THE UNIVERSITY OF CHICAGO

PALLADIUM CATALYZED CYCLIZATION AND C–O BOND FORMATION CASCADE, AND ITS APPLICATION IN TOTAL SYNTHESIS

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ABSTRACT

Palladium catalyzed cyclization and C–O bond formation cascade, and its application in total synthesis

Chapter 1. Total synthesis inspired cascade reactions

Total synthesis of complex natural products has long inspired many creative methodologies. Cascade reactions have shown their ability to construct complex structures in total synthesis. In our group's former work on *(-)-presilphiperfolan-8-ol*, a cascade cyclization was used to construct the highly strained molecule. Inspired by our former results and synthesis of terpenes possessing a 1,3-*trans* structure, such as *botrydial* family, we designed a cascade reaction.

Chapter 2. Palladium catalyzed cyclization and C–O bond formation cascade

Heck type cyclization and nucleophilic attack cascades matched the stereochemistry demand. However, a C–O bond formation process, which was required in those terpene syntheses, was not precedented. To find a solution of the challenge, we developed a cyclization and C–O bond formation cascade. The methodology worked for a wide scope of substrates, resulting in moderate to high yields. We investigated the mechanism and found that a S_N2 process though a cyclopropane intermediate would be the most possible, deferent from former proposals. The methodology was used in total synthesis of *botrydienal* and *epi-10-oxodehydro-dihydrobotrydial*, indicating the potential power of this methodology in organic synthesis.

Chapter 3. Synthetic study towards *paraliane* family of natural products

Paralianes are terpenes with complex tetracyclic structures. They are bioactive in an anti-inflammatory capacity. Though first isolated in 1998, none of the members in this family have been synthesized. We synthesized the east fragment with our palladium catalyzed methodology. The west fragment was synthesized from a commercial chiral starting material. The two fragments were coupled together by the Nozaki–Hiyama–Kishi reaction. In model study we achieved the

unprecedented Mukaiyama radical coupling of alkene and aldehyde for ring closure. Further study is still going on in real system to synthesize the target molecule.

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LIST OF ABBREVIATIONS

Ac	acetyl
acac	acetylacetonate
Ad	adamantyl
BDSB	bromodiethylsulfonium bromopentachloroantimate
Bn	benzyl
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DDQ	2,3-dicyano-5,6-dichlorobenzoquinone
DIBAL-H	diisobutylaluminum hydride
DIPA	diisopropylamine
DMF	*N*,*N*-dimethylformamide
DMP	Dess-Martin periodinane
DMSO	dimethylsulfoxide
dpm	2,2,6,6-tetramethyl-3,5-heptanedionate
HMPA	hexamethylphosphoramide
HOBt	1-hydroxybenzotriazole

IBX	2-iodoxybenzoic acid
KHMDS	potassium bis(trimethylsilyl)amide
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LHMDS	lithium bis(trimethylsilyl)amide
***m*CPBA**	*meta*-chloroperoxybenzoic acid
MPO	4-methoxypyridine *N*-oxide
MVK	methyl vinyl ketone
NBS	*N*-bromosuccinimide
NMO	4-methylmorpholine *N*-oxide
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
Phth	phthalimide
Piv	pivaloyl
PMB	*para*-methoxybenzyl
PMP	1,2,2,6,6-pentamethylpiperidine
***t*-AmylOH**	2-methylbutan-2-ol
TBAF	tetrabutylammonium fluoride

TBAI	tetrabutylammonium iodide
TBHP	*tert*-butyl hydroperoxide
TBS	*tert*-butyldimethylsilyl
TES	triethylsilyl
Tf	trifluoromethanesulfonate
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TMG	1,1,3,3-tetramethylguanidine
TMS	trimethylsilyl
Ts	tosyl

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CHAPTER 1

TOTAL SYNTHESIS INSPIRED CASCADE REACTIONS

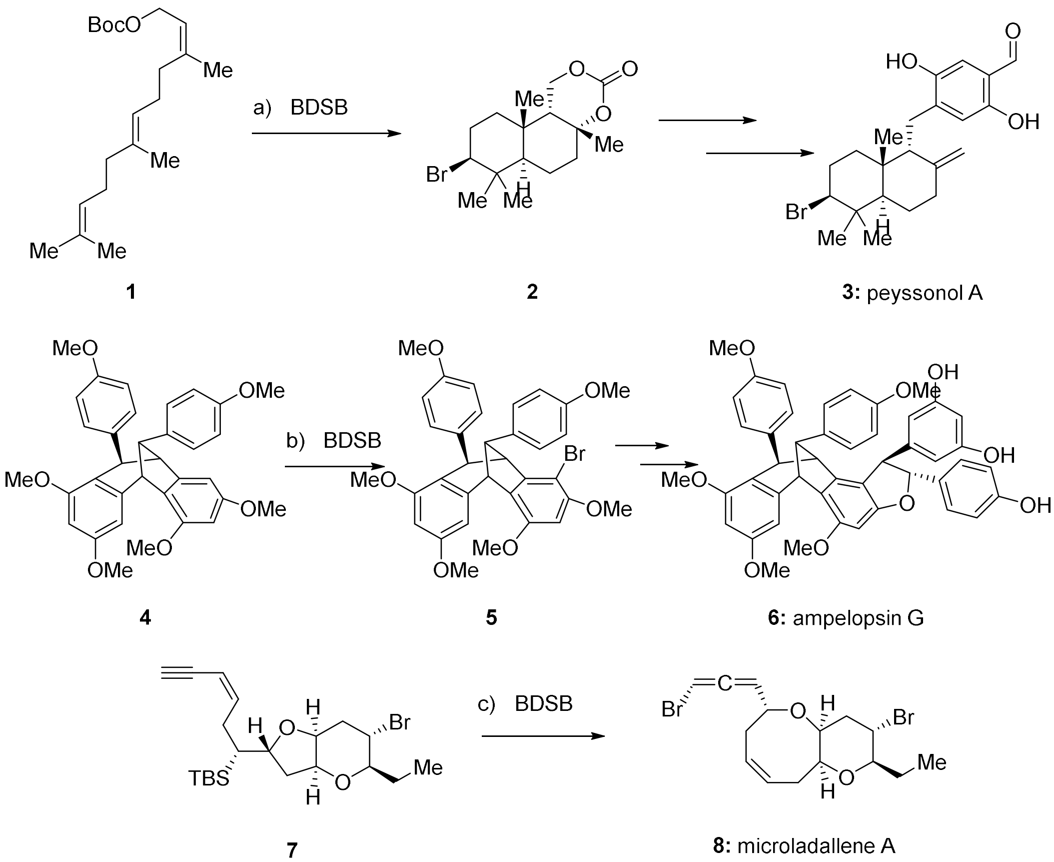
1.1 Total synthesis inspired methodology

Total synthesis of complex natural products is an arena of organic chemistry. The application in total synthesis often illustrated the power of one method. The challenging problems that are unable to draw upon previous methods are often the driving force for the discovery of new methodologies. Since the very start of total synthesis about 200 years ago,[1] chemists have been developing many new approaches for total synthesis. Stories laid on how new methodologies were inspired from difficulties met in total synthesis. The useful DCC esterification[2] was a fruit of long struggle with the β-lactam structure in *penicillin* synthesis and peptide formation. The demand for enantio-selective method to synthesize *prostaglandin* led to Corey's borane based asymmetric reduction of ketones, Corey-Bakshi-Shibata reaction.[3] In recent research, Lee's diazo radical tandem cyclization was closely related to their terpene total synthesis.[4]

Those examples are just the tip of a huge iceberg in the research history of organic synthesis. Our group has been working on total synthesis and inspired methodologies for a long time. For selective bromination and polyene cyclization in halogen-containing natural products, our group developed BDSB as a new and convenient reagent as a bromonium resource.[5] This reagent played an important role in the synthesis of *resveratrol* oligomers (**6**) as a selective bromination reagent of aromatic rings.[6] The bromonium introduced polyene cyclization also led to the synthesis of *peyssonol* (**3**) and *laurencia* (**8**) family natural products.[7] Those synthetic applications showed the power of BDSB as a bromination reagent. Our recent pyrone Diels-Alder reaction[8] and asymmetric Pictet-Spengler reaction[9] are also related to total synthesis. (Scheme 1-1)

Also inspired by oxidized terpene synthesis, herein we will introduce our development of a cyclization methodology and its application in total synthesis.

Scheme 1-1: BDSB in total synthesis

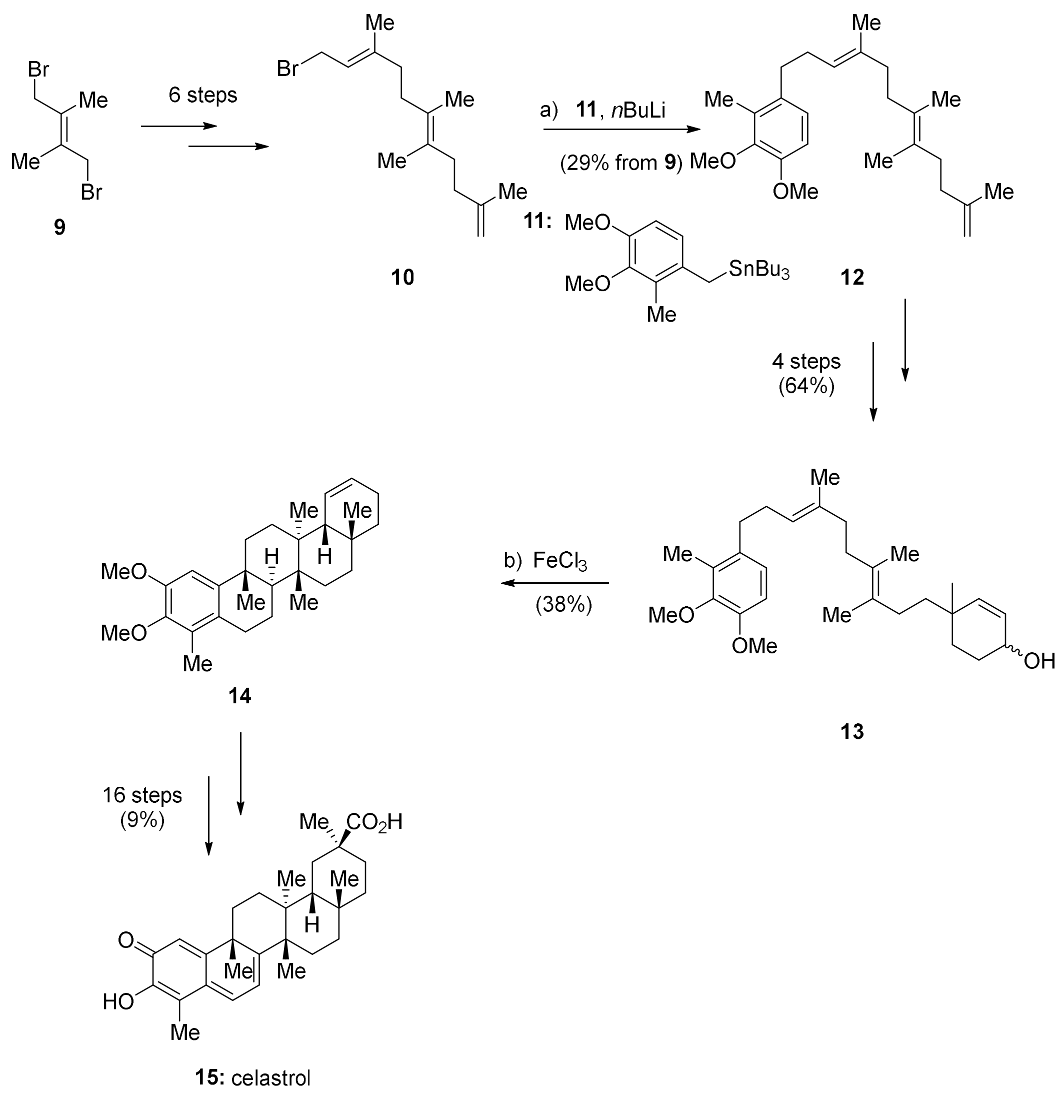


1.2 Cascade reaction in total synthesis

Cascade reactions can form complex ring structures, such as continuous stereocenters, in one step. Thus, they are very useful tools in the total synthesis of natural products. Robinson's famous synthesis of tropinone in 1917 was the first light of cascade cyclization.[10] From then on, many cascade reactions have been developed.

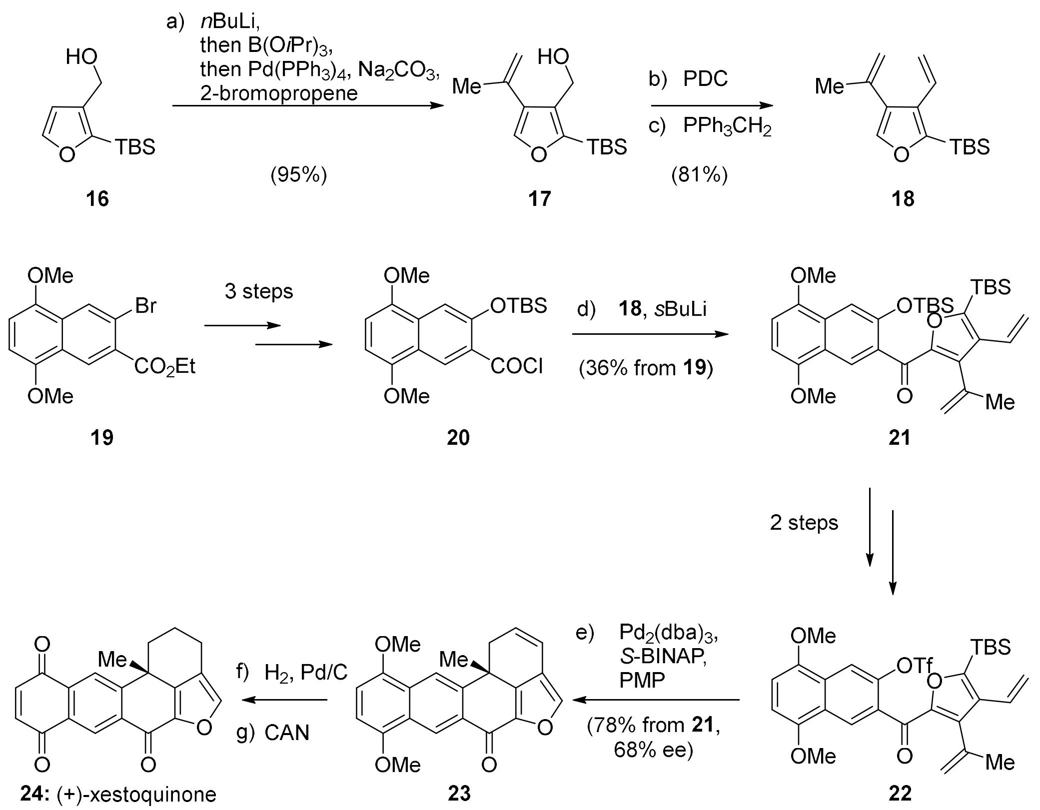
Polyene cyclization is typical of cascade reactions. They played a significant role in the natural synthesis of terpenes and steroids, and in total synthesis since the middle of the 20th century.[11] The BDSB research in our group described above was also closely related to polyene cyclization.[5,7] One more recent example would be Siegel's synthesis of *celastrol* (**15**) in 2015 from simple alkene **9**. **9** was elongated to triene **10**, which was coupled with organotin **11** to provide intermediate **12**. Then, **12** was transformed into cascade precursor **13** in 4 steps. Lewis acid $FeCl_3$ catalyzed polyene cyclization provided polycyclic structure **14** in moderate yield with all rings formed and all stereocenters stored correctly. Further transformations led to *celastrol* (**15**) in a total of 28 steps.[12] (Scheme 1-2)

Scheme 1-2: Siegel's synthesis of *celastrol*



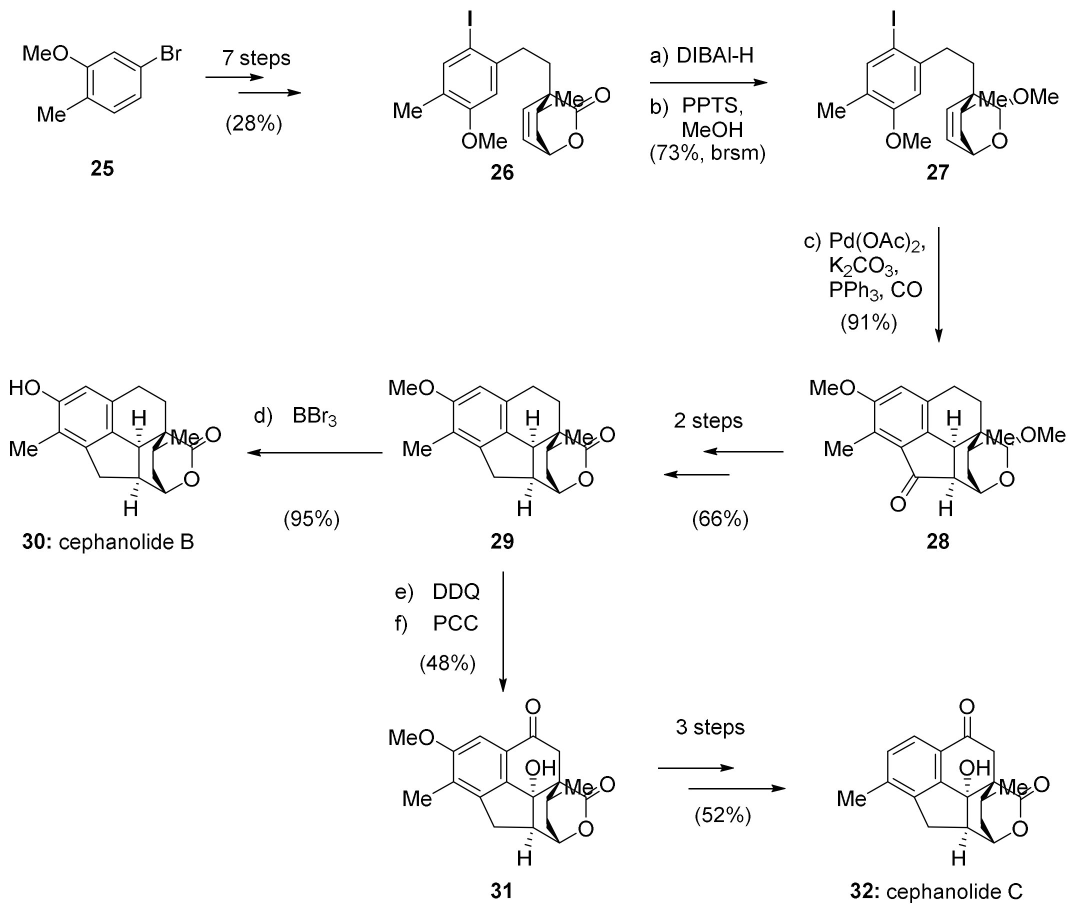
Transition metal-catalyzed cascade reactions are also useful tools in total synthesis. Early in 1996, Keay et al. reported a short synthesis of *(+)-xestoquinone* (**24**), with a Pd-catalyzed cascade Heck reaction as the key step. They first synthesized fragment **18** in 3 steps from **16** in high yield. Another fragment, **20**, was also prepared in 3 steps from **19**. Then, **18** and **20** were coupled by a nucleophilic attack to form **21**, which was transformed to cascade precursor **22**. Palladium catalyzed cascade Heck reaction, with *S*-(+)-BINAP as chiral ligand, provided **23** asymmetrically, forming two rings in one step and constructing all carbon skeleton. **23** could produce **24** after hydrogenation and dearomatization.[13] (Scheme 1-3)

Scheme 1-3: Keay's synthesis of *(+)-xestoquinone*



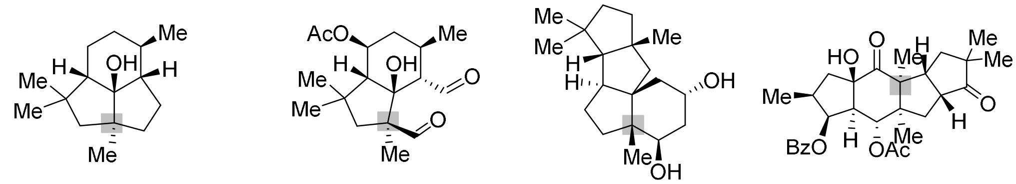
Zhao et al. synthesized *cephanolides*, providing another example of a Pd-catalyzed cascade reaction. They synthesized intermediate **26** from **25**, but **26** would give undesired diastereomer in the cascade Heck coupling and carbonylation, so, they transformed **26** into **27** which smoothly produced the desired **28**. **29** could be synthesized from **28** by oxidation and reduction, the deprotection would provide *cephanolide B* (**30**). *Cephanolide C* (**32**) could be synthesized by a further oxidation/reduction sequence. They also expanded the scope of their cascade reaction to other substrates and showed its potential use in organic synthesis.[14] (Scheme 1-4)

Scheme 1-4: Zhao's synthesis of *cephanolides*



In our group's former work of *(-)-presilphiperfolan-8-ol* synthesis, to solve the challenge of synthesizing a highly strained trans-5,5 bicyclic structure, a Pd-catalyzed cascade reaction was developed.[15] We noticed that the stereo-specific Heck reaction would result in an 1,3-*trans* structure, which also presents in other natural products.[16] (Figure 1-1) For **34-36**, structures of those terpenes also share a quaternary center and one C–O bond next to it. These common features inspired our development of a common solution of syntheses of such structures: a cascade reaction.

Figure 1-1: 1,3-*trans* structure in natural products



33: (-)-presilphiperfolan-8-ol **34:** botrydial **35:** conidiogenol **36:** paralianone D

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CHAPTER 2

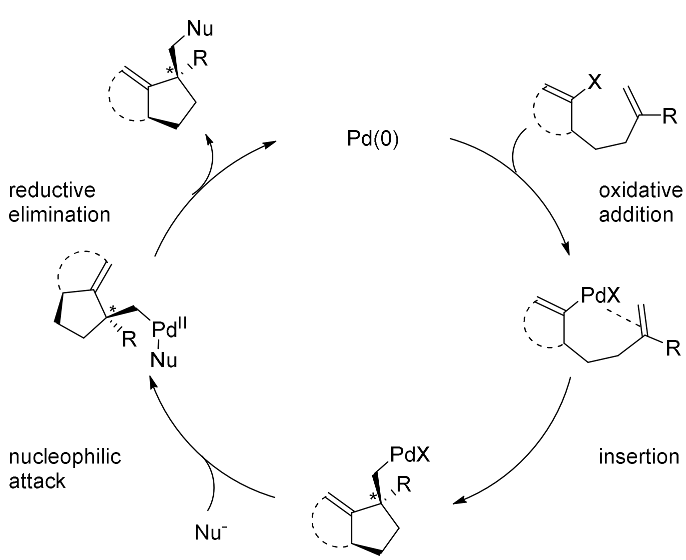
PALLADIUM CATALYZED CYCLIZATION AND C–O BOND FORMATION CASCADE

2.1 Introduction

2.1.1 Heck-type cyclization and nucleophile trapping cascade

Since its original development,[1] the Heck reaction has proven a powerful tool in organic synthesis.[2] The catalytic cycle of the Heck reaction ends with β-H elimination of the palladium intermediate and release of the product. When no β-H is available, Grigg et al. reported that in a 5-exo intramolecular cyclization, the addition of extra nucleophile could trap the intermediate and introduce a new C–X bond.[3] Their proposed cascade mechanism included a nucleophilic attack to the alkyl palladium next to the labeled quaternary center which prevented β-H elimination, followed by reductive elimination (Figure 2-1).

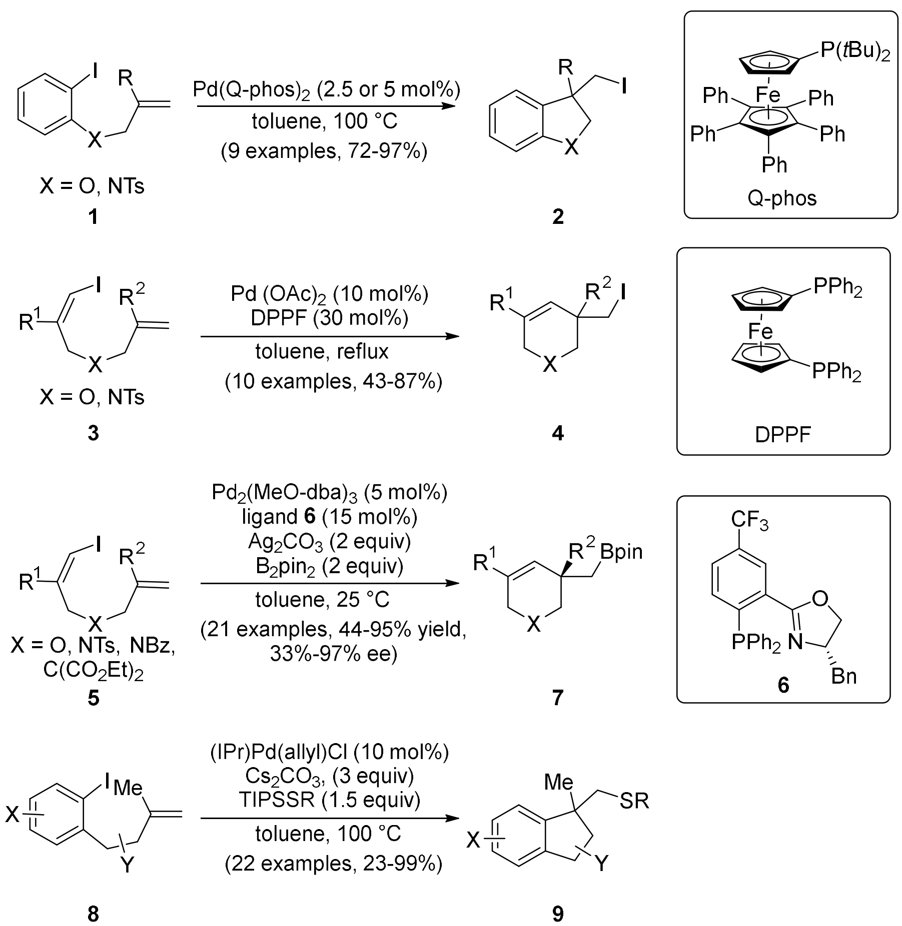
Figure 2-1: Proposed mechanism of nucleophile trapping



This process was widely studied and proved to have various applications.[4] The reaction generated a quaternary center and was stereospecific. As shown in Figure 2-1, the *cis* insertion guaranteed 1,3-*trans* stereochemistry, which perfectly matched the proposed molecules in **Chapter 1**, thus being a potential general solution of such structures in natural product synthesis.

A large scope of heteroatom nucleophiles has been investigated since Grigg's original discovery with carbon and hydride. Lautens et al. in 2011 reported that, starting from phenyl iodide **1**, with very bulky ligand Q-phos, they could achieve a cyclization and iodination cascade with high yields.[5a] In the same year, Tong et al. reported a similar process using vinyl iodide **3** instead, with the bident ligand DPPF.[5b] Later in 2017, Tong et al. succeeded in cyclization and C–B bond formation asymmetrically with chiral ligand **6**, resulting both high yields and enantiomeric excess in most examples.[6] Recently in 2019, Nakada et al. used the TIPS thioether as nucleophile to form C–S bond in this cascade.[7] (Scheme 2-1)

Scheme 2-1: Heteroatom nucleophiles in cyclization cascade



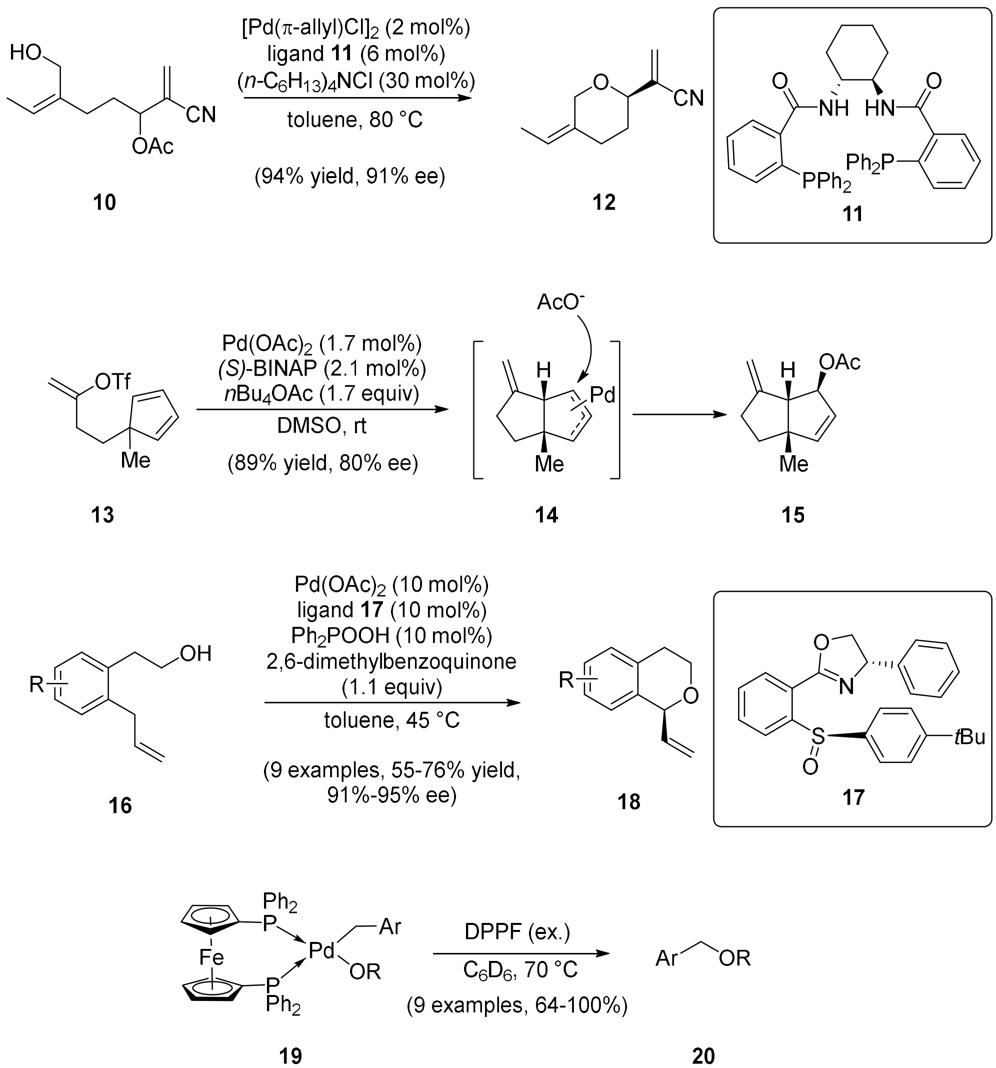
However, C–O bond formation, which is of interest to construct our proposed molecules, was still unprecedented to the best of our knowledge in this cascade. (One close example will be discussed in *2.3.2*)

2.1.2 Palladium catalyzed C–O bond formation

Many different C–O bond formation process catalyzed by palladium, with different mechanisms, have been reported.

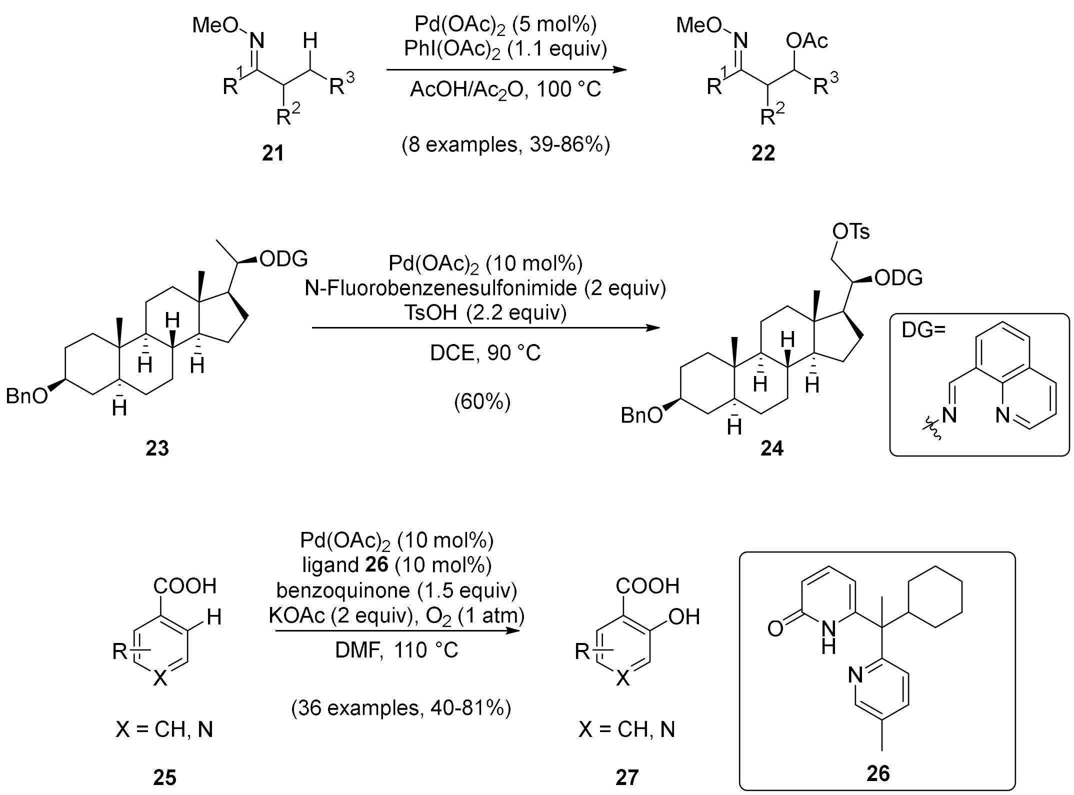
In contrast to the unactivated alkyl palladium(II) intermediate in cyclization cascade above, activated palladium(II), such as allyl palladium(II), was readily available for a nucleophilic attack to form a C–O bond. The Tsuji-Trost reaction, generating an allyl palladium(II) intermediate from allyl acetate, was a famous example. Trost et al. reported that using an intramolecular hydroxyl group as nucleophile, with chiral ligands, the asymmetric cyclic ether **12** could be synthesized from allyl acetate **10** via dynamic kinetic transformation.[8] In a process by Shibasaki et al. similar with Heck-type cyclization but via an allyl palladium intermediate **14**, a nucleophilic attack by *n*Bu_4NOAc could form an enantioenriched allylic acetate **15**.[9] The White group did a series of work on allylic oxidation with palladium(II) and sulfoxide ligands (known as the White catalyst), including the synthesis of asymmetric cyclic ether **18** through intramolecular allylic oxidation.[10] Recently this sulfoxide ligand catalysis was applied in the synthesis of artemisinic alcohols.[11] Other than allyl palladium(II), Hartwig et al. heated a pre-synthesized benzyl palladium(II) DPPF complex **19** with excess DPPF to trap Pd(0), and also observed C–O bond formation.[12] (Scheme 2-2)

Scheme 2-2: C-O bond formation via activated Pd(II) intermediate



In addition to C–O bond formation via the palladium(II) intermediate, C–O bond formation via palladium(IV) species is also well studied. The formation of these high valence intermediate generally requires the use of an extra oxidant, such as $PhI(OAc)_2$ or O_2. Sanford et al. found that oximes were a good directing group, activating its β-position, helping palladium insertion into C–H bond, and resulting in C–H bond oxidation.[13] Dong et al. expanded this chemistry. They established a methodology to introduce a tosyl group by oxime directed C–H bond oxidation on the α-position of the oxime oxygen. This would work with the pregnanediol derivative **23** and thus potentially work in late-stage oxidation in total synthesis.[14] The Yu group did intensive research on C–H bond oxidation, and recently reported an interesting methodology of sp^2 C–H bond oxidation using molecular oxygen. The tautomeric ligand **26** was essential, as its tautomerization between pyridone and hydroxyl pyridine accelerated proton extraction from the substrate and palladium(IV) intermediate formation.[15] (Scheme 2-3)

Scheme 2-3: C-O bond formation via Pd(IV) intermediate



2.2 Development of methodology

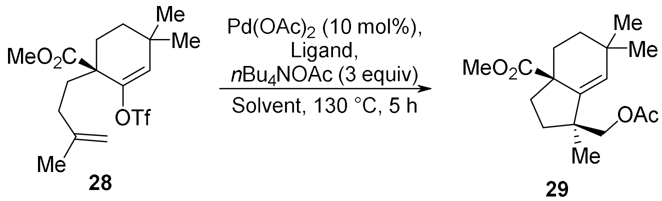
2.2.1 Original design

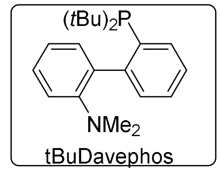
While oxidation via palladium(IV) intermediates are not compatible with Pd(0)/Pd(II) catalytic cycle of Heck-type cyclizations, we proposed a new methodology to achieve the cyclization and C–O bond formation cascade. In terms of oxygen nucleophiles, only nucleophilic attacks on activated allyl or benzyl palladium(II) were known. We deduced that a good nucleophile would help in the case of our unactivated alkyl palladium(II) intermediate. Thus, we chose the nucleophile $n\mathrm{Bu_4NOAc}$ used by Shibasaki et al.[9] as our acetate source and Buchwald's ligands were used[16] to achieve this transformation.

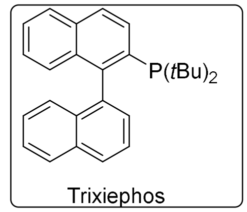
2.2.2 Optimization of conditions

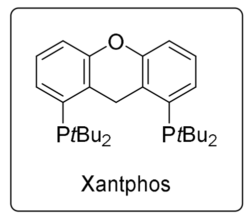
With Dr. Pengfei Hu, we started our investigation on Grigg's vinyl triflate **28**.[3b] To our delight, with Buchwald's bulky ligand Trixiephos[16a] and $n\mathrm{Bu_4NOAc}$ we observed a considerable amount of the desired cascade product, acetate **29** as a single diastereomer (entry 1). In contrast, KOAc as the nucleophile produced only trace amounts of **29** (entry 2), indicating that a suitable nucleophile was essential. When the amount of ligand was reduced to 15 mol%, the yield increased to 83% (entry 3). A decreased equivalence of nucleophiles, however, resulted in yield loss (entry 4). Then we screened other ligands, of which tBuMephos[16b] proved to be the best, providing a 95% yield (entries 5-8). A decrease in the loading of tBuMephos decreased the yield, so we insisted with 15 mol% (entry 9). Solvent screening showed that product was formed in comparable yields in both EtOAc and xylene, while DMF resulted in worse yields and no desired product was observed in DCE (entries 10-13). It was then found that the temperature could be lowered to 90 °C without a deduction of yield, providing the optimized reaction conditions (entry 14). This set of conditions would serve as our optimized reaction conditions. (Table 2-1)

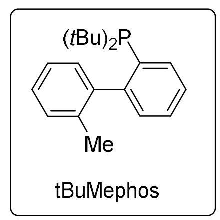
Table 2-1: Reaction condition screening[a]











Entry	Ligand	Solvent	NMR Yield(%)
1	Trixiephos (30 mol%)	toluene	61
2[b]	Trixiephos (30 mol%)	toluene	trace
3	Trixiephos (15 mol%)	toluene	83
4[c]	Trixiephos (15 mol%)	toluene	61
5	tBuDavephos (15 mol%)	toluene	82
6	Johnphos (15 mol%)	toluene	76
7	Xantphos (15 mol%)	toluene	52
8	tBuMephos (15 mol%)	toluene	95
9	tBuMephos (11 mol%)	toluene	86
10	tBuMephos (15 mol%)	EtOAc	93
11	tBuMephos (15 mol%)	xylene	91
12	tBuMephos (15 mol%)	DMF	73
13	tBuMephos (15 mol%)	DCE	0
14[d]	**tBuMephos (15 mol%)**	**toluene**	**96**

a. reaction conditions: **28** (0.1 mmol), $Pd(OAc)_2$ (0.01 mmol), solvent (1 ml), ligands and acetate salt (0.3 mmol) as indicated.
b. KOAc was used instead of *n*Bu_4NOAc;
c. *n*Bu_4NOAc was 1.2 equiv;
d. reaction temperature was 90 °C

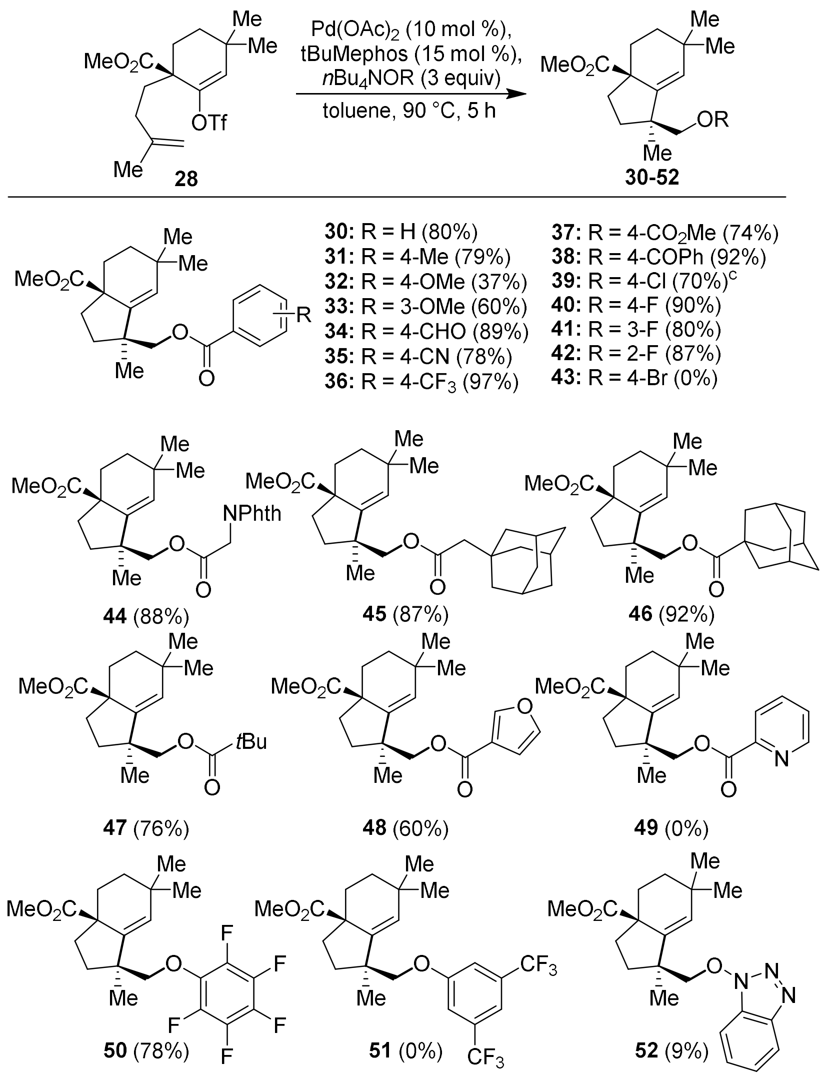
2.2.3 Substrate scope

With the optimized condition in hand, we expanded the oxygen nucleophile scope to various tetrabutylammonium salts. While these salts are highly hydroscopic, this reaction calls for anhydrous conditions. Thus, they have to be prepared and crystalized under anhydrous conditions carefully and stored in a dry box (see experiment section for more details). Improper storage of these salts resulted in a dramatic yield loss. The *n*Bu_4NOAc powder, which was exposed to open air for 10 min before setting up a reaction, resulted in a 45-50% yield of **29** with all other conditions unchanged. However, when kept free from moisture, they could be stored for months without a loss in reactivity. Phenolate salts (see table 2-2, **50**, **51**), however, are not stable and should be used freshly.

Many benzoic acid nucleophiles (**30**-**42**), both electron-rich and electron-poor ones, are compatible with our methodology. Substitutions such as carbonyls (**34**, **38**), esters (**37**), cyanide (**35**), fluoride (**40**-**42**) and chloride (**39**) on the benzene ring are tolerated in this reaction. With a bromide substitution (**43**), however, we observed no desired product. The proposed reason was that bromide was also prone to palladium oxidative addition. Those salts, in most cases, provided good yields of the desired product, higher than 70%. However, the two most electron-rich examples (**32**, **33**) only gave moderate yields. -OMe groups at para position (**32**), which were the most electron donating, resulted in the lowest yield. This trend indicated that an electron-poor nucleophile was better for this reaction.

We then investigated other types of nucleophiles. Alkyl acid nucleophiles like protected glycine (**44**), hindered adamentyl acids (**45**, **46**), and pivalate (**47**) all reacted smoothly to get high yields. 3-furoic acid (**48**) worked in 60% yield, while picolinic acid (**49**) was not compatible. The proposed reason was that picolinic acid itself was also a strong ligand to palladium[17] and poisoned the phosphine coordinating catalyst. When phenol was used instead of acid (**50**, **51**), only those highly electron deficient, with an acidity in the range of normal carboxyl acid, like pentafluorophenol (**50**) (pK_a = 5.5 in H_2O)[18a], could provide the desired product. No product was observed with 3,5-ditrifluoromethylphenol (**51**) which was not as electron poor, pK_a = 8.26 in H_2O.[18b] This proved consistent with the trend shown with electron poor benzoic acids serving as better nucleophiles. Additionally, acidic *N*-oxide HOBt could also act as nucleophile, though with a very low 9% yield (**52**). (Table 2-2)

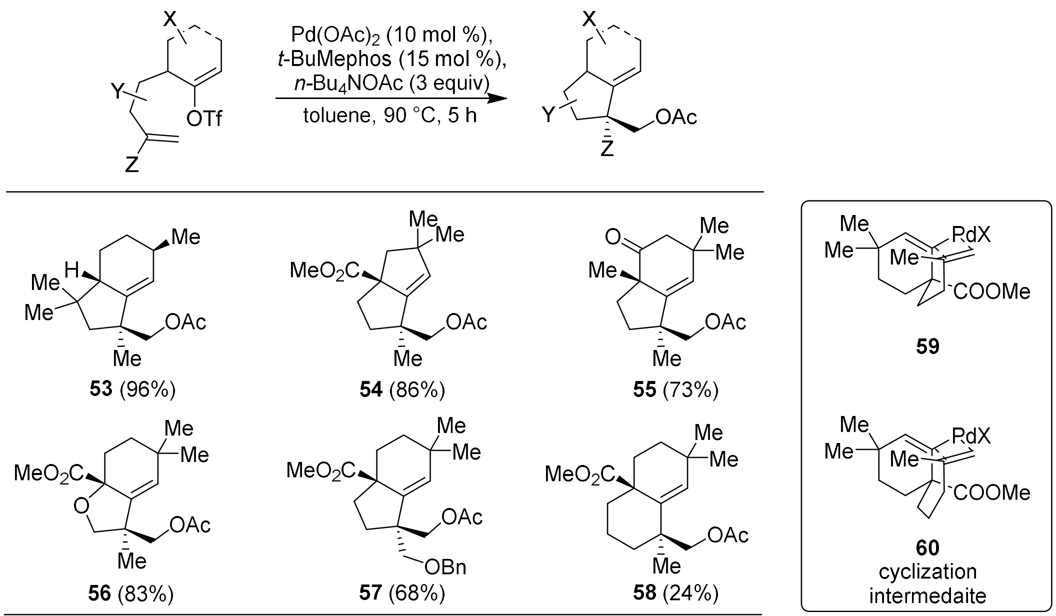
Table 2-2: Oxygen nucleophile scope of cyclization cascade.[a,b]



a. reaction conditions unless otherwise noted: **28** (0.1 mmol), Pd(OAc)$_2$ (0.01 mmol), tBuMephos (0.015 mol), ammonium salt (0.3 mmol), toluene (1 mL), 90 °C, 5 h;
b. isolated yields;
c. reaction temperature was 130 °C.

With the success of the nucleophile scope, we investigated other vinyl triflate substrates. A chiral substrate resulted in a single enantiomer product **53**. Besides 6,5-bicycle, a 5,5-bicyclic structure **54** could also be constructed in high yields. Carbonyl substitution in **55** did not influence the reactivity. A tetrahydrofuran structure **56** could be synthesized from triflate with an O-linked side chain. In **57,** two hydroxylmethyl substitutions on the same quaternary center could be differentiated by benzyl and acetate protecting groups. All examples above were 5-exo cyclizations, but the 6-exo cyclization product **58** could also been synthesized, though with much lower yield, because of a more strained cyclization intermediate **60**.[19] (Table 2-3)

Table 2-3: Vinyl triflate scope of cyclization cascade[a]



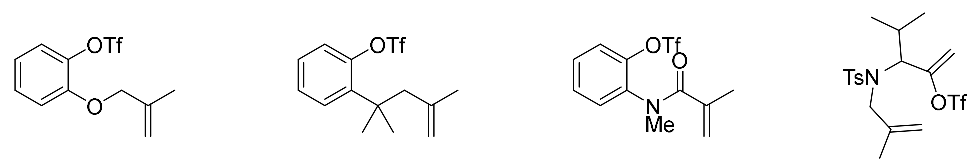
a. reaction conditions: substrate (0.1 mmol), $Pd(OAc)_2$ (0.01 mmol), tBuMephos (0.015 mol), *n*Bu_4NOAc (0.3 mmol), toluene (1 mL), 90 °C, 5 h.

2.2.4 Substrate limitations

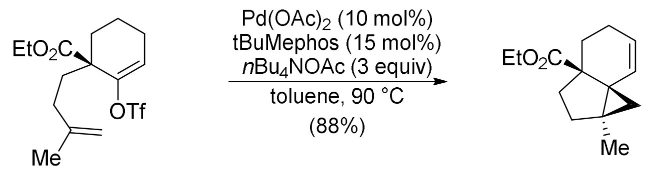
Though we showed the power of this reaction, the methodology also had its limitations. In addition to **43**, **49**, and **51** mentioned above, some other substrates failed in our system. All phenyl triflates and acyclic vinyl triflates we tried, such as **61-64**, failed to form any of the desired product. With **61-63**, only *ipso* substitution of triflate by acetate was observed. **64** resulted in decomposition.

Some substrates formed undesired products. When the gem-dimethyl structure was absent, we did not observe the desired product, rather, a 3-membered ring structure **66**, which was observed by Grigg et al. in a similar system.[20] Palladium insertion into styrene in **67** resulted in a polycyclic structure **69** instead of our desired product. Activation of benzene C–H bonds by the alkyl palladium(II) intermediate followed by an intramolecular Heck reaction should be responsible. Zhu et al. reported a similar example.[21] (Table 2-4)

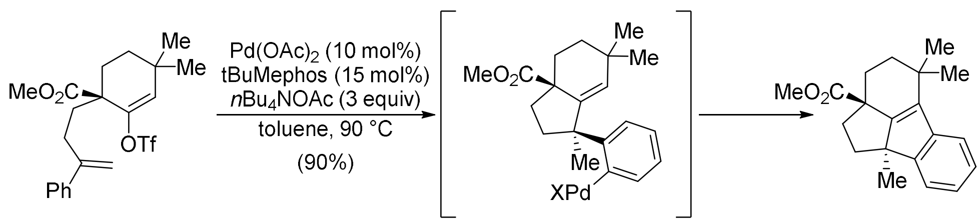
Table 2-4: Failed substrates



61 **62** **63** **64**



65 **66**



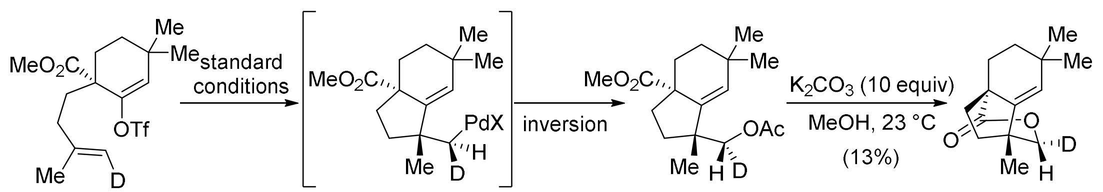
67 **68** **69**

2.3 Mechanism study

2.3.1 Isotope labeling experiment

To illustrate mechanism of the reaction, we first did an isotope labeling experiment. We synthesized a D-labeled vinyl triflate **D-28**.[22] Under our standard condition, the labeled cyclization product **D-29** was formed smoothly. As we observed a single product, a radical process did not tend to happen. For more stereochemical information, we tried several modifications and found that simply treating **D-29** with excess base could form a lactone **D-71**, though only in low yield. NOE NMR analysis of **D-71** revealed that the remained hydrogen had a NOE interaction with the angular methyl group, so the deuterium atom was found to be *trans* to that methyl, which indicated an inversion from cyclized intermediate **D-70**, where the deuterium atom was *cis* to the methyl, to cascade product **D-29**. This provided evidence for an S_N2 process in the mechanism. (Scheme 2-4)

Scheme 2-4: Isotope labeling study



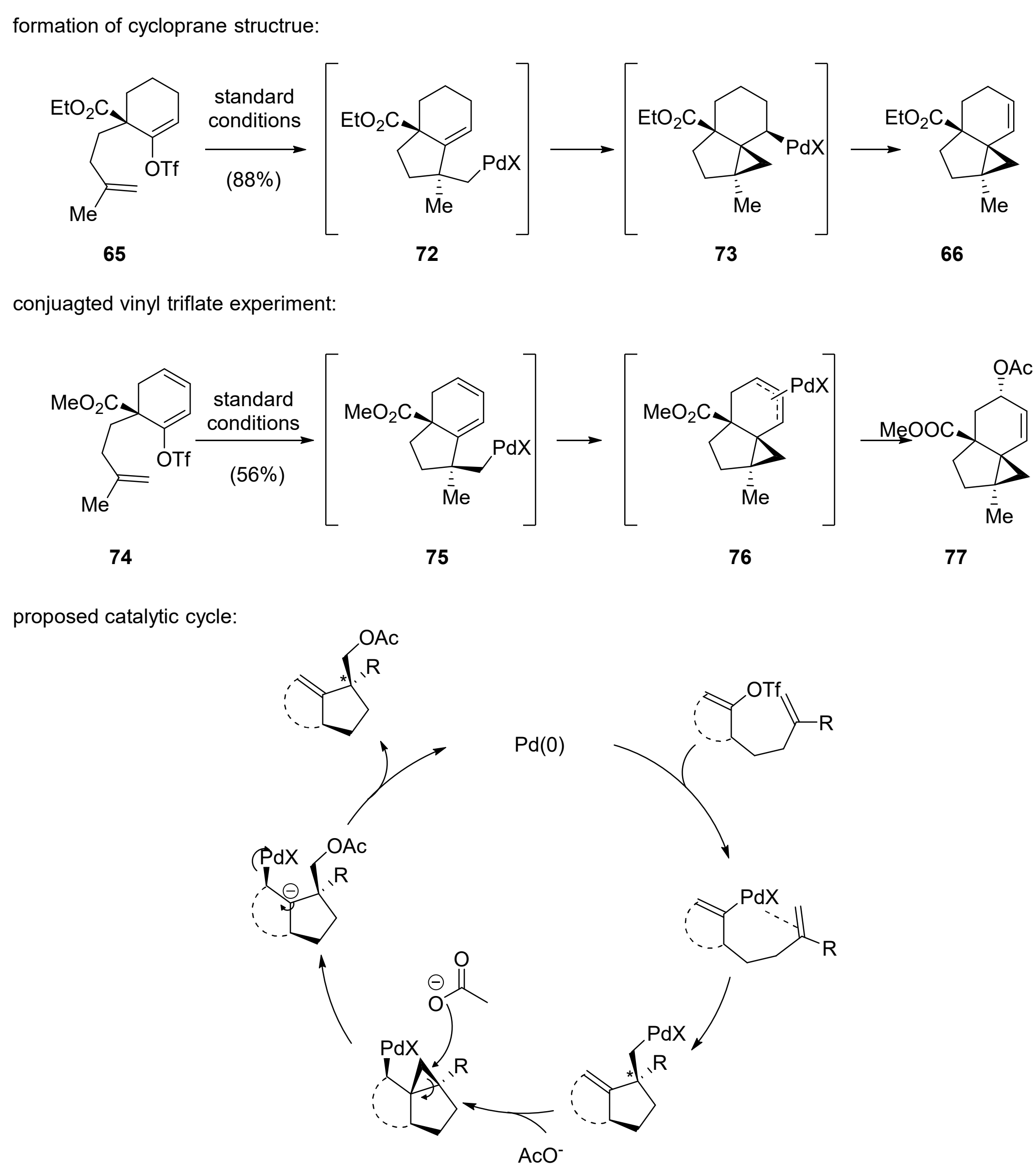
D-28 **D-70** **D-29** **D-71**
confirmed by NOE

2.3.2 Cyclopropane intermediate

As we confirmed a S_N2 mechanism of this reaction, the detailed mechanism was still of interest. The incompatibility of phenyl triflates in our reaction, while reported possible with halogen and sulfur nucleophiles,[5a,7] was of particular interest. Grigg et al. proposed a direct nucleophilic attack mechanism (Figure 2-1).[3] However in this case, C–O reductive elimination with inactivated alkyl palladium(II) would be difficult. As mentioned in *2.1.1*, Mulzer et al. observed a similar cyclization reaction on vinyl bromide substrate in the synthetic study of *bielschowskysin*, proposing an acetoxyl-palladation mechanism.[23] However, this was also difficult when oxidative addition was possible, and as shown on **43** (Table 2-2), oxidative addition of bromide might interfere with this cascade. Thus, those proposals were not satisfying.

One hint of the mechanism came from **66** with the 3-membered ring. An intramolecular Heck-type insertion to the double bond in alkyl palladium(II) intermediate **72** formed cyclopropane intermediate **73**. It was followed by β-H elimination, which is the termination of 'normal' Heck reactions, to provide **66**.[20] It was reasonable to propose that the cyclopropane intermediate was general for this type of reaction. This could also explain the necessity of the gem-dimethyl blocking group (or a blocking group *cis* to the palladium, like **53**) to prevent β-H elimination and allow nucleophilic attack. We also noted that the strain of the cyclopropane structure would enhance the reactivity and make it ready to nucleophilic attack and ring opening.[24]

Scheme 2-5: Cycloprane intermediate mechanism

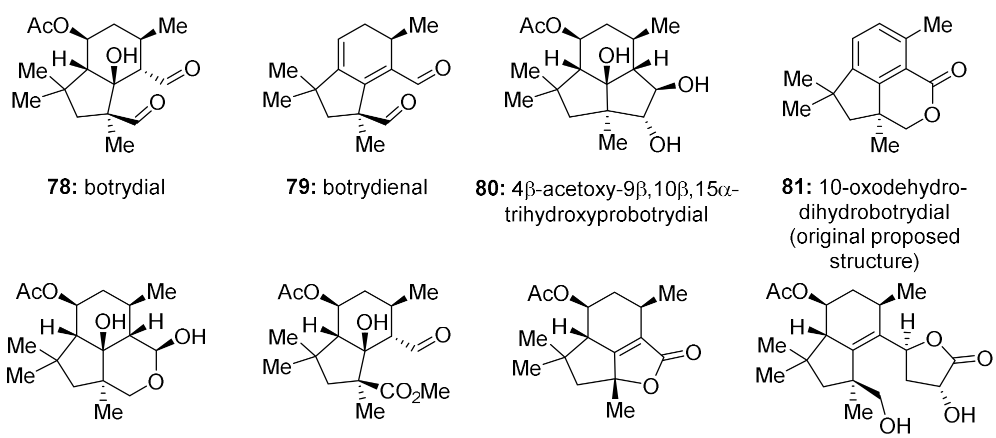


We proposed that the cyclopropane structure was the actual active intermediate. To provide more sound evidence, we synthesized conjugated vinyl triflate **74**. After intramolecular insertion, due to the additional double bond, the cyclopropane intermediate **76** would contain an activated allyl palladium(II) instead of alkyl. If a nucleophilic attack happened on **76**, the allyl palladium(II) species would be more reactive than cyclopropane ring, which was confirmed by the observed product **77** and the lack of the cascade product. Based on these results, we proposed the revised catalytic cycle of this reaction, with one extra cyclopropane intermediate. The strain of 3-membered ring was essential to allow the oxygen nucleophilic attack. As the elimination did not follow antiperiplanar manner, it was possibly a stepwise process, first ring-opening of the cyclopropane then cleavage of C–Pd bond. The relationship between acidity and reactivity (see *2.2.3*) was possibly because that a too strong nucleophile might attack palladium to replace the ligand, rather than the carbon on cyclopropane ring, thus making the palladium a bad leaving group and terminating this process.(Scheme 2-5)

2.4 Synthetic application: botrydienal

2.4.1 Introduction

Figure 2-2: Structures of selected members of *botrydial* family



78: botrydial **79:** botrydienal **80:** 4β-acetoxy-9β,10β,15α-trihydroxyprobotrydial **81:** 10-oxodehydro-dihydrobotrydial (original proposed structure) **82:** dihydrobotrydial **83:** methyl acetylbotryaloate **84:** norbotrydialone acetate **85:** 4β-acetoxy-tetrahydrobotryslactone

The *botrydial* family were first isolated in 1974 from *Botrytis cinerea*, a useful fungus in wine industry.[25] They are phytotoxic metabolites, causing 'noble rot' in grapes and have been made use of in production of trockenbeerenauslese, an expensive sweet wine, since the 18th century.

Botrydienal **79**, which was isolated in 1985,[26] proved to be highly bioactive, with ID_{50} = 0.1-1 μg/ml.[27]

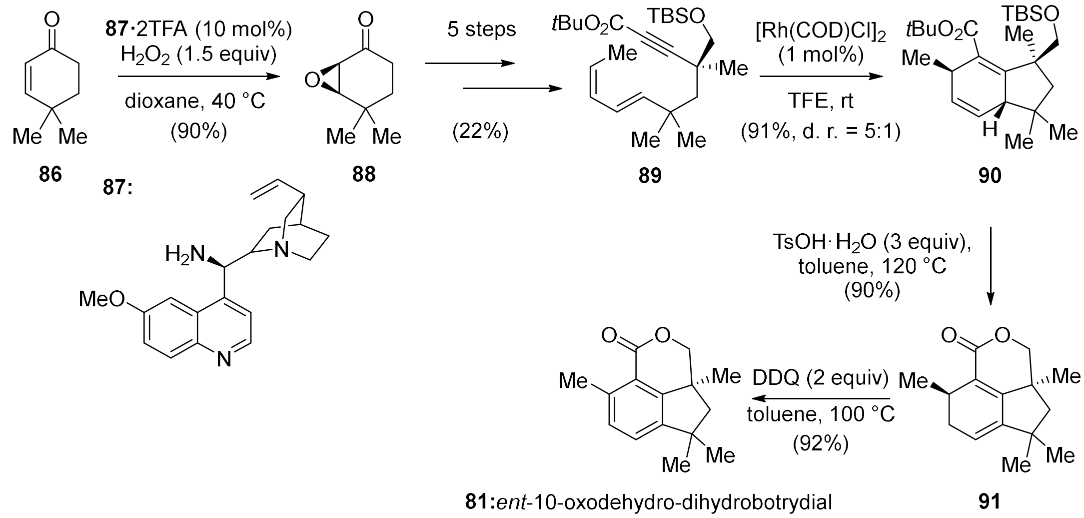
This terpene family, having more than 15 members, share a 6,5-bicyclic skeleton, with different oxidation statuses. Some of them have an extra lactone or acetal ring (**81**, **84**), or a highly strained *trans*-5,5-bicyclic structure (**80**). Many members have continuous stereocenters with oxygen (**78**, **80**, **82**, **83**, **85**) and are challenging targets of synthesis. (Figure 2-2)

Though first isolated decades ago, not many synthetic studies of the *botrydial* family were reported. Collado et al. reported some transformations between family members.[27] The Li group made significant contributions in this field with their Diels-Alder chemistry. In 2016 they reported the first asymmetric synthesis of proposed structure of *10-oxodehydro-dihydrobotrydial* in 9 steps.[28] They achieved asymmetric epoxidation of ketone **86** by quinine catalyst **87**. The enantio-rich epoxide **88** was then transferred to compound **89**. Then a Diels-Alder reaction catalyzed by rhodium provided bicyclic **90** stereo-selectively. Then lactonization and double bond migration by acid catalysis followed by oxidative aromatization provide natural product **81**. However, the product they synthesized had reversed optical rotation of the natural product, effectively proving to be an enantiomer of the target. In 2017 in a following study the transferred intermediate **91** to *botrydienal* **79** in 2 steps.[29]

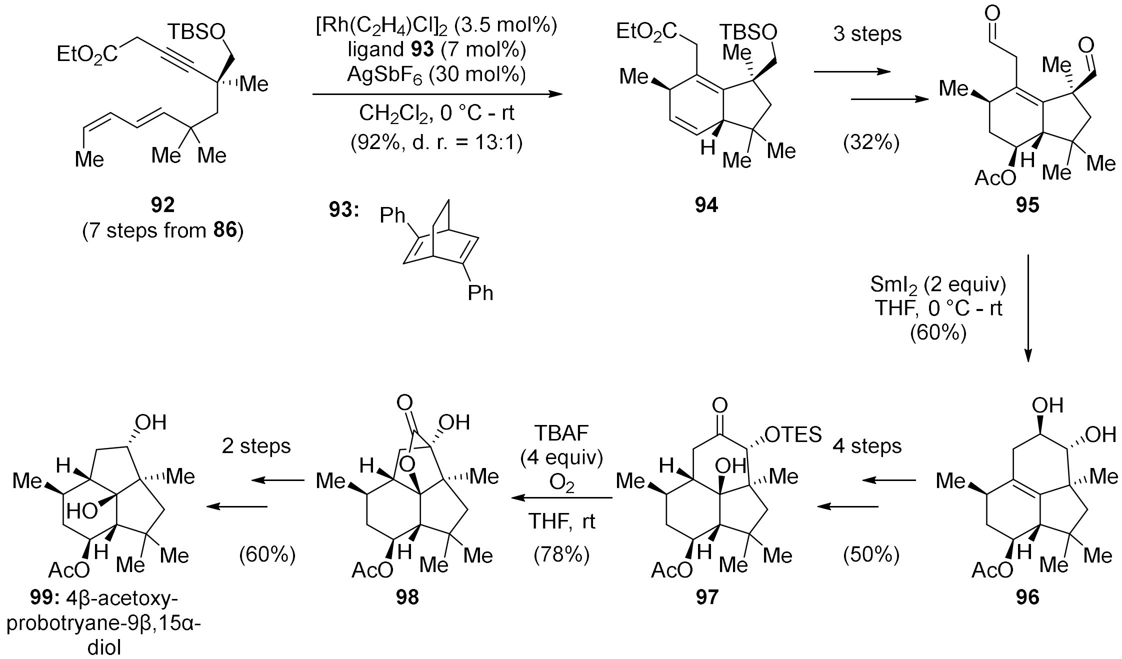
A more strained and challenging product *4β-acetoxyprobotryane-9β,15α-diol* **99** was also achieved by Li et al.[30] They synthesized Diels-Alder product **94** in a similar route. This was transferred to dial **95**, followed by SmI_2 reductive coupling to construct the third ring. After further oxidation and protection, oxidative ring contraction led to strained *trans*-5,5-bicylic structure **98**. Finally oxidative cleavage of the lactone and reduction produced natural product **99**. (Scheme 2-6)

Scheme 2-6: Li's synthesis of *botrydial* family

asymmetric total synthesis of proposed structure of *10-oxodehydro-dihydrobotrydial*:



asymmetric total synthesis of *4β-acetoxyprobotryane-9β,15α-diol*:

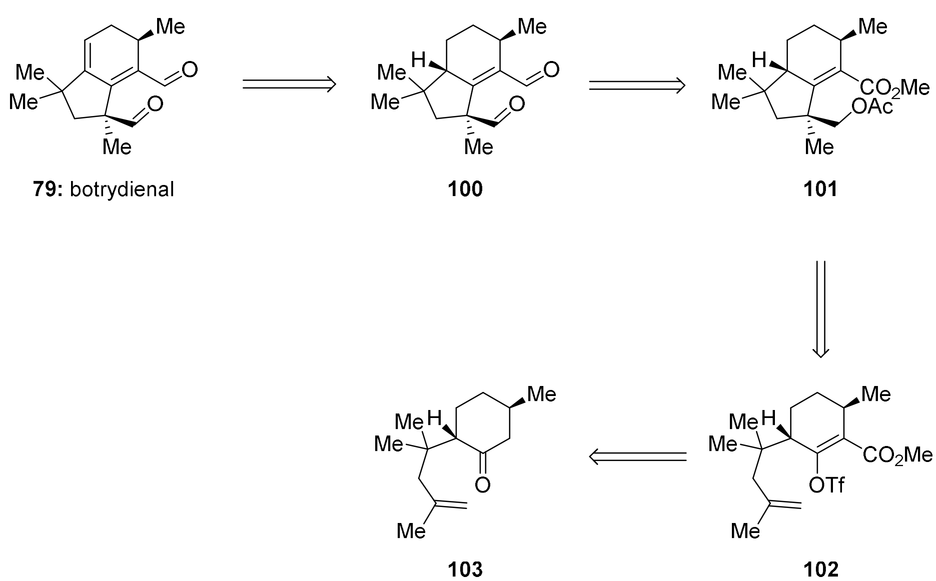


Li's total synthesis based on intramolecular Diels-Alder reactions and ring contraction was impressive. However, the synthesis of Diels-Alder precursor was not concise. We proposed that our cascade reaction would be an alternative and effective method to build up the bicyclic structure.

2.4.2 Overall design of synthetic route

To demonstrate the power of our cascade methodology we planned to achieve the synthesis of *botrydienal* (**79**). We proposed that the 5-membered ring and C–O bond could be built with our cascade chemistry in one step stereo-selectively. As shown in scheme 2-7, we proposed that the conjugated diene in our target **79** could be introduced in a later stage. The intermediate **100** can be traced back to **101** after oxidation status management. **101** could be synthesized by our cascade reaction from triflate **102**, which could be easily prepared from known chiral compound **103**.[31]

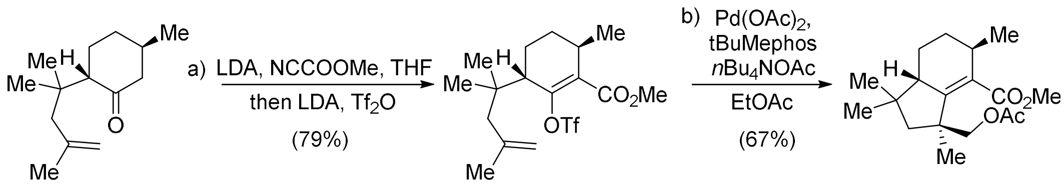
Scheme 2-7: Proposed synthetic route of *botrydienal*



2.4.3 Route to cyclization cascade and aromatization problem

Our synthesis started with known compound **103**, which was prepared from commercial *(+)-pulegone* in one step by Sakurai reaction with 50% yield.[31b] A one-pot α-acylation and triflation of **103** resulted in triflate **102**. This one-pot process produced better yields than the isolated two-step procedure, which exhibited a yield of less than 50%. Our optimized condition of methodology in toluene worked for this substrate to provide cascade product **101**, however with only 35% yield. After additional screening we found EtOAc (also good for the methodology, see Table 2-1, entry 10) was the optimized solvent for this specific reaction, resulting in 67% yield. (Scheme 2-8)

Scheme 2-8: Synthesis towards cyclization cascade[a]

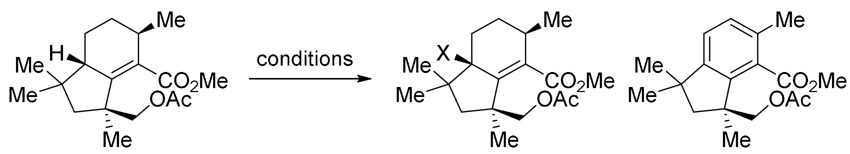


103 **102** **101**

a. reaction conditions: (a) LDA (3 equiv), THF, -78 °C - 0 °C, 90 min, then NCCOOMe (3.3 equiv), HMPA (3 equiv), -78 °C, 1 h, then LDA (10 equiv), Tf_2O (10 equiv), -78 °C, 4 h; (b) $Pd(OAc)_2$ (10 mol%), tBuMephos (15 mol%), $n$$Bu_4NOAc$ (3 equiv), EtOAc, 90 °C, 12 h.

Though the cyclization worked smoothly, the following step proved to be challenging. Li et al. showed that their intermediate **91** was readily susceptible to aromatization,[28a] which was also true of intermediate **101**. We tried various conditions, including radical substitution, allylic oxidation, and epoxidation, but the desired allylic functionalization was not successful. Only aromatization product was observed. We also tried other substrates, such as free diol **106**, mono alcohol **107** and lactone **108**, but all these reactants led to undesired aromatization. However, we made use of this aromatization of **108** to synthesis *10-oxodehydro-dihydrobotrydial*. Treatment of **101** with excess base formed lactone **108**, followed by aromatization, providing **81**. Optical data of our sample was consistent with Li's[28a] leading us to believe that this was the enantiomer of the natural product isolated by Collado et al..[28b] (Scheme 2-9)

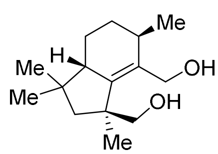
Scheme 2-9: Aromatization and synthesis of *10-oxodehydro-dihydrobotrydial*



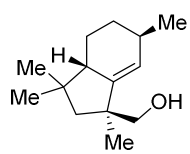
101 **104** **105**

Entry	Conditions	Results
1	NBS, CCl_4	**105** only
2	Br_2, *hv*, CCl_4	**105** only
3	SeO_2, 1,4-dioxane	**105** only
4	TBHP, *n*BuLi, THF	no reaction
5	*m*CPBA, K_2CO_3, CH_2Cl_2	no reaction

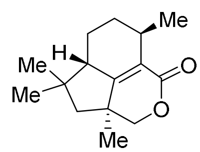
Other failed substrates:



106

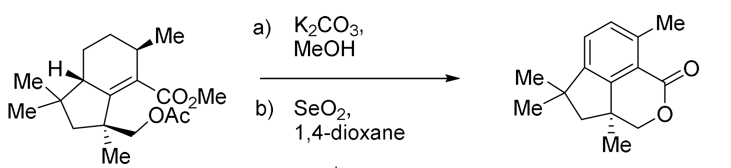


107



108

synthesis of 10-oxodehydro-dihydrobotrydial: [a]



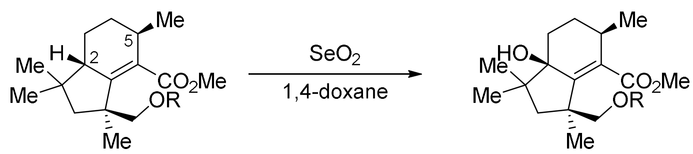
101 (17%[b], 2 steps) **81**:*ent*-10-oxodehydrodi-hydrobotrydial

a. reaction conditions: (a) K_2CO_3 (10 equiv), MeOH, 23 °C, 10 h; (b) SeO_2 (4 equiv), 1,4-dioxane, reflux, 12 h.
b. 32% **108** was recovered.

2.4.4 Final steps towards botrydienal

After extensive screening, we finally found that a bulky protection group of the hydroxyl, instead of acetate, could prevent aromatization. TBS protected **109c** (easily prepared from **101** by basic alcoholysis and TBS protection, see Scheme 2-10) was found to be the best, resulting in 49% yield with SeO_2 oxidation.[32] (Table 2-5) We proposed that aromatization was a 2-step process, consisting of oxidation of both allylic positions (C-2 and C-5 in **109**) and double elimination. The hindered TBS group, though remote, could mask the undesired allylic position at C-5 position and thus provided the desired mono oxidized product.

Table 2-5: Protection group and allylic oxidation[a]

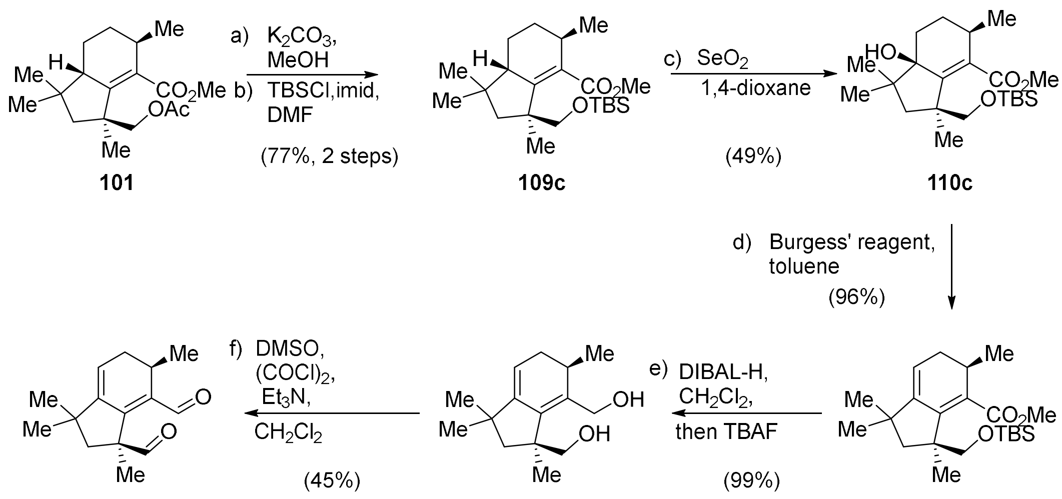


Substrate	R gorup	isolated yield of **110**
109a	piv	0%[b]
109b	TES	0%[b]
109c	TBS	49%[c]
109d	TIPS	37%[c]

a. reaction coditions: SeO_2 (4 equiv), 1,4-dioxane, reflux, 12 h.
b. only aromatized product was observed.
c. with some aromatized product.

With the allylic oxidation succeeded, we continued the synthesis toward *botrydienal*. Allylic hydroxyl in **110c** could be eliminated by Burgess' reagent[33] to produce the conjugated diene structure in **111**. Then a one-pot DIBAL-H reduction and deprotection of the TBS group provided diol **112** in nearly quantitative yield. DMP oxidation of **112** only resulted in trace amounts of the desired natural product **79**, but Swern oxidation with a high excess of the amount of reagents provided 45% yield of **79**. We finished the total synthesis of *botrydienal* in 9 steps from commercial *(+)-pulegone*, with 4.3% yield overall. (Scheme 2-10)

Scheme 2-10: Finish of synthesis of *botrydienal*[a]



101 **109c** **110c**

79: botrydienal **112** **111**

a. reaction conditions: (a) K_2CO_3 (1.05 equiv), MeOH, 23 °C, 10 h; (b) TBSCl (1.5 equiv), imidazole (1.6 equiv), DMF, 23 °C, 12 h; (c) SeO_2 (4 equiv), 1,4-dioxane, reflux, 12 h; (d) Burgess reagent (3 equiv), toluene, 80 °C, 12 h; (e) DIBAL-H (3 equiv), CH_2Cl_2, 0 °C, 1 h, then TBAF (3 equiv), 0 °C, 3 h; (f) DMSO (20 equiv), $(COCl)_2$ (10 equiv), CH_2Cl_2, -78 °C, 3 h, then Et_3N (30 equiv), 30 min.

2.5 Summary and outlook

Palladium catalyzed cyclization and nucleophile capture cascades have been widely investigated. However, C–O formation in such cascades were not well studied, as this via an inactivated alkyl palladium(II) intermediate was challenging. C–O bonds are very useful in organic synthesis for various further transformations. Such a stereospecific C–O bond formation cascade would be a potential solution to a series of natural products with 1,3-*trans* structures. Herein we developed an unprecedented cascade methodology of cyclization and C–O bond formation, via a Pd(0)/Pd(II) catalytic cycle. This reaction was compatible with many substrates with different substitutions, mostly resulting in high yields, and could construct various ring structures.

Mechanism study indicated that the reaction proceeded via a cyclopropane key intermediate which was proposed to be the actual intermediate of such a nucleophile capture cascade, different from former proposals. We also showed the power of our methodology by short asymmetric synthesis of *botrydienal* and *epi-10-oxodehydro-dihydrobotrydial*, in 9 and 5 steps respectively, more concise than former syntheses.

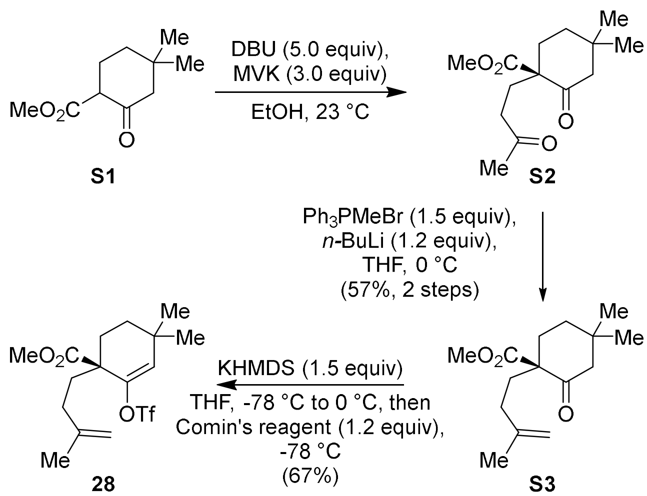
This methodology was also applied in our group's synthesis of *conidiogenones* to construct a 5,5-bycyclic moiety and a C–O bond.[34] Further studies, such as C–N bond formation cascades with azide salts are now under investigation in our group. We have found that azide nucleophiles could react smoothly to provide C–N bond formation product with the same substrate **28**.

2.6 Experiment section

General Procedures. All reactions were conducted under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), toluene, dimethylformamide (DMF), diethyl ether (Et_2O) and dichloromethane (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. SiliCycle silica gel plates silica gel plates (60F-254) using UV light as visualizing agent, and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. SiliCycle silica gel (60, academic grade, particle size 0.040–0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography separations were carried out on 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker 500 MHz and 400 MHz instruments and calibrated using residual undeuterated solvent as an internal reference ($\delta(CDCl_3) = 7.26$, δ(DMSO-d6) = 2.50 for ^{1}H NMR and $\delta(CDCl_3) = 77.0$, δ(DMSO-d6) = 39.5 for ^{13}C NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d

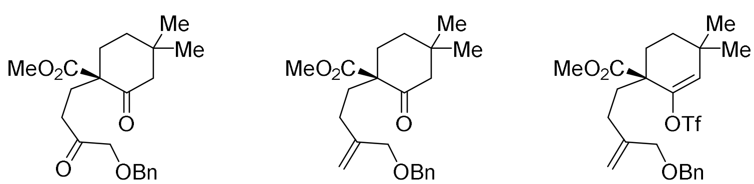
= doublet, t = triplet, q = quartet, sx = sextet, m = multiplet. IR spectra were recorded on a Perkin-Elmer 1000 series FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on an Agilent 6244 Tof-MS using ESI (Electrospray Ionization) at the University of Chicago Mass Spectroscopy Core Facility.

Methodology



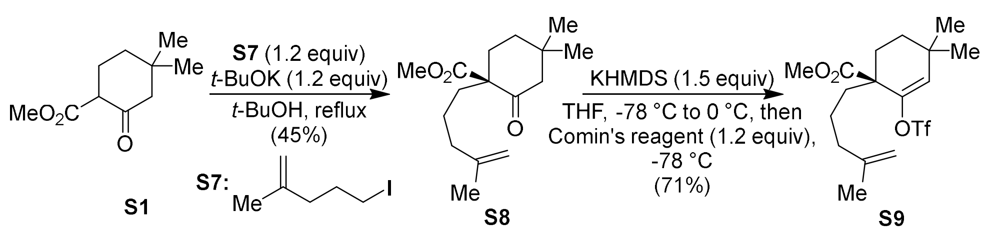
Triflate 28. To a solution of **methyl 4,4-dimethyl-2-oxocyclohexane-1-carboxylate (S1)** (1.84 g, 10.0 mmol, 1.0 equiv) in EtOH (50 mL) at 23 °C was added DBU (7.60 g, 50.0 mmol, 5.0 equiv) and methyl vinyl ketone (2.10 g, 30.0 mmol, 3.0 equiv). The resultant solution was then stirred at 23 °C for 3 h. Upon completion, the reaction contents were diluted with EtOAc (30 mL) and quenched by the addition of saturated aqueous NH_4Cl (30 mL). The resultant mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was then extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with H_2O (30 mL) and brine (30 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 5:1) to provide the desired Michael adduct **S2** (2.41 g, 95% yield) as a pale-yellow oil. **S2**: R_f = 0.23 (silica gel, hexanes: EtOAc = 5:1); IR (film) ν_{max} 3628, 3414, 2956, 1713, 1435, 1369, 1102, 1075, 940, 853

cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.72 (s, 3 H), 2.56–2.49 (m, 1 H); 2.43–2.39 (m, 1 H), 2.34 (d, J = 13.3 Hz, 1 H), 2.18–2.13 (m, 1 H), 2.12 (s, 3 H), 2.11– 2.07 (m, 1 H), 1.89–1.83 (m, 1 H), 1.65–1.49 (m, 2 H), 1.51–1.49 (m, 1 H), 1.02 (s, 3 H), 0.87 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7, 207.4, 172.4, 58.8, 53.8, 52.5, 38.8, 36.7, 35.6, 31.9, 31.1, 30.0, 28.1, 25.7; HRMS (ESI) calcd for $C_{14}H_{23}O_4^+$ [M + H$^+$] 255.1591, found: 255.1593. Next, to a suspension of Ph_3PCH_3Br (2.68 g, 7.50 mmol, 1.5 equiv) in THF (30 mL) at 0 °C was added *n*-BuLi (2.40 mL, 2.5 M in THF, 6.00 mmol, 1.2 equiv). The resultant mixture was stirred at 0 °C for 15 min and then a solution of the intermediate from above (1.27 g, 5.00 mmol, 1.0 equiv) in THF (20 mL) was added. The resultant mixture was stirred at 0 °C for 2 h. Upon completion, the reaction contents were diluted with EtOAc (30 mL) and quenched by the addition of saturated aqueous NH_4Cl (30 mL). The mixture was warmed to 23 °C, poured into a separatory funnel, and the resultant layers were separated. The aqueous layer was then extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine (30 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 50:1) to provide ketone **S3** (0.756 g, 60% yield) as a pale-yellow oil. **S3**: R_f = 0.68 (silica gel, hexanes:EtOAc, 5:1); IR (film) ν_{max} 2956, 2857, 1714, 1650, 1454, 1369, 1252, 1199, 1100, 887 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (s, 1 H), 4.68 (s, 1 H), 3.72 (s, 3 H), 2.46 (dt, J = 13.6, 3.7 Hz, 1 H), 2.31 (d, J = 13.1 Hz, 1 H), 2.15 (dd, J = 13.1, 2.4 Hz, 1 H), 2.06–2.00 (m, 1 H), 1.92–1.86 (m, 2 H), 1.72 (s, 3 H), 1.70–1.57 (m, 3 H), 1.51–1.47 (m, 1 H), 1.02 (s, 3 H), 0.87 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 172.3, 145.3, 110.0, 59.4, 53.9, 52.3, 36.7, 35.7, 32.7, 32.2, 31.4, 31.3, 25.5, 22.6; HRMS (ESI) calcd for $C_{15}H_{25}O_3^+$ [M + H$^+$] 253.1798, found: 253.1805. Finally, to a solution of ketone **S3** (1.26 g, 5.00 mmol) in THF (40 mL) at –78 °C was added KHMDS (7.50 mL, 1.0 M in THF, 7.50 mmol, 1.5 equiv). The resultant yellow solution was then stirred at 0 °C for 90 min before being cooled to –78 °C. A solution of Comin's reagent (2.35 g, 6.00 mmol, 1.2 equiv) in THF (10 mL) was then added. The resultant solution was stirred at –78 °C for 1 h before being diluted by EtOAc (30 mL) and quenched by the addition of saturated aqueous NH_4Cl (30 mL). The mixture was warmed to 0 °C, poured into a separatory funnel, and the resultant layers were separated. The aqueous layer was then extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine (30 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (Et_3N-buffered silica gel, hexanes) to provide triflate **17** (1.29 g, 67% yield) as a colorless oil. **17**: R_f = 0.69 (silica gel, hexanes: EtOAc, 10:1); IR (film) ν_{max} 2962, 2869, 1739, 1669, 1651, 1417, 1214, 1144, 1004, 950, 899, 816 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.63 (s, 1 H), 4.73 (s, 1 H), 4.67 (s, 1 H), 3.74 (s, 3 H), 2.23–2.18 (m, 1 H), 2.05–1.92 (m, 3 H), 1.87–1.76 (m, 2 H), 1.73 (s, 3 H), 1.50–1.48 (m, 2 H), 1.10 (s, 3 H), 1.06 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 146.8, 144.7, 129.9, 119.3, 117.0, 110.6, 52.3, 50.2, 33.48, 33.46, 33.3, 32.2, 29.9, 29.1, 27.8, 22.3; HRMS (ESI) calcd for $C_{16}H_{24}O_5F_3S^+$ [M + H^+] 385.1291, found: 385.1298.

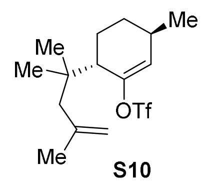


S4 S5 S6

Triflate S6. Prepared as described above starting from **4,4-dimethyl-2-oxocyclohexane-1-carboxylate** (0.552 g, 3.00 mmol, 1.0 equiv) and **1-(benzyloxy)but-3-en-2-one**[35] (1.58 g, 9.00 mmol, 3.0 equiv) to afford triflate S**6** (0.139 g, 9% overall yield) as a colorless oil. **S4**: R_f = 0.29 (silica gel, hexanes:EtOAc, 5:1); IR (film) ν_{max} 3510, 2954, 2866, 1712, 1454, 1248, 1201, 1101 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5 H), 4.57 (s, 2 H), 4.04 (s, 2 H), 3.70 (s, 3 H), 2.59–2.52 (m, 1 H), 2.45–2.37 (m, 2 H), 2.34 (d, J = 13.2 Hz, 1 H), 2.16–2.11 (m, 2 H), 1.92–1.86 (m, 1 H), 1.62–1.49 (m, 3 H), 1.02 (s, 3 H), 0.87 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.6, 207.2, 172.3, 137.2, 128.5, 128.0, 127.9, 74.8, 73.4, 58.8, 53.8, 52.4, 36.7, 35.6, 34.2, 31.8, 31.1, 27.6, 25.6; HRMS (ESI) calcd for $C_{21}H_{29}O_5^+$ [M + H^+] 361.2010, found: 361.2009. **S5**: R_f = 0.50 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 3443, 3030, 2954, 2863, 1713, 1652, 1496, 1368, 1199, 1098, 1028, 904, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5 H), 5.06 (s, 1 H), 4.96 (s, 1 H), 4.48 (s, 2 H), 3.96 (s, 2 H), 3.70 (s, 3 H), 2.58–2.52 (m, 1 H), 2.45–2.37 (m, 2 H), 2.33 (d, *J* = 13.2 Hz, 1 H), 2.16–2.09 (m, 2 H), 1.91–1.85 (m, 1 H), 1.64–1.56 (m, 2 H), 1.50–1.48 (m, 1 H), 1.01 (s, 3 H), 0.86 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.1, 172.2, 145.5, 138.4, 128.3, 128.1, 127.7, 127.5, 73.0, 72.0, 59.4, 53.9, 52.3, 36.7, 35.7, 35.1, 32.7, 31.31, 31.28; HRMS (ESI) calcd for $C_{22}H_{31}O_4^+$ [M + H^+] 359.2217, found: 359.2231. **S6**: R_f = 0.62 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 3032, 2959, 2866, 1738, 1669, 1454, 1416, 1365, 1213, 1144, 1093, 901, 817 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5 H), 5.63 (s, 1 H), 5.08(s, 1H), 4.96 (s, 1 H), 4.51–4.46 (m, 2 H), 3.96 (dd, *J* = 16.1, 12.5 Hz, 1 H), 3.72 (s, 3 H), 2.22–2.18 (m, 1 H), 2.12–2.02 (m, 3 H), 1.89–1.83 (m, 1 H), 1.80–1.75 (m, 1 H), 1.51–1.48 (m, 2 H), 1.09 (s, 3 H), 1.05 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 146.7, 145.0, 138.2, 130.1, 128.4, 127.7, 127.6, 122.1, 119.6, 117.0, 114.5, 112.6, 73.0, 72.0, 52.4, 50.2, 33.5, 33.4, 33.3, 29.9, 29.0, 27.8, 27.6; HRMS (ESI) calcd for $C_{23}H_{30}O_6F_3S^+$ [M + H^+] 491.1710, found: 491.1694.

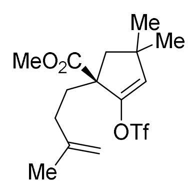


Triflate S9. To *t*-BuOK (2.4 mL, 1.0 M in *t*-BuOH, 2.40 mmol, 1.2 equiv) at 23 °C was added **methyl 4,4-dimethyl-2-oxocyclohexane-1-carboxylate** (0.368 g, 2.00 mmol, 1.0 equiv). The resultant mixture was stirred at 23 °C for 10 min before **5-iodo-2-methylpent-1-ene (S7)**[36] (0.504 g, 2.40 mmol, 1.2 equiv) was added. The resultant mixture was heated to 85 °C and stirred at that temperature for 18 h.[37] Upon completion, the reaction contents were cooled to 23 °C, diluted with EtOAc (10 mL), and quenched by the addition of saturated aqueous NH_4Cl (10 mL). The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was then extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (10 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 100:1→50:1) to provide ketone **S8** (0.241 g, 45% yield) as a pale-yellow oil. **S8**: R_f = 0.45 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 3073, 2956, 2869, 1712, 1649, 1456, 1255, 1199, 1168, 1101, 888, 749 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (s, 1 H), 4.66 (s, 1 H), 3.72 (s, 3 H), 2.44 (dt, *J* = 13.7, 3.6 Hz , 1 H), 2.30 (d, *J* = 13.1 Hz, 1 H), 2.14 (dd, *J* = 13.1, 2.3 Hz, 1 H), 2.00 (t, *J* = 7.4 Hz, 1 H), 1.88–1.82 (m, 1 H), 1.69 (s, 3 H), 1.65–1.46 (m, 4 H) 1.36–1.30 (m, 1 H), 1.01 (s, 3 H), 0.86 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 172.5, 145.2, 110.2, 59.6, 53.9, 52.2, 37.9, 36.7, 35.7, 34.0, 31.4, 31.3, 25.5, 22.2, 22.1; HRMS (ESI) calcd for $C_{16}H_{27}O_3^+$ [M + H$^+$] 267.1955, found: 267.1955. Pressing forward, triflate **S9** was prepared as described above starting from **S8** (0.084 g, 0.31 mmol, 1.0 equiv) to afford triflate **S9** (0.089 g, 71% yield) as a colorless oil. **S9**: R_f = 0.58 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2960, 2890, 1739, 1670, 1651, 1417, 1212, 1144, 1005, 900, 816 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 (s, 1 H), 4.71 (s, 1 H), 4.66 (s, 1 H), 3.72 (s, 3 H), 2.22–2.17 (m, 1 H), 2.06–1.97 (m, 2 H), 1.86–1.64 (m, 3 H), 1.68 (s, 3 H), 1.49–1.38 (m, 4 H), 1.09 (s, 3 H), 1.05 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 147.0, 144.9, 129.7, 119.6, 117.0, 110.5, 52.3, 50.2, 37.8, 34.6, 33.5, 33.4, 29.9, 29.3, 27.8, 22.1, 22.0; HRMS (ESI) calcd for $C_{17}H_{26}O_5F_3S^+$ [M + H$^+$] 399.1448, found: 399.1454.



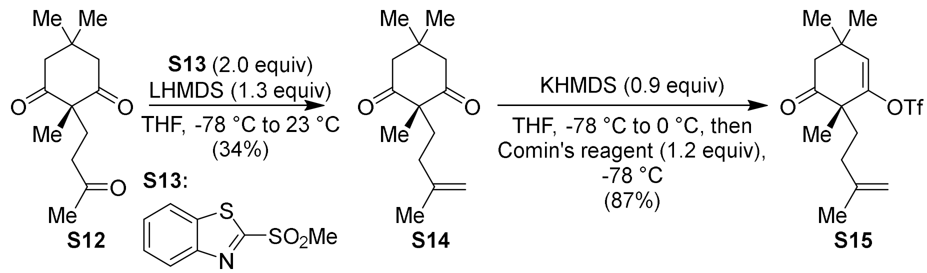
S10

Triflate S10. Prepared as described above starting from **103** (0.694 g, 3.33 mmol, 1.0 equiv) to afford triflate **S10** (0.985 g, 87% yield) as a colorless oil. **S10**: R_f = 0.48 (silica gel, hexanes); $[\alpha]_D^{20}$ = +57.0° (*c* = 0.53 in $CHCl_3$); IR (film) ν_{max} 2963, 2874, 1666, 1643, 1417, 1209, 1144, 969, 893 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (s, 1 H), 4.89–4.87 (m, 1 H), 4.68–4.67 (m, 1 H), 2.46–2.42 (m, 1 H), 2.32–2.26 (m, 1 H), 2.12 (d, *J* = 13.2 Hz, 1 H), 1.97 (d, *J* = 13.3 Hz, 1 H), 1.98–1.92 (m, 1 H), 1.82–1.77 (m, 1 H), 1.78 (s, 3 H), 1.59–1.52 (m, 1 H), 1.15–1.08 (m, 1 H), 1.05 (s, 3 H), 1.04 (d, *J* = 7.1 Hz, 3 H), 1.00 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 142.9, 128.2, 121.5, 119.8, 117.2, 114.9, 47.6, 46.6, 37.3, 30.4, 30.1, 26.7, 26.5, 25.6, 25.5, 21.2; HRMS (CI) calcd for $C_{15}H_{24}O_3F_3S^+$ [M + H^+] 341.1393, found: 341.1391.



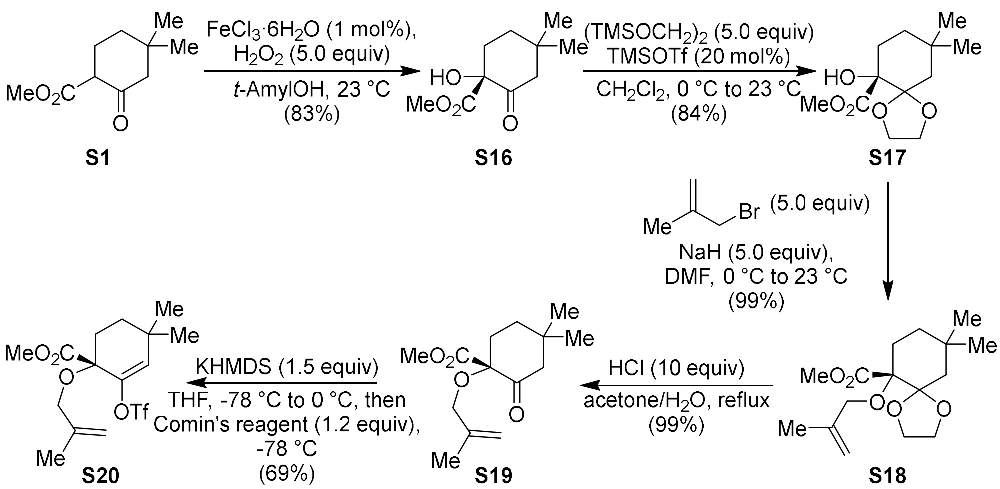
S11

Triflate S11. Prepared as described above starting from **methyl 4,4-dimethyl-2-oxocyclopentane-1-carboxylate**[38] (0.200 g, 1.17 mmol, 1.0 equiv) and **5-iodo-2-methylpent-1-ene** (0.275 g, 1.40 mmol, 1.2 equiv) to afford triflate **S11** (0.298 g, 69% yield) as a pale-yellow oil. **S11**: R_f = 0.58 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2960, 2870, 1740, 1654, 1424, 1366, 1249, 1215, 1142, 1047, 995, 842, 805, 762, 602 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 (s, 1 H), 4.73 (s, 1 H), 4.69 (s, 1 H), 3.74 (s, 3 H), 2.44 (d, *J* = 13.5 Hz, 1H), 2.10–2.04 (m, 1 H), 1.95–1.91 (m, 2 H), 1.78–1.73 (m, 1 H), 1.74 (d, *J* = 13.5 Hz, 1 H), 1.73 (s, 3 H), 1.17 (s, 3 H), 1.14 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 145.9, 144.5, 127.2, 122.2, 119.7, 117.2, 114.6, 110.5, 57.9, 52.4, 45.9, 40.0, 34.1, 32.6, 29.9, 28.9, 22.4; HRMS (ESI) calcd for $C_{15}H_{22}O_5F_3S^+$ [M + H$^+$] 371.1135, found: 371.1141.



Triflate S15. To a solution of **2-methanesulfonylbenzothiazole (S13)** (1.28 g, 6.00 mmol, 2.0 equiv) and **2,5,5-trimethyl-2-(3-oxobutyl)cyclohexane-1,3-dione (S12)**[39] (0.672 g, 3.00 mmol, 1.0 equiv) in THF (30 mL) at –78 °C was added LHMDS (3.90 mL, 1.0 M in THF, 3.90 mmol, 1.3 equiv). The resultant mixture was stirred at –78 °C for 3 h, and then the mixture was warmed to 23 °C and stirred for an additional 1 h. Upon completion, the reaction mixture was diluted with EtOAc (20 mL), cooled to 0 °C, quenched by the addition of saturated aqueous NH_4Cl (20 mL), and warmed to 23 °C. The resultant mixture was then poured into a separatory funnel and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine (30 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 20:1→10:1) to provide ketone **S14** (0.226 g, 34% yield) as a yellow oil. [Note: **S12** was not stable under strong basic conditions, thus attempts at a Wittig reaction variant gave only trace product]. **S14**: R_f = 0.47 (silica gel, hexanes:EtOAc, 4:1); IR (film) ν_{max} 2955, 2871, 1727, 1693, 1650, 1456, 1373, 1331, 1254, 1070, 955, 889 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.69 (s, 1 H), 4.63 (s, 1 H), 2.70 (d, J = 14.5 Hz, 2 H), 2.46 (d, J = 14.5 Hz, 2 H), 1.87–1.80 (m, 4 H), 1.67 (s, 3 H), 1.22 (s, 3 H), 1.06 (s, 3 H), 0.87 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.8, 144.6, 110.4, 64.4, 51.4, 35.9, 32.2, 30.6, 29.4, 27.6, 22.5, 17.9; HRMS (ESI) calcd for $C_{14}H_{23}O_2^+$

[M + H$^+$] 233.1693, found: 233.1699. Pressing forward, triflate **S15** was prepared as described above starting from **S15** (0.044 g, 0.20 mmol, 1.0 equiv) and using KHMDS (0.18 mL, 1.0 M in THF, 0.9 equiv) to afford triflate **S15** (0.063 g, 87% yield) as a colorless oil. **S15**: R_f = 0.68 (silica gel, hexanes: EtOAc, 10:1); IR (film) ν_{max} 2966, 2937, 1724, 1673, 1416, 1245, 1214, 1142, 1001, 887, 797 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (s, 1 H), 4.70 (s, 1 H), 4.66 (s, 1 H), 2.52 (d, J = 14.0 Hz, 2 H), 2.37 (d, J = 13.9 Hz, 2 H), 2.04–1.98 (m, 1 H), 1.82–1.78 (m, 2 H), 1.69 (s, 3 H), 1.66–1.61 (m, 1 H), 1.30 (s, 3 H), 1.16 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.2, 149.1, 144.5, 126.7, 119.6, 117.0, 110.5, 51.6, 50.9, 34.0, 33.1, 33.0, 29.8, 29.3, 23.4, 22.3; HRMS (ESI) calcd for $C_{15}H_{22}O_4F_3S^+$ [M + H$^+$] 355.1185, found: 355.1194.

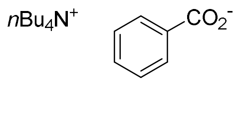


Triflate S20. **S16** (0.423 g, 83% yield b.r.s.m.) was prepared as a pale yellow oil following the reported procedure starting from **S1** (0.736 g, 4.00 mmol, 1.0 equiv).[40] **S16**: R_f = 0.26 (silica gel, hexanes:EtOAc, 5: 1); IR (film) ν_{max} 3459, 2958, 2870, 1720, 1456, 1436, 1370, 1289, 1258, 1200, 1164, 1123, 1099, 1039, 1006, 978, 796; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.31 (s, 1 H), 3.79 (s, 3 H), 2.60–2.56 (m, 1 H), 2.48–2.39 (m, 2 H), 1.83–1.79 (m, 1 H), 1.63–1.60 (m, 1H), 1.08 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.0, 170.5, 79.9, 53.0, 51.4, 36.9, 35.1, 33.4, 30.6, 26.1; HRMS (ESI) calcd for $C_{10}H_{15}O_3^+$ [M + H$^+$ – H_2O] 183.1016, found: 183.1022. Next, to a solution of **S16** (0.200 g, 1.00 mmol, 1.0 equiv) in CH_2Cl_2 (10 ml) at 0 °C was added 1,2-bis(trimethylsiloxyl)ethane (0.618 g, 5.00 mmol, 5.0 equiv) and TMSOTf (44.0 mg, 0.20 mmol, 20 mol %). The mixture was then stirred at 23 °C for 20 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous $NaHCO_3$ (10 mL). The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was then extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (hexanes:EtOAc, 10:1→5:1) to provide ketal **S17** (0.205 g, 84% yield) as a white solid. **S17**: R_f = 0.22 (silica gel, hexanes:EtOAc, 5:1); IR (film) ν_{max} 3505, 2952, 1732, 1449, 1388, 1264, 1217, 1168, 1074, 1043, 988, 826, 614; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94–3.89 (m, 3 H), 3.78–3.74 (m, 1 H), 3.77 (s, 3 H), 3.38 (d, J = 1.7 Hz, 1 H), 2.29–2.22 (m, 1 H), 1.78–1.74 (m, 2 H), 1.58–1.52 (m, 1 H), 1.45 (dd, J = 13.8, 1.4 Hz, 1 H), 1.32 (dtd, J = 13.6, 4.8, 1.3 Hz, 1 H), 1.04 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 110.1, 76.9, 65.8, 64.7, 52.8, 43.7, 32.9, 32.0, 31.2, 28.7, 26.7; HRMS (ESI) calcd for $C_{12}H_{19}O_4^+$ [M + H^+ – H_2O] 227.1278, found: 227.1281 Pressing forward, to a suspension of NaH (0.200 g, 60% dispersion in mineral oil, 5.00 mmol, 5.0 equiv) in DMF (5 ml) at 0 °C was added a solution of ketal **S17** (0.244 g, 1.00 mmol, 1.0 equiv) in DMF (5 ml). The resultant mixture was then stirred for 30 min at 0 °C before 3-bromo-2-methylpropene (0.675 g, 5.00 mmol, 5.0 equiv) was added. The reaction contents were then warmed to 23 °C and stirred at that temperature for 2 h. Upon completion, the reaction contents were cooled to 0 °C, diluted with Et_2O (10 ml), and quenched by the slow addition of H_2O. The resultant mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was then extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with H_2O (3 × 10 mL) and brine (10 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 5:1) to provide ketal **S18** (0.298 g, 99% yield) as a colorless oil. **S18**: R_f = 0.28 (silica gel, hexanes: EtOAc = 5:1); IR (film) ν_{max} 2951, 2913, 1735, 1453, 1254, 1214, 1165, 1083, 1057, 900; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.03 (s, 1 H), 4.85 (s, 1 H), 3.96–3.92 (m, 1 H), 3.89–3.85 (m, 2 H), 3.81–3.78 (m, 3 H), 3.75 (s, 3 H), 2.26 (ddd, *J* = 15.1, 13.6, 3.8 Hz, 1 H), 2.01 (dt, *J* = 15.2, 3.8 Hz, 1 H), 1.85 (d, *J* = 13.8 Hz, 1 H), 1.75 (s, 3 H), 1.40 (dd, *J* = 13.8, 1.7 Hz, 1 H), 1.37 (td, *J* = 13.5, 3.5 Hz, 1 H), 1.23 (ttd, *J* = 13.5, 5.6, 1.8 Hz, 1 H), 1.04 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 141.5, 111.4, 110.0, 82.4, 67.5, 65.0, 64.9, 52.2, 43.6, 32.9, 32.6, 31.3, 26.5, 24.7, 19.7; HRMS (ESI) calcd for $C_{16}H_{27}O_5^+$ [M + H$^+$] 299.1853, found: 299.1870. Next, to a solution of ketal **S18** (0.298 g, 1.00 mmol, 1.0 equiv) in acetone (15 ml) at 23 °C was added HCl (10.0 mL, 1.0 M in H_2O, 10.0 mmol, 10 equiv). The resultant solution was heated to 60 °C for 12 h. Upon completion, the reaction contents were cooled to 23 °C, poured into a separatory funnel, and the resultant layers were separated. The aqueous layer was then extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1) to provide ketone **S19** (0.254 g, 99% yield) as a colorless oil. Ketone **S19:** R_f = 0.30 (silica gel, hexanes: EtOAc = 10:1); IR (film) ν_{max} 2957, 2928, 2870, 1751, 1724, 1456, 1370, 1298, 1256, 1160, 1127, 1080, 1054, 899; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.03 (s, 1 H), 4.89 (s, 1 H), 4.15 (d, *J* = 12.0 Hz, 1 H), 3.79 (s, 3 H), 3.78 (d, *J* = 12.0 Hz, 1 H), 2.54 (d, *J* = 13.2 Hz, 1 H), 2.34 (ddd, *J* = 14.8, 5.6, 4.2 Hz, 1 H), 2.17 (dd, *J* = 13.2, 1.6 Hz, 1 H), 2.12 (ddd, *J* = 14.8, 11.3, 4.3 Hz, 1 H), 1.83 (ddd, *J* = 13.9, 11.2, 4.3 Hz, 1 H), 1.77 (s, 3 H), 1.36 (dddd, *J* = 13.8, 5.5, 4.3, 1.6 Hz, 1 H), 1.04 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 170.6, 141.8, 111.9, 85.4, 69.7, 52.3, 52.2, 36.5, 33.8, 31.3, 30.1, 26.7, 19.6; HRMS (ESI) calcd for $C_{14}H_{23}O_4^+$ [M + H$^+$] 255.1591, found:

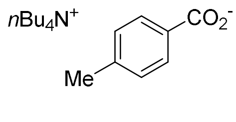
255.1599. Pressing forward, triflate **S20** was prepared as described above starting from **S19** (0.079 g, 0.31 mmol, 1.0 equiv) to afford triflate **S20** (0.083 g, 69% yield) as a yellow oil. **S20**: R_f = 0.32 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2961, 2870, 1759, 1661, 1454, 1419, 1366, 1211, 1145, 1093, 1056, 1007, 952, 901, 811; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (s, 1 H), 5.03 (s, 1 H), 4.88 (s, 1 H), 4.00 (dd, J = 28.3, 11.6 Hz, 2 H), 3.79 (s, 3 H), 2.25 (ddd, J = 13.8, 11.4, 3.4 Hz, 1 H), 2.10 (ddd, J = 13.8, 6.9, 3.4 Hz, 1 H), 1.78 (s, 3 H), 1.71 (ddd, J = 13.8, 11.2, 3.4 Hz, 1 H), 1.54 (ddd, J = 13.8, 6.9, 3.4 Hz, 1 H), 1.13 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 144.6, 141.9, 123.3, 119.6, 117.0, 112.0, 78.4, 69.6, 52.6, 33.6, 32.0, 30.0, 29.1, 27.6, 19.5; HRMS (ESI) calcd for $C_{15}H_{21}O_6F_3SNa^+$ [M + Na^+] 409.0903, found: 409.0907.

Preparation of nucleophilic salts

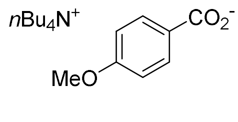
To a solution of corresponding acid or phenol (5.00 mmol) in anhydrous MeOH (5 mL) was added *n*-Bu_4NOH (5.05 mL, 1.0 M in MeOH, 5.05 mmol, 1.01 equiv) at 23 °C, and the resultant solution was stirred at 23 °C for 1 h. Upon completion, the resultant mixture was co-evaporated with benzene under an Ar atmosphere and the residue was dried over P_2O_5 on vacuum overnight. If the dried residue was a liquid, it was cooled to 0 °C to form a solid (>95% yield). The solid was then recrystallized from minimal EtOAc under Ar atmosphere, then the mother liquid was removed through a cannula, and the residue was dried on vacuum again to provide the anhydrous salt crystal (30–60% yield) used for subsequent reaction. The salts can be kept stable in dry box for months. [Note: the pentafluorophenoate salt (**S39**) was unstable and should be used immediately].



S21



S22



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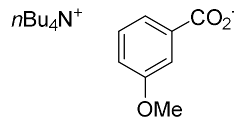

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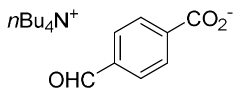

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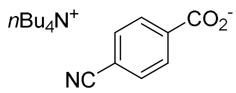
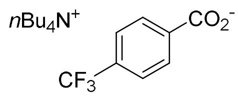
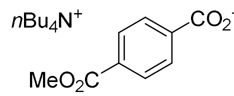


S26



S27



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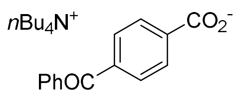

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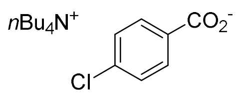

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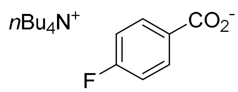
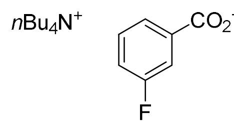
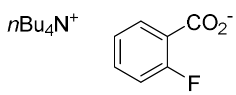


S31



S32



S33

nBu_4N^+ $PhthNCH_2CO_2^-$

S34

nBu_4N^+ $AdCH_2CO_2^-$

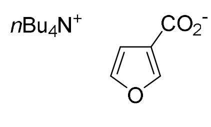
S35

nBu_4N^+ $AdCO_2^-$

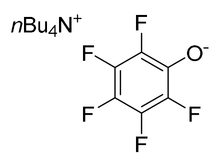
S36

n$Bu_4N^+PivO^-$

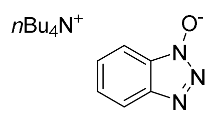
S37



S38



S39



S40

Tetrabutylammonium benzolate (S21). Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10–8.08 (m, 2 H), 7.30–7.28 (m, 3 H), 3.56–2.32 (m, 8 H), 1.66–1.59 (m, 8 H), 1.40 (sx, J = 7.4 Hz, 8 H), 0.96 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 141.4, 129.4, 128.2, 126.9, 58.5, 23.9, 19.6, 13.5.

Tetrabutylammonium 4-methylbenzoate (S22). Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2 H), 6.98 (d, J = 7.8 Hz, 2 H), 3.04–3.00 (m, 8 H), 2.23 (s, 3 H), 1.41–1.35 (m, 8 H), 1.27–1.19 (m, 8 H), 1.07 (sx, J = 7.4 Hz, 8 H), 0.83 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 138.3, 137.4, 129.4, 127.8, 58.0, 23.6, 21.1, 19.4, 13.5.

Tetrabutylammonium 4-methoxybenzoate (S23). Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.84 (m, 2 H), 6.61–6.58 (m, 2 H), 3.01–2.97 (m, 8 H), 1.36–1.29 (m, 8 H), 1.16 (sx, J = 7.4 Hz, 8 H), 0.74 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 160.0, 133.9, 130.9, 112.0, 58.3, 55.0, 23.8, 19.5, 13.5.

Tetrabutylammonium 3-methoxybenzoate (S24). White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.55 (m, 2 H), 7.09–7.06 (m, 1 H), 6.75–6.73 (m, 1 H), 3.71 (s, 3 H), 3.09–3.06 (m, 8 H), 1.46–1.39 (m, 8 H), 1.25 (sx, J = 7.3 Hz, 8 H), 0.83 (t, J = 7.2 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 158.9, 142.3, 128.0, 122.0, 115.3, 113.9, 58.4, 55.2, 23.8, 19.6, 13.6.

Tetrabutylammonium 4-formylbenzoate (S25). White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1 H); 8.12 (d, J = 8.0 Hz, 2 H), 7.73 (d, J = 8.0 Hz, 2 H), 3.20–3.17 (m, 8 H), 1.55–1.49 (m, 8 H), 1.30 (sx, J = 7.4 Hz, 8 H), 0.86 (t, J = 7.4 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 170.1, 146.6, 136.3, 129.8, 129.0, 58.6, 23.9, 19.6, 13.6.

Tetrabutylammonium 4-cyanobenzoate (S26). Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2 H), 7.36 (d, J = 8.4 Hz, 2 H), 3.09–3.06 (m, 8 H), 1.44–1.37 (m, 8 H), 1.18 (sx, J = 7.4 Hz, 8 H), 0.74 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 145.6, 131.0, 129.8, 119.6, 111.2, 58.5, 23.8, 19.5, 13.5.

Tetrabutylammonium 4-(trifluoromethyl)benzoate (S27). Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 7.9 Hz, 2 H), 7.52 (d, J = 8.1 Hz, 2 H), 3.32–3.30 (m, 8 H), 1.64–1.58 (m, 8 H), 1.41–1.34 (m, 8 H), 1.26 (sx, J = 7.4 Hz, 8 H), 0.94 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 144.7, 130.0, 129.8, 129.5, 125.6, 124.0, 123.9, 58.4, 23.8, 19.5, 13.4.

Tetrabutylammonium 4-(methoxycarbonyl)benzoate (S28). White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 2 H), 7.92 (d, J = 8.0 Hz, 2 H), 3.85 (s, 3 H), 3.26–3.22

(m, 8 H), 1.58–1.52 (m, 8 H), 1.34 (sx, J = 7.3 Hz, 8 H), 0.90 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 167.5, 145.6, 129.7, 129.2, 128.6, 58.7, 51.8, 24.0, 19.7, 13.6.

Tetrabutylammonium 4-benzoylbenzoate (S29). Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05–8.03 (m, 2 H), 7.63–7.61 (m, 2 H), 7.45–7.42 (m, 1 H), 7.34–7.31 (m, 2 H), 3.14–3.11 (m, 8 H), 1.49–1.42 (m, 8 H), 1.24 (sx, J = 7.4 Hz, 8 H), 0.80 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 170.2, 145.0, 137.8, 137.2, 132.2, 129.8, 129.2, 129.1, 128.1, 58.5, 23.8, 19.6, 13.6.

Tetrabutylammonium 4-chlorobenzoate (S30). Green solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2 H), 7.16–7.13 (m, 2 H), 3.15–3.12 (m, 8 H), 1.51–1.45 (m, 8 H), 1.28 (sx, J = 7.4 Hz, 8 H), 0.86 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 139.2, 134.4, 130.9, 127.2, 58.5, 23.9, 19.6, 13.6.

Tetrabutylammonium 4-fluorobenzoate (S31). White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00–7.97 (m, 2 H), 6.86–6.82 (m, 2 H), 3.13–3.10 (m, 8 H), 1.49–1.42 (m, 8 H), 1.27 (sx, J = 7.4 Hz, 8 H), 0.85 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 164.3, 162.4, 131.4, 131.3, 125.2, 113.6, 113.5, 58.8, 24.1, 19.7, 13.6.

Tetrabutylammonium 3-fluorobenzoate (S32). White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.73 (m, 1 H), 7.63–7.61 (m, 1 H), 7.13–7.09 (m, 1 H), 6.86–6.83 (m, 1 H), 3.14–3.10 (m, 8 H), 1.47–1.43 (m, 8 H), 1.26–1.21 (m, 8 H), 0.84–0.80 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 163.4, 161.4, 143.9, 128.3, 125.0, 116.0, 115.8, 115.1, 115.0, 58.5, 23.9, 19.6, 13.6.

Tetrabutylammonium 2-fluorobenzoate (S33). White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65–7.62 (m, 1 H), 7.06–7.02 (m, 1 H), 6.91–6.88 (m, 1 H), 6.82–6.78 (m, 1 H), 3.17–3.13 (m, 8 H), 1.49–1.45 (m, 8 H), 1.25 (sx, J = 7.4 Hz, 8 H), 0.83 (t, J = 7.4 Hz, 12 H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 169.0, 161.2, 159.2, 131.2, 131.1, 128.5, 123.0, 115.4, 115.2, 58.4, 23.9, 19.6, 13.6.

Tetrabutylammonium *N*-Phthaloylglycinate (S34). Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, J = 5.4, 3.0 Hz, 2 H), 7.62 (dd, J = 5.4, 3.0 Hz, 2 H), 4.21 (s, 2 H), 3.32–3.28 (m, 8 H), 1.66–1.60 (m, 8 H), 1.40 (sx, J = 7.4 Hz, 8 H), 0.97 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 168.6, 133.1, 122.7, 58.6, 42.5, 24.0, 19.7, 13.6.

Tetrabutylammonium 2-(adamantan-1-yl)acetate (S35). Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30–3.26 (m, 8 H), 1.87 (s, 2 H), 1.81 (s, 3 H), 1.63 (d, J = 2.2 Hz, 6 H), 1.59–1.53 (m, 14 H), 1.34 (sx, J = 7.4 Hz, 8 H), 0.90 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 58.7, 55.0, 43.0, 37.3, 32.1, 29.0, 24.1, 19.7, 13.7.

Tetrabutylammonium adamantane-1-carboxylate (S36). Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.28–3.26 (m, 8 H), 1.87–1.84 (m, 9 H), 1.63–1.55 (m, 14 H), 1.37 (sx, J = 7.4 Hz, 8 H), 0.94 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.2, 8.7, 49.8, 41.8, 40.7, 37.4, 29.0, 24.1, 19.7, 13.7.

Tetrabutylammonium pivalate (S37). Pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.24–3.20 (m, 8 H), 1.57–1.51 (m, 8 H), 1.33 (sx, J = 7.4 Hz, 8 H), 1.04 (s, 9 H), 0.89 (t, J = 7.4 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.4, 58.6, 39.5, 28.9, 24.0, 19.7, 13.7.

Tetrabutylammonium furan-3-carboxylate (S38). Brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63–7.62 (m, 1 H), 7.10 (t, J = 1.6 Hz, 1 H), 6.53–6.52 (m, 1 H), 3.09–3.06 (m, 8 H), 1.45–1.38 (m, 8 H), 1.22 (sx, J = 7.4 Hz, 8 H), 0.79 (t, J = 7.4 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8, 144.5, 141.5, 128.4, 111.6, 58.4, 23.8, 19.5, 13.5.

Tetrabutylammonium pentafluorophenonate (S39). Pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.13–3.09 (m, 8 H), 1.53–1.46 (m, 8 H), 1.28 (sx, J = 7.4 Hz, 8 H), 0.87 (t, J = 7.4 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 142.1, 140.3, 139.7, 137.8, 125.1, 58.4, 23.6, 19.4, 13.3.

Tetrabutylammonium 1H-benzo[d][1,2,3]triazol-1-olate (S40). Brown solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67–7.63 (m, 2 H), 7.07–7.01 (m, 2 H), 3.20–3.17 (m, 8 H), 1.55–1.49 (m, 8 H), 1.31 (sx, J = 7.4 Hz, 8 H), 0.89 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 127.8, 122.2, 121.1, 118.0, 112.4, 58.5, 23.8, 19.6, 13.6.

General procedure for the Pd-based cyclization

To a flame-dried seal tube was added $Pd(OAc)_2$ (2.2 mg, 0.010 mmol, 0.1 equiv), *t*-BuMephos (4.7 mg, 0.015 mmol, 0.15 equiv), and the tetrabutylammonium salt (0.30 mmol, 3.0 equiv). Next, a solution of the desired vinyl triflate (0.10 mmol, 1.0 equiv) in toluene (1 mL) was added at 23 °C. The resultant mixture was then stirred at 90 °C until palladium black completely crashed out, typically for 5 h. Upon completion, the reaction mixture was cooled to 23 °C and filtered through a pad of silica gel (EtOAc). The filtrate was concentrated, and the resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc) to provide the desired oxygenated product in the amount and form delineated below.

Product Acetate 29. Pale yellow oil, 28.2 mg, 96% yield; R_f = 0.26 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2930, 2863, 1739, 1729, 1597, 1564, 1448, 1385, 1274, 1218, 1150, 1034 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.27 (s, 1 H), 4.00 (dd, J = 27.2, 10.5 Hz, 2 H), 3.65 (s, 3 H), 2.26–2.22 (m, 1 H), 2.20–2.17 (m, 1 H), 2.06 (s, 3 H), 1.56–1.49 (m, 2 H), 1.47–1.40 (m, 2 H), 1.37–1.28 (m, 2 H), 1.09 (s, 3 H), 0.99 (s, 3 H), 0.92 (s, 3 H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 176.7, 144.1, 133.2, 72.4, 55.5, 51.8, 44.0, 35.8, 35.4, 32.5, 31.8, 30.5, 29.7, 29.4, 28.2, 27.4, 26.1, 21.0; HRMS (ESI) calcd for $C_{17}H_{27}O_4^+$ [M + H^+] 295.1904, found: 295.1907.

Product benzolate 30. Colorless oil, 28.4 mg, 80% yield; R_f = 0.26 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2864, 1722, 1451, 1362, 1274, 1205, 1176, 1151, 1114, 1070, 1026, 961, 711; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–8.05 (m, 2 H), 7.56 (tt, J = 7.4, 1.3 Hz, 1 H), 7.46–7.43 (m, 2 H), 5.36 (s, 1 H), 4.25 (dd, J = 16.5, 10.5 Hz, 2 H), 3.65 (s, 3 H), 2.30–2.27 (m, 1 H), 2.23–2.20 (m, 1 H), 1.71–1.58 (m, 2 H), 1.51–1.45 (m, 2 H), 1.40–1.25 (m, 2 H), 1.20 (s, 3 H), 1.00 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 166.7, 144.0, 133.4, 132.7, 130.7, 129.6, 128.3, 72.7, 55.5, 51.9, 44.4, 35.8, 35.6, 34.8, 32.6, 31.9, 30.5, 29.4, 26.2; HRMS (ESI) calcd for $C_{22}H_{28}O_4Na^+$ [M + Na^+] 379.1880, found: 379.1886.

Product 4-Me 31. White oil, 29.2 mg, 79% yield; R_f = 0.27 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2954, 2864, 1720, 1612, 1458, 1380, 1362, 1273, 1206, 1177, 1151, 1120, 1020, 961, 914, 841; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 2 H), 7.24 (d, J = 8.1 Hz, 2 H), 5.34 (s, 1 H), 4.22 (dd, J = 18.6, 10.6 Hz, 2 H), 3.65 (s, 3 H), 2.41 (s, 3 H), 2.30–2.26 (m, 1 H), 2.22–2.19 (m, 1 H), 1.70–1.57 (m, 2 H), 1.49–1.44 (m, 2 H), 1.40–1.27 (m, 2 H), 1.19 (s, 3 H), 1.00 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 166.8, 144.1, 143.3, 133.3, 129.6, 129.0, 128.0, 72.5, 55.5, 51.9, 44.4, 35.8, 35.6, 34.8, 32.6, 31.9, 30.5, 29.4, 26.2, 21.6; HRMS (ESI) calcd for $C_{23}H_{31}O_4^+$ [M + H^+] 371.2217, found: 371.2226.

Product 4-OMe 32. Pale yellow oil, 14.3 mg, 37% yield; R_f = 0.25 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2864, 1716, 1607, 1511, 1459, 1363, 1300, 1256, 1205, 1167, 1102, 1031, 847, 770 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.8 Hz, 2 H), 6.92 (d, J = 8.8 Hz, 2 H), 5.35 (s, 1 H), 4.21 (dd, J = 17.8, 10.5 Hz, 2 H), 3.86 (s, 3 H), 3.65 (s, 3 H), 2.30–2.26 (m, 1 H), 2.22–2.19 (m, 1 H), 1.70–1.57 (m, 2 H), 1.50–1.44 (m, 2 H), 1.40–1.27 (m, 2 H), 1.19 (s, 3 H), 1.00 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 166.4, 163.2, 144.1, 133.3, 131.5, 123.2, 113.6 ,72.4, 55.5, 55.4, 51.8, 44.4, 35.8, 35.6, 34.8, 32.6, 31.9, 30.5, 29.4, 26.2; HRMS (ESI) calcd for $C_{23}H_{31}O_5^+$ [M + H$^+$] 387.2166, found: 387.2179.

Product 3-OMe 33. Pale yellow oil, 23.2 mg, 60% yield; R_f = 0.44 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2864, 2838, 1721, 1587, 1457, 1321, 1278, 1151, 1104, 1046, 977, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 7.7, 1.0 Hz, 1 H), 7.58 (dd, *J* = 2.6, 1.5 Hz, 1 H), 7.35 (t, *J* = 7.9 Hz), 7.10 (ddd, *J* = 8.2, 2.6, 0.8 Hz, 1 H), 5.36 (s, 1 H), 4.24 (dd, *J* = 19.1, 10.5 Hz, 2 H), 3.86 (s, 3 H), 3.65 (s, 3 H), 2.30–2.26 (m, 1 H), 2.23–2.20 (m, 1 H), 1.70–1.58 (m, 2 H), 1.51–1.44 (m, 2 H), 1.40–1.29 (m, 2 H), 1.19 (s, 3 H), 1.00 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 166.5, 159.6, 144.0, 133.4, 132.0, 129.3, 121.2, 119.2, 114.2, 72.8, 55.5, 55.4, 51.9, 44.4, 35.8, 35.6, 34.8, 32.6, 31.9, 30.5, 29.4, 26.2; HRMS (ESI) calcd for $C_{23}H_{31}O_5^+$ [M + H$^+$] 387.2166, found: 387.2173.

Product 4-CHO 34. Colorless oil, 34.1 mg, 89% yield; R_f = 0.28 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2864, 1723, 1709, 1459, 1275, 1202, 1116, 1016, 759 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.1 (s, 1 H), 8.21 (d, *J* = 8.2 Hz, 2 H), 7.96 (d, *J* = 8.3 Hz, 2 H), 5.36 (s, 1 H), 4.28 (dd, *J* = 12.8, 10.6 Hz, 2 H), 3.65 (s, 3 H), 2.31–2.27 (m, 1 H), 2.23–2.20 (m, 1 H), 1.68–1.59 (m, 2 H), 1.52–1.45 (m, 2 H), 1.40–1.25 (m, 2 H), 1.21 (s, 3 H), 0.99 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 176.6, 165.6, 143.9, 139.1, 135.7, 133.5, 130.1, 129.5, 73.2, 55.6, 51.9, 44.3, 35.8, 35.5, 34.7, 32.6, 31.8, 30.5, 29.3, 26.2; HRMS (ESI) calcd for $C_{23}H_{29}O_5^+$ [M + H$^+$] 385.2010, found: 385.2009.

Product 4-CN 35. Yellow oil, 29.7 mg, 78% yield; R_f = 0.19 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2864, 2231, 1724, 1458, 1275, 1206, 1152, 1118, 1018, 956, 861, 767 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15–8.14 (m, 2 H), 7.76–7.74 (m, 2 H), 5.34 (s, 1 H), 4.28

(dd, J = 12.0, 10.6 Hz, 2 H), 3.65 (s, 3 H), 2.30–2.27 (m, 1 H), 2.23–2.20 (m, 1 H), 1.70–1.57 (m, 2 H), 1.52–1.45 (m, 2 H), 1.40–1.25 (m, 2 H), 1.19 (s, 3 H), 0.99 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 165.0, 143.8, 134.5, 133.6, 132.2, 130.0, 118.0, 116.3, 73.4, 55.6, 51.9, 44.3, 35.8, 35.5, 34.7, 32.6, 31.8, 30.5, 29.3, 26.2; HRMS (ESI) calcd for $C_{23}H_{28}O_4N^+$ [M + H^+] 382.2013, found: 382.2017.

Product 4-CF_3 36. Colorless oil, 41.1 mg, 97% yield; R_f = 0.50 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2956, 2865, 1726, 1412, 1357, 1281, 1132, 1066, 1018, 862 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.1 Hz, 2 H), 7.71 (d, J = 8.2 Hz, 2 H), 5.36 (s, 1 H), 4.28 (dd, J = 15.2 Hz, 10.6 Hz, 2 H), 3.66 (s, 3 H), 2.31–2.27 (m, 1 H), 2.23–2.20 (m, 1 H), 1.71–1.58 (m, 2 H), 1.52–1.46 (m, 2 H), 1.37–1.25 (m, 2 H), 1.20 (s, 3 H), 1.00 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 165.4, 143.9, 134.2, 133.9, 133.5, 139.9, 125.39, 125.36, 73.1, 55.6, 51.9, 44.3, 35.8, 35.5, 34.7, 32.6, 30.5, 29.3, 26.2; HRMS (ESI) calcd for $C_{23}H_{28}O_4F_3^+$ [M + H^+] 425.1934, found: 425.1942.

Product 4-COOMe 37. Yellow solid, 30.6 mg, 74% yield; R_f = 0.37 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2954, 2864, 1724, 1458, 1272, 1117, 1019, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 4 H), 5.35 (s, 1 H), 4.26 (dd, J = 13.7, 10.5 Hz, 2 H), 3.94 (s, 3 H), 3.64 (s, 3 H), 2.30–2.26 (m, 1 H), 2.22–2.19 (m, 1 H), 1.70–1.58 (m, 2 H), 1.51–1.48 (m, 2 H), 1.39–1.24 (m, 2 H), 1.20 (s, 3 H), 0.98 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 166.3, 165.8, 143.9, 134.5, 133.8, 133.5, 129.54, 129.51, 73.1, 55.6, 52.4, 52.0, 44.3, 35.8, 35.5, 34.7, 32.6, 31.8, 30.5, 29.3, 26.2; HRMS (ESI) calcd for $C_{24}H_{31}O_6^+$ [M + H^+] 415.2115, found: 415.2113.

Product 4-COPh 38. Yellow oil, 42.3 mg, 92% yield; R_f = 0.37 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2864, 1710, 1663, 1449, 1297, 1206, 1116, 926, 714 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17–8.15 (m, 2 H), 7.85–7.84 (m, 2 H), 7.81–7.79 (m, 2 H), 7.63–7.60 (m, 1 H), 7.51–7.48 (m, 2 H), 5.37 (s, 1 H), 4.29 (dd, J = 14.7, 10.5 Hz, 2 H), 3.66 (s, 3 H), 2.31–2.27 (m, 1 H), 2.23–2.20 (m, 1 H), 1.71–1.59 (m, 2 H), 1.52–1.46 (m, 2 H), 1.40–1.29 (m, 2 H), 1.22 (s, 3 H), 1.00 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 165.9, 143.9, 141.2, 137.0, 133.8, 133.5, 132.9, 130.1, 129.8, 129.4, 128.5, 73.1, 55.6, 51.9, 44.4, 35.8, 35.4, 34.7, 32.2, 31.8, 30.5, 29.4, 26.2; HRMS (ESI) calcd for $C_{29}H_{32}O_5Na^+$ [M + Na$^+$] 483.2142, found: 483.2146.

Product 4-Cl 39. Yellow oil, 27.4 mg, 70% yield; R_f = 0.54 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2956, 2864, 124, 1595, 1488, 1459, 1400, 1381, 1363, 1272, 1205, 1151, 1116, 1015, 960, 850, 760 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 2 H), 7.41 (d, J = 8.5 Hz, 2 H), 5.34 (s, 1 H), 4.24 (dd, J = 14.1, 10.6 Hz, 2 H), 3.65 (s, 3 H), 2.30–2.26 (m, 1 H), 2.22–2.19 (m, 1 H), 1.69–1.58 (m, 2 H), 1.51–1.44 (m, 2 H), 1.40–1.28 (m, 2 H), 1.19 (s, 3 H),0.99 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 165.8, 144.0, 139.2, 133.4, 130.9, 129.6, 129.2, 128.7, 128.3, 72.8, 55.5, 51.9, 44.3, 35.8, 35.5, 34.7, 32.6, 31.8, 30.5, 29.3, 26.2; HRMS (ESI) calcd for $C_{22}H_{28}O_4Cl^+$ [M + H$^+$] 391.1671, found: 391.1675.

Product 4-F 40. Pale yellow oil, 33.7 mg, 90% yield; R_f = 0.51 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2864, 1724, 1604, 1508, 1458, 1274, 1152, 1116, 854, 767 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08–8.05 (m, 2 H), 7.13–7.09 (m, 2 H), 5.34 (s, 1 H), 4.23 (dd, J = 13.7, 10.6 Hz, 2 H), 3.65 (s, 3 H), 2.30–2.26 (m, 1 H), 2.22–2.19 (m, 1 H), 1.70–1.57 (m, 2 H), 1.51–1.44 (m, 2 H), 1.40–1.25 (m, 2 H), 1.19 (s, 3 H), 0.99 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 166.7, 165.7, 164.7, 144.0, 133.4, 132.1, 132.0, 127.0, 126.9, 115.5, 115.3, 72.8, 55.5, 51.9, 44.4, 35.8, 35.5, 34.7, 32.6, 31.8, 30.5, 29.4, 26.2; HRMS (ESI) calcd for $C_{22}H_{28}O_4F^+$ [M + H$^+$] 375.1966, found: 375.1971.

Product 3-F 41. Colorless oil, 29.9 mg, 80% yield; R_f = 0.49 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2957, 2864, 1724, 1596, 1561, 1448, 1388, 1276, 1261, 1204, 1151, 1094, 858 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85–7.84 (m, 1 H), 7.74–7.71 (m, 1 H), 7.44–7.40 (m, 1 H), 7.27–7.23 (m, 1 H), 5.35 (s, 1 H), 4.25 (dd, J = 15.8, 10.5 Hz, 2 H), 3.65 (s, 3 H), 2.30–2.26 (m, 1 H), 2.23–2.20 (m, 1 H), 1.70–1.58 (m, 2 H), 1.51–1.45 (m, 2 H), 1.40–1.25 (m, 2 H), 1.19 (s, 3 H), 1.00 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 165.5, 161.6, 143.9, 133.5, 130.0, 129.9, 125.3, 125.2, 119.9, 119.7, 116.5, 116.3, 73.0, 55.5, 51.9, 44.3, 35.8, 35.5, 34.7, 32.6, 31.8, 30.5, 29.3, 26.2; HRMS (ESI) calcd for $C_{22}H_{28}O_4F^+$ [M + H$^+$] 375.1966, found: 375.1971.

Product 2-F 42. Colorless oil, 32.6 mg, 87% yield; R_f = 0.40 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2864, 1724, 1613, 1486, 1458, 1363, 1297, 1153, 1128, 1033, 960, 758 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (td, J = 7.6, 1.8 Hz, 1 H), 7.52–7.48 (m, 1 H), 7.19 (dt, J = 7.8, 0.5 Hz, 1 H), 7.12 (dd, J = 10.6, 8.7 Hz, 1 H), 5.36 (s, 1 H), 4.25 (dd, J = 12.8, 10.6 Hz, 2 H), 3.64 (s, 3 H), 2.28–2.24 (m, 1 H), 2.22–2.19 (m, 1 H), 1.70–1.57 (m, 2 H), 1.50–1.43 (m, 2 H), 1.39–1.24 (m, 2 H), 1.19 (s, 3 H), 0.98 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 164.7, 163.0, 160.9, 143.9, 134.3, 134.2, 133.3, 132.2, 123.9, 123.8, 117.0, 116.8, 73.2, 55.6, 51.9, 44.2, 35.8, 35.6, 34.8, 32.6, 31.8, 30.5, 29.4, 26.2; HRMS (ESI) calcd for $C_{22}H_{28}O_4F^+$ [M + H$^+$] 375.1966, found: 375.1959.

Product glycine 44. Colorless oil, 29.8 mg, 68% yield; R_f = 0.16 (silica gel, hexanes:EtOAc, 5:1); IR (film) ν_{max} 2925, 2857, 1778, 1749, 1724, 1457, 1417, 1388, 1206, 955, 731, 714; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, J = 5.5, 3.0 Hz, 2 H), 7.75 (dd, J = 5.4, 3.1 Hz, 2 H), 5.20 (s, 1 H), 4.46 (d, J = 4.1 Hz, 2 H), 4.09 (s, 1 H), 3.64 (s, 3 H), 2.20–2.16 (m, 2 H), 1.52–1.47 (m, 1H), 1.45–1.37 (m, 3 H), 1.34–1.29 (m, 2 H), 1.04 (s, 3 H), 0.96 (s, 3 H), 0.87 (s, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 167.4, 167.2, 143.8, 134.2, 133.4, 132.1, 123.6, 73.4, 55.5, 51.9, 44.0, 39.0, 35.7, 35.3, 34.8, 32.5, 31.8, 30.4, 29.7, 29.3, 25.9; HRMS (ESI) calcd for $C_{25}H_{29}O_6NNa^+$ [M + Na^+] 462.1887, found: 462.1889.

Product CH_2Ad 45. Colorless oil, 37.3 mg, 87% yield; R_f = 0.34 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2953, 2904, 2848, 1730, 1457, 1256, 1201, 1136, 1101, 1003 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 1 H), 3.96 (dd, J = 15.3, 10.6 Hz, 2 H), 3.65 (s, 3 H), 2.26–2.22 (m, 1 H), 2.19–2.17 (m, 1 H), 2.08 (s, 2 H), 1.96 (s, 3 H), 1.71–1.62 (m, 12 H), 1.55–1.49 (m, 2 H), 1.47–1.39 (m, 2 H), 1.37–1.27 (m, 2 H), 1.10 (s, 3 H), 0.98 (s, 3 H), 0.92 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 172.1, 144.2, 133.1, 72.1, 55.5, 51.8, 49.3, 43.9, 42.5, 36.8, 35.8, 35.7, 34.8, 32.7, 32.6, 31.9, 30.5, 29.4; HRMS (ESI) calcd for $C_{27}H_{41}O_4^+$ [M + H^+] 429.2999, found: 429.2989.

Product Ad 46. Colorless oil, 38.1 mg, 92% yield; R_f = 0.65 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2907, 2854, 1727, 1453, 1234, 1150, 1078, 991, 963, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.30 (s, 1 H), 3.93 (dd, J = 12.6, 10.6 Hz, 2 H), 3.64 (s, 3 H), 2.26–2.22 (m, 1 H), 2.19–2.16 (m, 1 H), 2.01 (s, 3 H), 1.91–1.90 (m, 6 H), 1.74–1.66 (m, 6 H), 1.54–1.47 (m, 2 H), 1.45–1.38 (m, 2 H), 1.37–1.24 (m, 2 H), 1.10 (s, 3 H), 0.99 (s, 3 H), 0.92 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 176.8, 144.0, 133.2, 71.8, 55.4, 51.9, 44.2, 40.9, 39.0, 36.6, 35.8, 35.5, 34.7, 32.6, 31.8, 30.6, 29.4, 28.0, 26.0; HRMS calcd for $C_{26}H_{39}O_4^+$ [M + H^+] 415.2843, found: 415.2847.

Product pivalate 47. Pale yellow oil, 25.5 mg, 76% yield; R_f = 0.37 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2957, 2866, 1728, 1597, 1563, 1481, 1448, 1396, 1286, 1217, 1150, 858, 798 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.29 (s, 1 H), 3.94 (dd, J = 12.2, 10.5 Hz, 2 H), 3.64 (s, 3 H), 2.25–2.22 (m, 1 H), 2.19–2.16 (m, 1 H), 1.54–1.48 (m, 2 H), 1.46–1.39 (m, 2 H), 1.37–1.26 (m, 2 H), 1.20 (s, 9 H), 1.10 (s, 3 H), 0.98 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 178.6, 176.8, 144.0, 133.2, 76.8, 72.1, 55.5, 51.9, 44.2, 35.7, 35.5, 34.7, 32.6, 31.8, 30.5, 29.4, 27.3, 26.0; HRMS (ESI) calcd for $C_{20}H_{33}O_4^+$ [M + H^+] 337.2373, found: 337.2377.

Product furan 48. Yellow oil, 20.6 mg, 60% yield; R_f = 0.32 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2955, 2864, 1725, 1579, 1506, 1461, 1304, 1205, 1161, 1076, 980, 874 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, J = 1.4, 0.7 Hz, 1 H), 7.43 (t, J = 1.7 Hz, 1 H), 6.75 (dd, J = 1.8, 0.7 Hz, 1 H), 5.32 (s, 1 H), 4.18 (dd, J = 15.2, 10.6 Hz, 2 H), 3.65 (s, 3 H), 2.28–2.25 (m, 1 H), 2.22–2.19 (m, 1 H), 1.67–1.52 (m, 2 H), 1.49–1.42 (m, 2 H), 1.39–1.28 (m, 2 H), 1.15 (s, 3 H), 1.00 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 163.2, 147.5, 144.0, 143.6, 133.3, 119.8, 109.8, 72.1, 55.5, 51.9, 44.3, 35.8, 35.4, 34.7, 32.6, 31.8, 30.5, 29.4, 26.2; HRMS (ESI) calcd for $C_{20}H_{27}O_5^+$ [M + H^+] 347.1853, found: 347.1854.

Product flourophenol 50. Pale yellow oil, 32.6 mg, 78% yield; R_f = 0.75 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2957, 2865, 1728, 1518, 1463, 1381, 1205, 1151, 1027, 996 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (s, 1 H), 4.08 (d, J = 8.6 Hz, 1 H). 4.00 (d, J = 8.6 Hz, 1 H), 3.64 (s, 3 H), 2.27–2.23 (m, 1 H), 2.22–2.19 (m, 1 H), 1.69–1.59 (m, 2 H), 1.50–1.44 (m, 2 H), 1.39–1.27 (m, 2 H), 1.26 (s, 3 H), 0.98 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 143.7, 142.8, 140.7, 139.1, 138.0, 137.1, 136.0, 134.5, 133.6, 83.8, 55.6, 51.8, 45.4, 35.8, 35.3, 34.8, 32.6, 31.6, 30.4, 29.3, 25.5; HRMS (ESI) calcd for $C_{21}H_{24}O_3F_5^+$ [M + H^+] 419.1640, found: 419.1649.

Product 52. Pale yellow oil, 3.3 mg, 9% yield; R_f = 0.16 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2956, 2864, 1725, 1462, 1376, 1358, 1263, 1239, 1206 1153, 1088, 952, 744; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 1 H), 7.63 (d, J = 8.3 Hz, 1 H), 7.49 (ddd, J = 8.4, 7.0, 0.7 Hz, 1 H), 7.37 (ddd, J = 8.4, 6.9, 0.9 Hz, 1 H), 5.46 (s, 1 H), 4.44 (dd, J = 43.2, 7.8 Hz, 2 H), 3.60 (s, 1 H), 2.33–2.30 (m, 1 H), 2.26–2.23 (m, 1 H), 1.79–1.69 (m, 2 H), 1.56–1.49 (m, 2 H), 1.43–1.30 (m, 2 H), 1.41 (s, 3 H), 1.03 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 143.7, 134.1, 127.7, 127.2, 124.5, 108.9, 88.5, 55.7, 52.0, 44.3, 35.7, 35.4, 34.7, 32.8, 31.6, 30.5, 29.3, 26.0, 20.3, 13.7; HRMS (ESI) calcd for $C_{21}H_{28}O_3N_3^+$ [M + H$^+$] 370.2125, found: 370.2113.

Product 53. Colorless oil, 24.0 mg, 96% yield; R_f = 0.64 (silica gel, hexanes:EtOAc, 10:1); $[\alpha]_D^{20}$ = +44.0° (*c* = 0.55 in $CHCl_3$); IR (film) ν_{max} 2955, 2868, 2865, 1744, 1455, 1383, 1370, 1242, 1034 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (s, 1 H), 3.84 (d, *J* = 10.4 Hz, 1 H), 3.72 (d, *J* = 10.4 Hz, 1 H), 3.71 (s, 3 H), 2.20–2.13 (m, 1 H), 2.12–2.08 (m, 1 H), 2.07 (s, 3 H), 1.88–1.84 (m, 1 H), 1.74–1.68 (m, 1 H), 1.56 (d, *J* = 13.2 Hz, 1 H), 1.40 (d, *J* = 13.2 Hz, 1 H), 1.20–1.13 (m, 1 H), 1.16 (s, 3 H), 1.06–1.00 (m, 1 H), 1.03 (s, 3 H), 0.95 (d, *J* = 7.0 Hz, 3 H), 0.79 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 148.2, 125.7, 73.5, 52.1, 51.0, 42.5, 39.4, 32.0, 31.2, 28.2, 24.4, 23.8, 23.0, 22.3, 21.0; HRMS (CI) calcd for $C_{16}H_{27}O_2^+$ [M + H$^+$] 251.2006, found: 251.2002.

Product 54. Yellow oil, 24.2 mg, 86% yield; R_f = 0.26 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2954, 2866, 1742, 1459, 1384, 1370, 1247, 1152, 1034, 848 cm^{-1} ;^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (s, 1 H), 4.00 (dd, *J* = 20.2, 10.5 Hz, 2 H), 3.69 (s, 3 H), 2.27–2.23 (m, 1 H), 2.16 (d, *J* = 12.9 Hz, 1 H), 2.06 (s, 3 H), 1.90 (td, *J* = 12.9, 6.9 Hz, 1 H), 1.72 (d, *J* = 13.0 Hz, 1 H), 1.68 (ddd, *J* = 13.3, 7.5, 1.0 Hz, 1H), 1.44 (td, *J* = 12.4, 7.5 Hz, 1 H), 1.14 (s, 3 H), 1.10 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 171.2, 10, 134.9, 70.9, 66.2, 52.2, 51.9, 50.9, 40.1, 39.6, 35.7, 30.8, 27.5, 25.9, 21.0; HRMS (CI) calcd for $C_{16}H_{25}O_4^+$ [M + H$^+$] 281.1753, found: 281.1757.

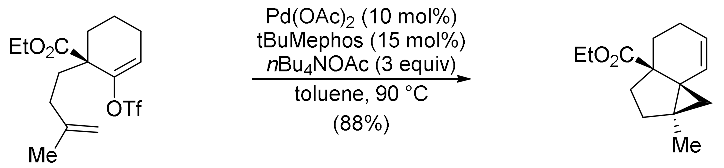
Product 55. Yellow oil, 26.4 mg, 73% yield; R_f = 0.29 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2959, 2870, 1742, 1714, 1462, 1384, 1372, 1245, 1036 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.29 (s, 1 H), 3.99 (s, 2 H), 2.73 (d, *J* = 14.2 Hz, 1 H), 2.13 (d, *J* = 14.2 Hz, 1 H), 2.08 (s, 3 H), 1.90 (td, *J* = 12.9, 6.8 Hz, 1 H), 1.72 (td, *J* = 12.6, 7.1 Hz, 1 H), 1.62–1.59 (m, 1 H), 1.53–1.51 (m, 1 H), 1.31 (s, 3 H), 1.17 (s, 3 H), 1.06 (s, 3 H), 1.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 213.8, 171.1, 148.6, 130.6, 71.9, 54.2, 49.2, 44.4, 38.8, 33.4, 31.0, 30.9, 30.8, 26.4, 26.0, 20.9; HRMS (ESI) calcd for $C_{16}H_{25}O_3^+$ [M + H$^+$] 265.1798, found: 265.1792.

Product O-tethered 56. Yellow oil, 24.5 mg, 83% yield; R_f = 0.18 (silica gel, hexanes: EtOAc = 10:1); IR (film) ν_{max} ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (s, 1H), 3.94 (dd, *J* = 35.7, 10.9 Hz, 2 H), 3.74 (dd, *J* = 54.8, 9.4 Hz, 2 H), 3.73 (s, 3 H), 2.19–2.15 (m, 1 H), 2.04 (s, 3 H), 1.64–1.59 (m, 1 H), 1.58–1.48 (m, 2 H), 1.20 (s, 3 H), 1.06 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 171.0, 140.0, 133.8, 84.8, 76.8, 69.6, 52.3, 44.3, 33.0, 32.9, 30.3, 30.2, 29.1, 23.8, 20.9; HRMS (ESI) calcd for $C_{16}H_{24}O_5Na^+$ [M + Na$^+$] 319.1516, found: 319.1523

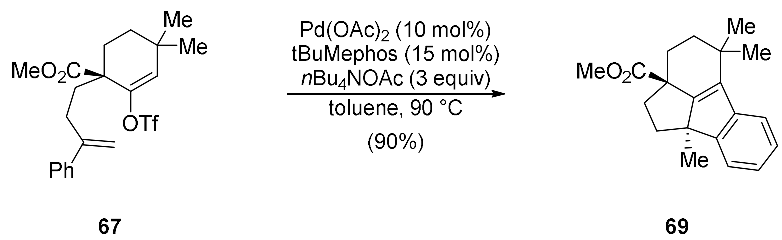
Product OBn 57. Pale yellow oil, 27.2 mg, 68% yield; R_f = 0.31 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2953, 2862, 1727, 1454, 1377, 1360, 1244, 1212, 1151, 1100, 1035, 731, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.27 (m, 5 H), 5.39 (s, 1 H), 4.50 (s, 2 H), 4.14 (dd, *J* = 21.0, 10.5 Hz, 2 H), 3.66 (s, 3 H), 3.45 (d, *J* = 8.8 Hz, 1 H), 3.23 (d, *J* = 8.8 Hz, 1 H), 2.22–2.16 (m, 2 H), 2.00 (s, 3 H), 1.90–1.86 (m, 1 H), 1.47–1.31 (m, 5 H), 0.99 (s, 3 H), 0.92 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 171.0, 140.5, 138.8, 134.0, 128.3, 127.4, 127.2, 74.0, 73.2, 67.6, 55.5, 51.9, 48.1, 36.1, 34.9, 32.6, 31.5, 30.7, 30.5, 29.5, 21.0; HRMS (ESI) calcd for $C_{24}H_{32}O_5Na^+$ [M + Na$^+$] 423.2142, found: 423.2117.

Product 6-member ring 58. Pale yellow oil, 7.4 mg, 24% yield; R_f = 0.18 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2951, 2863, 1726, 1453, 1386, 1371, 1241, 1154, 1058, 1031, 1000, 976 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (s, 1 H), 3.75 (s, 2 H), 3.63 (s, 3 H), 2.44–2.41 (m, 1 H), 2.03 (s, 3 H), 1.78–1.75 (m, 1 H), 1.68–1.64 (m, 1 H), 1.57–1.47 (m, 4 H), 1.33–1.30 (m, 1 H), 1.24–1.18 (m, 1 H), 1.13–1.06 (m, 1 H), 1.09 (s, 3 H), 1.00 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 171.2, 136.9, 136.4, 69.6, 51.8, 46.6, 39.0, 37.3, 35.5, 35.4, 32.9, 32.5, 30.8, 29.1, 25.8, 20.9, 19.2; HRMS (ESI) calcd for $C_{18}H_{29}O_4^+$ [M + H^+] 309.2060, found: 309.2051.

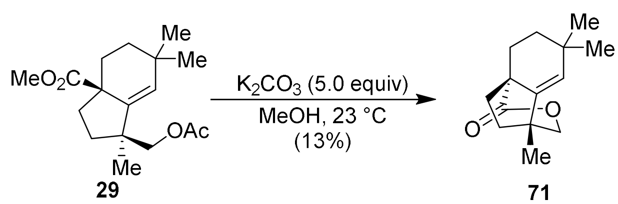


65 **66**

Undesired product 66. Triflate 65 (163 mg, 43% overall yield) was prepared as described above procedure toward **S9** from **ethyl 2-oxocyclohexane carboxylate** (340 mg, 2.0 mmol, 1.0 equiv) and **4-iodo-2-methyl-but-1-ene** (431 mg, 2.2 mmol, 1.1 equiv). **65**: colorless oil. R_f = 0.64 (silica gel, hexanes:EtOAc, 5:1); IR (film) ν_{max} 2941, 1734, 1416, 1248, 1210, 1145, 1032, 909 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (dd, *J* = 5.1 Hz, 3.1 Hz, 1 H), 4.72 (s, 1H), 4.69 (s, 1H), 4.25–4.17 (m, 2H), 2.31–2.25 (m, 2H), 2.22–2.16 (m, 1H), 2.04–1.95 (m, 3 H), 1.89–1.83 (m, 1H), 1.72 (s, 3 H), 1.67–1.57 (m, 3 H), 1.29 (t, *J* = 7.14 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 148.3, 144.8, 120.1, 110.6, 61.7, 50.2, 33.5, 33.3, 32.0, 24.4, 22.4, 18.8, 14.0; HRMS (ESI) calcd for $C_{15}H_{22}OSF_3^+$ [M + H^+] 371.1135, found 371.1147. **Undesired product 66** (19.4 mg, 88% yield) was prepared as described above from **65** (37.0 mg, 0.1 mmol, 1.0 equiv). **66:** colorless oil. R_f = 0.57 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2921, 2860, 1722, 1445, 1264, 1218, 1195, 1170, 1076, 1028, 681 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75–5.72 (m, 1 H), 5.27–5.24 (m, 1 H), 4.16–4.07 (m, 2 H), 2.21–2.13 (m, 1 H), 2.10–1.99 (m, 2 H), 1.63–1.51 (m, 3 H), 1.22 (t, *J* = 7.1 Hz), 1.19 (d, *J* = 5.5 Hz), 1.12 (s, 3 H), 0.54 (d, *J* = 5.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 128.9, 126.6, 125.1, 60.0, 52.5, 32.3, 32.3, 30.8, 27.0, 23.7, 22.2, 19.6, 14.3; HRMS (ESI) $C_{14}H_{21}O_2^+$ [M + H^+] 221.1536, found 221.1534.



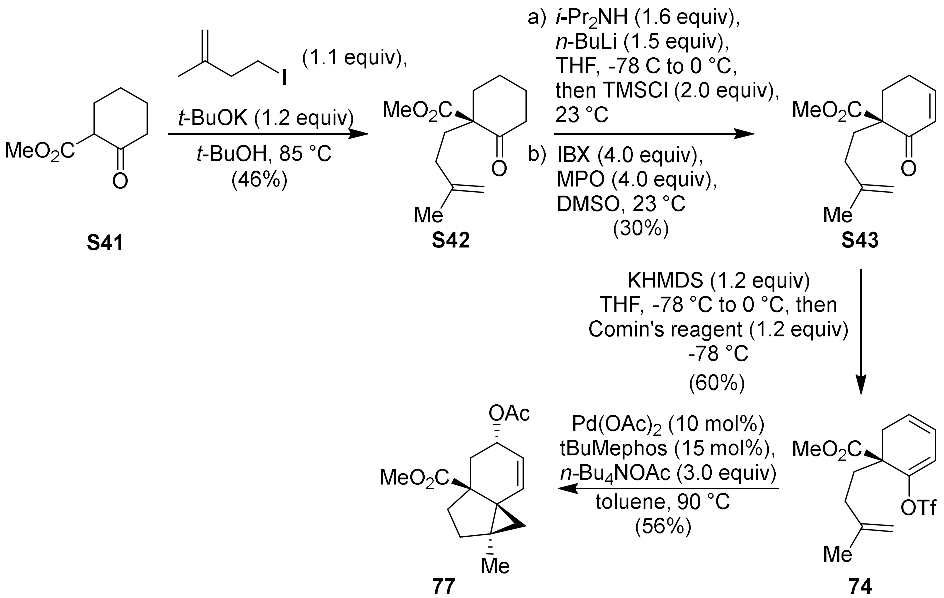
Undesired product 69. Triflate 67 (94.2 mg, 11% overall yield) was prepared as described above procedure toward **28** from **S1** (1.84g, 10.0 mmol, 1.0 equiv) and **phenyl vinyl ketone** (1.98 g, 15.0 mmol, 1.5 equiv). **67:** colorless oil. R_f = 0.58 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.37 (m, 2 H), 7.34–7.31 (m, 2 H), 7.29–7.26 (m, 1 H), 5.64 (s, 1 H), 5.30 (s, 1 H), 5.09 (s, 1 H), 3.72 (s, 3 H), 2.54–2.45 (m, 2 H), 2.23 (dt, J = 14.0 Hz, 4.2 Hz, 1 H), 2.02–1.96 (m, 1 H), 1.90–1.83 (m, 2 H), 1.51–1.49 (m, 2 H), 1.11 (s, 3 H), 1.07 (s, 3H). **Undesired product 69** (26.6 mg, 90% yield) was prepared as described above from **67** (44.6 mg, 0.1 mmol, 1.0 equiv). **69:** colorless oil. R_f = 0.66 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, DMSO-d6) δ 7.36 (dd, J = 13.2 Hz, 7.5 Hz, 2H), 7.21 (td, J = 7.6 Hz, 0.9 Hz, 1 H), 7.11 (td, J = 7.6 Hz, 0.9 Hz, 1 H), 3.66 (s, 3 H), 2.71–2.68 (m, 1 H), 2.22 (dd, J = 13.6 Hz, 8.4 Hz, 1 H), 2.14 (dt, J = 13.2 Hz, 2.7 Hz, 1 H), 1.35–1.30 (m , 1 H), 1.33 (s, 3 H), 1.29 (s, 3 H), 1.15 (s , 3H), 0.87 (dt, J = 8.7 Hz, 11.6 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d6) δ 176.7, 156.2, 153.4, 143.0, 141.7, 126.9, 124.8, 123.1, 122.1, 56.3, 52.4, 47.6, 42.4, 38.7, 33.8, 33.0, 32.1, 29.2, 25.4, 19.7.



Bicycle 71. To a solution of cyclized product **29** (0.294 g, 1.00 mmol, 1.0 equiv) in MeOH (10 mL) was added K_2CO_3 (0.690 g, 5.00 mmol, 5.0 equiv). The resultant mixture was then stirred

for 12 h at 23 °C. The reaction contents were diluted with EtOAc (10 mL) and quenched by the addition of saturated aqueous NH_4Cl (10 mL). The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was then extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with H_2O (10 mL) and brine (10 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:Et_2O, 20:1→10:1) to provide bicycle **71** (28.4 mg, 13% yield) as a yellow solid. **71**: R_f = 0.66 (silica gel, hexanes:EtOAc, 5:1); IR (film) ν_{max} 2955, 2870, 1743, 1597, 1563, 1467, 1395, 1351, 1219, 1126, 1104, 1054, 1034, 992, 880, 864 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 1 H), 4.02 (d, *J* = 9.6 Hz, 1 H), 3.83 (dd, *J* = 9.6 Hz, 1.7 Hz, 1 H), 2.60–2.53 (m, 1 H), 2.21 (ddd, *J* = 13.1, 9.6, 4.4 Hz, 1 H), 1.95 (ddd, *J* = 14.7, 9.5, 5.5 Hz, 1 H), 1.74 (tdd, *J* = 12.6, 4.3, 2.0 Hz, 1 H), 1.61 (td, *J* = 18.1 Hz, 5.4 Hz, 1 H), 1.48–1.42 (m, 1 H), 1.40–1.32 (m, 2 H), 1.13 (s, 3 H), 0.99 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 139.5, 126.6, 82.2, 50.7, 42.2, 36.8, 35.8, 35.0, 31.6, 30.6, 28.1, 26.2, 16.6; HRMS (ESI) calcd for $C_{14}H_{21}O_2^+$ [M + H^+] 221.1536, found: 221.1539. **See *2.8* for 2D NMR.**

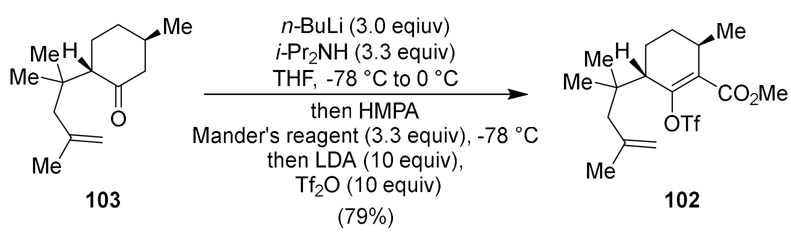
D-labeled 71 was prepared by the described procedure toward **S9**. The D-labeled side chain **(E)-4-iodo-2-methylbut-1-ene-1-*d*** is prepared according to Prof. Brown's method[22]. **D-labeled 71** : ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 1 H), 3.81 (s, 1 H), 2.62–2.54 (m, 1 H), 2.21 (ddd, *J* = 13.1, 9.6, 4.4 Hz, 1 H), 1.95 (ddd, *J* = 14.7, 9.5, 5.5 Hz, 1 H), 1.75 (tdd, *J* = 12.6, 4.3, 2.0 Hz, 1 H), 1.61 (td, *J* = 18.1 Hz, 5.4 Hz, 1 H), 1.49–1.42 (m, 1 H), 1.40–1.35 (m, 2 H), 1.13 (s, 3 H), 0.99 (s, 3 H), 0.98 (s, 3 H).



Cyclopropane 77. Ketone **S42** (0.103 g, 46% yield) was prepared as a colorless oil from commercial **methyl 2-oxocyclohexane-1-carboxylate (S41)** (0.156 g, 1.00 mmol, 1.0 equiv) and **4-iodo-2-methylbut-1-ene** (0.216 g, 1.10 mmol, 1.1 equiv) by the procedure described above. **S42**: R_f = 0.29 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2949, 2865, 1714, 1650, 1450, 1215, 1135, 889 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (s, 1 H), 4.68 (s, 1 H), 3.73 (s, 1 H), 2.54–2.51 (m, 1 H), 2.46–2.43 (m, 1 H), 2.05–2.00 (m, 2 H)1.96–1.84 (m, 1 H), 1.78–1.65 (m, 3 H), 1.72 (s, 3 H) 1.50–1.44 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7, 127.5, 145.3, 110.0, 60.1, 52.2, 41.1, 36.0, 32.9, 32.3, 27.6, 22.54, 22.52; HRMS (ESI) calcd for $C_{13}H_{21}O_3^+$ [M + H$^+$] 225.1485, found: 225.1472. Next, to a solution of *i*-Pr_2NH (0.440 mL, 3.20 mmol, 1.6 equiv) in THF (5 mL) at 0 °C was added *n*-BuLi (1.20 mL, 2.5 M in hexanes, 3.00 mmol, 1.5 equiv), The resultant solution was then stirred for 15 min at 0 °C. The reaction contents were then cooled to –78 °C and a solution of ketone **S42** (0.448 g, 2.00 mmol, 1.0 equiv) in THF (5 mL) was added dropwise. After warming to 0 °C and stirring at that temperature for 90 min, the solution was recooled to –78 °C and TMSCl (0.510 mL, 4.00 mmol, 2.0 equiv) was added. The resultant solution was slowly warmed to 23 °C and stirred for 12 h. Upon completion, the reaction contents

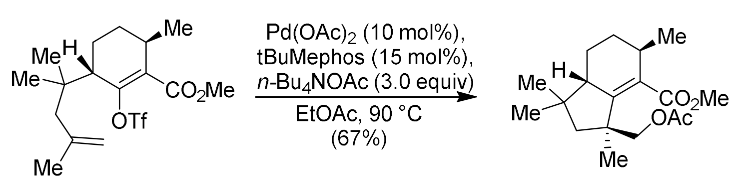
were quenched by the addition of saturated aqueous NH_4Cl (10 mL). The mixture was then poured into a separatory funnel and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layers were then washed with brine (10 mL) before being dried (Na_2SO_4), filtered, and concentrated to provide the desired crude TMS enol ether intermediate (2.00 mmol assumed) directly used for next step without any further purification. Passing forward, IBX (2.24 g, 8.00 mmol, 4.0 equiv) and MPO (1.00 g, 5.00 mmol, 2.5 equiv) was dissolved in DMSO (20 mL). This solution was then added to a solution of the crude enol ether (2.00 mmol assumed, 1.0 equiv) in DMSO (2.5 mL) at 23 °C. The resultant mixture was stirred at 23 °C for 6 h. Upon completion, the reaction contents were diluted with Et_2O (10 mL) and quenched by the addition of saturated aqueous $NaHCO_3$ (10 mL). The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was then extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL), H_2O (10 mL) and brine (10 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 20:1→10:1) to provide enone **S43** (0.242 g, 30% yield from ketone **S42**)[9] as a pale-yellow oil. **S43**: R_f = 0.46 (silica gel, hexanes:EtOAc, 5:1); IR (film) ν_{max} 2953, 1723, 1686, 1449, 1386, 1245, 1205, 1081, 889 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.91–6.88 (m, 1 H), 6.01 (dt, J = 10.1, 1.7 Hz, 1 H), 4.69 (s, 1 H), 4.68 (s, 1 H), 3.68 (s, 3 H), 2.54–2.46 (m, 2 H), 2.37–2.30 (m, 1 H), 2.09–2.03 (m, 1 H), 1.99–1.94 (m, 1 H), 1.87–1.81 (m, 1 H), 1.72 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2, 172.0, 149.5, 145.2, 129.1, 110.2, 56.8, 52.4, 32.6, 31.9, 29.9, 23.6, 22.5; HRMS (ESI) calcd for $C_{13}H_{19}O_3^+$ [M + H^+] 223.1329, found: 223.1333. Next, triflate **74** was prepared as described above starting from **S43** (0.111 g, 5.00 mmol, 1.0 equiv) to afford triflate **74** (0.104 g, 60% yield) as a colorless oil. **74**: R_f = 0.62 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2956, 1714, 1654, 1416, 1213, 1143, 1060, 891, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05–6.04 (m, 1 H), 5.87–5.82 (m, 1 H), 4.73 (s, 1 H), 4.71 (s, 1 H), 3.74 (s, 3 H), 3.07 (dd, *J* = 17.7, 4.2 Hz, 1 H), 2.53–2.49 (m, 1 H), 2.04–1.98 (m, 3 H), 1.94–1.88 (m, 1 H), 1.72 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 148.1, 144.5, 126.1, 120.8, 115.35, 115.34, 115.33, 110.6, 52.6, 49.5, 33.7, 32.7, 32.5, 22.4; HRMS (ESI) calcd for $C_{14}H_{18}O_5F_3S^+$ [M + H$^+$] 355.0822, found: 355.0822. Finally, **77** was prepared following the general Pd-cyclization procesure defined above from **74** (35.4 mg, 0.1 mmol) to provide **77** (14.9 mg, 56% yield) as a pale-yellow oil. **77**: R_f = 0.29 (silica gel, hexanes:EtOAc, 10:1); IR (film) ν_{max} 2952, 2926, 2863, 1738, 1442, 1370, 1240, 1152, 1113, 1055, 1023 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67–5.65 (m, 1 H), 5.59–5.55 (m, 1 H), 5.36 (dd, *J* = 10.0, 1.5 Hz, 1 H), 3.69 (s, 3H), 2.35–2.32 (m, 1 H), 2.06 (s, 3 H), 1.92–1.82 (m, 2 H), 1.71–1.62 (m, 2 H), 1.53–1.49 (m, 1 H), 1.29 (d, *J* = 5.8 Hz, 1 H), 1.16 (s, 3 H), 0.62 (d, *J* = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 170.6, 132.2, 126.7, 69.6, 54.2, 51.9, 35.82, 35.76, 32.6, 31.7, 31.3, 22.3, 21.3, 19.6; HRMS (ESI) calcd for $C_{15}H_{20}O_4Na^+$ [M + Na$^+$] 287.1254, found: 287.1246.

Synthetic application



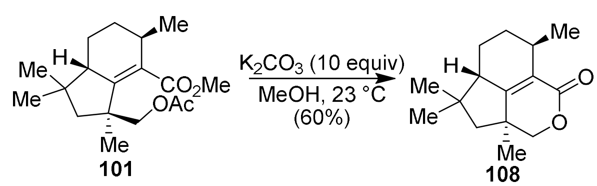
Triflate 102. To a solution of *i*-Pr_2NH (0.440 mL, 3.20 mmol, 3.2 equiv) in THF (3 mL) at 0 °C was added *n*-BuLi (1.20 mL, 2.5 M in hexanes, 3.00 mmol, 3.0 equiv) and the resultant solution was stirred at 0 °C for 15 min. The reaction contents were then cooled to –78 °C and a solution of **103** (0.208 g, 1.00 mmol, 1.0 equiv) in THF (5 mL) was added dropwise over the course of 5 min. The reaction mixture was then warmed to 0 °C and kept at that temperature for 90 min

before being cooled to –78 °C. HMPA (0.50 mL) and a solution of Mander's reagent (0.280 g, 3.30 mmol, 3.3 equiv) in THF (2 mL) were then added sequentially. After stirring the resultant mixture at –78 °C for 1 h, LDA (prepared from *n*-BuLi and *i*-Pr_2NH as described, 10.0 mL, 1.0 M in THF, 10.0 mmol, 10 equiv) was added at –78 °C and was followed by the addition of Tf_2O (1.68 mL, 10.0 mmol, 10 equiv). The reaction contents were stirred at –78 °C for 4 h before being quenched by the addition of saturated aqueous $NaHCO_3$ (10 mL). The mixture was then warmed to 23 °C, H_2O (10 mL) was added to dissolve any remaining solids, and the reaction contents was poured into a separatory funnel and the layers were separated. The aqueous layer was then extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (100 mL), H_2O (10 mL), and brine (10 mL), dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (Et_3N-buffered silica gel, hexanes) to provide triflate **102** (0.314 g, 79% yield) as a colorless oil. **102**: R_f = 0.65 (silica gel, hexanes:EtOAc, 15:1); $[\alpha]_D^{20}$ = +94.0° (*c* = 0.53, $CHCl_3$); IR (film) ν_{max} 2968, 1731, 1421, 1245, 1203, 1142, 1065, 1048, 961, 891, 810 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.91 (s, 1 H), 4.68 (s, 1 H), 3.80 (s, 3 H), 2.75–2.72 (m, 1 H), 2.41–2.39 (m, 1 H), 2.16 (d, *J* = 13.1 Hz, 1 H), 1.98 (d, *J* = 13.1 Hz, 1 H), 1.91–1.87 (m, 3 H), 1.78 (s, 3 H), 1.38–1.33 (m, 1 H), 1.18 (d, *J* = 7.0 Hz, 3 H), 1.05 (s, 3 H), 1.01 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 151.4, 142.5, 131.9, 122.1, 119.6, 117.0, 115.3, 114.5, 52.0, 48.2, 45.9, 39.0, 31.5, 27.5, 27.2, 26.6, 25.5, 22.3, 20.9; HRMS (ESI) calcd for $C_{17}H_{26}O_5F_3S^+$ [M + H^+] 399.1448, found: 399.1436.



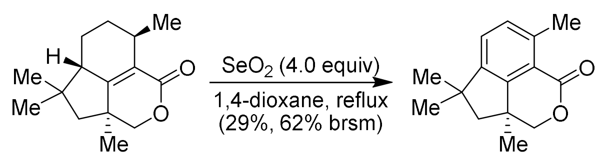
102 **101**

Acetate 101. To a flame-dried sealed tube was added $Pd(OAc)_2$ (0.112 g, 0.500 mmol, 10 mol %), *t*-BuMephos (0.234 g, 0.75 mmol, 15 mol %), and *n*-Bu_4NOAc (4.52 g, 15.0 mmol, 3.0 equiv). A solution of triflate **102** (1.99 g, 5.00 mmol, 1.0 equiv) in EtOAc (50 mL) was then added at 23 °C. The mixture was heated to 90 °C and stirred at this temperature for 12 h. Upon completion, the reaction contents were cooled to 23 °C and filtered through a pad of silica gel (EtOAc). The filtrate was concentrated, and the resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 30:1) to provide acetate **101** (1.03 g, 67% yield) as a pale-yellow oil. **101**: R_f = 0.48 (silica gel, hexanes:EtOAc, 10:1); $[\alpha]_D^{20}$ = +23.0° (*c* = 1.0 in $CHCl_3$); IR (film) ν_{max} 2932, 2865, 1742, 1726, 1373, 1226, 1061, 1030 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.24 (d, *J* = 10.3 Hz, 1 H), 4.05 (d, *J* = 10.3 Hz, 1 H), 3.71 (s, 3 H), 2.56–2.48 (m, 1 H), 2.15–2.11 (m, 1 H), 2.06 (s, 3 H), 1.93–1.88 (m, 1 H), 1.73 (d, *J* = 13.3 Hz, 1 H), 1.71–1.66 (m, 1 H), 1.40 (d, *J* = 13.2 Hz, 1 H), 1.25–1.06 (m, 2 H), 1.11 (s, 3 H), 1.00 (s, 3 H), 0.91 (d, *J* = 6.8 Hz, 3 H), 0.78 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 170.8, 149.8, 131.5, 73.1, 53.7, 53.1, 51.1, 44.1, 39.0, 33.1, 31.4, 27.9, 23.7, 22.9, 22.1, 21.0, 20.1; HRMS (ESI) calcd for $C_{18}H_{29}O_4^+$ [M + H$^+$] 309.2060, found: 309.2063.



Lactone 108. To a solution of acetate **101** (0.616 g, 2.00 mmol, 1.0 equiv) in MeOH (20 mL) at 23 °C was added K_2CO_3 (2.76 g, 20 mmol, 10 equiv), and the resultant mixture was stirred at 23 °C for 10 h. Upon completion, the reaction contents were diluted with EtOAc (10 mL) and quenched by the addition of saturated aqueous NH_4Cl (10 mL). The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was then extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with H_2O (2 × 10 mL) and brine (10 mL)

before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 20:1→10:1) to provide lactone **108** (0.281 g, 60% yield) as a colorless solid. **108**: R_f = 0.58 (silica gel, hexanes:EtOAc, 5:1); $[\alpha]_D^{20}$ = –53.0° (*c* = 0.30 in $CHCl_3$); IR (film) ν_{max} 2957, 2869, 1714, 1462, 1388, 1368, 1256, 1209, 1165, 1070, 1049, 1000, 974, 788 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.08 (d, *J* = 10.4 Hz, 1 H), 4.01 (d, *J* = 10.4 Hz, 1 H), 2.78–2.72 (m, 1 H), 2.45 (ddd, *J* = 10.3, 6.8, 2.3 Hz, 1 H), 1.68–1.58 (m, 1 H), 1.56 (d, *J* = 14.1 Hz, 1 H), 1.50, (d, *J* = 13.9 Hz, 1 H), 1.39–1.31 (m, 1 H), 1.24 (s, 3 H), 1.16 (s, 3 H), 1.02, (d, *J* = 7.0 Hz, 1 H), 0.83 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 124.6, 50.4, 49.1, 41.6, 38.4, 29.3, 29.2, 25.9, 25.1, 25.0, 19.3, 16.1; HRMS (ESI) calcd for $C_{15}H_{23}O_2^+$ [M + H^+] 235.1693, found: 235.1700.



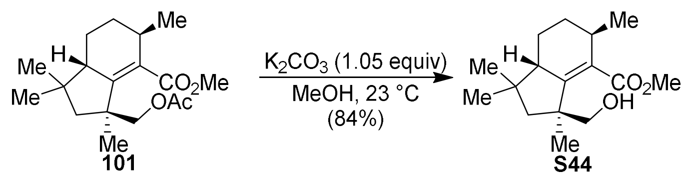
108
81

10-oxodehydrodihydrobotrydial (81). Lactone **108** (46.8 mg, 0.200 mmol, 1.0 equiv) in 1,4-dioxane (2 mL) was treated with SeO_2 (88.8 mg, 0.800 mmol, 4.0 equiv). The resultant mixture was then heated at 110 °C for 12 h. Upon completion, the resultant mixture was cooled to 23 °C and filtered through a pad of silica gel (EtOAc). The filtrate was then concentrated, and the resultant residue was purified by column chromatography (hexanes: EtOAc = 100:1→50:1) to provide recovered starting material (24.9 mg) along with 10-oxodehydrodihydrobotrydial (**81**, 13.3 mg, 29% yield, 62% yield brsm) as a white solid. **81:** R_f = 0.68 (silica gel, hexanes: EtOAc = 5:1); $[\alpha]_D^{20}$ = –95.0° (*c* = 1.0 in $CHCl_3$); lit: $[\alpha]_D^{28}$ = –166.5° (*c* = 1.0 in $CHCl_3$)[28a]; as such the rotation data showed this should be the enantiomer of natural **81** ($[\alpha]_D^{28}$ = +87° (*c* = 3.9 mg/ml in $CHCl_3$)[28b]); IR (film) ν_{max} 2961, 2927, 2867, 1759, 1584, 1484, 1245, 1067, 829, 801, 532 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.7 Hz, 1 H), 7.15 (d, *J* = 7.7 Hz, 1 H), 4.36 (d, *J* = 10.0

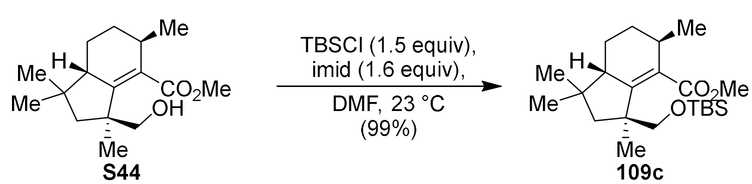
Hz, 1 H), 4.13 (d, J = 10.0 Hz, 1 H), 2.62 (s, 3 H), 1.98 (d, J = 12.8 Hz, 1 H), 1.86 (d, J = 12.9 Hz, 1 H), 1.51 (s, 3 H), 1.45 (s, 3 H), 1.32 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 151.4, 147.0, 139.6, 131.7, 127.2, 119.6, 79.2, 52.1, 45.1, 40.8, 30.8, 30.7, 24.7, 20.2; HRMS (ESI) calcd for $C_{15}H_{19}O_2^+$ [M + H$^+$] 231.1380, found: 231.1388.

Table 2-S1: Comparison of literature and obtained spectral values for *10-oxodehydrodihydrobotrydial* (**58**)[28b]

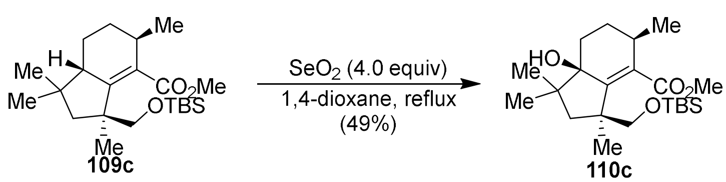
^{1}H NMR in $CDCl_3$	
Natural (Collado, 400 MHz)	Synthetic (This work, 500 MHz)
7.20 (d, J = 7.8 Hz, 1 H)	7.21 (d, J = 7.7 Hz, 1 H)
7.14 (d, J = 7.8 Hz, 1 H)	7.15 (d, J = 7.7 Hz, 1 H)
4.35 (d, J = 10.1 Hz, 1 H)	4.36 (d, J = 10.0 Hz, 1 H)
4.12 (d, J = 10.1 Hz, 1 H)	4.13 (d, J = 10.0 Hz, 1 H)
2.61 (s, 3 H)	2.62 (s, 3 H)
1.96 (d, J = 13.0 Hz, 1 H)	1.98 (d, J = 13.0 Hz, 1 H)
1.84 (d, J = 13.0 Hz, 1 H)	1.86 (d, J = 13.0 Hz, 1 H)
1.50 (s, 3 H)	1.50 (s, 3 H)
1.44 (s, 3 H)	1.45 (s, 3 H)
1.31 (s, 3 H)	1.32 (s, 3 H)
^{13}C NMR in $CDCl_3$	
Natural (Collado, 100 MHz)	Synthetic (This work, 125 MHz)
164.0	164.0
151.4	151.4
147.0	147.0
139.6	139.6
131.7	131.7
127.3	127.2
119.6	119.6
79.2	79.2
52.1	52.1
45.1	45.1
40.4	40.5
30.7	30.8
30.7	30.7
24.7	24.7
20.3	20.2



Alcohol S44. To a solution of acetate **101** (1.23 g, 4.00 mmol, 1.0 equiv) in MeOH (40 mL) at 23 °C was added K_2CO_3 (0.580 g, 4.20 mmol, 1.05 equiv), and the resultant mixture was stirred at 23 °C for 10 h. Upon completion, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl (30 mL), poured into a separatory funnel, and the resultant layers were separated. The aqueous layer was then extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with H_2O (30 mL) and brine (30 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→5:1) to provide alcohol **S44** (0.894 g, 84% yield) as a white solid. **S44**: R_f = 0.33 (silica gel, hexanes: EtOAc = 5:1); $[\alpha]_D^{20}$ = –19.0° (*c* = 0.53 in $CHCl_3$); IR (film) ν_{max} 3438, 2921, 2864, 1718, 1656, 1446, 1366, 1261, 1225, 1060, 981, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 3.75 (s, 3 H), 3.45–3.40 (m, 2 H), 3.21 (dd, *J* = 6.6, 5.8 Hz, 1 H), 2.56–2.48 (m, 1 H), 2.14–2.10 (m, 1 H), 1.93–1.88 (m, 1 H), 1.72–1.68 (m, 1 H), 1.59 (d, *J* = 13.0 Hz, 1 H), 1.40 (d, *J* = 12.9 Hz, 1 H), 1.25–1.08 (m, 2 H), 1.10 (s, 3 H), 1.01 (s, 3 H), 0.93 (d, *J* = 6.8 Hz, 3 H), 0.79 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 151.2, 131.2, 71.7, 54.1, 53.0, 51.6, 46.6, 38.5, 33.2, 31.4, 27.8, 23.9, 22.4, 22.1, 20.2; HRMS (ESI) calcd for $C_{16}H_{27}O_3^+$ [M + H^+] 267.1955, found: 267.1965.

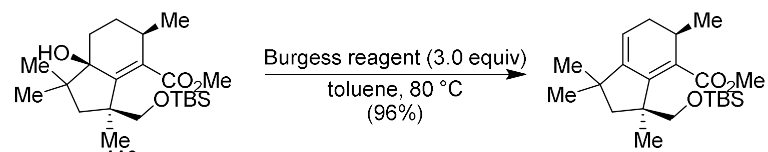


TBS-Protected Ether 109c. To a solution of alcohol **S46** (0.266 g, 1.00 mmol, 1.0 equiv) in DMF (10 mL) at 23 °C was sequentially added imidazole (0.109 g, 1.60 mmol, 1.6 equiv) and TBSCl (0.225 g, 1.50 mmol, 1.5 equiv). The resultant solution was stirred at 23 °C for 12 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (10 mL), poured into a separatory funnel, and the resultant layers were separated. The aqueous layer was then extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with H_2O (4 × 10 mL) and brine (10 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 20:1) to provide **109c** (0.380 g, 99% yield). **109c**: R_f = 0.39 (silica gel, hexanes:EtOAc, 20:1); $[\alpha]_D^{20}$ = +30.0° (*c* = 1.0 in $CHCl_3$); IR (film) ν_{max} 2930, 2857, 1727, 1432, 1385, 1254, 1226, 1212, 1060, 837 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.80 (d, *J* = 8.7 Hz, 1 H), 3.70 (s, 3 H), 3.39 (d, *J* = 8.7 Hz, 1 H), 2.54–2.48 (m, 1 H), 2.18–2.14 (m, 1 H), 2.04 (d, *J* = 12.7 Hz, 1 H), 1.90–1.86 (m, 1 H), 1.68–1.63 (m, 1 H), 1.23 (d, *J* = 12.8 Hz, 1 H), 1.17–1.08 (m, 2 H), 1.001 (s, 3 H), 0.995 (s, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H), 0.88 (s, 9 H), 0.77 (s, 3 H), 0.04 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 152.2, 129.4, 71.6, 53.9, 52.7, 50.9, 46.3, 38.9, 33.1, 27.9, 24.0, 22.8, 22.3, 20.1, 18.2, –5.3, –5.4; HRMS (ESI) calcd for $C_{22}H_{41}O_3Si^+$ [M + H$^+$] 381.2819, found: 381.2826.



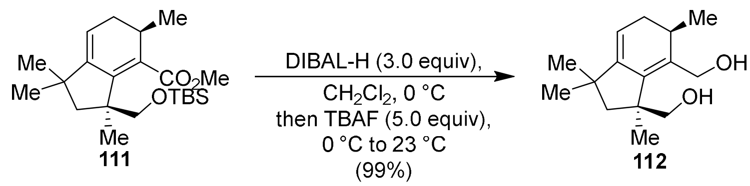
Allylic alcohol 110c. To a solution of **109c** (0.076 g, 0.200 mmol, 1.0 equiv) in 1,4-dioxane (2 mL) at 23 °C was added SeO_2 (0.089 g, 0.800 mmol, 4.0 equiv). The resultant mixture was then heated at 110 °C for 12 h. Upon completion, the resultant mixture was cooled to 23 °C and filtered through a pad of silica gel (EtOAc). The filtrate was then concentrated, and the resultant residue was purified by column chromatography (hexanes: EtOAc = 100:1→50:1) to provide allylic alcohol **110c** (0.039 g, 49% yield) as a colorless oil. **110c**: R_f = 0.53 (silica gel, hexanes:EtOAc, 10:1); $[\alpha]_D^{20}$ = +10.0° (*c* = 0.21 in $CHCl_3$); IR (film) ν_{max} 3426, 2951, 2931, 2860, 1720, 1471, 1251, 1215, 1065, 782 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.59 (d, *J* = 2.0 Hz, 1 H), 4.02 (d, *J* =

8.5 Hz, 1 H), 3.72 (s, 3 H), 3.21 (d, J = 8.5 Hz, 1 H), 2.49–2.44 (m, 1 H), 2.20 (d, J = 12.8 Hz, 1 H), 1.73−1.54 (m, 2 H), 1.39–1.34 (m, 1 H), 1.15 (d, J = 12.8 Hz, 1 H), 1.023 (s, 3 H), 1.017 (s, 3 H), 0.93 (d, J = 6.9 Hz, 1 H), 0.92 (s, 3 H), 0.85 (s, 3 H), 0.113 (s, 3 H), 0.111(s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 148.8, 134.2, 79.6, 71.8, 51.1, 49.7, 45.2, 43.4, 33.7, 27.0, 26.9, 26.7, 25.9, 23.3, 21.6, 19.8, 18.4, –5.5, –5.6; HRMS (ESI) calcd for $C_{22}H_{39}O_3Si^+$ [M + H^+ – H_2O] 379.2663, found: 379.2665.

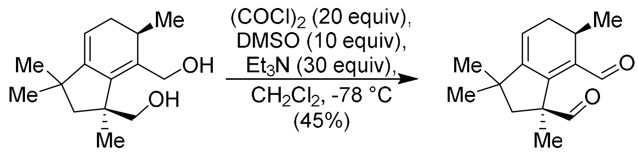


Diene 111. To a solution of allylic alcohol **110c** (0.070 g, 0.180 mmol, 1.0 equiv) in toluene (8 mL) at 23 °C was added the Burgess reagent (0.120 g, 0.500 mmol, 3.0 equiv). The resultant flask was then immersed in a pre-heated oil bath at 80 °C and stirring of the mixture was continued at 80 °C for 12 h. Upon completion, the reaction contents were cooled to 23 °C, diluted with Et_2O (10 mL), and poured into a separatory funnel. This organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL). The organic phase was then dried (Na_2SO_4) and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1) to provide diene **111** (0.064 g, 96% yield) as a pale-yellow oil. **111**: R_f = 0.62 (silica gel, hexanes: EtOAc = 10:1); $[\alpha]_D^{20}$ = +28° (c = 1.0 in $CHCl_3$); IR (film) ν_{max} 2955, 2928, 2859, 1711, 1463, 1432, 1230, 1096, 852, 836, 775 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.59 (dd, J = 5.6, 3.5 Hz, 1 H), 3.78 (d, J = 9.4 Hz, 1 H), 3.74 (s, 3 H), 3.58 (d, J = 9.4 Hz, 1 H), 2.67–2.62 (m, 1 H), 2.42–2.36 (m, 1 H), 2.20 (d, J = 13.2 Hz, 1 H), 2.06–2.00 (m, 1 H), 1.40 (d, J = 13.2 Hz, 1 H), 1.24 (s, 3 H), 1.16 (s, 3 H), 1.11 (s, 3 H), 1.04 (d, J = 6.9 Hz, 1 H), 0.04 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 151.4, 151.0, 126.0, 118.5, 67.7, 52.3, 50.69,

47.9, 38.5, 31.4, 31.3, 31.0, 30.2, 25.8, 24.1, 18.4, –5.5, –5.6; HRMS (ESI) calcd for $C_{22}H_{39}O_3Si^+$ [M + H$^+$] 379.2663, found: 379.2669.



Botrydienol (112). To a solution of diene **111** (37.8 mg, 0.100 mmol, 1.0 equiv) in CH_2Cl_2 (0.7 mL) at 0 °C was added DIBAL-H (0.3 mL, 1.0 M in CH_2Cl_2, 0.300 mmol, 3.0 equiv) dropwise over the course of 10 min. The resultant solution was then stirred at 0 °C for 1 h. Next, TBAF (0.500 mL, 1.0 M in THF, 0.500 mmol, 5.0 equiv) was added dropwise over the course of 10 min. The resultant mixture was then warmed to 23 °C and stirred at that temperature for an additional 3 h. Upon completion, the reaction contents were quenched by the slow addition of solid Na_2SO_4•$10H_2O$ at 0 °C until no further gas was released. The mixture was then filtered through Celite, and the residual solids were washed with EtOAc (5 × 1 mL). The combined organic layers were washed with saturated H_2O (3 × 5 mL) and brine (5 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 5:1→1:1) to provide botrydienol (**112**, 23.6 mg, 99% yield) as a white solid. **112**: R_f = 0.21 (silica gel, hexanes: EtOAc, 3:1); $[\alpha]_D^{20}$ = +53.0° (c = 0.80 in $CHCl_3$); IR (film) ν_{max} 3337, 2955, 2924, 2862, 1597, 1563, 1449, 1395, 1219, 1119, 1034 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (dd, J = 5.3, 3.1 Hz, 1 H), 4.35 (d, J = 11.3 Hz, 1 H), 4.20 (d, J = 11.3 Hz, 1 H), 3.65 (d, J = 11.1 Hz, 1 H), 3.53 (d, J = 11.1 Hz, 1 H), 2.42–2.30 (m, 2 H), 2.02 (dt, J = 17.1, 4.5 Hz, 1 H), 1.95 (d, J = 13.2 Hz, 1 H), 1.46 (d, J = 13.2 Hz, 1 H), 1.25 (s, 3 H), 1.15 (s, 3 H), 1.10 (s, 3 H), 1.08 (d, J = 6.8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 141.1, 134.2, 114.1, 70.4, 61.9, 53.1, 47.0, 39.7, 32.6, 31.7, 31.0, 30.7, 25.8, 18.8; HRMS (CI) calcd for $C_{15}H_{23}O^+$ [M + H$^+$ – H_2O] 219.1743, found: 219.1746.



112 79

Botrydienal (79). To a solution of $(COCl)_2$ (0.110 mL, 1.28 mmol, 20 equiv) in CH_2Cl_2 (0.5 mL) at –78 °C was added DMSO (0.045 mL, 0.64 mmol, 10 equiv) dropwise over the course of 5 min. After stirring the resultant solution at –78 °C for 15 min, a solution of botrydienol (**112**, 15.0 mg, 0.064 mmol, 1.0 equiv) in CH_2Cl_2 (0.5 mL) was added dropwise over the course of 10 min. The resultant solution was then stirred at –78 °C for 3 h, at which time Et_3N (0.26 mL, 1.9 mmol, 30 equiv) was added the reaction contents were stirred at –78 °C for another 30 min. Upon completion, the reaction contents were quenched by the addition of H_2O (2 mL), warmed to 23 °C, poured into a separatory funnel, and the resultant layers were separated. The aqueous layer was then extracted with CH_2Cl_2 (2 × 2 mL). The combined organic layers were washed with H_2O (3 mL) before being dried (Na_2SO_4), filtered, and concentrated. The resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→5:1) to provide botrydienal (**79**, 8.2 mg, 55% yield) as a white solid. **79**: R_f = 0.55 (silica gel, hexanes:EtOAc, 5:1); $[\alpha]_D^{20}$ = +167.0° (c = 0.18 in n-hexane); lit: $[\alpha]_D^{30}$ = +190° (c = 0.18 in n-hexane)[26]; IR (film) ν_{max} 2959, 2926, 2853, 2819, 2807, 2712, 1723, 1658, 1640, 1570, 1453, 1143, 924, 797, 404 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1 H), 9.67 (s, 1 H), 5.88 (dd, J = 6.3, 2.8 Hz, 1 H), 3.00–2.97 (m, 1 H), 2.45 (ddd, J = 18.4, 8.7, 6.7 Hz, 1 H); 2.23 (d, J = 13.6 Hz, 1H), 2.20 (dd, J = 19.2, 6.3 Hz, 1 H); 1.63 (d, J = 13.7 Hz, 1 H); 1.53 (s, 3 H), 1.26 (s, 3 H), 1.06 (s, 3 H), 0.92 (d, J = 7.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 189.8, 155.2, 149.5, 136.0, 123.7, 56.5, 50.6, 40.5, 30.62, 30.61, 28.8, 25.3, 24.2, 18.3; HRMS (ESI) calcd for $C_{15}H_{21}O_2^+$ [M + H^+] 233.1536, found: 233.1542.

Table 2-S2: Comparison of literature and obtained spectral values for *botrydienal* (**79**)[26]

^{1}H NMR in $CDCl_3$	
Natural (Marumo, 100 MHz)	Synthetic (This work, 500 MHz)
9.74 (s, 1 H)	9.74 (s, 1 H)
9.67 (s, 1 H)	9.67 (s, 1 H)
5.87 (ddd, J = 6.1, 3.2, 0.5 Hz, 1 H)	5.88 (dd, J = 6.3, 2.8 Hz, 1 H)
2.98 (m, 1 H)	3.00–2.97 (m, 1 H)
2.48 (ddd, J = 18, 8.1, 6.1 Hz, 2 H)	2.48 (ddd, J = 18.4, 8.7, 6.7 Hz, 2 H)
2.24 (d, J = 13.9 Hz, 2 H)	2.24 (d, J = 13.6 Hz, 2 H)
1.63 (d, J = 13.9 Hz, 3 H)	1.63 (d, J = 13.7 Hz, 3 H)
1.54 (s, 3 H)	1.53 (s, 3 H)
1.25 (s, 3 H)	1.26 (s, 3 H)
1.06 (s, 3 H)	1.06 (s, 3 H)
^{13}C NMR in $CDCl_3$	
Natural (Marumo, 25 MHz)	Synthetic (This work, 125 MHz)
199.5	199.9
189.5	189.8
154.9	155.2
149.2	149.5
135.7	136.0
123.5	123.7
56.3	56.5
50.4	50.6
40.4	40.5
30.5	30.6
30.5	30.5
28.7	28.8
25.3	25.3
24.2	24.2
18.3	18.3

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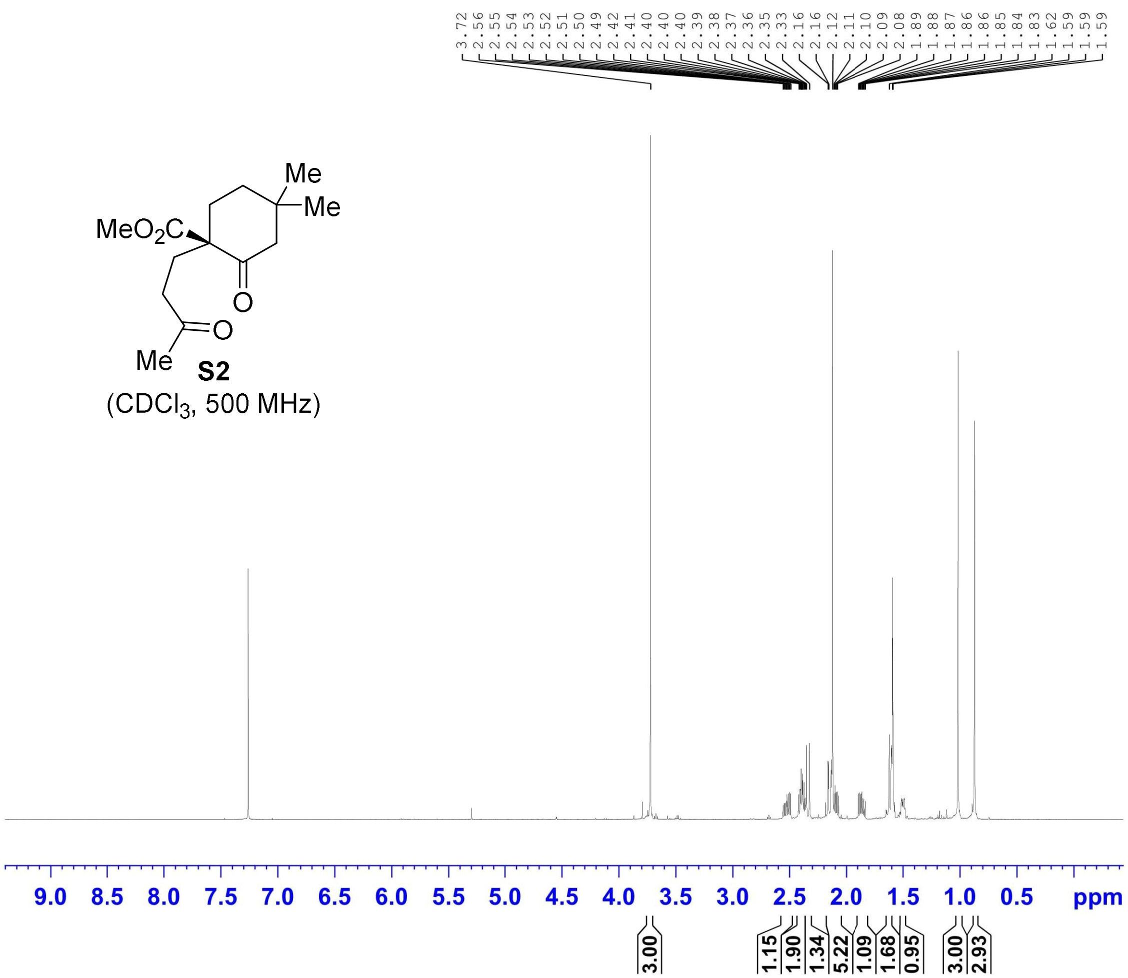
2.8 NMR data of selected intermediates



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PROCNO                  1

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PULPROG                zg
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D1             4.00000000 sec
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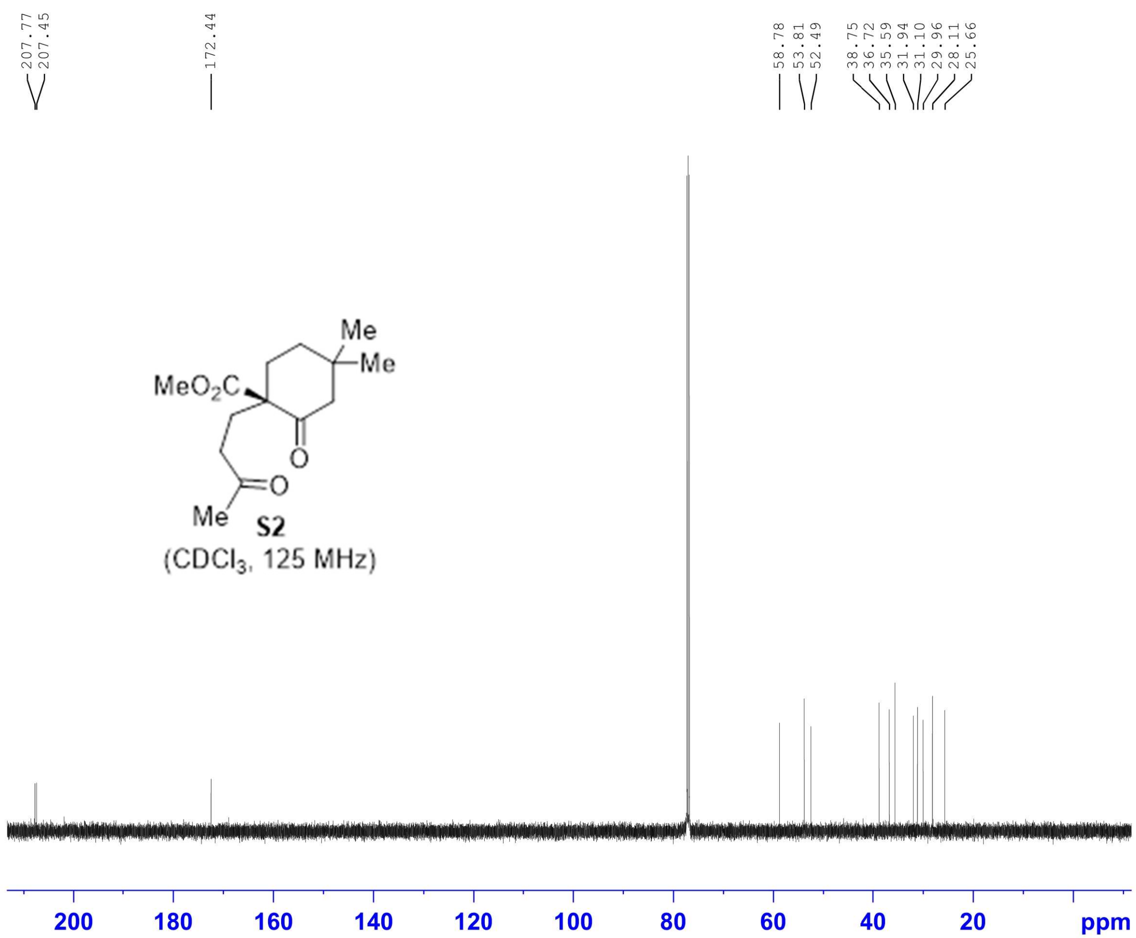

S2

($CDCl_3$, 125 MHz)

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TE                294.9 K
D1          10.00000000 sec
D11          0.03000000 sec
TD0                   1

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PL12              16.50 dB
PL13              17.00 dB
PL2W        24.54113007 W
PL12W        0.54940748 W
PL13W        0.48965994 W
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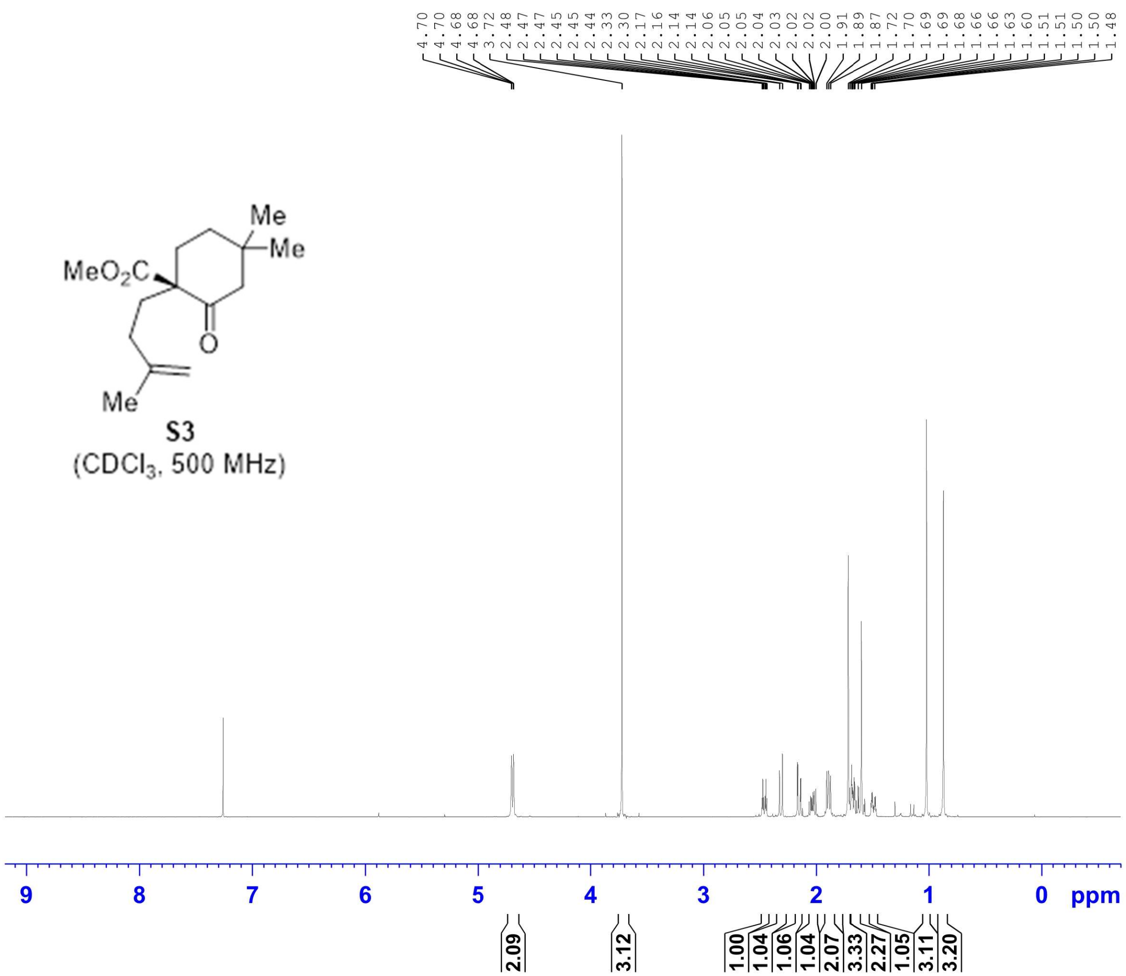

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TD0                    1

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PLW1         12.19999981 W

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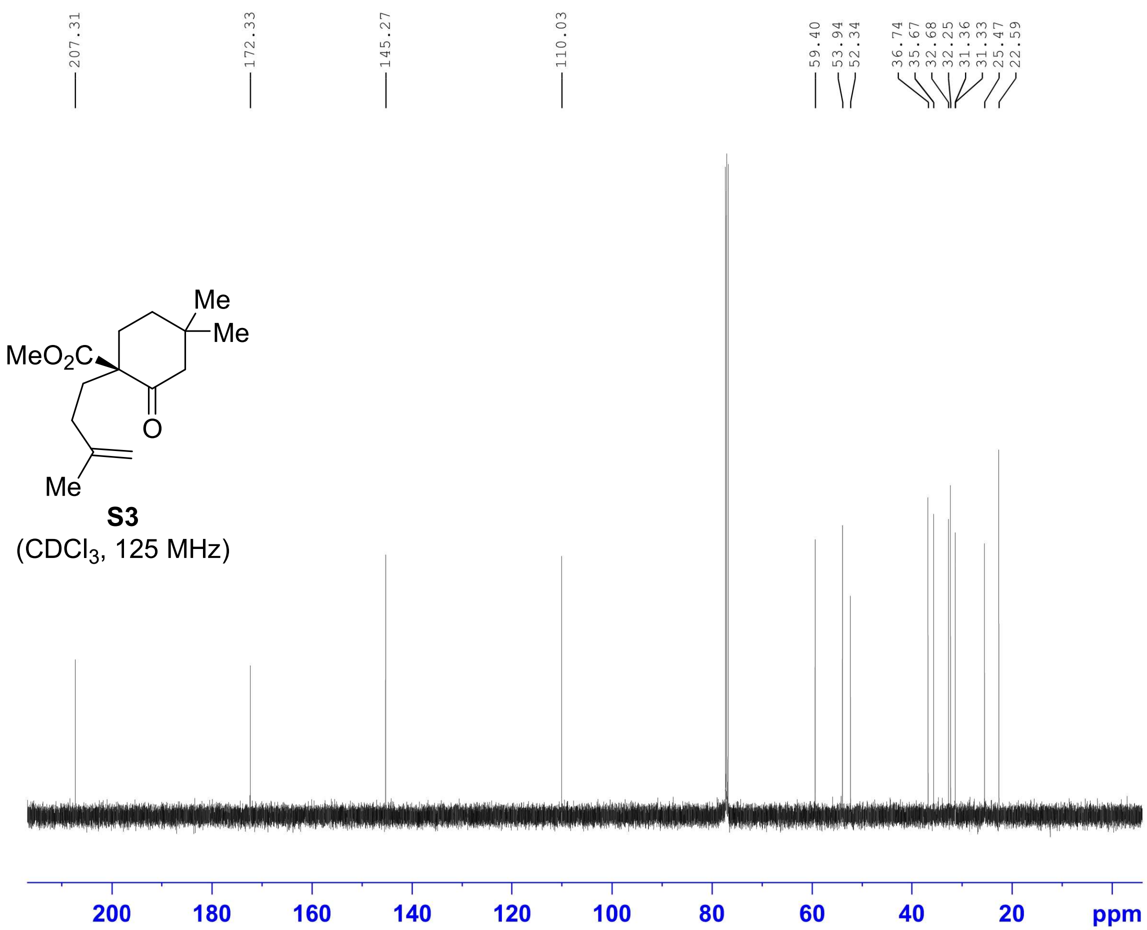


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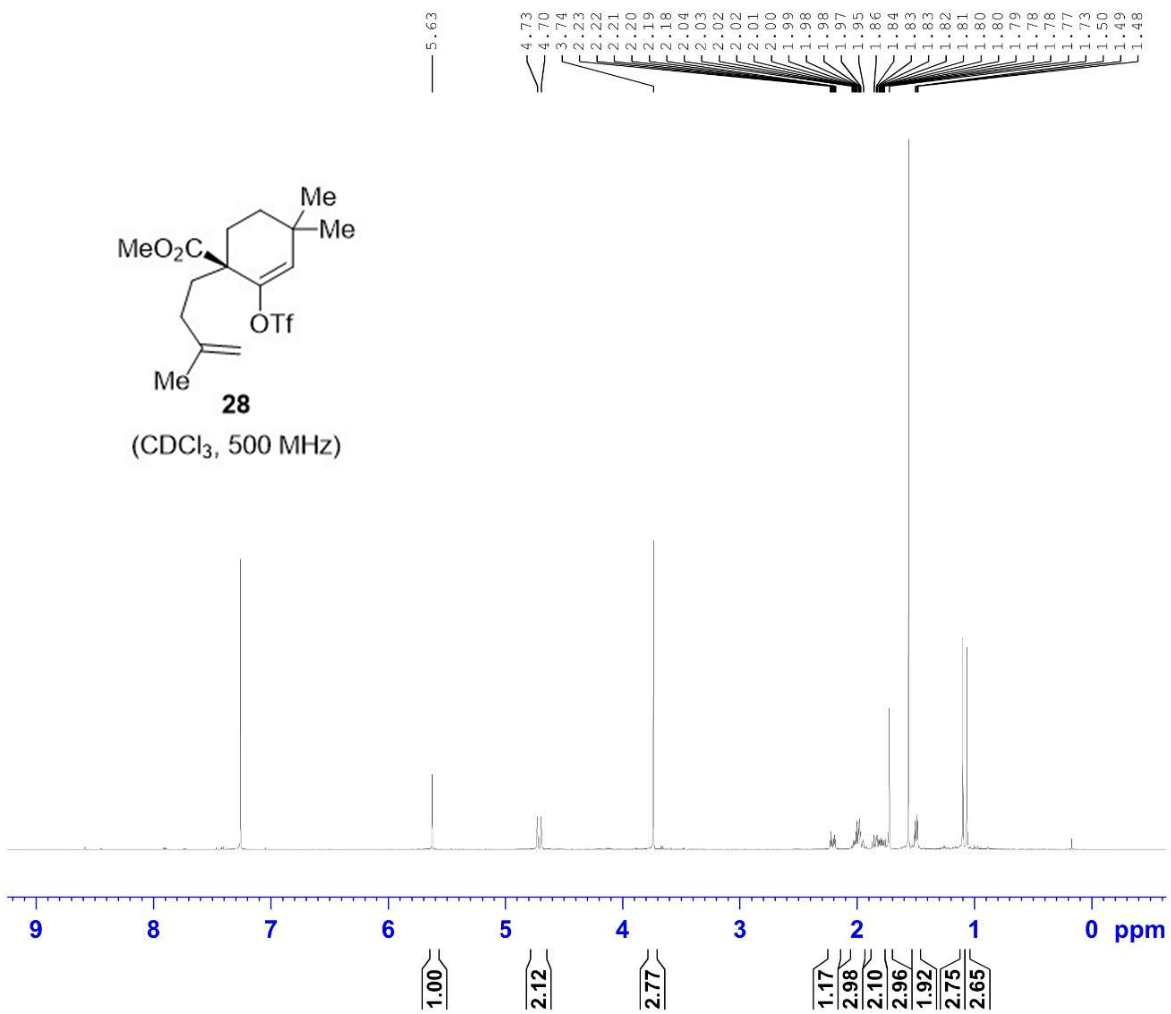
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                 1.00 dB
PL1W         72.42802429 W
SFO1         125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2      0 dB
PL12               16.50 dB
PL13               17.00 dB
PL2W         24.54113007 W
PL12W         0.54940748 W
PL13W         0.48965994 W
SFO2         500.1325006 MHz

F2 - Processing parameters
SI                131072
SF           125.7577890 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```



28

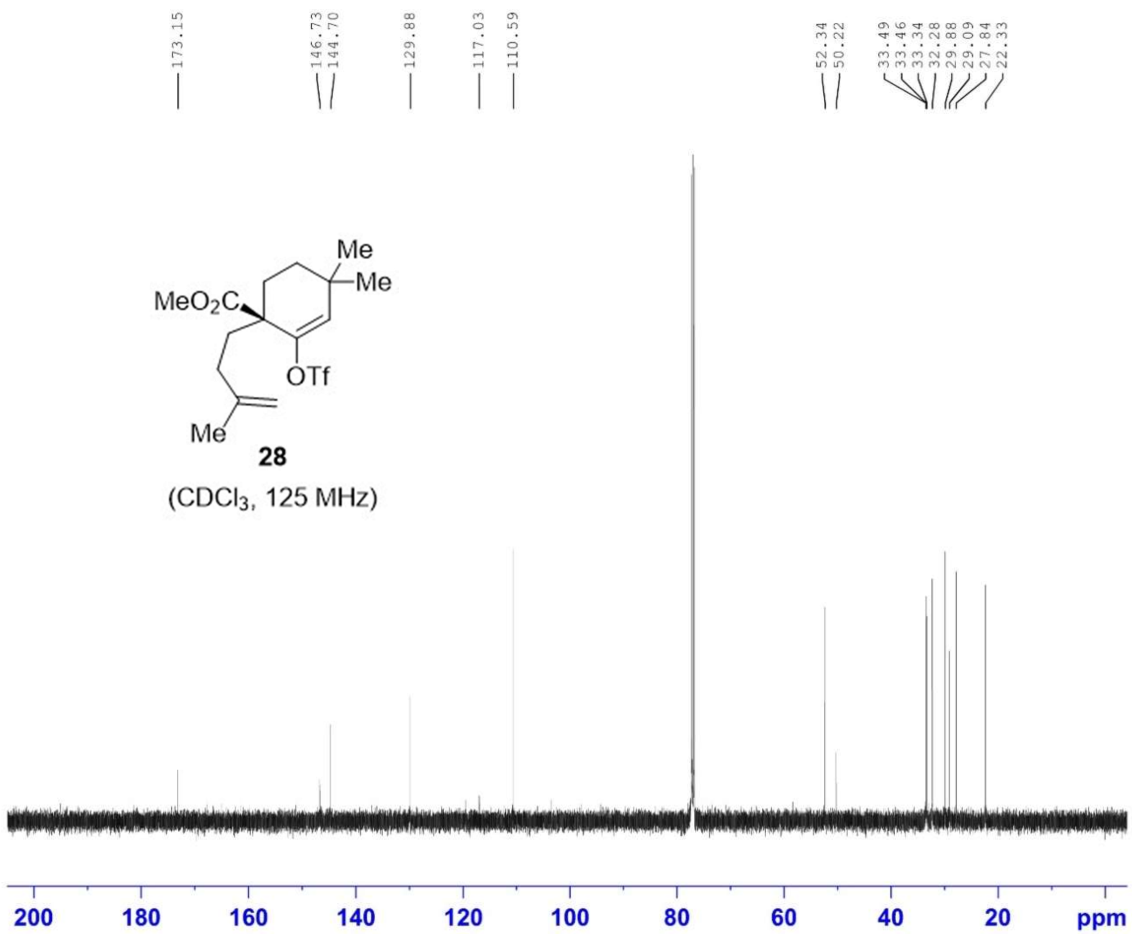
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             OTf(SM)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180730
Time               14.32
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                118.99
DW                50.000 usec
DE                  6.50 usec
TE                 295.5 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700123 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



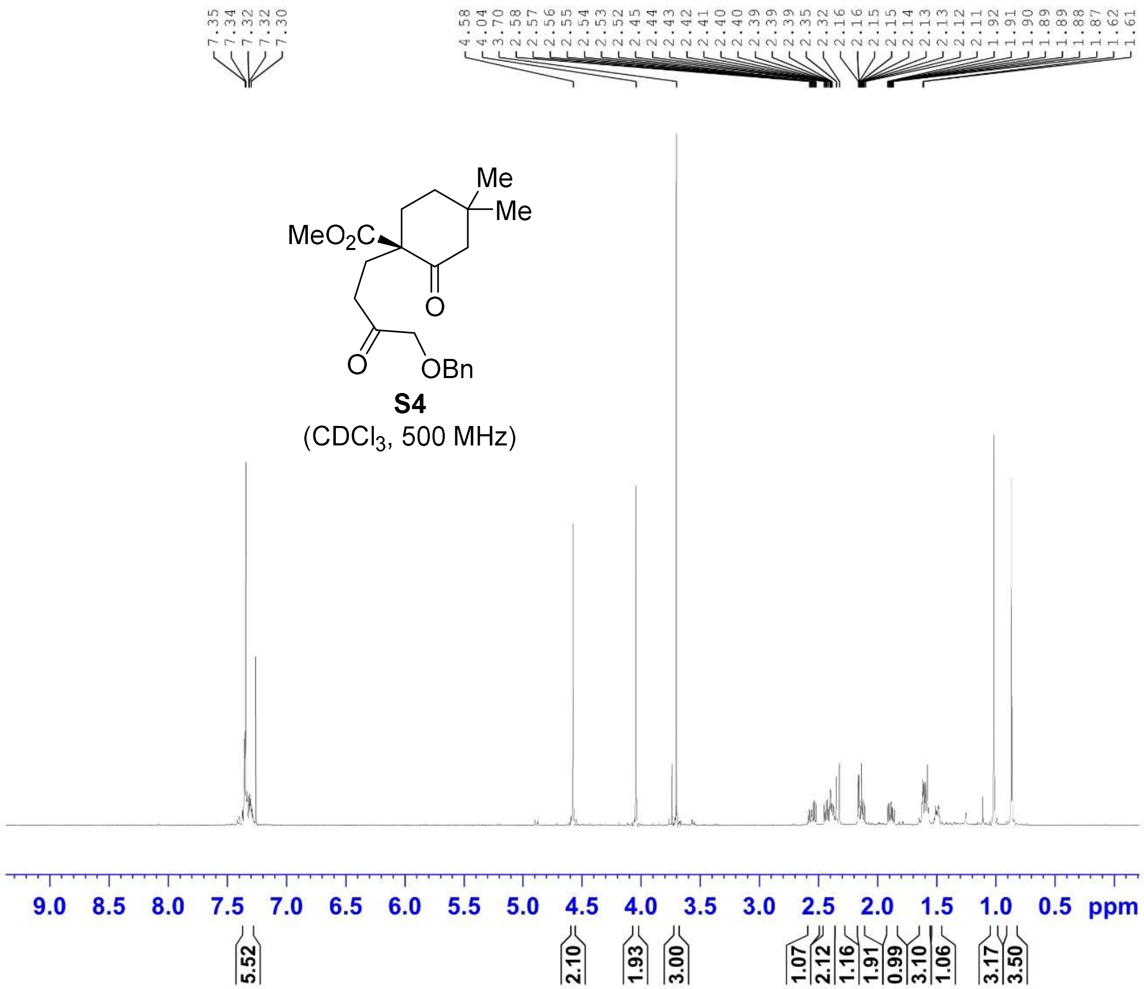

```
Current Data Parameters
NAME             OTf(SM)
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180730
Time_              22.15
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                   490
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 297.7 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```



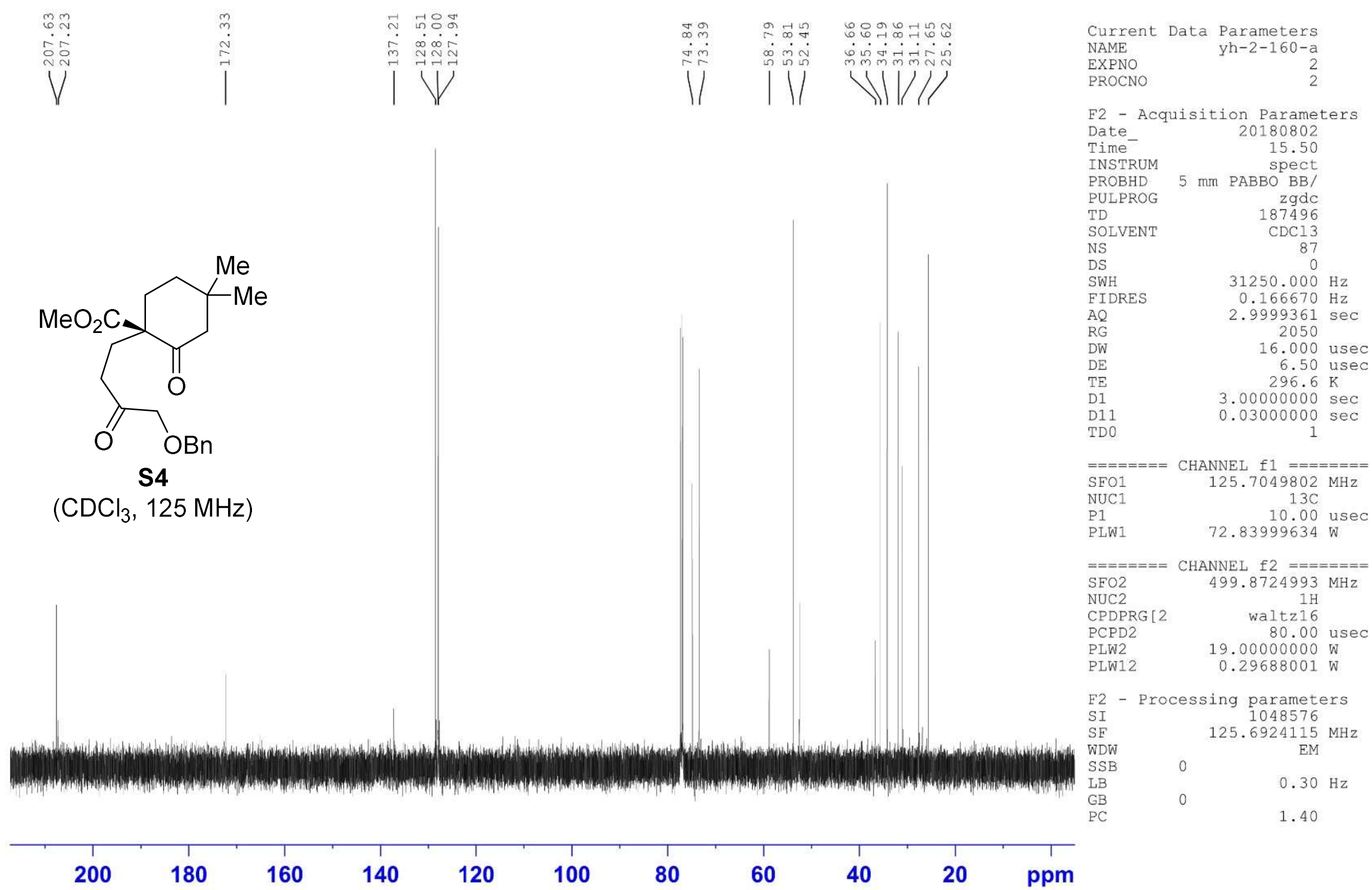
S4
($CDCl_3$, 500 MHz)

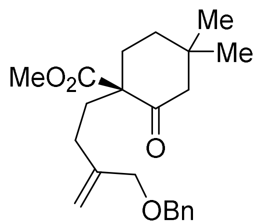
```
Current Data Parameters
NAME             yh-2-160-b
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20191020
Time                  18.31
INSTRUM               spect
PROBHD   5 mm PATXI 1H/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        1
DS                        0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                   110.37
DW               50.000 usec
DE                10.00 usec
TE                 297.0 K
D1           2.00000000 sec
TD0                       1

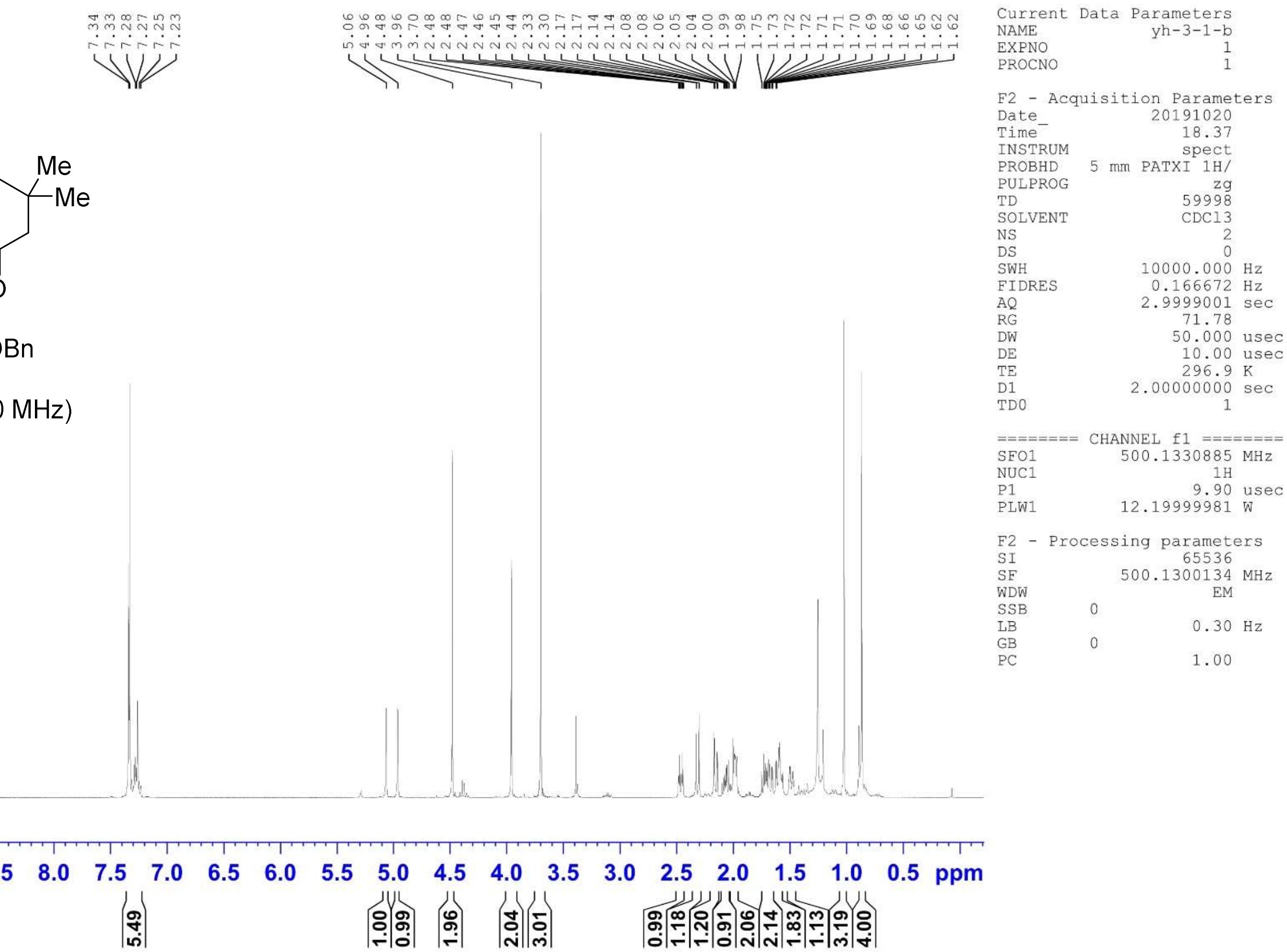
======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                     1H
P1                 9.90 usec
PLW1        12.19999981 W

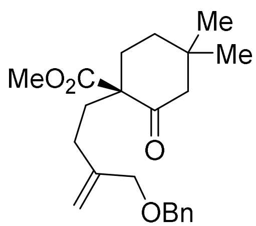
F2 - Processing parameters
SI                    65536
SF          500.1300133 MHz
WDW                      EM
SSB       0
LB                  0.30 Hz
GB        0
PC                     1.00
```


207.63
207.23
172.33
137.21
128.51
128.00
127.94
74.84
73.39
58.79
53.81
52.45
36.66
35.60
34.19
31.86
31.11
27.65
25.62
MeO2C
Me
Me
O
O
OBn
S4
(CDCl3, 125 MHz)
Current Data Parameters
NAME yh-2-160-a
EXPNO 2
PROCNO 2
F2 - Acquisition Parameters
Date_ 20180802
Time_ 15.50
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 87
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 296.6 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6924115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm

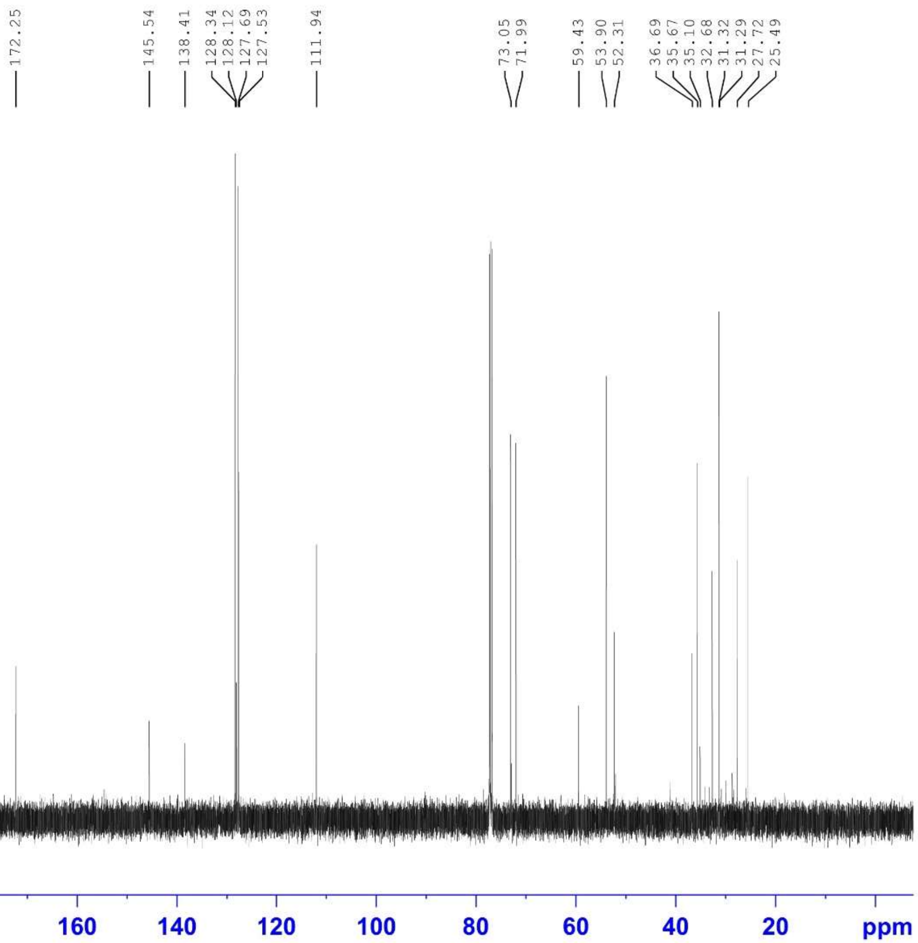


S5
($CDCl_3$, 500 MHz)





S5
($CDCl_3$, 125 MHz)



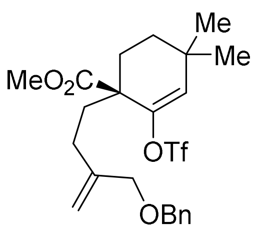
Current Data Parameters
NAME yh-3-1-a
EXPNO 2
PROCNO 2

F2 - Acquisition Parameters
Date_ 20180802
Time_ 16.08
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 121
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1

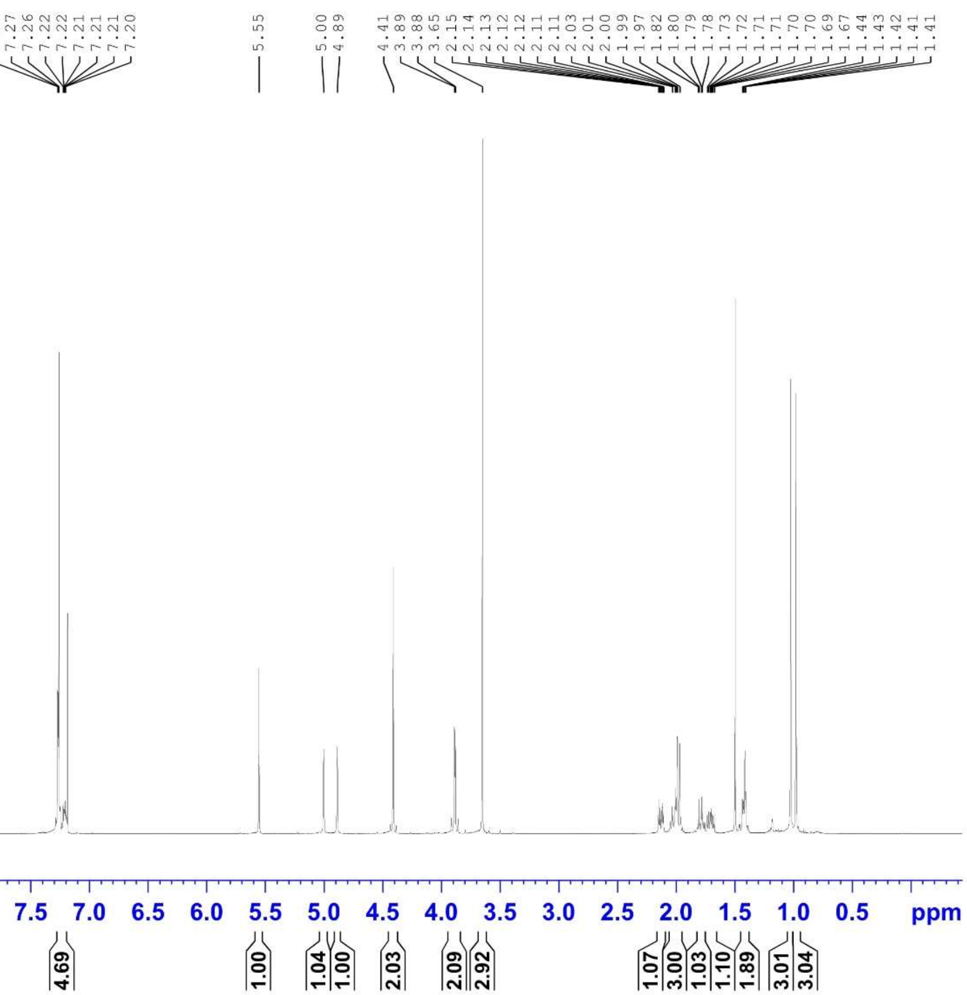
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W

======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W

F2 - Processing parameters
SI 1048576
SF 125.6924115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



S6
($CDCl_3$, 500 MHz)

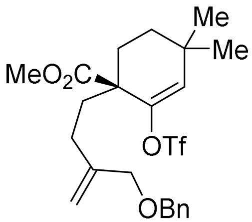



```
Current Data Parameters
NAME            yh-3-2-r
EXPNO                  1
PROCNO                 1

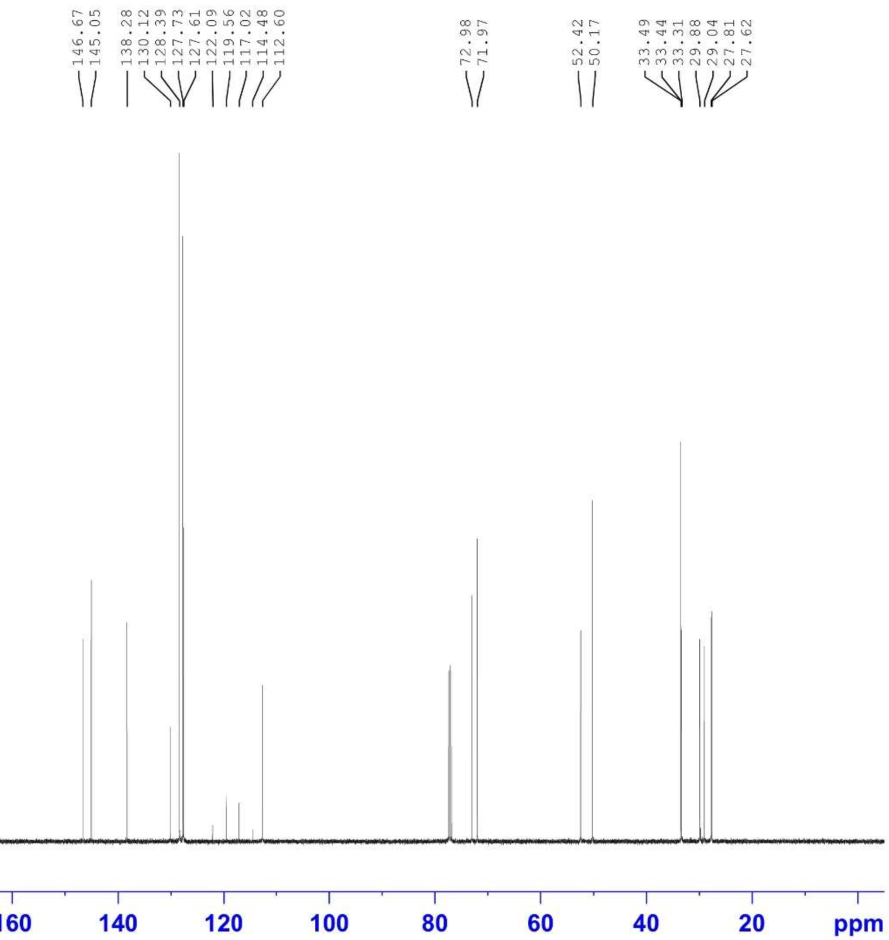
F2 - Acquisition Parameters
Date_           20180730
Time               19.39
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 86.16
DW                50.000 usec
DE                  6.50 usec
TE                 295.8 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700490 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



S6
($CDCl_3$, 125 MHz)



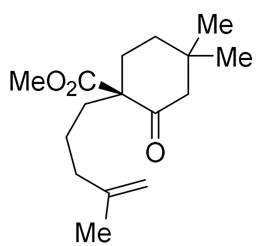

```
Current Data Parameters
NAME            yh-3-2-r
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180731
Time               21.00
INSTRUM            spect
PROBHD   5 mm PAQNP 1H/
PULPROG             zgpg
TD                197364
SOLVENT            CDCl3
NS                    61
DS                     4
SWH            32894.738 Hz
FIDRES          0.166670 Hz
AQ             2.9999328 sec
RG                  2050
DW                15.200 usec
DE                  6.00 usec
TE                 292.7 K
D1           10.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                 1.00 dB
PL1W         72.42802429 W
SFO1         125.7716224 MHz

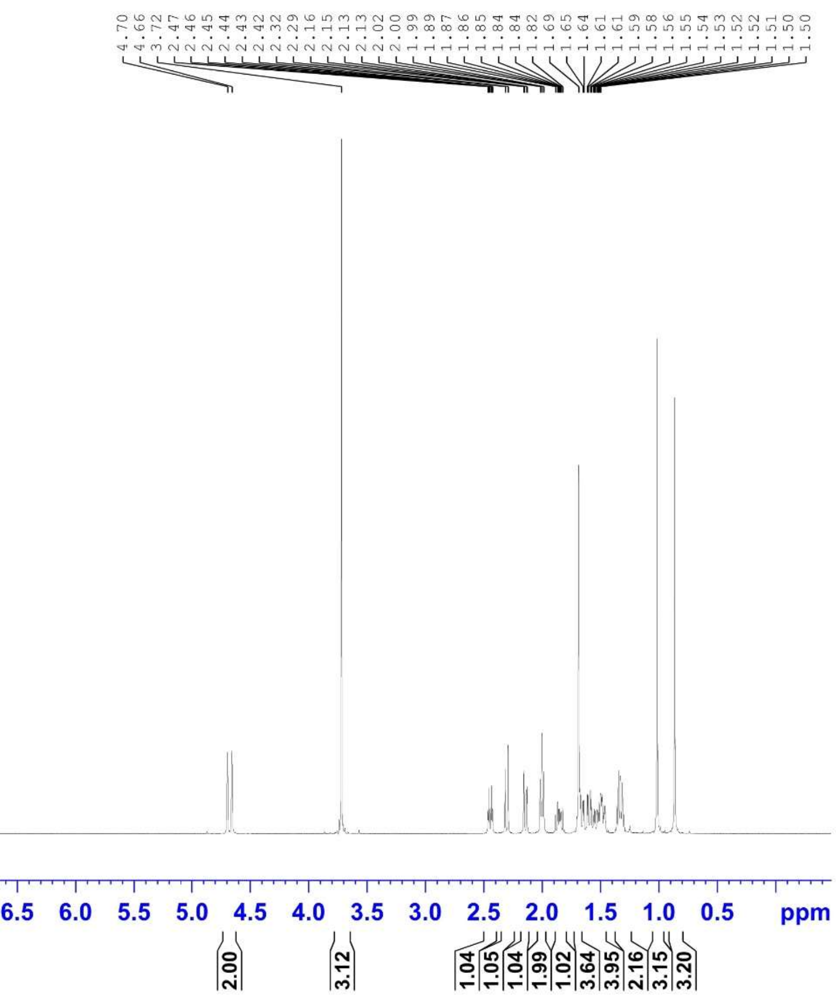
======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2       0 dB
PL12               16.50 dB
PL13               17.00 dB
PL2W         24.54113007 W
PL12W         0.54940748 W
PL13W         0.48965994 W
SFO2         500.1325006 MHz

F2 - Processing parameters
SI                131072
SF           125.7577890 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.40
```



S8

($CDCl_3$, 500 MHz)

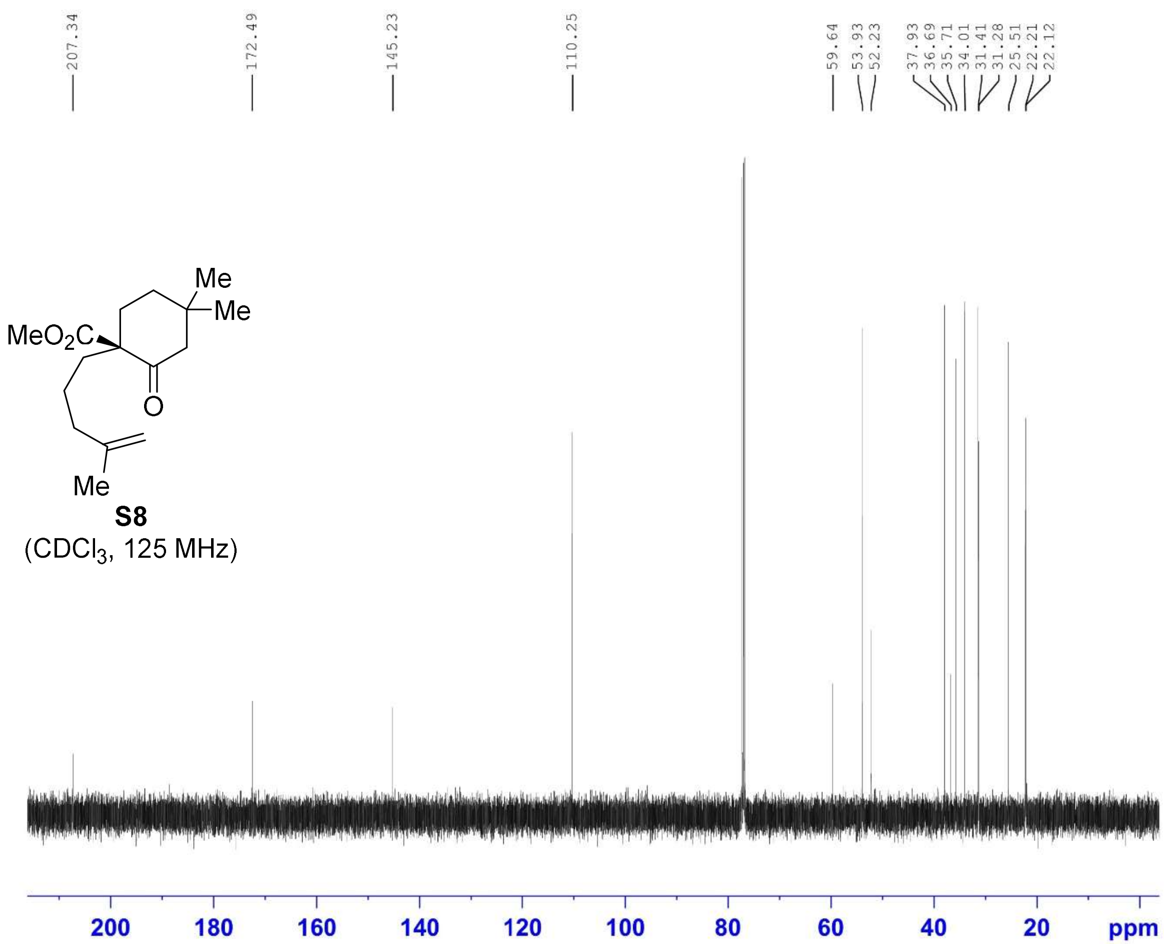



```
Current Data Parameters
NAME            yh-5-17-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180812
Time_               20.00
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      3
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                 141.13
DW                 50.000 usec
DE                  10.00 usec
TE                  294.3 K
D1             3.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                   2.67 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                  65536
SF            500.1300138 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```



S8
($CDCl_3$, 125 MHz)

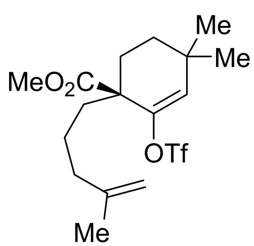
```
Current Data Parameters
NAME              yh-5-17-a
EXPNO                     2
PROCNO                    2

F2 - Acquisition Parameters
Date_              20180812
Time                  21.14
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT               CDCl3
NS                      153
DS                        0
SWH               31250.000 Hz
FIDRES             0.166670 Hz
AQ                2.9999361 sec
RG                     2050
DW                   16.000 usec
DE                     6.50 usec
TE                    297.2 K
D1               3.00000000 sec
D11              0.03000000 sec
TD0                       1

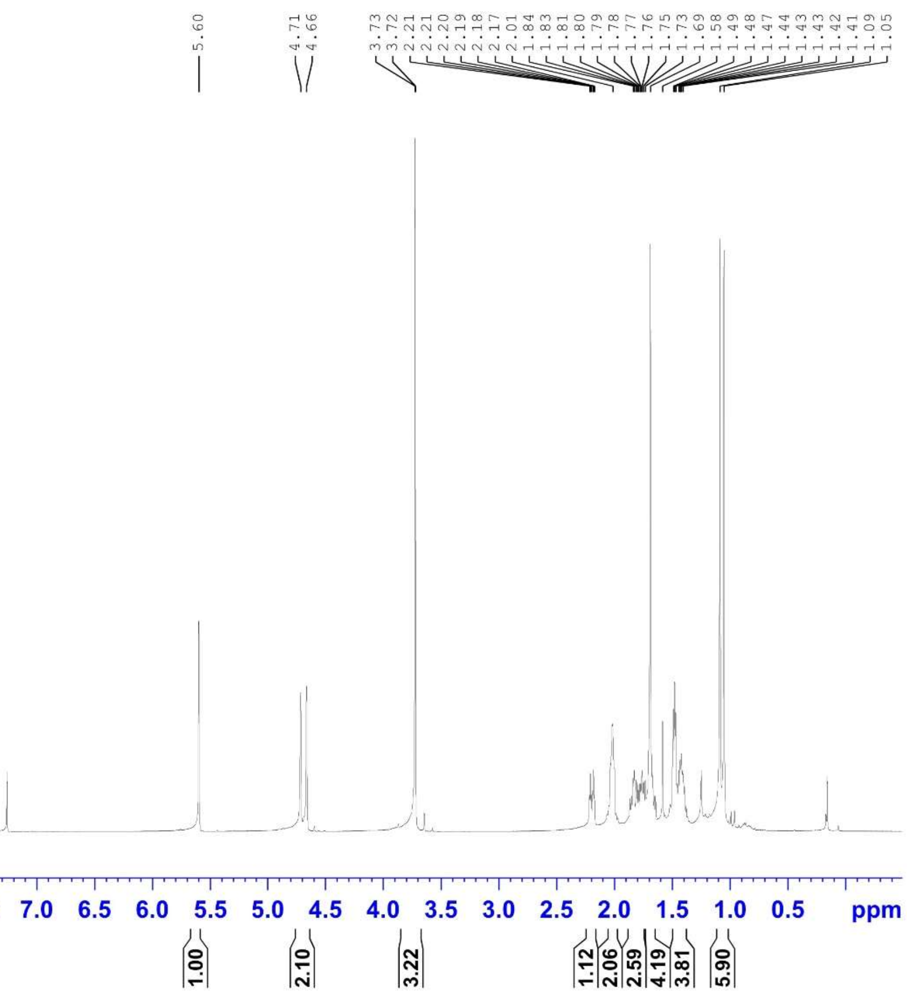
======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



S9
($CDCl_3$, 500 MHz)

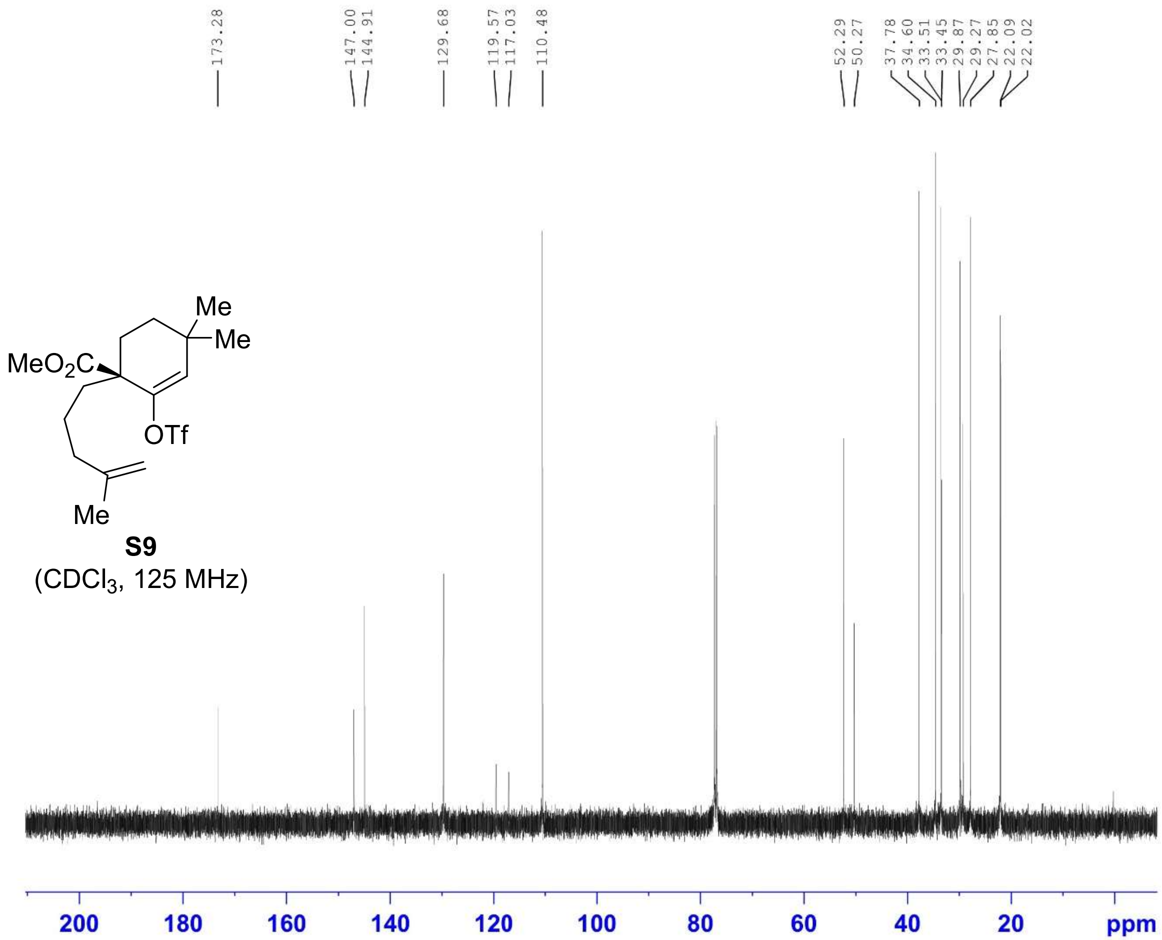



```
Current Data Parameters
NAME             yh-5-18-r
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180730
Time                 15.21
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                      16
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                   51.11
DW                  50.000 usec
DE                    6.50 usec
TE                   295.6 K
D1              4.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                     1H
P1                     3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                   65536
SF             499.8700129 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



S9
($CDCl_3$, 125 MHz)

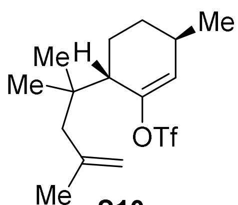
```
Current Data Parameters
NAME          yh-5-18-r
EXPNO                 2
PROCNO                2

F2 - Acquisition Parameters
Date_          20180730
Time              21.08
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zgdc
TD               187496
SOLVENT           CDCl3
NS                  191
DS                    0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                 2050
DW               16.000 usec
DE                 6.50 usec
TE                297.3 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1

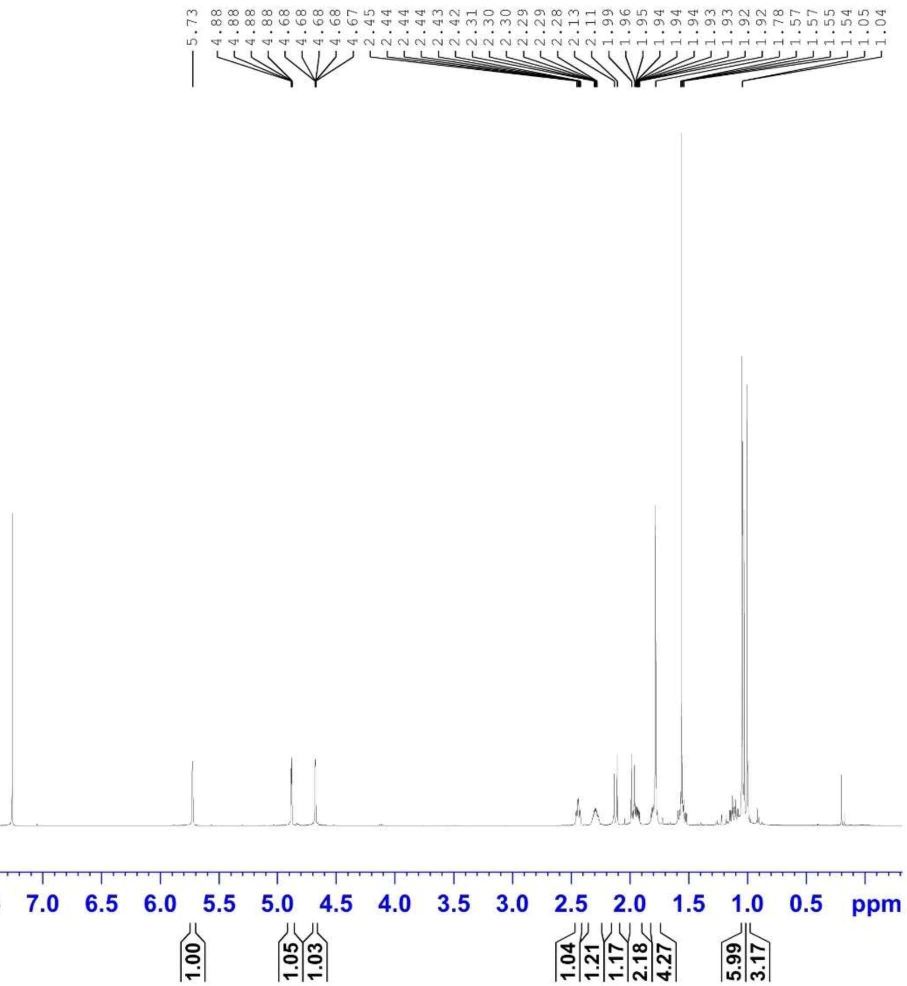
======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                13C
P1                10.00 usec
PLW1        72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI              1048576
SF          125.6924115 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.40
```



S10
($CDCl_3$, 500 MHz)

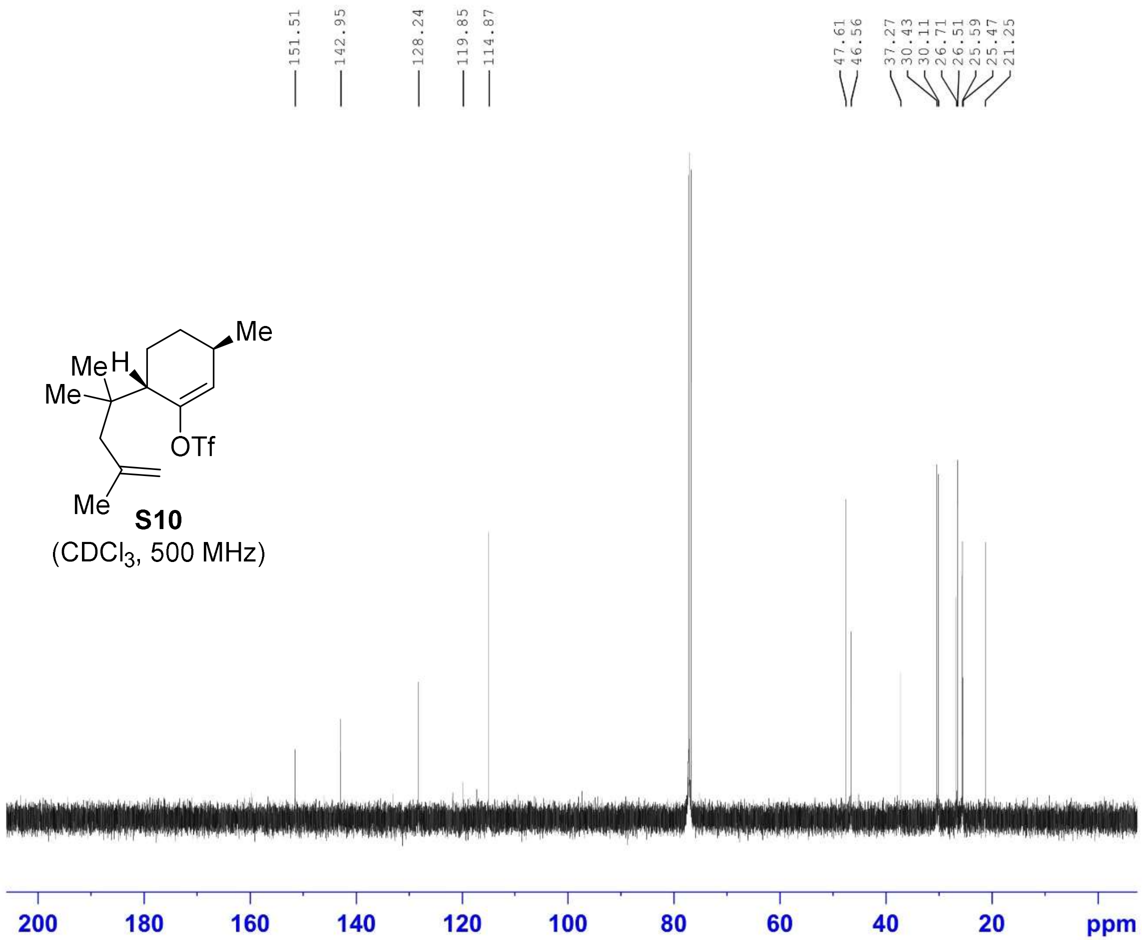



```
Current Data Parameters
NAME              yh-4-1-r
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180730
Time                 19.46
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                      16
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                  100.96
DW                  50.000 usec
DE                    6.50 usec
TE                   295.8 K
D1              4.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                    1H
P1                    3.58 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                   65536
SF          499.8700122 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



S10
($CDCl_3$, 500 MHz)

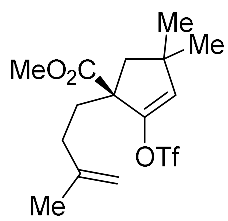
```
Current Data Parameters
NAME              yh-4-1-r
EXPNO                    3
PROCNO                   3

F2 - Acquisition Parameters
Date_             20180730
Time_                21.45
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                     306
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   297.7 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

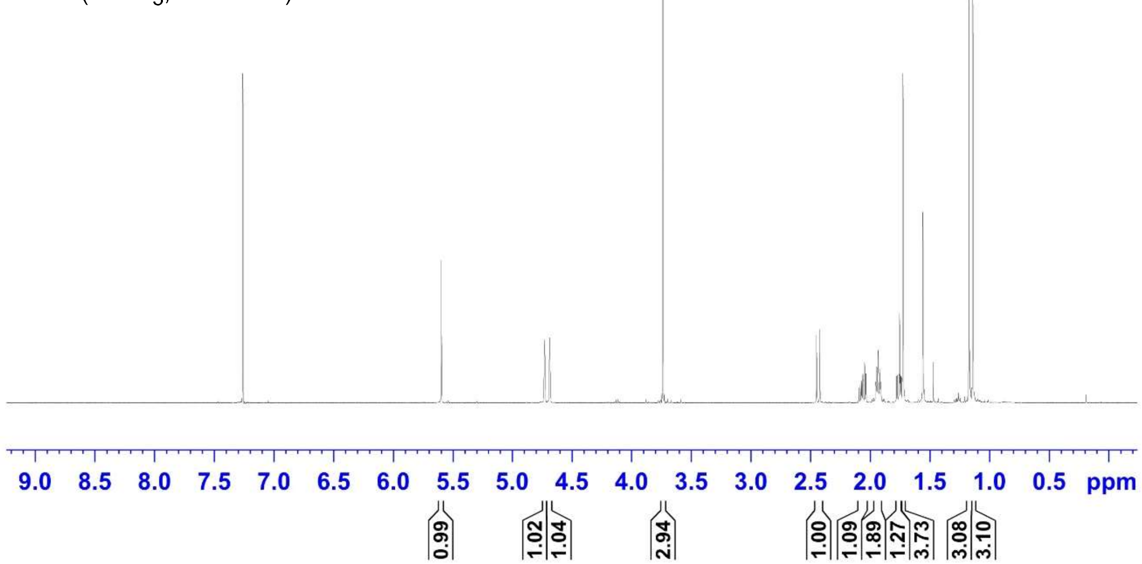
======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6924115 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.40
```



S11
($CDCl_3$, 500 MHz)

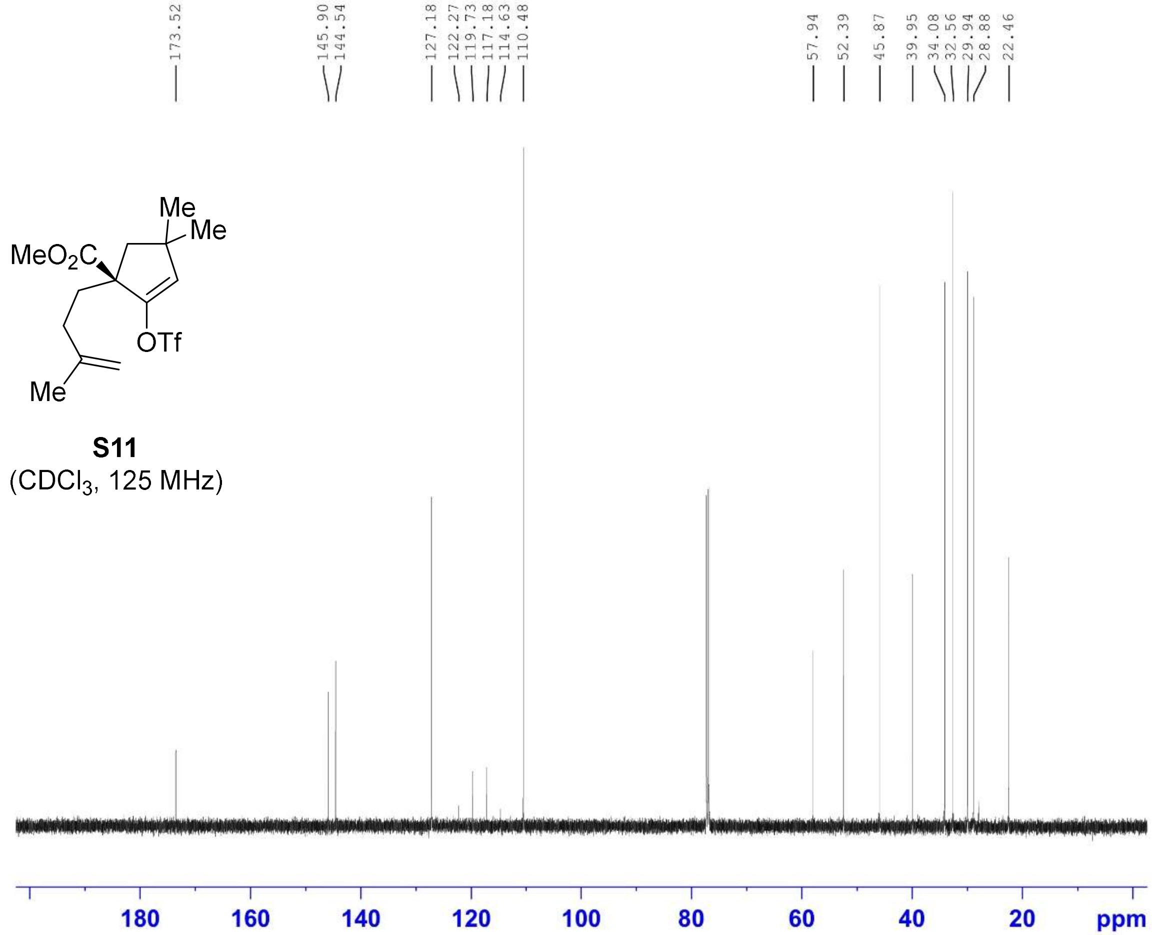



```
Current Data Parameters
NAME      5-member-ring-OTf
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20190812
Time                  14.30
INSTRUM               spect
PROBHD   5 mm PATXI 1H/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        4
DS                        0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                  196.79
DW               50.000 usec
DE                10.00 usec
TE                293.4 K
D1            4.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                     1H
P1                 3.30 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                    65536
SF          500.1300138 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.00
```



S11
($CDCl_3$, 125 MHz)

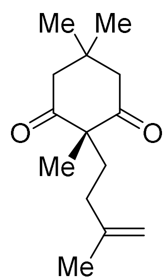
```
Current Data Parameters
NAME      5-member-ring-OTf
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20190812
Time                21.48
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    329
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.3 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

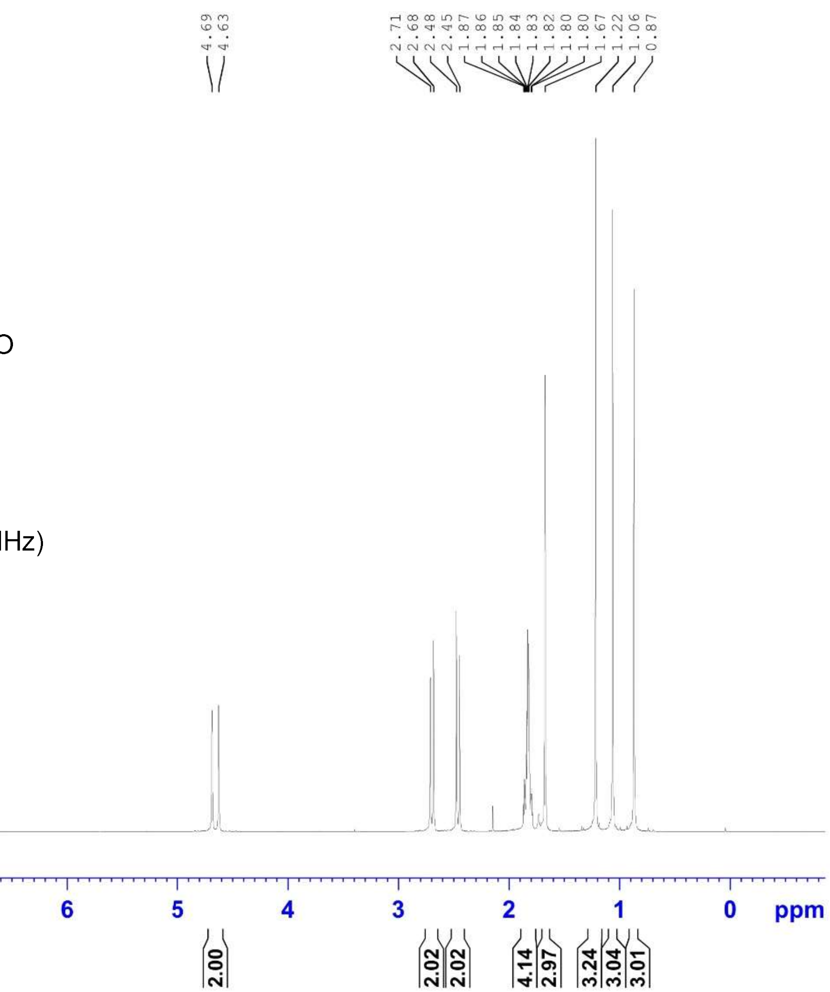
======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                  10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                1048576
SF           125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



S14
($CDCl_3$, 500 MHz)

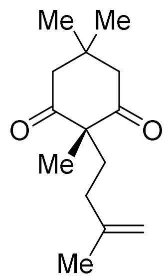



```
Current Data Parameters
NAME          yh-5-36-r
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20180801
Time              13.14
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    6
DS                    0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                30.11
DW               50.000 usec
DE                10.00 usec
TE                294.1 K
D1           3.00000000 sec
TD0                   1

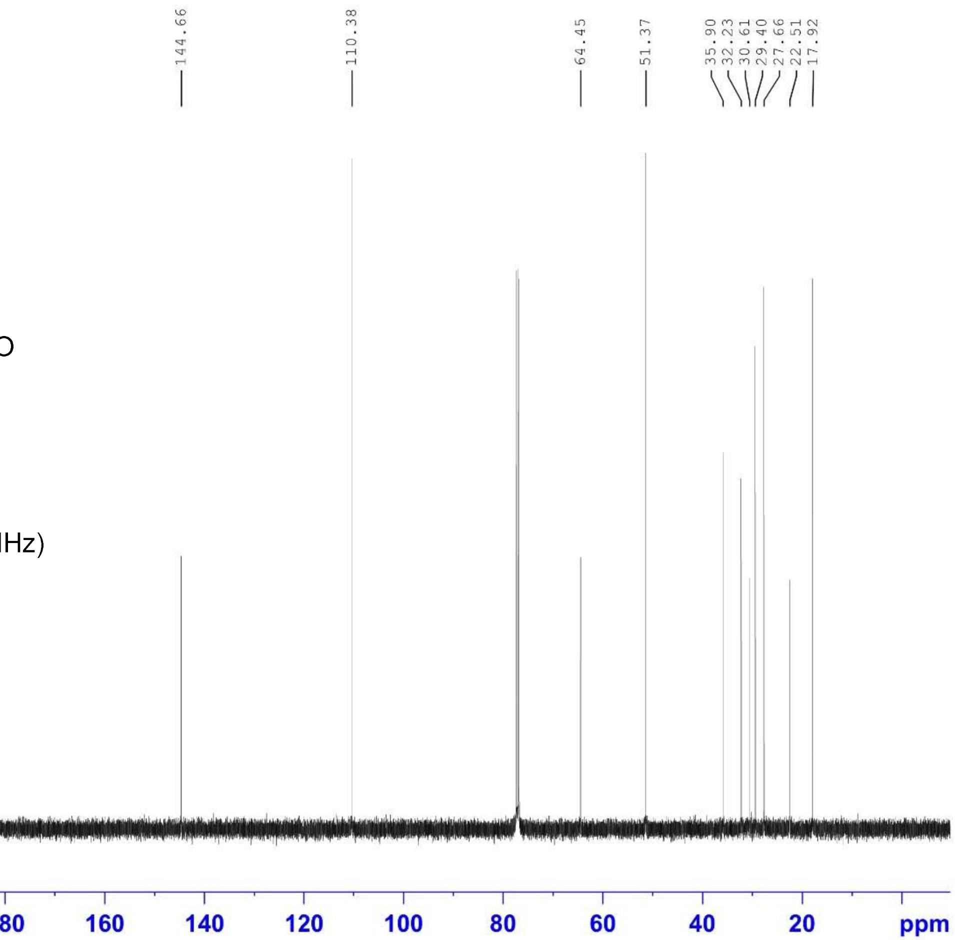
======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                 1H
P1                 2.67 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                65536
SF          500.1300136 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



S14

($CDCl_3$, 125 MHz)



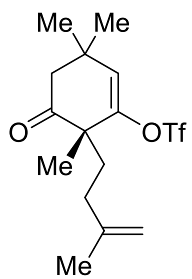

```
Current Data Parameters
NAME          yh-5-36-r
EXPNO                 2
PROCNO                2

F2 - Acquisition Parameters
Date_          20180801
Time              13.41
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zgdc
TD               187496
SOLVENT           CDCl3
NS                   97
DS                    0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                 2050
DW               16.000 usec
DE                 6.50 usec
TE                296.6 K
D1           4.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                13C
P1                 3.58 usec
PLW1        72.83999634 W

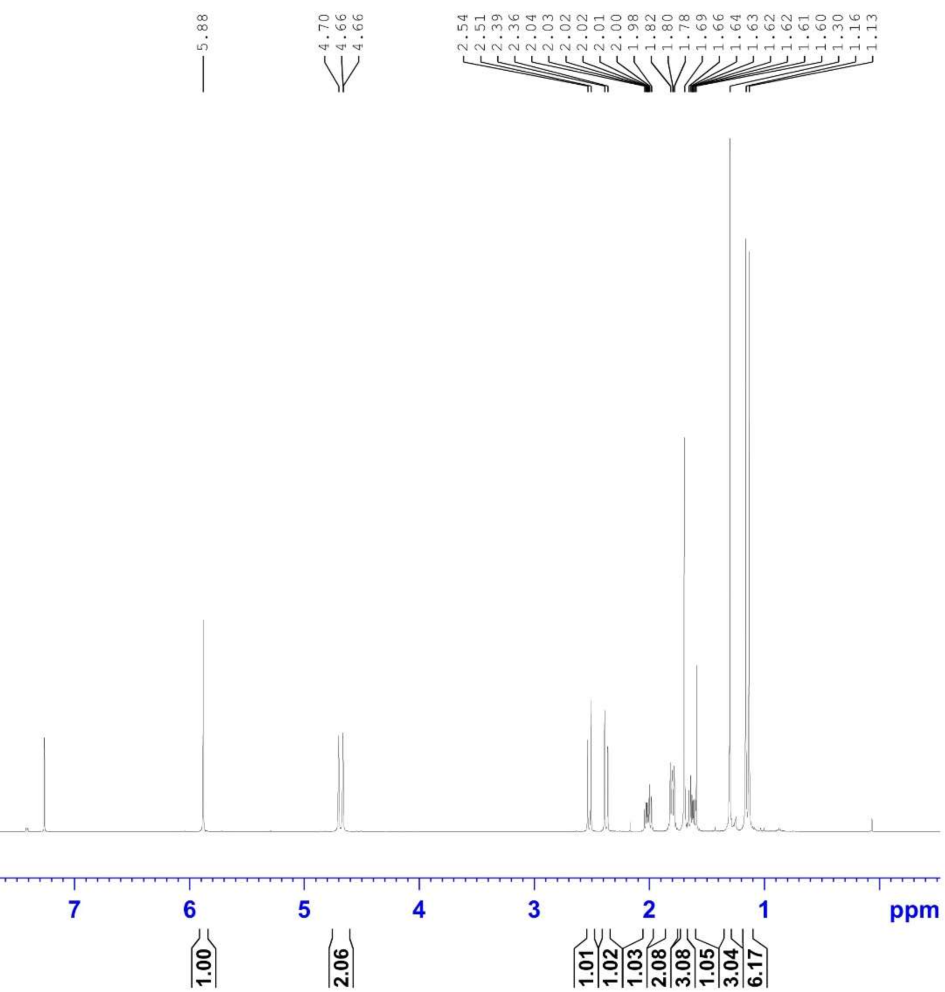
======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI              1048576
SF          125.6924115 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.40
```



S15

($CDCl_3$, 500 MHz)

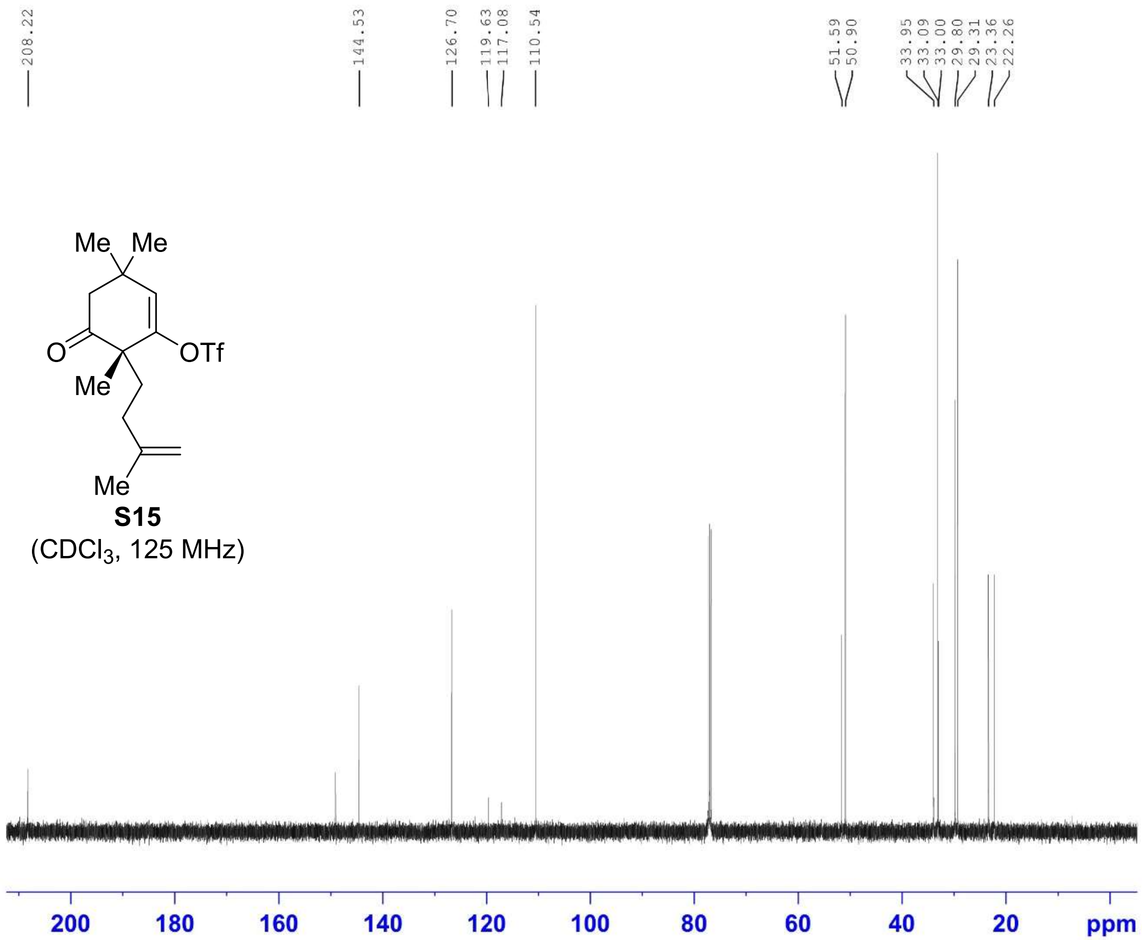



```
Current Data Parameters
NAME            yh-5-38-1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180801
Time                13.54
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  97.37
DW                 50.000 usec
DE                  10.00 usec
TE                  294.2 K
D1             3.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                   2.67 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                  65536
SF            500.1300138 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S15
($CDCl_3$, 125 MHz)

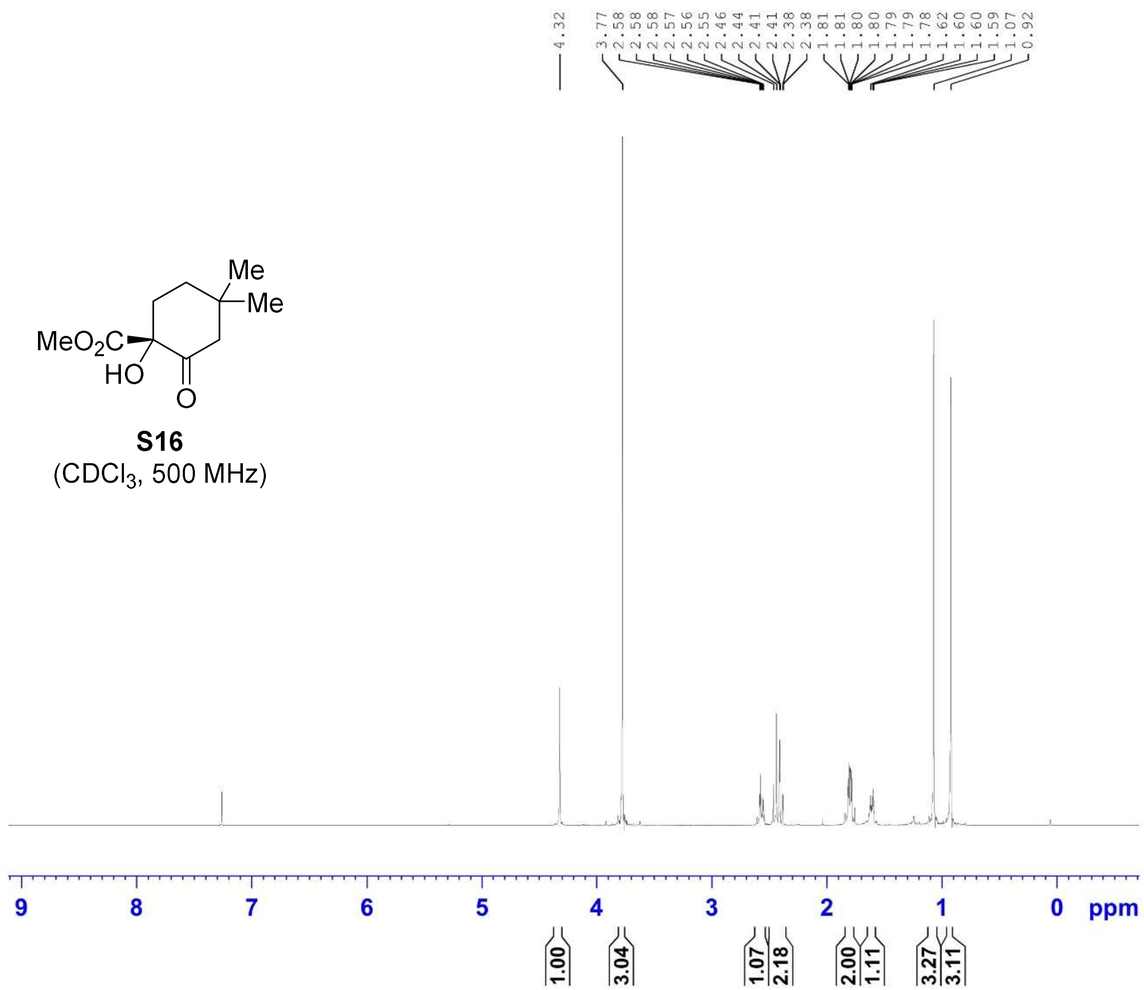
```
Current Data Parameters
NAME            yh-5-38-1
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180801
Time                14.37
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    158
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  297.1 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



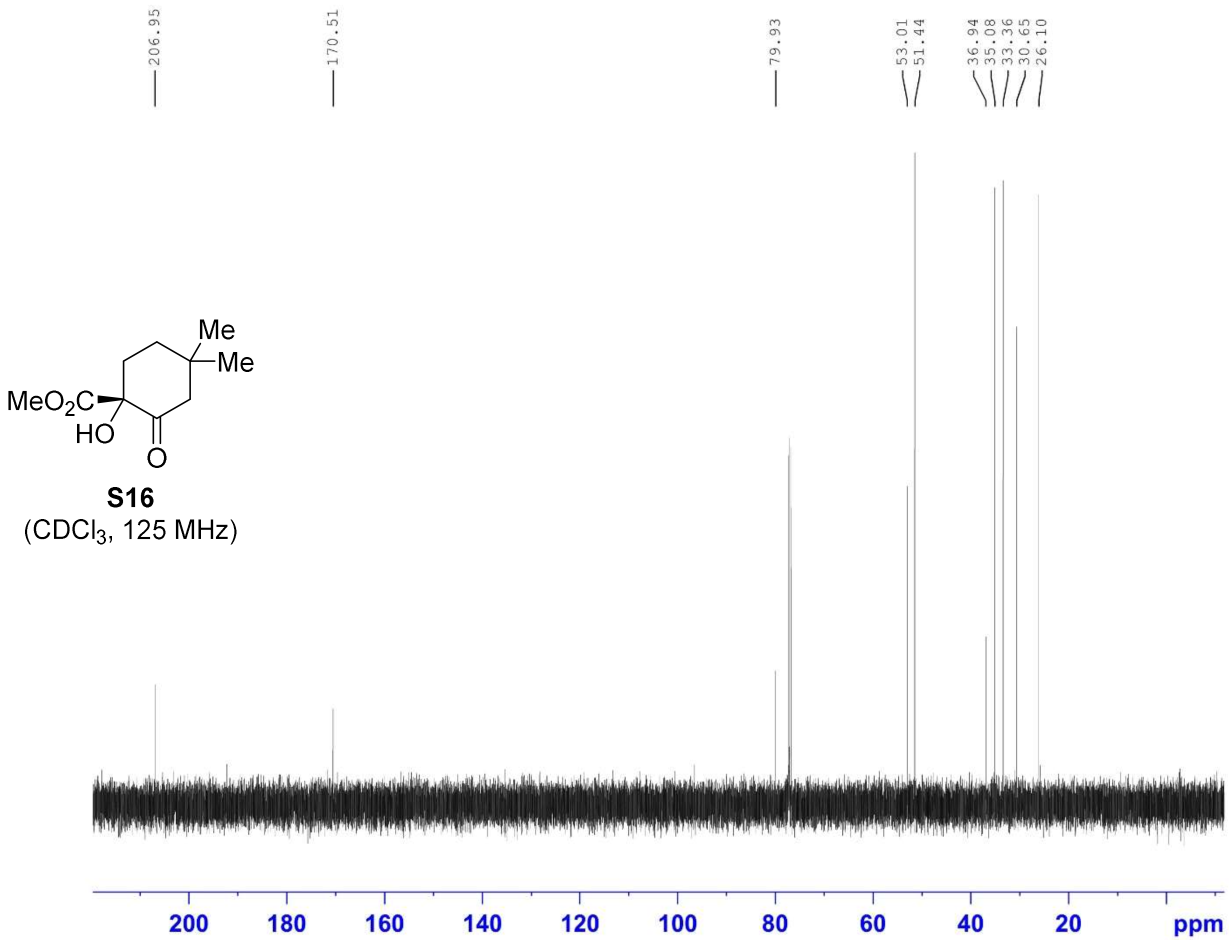
S16
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME            yh-5-52-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190711
Time_               23.52
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      1
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  56.75
DW                 50.000 usec
DE                   6.50 usec
TE                  296.1 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700118 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S16
($CDCl_3$, 125 MHz)

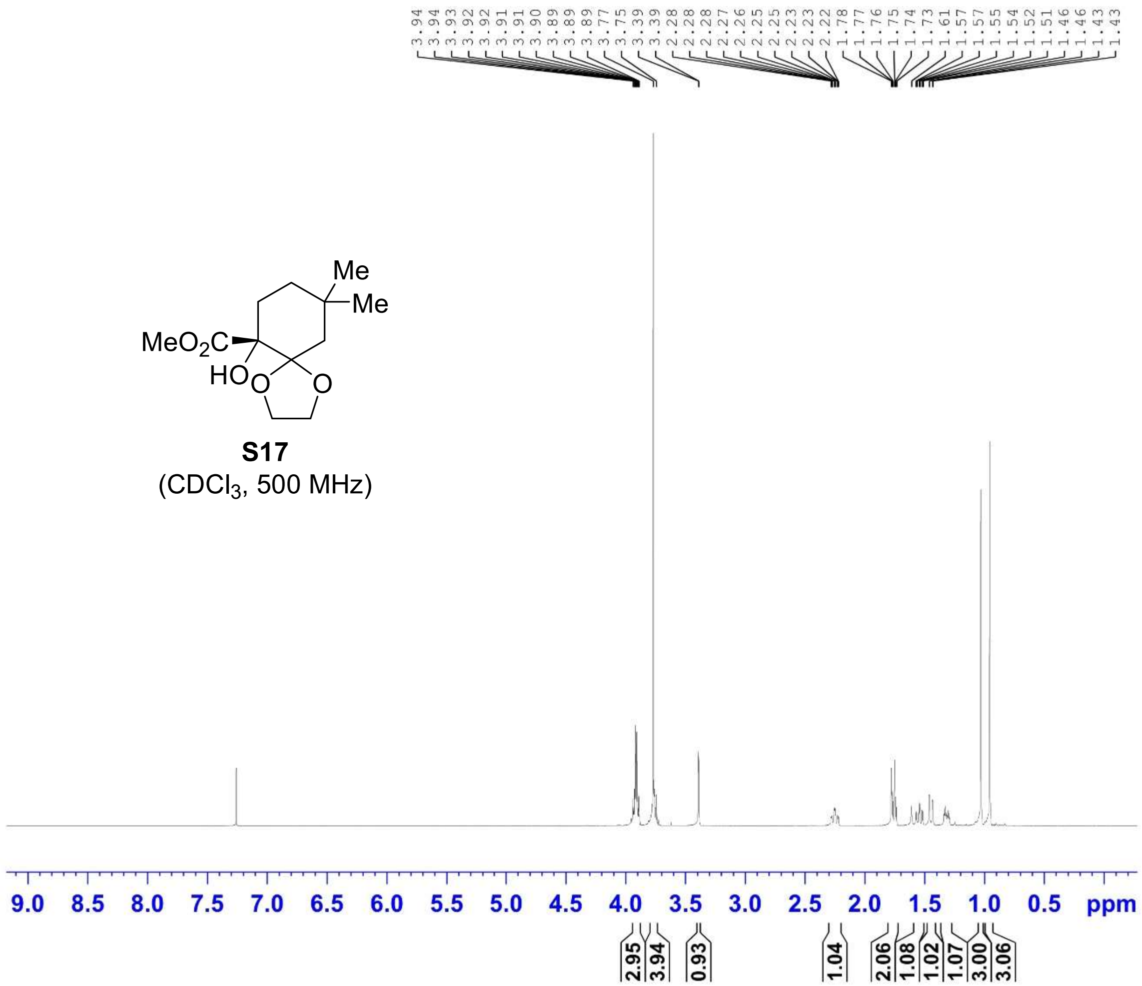
```
Current Data Parameters
NAME            yh-5-52-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20190711
Time                23.58
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                      7
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.3 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.40
```



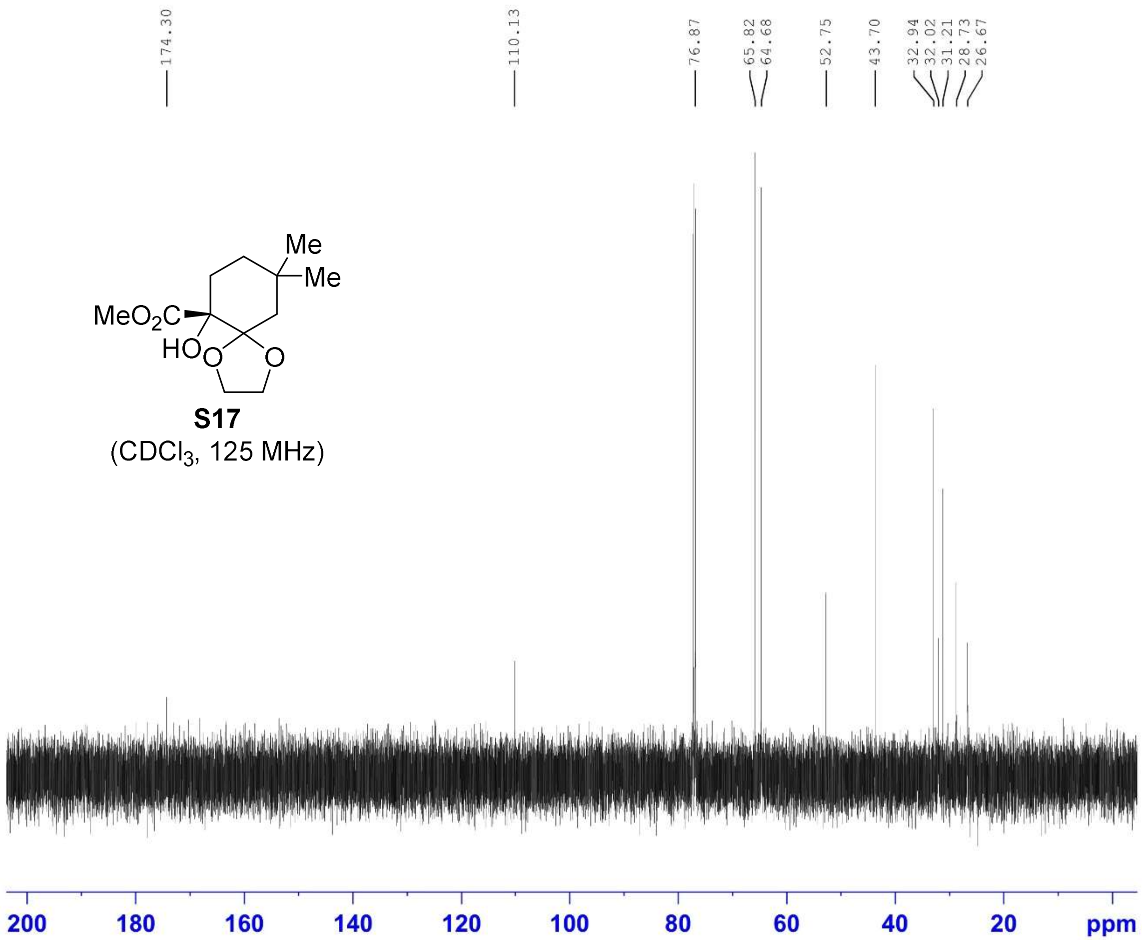
S17
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME          yh-5-77-a
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190711
Time_             14.56
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    2
DS                    0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                70.49
DW               50.000 usec
DE                 6.50 usec
TE                295.4 K
D1           4.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                 1H
P1                 3.58 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                65536
SF          499.8700119 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



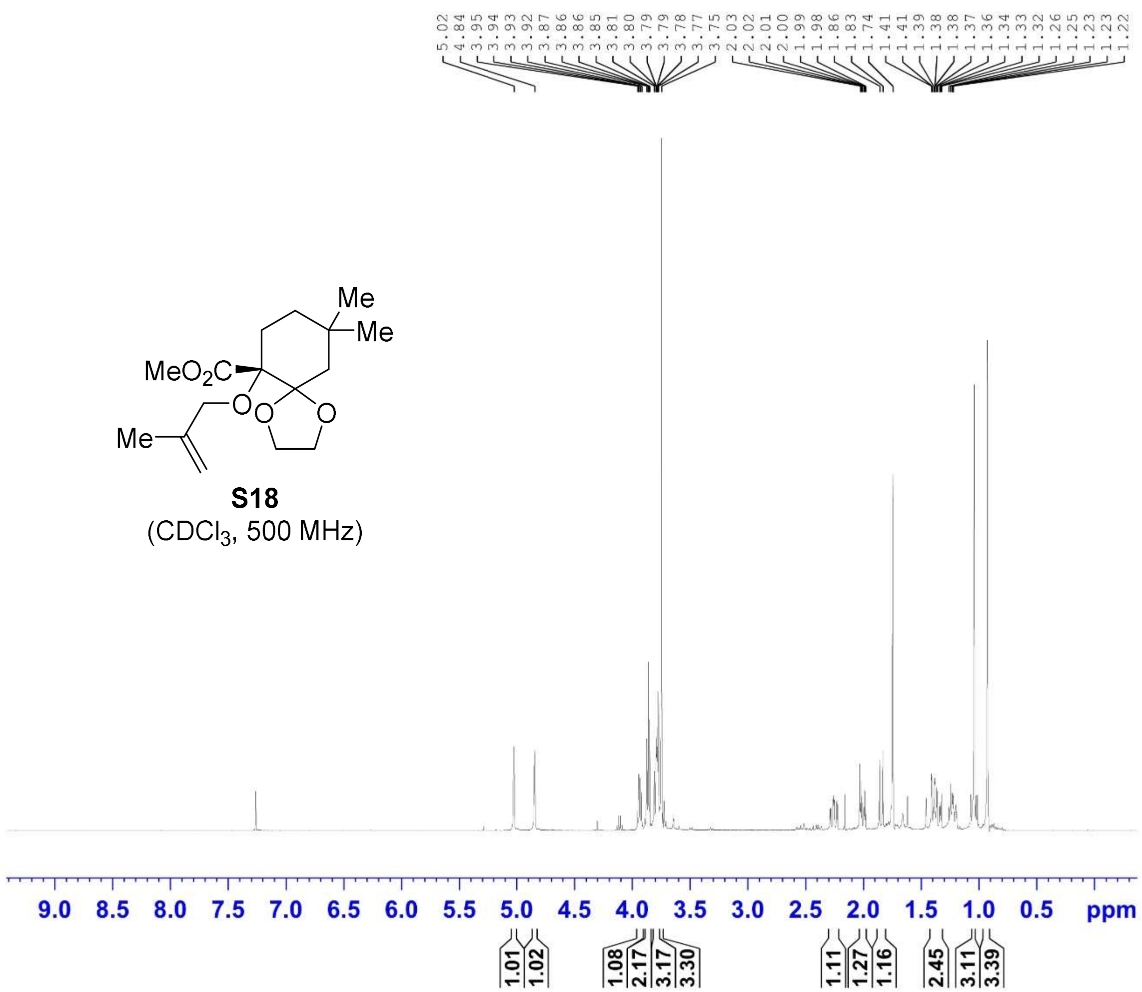

```
Current Data Parameters
NAME            yh-5-77-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20190711
Time                15.02
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                     21
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  295.8 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



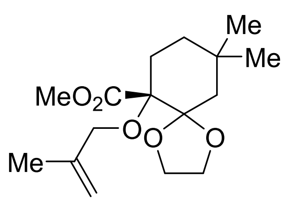
S18
($CDCl_3$, 500 MHz)


```
Current Data Parameters
NAME            yh-5-78-c
EXPNO                   1
PROCNO                  1

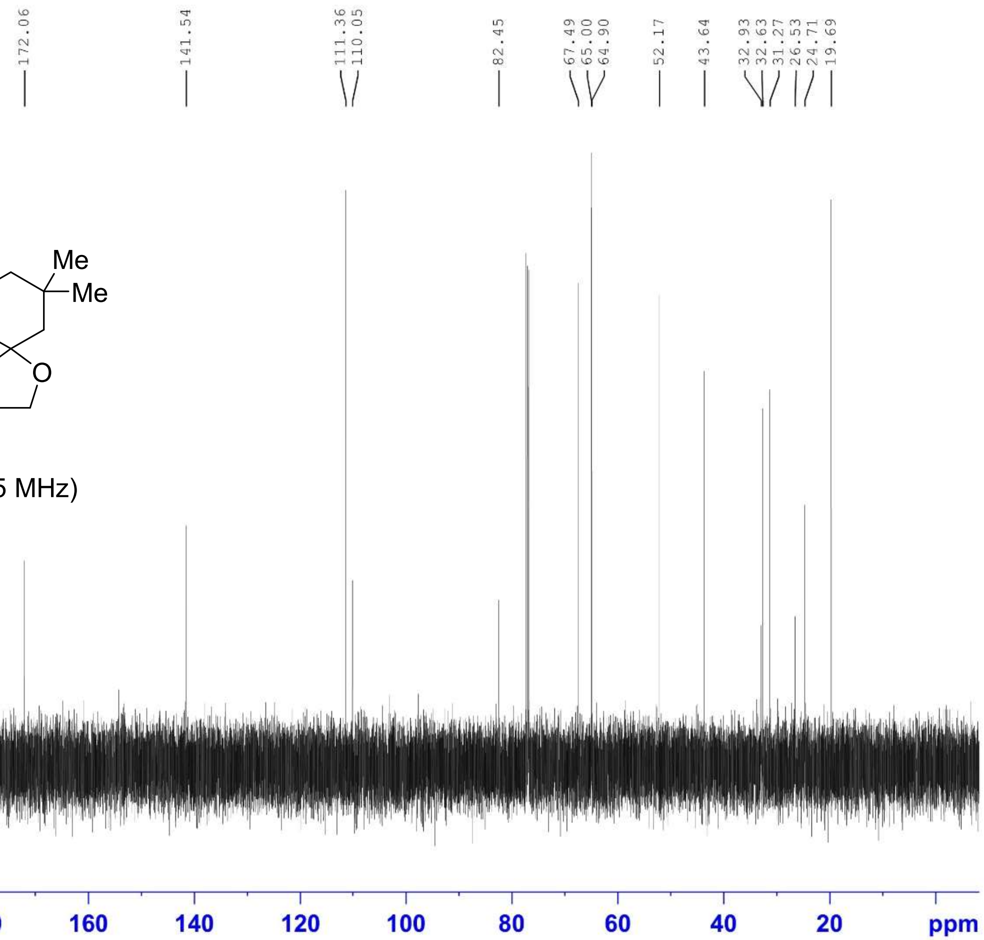
F2 - Acquisition Parameters
Date_            20190712
Time                17.20
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      1
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  44.57
DW                 50.000 usec
DE                   6.50 usec
TE                  297.0 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700120 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S18
($CDCl_3$, 125 MHz)



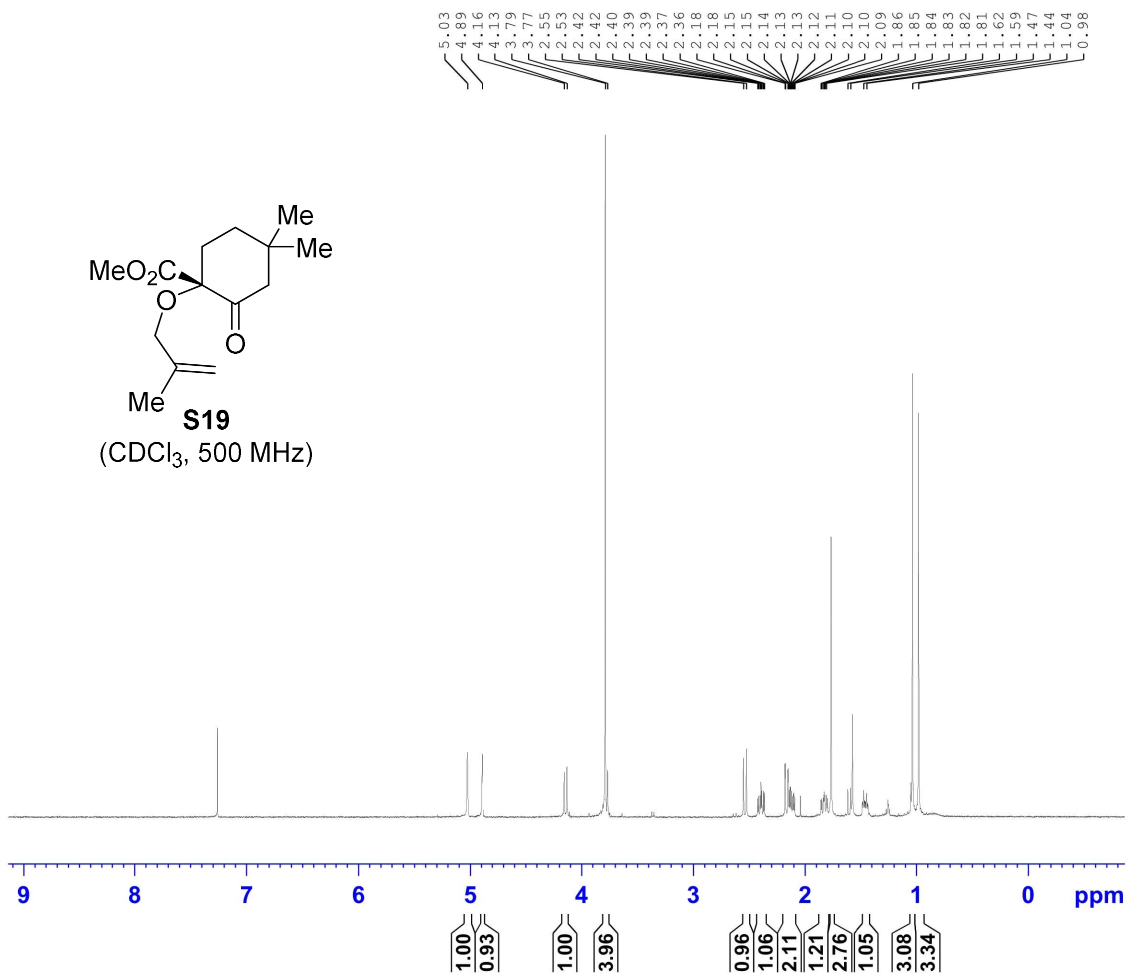

```
Current Data Parameters
NAME            yh-5-78-c
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20190712
Time                17.23
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                      3
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  297.1 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB        0
LB                   0.30 Hz
GB         0
PC                   1.40
```



S19

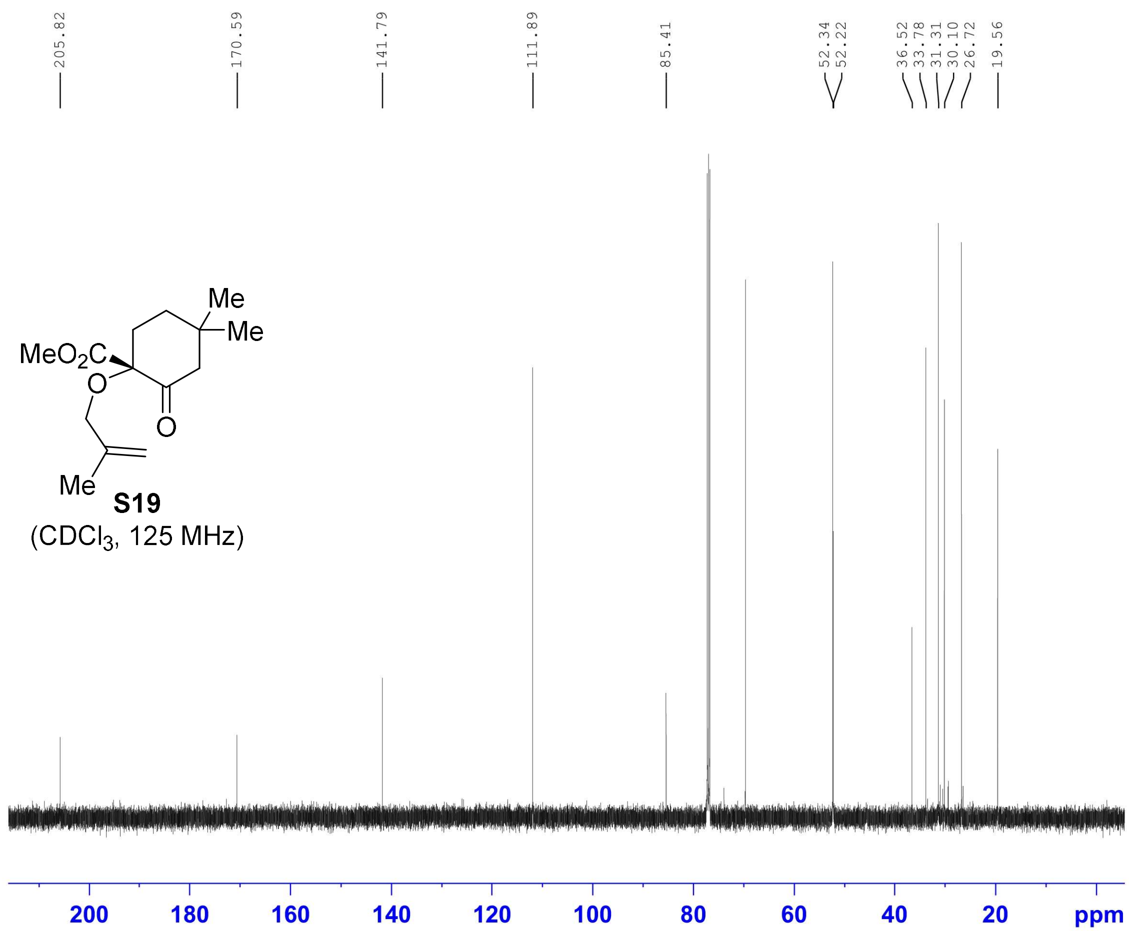
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             yh-5-86-b
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20190712
Time                 17.30
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       2
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                    0.98
DW                  50.000 usec
DE                    6.50 usec
TE                   297.1 K
D1              4.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           499.8730869 MHz
NUC1                    1H
P1                    3.58 usec
PLW1           18.25000000 W

F2 - Processing parameters
SI                   65536
SF             499.8700121 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



S19

($CDCl_3$, 125 MHz)

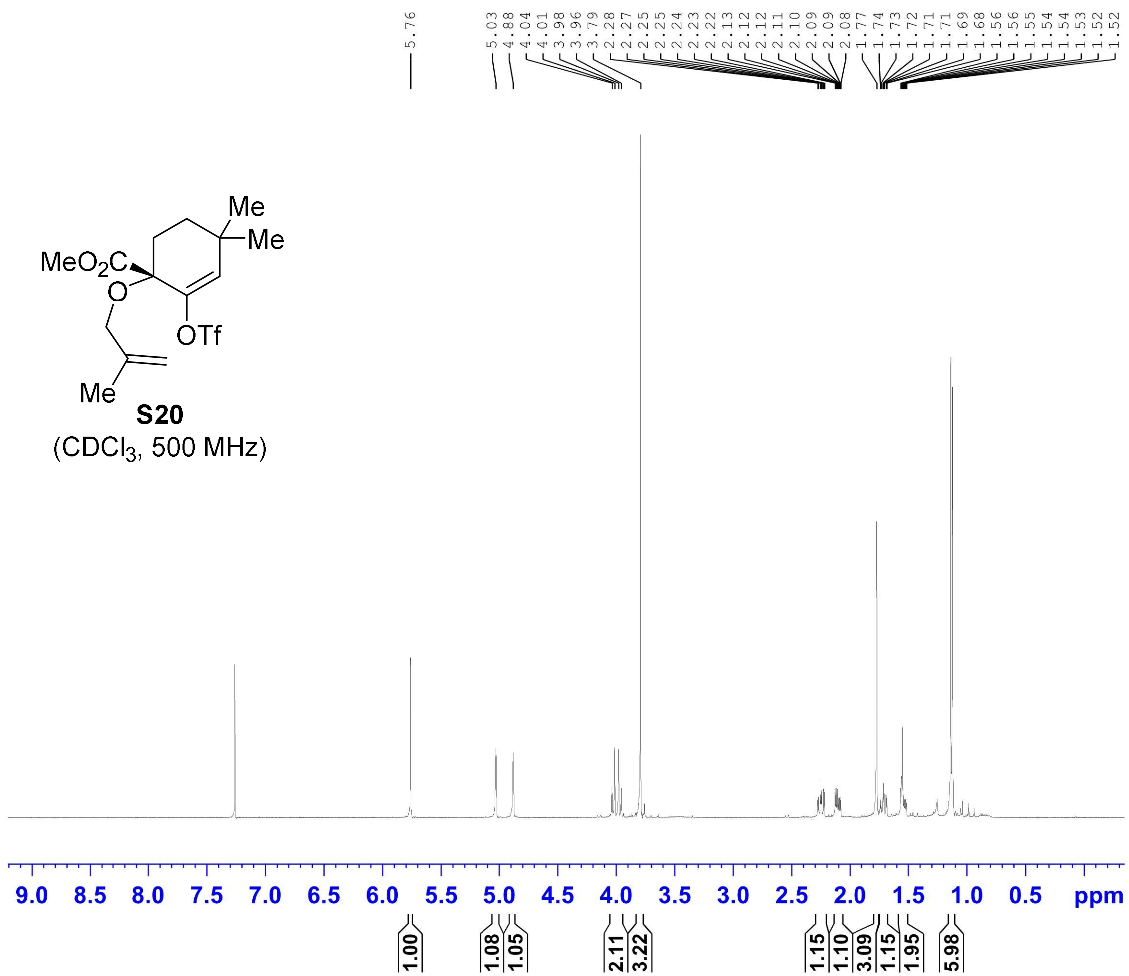
```
Current Data Parameters
NAME             yh-5-86-b
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20190712
Time                 22.36
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                     387
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   299.3 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6924115 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



S20

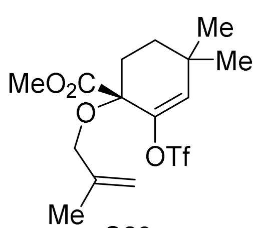
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME            yh-5-87-c
EXPNO                   1
PROCNO                  1

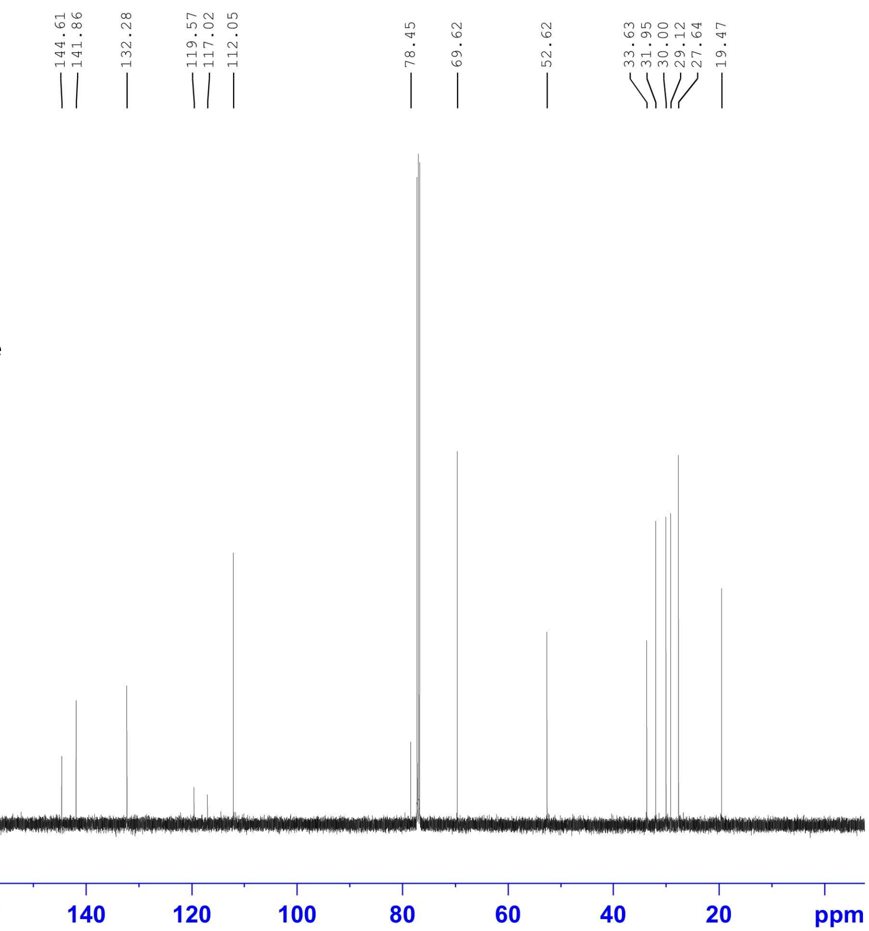
F2 - Acquisition Parameters
Date_            20190712
Time                21.21
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                 100.96
DW                 50.000 usec
DE                   6.50 usec
TE                  297.5 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF           499.8700122 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S20
($CDCl_3$, 125 MHz)



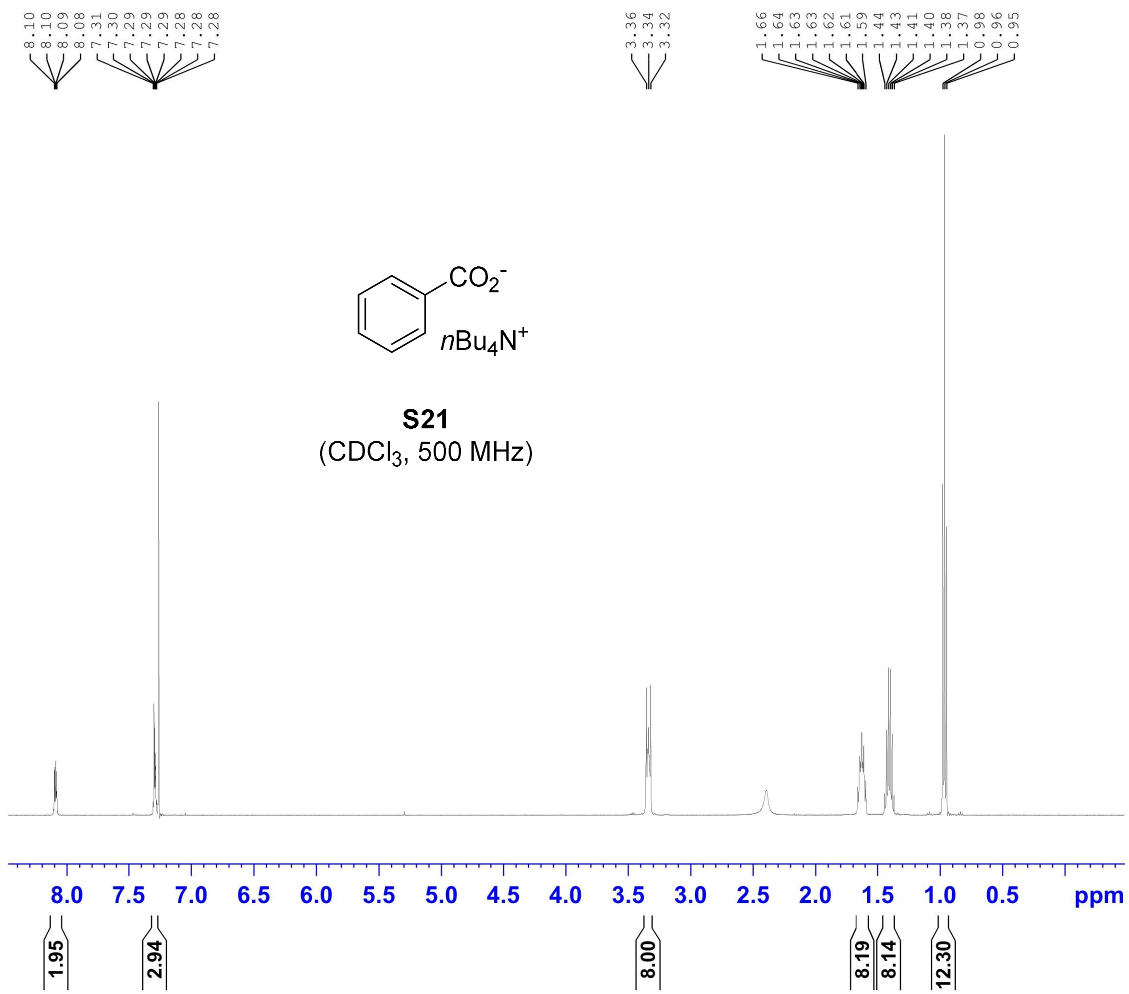

```
Current Data Parameters
NAME              yh-5-87-c
EXPNO                     3
PROCNO                    3

F2 - Acquisition Parameters
Date_              20190713
Time                   0.02
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT               CDCl3
NS                      803
DS                        0
SWH               31250.000 Hz
FIDRES             0.166670 Hz
AQ                2.9999361 sec
RG                     2050
DW                   16.000 usec
DE                     6.50 usec
TE                    299.5 K
D1               3.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            125.7049802 MHz
NUC1                    13C
P1                    10.00 usec
PLW1            72.83999634 W

======== CHANNEL f2 ========
SFO2            499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2            19.00000000 W
PLW12            0.29688001 W

F2 - Processing parameters
SI                  1048576
SF              125.6924115 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.40
```



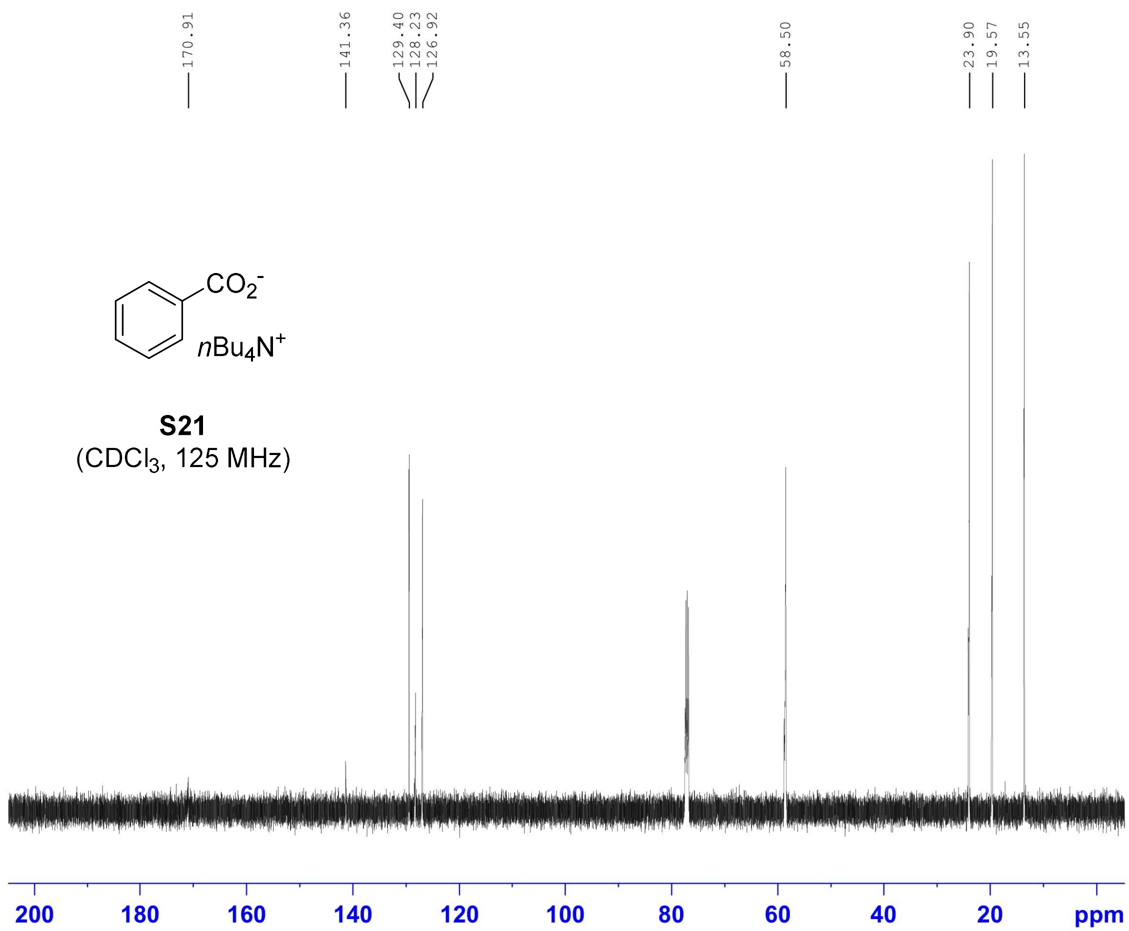
S21
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             yh-7-32-a
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20191010
Time                 13.42
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       4
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                  196.79
DW                  50.000 usec
DE                   10.00 usec
TE                   297.0 K
D1              4.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                    1H
P1                    3.30 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                   65536
SF            500.1300135 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

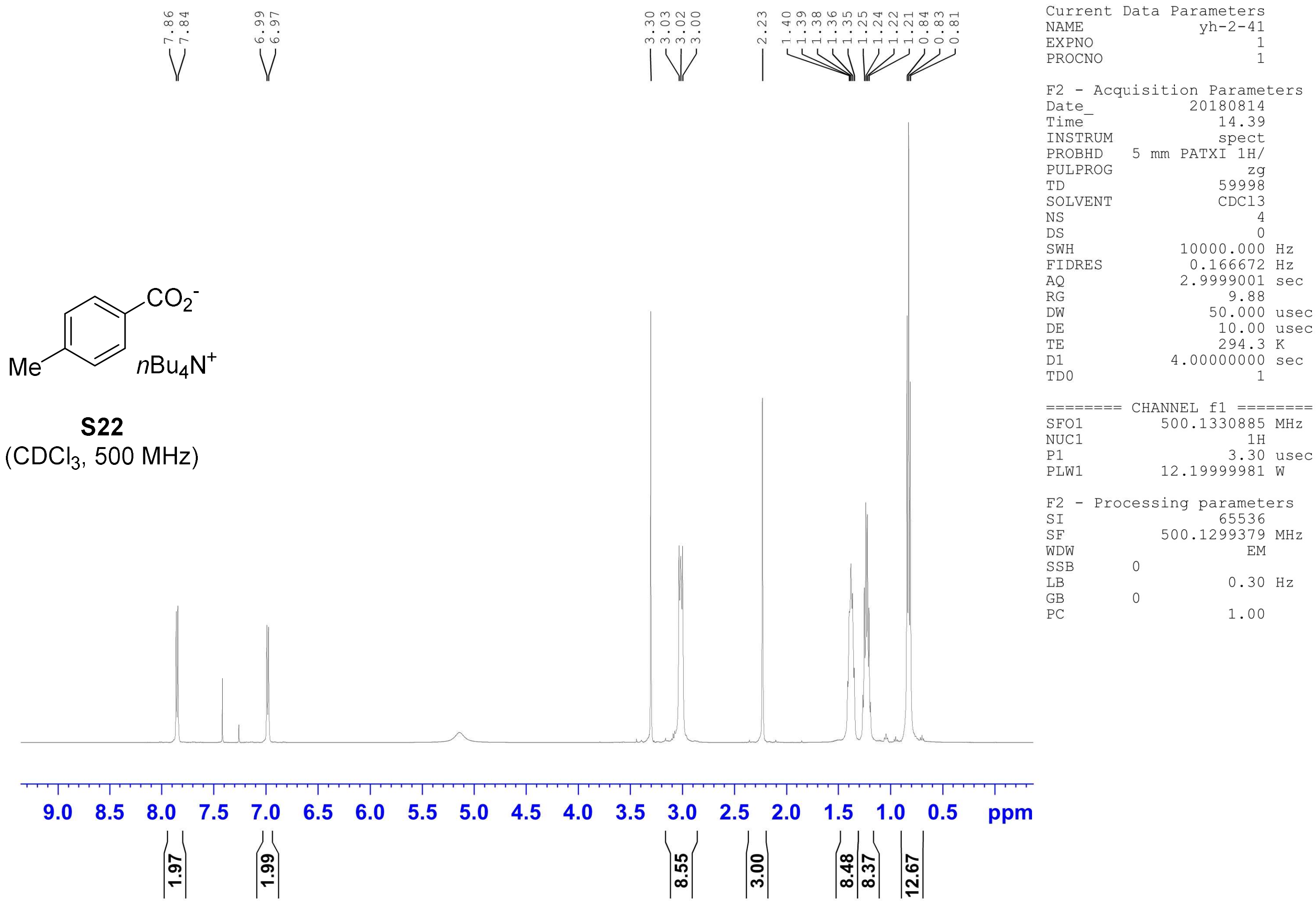


S21
($CDCl_3$, 125 MHz)

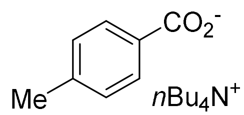
```
Current Data Parameters
NAME              yh-7-32
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20191005
Time                15.02 h
INSTRUM             spect
PROBHD   Z113652_0187 (
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    153
DS                      0
SWH             31250.000 Hz
FIDRES           0.333340 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.7 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1         125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1         72.83999634 W
SFO2         499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

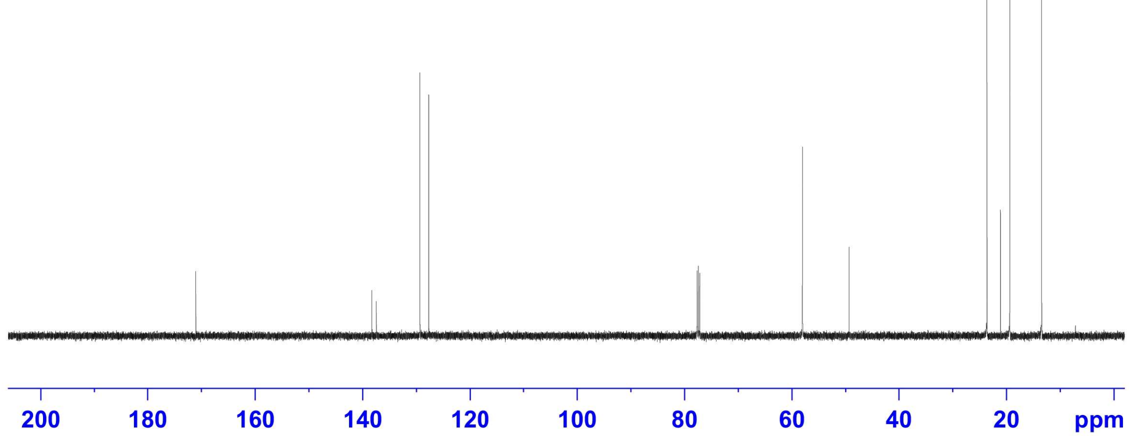
F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



S22
($CDCl_3$, 500 MHz)



S22
($CDCl_3$, 125 MHz)



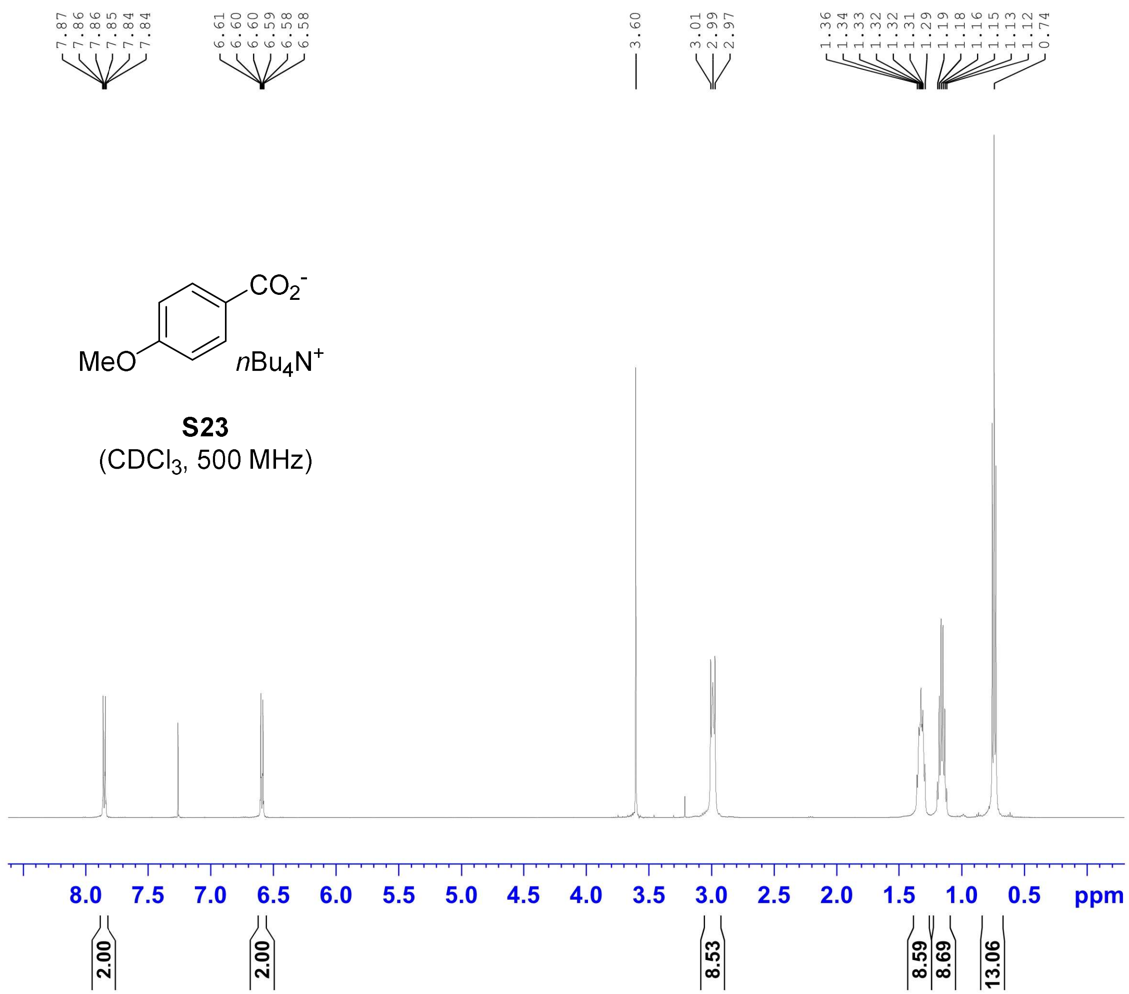

```
Current Data Parameters
NAME              yh-2-41
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180814
Time                15.10
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                      5
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  295.9 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



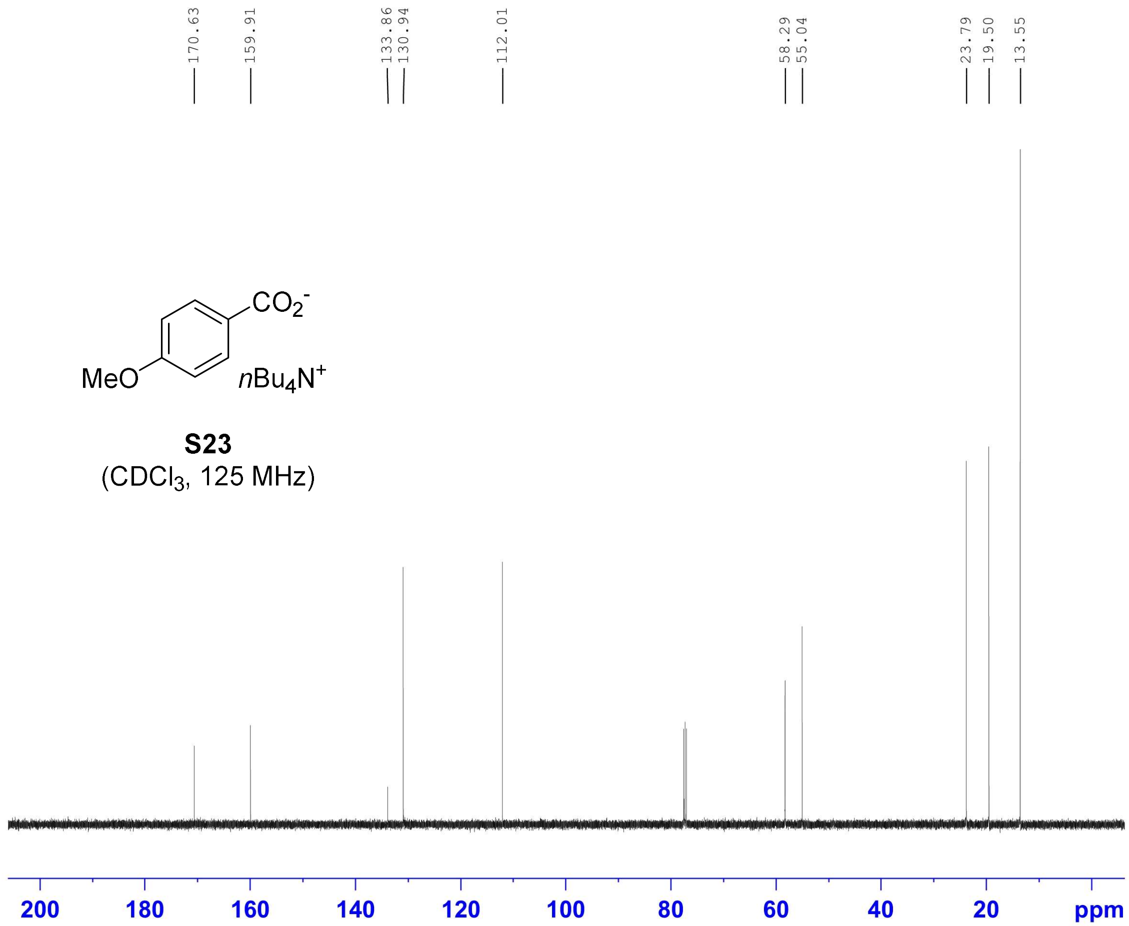
S23
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME              yh-2-29
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180827
Time                20.40
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      1
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  13.94
DW                 50.000 usec
DE                   6.50 usec
TE                  296.3 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF           499.8700148 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S23
($CDCl_3$, 125 MHz)

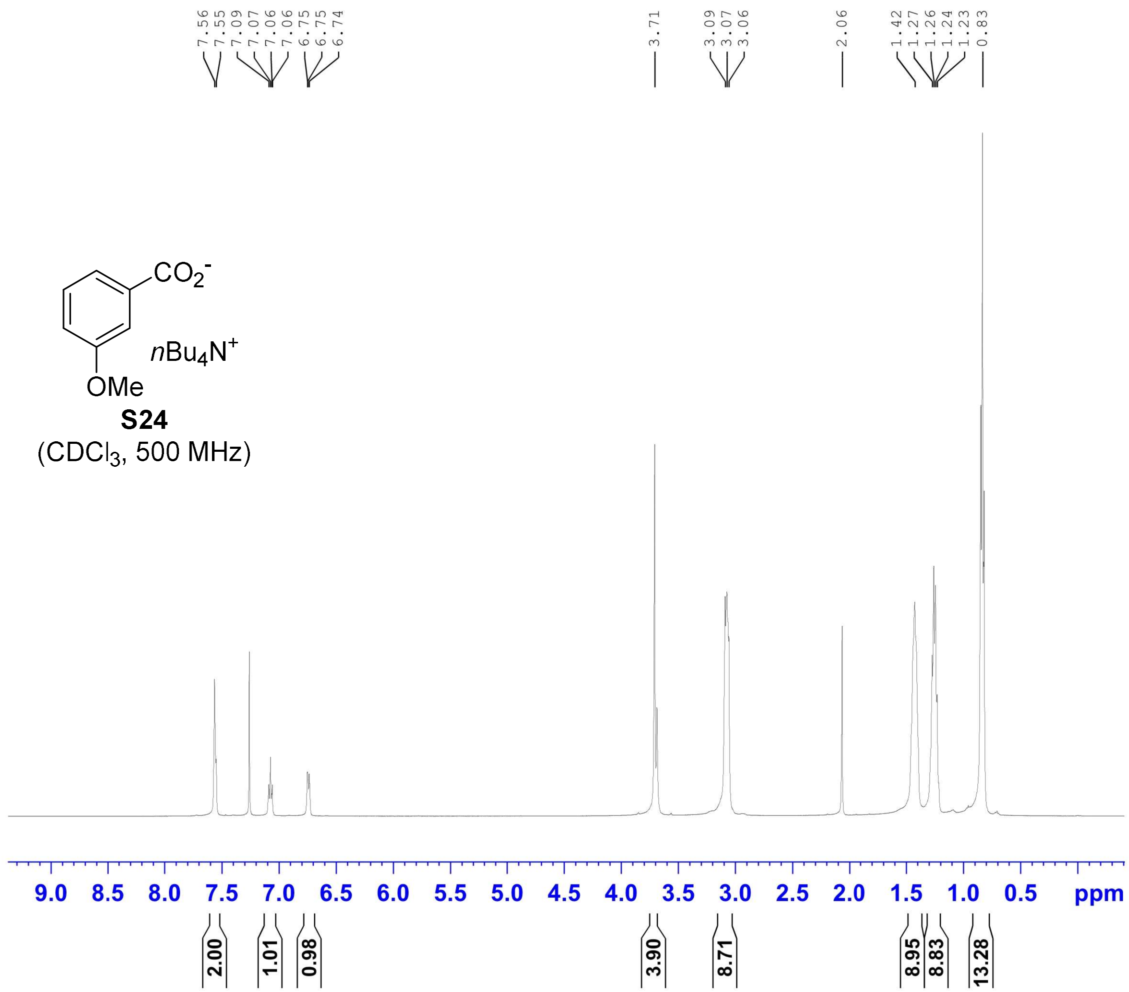
```
Current Data Parameters
NAME              yh-2-29
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180827
Time                20.44
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                      4
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.3 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



S24

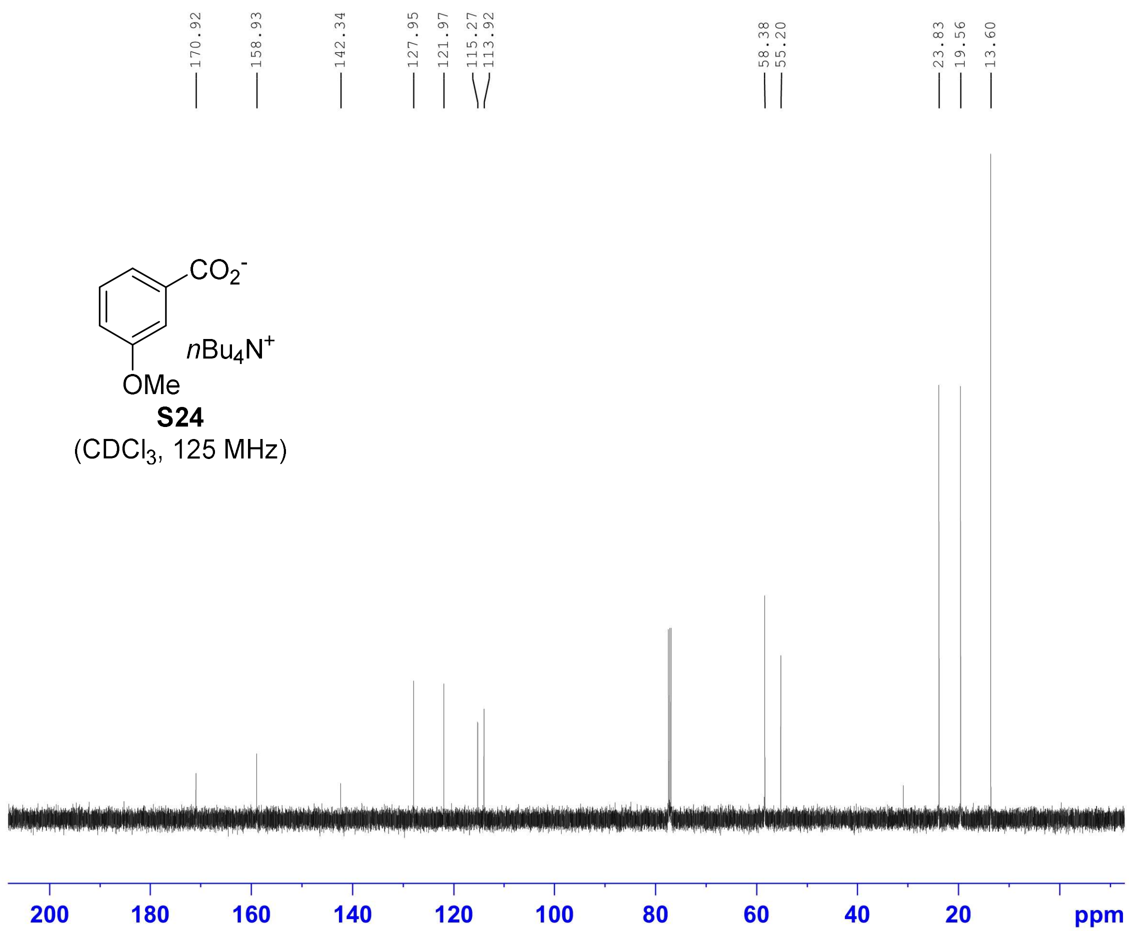
(CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME              yh-2-58
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180814
Time                21.20
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  22.37
DW                 50.000 usec
DE                   6.50 usec
TE                  295.9 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700130 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



nBu_4N^+

S24

($CDCl_3$, 125 MHz)

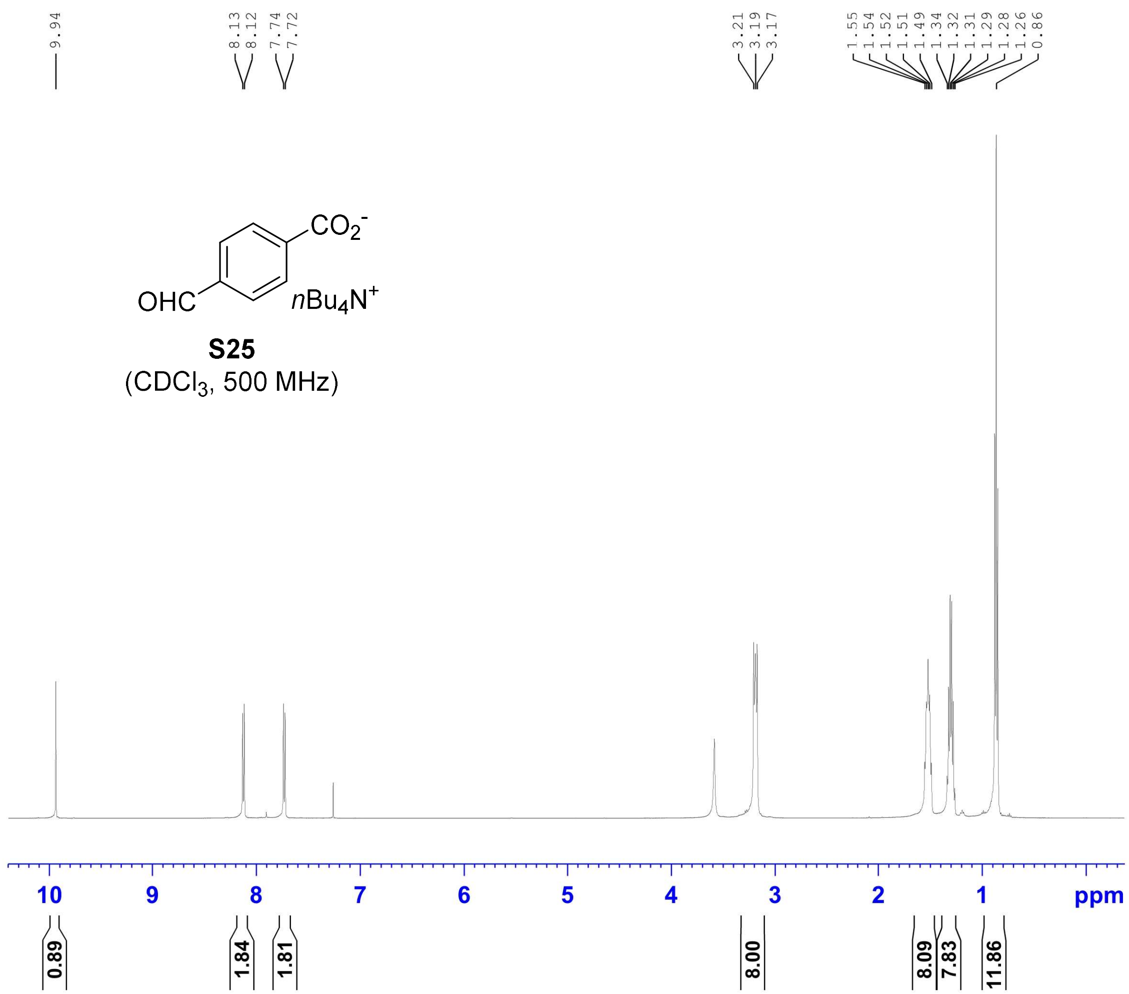
```
Current Data Parameters
NAME              yh-2-58
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180814
Time                21.25
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                      6
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.0 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



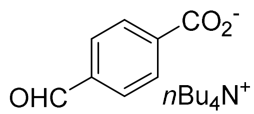
S25
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             yh-2-75
EXPNO                  1
PROCNO                 1

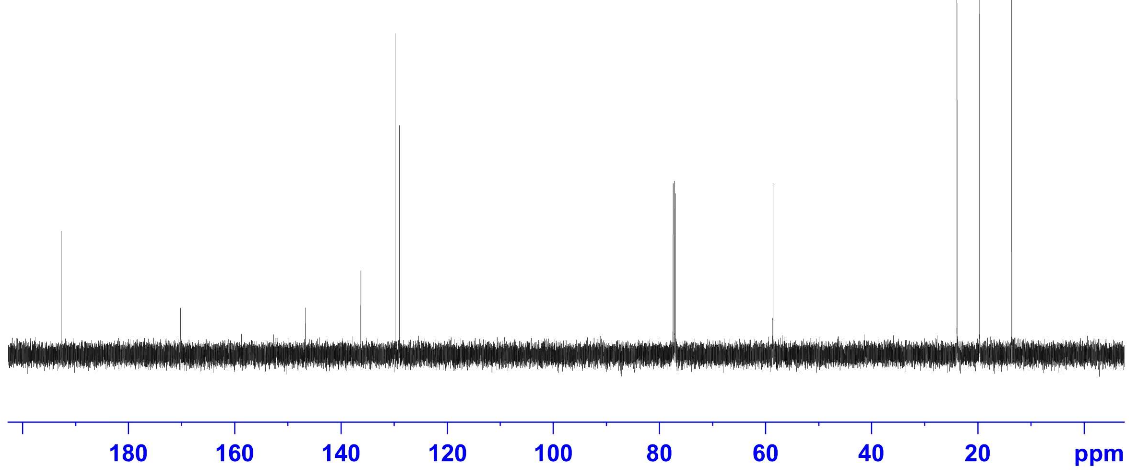
F2 - Acquisition Parameters
Date_           20180814
Time               22.45
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     1
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 25.24
DW                50.000 usec
DE                  6.50 usec
TE                 296.1 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700126 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



S25
($CDCl_3$, 125 MHz)



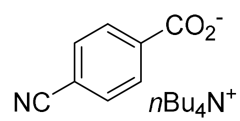

```
Current Data Parameters
NAME              yh-2-75
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180814
Time                22.48
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                      3
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.1 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

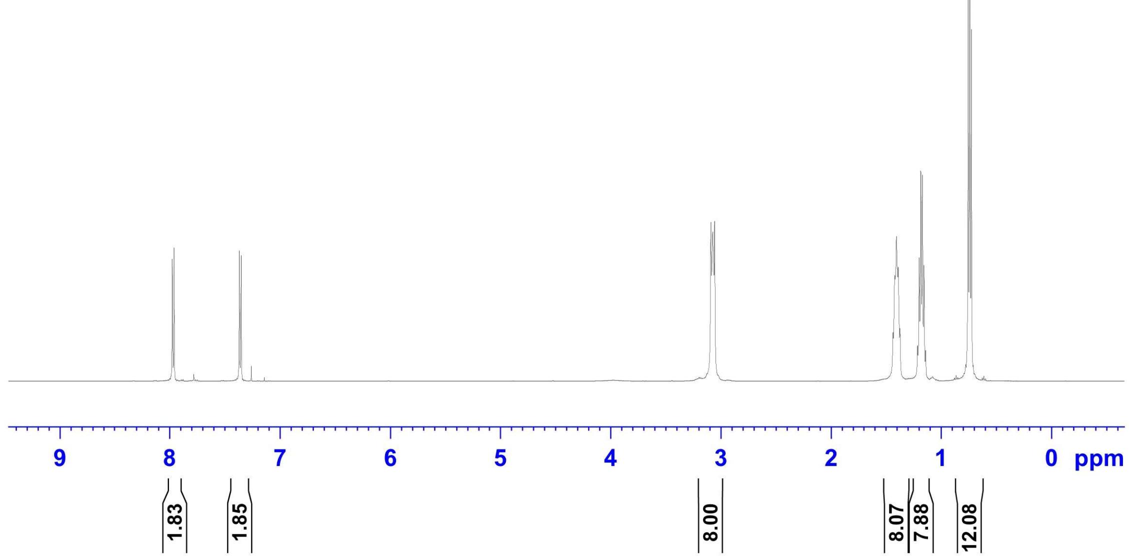
======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



S26

($CDCl_3$, 500 MHz)

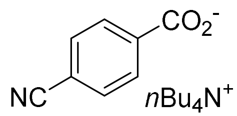



```
Current Data Parameters
NAME              yh-2-53
EXPNO                   1
PROCNO                  1

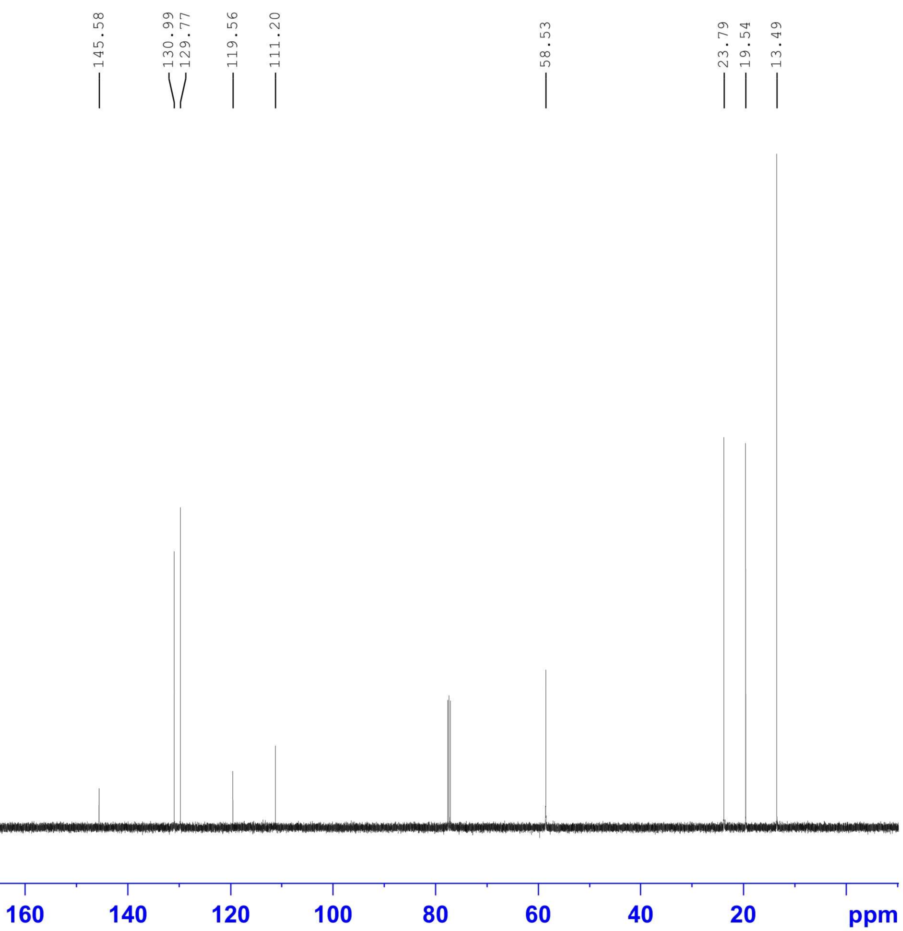
F2 - Acquisition Parameters
Date_            20180814
Time                16.03
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      1
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  13.94
DW                 50.000 usec
DE                   6.50 usec
TE                  295.8 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700143 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S26
($CDCl_3$, 125 MHz)



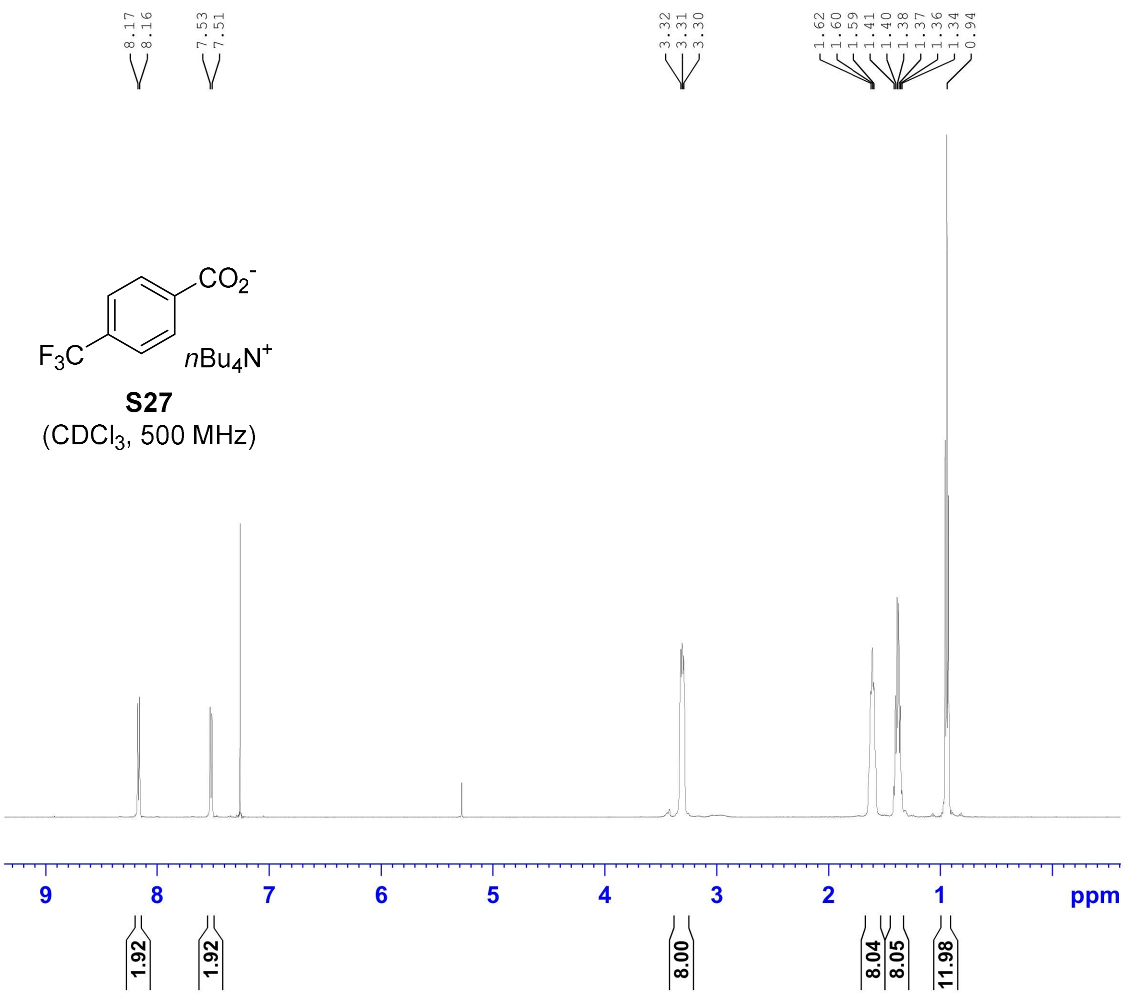

```
Current Data Parameters
NAME             yh-2-53
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180814
Time               16.07
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                     3
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 295.8 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```



S27

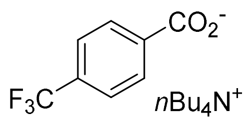
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME           yh-2-40-a
EXPNO                  1
PROCNO                 1

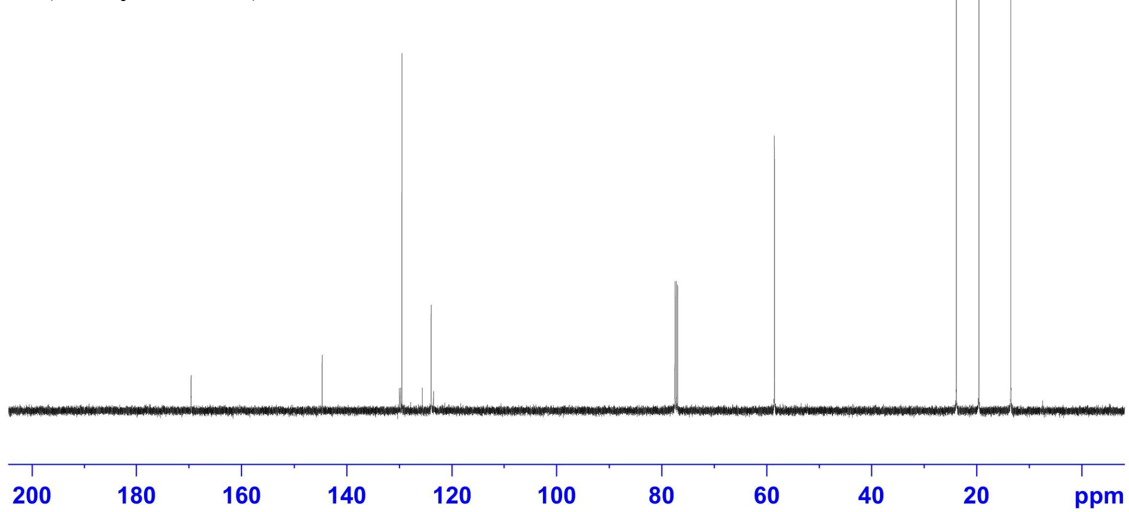
F2 - Acquisition Parameters
Date_           20180829
Time               22.24
INSTRUM            spect
PROBHD   5 mm PATXI 1H/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     1
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 97.37
DW                50.000 usec
DE                 10.00 usec
TE                 294.1 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                  1H
P1                  3.30 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                 65536
SF           500.1300140 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



S27
($CDCl_3$, 125 MHz)



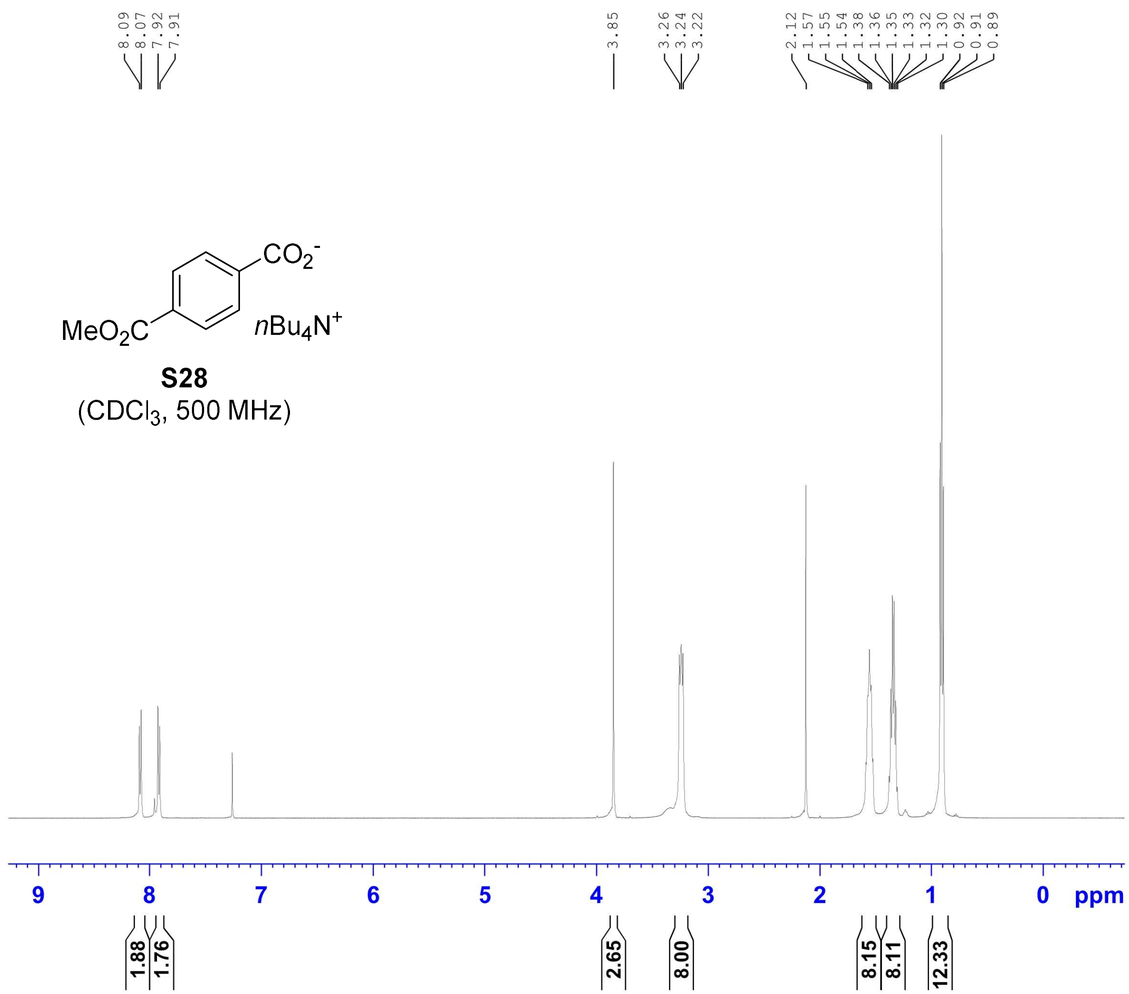

```
Current Data Parameters
NAME            yh-2-40-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180829
Time                22.11
INSTRUM             spect
PROBHD   5 mm PAQNP 1H/
PULPROG              zgpg
TD                 197364
SOLVENT             CDCl3
NS                     42
DS                      0
SWH             32894.738 Hz
FIDRES           0.166670 Hz
AQ              2.9999328 sec
RG                   2050
DW                 15.200 usec
DE                   6.00 usec
TE                  295.8 K
D1            10.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.90 usec
PL1                  1.00 dB
PL1W          72.42802429 W
SFO1         125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2       0 dB
PL12                16.50 dB
PL13                17.00 dB
PL2W          24.54113007 W
PL12W          0.54940748 W
PL13W          0.48965994 W
SFO2         500.1325006 MHz

F2 - Processing parameters
SI                 131072
SF           125.7577890 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.40
```



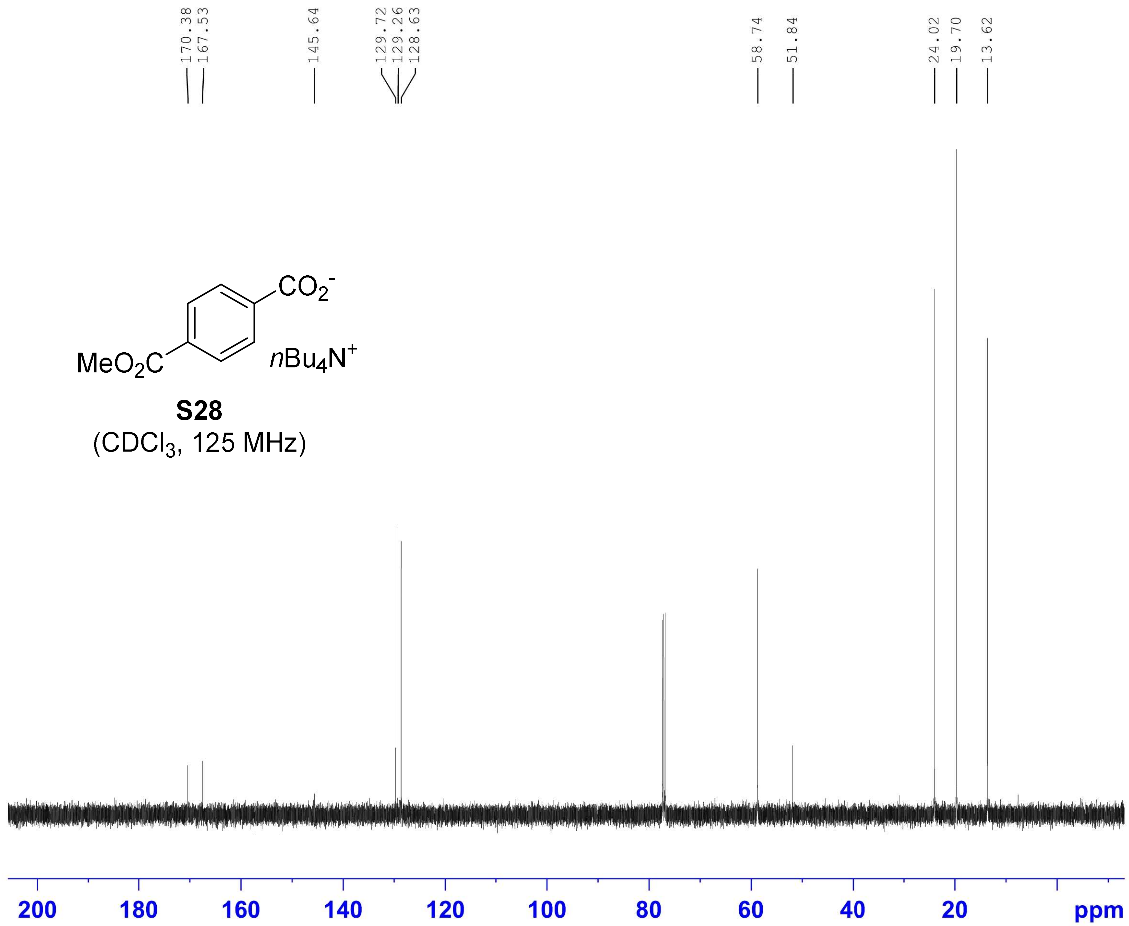
S28
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME              yh-2-65
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180814
Time                21.31
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  44.57
DW                 50.000 usec
DE                   6.50 usec
TE                  296.0 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700123 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S28
($CDCl_3$, 125 MHz)

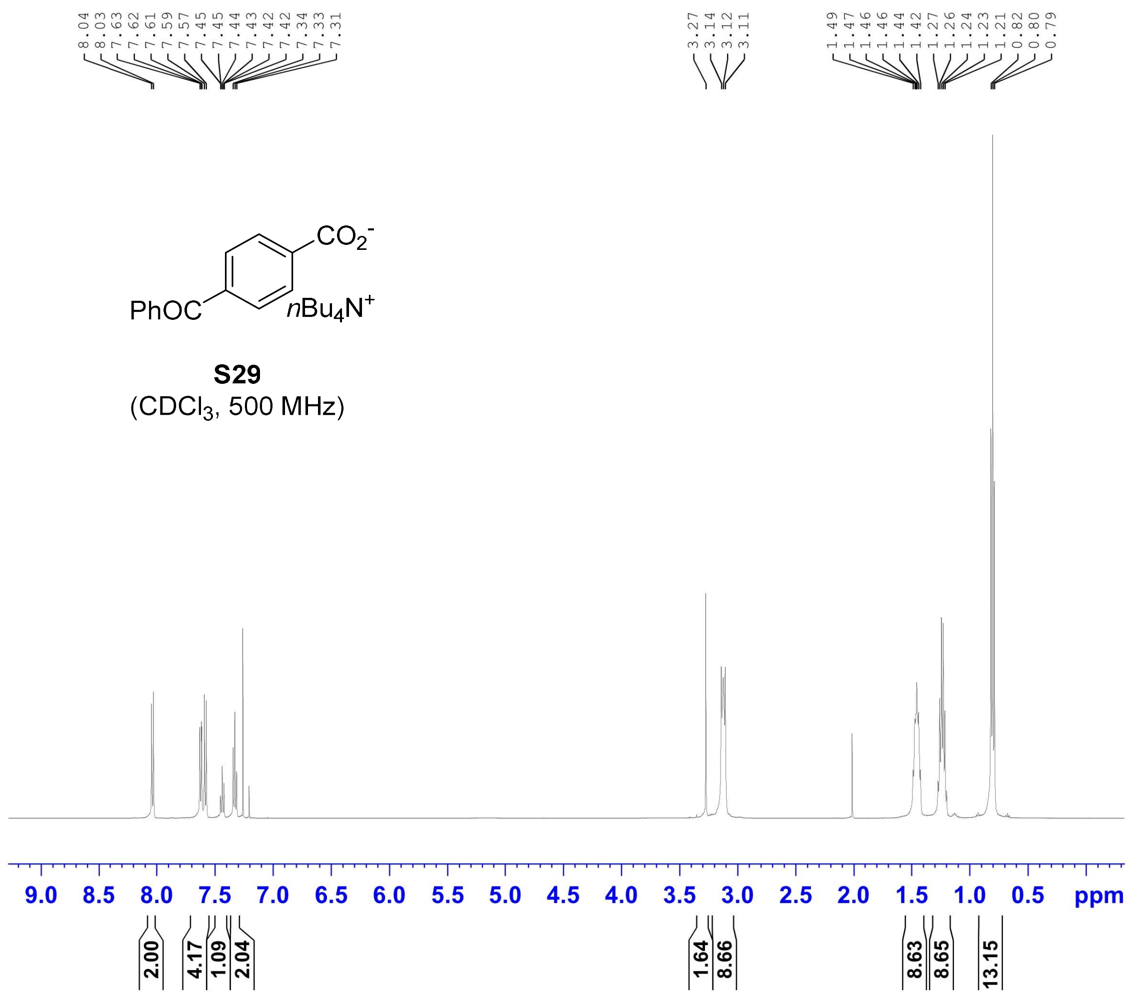
```
Current Data Parameters
NAME              yh-2-65
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180814
Time                21.45
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                     47
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.8 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



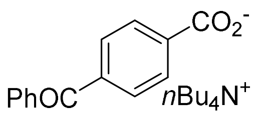
S29
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             yh-2-70
EXPNO                  1
PROCNO                 1

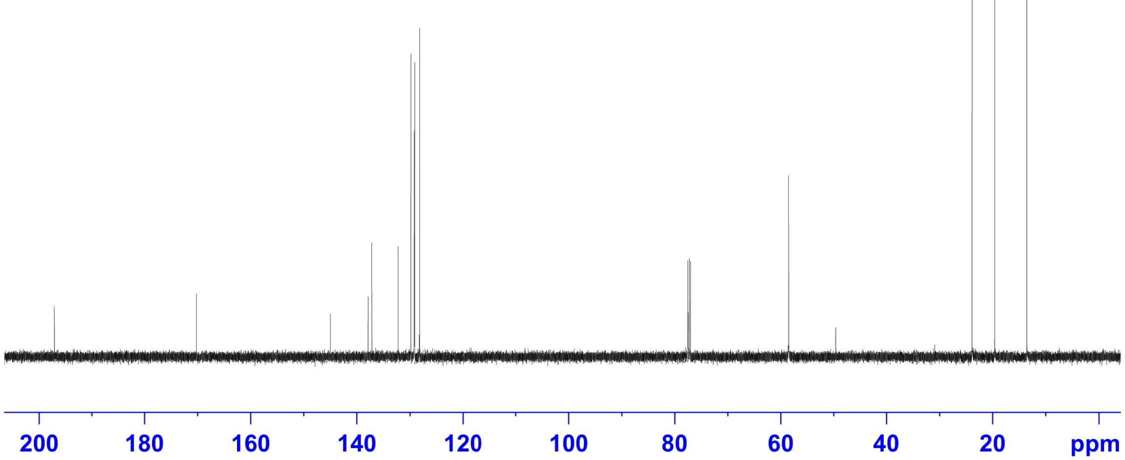
F2 - Acquisition Parameters
Date_           20180814
Time               21.49
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     3
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 15.35
DW                50.000 usec
DE                  6.50 usec
TE                 296.4 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700134 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



S29
($CDCl_3$, 125 MHz)



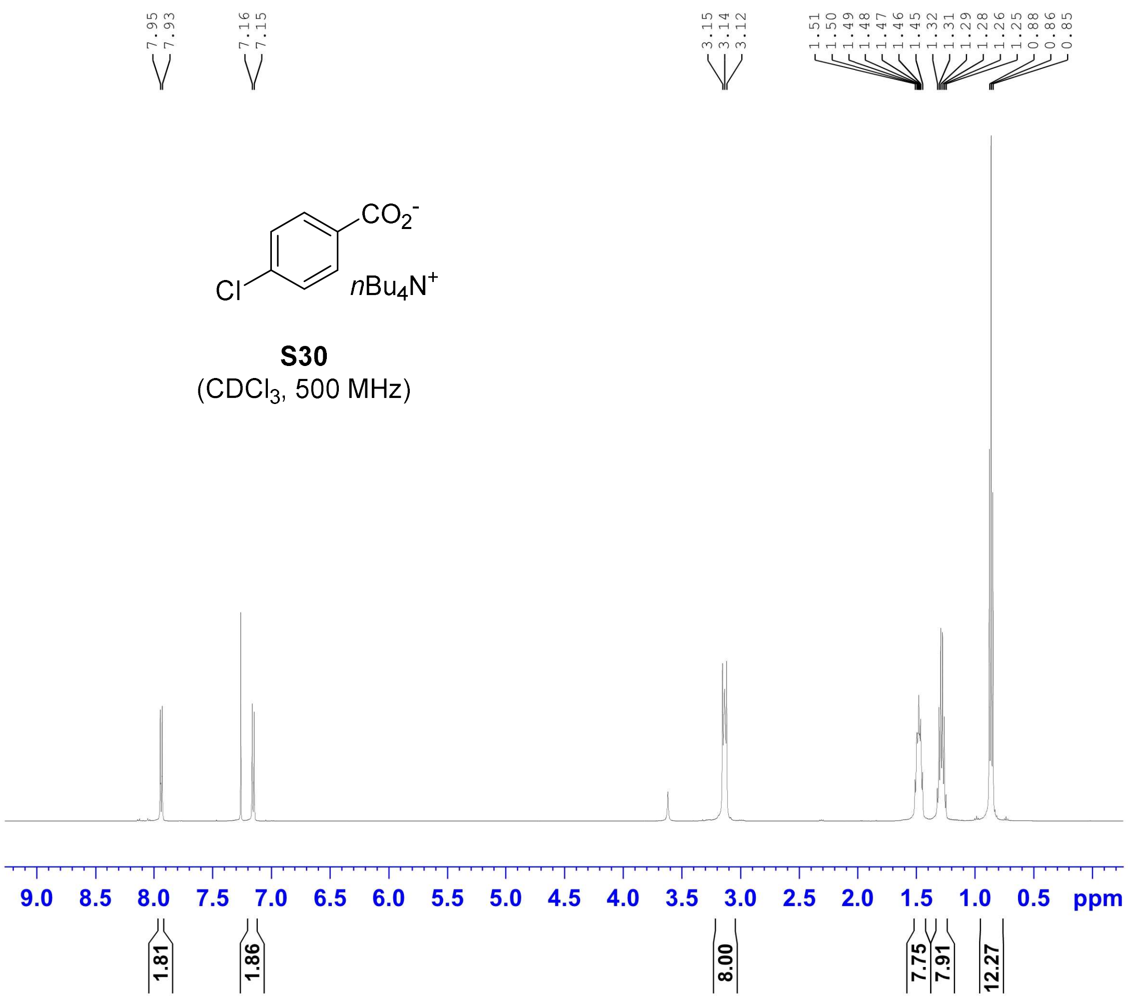

```
Current Data Parameters
NAME             yh-2-70
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180814
Time               21.59
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                     6
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 296.4 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```

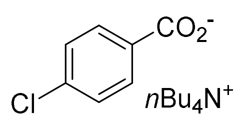



```
Current Data Parameters
NAME            yh-2-44
EXPNO                 1
PROCNO                1

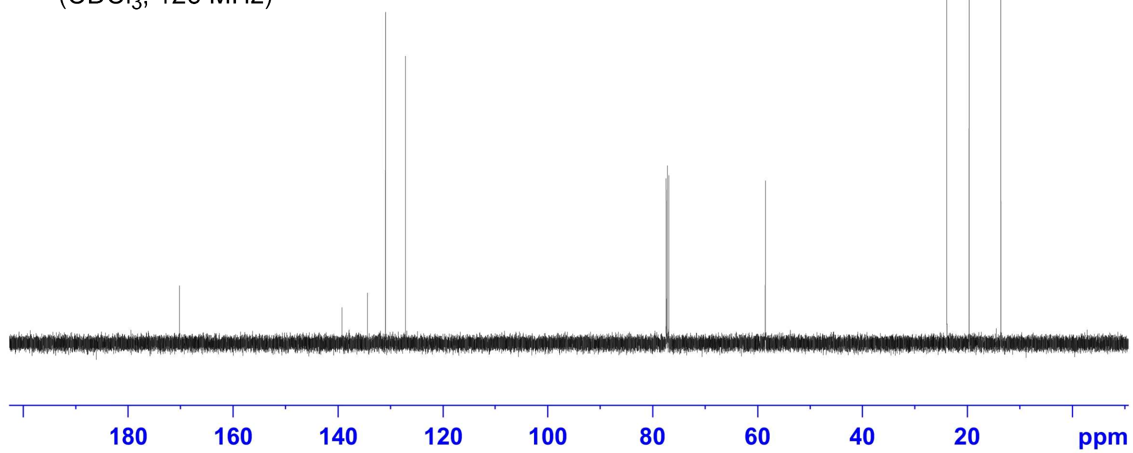
F2 - Acquisition Parameters
Date_          20180814
Time              15.54
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    6
DS                    0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                25.24
DW               50.000 usec
DE                 6.50 usec
TE                295.7 K
D1           4.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                 1H
P1                 3.58 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                65536
SF          499.8700130 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



S30
($CDCl_3$, 125 MHz)



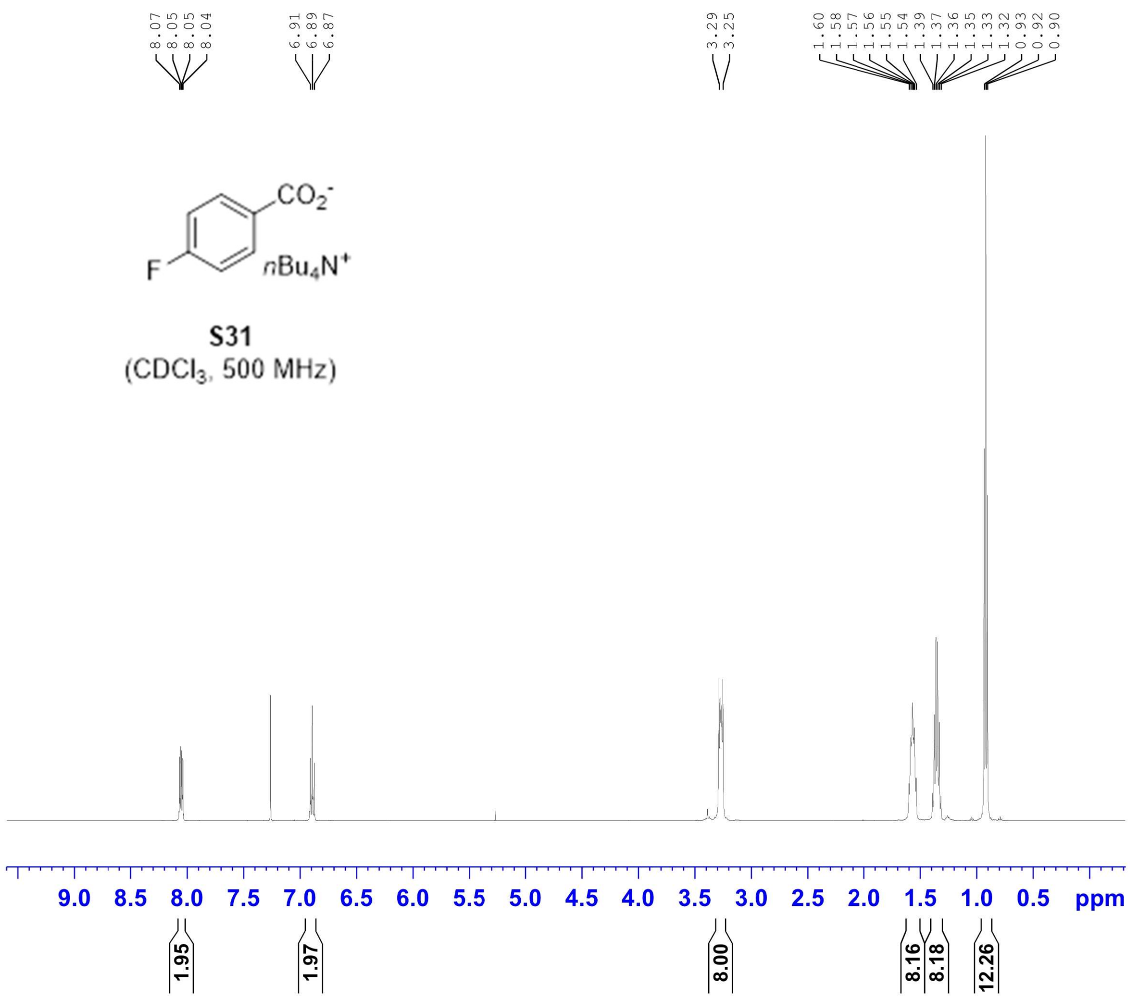

```
Current Data Parameters
NAME             yh-2-44
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180814
Time               15.58
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                     4
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 295.8 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```



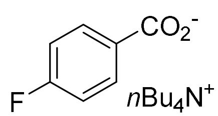
S31
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             yh-2-51-a
EXPNO                    1
PROCNO                   1

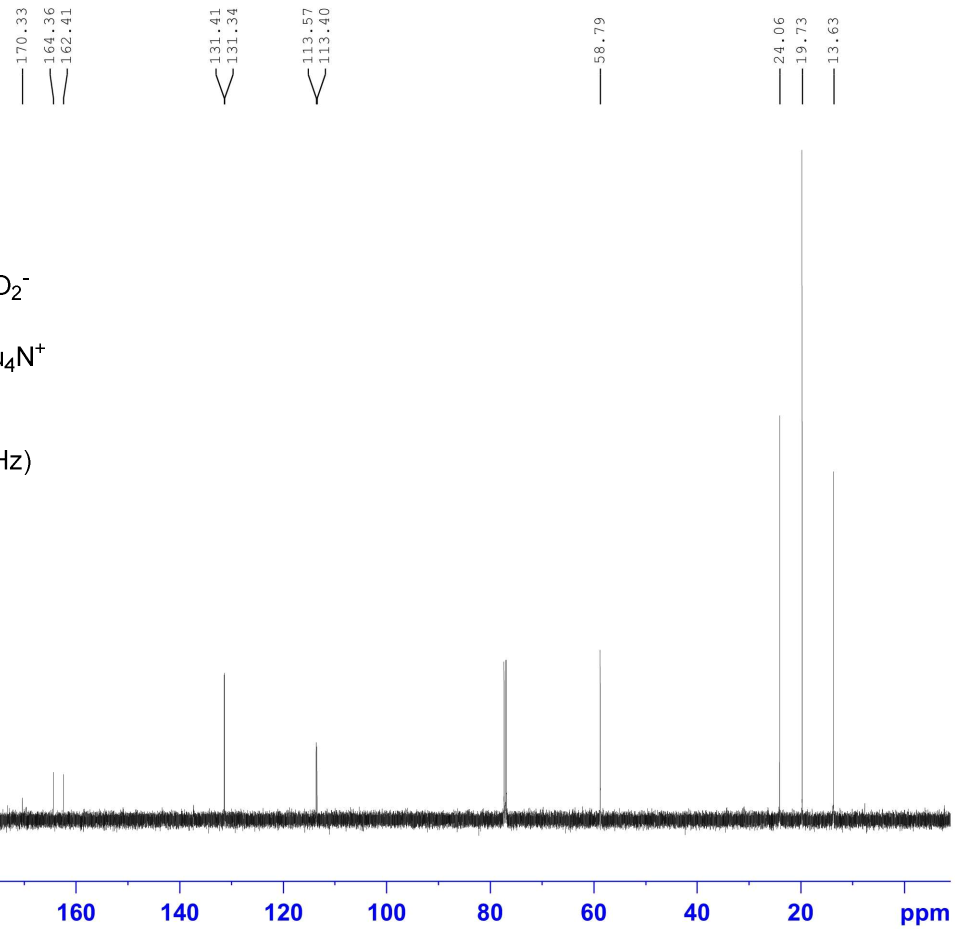
F2 - Acquisition Parameters
Date_             20180829
Time                 19.37
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       2
DS                       0
SWH          10000.000 Hz
FIDRES        0.166672 Hz
AQ           2.9999001 sec
RG                   71.78
DW              50.000 usec
DE               10.00 usec
TE                294.2 K
D1          4.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1       500.1330885 MHz
NUC1                    1H
P1                3.30 usec
PLW1       12.19999981 W

F2 - Processing parameters
SI                   65536
SF         500.1300143 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```



S31
($CDCl_3$, 125 MHz)



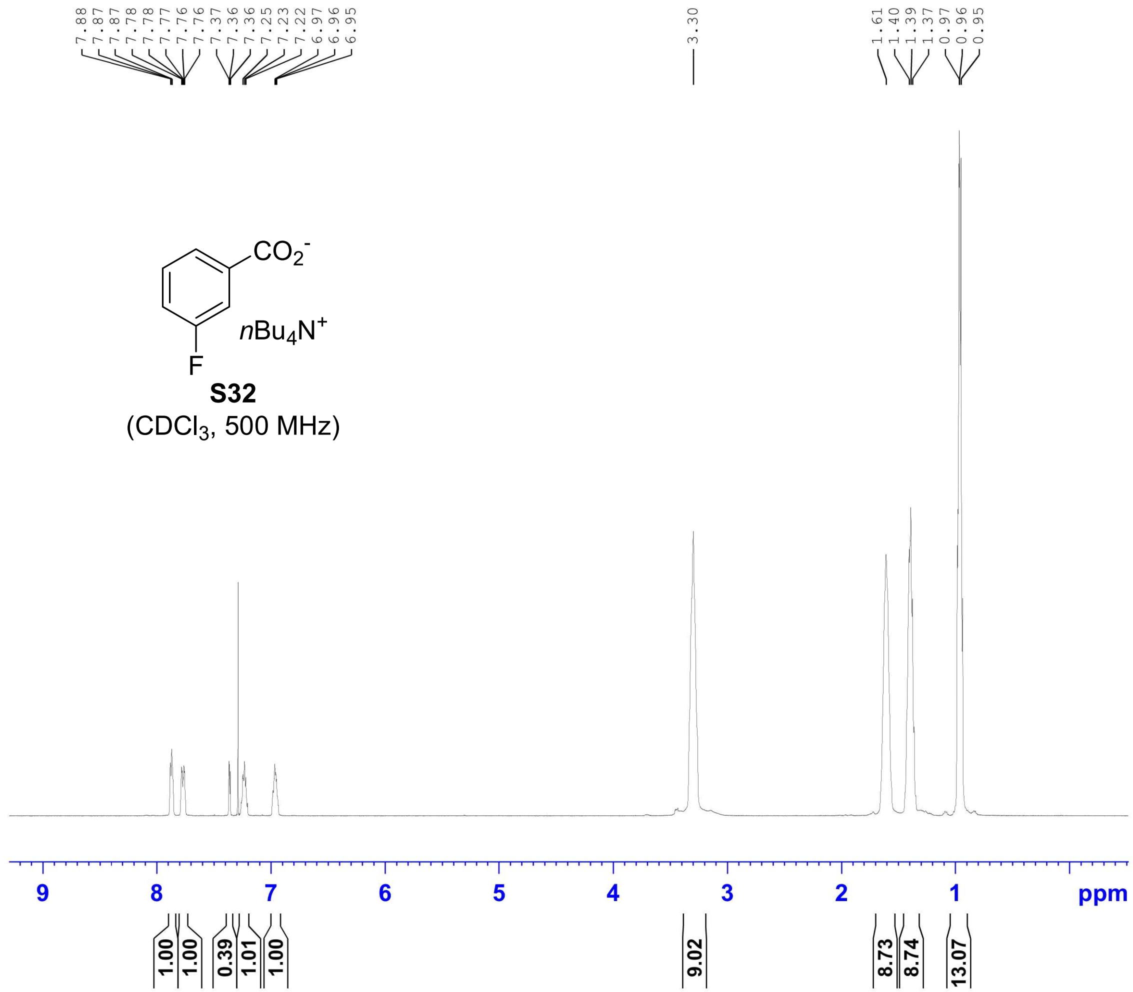

```
Current Data Parameters
NAME            yh-2-51-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180829
Time                19.56
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                     52
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.7 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```

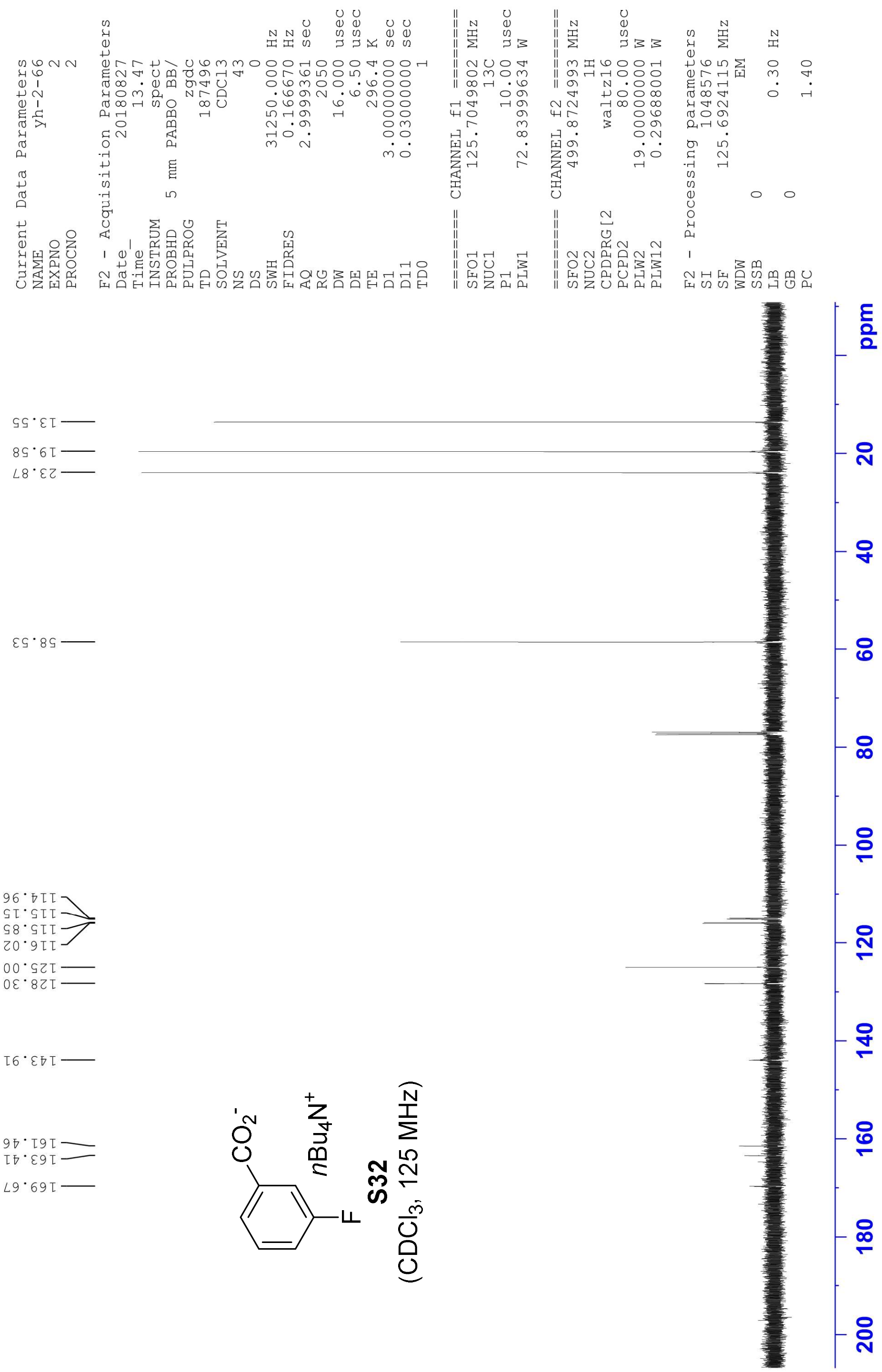


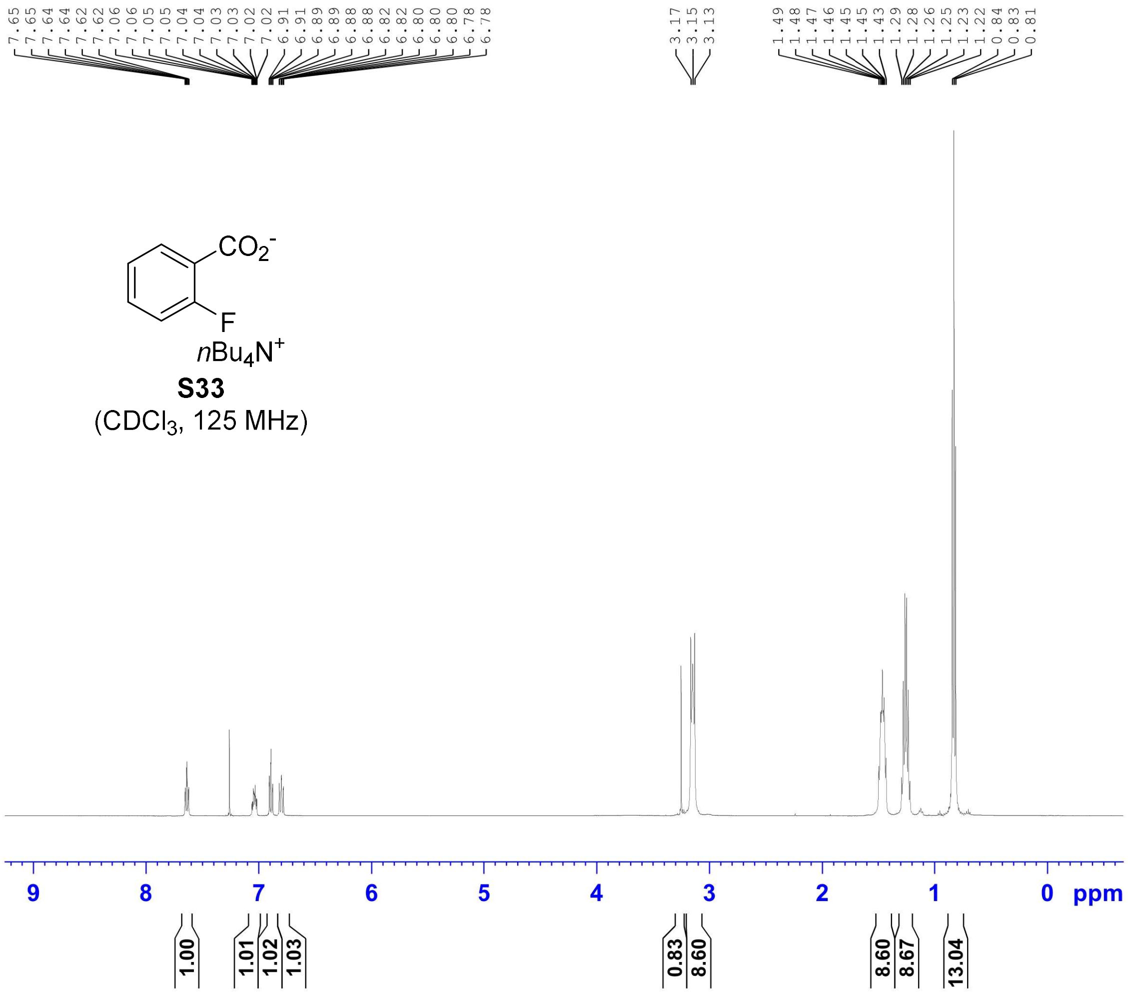

```
Current Data Parameters
NAME            yh-2-66-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180829
Time                22.43
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  79.04
DW                 50.000 usec
DE                  10.00 usec
TE                  294.2 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                   3.30 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                  65536
SF            500.1300000 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```


Current Data Parameters
NAME yh-2-66
EXPNO 2
PROCNO 2
F2 - Acquisition Parameters
Date_ 20180827
Time_ 13.47
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 43
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 296.4 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6924115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
13.55
19.58
23.87
58.53
114.96
115.15
115.85
116.02
125.00
128.30
143.91
161.46
163.41
169.67
CO2-
nBu4N+
F
S32
(CDCl3, 125 MHz)
ppm
20
40
60
80
100
120
140
160
180
200



S33

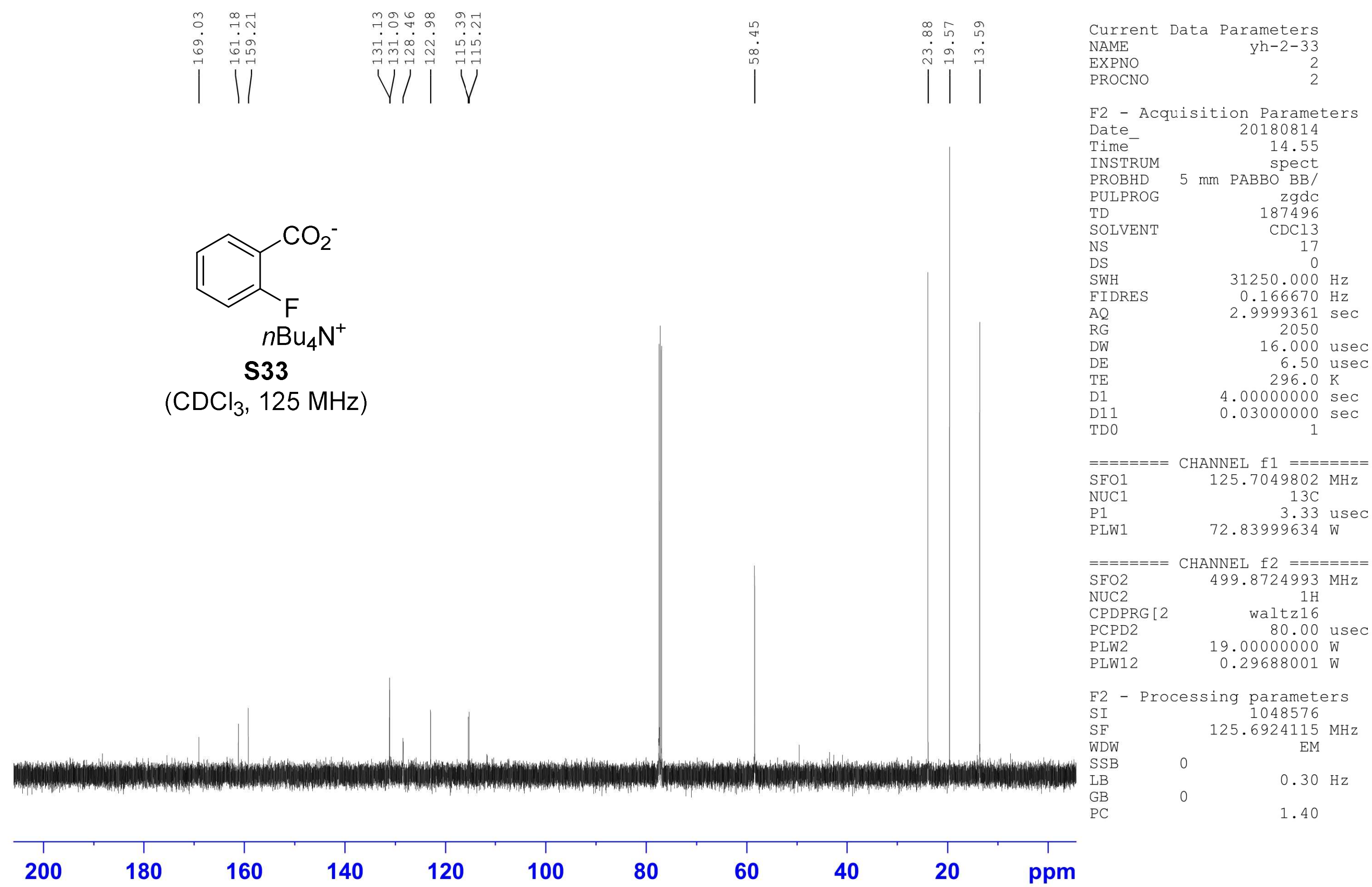
($CDCl_3$, 125 MHz)


```
Current Data Parameters
NAME             yh-2-33
EXPNO                  1
PROCNO                 1

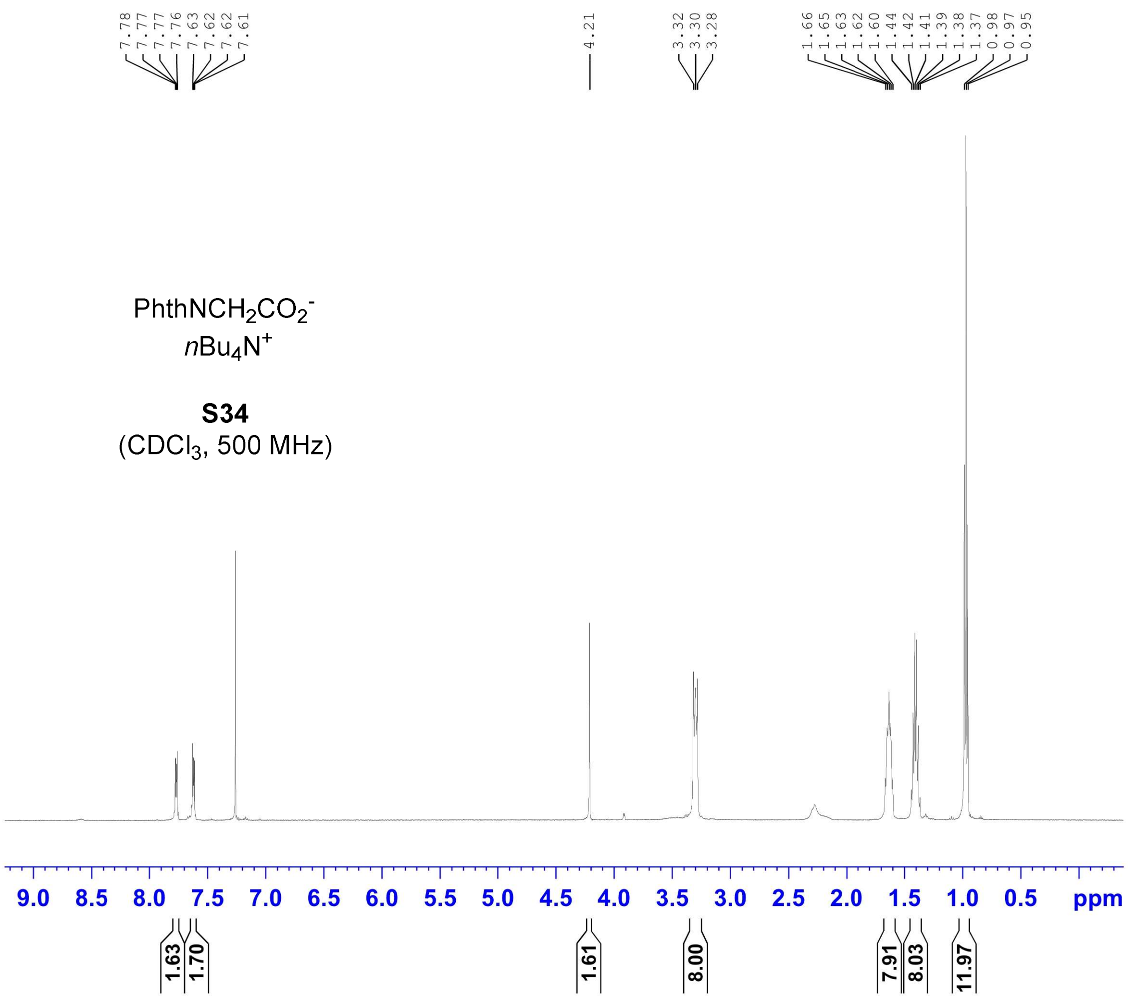
F2 - Acquisition Parameters
Date_           20180814
Time               14.28
INSTRUM            spect
PROBHD   5 mm PATXI 1H/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     1
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 20.66
DW                50.000 usec
DE                 10.00 usec
TE                 294.3 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                  1H
P1                  3.30 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                 65536
SF          500.1300150 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



169.03
161.18
159.21
131.13
131.09
128.46
122.98
115.39
115.21
58.45
23.88
19.57
13.59
CO_2^-
F
nBu$_4$N$^+$
S33
($CDCl_3$, 125 MHz)
Current Data Parameters
NAME yh-2-33
EXPNO 2
PROCNO 2
F2 - Acquisition Parameters
Date_ 20180814
Time_ 14.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 17
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 296.0 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 3.33 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6924115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm



$PhthNCH_2CO_2^-$
$n Bu_4N^+$

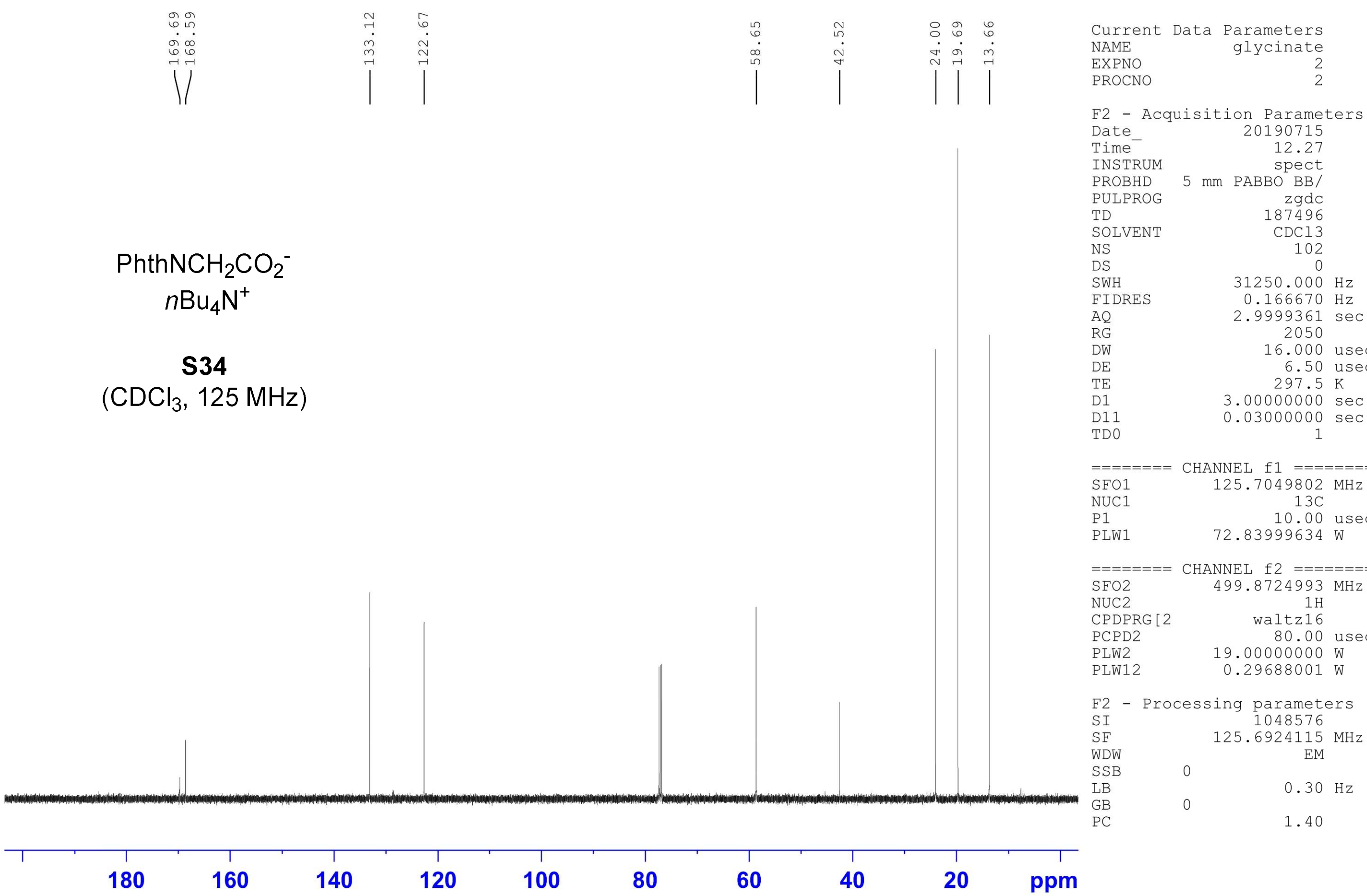
S34
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME            glycinate
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190715
Time                11.52
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      4
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                 159.35
DW                 50.000 usec
DE                   6.50 usec
TE                  295.7 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700120 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

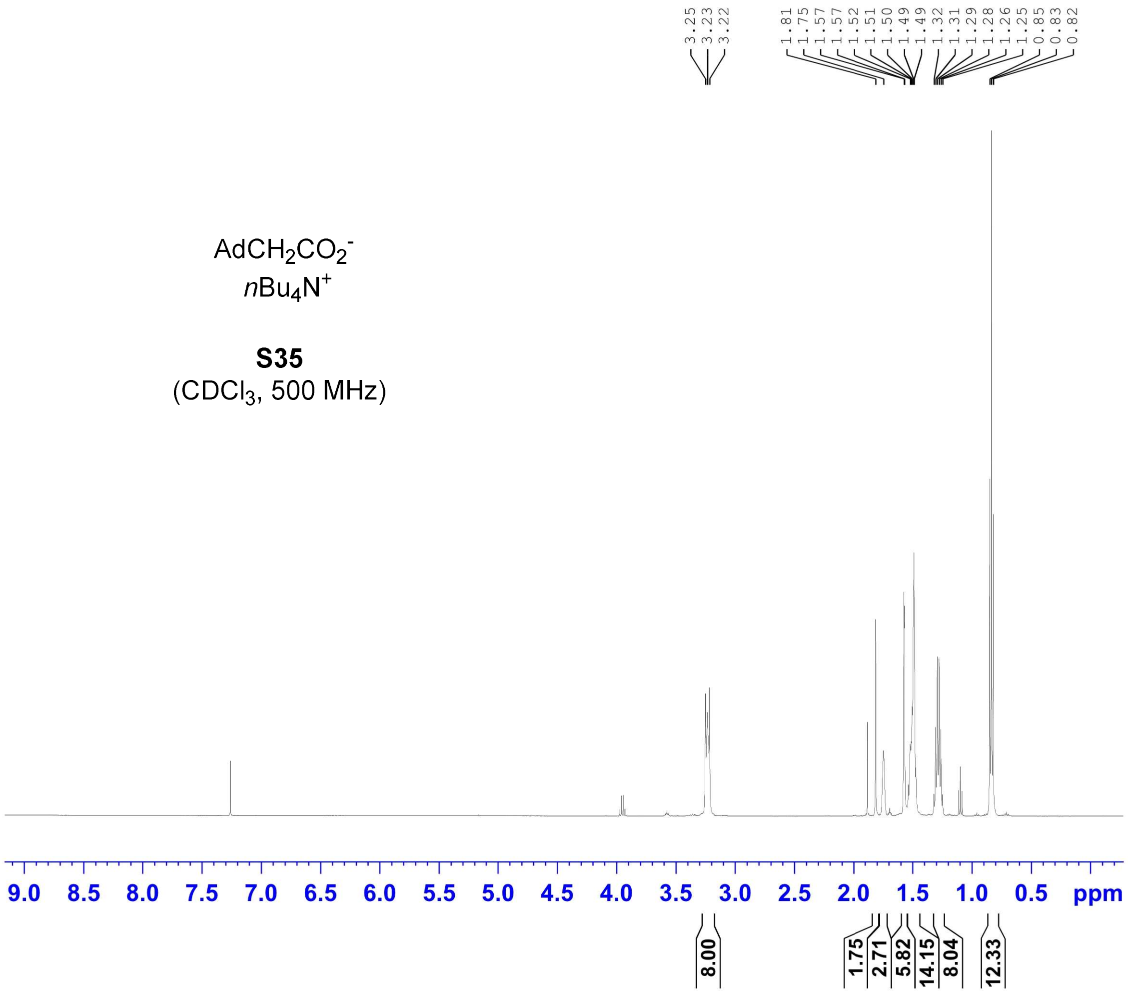


$PhthNCH_2CO_2^-$
$n$$Bu_4N^+$

S34
($CDCl_3$, 125 MHz)

AdCH$_2$CO$_2^-$
nBu$_4$N$^+$

S35
(CDCl$_3$, 500 MHz)

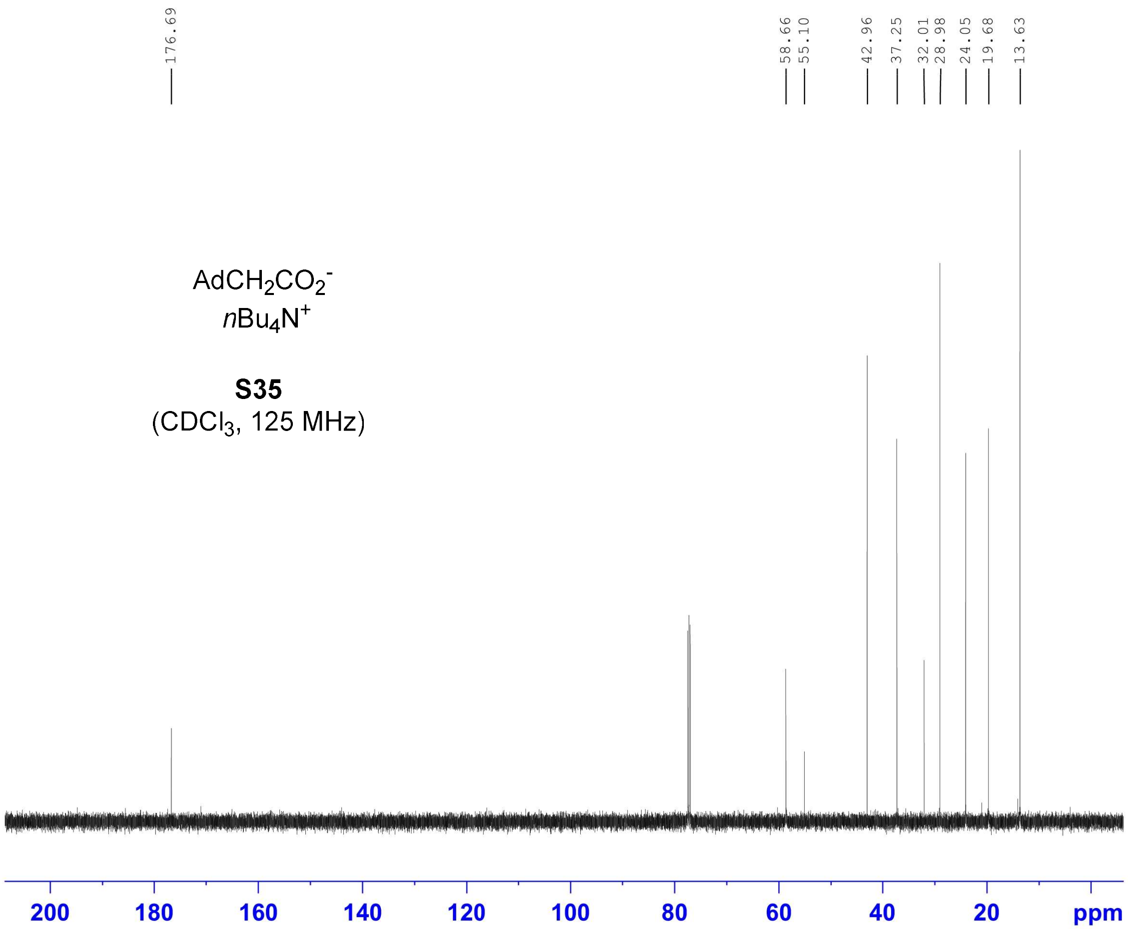



```
Current Data Parameters
NAME             yh-2-23
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180829
Time_              11.09
INSTRUM            spect
PROBHD   5 mm PAQNP 1H/
PULPROG               zg
TD                 44998
SOLVENT            CDCl3
NS                     1
DS                     0
SWH             7500.000 Hz
FIDRES          0.166674 Hz
AQ             2.9998667 sec
RG                    16
DW                66.667 usec
DE                 71.43 usec
TE                 295.0 K
D1            3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.50 usec
PL1       0 dB
PL1W         24.54113007 W
SFO1         500.1330008 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300168 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



$AdCH_2CO_2^-$
$n Bu_4N^+$

S35
($CDCl_3$, 125 MHz)

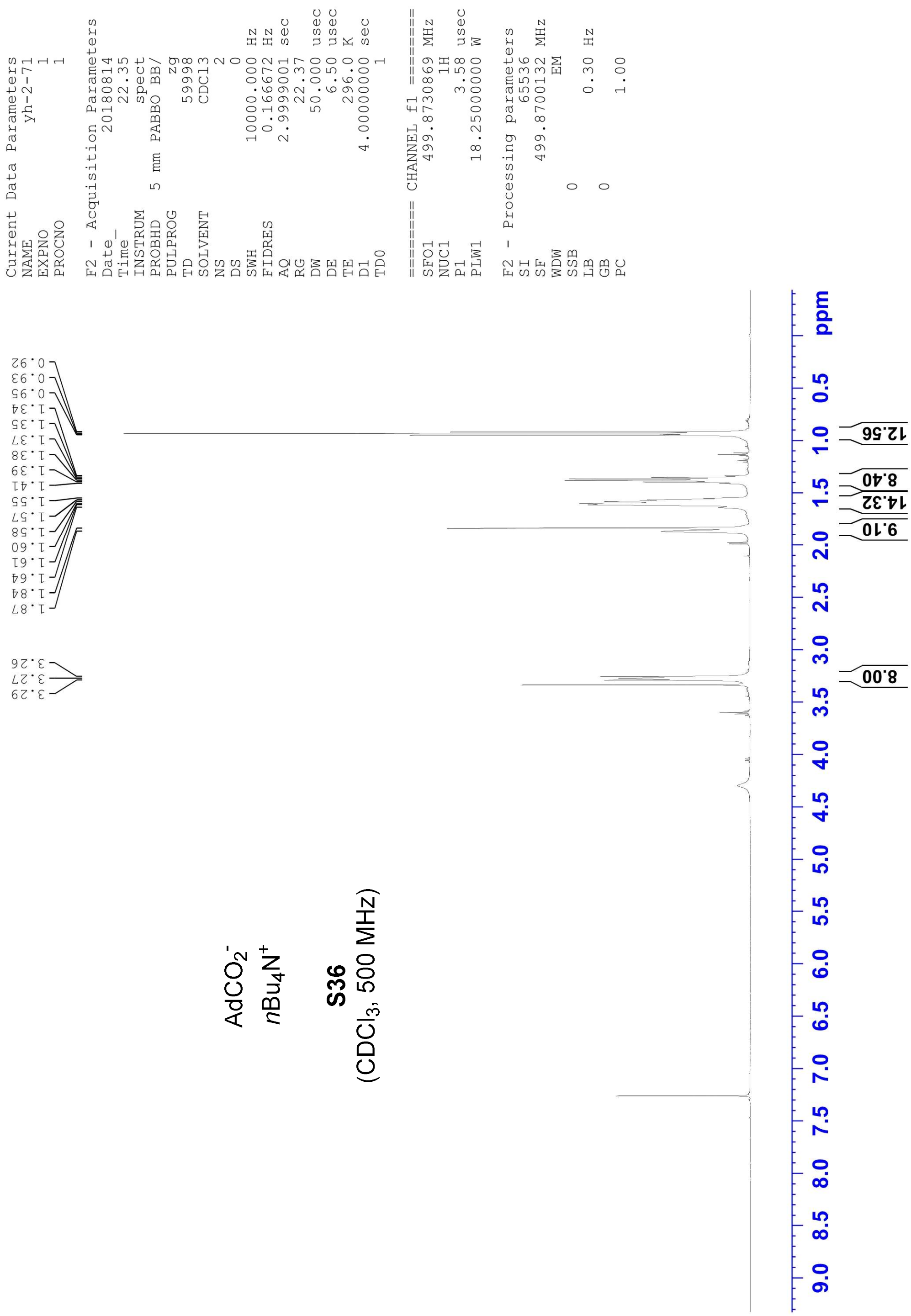
```
Current Data Parameters
NAME              yh-2-23
EXPNO                   2
PROCNO                  2

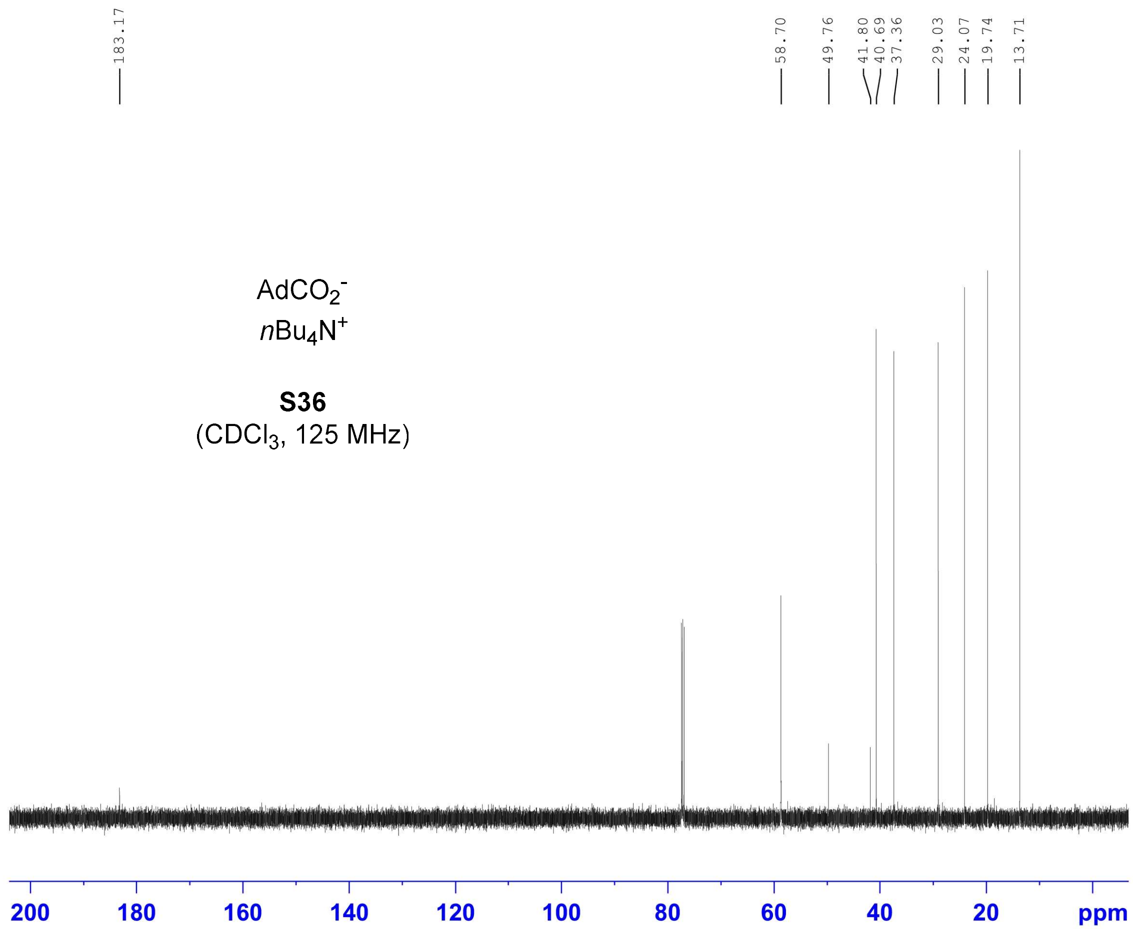
F2 - Acquisition Parameters
Date_            20180829
Time                11.15
INSTRUM             spect
PROBHD   5 mm PAQNP 1H/
PULPROG              zgpg
TD                 197364
SOLVENT             CDCl3
NS                      2
DS                      0
SWH            32894.738 Hz
FIDRES          0.166670 Hz
AQ             2.9999328 sec
RG                   2050
DW                 15.200 usec
DE                   6.00 usec
TE                  295.3 K
D1           10.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.90 usec
PL1                  1.00 dB
PL1W          72.42802429 W
SFO1          125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2         0 dB
PL12                16.50 dB
PL13                17.00 dB
PL2W          24.54113007 W
PL12W          0.54940748 W
PL13W          0.48965994 W
SFO2          500.1325006 MHz

F2 - Processing parameters
SI                 131072
SF            125.7577890 MHz
WDW                    EM
SSB         0
LB                   0.30 Hz
GB          0
PC                   1.40
```


AdCO2-
nBu4N+
S36
(CDCl3, 500 MHz)
0.92
0.93
0.95
1.34
1.35
1.37
1.38
1.39
1.41
1.55
1.57
1.58
1.60
1.61
1.64
1.84
1.87
3.26
3.27
3.29
12.56
8.40
14.32
9.10
8.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
Current Data Parameters
NAME yh-2-71
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180814
Time_ 22.35
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 2
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 22.37
DW 50.000 usec
DE 6.50 usec
TE 296.0 K
D1 4.00000000 sec
TD0 1
======= CHANNEL f1 =======
SFO1 499.8730869 MHz
NUC1 1H
P1 3.58 usec
PLW1 18.25000000 W
F2 - Processing parameters
SI 65536
SF 499.8700132 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



AdCO$_2^-$
nBu$_4$N$^+$

S36
(CDCl$_3$, 125 MHz)

```
Current Data Parameters
NAME             yh-2-71
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180814
Time               22.40
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                     7
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 296.1 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

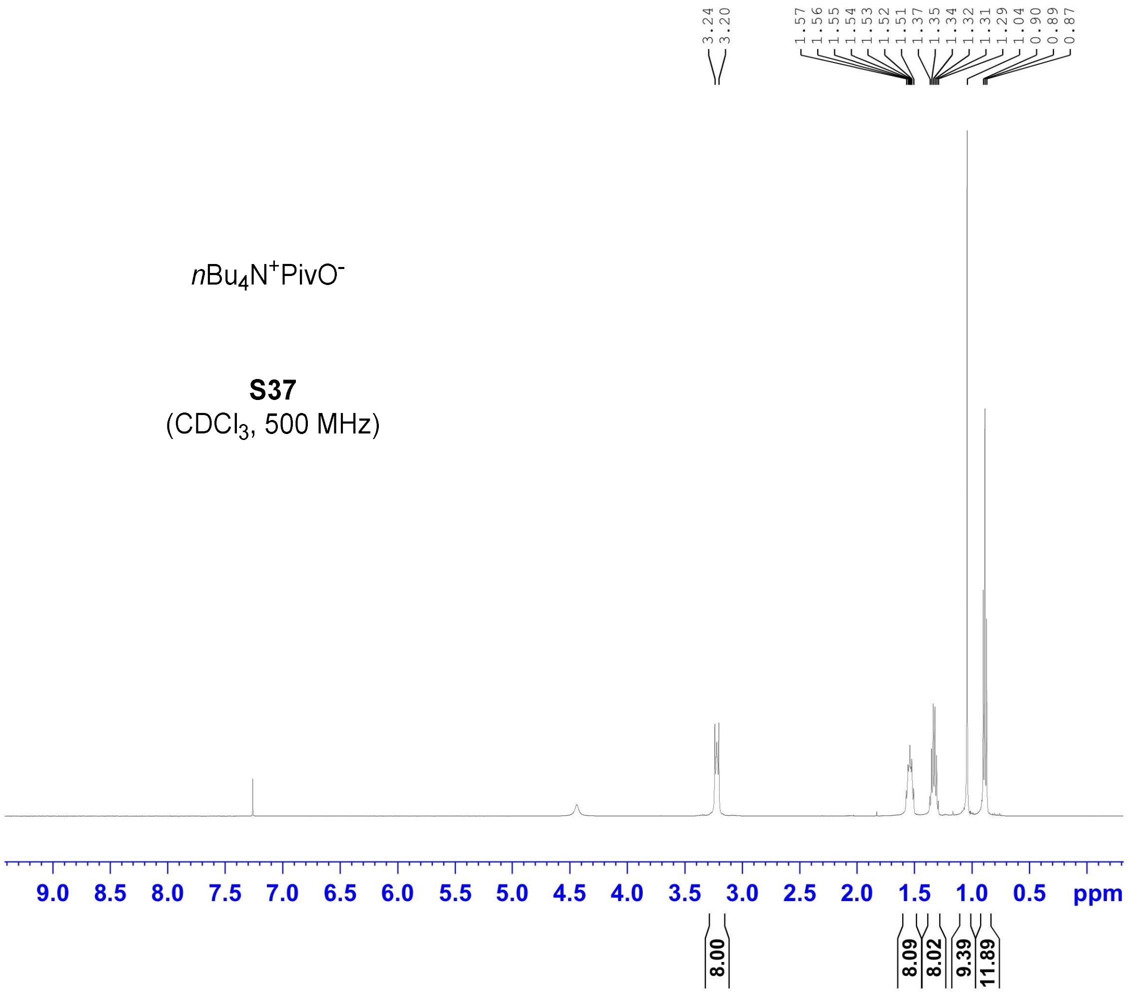
======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```

nBu$_4$N$^+$PivO$^-$

S37
($CDCl_3$, 500 MHz)

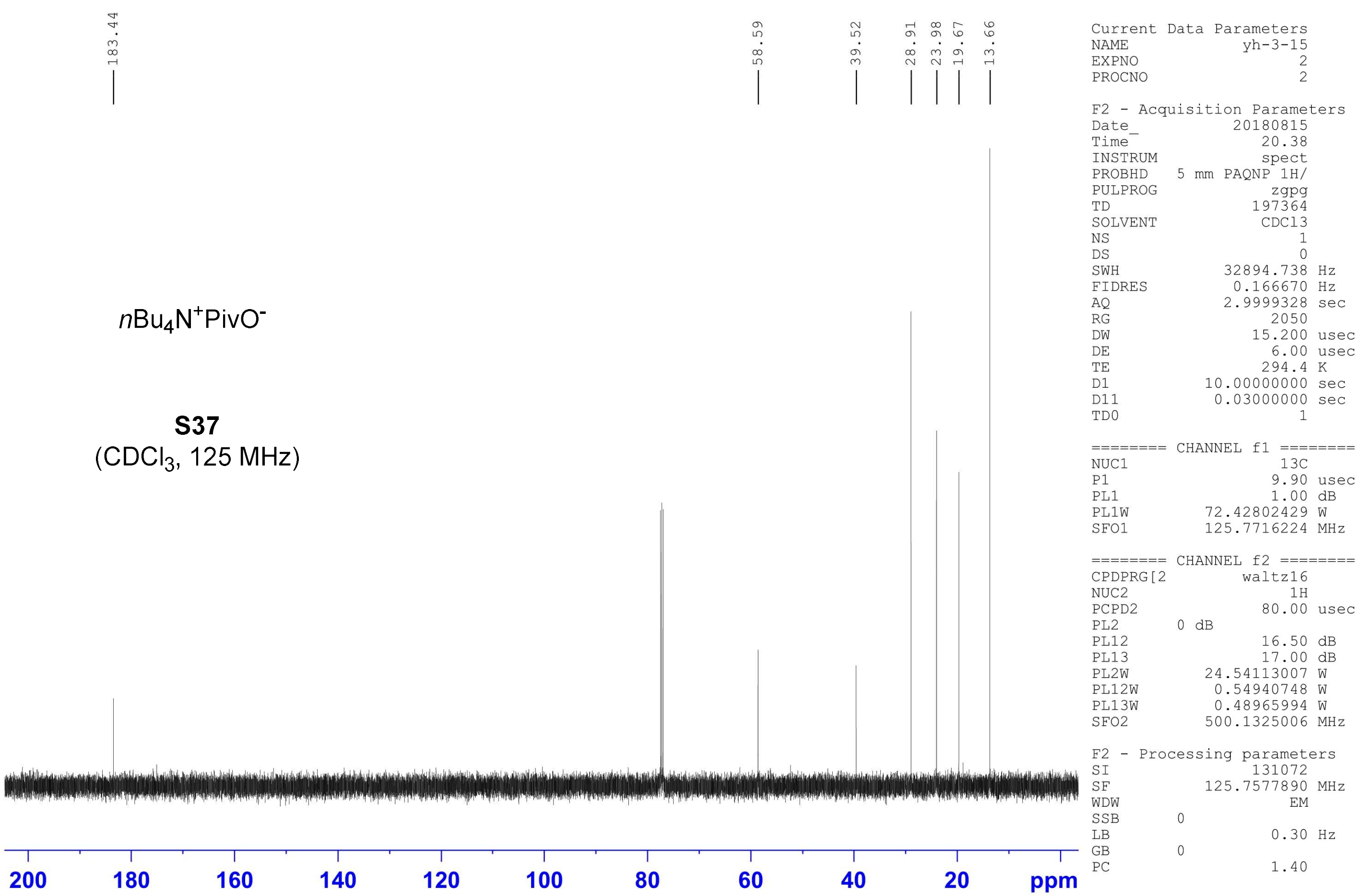



```
Current Data Parameters
NAME             yh-3-15
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180815
Time               20.23
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     3
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 19.64
DW                50.000 usec
DE                  6.50 usec
TE                 296.0 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

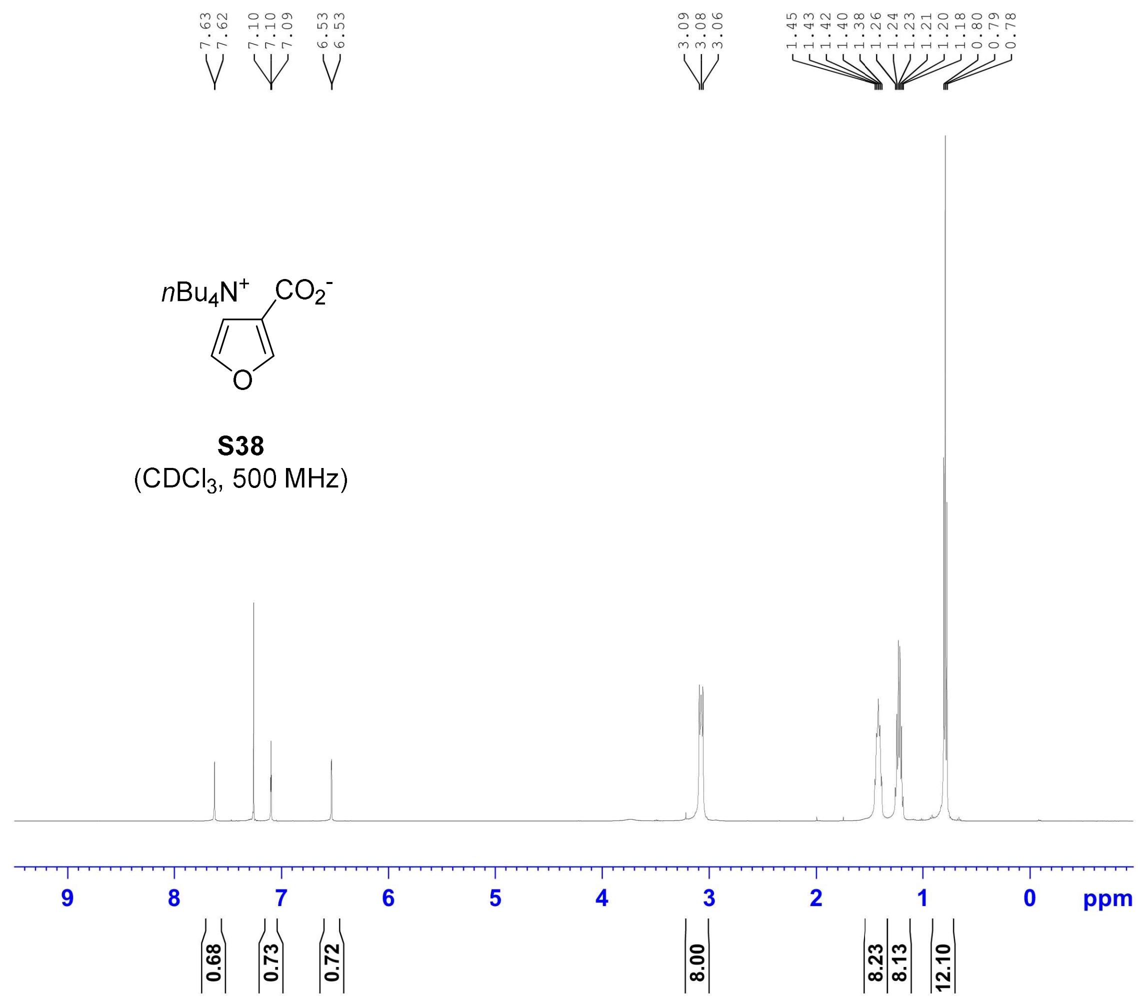
F2 - Processing parameters
SI                 65536
SF           499.8700134 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



n$Bu_4N^+PivO^-$

S37
($CDCl_3$, 125 MHz)

S38
($CDCl_3$, 500 MHz)

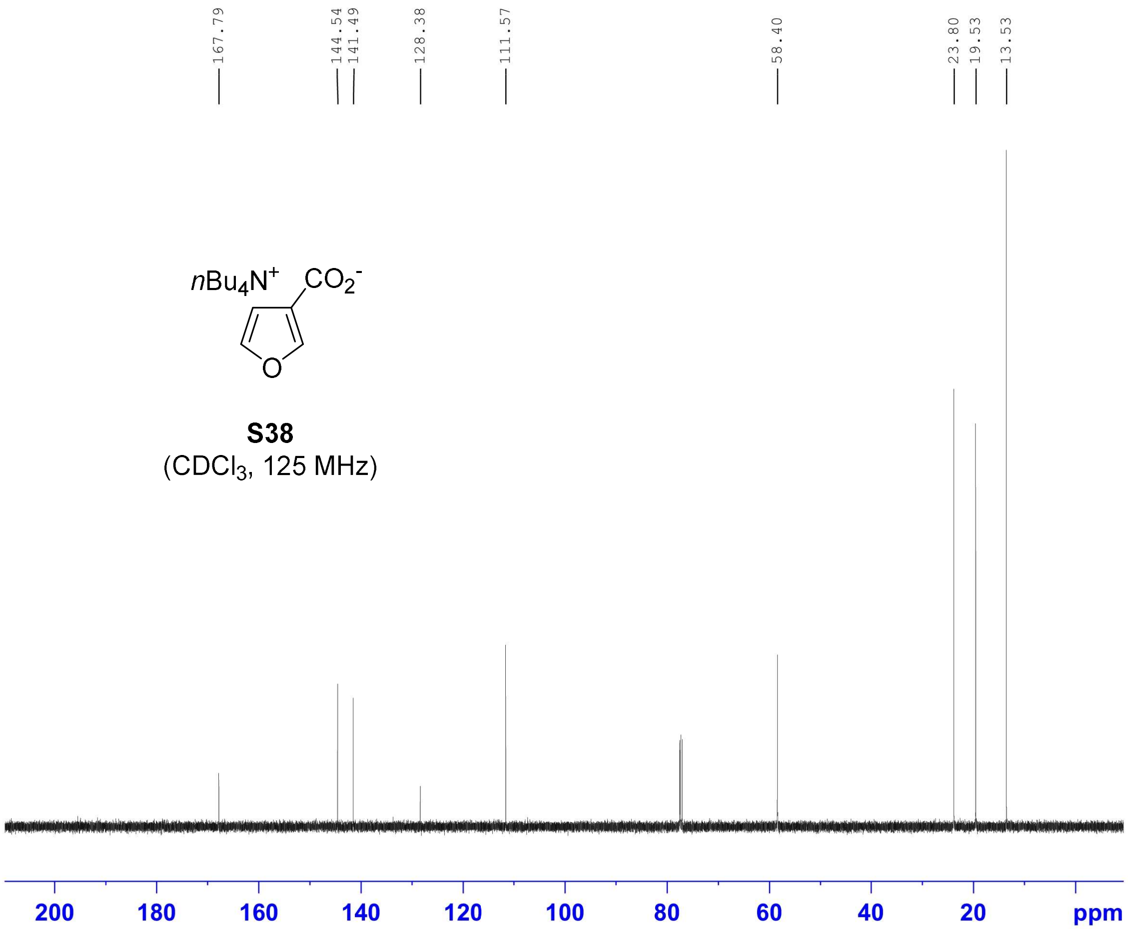



```
Current Data Parameters
NAME            yh-2-139
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180814
Time               22.52
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     2
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                  5.87
DW                50.000 usec
DE                  6.50 usec
TE                 296.1 K
D1            3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                 10.75 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700140 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



S38
($CDCl_3$, 125 MHz)

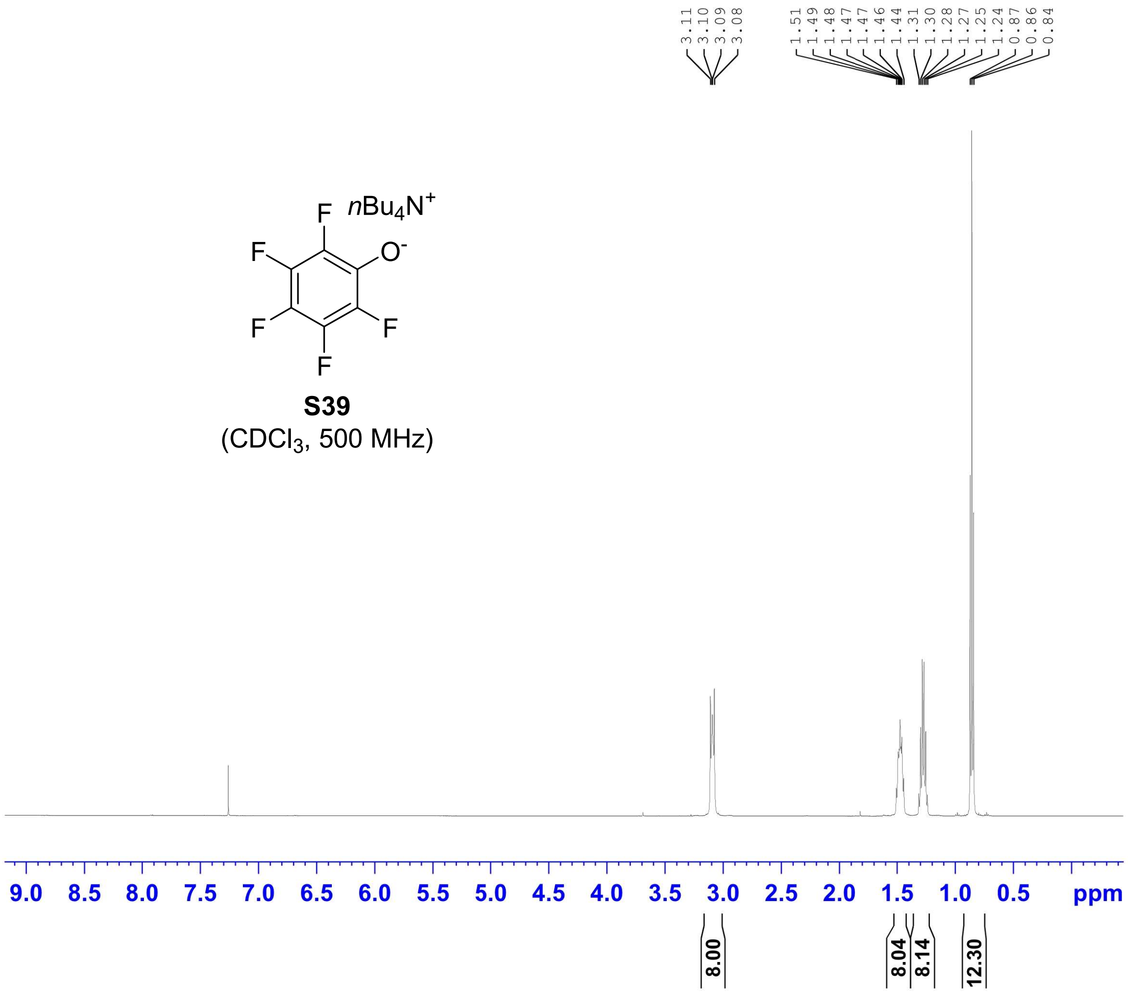
```
Current Data Parameters
NAME              yh-2-139
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20180814
Time                 22.55
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                       4
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   296.1 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                     13C
P1                     10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                   1048576
SF           125.6924115 MHz
WDW                       EM
SSB      0
LB                      0.30 Hz
GB       0
PC                      1.40
```



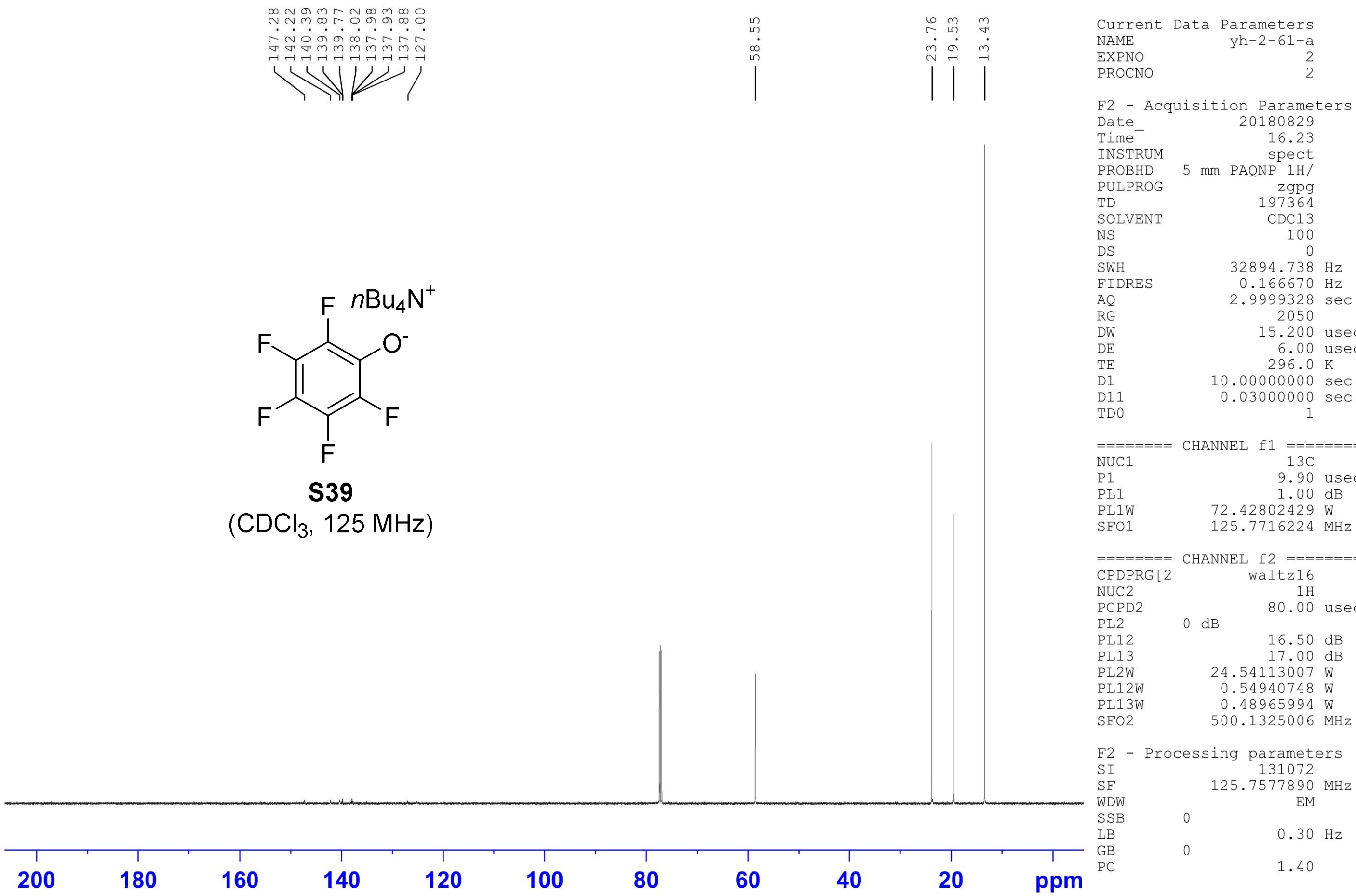
S39
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME            yh-2-61-a
EXPNO                   1
PROCNO                  1

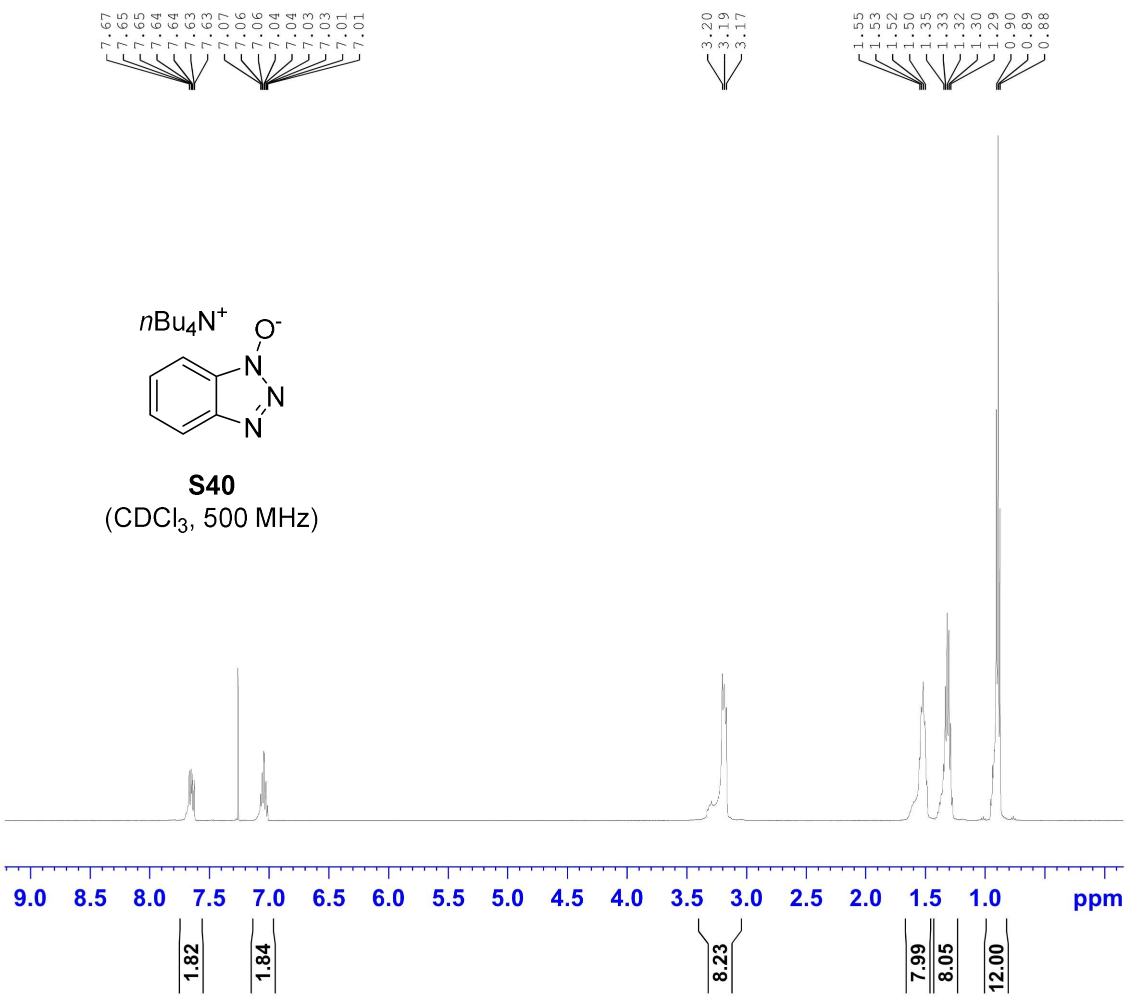
F2 - Acquisition Parameters
Date_            20180829
Time                15.56
INSTRUM             spect
PROBHD   5 mm PAQNP 1H/
PULPROG                zg
TD                  44998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH              7500.000 Hz
FIDRES           0.166674 Hz
AQ              2.9998667 sec
RG                   22.6
DW                 66.667 usec
DE                  71.43 usec
TE                  295.2 K
D1             3.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.50 usec
PL1       0 dB
PL1W          24.54113007 W
SFO1          500.1330008 MHz

F2 - Processing parameters
SI                  32768
SF            500.1300156 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```



S39
(CDCl$_3$, 125 MHz)



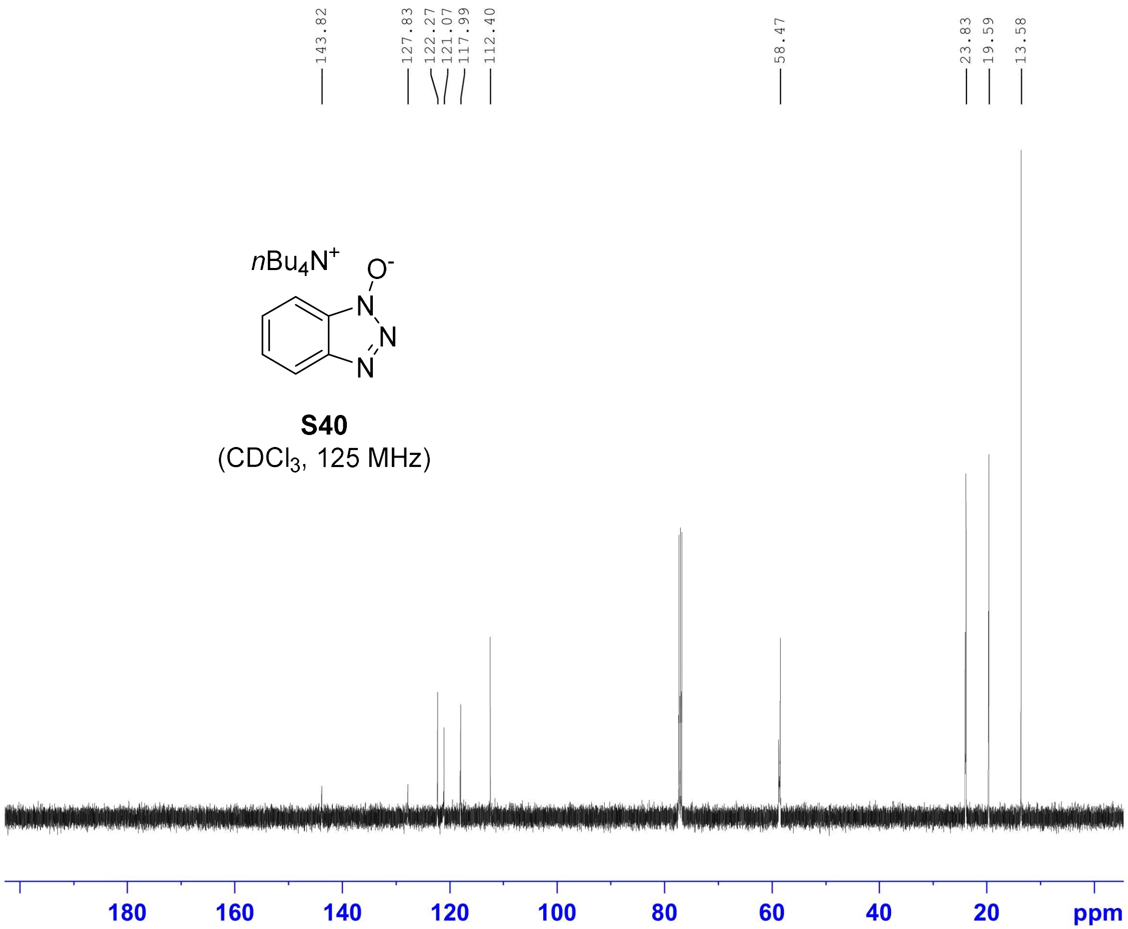
S40
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             HOBt salt
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20190927
Time                 16.44
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       4
DS                       0
SWH          10000.000 Hz
FIDRES        0.166672 Hz
AQ           2.9999001 sec
RG              110.37
DW              50.000 usec
DE               10.00 usec
TE               297.0 K
D1          4.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1       500.1330885 MHz
NUC1                    1H
P1                 3.30 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                   65536
SF         500.1300141 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```



S40
($CDCl_3$, 125 MHz)

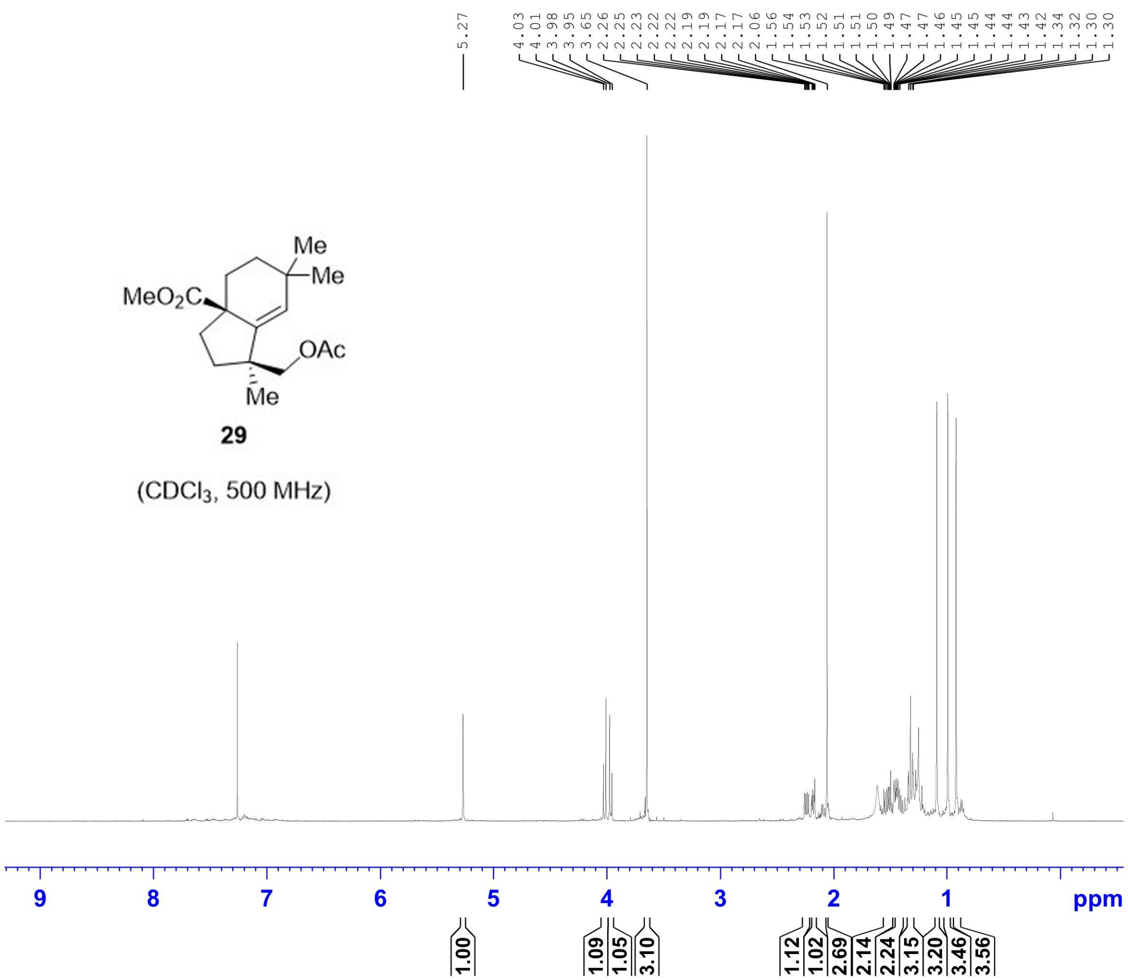

```
Current Data Parameters
NAME          HOBt salt
EXPNO                 2
PROCNO                2

F2 - Acquisition Parameters
Date_          20190930
Time              16.46
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zgdc
TD               187496
SOLVENT           CDCl3
NS                  151
DS                    0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                 2050
DW               16.000 usec
DE                 6.50 usec
TE                298.0 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                13C
P1                10.00 usec
PLW1        72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI              1048576
SF          125.6924115 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.40
```



29

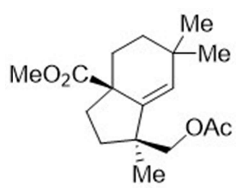
($CDCl_3$, 500 MHz)


```
Current Data Parameters
NAME     acetate product
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180820
Time               15.39
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     2
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 77.07
DW                50.000 usec
DE                  6.50 usec
TE                 296.0 K
D1            4.00000000 sec
TD0                    1

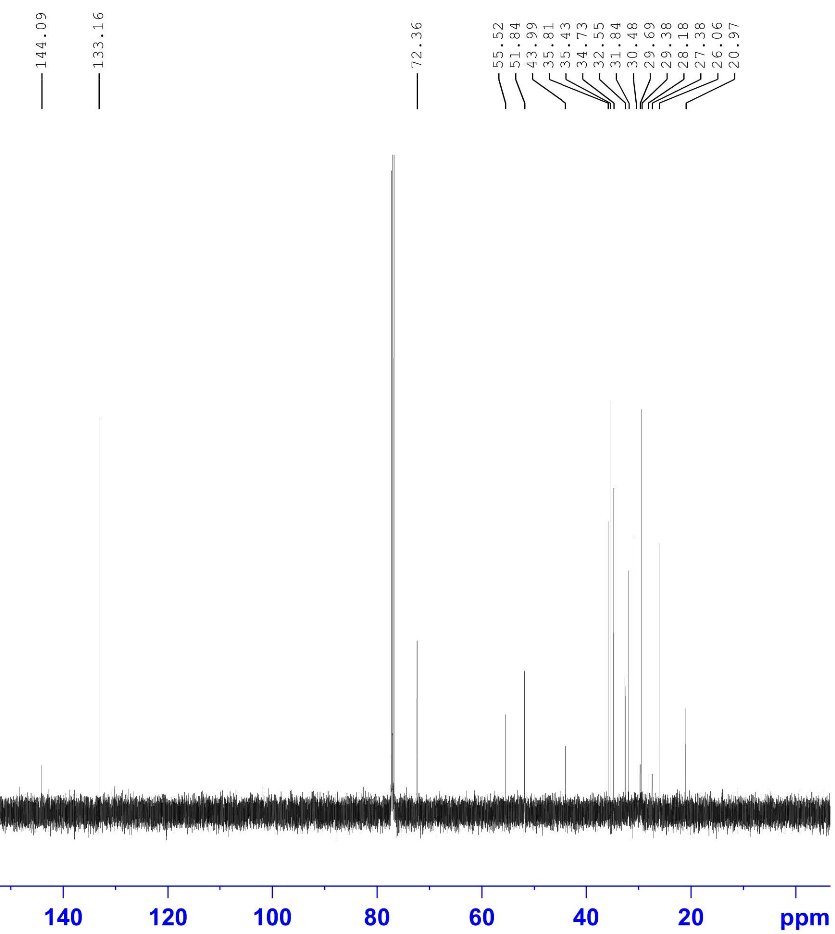
======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700122 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



29

($CDCl_3$, 125 MHz)



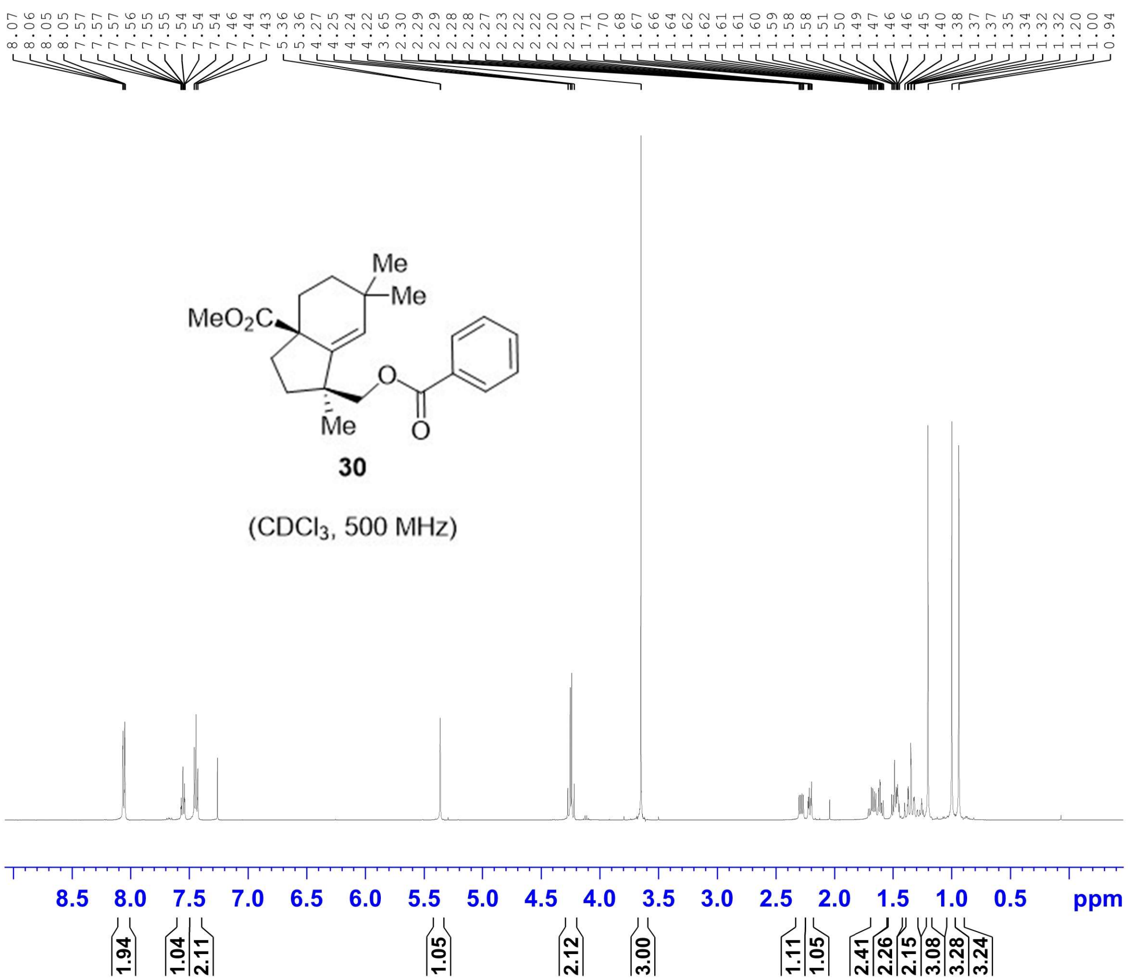

```
Current Data Parameters
NAME      acetate product
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180820
Time                15.59
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    159
DS                      0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                   2050
DW               16.000 usec
DE                 6.50 usec
TE                297.3 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1        72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI                1048576
SF          125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



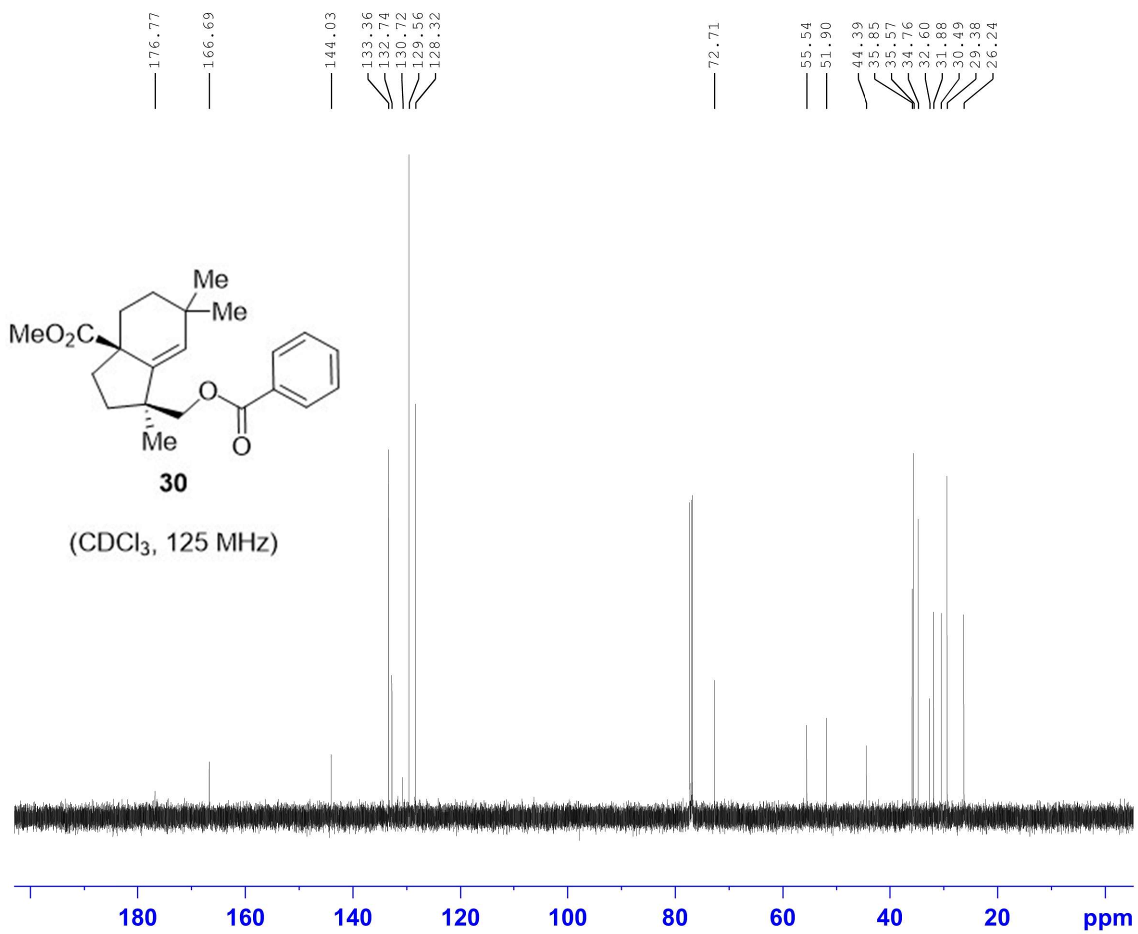
30

(CDCl$_3$, 500 MHz)

Current Data Parameters
NAME yh-7-35-b
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191005
Time_ 15.10 h
INSTRUM spect
PROBHD Z113652_0187 (
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 4
DS 0
SWH 10000.000 Hz
FIDRES 0.333344 Hz
AQ 2.9999001 sec
RG 37.92
DW 50.000 usec
DE 6.50 usec
TE 296.0 K
D1 3.00000000 sec
TD0 1
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



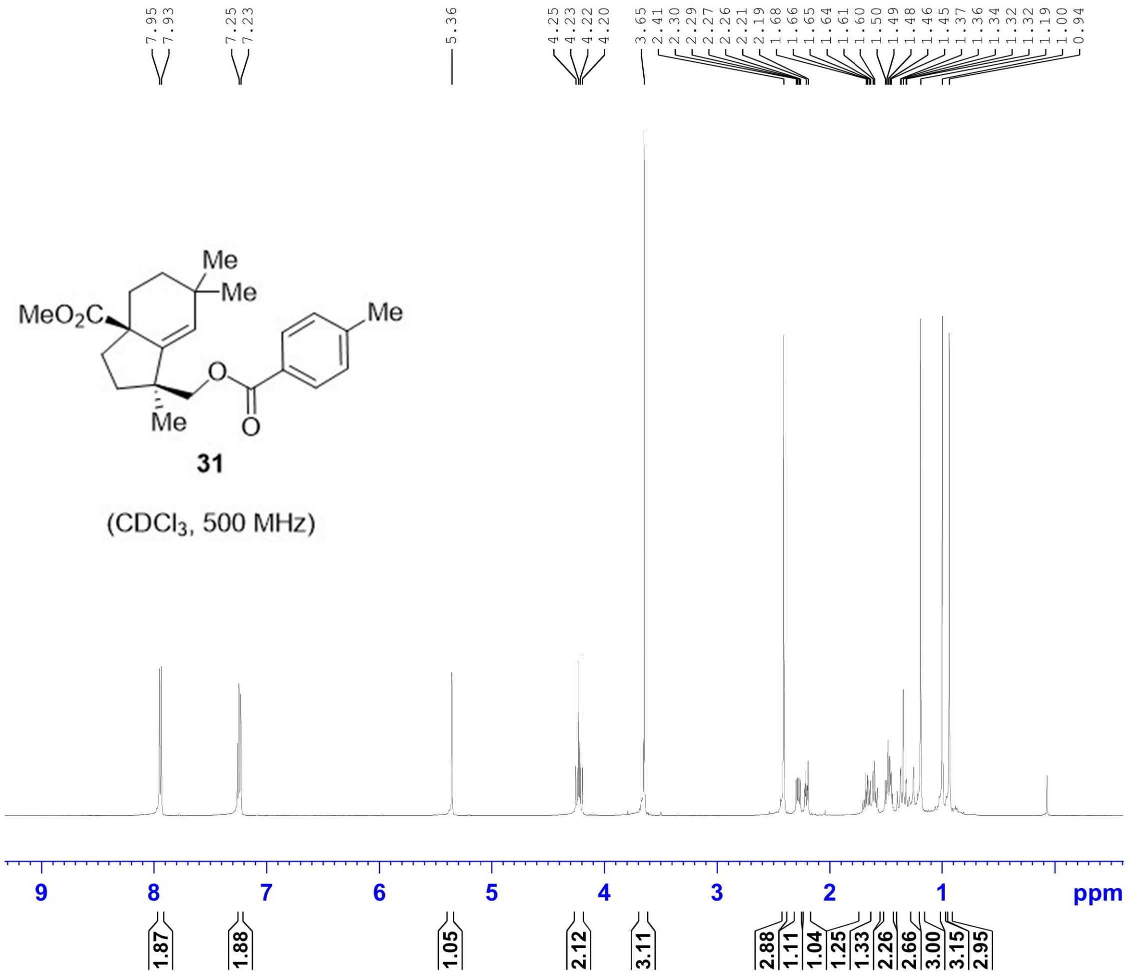
30

($CDCl_3$, 125 MHz)

```
Current Data Parameters
NAME          yh-7-35-b
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20191005
Time_             15.28 h
INSTRUM           spect
PROBHD   Z113652_0187 (
PULPROG            zgdc
TD               187496
SOLVENT           CDCl3
NS                   56
DS                    0
SWH           31250.000 Hz
FIDRES         0.333340 Hz
AQ            2.9999361 sec
RG                 2050
DW               16.000 usec
DE                 6.50 usec
TE                296.7 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7049802 MHz
NUC1                13C
P1                10.00 usec
PLW1        72.83999634 W
SFO2        499.8724993 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

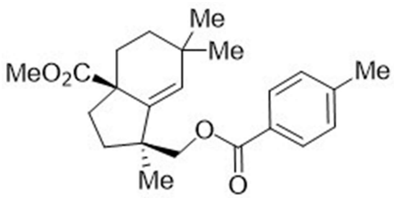
F2 - Processing parameters
SI              1048576
SF          125.6924115 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.40
```



31

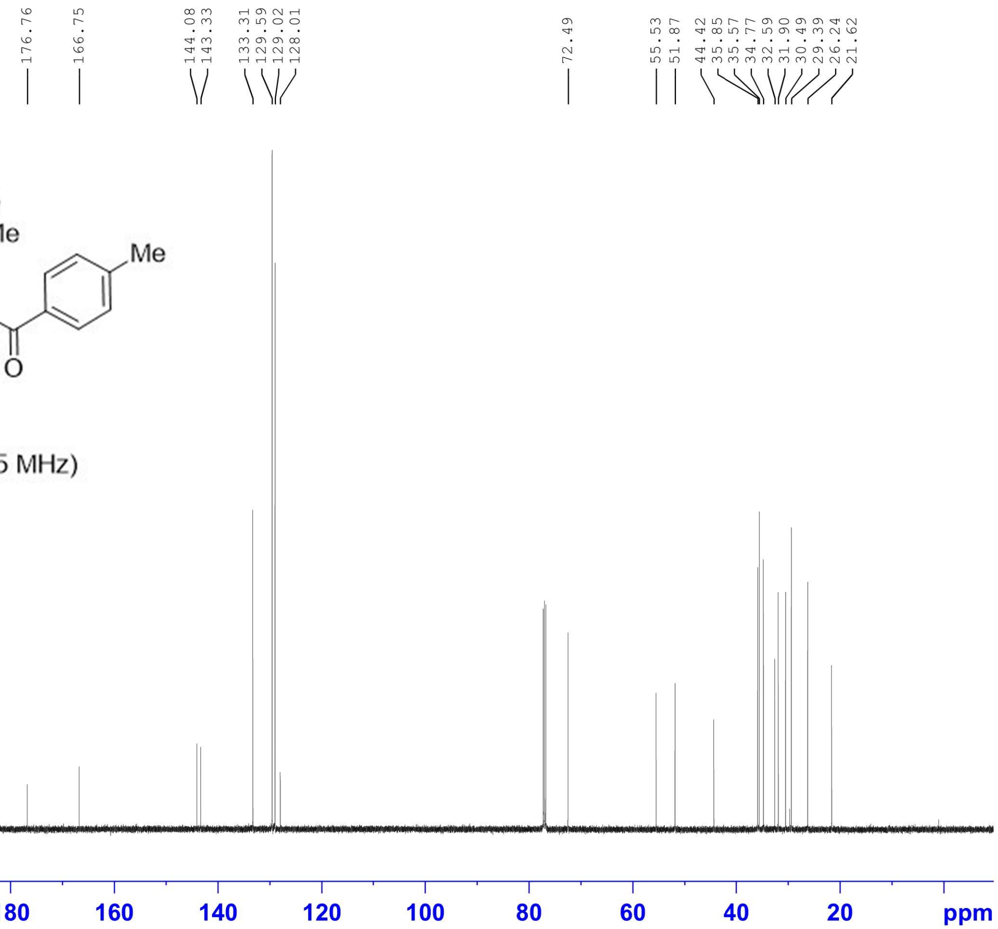
(CDCl$_3$, 500 MHz)

Current Data Parameters	
NAME	yh-2-42-a
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20171226
Time	21.24
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	4
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	28.76
DW	50.000 usec
DE	6.50 usec
TE	296.0 K
D1	3.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	499.8730869 MHz
NUC1	1H
P1	10.75 usec
PLW1	18.25000000 W
F2 - Processing parameters	
SI	65536
SF	499.8700123 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



31

($CDCl_3$, 125 MHz)



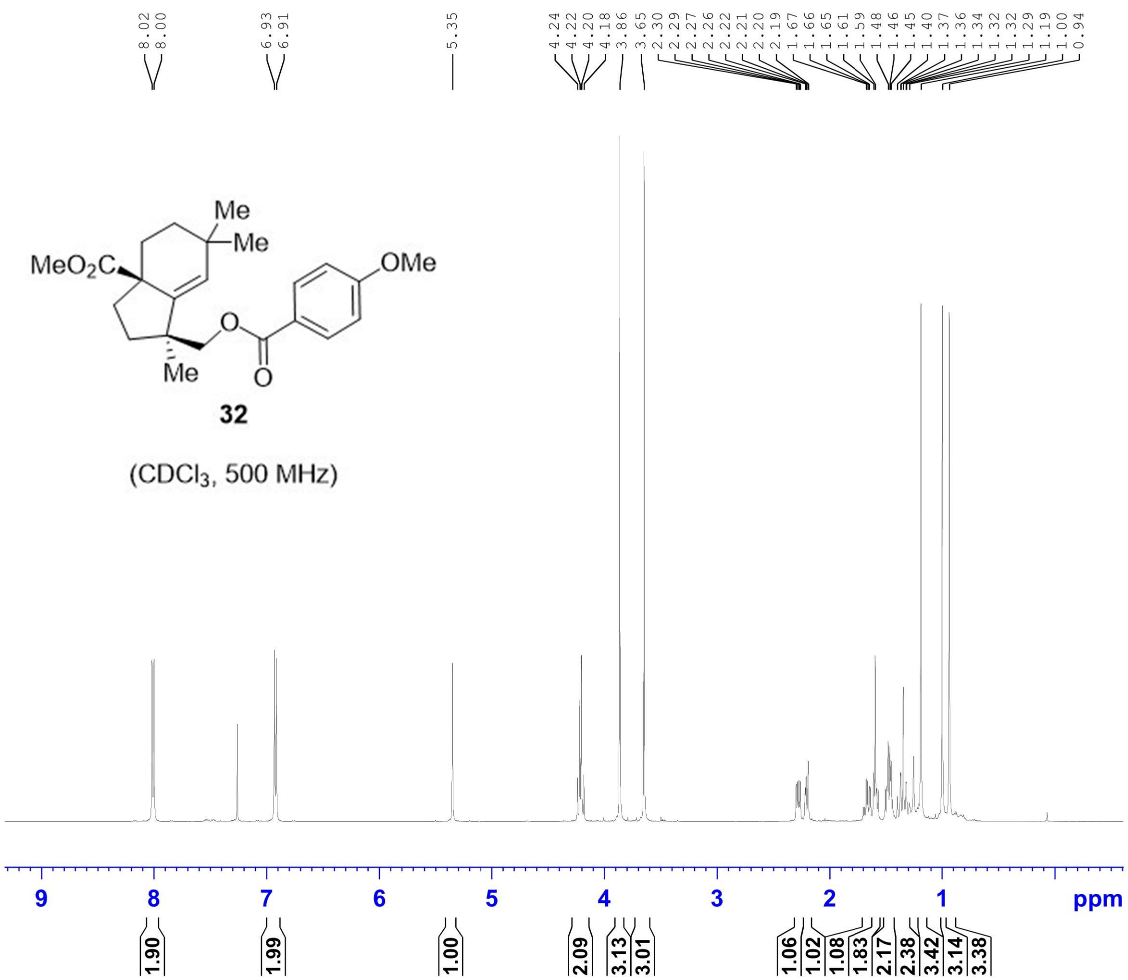

```
Current Data Parameters
NAME              yh-2-42-a
EXPNO                     2
PROCNO                    2

F2 - Acquisition Parameters
Date_              20171226
Time                  22.26
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT               CDCl3
NS                      482
DS                        0
SWH               31250.000 Hz
FIDRES             0.166670 Hz
AQ                2.9999361 sec
RG                     2050
DW                   16.000 usec
DE                     6.50 usec
TE                    297.7 K
D1               3.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            125.7049802 MHz
NUC1                    13C
P1                    10.00 usec
PLW1            72.83999634 W

======== CHANNEL f2 ========
SFO2            499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2            19.00000000 W
PLW12            0.29688001 W

F2 - Processing parameters
SI                  1048576
SF              125.6924115 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.40
```



32

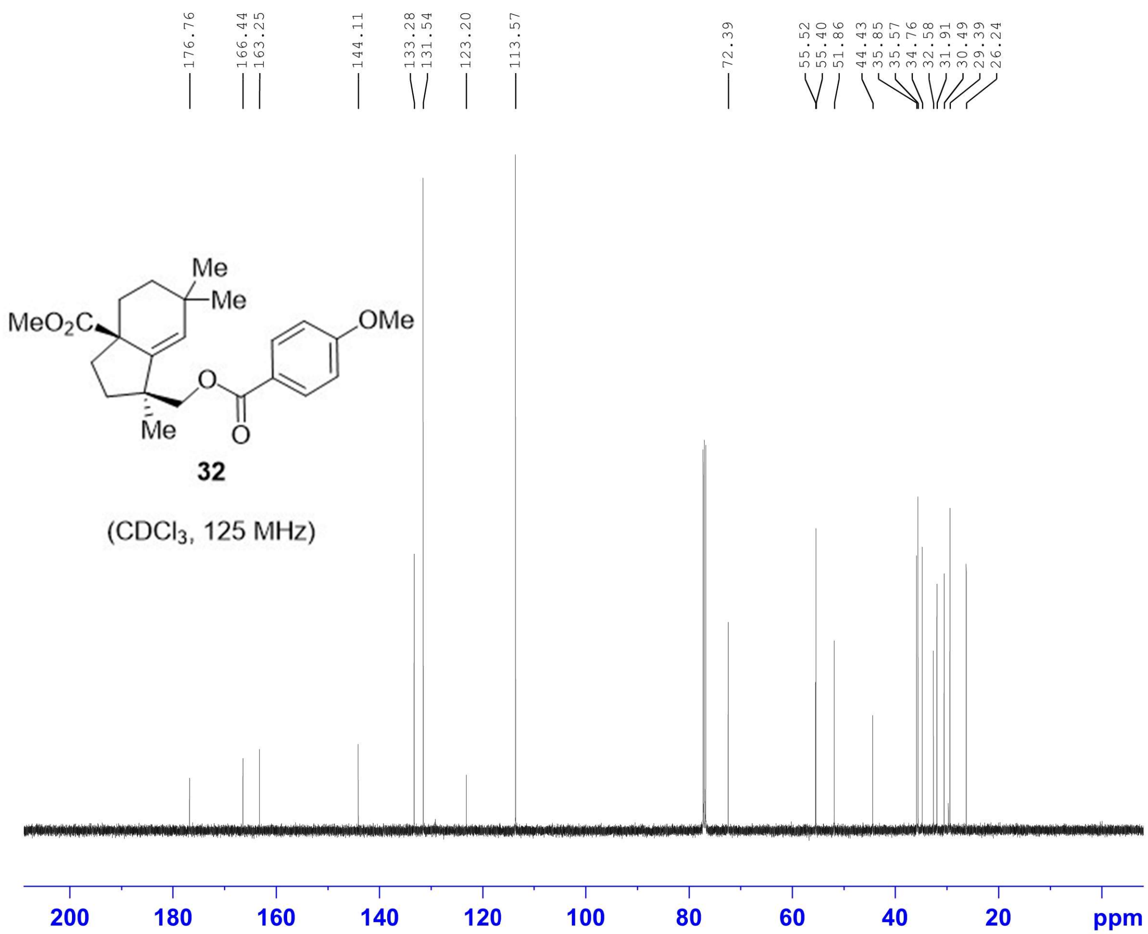
($CDCl_3$, 500 MHz)


```
Current Data Parameters
NAME          yh-2-31-1-r
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171114
Time                17.29
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  79.04
DW                 50.000 usec
DE                  10.00 usec
TE                  294.6 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                   8.00 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                  65536
SF            500.1300132 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```




```
Current Data Parameters
NAME            yh-2-31-r
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20171122
Time                21.57
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    559
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  298.8 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

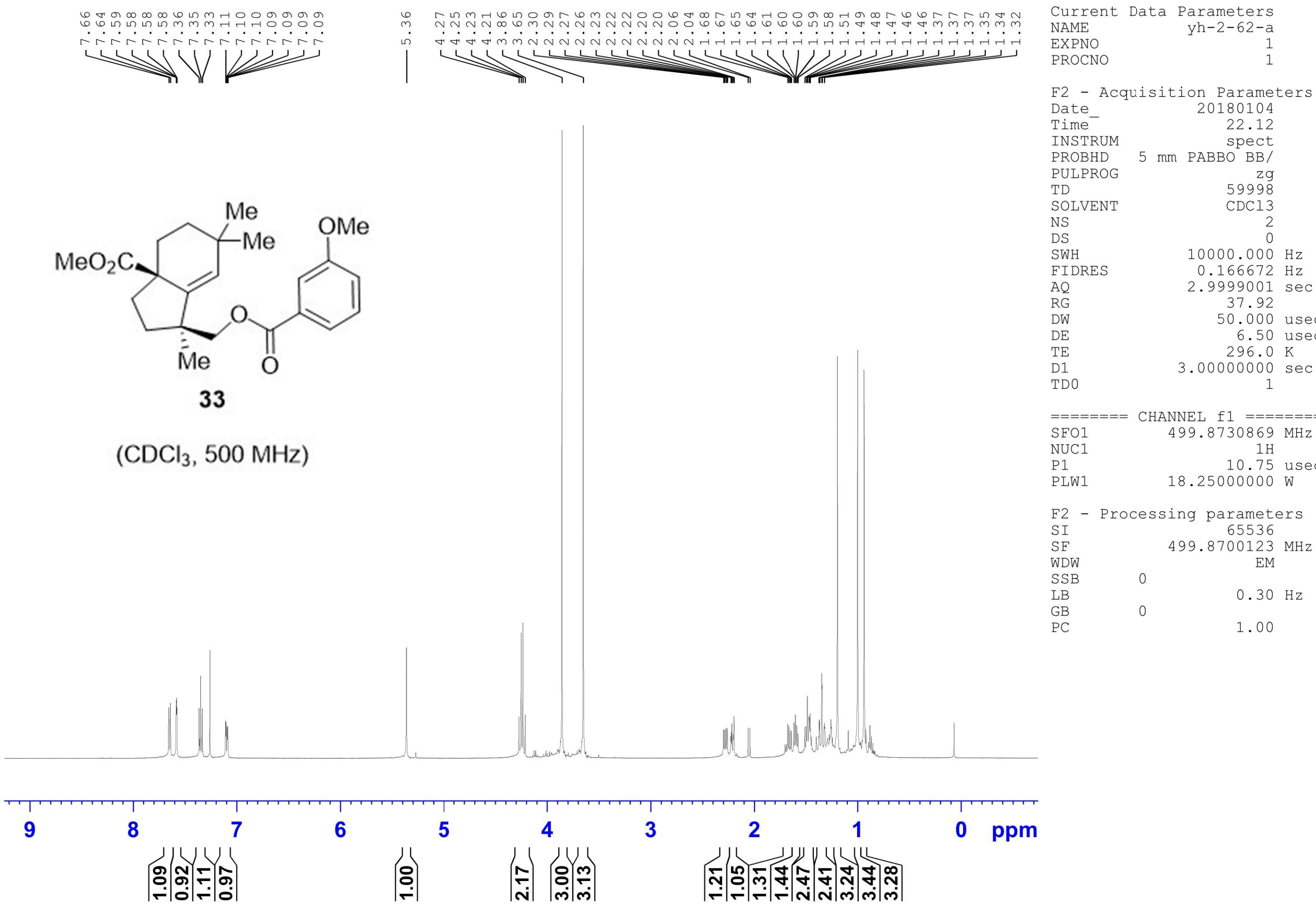
======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

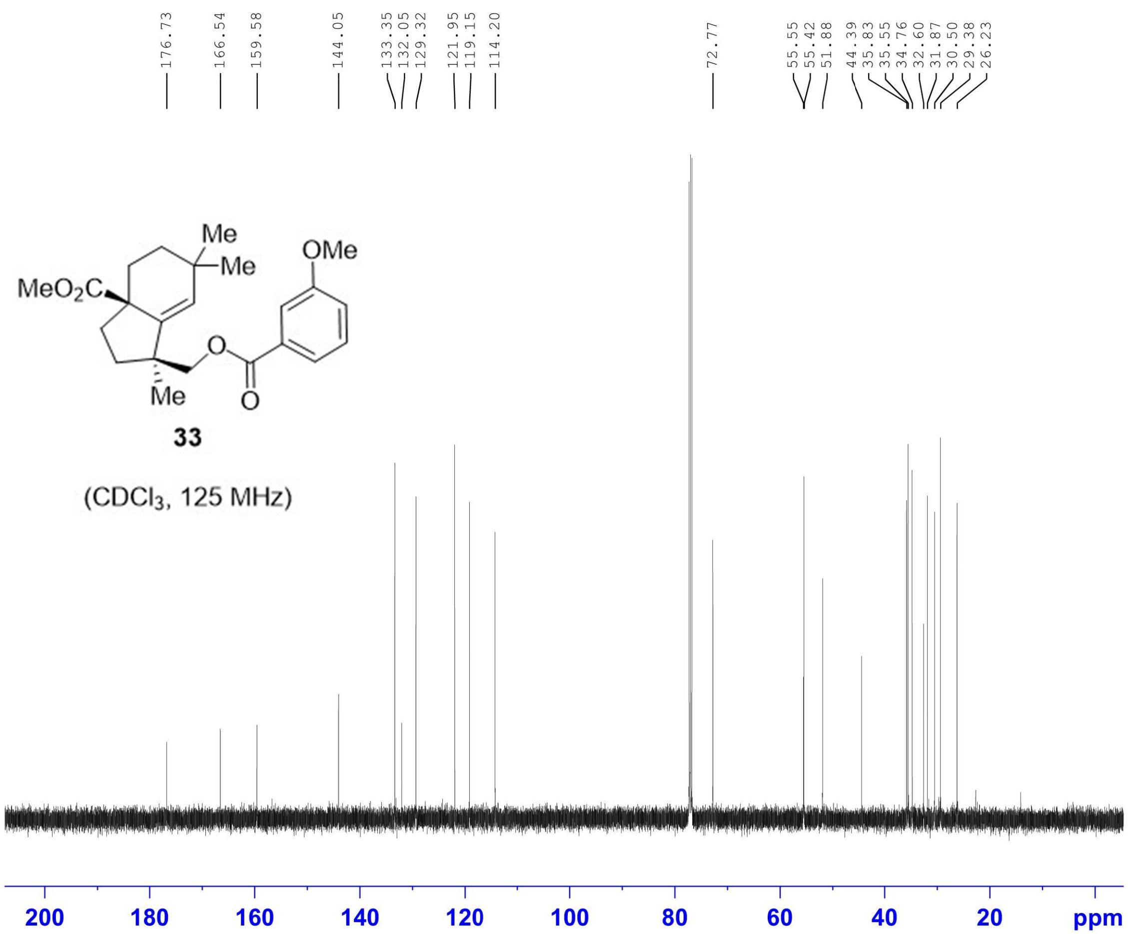
======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```

33

($CDCl_3$, 500 MHz)






```
Current Data Parameters
NAME            yh-2-62-a
EXPNO                   4
PROCNO                  4

F2 - Acquisition Parameters
Date_            20180104
Time                22.55
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    366
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  297.7 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

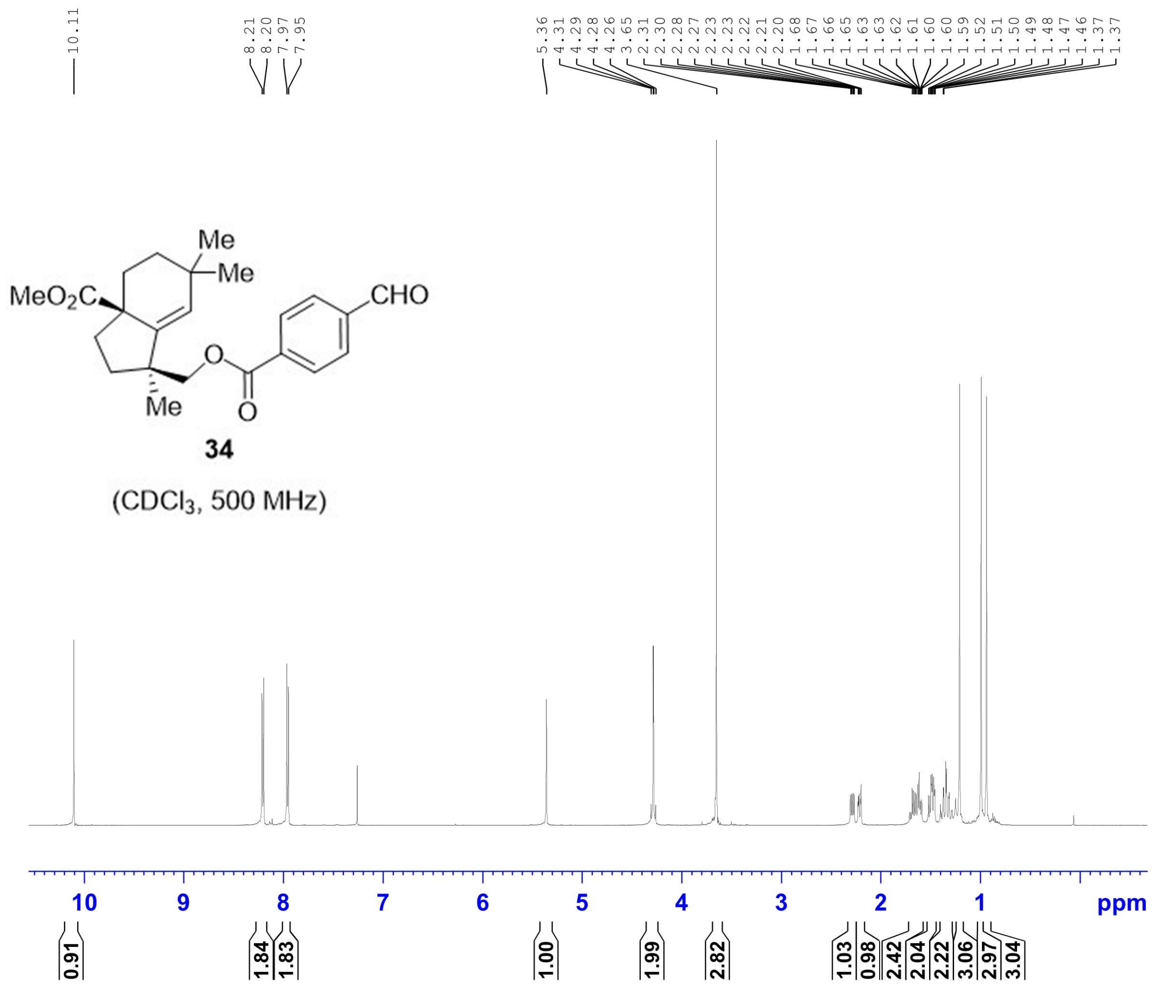
======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```

34

(CDCl$_3$, 500 MHz)

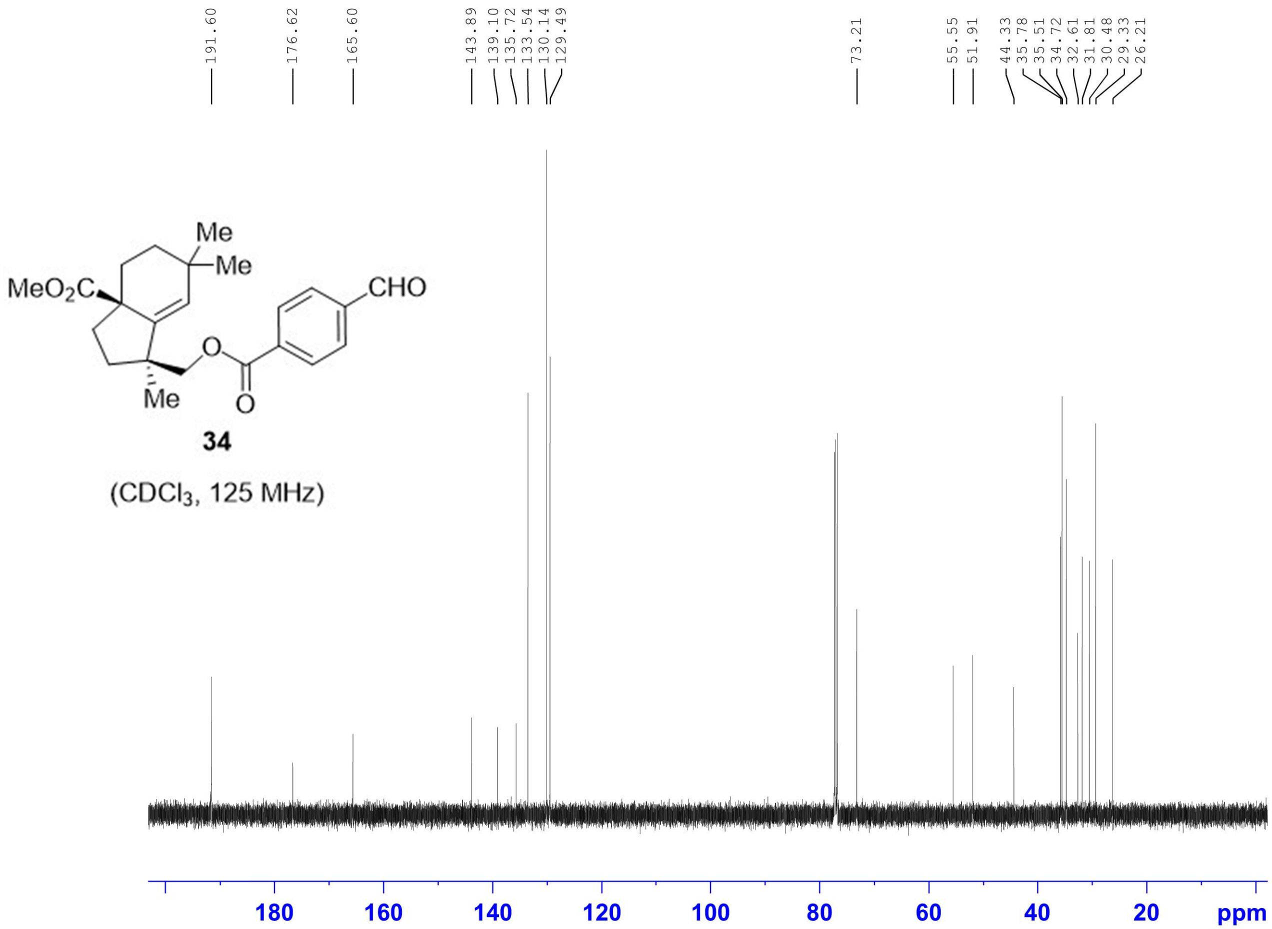



```
Current Data Parameters
NAME            yh-2-77-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180124
Time                22.13
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                  35.92
DW                 50.000 usec
DE                   6.50 usec
TE                  296.9 K
D1            3.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                   1H
P1                  10.75 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF           499.8700124 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```



34

(CDCl$_3$, 125 MHz)

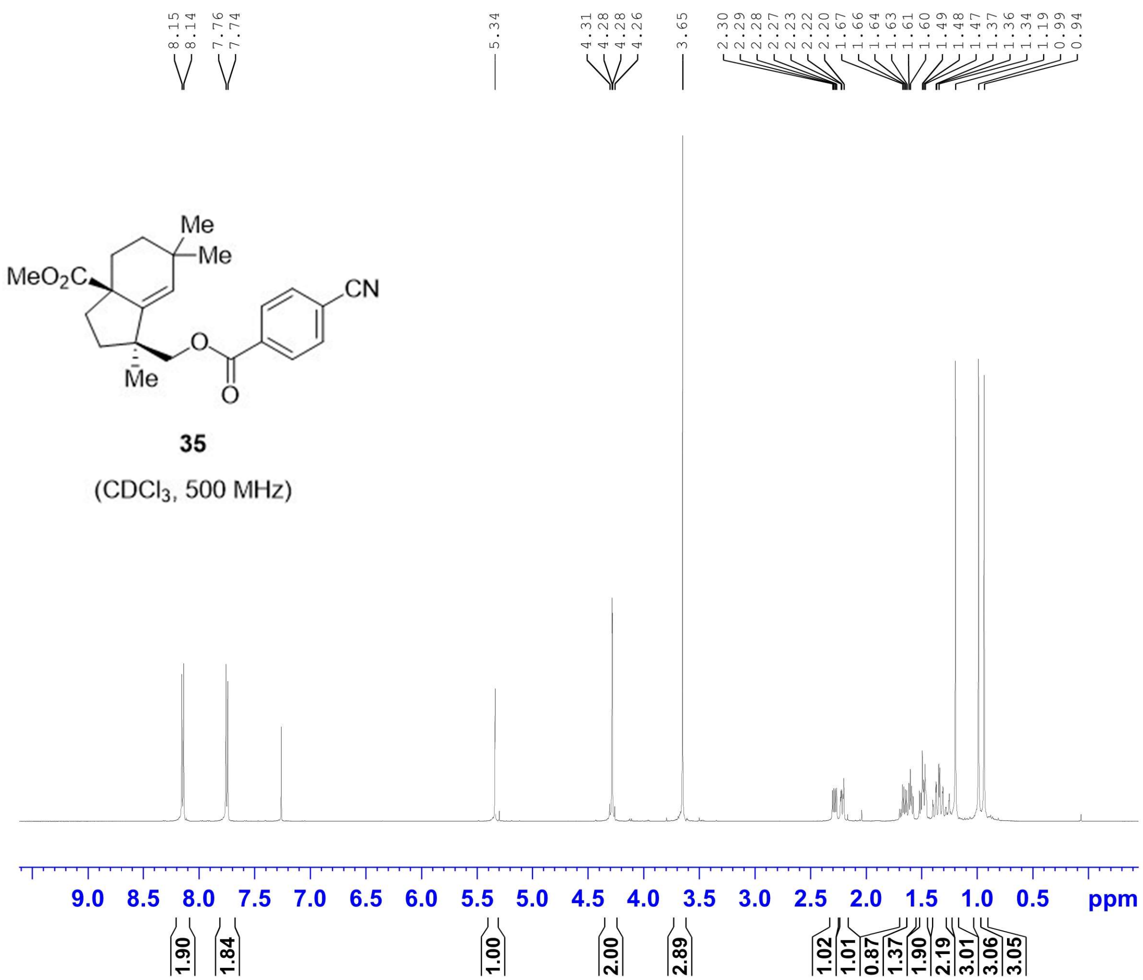
```
Current Data Parameters
NAME            yh-2-77-a
EXPNO                   3
PROCNO                  3

F2 - Acquisition Parameters
Date_            20180124
Time_               22.35
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    135
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  298.2 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



35

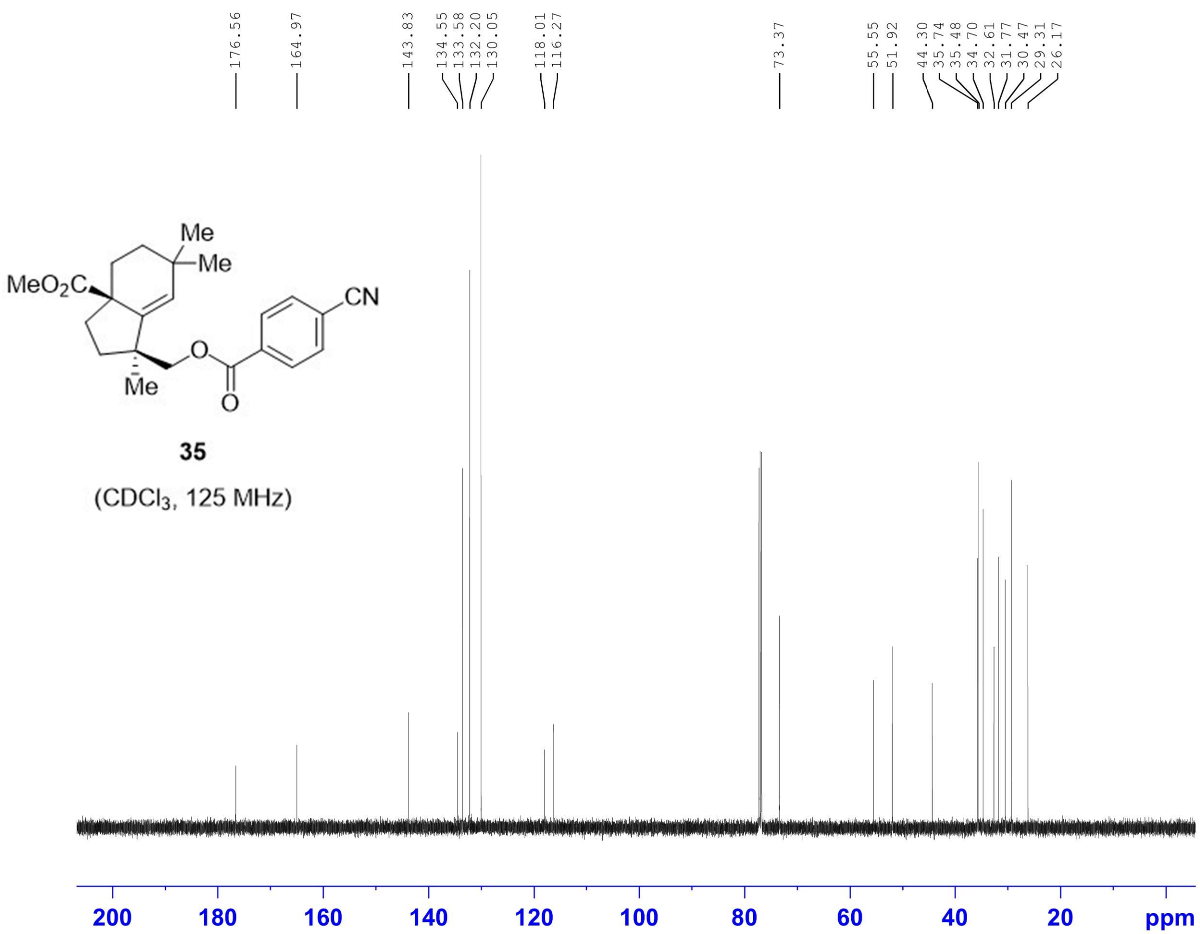
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME            yh-2-53-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180102
Time                21.59
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      4
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  35.92
DW                 50.000 usec
DE                   6.50 usec
TE                  296.1 K
D1             3.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                   1H
P1                  10.75 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF           499.8700122 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



35

($CDCl_3$, 125 MHz)

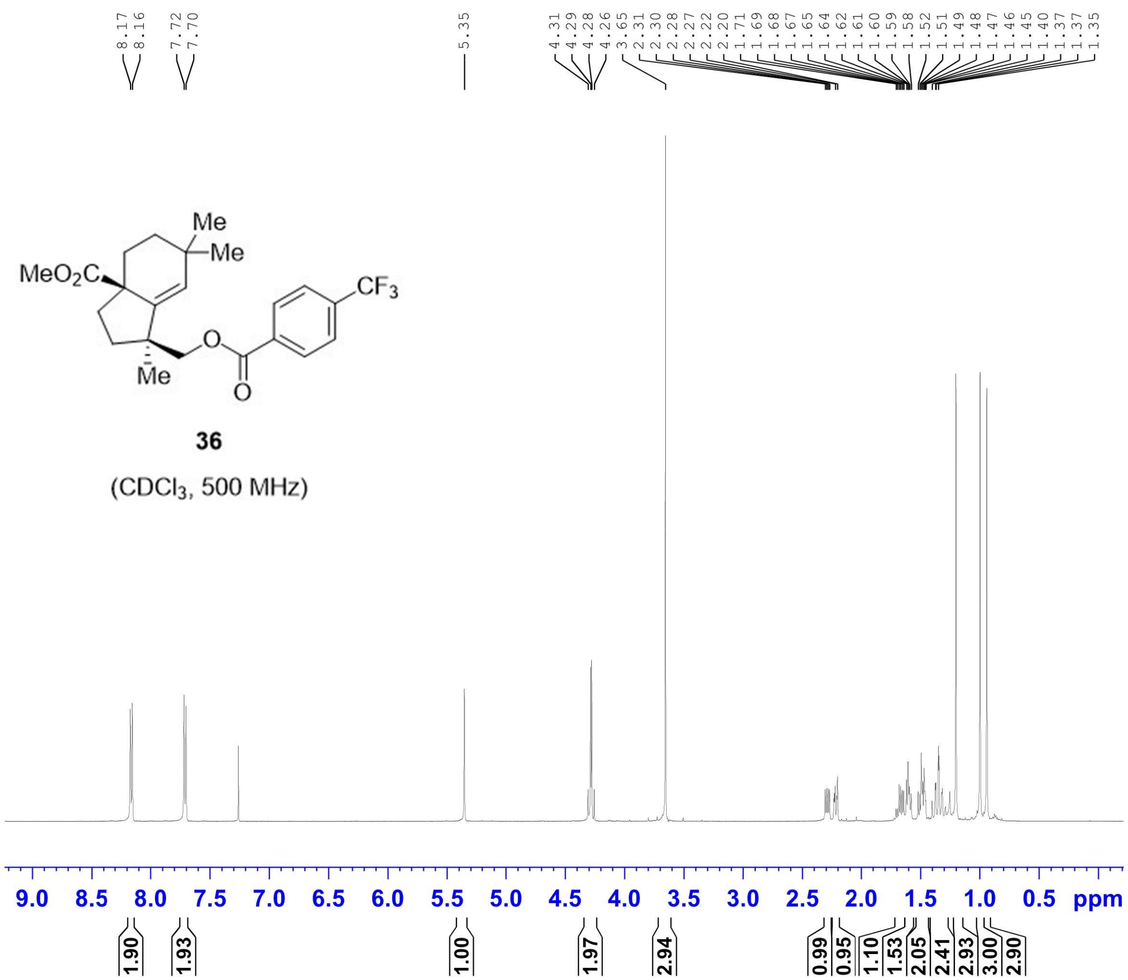

```
Current Data Parameters
NAME             yh-2-53-a
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20180102
Time                 22.29
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                     273
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   297.5 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2           499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6924115 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



36

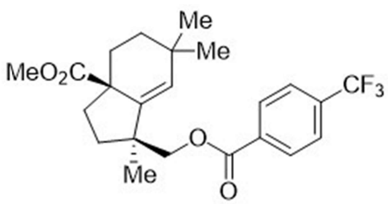
(CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME              yh-2-43-a
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20180812
Time_                 22.11
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        5
DS                        0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                    62.78
DW                50.000 usec
DE                  6.50 usec
TE                  296.8 K
D1            4.00000000 sec
TD0                       1

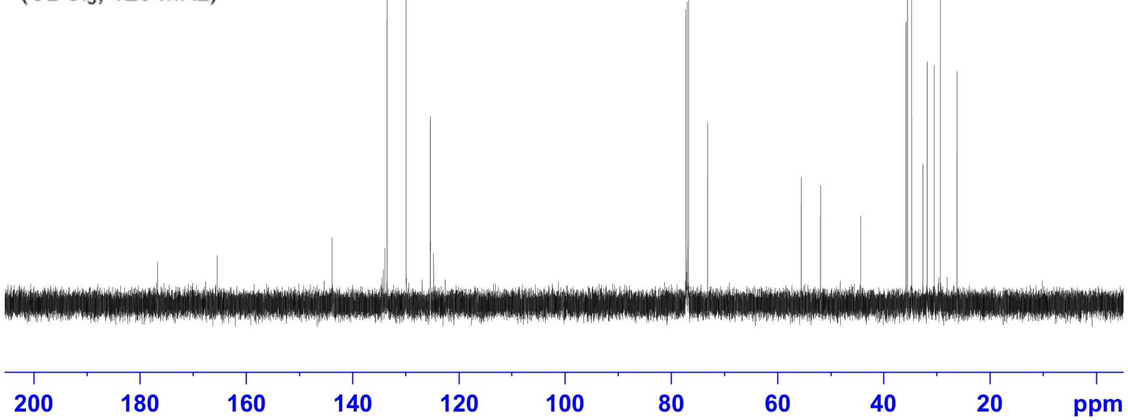
======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                     1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                    65536
SF           499.8700121 MHz
WDW                      EM
SSB       0
LB                  0.30 Hz
GB        0
PC                     1.00
```



36

($CDCl_3$, 125 MHz)



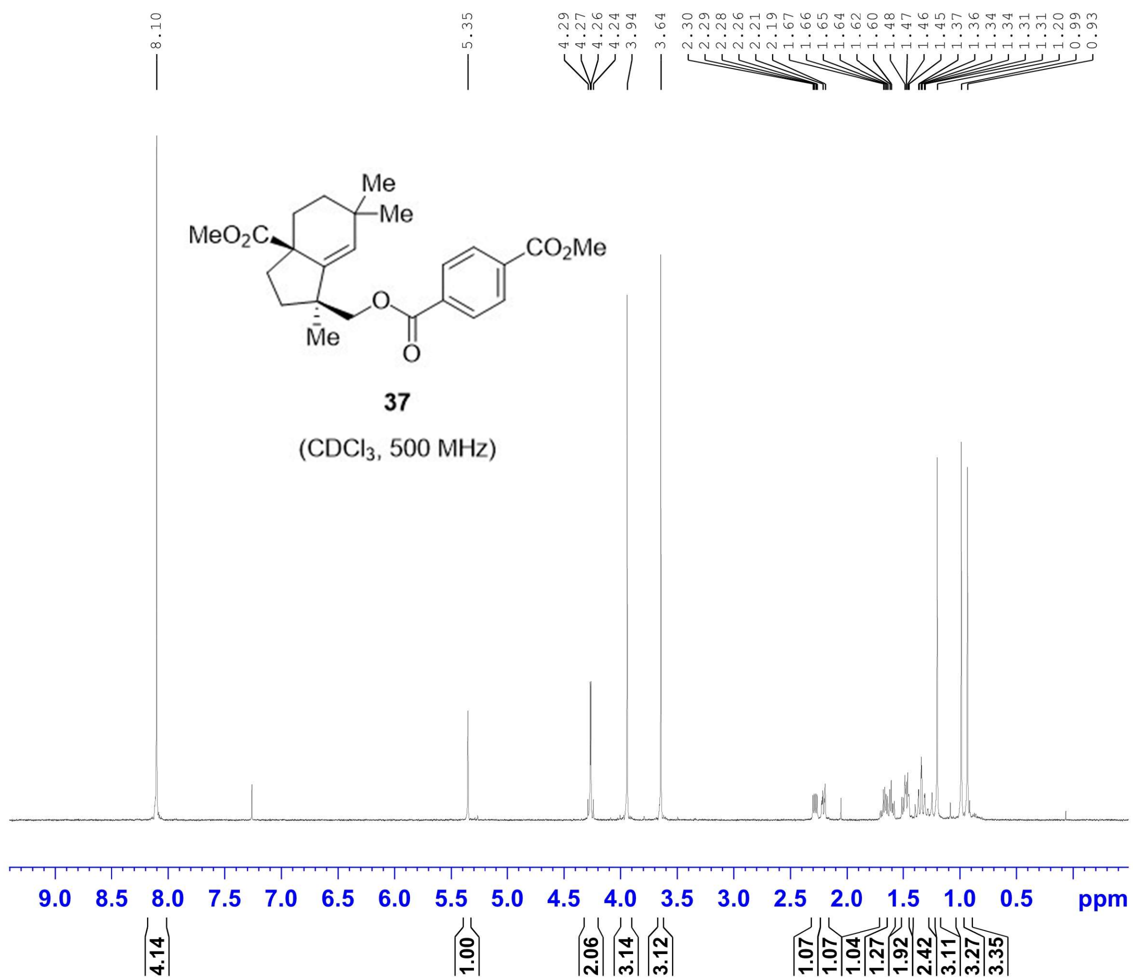

```
Current Data Parameters
NAME            yh-2-43-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180812
Time                22.23
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                     64
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  297.2 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



37

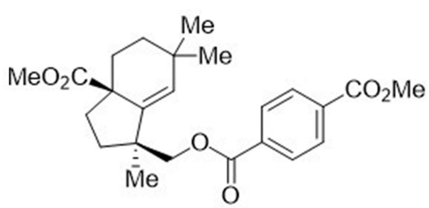
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME            yh-2-69-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180119
Time                21.15
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      3
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  893.6
DW                 50.000 usec
DE                   6.50 usec
TE                  297.2 K
D1             3.00000000 sec
TD0                     1

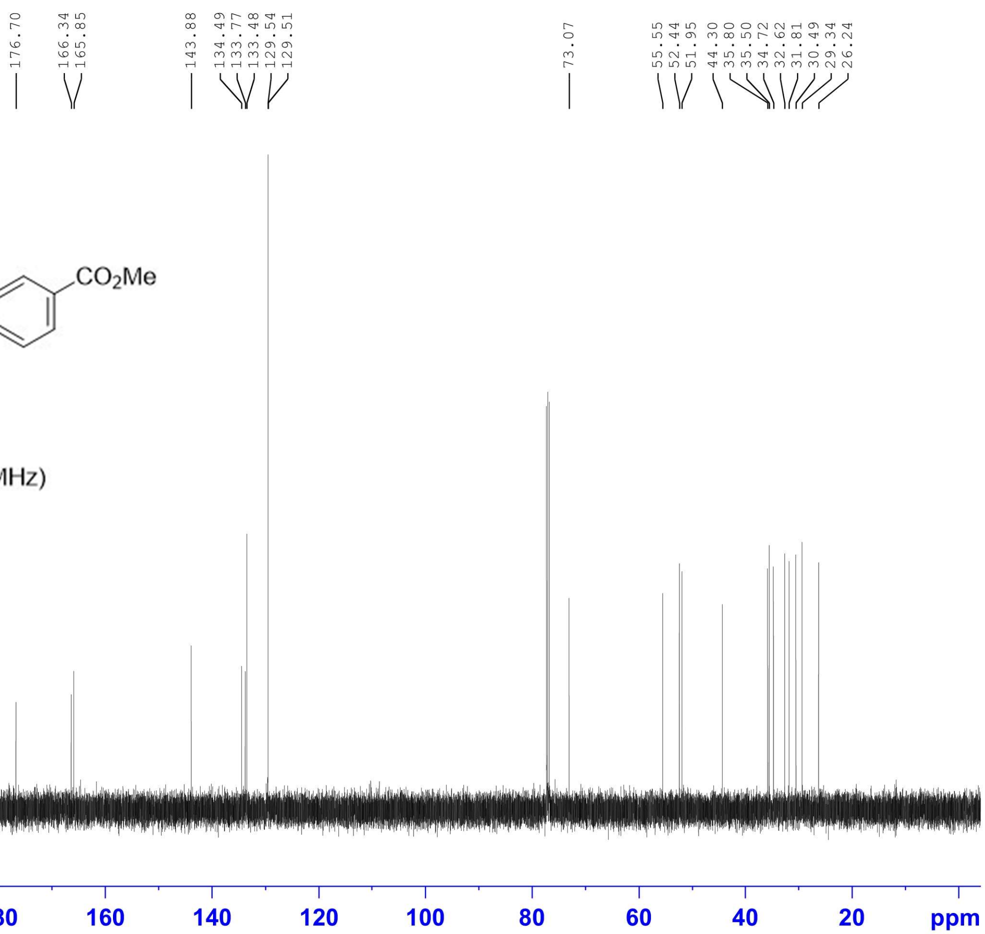
======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                  10.75 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700123 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



37

(CDCl$_3$, 125 MHz)



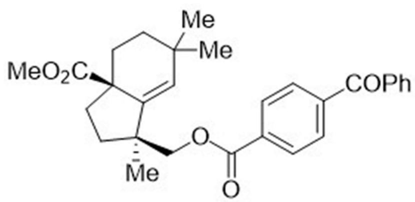

```
Current Data Parameters
NAME            yh-2-69-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180119
Time                21.22
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                      6
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  297.2 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                13C
P1                  10.00 usec
PLW1        72.83999634 W

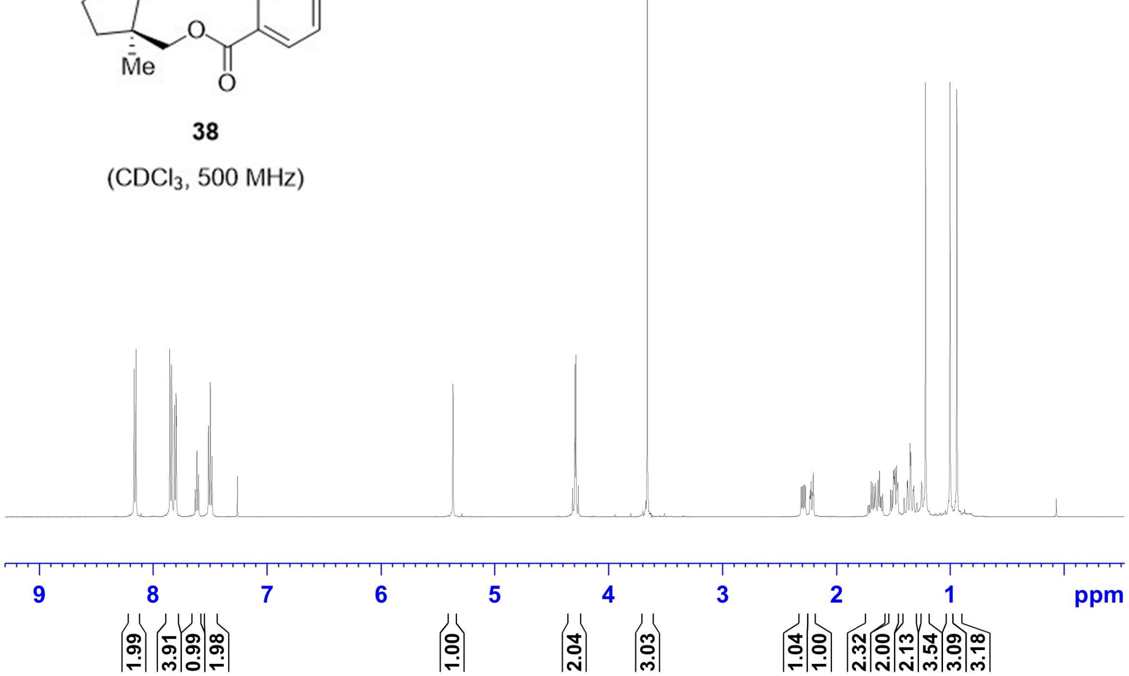
======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



38

(CDCl$_3$, 500 MHz)

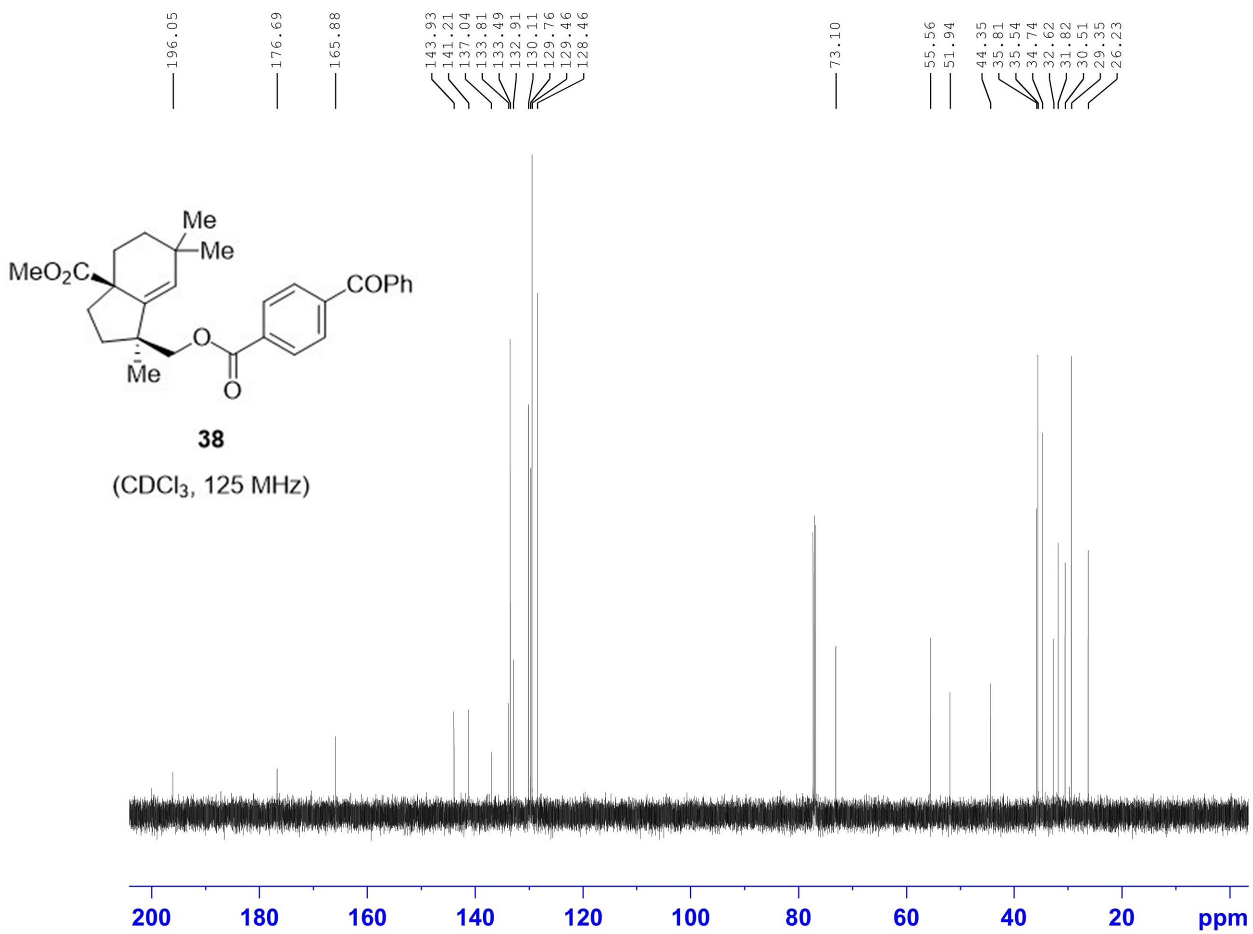



```
Current Data Parameters
NAME            yh-2-72-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180111
Time                22.37
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  28.76
DW                 50.000 usec
DE                   6.50 usec
TE                  296.7 K
D1             3.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                  10.75 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700124 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



38

($CDCl_3$, 125 MHz)

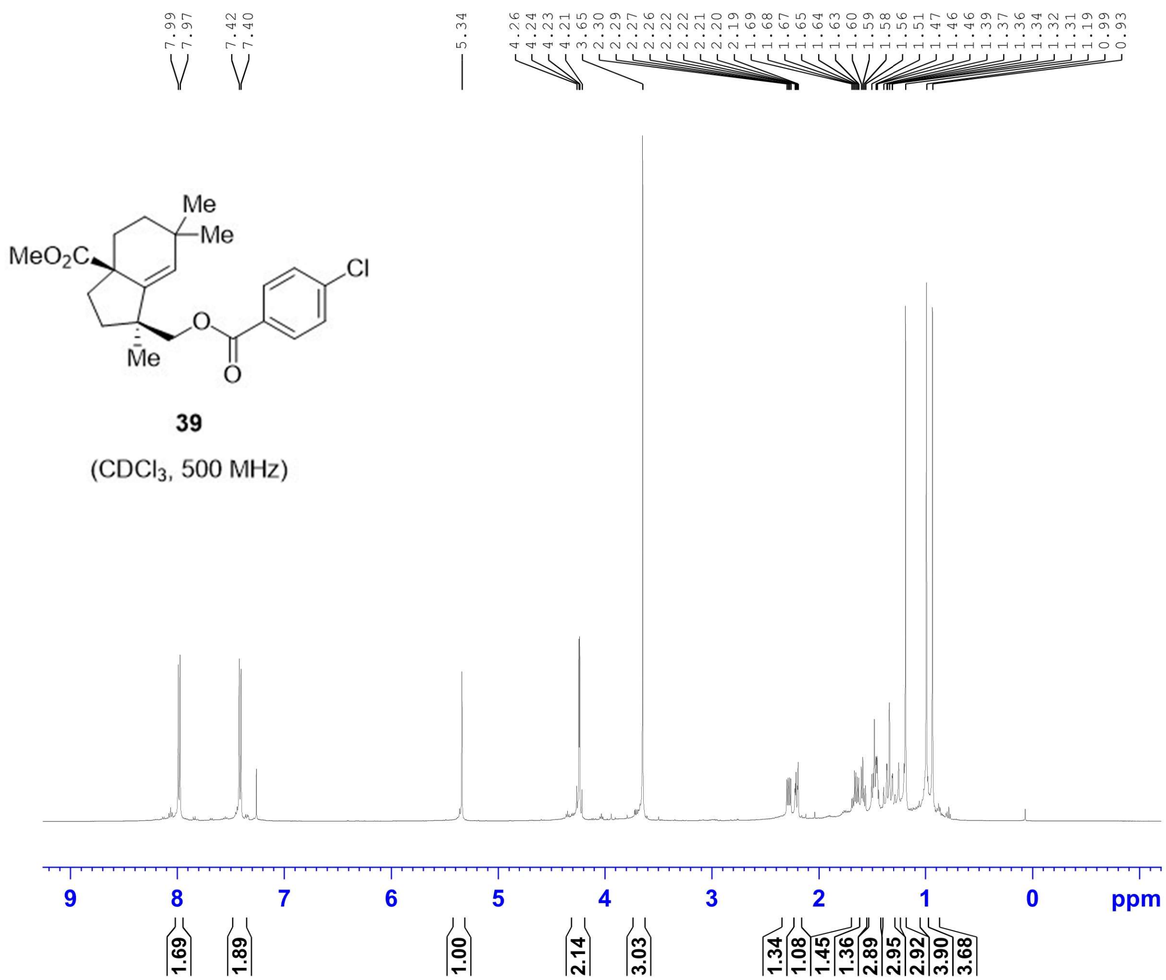
```
Current Data Parameters
NAME             yh-2-72-a
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20180111
Time                 22.44
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                      43
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   297.4 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                     13C
P1                     10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                   1048576
SF           125.6924115 MHz
WDW                       EM
SSB      0
LB                      0.30 Hz
GB       0
PC                      1.40
```



39

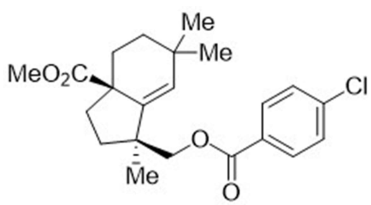
(CDCl$_3$, 500 MHz)


```
Current Data Parameters
NAME             yh-2-47-a
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180101
Time                 21.59
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                      16
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                   28.76
DW                  50.000 usec
DE                    6.50 usec
TE                   296.7 K
D1              3.00000000 sec
TD0                      1

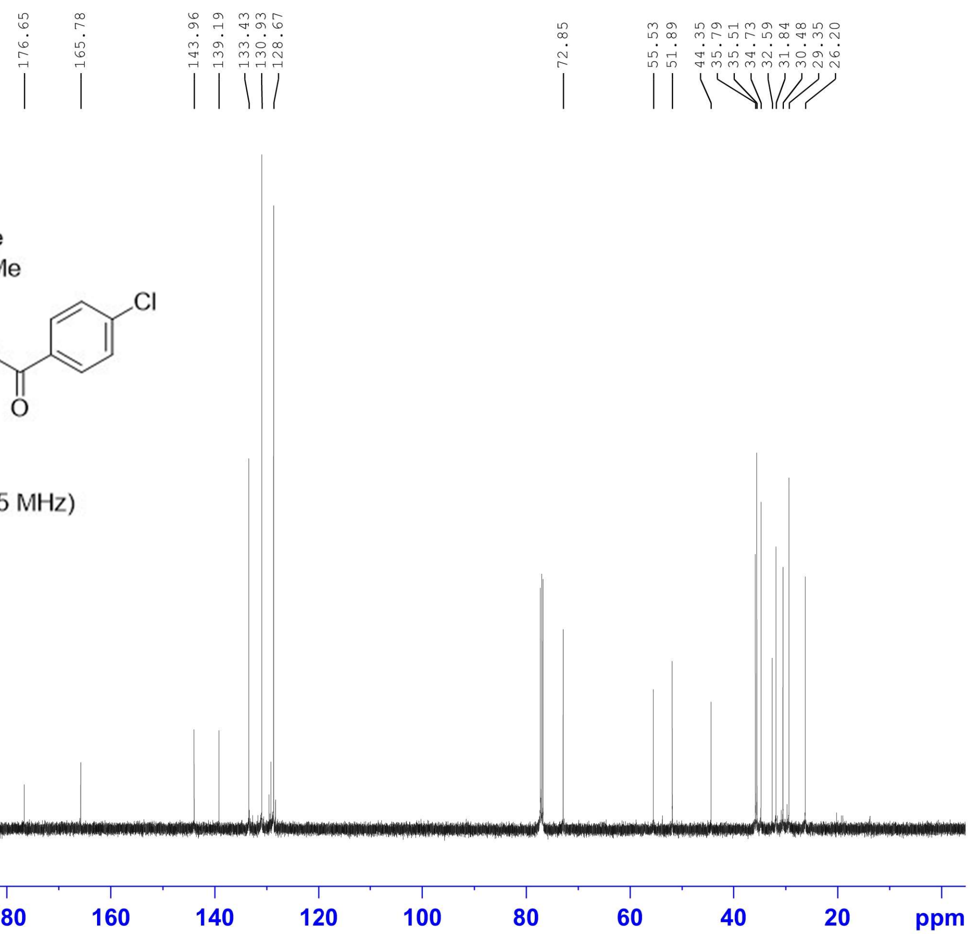
======== CHANNEL f1 ========
SFO1           499.8730869 MHz
NUC1                    1H
P1                   10.75 usec
PLW1           18.25000000 W

F2 - Processing parameters
SI                   65536
SF             499.8700122 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



39

($CDCl_3$, 125 MHz)



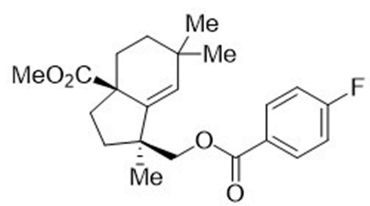

```
Current Data Parameters
NAME          yh-2-47-a
EXPNO                 2
PROCNO                2

F2 - Acquisition Parameters
Date_          20180101
Time              22.30
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zgdc
TD               187496
SOLVENT           CDCl3
NS                  261
DS                    0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                 2050
DW               16.000 usec
DE                 6.50 usec
TE                297.7 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                13C
P1                10.00 usec
PLW1        72.83999634 W

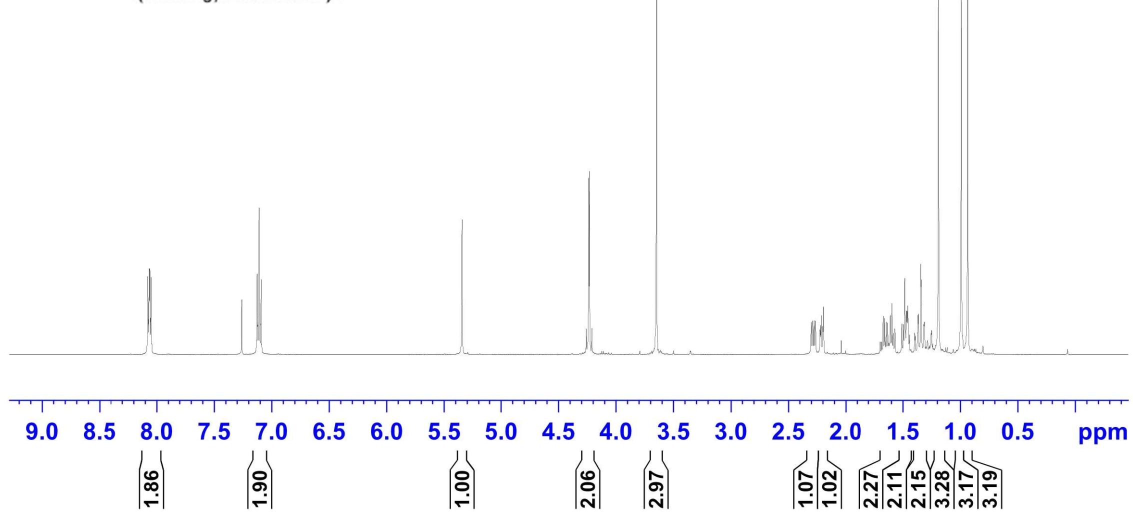
======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI              1048576
SF          125.6924115 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.40
```



40

($CDCl_3$, 500 MHz)

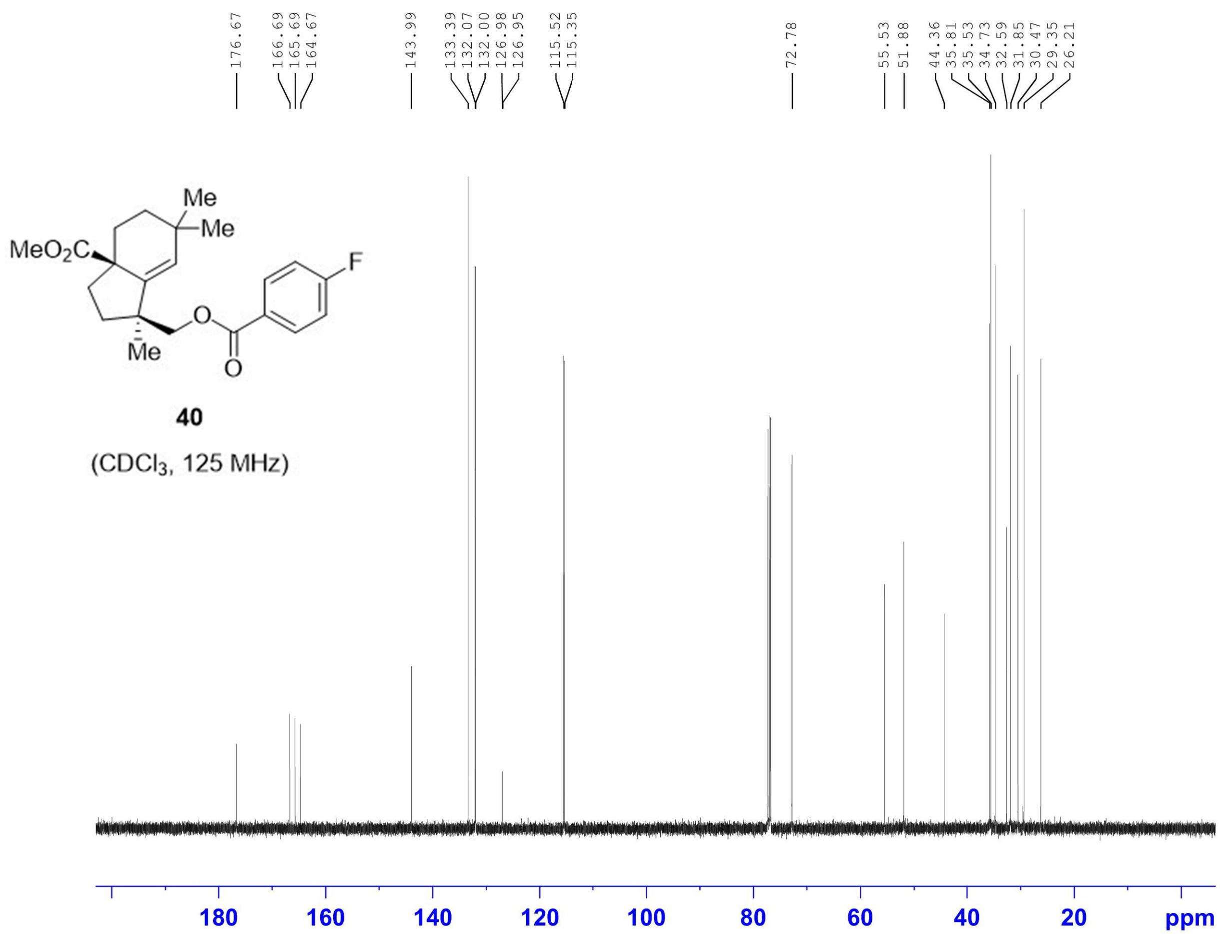



```
Current Data Parameters
NAME             yh-2-55-a
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180103
Time                 21.58
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       4
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                   29.95
DW                  50.000 usec
DE                    6.50 usec
TE                   296.2 K
D1              3.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                    1H
P1                   10.75 usec
PLW1       18.25000000 W

F2 - Processing parameters
SI                   65536
SF          499.8700123 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



40

($CDCl_3$, 125 MHz)

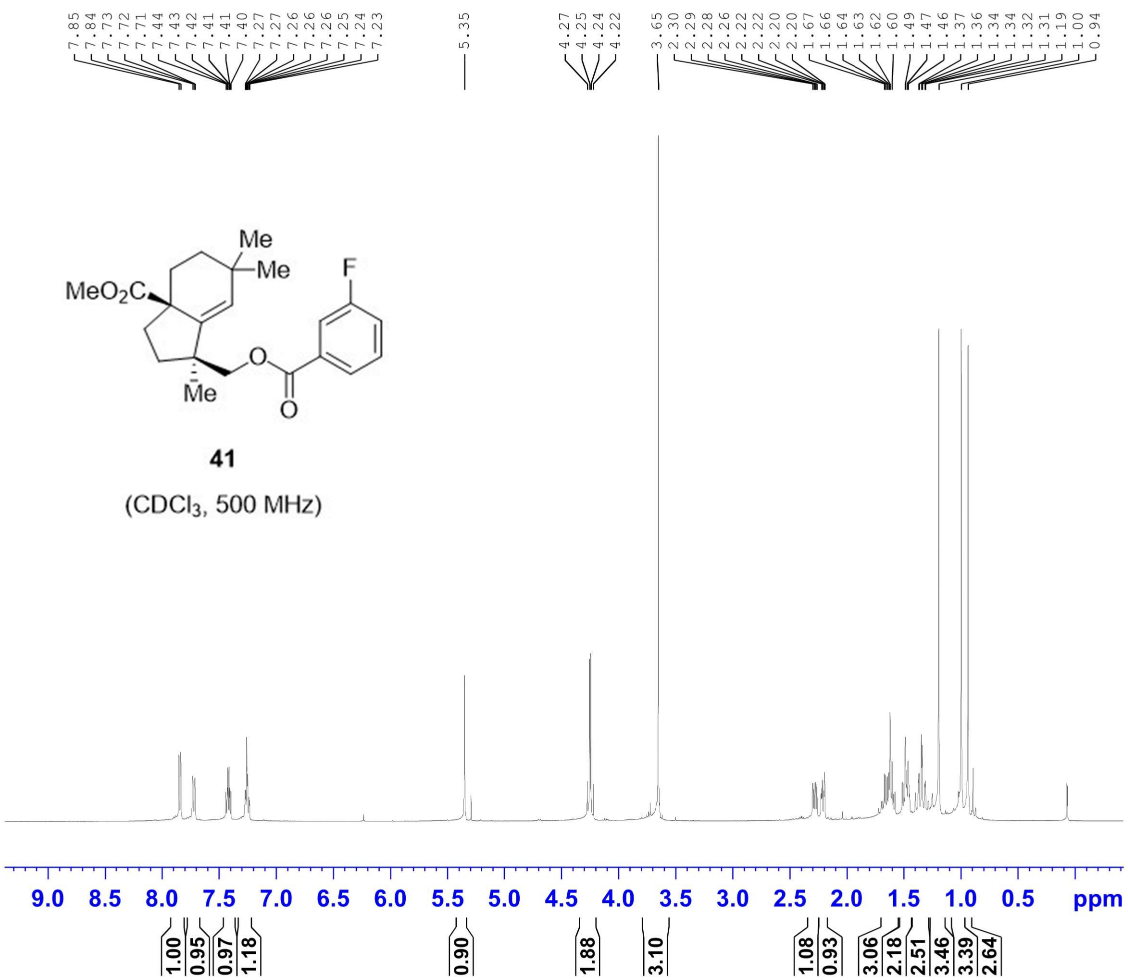
```
Current Data Parameters
NAME            yh-2-55-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180103
Time                22.36
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    354
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  297.9 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```

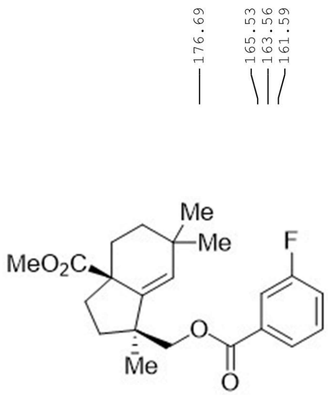



```
Current Data Parameters
NAME          yh-2-68-a
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20180821
Time              16.51
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    5
DS                    0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                62.78
DW               50.000 usec
DE                 6.50 usec
TE                295.7 K
D1           4.00000000 sec
TD0                   1

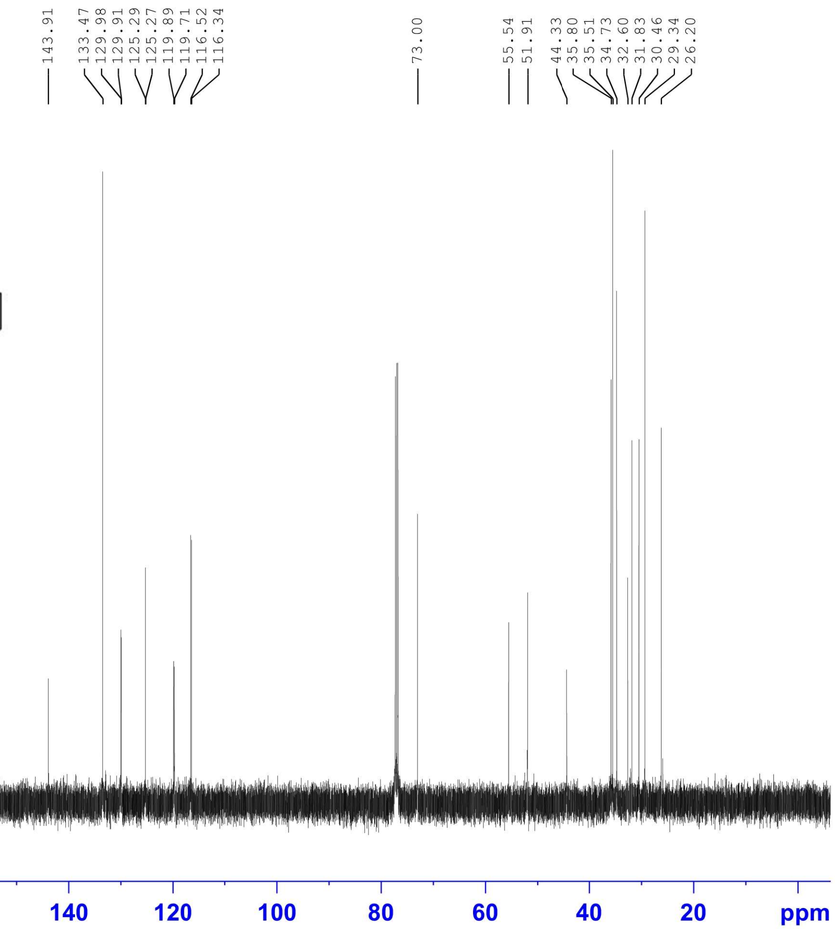
======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                 1H
P1                 3.58 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                65536
SF          499.8700123 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



41

(CDCl$_3$, 125 MHz)



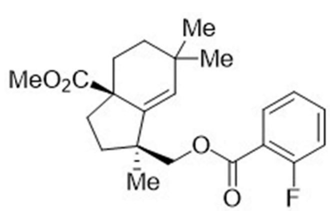

```
Current Data Parameters
NAME              yh-2-68-a
EXPNO                     2
PROCNO                    2

F2 - Acquisition Parameters
Date_              20180821
Time                  17.07
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT               CDCl3
NS                      115
DS                        0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                     2050
DW                   16.000 usec
DE                     6.50 usec
TE                    297.0 K
D1               3.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                     13C
P1                     10.00 usec
PLW1         72.83999634 W

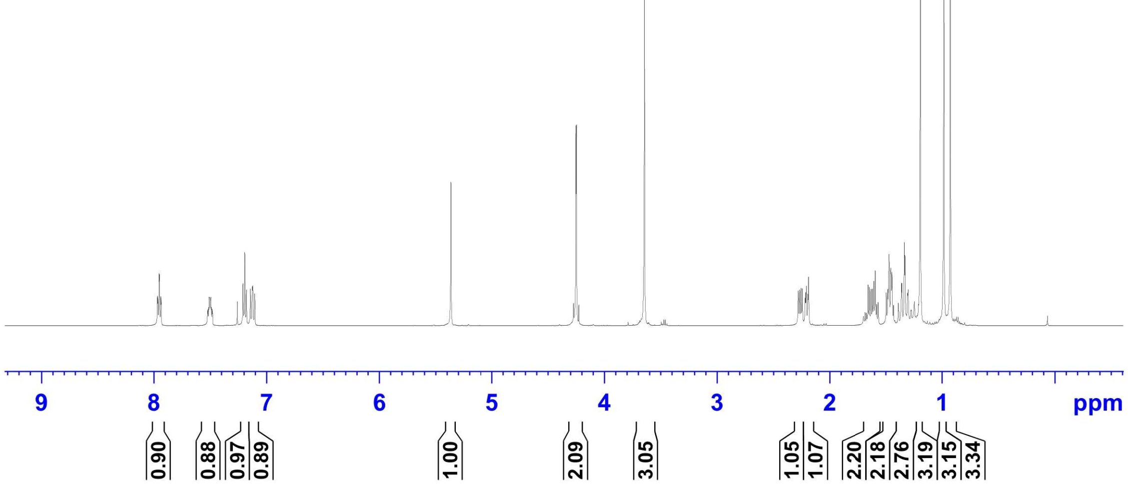
======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                   1048576
SF           125.6924115 MHz
WDW                       EM
SSB      0
LB                      0.30 Hz
GB       0
PC                      1.40
```



42

(CDCl$_3$, 500 MHz)

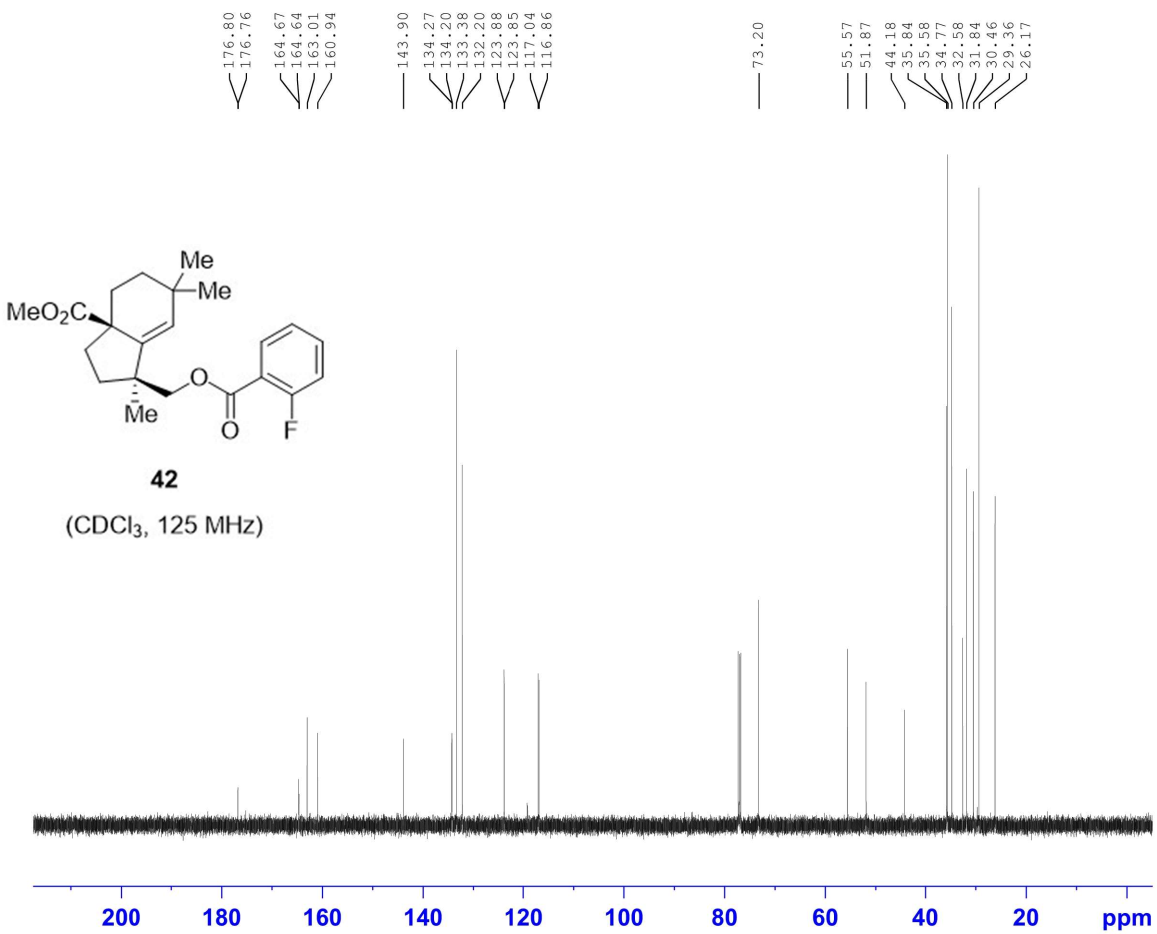



```
Current Data Parameters
NAME          yh-2-34-a
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20171218
Time              21.22
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                   16
DS                    0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                16.71
DW               50.000 usec
DE                 6.50 usec
TE                296.8 K
D1           3.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                 1H
P1                10.75 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                65536
SF          499.8700122 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



42

(CDCl$_3$, 125 MHz)

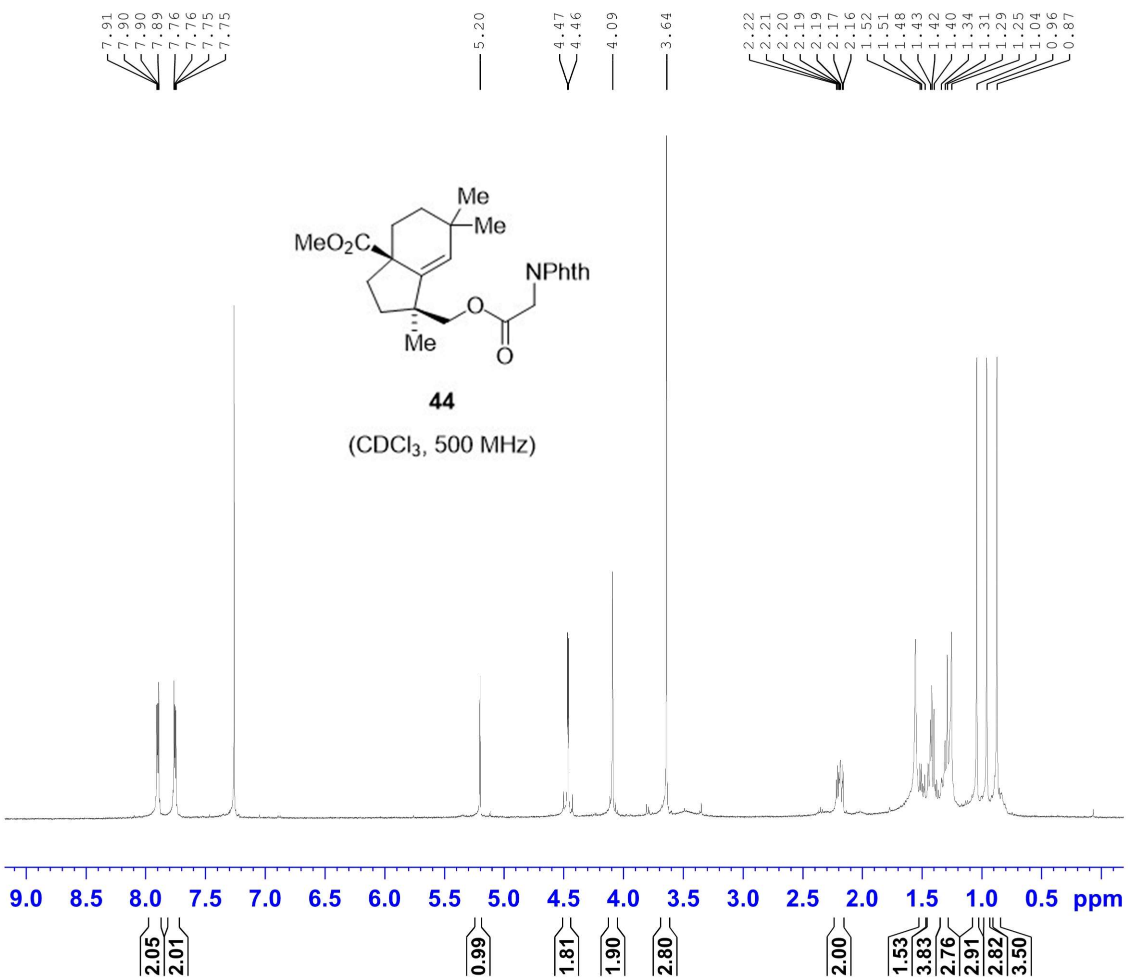
```
Current Data Parameters
NAME              yh-2-34-a
EXPNO                     2
PROCNO                    2

F2 - Acquisition Parameters
Date_              20171218
Time                  21.35
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT               CDCl3
NS                       52
DS                        0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                     2050
DW              16.000 usec
DE                6.50 usec
TE                297.6 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1       125.7049802 MHz
NUC1                    13C
P1               10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2       499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2            80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                  1048576
SF          125.6924115 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.40
```



44

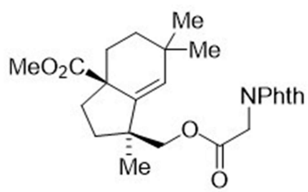
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME          yh-5-55-d
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190712
Time              21.14
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    4
DS                    0
SWH          10000.000 Hz
FIDRES        0.166672 Hz
AQ           2.9999001 sec
RG               105.66
DW               50.000 usec
DE                 6.50 usec
TE                297.5 K
D1           4.00000000 sec
TD0                   1

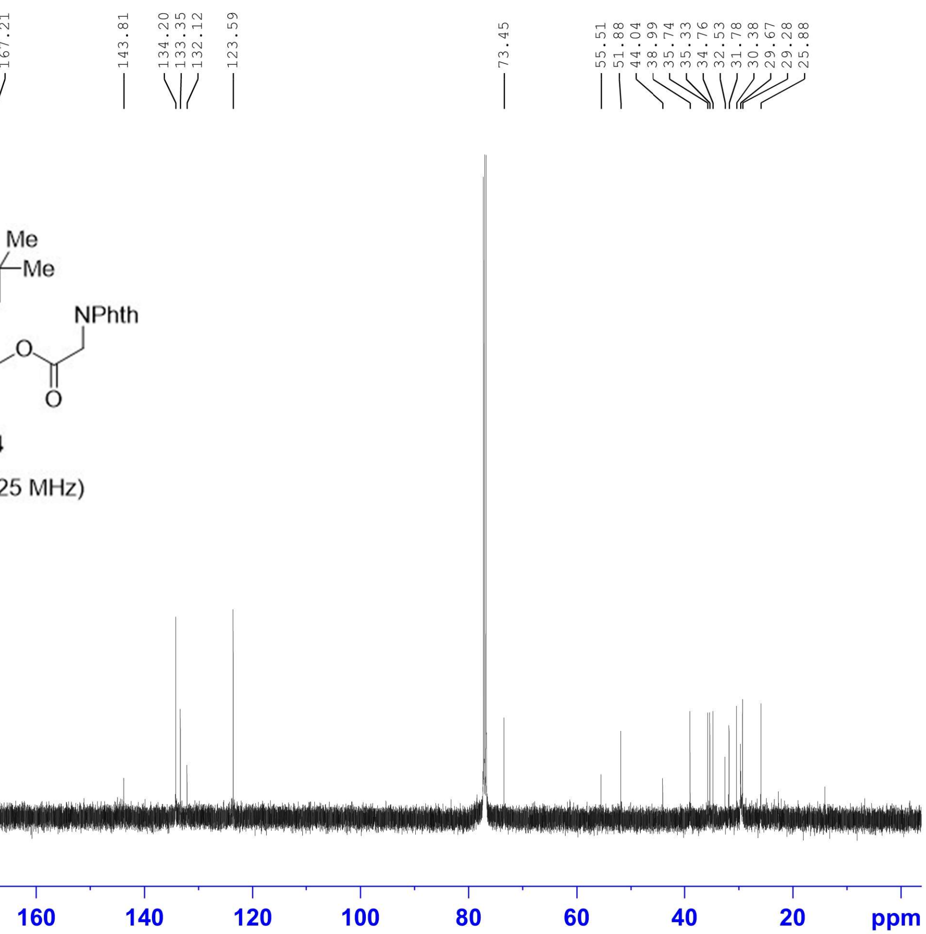
======== CHANNEL f1 ========
SFO1       499.8730869 MHz
NUC1                 1H
P1                 3.58 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                65536
SF         499.8700124 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



44

(CDCl$_3$, 125 MHz)



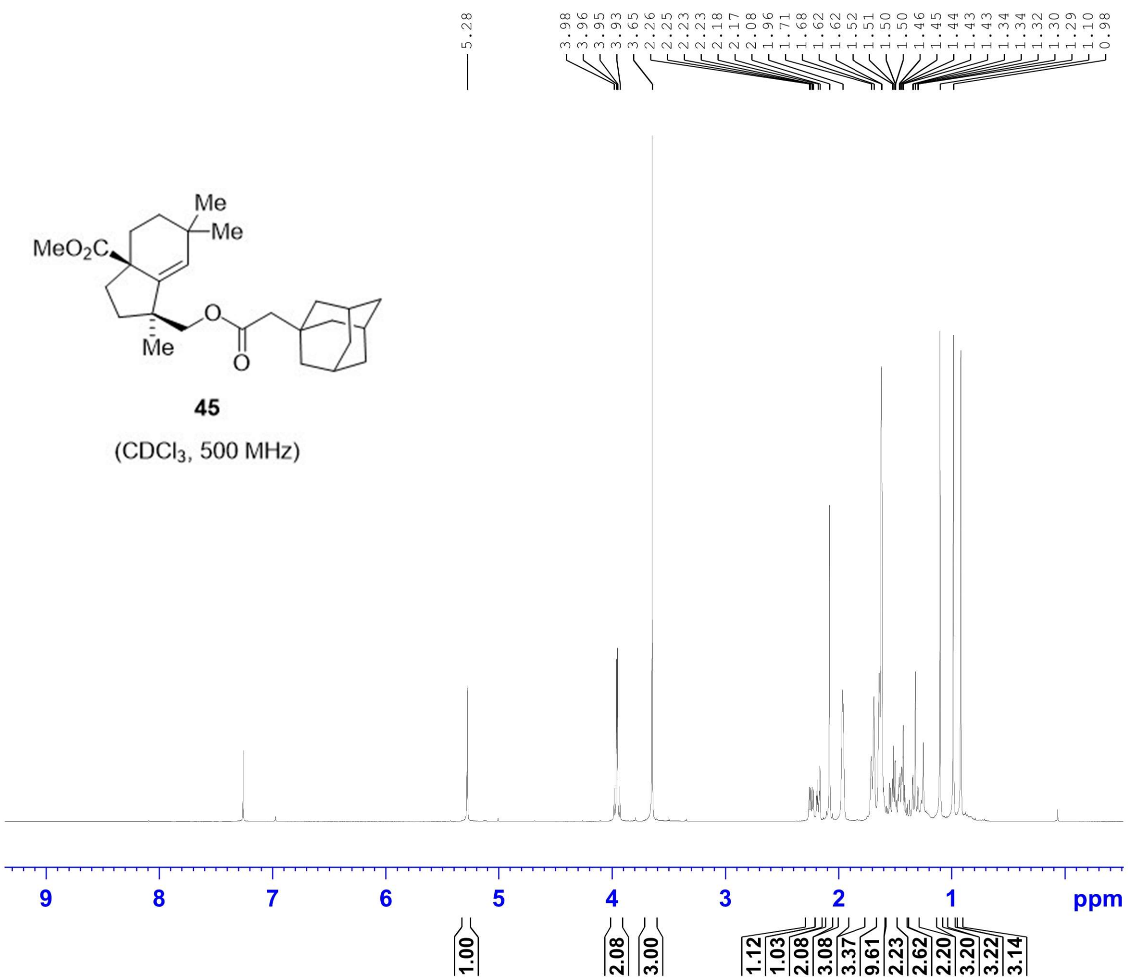

```
Current Data Parameters
NAME             yh-5-51-a
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20180926
Time                 23.03
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                    1083
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   301.2 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                    13C
P1                    10.00 usec
PLW1        72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI                  1048576
SF           125.6924115 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.40
```

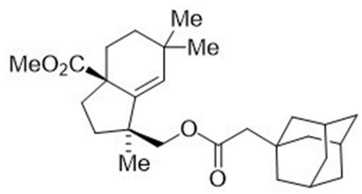



```
Current Data Parameters
NAME            yh-2-25-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171214
Time                21.05
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                     16
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  28.76
DW                 50.000 usec
DE                   6.50 usec
TE                  296.9 K
D1             3.00000000 sec
TD0                     1

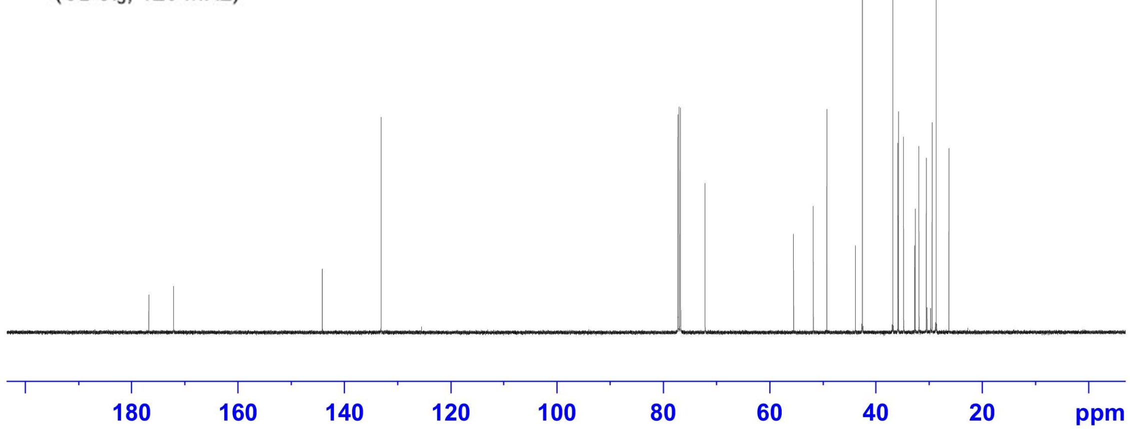
======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                  10.75 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700123 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



45

($CDCl_3$, 125 MHz)



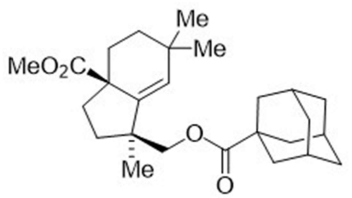

```
Current Data Parameters
NAME             yh-2-25-a
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20171214
Time                 22.48
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                     978
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   298.9 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                     13C
P1                     10.00 usec
PLW1            72.83999634 W

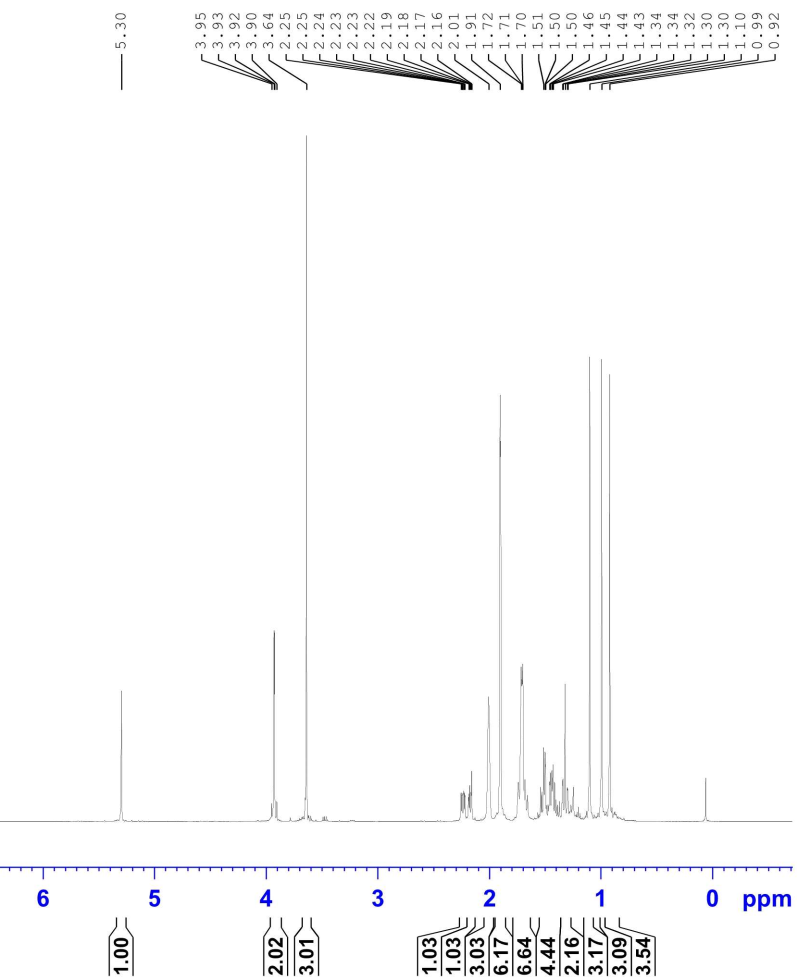
======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                  80.00 usec
PLW2            19.00000000 W
PLW12            0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6924115 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



46

($CDCl_3$, 500 MHz)

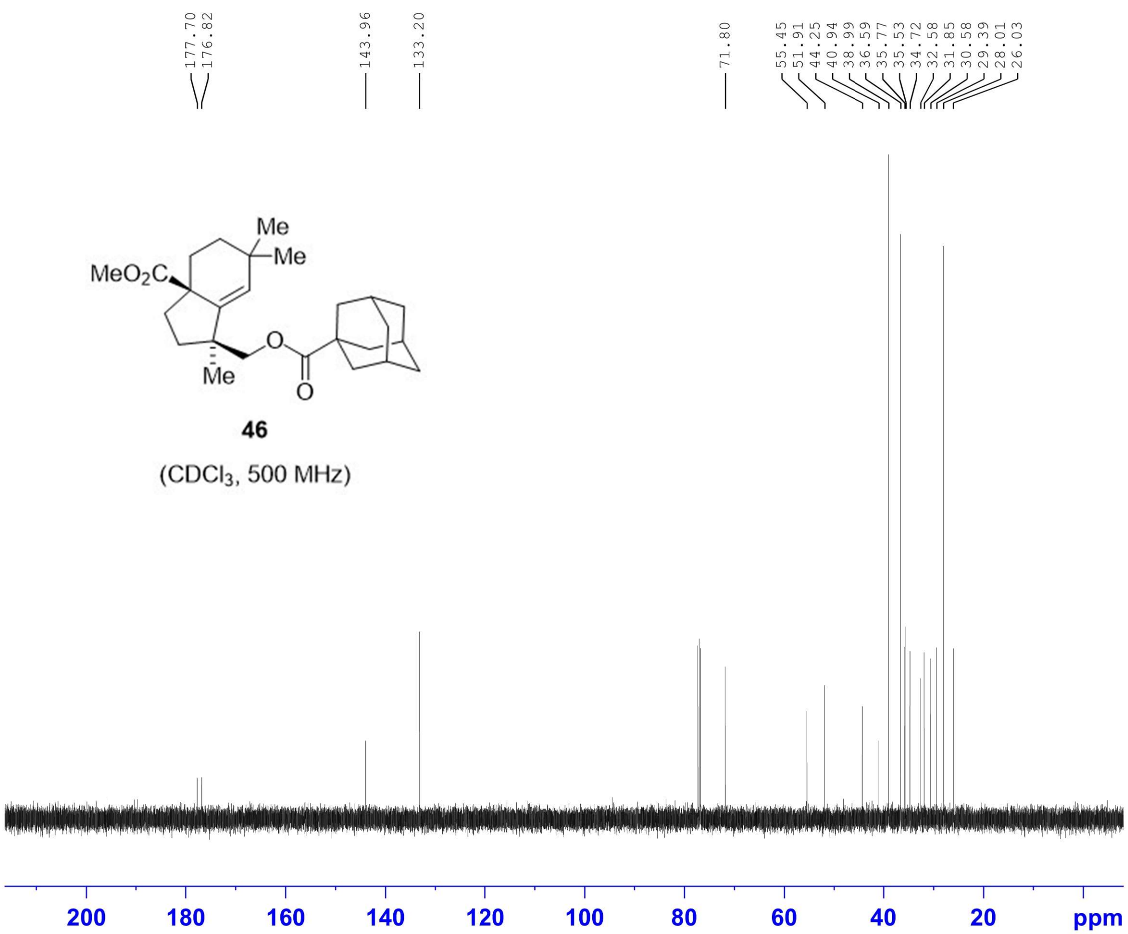



```
Current Data Parameters
NAME             yh-2-73-a
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180121
Time                 22.32
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       2
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                   19.64
DW                  50.000 usec
DE                    6.50 usec
TE                   296.8 K
D1              3.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           499.8730869 MHz
NUC1                    1H
P1                   10.75 usec
PLW1           18.25000000 W

F2 - Processing parameters
SI                   65536
SF             499.8700124 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



46

($CDCl_3$, 500 MHz)

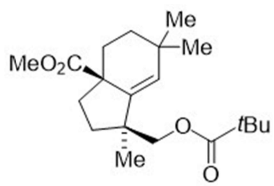

```
Current Data Parameters
NAME            yh-2-73-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180121
Time                22.35
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                      7
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.9 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

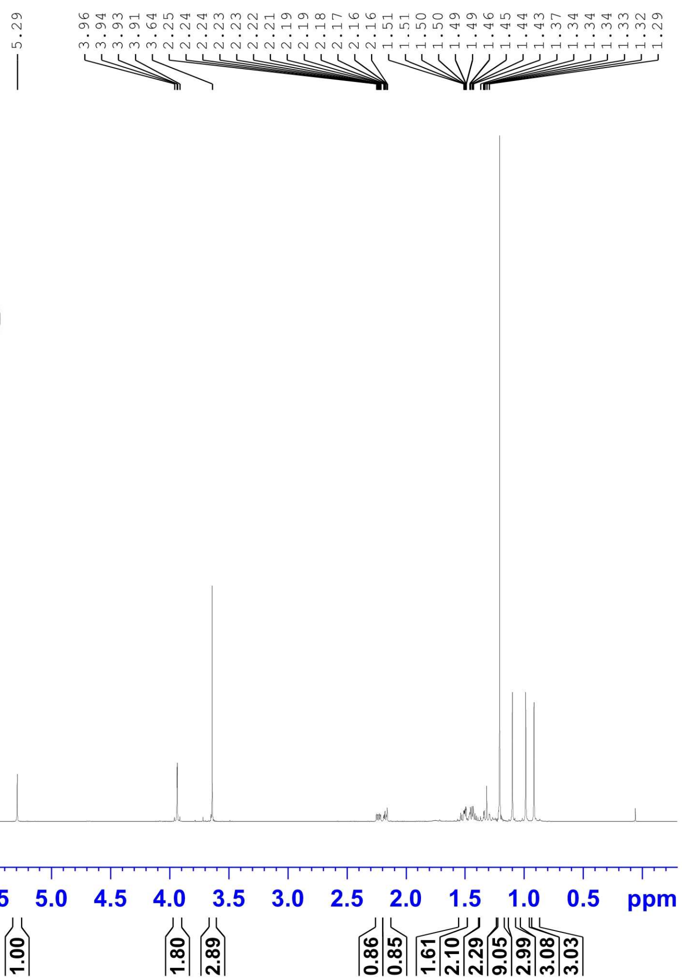
======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



47

($CDCl_3$, 500 MHz)

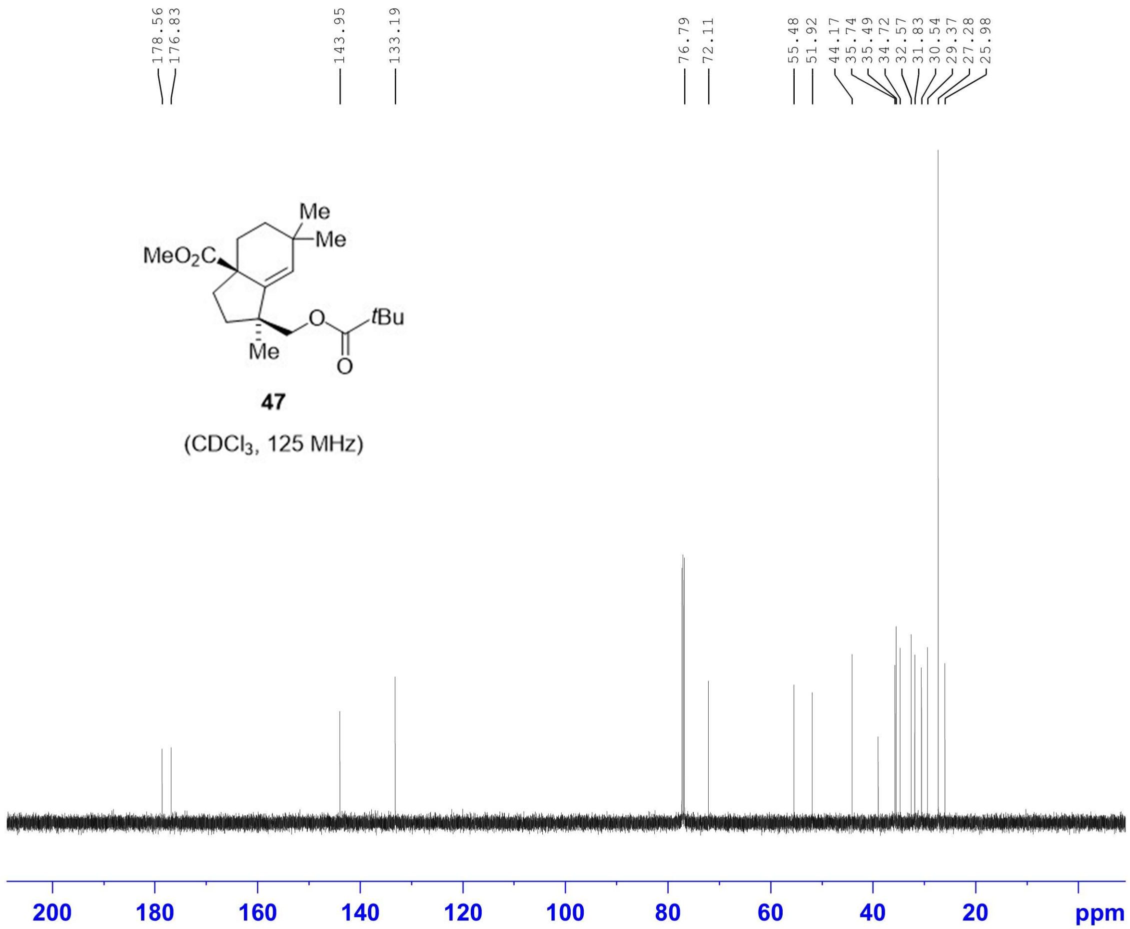



```
Current Data Parameters
NAME             yh-3-18-a
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180815
Time                 16.03
INSTRUM              spect
PROBHD   5 mm PAQNP 1H/
PULPROG                 zg
TD                   44998
SOLVENT              CDCl3
NS                       1
DS                       0
SWH               7500.000 Hz
FIDRES            0.166674 Hz
AQ               2.9998667 sec
RG                    50.8
DW                  66.667 usec
DE                   71.43 usec
TE                   294.5 K
D1              3.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.50 usec
PL1        0 dB
PL1W         24.54113007 W
SFO1        500.1330008 MHz

F2 - Processing parameters
SI                   32768
SF          500.1300138 MHz
WDW                     EM
SSB        0
LB                    0.30 Hz
GB         0
PC                    1.00
```



47

($CDCl_3$, 125 MHz)

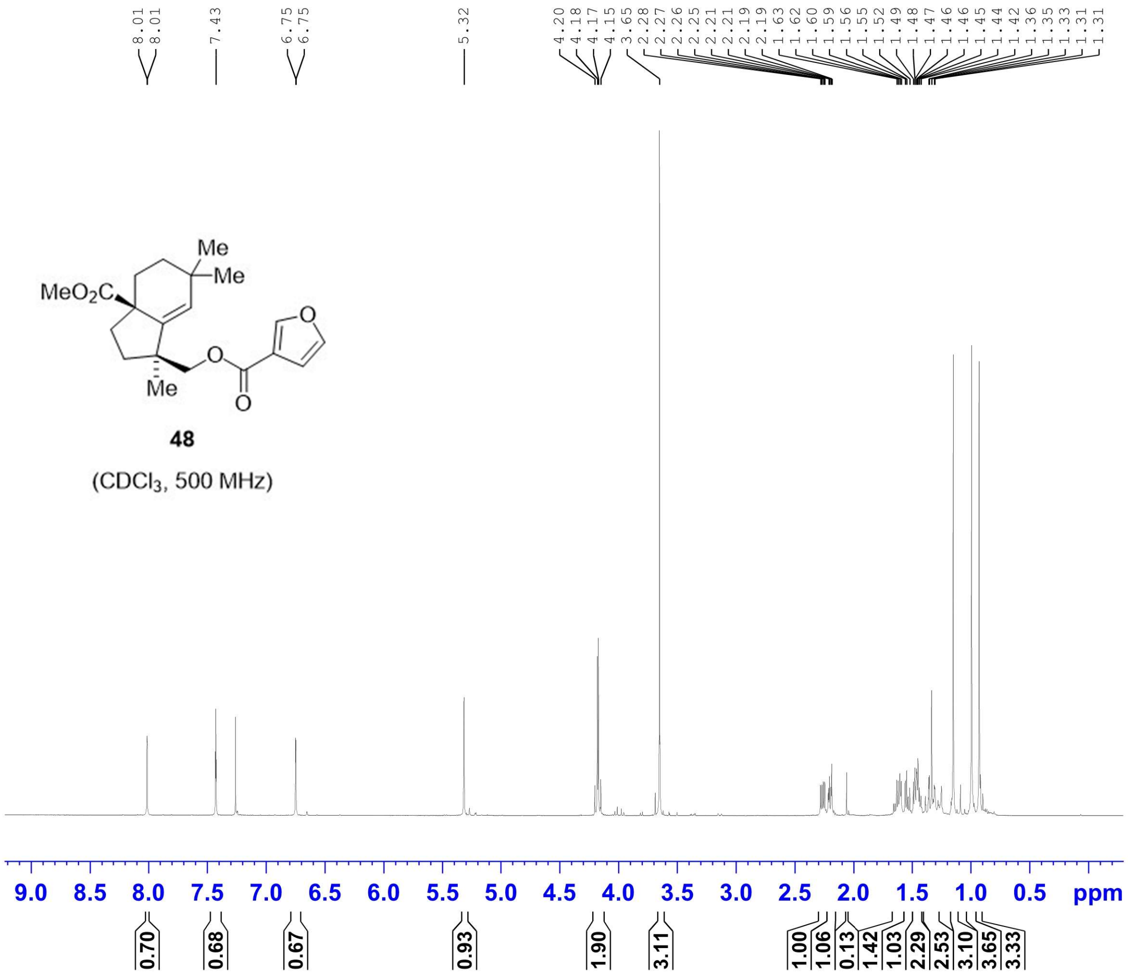

```
Current Data Parameters
NAME            yh-3-18-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180815
Time                16.16
INSTRUM             spect
PROBHD   5 mm PAQNP 1H/
PULPROG              zgpg
TD                 197364
SOLVENT             CDCl3
NS                     15
DS                      0
SWH             32894.738 Hz
FIDRES           0.166670 Hz
AQ              2.9999328 sec
RG                   2050
DW                 15.200 usec
DE                   6.00 usec
TE                  295.0 K
D1            10.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.90 usec
PL1                  1.00 dB
PL1W          72.42802429 W
SFO1         125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2       0 dB
PL12                16.50 dB
PL13                17.00 dB
PL2W          24.54113007 W
PL12W          0.54940748 W
PL13W          0.48965994 W
SFO2         500.1325006 MHz

F2 - Processing parameters
SI                 131072
SF           125.7577890 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.40
```



48

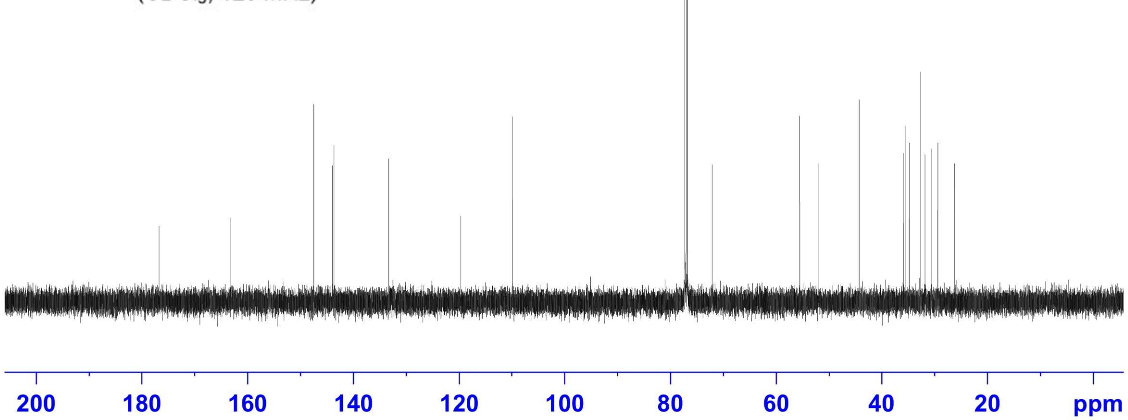
(CDCl$_3$, 500 MHz)

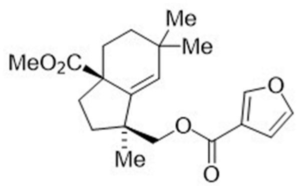
```
Current Data Parameters
NAME          yh-2-143-a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180419
Time_              20.41
INSTRUM            spect
PROBHD   5 mm PAQNP 1H/
PULPROG               zg
TD                 44998
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             7500.000 Hz
FIDRES          0.166674 Hz
AQ             2.9998667 sec
RG                   181
DW                66.667 usec
DE                 71.43 usec
TE                 295.1 K
D1            3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1       0 dB
PL1W         24.54113007 W
SFO1         500.1330008 MHz

F2 - Processing parameters
SI                 16384
SF           500.1300133 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```





48

($CDCl_3$, 125 MHz)

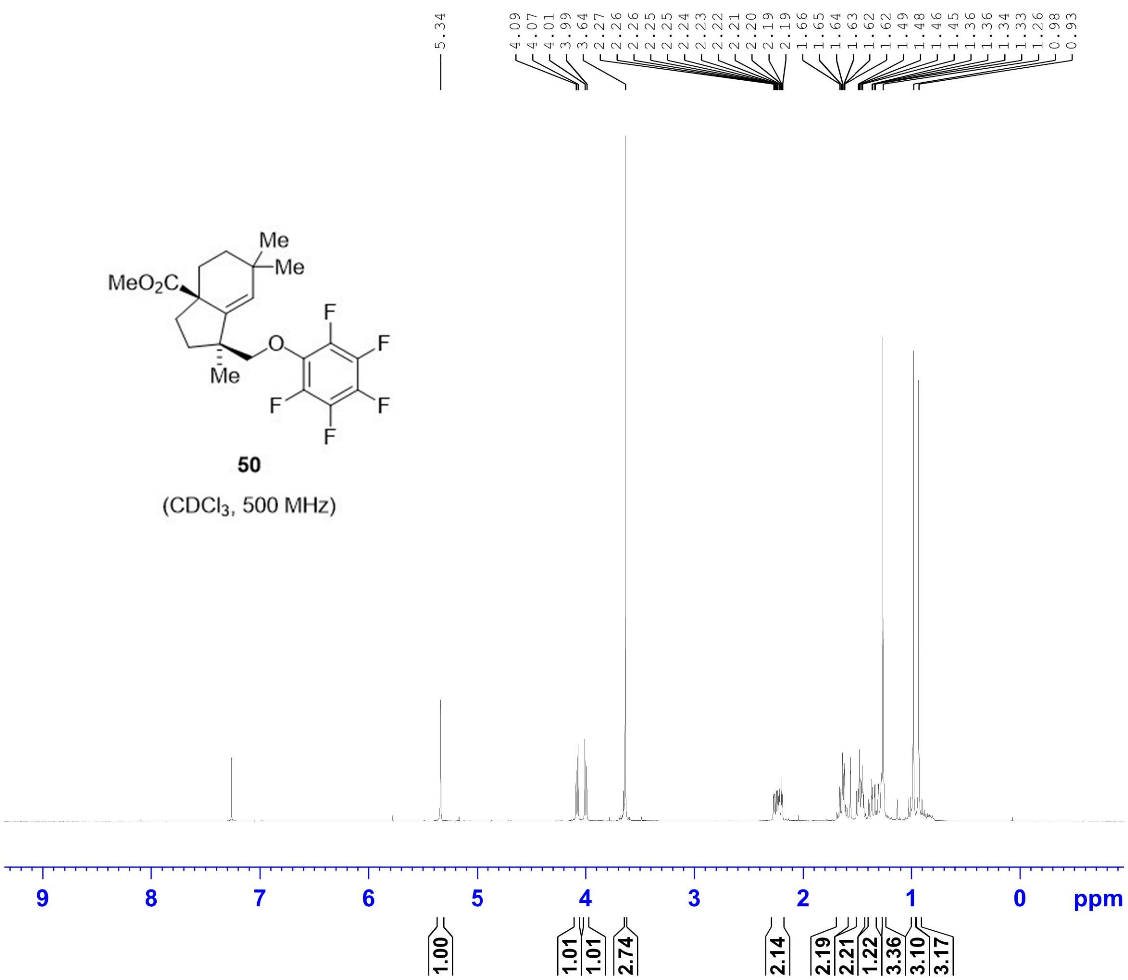
```
Current Data Parameters
NAME            yh-2-143-a
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20180419
Time                 20.58
INSTRUM              spect
PROBHD   5 mm PAQNP 1H/
PULPROG               zgpg
TD                  197364
SOLVENT              CDCl3
NS                      27
DS                       4
SWH             32894.738 Hz
FIDRES           0.166670 Hz
AQ              2.9999328 sec
RG                    2050
DW                  15.200 usec
DE                    6.00 usec
TE                   295.6 K
D1            10.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                   1.00 dB
PL1W           72.42802429 W
SFO1          125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2         0 dB
PL12                 16.50 dB
PL13                 17.00 dB
PL2W           24.54113007 W
PL12W           0.54940748 W
PL13W           0.48965994 W
SFO2          500.1325006 MHz

F2 - Processing parameters
SI                  131072
SF            125.7577890 MHz
WDW                     EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.40
```

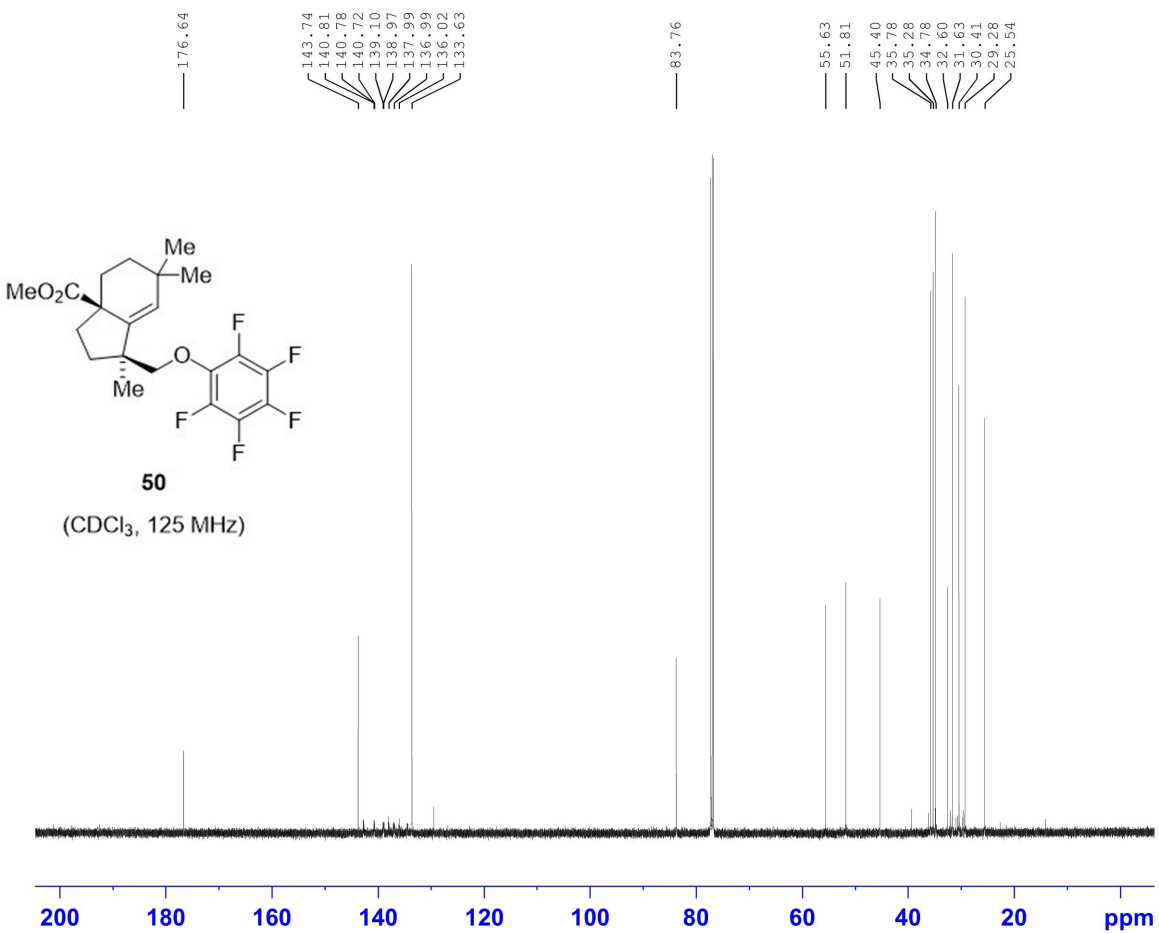



```
Current Data Parameters
NAME            yh-2-63-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180110
Time_               21.27
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                  37.92
DW                 50.000 usec
DE                   6.50 usec
TE                  296.7 K
D1            3.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                   1H
P1                  10.75 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                  65536
SF           499.8700123 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



50

($CDCl_3$, 125 MHz)

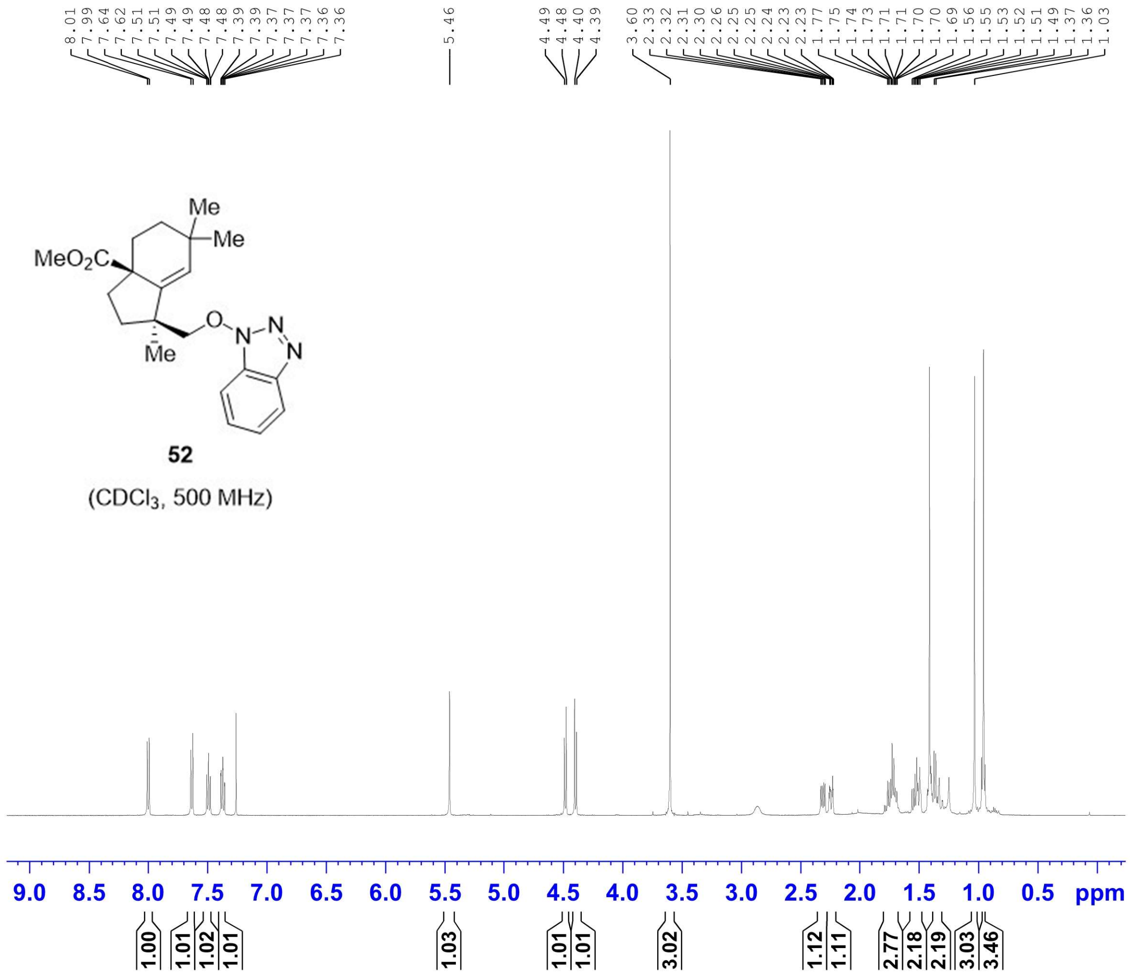

```
Current Data Parameters
NAME             yh-2-63-a
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20180111
Time                  0.59
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                    2048
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   298.7 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2           499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6924115 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



52

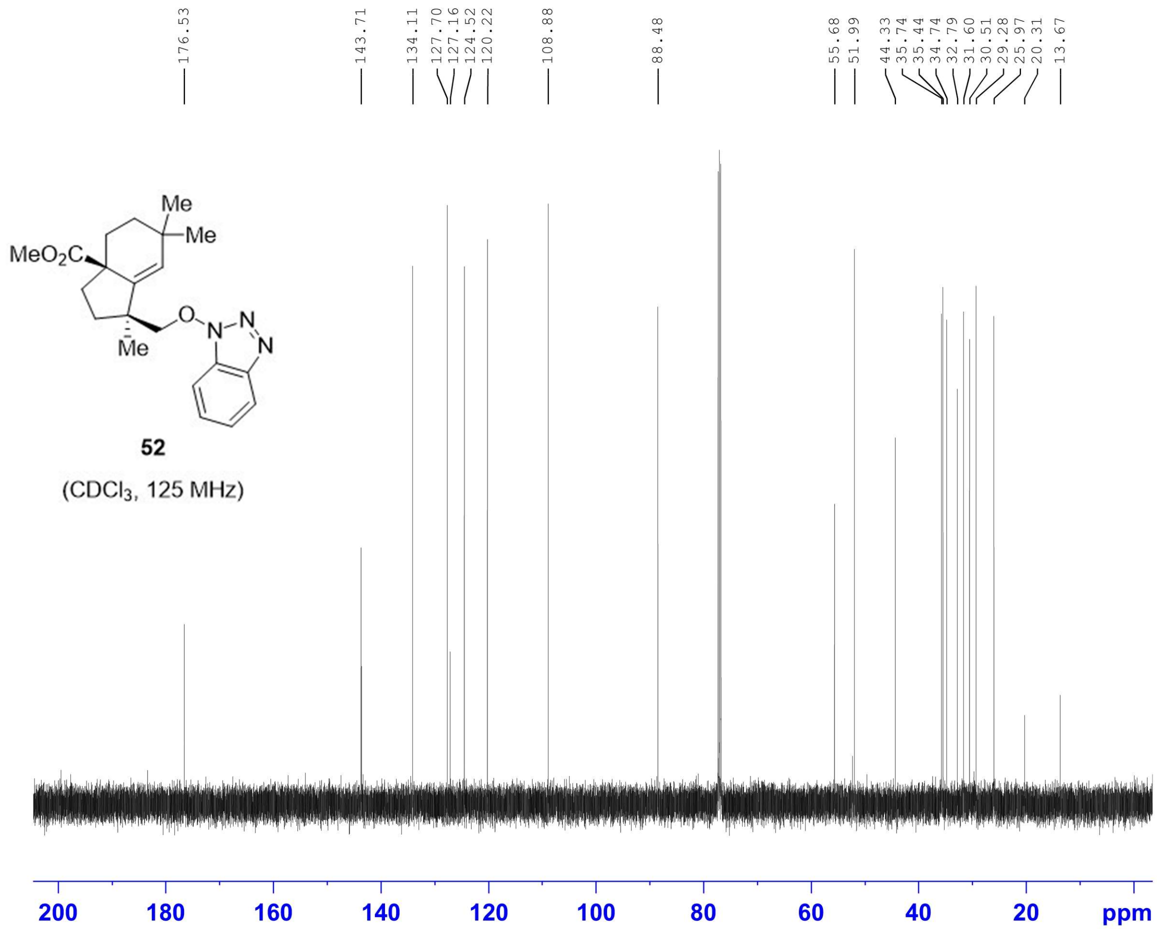
($CDCl_3$, 500 MHz)


```
Current Data Parameters
NAME          yh-7-27-b
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190930
Time              15.25
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    4
DS                    0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                70.49
DW               50.000 usec
DE                 6.50 usec
TE                298.0 K
D1           4.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                 1H
P1                 3.58 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                65536
SF          499.8700109 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



52

(CDCl$_3$, 125 MHz)

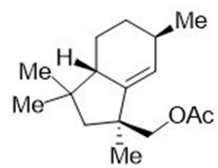
```
Current Data Parameters
NAME             yh-7-27-b
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_            20190930
Time                16.10
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                     67
DS                      0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                   2050
DW               16.000 usec
DE                 6.50 usec
TE                298.0 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                    13C
P1                    10.00 usec
PLW1        72.83999634 W

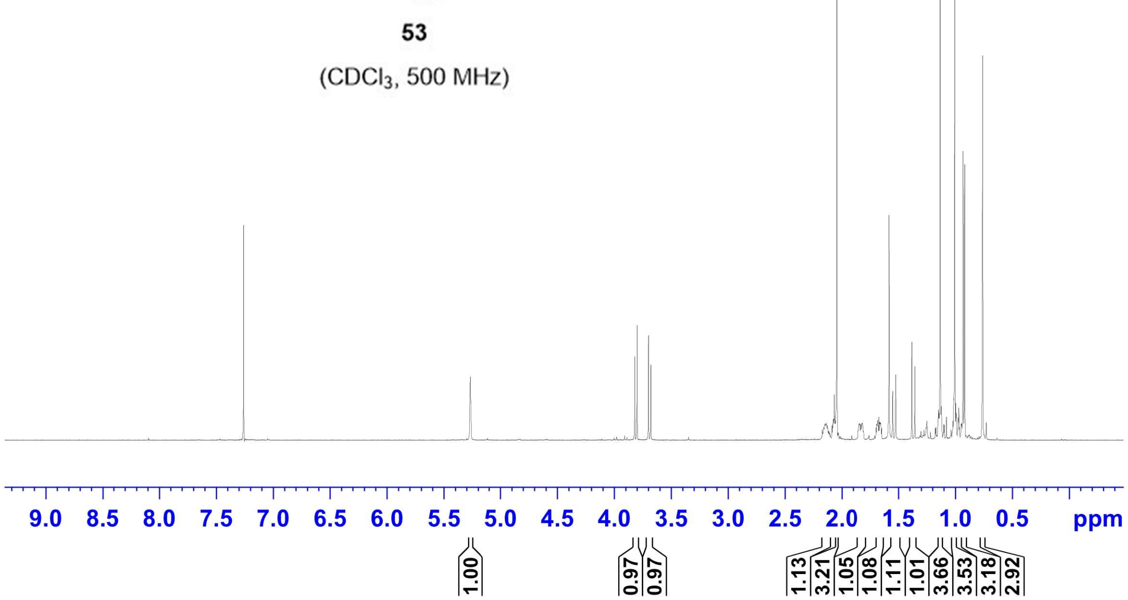
======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI                  1048576
SF          125.6924115 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.40
```



53

($CDCl_3$, 500 MHz)

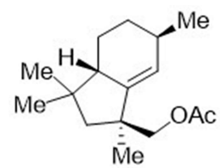



```
Current Data Parameters
NAME          yh-5-46-r
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20180731
Time              20.07
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    3
DS                    0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG               196.79
DW               50.000 usec
DE                10.00 usec
TE                294.1 K
D1           3.00000000 sec
TD0                   1

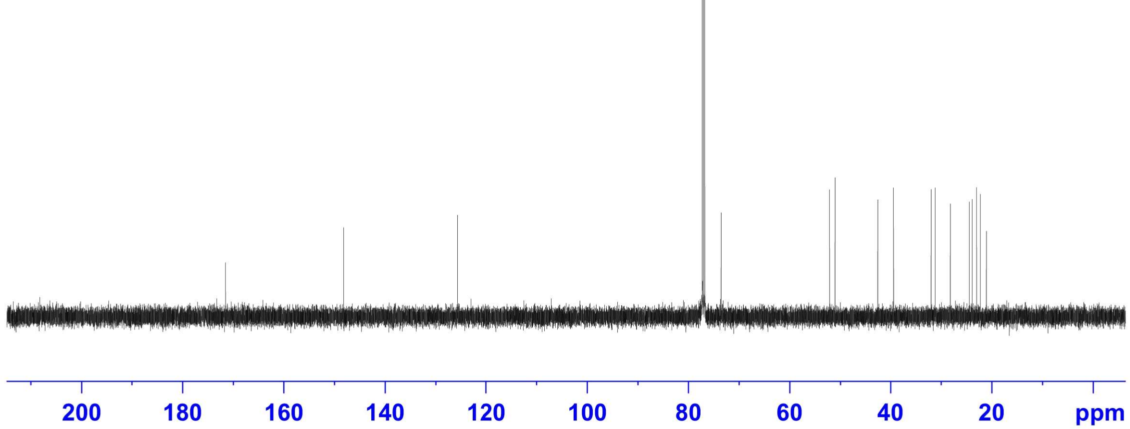
======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                 1H
P1                 2.67 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                65536
SF          500.1300138 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



53

($CDCl_3$, 125 MHz)



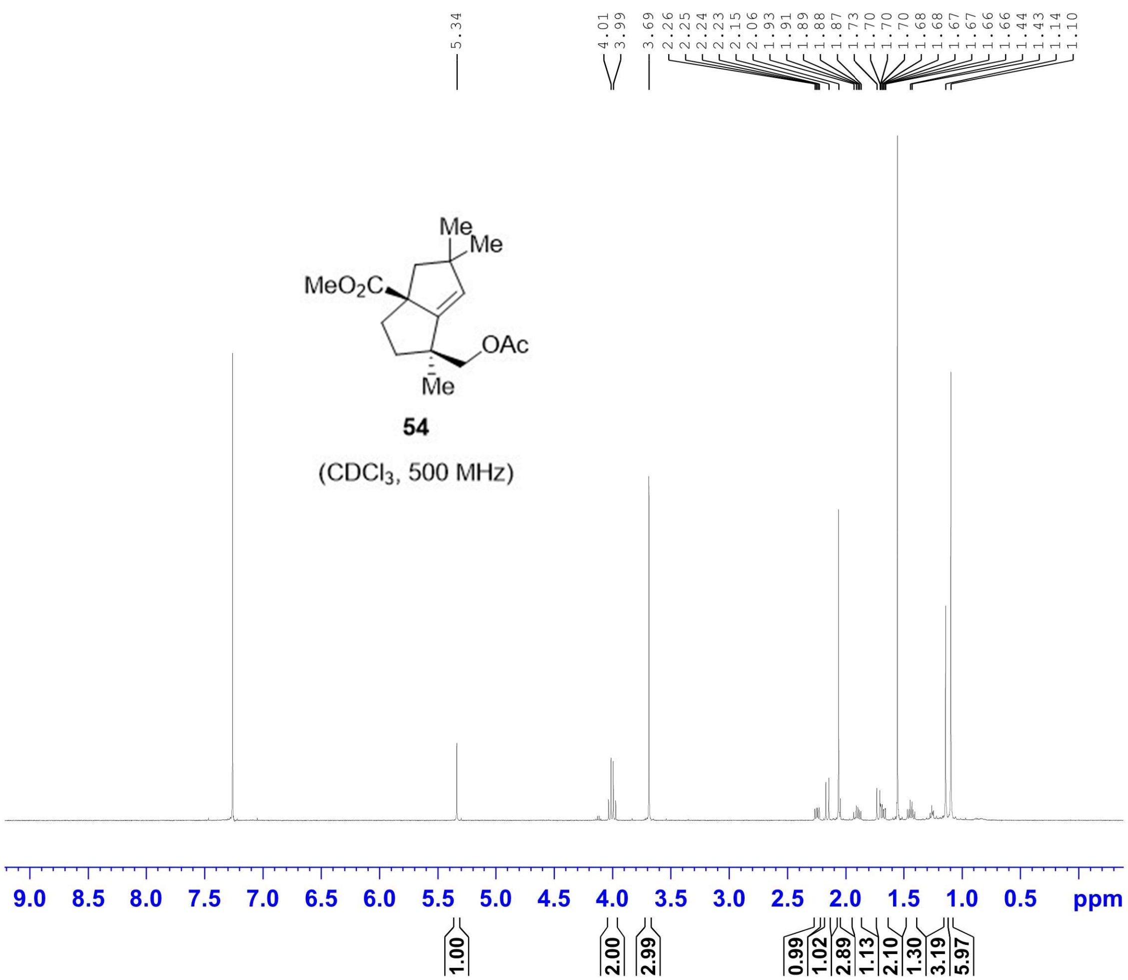

```
Current Data Parameters
NAME          yh-5-46-r
EXPNO                2
PROCNO               2

F2 - Acquisition Parameters
Date_          20180731
Time              20.37
INSTRUM           spect
PROBHD   5 mm PAQNP 1H/
PULPROG            zgpg
TD               197364
SOLVENT           CDCl3
NS                   41
DS                    4
SWH          32894.738 Hz
FIDRES        0.166670 Hz
AQ           2.9999328 sec
RG                 2050
DW               15.200 usec
DE                 6.00 usec
TE                292.6 K
D1          10.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.00 usec
PL1                1.00 dB
PL1W        72.42802429 W
SFO1        125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2      0 dB
PL12              16.50 dB
PL13              17.00 dB
PL2W        24.54113007 W
PL12W        0.54940748 W
PL13W        0.48965994 W
SFO2        500.1325006 MHz

F2 - Processing parameters
SI               131072
SF          125.7577890 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.40
```



54

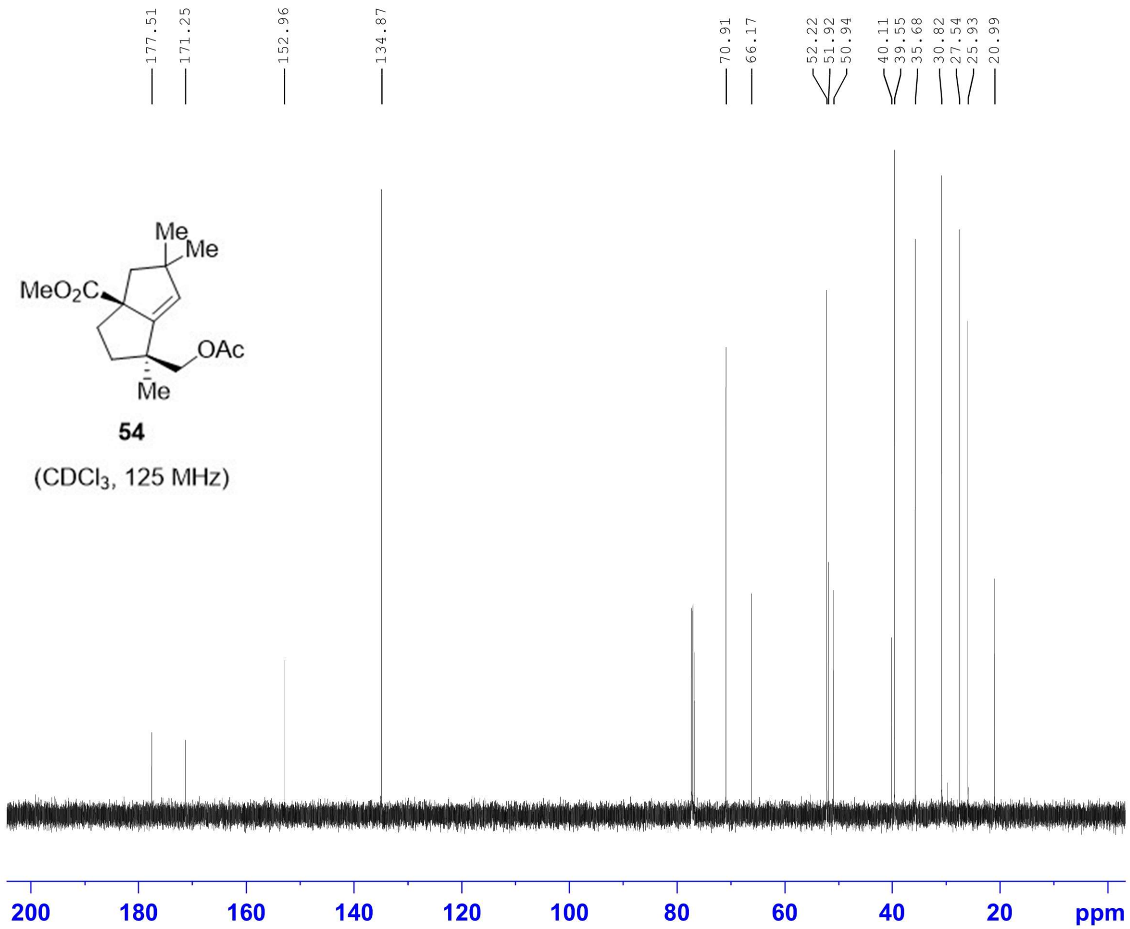
(CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME         5-member-ring
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20190812
Time                 11.28
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       6
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                  196.79
DW                  50.000 usec
DE                   10.00 usec
TE                   294.4 K
D1              4.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.1330885 MHz
NUC1                    1H
P1                    3.30 usec
PLW1           12.19999981 W

F2 - Processing parameters
SI                   65536
SF             500.1300138 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



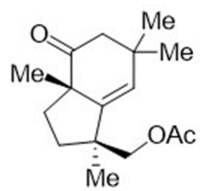

```
Current Data Parameters
NAME        5-member-ring
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20190812
Time_               21.07
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                     15
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  294.5 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                  10.00 usec
PLW1         72.83999634 W

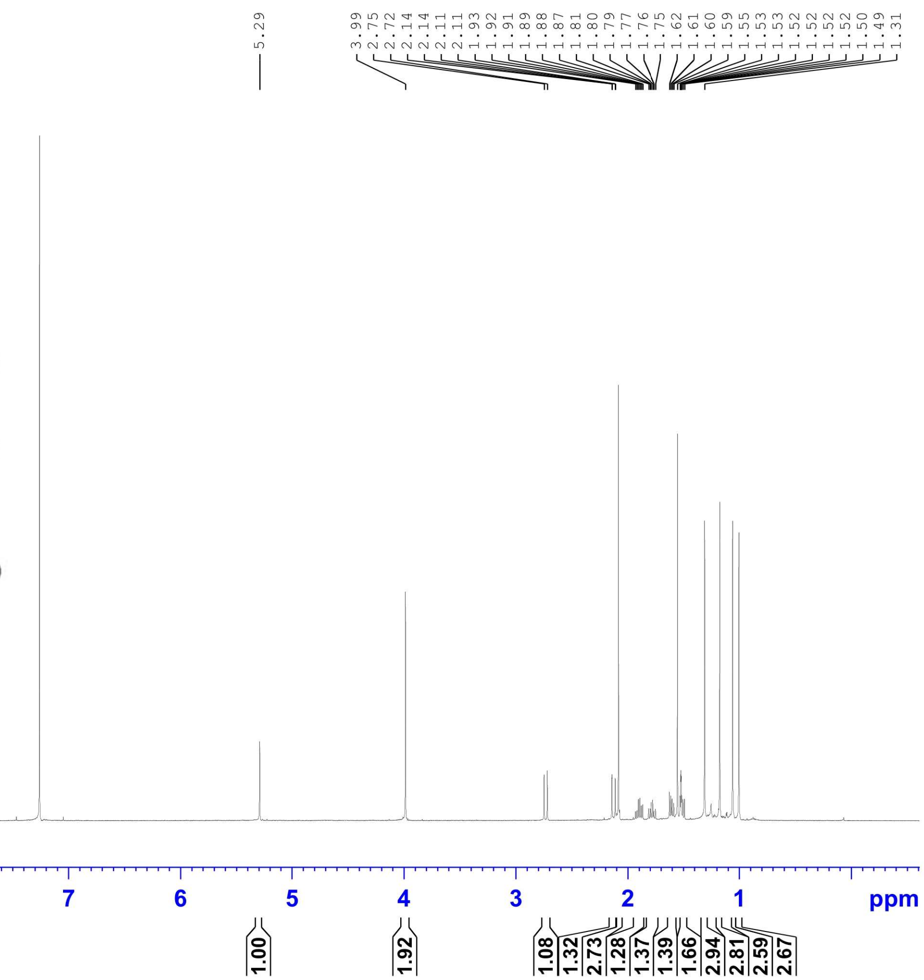
======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



55

(CDCl$_3$, 500 MHz)

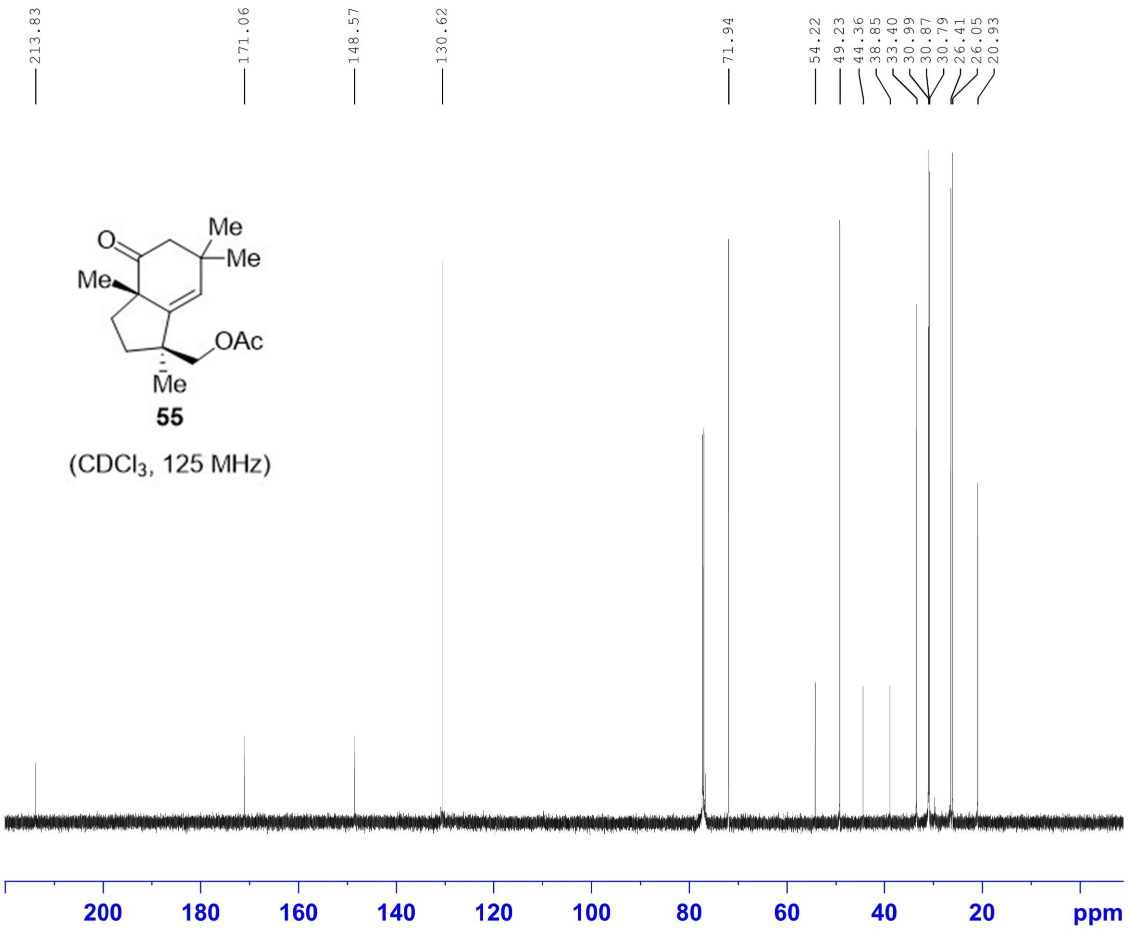



```
Current Data Parameters
NAME              yh-5-39
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180724
Time                15.25
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                     16
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                 118.99
DW                 50.000 usec
DE                   6.50 usec
TE                  296.2 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700122 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



55

($CDCl_3$, 125 MHz)

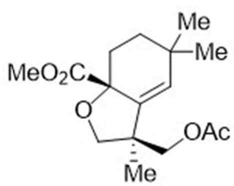
```
Current Data Parameters
NAME              yh-5-39
EXPNO                   3
PROCNO                  3

F2 - Acquisition Parameters
Date_            20180725
Time                22.44
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    507
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  298.2 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

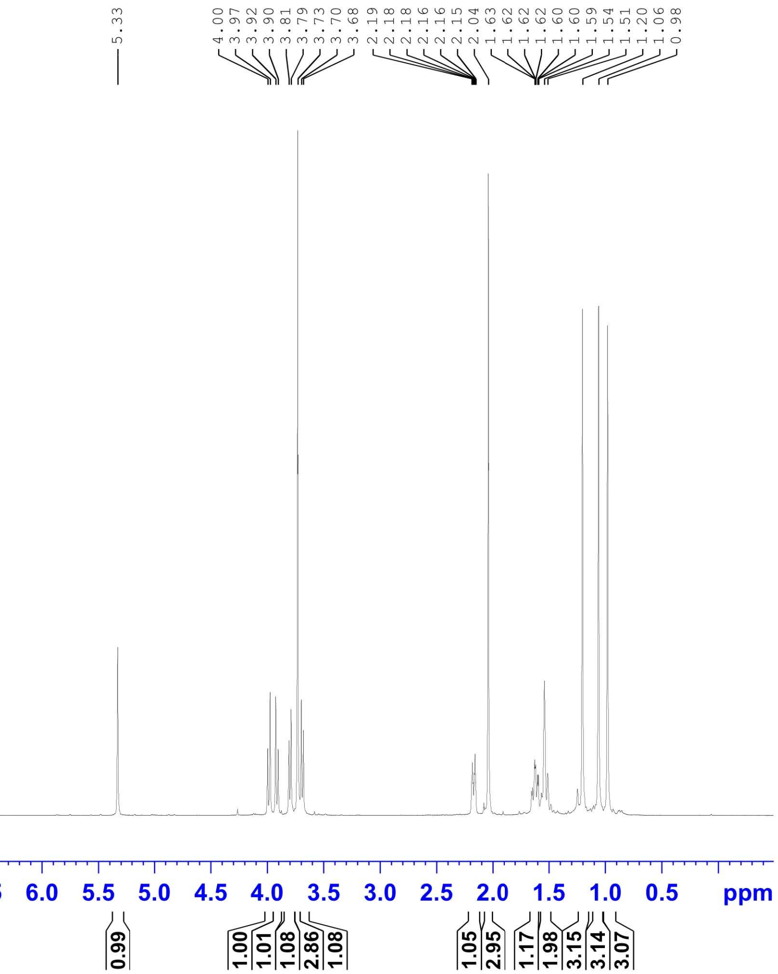
======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



56

($CDCl_3$, 500 MHz)

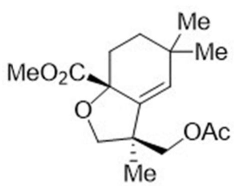



```
Current Data Parameters
NAME          yh-5-88-a
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20181022
Time              11.53
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    8
DS                    0
SWH          10000.000 Hz
FIDRES        0.166672 Hz
AQ           2.9999001 sec
RG                56.75
DW              50.000 usec
DE                6.50 usec
TE               297.2 K
D1          4.00000000 sec
TD0                   1

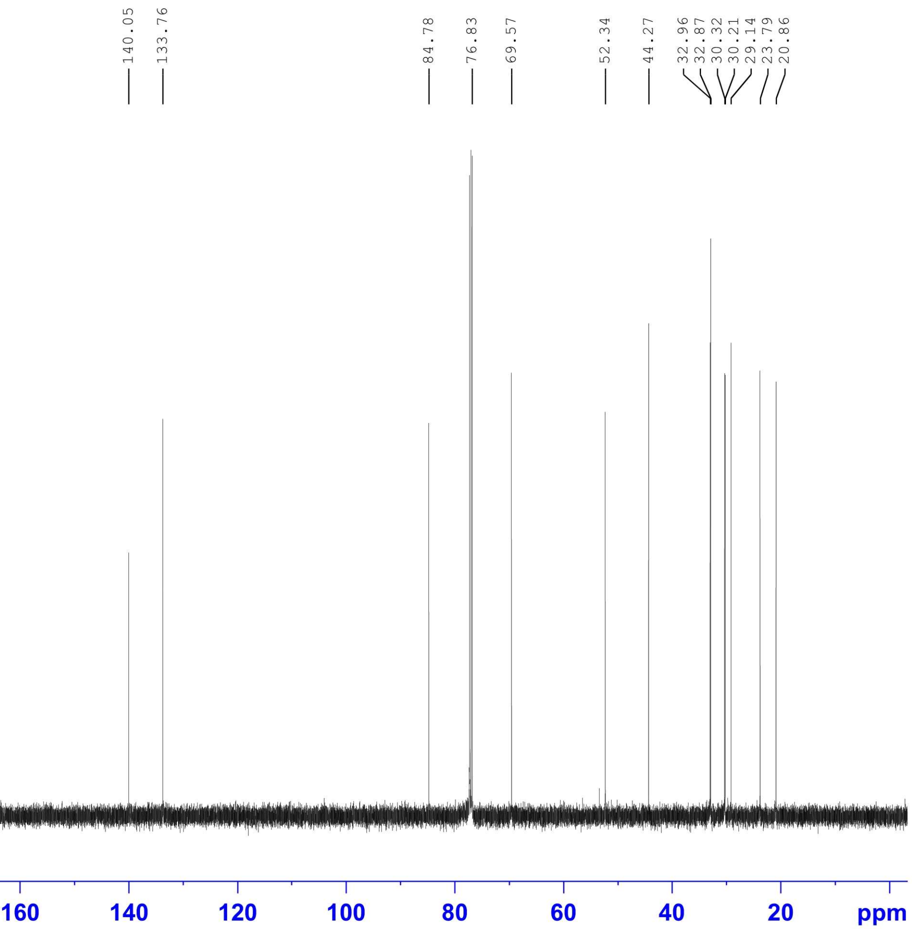
======== CHANNEL f1 ========
SFO1       499.8730869 MHz
NUC1                 1H
P1                 3.58 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                65536
SF         499.8700120 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



56

($CDCl_3$, 125 MHz)



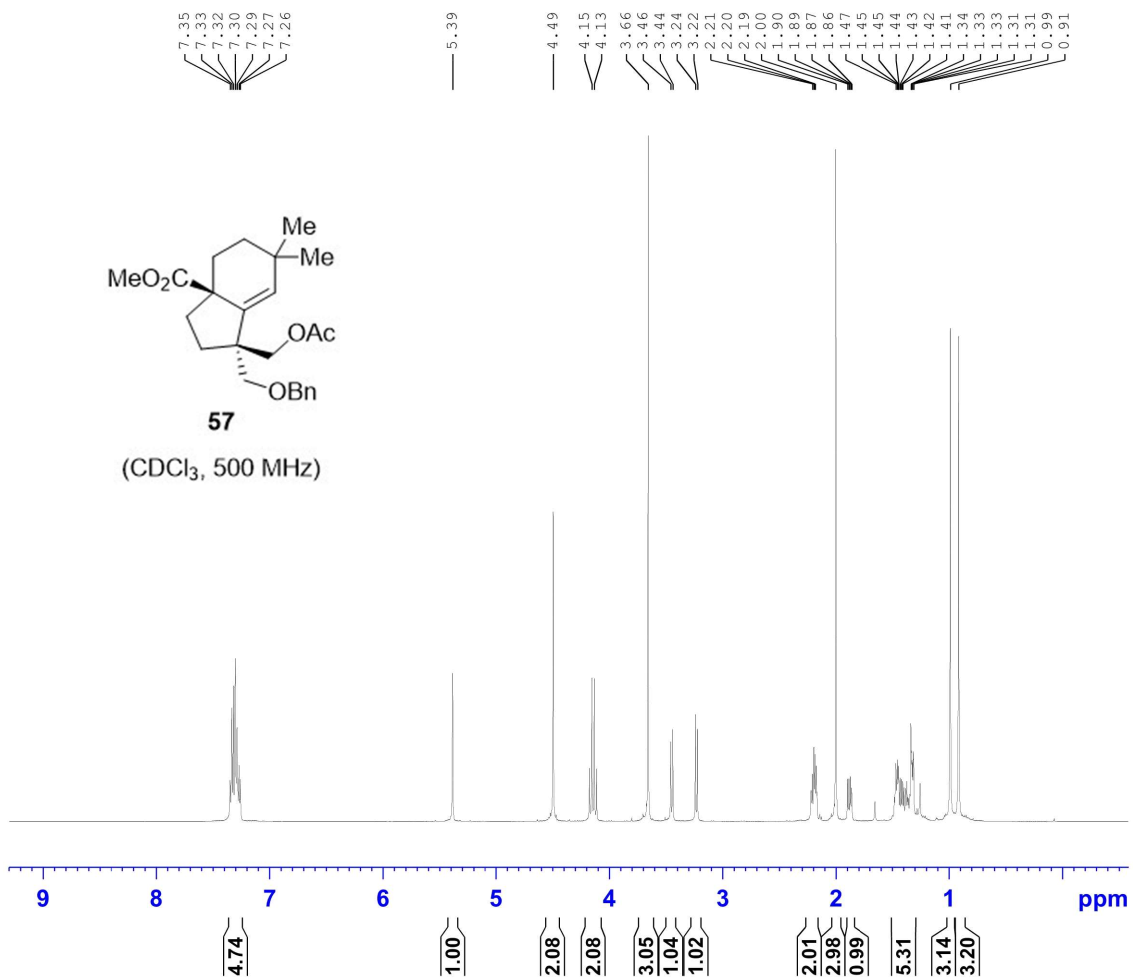

```
Current Data Parameters
NAME             yh-5-88-a
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20181022
Time                 13.52
INSTRUM              spect
PROBHD   5 mm PAQNP 1H/
PULPROG               zgpg
TD                  197364
SOLVENT              CDCl3
NS                      64
DS                       0
SWH             32894.738 Hz
FIDRES           0.166670 Hz
AQ              2.9999328 sec
RG                    2050
DW                  15.200 usec
DE                    6.00 usec
TE                   295.5 K
D1            10.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.90 usec
PL1                   1.00 dB
PL1W           72.42802429 W
SFO1           125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2          0 dB
PL12                 16.50 dB
PL13                 17.00 dB
PL2W           24.54113007 W
PL12W           0.54940748 W
PL13W           0.48965994 W
SFO2           500.1325006 MHz

F2 - Processing parameters
SI                  131072
SF             125.7577890 MHz
WDW                     EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.40
```



57

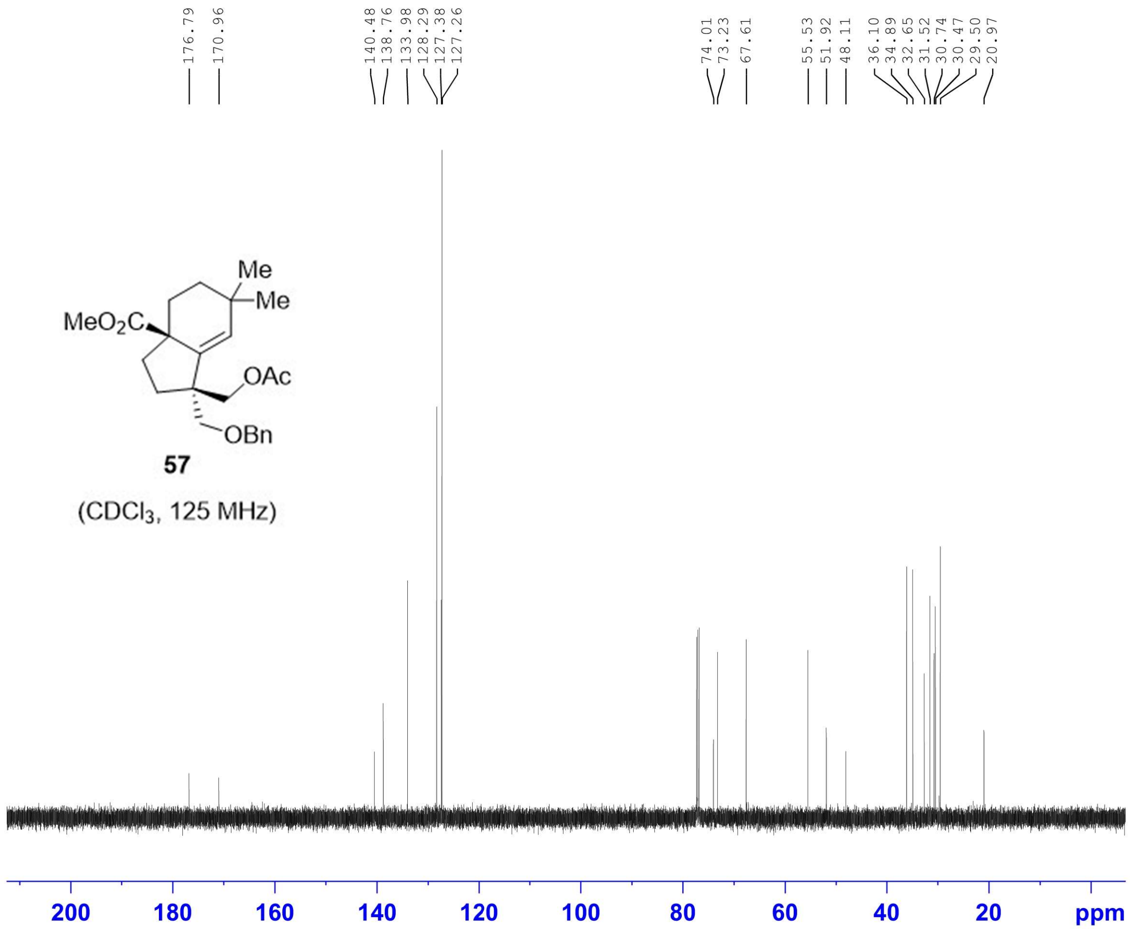
(CDCl$_3$, 500 MHz)


```
Current Data Parameters
NAME             yh-3-3-a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180131
Time                22.59
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      4
DS                      0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                  22.37
DW                 50.000 usec
DE                   6.50 usec
TE                  296.8 K
D1             3.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                   1H
P1                  10.75 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                  65536
SF          499.8700120 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



57

($CDCl_3$, 125 MHz)

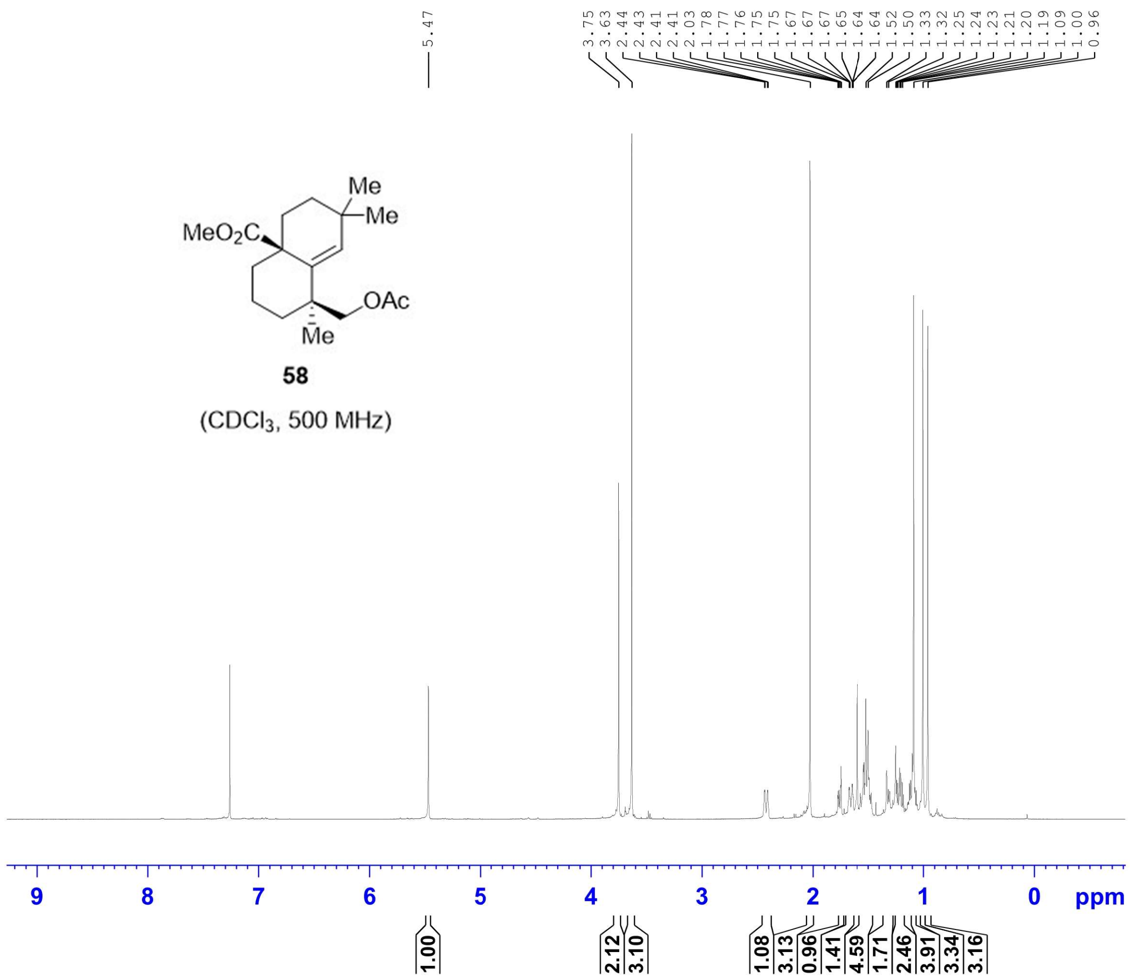
```
Current Data Parameters
NAME              yh-3-3-a
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20180131
Time                 23.09
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                      18
DS                       0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   297.1 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                 1048576
SF          125.6924115 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



58

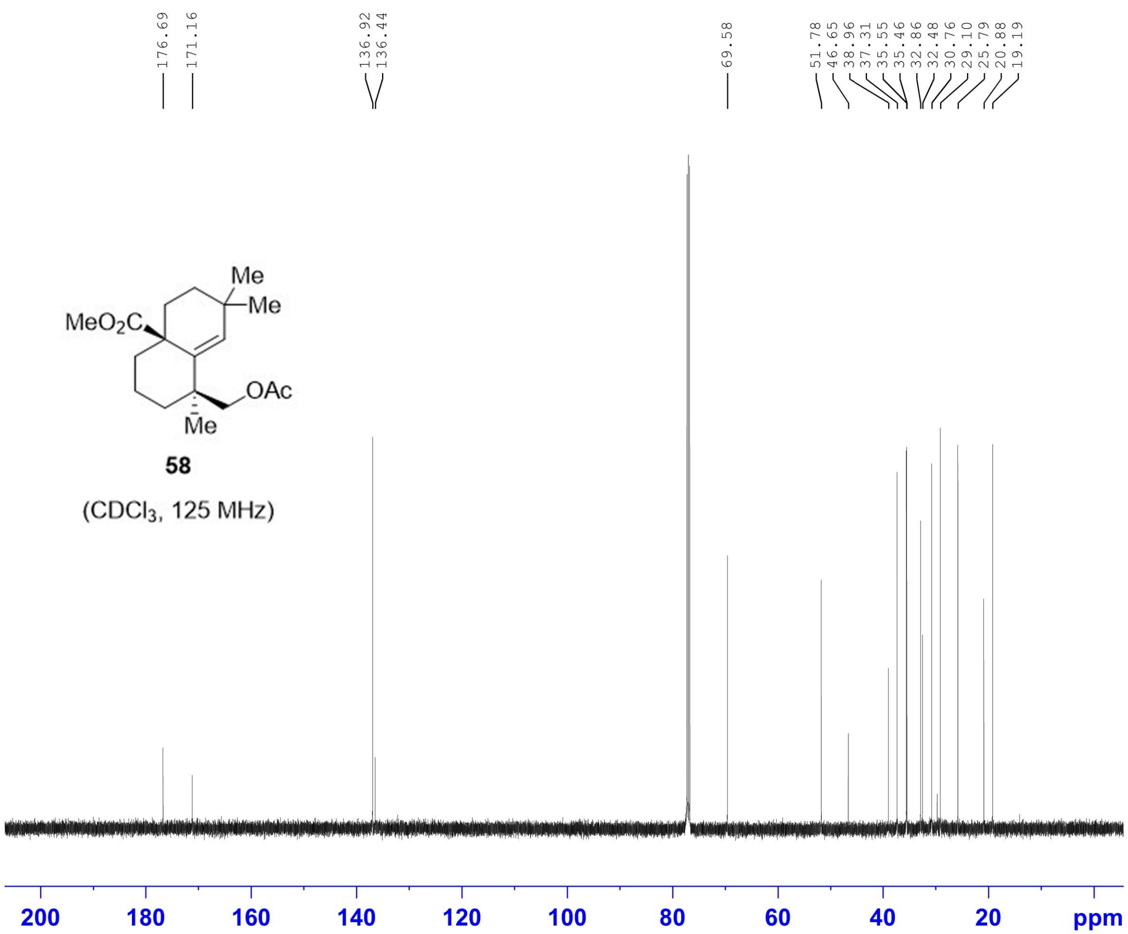
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             yh-5-21
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180711
Time               21.11
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 77.07
DW                50.000 usec
DE                  6.50 usec
TE                 296.7 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700122 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



58

(CDCl$_3$, 125 MHz)

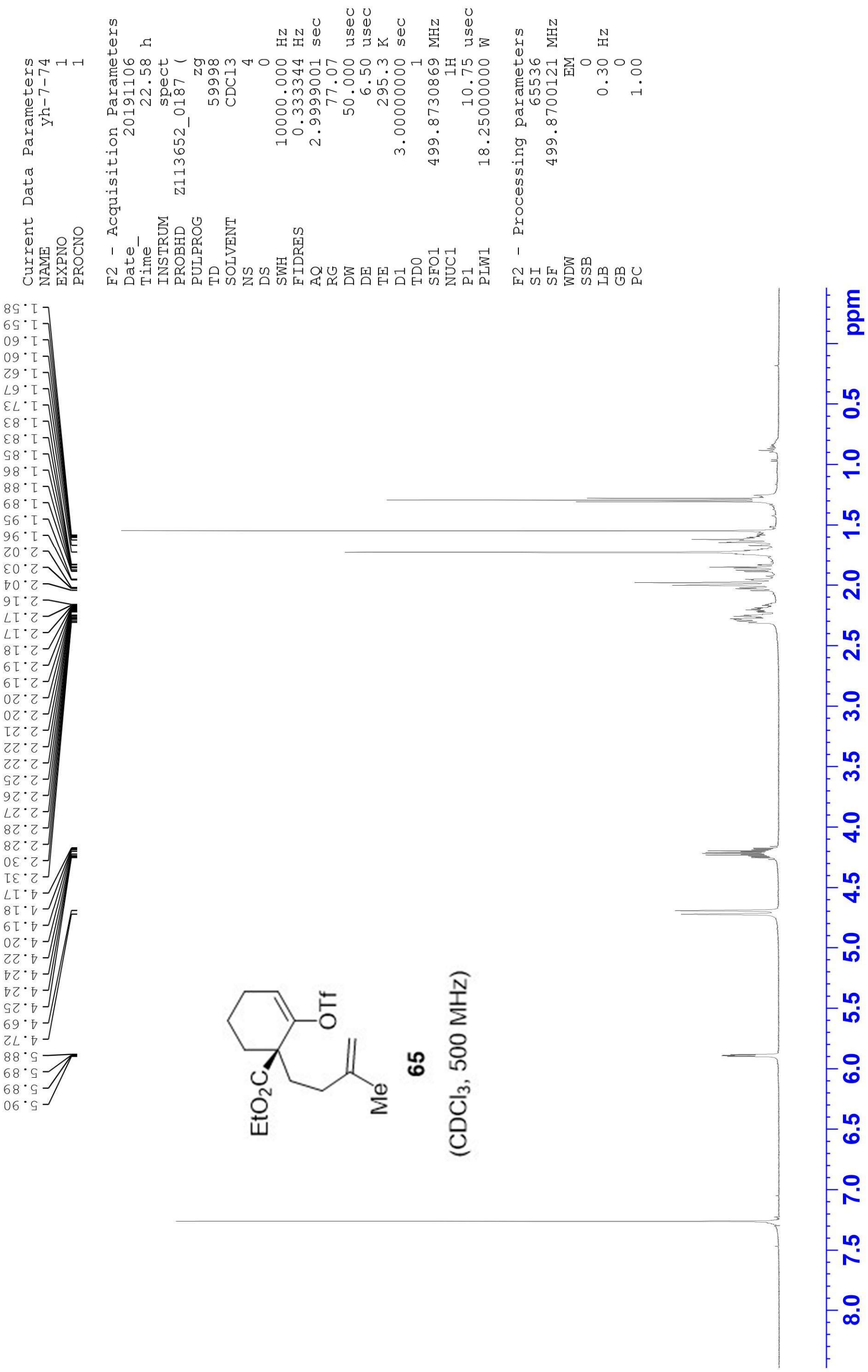
```
Current Data Parameters
NAME              yh-5-21
EXPNO                   2
PROCNO                  2

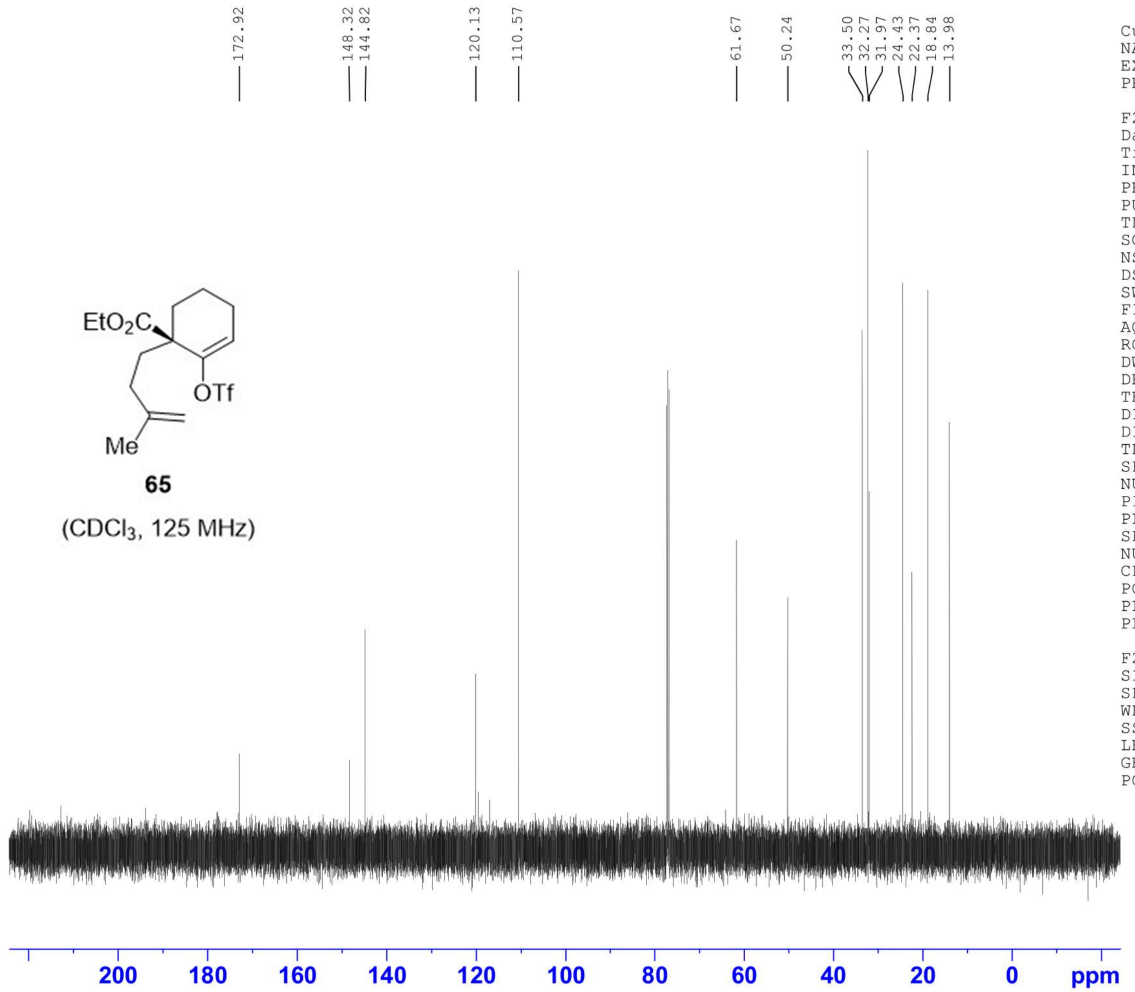
F2 - Acquisition Parameters
Date_            20180711
Time_               22.40
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    810
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  298.4 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                  10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                1048576
SF           125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```


Current Data Parameters
NAME yh-7-74
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191106
Time 22.58 h
INSTRUM spect
PROBHD Z113652_0187 (
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 4
DS 0
SWH 10000.000 Hz
FIDRES 0.333344 Hz
AQ 2.9999001 sec
RG 77.07
DW 50.000 usec
DE 6.50 usec
TE 295.3 K
D1 3.00000000 sec
TD0 1
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W
F2 - Processing parameters
SI 65536
SF 499.8700121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
EtO2C
OTf
Me
65
(CDCl3, 500 MHz)
ppm



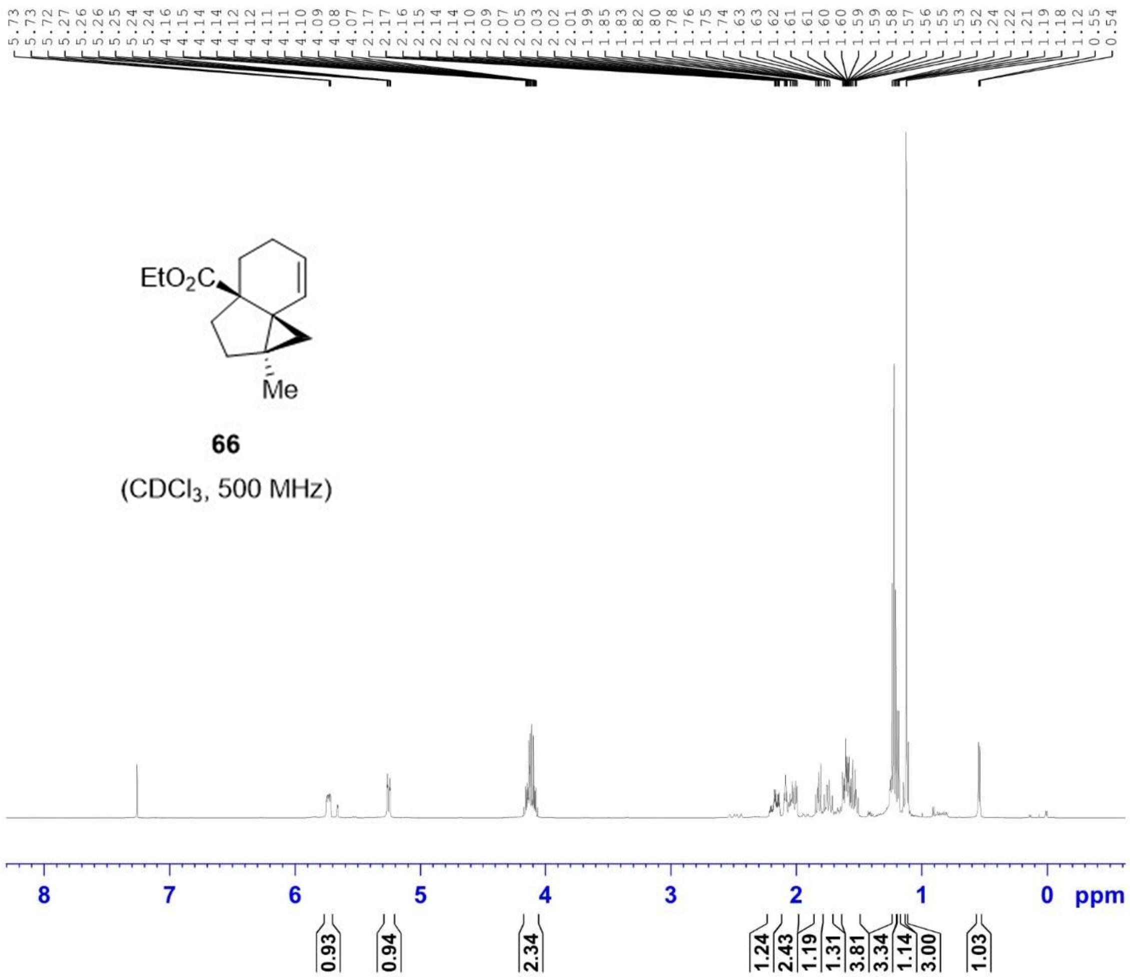
65

($CDCl_3$, 125 MHz)

```
Current Data Parameters
NAME              yh-7-74
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20191107
Time                22.20 h
INSTRUM             spect
PROBHD   Z113652_0187 (
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                     13
DS                      0
SWH           31250.000 Hz
FIDRES         0.333340 Hz
AQ            2.9999361 sec
RG                   2050
DW               16.000 usec
DE                 6.50 usec
TE                295.7 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                     1
SFO1        125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1        72.83999634 W
SFO2        499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI                1048576
SF          125.6924115 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.40
```



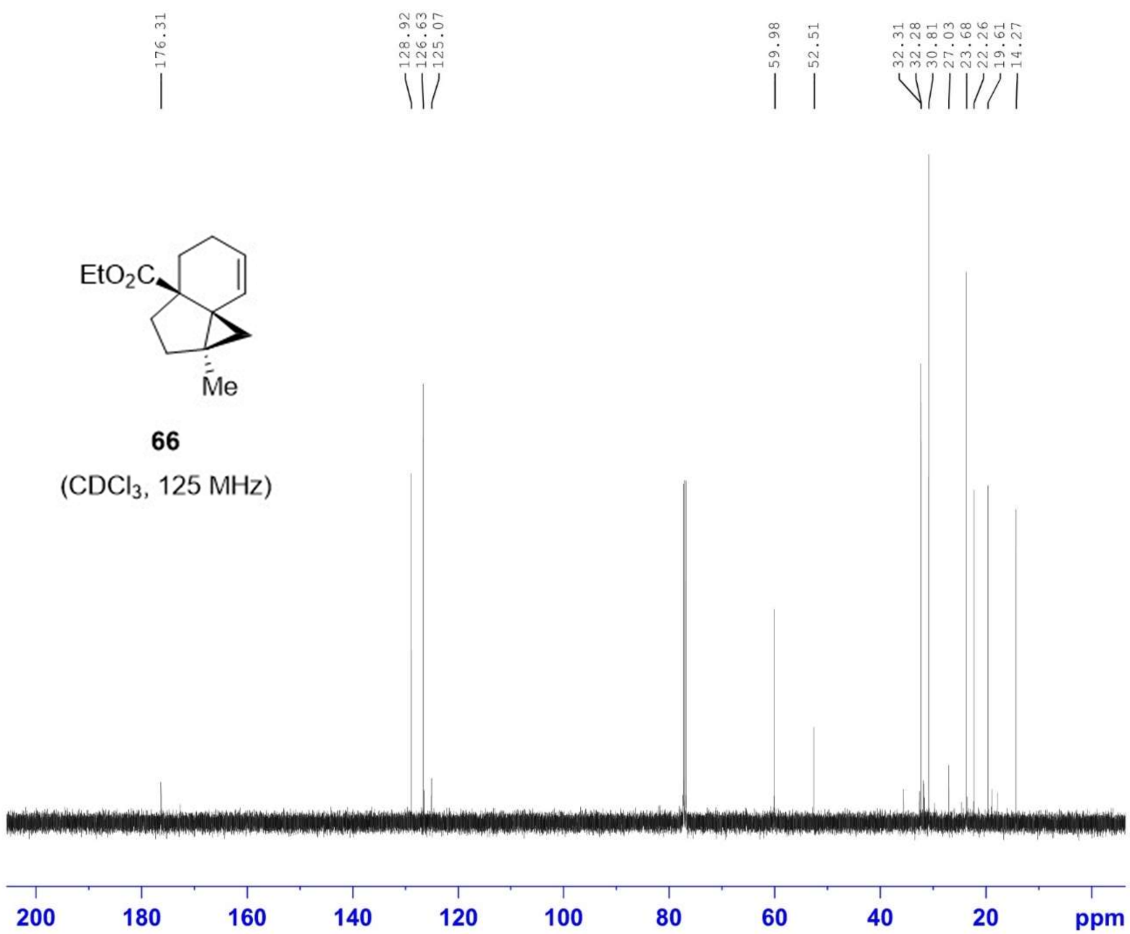
66

($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME              yh-7-76-a
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20191108
Time                 0.02 h
INSTRUM               spect
PROBHD    Z113652_0187 (
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        4
DS                        0
SWH            10000.000 Hz
FIDRES          0.333344 Hz
AQ             2.9999001 sec
RG                    29.95
DW                50.000 usec
DE                  6.50 usec
TE                  295.4 K
D1            3.00000000 sec
TD0                       1
SFO1         499.8730869 MHz
NUC1                     1H
P1                  10.75 usec
PLW1         18.25000000 W

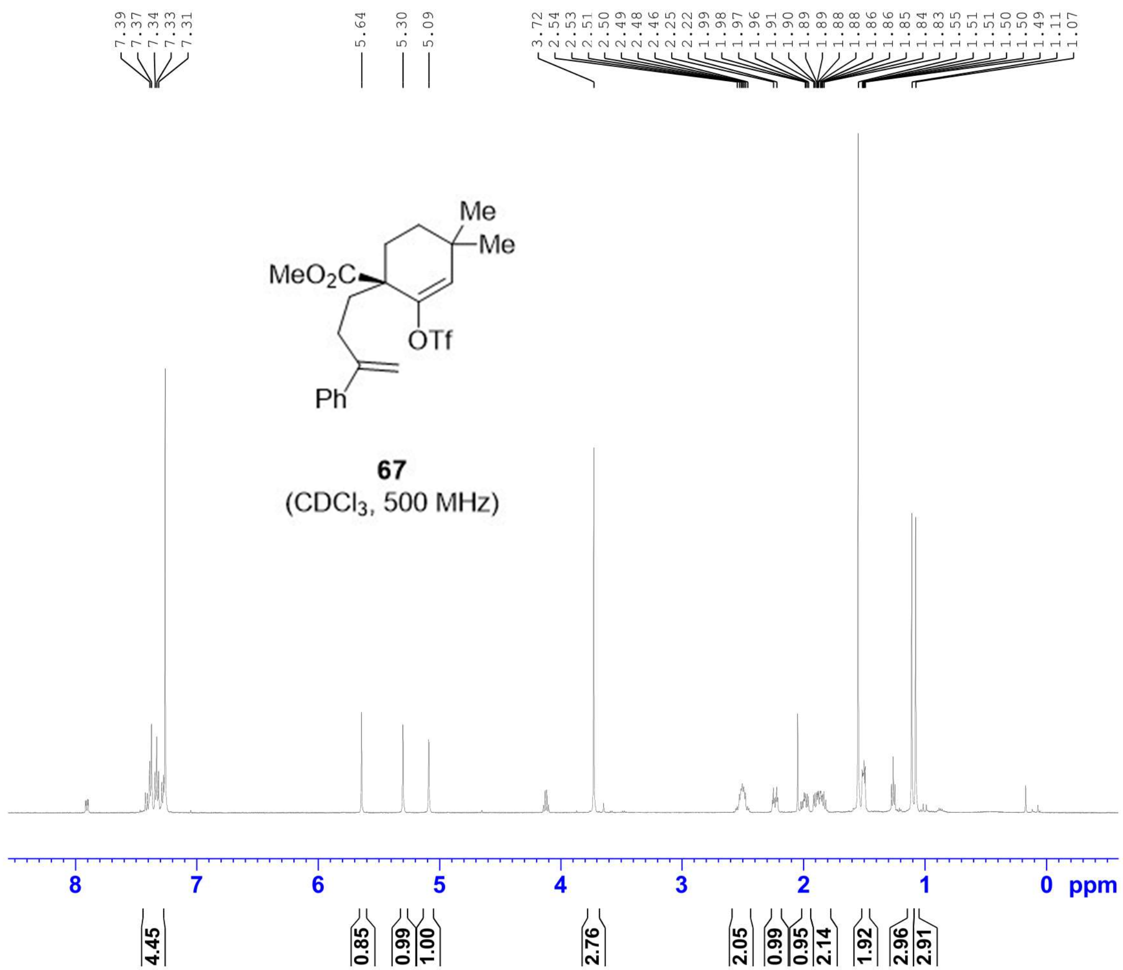
F2 - Processing parameters
SI                    65536
SF           499.8700125 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.00
```




```
Current Data Parameters
NAME          yh-7-76-a
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20191108
Time               0.24 h
INSTRUM           spect
PROBHD   Z113652_0187 (
PULPROG            zgdc
TD               187496
SOLVENT           CDCl3
NS                  103
DS                    0
SWH           31250.000 Hz
FIDRES         0.333340 Hz
AQ            2.9999361 sec
RG                 2050
DW               16.000 usec
DE                 6.50 usec
TE                296.6 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7049802 MHz
NUC1                13C
P1                10.00 usec
PLW1        72.83999634 W
SFO2        499.8724993 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI              1048576
SF          125.6924115 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.40
```



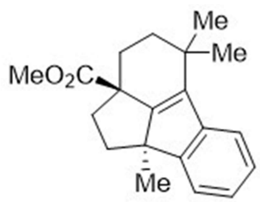
67
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME              yh-2-149
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170906
Time                 23.05
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                  196.79
DW                  50.000 usec
DE                   10.00 usec
TE                   295.0 K
D1              2.00000000 sec
TD0                      1

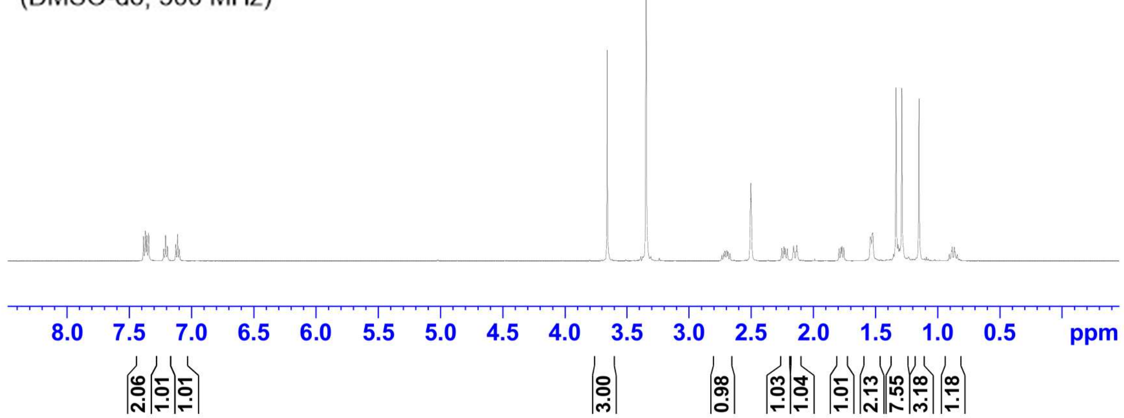
======== CHANNEL f1 ========
SFO1           500.1330885 MHz
NUC1                    1H
P1                    8.00 usec
PLW1           12.19999981 W

F2 - Processing parameters
SI                   65536
SF             500.1300134 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



69

(DMSO-d6, 500 MHz)

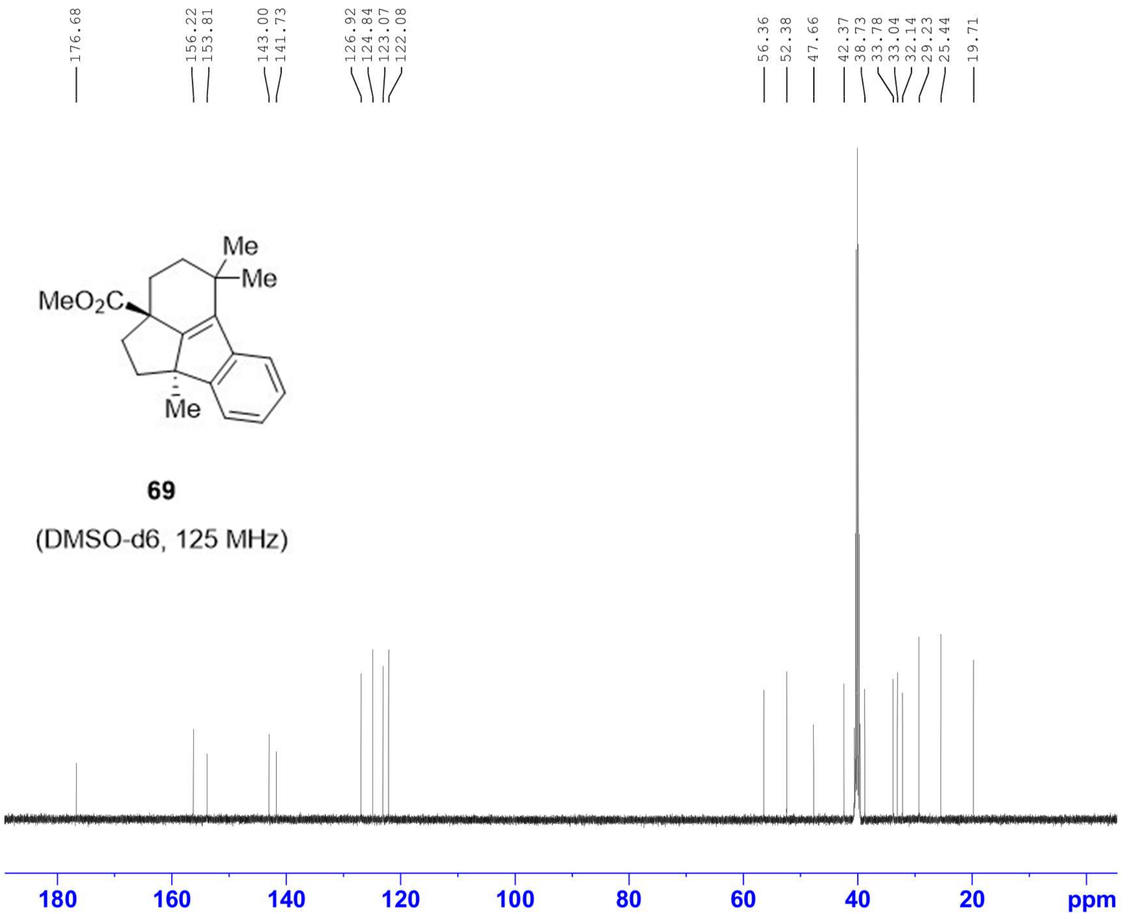



```
Current Data Parameters
NAME          yh-2-150-1-r
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170908
Time                 15.30
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT               DMSO
NS                       8
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                  110.37
DW                  50.000 usec
DE                   10.00 usec
TE                   293.4 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.1330885 MHz
NUC1                    1H
P1                    8.00 usec
PLW1           12.19999981 W

F2 - Processing parameters
SI                   65536
SF             500.1300049 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



69

(DMSO-d6, 125 MHz)

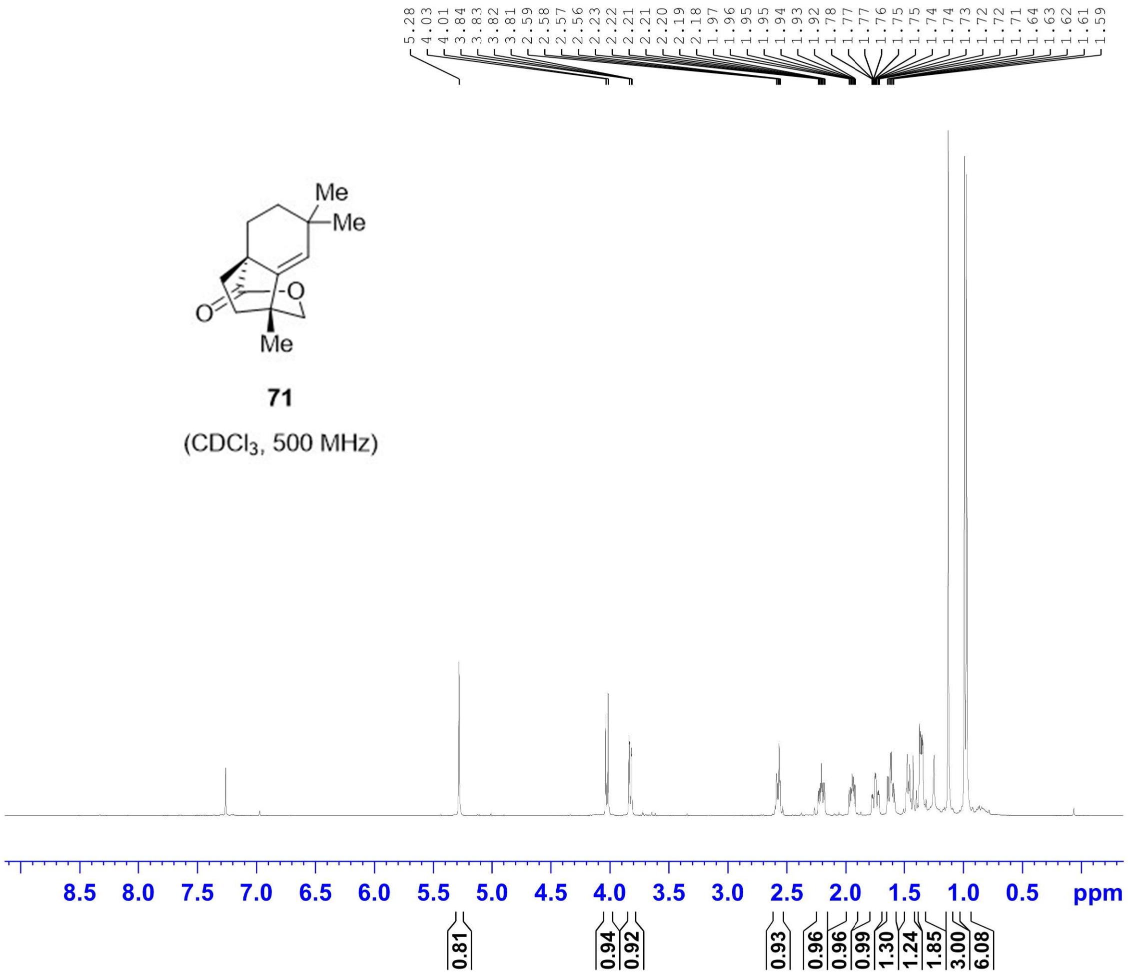
```
Current Data Parameters
NAME          yh-2-150-1-rc
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20170917
Time_                 21.21
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT                DMSO
NS                      530
DS                        0
SWH               31250.000 Hz
FIDRES             0.166670 Hz
AQ                2.9999361 sec
RG                     2050
DW                   16.000 usec
DE                     6.50 usec
TE                    297.3 K
D1               3.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            125.7049802 MHz
NUC1                    13C
P1                    10.00 usec
PLW1            72.83999634 W

======== CHANNEL f2 ========
SFO2            499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2            19.00000000 W
PLW12            0.29688001 W

F2 - Processing parameters
SI                  1048576
SF              125.6924115 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.40
```



71

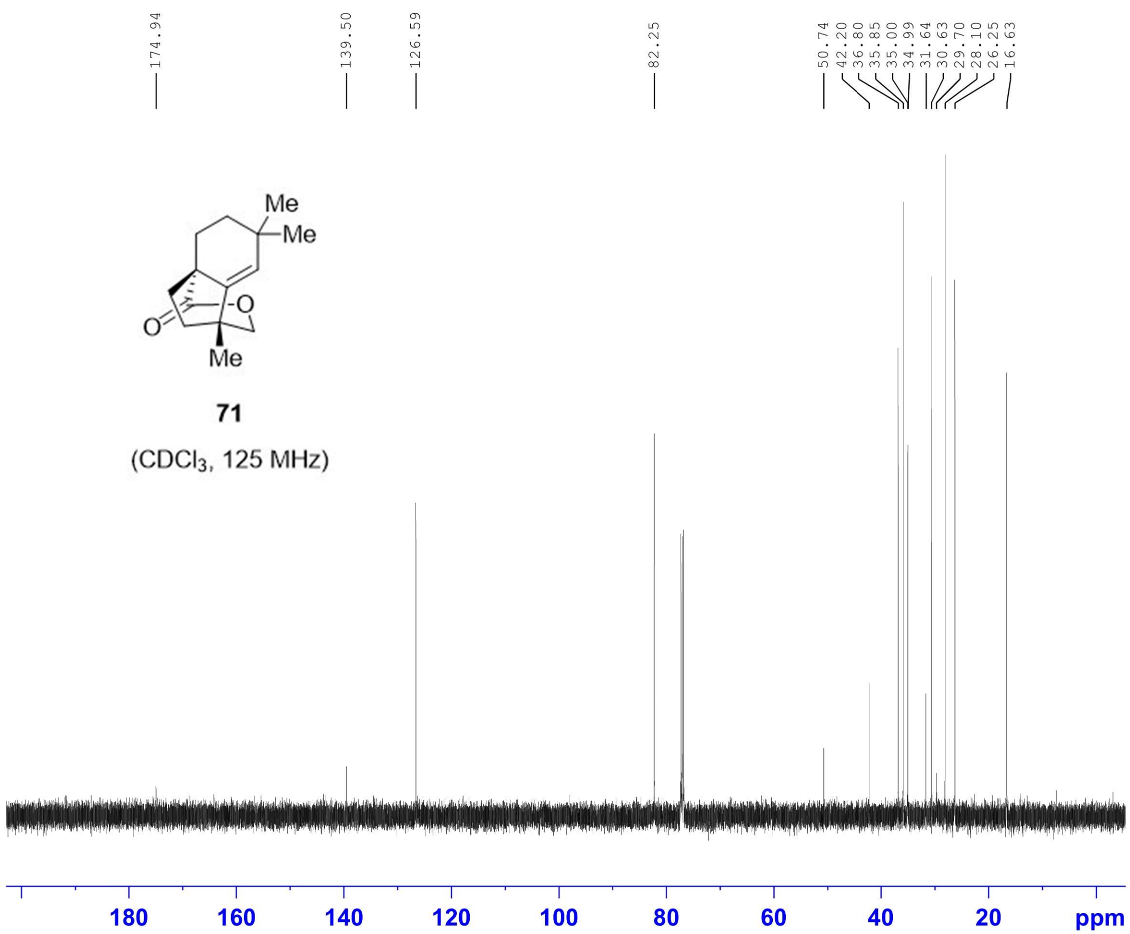
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME          yh-3-36-rH
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171104
Time_              21.34
INSTRUM            spect
PROBHD   5 mm PATXI 1H/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                  55.8
DW                50.000 usec
DE                 10.00 usec
TE                 294.7 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                 65536
SF           500.1300131 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



71

(CDCl$_3$, 125 MHz)

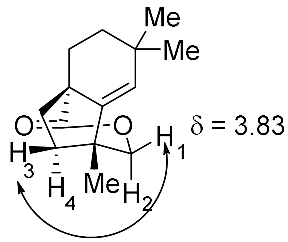
```
Current Data Parameters
NAME          yh-3-36-rC
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180822
Time               14.15
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                   147
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 296.7 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

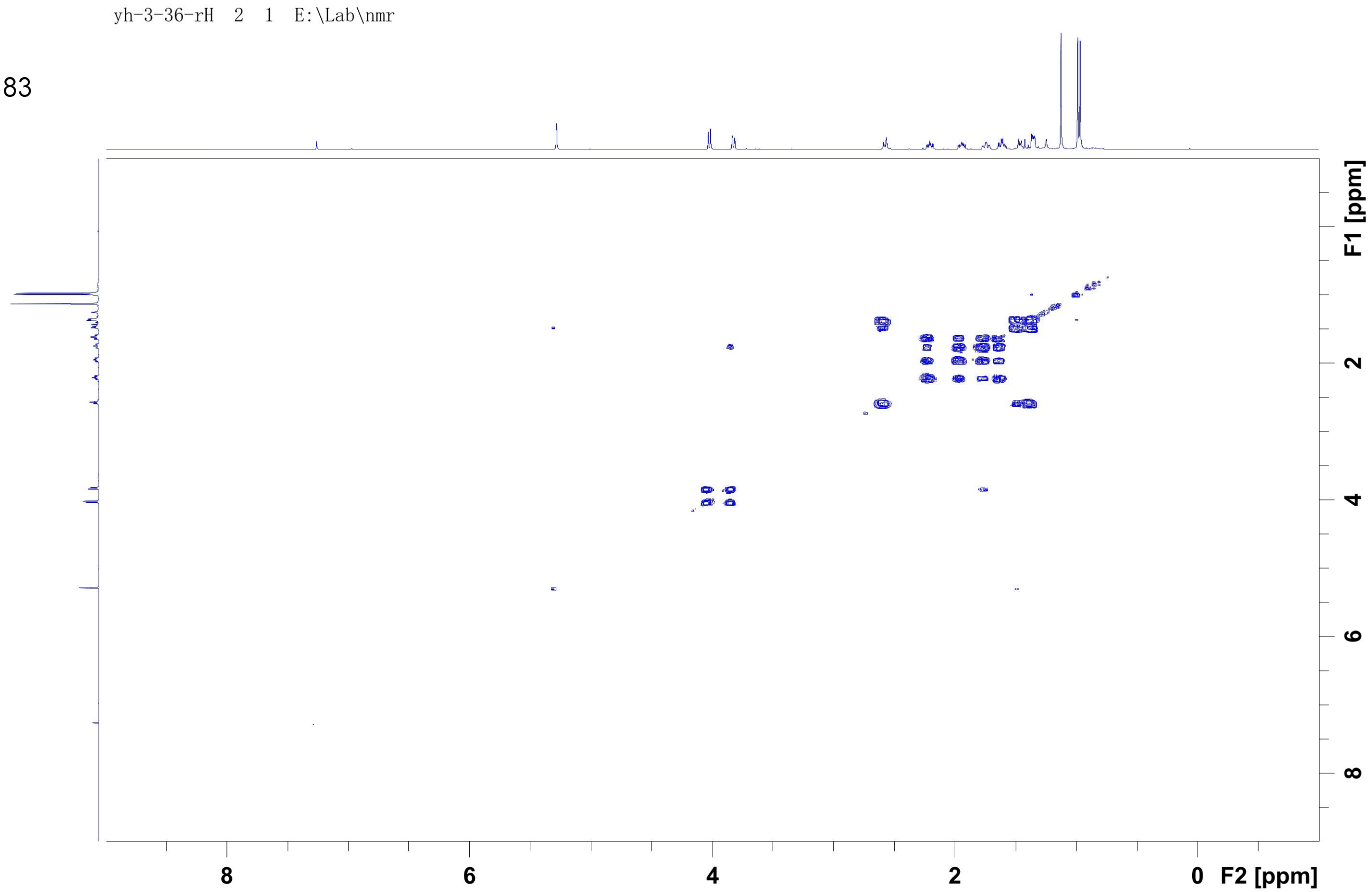
======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

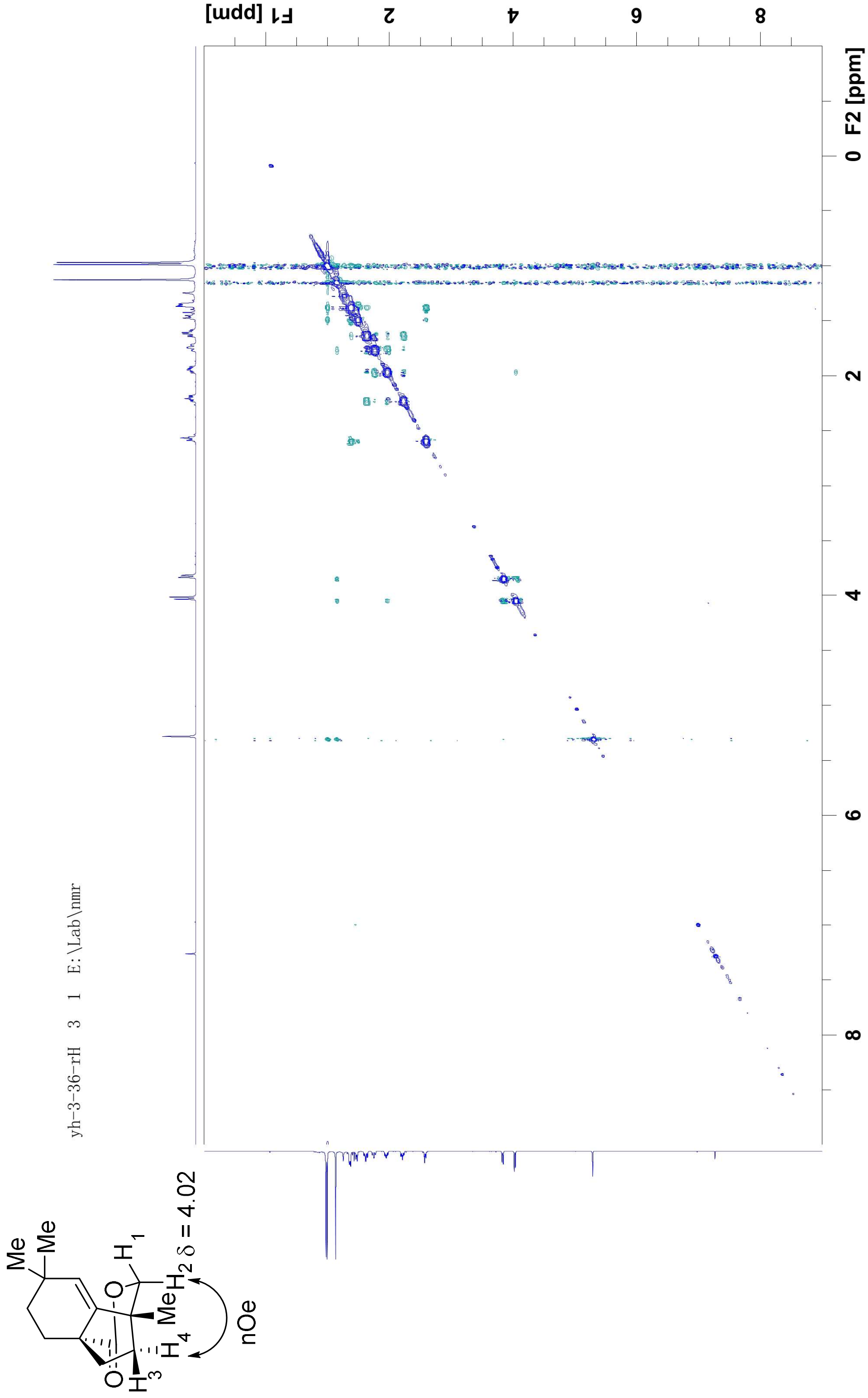
======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

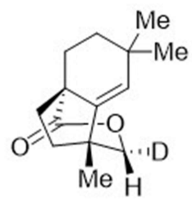
F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```



cosey (W coupling)

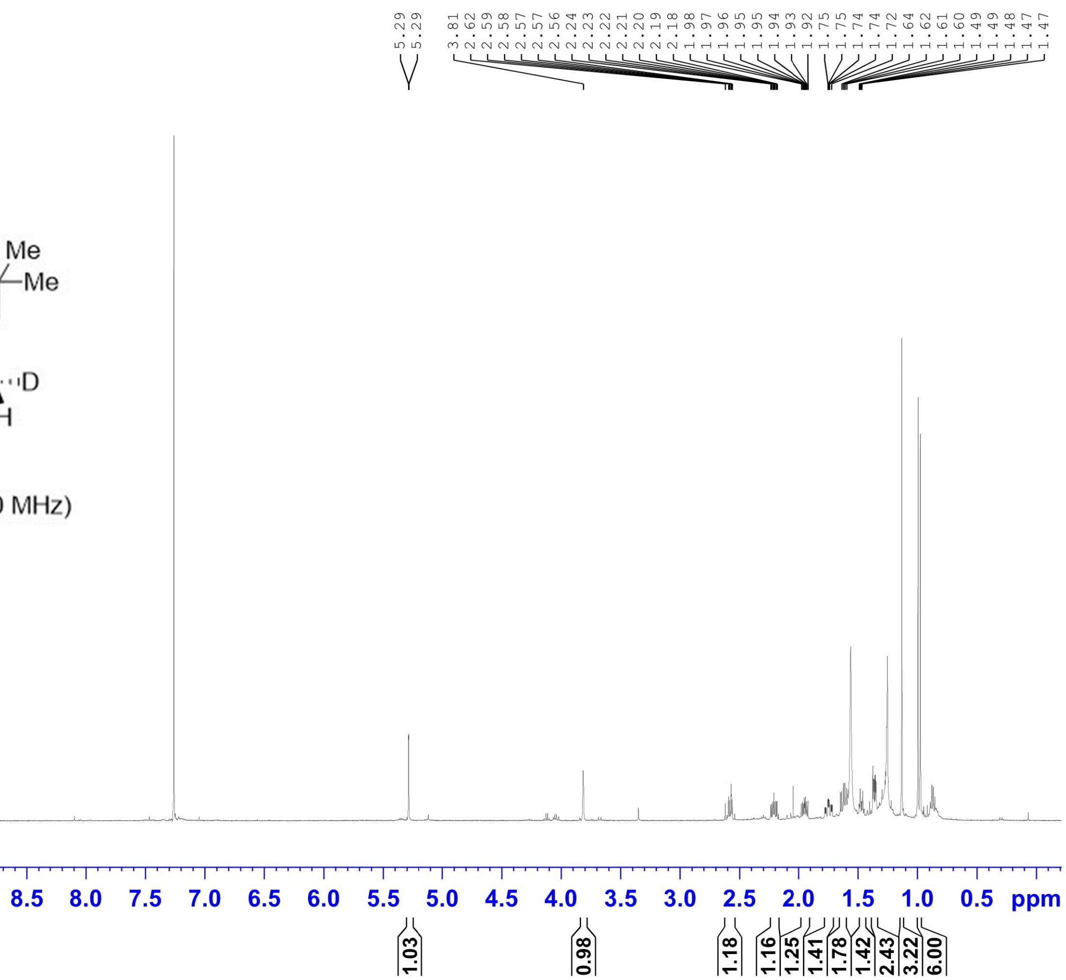



yh-3-36-rH 3 1 E:\Lab\nmr
F1 [ppm]
F2 [ppm]
nOe
δ = 4.02



D-71

(CDCl$_3$, 500 MHz)

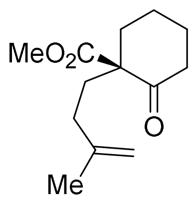



```
Current Data Parameters
NAME          yh-6-146-3-a
EXPNO                    1
PROCNO                   1

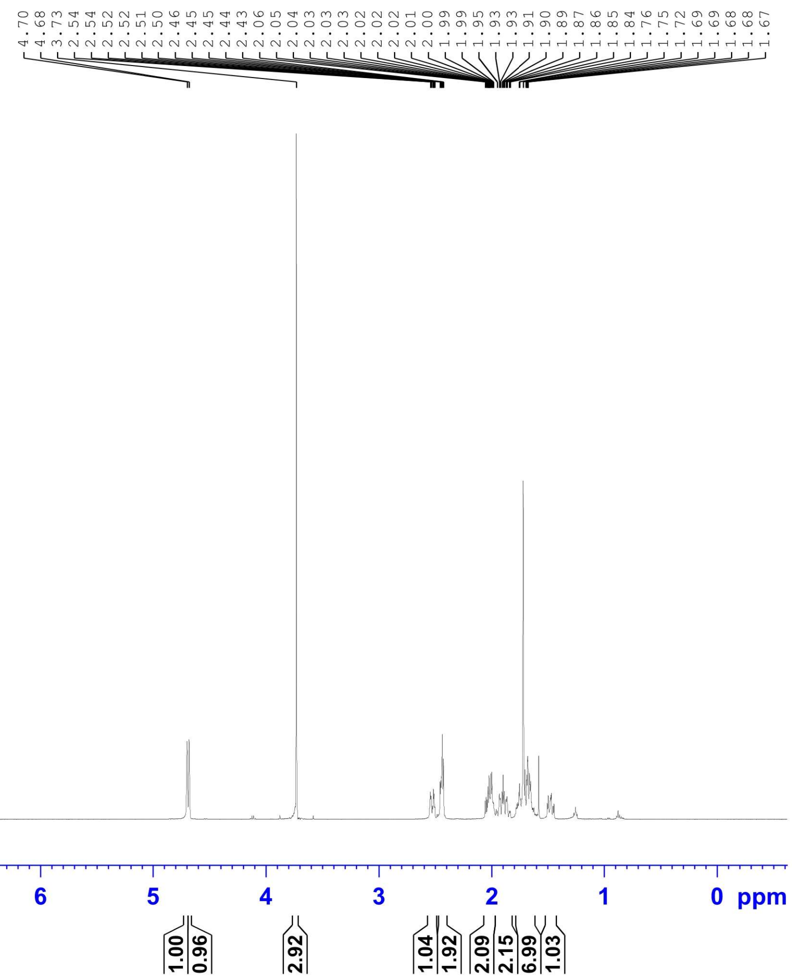
F2 - Acquisition Parameters
Date_             20190811
Time                 21.15
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                  196.79
DW                  50.000 usec
DE                   10.00 usec
TE                   294.8 K
D1              4.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                    1H
P1                    3.30 usec
PLW1           12.19999981 W

F2 - Processing parameters
SI                   65536
SF             500.1300138 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



S42
($CDCl_3$, 500 MHz)

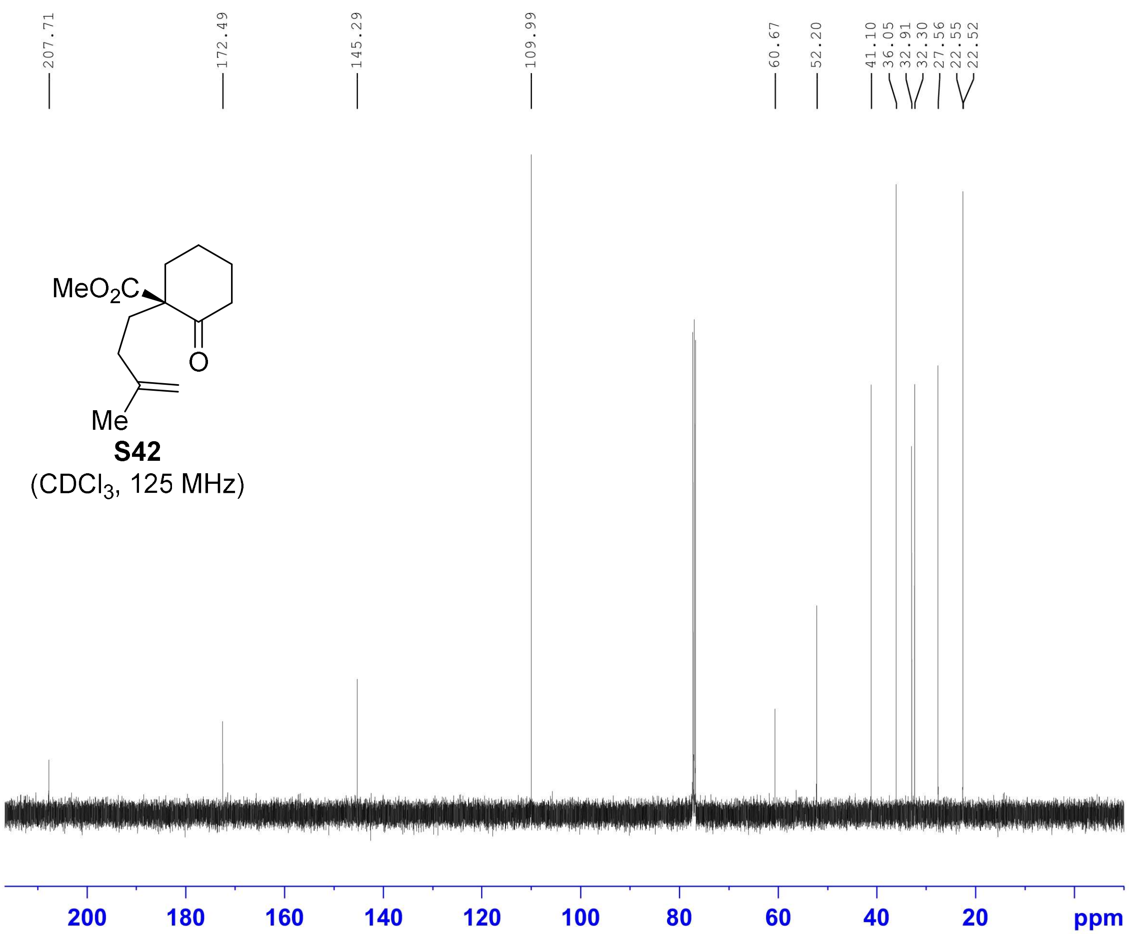



```
Current Data Parameters
NAME              yh-5-49
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180813
Time                15.54
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  77.07
DW                 50.000 usec
DE                   6.50 usec
TE                  295.7 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700122 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S42

($CDCl_3$, 125 MHz)

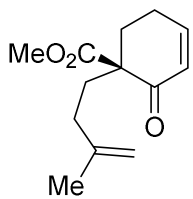
```
Current Data Parameters
NAME              yh-5-49
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180813
Time                20.19
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    165
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  297.3 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

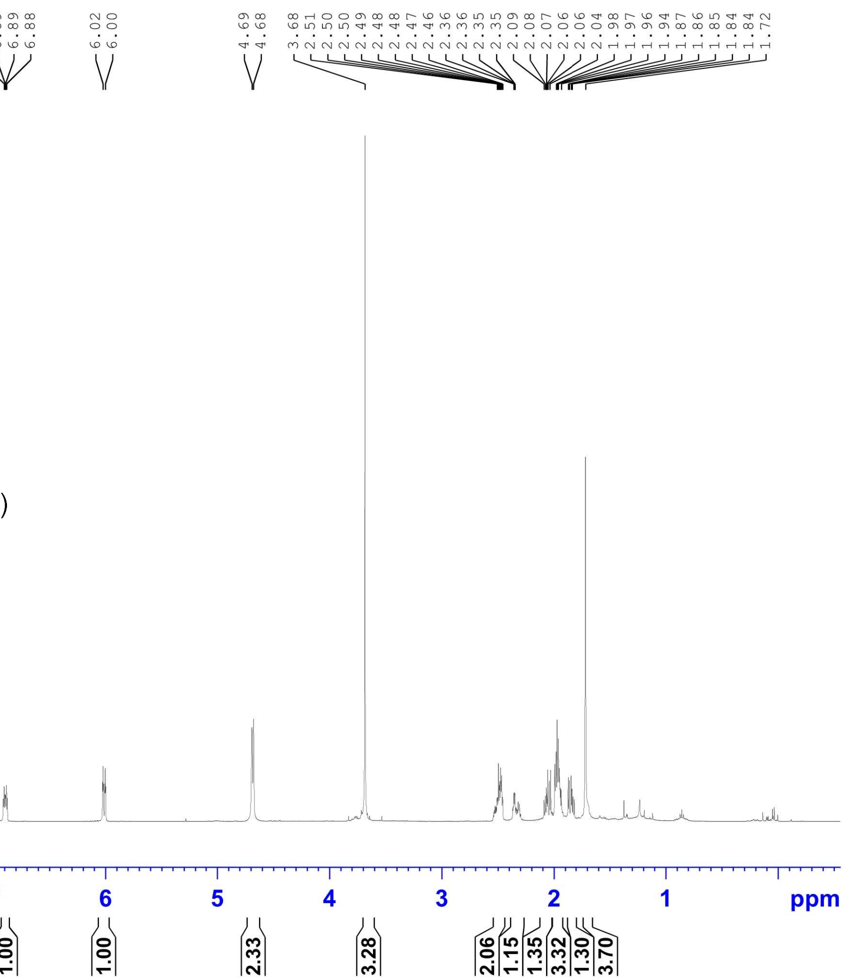
======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                1048576
SF           125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



S43
(CDCl$_3$, 500 MHz)

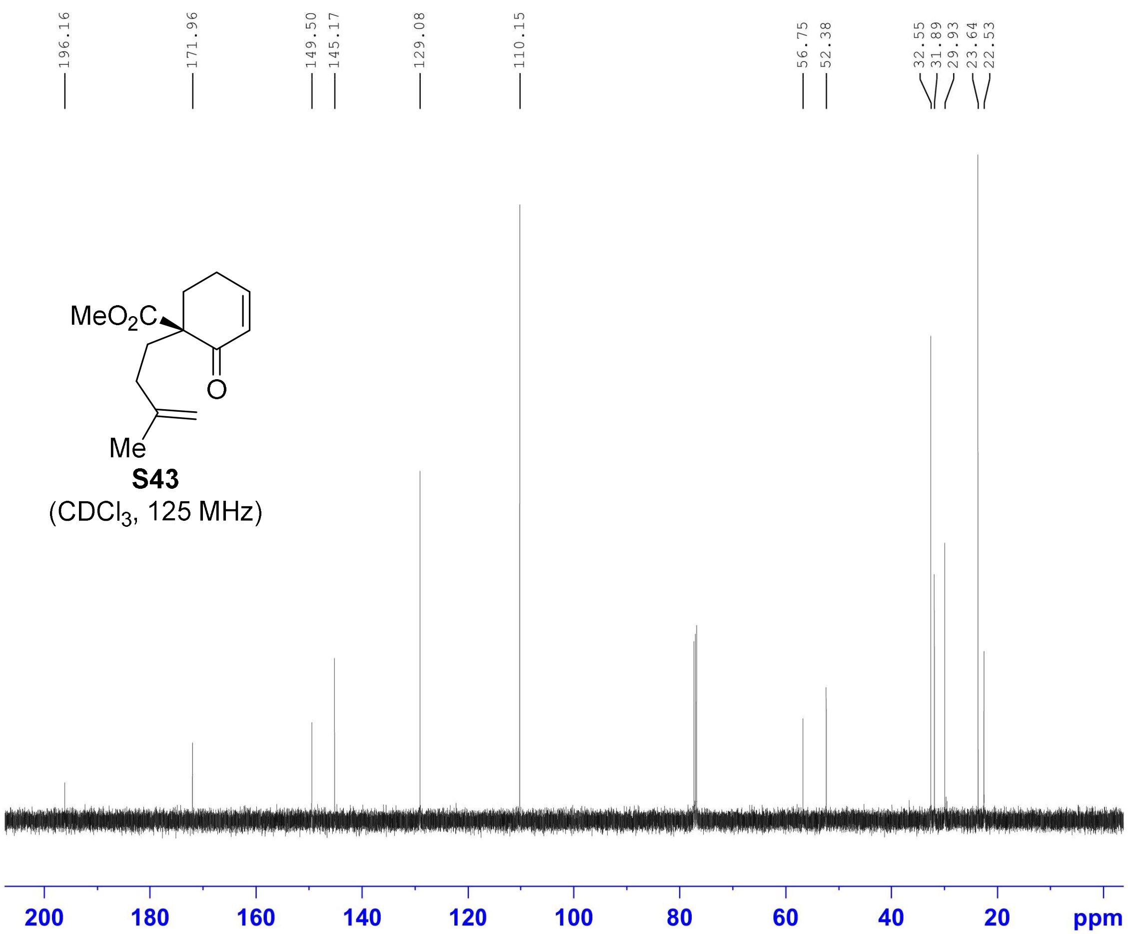



```
Current Data Parameters
NAME              yh-4-22-a
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_             20180812
Time                 20.18
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       8
DS                       0
SWH          10000.000 Hz
FIDRES        0.166672 Hz
AQ           2.9999001 sec
RG               52.86
DW              50.000 usec
DE               10.00 usec
TE               294.2 K
D1          3.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1       500.1330885 MHz
NUC1                    1H
P1                2.67 usec
PLW1       12.19999981 W

F2 - Processing parameters
SI                   65536
SF         500.1300136 MHz
WDW                     EM
SSB      0
LB                0.30 Hz
GB       0
PC                    1.00
```



S43

($CDCl_3$, 125 MHz)

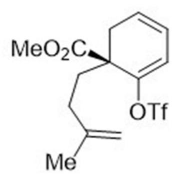
```
Current Data Parameters
NAME            yh-4-22-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180812
Time                20.53
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                     23
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  296.3 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

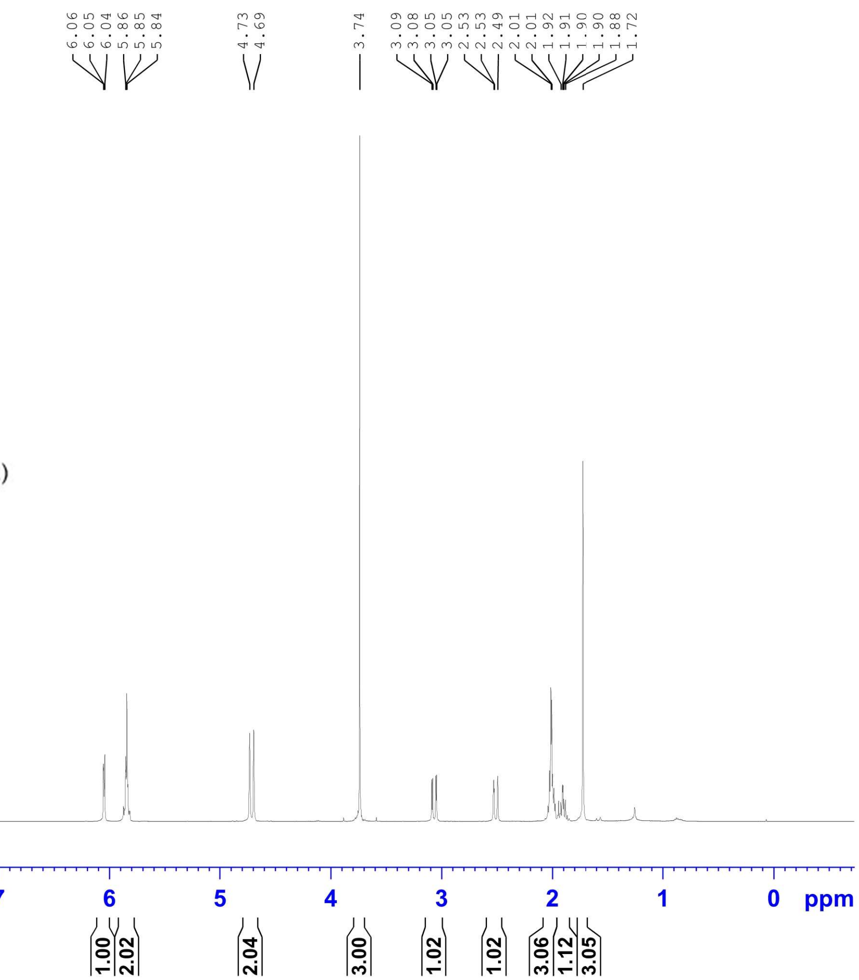
======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



74

(CDCl$_3$, 500 MHz)

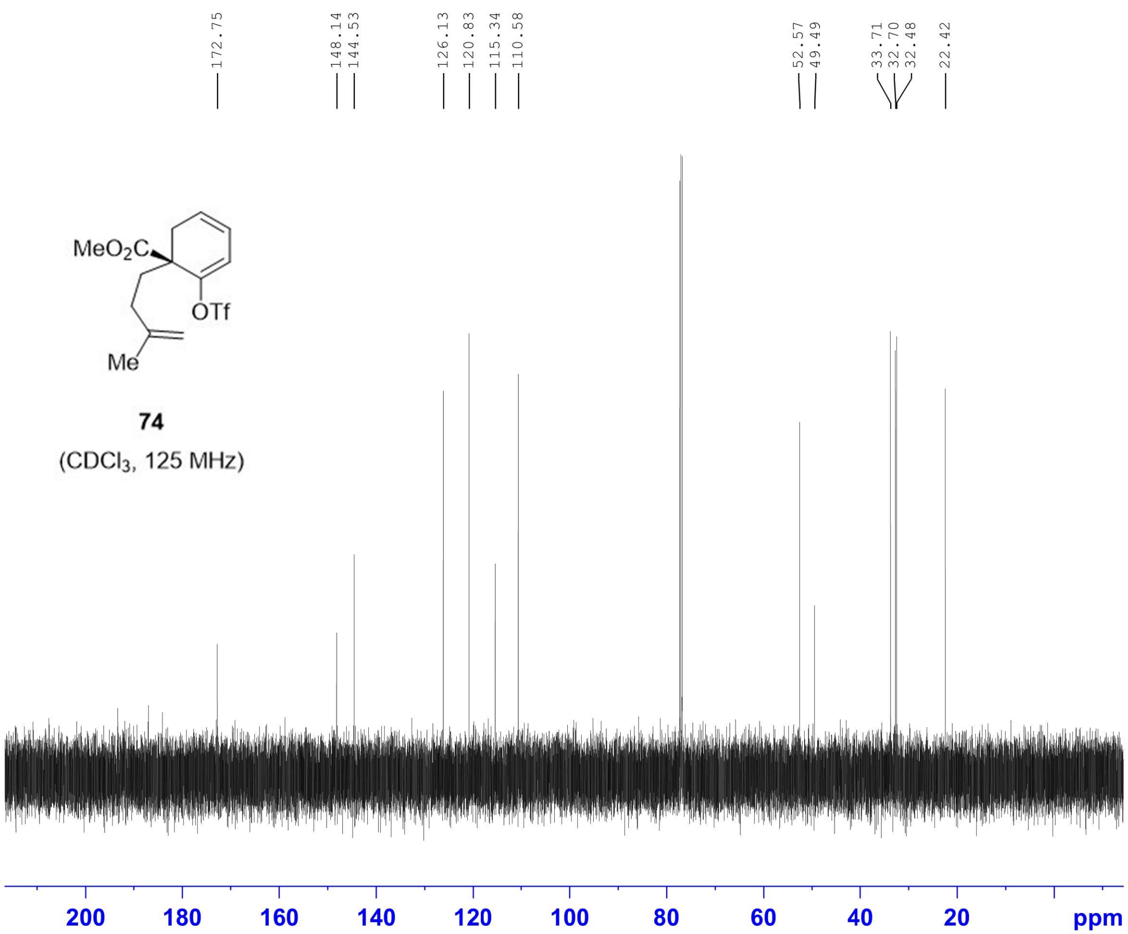



```
Current Data Parameters
NAME          yh-4-24-a
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20180314
Time              22.08
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                29.95
DW               50.000 usec
DE                 6.50 usec
TE                296.7 K
D1           4.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                 1H
P1                 3.58 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                32768
SF          499.8700123 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



74

($CDCl_3$, 125 MHz)

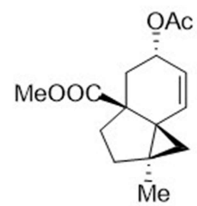
```
Current Data Parameters
NAME           yh-4-24-a
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180314
Time_              22.16
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                     2
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 296.9 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

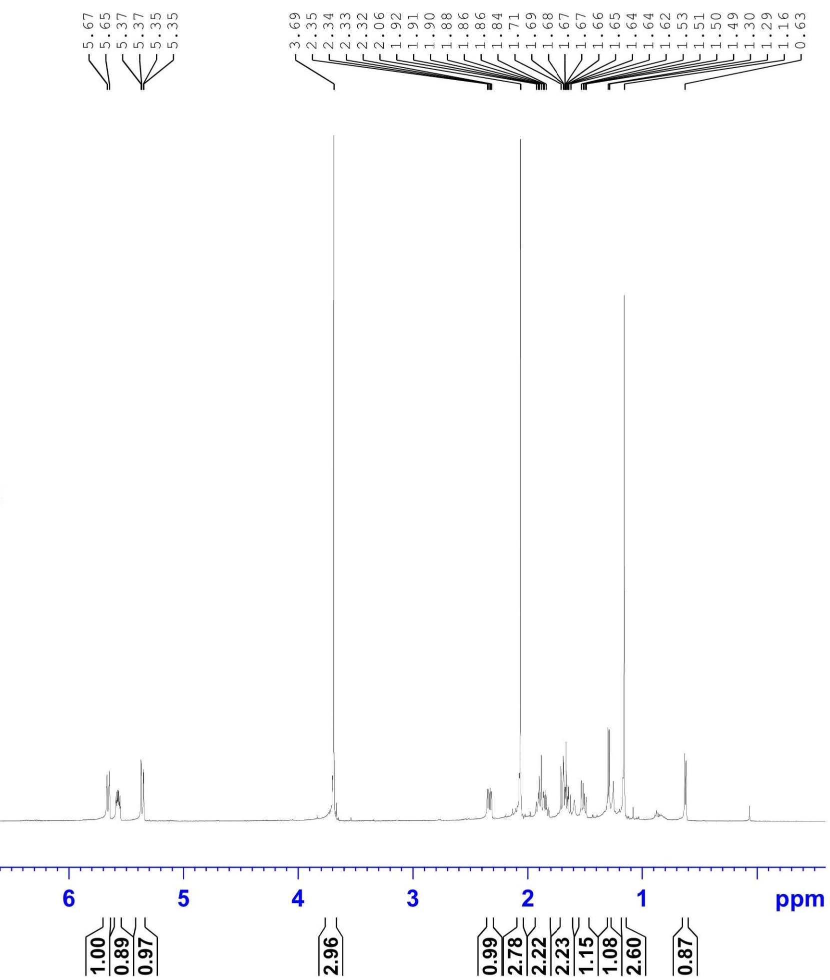
======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```



77

($CDCl_3$, 500 MHz)

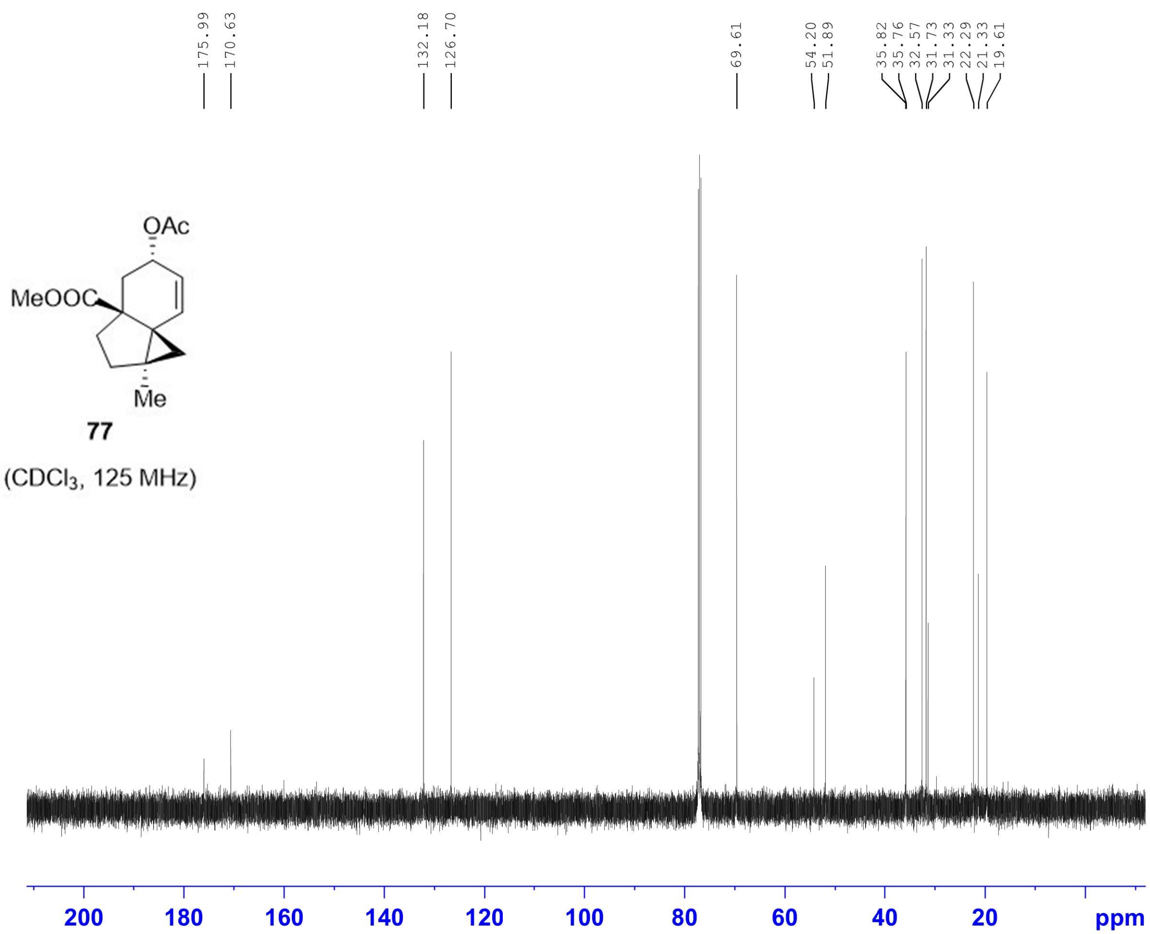



```
Current Data Parameters
NAME          yh-4-25-2-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180313
Time                21.11
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  51.11
DW                 50.000 usec
DE                   6.50 usec
TE                  296.9 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700123 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



77

($CDCl_3$, 125 MHz)

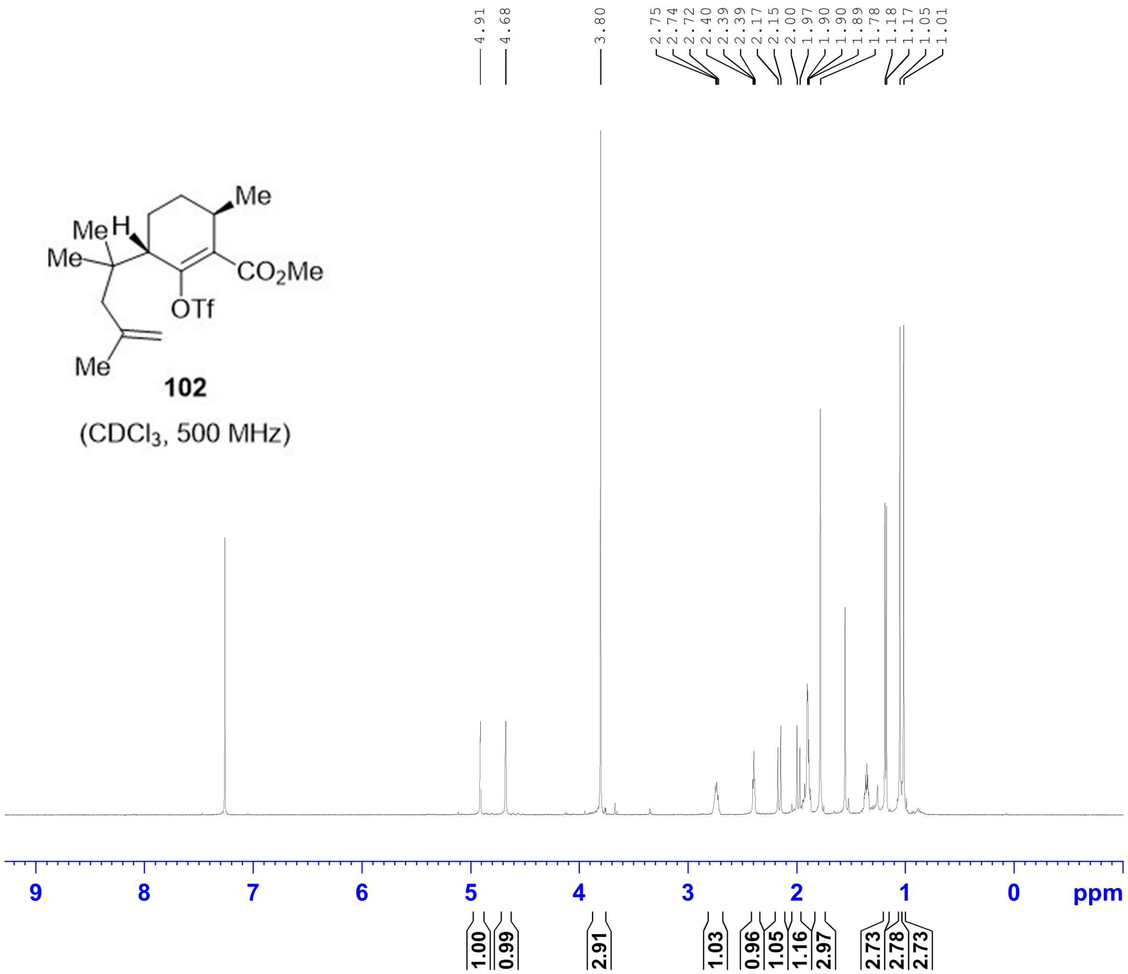

```
Current Data Parameters
NAME          yh-4-25-2-a
EXPNO                   3
PROCNO                  3

F2 - Acquisition Parameters
Date_            20180313
Time                21.47
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    329
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  298.5 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



102

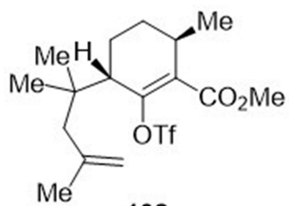
($CDCl_3$, 500 MHz)


```
Current Data Parameters
NAME             yh-4-121
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180725
Time                21.16
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      3
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                 105.66
DW                 50.000 usec
DE                   6.50 usec
TE                  296.5 K
D1             4.00000000 sec
TD0                     1

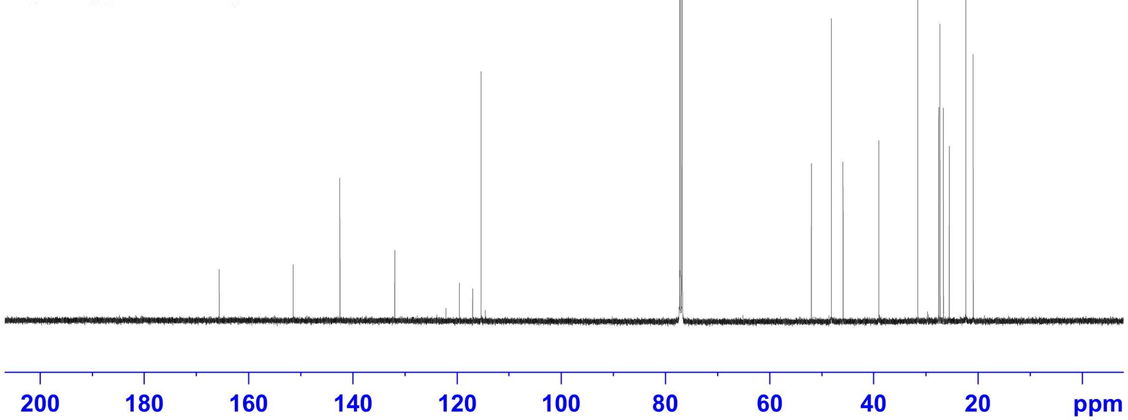
======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700122 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



102

($CDCl_3$, 125 MHz)



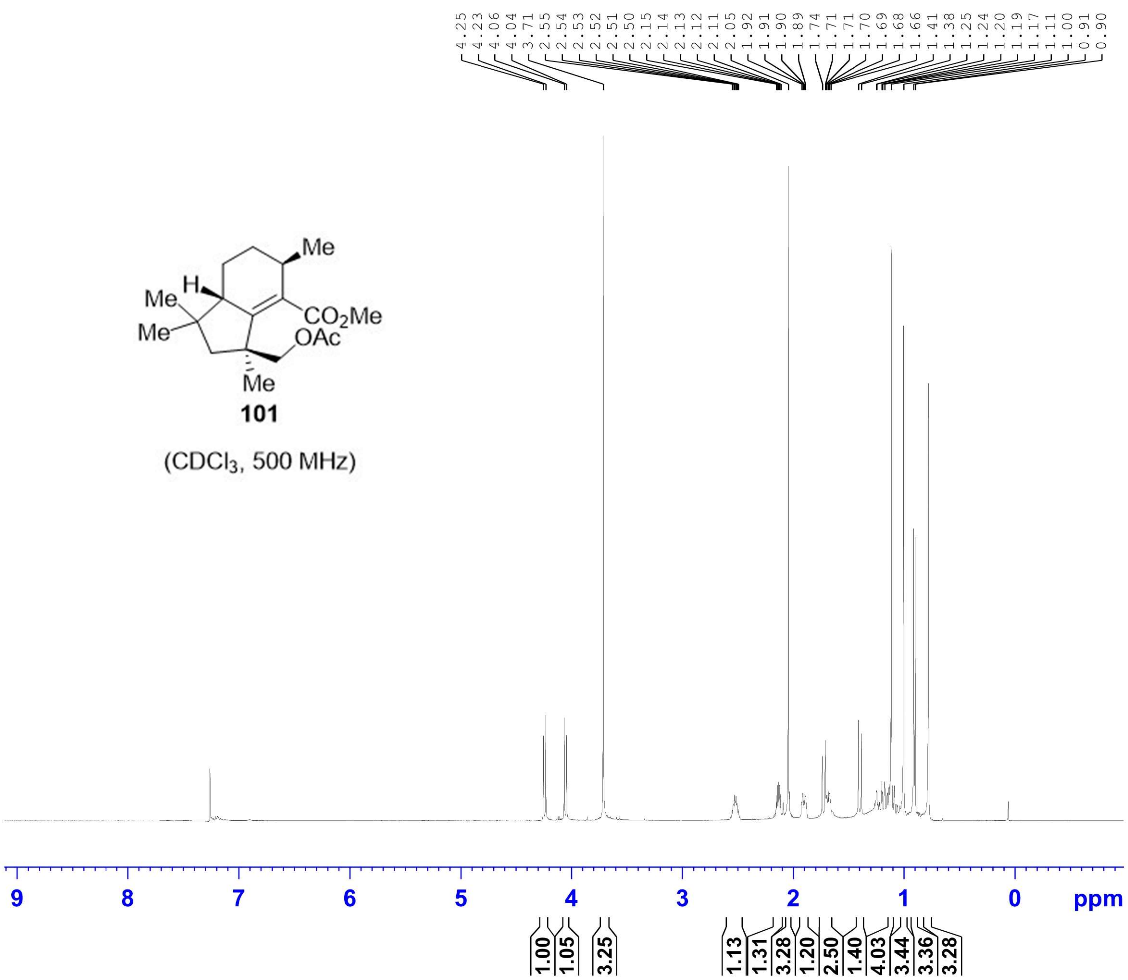

```
Current Data Parameters
NAME            yh-4-121
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180726
Time                7.14
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                  5000
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 298.4 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```

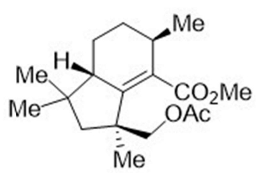



```
Current Data Parameters
NAME              yh-5-48
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180809
Time                21.01
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      3
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  51.11
DW                 50.000 usec
DE                   6.50 usec
TE                  296.3 K
D1             4.00000000 sec
TD0                     1

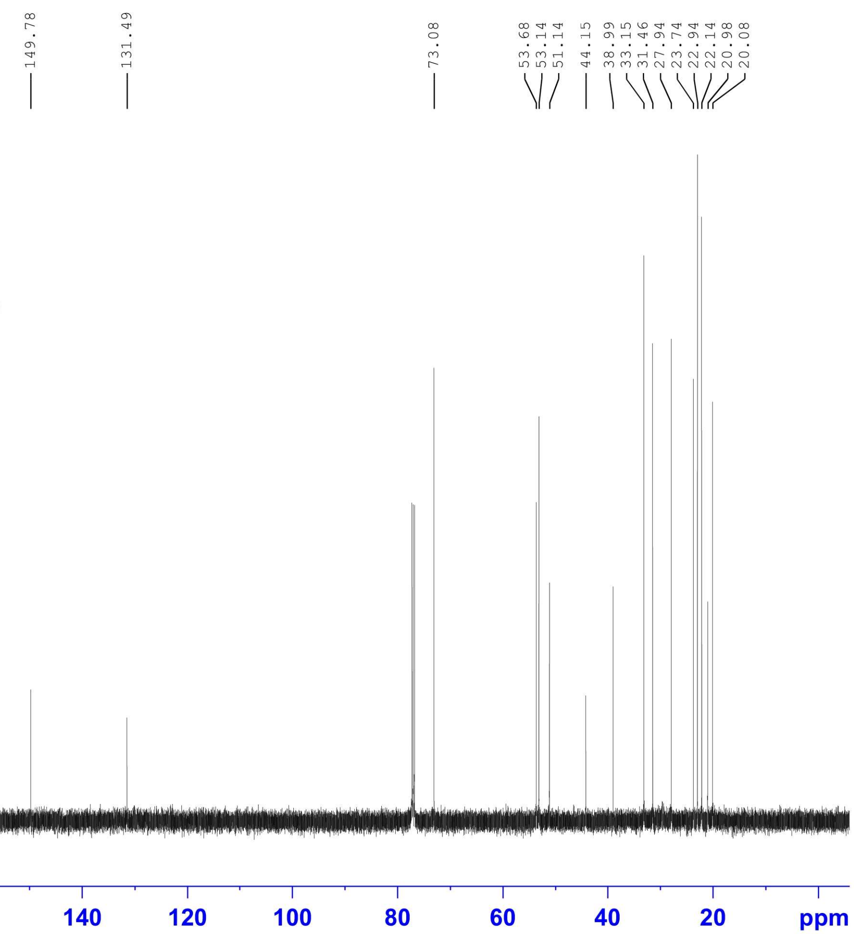
======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700123 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



101

(CDCl$_3$, 125 MHz)



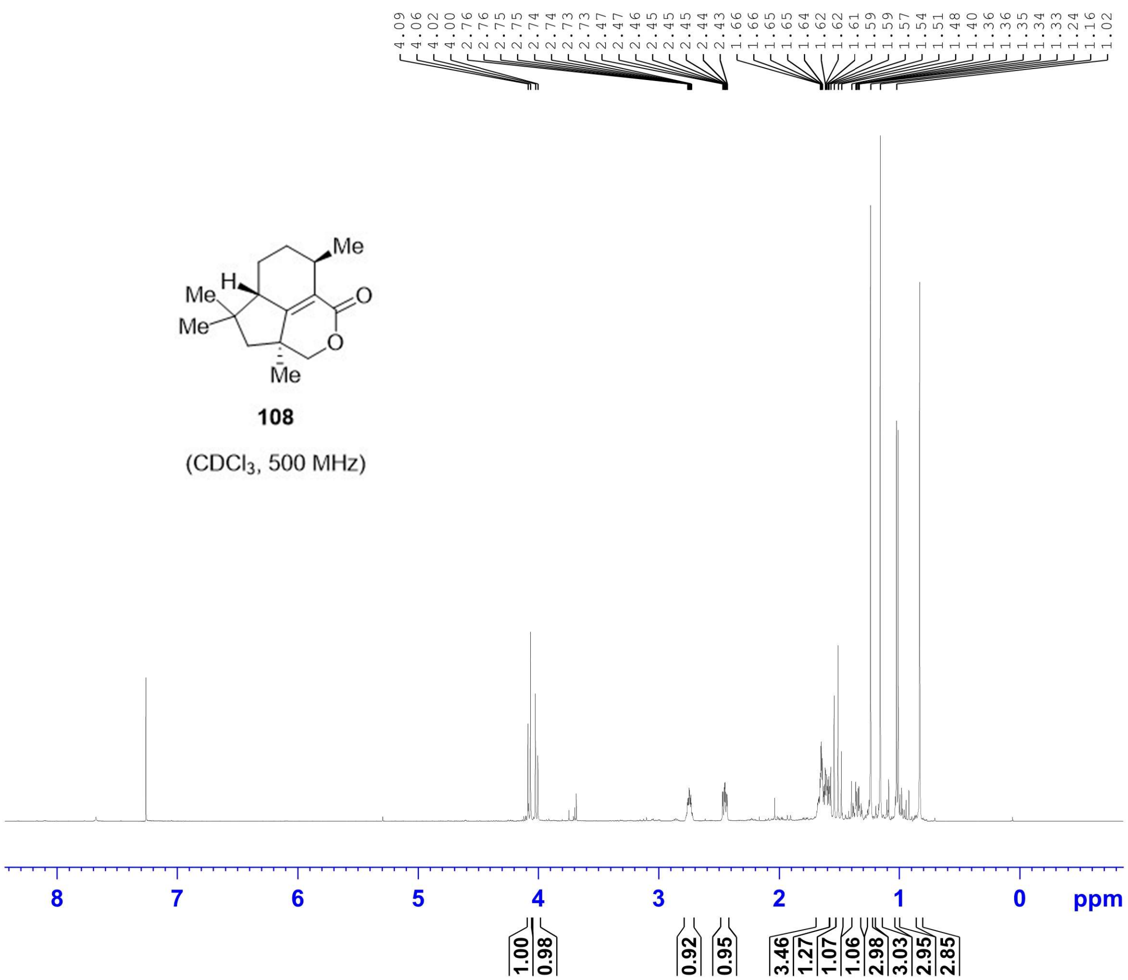

```
Current Data Parameters
NAME             yh-5-48
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180809
Time               21.22
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                   149
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 297.3 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```



108

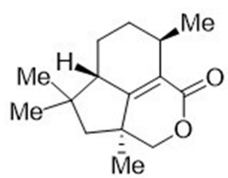
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME          yh-4-57-b
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20180803
Time              11.05
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    8
DS                    0
SWH          10000.000 Hz
FIDRES        0.166672 Hz
AQ           2.9999001 sec
RG              110.37
DW              50.000 usec
DE               10.00 usec
TE               294.1 K
D1          3.00000000 sec
TD0                   1

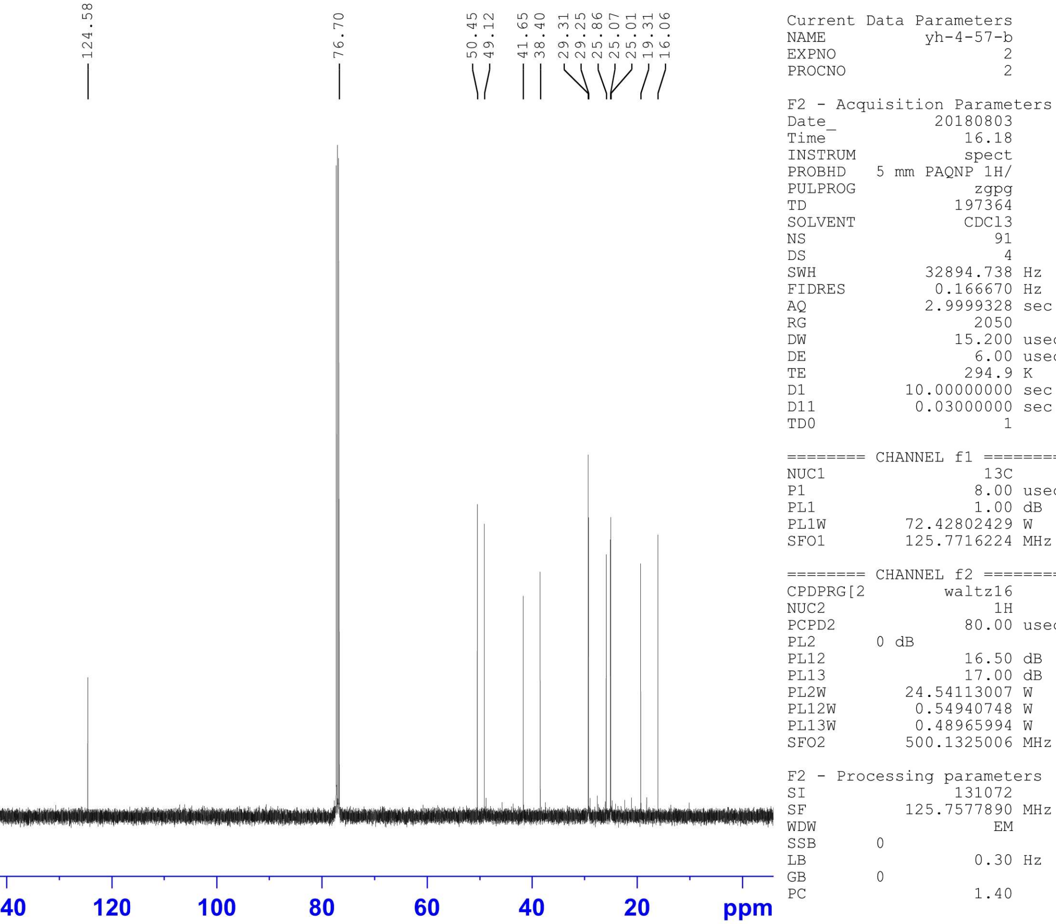
======== CHANNEL f1 ========
SFO1       500.1330885 MHz
NUC1                 1H
P1                 2.67 usec
PLW1        12.19999981 W

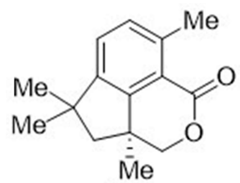
F2 - Processing parameters
SI                65536
SF          500.1300137 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



108

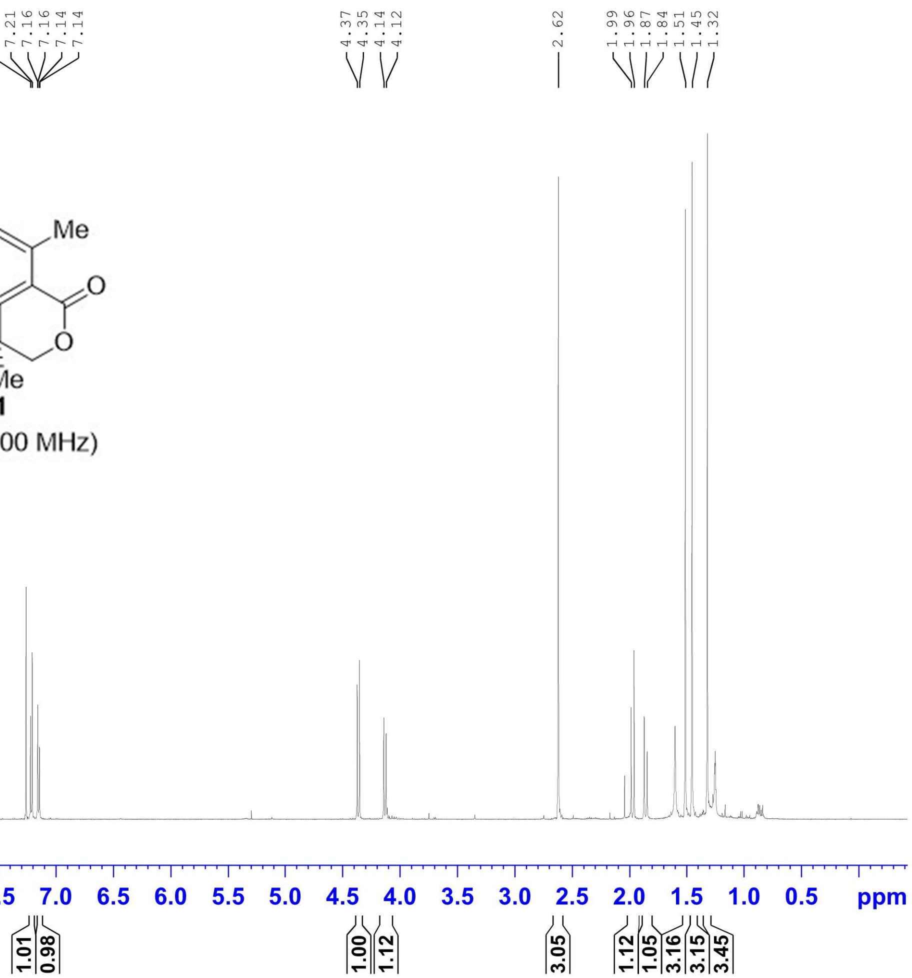
(CDCl$_3$, 125 MHz)





81

(CDCl$_3$, 500 MHz)



Current Data Parameters

NAME	yh-5-47
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

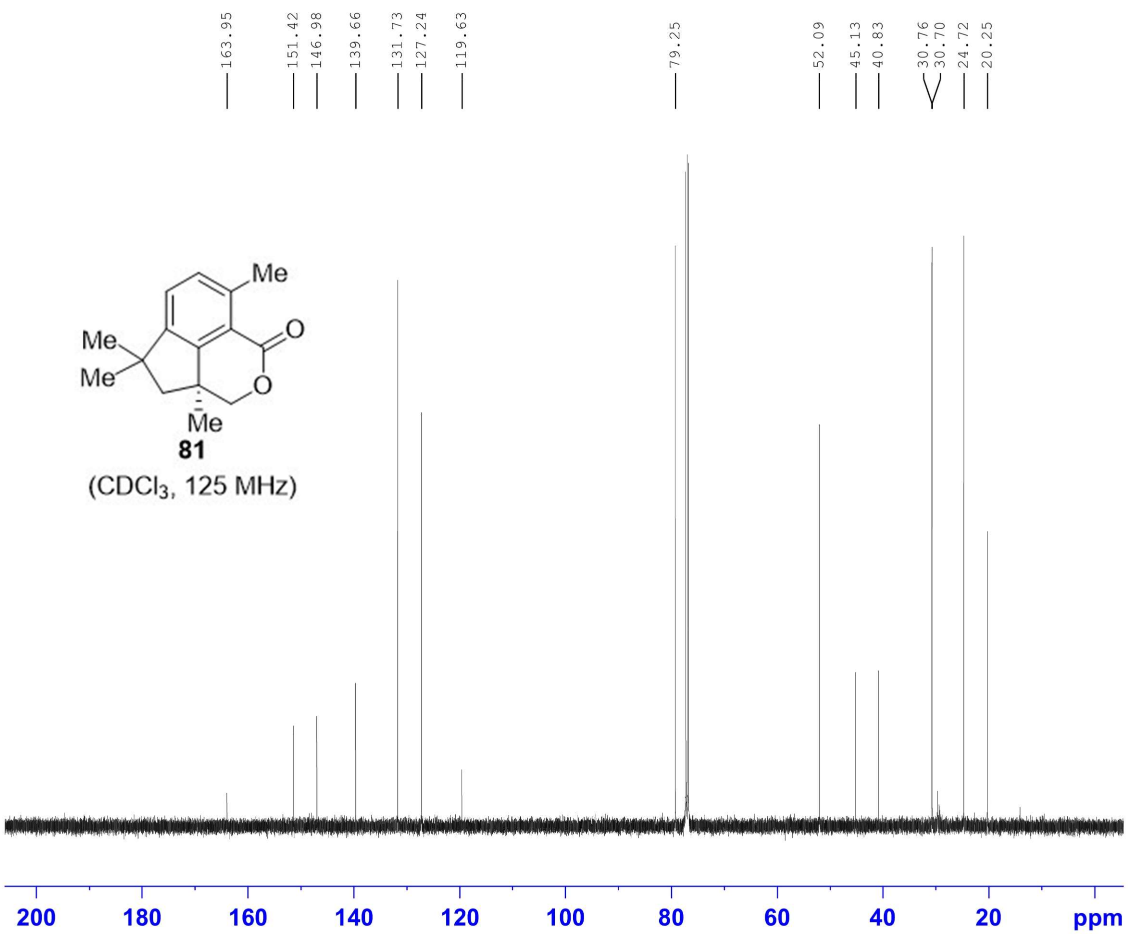
Date_	20180804
Time_	22.32
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	2
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	196.79
DW	50.000 usec
DE	10.00 usec
TE	294.4 K
D1	3.00000000 sec
TD0	1

======== CHANNEL f1 ========

SFO1	500.1330885 MHz
NUC1	1H
P1	2.67 usec
PLW1	12.19999981 W

F2 - Processing parameters

SI	65536
SF	500.1300138 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



81

($CDCl_3$, 125 MHz)

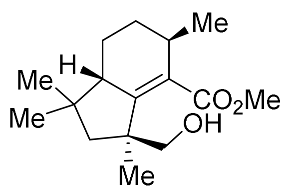
```
Current Data Parameters
NAME            yh-5-47-a
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180805
Time                20.54
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                    872
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  297.9 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

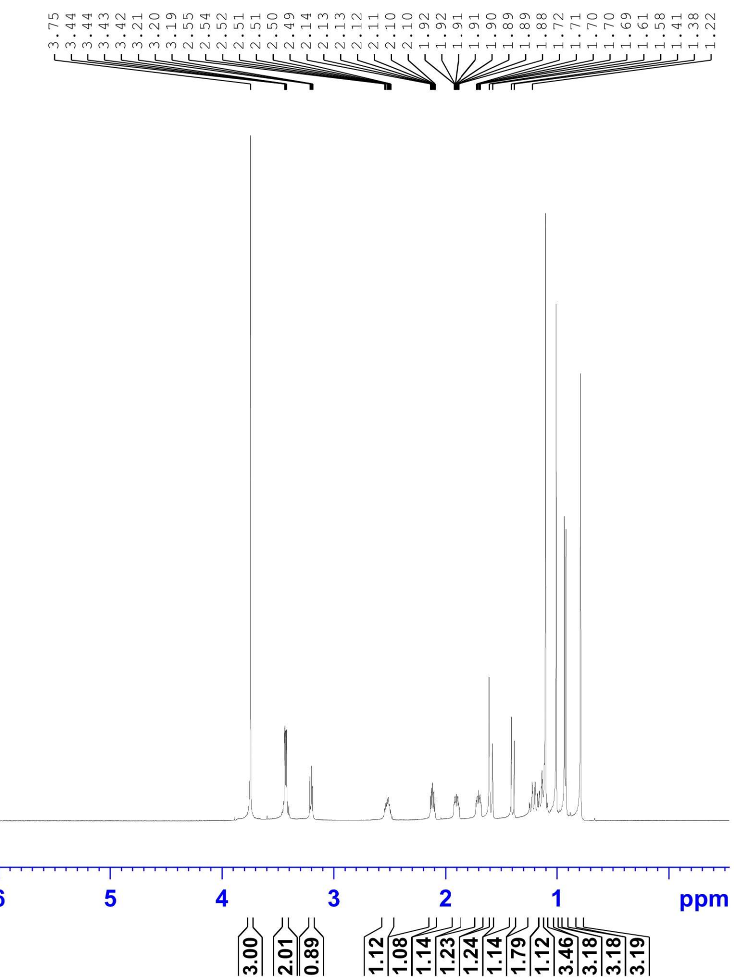
======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                1048576
SF           125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



S44
($CDCl_3$, 500 MHz)

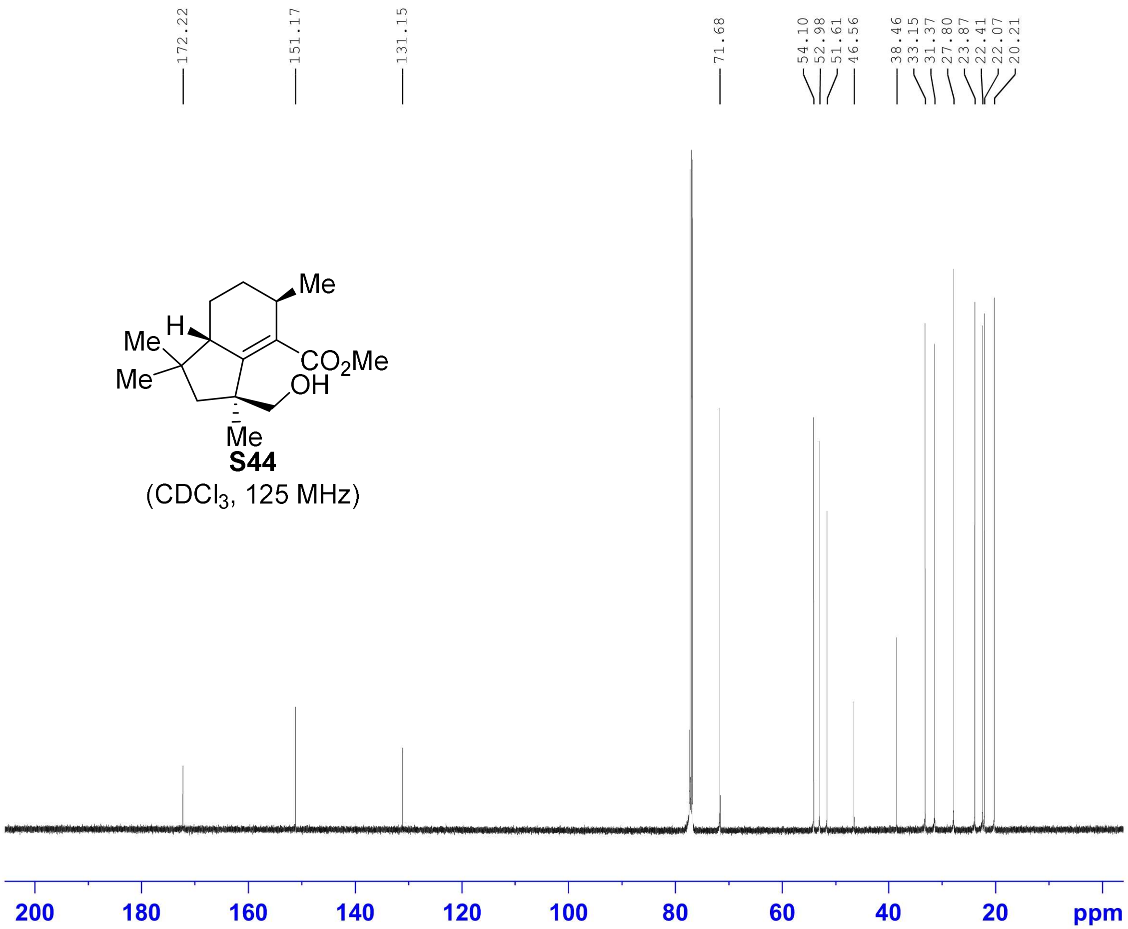



```
Current Data Parameters
NAME            yh-4-107
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180525
Time               21.45
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     7
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 77.07
DW                50.000 usec
DE                  6.50 usec
TE                 296.3 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700122 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



S44

($CDCl_3$, 125 MHz)

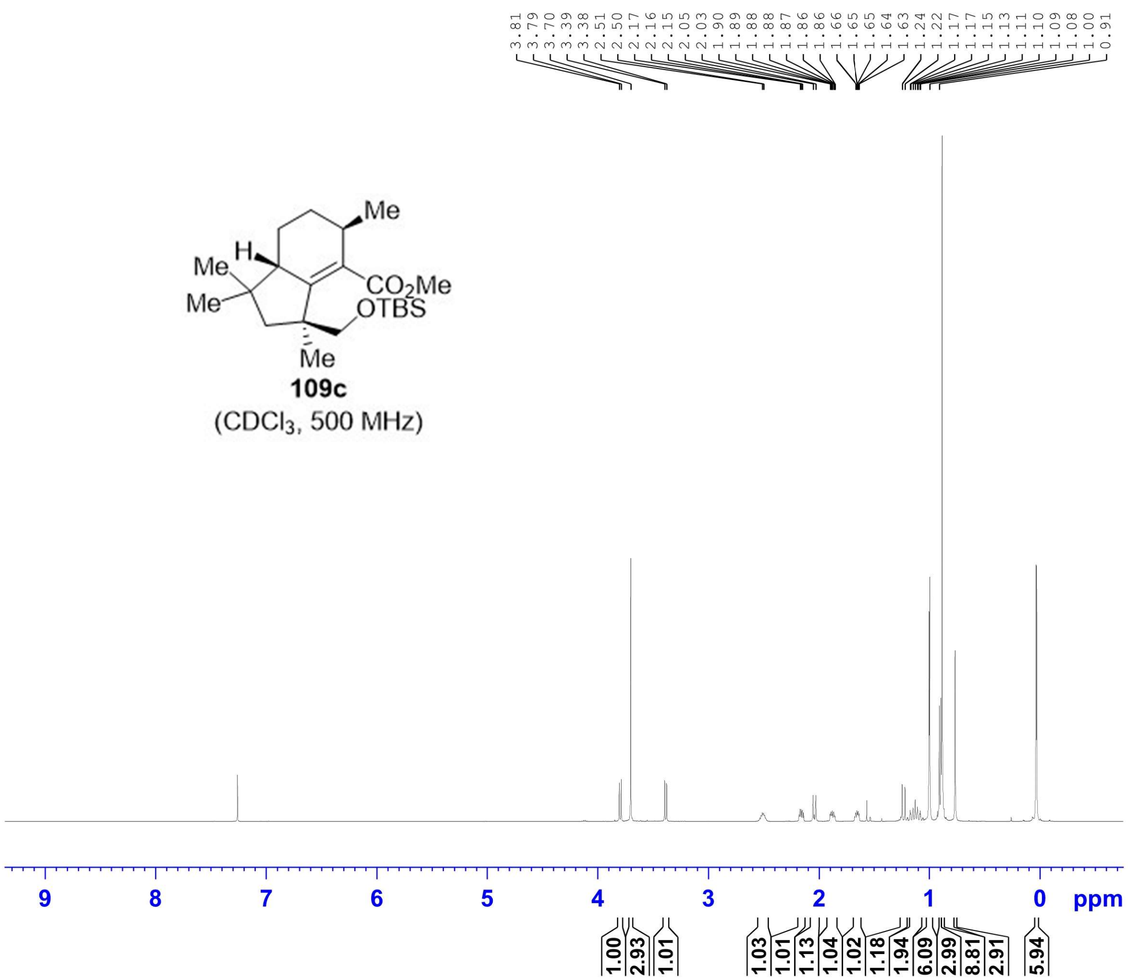
```
Current Data Parameters
NAME             yh-4-107
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20180526
Time                 8.04
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                   6000
DS                      0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                 16.000 usec
DE                   6.50 usec
TE                  297.7 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6924115 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```



109c
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             yh-4-92
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180525
Time               21.06
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     4
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 56.75
DW                50.000 usec
DE                  6.50 usec
TE                 295.6 K
D1            4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700123 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
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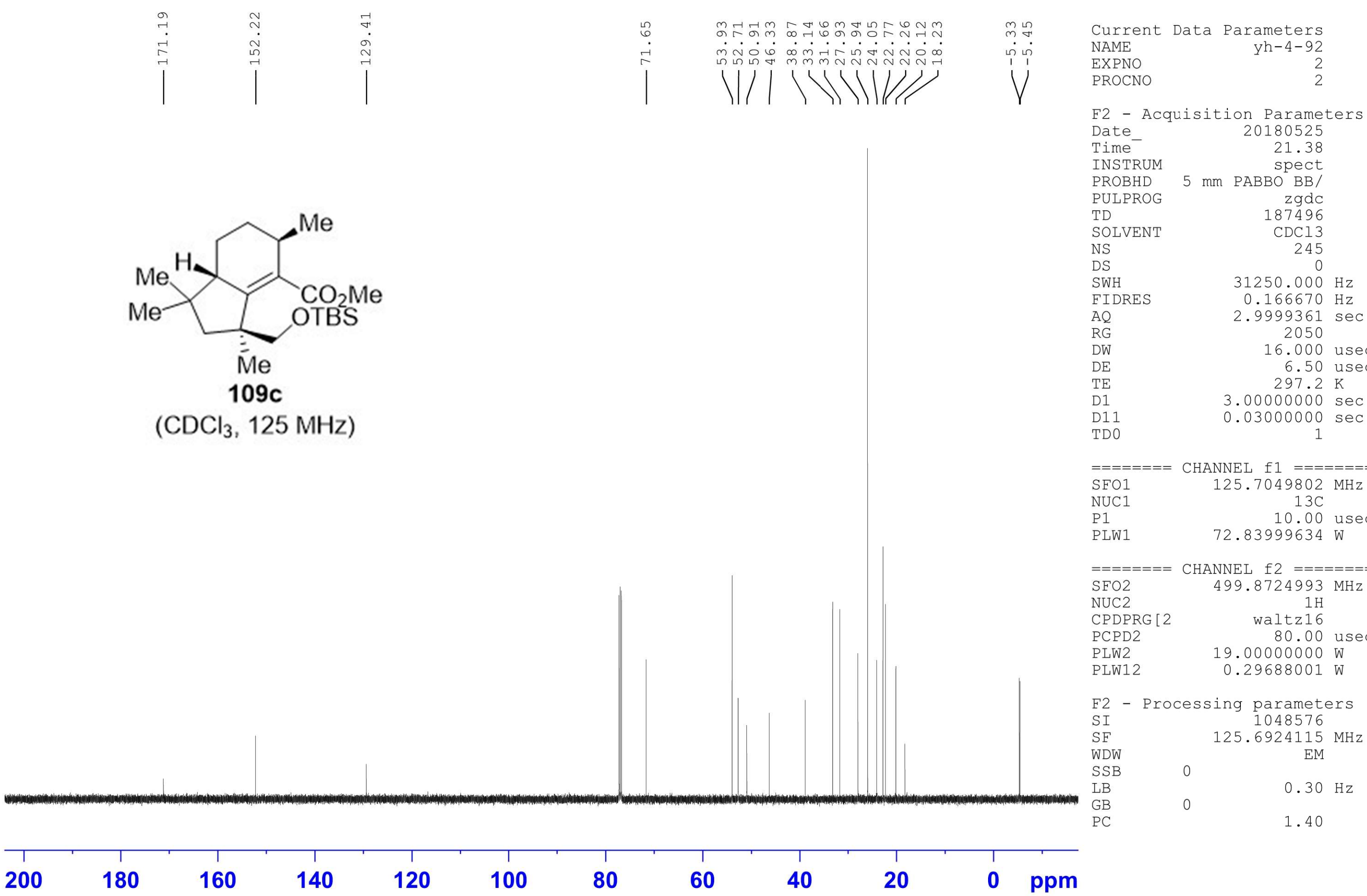
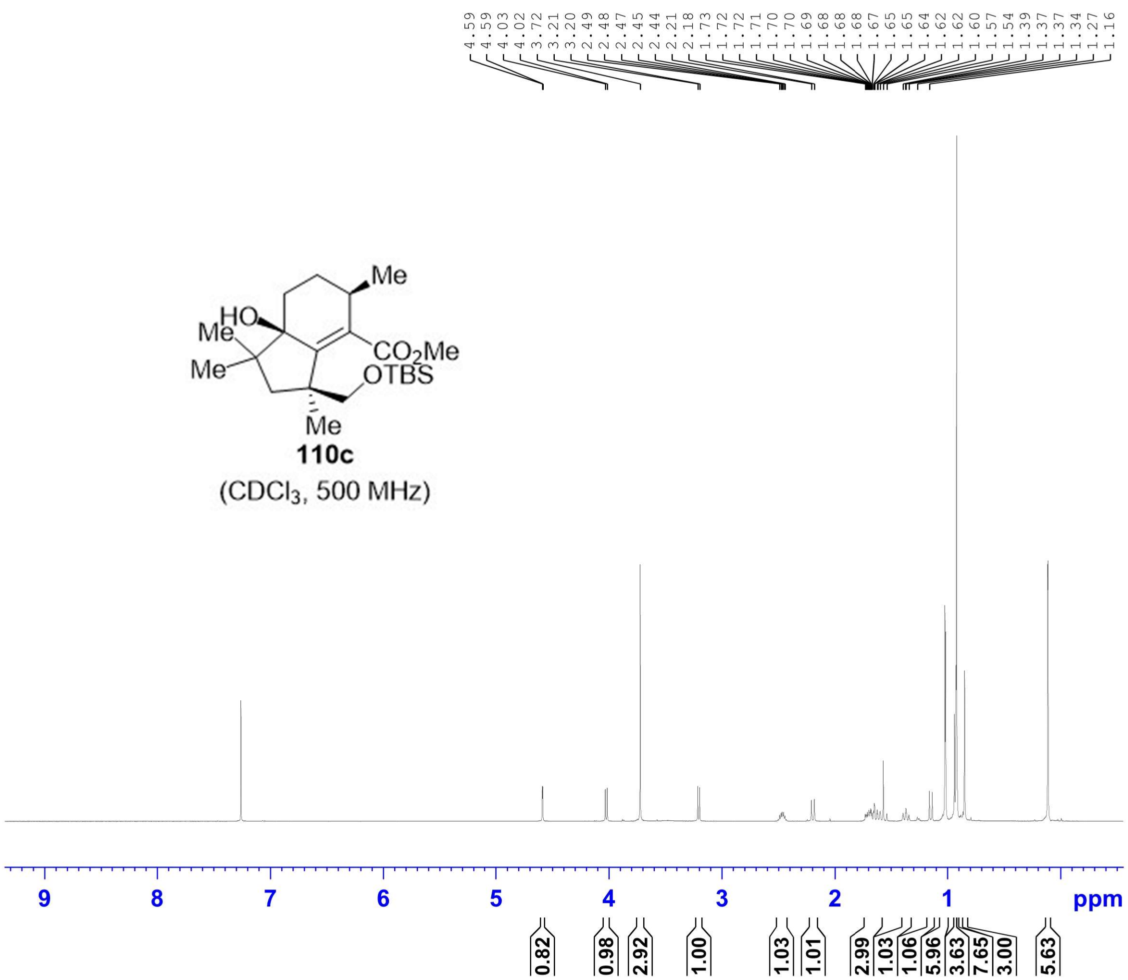


109c

($CDCl_3$, 125 MHz)



110c

($CDCl_3$, 500 MHz)

```
Current Data Parameters
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EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180526
Time                23.03
INSTRUM             spect
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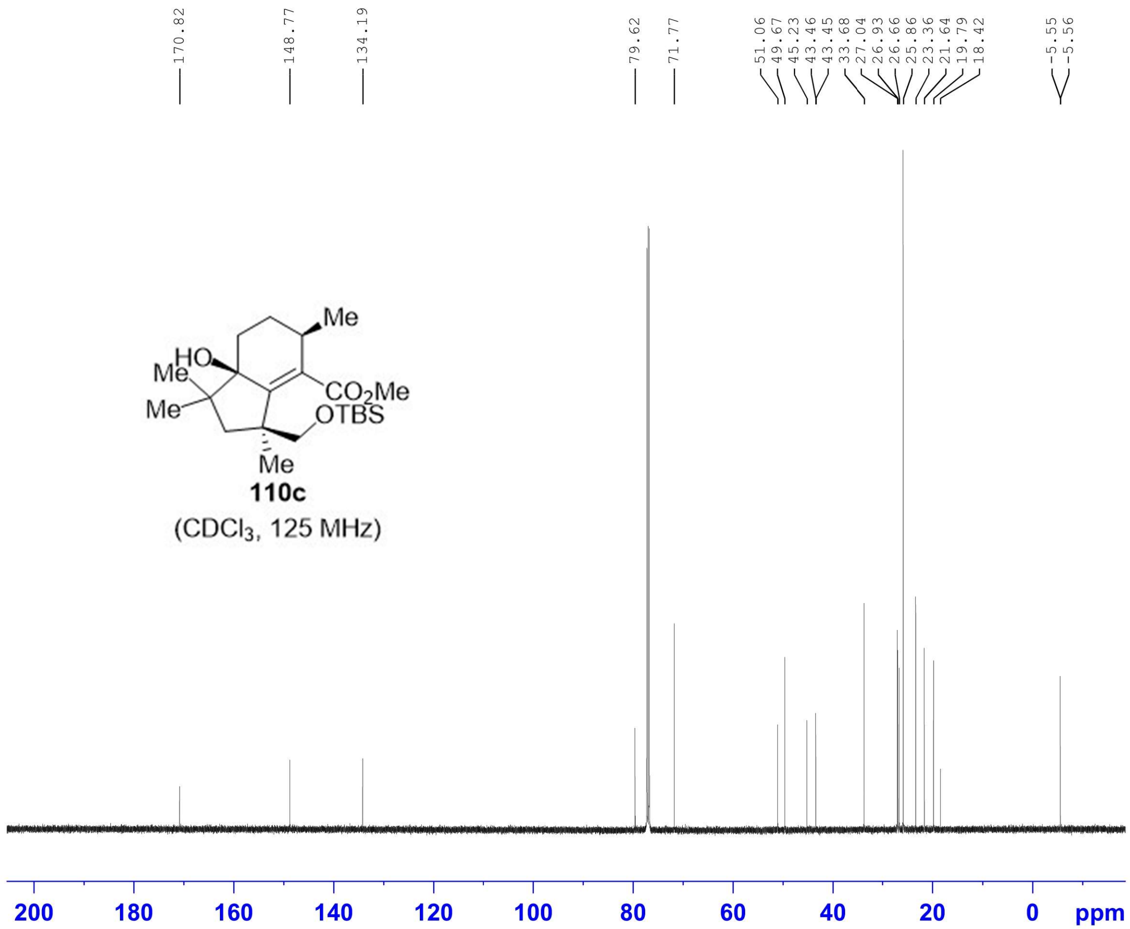
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      5
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  86.16
DW                 50.000 usec
DE                   6.50 usec
TE                  295.5 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700122 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



110c

(CDCl$_3$, 125 MHz)

```
Current Data Parameters
NAME              yh-4-112
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20180527
Time                  7.01
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                    4661
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   297.6 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2           499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
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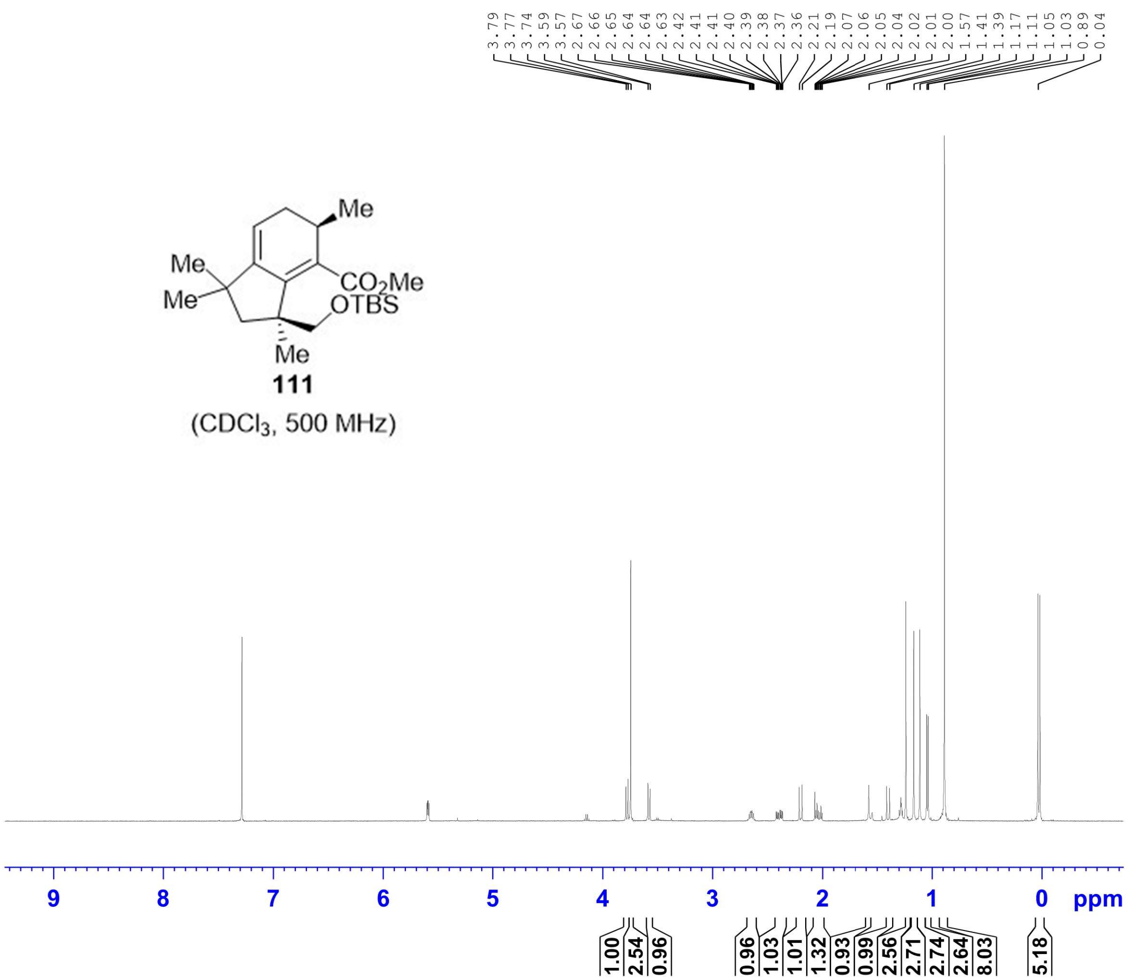
SF             125.6924115 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



111

($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME             yh-4-114
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
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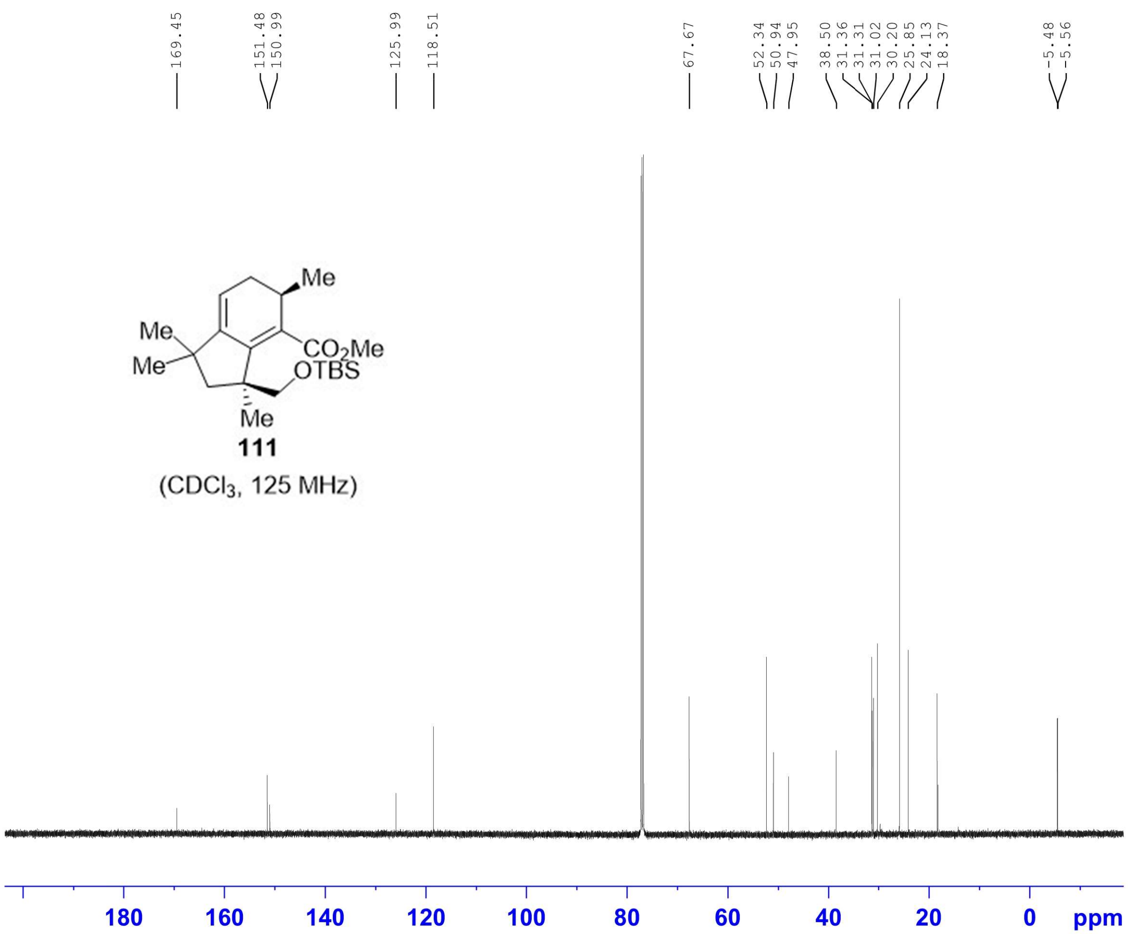
Time                23.38
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      2
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                 105.66
DW                 50.000 usec
DE                   6.50 usec
TE                  296.1 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   3.58 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                  65536
SF            499.8700000 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



111

($CDCl_3$, 125 MHz)

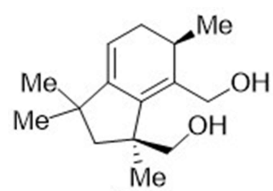
```
Current Data Parameters
NAME              yh-4-114
EXPNO                    2
PROCNO                   2

F2 - Acquisition Parameters
Date_             20180530
Time                  8.10
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                    5000
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   297.7 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                      1

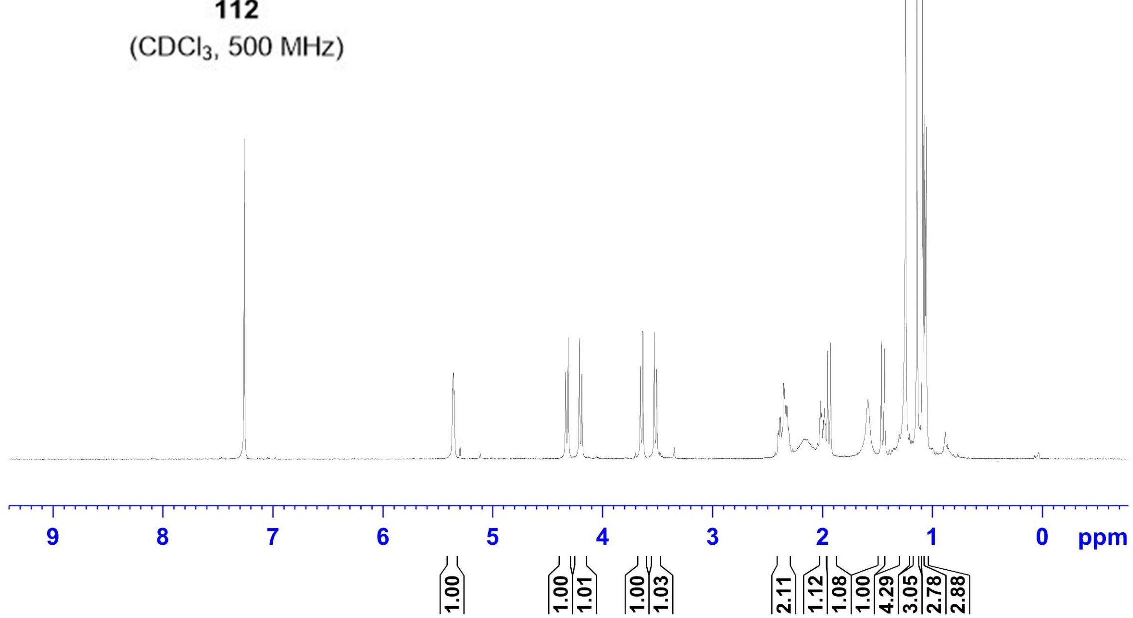
======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF           125.6924115 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



112
($CDCl_3$, 500 MHz)

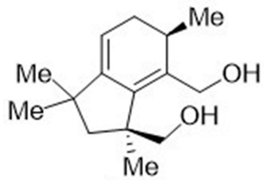



```
Current Data Parameters
NAME             yh-4-116
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180528
Time                15.46
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                 196.79
DW                 50.000 usec
DE                  10.00 usec
TE                  293.8 K
D1             3.00000000 sec
TD0                     1

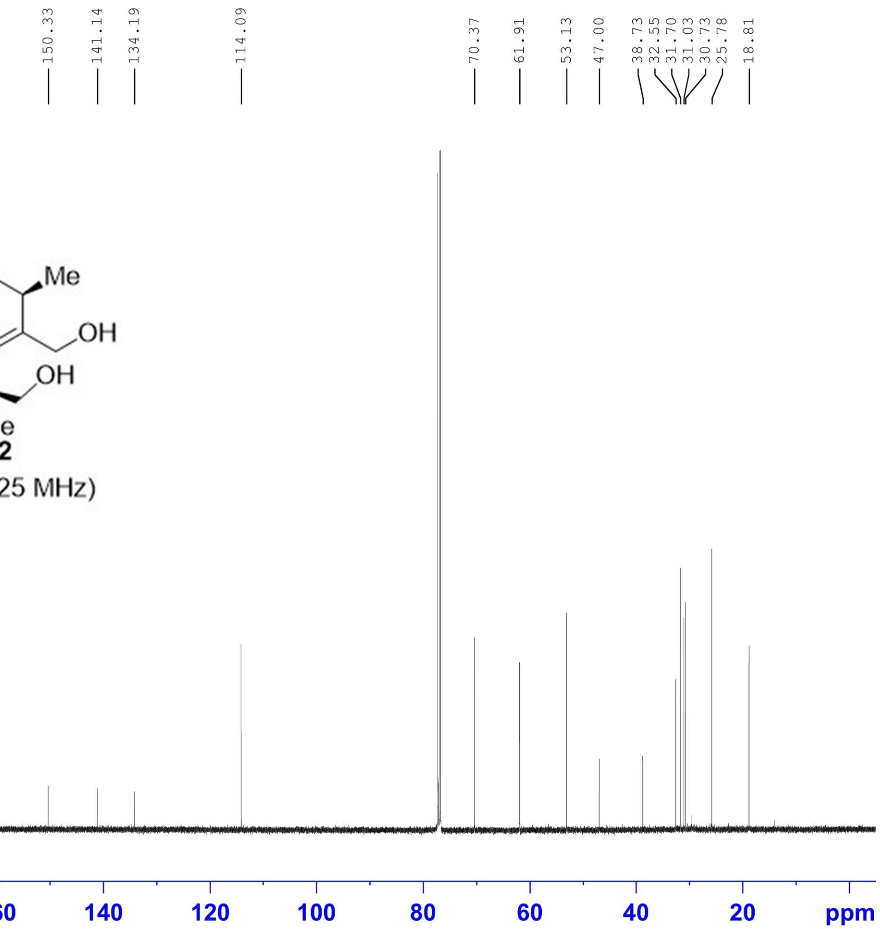
======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                    1H
P1                    2.67 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                  65536
SF           500.1300137 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



112

(CDCl$_3$, 125 MHz)



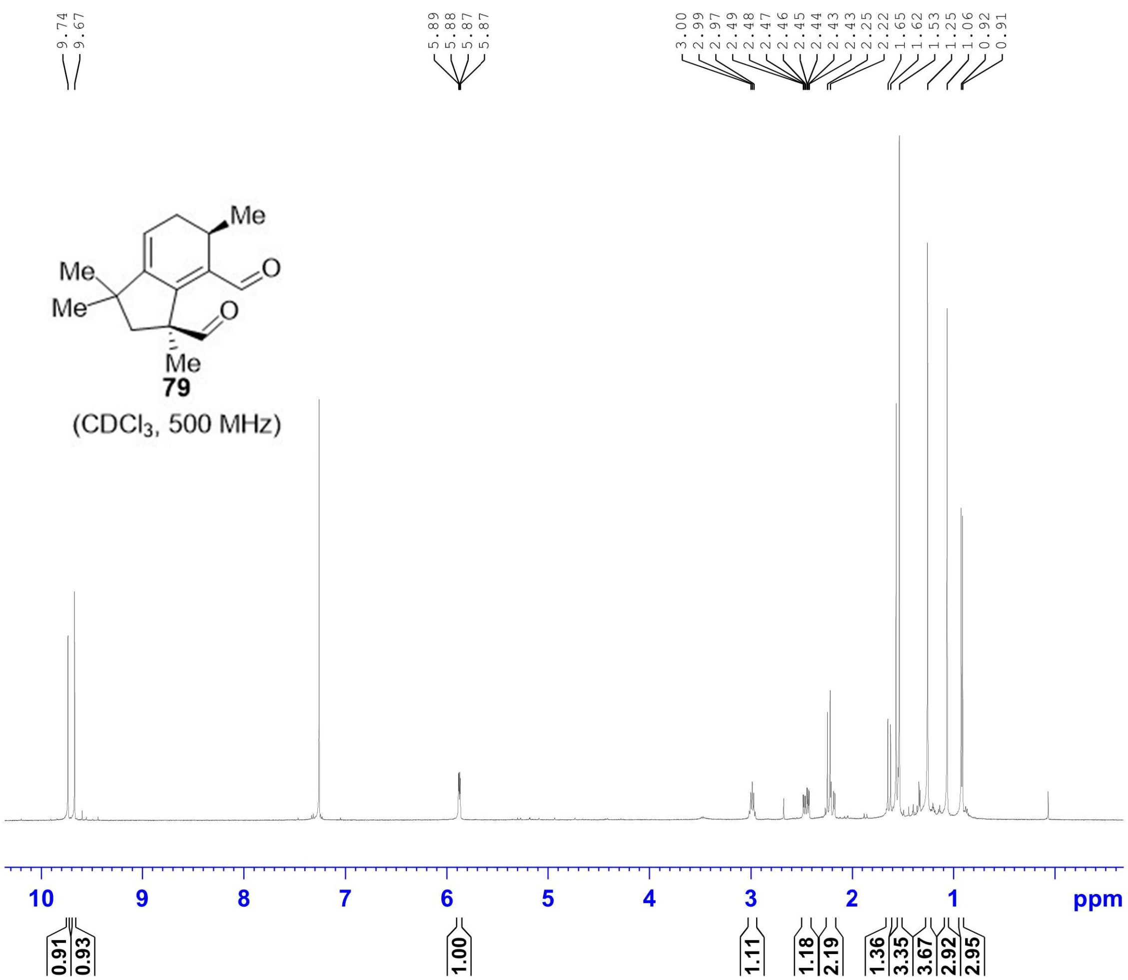

```
Current Data Parameters
NAME            yh-4-116
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180529
Time                5.53
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                  5000
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 297.7 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```



79

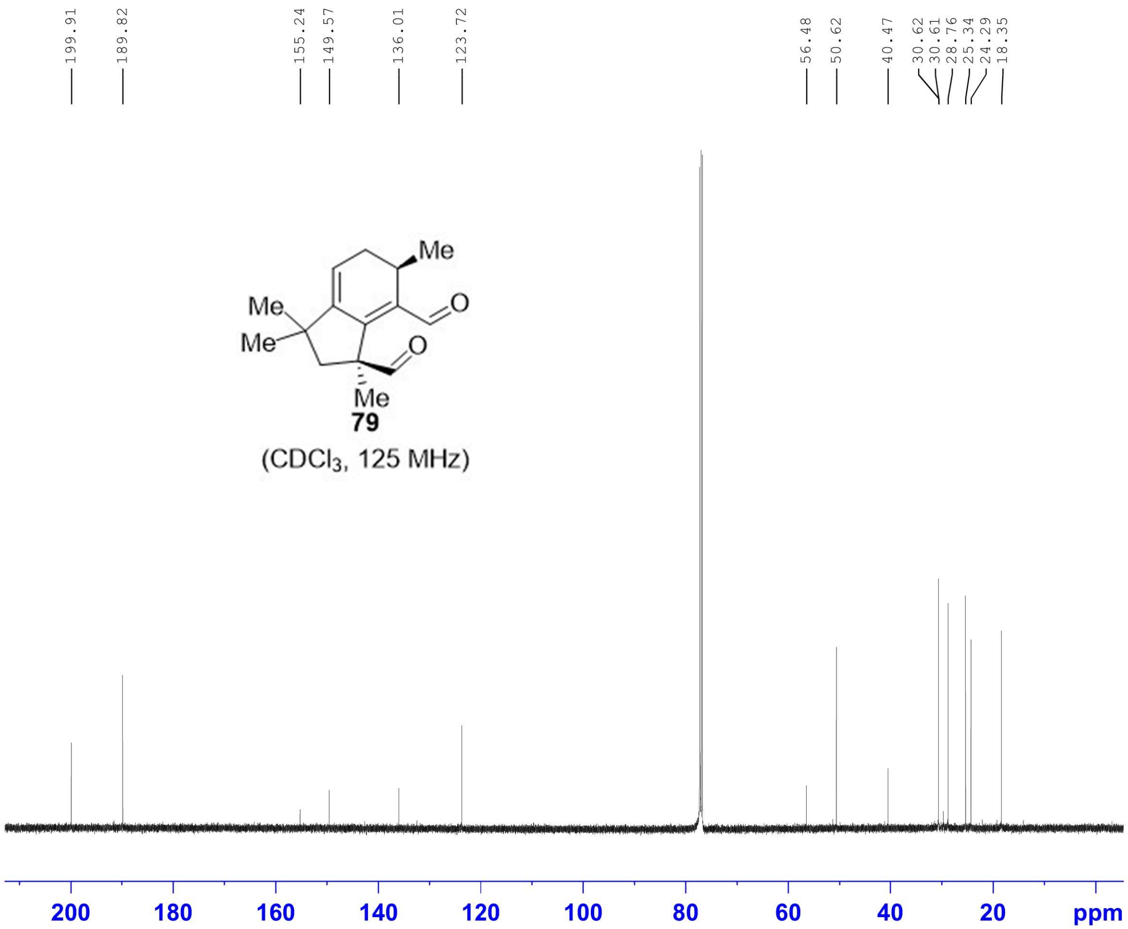
($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME            yh-4-106-2
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180523
Time                 21.50
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       4
DS                       0
SWH          10000.000 Hz
FIDRES        0.166672 Hz
AQ           2.9999001 sec
RG              133.95
DW              50.000 usec
DE                6.50 usec
TE               295.5 K
D1          4.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1       499.8730869 MHz
NUC1                    1H
P1                3.58 usec
PLW1       18.25000000 W

F2 - Processing parameters
SI                   65536
SF         499.8700123 MHz
WDW                     EM
SSB      0
LB                0.30 Hz
GB       0
PC                    1.00
```




```
Current Data Parameters
NAME          yh-4-106-2
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20180524
Time                6.47
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT            CDCl3
NS                  5200
DS                     0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                  2050
DW                16.000 usec
DE                  6.50 usec
TE                 297.5 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI               1048576
SF           125.6924115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.40
```

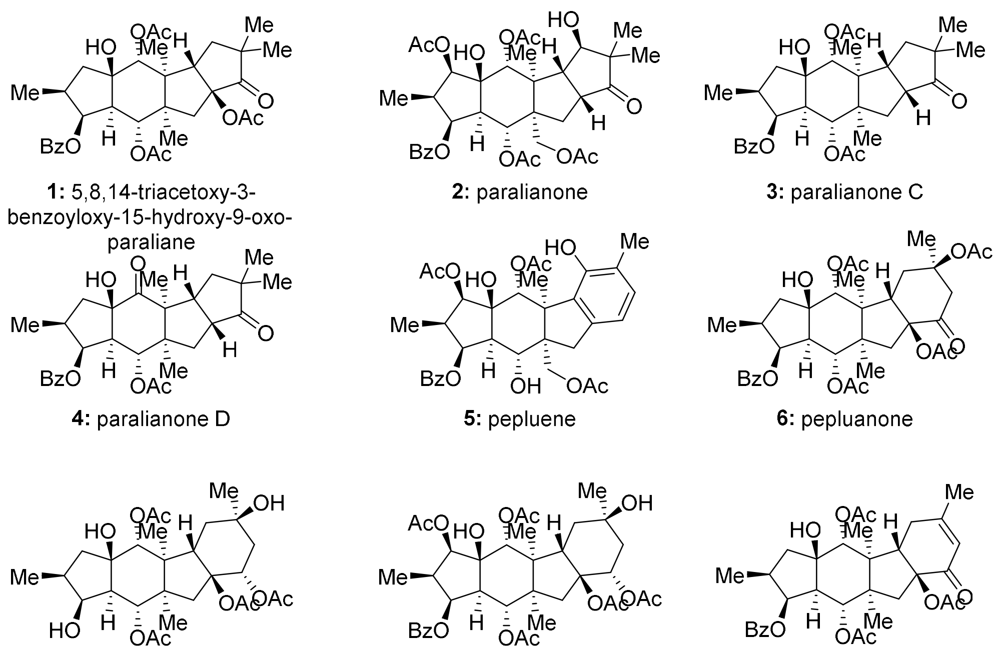
CHAPTER 3

SYNTHETIC STUDY TOWARDS *PARALIANE* FAMILY OF NATURAL PRODUCTS

3.1 Introduction

3.1.1 Structures of selected members of the paraliane family of natural products

Figure 3-1: Structure of selected members of *paraliane* and *pepluane* family



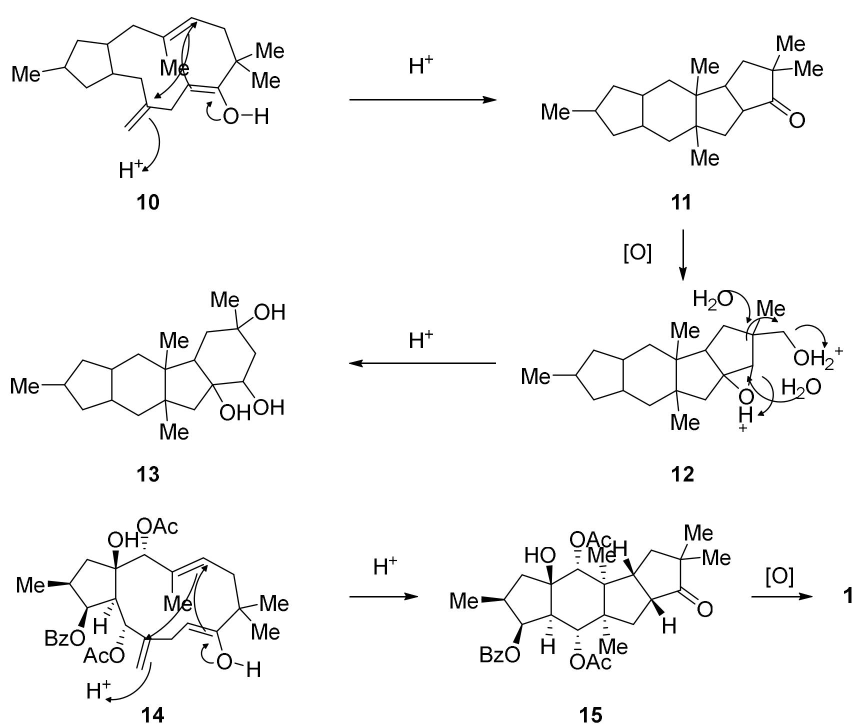
1: 5,8,14-triacetoxy-3-benzoyloxy-15-hydroxy-9-oxo-paraliane; **2:** paralianone; **3:** paralianone C; **4:** paralianone D; **5:** pepluene; **6:** pepluanone; **7:** pepluanol C; **8:** pepluanol D; **9:** pepluanol G

The *paraliane* family of natural products is comprised of complex tetracyclic terpenes. The first member **1** was first isolated in 1998 by the Jakupovic group from the plant *Euphorbia paralias*.[1] Other members of the family have since been further isolated from *E. paralias* and the related traditional herb *Euphorbia peplus*, together with the similar *pepluane* family.[2] The *paraliane* family (**1-4**) compounds share a special 5,5,6,5-tetracyclic skeleton while the *pepluane* (**5-9**) skeleton is 6,5,6,5-tetracyclic. All *paraliane* family members (**1-4**) are highly oxidized terpenes, and the density of continuous stereocenters makes them even more challenging targets of organic synthesis. As for as we know, no total synthesis of *paraliane* family members have been reported. (Figure 3-1)

3.1.2 Biochemistry and biosynthesis study on paraliane family

E. peplus has been used in the treatment of skin diseases since the ancient times in Europe. The extraction of *E. peplus* was reported to be effective in the treatment against nonmelanoma skin cancer.[3] Researchers have been working on isolating the active ingredients from those plants.[4] *Paralianones* were reported to be anti-inflammatorily bioactive, though moderate, with the best IC_{50} equaling 33.7 μM for *paralinaone C* (**3**).[2b,5]

Scheme 3-1: Proposed biosynthesis of *pepluane* and *paraliane* skeleton



As *jatrophanes* were co-isolated with *paralianes* from same plant[2b], it was proposed that the biosynthesis process of *paralianes* started from relatively simple *jatrophanes*. The acid catalyzed polyene cyclization of *jatrophane* skeleton **10** could directly provide *paraliane* skeleton **11** in one step. Following oxidation and ring expansion would result in *pepluane* skeleton **13**.[4] Jakupovic et al. proposed that **1** was synthesized by nature from a hypothetical precursor **14**, via cyclization forming **15** and following α-oxidation of ketone.[1] However, though **14** is similar to natural product *guyonianin E*,[2c] it has been neither isolated nor synthesized so far. (Scheme 3-1)

3.2 Synthetic study of paralianones via Pd-catalyzed cyclization cascade

3.2.1 Overview of the design

The proposed biosynthesis of the *paraliane* skeleton was based on the acid-catalyzed polyene cyclization. And herein we proposed that our palladium chemistry could be applied to construct the complex ring structures.

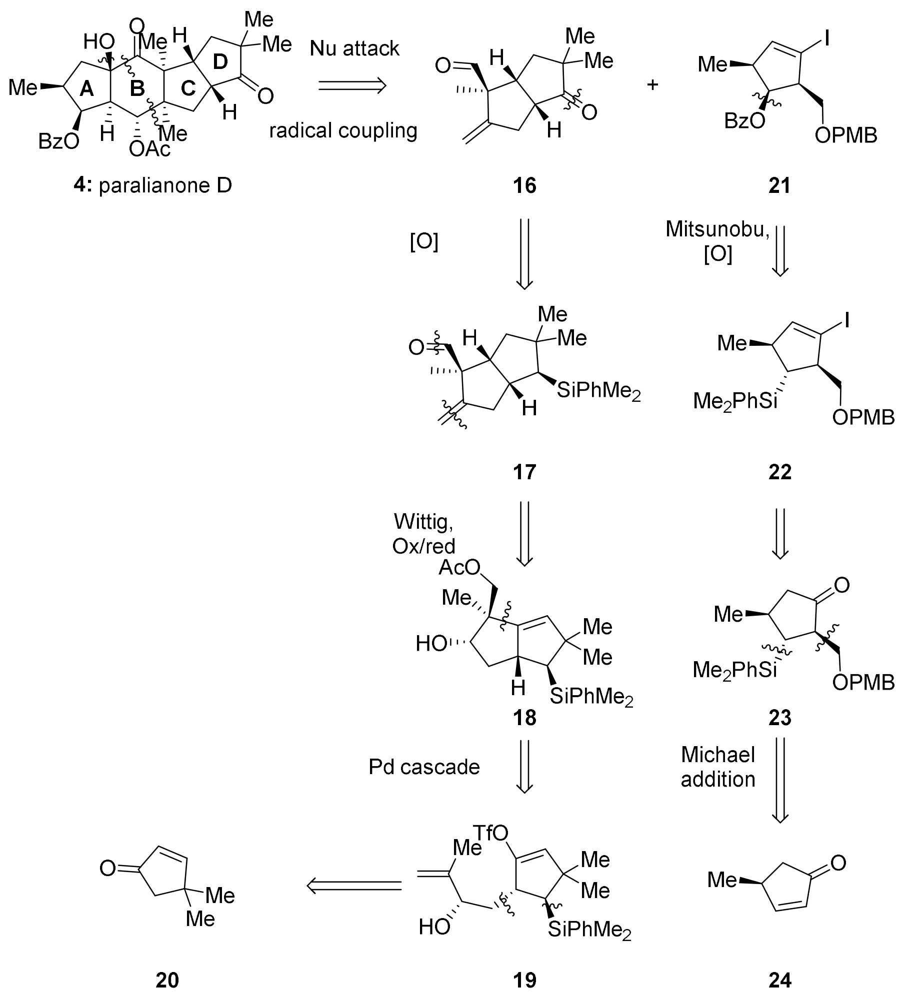
All members of the *paraliane* family have the same stereochemistry in all four rings. We noticed that the 1,3-*trans* stereochemistry and gem-dimethyl quaternary center of the C and D rings, as well as the C–O bond (acetate) on the B ring, could be the target of our cascade chemistry. So, we proposed this stereospecific cascade would be a potential method for the convergent synthesis of the *paraliane* family. (Scheme 3-2)

The retrosynthetic analysis of *paralianone D*, as an example, was shown in Scheme 3-2. The first disconnection focused on the B ring of natural product **4**. This 6-membered ring could be synthesized by a nucleophilic attack to the carbonyl and reductive radical coupling of the alkene and aldehyde, to form the upper and lower bonds, respectively. Then, **4** could be traced back to 2 fragments: east fragment **16** and west fragment **21**.

The ketone of **16** could be introduced by oxidation of a silyl group.[6] Intermediate **17** could be the product of a Wittig reaction and oxidation/hydrogenation from acetate **18**. The stereochemistry and C–O bond next to quaternary center in **18** indicated that we could synthesize it via our Pd-catalyzed cascade chemistry from triflate **19**. Finally, **19** could be traced back to commercial enone **20** by an asymmetrical Michael addition.

For the west fragment **21**, the benzoate group could be introduced by the Mitsunobu reaction[7] and oxidation, so it could also be traced back to a silyl intermediate **22**. The vinyl iodide could be readily synthesized from ketone, and ketone **23** would be easily produced by a silyl Michael addition from chiral enone **24**.

Scheme 3-2: Retrosynthetic analysis of *paralianone D*

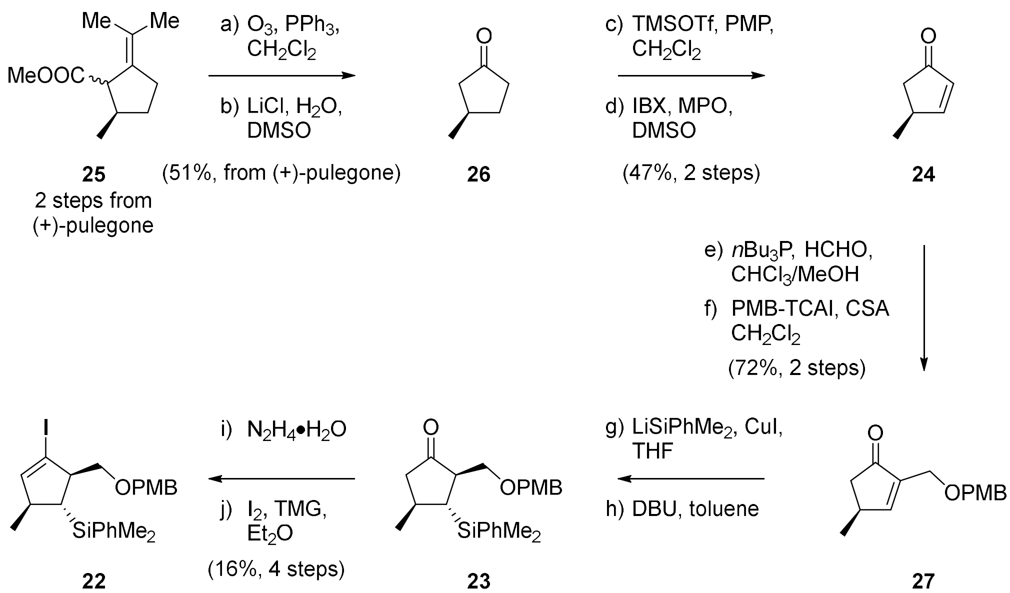


3.2.2 Synthesis of west fragment

We started the synthesis from chiral ketone **26**. Though commercially available, we also developed a synthesis of **26** due to its cost ($ 96/g from Sigma-Aldrich). The chiral compound **25** was readily prepared on a decagram scale from cheap commercially available natural product, *(+)-*

pulegone ($ 1.24/g from Sigma-Aldrich), by bromination then one-pot Favorskii rearrangement and elimination (see experimental section for detailed procedures).[8] Ozonolysis cleavage of the alkene[9] followed by decarboxylation of the resulting keto-ester provided chiral ketone **26**. Selective formation of silyl enol ether with hindered base 1,2,2,6,6-pentamethylpiperidine (PMP)[10] followed by IBX oxidation[11] would provide enone **24** in moderate yield. (Scheme 3-3)

Scheme 3-3: Synthesis of west fragment[a]



a. reaction conditions: (a) O_3, CH_2Cl_2, -78 °C, then PPh_3 (1.1 equiv), -78 °C - 23 °C, 12 h; (b) LiCl (2.0 equiv), DMSO/H_2O (200:1), 120 °C, 7 h; (c) PMP (1,2,2,6,6-pentamethylpiperidine, 1.2 equiv), TMSOTf (1.1 equiv), CH_2Cl_2, -78 °C, 8 h; (d) IBX (2.0 equiv), MPO (1.3 equiv), DMSO, 23 °C, 3 h; (e) *n*Bu_3P (10 mol%) , HCHO (37% in H_2O, 2.0 equiv), $CHCl_3$/MeOH (3:2), 0 °C, 1 h; (f) PMB-TCAI (O-(4-methoxybenzyl)-trichloroacetimidate, 3.0 equiv), CSA (10 mol%), CH_2Cl_2, 0 °C - 23 °C, 24 h; (g) $LiSiPhMe_2$ (2.6 equiv), CuI (1.3 equiv), THF, -78 °C, 15 min; (h) DBU (2.0 equiv), toluene, 23 °C, 12 h; (i) N_2H_4•H_2O, neat, 120 °C, 8 h; (j) I_2 (1.1 equiv), TMG (1,1,3,3-tetramethylguanidine, 6.0 equiv), Et_2O, 23 °C, 10 h, then 45 °C, 2 h, then neat, 3 h.

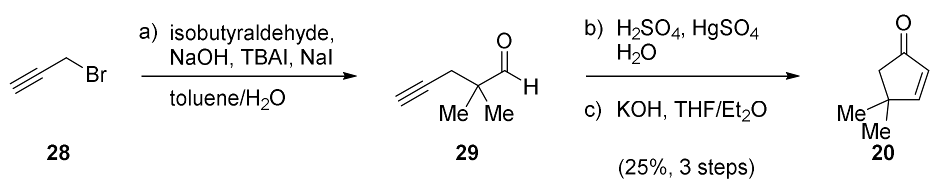
Starting from **24**, we introduced the hydroxyl group by the Baylis–Hillman reaction with formalin.[12] The free hydroxyl group should be protected before following silyl Michael addition, but all silyl ether protection groups were proved to be incompatible with the strongly basic lithium reagent, leading to decomposition in the next step. After screening we found that PMB was a good protection group in this stage, which could be installed easily under acidic conditions with PMB-

TCAI[13]. The silyl Michael addition with CuI[14] worked well on the PMB protected intermediate **27** to form a pair of inseparable diastereomers, which could be epimerized to the desired diastereomer **23** by DBU treatment. Ketone **23** could be transferred to iodide **24** in 2 steps by Prof. Barton's methodology in moderate yield.[15] (Scheme 3-3)

3.2.3 To Pd-catalyzed cascade

To synthesize the precursor of the key step in the Pd-catalyzed cyclization cascade, we started from commercially available enone **20**. However as **20** is expensive ($ 540/g from Sigma-Aldrich), we synthesized **20** on a decagram scale in our lab. Many known procedures[16] turned out to be difficult to handle or have low yields in large scale, so we developed a sequence that required only one purification and no column. Propargyl aldehyde **29** could be synthesized via phase transfer catalysis.[17] The neutralized crude product of **29**, without further purification, could be hydrated to form a keto-aldehyde,[18] followed by intramolecular aldol condensation and distillation to provide desired enone **20**.[16a] (Scheme 3-4)

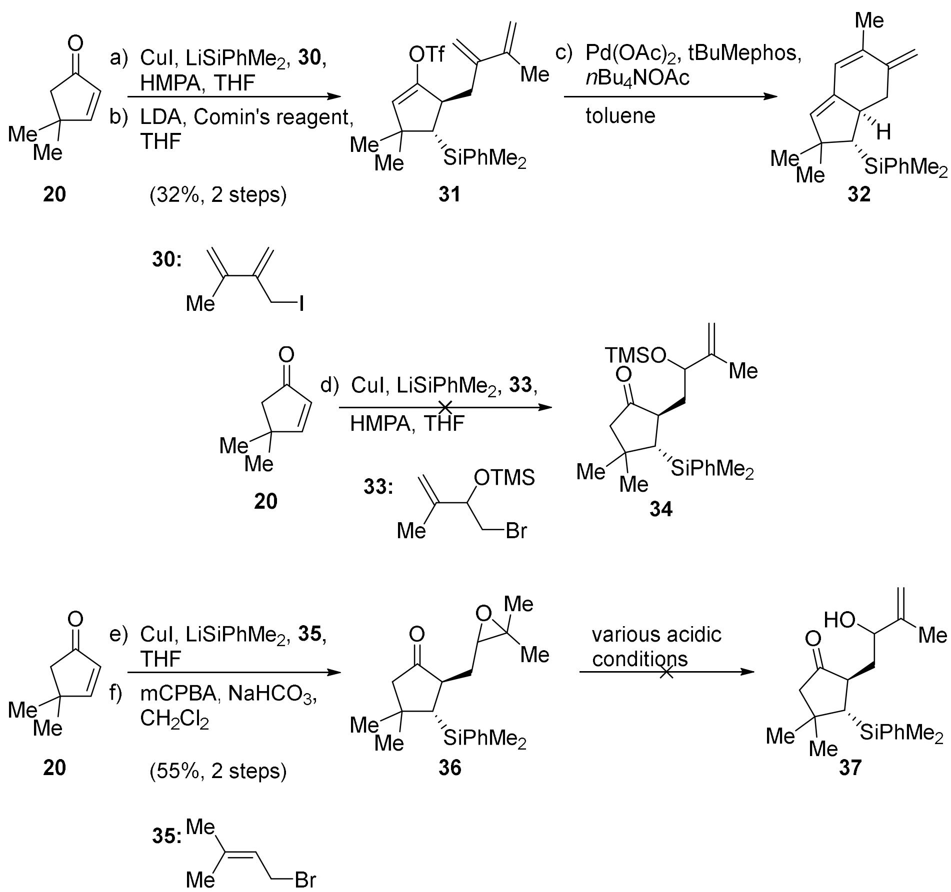
Scheme 3-4: Synthesis of enone 20[a]



a. reaction conditions: (a) isobutyraldehyde (2.0 equiv), NaOH (2.0 equiv), NaI (10 mol%), TBAI (2 mol%), toluene/H_2O (2:1), 50 °C, 12 h; (b) H_2SO_4 (ex.), $HgSO_4$ (2 mol%), H_2O, 23 °C, 12 h; (c) KOH (5% in H_2O), THF/Et_2O (1:4), 45 °C, 12 h.

With abundant supply of **20**, we went on to explore an optimized route for the Pd-catalyzed cascade. The first trial started with conjugated diene side chain. After a one-pot Michael addition and allylation of **20**, using LDA as a base, triflate **31** could be formed with desired selectivity (KHMDS provided the undesired regioisomer). When **31** was treated with Pd-catalyzed cascade condition, only a triene, tentatively assigned as **32**, was observed. We proposed that **32** was the product of β-H elimination of the allyl Pd(II) intermediate. (Scheme 3-5)

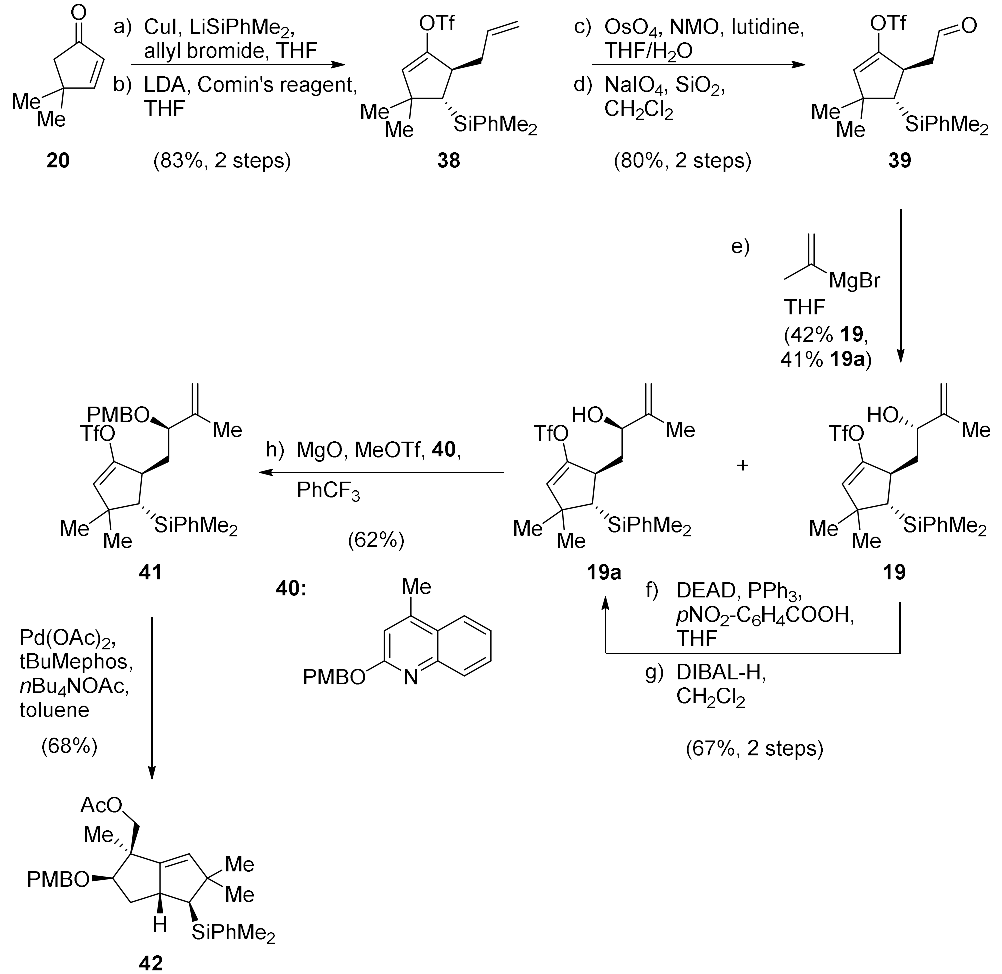
Scheme 3-5: Failed attempts on Pd-catalyzed cascade[a]



a. reaction conditions: (a) CuI (1.0 equiv), $LiSiPhMe_2$ (2.0 equiv), THF, -78 °C, 20 min, then **30** (1.5 equiv), HMPA (2.5 equiv), -78 °C - 23 °C, 12 h; (b) LDA (4.0 equiv), Comin's reagent (3.0 equiv), THF, -78 °C, 3 h; (c) $Pd(OAc)_2$ (10 mol%), tBuMephos (15 mol%), *n*Bu_4NOAc (3.0 equiv), toluene, 90 °C, 12 h; (d) CuI (1.0 equiv), $LiSiPhMe_2$ (2.0 equiv), THF, -78 °C, 20 min, then **33** (1.5 equiv), HMPA (2.5 equiv), -78 °C - 23 °C, 12 h; (e) CuI (1.0 equiv), $LiSiPhMe_2$ (2.0 equiv), THF, -78 °C, 20 min, then **35** (1.5 equiv), -78 °C - 23 °C, 12 h; (f) mCPBA (1.2 equiv), $NaHCO_3$ (5.0 equiv), CH_2Cl_2, 0 °C.

As the conjugated diene side chain was proved to be incompatible, we proposed the allyl alcohol side chain instead. However, alkylation with bromide **33** failed to yield any desired product. We returned to allylation. Michael addition and allylation with bromide **35** worked smoothly. Epoxidation with *m*CPBA provided **36**, on which we tried many acidic conditions for rearrangement to the desired compound **37,** with all proposed conditions failing. (Scheme 3-5)

Scheme 3-6: Roue to Pd-catalyzed cascade precursor[a]

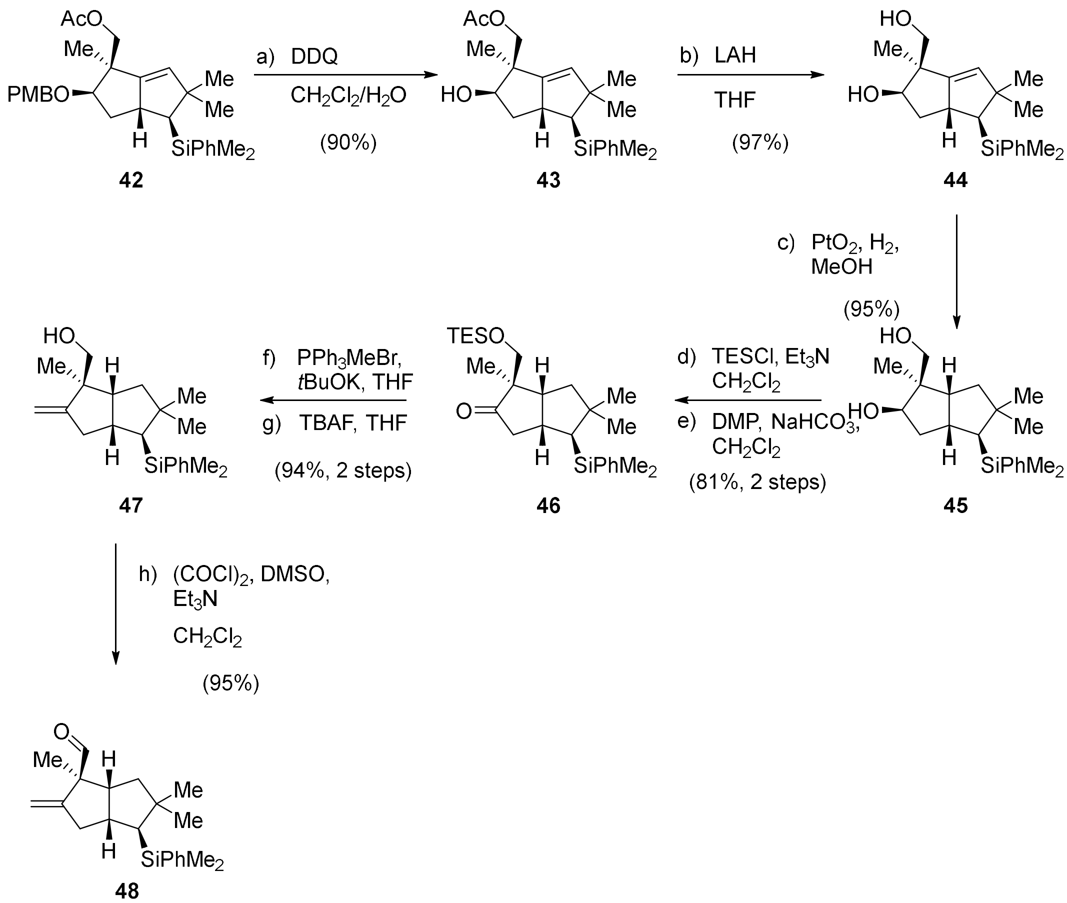


a. reaction conditions: (a) CuI (1.0 equiv), $LiSiPhMe_2$ (2.0 equiv), THF, -78 °C, 20 min, then allyl bromide (1.5 equiv), -78 °C - 23 °C, 12 h; (b) LDA (4.0 equiv), Comin's reagent (3.0 equiv), THF, -78 °C - 23 °C, 12 h; (c) OsO_4 (2 mol%), NMO (1.5 equiv), 2,6-lutidine (2.0 equiv), THF/H_2O (4:1), 0 °C - 23 °C, 12 h; (d) $NaIO_4$ (on SiO_2), CH_2Cl_2, 23 °C, 2 h; (e) isopropenylmagnesium bromide (1.5 equiv), THF, -78 °C, 2 h; (f) DEAD (2.0 equiv), PPh_3 (2.0 equiv), 4-nitrobenzoic acid (2.0 equiv), THF, 23 °C, 12 h; (g) DIBAL-H (3.5 equiv), CH_2Cl_2, 0 °C, 3 h; (h), MgO (3.0 equiv), MeOTf (3.0 equiv), **40** (3.0 equiv), $PhCF_3$, 0 °C - 23 °C, 12 h; (i) $Pd(OAc)_2$ (10 mol%), tBuMephos (15 mol%), nBu_4NOAc (3.0 equiv), toluene, 90 °C, 12 h.

We then turned to build the allyl alcohol side chain with a nucleophilic attack. Triflate **38** could be synthesized via a similar route as **31** with allyl bromide. As the vinyl triflate was electron deficient, the double bond on side chain was selectively cleaved to form aldehyde **39**. The two-step sequence with $NaIO_4$ supported on silica gel[19] provided better yield than the traditional one-pot procedure which provided a 60% yield. A Grignard attack to **39** resulted in a pair of separable diastereomers, **19** and **19a**, with 1:1 ratio (the stereochemistry was tentatively assigned). We tested the cascade reaction with **19** and **19a**. Trace amounts of the desired cyclized product was observed only with **19**, and **19a** led to total decomposition. We proposed that the free alcohol was not good in palladium chemistry possibly due to protonation of organometallic intermediates. Silyl protection groups were put on first, but no improvement was observed. PMB protection was tested next. As the triflate **19a** was sensitive to both acidic and basic conditions, we found that PMB groups could be installed via neutral conditions[20] and protected **41** worked well with Pd catalysis to form our desired bicycle **42**. However, the corresponding diastereomer of **41** from **19** resulted in low yields (<30%) in the cascade reaction. Thus, we inverted stereochemistry of **19** to **19a** via Mitsunobu reaction to push to **41**. (Scheme 3-6)

3.2.4 Synthesis of east fragment

Scheme 3-7: Synthesis of east fragment[a]

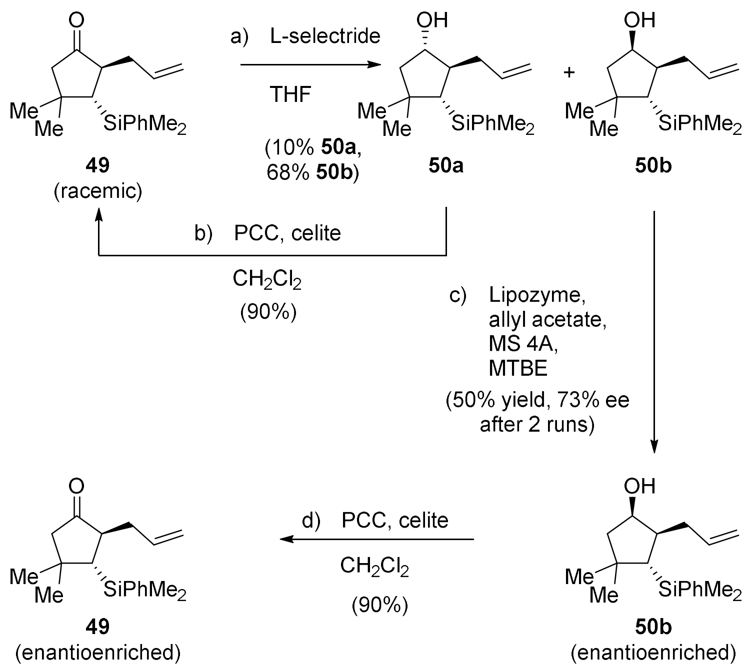


a. reaction conditions: (a) DDQ (1.5 equiv), CH_2Cl_2/H_2O (10:1), 23 °C, 1 h; (b) LAH (1.2 equiv), THF, 0 °C, 1 h; (c) PtO_2 (10 mol%), H_2 (5 atm), MeOH, 23 °C, 12 h; (d) TESCl (1.05 equiv), Et_3N (3.0 equiv), CH_2Cl_2, 0 °C - 23 °C, 12 h;(e) DMP (1.5 equiv), $NaHCO_3$, CH_2Cl_2, 0 °C - 23 °C, 3 h; (f) PPh_3MeBr (5.0 equiv), *t*BuOK (4.0 equiv), THF, 23 °C, 6 h; (g) TBAF (1.1 equiv), THF, 0 °C, 2 h; (h) $(COCl)_2$ (10 equiv), DMSO (20 equiv), CH_2Cl_2, -78 °C, 3 h, then Et_3N (30 equiv), 2 h.

With the success on the Pd-catalyzed cascade key step, we continued to the desired east fragment. The alkene in **42** was extremely hindered such that both PMB and acetate groups had to be removed to get diol **44** before hydrogenation of the double bond to provide reasonable conversion. The hydrogenation of **44** only worked under elevated pressure, 5 atm, and with PtO_2 as catalyst, with 95% yield. To selectively protect the primary alcohol, we treated **45** with small excess amount of TESCl, and followed with a DMP oxidation to provide **46**. Then via a Wittig reaction, deprotection followed by Swern oxidation with large excess amount of reagents, we could synthesize the east fragment **48**.

3.2.5 Route to enantioenriched intermediates

Scheme 3-8: Resolution of ketone 49[a]



a. reaction conditions: (a) L-selectride (1.5 equiv), THF, -78 °C - 0 °C, 2 h; (b) PCC (1.5 equiv), celite, CH_2Cl_2, 23 °C, 1.5 h; (c) Lipozyme, MS 4A, allyl acetate (5.0 equiv), MTBE, 50 °C, 18 h. (d) PCC (1.5 equiv), celite, CH_2Cl_2, 23 °C, 1.5 h.

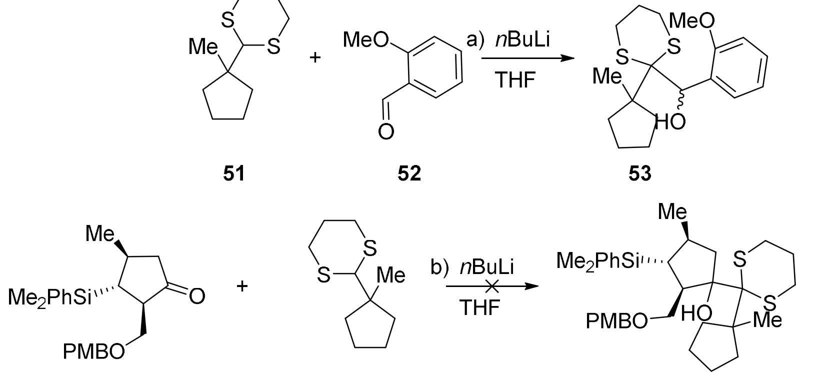
To achieve asymmetric synthesis, with the enantioenriched west fragment, we needed to synthesize the east fragment asymmetrically. Prof. Hoveyda reported a methodology of asymmetrical silyl addition on **20** to provide **49**,[21] which we succeeded on a 0.1 mmol scale (60% yield, 92% e.e.), but failed to reproduce on larger scales. For a better supply of material, we chose to do resolution on the racemic **49**. After extensive screening including CBS kinetic resolution,[22] chiral sulfinamide resolution,[23] we finally found that **49** could be selectively reduced by L-selectride to corresponding alcohol **50b,** while **50a** could be oxidized to recover ketone **49**. For resolution of **50b**, many enzymes including Lipase and Novozyme® 435 were tested. Finally, Lipozyme® was found to be the good enzyme to resolute **50b**[24] to provide desired enantiomer with 73% e.e. after 2 runs, and **49** by following PCC oxidation. By this process we could go on to synthesize enantioenriched **48** for further study on final B ring closure. (Scheme 3-8)

3.2.6 Model study on B ring formation

To construct the B ring, the first step would be a nucleophilic attack to couple the east and west fragments. As the reaction would be challenging due to hindrance, we tested a series of conditions with model compounds to explore possible solutions. The first attempt was the umpolung Corey-Seebach reaction.[25] Model dithiane **51** could attack aldehyde **52** with *n*BuLi, but on the real hindered west fragment **23**, the dithiane attack did not result in any of the desired adduct. As the formation of continuous quaternary centers in one step was difficult, we turned to use the west fragment in the nucleophilic to attack on the aldehyde of east fragment. For model aldehyde **56**, simple Grignard reaction with **55** resulted in only reduction. The Grignard reaction catalyzed by La(III) salt, however, provided adduct **57** in moderate yield.[26] But with real west fragment **58**, again no desired product was observed, only decomposition. Vinyl lithium reagents led to comparable results, working well with simple compound **60** but not real fragment **22**. We separated reduced product **63**, indicating that Li species did form but no nucleophilic attack happened. Finally, we tried the Nozaki–Hiyama–Kishi reaction.[27] To our delight, we separated the desired adduct **64** with real fragment **22** and benzaldehyde. (Scheme 3-9)

Scheme 3-9: Model study on nucleophilic attack[a]

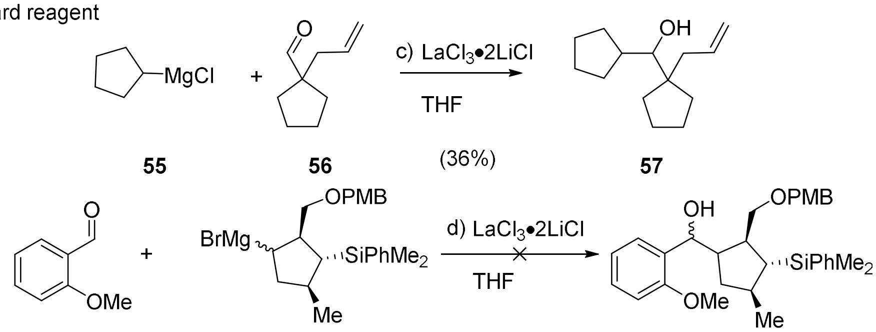
a) Dithiane



51 52 53

23 51 54

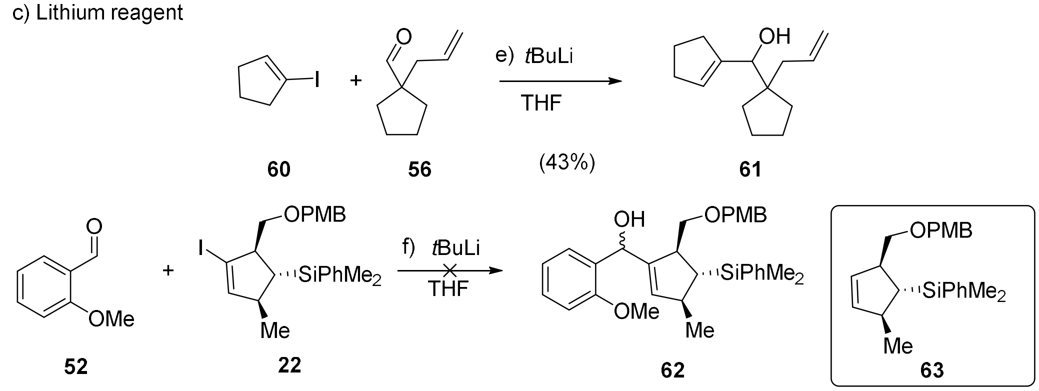
b) Grignard reagent



55 56 57

52 58 59

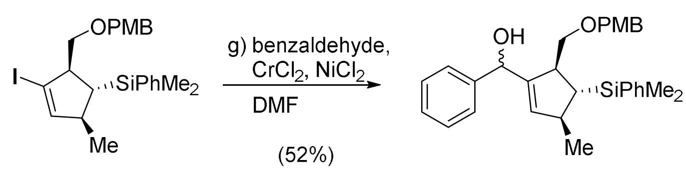
c) Lithium reagent



60 56 61

52 22 62 63

d) NHK reaction

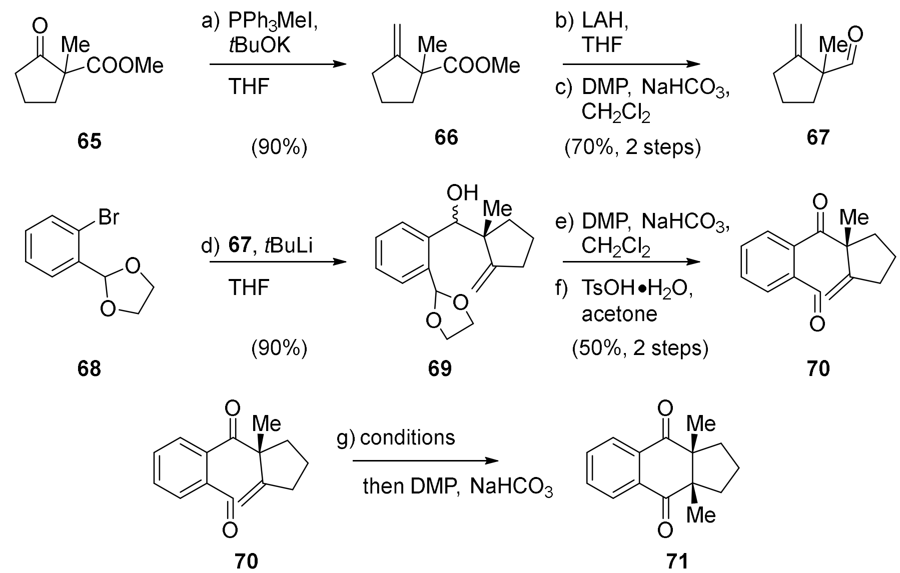


22 64

a. reaction conditions: (a) **51** (1.0 equiv), **52** (1.2 equiv), *n*BuLi (2.0 equiv), THF, 0 °C - 23 °C, 12 h; (b) **51** (1.0 equiv), **23** (1.2 equiv), *n*BuLi (2.0 equiv), THF, 0 °C - 23 °C, 12 h; (c) **56** (1.0 equiv), **55** (1.2 equiv), $LaCl_3 \cdot 2LiCl$ (1.0 equiv), THF, 0 °C - 23 °C, 12 h; (d) **52** (1.0 equiv), **58** (2.0 equiv), $LaCl_3 \cdot 2LiCl$ (1.0 equiv), THF, 0 °C - 23 °C, 12 h; (e) **56** (1.0 equiv), **60** (1.2 equiv), *t*BuLi (2.5 equiv), THF, -78 °C, 1 h; (f) **22** (1.0 equiv), **52** (2.0 equiv), *t*BuLi (2.0 equiv), THF, -78 °C - 0 °C, 1 h; (g) **22** (1.3 equiv), benzaldehyde (1.0 equiv), $CrCl_2$ (7.0 equiv), $NiCl_2$ (5 mol%), DMF, 23 °C, 12 h.

We continued to explore on the radical cyclization for B ring closure. For a model compound with hindrance, we synthesized aldehyde **67** with quaternary center in 3 steps from keto-ester **65**. Then **67** was coupled with aryl bromide **68**[28] to form model compound **70** after oxidation and deprotection. (Scheme 3-10)

Scheme 3-10: Benzaldehyde model study of radical cyclization[a]



entry	conditions	yield[b]
1	SmI_2 (2.5 equiv), tBuOH (2.5 equiv), THF, -78 °C	<10%
2	$Fe(acac)_3$ (1.0 equiv), $PhSiH_3$ (2.5 equiv), iPrOH (0.25M), 60 °C	32%
3	$Fe(acac)_3$ (1.0 equiv), $PhSiH_2(OiPr)$ (2.5 equiv), iPrOH (0.25M), 60 °C	58%
4	$Mn(dpm)_3$ (1.0 equiv), $PhSiH_2(OiPr)$ (2.5 equiv), iPrOH (0.25M), 23 °C	62%
5	**$Mn(dpm)_3$ (1.0 equiv), $PhSiH_2(OiPr)$ (2.5 equiv), iPrOH (0.1M), 23 °C**	**66%**
6	$Co(dpm)_2$ (1.0 equiv), $PhSiH_2(OiPr)$ (2.5 equiv), TBHP (1.5 equiv), iPrOH (0.25M), 23 °C	31%[c]

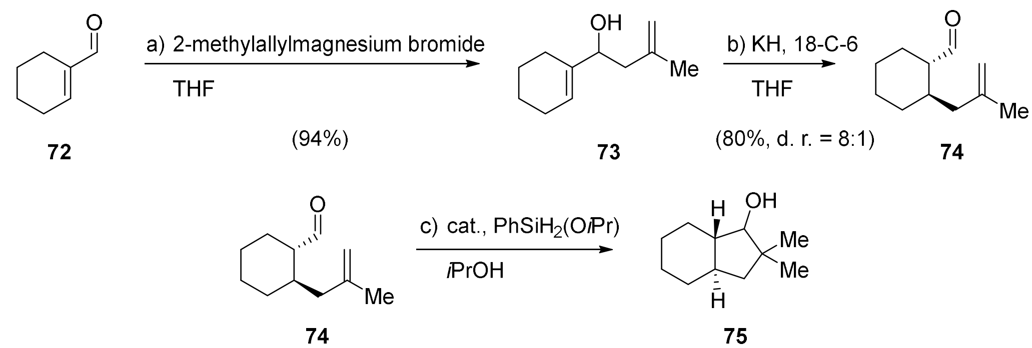
a. reaction conditions: (a) PPh_3MeI (1.3 equiv), tBuOK (1.2 equiv), THF, 70 °C, 2 h; (b) LAH (1.0 equiv), THF, 23 °C, 90 min; (c) DMP (1.3 equiv), $NaHCO_3$, CH_2Cl_2, 0 °C - 23 °C, 1 h; (d) **67** (1.0 equiv), **68** (1.5 equiv), tBuLi (3.0 equiv), THF, -78 °C - 23 °C, 12 h; (e) DMP (1.3 equiv), $NaHCO_3$, CH_2Cl_2, 23 °C, 1 h; (f) $TsOH \cdot H_2O$ (10 mol%), acetone, 23 °C, 18 h.

b. isolated yield

c. provide **71** without DMP oxidation, NMR yield

We tried a series of conditions on **70** for cyclization. To eliminate diastereomers for a better NMR to compare yields, the cyclized product was oxidized by DMP. SmI_2 reductive coupling provided only trace amounts of product (entry 1). We then turned to Mukaiyama radical conditions reported by Prof. Bonjoch and Prof. Bradshaw et al.,[29] which provided 32% yield (entry 2). Using Shenvi's silane[30] instead of phenyl silane, a much better yield 58% could be achieved (entry 3). Further screening showed that Mn(dpm)$_3$ was a better catalyst (entry 4), and the yield was slightly better in lower concentration (entry 5). The cobalt catalyst directly resulted in diketone **71** without further oxidation, possibly because of Co(IV) as an oxidant, but the yield was lower (entry 6). (Scheme 3-10)

Scheme 3-11: Alkyl aldehyde model of radical cyclization[a]



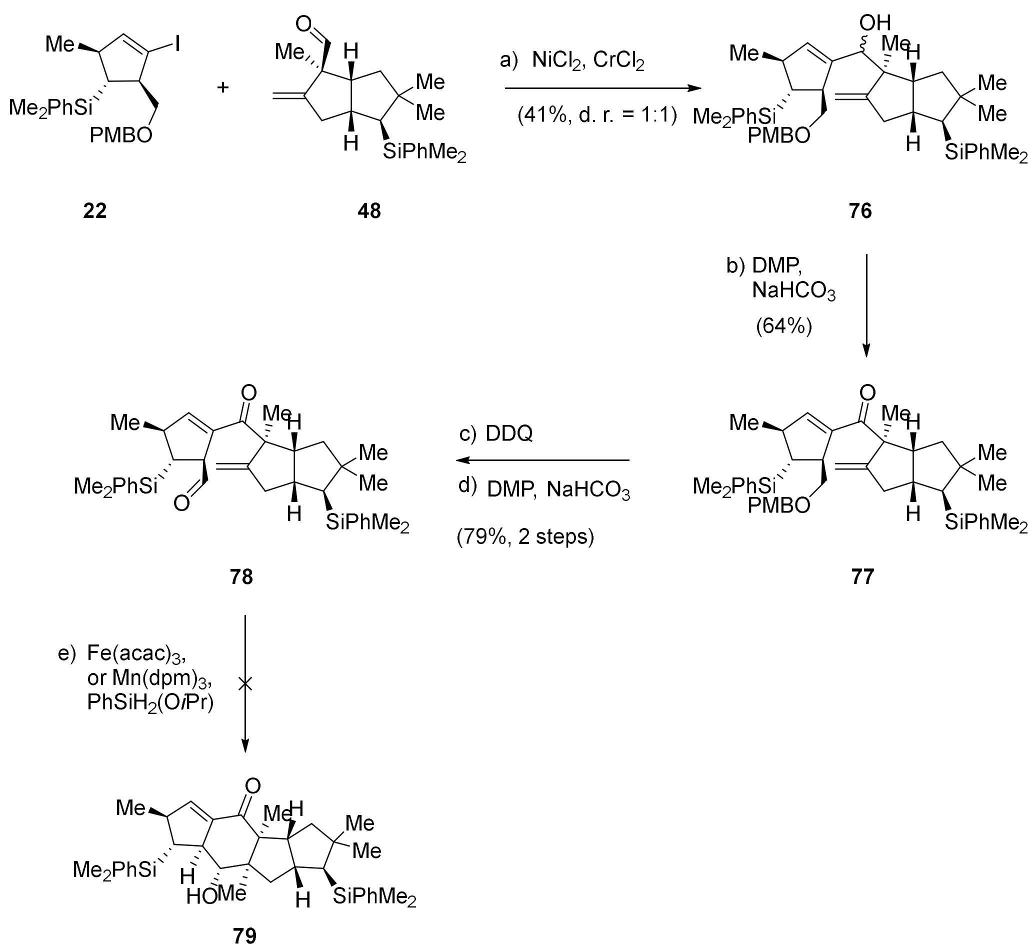
entry	catalyst	yield[b]
1	**$Fe(acac)_3$ (1.0 equiv)**	**60%**
2	$Co(dpm)_2$ (1.0 equiv), TBHP (1.5 equiv)	trace
3	$Co(dpm)_2$ (10 mol%), TBHP (1.0 equiv)	18%
4	$Mn(dpm)_3$ (1.0 equiv)	45%

a. reaction conditions: (a) 2-methylallylmagnesium bromide (1.5 equiv), THF, 0 °C, 1 h; (b) KH (4.0 equiv), 18-C-6 (4.0 equiv), THF, 23 °C, 8 h; (c) cat., $PhSiH_2(O\textit{i}Pr)$ (2.5 equiv), *i*PrOH, 23 °C, 12 h
b. isolated yield

As the real system would be alkyl aldehyde, we also tested the Mukaiyama reaction on model **74**, which could be synthesized from **72** by Grignard addition and oxy-Cope rearrangement. Different conditions of Mukaiyama radical reaction were tested on aldehyde **74**. A single diastereomer **75** was formed and Fe(acac)$_3$ was found to be the best catalyst (entry 1). (Scheme 3-11)

3.2.7 Trial of B ring formation

Scheme 3-12: Trial of B ring formation[a]



a. reaction conditions: a) **48** (1.0 equiv), **22** (3.0 equiv), $NiCl_2$ (1 mol%), $CrCl_2$ (7.0 equiv), DMF, 40 °C, 48 h; (b) DMP (2.5 equiv), $NaHCO_3$, CH_2Cl_2, 23 °C, 3 h; (c) DDQ (1.5 equiv), CH_2Cl_2/H_2O, 23 °C, 1 h; (d) DMP (1.5 equiv), $NaHCO_3$, CH_2Cl_2, 23 °C, 1 h; (e) $Fe(acac)_3$ (1.0 equiv) or $Mn(dpm)_3$ (1.0 equiv), $PhSiH_2(O\textit{i}Pr)$ (2.5 equiv), *i*PrOH, 23 °C, 3 h.

With the success of model study, we turned to our real fragments **22** and **48**. The described Nozaki–Hiyama–Kishi reaction condition for **64** worked on them, however the conversion was very low. After screening, we found the optimized condition. With only 1 mol% $NiCl_2$ and higher concentration, we could separate 41% yield of the desired coupling product **76** as a pair of diastereomers (d. r. = 1:1). Then the two diastereomers was oxidized to one ketone **77**. Further deprotection and oxidation provided aldehyde **78**. Unfortunately, trial of Mukaiyama radical cyclization on **78** resulted in only decomposition. It might be because that such HAT conditions could also react with enone[31] and undesired transformation could happen.

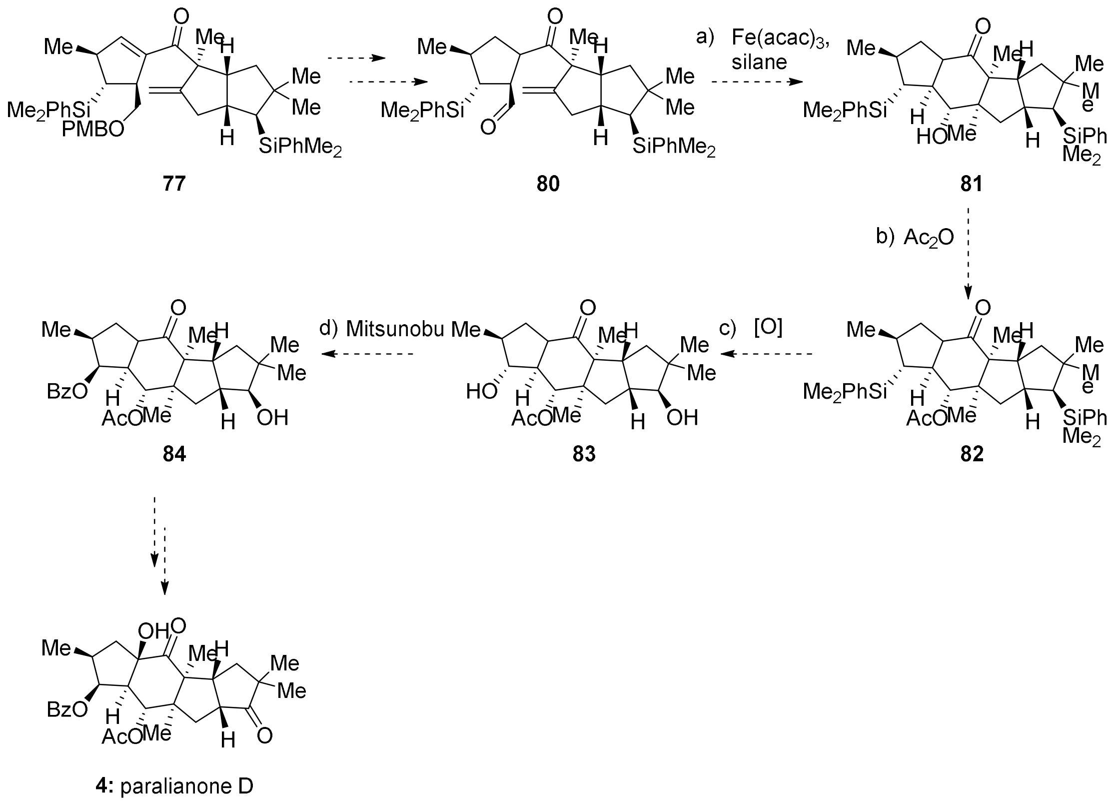
3.3 Summary and outlook

Based on our cascade methodology, we designed a synthetic route towards natural product *paralianone D*. We synthesized the west fragment in 8 steps form commercial chiral compound **26**. The east fragment was synthesized with our methodology in 18 steps from commercial enone **20**. To achieve enantioenriched east fragment, we used enzymatic resolution.

In model study, we succeeded in the Nozaki–Hiyama–Kishi coupling of two fragments and discovered an unprecedented Mukaiyama type radical cyclization of alkene and aldehyde. The Nozaki–Hiyama–Kishi reaction combined two fragments in the real system. However, the radical cyclization was not successful so far. We plan to try on other substrate without enone moiety for the cyclization, such as a 1,4-reduction to synthesis intermediate **80** prior to cyclization. Other reductive coupling like SmI_2 can also be considered. After the cyclization, we will build the whole skeleton of *paralianone D* (**4**), and a series of oxidation reactions and Mitsunobu reaction will lead to the target natural product. (Scheme 3-13)

The final steps of west fragment preparation also need optimization, due to very low yields and low purity. Prof. Reisman's vinyl iodide synthesis[32] may be a possible choice.

Scheme 3-13 Future plan

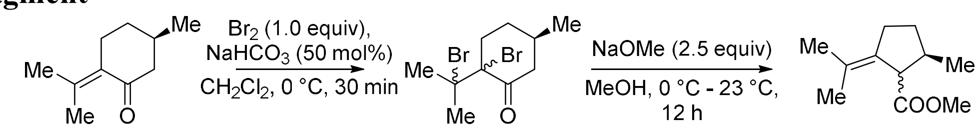


3.4 Experimental section

General Procedures. All reactions were conducted under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), toluene, dimethylformamide (DMF), diethyl ether (Et_2O) and dichloromethane (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^1H and ^{13}C NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. SiliCycle silica gel plates silica gel plates (60F-254) using UV light as visualizing agent, and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents.

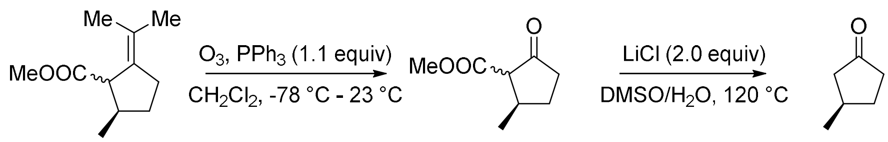
SiliCycle silica gel (60, academic grade, particle size 0.040–0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography separations were carried out on 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker 500 MHz and 400 MHz instruments and calibrated using residual undeuterated solvent as an internal reference ($\delta(CDCl_3)$ = 7.26 for ^{1}H NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet.

West Fragment



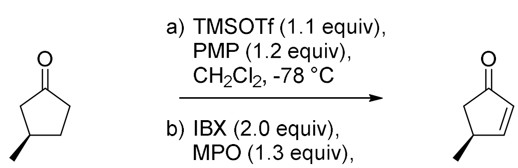
S1: (+)-pulegone **S2** **25**

Ester 25. To a solution of **S1** (30.4 g, 0.20 mol, 1.0 equiv) and $NaHCO_3$ (8.4 g, 0.10 mol, 50 mol%) in CH_2Cl_2 (200 mL) at 0 °C was added Br_2 (10.5 mL, 0.20 mol, 1.0 equiv) dropwise over the course of 30 min. The mixture was filtered, and this solution containing **S2** was added to a solution of NaOMe (27 g, 0.50 mol, 2.5 equiv) in MeOH (200 mL) at 0 °C. The resulting mixture was slowly warmed to 23 °C and stirred at that temperature for 12 h. Upon completion, the reaction was quenched by the addition of HCl solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (3× 200 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. To remove ketone impurities, the yellow residue was dissolved in H_2O (200 mL). NaOAc (15 g) and semicarbazide hydrochloride (15 g) was added. EtOH was added till the solution was clean. Then the mixture was refluxed for 2 h and stirred for 12 h at 23 °C. The mixture was extracted by hexane (3× 200 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The resultant residue was purified by column chromatography (hexanes: EtOAc = 20:1→10:1) to provide ester **25** (24 g). All data were identical with literature report.[8]



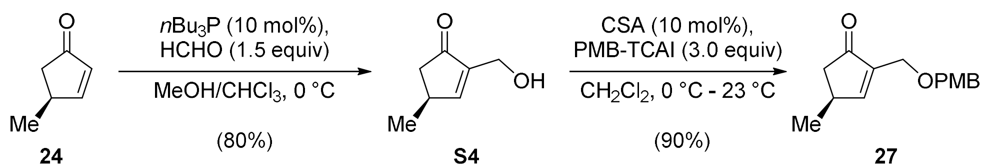
25 (57% from (+)-pulegone) **S3** (90%) **26**

Ketone 26. To a solution of **25** (29.1 g, 0.16 mol, 1.0 equiv) in CH_2Cl_2 (200 mL) at -78 °C was bubbled O_3 for 2 h until the solution turned blue, then PPh_3 (47 g, 0.18 mol, 1.1 equiv) was added. The solution was slowly warmed to 23 °C and stirred for 12 h. Then it was concentrated and diluted by hexane. The resulted mixture was filtered through a pad of silica gel (hexanes: EtOAc = 3:1). The filtrate was concentrated, and the resultant residue was purified by column chromatography (hexanes: EtOAc = 30:1→20:1→3:1→2:1) to provide keto-ester **S3** (21.95 g, 57% from **S1**). All data were identical with literature report.[9] To a solution of **S3** (21.8 g, 0.14 mol, 1.0 equiv) in DMSO (200 mL) and H_2O (10 mL) was added LiCl (12 g, 0.28 mol, 2.0 equiv). The mixture was heated to 120 °C and stirred at that temperature for 12 h. Upon completion, the reaction contents were cooled to 23 °C, diluted with water and extracted with Et_2O (2 × 200 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated (40 °C, 500 mm Hg). The resultant residue was purified by column chromatography (pentanes: Et_2O = 1:1) to provide ketone **26** (12.3 g, 90%). All data were identical with commercial sample from Sigma-Aldrich.

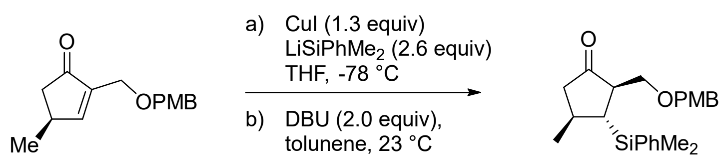


26 (47%, 2 steps) **24**

Enone 24. To a solution of **26** (3.92 g, 40 mmol, 1.0 equiv) in CH_2Cl_2 (120 ml) at -78 °C was added PMP (7.44g, 48 mmol. 1.2 equiv) then TMSOTf (7.94 mL, 44 mmol, 1.1 equiv). The resulted mixture was stirred at that temperature for 8 h. Upon completion, the reaction was quenched by addition of $NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The organic layer was concentrated (40 °C, 500 mmHg). The residue was used in the next step without further purification. The IBX oxidation was conducted via reported procedure.[11] The resulted mixture was purified by column chromatography (pentanes: Et_2O = 3:1→2:1) to provide enone **24** (1.8 g, 47% over 2 steps) as a pale-yellow oil. **24**: R_f = 0.31 (silica gel, hexanes:Et_2O, 2:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 5.6 Hz, 2.5 Hz, 1 H), 6.12 (dd, *J* = 5.6 Hz, 2.1 Hz, 1 H), 3.06–2.99 (m, 1H), 2.59 (dd, *J* = 18.8 Hz, 6.4 Hz, 1 H), 1.94 (dd, *J* = 18.8 Hz, 2.2 Hz, 1 H), 1.04 (s, 3 H).

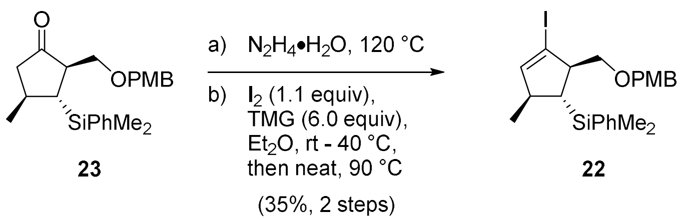


PMB ether 27. To a solution of **24** (2.97 g, 31 mmol, 1.0 equiv) and HCHO (37% in H_2O, 4.6 mL, 62 mmol, 2.0 equiv) in MeOH (60 ml) and $CHCl_3$ (60 ml) at 0 °C was added *n*Bu_3P (0.77 mL, 3.1 mmol, 10 mol%) in $CHCl_3$ (30 ml) dropwise over the course of 15 min. The mixture was stirred at that temperature for 1 h. Upon completion, the reaction was quenched by addition of water. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (5× 100 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 1:1) to provide **S4** (3.21 g, 80%) as a colorless oil. **S4**: R_f = 0.23 (silica gel, hexanes:EtOAc, 1:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (dt, *J* = 2.5 Hz, 1.3 Hz, 1 H), 4.37–4.36 (m, 2 H), 2.98–2.95 (m, 1 H), 2.68 (dd, *J* = 19.0 Hz, 6.3 Hz, 1 H), 2.02 (dd, *J* = 19.0 Hz, 2.1 Hz, 1 H), 1.21 (d, *J* = 7.2 Hz, 3 H). To a solution of **S2** (3.15 g, 25 mmol, 1.0 equiv) and PMB-TCAI (21.1 g, 75 mmol, 3.0 equiv) in CH_2Cl_2 (100 mL) at 0 °C was added CSA (0.58 g, 2.5 mmol, 10 mol%). The mixture was slowly warmed to 23 °C and stirred for 24 h. Upon completion, the reaction was quenched by addition of $NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2× 100 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was diluted by hexane (100 mL) and filtered to remove CCl_3CONH_2. The filtrate was concentrated and purified by column chromatography (hexanes:EtOAc = 10:1→5:1) to provide **27** (5.53 g, 90%) as a pale-yellow oil. **27**: R_f = 0.35 (silica gel, hexanes:EtOAc, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.47 (m, 1 H), 7.28–7.26 (m, 2 H), 6.9–6.87 (m, 2 H), 4.50 (s, 2H), 4.16–4.15 (m, 2 H), 3.81 (s, 3 H), 2.95–2.93 (m, 1 H), 2.66 (dd, J = 18.9 Hz, 6.3 Hz, 1 H), 2.00 (dd, J = 18.9 Hz, 2.1 Hz, 1 H), 1.19 (d, J = 7.2 Hz, 3 H).



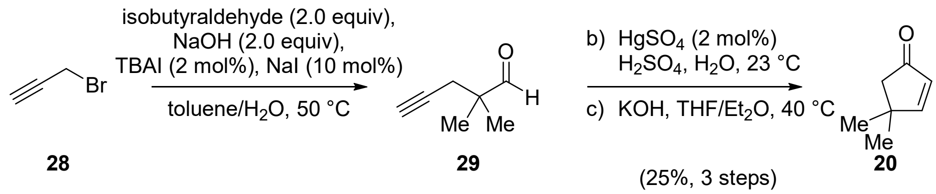
27 23

Ketone 23. To a suspension of CuI (2.72 g, 14.3 mmol, 1.3 equiv) in THF (50 mL) at 0 °C was added $LiSiPhMe_2$ (1.0 M in THF, 28.6 mL, 28.6 mmol, 2.6 equiv). The mixture was stirred at that temperature for 30 min. Then the mixture was cooled to -78 °C. A solution of **27** (2.71 g, 11 mmol, 1.0 equiv) in THF (30 mL) was added slowly over the course of 5 min. The mixture was stirred for additional 15 min. The reaction was quenched by addition of NH_4Cl solution. The mixture was warmed to 23 °C and poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2× 100 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 10:1) to provide a mixture of diastereomers (2.05 g, 49%) with inseparable $PhMe_2SiOH$. The diastereomers were dissolved in toluene (40 mL) and DBU (1.64 mL, 11 mmol, 2.0 equiv) was added at 23 °C. The mixture was stirred at that temperature for 12 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2× 50 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 10:1) to provide **23** (1.89 g, 45%) as a yellow oil with inseparable $PhMe_2SiOH$. **23:** R_f = 0.33 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2 H), 7.36–7.32 (m, 3 H), 7.16 (d, J = 8.7 Hz, 2 H), 6.86 (d, J = 8.7 Hz, 2 H), 4.25 (dd, J = 39.8 Hz, 11.8 Hz, 2 H), 3.81 (s, 3 H), 3.62 (dd, J = 9.1 Hz, 2.9 Hz, 1 H), 3.05 (dd, J = 9.2 Hz, 3.4 Hz, 1 H), 2.37 (dd, J = 17.4 Hz, 6.4 Hz, 1 H), 2.11–2.02 (m, 2 H), 1.87 (dd, J = 17.5 Hz, 10.9 Hz, 1 H), 1.47 (d, J = 11.1 Hz, 1 H), 1.06 (d, J = 6.4 Hz, 3 H), 0.34 (s, 3 H), 0.32 (s, 3 H).

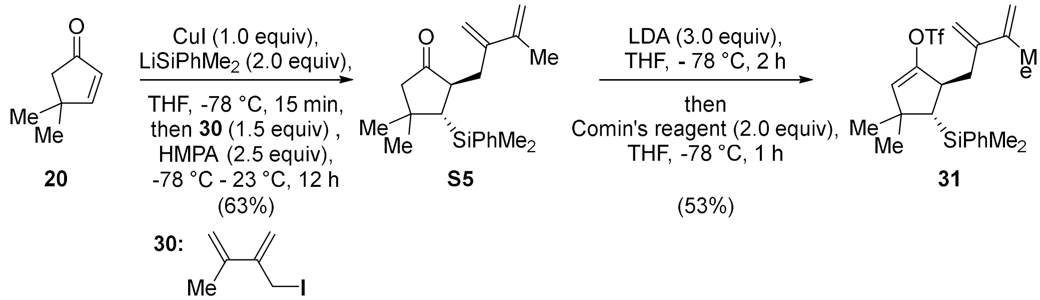


Iodide 22. **22** (0.96 g, 35%) was prepared via reported procedure[15] from **23** (2.13 g, 5.6 mmol) **22:** R_f = 0.58 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2 H), 7.36–7.33 (m, 3 H), 7.24–7.22 (m , 2 H), 6.88–6.86 (m, 2 H), 6.01 (t, J = 2.25 Hz, 1 H), 4.39 (dd, J = 31.1 Hz, 11.8 Hz, 2 H), 3.81 (s, 3 H), 3.40 (dd, J = 9.6 Hz, 4.5 Hz, 1 H), 3.17 (dd, J = 9.6 Hz, 3.6 Hz, 1 H), 2.77–2.74 (m, 1 H), 2.66–2.63 (m, 1 H), 1.28 (dd, J = 6.3 Hz, 5.7 Hz, 1 H), 0.96 (d, J = 6.8 Hz, 3 H), 0.25 (s, 3 H), 0.24 (s, 3 H).

East fragment

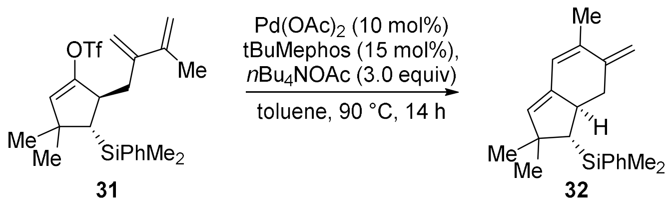


Enone 20. To a vigorously stirred solution of NaOH (96 g, 2.4 mol, 2.0 equiv), TBAI (8.8 g, 24 mmol, 2 mol%) and NaI (18 g, 0.12 mol, 10 mol%) in toluene (200 mL) and H_2O (150 mL) at 50 °C was added a solution of isobutyraldehyde (219 mL, 2.4 mol, 2.0 equiv) and **28** (132 mL, 1.2 mol, 1.0 equiv) in toluene (100 mL) slowly over the course of 5 h. The stirring was continued at that temperature for 18 h. Upon completion, the reaction was quenched and neutralized by HCl solution. The mixture was poured into a separatory funnel and the layers were separated. The organic layer was directly poured into a flask filled with H_2SO_4 (0.7 M in H_2O, 300 mL) and $HgSO_4$ (4.1 g, 14 mmol). And the mixture was stirred at 23 °C for 12 h. Upon completion, the reaction was quenched and neutralized by $NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2× 200 mL). The combined organic layer was concentrated. The residue was added to a flask with KOH (5 % in H_2O, 250 mL), THF (80 mL) and Et_2O (300 mL). The mixture was heated to 40 °C and refluxed at that temperature for 18 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by Et_2O (200 mL). The mixture was distilled at 95 °C under atmosphere pressure to remove solvents. And following reduced pressure distillation (130 °C, 60-30 mmHg) provided **20** (33 g, 25% over 3 steps) as a yellow oil. All data of **20** were identical with commercial sample from Sigma-Aldrich.

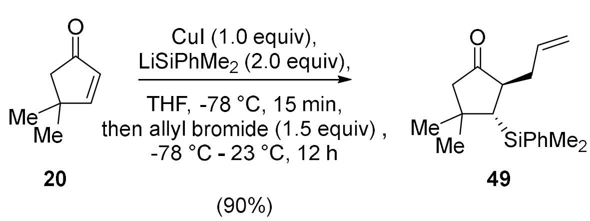


Triflate 31: To a suspension of CuI (190 mg, 1.0 mmol, 1.0 equiv) in THF (5 mL) was added $LiPhSiMe_2$ (1.0 M in THF, 2 mL, 2.0 equiv) and the mixture was stirred at that temperature for 30 min. Then it was cooled to -78 ℃ and a solution of **20** (110 mg, 1.0 mmol, 1.0 equiv) in THF (3 mL) was added over the course of 5 min. The mixture was stirred at that temperature for 15 min. HMPA (0.4 mL) and **30** (312 mg, 1.5 mmol, 1.5 equiv) was added and the mixture was slowly warmed to 23 ℃. The stirring was continued for 12 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was warmed to 23 ℃ and poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2× 10 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 40:1) to provide **S5** (205 mg, 63%) as a pale-yellow oil. **S5:** R_f = 0.41 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2 H), 7.35–7.33 (m, 3 H), 5.07 (s, 1 H), 4.88 (s, 1 H), 4.84 (s, 1 H), 4.70 (s, 1 H), 2.55–2.51 (m, 1 H), 2.33 (ddd, J = 36.5 Hz, 14.7 Hz, 6.4 Hz, 2 H), 2.14 (d, J = 16.5 Hz, 1 H), 1.98 (dd, J = 16.7 Hz, 1.3 Hz, 1 H), 1.84 (s, 3 H), 1.45 (d, J = 9.7 Hz, 1 H), 1.11 (s, 3 H), 1.02 (s, 3 H), 0.38 (s, 3 H), 0.37 (s, 3 H). To a solution of $i$$Pr_2$NH (0.17 mL, 1.2 mmol) in THF (2 mL) at 0 ℃ was added nBuLi (2.5 M in THF, 0.4 mL, 1.0 mmol, 3.0 equiv). The mixture was stirred at that temperature for 15 min. Then the mixture was cooled to -78 ℃ and a solution of **S5** (108 mg, 0.33 mmol, 1.0 equiv) in THF (1 mL) was added. The mixture was stirred at that temperature for 2 h, and a solution of Comin's reagent (259 mg, 0.66 mmol, 2.0 equiv) in THF (1 mL) was added. The

stirring was continued at that temperature for 1 h. Upon completion, the reaction was quenched by addition of $NaHCO_3$ solution. The mixture was warmed to 23 °C and poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 5 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (Et_3N-buffered silica gel, hexanes) to provide **31** (86.1 mg, 53%) as a colorless oil. **31:** R_f = 0.69 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2 H), 7.36–7.34 (m, 3 H), 5.40 (s, 1 H), 5.13 (s, 1 H), 4.96 (s, 1 H), 4.92 (s, 1 H), 4.73 (s, 1 H), 3.12–3.08 (m, 1 H), 2.50 (d, J = 14.0 Hz, 7.1 Hz, 1 H), 2.31 (d, J = 13.9 Hz, 6.9 Hz, 1 H), 1.84 (s , 3H), 1.49 (d, J = 5.2, 1 H), 1.18 (s , 3H), 1.07 (s , 3H), 0.40 (s , 3H), 0.30 (s , 3H).

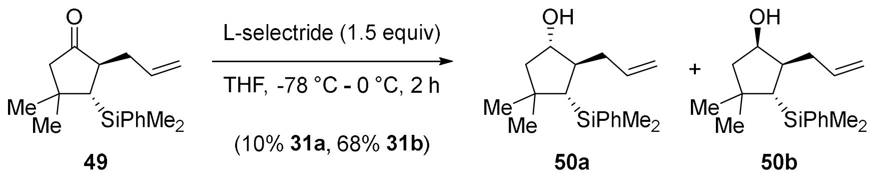


Triene 32. 31 (22.9 mg, 0.05 mmol, 1.0 equiv) was treated with standard procedure described in chapter 2. But only **32** was observed. **32:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.55 (m, 2 H), 7.36–7.34 (m, 3 H), 5.94 (s, 1 H), 5.39 (d, J = 1.8 Hz, 1 H), 4.75 (s, 1 H), 4.59 (s, 1 H), 2.86–2.80 (m, 1 H), 2.22 (dd, J = 14.1 Hz, 5.1 Hz, 1 H), 1.85 (s, 3 H), 1.83 (tt, J = 13.7 Hz, 2.6 Hz, 1 H), 1.09 (d, J = 10.6 Hz, 1 H), 1.07 (s, 3 H), 1.01 (s, 3 H), 0.43 (s, 3 H), 0.41 (s, 3 H).

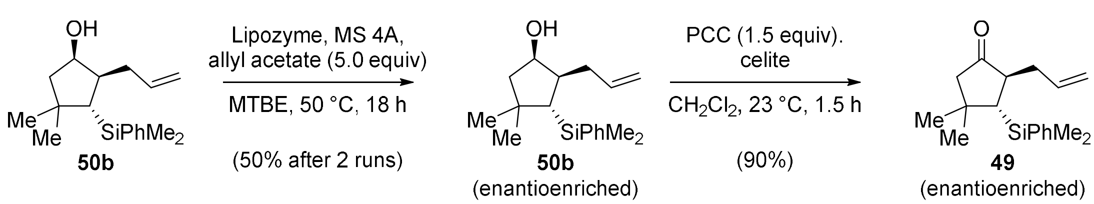


Ketone 49. 49 (53.9 g, 90%) was prepared by the procedure described for **S3** from **20** (23.1g, 0.21 mol, 1.0 equiv) as a yellow oil. **49:** R_f = 0.44 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2 H), 7.37–7.35 (m, 3 H), 5.47–5.39 (m, 1 H), 4.90 (d,

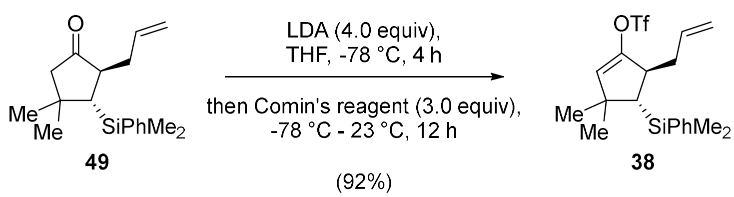
J = 10.2 Hz, 1H), 4.62 (d, J = 16.2 Hz, 1 H), 2.45–2.37 (m, 2 H), 2.01 (dd, J = 48.6 Hz, 16.4 Hz, 2 H), 1.55 (s, 3 H), 1.41 (d, J = 11.8 Hz, 1 H), 1.13 (s, 3 H), 1.01 (s, 3 H), 0.43 (s, 6 H).



Alcohol 50a and 50b. To a solution of **49** (30.1 g, 105 mmol, 1.0 equiv) in THF (200 mL) at -78 °C was added L-selectride (1.0 M in THF, 160 mL, 160 mmol, 1.5 equiv). The mixture was stirred at that temperature for 1 h. Then it was warmed to 0 °C and stirred at that temperature for 1 h. Upon completion, the react5ion was quenched by addition of NH_4Cl. The mixture was warmed to 23 °C and poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 100 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by careful column chromatography (hexanes:EtOAc = 100:1→40:1→30:1→20:1) to provide **50b** (18.1 g, 60%) as a colorless oil, and a mixture of **50a** and **50b** (5.44 g, 18%, 5:4) was collected for recovery of **49**. **50a**: R_f = 0.43 (silica gel, hexanes:EtOAc, 5:1). **50b:** R_f = 0.46 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2 H), 7.34–7.32 (m, 3 H), 5.86–5.75 (m, 1 H), 5.02–4.95 (m, 2 H), 4.25–4.21 (m, 1 H), 2.13–2.06 (m, 2 H), 1.99–1.88 (m, 1 H), 1.77 (dd, J = 13.8 Hz, 5.9 Hz, 1 H), 1.49 (d, J = 13.8 Hz, 3.9 Hz, 1 H), 1.23 (d, J = 5.2 Hz, 1 H), 1.05 (s, 3 H), 0.98 (s, 3 H), 0.37 (s, 3 H), 0.36 (s, 3 H).

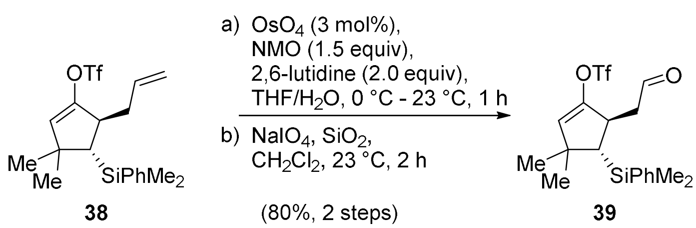


Enantioenriched 49. To a solution of **50b** (33.7 g, 117 mmol, 1.0 equiv) in *t*BuOMe (MTBE, 580 mL) at 50 °C was added Lipozyme® (11.6 g) and activated MS 4Å (104 g). Then allyl acetate (54 mL, 0.58 mol, 5.0 equiv) was added. The mixture was refluxed at that temperature for 18 h. Then it was cooled to 23 °C and filtered. The filtrate was concentrated, and the residue was purified by column chromatography (hexanes:EtOAc = 40:1) to provide enantioenriched **50b** (24.3 g). The it was put in a second run with Lipozyme® (8.4 g), activated MS 4Å (75 g) and MTBE (420 mL) for 18 h. Then the mixture was cooled to 23 °C and filtered. The filtrate was concentrated, and the residue was purified by column chromatography (hexanes:EtOAc = 40:1) to provide enantioenriched **50b** (16.8 g, 50%, 70% e. e.) as a colorless oil. To a suspension of PCC (20.4 g, 95 mmol, 1.5 equiv) and celite (40 g) in CH_2Cl_2 (400 mL) at 23 °C was added enantioenriched **50b** (18.1 g, 63 mmol, 1.0 equiv). The mixture was stirred at that temperature for 90 min. Upon completion, the mixture was diluted by hexane (400 mL) and filtered through a pad of silica gel (hexanes:EtOAc = 5:1). The filtrate was concentrated, and the residue was purified by column chromatography (hexanes:EtOAc = 10:1) to provide enantioenriched **49** (17.2 g, 90%) as a pale-yellow oil. The mixture of racemic **50a** and **50b** was treated by the same condition to recover racemic **49** (4.87 g, 90%).



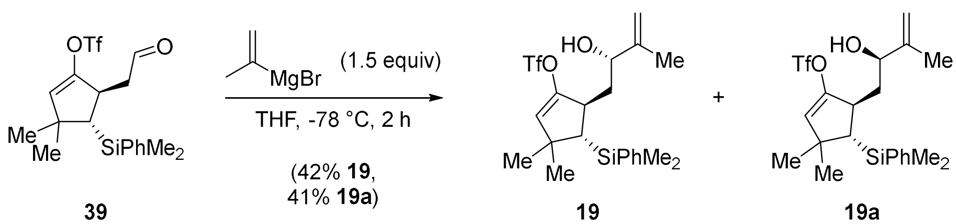
Triflate 38. To a solution of *i*Pr_2NH (19.6 mL, 0.14 mol) in THF (100 mL) at 0 °C was added *n*BuLi (2.5 M in THF, 48 mL, 0.12 mmol, 4.0 equiv). The mixture was stirred at that temperature for 15 min. Then the mixture was cooled to -78 °C and a solution of **49** (8.58 g, 30 mmol, 1.0 equiv) in THF (50 mL) was added. The mixture was stirred at that temperature for 4 h, and a solution of Comin’s reagent (35.8 g, 90 mmol, 3.0 equiv) in THF (50 mL) was added. The mixture was slowly warmed to 23 °C and stirred at that temperature for 12 h. Upon completion,

the reaction was quenched by addition of $NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 200 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was filter through a pad of Et_3N-buffered silica gel (hexanes:EtOAc = 10:1). The filtrate was concentrated, and the residue was purified by column chromatography (Et_3N-buffered silica gel, hexanes) to provide **38** (22.9 g, 92%) as a colorless oil. **38:** R_f = 0.90 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2 H), 7.37–7.35 (m, 3 H), 5.58–5.48(m, 1 H), 5.44 (d, J = 1.8 Hz, 1 H), 5.03–5.01 (m, 1 H), 4.81–4.76 (m, 1 H), 3.09–3.04 (m, 1 H), 2.24–2.17 (m, 1 H), 1.70 (ddd, J = 14.7 Hz, 8.8 Hz, 4.9 Hz, 1 H), 1.37 (d, J = 8.5 Hz, 1 H), 1.11 (s, 3H), 1.09 (s, 3H), 0.43 (s, 3H), 0.41 (s, 3H).



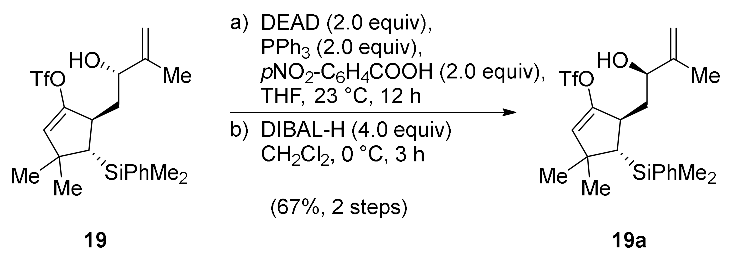
Aldehyde 39. To a solution of **38** (11.5 g, 27.5 mmol, 1.0 equiv) in THF (160 mL) at 0 °C was added OsO_4 (4% in H_2O, 0.8 mmol, 3 mol%). Then a solution NMO (4.83 g, 41 mmol, 1.5 equiv) in H_2O (40 mL) was added, followed by addition of 2,6-lutidine (7.1 ml, 55 mmol, 2.0 equiv). The mixture was slowly warmed to 23 °C and was stirred at that temperature for 1 h. Upon completion, the reaction was quenched by addition of $Na_2S_2O_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 100 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was filter through a pad silica gel (EtOAc). The filtrated was concentrated and used in next step without further purification. $NaIO_4$ supported on SiO_2 was prepared by reported procedure[19] from $NaIO_4$ (25.7 g, 120 mmol) and SiO_2 (100 g) in H_2O (50 mL). That supported $NaIO_4$ (110 g)

was suspended in CH_2Cl_2 (200 mL) and a solution of crude from the last step in CH_2Cl_2 (100 mL) was added. The mixture was stirred at 23 °C for 1 h. Upon completion, the reaction was filtered. The filtrate was concentrated, and the residue was purified by column chromatography (hexanes:EtOAc = 40:1→30:1) to provide **39** (18.5 g, 80%) as a colorless oil. **39:** R_f = 0.46 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (m, 1 H), 7.50–7.48 (m, 2 H), 7.37–7.35 (m, 3 H), 5.51 (d, J = 1.9 Hz, 1 H), 3.49–3.44 (m, 1 H), 2.25 (ddd, J = 17.7 Hz, 7.0 Hz, 2.0 Hz, 1 H), 2.05 (dd, J = 17.5 Hz, 3.8 Hz, 1 H), 1.30 (d, J = 9.2 Hz, 1 H), 1.17 (s, 3H), 1.16 (s, 3H), 0.46 (s, 3H), 0.45 (s, 3H).

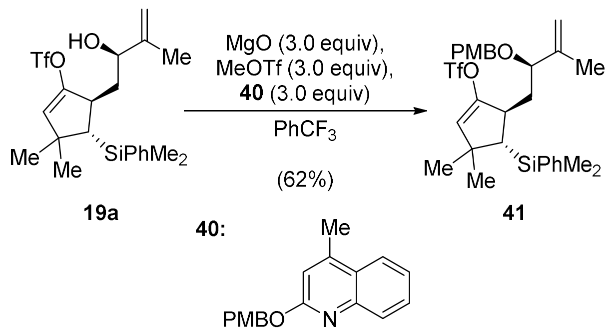


Alcohol 19 and 19a. To a solution of **39** (9.24 g, 22 mmol, 1.0 equiv) in THF (200 mL) at -78 °C was added isopropenylmagnesium bromide (0.5 M in THF, 66 mL, 33 mmol, 1.5 equiv). The mixture was stirred at that temperature for 2 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was warmed to 23 °C and poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 200 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by careful column chromatography (hexanes:EtOAc = 100:1→50:1→10:1) to provide **19** (8.48 g, 42%) and **19a** (8.37 g, 41%) as colorless oil. **19:** R_f = 0.55 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.48 (m, 2 H), 7.37–7.35 (m, 3 H), 5.43 (d, J = 1.6 Hz, 1 H), 4.77 (s,1 H), 4.69 (s, 1 H), 4.08–4.05 (m, 1 H), 3.25 (tt, J = 8.8 Hz, 2.3 Hz, 1 H), 1.50 (s, 3 H), 1.48–1.44 (m, 1 H), 1.36–1.30 (m, 1 H), 1.14 (s, 3 H), 1.11–1.10 (m, 4 H), 0.46 (s, 3 H), 0.46 (s, 3H). **19a:** R_f = 0.48 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.55

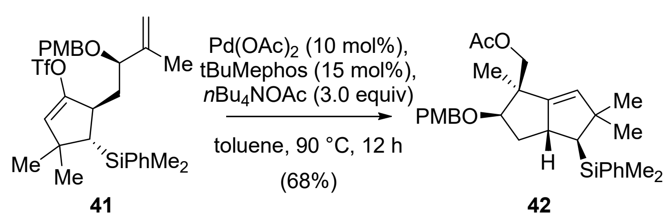
(m, 2 H), 7.38–7.37 (m, 3 H), 5.46 (d, J = 1.4 Hz, 1 H), 4.79 (s, 1 H), 4.74 (t, J = 1.5 Hz, 1 H), 3.79 (qui, J = 4.1 Hz, 1 H), 3.00–2.97 (m , 1 H), 1.61–1.57 (m, 2 H), 1.53 (s, 1 H), 1.51–1.50 (m, 1 H), 1.16 (s, 3 H), 1.14 (s, 3 H), 0.95 (d, J = 4.1 Hz, 1 H), 0.44 (s, 3 H), 0.42 (s, 3H).



Inversion. To a solution of **19** (8.48 g, 18.3 mmol, 1.0 equiv), PPh_3 (9.4 g, 36 mmol, 2.0 equiv) and 4-nitrobenzoic acid (6.0 g, 36 mmol, 2.0 equiv) in THF (100 mL) at 23 °C was added DEAD (40% in toluene, 16.4 mL, 36 mmol, 2.0 equiv) dropwise over the course of 10 min. The mixture was stirred at that temperature for 12 h. Upon completion, the reaction was quenched by addition of $NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by Et_2O (2 × 100 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was filtered through a pad of silica gel (hexanes:EtOAc = 10:1). The filtrate was concentrated and purified by column chromatography (hexanes:EtOAc = 100:1→50:1) to provide a yellow oil. The yellow oil was dissolved in CH_2Cl_2 (50 mL) and DIBAL-H (1.0 M in CH_2Cl_2, 50 mL, 50 mmol) was added at 0 °C. The mixture was stirred at that temperature for 3 h. Upon completion, the reaction was quenched by addition of Rochelle salt solution. The mixture was warmed to 23 °C and poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 100 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 100:1→50:1) to provide **19a** (5.59 g, 67% over 2 steps).

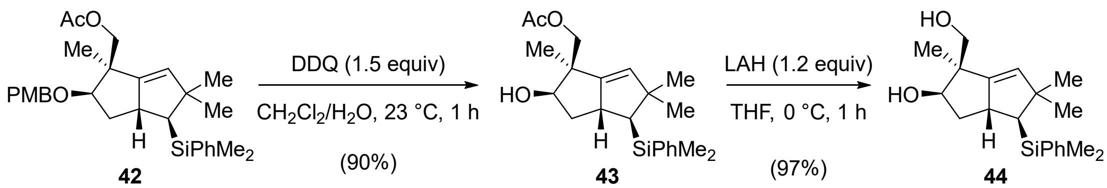


PMB ether 42. To **19a** (13.9 g, 30 mmol, 1.0 equiv), MgO (3.6 g, 90 mmol, 3.0 equiv) and **40**[20] (25.1 g, 90 mmol, 3.0 equiv) in $PhCF_3$ (200 mL) was added MeOTf (9.84 mL, 90 mmol, 3.0 equiv) at 0 °C. The mixture was warmed to 23 °C and stirred at that temperature for 12 h. Upon completion, the mixture was filtered through celite (EtOAc). The filtrate was concentrated and filtered through a pad of Et_3N-buffered silica gel (hexanes:EtOAc = 50:1). The filtrate was concentrated, and the residue was purified by column chromatography (Et_3N-buffered silica gel, hexanes) to provide **41** as a pale-yellow oil (10.8 g, 62%). **41:** R_f = 0.63 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2 H), 7.32–7.23 (m, 5 H), 6.89–6.87 (m, 2 H), 5.36 (d, *J* = 1.8 Hz, 1 H), 4.86 (d, *J* = 1.0 Hz, 2 H), 4.35 (d, *J* = 11.1 Hz, 1 H), 4.11 (d, *J* = 11.1 Hz, 1 H), 3.84–3.80 (m, 1 H), 3.81 (s, 3 H), 3.26 (tt, *J* = 8.9 Hz, 2.0 Hz, 1 H), 1.67 (ddd, *J* = 14.5 Hz, 10.8 Hz, 2.1 Hz, 1 H), 1.54 (s, 3 H), 1.39 (ddd, *J* = 14.7 Hz, 8.7 Hz, 2.6 Hz, 1 H), 1.22 (d, *J* = 9.1 Hz, 1 H), 1.06 (s, 3 H), 1.03 (s, 3H), 0.39 (s, 3 H), 0.38 (s, 3 H).



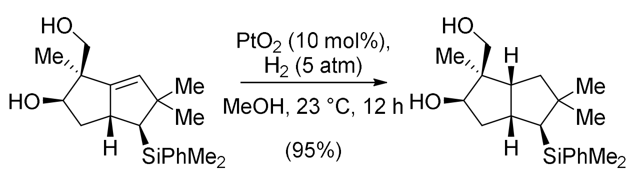
Acetate 42. To $Pd(OAc)_2$ (142 mg, 0.63 mmol, 10 mol%), tBuMephos (298 mg, 0.96 mmol, 15 mol%), *n*Bu_4OAc (5.74 g, 19 mmol, 3.0 equiv) in toluene (65 mL) was added **41** (3.70 g, 6.4 mmol, 1.0 equiv). The mixture in a sealed tube was heated to 90 °C and stirred at that temperature

for 12 h. Upon completion, the mixture was cooled to 23 °C and filtered through a pad of silica gel (EtOAc). The filtrate was concentrated, and the residue was purified by column chromatography (silica gel, hexanes:EtOAc = 30:1→20:1) to provide **42** (2.13 g, 68%) as a yellow oil. **42:** R_f = 0.60 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2 H), 7.35–7.33 (m, 3 H), 7.22–7.20 (m, 2 H), 6.87–6.85 (m, 2 H), 5.12 (d, J = 2.6 Hz, 1 H), 3.89 (q, J = 11.2 Hz, 2 H), 3.85–3.81 (m, 1 H), 3.80 (s, 3 H), 2.77–2.71 (m, 1 H), 2.00 (s, 3 H), 1.96–1.92 (m, 1 H), 1.08 (d, J = 10.1 Hz, 1 H), 1.06 (s, 3 H), 1.00–0.94 (m, 1 H), 0.98 (s, 3 H), 0.96 (s, 3H), 0.36 (s, 3 H), 0.35 (s, 3 H).



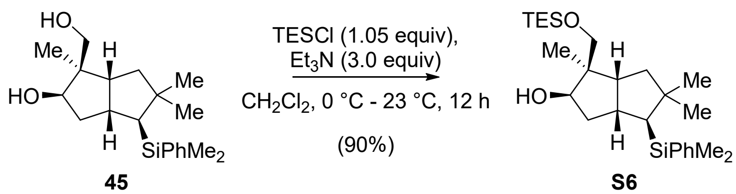
Diol 44. To a solution of **42** (3.34 g, 6.8 mmol, 1.0 equiv) in CH_2Cl_2 (60 mL) and H_2O (6 mL) was added DDQ (2.31 g, 10.2 mmol, 1.5 equiv). The mixture was stirred at 23 °C for 1 h. Upon completion, the reaction was quenched by addition of $NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 50 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 5:1) to provide **43** (2.27 g, 90%) as a pale-yellow oil. **43:** R_f = 0.18 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2 H), 7.34–7.33 (m, 3 H), 5.17 (d, J = 2.6 Hz, 1 H), 4.12–4.09 (m, 1 H), 3.92 (q, J = 10.8 Hz, 2 H), 2.81 (tdd, J = 11.1 Hz, 6.7 Hz, 2.6 Hz, 1 H), 2.04 (s, 3 H), 1.92 (dt, J = 11.8 Hz, 6.3 Hz, 1 H), 1.07 Hz (d, J = 10.8 Hz, 1H), 1.01 (s, 3 H), 1.01 (s, 3 H), 0.98 (s, 3 H), 0.95–0.88 (m, 1H), 0.37 (s, 3 H), 0.37 (s, 3H). To a solution of **43** (2.23 g, 6.0 mmol, 1.0 equiv) in THF (50 mL) was added LAH (1.0 M in THF, 7.2 mL, 7.2 mmol, 1.2 equiv) at 0 °C. The mixture

was stirred at that temperature for 1 h. Upon completion, the reaction was quenched by addition of Rochelle salt solution. The mixture was warmed to 23 °C and poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 50 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 2:1) to provide **44** (1.92 g, 97%) as a white solid. **44:** R_f = 0.40 (silica gel, hexanes:EtOAc, 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2 H), 7.34–7.33 (m, 3 H), 5.19 (d, J = 2.6 Hz, 1 H), 4.15–4.11 (m, 1 H), 3.43 (s, 2 H), 2.80–2.76 (tdd, J = 10.8 Hz, 6.6 Hz, 2.6 Hz, 1 H), 1.91 (dt, J = 11.6 Hz, 6.2 Hz, 1 H), 1.09 (d, J = 10.3 Hz, 1 H), 1.02 (s, 3 H), 1.00 (s, 3 H), 0.99 (s, 3 H), 0.96–0.91 (m, 1 H), 0.37 (s, 3 H), 0.37 (s, 3 H).

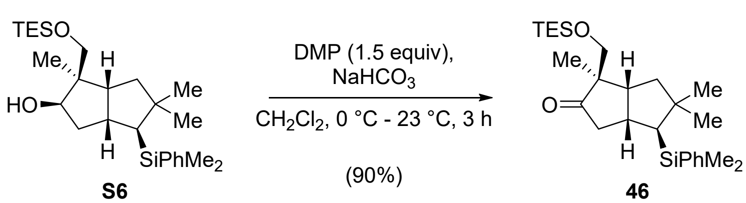


44 **45**

Diol 45. A Q-tube was equipped with PtO_2 (45 mg, 0.2 mmol, 10 mol%) and a solution of **44** (0.66 g, 2.0 mmol, 1.0 equiv) in MeOH (20 mL) was added. The Q-tube was purged with H_2 (5 atm), and the mixture was stirred at 23 °C for 12 h. Upon completion, the mixture was filtered through a pad of silica gel (EtOAc). The filtrate was concentrated to provide **45** (0.63 g, 95%) as a white solid. **45:** R_f = 0.40 (silica gel, hexanes:EtOAc, 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.49 (m, 2 H), 7.33–7.32 (m, 3 H), 3.96–3.92 (m, 1 H), 3.48–3.41 (m, 2 H), 2.47–2.40 (m, 1 H), 2.13–2.07 (m, 1 H), 1.91–1.86 (m, 1 H), 1.84 (d, J = 4.4 Hz, 1 H), 1.65 (t, J = 5.2 Hz, 1 H), 1.47 (t, J = 11.4 Hz, 1 H), 1.27 (dd, J = 12.2 Hz, 8.4 Hz, 1 H), 1.14–1.06 (m, 1 H), 0.94 (s, 3 H), 0.91 (s, 3 H), 0.86 (s, 3 H), 0.76 (d, J = 11.0 Hz, 1 H), 0.34 (s, 6 H).

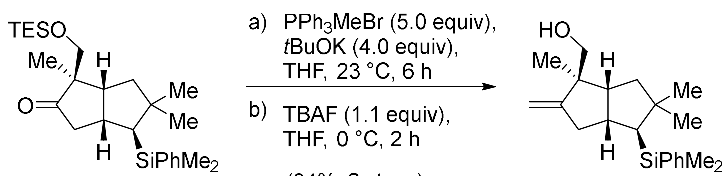


TES ether S6. To a solution of **45** (1.98 g, 6.0 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL) was added TESCl (0.93 g, 6.18 mmol, 1.05 equiv) and Et_3N (2.46 mL, 17.7 mmol, 3.0 equiv) at 0 °C. The mixture was slowly warmed to 23 °C and stirred at that temperature for 12 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 50 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 40:1→20:1→10:1) to provide **S6** (2.40 g, 90%) as a colorless oil. **S6:** R_f = 0.50 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2 H), 7.33–7.31 (m, 3 H), 3.94 (ddd, J = 10.4 Hz, 6.1 Hz, 2.1 Hz, 1 H), 3.41 (dd, J = 33.9 Hz, 9.1 Hz, 2 H), 2.46–2.38 (m, 1 H), 2.38 (d, J = 2.1 Hz, 1 H). 2.02 (td, J = 10.6 Hz, 8.3 Hz, 1 H), 1.88 (ddd, J = 14.1 Hz, 7.9 Hz, 6.2 Hz, 1 H), 1.45 (t, J = 11.5 Hz, 1 H), 1.23 (dd, J = 12.2 Hz, 8.2 Hz, 1 H), 1.16–1.09 (m, 1 H), 0.94 (t, J = 8.0 Hz, 9 H), 0.92 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H), 0.74 (d, J = 11.0 Hz, 1 H), 0.58 (q, J = 8.0 Hz, 6 H), 0.33 (s, 3H), 0.33 (s, 3H).



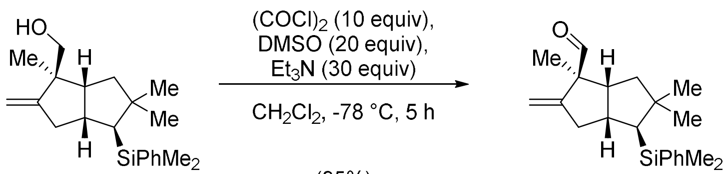
Ketone 46. DMP (1.84 g, 4.3 mmol, 1.5 equiv) and $NaHCO_3$ (1.8 g) was stirred in CH_2Cl_2 (10 mL) at 23 °C for 15 min. Then the mixture was cooled to 0 °C and a solution of **S6** (1.38 g, 2.9 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was added. The mixture was slowly warmed to 23 °C and

stirred at that temperature for 3 h. Upon completion, the reaction was quenched by $Na_2S_2O_3$/$NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 20 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 10:1) to provide **46** (1.14 g, 90%) as a pale-yellow oil. **46**: R_f = 0.50 (silica gel, hexanes:EtOAc, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.48 (m, 2 H), 7.34–7.31 (m, 3 H), 3.51 (d, J = 9.0 Hz, 1 H), 3.37 (d, J = 9.0 Hz, 1 H), 2.81–2.75 (m, 1 H), 2.71–2.66 (m, 1 H), 2.34 (dd, J = 19.4 Hz, 10.5 Hz, 1 H), 1.55 (dd, J = 19.6 Hz, 6.1 Hz, 1 H), 1.42 (dd, J = 12.0 Hz, 6.9 Hz, 1 H), 1.17 (t, J = 12.4 Hz, 1 H), 0.97 (s, 3 H), 0.97 (s, 3 H), 0.94 (t, J = 8.0 Hz, 9 H), 0.84 (s, 3 H), 0.75 (d, J = 8.1 Hz, 1 H), 0.56 (q, J = 8.0 Hz, 6 H), 0.38 (s, 3 H), 0.35 (s, 3 H).



46 **47**

Alkene 47. PPh_3MeBr (4.64 g, 13.0 mmol, 5.0 equiv) and *t*BuOK (1.16 g, 10.3 mmol, 4.0 equiv) was stirred in THF (15 mL) at 23 °C for 15 min. Then a solution of **46** (1.15 g, 2.6 mmol, 1.0 equiv) in THF (10 mL) was added. The mixture was stirred at that temperature for 6 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by Et_2O (2 × 20 mL). The combined organic layer was washed by H_2O and brine, dried (Na_2SO_4), filtered and concentrated. The residue was filtered through a pad of silica gel (hexanes:EtOAc = 40:1). The filtrate was concentrated, and the residue was used in the next step. To a solution of the residue in THF (25 mL) was added TBAF (1.0 M in THF, 2.8 mL, 2.8 mmol, 1.1 equiv) at 0 °C. The mixture was stirred at that temperature for 2 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 20 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 20:1→10:1) to provide **47** (802 mg, 94% over 2 steps) as a colorless oil. **47:** R_f = 0.28 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2 H), 7.35–7.32 (m, 3 H), 4.90 (s, 1 H), 4.76–4.75 (m, 1 H), 3.30 (dd, J = 10.4 Hz, 2.8 Hz, 1 H), 3.19 (t, J = 10.2 Hz, 1 H), 2.48–2.26 (m, 2 H), 2.22–2.17 (m, 1H), 1.58 (d, J = 15.4 Hz, 1 H), 1.30 (dd, J = 11.8 Hz, 7.0 Hz, 1 H), 1.25 (dd, J = 10.0 Hz, 3.0 Hz, 1 H), 1.05 (q, J = 10.6 Hz, 1 H), 0.98 (s, 3 H), 0.89 (s, 3 H), 0.87 (s, 3 H), 0.65 (d, J = 8.5 Hz, 1 H), 0.37 (s, 3 H), 0.33 (s, 3 H).

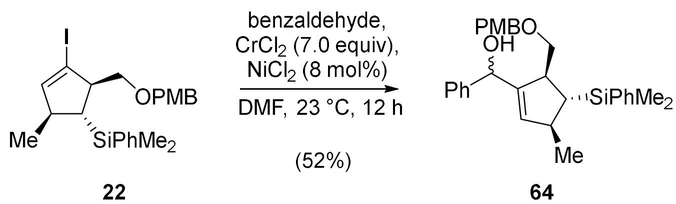


47 **48**

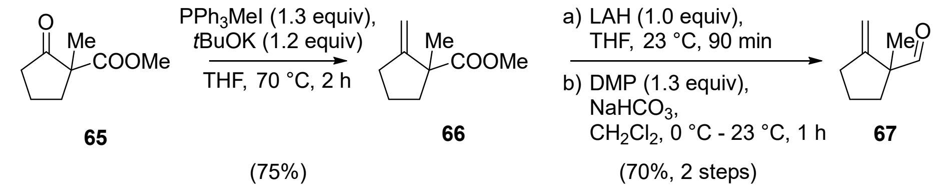
Aldehyde 48. To a solution of $(COCl)_2$ (86 µL, 1.0 mmol, 10 equiv) in CH_2Cl_2 (1 mL) was added DMSO (0.14 mL, 2.0 mmol, 20 equiv) at -78 °C. The mixture was stirred at that temperature for 15 min. A solution of **47** (32.8 mg, 0.1 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) was added. The mixture was stirred at -78 °C for 3 h. Then Et_3N (0.42 mL, 3.0 mmol, 30 equiv) was added, and the stirring was continued at -78 °C for 2 h. Upon completion, the reaction was quenched by addition of H_2O. The mixture was warmed to 23 °C and poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 2 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 10:1) to provide **48** (30.9 mg, 95%) as a pale-yellow oil. **48:** R_f = 0.52 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1 H), 7.52–

7.48 (m, 2 H), 7.35–7.32 (m, 3 H), 5.00 (s, 1 H), 4.87 (d, *J* = 2.2 Hz, 1 H), 2.85 (ddd, *J* = 8.8 Hz, 7.3 Hz, 12.1 Hz, 1 H), 2.63 (qd, *J* = 9.5 Hz, 2.9 Hz, 1 H), 2.27 (ddt, *J* = 16.6 Hz, 10.2 Hz, 2.8 Hz, 1 H), 1.58–1.53 (m, 1 H), 1.30 (dd, *J* = 11.8 Hz, 7.2 Hz, 1 H), 1.10 (s, 3 H), 1.08–1.02 (m, 1 H), 0.92 (s, 3 H), 0.90 (s, 3 H), 0.63 (d, *J* = 9.1 Hz, 1 H), 0.38 (s, 3 H), 0.34 (s, 3 H).

Model Study

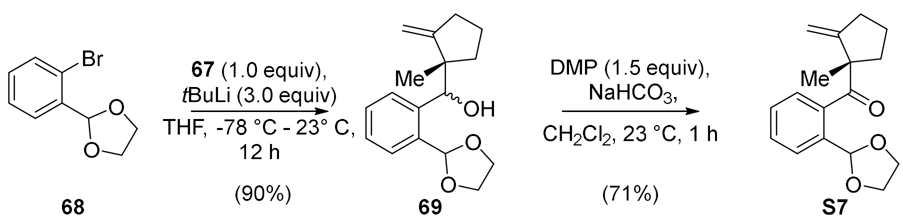


64. In glove box, to a solution of $CrCl_2$ (25 mg, 0.2 mmol, 7.0 equiv) in degassed DMF (0.5 mL) was added benzaldehyde (3.2 mg, 0.03 mmol, 1.0 equiv) and **22** (22 mg, 0.05 mmol, 1.3 equiv). Then $NiCl_2$ (0.3 mg, 8 mol%) was added. The mixture was stirred in glove box at 23 °C for 12 h. Upon completion, the reaction was diluted by Et_2O and quenched by addition of H_2O. The mixture was poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted by Et_2O (2 × 2 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 10:1) to provide **64** (7.3 mg, 52%, mixture of diastereomers) as a yellow oil. **64**(minor diastereomer)**:** R_f = 0.62 (silica gel, hexanes:EtOAc, 5:1). **64**(major diastereomer)**:** R_f = 0.47 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.20 (m, 10 H), 7.15 (d, *J* = 8.6 Hz, 2 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 5.48 (s, 1 H), 4.75 (d, *J* = 8.2 Hz, 1 H), 4.28 (dd, *J* = 25.4 Hz, 10.4 Hz, 2 H), 3.81 (s, 3 H), 3.29 (t, *J* = 9.2 Hz, 1 H), 3.16 (dd, *J* = 9.2 Hz, 3.9 Hz, 1 H), 2.75–2.70 (m, 1 H), 2.65–2.61 (m, 1 H), 2.35 (t, *J* = 7.5 Hz, 1 H), 0.96 (d, *J* = 6.8 Hz, 3 H), 0.62 (t, *J* = 6.0 Hz, 1 H), 0.16 (s, 3 H), 0.14 (s, 3 H).

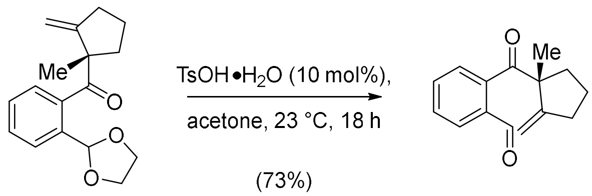


Aldehyde 67. To a solution of PPh_3MeI (9.05 g, 22 mmol, 1.3 equiv) in THF (50 mL) was added *t*BuOK (2.32 g, 20 mmol, 1.2 equiv). The mixture was heated to 70 °C and refluxed at that temperature for 1h. Then a solution of **65** (2.65 g, 17 mmol, 1.0 equiv) in THF (30 mL) was added. Reflux was continued at that temperature for 1 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was cooled to 23 °C and poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted by Et_2O (2 × 30 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated (40 °C, 500 mmHg). The residue was purified by column chromatography (petanes:Et_2O = 10:1) to provide **66** (1.98 g, 75%) as a pale-yellow oil. **66:** R_f = 0.77 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.98 (t, J = 2.0 Hz, 1 H), 4.95 (t, J = 2.3 Hz, 1 H), 3.67 (s, 3 H), 2.51–2.38 (m, 2 H), 2.34 (dt, J = 12.5 Hz, 6.9 Hz, 1 H), 1.83–1.78 (m, 1 H), 1.69–1.65 (m, 1 H), 1.61–1.59 (m, 1 H), 1.33 (s, 3 H). To suspension of LAH (684 mg, 18 mmol, 1.0 equiv) in THF (20 mL) was added a solution of **66** (2.77 g, 18 mmol, 1.0 equiv) in THF (30 mL). The mixture was stirred at 23 °C for 90 min. Upon completion, the reaction was quenched by addition of Rochelle salt solution. The mixture was poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted by Et_2O (2 × 30 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was filtered through a pad of silica gel (Et_2O). The filtrate was concentrated (40 °C, 500 mmHg) and used in next step. DMP (5.5 g, 13 mmol, 1.3 equiv) and $NaHCO_3$ (12 g) was stirred in CH_2Cl_2 (20 mL) at 23 °C for 15 min. Then a solution of the residue (10 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) was added at 0 °C. The mixture was slowly warmed to

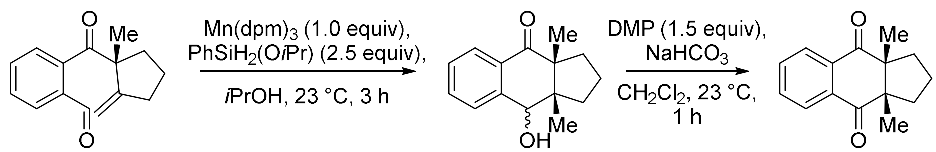
23 °C and stirred at that temperature for 1 h. Upon completion, the reaction was quenched by $Na_2S_2O_3$/$NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 20 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated (40 °C, 550 mmHg). The residue was purified by column chromatography (petanes:Et_2O = 10:1) to provide **67** (0.97 g, 70% over 2 steps) as a pale-yellow oil. **67:** R_f = 0.64 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.31 (s, 1 H), 5.14 (t, J = 2.3 Hz, 1 H), 4.83 (t, J = 2.3 Hz, 1 H), 2.50–2.35 (m, 2 H), 2.20 (dt, J = 12.8 Hz, 6.8 Hz, 1 H), 1.76–1.70 (m, 2 H), 1.54 (qui, J = 6.6 Hz, 1 H), 1.21 (s, 3 H).



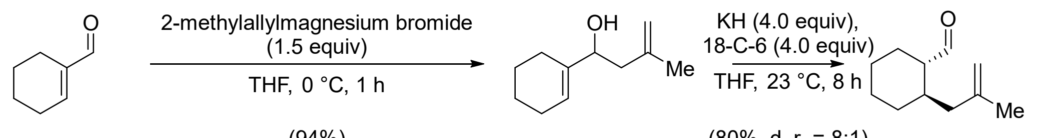
S7. To a solution of **68**[28] (1.37 g, 6.0 mmol, 1.5 equiv) in THF (20 mL) was added *t*BuLi (1.6 M in THF, 7.5 mL, 12 mmol, 3.0 equiv) at -78 °C. The mixture was stirred at that temperature for 1 h. Then a solution of **67** (0.50 g, 4.0 mmol, 1.0 equiv) in THF (10 mL) was added. The mixture was slowly warmed to 23 °C and stirred at that temperature for 12 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 20 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 15:1→5:1) to provide **69** (0.99 g, 90%) as a mixture of diastereomers. DMP (193 mg, 0.45 mmol, 1.5 equiv) and $NaHCO_3$ (400 mg) was stirred in CH_2Cl_2 (2 mL) at 23 °C for 15 min. Then a solution of **69** (83 mg, 0.3 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) was added. The mixture was stirred at 23 °C for 1 h. Upon completion, the reaction was quenched by $Na_2S_2O_3$/$NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 3 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 10:1) to provide **S7** (59 mg, 71%) as a yellow oil. **S7:** R_f = 0.75 (silica gel, hexanes:EtOAc, 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 1 H), 7.38–7.34 (m, 1 H), 7.30–7.27 (m, 2 H), 5.94 (s, 1 H), 5.12 (t, J = 1.9 Hz, 1 H), 5.04 (t, J = 2.0 Hz, 1 H), 4.00–3.93 (m, 4 H), 2.53–2.48 (m, 1 H), 2.42–2.34 (m, 1 H), 2.13–2.04 (m, 1 H), 1.72–1.62 (m, 3 H), 1.38 (s, 3 H).



Model 70. To a solution of **S7** (59 mg, 0.22 mmol, 1.0 equiv) in acetone (2.5 mL) was added $TsOH{\cdot}H_2O$ (4 mg, 0.02 mmol, 10 mol%). The mixture was stirred at 23 °C for 18 h. Upon completion, the reaction was diluted by EtOAc and quenched by addition of NH_4Cl solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 2 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 8:1) to provide **70** (36 mg, 73%) as a pale-yellow oil. **70:** R_f = 0.46 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1 H), 7.86–7.84 (m, 1 H), 7.59–7.52 (m, 2 H), 7.34–7.33 (m, 1 H), 5.13 (t, J = 2.0 Hz, 1 H), 5.00 (t, J = 2.1 Hz, 1 H), 2.52–2.47 (m, 1 H), 2.33–2.26 (m, 1 H), 2.10–2.04 (m, 1 H), 1.76–1.72 (m, 1 H), 1.67–1.61 (m, 2 H), 1.46 (s, 2 H).

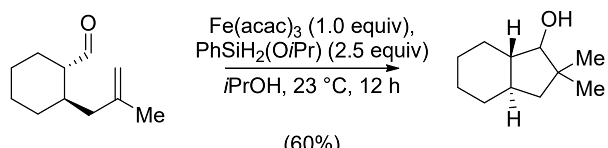


Diketone 71. To a flask equipped with Mn(dpm)$_3$ (30.2 mg, 0.5 mmol, 1.0 equiv) was added a solution of **70** (11.4 mg, 0.5 mmol, 1.0 equiv) in *i*PrOH (0.5 mL). Then Shenvi's silane (22 μL, 1.25 mmol, 2.5 equiv) was added. The mixture was stirred at 23 °C for 3 h. Upon completion, the reaction was diluted with EtOAc and quenched by addition of H_2O. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 2 mL). The combined organic layer was concentrated. The residue was filtered through a pad of silica gel (hexanes:EtOAc = 5:1) to provide a mixture of **S8** (2 diastereomers) and **71**. This mixture was then treated with DMP and $NaHCO_3$ via described procedure. Then column chromatography (hexanes:EtOAc = 10:1) provide **71** (7.5 mg, 66%) as a yellow oil. **71:** R_f = 0.64 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08–8.06 (m, 2 H), 7.74–7.72 (m, 2 H), 2.39–2.34 (m, 2 H), 1.83–1.77 (m, 2 H), 1.71–1.66 (m, 2 H), 1.26 (s, 6 H).



72 73 74

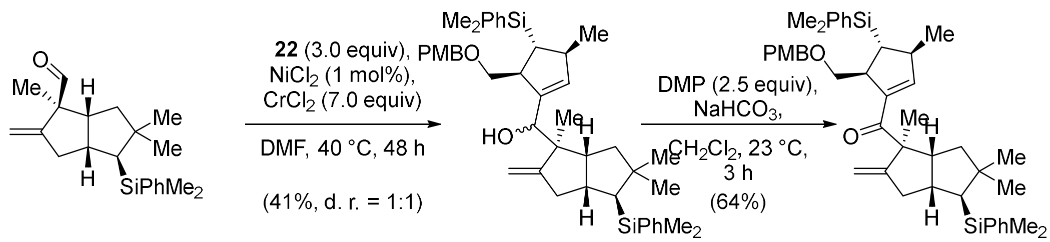
Model 74. To a solution of **72** (550 mg, 5.0 mmol, 1.0 equiv) in THF (30 mL) was added 2-methylallylmagnesium bromide (0.5 M in THF, 15 mL, 7.5 mmol, 1.5 equiv) at 0 °C. The mixture was stirred at that temperature for 1 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was warmed to 23 °C and poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted by EtOAc (2 × 30 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 1:1) to provide **73** (777 mg, 94%) as a colorless oil. **73:** R_f = 0.43 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72–5.70 (m, 1 H), 4.88–4.87 (m, 1 H), 4.82–4.81 (m, 1 H), 4.10–4.08 (m, 1 H), 2.26–2.24 (m, 2 H), 2.10–2.02 (m, 2 H), 1.97–1.92 (m, 1 H), 1.70–1.53 (m, 4 H), 1.67 (d, J = 2.8 Hz, 1 H). To a suspension of KH (80 mg, 2.0 mmol, 4.0 equiv) in THF (4 mL) was added a solution of **73** (83 mg, 0.5 mmol, 1.0 equiv) in THF (3 mL) at 0 °C. Then a solution of 18-C-6 (528 mg, 2.0 mmol, 4.0 equiv) in THF (3 mL) was added at 0 °C. The mixture was slowly warmed to 23 °C and stirred at that temperature for 8 h. Upon completion, the reaction was quenched by addition of NH_4Cl solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by Et_2O (2 × 10 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated (40 °C, 550 mmHg). The residue was purified by column chromatography (petanes:Et_2O = 30:1→20:1) to provide **74** (66 mg, 80%, d. r. = 8:1) as a pale-yellow oil. **74:** R_f = 0.66 (silica gel, hexanes:EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (d, *J* = 3.6 Hz, 1 H), 4.76 (s, 1 H), 4.68 (s, 1 H), 2.13–2.10 (m, 1 H), 2.04–2.00 (m, 1 H), 1.86–1.81 (m, 3 H), 1.77–1.71 (m, 3 H), 1.69 (s, 3 H), 1.41–1.36 (m, 1 H), 1.34–1.25 (m, 3 H), 0.97–0.92 (m, 1 H).



74 75

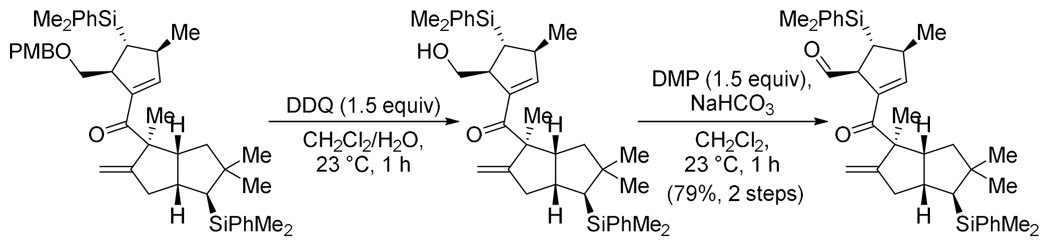
Alcohol 75. To a flask equipped with $Fe(acac)_3$ (17.6 mg, 0.05 mmol, 1.0 equiv) was added a solution of **74** (8.3 mg, 0.05 mmol, 1.0 equiv) in *i*PrOH (0.5 mL). Then Shenvi's silane (22 µL, 0.12 mmol, 2.5 equiv) was added. The mixture was stirred 23 °C for 12 h. Upon completion, the mixture was concentrated, and the residue was purified by column chromatography (hexanes:EtOAc = 10:1) to provide **75** (5.0 mg, 60%, single diastereomer) as a colorless oil. **75:** R_f = 0.30 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.24 (dd, *J* = 8.6 Hz, 5.5 Hz, 1 H), 1.98–1.96 (m, 1 H), 1.78–1.75 (m, 2 H), 1.73–1.71 (m, 1 H), 1.59–1.58 (m, 1 H), 1.26–1.25 (m, 1 H), 1.18–1.08 (m, 6 H), 1.04 (s, 3 H), 0.93 (s, 3H).

Ring B formation



Ketone 77. To a vial equipped with $CrCl_2$ (35 mg, 0.3 mmol, 7.0 equiv) in glove box was added a solution of **48** (13.7 mg, 42 μmol, 1.0 equiv) in degassed DMF (0.15 mL). Then **22** (62 mg, 0.13 mmol, 3.0 equiv) and $NiCl_2$ (0.8mg/mL in DMF, 65 μL, 0.42 μmol, 1 mol%) was added. The mixture was stirred at 40 °C for 48 h. Then the mixture was moved out from glove box and cooled to 23 °C. H_2O (0.5 mL) and Et_2O (0.5 mL) was added. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by Et_2O (2 × 1 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 20:1→5:1) to provide **76** (12.0 mg, 41%, d. r. = 1:1) as a pale-yellow oil. And 3.0 mg of **48** and 13 mg of **22** was recovered. **76:** R_f = 0.32 and 0.41 (silica gel, hexanes:EtOAc, 10:1). A suspension of DMP (34 mg, 80 μmol, 2.5 equiv) and $NaHCO_3$ (60 mg) in CH_2Cl_2 (0.2 mL) was stirred for 15 min at 23 °C and a solution of **76** (22 mg, 32 μmol, 1.0 equiv) in CH_2Cl_2 was added. The mixture was stirred at that temperature for 3 h. Upon completion, the reaction was quenched by addition of $Na_2S_2O_3$/$NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 1 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 10:1→5:1) to provide **78** (14.1 mg, 64%) as a colorless oil. **78:** R_f = 0.60 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.43 (m, 4 H), 7.33–7.26 (m, 6 H), 7.18–7.17 (m, 2 H), 6.87–6.84 (m, 2 H), 6.61 (dd, J = 2.6 Hz, 1.6 Hz, 1 H), 4.89 (s, 1 H), 4.85 (s, 1 H), 4.31(dd, J = 28.0 Hz,

11.7 Hz, 2 H), 3.81 (s, 3 H), 3.40 (dd, J = 9.2 Hz, 5.7 Hz, 1 H), 3.31 (dd, J = 9.2 Hz, 3.7 Hz, 1 H), 3.20–3.19 (m, 1 H), 3.16–3.12 (m, 1 H), 2.72–2.69 (m, 1 H), 2.45–2.40 (m, 1 H), 2.22–2.17 (m, 1 H), 1.36–1.33 (m, 1 H), 1.23–1.19 (m, 1 H), 1.11 (s, 3 H), 0.97 (d, J = 7.0 Hz, 3 H), 0.92–0.87 (m, 2 H), 0.88 (s, 3 H), 0.85 (s, 3 H), 0.56 (d, J = 9.2 Hz, 1 H), 0.32 (s, 3 H), 0.27 (s, 3 H), 0.23 (s, 3 H), 0.22 (s, 3 H).



Aldehyde 78. To a solution of **77** (14 mg, 20 μmol, 1.0 equiv) in CH_2Cl_2 (0.4 mL) and H_2O (40 μL) was added DDQ (6.8 mg, 30 μmol, 1.5 equiv). The mixture was stirred at 23 °C for 1 h. Upon completion, the reaction was quenched by addition of $NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 1 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 20:1→10:1) to provide **S9** (inseparable with 4-methoxylbenzaldehyde, 86% NMR yield) as a pale-yellow oil. **S9:** R_f = 0.35 (silica gel, hexanes:EtOAc, 10:1). The mixture was used in the next step. A suspension of DMP (10 mg, 24 μmol, 1.5 equiv) and $NaHCO_3$ (20 mg) in CH_2Cl_2 (0.1 mL0was stirred at 23 °C for 15 min. Then a solution of **S9** (16 μmol) in CH_2Cl_2 (0.1 mL) was added. The mixture was stirred at that temperature for 1 h. Upon completion, the reaction was quenched by addition of $Na_2S_2O_3$/$NaHCO_3$ solution. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted by CH_2Cl_2 (2 × 0.5 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column

chromatography (hexanes:EtOAc = 10:1) to provide **78** (8.5 mg, 79 % in 2 steps) as a pale-yellow oil. **78:** R_f = 0.50 (silica gel, hexanes:EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (d, J = 3.0 Hz, 1 H), 7.49–7.46 (m, 4 H), 7.36–7.31 (m, 6 H), 6.88 (dd, J = 2.5 Hz, 1.9 Hz, 1 H), 4.94–4.93 (m, 2 H), 3.63–3.61 (m, 1 H), 3.14–3.09 (m, 1 H), 2.89–2.86 (m,1 H), 2.49–2.44 (m, 1 H), 2.07–2.02 (m, 1 H), 1.33 (m, 1 H), 1.21–1.18 (m, 1 H), 1.10 (s, 3 H), 0.97 (d, J = 7.0 Hz, 3 H), 0.89 (s, 3 H), 0.88–0.84 (m, 2 H), 0.85 (s, 3 H), 0.47 (d, J = 9.3 Hz, 1 H), 0.35 (s, 3 H), 0.30 (s, 3 H), 0.29 (s, 3 H), 0.29 (s, 3 H).

3.5 References

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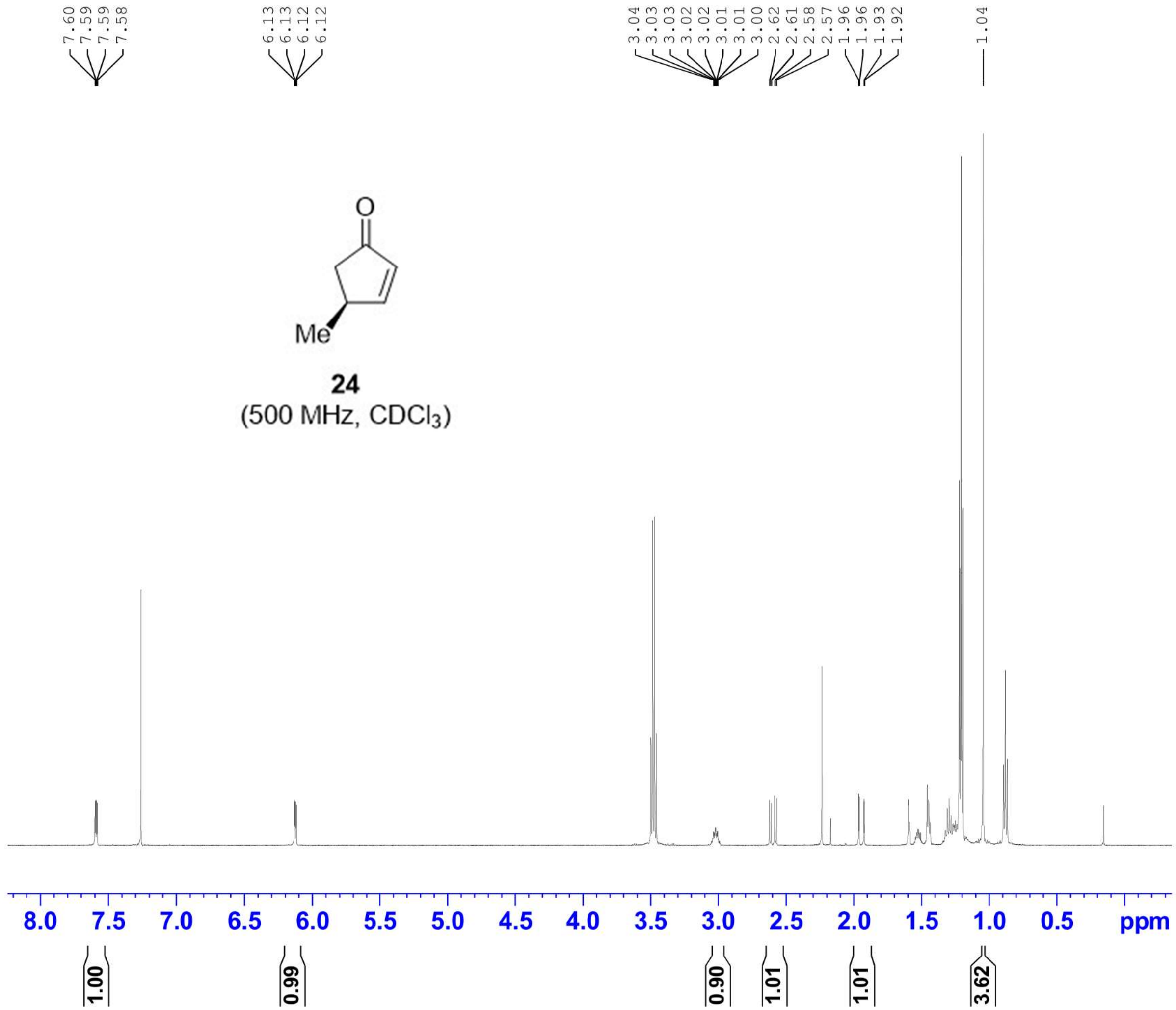
3.6 NMR data of selected intermediates



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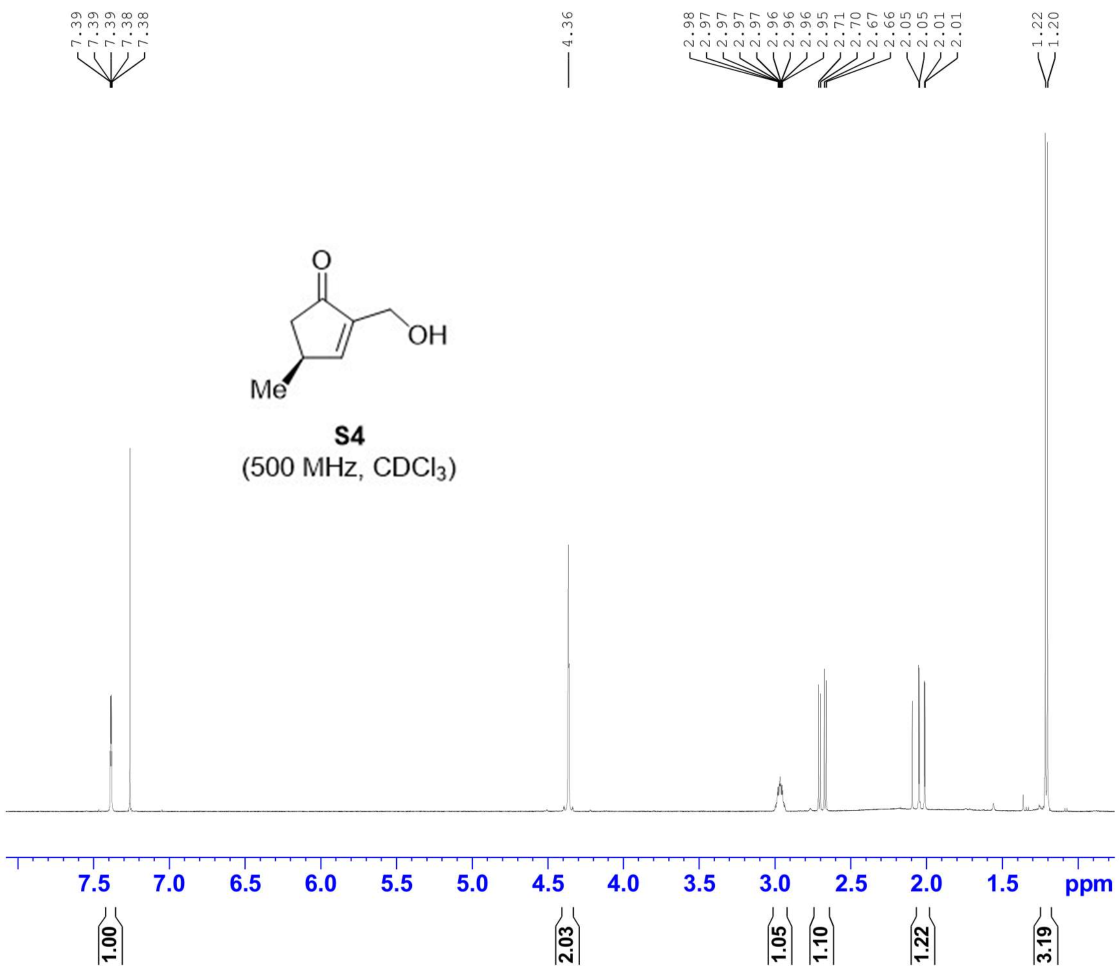

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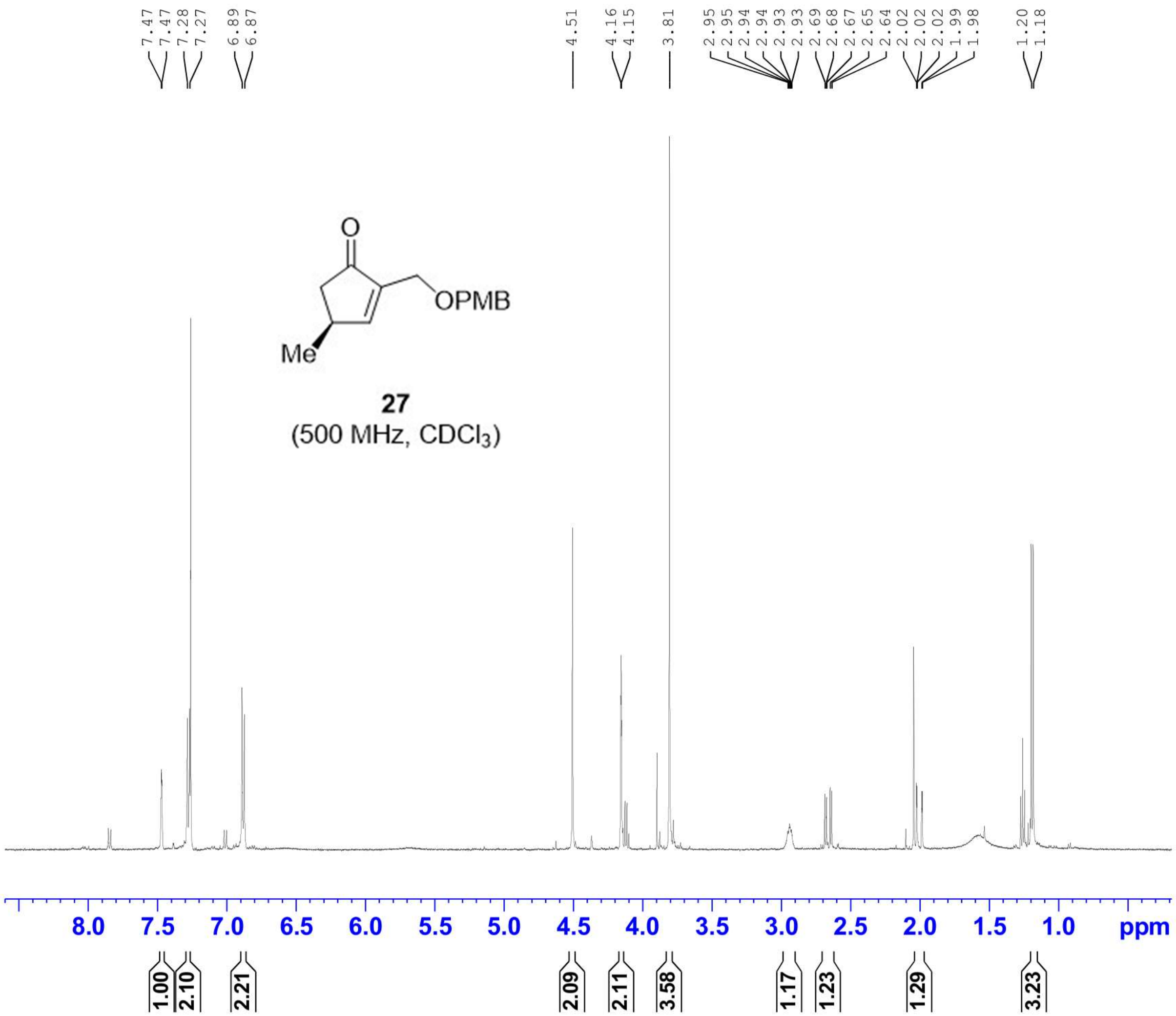


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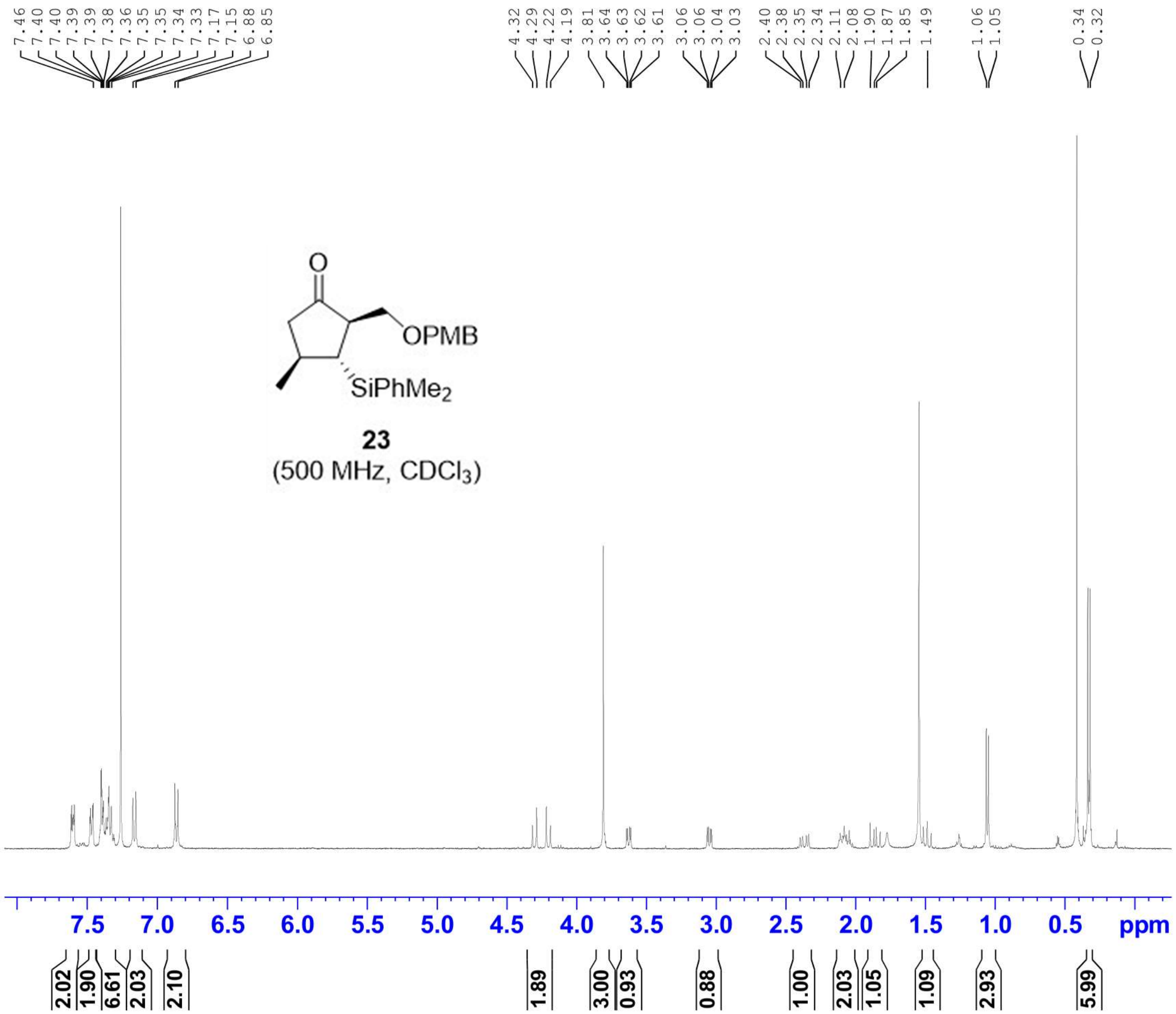
SFO1        500.1335009 MHz
NUC1                 1H
P0                 3.37 usec
P1                10.10 usec
PLW1        25.00300026 W

F2 - Processing parameters
SI               131072
SF          500.1300121 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



23
(500 MHz, $CDCl_3$)

Current Data Parameters

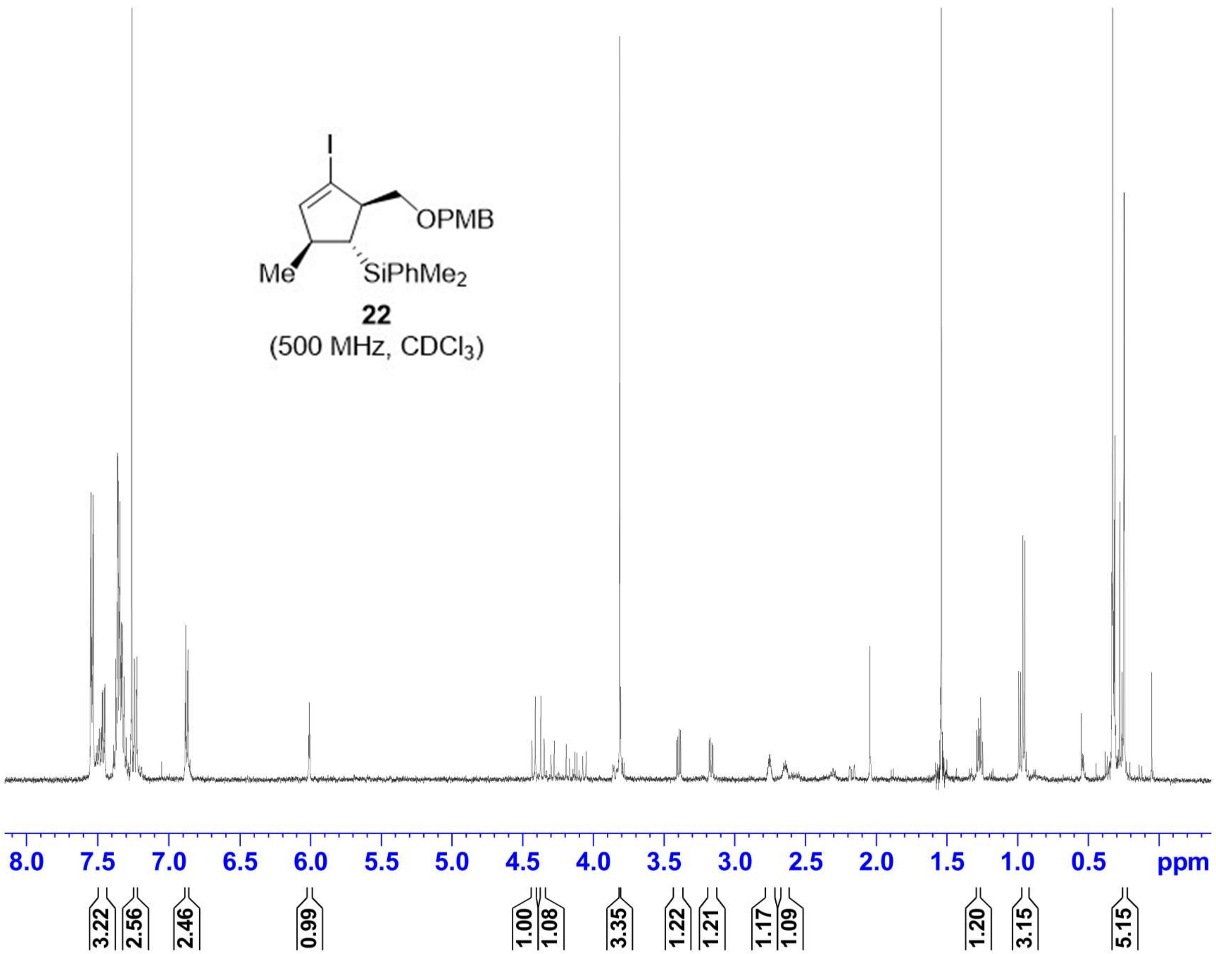
NAME	yh-8-71
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20200708
Time	19.22 h
INSTRUM	spect
PROBHD	Z140678_0010 (
PULPROG	zg30
TD	38460
SOLVENT	CDCl3
NS	8
DS	0
SWH	6410.256 Hz
FIDRES	0.333347 Hz
AQ	2.9998801 sec
RG	187.66
DW	78.000 usec
DE	6.50 usec
TE	297.1 K
D1	1.50000000 sec
TD0	1
SFO1	400.1528010 MHz
NUC1	1H
P0	2.28 usec
P1	6.85 usec
PLW1	31.98900032 W

F2 - Processing parameters

SI	131072
SF	400.1500097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

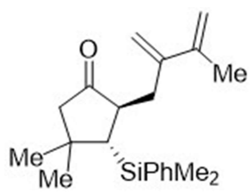


22
(500 MHz, $CDCl_3$)

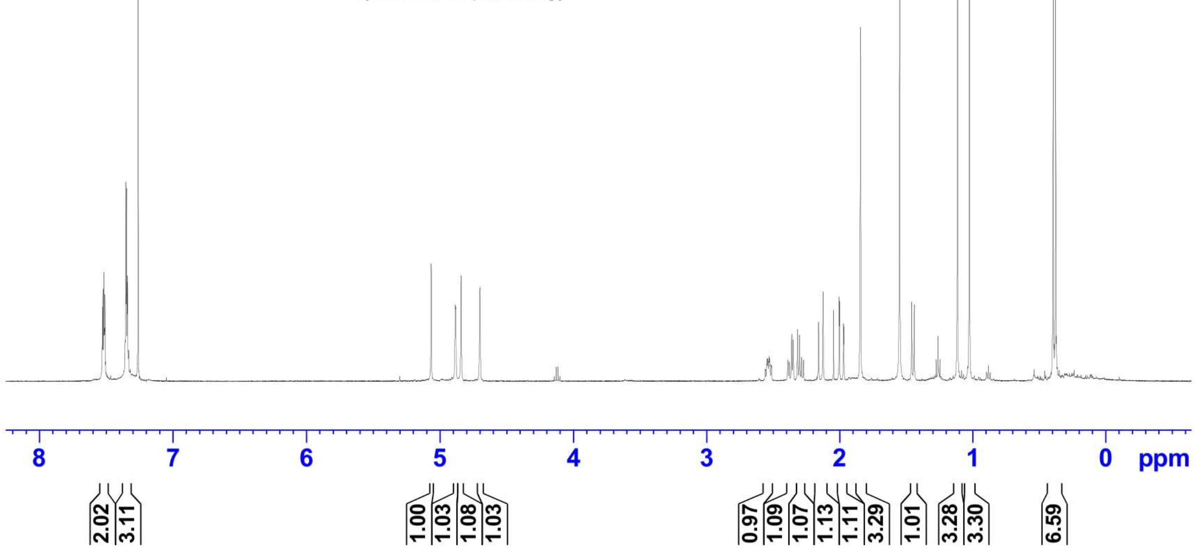
```
Current Data Parameters
NAME          yh-10-127
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210907
Time              19.46 h
INSTRUM           spect
PROBHD   Z800701_0094 (
PULPROG            zg30
TD                48076
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8012.820 Hz
FIDRES         0.333340 Hz
AQ            2.9999423 sec
RG               196.79
DW               62.400 usec
DE                 6.50 usec
TE                298.2 K
D1           1.50000000 sec
TD0                   1
SFO1        500.1335009 MHz
NUC1                 1H
P0                 3.37 usec
P1                10.10 usec
PLW1        25.00300026 W

F2 - Processing parameters
SI               131072
SF          500.1300124 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



S5
(500 MHz, $CDCl_3$)

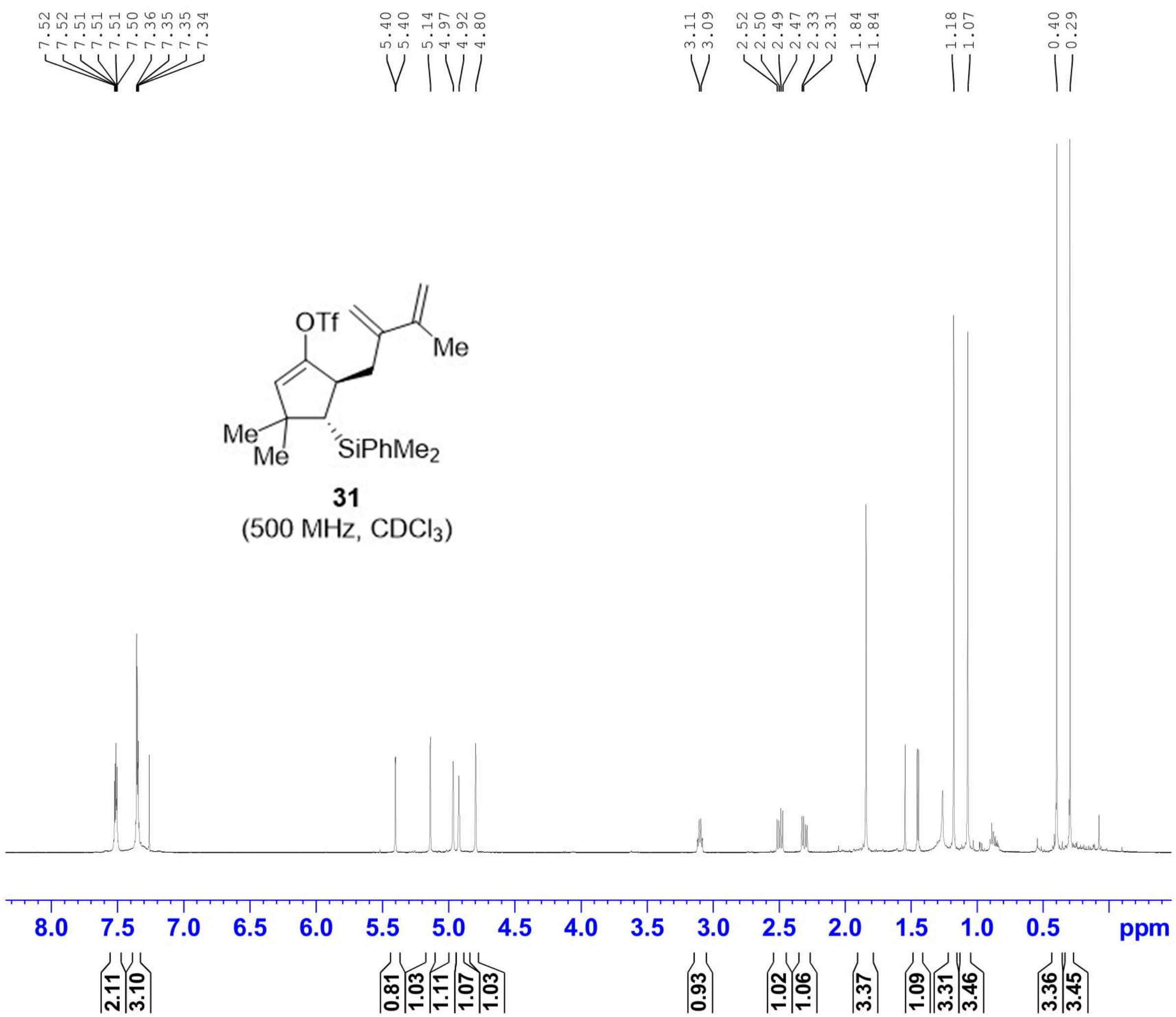



```
Current Data Parameters
NAME            yh-7-58-1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20191017
Time                21.21
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      6
DS                      0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 196.79
DW                 50.000 usec
DE                  10.00 usec
TE                  297.0 K
D1            2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                   9.90 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                  65536
SF           500.1300134 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



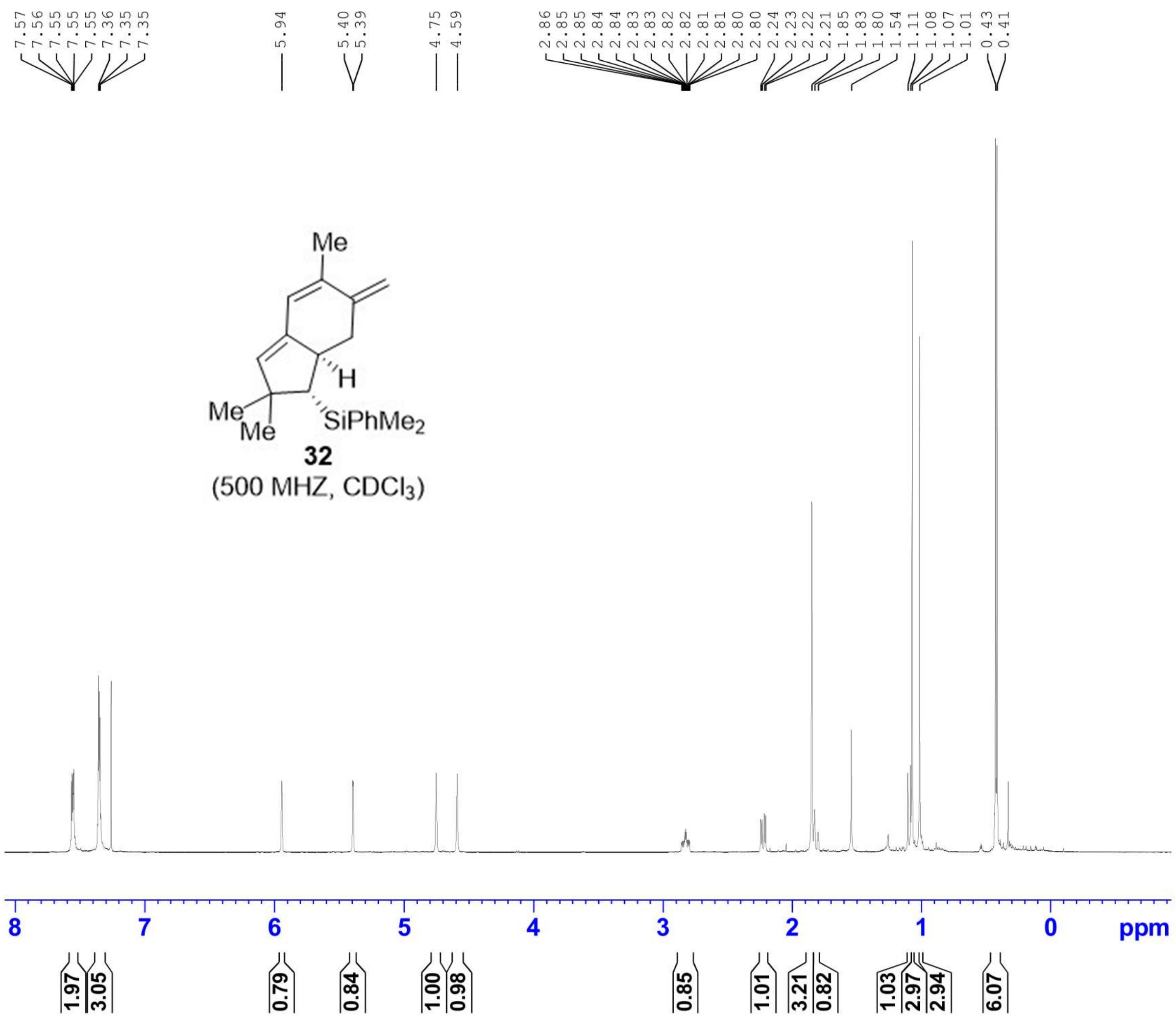
31
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME             yh-7-60
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191018
Time               21.53
INSTRUM            spect
PROBHD   5 mm PATXI 1H/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     6
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 71.78
DW                50.000 usec
DE                 10.00 usec
TE                 297.1 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                  1H
P1                  9.90 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                 65536
SF           500.1300133 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

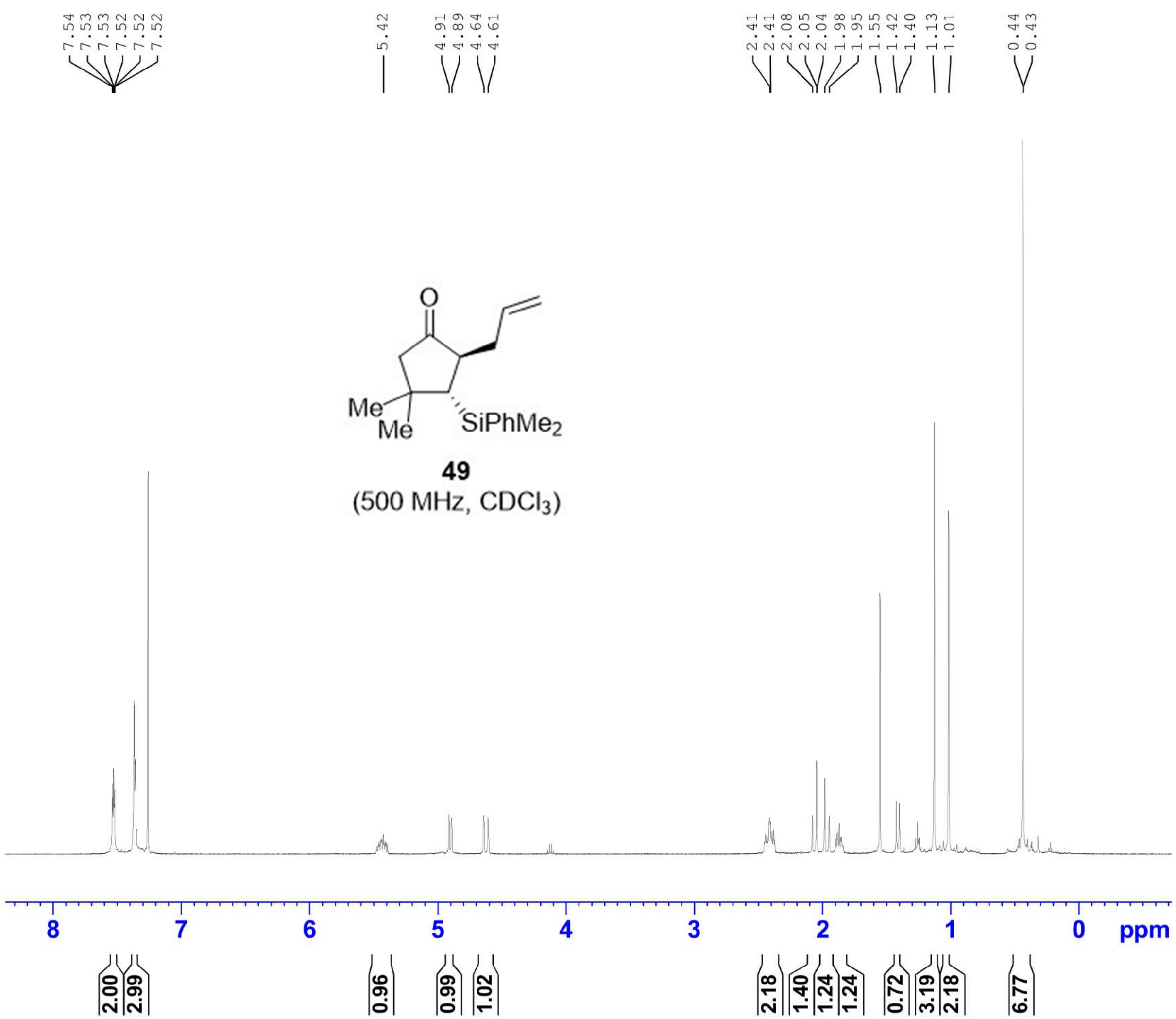



```
Current Data Parameters
NAME              yh-7-62
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20191020
Time                18.23
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      6
DS                      0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                 141.13
DW                 50.000 usec
DE                  10.00 usec
TE                  297.1 K
D1            2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                   9.90 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                  65536
SF           500.1300133 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



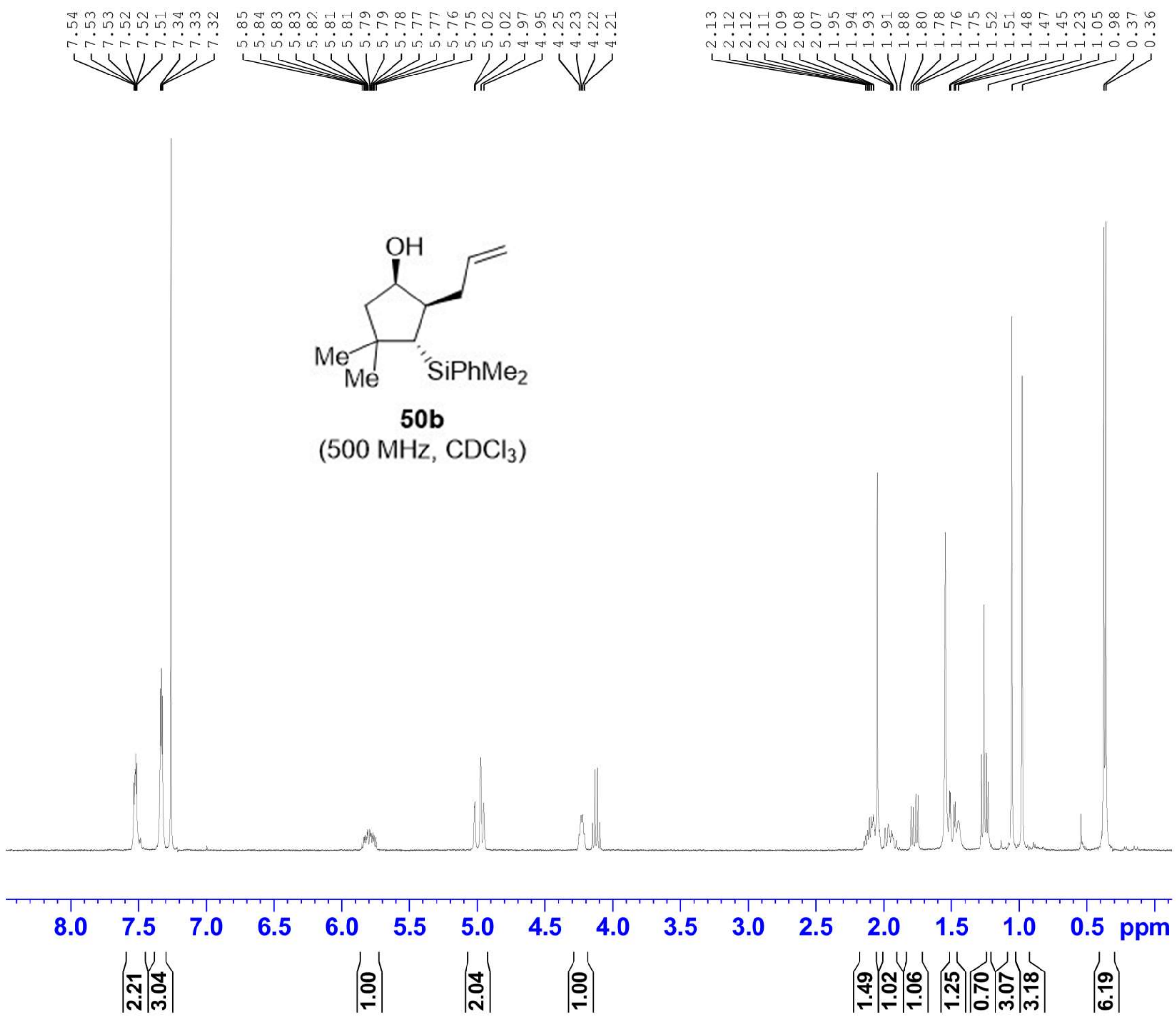
49
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME               yh-7-77
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20191108
Time                 17.05
INSTRUM              spect
PROBHD    5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       4
DS                       0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                  196.79
DW                  50.000 usec
DE                   10.00 usec
TE                   294.3 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                     1H
P1                     9.90 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                   65536
SF          500.1300134 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

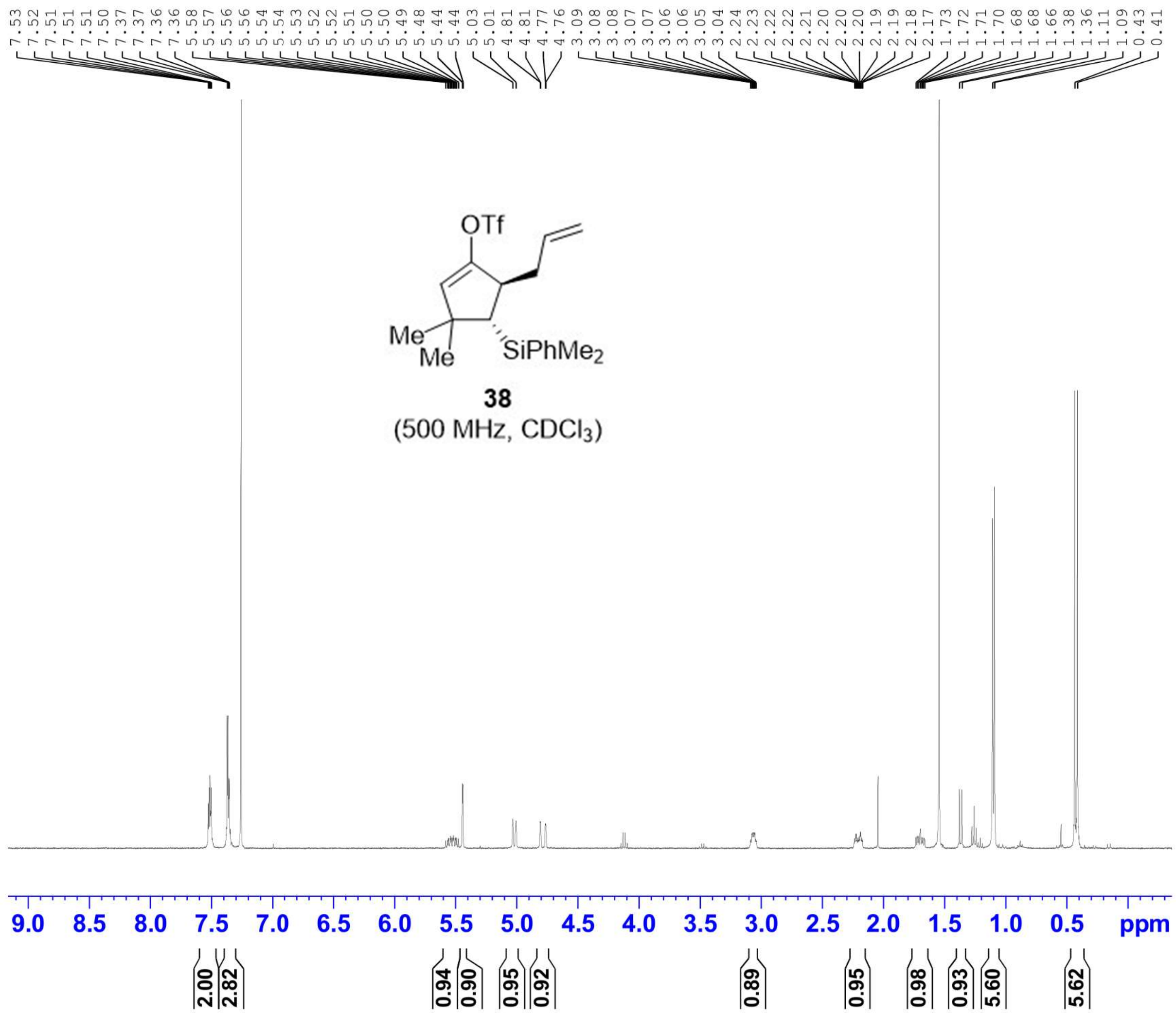


50b
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME             yh-8-62-1
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200704
Time                 17.23 h
INSTRUM              spect
PROBHD   Z140678_0010 (
PULPROG               zg30
TD                   38460
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               6410.256 Hz
FIDRES            0.333347 Hz
AQ               2.9998801 sec
RG                   211.9
DW                  78.000 usec
DE                    6.50 usec
TE                   297.1 K
D1              1.50000000 sec
TD0                      1
SFO1           400.1528010 MHz
NUC1                    1H
P0                    2.28 usec
P1                    6.85 usec
PLW1           31.98900032 W

F2 - Processing parameters
SI                  131072
SF             400.1500096 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



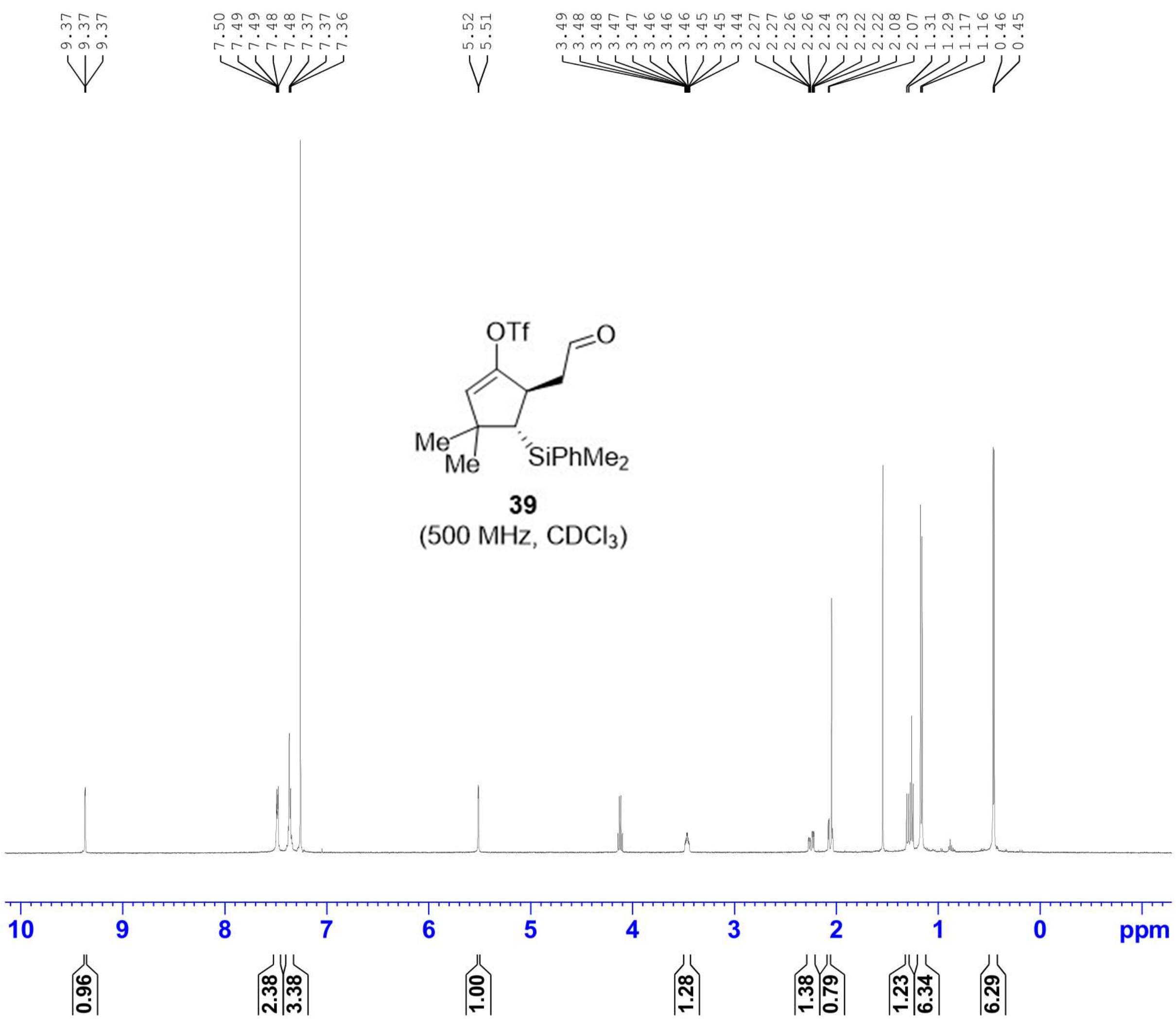
38

(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME            yh-8-119
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200810
Time               20.29 h
INSTRUM            spect
PROBHD   Z140678_0010 (
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             6410.256 Hz
FIDRES          0.333347 Hz
AQ             2.9998801 sec
RG                 211.9
DW                78.000 usec
DE                  6.50 usec
TE                 297.2 K
D1            1.50000000 sec
TD0                    1
SFO1         400.1528010 MHz
NUC1                  1H
P0                  2.28 usec
P1                  6.85 usec
PLW1         31.98900032 W

F2 - Processing parameters
SI                131072
SF           400.1500098 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

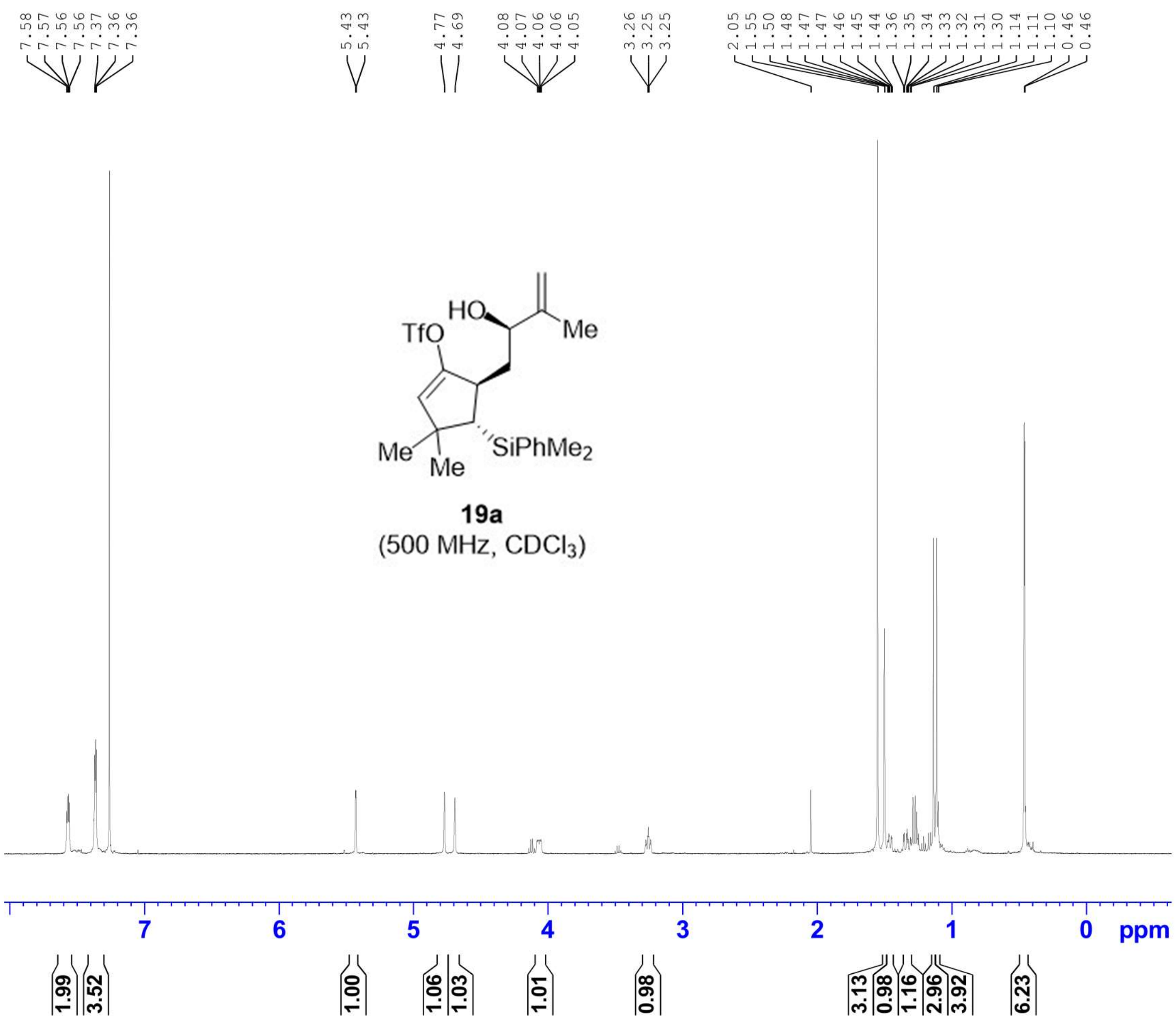


39
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME        yh-7-117-r-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191208
Time_              16.28 h
INSTRUM            spect
PROBHD   Z113652_0187 (
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     6
DS                     0
SWH            10000.000 Hz
FIDRES          0.333344 Hz
AQ             2.9999001 sec
RG                178.15
DW                50.000 usec
DE                  6.50 usec
TE                 295.2 K
D1            4.00000000 sec
TD0                    1
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700123 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



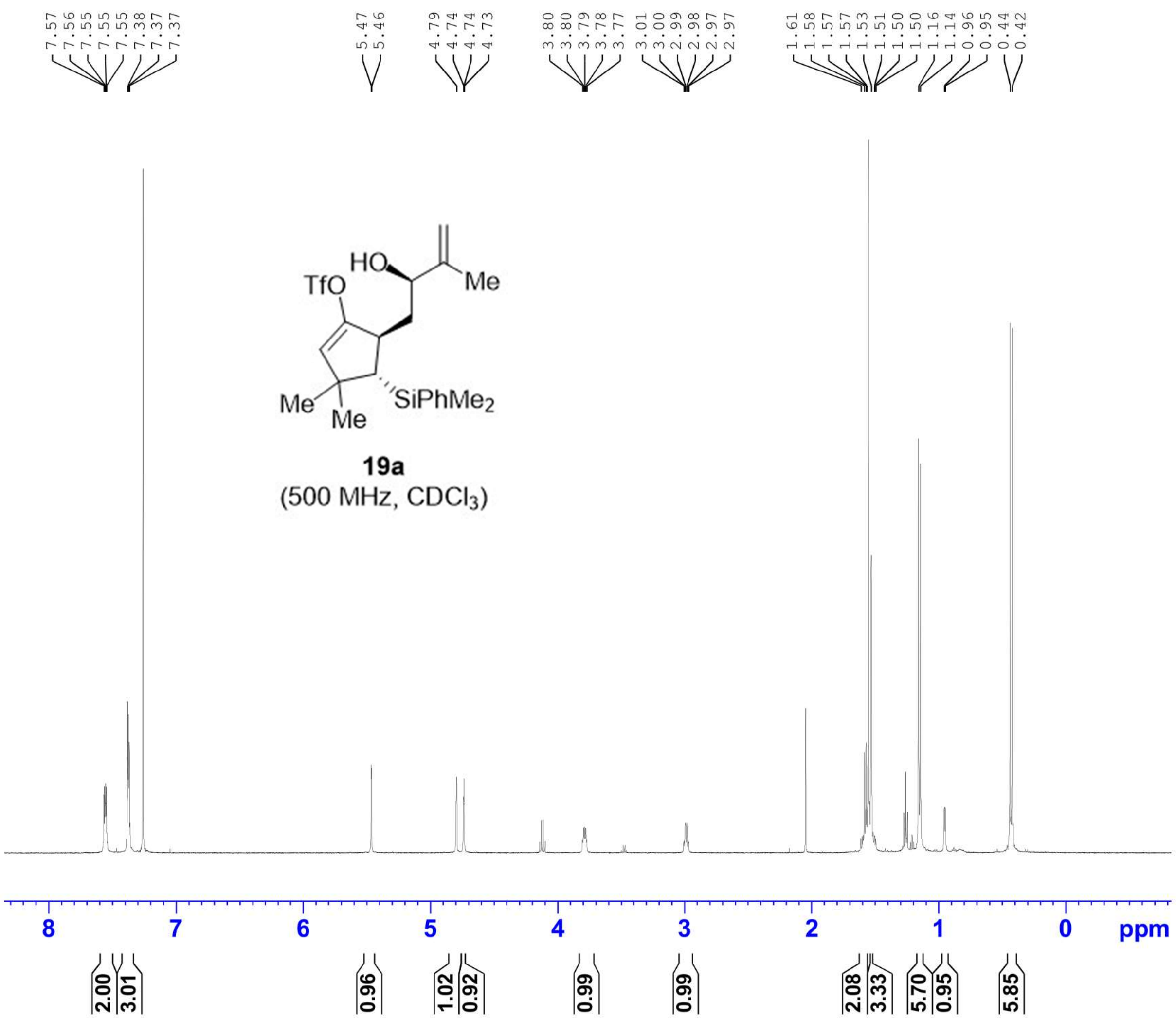
19a
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME              yh-7-94-1
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20191124
Time                  19.54
INSTRUM               spect
PROBHD   5 mm PATXI 1H/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        6
DS                        0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                   196.79
DW               50.000 usec
DE                10.00 usec
TE                  294.6 K
D1           4.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                     1H
P1                 3.30 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                    65536
SF          500.1300134 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```



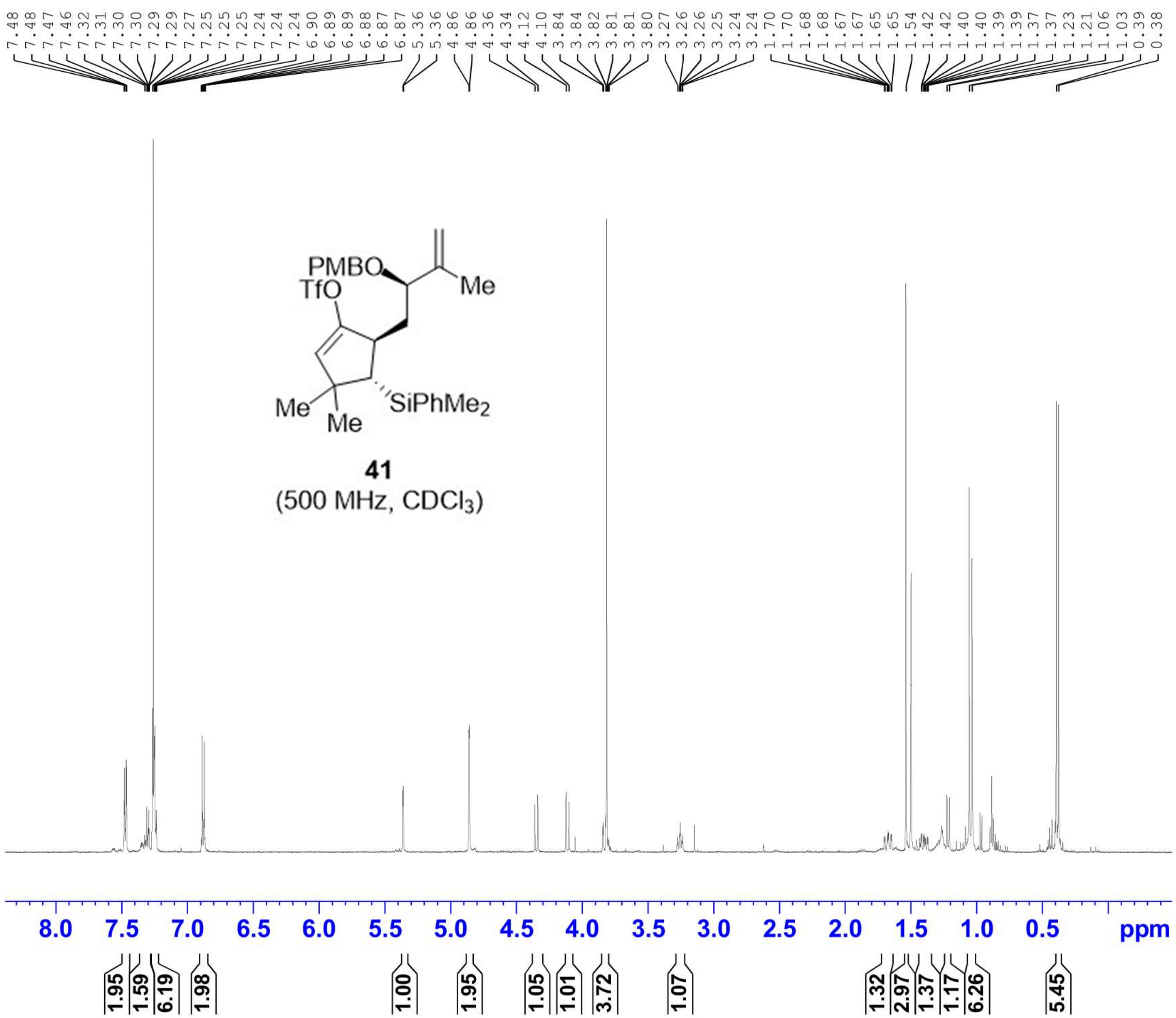
19a
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME            yh-7-94-2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20191124
Time                19.58
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      6
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                 196.79
DW                 50.000 usec
DE                  10.00 usec
TE                  294.7 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                   3.30 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                  65536
SF            500.1300135 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

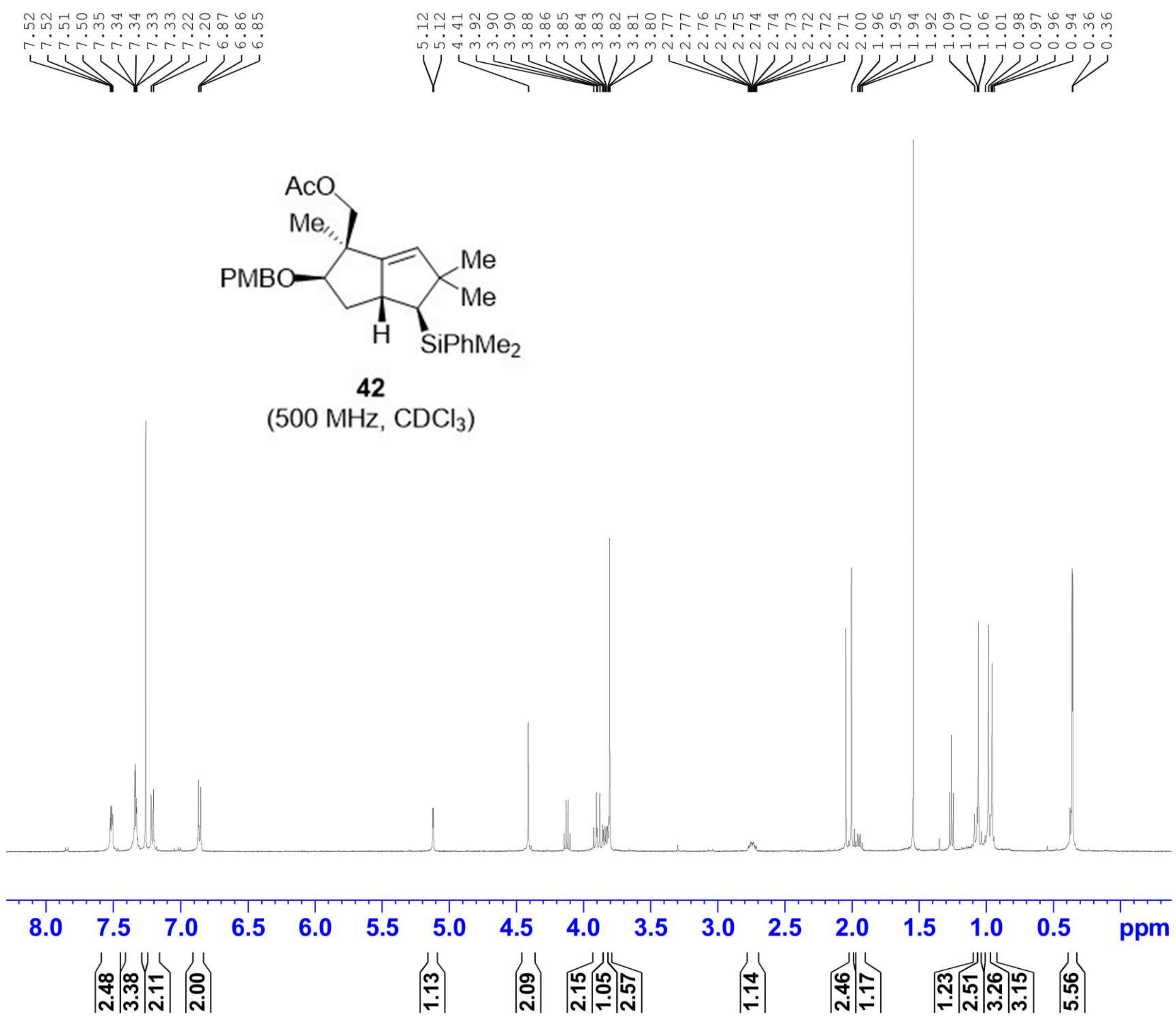


41
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME            yh-10-106
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210806
Time                17.17 h
INSTRUM             spect
PROBHD   Z800701_0094 (
PULPROG              zg30
TD                  48076
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8012.820 Hz
FIDRES           0.333340 Hz
AQ              2.9999423 sec
RG                 196.79
DW                 62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.50000000 sec
TD0                     1
SFO1         500.1335009 MHz
NUC1                   1H
P0                   3.37 usec
P1                  10.10 usec
PLW1          25.00300026 W

F2 - Processing parameters
SI                 131072
SF           500.1300130 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

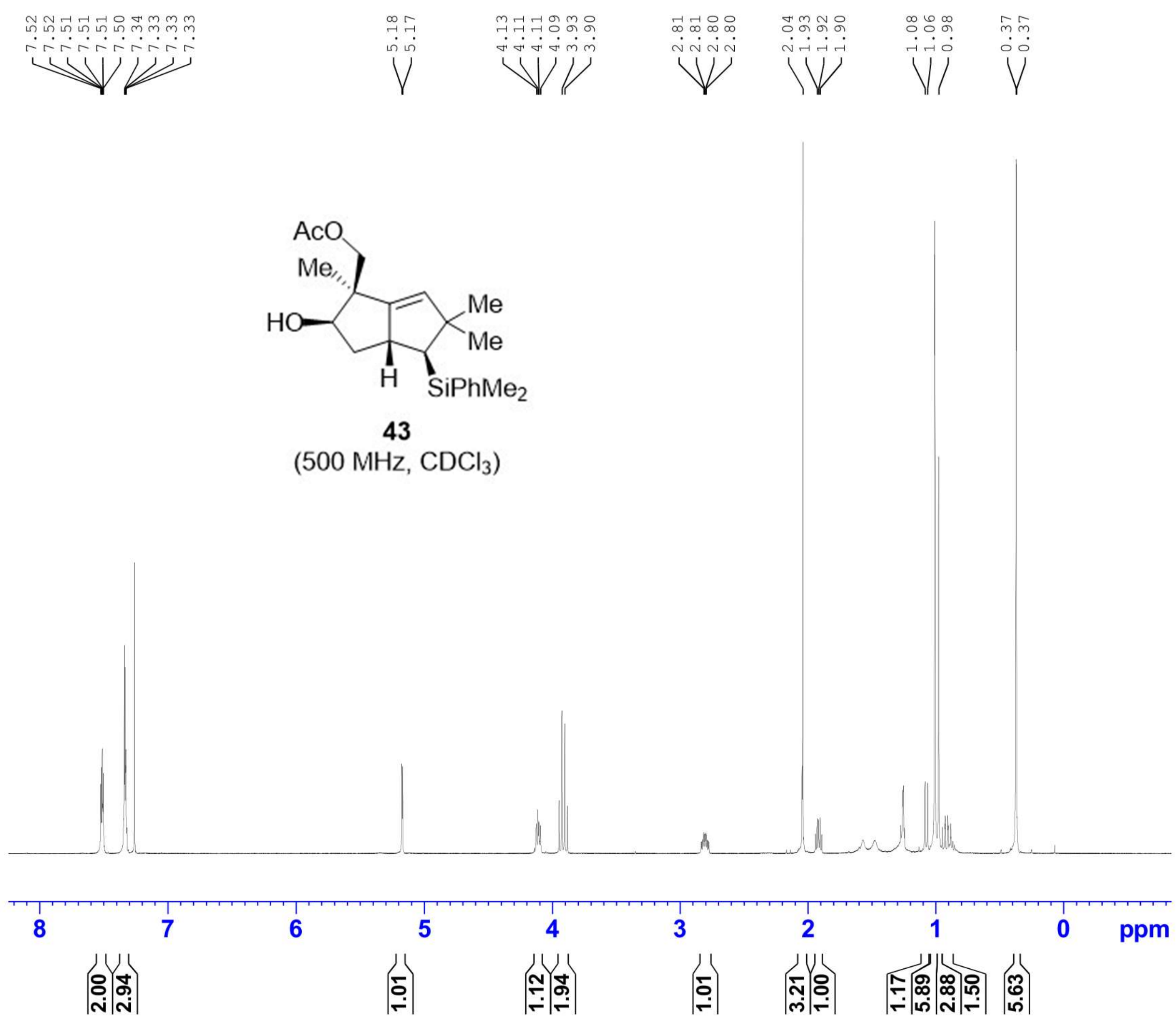


42
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME          yh-10-116
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210824
Time              18.04 h
INSTRUM           spect
PROBHD   Z113652_0187 (
PULPROG            zg30
TD                48076
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8012.820 Hz
FIDRES         0.333340 Hz
AQ            2.9999423 sec
RG               105.66
DW               62.400 usec
DE                 6.50 usec
TE                298.1 K
D1           1.50000000 sec
TD0                   1
SFO1        499.8734991 MHz
NUC1                 1H
P0                 3.20 usec
P1                 9.60 usec
PLW1        20.98900032 W

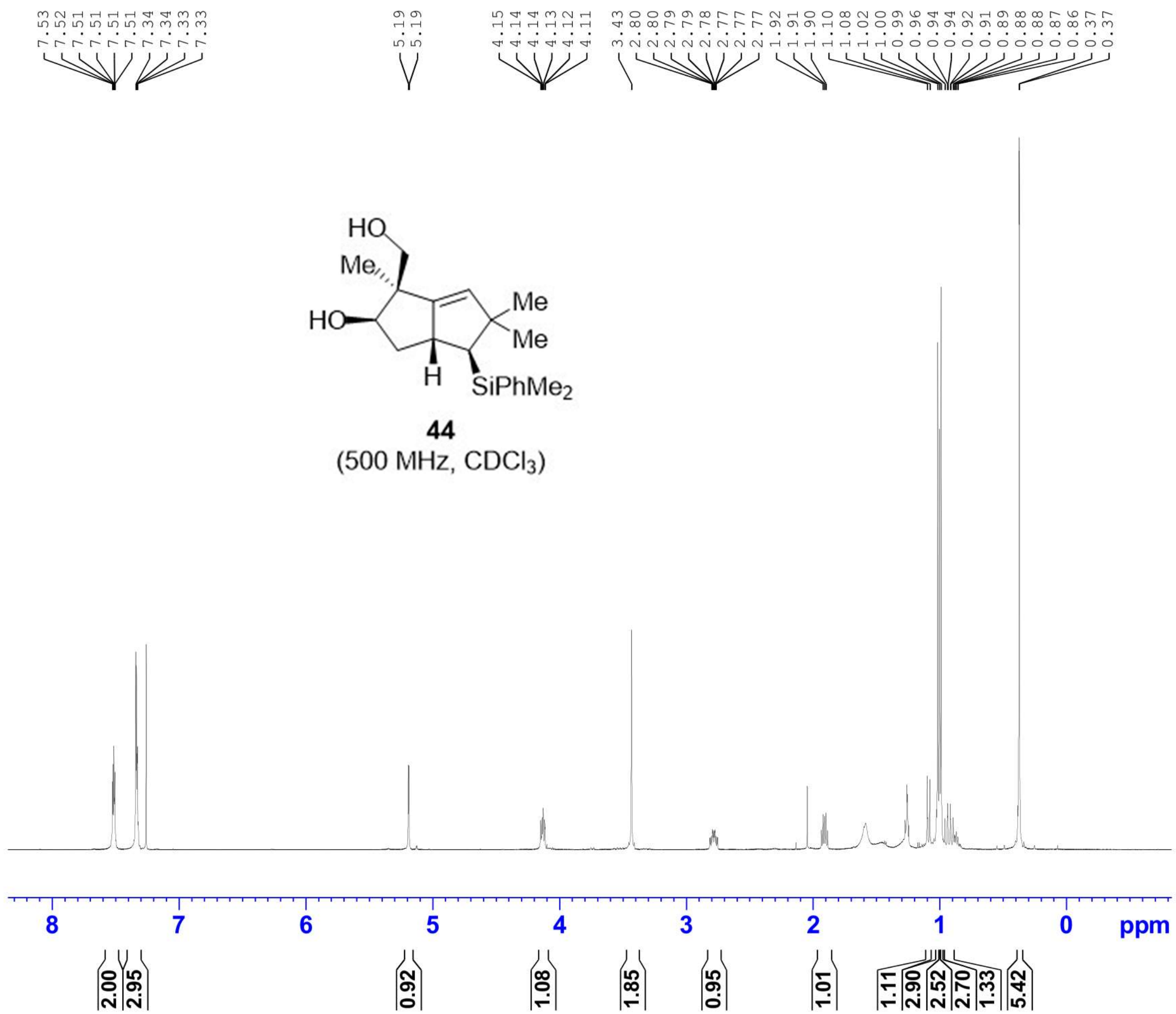
F2 - Processing parameters
SI               131072
SF          499.8700124 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




```
Current Data Parameters
NAME              yh-7-110
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20191205
Time                 17.30 h
INSTRUM              spect
PROBHD   Z113652_0187 (
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       6
DS                       0
SWH              10000.000 Hz
FIDRES            0.333344 Hz
AQ               2.9999001 sec
RG                   86.16
DW                  50.000 usec
DE                    6.50 usec
TE                   295.0 K
D1              4.00000000 sec
TD0                      1
SFO1           499.8730869 MHz
NUC1                    1H
P1                    3.58 usec
PLW1           18.25000000 W

F2 - Processing parameters
SI                   65536
SF             499.8700124 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

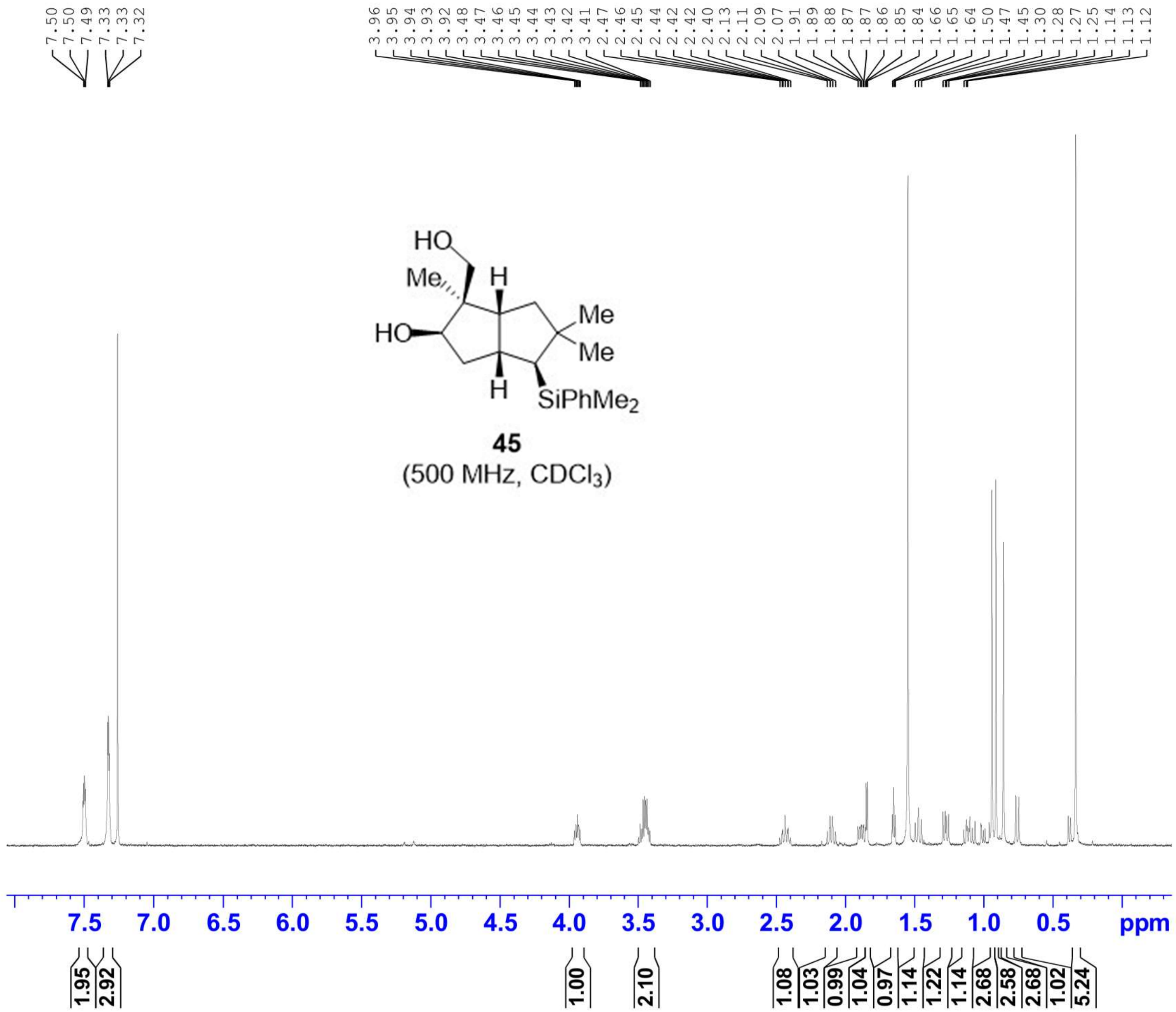


44
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME          yh-7-148-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200122
Time               21.20 h
INSTRUM            spect
PROBHD   Z113652_0187 (
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES          0.333344 Hz
AQ             2.9999001 sec
RG                105.66
DW                50.000 usec
DE                  6.50 usec
TE                 297.0 K
D1            4.00000000 sec
TD0                    1
SFO1         499.8730869 MHz
NUC1                  1H
P1                  3.58 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700125 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

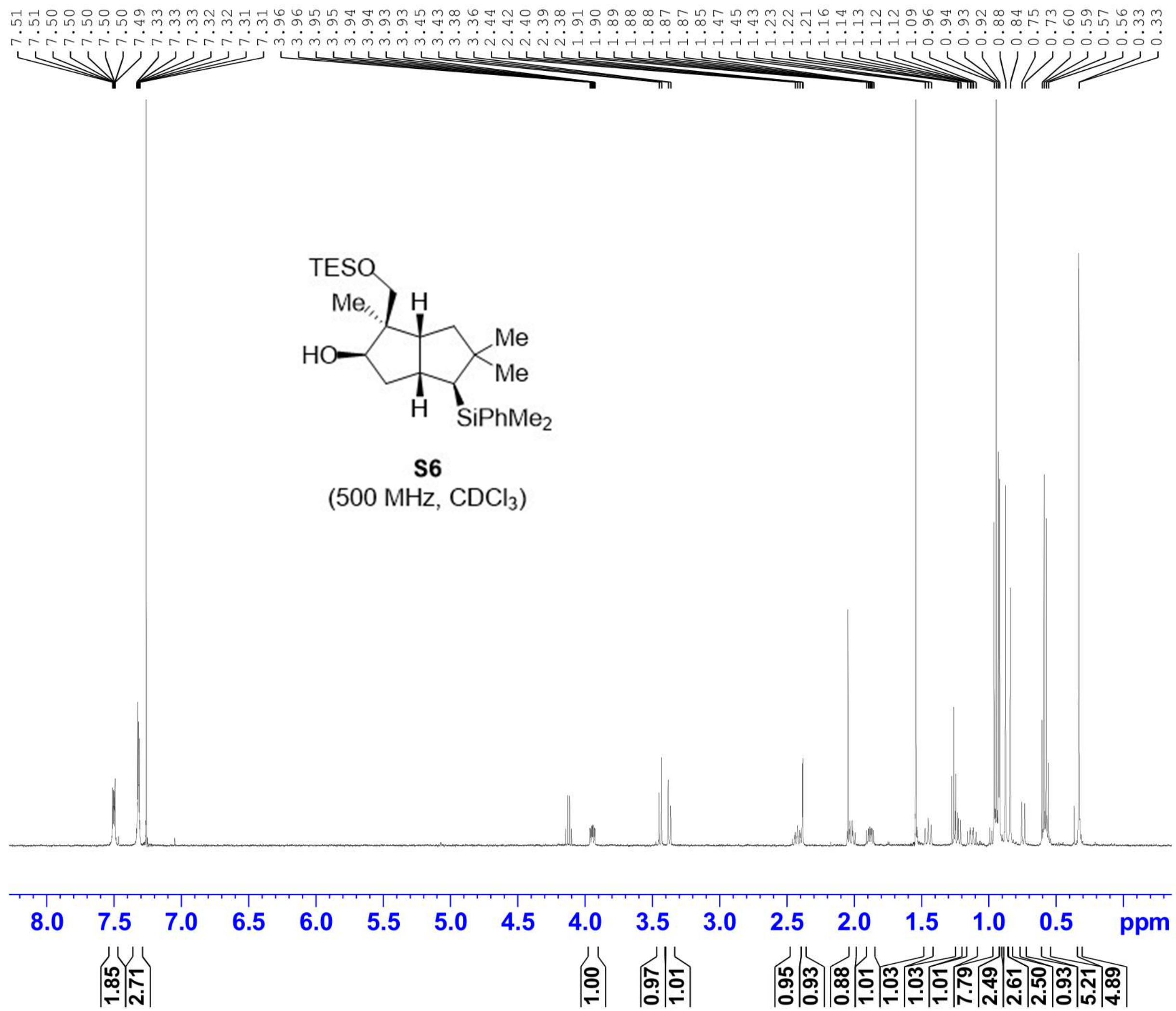


45
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME      yh-10-122-1-crude-2
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_             20210831
Time_                11.10 h
INSTRUM              spect
PROBHD   Z800701_0094 (
PULPROG               zg30
TD                   48076
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               8012.820 Hz
FIDRES            0.333340 Hz
AQ               2.9999423 sec
RG                  196.79
DW                  62.400 usec
DE                    6.50 usec
TE                   298.1 K
D1              1.50000000 sec
TD0                      1
SFO1           500.1335009 MHz
NUC1                    1H
P0                    3.37 usec
P1                   10.10 usec
PLW1           25.00300026 W

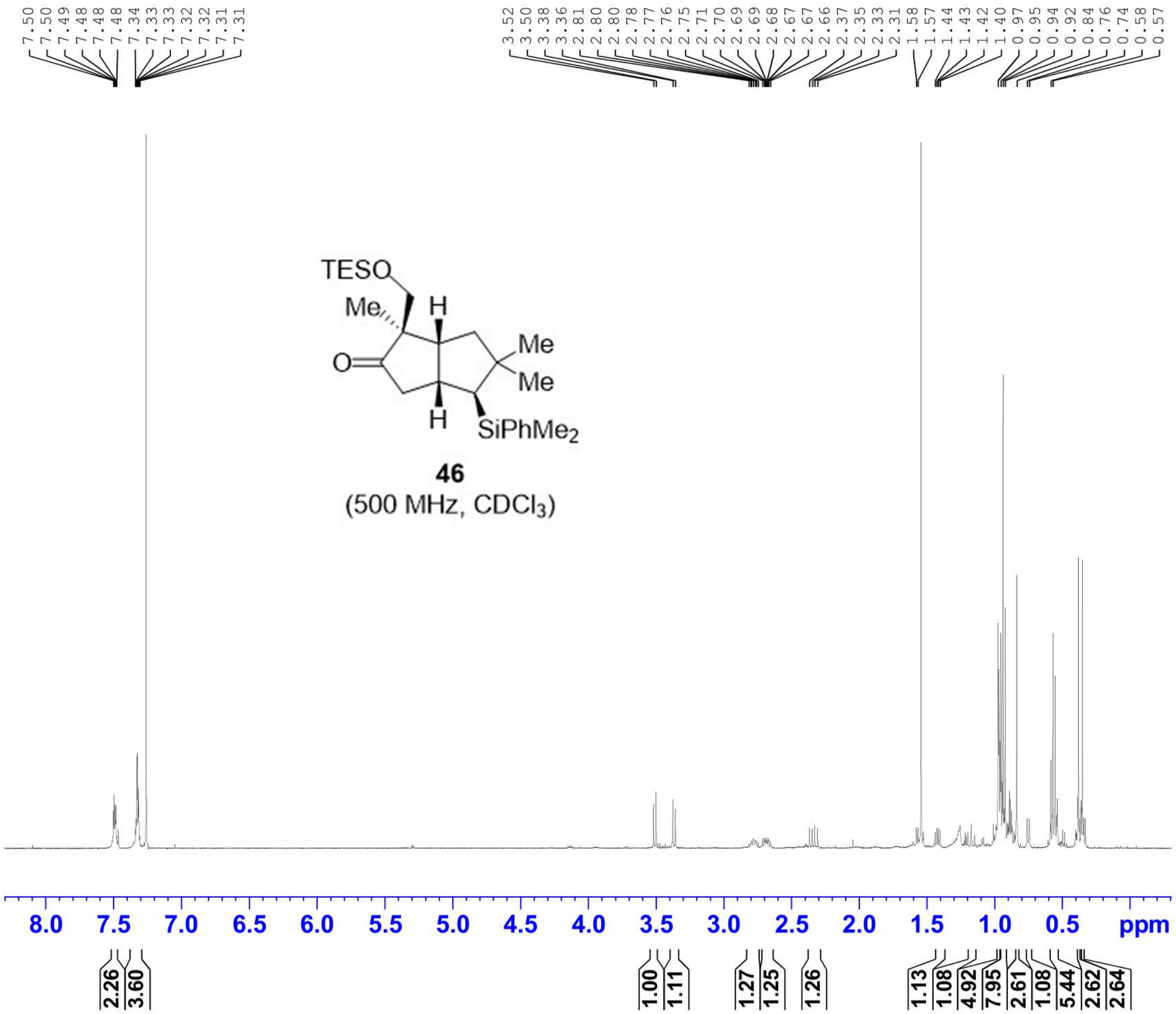
F2 - Processing parameters
SI                  131072
SF             500.1300128 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```




```
Current Data Parameters
NAME          yh-10-123-2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210901
Time_               16.29 h
INSTRUM             spect
PROBHD   Z800701_0094 (
PULPROG              zg30
TD                  48076
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8012.820 Hz
FIDRES           0.333340 Hz
AQ              2.9999423 sec
RG                 196.79
DW                 62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.50000000 sec
TD0                     1
SFO1          500.1335009 MHz
NUC1                   1H
P0                   3.37 usec
P1                  10.10 usec
PLW1          25.00300026 W

F2 - Processing parameters
SI                 131072
SF            500.1300126 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

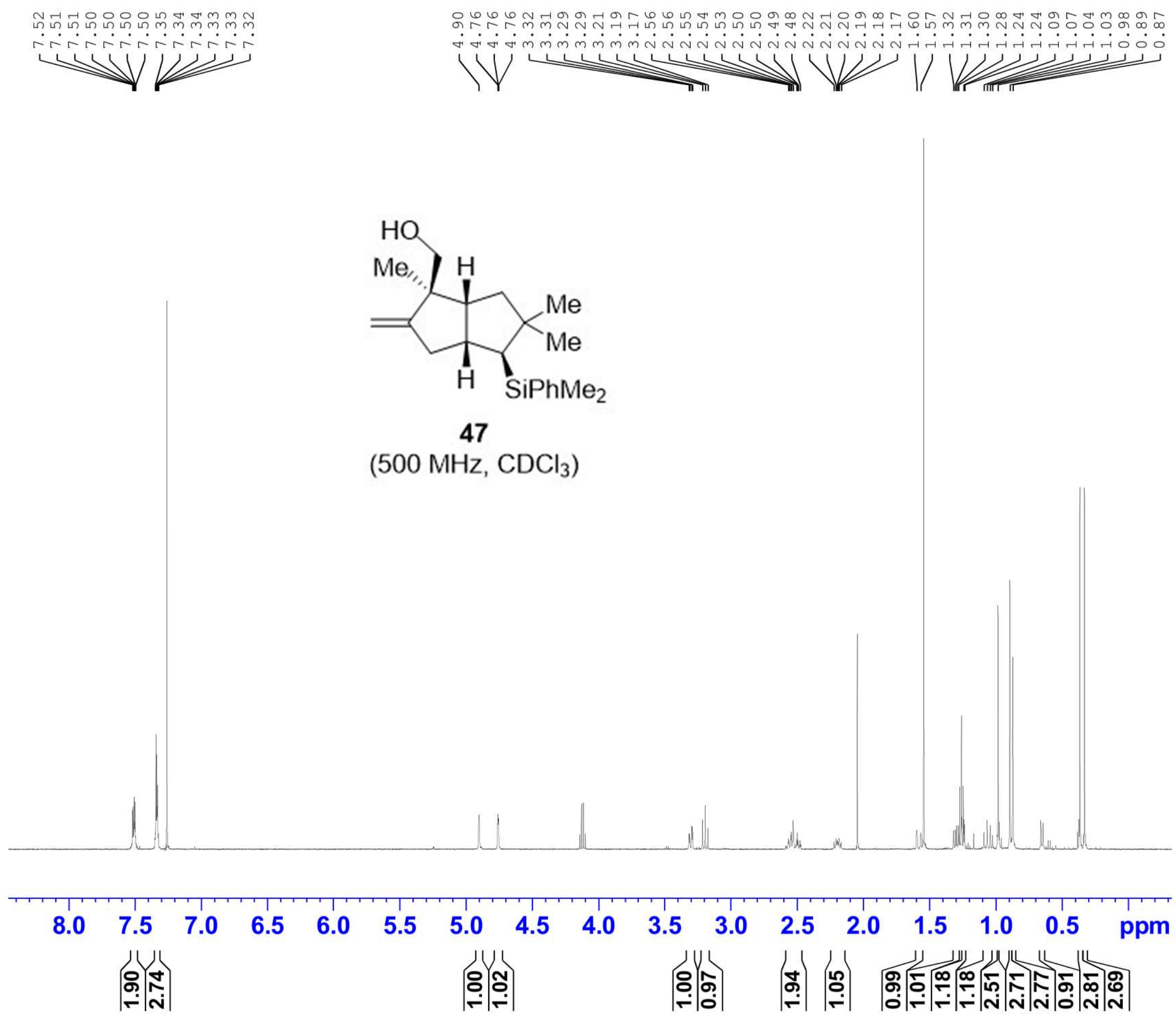


46
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME              yh-9-30
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20201012
Time                23.15 h
INSTRUM             spect
PROBHD   Z113652_0187 (
PULPROG              zg30
TD                  48076
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8012.820 Hz
FIDRES           0.333340 Hz
AQ              2.9999423 sec
RG                 189.89
DW                 62.400 usec
DE                   6.50 usec
TE                  297.1 K
D1             1.50000000 sec
TD0                     1
SFO1          499.8734991 MHz
NUC1                   1H
P0                   3.03 usec
P1                   9.10 usec
PLW1          23.98800087 W

F2 - Processing parameters
SI                 131072
SF            499.8700123 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



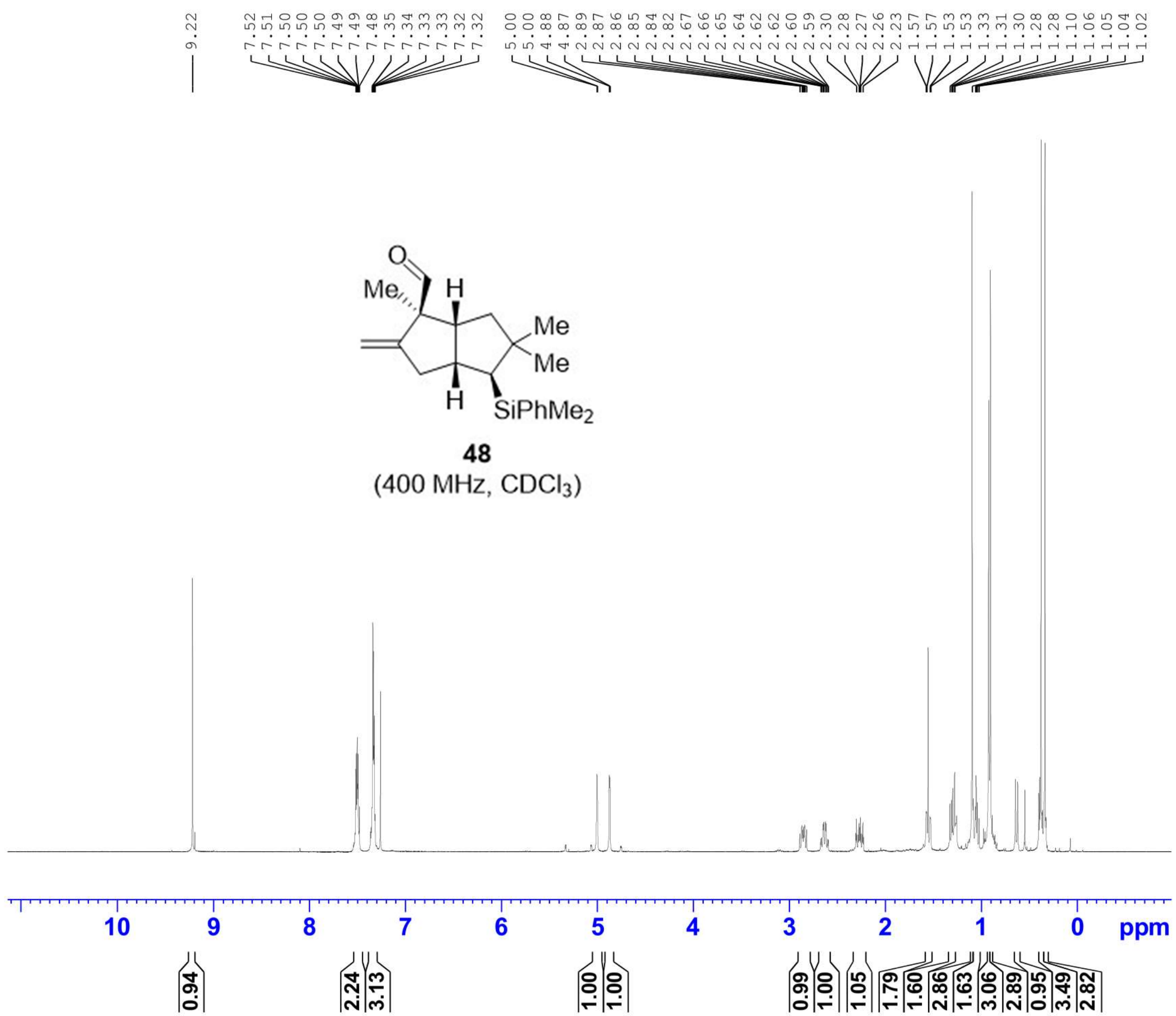
47
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME            yh-10-126
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20211019
Time                20.43 h
INSTRUM             spect
PROBHD   Z800701_0094 (
PULPROG              zg30
TD                  48076
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8012.820 Hz
FIDRES           0.333340 Hz
AQ              2.9999423 sec
RG                 196.79
DW                 62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.50000000 sec
TD0                     1
SFO1          500.1335009 MHz
NUC1                   1H
P0                   3.37 usec
P1                  10.10 usec
PLW1          25.00300026 W

F2 - Processing parameters
SI                 131072
SF            500.1300120 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

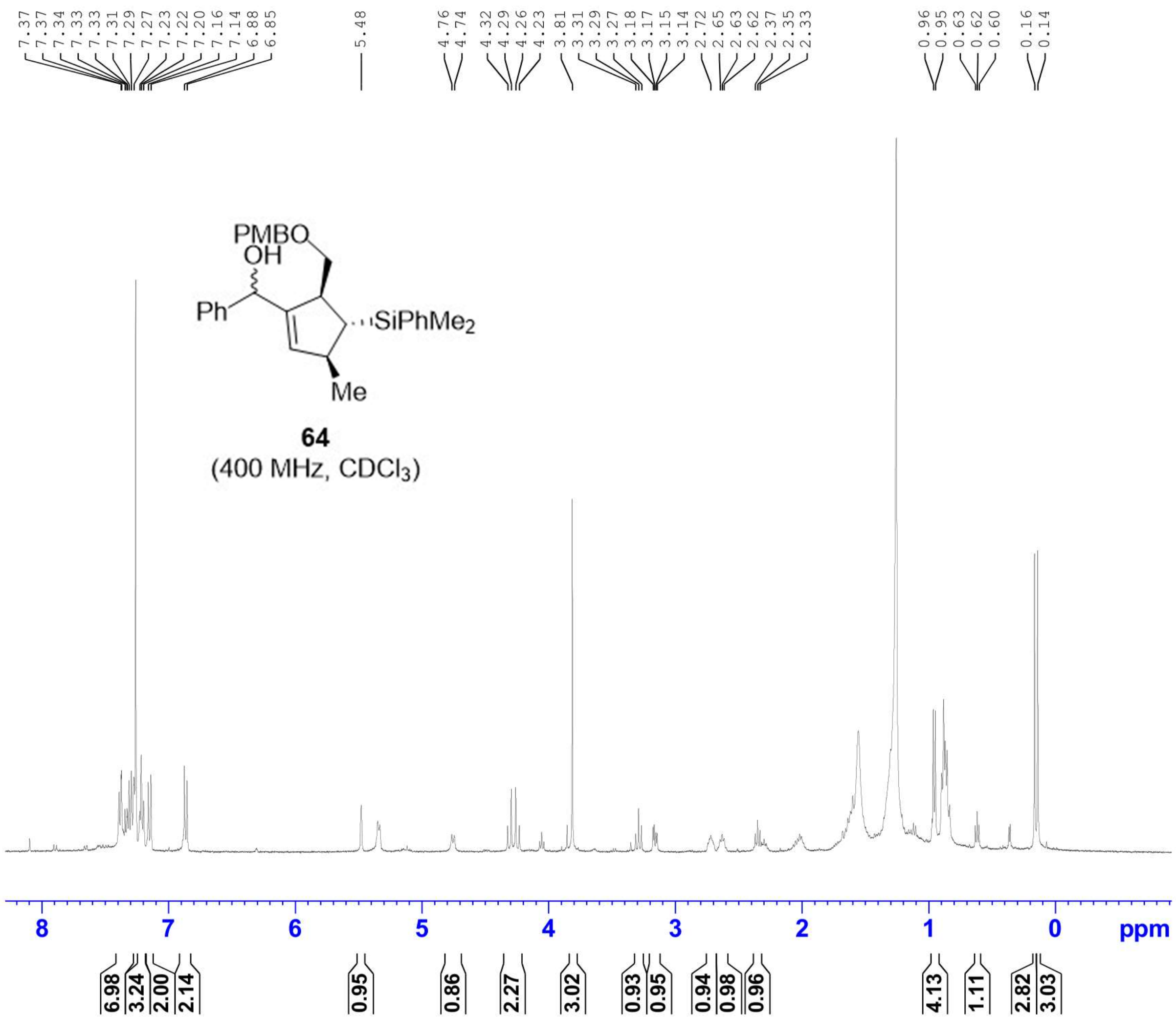
48
(400 MHz, $CDCl_3$)




```
Current Data Parameters
NAME              yh-9-47
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20201022
Time                 1.41 h
INSTRUM             spect
PROBHD   Z140678_0010 (
PULPROG              zg30
TD                  38460
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              6410.256 Hz
FIDRES           0.333347 Hz
AQ              2.9998801 sec
RG                 103.18
DW                 78.000 usec
DE                   6.50 usec
TE                  297.2 K
D1             1.50000000 sec
TD0                     1
SFO1          400.1528010 MHz
NUC1                   1H
P0                   2.28 usec
P1                   6.85 usec
PLW1          31.98900032 W

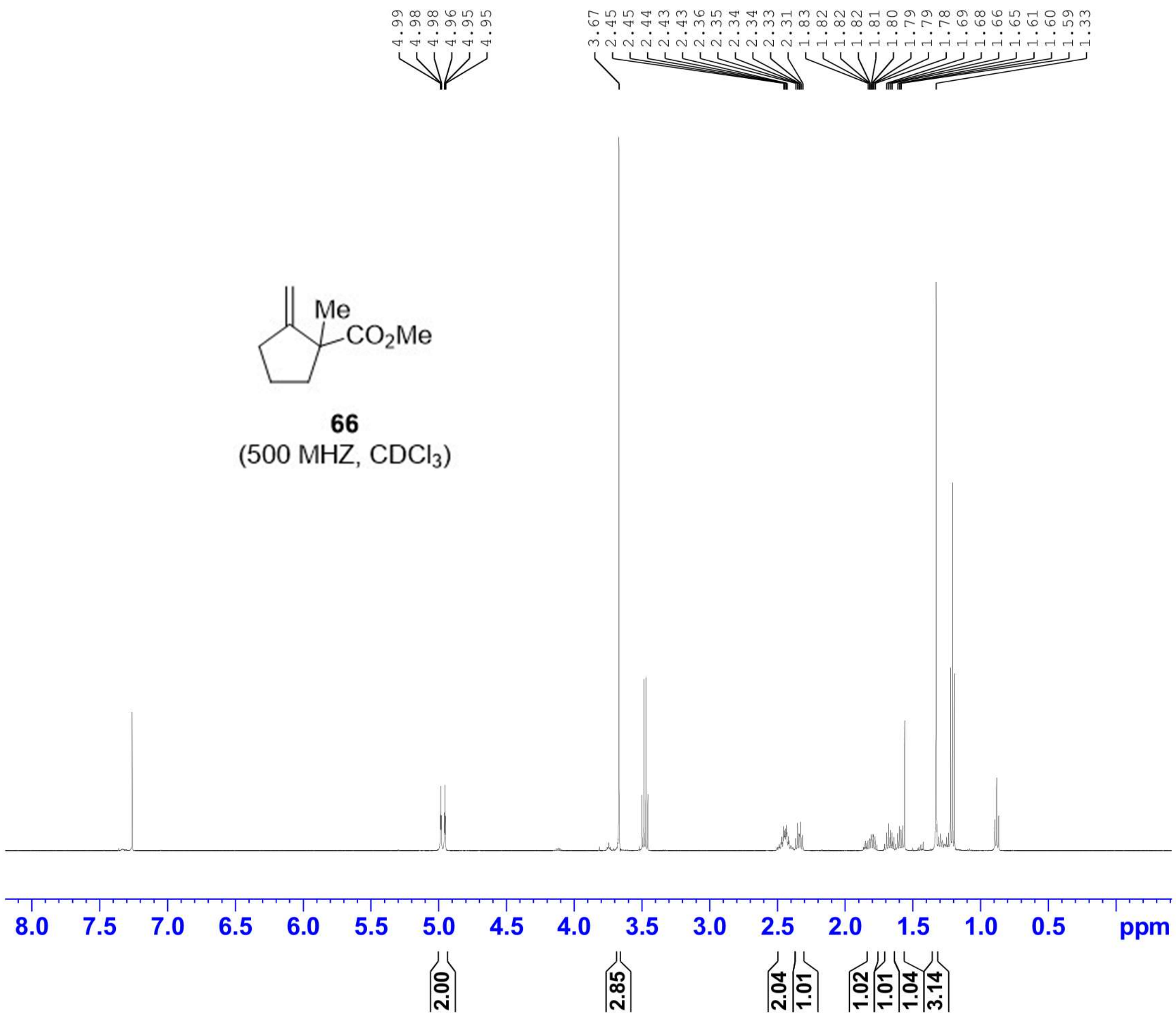
F2 - Processing parameters
SI                 131072
SF            400.1500096 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME            yh-10-5-a
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20211020
Time                18.51 h
INSTRUM             spect
PROBHD   Z140678_0010 (
PULPROG              zg30
TD                  38460
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              6410.256 Hz
FIDRES           0.333347 Hz
AQ              2.9998801 sec
RG                 165.16
DW                 78.000 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.50000000 sec
TD0                     1
SFO1          400.1528010 MHz
NUC1                   1H
P0                   2.28 usec
P1                   6.85 usec
PLW1          31.98900032 W

F2 - Processing parameters
SI                 131072
SF            400.1500099 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



66
(500 MHZ, $CDCl_3$)

Current Data Parameters

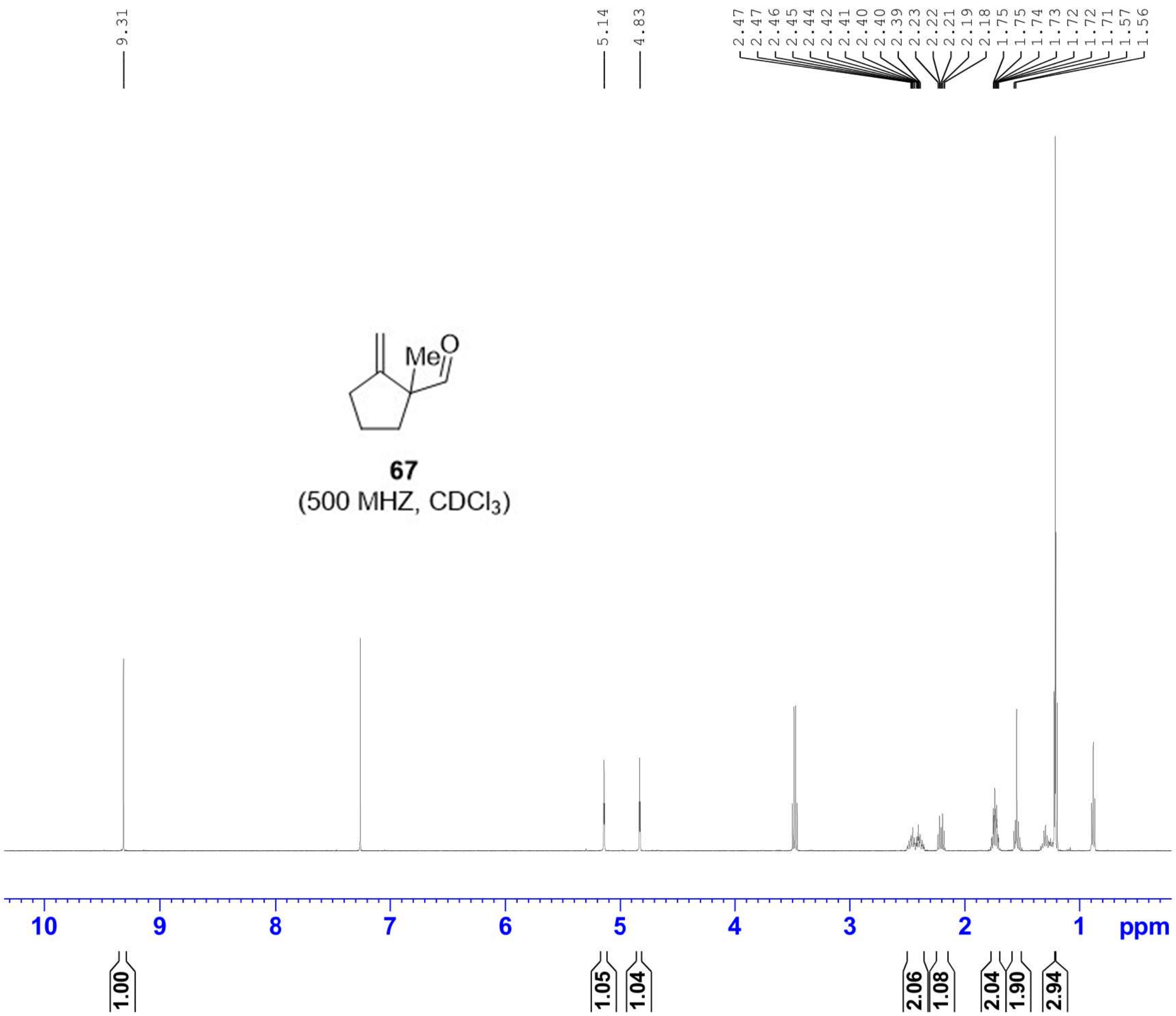
NAME	yh-10-41
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20210512
Time	14.19 h
INSTRUM	spect
PROBHD	Z800701_0094 (
PULPROG	zg30
TD	48076
SOLVENT	CDCl3
NS	8
DS	0
SWH	8012.820 Hz
FIDRES	0.333340 Hz
AQ	2.9999423 sec
RG	196.79
DW	62.400 usec
DE	6.50 usec
TE	298.2 K
D1	1.50000000 sec
TD0	1
SFO1	500.1335009 MHz
NUC1	1H
P0	3.37 usec
P1	10.10 usec
PLW1	25.00300026 W

F2 - Processing parameters

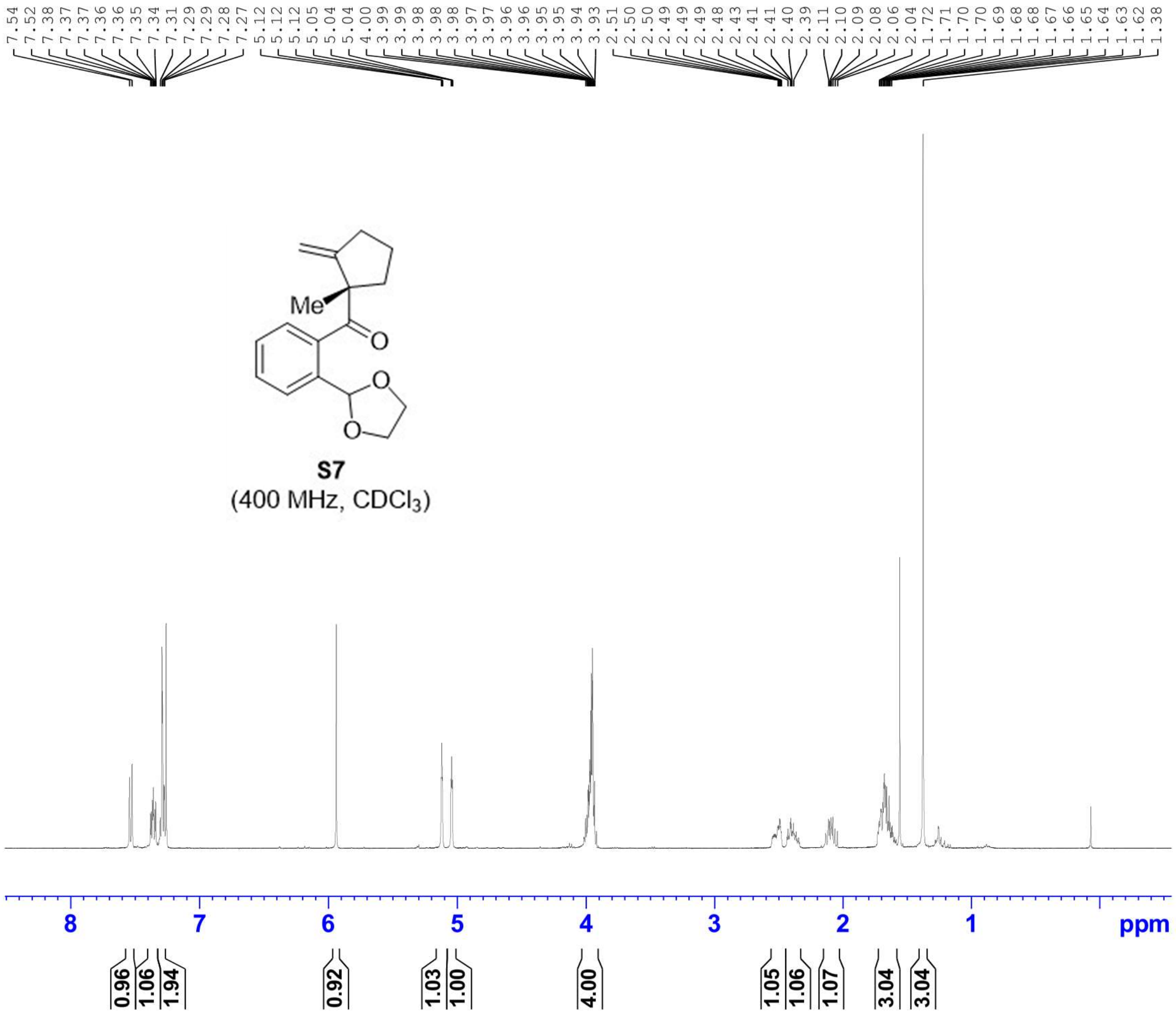
SI	131072
SF	500.1300125 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00




```
Current Data Parameters
NAME            yh-10-44
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210514
Time_              12.56 h
INSTRUM            spect
PROBHD    Z800701_0094 (
PULPROG             zg30
TD                 48076
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8012.820 Hz
FIDRES          0.333340 Hz
AQ             2.9999423 sec
RG                196.79
DW                62.400 usec
DE                  6.50 usec
TE                 298.1 K
D1            1.50000000 sec
TD0                    1
SFO1         500.1335009 MHz
NUC1                  1H
P0                  3.37 usec
P1                 10.10 usec
PLW1         25.00300026 W

F2 - Processing parameters
SI                131072
SF           500.1300125 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

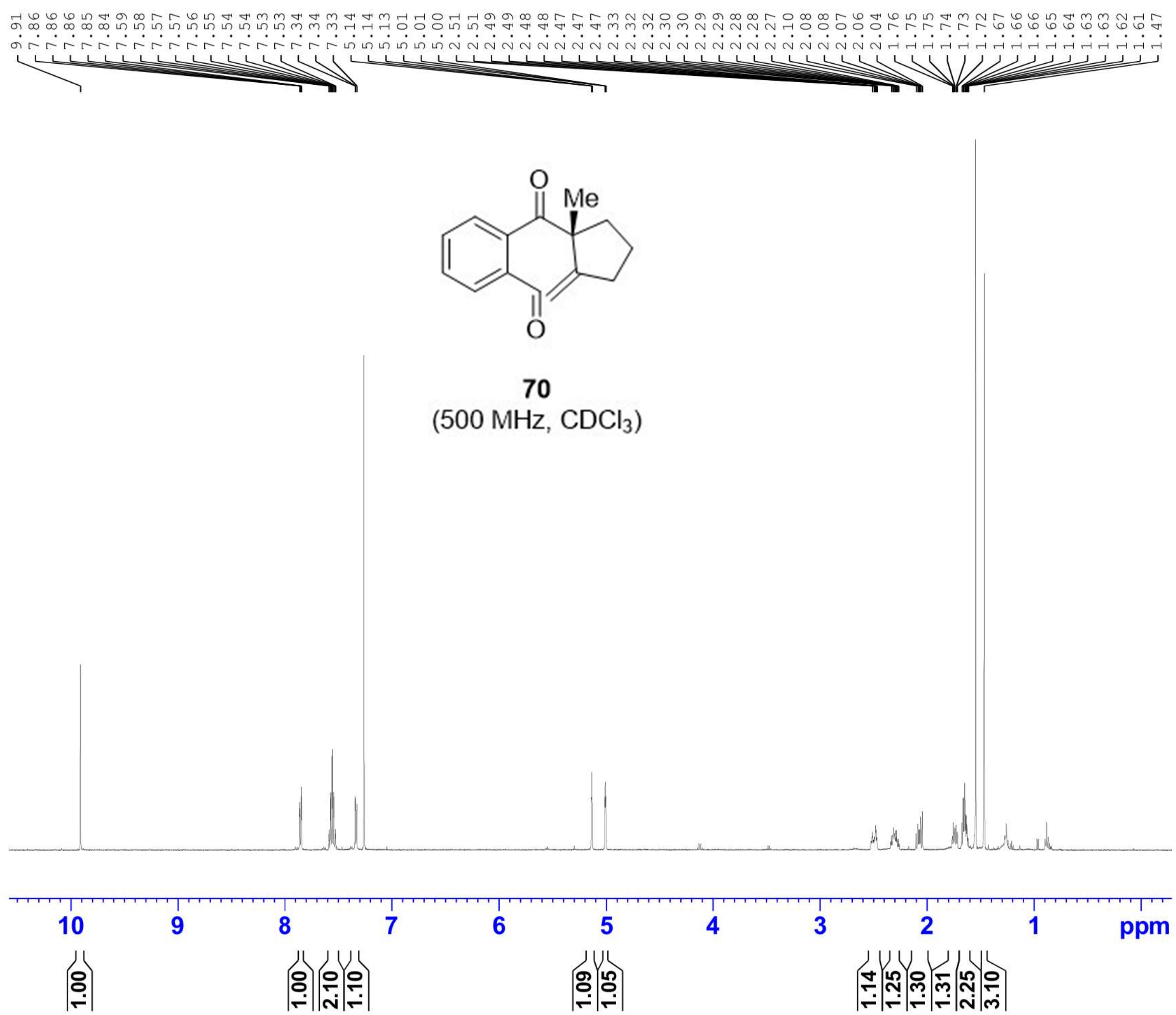


S7
(400 MHz, $CDCl_3$)

```
Current Data Parameters
NAME              yh-10-47
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210518
Time                 14.35 h
INSTRUM              spect
PROBHD   Z140678_0010 (
PULPROG               zg30
TD                   38460
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               6410.256 Hz
FIDRES            0.333347 Hz
AQ               2.9998801 sec
RG                  143.42
DW                  78.000 usec
DE                    6.50 usec
TE                   298.2 K
D1              1.50000000 sec
TD0                      1
SFO1           400.1528010 MHz
NUC1                    1H
P0                    2.28 usec
P1                    6.85 usec
PLW1           31.98900032 W

F2 - Processing parameters
SI                  131072
SF             400.1500097 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

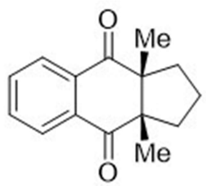


70
(500 MHz, $CDCl_3$)

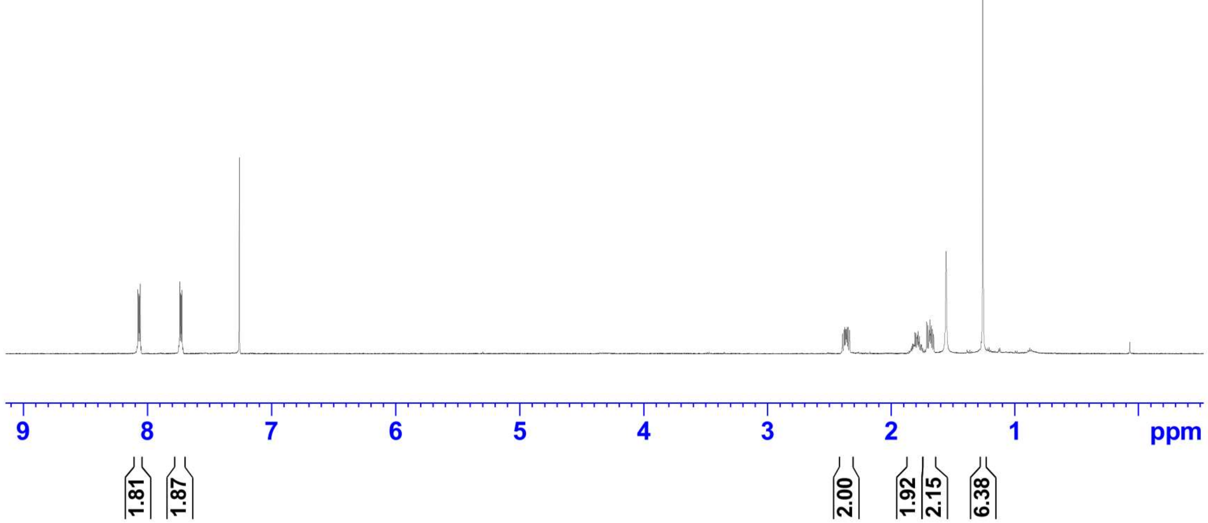
```
Current Data Parameters
NAME             yh-10-49
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210520
Time                11.26 h
INSTRUM             spect
PROBHD   Z800701_0094 (
PULPROG              zg30
TD                  48076
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8012.820 Hz
FIDRES           0.333340 Hz
AQ              2.9999423 sec
RG                 196.79
DW                 62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.50000000 sec
TD0                     1
SFO1          500.1335009 MHz
NUC1                   1H
P0                   3.37 usec
P1                  10.10 usec
PLW1          25.00300026 W

F2 - Processing parameters
SI                 131072
SF            500.1300126 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



71
(500 MHz, $CDCl_3$)



Current Data Parameters

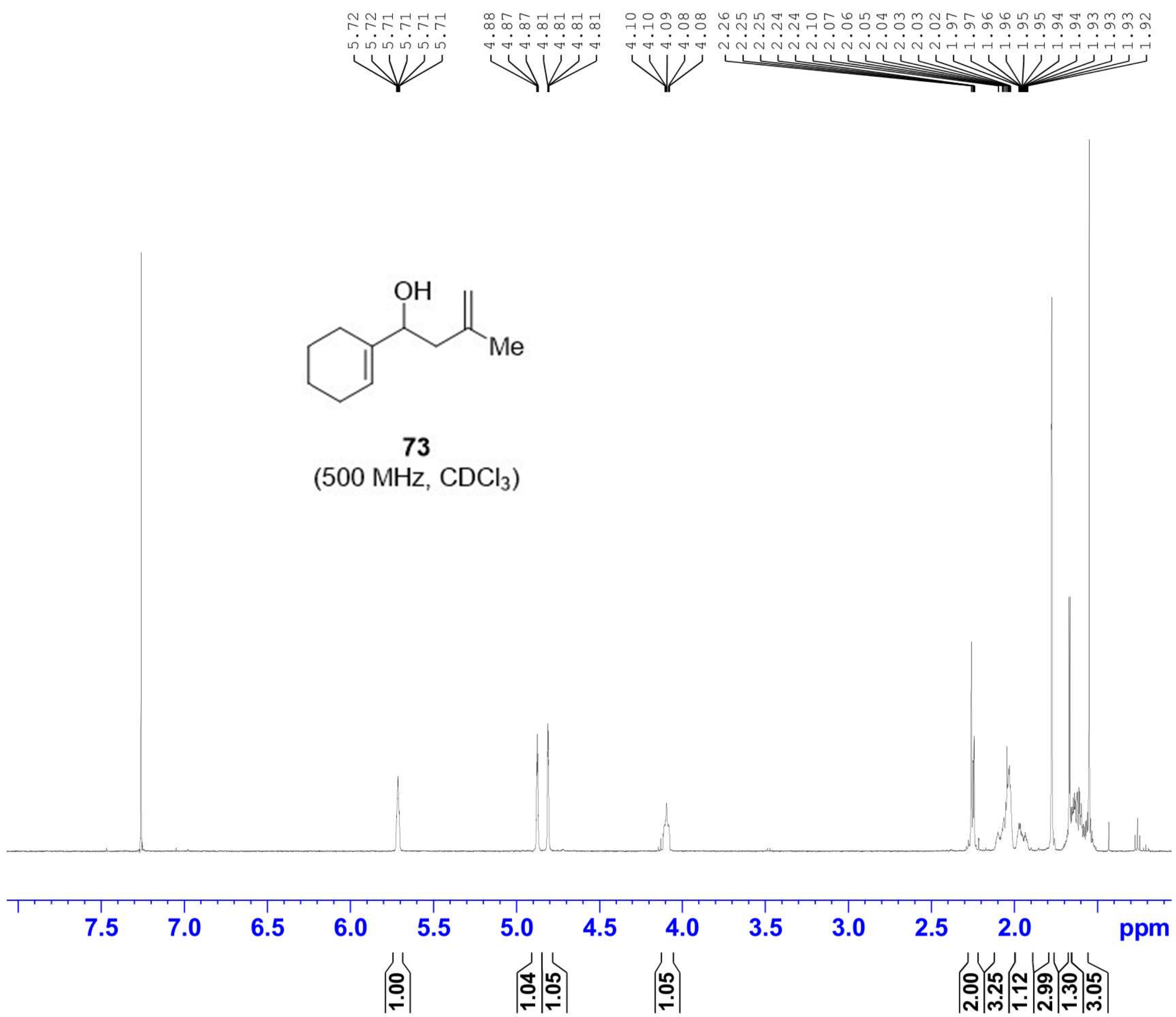
NAME	yh-10-52-1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20210523
Time	12.45 h
INSTRUM	spect
PROBHD	Z800701_0094 (
PULPROG	zg30
TD	48076
SOLVENT	CDCl3
NS	8
DS	0
SWH	8012.820 Hz
FIDRES	0.333340 Hz
AQ	2.9999423 sec
RG	196.79
DW	62.400 usec
DE	6.50 usec
TE	298.1 K
D1	1.50000000 sec
TD0	1
SFO1	500.1335009 MHz
NUC1	1H
P0	3.37 usec
P1	10.10 usec
PLW1	25.00300026 W

F2 - Processing parameters

SI	131072
SF	500.1300126 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

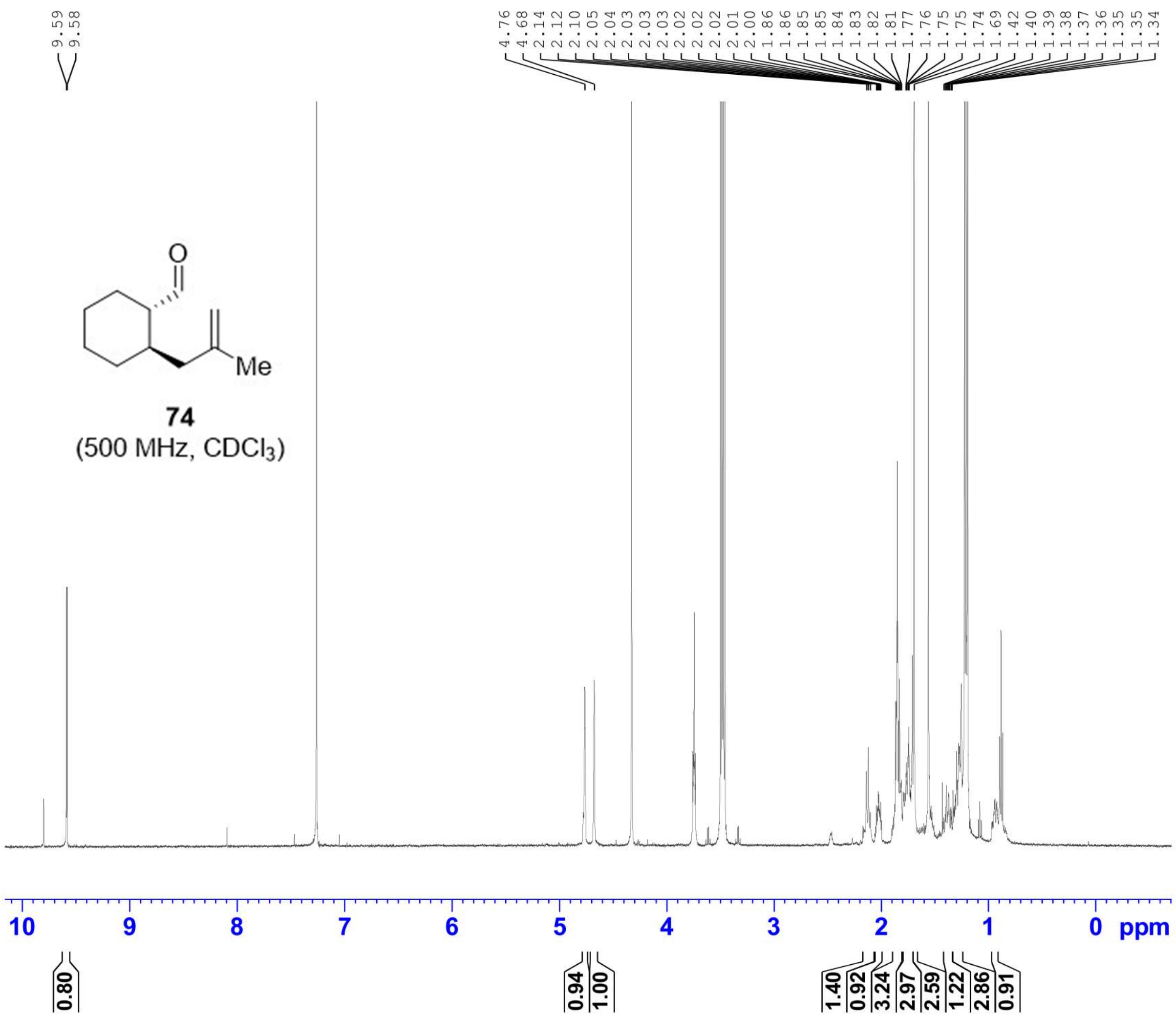


73
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME            yh-10-155
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20211006
Time                22.08 h
INSTRUM             spect
PROBHD   Z800701_0094 (
PULPROG              zg30
TD                  48076
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8012.820 Hz
FIDRES           0.333340 Hz
AQ              2.9999423 sec
RG                 196.79
DW                 62.400 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.50000000 sec
TD0                     1
SFO1          500.1335009 MHz
NUC1                   1H
P0                   3.37 usec
P1                  10.10 usec
PLW1          25.00300026 W

F2 - Processing parameters
SI                 131072
SF            500.1300120 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

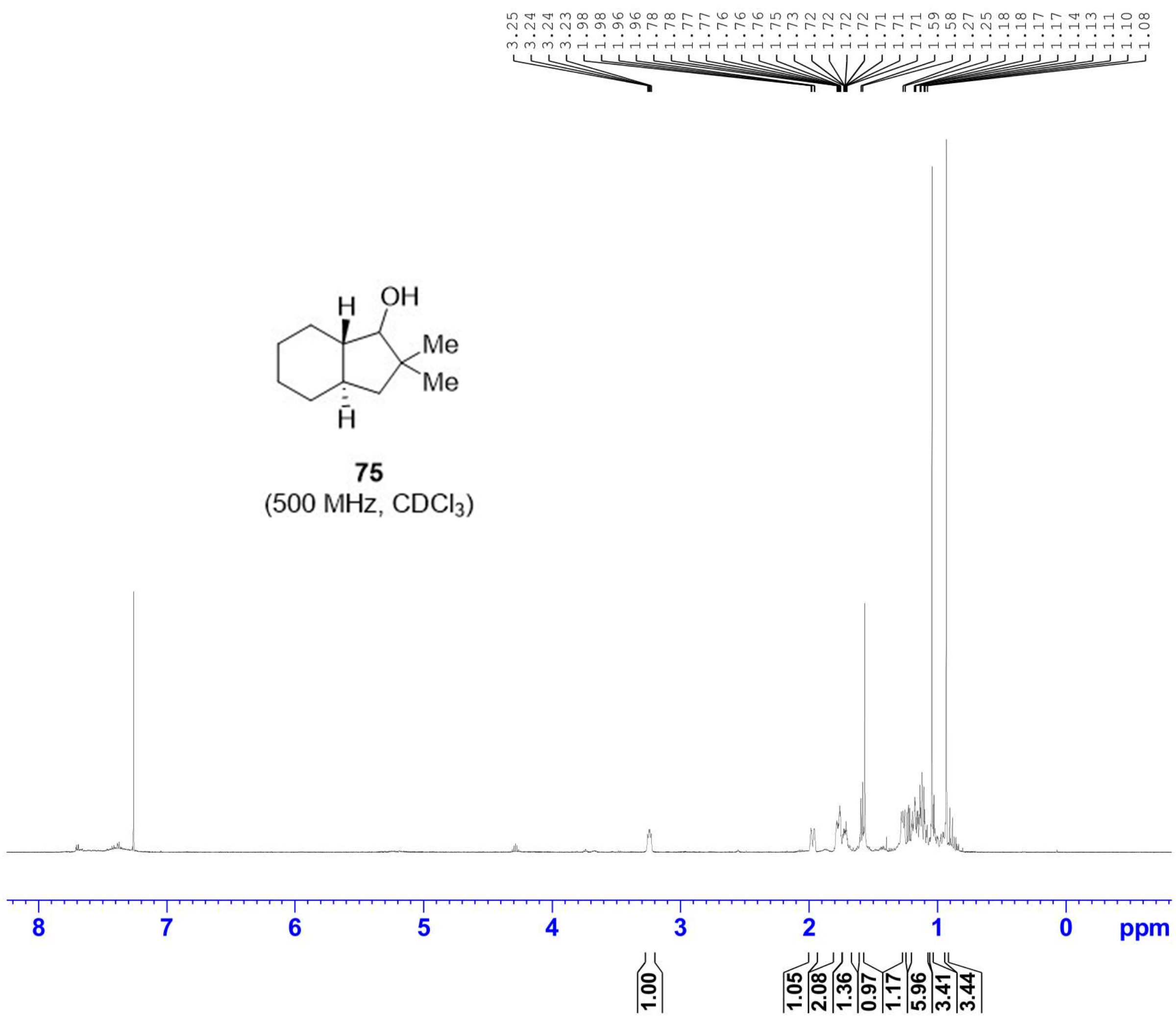


74
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME          yh-10-152-sm
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210930
Time                 17.05 h
INSTRUM              spect
PROBHD   Z113652_0187 (
PULPROG               zg30
TD                   48076
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               8012.820 Hz
FIDRES            0.333340 Hz
AQ               2.9999423 sec
RG                  189.89
DW                  62.400 usec
DE                    6.50 usec
TE                   298.1 K
D1              1.50000000 sec
TD0                      1
SFO1           499.8734991 MHz
NUC1                    1H
P0                    3.20 usec
P1                    9.60 usec
PLW1           20.98900032 W

F2 - Processing parameters
SI                  131072
SF             499.8700123 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

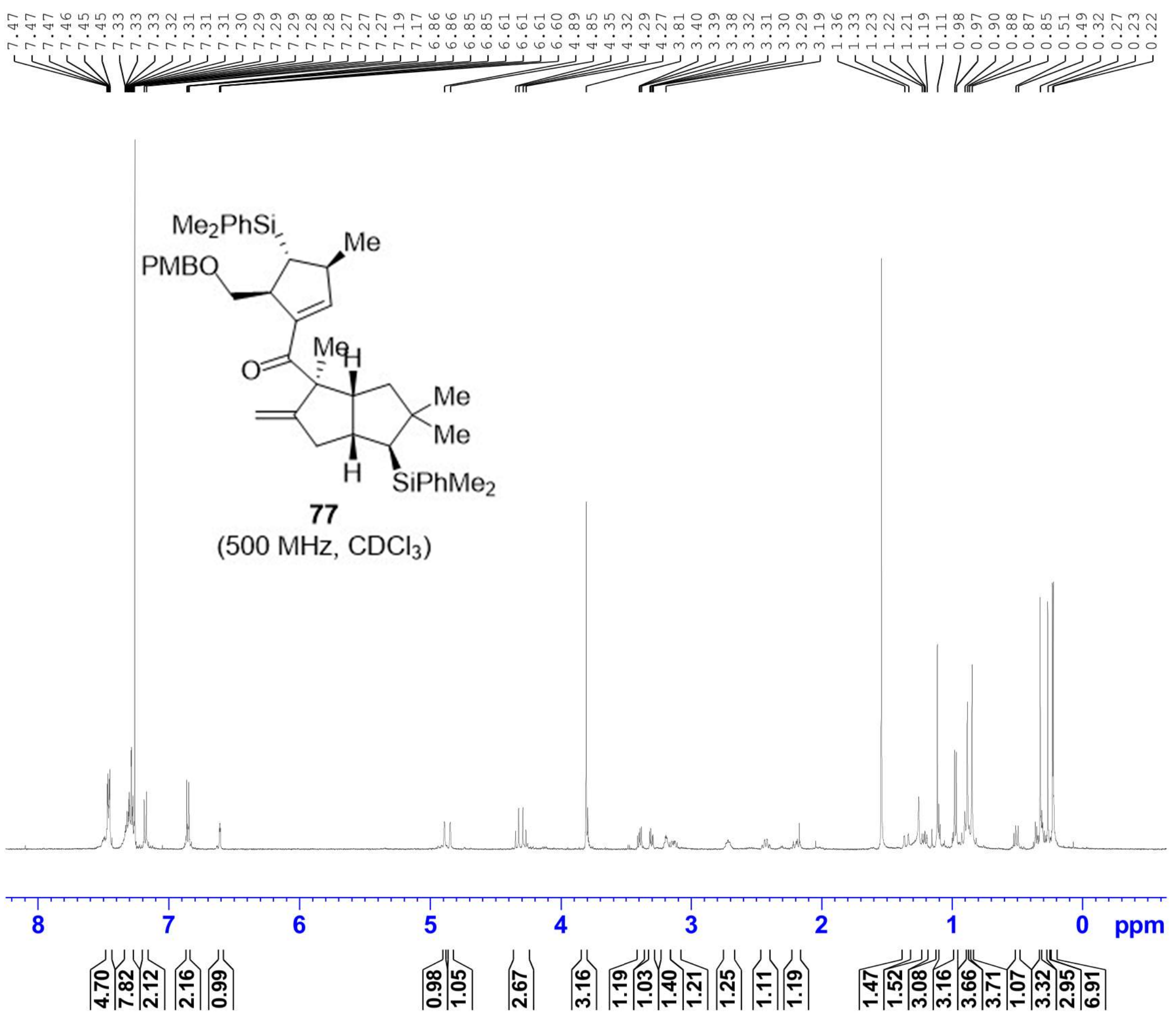


75
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME          yh-10-152-3
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20211001
Time                21.11 h
INSTRUM             spect
PROBHD   Z800701_0094 (
PULPROG              zg30
TD                  48076
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8012.820 Hz
FIDRES           0.333340 Hz
AQ              2.9999423 sec
RG                 196.79
DW                 62.400 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.50000000 sec
TD0                     1
SFO1          500.1335009 MHz
NUC1                   1H
P0                   3.37 usec
P1                  10.10 usec
PLW1          25.00300026 W

F2 - Processing parameters
SI                 131072
SF            500.1300118 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

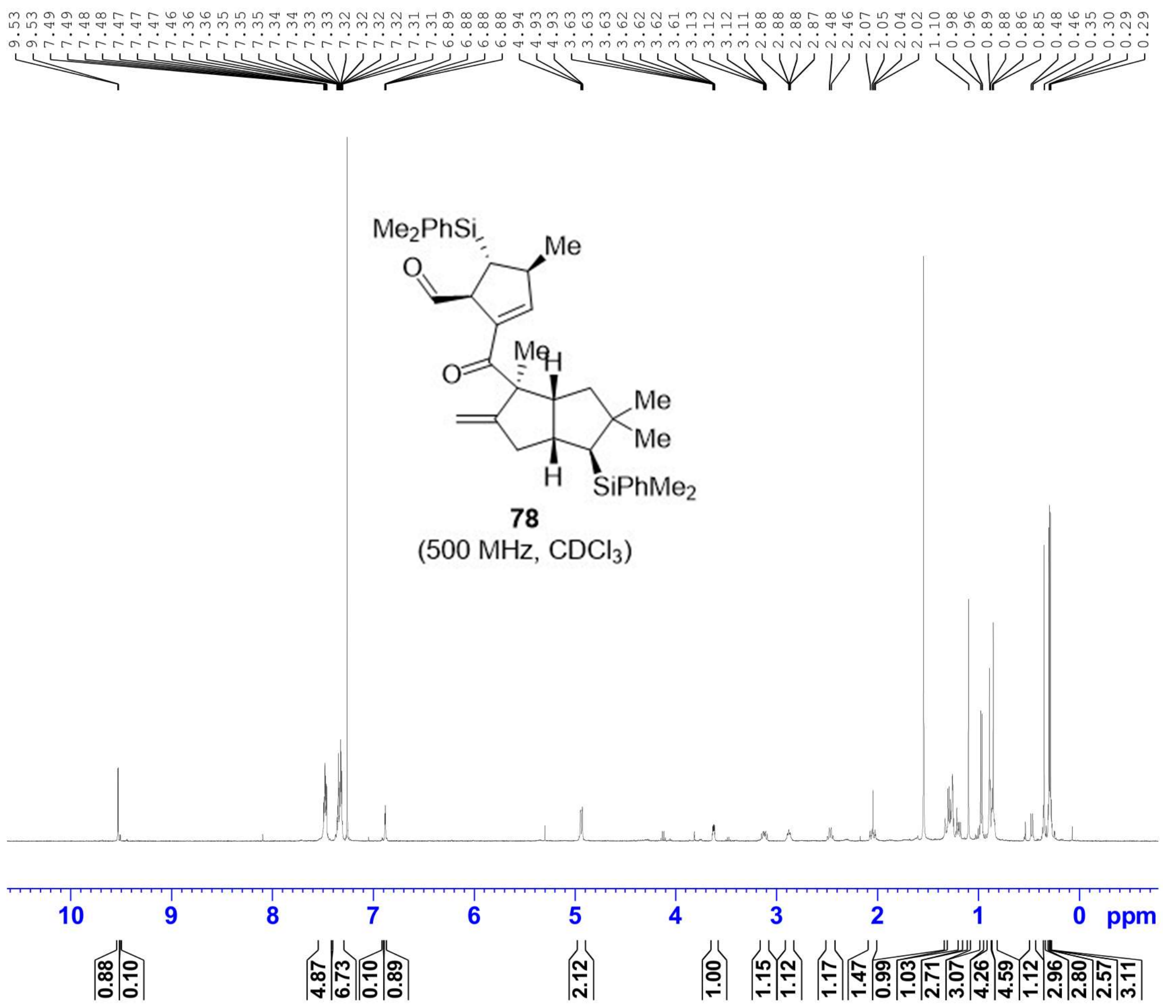


77
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME                yh-11-1
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211023
Time_                 17.03 h
INSTRUM               spect
PROBHD   Z800701_0094 (
PULPROG                zg30
TD                    48076
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8012.820 Hz
FIDRES             0.333340 Hz
AQ                2.9999423 sec
RG                   196.79
DW                   62.400 usec
DE                     6.50 usec
TE                    298.1 K
D1               1.50000000 sec
TD0                       1
SFO1            500.1335009 MHz
NUC1                     1H
P0                     3.37 usec
P1                    10.10 usec
PLW1            25.00300026 W

F2 - Processing parameters
SI                   131072
SF              500.1300121 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



78
(500 MHz, $CDCl_3$)

```
Current Data Parameters
NAME             yh-11-3
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211025
Time               19.22 h
INSTRUM            spect
PROBHD   Z800701_0094 (
PULPROG             zg30
TD                 48076
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             8012.820 Hz
FIDRES          0.333340 Hz
AQ             2.9999423 sec
RG                196.79
DW                62.400 usec
DE                  6.50 usec
TE                 298.2 K
D1            1.50000000 sec
TD0                    1
SFO1         500.1335009 MHz
NUC1                  1H
P0                  3.37 usec
P1                 10.10 usec
PLW1         25.00300026 W

F2 - Processing parameters
SI                131072
SF           500.1300118 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```