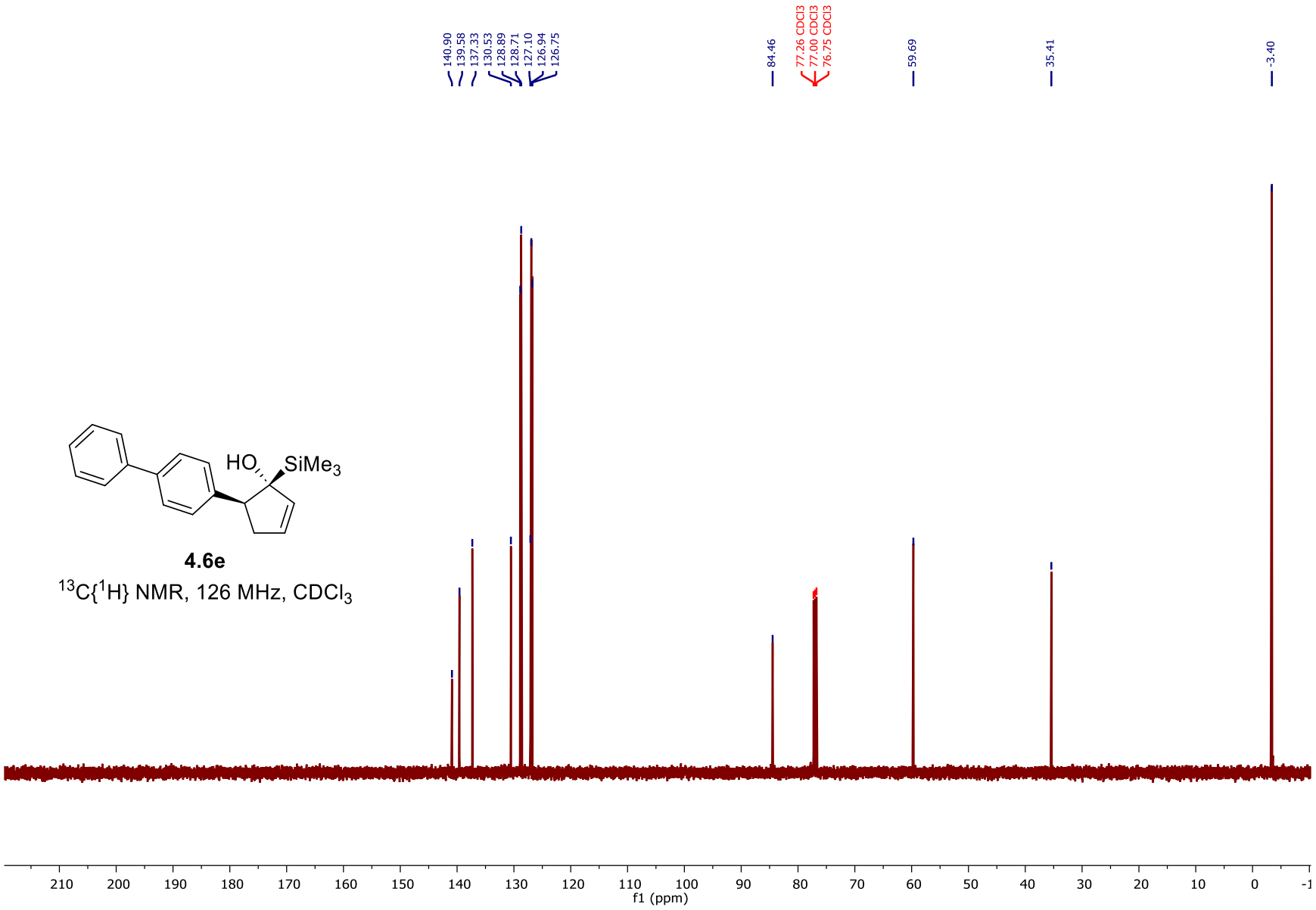
4.11c

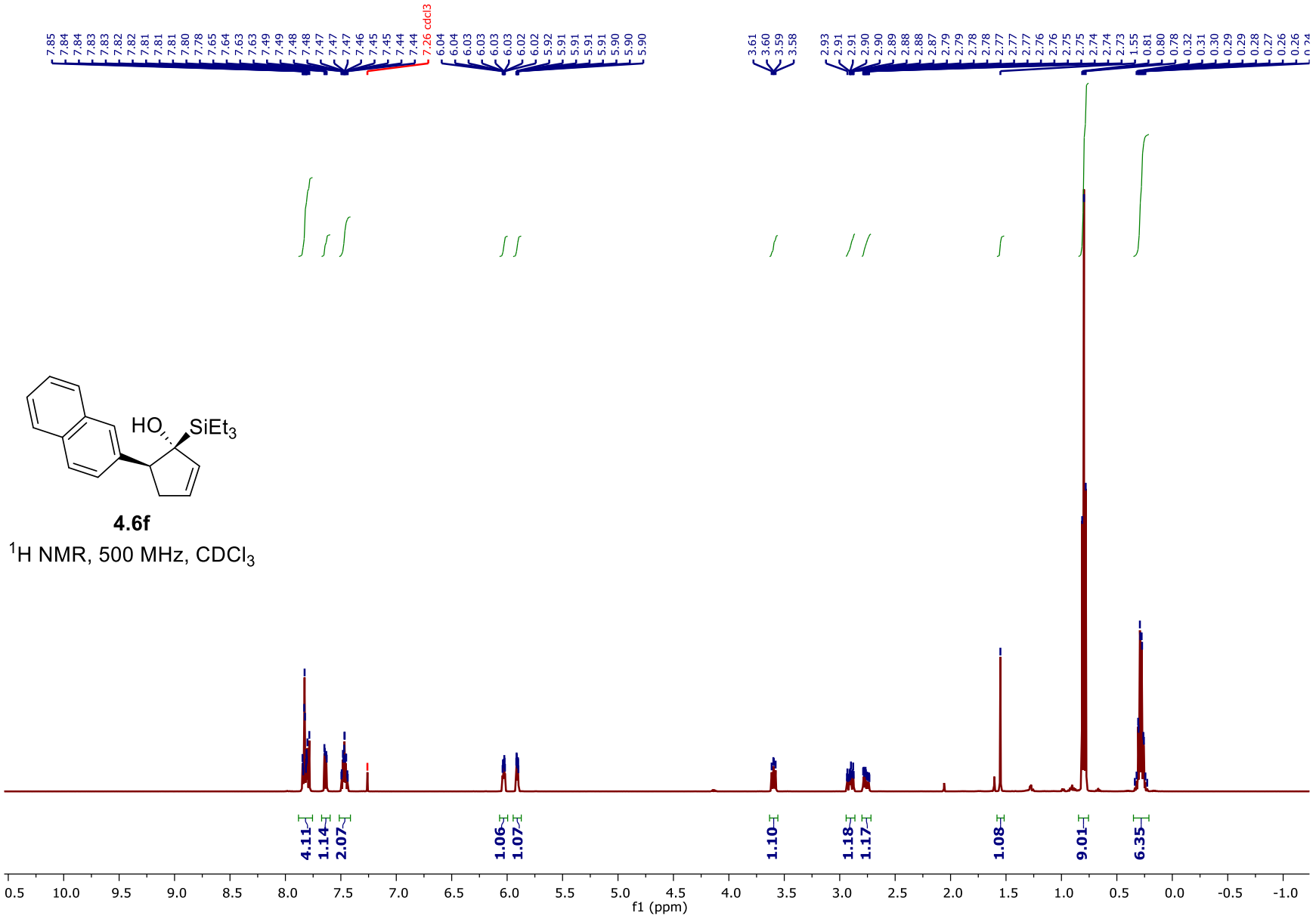
^{19}F NMR, 470 MHz, $CDCl_3$

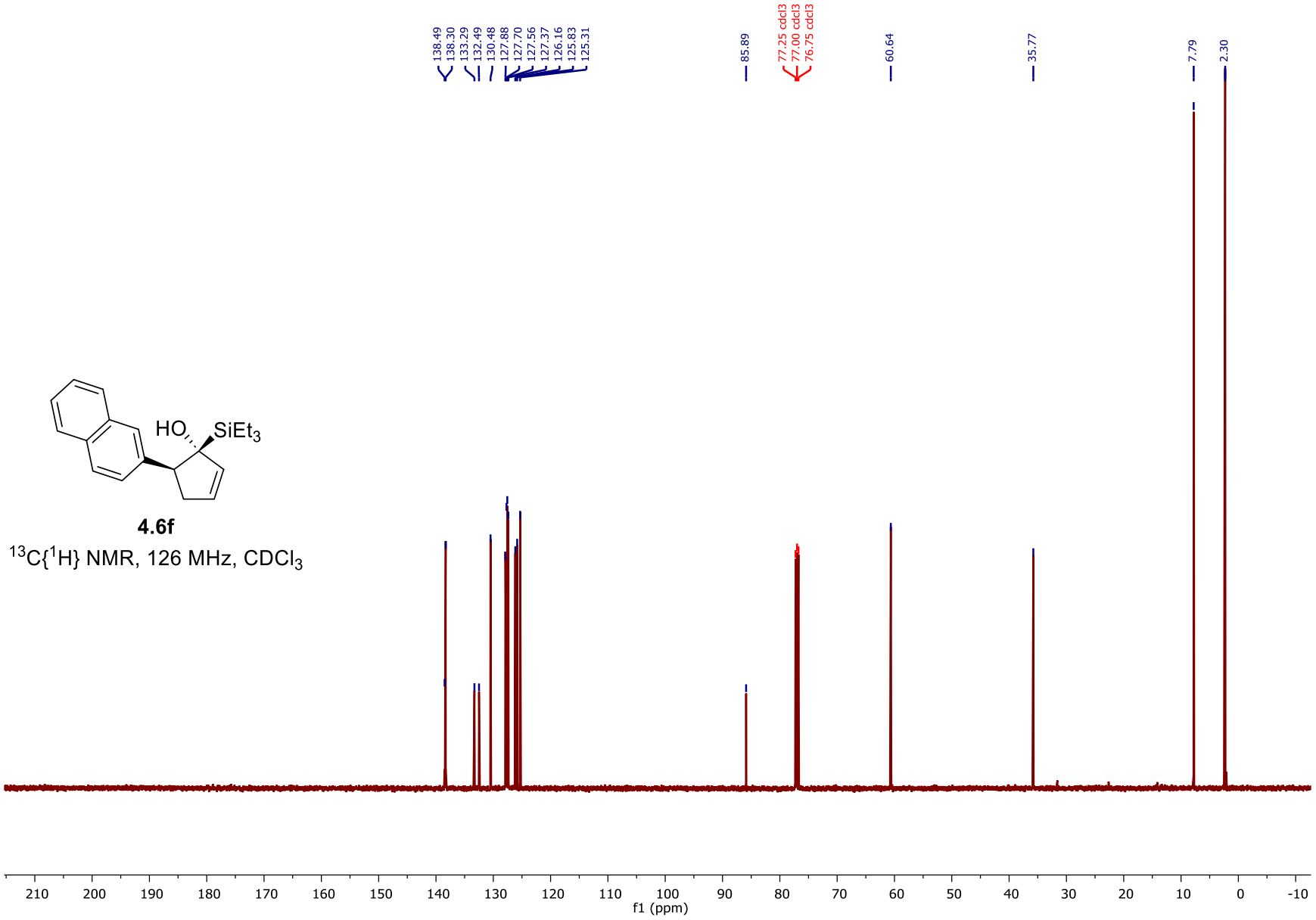

8.63 8.61 7.87 7.85 7.78 7.77 7.64 7.63 7.55 7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.50 7.49 7.49 7.49 7.48 7.47 7.47 7.45 7.43 7.26 cdcl3
6.11 6.10 6.10 6.10 6.09 6.09 6.09 5.82 5.81 5.81 5.81 5.80 5.80 5.80 5.80
4.49 4.48 4.47 4.46
3.07 3.06 3.06 3.05 3.04 3.04 3.04 3.03 3.03 3.02 3.01 3.01 2.84 2.83 2.83 2.83 2.82 2.82 2.81 2.81 2.80 2.80 2.80 2.80 2.79 2.78 2.78 1.72
-0.43
HO
SiMe3
4.6d
1H NMR, 500 MHz, CDCl3
1.05 0.99 0.99 1.04 1.97 1.00 0.96 0.95 1.06 1.14 1.12 0.92 8.78
f1 (ppm)

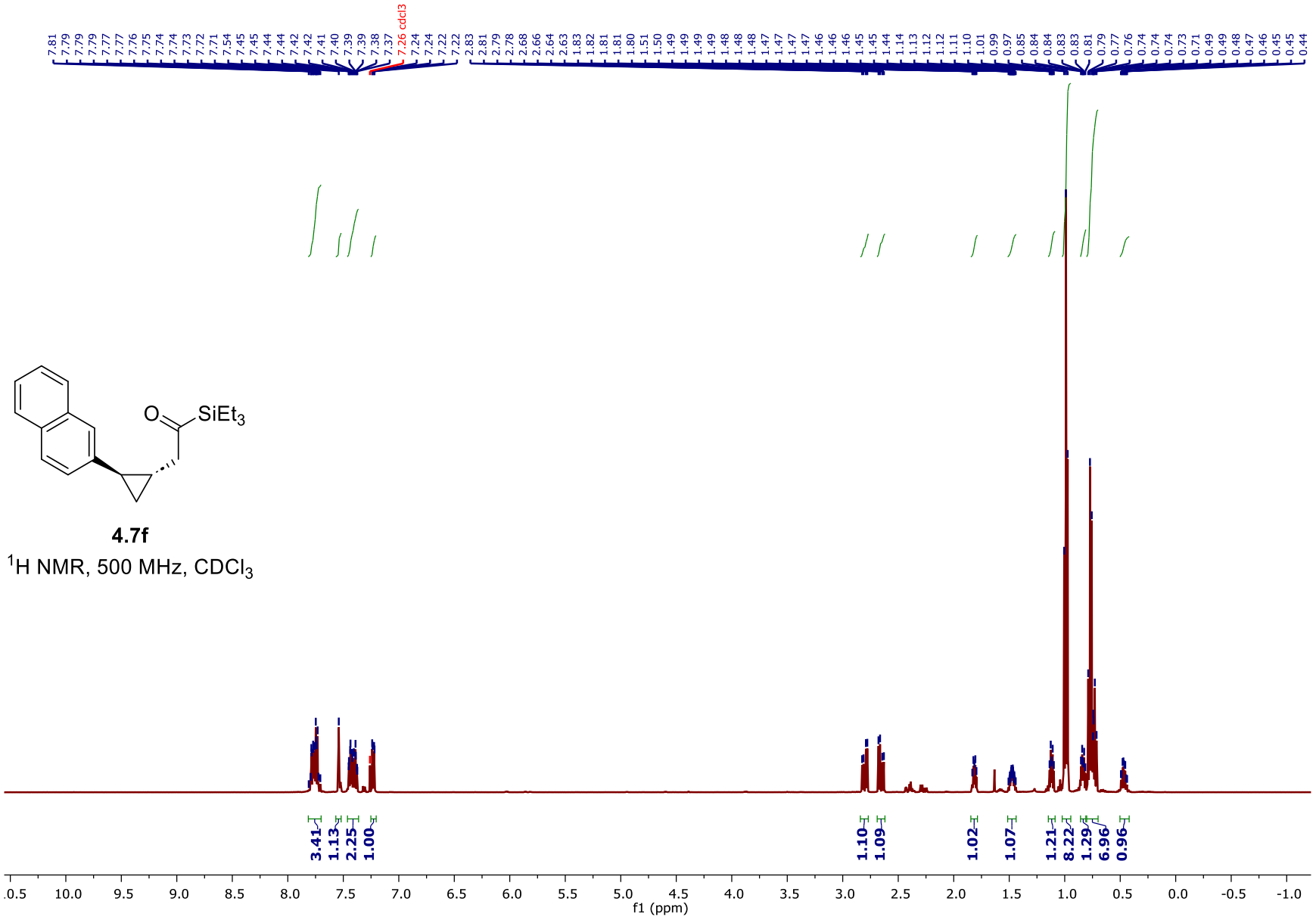

137.36
136.18
134.03
133.76
130.82
128.58
127.37
125.79
125.49
124.98
124.97
124.11
85.97
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
53.82
37.43
-3.60
HO
SiMe3
4.6d
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
SiMe3
4.6e
1H NMR, 500 MHz, CDCl3
CDCl3
f1 (ppm)


140.90
139.58
137.33
130.53
128.89
128.71
127.10
126.94
126.75
84.46
77.26 CDCl3
77.00 CDCl3
76.75 CDCl3
59.69
35.41
-3.40
HO
SiMe3
4.6e
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

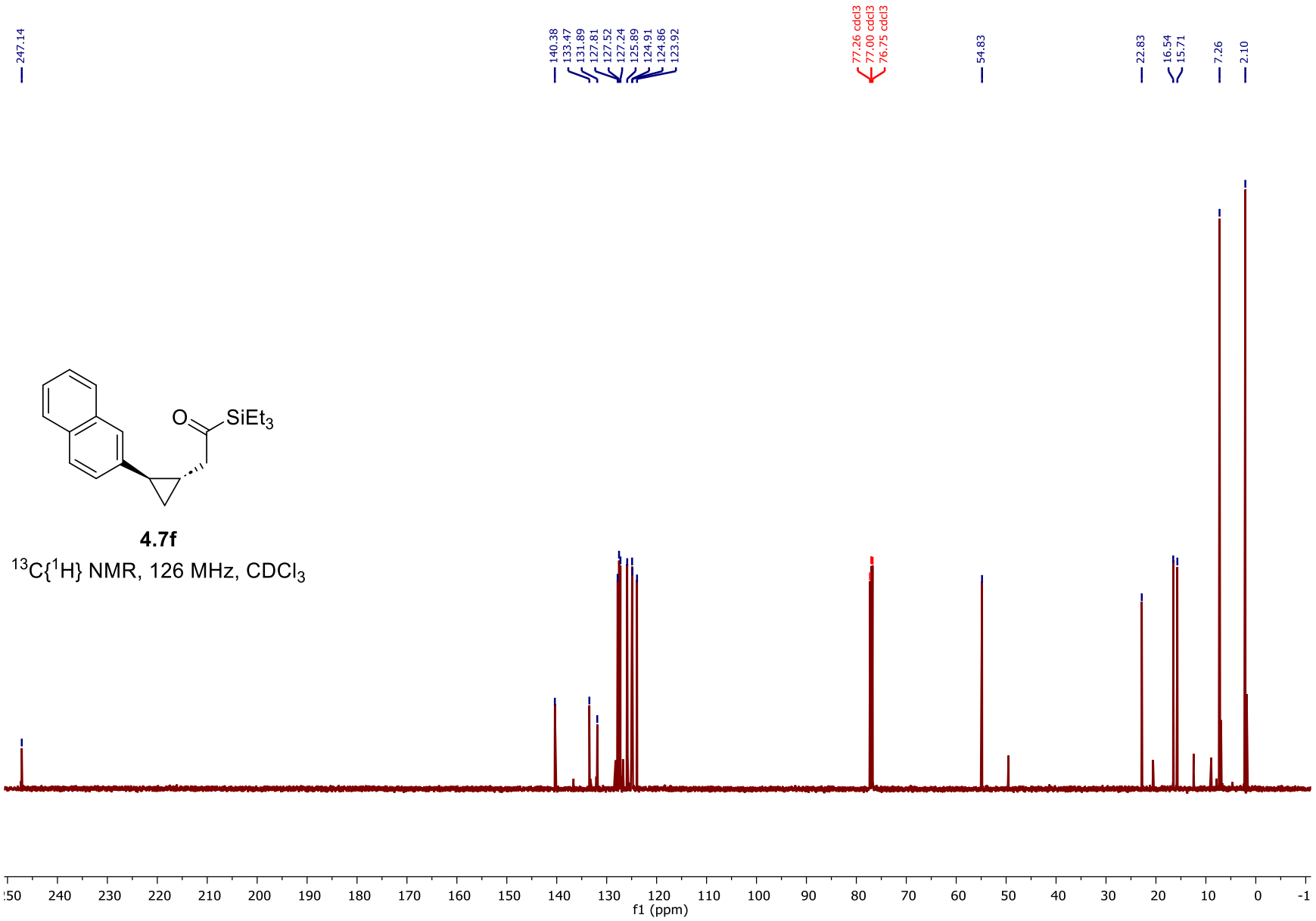

HO
SiEt3
4.6f
1H NMR, 500 MHz, CDCl3
7.26 cdcl3
4.11
1.14
2.07
1.06
1.07
1.10
1.18
1.17
1.08
9.01
6.35
f1 (ppm)

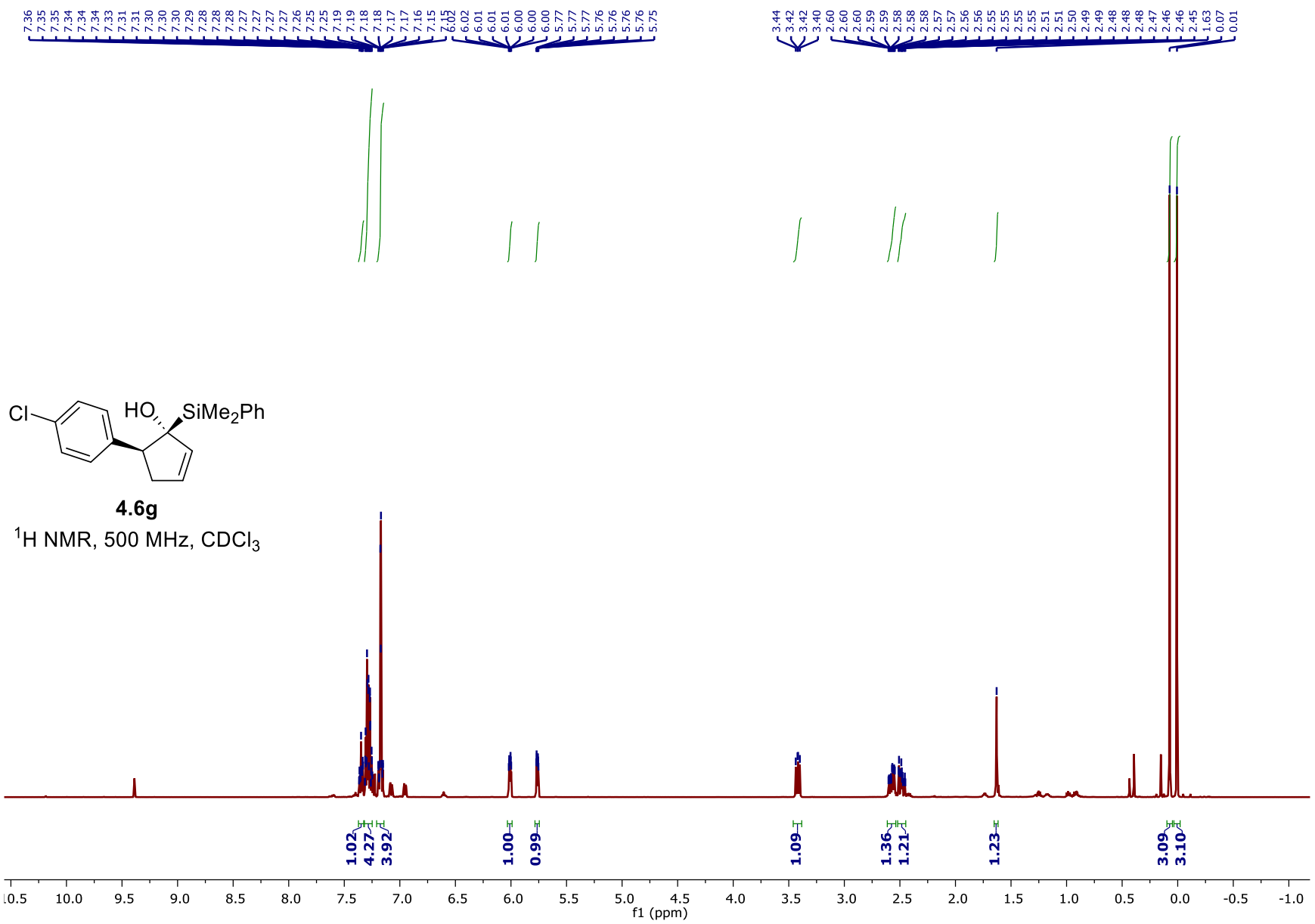

138.49
138.30
133.29
132.49
130.48
127.88
127.70
127.56
127.37
126.16
125.83
125.31
85.89
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
60.64
35.77
7.79
2.30
HO
SiEt3
4.6f
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

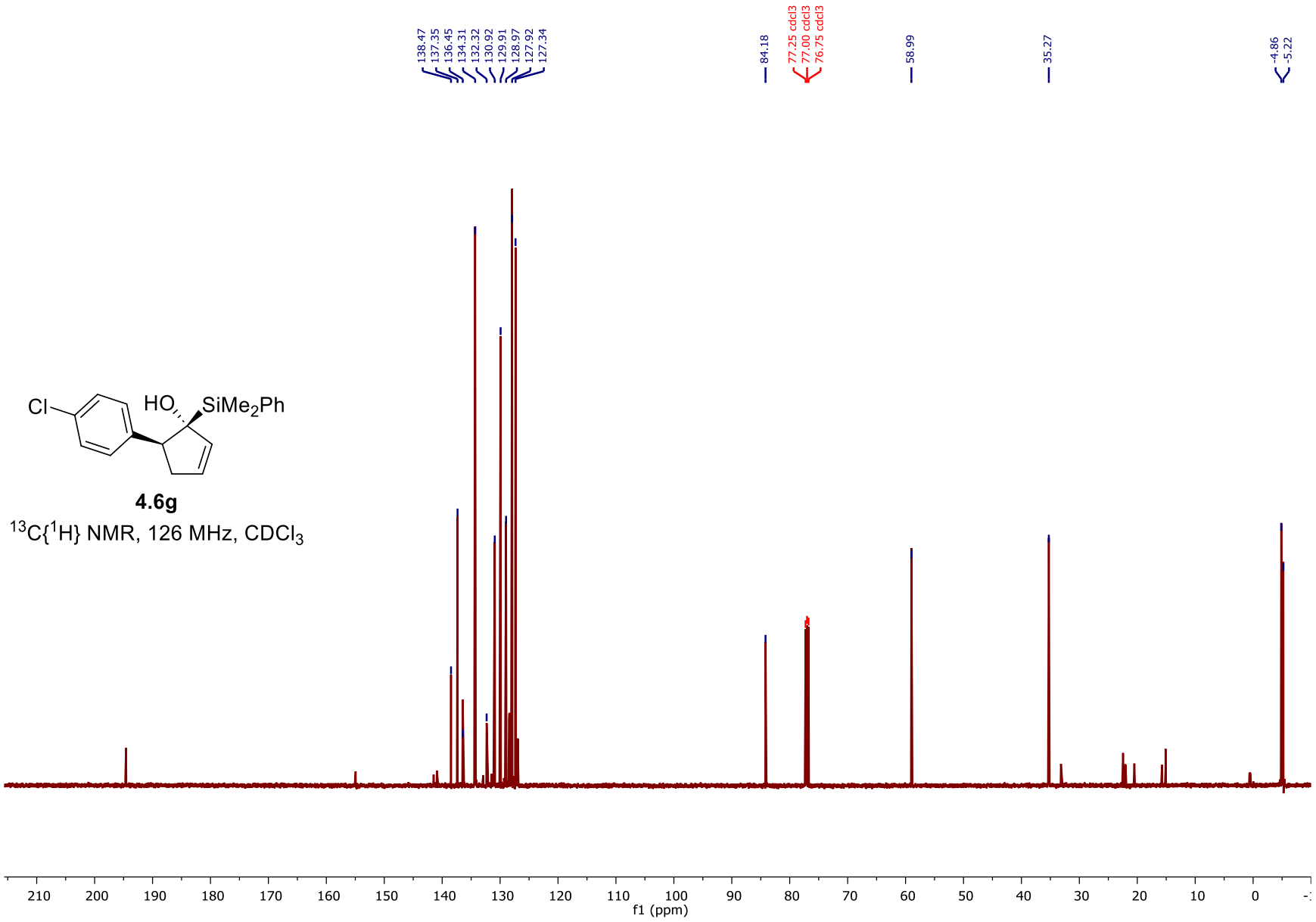


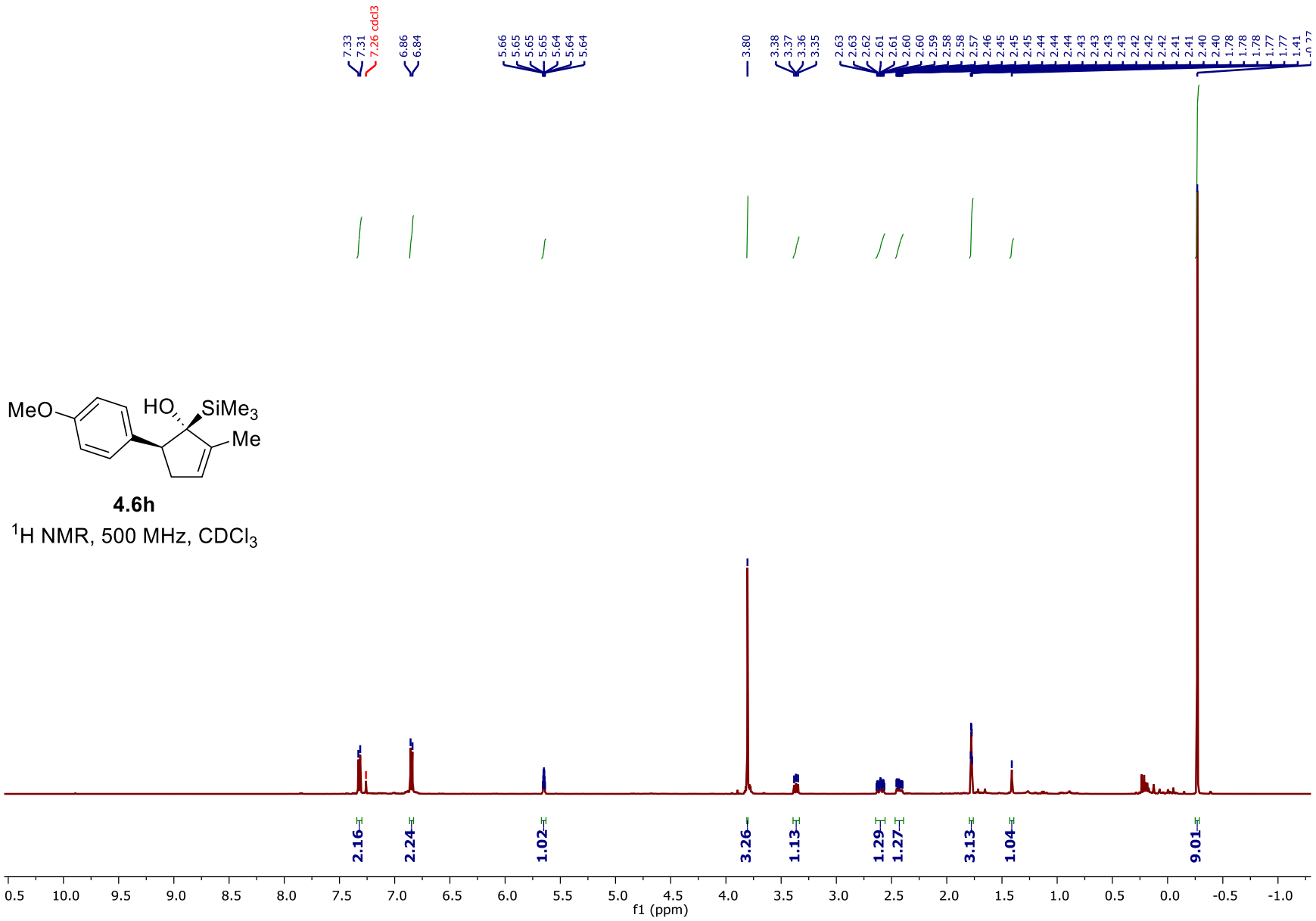
4.7f

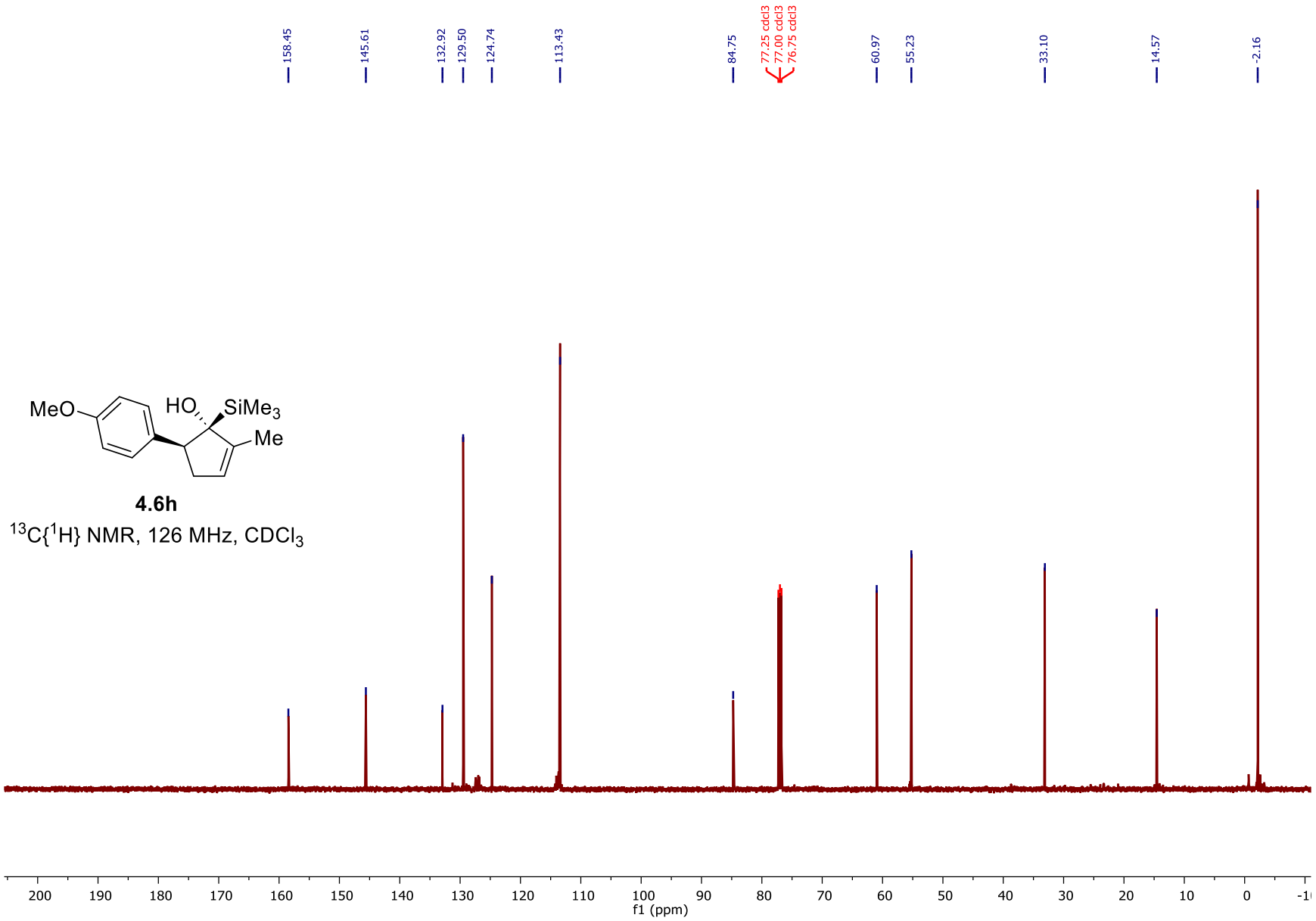
^{1}H NMR, 500 MHz, $CDCl_3$

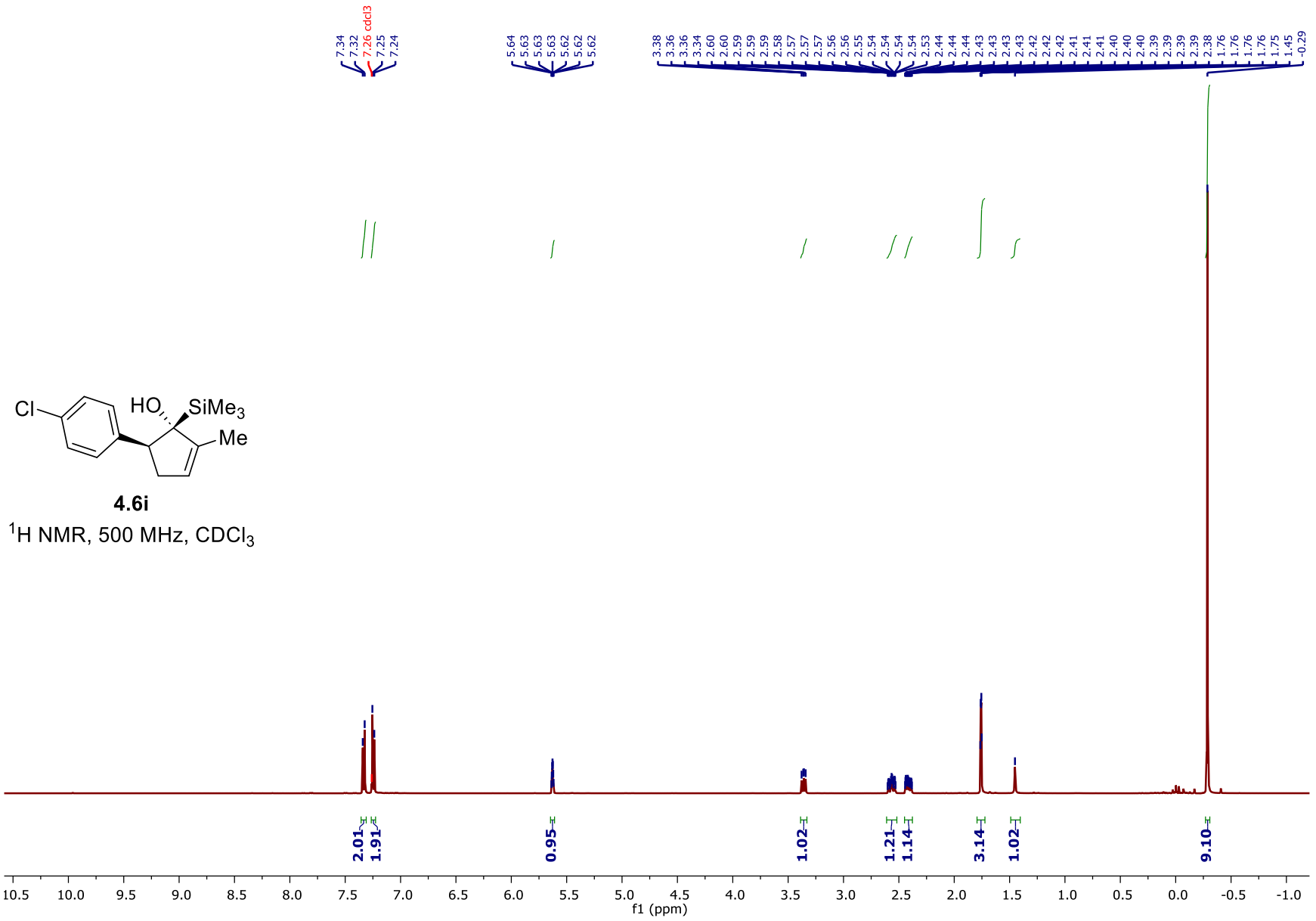

247.14
140.38
133.47
131.89
127.81
127.52
127.24
125.89
124.91
124.86
123.92
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
54.83
22.83
16.54
15.71
7.26
2.10
O
SiEt3
4.7f
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)


7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.27 7.26 7.25 7.25 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.15 7.15 6.02 6.02 6.01 6.01 6.01 6.00 6.00 6.00 5.77 5.77 5.76 5.76 5.76 5.75
3.44 3.42 3.42 3.40 2.60 2.60 2.60 2.59 2.59 2.58 2.58 2.58 2.57 2.57 2.56 2.56 2.55 2.55 2.55 2.55 2.51 2.51 2.50 2.49 2.49 2.48 2.48 2.48 2.47 2.46 2.46 2.45 1.63 0.07 0.01
Cl
HO
SiMe2Ph
4.6g
1H NMR, 500 MHz, CDCl3
1.02
4.27
3.92
1.00
0.99
1.09
1.36
1.21
1.23
3.09
3.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


138.47
137.35
136.45
134.31
132.32
130.92
129.91
128.97
127.92
127.34
84.18
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
58.99
35.27
-4.86
-5.22
Cl
HO
SiMe2Ph
4.6g
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)

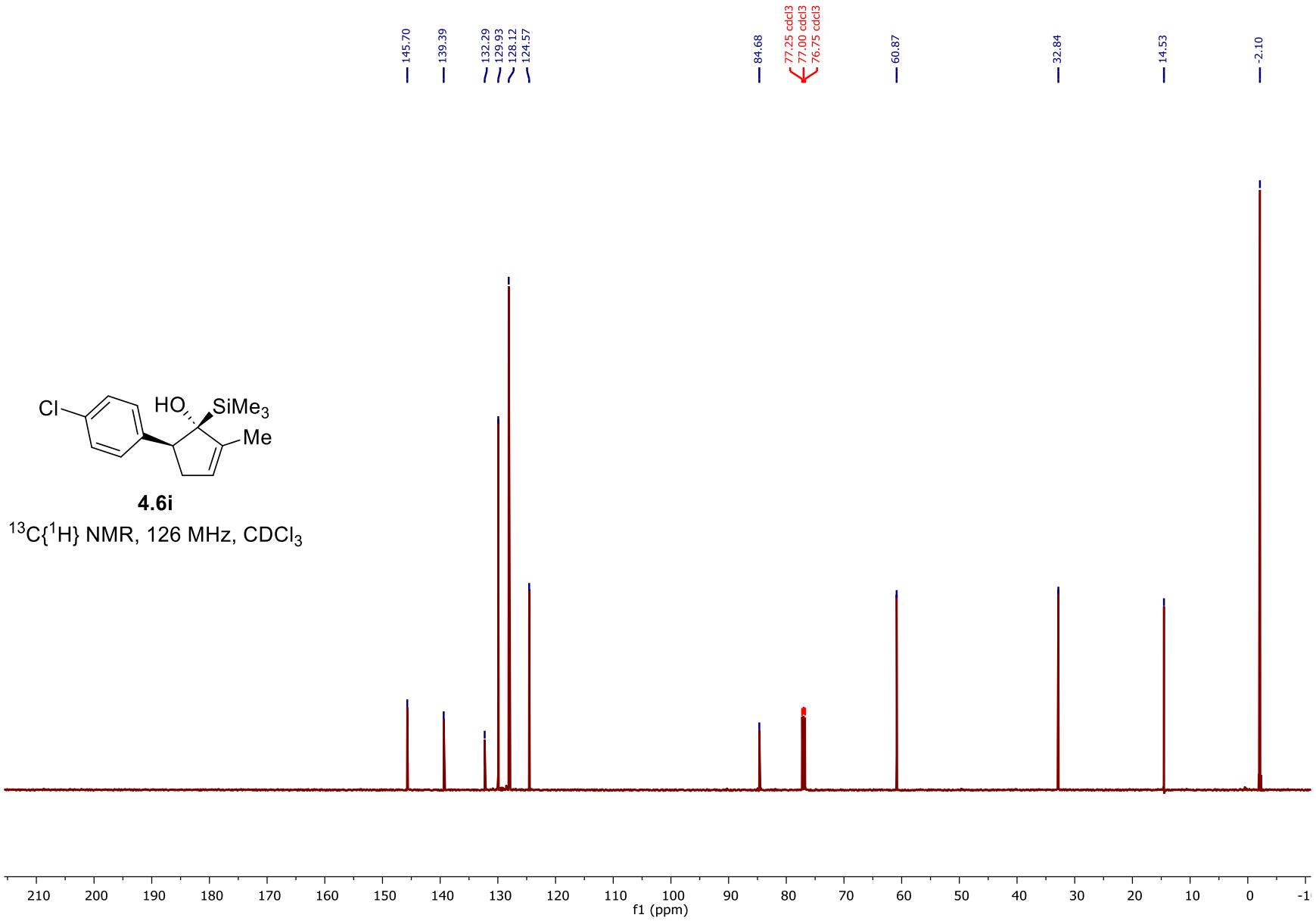

7.33
7.31
7.26 cdcl3
6.86
6.84
5.66
5.65
5.65
5.65
5.64
5.64
5.64
3.80
3.38
3.37
3.36
3.35
2.63
2.63
2.62
2.61
2.61
2.60
2.60
2.59
2.58
2.58
2.57
2.46
2.45
2.45
2.44
2.44
2.44
2.43
2.43
2.43
2.42
2.42
2.42
2.41
2.41
2.40
2.40
1.78
1.78
1.78
1.77
1.77
1.41
MeO
HO
SiMe3
Me
4.6h
1H NMR, 500 MHz, CDCl3
2.16
2.24
1.02
3.26
1.13
1.29
1.27
3.13
1.04
9.01
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

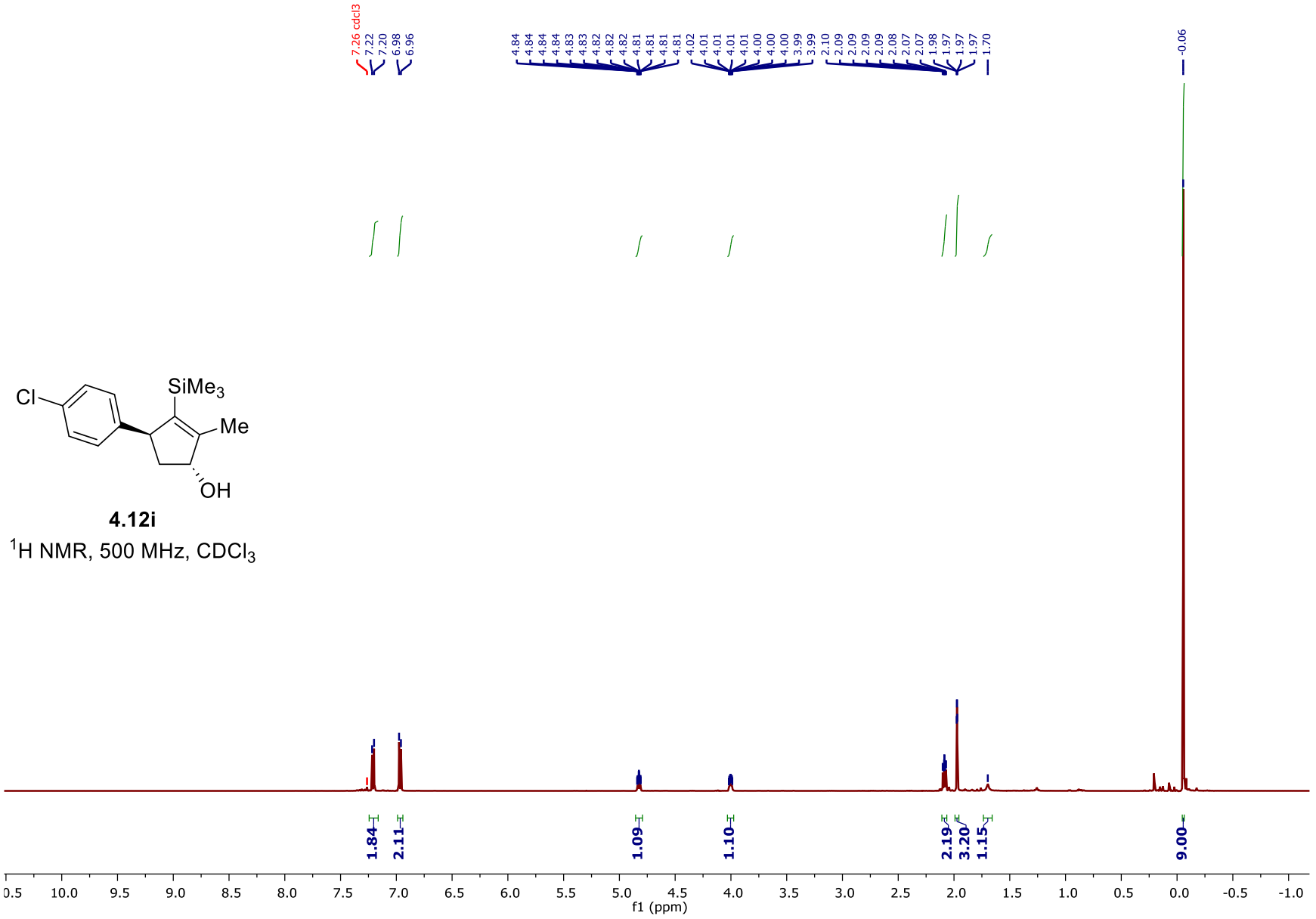

158.45
145.61
132.92
129.50
124.74
113.43
84.75
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
60.97
55.23
33.10
14.57
-2.16
MeO
HO
SiMe3
Me
4.6h
13C{1H} NMR, 126 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4.6i

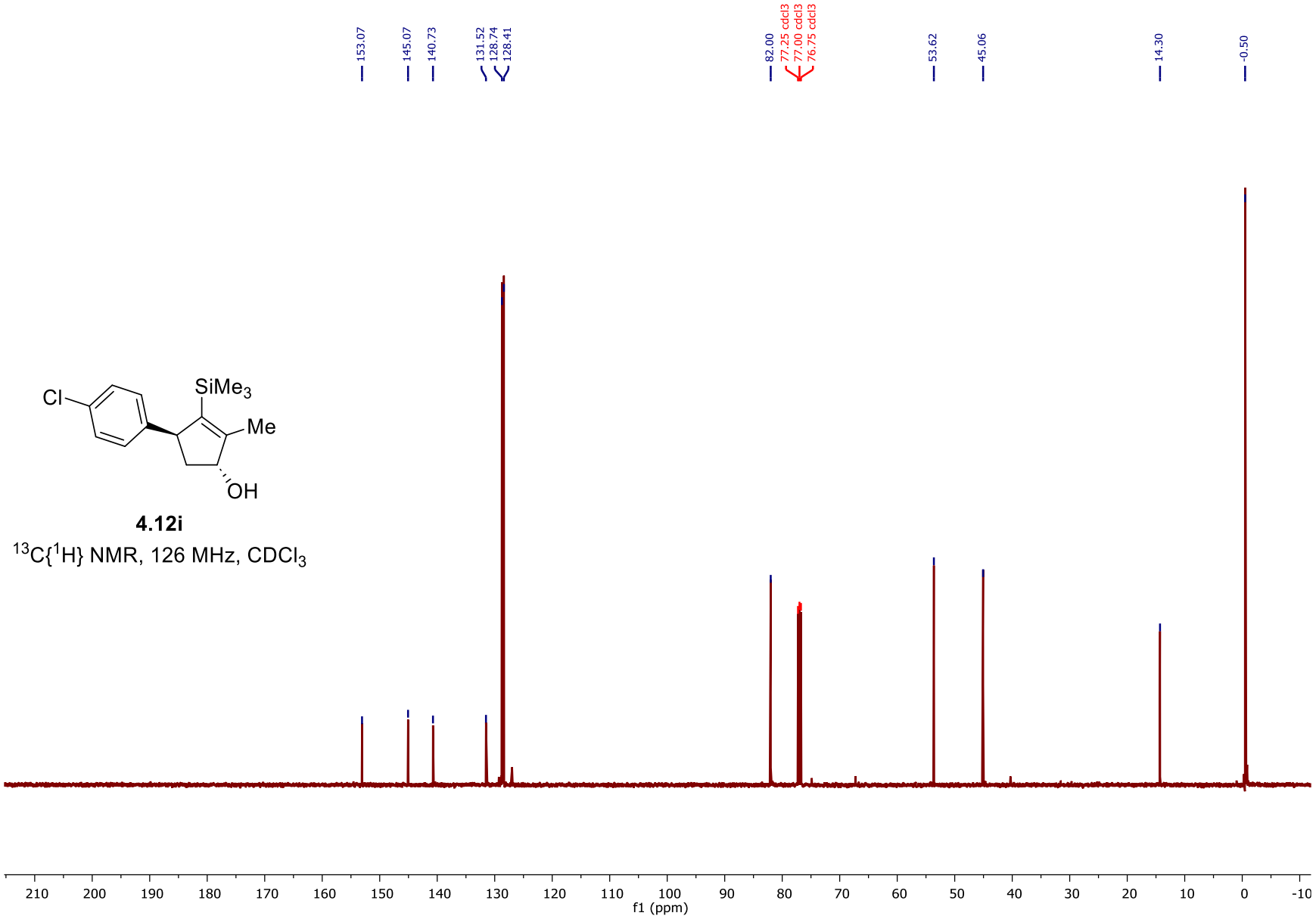
^{1}H NMR, 500 MHz, $CDCl_3$

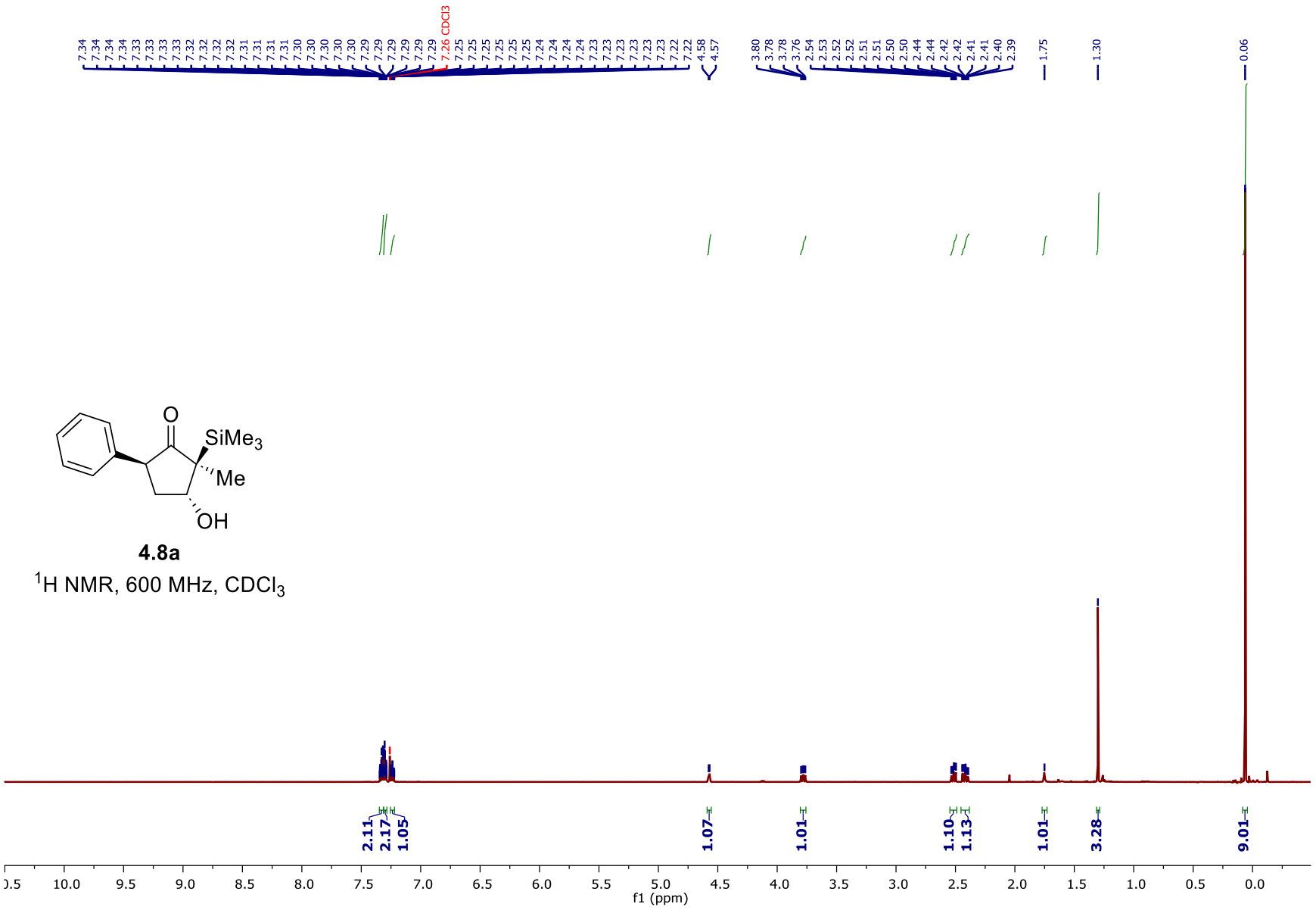

145.70
139.39
132.29
129.93
128.12
124.57
84.68
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
60.87
32.84
14.53
-2.10
Cl
HO
SiMe3
Me
4.6i
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

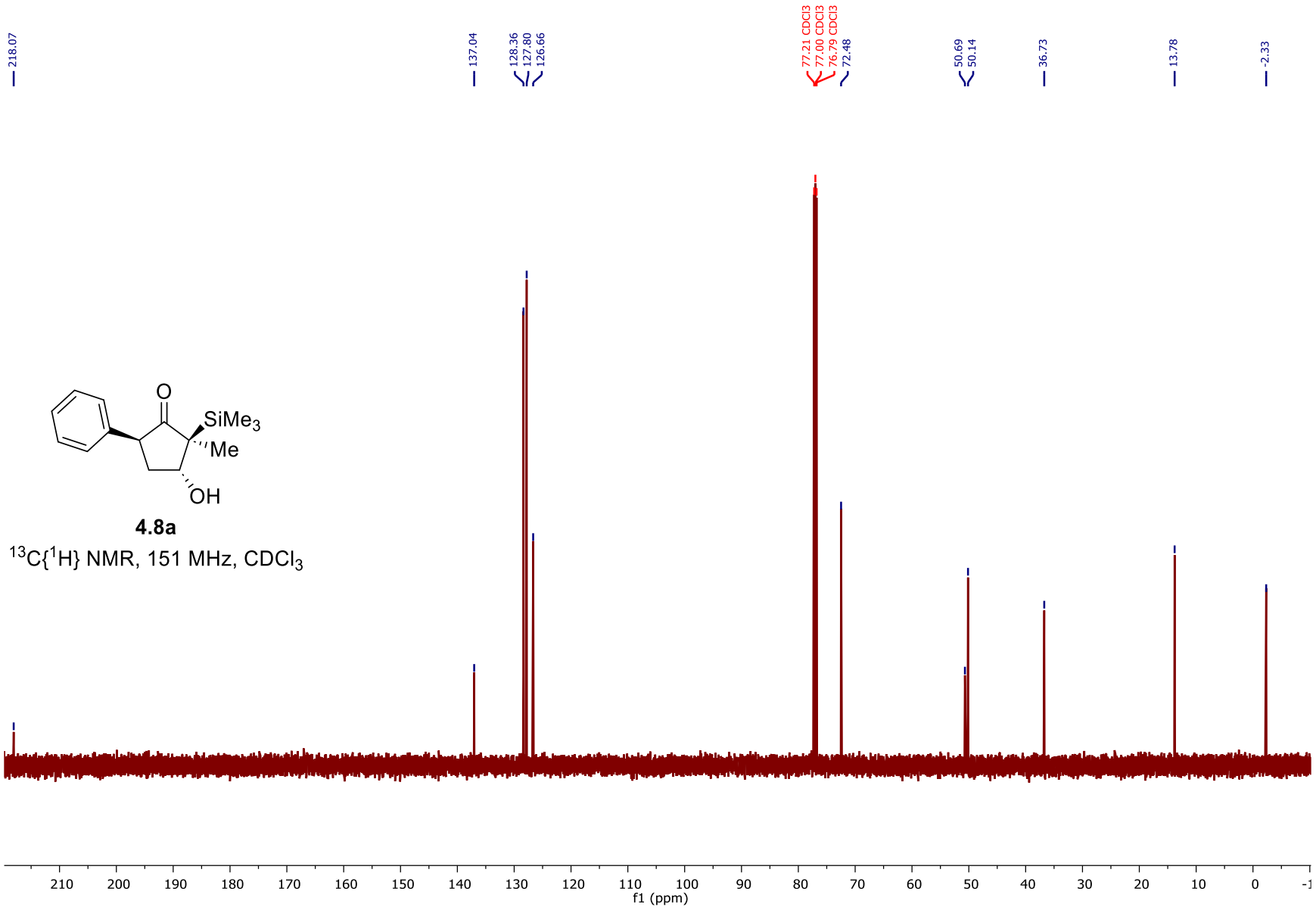


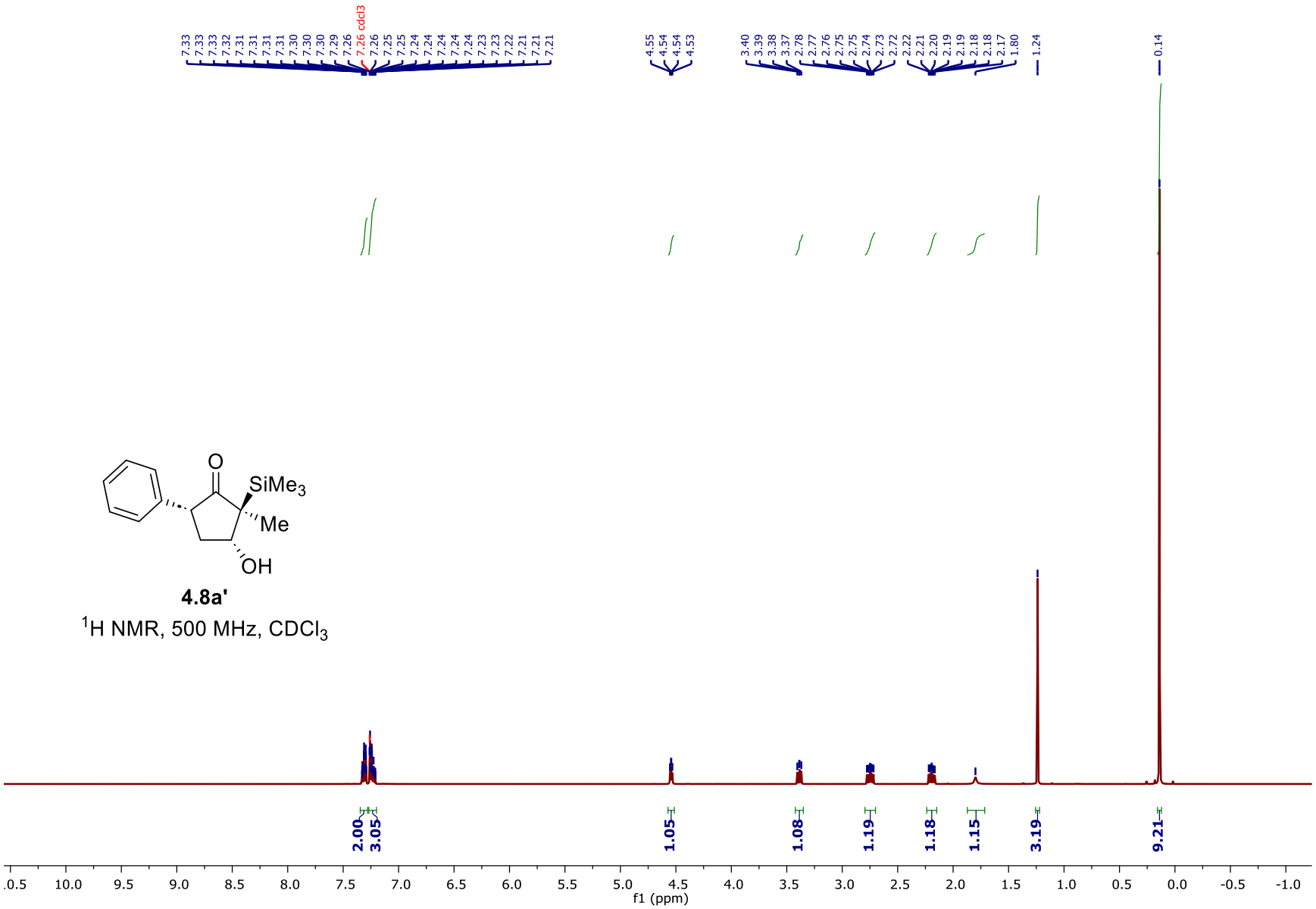
4.12i

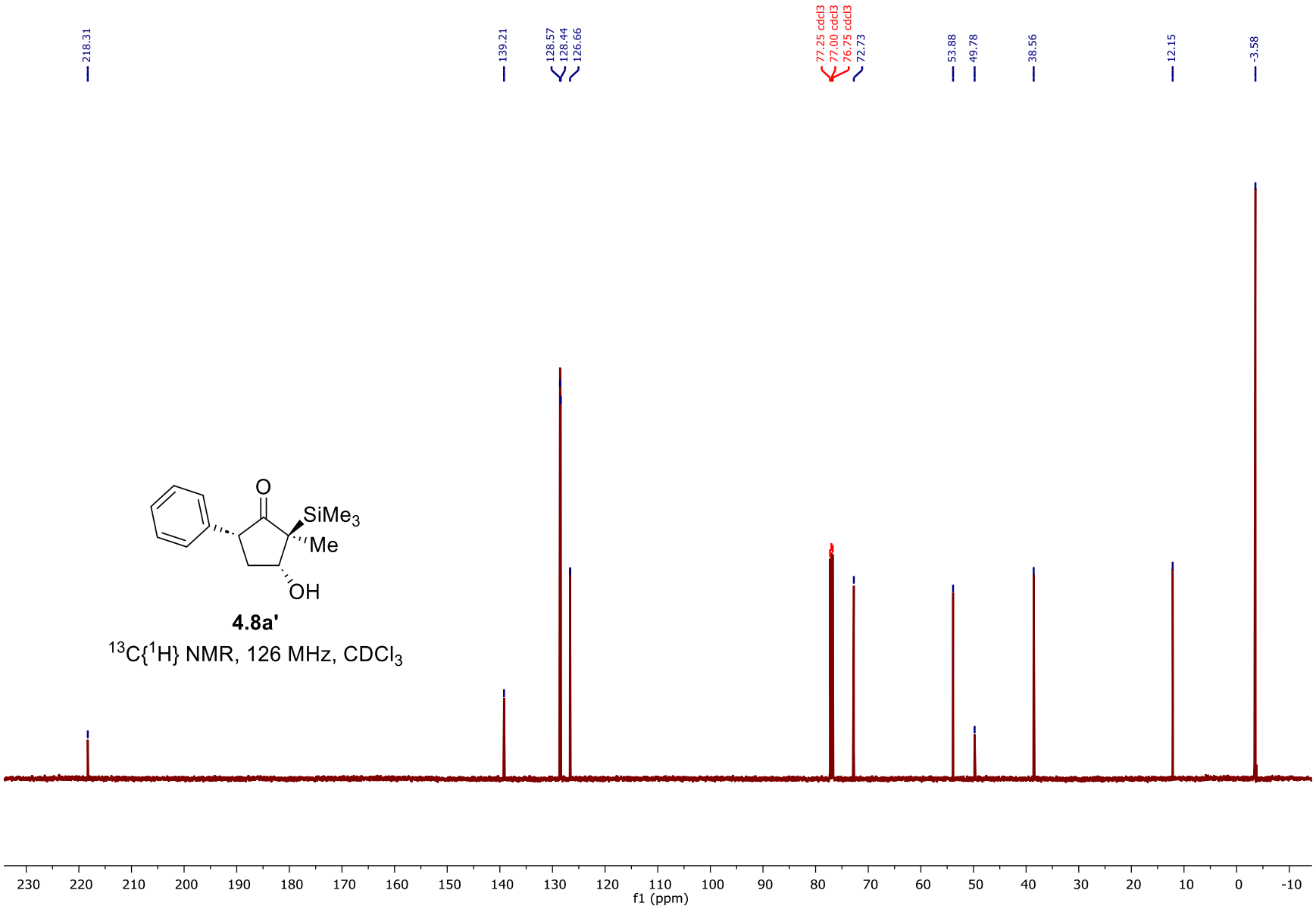
^{1}H NMR, 500 MHz, $CDCl_3$

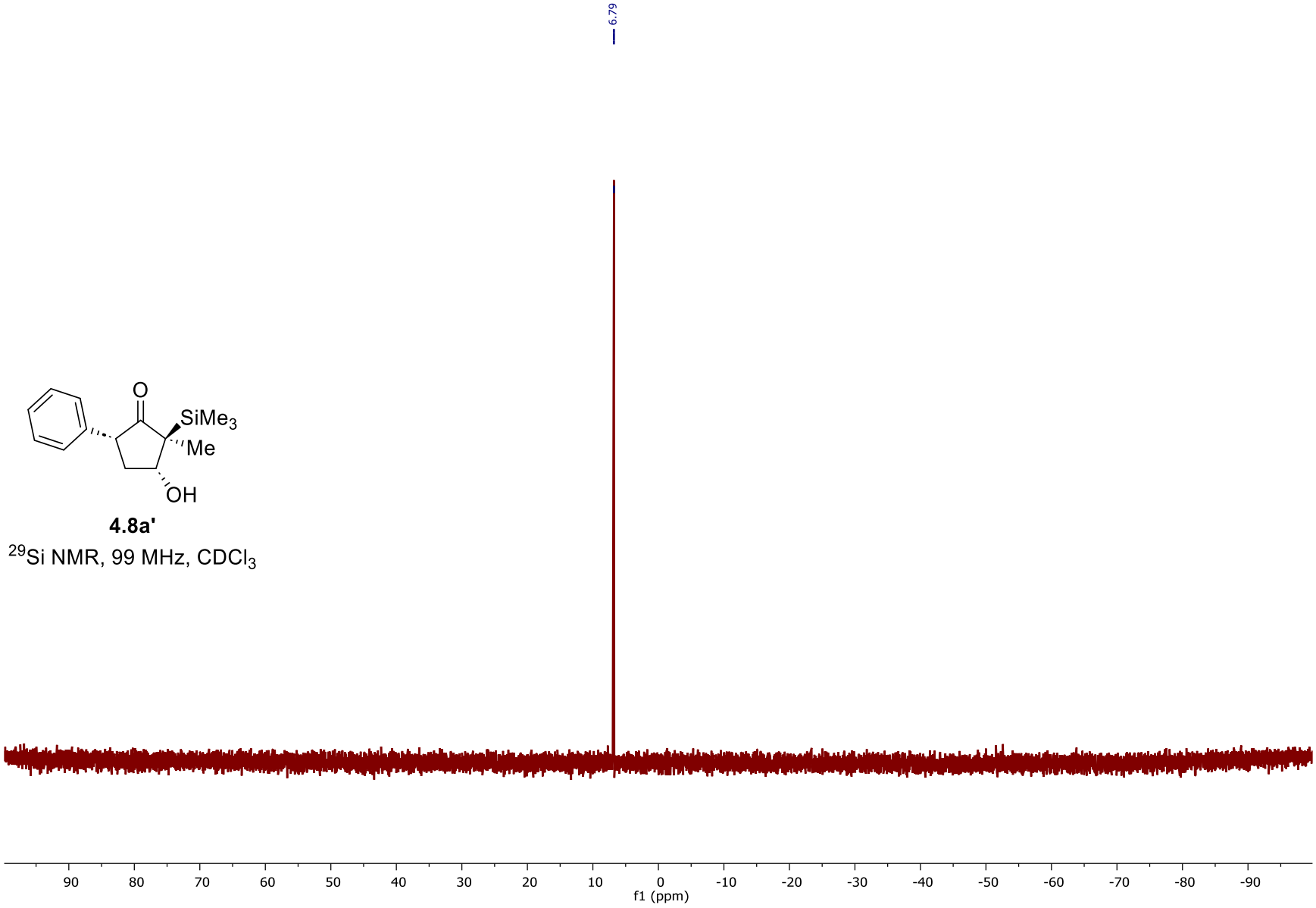

153.07
145.07
140.73
131.52
128.74
128.41
82.00
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
53.62
45.06
14.30
-0.50
Cl
SiMe3
Me
OH
4.12i
13C{1H} NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
SiMe3
Me
OH
4.8a
1H NMR, 600 MHz, CDCl3
7.26 CDCl3
2.11
2.17
1.05
1.07
1.01
1.10
1.13
1.01
3.28
9.01
f1 (ppm)


218.07
137.04
128.36
127.80
126.66
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
72.48
50.69
50.14
36.73
13.78
-2.33
O
SiMe3
Me
OH
4.8a
13C{1H} NMR, 151 MHz, CDCl3
f1 (ppm)

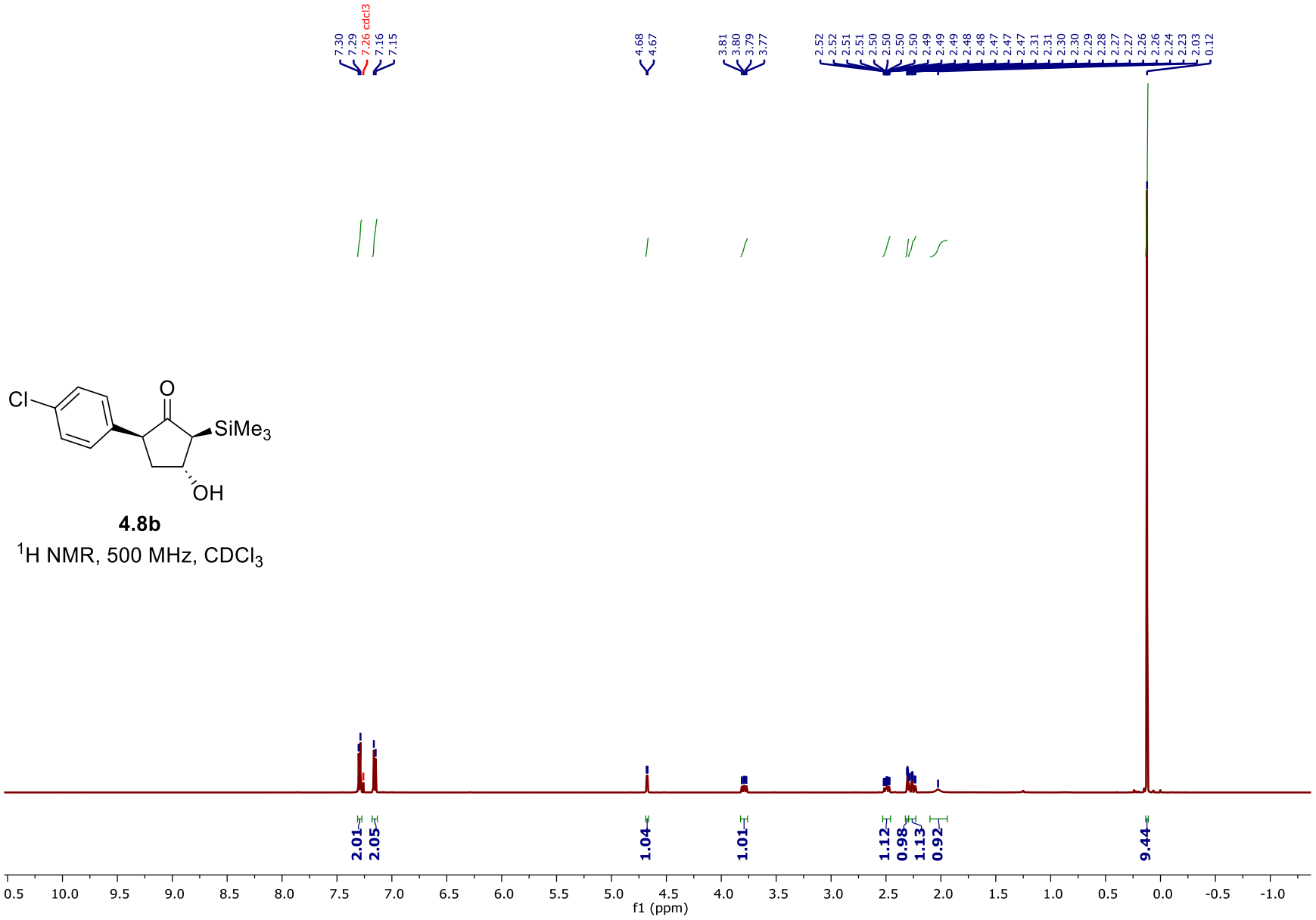

7.33 7.33 7.33 7.32 7.31 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.26 7.26 cdcl3 7.26 7.25 7.25 7.24 7.24 7.24 7.24 7.24 7.23 7.22 7.21 7.21 7.21
4.55 4.54 4.54 4.53
3.40 3.39 3.38 3.37 2.78 2.77 2.76 2.75 2.75 2.74 2.73 2.72 2.22 2.21 2.20 2.19 2.19 2.18 2.18 2.17 1.80
1.24
0.14
O
SiMe3
Me
OH
4.8a'
1H NMR, 500 MHz, CDCl3
2.00
3.05
1.05
1.08
1.19
1.18
1.15
3.19
9.21
f1 (ppm)

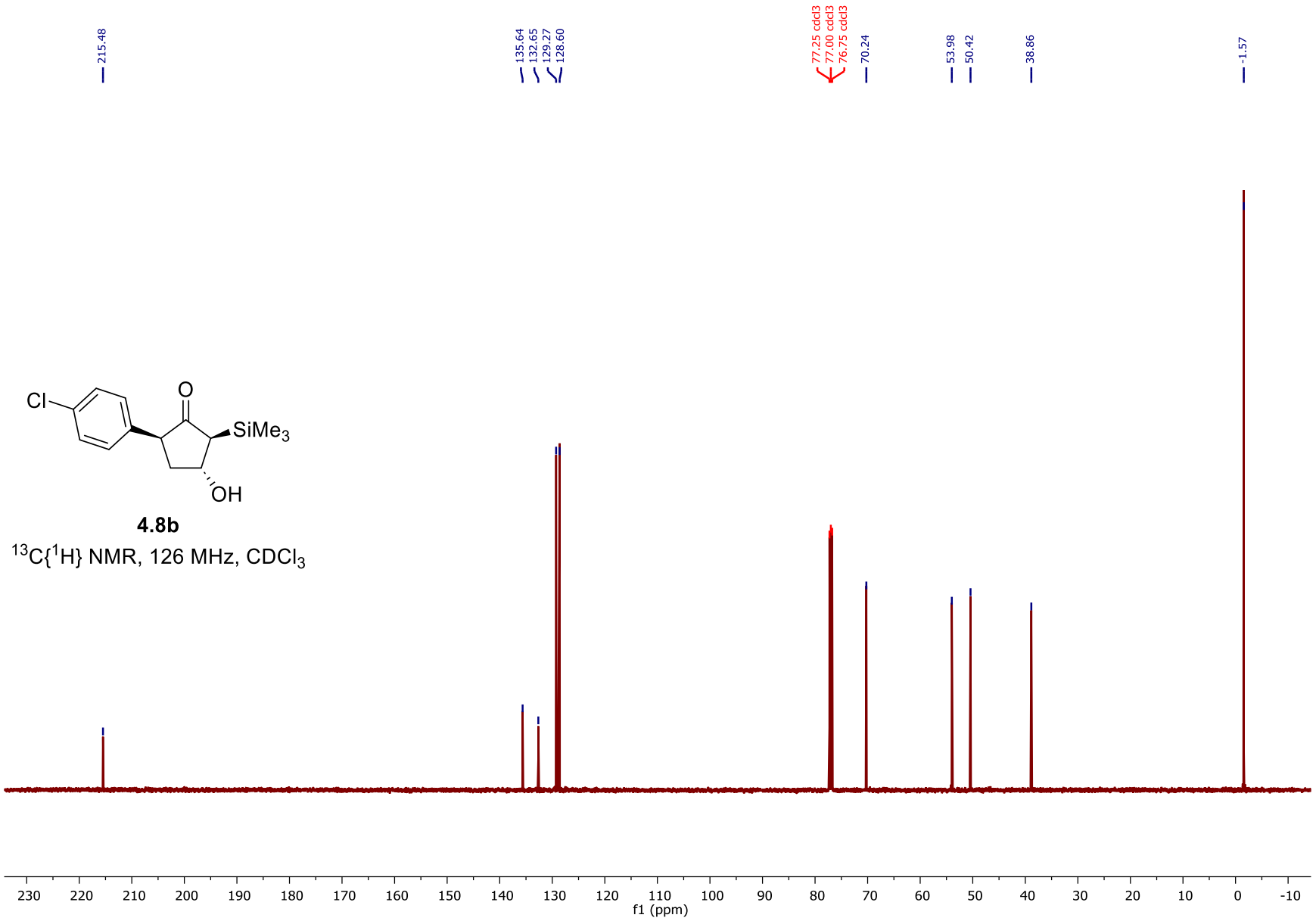

218.31
139.21
128.57
128.44
126.66
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
72.73
53.88
49.78
38.56
12.15
-3.58
O
SiMe3
Me
OH
4.8a'
13C{1H} NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

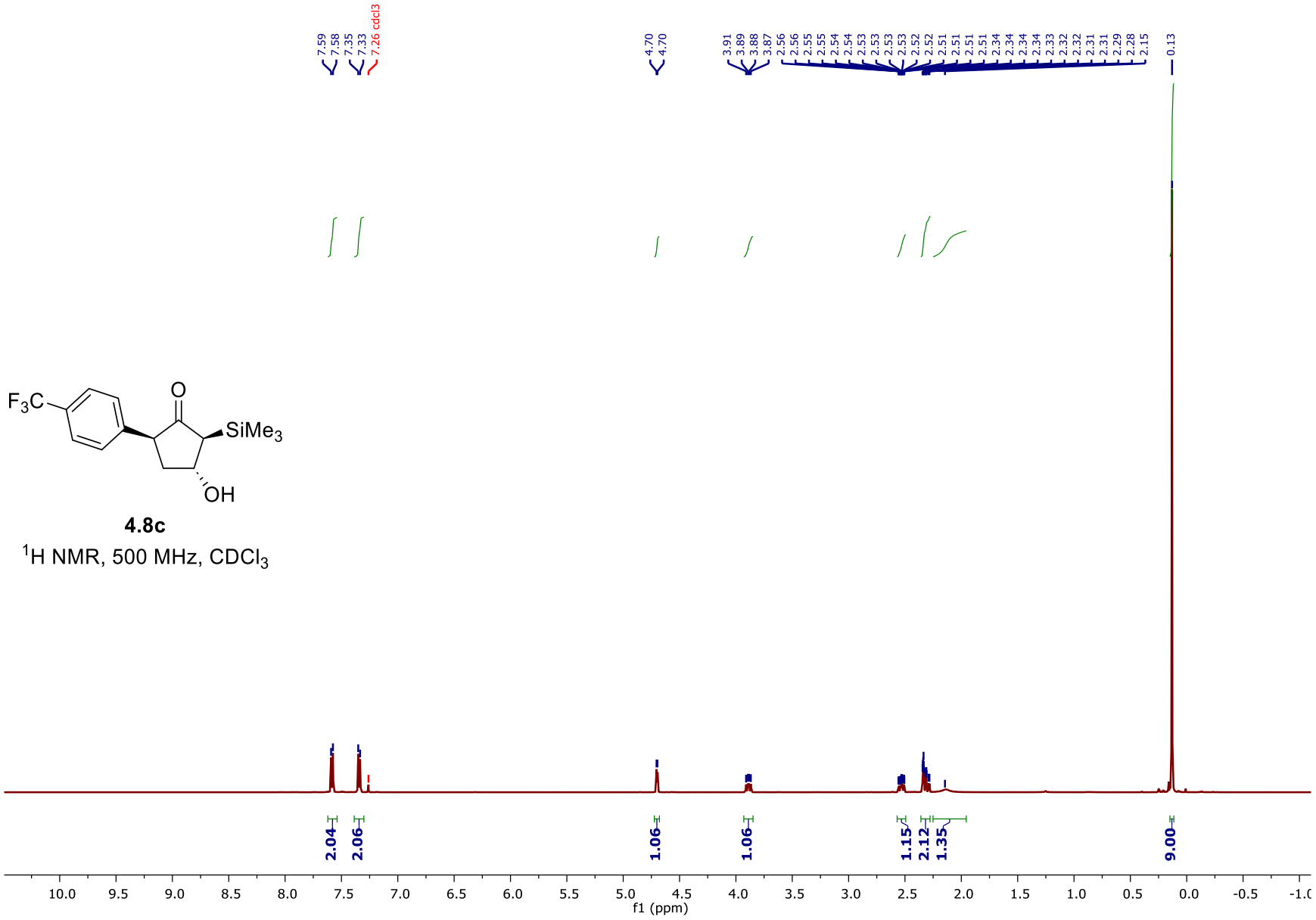


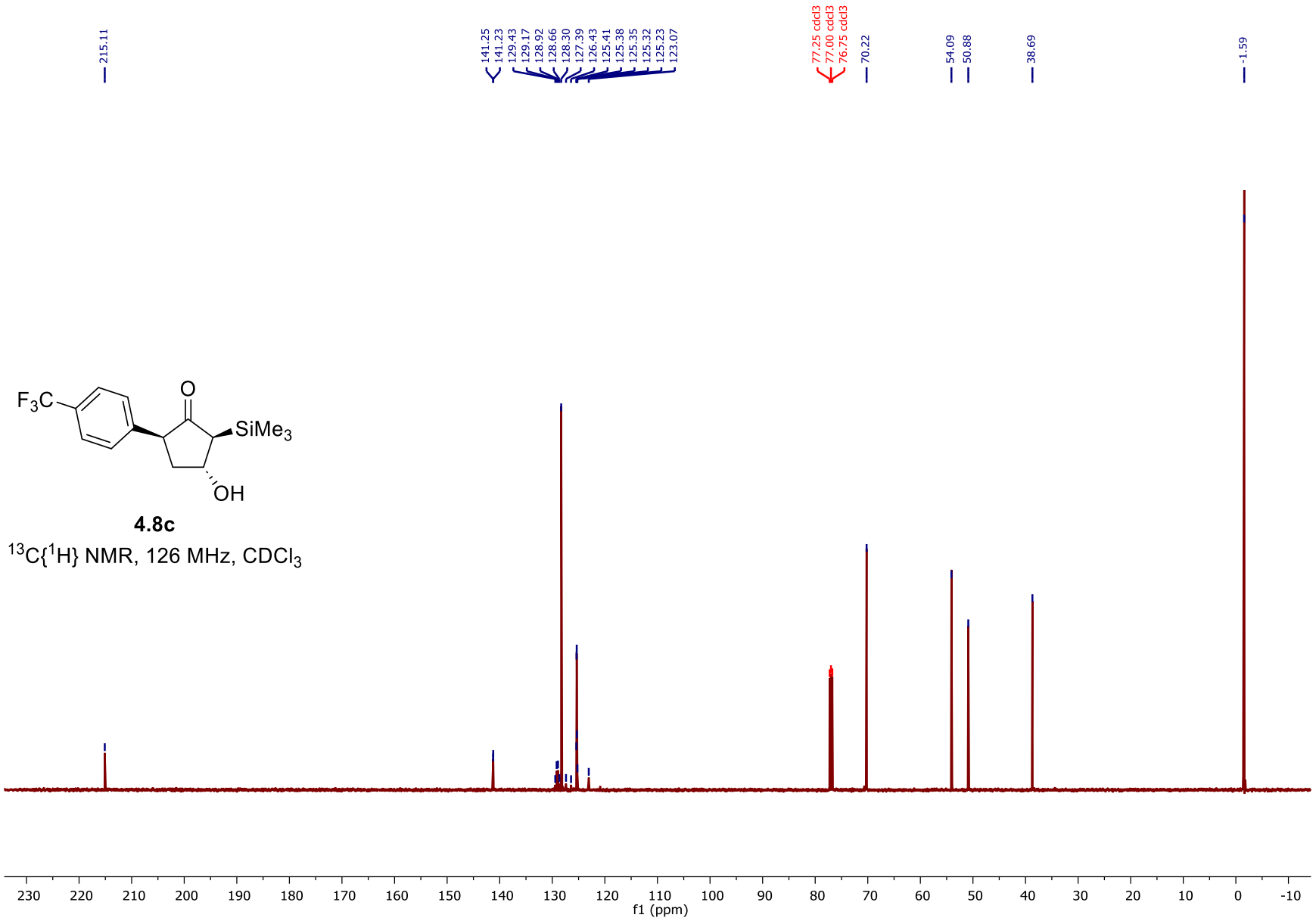
4.8a'

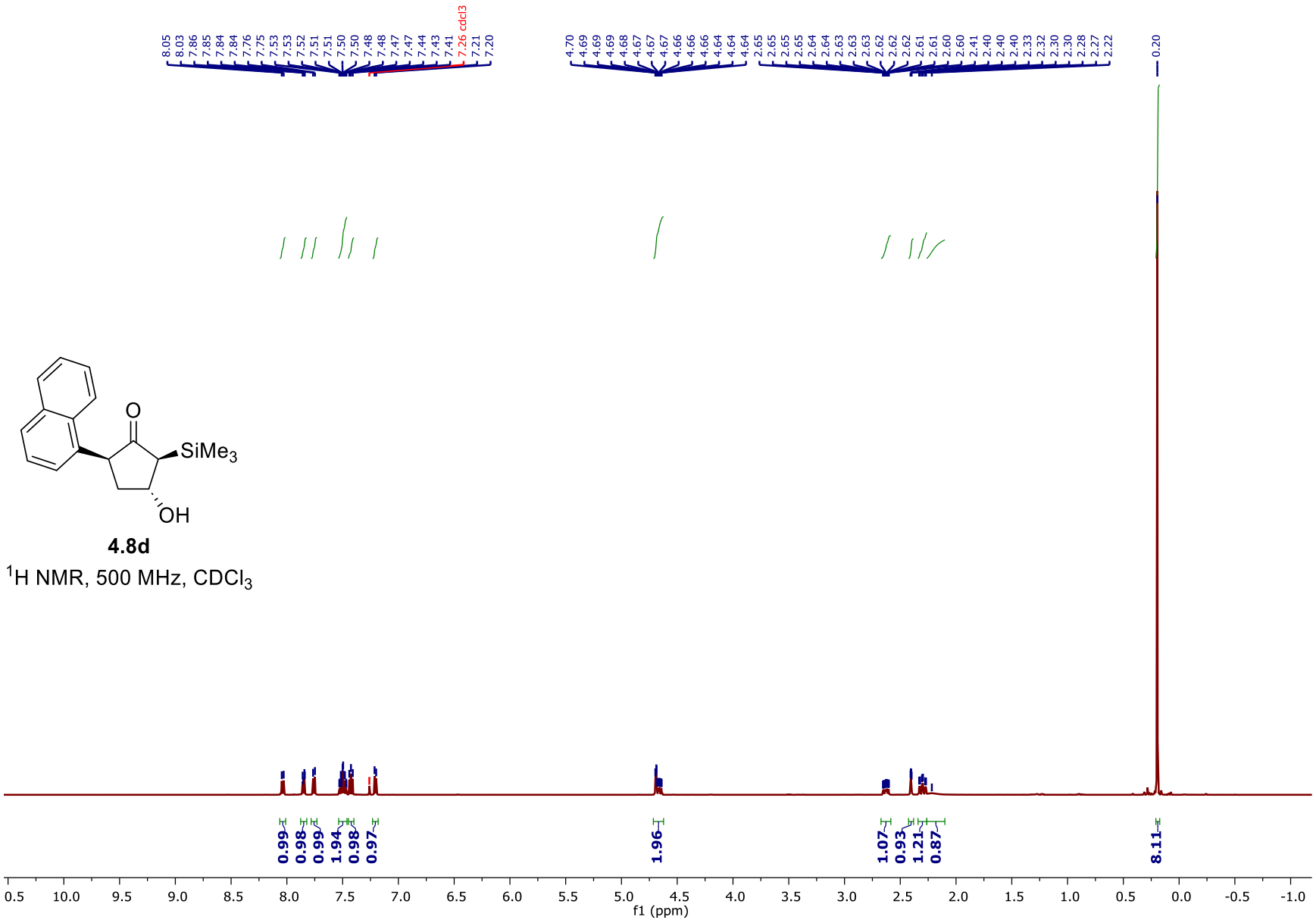
^{29}Si NMR, 99 MHz, $CDCl_3$


7.30
7.29
7.26 cdcl3
7.16
7.15
4.68
4.67
3.81
3.80
3.79
3.77
2.52
2.52
2.51
2.51
2.50
2.50
2.50
2.50
2.49
2.49
2.49
2.48
2.48
2.47
2.47
2.47
2.31
2.31
2.30
2.30
2.29
2.28
2.27
2.27
2.26
2.26
2.24
2.23
2.03
0.12
Cl
O
SiMe3
OH
4.8b
1H NMR, 500 MHz, CDCl3
2.01
2.05
1.04
1.01
1.12
0.98
1.13
0.92
9.44
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


215.48
135.64
132.65
129.27
128.60
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.24
53.98
50.42
38.86
-1.57
Cl
O
SiMe3
OH
4.8b
13C{1H} NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

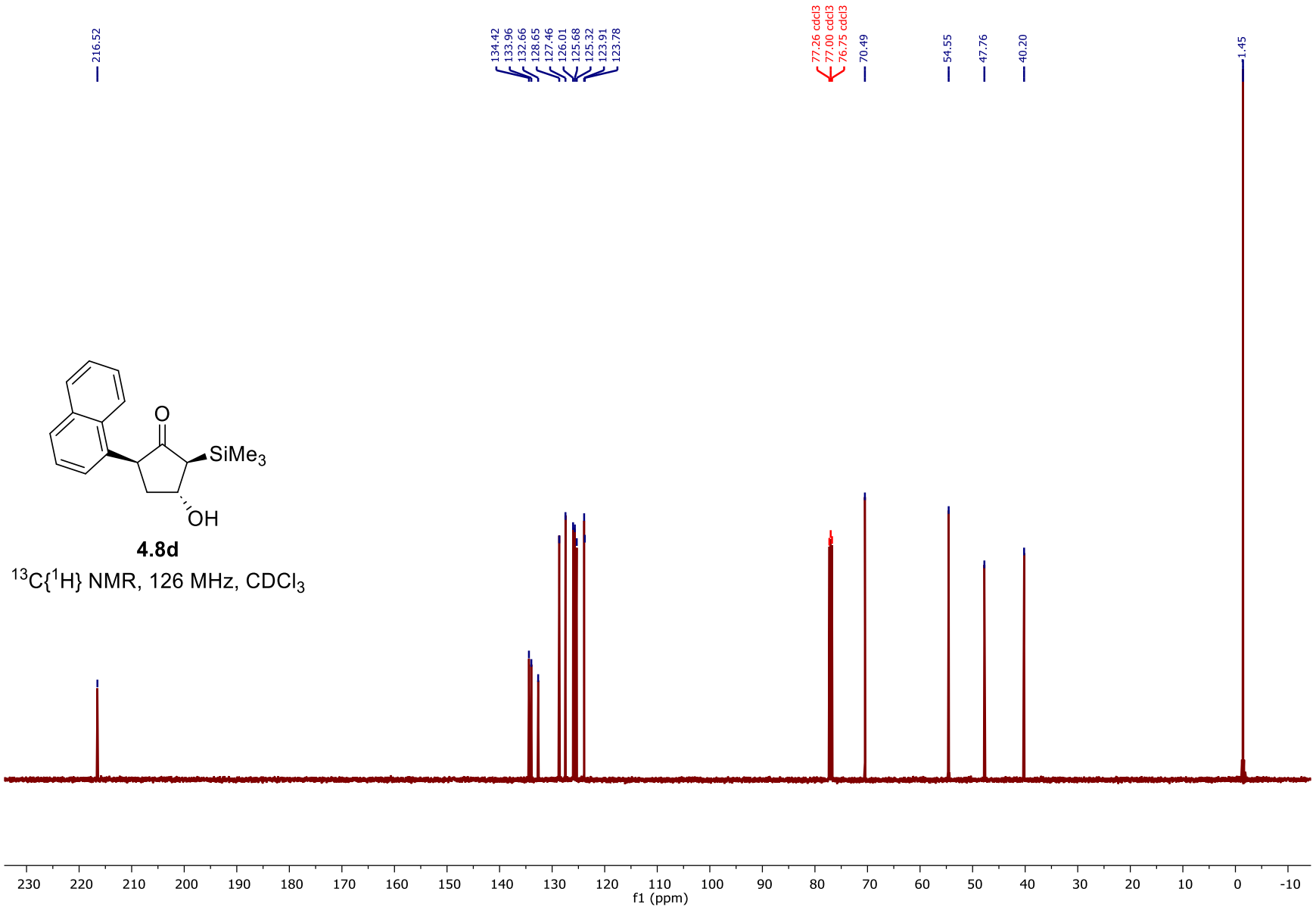

7.59
7.58
7.35
7.33
7.26 cdcl3
4.70
4.70
3.91
3.89
3.88
3.87
2.56
2.56
2.55
2.55
2.55
2.54
2.54
2.53
2.53
2.53
2.53
2.52
2.52
2.51
2.51
2.51
2.51
2.34
2.34
2.34
2.34
2.33
2.32
2.32
2.31
2.31
2.29
2.28
2.15
0.13
F3C
O
SiMe3
OH
4.8c
1H NMR, 500 MHz, CDCl3
2.04
2.06
1.06
1.06
1.15
2.12
1.35
9.00
10.0
9.5
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)

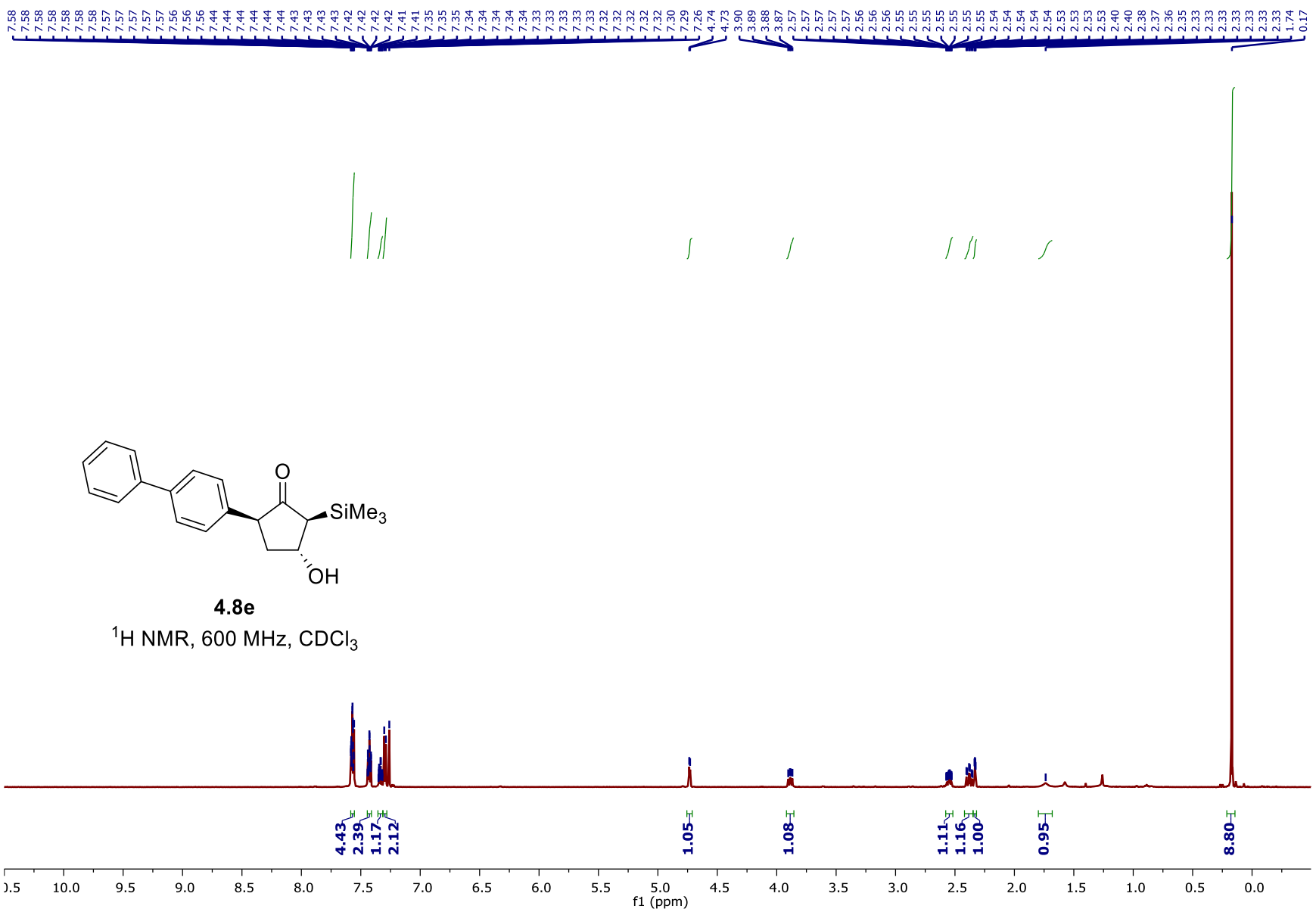

215.11
141.25
141.23
129.43
129.17
128.92
128.66
128.30
127.39
126.43
125.41
125.38
125.35
125.32
125.23
123.07
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.22
54.09
50.88
38.69
-1.59
F3C
O
SiMe3
OH
4.8c
13C{1H} NMR, 126 MHz, CDCl3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

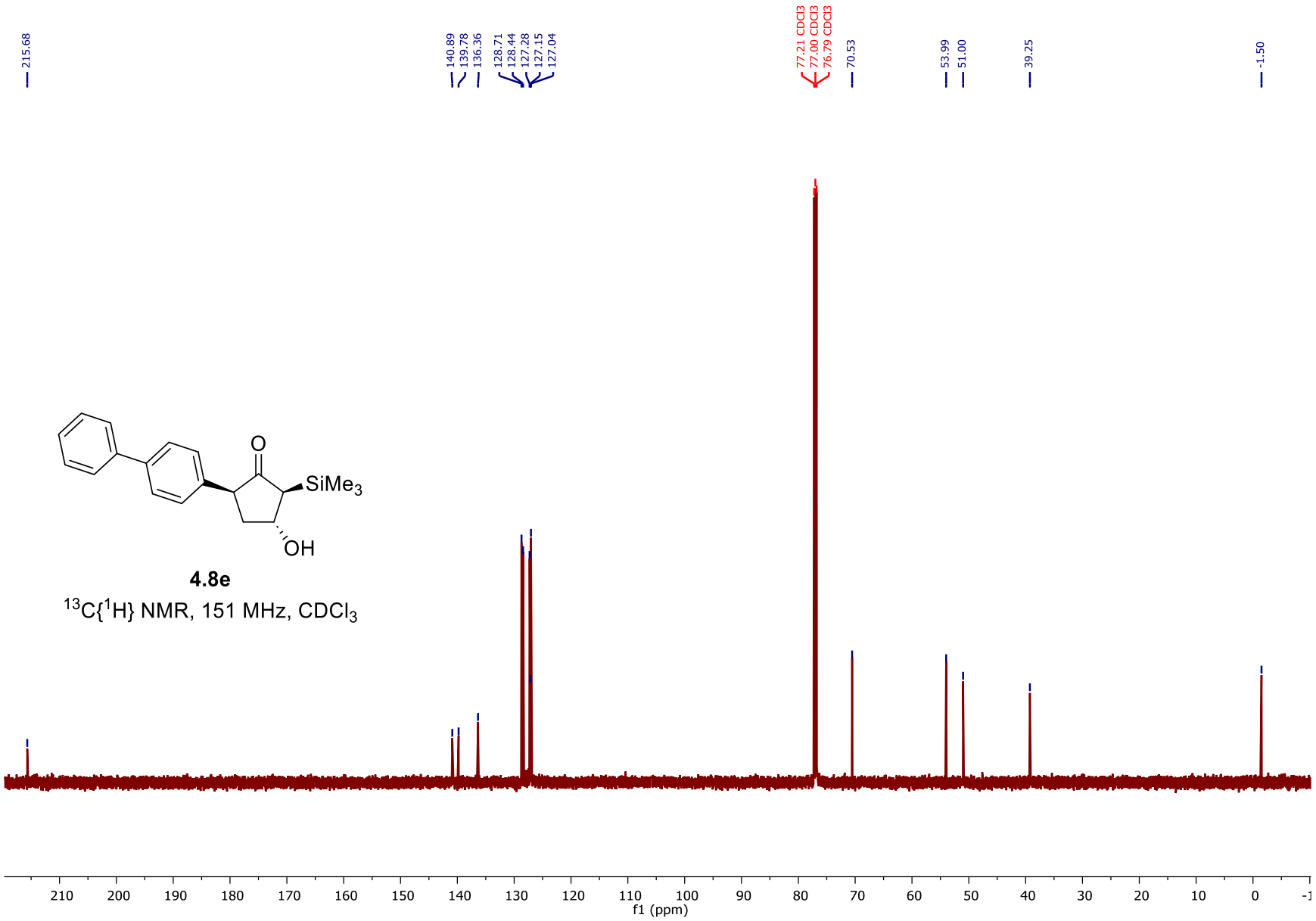


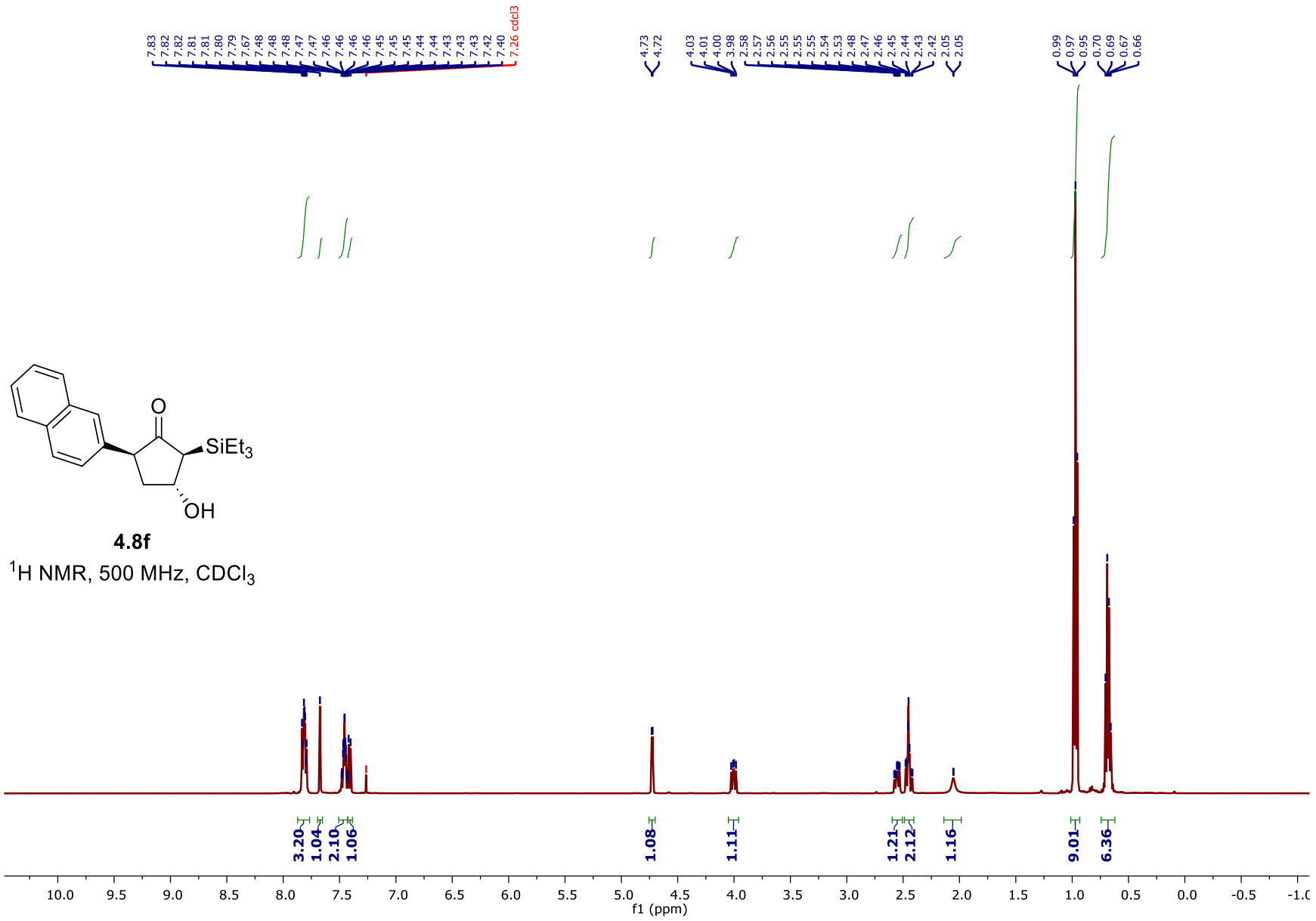
4.8d

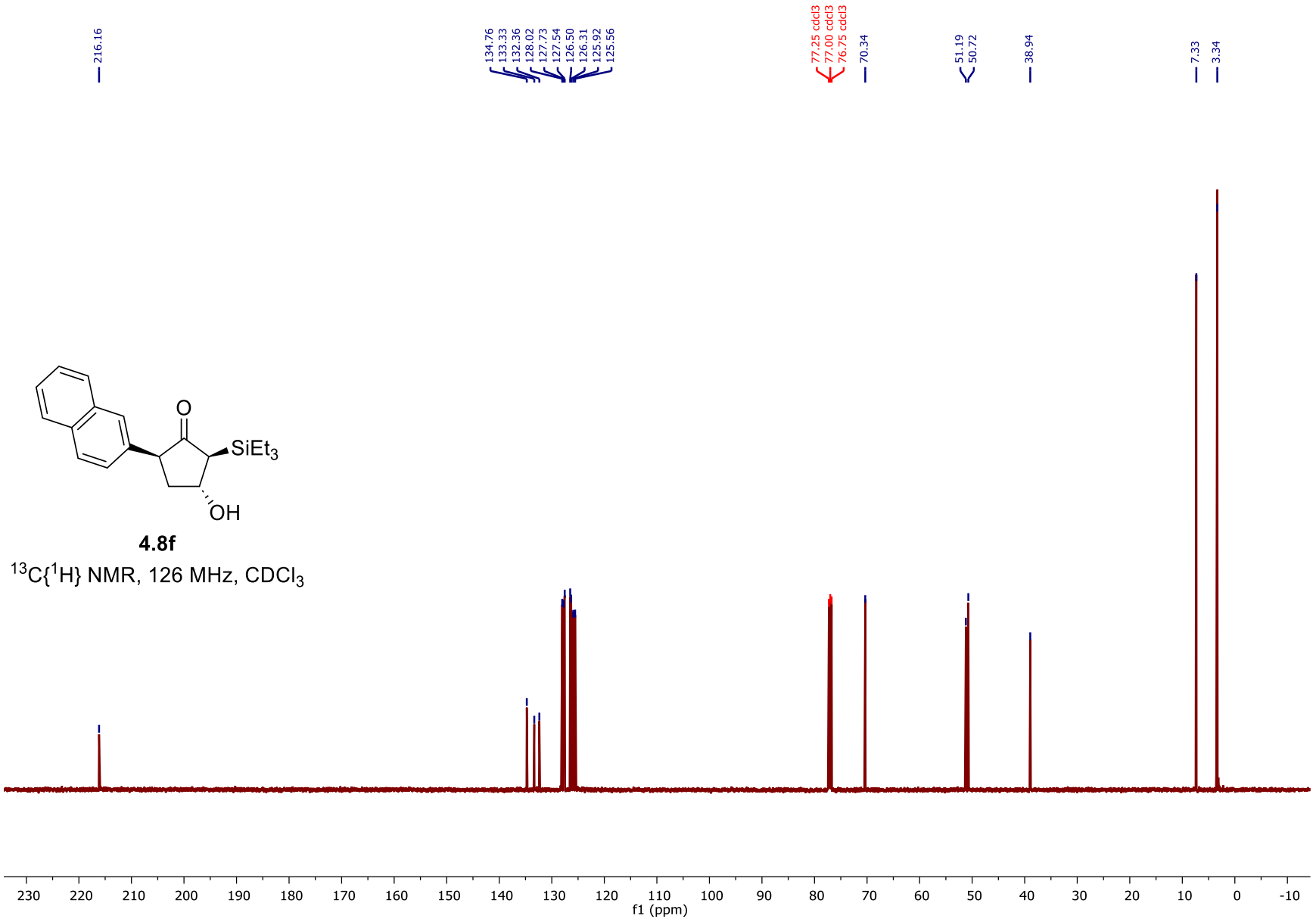
^{1}H NMR, 500 MHz, $CDCl_3$

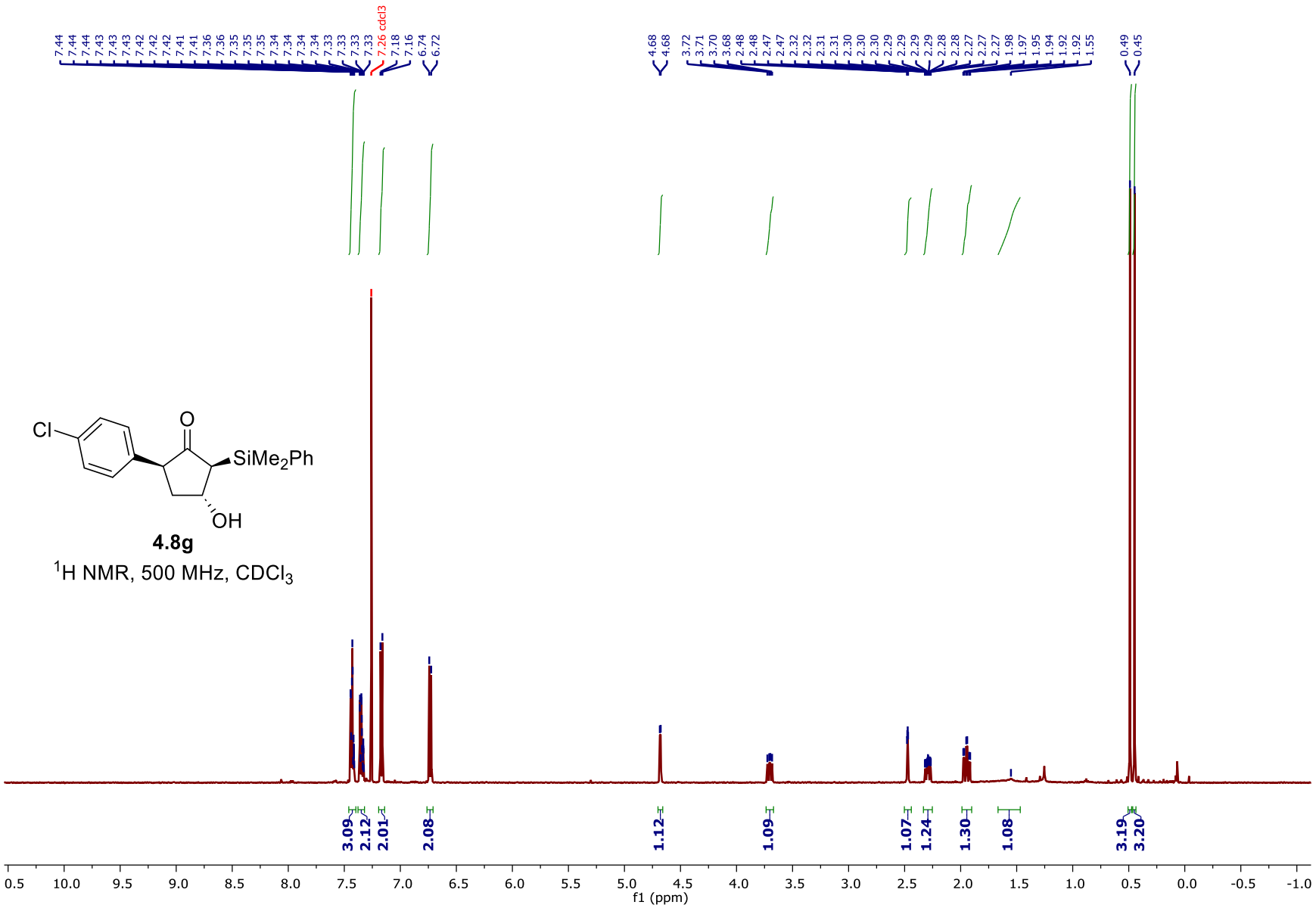

216.52
134.42
133.96
132.66
128.65
127.46
126.01
125.68
125.32
123.91
123.78
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
70.49
54.55
47.76
40.20
1.45
O
SiMe3
OH
4.8d
13C{1H} NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.58 7.58 7.58 7.58 7.58 7.58 7.57 7.57 7.57 7.57 7.56 7.56 7.56 7.44 7.44 7.44 7.44 7.44 7.44 7.43 7.43 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.35 7.35 7.35 7.34 7.34 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.32 7.32 7.32 7.30 7.29 7.26 4.74 4.73 3.90 3.89 3.88 3.87 2.57 2.57 2.57 2.57 2.57 2.56 2.56 2.56 2.55 2.55 2.55 2.55 2.55 2.55 2.55 2.55 2.54 2.54 2.54 2.54 2.54 2.53 2.53 2.53 2.53 2.40 2.40 2.38 2.37 2.36 2.35 2.33 2.33 2.33 2.33 2.33 2.33 1.74 0.17
O
SiMe3
OH
4.8e
1H NMR, 600 MHz, CDCl3
4.43
2.39
1.17
2.12
1.05
1.08
1.11
1.16
1.00
0.95
8.80
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


215.68
140.89
139.78
136.36
128.71
128.44
127.28
127.15
127.04
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.53
53.99
51.00
39.25
-1.50
O
SiMe3
OH
4.8e
13C{1H} NMR, 151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.83 7.82 7.82 7.81 7.81 7.80 7.79 7.67 7.48 7.48 7.48 7.47 7.47 7.46 7.46 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.40 7.26 cdcl3
4.73 4.72 4.03 4.01 4.00 3.98 2.58 2.57 2.56 2.55 2.55 2.55 2.54 2.53 2.48 2.47 2.46 2.45 2.44 2.43 2.42 2.05 2.05
0.99 0.97 0.95 0.70 0.69 0.67 0.66
O
SiEt3
OH
4.8f
1H NMR, 500 MHz, CDCl3
3.20 1.04 2.10 1.06 1.08 1.11 1.21 2.12 1.16 9.01 6.36
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)


216.16
134.76
133.33
132.36
128.02
127.73
127.54
126.50
126.31
125.92
125.56
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.34
51.19
50.72
38.94
7.33
3.34
O
SiEt3
OH
4.8f
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)


7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.34
7.33
7.33
7.33
7.26 cdcl3
7.18
7.16
6.74
6.72
4.68
4.68
3.72
3.71
3.70
3.68
2.48
2.48
2.47
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2.31
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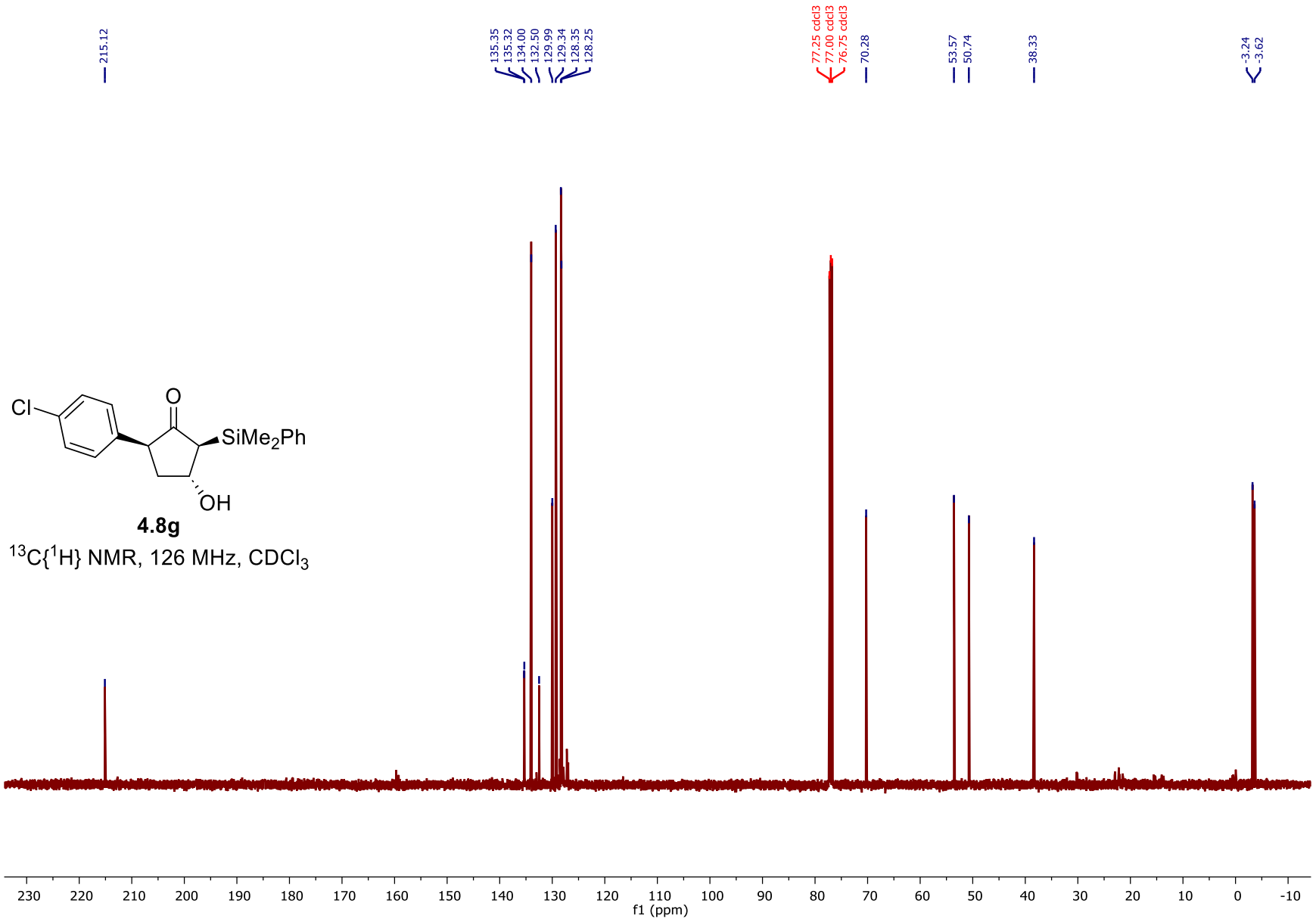
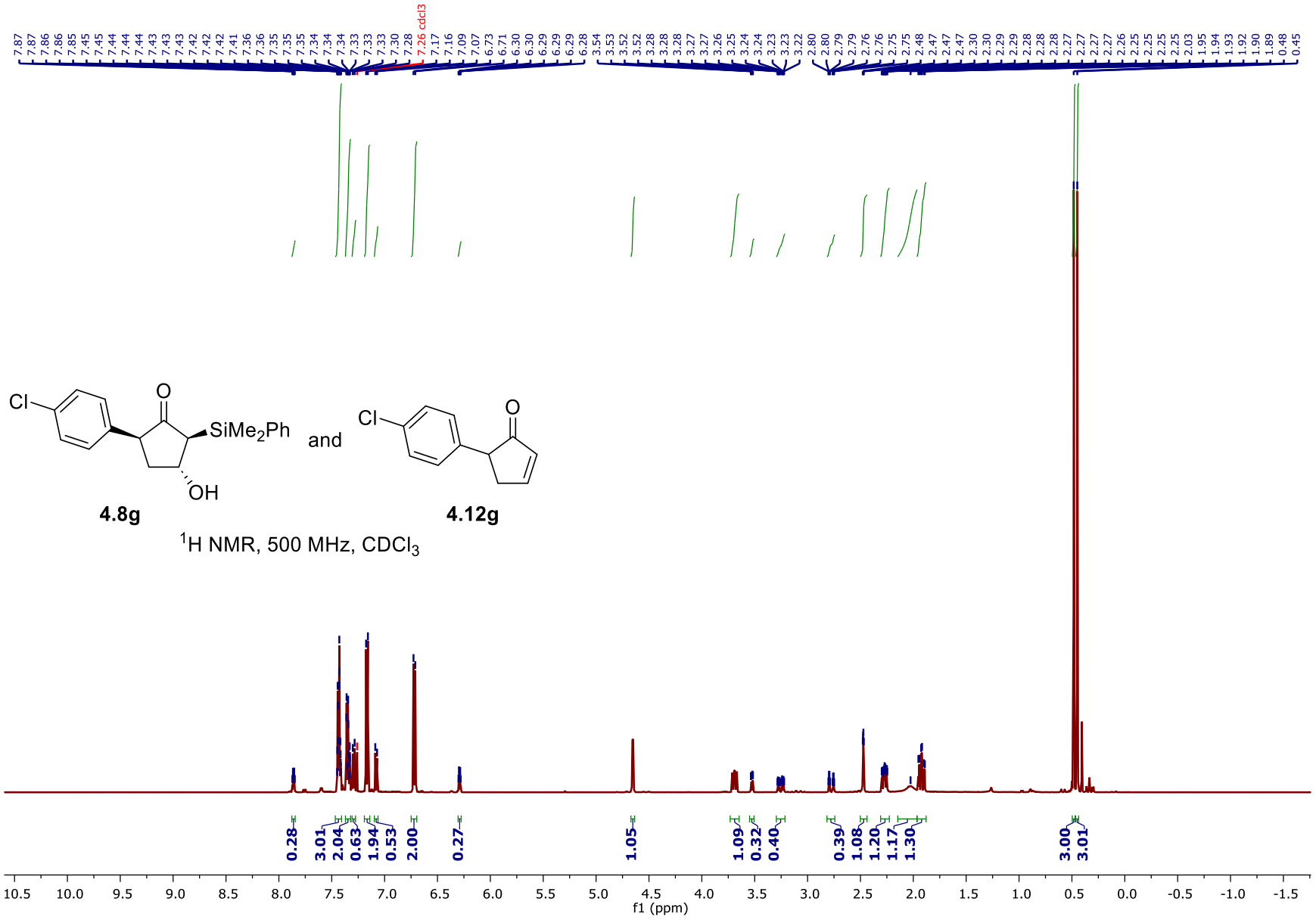
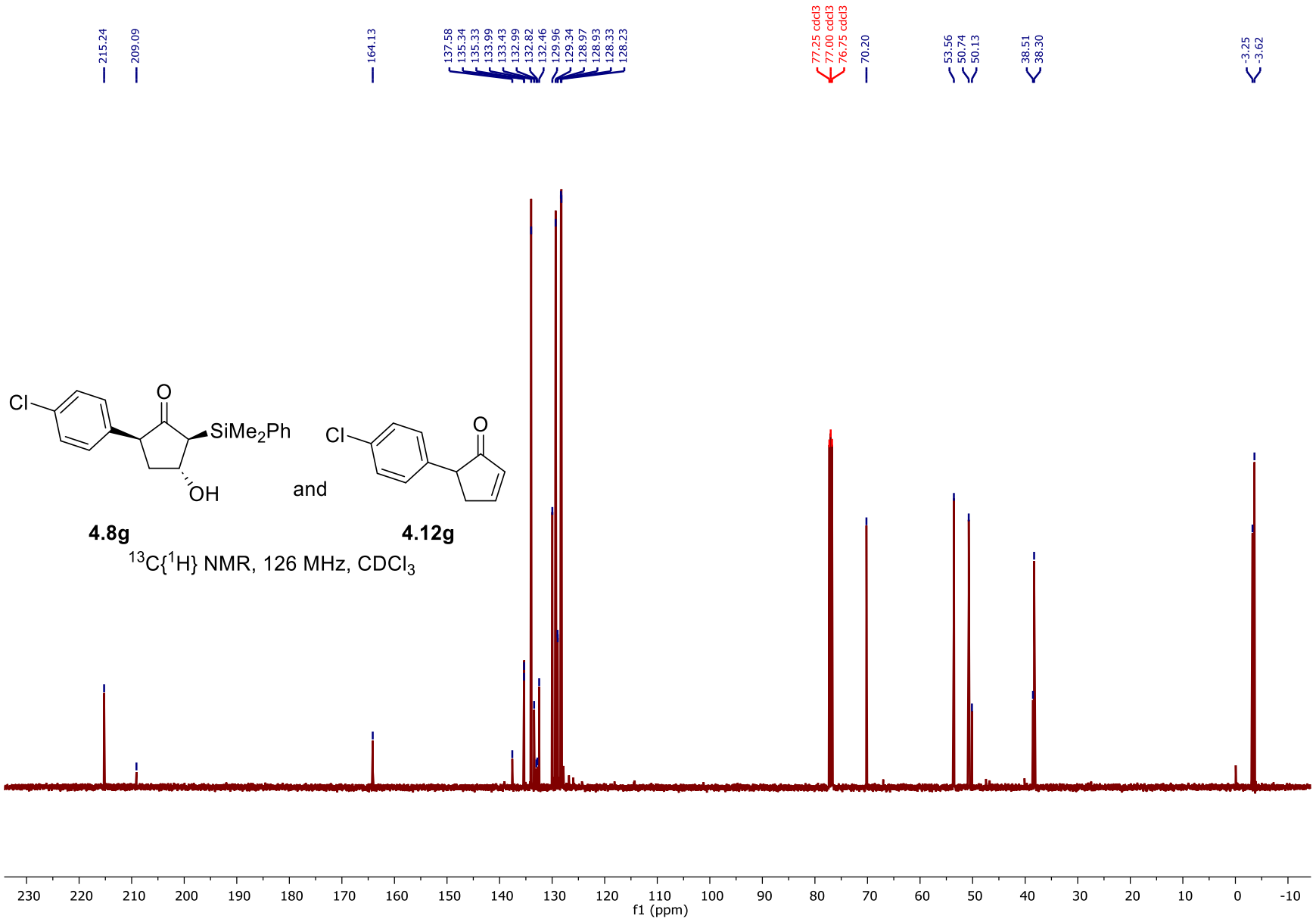
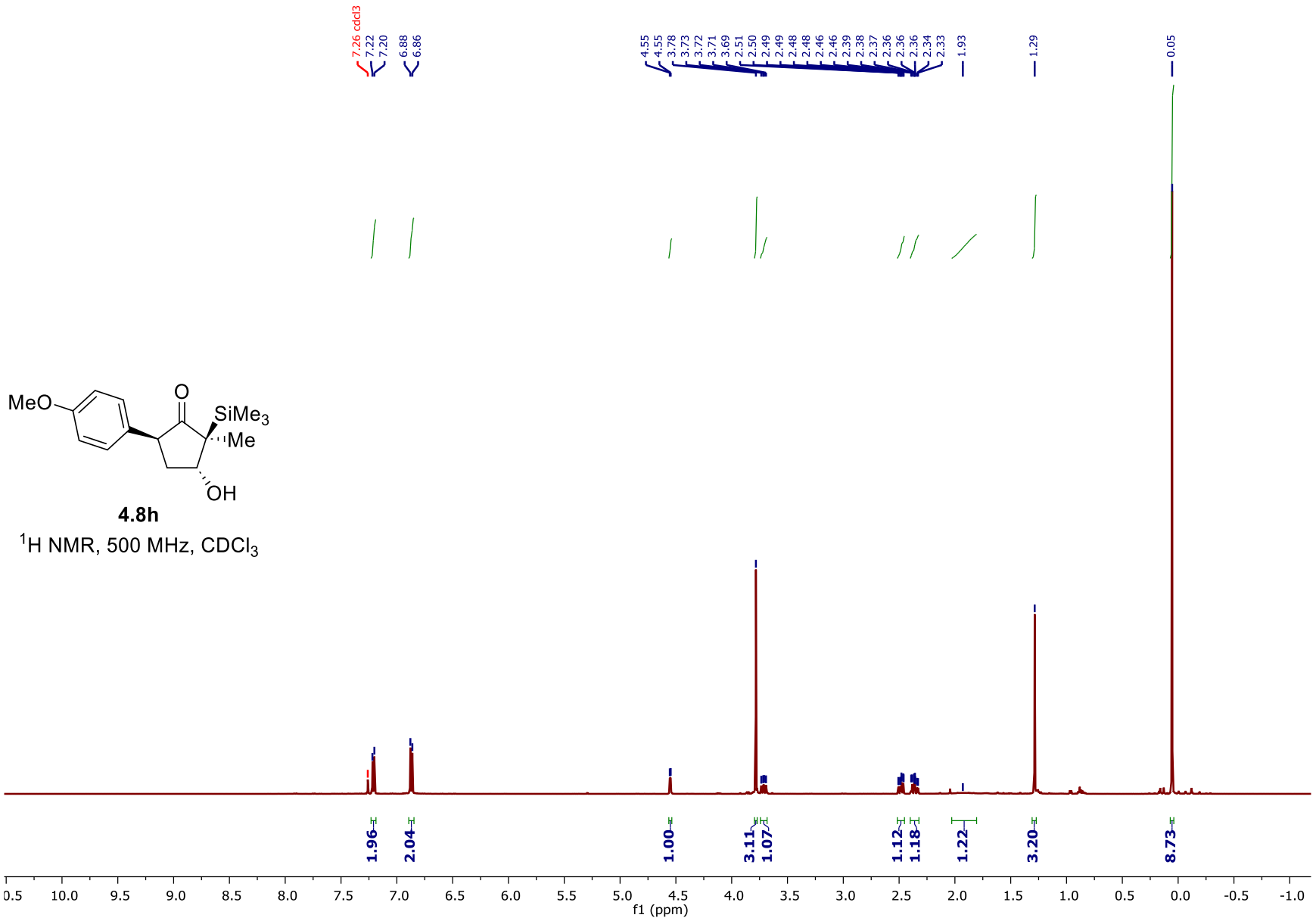
2.30
2.29
2.29
2.29
2.29
2.28
2.28
2.27
2.27
2.27
1.98
1.97
1.95
1.94
1.92
1.92
1.55
0.49
0.45
Cl
O
SiMe2Ph
OH
4.8g
1H NMR, 500 MHz, CDCl3
3.09
2.12
2.01
2.08
1.12
1.09
1.07
1.24
1.30
1.08
3.19
3.20
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


215.12
135.35
135.32
134.00
132.50
129.99
129.34
128.35
128.25
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.28
53.57
50.74
38.33
-3.24
-3.62
Cl
O
SiMe2Ph
OH
4.8g
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)

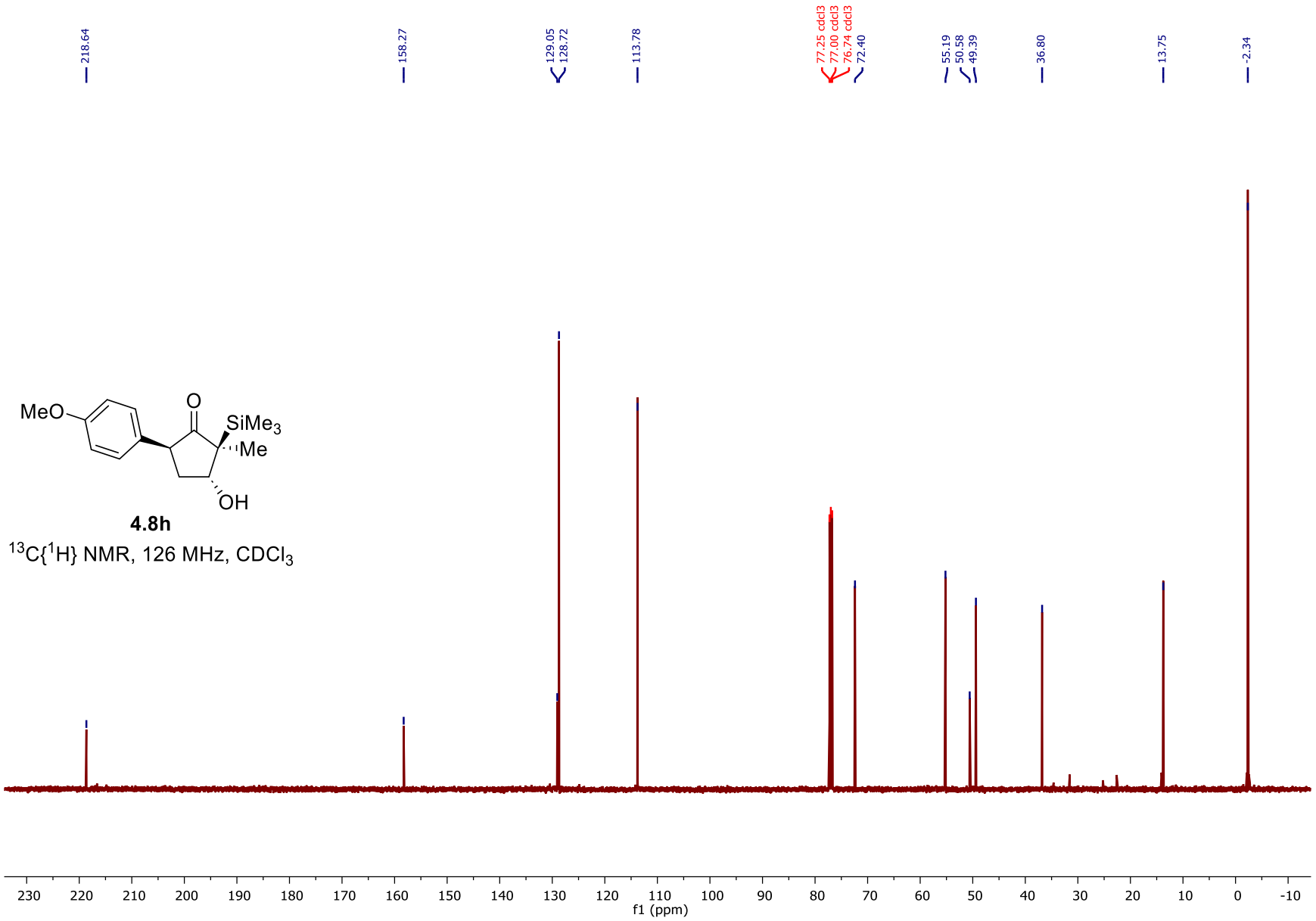

7.87 7.87 7.86 7.86 7.85 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.30 7.28 7.26 cdcl3 7.17 7.16 7.09 7.07 6.73 6.71 6.30 6.30 6.29 6.29 6.29 6.28
3.54 3.53 3.52 3.52 3.28 3.28 3.28 3.27 3.27 3.26 3.25 3.24 3.24 3.23 3.23 3.22
2.80 2.80 2.79 2.79 2.76 2.76 2.75 2.75 2.48 2.47 2.47 2.47 2.30 2.29 2.29 2.28 2.28 2.28 2.27 2.27 2.27 2.27 2.26 2.25 2.25 2.25 2.25 2.03 1.95 1.94 1.93 1.92 1.90 1.89 0.48 0.45
Cl
O
SiMe2Ph
OH
and
Cl
O
4.8g
4.12g
1H NMR, 500 MHz, CDCl3
0.28 3.01 2.04 0.63 1.94 0.53 2.00 0.27 1.05 1.09 0.32 0.40 0.39 1.08 1.20 1.17 1.30 3.00 3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

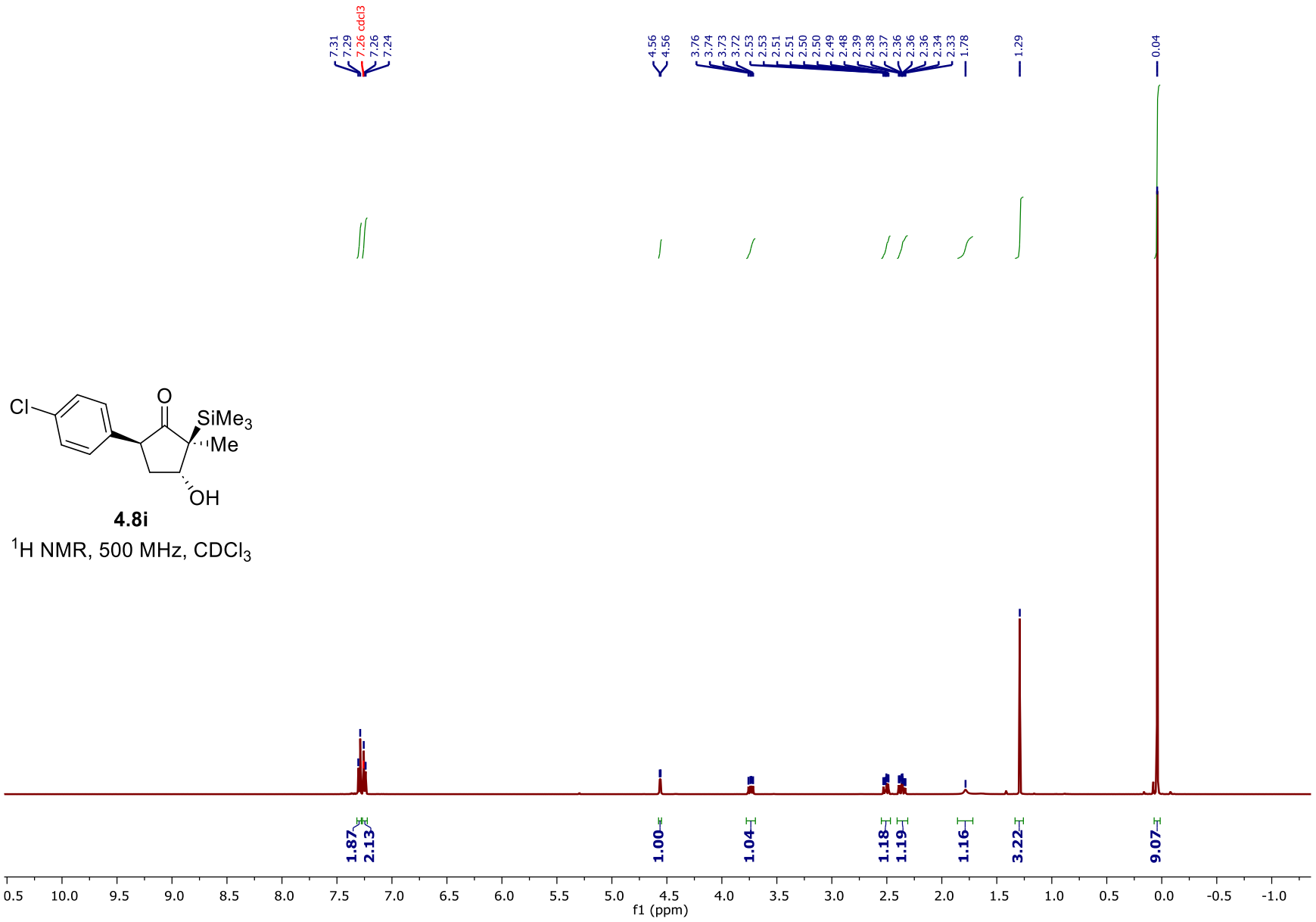

215.24
209.09
164.13
137.58
135.34
135.33
133.99
133.43
132.99
132.82
132.46
129.96
129.34
128.97
128.93
128.33
128.23
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.20
53.56
50.74
50.13
38.51
38.30
-3.25
-3.62
Cl
O
SiMe2Ph
OH
and
Cl
O
4.8g
4.12g
13C{1H} NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



4.8h

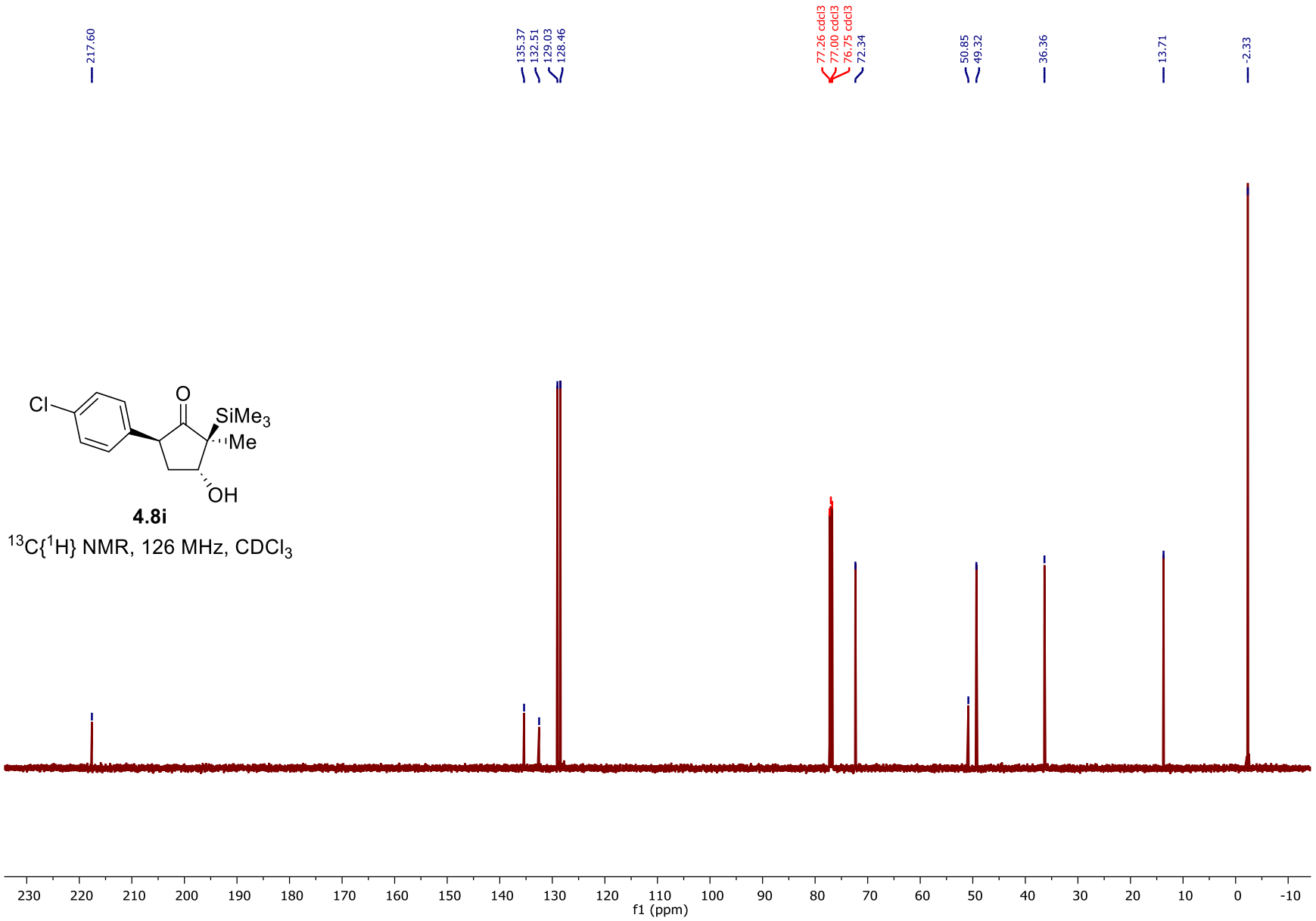
^{1}H NMR, 500 MHz, $CDCl_3$

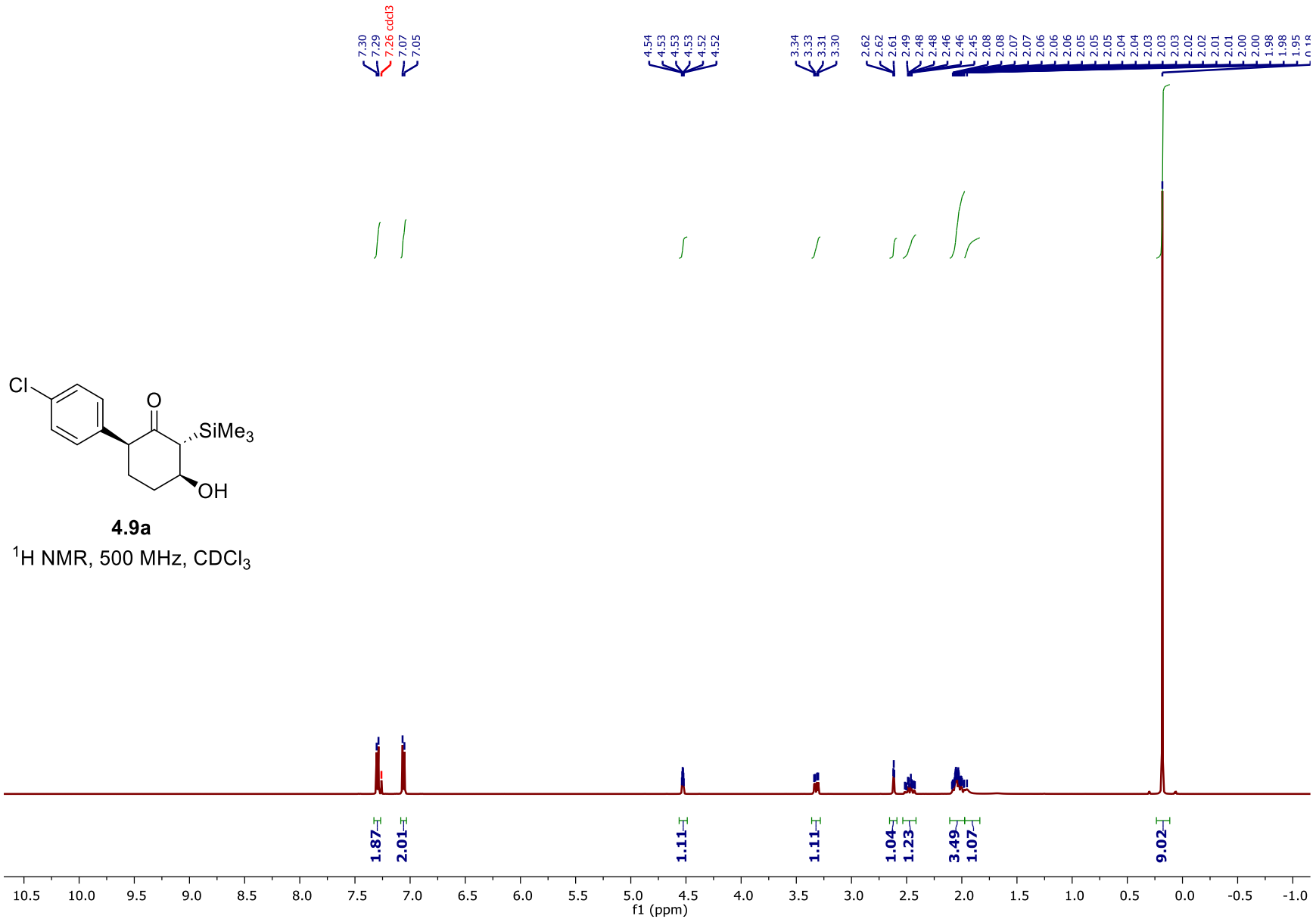

218.64
158.27
129.05
128.72
113.78
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
72.40
55.19
50.58
49.39
36.80
13.75
-2.34
MeO
O
SiMe3
Me
OH
4.8h
13C{1H} NMR, 126 MHz, CDCl3
f1 (ppm)



4.8i

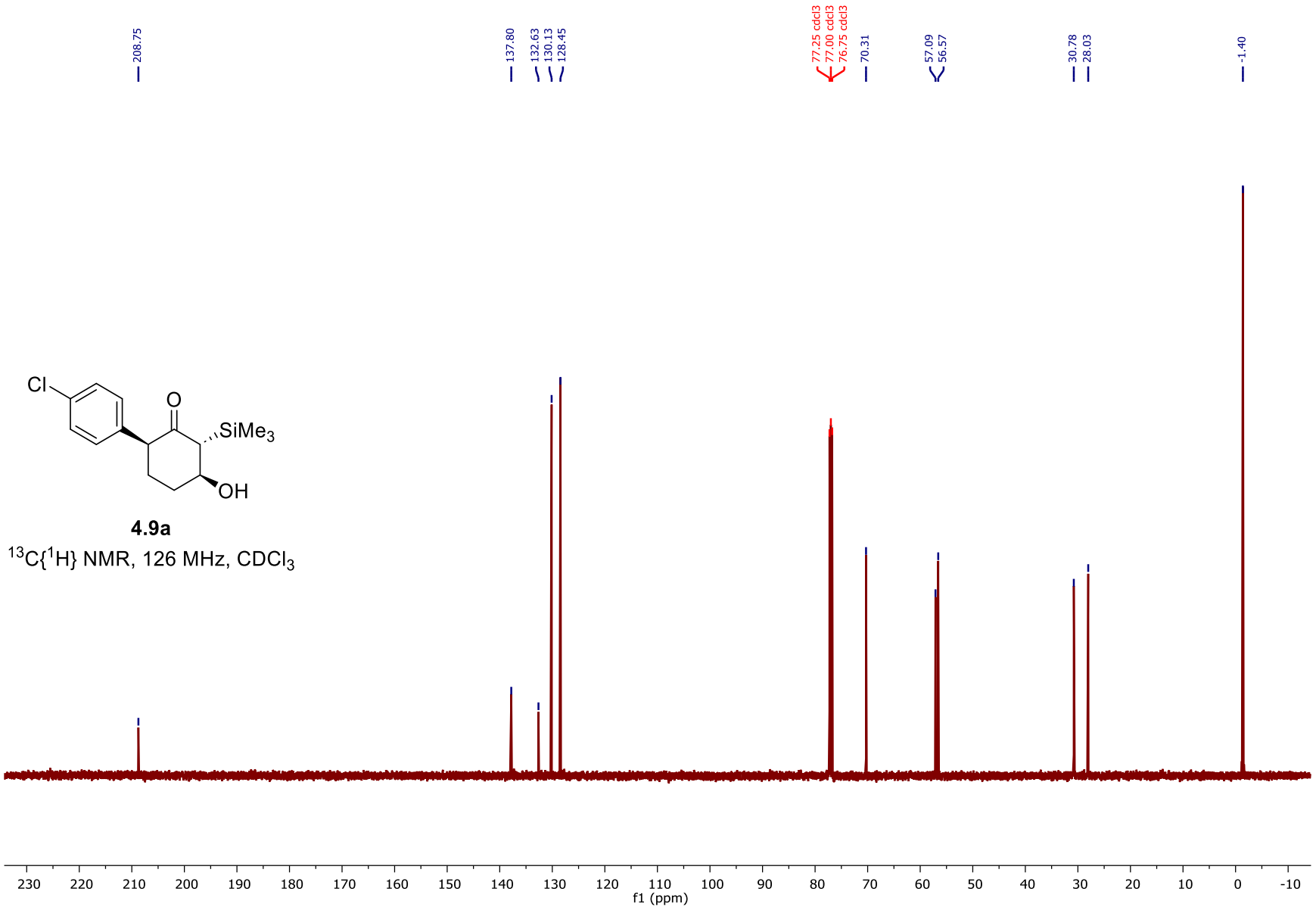
^{1}H NMR, 500 MHz, $CDCl_3$

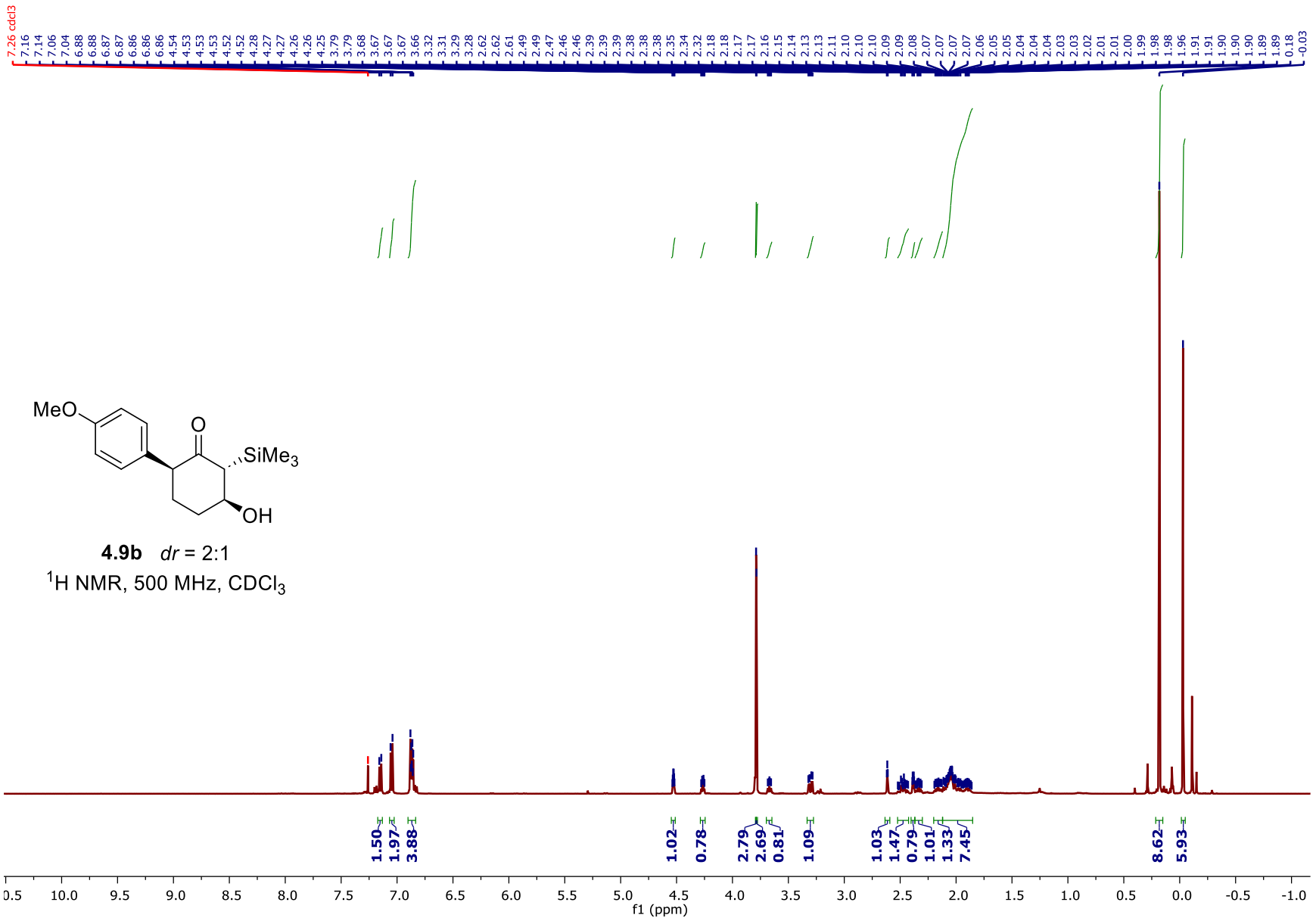

217.60
135.37
132.51
129.03
128.46
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
72.34
50.85
49.32
36.36
13.71
-2.33
Cl
O
SiMe3
Me
OH
4.8i
13C{1H} NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

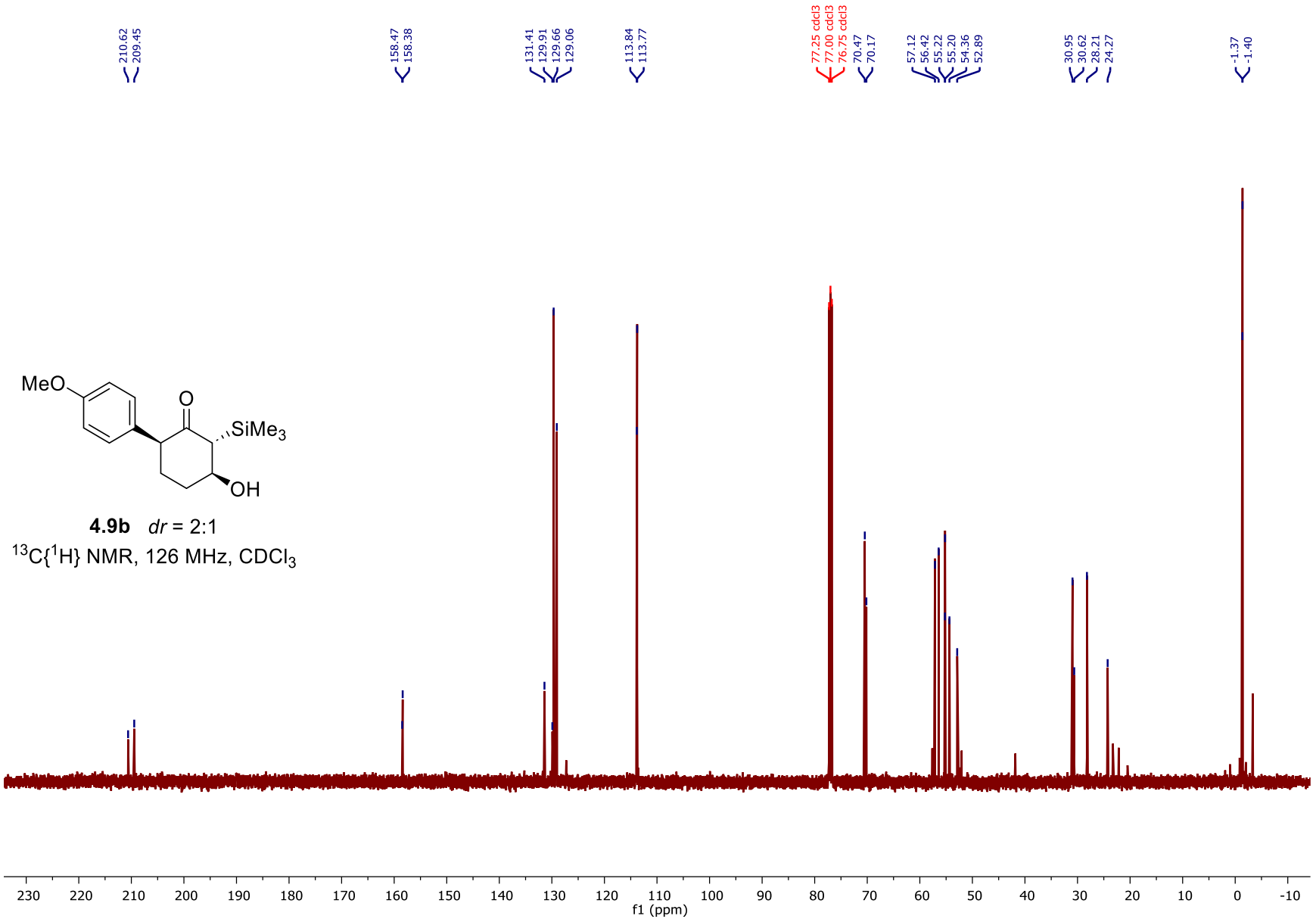


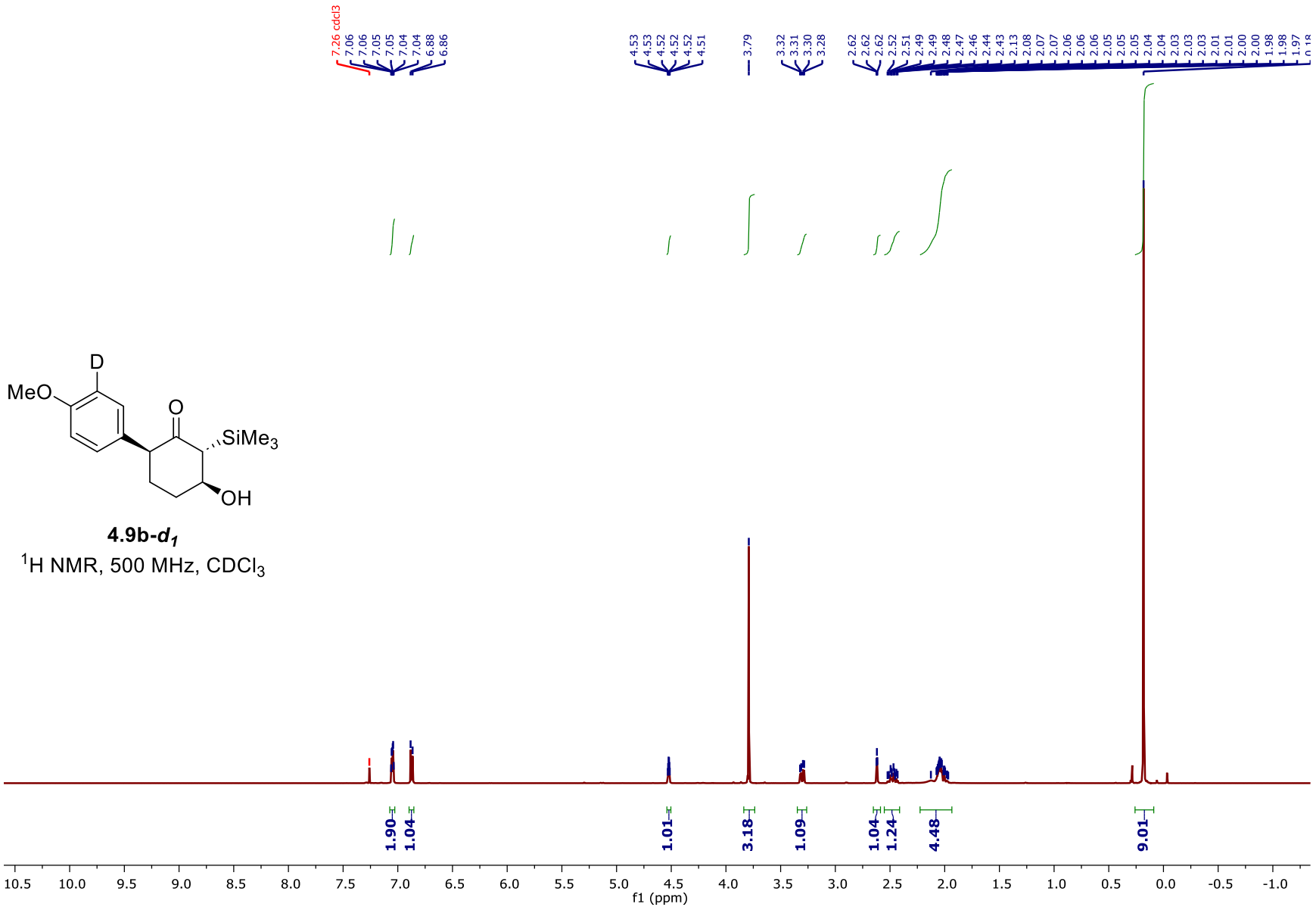
4.9a

^{1}H NMR, 500 MHz, $CDCl_3$


208.75
137.80
132.63
130.13
128.45
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.31
57.09
56.57
30.78
28.03
-1.40
Cl
O
SiMe3
OH
4.9a
13C{1H} NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
O
SiMe3
OH
4.9b dr = 2:1
1H NMR, 500 MHz, CDCl3
f1 (ppm)


210.62
209.45
158.47
158.38
131.41
129.91
129.66
129.06
113.84
113.77
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.47
70.17
57.12
56.42
55.22
55.20
54.36
52.89
30.95
30.62
28.21
24.27
-1.37
-1.40
MeO
O
SiMe3
OH
4.9b dr = 2:1
13C{1H} NMR, 126 MHz, CDCl3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26 cdcl3
7.06
7.06
7.05
7.05
7.04
7.04
6.88
6.86
4.53
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4.52
4.52
4.52
4.51
3.79
3.32
3.31
3.30
3.28
2.62
2.62
2.62
2.52
2.51
2.49
2.49
2.48
2.47
2.46
2.44
2.43
2.13
2.08
2.07
2.07
2.06
2.06
2.06
2.05
2.05
2.05
2.04
2.04
2.03
2.03
2.03
2.01
2.01
2.00
2.00
2.00
1.98
1.97
D
MeO
O
SiMe3
OH
4.9b-d1
1H NMR, 500 MHz, CDCl3
1.90
1.04
1.01
3.18
1.09
1.04
1.24
4.48
9.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
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0.0
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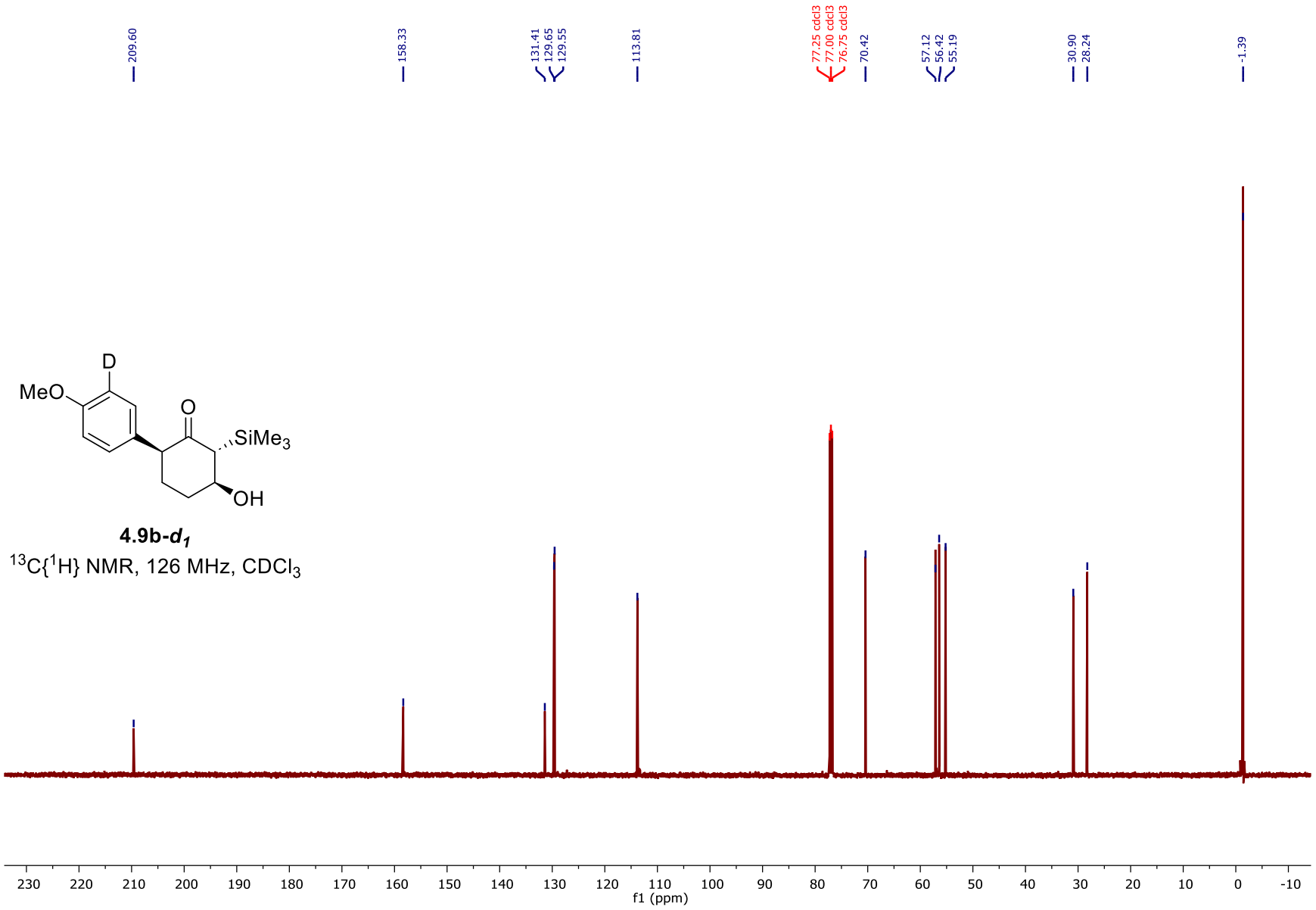
-1.0
f1 (ppm)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129.65
129.55
113.81
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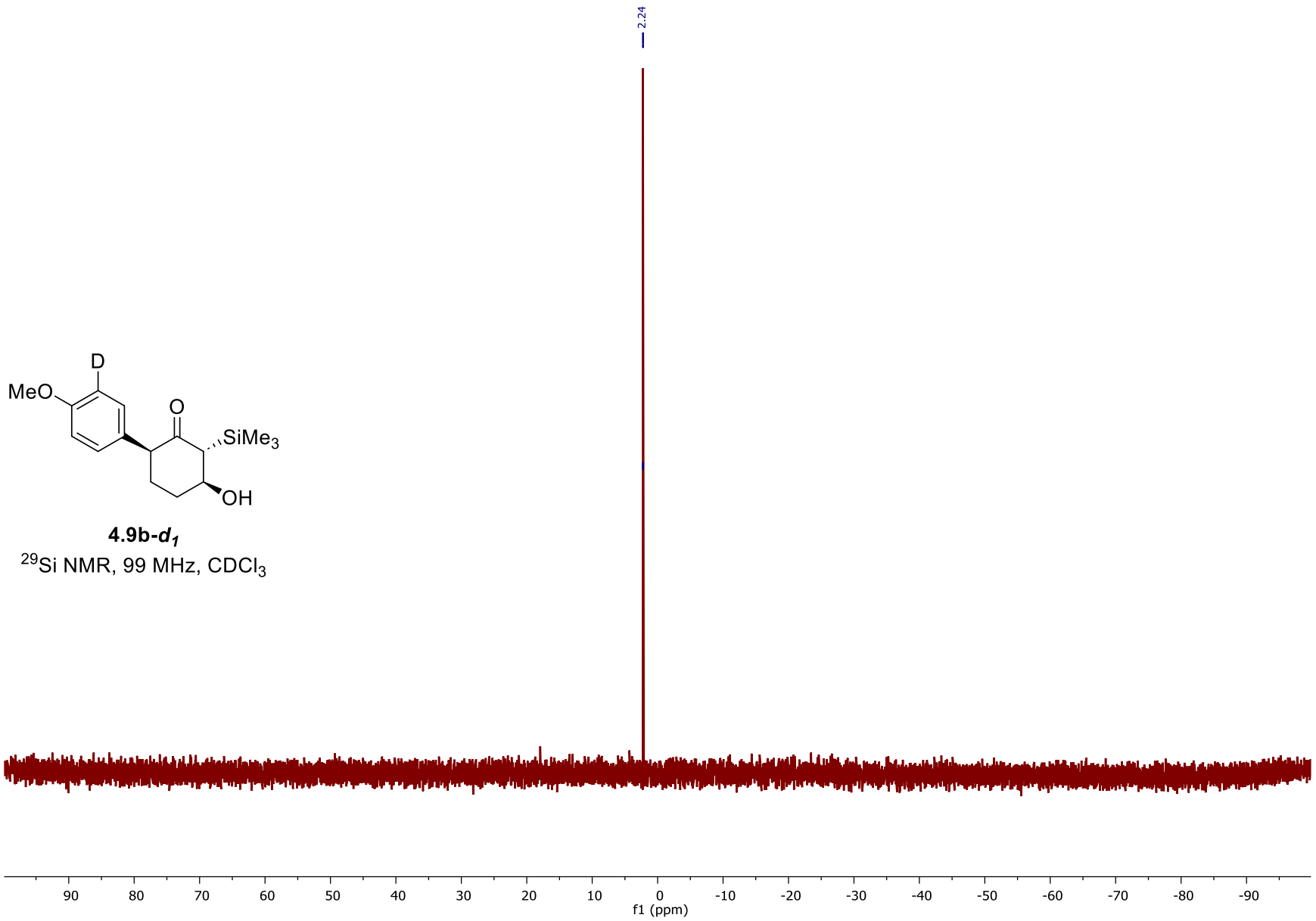
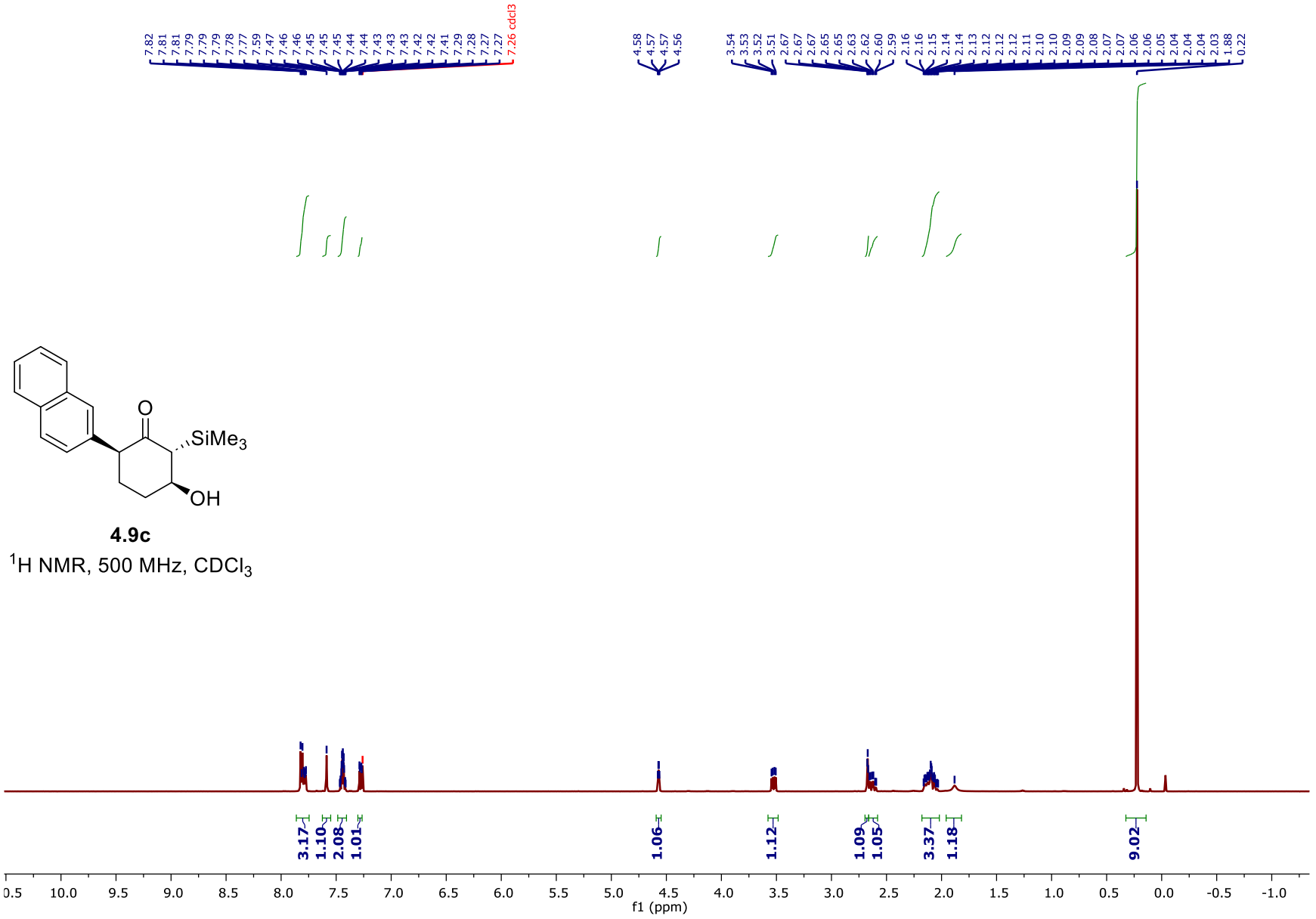
76.75 cdcl3
70.42
57.12
56.42
55.19
30.90
28.24
-1.39
D
MeO
O
SiMe3
OH
4.9b-d1
13C{1H} NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



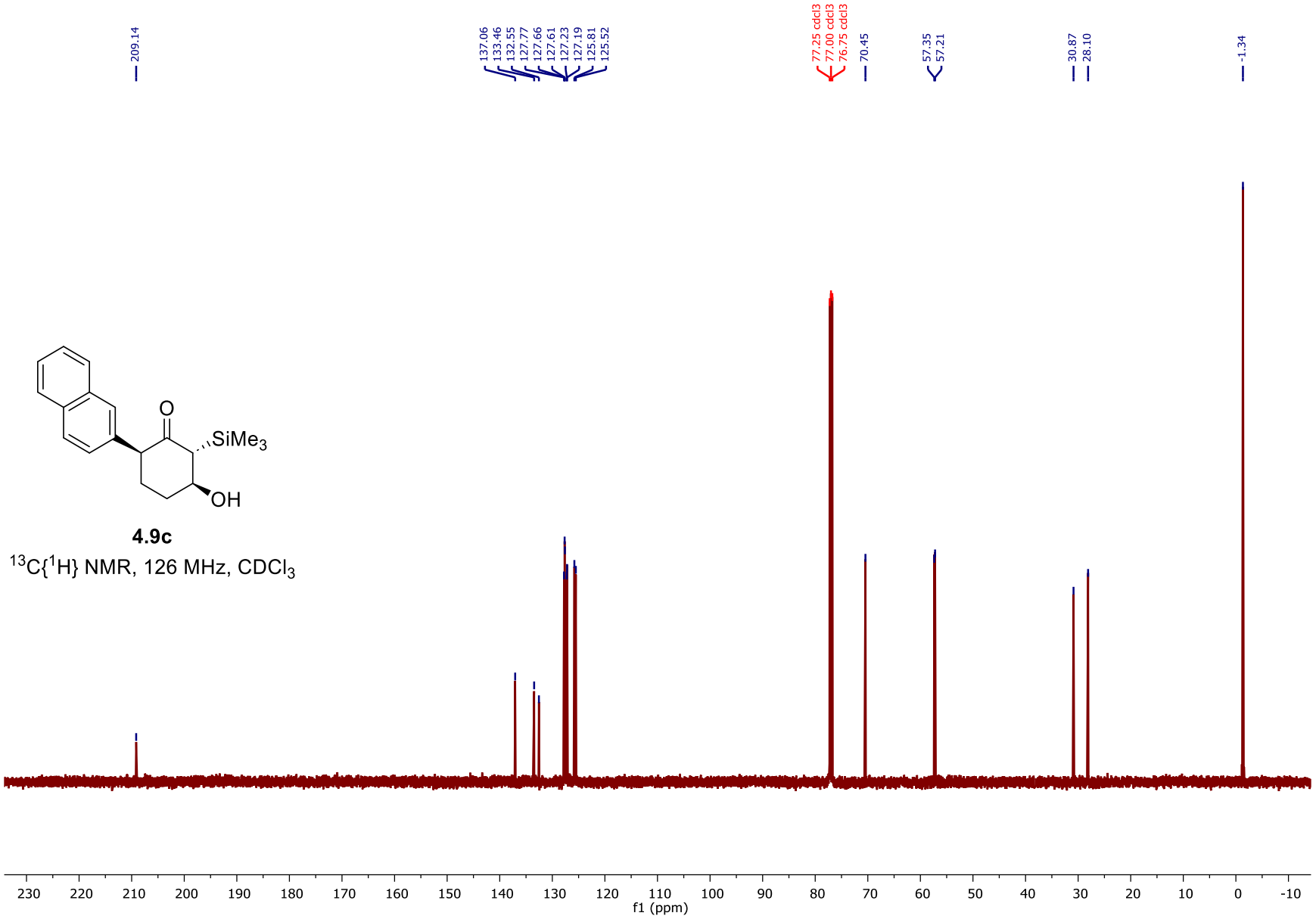
4.9b-*d*$_1$

^{29}Si NMR, 99 MHz, $CDCl_3$



4.9c

^{1}H NMR, 500 MHz, $CDCl_3$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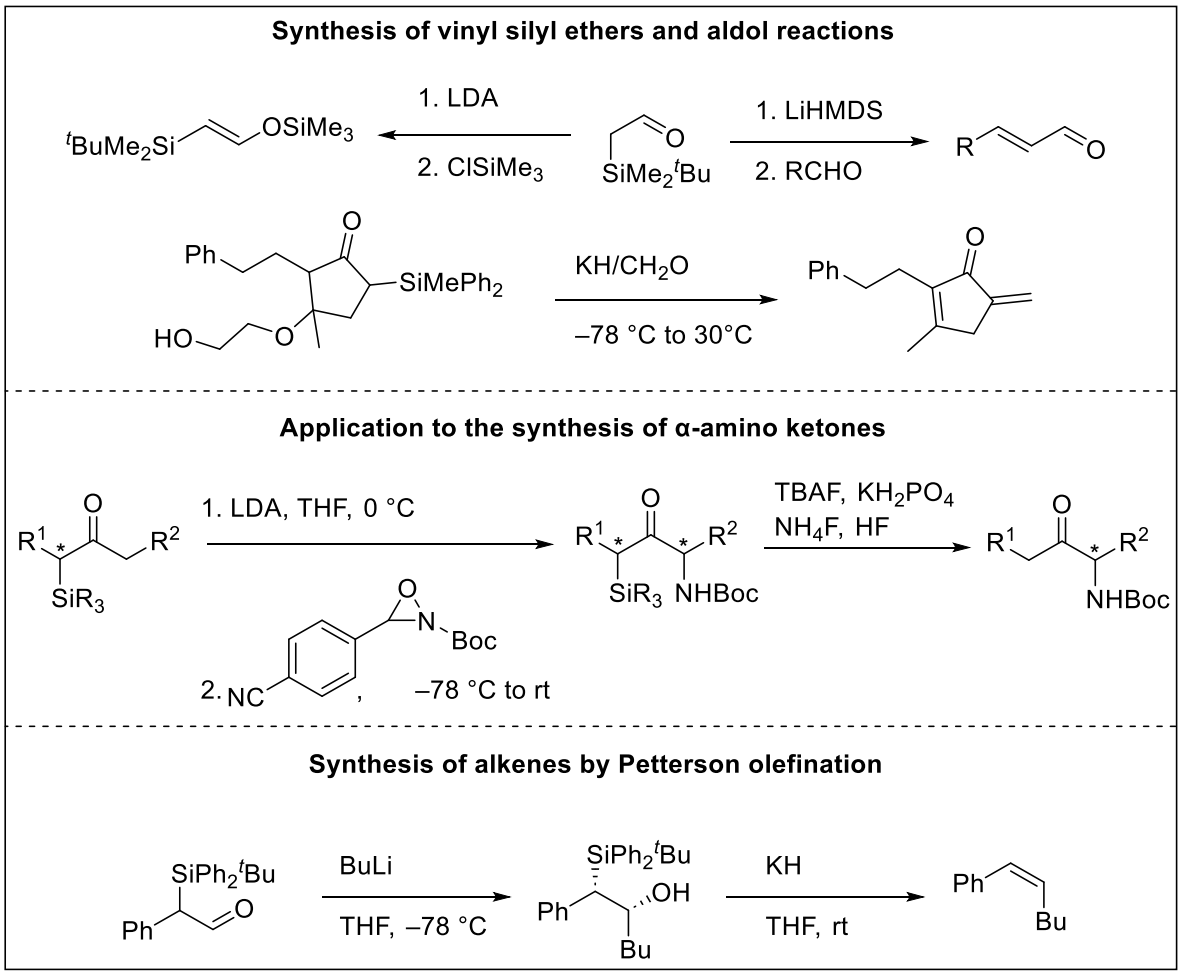
132.55
127.77
127.66
127.61
127.23
127.19
125.81
125.52
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.45
57.35
57.21
30.87
28.10
-1.34
O
SiMe3
OH
4.9c
13C{1H} NMR, 126 MHz, CDCl3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

CHAPTER 5.

SERENDIPITOUS [1,2]-CARBON-TO-CARBON SILYL MIGRATION IN α-HYRDOXY ALLYL SILANES: ACCESS TO α-SILYL ALKANALS

5.1. Introduction

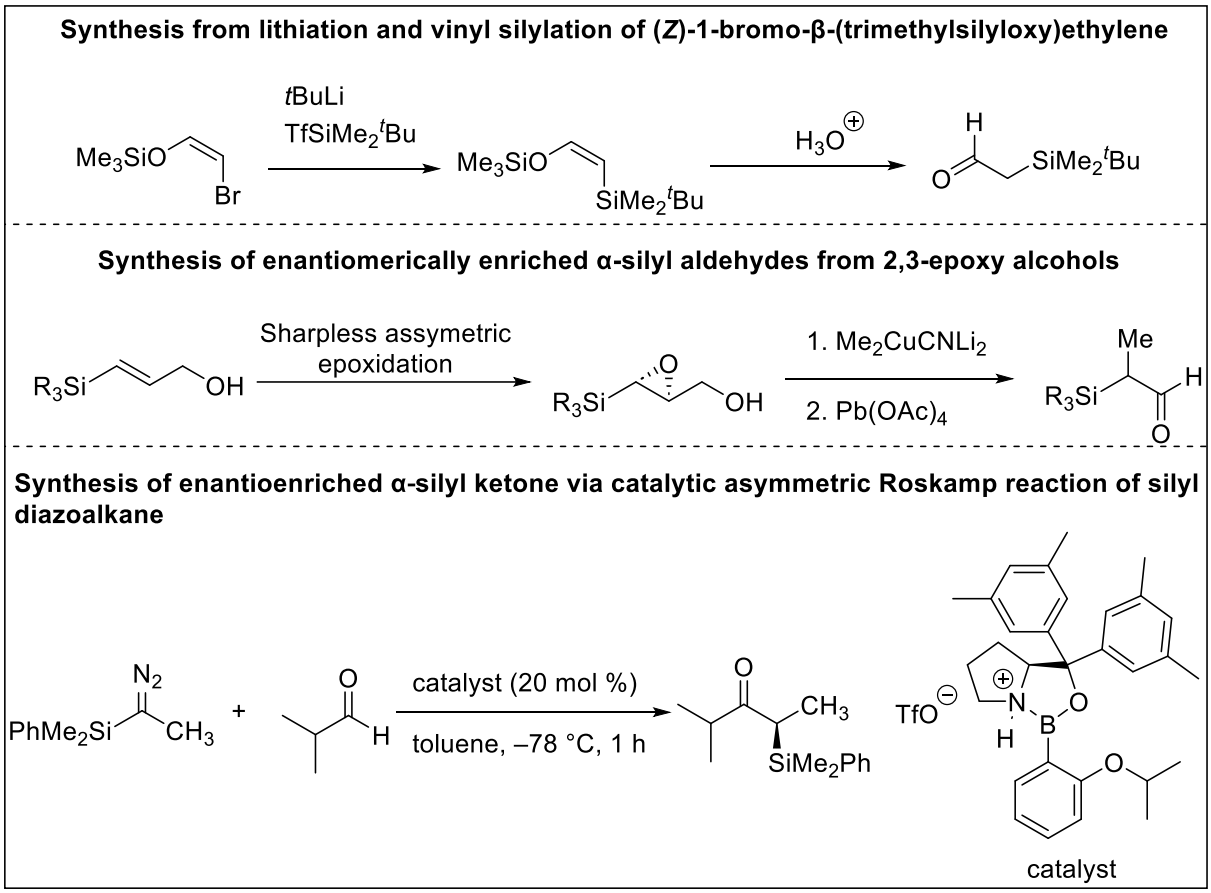
As we have seen in chapter 4, carbon to carbon silyl migration is rare compared to carbon to oxygen (Brook rearrangement)[1-4] or oxygen to carbon (retro-Brook rearrangement)[5-10] silyl shifts. Aldehydes and ketones with a silyl group at the α-position are good precursors for vinyl silyl ethers,[11] aldol reactions,[12] α-amino ketones,[13] and Peterson olefinations[14,15] (Scheme 5.1)



Scheme 5.1: Selected synthetic applications of α-silyl ketones and aldehydes

Despite their synthetic usefulness, few methods of accessing α-silyl ketones and aldehydes have been reported. Example of these methods are lithiation followed by silyl vinylation,[11]

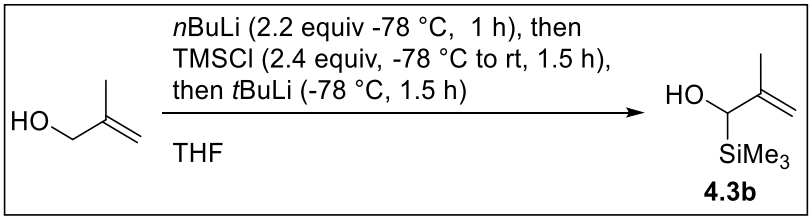
synthesis from 3-silyl-2,3-epoxy alcohols,[16] and catalytic asymmetric Roskamp reaction[17] (Scheme 5.2).



Scheme 5.2: Selected syntheses of α-silyl ketones and aldehydes

5.2. Serendipitous [1,2]-carbon-to-carbon silyl migration

During preparation of one of the intermediates for Wittig rearrangement in Chapter 4 (Scheme 5.3), a peak at around 9.5 ppm in ^{1}H NMR corresponding to an aldehyde was observed (Figure 5.1).



Scheme 5.3: Synthesis of 2-methyl-1-(trimethylsilyl)prop-2-en-1-ol **4.3b** by retro-Brook rearrangement

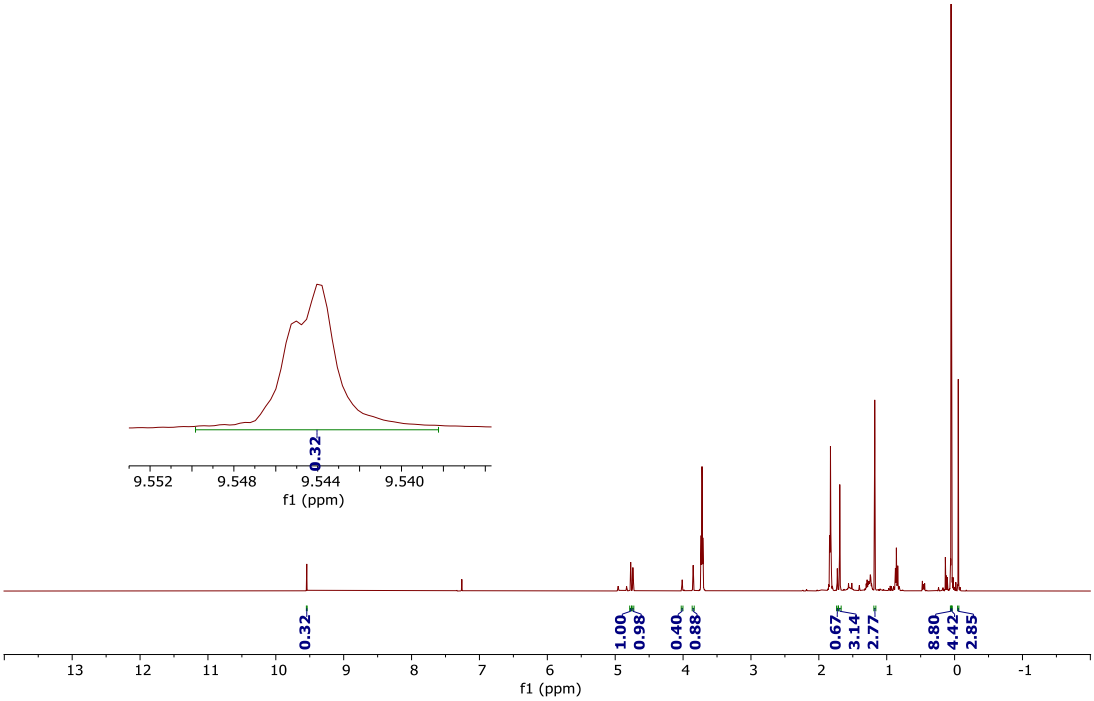


Figure 5.1: ^{1}H NMR of crude reaction mixture

At first, the peak was thought to be from a byproduct or impurity in the crude reaction mixture. After purification by column chromatography, the peak remained as a ~1:1 mixture with the compound of interest (Figure 5.2).

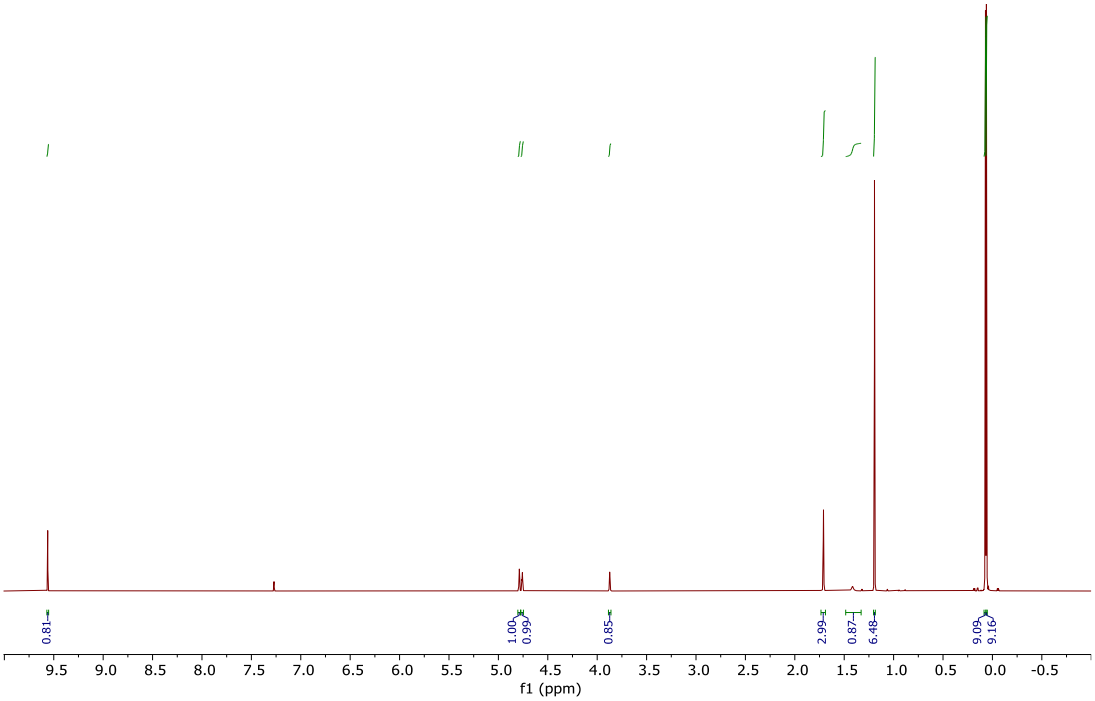


Figure 5.2: ^{1}H NMR of purified material in $CDCl_3$

At a glance, it was unclear whether this unknown compound had the same R_f value as the compound of interest or if it was being formed from that compound in the NMR tube. To further investigate this, the sample in the NMR tube was left overnight (~12 hours) and resubmitted for NMR analysis the following day. Surprisingly, the aldehyde peak had increased in intensity, overshadowing the compound of interest (Figure 5.3).

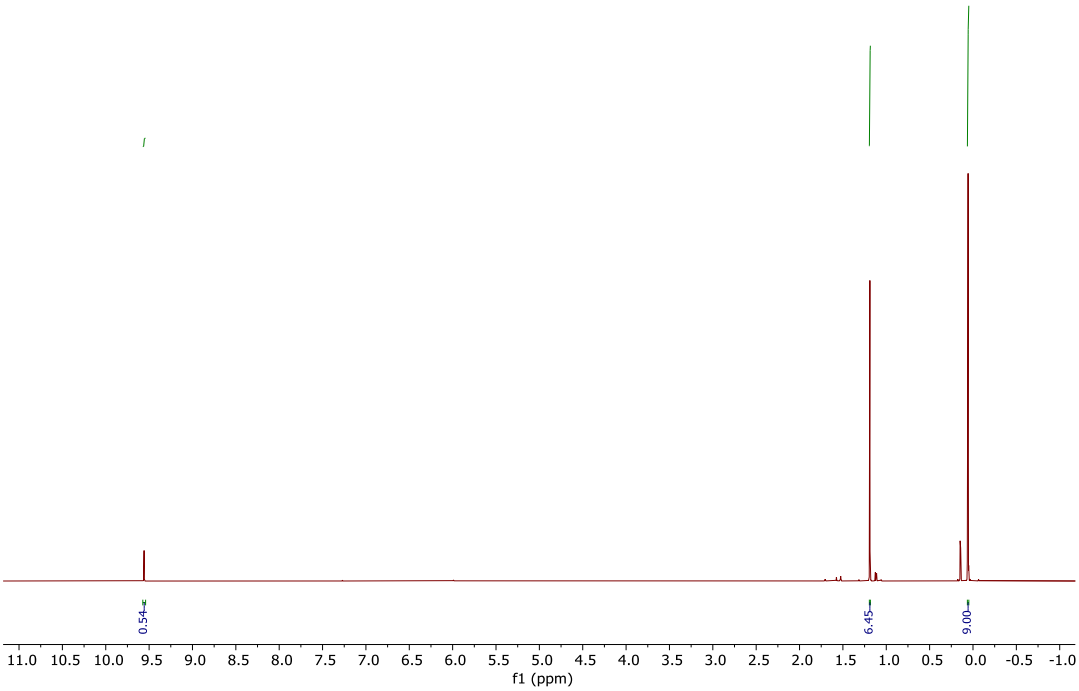
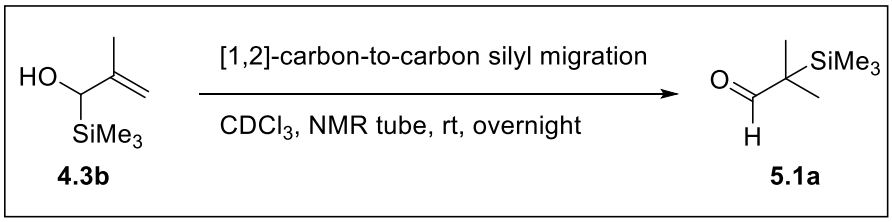


Figure 5.3: ^{1}H NMR of purified material in $CDCl_3$ after 12 hours

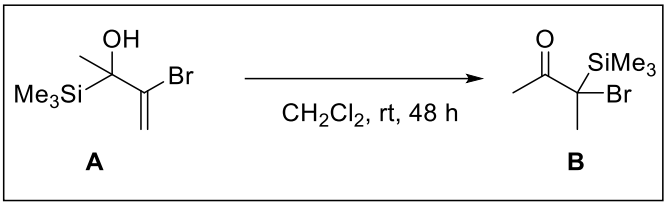
Having determined that the unknown compound was being formed from the compound of interest, we embarked on deducing its structure. It turned out to be 2-methyl-2-(trimethylsilyl)propanal, which is formed as a result of an irreversible [1,2]-carbon-to-carbon silyl migration of 2-methyl-1-(trimethylsilyl)prop-2-en-1-ol (Scheme 5.4).



Scheme 5.4: The [1,2]-carbon-to-carbon silyl migration of 2-methyl-1-(trimethylsilyl)prop-2-en-1-ol

Although this rearrangement looks trivial, we were surprised to find only one report of such migration in the literature (Scheme 5.5).[18] In this paper, the authors stated, "This unusual rearrangement reaction was **NOT** appreciably accelerated by the presence of acids (HCl gas, TsOH), and was completely **inhibited by weak bases** (pyridine, Et_3N) and even THF. We are not

aware of a precedent for this rearrangement process."



Scheme 5.5: Silyl migration of compound **5.2** in DCM

With this information, we decided to do further experiments to determine why this migration was occurring. Knowing that over many months of storage at room temperature, deuterated chloroform can become acidic,[19] we acquired the ^{1}H NMR in deuterated chloroform that was stored over K_2CO_3. Compound **5.1a** did not form immediately, but the transformation of compound **4.3b** to **5.1a** slowly occurred. Thus, the chloroform stored over K_2CO_3 only slows the reaction but it does not stop the process. Notably even with new bottle of chloroform, the aldehyde was formed overnight. However, compound **4.3b** was stable in deuterated benzene and the aldehyde was not formed even after weeks (Figure 5.4).

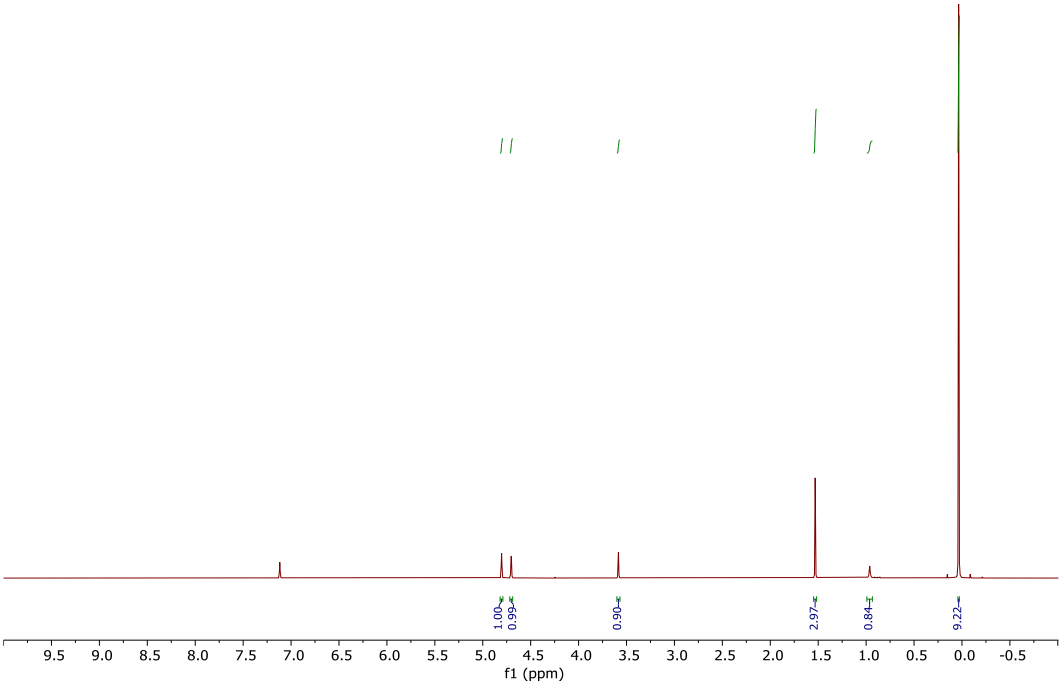
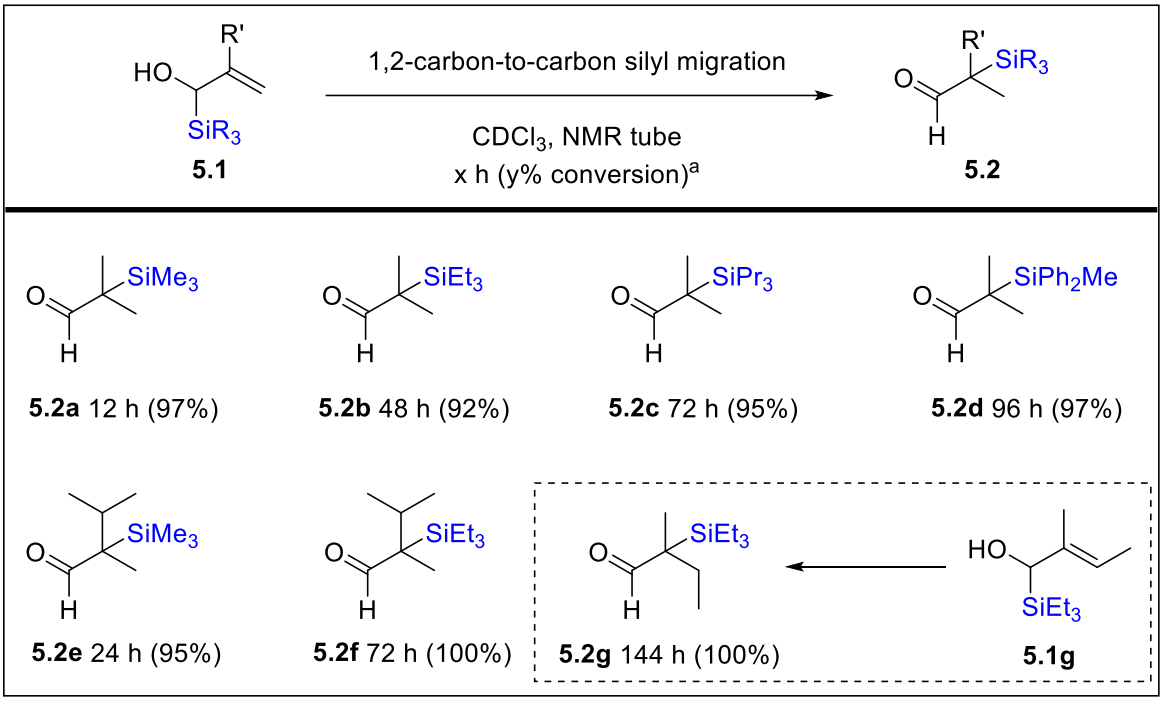


Figure 5.4: ^{1}H NMR of purified material in C_6D_6

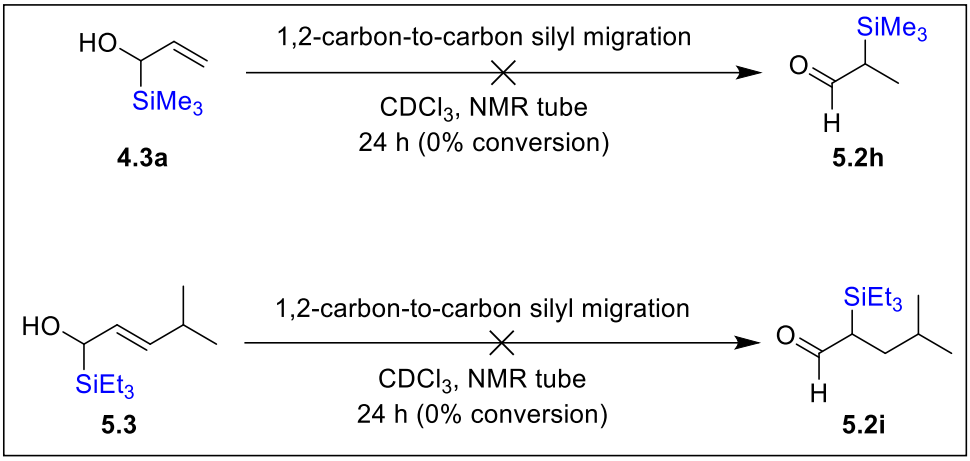
5.3. Substrate scope for [1,2]-carbon-to-carbon silyl migration

Next, we looked at the substrate scope of this migration. We began by modifying the substituents on silicon: Moving from trimethyl to triethyl, tripropyl and diphenyl methyl groups all effected the migration in varying amount of time (Scheme 5.6, substrates **5.1b** – **5.1d**). Having an isopropyl group in place of methyl at the olefin carbon proximal to silicon also worked well (Scheme 5.6, substrates **5.1e** and **5.1f**). Finally, [1,2]-silyl migration also occurred on a trisubstituted olefin **5.1g**.



Scheme 5.6: Substrate scope for [1,2]-carbon to carbon migration in NMR tube
[a]Conversion (y%) was determined by ^{1}H NMR integration

We then tested the importance of having an alkyl substituent on the olefin carbon β to silicon. The silyl migration was not observed in compounds **4.3a** and **5.3** even after days of sitting in NMR tube with $CDCl_3$ as a solvent (Scheme 5.7).



Scheme 5.7: Substrate scope limitation

When a mixture of **5.3** and **5.1f** was dissolved in $CDCl_3$ from a bottle that contained K_2CO_3, both alcohols could be observed at time zero. After 18 hours, alcohol **5.1f** had converted to aldehyde **5.2f** while alcohol **5.3** remained unchanged. On the fifth day, alcohol **5.1f** had completely transformed to aldehyde **5.2f** while silyl migration was not detected on alcohol **5.3**. (Figure 5.5)

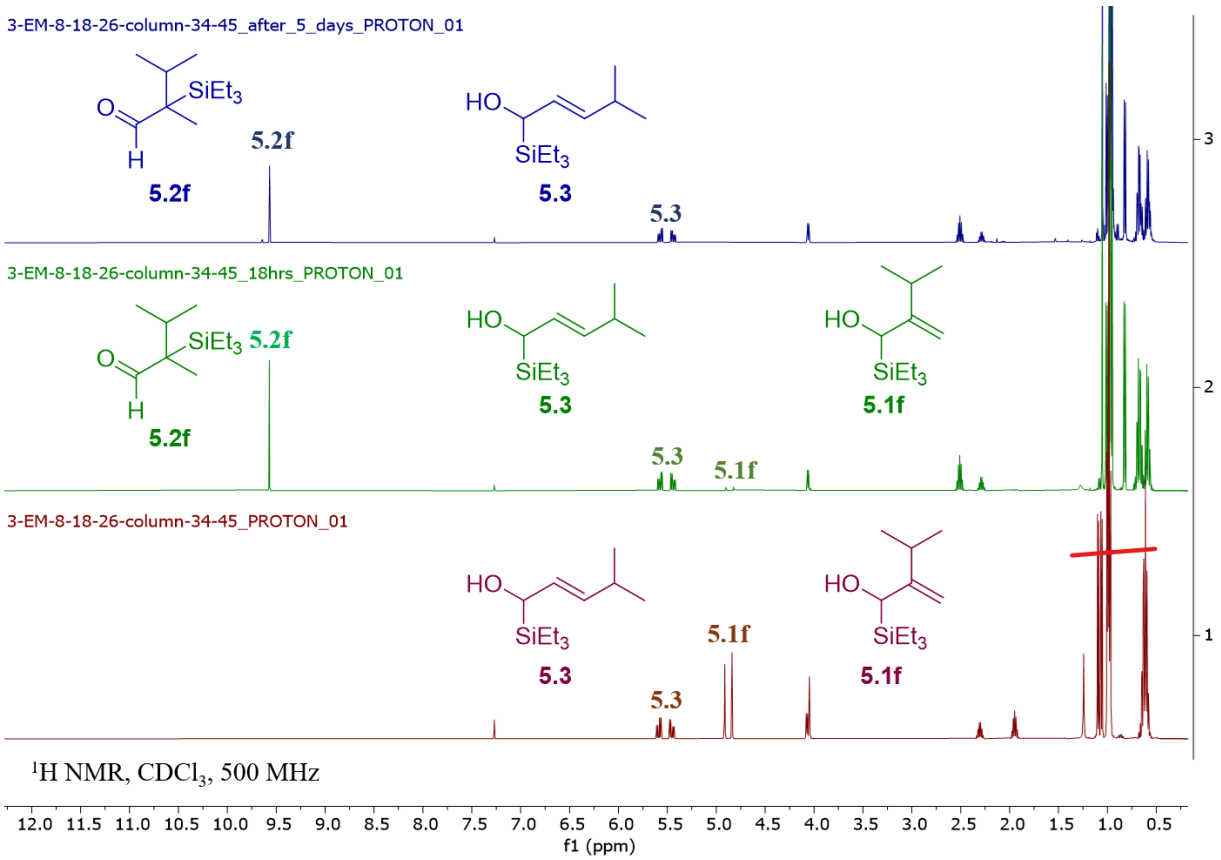
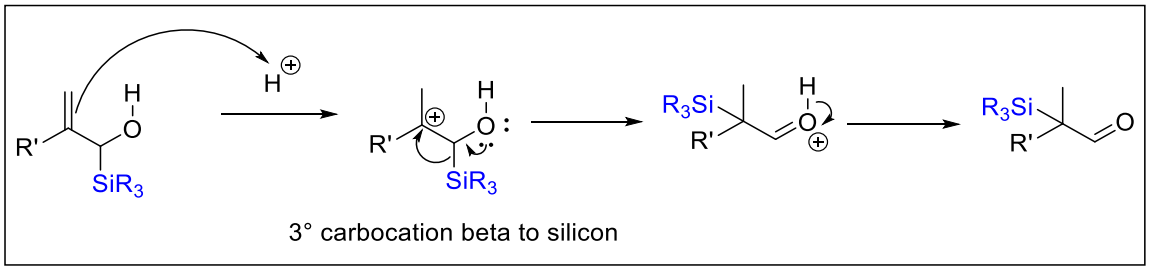


Figure 5.5: ^{1}H NMR of compounds **5.1f** and **5.3** over time

5.4. Proposed reaction mechanism of the [1,2]-carbon-to-carbon silyl migration

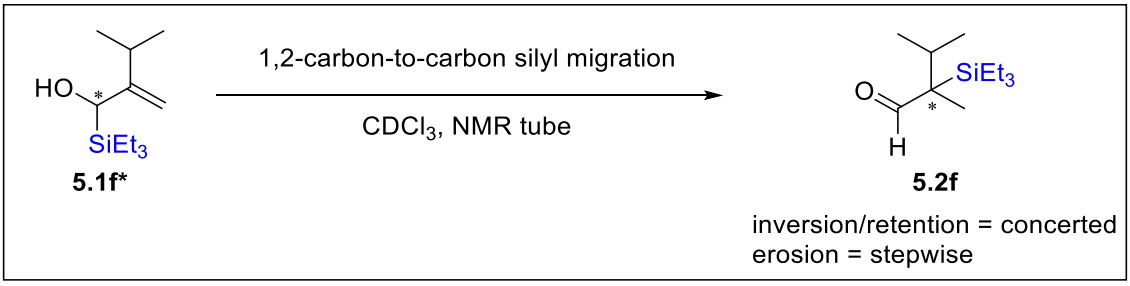
With the above observations of importance of having the alkyl group at the olefin carbon β to the silyl group, we propose that this reaction is acid catalyzed and proceeds by the olefin abstracting proton followed by subsequent silyl migration which is facilitated by carbonyl formation (Scheme 5.8).



Scheme 5.7: Proposed reaction mechanism of the silyl shift

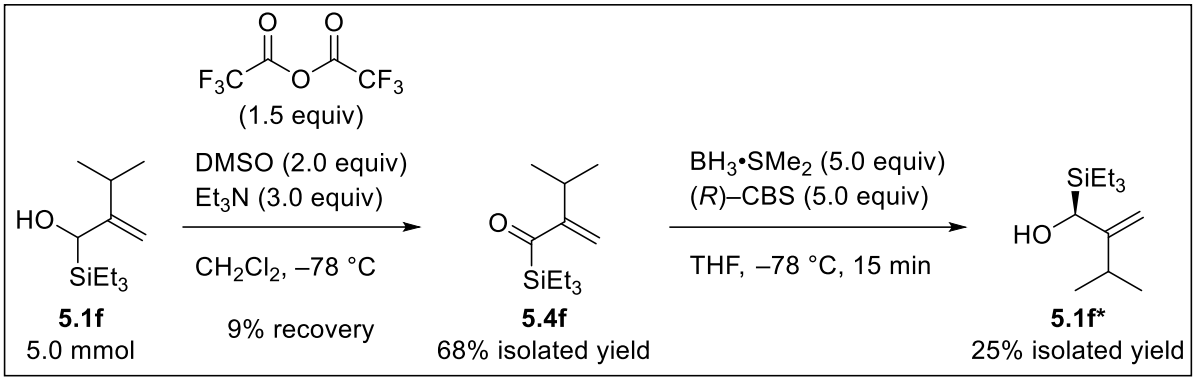
5.5. Attempted mechanistic investigation of the [1,2]-carbon-to-carbon silyl migration

To investigate whether the proposed mechanism is concerted or stepwise. Compound **5.1f** was studied since the silyl migration would create a new stereogenic center. An enantiomerically enriched **5.1f** will lead to **5.2f** with inversion / retention of stereochemistry (concerted) or erosion of stereochemistry (stepwise) with carbocation intermediate (Scheme 5.8).



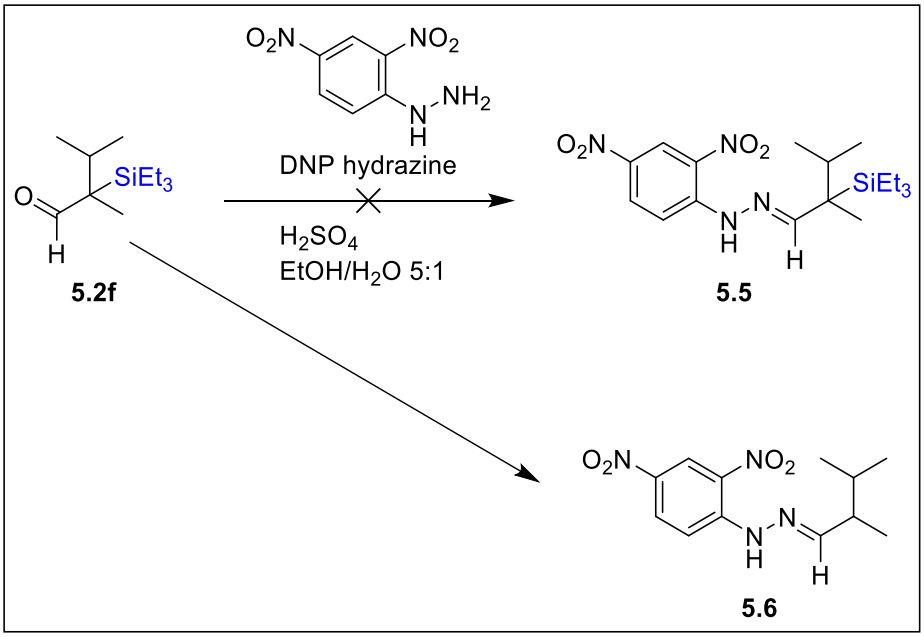
Scheme 5.8: Reaction design to investigate mechanistic pathways

With the above idea, we began with synthesizing the enantiomerically enriched **5.1f** by first oxidizing the racemic **5.1f** followed by asymmetric reduction of the resulting acyl silane **5.4f** using Corey-Bakshi-Shibata (CBS) catalyst[36] to generate **5.1f*** (Scheme 5.9).

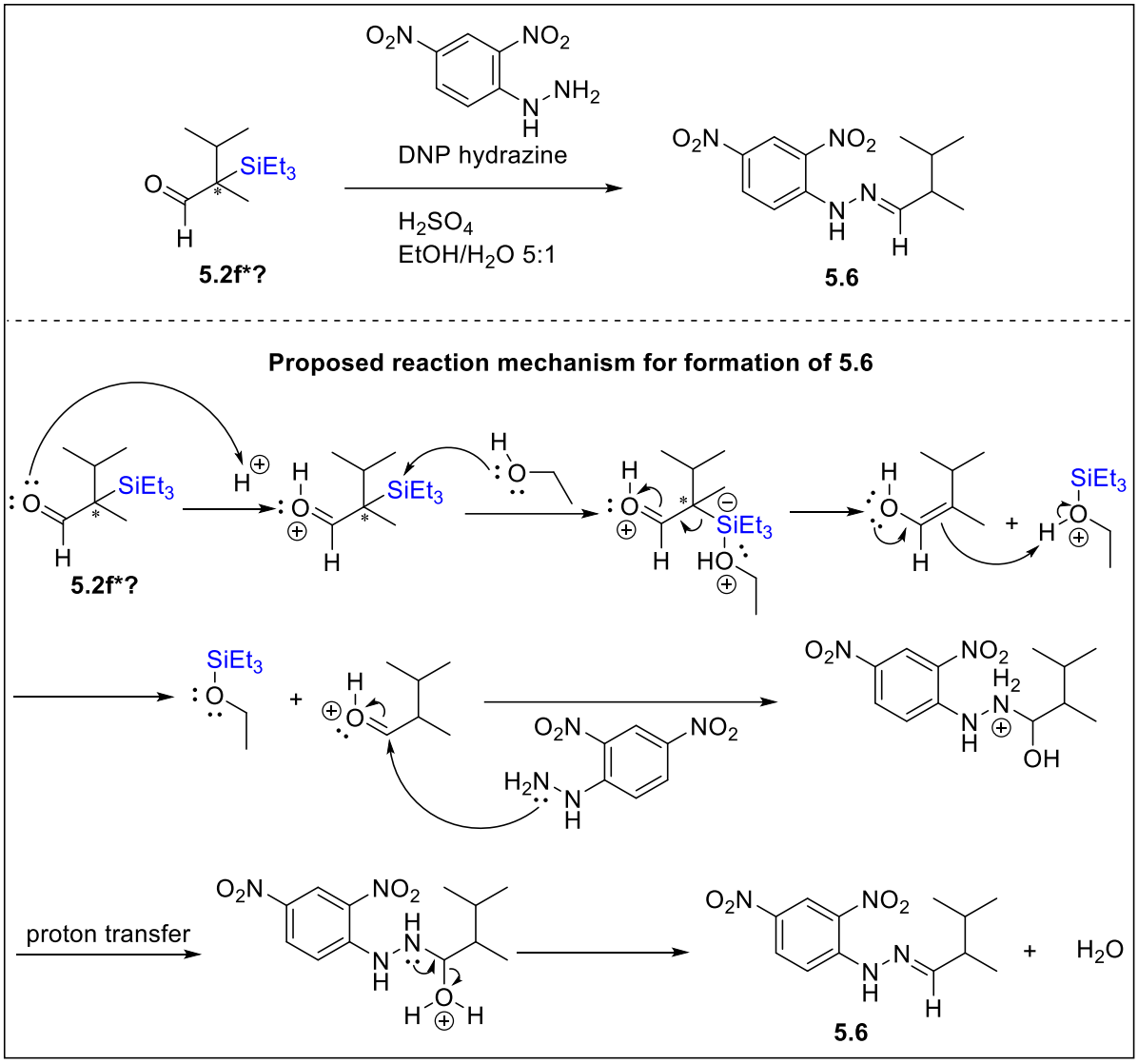


Scheme 5.9: Synthesis of enantioenriched **5.1f**

With compound **5.1f*** at hand, we subjected it to conditions leading to [1,2]-carbon-to-carbon silyl shift. Unfortunately, attempts to derivatize the resulting aldehyde with the purpose of determining absolute stereochemistry were unsuccessful. Aldehyde **5.2f** was reacted with 2,4-dinitrophenyl hydrazine with intention of forming 2,4-dinitrophenyl hydrazone (**5.5**), but instead, desilylated hydrazone **5.6** was formed (Scheme 5.10). The proposed mechanism is shown in Scheme 5.11.



Scheme 5.10: Attempted derivatization of **5.2f**



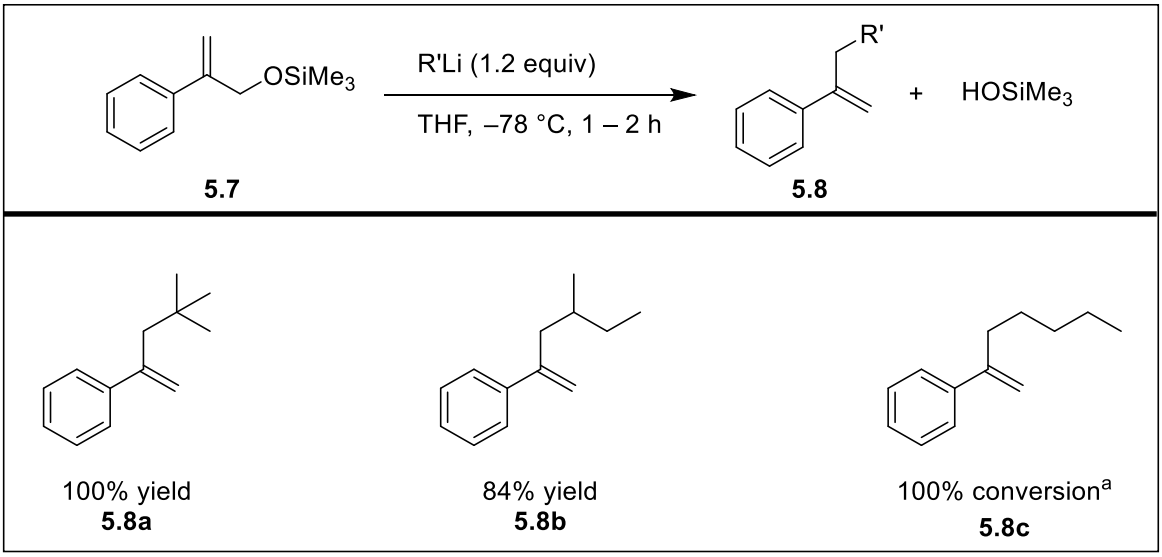
Scheme 5.11: Proposed reaction mechanism for the formation of the observed product **5.6**

Whether the mechanism of the [1,2]-carbon to carbon silyl migration is stepwise (involving carbocation formation) or concerted is not known at this time. Formation of carbocation intermediate is more likely since it would be doubly stabilized: a tertiary carbocation[20-22] and β to silicon.[23-35] Further investigations will be performed by others.

5.6. Unexpected S_N2-like reaction between the O-silylated 2-phenylprop-2-en-1-ol and butyl lithiums

Knowing the importance of having a substituent other than proton on the olefin carbon β to silicon, we embarked on synthesizing substrates containing aromatic groups at this position. In our

quest to expand the substrate scope of the silyl migration, we saw an unexpected transformation involving S_N2-like reaction between the O-silylated 2-phenylprop-2-en-1-ol and butyl lithiums (Scheme 5.12). To the best of our knowledge, this reaction had no literature precedence. Use of *tert*-butyllithium and *sec*-butyllithium resulted in the formation of products **5.8a** and **5.8b** in high yields. However, when we employed *n*-butyllithium, product **5.8c** was formed as a mixture with desilylated alcohol **5.9h** which could have resulted from unreacted starting material during workup. Lastly, there exists a challenge to access molecules with all C-sp^3 quaternary center by C–C coupling reactions.[37-50] This discovery will be helpful in accessing such products.



Scheme 5.12: Unexpected S_N2-like reactions
[a]The product was formed as a mixture with 2-phenyl ally alcohol

5.7. Conclusion

In summary, we have serendipitously discovered an irreversible [1,2]-carbon-to-carbon silyl migration leading to α-silylated alkanals. This migration proceeds even when the substituents on silicon are modified but requires an alkyl group at the olefin carbon β to silicon. Preliminary studies have also shown that the migration is acid catalyzed.

Further experimental studies to determine the mechanistic pathway of this migration are

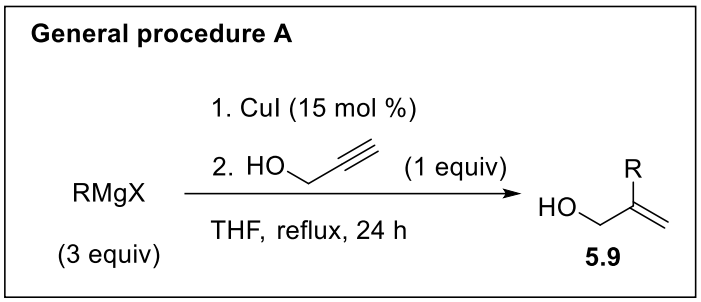
underway. Lastly, we have seen unexpected S_N2-like reaction between the O-silylated 2-phenylprop-2-en-1-ol and butyl lithiums in attempted retro-Brook rearrangement to expand the substrate scope. This reaction not only takes place on an *in situ* generated O-Silylated alcohol but also occurs when the O-silyl alcohol is prepared separately.

5.8. Experimental section

5.8.1. General information

Unless otherwise noticed all reactions were run under a positive atmosphere of nitrogen in oven- dried (at least 4 hours) or flame-dried round bottom flasks or disposable drum vials capped with rubber septa. Solvents were removed by rotary evaporation at temperatures lower than 45 ºC. Column chromatography was run on 230–400 mesh silica gel. Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone ketyl; dichloromethane and trimethylsilyl chloride were distilled from calcium hydride. Triethylsilyl chloride, tripropylsilyl chloride, and diphenylmethylsilyl chloride were used as received. *n*-Butyllithum (2.5 M in hexanes) and *sec*-butyllithium (1.4 M in cyclohexane) were purchased from Aldrich and their concentration calculated by titration with diphenylacetic acid (average of three runs). ^{1}H NMR spectra was collected in 500 MHz Varian instruments using $CDCl_3$ as solvent, which was referenced at 7.26 ppm (residual chloroform proton) and ^{13}C NMR spectra was collected in $CDCl_3$ at 126 MHz or 151 MHz and referenced at 77.0 ppm. Another deuterated solvent used for NMR analysis was benzene (referenced at 7.16 for ^{1}HNMR and 128.39 for ^{13}CNMR). High resolution mass spectrometric (HRMS) analysis was run in TOF instruments.

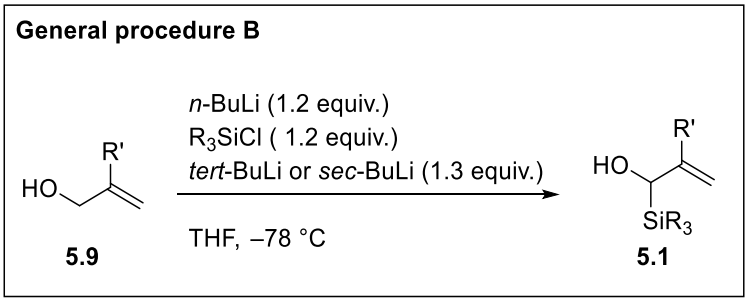
5.8.2. Synthesis of ally alcohols 5.9 from propargyl alcohols: General procedure A



Following a reported procedure,[51] for a 50 mmol scale reaction, to a dry 500 mL 3-neck round bottomed flask fitted with a magnetic stir bar was weighed 4.01 g of magnesium powder (165 mmol, 3.3 equiv), 3 crystals of iodine and 125 mL of freshly distilled dry THF. The two side necks of the flask were sealed with rubber septa and a reflux condenser was attached to the middle neck and the whole system purged with nitrogen after placing an oil bath was placed underneath the flask. On a separate 250 mL round bottomed flask a solution corresponding to 150 mmol (3.0 equiv) of alkyl/aryl halide in 100 mL dry THF was prepared. The 250 mL flask was sealed with a rubber septum and purged with nitrogen. The 250 mL flask was then connected to the 500 mL flask via canula. The alkyl/aryl halide solution was transferred in a dropwise manner for ~30 minutes to the 500 mL flask via canula while stirring and monitoring both the temperature of the oil bath and the reaction mixture in the 500 mL flask. After complete addition, the temperature of the oil bath had risen to 35 – 40 °C. The canula was removed and the oil bath was heated to 75 °C to allow the Grignard reagent to form over 1.5 hours. The heat was then turned off and the reaction mixture allowed to cool down to room temperature slowly without removing the oil bath. This was followed by addition of 1.43 g of copper (I) iodide (7.5 mmol, 0.15 equiv) which was done by removing one of the side neck rubber septum, quickly adding the CuI and replacing the septum fast enough to minimize contact with air. The resulting mixture was stirred at room temperature for 30 minutes after which 2.91 mL (50 mmol, 1 equiv) of propargyl alcohol as a solution in 25

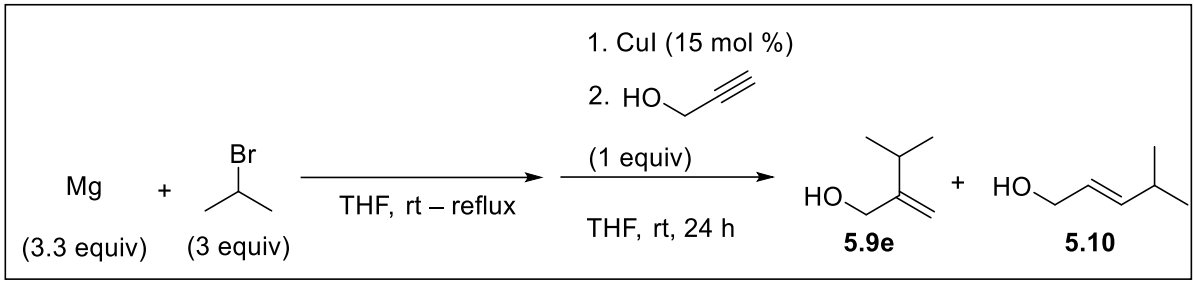
mL dry THF was added dropwise via syringe. After complete addition, the mixture was heated to 75 °C and stirred at this temperature for 24 hours. This was followed by turning off the heat and allowing the mixture to cool to room temperature. The oil bath was removed and replaced with an ice bath to cool down the mixture further to 0 °C. The mixture was quenched by slow addition of 80 mL of water. The reaction mixture was transferred to a 1000 mL separatory funnel and diluted with 100 mL ethyl ether. The layers were separated, and the aqueous layer was extracted with ether (80 mL X 3). Combined organic layers were washed with 80 mL water and 80 mL brine respectively then dried over anhydrous magnesium sulfate. The mixture was filtered, and the filtrate was concentrated on a rotorvap under reduced pressure to afford allyl alcohol **5.9** which was purified by column chromatography (Hexanes/EtOAc).

5.8.3. Preparation of α-hydroxy allyl silanes 4.3 – general procedure B:[52]



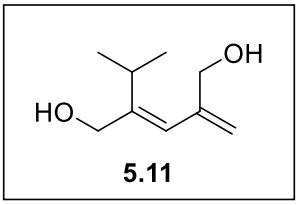
A solution of the corresponding allylic alcohol in THF was cooled at −78 °C, and *n*-butyllithium (1.6 M or 2.5 M in hexanes) was added dropwise over 5 min. After 30 min the corresponding chlorosilane was added dropwise via syringe. After the resulting solution was stirred for a given amount of time (see individual compounds procedure below), *sec*-butyllithium or *tert*-butyllithium (see below for details) was added dropwise over 30−60 min, and then the reaction was kept at the indicated temperature.

Synthesis of 3-methyl-2-methylenebutan-1-ol (5.9e) and (*E*)-4-methylpent-2-en-1-ol (5.10)



Following the general procedure A with slight modification compounds **5.9e** and **5.10** were synthesized from 8.00 g (330 mmol, 3.3 equiv) of magnesium, 28 mL (300 mmol, 3.0 equiv) of isopropyl bromide, 2.86 g CuI (15 mmol, 0.15 equiv) and 5.85 mL (100 mmol, 1.0 equiv) of propargyl alcohol: After reflux (formation of the Grignard reagent) the Grignard reagent was allowed to cool down to around 40 degrees Celsius. On a separate flask, copper (I) iodide and propargyl alcohol were stirred at 0 °C in THF (100 mL). The Grignard reagent was transferred to this flask via cannula and the reaction proceeded at room temperature for 24 hours and then quenched at minus 10 degrees Celsius, worked up and solvent evaporated. Purification by column chromatography (30% Et_2O in hexanes) afforded total of 7428 mg, 74 mmol (74% isolated yield) of **5.9e** and **5.10**, as a 5:1 mixture: a 74% yield. 803 mg of another side product **5.11** was also formed (see structure below).

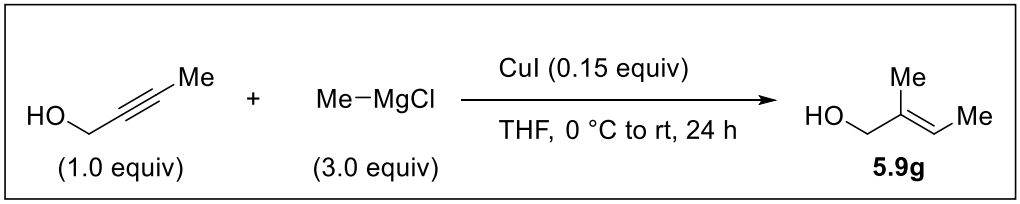
Spectroscopic data for **5.9e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.97 (q, *J* = 1.5 Hz, 1H), 4.86 (p, *J* = 1.2 Hz, 1H), 4.08 (t, *J* = 1.3 Hz, 2H), 2.29 (hept, *J* = 6.4 Hz, 1H), 2.18 (s, 1H), 1.04 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 106.8, 64.7, 30.9, 21.7. Spectroscopic data were similar to those reported in the literature.[53] The minor product **5.10** spectroscopic data also matched the literature report.[54]



5.11

Spectroscopic data for (*E*)-2-isopropyl-4-methylenepent-2-ene-1,5-diol **5.11**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (dt, *J* = 10.2, 1.1 Hz, 1H), 5.26 (q, *J* = 1.5 Hz, 1H), 4.91 (dd, *J* = 1.9, 1.0 Hz, 1H), 4.10 – 4.06 (m, 2H), 4.02 (d, *J* = 1.1 Hz, 2H), 3.43 (s, 2H), 2.48 (dp, *J* = 10.1, 6.6 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 138.4, 136.2, 114.7, 67.4, 65.6, 27.9, 23.1.

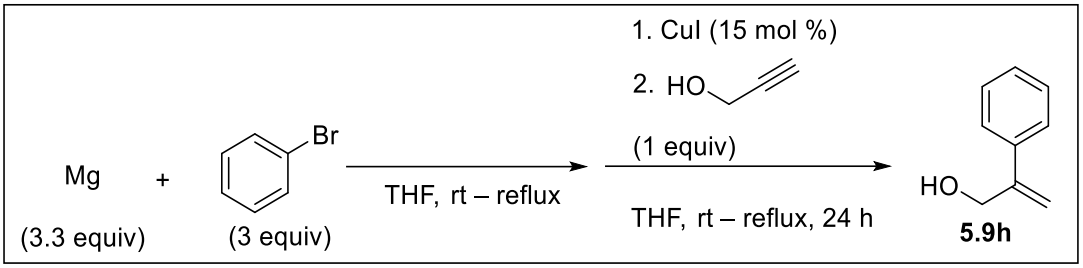
Synthesis of (*E*)-2-methylbut-2-en-1-ol (5.9g)



(1.0 equiv) (3.0 equiv) **5.9g**

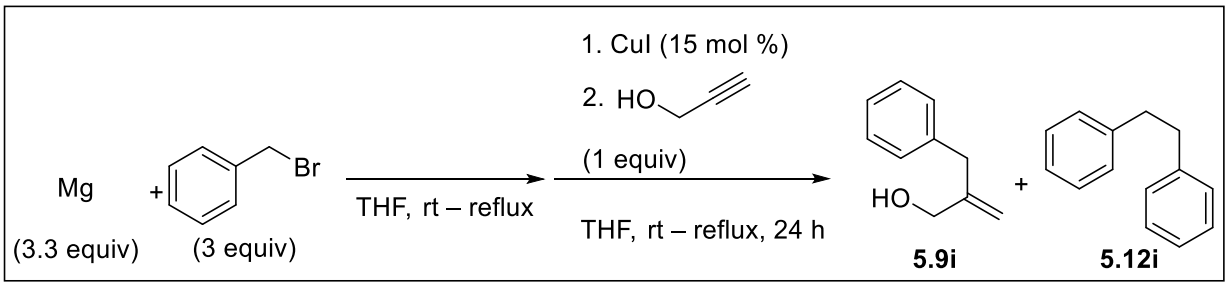
Following procedure A: This time around having the propargyl alcohol and CuI in a 500 mL RB flask at 0 °C, MeMgCl as a solution in THF (3M) was added. Accidentally, the flask cracked while quenching and spilled the reaction mixture in the hood. A small amount of the reaction mixture was recovered and worked up. Purification by column chromatography afforded 731 mg as a mixture of **5.9g** and the starting propargyl alcohol (**5.9g** 66% W/W with but-2-yn-1-ol). Spectroscopic data for **5.9g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (q, *J* = 6.8 Hz, 1H), 3.96 (s, 2H), 2.14 (s, 2H), 1.63 (s, 3H), 1.59 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.3, 120.5, 68.8, 13.2, 13.0. Spectroscopic data were similar to those reported in the literature.[55]

Synthesis of 2-phenylprop-2-en-1-ol (5.9h)



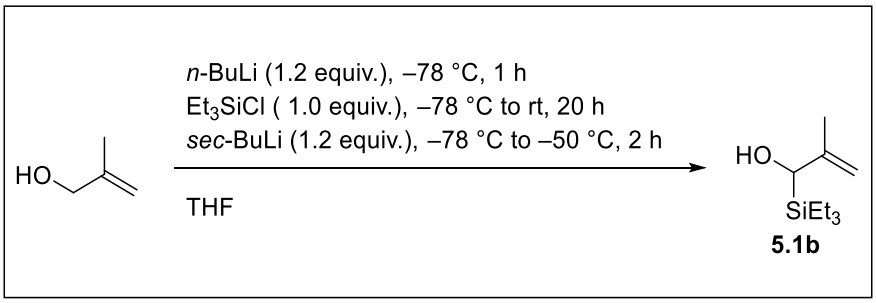
Applying procedure A to 4 g (165 mmol, 3.3 equiv) of magnesium, 15.8 mL (150 mmol, 3.0 equiv) of bromobenzene, 1.43 g CuI (7.5 mmol, 0.15 equiv) and 2.88 mL (50 mmol, 1.0 equiv) of propargyl alcohol, alcohol **5.9h** was prepared in quantitative yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 5.48 (q, *J* = 1.0 Hz, 1H), 5.36 (q, *J* = 1.4 Hz, 1H), 4.53 (dd, *J* = 1.5, 0.9 Hz, 2H), 2.22 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 138.4, 128.4, 127.8, 126.0, 112.5, 64.7. Spectroscopic data were similar to those reported in the literature.[56]

Attempted synthesis of 2-benzylprop-2-en-1-ol (5.9i)



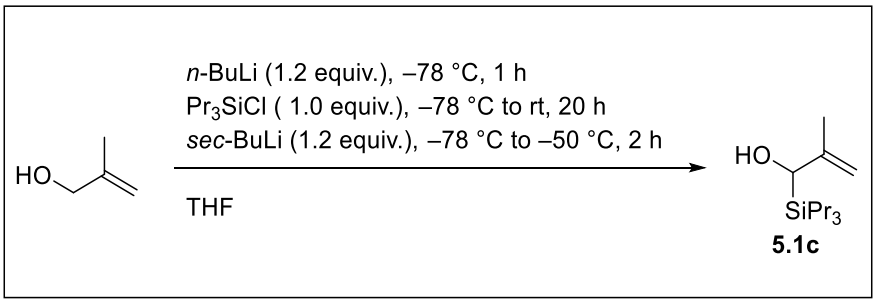
Applying general procedure A to 3.65 g (150 mmol, 3.0 equiv) of magnesium, 16.04 mL (135 mmol, 2.7 equiv) of benzyl bromide, 1.43 g CuI (7.5 mmol, 0.15 equiv) and 2.88 mL (50 mmol, 1.0 equiv) of propargyl alcohol, compound **5.9i** could not be obtained. Instead, 1,2-diphenylethane **5.12i** was formed in quantitative yield. Spectroscopic data for **5.12i**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.33 – 7.25 (m, 6H), 3.03 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 128.4, 128.3, 125.9, 37.9. Spectroscopic data were similar to those reported in the literature.[57]

Synthesis of 2-methyl-1-(triethylsilyl)prop-2-en-1-ol (5.1b)



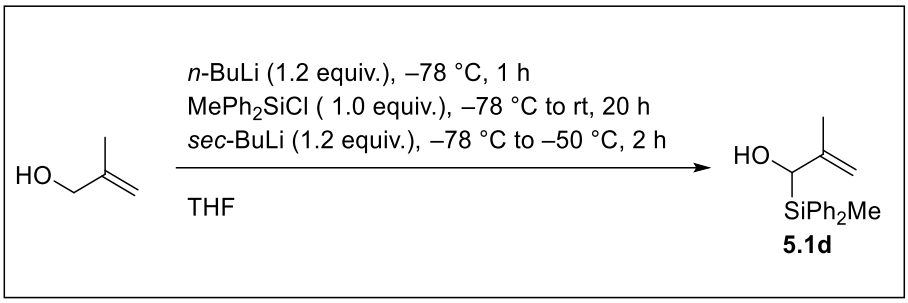
Following general procedure B, a solution of 1.26 mL 2-methyl allyl alcohol (1081.7 mg, 15 mmol, 1 equiv.) in THF (25 mL) was cooled to −78 °C. *n*-BuLi (2.4 M in hexanes, 7.5 mL, 18 mmol, 1.2 equiv.) was added dropwise and the mixture stirred at –78 °C for 1 h. Chlorotriethylsilane (2.52 mL, 15 mmol, 1.0 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –78 °C to room temperature for 18 hours resulting in the formation of a white suspension. The mixture was cooled back to –78 °C followed by dropwise addition of *sec*-butyllithium (1.4 M in cyclohexane, 12.9 mL, 18 mmol, 1.2 equiv.) and the reaction stirred for an additional 2 hours at –78 °C to –50 °C. The reaction mixture was cooled back to –78 °C and quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 20 mL). Then all the organic phases were combined, washed with H_2O (20 mL) and brine (20 mL) respectively, and dried over anhydrous $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography, R_f = 0.3 (15% Et_2O in hexanes) to afford 1.4 g, 7.5 mmol (50% isolated yield) of compound **5.1b** as a colorless liquid. ^{1}H NMR (500 MHz, C_6D_6) δ 4.88 (tq, *J* = 1.7, 0.8 Hz, 1H), 4.74 (h, *J* = 1.3 Hz, 1H), 3.80 (s, 1H), 1.61 (dt, *J* = 1.3, 0.7 Hz, 3H), 1.23 (s, 1H), 1.02 (t, *J* = 7.9 Hz, 9H), 0.65 (qd, *J* = 14.9, 7.6 Hz, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 149.4, 107.1, 70.1, 21.0, 8.1, 2.8.

Synthesis of 2-methyl-1-(tripropylsilyl)prop-2-en-1-ol (5.1c)



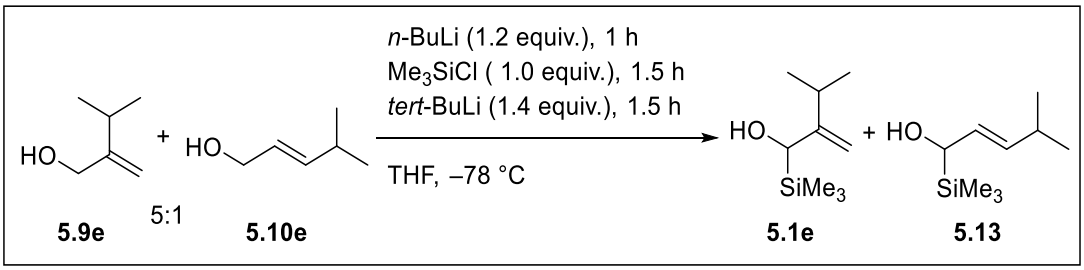
Following general procedure B, a solution of 0.84 mL 2-methyl allyl alcohol (721.1 mg, 10 mmol, 1 equiv.) in THF (25 mL) was cooled to −78 °C. *n*-BuLi (2.4 M in hexanes, 5 mL, 12 mmol, 1.2 equiv.) was added dropwise and the mixture stirred at –78 °C for 1 h. Chlorotripropylsilane (2.2 mL, 10 mmol, 1.0 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –78 °C to room temperature for 18 hours resulting in the formation of a white suspension. The mixture was cooled back to –78 °C followed by dropwise addition of *sec*-butyllithium (1.4 M in cyclohexane, 8.6 mL, 12 mmol, 1.2 equiv.) and the reaction stirred for an additional 2 hours at –78 °C to –50 °C. The reaction mixture was cooled back to –78 °C and quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 20 mL). Then all the organic phases were combined, washed with H_2O (20 mL) and brine (20 mL) respectively, and dried over anhydrous $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography (10% Et_2O in hexanes) to afford 491 mg, 2.2 mmol (22% isolated yield) of compound **5.1c** as a colorless liquid. ^{1}H NMR (500 MHz, C_6D_6) δ 4.89 (tt, *J* = 1.7, 0.7 Hz, 1H), 4.75 (p, *J* = 1.4 Hz, 1H), 3.80 (s, 1H), 1.63 (dd, *J* = 1.6, 0.7 Hz, 3H), 1.42 (dddd, *J* = 14.4, 12.8, 11.1, 7.3 Hz, 6H), 1.01 (t, *J* = 7.3 Hz, 9H), 0.97 (s, 1H), 0.74 – 0.59 (m, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 149.4, 107.2, 70.5, 21.1, 19.3, 18.3, 14.7.

Synthesis of 2-methyl-1-(methyldiphenylsilyl)prop-2-en-1-ol (5.1d)



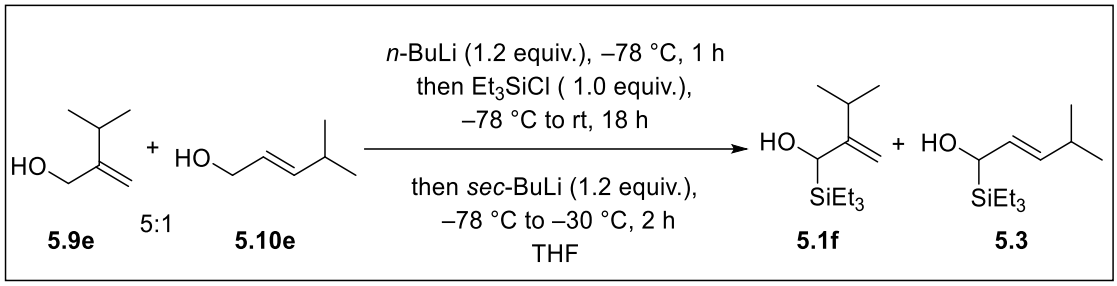
Following general procedure B, a solution of 1.26 mL 2-methyl allyl alcohol (1081.7 mg, 15 mmol, 1 equiv.) in THF (25 mL) was cooled to −78 °C. *n*-BuLi (2.4 M in hexanes, 7.5 mL, 18 mmol, 1.2 equiv.) was added dropwise and the mixture stirred at –78 °C for 1 h. Chloromethyldiphenylsilane (3.15 mL, 15 mmol, 1.0 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –78 °C to room temperature for 18 hours resulting in the formation of a white suspension. The mixture was cooled back to –78 °C followed by dropwise addition of *sec*-butyllithium (1.4 M in cyclohexane, 12.9 mL, 18 mmol, 1.2 equiv.) and the reaction stirred for an additional 2 hours at –78 °C to –50 °C. The reaction mixture was cooled back to –78 °C and quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 20 mL). Then all the organic phases were combined, washed with H_2O (20 mL) and brine (20 mL) respectively, and dried over anhydrous $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography (12% Et_2O in hexanes) to afford 391 mg, 1.5 mmol (10% isolated yield) of compound **5.1d** as a colorless liquid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.73 – 7.64 (m, 2H), 7.61 – 7.54 (m, 2H), 7.21 – 7.10 (m, 6H), 4.86 (dq, *J* = 1.7, 0.9 Hz, 1H), 4.72 (h, *J* = 1.4 Hz, 1H), 4.22 (s, 1H), 1.34 (s, 3H), 1.21 (s, 1H), 0.55 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 148.3, 136.1, 135.8, 135.8, 130.1, 128.5, 128.4, 108.7, 70.8, 21.6, -6.1.

Synthesis of 3-methyl-2-methylene-1-(trimethylsilyl)butan-1-ol (5.1e) and (*E*)-4-methyl-1-(trimethylsilyl)pent-2-en-1-ol (5.13)



Following general procedure B, a solution of 3-methyl-2-methylenebutan-1-ol **5.9e** and (*E*)-4-methylpent-2-en-1-ol **5.10e** (501 mg, 5.0 mmol, 1 equiv.) in THF (10 mL) was cooled to −78 °C. *n*-BuLi (2.4 M in hexanes, 2.5 mL, 12 mmol, 1.2 equiv.) was added dropwise and the mixture stirred at –78 °C for 1 h. Chlorotrimethylsilane (0.65 mL, 5.0 mmol, 1.0 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –78 °C for 1.5 hours resulting in the formation of a white suspension. This was followed by dropwise addition of *tert*-butyllithium (1.6 M in pentane, 4.4 mL, 7.0 mmol, 1.4 equiv.) and the reaction stirred for an additional 1.5 hours at –78 °C and quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 20 mL). Then all the organic phases were combined, washed with H_2O (20 mL) and brine (20 mL) respectively, and dried over anhydrous $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography (10% Et_2O in hexanes) to afford 51 mg, 0.3 mmol (6% isolated yield) of compound **5.1e** as a colorless liquid. The very low isolated yield could be attributed to impure starting material. Alcohol **5.13** was observed in crude reaction mixture but could not be isolated. Spectroscopic data for **5.1e**: ^{1}H NMR (500 MHz, C_6D_6) δ 4.94 (dd, *J* = 1.5, 1.0 Hz, 1H), 4.82 (q, *J* = 1.0 Hz, 1H), 3.74 (s, 1H), 1.86 (hept, *J* = 6.7 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 4H), 0.92 (s, 1H), 0.09 (s, 9H). ^{13}C NMR (126 MHz, C_6D_6) δ 160.6, 103.1, 70.5, 32.0, 24.4, 21.7, -3.00.

Synthesis of 3-methyl-2-methylene-1-(triethylsilyl)butan-1-ol (5.1f) and (E)-4-methyl-1-(triethylsilyl)pent-2-en-1-ol (5.3)



Following general procedure B, a solution of 3-methyl-2-methylenebutan-1-ol **5.9e** and (*E*)-4-methylpent-2-en-1-ol **5.10e** (4.01 g, 40 mmol, 1 equiv.) in THF (80 mL) was cooled to −78 °C. *n*-BuLi (2.5 M in hexanes, 19.2 mL, 48 mmol, 1.2 equiv.) was added dropwise and the mixture stirred at –78 °C for 1 h. Chlorotriethylsilane (8.4 mL, 50 mmol, 1.25 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –78 °C to room temperature for 18 hours resulting in the formation of a white suspension. The mixture was cooled back to –78 °C followed by dropwise addition of *sec*-butyllithium (1.4 M in cyclohexane, 39.3 mL, 55 mmol, 1.38 equiv.) and the reaction stirred for an additional 2 hours at –78 °C to –30 °C. The reaction mixture was cooled back to –78 °C and quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 20 mL). Then all the organic phases were combined, washed with H_2O (20 mL) and brine (20 mL) respectively, and dried over anhydrous $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography (15% Et_2O in hexanes) to afford a colorless liquid 4037 mg, 18.8 mmol (47% isolated yield) of compounds **5.1f** and **5.3** as 2:1 mixture. This mixture was further purified by column chromatography (2.5% Et_2O in hexanes) to afford both compound **5.1f** and **5.3** as pure compounds.

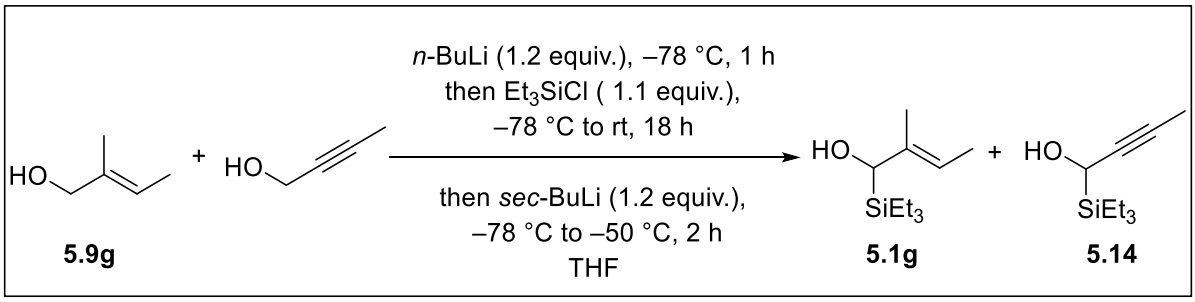
Spectroscopic data of **5.1f** in C_6D_6: ^{1}H NMR (500 MHz, C_6D_6) δ 4.99 (dd, *J* = 1.6, 1.0 Hz, 1H), 4.83 (q, *J* = 1.0 Hz, 1H), 3.94 (t, *J* = 1.3 Hz, 1H), 1.91 (heptd, *J* = 6.8 Hz, 1H), 1.08 – 1.01

(m, 12H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.95 (s, 1H), 0.74 – 0.60 (mq 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 161.0, 103.3, 68.8, 31.7, 24.4, 21.9, 8.2, 2.8.

Spectroscopic data of **5.1f** in $CDCl_3$ stored over K_2CO_3: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.90 (dd, *J* = 1.6, 0.9 Hz, 1H), 4.83 (q, *J* = 0.9 Hz, 1H), 4.04 (t, *J* = 1.2 Hz, 1H), 1.94 (heptd, *J* = 6.8, 1.0 Hz, 1H), 1.21 (s, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.62 (qd, *J* = 7.9, 3.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 102.7, 68.3, 31.2, 23.9, 21.2, 7.5, 1.9.

Spectroscopic data of **5.3**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.58 (ddd, *J* = 15.4, 6.7, 1.2 Hz, 1H), 5.45 (ddd, *J* = 15.4, 6.6, 1.6 Hz, 1H), 4.06 (ddd, *J* = 6.6, 1.6, 0.9 Hz, 1H), 2.29 (dqt, *J* = 13.4, 6.7, 1.1 Hz, 1H), 1.25 (s, 1H), 1.03 – 0.91 (m, 18H), 0.59 (qd, *J* = 8.0, 1.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1, 128.8, 66.7, 31.0, 22.6, 7.4, 1.6.

Synthesis of 3-methyl-2-methylene-1-(triethylsilyl)butan-1-ol (5.1g) and (E)-4-methyl-1-(triethylsilyl)pent-2-en-1-ol (5.14)

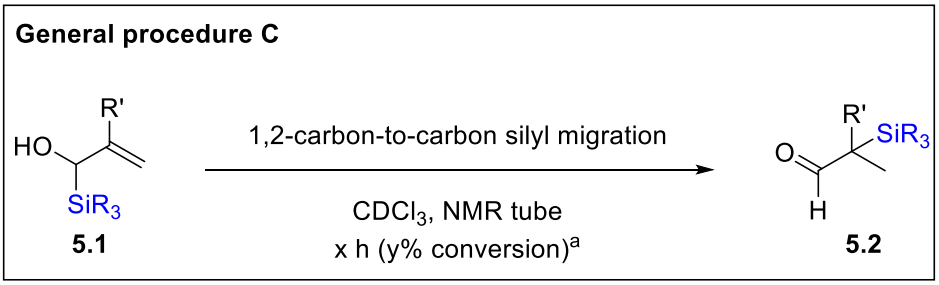


Following general procedure B, to a 50 mL round bottom flask was weighed 600 mg of (E)-2-methylbut-2-en-1-ol **5.9g** 66% W/W with but-2-yn-1-ol (a total of 7.51 mmol, 1 equiv). 20 mL of freshly distilled THF was added to the flask, purged with nitrogen and the solution was cooled to −78 °C. *n*-BuLi (2.4 M in hexanes, 3.75 mL, 9.0 mmol, 1.2 equiv.) was added dropwise and the mixture stirred at –78 °C for 1 h. Chlorotriethylsilane (1.4 mL, 8.3 mmol, 1.1 equiv.) was then added slowly from a syringe and the resulting mixture was stirred at –78 °C to room temperature

for 18 hours resulting in the formation of a white suspension. The mixture was cooled back to –78 °C followed by dropwise addition of *sec*-butyllithium (1.4 M in cyclohexane, 6.4 mL, 9 mmol, 1.2 equiv.) and the reaction stirred for an additional 2 hours at –78 °C to –30 °C. The reaction mixture was cooled back to –78 °C and quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 20 mL). Then all the organic phases were combined, washed with H_2O (20 mL) and brine (20 mL) respectively, and dried over anhydrous $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography (10% Et_2O in hexanes) to afford 463 mg, 2.31 mmol of **5.1g** (50% based on starting alcohol **5.10g**) and 102 mg, 0.55 mmol of **5.14** (19% based on starting propargyl alcohol) as colorless liquids.

Spectroscopic data of **5.1g**: ^{1}H NMR (500 MHz, C_6D_6) δ 5.31 (qt, *J* = 6.7, 1.3 Hz, 1H), 3.81 (s, 1H), 1.56 (dt, *J* = 6.7, 1.3 Hz, 3H), 1.53 (s, 3H), 1.04 (t, *J* = 7.9 Hz, 9H), 0.86 (s, 1H), 0.65 (qq, *J* = 16.0, 7.9 Hz, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 140.0, 116.1, 71.5, 14.9, 13.5, 8.2, 3.0. Spectroscopic data for **5.14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (q, *J* = 2.7 Hz, 1H), 1.86 (d, *J* = 2.5 Hz, 3H), 1.42 (s, 1H), 1.00 (t, *J* = 8.0 Hz, 9H), 0.68 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.8, 79.8, 54.6, 7.3, 3.8, 1.6.

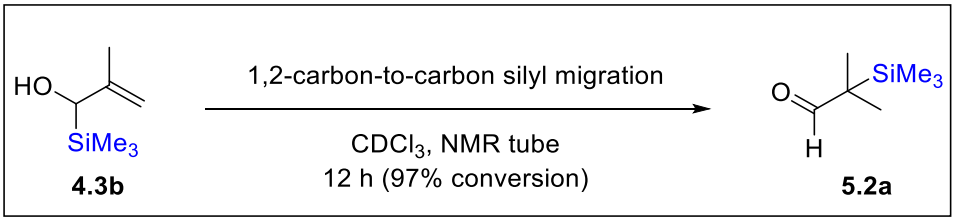
4.7.3. The [1,2]-carbon to carbon silyl migration: general procedure C



Alcohol **5.1** was dissolved in $CDCl_3$ and the solution transferred into NMR tube. The reaction in the NMR tube was monitored by NMR analysis until over 90% conversion had been achieved,

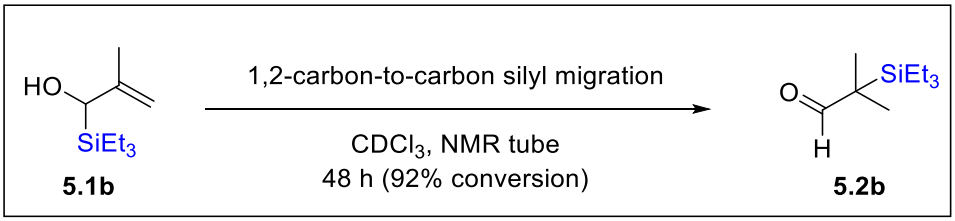
obtaining aldehyde **5.2**.

Synthesis of 2-methyl-2-(trimethylsilyl)propanal (5.2a)



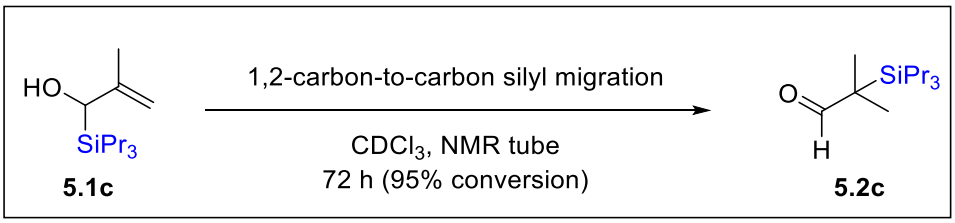
Aldehyde **5.2a** was synthesized from alcohol **4.3b** following general procedure C in 97% conversion after 12 hours: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 1.19 (s, 6H), 0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.8, 42.1, 17.3, -4.2.

Synthesis of 2-methyl-2-(triethylsilyl)propanal (5.2b)



Aldehyde **5.2b** was synthesized from alcohol **5.1b** following general procedure C in 92% conversion after 48 hours: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H), 1.21 (s, 6H), 0.97 (t, J = 7.9 Hz, 9H), 0.65 (q, J = 7.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.3, 43.0, 18.2, 7.7, 1.8.

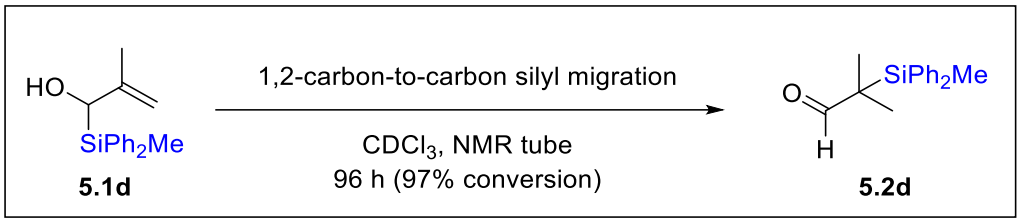
Synthesis of 2-methyl-2-(tripropylsilyl)propanal (5.2c)



Aldehyde **5.2c** was synthesized from alcohol **5.1c** following general procedure C in 95% conversion after 72 hours: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 1.38 – 1.27 (m, 6H), 1.19 (s, 6H), 0.95 (t, J = 7.2 Hz, 9H), 0.64 – 0.58 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.4, 42.8,

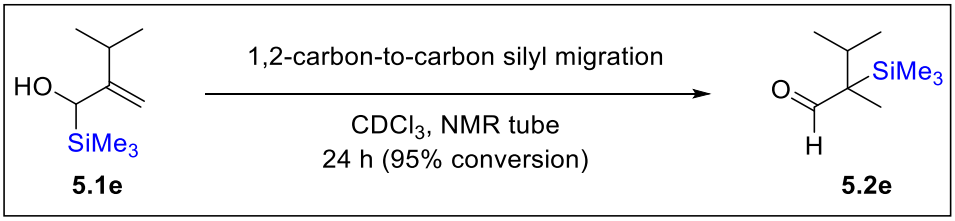
18.7, 18.3, 17.6, 13.5.

Synthesis of 2-methyl-2-(methyldiphenylsilyl)propanal (5.2d)



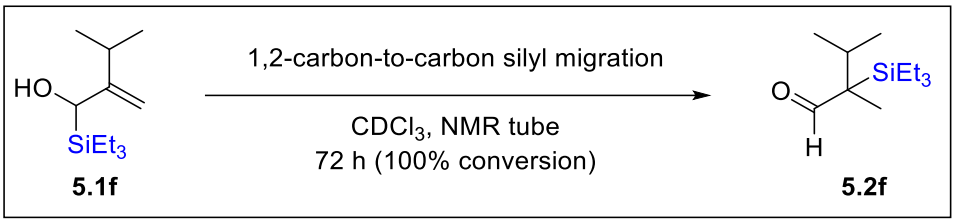
Aldehyde **5.2d** was synthesized from alcohol **5.1d** following general procedure C in 97% conversion after 96 hours: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.64 – 7.59 (m, 4H), 7.46 – 7.38 (m, 6H), 1.32 (s, 6H), 0.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.7, 135.2, 133.2, 129.8, 128.0, 41.9, 18.5, -6.3.

Synthesis of 2,3-dimethyl-2-(trimethylsilyl)butanal (5.2e)



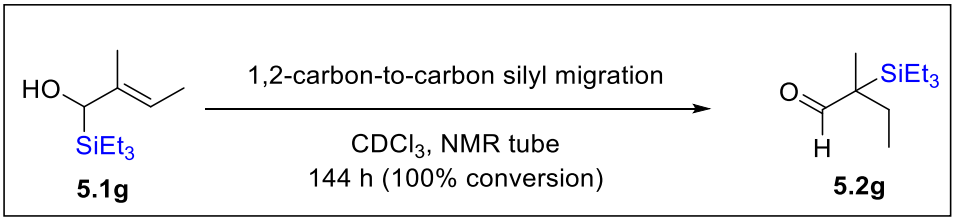
Aldehyde **5.2e** was synthesized from alcohol **5.1e** following general procedure C in 95% conversion after 24 hours. NMR analysis was done on a mixture of **5.1e**:**5.2e** (1.4:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (s, 1H), 4.85 (dt, *J* = 1.5, 0.8 Hz, 1H), 4.83 (q, *J* = 0.9 Hz, 1H), 3.90 (s, 1H), 2.53 (hept, *J* = 6.8 Hz, 1H), 1.94 (h, *J* = 6.8 Hz, 1H), 1.27 (s, 2H), 1.10 – 1.02 (m, 12H), 1.00 (d, *J* = 7.0 Hz, 4H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.08 (s, 9H), 0.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.0, 160.1, 102.5, 70.2, 50.9, 31.5, 29.4, 23.8, 21.0, 19.6, 19.2, 8.8, -2.3, -3.6.

Synthesis of 2,3-dimethyl-2-(triethylsilyl)butanal (5.2f)



Aldehyde **5.2f** was synthesized from alcohol **5.1f** following general procedure C in 100% conversion after 72 hours: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 2.50 (hept, *J* = 6.9 Hz, 1H), 1.04 (s, 3H), 1.00 (d, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.82 (d, *J* = 6.8 Hz, 3H), 0.66 (qd, *J* = 7.9, 3.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.1, 52.3, 29.5, 19.6, 19.4, 9.4, 7.8, 3.0. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 8.71.

Synthesis of 2-methyl-2-(triethylsilyl)butanal (5.2g)

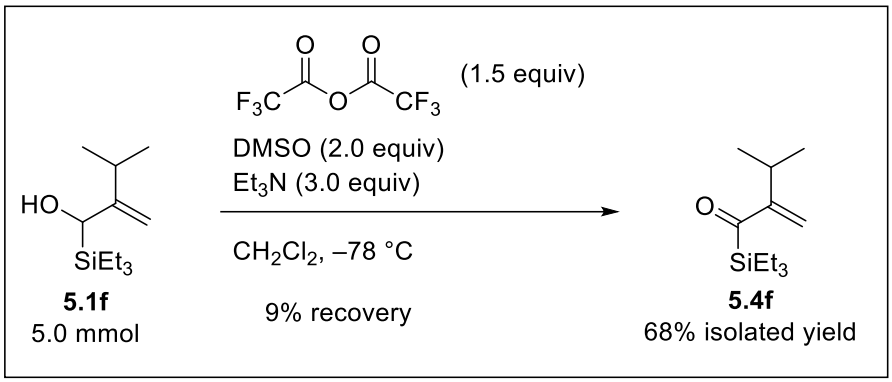


Aldehyde **5.2g** was synthesized from alcohol **5.1g** following general procedure C in 100% conversion after 144 hours: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (s, 1H), 2.16 (dq, *J* = 13.9, 7.0 Hz, 1H), 1.53 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.15 (s, 3H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.82 (t, *J* = 7.4 Hz, 3H), 0.64 (q, *J* = 8.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.5, 48.3, 24.5, 13.2, 9.9, 7.7, 1.8.

5.8.4. Synthesis of enantioenriched 5.1f

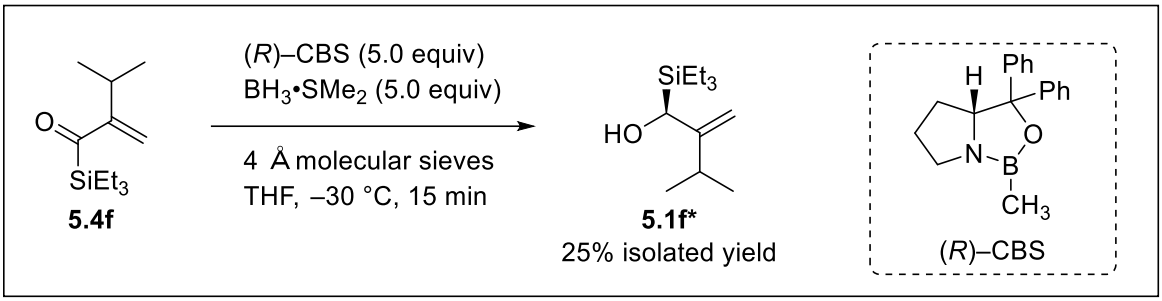
Compound **5.1f*** was synthesized from **5.1f** in two steps as indicated on scheme 5.9.

Synthesis of 3-methyl-2-methylene-1-(triethylsilyl)butan-1-one (5.4f)



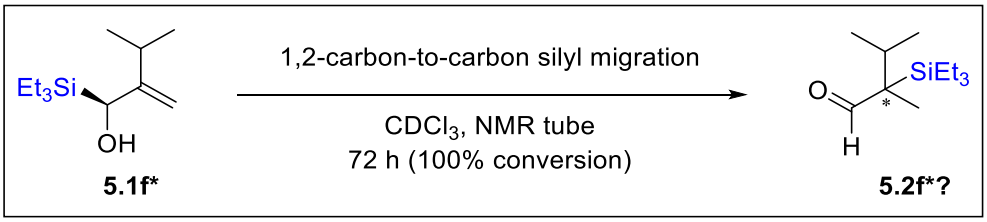
Following a reported procedure; a dry 100 mL round bottom flask fitted with a magnetic stir bar was sealed with a rubber septum and cooled under nitrogen. 25 mL of dry DCM was then added to the flask via syringe followed by 1.04 mL trifluoroacetic anhydride (7.5 mmmol, 1.5 equiv). The mixture was cooled on a dry ice-acetone bath to –78 °C followed by dropwise addition of 0.71 mL of DMSO (10 mmol, 2.0 equiv). After complete addition of DMSO, the resulting mixture was stirred at –78 °C for additional 30 minutes after which a solution of α-hydroxyallylsilane **5.1f** 1072.1 mg in dry DCM (5.0 mmol, 1.0 equiv) was added dropwise and resulting solution stirred at –78 °C for one hour. This was followed by slow addition of 2.09 mL of freshly distilled triethylamine (15 mmol, 3.0 equiv) and the resulting mixture stirred at –78 °C for another one hour. The reaction mixture was quenched with water and allowed to warm up slowly to room temperature. The layers were separated and the aqueous phase was extracted twice with DCM. The combined organic phases were dried over anhydrous magnesium sulfate filtered and concentrated in vacuo followed by column chromatography (5% EtOAc in hexanes) to afford 722 mg, 3.4 mmol (68% isolated yield) of **5.4f** as a colorless oil and 95 mg of **5.1f** (9% recovery). Spectroscopic data for **5.4f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 (d, *J* = 1.2 Hz, 1H), 5.88 (s, 1H), 2.83 (hept, *J* = 6.9, 1.2 Hz, 1H), 0.98 – 0.89 (m, 15H), 0.76 (qd, *J* = 7.8, 1.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 237.9, 161.5, 124.7, 26.1, 21.6, 7.3, 3.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ -0.88.

Synthesis of (*S*)-3-methyl-2-methylene-1-(triethylsilyl)butan-1-ol (5.1f*)



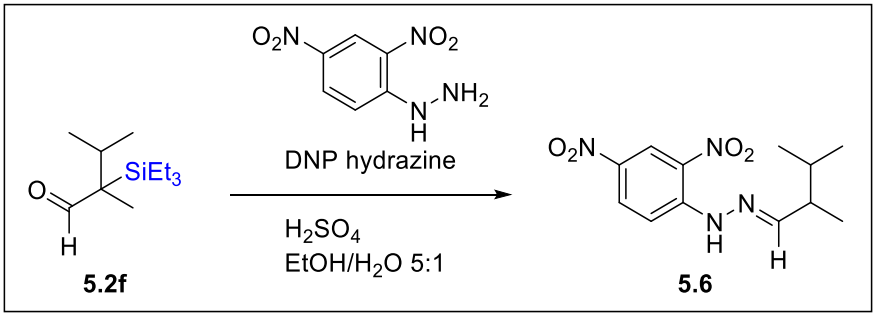
Following a reported procedure,[58] to a solution of 659 mg **5.4f** (3.1 mmol, 1.0 equiv) in 10 mL of freshly distilled anhydrous THF was added 2 g of 4Å molecular sieves at room temperature under nitrogen atmosphere and the mixture stirred at room temperature for 2 h. To the mixture was added 4.3 g (*R*)-CBS as a solution in 5 mL dry THF 5(15.5 mmol, 5.0 equiv) and reaction mixture was cooled to –30 °C and stirred at this temperature for 10 min. This was followed by dropwise dropwise addition of 1.5 mL BH_3•SMe_2 (15.5 mmol, 5.0 equiv) at –30 °C. The resulting mixture was stirred at –30 °C for 15 min, quenched with MeOH and saturated NH_4Cl, and extracted with Et_2O (20 mL x 2). The combined organic layers were washed with brine, dried over MgSO4, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (30% Et_2O in hexanes) to give 165 mg, 0.78 mmol of **5.1f*** (25% isolated yield) as a colorless oil. The optical purity and absolute configuration of 5.1f* were not determined experimentally but compared to similar structures in the literature.[58] The other spectral data were identical with those of **5.1f**.

Synthesis of 2,3-dimethyl-2-(triethylsilyl)butanal (5.2f*?)



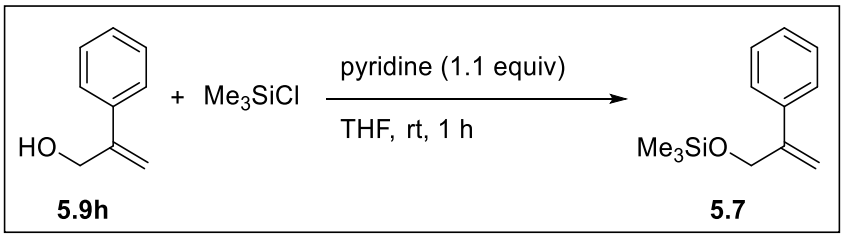
Aldehyde **5.2f*?** was synthesized from alcohol **5.1f*** following general procedure C in 100% conversion after 72 hours: Spectroscopic data was identical to those of **5.2f.**

Attempted derivatization of 5.2f*?: Synthesis of (*E*)-1-(2,3-dimethylbutylidene)-2-(2,4-dinitrophenyl)hydrazine



Compound **5.6** was synthesized following the same procedure for the synthesis of **3.16** in Chapter 3. Spectroscopic data for **5.6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.00 (s, 1H), 9.11 (d, *J* = 2.6 Hz, 1H), 8.29 (ddd, *J* = 9.6, 2.6, 0.8 Hz, 1H), 7.93 (d, *J* = 9.6 Hz, 1H), 7.46 (dd, *J* = 6.1, 0.7 Hz, 1H), 2.41 (h, *J* = 7.0 Hz, 1H), 1.90 – 1.78 (m, *J* = 6.8 Hz, 1H), 1.16 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 2.7 Hz, 3H), 0.97 (d, *J* = 2.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 145.2, 137.6, 129.9, 128.7, 123.5, 116.6, 43.0, 31.6, 20.1, 19.5, 14.3. Compound **5.6** is known.[59]

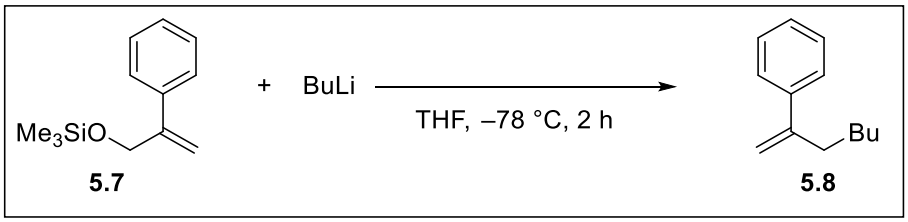
Synthesis of trimethyl((2-phenylallyl)oxy)silane (5.7)



To a 100 mL round bottom flask was weighed 1342 mg ally alcohol **5.9h** (10 mmol, 1.0 equiv) and 50 mL of dry THF added. The flask was sealed with a rubber septum and purged with nitrogen. This was followed by addition of 0.89 mL of pyridine (11 mmol, 1.1 equiv) and the resulting mixture stirred in dry THF for 5 minutes. This was followed by addition of 1.27 mL of TMSCl

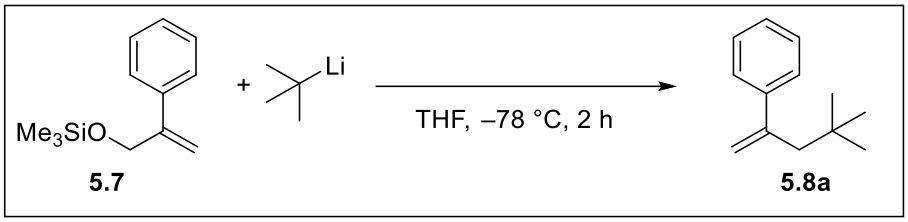
(10 mmol, 1.0 equiv) and the resulting mixture stirred for an additional one hour at room temperature. The THF was removed by rotavap and the resulting residue diluted with hexanes. The mixture was filtered, and the filtrate was concentrated under reduced pressure to give the expected product. The product was further purified by column chromatography (10% EtOAc in hexanes) to give 2046 mg, 9.9 mmol (99% isolated yield) of **5.7**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 5.47 (q, *J* = 1.4 Hz, 1H), 5.41 (q, *J* = 1.7 Hz, 1H), 4.54 (t, *J* = 1.5 Hz, 2H), 0.19 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 139.0, 128.3, 127.6, 126.0, 111.9, 64.3. Spectroscopic data were in agreement with those reported in the literature.[60]

5.8.5. Unexpected S_N2-like reactions: general procedure D



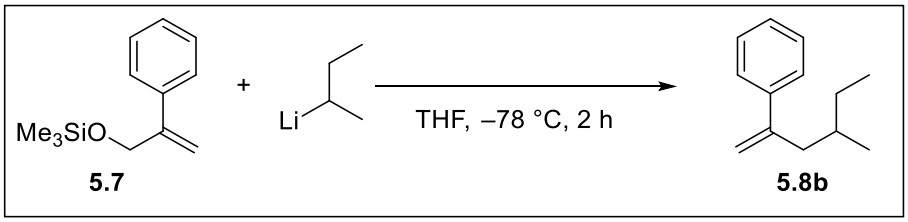
To a 50 mL round bottom flask was added as a solution of **5.7** in 12 mL dry THF. The mixture was cooled to –78 °C then butyllithium was added dropwise resulting in a colored solution. The mixture was stirred at –78 °C for two hours then quenched with saturated ammonium chloride solution and diluted with 20 mL of ether 10 mL of water. The layers were separated and the aqueous layer was extracted with ether (20 mL X 3). Combined organics were washed with saturated ammonium chloride, water and brine respectively and then dried over anhydrous magnesium sulfate. Filtration and concentration gave the substitution product.

Synthesis of (4,4-dimethylpent-1-en-2-yl)benzene 5.8a



Applying general procedure D to silyl ether **5.7** 412.72 mg (2.0 mmol, 1.0 equiv) and 1.5 mL of *tert*-butyllithium (1.6 M in pentane, 2.4 mmol, 1.2 equiv), compound **5.8a** was synthesized in quantitative yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 5.28 (d, *J* = 2.1 Hz, 1H), 5.05 (dd, *J* = 2.0, 0.9 Hz, 1H), 2.50 (s, 2H), 0.84 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 143.7, 128.1, 126.9, 126.5, 116.3, 48.9, 31.7, 30.1. Spectroscopic data were in agreement with those reported in the literature.[61]

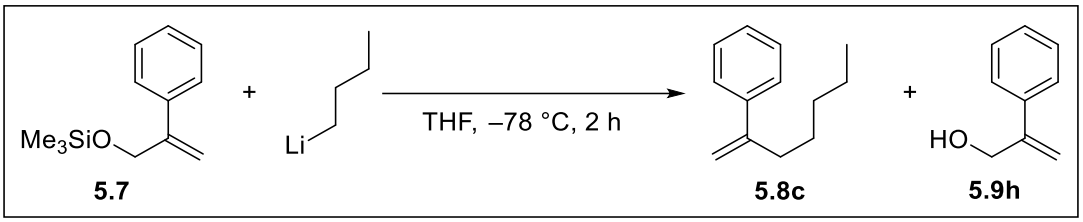
Synthesis of (4-methylhex-1-en-2-yl)benzene 5.8b



Applying general procedure D to silyl ether **5.7** 412.72 mg (2.0 mmol, 1.0 equiv) and 1.71 mL of *sec*-butyllithium (1.4 M in cyclohexane, 2.4 mmol, 1.2 equiv). After workup and column chromatography (1.5% EtOAc in hexanes), compound **5.8b** was synthesized in 292.81 mg, 1.68 mmol (84% isolated yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.37 – 7.26 (m, 3H), 5.29 (d, *J* = 1.8 Hz, 1H), 5.06 (q, *J* = 1.2 Hz, 1H), 2.62 (ddd, *J* = 14.1, 5.8, 1.3 Hz, 1H), 2.25 (ddd, *J* = 14.0, 8.3, 1.0 Hz, 1H), 1.52 – 1.43 (m, 1H), 1.22 – 1.14 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 4H), 0.80 (ddd, *J* = 14.1, 7.0, 2.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 141.5, 128.2, 127.2, 126.3, 113.6, 43.0, 32.6, 29.4, 18.9, 11.3. Spectroscopic data were in

agreement with those reported in the literature.[62]

Synthesis of hept-1-en-2-ylbenzene 5.8c



Applying general procedure D to silyl ether **5.7** 412.72 mg (2.0 mmol, 1.0 equiv) and 1 mL of *n*-butyllithium (2.4 M in cyclohexane, 2.4 mmol, 1.2 equiv). After workup compound **5.8c** and **5.9h** as a mixture 100% conversion by NMR of the crude material: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 4H), 7.42 – 7.28 (m, 6H), 5.51 (q, *J* = 1.0 Hz, 1H), 5.38 (q, *J* = 1.4 Hz, 1H), 5.31 (d, *J* = 1.5 Hz, 1H), 5.10 (q, *J* = 1.4 Hz, 1H), 4.56 (dd, *J* = 1.6, 0.9 Hz, 2H), 2.57 – 2.50 (m, 1H), 1.91 (s, 1H), 1.55 – 1.44 (m, 2H), 1.43 – 1.31 (m, 4H), 0.98 – 0.86 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 147.2, 141.4, 138.4, 128.5, 128.2, 127.9, 127.2, 126.0, 126.0, 112.5, 111.9, 64.9, 35.3, 31.5, 27.9, 22.4, 14.0. Spectroscopic data of **5.8c** were in agreement with those reported in the literature.[63]

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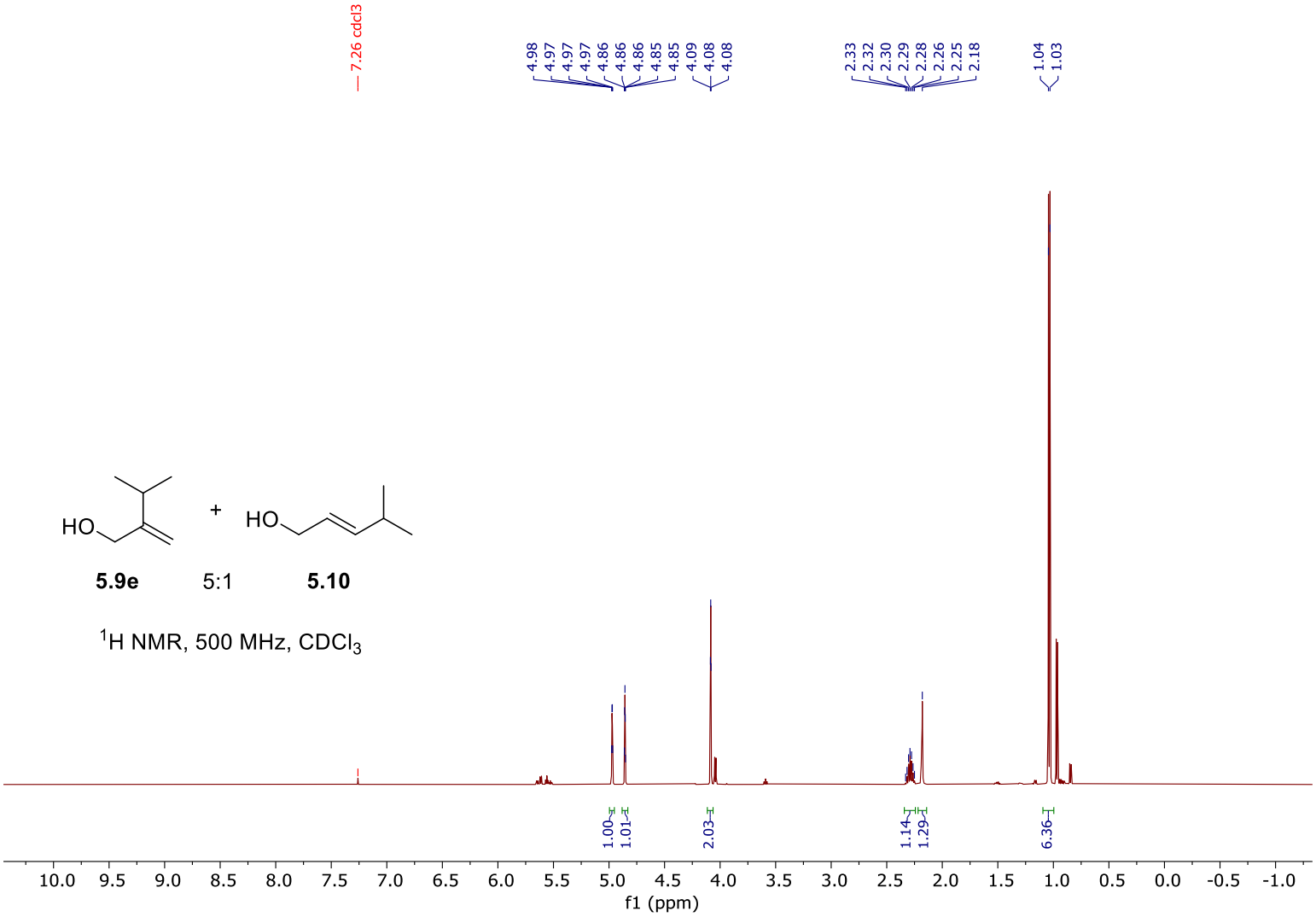
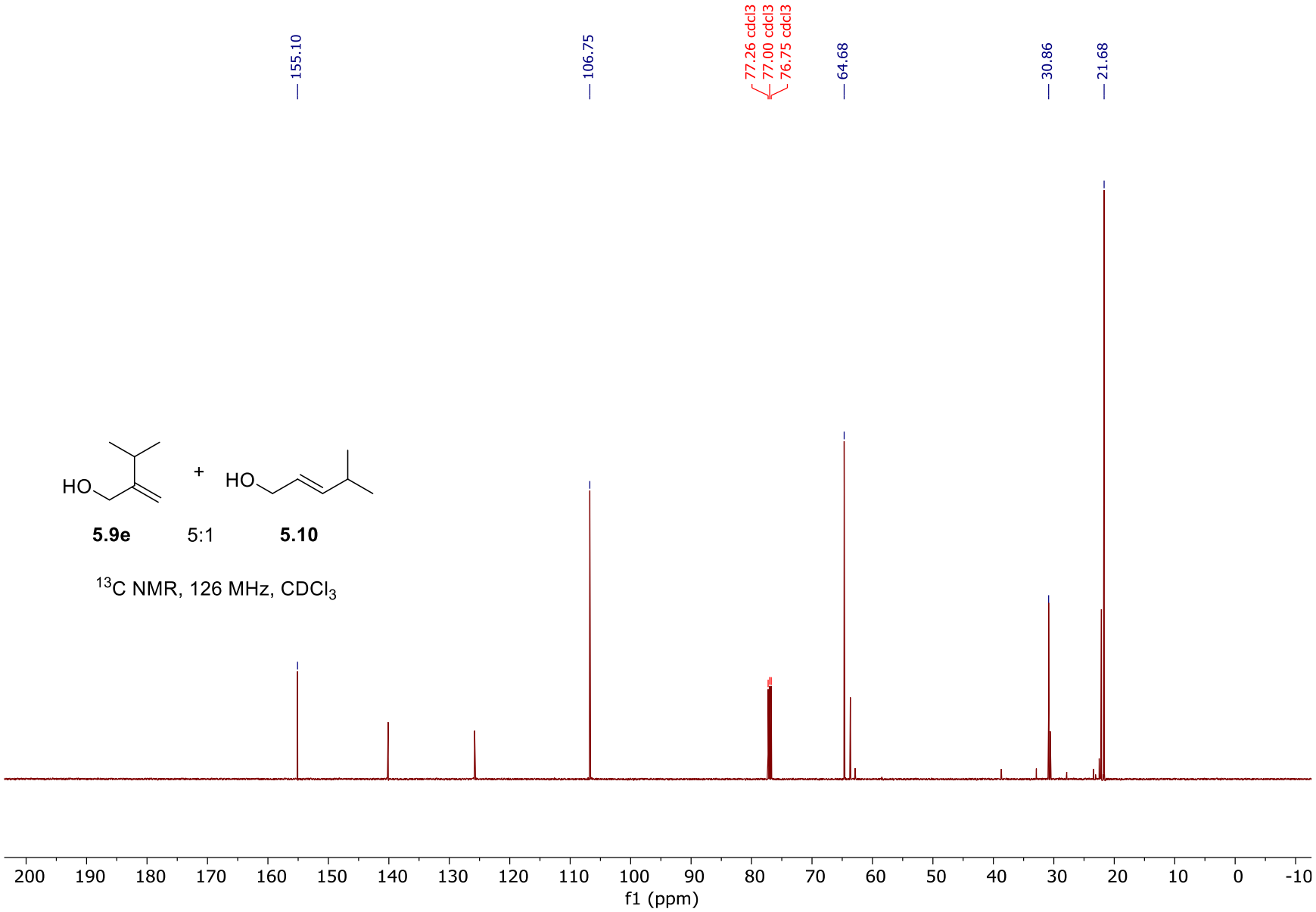
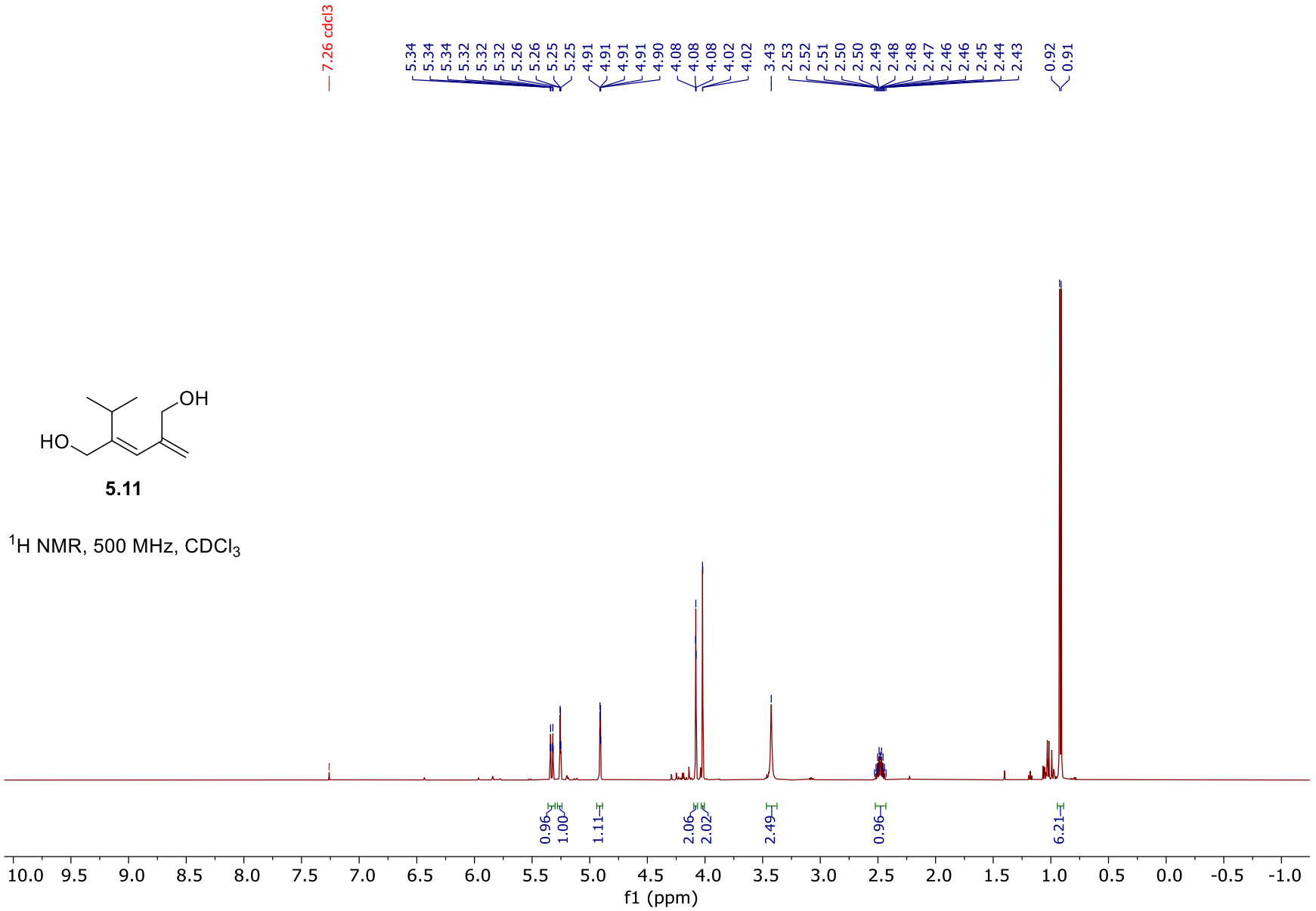
APPENDIX

Copies of NMR spectra

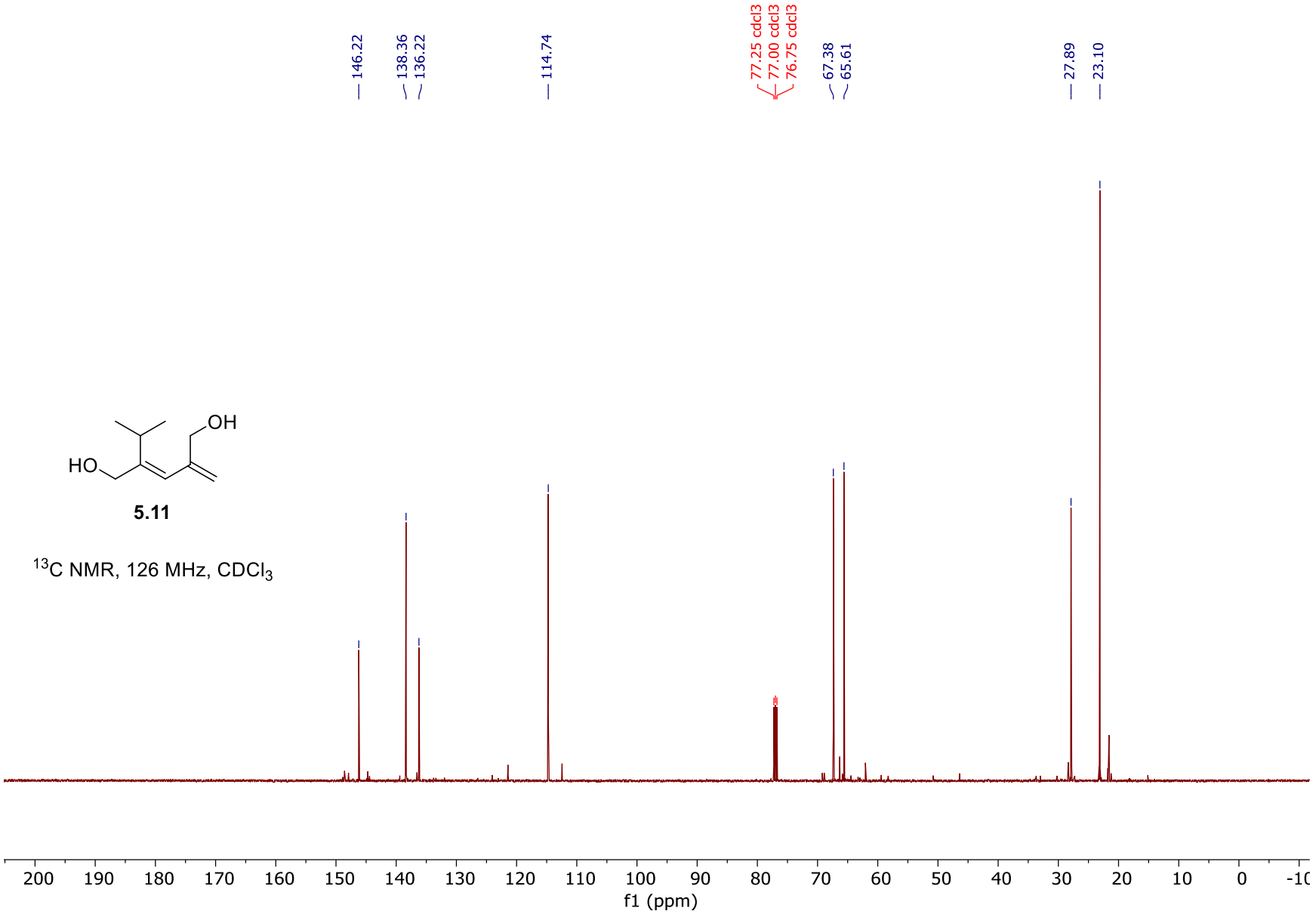


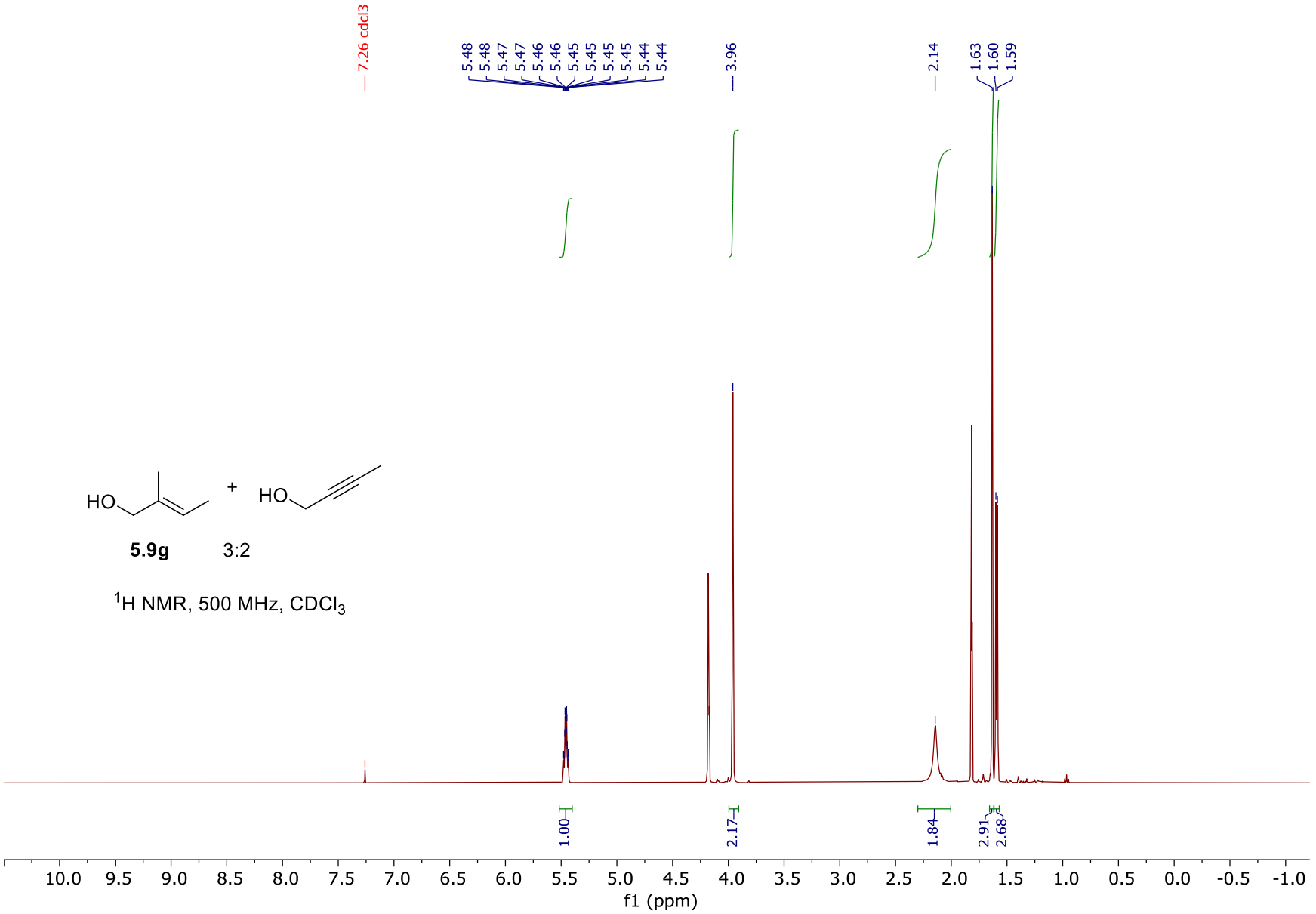

155.10
106.75
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
64.68
30.86
21.68
HO
+
HO
5.9e
5:1
5.10
13C NMR, 126 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

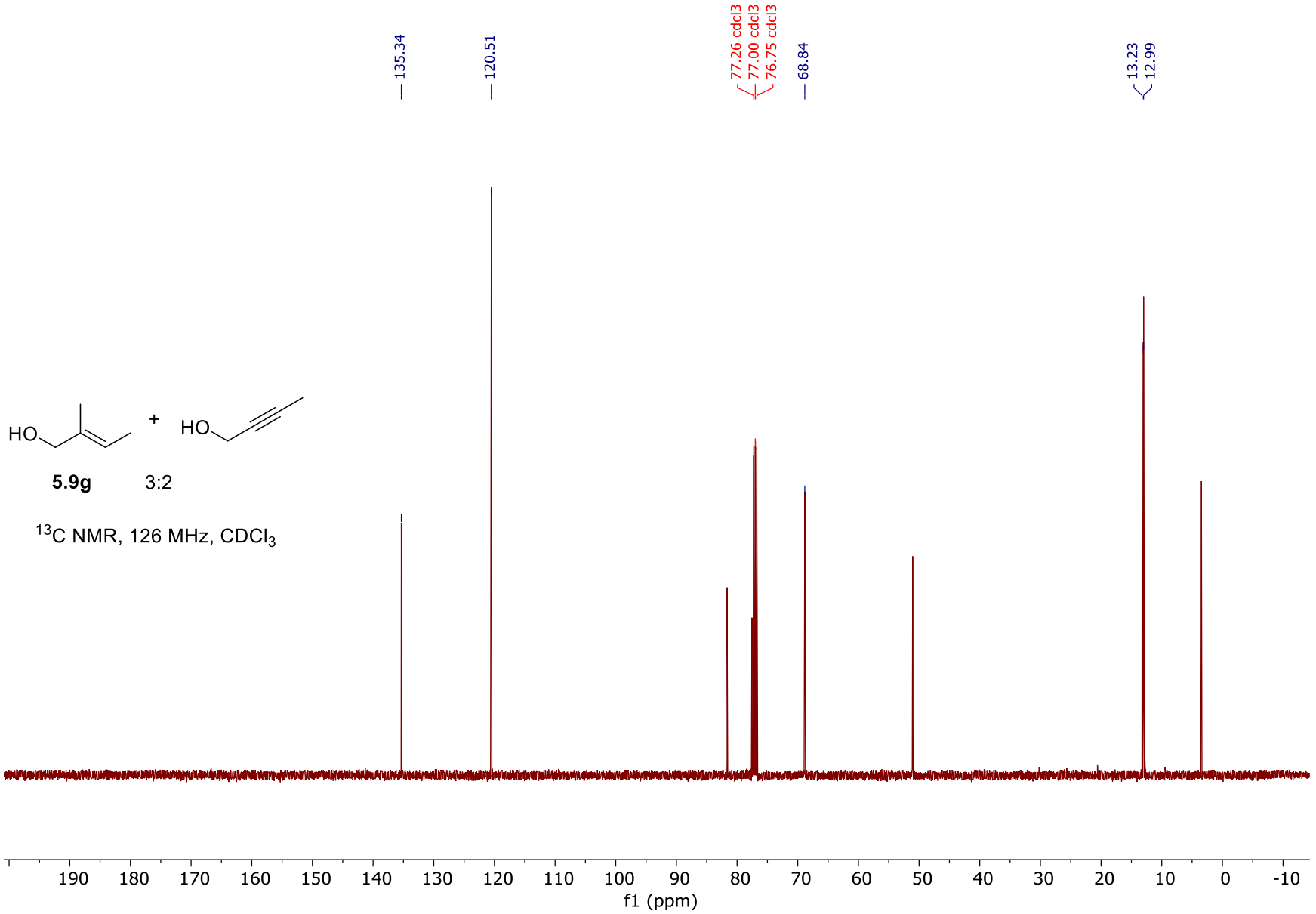


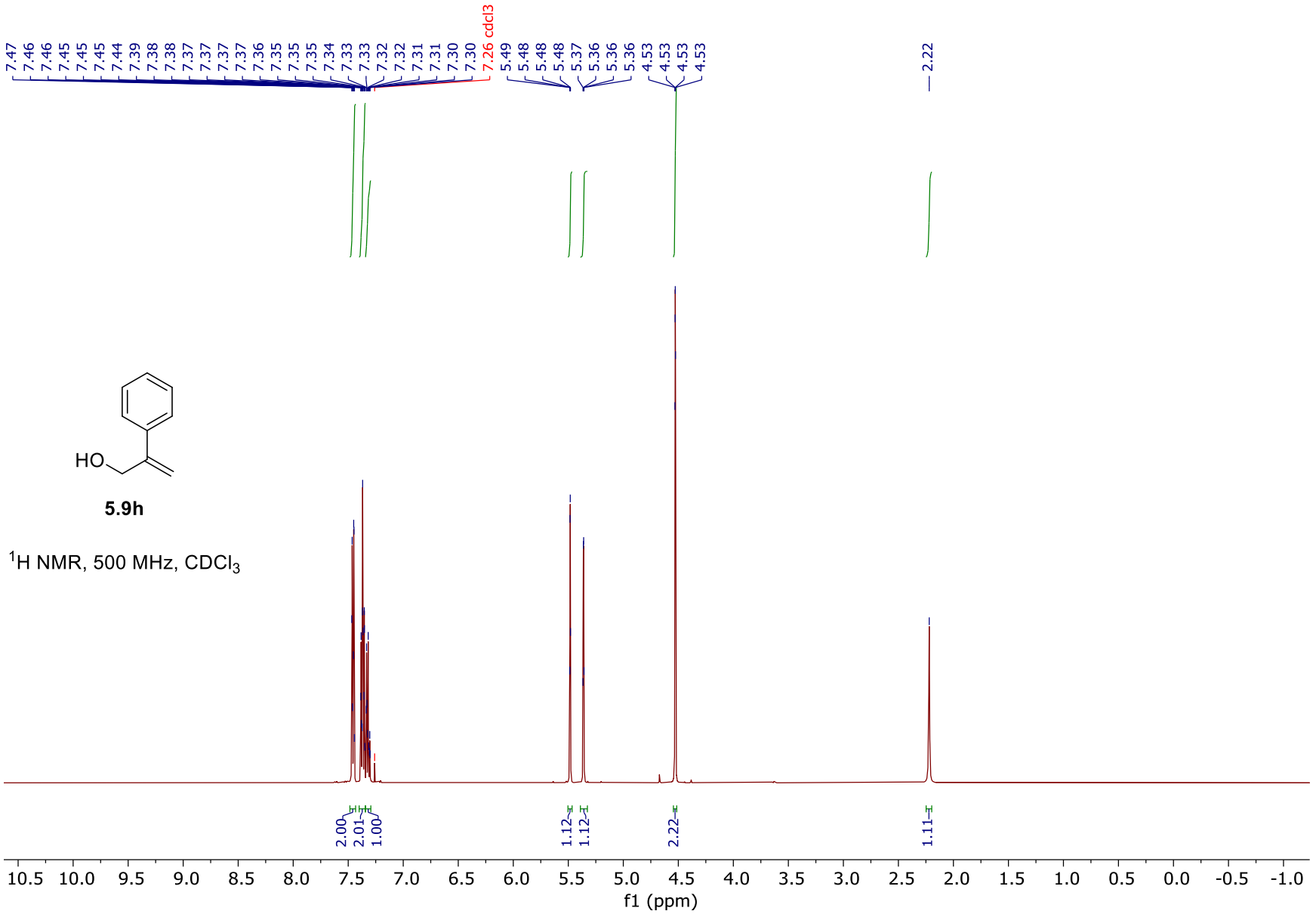
5.11

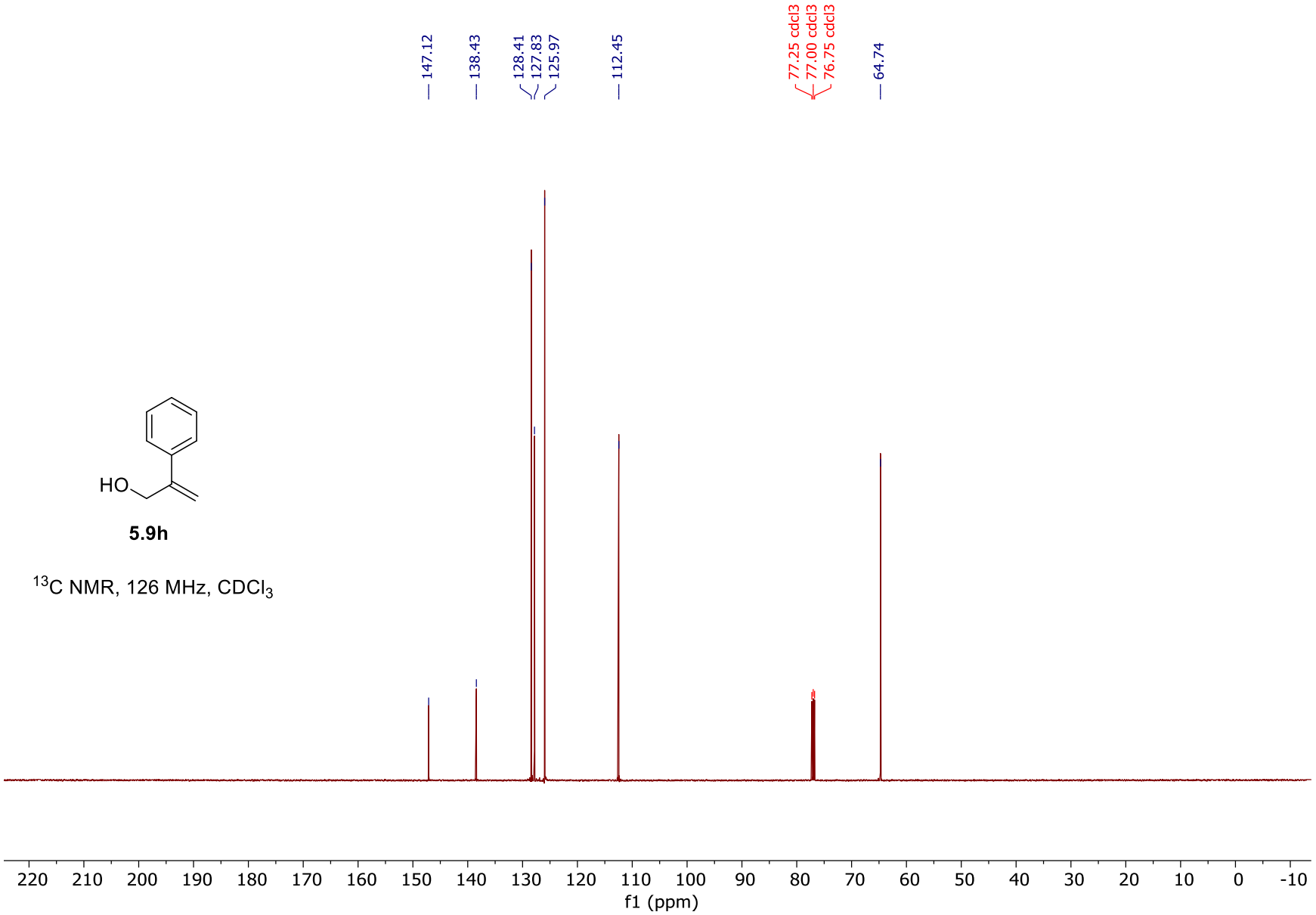
^{1}H NMR, 500 MHz, $CDCl_3$

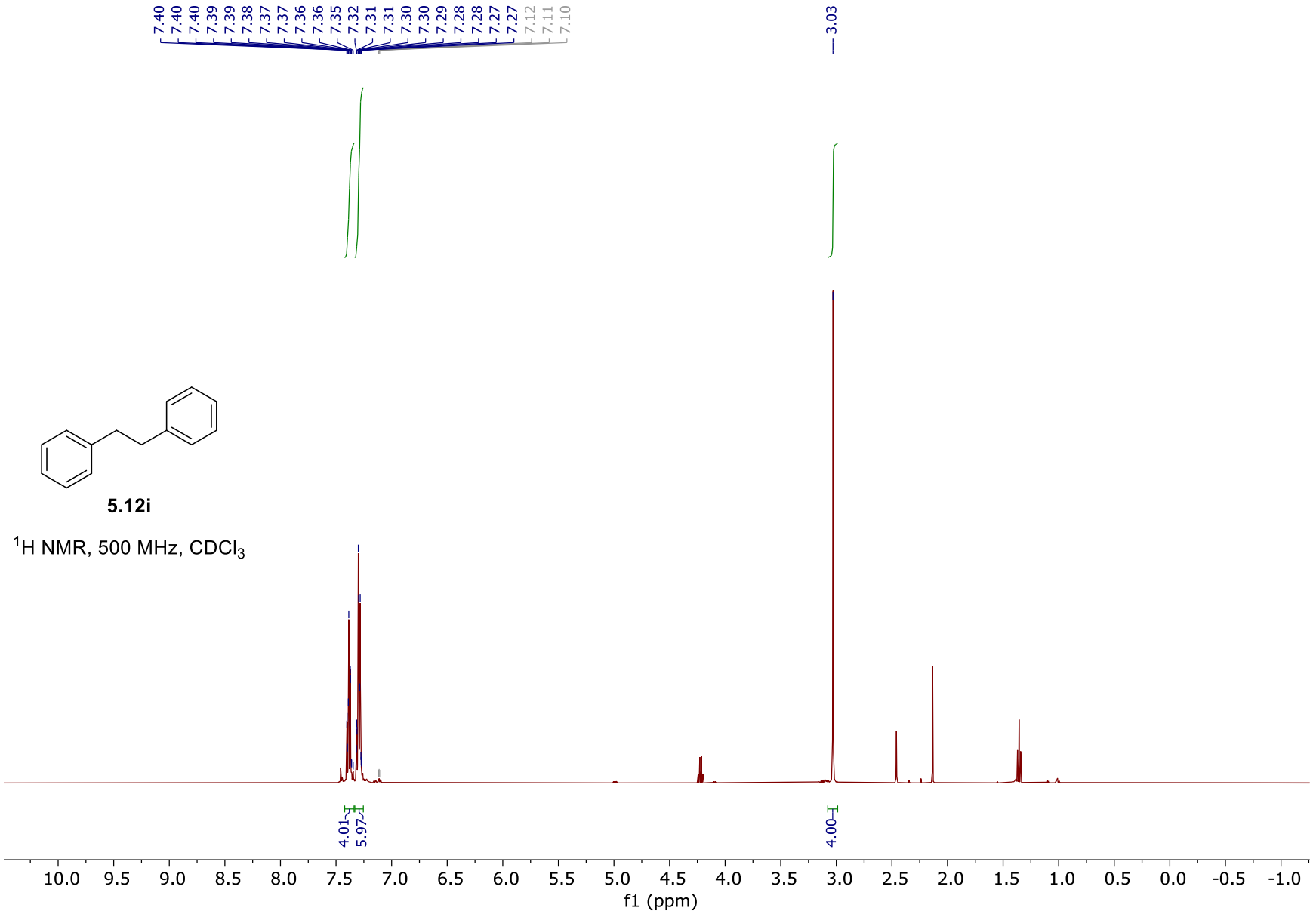

146.22
138.36
136.22
114.74
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
67.38
65.61
27.89
23.10
OH
HO
5.11
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

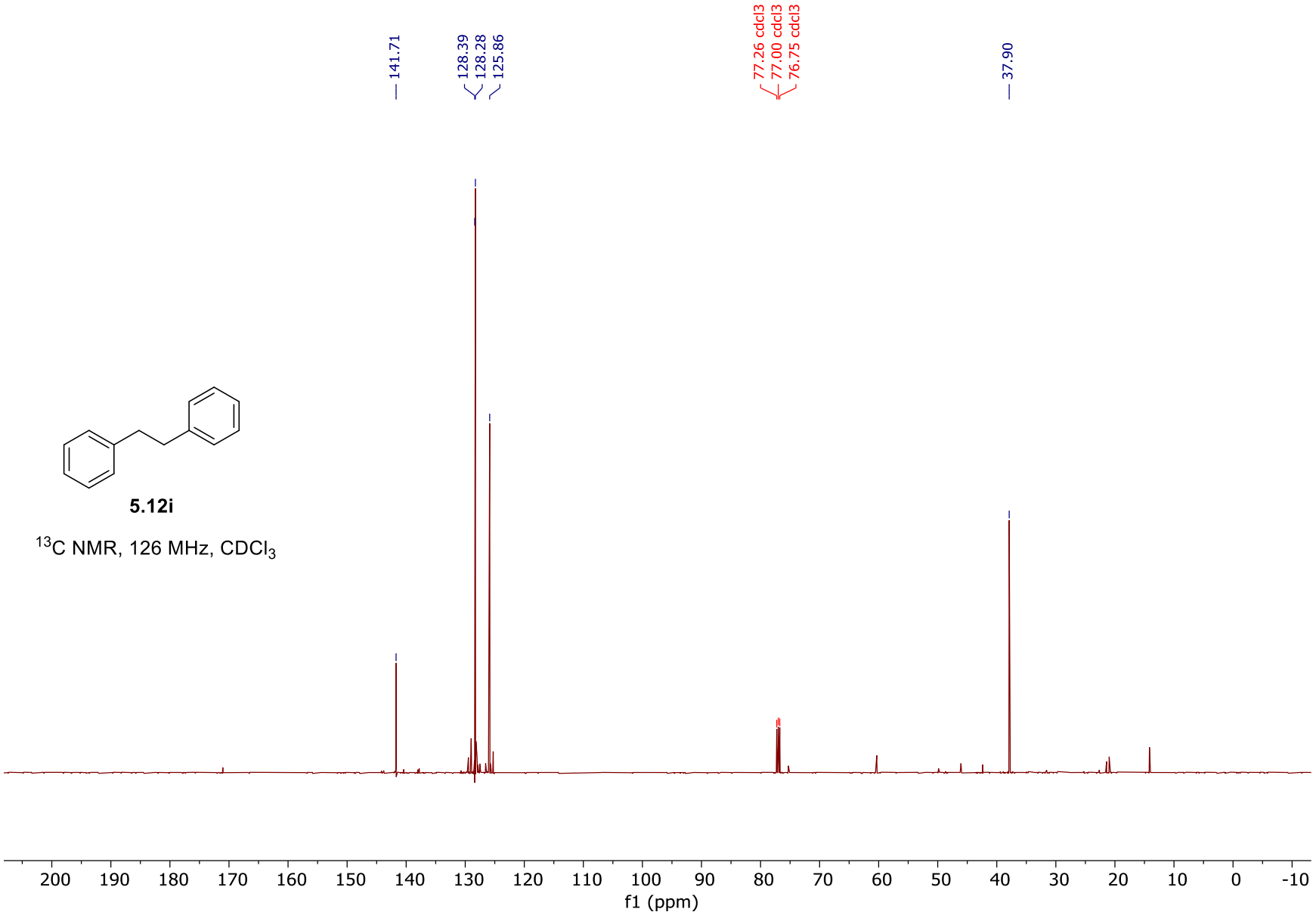

7.26 cdcl3
5.48
5.48
5.47
5.47
5.46
5.46
5.45
5.45
5.45
5.45
5.44
5.44
3.96
2.14
1.63
1.60
1.59
HO
+
HO
5.9g
3:2
1H NMR, 500 MHz, CDCl3
1.00
2.17
1.84
2.91
2.68
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

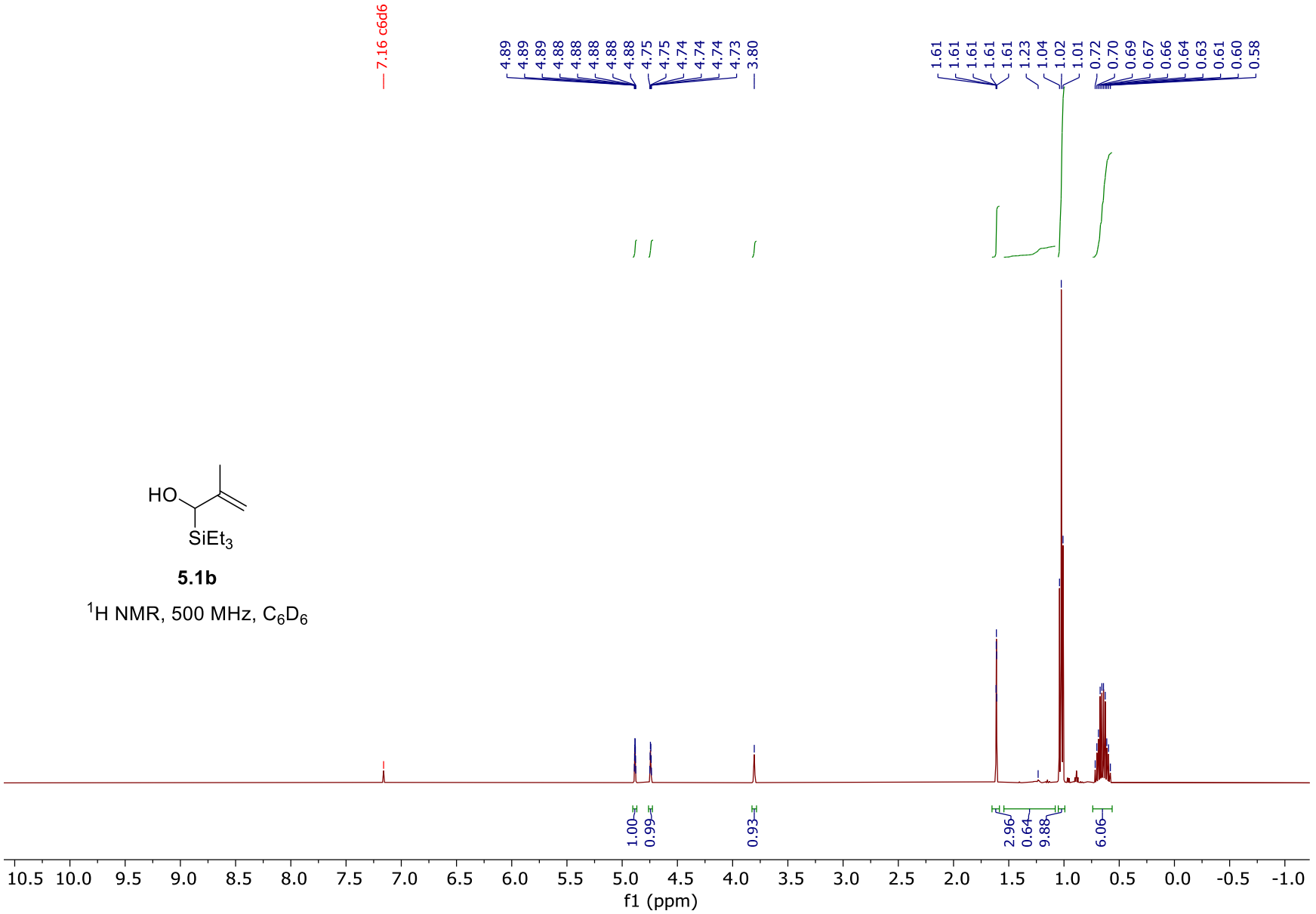

135.34
120.51
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
68.84
13.23
12.99
HO
+
HO
5.9g
3:2
^{13}C NMR, 126 MHz, $CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

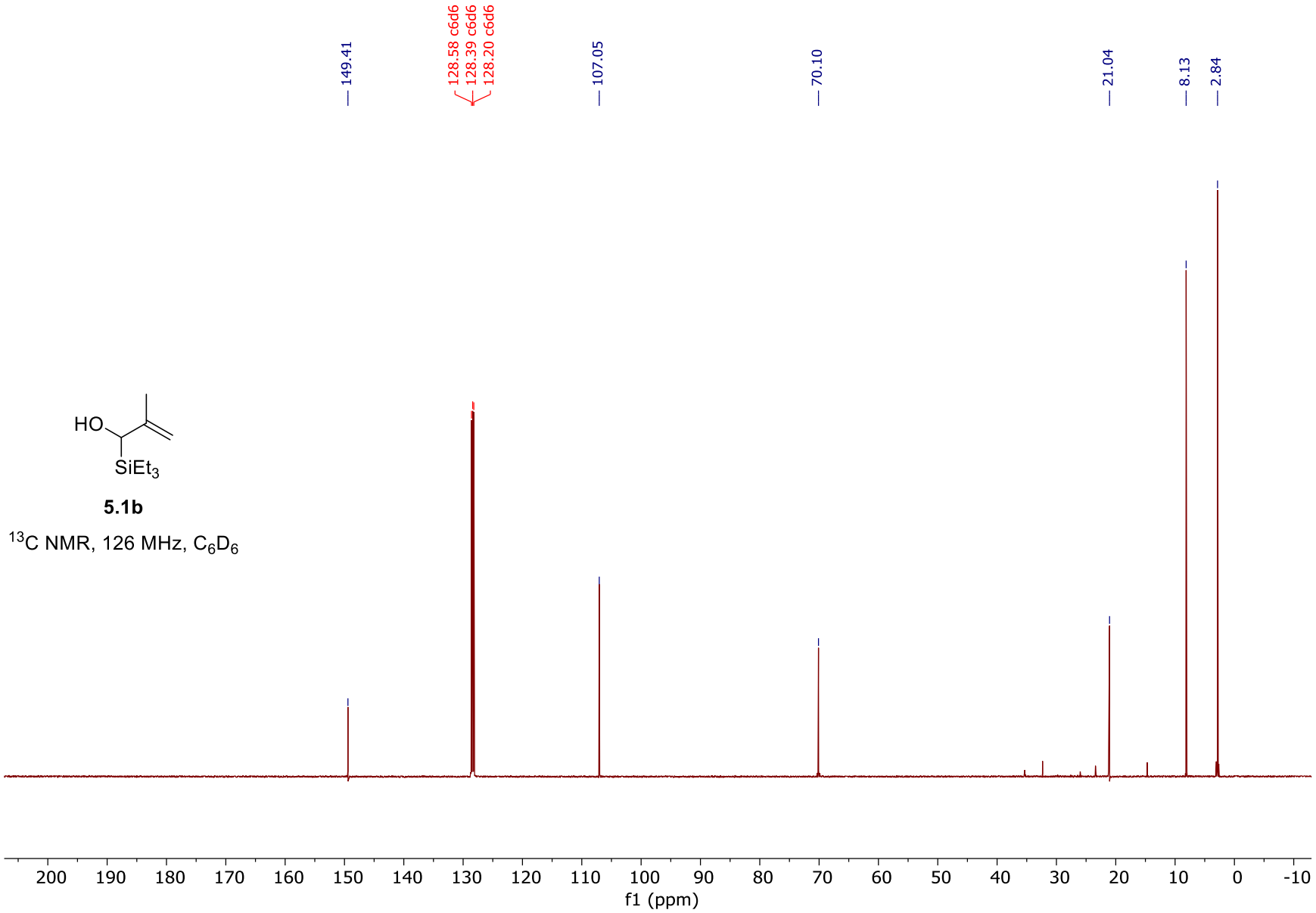

7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.39
7.38
7.38
7.37
7.37
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.26 cdcl3
5.49
5.48
5.48
5.48
5.37
5.36
5.36
5.36
4.53
4.53
4.53
2.22
HO
5.9h
1H NMR, 500 MHz, CDCl3
2.00
2.01
1.00
1.12
1.12
2.22
1.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

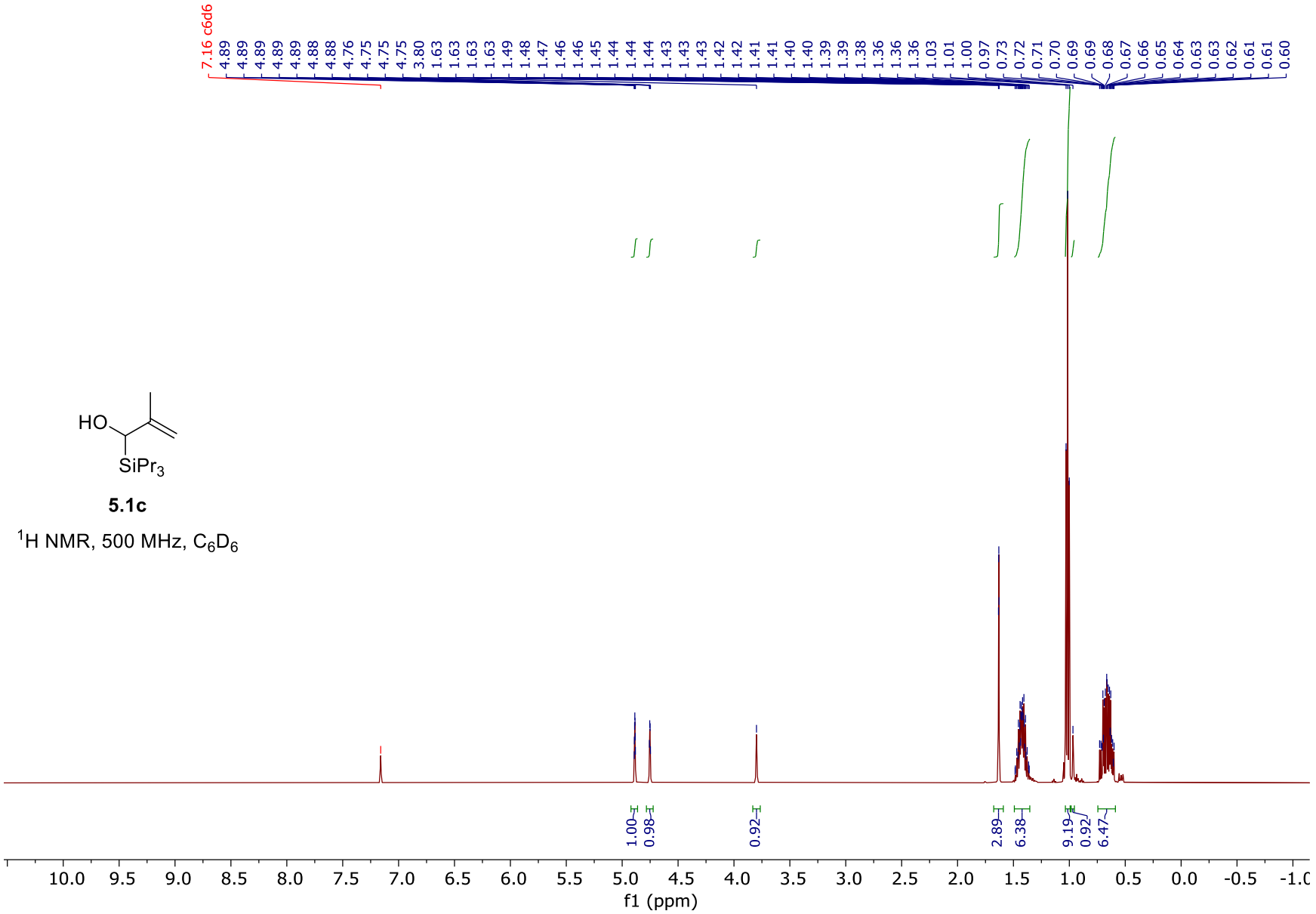

147.12
138.43
128.41
127.83
125.97
112.45
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
64.74
HO
5.9h
13C NMR, 126 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

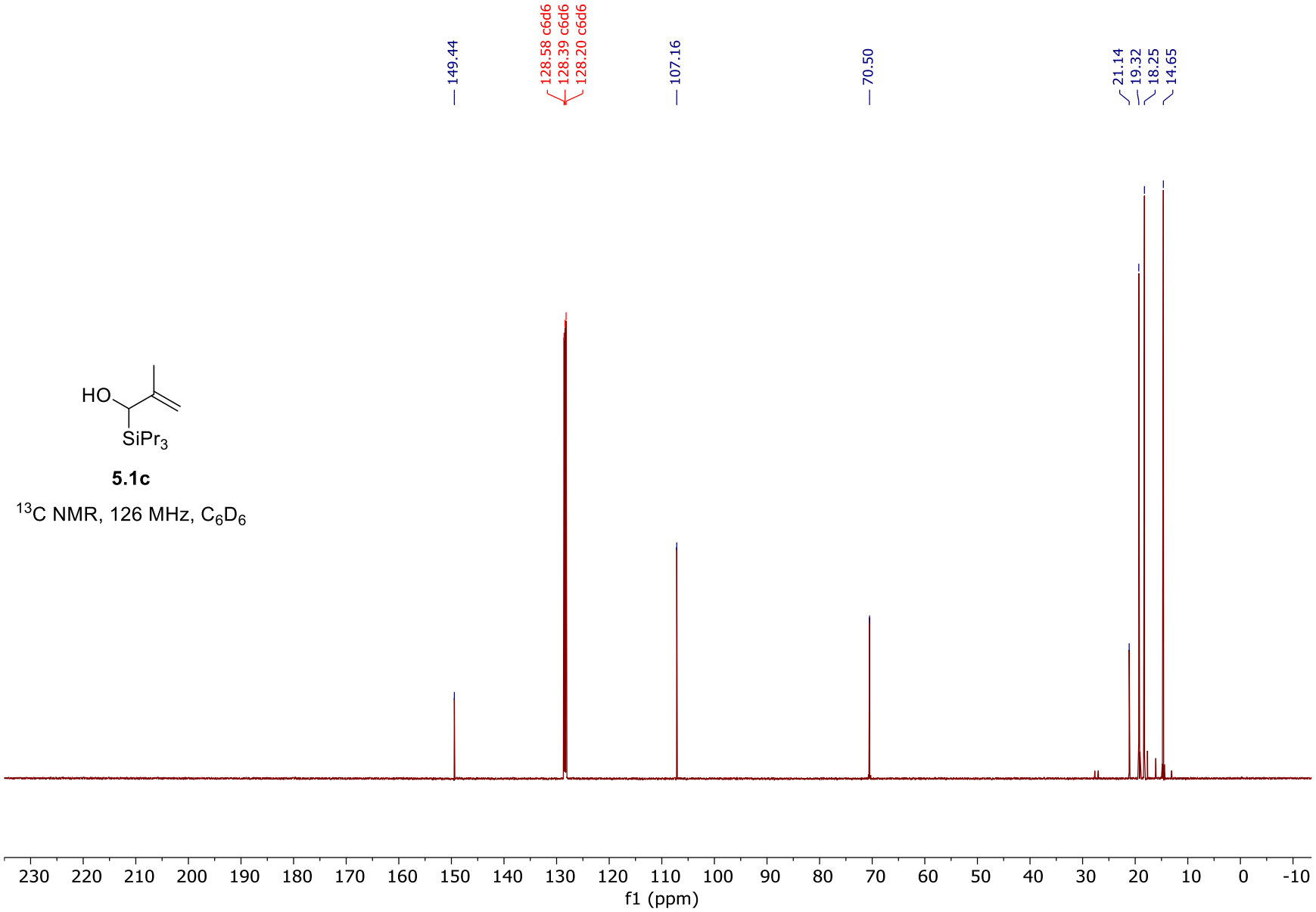

7.40
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.12
7.11
7.10
3.03
5.12i
1H NMR, 500 MHz, CDCl3
4.01
5.97
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

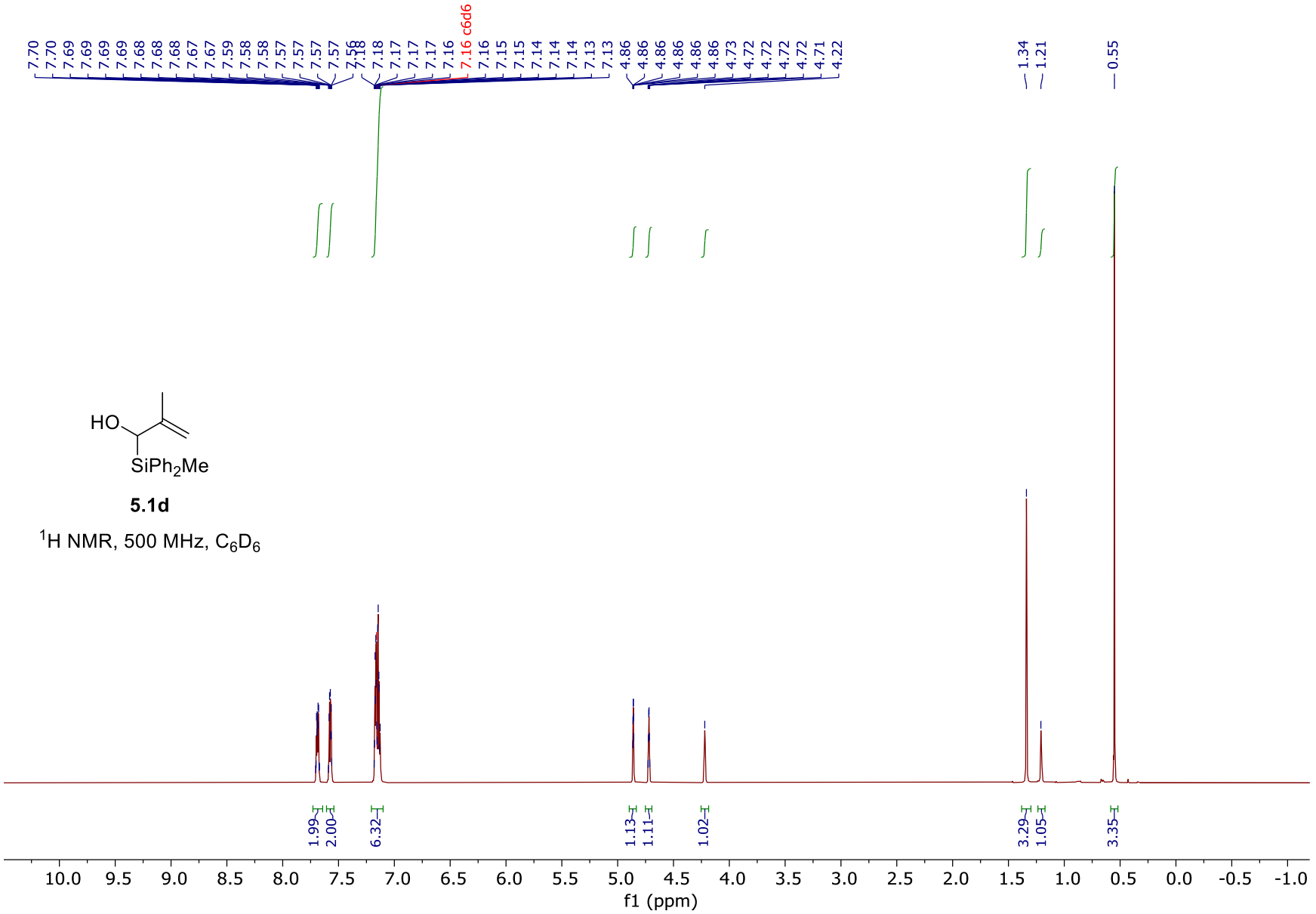

141.71
128.39
128.28
125.86
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
37.90
5.12i
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

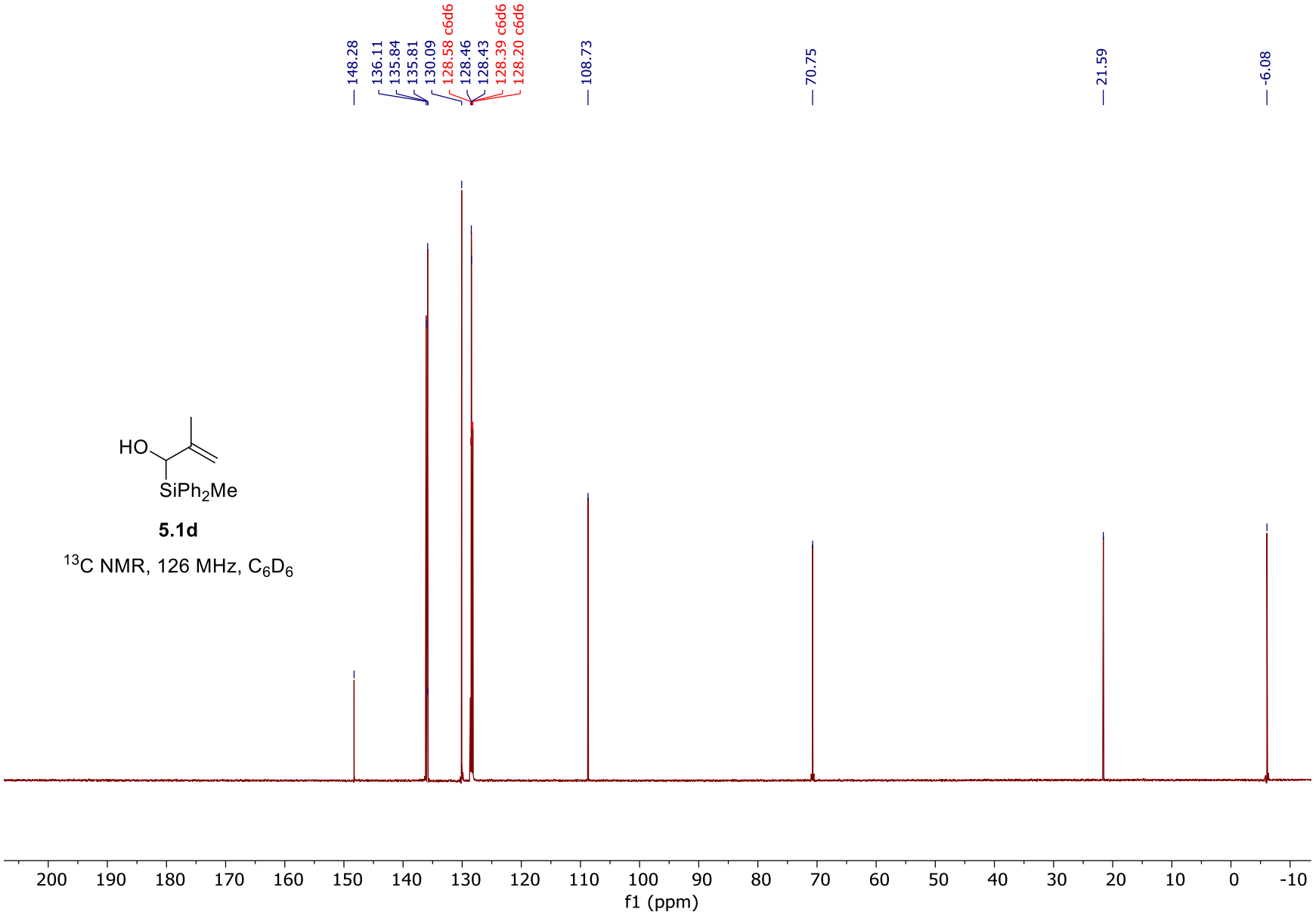

7.16 c6d6
4.89
4.89
4.89
4.88
4.88
4.88
4.88
4.88
4.75
4.75
4.74
4.74
4.74
4.73
3.80
1.61
1.61
1.61
1.61
1.61
1.23
1.04
1.02
1.01
0.72
0.70
0.69
0.67
0.66
0.64
0.63
0.61
0.60
0.58
HO
SiEt3
5.1b
1H NMR, 500 MHz, C6D6
1.00
0.99
0.93
2.96
0.64
9.88
6.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

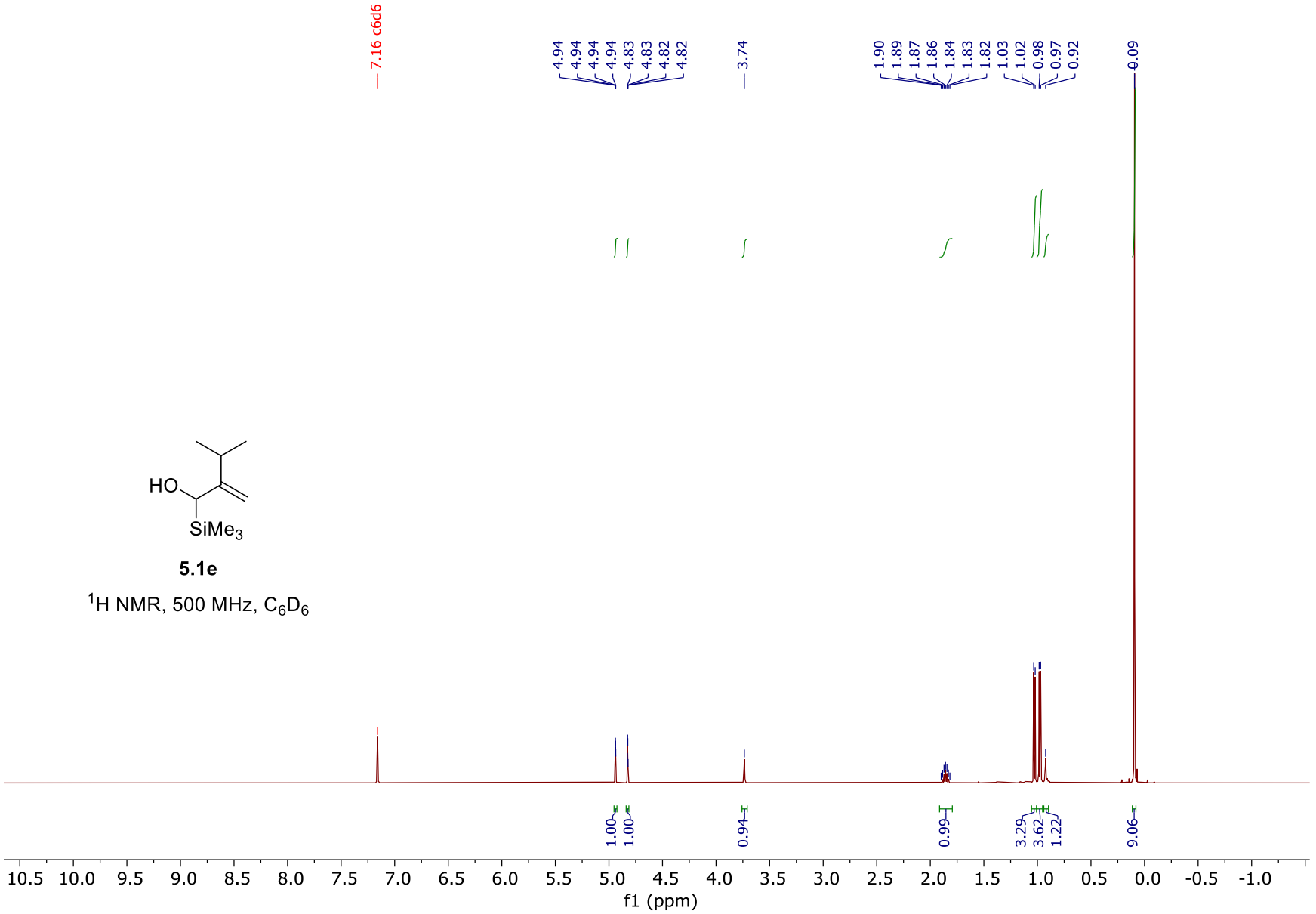

149.41
128.58 c6d6
128.39 c6d6
128.20 c6d6
107.05
70.10
21.04
8.13
2.84
HO
SiEt3
5.1b
13C NMR, 126 MHz, C6D6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

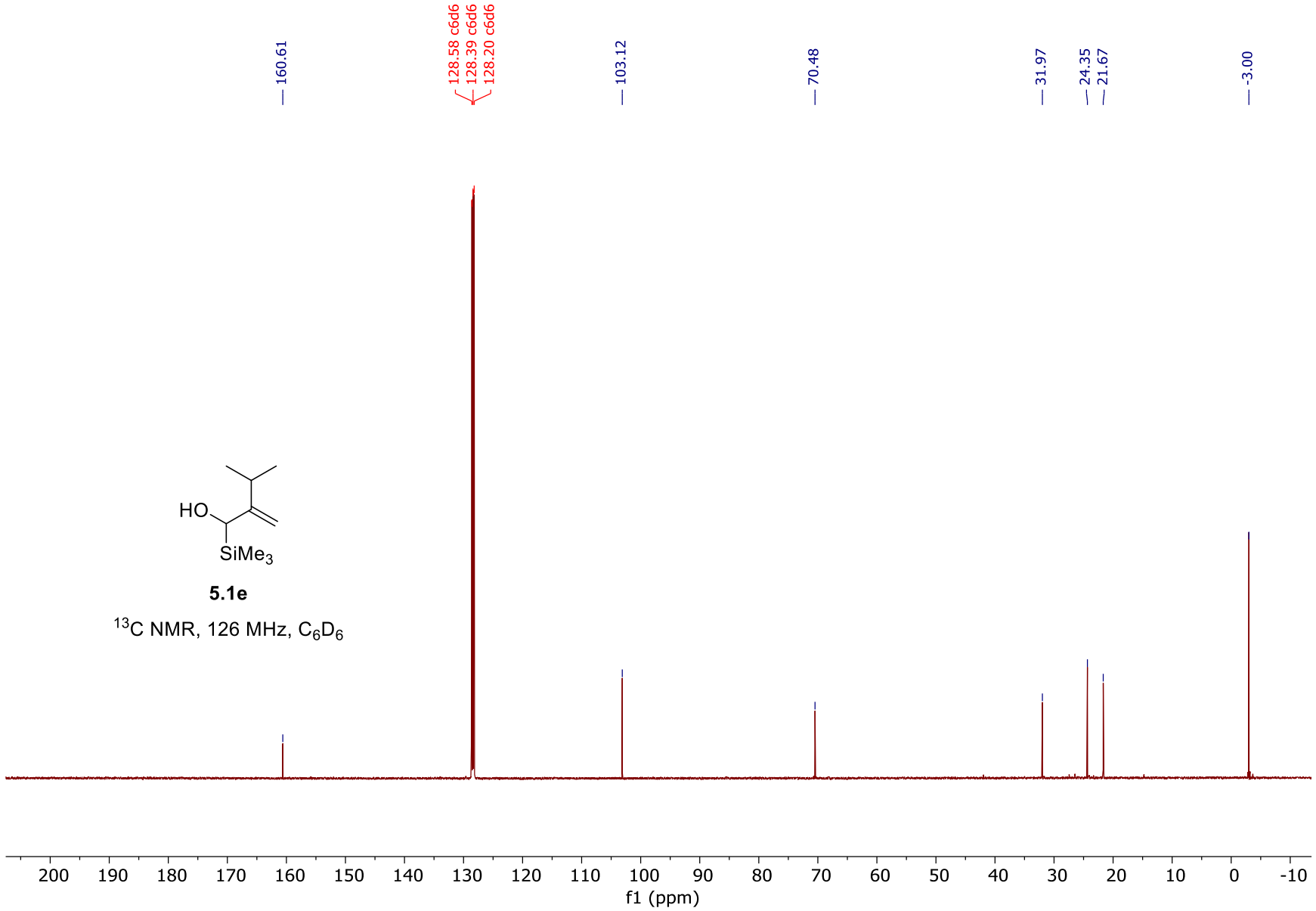

7.16 c6d6
4.89 4.89 4.89 4.89 4.89 4.88 4.88 4.76 4.75 4.75 4.75 3.80 1.63 1.63 1.63 1.63 1.49 1.48 1.47 1.46 1.46 1.45 1.44 1.44 1.44 1.43 1.43 1.43 1.42 1.42 1.41 1.41 1.40 1.40 1.39 1.39 1.38 1.36 1.36 1.03 1.01 1.00 0.97 0.73 0.72 0.71 0.70 0.69 0.69 0.68 0.67 0.66 0.65 0.64 0.63 0.63 0.62 0.61 0.61 0.60
HO
SiPr3
5.1c
1H NMR, 500 MHz, C6D6
1.00 0.98 0.92 2.89 6.38 9.19 0.92 6.47
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 -1.0
f1 (ppm)

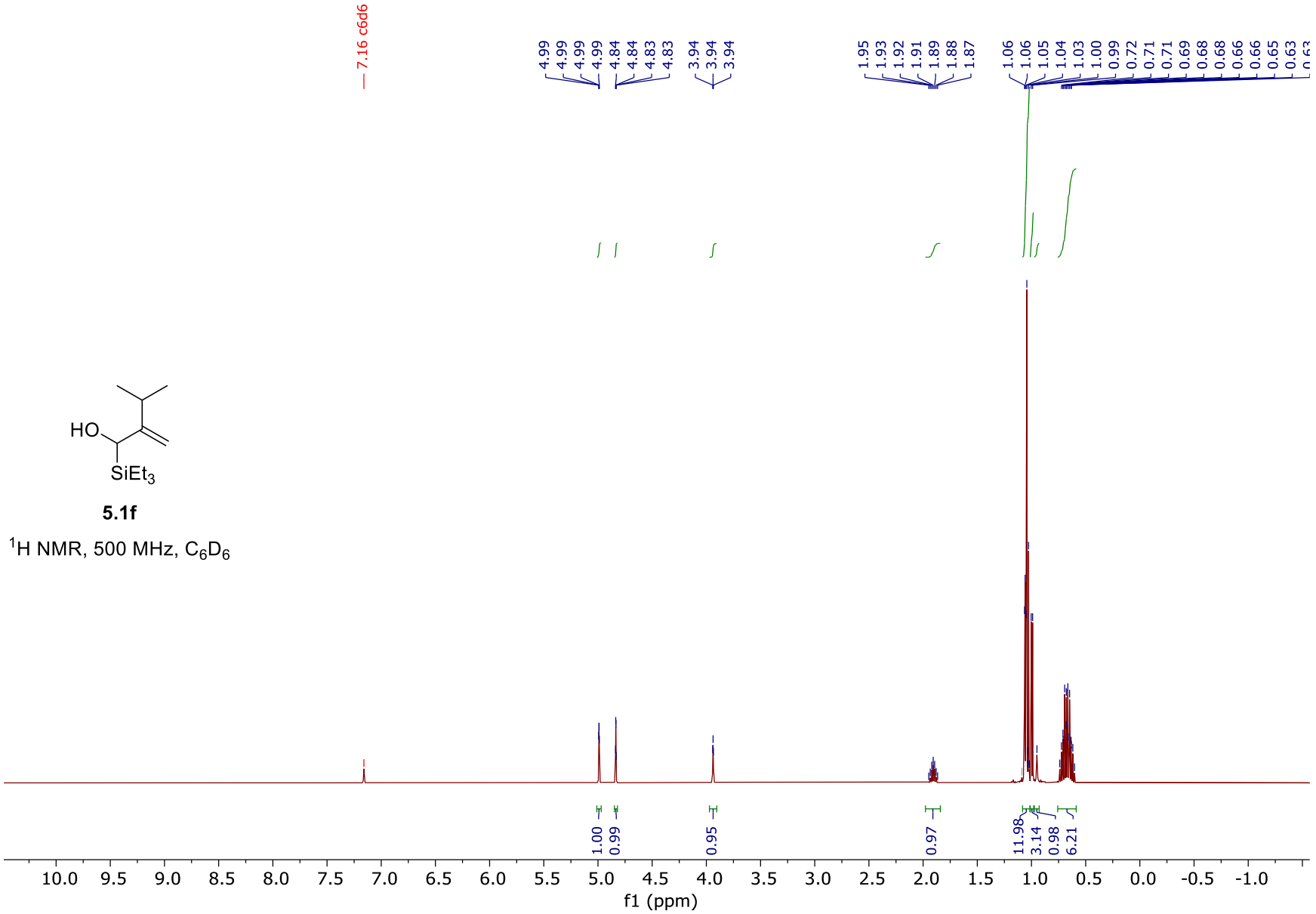

149.44
128.58 c6d6
128.39 c6d6
128.20 c6d6
107.16
70.50
21.14
19.32
18.25
14.65
HO
SiPr3
5.1c
13C NMR, 126 MHz, C6D6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.70 7.70 7.69 7.69 7.69 7.69 7.68 7.68 7.68 7.67 7.67 7.59 7.58 7.58 7.57 7.57 7.57 7.57 7.56 7.18 7.18 7.17 7.17 7.17 7.16 7.16 c6d6 7.16 7.15 7.15 7.14 7.14 7.14 7.13 7.13 4.86 4.86 4.86 4.86 4.86 4.86 4.73 4.72 4.72 4.72 4.72 4.71 4.22
1.34 1.21 0.55
HO
SiPh2Me
5.1d
1H NMR, 500 MHz, C6D6
1.99 2.00 6.32 1.13 1.11 1.02 3.29 1.05 3.35
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 -1.0
f1 (ppm)


148.28
136.11
135.84
135.81
130.09
128.58 c6d6
128.46
128.43
128.39 c6d6
128.20 c6d6
108.73
70.75
21.59
-6.08
HO
SiPh2Me
5.1d
13C NMR, 126 MHz, C6D6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

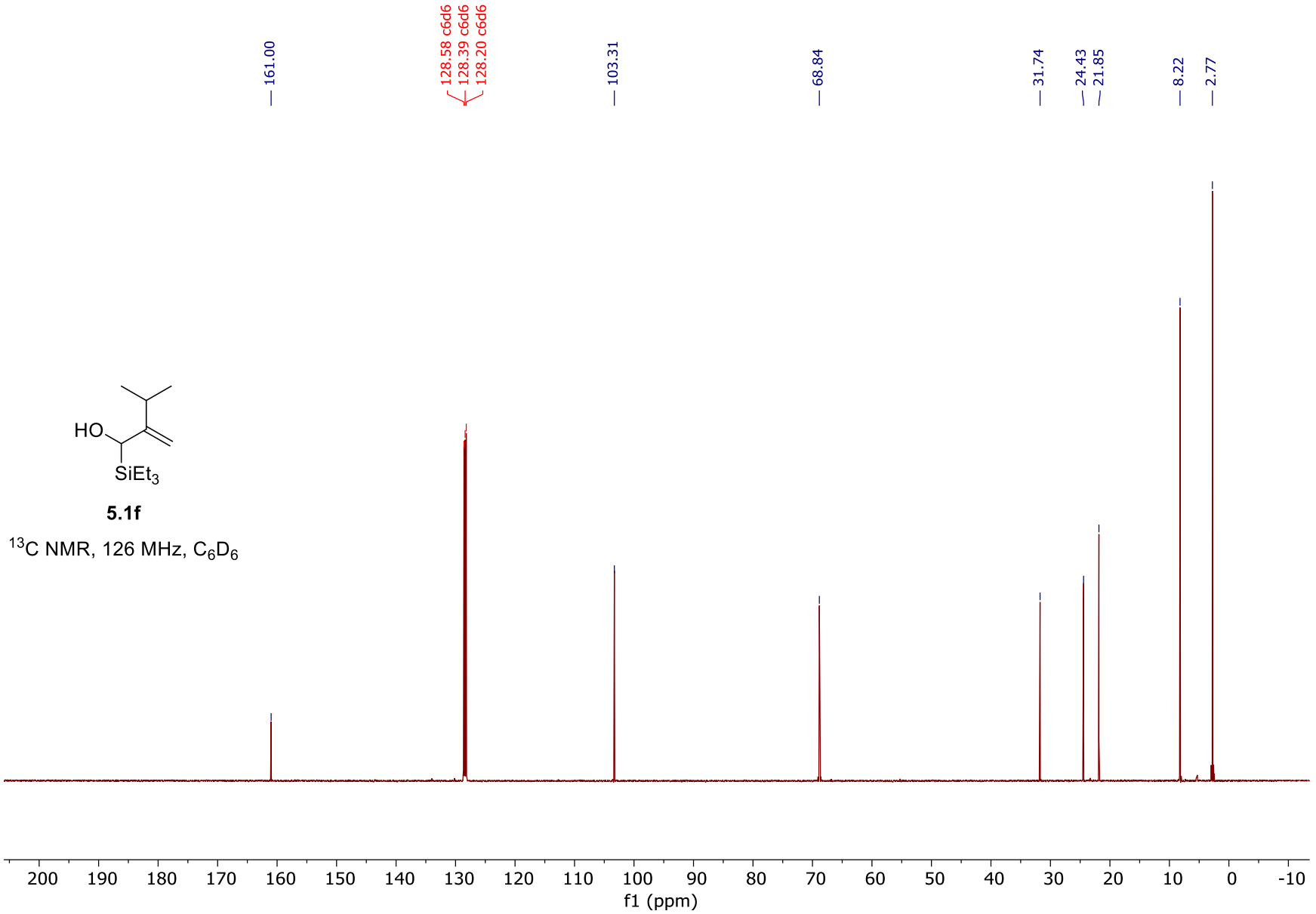

7.16 c6d6
4.94
4.94
4.94
4.94
4.83
4.82
4.82
3.74
1.90
1.89
1.87
1.86
1.84
1.83
1.82
1.03
1.02
0.98
0.97
0.92
0.09
HO
SiMe3
5.1e
1H NMR, 500 MHz, C6D6
1.00
1.00
0.94
0.99
3.29
3.62
1.22
9.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

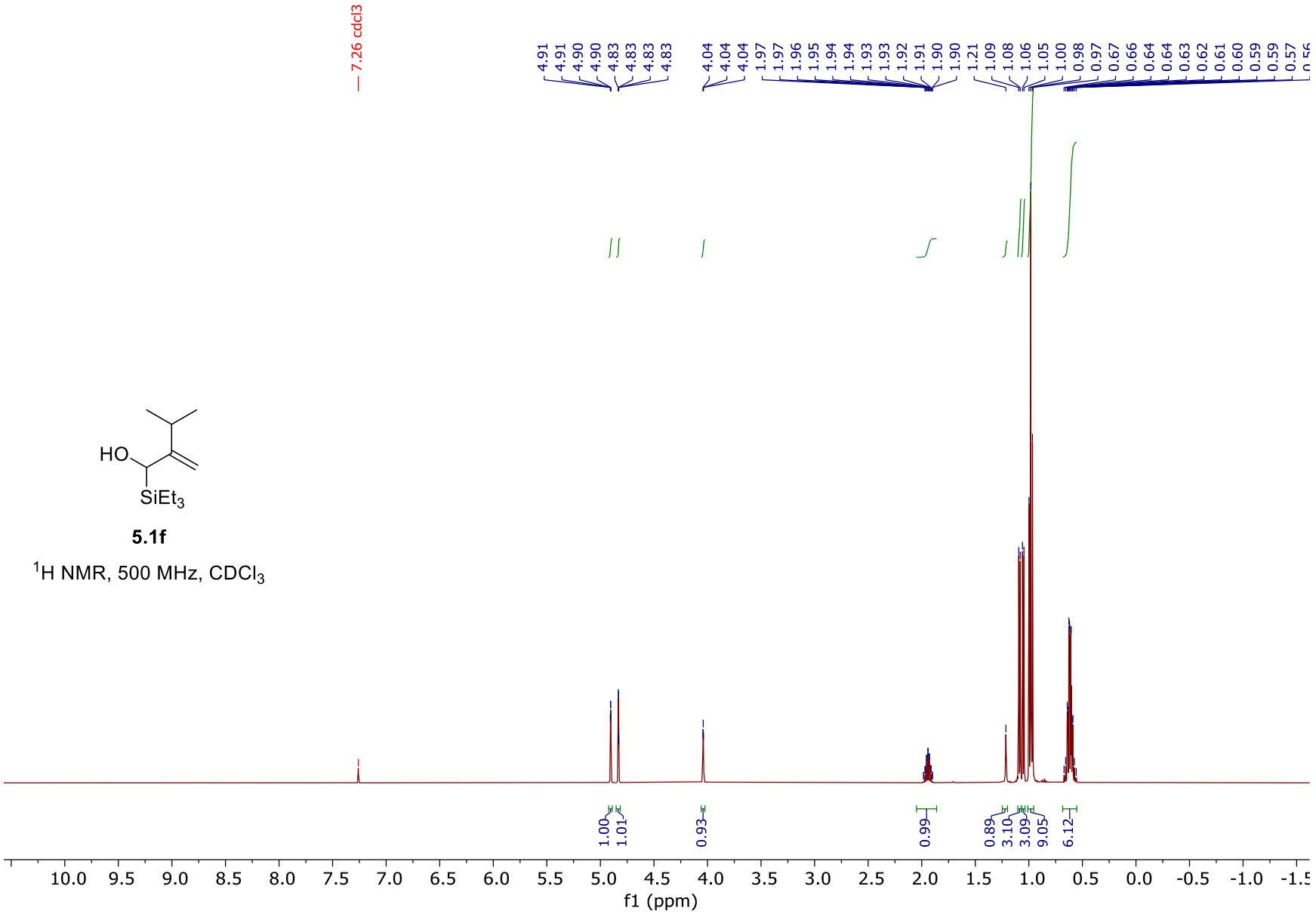

160.61
128.58 c6d6
128.39 c6d6
128.20 c6d6
103.12
70.48
31.97
24.35
21.67
-3.00
HO
SiMe3
5.1e
13C NMR, 126 MHz, C6D6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

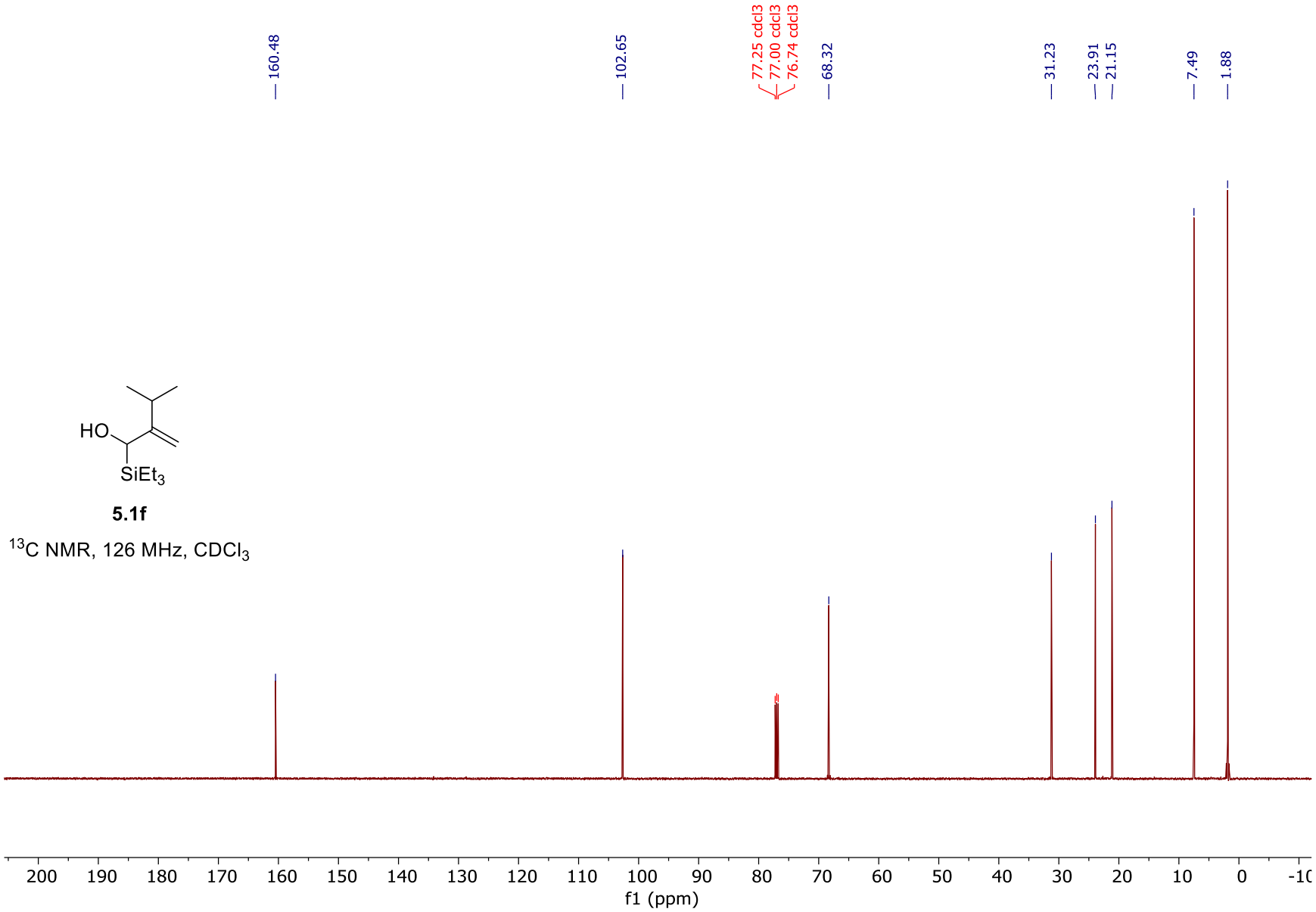


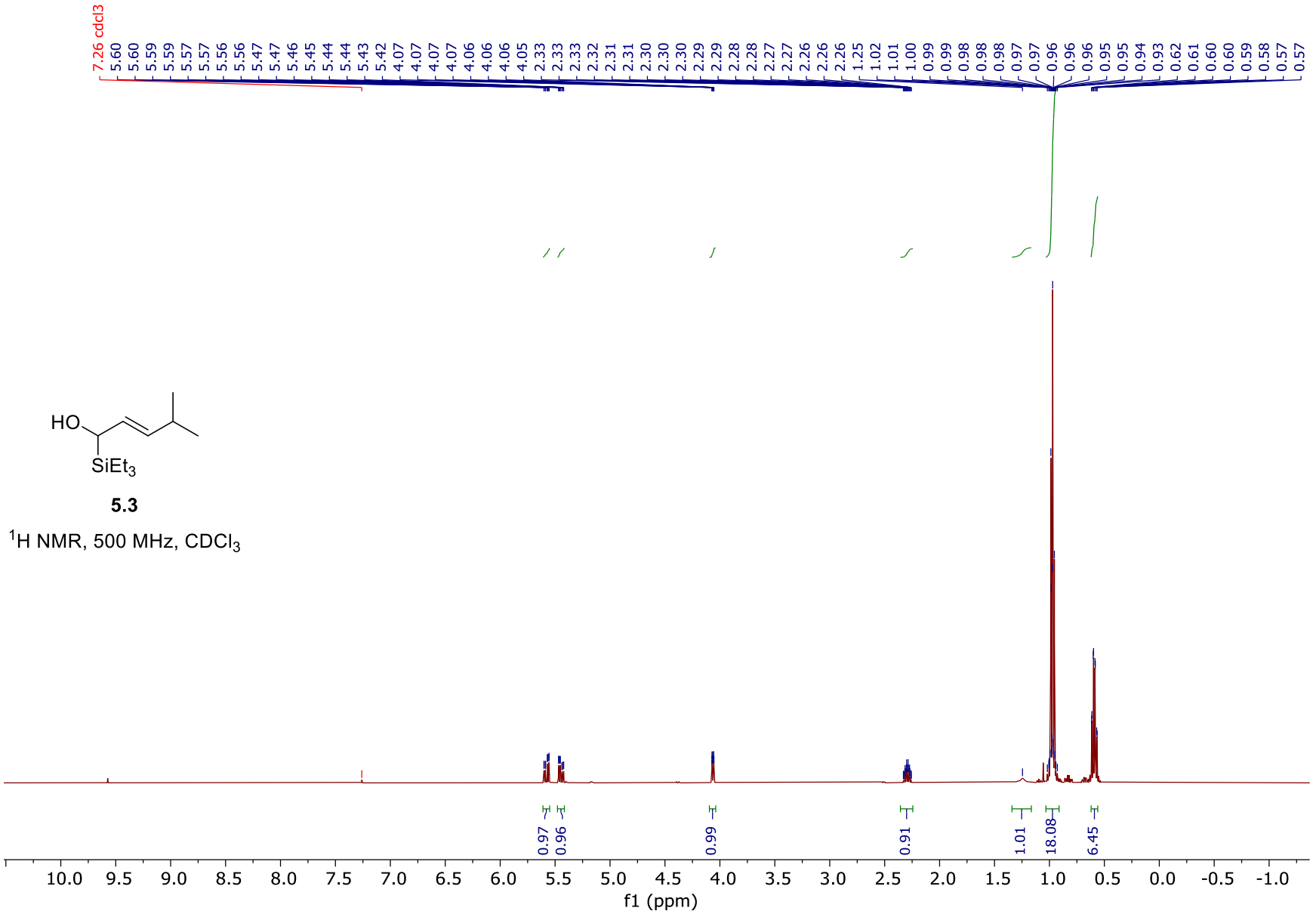
5.1f

^{1}H NMR, 500 MHz, C_6D_6


161.00
128.58 c6d6
128.39 c6d6
128.20 c6d6
103.31
68.84
31.74
24.43
21.85
8.22
2.77
HO
SiEt3
5.1f
13C NMR, 126 MHz, C6D6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

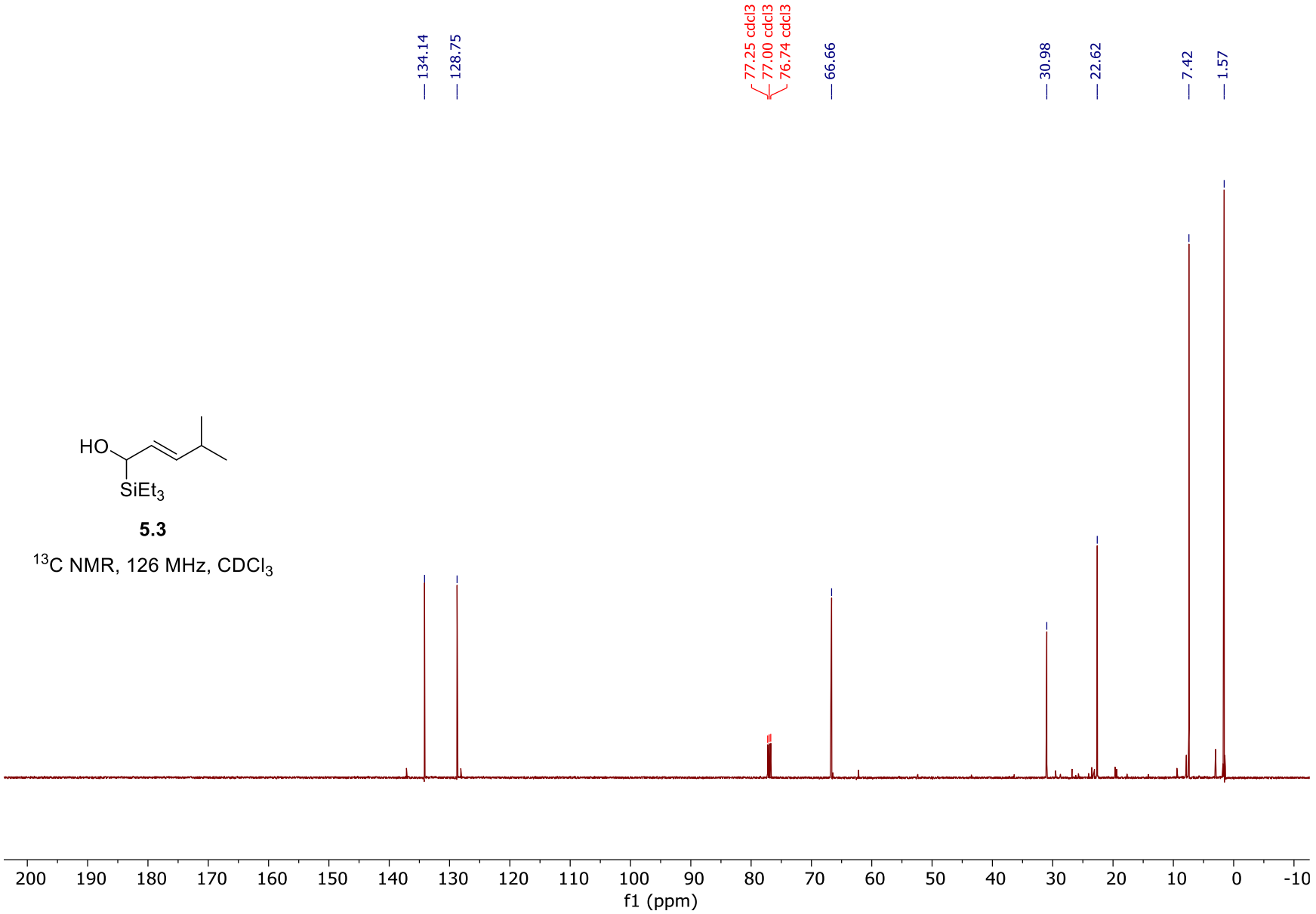

7.26 cdcl3
4.91 4.91 4.90 4.90 4.83 4.83 4.83 4.83
4.04 4.04 4.04
1.97 1.97 1.96 1.95 1.94 1.94 1.93 1.93 1.92 1.91 1.90 1.90
1.21 1.09 1.08 1.06 1.05 1.00 0.98 0.97 0.67 0.66 0.64 0.64 0.63 0.62 0.61 0.60 0.59 0.59 0.57
HO
SiEt3
5.1f
1H NMR, 500 MHz, CDCl3
1.00 1.01 0.93 0.99 0.89 3.10 3.09 9.05 6.12
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 -1.0
f1 (ppm)

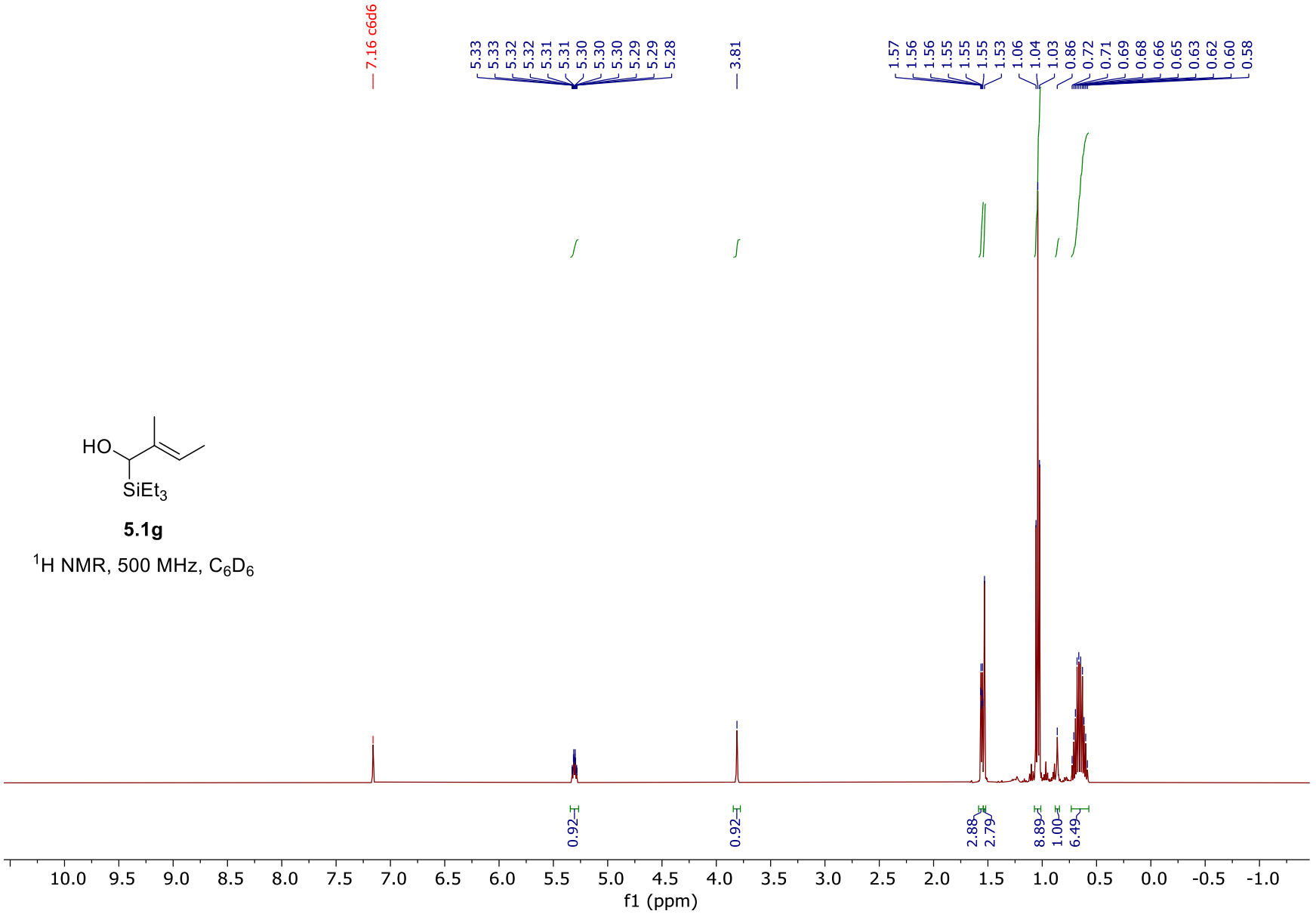

160.48
102.65
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
68.32
31.23
23.91
21.15
7.49
1.88
HO
SiEt3
5.1f
13C NMR, 126 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

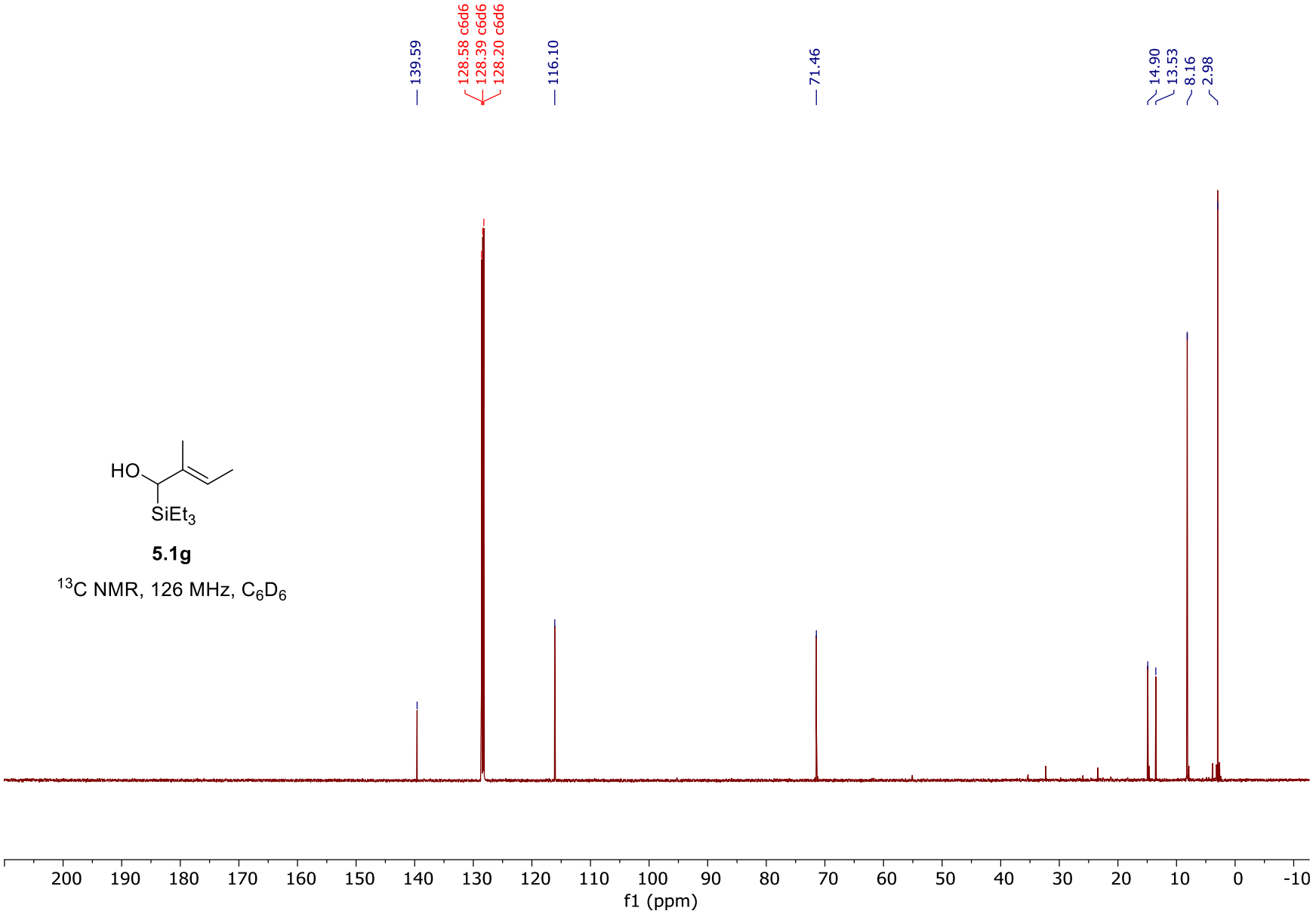


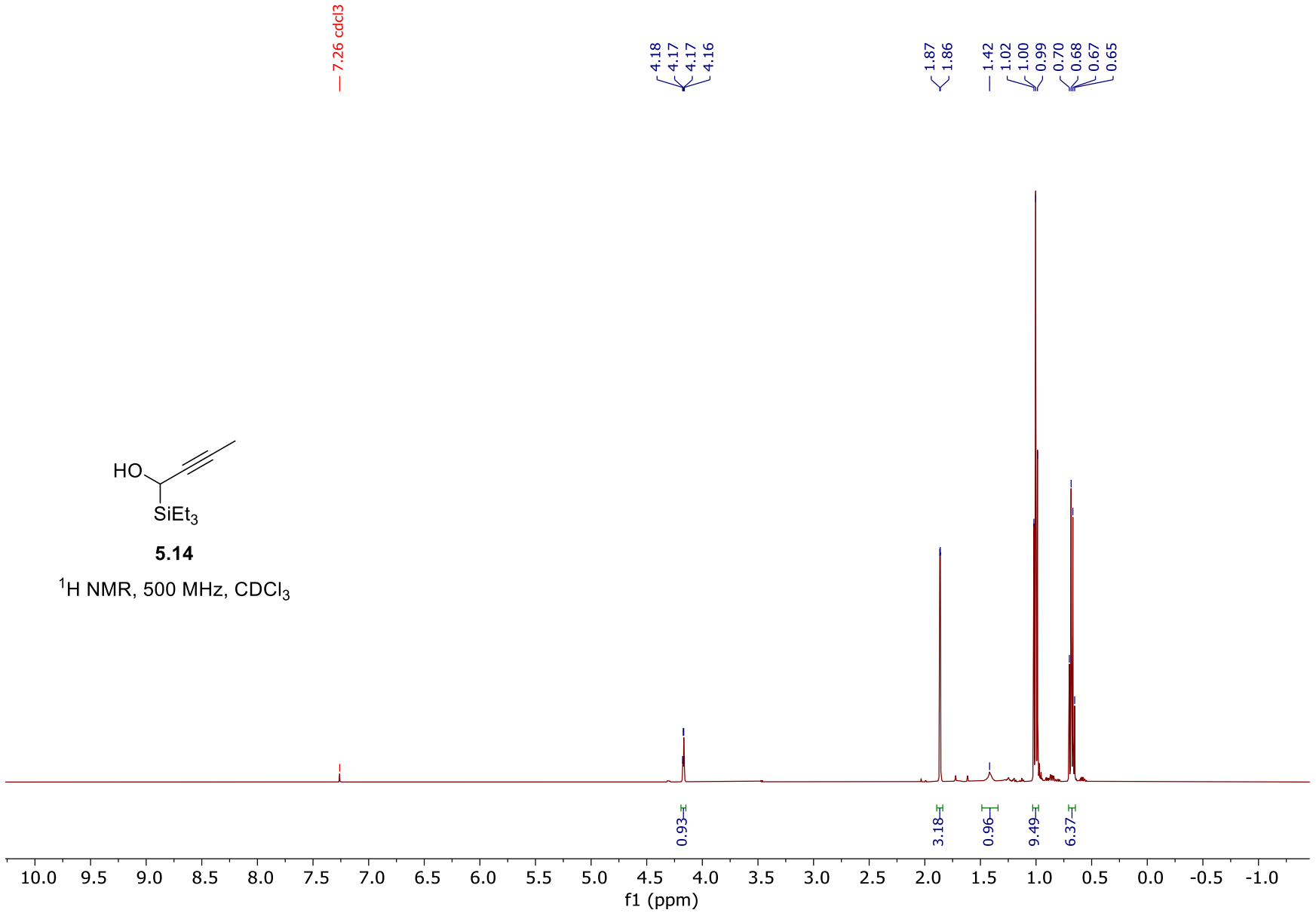
5.3

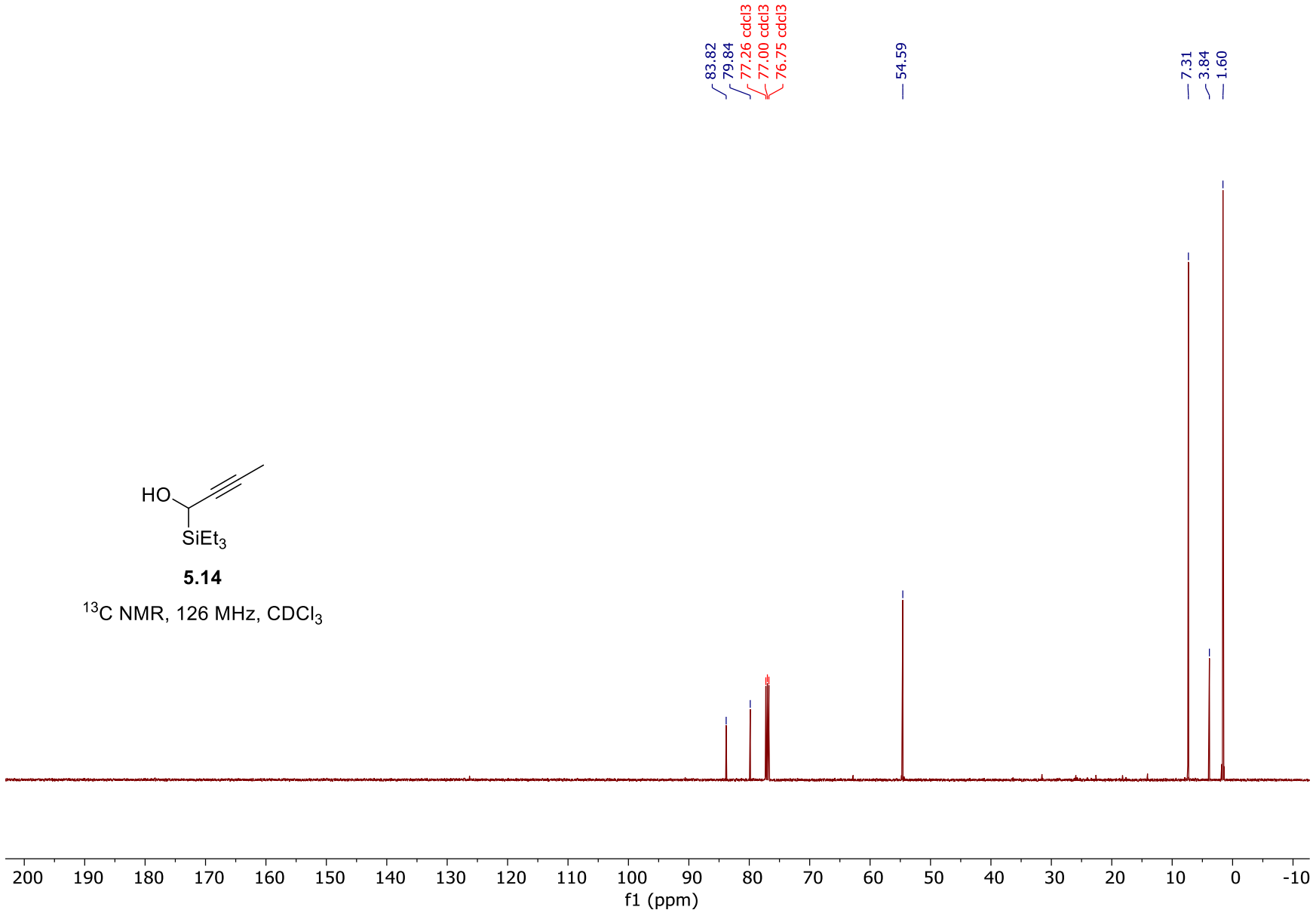
^{1}H NMR, 500 MHz, $CDCl_3$

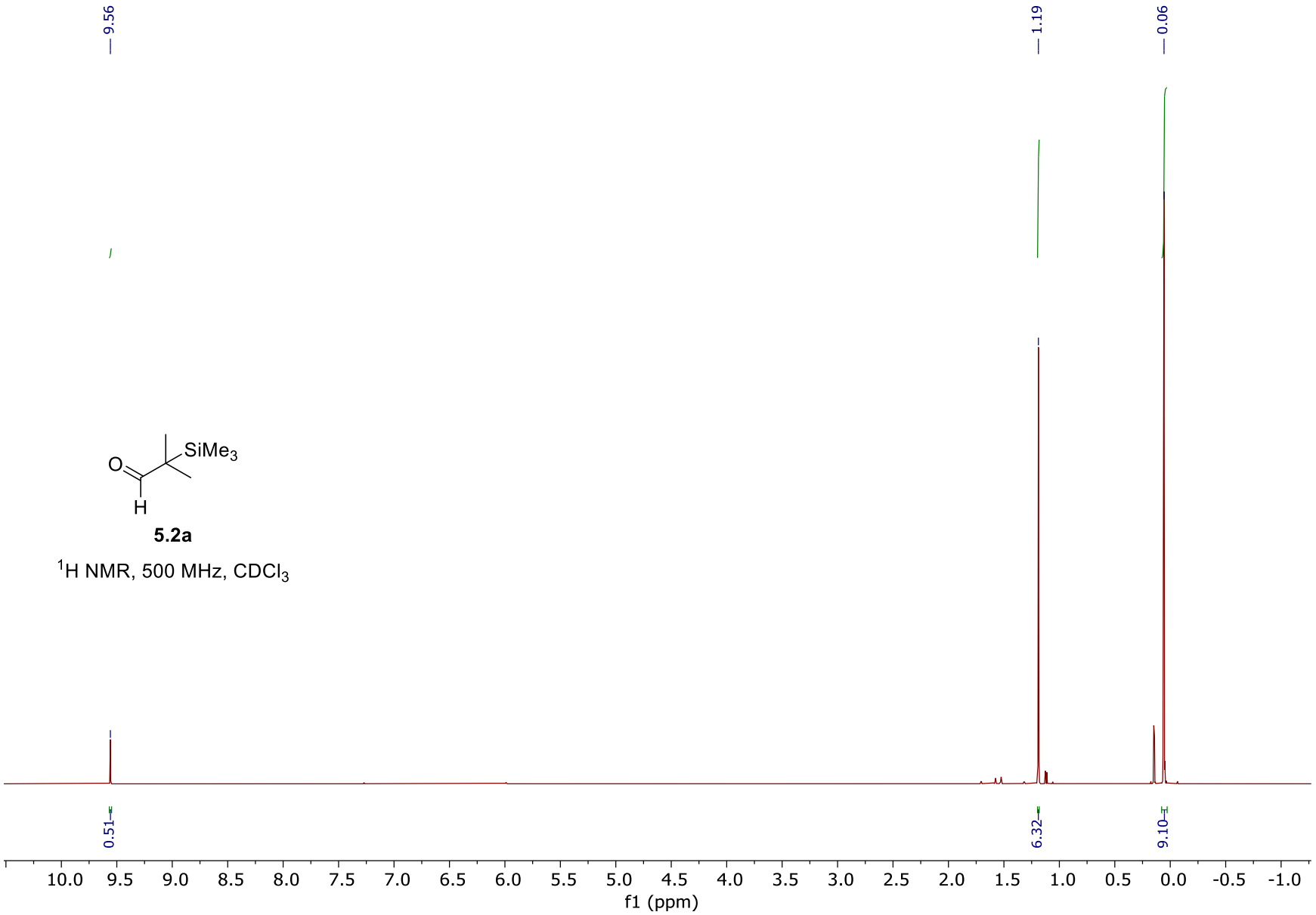

134.14
128.75
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
66.66
30.98
22.62
7.42
1.57
HO
SiEt3
5.3
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.16 c6d6
5.33
5.33
5.32
5.32
5.31
5.31
5.30
5.30
5.30
5.29
5.29
5.28
3.81
1.57
1.56
1.56
1.55
1.55
1.55
1.53
1.06
1.04
1.03
0.86
0.72
0.71
0.69
0.68
0.66
0.65
0.63
0.62
0.60
0.58
HO
SiEt3
5.1g
1H NMR, 500 MHz, C6D6
0.92
0.92
2.88
2.79
8.89
1.00
6.49
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 -1.0
f1 (ppm)


139.59
128.58 c6d6
128.39 c6d6
128.20 c6d6
116.10
71.46
14.90
13.53
8.16
2.98
HO
SiEt3
5.1g
13C NMR, 126 MHz, C6D6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

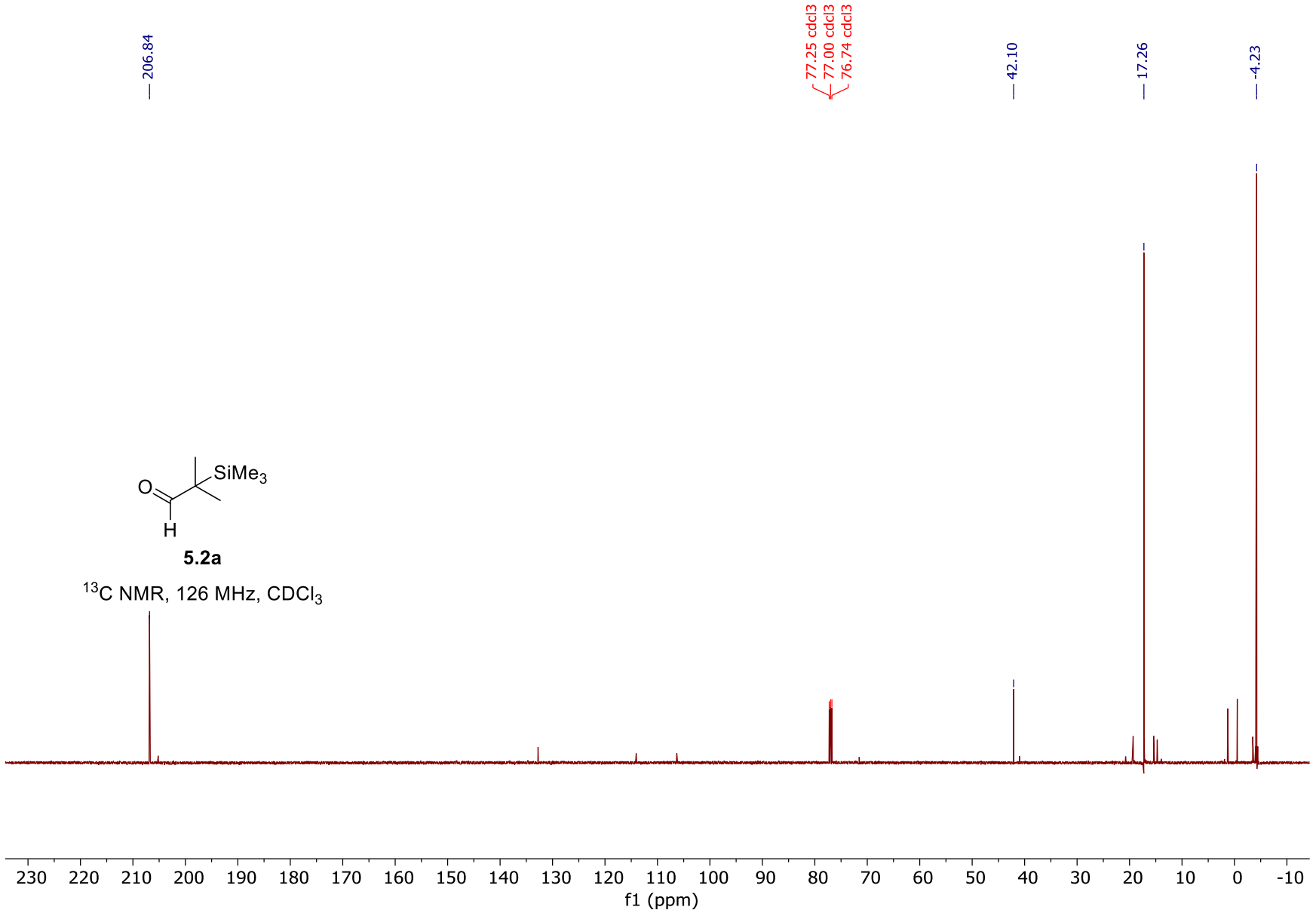

7.26 cdcl3
4.18
4.17
4.17
4.16
1.87
1.86
1.42
1.02
1.00
0.99
0.70
0.68
0.67
0.65
HO
SiEt3
5.14
1H NMR, 500 MHz, CDCl3
0.93
3.18
0.96
9.49
6.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

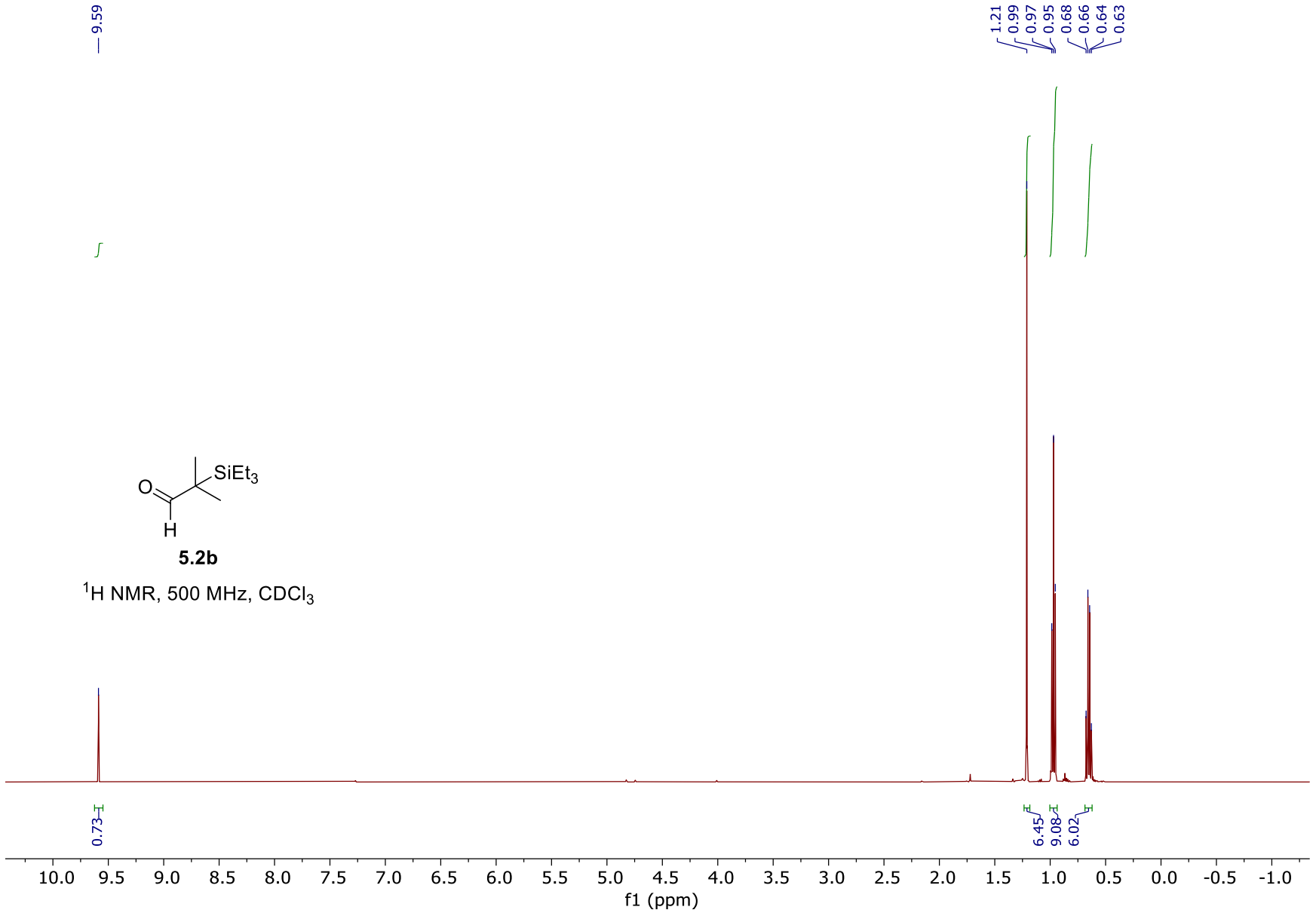

83.82
79.84
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
54.59
7.31
3.84
1.60
HO
SiEt3
5.14
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

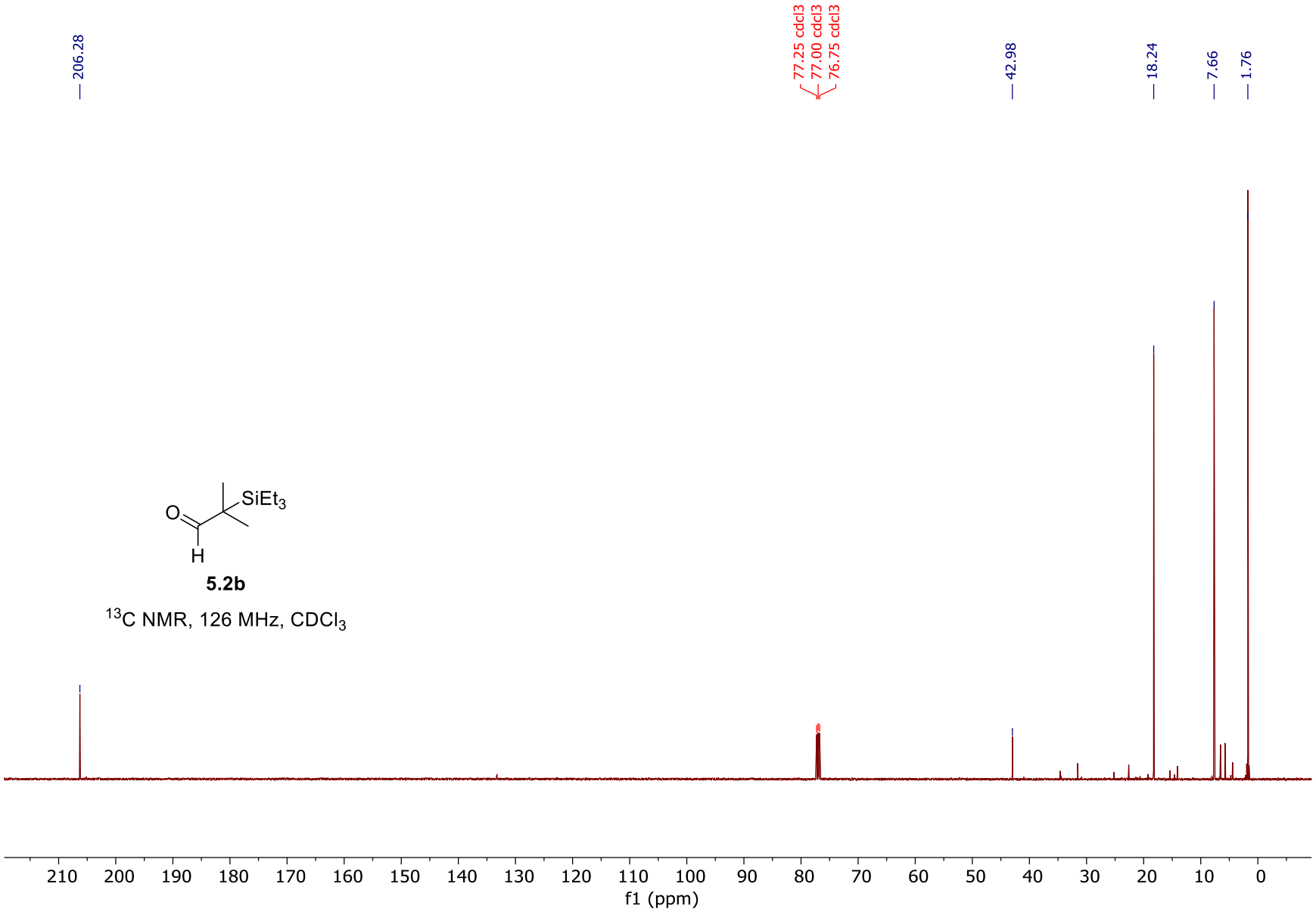


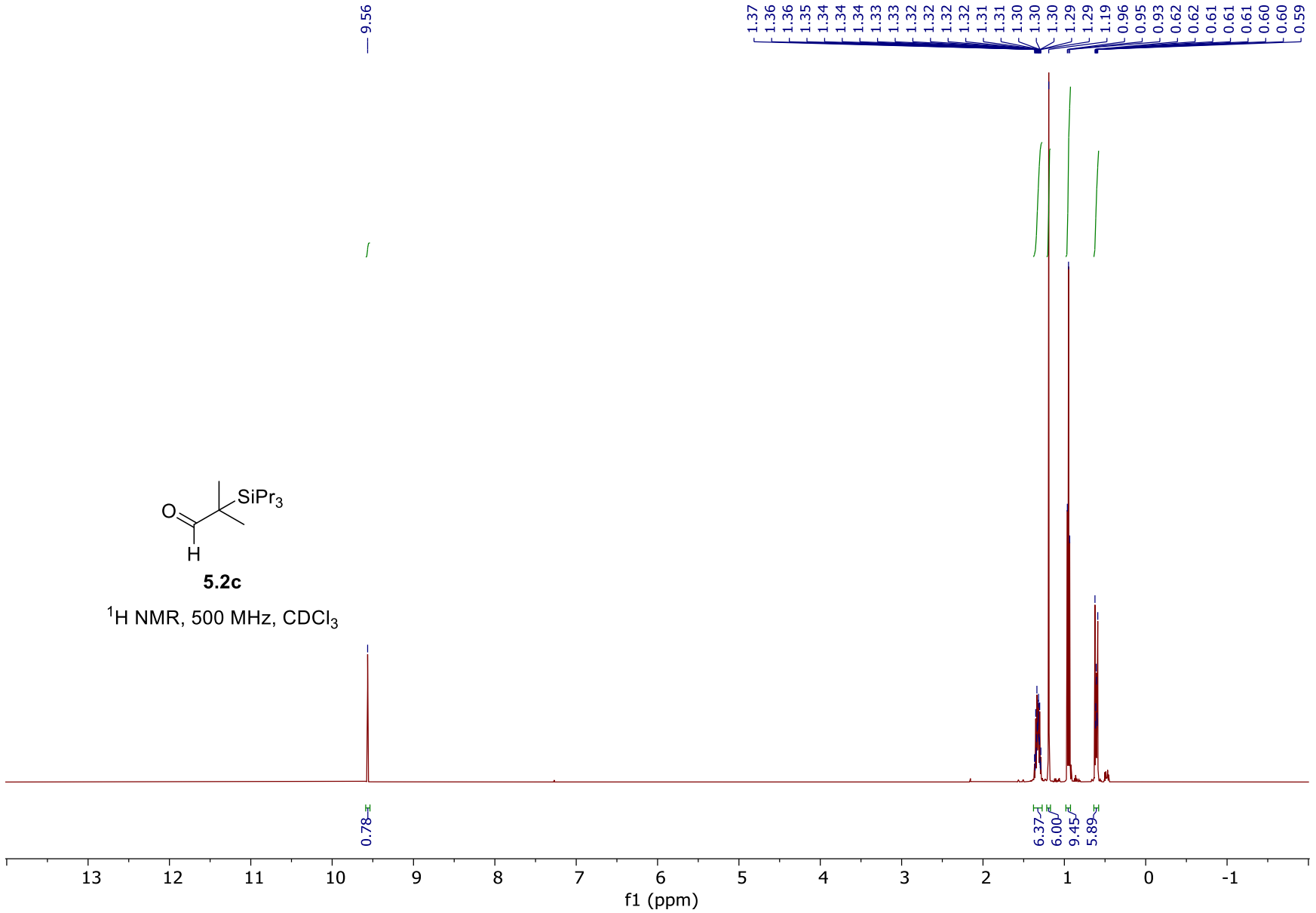
5.2a

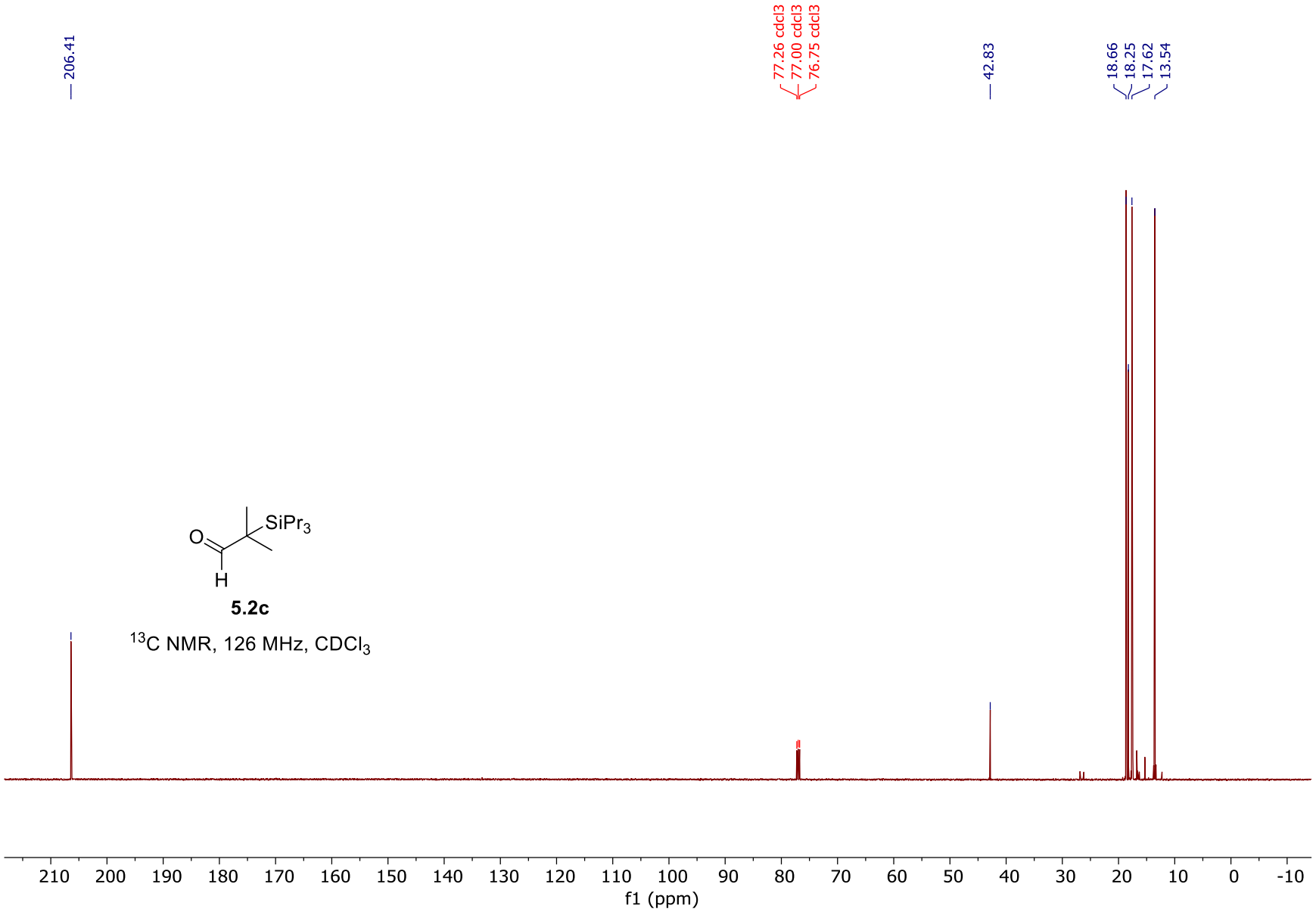
^{1}H NMR, 500 MHz, $CDCl_3$

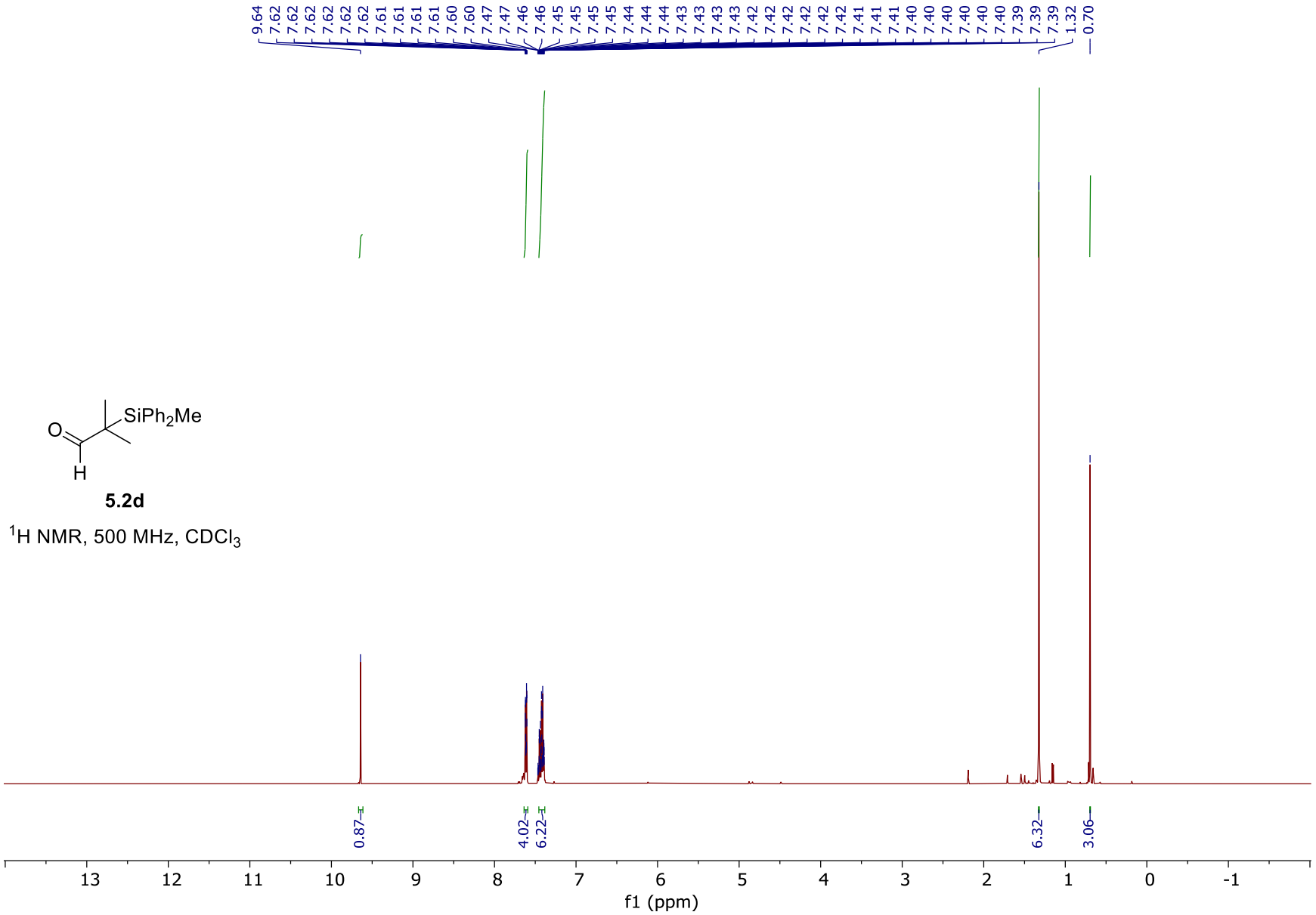

206.84
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
42.10
17.26
-4.23
SiMe3
O
H
5.2a
13C NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

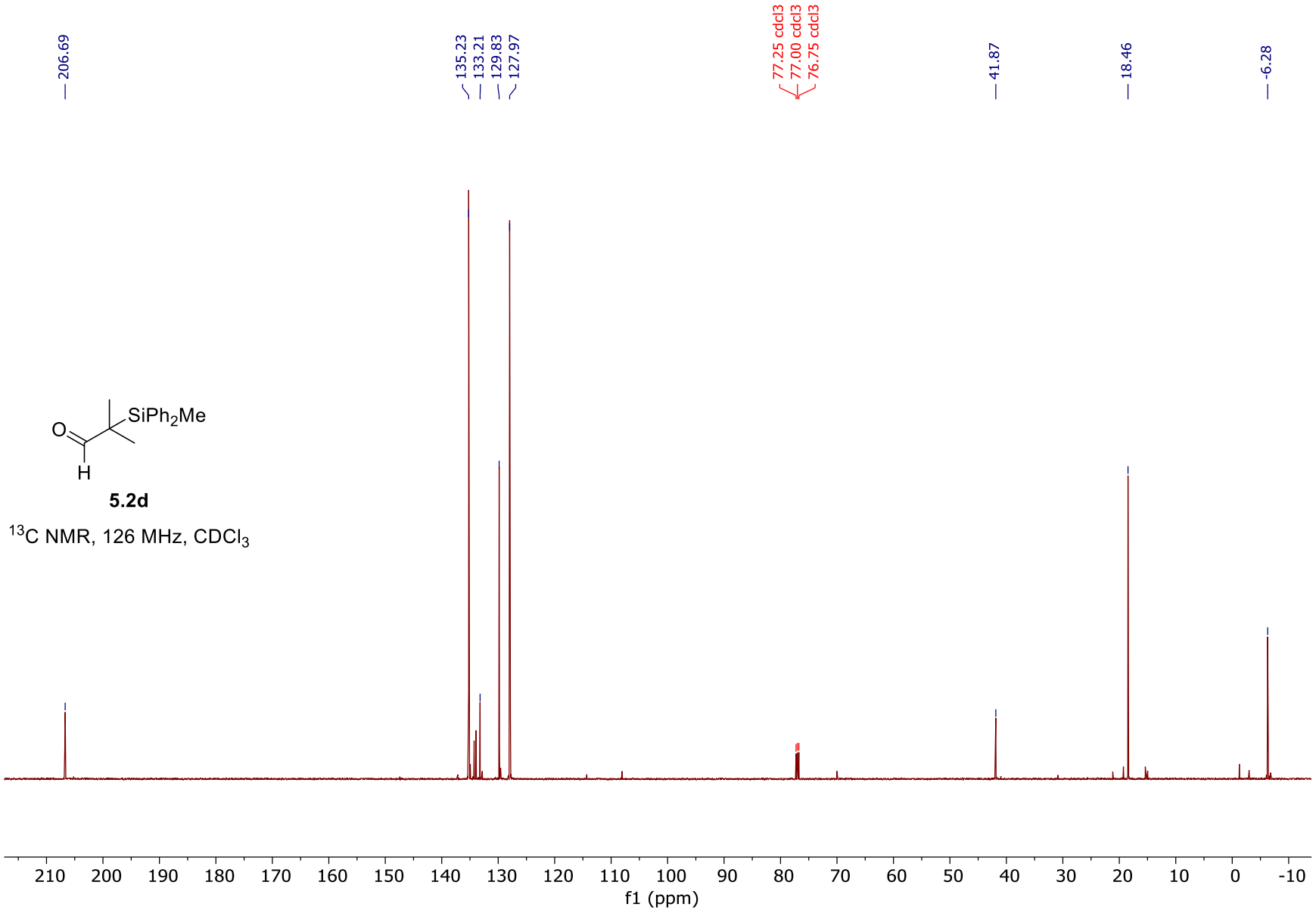

9.59
1.21
0.99
0.97
0.95
0.68
0.66
0.64
0.63
SiEt3
O
H
5.2b
1H NMR, 500 MHz, CDCl3
0.73
6.45
9.08
6.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

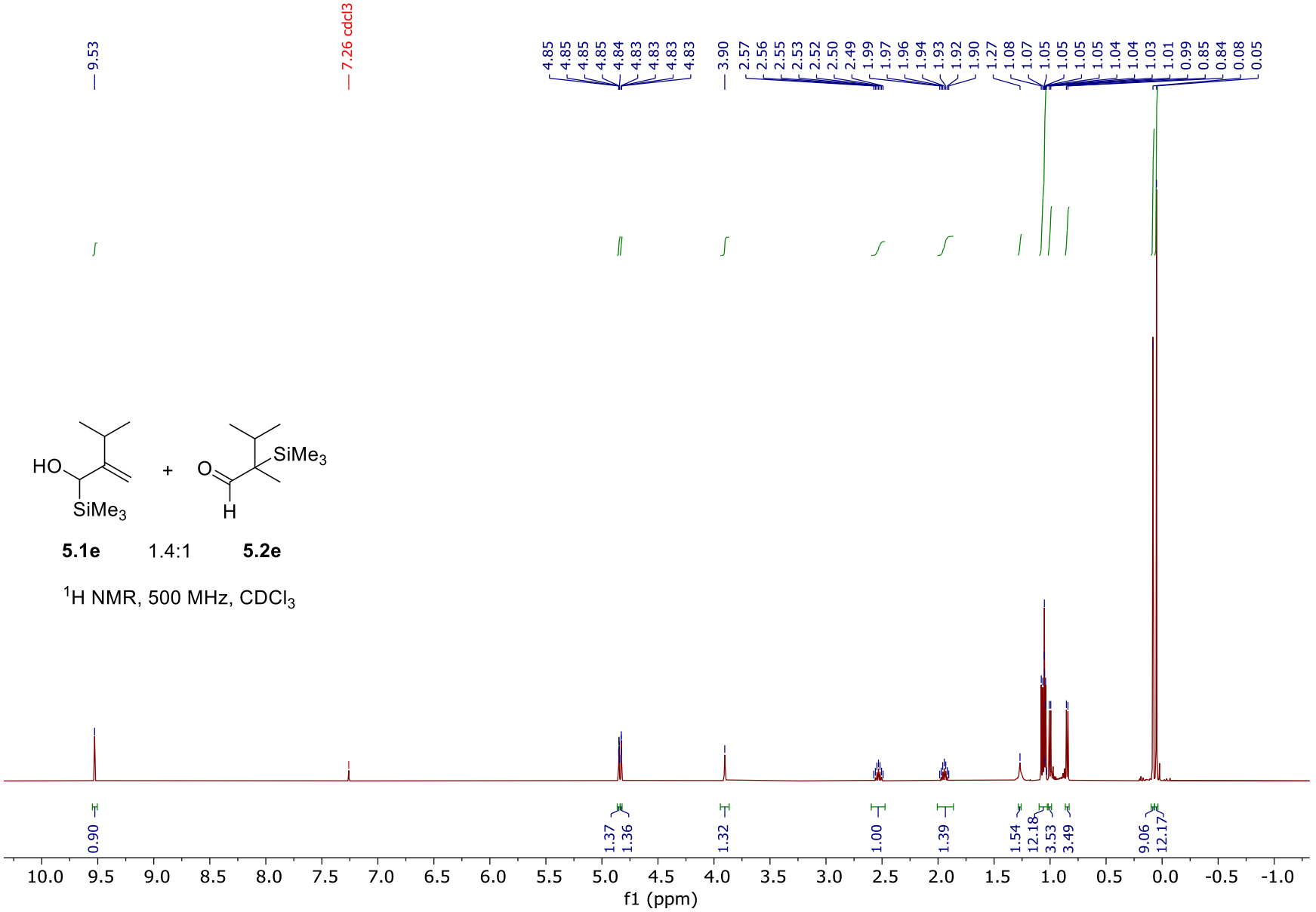

206.28
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
42.98
18.24
7.66
1.76
O
SiEt3
H
5.2b
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

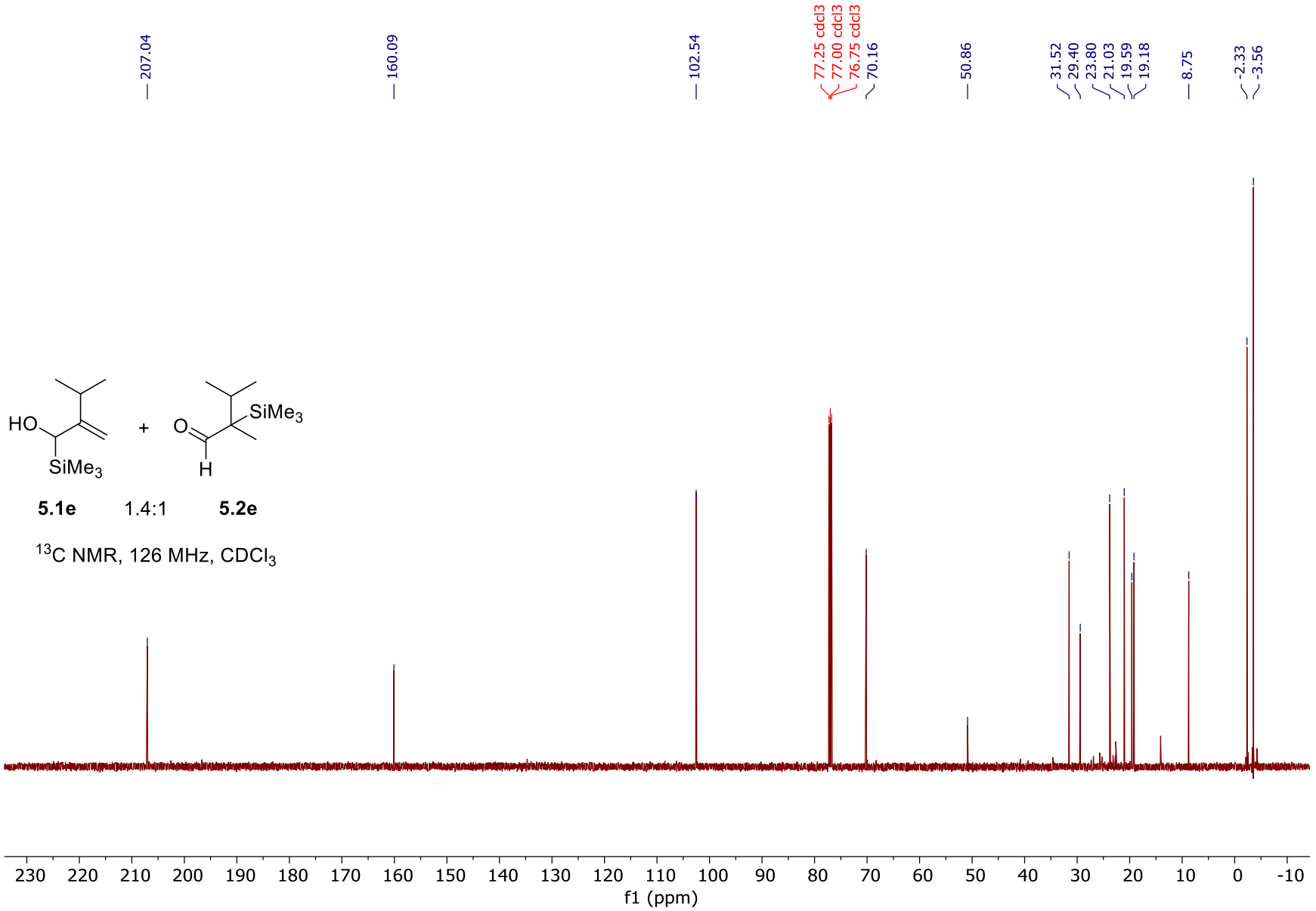

9.56
1.37
1.36
1.36
1.35
1.34
1.34
1.34
1.33
1.33
1.32
1.32
1.32
1.32
1.31
1.31
1.30
1.30
1.30
1.29
1.29
1.19
0.96
0.95
0.93
0.62
0.62
0.61
0.61
0.61
0.60
0.60
0.59
O
SiPr3
H
5.2c
1H NMR, 500 MHz, CDCl3
0.78
6.37
6.00
9.45
5.89
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

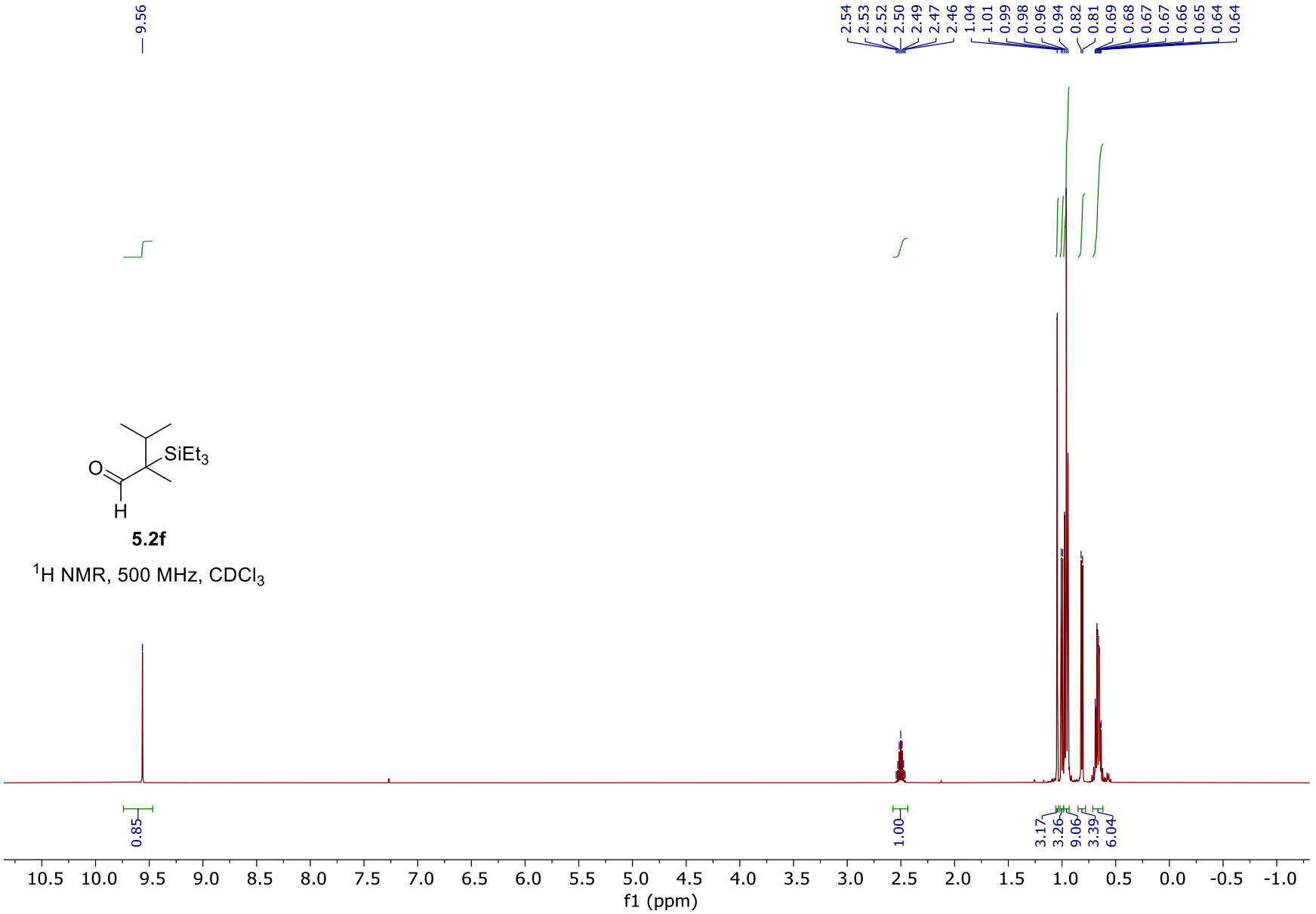

206.41
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
42.83
18.66
18.25
17.62
13.54
O
SiPr3
H
5.2c
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

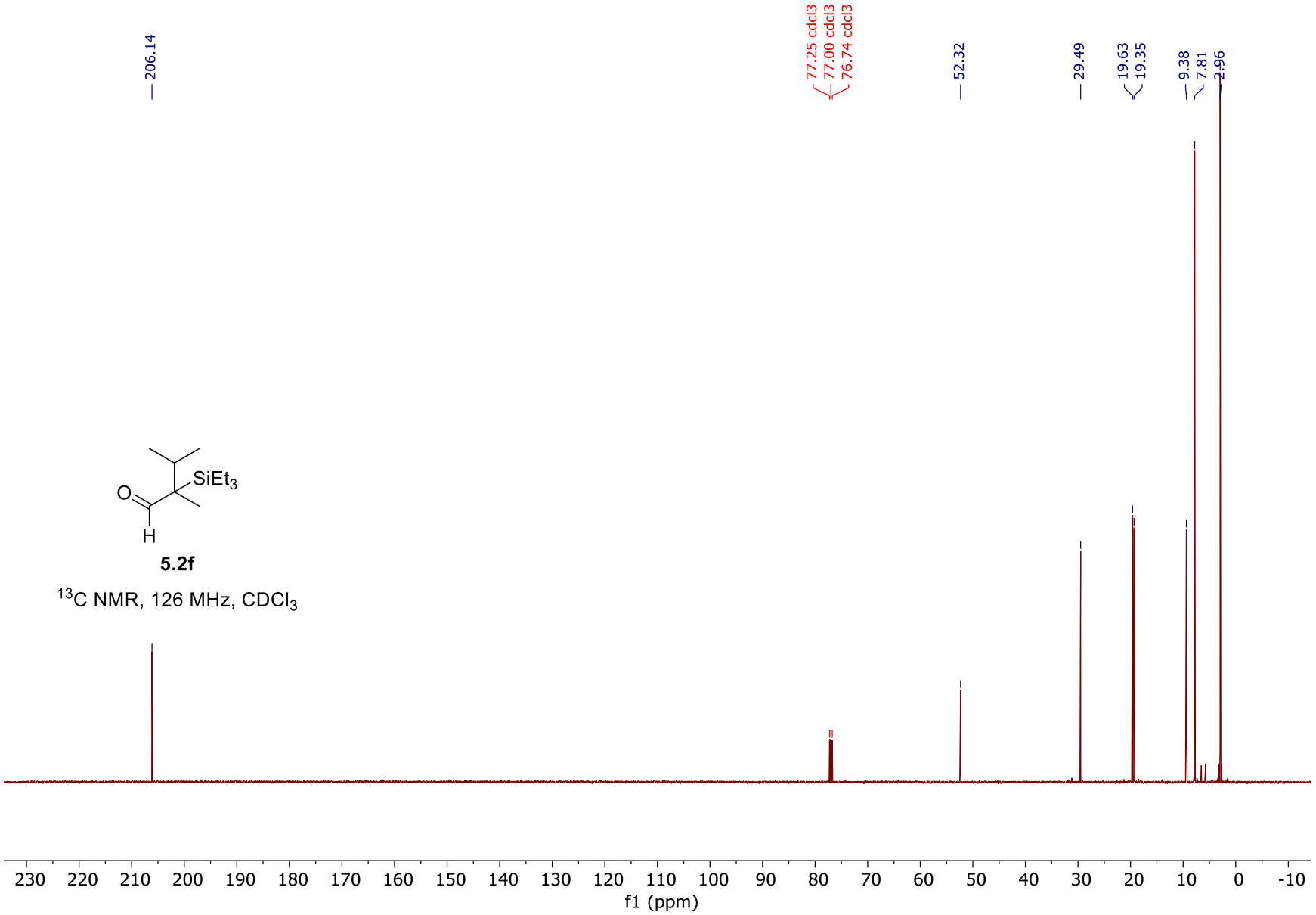

9.64
7.62
7.62
7.62
7.62
7.62
7.62
7.61
7.61
7.61
7.61
7.60
7.60
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.43
7.43
7.42
7.42
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.40
7.40
7.39
7.39
7.39
1.32
0.70
SiPh2Me
O
H
5.2d
1H NMR, 500 MHz, CDCl3
0.87
4.02
6.22
6.32
3.06
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

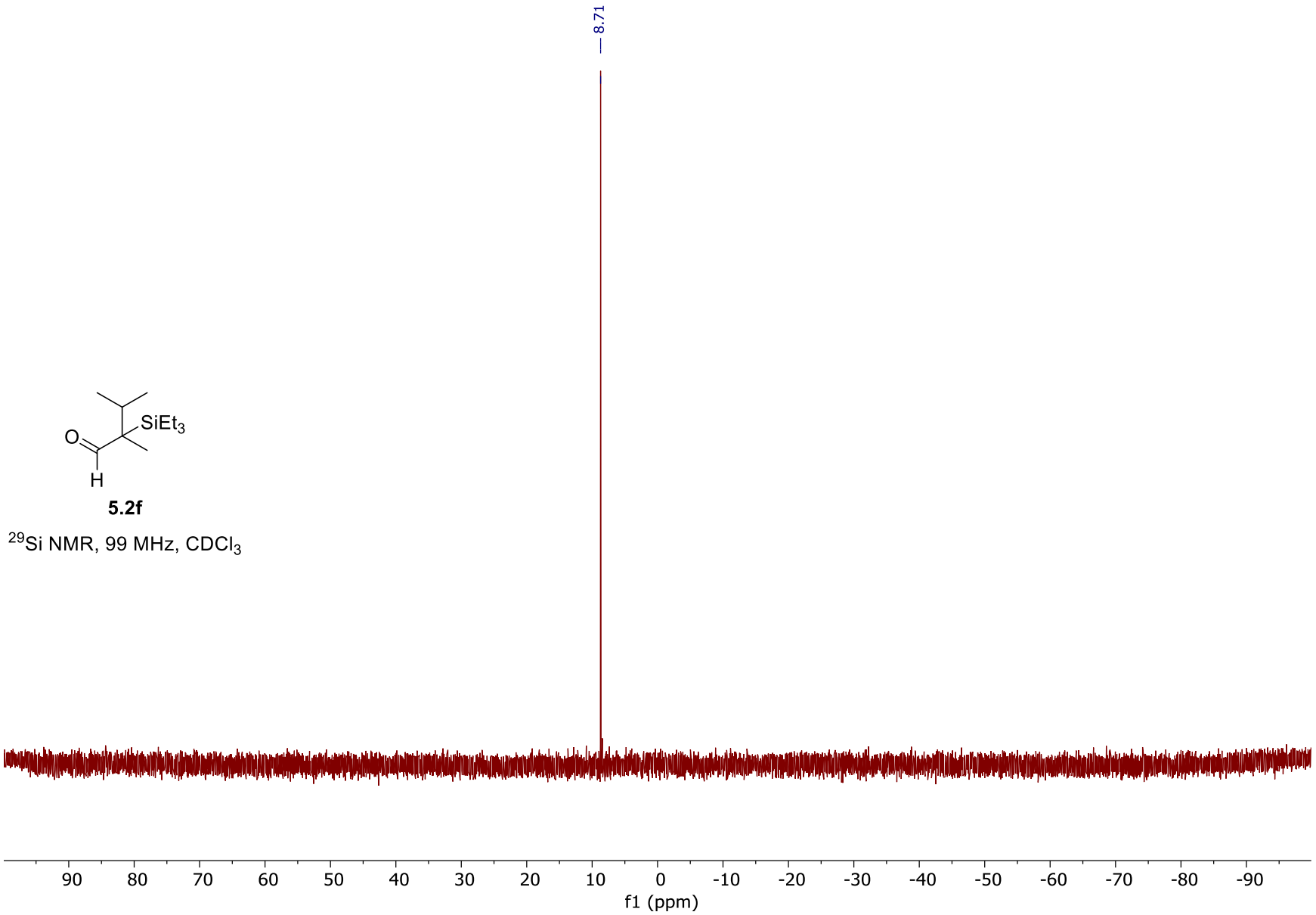

206.69
135.23
133.21
129.83
127.97
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
41.87
18.46
-6.28
O
SiPh2Me
H
5.2d
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.53
7.26 cdcl3
4.85 4.85 4.85 4.85 4.84 4.83 4.83 4.83 4.83
3.90
2.57 2.56 2.55 2.53 2.52 2.50 2.49 1.99 1.97 1.96 1.94 1.93 1.92 1.90
1.27 1.08 1.07 1.05 1.05 1.05 1.05 1.04 1.04 1.03 1.01 0.99 0.85 0.84 0.08 0.05
HO
SiMe3
+
O
SiMe3
H
5.1e 1.4:1 5.2e
1H NMR, 500 MHz, CDCl3
0.90
1.37 1.36
1.32
1.00
1.39
1.54
12.18
3.53
3.49
9.06
12.17
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 -1.0
f1 (ppm)


207.04
160.09
102.54
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
70.16
50.86
31.52
29.40
23.80
21.03
19.59
19.18
8.75
-2.33
-3.56
HO
SiMe3
+
O
SiMe3
H
5.1e 1.4:1 5.2e
13C NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

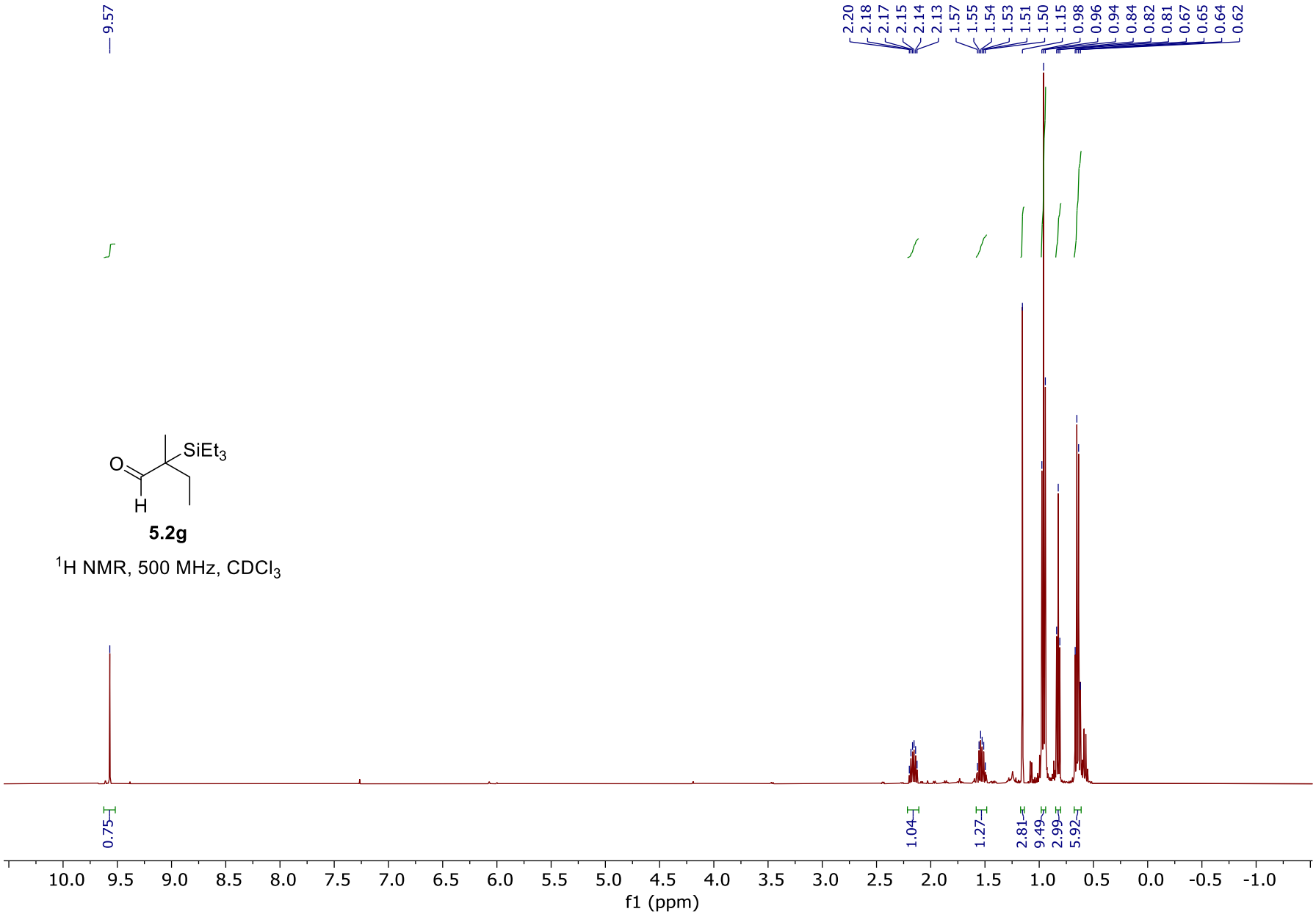

9.56
2.54
2.53
2.52
2.50
2.49
2.47
2.46
1.04
1.01
0.99
0.98
0.96
0.94
0.82
0.81
0.69
0.68
0.67
0.67
0.66
0.65
0.64
0.64
SiEt3
O
H
5.2f
1H NMR, 500 MHz, CDCl3
0.85
1.00
3.17
3.26
9.06
3.39
6.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

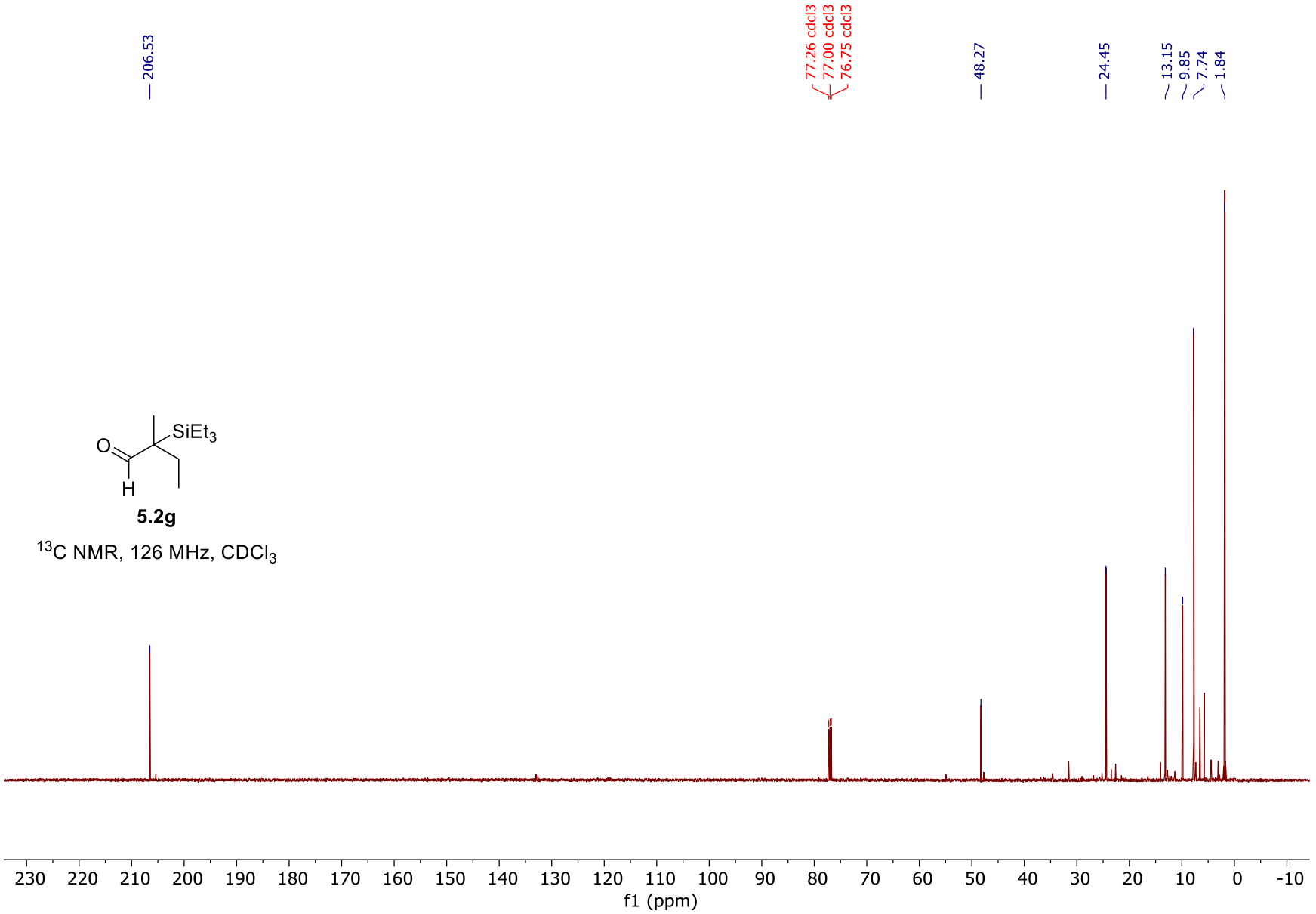

206.14
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
52.32
29.49
19.63
19.35
9.38
7.81
2.96
SiEt3
O
H
5.2f
13C NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

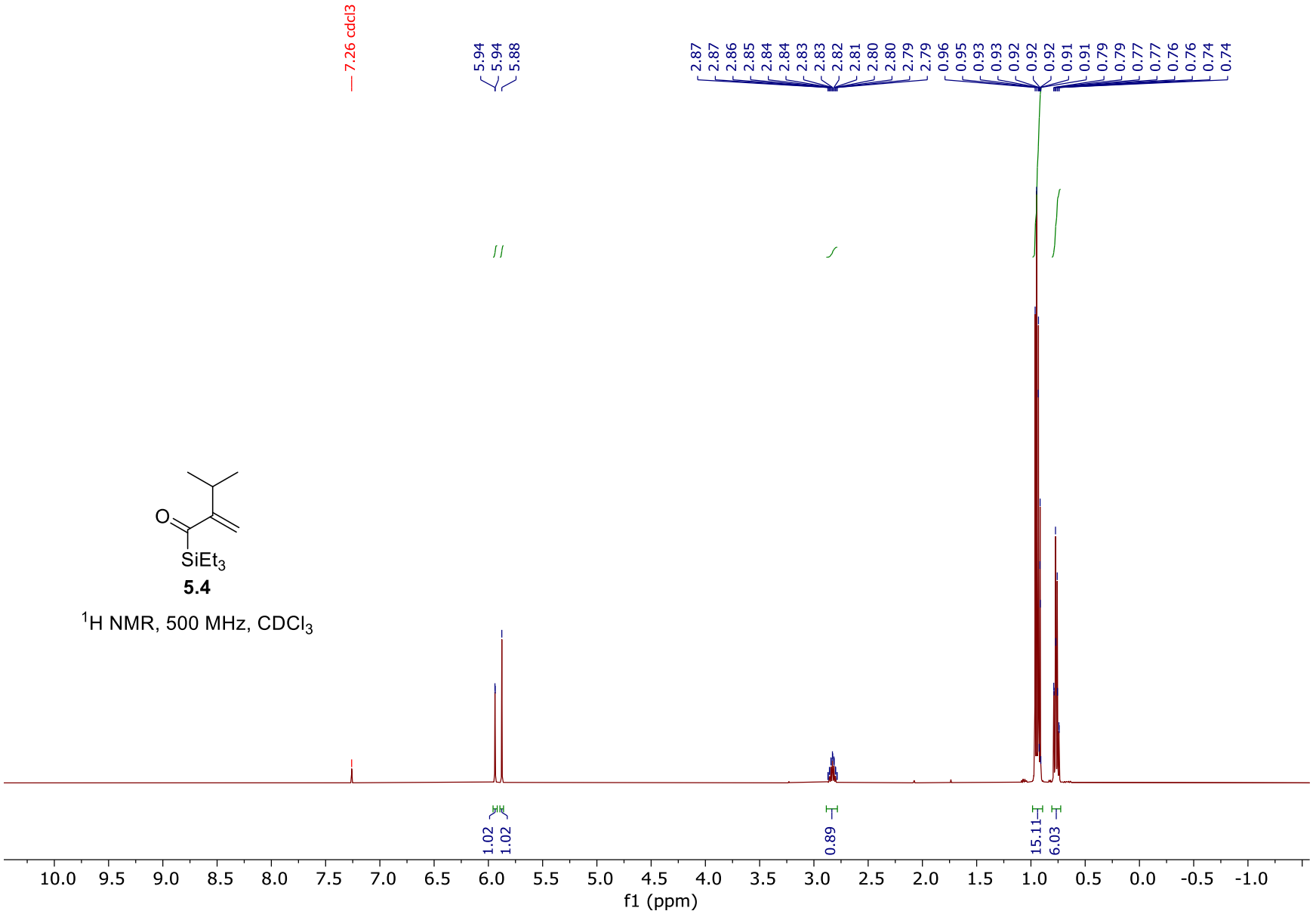


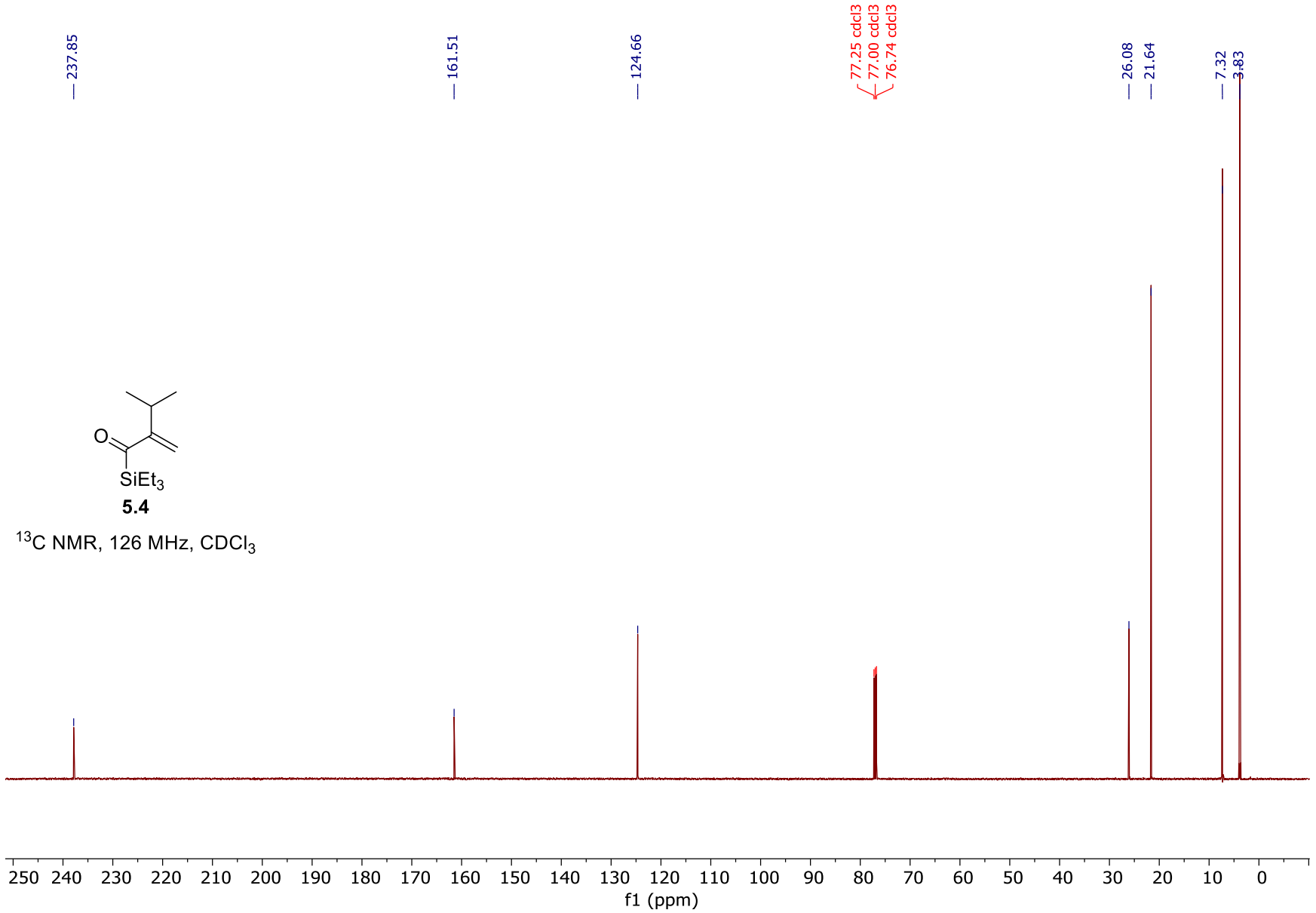
5.2f

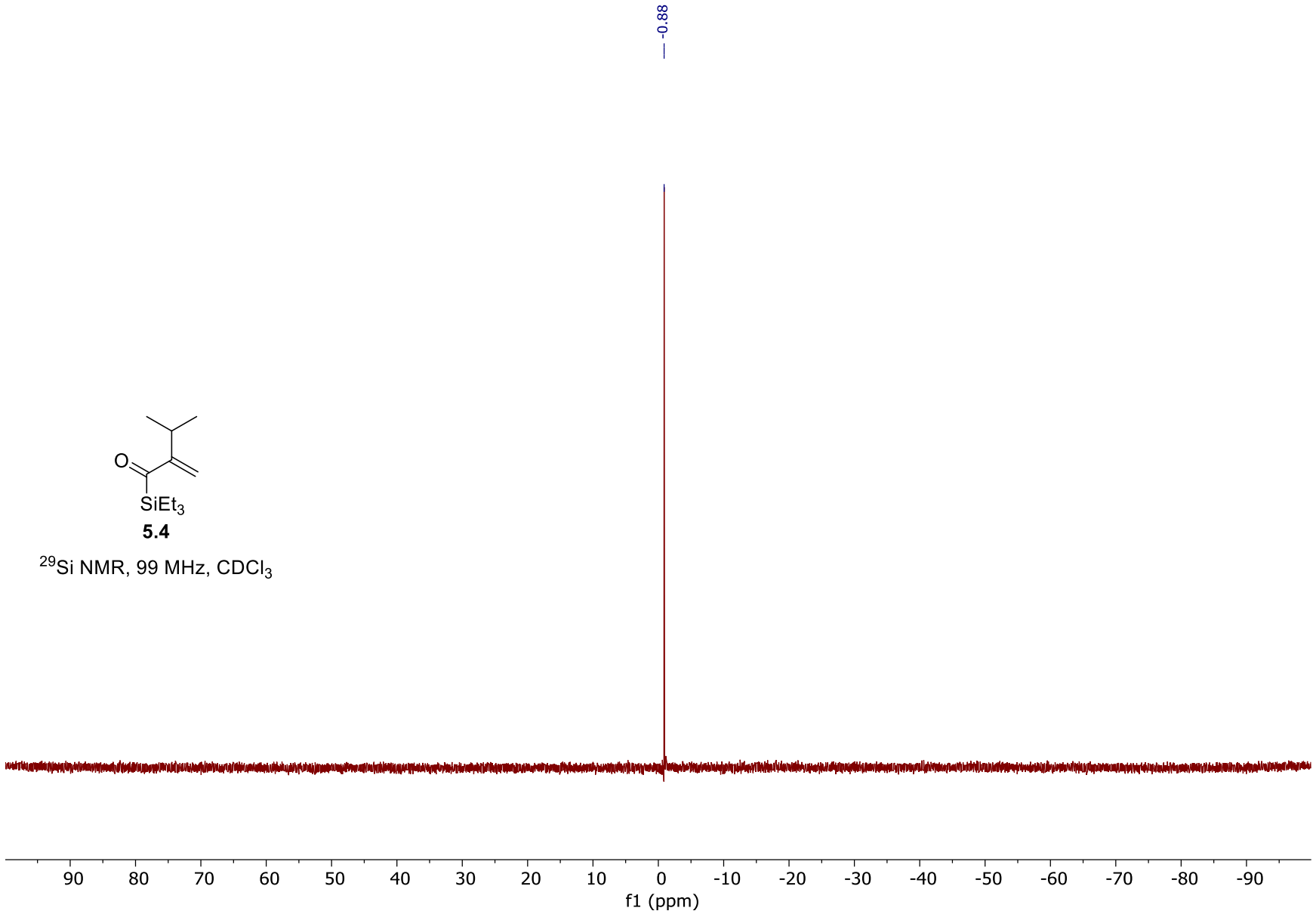
^{29}Si NMR, 99 MHz, $CDCl_3$


9.57
2.20
2.18
2.17
2.15
2.14
2.13
1.57
1.55
1.54
1.53
1.51
1.50
1.15
0.98
0.96
0.94
0.84
0.82
0.81
0.67
0.65
0.64
0.62
SiEt3
O
H
5.2g
1H NMR, 500 MHz, CDCl3
0.75
1.04
1.27
2.81
9.49
2.99
5.92
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 -1.0
f1 (ppm)


206.53
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
48.27
24.45
13.15
9.85
7.74
1.84
SiEt3
O
H
5.2g
13C NMR, 126 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

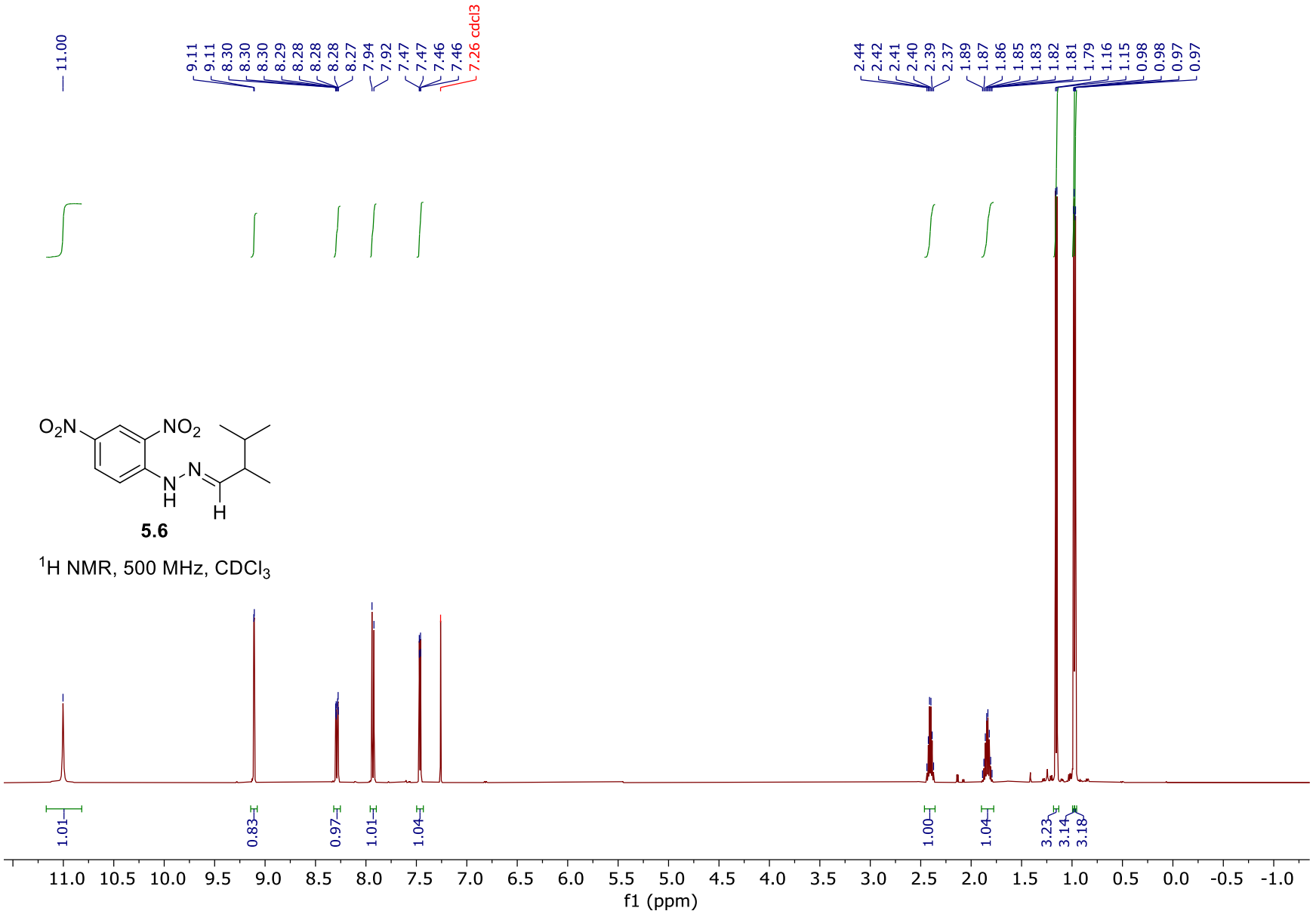

7.26 cdcl3
5.94
5.94
5.88
2.87
2.87
2.86
2.85
2.84
2.84
2.83
2.83
2.82
2.81
2.80
2.80
2.79
2.79
0.96
0.95
0.93
0.93
0.92
0.92
0.92
0.91
0.91
0.79
0.79
0.77
0.77
0.76
0.76
0.74
0.74
O
SiEt3
5.4
1H NMR, 500 MHz, CDCl3
1.02
1.02
0.89
15.11
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

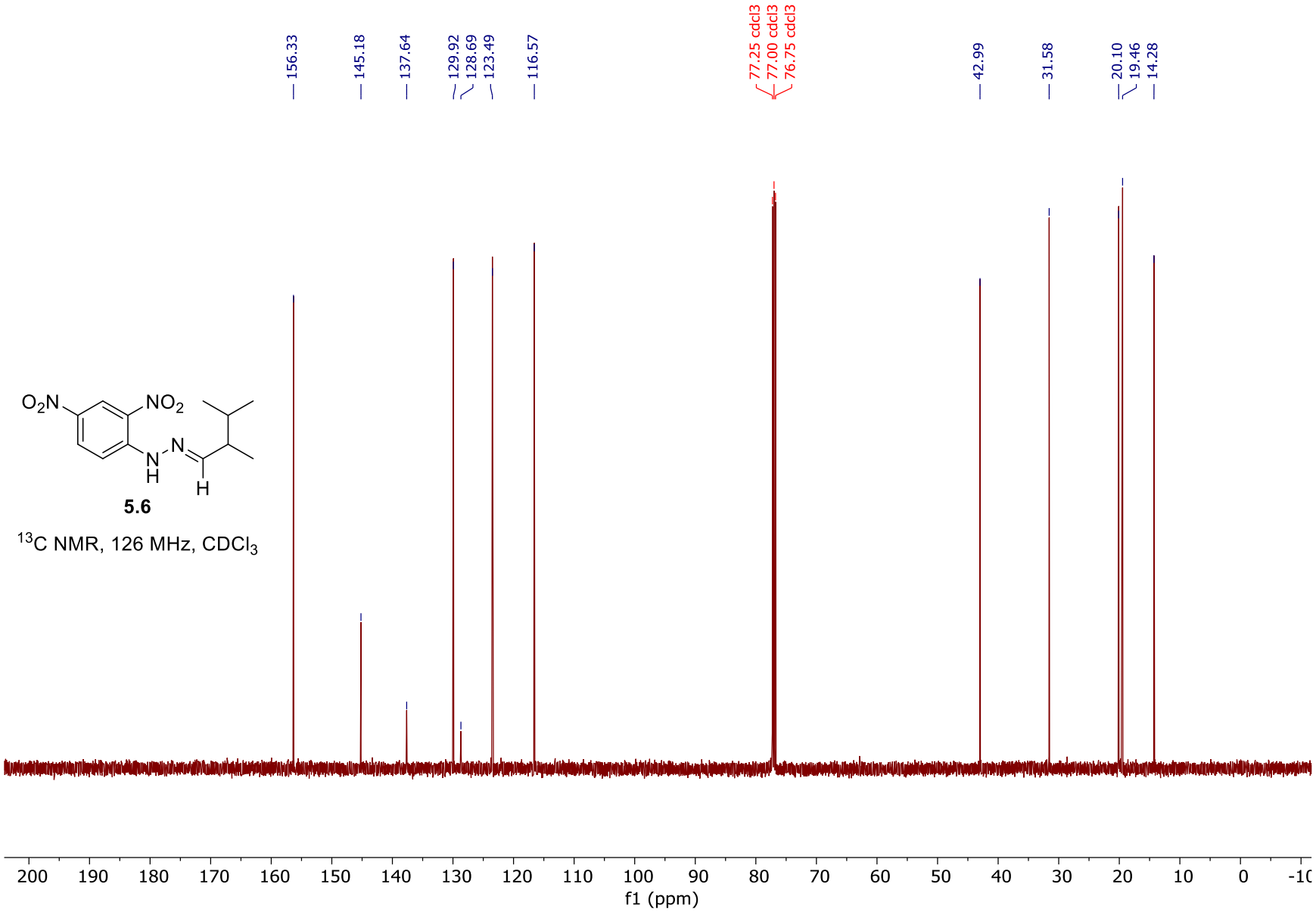

237.85
161.51
124.66
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
26.08
21.64
7.32
3.83
O
SiEt3
5.4
13C NMR, 126 MHz, CDCl3
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

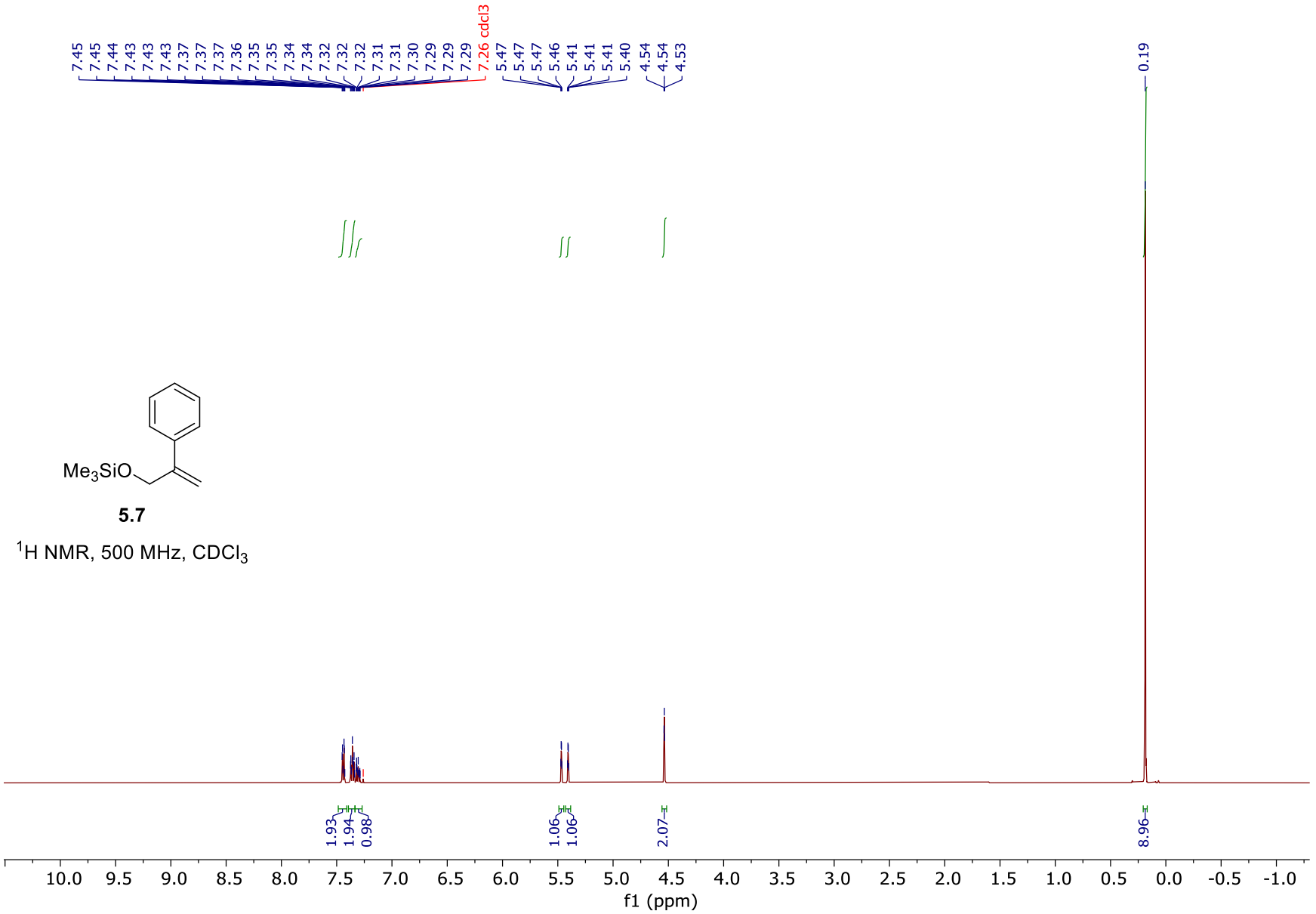


5.4

^{29}Si NMR, 99 MHz, $CDCl_3$

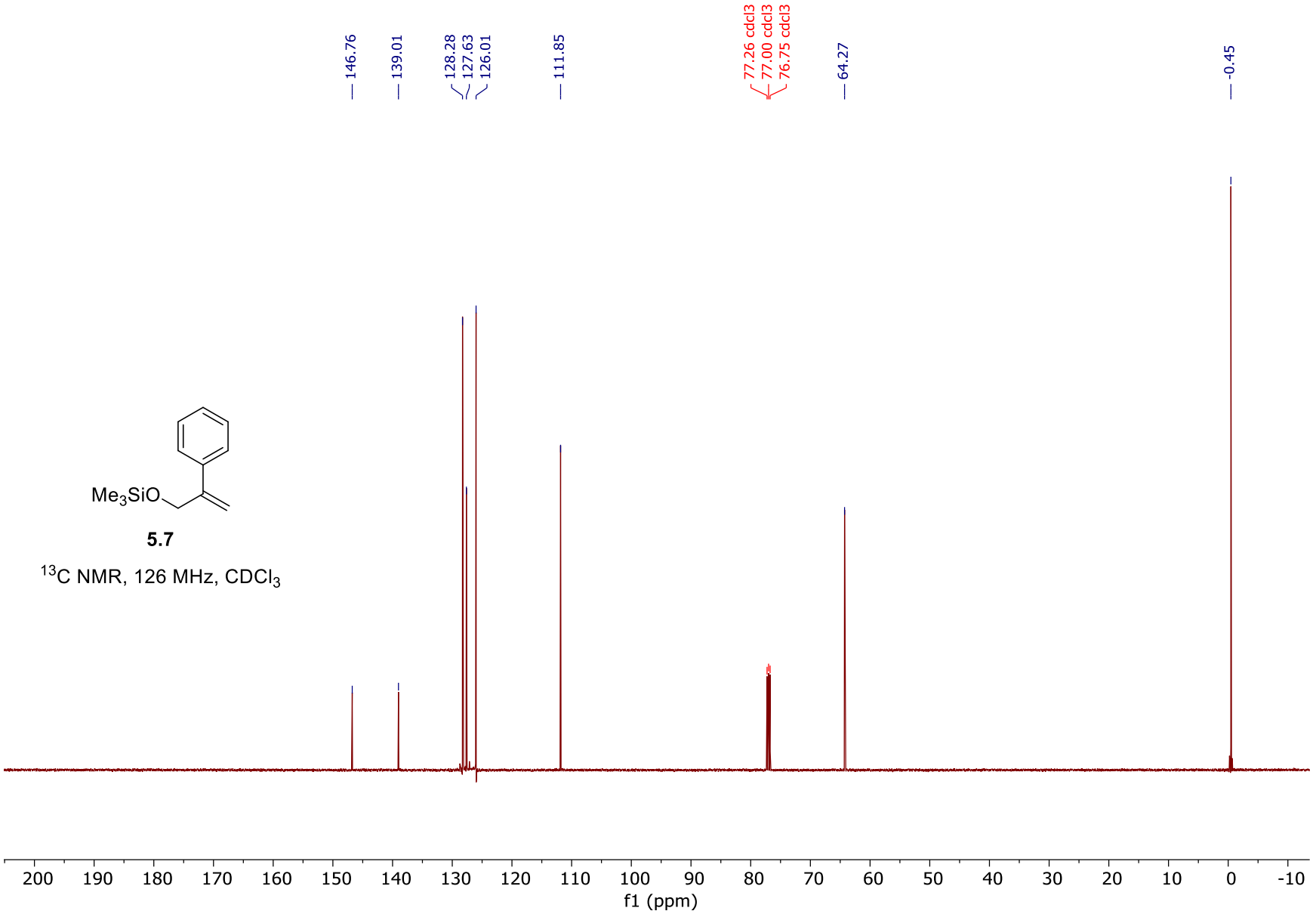

11.00
9.11
9.11
8.30
8.30
8.29
8.28
8.28
8.28
8.27
7.94
7.92
7.47
7.47
7.46
7.46
7.26 cdcl3
2.44
2.42
2.41
2.40
2.39
2.37
1.89
1.87
1.86
1.85
1.83
1.82
1.81
1.79
1.16
1.15
0.98
0.98
0.97
0.97
O2N
NO2
N
N
H
H
5.6
1H NMR, 500 MHz, CDCl3
1.01
0.83
0.97
1.01
1.04
1.00
1.04
3.23
3.14
3.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

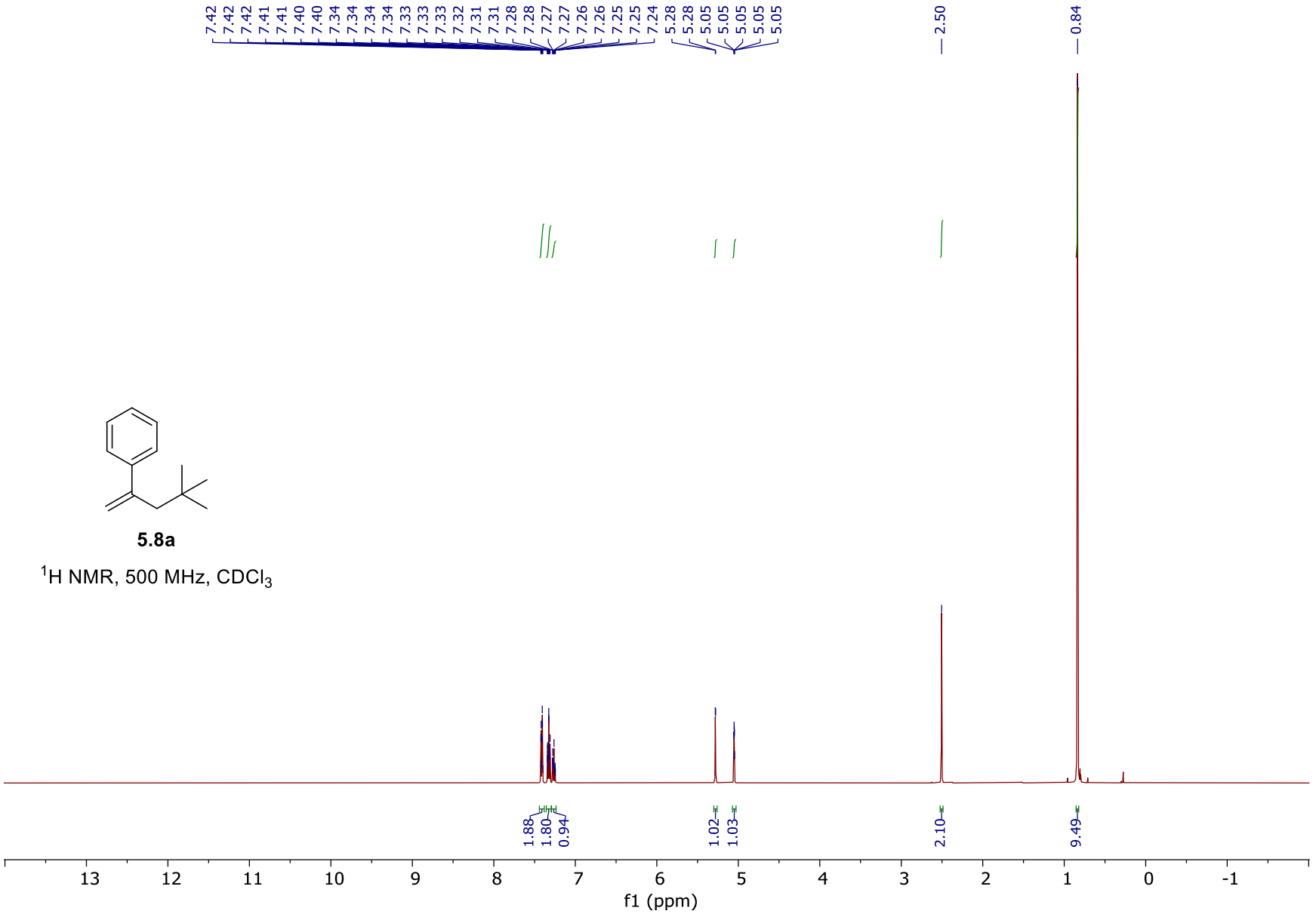

156.33
145.18
137.64
129.92
128.69
123.49
116.57
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
42.99
31.58
20.10
19.46
14.28
O2N
NO2
N
H
N
H
5.6
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



5.7

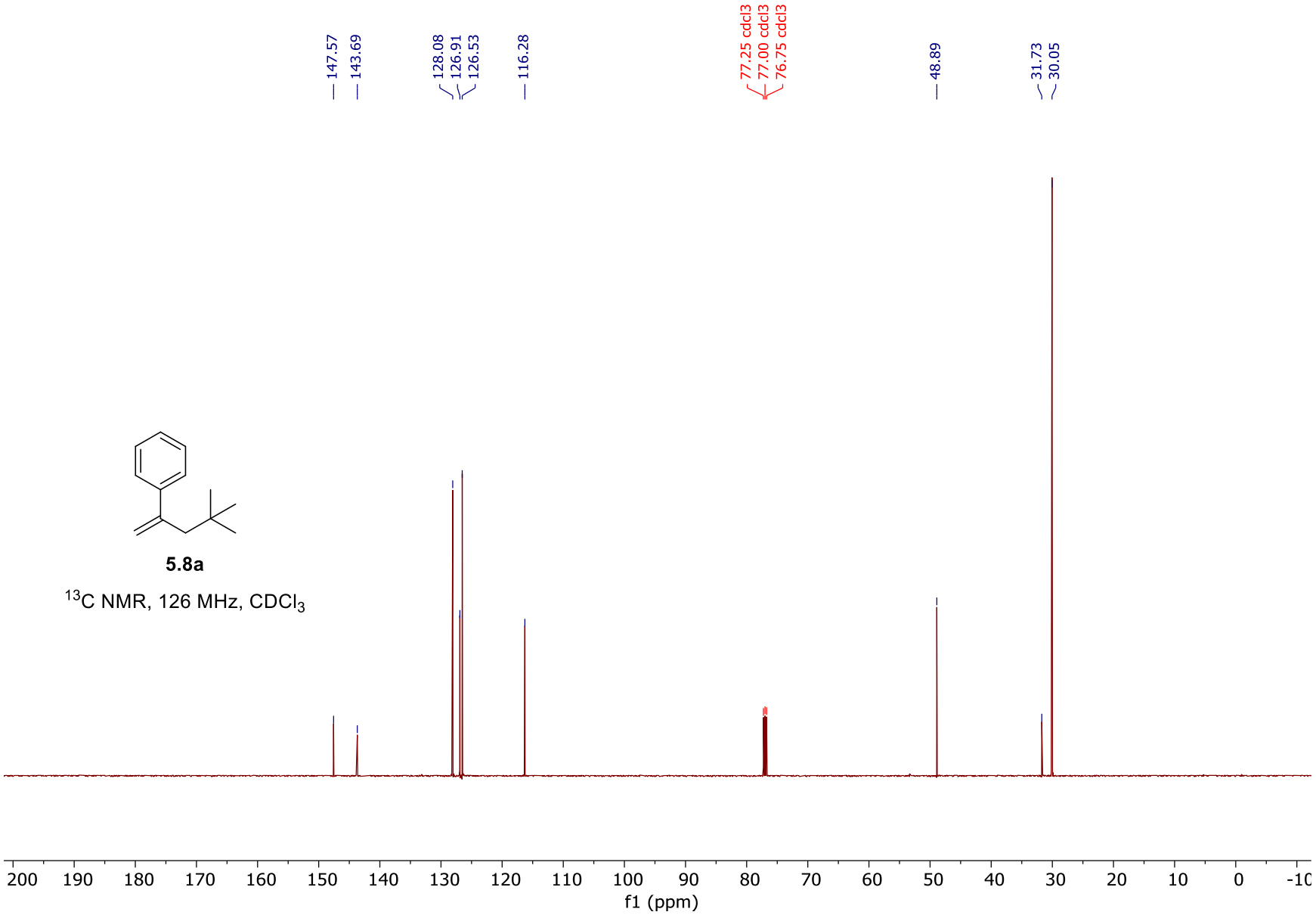
^{1}H NMR, 500 MHz, $CDCl_3$

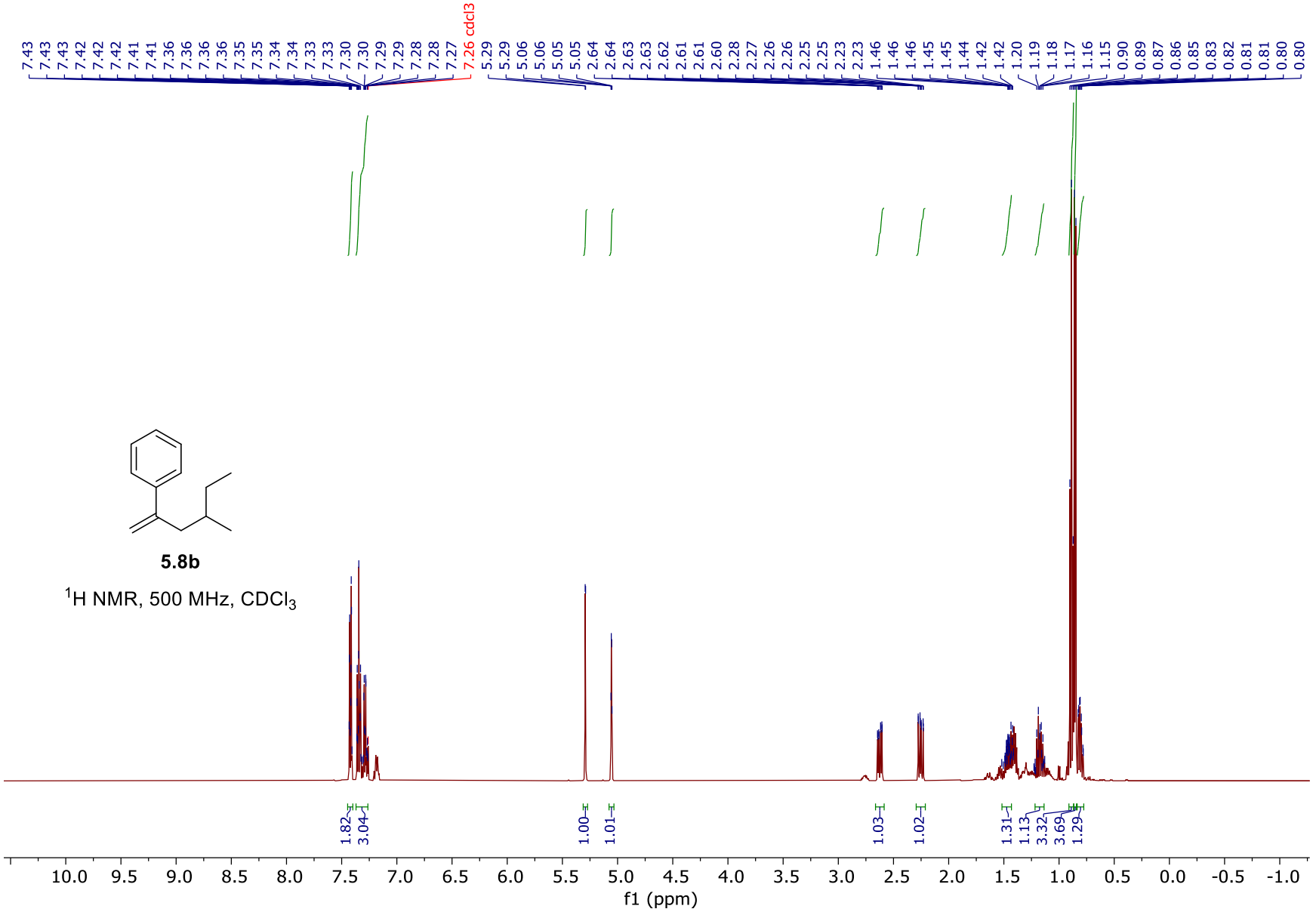

146.76
139.01
128.28
127.63
126.01
111.85
77.26 cdcl3
77.00 cdcl3
76.75 cdcl3
64.27
-0.45
Me3SiO
5.7
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

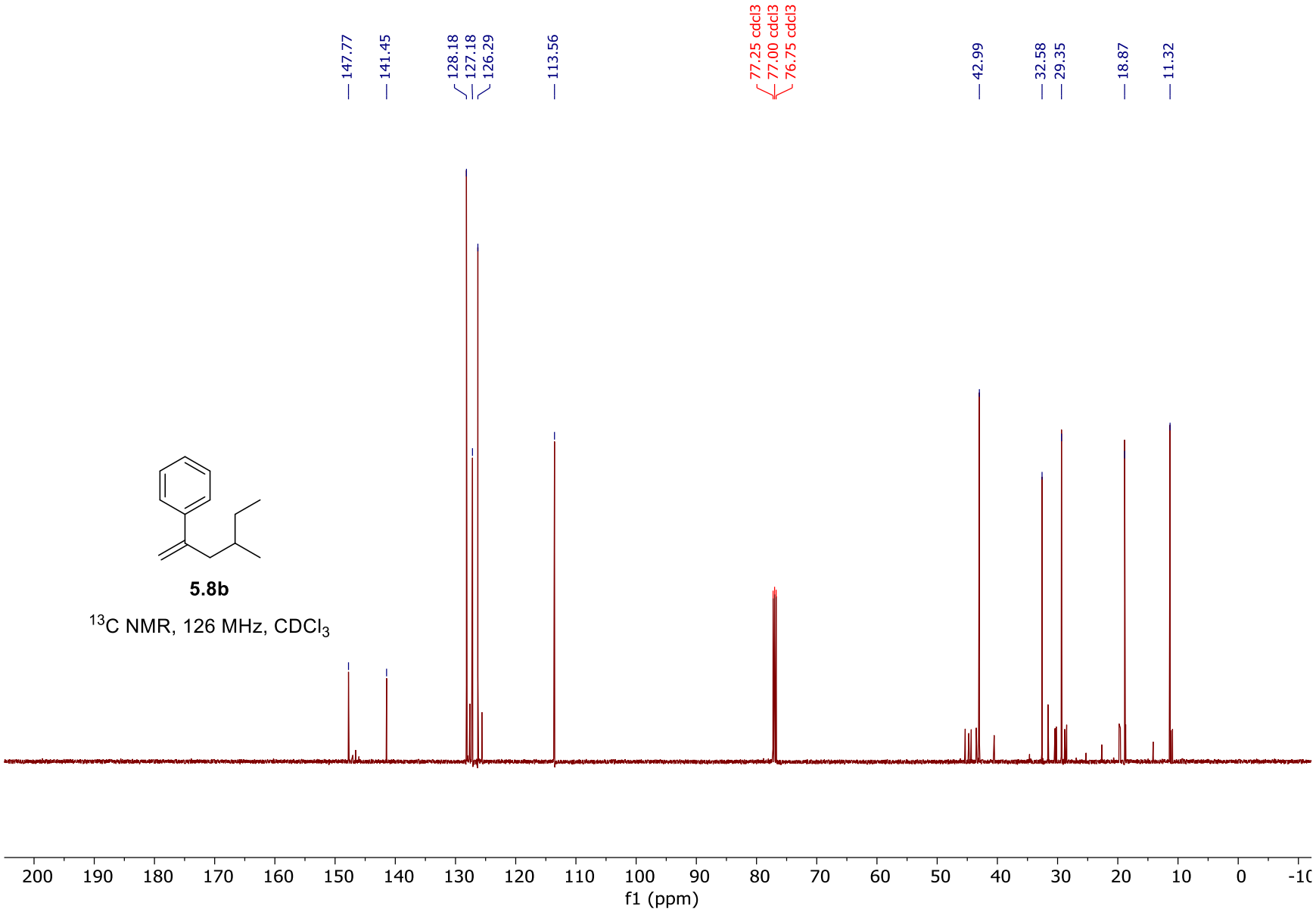


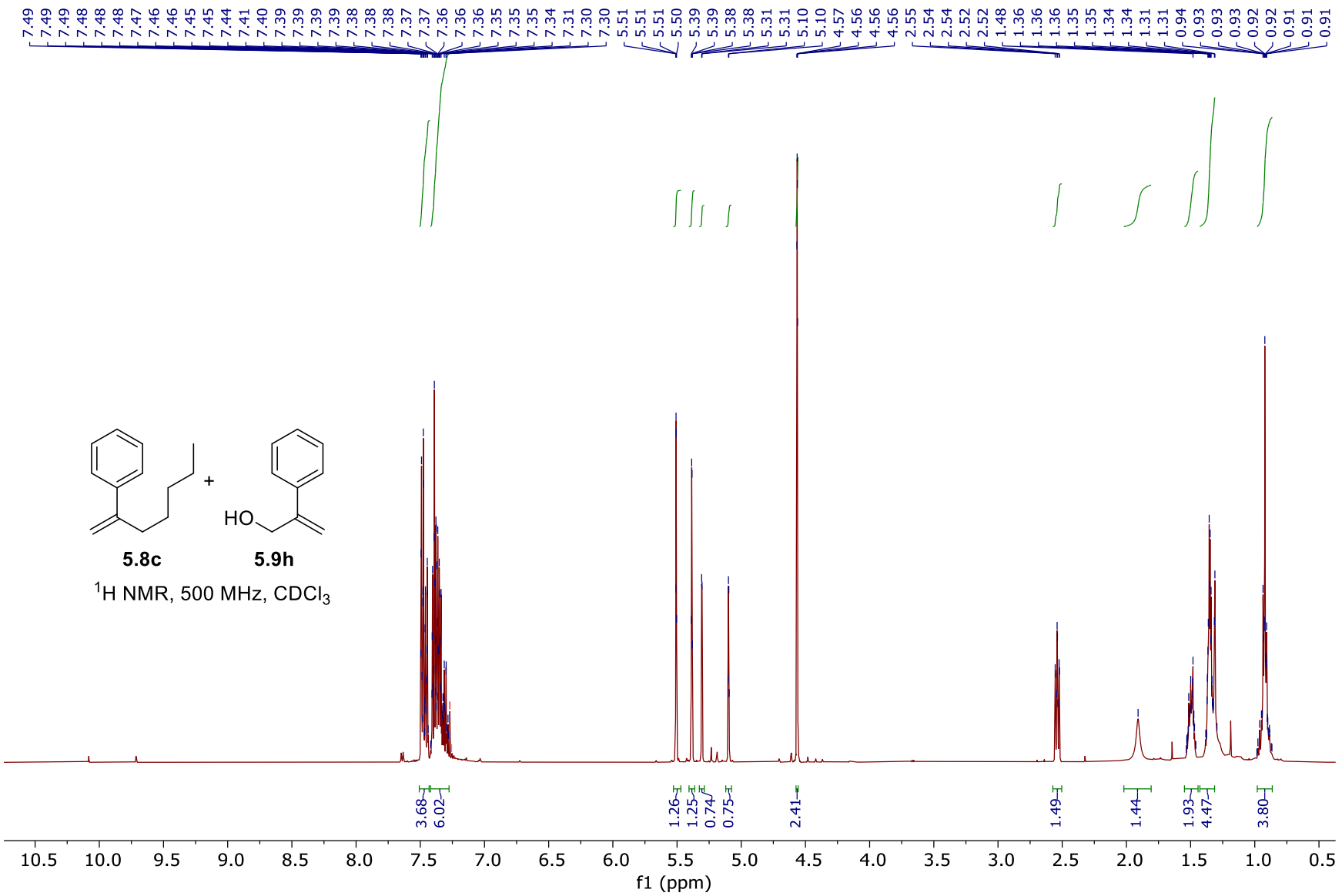
5.8a

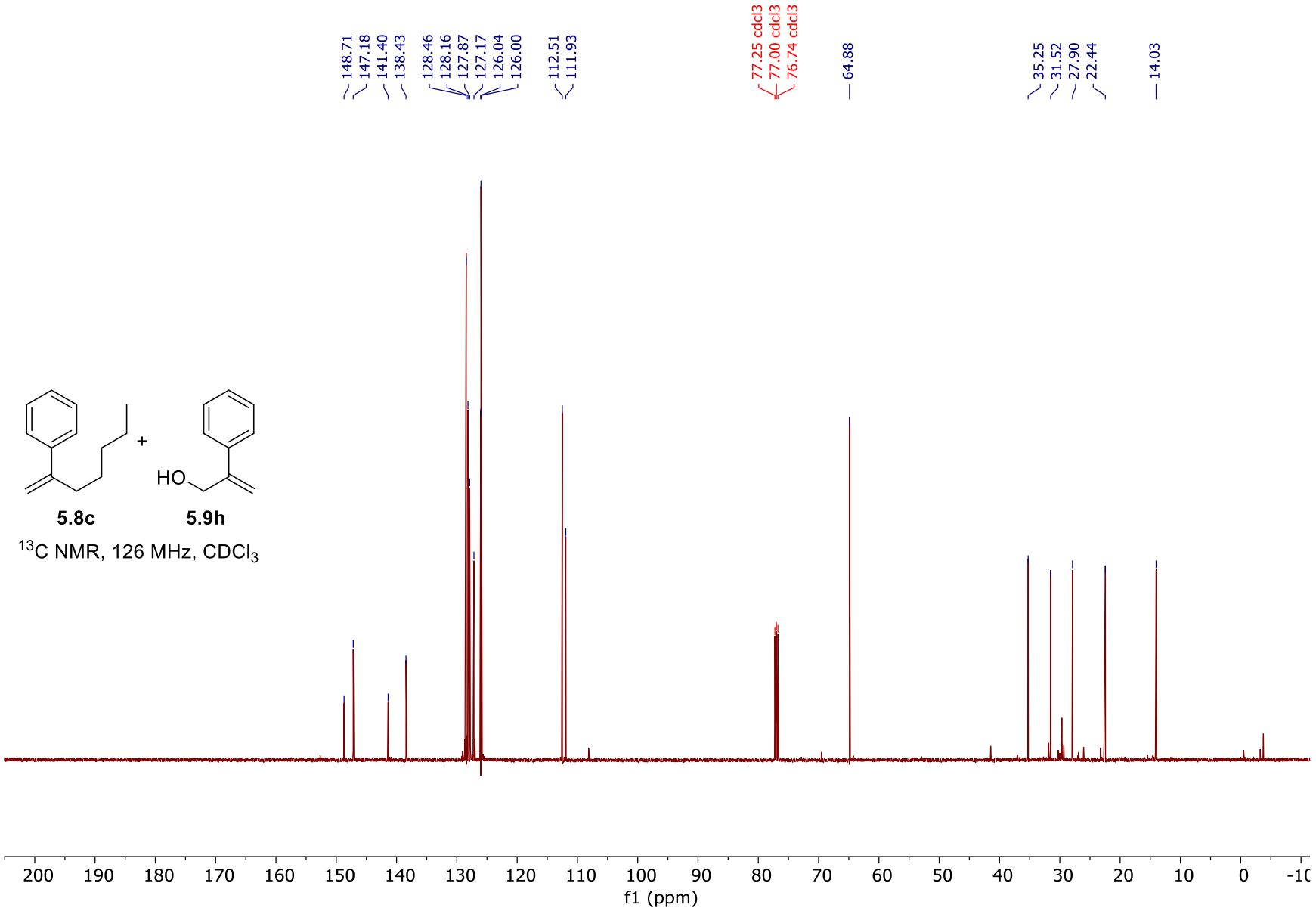
^{1}H NMR, 500 MHz, $CDCl_3$


147.57
143.69
128.08
126.91
126.53
116.28
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
48.89
31.73
30.05
5.8a
^{13}C NMR, 126 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.26 cdcl3
5.29 5.29 5.06 5.06 5.05 5.05 2.64 2.64 2.63 2.63 2.62 2.61 2.61 2.60 2.28 2.27 2.26 2.26 2.25 2.25 2.23 2.23 1.46 1.46 1.46 1.45 1.45 1.44 1.42 1.42 1.20 1.19 1.18 1.17 1.16 1.15 0.90 0.89 0.87 0.86 0.85 0.83 0.82 0.81 0.81 0.80 0.80
5.8b
1H NMR, 500 MHz, CDCl3
1.82 3.04 1.00 1.01 1.03 1.02 1.31 1.13 3.32 3.69 1.29
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 -1.0
f1 (ppm)


147.77
141.45
128.18
127.18
126.29
113.56
77.25 cdcl3
77.00 cdcl3
76.75 cdcl3
42.99
32.58
29.35
18.87
11.32
5.8b
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.49 7.49 7.49 7.48 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.44 7.41 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.31 7.30 7.30
5.51 5.51 5.51 5.50 5.39 5.39 5.38 5.38 5.31 5.31 5.10 5.10 4.57 4.56 4.56 4.56
2.55 2.54 2.54 2.52 2.52 1.48 1.36 1.36 1.36 1.35 1.35 1.34 1.34 1.31 1.31 0.94 0.93 0.93 0.92 0.92 0.91 0.91 0.91
+
HO
5.8c
5.9h
^{1}H NMR, 500 MHz, $CDCl_3$
3.68 6.02 1.26 1.25 0.74 0.75 2.41 1.49 1.44 1.93 4.47 3.80
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


148.71
147.18
141.40
138.43
128.46
128.16
127.87
127.17
126.04
126.00
112.51
111.93
77.25 cdcl3
77.00 cdcl3
76.74 cdcl3
64.88
35.25
31.52
27.90
22.44
14.03
HO
5.8c
5.9h
13C NMR, 126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

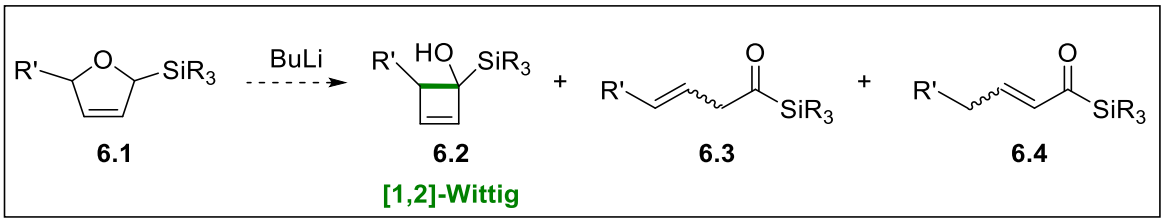
CHAPTER 6.

FUTURE WORK

6.1. Future work on Wittig rearrangements

6.1.1. Wittig rearrangement on a contracted ring

So far, we have seen the Wittig rearrangement of dihydropyrans and tetrahydrooxepins whereby regioselectivity is controlled by having a silyl group either at the 2- or 4-position.The future work on Wittig rearrangements will entail reducing the ring system to 2-silyl-2,5-dihydrofuran **6.1**. This might lead to formation of 2-silylcyclobutenols **6.2** via [1,2]-Wittig rearrangement and/or the two ring opened products **6.3** and **6.4** (Scheme 6.1).

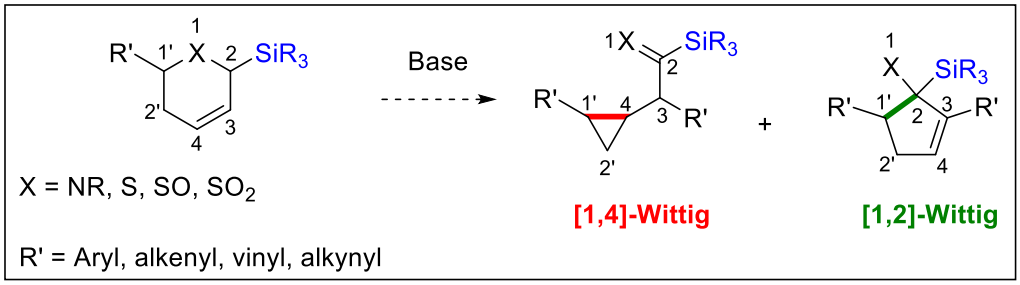


Scheme 6.1: Proposed Wittig rearrangement of 2-silyl-2,5-dihydrofuran

The above transformation has not been able to be accomplished due to difficulties in accessing the dihydrofuran via ring closing metathesis. This problem was solved in 2005 by Grubbs (Hong, S. H.; Sanders, D. P.; Lee, C. W.; Grubbs, R. H. Prevention of undesirable isomerization during olefin metathesis. *J. Am. Chem. Soc.* **2005**, *127*, 17160).

6.1.2. Use of other heteroatoms on Wittig rearrangement

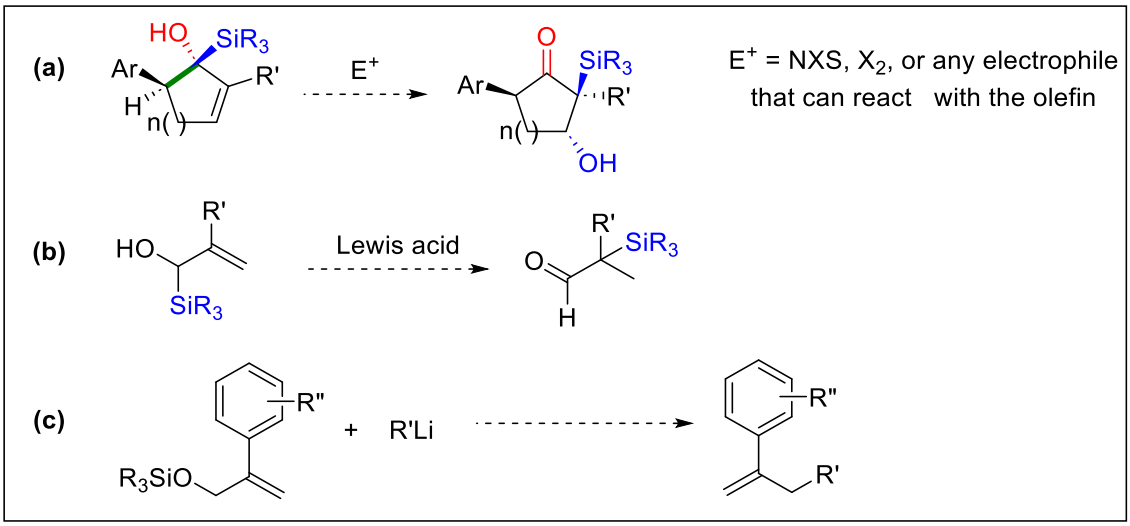
All the Wittig rearrangements discussed in this dissertation use oxygen as the heteroatom. The future work will involve the use of other atoms in place of oxygen (Scheme 6.2).



Scheme 6.2: Proposed Wittig rearrangement on a six-member ring with other heteroatoms

6.2. Future Work on silyl migrations

For silyl migrations, future work will involve use of other electrophiles apart from *m*-CPBA (Scheme 6.3a). For the acid catalyzed silyl migration, future work will entail the use of Lewis acid (Scheme 6.3b). Lastly, for the unusual S_N2-like reaction, the future work will involve expanding the substrate scope by modifying the aromatic ring and/or use of other alkyl/aryl lithiums in place of butyllithiums (Scheme 6.3c).



Scheme 6.3: Future work on silyl migrations