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Using Planar Chiral Iron(0) Tricarbonyl Diene Complexes: A Focus on Azaspirocycles and the Use of an Oxazolidinone Chiral Auxiliary

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Using Planar Chiral Iron(0) Tricarbonyl Diene Complexes: A Focus on Azaspirocycles and the Use of an Oxazolidinone Chiral Auxiliary

An Honors Thesis presented by

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List of Common Abbreviations

Ac	acetate
Ar	either aryl or argon, depending on context
bda	benzylideneacetone
Bn	benzyl
Boc	*tert*-butyloxycarbonyl
br	broad
brine	saturated aqueous NaCl solution
cat.	catalyst
CSA	camphorsulfonic acid
DBU	1,8-diazabicycloundec-7-ene
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
decomp.	decomposition
DIAD	diisopropyl azodicarboxylate
DIBAL	diisobutylaluminum hydride
DMAP	dimethyl amino pyridine
DMF	*N,N*-dimethylformamide
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone
DMSO	dimethylsulfoxide
DPPA	diphenylphosphoryl azide
dr	diastereomeric ratio
Et	ethyl
HRMS	high resolution mass spectrometry
i-Pr	isopropyl
IR	infrared
LDA	lithium di *i*-propylamine
Me	methyl
MHz	megahertz
MOZ	*para*-methoxybenzyl carbamate
Ms	mesylate

n-Bu/Bu	*n*-butyl
NIS	*N*-iodosuccinimide
NMR	nuclear magnetic resonance
Ns	Nosyl
Ph	phenyl
PMB	*para*-methoxybenzene
ppm	parts per million
PTSA	*para*-toluene sulfonic acid
pyr	pyridine
RT	room temperature
S*	(R)-*p*-tolylsulfoxide
t-Bu	*tert*-butyl
TBAF	tetra-*n*-butylammonium fluoride
TBDPS	*tert*-butyldiphenylsilyl
TBS	*tert*-butyldimethylsilyl
TEOC	2-(trimethylsilyl)ethyl carbamate
Tf	triflate
THP	tetrahydropyran
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMANO	trimethylamine *N*-oxide
TMS	trimethyl silyl
TMSE	trimethyl silyl ethanol
TsOH	*para*-toluene sulfonic acid

Abstract

For many years, the Paley laboratory has developed the use of planar chiral η^4 iron(0) tricarbonyl complexes for use in directing the central chirality of adjacent centers. This work examines the use of dienes functionalized at C2 with a chiral auxiliary.

The functionalization of a stereocontrolled [6,6]-azaspirocycle was taken on to great success. This sequence involved a 2-sulfinyl diene complex. The keystone Grignard addition to the cyclic imine was accomplished to afford a single diastereomer. Ring closing metathesis was used to form the final ring of the azaspirocycle framework.

Two more sequences were attempted to form azaspirocycle centers. The first was an attempt to employ an intramolecular Mannich. In this sequence, the cyclic imine and an enol would form in situ in order to avoid isolating the imine species which has been known to decompose. The final attempt at azaspirocycle formation was an attempt to directly replace a tertiary alcohol with an amine, again in an attempt to avoid the imine species.

An alternative project working to use an alternative chiral auxiliary, an oxazolidinone, was also developed. The 2-oxazolidinyl diene complex was successfully complexed and new developments in this sequence included the development of a stannylcupration directed by a propargylic acetal in order to have an aldehyde adjacent to the diene complex.

Introduction

The stereochemistry of different centers in a molecule can have a huge impact on its activity. Considering nature essentially only contains one of two forms as far as stereochemistry is concerned, it is crucial for synthetic chemists to appreciate chirality. In the past, organic synthesis has been focused on making molecules regardless of stereochemistry and either trying to separate the two enantiomers after synthesis or leaving them as a racemic mixture. Conceptually, this at best leaves half of the material unused, and at worst enables the possibility for the opposite enantiomer to produce negative effects. Due to the downfalls of having a mixture of enantiomers, recent organic synthesis has evolved to develop methodology that preferentially forms one enantiomer.

There are many different techniques employed to produce enantiomerically pure compounds. One method that has emerged is the use of planar chirality to direct the central chirality of a molecule through catalysis[3] or diastereoselective complexation[4]. The work done in the Paley laboratory, including the work done for this thesis, continues to follow this strategy.

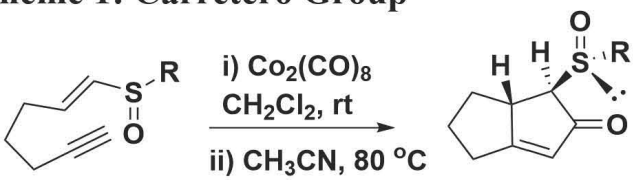
For many years, the Paley laboratory has developed techniques to make enantiomerically pure planar chiral η^4 iron(0) tricarbonyl diene complexes through diastereoselective complexation. These complexes are then used to direct reactions at adjacent centers. The preferential complexation of the iron(0) tricarbonyl fragment to one of the diastereotopic faces of the diene is accomplished using chiral auxiliaries, in this case either the (*R*)-*p*-tolyl sulfoxide or the (*S*)-4-isopropyl-2-oxazolidinone groups. One benefit of this methodology is if the opposite center is desired, the chirality of the auxiliary need only to be switched, which would hypothetically install the iron on the opposite face and direct the adjacent centers to be of the opposite form.

The work presented here falls into two general projects: the diastereomerically controlled formation of azaspirocycles and the development of the use of the oxazolidinone as a chiral auxiliary on the diene. A significant amount of chemistry has been utilized in each of these projects, but earlier development of the methodology employed in Paley laboratory must first be discussed.

i) Use of the sulfoxide chiral auxiliary

Enantiomerically pure sulfoxides have been used as chiral auxiliaries outside of the context of planar chirality for some time[5, 6]. Using them in the context of transition metal chemistry was an early motivation for the development of the methodology described by the Paley laboratory, and an early example comes from the Carretero group. They used a sulfoxide as a chiral auxiliary to dictate the stereochemistry for intramolecular Pauson-Khand cyclization[7] as shown in **Scheme 1**[7]. These results seem to indicate the compatibility of the sulfoxide unit in the context of challenging organometallic reactions.

Scheme 1: Carretero Group



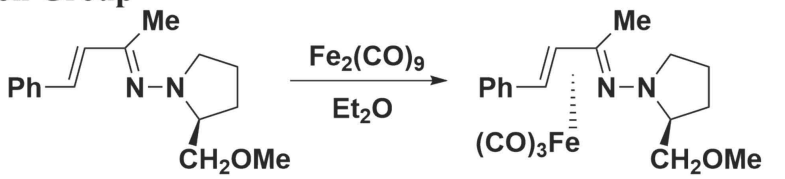
At roughly the same time, the use of chiral auxiliaries to create planar chiral η^4 iron complexes via diastereoselective complexation was becoming established. Early work by the Helquist group involved preparing an enone with a side group that included a phosphine group that directed complextion via chelation (**Scheme 2**)[8]. The Pearson group later demonstrated the diastereoselective complexation of azadienes using $Fe_2(CO)_9$ using the chiral hydrazine SAMP (**Scheme 2**)[9]; this work showed that the facial selectivity of this type of complexation could be

quite good (up to 95:5 under certain conditions). Their work with diene systems equipped with chiral amides was similarly successful and showed that the facial selectivities were determined to some extent by the proximity to the diene complex of the chiral auxiliary[9].

Scheme 2

Halquist Group

Pearson Group



dr 95:5

In the Paley laboratory, the use of a sulfoxide auxiliary did afford with the opportunity to form η^4 iron(0) tricarbonyl complexes with good facial selectivity. The maturation of this methodology began with the development of synthesis for enantiomerically pure 1- and 2-sulfinyl dienes[10, 11].

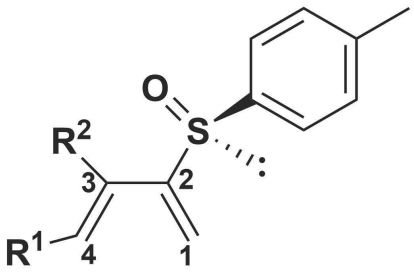
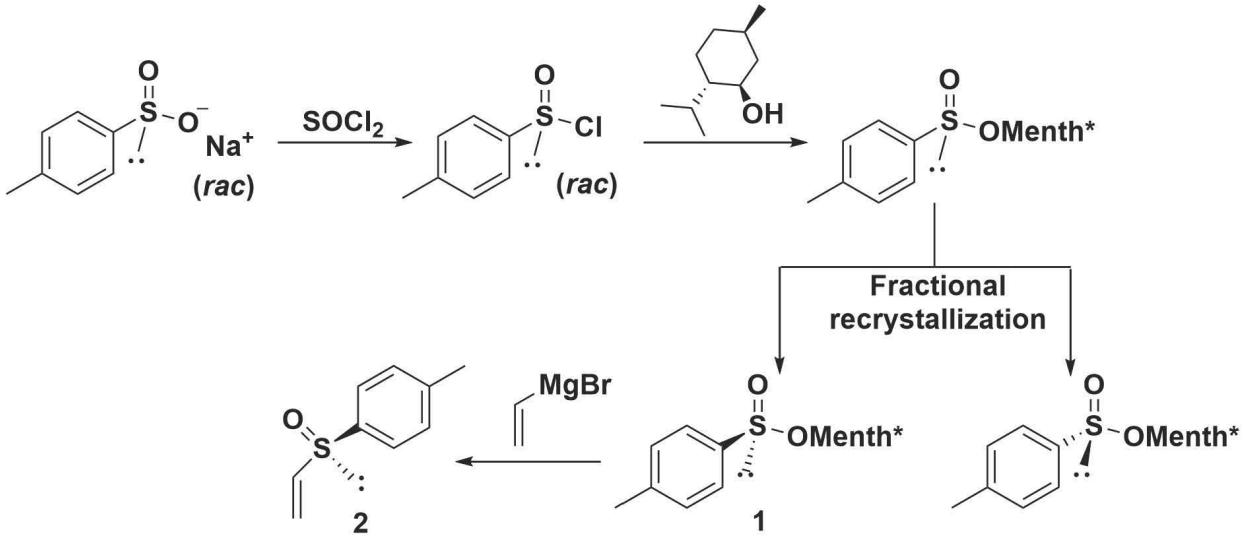


Figure 1: An enantiomerically pure 2-sulfinyl diene, with the numbering scheme used throughout this thesis

Formation of these sulfinyl dienes, and in particular the 2-sulfinyl dienes which are featured in this thesis (Fig. 1) is based on the Stille reaction. As the methodology developed, the ability to prepare increasingly complicated vinyl stannanes to be coupled to an enantiomerically

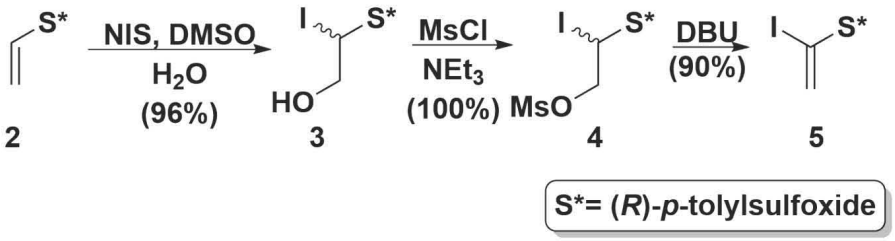
pure halovinyl sulfoxide became vital. Indeed, this is an important aspect of the results presented in this thesis. However, the synthesis of the iodovinyl sulfoxide was developed some years earlier.

Scheme 3: Andersen preparation of chiral sulfoxide



Using the classic methodology first developed by the Andersen group (**Scheme 3**)[12], the Paley laboratory developed a sequence to prepare the iodovinyl sulfoxide **5**, as seen in **Scheme 4**[10].

Scheme 4



The menthyl sulfinate ester **1**, which is now commercially available, was originally prepared by fractional recrystallization after addition of enantiomerically pure menthol to racemic *p*-tolyl sulfinyl chloride. Addition of Grignard reagents effectively displaces the

menthoxide anion, with inversion. To access the required iodovinyl sulfoxide **5**, vinyl Grignard was employed as the nucleophile, producing *p*-tolyl vinyl sulfoxide **2**.

To prepare the required Stille partner, iodovinyl sulfoxide **5**, NIS is used to form iodohydrin **3**. Presumably, this reaction proceeds via an intermediate iodonium ion, which is trapped by addition of water to the less substituted position. A diastereomeric mixture is formed, but this is inconsequential. The alcohol is converted to the corresponding mesylate **4**, and elimination using DBU affords the desired iodovinyl sulfoxide **5**.

As it turned out, the Stille reaction with this vinyl iodide was particularly sluggish using standard conditions because the vinyl sulfoxide is inherently electron poor and the carbon bearing the iodide is rather hindered. The problem is exacerbated when the vinyl stannane is electron deficient. This is often the case because the use of electron withdrawing groups along the diene periphery grew as the methodology matured. Thus, the Stille coupling of two electron deficient partners, which are also rather sterically hindered can be challenging. The Paley laboratory employs the modification developed by Fürstner[13, 14]. This methodology capitalizes on the tendency for copper to perform transmetallations better than tin. Thus the addition of a copper reagent (CuO_2PPh_2; Fürstner employs CuTC and $Bu_4NO_2PPh_2$) with the palladium catalyst, encourages the vinyl stannane to convert to a vinyl copper species which then undergoes the key transmetallation of the Stille catalytic cycle. Furthermore, the tributylstannyl diphenyl phosphinate ($Bu_3SnO_2PPh_2$) precipitates, driving the reaction to completion and aiding in the removal of the tin-containing by-products.

Once the diene has been synthesized, the iron(0) tricarbonyl fragment is installed. Either bdaFe$(CO)_3$ or $Fe_2(CO)_9$ are used to accomplish this complexation (the differences and benefits of each will be discussed later).

The preference for the complexation to the top face as shown in Fig. 2 can be explained by the minimization of 1,3-allylic strain between the oxygen atom of the sulfoxide and the R^2 group. Rotation about the C-S bond leads to the more favored conformation in which one face of the diene is sterically hindered. This facilitates preferential complexation to the opposite face.

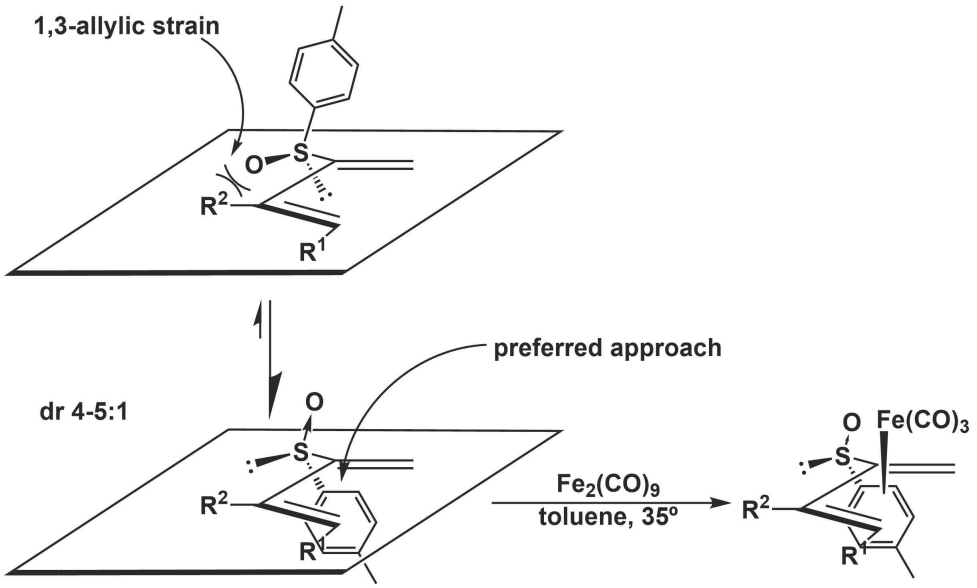
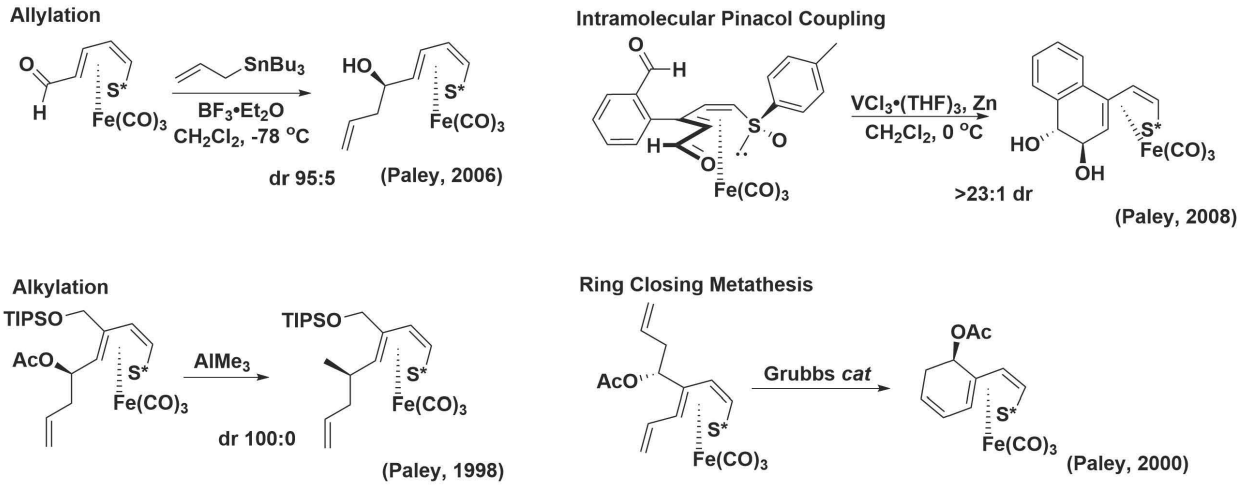


Fig. 2: Facial selectivity of complexation of 2-sulfinyl diene using the (*R*)-*p*-tolyl sulfoxide auxiliary

As indicated in Fig. 2 facial selectivities of about 4 or 5 to 1 are typically achieved. Luckily, the major and minor diastereomers are generally separable using column chromatography in this step or consequent steps.

The Paley laboratory has been using sulfinyl iron(0) tricarbonyl diene complexes for many years, and as such, has developed a good understanding of the reactions that are compatible with the unit. Some of the major reactions developed include diastereoselective allylations[15, 16], alkylations[16], and intramolecular pinacol couplings[17], and we have also demonstrated the compatibility of the complexes with ring-closing metathesis[11]. An example of each of these transformations is grouped together in **Scheme 5**.

Scheme 5



We have acquired substantial experience preparing and manipulating these compounds. The complexes may be handled with no special precautions, though they should be stored in the dark due to light sensitivity over prolonged periods. They are chromatographically stable and diastereomeric complexes are generally easy to separate. Fortunately Grignard reagents (as well as $NaBH_3CN$) can be used to transform carbonyls (or imines) at positions adjacent to the diene complex. Bronsted and Lewis acids have also been successful used. While many standard organic transformations may be performed on these iron(0) diene complexes, there are significant limitations. For example, strongly oxidizing conditions, such as $NaOH/H_2O_2$, leads to decomposition. Treatment with amine bases or some basic reagents (such as TBAF) are tolerated but some stronger bases (alkoxides, sodium hydride, LDA, alkyl lithiums) are not. Finally, strongly electrophilic reagents such as acid chlorides and oxalyl chloride lead to decomposition; esterifications and oxidations need to be carried with with anhydrides and SO_3•pyr/DMSO, respectively.

Perhaps a more worrisome drawback to the sulfoxide, other than some challenges with conditions that it is compatible with, has been its removal so that different parts of the molecule can be manipulated. Once the diene is decomplexed, it is more of a liability than a benefit if the

sulfoxide itself cannot be manipulated. Paley laboratory did accomplish a reduction of the vinyl sulfoxide to a terminal alkene using SmI_2[11]. However, this reaction was originally attempting to reduce to the sulfoxide to a sulfide, so it is hard to be confident in this methodology. Attempts at utilizing the Pummerer reaction have also been largely unsuccessful.

A brief note on decomplexation: obviously, in order for this methodology to be applied to ttal synthesis, the iron(0) triarbonyl fragment must be removed. This decomplexation has been accomplished successfully without racemization using trimethylamine *N*-oxide (TMANO)[14] and ceric ammonium nitrate (CAN)[15]. It should be noted that these decomplexations were accomplished on the 1-sulfinyldienes, not the 2-sulfinyldienes used in this work. Also, the Paley Lab has had some trouble with the use of CAN; it caused racemized spiroketal stereocenters that had been assembled adjacent to the dienes[14].

ii) Use of the Oxazolidinone Chiral Auxiliary

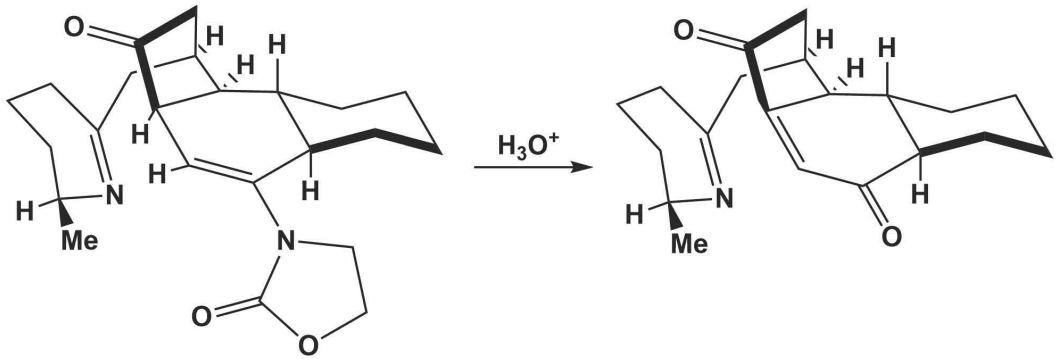
Although the Paley laboratory has been successful with the sulfoxide auxiliary, it would be beneficial to the methodology being developed to use a chiral auxiliary that could be easily manipulated into a useable "handle." An oxazolidinone, attached to the diene through the nitrogen atom, seemed like a great candidate.

Evans group first developed the use of chiral oxazolidinones in the context of diastereoselective alkylations[18] and aldol reactions[19]. Pericyclic reactions are also commonly directed by Evans' oxazolidinones[5, 20]. An extensive volume of work has been done using the oxazolidinone auxiliary[21], and as such, the chemistry of its use is well known.

Indeed, it was envisioned that installed in place of the sulfoxide in the sequences employed by the Paley laboratory, simple hydrolysis of the dienyloxazolidinone (that would

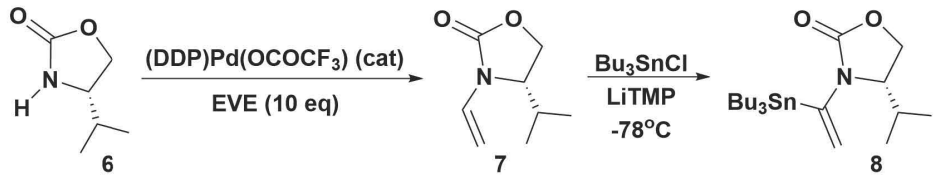
remerge after the decomplexation of the iron(0) tricarbonyl unit) would yield an enone. Clearly, this suggests useful manipulation and further functionalization, suggesting the application for total synthesis. It is worth noting that the hydrolysis of a similar *N*-dienyloxazolidinone is featured in the synthesis of Galbulimima Alkaloid 13[22].

Scheme 7: Galbulimima Alkaloid 13



Due to the apparent benefit of the oxazolidinone auxiliary, the Paley laboratory began investigating its compatibility with the stategies developed using the sulfoxide auxiliary. Even before complexation of the diene, some differences between the sequences to prepare the diene precursors were apparent. The iodovinyl oxazolidinone is unknown, so the required vinyl stannane must be converted into an iodide and a stannyl vinyl oxazolidinone would be required, essentially switching the coupling partners for the Stille step. Fortunately, Hegedus reported the synthesis of such a compound[23], though the synthesis of the vinyl oxazolidinone precursor was not routine until the 2004 report by Stahl[24]. **Scheme 8** demonstrates the basic steps needed. A palladium catalyzed vinylation of the chiral oxazolidinone **6**, using ethylvinylether as the vinyl source to form **7**, is followed by the regioselective stannylation via a directed metalation of the vinylic C-H bond adjacent to the oxazolidinone unit to afford **8**.

Scheme 8



For some time, the use of the oxazolidinone in Paley laboratory could not move forward, because the absolute stereochemistry of the complexation had not been determined. My predecessor, Alice Wong, was able to crystallize one of her complexes that bore the oxazolidinone derived from the amino acid valine: (*S*)-4-isopropyl-2-oxazolidinone (Fig. 3)[1].

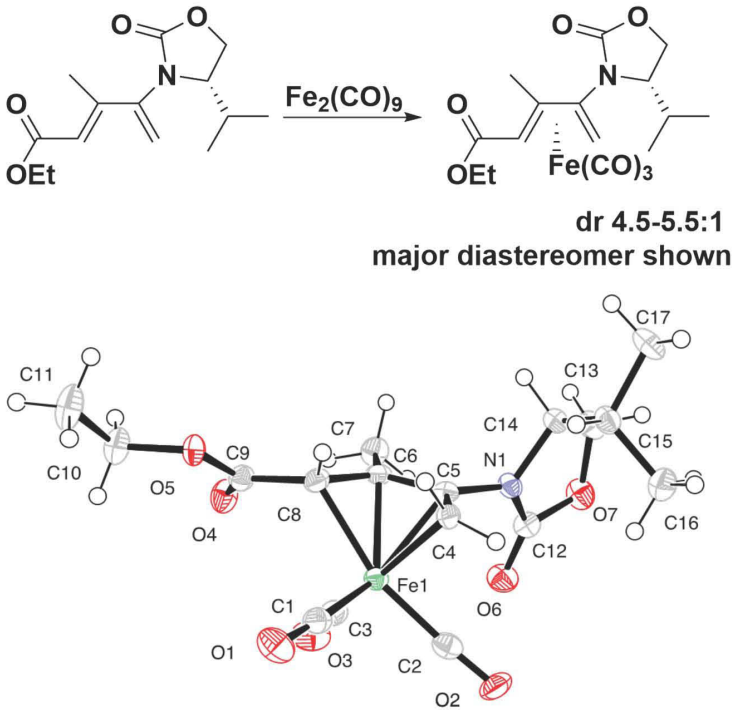


Figure 3. Determination of absolute stereochemistry of 2-oxazolidonyldiene using (*S*)-4-isopropyl-2-oxazolidinone. [1]

Notably, both diastereomers could be crystallized; it was the minor complex, however, that gave the higher quality structure by X-ray crystallography. An ORTEP diagram of the major

diastereomer is shown in Fig. 3. These crystals indicated that the iron complexed to the opposite face of where our sulfoxide directs, using one of the simplest Evan's auxiliaries is derived from.

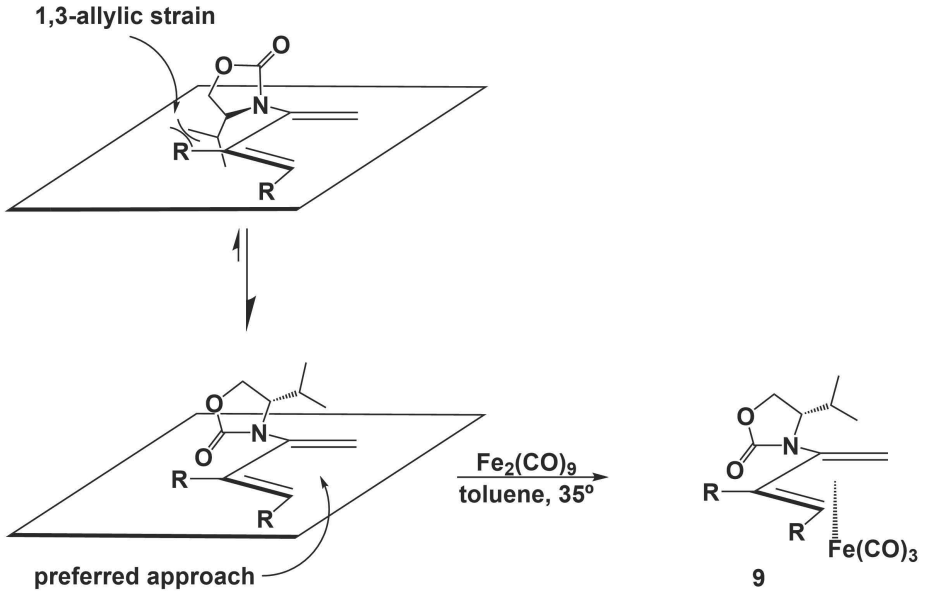


Figure 4. Schematic of 2-oxazolidynldiene complexation using (*S*)-4-isopropyl-2-oxazolidinone as the auxiliary

A more schematic view of this structure can be seen in Fig. 4. Again, in an analogous to the sulfinyl dienes, 1,3-allylic strain causes the facial selectivity. It is worth noting that the selectivities with the oxazolidinone are comparable or better to the sulfoxide cases. Selectivities up to 8:1 have now been obtained.

Having determined the absolute stereochemistry of the planar chiral complex, the use of the oxazolidinyl diene iron(0) tricarbonyl complexates (**9**) in reaction sequences commonly used in Paley laboratory as well as other chemistry became possible. Some of the work presented in this thesis is part of that investigation.

One benefit immediately found using the new oxazolidinyl-based systems was an improvement in the efficiency of the Stille Coupling. The Stille coupling to prepare the sulfinyl dienes can be challenging, with average yields typically in the 55-70% range. However, with the

oxazolidinyl dienes, yields of this coupling are excellent: 75-85% is common. Indeed, in some cases yields have been as high as 97%. This improvement is likely due to the nature of the auxiliary as an electron donating group. The sulfoxide is an electron withdrawing group, which makes the coupling more challenging. Additionally, the sulfur atom is the stereocenter and therefore has considerably more steric volume. On the other hand, the stereochemistry of the oxazolidinone is on the hetereocyclic ring. The nitrogen atom itself has significant sp^2 character, which reduces the steric volume and should render the Stille coupling at the adjacent center more feasible.

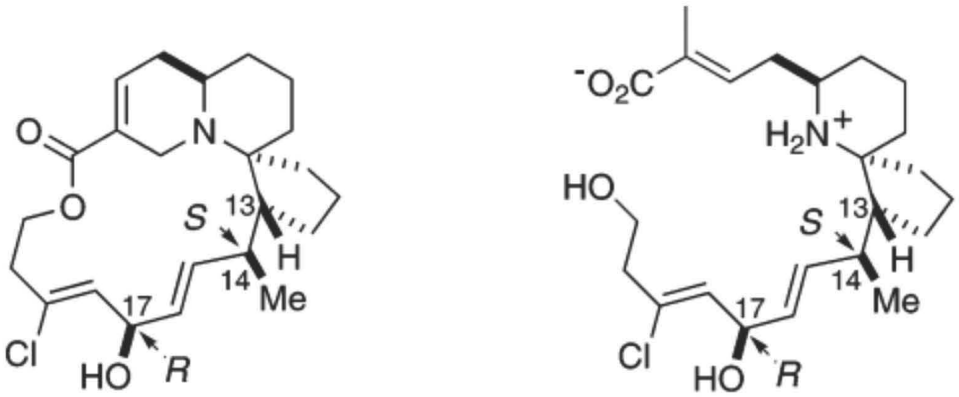
An additional advantage is offered in the complexation as well. While selectivities for the diastereoselective complexation to afford the iron(0) tricarbonyl complexes are good or even better than previously observed with the sulfoxide bearing analogs, the complexation can be achieved with commercially available $Fe_2(CO)_9$. This is in contrast to the use of $bdaFe(CO)_3$ for the sulfinyl dienes. Furthermore, use of $Fe_2(CO)_9$ provides cleaner reaction mixtures; excess reagent is easily removed by filtration, and neither $bdaFe(CO)_3$ nor bda are present, simplifying the chromatography. The Paley laboratory has employed $bdaFe(CO)_3$ for many years with the sulfinyl dienes due to early success with this iron(0) tricarbonyl source. Also, the complexation of the sulfinyl dienes using $Fe_2(CO)_9$ was not as clean as with the oxazolidinyl analogs. As the sulfinyl dienes became more complex, the separation of bda and $bdaFe(CO)_3$ became more and more challenging. Also, the complexation products of the sulfinyl diene were inseparable from bda and $bdaFe(CO)_3$. Due to these challenges the switch was made to using $Fe_2(CO)_9$ almost exclusively in recent work.

The Paley laboratory has experienced some unexpected setbacks with this oxazolidinyl chemistry. For example, attempted deprotection of complex **10** led to a complicated mixture of product that appeared to include the rearranged complex **11** (**Scheme 9**)[25].

Scheme 9

iii) Azaspirocycle Synthesis

The other project that this work encompasses is the formation of an diastereomerically pure azaspirocycle. The azaspirocycle is a motif found in many biologically active molecules and has been a recent focus for synthetic chemists. Halichlorine and the pinnaic acids, seen in **Figure 5** have been of particular focus[2].



halichlorine a pinnaic acid

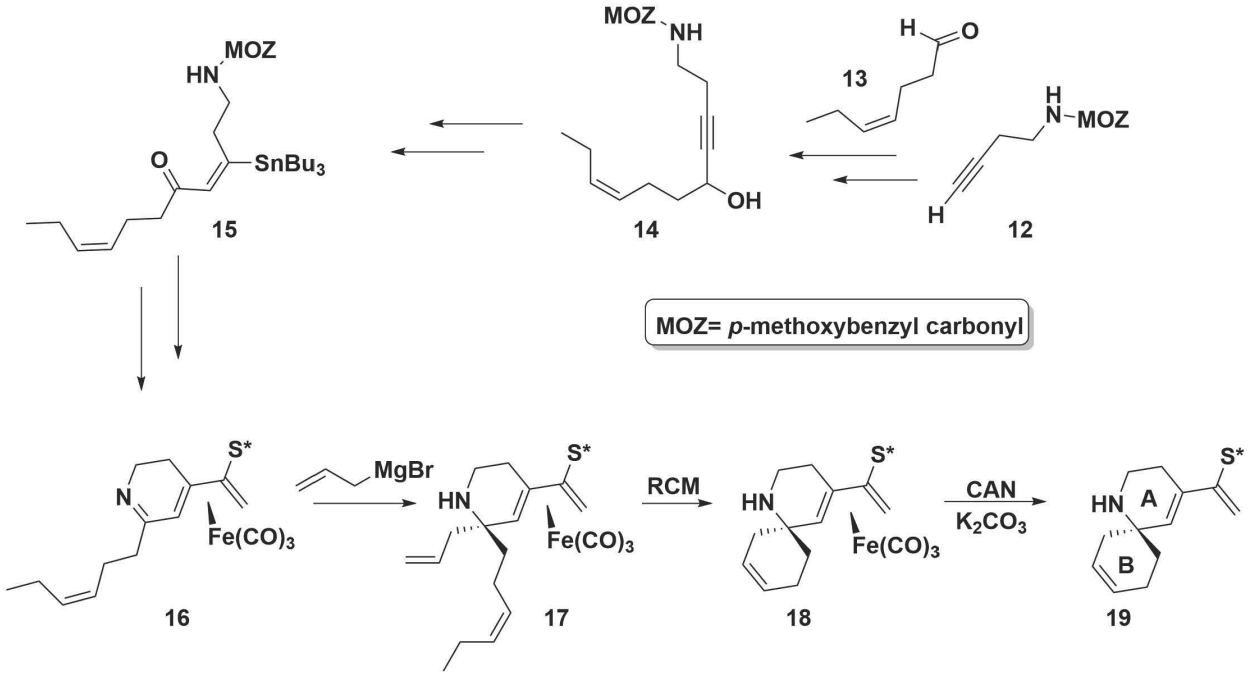
Figure 5: naturally occurring azaspirocycles[2]

Forming the azaspirocycle portion of these molecules is of especial interest. A variety of methodologies have been used to enantioselectively form this bicyclic system including: NBS-promoted semipinacol rearrangment[26], C-methylation of the spirotricyclic lactam followed by

lactam ring-opening and subsequent ring closing metathesis[27], and Grignard additions to afford intermediates that undergo ring closing metathesis[28] to name a few.

In the context of the chemistry being developed in the Paley laboratory, azaspirocylce synthesis was a natural offshoot of the successful work in synthesizing the similar spiroketals[14] in a diastereoselective manner. To accomplish this, it was necessary to install tethers on the diene such that the cyclization will be directed by the iron(0) tricarbonyl fragment. My predecessor, Alice Wong, was able to successfully synthesize a single, simple diastereomerically pure azaspirocycle; her work on this project is summarized below (**Scheme 10**)[1].

Scheme 10



The homopropargylic carbamate, **12**, that begins this sequence was made using the Curtius rearrangement of the corresponding homopropargylic carboxylic acid[29]; the intermediate isocyanate was trapped with *para*-methoxybenzyl alcohol to get carbamate-protected amine. The alkyne was subsequently deprotonated to form the nucleophile used to reaction with the aldehyde **13**. The resulting propargylic alcohol **14** underwent a Pd-catalyzed hydrostannylation that was

only moderately regioselective. Then, the allylic alcohol was oxidized using Parikh-Doering oxidation conditions. This β-stannyl enone **15** was used in the modified Stille reaction previously discussed, and the complexation of the iron(0) fragment was accomplished with $bdaFe(CO)_3$. Deprotection of the carbamate and concomitant cyclization of the resulting primary amine with the ketone produced the unstable cyclic imine **16** (**Scheme 10)**. Allyl Grignard addition was accomplished to afford **17** using a Lewis acid to increase the electrophilicity of the imine. Significantly, this addition afforded a single diastereomer, suggesting that the strategy of preparing the azaspirocycle with a quaternary stereocenter adjacent to the planar chiral unit was viable. The actual closure of the second ring in azaspirocycle **18**, spiro fused to the first, was performed using ring-closing metathesis with Grubbs-Hoveyda 2nd generation catalyst. This approach is reminiscent of that used by Hsung in the synthesis of stereocontrolled spiroketals[30]. The discovery that Grubbs' ring closing metathesis was compatible with the sulfinyl iron(0) dienes had been made some years earlier[11]. Excitingly, Alice was able to decomplex this molecule to again reveal a sulfinyl diene **19** using CAN and potassium carbonate. The planned research for this thesis included studies on the functionalization of the B ring; this is described in the next section of this thesis.

Results and discussion

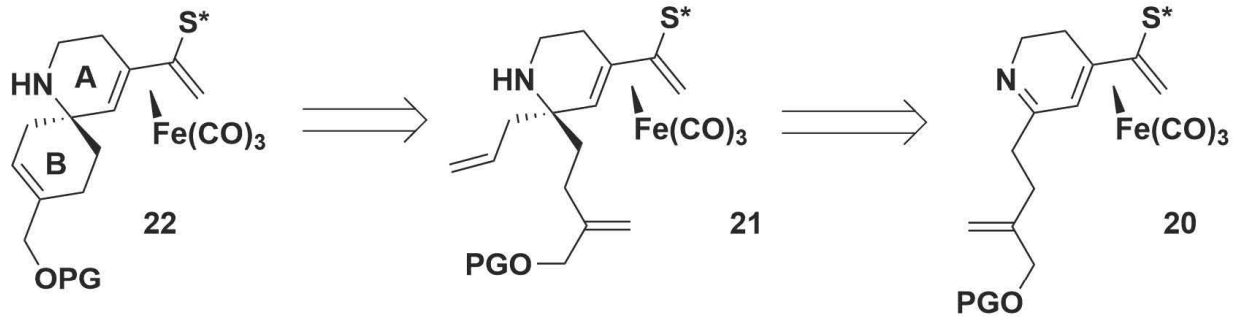
I. Azaspirocycle

i) Via ring closing metathesis

This project was developed to attempt to functionalize the azaspirocycle previously synthesized by Alice Wong in the Paley lab (**Scheme 10**). The functional group, in this case the incorporation of an allylic alcohol, was installed at the beginning of the sequence and the subsequent major steps used followed the protocols that had been developed by her to form the original azaspirocycle.

A retrosynthetic synthesis of the functionalized azspirocycle can be seen in **Scheme 11**. The concept behind this sequence is to build a compound so that a cyclic imine **20**, as the A ring, can be formed adjacent to the planar chiral iron(0) complex. To this imine an allylic nucleophile would be added affording **21**, and then the B ring in **22** would be formed using ring closing metathesis.

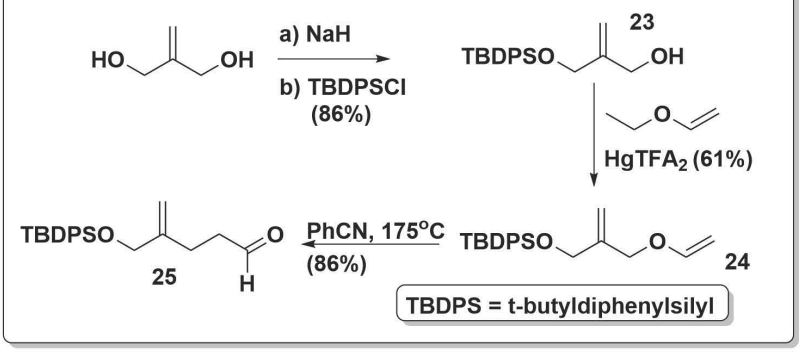
Scheme 11



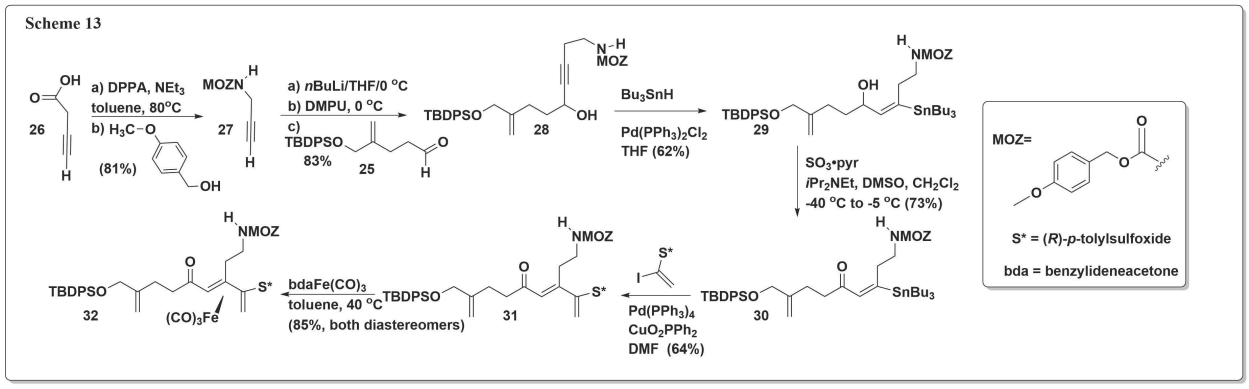
. The sequence was begun by desymmetrizing 2-methylene-1,3-propanediol by monoprotection with *tert*-butyldiphenylsilylchloride[31]. This reaction was actually more successful than expected considering the chance to protect both alcohol groups. The remaining

alcohol **23** was converted into vinylic ether **24**[32]. The next step was a known Claisen [3,3] sigmatropic rearrangement[32] to form the aldehyde **25** (**Scheme 12**).

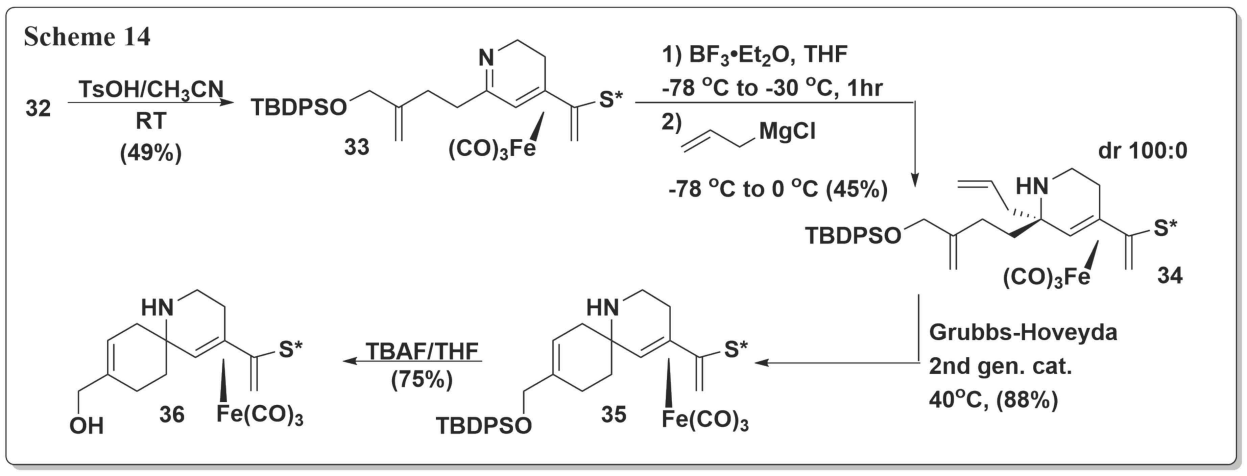
Scheme 12



To form the other "branch" of the molecule, the carboxylic acid **26** underwent the Curtius rearrangement and then reacted with 4-methoxybenzyl alcohol to form carbamate[29] **27** as seen in **Scheme 13**. This alkyne was deprotonated with two equivalents of *n*-butyl lithium and reacted with the aldehyde **25**, prepared using the Claisen rearrangment, to afford **28**. The addition of the aldehyde preferentially occurs at the more reactive acetylide position. This reaction is noteworthy because it is the basis of a large portion of my work and work in the Paley laboratory. This alkylation[33] is used to prepare alkynes for hydrostannylations and a lot of previous work has gone into developing substrates that are compatible with these basic reaction conditions. The alkyne underwent Pd-catalyzed hydrostannylation with good regioselectivity although exact values could not be obtained (2 to 2.5:1 are typical in cases wehere the ratio can be evaluated by ^{1}H NMR spectroscopy). The yield of this reaction was 62% which is typical for this transformation in our lab. The allylic alcohol **29** was then successfully oxidized to **30** using Parikh-Doering conditions[16], which are often employed in the Paley laboratory.



The next step is crucial for the installment of planar chirality, and thus a focus in the Paley laboratory. The vinyl stannane **30** was reacted with the iodovinyl sulfoxide **5** via a modified Stille reaction[13, 14]. The enantiomerically pure iodovinyl sulfoxide is prepared using methodology developed in 1997 and was described earlier in this thesis[10]. The sulfinyl diene **31** was formed with a typical yield of 64%. Planar chirality was installed by reacting the diene with bdaFe(CO)$_3$, producing the corresponding iron(0) tricarbonyl complex **32**, with a diastereomeric ratio of 2.6:1. This ratio is rather low for these compounds; a rationalization is not obvious though it is possible that temporary coordination to the substituted terminal alkene helps deliver the Fe(CO)$_3$ fragment to the diene with a greater degree of randomness.



With these benefits in mind, the carbamate was deprotected with *p*-toluenesulfonic acid and with a subsequent loss of water, the cyclic imine **33** was formed (**Scheme 14**). Boron

trifluoride was added to produce an iminium ion, a stronger nucleophile, and then allyl Grignard was added producing amine **34**. The diastereoselective ratio was 100:0 for this addition, which is quite exciting. The adjacent planar chirality is a highly effective controlling element for stereoselective additions, particularly in this case. However, the yield of 45% was deplorable. The intermediate cyclicimine species **33** was just too fragile, as it tends to decompose even under fairly dilute conditions. When concentrated, this imine species becomes noticeably darker over time, which is quite discouraging. It is suspected that the instability of these compounds is either a result of intermolecular transfer of the $Fe(CO)_3$ fragment from one diene to the imine nitrogen atom of another complex. Another possibility is enamine formation that triggers a loss of the $Fe(CO)_3$ fragment from the diene. This was observed in the less substituted imine **16** prepared by Alice Wong[1]. It was hoped that increasing the substitution would lead to increasing stability. Unfortunately, this was not the case.

Although the stability of the imine is unfortunate, the material was pushed on and Grubbs-Hoveyda 2nd generation catalyst was used successfully for ring closing metathesis[11, 34]. Thus the azaspirocycle **35** was successfully formed with the additional functionalization of the protected allylic alcohol.

In order to determine absolute stereochemistry of the azaspirocycle, some effort was made to crystallize a derivative of the material. This effort was mainly in the form of an attempted tosylation of the amine. This reaction did not yield promising results so that goal was abandoned.

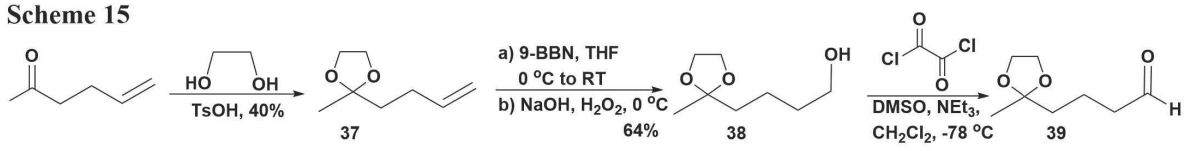
Finally, we were able to deprotect the silyl ether to form an allylic alcohol **36** which has a promising handle for further functionalization on the B ring of the azaspirocycle.

ii) Via intramolecular Mannich

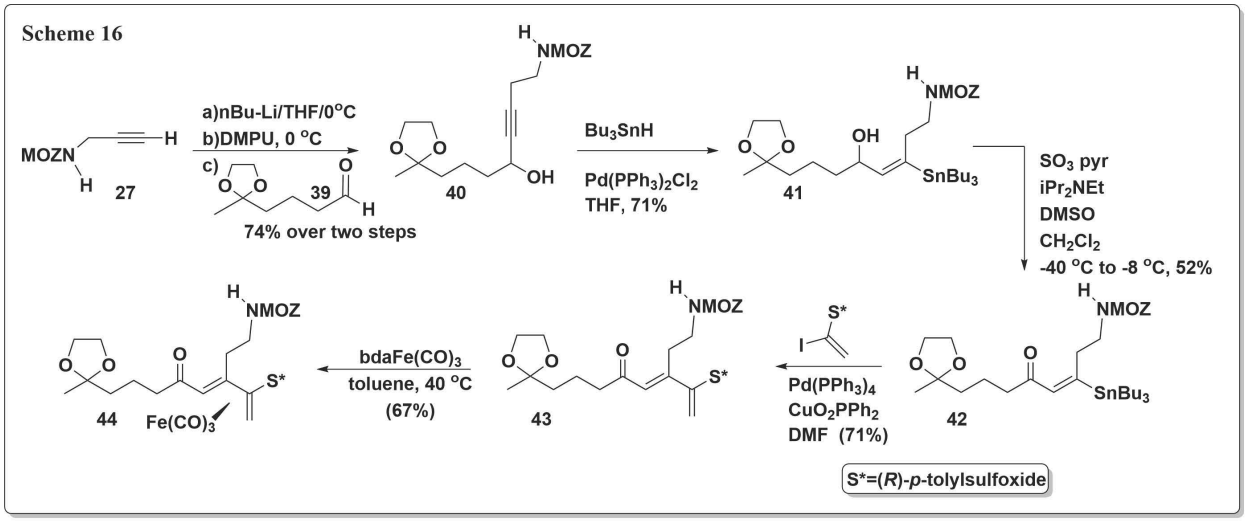
Given the apparent instability of the imine, we strove to find a pathway to the azaspirocycle that did not require the isolation of an imine. Using an intramolecular Mannich seemed like a promising idea.

Hypothetically, we wanted to assemble a molecule such that, in one step, we could form a cylic imine would then undergo nucleophilic attack from an appropriately positioned enol. As is fitting in the Paley laboratory, we wanted the formation of the azaspirocycle to be diastereoselective, so we chose to assemble the piece so that the transient imine intermediate would form adjacent to the iron(0) tricarbonyl complex. The enol could then add preferentially opposite the iron(0) tricaronyl fragment.

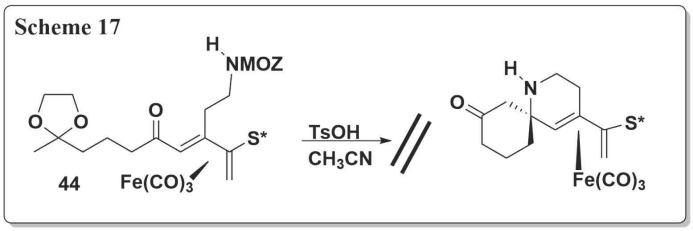
Scheme 15



Our aim was still to form a 6,6 azaspirocycle, so to begin this project, we made the chain that was to become the B ring as seen in **Scheme 15**. Beginning with commercially available hex-5-en-2-one, the ketone was readily protected with ethylene glycol to afford **37**. This protecting group was chosen because it would hold up through primary steps of the sequence, but could be removed with the acidic hydrolytic conditions planned for the Mannich reaction. Once protected, a hydroboration was performed and the resulting primary alcohol **38** was oxidized to the aldehyde **39** using dimethylsulfoxide and oxalyl chloride.

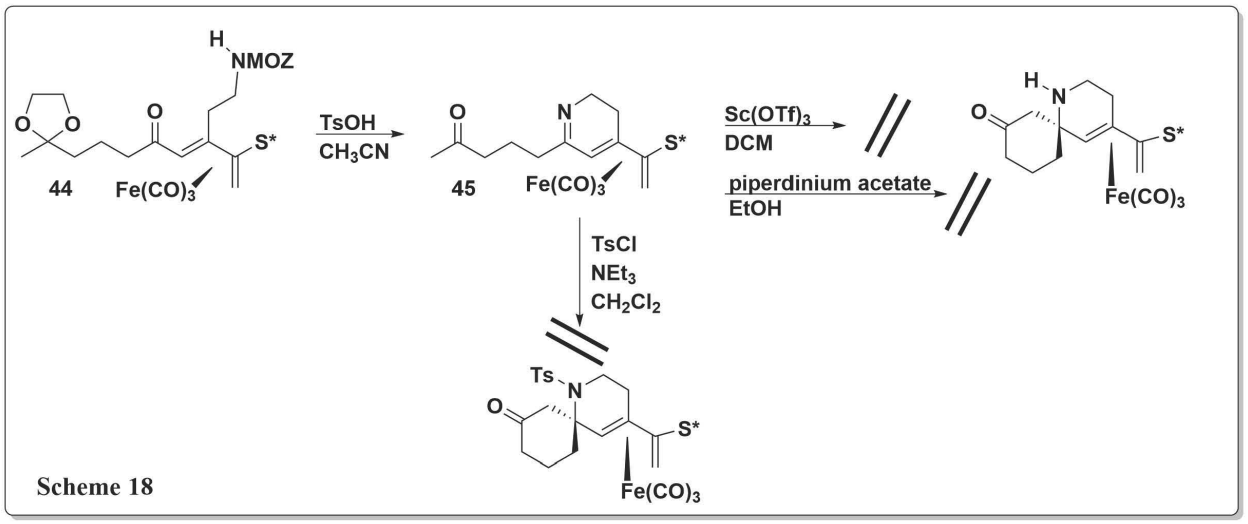


In analogy to the sequence described earlier, **Scheme 16**, shows the deprotonation of alkyne **27** and the subsequent nucleophlic attack on the recently prepared aldehyde **39**. As expected, the aldehyde was preferentially added to the acetylide instead of the carbamate anion in the MOZ protecting group to form **40**. A hydrostannylation using tributyltin hydride was accomplished but the regioisomeric ratio was not obtained. The resulting allylic alcohol **41** was oxidized using the Parikh-Doering conditions to stannyl enone **42**. The Stille reaction using Paley-adjusted Fürstner conditions was again successful to form the sulfinyl diene **43**. The subsequent complexation also went off without a hitch to afford **44** (dr not measured).



Feeling confident about the synthesis of the framework for the intramolecular Mannich, the ketone **44** was subjected to *p*-toluenesulfonic acid. Unfortunately, there was no reaction, which was a surprising outcome given the ease of formation of the imine in the earlier series (**Scheme 17**). A variety of conditions were then tried, all using tosic acid, but no length of time

seemed to coax the compound to react. Finally, we raised the temperature and a reaction did occur. Unfortunately, while the acetal and the amine were deprotected, and imine **45** formed, the sought-after Mannich reaction did not happen. This result was very discouraging because the whole concept of the sequence was to avoid the isolation of the imine.



Scheme 18

Conversion of this material was attempted anyway as shown in **Scheme 18**. Use of a soft Lewis Acid, scandium triflate, gave no product. Similarly, use of mild Bronsted neutral conditions using piperdinium acetate also failed. The final attempt we made was to form a tosyliminium ion to make the imine a better electrophile. Unfortunately this attempt was also unsuccessful.

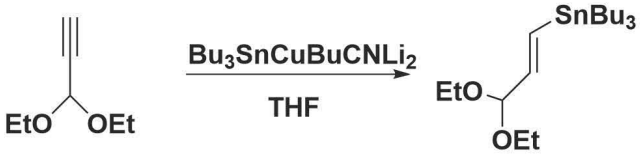
iii) Via direct replacement of a tertiary alcohol

The instability of the imine in the previous sequences was very disappointing, but the azaspirocycle was still on our minds as a worthy target. We were inspired by a report[35] in which a tertiary amine was created by intramolecular replacement of an ester with a secondary amine using a ruthenium catalyst.

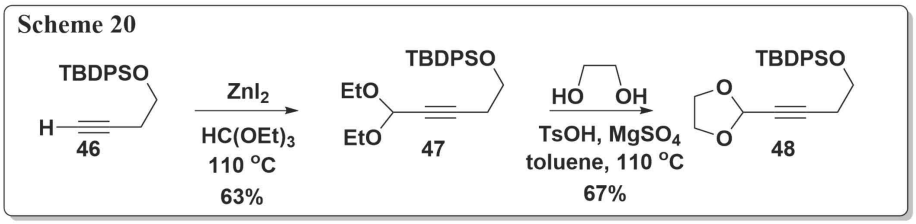
Recognizing the potential to have this step be the formation of our A ring, we set out to form the necessary precursor. We were seeking a way to have an aldehyde adjacent to the diene complex. As discussed, the iron(0) tricarbonyl complex is not compatible with all of the reactions we might be able to employ in other sequences. Thus, the oxidation state of an aldehyde presented a serious challenge. Selective reduction of an ester or amide at this position was not viable. Potentially, a silyl-protected alcohol could have been installed, but with the TEOC group protecting the amine, selectively deprotecting the alcohol was not feasible as both are removed using TBAF. Also, installing the aldehyde itself would not work as it is too reactive to undergo the stannylcupration, Stille coupling, or complexation reactions.

An acetal seemed like a great option to have the oxidation state of an aldehyde without the same reactivity. This choice implied that the hydrostannylation (or stannylcupration) could be performed, with regioselectivity, on an alkynyl acetal. There was only scant evidence in the literature that this could be feasible. Indeed, only one example was identified by a database (SciFinder Scholar) search, and this utilized a terminal alkyne[36] as seen in **Scheme 19**.

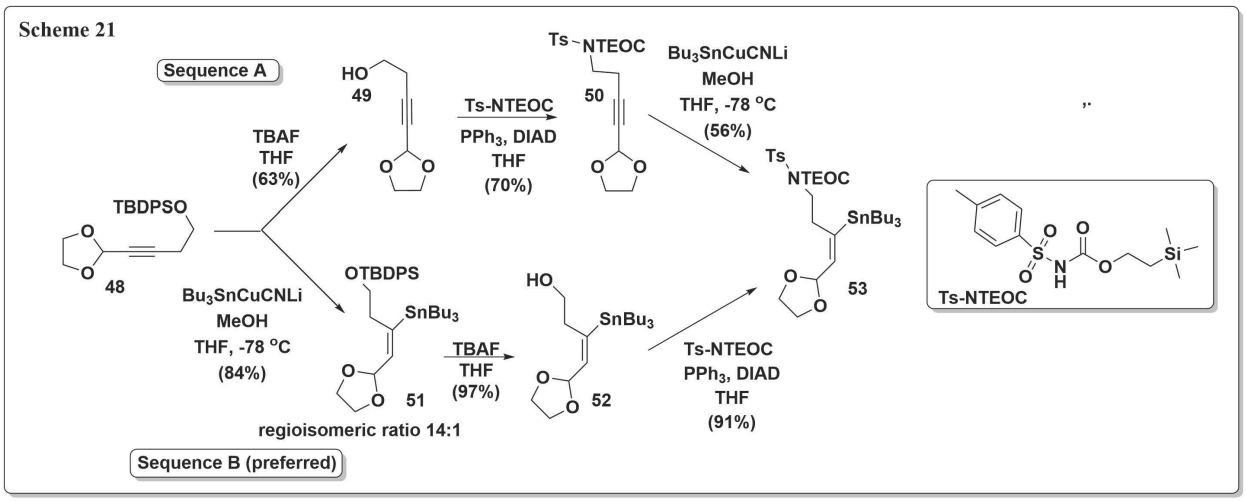
Scheme 19: Previous stannylcupration using an acetal as a directing group



With this in mind, our sequence began by forming a propargylic acetal **47** using ZnI_2 and triethylorthoformate based on a literature procedure[37]. The diethyl acetal seemed too reactive for the subsequent reactions that were planned, so the acetal was exchanged using ethylene glycol to form **48** (**Scheme 20**).



Here is where the chemistry really gets interesting for this sequence. We chose to divide the material into two different parallel sequences as seen in **Scheme 21**. The next major step in forming our sulfinyl iron(0) tricarbonyl complex requires the formation of a vinyl stannane, and two strategies seemed worthy of pursuit and comparison.

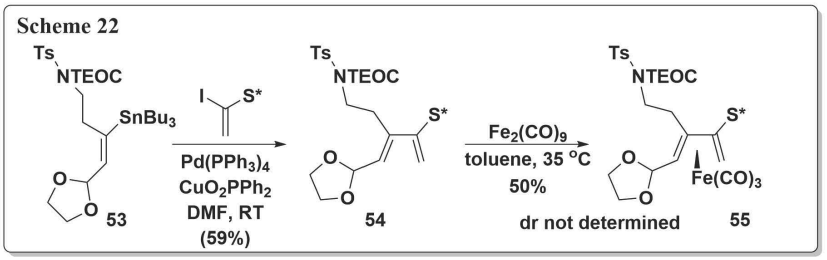


In Sequence A, we chose to install the tosylcarbamate on the substrate first and then perform the stannylcupration. The opposite order was chosen for sequence B. As it turned out, it was possible to prepare the desired amino vinyl stannane **53**, but the yields of the individual steps to obtain the homopropargylic alcohol **49** and the subsequent homopropargylic carbamate **50** were modest.

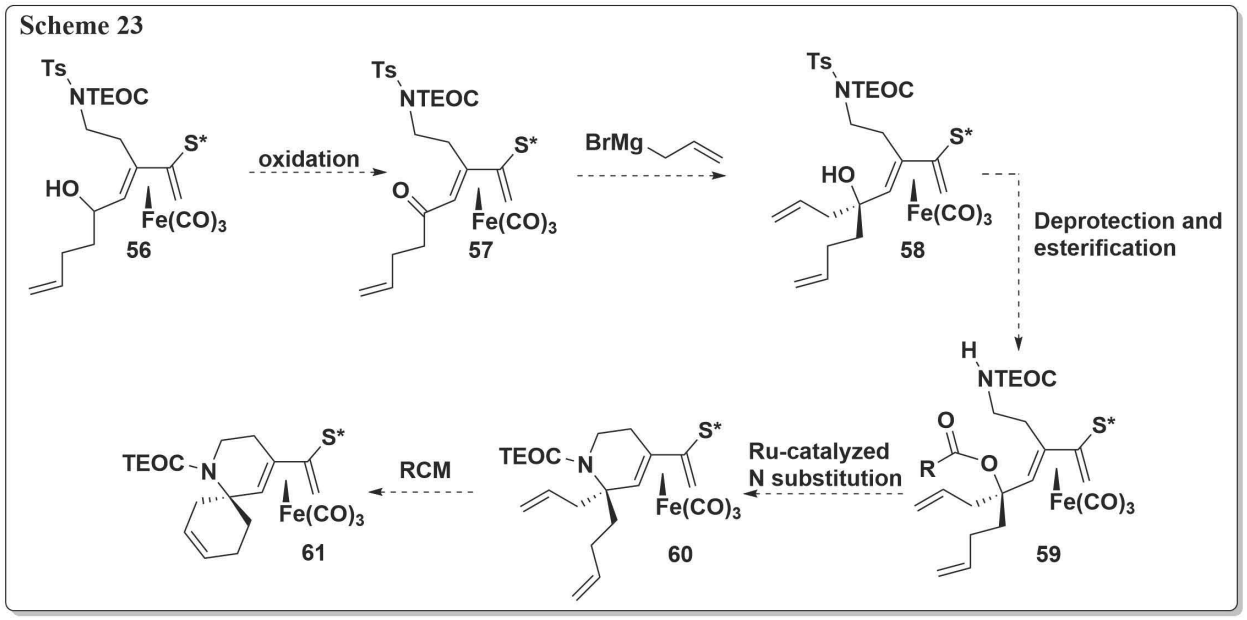
Conversely, in Sequence B, we chose to perform the stannylcupration on the silylether species (forming **51**) and then use the Mitsunobu reaction to install the tosyl carbamate **53** via alcohol **52**. The yields in this sequence were significantly better than those in Sequence A. But most notably, however, was the highly encouraging 14:1 regioisomeric ratio of the

stannylcupration. To our knowledge, this is the first example of a stannylcupration using an acetal as a directing group on an internal alkyne. The ability to have an easily accessible protected enal could be quite useful in future syntheses, both in the Paley laboratory and beyond.

After forming the vinylstannane **53**, the modified Stille was accomplished with the iodovinyl sulfoxide with a reasonable yield of sulfinyl diene **54** of 59%. The following complexation was accomplished with iron(0) nonacarbonyl to yield **55** (**Scheme 22**).

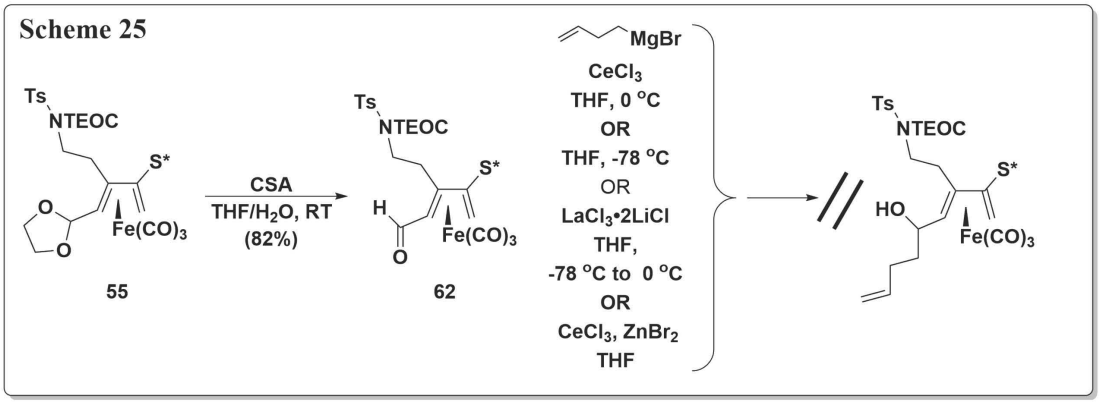


With the planar chirality installed, it was time to begin the assembly of the B ring precursors. Importantly, the acetal deprotection went smoothly using camphor sulfonic acid, proving to us that aldehyde **62** was truly accessible using this methodology. The next steps in the synthesis are proposed synthesis in **Scheme 23**. An addition to the aldehyde to yield **56** followed by an oxidation to form the ketone adjacent to the diene complex seemed trivial. After isolating the ketone **57**, the hope was to perform the defining diasteroselective addition. The resulting tertiary alcohol **58** was to be transformed into ester **59** and the ruthenium catalyzed replacement of the oxygen with our nitrogen seemed plausible. After this step formed **60** which would contain the A ring of the azaspirocycle, ring closing metathesis was going to be used to form the full azaspirocycle **61**. Based on our success with using ring closing metathesis in previous azaspirocycle sequences, this step seemed insignificant.

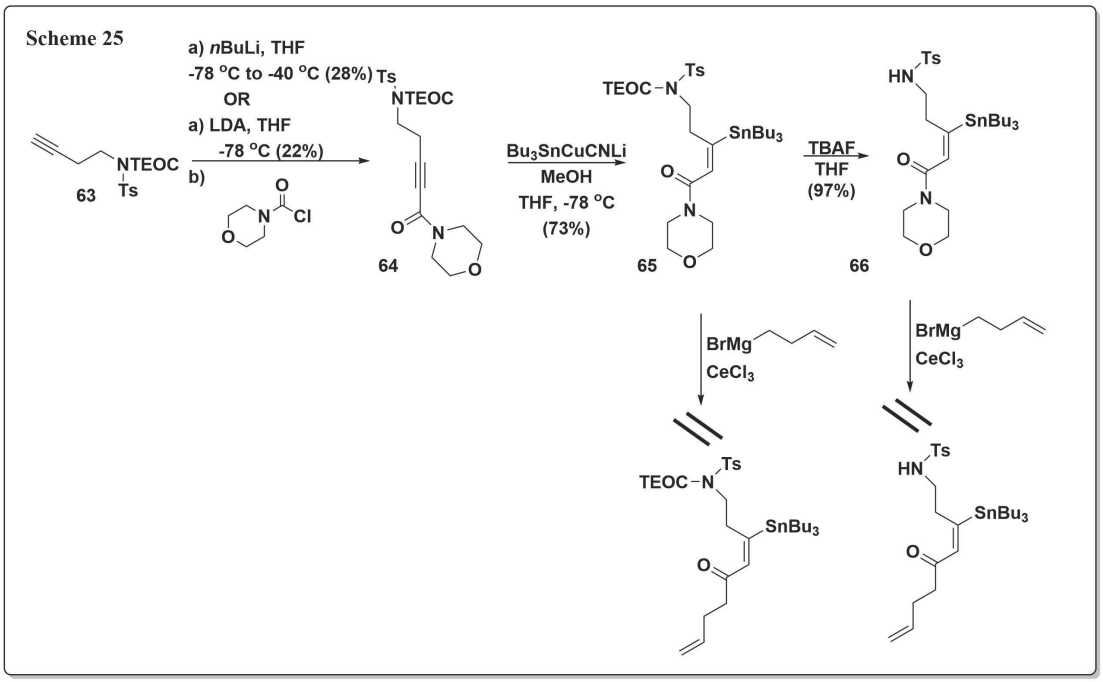


Hypothetically, this sequence was promising, but the first addition to the aldehyde was incredibly challenging (**Scheme 24**). The aldehyde **62** that we were so excited to have present adjacent to the diene complex turned out to be recalcitrant. Extensive attempts were made to add the butene group, but they were all unsuccessful. We tried forming the cerium analogue to the Grignard, thinking that the softer nucleophile would be successful. It was not. The hard butenyl Grignard reagent was itself unsuccessful. We tried lanthanum because this was reported to work at temperatures above -78 ^{o}C[38]. Feeling fairly discouraged, we tried to justify the problems we were having by scrutinizing our molecule further. The aldehyde was present, but so was the carbamate. Carbamates in general are softer than aldehydes, so perhaps it was interfering with the soft nucleophiles. However, the much greater tendency for aldehydes to react gives me pause about this conclusion. It is possible that the metal centers we were trying to use were coordinating to the carbamate, or possibly the extremely polar sulfoxide. Competitive coordination seemed likely, so we attempted to include $ZnBr_2$ in solution and again make the cerium reagent. Hypothetically, the Zn atom would coordinate preferentially to the interfering part of the molecule, leaving the aldehyde available for the nucleophilic attack. This was not the

case. These conditions also failed to yield the desired product. Notably, the nucleophile did not seem to add to the other parts of the molecule mentioned, there just seemed to be a lack of reactivity.



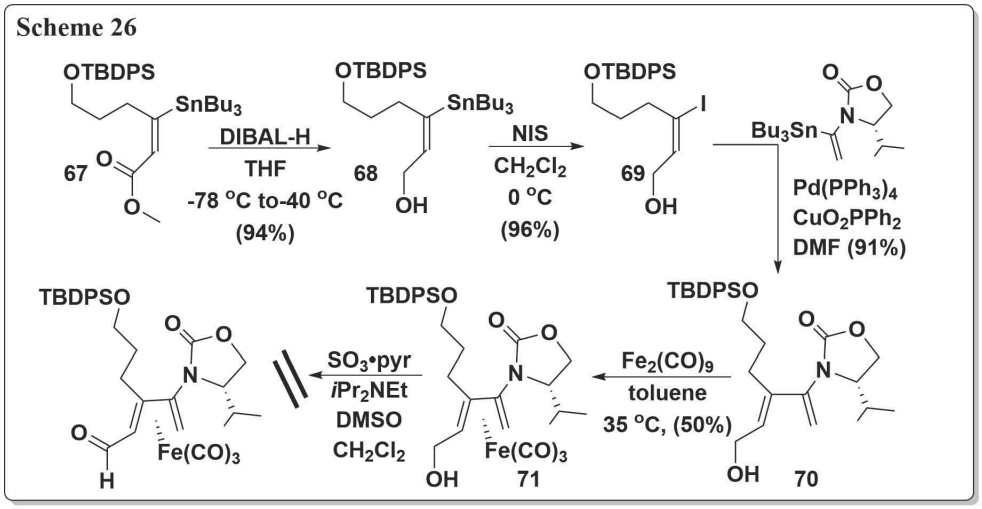
With the challenge adding to the aldehyde fresh in our mind, we tried to make the ketone from the morpholine amide, a tactic employed by the Paley group as part of their earlier approaches toward spiroketal synthesis[14]. This sequence would remove the need to add to the aldehyde and then oxidize the alcohol to synthesize the same ketone.



As seen in **Scheme 25** the alkyation of carbamoyl chloride was disappointing. Under both butyl lithium and LDA conditions, the yields were deplorable (<30%). It is possible that the TEOC group was getting competitively deprotonated instead of the alkyne. This reaction was not optimized further before the material was used. The stannylcupration on the propargylic amide was very successful. The next step involved adding the butene group. We first attempted to add it to the vinyl stannane with the tosyl carbamate. We attempted to make the cerium derivative of butenyl Grignard as the soft nucleophile of the cerium species is known to be compatible with the soft amide[14]. Again, the TEOC group seemed to be the culprit of failure. It is possible that the carbamate was coordinating to the cerium and/or magnesium to prevent the desired reaction. We removed the TEOC group using TBAF and tried the addition using cerium again. Unfortunately, this sequence also failed, suggesting that it might not have been the competitive presence of the carbamate that was the problem. It is possible that the butenyl Grignard reagent was bad, although it was freshly purchased, so that would just be bad luck. Limited by time and frustrated with the failure so early in the sequence, this sequence to the azaspirocycle was dropped. Despite our prior accomplishment of preparing a somewhat more functionalized azaspirocycle than had been previously made, this methodology was plagued by unreactive or unstable intermediate compounds. It was time to move on to a different project, but one that could at least leverage the discovery that alkynyl acetals could be regioselectively stannylated.

II. Oxazolidinone Project

i) An example of some difficulty: oxidation with SO_3



The sequence depicted in **Scheme 26** is the first I worked on involving the oxazolidinone chiral auxiliary. It is an informative sequence because it is a good example of the differences between the sequences using the oxazolidinone auxiliary and those involving the sulfoxide. The goal of this sequence was to form the aldehyde adjacent to the diene in order to be able to make diastereoselective additions at that center further into the sequence. As previously mentioned, constructing an aldehyde adjacent to the iron complex has been very challenging. This sequence occurred prior to the development of the stannylcupration using an acetal as a directing group. As such, the ester was the directing group for the stannylation (not shown), a transformation known for many years[39].

The sequence depicted in **Scheme 26** begins with the reduction of the ester **67** into an alcohol **68**. Unlike the case using the sulfoxide auxiliary, the iodovinyl oxazolidinone cannot be synthezised. The stannane must be converted into the iodide in order to couple with the vinyl stannane oxazolidinone. *N*-iodosuccinimide was used for the iodination to form **69**. The modified Stille used in the Paley lab tends to work very well with the vinyl stannane oxazolidinone, and

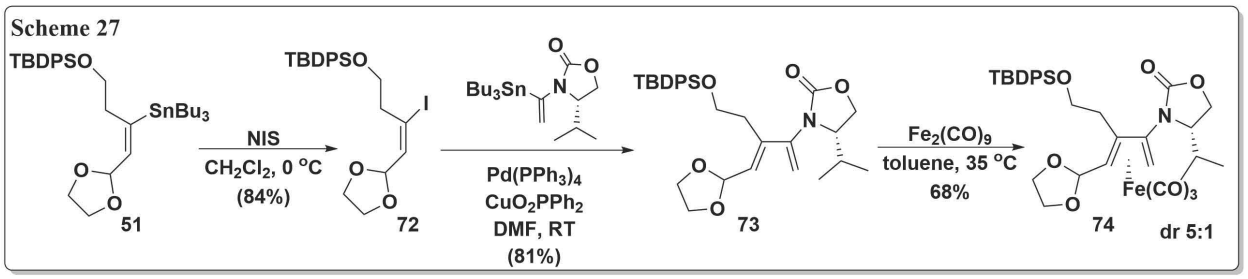
this sequence showed no deviation from that trend. The 90% yield of **70** was typical for these sequences and further encouragement for the investigation into this chemistry.

The complexation of the resulting diene **71** was not ideal, the yield was a low 50%, but nevertheless, the planar chirality was installed. The Parikh-Doering oxidation additions were attempted, as we know them to be compatible with the iron(0) tricarbonyl fragment from the sulfoxide series. Unfortunately, they were not compatible with the oxazolidinone and a measly 8% of the desired product was made. Although this result was disappointing, it partially inspired the development of the acetal chemistry described earlier (**Scheme 20 and 21**) which was very exciting. It is also important for the Paley laboratory to understand the adjustments that must be made when changing chiral auxiliaries. Oxidation is often a key step, and so understanding the need to adjust the visualization of sequences is crucial.

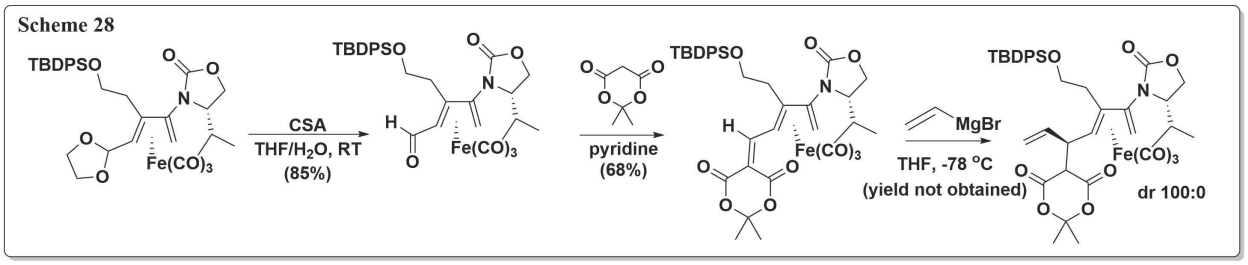
ii) Alkylidene malonate:

a) Oxazolidinone--- an aldehyde derivative and selective addition

A large portion of this thesis has discussed the benefit of an aldehyde adjacent to the diene complex. The following sequence provides one example of the benefits of this oxidation state at that position. Conceptually, we are forming the aldehyde and then replacing it with an alkylidene malonate via a Knoevenagel type aldol reaction. The addition to the alkylidene malonate should be perfectly diastereoselective, as has been shown in the 1-sulfinyl series[11].



Scheme 27 shows that this sequence begins with the product of the recently developed stannylcupration using an acetal as a directing group. Converting the resulting stannane **51** into iodide **72** and preforming the modified Stille afforded diene **73**. The complexation went reasonably well with a yield of 68% for **74** and the planar chirality was ready to be exploited.

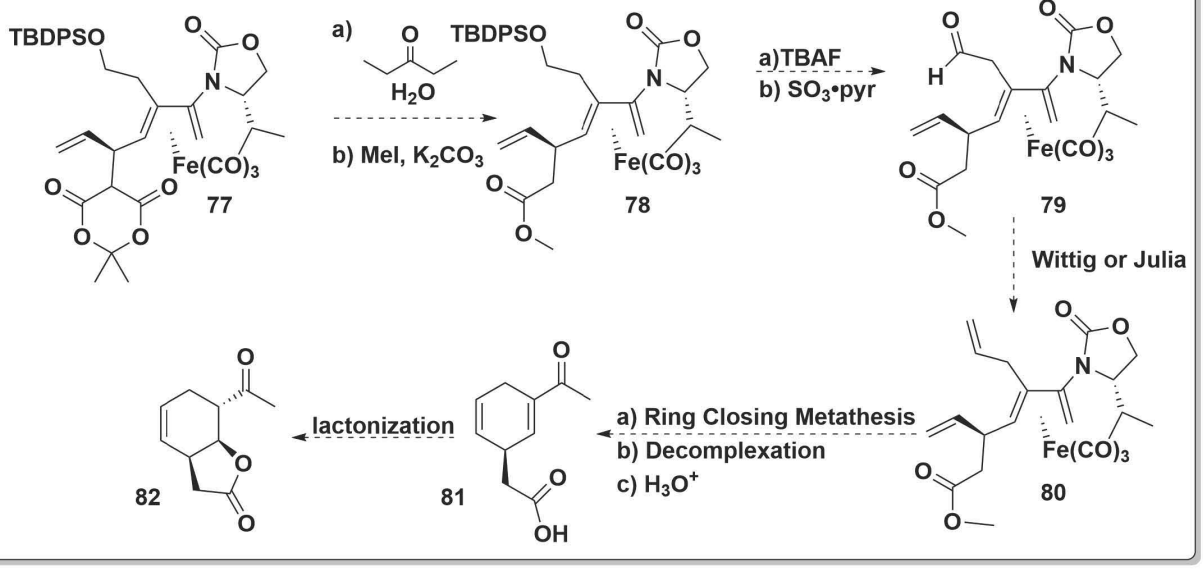


Excitingly, the oxazolidinone held up to the acid conditions we used to hydrolyze the acetal to aldehyde **75**. The oxazolidinone was also compatible with the mildly basic conditions used to install the alkylidene malonate **76** using a Knoevenagel type aldol reaction with Meldrum's acid. This addition was very exciting because it provides a framework to ensure that the planar chirality will be influential on the addition of the incoming nucleophile. I say this because hypothetically, if we added to the aldehyde, neither face would be overwhelmingly preferred.

If visualized as drawn in **Scheme 28**, the nucleophile would likely add from the top face, opposite the iron fragment. However, it is possible that the aldehyde could also take the conformation where the oxygen would be pointed up as drawn in **Scheme 28**. In this case the same face of the molecule would be attacked, but the stereocenter formed would be opposite. This possibility would essentially negate the purpose of our asymetric synthesis. Thus the installation of the alkylidene malonate is extremely important. It is huge in comparison to the aldehyde, so there is no conceivable way for it to rotate about the C-C bond in order to expose

the other face. Commentary aside, the addition of vinyl Grignard to afford **77** was accomplished with perfectly diastereoselectivity, to our great excitement.

Scheme 29



This sequence was stopped due to time limitation, but **Scheme 29** demonstrates the direction it was heading. The next step would have been a decarboxylation followed by a methylation to form the ester **78**. The goal moving forward with the upper tail of the molecule was to form a terminal alkene **80** from the protected alcohol. Using ring closing metathesis with this terminal alkene and the alkene added during the diastereoselective addition, we could form a ring with an incorporated stereocenter. The terminal alkene was to be formed by deprotecting the silyl ether **78** and oxidizing the resulting alcohol into the aldehyde **79**. Then, the Wittig or Julia reaction could be used to add a carbon (**80**) and the cyclization could occur to afford **81**.

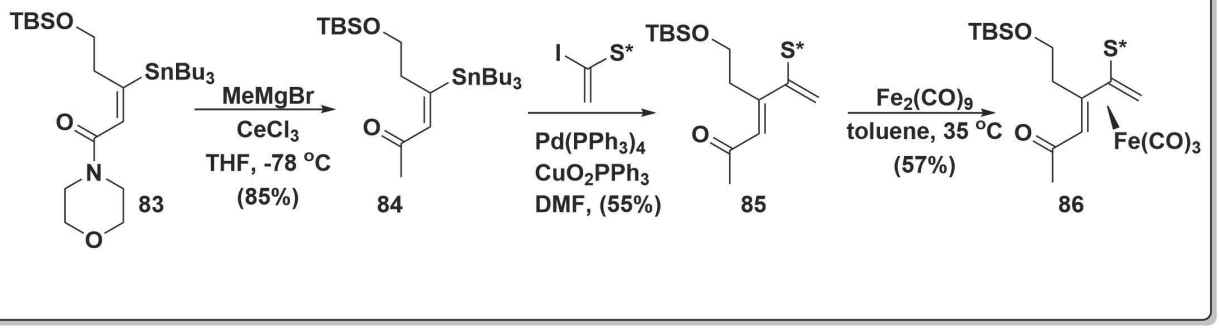
This is where the sequence could have really gotten exciting. The iron(0) tricarbonyl fragment was to be removed using reactions investigated in Paley lab in the past[14], and hydrolysis of the oxazolidinone into enone **81** was planned. This possibility is a huge benefit to using the oxazolidinone auxiliary because hypothetically that portion of the molecule now has a

handle to expand upon. Likely, the ester derived from the alkylidene malonate would hypothetically become a carboxylic acid and this acid could then cyclize to form lactone **82**. This possibility was very exciting because the lactone would most preferentially add on top (as drawn) and thermodynamically it makes sense that the ketone would occupy the opposite face. Thus, this sequence would have hypothetically formed three (3!) stereocenters on one ring.

b) Ketone derivative of alkylidene malonate: an attempt to make a controlled quaternary center

The goal of this variation of the project was to install an alkylidene malonate in place of a ketone adjacent to the diene complex in order to, after a diastereoselective addition, form a controlled quaternary center. We actually attempted this chemistry with both the sulfoxide and the oxazolidinone chiral auxiliaries.

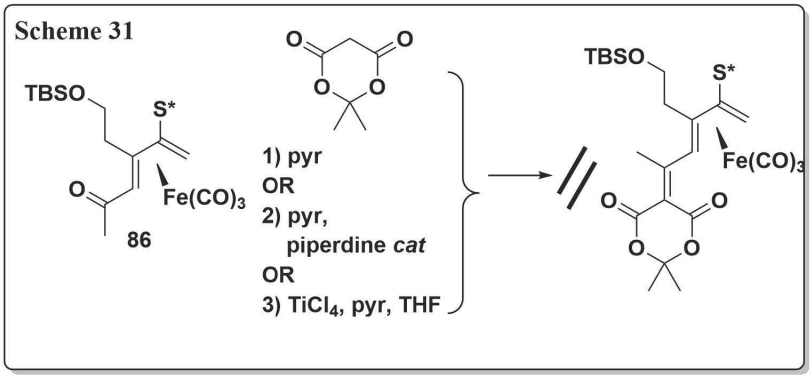
Scheme 30



We first attempted the ketone derivative of the alkylidene malonate with the sulfoxide, because as a lab we understand the limitations of the sulfoxide better than those of the oxazolidinone. As seen in **Scheme 30** the vinyl stannane **83** was synthesized using a stannylcupration directed by the morpholine amide. To form ketone **84**, we prepared the cerium derivative of methyl Grignard *in situ*. Cerium is much softer than magnesium, so it has been found to improve additions to amides, which are also soft[40]. This tactic was reported by the Paley

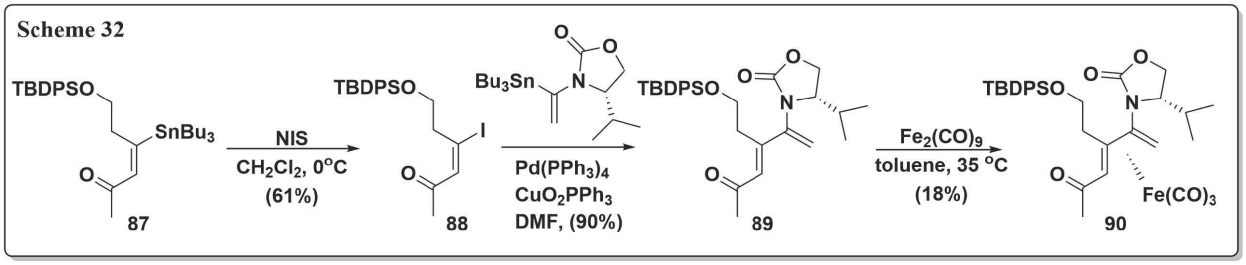
laboratory several years ago[14]. The modified Stille was performed with an adequate yield of 55% of diene **85**. This is just another example of disadvantage of the Paley sequence using the sulfoxide auxiliary. Complexation was accomplished to yield **86**, but again the yield was not exciting at 57%.

Scheme 31



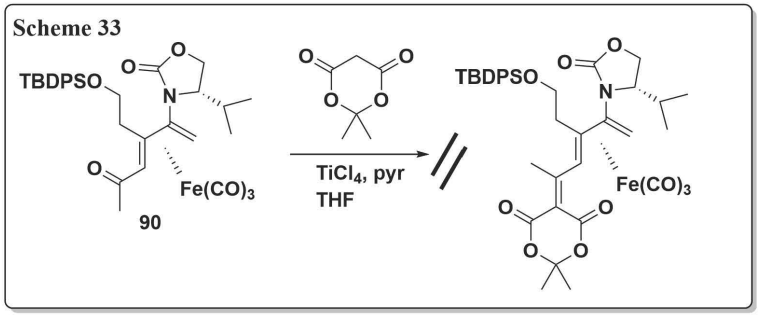
The new aspect of the chemistry, the formation of an alkylidene malonate derived from a ketone, can be seen in **Scheme 31**. Previous installation of Meldrum's acid, using an aldehyde in the Paley laboratory have needed simply the acid and pyridine to install the alkylidene malonate. Those basic conditions were tried, but to no avail. Recent literature suggested that the addition of piperdine as a catalyst may assist in the installation[41], but our attempt using piperdine also failed. A last attempt was made to install the alkylidene malonate in place of the ketone involved using a Lewis acid, $TiCl_4$, which has been found to promote this transformation[42]. A trace of product was detected, but 74% of the starting material was recovered which was not encouraging.

Without much confidence in our procedure, we attempted to use an analogous pathway with the oxazolidinone as the chiral auxiliary. We thought that perhaps the electron-withdrawing nature of the sulfoxide was preventing the Meldrum's acid from reacting at the ketone where we wanted it to.



This sequence begins with the same compound as the last one. The first difference, as seen in **Scheme 32**, is the need to iodinate the vinyl stannane **87**. The modified Stille was undertaken successfully with iodide **88** and the stannane containing the oxazolidinone to form the diene **89**. Notably, the yield of the Stille reaction was outstanding at 90%. Unfortunately, the complexation to yield **90** went very poorly, with an 18% yield, and it is unclear why. Perhaps the ketone adjacent to the diene interfered as the iron(0) could potentially form and η^4 complex with the ketone and its neighboring alkene.

Nevertheless, the material was pushed on to see if the Knoevenagel step was possible. **Scheme 33** shows that we chose to use the $TiCl_4$ conditions because they showed a chance of success in the sulfoxide sequence. Unfortunately, no product was detected from this reaction.

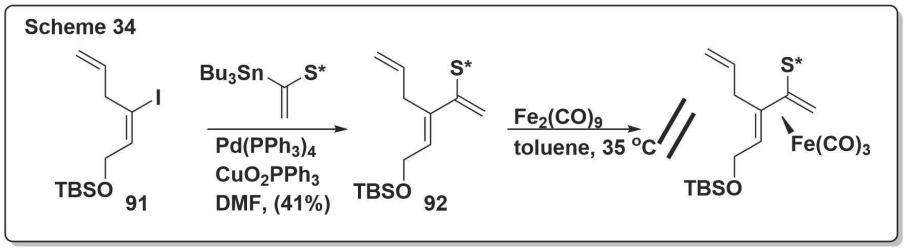


In the end, sterics are likely the culprit of all of this failure to install the alkylidene malonate. In order to have the alkylidene malonate installed, the ketone must be in a conformation such that the oxygen is pointed away from the rest of the molecule, and the methyl group is pointing toward the other tail of the molecule. This methyl must interact with the

methylene attached to the far side of the alkene in the diene, and this unfavorable interaction disables the conformation needed for the Knoevenagel reaction to occur.

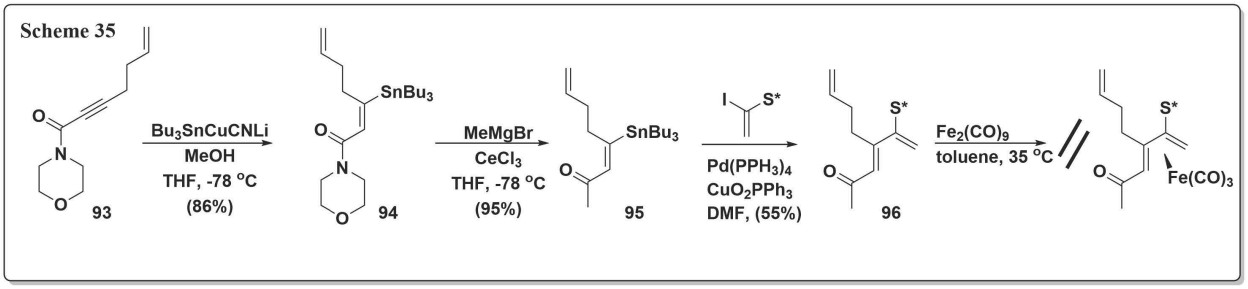
iii) Complexation with preinstalled alkene

Based on the end of **Scheme 29** it is apparent that a terminal alkene on the "upper branch" of the molecule as drawn would be incredibly beneficial. Given that it takes at least four steps (protecting, deprotection, oxidation, Wittig or Julia) to make this alkene from a primary alcohol, we wanted to try to install it prior to complexation to be able to cut out some steps, especially considering the challenges we have faced with oxidizing in the presence of the oxazolidinone. The next few sequences discussed actually involve the sulfoxide chiral auxiliary because we wanted to only change one aspect of the chemistry at a time.



Our first attempt, in **Scheme 34**, involved a terminal alkene two carbons away from the diene. The iodide **91** was prepared by Professor Paley. The Stille coupling was accomplished to yield **92**, albeit with a poor yield of 41%. Our attempt to complex the diene was a complete failure and four distinct compounds were observed via NMR. At first we thought these were the major and minor isomers of this product and the isomerized (with regards to the sulfoxide). We now believe that the side-chain alkene was incorporated into the organic ligand, that is, at least one of the four products is an η^2- η^4 bidentate complex. It occurred to us that the proximity of the terminal alkene could have been the problem.

As such, for our next attempt in **Scheme 35**, we built a molecule with two methylenes between the diene and the alkene. To do so, we did a stannylcupration on the propargylic morpholine amide **93** to afford **94**. We then used the cerium analogue to methyl Grignard to form methyl ketone **95** with a great yield (95%). The Stille reaction went typically for the iodosulfoxide partner with a yield of 55% of diene **96**. Then we got to the complexation step and, again, we got an intractable mess.



Some close NMR analysis of the products of these unsuccessful complexations and other like them indicated that the alkene was likely coordinating to the iron in an η^2 fashion, along with the η^4 complex desired. This result was disappointing because having an available alkene on the upper tether of the compound could be incredibly useful in future syntheses, especially considering the compatibility of the complexed compounds with ring closing metathesis.

Concluding Remarks

In conclusion, the functionalization of a [6,6]-azaspirocycle was developed confirming that the major reactions performed by my predecessor were compatible with a silyl-protected allylic alcohol. Unfortunately, the work presented in this thesis confronted the same problem with an unstable imine as a crucial part of the sequence. It is noteworthy, however, that the planar chirality installed using a 2-sulfinyl iron(0) tricarbonyl diene complex directed the addition to this loathsome imine to yield a single diastereomer.

Due to the instability of the intermediate imine, two different sequences were developed in an attempt to bypass the isolation of such a species. The first attempt was the potential use of an intramolecular Mannich. Unfortunately, our attempts to perform the Mannich could only produce a similarly unstable imine to the first sequence. The third attempt was to directly replace a tertiary alcohol with a functionalized amine. This sequence was unfortunately unfruitful due to a recalcitrant aldehyde that would not undergo any addition reaction that we tried.

The second piece of the work presented here was the development of the use of an oxazolidinone as a chiral auxiliary to direct the complexation of the diene. Fortunately, we were able to use this auxiliary in a sequence employing an alkylidene malonate to which a nucleophile was added with perfect diastereoselectivity. Unfortunately, attempts to extend this project to ketone derivatives of the alkylidene malonate, as opposed to an aldehyde, failed.

Other sequences were attempted in which we sought to install terminal alkenes prior to complexation of the diene. Unfortunately, the complexation reactions produced confusing messes that appeared to incorporate compounds in which the iron was coordinating to the terminal alkene.

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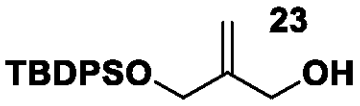
Experimental Section

All reactions were carried out on a Schlenk line under argon atmosphere. The solvents used in these methods were all anhydrous unless otherwise noted. THF, toluene, and dichloromethane solvents were purchased from J.T. Baker and kept in an anhydrous solvent dispenser. When being utilized, the collection flasks for these solvents were either purged with alternating evacuation and argon flow or sufficiently dried in a glassware oven. Upon collection, the solvents were run through a netural alumina/copper(II) oxide columns to assure that they were anhydrous. All other liquids were measured and transferred using gastight syringes or cannulas, and all solids were weighed using an analytical balance. All air-sensitive reagents were stored under inert nitrogen atmosphere in a glovebox.

All crude products were purified by flash column chromatography using Merck 200-400 silica gel as the solid phase and mixtures of hexanes, ethyl acetate, and sometimes trimethylamine as eluents. Compounds with limited solubility in these solvents were loaded onto the column using either toluene or chloroform.

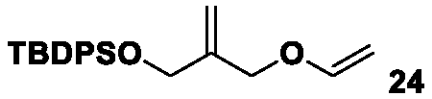
Thin layer chromatography was carried out using uniplate 150 micron precoated glass plates purchased from Analtech. Visualization of product spots achieved using ultraviolet light, vanillin dip, and/or permanganate dip. Products were characterized by NMR using a Bruker Ascend 400MHz NMR with autosample (400 MHz for ^{1}H, 100 MHz for ^{13}C). Fourier transform IR spectra were taken using a DigiLab Excalibur Series spectrometer at 4 cm^{-1} resolution. Rotational analysis was carried out using a Jasco P-2000 series polarimeter. HRMS was performed by the Mass Spectrometry Facility in the Department of Chemistry at the University of California at Riverside.

NMR abbreviations: s=singlet, d=doublet, t=triplet, dd=doublet of doublets, dt=doublet of triplets, td=triplet of doublets, m=multiplet, obs=obscured.



Alcohol **23**: NaH (60% dispersion in mineral oil) (228 mg, 5.7 mmol, 1 eq) was weighed into a Schlenk flask in the glovebox. Under Ar, dry THF (4.5 mL) was added and the solution was cooled to 0°C. 2-methylene-1,3-pronediol (507 mg, 11.4 mmol, 1 eq) was added dropwise. The reaction was stirred for 70 min at room temperature. The solution was recooled to 0°C and t-butyldiphenylsilylchloride (1.41 mL, 10.83 mmol, 0.95 eq) was added over 2 min. The reaction was quenched with 5 mL of H_2O. The solution was diluted with Et_2O (50 mL) and water (10 mL). The aqueous layer was extracted with Et_2O (2 x 15 mL). The organic layer was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified via column chromatography (silica, 7:1 hexanes: EtOAc) to yield alcohol **23** (1.86 g, 100%) as a clear oil.

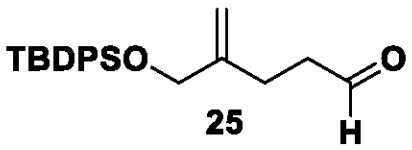
^{1}H NMR (400 MHz) **δ** 1.06 (s, 9H, *t*-butyl H), 1.78 (t, 1H, O<u>H</u>), 4.28 (d, 2H, C<u>H</u>$_2$OH, *J*= 5.6Hz), 4.26 (s, 2H, C<u>H</u>$_2$OSi), 5.11 (q, 1H, one of the vinylic H, *J*= 1.2 Hz), 5.15 (q, 1H, one of the vinylic H, *J*= 0.7 Hz), 7.41 (m, 6H, Ar), 7.68 (m, 4H, Ar).



24

Ether **24**: Alcohol **23** (1.86 g, 5.70 mmol, 1 eq) was dissolved in ethylvinyl ether (24.2 mL) and mercuric trifluoroacetate (365 mg, 0.855 mmol, 0.15 eq) was added. After 2.5 h, an additional portion of mercuric trifluoroacetate (122 mg, 0.285 mmol, 0.05eq) was added and the reaction was refluxed for 20 h. The reaction was cooled to 0°C and poured into 10% Na_2CO_3 solution (40 mL). The subsequent mixture was extracted with ether (50 mL). The organic layer was washed with brine (20 mL) and was dried over $MgSO_4$ then filtered. The solution was concentrated via rotary evaporation and purified via column chromatography (silica, 50:1 hexanes: EtOAc) to yield ether **24** (1.588 g, 79%) as a clear oil.

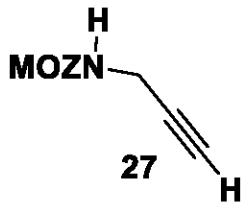
^{1}H NMR (400 MHz) **δ** 1.06 (s, 9H, *t*-butyl H), 4.02 (dd, 2H, one of $C\underline{H}_2OCHCH_2$, *J*= 6.8 Hz, 2.0 Hz), 4.25 (m, 5H, one of $C\underline{H}_2OCHCH_2$ + $C\underline{H}_2OSi$ + $CH_2OCHC\underline{H}_2$), 5.19 (q, 1H, one of $C\underline{H}_2C(CH_2O)_2$, *J*= 1.4 Hz), 5.32 (q, 1H, one of $C\underline{H}_2C(CH_2O)_2$, *J*= 0.8 Hz), 6.43 (dd, 1H, $CH_2OC\underline{H}CH_2$, *J*= 14 Hz, 6.6 Hz), 7.41 (m, 6H, Ar), 7.68 (m, 4H, Ar).



25

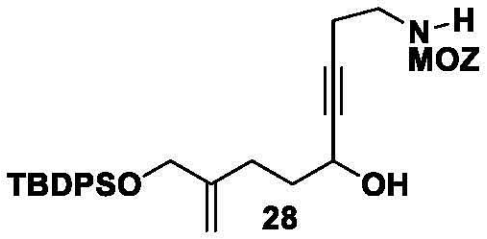
Aldehyde **25**: The flask with the vinyl ether **24** (2.11 g, 5.99 mmol, 1eq), was equipped with a stir ba r and placed under Ar. Benzonitrile (4.25 mL) was added and heated at 175°C overnight (16 h). The reaction was distilled using a Kuglrohr oven. The resulting residue was purified via column chromatography (silica, 12:1 hexanes: EtOAc) to yield aldehyde **25** (1.8219 g, 86%) as a clear oil.

^{1}H NMR (400 MHz) **δ** 1.04 (s, 9H, *t*-butyl H), 2.34 (t, 2H, C$\underline{H}_2$CH$_2$C(O)H, *J*= 7.5 Hz), 2.54 (td, 2H, CH$_2$C$\underline{H}_2$C(O)H, *J*= 7.5 Hz, 1.4Hz), 4.12 (s, 2H, C$\underline{H}_2$OSi), 4.77 (q, 1H, one of the vinylic H, *J*= 1.3 Hz), 5.19 (d, 1H, one of the vinylic H, *J*= 0.7 Hz), 7.41 (m, 6H, Ar), 7.67 (m, 4H, Ar), 9.73 (t, 1H, C(O)$\underline{H}$, *J*= 1.6 Hz)



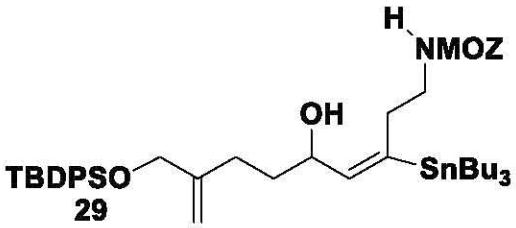
Carbamate **27**: The flask was flame dried under Ar, and the carboxylic acid (981 mg, 10 mmol, 1 eq) was added, followed by toluene (15 mL) and NEt_3 (1.39 mL, 10 mmol, 1eq). DPPA (2.16 mL, 10 mmol, 1.eq) was added slowly and the reaction mixture was placed in an 80°C oil bath for 3h. After being removed from the bath, 4-methyoxybenzyl alcohol (1.37 mL, 11 mmol, 1.1 eq) and DMAP (244 mg, 2 mmo, 0.2 eq) were added. The flask was sealed and placed in a 50°C oil bath overnight. The mixture was concentrated using rotary evaporation and the resulting residue was purified via column chromatography (silica, 4:1 hexanes: EtOAc) to yield carbamate **27** (1.89 g, 81%) as a clear oil.

^{1}H NMR (400 MHz) **δ** 1.99 (t, 1H, alkynyl H, *J*= 1.7Hz), 2.41 (td, 2H, propargylic H, *J*= 6.2 Hz, 2.3Hz), 3.35 (q, 2H, C$\underline{H}_2$NH, *J*= 6.3Hz), 3.81 (s, 3H, OC$\underline{H}_3$), 5.04 (s, 2H, benzylic H), 6.90 (m, 2H, Ar), 7.31 (m, 2H, Ar)



Propargylic alcohol **28**: Alkyne **27** (1.147 g, 4.922 mmol, 1 eq) was dissolved in dry THF (30 mL) and cooled to 0°C. n-BuLi (1.6M in hexanes, 6.15 mL, 9.844 mmol, 2 eq) was added dropwise via syringe. Stirred for 20 minutes and the 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) (1.190 mL, 9.844 mmol, 2 eq) was added dropwise via syringe. Stirred for 10 min at 0°C, the aldehyde **25** (1.8219 g, 5.168 mmol, 1.05 eq) in THF (11.5 mL) was added via cannula. Stirred for 1 h at 0°C. Reaction was quenched with H_2O (10mL). Separated with Et_2O (45 mL). Layers separated and organic layer washed with H_2O (20 mL) then brine (20 mL). The solution was dried over $MgSO_4$ and concentrated via rotary evaporator. The resulting residue was purified via column chromatography (silica, 2.5:1 hexanes: EtOAc) to yield **28** (2.39 g, 83%).

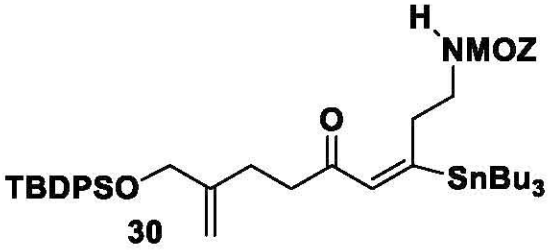
^{1}H NMR (400 MHz) **δ** 1.05 (s, 9H, *t*-butyl), 1.76 (m, 2H, C$\underline{H}_2$CHOH), 1.84 (broad s, 1H, O$\underline{H}$), 2.13 (t, 2H, *J*= 7.7 Hz), 2.40 (t, 2H, propargylic H, *J*= 6.1 Hz), 3.31 (dt, 2H, C$\underline{H}_2$NH, *J*=), 3.80 (s, ArOC$\underline{H}_3$), 4.11 (s, 2H, C$\underline{H}_2$OSi), 4.31 (dt, 1H, CHOH), 4.89 (s, 1H, one of the terminal vinyl H), 5.04 (s, 2H, C(O)OC$\underline{H}_2$), 5.19 (s, 1H, one of the terminal vinyl H), 6.87 (d, 2H, Ar, *J*= 8.7 Hz), 7.28 (partially obscured d, 2H, Ar), 7.39 (m, 6H, Ar), 7.68 (m, 4H, Ar); **^{13}C NMR** (100 MHz) **δ** 19.27, 20.24, 26.80, 28.27, 36.00, 39.82, 55.29, 62.15, 66.38, 66.64, 82.45, 82.74, 109.32, 113.92, 127.68, 113.92, 127.68, 128.47, 129.67, 130.08, 133.54, 135.52, 147.17, 156.34, 159.59; **IR** (neat) 1112, 1248, 1428, 1519, 1531, 1705, 2857, 2932, 2955, 3072, 3361, 3407 cm^{-1}; **HRMS** (M+Na$^+$) calcd for $C_{35}H_{43}NO_5Si$ 608.2803 found 608.2818.



29

Vinyl stannane **29**: Under an Ar atmosphere, the alkyne **28** (2.39 g, 4.080 mmol, 1 eq), tributyltin (1.41 mL, 5.304 mmol, 1.3 eq), and catalyst $Pd(PPh_3)Cl_2$ (85.9 mg, 0.1224 mmol, 0.03 eq) were dissolved in THF (30 mL) and stirred for 24 h. A second portion of both tributyltin (0.937 mL, 3.535 mmol, 0.86 eq), and catalyst $Pd(PPh_3)Cl_2$ (57.2 mg, 0.081 mmol, 0.02 eq) were added and the reaction was stirred for 24 h. The solution was concentrated via rotary evaporation and the residue was purified via column chromatography (silica, 6:1 hexanes: EtOAc with 0.5% NEt_3 three times) to yield the vinyl stannane **29** (2.24 g, 62%) as a pale yellow oil.

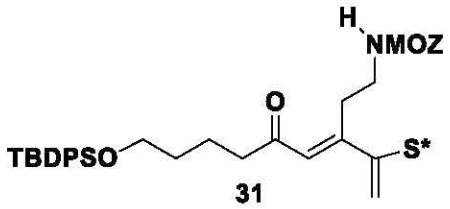
^{1}H NMR (400 MHz) **δ** 0.88 (m, 15H, $Sn(C\underline{H}_2CH_2CH_2C\underline{H}_3)_3$), 1.05 (s, 9H, *t*-butyl), 1.22-1.49 (2m, 12H, $Sn(CH_2C\underline{H}_2C\underline{H}_2CH_3)_3$), 1.55 (partially obscured m, 1H, one of $C\underline{H}_2CHOH$), 1.63 (partially obscured m, 1H, one of $C\underline{H}_2CHOH$), 1.79 (d, 1H, O<u>H</u>, *J*= 3.8 Hz), 2.01 (m, 2H, $C(CH_2)C\underline{H}_2CH_2CHOH$), 2.35 (m, 1H, one of $C(SnBu_3)C\underline{H}_2$), 2.63 (m, 1H, one of $C(SnBu_3)C\underline{H}_2$), 3.08 (m, 1H, one of $C\underline{H}_2NH$), 3.28 (m, 1H, one of $C\underline{H}_2NH$), 3.78 (s, 3H, $ArOCH_3$), 4.10 (s, 2H, CH_2OSi), 4.39 (m, 1H, C<u>H</u>OH), 4.88 (s, 1H, one of the terminal vinyl H), 5.01 (m, 3H, N<u>H</u> + $C(O)OC\underline{H}_2Ar$), 5.20 (s, 1H, one of the terminal vinyl H), 5.61 (d with Sn satellites, vinylic H β to Sn, *J*= 8.2 Hz), 6.85 (m, 2H, Ar), 7.27 (m, 2H, Ar), 7.40 (m, 6H, Ar), 7.79 (m, 2H, Ar); **^{13}C NMR** (100 MHz) **δ** 9.67, 13.70, 19.25, 26.79, 27.35, 28.67, 29.06, 33.00, 35.62, 40.50, 55.24, 66.36, 66.70, 108.81, 113.84, 127.67, 129.65, 130.02, 133.53, 135.50, 147.64, 159.49; **IR** (neat) 1112, 1247, 1428, 1463, 1519, 1705, 2855, 2922, 3361, 3414 cm^{-1}; **HRMS** ($M+H^+$) calcd for $C_{47}H_{72}NO_5Si^{120}Sn$ 878.4196, found 878.4205



Stannylenone **30**: The allylic alcohol **29** (598.2 mg, 0.682 mmol, 1 eq) was dissolved in dichloromethane under an Ar atmosphere. DMSO (1.6 mL) and diisopropylethylamine (0.475 mL, 2.729 mmol, 4 eq) were added and the solution was cooled to -40°C. SO_3·pyr (307 mg, 2.047 mmol, 3eq) was added and the reaction was allowed to warm to -8°C over 90 min. The reaction solution diluted with saturated $NaHCO_3$ (10 mL) and transferred to separatory funnel with EtOAc (35 mL). The layers were separated and the organics were washed with H2O (2 x 10), brine (1 x 10). The solution was dried over $MgSO_4$ and then filtered and concentrated via rotary evaporation. The resulting residue was purified via column chromatography (silica, 12:1 hexanes: EtOAc with 0.5% NEt_3) to yield ketone **30** (436.3 mg, 73%) as a clear oil.

^{1}H NMR (400 MHz) **δ** 0.88 (t, 9H, $Sn(CH_2CH_2CH_2C\underline{H}_3)_3$), 0.97 (t with Sn satellites, 6H, $Sn(C\underline{H}_2CH_2CH_2CH_3)_3$) 1.06 (s, 9H, t-butyl), 1.22-1.57 (two m, 12 H, $Sn(CH_2C\underline{H}_2C\underline{H}_2CH_3)_3$), 2.28 (t, 2H, $C(CH_2)C\underline{H}_2CH_2C(O)$), *J*=15 Hz), 2.55 (t, 2H, $C\underline{H}_2COC$, *J*= 7.6 Hz), 2.85 (t with satellites, 2H, CH_2CSnBu_3, *J*= 6.5 Hz), 3.30 (dt, 2H, CH_2NH), 3.79 (s, 3H, $ArOCH_3$), 4.10 (s, 2H, $C\underline{H}_2OSi$), 4.82 (s, 1H, one of terminal vinyl H), 4.95 (s, 2H, $C(O)OC\underline{H}_2Ar$), 5.18 (s, 1H, one of the terminal vinyl H), 5.57 (t, 1H, NH), 6.39 (s with satelittes, 1H, $C\underline{H}CSnBu_3$), 6.85 (d, 2H, Ar, *J*=8.64 Hz), 7.28 (partially obscured d, 2H, Ar), 7.40 (m, 6H, Ar), 7.67 (m, 4H, Ar); **^{13}C NMR (100 MHz) δ** 9.94, 13.66, 19.26, 26.75, 26.81, 27.04, 27.32, 28.87, 28.97, 29.01, 40.38, 41.92, 55.26, 66.07, 66.42, 109.19, 113.77, 127.68, 129.07, 129.67, 129.87, 133.51, 133.51, 135.52, 138.31, 146.95, 156.95, 159.37, 167.69, 199.24; **IR** (neat) 1112, 1246, 1515, 1722, 2856,

2929, 2956, 3072, 3349 cm^{-1}; **HRMS** ($M+H^+$) calcd for $C_{47}H_{70}NO_5{}^{120}Sn$ 876.4040, found 876.4044

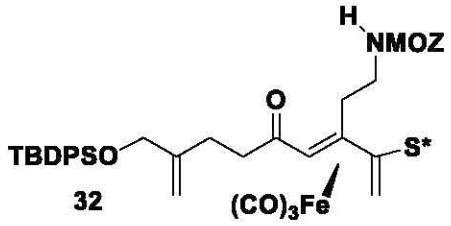


31

Sulfinyl diene **31**: Stannylenone **30** (436.3 mg, 0.4987 mmol, 1 eq) was placed in a schlenk flask and brought into the glovebox. It was dissolved in dichloromethane (5.0 mL). Iodovinyl sulfoxide (145.7 mg, 0.4987 mmol, 1 eq) was added. Next, CuO_2PPh_2 (161 mg, 0.5735 mmol, 1.15 eq) and $Pd(PPh_3)_4$ catalyst (57.6 mg, 0.0499 mmol, 0.1 eq) were added and the reaction was stirred overnight. The reaction was removed from the glove box and filtered through a silica gel plug with EtOAc. The solution was concentrated via rotary evaporation and transferred to separatory funnel with diethyl ether (90 mL). The organic layer was washed with H_2O (2 x 25 mL) and brine (30 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 1.5:1 hexanes: EtOAc, loaded in chloroform) to yield sulfoxide diene **31** (258.9 mg, 70%).

^{1}H NMR (400 MHz) **δ** 1.07 (s, 9H, *t*-butyl), 2.21 (t, 2H, C$\underline{H}_2$C(O), *J*= 7.5 Hz), 2.31 (s, 3H, ArC$\underline{H}_3$), 2.50 (dt, 2H, C(CH$_2$)C$\underline{H}_2$, *J*=7.5, 2.2 Hz), 2.58 (m, 1H, one C=C(CS*)C$\underline{H}_2$), 2.85 (m, 1H, one C=C(CS*)C$\underline{H}_2$), 2.83 (m, 1H, C$\underline{H}_2$NH), 3.05 (m, 1H, C$\underline{H}_2$NH), 3.79 (s, 3H, ArOC$\underline{H}_3$), 4.09 (s, 2H, C$\underline{H}_2$OSi), 4.78 (s, 1H, one of CS*C$\underline{H}_2$), 4.95 (m, 3H, NH + C(O)OC$\underline{H}_2$Ar), 5.13 (s, 1H, one of CS*C$\underline{H}_2$), 6.18 (s, 1H, one of terminal vinyl H), 6.29 (s, 1H, C(O)C$\underline{H}$C), 6.39 (s, 1H, one of terminal vinyl H), 6.86 (d, 2H, Ar, *J*= 8.6 Hz), 7.18 (d, 2H, Ar, *J*= 8.0 Hz), 7.25 (partially obscured d, 2H, Ar), 7.40 (m, 8H, Ar), 7.67 (m, 4H, Ar); **^{13}C NMR (100 MHz) δ** 19.27, 21.45, 26.58, 26.80, 31.96, 39.54, 42.73, 55.28, 66.26, 66.36, 109.32, 113.84, 120.19, 125.61, 127.56, 127.71, 128.74, 129.74, 129.92, 130.04, 133.43, 135.50, 139.25,

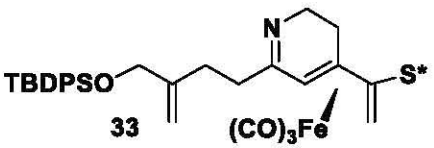
142.60, 146.46, 146.57, 153.61, 156.29, 159.50, 200.04; **IR** (neat) 1112, 1246, 1515, 1723, 2857, 2894, 3340 cm^{-1}; Diastereomeric (facial) mixture: $[\alpha]_D^{22.7}$ = +58.8 (*c* 0.375, $CHCl_3$)



Diene complex **32**: Under an Ar atmosphere, the sulfinyl diene **31** (479.3 mg, 0.639 mmol, 1 eq) was dissolved in toluene (7 mL). $BdaFe(CO)_3$ (731.3 mg, 2.556 mmol, 4 eq) was added. The reaction was placed in a 40°C bath and stirred for 20 h. Reaction mixture was filtered through silica gel on a glass frit and rinsed with EtOAc. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 9:1 to 7:1 to 3:1 hexanes: EtOAc) to yield the complexed diene **32** (480.5, 85%) as a yellow foam with dr 3.3:1.

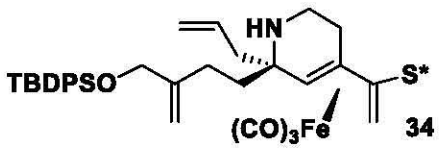
Major **^{1}H NMR** (400 MHz) **δ** 0.29 (d, 1H, one of the CS*C$\underline{H}_2$, *J*= 3.4 Hz), 0.52 (s, 1H, C(O)C$\underline{H}$C), 1.04 (s, 9H, *t*-butyl), 2.20 (t, 2H, C$\underline{H}_2$C(O), *J*= 6.6 Hz), 2.40 (partially obscured s, 3H, $ArCH_3$), 2.48 (m, 2H, $C(CH_2)CH_2$), 2.88 (m, 2H, C(CS*)C$\underline{H}_2$), 3.30 (m, 1H, one of C$\underline{H}_2$NH), 3.66 (m, 1H, one of C$\underline{H}_2$NH), 3.80 (s, 3H, ArOC$\underline{H}_3$), 4.07 (partially obscured s, 2H, C$\underline{H}_2$OSi), 4.59 (t, 1H, N$\underline{H}$), 4.80 (partially obscured s, 1H, one of terminal vinyl H), 5.16 (partially obscured s, 1H, one of terminal vinyl H), 4.95 (partially obscured m, 2H, $C(O)OCH_2Ar$), 6.89 (partially obscured d, 2H, Ar), 7.23 (partially obscured d, 2H, Ar), 7.38 (m, 6H, Ar), 7.65 (m, 4H, Ar), 7.83 (d, 2H, Ar); Unobscured peaks of minor **^{1}H NMR** (400 MHz) **δ** 0.47 (d, 1H, one of the CS*C$\underline{H}_2$), 0.49 (s, 1H, C(O)C$\underline{H}$C), 1.05 (s, 9H, *t*-butyl), 2.12 (d, 1H, one of the CS*C$\underline{H}_2$), 2.39 (partially obscured s, 3H, $ArCH_3$), 3.07 (m, 1H, one of C$\underline{H}_2$NH), 3.45 (m, 1H, one of C$\underline{H}_2$NH), 3.78 (s, 3H, ArOC$\underline{H}_3$), 4.08 (s, 3H, ArOC$\underline{H}_3$), 4.39 (t, 1H, N$\underline{H}$), 4.82 (partially obscured s, 1H, one of terminal vinyl H), 5.19 (partially obscured s, 1H, one of terminal vinyl H), 4.95 (partially obscured m, 2H, $C(O)OCH_2Ar$); **^{13}C NMR** (100 MHz) **δ** 19.25, 21.08, 21.59, 15.61, 26.77, 28.26, 29.74, 41.22, 42.00, 52.39, 55.28, 66.35, 66.49, 105.09,

109.01, 113.86, 115.21, 125.64, 127.67, 129.66, 130.05, 130.48, 133.53, 135.48, 141.38, 143.01, 146.85, 156.24, 159.60; **IR** (film, $CHCl_3$) 1112, 1246, 1428, 1515, 1715, 1997, 2066, 2858, 2895, 2932, 2957, 3012, 3334 cm^{-1}; **HRMS** ($M+H^+$) calcd for $C_{47}H_{52}NO_9Si^{56}Fe$ 890.2476 found 890.2493; Diastereomeric (facial) mixture: $\mathbf{[\alpha]_D^{24.6}}$ = +138.7 (*c* 0.545, $CHCl_3$)



Imine **33**: Diene complex **32** (384.4 mg, 0.4320 mmol, 1 eq) was dissolved in acetonitrile (8 mL). *Para*-toluenesulfonic acid monohydrate (164.3 mg, 0.8639 mmol, 2 eq) was added. The reaction mixture was stirred at room temperature for 3.5 h. The reaction was quenched with K_2CO_3 (119 mg in 5 mL H_2O). The mixture was diluted with EtOAc (40 mL) and H_2O (20 mL). It was then transferred to a separatory funnel and the layer were separated. The organic layer was washed with brine (20 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 2:1 hexanes: EtOAc with 0.5% NEt_3) to yield imine **33** (230 mg, 75%).

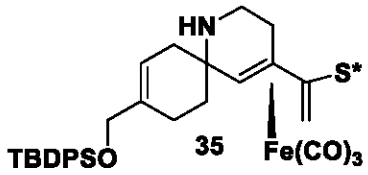
No spectra were taken due to the instability of the imine.



Cyclic amine **34**: Under an Ar atmosphere, $BF_3 \cdot Et_2O$ (0.120 mL, 0.9757 mmol, 3 eq) was added dropwise to a solution of iminodiene **33** (230 mg, 0.3252 mmol, 1 eq) in THF (8 mL) at -78°C. Gradually, the solution was warmed to -30°C over 1 h. The solution was then recooled to -78°C and ally-MgCl (1.7M in THF, 0.574 mL, 0.9757 mmol, 3 eq) was added dropwise via syringe. The solution was warmed to 0°C over 3 h. The reaction was quenched with $NaHCO_3$ (20 mL) and then diluted and transferred to a separatory funnel with EtOAc (40 mL). The layers were separated and the aqueous layer was washed with EtOAc (2 x 30 mL). The combined organics were dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 4:1 hexanes: EtOAc with 0.5% NEt_3) to yield the cyclic amine **34** (110.5 mg, 45% dr 100:0.

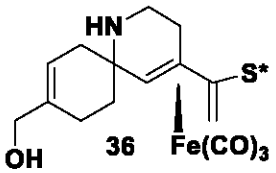
Major: **^{1}H NMR** (400 MHz) **δ** -0.23 (d, 1H, one of the CS*C$\underline{H}_2$, *J*= 3.2 Hz), 1.08 (s, 9H, *t*-butyl), 1.28 (s, 1H, C$\underline{H}$=CCS*), 1.55 (t, 2H, C$\underline{H}_2$C(CR)NCH, *J*= 8.4 Hz), 2.05 (m, 3H, N$\underline{H}$ + C(CH$_2$)C$\underline{H}_2$CH$_2$C(CR)N), 2.15-2.40 (ABX system, 2H, allylic and α to N), 2.41 (s, 3H, ArC$\underline{H}_3$), 2.52 (d, 1H, one of the CS*C$\underline{H}_2$, *J*= 3.2 Hz), 2.65 (dd, 1H, one of NCH$_2$C$\underline{H}_2$), 3.02 (m, 2H, one of each NC$\underline{H}_2$C$\underline{H}_2$), 3.20 (m, 1H, one of NC$\underline{H}_2$CH$_2$), 4.12 (dt, 2H, C$\underline{H}_2$OSi, *J*(small)= 3.5 Hz), 5.92 (partially obscured s, 1H, one of terminal vinyl H γ to OSi), 5.01 (partially obscured q, 2H, terminal vinyl H), 5.22 (s, 1H, one of terminal vinyl H γ to OSi), 5.61 (m, 1H, vinylic H γ to N), 7.38 (m, 10H, Ar), 7.67 (m, 4H, Ar); Unobscured peaks of the minor: **^{1}H NMR** (400 MHz) **δ** 1.25 (s, 1H, C$\underline{H}$=CCS*), 2.89 (dd, 1H, one of NCH$_2$C$\underline{H}_2$); **^{13}C NMR (100 MHz) δ** 19.28, 21.58, 25.31, 25.80, 26.80, 55.03, 66.69, 74.68, 104.29, 106.07, 108.43, 118.67, 125.31, 127.31, 129.63, 130.21, 133.07, 133.58, 133.62, 141.92, 142.34, 147.48; **IR** (film, $CHCl_3$) 1981, 2050, 2857,

2931, 3000, 3072, 3339 cm^{-1}; **HRMS** ($M+H^+$) calcd for $C_{41}H_{48}NO_5SiS^{56}Fe$ 750.2366, found 750.2374; Diastereomeric (facial) mixture: $[\alpha]_D^{23.6}$ = +155.8 (*c* 0.155, $CHCl_3$);

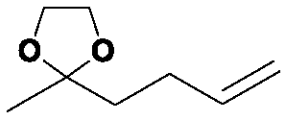


Azaspirocycle **35**: The amine **34** (110.5 mg, 0.1475 mmol, 1eq) was dissolved in toluene (5 mL) in a dry Schlenk flask under Ar atmosphere. Grubbs Hoyveda second generation catalyst (4.6 mg 0.0074 mmol, .05 eq) was added and the reaction was stirred for 24 h. Another portion of catalyst (4.6 mg 0.0074 mmol, .05 eq) was added and the reaction was stirred for another 24 h. The reaction mixture was concentrated via rotary evaporation and purified using column chromatography (silica, 4:1 hexanes: EtOAc with 0.5% NEt_3) to yield the azaspirocycle **35** (93.9 mg, 88%) as a yellow oil.

^{1}H NMR (400 MHz) **δ** -0.21 (d, 1H, one of the CS*C$\underline{H}_2$, *J*= 3.2 Hz), 1.04 (s, 9H, *t*-butyl), 1.25 (d, 1H, homoallylic, *J*= 2.6 Hz), 1.30 (s, 1H, CH=CCS*), 1.65 (m, 1H, one of allylic H on B-ring), 1.74 (m, 1H, one of allylic H on B-ring), 2.05 (broad t, 1H, NH), 2.18 (m, 1H, homoallylic), 2.35 (broad d, 1H, *J*= Hz), 2.42 (s, 3H, ArC$\underline{H}_3$), 2.52 (d, 1H, one of the CS*C$\underline{H}_2$, *J*= 3.4 Hz), 2.72 (dt, 1H, one of the allylic H to complex, *J*= 16 Hz, Hz), 3.01 (m, 2H, C$\underline{H}_2$N), 3.21 (m, 1H, one of the allylic H to complex), 4.05 (s, 2H, C$\underline{H}_2$OSi), 5.49 (s, 1H, vinylic H not on complex), 7.38 (m, 8H, Ar), 7.67 (m, 6H, Ar); **^{13}C NMR (100 MHz) δ** 19.27, 21.58, 22.52, 25.79, 26.55, 26.84, 36.12, 38.50, 51.54, 67.05, 104.56, 105.86, 118.12, 125.33, 127.62, 129.63, 130.19, 133.59, 133.61, 135.52, 136.33, 141.95, 142.35; **IR** (neat) 1977, 2049, 2856, 2929, 3407 cm^{-1}; **HRMS** (M+ H+) calcd for $C_{39}H_{44}NO_5SiS^{56}Fe$ 722.2053, found 722.2082; Diastereomeric (facial) mixture: $[\alpha]_D^{23}$ = +159.9 (*c* 0.595, $CHCl_3$);



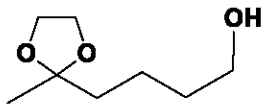
Allylic alcohol **36**: The silyl ether (PAGE 42) (13.6 mg, 0.0188 mmol, 1 eq) was dissolved in THF (0.3 mL). TBAF (1.0 M in THF, 0.0226 mL, 0.0226 mmol, 1.2 eq) was added. The reaction was stirred overnight. The reaction was transferred to separatory funnel with EtOAc (10 mL). The organic layer was washed with saturated $NaHCO_3$ (4 mL) and brine (4 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, EtOAc with 0.5% NEt_3) to yield alcohol PAGE 63 (6.8 mg, 75%) as a yellow oil.



37

Acetal **37**: Hex-5-en-2-one (2.95 mL, 25.5 mmol, 1eq) was dissolved in toluene (25 mL) and ethylene glycol (5.68 mL, 101.9 mmol, 4 eq) and tosic acid (485 mg, 2.55 mmol, 0.1 eq) were added. A Dean-Stark trap was attached with the condenser and the solution was refluxed for 5 h. The reaction mixture was diluted with EtOAc (75 mL) and washed with $NaHCO_3$ (2 x 20 mL) then brine (20 mL). The resulting mixture was dried over $MgSO_4$ then filtered. The solution was concentrated via rotary evaporation and purified via column chromatography (silica, 9:1 hexanes: EtOAc) to yield acetal **37** (1.45 g, 40%) as a clear oil.

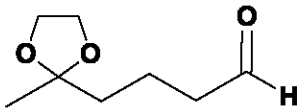
^{1}H NMR (400 MHz) **δ** 1.33 (s, 3H, terminal methyl H), 1.74 (m, 2H, $C\underline{H}_2C(OCH_2CH_2O)$, 2.16 (m, 2H, allylic H), 3.95 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$), 4.95 (dq, 1H, terminal vinyl H *cis* to internal, *J*= 10.2 Hz, 1.3 Hz), 5.14 (dt, 1H, terminal vinyl H *trans* to internal, *J*= 17 Hz, 1.9 Hz).



38

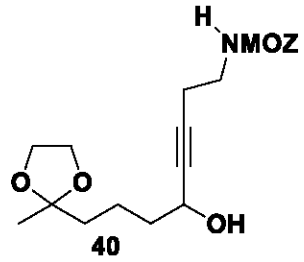
Alcohol **38**: The alkene **37** (1.45g, 10.2 mmol, 1eq) was dissolved in THF (30 mL) under Ar and cooled to 0°C. 9-BBN (0.5M in THF) (22.4mL, 11.2 mmol, 1.1 eq) was added over 10 min via syringe. It was allowed to warm to room temperature overnight. The reaction was recooled to 0oC. A premixed solution of $NaOH/H_2O_2/H_2O$ (NaOH: 1.2 g in 10 mL H_2O; H_2O_2: 10 mL of 30% aq solution) via pipette. The reaction was stirred for 3h at 0oC. The reaction was diluted with Et2O (150 mL) and water (50 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 50 mL). The combined organics were washed with brine (40 mL), dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified via column chromatography (silica, 1:1 hexanes: EtOAc) to yield alcohol **38** (1.0402 g, 64%) as a clear oil.

^{1}H NMR (400 MHz) **δ** 1.30 (s, 3H, terminal methyl H), 1.45 (br s, 1H, O<u>H</u>), 1.48 (m, 2H, $CH_2CH_2C\underline{H}_2CH_2OH$), 1.58 (m, 2H, $CH_2C\underline{H}_2CH_2CH_2OH$), 1.67 (m, 2H, $C\underline{H}_2CH_2CH_2CH_2OH$), 3.65 (q, 2H, $C\underline{H}_2OH$, J= 5. 1 Hz), 3.86 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$)



39

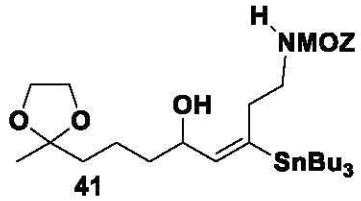
Aldehyde **39**: Under Ar, a Schlenk flask was equipped with CH_2Cl_2 (25 mL), followed by oxalyl chloride (0.836 mL, 9.740 mmol, 1.5 eq). The solution was cooled to -78°C. DMSO (1.384 mL, 19.48 mmol, 3 eq) was added via syringe. After stirring for 5 min, a solution of alcohol PAGE 8 (1.0402g, 6.493 mmol, 1eq) in CH_2Cl_2 (10 mL) was added via cannula. After 15 min, NEt3 (4.524 mL, 32.46 mmol, 5 eq) was added. The reaction was stirred at -78°C for 4 h and then quenched with H_2O (15 mL). It was then diluted with Et_2O (175 mL) and H_2O (30 mL) The aqueous layer was extracted with Et_2O (40 mL). The combined organics were washed with H_2O (40 mL), brine (40 mL) and dried over $MgSO_4$ then filtered. After being concentrated via rotary evaporation, the residue was taken up in hexanes and filtered through glass wool. No chromatography was done (assumed 100% yield). No spectra were taken.



40

Propargylic alcohol **40**: Under Ar, alkyne **27** was dissolved in dry THF (40 mL) and then cooled to 0°C. *n*BuLi (1.6 M in hexanes, 7.73 mL, 12.368 mmol, 2 eq) was added dropwise via syringe. This solution was stirred for 20 min and then DMPU (1.50 mL, 12.368 mmol, 2eq) was added dropwise via syringe. After 10 min of stirring at 0°C, the aldehyde **39** (1.027 g, 6.493, 1.05 eq) in THF (15 mL) was added via cannula. The reaction was stirred for 1 h at 0°C and then quenched with H_2O (20 mL). The mixture was transferred to a separatory funnel and Et_2O (60 mL). The layers were separated and washed with H_2O (30 mL) and then brine (30 mL) then dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified via column chromatography (silica, 1:1 hexanes: EtOAc) to yield **40** (1.79 g, 74%) as a yellow oil.

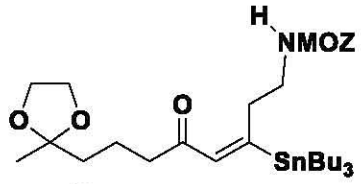
^{1}H NMR (400 MHz) **δ** 1.52 (s, 3H, terminal methyl H), 1.48-1.61 (m, 6H, C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$CHOH), 1.88 (m, 1H, N$\underline{H}$), 2.41 (t, 2H, C$\underline{H}_2$CH$_2$NH, *J*= 6.3 Hz), 3.31 (q, 2H, C$\underline{H}_2$CH$_2$NH, *J*= 6.3 Hz), 3.81 (s, 3H, OC$\underline{H}_3$), 3.91 (d, 4H, OC$\underline{H}_2$C$\underline{H}_2$O, *J*= 3.2 Hz), 4.34 (q, 1H, C$\underline{H}$OH, *J*= 5.52 Hz), 5.02 (s, 2H, benzylic methylene), 5.12 (br s, 1H, O$\underline{H}$), 6.88 (m, 2H, Ar), 7.31 (m, 2H, Ar); **^{13}C NMR (100 MHz) δ** 14.21, 19.74, 20.25, 21.08, 23.78, 37.92, 38.59, 39.88, 55.30, 60.42, 62.45, 64.64, 66.62, 82.40, 82.85, 109.95, 113.91, 128.48, 130.08, 156.39, 159.58, 171.21; **IR** (neat) 1035, 1067, 1246, 1515, 1538, 1698, 1714, 2882, 2953, 2980, 3354 cm^{-1};



41

Vinyl stannane **41**: Under an Ar atmosphere, the alkyne **40** (1.79 g, 4.575 mmol, 1 eq), tributyltin (1.58 mL, 5.948 mmol, 1.3 eq), and catalyst $Pd(PPh_3)Cl_2$ (96 mg, 0.137 mmol, 0.03 eq) were dissolved in THF (35 mL) and stirred for 24 h. A second equivalent of both tributyltin (1.58 mL, 5.948 mmol, 1.3 eq), and catalyst $Pd(PPh_3)Cl_2$ (96 mg, 0.137 mmol, 0.03 eq) were added. The solution was concentrated via rotary evaporation and the residue was purified via column chromatography (silica, 4:1 to 2.5:1 hexanes: EtOAc with 0.5% NEt_3 twice) to yield the vinyl stannane **41** (2.21 g, 71%) as a clear oil.

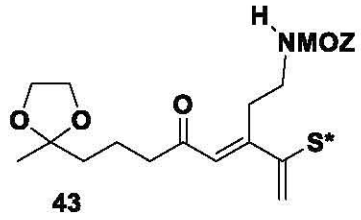
^{1}H NMR (400 MHz) **δ** 0.88 (two t, 15H, $Sn(C\underline{H}_2CH_2CH_2C\underline{H}_3)_3$), 1.23-1.51 (two m, 12 H, $Sn(CH_2C\underline{H}_2C\underline{H}_2CH_3)_3$), 1.40 (partially obscured s, 3H, $CO_2C\underline{H}_3$), 1.41-1.77 (obscured m, 7H, $CO_2C\underline{H}_2C\underline{H}_2C\underline{H}_2$ and O<u>H</u>), 2.38 (m, 1H, one of allylic H), 2.63 (m, 1H, one of allylic H), 3.09 (m, 1H, one of $C\underline{H}_2NH$), 3.28 (m, 1H, one of $C\underline{H}_2NH$), 3.80 (s, 3H, $ArOCH_3$), 3.92 (m, 4H, OCH_2CH_2O), 4.42 (m, 1H, C<u>H</u>OH), 5.05 (m, 3H, N<u>H</u> + $C(O)OC\underline{H}_2Ar$), 5.62 (d with satellites, 1H, vinylic H, *J*= 8.3 Hz), 6.87 (d, 2H, Ar, *J*= 8.6 Hz), 7.29 (d, 2H, Ar, *J*= 8.5 Hz); **^{13}C NMR (100 MHz) δ** 9.69, 13.68, 14.21, 20.03, 23.74, 27.36, 29.07, 33.50, 37.66, 38.97, 40.65, 55.23, 60.41, 64.62, 66.39, 66.93, 109.99, 113.87, 128.75, 130.01, 145.78, 156.44, 159.52; **IR** (neat) 1247, 1516, 1706, 2927, 2955, 3352 cm^{-1}; **HRMS** sample submitted for exact mass determination.



42

Stannylenone **42**: The alcohol **41** (2.21, 3.239 mmol, 1 eq) was dissolved in dichloromethane (40 mL) under an Ar atmosphere. DMSO (7.6 mL) and diisopropylethylamine (2.26 mL, 12.956, mmol, 4 eq) were added and the solution was cooled to -40°C. SO_3·pyr (1.46 g, 9.716 mmol, 3eq) was added and the reaction was allowed to warm to -8°C over 90 min. The reaction solution diluted with saturated $NaHCO_3$ (30 mL) and transferred to separatory funnel with EtOAc (110 mL) and H_2O (60 mL). The layers were separated and the organics were washed with H_2O (45 mL), brine (45 mL). The solution was dried over $MgSO_4$ and then filtered and concentrated via rotary evaporation. The resulting residue was purified via multiple column chromatography (silica, 5:1 hexanes: EtOAc with 0.5% NEt_3) to yield ketone **42** (1.15 mg, 52%) as a clear oil.

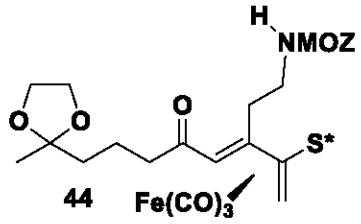
^{1}H NMR (400 MHz) **δ** 0.80 (t, 9H, $Sn(CH_2CH_2CH_2C\underline{H}_3)_3$), 0.98 (t with satellites, 6H, $Sn(C\underline{H}_2CH_2CH_2CH_3)_3$, 1.25-1.78 (m, 18 H, terminal methyl + N$\underline{H}$ + $Sn(CH_2C\underline{H}_2C\underline{H}_2CH_3)_3$ + $C\underline{H}_2C\underline{H}_2CH_2C(O)H$), 2.48 (t, 2H, $C\underline{H}_2C(O)H$, *J*= 6.8 Hz), 2.87 (t with satellites, 2H, allylic H, *J*= 6.5 Hz), 3.30 (q, 2H, $C\underline{H}_2NH$, *J*= 6 Hz), 3.80 (s, 3H, $OC\underline{H}_3$), 3.95 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$), 4.99 (s, 2H, benzylic H), 5.62 (br t, 1H, NH), 6.43 (s with satellites, 1H, vinylic H), 6.88 (m, 2H, Ar), 7.32 (m, 2H, Ar); **^{13}C NMR (100 MHz) δ** 9.92, 13.69, 18.44, 23.78, 27.04, 27.33, 27.61, 28.86, 28.96, 29.06, 34.73, 38.31, 40.39, 43.54, 55.27, 64.65, 66.05, 109.82, 113.76, 129.07, 129.88, 138.54, 156.58, 159.35, 167.30, 200.01; **IR** (neat) 1247, 1516, 1722, 2928, 2956, 3348 cm^{-1}.



43

Sulfinyl diene **43**: Stannylenone **42** (1.15 g, 1.690 mmol, 1 eq) was placed in a schlenk flask and brought into the glovebox. It was dissolved in DMF (17 mL). The iodovinyl sulfoxide (494 mg, 1.690 mmol, 1 eq) was added. Next, CuO_2PPh_2 (546 mg, 1.944 mmol, 1.15 eq) and $Pd(PPh_3)_4$ catalyst (195 mg, 0.169 mmol, 0.1 eq) were added and the reaction was stirred overnight. The reaction was removed from the glove box and filtered through a silica gel plug with EtOAc. The solution was concentrated via rotary evaporation and transferred to separatory funnel with diethyl ether (150 mL). The organic layer was washed with H_2O (50 mL) and brine (50 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, three columns 1:2, 1:2 to pure EtOAc, and 1:2 hexanes: EtOAc) to yield sulfinyl diene **43** (668.4 mg, 71%).

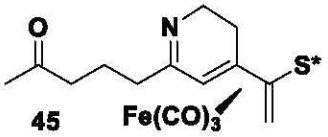
^{1}H NMR (400 MHz) **δ** 1.28 (s, 3H, $C\underline{H}_3CO_2$), 1.62 (partially obscured m, 4H, $CO_2C\underline{H}_2C\underline{H}_2$), 2.34 (s, 3H, $ArC\underline{H}_3$), 2.45 (t, 2H, $C\underline{H}_2C(O)$, *J*= 6.4 Hz), 2.60 (m, 1H, one of allylic H), 2.86 (partially obscured m, 1H, one of allylic H), 2.93 (m, 1H, one of $C\underline{H}_2NH$), 3.08 (m, 1H, one of $C\underline{H}_2NH$), 3.80 (s, 3H, $ArOC\underline{H}_3$), 3.92 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$), 4.96 (m, 3H, N$\underline{H}$ and $C(O)OC\underline{H}_2Ar$), 6.18 (s, 1H, one of vinylic), 6.35 (s, 1H, one of vinylic), 6.40 (s, 1H, one of vinylic), 6.88 (d, 2H, Ar, *J*= 8.6 Hz), 7.25 (2d, 4H, Ar), 7.48 (d, 2H, Ar, *J*= 8.1 Hz); **^{13}C NMR (100 MHz) δ** 18.32, 21.48, 23.77, 31.03, 38.20, 39.55, 44.47, 55.30, 64.66, 66.26, 109.72, 113.85, 120.09, 125.62, 127.73, 128.77, 130.054, 139.28, 142.58, 146.23, 153.66, 156.31, 159.50, 200.73; **IR** (neat) 1051, 1246, 1519, 1715, 2883, 2956, 3339 cm^{-1}; Diastereomeric (facial) mixture: $[\alpha]_D^{22.8}$ = +58.9 (*c* 0.42, $CHCl_3$);



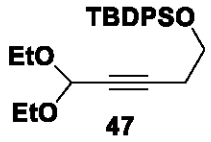
Diene complex **44**: Under an Ar atmosphere, the sulfinyl diene **43** (668.4 mg, 1.203 mmol, 1 eq) was dissolved in toluene (12.2 mL). Bda iron(0)tricarbonyl (1.377 g, 4.813 mmol, 4 eq) was added. The reaction was placed in a 40°C bath and stirred for 20 h. Reaction mixture was filtered through silica gel on a glass frit and rinsed with EtOAc. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 1.5: 1 hexanes: EtOAc, loaded in chloroform) to yield the complexed diene **44** (563.4 mg, 67%) as a yellow foam.

Major: **^{1}H NMR** (400 MHz) **δ** 0.32 (d, 1H, one of CS*C$\underline{H}_2$, *J*= 3.6 Hz), 0.59 (s, 1H, C(O)C$\underline{H}$C), 1.29 (s, 3H, C$\underline{H}_3$CO$_2$), 1.65 (m, 4H, CO$_2$C$\underline{H}_2$C$\underline{H}_2$), 2.39 (m, 6H, ArC$\underline{H}_3$ + C$\underline{H}_2$C(O) + one of the allylic H), 2.90 (partially obscured, 1H, one of CS*C$\underline{H}_2$, *J*= 3.6Hz), 2.91 (partially obscured m, 1H, one of C$\underline{H}_2$NH), 3.29 (m, 1H, one of C$\underline{H}_2$NH), 3.68 (m, one of the allylic H), 3.82 (s, 3H, ArOC$\underline{H}_3$), 3.91 (m, 4H, OC$\underline{H}_2$C$\underline{H}_2$O), 4.63 (t, 1H, NH), 4.98 (s, 2H, C(O)OC$\underline{H}_2$Ar), 6.78 (partially obscured d, 2H, Ar), 7.25 (partially obscured d, 2H, Ar), 7.34 (partially obscured d, 2H, Ar), 7.80 (d, 2H, Ar, *J*= 8.1 Hz); Unobscured peaks from minor: **^{1}H NMR** (400 MHz) **δ** 0.48 (d, 1H, one of CS*C$\underline{H}_2$, *J*= 3.7 Hz), 0.55 (s, 1H, C(O)OC$\underline{H}$C), 2.13 (d, 1H, one of CS*C$\underline{H}_2$, *J*= 3.7 Hz), 3.09 (m, 1H, one of allylic), 3.46 (m, 1H, one of C$\underline{H}_2$NH), 4.42 (t, 1H, NH), 4.90 (partially obscured AB system, 2H) 7.66 (d, 2H, Ar, *J*= 8.2 Hz); **^{13}C NMR (100 MHz) δ** 18.62, 21.58, 23.73, 28.20, 29.82, 38.20, 41.23, 52.60, 55.29, 64.62, 66.47, 77.226, 105.19, 109.80, 113.87, 115.089, 124.69, 125.67, 128.85, 130.16, 130.48, 141.36, 143.02, 156.26, 159.60, 206.321; **IR** (film, $CHCl_3$) 1054, 1246, 1515, 1716, 1996, 2066, 2885, 2957, 3334 cm^{-1}; **HRMS**

sample submitted for exact mass determination; Diastereomeric (facial) mixture: $[\alpha]_D^{23}$ = +172.6 (*c* 2.755, $CHCl_3$);



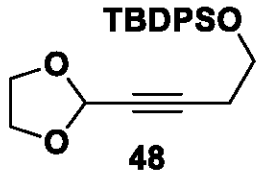
Imine **45**: Diene complex **44** (52.8 mg, 0.0759 mmol, 1 eq) was dissolved in acetonitrile (7 mL). *Para*-toluenesulfonic acid monohydrate (57.8 mg, 0.3037 mmol, 4 eq) was added. The reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with K_2CO_3 (42 mg in 5 mL H_2O). The mixture was diluted with EtOAc (205mL) and H_2O (10 mL). It was then transferred to a separatory funnel and the layer were separated. The organic layer was washed with brine (10 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 10:1 EtOAc: methanol with 0.5% NEt_3) to yield imine **45** (33.2 mg, 90%). No spectra were taken due to visible decomposition of product.



47

Acetal **47**: The alkyne **46** (1.1857 g, 3.241 mmol, 1 eq) was dissolved in triethylorthoformate (44 mL) under an Ar atmosphere. ZnI_2 (1.035 g, 3.241 mmol, 1 eq) was removed from the glove box and added. The reaction mixture was placed in a 110°C oil bath for 4 h. The solvent was removed via vacuum distillation into a dry ice cooled receiver. The mixture was filtered through a silica gel plug with 9:1 hexanes: EtOAc with 1% NEt_3. The mixture was concentrated via rotary evaporation and the resulting residue was purified via column chromatography (silica, 30:1 hexanes: EtOAc with 0.5% NEt3) to yield acetal **47** (1.0211g, 77%).

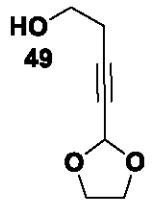
^{1}H NMR (400 MHz) **δ** 1.04 (s, 9H, *t*-butyl), 1.21 (t, 6H, $C\underline{H}_3CH_2O$, *J*= 7.2 Hz), 2.50 (td, 2H, propargylic H, *J*= 6.8 Hz, 1.6 Hz), 3.55 (m, 2H, two of $CH_3C\underline{H}_2O$), 3.70 (m, 2H, two of $CH_3C\underline{H}_2O$), 3.77 (t, 2H, $C\underline{H}_2OSi$, *J*= 6.8 Hz), 5.21 (t, 1H, $CCC\underline{H}Et_2$, *J*= 1.6 Hz), 7.40 (m, 6H, Ar), 7.67 (m, 4H, Ar); **^{13}C NMR** (100 MHz) **δ** 15.07, 19.17, 22.78, 26.75, 60.64, 62.10, 76.20, 83.34, 91.42, 127.69, 129.69, 133.51, 135.56; **IR** (neat) 702, 1053, 1112, 2858, 2884, 2931, 2974, 3049, 3071 cm^{-1}, **HRMS** sample submitted for exact mass determination;



48

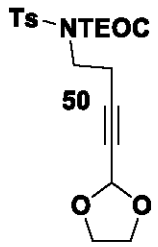
Acetal **48**: The acetal **47** (460.3mg, 1.121 mmol, 1eq) was dissolved in toluene (6.75 mL). Ethylene glycol (0.125 mL, 2.242 mmol, 2 eq) was added followed by tosylic acid (26.0 mg, 0.140 mmol, 0.125 eq) and $MgSO_4$ (1.2 g). The reaction was placed in an oil bath and refluxed for 2.5 h. Another portion of both ethylene glycol (0.187 mL, 3.363 mmol, 3 eq) and tosylic acid (26.0 mg, 0.140 mmol, 0.125 eq) were added. The reaction was refluxed for 5 h. The reaction was removed from the bath and filtered through a glass funnel with diethyl ether (20 mL). Saturated $NaHCO_3$ (15 mL) was added and the mixture was transferred to a separatory funnel. The layers were separated and the aqueous was extracted with diethyl ether (2 x 15 mL). The combined organics were dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified via column chromatography (silica, 30: 1 then 19:1 hexanes: EtOAc with 0.5% NEt_3) yielding the cyclic acetal **48** (402.4 mg, 94%) as a clear oil.

^{1}H NMR (400 MHz) **δ** 1.05 (s, 9H, *t*-butyl), 2.50 (td, 2H, propargylic H, *J*= 7.2 Hz, 1.2 Hz), 3.78 (t, 2H, $C\underline{H}_2OSi$, *J*= 7.2 Hz), 3.75-4.05 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$), 5.59 (t, 1H, $C\underline{H}(OCH_2CH_2O)$, *J*= 1.6 Hz), 7.38 (m, 6H, Ar), 7.65 (m, 4H, Ar); **^{13}C NMR (100 MHz) δ** 19.18, 22.74, 26.76, 61.99, 64.44, 77.01, 83.58, 93.10, 127.70, 129.70, 133.48, 135.56; **IR** (neat) 614, 702, 1112, 1428, 1589, 2857, 2931, 3049, 3071 cm^{-1}; **HRMS** sample submitted for exact mass determination;



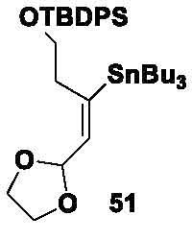
Homopropargylic alcohol **49**: The silyl ether **48** (218.6 mg, 0.574 mmol, 1 eq) was dissolved in THF (5.7 mL). TBAF (1.0 M in THF, 0.632 mL, 0.632 mmol, 1.1 eq) was added. The reaction was stirred overnight. The reaction was transferred to separatory funnel with EtOAc (25 mL). The organic layer was washed with saturated $NaHCO_3$ (10 mL) and brine (10 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 1:1 hexanes: EtOAc) to yield alcohol **49** (51.0 mg, 63%) as a yellow oil.

^{1}H NMR (400 MHz) **δ** 1.90 (broad s, 1H, O<u>H</u>), 2.51 (td, 2H, propargylic H, *J*= 6.0 Hz, 1.2 Hz), 3.72 (t, 2H, C<u>H</u>$_2$OH, *J*= 6.4 Hz), 3.78-4.10 (m, 4H, OC<u>H</u>$_2$C<u>H</u>$_2$O), 5.61 (t, 1H, C<u>H</u>(OCH$_2$CH$_2$O), *J*= 1.6 Hz); **^{13}C NMR (100 MHz) δ** 23.01, 60.69, 64.55, 77.85, 83.19, 93.04; **HRMS** sample submitted for exact mass determination;



Carbamate **50**: Under an Ar atmosphere, the protected amine (91.9 mg, .2914 mmol, 1 eq), triphenylphosphine (152.8g, 0.5827 mmol, 2 eq), and the alcohol **49** (49.7 mg, 0.3496 mmol, 1.2 eq) were dissolved in THF (3 mL) and cooled to 0°C. DIAD (0.1016 mL, 0.5244 mmol, 1.8 eq) was added dropwise and the bath was removed. The reaction was stirred overnight. The solvent was removed via rotary evaporation and the resulting residue was purified using multiple column chromatography (4:1 then 3:1 hexanes:EtOAc with 1.5% NEt_3) to yield carbamate **50** (89.4 mg, 70%) as a clear oil.

^{1}H NMR (400 MHz) **δ** 0.00 (s, 9H, $Si(C\underline{H}_3)_3$), 0.95 (m, 2H, $C\underline{H}_2Si$), 2.43 (s, 3H, $ArC\underline{H}_3$), 2.70 (td, 2H, propargylic H, *J*= 4.4 Hz, 1.6 Hz), 3.85-4.05 (m, 6H, $OC\underline{H}_2C\underline{H}_2O$ + $C\underline{H}_2N$), 5.61 (t, 1H, $C\underline{H}(OCH_2CH_2O$, *J*= 1.2 Hz),7.32 (dd, 2H, Ar, *J*= 8.8 Hz, 0.8Hz), 7.85 (dt, 2H, Ar, *J*=3.6 Hz, 2.0 Hz); **^{13}C NMR** (100 MHz) **δ** 17.45, 20.12, 21.64, 45.01, 64.41, 66.22, 82.19, 92.94, 128.46, 129.35, 136.51, 144.65, 152.19; **IR** (neat) 704, 1251, 1357, 1732, 1809, 2242, 2899, 2956 cm^{-1}, **HRMS** sample submitted for exact mass determination;

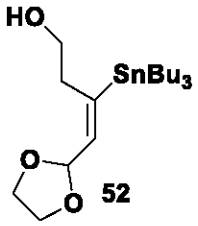


51

Vinyl stannane **51**: Ditributyltin (0.537 mL, 1.063 mmol, 2.2 eq) was dissolved in THF (6 mL) in a flame dried Schlenk flask under an Ar atmosphere. Solution cooled to -78°C. Butyllithium (1.6 M in hexanes, 0.634 mL, 1.015 mmol, 2.1 eq) was added via syringe. Solution was stirred at -40°C for 30 min. The mixture was recooled to -78°C and copper cyanide (86.6 mg, 0.9664 mmol, 2 eq) was added. The reaction mixture was stirred at -40°C for 30 min and then recooled to -78°C. Methanol (0.029 mL, 0.7248 mmol, 1.5 eq) was added to the reaction. The alkyne **148** (183.9 mg, 0.4832 mmol, 1 eq) was dissolved in THF (6 mL) and this solution was added via cannula to the reaction mixture. The reaction was stirred at -78°C for 2h. The temperature was raised to -25°C and then the reaction was quenched with saturated NH_4Cl/NH_4OH (9:1, 40 mL). The mixture was transferred to a separatory funnel with EtOAc (60 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 30 mL). The combined organics were washed with brine (20 mL). The solution was dried over $MgSO_4$ and filtered. The mixture was concentrated via rotary evaporation and the resulting residue was purified via column chromatography (silica, 40:1 hexanes: EtOAc) to yield a mixture of isomers of the vinyl stannane **51** (311.7 mg, 96%).

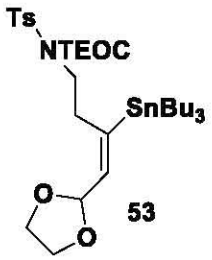
^{1}H NMR (400 MHz) **δ** 0.83 (m, 15H, $Sn(C\underline{H}_2CH_2CH_2C\underline{H}_3)_3$), 1.24 (m, 6H, $Sn(CH_2CH_2C\underline{H}_2CH_3)_3$), 1.46 (m, 6H, $Sn(CH_2C\underline{H}_2CH_2CH_3)_3$), 2.68 (td with satellites, 2H, allylic H, *J*= 7.5 Hz, 1.1 Hz), 3.60 (t, 2H, $C\underline{H}_2OSi$, *J*= 8.0 Hz), 3.79-3.98 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$), 5.37 (d, 1H, vinylic H, *J*= 6.4 Hz), 5.60 (d, 1H, $C\underline{H}(OCH_2CH_2O)$, *J*= 6.4 Hz), 7.39 (m, 6H, Ar), 7.64 (m, 4H, Ar); **^{13}C NMR** (100 MHz) **δ** 9.57, 13.62, 19.17, 26.86, 27.42, 28.96, 37.37, 63.65, 98.17,

127.62, 129.56, 133.88, 135.59, 137.78, 149.56; **IR** (neat) 701, 742, 958, 1111, 1428, 2928 cm^{-1}, **HRMS** sample submitted for exact mass determination;



Homoallylic alcohol **52**: The silyl ether **51** (1.387 g, 2.065 mmol, 1 eq) was dissolved in THF (20 mL). TBAF (1.0 M in THF, 2.272 mL, 2.272 mmol, 1.1 eq) was added. The reaction was stirred overnight. The reaction was transferred to separatory funel with EtOAc (60 mL). The organic layer was washed with saturated $NaHCO_3$ (25 mL) and brine (25 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 3:1 hexanes: EtOAc with 0.5% NEt_3) to yield alcohol **52** (0.8698 g, 97%) as a clear oil.

^{1}H NMR (400 MHz) **δ** 0.90 (m, 15H, $Sn(C\underline{H}_2CH_2CH_2C\underline{H}_3)_3$), 1.38 (m, 6H, $Sn(CH_2CH_2C\underline{H}_2CH_3)_3$), 1.50 (m, 6H, $Sn(CH_2C\underline{H}_2CH_2CH_3)_3$), 2.08 (t, 1H, OH, *J*= 5.6 Hz), 2.66 (td with satellites, 2H, allylic H, *J*= 6.0 Hz, 1.2 Hz), 3.62 (partially obscured q, 2H, $C\underline{H}_2OH$, *J*= 5.6 Hz), 3.86- 4.08 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$), 5.54 (d with satellites, 1H, $C\underline{H}(OCH_2CH_2O)$, *J*= 6.0 Hz)

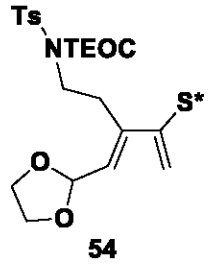


Carbamate **53**: Ditributyltin (0.223 mL, 0.4389 mmol, 2.2 eq) was dissolved in THF (2.5 mL) in a flame dried Schlenk flask under an Ar atmosphere. Solution cooled to -78°C. Butyllithium (1.6 M in hexanes, 0.261 mL, 0.4190 mmol, 2.1 eq) was added via syringe. Solution was stirred at -40°C for 30 min. The mixture was recooled to -78°C and copper cyanide (35.7 mg, 0.3990 mmol, 2 eq) was added. The reaction mixture was stirred at -40°C for 30 min and then recooled to -78°C. Methanol (0.012 mL, 0.2993 mmol, 1.5 eq) was added to the reaction. The alkyne **50** (87.7 mg, 0.1995 mmol, 1 eq) was dissolved in THF (2.5 mL) and this solution was added via cannula to the reaction mixture. The reaction was stirred at -78°C for 2h. The temperature was raised to -25°C and then the reaction was quenched with saturated NH_4Cl/NH_4OH (9:1, 20 mL). The mixture was transferred to a separatory funnel with EtOAc (30 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 15 mL). The combined organics were washed with brine (10 mL). The solution was dried over $MgSO_4$ and filtered. The mixture was concentrated via rotary evaporation and the resulting residue was purified via column chromatography (silica, 9:1 hexanes: EtOAc with 1.5% NEt_3) to yield the major isomers of the vinyl stannane **53** (82.2 mg, 56%) as a clear oil.

Under an Ar atmosphere, the alcohol **52** (200.0 mg, 4.617 mmol, 1 eq), triphenylphosphine (242 mg, 0.9234 mmol, 2eq), and protected amine (175 mg, 554.0 mmol, 1.2 eq) were dissolved in THF (4.6 mL) and cooled to 0°C. DIAD (0.161 mL, 0.8311 mmol, 1.8 eq)

was added dropwise and the bath was removed. The reaction was stirred overnight. The solvent was removed via rotary evaporation and the resulting residue was purified using column chromatography (12:1 hexanes: EtOAc with 1.5% NEt_3) to yield carbamate **53** (295.2 mg, 88%) as a clear oil.

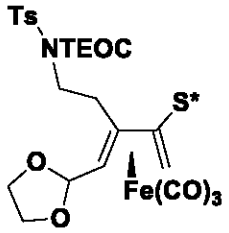
^{1}H NMR (400 MHz) **δ** -0.01 (s, 9H, $Si(C\underline{H}_3)_3$), 0.85-1.08 (m, 17H, $Sn(C\underline{H}_2CH_2CH_2C\underline{H}_3)_3$ + $C\underline{H}_2Si$), 1.32 (m, 6H, $Sn(CH_2CH_2C\underline{H}_2CH_3)_3$), 1.50 (partially obscured m, 6H, $Sn(CH_2C\underline{H}_2CH_2CH_3)_3$), 2.43 (s with satellites, 3H, $ArC\underline{H}_3$), 2.83 (t with satellites, 2H, allylic H, *J*= 6.0 Hz), 3.75 (m, 2H, $C\underline{H}_2N$), 3.86-4.08 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$), 4.15 (m, 2H, $C\underline{H}_2OC(O)$), 5.62 (d, 1H, $C\underline{H}(OCH_2CH_2O)$, *J*= 6.8 Hz), 5.71 (d, 1H, vinylic H, *J*= 6.8 Hz), 7.31 (d, 2H, Ar, *J*= 8.8 Hz), 7.84 (d, 2H, Ar, *J*= 8.8 Hz); **^{13}C NMR** (100 MHz) **δ** -1.68, 8.02, 9.56, 13.69, 17.66, 21.63, 27.40, 29.05, 34.51, 64.98, 66.00, 98.06, 128.37, 129.30, 137.01, 144.44, 152.46, 159.08;



54

Sulfinyl diene **54**: In the glove box, the vinyl stannane **53** (3.774 g, 0.5165 mmol, 1 eq) was dissolved in DMF (9 mL). The iodovinyl sulfoxide (150.9 mg, 0.5165 mmol, 1 eq) was added. Next, CuO_2PPh_2 (166.8 mg, 0.5940 mmol, 1.15 eq) and $Pd(PPh_3)_4$ catalyst (59.8 mg, 0.0517 mmol, 0.1 eq) were added and the reaction was stirred overnight. The reaction was removed from the glove box and filtered through a silica gel plug with EtOAc. The solution was concentrated via rotary evaporation and transferred to separatory funnel with diethyl ether (60 mL). The organic layer was washed with H_2O (2 x 20 mL) and brine (20 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 2.5:1 to 1:1 hexanes: EtOAc) to yield Sulfinyl diene **54** (176.5 mg, 56%).

^{1}H NMR (400 MHz) **δ** 0.01 (s, 9H, $Si(C\underline{H}_3)_3$), 0.91 (m, 2H, $C\underline{H}_2Si$), 2.38 (s, 3H, one of $ArC\underline{H}_3$), 2.42 (s, 3H, one of $ArC\underline{H}_3$), 2.71 (m, 2H, allylic H), 3.89-4.05 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$), 4.15 (m, 2H, $C\underline{H}_2OC(O)$), 5.57 (d, 1H, $C\underline{H}(OCH_2CH_2O)$, *J*= 6.8 Hz), 5.82 (d, 1H, vinylic H, *J*= 6.8 Hz), 6.10 (d, 1H, one of $CS^*C\underline{H}_2$, *J*= 1.2 Hz), 6.31 (d, 1H, one of $CS^*C\underline{H}_2$, *J*= 0.8 Hz), 7.26 (partially obscured 2 d, 4H, Ar), 7.51 (dd, 2H, Ar, *J*= 6.4 Hz, 1.6 Hz), 7.72 (dd, 2H, Ar, *J*= 6.4 Hz, 1.6 Hz); **^{13}C NMR** (100 MHz) **δ** -1.67, 17.47, 21.50, 21.65, 31.33, 45.36, 65.12, 65.19, 66.24, 99.13, 115.58, 125.80, 128.22, 129.34, 129.66, 129.81, 135.65, 136.49, 140.17, 142.02, 144.67, 152.19, 153.25

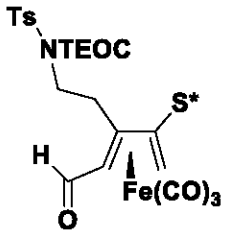


55

Diene complex **55**: In the glove box, diiron nonacarbonyl (423.8 mg, 1.165 mmol, 4 eq) was placed in a Schlenk flask which had been equipped with a stir bar. This flask was sealed and brought into the fume and placed under Ar atmosphere. Meanwhile, the sulfoxide diene **54** (176.5 mg, 0.2913 mmol, 1eq) was dissolved in dry toluene and cannulated into the Schlenk flask containing the diiron nonacarbonyl. This flask was sealed and removed from Ar and then placed in a 35°C oil bath and stirred for 20 h. Reaction mixture was filtered through silica gel on a glass frit and rinsed with EtOAc. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 4:1 hexanes: EtOAc with 0.5% NEt_3) to yield yellow oil **55** (131.9 mg, 61%).

Major: **^{1}H NMR** (400 MHz) **δ** 0.00 (s, 9H, $Si(C\underline{H}_3)_3$), 0.70 (d, 1H, one of $CS^*C\underline{H}_2$, *J*= 3.6 Hz), 0.68 (d, 1H, $C\underline{H}CCS^*$, *J*= 6.8 Hz), 0.96 (m, 2H, $C\underline{H}_2Si$), 2.41 (s, 3H, one of $ArC\underline{H}_3$), 2.45 (s, 3H, one of $ArC\underline{H}_3$), 2.55 (d, 1H, one of $CS^*C\underline{H}_2$, *J*= 3.6 Hz), 3.06 (td, 1H, one of the allylic H, *J*= 12.8 Hz, 4.8 Hz), 3.68 (td, 1H, one of the allylic H, *J*= 12.8 Hz, 4.8 Hz), 3.87- 4.32 (m, 8H, $C\underline{H}_2OC(O)$ + $OC\underline{H}_2C\underline{H}_2O$ + $C\underline{H}_2N$), 5.10 (d, 1H, $CHC\underline{H}CCS^*$, *J*= 7.2 Hz), 7.35 (m, 4H, Ar), 7.85 (m, 4H, Ar). Unobscured peaks of the the Minor: **δ** 0.29 (d, 1H, one of $CS^*C\underline{H}_2$), 2.43 (s, 3H, one of $ArC\underline{H}_3$), 7.78 (d, 2H, Ar); **^{13}C NMR (100 MHz) δ** -1.65, 14.21, 17.63, 21.07, 21.52, 28.73, 30.26, 46.57, 58.67, 60.41, 65.25, 65.71, 66.49, 102.37, 102.80, 114.36, 125.35, 128.39, 129.47, 130.15, 136.60, 142.24, 144.80; **IR** (neat) 671, 1089, 1167, 1278, 1375, 1457,

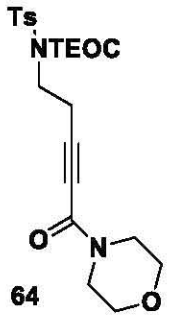
1493, 1597, 1996, 2067, 2895, 2956 cm^{-1}, **HRMS** sample submitted for exact mass determination; Diastereomeric (facial) mixture: $\mathbf{[\alpha]_D^{23}}$ = +115.0 (*c* 0.515, $CHCl_3$);



62

Aldehyde **62**: The acetal **55** (400.0 mg, 0.5364 mmol, 1 eq) was dissolved in THF (5 mL) and H_2O (1 mL). Camphor sulfonic acid (CSA) (24.9 mg, 0.1073 mmol, 0.2 eq) was added and the reaction was stirred for 72 h. The reaction was diluted with EtOAc (50 mL). Layers were separated and the organic layer was washed with saturated $NaHCO_3$ (20 mL). The combined organics washed with brine (20 mL). The solution was dried over $MgSO_4$ and filtered. Solution was concentrated via rotary evaporation and purified via column chromatography (silica, 4:1 hexanes: EtOAc) to yield aldehyde **62** (309.0 mg, 82%) as a yellow oil.

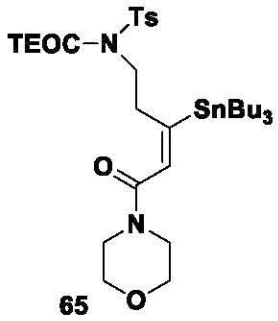
^{1}H NMR (400 MHz) **δ** 1.02 (s, 9H, Si(C$\underline{H}_3$)$_3$), 0.59 (d, 1H, one of CS*C$\underline{H}_2$, *J*= 4.0 Hz), 0.91 (partially obscured d, 1 H, vinylic), 0.95 (m, 2H, C$\underline{H}_2$Si), 2.45 (s, 6H, 2 ArC$\underline{H}_3$), 2.92 (d, 1H, one of CS*C$\underline{H}_2$, *J*= 4.0 Hz), 3.48 (m, 1H, one of allylic), 3.72 (m, 2H, C$\underline{H}_2$N), 3.90 (m, 1H, one of allylic), 4.18 (m, 2H, C$\underline{H}_2$O), 7.30 (d, 2H, Ar, *J*= 8.0 Hz), 7.37 (d, 2H, Ar, *J*= 8.0 Hz), 7.78 (m, 2H, Ar), 7.88 (m, 2H, Ar), 9.52 (d, 2H, CH(O), *J*= 5.6 Hz); **^{13}C NMR (100 MHz) δ** - 1.66, 14.20, 17.47, 21.60, 29.42, 31.19, 47.42, 55.04, 60.40, 66.74, 104.67, 116.60, 125.82, 128.37, 129.47, 130.44, 136.28, 141.00, 142.98, 144.95, 152.10, 194.74; **IR** (neat) 672, 1053, 1086, 1169, 1251, 1374, 1452, 1685, 1735, 1996, 2067, 2956 cm^{-1}, **HRMS** sample submitted for exact mass determination; Diastereomeric (facial) mixture: **[α]$_D^{22}$** = +84.815 (*c* 0.45, $CHCl_3$);



64

Morpholine amide **64**: The alkyne **63** (128.8 mg, 0.3504 mmol, 1 eq) was dissolved in THF (2 mL) under an Ar atmosphere and cooled to -78°C. n-Butyllithium (1.6 M in hexanes, 0.285 mL, 0.4556 mmol, 1.3 eq) was added dropwise and the reaction was allowed to warm to room temperature over 5h. The reaction was then recooled to -78°C and carbamoyl chloride (0.104 mL, 0.9111 mmol, 2.6 eq) was added. The reaction was warmed to room temperature overnight and then quenched with a saturated solution of NH_4Cl (10 mL). The mixture was diluted with EtOAc (40 mL) and the organics were washed with brine (10 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 1.5:1 hexanes: EtOAc) to yield amide **64** (46.5 mg, 28%) as a clear oil.

^{1}H NMR (400 MHz) **δ** 0.01 (s, 9H, $Si(C\underline{H}_3)_3$), 0.95 (m, 2H, $C\underline{H}_2Si$), 2.45 (s, 3H, $ArC\underline{H}_3$), 2.87 (t, 2H, propargylic H, *J*= 7.0 Hz), 3.70 (m, 8H, methylenes on heterocycle), 4.04 (t, 2H, $C\underline{H}_2N$, *J*= 7.0 Hz), 4.16 (m, 2H, $C\underline{H}_2OC(O)$), 7.32 (dd, 2H, Ar, *J*= 8.4 Hz, 0.8 Hz), 7.85 (d, 2H, Ar, *J*= 6.4 Hz); **^{13}C NMR (100 MHz) δ** -1.65, 17.50, 20.55, 21.67, 41.89, 44.65, 47.25, 66.46, 67.03, 75.16, 89.45, 128.41, 129.45, 136.38, 144.86, 152.15, 152.83;

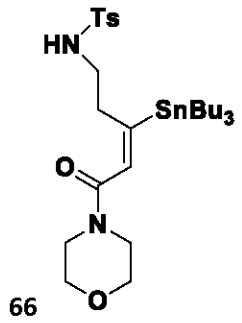


65

Vinyl stannane **65**: Ditributyltin (0.276 mL, 0.546 mmol, 2.2 eq) was dissolved in THF (3 mL) in a flame dried Schlenk flask under an Ar atmosphere. Solution cooled to -78°C. n-Butyllithium (1.6 M in hexanes, 0.326 mL, 0.521 mmol, 2.1 eq) was added via syringe. Solution was stirred at -40°C for 30 min. The mixture was recooled to -78°C and copper cyanide (44.4 mg, 0.496 mmol, 2 eq) was added. The reaction mixture was stirred at -40°C for 30 min and then recooled to -78°C. Methanol (0.015 mL, 0.372 mmol, 1.5 eq) was added to the reaction. The alkyne **64** (183.9 mg, 0. mmol, 1 eq) was dissolved in THF (6 mL) and this solution was added via cannula to the reaction mixture. The reaction was stirred at -78°C for 2h. The temperature was raised to -25°C and then the reaction was quenched with saturated NH_4Cl/NH_4OH (9:1, 20 mL). The mixture was transferred to a separatory funnel with EtOAc (30 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organics were washed with brine (10 mL). The solution was dried over $MgSO_4$ and filtered. The mixture was concentrated via rotary evaporation and the resulting residue was purified via column chromatography (silica, 3:1 hexanes: EtOAc with 0.5% NEt_3) to yield a mixture of isomers of the vinyl stannane **65** (139.9 mg, 73%).

^{1}H NMR (400 MHz) **δ** 0.01 (s, 9H, $Si(C\underline{H}_3)_3$), 0.90 (t, 9H, $Sn(CH_2CH_2CH_2C\underline{H}_3)_3$), 0.95 (m, 2H, $C\underline{H}_2Si$), 1.02 (m, 6H, $Sn(C\underline{H}_2CH_2CH_2CH_3)_3$), 1.32 (m, 6H, $Sn(CH_2CH_2C\underline{H}_2CH_3)_3$), 1.53 (m, 6H, $Sn(CH_2C\underline{H}_2CH_2CH_3)_3$), 2.83 (t with satellites, 2H, allylic H, *J*= 8.2 Hz), 3.52 (m, 2H, one of the methylenes on the heterocycle), 3.70 (m, 6H, 3 methylenes on the heterocycle), 3.78

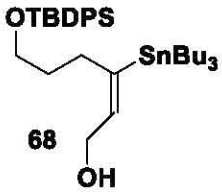
(m, 2H, C<u>H</u>$_2$N), 4.15 (m, 2H, C<u>H</u>$_2$OC(O)), 6.17 (s with satellites, 1H, vinylic H), 7.30 (dd, 2H, Ar, *J*= 8.4 Hz, 0.4 Hz), 7.84 (d, 2H, Ar, *J*= 8.4 Hz); **^{13}C NMR (100 MHz) δ** -1.67, 9.93, 13.71, 17.62, 21.63, 27,39, 29.13, 35.87, 41.54, 46.16, 46.80, 65.99, 66.76, 128.45, 129.30, 134.96, 136.76, 144.42, 151.64, 152.21, 166.56;



66

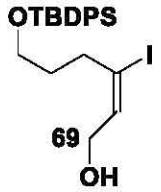
Tosylamine **66**: The protected amine **65** (125.4 mg, 0.162 mmol, 1 eq) was dissolved in THF (1.6 mL). TBAF (1.0 M in THF, 0.179 mL, 0.179 mmol, 1.1 eq) was added. The reaction was stirred overnight. The reaction was transferred to separatory funnel with EtOAc (15 mL). The organic layer was washed with saturated $NaHCO_3$ (5 mL) and brine (5 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 1:1 hexanes: EtOAc with 1% NEt_3) to yield amine **66** (99.4 mg, 97%).

^{1}H NMR (400 MHz) **δ** 0.98 (m, 15H, $Sn(C\underline{H}_2CH_2CH_2C\underline{H}_3)_3$), 1.29 (m, 6H, $Sn(CH_2CH_2C\underline{H}_2CH_3)_3$), 1.56 (m, 6H, $Sn(CH_2C\underline{H}_2CH_2CH_3)_3$), 2.39 (s, 3H, $ArC\underline{H}_3$), 2.52 (t with satellites, 2H, allylic H, *J*= 5.9 Hz), 3.01 (m, 2H, $C\underline{H}_2NH$), 6.20 (s with satellites, 1H, vinylic H), 7.26 (m, 2H, Ar), 7.75 (m, 2H, Ar); **^{13}C NMR (100 MHz) δ** 9.88, 13.90, 21.47, 27.60, 29.01, 34.43, 41.22, 41.91, 46.68, 66.88, 127.21, 129.38, 132.83, 137.59, 142.48, 159.03, 165.68; **IR** (neat) 661, 961, 1021, 1071, 1115, 1329, 1434, 1612, 1738, 2924, 3110 cm^{-1}, **HRMS** sample submitted for exact mass determination;



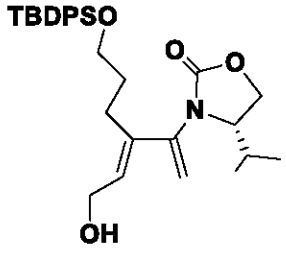
Vinyl stannane **68**: Under an Ar atmosphere, the stannyl enone **67** (680 mg, 1.013 mmol, 1 eq) was dissolved in dry THF (8 mL). The solution was cooled to -78°C. DIBAL (neat, 0.433 mL, 2.431 mmol, 2.4 eq) was added slowly and the reaction was maintained at -78°C for 1 h. The reaction was warmed to -40°C and maintained for 1 h. The reaction was then put in a 0°C bath and a saturated solution of sodium potassium tartrate (10 mL) was added slowly. The reaction was allowed to warm to room temperature over 2 h and maintained at room temperature overnight. The reaction was then diluted with EtOAc (40 mL) and transferred to a separatory funnel. Brine (10 mL) was added and the layers were separated. The aqueous was extracted with EtOAc (3 x 10 mL). The organics were washed with H_2O (10 mL) and brine (10 mL). The combined organics were dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 9:1 hexanes: EtOAc with 0.5% NEt_3) to yield the allylic alcohol **68** (610.8 mg, 94%).

No spectra taken.



Vinyl iodide **69**: The vinyl stannane **68** (610.8 mg, 0.9490 mmol, 1 eq) was dissolved in dichloromethane (5 mL). N-Iodosuccinimide (256.0 mg, 1.139 mmol, 1.2 eq) was taken from the glovebox and added to the solution of the vinyl stannane at 0°C and stirred at 0°C for 2h. The reaction was quenched with saturated $NaHCO_3$ (15 mL) and saturated $Na_2S_2O_3$ (15 mL). The mixture was diluted with EtOAc (20 mL) and transferred to a separatory funnel. Layers separated and organic layer was washed with brine (15 mL). This solution was filtered and concentrated via rotary evaporation. The resulting residue was purified with column chromatography (silica, 9:1 hexanes: EtOAc with 0.5% NEt_3) to yield vinyl iodide **69** (437.4 mg, 96%) as a pale yellow oil.

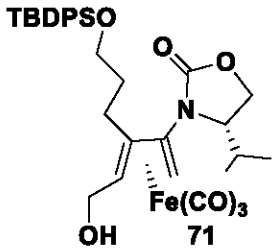
^{1}H NMR (400 MHz) **δ** 1.08 (s, 9H, *t*-butyl), 1.25 (t, 1H, O<u>H</u>, *J*=7.1 Hz), 1.66 (m, 2H, $SiOCH_2C\underline{H}_2CH_2$), 2.62 (t, 2H, allylic H, *J*= 7.0 Hz), 3.68 (t, 2H, $C\underline{H}_2OH$, *J*=5.7 Hz), 4.08 (m, 2H, $C\underline{H}_2OSi$), 6.51 (t, 1H, vinylic H, *J*= 7.2 Hz), 7.40 (m, 6H, Ar), 7.65 (m, 4H, Ar); **^{13}C NMR (100 MHz) δ** 19.15, 26.88, 31.47, 35.00, 59.86, 61.72, 107.91, 127.74, 129.79, 133.44, 135.56, 140.74; **HRMS** sample submitted for exact mass determination;



70

Oxazolidinyl diene **70**: In the glove box, the vinyl stannane (404.8 mg, 0.9113 mmol, 1eq) was dissolved in DMF and transferred into the flask containing the vinyl iodide **69** (437.4 mg, 0.9113 mmol, 1 eq). CuO_2PPh_2 (294 mg, 1.048 mmol, 1.15 eq) and $Pd(PPh_3)_4$ catalyst (105.3 mg, 0.0911 mmol, 0.1 eq) added and the reaction was stirred overnight. The reaction was removed from the glove box and filtered through a silica gel plug with EtOAc. The solution was concentrated via rotary evaporation and transferred to separatory funnel with diethyl ether (120 mL) and H_2O (50 mL). The organic layer was washed with H_2O (50 mL) and brine (50 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 1:1 hexanes: EtOAc, twice) to yield oxazolidinone diene **70** (422.3 mg, 91%).

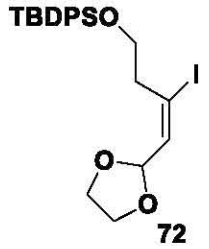
^{1}H NMR (400 MHz) **δ** 0.87 (2d, 6H, $CH(C\underline{H}_3)_2$, *J*= 7.0 Hz, 7.0 Hz), 1.08 (s, 9H, *t*-butyl), 1.56 (partially obscured m, 2H, $CH_2C\underline{H}_2CH_2$), 1.81 (broad m, 1H, O<u>H</u>), 1.89 (m, 1H, $C\underline{H}(CH_3)_2$), 2.18 (m, 1H, one of $CH_2C\underline{H}_2C{=}CH$), 2.52 (m, 1H, one of $CH_2C\underline{H}_2C{=}CH$), 3.62 (t, 2H, $C\underline{H}_2OSi$, *J*= 5.6 Hz), 3.82 (m, 1H, NC<u>H</u>), 4.10-4.49 (2 m, 4H, $C\underline{H}_2OH$ + $C\underline{H}_2OC(O)$), 5.21 (s, 1H, one of $C\underline{H}_2{=}CN$), 5.34 (s, 1H, one of $C\underline{H}_2{=}CN$), 5.87 (t, 1H, $C{=}C\underline{H}CH_2OH$, *J*= 6.3 Hz), 7.41 (m, 6H, Ar), 7.67 (m, 4H, Ar); **^{13}C NMR (100 MHz) δ** 14.43, 17.87, 19.17, 24.32, 26.87, 28.87, 31.21, 59.07, 60.29, 62.74, 112.65, 127.70, 129.72, 133.55, 135.53, 135.59, 137.12, 141.63, 156.60;



71

Diene complex **71**: In the glove box, diiron nonacarbonyl (907.7 mg, 2.495 mmol, 3 eq) was placed in a Schlenk flask which had been equipped with a stir bar. This flask was sealed and brought into the fume and placed under Ar atmosphere. Meanwhile, the oxazolidynl diene **70** (422.3 mg, 0.83.17 mmol, 1eq) was dissolved in dry toluene and cannulated into the Schlenk flask containing the diiron nonacarbonyl. This flask was sealed and removed from Ar and then placed in a 35°C oil bath and stirred for 23 h. Reaction mixture was filtered through silica gel on a glass frit and rinsed with EtOAc. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 3:1 hexanes: EtOAc, twice) to yield the complexed diene **71** (270 mg, 50%) as a white foam.

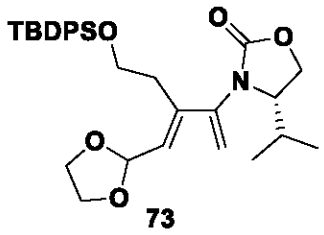
Poor spectra quality, assignment not possible.



72

Vinyl iodide **72**: Vinyl stannane **51** (456.0 mg, 0.6789 mmol, 1 eq) was dissolved in dichloromethane (7 mL). N-Iodosuccinimide (168.0 mg, 0.7468 mmol, 1.1 eq) was taken from the glovebox and added to the solution of the vinyl stannane at 0°C and stirred at 0°C for 2h. The reaction was quenched with saturated NaHCO3 (10 mL) and saturated Na2S2O3 (10 mL). The mixture was diluted with EtOAc (60 mL) and transferred to a separatory funnel. Layers separated and organic layer was washed with brine (20 mL). This solution was filtered and concentrated via rotary evaporation. The resulting residue was purified with column chromatography (silica, 40:1 hexanes: EtOAc with 0.5 NEt3) to yield vinyl iodide **72** (289.6 mg, 84%).

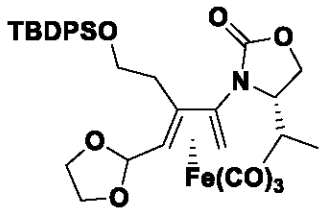
^{1}H NMR (400 MHz) **δ** 1.08 (s, 9H, *t*-butyl), 2.80 (td, 2H, allylic H, *J*=6.4 Hz, 0.8Hz) 3.76 (t, 2H, C$\underline{H}_2$OSi, *J*= 6.4 Hz), 3.78 (m, 4H, OC$\underline{H}_2$C$\underline{H}_2$O), 5.43 (d, 1H, vinylic, *J*= 6.4 Hz), 6.30 (d, 1H, C$\underline{H}$(OCH$_2$CH$_2$O), *J*= 6.4 Hz), 7.43 (m, 6H, Ar), 7.65 (m, 4H, Ar); **^{13}C NMR** (100 MHz) **δ** 19.16, 26.77, 26.87, 42.89, 62.31, 64.81, 99.43, 106.68, 127.68, 129.65, 133.45, 135.66, 139.74



73

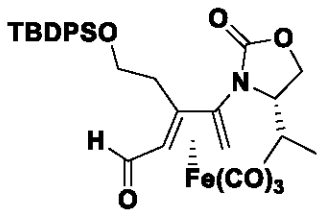
Oxazolidynldiene **73**: In the glove box, the vinyl stannane (253.0 mg, 0.5695 mmol, 1 eq) was dissolved in DMF and transferred into the flask containing the vinyl iodide (289.6 mg, 0.5695 mmol, 1 eq). CuO_2PPh_2 (183.9 mg, 0.6549 mmol, 1.15 eq) and $Pd(PPh_3)_4$ catalyst (65.9 mg, 0.0570 mmol, 0.1 eq) added and the reaction was stirred overnight. The reaction was removed from the glove box and filtered through a silica gel plug with EtOAc. The solution was concentrated via rotary evaporation and transferred to separatory funnel with diethyl ether (40 mL). The organic layer was washed with H_2O (2 x 12 mL) and brine (12 mL). The solution was dried over MgSO4 and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 3:1 hexanes: EtOAc with 0.5 NEt_3) to yield oxazolidinone diene **73** (247.4 mg, 81%).

^{1}H NMR (400 MHz) **δ** 0.81 (2 d, 6H, $CH(C\underline{H}_3)_2$, *J*= 7.2, *J*= 6.8 Hz), 1.04 (s, 9H, *t*-butyl), 1.71 (m, 1H, $C\underline{H}(CH_3)_2$), 2.42 (m, 1H, one of allylic H), 2.66 (m, 1H, one of allylic H), 3.75 (m, 5H, $OC\underline{H}_2C\underline{H}_2O$ and $C\underline{H}OC(O)$), 3.95 (m, 2H, $C\underline{H}_2N$), 4.10 (m, 1H, one of $C\underline{H}_2OSi$), 4.22 (t, 1H, one of $C\underline{H}_2OSi$, *J*= 9.0 Hz), 5.22 (s, 1H, one of $C\underline{H}_2$=CN), 5.25 (s, 1H, one of $C\underline{H}_2$=CN), 5.41 (d, 1H, vinylic, *J*= 6.8 Hz), 5.62 (d, 1H, $C\underline{H}(OCH_2CH_2O)$, *J*= 6.8 Hz), 7.43 (m, 6H, Ar), 7.65 (m, 4H, Ar); **^{13}C NMR (100 MHz) δ** 14.29, 17.76, 19.13, 26.82, 28.80, 32.15, 59.93, 62.60, 62.64, 64.93, 99.63, 113.64, 127.69, 128.04, 129.68, 133.61, 135.60, 137.88, 140.99, 156.39;



74 dr 5:1

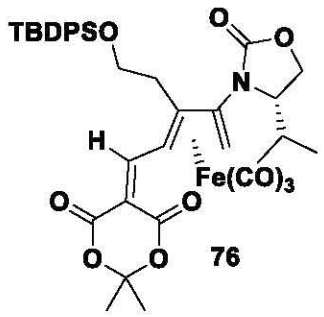
Diene complex **74**: In the glove box, diiron nonacarbonyl (587.0 mg, 1.615 mmol, 3.5 eq) was placed in a Schlenk flask which had been equipped with a stir bar. This flask was sealed and brought into the fume and placed under Ar atmosphere. Meanwhile oxazolidinone diene **73** (247.4 mg, 0.4613 mmol, 1eq) was dissolved in dry toluene and cannulated into the Schlenk flask containing the diiron nonacarbonyl. This flask was sealed and removed from Ar and then placed in a 35°C oil bath and stirred for 23 h. Reaction mixture was filtered through silica gel on a glass frit and rinsed with EtOAc. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 12:1 then 7:1 hexanes: EtOAc) to yield yellow oil **74** (210.8 mg, 68%). Note that green iron complex eluted with the compound.



75

Aldehyde **75**: Acetal **74** was dissolved with THF (2.5 mL) and H_2O (0.5 mL). One portion of camphor sulfonic acid (CSA) (7.2 mg, 0.0312 mmol, 0.1 eq) was added and the reaction was stirred for 2 h at room temperature. A second portion of CSA was added (7.2 mg, 0.0312 mmol, 0.1 eq) and stirred overnight. Reaction was diluted with EtOAc (30 mL). Layers were separated and the organic layer was washed with saturated $NaHCO_3$ (15 mL). The aqueous layer was extracted with EtOAc (2 x 10 mL). Combined organics washed with brine (15 mL). Solution was dried over $MgSO_4$ and filtered. Solution was concentrated via rotary evaporation and purified via column chromatography (silica, 3:1 hexanes: EtOAc with 0.5% NEt_3) to yield aldehyde **75** (168.1 mg, 85%) as a yellow oil.

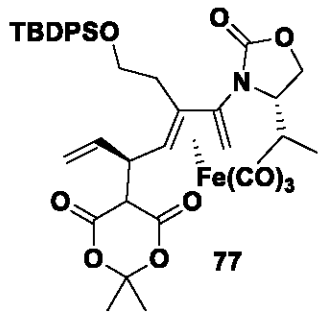
^{1}H NMR (400 MHz) **δ** 0.59 (d, 3H, one of $CH(C\underline{H}_3)_2$, *J*= 7.2 Hz), 0.69 (d, 1H, one of $C\underline{H}_2$=CN, *J*= 6.0 Hz), 0.85 (d, 3H, one of $CH(C\underline{H}_3)_2$, *J*= 6.8 Hz), 0.85 (partially obscured d, 1H, one of $C\underline{H}_2$=CN), 1.05 (s, 9H, *t*-butyl), 2.11 (d, 1H, CH(O)CH, *J*= 3.9 Hz), 2.22 (m, 1H, $C\underline{H}(CH_3)_2$), 2.87 (m, 1H, one of the allylic H), 3.04 (m, 1H, one of the allylic H), 3.75 (m, 1H, C<u>H</u>O), 3.85 (m, 1H, one of $C\underline{H}_2$N), 3.98 (m, 3H, $C\underline{H}_2$OSi and one of $C\underline{H}_2$N), 7.40 (m, 6H, Ar), 7.59 (m, 4H, Ar), 9.30 (d, 1H, C<u>H</u>(O), *J*= 6.0 Hz); **^{13}C NMR (100 MHz) δ** 13.52, 17.43, 19.36, 26.92, 28.78, 31.55, 39.11, 53.33, 61.34, 63.75, 64.55, 102.70, 104.03, 127.82, 129.99, 133.10, 135.34, 156.31, 195.12; **IR** (neat) 1111, 1428, 1672, 1745, 1974, 2002, 2059, 2869, 2962 cm^{-1}; **HRMS** ($M+Na^+$) cacld for $C_{32}H_{37}NO_7NaSi^{56}Fe$ 654.1581, found 654.1605.



76

Alkylidene malonate **76**: Under an Ar atmosphere, aldehyde **75**, dissolved in pyridine. 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) (42.2 mg, 0.293 mmol, 1.1 eq) was added. The reaction was stirred overnight. The reaction mixture was diluted with EtOAc (60 mL). The organic layer was washed with saturated $CuSO_4$ (2 x 20 mL) and brine (2 x 20 mL). Dried over $MgSO_4$. The solution was filtered and concentrated via rotary evaporation. The crude mixture was purified via column chromatography (silica, 5:1 hexanes: EtOAc with 0.5% formic acid) to yield an orange semisolid **76** (137.3 mg, 68%).

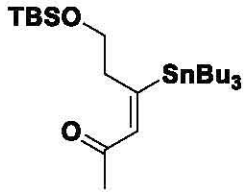
^{1}H NMR (400 MHz) **δ** 0.62 (d, 3H, one of $CH(C\underline{H}_3)_2$, *J*= 7.0 Hz), 0.87 (d, 3H, one of $CH(C\underline{H}_3)_2$, *J*= 7.0 Hz), 1.00 (s, 9H, *t*-butyl), 1.50 (d, 1H, one of the $CNC\underline{H}_2$, *J*= 4.0 Hz), 1.62 (s, 3H, one of $C(C\underline{H}_3)O_2$), 1.71 (s, 3H, one of $C(C\underline{H}_3)O_2$), 2.25 (partially obscured m, 1H, $C\underline{H}(CH_3)_2$), 2.30 (d, 1H, one of the $CNC\underline{H}_2$, *J*= 3.9 Hz), 2.77 (d, 1H, $C\underline{H}$=CCN, *J*= 12.2 Hz), 2.81 (partially obscured m, 1H, one of the allylic H), 2.94 (m, 1H, one of the allylic H), 3.75 (m, 2H,$C(O)OC\underline{H}_2$), 3.90 (m, 1H, $C\underline{H}N$), 4.00 (m, 2H, $C\underline{H}_2OSi$), 7.38 (m, 6H, Ar), 7.55 (m, 4H, Ar), 7.93 (d, 1H, $(C(O))_2CC\underline{H}$); **^{13}C NMR (100 MHz) δ** 13.54, 17.50, 19.29, 26.90, 27.46, 27.57, 28.85, 31.30, 39.91, 51.04, 61.47, 63.88, 64.16, 104.43, 104.84, 105.03, 127.86, 130.04, 130.08, 132.90, 135.32, 135.42, 156.21; **IR** (neat) 1111, 1428, 1672, 1745, 1974, 2002, 2059, 2869, 2962 cm^{-1}; **HRMS** ($M+Na^+$) cacld for $C_{32}H_{37}NO_7NaSi^{56}Fe$ 654.1581, found 654.1605.



77

77: Under an Ar atmosphere, compound **76** (83.3 mg, 0.1099 mmol) was dissolved in THF (1.1 mL) and cooled to -78°C. Vinyl magnesium bromide (1.0 M in hexanes, 0.1648 mL, 0.1648 mmol, 1.5 eq) added and solution stirred at -78°C for 90 min. Quenched with saturated NH_4Cl (25 mL). Extracted with EtOAc (45 mL). Organic layer washed with brine (20 mL) and dried over $MgSO_4$. Solution was filtered and concentrated via rotary evaporation. Not purified.

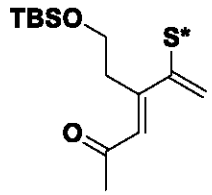
Crude: **^{1}H NMR** (400 MHz) **δ** 0.43 (d, 1H, one of the CNC$\underline{H}_2$, *J*= 3.4 Hz), 0.61 (d, 3H, one of CH(C$\underline{H}_3$)$_2$, *J*= 6.9 Hz), 0.77 (d, 3H, one of CH(C$\underline{H}_3$)$_2$, *J*= 6.8 Hz), 1.05 (s, 9H, *t*-butyl), 1.32 (partially obscured d, 1H, one of the CNC$\underline{H}_2$), 1.42 (d, 1H, C$\underline{H}$=CCN, *J*= 10.7 Hz), 1.60 (m, 1H, N$\underline{H}$), 1.75 (s, 3H, one of C(C$\underline{H}_3$)O$_2$), 1.81 (s, 3H, one of C(C$\underline{H}_3$)O$_2$), 2.15 (m, 1H, C$\underline{H}$(CH$_3$)$_2$), 2.70 (m, 1H, one of C$\underline{H}_2$CH$_2$OSi), 3.01 (m, 1H, one of C$\underline{H}_2$CH$_2$OSi), 3.38 (m, 2H, C$\underline{H}_2$OC(O)), 3.52 (m, 1H, C$\underline{H}$(C(O))$_2$), 3.75 (m, 2H, CH$_2$=CHC$\underline{H}$ and NC$\underline{H}$), 3.89 (m, 2H, C$\underline{H}_2$OSi), 5.02 (d, 1H, terminal vinyl H trans to chain, *J*= 10.4 Hz), 5.30 (d, 1H, terminal vinyl H cis to chain, *J*= 17.0 Hz), 5.72 (pd, 1H, vinylic H, *J*= 8.2 Hz, 1.5 Hz), 7.42 (m, 6H, Ar), 7.65 (m, 4H, Ar)



84

Stannyl enone **84**: $CeCl_3$ (anhydrous, 132.7 mg, 0.5385 mmol, 2.5 eq) was placed in a Schlenk flask in the glovebox, sealed, and placed in the fume hood. Under Ar, it was dissolved in THF (2 mL) and stirred for 2 h. The suspension was cooled to -78°C and the methyl Grignard (3.0 M in Et_2O, 0.144 mL, 2eq) was added and stirred at -78°C for 1 h. The amide **83** (126.7 mg, 0.2154 mmol, 1 eq) was dissolved in THF (2 mL) and cannulated into the cerium reagent. This mixture was stirred at -78°C for 1h, and then warmed to -40°Cnd maintained for 30 min. The reaction was quenched with saturated NH_4Cl (1 mL) and upon warming to room temperatue, diluted with H_2O (10 mL) and Et_2O (20 mL). The aqueous layer was extracted with Et_2O (2 x 10mL) and the combined organics were dried over $MgSO_4$ and filtered. The mixture was concentrated via rotary evaporation and the resulting residue was purified via column chromatography (silica, 30:1 hexanes: EtOAc with 0.5% NEt_3) to yield the vinyl stannane **84** (94.2 mg, 85%) as a pale yellow oil.

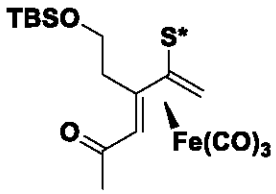
^{1}H NMR (400 MHz) **δ** 0.05 (s, 6H, $Si(C\underline{H}_3)_2C((CH_3)_3)$), 0.88 (partially obscured s, 9H, $Si(CH_3)_2C((C\underline{H}_3)_3)$), 0.95 (m, 15H, $Sn(C\underline{H}_2CH_2CH_2C\underline{H}_3)_3$), 1.31 (m, 6H, $Sn(CH_2CH_2C\underline{H}_2CH_3)_3$), 1.49 (m, 6H, $Sn(CH_2C\underline{H}_2CH_2CH_3)_3$), 2.19 (s with satellites, 3H, $C\underline{H}_3C(O)$), 3.01 (td with satellites, 2H, allylic H, *J*= 7.2 Hz, 1.2 Hz), 3.64 (t, 2H, $C\underline{H}_2OSi$, *J*= 7.2 Hz), 6.38 (t, with satellites, vinylic H, *J*= 1.2 Hz); **^{13}C NMR (100 MHz) δ** -5.21, 8.50, 11.74, 18.43, 26.03, 27.38, 29.00, 31.45, 39.18, 62.70, 138.06, 167.55, 196.89; **HRMS** sample submitted for exact mass determination



85

Sulfinyl diene **85**: In the glove box, the vinyl stannane **84** (92.8 mg, 0.179 mmol, 1 eq) was dissolved in DMF and transferred into the flask containing the iodo-vinyl sulfoxide (52.2 mg, 0.179 mmol, 1 eq). CuO_2PPh_2 (57.8 mg, 0.206 mmol, 1.15 eq) and $Pd(PPh_3)_4$ catalyst (20.8 mg, 0.018 mmol, 0.1 eq) added and the reaction was stirred overnight. The reaction was removed from the glove box and filtered through a silica gel plug with EtOAc. The solution was concentrated via rotary evaporation and transferred to separatory funnel with diethyl ether (35 mL). The organic layer was washed with H_2O (2 x 10 mL) and brine (10 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 3:1 hexanes: EtOAc with 0.5 NEt_3) to yield sulfinyl diene **85** (45.6 mg, 65%).

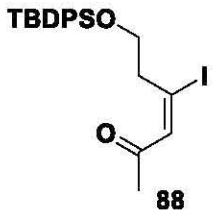
^{1}H NMR (400 MHz) **δ** -0.04 (s, 6H, $Si(C\underline{H}_3)_2C((CH_3)_3)$), 0.80 (s, 9H, $Si(CH_3)_2C((C\underline{H}_3)_3)$, 2.21 (s, 3H, $C\underline{H}_3C(O)$), 2.39 (s, 3H, $ArC\underline{H}_3$), 2.61 (m, 1H, one of the allylic H), 2.96 (m, 1H, one of the allylic H), 3.30 (m, 1H, one of $C\underline{H}_2OSi$), 3.39 (m, 1H, one of $C\underline{H}_2OSi$), 6.16 (s, 1H, one of the vinylic H), 6.31 (s, 1H, one of the vinylic H), 6.38 (s, 1H, one of the vinylic H), 7.21 (partially obscured d, 2H, Ar), 7.46 (d, 2H, *J*= 8.0 Hz); **^{13}C NMR (100 MHz) δ** -5.48, 18.26, 21.46, 25.88, 32.14, 35.00, 61.36, 119.40, 125.70, 127.28, 129.95, 139.54, 142.42, 147.13, 154.88, 197.60



86

Diene complex **86**: In the glove box, diiron nonacarbonyl (169.0 mg, 0.464 mmol, 4 eq) was placed in a Schlenk flask which had been equipped with a stir bar. This flask was sealed and brought into the fume and placed under Ar atmosphere. Meanwhile the sulfoxide diene **85** (45.6 mg, 0.1161 mmol, 1eq) was dissolved in dry toluene (1.2 mL) and cannulated into the Schlenk flask containing the diiron nonacarbonyl. This flask was sealed and removed from Ar and then placed in a 35°C oil bath and stirred for 20 h. Reaction mixture was filtered through silica gel on a glass frit and rinsed with EtOAc. The solution was concentrated via rotary evaporation and purified using multiple column chromatography (silica, 7:1 hexanes: EtOAc with 0.5% NEt_3) to yield the diene complex **86** (35.3 mg, 57%) as a yellow solid.

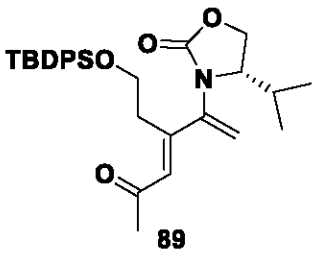
^{1}H NMR (400 MHz) **δ** -0.80 (s, 3H, one of the $Si(C\underline{H}_3)_2C((CH_3)_3)$, -0.40 (s, 3H, $Si(C\underline{H}_3)_2C((CH_3)_3)$, 0.38 (d, 1H, one of $CS^*C\underline{H}_2$, *J*= 4.0 Hz), 0.62 (d, 1H, $C(O)C\underline{H}$), 0.81 (s, 9H, $Si(CH_3)_2C((C\underline{H}_3)_3)$, 2.12 (s, 3H, $C\underline{H}_3C(O)$), 2.42 (s, 3H, $ArC\underline{H}_3$), 2.83 (d, 1H, one of $CS^*C\underline{H}_2$, *J*= 3.6 Hz), 3.22 (m, 1H, one of the allylic H), 3.45 (m, 2H, one of the allylic H + one of the $C\underline{H}_2OSi$), 3.81 (m, 1H one of the $C\underline{H}_2OSi$), 7.32 (d, 2H, Ar, *J*= 8.0 Hz), 7.72 (dd, 2H, Ar, *J*= 7.6 Hz, 1.6 Hz); **^{13}C NMR (100 MHz) δ** -5.47, -5.35, 18.42, 21.53, 25.92, 30.08, 30.52, 31.55, 53.28, 63.07, 106.62, 114.47, 125.88, 130.21, 141.77, 142.69, 203.08; **IR** (ATR) 1084, 1057, 1991, 2060, 2857, 2929 cm^{-1}; **HRMS** sample submitted for exact mass determination; Diastereomeric (facial) mixture: $[\alpha]_D^{23}$ = +293.5 (*c* 0.34, $CHCl_3$)



88

Vinyl iodide **88**: Vinyl stannane **87** (442.4mg, 0.6895 mmol, 1 eq) was dissolved in dichloromethane (7 mL). N-Iodosuccinimide (170.6 mg, 0.7585 mmol, 1.1 eq) was taken from the glovebox and added to the solution of the vinyl stannane at 0°C and stirred at 0°C for 2h. The reaction was concentrated via rotary evaporation. The resulting residue was purified with column chromatography (silica, 30:1 hexanes: EtOAc) to yield vinyl iodide **88** (200 mg, 61%).

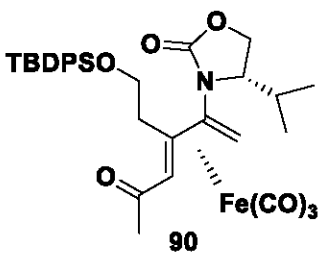
^{1}H NMR (400 MHz) **δ** 1.04 (s, 9H, *t*-butyl), 2.14 (s, 3H, C$\underline{H}_3$C(O)), 3.38 (td, 2H, allylic H, *J*= 6.2 Hz, 0.8 Hz), 3.81 (t, 2H, C$\underline{H}_2$OSi, *J*= 6.0Hz), 7.12 (s, 1H, vinylic H), 7.40 (m, 6H, Ar), 7.67 (m, 4H, Ar); **^{13}C NMR (100 MHz) δ** 19.20, 26.74, 31.22, 43.77, 63.01, 125.12, 127.66, 129.63, 133.45, 135.63, 140.51, 195.38; **IR** (neat) 1111, 1174, 1354, 1428, 1584, 1698, 2857, 2929, 3070 cm^{-1}



89

Oxazolidinyl diene **89**: In the glove box, the vinyl stannane (185.8 mg, 0.4180 mmol, 1 eq) was dissolved in DMF (2.2 mL) and transferred into the flask containing the vinyl iodide **88** (200 mg, 0.4186 mmol, 1 eq). CuO_2PPh_2 (135 mg, 0.4807 mmol, 1.15 eq) and $Pd(PPh_3)_4$ catalyst (48.3 mg, 0.0418 mmol, 0.1 eq) added and the reaction was stirred overnight. The reaction was removed from the glove box and filtered through a silica gel plug with EtOAc. The solution was concentrated via rotary evaporation and transferred to separatory funnel with diethyl ether (30 mL). The organic layer was washed with H_2O (2 x 10 mL) and brine (10 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 3:1 hexanes: EtOAc) to yield oxazolidinone diene **89** (189.8 mg, 90%) as a yellow foam.

^{1}H NMR (400 MHz) **δ** 0.78 (d, 3H, one of $CH(C\underline{H}_3)_2$, *J*= 6.8 Hz), 0.82 (d, 3H, one of $CH(C\underline{H}_3)_2$, *J*= 6.8 Hz), 1.04 (s, 9H, *t*-butyl), 1.82 (m, 1H, $C\underline{H}(CH_3)_2$), 2.21 (s, 3H, $C\underline{H}_3C(O)$), 2.72 (m, 1H, one of allylic H), 3.80 (m, 1H, one of allylic H), 3.75 (m, 3H, $C\underline{H}_2N$ + $C\underline{H}O$), 4.15 (m, 1H, one of $C\underline{H}_2OSi$), 4.30 (t, 1H, one of $C\underline{H}_2OSi$, *J*= 9.2 Hz), 5.42 (s, 1H, one of $C\underline{H}_2$=CN), 5.55 (s, 1H, one of $C\underline{H}_2$=CN), 6.79 (s, 1H, vinylic), 7.40 (m, 6H, Ar), 7.65 (m, 4H, Ar); **^{13}C NMR** (100 MHz) **δ** 14.30, 17.86, 19.14, 26.82, 28.40, 32.30, 32.55, 60.25, 62.77, 62.95, 116.21, 126.07, 127.85, 129.61, 133.56, 135.57, 142.01, 148.45, 156.31, 198.31; **IR** (neat), 1408, 1589, 1764, 2929.4, 3071, 3406 cm^{-1}

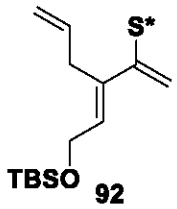


90

Diene complex **90**: In the glove box, diiron nonacarbonyl (545 mg, 1.499 mmol, 4 eq) was placed in a Schlenk flask which had been equipped with a stir bar. This flask was sealed and brought into the fume and placed under Ar atmosphere. Meanwhile, the oxazolidinone diene **89** (189.8 mg, 0.3749 mmol, 1eq) was dissolved in dry toluene and cannulated into the Schlenk flask containing the diiron nonacarbonyl. This flask was sealed and removed from Ar and then placed in a 35°C oil bath and stirred for 20 h. Reaction mixture was filtered through silica gel on a glass frit and rinsed with EtOAc. The solution was concentrated via rotary evaporation and purified using multiple column chromatography (silica, 5:1 hexanes: EtOAc with 1% NEt_3) to complexed diene **90** (44.3 mg, 18.3%).

Major: **^{1}H NMR** (400 MHz) **δ** 0.34 (s, 1H, C(O)C<u>H</u>), 0.47 (d, 3H, one of CH(C<u>H</u>$_3$)$_2$, *J*= 7.2 Hz), 0.61 (d, 1H, one of C<u>H</u>$_2$=CN, *J*= 3.6 Hz), 0.70 (d, 3H, one of CH(C<u>H</u>$_3$)$_2$, *J*= 6.8 Hz), 1.04 (s, 9H, *t*-butyl), 1.95 (d, 1H, one of C<u>H</u>$_2$=CN, *J*= 3.6 Hz), 2.01 (s, 3H, C<u>H</u>$_3$C(O)), 2.18 (m, 1H, C<u>H</u>(CH$_3$)$_2$), 2.65 (m, 1H, one of allylic H), 3.55 (m, 1H, one of the allylic), 3.70 (td, 1H, CHO, *J*= 10 Hz, 3.2 Hz), 4.85 (m, 1H, one of C<u>H</u>$_2$N), 4.93 (m, 1H, one of C<u>H</u>$_2$N), 4.01 (m, 2H, C<u>H</u>$_2$OSi), 7.43 (m, 6H, Ar), 7.55 (m, 4H, Ar); Unobscured peaks of the minor: **^{1}H NMR** (400 MHz) **δ** 1.25 (partially obscured d, 1H, vinylic), 2.05 (partially obscured d, 1H, vinylic), 7.65 (m, 4H, Ar)

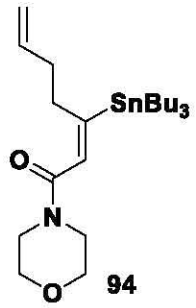
^{13}C NMR (100 MHz) **δ** 13.57, 17.28, 19.52, 27.06, 28.71, 30.45, 31.43, 38.45, 50.20, 61.23, 63.59, 64.73, 103.62, 104.16, 127.75, 129.86, 133.56, 135.31, 156.42;



92

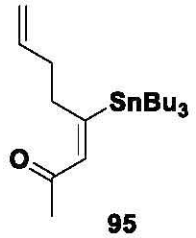
Sulfinyl diene **92**: In the glove box, the vinyl stannane (253.1 mg, 0.556 mmol, 1eq) was dissolved in DMF and transferred into the flask containing the vinyl iodide **91** (188.2 mg, 0.556 mmol, 1 eq). CuO_2PPh_2 (179.6 mg, 0.6398 mmol, 1.15 eq) and $Pd(PPh_3)_4$ catalyst (64.3 mg, 0.0556 mmol, 0.1 eq) added and the reaction was stirred overnight. The reaction was removed from the glove box and filtered through a silica gel plug with EtOAc. The solution was concentrated via rotary evaporation and transferred to separatory funnel with diethyl ether (40 mL). The organic layer was washed with H_2O (2 x 15 mL) and brine (15 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 4:1 hexanes: EtOAc) to yield sulfinyl diene **92** (84.7 mg, 41%).

^{1}H NMR (400 MHz) **δ** 0.01 (s, 6H, $Si(C\underline{H}_3)_2C((CH_3)_3)$), 0.88 (s, 9H, $Si(CH_3)_2C((C\underline{H}_3)_3)$), 2.36 (s, 3H, $ArC\underline{H}_3$), 2.82 (m, 2H, allylic H), 4.18 (d, 2H, $C\underline{H}_2OSi$, *J*= 6 Hz), 4.83 (m, 2H, $C\underline{H}_2$=CS*), 5.40 (m, 1H, CH_2=C<u>H</u>), 5.72 (s, 1H, one of $C\underline{H}_2CS$*), 5.80 (t, 1H, $SiOCH_2C\underline{H}$, *J*= 6 Hz), 6.15 (s, 1H, one of $C\underline{H}_2CS$*), 7.18 (m, 2H, Ar), 7.50 (dd, 2H, Ar, *J*= 6.4 Hz, 1.6 Hz).



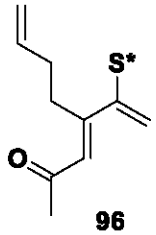
94

Vinyl stannane **94**: Ditributyltin (4.95 mL, 9.790 mmol, 2.2 eq) was dissolved in THF (12.5 mL) in a flame dried Schlenk flask under an Ar atmosphere. Solution cooled to -78°C. n-Butyllithium (1.6 M in hexanes, 5.84 mL, 9.345 mmol, 2.1 eq) was added via syringe. Solution was stirred at -40°C for 30 min. The mixture was recooled to -78°C and copper cyanide (79.7 mg, 8.900 mmol, 2 eq) was added. The reaction mixture was stirred at -40°C for 30 min and then recooled to -78°C. Methanol (0.270 mL, 6.675 mmol, 1.5 eq) was added to the reaction. The alkyne **93** (860 mg, 4.450 mmol, 1 eq) was dissolved in THF (6 mL) and this solution was added via cannula to the reaction mixture. The reaction was stirred at -78°C for 2h. The temperature was raised to -25°C and then the reaction was quenched with saturated NH_4Cl/NH_4OH (9:1, 40 mL). The mixture was transferred to a separatory funnel with EtOAc (25 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 25 mL). The combined organics were washed with brine (15 mL). The solution was dried over $MgSO_4$ and filtered. The mixture was concentrated via rotary evaporation and the resulting residue was purified via column chromatography (silica, 4:1 hexanes: EtOAc with 0.5% NEt_3) to yield the vinyl stannane **94** (1.858 g, 86%).



95

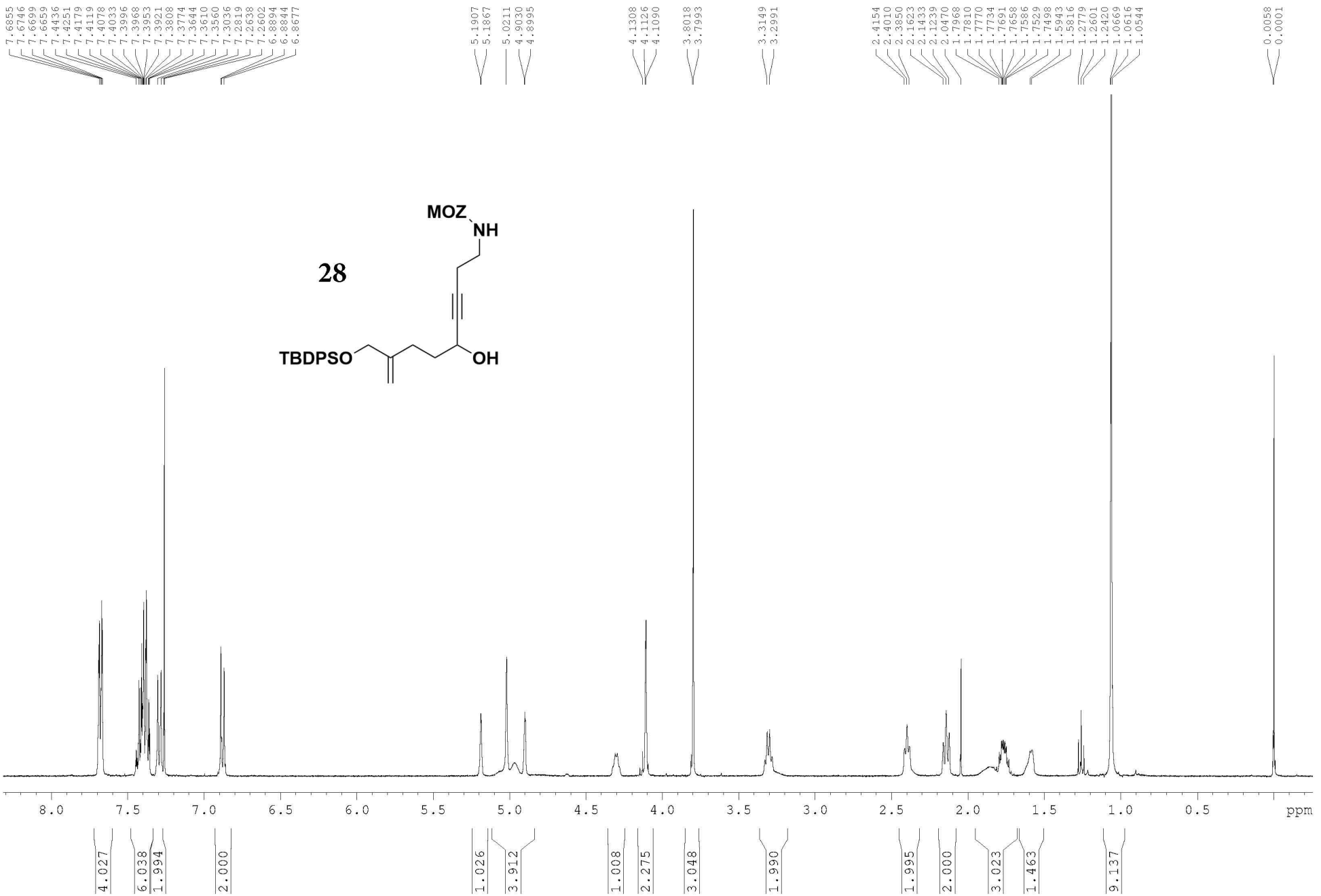
Stannyl enone **95**: $CeCl_3$ (anhydrous, 670 mg, 2.717 mmol, 2.5 eq) was placed in a Schlenk flask in the glovebox, sealed, and placed in the fume hood. Under Ar, it was dissolved in THF (11 mL) and stirred for 2 h. The suspension was cooled to -78°C and the methyl Grignard (3.0 M in Et_2O, 0.724 mL, 2.173 mmol, 2eq) was added and stirred at -78°C for 1 h. The amide **94** (526.3 mg, 1.087 mmol, 1 eq) was dissolved in THF (11 mL) and cannulated into the cerium reagent. This mixture was stirred at -78°C for 1h, and then warmed to -40°Cnd maintained for 30 min. The reaction was quenched with saturated NH_4Cl (20 mL) and upon warming to room temperatue, diluted with H_2O (30 mL) and Et_2O (50 mL). The aqueous layer was extracted with Et_2O (2 x 20mL) and the combined organics were dried over $MgSO_4$ and filtered. The mixture was concentrated via rotary evaporation and the resulting residue was purified via column chromatography (silica, 40:1 hexanes: EtOAc with 0.5% NEt_3) to yield stannyl enone **95** (428.0 mg, 95%).



96

Sulfinyl diene **96**: In the glove box, the vinyl stannane **95** (0.4280 mg, 1.035 mmol, 1 eq) was dissolved in DMF (5 mL). The iodovinyl sulfoxide (302 mg, 1.035 mmol, 1 eq) was added. Next, CuO_2PPh_2 (334 mg, 1.190 mmol, 1.15 eq) and $Pd(PPh_3)_4$ catalyst (119.0 mg, 0.103 mmol, 0.1 eq) were added and the reaction was stirred overnight. The reaction was removed from the glove box and filtered through a silica gel plug with EtOAc. The solution was concentrated via rotary evaporation and transferred to separatory funnel with diethyl ether (100 mL). The organic layer was washed with H_2O (2 x 30 mL) and brine (30 mL). The solution was dried over $MgSO_4$ and filtered. The solution was concentrated via rotary evaporation and purified using column chromatography (silica, 3:1 hexanes: EtOAc) to yield sulfoxide diene **96** (163.6 mg, 55%).

^{1}H NMR (400 MHz) **δ** 1.82 (m, 2H, $C\underline{H}_2C(CH_2)CS^*$), 2.16 (s, 3H, $C\underline{H}_3C(O)$), 2.38 (s, 3H, $ArC\underline{H}_3$), 2.42 (m, 1H, one of the allylic H to the terminal alkene), 2.97 (m, 1H, one of the allylic H to the terminal alkene), 4.85 (m, 2H, terminal vinylic H), 5.62 (m, 1H, internal H on the terminal alkene), 6.01 (s, 1H, one of the vinylic H on the diene), 6.27 (1H, one of the vinylic H on the diene), 6.36 (1H, one of the vinyliv H on the diene), 7.21 (partially obscured d, 2H, Ar), 7.49 (m, 2H, Ar); **^{13}C NMR (100 MHz) δ** 21.45, 30.23, 31.88, 32.20, 115.11, 118.48, 125.74, 126.46, 130.05 137.13, 139.36, 142.49, 149.54, 154.73, 197.74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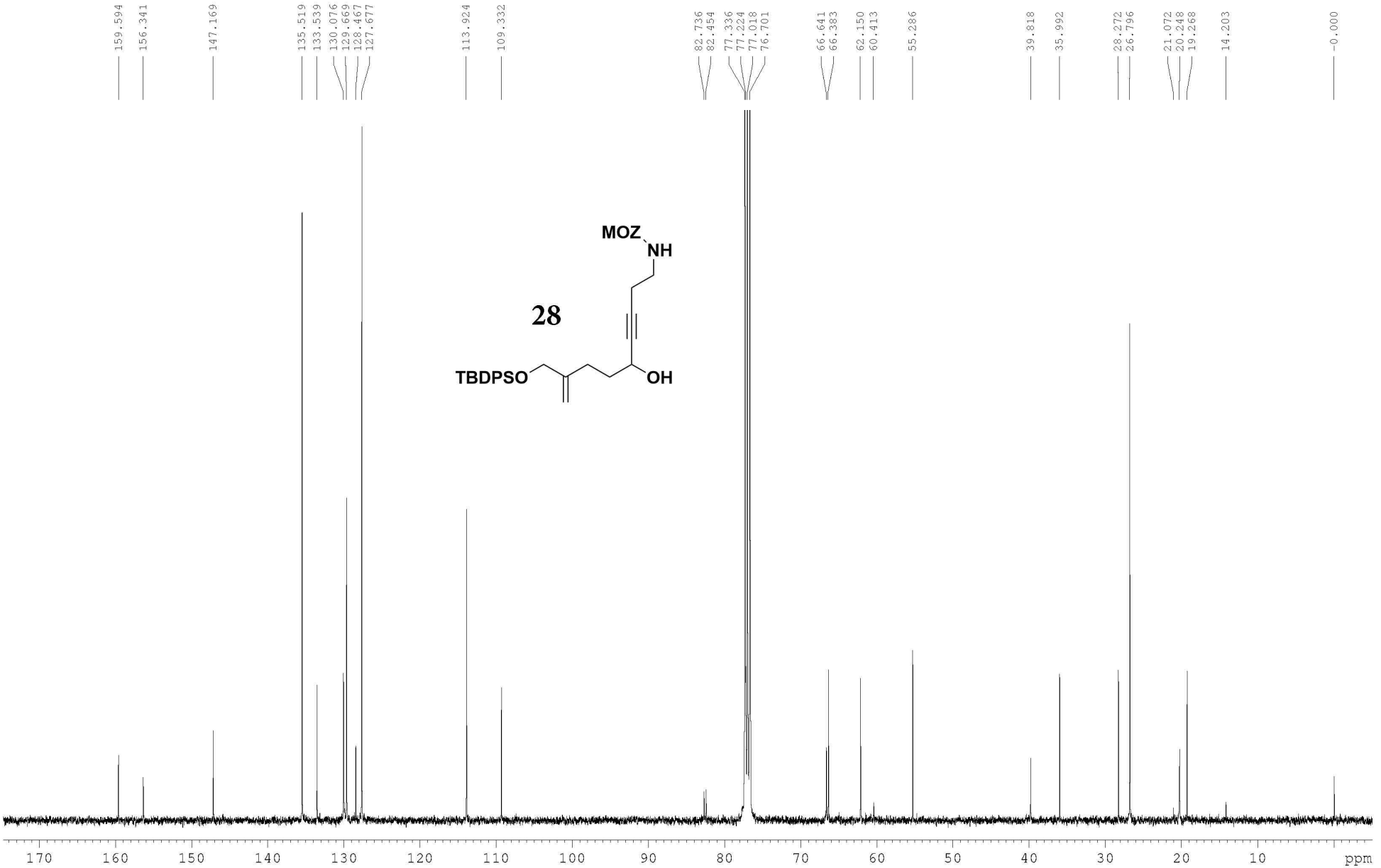
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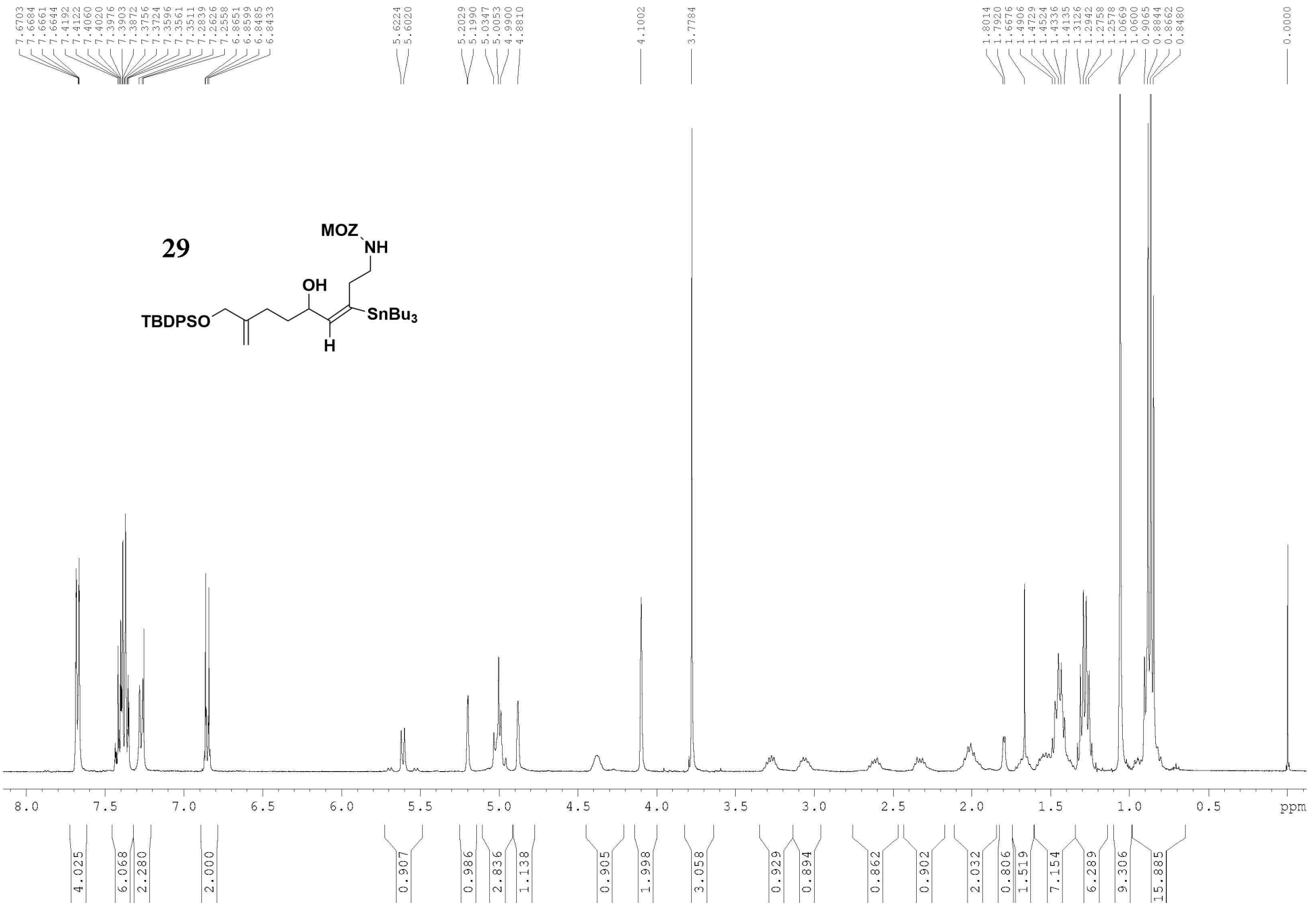
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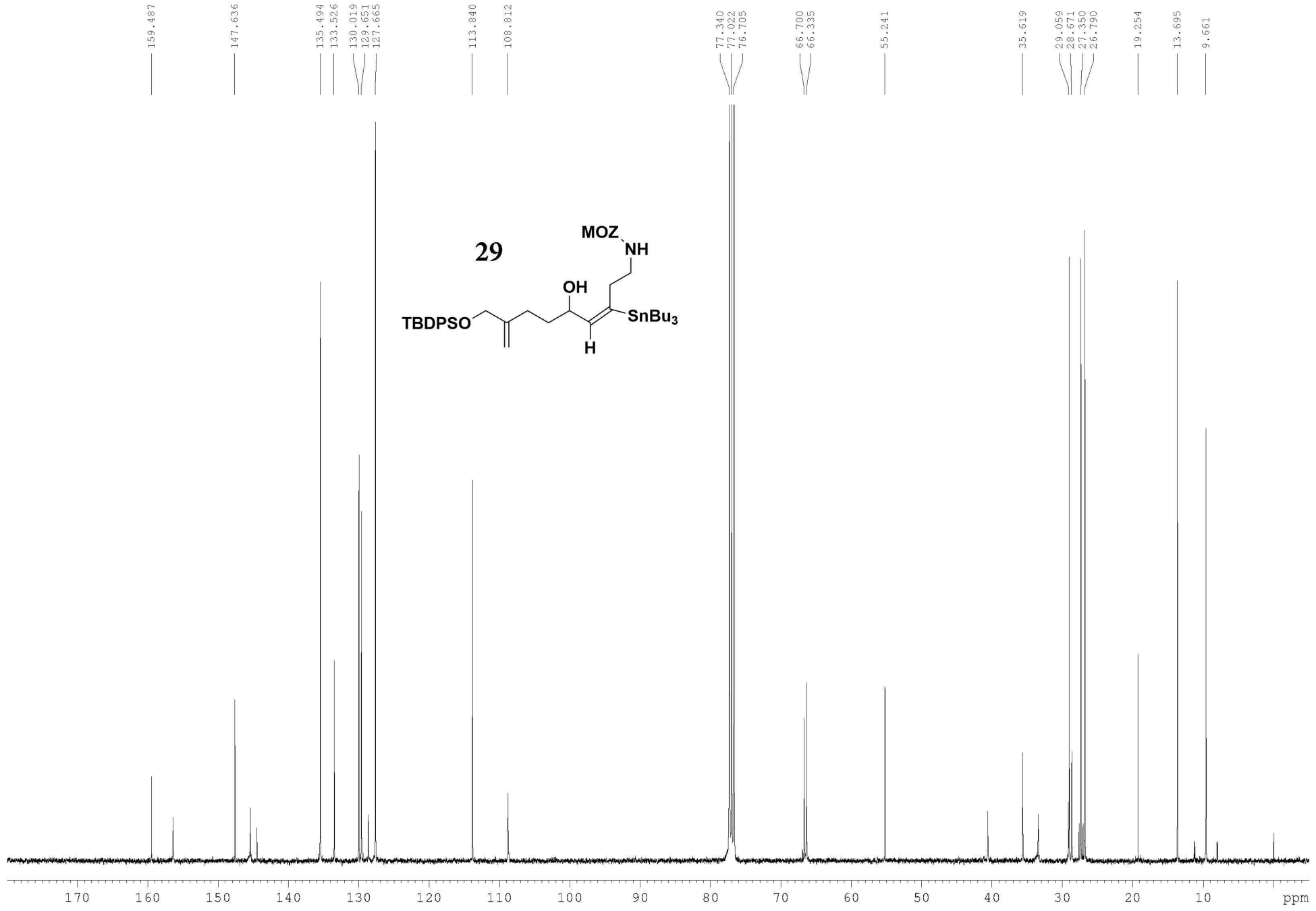
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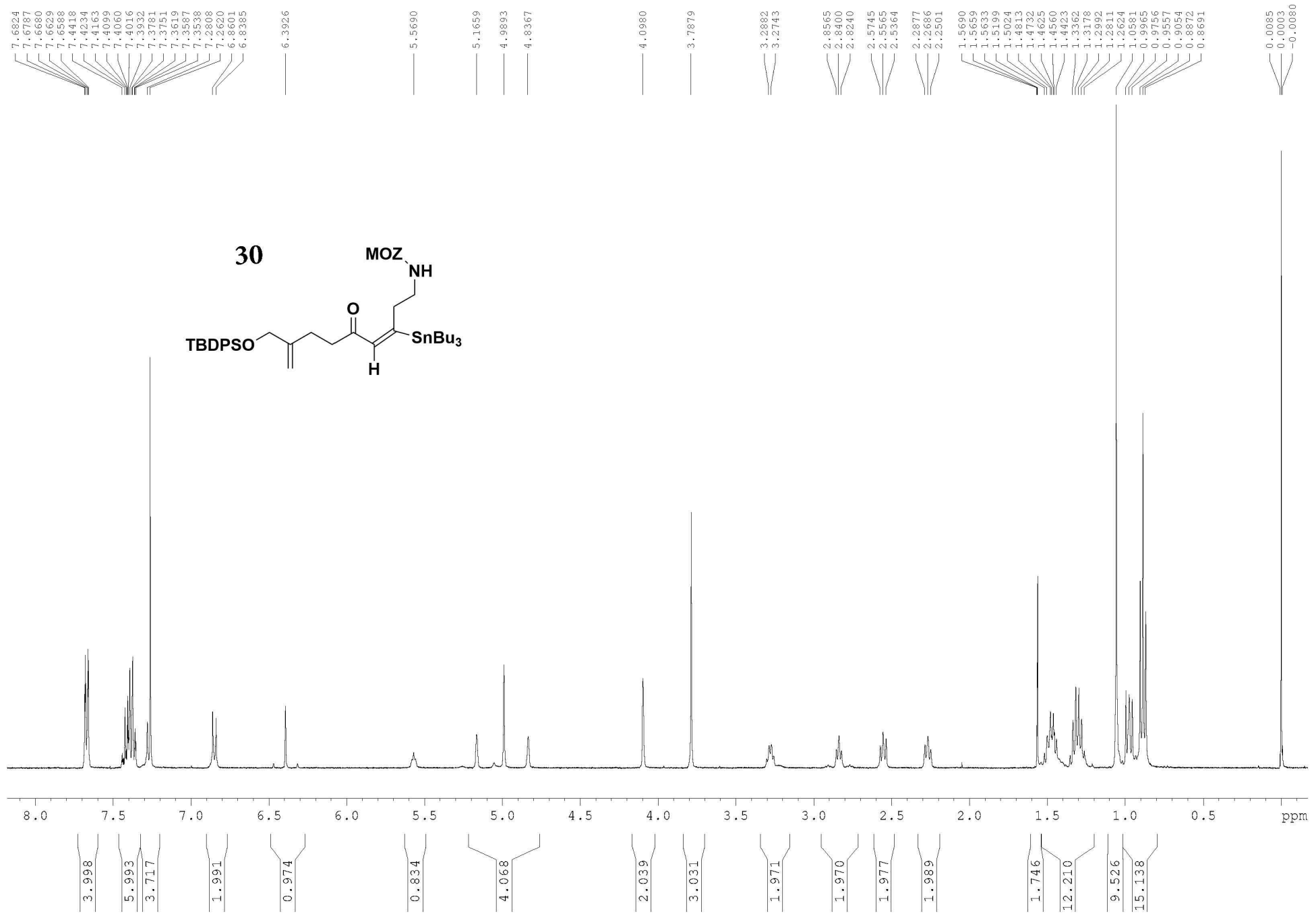
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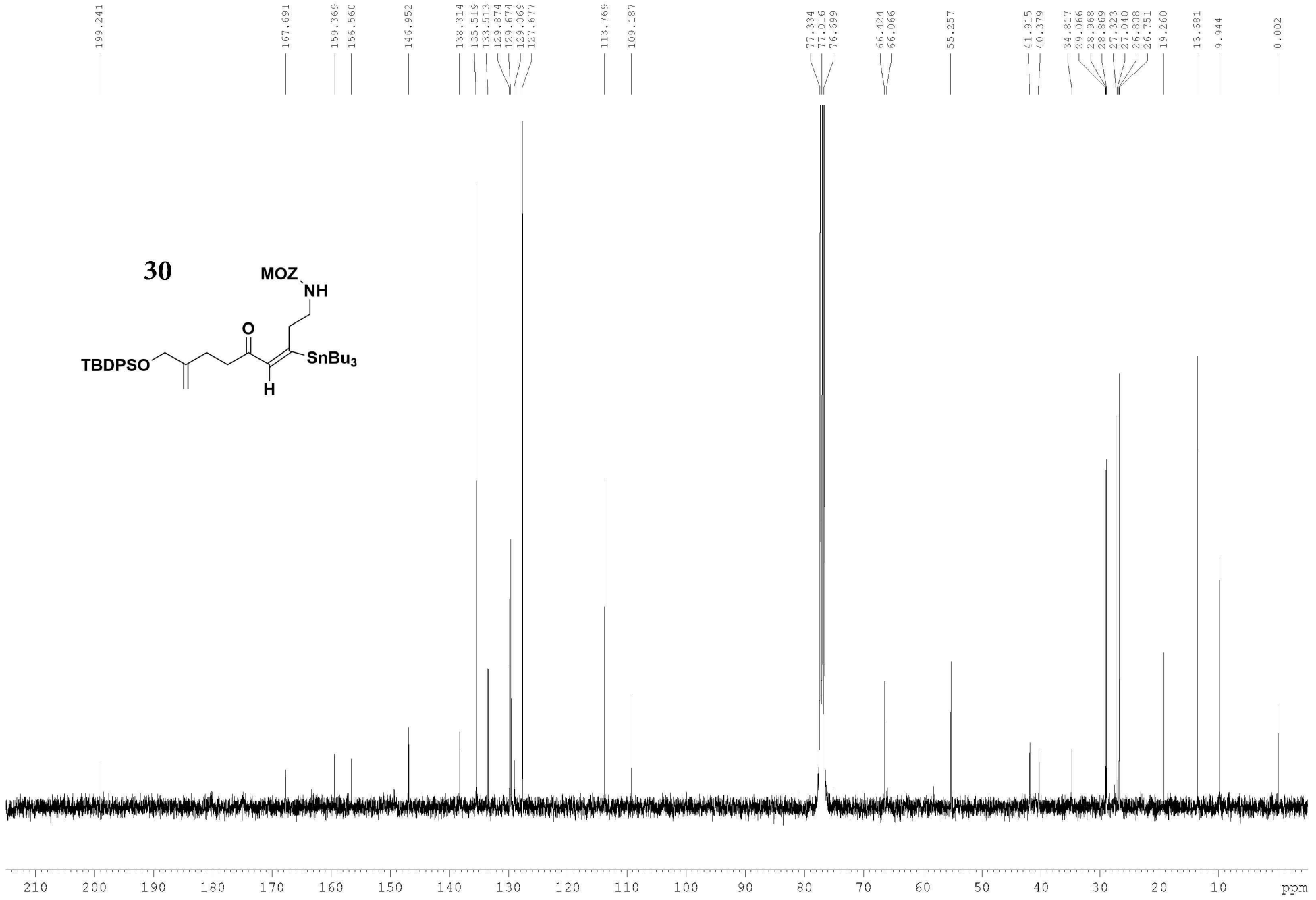
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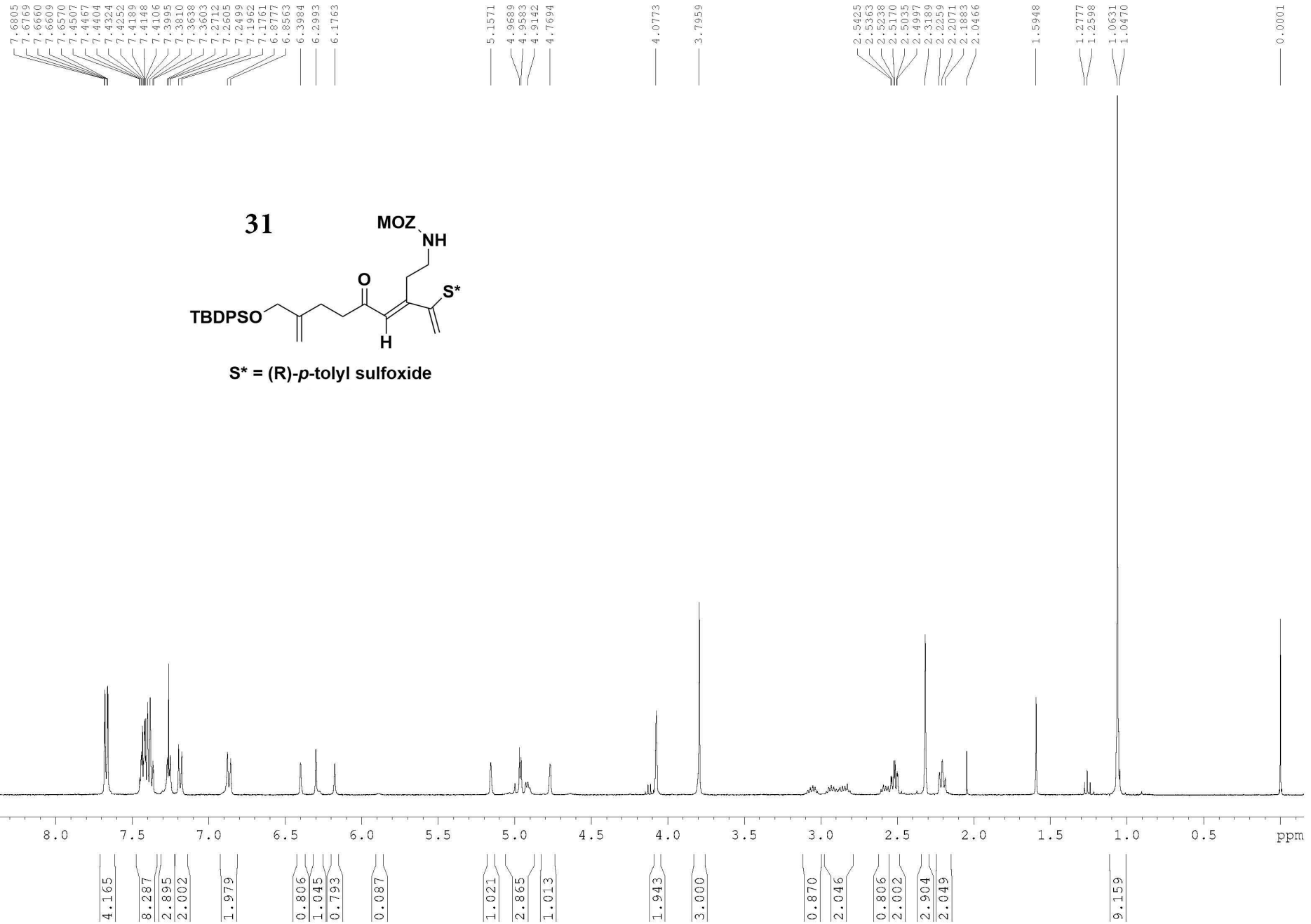
167.691
159.369
156.560
146.952
138.314
135.519
133.513
129.874
129.674
129.069
127.677
113.769
109.187
77.334
77.016
76.699
66.424
66.066
55.257
41.915
40.379
34.817
29.066
28.968
28.869
27.323
27.040
26.808
26.751
19.260
13.681
9.944
0.002
30
MOZ
NH
O
TBDPSO
SnBu3
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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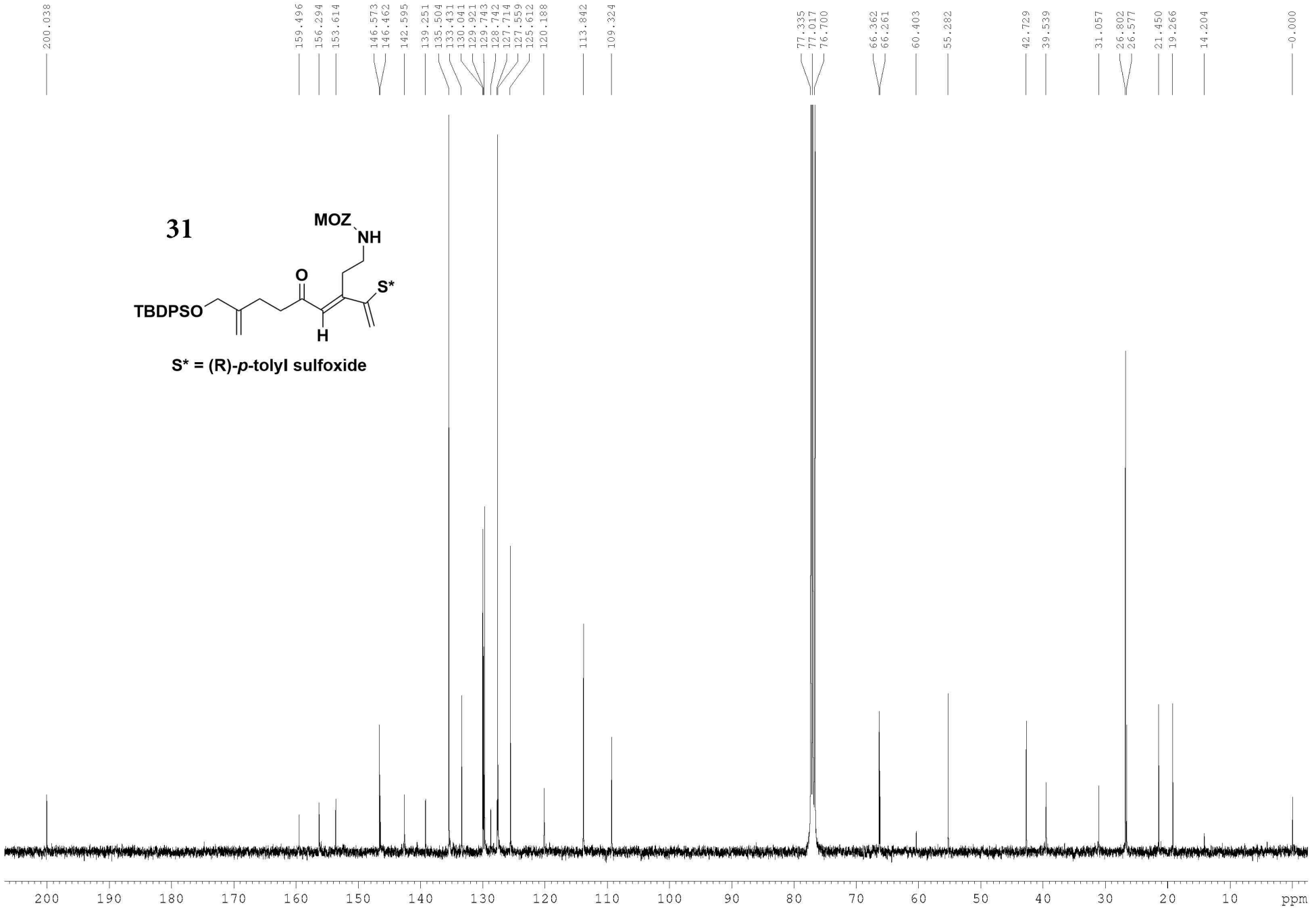
7.6660
7.6609
7.6570
7.4507
7.4467
7.4404
7.4324
7.4252
7.4189
7.4148
7.4106
7.3995
7.3810
7.3638
7.3603
7.2712
7.2605
7.2499
7.1962
7.1761
6.8777
6.8563
6.3984
6.2993
6.1763
5.1571
4.9689
4.9583
4.9142
4.7694
4.0773
3.7959
2.5425
2.5363
2.5238
2.5170
2.5035
2.4997
2.3189
2.2259
2.2071
2.1883
2.0466
1.5948
1.2777
1.2598
1.0631
1.0470
0.0001
31
MOZ
NH
O
S*
TBDPSO
H
S* = (R)-p-tolyl sulfoxide
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
4.165
8.287
2.895
2.002
1.979
0.806
1.045
0.793
0.087
1.021
2.865
1.013
1.943
3.000
0.870
2.046
0.806
2.002
2.904
2.049
9.159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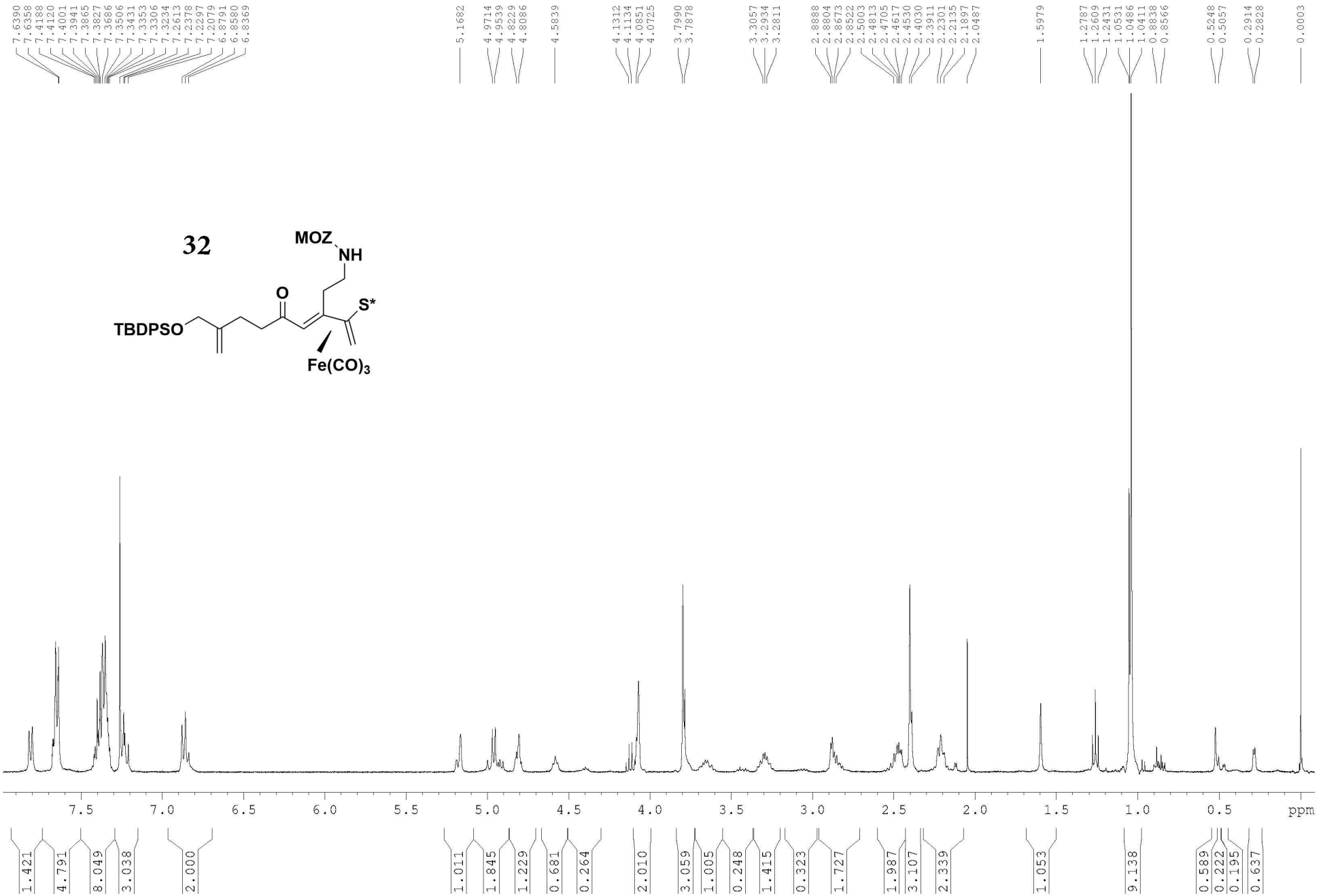
159.496
156.294
153.614
146.573
146.462
142.595
139.251
135.504
133.431
130.041
129.921
129.743
128.742
127.714
127.559
125.612
120.188
113.842
109.324
77.335
77.017
76.700
66.362
66.261
60.403
55.282
42.729
39.539
31.057
26.802
26.577
21.450
19.266
14.204
-0.000
31
MOZ
NH
O
S*
TBDPSO
H
S* = (R)-p-tolyl sulfoxide
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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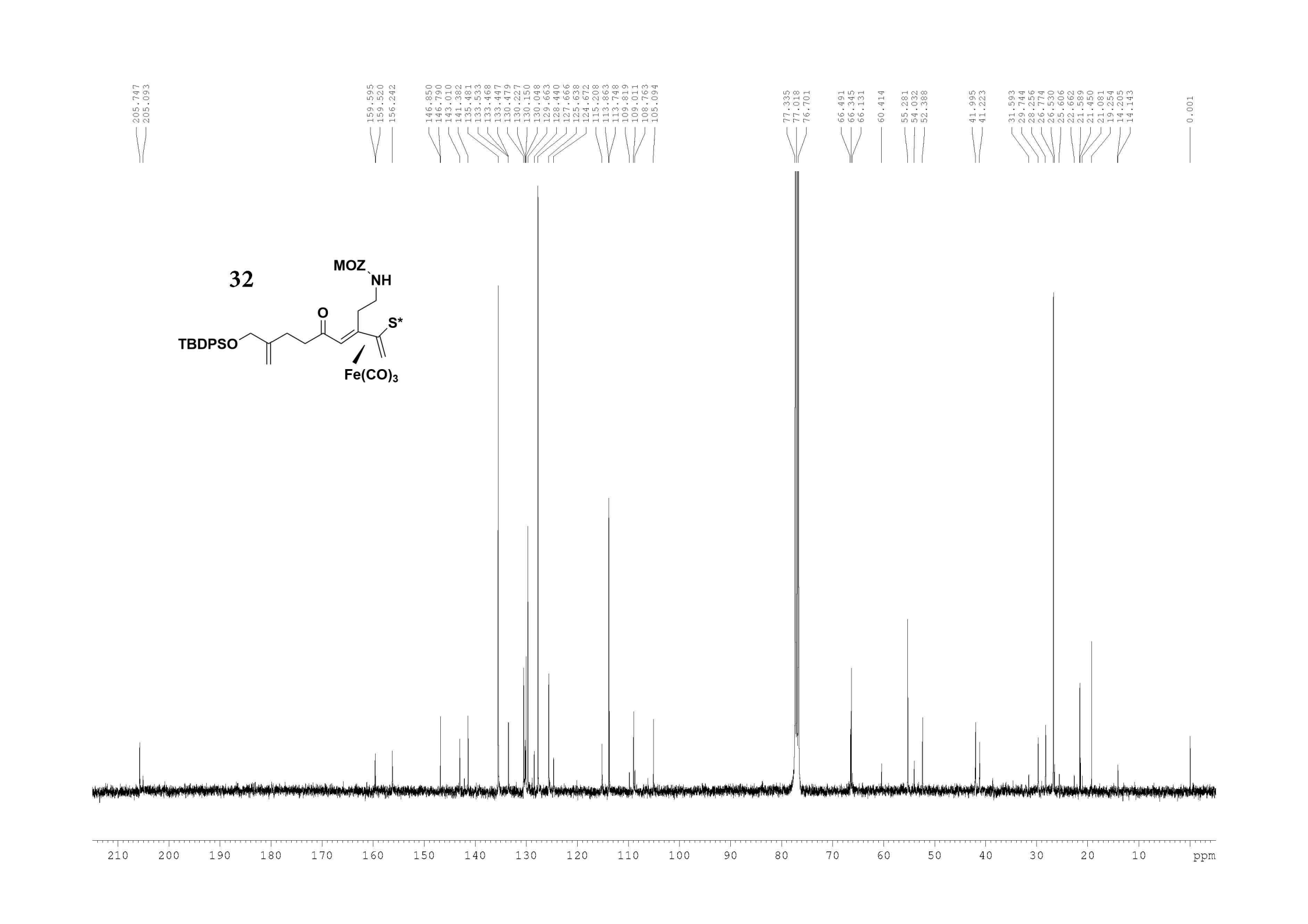
7.6358
7.4188
7.4120
7.4001
7.3941
7.3865
7.3827
7.3686
7.3506
7.3431
7.3353
7.3306
7.3234
7.2613
7.2378
7.2297
7.2079
6.8791
6.8580
6.8369
5.1682
4.9714
4.9539
4.8229
4.8086
4.5839
4.1312
4.1134
4.0851
4.0725
3.7990
3.7878
3.3057
3.2934
3.2811
2.8888
2.8804
2.8673
2.8522
2.5003
2.4813
2.4705
2.4617
2.4530
2.4030
2.3911
2.2301
2.2135
2.1897
2.0487
1.5979
1.2787
1.2609
1.2431
1.0531
1.0486
1.0411
0.8838
0.8566
0.5248
0.5057
0.2914
0.2828
0.0003
32
MOZ
NH
O
S*
TBDPSO
Fe(CO)3
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
1.421
4.791
8.049
3.038
2.000
1.011
1.845
1.229
0.681
0.264
2.010
3.059
1.005
0.248
1.415
0.323
1.727
1.987
3.107
2.339
1.053
9.138
0.589
0.222
0.195
0.637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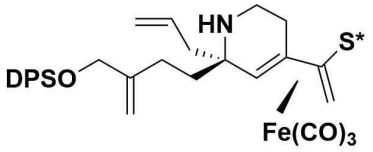
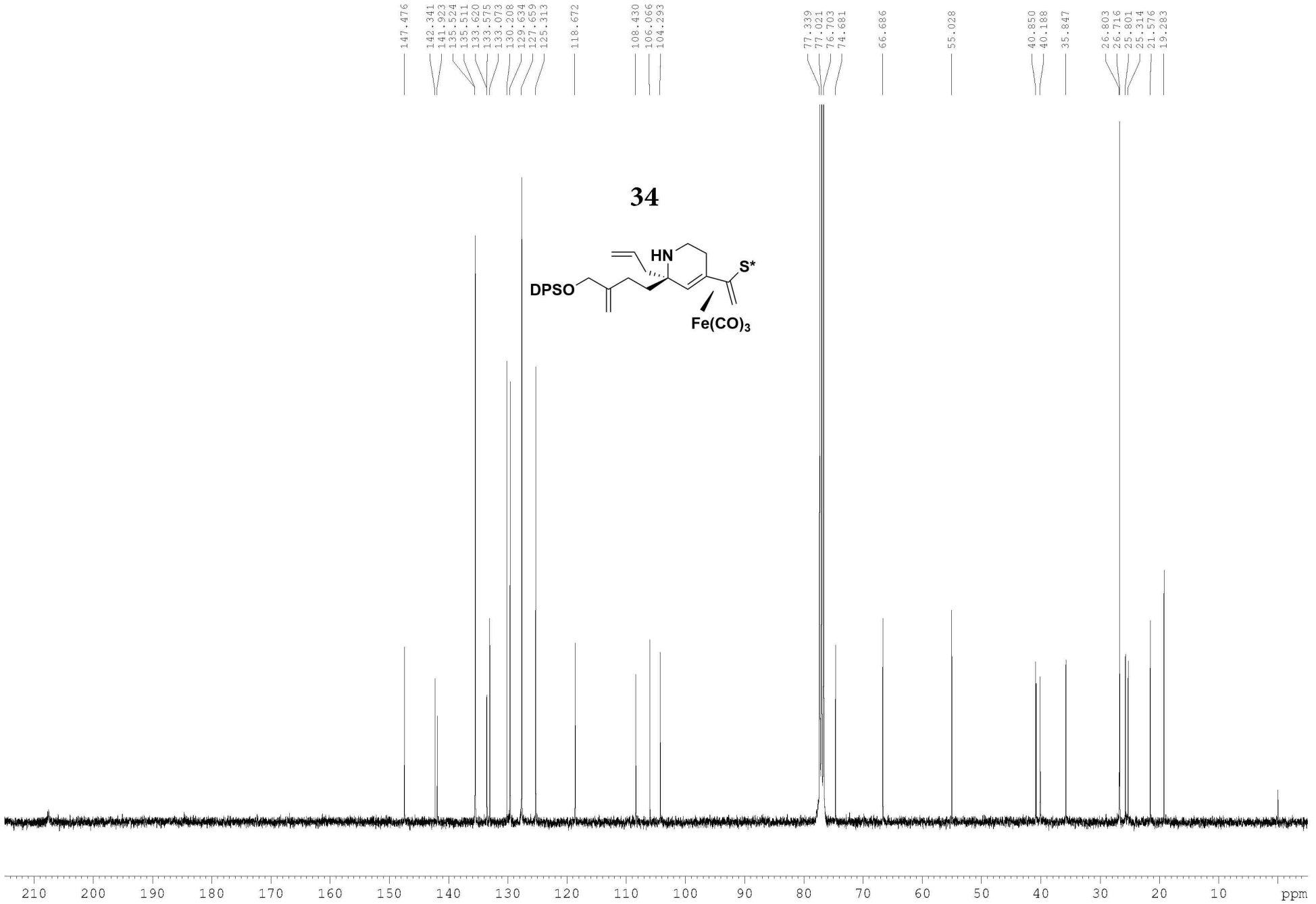
205.093
159.595
159.520
156.242
146.850
146.790
143.010
141.382
135.481
133.533
133.468
133.447
130.479
130.227
130.150
130.048
129.663
128.440
127.666
125.638
124.672
115.208
113.863
113.748
109.819
109.011
108.763
105.094
77.335
77.018
76.701
66.491
66.345
66.131
60.414
55.281
54.032
52.388
41.995
41.223
31.593
29.744
28.256
26.774
26.530
25.606
22.662
21.589
21.450
21.081
19.254
14.205
14.143
0.001
32
MOZ
NH
O
S*
TBDPSO
Fe(CO)3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

34


HN
S*
DPSO
Fe(CO)3

7.6727
7.6660
7.6605
7.4305
7.4252
7.4172
7.4127
7.4083
7.3962
7.3807
7.3642
7.3604
7.3507
7.3307
7.2584
5.6244
5.6067
5.2193
5.0553
5.0297
5.0055
4.9594
4.9447
4.1397
4.1302
3.1872
3.0503
3.0346
3.0280
3.0115
2.9956
2.9892
2.5292
2.5208
2.4288
2.3508
2.3325
2.1881
2.1699
2.0740
2.0624
2.0462
2.0360
1.5717
1.5526
1.5478
1.5294
1.2859
1.0657
0.0000
-0.2187
-0.2269
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
6.008
8.035
0.975
1.000
1.025
1.978
2.045
0.962
1.927
0.995
0.986
2.969
1.060
1.068
2.099
3.039
1.206
9.356
0.928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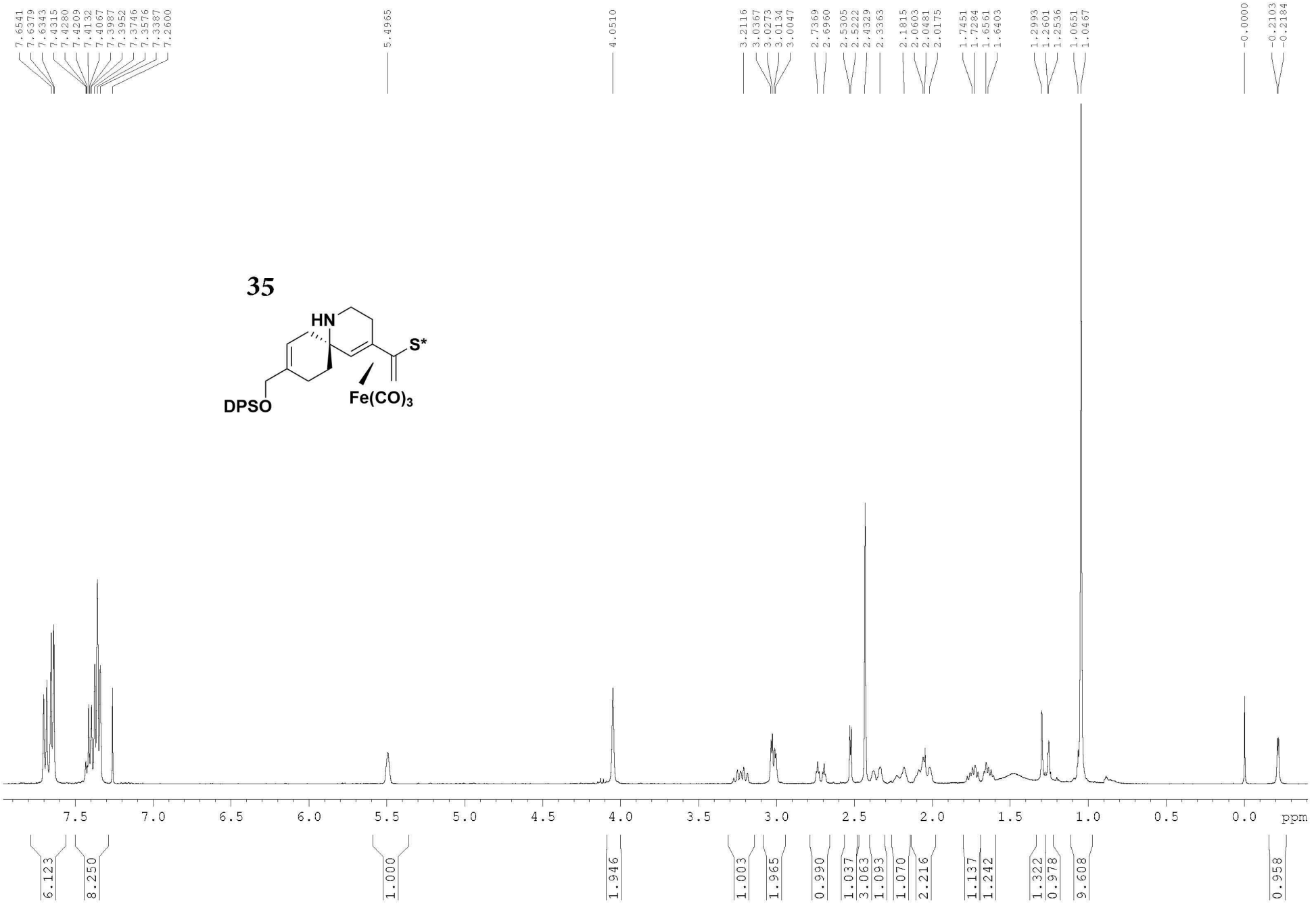
142.341
141.923
135.524
135.511
133.620
133.575
133.073
130.208
129.634
127.659
125.313
118.672
108.430
106.066
104.293
77.339
77.021
76.703
74.681
66.686
55.028
40.850
40.188
35.847
26.803
26.716
25.801
25.314
21.576
19.283
34
HN
S*
DPSO
Fe(CO)3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.6379
7.6343
7.4315
7.4280
7.4209
7.4132
7.4067
7.3987
7.3952
7.3746
7.3576
7.3387
7.2600
5.4965
4.0510
3.2116
3.0367
3.0273
3.0134
3.0047
2.7369
2.6960
2.5305
2.5222
2.4329
2.3363
2.1815
2.0603
2.0481
2.0175
1.7451
1.7284
1.6561
1.6403
1.2993
1.2601
1.2536
1.0651
1.0467
-0.0000
-0.2103
-0.2184
35
HN
S*
DPSO
Fe(CO)3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
6.123
8.250
1.000
1.946
1.003
1.965
0.990
1.037
3.063
1.093
1.070
2.216
1.137
1.242
1.322
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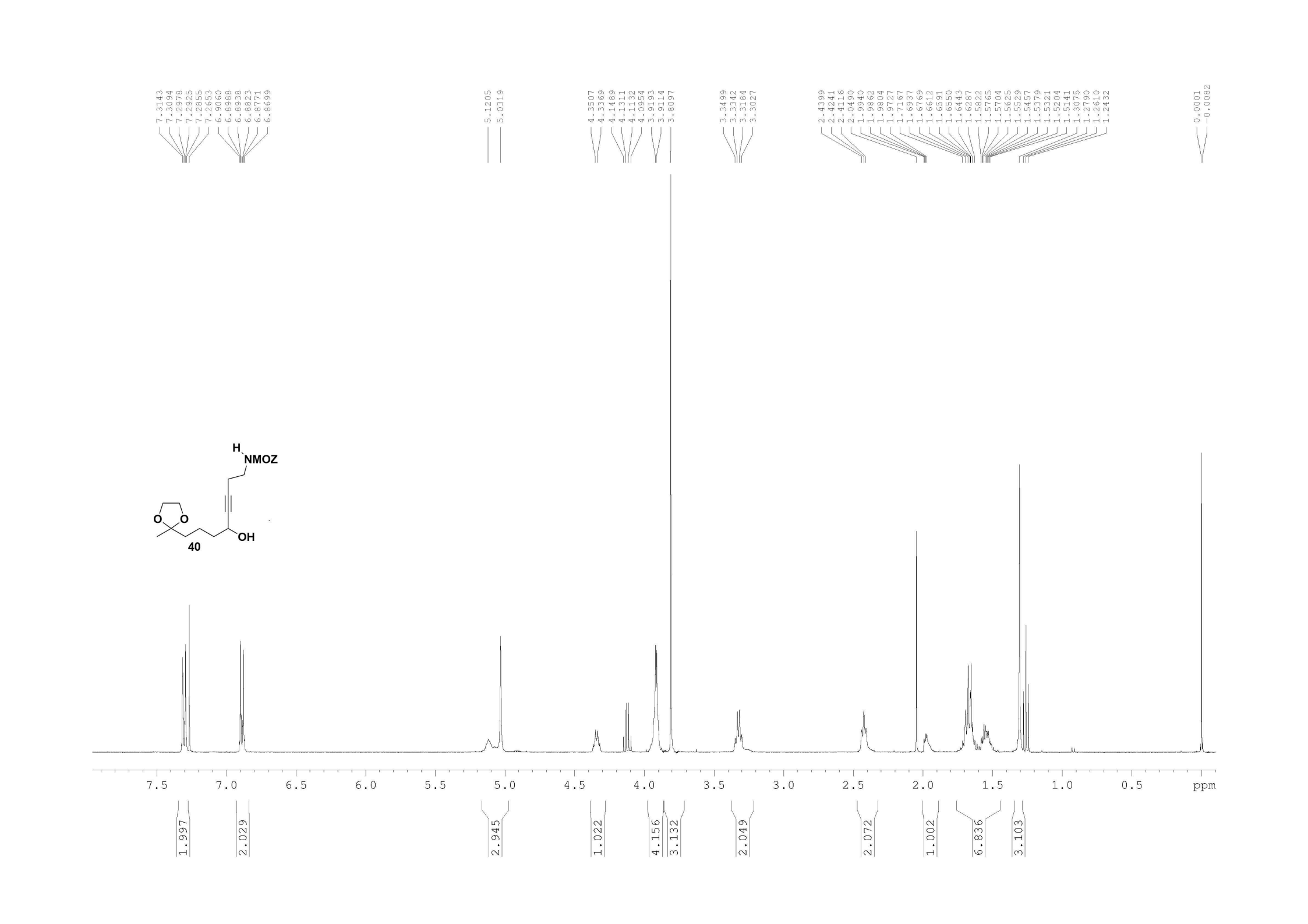
0.958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7.2978
7.2925
7.2855
7.2653
6.9060
6.8988
6.8938
6.8823
6.8771
6.8699
5.1205
5.0319
4.3507
4.3369
4.1489
4.1311
4.1132
4.0954
3.9193
3.9114
3.8097
3.3499
3.3342
3.3184
3.3027
2.4399
2.4041
2.4116
2.0490
1.9940
1.9862
1.9804
1.9727
1.7167
1.6937
1.6769
1.6612
1.6591
1.6550
1.6443
1.6287
1.5822
1.5765
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1.5529
1.5457
1.5379
1.5321
1.5204
1.5141
1.3075
1.2790
1.2610
1.2432
0.0001
-0.0082
H
NMOZ
O
O
OH
40
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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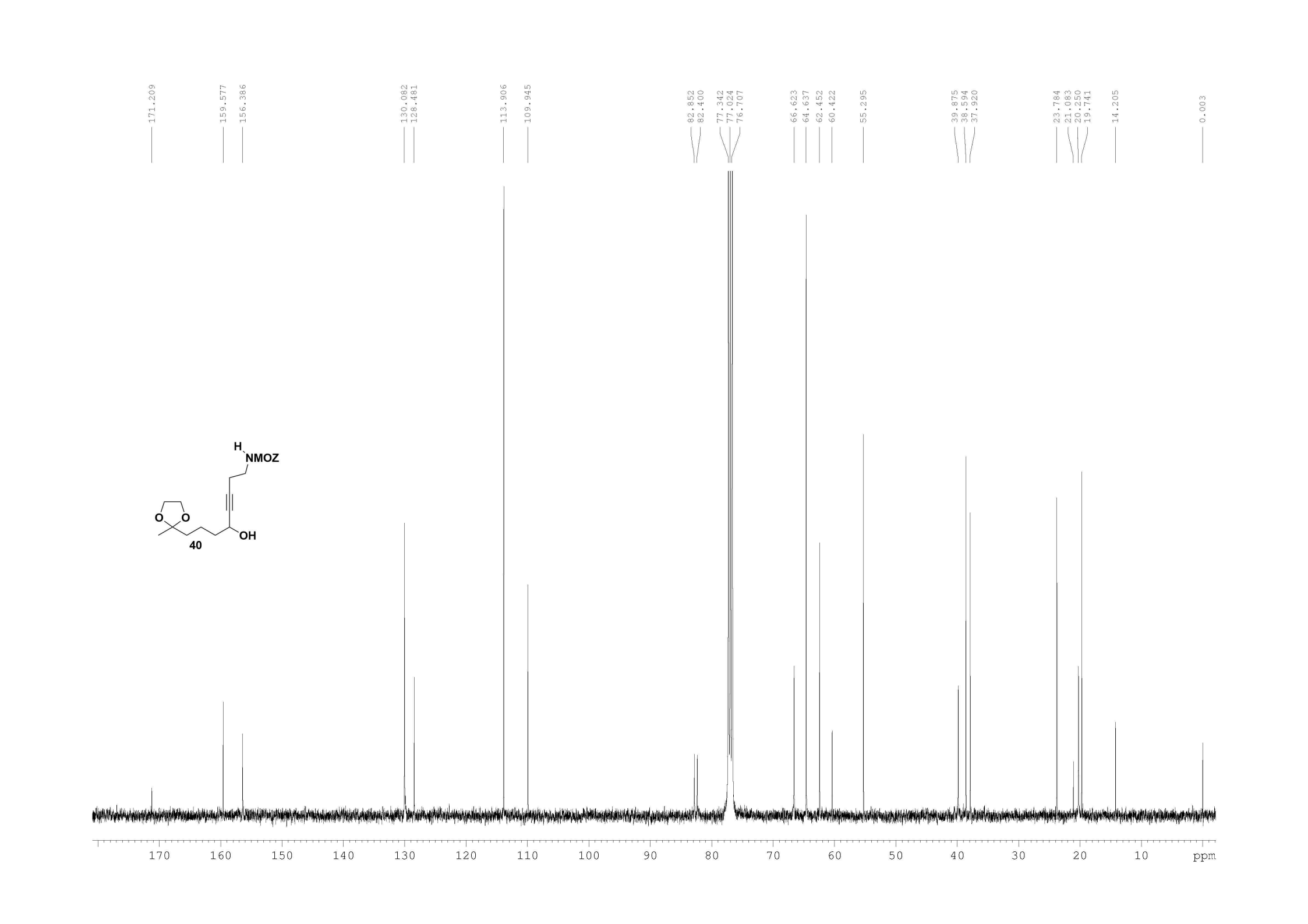
1.022
4.156
3.132
2.049
2.072
1.002
6.836
3.103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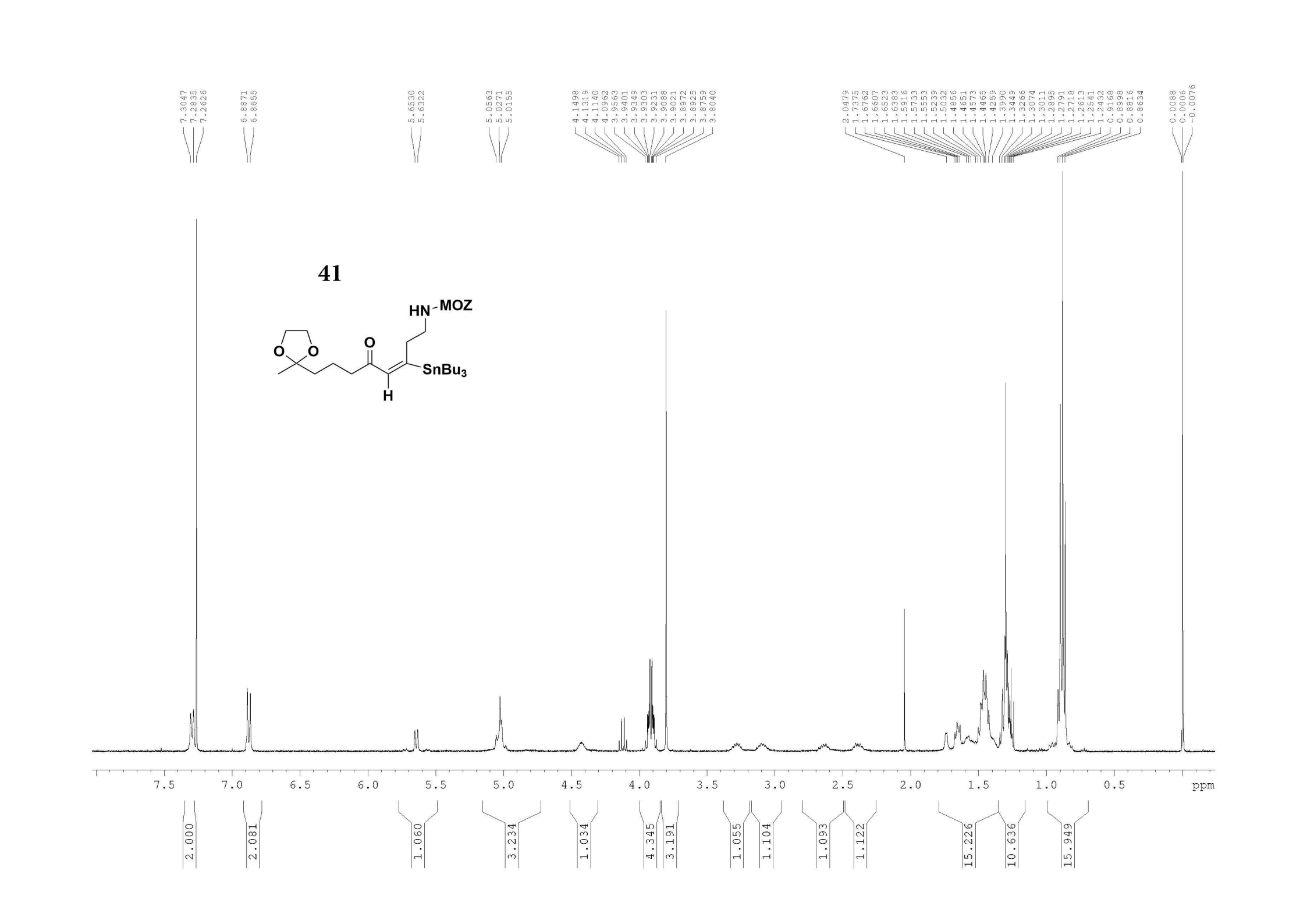
113.906
109.945
82.852
82.400
77.342
77.024
76.707
66.623
64.637
62.452
60.422
55.295
39.875
38.594
37.920
23.784
21.083
20.250
19.741
14.205
0.003
H
NMOZ
O
O
OH
40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


41
HN-MOZ
O
O
O
SnBu3
H
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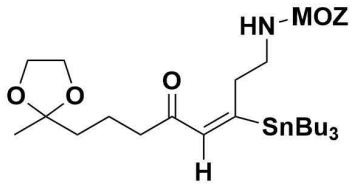
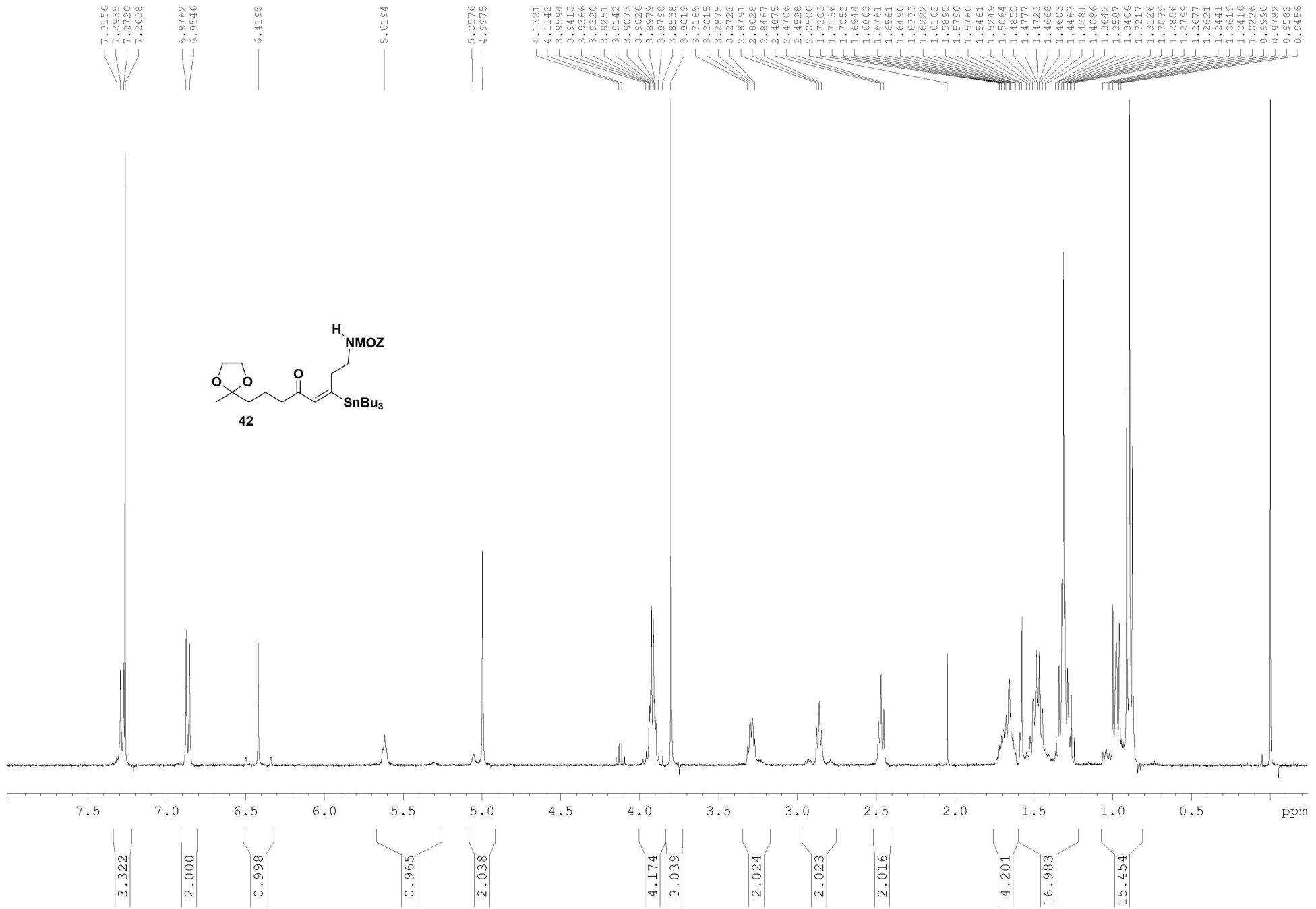
7.2626
6.8871
6.8655
5.6530
5.6322
5.0563
5.0271
5.0155
4.1498
4.1319
4.1140
4.0962
3.9563
3.9401
3.9349
3.9303
3.9231
3.9088
3.9021
3.8972
3.8925
3.8759
3.8040
2.0479
1.7375
1.6762
1.6607
1.6523
1.6383
1.5916
1.5733
1.5553
1.5239
1.5032
1.4856
1.4651
1.4573
1.4465
1.4259
1.3990
1.3449
1.3266
1.3074
1.3011
1.2895
1.2791
1.2718
1.2613
1.2541
1.2432
0.9168
0.8998
0.8816
0.8634
0.0088
0.0006
-0.0076
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
2.000
2.081
1.060
3.234
1.034
4.345
3.191
1.055
1.104
1.093
1.122
15.226
10.636
15.949

41


HN
MOZ
O
O
O
SnBu3
H

159.520
156.440
145.778
130.011
128.746
113.872
109.986
77.333
77.015
76.698
66.932
66.388
64.622
60.407
55.275
40.647
38.968
37.661
33.504
29.160
29.065
28.965
27.646
27.360
27.076
23.739
21.073
20.032
14.206
13.682
9.689
0.000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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5.0576
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4.1321
4.1142
3.9594
3.9413
3.9366
3.9320
3.9251
3.9142
3.9073
3.9026
3.8979
3.8798
3.8538
3.8019
3.3165
3.3015
3.2875
3.2722
2.8791
2.8628
2.8467
2.4875
2.4706
2.4528
2.0500
1.7203
1.7136
1.7052
1.6944
1.6863
1.6761
1.6561
1.6490
1.6333
1.6222
1.6162
1.5995
1.5790
1.5760
1.5461
1.5249
1.5064
1.4855
1.4777
1.4723
1.4668
1.4603
1.4463
1.4281
1.4086
1.3642
1.3587
1.3406
1.3217
1.3126
1.3039
1.2856
1.2799
1.2677
1.2621
1.2441
1.0619
1.0416
1.0226
0.9990
0.9782
0.9582
0.9456
H
NMOZ
O
O
O
SnBu3
42
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
3.322
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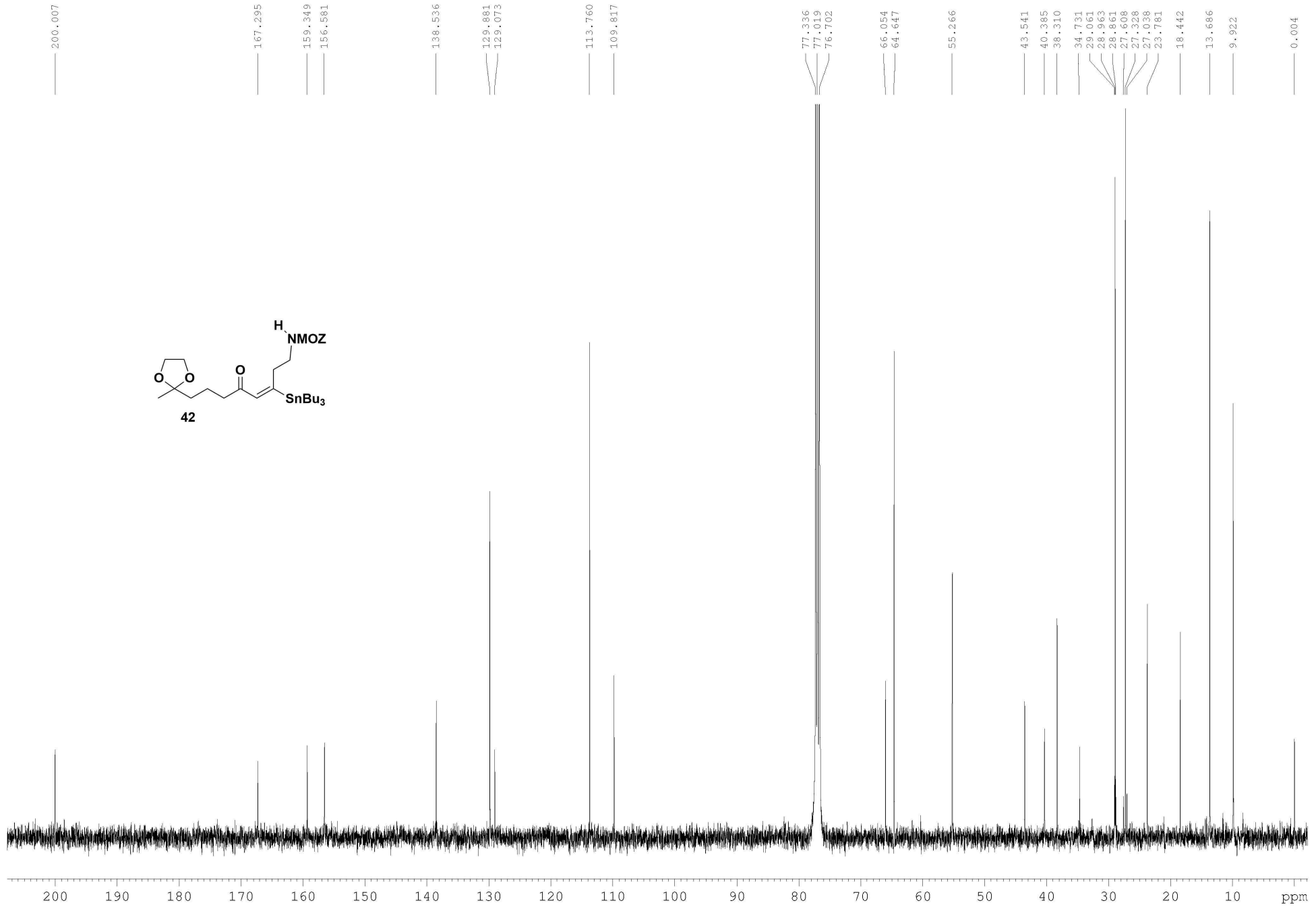
2.038
4.174
3.039
2.024
2.023
2.016
4.201
16.983
15.454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129.073
113.760
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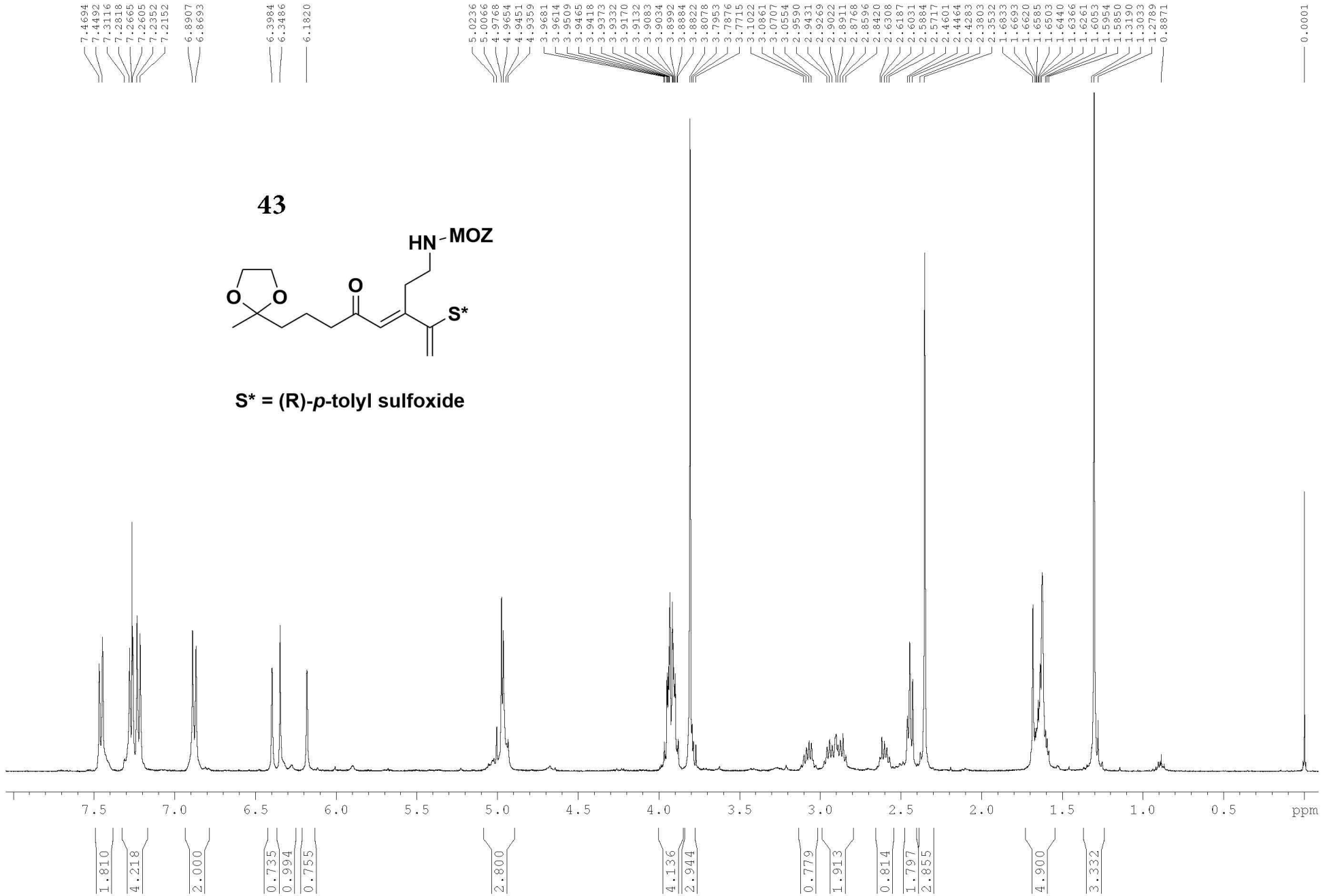
77.336
77.019
76.702
66.054
64.647
55.266
43.541
40.385
38.310
34.731
29.061
28.963
28.861
27.608
27.328
27.038
23.781
18.442
13.686
9.922
0.004
H
NMOZ
O
O
O
SnBu3
42
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.2605
7.2352
7.2152
6.8907
6.8693
6.3984
6.3486
6.1820
5.0236
5.0066
4.9768
4.9654
4.9451
4.9359
3.9681
3.9614
3.9509
3.9465
3.9418
3.9373
3.9332
3.9170
3.9132
3.9083
3.9034
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3.8884
3.8822
3.8078
3.7953
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3.0707
3.0554
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2.9431
2.9269
2.9022
2.8911
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2.8596
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2.6031
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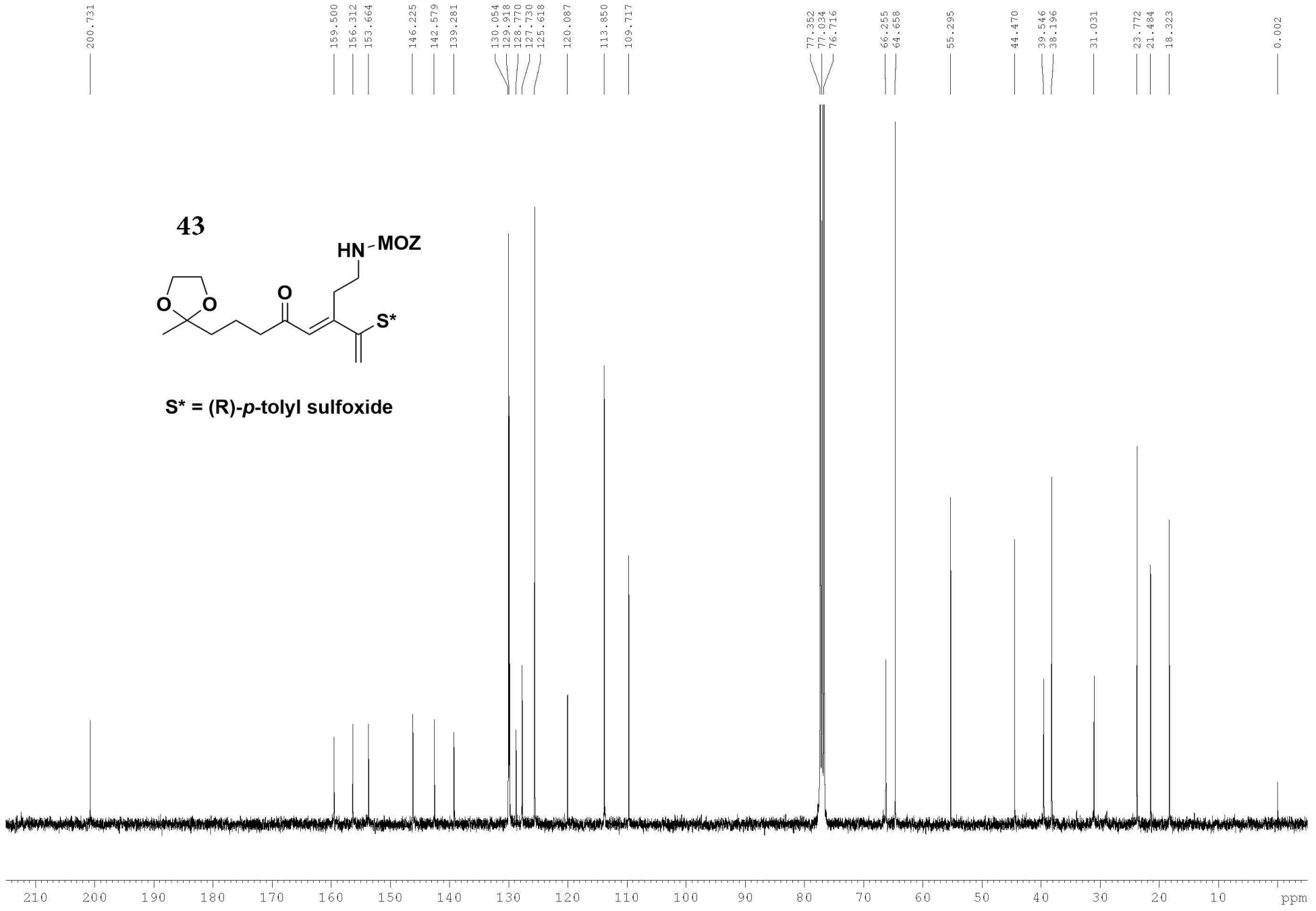
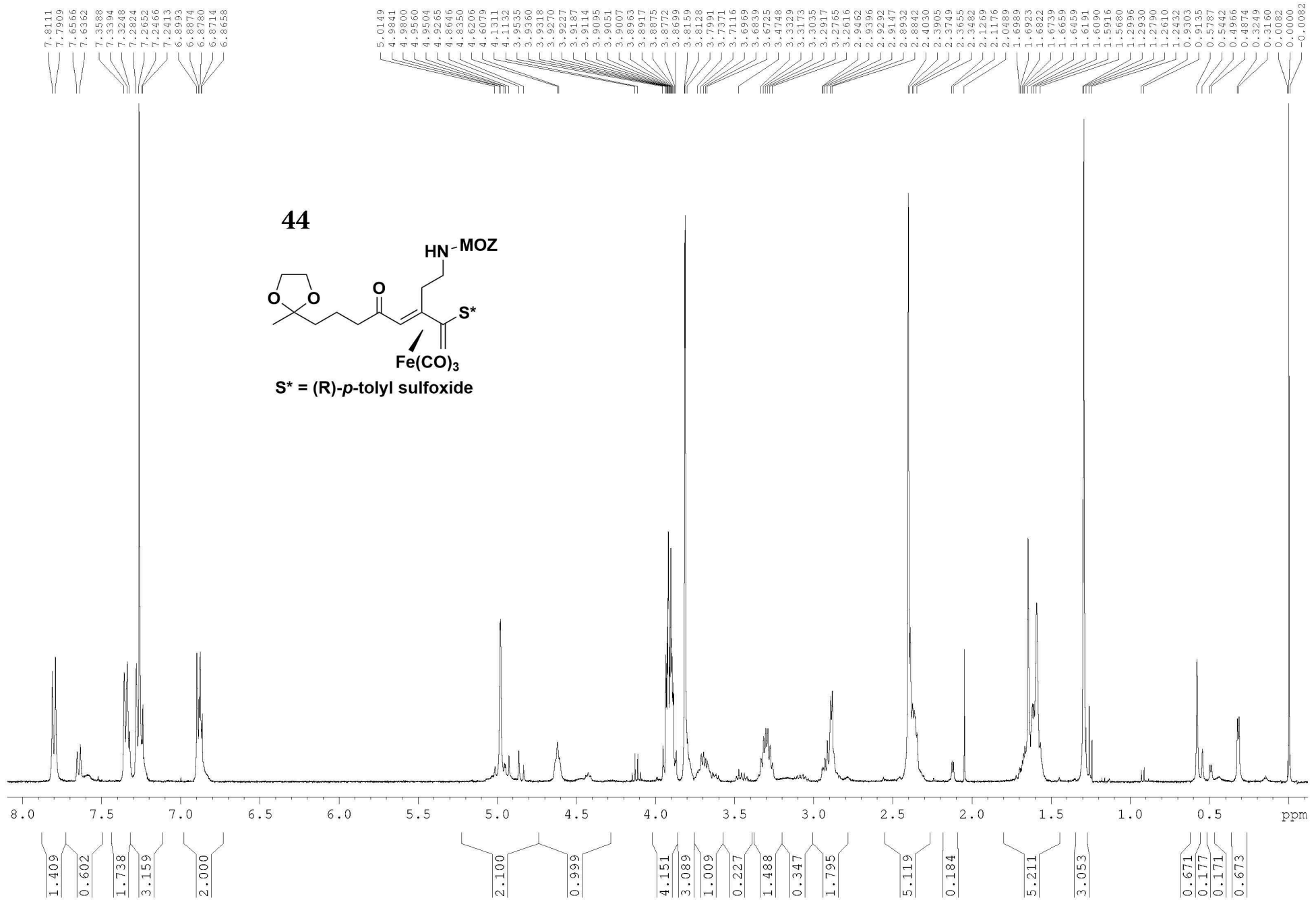
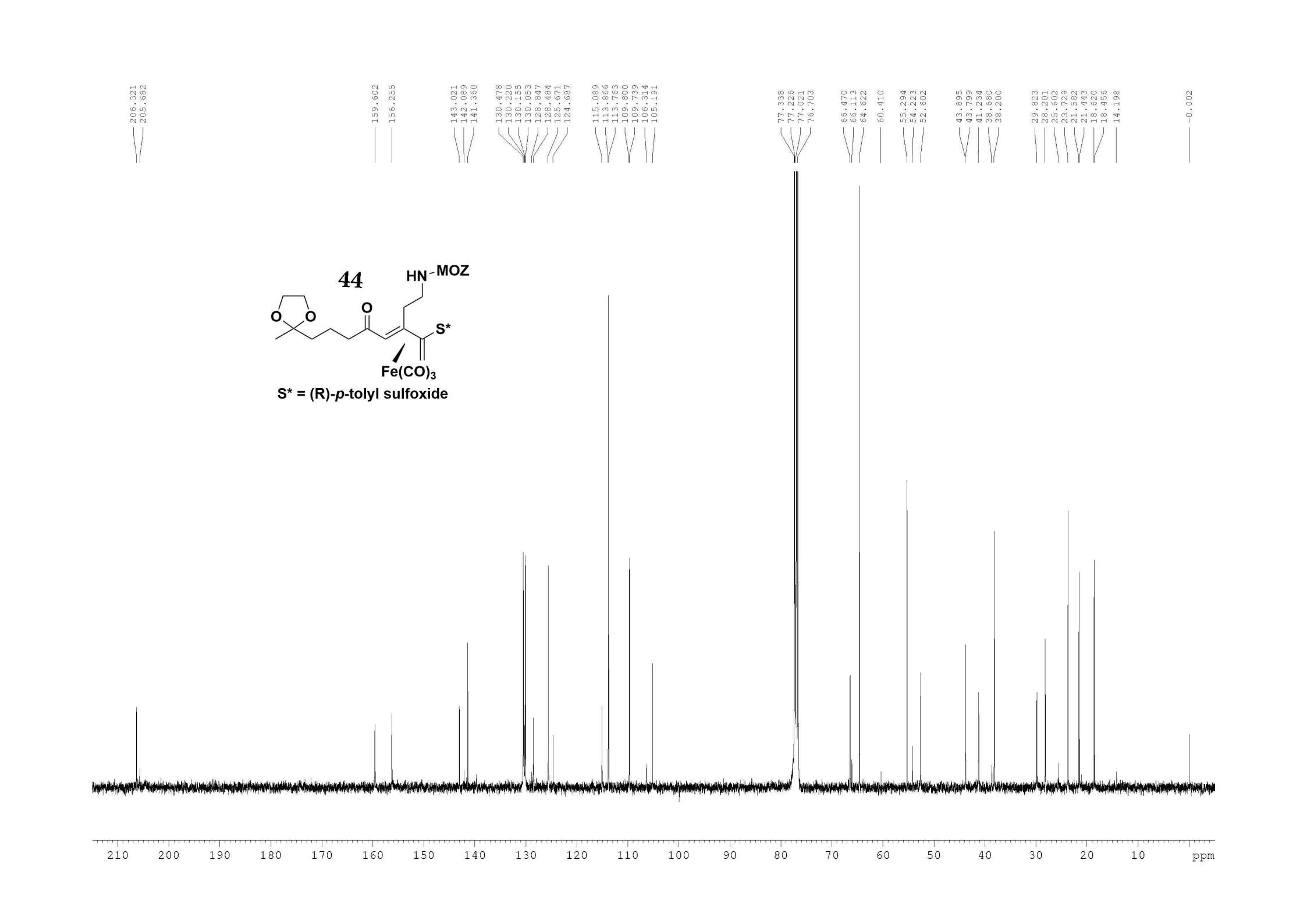
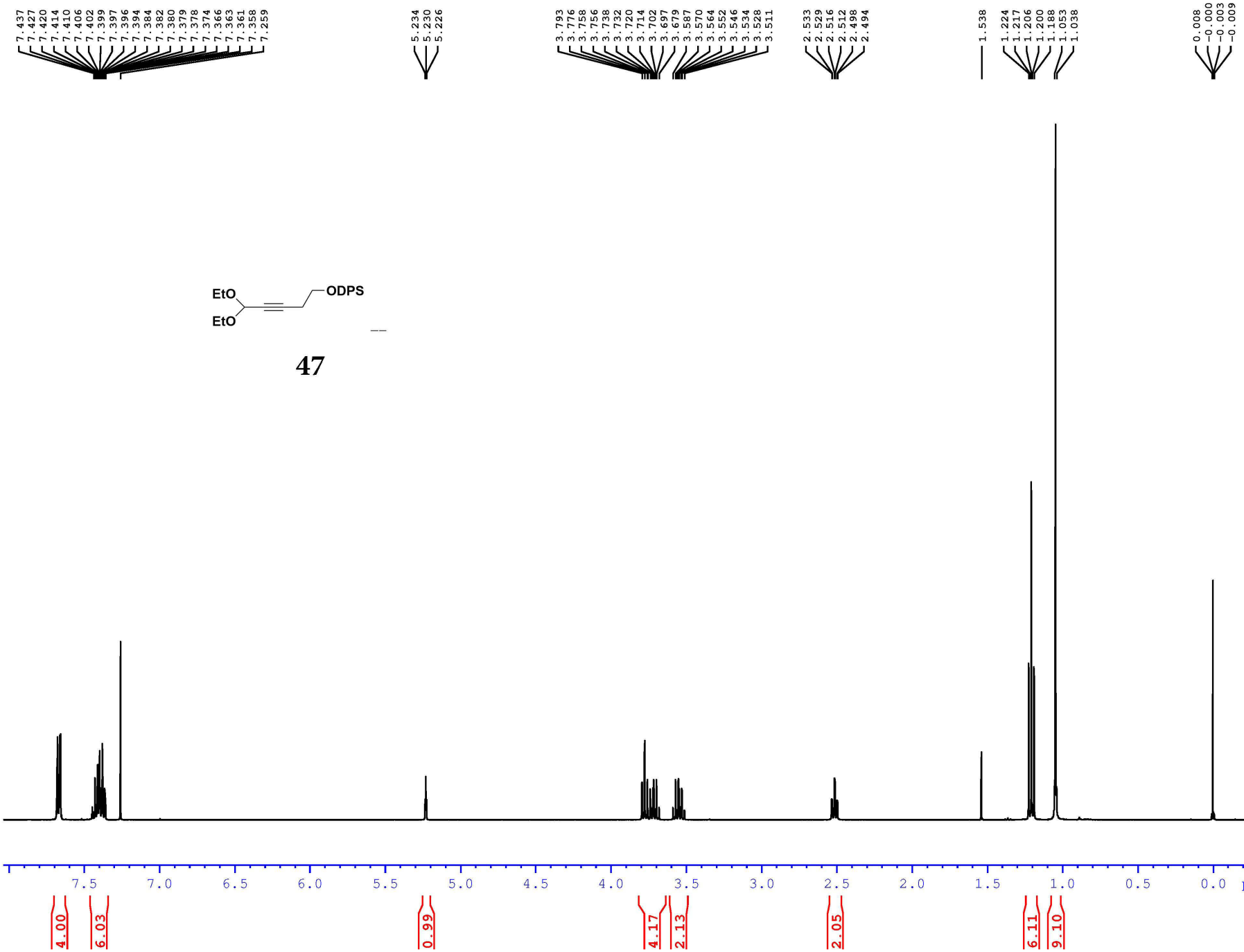
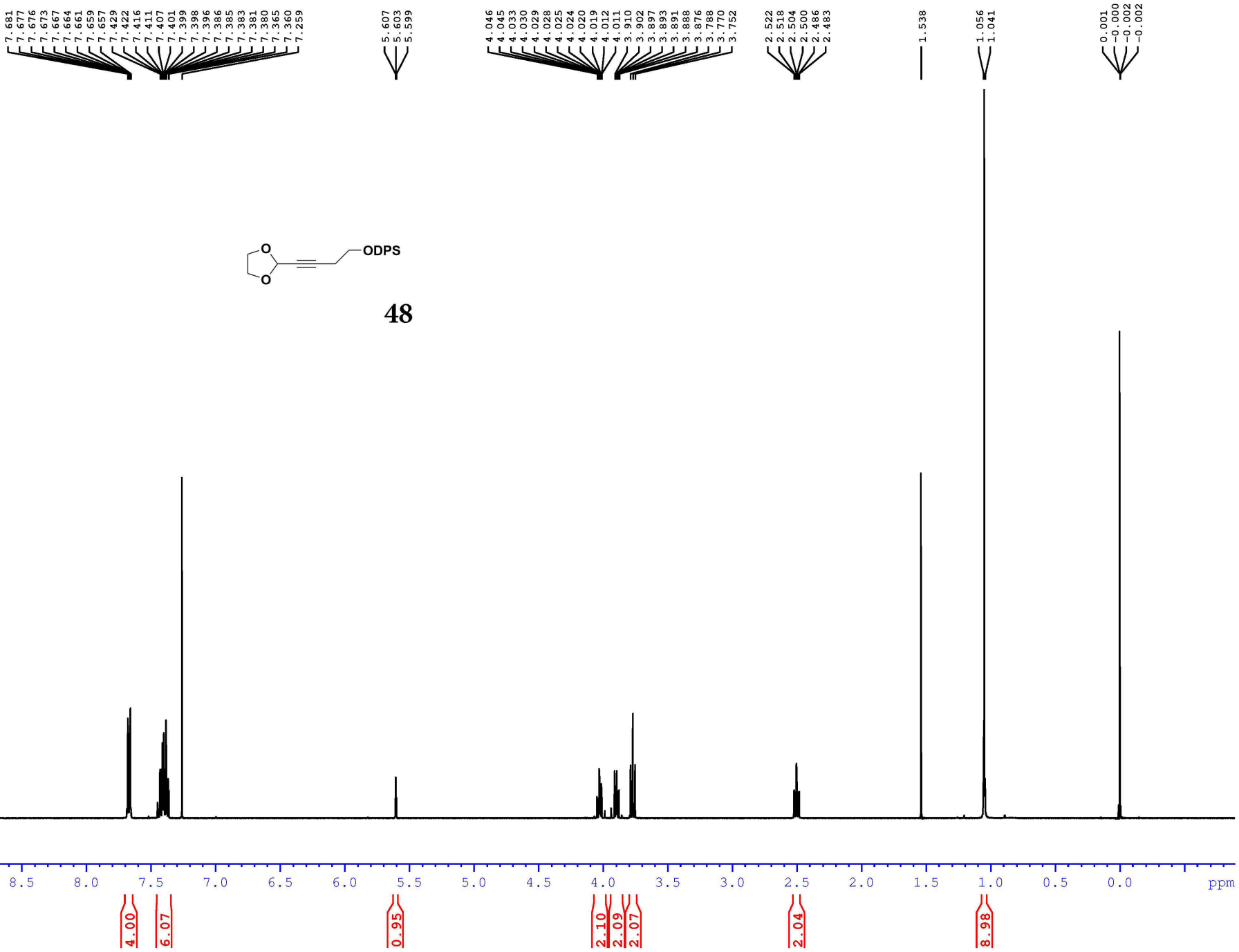
2.5717
2.4601
2.4464
2.4283
2.3803
2.3532
1.6833
1.6693
1.6620
1.6585
1.6503
1.6440
1.6366
1.6261
1.6053
1.5954
1.5850
1.3190
1.3033
1.2789
0.8871
0.0001
43
HN
MOZ
O
O
O
S*
S* = (R)-p-tolyl sulfoxide
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.810
4.218
2.000
0.735
0.994
0.755
2.800
4.136
2.944
0.779
1.913
0.814
1.797
2.855
4.900
3.332

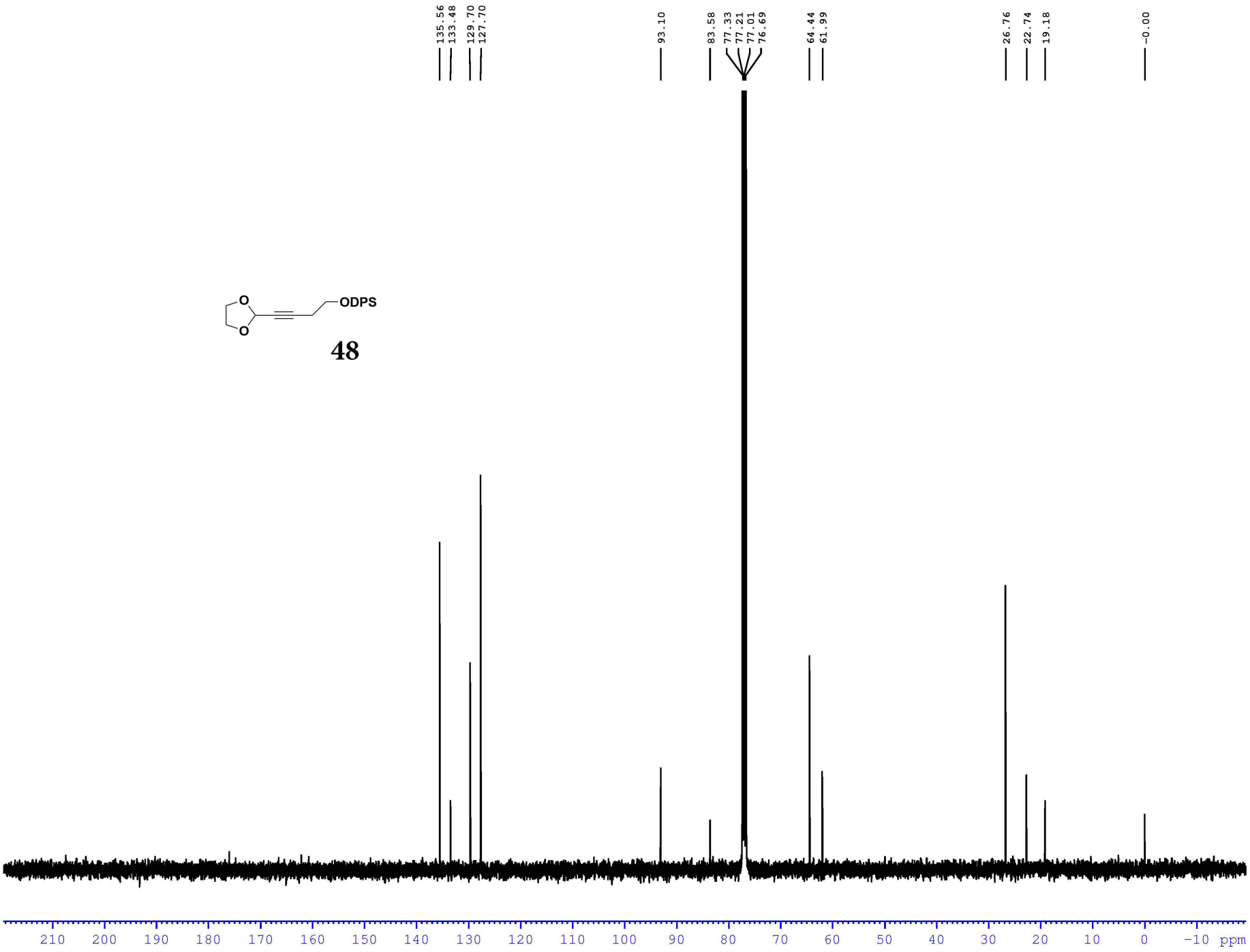

200.731
159.500
156.312
153.664
146.225
142.579
139.281
130.054
129.918
128.770
127.730
125.618
120.087
113.850
109.717
77.352
77.034
76.716
66.255
64.658
55.295
44.470
39.546
38.196
31.031
23.772
21.484
18.323
0.002
43
HN-MOZ
O
O
O
S*
S* = (R)-p-tolyl sulfoxide
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

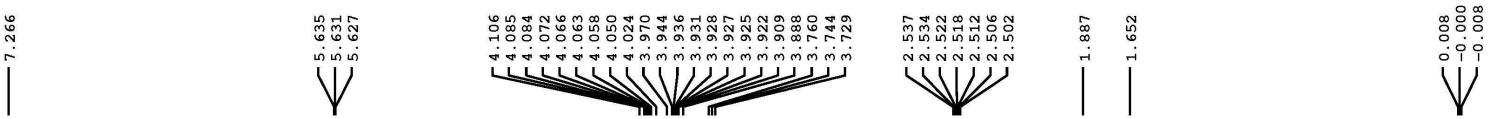

7.8111
7.7909
7.6566
7.6362
7.3588
7.3394
7.3248
7.2824
7.2652
7.2466
7.2413
6.8993
6.8874
6.8780
6.8714
6.8658
5.0149
4.9841
4.9800
4.9560
4.9504
4.9265
4.8646
4.8350
4.6206
4.6079
4.1311
4.1132
3.9535
3.9360
3.9318
3.9270
3.9227
3.9187
3.9114
3.9095
3.9051
3.9007
3.8963
3.8917
3.8875
3.8772
3.8699
3.8159
3.8128
3.7991
3.7371
3.7116
3.6969
3.6839
3.6725
3.4748
3.3329
3.3173
3.3035
3.2917
3.2765
3.2616
2.9462
2.9396
2.9292
2.9147
2.8932
2.8842
2.4030
2.3905
2.3749
2.3655
2.3482
2.1269
2.1176
2.0489
1.6989
1.6923
1.6822
1.6739
1.6659
1.6459
1.6191
1.6090
1.5916
1.5680
1.2996
1.2930
1.2790
1.2610
1.2432
0.9303
0.9135
0.5787
0.5442
0.4966
0.4874
0.3249
0.3160
0.0082
0.0000
-0.0082
44
HN-MOZ
O
O
O
S*
Fe(CO)3
S* = (R)-p-tolyl sulfoxide
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
1.409
0.602
1.738
3.159
2.000
2.100
0.999
4.151
3.089
1.009
0.227
1.488
0.347
1.795
5.119
0.184
5.211
3.053
0.671
0.177
0.171
0.673

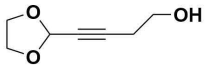

206.321
205.682
159.602
156.255
143.021
142.089
141.360
130.478
130.220
130.155
130.053
128.847
128.484
125.671
124.687
115.089
113.866
113.763
109.800
109.739
106.314
105.191
77.338
77.226
77.021
76.703
66.470
66.113
64.622
60.410
55.294
54.223
52.602
43.895
43.799
41.234
38.680
38.200
29.823
28.201
25.602
23.729
21.582
21.443
18.620
18.456
14.198
-0.002
44
HN-MOZ
O
O
O
S*
Fe(CO)3
S* = (R)-p-tolyl sulfoxide
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.437
7.427
7.420
7.414
7.410
7.406
7.402
7.399
7.397
7.396
7.394
7.384
7.382
7.380
7.379
7.378
7.374
7.366
7.363
7.361
7.358
7.259
5.234
5.230
5.226
3.793
3.776
3.758
3.756
3.738
3.732
3.720
3.714
3.702
3.697
3.679
3.587
3.570
3.564
3.552
3.546
3.534
3.528
3.511
2.533
2.529
2.516
2.512
2.498
2.494
1.538
1.224
1.217
1.206
1.200
1.188
1.053
1.038
0.008
-0.000
-0.003
-0.009
EtO
EtO
ODPS
47
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.00
6.03
0.99
4.17
2.13
2.05
6.11
9.10

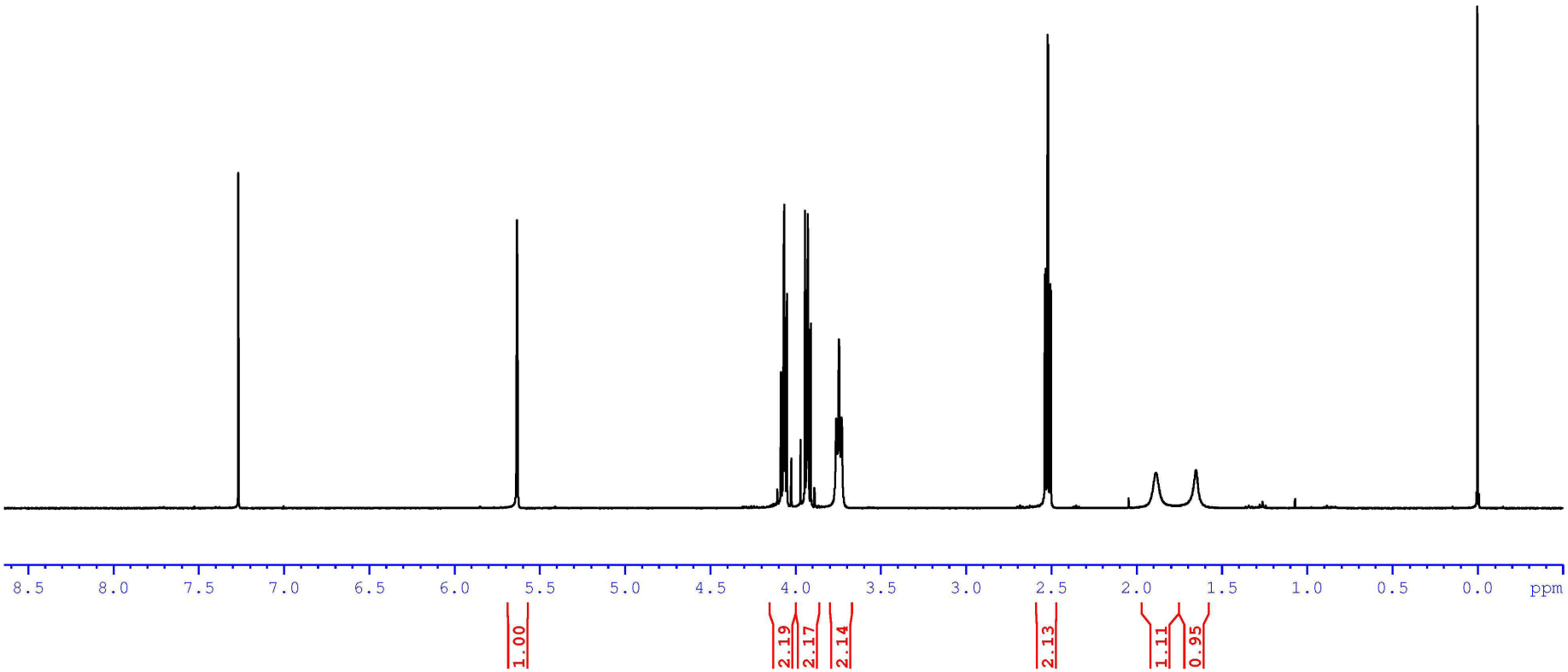

7.681
7.677
7.676
7.673
7.667
7.664
7.661
7.659
7.657
7.429
7.422
7.416
7.411
7.407
7.401
7.399
7.398
7.396
7.386
7.385
7.383
7.381
7.380
7.365
7.360
7.259
5.607
5.603
5.599
4.046
4.045
4.033
4.030
4.029
4.028
4.025
4.024
4.020
4.019
4.012
4.011
3.910
3.902
3.897
3.893
3.891
3.888
3.876
3.788
3.770
3.752
2.522
2.518
2.504
2.500
2.486
2.483
1.538
1.056
1.041
0.001
-0.000
-0.002
-0.002
ODPS
48
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.00
6.07
0.95
2.10
2.09
2.07
2.04
8.98

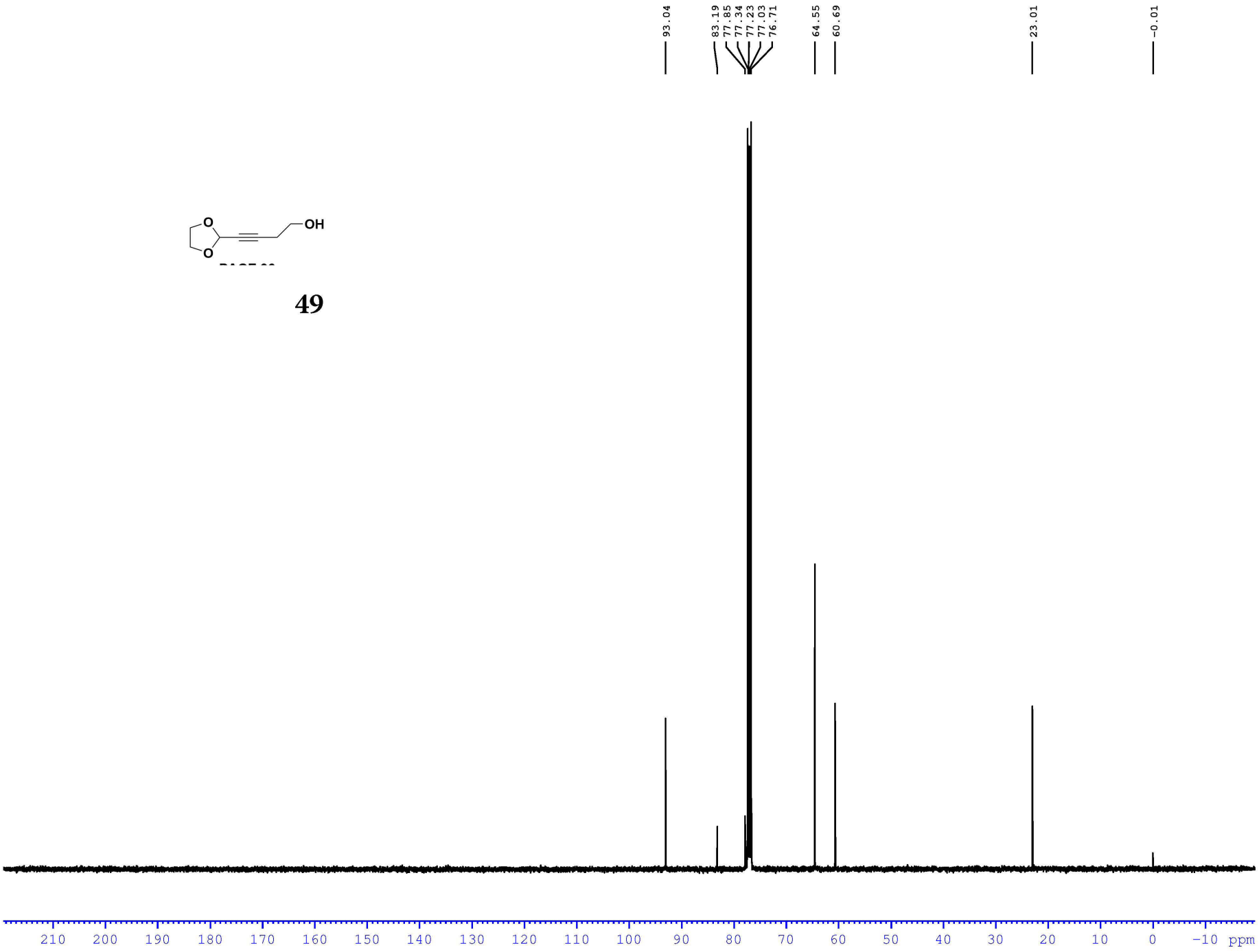

135.56
133.48
129.70
127.70
93.10
83.58
77.33
77.21
77.01
76.69
64.44
61.99
26.76
22.74
19.18
-0.00
ODPS
48
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


7.266
5.635
5.631
5.627
4.106
4.085
4.084
4.072
4.066
4.063
4.058
4.050
4.024
3.970
3.944
3.936
3.931
3.928
3.927
3.925
3.922
3.909
3.888
3.760
3.744
3.729
2.537
2.534
2.522
2.518
2.512
2.506
2.502
1.887
1.652
0.008
-0.000
-0.008

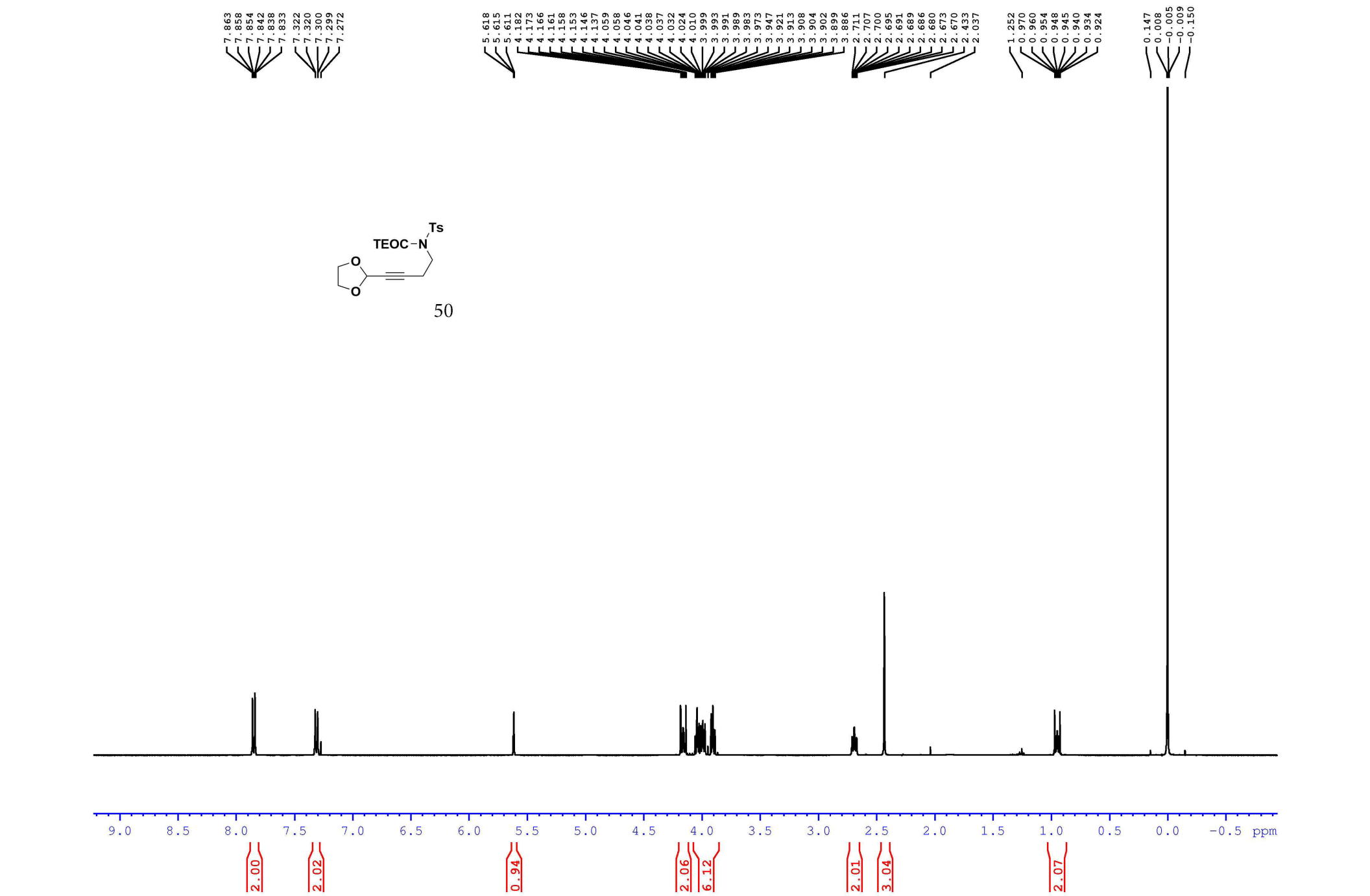

O
O
OH

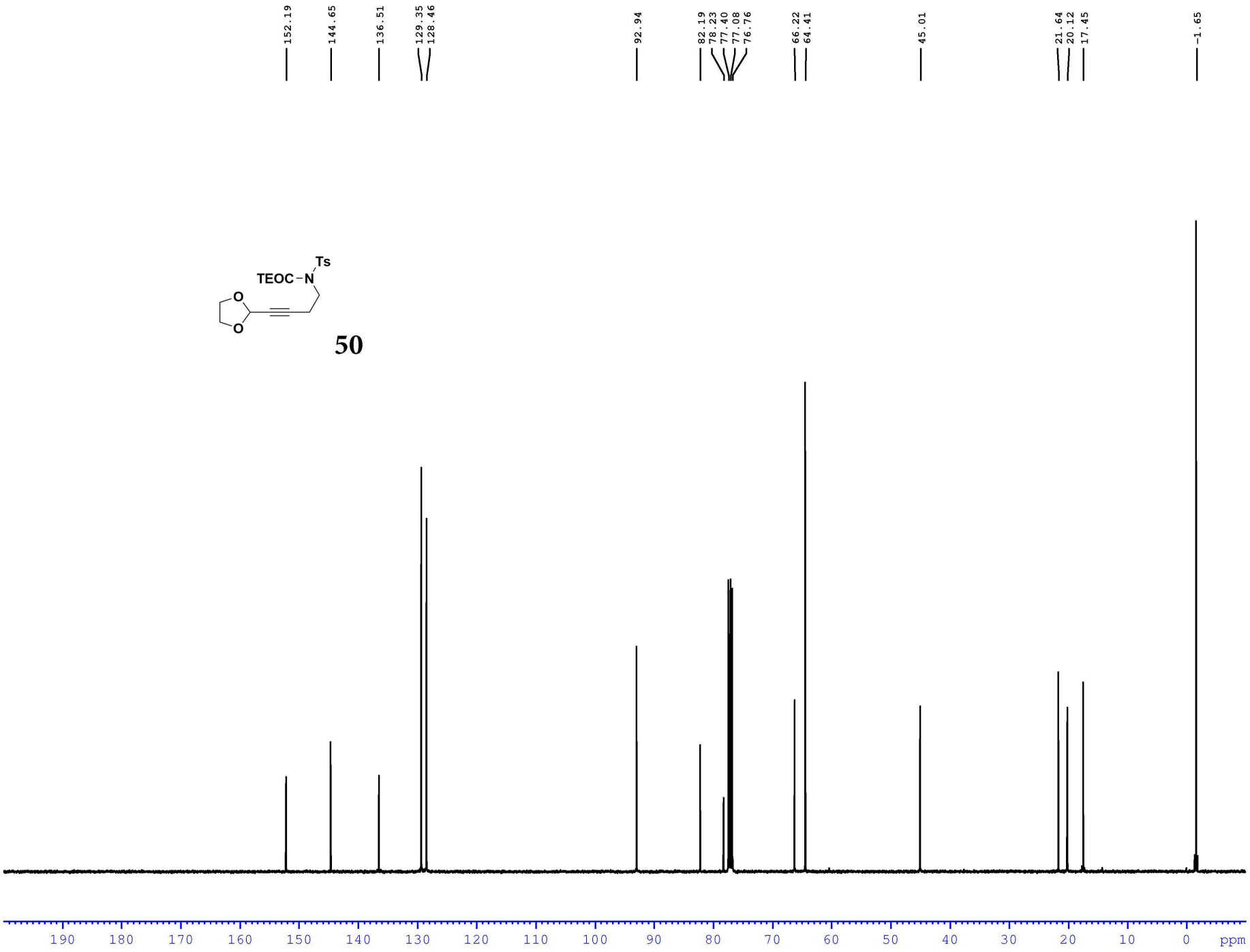
49

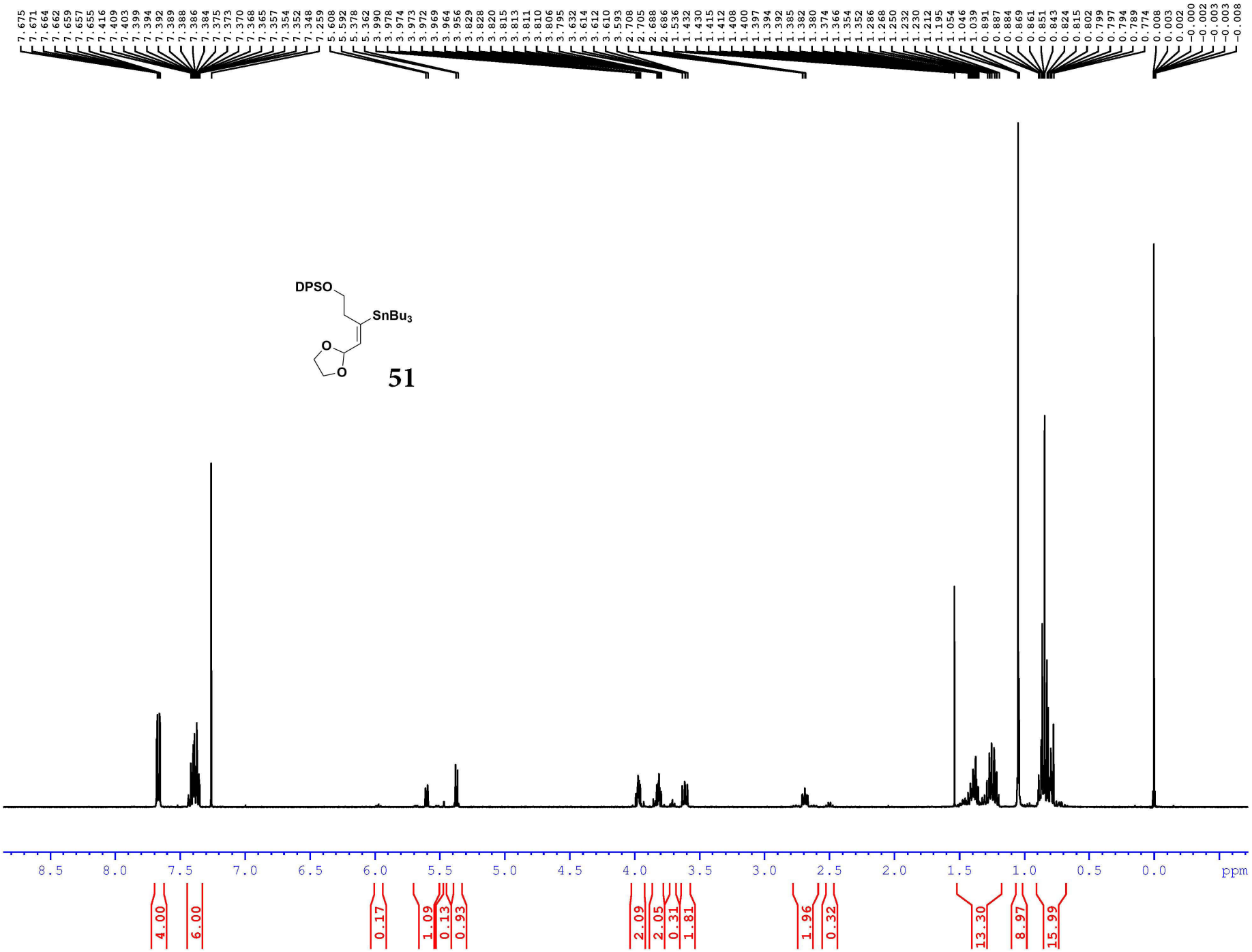

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.19
2.17
2.14
2.13
1.11
0.95


93.04
83.19
77.85
77.34
77.23
77.03
76.71
64.55
60.69
23.01
-0.01
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

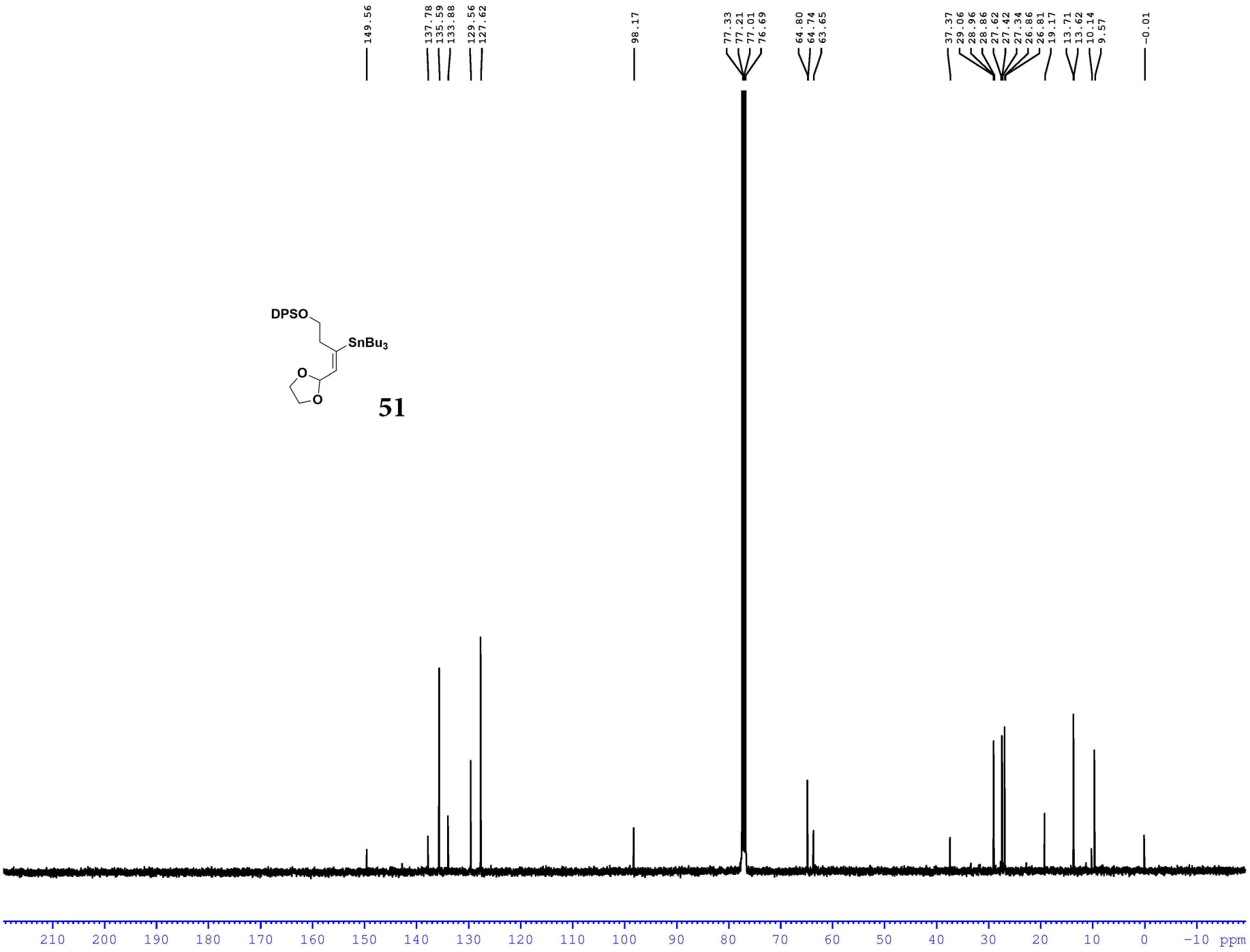
49

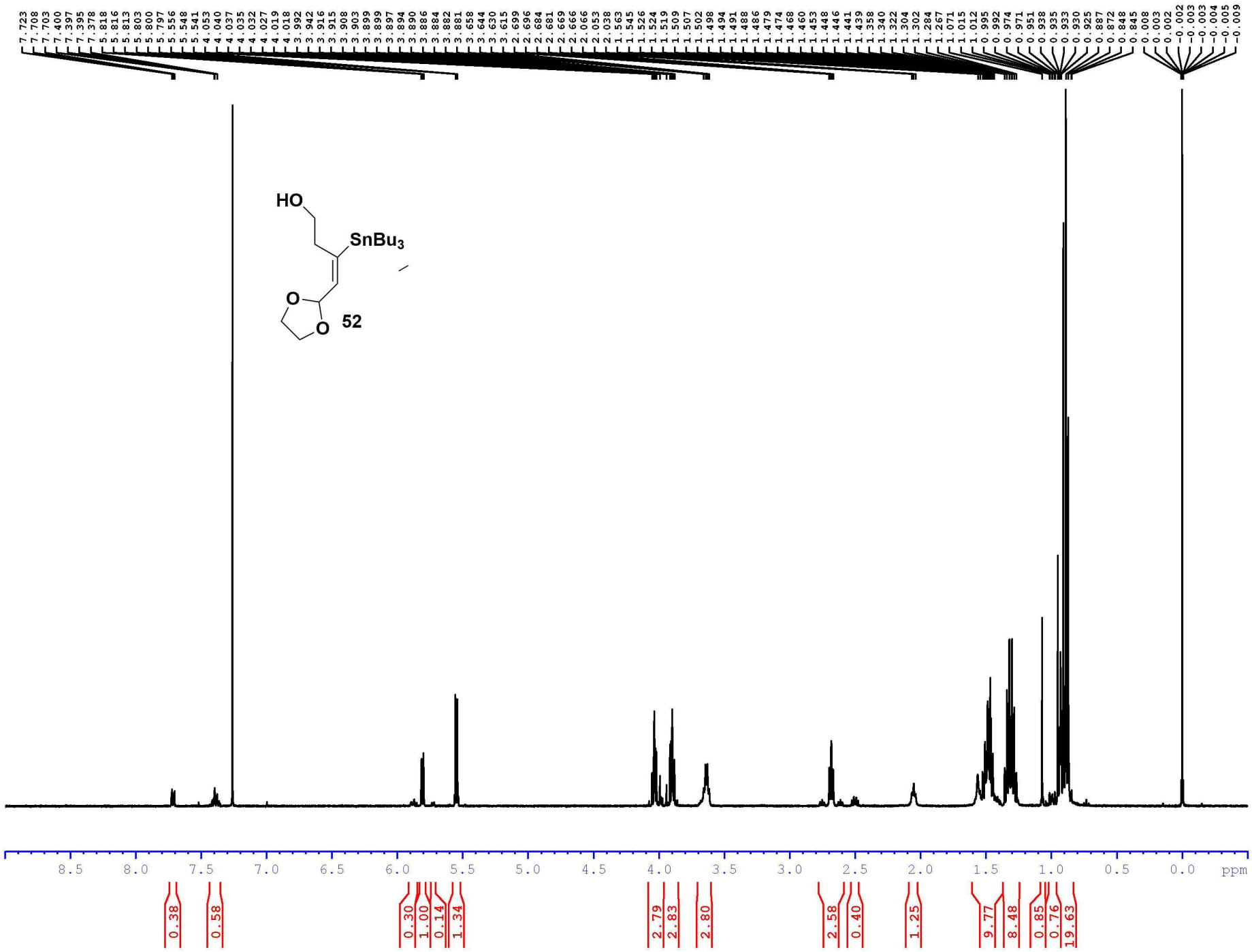

7.863
7.858
7.854
7.842
7.838
7.833
7.322
7.320
7.300
7.299
7.272
5.618
5.615
5.611
4.182
4.173
4.166
4.161
4.158
4.153
4.146
4.137
4.059
4.058
4.046
4.041
4.038
4.037
4.032
4.024
4.010
3.999
3.993
3.991
3.989
3.983
3.973
3.947
3.921
3.913
3.908
3.904
3.902
3.899
3.886
2.711
2.707
2.700
2.695
2.691
2.689
2.686
2.680
2.673
2.670
2.433
2.037
1.252
0.970
0.960
0.954
0.948
0.945
0.940
0.934
0.924
0.147
0.008
-0.005
-0.009
-0.150
Ts
TEOC−N
O
O
50
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
2.00
2.02
0.94
2.06
6.12
2.01
3.04
2.07

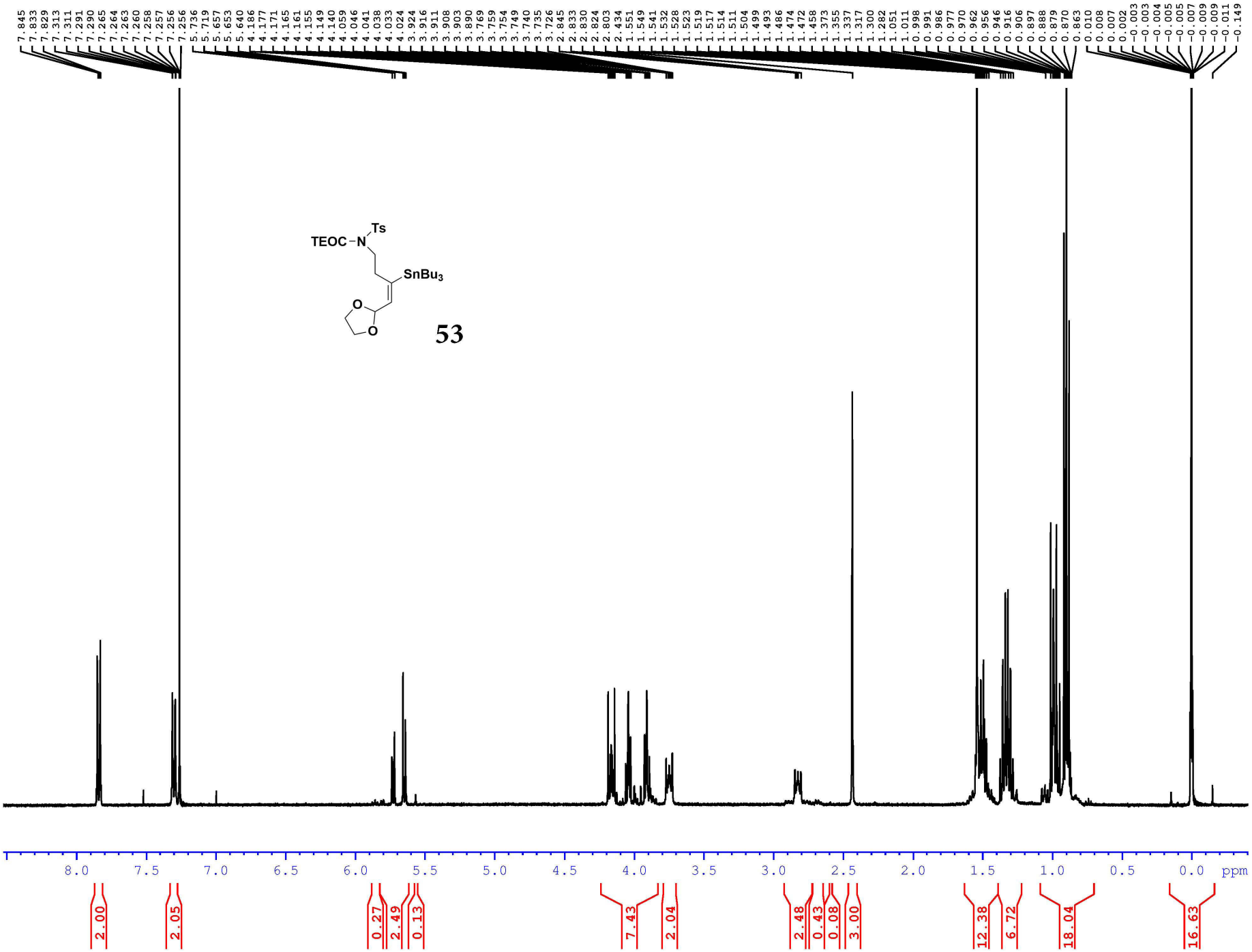

152.19
144.65
136.51
129.35
128.46
92.94
82.19
78.23
77.40
77.08
76.76
66.22
64.41
45.01
21.64
20.12
17.45
-1.65
Ts
TEOC
N
O
O
50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.675 7.671 7.664 7.662 7.659 7.657 7.655 7.416 7.409 7.403 7.399 7.394 7.392 7.389 7.388 7.386 7.384 7.375 7.373 7.370 7.368 7.365 7.357 7.354 7.352 7.348 7.259
5.608 5.592 5.378 5.362 3.990 3.978 3.974 3.973 3.972 3.969 3.964 3.956 3.829 3.828 3.820 3.815 3.813 3.811 3.810 3.806 3.795 3.632 3.614 3.612 3.610 3.593 2.708 2.705 2.688 2.686 1.536 1.432 1.430 1.415 1.412 1.408 1.400 1.397 1.394 1.392 1.385 1.382 1.380 1.374 1.366 1.354 1.352 1.286 1.268 1.250 1.232 1.230 1.212 1.195 1.054 1.046 1.039 0.891 0.887 0.884 0.869 0.861 0.851 0.843 0.824 0.815 0.802 0.799 0.797 0.794 0.789 0.774
0.008 0.003 0.002 -0.000 -0.002 -0.003 -0.003 -0.008
DPSO
SnBu3
O
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.00 6.00 0.17 1.09 0.13 0.93 2.09 2.05 0.31 1.81 1.96 0.32 13.30 8.97 15.99

51


149.56
137.78
135.59
133.88
129.56
127.62
98.17
77.33
77.21
77.01
76.69
64.80
64.74
63.65
37.37
29.06
28.96
28.86
27.62
27.42
27.34
26.86
26.81
19.17
13.71
13.62
10.14
9.57
-0.01
DPSO
SnBu3
O
O
51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


HO
SnBu3
O
O
52
7.723 7.708 7.703 7.400 7.397 7.395 7.378 5.818 5.816 5.813 5.803 5.800 5.797 5.556 5.548 5.541 4.053 4.040 4.037 4.035 4.032 4.027 4.019 4.018 3.992 3.942 3.916 3.915 3.908 3.903 3.899 3.899 3.897 3.894 3.890 3.886 3.884 3.882 3.881 3.658 3.644 3.630 3.615 2.699 2.696 2.684 2.681 2.669 2.666 2.066 2.053 2.038 1.563 1.545 1.526 1.524 1.519 1.509 1.507 1.502 1.498 1.494 1.491 1.488 1.486 1.479 1.474 1.468 1.460 1.453 1.448 1.446 1.441 1.439 1.358 1.340 1.322 1.304 1.302 1.284 1.267 1.071 1.015 1.012 0.995 0.992 0.974 0.971 0.951 0.938 0.935 0.933 0.930 0.925 0.887 0.872 0.848 0.845 0.008 0.003 0.002 0.002 -0.002 -0.003 -0.003 -0.004 -0.005 -0.009
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.38 0.58 0.30 1.00 0.14 1.34 2.79 2.83 2.80 2.58 0.40 1.25 9.77 8.48 0.85 0.76 19.63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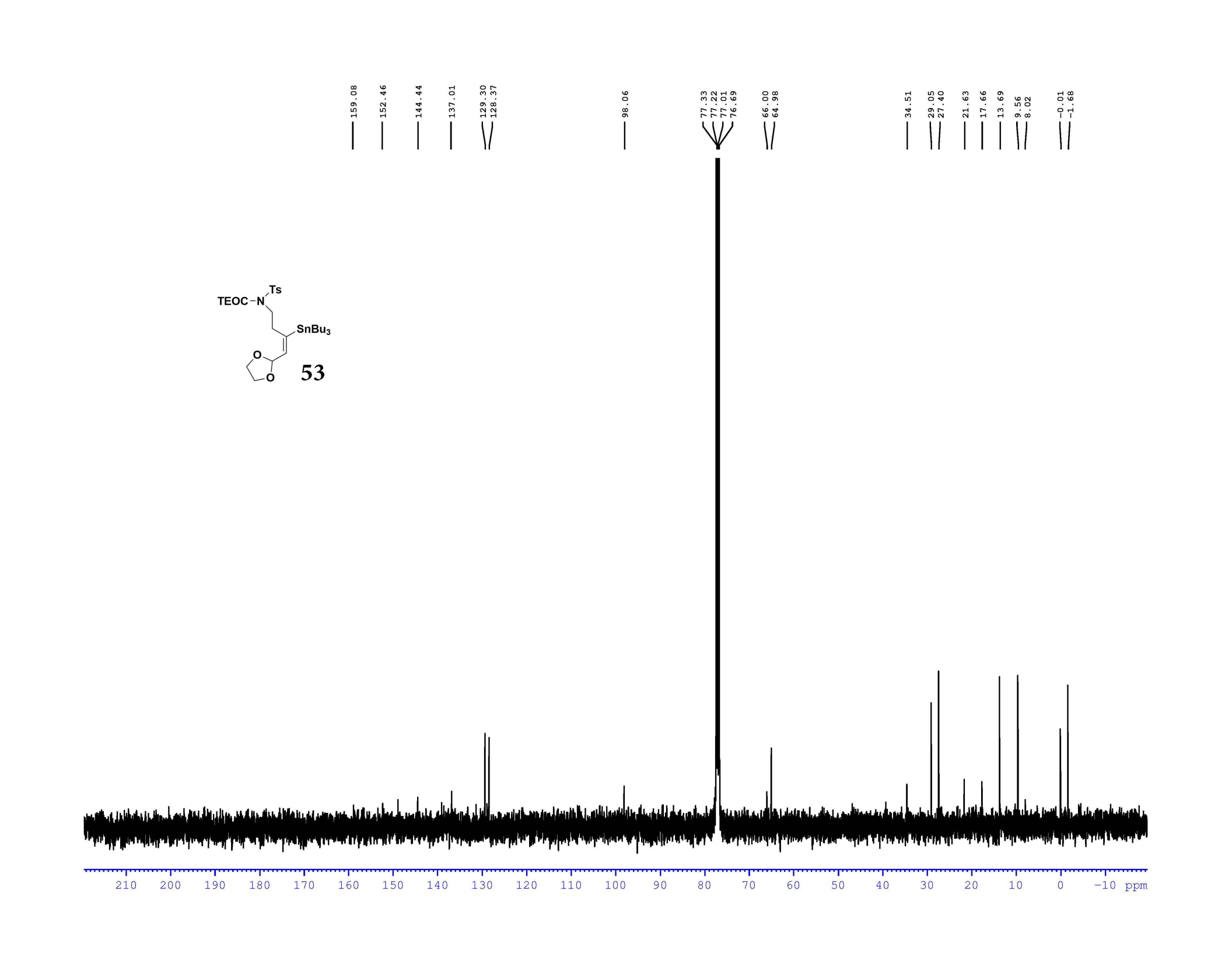
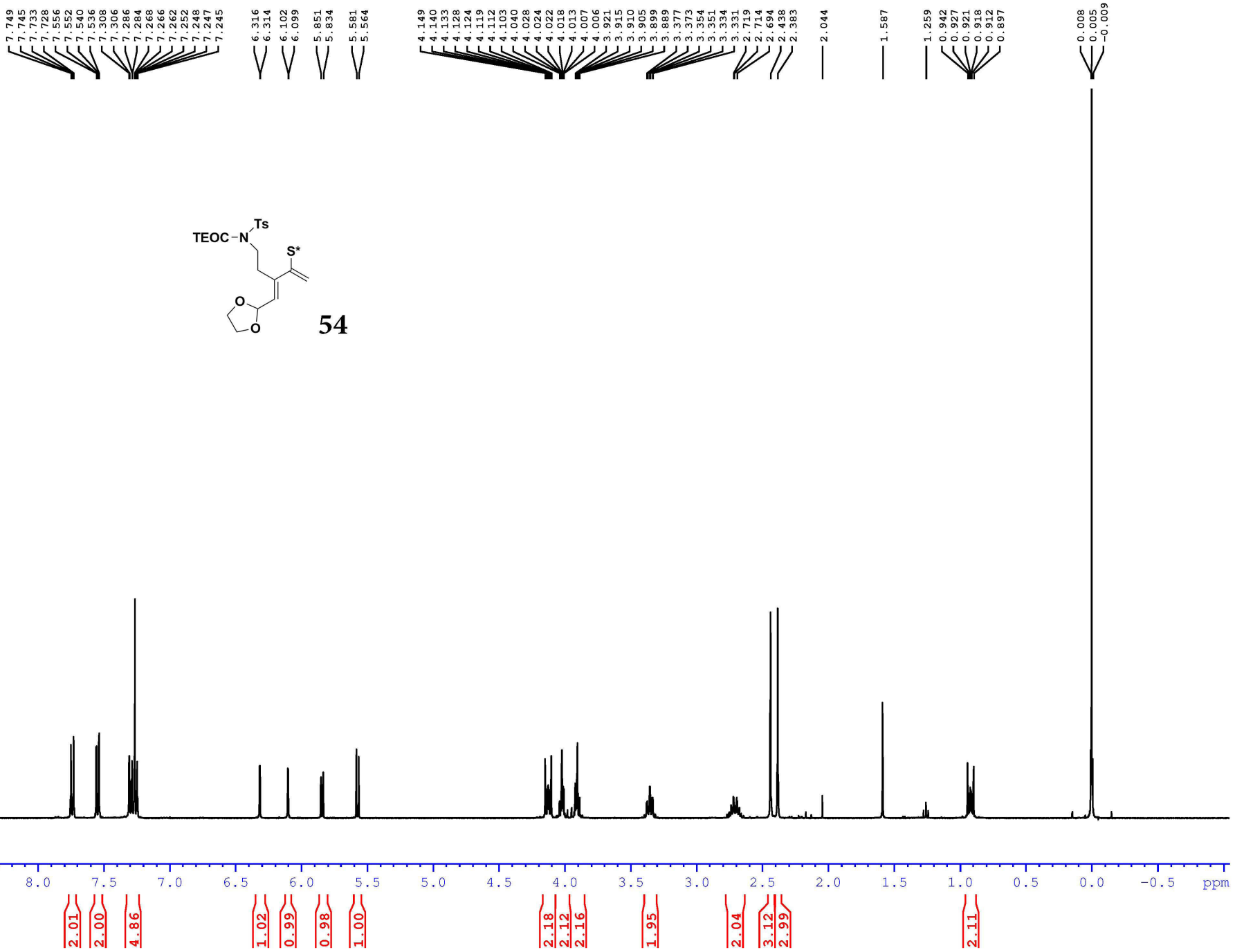
5.736 5.719 5.657 5.653 5.640 4.186 4.177 4.171 4.165 4.161 4.155 4.149 4.140 4.059 4.046 4.041 4.038 4.033 4.024 3.924 3.916 3.911 3.908 3.903 3.890 3.769 3.759 3.754 3.749 3.740 3.735 3.726 2.845 2.833 2.830 2.824 2.803 2.434 1.551 1.549 1.541 1.532 1.528 1.523 1.519 1.517 1.514 1.511 1.504 1.499 1.493 1.486 1.474 1.472 1.458 1.373 1.355 1.337 1.317 1.300 1.282 1.051 1.011 0.998 0.991 0.986 0.977 0.970 0.962 0.956 0.946 0.916 0.906 0.897 0.888 0.879 0.870 0.863 0.010 0.008 0.007 0.002 -0.003 -0.003 -0.004 -0.005 -0.005 -0.007 -0.009 -0.009 -0.011 -0.149
TEOC
N
Ts
SnBu3
O
O
53
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00 2.05 0.27 2.49 0.13 7.43 2.04 2.48 0.43 0.08 3.00 12.38 6.72 18.04 16.63


159.08
152.46
144.44
137.01
129.30
128.37
98.06
77.33
77.22
77.01
76.69
66.00
64.98
34.51
29.05
27.40
21.63
17.66
13.69
9.56
8.02
-0.01
-1.68
TEOC
N
Ts
SnBu3
O
O
53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


7.749
7.745
7.733
7.728
7.556
7.552
7.540
7.536
7.308
7.306
7.286
7.284
7.268
7.266
7.262
7.252
7.248
7.247
7.245
6.316
6.314
6.102
6.099
5.851
5.834
5.581
5.564
4.149
4.140
4.133
4.128
4.124
4.119
4.112
4.103
4.040
4.028
4.024
4.022
4.018
4.013
4.007
4.006
3.921
3.915
3.910
3.905
3.899
3.889
3.377
3.373
3.354
3.351
3.334
3.331
2.719
2.714
2.694
2.438
2.383
2.044
1.587
1.259
0.942
0.927
0.921
0.918
0.912
0.897
0.008
0.005
-0.009
TEOC
N
Ts
S*
O
O
54
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
2.01
2.00
4.86
1.02
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0.98
1.00
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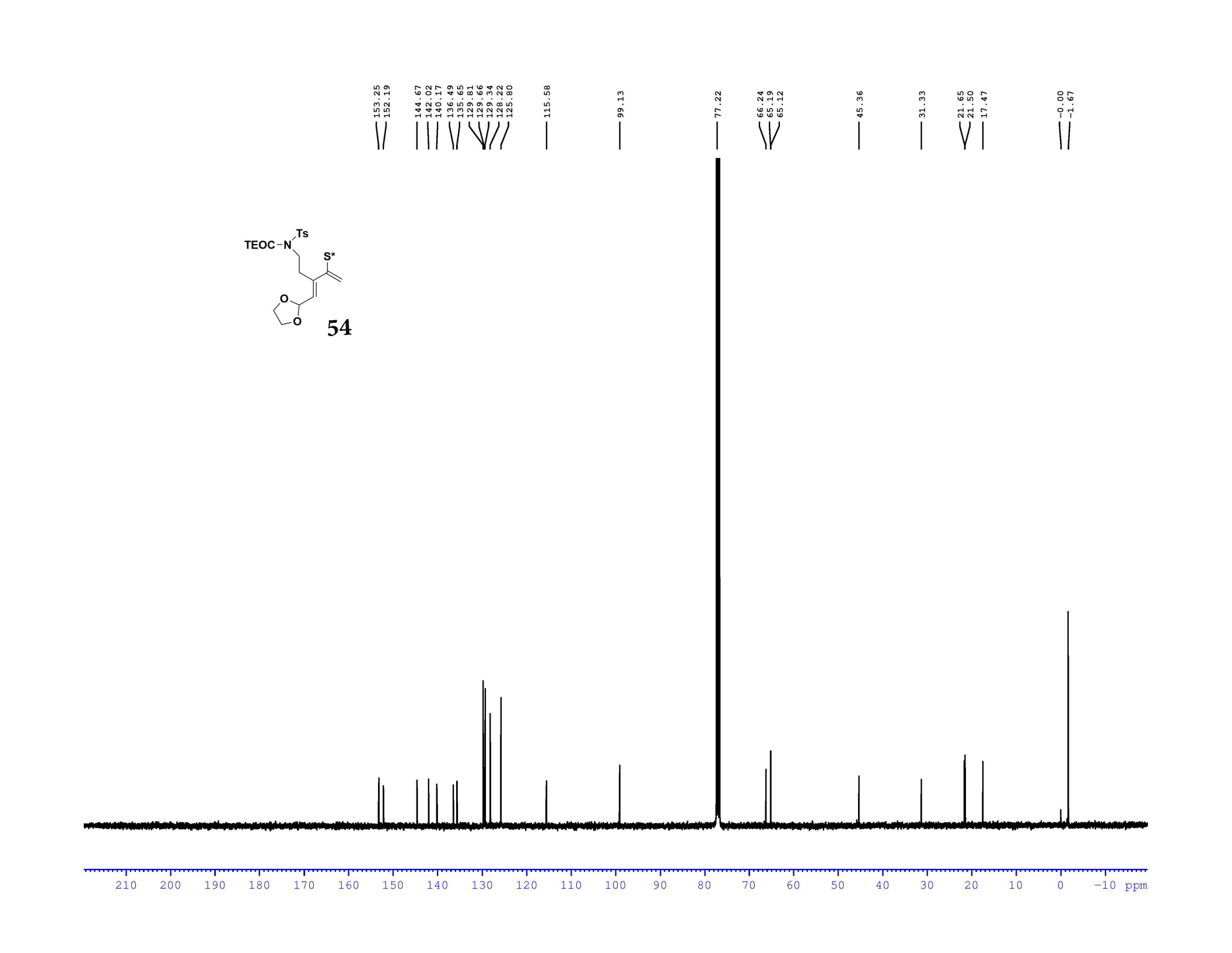
2.16
1.95
2.04
3.12
2.99
2.11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136.49
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115.58
99.13
77.22
66.24
65.19
65.12
45.36
31.33
21.65
21.50
17.47
-0.00
-1.67
TEOC
N
Ts
S*
O
O
54
210
200
190
180
170
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130
120
110
100
90
80
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50
40
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20
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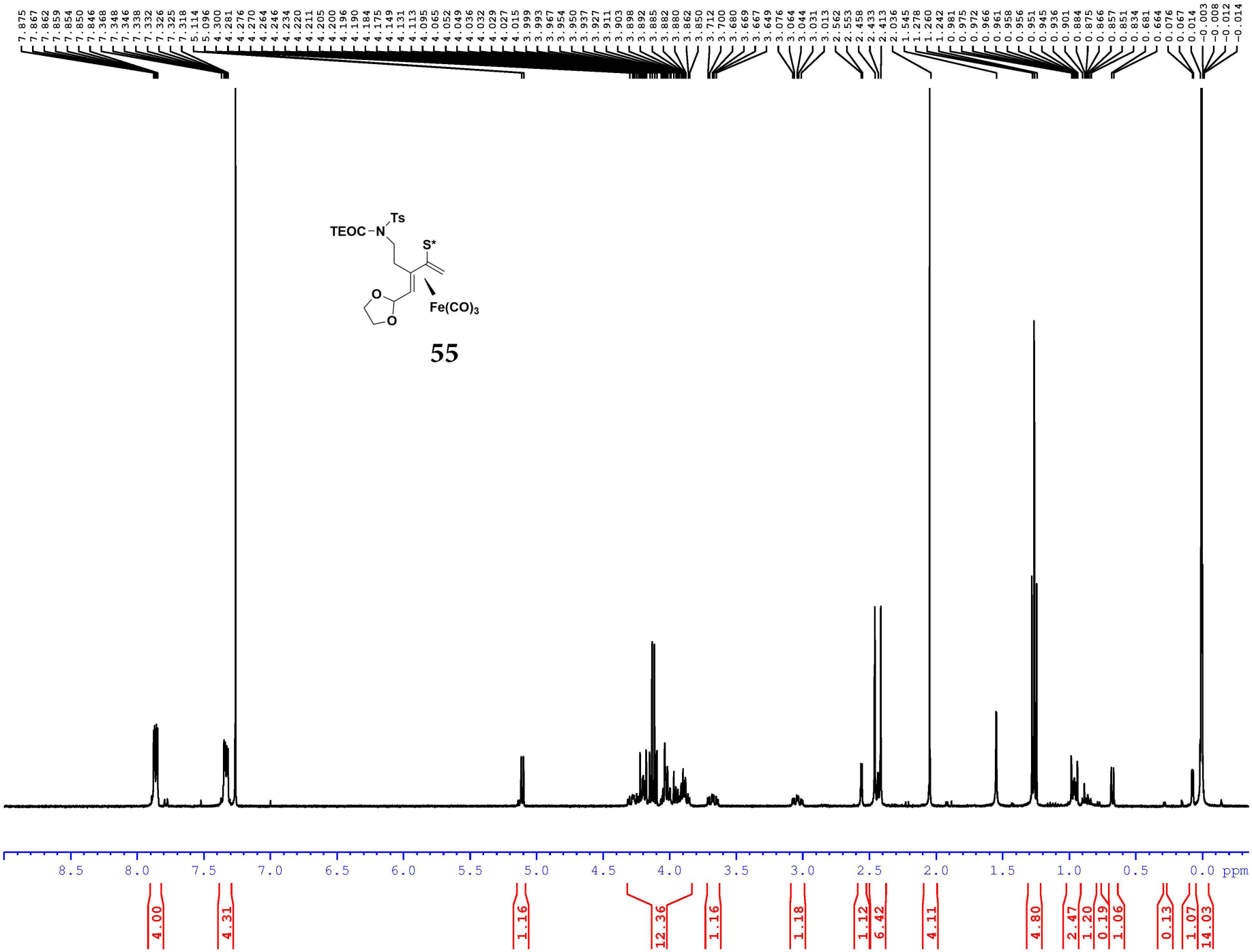
0
-10
ppm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7.332
7.326
7.325
7.318
5.114
5.096
4.300
4.281
4.276
4.270
4.264
4.246
4.234
4.220
4.211
4.205
4.200
4.196
4.190
4.184
4.175
4.149
4.131
4.113
4.095
4.065
4.052
4.049
4.036
4.032
4.029
4.027
4.015
3.999
3.993
3.967
3.954
3.950
3.937
3.927
3.911
3.903
3.898
3.892
3.885
3.882
3.880
3.862
3.850
3.712
3.700
3.680
3.669
3.667
3.649
3.076
3.064
3.044
3.031
3.013
2.562
2.553
2.458
2.433
2.413
2.036
1.545
1.278
1.260
1.242
0.981
0.975
0.972
0.966
0.961
0.958
0.956
0.951
0.945
0.936
0.901
0.884
0.875
0.866
0.857
0.851
0.834
0.681
0.664
0.076
0.067
0.014
-0.003
-0.008
-0.012
-0.014
TEOC
N
Ts
S*
O
O
Fe(CO)3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
4.00
4.31
1.16
12.36
1.16
1.18
1.12
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4.11
4.80
2.47
1.20
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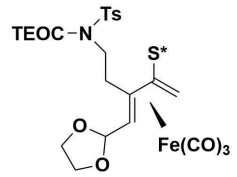
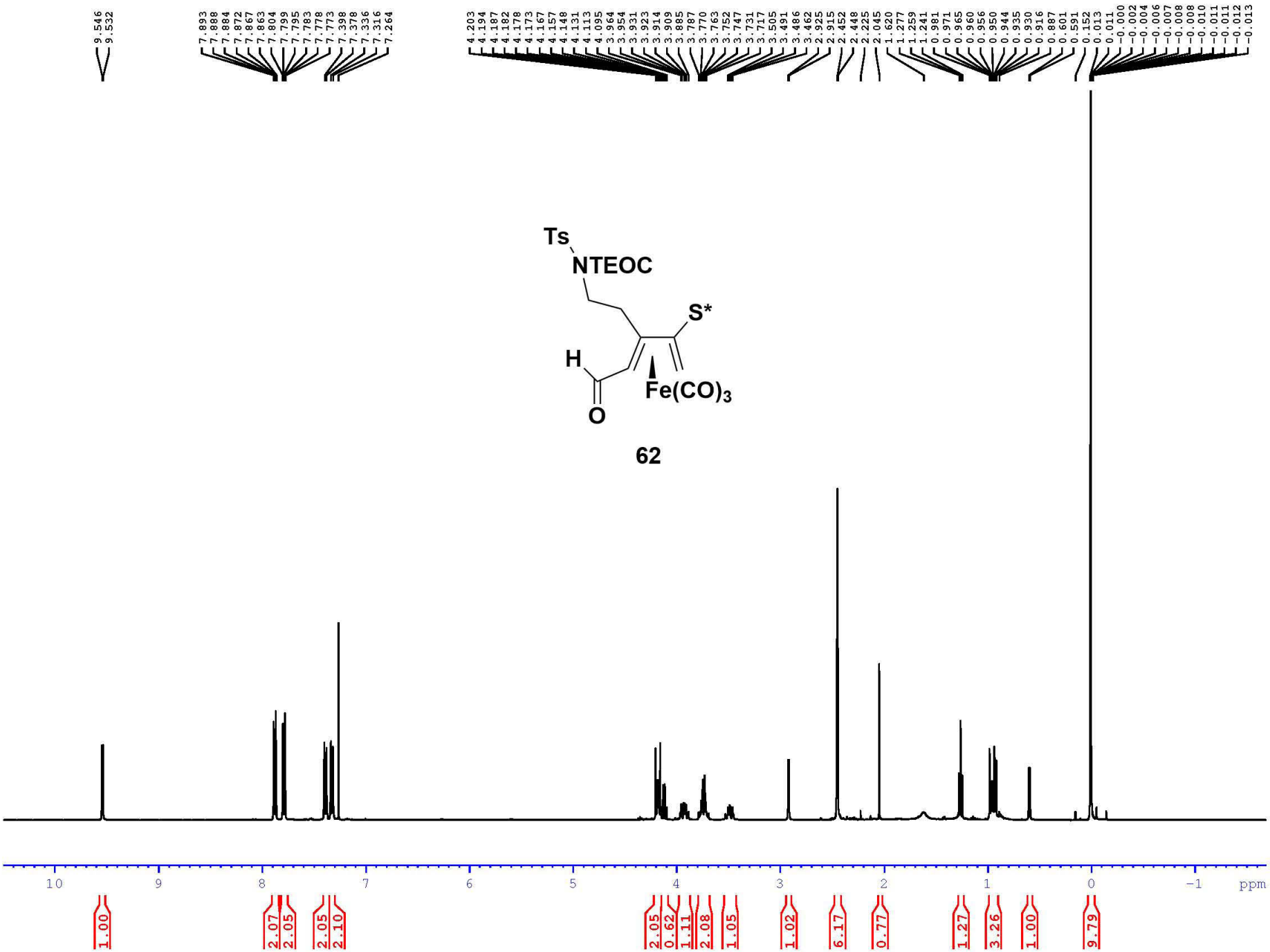
1.06
0.13
1.07
14.03

55


TEOC
N
Ts
S*
O
O
Fe(CO)3

55

144.80
142.24
142.18
136.60
130.15
129.47
128.39
125.35
114.36
102.80
102.37
77.23
66.49
65.71
65.25
60.41
58.67
46.57
30.26
28.73
21.68
21.52
21.07
17.63
14.21
0.00
-1.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm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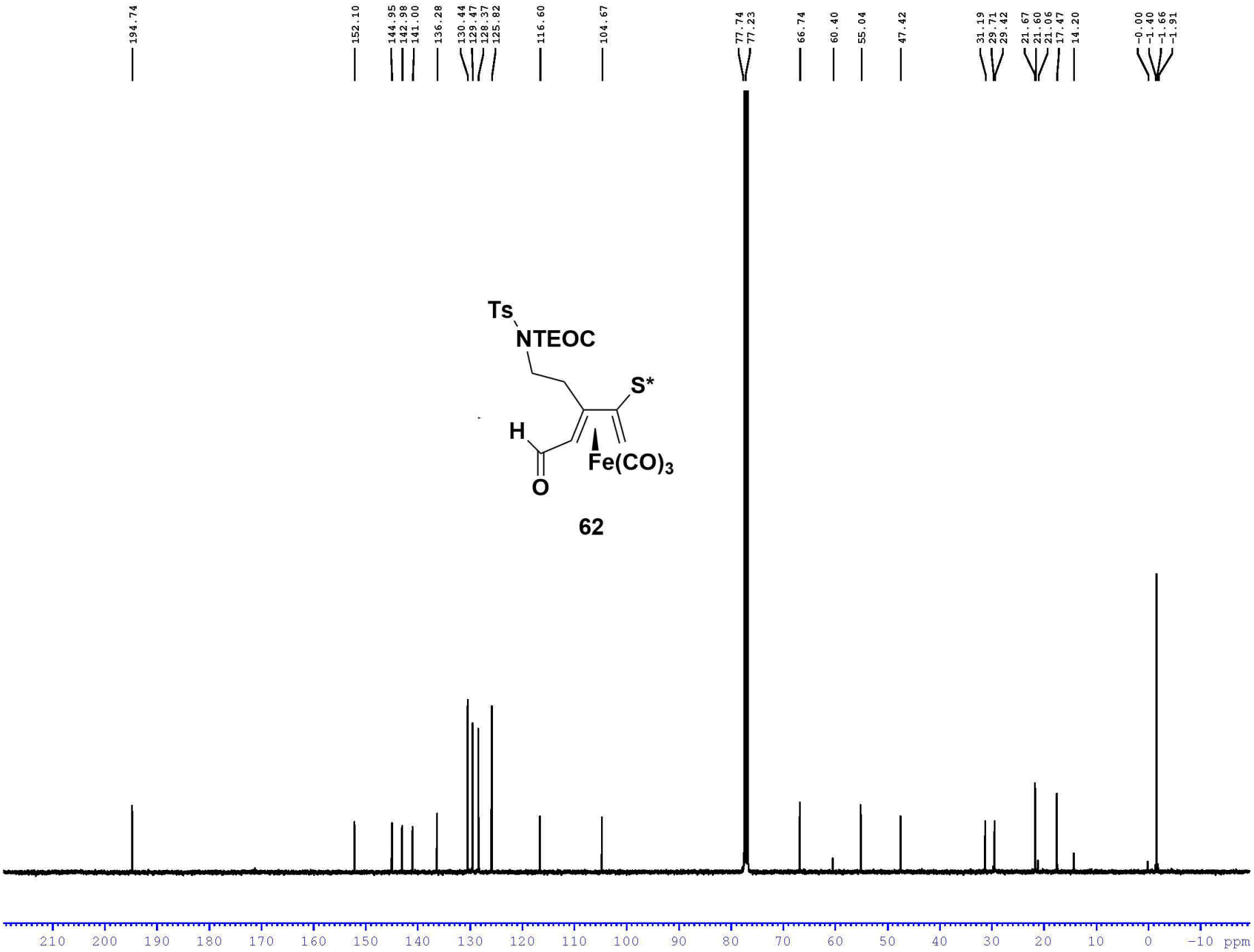
7.783
7.778
7.773
7.398
7.378
7.336
7.316
7.264
4.203
4.194
4.187
4.182
4.178
4.173
4.167
4.157
4.148
4.131
4.113
4.095
3.964
3.954
3.931
3.923
3.914
3.909
3.885
3.787
3.770
3.763
3.752
3.747
3.731
3.717
3.505
3.491
3.486
3.462
2.925
2.915
2.452
2.448
2.225
2.045
1.620
1.277
1.259
1.241
0.981
0.971
0.965
0.960
0.956
0.950
0.944
0.935
0.930
0.916
0.887
0.601
0.591
0.152
0.013
0.011
-0.000
-0.002
-0.004
-0.006
-0.007
-0.008
-0.008
-0.010
-0.011
-0.011
-0.012
-0.013
Ts
NTEOC
S*
H
O
Fe(CO)3
62
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.00
2.07
2.05
2.05
2.10
2.05
0.62
1.11
2.08
1.05
1.02
6.17
0.77
1.27
3.26
1.00
9.79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152.10
144.95
142.98
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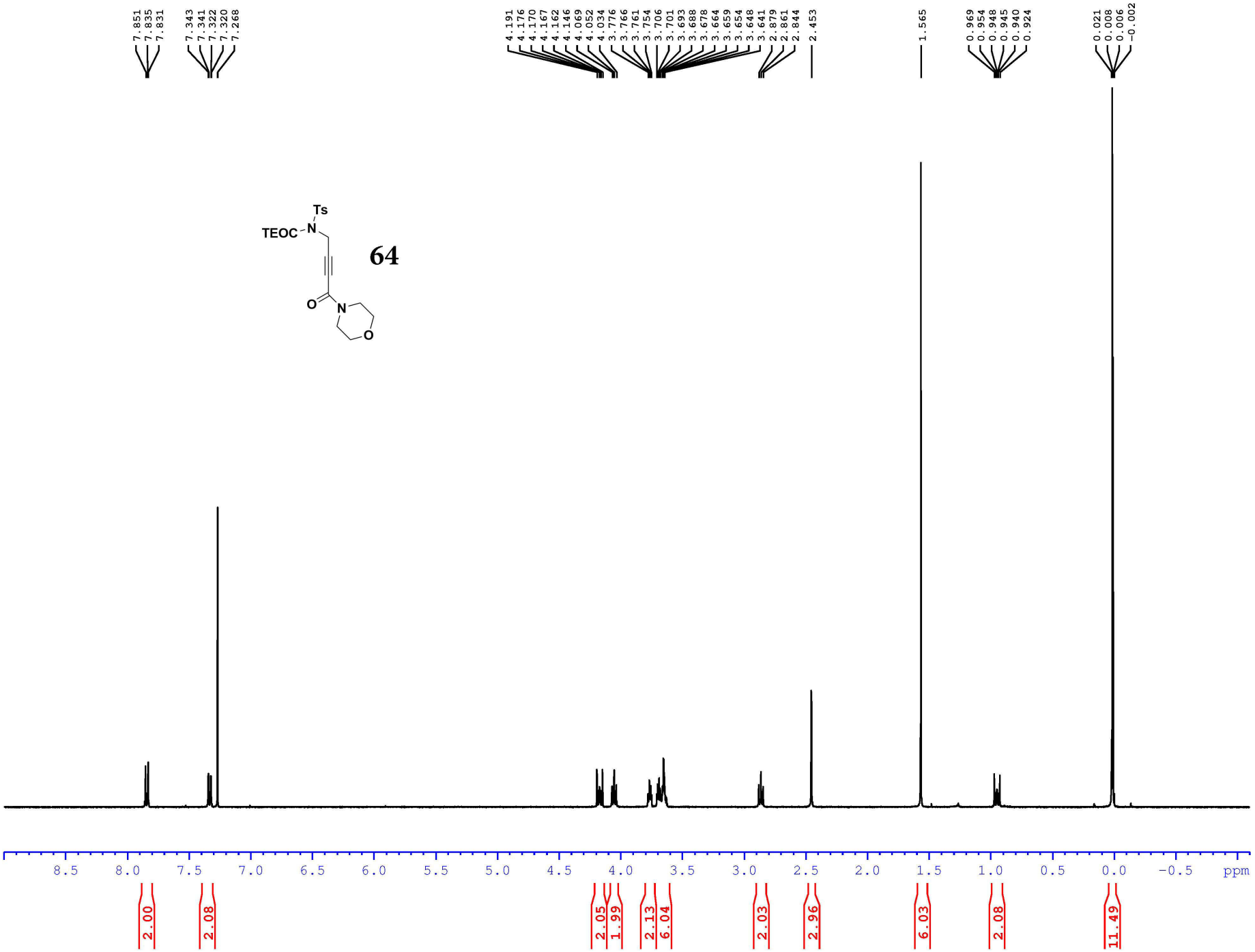
136.28
130.44
129.47
128.37
125.82
116.60
104.67
77.74
77.23
66.74
60.40
55.04
47.42
31.19
29.71
29.42
21.67
21.60
21.06
17.47
14.20
-0.00
-1.40
-1.66
-1.91
Ts
NTEOC
S*
H
O
Fe(CO)3
62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10 ppm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7.831
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7.341
7.322
7.320
7.268
4.191
4.176
4.170
4.167
4.162
4.146
4.069
4.052
4.034
3.776
3.766
3.761
3.754
3.706
3.701
3.693
3.688
3.678
3.664
3.659
3.654
3.648
3.641
2.879
2.861
2.844
2.453
1.565
0.969
0.954
0.948
0.945
0.940
0.924
0.021
0.008
0.006
-0.002
Ts
TEOC
N
O
N
O
64
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
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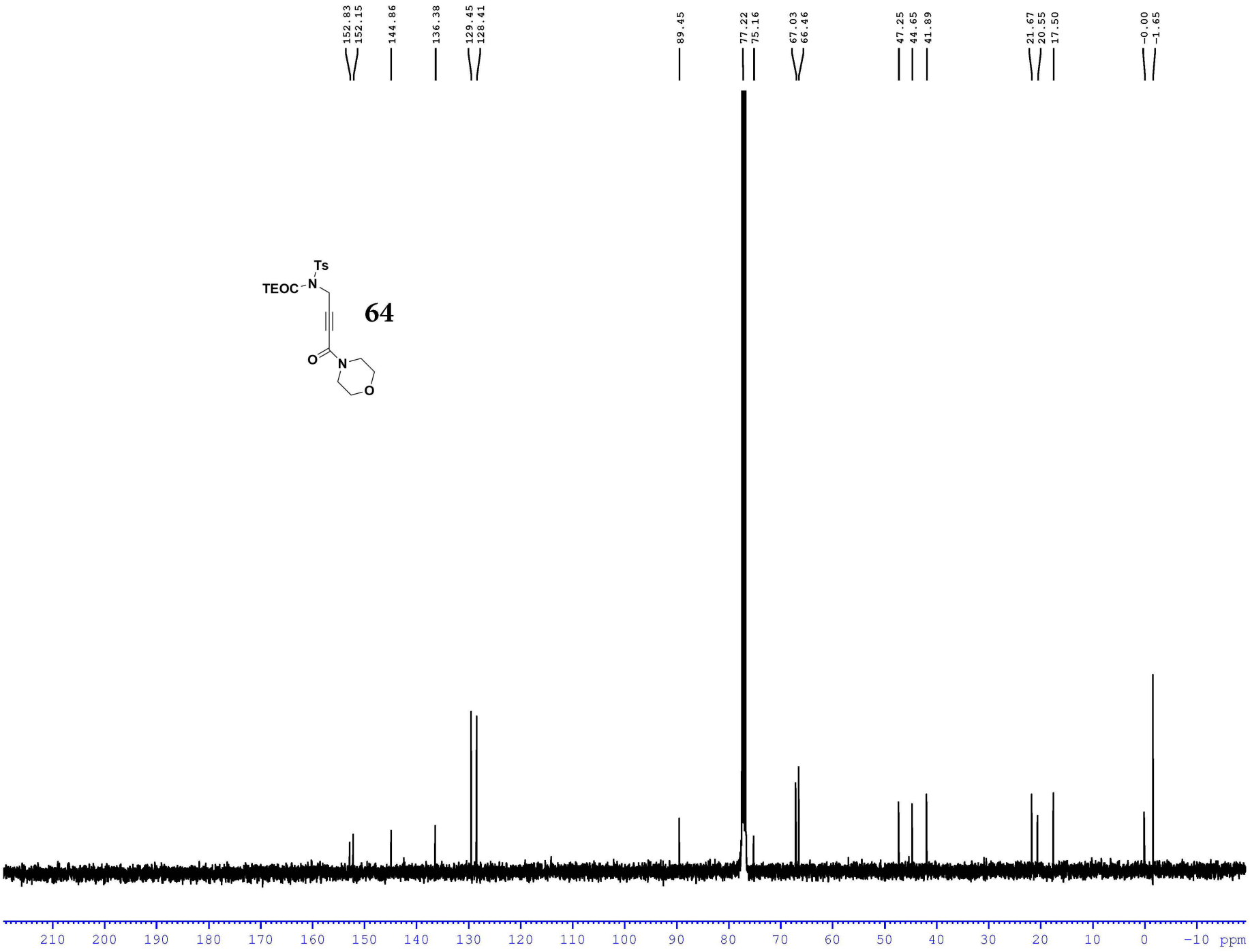
2.08
2.05
1.99
2.13
6.04
2.03
2.96
6.03
2.08
11.49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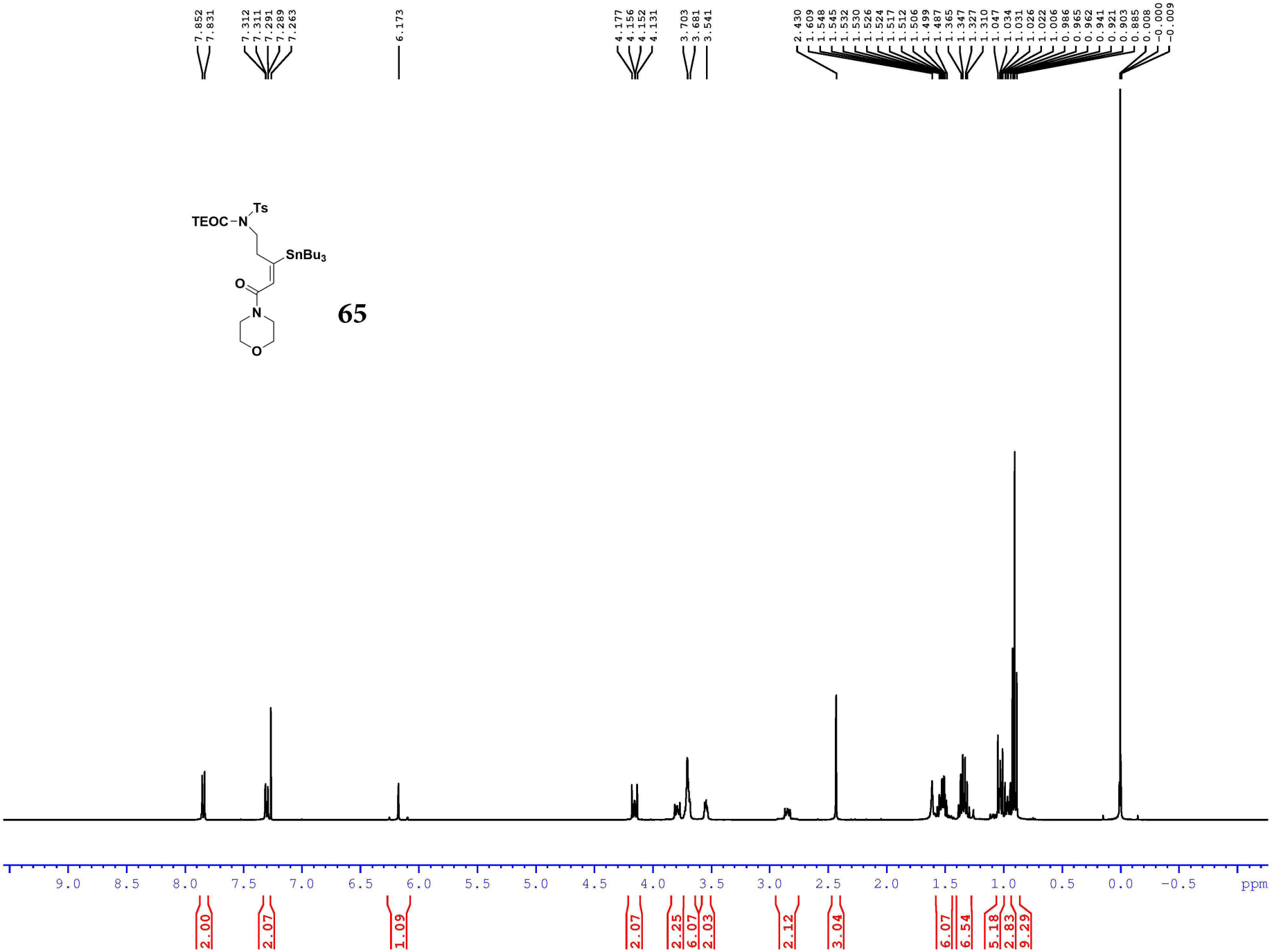
152.15
144.86
136.38
129.45
128.41
89.45
77.22
75.16
67.03
66.46
47.25
44.65
41.89
21.67
20.55
17.50
-0.00
-1.65
Ts
TEOC
N
O
N
O
64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm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7.311
7.291
7.289
7.263
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4.152
4.131
3.703
3.681
3.541
2.430
1.609
1.548
1.545
1.532
1.530
1.526
1.524
1.517
1.512
1.506
1.499
1.487
1.365
1.347
1.327
1.310
1.047
1.034
1.031
1.026
1.022
1.006
0.986
0.965
0.962
0.941
0.921
0.903
0.885
0.008
-0.000
-0.009
TEOC
N
Ts
SnBu3
O
N
O
65
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
2.00
2.07
1.09
2.07
2.25
6.07
2.03
2.12
3.04
6.07
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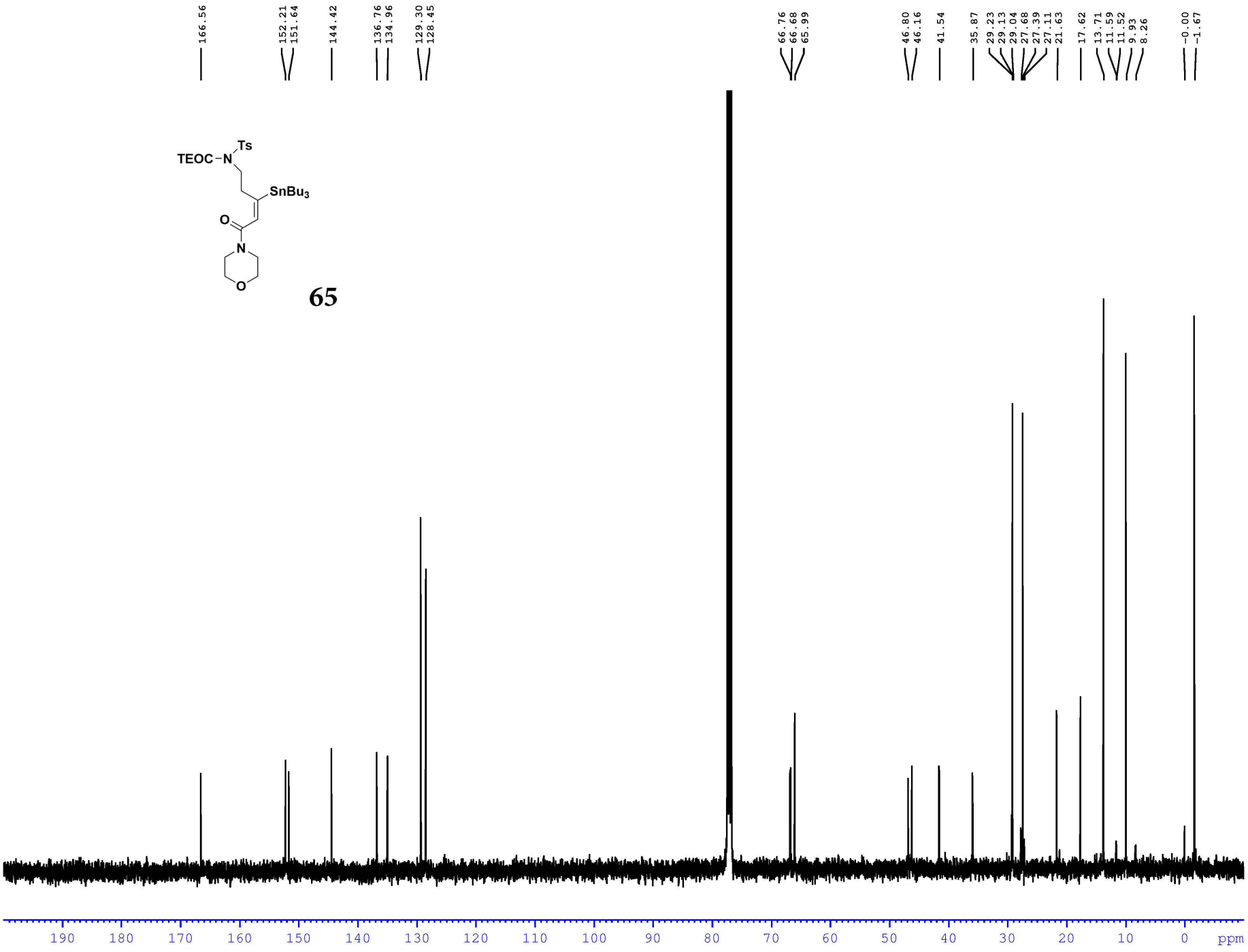
5.18
2.83
9.29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128.45
66.76
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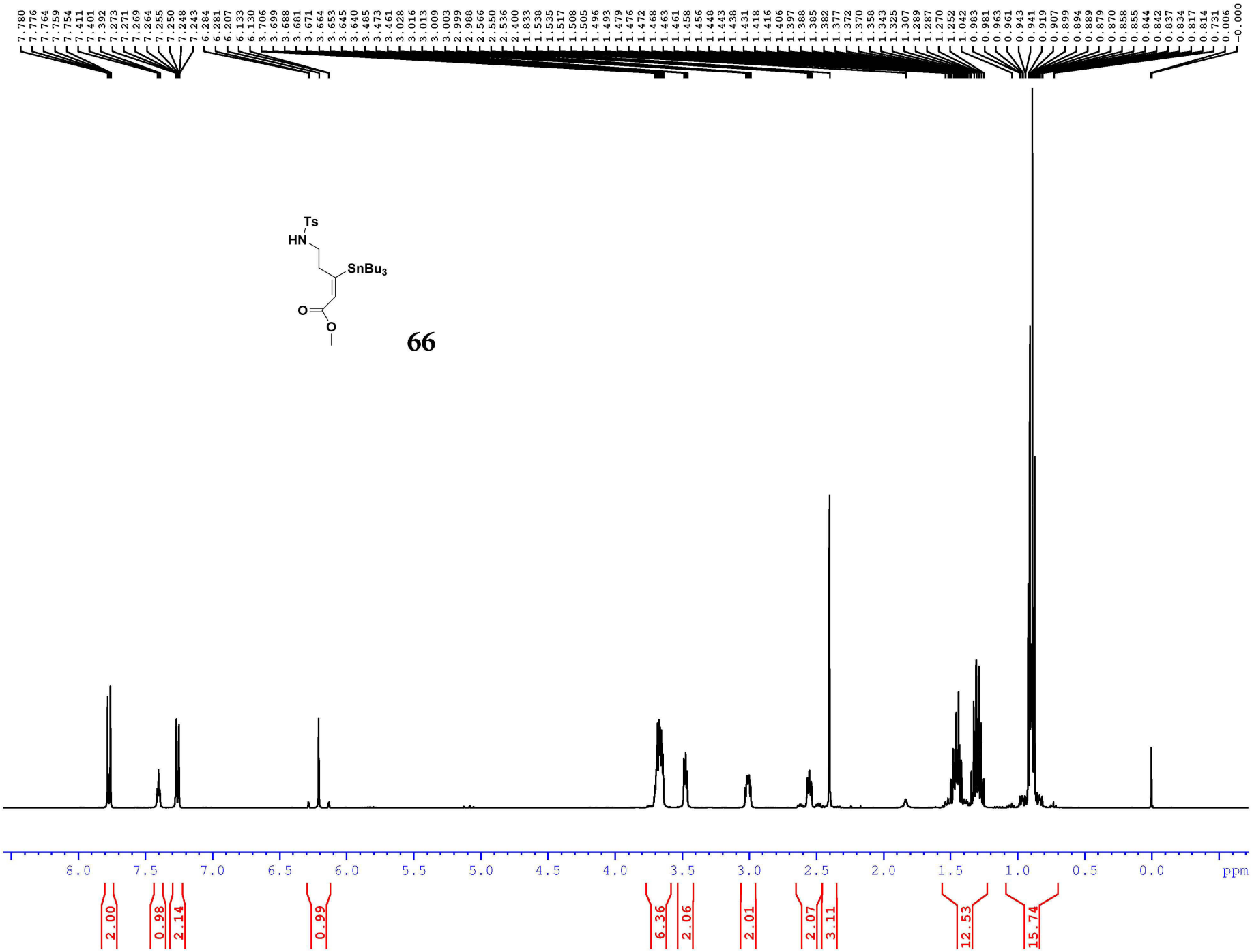
65.99
46.80
46.16
41.54
35.87
29.23
29.13
29.04
27.68
27.39
27.11
21.63
17.62
13.71
11.59
11.52
9.93
8.26
-0.00
-1.67
TEOC
N
Ts
SnBu3
O
N
O
65
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.264
7.255
7.250
7.248
7.243
6.284
6.281
6.207
6.133
6.130
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3.699
3.688
3.681
3.671
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3.640
3.485
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3.016
3.013
3.009
3.003
2.999
2.988
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2.550
2.536
2.400
1.833
1.538
1.535
1.517
1.508
1.505
1.496
1.493
1.479
1.476
1.472
1.468
1.463
1.461
1.458
1.456
1.448
1.443
1.438
1.431
1.418
1.416
1.406
1.397
1.388
1.385
1.382
1.377
1.372
1.370
1.358
1.343
1.325
1.307
1.289
1.287
1.270
1.252
1.042
0.983
0.981
0.963
0.961
0.943
0.941
0.919
0.907
0.899
0.894
0.889
0.879
0.870
0.858
0.855
0.844
0.842
0.837
0.834
0.817
0.814
0.731
0.006
-0.000
Ts
HN
SnBu3
O
O
66
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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2.01
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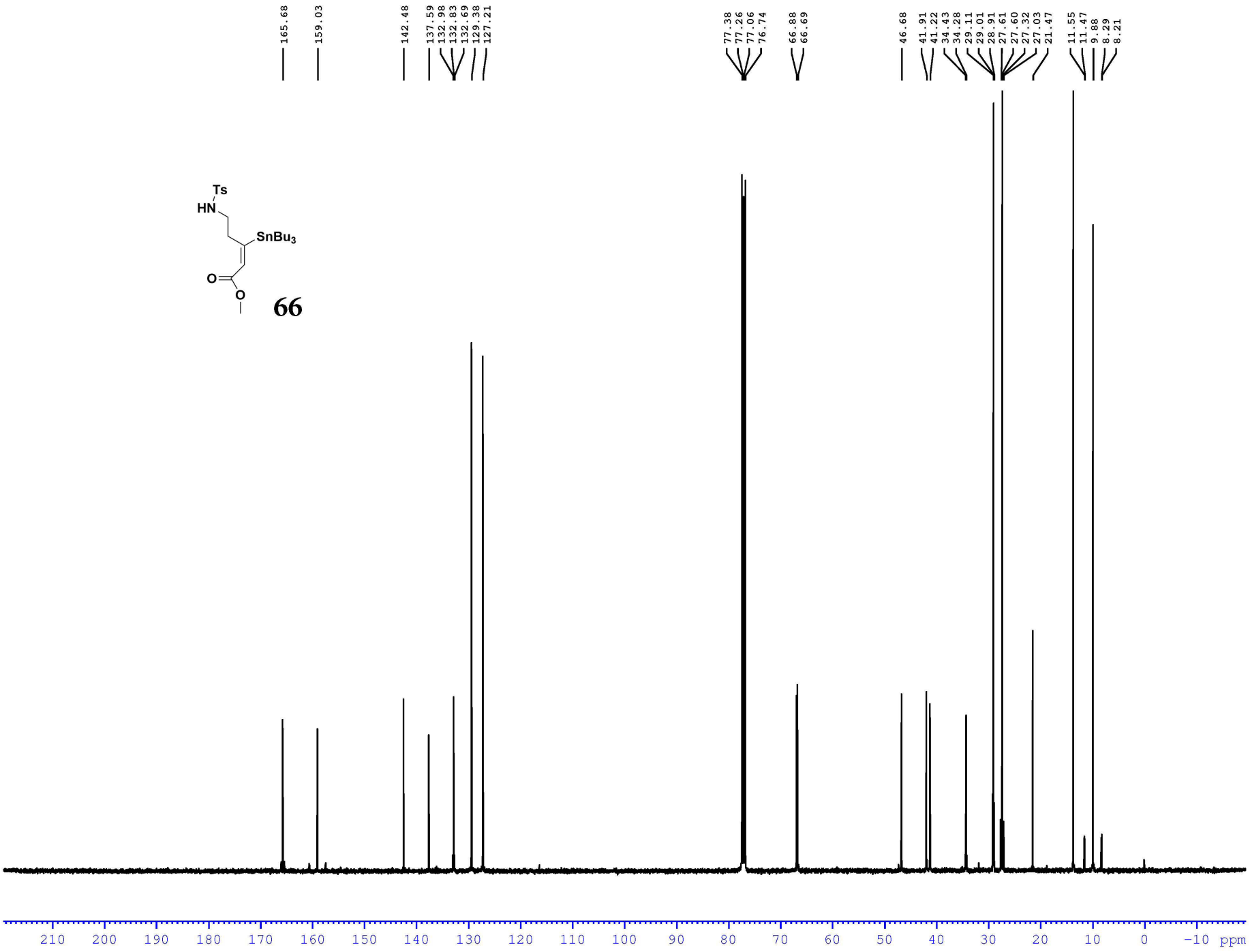
15.74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132.83
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129.38
127.21
77.38
77.26
77.06
76.74
66.88
66.69
46.68
41.91
41.22
34.43
34.28
29.11
29.01
28.91
27.61
27.60
27.32
27.03
21.47
11.55
11.47
9.88
8.29
8.21
Ts
HN
SnBu3
O
O
66
210
200
190
180
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150
140
130
120
110
100
90
80
70
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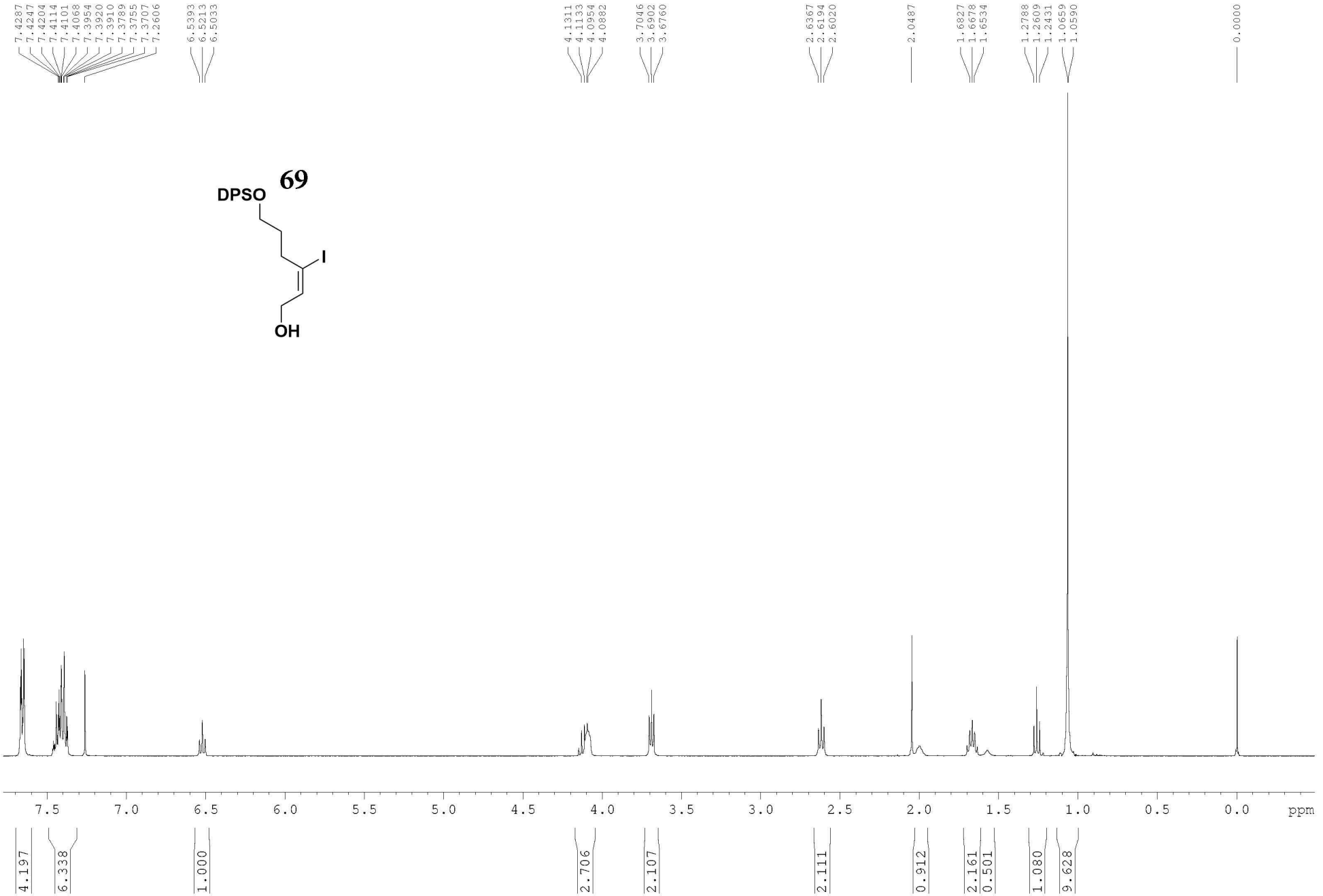
50
40
30
20
10
0
−10
ppm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7.3954
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7.3910
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7.3755
7.3707
7.2606
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6.5213
6.5033
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4.1133
4.0954
4.0882
3.7046
3.6902
3.6760
2.6367
2.6194
2.6020
2.0487
1.6827
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1.6534
1.2788
1.2609
1.2431
1.0659
1.0590
0.0000
69
DPSO
I
OH
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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
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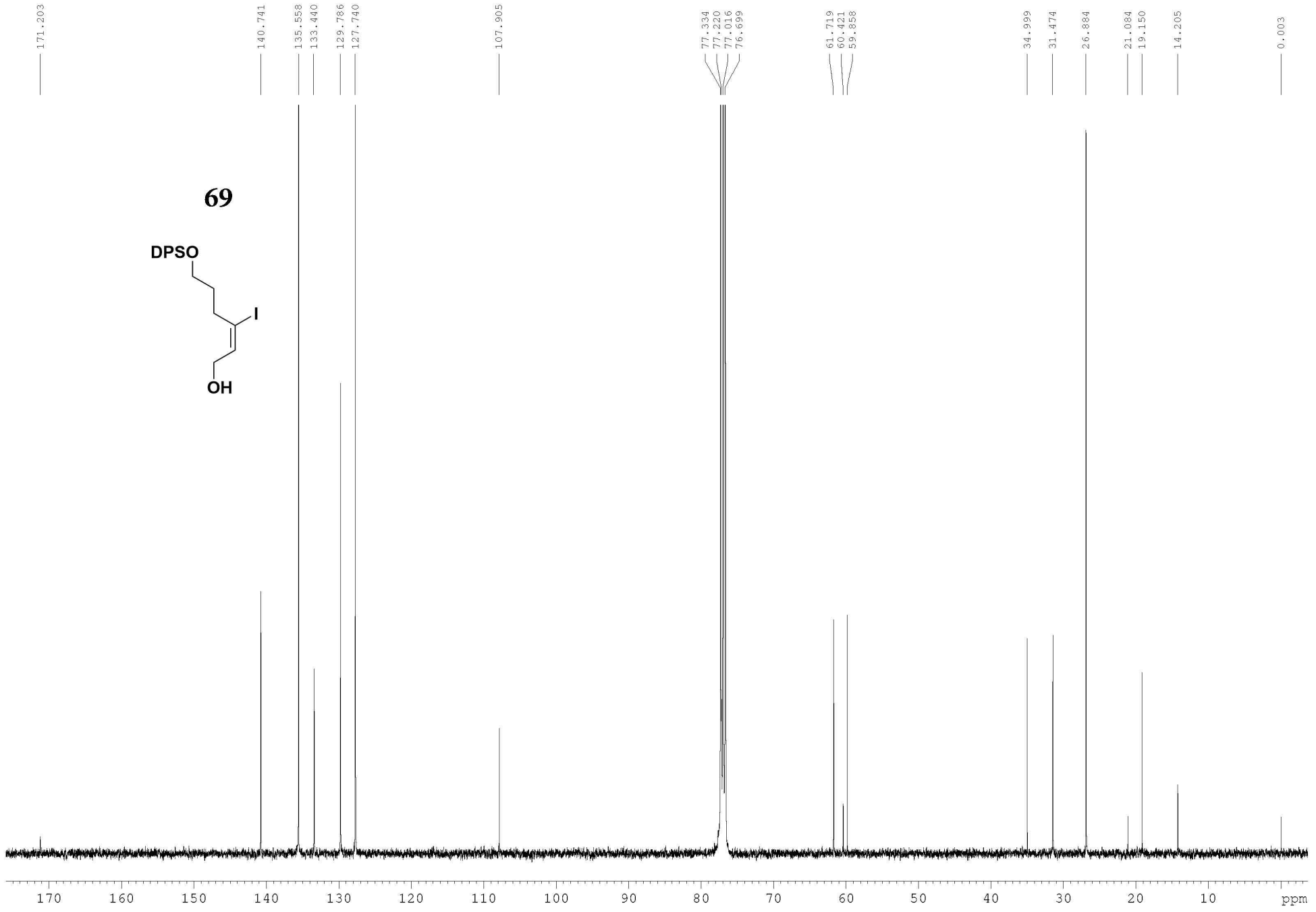
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77.016
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60.421
59.858
34.999
31.474
26.884
21.084
19.150
14.205
0.003
69
DPSO
I
OH
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150
140
130
120
110
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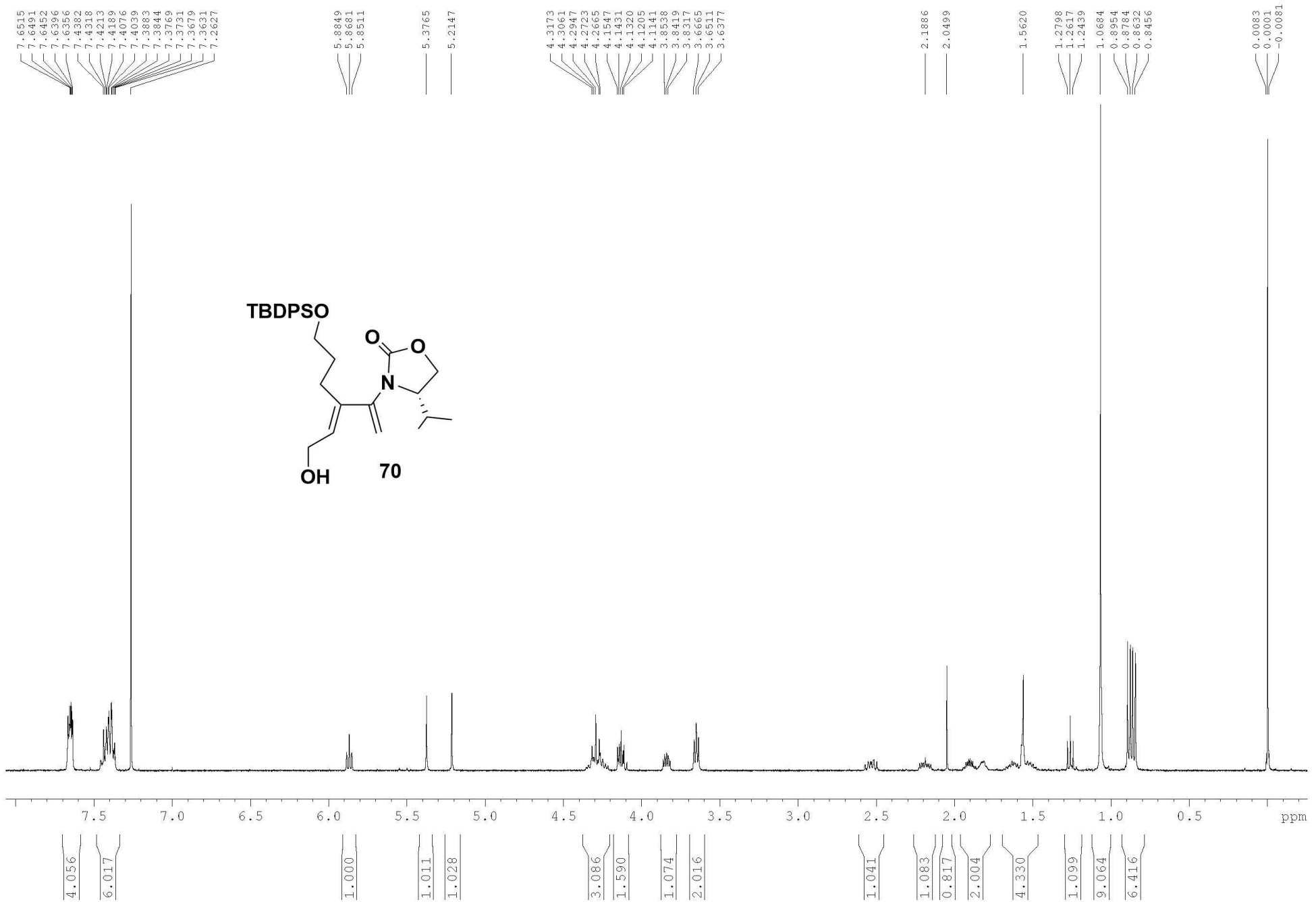
70
60
50
40
30
20
10
ppm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7.4039
7.3883
7.3844
7.3769
7.3731
7.3679
7.3631
7.2627
5.8849
5.8681
5.8511
5.3765
5.2147
4.3173
4.3061
4.2947
4.2723
4.2665
4.1547
4.1431
4.1320
4.1205
4.1141
3.8538
3.8419
3.8317
3.6665
3.6511
3.6377
2.1886
2.0499
1.5620
1.2798
1.2617
1.2439
1.0684
0.8954
0.8784
0.8632
0.8456
0.0083
0.0001
-0.0081
TBDPSO
O
O
N
OH
70
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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
4.056
6.017
1.000
1.011
1.028
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2.016
1.041
1.083
0.817
2.004
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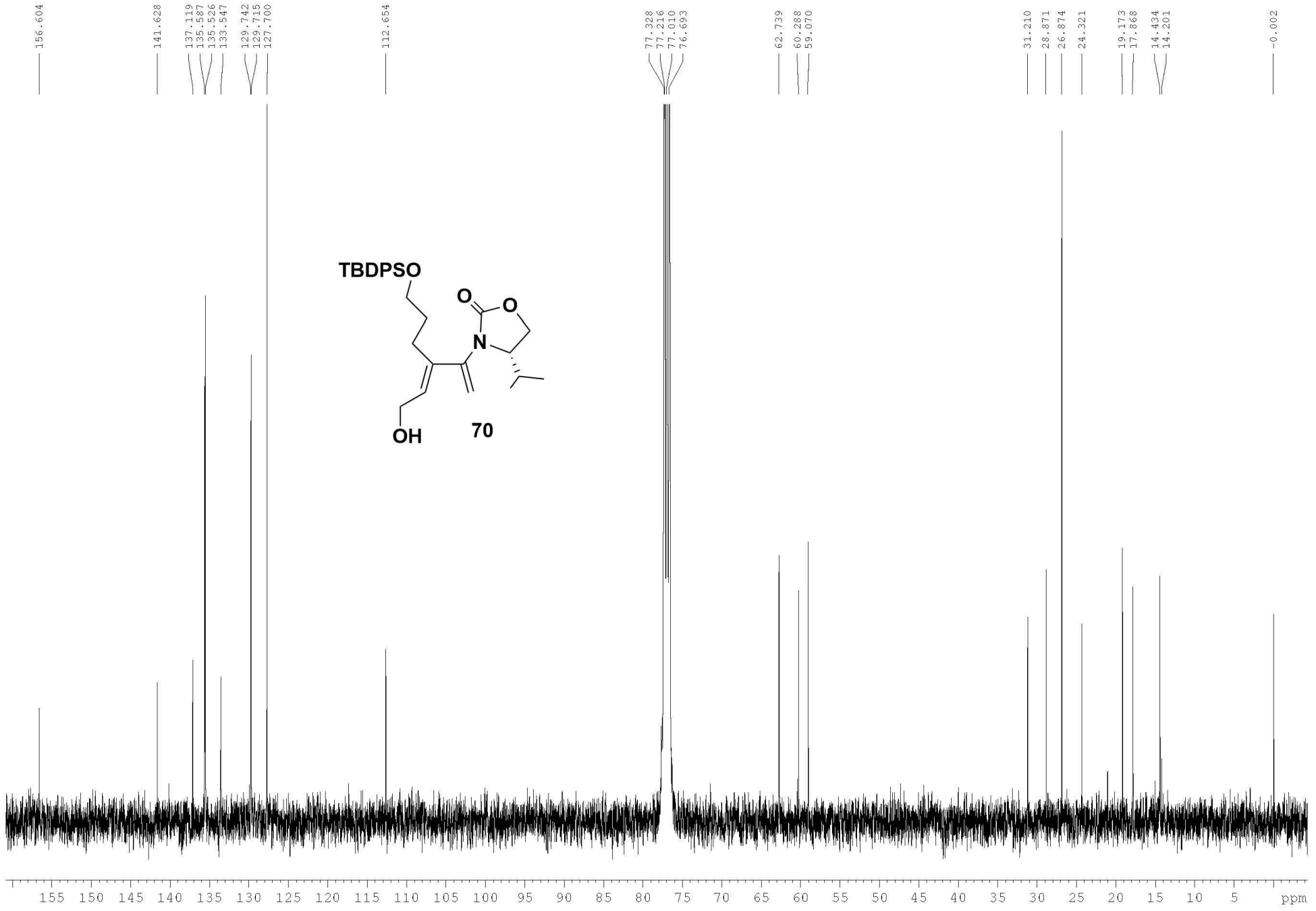
9.064
6.416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76.693
62.739
60.288
59.070
31.210
28.871
26.874
24.321
19.173
17.868
14.434
14.201
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O
N
OH
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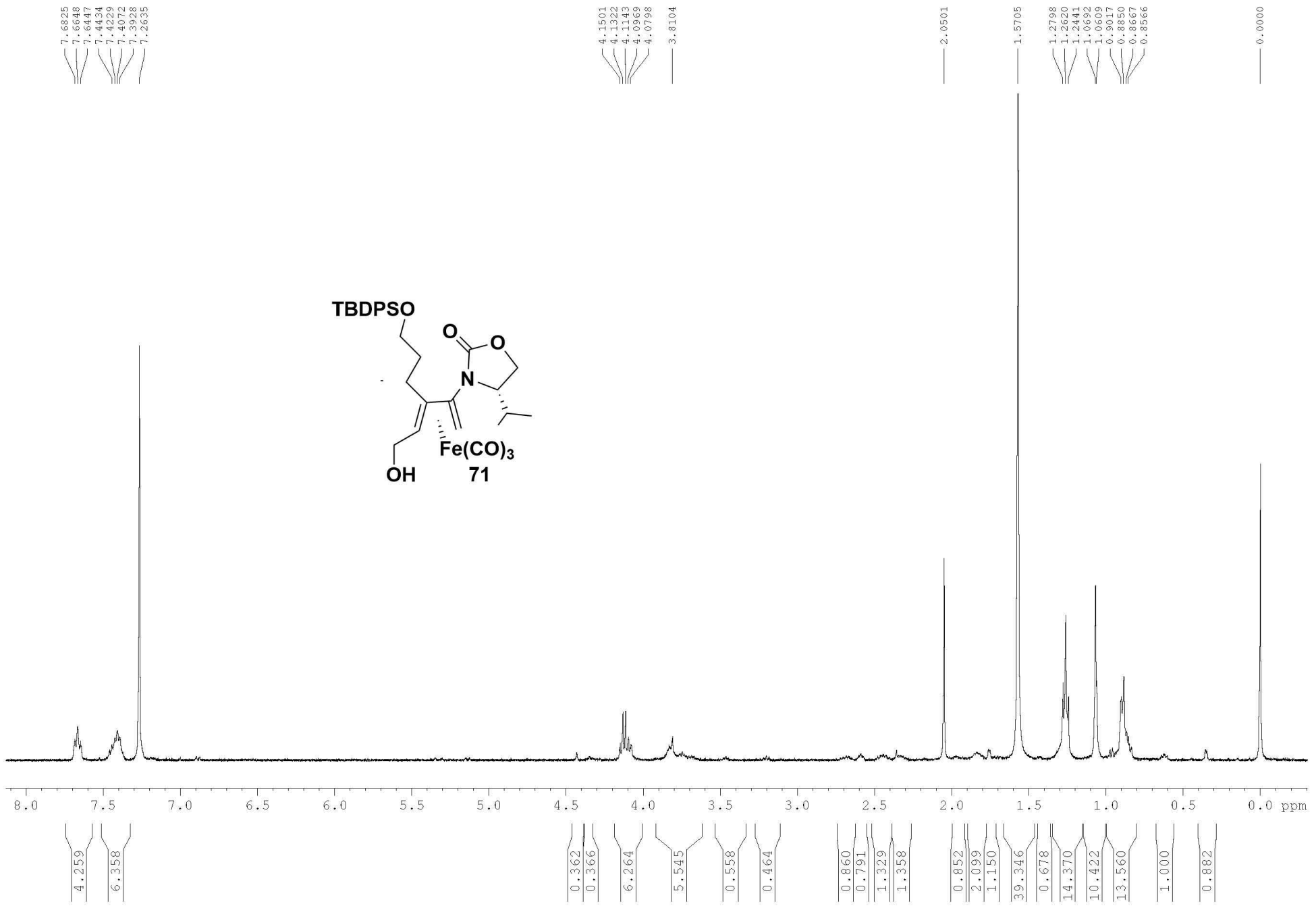
ppm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4.0969
4.0798
3.8104
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1.5705
1.2798
1.2620
1.2441
1.0692
1.0609
0.9017
0.8850
0.8667
0.8566
0.0000
TBDPSO
O
O
N
Fe(CO)3
OH
71
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
4.259
6.358
0.362
0.366
6.264
5.545
0.558
0.464
0.860
0.791
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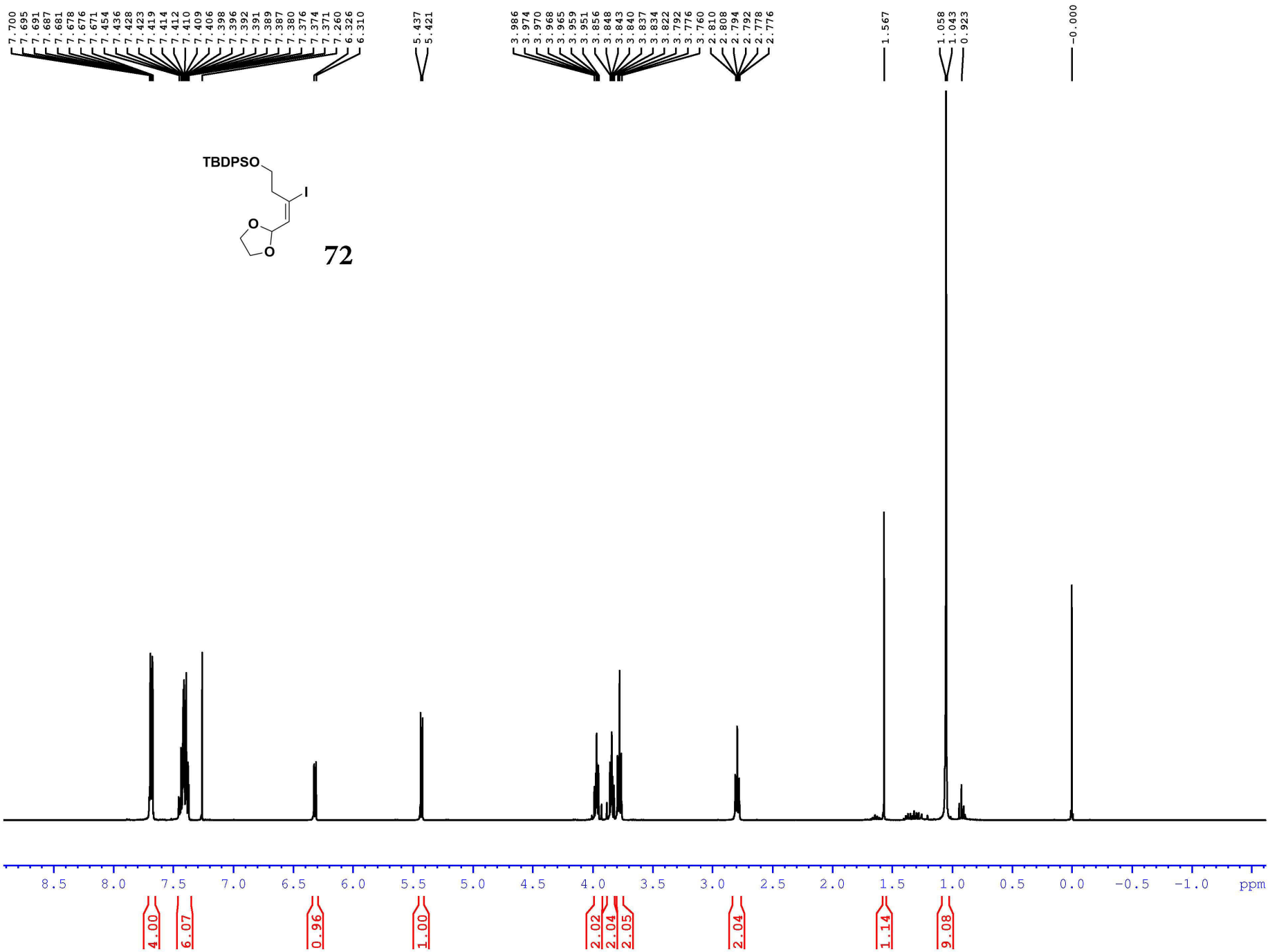
0.882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7.414
7.412
7.410
7.409
7.406
7.398
7.396
7.392
7.391
7.389
7.387
7.380
7.376
7.374
7.371
7.260
6.326
6.310
5.437
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3.986
3.974
3.970
3.968
3.965
3.959
3.951
3.856
3.848
3.843
3.840
3.837
3.834
3.822
3.792
3.776
3.760
2.810
2.808
2.794
2.792
2.778
2.776
1.567
1.058
1.043
0.923
-0.000
TBDPSO
I
O
O
72
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
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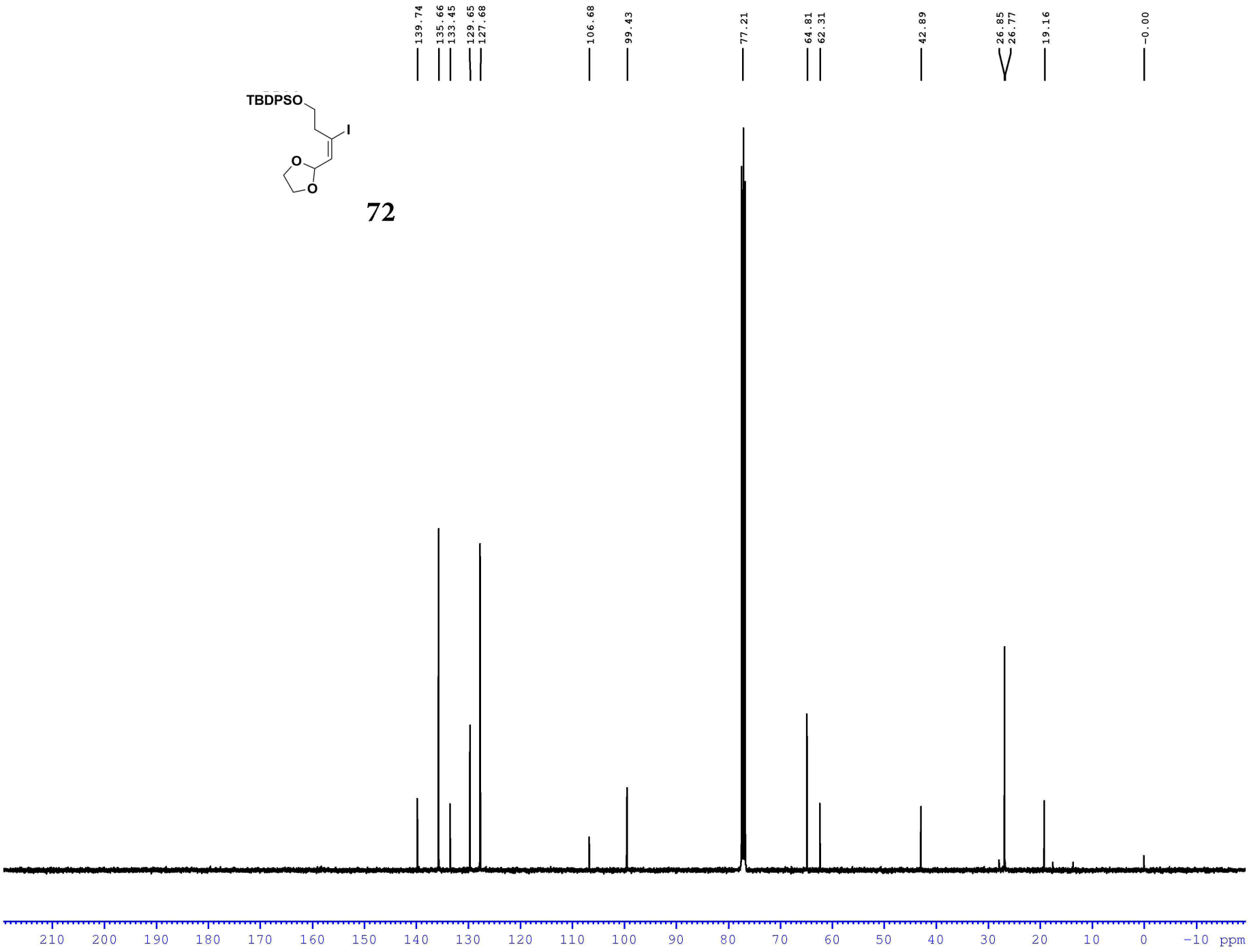
0.96
1.00
2.02
2.04
2.05
2.04
1.14
9.08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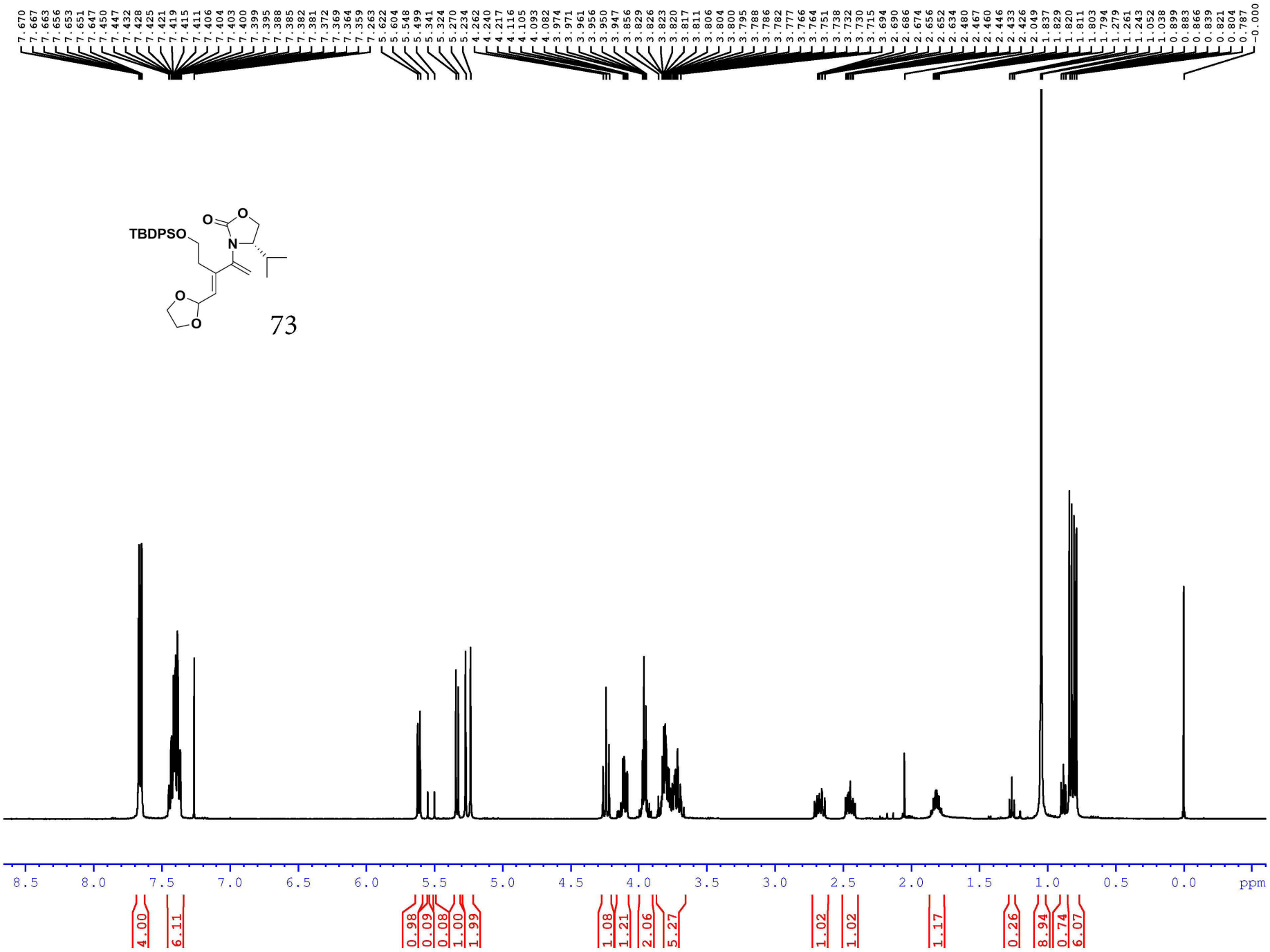
135.66
133.45
129.65
127.68
106.68
99.43
77.21
64.81
62.31
42.89
26.85
26.77
19.16
-0.00
TBDPSO
I
O
O
72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm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7.667
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7.428
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7.421
7.419
7.415
7.411
7.406
7.404
7.403
7.400
7.399
7.395
7.388
7.385
7.382
7.381
7.372
7.369
7.364
7.359
7.263
5.622
5.604
5.548
5.499
5.341
5.324
5.270
5.234
4.262
4.240
4.217
4.116
4.105
4.093
4.082
3.974
3.971
3.961
3.956
3.950
3.947
3.856
3.829
3.826
3.823
3.820
3.817
3.811
3.806
3.804
3.800
3.795
3.788
3.786
3.782
3.777
3.766
3.764
3.751
3.738
3.732
3.730
3.715
3.694
2.690
2.686
2.674
2.656
2.652
2.634
2.480
2.467
2.460
2.446
2.433
2.426
2.049
1.837
1.829
1.820
1.811
1.803
1.794
1.279
1.261
1.243
1.052
1.038
0.899
0.883
0.866
0.839
0.821
0.804
0.787
-0.000
TBDPSO
O
O
N
O
O
O
73
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.00
6.11
0.98
0.09
0.08
1.00
1.99
1.08
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2.06
5.27
1.02
1.02
1.17
0.26
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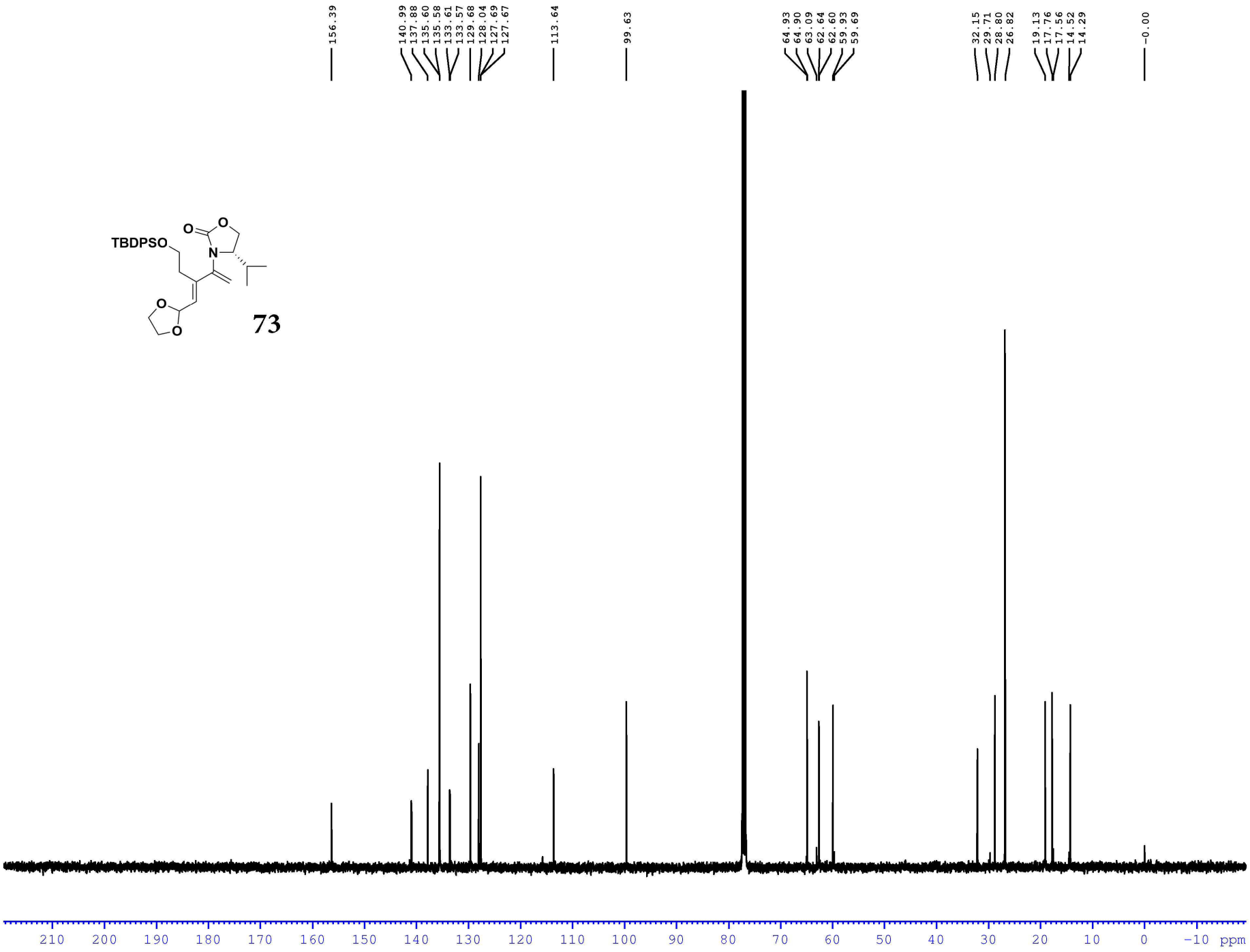
0.74
6.07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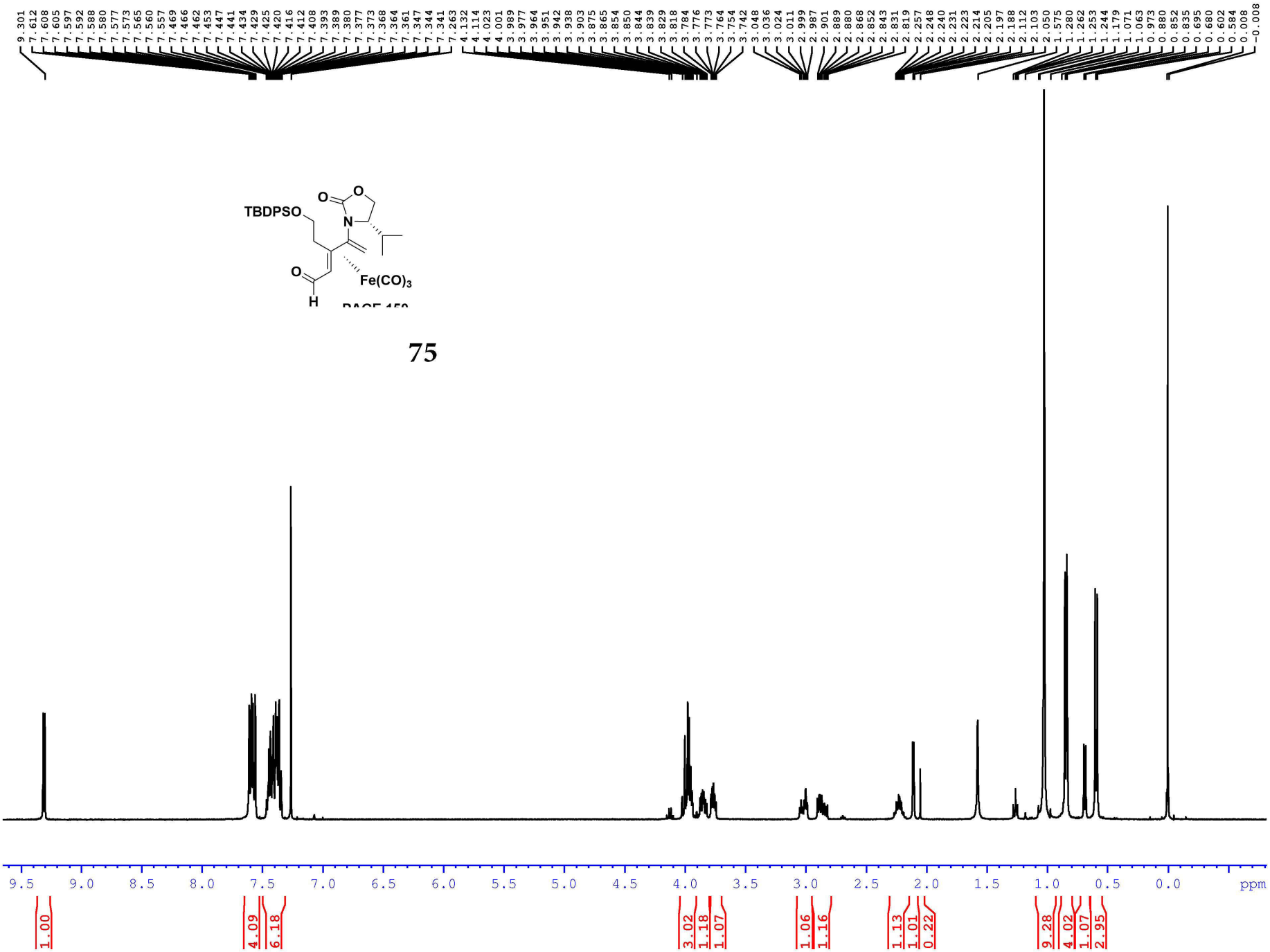
133.57
129.68
128.04
127.69
127.67
113.64
99.63
64.93
64.90
63.09
62.64
62.60
59.93
59.69
32.15
29.71
28.80
26.82
19.13
17.76
17.56
14.52
14.29
-0.00
TBDPSO
O
O
N
O
O
O
73
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm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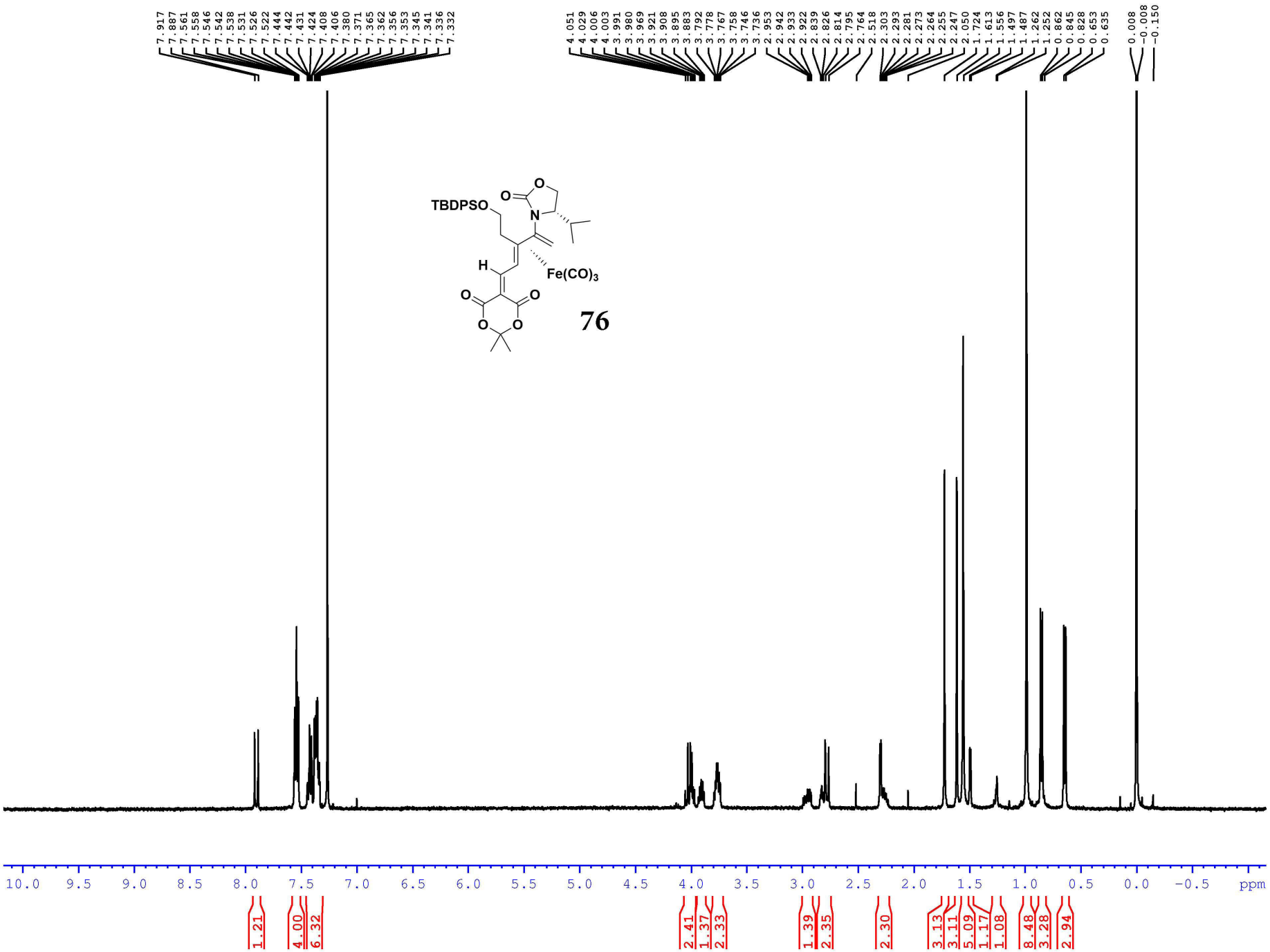
7.608
7.605
7.597
7.592
7.588
7.580
7.577
7.573
7.565
7.560
7.557
7.469
7.466
7.462
7.453
7.447
7.441
7.434
7.429
7.425
7.420
7.416
7.412
7.408
7.393
7.389
7.380
7.377
7.373
7.368
7.364
7.361
7.347
7.344
7.341
7.263
4.132
4.114
4.023
4.001
3.989
3.977
3.964
3.951
3.942
3.938
3.903
3.875
3.865
3.854
3.850
3.844
3.839
3.829
3.818
3.784
3.776
3.773
3.764
3.754
3.742
3.048
3.036
3.024
3.011
2.999
2.987
2.901
2.889
2.880
2.868
2.852
2.843
2.831
2.819
2.257
2.248
2.240
2.231
2.223
2.214
2.205
2.197
2.188
2.112
2.103
2.050
1.575
1.280
1.262
1.253
1.244
1.179
1.071
1.063
0.973
0.880
0.852
0.835
0.695
0.680
0.602
0.584
0.008
−0.008
TBDPSO
O
O
N
O
H
Fe(CO)3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
4.09
6.18
3.02
1.18
1.07
1.06
1.16
1.13
1.01
0.22
9.28
4.02
1.07
2.95

75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7.442
7.431
7.424
7.408
7.406
7.380
7.371
7.365
7.362
7.356
7.353
7.345
7.341
7.336
7.332
4.051
4.029
4.006
4.003
3.991
3.980
3.969
3.921
3.908
3.895
3.883
3.792
3.778
3.767
3.758
3.746
3.736
2.953
2.942
2.933
2.922
2.839
2.826
2.814
2.795
2.764
2.518
2.303
2.293
2.281
2.273
2.264
2.255
2.247
2.050
1.724
1.613
1.556
1.497
1.487
1.262
1.252
0.862
0.845
0.828
0.653
0.635
0.008
-0.008
-0.150
TBDPSO
O
O
N
H
Fe(CO)3
O
O
O
O
76
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
1.21
4.00
6.32
2.41
1.37
2.33
1.39
2.35
2.30
3.13
3.11
5.09
1.17
1.08
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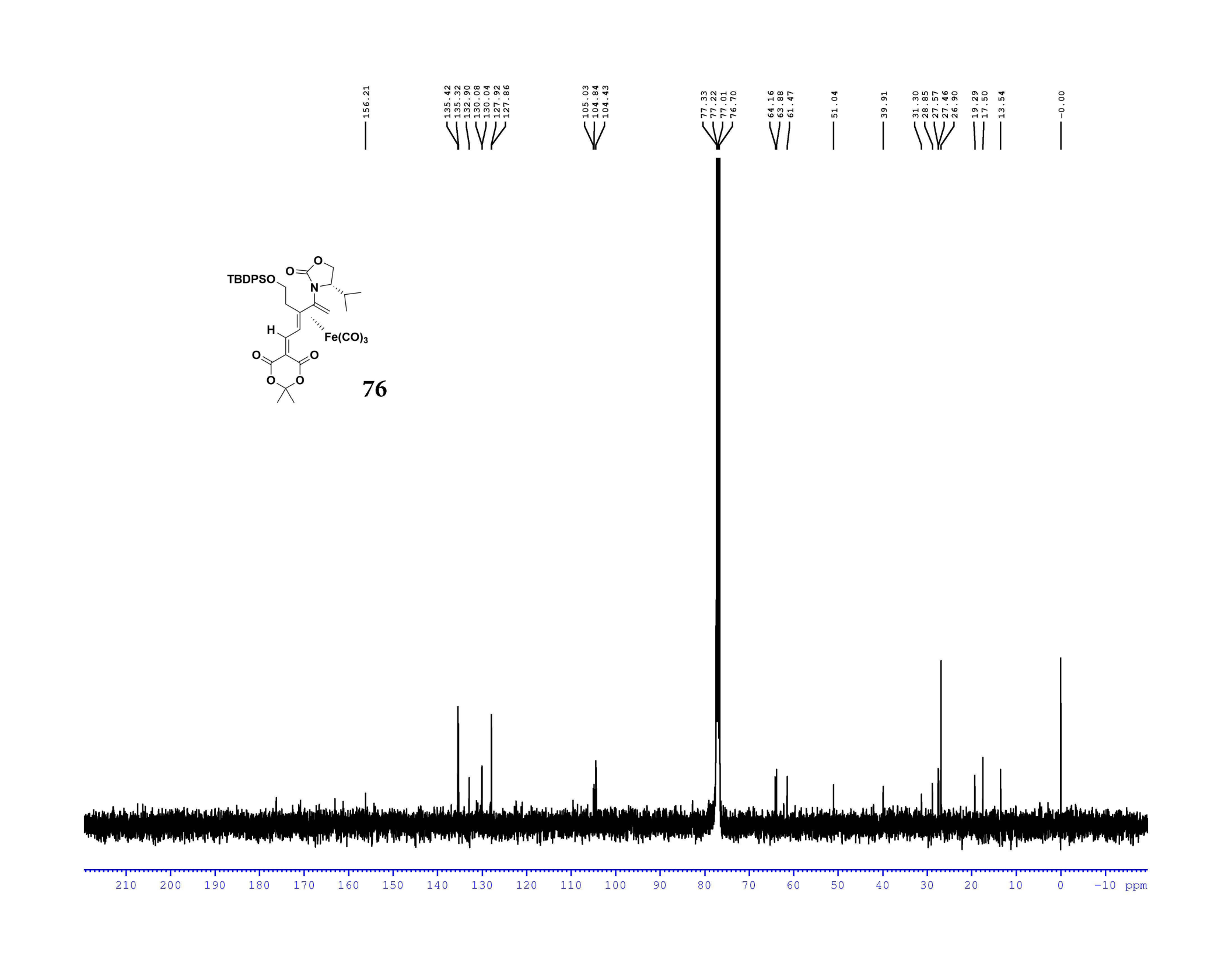
3.28
2.94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130.04
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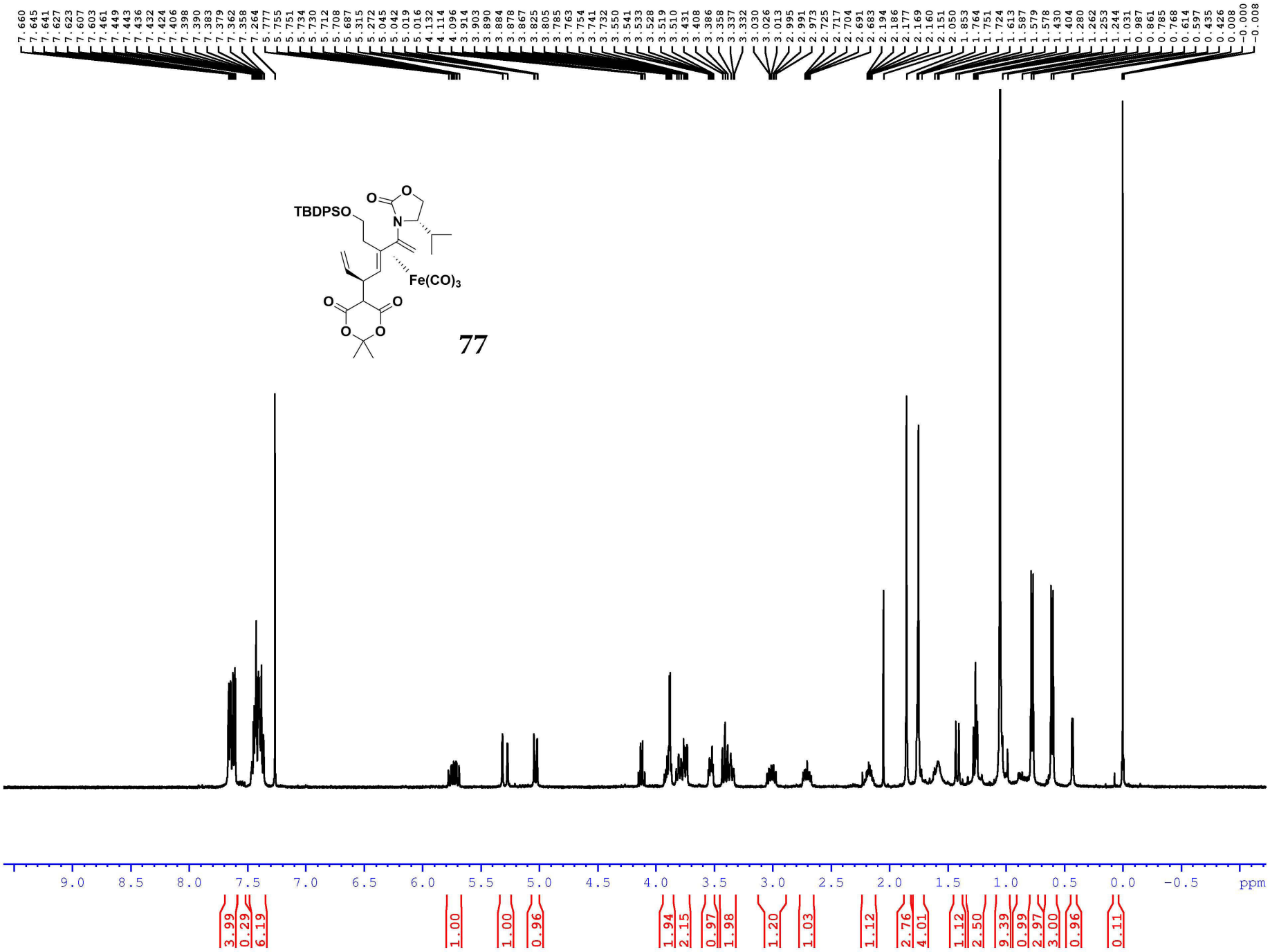
127.86
105.03
104.84
104.43
77.33
77.22
77.01
76.70
64.16
63.88
61.47
51.04
39.91
31.30
28.85
27.57
27.46
26.90
19.29
17.50
13.54
-0.00
TBDPSO
O
O
N
H
Fe(CO)3
O
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

76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7.443
7.436
7.432
7.424
7.406
7.398
7.390
7.383
7.379
7.362
7.358
7.264
5.777
5.755
5.751
5.734
5.730
5.712
5.708
5.687
5.315
5.272
5.045
5.042
5.019
5.016
4.132
4.114
4.096
3.914
3.903
3.890
3.884
3.878
3.867
3.825
3.805
3.785
3.763
3.754
3.741
3.732
3.550
3.541
3.533
3.528
3.519
3.510
3.431
3.408
3.386
3.358
3.337
3.332
3.030
3.026
3.013
2.995
2.991
2.973
2.725
2.717
2.704
2.691
2.683
2.194
2.186
2.177
2.169
2.160
2.151
2.050
1.853
1.764
1.751
1.724
1.613
1.587
1.579
1.578
1.430
1.404
1.280
1.262
1.253
1.244
1.031
0.987
0.861
0.785
0.768
0.614
0.597
0.435
0.426
0.008
-0.000
-0.008
TBDPSO
O
O
N
Fe(CO)3
O
O
O
O
77
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
3.99
0.29
6.19
1.00
1.00
0.96
1.94
2.15
0.97
1.98
1.20
1.03
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4.01
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0.99
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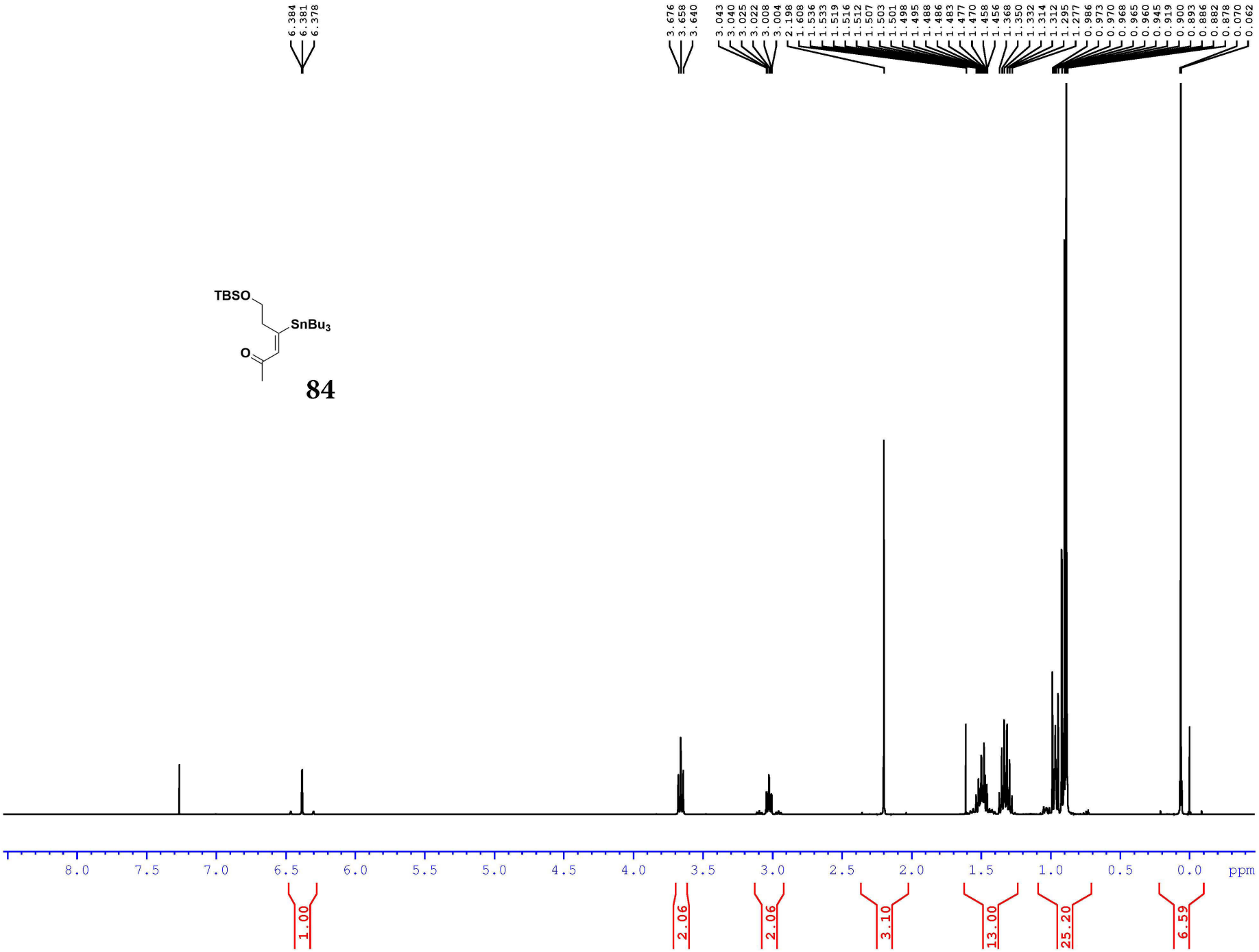
3.00
0.96
0.11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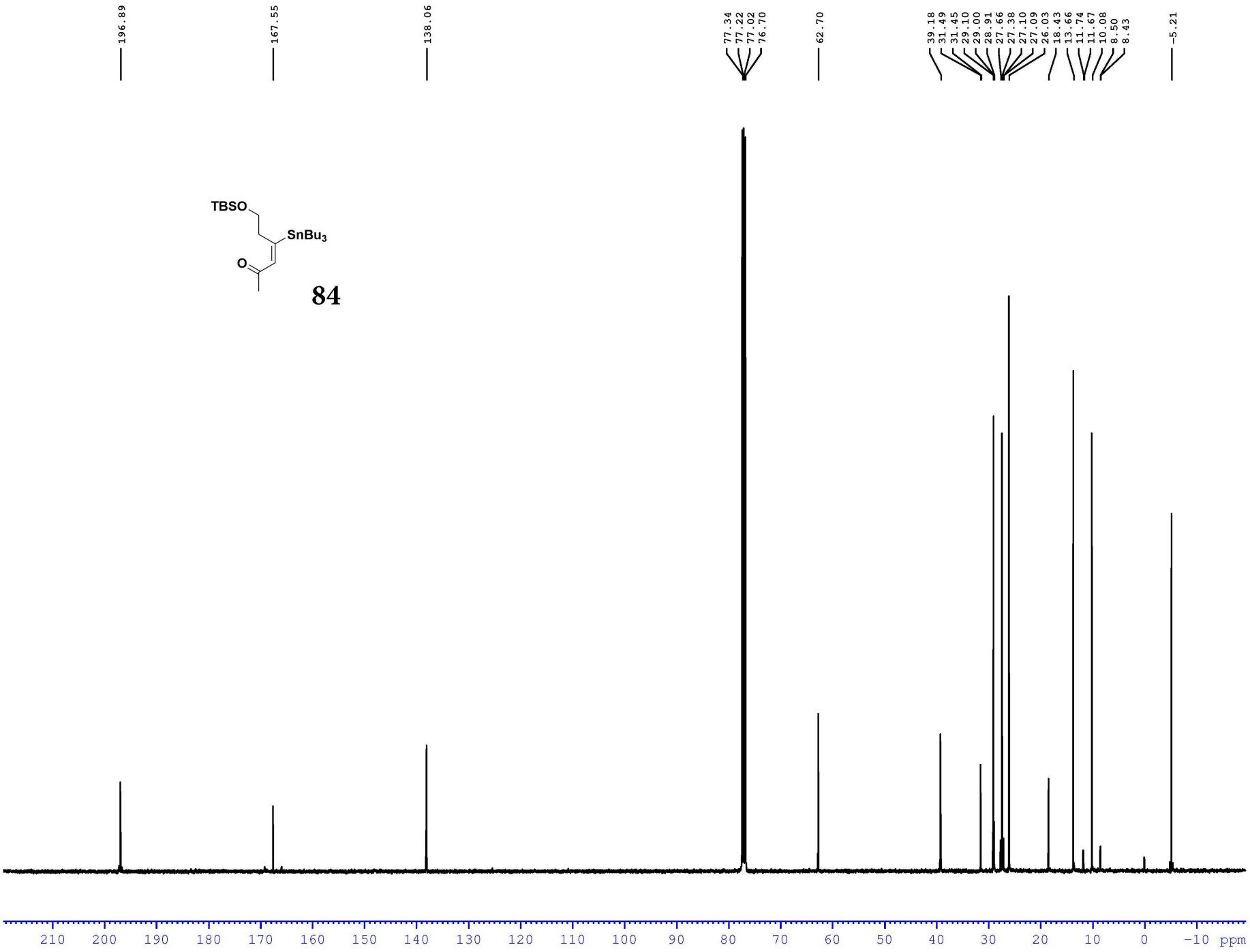
3.640
3.043
3.040
3.025
3.022
3.008
3.004
2.198
1.608
1.536
1.533
1.519
1.516
1.512
1.507
1.503
1.501
1.498
1.495
1.488
1.486
1.483
1.477
1.470
1.458
1.456
1.368
1.350
1.332
1.314
1.312
1.295
1.277
0.986
0.973
0.970
0.968
0.965
0.960
0.945
0.919
0.900
0.893
0.886
0.882
0.878
0.070
0.062
TBSO
SnBu3
O
84
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.06
2.06
3.10
13.00
25.20
6.59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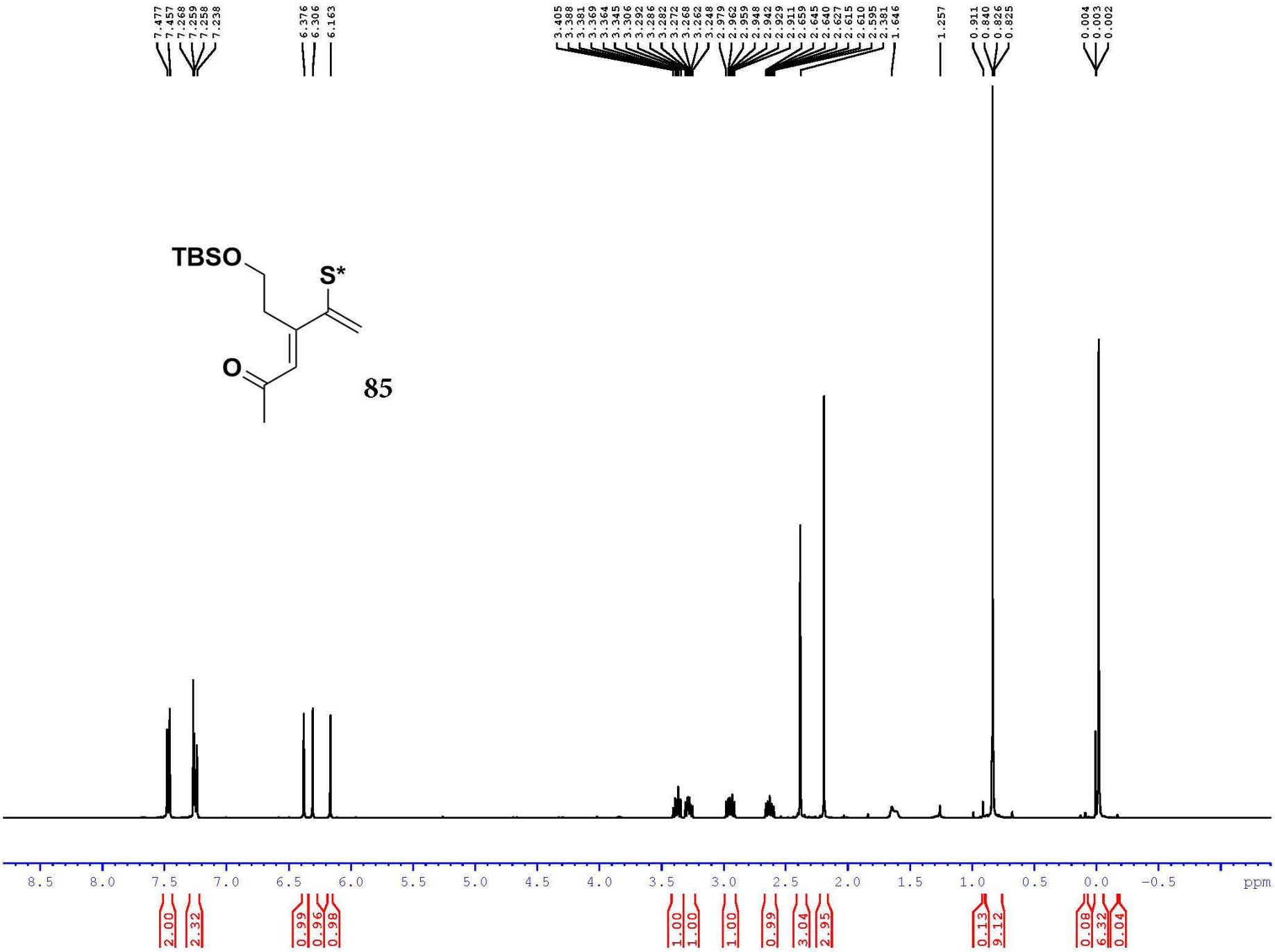
167.55
138.06
77.34
77.22
77.02
76.70
62.70
39.18
31.49
31.45
29.10
29.00
28.91
27.66
27.38
27.10
27.09
26.03
18.43
13.66
11.74
11.67
10.08
8.50
8.43
-5.21
TBSO
SnBu3
O
84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm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7.259
7.258
7.238
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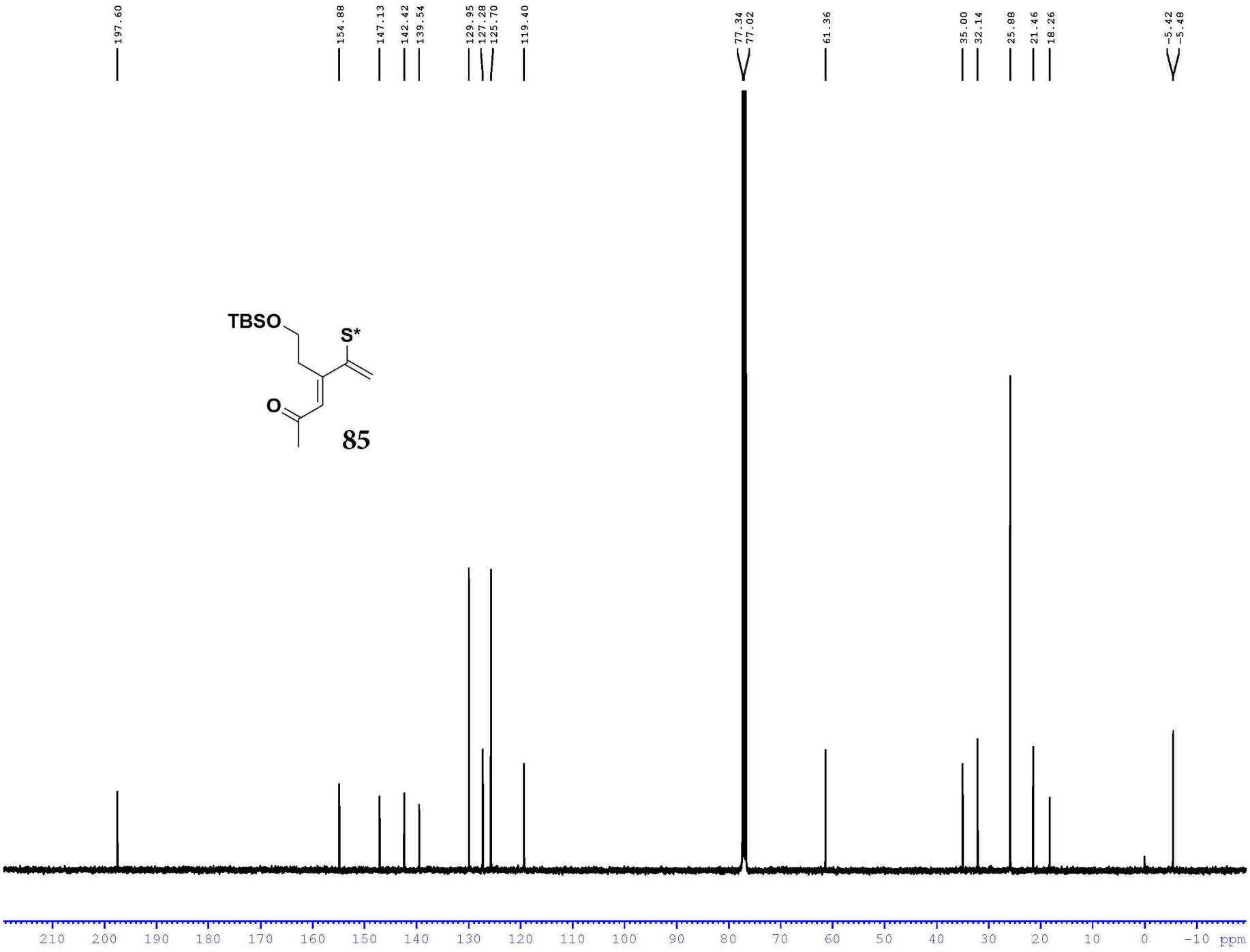
6.306
6.163
3.405
3.388
3.381
3.369
3.364
3.345
3.306
3.292
3.286
3.282
3.272
3.268
3.262
3.248
2.979
2.962
2.959
2.948
2.942
2.929
2.911
2.659
2.645
2.640
2.627
2.615
2.610
2.595
2.381
1.646
1.257
0.911
0.840
0.826
0.825
0.004
0.003
0.002
TBSO
S*
O
85
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
2.00
2.32
0.99
0.96
0.98
1.00
1.00
1.00
0.99
3.04
2.95
0.13
9.12
0.08
6.32
0.04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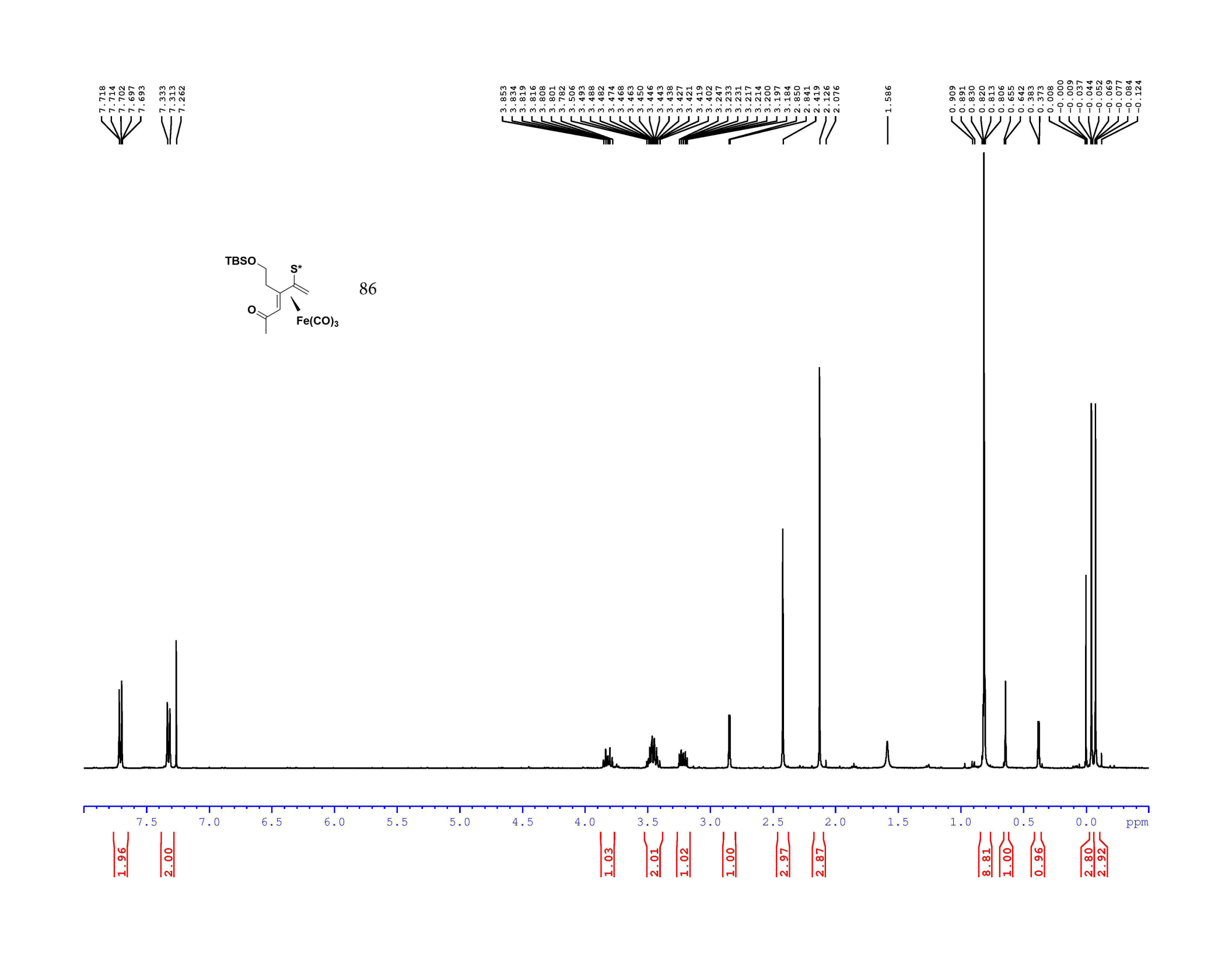
154.88
147.13
142.42
139.54
129.95
127.28
125.70
119.40
77.34
77.02
61.36
35.00
32.14
25.88
21.46
18.26
-5.42
-5.48
TBSO
S*
O
85
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm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7.693
7.333
7.313
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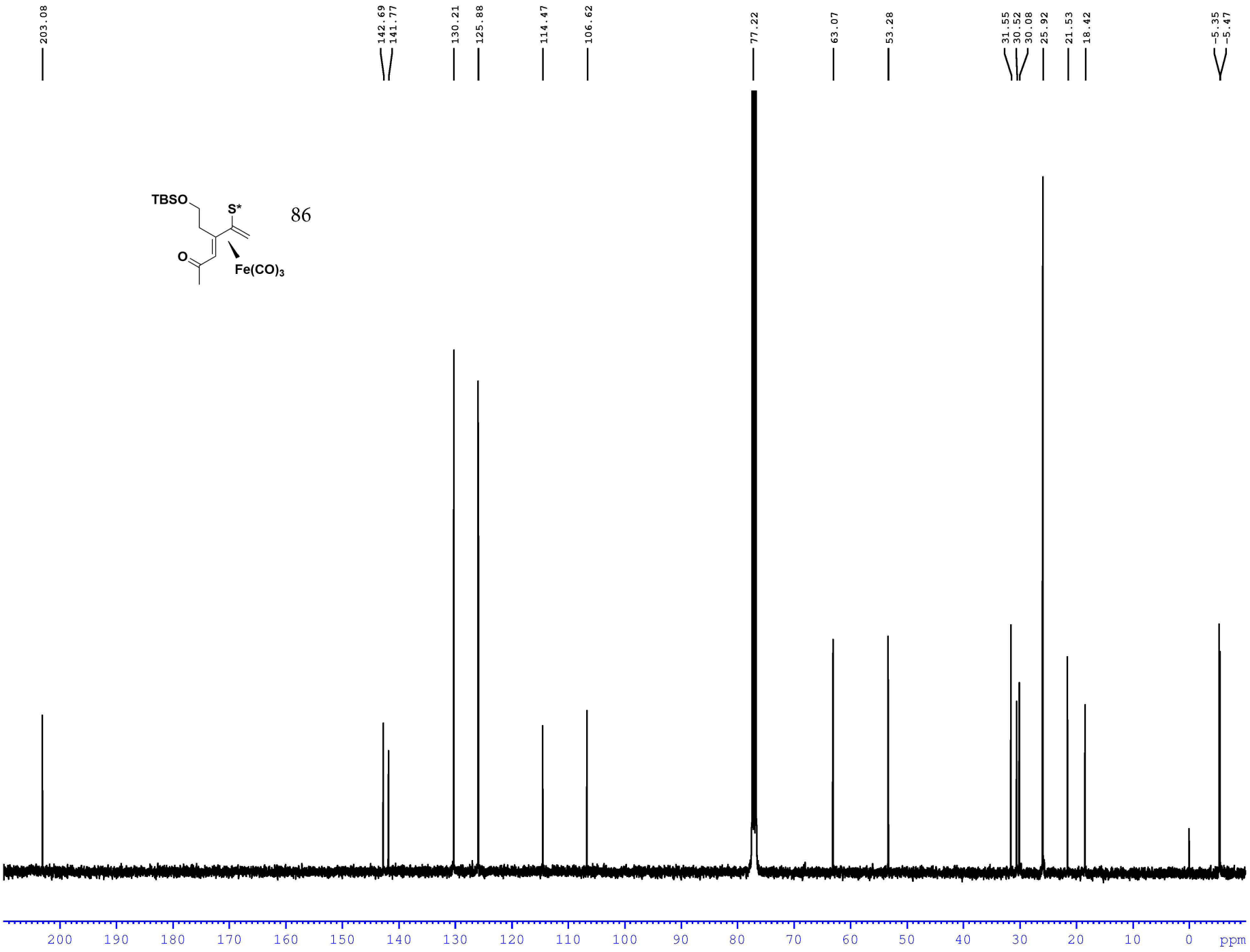
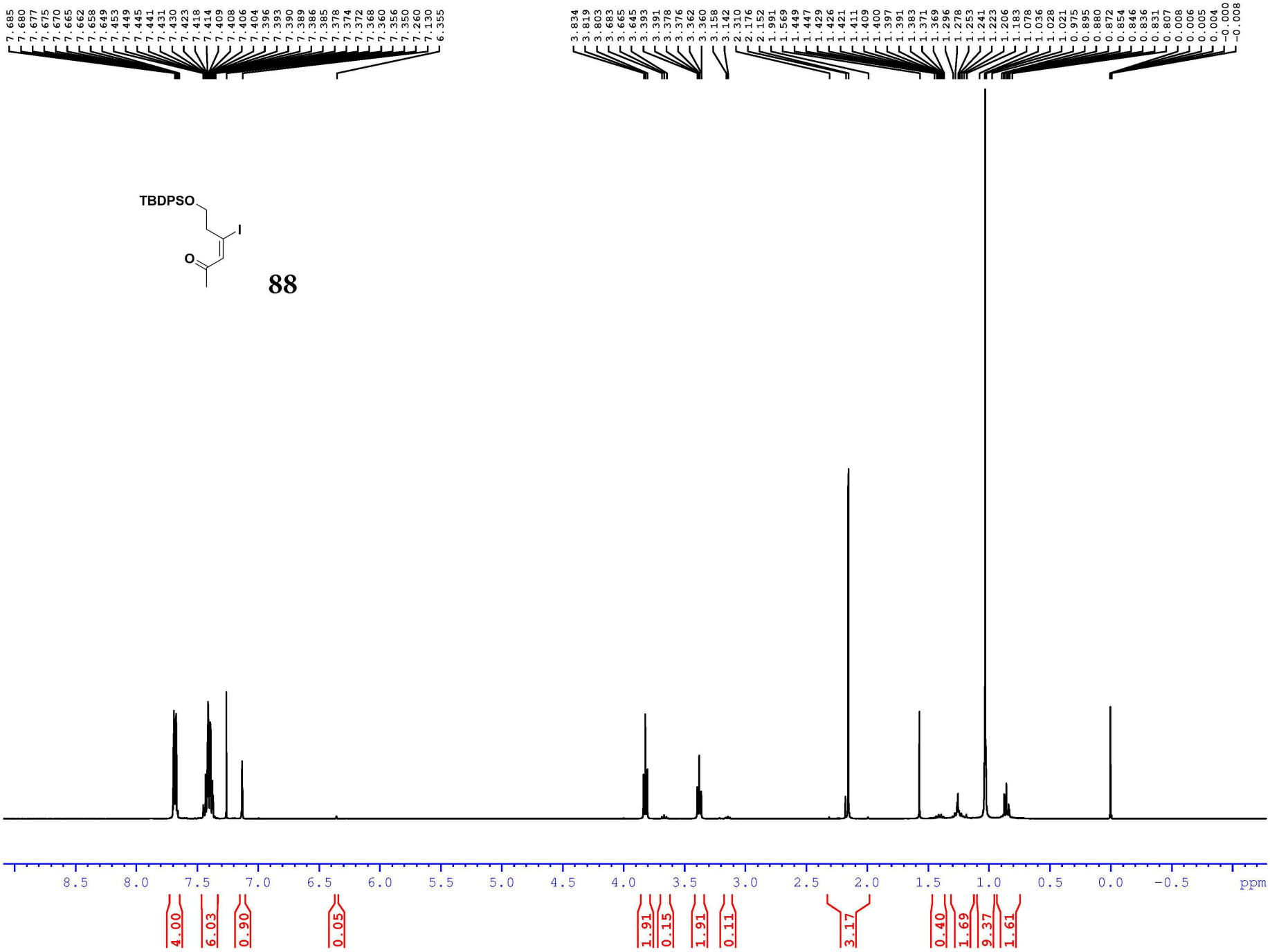
3.834
3.819
3.816
3.808
3.801
3.782
3.506
3.493
3.488
3.482
3.474
3.468
3.463
3.450
3.446
3.443
3.438
3.427
3.421
3.419
3.402
3.247
3.233
3.231
3.217
3.214
3.200
3.197
3.184
2.850
2.841
2.419
2.126
2.076
1.586
0.909
0.891
0.830
0.820
0.813
0.806
0.655
0.642
0.383
0.373
0.008
-0.000
-0.009
-0.037
-0.044
-0.052
-0.069
-0.077
-0.084
-0.124
TBSO
S*
O
Fe(CO)3
86
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.96
2.00
1.03
2.01
1.02
1.00
2.97
2.87
8.81
1.00
0.96
2.80
2.92


203.08
142.69
141.77
130.21
125.88
114.47
106.62
77.22
63.07
53.28
31.55
30.52
30.08
25.92
21.53
18.42
-5.35
-5.47
TBSO
S*
O
Fe(CO)3
86
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.431
7.430
7.423
7.418
7.414
7.409
7.408
7.406
7.404
7.396
7.393
7.390
7.389
7.386
7.385
7.378
7.374
7.372
7.368
7.360
7.356
7.350
7.260
7.130
6.355
3.834
3.819
3.803
3.683
3.665
3.645
3.393
3.391
3.378
3.376
3.362
3.360
3.158
3.142
2.310
2.176
2.152
1.991
1.569
1.449
1.447
1.429
1.426
1.421
1.411
1.409
1.400
1.397
1.391
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1.369
1.296
1.278
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1.241
1.223
1.206
1.183
1.078
1.036
1.028
1.021
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0.880
0.872
0.854
0.846
0.836
0.831
0.807
0.008
0.006
0.005
0.004
-0.000
-0.008
TBDPSO
I
O
88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
4.00
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0.05
1.91
0.15
1.91
0.11
3.17
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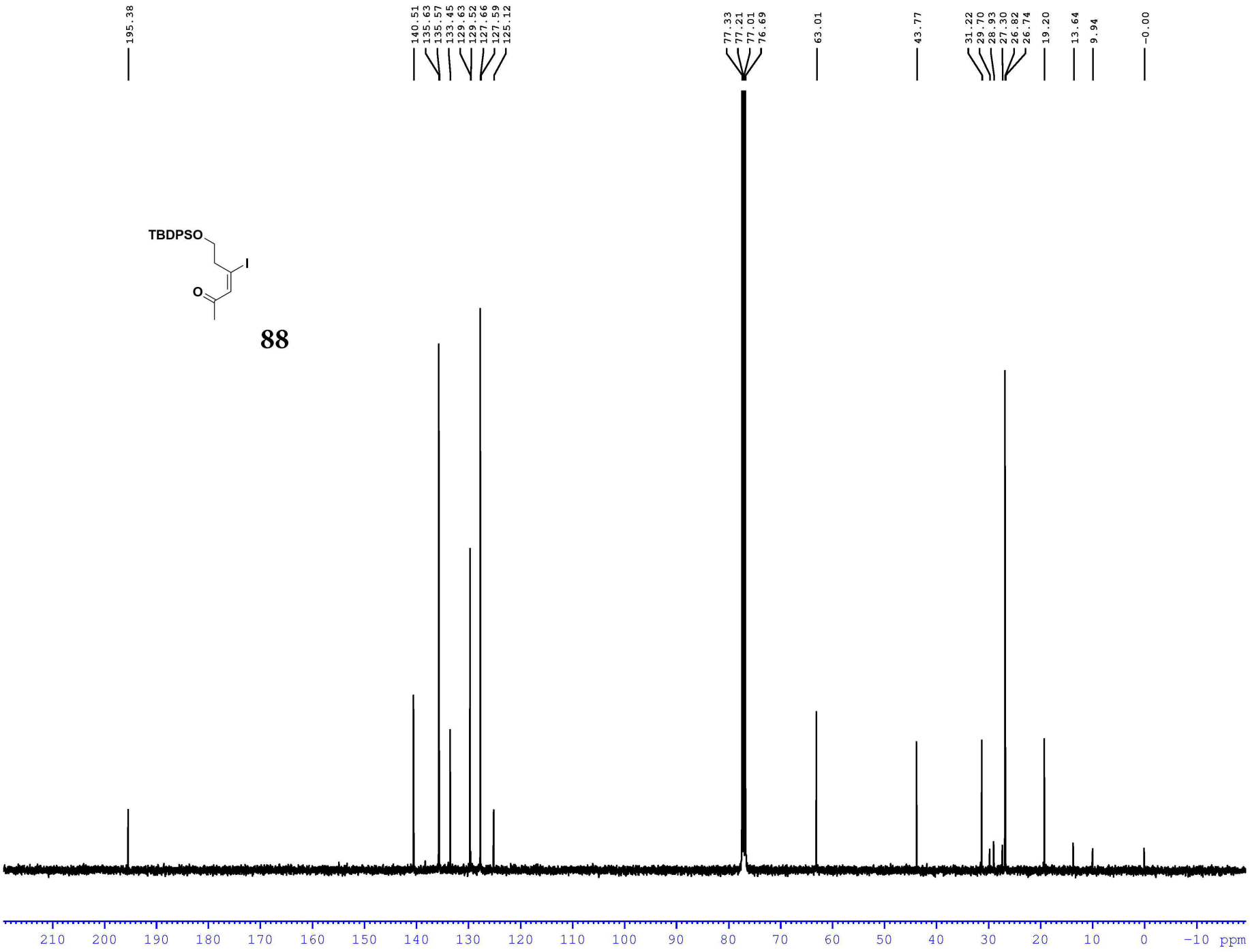
1.61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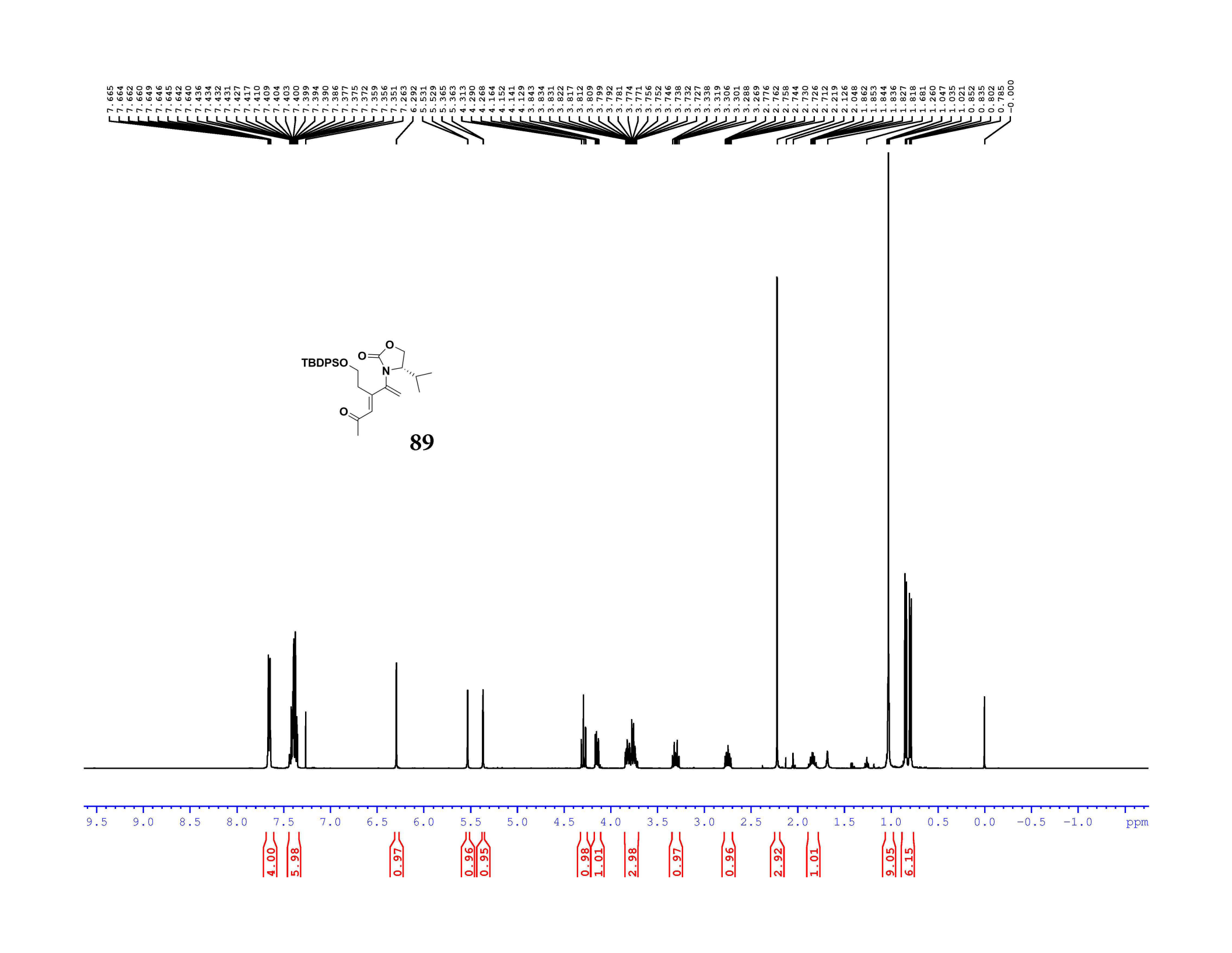
129.52
127.66
127.59
125.12
77.33
77.21
77.01
76.69
63.01
43.77
31.22
29.70
28.93
27.30
26.82
26.74
19.20
13.64
9.94
-0.00
TBDPSO
I
O
88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm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7.427
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7.409
7.404
7.403
7.400
7.399
7.394
7.390
7.386
7.377
7.375
7.372
7.359
7.356
7.351
7.263
6.292
5.531
5.529
5.365
5.363
4.313
4.290
4.268
4.164
4.152
4.141
4.129
3.843
3.834
3.831
3.822
3.817
3.812
3.809
3.799
3.792
3.781
3.774
3.771
3.756
3.752
3.746
3.738
3.732
3.727
3.338
3.319
3.306
3.301
3.288
3.269
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2.758
2.744
2.730
2.726
2.712
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1.827
1.818
1.681
1.260
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1.035
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0.852
0.835
0.802
0.785
-0.000
TBDPSO
O
O
N
O
89
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm
4.00
5.98
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0.98
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0.96
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1.01
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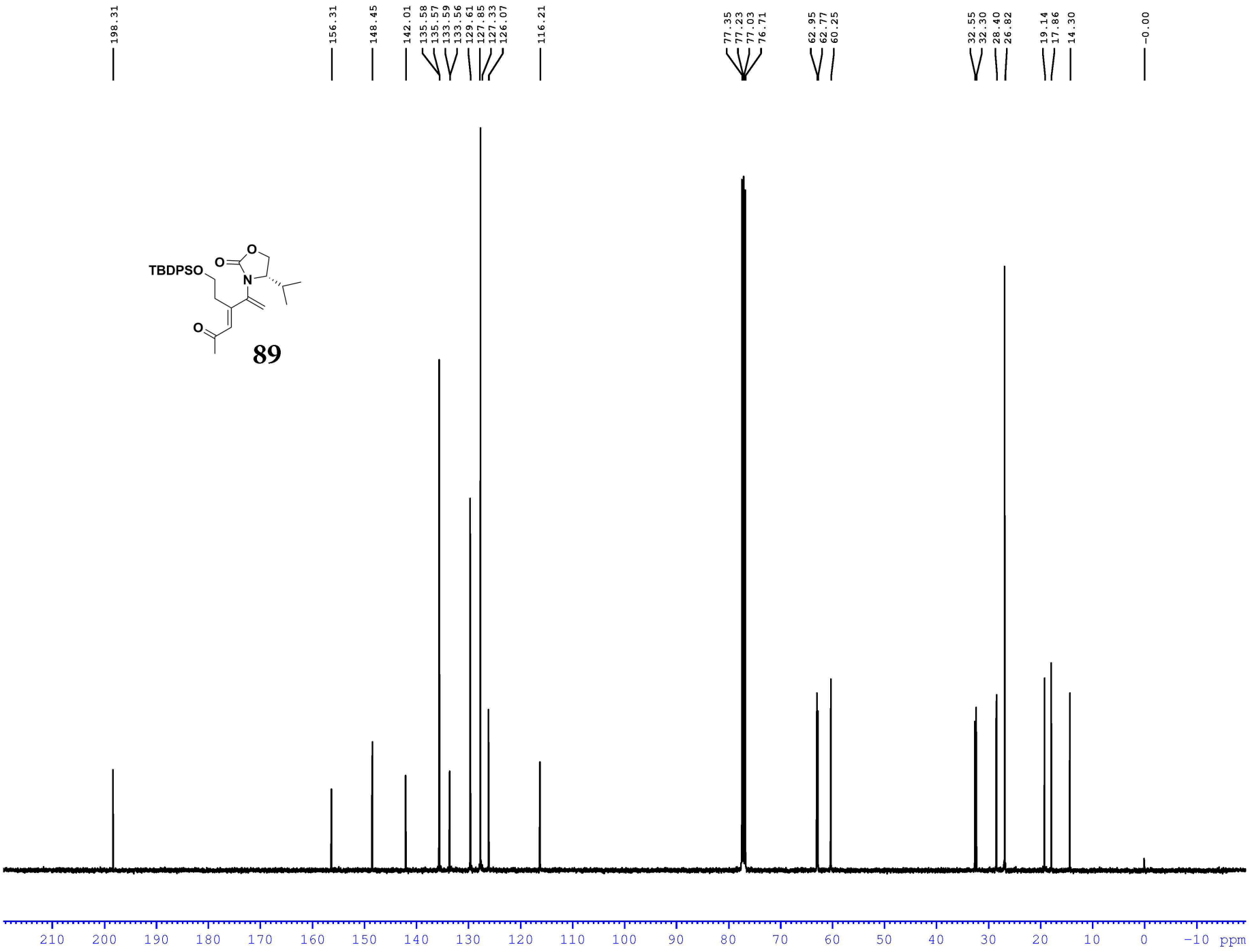
6.15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133.56
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127.33
126.07
116.21
77.35
77.23
77.03
76.71
62.95
62.77
60.25
32.55
32.30
28.40
26.82
19.14
17.86
14.30
-0.00
TBDPSO
O
O
N
O
89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
10
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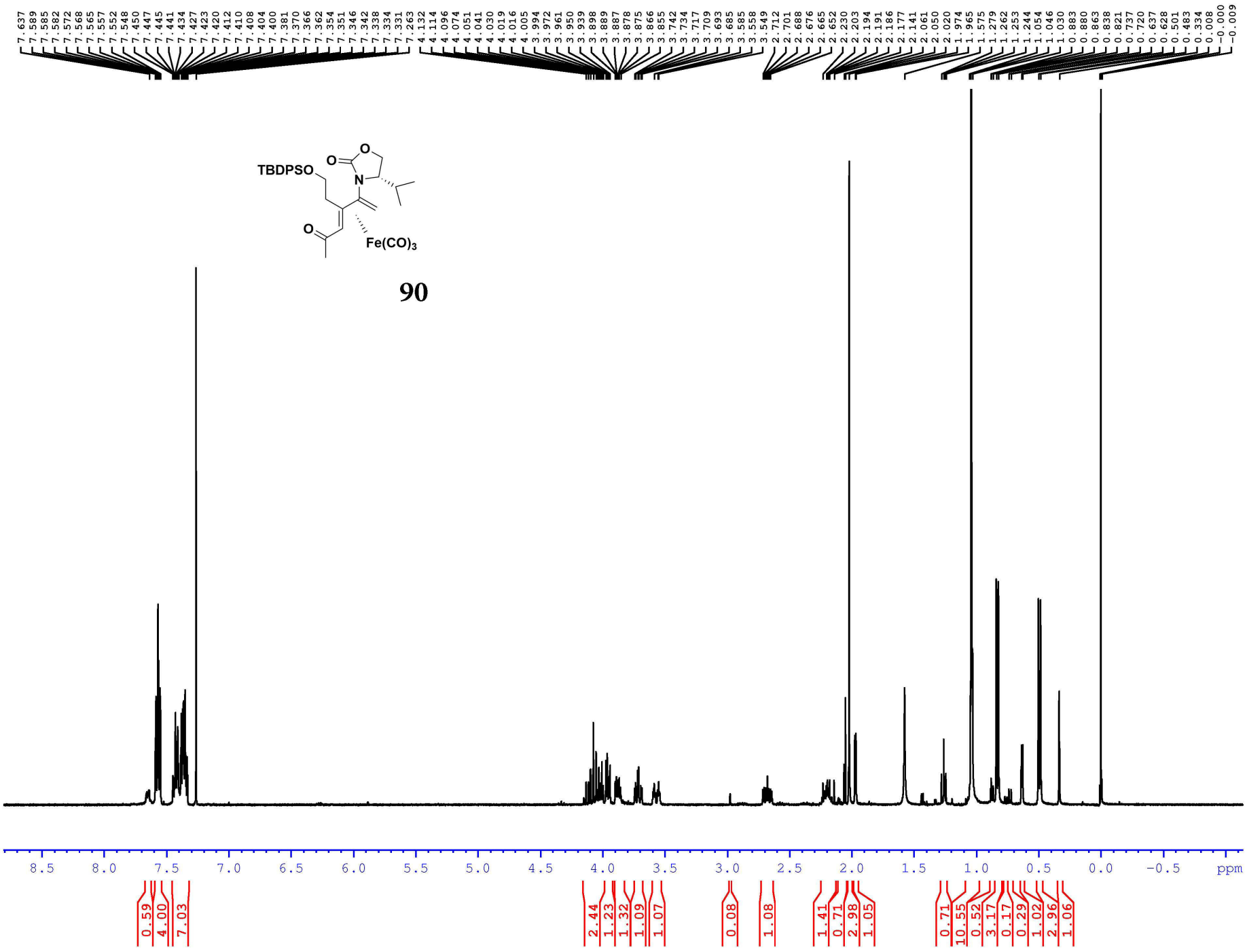
ppm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O
N
O
Fe(CO)3
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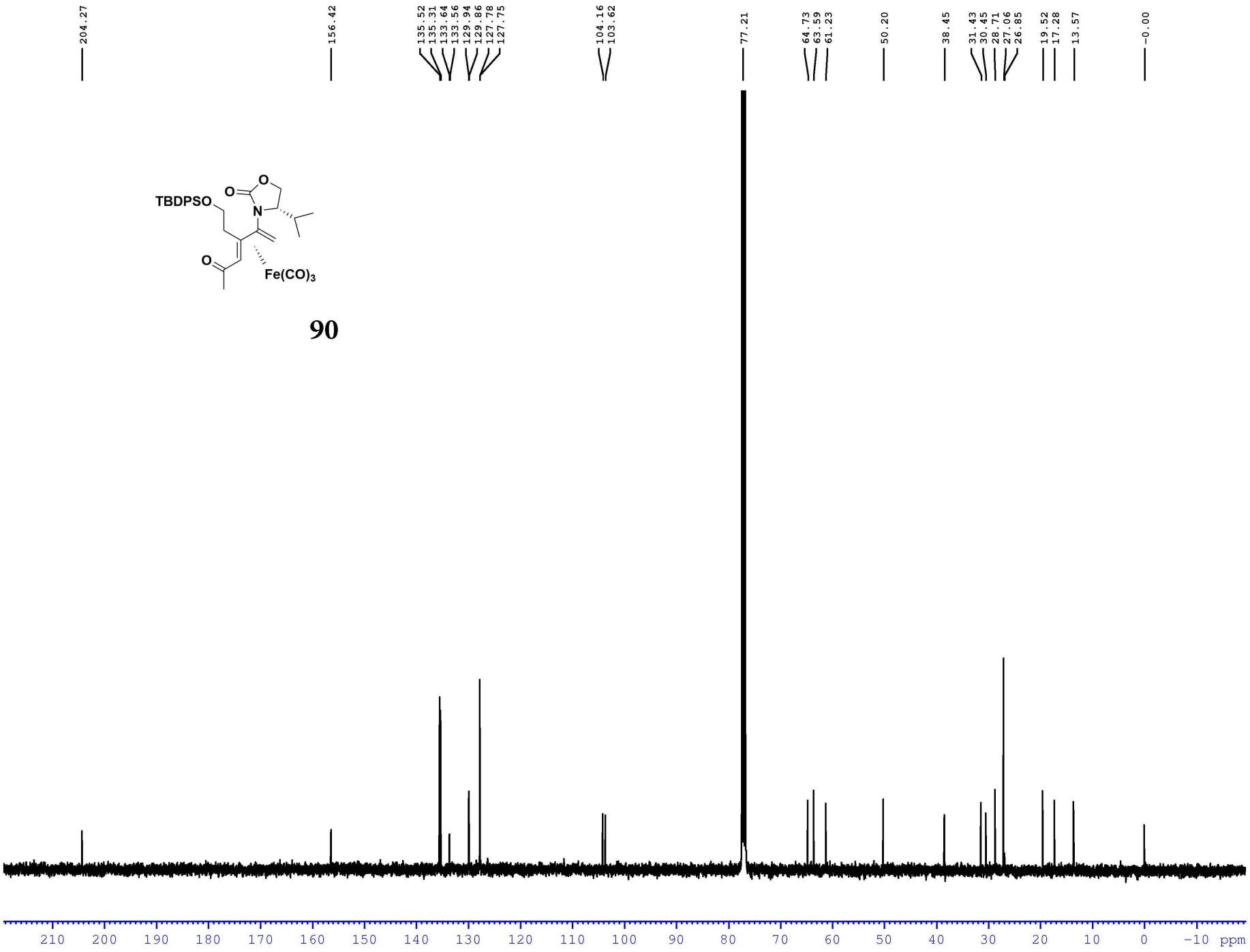
ppm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133.56
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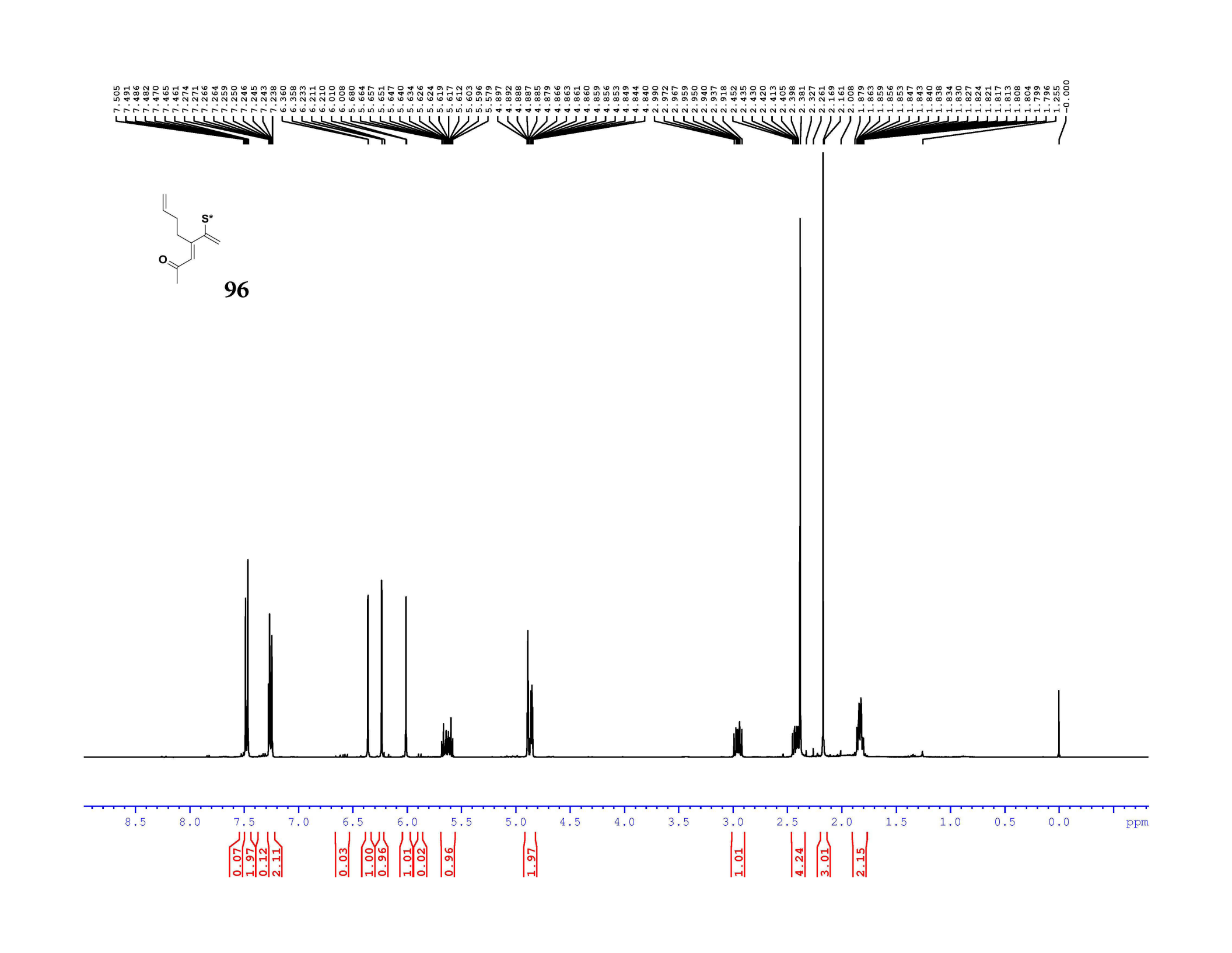
129.86
127.78
127.75
104.16
103.62
77.21
64.73
63.59
61.23
50.20
38.45
31.43
30.45
28.71
27.06
26.85
19.52
17.28
13.57
-0.00
TBDPSO
O
O
N
O
Fe(CO)3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

90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7.250
7.246
7.245
7.243
7.238
6.360
6.358
6.233
6.211
6.210
6.010
6.008
5.680
5.664
5.657
5.651
5.647
5.640
5.634
5.626
5.624
5.619
5.617
5.612
5.603
5.596
5.579
4.897
4.892
4.888
4.887
4.885
4.879
4.866
4.863
4.861
4.860
4.859
4.856
4.853
4.849
4.844
4.840
2.990
2.972
2.967
2.959
2.950
2.940
2.937
2.918
2.452
2.435
2.430
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2.405
2.398
2.381
2.327
2.261
2.169
2.161
2.008
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1.863
1.859
1.856
1.853
1.847
1.843
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1.838
1.834
1.830
1.827
1.824
1.821
1.817
1.813
1.808
1.804
1.799
1.796
1.255
-0.000
S*
O
96
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.07
1.97
0.12
2.11
0.03
1.00
0.96
1.01
0.02
0.96
1.97
1.01
4.24
3.01
2.15