Preparation of Organoboronates through Nickel-Catalyzed Conjunctive Coupling Reactions and Their Applications:

Author: Seung Moh Koo

Preparation of Organoboronates through Nickel-Catalyzed Conjunctive Coupling Reactions and Their Applications

Seung Moh Koo

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Preparation of Organoboronates through Nickel-Catalyzed Conjunctive Coupling Reactions and Their Applications

Seung Moh Koo

Advisor: Professor James P. Morken

Abstract: This thesis will describe the development of two transition metal catalyzed syntheses of organoboronic compounds. The first section describes relevant concepts and precedents for the conjunctive coupling reaction. In the second section of this thesis, nickel catalyzed conjunctive coupling reaction of carboxylic acid derivatives with 9-BBN derived ate complexes will be discussed, where β-trialkylboryl ketones are obtained as the product. In the third section, the development of alkyl group migration in nickel-catalyzed conjunctive coupling with $C(sp^3)$ electrophiles will be discussed. Enantioenriched secondary boronic esters can be prepared from this reaction, and two alkaloid syntheses are disclosed as the application of the method.

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List of Abbreviations

dr = diastereomeric ratio

er = enantiomeric ratio

ee = enantiomeric excess

pin = pinacol

neo = neopentyl glycol

mac = methylated acenaphthoquinone

9-BBN = 9-borabicyclo[3.3.1]nonane

n-Hex = *n*-hexyl

n-Bu = *n*-butyl

i-Pr = isopropyl

t-Bu = *tert*-butyl

Cy = cyclohexyl

THF = tetrahydrofuran

DMSO = dimethylsulfoxide

TMEDA = tetramethylethylenediamine

o-Tol = ortho-tolyl

Boc = *tert*-butoxycarbonyl

Bn = benzyl

Bz = benzoyl

Ph = phenyl

BOx = bis(oxazoline)

PyBOx = pyridine bis(oxazoline)

eq. = equation

equiv. = equivalence

EtOAc = ethyl acetate

DCM, or CH_2Cl_2 = dichloromethane

NMR = nuclear magnetic resonance

ppm = parts per million

HRMS = high resolution mass spectrometry

SFC = supercritical fluid chromatography

temp = temperature

min = minutes

h = hours

$C(sp^3)$ = electrophile bearing reactive site on the sp^3 hybridized carbon

α = alpha

β = beta

M = molar

rt = room temperature (generally 22 °C)

Et_2O = diethyl ether

rac = racemic

Acknowledgments

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I'd like to also thank all of Morken group members for many helpful discussion of chemistry during my time in the lab. I'd like to thank Adam, Marshall, Sheila, Alex, and Charlie for making days in lab more enjoyable. Outside of our group members, I'd like to thank Jaehee and KyungA for being great mentors and being supportive over the years. I'd like to also thank BC chemistry department staff members—Dale, Lynne, Ian and TJ—for helping me troubleshoot problems whether chemistry related or not.

Lastly, I'd like to thank my family members; my parents and my brother for all of the encouragements and support they have given to me.

1. Introduction

Since the development of palladium catalyzed cross-coupling reactions,[1] transition metal catalyzed reactions have become widely adopted both in academia as well as in industry, becoming an integral part of modern organic chemistry as they enable challenging carbon-carbon and carbon-heteroatom bond formation by coupling nucleophilic and electrophilic species together. The Nobel Prize in Chemistry in 2010 was jointly awarded to Heck, Negishi, and Suzuki, "for palladium-catalyzed cross couplings in organic synthesis"[2] which highlights the contribution of transition metal catalysis to the organic chemistry today.

Among many classes of compounds, organoboron species are widely used motifs due to their versatile reactivity. For instance, carbon-boron bond in organoboron species can be stereospecifically transformed into carbon-carbon or carbon-heteroatom bonds.[3] Moreover, organoboronates can be used in Suzuki-Miyaura cross-coupling reactions.[4]

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[1] (a) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374., (b) Heck, R. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320. (c) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tet. Lett.* **1975**, *16*, 4467. (d) King, A. O.; Okukado, N.; Negishi, E. *J. Chem. Soc., Chem. Comm.* **1977**, *19*, 683. (e) Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636. (f) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3437.
[2] <https://www.nobelprize.org/prizes/chemistry/2010/summary/> Accessed: 3 Feb 2020.
[3] Sandford, C.; Aggarwal, V. K. *Chem. Comm.* **2017**, *53*, 5481.
[4] For review of Suzuki-Miyaura cross-coupling see: Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457

Additionally, depending on the ligand on boron, these compounds can be stable to air and moisture, unlike many other organometallic reagents such as Grignard reagents.

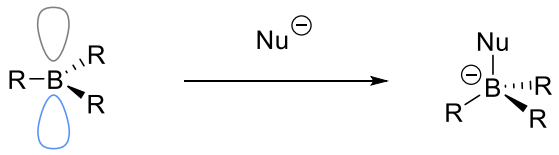
While much progress has been made, there still exists the gap where not all organoboronates are easily accessible by currently available methods. Therefore, developing preparative methods for organoboron species that start from simple starting materials is desirable. We wanted to tackle this challenge by developing transition metal catalyzed methodologies to synthesize organoboronates. Specifically, we utilized a process that was inspired from the Suzuki cross coupling reaction. In general terms, the mechanism of the Suzuki-Miyaura reaction involves oxidative addition of the transition metal catalyst into the electrophile, transmetalation of the transition metal catalyst with the organoboron reagent, and finally, reductive elimination of the C-C bonded product regenerates the catalyst to turn over the catalyst. For the newly developed conjunctive coupling reaction, instead of transmetallation of the functional group with the organoboron reagent, 1,2-metallate rearrangement of the vinyl boron ate complex enables regioselective dicarbonfunctionalization of vinyl boronates.

In this section of the thesis, the underlying reactivity principle that inspired the conjunctive coupling reaction from the organoboronates (1,2-metallate rearrangment) as well as recent advances in the conjunctive coupling reactions using palladium and nickel will be discussed. The following two sections will demonstrate our contribution to the conjunctive coupling using nickel catalysts, and will describe the synthetic utility of such methodologies by application to targets of interest.

1.1 1,2-Metallate Rearrangement

1.1.1 Background

Scheme 1.1: Reactivity of organoboronates and formation of the "ate" complex



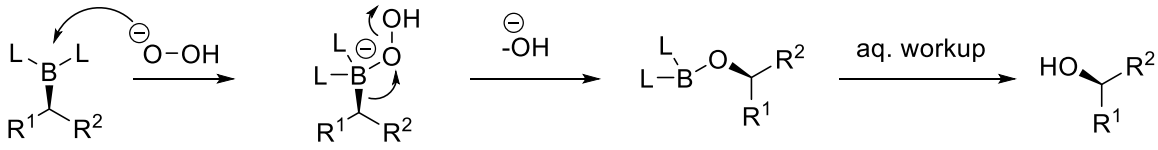
1.1 **1.2**

An organoborane **(1.1)** typically exists in a trigonal planar geometry because it can only have three bonds in its neutral form by employing its three valence electrons. As this bonding does not satisfy the full octet, the boron atom contains an empty p-orbital that is orthogonal to the sp^2-hybridized boron orbitals and can accept a pair of electrons. Lewis acidity of organoboranes originates from the tendency of the boron atom to accept a pair of electrons and achieve a full octet. Upon accepting a pair of electrons from a donor, it forms a boron "ate" complex **(1.2)**. Although the formal negative charge is on boron atom for the "ate" complex, due to differences in electronegativity, the actual distribution of electron density is generally polarized away from boron atom.[5] Typical ligands for boron are carbon (Pauling electronegativity = 2.55), oxygen (3.44), and nitrogen (3.04), all of which are more electronegative than the boron atom (2.04). The presence of electron density on the atoms adjacent to boron is considered to be the driving force that enables 1,2-metallate rearrangements.

[5] Boron is less electronegative than many of typical atoms bonded to boron.

One of the most widely used examples of 1,2-metallate rearrangment of boronic esters and boranes is the oxidation to alcohols. In 1961, Brown and coworker[6] have demonstrated that boranes can be stereoselectively oxidized by basic peroxides, where the alcohol is obtained with retention of configuration at the reacting carbon stereocenter (Scheme 1.2). It was later found that boronic esters could also be oxidized in similar manner.[7]

Scheme 1.2: 1,2-metallate rearrangement used for the oxidation of organoboronates



1.3 **1.4** **1.5** **1.6**

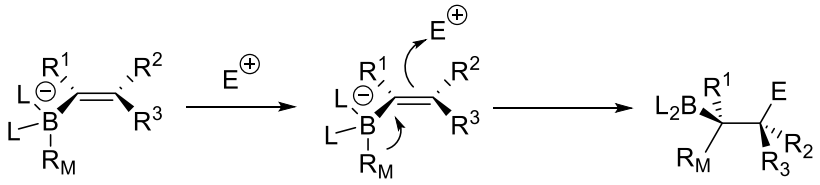
As for the mechanism, first, when a trisubstituted organoboron **(1.3)** is treated with a basic peroxide, a four coordinate boron "ate" **(1.4)** is formed by peroxide anion attack on the empty p-orbital. The "ate" complex can then undergo 1,2-metallate rearrangement, where α-carbon migrates to the adjacent oxygen atom, thereby displacing hydroxide by O-O σ-bond cleavage. Upon aqueous workup, the O-B bond is cleaved and the alcohol product **(1.6)** is obtained. It is notable that the configuration at the migrating carbon is retained, thus making this a stereospecific process. Since Brown's report, a wide variety of stereospecific transformations that replace the C-B bond with C-C bond as well as C-heteroatom bonds have been developed that take advantage of the reactivity of boron.[3]

[6] Brown, H. C.; Zweifel G. *J. Am. Chem. Soc.*, **1961**, *83*, 2544.
[7] Stymiest, J. L.; Bagutski, V.; French, R. M.; Aggarwal, V. K. *Nature* **2008**, *456*, 778.

1.1.2 1,2-Metallate Rearrangements Induced by External Electrophiles

When an alkenyl boron ate complex **(1.7)**, that lacks a leaving group is formed, the 1,2-metallate rearrangement does not occur (Scheme 1.3). However, when an appropriate external electrophile is introduced, it can induce rearrangement, leading to 1,2-difunctionalized product **1.8**.

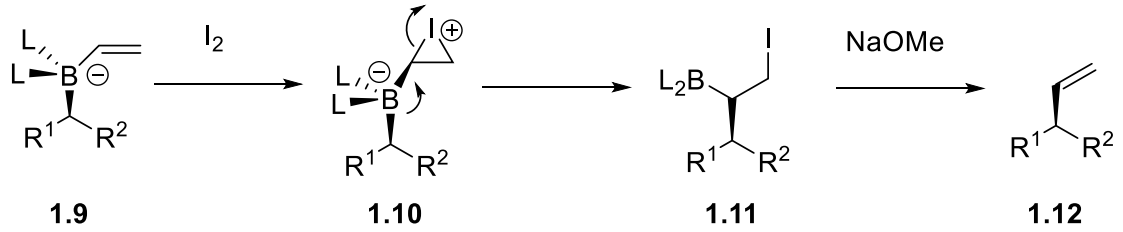
Scheme 1.3: Generalized scheme for external electrophile induced 1,2-metallate rearrangement



An example of this type of reactivity was disclosed by Zweifel and coworkers in an olefination method.[8] When an alkenyl derived boron ate complex **(1.9)** is treated with iodine, it is proposed to form an iodonium intermediate **(1.10)**, which can undergo 1,2-rearrangement to generate boryl iodide intermediate **(1.11)**. Upon treatment with sodium methoxide, B-I elimination produces terminal olefin product **(1.12)**.

[8] (a) Zweifel, G.; Arzoumanian, H.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 3652., (b) Evans, D. A.; Crawford, T. C.; Thomas, R. C.; Walker, J. A. *J. Org. Chem.* **1976**, *41*, 3947.

Scheme 1.4: Zweifel olefination

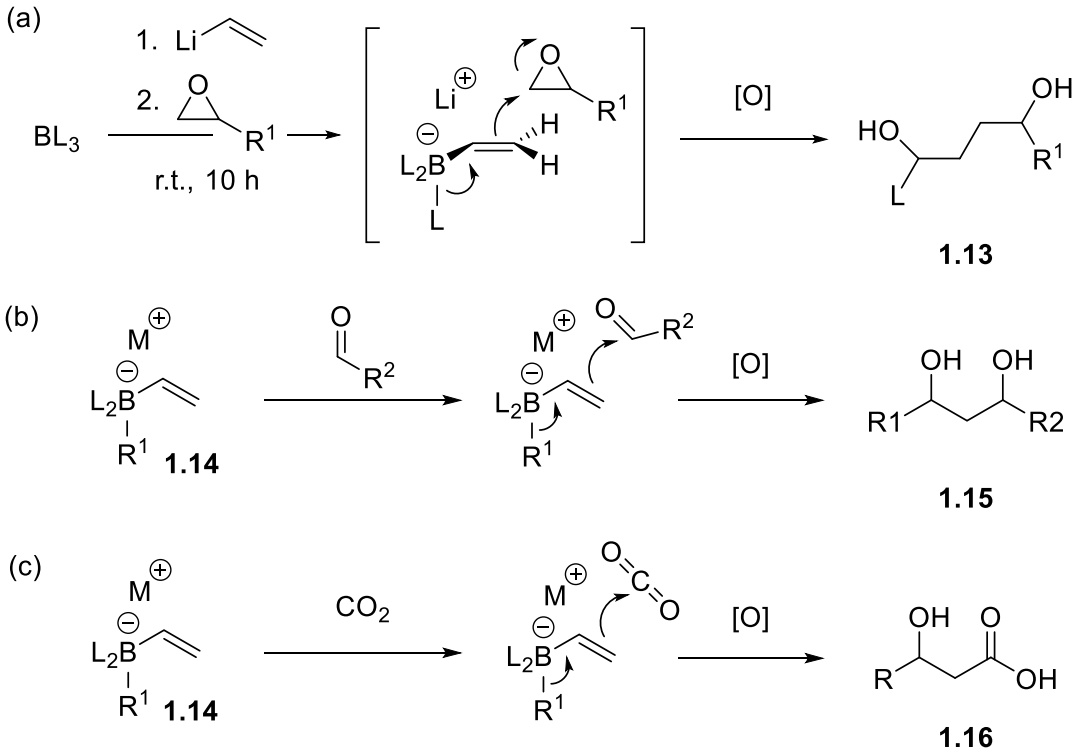


1.9 **1.10** **1.11** **1.12**

Additionally, there are examples of 1,2-metallate rearrangement induced by carbon electrophiles that proceed without the elimination of the boryl functional group. Utimoto and coworkers have reported that the ate complex derived from borane can participate in 1,2-rearrangment with epoxides[9] and aldehydes[10] to produce diols after oxidation (Scheme 1.5, (a) and (b)). Similarly, Deng and coworkers have reported that carbon dioxide can be used as the electrophile to obtain β-hydroxy carboxylic acids as the product (Scheme 1.5, (c)).[11]

[9] Utimoto, K., Uchida, K.; Nozaki, H. *Tetrahedron Lett.* **1973**, *14*, 4527.
[10] Utimoto, K.; Uchida, K.; Nozaki, H. *Tetrahedron*, **1977**, *33*, 1949.
[11] Deng, M.-Z.; Lu, D. A.; Xu, W.-H. *J. Chem. Soc. Chem. Commun.* **1985**, *21*, 1478.

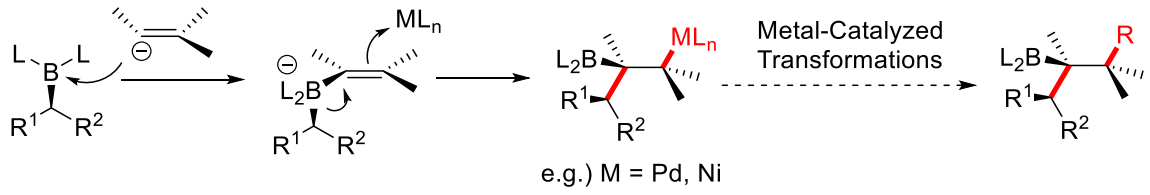
Scheme 1.5: 1,2-metallate rearrangement induced by carbon electrophiles



1.1.3 Metal-Induced 1,2-Metallate Rearrangements

As one can imagine, a transition metal species that is electron deficient may induce 1,2-rearrangement, and the product resulting from that may be used in cross coupling reactions (Scheme 1.6).

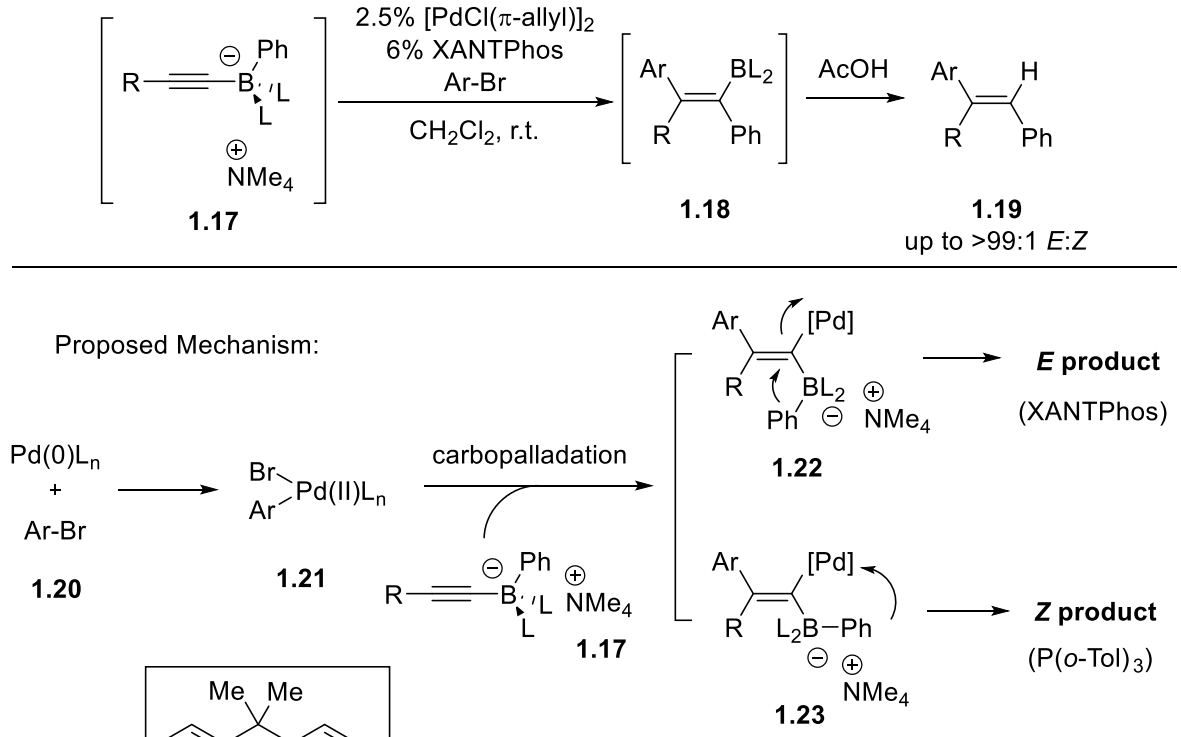
Scheme 1.6: General Scheme for metal-induced 1,2-metallate rearrangements



Along this line, Murakami and coworkers have developed methods that produce *E*-trisubstituted alkenylboranes **(1.18)** by palladium induced 1,2-rearrangement of alkynylborate **(1.17)** (Scheme 1.7).[12] The authors propose a mechanism where oxidative addition of an aryl bromide gives aryl palladium species **(1.21)**, it can then carbopalladate the alkyne in a *syn* fashion to produce **(1.22)**. Subsequently, when XANTPhos is the ligand, the phenyl group on boron undergoes substitutive 1,2-migration to invert the stereochemistry, giving *trans* alkene product. Interestingly, the authors mention the use of $P(o\text{-}tol)_3$ instead of XANTPhos results in the Z-isomer, which likely arises due to the less bulkier ligand on palladium allowing 1,3-phenyl migration pathway **(1.23)** that does not invert stereochemistry.[13]

[12] Ishida, N.; Shimamoto, Y.; Murakami, M. *Org. Lett.* **2009**, *11*, 5434.
[13] Ishida, N.; Miura, T.; Murakami, M. *Chem. Commun.* **2007**, *42*, 4381.

Scheme 1.7: Metal induced 1,2-metallate rearrangement and proposed mechanism

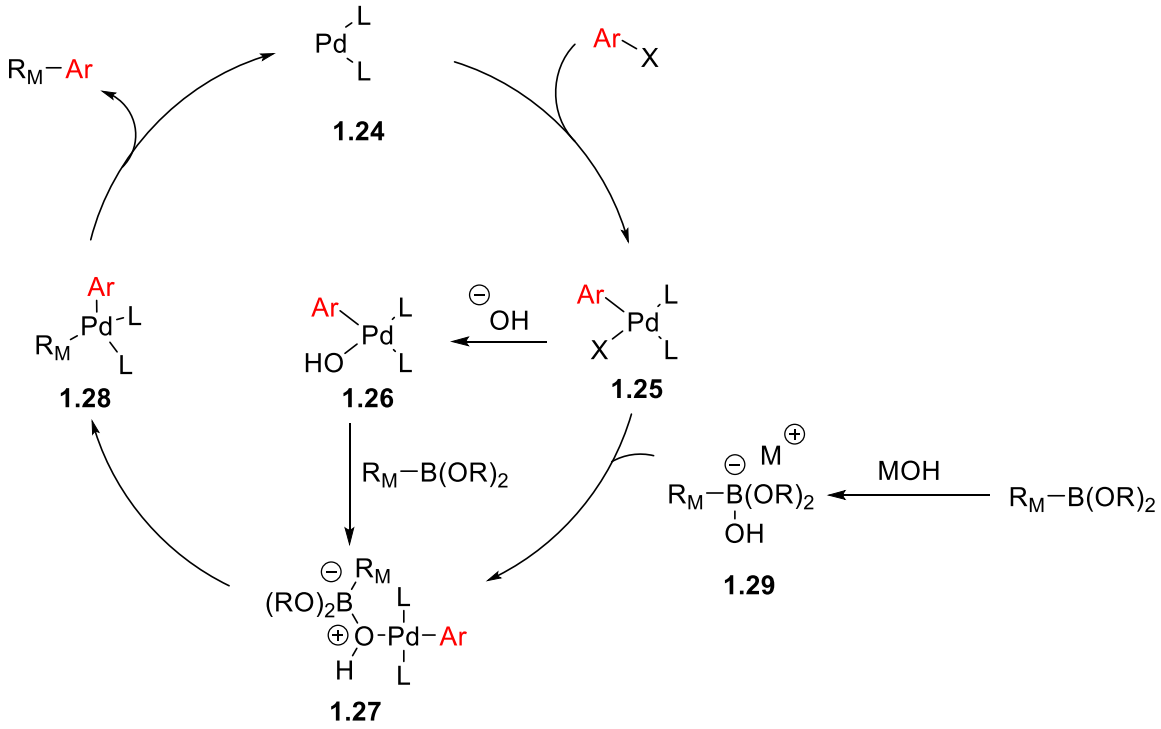


1.2 Suzuki-Miyaura Cross-Coupling

A general reaction mechanism for the Suzuki-Miyaura cross-coupling is represented below (Scheme 1.8).[4] In the generalized scheme, the catalytic cycle for the Suzuki-Miyaura cross coupling proceeds with the oxidative addition of aryl halide to form aryl palladium (II) species **(1.25)**. Then, in order for the transmetallation to occur, association of an activated boron "ate" complex **(1.29)** can lead to formation of transmetallation intermediate **(1.27)**. Alternatively, palladium (II) hydroxide **(1.26)** can

form first, and when organoboron species is added, it can also form transmetallation intermediate **(1.27)**. After the transmetallation, palladium (II) species **(1.28)** is generated. Finally, after reductive elimination, two groups are coupled together into the desired product and regenerates catalyst **(1.24)**.

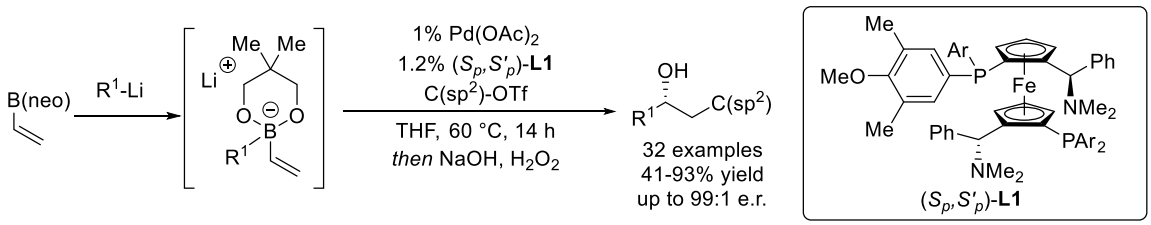
Scheme 1.8: Generalized mechanism of the Suzuki-Miyaura Cross-Coupling



1.3 Conjunctive Coupling Reaction and Recent Advances

In 2016, the Morken group reported the first instance of the conjunctive coupling reaction with palladium and Mandyphos **L1** catalyst complex (Scheme 1.9).[14] In this report, enantioenriched secondary organoboronic esters can be prepared from vinylboron ate complex and C(sp^2)-OTf.

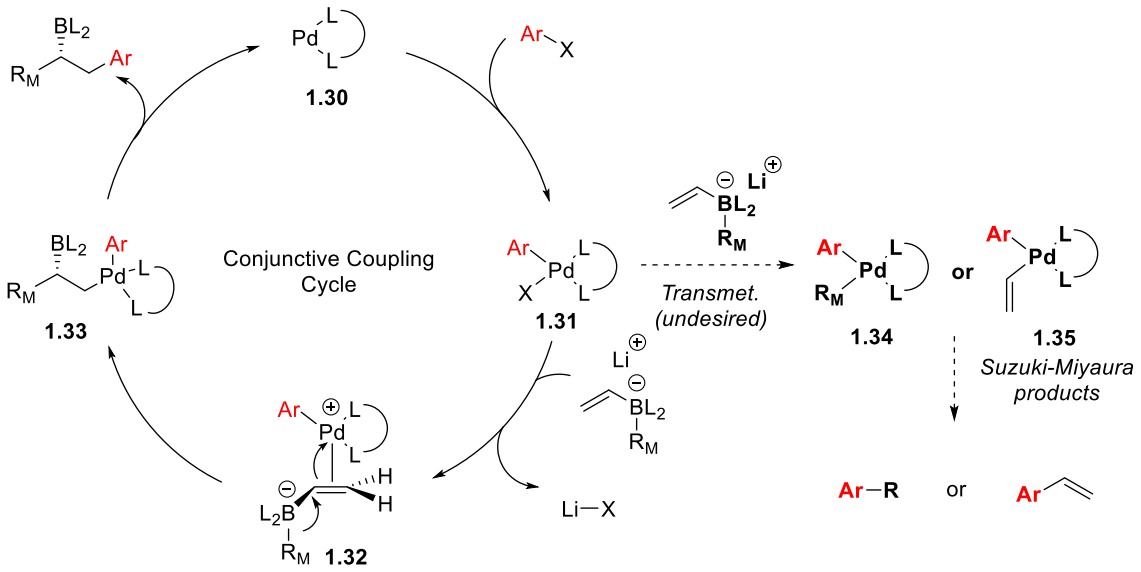
Scheme 1.9: Palladium-catalyzed conjunctive coupling reaction



In contrast to the Suzuki-Miyaura cross-coupling reaction, the following catalytic cycle is proposed for a conjunctive coupling (Scheme 1.10). The cycle begins with the oxidative addition of an electrophile to form Pd(II) species **(1.31)**. Then, the electrophilic palladium species can coordinate to alkene of the vinyl boron ate complex as shown in **(1.32)**. After 1,2-rearrangement induced by palladium catalyst, **(1.33)** forms. Subsequent reductive elimination produces the desired secondary boronic ester and regenerates Pd(0) catalyst **(1.30)**. There is a possibility that **(1.31)** can undergo transmetallation to form **(1.34)** or **(1.35)**, which produces undesired Suzuki-Miyaura products.

[14] Zhang, L.; Lovinger, G. J.; Edelstein, E. K.; Szymaniak, A. A.; Chierchia, M. P.; Morken, J. P. *Science*, **2016**, *351*, 70.

Scheme 1.10: Proposed mechanism for Pd-catalyzed conjunctive coupling reaction

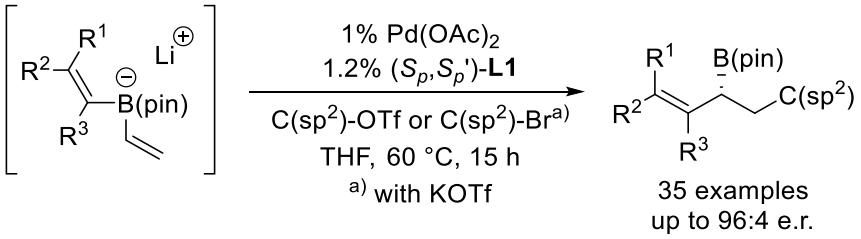


1.3.1 Catalytic Conjunctive Coupling Reactions with Palladium Catalysts

Studies from the Morken group have demonstrated that Grignard reagents may be used instead of organolithium reagents.[15] Additionally, the Morken group has found that bis(alkenyl) boron ate complexes may participate in the conjunctive coupling reaction with palladium catalyst, producing enantioenriched allylic boronates as product (Scheme 1.11).[16]

[15] Lovinger, G. J.; Aparece, M. D.; Morken, J. P. *J. Am. Chem. Soc.* **2017**, *139*, 3153.
[16] Edelstein, E. K.; Namirembe, S.; Morken, J. P. *J. Am. Chem. Soc.* **2017**, *139*, 5027.

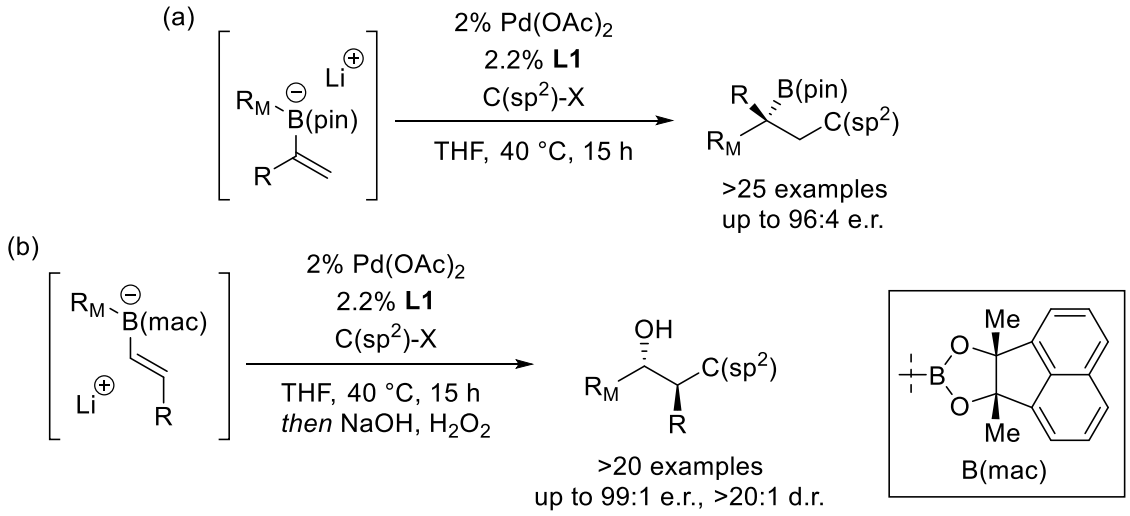
Scheme 1.11: Pd-catalyzed conjunctive coupling reaction with bis(alkenyl) boron ate complex



More recently, the Morken group has developed conjunctive coupling methods that enable migration to substituted alkenes such as 1,1-disubstituted alkenes (Scheme 1.12, (a)), and 1,2-disubstituted alkenes (Scheme 1.12, (b)).[17] When the boron ate complex derived from 1,1-disubstituted alkene is subjected to the reaction conditions, enantioenriched tertiary boronic esters can be obtained. For reaction with 1,2-disubstituted alkenes, high levels of enantioselectivity as well as the diastereoselectivity is observed for the product. For this reaction, a different diol ligand on boron was used to suppress undesired Suzuki-Miyaura coupling byproduct.

[17] a) Myhill, J. A.; Zhang, L.; Lovinger, J. P.; Morken, J. P. *Angew. Chem. Int. Ed.* **2018**, *57*, 12799., b) Myhill, J. A.; Wilhelmsen, C. A.; Zhang, L.; Morken, J. P. *J. Am. Chem. Soc.* **2018**, *140*, 15181.

Scheme 1.12: Migration to (a) 1,1-disubstituted alkenes, and (b) 1,2-disubstituted alkenes

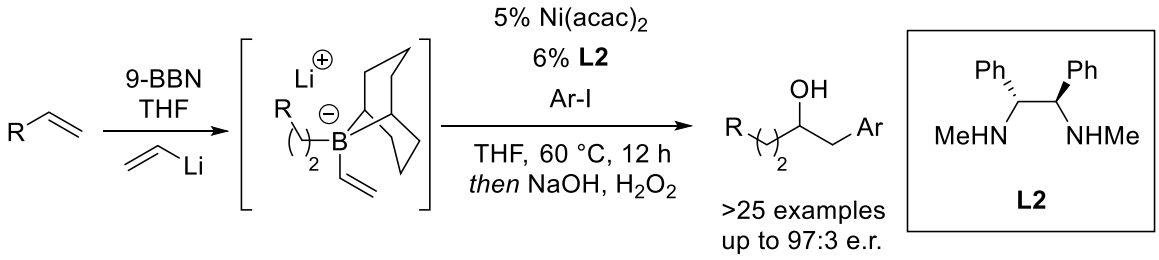


1.3.2 Catalytic Conjunctive Coupling Reactions with Nickel Catalysts

In addition to palladium as the catalyst, the Morken group has reported that nickel catalysts can also induce 1,2-metallate rearrangement to facilitate conjunctive coupling reactions. Using nickel and a chiral diamine catalyst, the conjunctive coupling reaction with boron ate complexes derived from alkyl 9-BBN was demonstrated, which produces enantioenriched secondary organoboronates (Scheme 1.13).[18]

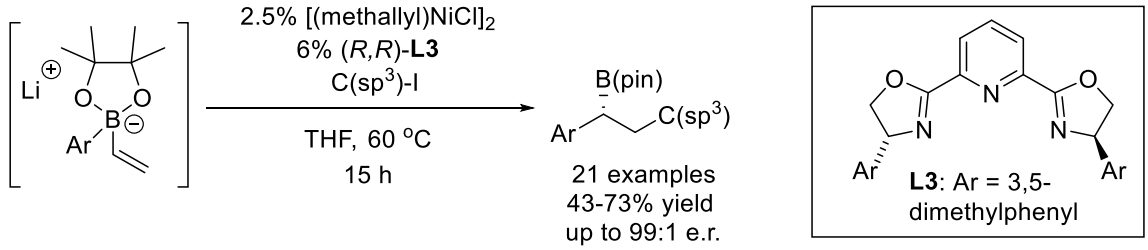
[18] Chierchia, M. P.; Law, C.; Morken, J. P. *Angew. Chem. Int. Ed.* **2017**, *56*, 11870.

Scheme 1.13: Ni-catalyzed conjunctive coupling reaction with 9-BBN derived ate complexes



Following the report of Ni-catalyzed conjunctive coupling reaction, the Morken group also demonstrated that alkyl electrophiles can be engaged in the reaction system using nickel/PyBOx catalysts (Scheme 1.14).[19] This allowed the expansion of the class of competent electrophiles for the conjunctive coupling reaction, which were previously limited to aryl and alkenyl groups.

Scheme 1.14: Ni-catalyzed conjunctive coupling reaction with C(sp^3) electrophiles



[19] Lovinger, G. J.; Morken, J. P. *J. Am. Chem. Soc.* **2017**, *139*, 17293.

2. Catalytic Conjunctive Coupling of Carboxylic Acid Derivatives with 9-BBN-Derived Ate Complexes

2.1 Introduction

Since the initial development of the conjunctive coupling reactions, all of the reports had been limited to aryl, alkenyl, and alkyl electrophiles.[20] Therefore, we wanted to expand the scope of the reaction by engaging carboxylic acid derivatives as electrophiles. This modification produces β-boryl carbonyl compounds, which is a useful type of compound as it contains two functional groups (ketone, and boryl) that may be transformed to other functionalized motifs. While a typical method to prepare this type of compound is conjugate borylation,[21] the conjunctive coupling method produces the product from a different set of starting materials, (three-component reaction) thereby making this complementary to existing methods. Additionally, since the products formed are β-trialkylboryl carbonyl compounds, they are novel compounds that had not been

[20] a) Zhang, L.; Lovinger, G. J.; Edelstein, E. K.; Szymaniak, A. A.; Chierchia, M. P.; Morken, J. P. *Science*, **2016**, *351*, 70. b) Lovinger, G. J.; Aparece, M. D.; Morken, J. P. *J. Am. Chem. Soc.* **2017**, *139*, 3153. c) Edelstein, E. K.; Namirembe, S.; Morken, J. P. *J. Am. Chem. Soc.* **2017**, *139*, 5027. d) Chierchia, M. P.; Law, C.; Morken, J. P. *Angew. Chem. Int. Ed.* **2017**, *56*, 11870. e) Lovinger, G. J.; Morken, J. P. *J. Am. Chem. Soc.* **2017**, *139*, 17293. f) Myhill, J. A.; Zhang, L.; Lovinger, J. P.; Morken, J. P. *Angew. Chem. Int. Ed.* **2018**, *57*, 12799. g) Myhill, J. A.; Wilhelmsen, C. A.; Zhang, L.; Morken, J. P. *J. Am. Chem. Soc.* **2018**, *140*, 15181.

[21] Wu, H.; Garcia, J. M.; Haeffner, F.; Radomkit, S.; Zhugralin, A. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2015**, *137*, 10585. Review: Collins, B. S. L.; Wilson, C. M.; Myers, E. L.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2017**, *56*, 11700.

previously studied, and may exhibit interesting reactivity that is absent in boronic ester counterpart.

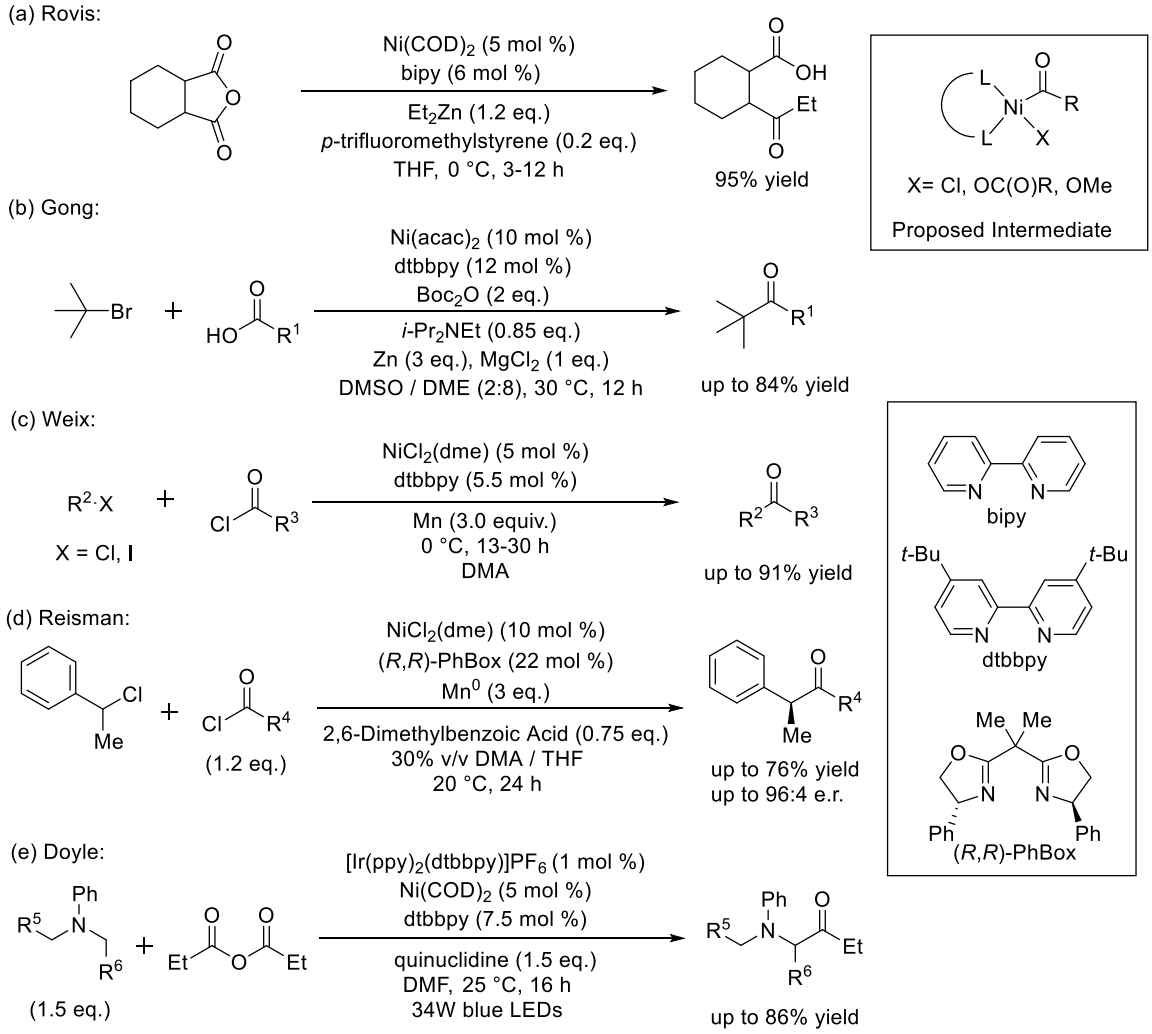
2.2 Background

In the recent years, many research groups have reported a variety nickel catalyzed cross-coupling reactions with carboxylic acid derivatives as the electrophile (Scheme 2.1). Rovis and coworkers reported monoalkylation of cyclic anhydrides (Scheme 2.1, (a)).[22] Gong and coworkers have demonstrated the synthesis of ketones by reductive coupling of alkyl carboxylic acid and *tertiary* alkyl halides (Scheme 2.1, (b)).[23] Another example of dialkyl ketone synthesis is shown by Weix and coworkers by reductive coupling of acid chloride and alkyl halides (Scheme 2.1, (c)).[24] Reisman and coworkers have developed an enantioconvergent reductive coupling method to produce enantioenriched α,α-disubstituted ketones from racemic secondary benzyl chlorides and acid chlorides (Scheme 2.1, (d)).[25] Lastly, Doyle and coworkers showcased a method for direct acylation of alkylamines with nickel and photoredox catalysts (Scheme 2.1, (e)).[26] In the examples in Scheme 2.1, nickel catalysts and bidentate ligands are employed (bipy or bis(oxazoline) ligands), and they are able to couple acyl group to various reaction partners. It is noteworthy that in these cases, the Ni-acyl adduct was proposed as an

[22] Bercot, E. A.; Rovis, T. *J. Am. Chem. Soc.* **2002**, *124*, 174.
[23] Zhao, C.; Jia, X.; Wang, X.; Gong, H. *J. Am. Chem. Soc.* **2014**, *136*, 17645.
[24] Wotal, A. C.; Weix, D. J. *Org. Lett.* **2012**, *14*, 1476.
[25] Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 7442.
[26] Joe, C. L.; Doyle, A. G. *Angew. Chem. Int. Ed.* **2016**, *55*, 4040

intermediate. Additionally, Coates and Rovis undertook a ^{13}C labeling study and showed that the Ni-acyl adduct could undergo direct transmetalation with organozinc reagents.[27] This led us to hypothesize that the intermediate may be competent in conjunctive coupling reactions with nickel, and we decided to investigate the reaction.

Scheme 2.1: Ni-catalyzed cross-coupling reactions with acyl electrophiles



[27] Johnson, J. B.; Bercot, E. A.; Rowley, J. M.; Coates, G. W.; Rovis, T. *J. Am. Chem. Soc.* **2007**, *129*, 2718.

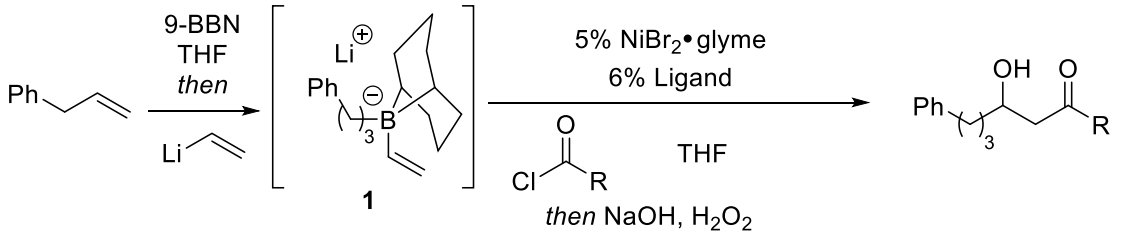
2.3 Development of Conjunctive Coupling Reaction with Acyl Electrophiles[28]

2.3.1 Reaction Optimization

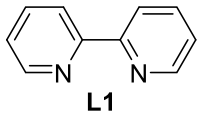
The reaction optimization began with allylbenzene and 9-BBN derived boron ate complex **(1)**, butyryl chloride, and nickel / bipyridine catalyst complex. Pinacolboratoboron-derived ate complex was not reactive and it did not yield product. With bipyridine ligand **L1**, after 1 hour of reaction time at room temperature, the product can be obtained in 65% yield after oxidation (Table 2.1, entry 1). Without the ligand **L1**, there is minimal background reaction between the boron ate complex and the electrophile (entry 2). At higher reaction temperature, the yield is diminished to 48% (entry 3). When bipyridine ligands **L1-L5** with different electronic profile were examined, the ligand **L3** with electron withdrawing CF_3 groups at 5,5'-position was able to offer highest yield (entry 1, 4, 7, 9, and 10). Although the reactivity difference between **L1** and **L3** was small for aliphatic acid chlorides, it was significant for aromatic acid chlorides (entry 5 and 6), so the ligand **L3** was chosen as the ligand for further study. Lastly, with ligand **L3**, the reaction is very fast, where the reaction is completed in two minutes (entry 8).

[28] Law, C.; Meng, Y.; Koo, S. M.; Morken, J. P. *Angew. Chem. Int. Ed.* **2019**, *58*, 6654.

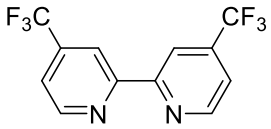
Table 2.1: Optimzation of the reaction conditions



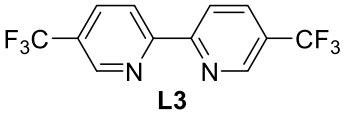
Entry	R	time	Temperature (°C)	Ligand	Yield (%)
1	*n*-Pr	1 h	22	**L1**	65
2	*n*-Pr	1 h	22	none	<5
3	*n*-Pr	1 h	40	**L1**	48
4	*n*-Pr	1 h	22	**L2**	72
5	Ph	1 h	22	**L1**	40
6	Ph	1 h	22	**L3**	75
7	*n*-Pr	1 h	22	**L3**	78
8	*n*-Pr	2 min	22	**L3**	75
9	*n*-Pr	1 h	22	**L4**	32
10	*n*-Pr	1 h	22	**L5**	40



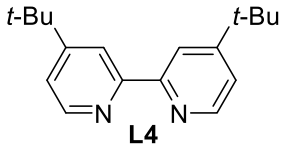
L1



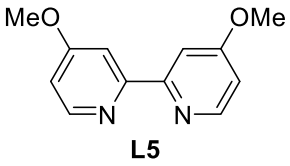
L2



L3

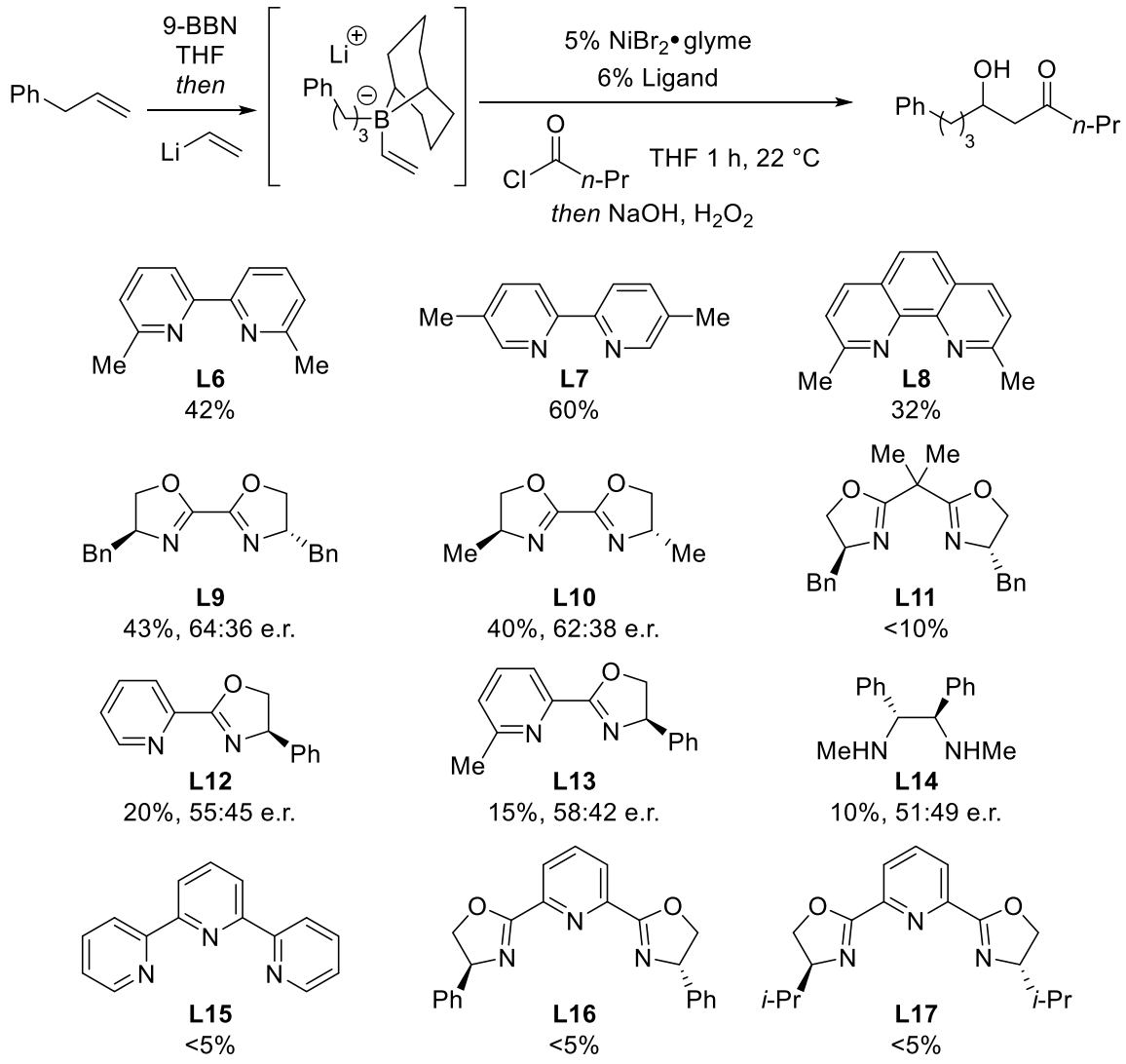


L4



L5

Scheme 2.2: Additional survey of ligands



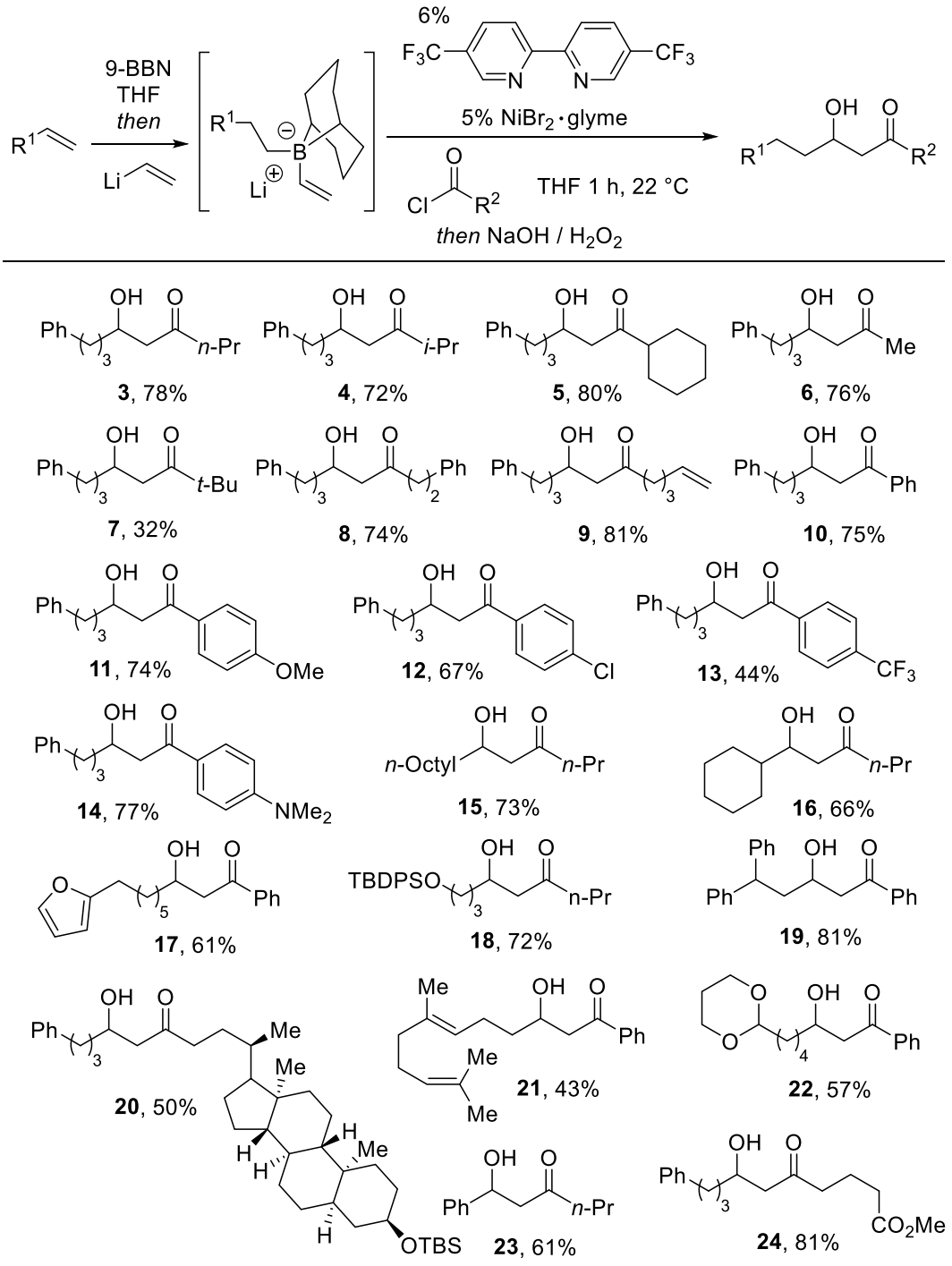
In addition to ligands **L1-5** that were shown in Table 2.1, more ligands were investigated. Bidentate ligands **L6**, **L7**, and **L8** demonstrated modest to good yields. Additionally, in efforts to render the reaction enantioselective, various chiral bidentate ligands such as BOx ligands (**L9-11**), PyOx ligands (**L12**, **L13**), and diamine ligand (**L14**) were examined. However, only a modest enantioselectivity could be achieved. Therefore, we decided to focus on developing the racemic reaction. Lastly, tridentate ligands **L15**, **L16**, and **L17** were not efficient for the conjunctive coupling reaction.

2.3.2 Substrate Scope

The scope of the conjunctive coupling with acyl electrophiles was investigated next (Scheme 2.3). In this study, various alkenes were used for the preparation of boron ate complexes with 9-BBN and vinyllithium. It was found that a variety of functional groups on the electrophile and migrating group are tolerated while products are produced in 43-81% yield. Both the unbranched and branched aliphatic acid chlorides (**3-6, 8**) produce good yields. Sterically bulkier *tert*-butyl substituents (**7**) on the carboxylic acid can be accommodated, while the yield is diminished at 32%. Aroyl chloride substituents with electron donating groups at the *para* position of the aromatic ring such as methoxy and dimethylamine groups (**11, 14**) were good yielding, while the electron withdrawing trifluoromethyl group at the *para* position (**13**) was lower yielding. It was later observed that the electrophile can undergo decarbonylation, which may contribute to lower yield.

Using the silyl protected lithocholic acid derivative can also afford the product **20** in 50% yield. Cyclohexene derived migrating group affords product in reasonable yield, without forming product from bicyclooctyl ligand migration from BBN ligand. Appended alkene (**21**), acetal (**22**), and silyl ether (**18**) can also be engaged in the reaction system.

Scheme 2.3: Ni-catalyzed conjunctive coupling with alkenes and acid chlorides

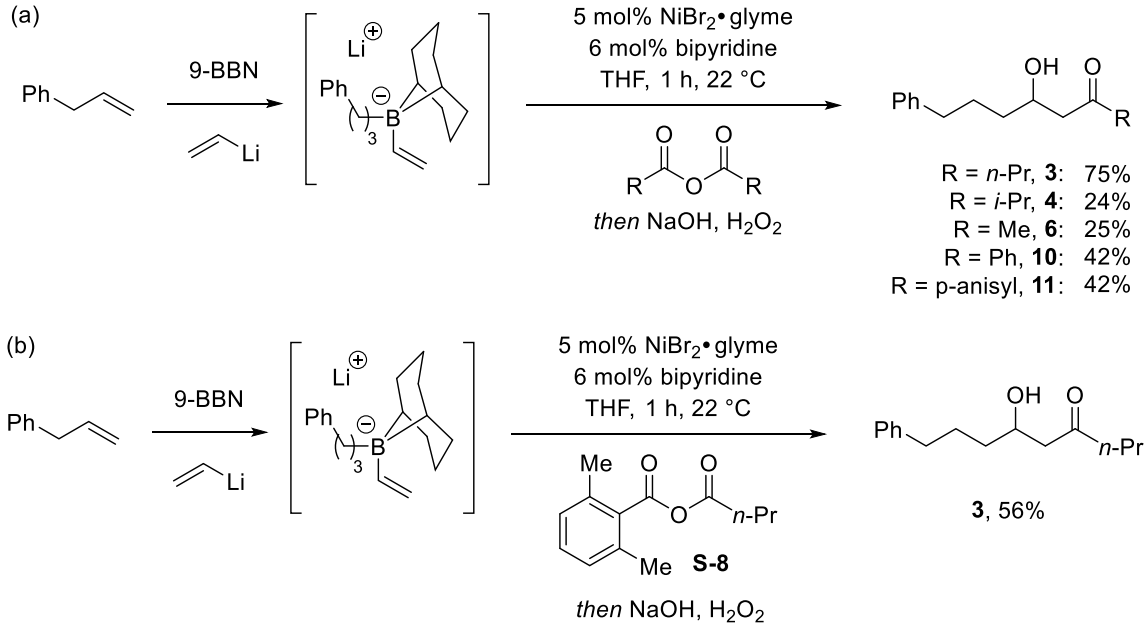


Under the optimized reaction conditions, the use of acid anhydrides resulted in a lower amount of product. This may be due to the lower electrophilicity of acid

anhydrides compared to acid chloride, which results in slower oxidative addition process.[29] In order to overcome this issue, a more electron donating ligand was used with the catalyst to accelerate the oxidative addition. Upon changing the ligand for the catalyst to unsubstituted bipyridine instead of CF_3-bipyridine ligand, the reaction was more efficient (Scheme 2.4 (a)).

Additionally, the reaction was tested to see if the product will be selective with a mixed anhydride (Scheme 2.4 (b)). When the mixed anhydride **S-8** is used in the reaction as the electrophile, the reaction yielded only the product with incorporation of less substituted carbonyl.

Scheme 2.4: Ni-catalyzed conjunctive coupling with (a) anhydride electrophiles and with (b) a mixed anhydride

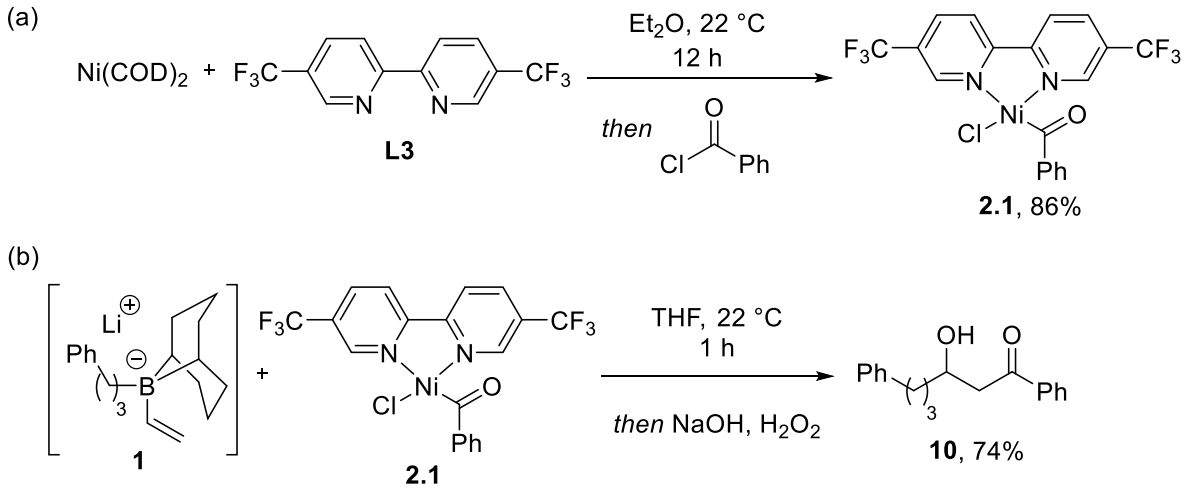


[29] Meng, G.; Szostak, M. *Org. Biomol. Chem.* **2016**, *14*, 5690.

2.3.3 Mechanistic Study

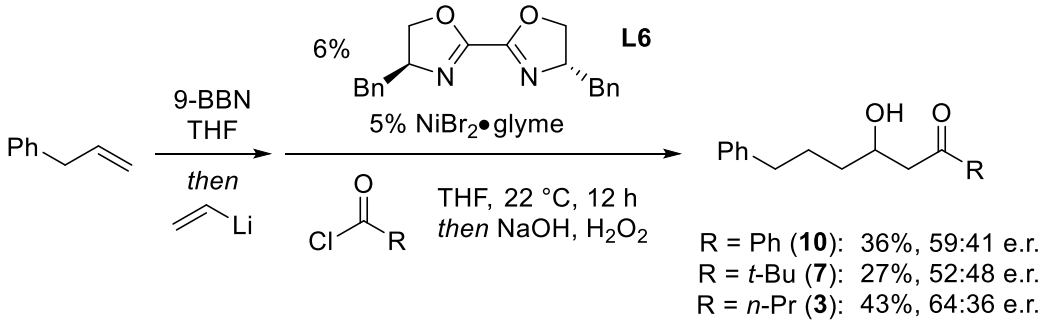
In order to gain more mechanistic insight, some preliminary experiments for mechanistic studies were performed. A Ni(II)-acyl adduct **2.1** was independently synthesized and isolated according to a method reported by the Gong group (Scheme 2.5, (a)).[23] This was performed to see whether Ni(II)-acyl adduct **2.1** is a catalytically competent species. When the reaction is conducted with stoichiometric amount of the nickel complex, conjunctive coupling product **10** can be obtained in 74% yield after oxidation, indicating that the Ni(II)-acyl adduct **2.1** is a competent species for the conjunctive coupling reaction (Scheme 2.5, (b)). In comparison to the catalytic reaction performed with ligand **L3**, the yield is similar.

Scheme 2.5 (a) preparation of Ni-acyl oxidative addition adduct, and (b) stoichiometric experiment



Prior to my participation in the project, my coworkers[30] have found that when a chiral BOx ligand **L6** is used for the reaction, variation of enantioselectivity based on the identity of the acid chloride electrophile can be observed (Scheme 2.6). This trend indicates that the oxidative addition of acid chloride electrophile to nickel occurs prior to the stereodetermining step, which is likely the irreversible 1,2-metallate rearrangement.

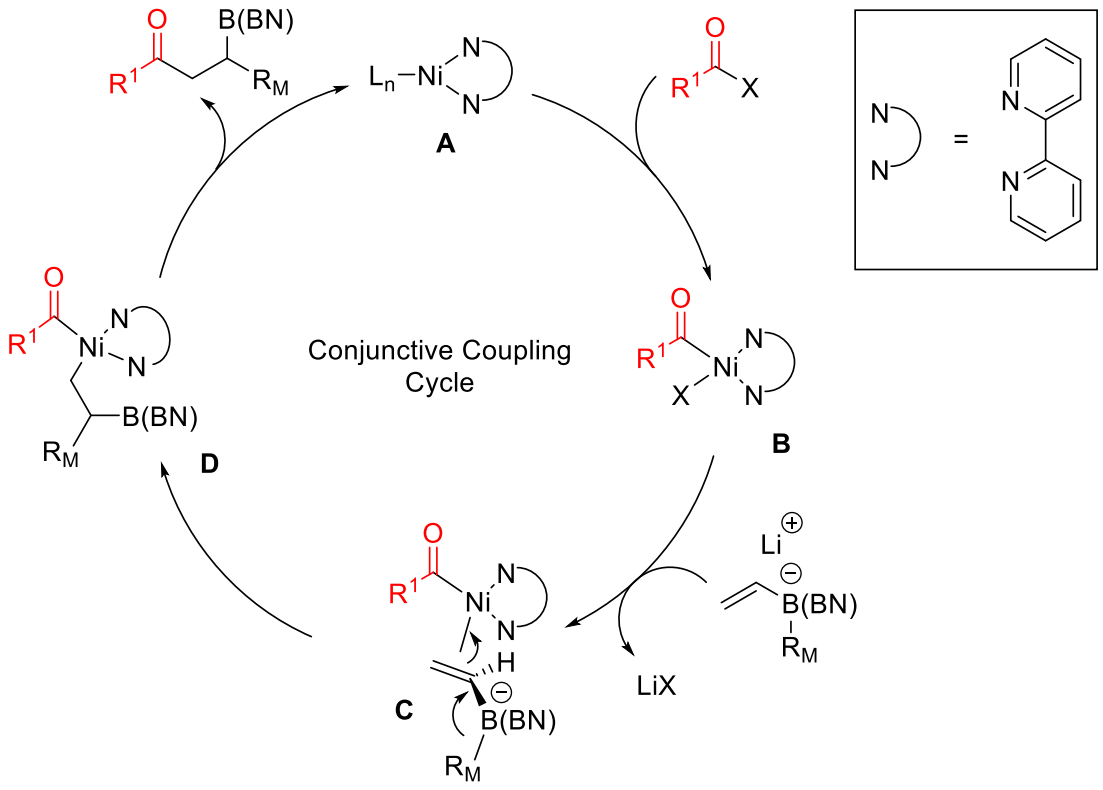
Scheme 2.6: Electrophile dependent enantioselectivity trends



With these data, the mechanism of the reaction is proposed as following (Scheme 2.7): carboxylic acid derivative as the electrophile is first oxidatively added to the Ni-bipyridine catalyst (**A**) to form complex (**B**). Then 1,2-metallate rearrangment occurs on the 9-BBN derived boron ate complex (**C**). Finally, reductive elimination of (**D**) yields β-boryl carbonyl compound and regenerates Ni-bipyridine catalyst complex (**A**) to turn over the cycle.

[30] Chunyin Law, and Yan Meng

Scheme 2.7: Proposed catalytic cycle for the conjunctive coupling reaction with acyl electrophiles



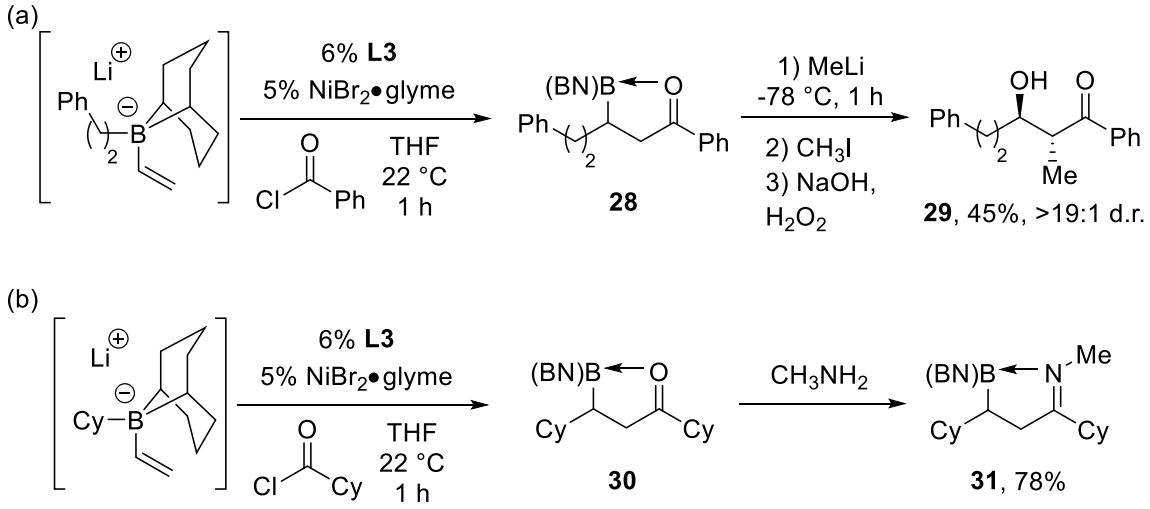
2.3.4 Brief Investigation of Properties of β-trialkylboryl Ketones

Because β-trialkylboryl carbonyl compounds are novel set of compounds, their properties and reactivities were briefly investigated. For a typical trialkyl borane, the ^{11}B NMR resonance is around δ 70-80 ppm.[31] However, the β-trialkylboryl ketone **28**'s ^{11}B NMR resonance was found to be δ 22.0 ppm. The upfield shift indicates that there is coordination between the boron and oxygen. Based on this finding, we hypothesized that the α-proton of the carbonyl will have increased acidity due to lewis acid activation.

[31] Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61.

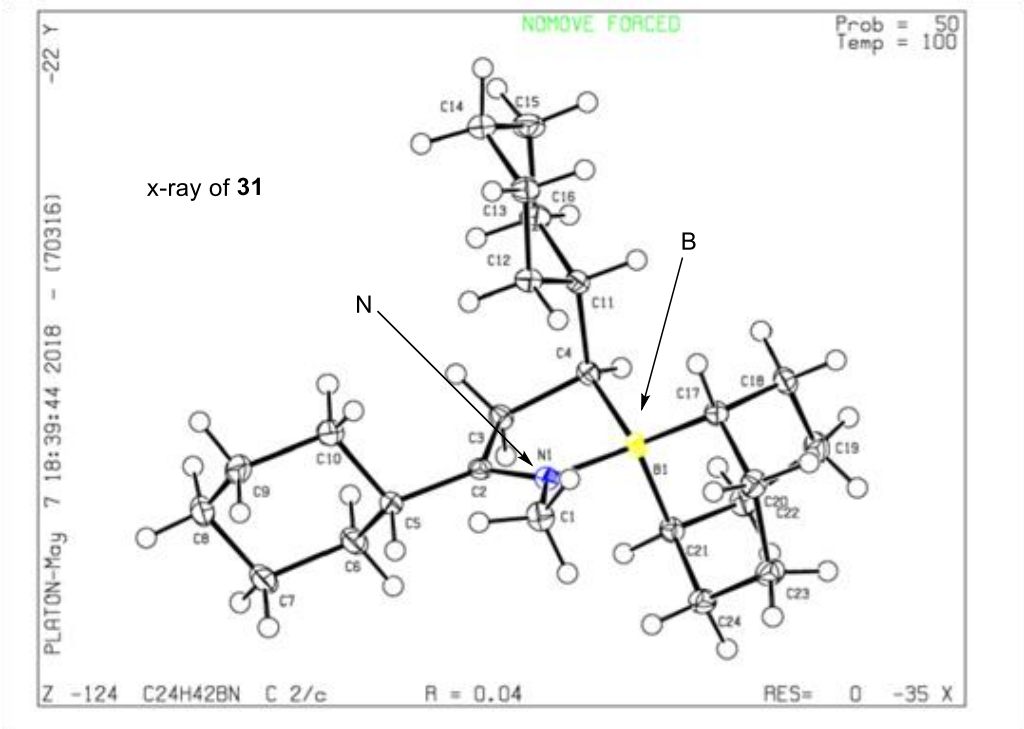
When **28** was treated with methyllithium, then with MeI, alkylation product **29** was obtained with high d.r. favoring the *anti*-alkylation product. The direct addition of methyllithium to the carbonyl was not observed.

Scheme 2.8: Reactivity of β-trialkylboryl carbonyl compounds.



To get a better idea for the rationale of the observed diastereoselectivity, we attempted to get a crystal structure for **28**. Although the attempts were unsuccessful, we were able to obtain a crystal structure for the imine **31**.

Scheme 2.9: X-ray structure of the derivative (31)



X-ray structure of **31** (Scheme 2.9) demonstrates that there is coordination between boron and nitrogen. In **31**'s crystal structure, the cyclohexyl group adjacent to boron is in axial position and may be able to block one face of the α-carbon atom. Therefore, if a similar conformation is taken by **28** during the enolate formation, the electrophile will approach from more accessible side, leading to the *anti* diastereomer.

2.4 Conclusion

In this section of the thesis, we describe a conjunctive coupling reaction where 9-BBN derived boron ate complex and acyl electrophile is coupled together to form β-carbonyl boryl compounds. It presents a complementary route to such class of product, where the starting materials used are different from conjugate borylation. The product, β-trialkylboryl ketone, is a novel class of compound, which may present more opportunities for studies, such as investigating transformations as well as the characteristics may be possible.

2.5 EXPERIMENTAL INFORMATION

2.5.1 General Information

^{1}H NMR spectra were recorded on either a Varian Gemini-500 (500 MHz), Varian Gemini-600 (600 MHz), or Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.24 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian Gemini-500 (125 MHz), Varian Gemini-600 (150 MHz) or a Varian Inova-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). Chemical shifts are reported in ppm using phosphoric acid as the external standard (H_3PO_4: 0.0 ppm). ^{11}B NMR spectra were recorded on a Varian Gemini-500 (128 MHz) spectrometer. ^{19}F NMR spectra were recorded on a Varian Gemini-500 (470 MHz) spectrometer. Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. High-resolution mass spectrometry (DART+) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography (TLC) was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), ceric ammonium molybdate (CAM) in ethanol or phosphomolybdic acid, and cerium(IV) sulfate in ethanol with sulfuric acid (Seebach).

Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector with isopropanol as the modifier.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (DCM) and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after purging with argon. Nickel(II) bromide-glyme was purchased from Sigma Aldrich, 9-Borabicyclo[3.3.1]nonane 0.5 M solution in THF was purchased from Alfa Aesar (of note, cross coupling reactions resulted in slightly diminished yields when a BBN solution from Sigma Aldrich was employed, or when borane reagents were prepared from BBN dimer). All other reagents were purchased from

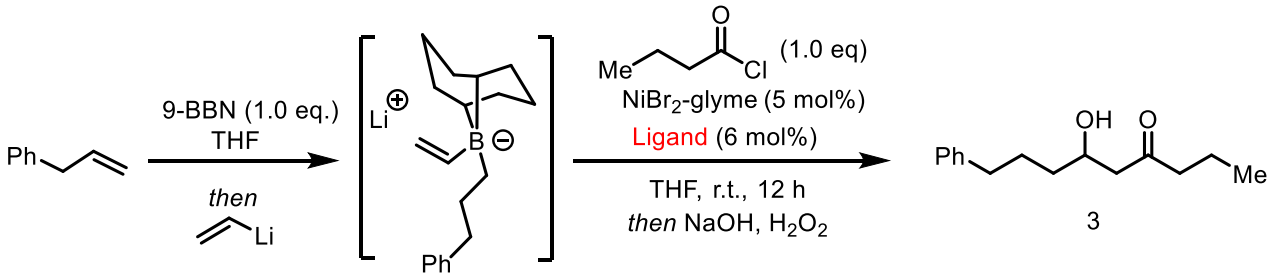
Sigma Aldrich, Alfa Aesar, Oakwood Chemicals, Combi-Blocks, or Acros Organics and used without further purification.

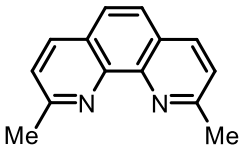
Optimization Studies (Tables 1 and S1)

In a glovebox, under argon, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with a solution of 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.). The vial was cooled to 0 ℃, and allylbenzene (0.26 mmol, 1.30 equiv.) was added via a syringe. The reaction mixture was allowed to warm to room temperature and stir for 3 hours before being cooled back to 0 ℃. A solution of vinyllithium (for synthesis of halide free vinyllithium see ref[32]) in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.) was added to the reaction mixture which was then warmed to room temperature and stirred for 5 minutes. Meanwhile a solution of the appropriate nickel pre-catalyst (0.010 mmol, 0.050 equiv.) and ligand (0.012 mmol, 0.060 equiv.) in THF (0.4 mL) was allowed to complex for 5 minutes under inert atmosphere. The catalyst solution was added to the boron 'ate' mixture at room temperature followed by addition of acyl chloride (0.20 mmol, 1.00 equiv.) The reaction vial was sealed with a septum cap, taken out of the glovebox and stirred at the appropriate temperature for the designated amount of time, after which point the reaction mixture was cooled to 0℃ and 30% H_2O_2 (0.5 mL) were added along with 3 M NaOH (0.5 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 3 hours. Aq. saturated $Na_2S_2O_3$ (1 mL) solution was then added to quench the remaining H_2O_2. The aqueous phase was EtOAc (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and subsequently purified via silica gel column chromatography (20% EtOAc in hexanes) to obtain an isolated yield.

[32] E. Edelstein, S. Namirembe, J. Morken, *J. Am. Chem. Soc.* **2017**, *139*, 5027.

Table S1: Additional Survey of Ligands

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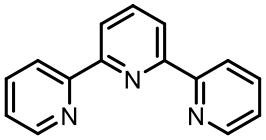
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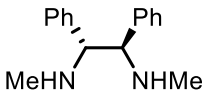
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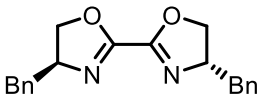
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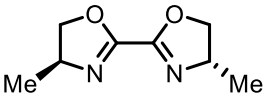
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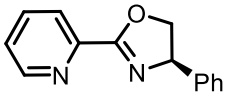
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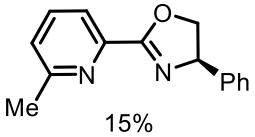
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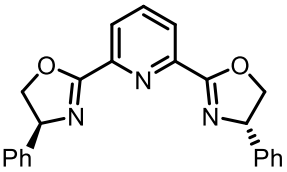
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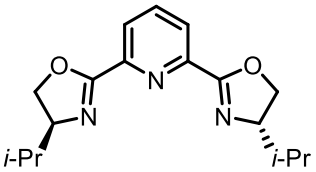
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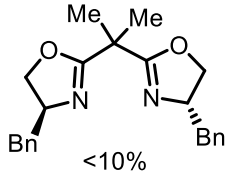
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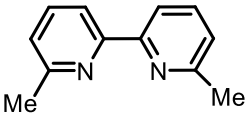
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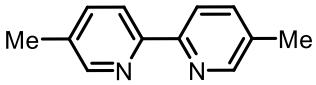
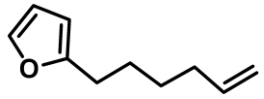

60%

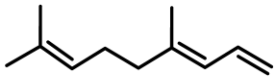
2.5.2 Experimental Procedures

2.5.2.1 *Procedure for Preparation of Alkenyl Substrates and Acyl Electrophiles*

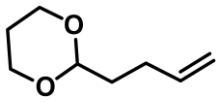
All alkenyl starting material and acyl electrophiles not mentioned below are commercially available and used as received.



2-(hex-5-enyl)furan (S-1). The title compound was prepared according to the procedure reported in the literature.[33] All spectral data was in accordance with previously published results.



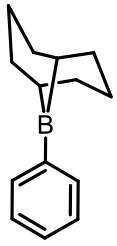
***(E)*-4,8-dimethylnona-1,3,7-triene (S-2).** The title compound was synthesized in two steps starting with oxidation of geraniol as reported by Stahl *et al.*[34] followed by Wittig olefination. The spectral data was in accordance with the literature.[35]



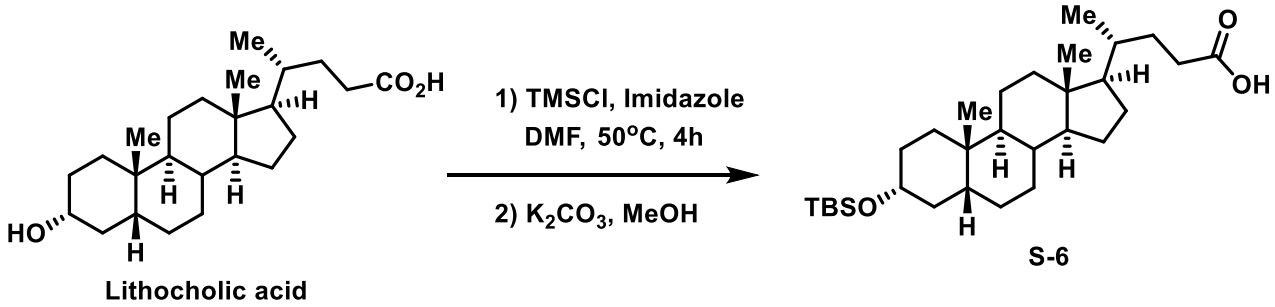
2-(but-3-en-1-yl)-1,3-dioxane (S-3). The title compound was synthesized from 4-pentenal according to the procedure reported by Karimi *et al*.[36] The spectral data was in accordance with the literature.

(allyloxy)(tert-butyl)diphenylsilane (S-4). The title compound was prepared according to the procedure reported in the literature. All spectral data was in accordance with previously published results.[37]

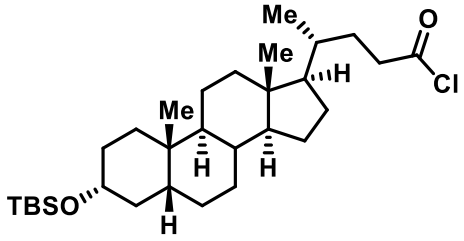
[33] S. Hobson, R. Marquez, *Org. Biomol. Chem.* **2006**, *4*, 3808.
[34] J. Hoover, S. Stahl, *J. Am. Chem. Soc.* **2011**, *133*, 16901.
[35] H. Davies, Ø Loe, D. Stafford*, Org. Lett.* **2005**, *7*, 5561.
[36] H. Firouzabadi, N, Iranpoor, B. Karimi, *Synlett*. **1999**, 321.
[37] B. Lin, Y, Zhao, Y. Lai, T. Loh, *Angew. Chem. Int. Ed.* **2012**, *51*, 8041.



9-phenyl-9-borabicyclo[3.3.1]nonane (S-5). The title compound was prepared according to the procedure reported in literature. All spectral data was in accordance with the literature.[38]



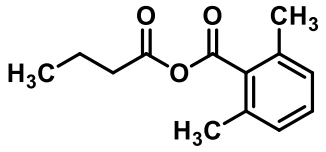
(4R)-4-((3R,5R,9S,10S,13R,14S,17R)-3-((tert-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoic acid (S-6). The title compound was prepared according to the procedure reported in literature.[39] All spectral data was in accordance with the literature.



(4R)-4-((3R,5R,9S,10S,13R,14S,17R)-3-((tert-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoyl chloride (S-7). To an oven-dried scintillation vial was added **S-6** (500 mg, 0.98 mmol). The vial was purged with nitrogen for 2 minutes. To it was added THF (1 mL) and Et_2O (1 mL). The reaction mixture was cooled to 0°C at which point oxalyl chloride (137 mg, 1.08 mmol) was added followed by 1 small drop of DMF. The reaction mixture was warmed up to room temperature and stirred overnight. Solvent was evaporated under vacuum to afford the product as a white solid (394mg, 79%).

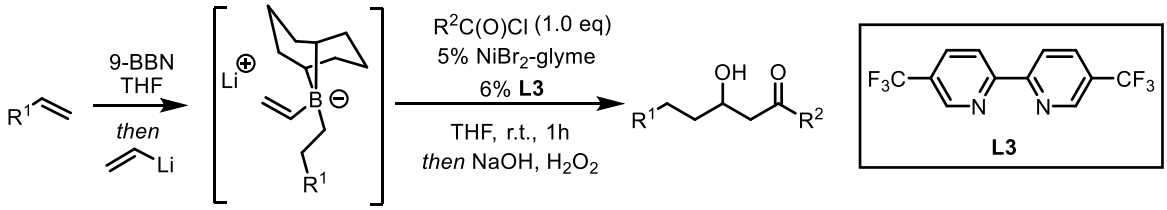
[38] G. Fang, O. Wallner, N. Di Blasio, X. Ginesta, J. Harvey, V. Aggarwal, *J. Am. Chem. Soc*. **2007**, *129*, 14632.
[39] C. Joe, A. Doyle, *Angew. Chem. Int. Ed.* **2016**, *55*, 4040.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66-3.49 (m, 1H), 2.96-2.88 (m, 1H), 2.85-2.76 (m, 1H), 1.95-1.02 (m, 26H), 0.92 (s, 3 H), 0.91 (s, 3H), 0.89 (s, 9H), 0.63 (s, 3H), 0.06 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.4, 73.0, 56.5, 56.0, 44.6, 42.9, 42.4, 40.34, 40.26, 37.1, 36.0, 35.7, 35.1, 34.7, 31.2, 31.2, 28.3, 27.4, 26.5, 26.1, 24.3, 23.5, 20.9, 18.5, 18.4, 12.2, -4.4. **IR** (neat) ν_{max} 2930(s), 2863 (s), 1708 (s), 1447 (m), 1249 (m), 1093 (m), 870 (m), 854 (m), 774 (m). **HRMS** (DART) for $C_{30}H_{53}O_2Si$ $(M\text{-}Cl)^+$: Calc'd: 473.3815, found: 473.3753.



butyric 2,6-dimethylbenzoic anhydride (S-8). The title compound was prepared according to the procedure reported in literature.[7] All spectral data was in accordance with the literature.

2.5.2.2 *General Procedure for Conjunctive Cross-Coupling*



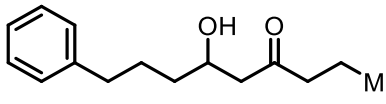
In a glovebox, under argon, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with a solution of 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.). The vial was cooled to 0°C, and the olefin (0.26 mmol, 1.30 equiv.) was added. The reaction mixture was allowed to warm to room temperature and stir for 3 hours before being cooled back to 0°C. A solution of vinyllithium (for synthesis of halide free vinyllithium see ref) in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.) was added to the reaction mixture which was then warmed to room temperature and stirred for 5 minutes. Meanwhile a solution of $NiBr_2$-glyme (0.010 mmol, 0.050 equiv.) and **L3** (see ref[40] for its synthesis) (0.012 mmol, 0.060 equiv.) in THF (0.4 mL) was allowed to complex for 5 minutes under inert atmosphere. The catalyst solution was added to the boron 'ate' mixture at room temperature followed by addition of acyl chloride (0.20 mmol, 1.00 equiv.) The reaction vial was sealed with a septum cap, taken out of the glovebox and stirred at room temperature for 1h, after which point the reaction mixture was cooled to 0°C and 30% H_2O_2 (0.5 mL) were added along with 3 M NaOH (0.5 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 3 hours. Aq. saturated $Na_2S_2O_3$ (1 mL) solution was then added to quench the reamining H_2O_2. The aqueous phase was EtOAc (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and subsequently purified via silica gel column chromatography to provide the desired products.

Note: In all cases, a stock solution of 9-BBN derivatives could be prepared and stored in a freezer for as long as one month, before addition of vinyllithium, without any diminishing yield.

The procedure for conjunctive cross-coupling reaction utilizing anhydrides as electrophiles is identical to the one reported above except the commercially available 2,2'-bipyridine is used as the ligand.

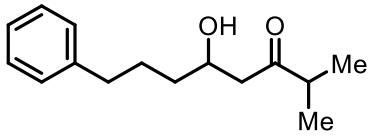
[40] Y. Forst, S. Becker, P. Caubere, *Tetrahedron*, **1994**, *50*, 11893.

2.5.2.3 *Characterization of Conjunctive Cross Coupling Products*



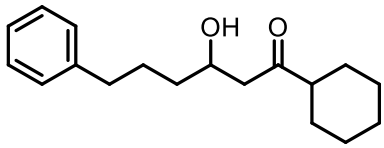
6-hydroxy-9-phenylnonan-4-one (3). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), butanoyl chloride (21.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (37 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.23-7.14 (m, 3H), 4.11-4.02 (m, 1H), 3.06 (d, J = 3.4 Hz, 1H), 2.68-2.54 (m, 3H), 2.48 (dd, J = 17.6, 9.1 Hz, 1H), 2.39 (t, J = 7.3 Hz, 2H), 1.87-1.74 (m, 1H), 1.73-1.48 (m, 4H), 1.46-1.36 (m, 1H), 0.91 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 212.5, 142.4, 128.5, 128.4, 125.9, 67.6, 49.0, 45.6, 36.1, 35.8, 27.4, 17.2, 13.8. **IR** (neat) ν_{max} 3398 (br, s), 2932 (s), 1707 (s), 1603 (w), 1496 (w), 1408 (m), 1375 (m), 1096 (m), 750 (s), 700 (s) cm^{-1}. **HRMS** (DART) for $C_{15}H_{23}O_2$ $[M+H]^+$: Calc'd: 235.1691, found: 235.1693.



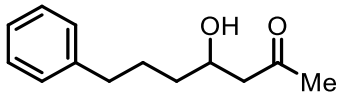
5-hydroxy-2-methyl-8-phenyloctan-3-one (4). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), isobutyryl chloride (21.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (33.7 mg, 72% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.20-7.15 (m, 3H), 4.10-3.99 (m, 1H), 3.28-3.01 (br s, 1H). 2.71-2.46 (m, 5H), 1.88-1.73 (m, 1H), 1.72-1.62 (m, 1H), 1.59-1.50 (m, 1H), 1.48-1.38 (m, 1H), 1.10 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 216.3, 142.4, 128.5, 128.4, 125.9, 67.6, 46.6, 41.6, 36.1, 35.9, 27.4, 18.2, 18.1. **IR** (neat) 3479 (br, m), 2969 (m), 2932 (s), 1706 (s), 1603 (w), 1496 (m), 1094 (m), 1043 (w), 751 (m), 701 (m) cm^{-1}. **HRMS** (DART) for $C_{15}H_{23}O_2$ $[M+H]^+$: Calc'd: 235.1693, found: 235.1703.



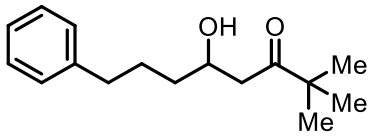
1-cyclohexyl-3-hydroxy-6-phenylhexan-1-one (5). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), cyclohexanecarbonyl chloride (29.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (43.9 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.28-7.22 (m, 3H), 4.17-4.04 (m, 1H), 3.26 (d, *J* = 3.2 Hz, 1H), 2.74-2.66 (m, 3H), 2.57 (dd, *J* = 17.7, 9.2 Hz, 1H), 2.42-2.34 (m, 1H), 1.96-1.82 (m, 5H), 1.78-1.69 (m, 2H), 1.65-1.57 (m, 1H), 1.55-1.46 (m, 1H), 1.44-1.22 (m, 5H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 215.8, 142.4, 128.6, 128.4, 125.9, 67.6, 51.5, 46.9, 36.1, 35.9, 28.4, 27.4, 25.9, 25.7. **IR** (neat) ν_{max} 3457 (m), 2925 (m), 1670 (s), 1602 (s), 1222 (m), 1023 (m), 969 (m), 827 (s), 613 (w), 580 (w) cm^{-1}. **HRMS** (DART) for $C_{18}H_{27}O_2$ $[M+H]^+$: Calc'd: 275.2006, found: 275.1996.



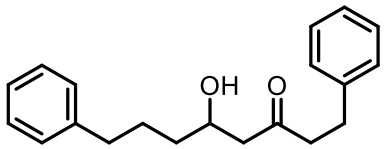
4-hydroxy-7-phenylheptan-2-one (6). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), acetyl chloride (15.7 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (37 mg, 76% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 7.20-7.14 (m, 3H), 4.08-4.00 (m, 1H), 3.02-2.94 (s, 1H), 2.66-2.57 (m, 3H), 2.51 (dd, *J* = 17.8, 9.2 Hz, 1H), 2.15 (s, 3H), 1.83-1.74 (m, 1H), 1.70-1.60 (m, 1H), 1.56-1.49 (m, 1H), 1.45-1.38 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.1, 142.4, 129.5, 128.4, 125.9, 67.5, 50.1, 36.0, 35.8, 30.9, 27.4. **IR** (neat) ν_{max} 3457 (m), 2923 (m), 1668 (s), 1596 (s), 1459 (m), 1262 (m), 988 (m), 826 (m), 746 (m), 701 (m), 580 (s), 552 (m). **HRMS** (DART) for $C_{13}H_{19}O_2$ $(M+H)^+$: Calc'd: 207.1380, found: 207.1370.



5-hydroxy-2,2-dimethyl-8-phenyloctan-3-one (7). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (2.20 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), pivaloyl chloride (24.1 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (15.9 mg, 32% yield).

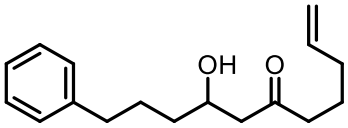
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.18 (m, 3H), 4.02 (m, 1H), 3.27 (d, *J* = 3.1 Hz, 1H), 2.67 (dd, *J* = 17.8, 2.5 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.53 (dd, *J* = 17.8, 9.2 Hz, 1H), 1.81 (m, 1H), 1.69 (m, 1H), 1.56 (m, 1H), 1.45 (m, 1H), 1.13 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 218.0, 142.4, 128.54, 128.45, 128.43, 128.41, 125.9, 67.8, 44.5, 43.19, 43.16, 36.1, 35.9, 27.5, 26.44, 26.40, 26.35. **IR** (neat) ν_{max} 3454 (br, w), 3026 (w), 2929 (m), 2861 (m), 1698 (s), 1603 (w), 1496 (m), 1478 (m), 1453 (m), 1394 (w), 1366 (m), 1067 (m), 1030 (w), 1008 (w), 844 (w), 748 (s), 699(s), 578 (w), 537 (w) cm^{-1}. **HRMS** (DART) for $C_{16}H_{25}O_2$ $[M+H]^+$: Calc'd: 249.1849, found: 249.1840.



5-hydroxy-1,8-diphenyloctan-3-one (8). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), hydrocinnamoyl chloride (33.7 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (43.9 mg, 79% yield).

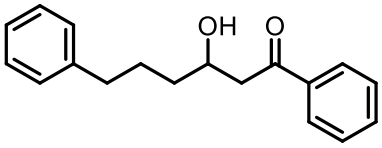
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (m, 4H), 7.19 (m, 6H), 4.06 (m, 1H), 2.99 (m, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.55 (dd, *J* = 17.5, 3.0 Hz, 1H), 2.49 (dd, J = 17.5, 8.9 Hz, 1H), 1.79 (m, 1H), 1.67 (m, 1H), 1.53 (m, 1H), 1.43 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 211.2, 142.3, 140.8, 128.6, 128.6, 128.5, 128.5, 128.40, 128.39, 128.37, 126.3, 125.9, 67.6, 49.4, 45.11, 36.0, 35.8, 29.6, 27.3. **IR** (neat) ν_{max} 3445 (br, w), 3026 (w), 2923 (w), 2856 (w), 1705 (s), 1603 (w), 1496 (m), 1453

(m), 1406 (m), 1371 (m), 1091 (m), 1030 (m), 748 (m), 698 (s), 563 (w) cm^{-1}. **HRMS** (DART) for $C_{20}H_{25}O_2$ $[M+H]^+$: Calc'd: 297.1849, found: 297.1838.



8-hydroxy-11-phenylundec-1-en-6-one (9). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), hex-5-enoyl chloride (26.5 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (42.2 mg, 81% yield).

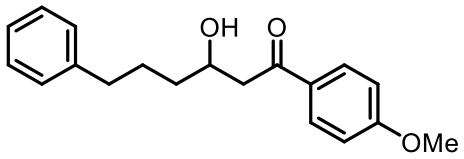
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.19-7.15 (m, 3H), 5.74 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03-4.95 (m, 2H), 4.11-4.01 (m, 1H), 3.09 (br s, 1H), 2.63 (t, *J* = 7.7,Hz, 2H), 2.55 (dd, *J* = 17.5, 2.8 Hz, 1H), 2.48 (dd, *J* = 17.5, 9.1 Hz, 1H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.04 (q, *J* = 7.1 Hz, 2H), 1.83-1.75 (m, 1H), 1.71-1.62 (m, 3H), 1.57-1.49 (m, 1H), 1.46-1.38 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 212.2, 142.3, 137.9, 128.5, 128.4, 125.8, 115.5, 67.6, 49.2, 42.8, 36.0, 35.8, 33.1, 27.4, 22.6. **IR** (neat) ν_{max} 3448.8 (br, m), 2933 (m), 1705 (m), 1640 (w), 1408 (m), 1276 (w), 1097 (m), 912 (m), 750 (s), 700 (s) cm^{-1}. **HRMS** (DART) for $C_{17}H_{25}O_2$ $[M+H]^+$: Calc'd: 261.1849, found: 261.1853.



3-hydroxy-1,6-diphenylhexan-1-one (10). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), benzoyl chloride (28.1 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (40.3 mg, 75% yield).

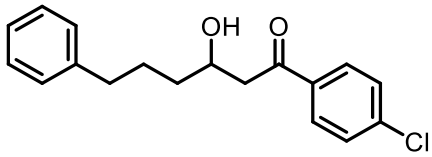
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.24-7.16 (m, 3H), 4.30-4.19 (m, 1H), 3.28 (d, *J* = 3.3 Hz, 1H), 3.15 (dd, *J* = 17.7, 2.6 Hz, 1H), 3.04 (dd, *J* = 17.9, 9.1 Hz, 1H), 2.68 (t, *J* = 7.6 Hz, 1H), 1.94-1.83 (m, 1H), 1.80-1.71 (m, 1H), 1.71-1.63 (m, 1H), 1.61-1.52 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 201.0, 142.4, 136.9, 133.7, 128.8, 128.6, 128.4, 128.2,

125.9, 67.7, 45.2, 36.2, 35.9, 27.5. **IR** (neat) ν_{max} 3481 (m), 2931 (w), 2901 (w), 1676 (s), 1595 (w), 1219 (w), 1098 (m), 749 (m), 699 (m), 686 (s), 583 (m) cm^{-1}. **HRMS** (DART) for $C_{18}H_{21}O_2$ $[M+H]^+$: Calc'd: 269.1536, found: 269.1545.



3-hydroxy-1-(4-methoxyphenyl)-6-phenylhexan-1-one (11). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), 4-methoxybenzoyl chloride (34.1 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a white solid (44.1 mg, 74% yield).

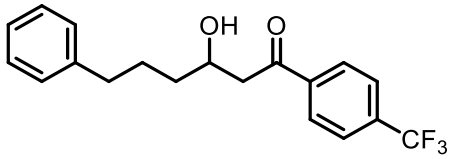
^{1}H NMR (400 MHz, $CDCl_3$) 7.92 (d, *J* = 8.9 Hz, 2H), 7.33-7.24 (m, 2H), 7.21-7.13 (m, 3H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.30-4.10 (m, 1H), 3.86 (s, 3H), 3.41 (br s, 1H), 3.10 (dd, *J* = 17.5, 2.5 Hz, 1H), 2.95 (dd, *J* = 17.5, 9.1 Hz 1H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.93-1.81 (m, 1H), 1.80-1.59 (m, 2H), 1.58-1.46 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.6, 164.0, 142.5, 130.5, 130.0, 128.6, 128.4, 125.9, 114.0, 67.9, 55.7, 44.7, 36.2, 35.9, 27.5. **IR** (neat) ν_{max} 3483 (br, s), 2926 (s), 1709 (s), 1603 (w), 1496 (w), 1168 (m), 1094 (m), 751 (m), 702 cm^{-1}. **HRMS** (DART) for $C_{19}H_{23}O_3$ $[M+H]^+$: Calc'd: 299.1642, found: 299.1649.



1-(4-chlorophenyl)-3-hydroxy-6-phenylhexan-1-one (12). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), 4-chlorobenzoyl chloride (35.0 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (40.6 mg, 67% yield).

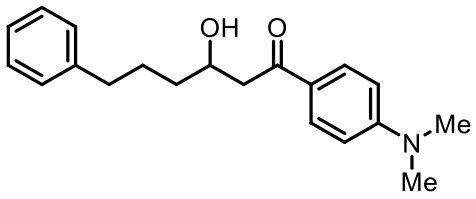
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.28 (t, 2H, *J* = 7.5 Hz, 2H), 7.22-7.16 (m, 3H), 4.28-4.19 (m, 1H), 3.17 (d, *J* = 3.4 Hz, 1H), 3.08 (dd, *J* = 17.7, 2.7 Hz, 1H), 3.01 (dd, *J* = 17.7, 9.1 Hz, 1H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.92-1.84 (m, 1H), 1.78-1.70 (m, 1H), 1.68-1.62 (m, 1H), 1.58-1.51 (m, 1H). **^{13}C NMR** (150

MHz, $CDCl_3$) δ 199.7, 142.3, 140.2, 135.2, 129.6, 129.1, 128.6, 128.5, 125.9, 67.6, 45.2, 36.1, 35.9, 27.5. **IR** (neat) ν_{max} 3484 (br, s), 2932 (w), 2901 (w), 1675 (s), 1588 (w), 1494 (m), 1400 (m), 1092 (s), 1039 (m), 986 (m), 832 (m), 817 (s), 733 (s), 534 (s) cm^{-1}. **HRMS** (DART) for $C_{18}H_{21}O_2Cl$ $[M+H]^+$: Calc'd: 303.1146, found: 303.1143.



3-hydroxy-6-phenyl-1-(4-(trifluoromethyl)phenyl)hexan-1-one (13). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), 4-(trifluoromethyl)benzoyl chloride (41.7 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a white solid (30.0 mg, 44% yield).

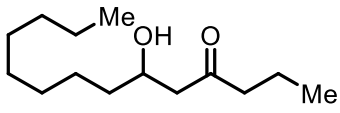
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.21-7.16 (m, 3H), 4.34-4.22 (m, 1H), 3.14 (dd, *J* = 17.7, 2.9 Hz, 1H), 3.08 (dd, *J* = 17.7, 8.7 Hz, 1H), 3.02 (s, 1H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.93-1.84 (m, 1H), 1.79-1.71 (m, 1H), 1.70-1.63 (m, 1H), 1.60-1.52 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.9, 142.3, 139.5, 128.58, 128.56, 128.5, 126.0, 125.9, 125.91, 125.88, 67.6, 45.7, 36.2, 35.9, 27.5. **IR** (neat) ν_{max} 3485 (s), 2931 (w), 2900 (w), 1682 (s), 1579 (w), 1509 (m), 1327 (s), 1169 (m), 892 (m), 844 (m), 703 (w), 606 (w) cm^{-1}. **HRMS** (DART) for $C_{19}H_{20}O_2F_3$ $[M+H]^+$: Calc'd: 337.1410, found: 337.1396.



1-(4-(dimethylamino)phenyl)-3-hydroxy-6-phenylhexan-1-one (14). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), 4-(dimethylamino)benzoyl chloride (36.7 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography

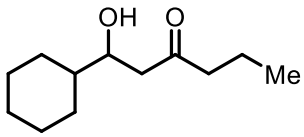
(20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (48.0 mg, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.1 Hz, 2H), 7.34-7.26 (m, 2H), 7.22-7.13 (m, 3H), 6.64 (d, *J* = 9.1 Hz, 2H), 4.24-4.16 (m, 1H), 3.73 (s, 1H), 3.10 (dd, *J* = 17.3, 2.4 Hz, 1H), 3.06 (s, 6H), 2.88 (dd, *J* = 17.3, 9.3 Hz, 1H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.93-1.83 (m, 1H), 1.79-1.70 (m, 1H), 1.69-1.61 (m, 1H), 1.58-1.50 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.1, 153.8, 142.5, 130.5, 128.6, 128.4, 125.8, 124.8, 110.7, 68.1, 43.9, 40.1, 36.3, 36.0, 27.5. **IR** (neat) ν_{max} 3468 (br, w), 2926 (w), 1650 (w), 1595 (s), 1530 (w), 1371 (m), 1186 (m), 1169 (m), 819 (w), 750 (m), 700 (w), 579 (w) cm^{-1}. **HRMS** (DART) for $C_{20}H_{26}NO_2$ $[M+H]^+$: Calc'd: 312.1952, found: 312.1958.



6-hydroxytetradecan-4-one (15). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), 1-octene (mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), butanoyl chloride (21.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (33.3 mg, 73% yield).

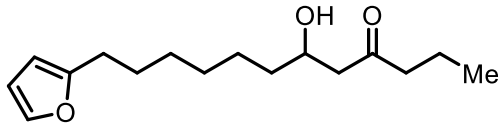
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.05-3.97 (m, 1H), 3.06 (br s, 1H), 2.57 (dd, *J* = 17.5, 2.8 Hz, 1H), 2.47 (dd, 1H), 2.39 (t, *J* = 7.3 Hz, 2H), 1.59 (h, *J* = 7.3 Hz, 2H), 1.52-1.17 (m, 14H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 212.6, 67.8, 49.1, 45.7, 36.6, 32.0, 29.69, 29.67, 29.4, 25.6, 22.8, 17.2, 14.2, 13.8. **IR** (neat) ν_{max} 3244 (br, m), 2957 (m), 2916
(s), 2848 (m), 1701 (s), 1465 (m), 1386 (m), 1132 (m), 1094 (m), 1027 (m), 889 (m), 724 (m), 628 (m) cm^{-1}. **HRMS** (DART) for $C_{14}H_{29}O_2$ $[M+H]^+$: Calc'd: 229.2162, found: 229.2172.



1-cyclohexyl-1-hydroxyhexan-3-one (16). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), cyclohexene (21.4 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF

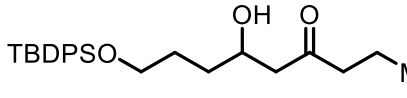
(0.4 mL), butanoyl chloride (21.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (26.2 mg, 66% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.79 (m, 1H), 2.97 (s, 1H), 2.58 (dd, *J* = 17.3, 2.4 Hz, 1H), 2.49 (dd, *J* = 17.3, 9.6 Hz, 1H), 2.41 (t, *J* = 7.3 Hz, 2H), 1.85-1.80 (m, 1H), 1.77-1.70 (m, 2H), 1.67-1.56 (m, 4H), 1.36-1.30 (m, 1H), 1.26-1.09 (m, 3H), 1.06-0.95 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 212.9, 71.9, 46.2, 45.8, 43.1, 29.0, 28.4, 26.6, 26.3, 26.2, 17.2, 13.8. **IR** (neat) ν_{max} 3448 (br, w), 2923 (s), 2852 (s), 1703 (s), 1450 (m), 1407 (m), 1371 (m), 1308 (m), 1274 (m), 1127 (m), 1108 (m), 1065 (m), 1027 (m), 989 (m), 957 (w), 892 (w), 531 (w) cm^{-1}. **HRMS** (DART) for $C_{12}H_{23}O_2$ $[M+H]^+$: Calc'd: 199.1693, found: 199.1688.



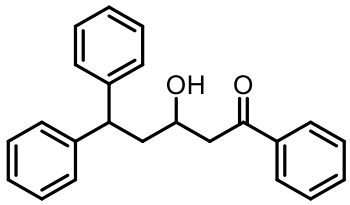
12-(furan-2-yl)-6-hydroxydodecan-4-one (17). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), **S-1** (39.0 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), butanoyl chloride (21.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (32.5 mg, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.29 (s, 1H), 6.29 – 6.24 (m, 1H), 5.97 (d, *J* = 3.1 Hz, 1H), 4.22 (m, 1H), 3.24 (d, *J* = 3.2 Hz, 1H), 3.17 (dd, *J* = 17.6, 2.6 Hz, 1H), 3.04 (dd, *J* = 17.6, 9.0 Hz, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.69-1.58 (m, 3H), 1.56-1.47 (m, 2H), 1.46-1.31 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.1, 156.6, 140.8, 136.9, 133.6, 128.8, 128.2, 110.2, 104.7, 67.9, 45.2, 36.6, 29.4, 29.2, 28.11, 28.07, 25.6. **IR** (neat) ν_{max} 3454 (br, w), 2929 (m), 2856 (w), 1677 (s), 1597 (m), 1580 (w), 1507 (w), 1449 (m), 1283 (w), 1210 (s), 1180 (w), 1146 (m), 1072 (w), 1003 (s), 922 (w), 884 (w), 797 (w), 752 (s), 727 (s), 689 (s), 662 (w), 599 (s), 587 (m), 536 (w) cm^{-1}. **HRMS** (DART) for $C_{19}H_{25}O_3$ $[M+H]^+$: Calc'd: 301.1798, found: 301.1796.



9-((tert-butyldiphenylsilyl)oxy)-6-hydroxynonan-4-one (18). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), **S-4** (77.1 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (2.20 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), butanoyl chloride (21.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (59.4 mg, 72% yield).

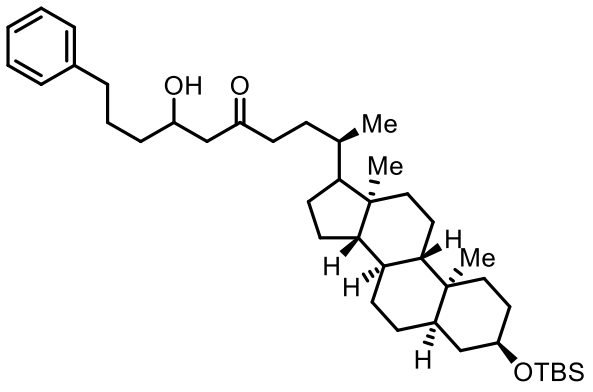
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.64 (m, 4H), 7.46-7.34 (m, 6H), 4.11-4.01 (m, 1H), 3.69 (t, *J* = 5.4 Hz, 1H), 3.24 (d, *J* = 3.2 Hz, 1H), 2.60-2.46 (m, 2H), 2.41 (t, *J* = 7.3 Hz, 2H), 1.84-1.51 (m, 6H), 1.05 (s, 9H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}CNMR** (126 MHz, $CDCl_3$) δ 212.3, 135.7, 135.7, 129.7, 127.8, 67.6, 64.0, 49.2, 45.7, 33.3, 28.7, 27.0, 19.3, 17.2, 13.8. **IR** (neat) ν_{max} 3399 (br, s), 2938 (s), 2857 (s), 1705 (s), 1472 (w), 1428 (m), 1112 (s), 741 (m), 705 (s), 615 (m) cm^{-1}. **HRMS** (DART) for $C_{25}H_{37}O_3Si$ $[M+H]^+$: Calc'd: 413.2507, found: 413.2505.



3-hydroxy-1,5,5-triphenylpentan-1-one (19). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), 1,1-diphenylethylene (46.9 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), benzoyl chloride (28.1 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (53.5 mg, 66% yield).

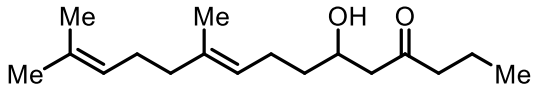
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.28-7.33 (m, 7H), 7.22-7.14 (m, 2H), 4.37 (dd, *J* = 10.4, 5.3 Hz, 1H), 4.06-4.13 (m, 1H), 3.29 (d, *J* = 3.0 Hz, 1H), 3.15 (dd, *J* = 17.7, 3.0 Hz, 1H), 3.09 (dd, *J* = 17.9, 8.6 Hz, 1H), 2.37-2.30 (m, 1H), 2.29-2.22 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.8, 145.3, 144.1, 136.8, 133.7, 128.8, 128.7, 128.6, 128.3, 128.1, 127.8, 126.5, 126.3, 65.7, 47.1, 45.4, 42.4. **IR** (neat) ν_{max} 3454 (br, w), 3059 (w), 3026 (w), 2933 (w), 1677 (m), 1597 (m), 1580 (w), 1493 (m), 1449 (m), 1409 (w), 1361 (w), 1280 (w), 1207 (m), 1181 (w), 1158 (w), 1076 (w), 1057 (w), 1031 (m), 1001 (w), 985 (w), 917 (w), 868 (w), 782 (w),

752 (s), 739 (m), 698 (s), 619 (w), 590 (w), 551 (w) cm^{-1}. **HRMS** (DART) for $C_{23}H_{23}O_2$ $[M+H]^+$: Calc'd: 331.1693, found: 331.1695.



(2R)-2-((3R,5R,8R,9S,10S,13R,14S)-3-((tert-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-7-hydroxy-10-phenyldecan-5-one (20). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), **S-7** (101.9 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (63.7 mg, 50% yield).

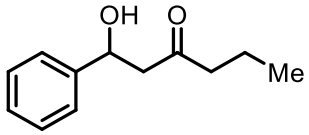
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 4.10-3.99 (m, 1H), 3.62-3.53 (m, 1H), 3.09 (dd, *J* = 8.1, 3.4 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.59-2.39 (m, 3H), 2.37-2.27 (m, 1H), 1.96-1.01 (m, 34H), 0.93-0.85 (m, 15H), 0.62 (s, 3H), 0.06 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 213.1, 142.4, 128.5, 128.4, 125.9, 73.0, 67.63, 67.59, 56.5, 56.1, 49.02, 49.01, 42.9, 42.4, 40.7, 40.4, 40.3, 37.1, 36.1, 36.0, 35.9, 35.7, 35.4, 34.7, 31.2, 29.7, 28.4, 27.43, 27.39, 26.5, 26.1, 24.3, 23.5, 21.0, 18.6, 18.5, 12.2, -4.4. **IR** (neat) ν_{max} 3480 (br, m), 2929 (s), 2854 (m), 1699 (s), 1603 (w), 1496 (w), 1451 (m), 750 (m), 700 (m) cm^{-1}. **HRMS** (DART) for $C_{41}H_{69}O_3Si$ $[M+H]^+$: Calc'd: 637.5016, found: 637.5005.



(E)-6-hydroxy-10,14-dimethylpentadeca-9,13-dien-4-one (21). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), **S-2** (39.1 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), butanoyl chloride (21.3 mg, 0.20 mmol, 1.00

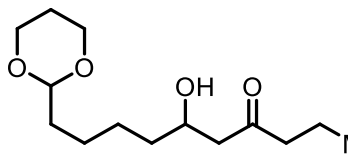
equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (22.9 mg, 43% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14-5.10 (t, *J* = 6.8 Hz, 1H), 5.09-5.06 (t, *J* = 6.6 Hz, 1H), 4.07-4.01 (m, 1H), 3.01 (d, *J* = 3.5 Hz, 1H), 2.59 (dd, *J* = 17.5, 2.8 Hz, 1H), 2.50 (dd, *J* = 17.5, 9.1 Hz, 1H), 2.40 (t, *J* = 7.3 Hz, 2H), 2.17-2.03 (m, 4H), 2.01-1.95 (m, 2H), 1.67 (s, 3H), 1.65-1.52 (m, 9H), 1.45-1.37 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 212.5, 136.0, 131.5, 124.4, 123.8, 67.4, 49.1, 45.7, 39.9, 36.6, 26.8, 25.8, 24.1, 17.8, 17.2, 16.2, 13.8. **IR** (neat) ν_{max} 3458 (br, m), 2963 (s), 2925 (s), 1707 (s), 1448 (m), 1376 (m), 1127 (w), 1103 (m), 1037 (w), 835 (w)cm^{-1}. **HRMS** (DART) for $C_{16}H_{25}O_3$ $[M+H]^+$: Calc'd: 265.1804, found: 265.1796.



1-hydroxy-1-phenylhexan-3-one (22). The reaction was performed according to the general procedure with slight modification. 9-phenyl-9-borabicyclo[3.3.1]nonane (**S-5**) (51.5 mg, 0.26 mmol, 1.30 equiv.) was synthesized independently as mentioned above, diluted with 0.5 mL THF, and to it was added halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (2.20 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), followed by butanoyl chloride (21.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (23.5 mg, 61% yield).

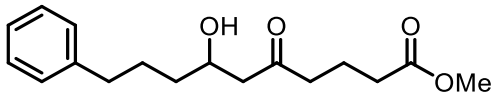
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.19 (m, 5H), 5.16 (dd, *J* = 8.7, 3.5 Hz, 1H), 3.38 (s, 1H), 2.85 (dd, *J* = 17.4, 8.8 Hz, 1H), 2.78 (dd, *J* = 17.4, 3.6 Hz, 1H), 2.41 (t, *J* = 7.3 Hz, 2H), 1.62 (h, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}CNMR** (150 MHz, $CDCl_3$) δ 211.7, 143.0, 128.7, 127.8, 125.8, 70.1, 51.2, 45.7, 17.2, 13.8. **IR** (neat) ν_{max} 3400 (br, m), 2961 (m), 1702 (s), 1494 (w), 1453 (m), 1370 (m), 1067 (m), 1030 (m), 757 (m), 701 (s) cm^{-1}. **HRMS** (DART) for C12H20NO_2 $[M+H]^+$: Calc'd: 210.1489, found: 210.1488.



10-(1,3-dioxan-2-yl)-6-hydroxydecan-4-one (23). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), **S-3** (37.0 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), butanoyl chloride (21.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was

purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (29.5 mg, 57% yield).

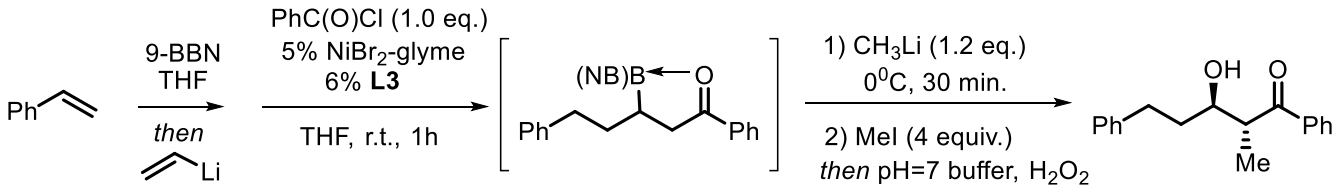
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.51 (t, *J* = 5.1 Hz, 1H), 4.21 (m, 1H), 4.08 (dd, *J* = 10.7, 5.0 Hz, 2H), 3.74 (td, *J* = 11.0, 2.0 Hz, 2H). 3.26 (m, 1H), 3.14 (dd, *J* = 17.5, 2.5 Hz, 1H), 3.02 (dd, *J* = 17.6, 9.0 Hz, 1H), 2.11-2.01 (m, 1H), 1.67-1.56 (m, 3H), 1.55-1.47 (m, 2H), 1.46-1.35 (m, 3H), 1.33-1.31 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.1, 136.9, 133.6, 128.8, 128.2, 102.4, 67.8, 67.0, 45.1, 36.5, 35.3, 26.0, 25.6, 24.0. **IR** (neat) ν_{max} 3454 (br, w), 2927 (w), 2855 (w), 1678 (m), 1597 (w), 1580 (w), 1449 (w), 1431(w), 1404 (w), 1377 (w), 1283 (w), 1240 (m), 1213 (m), 1181 (w), 1142 (s), 1092 (m), 993 (m), 936 (w), 894 (w), 864 (w), 838 (w), 754 (m), 691 (m), 662 (w), 644 (w), 587 (w), 535 (w) cm^{-1}. **HRMS** (DART) for $C_{17}H_{25}O_4$ $[M+H]^+$: Calc'd: 293.1747, found: 293.1751.



methyl 7-hydroxy-5-oxo-10-phenyldecanoate (24). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), methyl 5-chloro-5-oxopentanoate (32.9 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (47.4 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 2H), 7.18-7.13 (m, 3H), 4.07-3.98 (m, 1H), 3.64 (s, 3H), 2.61 (t, *J* = 7.4 Hz, 2H), 2.57-2.43 (m, 4H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.87 (p, *J* = 7.2 Hz, 2H), 1.80-1.71 (m, 1H), 1.70-1.57 (m, 1H), 1.56-1.46 (m, 1H), 1.45-1.34 (m, 1H) .**^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.2, 173.6, 142.3, 128.5, 128.4, 125.9, 77.5, 77.2, 76.8, 67.6, 51.7, 49.2, 42.4, 36.1, 35.8, 33.0, 27.3, 18.7. **IR** (neat) ν_{max} 3407 (br, w), 2937 (m), 1734 (s), 1710 (m), 1603 (w), 1172 (m), 1086 (m), 750 (m), 701 (m) cm^{-1}. **HRMS** (DART) for $C_{17}H_{25}O_4$ $[M+H-H_2O]^+$: Calc'd: 293.1747, found: 203.1737.

2.5.2.4 *Procedures and Characterization for Boron-Enolate Alkylation*



***anti*-3-hydroxy-2-methyl-1,5-diphenylpentan-1-one (29).** In a glovebox, under argon, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with a solution of 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.). The vial was cooled to 0°C, and styrene (27.1 mg, 0.26 mmol, 1.30 equiv.) was added. The reaction mixture was allowed to warm to room temperature and stir for 3 hours before being cooled back to 0°C. A solution of vinyllithium (for synthesis of halide free vinyllithium see ref[1]) in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.) was added to the reaction mixture which was then warmed to room temperature and stirred for 5 minutes. Meanwhile a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (see ref[10] for its synthesis) (3.51mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL) was allowed to complex for 5 minutes under inert atmosphere. The catalyst solution was added to the boron 'ate' mixture at room temperature followed by addition of benzoyl chloride (28.1 mg, 0.20 mmol, 1.00 equiv.). The reaction vial was sealed with a septum cap, taken out of the glovebox and stirred at room temperature for 1h, after which point the reaction mixture was cooled to -78°C and methyllithium in Et_2O (0.15 mL, 1.6M, 0.24 mmol, 1.2 equiv.) was added dropwise through a syringe under inert atmosphere. The reaction mixture was allowed to warm up to 0°C and stir for 30 minutes. After cooling the reaction mixture back to -78°C, iodomethane (113 mg, 0.60 mmol, 4.0 equiv.) was added dropwise. The reaction mixture was then warmed up to room temperature and stir for 2 hours. After cooling the reaction mixture to 0°C, 30% H_2O_2 (0.5 mL) was added along with pH=7 buffer solution (0.5 mL). The reaction mixture was allowed to warm up to room temperature and stir for 3 hours. Aq. saturated $Na_2S_2O_3$ (1 mL) solution was then added to quench the remaining H_2O_2. The aqueous phase was EtOAc (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and the crude mixture was purified by 2 runs of column chromatography (1st: 20% EtOAc in hexane, 2nd: 100% chloroform, stain in $KMnO_4$) to afford the product as a colorless oil (24.2 mg, 45% yield, >19:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.29-7.25 (m, 3H), 7.22-7.16 (m, 2H), 3.93-3.85 (m, 1H), 3.59-3.52 (m, 1H), 3.04 (d, *J* = 7.1 Hz, 1H), 2.96-2.88(m, 1H), 2.75-2.69 (m, 1H), 1.91-1.78 (m, 1H), 1.27 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 206.0, 142.2, 136.7, 133.6, 128.9, 128.6, 128.54, 128.52, 126.0, 73.6, 45.9, 37.0, 32.3, 29.9, 15.8. **IR** (neat) ν_{max} 3489 (br, m), 2927 (m), 1678 (s), 1596 (w), 1496 (m), 1454 (m), 1376 (w), 1210 (m), 972 (m), 702 (s) cm^{-1}. **HRMS** (DART) for $C_{18}H_{21}O_2$ $[M+H]^+$: Calc'd: 269.1542, found: 269.1536.

The relative stereochemistry of the product was deteremined by comparison of ^{1}H NMR spectrum with diastereochemically-enriched authentic sample prepared according to the procedure reported by Evans.[41]

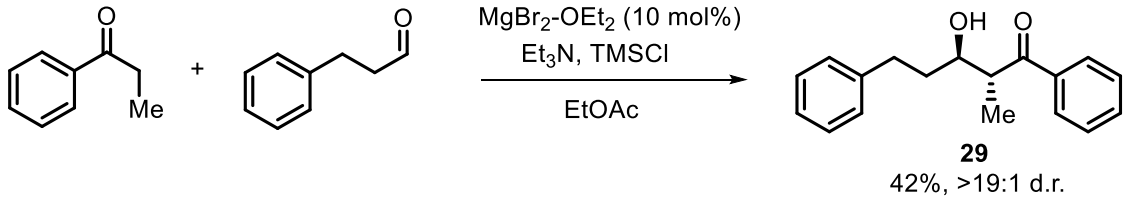
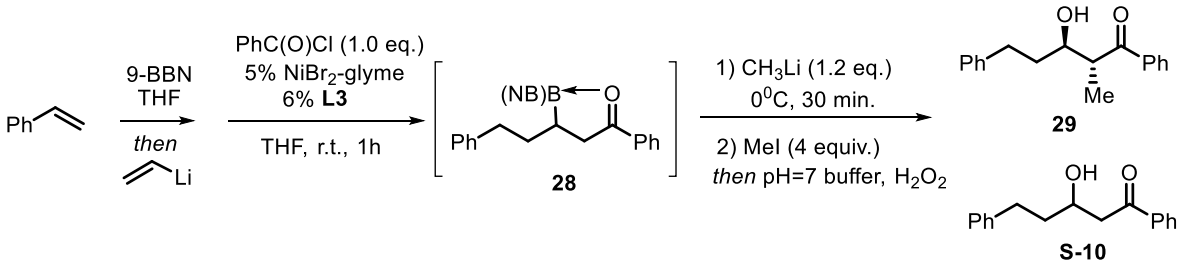


Table S2. Survey of Base for Boron-Enolate Alkylation

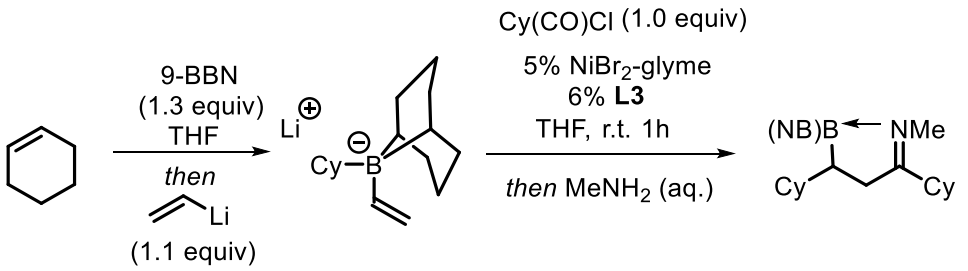


Base	29 (%)	S-6 (%)
*i*PrLi (1.7M pentane solution)	17%	0%
*n*BuLi (2.6M hexane solution)	39%	0%
MeLi (1.42M Et_2O solution)	45%	0%
LDA	0%	62%
iPr_2NEt	0%	58%

The formation of **S-10** is presumably due to the inefficient deprotonation of **28** and its subsequent oxidation.

[41] D. Evans, J. Tedrow, J. Shaw, C. Downey, *J. Am. Chem. Soc*. **2002**, *124*, 392.

2.5.2.5 *Synthesis and Characterization of 9-BBN-Schiff-Base*

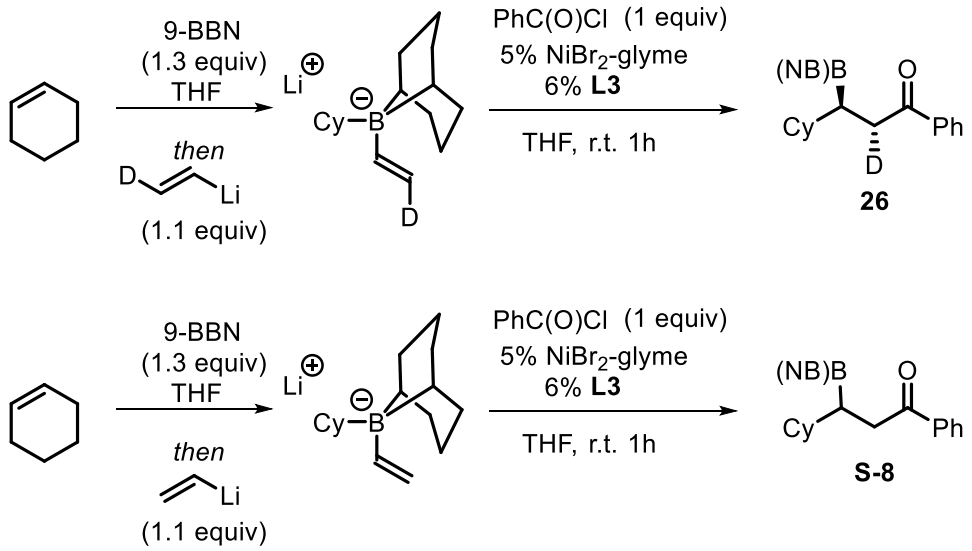


(E)-3-(9-borabicyclo[3.3.1]nonan-9-yl)-1,3-dicyclohexyl-N-methylpropan-1-imine (31). In a glovebox, under argon, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with a solution of 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.). The vial was cooled to 0°C, and cyclohexene (21.4 mg, 0.26 mmol, 1.30 equiv.) was added. The reaction mixture was allowed to heat up to 60°C and stir for 3 hours before being cooled back to 0°C. A solution of vinyllithium (for synthesis of halide free vinyllithium see ref[1]) in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.) was added to the reaction mixture which was then warmed to room temperature and stirred for 5 minutes. Meanwhile a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (see ref[10] for its synthesis) (0.012 mmol, 0.060 equiv.) in THF (0.4 mL) was allowed to complex for 5 minutes under inert atmosphere. The catalyst solution was added to the boron 'ate' mixture at room temperature followed by addition of cyclohexanecarbonyl chloride (29.3 mg, 0.20 mmol, 1.00 equiv.). The reaction vial was sealed with a septum cap, taken out of the glovebox and stirred at room temperature for 1h, after which point the reaction mixture was cooled to 0°C and 40% methylamine aqueous solution (1 mL) was added. The reaction mixture was allowed to warm up to room temperature and stirred for 1h. The aqueous phase was EtOAc (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and subsequently purified via silica gel column chromatography (20% CH_2Cl_2 in hexanes, stain in $KMnO_4$) to provide **31** as a white solid (55.4 mg, 78%).

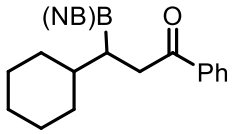
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (s, 3H), 2.61-2.51 (m, 1H), 2.50-2.37 (m, 2H), 2.30-2.18 (m, 1H), 2.10-1.94 (m, 1H), 1.93-0.98 (m, 31H), 0.94 (s, 1H), 0.39 (qd, J = 12.3, 3.6 Hz, 1H), 0.31 (s, 1H) .**^{13}C NMR** (126 MHz, $CDCl_3$) δ 189.1, 40.4, 37.7, 36.9, 35.8, 35.1, 34.3, 33.2, 31.9, 30.8, 30.7, 29.5, 29.4, 27.4, 27.3, 27.2, 26.0, 25.9, 25.8, 25.2, 24.2. **IR** (neat) ν_{max} 2917 (s), 2840 (s), 1637 (m), 1447 (m), 1332 (w), 1029 (m), 905 (s), 734 (s) cm^{-1}. **HRMS** (DART) for $C_{24}H_{43}BN$ $[M+H]^+$: Calc'd: 356.3483, found: 356.3489.

The structure was characterized by X-ray crystallography. Crystals were grown by slow evaporation with Et_2O in a 1-dram vial at room temperature.

2.5.2.6 *Deuterium-Labeling Experiments*



The trans-deuterium labeled vinyl lithium was prepared as described in previous reports.[42]



3-(9-borabicyclo[3.3.1]nonan-9-yl)-3-cyclohexyl-1-phenylpropan-1-one (S-9). In a glovebox, under argon, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with a solution of 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.). The vial was cooled to 0 ℃, and cyclohexene (21.4 mg, 0.26 mmol, 1.30 equiv.) was added via syringe. The reaction mixture was heated to 60 ºC and stir for 3 hours before being cooled back to 0 ℃. A solution of vinyllithium (for synthesis of halide free vinyllithium see ref[1]) in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.) was added to the reaction mixture which was then warmed to room temperature and stirred for 5 minutes. Meanwhile a solution of $NiBr_2$-glyme (0.010 mmol, 0.050 equiv.) and **L3** (see ref[10] for its synthesis) (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL) was allowed to complex for 5 minutes under inert atmosphere. The catalyst solution was added to the boron 'ate' mixture at room temperature followed by addition of benzoyl chloride (28.1 mg, 0.20 mmol, 1.00 equiv.). The reaction vial was sealed with a septum cap, taken out of the glovebox and stirred at room temperature for 1h. The crude mixture was concentrated in vacuo and purified by silica gel column chromatography (20% CH_2Cl_2 in hexane, stain in $KMnO_4$) to afford the product as a yellow oil (37.0 mg, 55% yield).

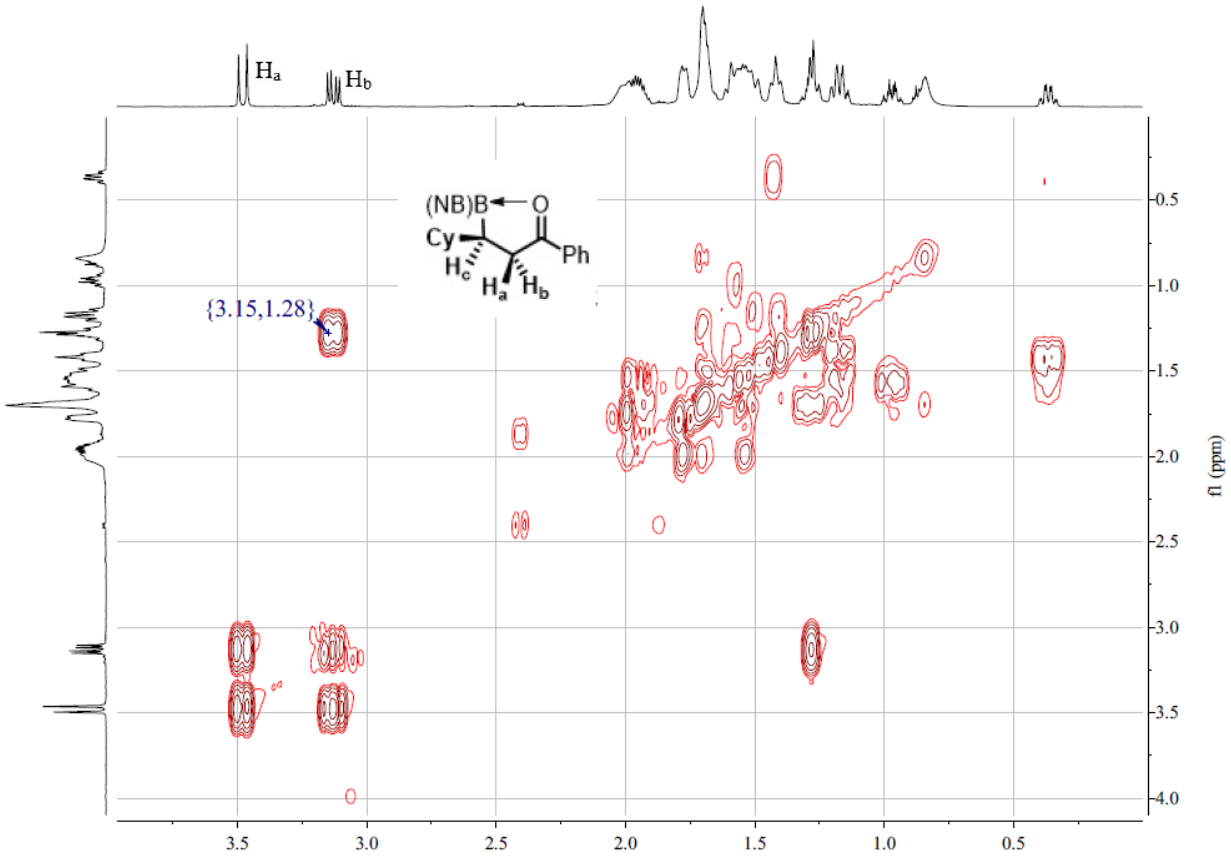
[42] L. Zhang, G. Lovinger, E. Edelstein, A. Szymaniak, M. Chierchia, J. Morken, *Science* **2015**, *351*, 70.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 2H), 7,74 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 8.1 Hz, 2H), 3.48 (d, *J* = 19.4 Hz, 1H), 3.15 (dd, *J* = 19.4, 8.3 Hz, 1H), 2.06-1.87 (m, 4H), 1.80-1.12 (m, 18H), 1.02-0.92 (m, 1H), 0.89-0.77 (m, 2H), 0.37 (dq, *J* = 12.2, 3.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 212.9, 136.4, 131.2, 130.9, 129.4, 40.0, 38.1, 33.5, 33.2, 32.6, 30.1, 27.2, 26.82, 26.77, 25.1. **^{11}B NMR** (150 MHz, $CDCl_3$) δ 21.5. **IR** (neat) ν_{max} 2917 (s), 2840 (s), 1637 (m), 1447 (m), 1332 (w), 1029 (m), 905 (s), 734 (s) cm^{-1}. **HRMS** (DART) for $C_{23}H_{34}BO$ $[M+H]^+$: Calc'd: 337.2697, found: 337.2700.

The resonances of the two diastereotopic protons adjacent to the carbonyl group in ^{1}H NMR are identified by a series of COESY NMR and 1D NOESY NMR analysis presented below.

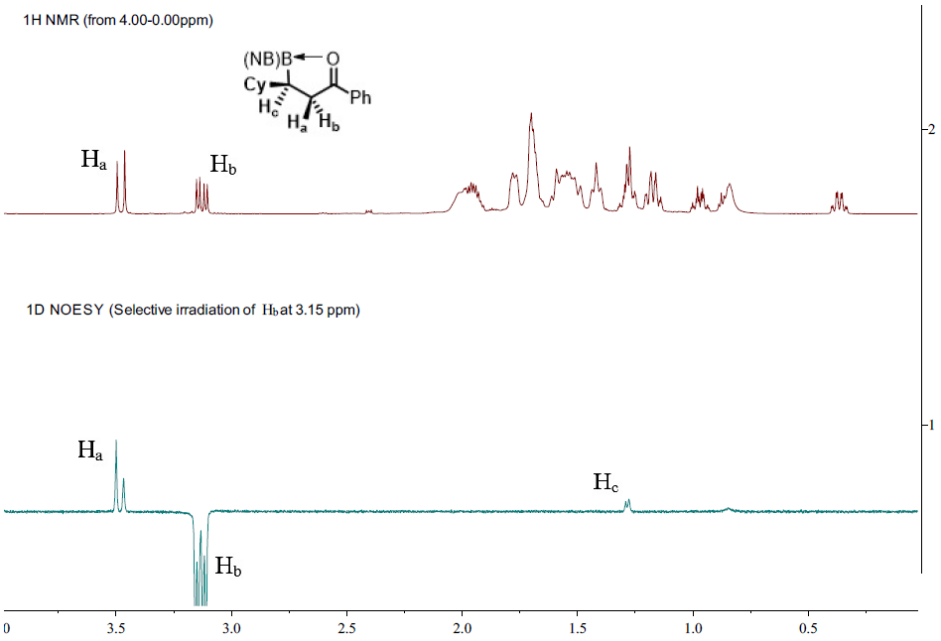
From COESY NMR spectrum, it is clearly seen that the proton with resonance at 3.15 ppm couples with H_c with a resonance at 1.28 ppm, whereas the resonance at 3.48 ppm shows no appreciable coupling with H_c. Therefore, it is determined that the 3.15 ppm resonance corresponds to H_b while the 3.48 ppm resonance corresponds to H_a.

COESY NMR of **S-9**

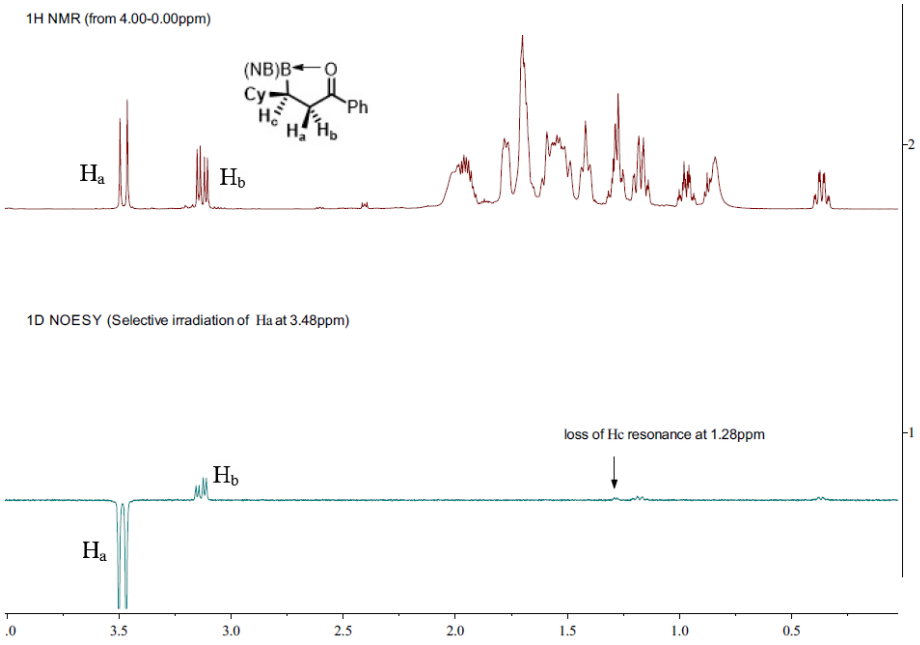


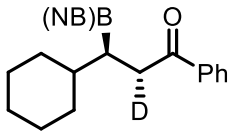
NOESY NMR was also carried out to support the findings about the resonances of the two diasterotopic protons. Selective irradiation of the resonance at 3.15 ppm led to NOE of H_c with resonance at 1.28ppm, whereas selective irradiation of the resonance at 3.48 ppm led to no observable NOE of H_c.

1D-NOESY NMR of **S-9** (selective irradiation at 3.15 ppm)



1D-NOESY NMR of **S-9** (selective irradiation at 3.48 ppm)

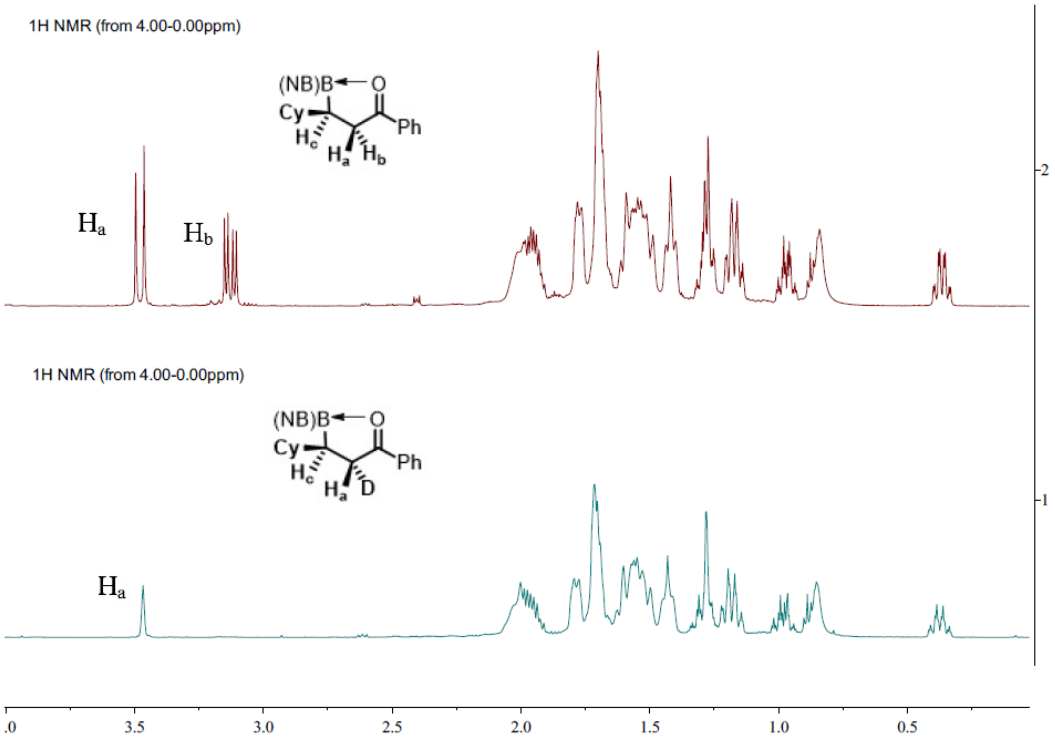




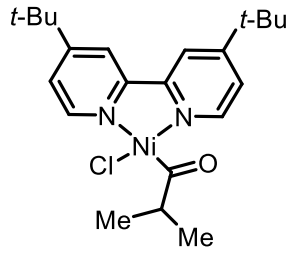
***anti*-3-(9-borabicyclo[3.3.1]nonan-9-yl)-3-cyclohexyl-1-phenylpropan-1-one-2-d (26).** The reaction was performed according to the procedure for synthesis of **S-7** with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), cyclohexene (21.4 mg, 0.26 mmol, 1.30 equiv.), deuterium labeled vinyl lithium in THF (0.27 mL, 0.82 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L3** (3.51 mg, 0.012 mmol, 0.060 equiv.) in THF (0.4 mL), benzoyl chloride (28.1 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% CH_2Cl_2 in hexane, stain in $KMnO_4$) to afford the product as a yellow oil (21.1 mg, 30% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.8 Hz, 2H), 7,75 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 3.48 (s, 1H), 2.13-1.88 (m, 3H), 1.81-1.40 (m, 3H), 1.36-1.11 (m, 5H), 1.04-0.94 (m, 1H), 0.91-0.71 (m, 2H), 0.37 (dq, J = 12.2, 3.4 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 213.0, 136.4, 131.3, 130.9, 129.4, 38.1, 33.50, 33.48, 32.6, 30.22, 30.15, 27.2, 26.83, 26.77, 25.1. **^{11}B NMR** (150 MHz, $CDCl_3$) δ 21.5. **IR** (neat) ν_{max} 2922 (s), 2852 (m), 1679 (m), 1598 (w), 1447 (s), 1272 (m), 1206 (m), 746 (s), 689 (s), 651 (w) cm^{-1}.

The relative stereochemistry was determined by comparison of its ^{1}H NMR spectrum with its non-deuterium labeled counterpart (**S-9**).



2.5.2.7 *Stoichiometric Experiments*

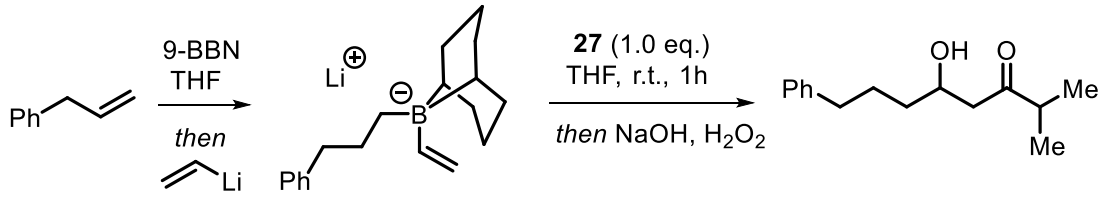


27

Ni(II) oxidative addition complex (27). The title compound was prepared according to the procedure reported by Gong with slight modifications.[43] In an argon filled glovebox, to an oven-dried scintillation vial was added $Ni(COD)_2$ (248 mg, 0.90 mmol, 1.0 equiv.) and Et_2O (4 mL). The reaction mixture was allowed to stir for 0.5h at room temperature at which point 4,4'-di-tert-butyl-2,2'-bipyridine (341 mg, 0.90 mmol, 1.0 equiv.) in Et_2O (4 mL) was added dropwise. The resulting mixture was allowed to stir at room temperature, at which point, a solution of *iso*-butyryl chloride (96.0 mg, 0.90 mmol, 1.0 equiv.) in Et_2O (1 mL) was added via a syringe. The mixture was allowed to stir for 1h. The suspension was then allowed to settle down and the supernatant was removed via syringe leaving behind red solid which was triturated with Et_2O (2 mL x 4). The red solid was then dried under vacuum, affording **27** (351 mg, 90%). All spectral data was in accordance with the literature.[13]

^{1}H NMR (500 MHz, DMF-d_7) δ 8.99 (br s, 1H), 8.72 (br s, 2H), 8.21 (br s, 1H), 7.88 (d, J = 40.3 Hz, 2H), 3.49 (s, 1H), 1.58 (s, 18H), 1.47 (s, 6H). **^{13}C NMR** (150 MHz, DMF-d_7) δ 260.0, 164.2, 163.3, 155.3, 152.2, 150.6, 148.0, 124.2, 123.2, 119.9, 118.7, 45.2, 35.6, 18.5.

Stoichiometric Conjunctive Cross-Coupling Reaction

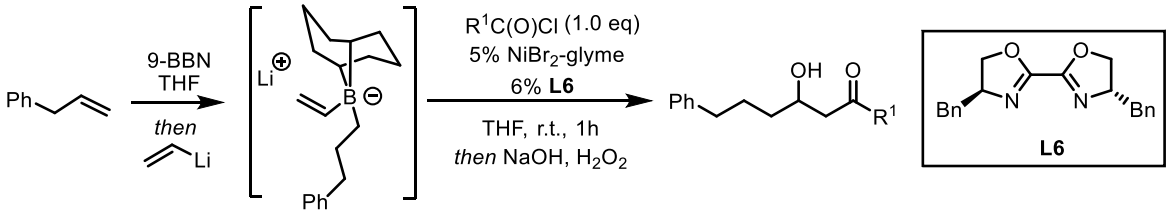


In a glovebox, under argon, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with a solution of 9-BBN in THF (0.40 mL, 0.5 M, 0.20 mmol, 1.00 equiv.). The vial was cooled to 0°C, and allylbenzene (23.6 mg, 0.20 mmol, 1.00 equiv.) was added. The reaction mixture was allowed to warm to room temperature and stir for 3 hours before being cooled back to 0°C. A solution of vinyllithium (for synthesis of halide free

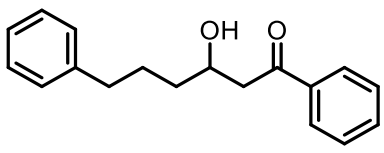
[43] C. Zhao, J. Xiao, X. Wang, H. Gong, *J. Am. Chem. Soc.* **2014**, *136*, 17645.

vinyllithium see ref[1]) in THF (0.15 mL, 1.38 M, 0.22 mmol, 1.00 equiv.) was added to the reaction mixture which was then warmed to room temperature and stirred for 5 minutes. To the vial was added **27** (86.7 mg, 0.20 mmol, 1.0 equiv.) in one portion at room temperature. The reaction vial was sealed with a septum cap, taken out of the glovebox and stirred at room temperature for 1h, after which point the reaction mixture was cooled to 0°C and 30% H_2O_2 (0.5 mL) were added along with 3 M NaOH (0.5 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 3 hours. Aq. saturated $Na_2S_2O_3$ (1 mL) solution was then added to quench the reaction. The aqueous phase was EtOAc (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and subsequently purified via silica gel column chromatography to provide **4** as a colorless oil (20.2 mg, 43%).

2.5.2.8 *Experiments with Chiral Bis(oxazoline) Ligands*



In a glovebox, under argon, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with a solution of 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.). The vial was cooled to 0°C, and the olefin (0.26 mmol, 1.30 equiv.) was added via syringe. The reaction mixture was allowed to warm to room temperature and stir for 3 hours before being cooled back to 0°C. A solution of vinyllithium (for synthesis of halide free vinyllithium see ref[1]) in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.) was added to the reaction mixture which was then warmed to room temperature and stirred for 5 minutes. Meanwhile a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L6** (0.012 mmol, 0.060 equiv.) in THF (0.4 mL) was allowed to complex for 5 minutes under inert atmosphere. The catalyst solution was added to the boron 'ate' mixture at room temperature followed by addition of acyl chloride (0.20 mmol, 1.00 equiv.) The reaction vial was sealed with a septum cap, taken out of the glovebox and stirred at room temperature for 1h, after which point the reaction mixture was cooled to 0°C and 30% H_2O_2 (0.5 mL) were added along with 3 M NaOH (0.5 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 3 hours. Aq. saturated $Na_2S_2O_3$ (1 mL) solution was then added to quench the reaction. The aqueous phase was EtOAc (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and subsequently purified via silica gel column chromatography to provide the desired products.

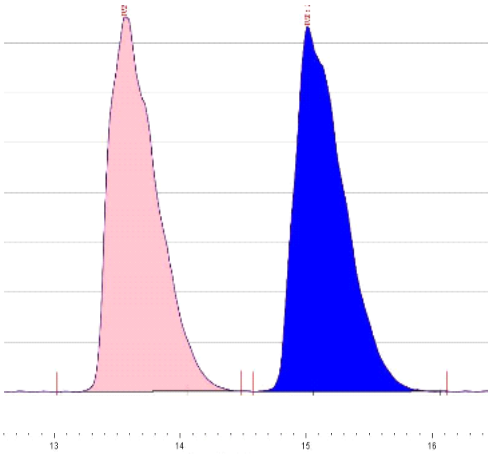


3-hydroxy-1,6-diphenylhexan-1-one (10). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L6** (0.012 mmol, 0.060 equiv.) in THF (0.4 mL), benzoyl chloride (28.1 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (19.3 mg, 36% yield). Its corresponding spectral data can be found above in the section ***"Characterization of Conjunctive Cross Coupling Products"***.

Enantioselectivity was determined by chiral SFC. Racemic compound was prepared according to the general procedure with **L3** (6 mol%) as the ligand.

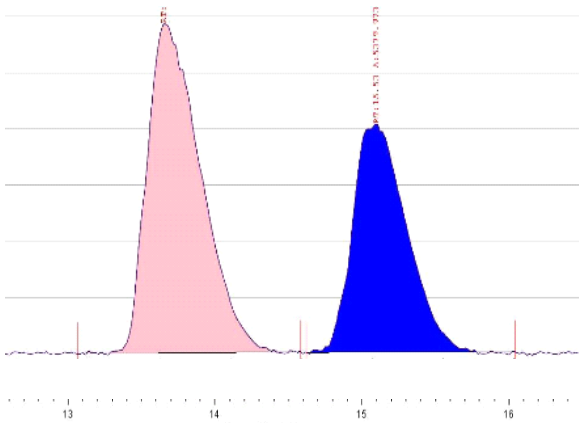
Chiral SFC (Chiracel AS-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)

Racemic material

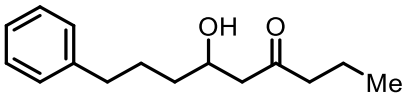


Peak No	% Area	Area	RT (min)
1	49.9903	19738.0387	13.5
2	50.0097	19745.7246	14.95
Total:	100	39483.7633	

Enantioenriched material



Peak No	% Area	Area	RT (min)
1	59.0118	7745.7033	14.03
2	40.9882	5379.9731	15.53
Total:	100	13125.6764	

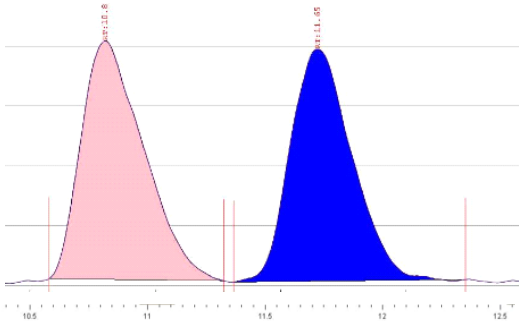


6-hydroxy-9-phenylnonan-4-one (3). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (3.09 mg, 0.010 mmol, 0.050 equiv.) and **L6** (0.012 mmol, 0.060 equiv.) in THF (0.4 mL), butanoyl chloride (21.3 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (20.2 mg, 43% yield). Its corresponding spectral data can be found above in the section ***"Characterization of Conjunctive Cross Coupling Products"***.

Enantioselectivity was determined by chiral SFC. Racemic compound was prepared according to the general procedure with **L3** (6 mol%) as the ligand.

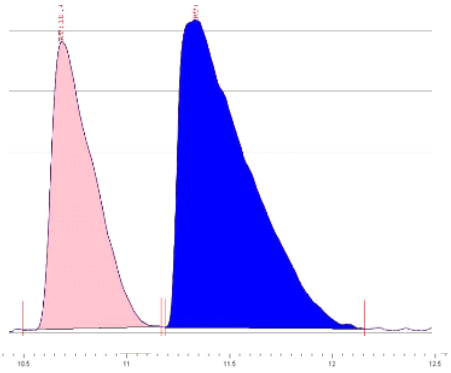
Chiral SFC (Chiracel AS-H, 2% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)

Racemic material

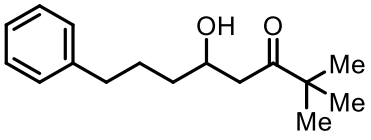


Peak No	% Area	Area	RT (min)
1	51.0302	3457.9941	10.8
2	48.9698	3318.3731	11.65
Total:	100	6776.3672	

Enantioenriched material



Peak No	% Area	Area	RT (min)
1	36.1664	4258.9027	10.41
2	63.8336	7516.955	11.24
Total:	100	11775.8577	

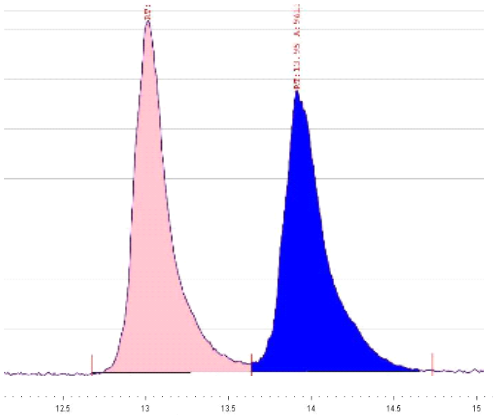


5-hydroxy-2,2-dimethyl-8-phenyloctan-3-one (7). The reaction was performed according to the general procedure with 9-BBN in THF (0.52 mL, 0.5 M, 0.26 mmol, 1.30 equiv.), allylbenzene (30.7 mg, 0.26 mmol, 1.30 equiv.), halide-free vinyllithium in THF (0.16 mL, 1.38 M, 0.22 mmol, 1.10 equiv.), a solution of $NiBr_2$-glyme (2.20 mg, 0.010 mmol, 0.050 equiv.) and **L6** (0.012 mmol, 0.060 equiv.) in THF (0.4 mL), pivaloyl chloride (24.1 mg, 0.20 mmol, 1.00 equiv.). The crude mixture was purified by column chromatography (20% EtOAc in hexanes, stain in $KMnO_4$) to afford the product as a colorless oil (13.4 mg, 27% yield). Its corresponding spectral data can be found above in the section ***"Characterization of Conjunctive Cross Coupling Products"***.

Enantioselectivity was determined by chiral SFC. Racemic compound was prepared according to the general procedure with **L3** (6 mol%) as the ligand.

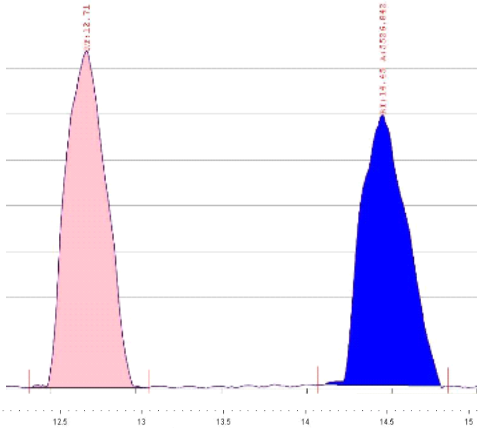
Chiral SFC (Chiracel OJ-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm)

Racemic material



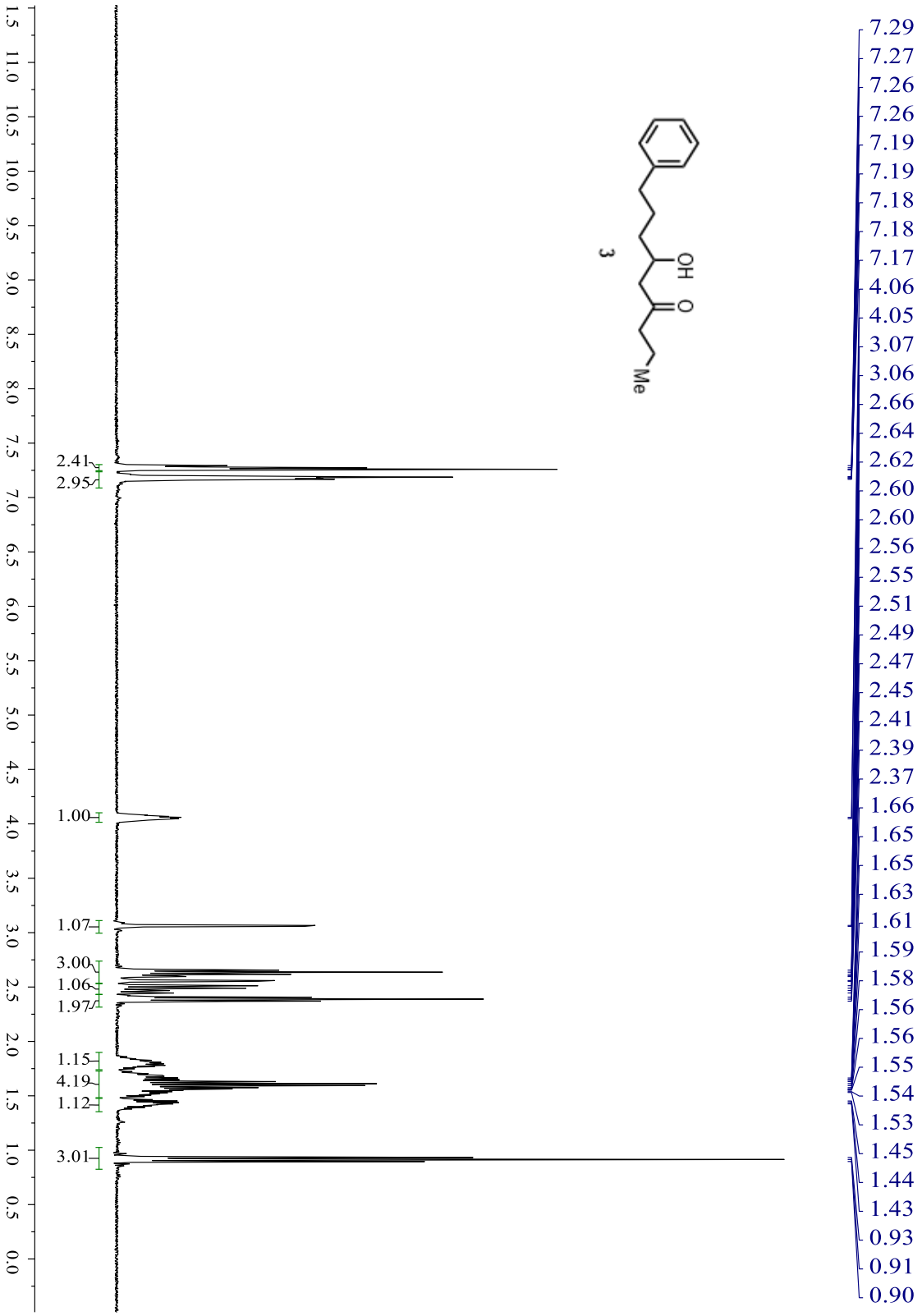
Peak No	% Area	Area	RT (min)
1	51.5896	10244.8632	12.2
2	48.4104	9613.5239	13.95
Total:	100	19858.3871	

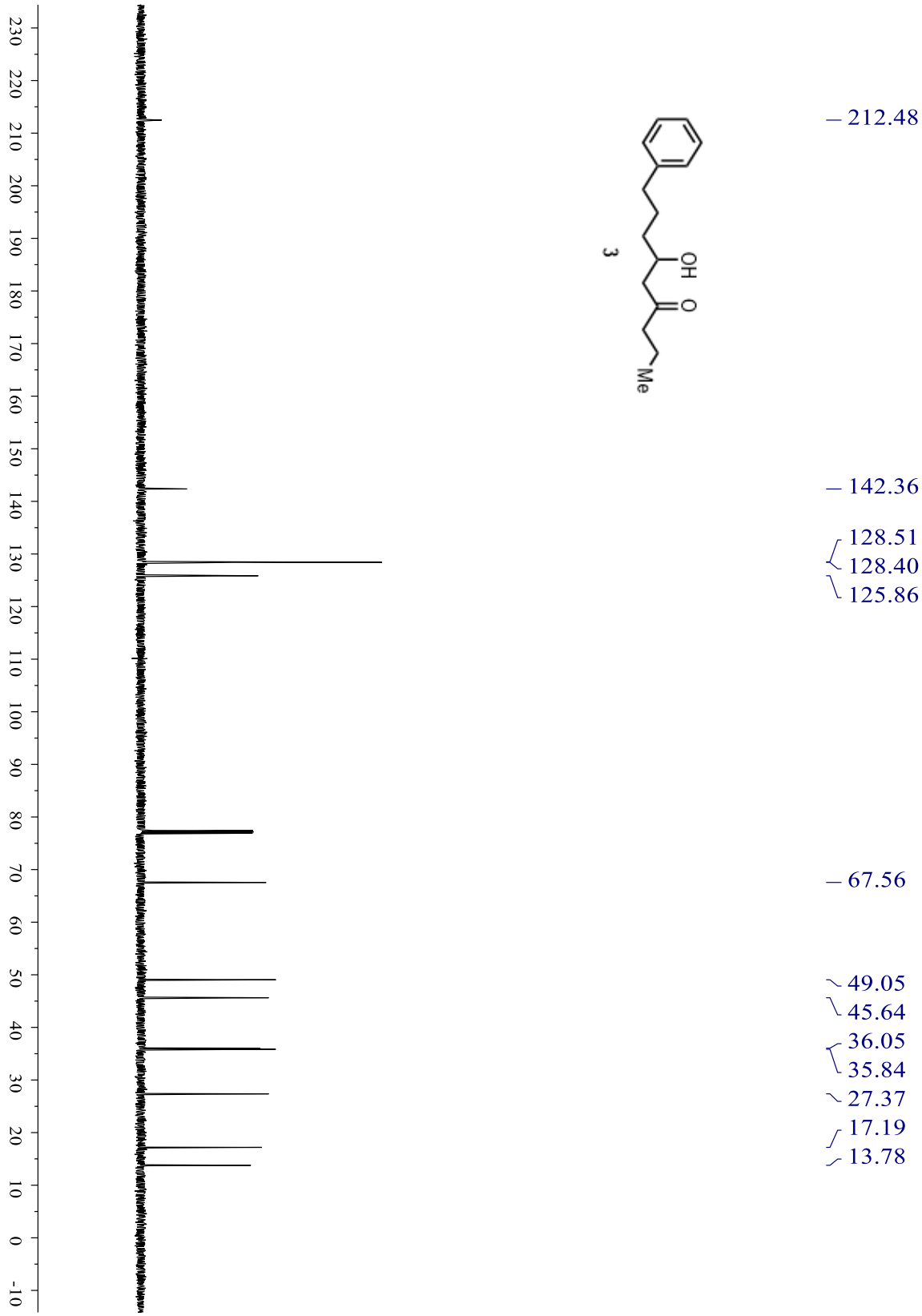
Enantioenriched material



Peak No	% Area	Area	RT (min)
1	52.339	6069.3027	12.71
2	47.661	5526.842	14.45
Total:	100	11596.1447	

2.5.3 Spectral Data

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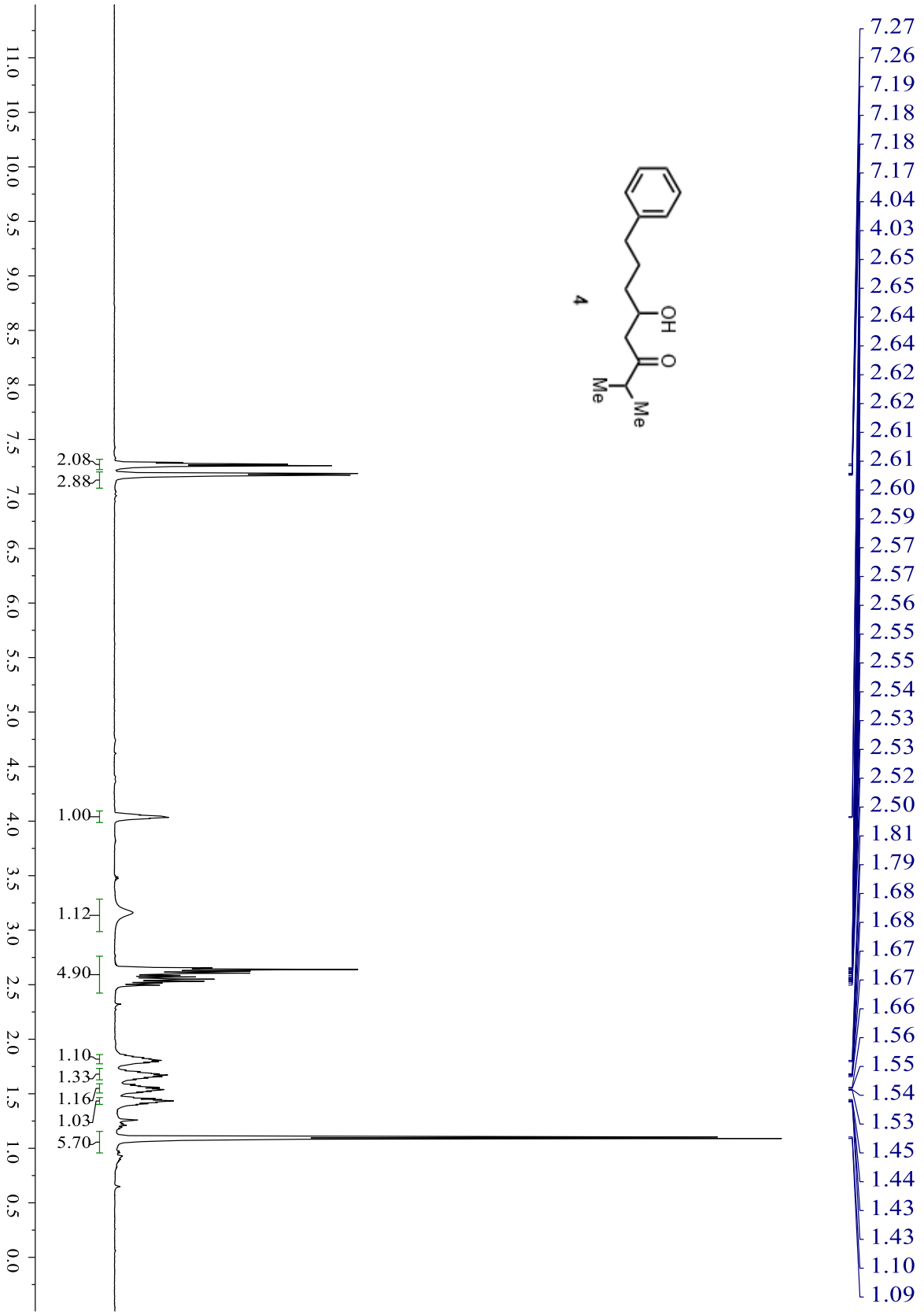
142.36
128.51
128.40
125.86
67.56
49.05
45.64
36.05
35.84
27.37
17.19
13.78
OH
O
Me
3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


4
OH
O
Me
Me
2.08
2.88
1.00
1.12
4.90
1.10
1.33
1.16
1.03
5.70
7.27
7.26
7.19
7.18
7.18
7.17
4.04
4.03
2.65
2.65
2.64
2.64
2.62
2.62
2.61
2.61
2.60
2.59
2.57
2.57
2.56
2.55
2.55
2.54
2.53
2.53
2.52
2.50
1.81
1.79
1.68
1.68
1.67
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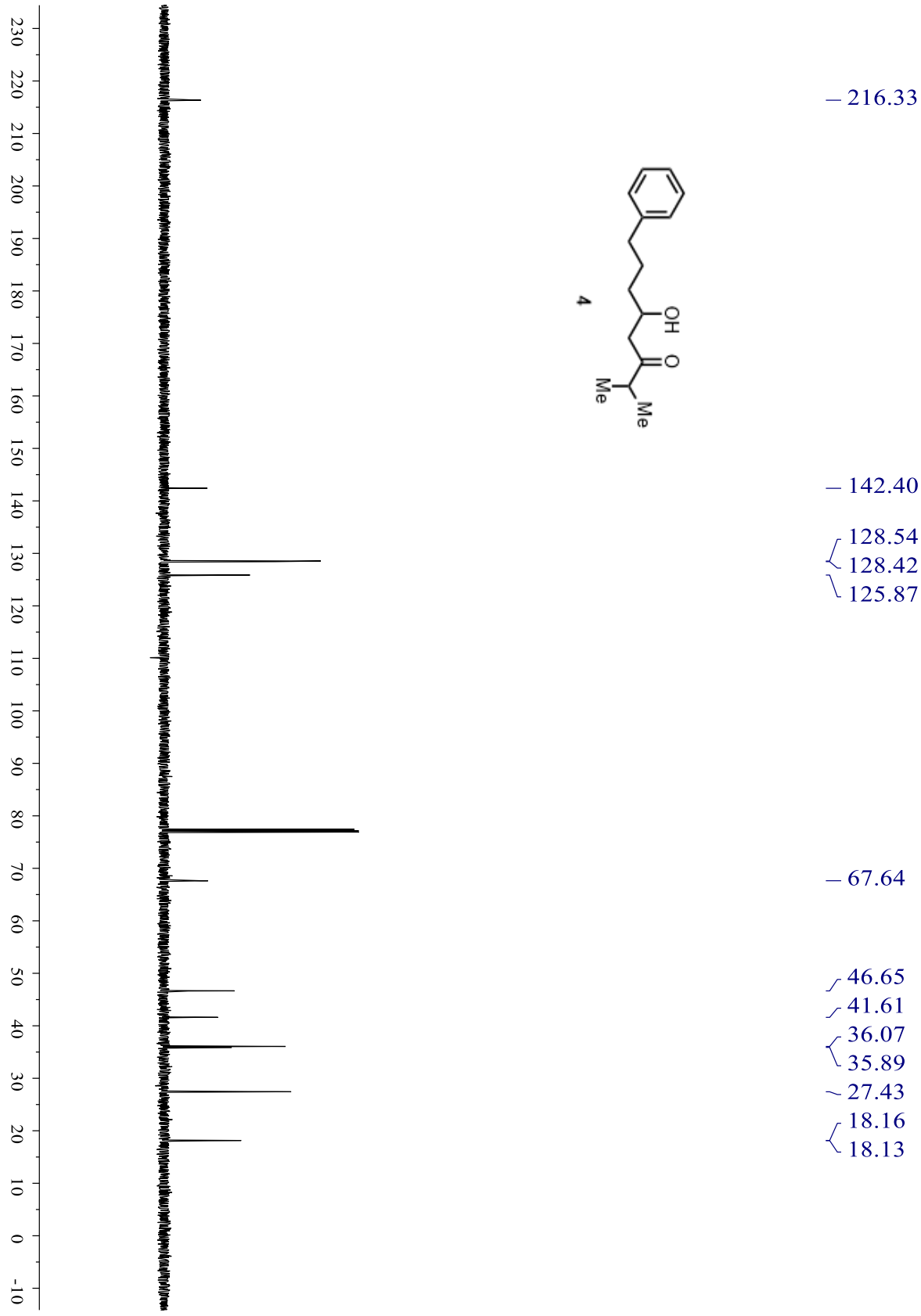
1.45
1.44
1.43
1.43
1.10
1.09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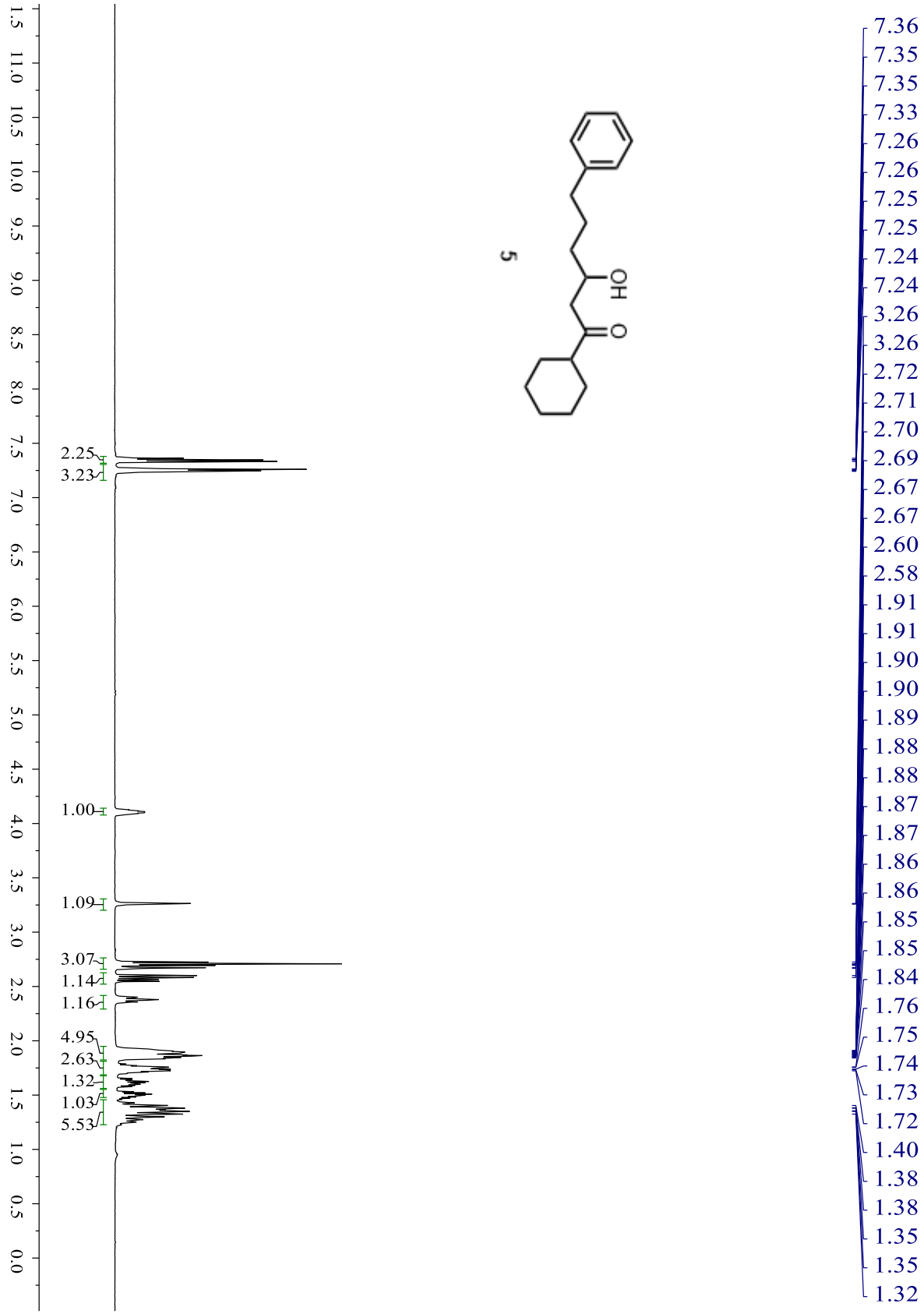
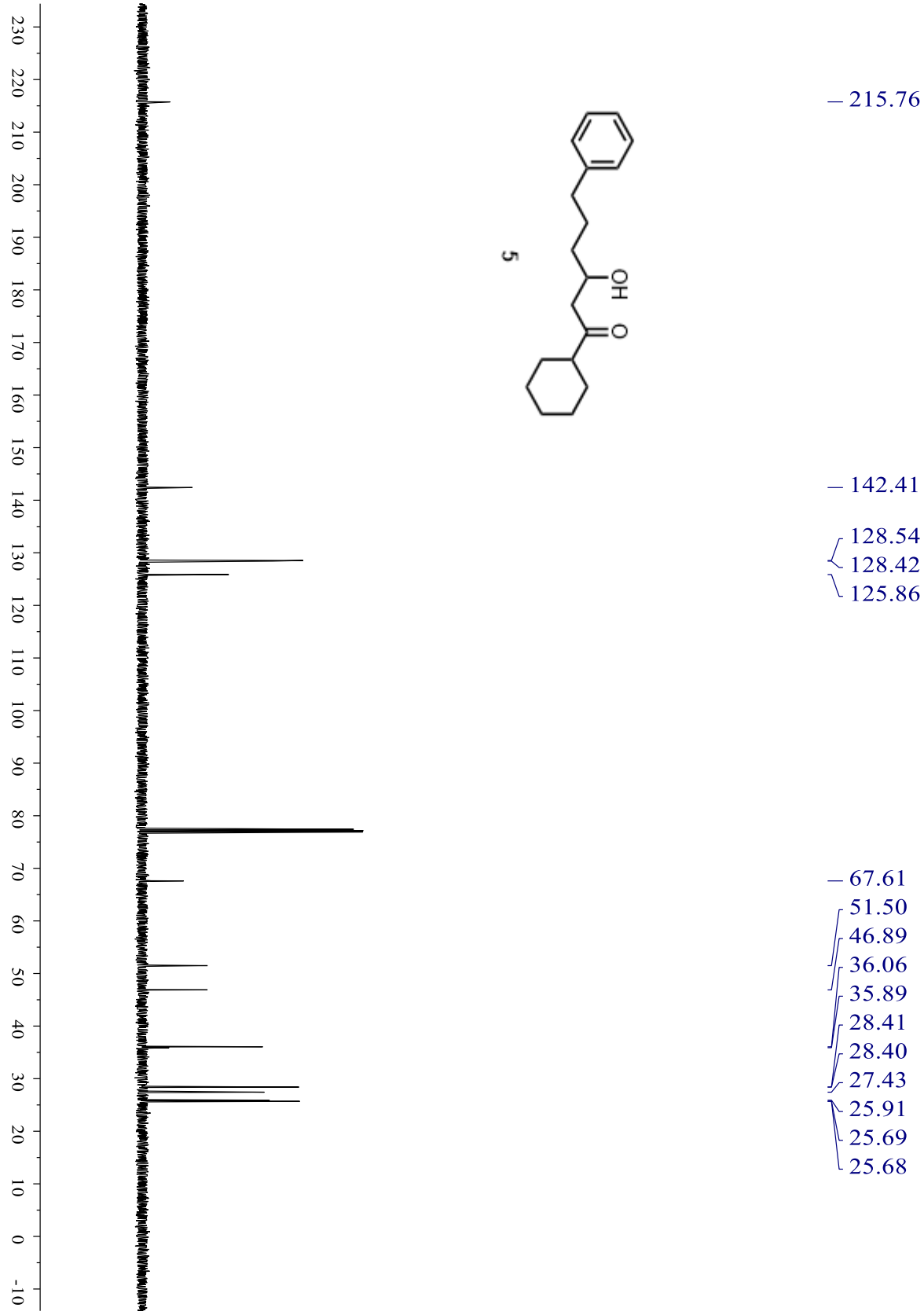
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
OH
O
Me
Me
4
216.33
142.40
128.54
128.42
125.87
67.64
46.65
41.61
36.07
35.89
27.43
18.16
18.13


5
HO
O
2.25
3.23
1.00
1.09
3.07
1.14
1.16
4.95
2.63
1.32
1.03
5.53
7.36
7.35
7.35
7.33
7.26
7.26
7.25
7.25
7.24
7.24
3.26
3.26
2.72
2.71
2.70
2.69
2.67
2.67
2.60
2.58
1.91
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.87
1.86
1.86
1.85
1.85
1.84
1.76
1.75
1.74
1.73
1.72
1.40
1.38
1.38
1.35
1.35
1.32


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
OH
O
5
215.76
142.41
128.54
128.42
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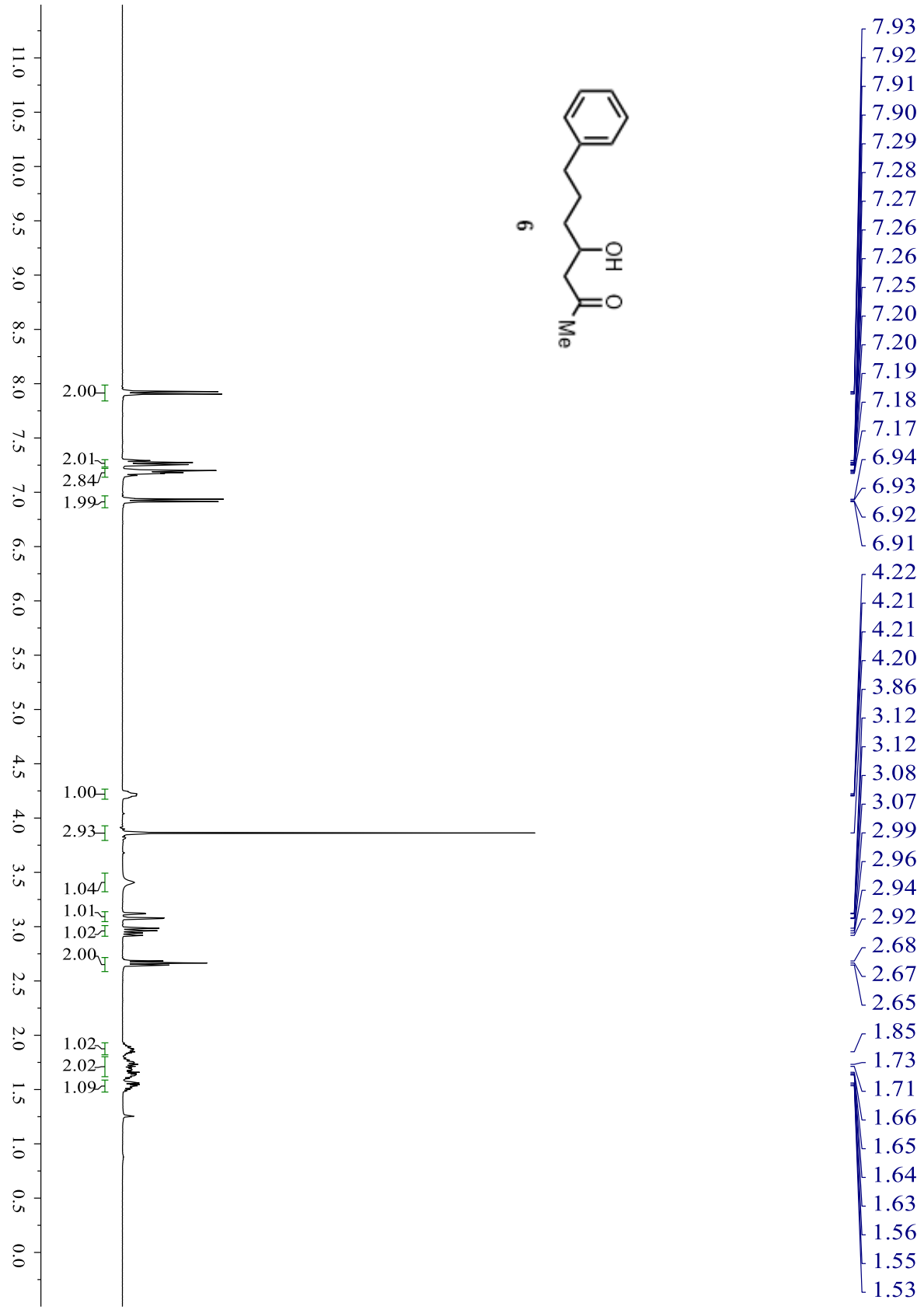
28.41
28.40
27.43
25.91
25.69
25.68


6
OH
O
Me
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
2.00
2.01
2.84
1.99
1.00
2.93
1.04
1.01
1.02
2.00
1.02
2.02
1.09
7.93
7.92
7.91
7.90
7.29
7.28
7.27
7.26
7.26
7.25
7.20
7.20
7.19
7.18
7.17
6.94
6.93
6.92
6.91
4.22
4.21
4.21
4.20
3.86
3.12
3.12
3.08
3.07
2.99
2.96
2.94
2.92
2.68
2.67
2.65
1.85
1.73
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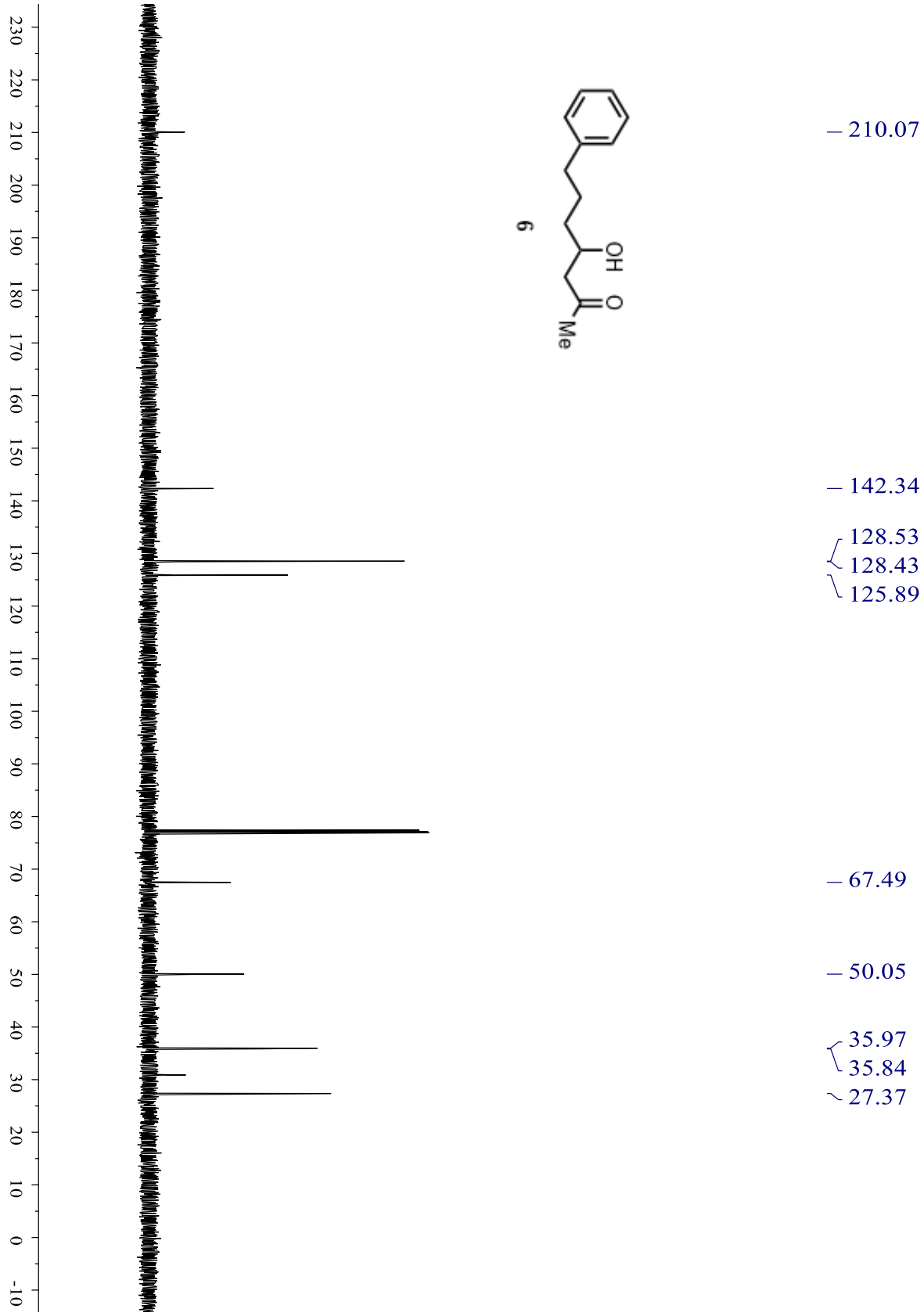
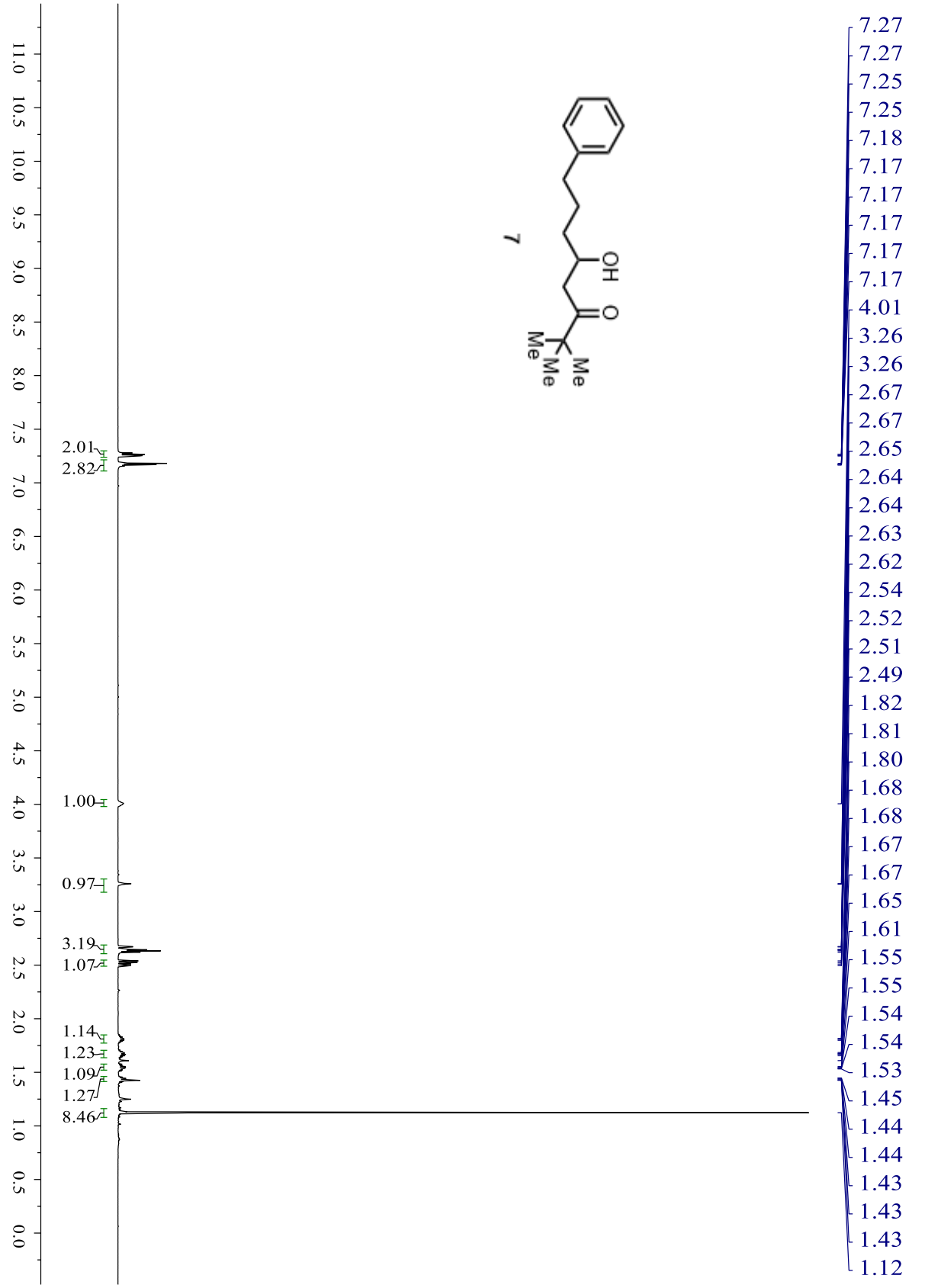
1.66
1.65
1.64
1.63
1.56
1.55
1.53


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
OH
O
Me
6
210.07
142.34
128.53
128.43
125.89
67.49
50.05
35.97
35.84
27.37


7
OH
O
Me
Me
Me
2.01
2.82
1.00
0.97
3.19
1.07
1.14
1.23
1.09
1.27
8.46
7.27
7.27
7.25
7.25
7.18
7.17
7.17
7.17
7.17
7.17
4.01
3.26
3.26
2.67
2.67
2.65
2.64
2.64
2.63
2.62
2.54
2.52
2.51
2.49
1.82
1.81
1.80
1.68
1.68
1.67
1.67
1.65
1.61
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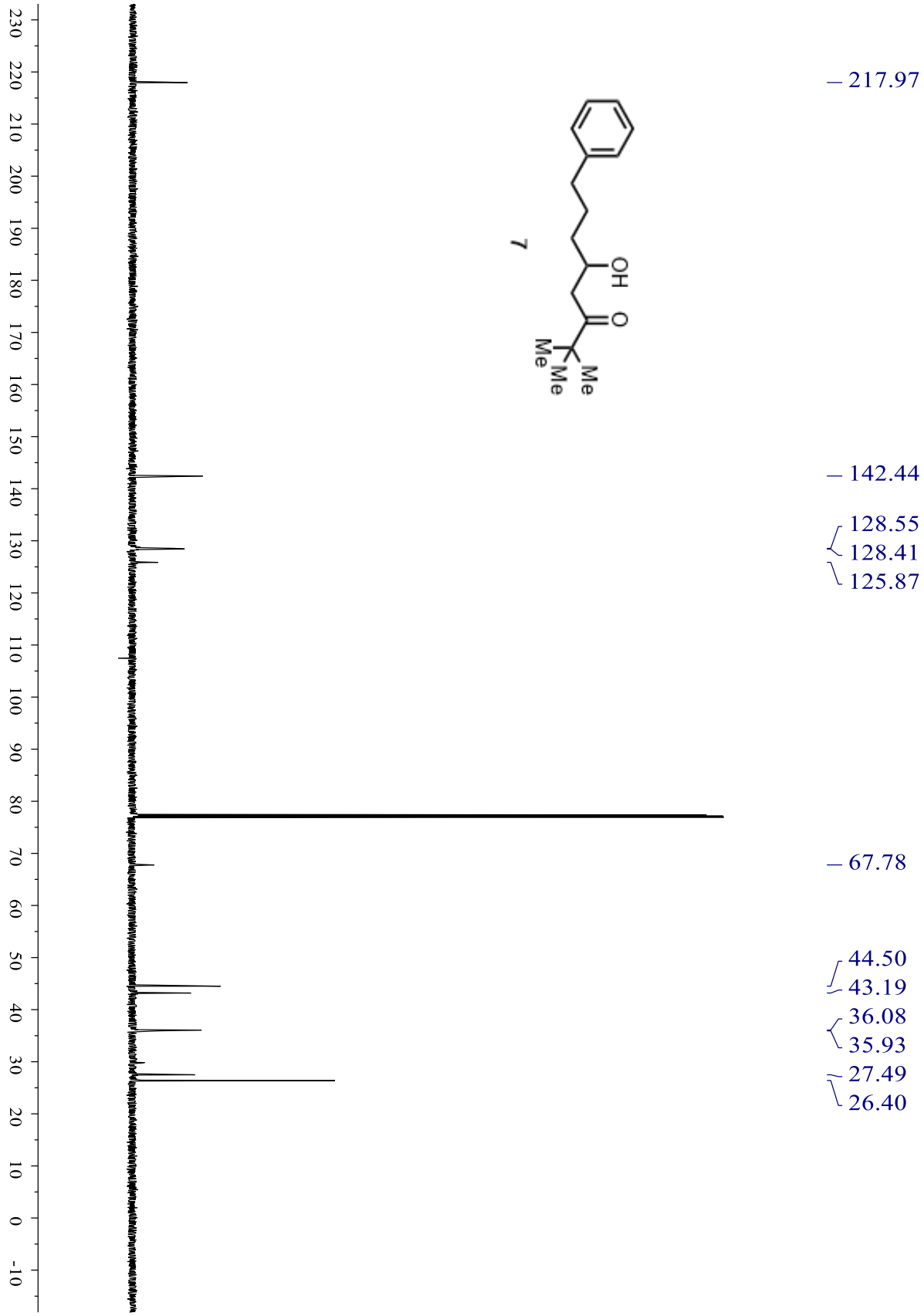
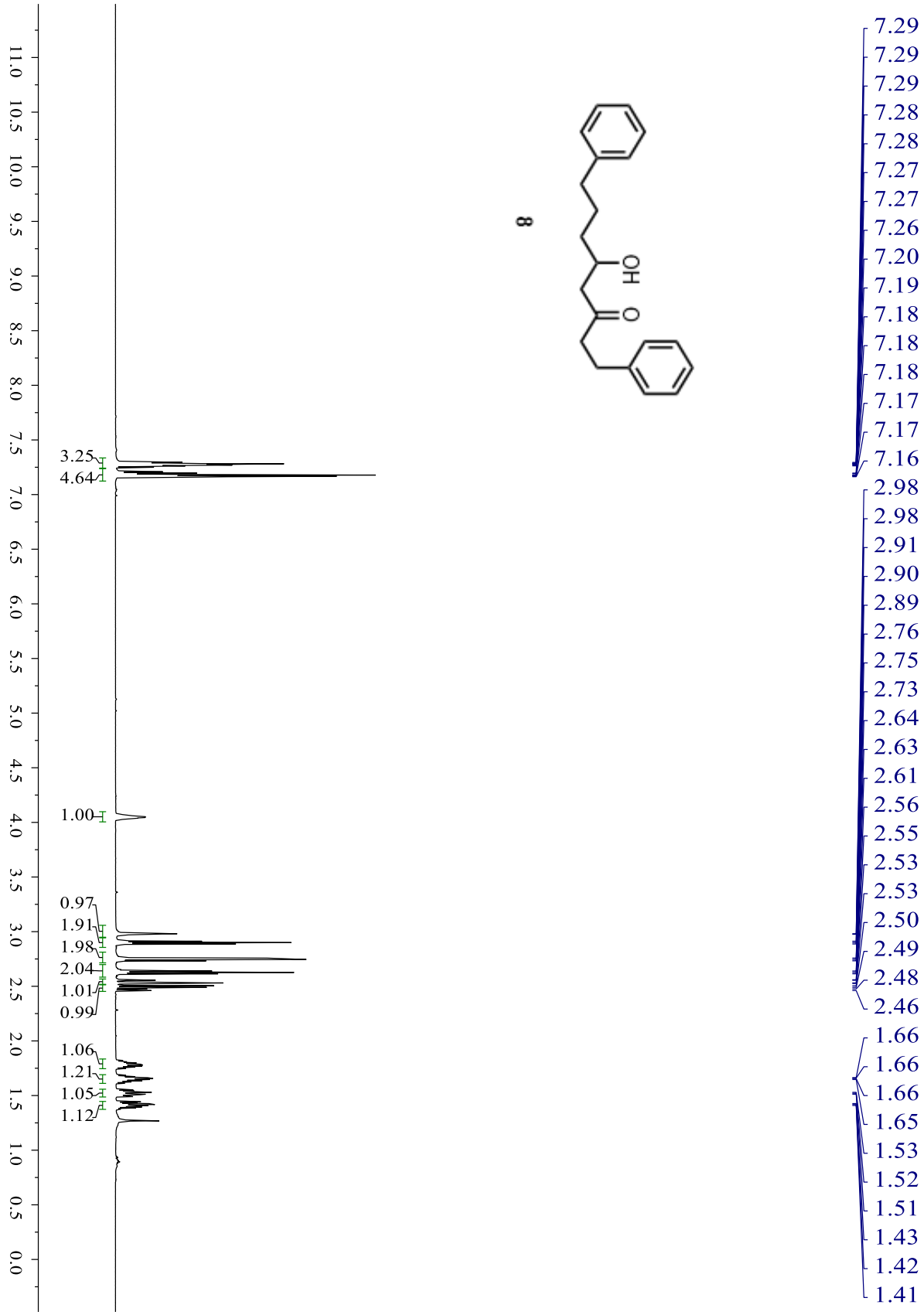
1.44
1.43
1.43
1.43
1.12


217.97
142.44
128.55
128.41
125.87
67.78
44.50
43.19
36.08
35.93
27.49
26.40
7
OH
O
Me
Me
Me


8
OH
O
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
3.25
4.64
1.00
0.97
1.91
1.98
2.04
1.01
0.99
1.06
1.21
1.05
1.12
7.29
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.20
7.19
7.18
7.18
7.18
7.17
7.17
7.16
2.98
2.98
2.91
2.90
2.89
2.76
2.75
2.73
2.64
2.63
2.61
2.56
2.55
2.53
2.53
2.50
2.49
2.48
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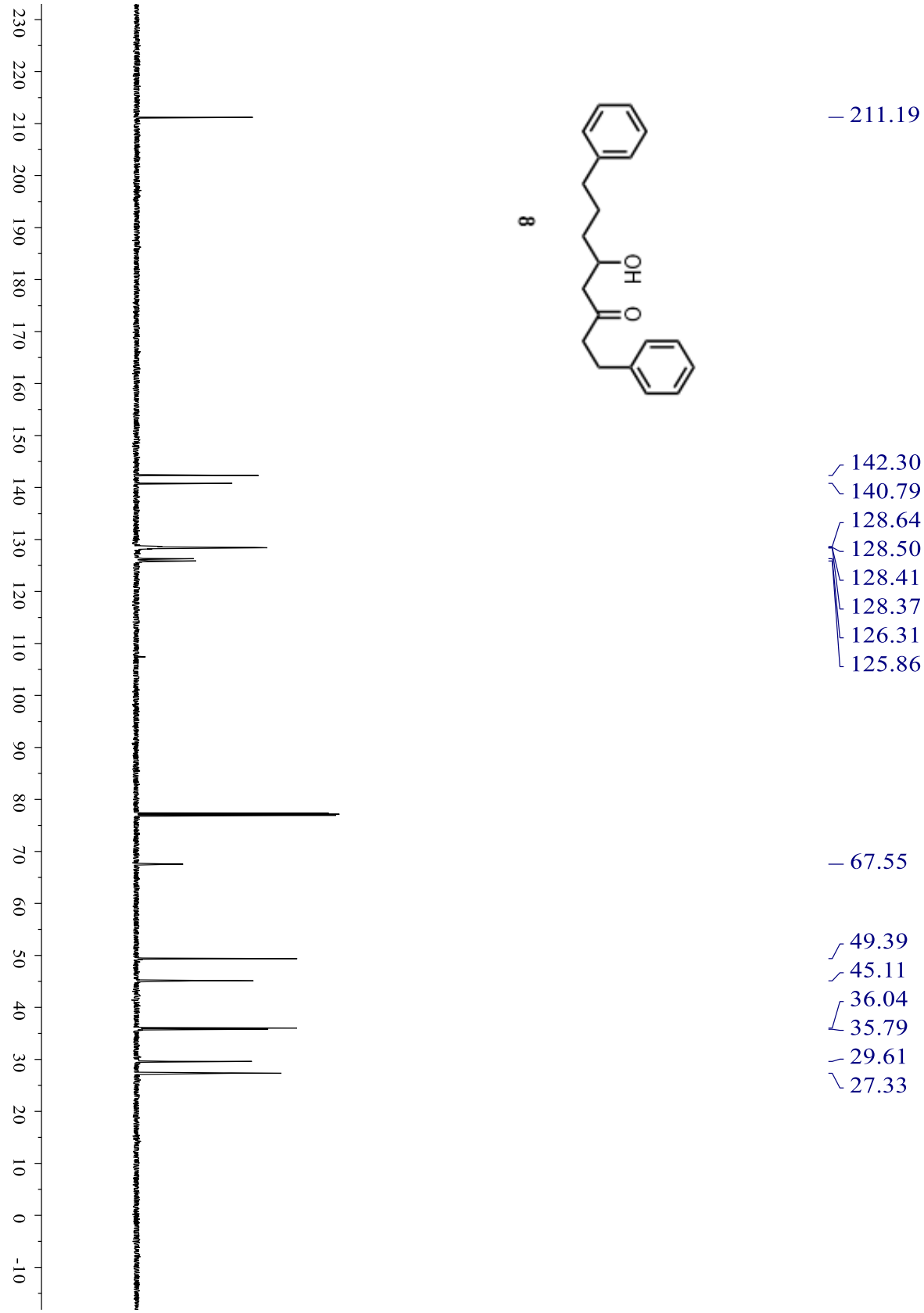
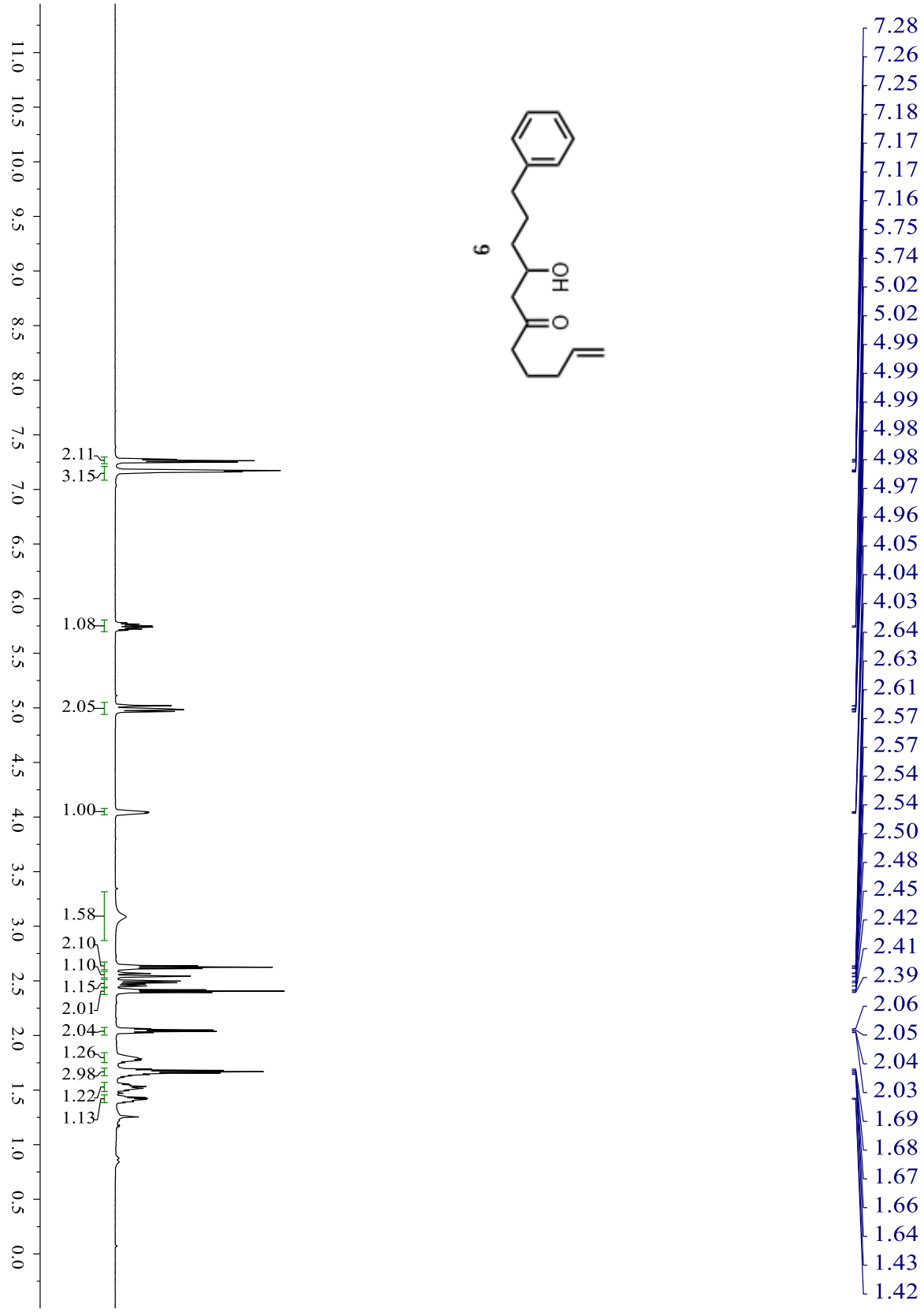
1.66
1.66
1.65
1.53
1.52
1.51
1.43
1.42
1.41


8
OH
O
211.19
142.30
140.79
128.64
128.50
128.41
128.37
126.31
125.86
67.55
49.39
45.11
36.04
35.79
29.61
27.33
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
2.11
3.15
1.08
2.05
1.00
1.58
2.10
1.10
1.15
2.01
2.04
1.26
2.98
1.22
1.13
6
HO
O
7.28
7.26
7.25
7.18
7.17
7.17
7.16
5.75
5.74
5.02
5.02
4.99
4.99
4.99
4.98
4.98
4.97
4.96
4.05
4.04
4.03
2.64
2.63
2.61
2.57
2.57
2.54
2.54
2.50
2.48
2.45
2.42
2.41
2.39
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1.67
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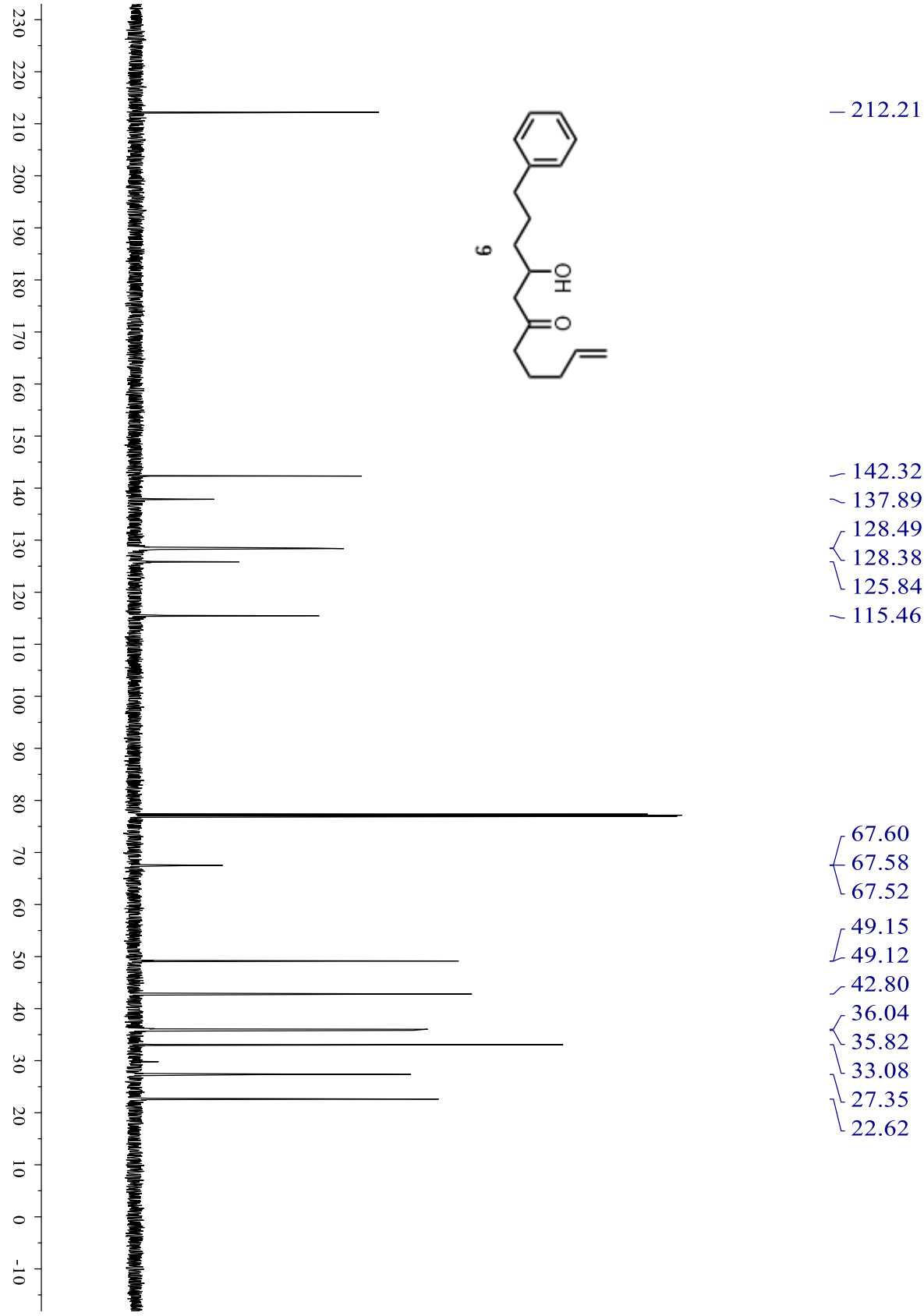
1.43
1.42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125.84
115.46
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49.15
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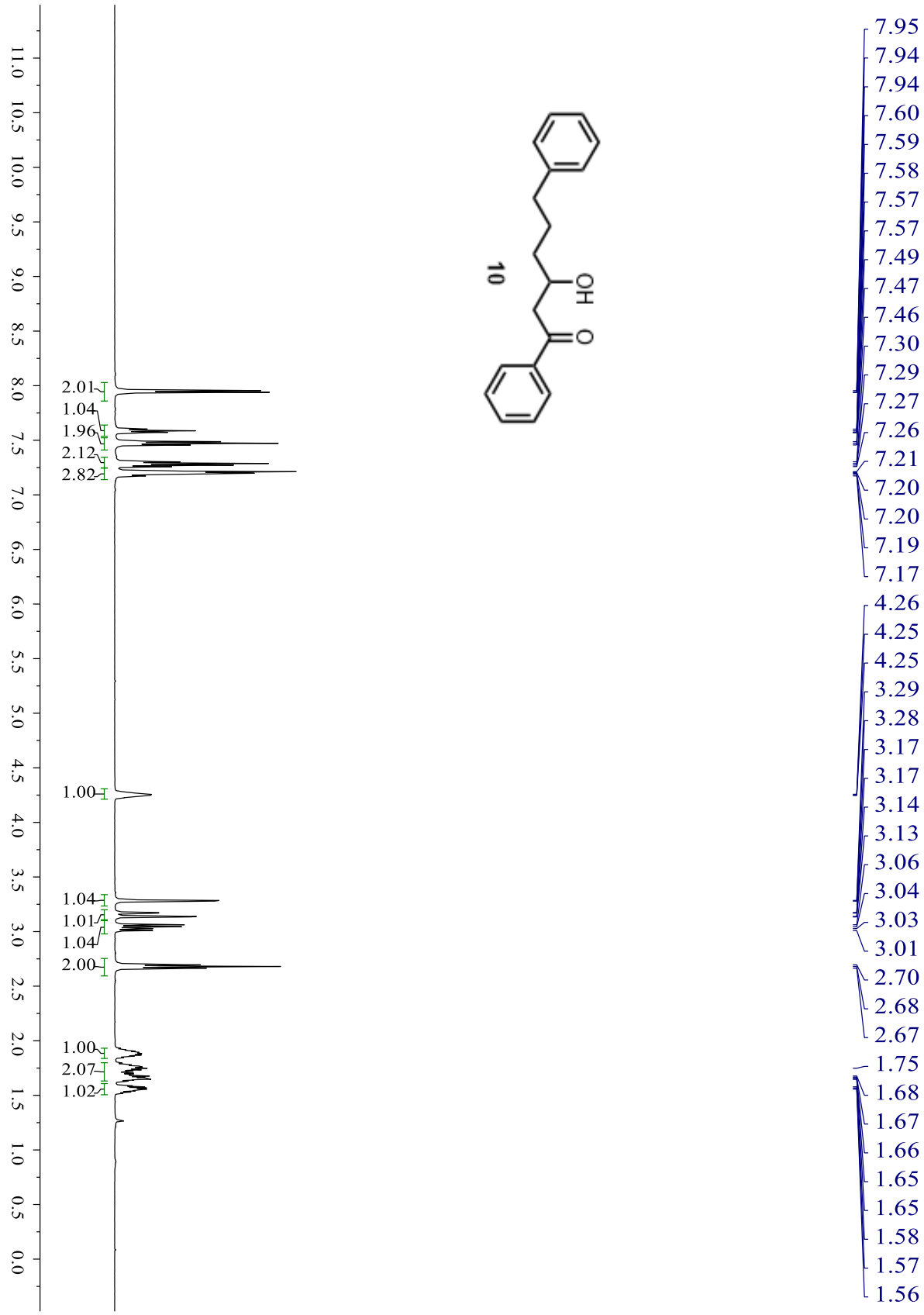
33.08
27.35
22.62
9
OH
O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2.01
1.04
1.96
2.12
2.82
1.00
1.04
1.01
1.04
2.00
1.00
2.07
1.02
10
OH
O
7.95
7.94
7.94
7.60
7.59
7.58
7.57
7.57
7.49
7.47
7.46
7.30
7.29
7.27
7.26
7.21
7.20
7.20
7.19
7.17
4.26
4.25
4.25
3.29
3.28
3.17
3.17
3.14
3.13
3.06
3.04
3.03
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1.65
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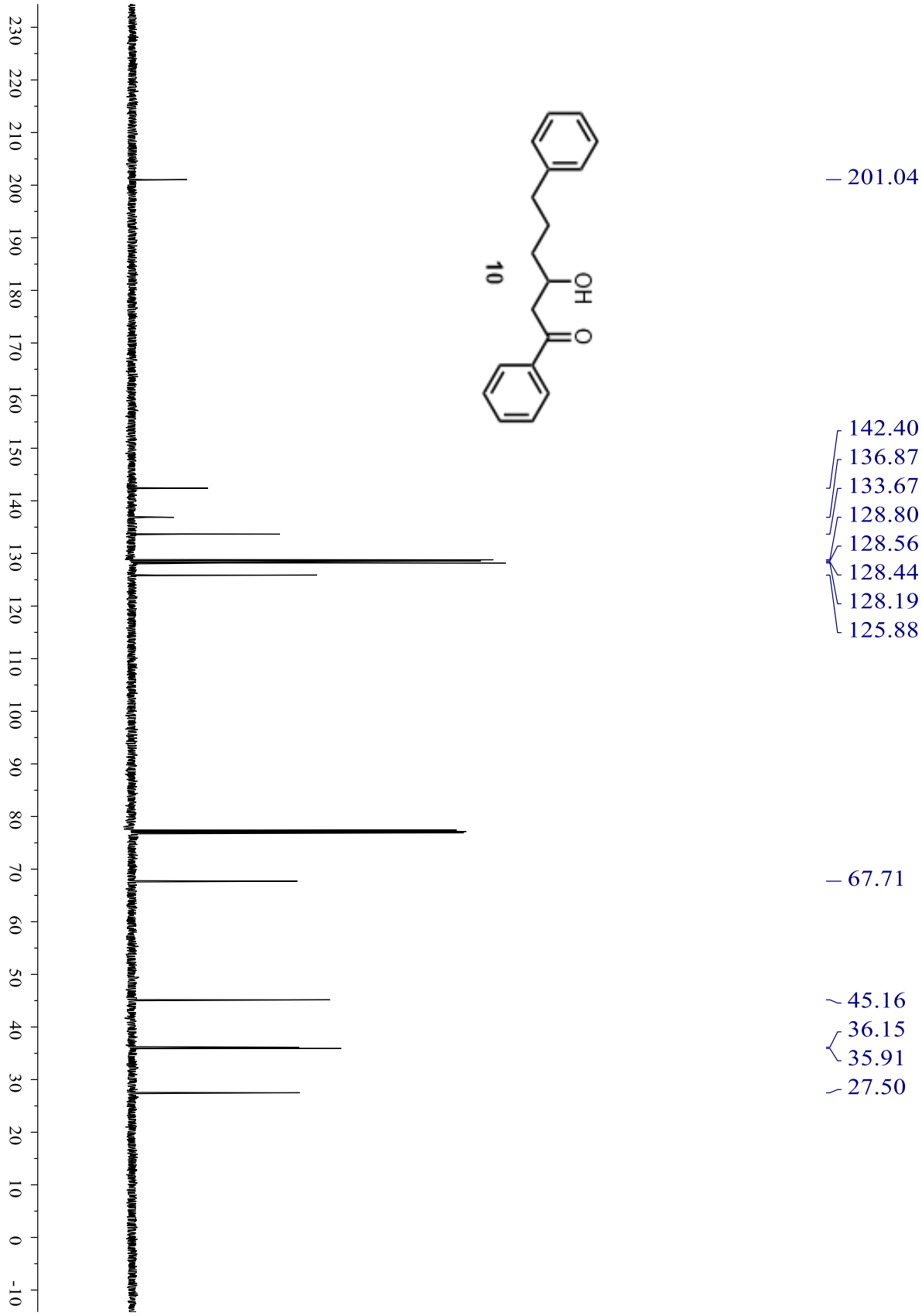
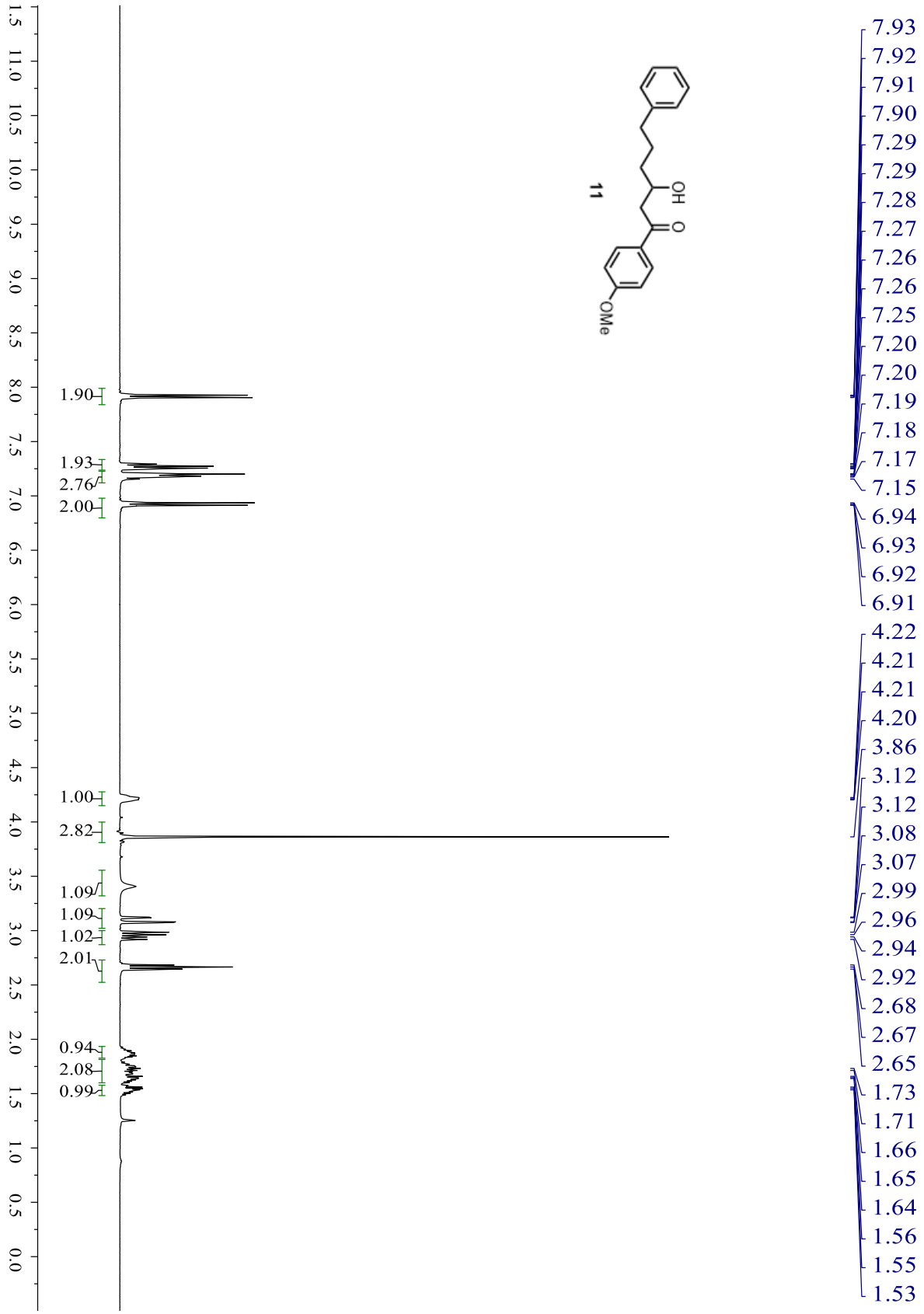
1.57
1.56


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
10
OH
O
201.04
142.40
136.87
133.67
128.80
128.56
128.44
128.19
125.88
67.71
45.16
36.15
35.91
27.50


11
OH
O
OMe
1.90
1.93
2.76
2.00
1.00
2.82
1.09
1.09
1.02
2.01
0.94
2.08
0.99
7.93
7.92
7.91
7.90
7.29
7.29
7.28
7.27
7.26
7.26
7.25
7.20
7.20
7.19
7.18
7.17
7.15
6.94
6.93
6.92
6.91
4.22
4.21
4.21
4.20
3.86
3.12
3.12
3.08
3.07
2.99
2.96
2.94
2.92
2.68
2.67
2.65
1.73
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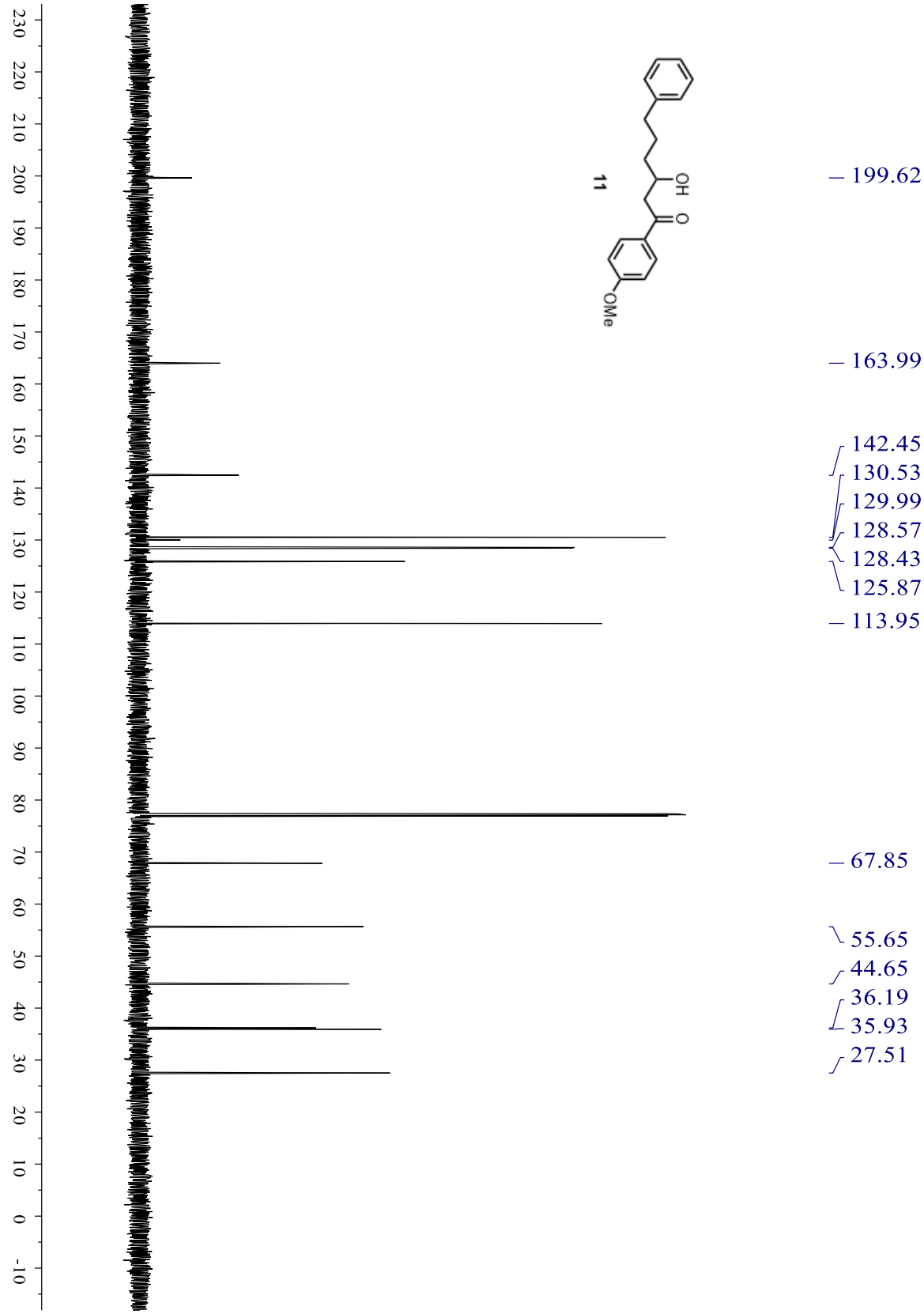
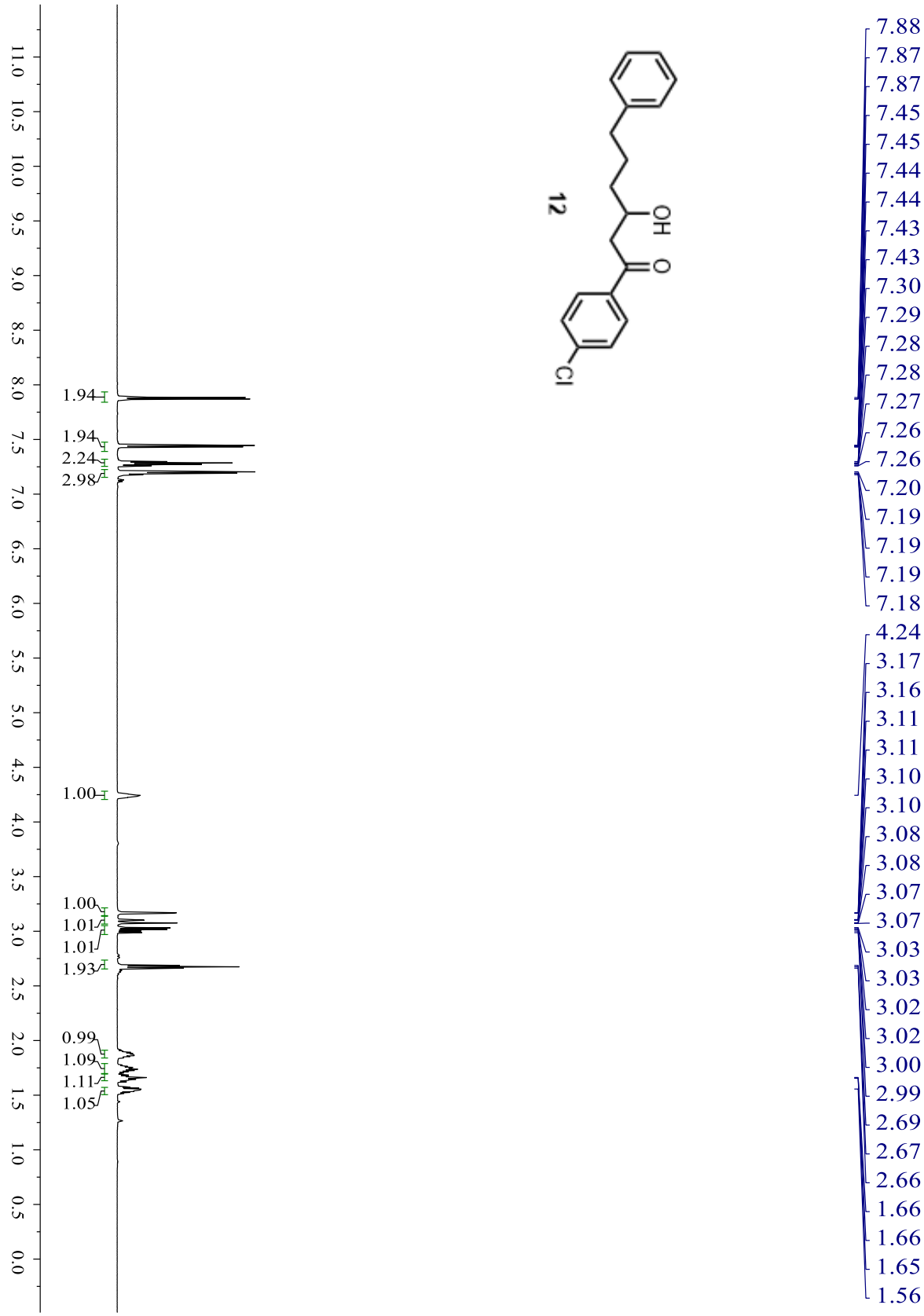
1.66
1.65
1.64
1.56
1.55
1.53


11
OH
O
OMe
199.62
163.99
142.45
130.53
129.99
128.57
128.43
125.87
113.95
67.85
55.65
44.65
36.19
35.93
27.51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7.28
7.27
7.26
7.26
7.20
7.19
7.19
7.19
7.18
4.24
3.17
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3.11
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3.10
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3.08
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3.07
3.07
3.03
3.03
3.02
3.02
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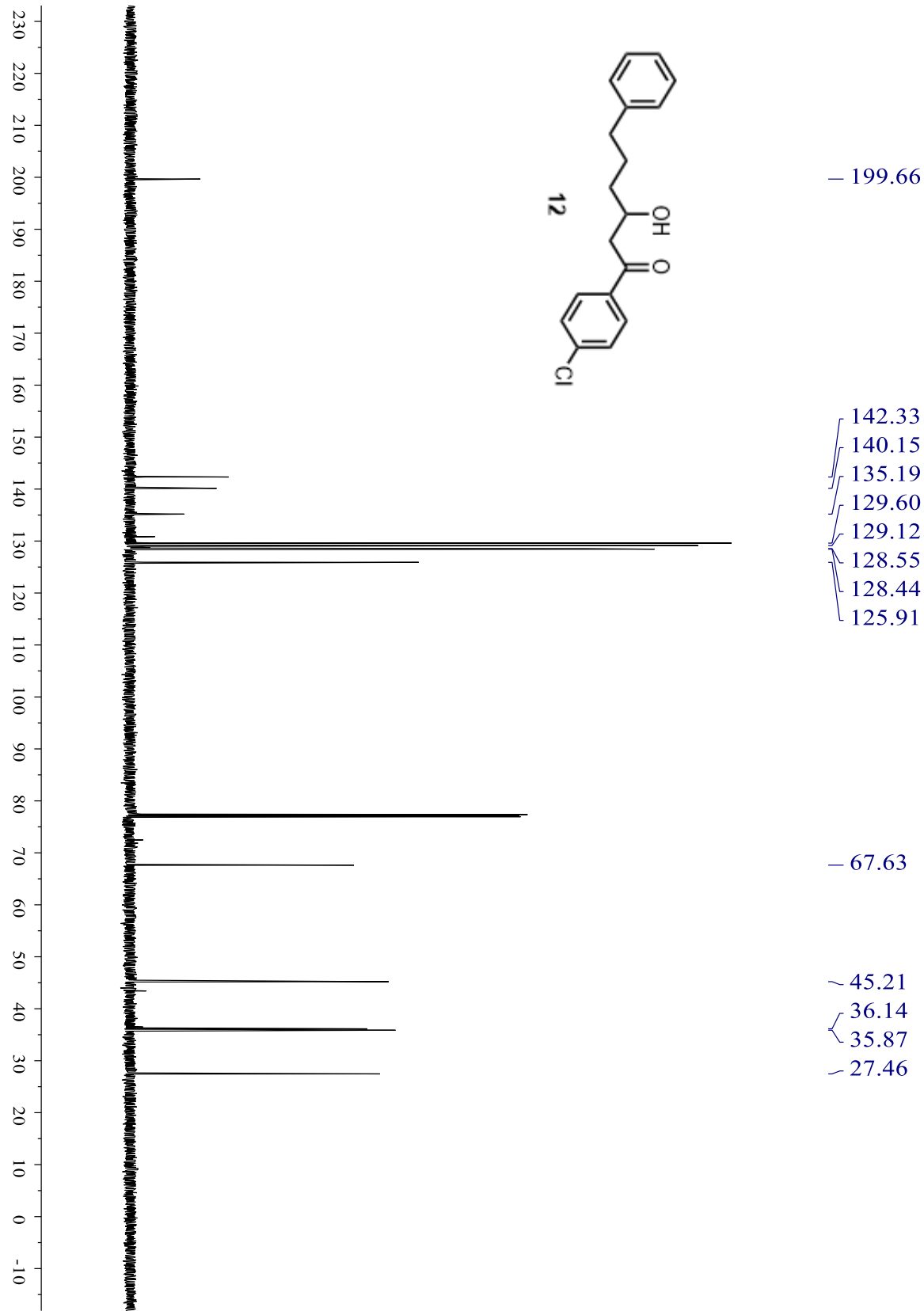
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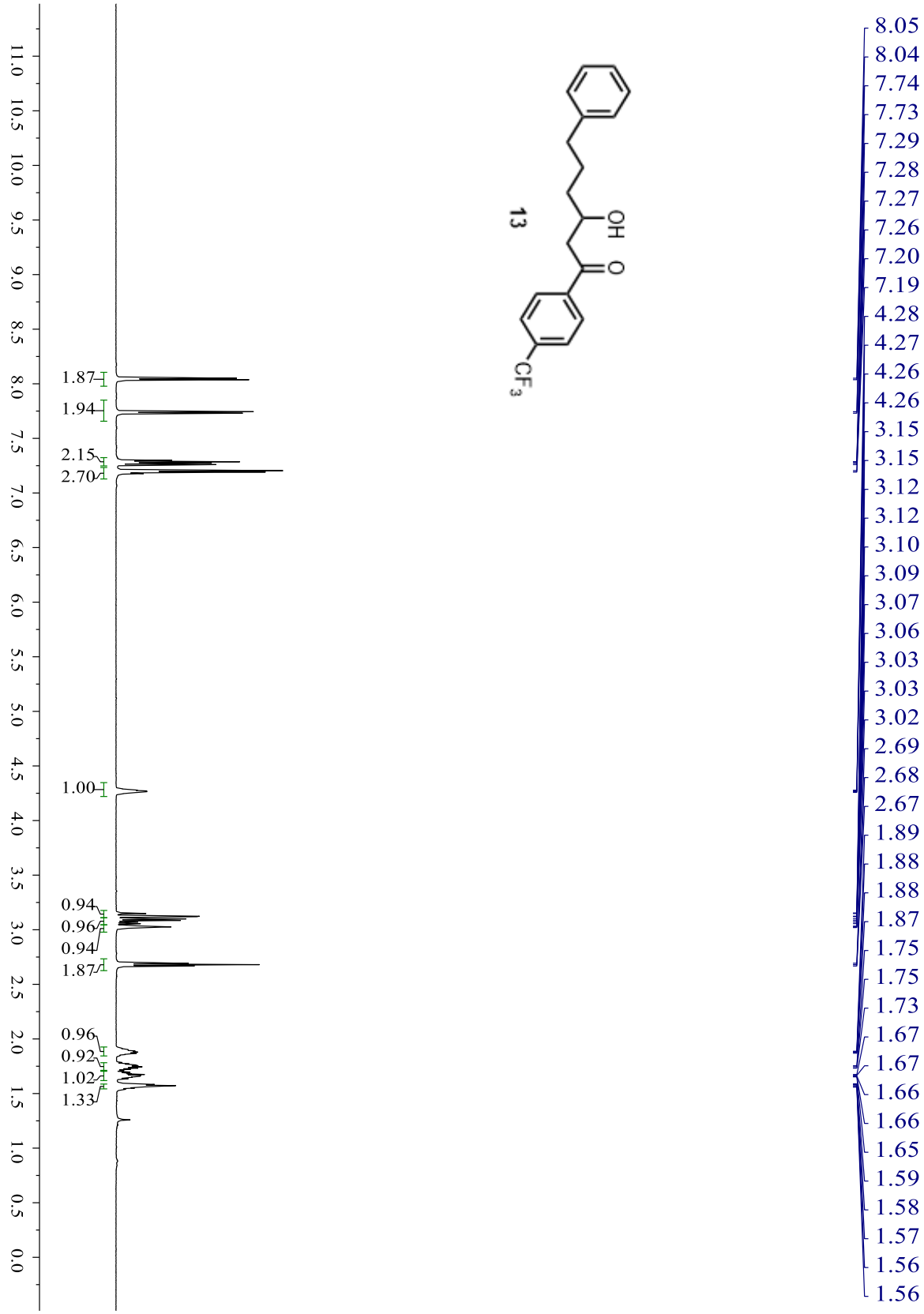
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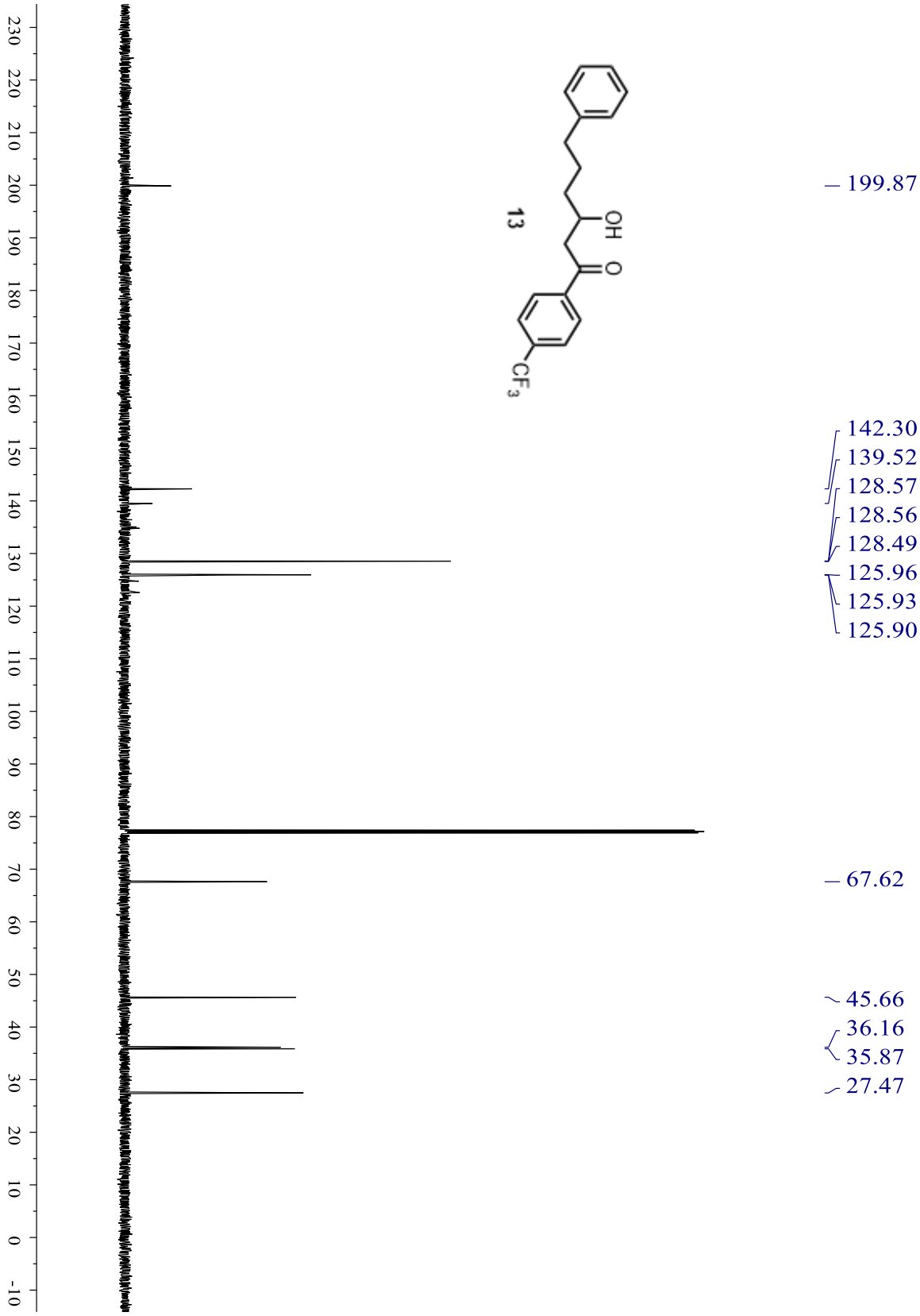
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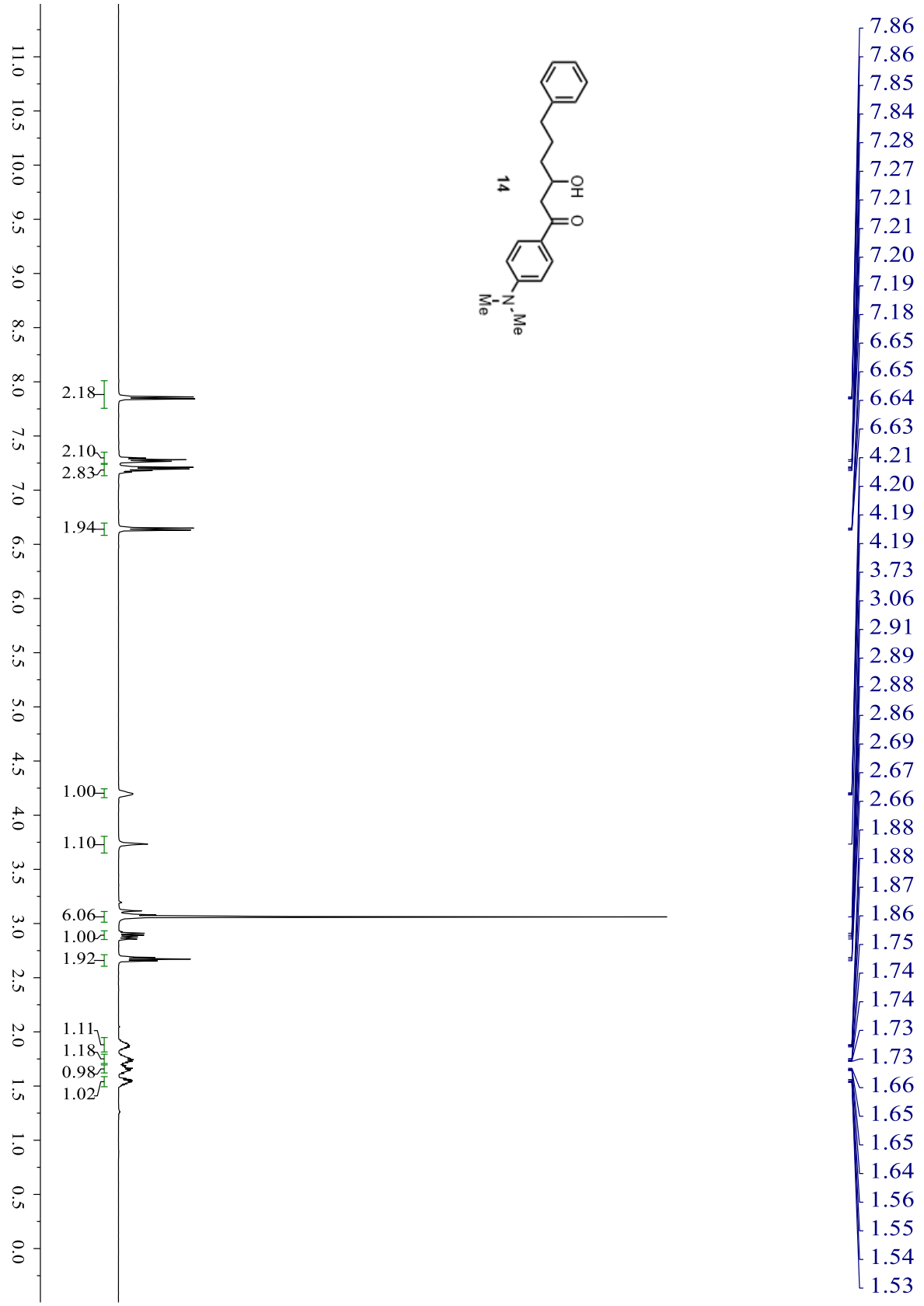
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6.64
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4.19
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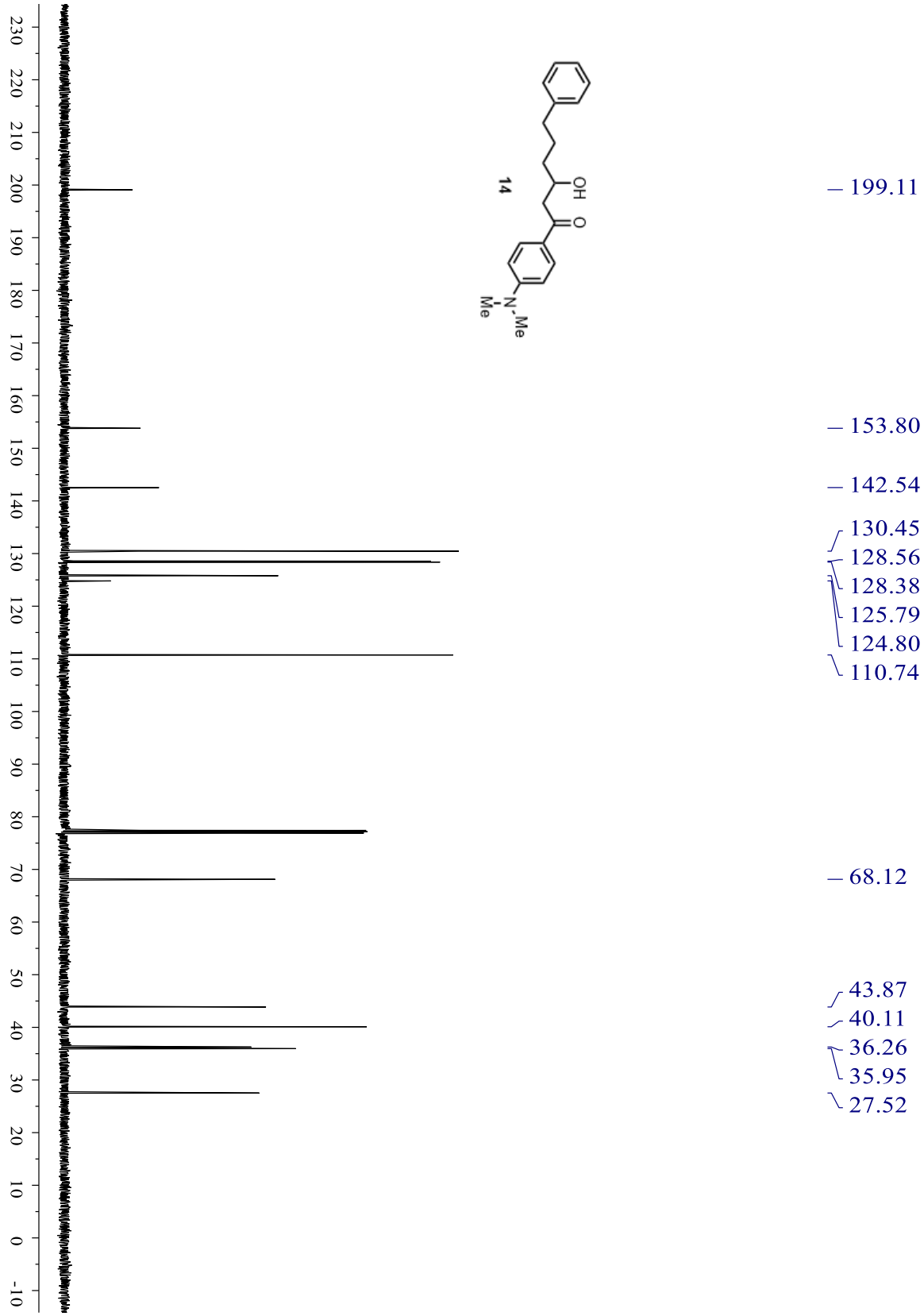
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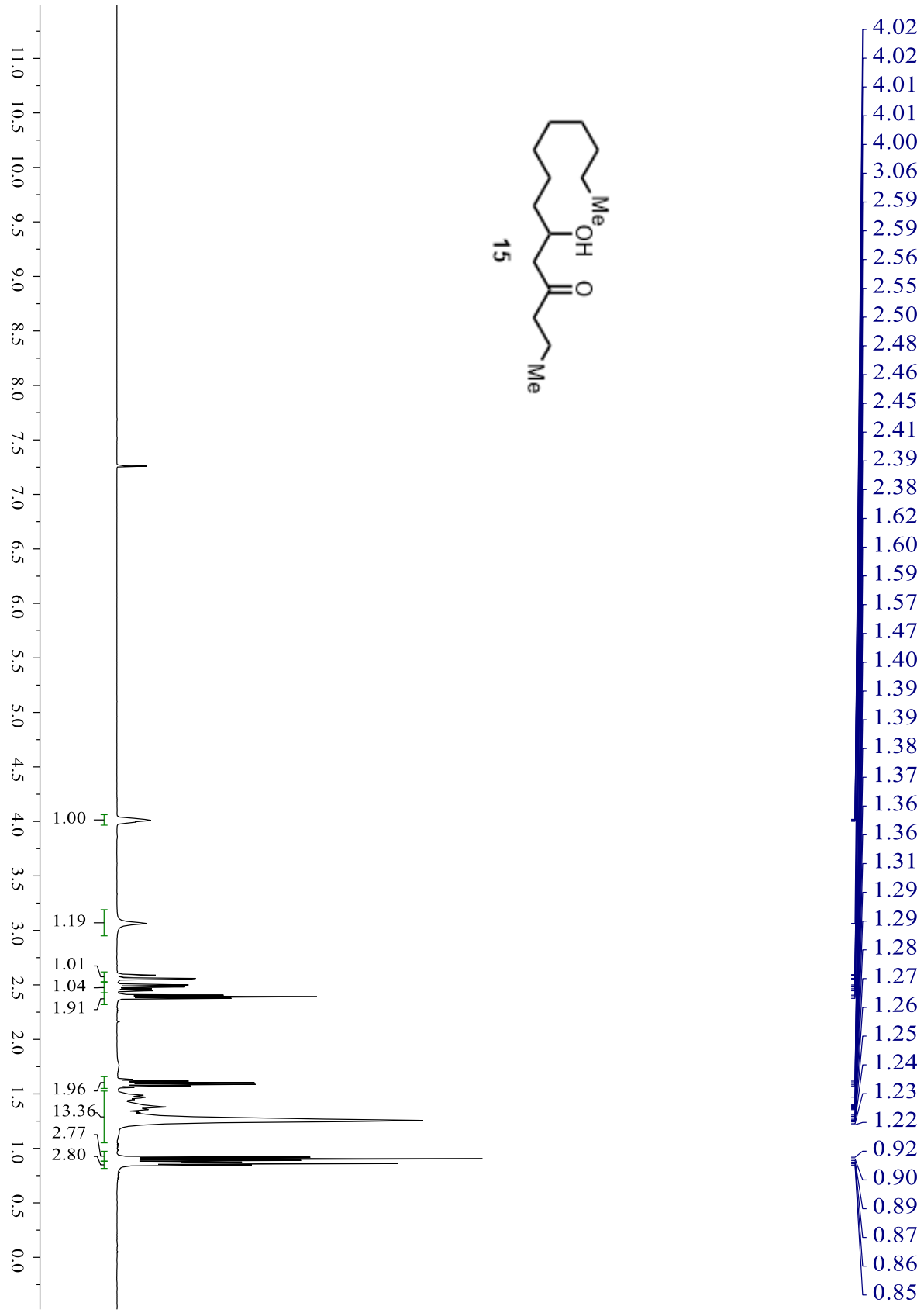
27.52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1.04
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1.96
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2.80
Me
OH
O
Me
15
4.02
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4.01
4.01
4.00
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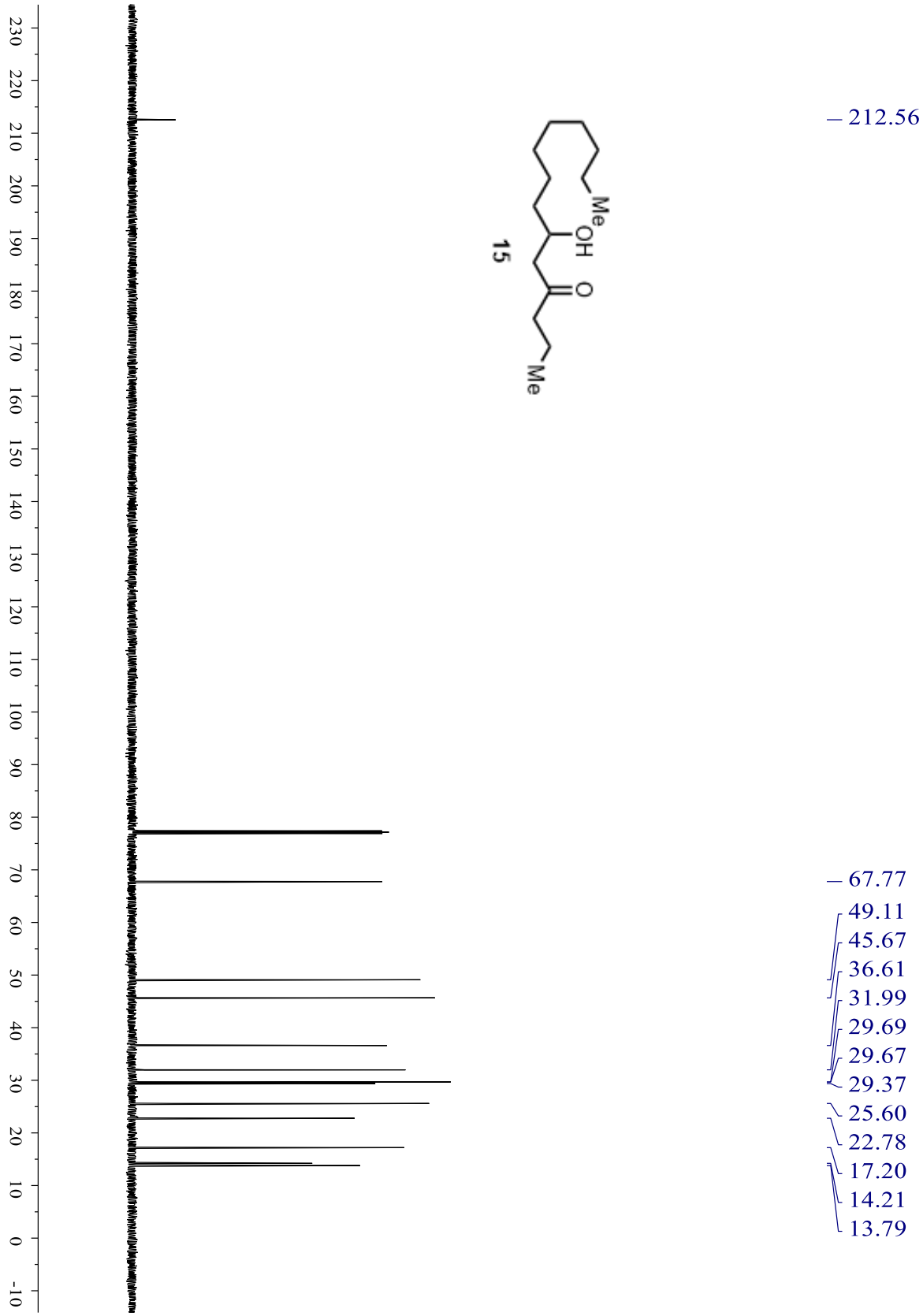
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10
0
-10
Me
OH
O
Me
15
212.56
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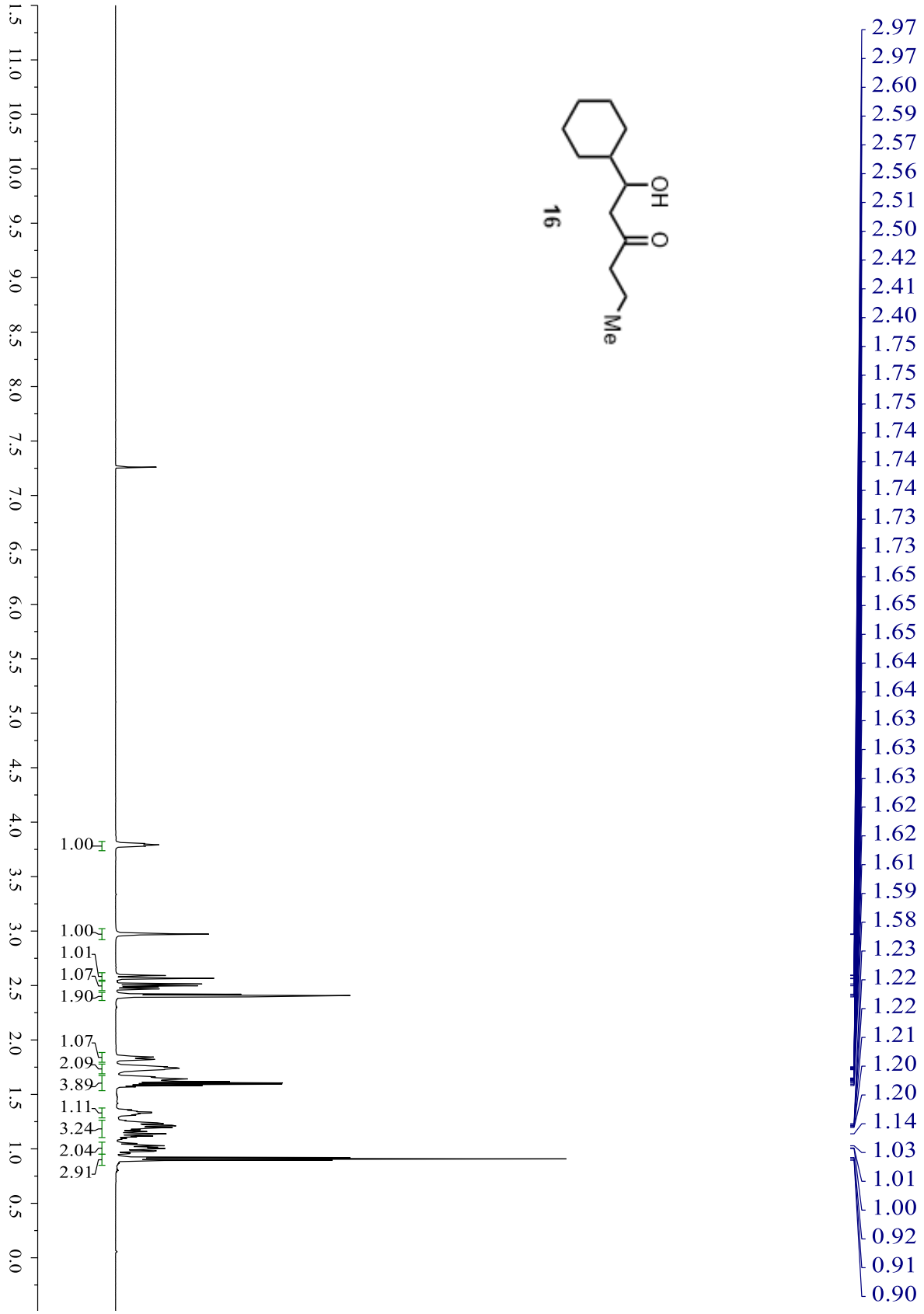
13.79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1.58
1.23
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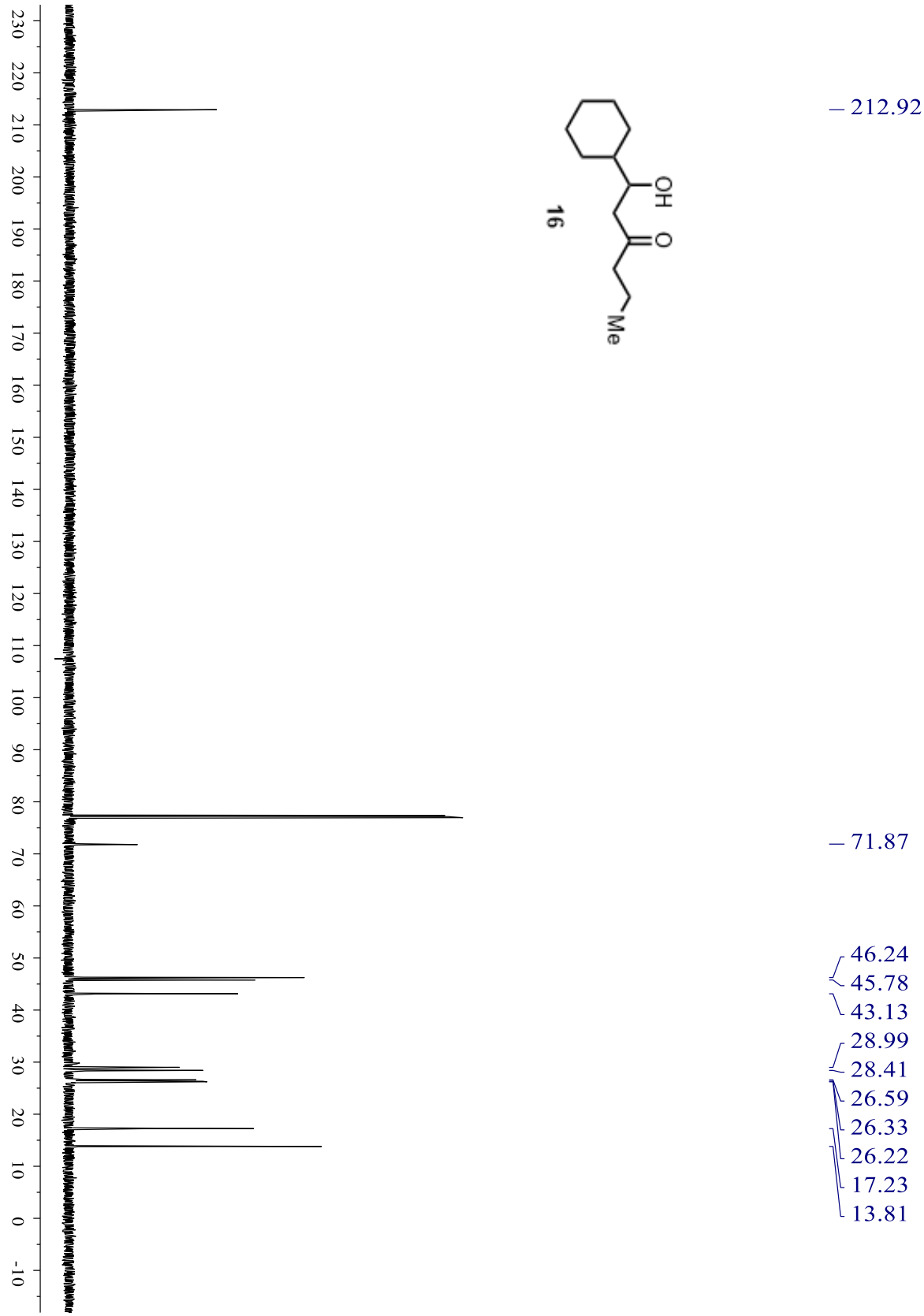
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80
70
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50
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30
20
10
0
-10
OH
O
Me
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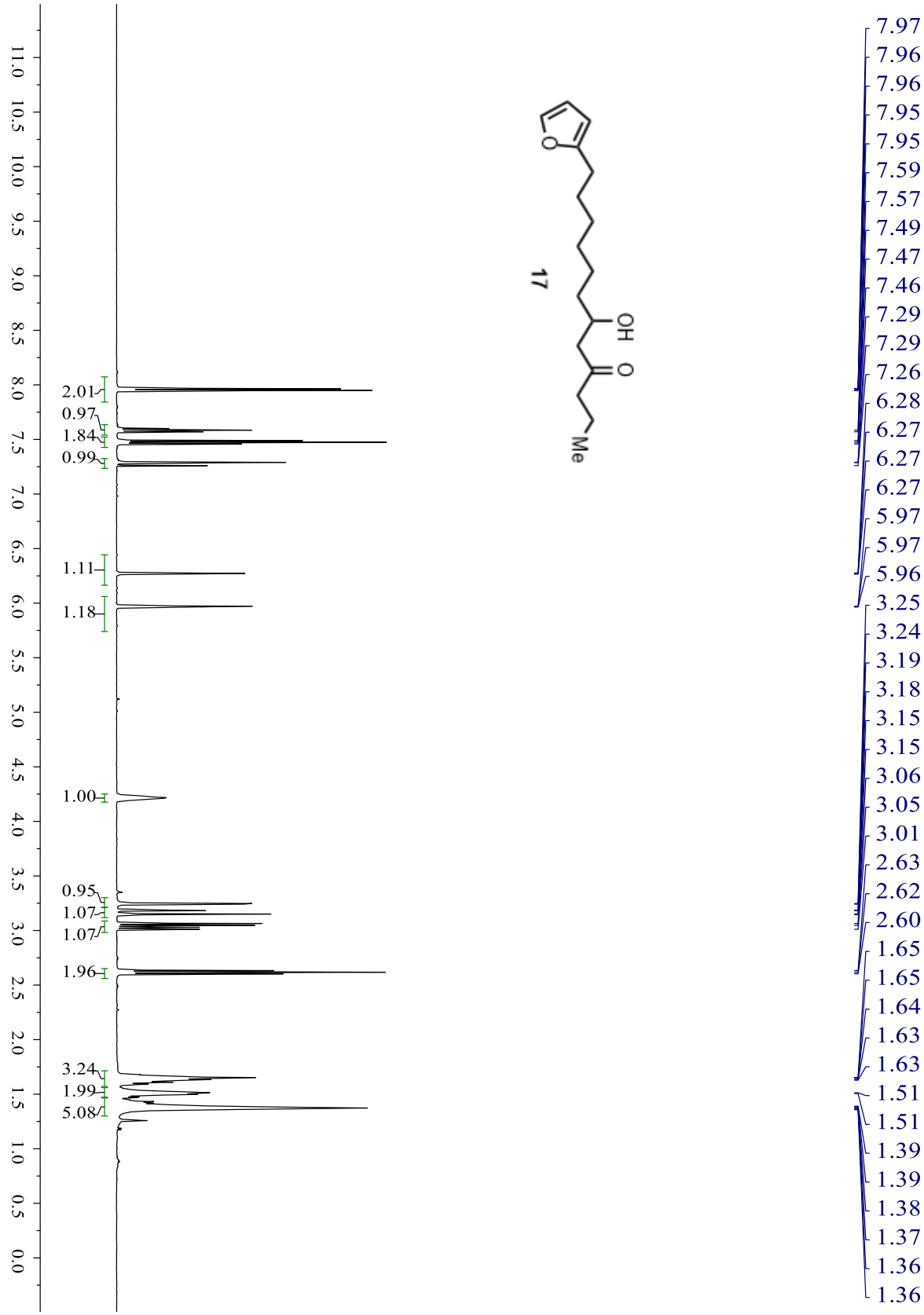
13.81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2.01
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1.84
0.99
1.11
1.18
1.00
0.95
1.07
1.07
1.96
3.24
1.99
5.08
17
OH
O
Me
7.97
7.96
7.96
7.95
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3.24
3.19
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3.15
3.15
3.06
3.05
3.01
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2.62
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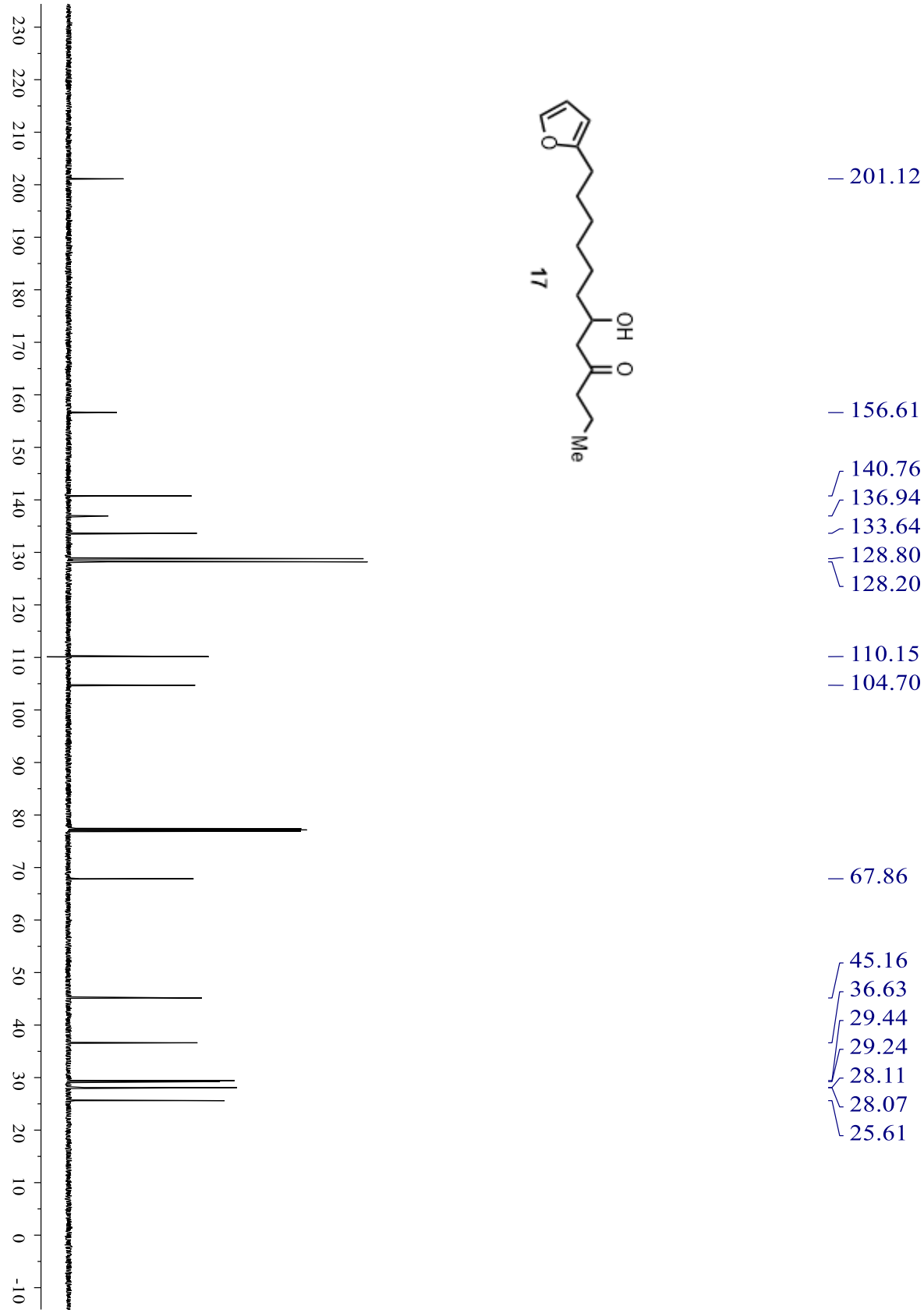
1.36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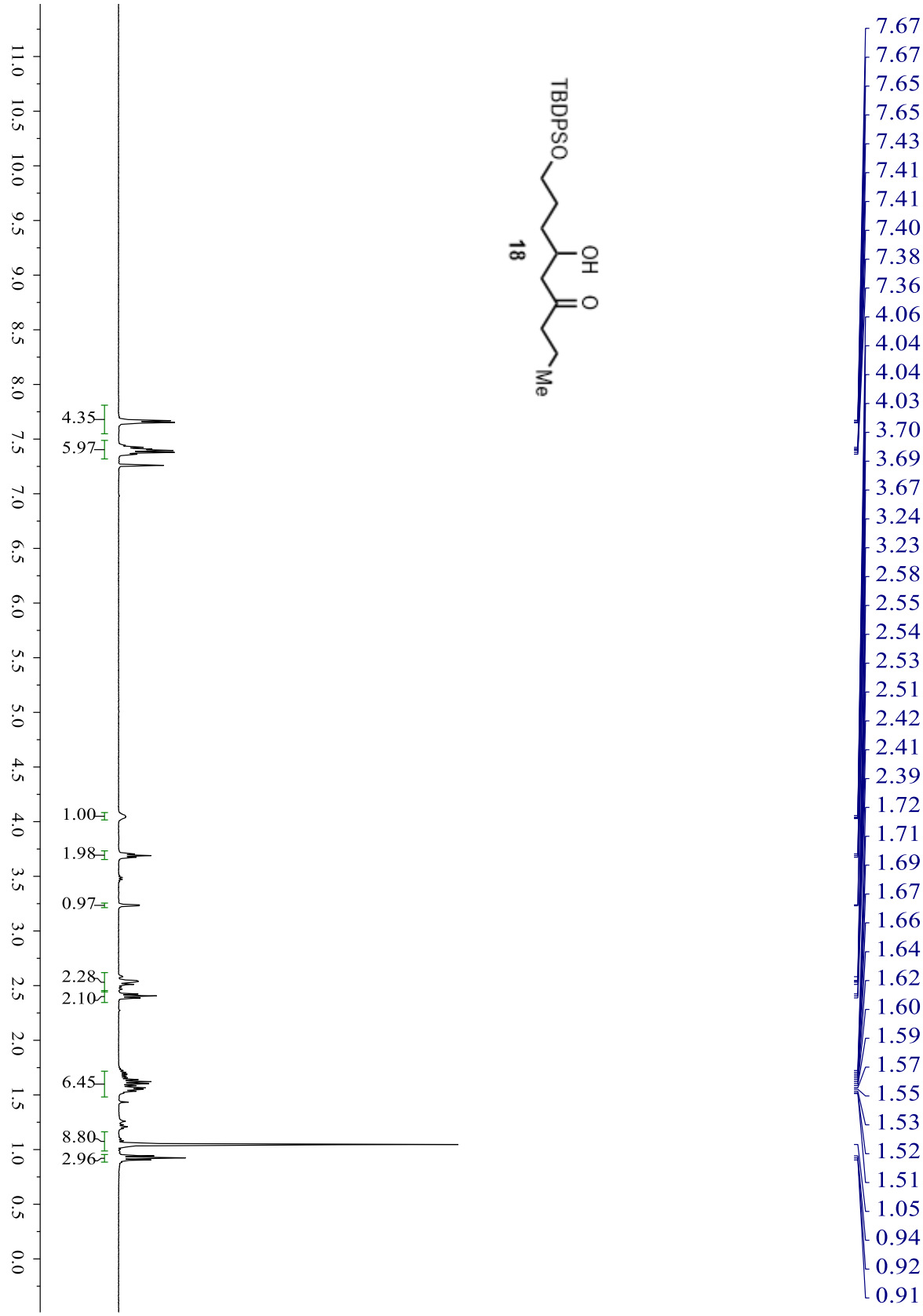
28.07
25.61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6.45
8.80
2.96
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7.67
7.65
7.65
7.43
7.41
7.41
7.40
7.38
7.36
4.06
4.04
4.04
4.03
3.70
3.69
3.67
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3.23
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2.55
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2.53
2.51
2.42
2.41
2.39
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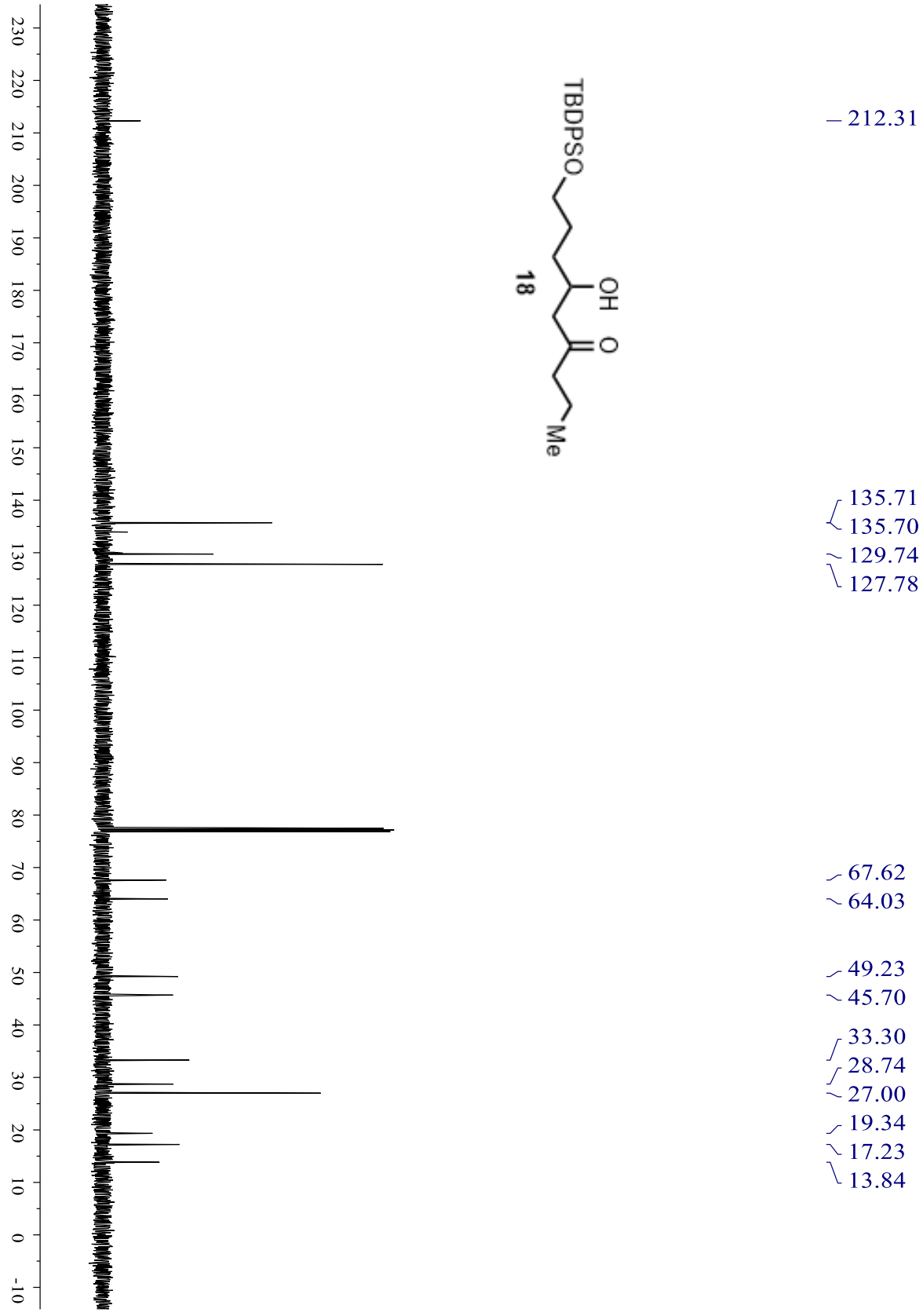
TBDPSO
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27.00
19.34
17.23
13.84
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220
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200
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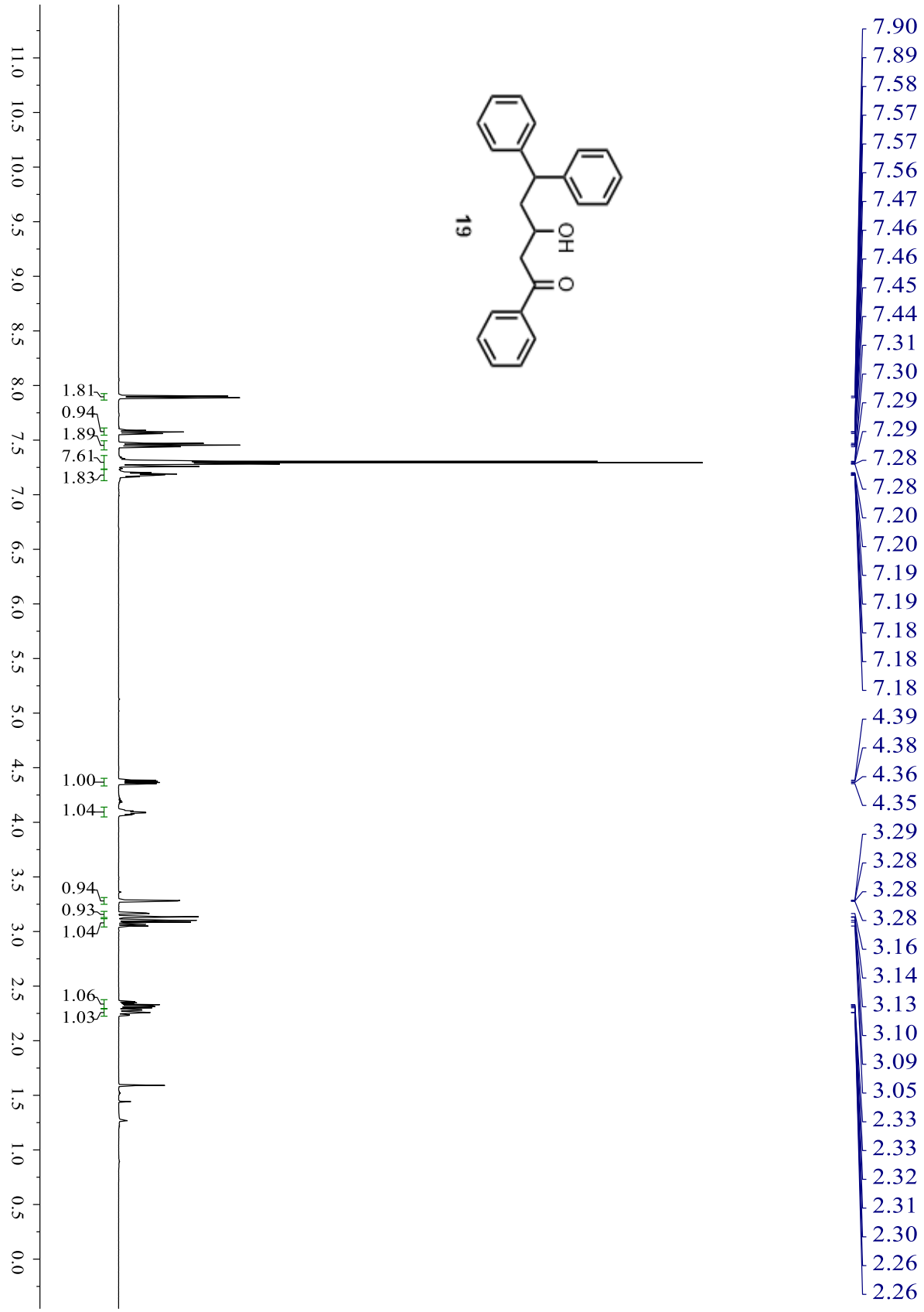
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0.93
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1.06
1.03
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7.89
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7.57
7.57
7.56
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7.46
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7.45
7.44
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7.18
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3.28
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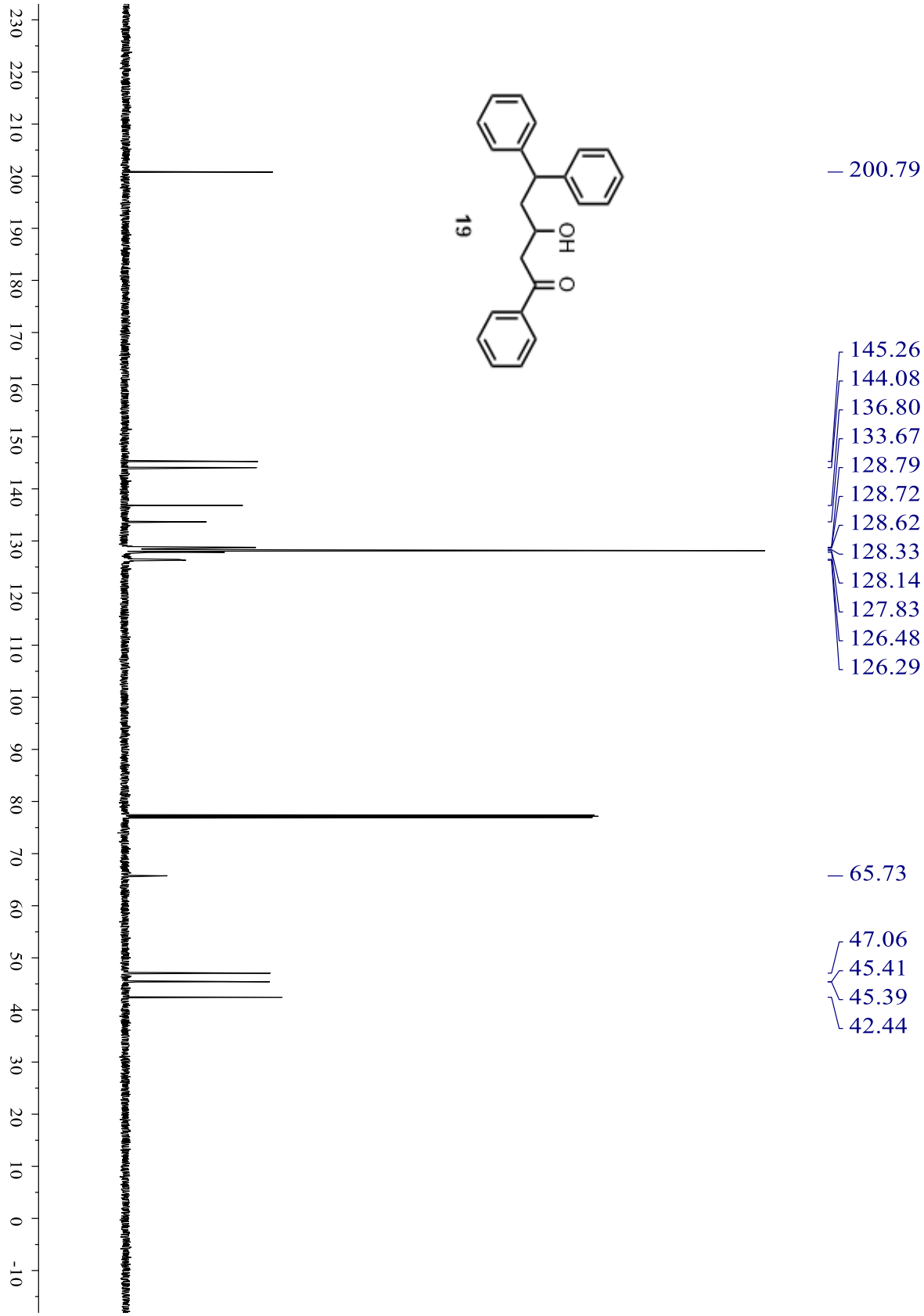
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O
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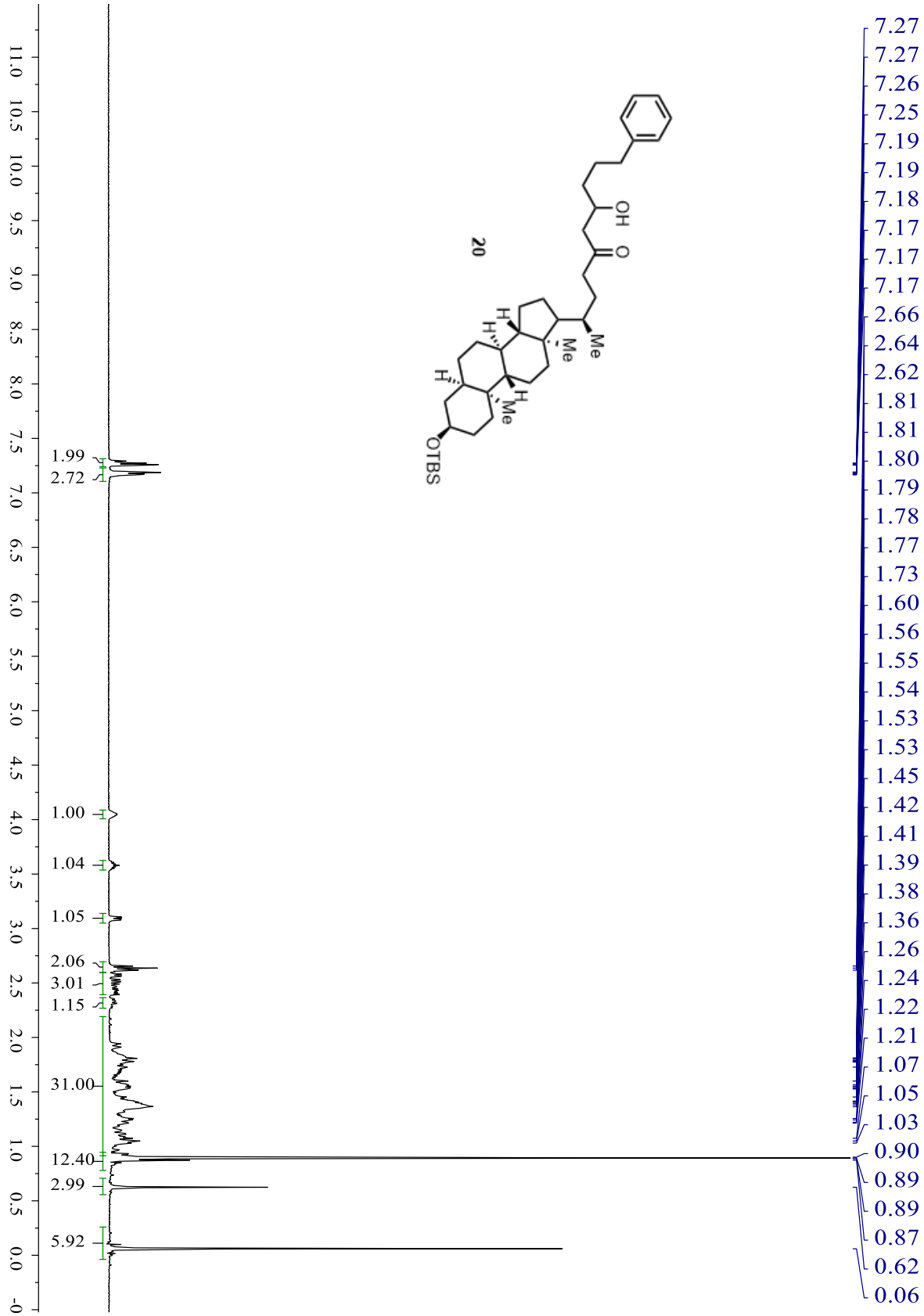
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O
Me
Me
Me
H
H
H
OTBS
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1.00
1.04
1.05
2.06
3.01
1.15
31.00
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7.27
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2.62
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1.81
1.80
1.79
1.78
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1.54
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1.53
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1.39
1.38
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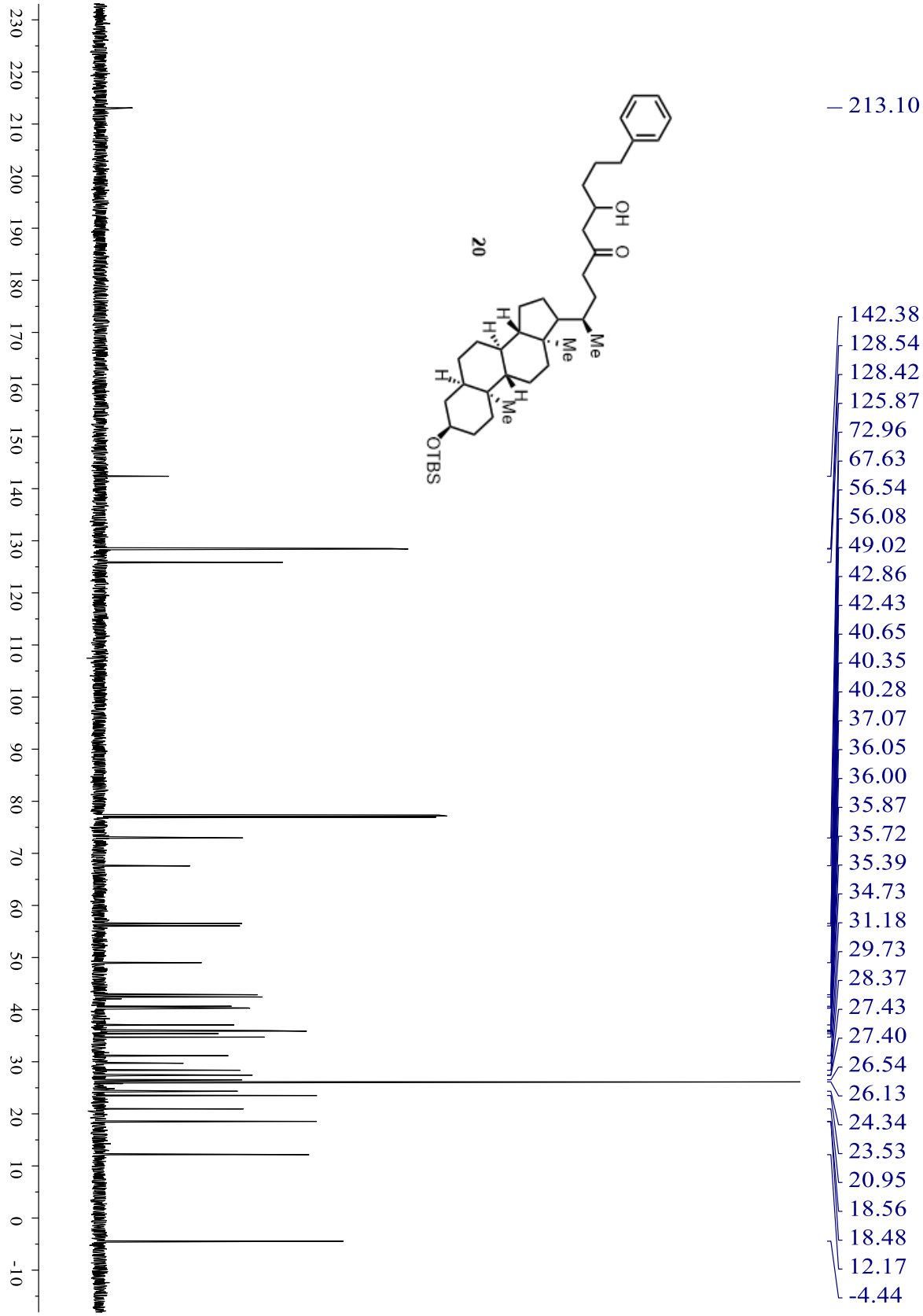
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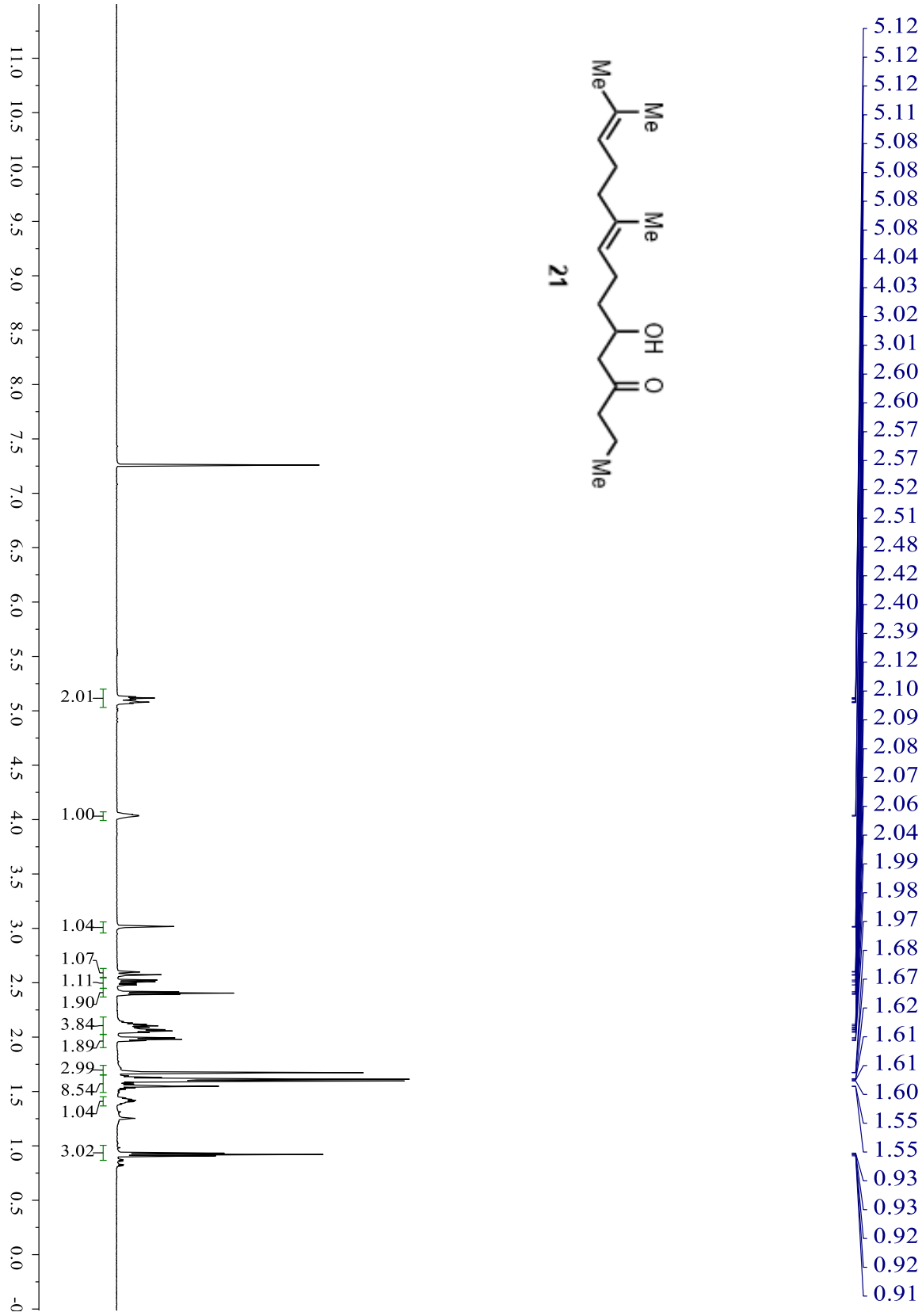
H
OTBS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Me
Me
OH
O
Me
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1.00
1.04
1.07
1.11
1.90
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1.89
2.99
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1.04
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2.12
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2.07
2.06
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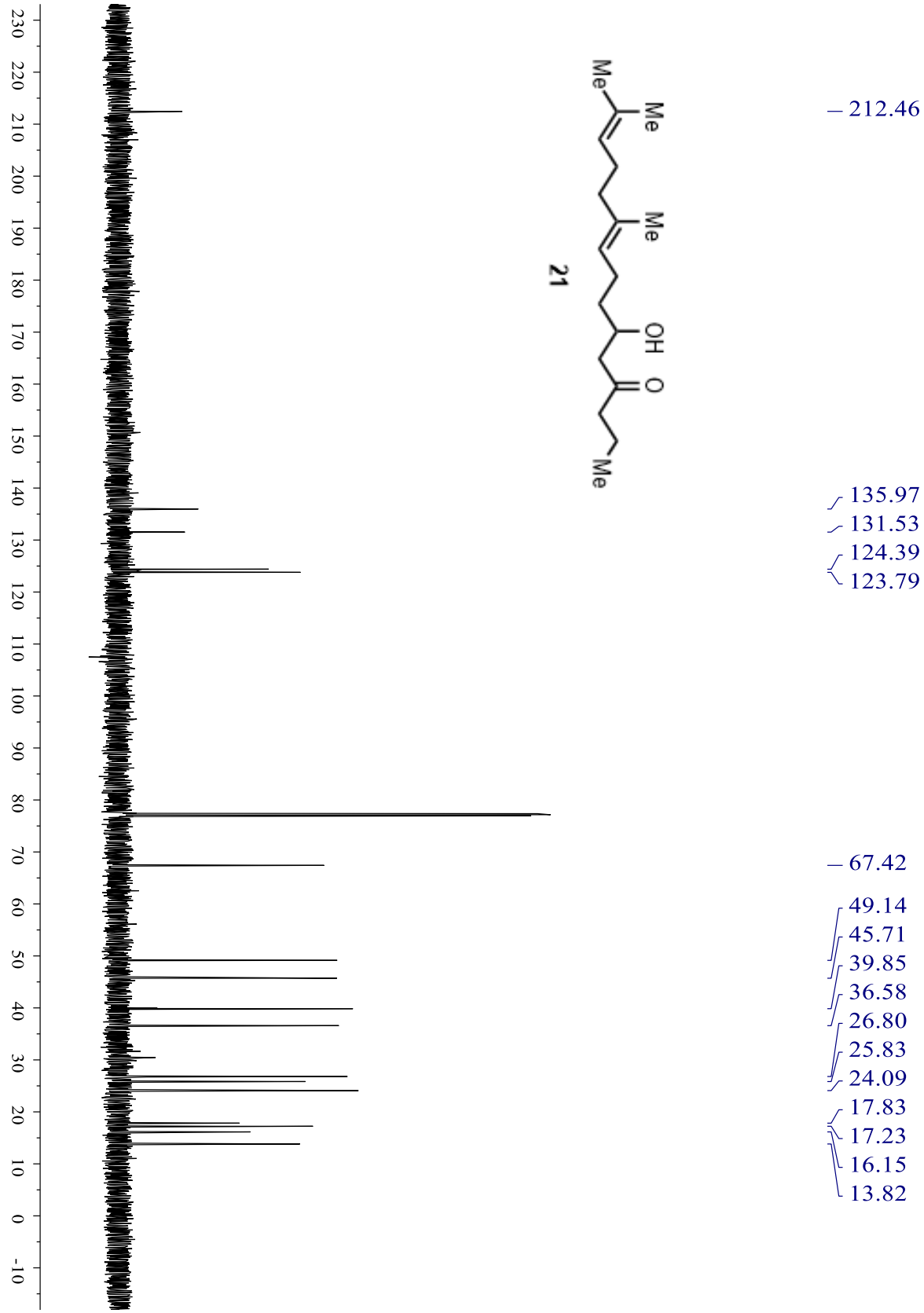
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39.85
36.58
26.80
25.83
24.09
17.83
17.23
16.15
13.82
230
220
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190
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100
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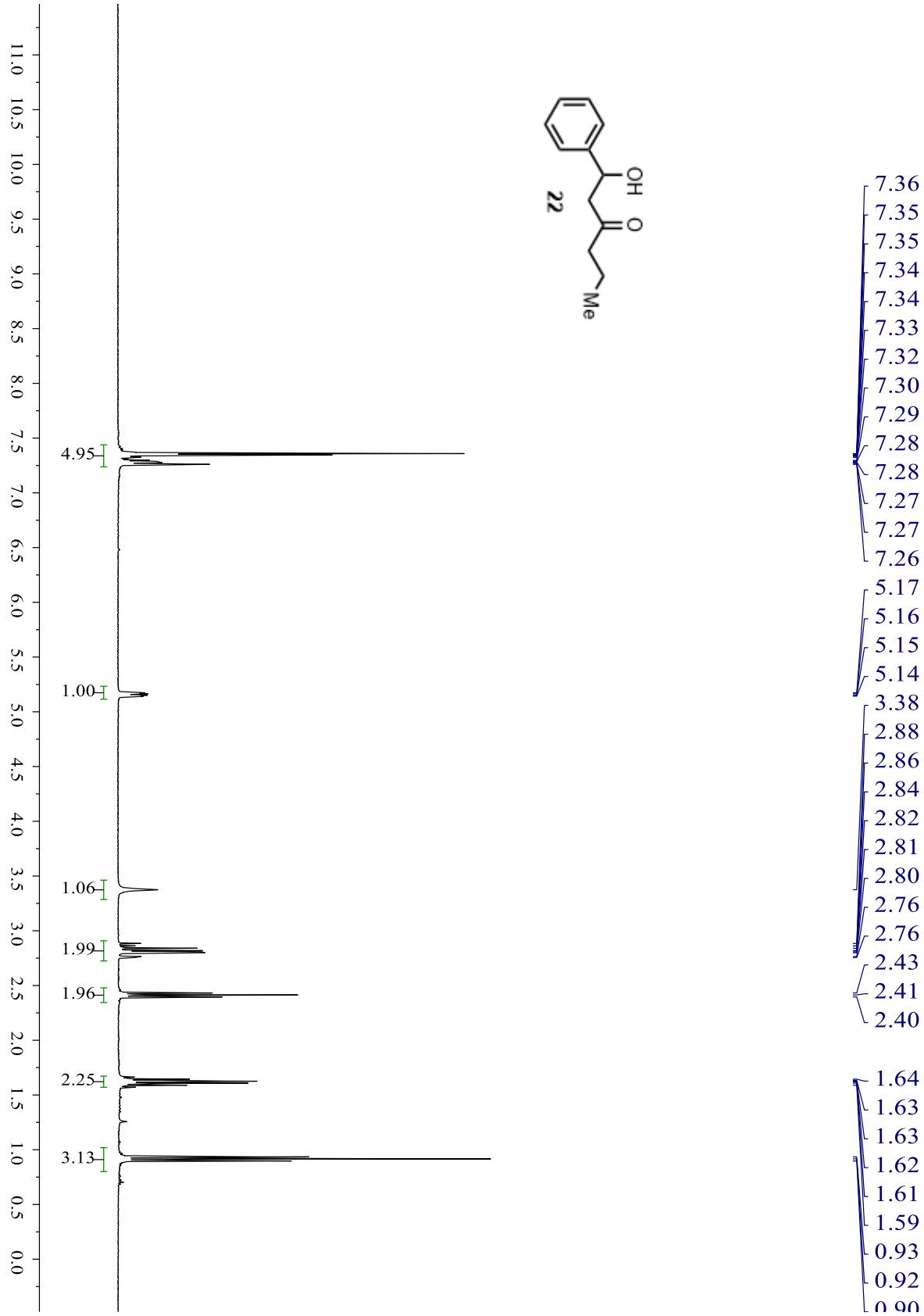
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1.06
1.99
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2.25
3.13
OH O
22
Me
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7.35
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7.34
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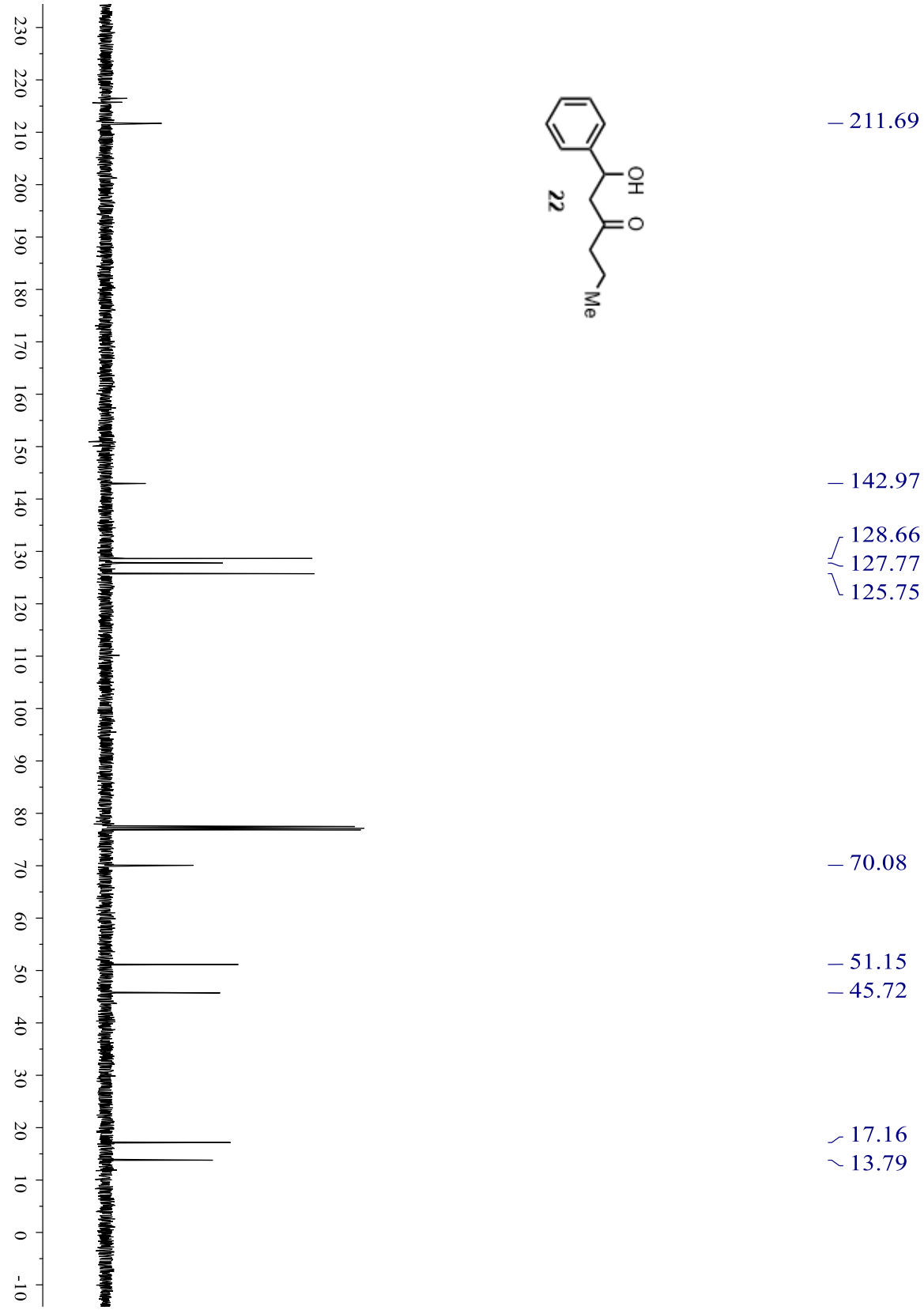
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30
20
10
0
-10
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O
Me
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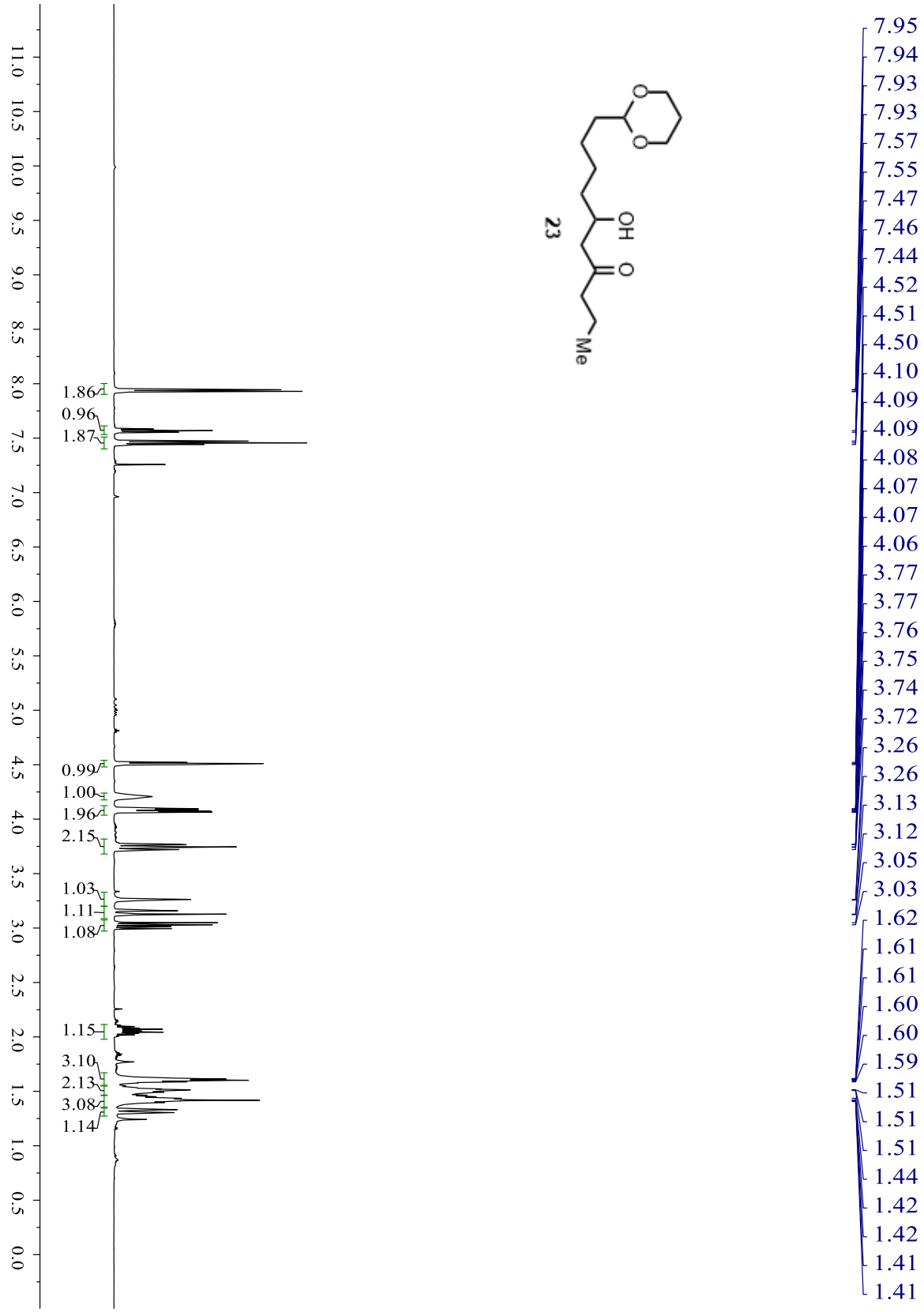
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0.96
1.87
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2.15
1.03
1.11
1.08
1.15
3.10
2.13
3.08
1.14
OH
O
Me
23
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7.94
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7.93
7.57
7.55
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7.46
7.44
4.52
4.51
4.50
4.10
4.09
4.09
4.08
4.07
4.07
4.06
3.77
3.77
3.76
3.75
3.74
3.72
3.26
3.26
3.13
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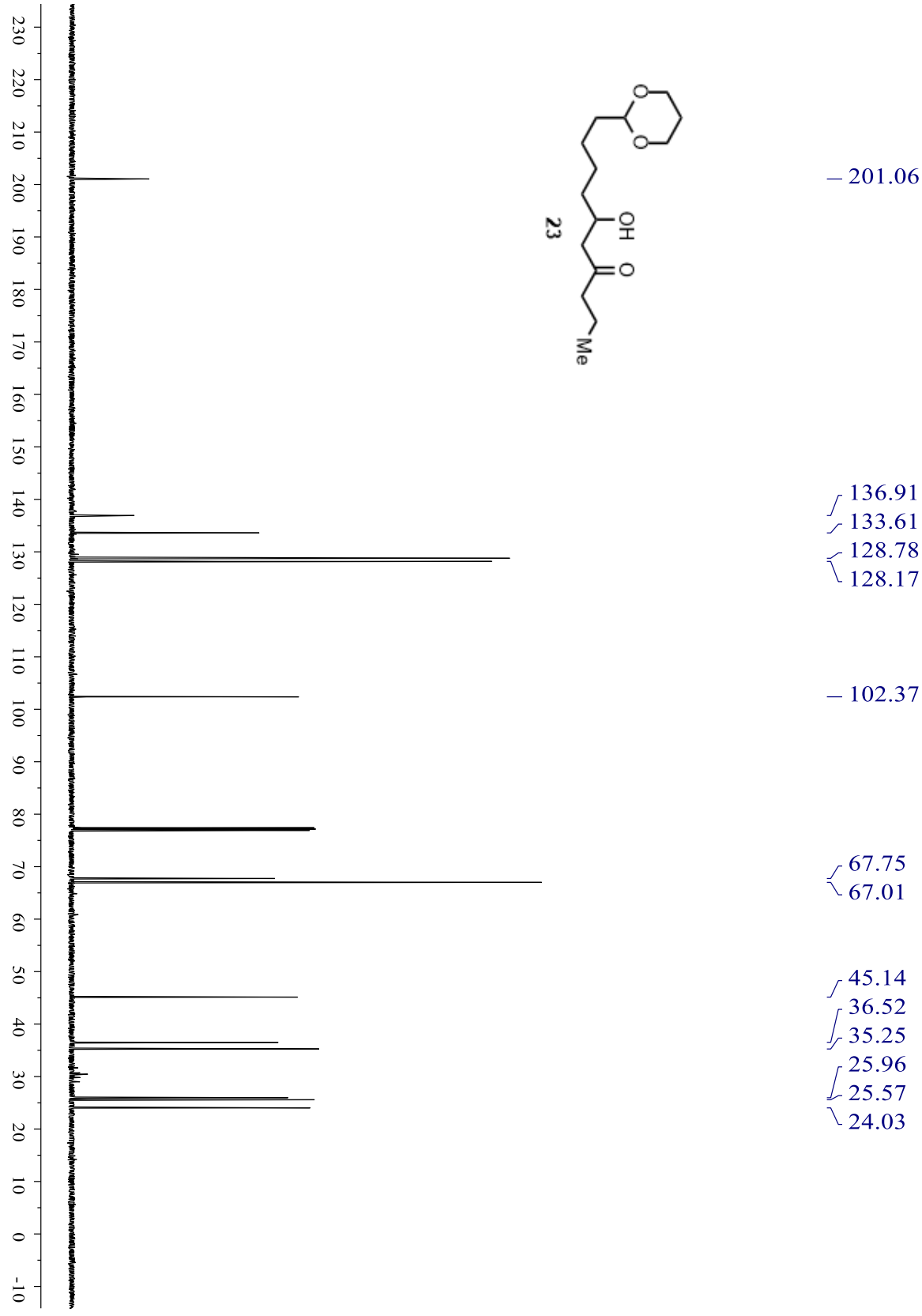
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10
0
-10
OH
O
Me
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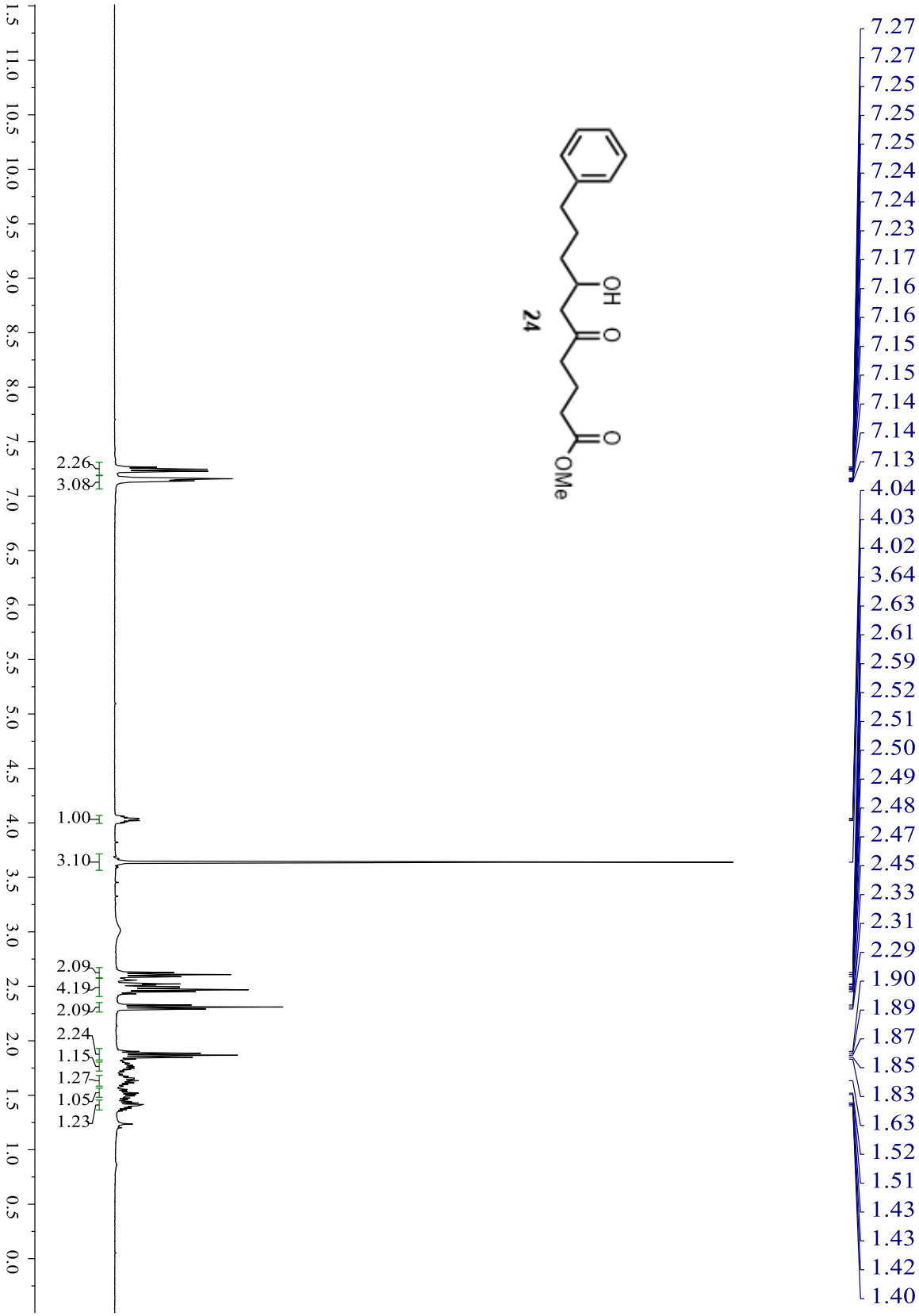
24.03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O
OMe
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2.09
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2.09
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1.27
1.05
1.23
7.27
7.27
7.25
7.25
7.25
7.24
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7.23
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.13
4.04
4.03
4.02
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2.61
2.59
2.52
2.51
2.50
2.49
2.48
2.47
2.45
2.33
2.31
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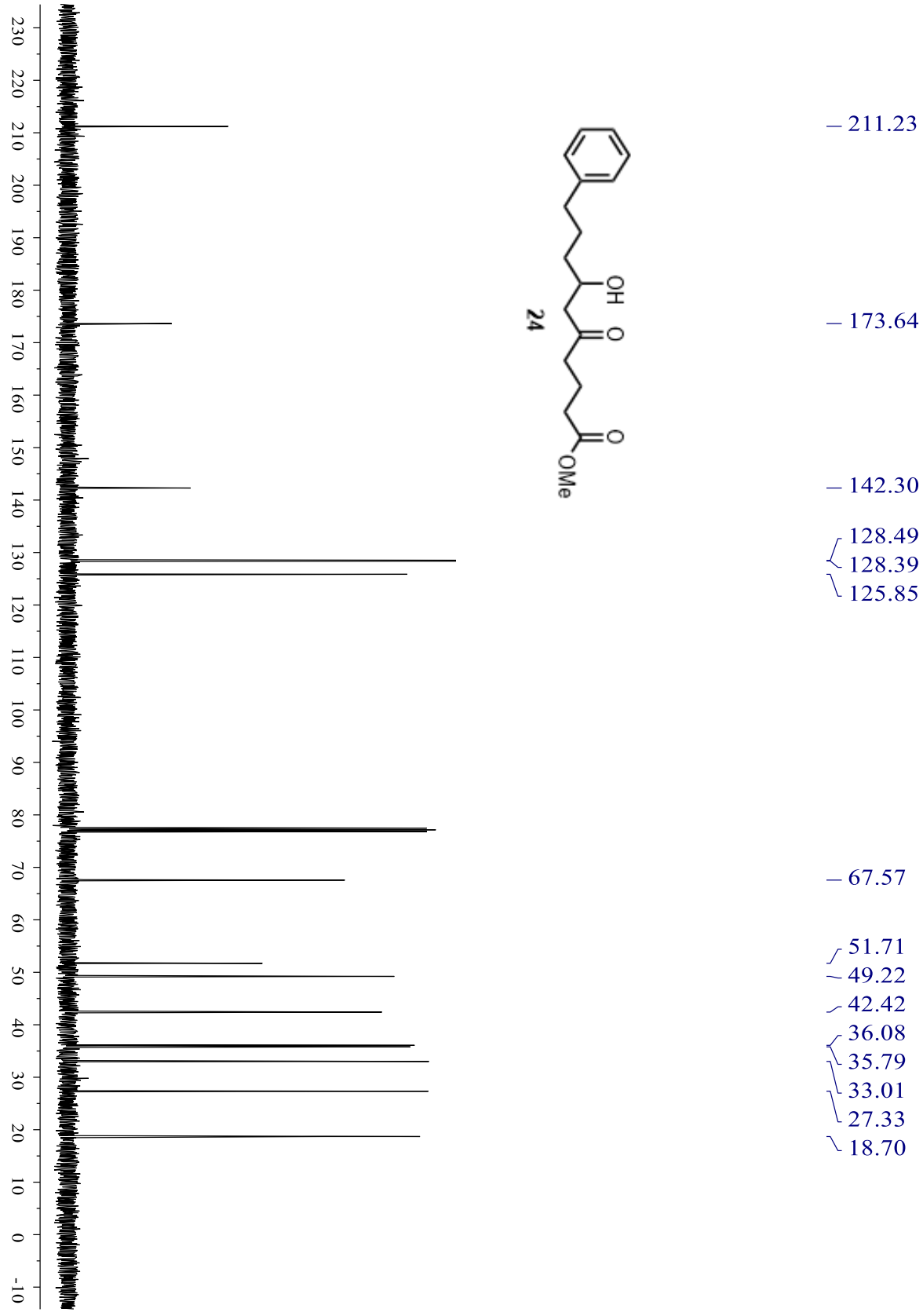
1.40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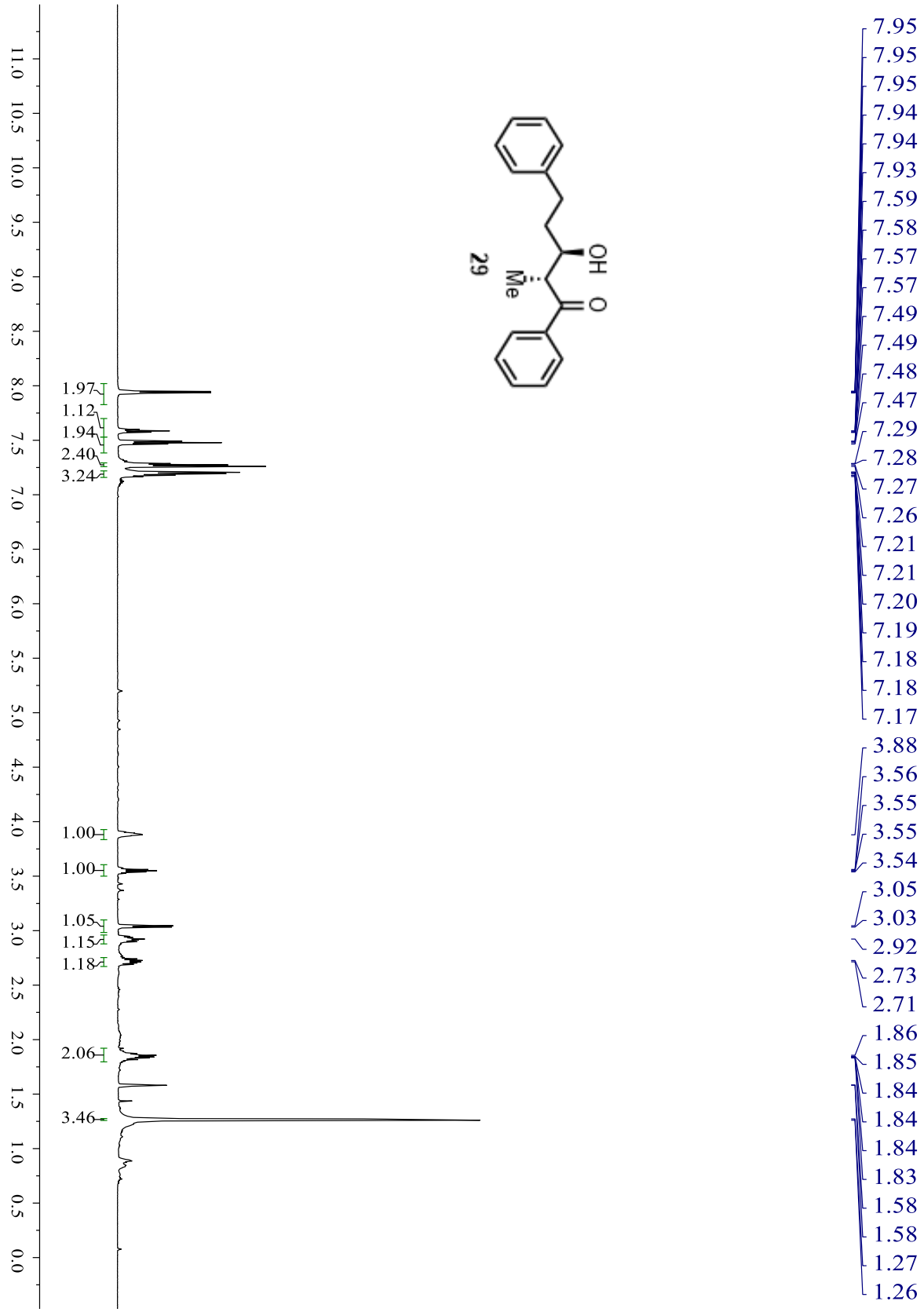
O
OMe
24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1.00
1.05
1.15
1.18
2.06
3.46
OH
O
Me
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7.47
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3.54
3.05
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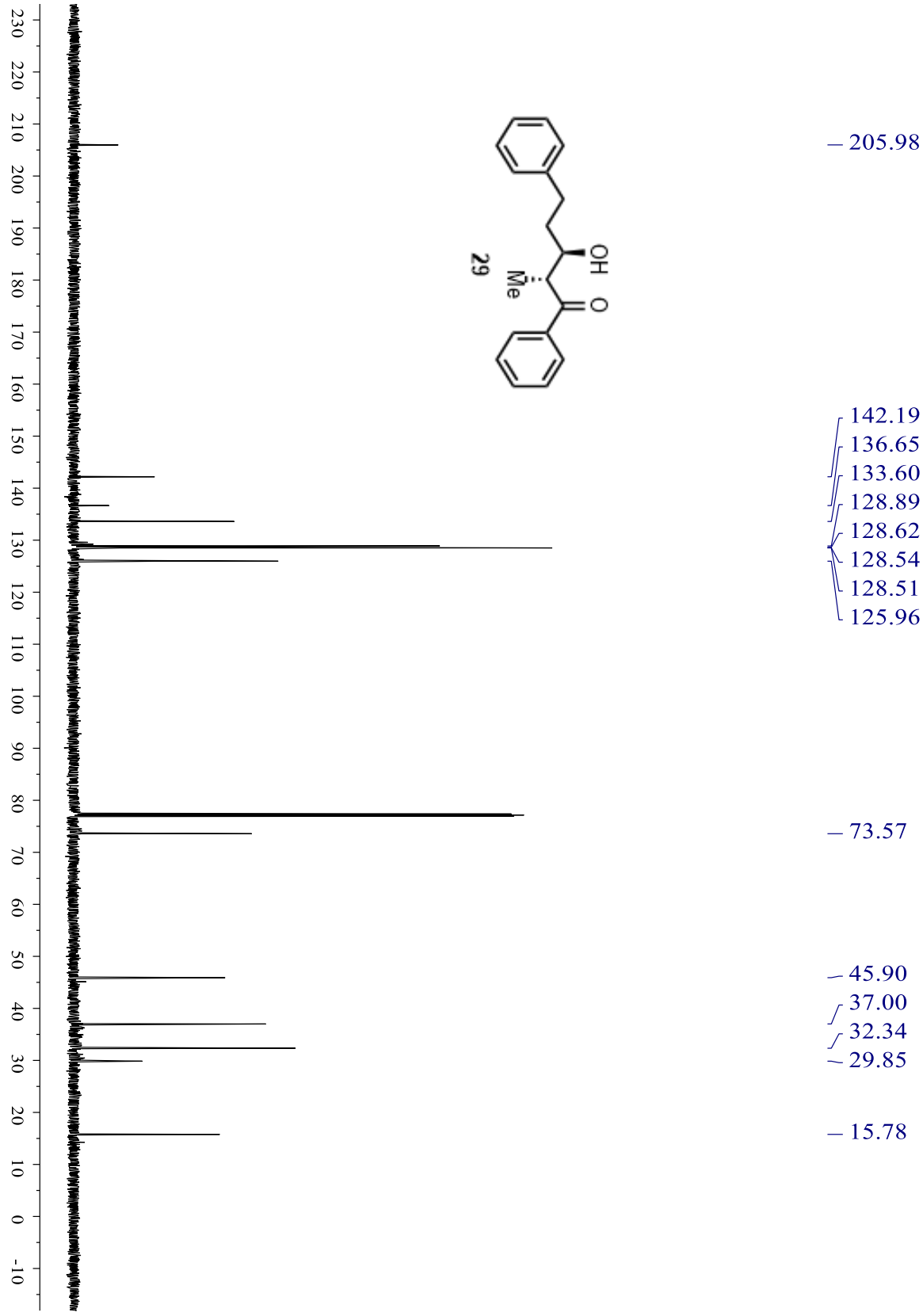
1.26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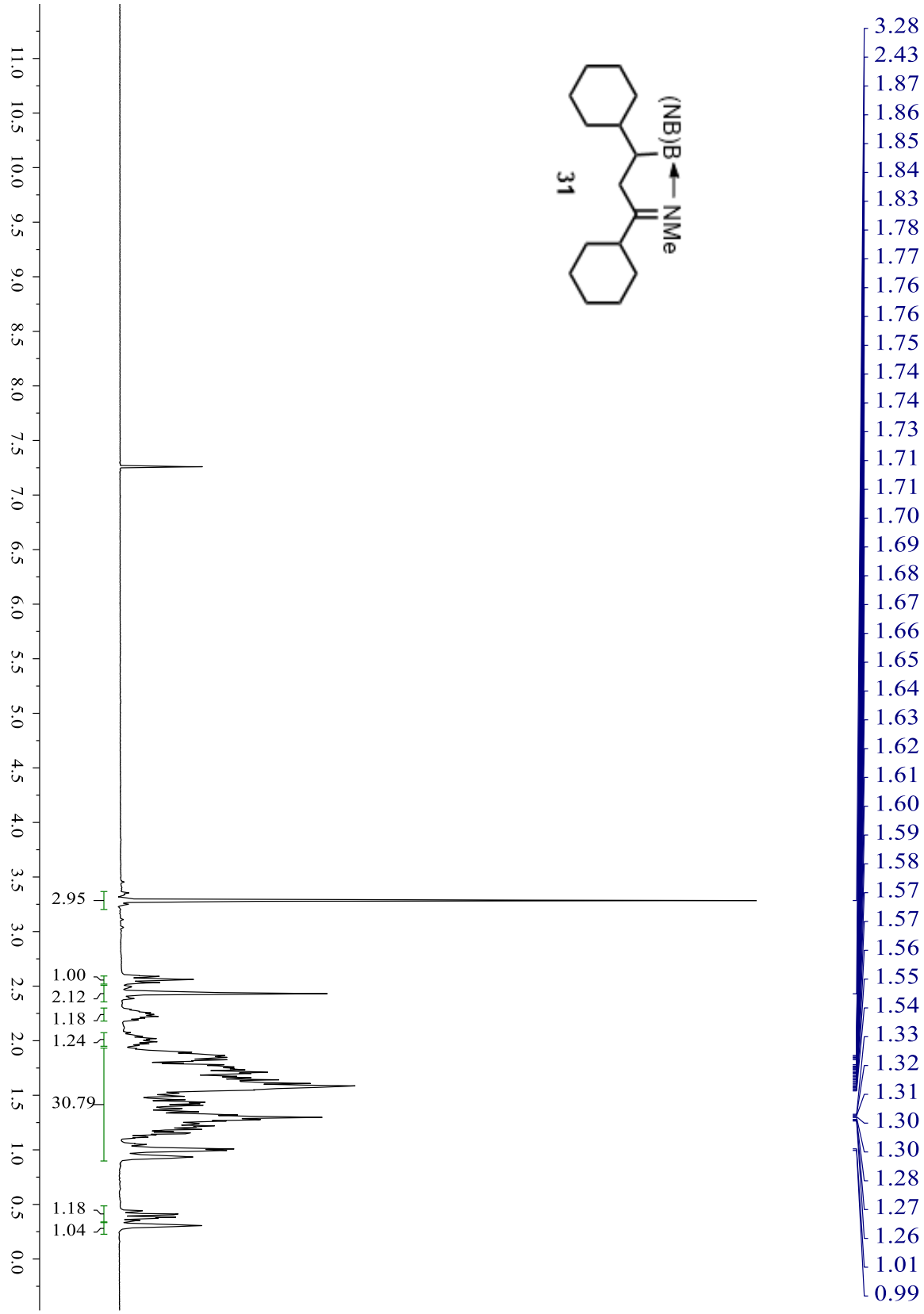
Me
29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2.95
1.00
2.12
1.18
1.24
30.79
1.18
1.04
3.28
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1.85
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1.56
1.55
1.54
1.33
1.32
1.31
1.30
1.30
1.28
1.27
1.26
1.01
0.99

(NB)B
NMe
31
189.07
40.42
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36.94
35.78
35.14
34.34
33.24
31.91
30.77
30.65
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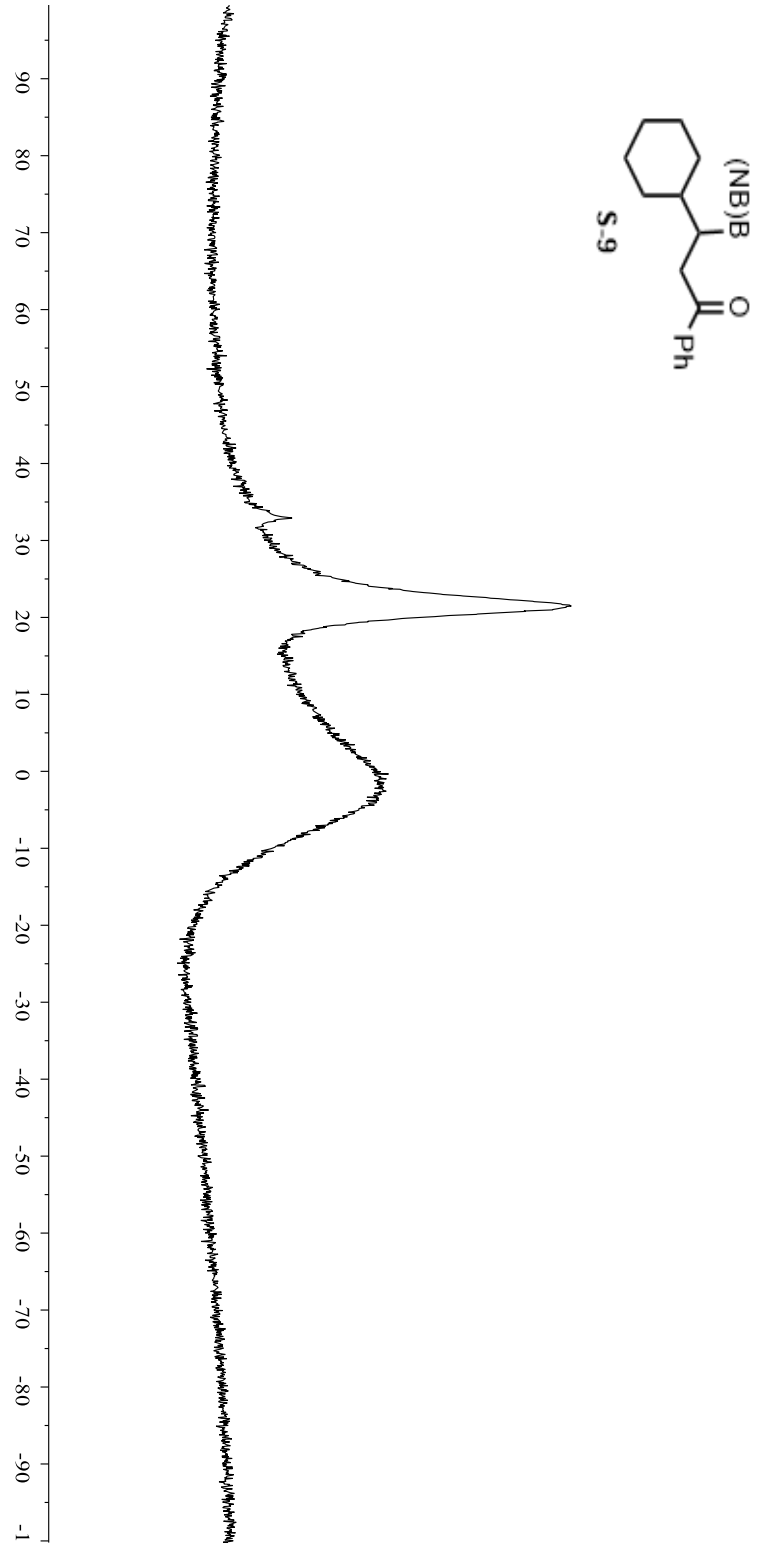
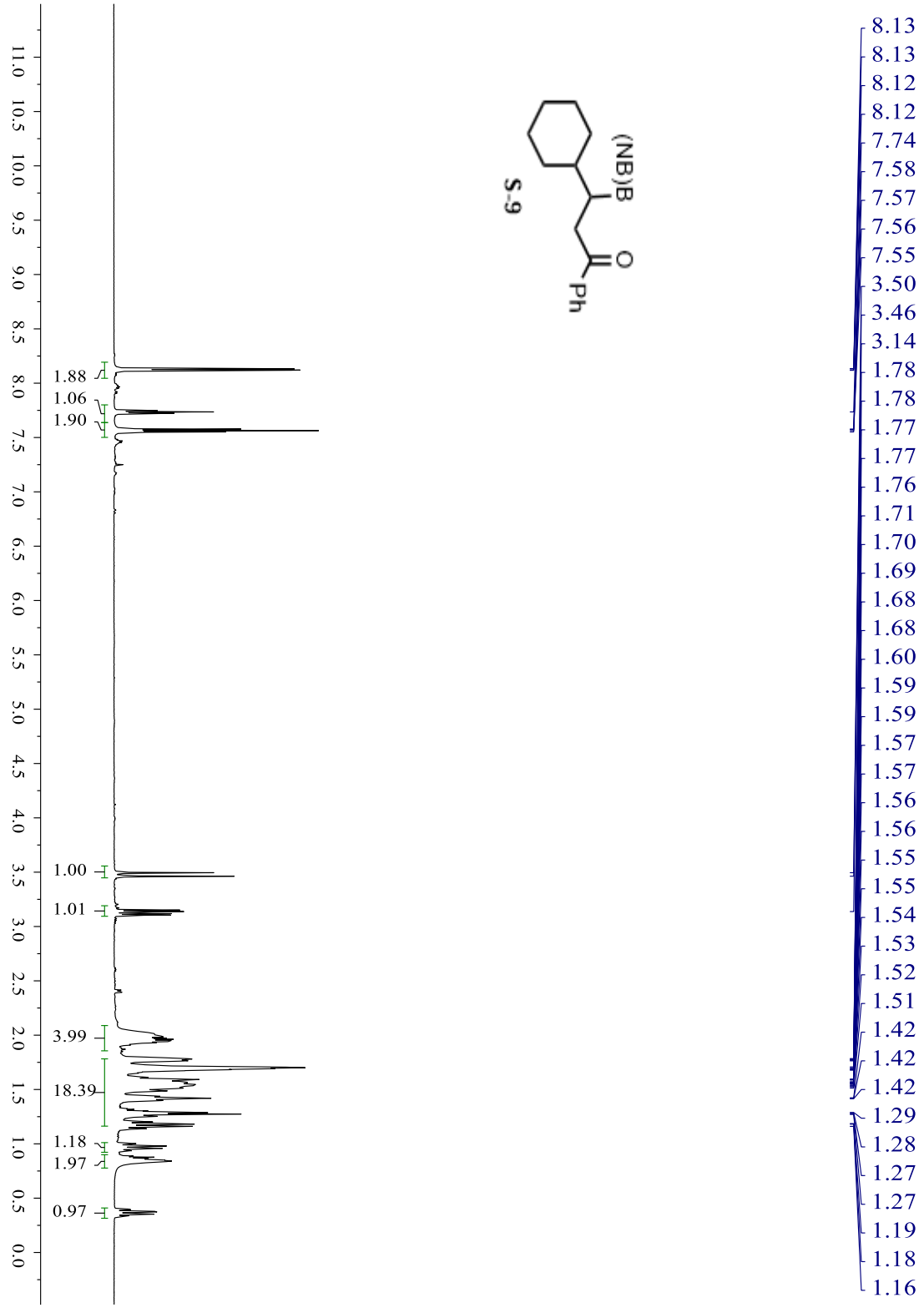
24.23

^{11}B NMR of S-9



– 21.52


S-9
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0.97
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8.13
8.12
8.12
7.74
7.58
7.57
7.56
7.55
3.50
3.46
3.14
1.78
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1.57
1.56
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1.55
1.55
1.54
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1.52
1.51
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1.29
1.28
1.27
1.27
1.19
1.18
1.16

S-9
(NB)B
O
Ph
212.92
136.40
131.24
130.88
129.37
40.00
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30.13
27.22
26.83
26.77
25.12
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220
210
200
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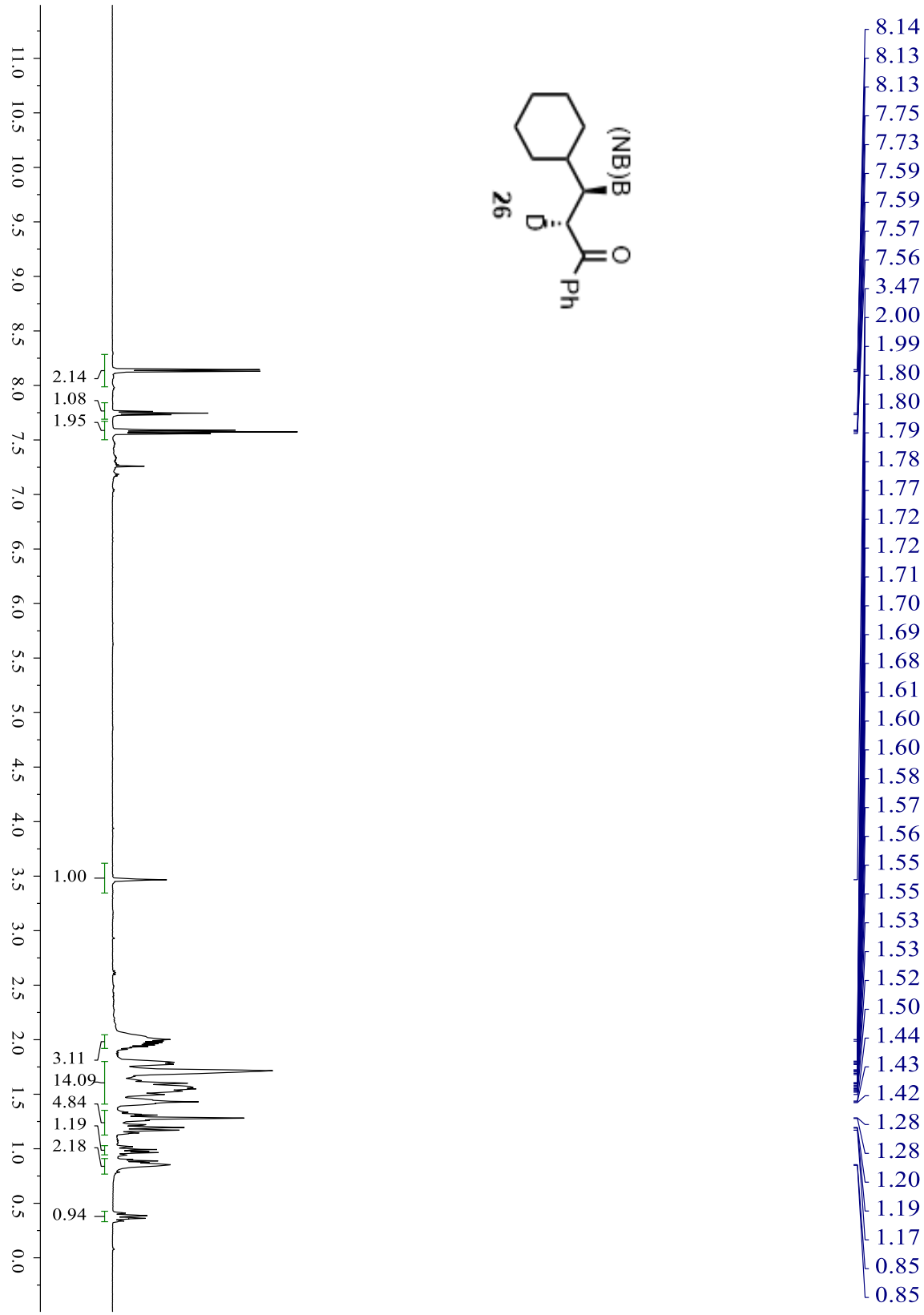
(NB)B
O
Ph
D
26
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2.14
1.08
1.95
1.00
3.11
14.09
4.84
1.19
2.18
0.94
8.14
8.13
8.13
7.75
7.73
7.59
7.59
7.57
7.56
3.47
2.00
1.99
1.80
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1.79
1.78
1.77
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1.56
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1.52
1.50
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1.28
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1.17
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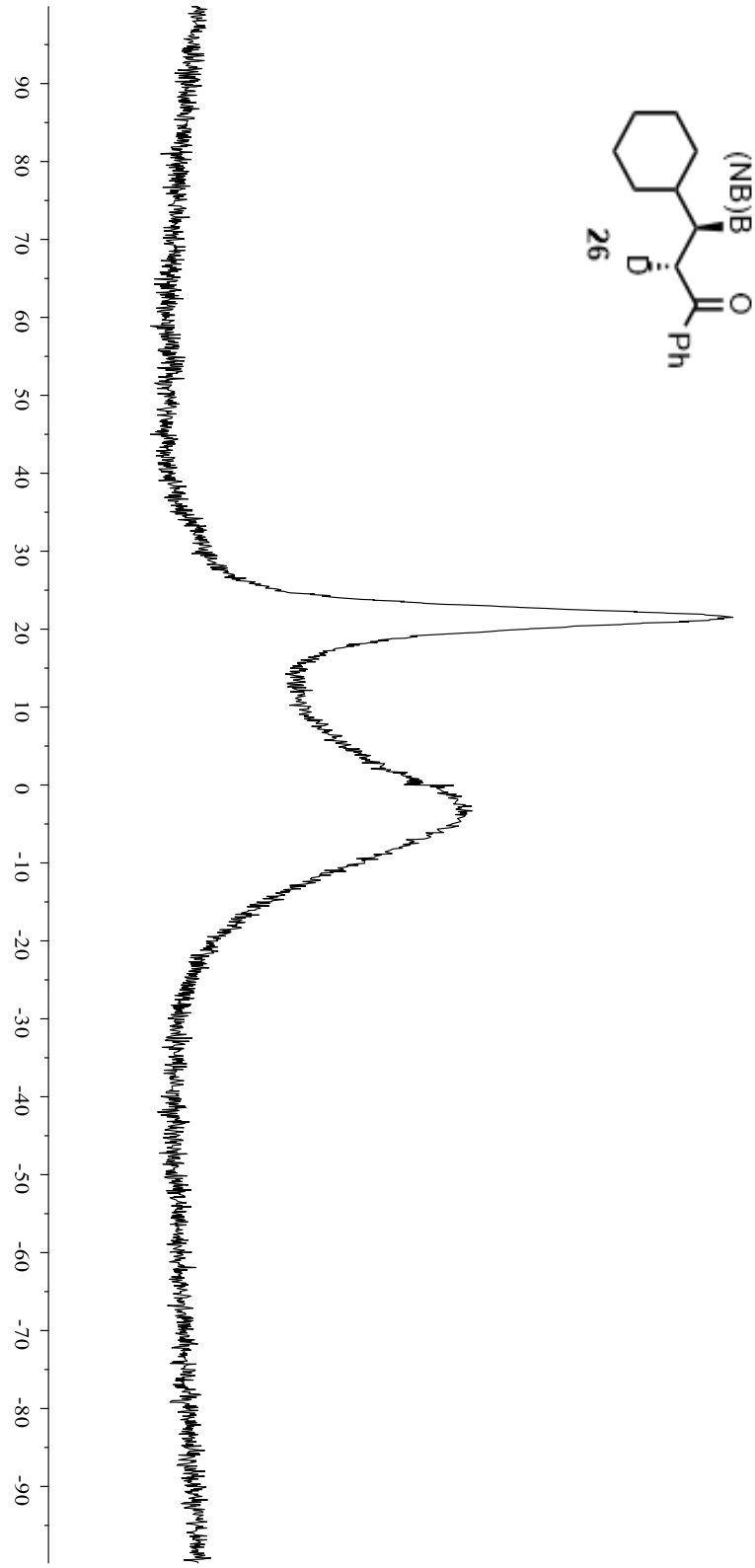
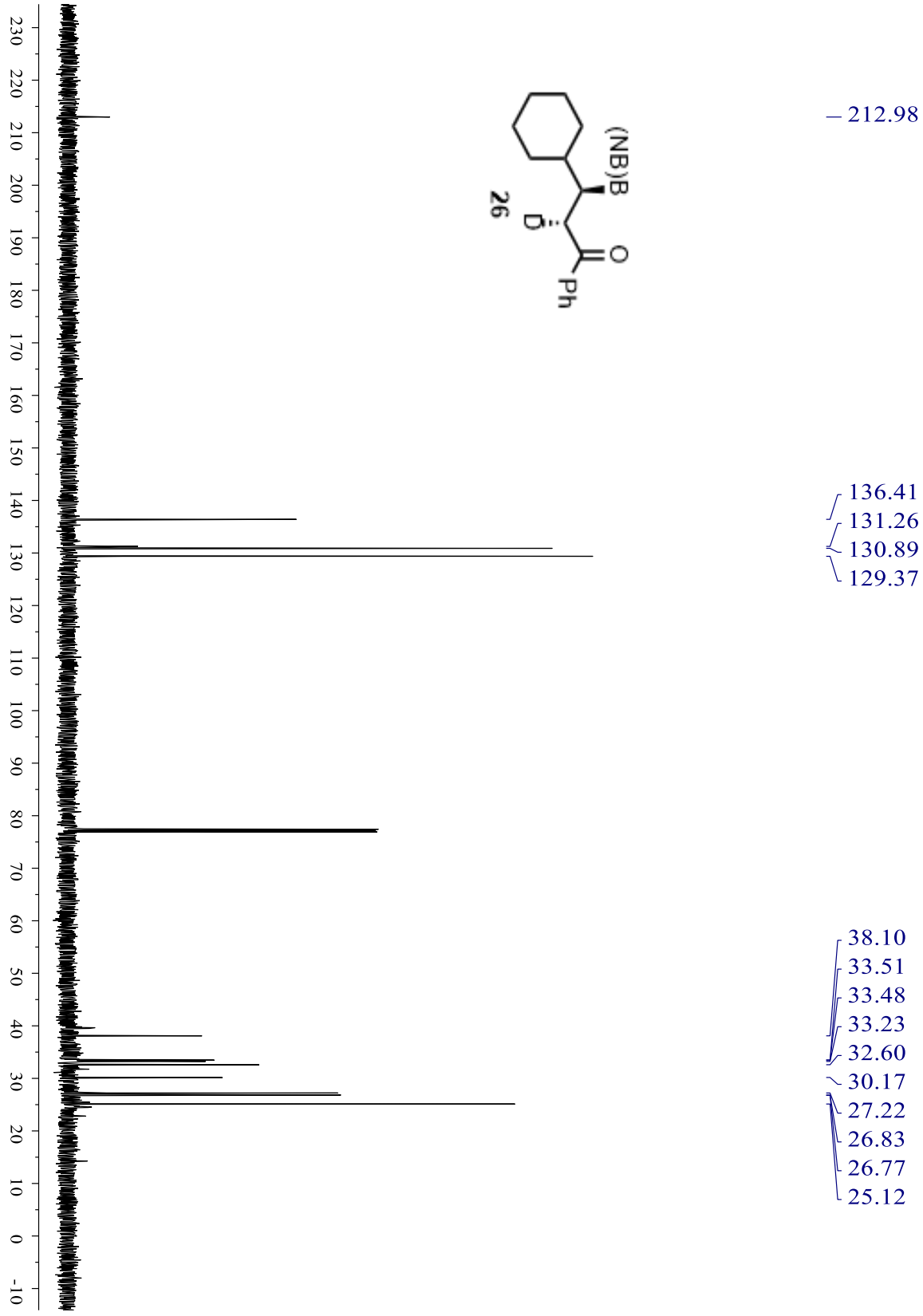
0.85

^{11}B NMR of 26



– 21.46


(NB)B
O
Ph
D
26
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38.10
33.51
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33.23
32.60
30.17
27.22
26.83
26.77
25.12
230
220
210
200
190
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120
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100
90
80
70
60
50
40
30
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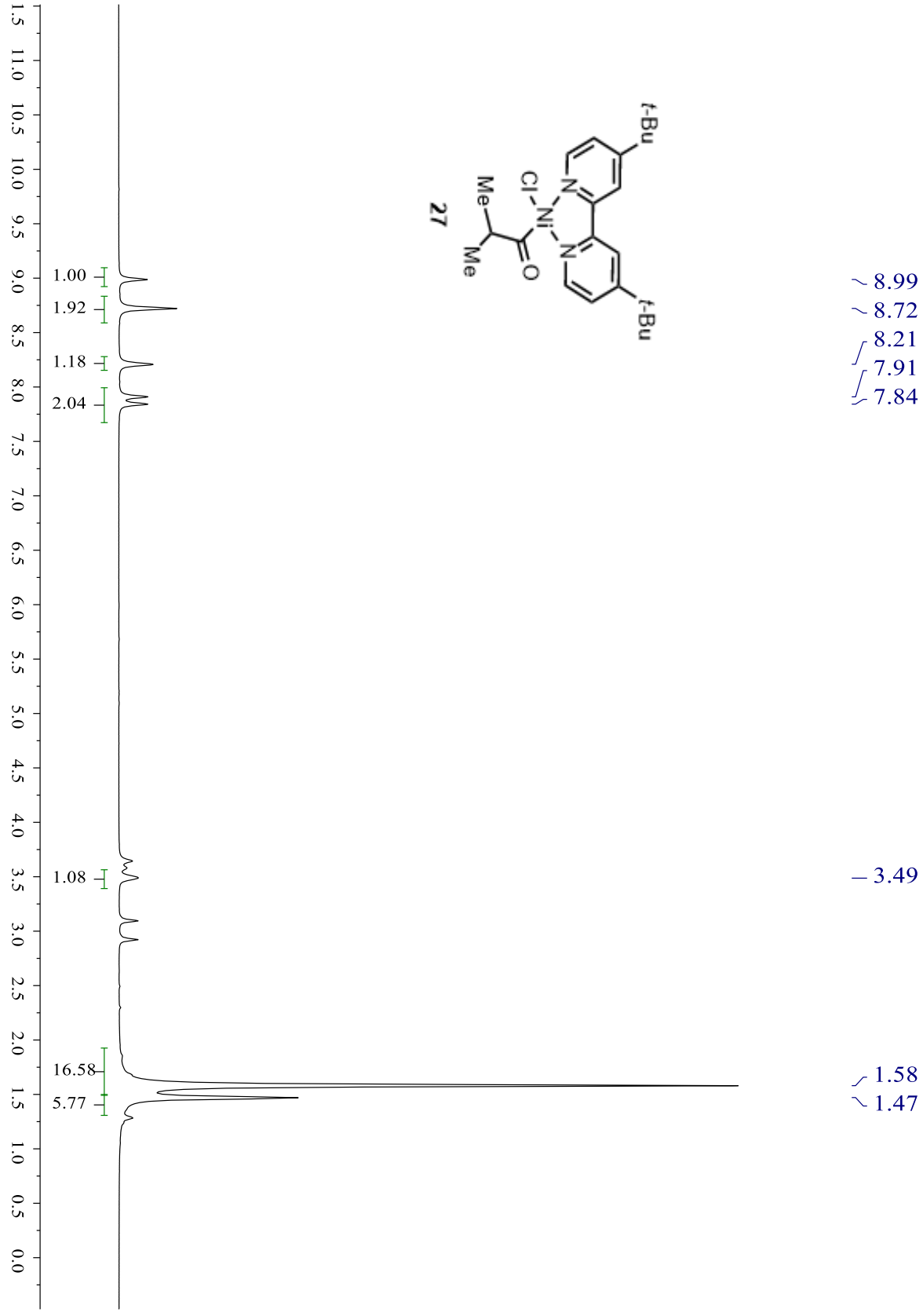
10
0
-10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1.00
1.92
1.18
2.04
1.08
16.58
5.77
t-Bu
Cl
Ni
N
N
O
Me
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t-Bu
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7.91
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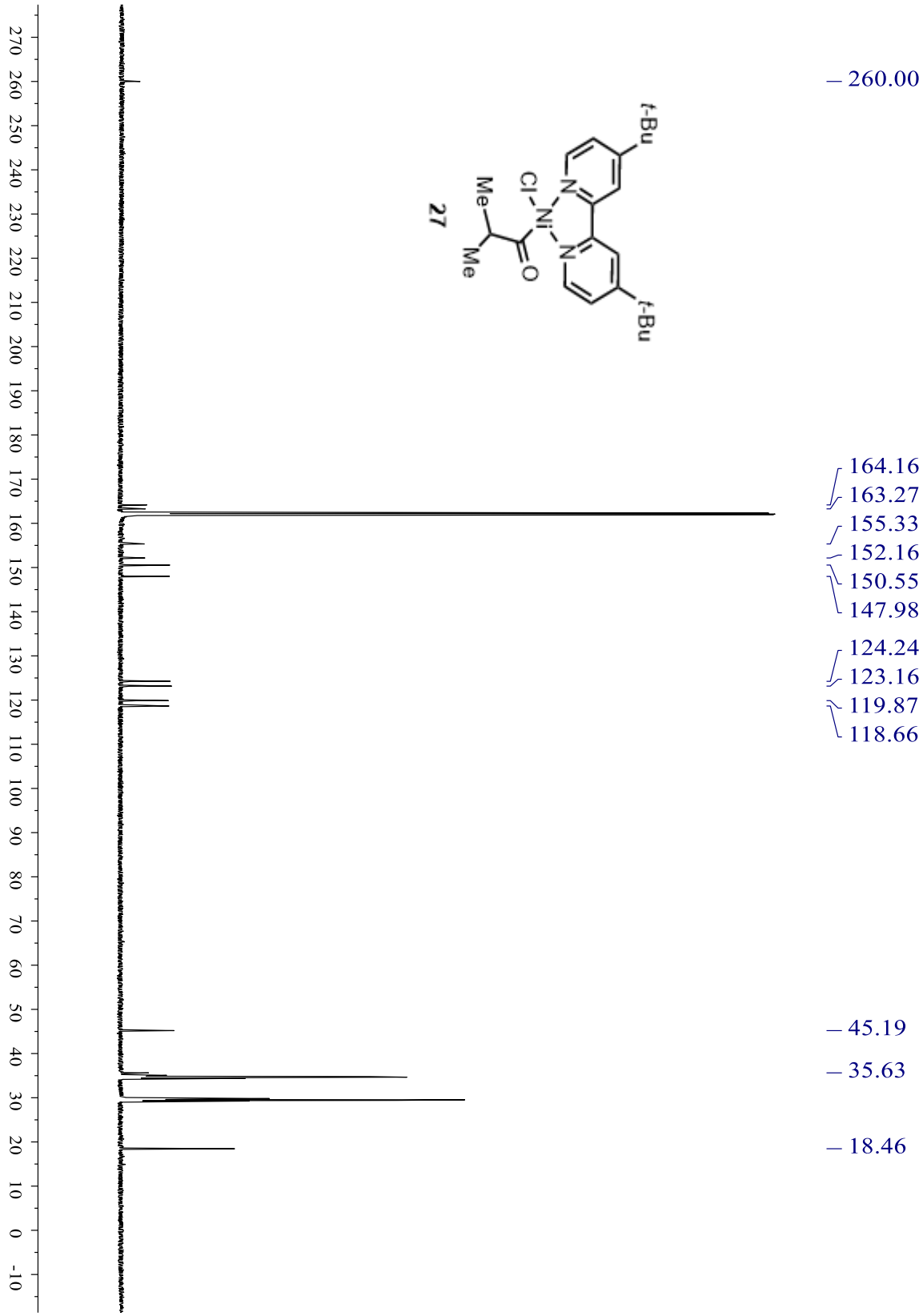
1.47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Cl
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N
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Me
Me
O
t-Bu
27
260.00
164.16
163.27
155.33
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123.16
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118.66
45.19
35.63
18.46

Crystallographic Data

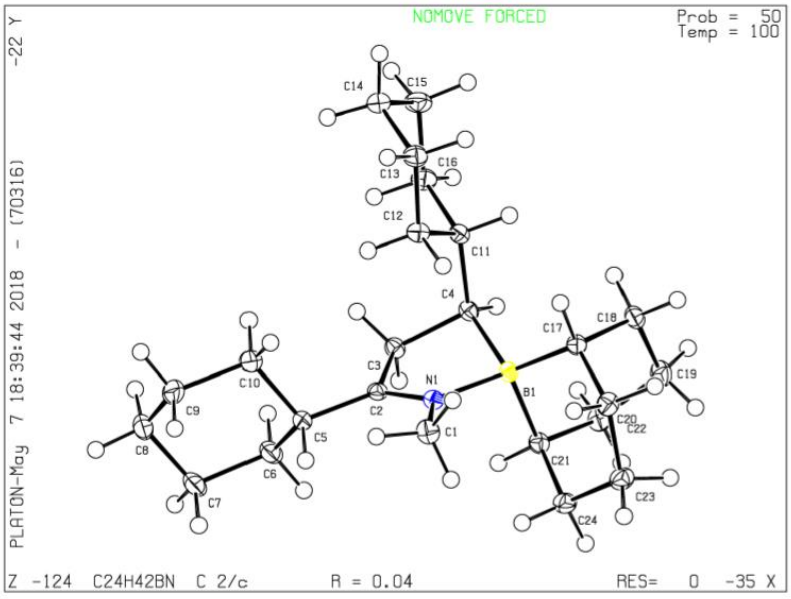


Table 1. Crystal data and structure refinement for C24H42BN.

Identification code	C24H42BN	
Empirical formula	C24 H42 B N	
Formula weight	355.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 17.528(3) Å	α= 90°.
	b = 9.8218(11) Å	β= 96.902(3)°.
	c = 24.925(3) Å	γ = 90°.
Volume	4259.8(9) $Å^3$	
Z	8	
Density (calculated)	1.108 Mg/m^3	
Absorption coefficient	0.062 mm^{-1}	
F(000)	1584	
Crystal size	0.500 x 0.360 x 0.220 mm^3	
Theta range for data collection	1.646 to 28.776°.	
Index ranges	-23<=h<=23, -13<=k<=13, -33<=l<=33	
Reflections collected	46241	

Independent reflections	5543 [R(int) = 0.0329]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.7053
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5543 / 0 / 236
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0416, wR2 = 0.1070
R indices (all data)	R1 = 0.0505, wR2 = 0.1137
Extinction coefficient	n/a
Largest diff. peak and hole	0.387 and -0.225 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for C24H42BN. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	5451(1)	5931(1)	3711(1)	13(1)
C(1)	4978(1)	6901(1)	3972(1)	18(1)
C(2)	5929(1)	6309(1)	3385(1)	13(1)
C(3)	6421(1)	5158(1)	3231(1)	14(1)
C(4)	6335(1)	4019(1)	3645(1)	13(1)
C(5)	6011(1)	7718(1)	3162(1)	16(1)
C(6)	6100(1)	7651(1)	2555(1)	21(1)
C(7)	6152(1)	9084(1)	2325(1)	28(1)
C(8)	6828(1)	9858(1)	2623(1)	35(1)
C(9)	6780(1)	9900(1)	3229(1)	32(1)
C(10)	6700(1)	8478(1)	3467(1)	23(1)
C(11)	6957(1)	4094(1)	4141(1)	14(1)
C(12)	6958(1)	5424(1)	4466(1)	16(1)
C(13)	7550(1)	5397(1)	4970(1)	18(1)
C(14)	8356(1)	5150(1)	4819(1)	20(1)
C(15)	8382(1)	3833(1)	4496(1)	22(1)
C(16)	7774(1)	3827(1)	3999(1)	19(1)
C(17)	5191(1)	3569(1)	4313(1)	14(1)
C(18)	5306(1)	2015(1)	4253(1)	18(1)
C(19)	4844(1)	1357(1)	3755(1)	20(1)
C(20)	4858(1)	2161(1)	3226(1)	19(1)
C(21)	4794(1)	3718(1)	3282(1)	15(1)
C(22)	4361(1)	3905(1)	4415(1)	17(1)
C(23)	3737(1)	3736(1)	3928(1)	19(1)
C(24)	3978(1)	4158(1)	3378(1)	18(1)
B(1)	5441(1)	4243(1)	3766(1)	13(1)

Table 3. Bond lengths [Å] and angles [°] for C24H42BN.

N(1)-C(2)	1.2889(12)
N(1)-C(1)	1.4663(12)
N(1)-B(1)	1.6638(13)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.5002(13)
C(2)-C(5)	1.5051(13)
C(3)-C(4)	1.5417(13)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(11)	1.5491(13)
C(4)-B(1)	1.6463(14)
C(4)-H(4)	1.0000
C(5)-C(10)	1.5402(14)
C(5)-C(6)	1.5406(14)
C(5)-H(5)	1.0000
C(6)-C(7)	1.5267(15)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.5230(18)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.523(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.5311(15)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.5375(13)
C(11)-C(16)	1.5388(13)
C(11)-H(11)	1.0000

C(12)-C(13)	1.5290(13)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.5237(15)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.5274(15)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.5341(14)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(22)	1.5428(13)
C(17)-C(18)	1.5493(14)
C(17)-B(1)	1.6225(14)
C(17)-H(17)	1.0000
C(18)-C(19)	1.5406(14)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.5382(14)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.5415(14)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(24)	1.5387(14)
C(21)-B(1)	1.6364(14)
C(21)-H(21)	1.0000
C(22)-C(23)	1.5426(14)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.5392(14)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900

C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900

C(2)-N(1)-C(1)	122.50(8)
C(2)-N(1)-B(1)	110.70(8)
C(1)-N(1)-B(1)	126.77(8)
N(1)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(1)-C(2)-C(3)	112.44(8)
N(1)-C(2)-C(5)	126.55(9)
C(3)-C(2)-C(5)	121.01(8)
C(2)-C(3)-C(4)	105.66(8)
C(2)-C(3)-H(3A)	110.6
C(4)-C(3)-H(3A)	110.6
C(2)-C(3)-H(3B)	110.6
C(4)-C(3)-H(3B)	110.6
H(3A)-C(3)-H(3B)	108.7
C(3)-C(4)-C(11)	112.56(8)
C(3)-C(4)-B(1)	101.41(7)
C(11)-C(4)-B(1)	116.15(7)
C(3)-C(4)-H(4)	108.8
C(11)-C(4)-H(4)	108.8
B(1)-C(4)-H(4)	108.8
C(2)-C(5)-C(10)	111.55(8)
C(2)-C(5)-C(6)	110.37(8)
C(10)-C(5)-C(6)	109.84(9)
C(2)-C(5)-H(5)	108.3
C(10)-C(5)-H(5)	108.3
C(6)-C(5)-H(5)	108.3
C(7)-C(6)-C(5)	110.28(9)
C(7)-C(6)-H(6A)	109.6
C(5)-C(6)-H(6A)	109.6

C(7)-C(6)-H(6B)	109.6
C(5)-C(6)-H(6B)	109.6
H(6A)-C(6)-H(6B)	108.1
C(8)-C(7)-C(6)	110.80(9)
C(8)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7A)	109.5
C(8)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	108.1
C(7)-C(8)-C(9)	111.36(10)
C(7)-C(8)-H(8A)	109.4
C(9)-C(8)-H(8A)	109.4
C(7)-C(8)-H(8B)	109.4
C(9)-C(8)-H(8B)	109.4
H(8A)-C(8)-H(8B)	108.0
C(8)-C(9)-C(10)	112.23(10)
C(8)-C(9)-H(9A)	109.2
C(10)-C(9)-H(9A)	109.2
C(8)-C(9)-H(9B)	109.2
C(10)-C(9)-H(9B)	109.2
H(9A)-C(9)-H(9B)	107.9
C(9)-C(10)-C(5)	110.70(9)
C(9)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1
C(12)-C(11)-C(16)	108.90(8)
C(12)-C(11)-C(4)	114.71(8)
C(16)-C(11)-C(4)	113.13(8)
C(12)-C(11)-H(11)	106.5
C(16)-C(11)-H(11)	106.5
C(4)-C(11)-H(11)	106.5
C(13)-C(12)-C(11)	112.08(8)
C(13)-C(12)-H(12A)	109.2
C(11)-C(12)-H(12A)	109.2

C(13)-C(12)-H(12B)	109.2
C(11)-C(12)-H(12B)	109.2
H(12A)-C(12)-H(12B)	107.9
C(14)-C(13)-C(12)	110.94(8)
C(14)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13A)	109.5
C(14)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	108.0
C(13)-C(14)-C(15)	110.61(9)
C(13)-C(14)-H(14A)	109.5
C(15)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
C(15)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.1
C(14)-C(15)-C(16)	111.55(8)
C(14)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15A)	109.3
C(14)-C(15)-H(15B)	109.3
C(16)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0
C(15)-C(16)-C(11)	112.81(8)
C(15)-C(16)-H(16A)	109.0
C(11)-C(16)-H(16A)	109.0
C(15)-C(16)-H(16B)	109.0
C(11)-C(16)-H(16B)	109.0
H(16A)-C(16)-H(16B)	107.8
C(22)-C(17)-C(18)	111.30(8)
C(22)-C(17)-B(1)	114.06(8)
C(18)-C(17)-B(1)	105.59(8)
C(22)-C(17)-H(17)	108.6
C(18)-C(17)-H(17)	108.6
B(1)-C(17)-H(17)	108.6
C(19)-C(18)-C(17)	115.43(8)
C(19)-C(18)-H(18A)	108.4
C(17)-C(18)-H(18A)	108.4

C(19)-C(18)-H(18B)	108.4
C(17)-C(18)-H(18B)	108.4
H(18A)-C(18)-H(18B)	107.5
C(20)-C(19)-C(18)	114.45(8)
C(20)-C(19)-H(19A)	108.6
C(18)-C(19)-H(19A)	108.6
C(20)-C(19)-H(19B)	108.6
C(18)-C(19)-H(19B)	108.6
H(19A)-C(19)-H(19B)	107.6
C(19)-C(20)-C(21)	115.03(8)
C(19)-C(20)-H(20A)	108.5
C(21)-C(20)-H(20A)	108.5
C(19)-C(20)-H(20B)	108.5
C(21)-C(20)-H(20B)	108.5
H(20A)-C(20)-H(20B)	107.5
C(24)-C(21)-C(20)	111.84(8)
C(24)-C(21)-B(1)	111.86(8)
C(20)-C(21)-B(1)	109.10(8)
C(24)-C(21)-H(21)	108.0
C(20)-C(21)-H(21)	108.0
B(1)-C(21)-H(21)	108.0
C(23)-C(22)-C(17)	116.10(8)
C(23)-C(22)-H(22A)	108.3
C(17)-C(22)-H(22A)	108.3
C(23)-C(22)-H(22B)	108.3
C(17)-C(22)-H(22B)	108.3
H(22A)-C(22)-H(22B)	107.4
C(24)-C(23)-C(22)	115.30(8)
C(24)-C(23)-H(23A)	108.4
C(22)-C(23)-H(23A)	108.4
C(24)-C(23)-H(23B)	108.4
C(22)-C(23)-H(23B)	108.4
H(23A)-C(23)-H(23B)	107.5
C(21)-C(24)-C(23)	114.99(8)
C(21)-C(24)-H(24A)	108.5
C(23)-C(24)-H(24A)	108.5

C(21)-C(24)-H(24B)	108.5
C(23)-C(24)-H(24B)	108.5
H(24A)-C(24)-H(24B)	107.5
C(17)-B(1)-C(21)	104.89(8)
C(17)-B(1)-C(4)	117.37(8)
C(21)-B(1)-C(4)	114.44(8)
C(17)-B(1)-N(1)	118.85(8)
C(21)-B(1)-N(1)	105.40(7)
C(4)-B(1)-N(1)	95.63(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C24H42BN. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	14(1)	12(1)	13(1)	-1(1)	1(1)	1(1)
C(1)	20(1)	15(1)	20(1)	-2(1)	6(1)	3(1)
C(2)	14(1)	13(1)	12(1)	0(1)	-2(1)	0(1)
C(3)	16(1)	15(1)	13(1)	1(1)	3(1)	1(1)
C(4)	16(1)	11(1)	12(1)	-1(1)	2(1)	1(1)
C(5)	13(1)	14(1)	19(1)	4(1)	1(1)	0(1)
C(6)	20(1)	23(1)	21(1)	8(1)	4(1)	3(1)
C(7)	21(1)	28(1)	34(1)	19(1)	5(1)	4(1)

C(8)	18(1)	28(1)	58(1)	26(1)	4(1)	0(1)
C(9)	21(1)	16(1)	55(1)	10(1)	-6(1)	-4(1)
C(10)	20(1)	15(1)	31(1)	4(1)	-5(1)	-2(1)
C(11)	15(1)	14(1)	14(1)	2(1)	2(1)	2(1)
C(12)	15(1)	17(1)	14(1)	0(1)	1(1)	2(1)
C(13)	20(1)	21(1)	14(1)	0(1)	-1(1)	0(1)
C(14)	16(1)	22(1)	21(1)	3(1)	-2(1)	0(1)
C(15)	17(1)	23(1)	25(1)	2(1)	-1(1)	5(1)
C(16)	17(1)	21(1)	20(1)	-1(1)	3(1)	5(1)
C(17)	16(1)	15(1)	11(1)	0(1)	1(1)	-2(1)
C(18)	21(1)	16(1)	17(1)	4(1)	2(1)	-1(1)
C(19)	25(1)	14(1)	21(1)	-1(1)	2(1)	-3(1)
C(20)	23(1)	17(1)	16(1)	-4(1)	1(1)	-2(1)
C(21)	18(1)	16(1)	11(1)	0(1)	2(1)	-1(1)
C(22)	18(1)	21(1)	14(1)	-1(1)	4(1)	-2(1)
C(23)	16(1)	24(1)	18(1)	1(1)	3(1)	-1(1)
C(24)	16(1)	22(1)	15(1)	2(1)	-1(1)	-1(1)
B(1)	15(1)	11(1)	12(1)	0(1)	1(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for C24H42BN.

	x	y	z	U(eq)
H(1A)	5152	7830	3911	27
H(1B)	5026	6717	4361	27
H(1C)	4439	6804	3818	27
H(3A)	6965	5449	3247	17
H(3B)	6245	4840	2859	17
H(4)	6376	3118	3463	16
H(5)	5533	8242	3206	19
H(6A)	6571	7134	2503	25
H(6B)	5654	7170	2360	25
H(7A)	6215	9027	1937	33
H(7B)	5670	9583	2360	33
H(8A)	6833	10799	2482	42
H(8B)	7314	9412	2556	42
H(9A)	6333	10461	3299	38
H(9B)	7249	10339	3413	38
H(10A)	6627	8557	3854	27
H(10B)	7176	7952	3442	27
H(11)	6840	3346	4390	17
H(12A)	7074	6196	4233	19
H(12B)	6441	5574	4576	19
H(13A)	7538	6276	5163	22
H(13B)	7416	4666	5216	22
H(14A)	8724	5092	5152	24
H(14B)	8509	5924	4601	24
H(15A)	8293	3049	4730	26
H(15B)	8898	3728	4379	26
H(16A)	7785	2934	3816	23
H(16B)	7907	4534	3742	23
H(17)	5550	3900	4628	17
H(18A)	5859	1839	4237	21

H(18B)	5163	1560	4581	21
H(19A)	5052	434	3705	24
H(19B)	4304	1254	3826	24
H(20A)	4429	1841	2962	22
H(20B)	5343	1950	3077	22
H(21)	4911	4141	2936	18
H(22A)	4225	3314	4711	21
H(22B)	4348	4859	4543	21
H(23A)	3576	2770	3906	23
H(23B)	3283	4283	3995	23
H(24A)	3608	3765	3088	22
H(24B)	3943	5162	3346	22

Table 6. Torsion angles [°] for C24H42BN.

C(1)-N(1)-C(2)-C(3)	172.08(8)
B(1)-N(1)-C(2)-C(3)	-9.74(10)
C(1)-N(1)-C(2)-C(5)	-8.54(14)
B(1)-N(1)-C(2)-C(5)	169.64(8)
N(1)-C(2)-C(3)-C(4)	-15.66(10)
C(5)-C(2)-C(3)-C(4)	164.92(8)
C(2)-C(3)-C(4)-C(11)	-91.76(9)
C(2)-C(3)-C(4)-B(1)	33.04(9)
N(1)-C(2)-C(5)-C(10)	100.75(11)
C(3)-C(2)-C(5)-C(10)	-79.92(11)
N(1)-C(2)-C(5)-C(6)	-136.85(10)
C(3)-C(2)-C(5)-C(6)	42.48(11)
C(2)-C(5)-C(6)-C(7)	177.81(8)
C(10)-C(5)-C(6)-C(7)	-58.79(11)
C(5)-C(6)-C(7)-C(8)	58.54(12)
C(6)-C(7)-C(8)-C(9)	-55.81(13)
C(7)-C(8)-C(9)-C(10)	54.02(13)
C(8)-C(9)-C(10)-C(5)	-54.47(13)
C(2)-C(5)-C(10)-C(9)	179.14(9)
C(6)-C(5)-C(10)-C(9)	56.43(12)
C(3)-C(4)-C(11)-C(12)	60.10(10)
B(1)-C(4)-C(11)-C(12)	-56.18(11)
C(3)-C(4)-C(11)-C(16)	-65.66(10)
B(1)-C(4)-C(11)-C(16)	178.06(8)
C(16)-C(11)-C(12)-C(13)	-55.74(10)
C(4)-C(11)-C(12)-C(13)	176.33(8)
C(11)-C(12)-C(13)-C(14)	58.13(11)
C(12)-C(13)-C(14)-C(15)	-56.44(11)
C(13)-C(14)-C(15)-C(16)	54.71(11)
C(14)-C(15)-C(16)-C(11)	-54.67(12)
C(12)-C(11)-C(16)-C(15)	54.06(11)
C(4)-C(11)-C(16)-C(15)	-177.12(8)
C(22)-C(17)-C(18)-C(19)	65.62(11)
B(1)-C(17)-C(18)-C(19)	-58.65(11)

C(17)-C(18)-C(19)-C(20)	44.62(12)
C(18)-C(19)-C(20)-C(21)	-40.46(13)
C(19)-C(20)-C(21)-C(24)	-72.25(11)
C(19)-C(20)-C(21)-B(1)	52.03(11)
C(18)-C(17)-C(22)-C(23)	-72.35(11)
B(1)-C(17)-C(22)-C(23)	46.99(12)
C(17)-C(22)-C(23)-C(24)	-37.55(13)
C(20)-C(21)-C(24)-C(23)	68.17(11)
B(1)-C(21)-C(24)-C(23)	-54.56(11)
C(22)-C(23)-C(24)-C(21)	41.70(12)
C(22)-C(17)-B(1)-C(21)	-55.49(10)
C(18)-C(17)-B(1)-C(21)	67.03(9)
C(22)-C(17)-B(1)-C(4)	176.21(8)
C(18)-C(17)-B(1)-C(4)	-61.27(10)
C(22)-C(17)-B(1)-N(1)	61.91(11)
C(18)-C(17)-B(1)-N(1)	-175.57(8)
C(24)-C(21)-B(1)-C(17)	59.02(10)
C(20)-C(21)-B(1)-C(17)	-65.25(9)
C(24)-C(21)-B(1)-C(4)	-170.93(8)
C(20)-C(21)-B(1)-C(4)	64.80(10)
C(24)-C(21)-B(1)-N(1)	-67.22(9)
C(20)-C(21)-B(1)-N(1)	168.51(7)
C(3)-C(4)-B(1)-C(17)	-161.46(8)
C(11)-C(4)-B(1)-C(17)	-39.11(11)
C(3)-C(4)-B(1)-C(21)	74.95(9)
C(11)-C(4)-B(1)-C(21)	-162.69(8)
C(3)-C(4)-B(1)-N(1)	-34.80(8)
C(11)-C(4)-B(1)-N(1)	87.55(8)
C(2)-N(1)-B(1)-C(17)	154.28(8)
C(1)-N(1)-B(1)-C(17)	-27.63(13)
C(2)-N(1)-B(1)-C(21)	-88.59(9)
C(1)-N(1)-B(1)-C(21)	89.50(10)
C(2)-N(1)-B(1)-C(4)	28.70(9)
C(1)-N(1)-B(1)-C(4)	-153.21(8)

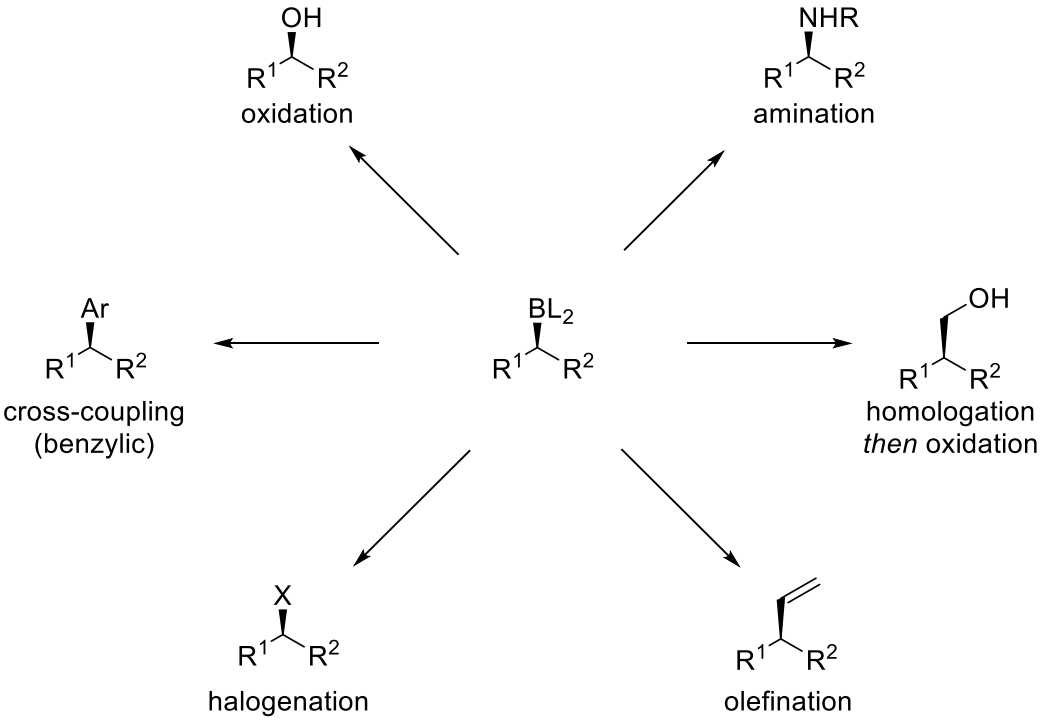
Symmetry transformations used to generate equivalent atoms:

3. Alkyl Group Migration in Ni-Catalyzed Conjunctive Coupling Reaction with C(sp^3) Electrophiles

3.1 Introduction

Chiral organoboronic esters are a widely used class of chemicals in modern chemistry as they can be transformed into various functional groups in a stereospecific fashion[44] (Scheme 3.1).

Scheme 3.1: Some examples of stereospecific transformations of organoboronates



[44] Sandford, C.; Aggarwal, V. K. *Chem. Comm.* **2017**, *53*, 5481.

Therefore, enantioselective methods to synthesize non-racemic alkyl boronates are highly desirable to many organic chemists.[45] There are many literature precedents for the preparation of secondary boronic esters in catalytic and enantioselective fashion, such as hydroboration of an alkene.

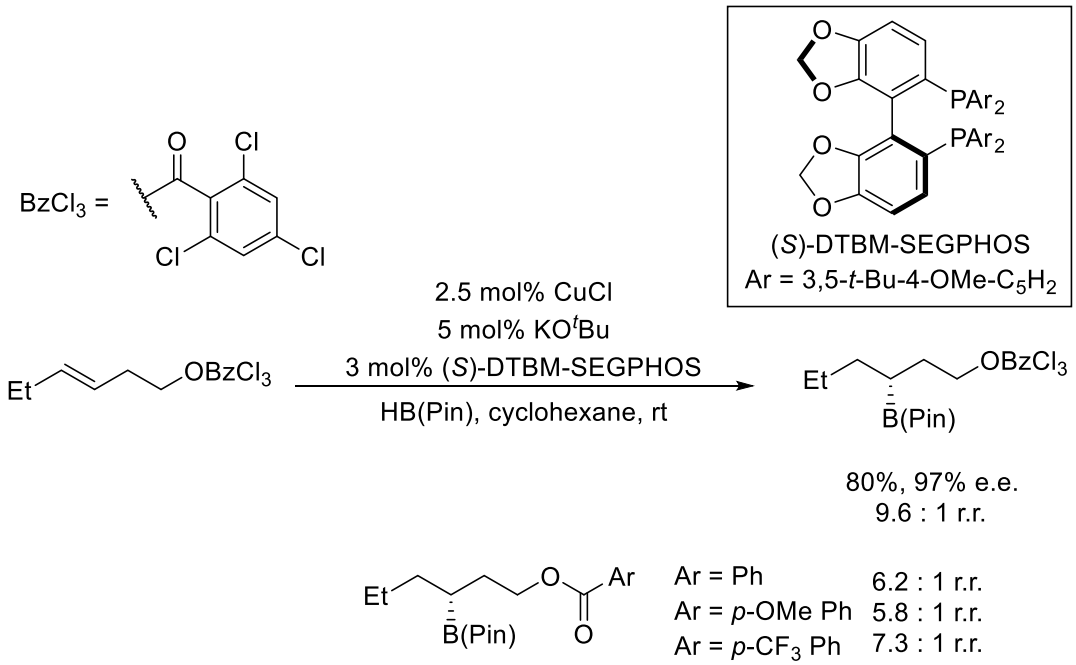
However, there are synthetic challenges. In many enantioselective catalytic methods for the preparation of secondary boronic esters, a directing group or functional group at a specific location of the substrate is required to achieve regioselectivity or enantioselectivity. To our knowledge, there is only one precedent, reported by Fu and coworkers, where there isn't the requirement for specialized substrate.[46]

[45] Collins, B. S. L; Wilson, C. M.; Myers, E. L., Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2017**, *56*, 11700.
[46] Schmidt, J.; Choi, J.; Liu, A. T.; Slusarczyk, M.; Fu, G. C. *Science* **2016**, *354*, 1265.

3.2 Background

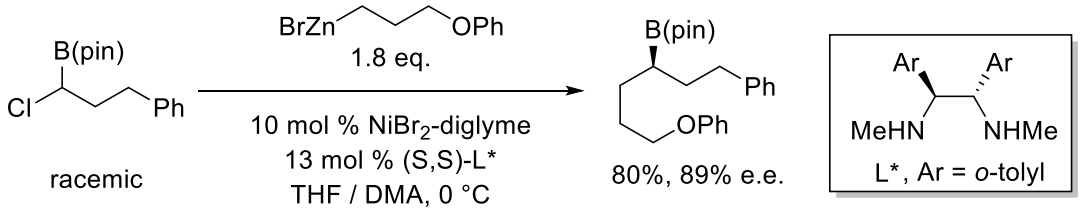
One method to prepare secondary enantioenriched boronic esters by regio- and enantioselective copper catalyzed hydroboration was reported by the Hartwig group.[47] This reaction can yield enantioenriched secondary boronic ester in 80% yield, 97% e.e. and 9.6 : 1 r.r. However, according to authors, changing the electronic nature of the benzoyl group would affect the regioselectivity of the hydroboration. For instance, with *p*-OMe benzoyl group, regioselectivity of the reaction is diminished to 5.8 : 1 r.r. This observation hints that the regioselectivity depends on the electronic bias of the parent alkene and is therefore substrate dependent.

Scheme 3.2: Regio- and enantioselective Cu-catalyzed hydroboration of alkenes



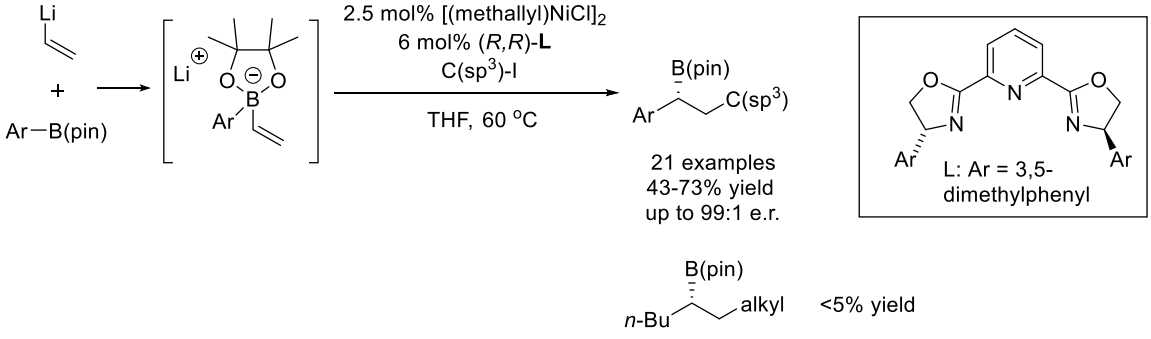
[47] Xi, Y.; Hartwig, J. F. *J. Am. Chem. Soc.* **2016**, *138*, 6703.

Scheme 3.3: Enantioconvergent Ni-catalyzed Negishi coupling reaction



In a separate study, Fu and coworkers reported a method to produce enantioenriched secondary boronic esters.45[45] In a stereoconvergent manner, enantioenriched secondary organoboronic esters were synthesized from racemic α-halo boronates as the starting material. The α-chloroboronate can be prepared as a racemic mixture from a primary alkylboronate by Matteson homologation reaction.[48] It is notable that this approach is modular and is not limited to a specialized set of substrates.

Scheme 3.4: Ni-catalyzed enantioselective conjunctive coupling reaction with C(sp^3) electrophiles



After the initial report of conjunctive coupling reaction in 2016 with palladium catalyst,[49] the Morken group also reported the conjunctive coupling reaction with C(sp^3)

[48] Matteson, D. S.; Majumdar, D. *J. Am. Chem. Soc.* **1980**, *102*, 7588
[49] Zhang, L.; Lovinger, G. J.; Edelstein, E. K.; Szymaniak, A. A.; Chierchia, M. P.; Morken, J. P. *Science* **2016**, *351*, 70.

electrophiles[50] (Scheme 3.4). In the presence of a nickel catalyst, a boron ate complex derived from arylB(pin) and vinyllithium can undergo a 1,2-metallate rearrangement across the olefin in an *anti*-fashion and cross-couple to a C(sp^3) electrophile to generate enantioenriched secondary boronic esters as products. A limitation to this process is that using alkyl migrating groups with C(sp^3) electrophiles were low yielding. We sought to address this challenge as it can be used to prepare secondary boronic esters with various chain lengths in an enantioselective and regioselective fashion.

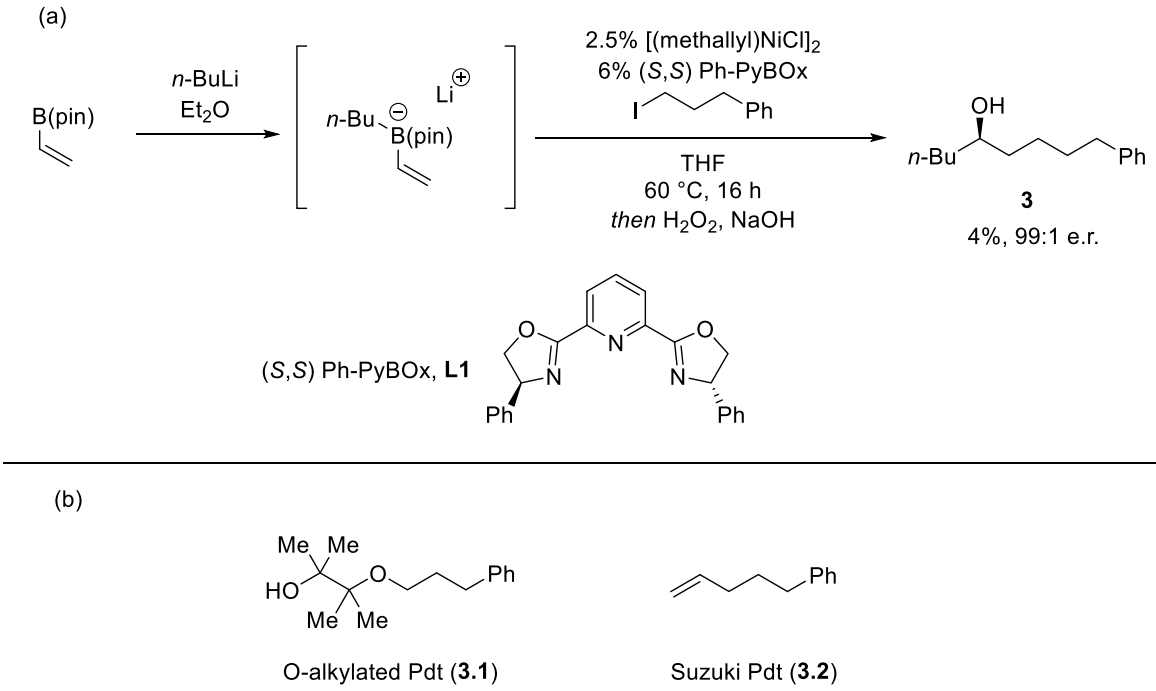
3.3 Development of C(sp^3)-C(sp^3) Conjunctive Coupling Reaction[51]

3.3.1 Initial Experiments and Optimization

Our initial investigation started with the use of the boron ate complex derived from vinylB(pin) and *n*-butyllithium, and used iodopropylbenzene as the electrophile. The nickel/pybox catalyst complex reported in the previous report from our group[4950] (Scheme 3.5, (a)) was also employed. While this reaction was very poor yielding (4% yield), enantioselectivity was good at 99:1 e.r. Investigation of the byproducts revealed that O-alkylated product such as **3.1**[52] was one of the byproduct as well as presence of Suzuki product such as **3.2** (Scheme 3.5, (b)).

[50] Lovinger, G. J; Morken, J. P. *J. Am. Chem. Soc.* **2017**, *139*, 17293.
[51] Koo, S. M.; Vendola, A. J.; Momm, S. N.; Morken, J. P. *Org. Lett.* **2020**, *22*, 666.
[52] Proposed to form from (i) the nucloephilic S_N2 reaction between the pinacolato boron ate complex and alkyliodide electrophile, or (ii) nucleophilic displacement of nickel-electrophile adduct by pinacolato boron ate complex, followed by reductive elimination.

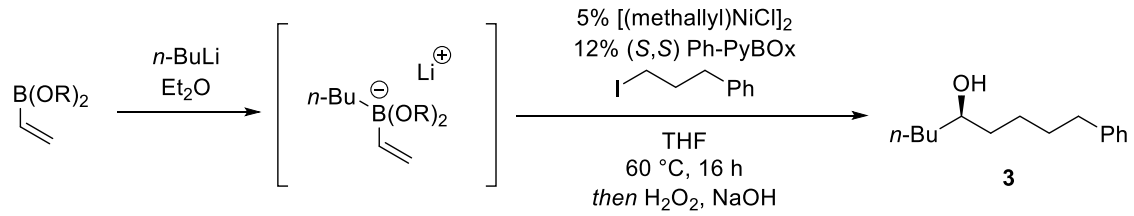
Scheme 3.5: (a) Results of initial investigation. (b) Undesired side products

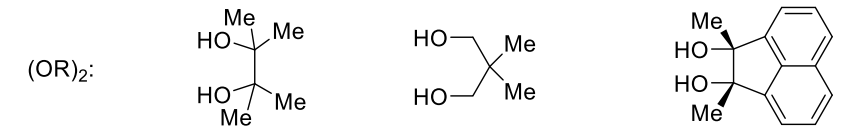


After the preliminary analysis, it was hypothesized that the steric environment as well as the nucleophilicity of the boron ate complex may be crucial for the reaction efficiency, we sought to change the nature of the boron ligands. Therefore, pinacol, neopentylglycol, and mac[53] (methylated acenaphoquinone) diol were investigated (Scheme 3.6). The yield of the product was increased significantly to 41%, with the mac ligand on boron. The improvement may be because the mac ligand is less nucleophilic on the oxygen, and the mac ligand can provide enough steric environments to reduce the amount of transmetallation between the boron ate complex and the nickel catalyst, leading to Suzuki byproducts.

[53] Myhill, J. A.; Wilhelmsen, C. A.; Zhang, L.; Morken, J. P. *J. Am. Chem. Soc.* **2018**, *140*, 15181.

Scheme 3.6: Investigation of the ligand on boron

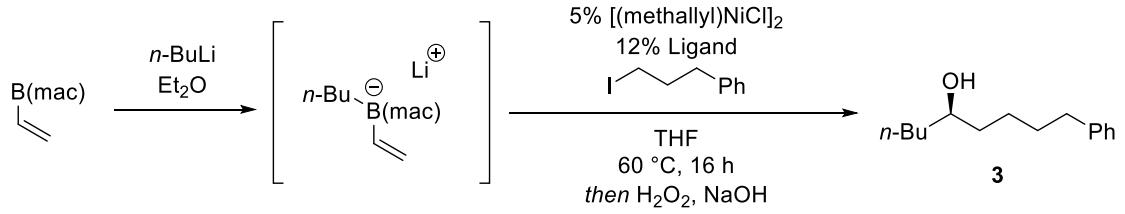




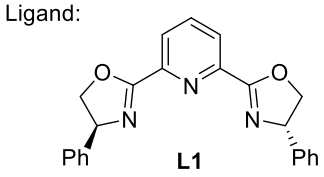
Yield (**3**):	4%, 99:1 e.r.	6%, e.r. n/d	41%, 99:1 e.r.

Next, the ligand for the catalyst was examined. In comparison to Ph-PyBOx **L1**, other PyBOx ligands that were tested (methyl **L2**, isopropyl **L3**, indenyl **L4**, naphthyl **L5**, and *o*-chlorophenyl **L6**) showed substantially lower yields ranging between 3-24% (Scheme 3.7). Therefore, Ph-PyBOx was chosen as the ligand for nickel catalyst for further optimization studies.

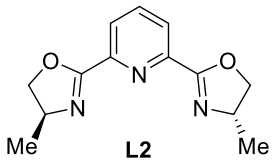
Scheme 3.7: Investigation of the ligand for nickel catalyst



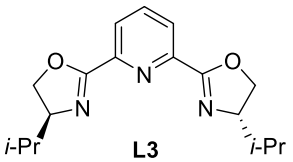
Ligand:



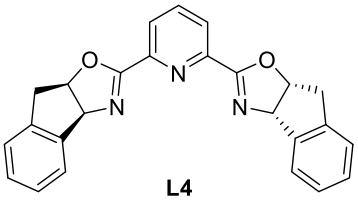
L1
41%



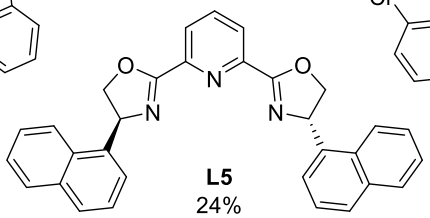
L2
3%



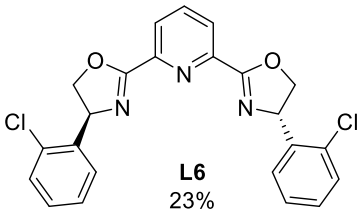
L3
5%



L4
4%

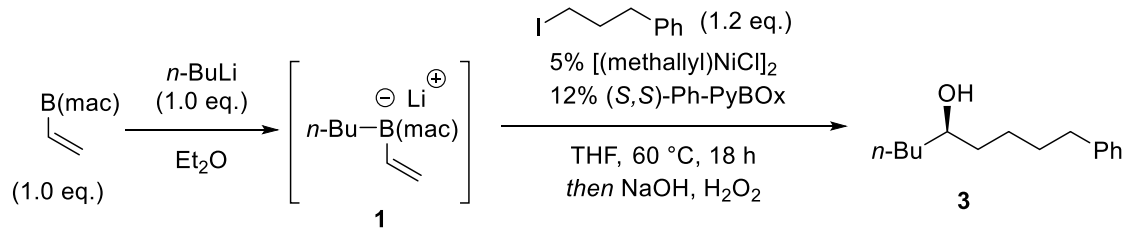


L5
24%



L6
23%

Table 3.1: Additional optimization of the reaction conditions



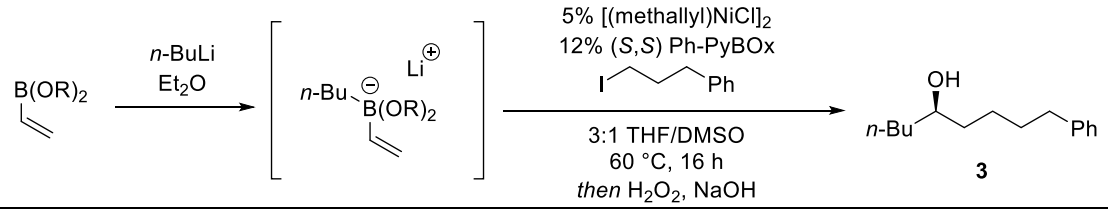
Entry	Modifications from Above	Yield	e.r.
1	none	41%	99:1
2	$Ni(COD)_2$ as [Ni]	16%	n/d
3	$NiBr_2$glyme as [Ni]	11%	n/d
4	$Ni(acac)_2$ as [Ni]	4%	n/d
5	2:1 THF/DMA as solvent	trace	n/a
6	2:1 THF/Tol as solvent	22%	n/d
7	2:1 THF/Et_2O as solvent	13%	n/d
8	2:1 THF/2-Me THF as solvent	16%	n/d
9	2:1 THF/Tetrahydropyran as solvent	9%	n/d
10	5:1 THF/DMSO as solvent	48%	93:7
11	3:1 THF/DMSO as solvent	53%	99:1
12	1.1 (equiv.) vinyl-B(mac), and 3:1 THF/DMSO as solvent	65%	98:2

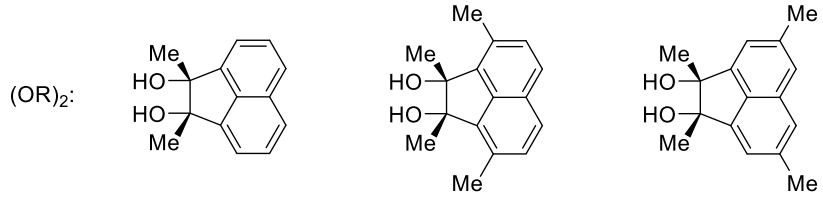
Nickel pre-catalysts such as $Ni(COD)_2$, $NiBr_2$-glyme, and $Ni(acac)_2$ were surveyed but were lower yielding compared to the reaction with methallyl nickel chloride dimer (Table 3.1, **entry 1-4**). A variety of solvent mixtures were tested (Table 3.1, **entry 5-11**), but only THF/DMSO mixture was able to improve the yield. The effects of DMSO are proposed as the following. i) DMSO may be able to sequester lithium cation and increase the nucleophilicity of the boron ate complex,[54] or ii) DMSO may coordinate to

[54] a) For effects of lithium cation sequestering by crown ether, see: Feeney, K.; Berionni, G.; Mayr, H.; Aggarwal, V. K. *Org. Lett.* **2015**, *17*, 2614. b) For an example of lithium-DMSO interaction, see: Eldik, R. V.; *et. al. ChemPhysChem* **2007**, *8*, 1315.

nickel and change the electronic nature of the catalyst.[55] Lastly, by changing the ratio for the boron ate complex, where an excess boronic ester is introduced, the reaction yield was improved (Table 3.1, **entry 12**). The reason for the increased yield is proposed that any excess organolithium added during the boron ate formation is detrimental to the reaction efficiency, and by introducing additional boronic ester, that situation can be avoided.

Scheme 3.8: Effects of mac ligand modifications





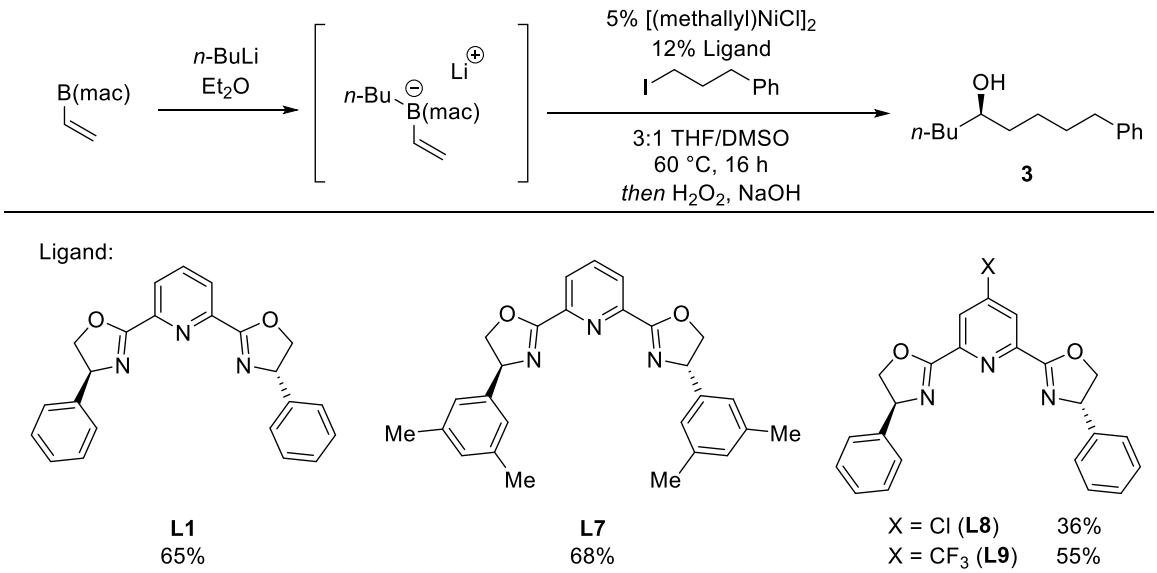
Yield (**3**): 65%, 99:1 e.r. 66%, 93:7 e.r. 65%, 98.5:1.5 e.r.

After obtaining workable reaction conditions, an additional set of experiments were done to see if the mac ligand can be tuned further to increase the yield (Scheme 3.8). Methyl substitution on the naphthyl ring were considered and *o*-dimethyl and *m*-dimethyl mac were prepared. For both *o*- and *m*-dimethyl mac ligands, yields were similar. However, the drop in enantioselectivity for *o*-dimethyl mac indicates that the

[55] Calculated value for the coordinating ability to transition metals of DMSO (0.3) is higher than that of THF (-0.3). Diaz-Torres, R.; Alvarez, S. *Dalton Trans.* **2011**, *40*, 10742.

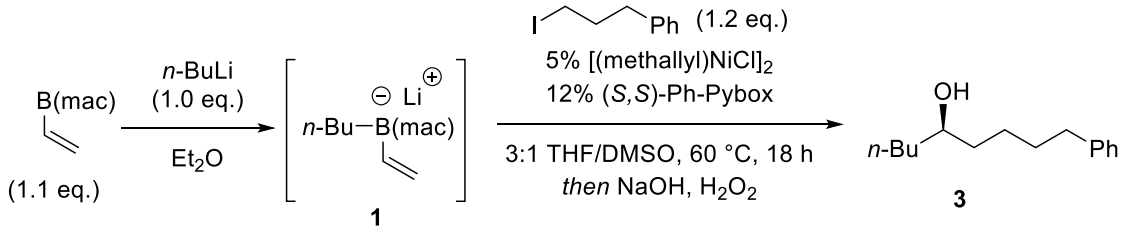
steric conjestion presents challenge. With *m*-dimethyl mac, yield is less affected, but a slight loss of enantioselectivity at 98.5:1.5 e.r. was observed.

Scheme 3.9: Survey of additional ligands similar to Ph-PyBOx as the ligand for nickel catalyst



A further study of PyBOx ligands revealed that Ph-PyBOx **L1** and 3,5-dimethylphenyl-PyBOx **L7** are the most competent amongst the ligands tested so far (Scheme 3.9). PyBOx ligands with substitution on 4-position of the pyridine ring with Cl **L8**, or CF_3 group **L9** diminished the yields. 3,5-dimethylphenyl-PyBOx **L7** is able to yield 3-5% more product than with Ph-PyBOx **L1**. Although improvement in yield was observed, due to the fact that synthesis of 3,5-dimethylphenyl-PyBOx **L7**[50] requires a lengthy sequence, we settled on using commercially available Ph-PyBOx **L1** as it is more practical.

Table 3.2: Optimization for a more reproducible conjunctive coupling reaction



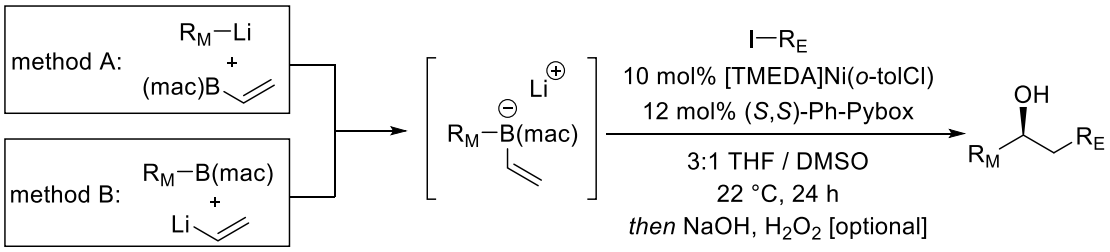
Entry	Modifications from Above	Yield	e.r.
1	none	64%	98:2
2	[(TMEDA)Ni(*o*-Tol)Cl] as [Ni]	55%	99:1
3	Same as **Entry 2**, but reaction run at room. temp.	65%	>99:1

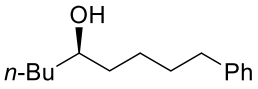
During the optimization efforts, it was discovered that the reaction was not reproducible. We hypothesized that the issue originated from poor solubility of nickel pre-catalyst in THF, as well as the temperature dependent stability of methallyl nickel chloride dimer as the nickel pre-catalyst. In order to see if the issue can be circumvented, we investigated whether a more stable nickel pre-catalyst such as [(TMEDA)Ni(*o*-Tol)Cl][56] could render the reaction to be more reliable. [(TMEDA)Ni(*o*-Tol)Cl] is bench stable and can be kept at room temperature, while methallyl nickel chloride dimer is moisture, and air sensitive, and requires refrigeration for storage. Compared to methallyl nickel chloride dimer, reaction with [(TMEDA)Ni(*o*-Tol)Cl] was more reproducible at 55% yield, with 99:1 e.r. (Table 3.2, **entry 2**). Upon lowering the reaction temperature to room temperature from 60 °C, we were pleased to find the reactivity improved and oxidized product **3** was obtained in 65% yield, with >99:1 e.r. This was the reaction condition used for the substrate scope investigation (Table 3.2, **entry 3**).

[56] Shields, J. D.; Gray, E. E.; Doyle, A. G. *Org. Lett.* **2015**, *17*, 2166.

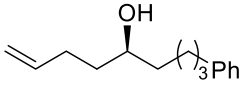
3.3.2 Substrate scope

Scheme 3.10: Substrate scope of the nickel-catalyzed conjunctive coupling reaction of alkyl migrating group and C(sp^3) electrophiles

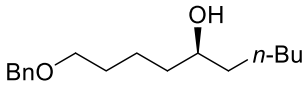




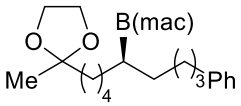
3, 65%, >99:1 e.r.



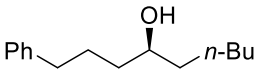
4, 55%, >99:1 e.r



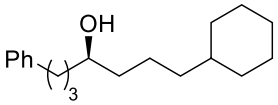
5, 60%, 99:1 e.r.



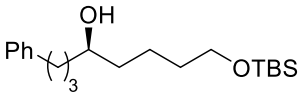
6, 52%, >99:1 e.r.



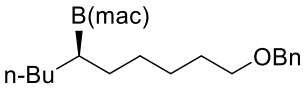
7, 62%, >99:1 e.r



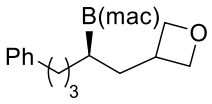
8, 62%, >99:1 e.r.



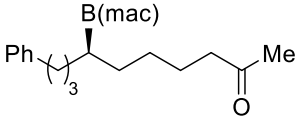
9, 59%, >99:1 e.r.



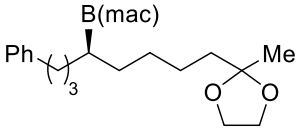
10, 55%, >99:1 e.r.



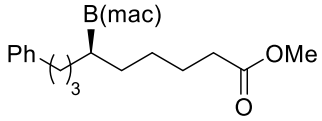
11, 44%, 99:1 e.r.[a)]



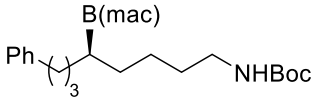
12, 22%, >99:1 e.r.



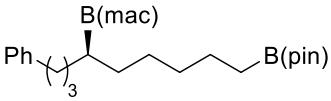
13, 56%, >99:1 e.r.



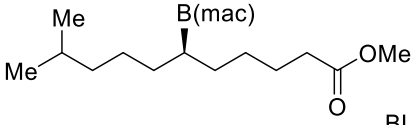
14, 60%, 99:1 e.r.



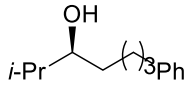
15, 60%, 99:1 e.r.



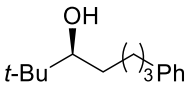
16, 55%, 99:1 e.r.



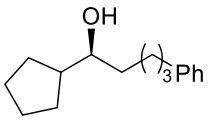
17, 54%, >99:1 e.r.



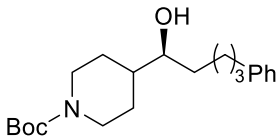
18,
BL_2 = B(mac): 32%, >99:1 e.r.
B(pin): 51%, 98:2 e.r.



19,
BL_2 = B(mac): 10%, 97:3 e.r.
B(pin): 25%, 98:2 e.r. [b)]



20, 47%, 99:1 e.r.



21, 53%, 99:1 e.r.

a) Reaction conducted at 60 °C
b) Reaction conducted at 45 °C

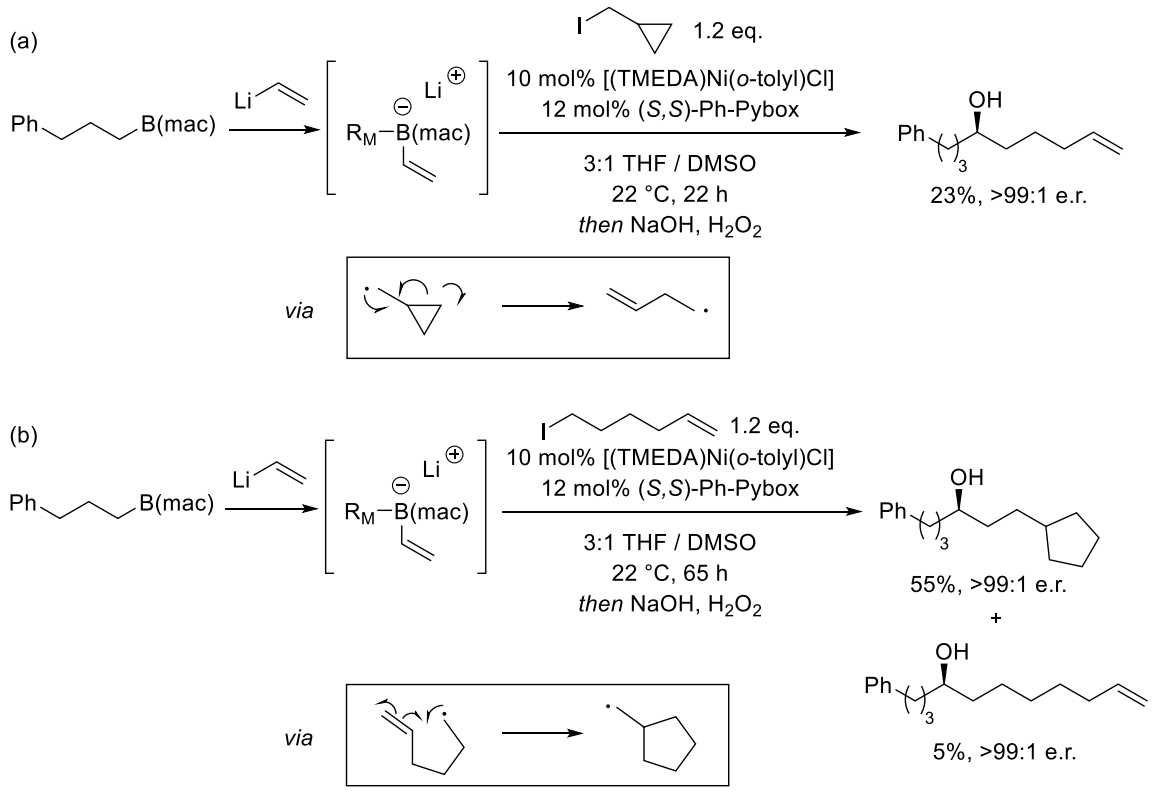
With optimized condition in hand, the scope of the reaction was investigated (Scheme 3.10). The boron ate complex, can be prepared either from organolithium and vinylB(mac) (method A), or from alkylB(mac) and vinyllithium (method B). Results show that a variety of functional groups were compatible. Except for a few substrates, the products obtained demonstrated very high levels of enantioselectivity of 99:1 e.r. or higher. Substrate investigation revealed alkene, ether, ketal, and carbamate containing-migrating groups can be accommodated (**4**-**6**, **21**). Sterically bulkier migrating groups such as secondary and tertiary alkyl migrating groups showed lower yields, indicating that the reaction is sensitive to steric effects (**18**-**20**). It is notable that for these hindered substrates, using the boron ate complex derived from pinacolatoboronate for (**18**) and (**19**) resulted in slight boost in yield.

For the electrophile, functional groups that are competent in the conjunctive coupling reaction are ethers (**10**-**11**), ketals (**13**), esters (**14**), Boc-protected amines (**15**), and boronic ester (**16**). Although it is lower yielding compared to that of primary alkyl iodides, secondary alkyl iodide electrophiles (**11**) can be engaged.

3.3.3 Mechanistic Studies

After the substrate scope was investigated, in order to gain some insight, experiments that probe the mechanism of the reaction were done. The reaction system behaved similarly with the previous report utilizing C(sp3)-I electrophiles from the Morken group, and similar results were obtained for the study with radical clock substrates. Radical clock substrates can be used to determine if the reaction involves radical behavior. As shown in (Scheme 3.11, (a)), when cyclopropylmethyliodide is used as the electrophile, a ring-opened butene fragment is incorporated into the product. Similarly, when 1-iodohexene is used as the electrophile, the presence of the ring-closed cyclopentylmethyl group is indicative of radical behavior (Scheme 3.11, (b)). Notably, it was possible to observe uncyclized substrate in the case of 1-iodohexene as the electrophile, which indicates that the rate of radical ring closure is within an order of magnitude to the rate of the chemoselectivity-determining step.

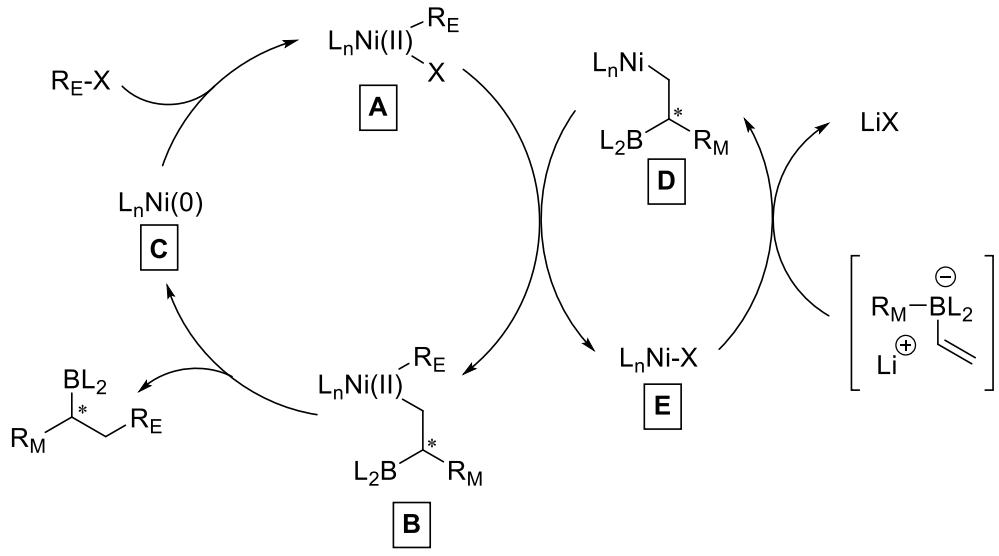
Scheme 3.11: Radical clock substrates for a) ring opening and b) cyclization



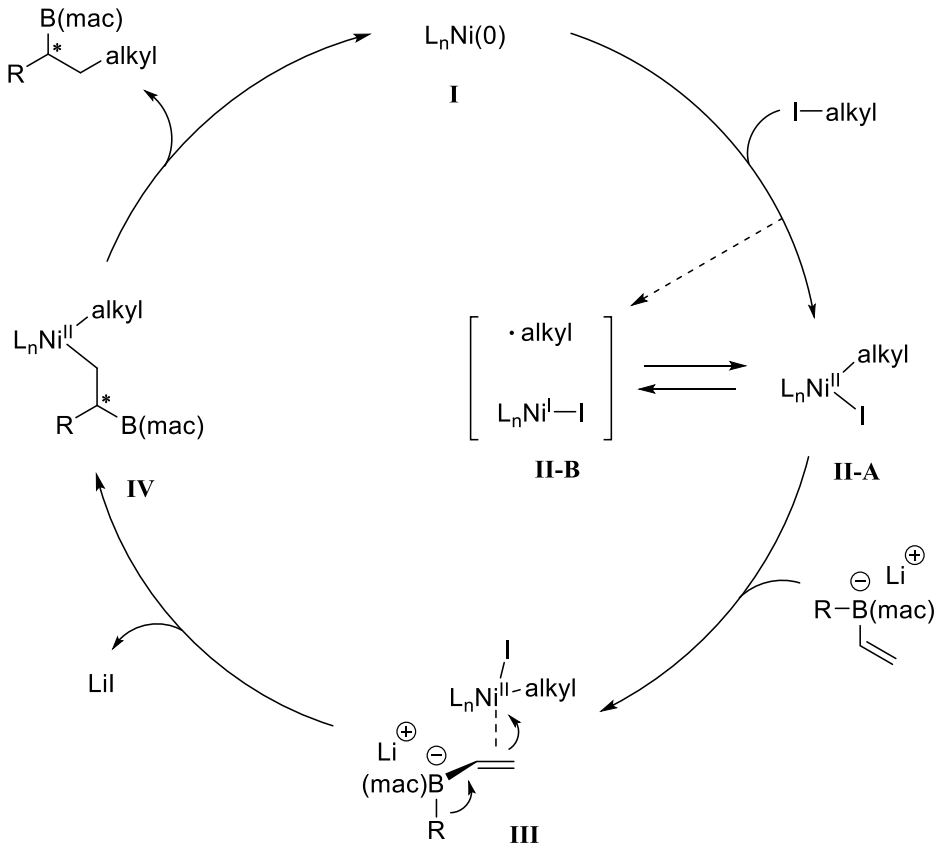
Unlike previous enantioselective conjunctive coupling reactions, steric effects of the electrophile did not have observable impact on the enantioselectivity. As demonstrated in the substrate survey, in almost all cases, the enantioselectivity remained very high. In order to investigate this trend, secondary alkyl iodide electrophiles were used for the conjunctive coupling reaction. In these cases, no decrease in enantioselectivity was observed despite the lower yield. For example, with cyclohexyl iodide as the electrophile, product is obtained in 17% yield, with 99:1 e.r. However, for isopropyl and *tert*-butyl migrating groups, the enantioselectivity was lower than 99:1. Thus, it was proposed that the 1,2-metalate shift onto metal could be occurring first, then followed by the oxidative addition of electrophile (Case 1). In this case, the e.r. could be independent of electrophile, but dependent on migrating group. Or, there may be two active nickel species in operation,

where nickel-electrophile complex (**A**) and nickel-nucleophile complex (**D**) may exchange ligands (or transmetallate), and lead to product formation by reductive elimination (Case 2, Scheme 3.12). Additional experiments were conducted such as increasing the amount of boron ate complex added to hexenyl iodide substrate, in order to monitor if the ratio of cyclized to uncyclized product changes. However, the results were inconclusive as the change in ratio was not significant. Therefore, we concluded that the absence of enantioselectivity variation based on the steric effects of the electrophile may be because the reduction in enantioselectivity caused by the electrophiles may be too small to be observable, and sterically demanding electrophiles simply lead to more unproductive consumption of the starting materials.

Scheme 3.12: A possible catalytic cycle involving two active nickel catalytic species



Scheme 3.13: Proposed catalytic cycle

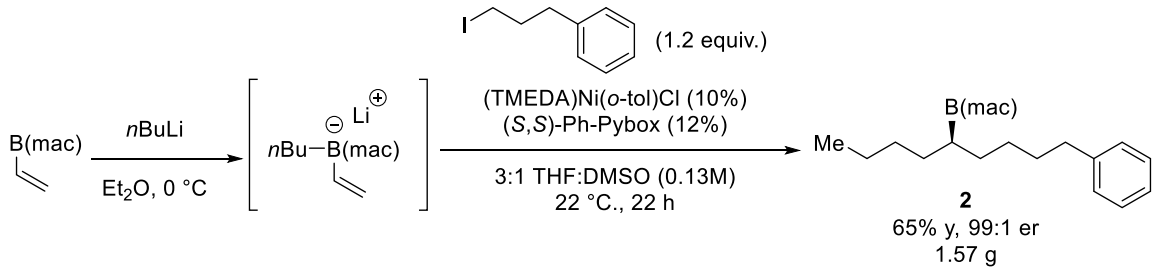


In summary, the proposed mechanism (Scheme 3.13) remains similar as the previous work[50], where the electrophile is oxidatively added to the nickel catalyst first (**II-A**), which is under equilibrium with the alkyl radical species (**II-B**). An alternative pathway is where alkyl radical is initially generated by halide abstraction (**II-B**), followed by the radical recombination with the metal catalyst to generate (**II-A**).[50] The 1,2-metallate rearrangement is proposed to be the next step (**III**). Upon reductive elimination of (**IV**), the secondary boronic ester is generated as the product and the catalyst (**I**) is regenerated.

3.3.4 Gram Scale Synthesis

The typical reaction was run in a small scale for the reaction development, In order to demonstrate the applicability of this method in a larger scale setting, a gram scale reaction was conducted (Scheme 3.14). VinylB(mac) was first placed in an oven dried 100 mL round bottom flask, then *n*-BuLi was added over about 5 min. Subsequently, solvents were removed under reduced pressure. While the boron ate complex was being prepared in a 100 mL RBF, a catalyst complex solution was prepared in a 20 mL scintillation vial and allowed to stir for about 30 minutes. After the electrophile was added to the flask containing boron ate complex, the catalyst complex solution was added. After letting the reaction mixture stir for 22 hours at the room temperature, the scaled up reaction resulted in similar yields and enantioselectivity as the smaller counterpart, yielding 1.57 g of enantioenriched product **2**, which demonstrates that reaction behavior is similar in larger scale.

Scheme 3.14: Gram-scale conjunctive coupling reaction



3.3.5 Application of the Method for Syntheses of Alkaloid Targets

In order to demonstrate the utility of this Ni-catalyzed coupling method, we investigated whether it can be used for the synthesis of alkaloids. Two targets (Scheme 3.15), (*R*)-N-Boc-Coniine, **24**, and (-)-Indolizidine 209D, **28**, were selected for study.[57,58]

Scheme 3.15: Alkaloid targets of interest

(*R*)-N-Boc-Coniine (**24**) (-)-Indolizidine 209D (**28**)

3.3.5.1 Synthesis of (R)-N-Boc-Coniine

One of the first alkaloids we sought to synthesize was coniine, as it has a relatively simple molecular structure, which contains only one stereocenter. To reach the goal, we considered applying stereospecific amination methods that were reported by the Morken group.[59,60] However, one challenge remained that in both cases, the substituted amine (RNHOMe) was not a substrate that was compatible with the methodology. Although it was unreactive in the intermolecular reaction, we proposed that for an appropriately sized ring, intramolecular amination of a substituted amine may be possible. Thus, it was planned that the secondary boronic ester resulting from the conjunctive coupling reaction would be subjected to intramolecular amination to furnish the product.

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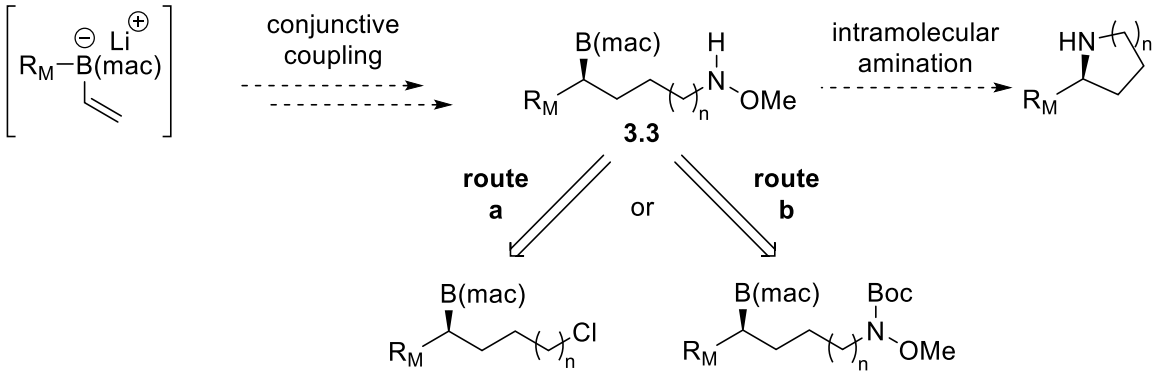
[57] Hotti, H.; Rischer, H. *Molecules* **2017**, *22*, 1962.
[58] Daly, J. W.; Spande, T. F.; Garraffo, H. M. *J. Nat. Prod.* **2005**, *68*, 1556.
[59] Mlynarski, S. N.; Karns, A. S.; Morken, J. P. *J. Am. Chem. Soc*. **2012**, *134*, 16449
[60] Edelstein, E. K.; Grote, A. C.; Palkowitz, M. D.; Morken, J. P. *Synlett* **2018**, *29*, 1749

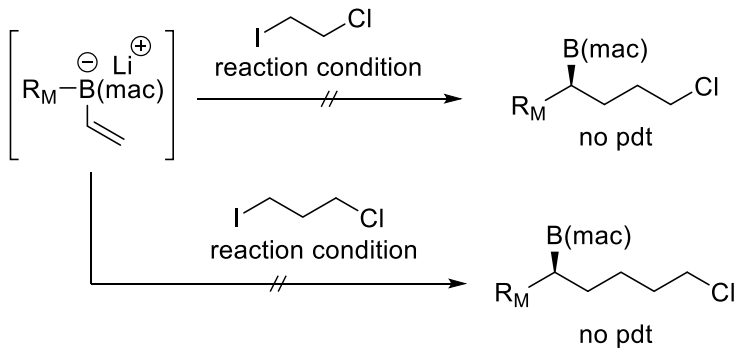
In order to test the hypothesis for intramolecular amination, we had to access the precursor (**3.3**). Two different approaches were proposed (Scheme 3.16), where a methoxyaminoboronate can be prepared from either nucloephilic substitution of a chloride (Scheme 3.16, **route a**), or deprotection of Boc-protected methoxyamine (Scheme 3.16, **route b**). After finding out that the chloride electrophile was unreactive to the reaction conditions during the optimization stage, we sought to investigate the iodo-chloro electrophiles.

Scheme 3.16: Initial proposals for the alkaloid synthesis

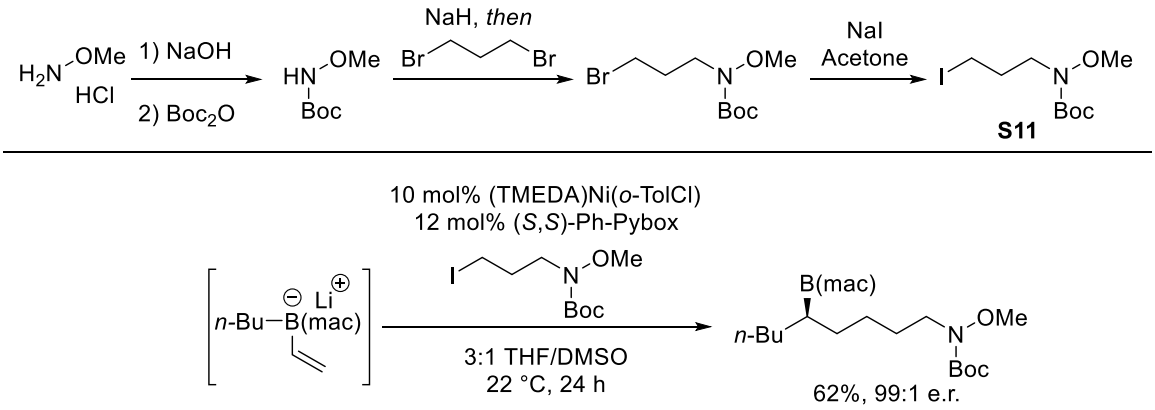


Efforts testing the conjunctive reaction with 1-chloro-2-iodoethane or 1-chloro-3-iodopropane were not successful (Scheme 3.17). Therefore, the alternate route was employed to test the hypothesis. Instead of installing the methoxyamine group after the conjunctive coupling reaction, the electrophile that contains Boc-protected methoxyamine pre-installed was examined.

Scheme 3.17: Unsuccessful conjunctive coupling with iodochloro electrophiles



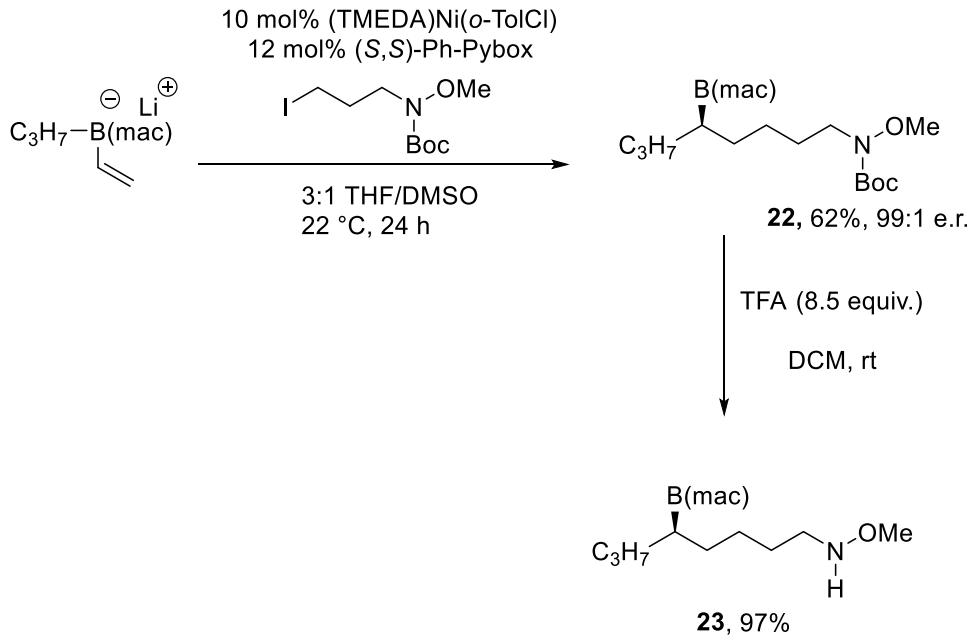
Scheme 3.18: Preparation of the electrophile for the synthesis of coniine and test reaction



First, an electrophile with appropriate carbon linker was synthesized (Scheme 3.18). Starting from methoxyamine hydrochloride, the amine can be Boc protected[61] and then undergo nucleophilic aliphatic substitution, followed by Finkelstein reaction[51] to form the alkyl iodide electrophile (**S11**). Compound **S11** was used in the test reaction with boron ate complex derived from *n*-butylB(mac) and vinyllithium to yield aminoboronate in 62% yield with 99:1 e.r.

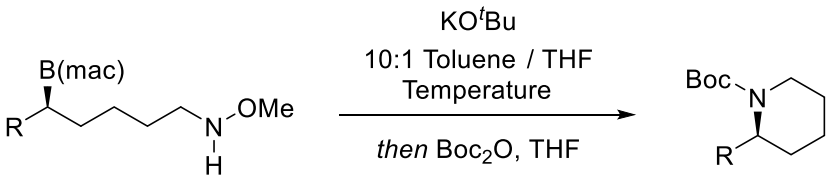
[61] Miyabe, H.; Asada, R.; Takemoto, Y. *Org. Biomol. Chem.* **2012**, *10*, 3519.

Scheme 3.19: Synthesis of aminoboronate (23) by Ni-catalyzed conjunctive coupling reaction for the (*R*)-N-Boc-coniine



The synthetic route for the (*R*)-N-Boc-Coniine is shown (Scheme 3.19). With the knowledge that conjunctive coupling reaction works well with the electrophile (**S11**), the boron ate complex derived from propylB(mac) and vinyllithium and electrophile (**S11**) were subjected to conjunctive coupling reaction. The secondary boronic ester (**22**) is obtained in good yield and excellent enantioselectivity. The boronic ester (**22**) was treated with trifluoroacetic acid to remove Boc group, which we did not observe any protodeboration. With aminoboronate (**23**) in hand, the reaction conditions for intramolecular amination were investigated.

Table 3.3: Optimization table for the intramolecular amination

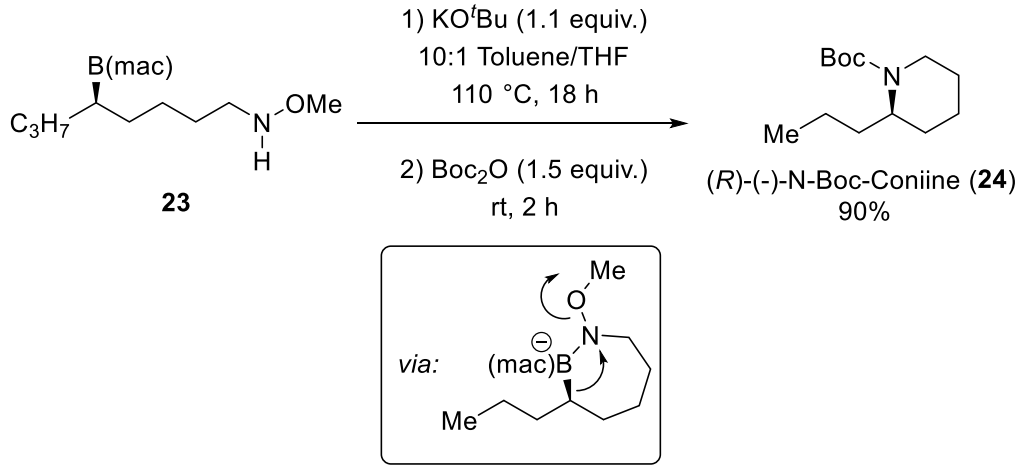


Entry	R	KO^{t}Bu (equiv.)	Temperature (°C)	Isolated Yield (%)
1	*n*-Bu	1.5	110	68
2	*n*-Bu	1.5	100	<5
3	*n*-Bu	1.5	120	50[1)]
4	*n*-Bu	4	110	25
5	*n*-Bu	6	110	<5
6	***n*-Pr**	**1.1**	**110**	**90**
7	*n*-Pr	1.5	110	79
8	*n*-Pr	2.0	110	64

Reactions were conducted in 0.05 mmol scale. [1)] NMR Yield, not Isolated Yield.

Initially, the intramolecular amination was tested on a model substrate with similar reaction condition as the one reported for the Morken group,[60] but with modification of the reaction temperature to 110 °C. Subsequent optimization efforts revealed that 110 °C was optimal reaction temperature (Table 3.3, **entry 1, 2, and 3**). After the optimal reaction temperature was found, the number of equivalents of potassium *tert*-butoxide was investigated. It was found that a higher amount of KOtBu led to diminished yield of amination product (Table 3.3, **entry 4, and 5**). Lastly, further fine tuning of the reaction condition was conducted for coniine, changing the amount of KOtBu was done to demonstrate 1.1 equiv. of KOtBu was optimal (Table 3.3, **entry 6, 7, and 8**) and was used to obtain 90% isolated yield.

Scheme 3.20: Synthesis of (*R*)-N-Boc-coniine by intramolecular amination

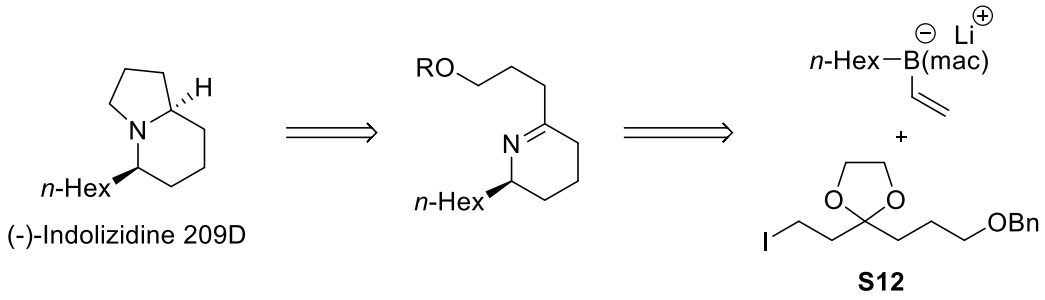


Then, using the optimized condition as described in Table 3.3, intramolecular amination was performed with aminoboronate (**23**). Product (**24**) was successfully obtained after Boc protection for the ease of isolation (Scheme 3.20). Additionally, we were able to compare the specific optical rotation for the product and compare to a known literature value to confirm the absolute stereochemistry.

3.3.5.2 Synthesis of (-)-indolizidine 209D

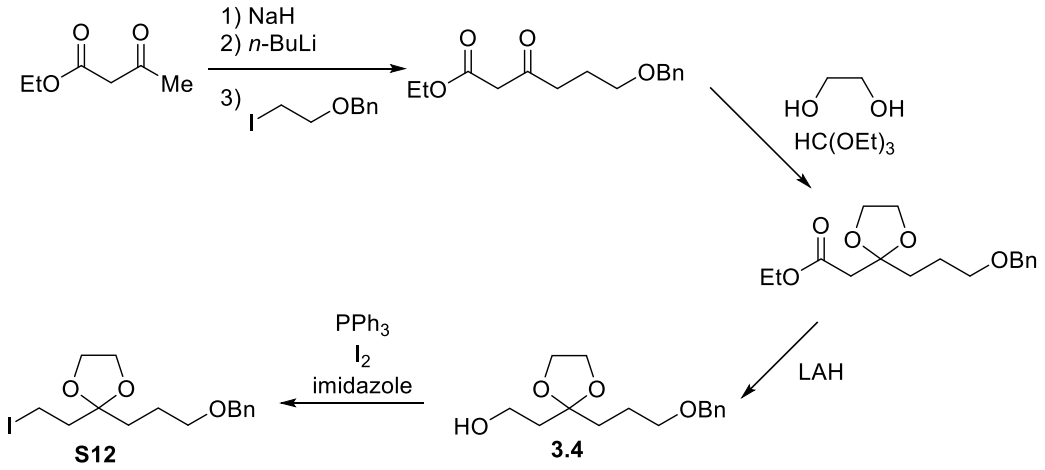
Another application in alkaloid synthesis was undertaken in the preparation of (-)-indolizidine 209D. In this synthesis, diastereoselective reductive amination was proposed as the key step to form the product as shown in the retrosynthetic analysis (Scheme 3.21).

Scheme 3.21: Retrosynthetic analysis for (-)-indolizidine 209D



In order to test the proposed synthetic route, the alkyl electrophile **S12** with appropriately distanced acetal can be prepared from a known intermediate **3.4** (alcohol)[62] by an Appel reaction[51] (Scheme 3.22).

Scheme 3.22: Preparation of electrophile for indolizidine 209D synthesis

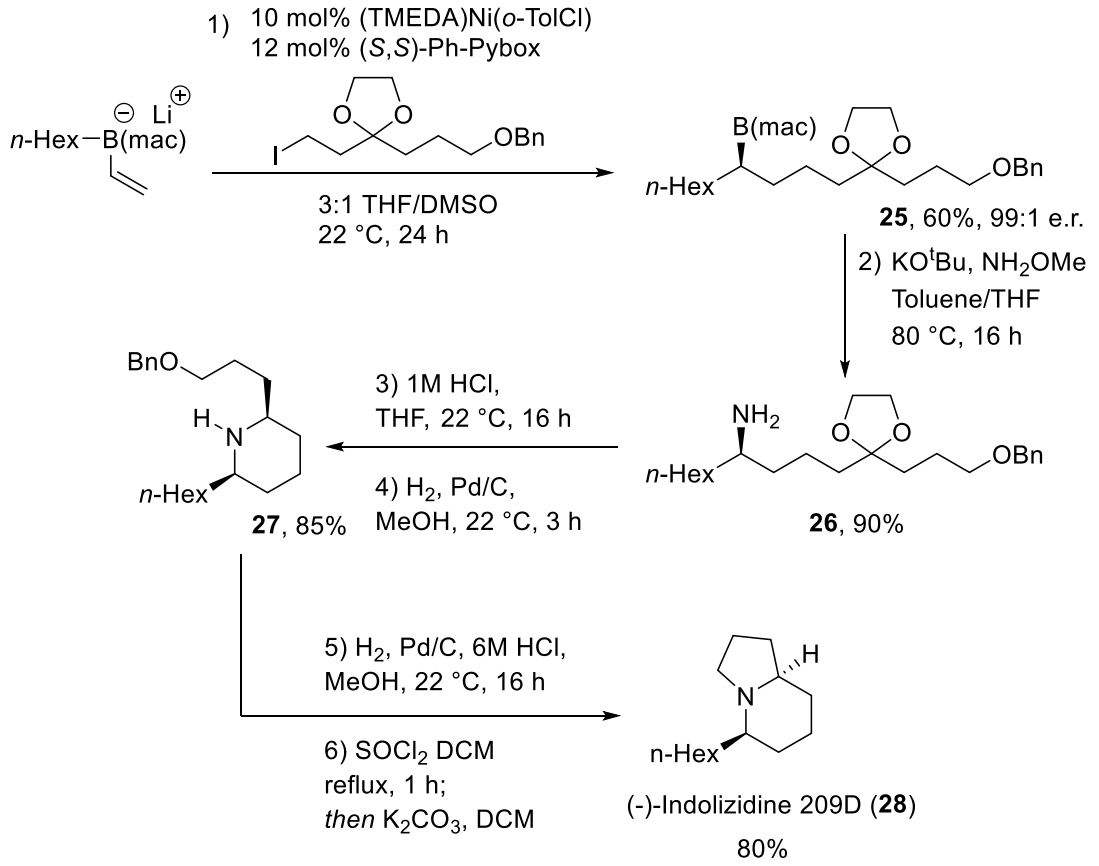


The synthetic route for the (-)-indolizidine 209D is shown (Scheme 3.23). Using the conjunctive coupling method with the boron ate derived from *n*-hexylB(mac) and vinyllithium, and with **S12** as the electrophile, the secondary boronic ester product **25** can be obtained in good yield and enantioselectivity. Following the procedure for the amination of boronic esters,[60] the free amine intermediate **26** can be obtained in 90%

[62] Liu, J.-H.; Song, L.-D.; Long, Y.-Q. *Tetrahedron Lett.* **2009**, *50*, 4587.

yield. Upon treatment of the intermediate with acid, it results in both the deprotection of the acetal as well as formation of the imine. The imine intermediate can then be diastereoselectively hydrogenated to produce syn-2,6-substituted piperidine **27**,[63] which is a known intermediate to indolizidine 209D, **28**.[64] The piperidine intermediate **27** is first debenzylated under acidic reduction condition, and then it was cyclized to indolizidine 209D.[64]

Scheme 3.23: Synthesis of (-)-indolizidine 209D by Ni-catalyzed conjunctive coupling reaction



[63] Simon, R. C.; Grischek, B.; Zepeck, F.; Steinreiber, A.; Belaj, F.; Kroutil, W. *Angew. Chem. Int. Ed.* **2012**, *51*, 6713.
[64] Coia, N.; Mokhtari, N.; Vasse, J.-L.; Szymoniak, J. *Org. Lett.* **2011**, *13*, 6292.

Similarly as with coniine, we were able to compare the specific optical rotation for the product and compare to a known literature value to confirm the absolute stereochemistry.

3.4 Conclusion

In this chapter, I have discussed the development of the conjunctive coupling reaction using alkyl migrating groups with C(sp^3)-iodide electrophiles. This methodology contributes to the area expanding the use of non-specialized substrates that do not contain directing groups or functional groups for reaction. This work represents a step towards broadening the scope of the conjunctive coupling reaction as a wide variety of functional groups are compatible with the method, and its utility is demonstrated by showcasing syntheses of two alkaloid targets, coniine and indolizidine 209D. However, the limitation still remains that the nature of alkene that is being difunctionalized have to be monosubstituted, with disubstituted alkenyl boronates like isopropenyl and propenyl boronates not competent in the reaction. Therefore, developing the reaction that accommodates such limitation may be helpful.

3.5 EXPERIMENTAL INFORMATION

3.5.1 General Information

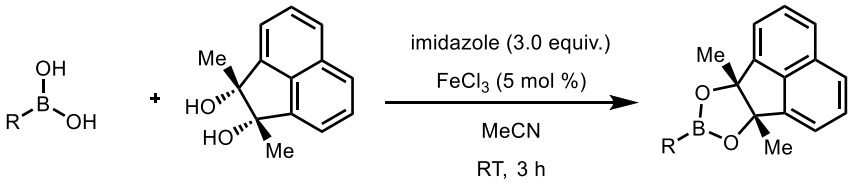
^{1}H NMR spectra were recorded on either a Varian Gemini-500 (500 MHz), Varian Gemini-600 (600 MHz), or Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian Gemini-500 (126 MHz), Varian Gemini-600 (151 MHz) or a Varian Inova-500 (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). ^{11}B NMR spectra were recorded on a Varian Gemini-500 (128 MHz) spectrometer. Chemical shifts are reported in ppm using BF_3-Et_2O as the external standard (BF_3-Et_2O: 0.0ppm). Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. High-resolution mass spectrometry (DART+) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography (TLC) was performed on aluminum backed 200 μm silica gel plates from Silicycle with F254nm indicator. Visualization was performed using ultraviolet light (254 nm), ceric ammonium molybdate (CAM), potassium permanganate ($KMnO_4$), or ninhydrin.

Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector with isopropanol as the modifier.

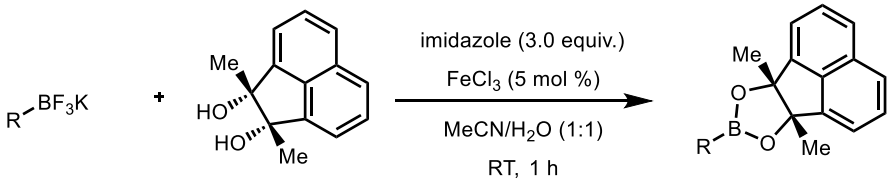
All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2) and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after purging with argon. VinylB(pin) was purchased from Combi-Blocks and was distilled prior to use. Anhydrous DMSO was purchased from Acros Organics and used without further purification. [(TMEDA)Ni(*o*-tol)Cl] and *(R,R)*-Ph-Pybox were purchased from Strem Chemicals and used without further purification. *(S,S)*-Ph-Pybox was purchased from Combi-Blocks and used without further purification. All other reagents were purchased from Sigma-Aldrich, Alfa Aesar, Oakwood Chemicals, Combi-Blocks, Frontier Scientific, or Acros Organics and used without further purification unless noted.

3.5.2 Experimental Procedures

3.5.2.1 *Procedures for the Preparation of Alkenyl and Alkyl Boronic Esters*

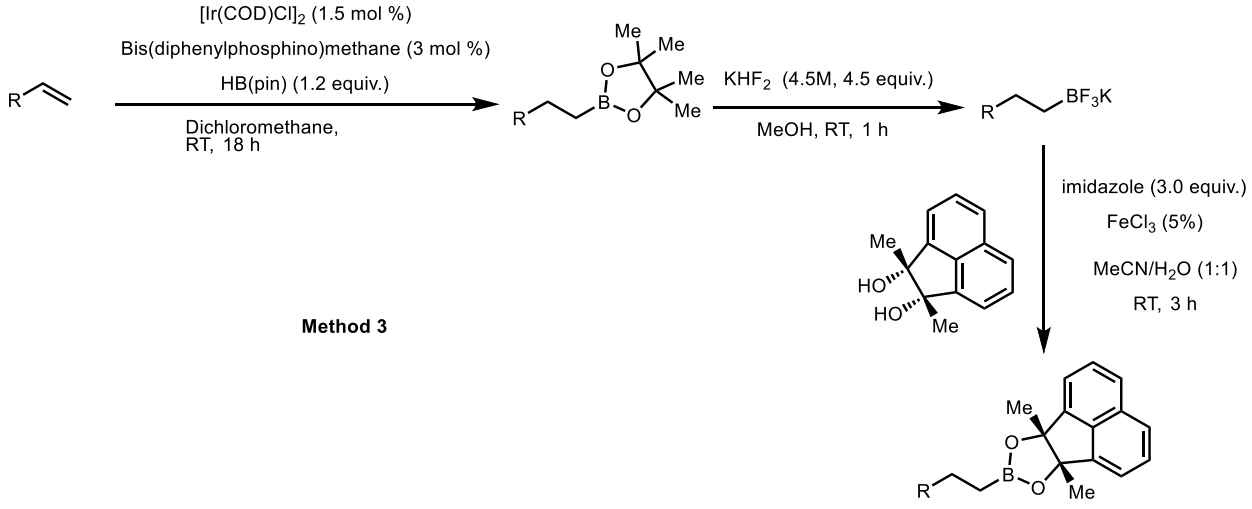


Method 1: According to a modified literature procedure[1]. Into a flame-dried 50 mL round bottom flask with a stir bar, boronic acid (4.67 mmol, 1.0 equiv.) was added. Acetonitrile (23.4 mL), and iron trichloride (37.9 mg, 0.234 mmol, 5 mol %) were then added, followed by imidazole (953.8 mg, 14.01 mmol, 3.0 equiv.), and then 1,2-dimethylacenaphthylene-1,2-diol[1] (1.00 g, 4.67 mmol, 1.0 equiv). The solution was allowed to stir at room temperature for three hours. The reaction mixture was then dried over sodium sulfate, filtered, and then concentrated under reduced pressure. The boronic ester was purified by silica gel chromatography to afford the pure product. (In cases of alkyl boronic esters of low polarity, passing the raw reaction mixture through a pad of silica gel eluting with Et_2O or DCM may afford a pure compound).

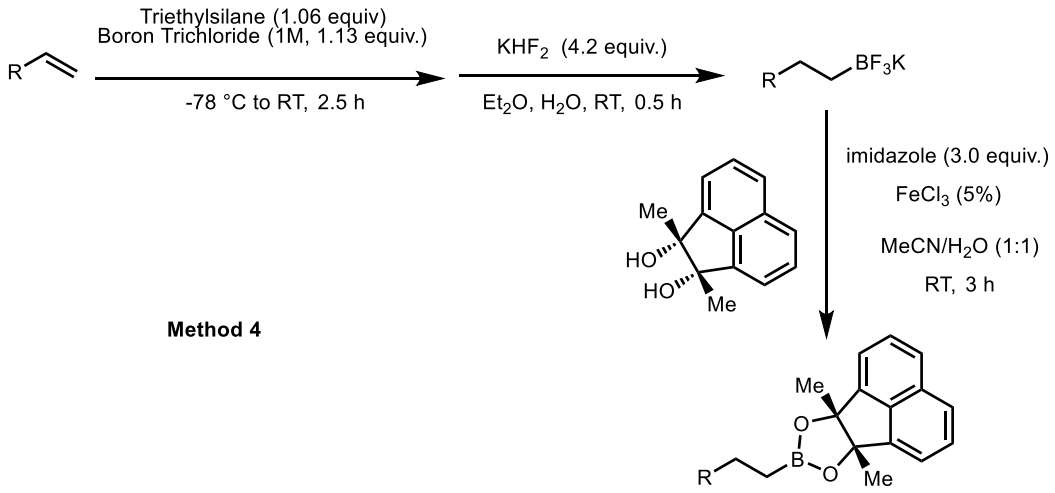


Method 2: According to a modified literature procedure[1]. Into a flame-dried 50 mL round bottom flask with a stir bar, alkyl potassium trifluoroborate salt (4.67 mmol, 1.0 equiv.) was added, then MeCN:H_2O (1:1, 23.4 mL), iron trichloride (37.9 mg, 0.234 mmol, 5 mol %) was then added, followed by imidazole (953.8 mg, 14.01 mmol, 3.0 equiv.), and then 1,2-dimethylacenaphthylene-1,2-diol[1] (1.00 g, 4.67 mmol, 1.0 equiv.). The solution was allowed to stir at room temperature for one hour. The reaction mixture was then passed through a fritted funnel containing silica gel, eluting with CH_2Cl_2, and then concentrated under reduced pressure. The boronic ester was then purified via silica gel chromatography to afford the pure product. (In cases of alkyl boronic esters of low polarity, passing the raw

reaction mixture through a pad of silica gel using Et_2O or DCM was able to afford a pure compound).

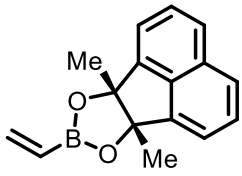


Method 3: Step one was performed in direct correlation with a literature procedure to afford the pinacol boronic ester.[2] The transformation of the boronic ester into the trifluoroborate salt was performed according to a modified literature procedure as follows.[3] In a scintillation vial equipped with a stir bar was added alkylB(pin) (2.28 mmol, 1.0 equiv.), followed by MeOH (11.4 mL). KHF_2 (4.5 M in H_2O, 2.28 mL, 10.26 mmol, 4.5 equiv.) was then added dropwise to the solution, and then allowed to stir for one hour. The solution was then concentrated under reduced pressure, and then redissolved in a minimal amount of acetone. The salt was then precipitated with diethyl ether, and was filtered on a Buchner funnel and collected as solid. **Method 2** was then used to prepare the boronic ester.



Method 4: This method was adapted from a literature procedure.[4] In a flame dried round bottom flask was added alkene (15 mmol, 1.0 equiv.) and triethylsilane (15.90 mmol, 1.13 equiv.), and then the flask was purged with nitrogen gas and cooled to -78 °C. Then, boron trichloride (1 M in hexanes, 16.95 mL, 16.95 mmol, 1.13 equiv.) was added dropwise and allowed to stir for 40 minutes. The solution was then allowed to warm to room temperature over the course of two hours. The reaction was then cooled to 0 °C, and ether and water (20 mL of each) were added and the reaction was allowed to stir for 30 minutes at room temperature. The crude mixture was then washed with ether three times, the organic layers dried with sodium sulfate, and then concentrated under reduced pressure. To the unpurified mixture was then added KHF_2 (63.0 mmol, 4.2 equiv.), and 20 mL of ether. Next, 1 mL of H_2O was added dropwise over the course of an hour. Sodium sulfate was then added; acetone was then added and the mixture filtered and concentrated. The crude material was redissolved in a minimal amount of acetone, and the borate salt precipitated by addition of ether. **Method 2** was then used to prepare the boronic ester. (**Method 4** provides for a faster route to boronic esters from available alkenes without the use of a pinacol boronic ester intermediate).

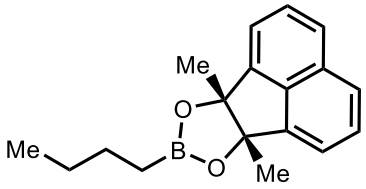
^{11}B NMR spectra were recorded on a Varian Gemini-500 (160 MHz), with external standard ($BF_3 \cdot Et_2O$): 0.0 ppm. If the value is not specified, the ^{11}B chemical shifts for the compounds are 35-36 ppm.



S1

6b,9a-dimethyl-8-vinyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (S1); vinylB(mac).

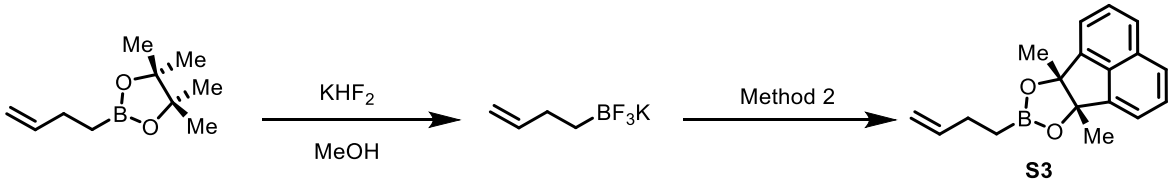
Title compound was prepared by **Method 2** with commercially available potassium vinyltrifluoroborate. The crude product was purified using silica gel chromatography (1% EtOAc/hexanes, stained in CAM) to afford white solid (98% yield). Title compound was recrystallized in hot hexanes to afford colorless, clear, and crystalline solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.63 – 7.55 (m, 4H), 6.11 (dd, *J* = 19.7, 4.0 Hz, 1H), 5.95 (dd, *J* = 13.8, 4.0 Hz, 1H), 5.80 (dd, *J* = 19.6, 13.7 Hz, 1H), 1.81 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 137.4, 134.9, 131.5, 128.6, 125.4, 119.6, 92.1, 22.2. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.5. IR (neat) ν_{max} 3061 (w), 2974 (w), 2110 (w), 1618 (m), 1499 (w), 1434 (m), 1373 (w), 1317 (s), 1250 (m), 1212 (w), 1175 (w), 1117 (m), 1077 (m), 1015 (w), 968 (m), 892 (w), 826 (m), 805 (w), 779 (m), 760 (w), 731 (w), 710 (m), 668 (w), 639 (w), 573 (w), 545 (w), 538 (w) cm^{-1}. HRMS (DART+) for $C_{16}H_{16}BO_2$ $[M+H]^+$: Calc'd: 251.1238, found: 251.1237.



S2

8-butyl-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (S2).

The reaction was performed according to **Method 1** with *n*-butylboronic acid (952.1 mg, 9.34 mmol, 1.0 equiv.), 1,2-dimethylacenaphthylene-1,2-diol (2.00 g, 9.34 mmol, 1.0 equiv.), iron trichloride (75.8 mg, 0.467 mmol, 5 mol %), imidazole, (1.91 g, 28.0 mmol, 3.0 equiv.), and MeCN (46.7 mL). The product was then purified by silica gel chromatography (15% EtOAc in hexanes, stained in CAM) to afford a yellow solid. (2.3 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 6.9 Hz, 2H), 1.77 (s, 6H), 1.32 (p, *J* = 7.6 Hz, 2H), 1.23 (tq, *J* = 14.6, 7.7 Hz, 2H), 0.80 (t, *J* = 7.3 Hz, 3H), 0.72 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 134.7, 131.4, 128.5, 125.3, 119.5, 91.7, 26.2, 25.4, 22.2, 13.9. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. IR (neat) ν_{max} 3044 (w), 2955 (w), 2928 (w), 2870 (w), 1348 (m), 1308 (m), 1116 (s), 1077 (s), 825 (s), 776 (s) cm^{-1}. HRMS (DART+) for $C_{18}H_{22}BO_2$ $[M+H]^+$: Calc'd: 281.1707, found: 281.1707.

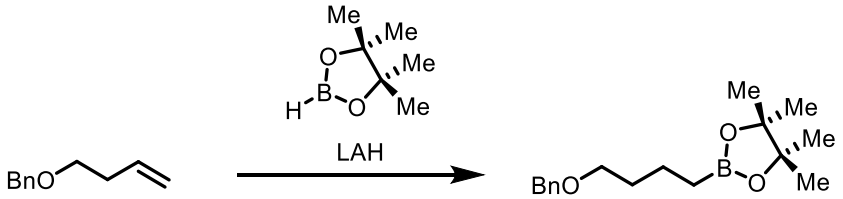


S3

8-(but-3-en-1-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (S3).

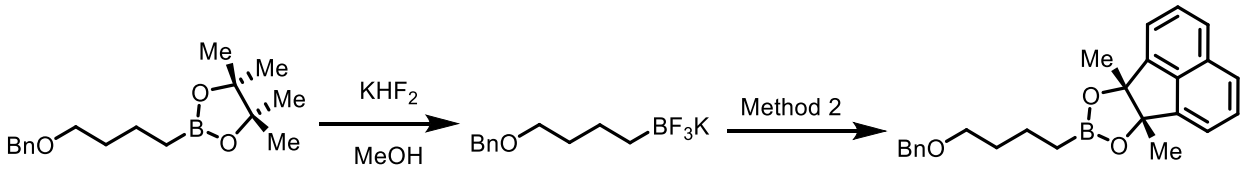
Title compound was prepared from following **Method 2** using but-3-en-1-yltrifluoro-λ^4-borane, potassium salt (prepared from commercially available 2-(but-3-en-1-yl)-4,4,5,5-

tetramethyl-1,3,2-dioxaborolane, following a literature procedure[3]). The crude product was purified using silica gel chromatography (1% EtOAc/Hexanes, stained in CAM) to afford a white solid (64% yield over 2 steps). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.60 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.55 (d, *J* = 6.9 Hz, 2H), 5.80 (ddt, *J* = 16.9, 10.2, 6.4 Hz, 1H), 4.89 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.79 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 2.10 (tdt, *J* = 7.8, 6.4, 1.4 Hz, 2H), 1.77 (s, 6H), 0.84 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 140.7, 134.8, 131.5, 128.6, 125.4, 119.6, 113.2, 91.9, 28.1, 22.3. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.6. IR (neat) ν_{max} 3044 (w), 2975 (w), 2930 (w), 1640 (w), 1499 (w), 1433 (w), 1402 (w), 1370 (s), 1307 (s), 1263 (w), 1246 (m), 1212 (w), 1174 (m), 1116 (s), 1078 (s), 1041 (w), 995 (w), 967 (m), 907 (m), 825 (s), 805 (w), 777 (s), 638 (w), 552 (w) cm^{-1}. HRMS (DART+) for $C_{18}H_{20}BO_2$ $[M+H]^+$: Calc'd: 279.1551, found: 279.1550.



2-(4-(benzyloxy)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Title compound was prepared from ((but-3-en-1-yloxy)methyl)benzene[5] using literature procedure.[6] All spectral data was in accord with the literature.[7]

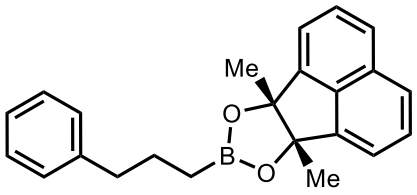


S4

(pk571) 8-(4-(benzyloxy)butyl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (S4).

The title compound was prepared from following **Method 2** using (4-(benzyloxy)butyl)trifluoro-λ^4-borane, potassium salt (which was prepared from 2-(4-(benzyloxy)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following literature procedure[3]). The crude product was purified using silica gel chromatography (5% EtOAc/Hexanes, stained in CAM) to afford a white solid (57% over two steps). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, , 2H), 7.59 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.55-7.53 (m, 2H), 7.33 – 7.28 (m, 4H), 7.27 – 7.24 (m, 1H), 4.41 (s, 2H), 3.39 (t, *J* = 6.7 Hz, 2H), 1.77 (s, 6H), 1.58 – 1.52 (m, 2H), 1.43 (p, *J* = 7.5 Hz, 2H), 0.75 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 138.9, 134.8, 131.5, 128.6, 128.4, 127.7, 127.5, 125.4, 119.6, 91.8, 72.8, 70.4, 32.3, 22.3, 20.6. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.6. IR (neat) ν_{max} 3030 (w), 2972 (w), 2932 (m), 2861 (m), 2362 (w), 1497 (w), 1454 (w), 1375 (s), 1310 (m), 1263 (m), 1232 (w), 1213 (w), 1175 (m), 1117 (s), 1079 (s), 1029 (w), 967 (w), 894

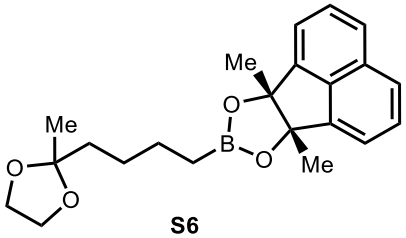
(w), 826 (s), 779 (s), 736 (m), 698 (m), 669 (w), 639 (w), 609 (w), 572 (w), 546 (w), 537 (w) cm^{-1}. HRMS (DART+) for $C_{25}H_{28}BO_3$ $[M+H]^+$: Calc'd: 387.2126, found: 387.2125.



S5

6b,9a-dimethyl-8-(3-phenylpropyl)-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (S5).

The reaction was performed according to **Method 2** with trifluoro-(3-phenylpropyl)-potassio-boron (1.60 g, 7.08 mmol, 1.0 equiv.), 1,2-dimethylacenaphthylene-1,2-diol (1.52 g, 7.08 mmol, 1.0 equiv.), iron trichloride (57.4 mg, 0.354 mmol, 5 mol %), imidazole, (1.45 g, 21.2 mmol, 3.0 equiv.), and MeCN:H_2O (1:1, 35.4 mL). The product was then purified by silica gel chromatography (15% ether in pentane, stained in CAM) to afford a yellow solid. (2.0 g, 83%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 2H), 7.59 (t, J = 7.7 Hz, 2H), 7.53 (d, J = 6.9 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 2.52-2.47 (m, 2H), 1.76 (s, 6H), 1.66 (p, J = 7.7 Hz, 2H), 0.77 (t, J = 7.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 142.7, 134.7, 131.5, 128.6 (2), 128.2, 125.6, 125.3, 119.5, 91.7, 38.5, 26.1, 22.2. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. IR (neat) ν_{max} 3025 (w), 2978 (w), 2932 (w), 1496 (w), 1372 (s), 1308 (m), 1116 (m), 1078 (m), 778 (s), 744 (m), 699 (m) cm^{-1}. HRMS (DART+) for $C_{23}H_{24}BO_2$ $[M+H]^+$: Calc'd: 343.1864, found: 343.1856.

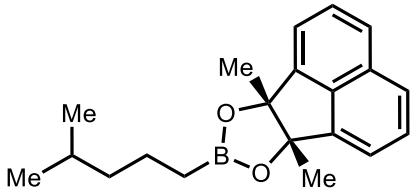


S6

6b,9a-dimethyl-8-(4-(2-methyl-1,3-dioxolan-2-yl)butyl)-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (S6).

The reaction was performed according to **Method 3** with 2-but-3-enyl-2-methyl-1,3-dioxolane (526.1 mg, 3.70 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (568.2 mg, 4.44 mmol, 1.2 equiv.), Bis(1,5-cyclooctadiene)diiridium(I) dichloride (37.3 mg, 0.056 mmol, 1.5 mol %), bis(diphenylphosphino)methane (42.7 mg, 0.111 mmol, 3.0 mol %), and dichloromethane (12.33 mL) to afford the 4,4,5,5-tetramethyl-2-[4-(2-methyl-1,3-dioxolan-2-yl)butyl]-1,3,2-dioxaborolane intermediate. Then, to this intermediate was added KHF_2 (4.5 M in H_2O, 3.7 mL, 16.65 mmol, 4.5 equiv.), followed by MeOH (11.4 mL), to afford the trifluoro-[4-(2-methyl-1,3-dioxolan-2-yl)butyl]-potassio-boron intermediate. Then to this was added 1,2-dimethylacenaphthylene-1,2-diol (353.8 mg, 1.65 mmol, 1.0 equiv.), iron trichloride (13.4 mg, 0.083 mmol, 5 mol %), imidazole, (337.3 mg,

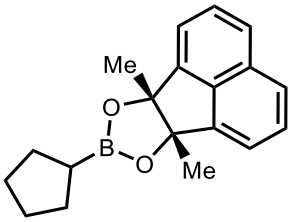
4.95 mmol, 3.0 equiv.), and MeCN:H_2O (1:1, 8.3 mL). The product was then purified by silica gel chromatography (50% ether in hexanes) to afford a white solid. (469 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 6.8 Hz, 2H), 3.91-3.81 (m, 4H), 1.77 (s, 6H), 1.56-1.51 (m, 2H), 1.39-1.32 (m, 2H), 1.32-1.25 (m, 2H), 1.21 (s, 3H), 0.74 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 134.6, 131.4, 128.5, 125.2, 119.4, 110.1, 91.6, 64.5, 38.8, 26.7, 24.2, 23.7, 22.1. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. IR (neat) ν_{max} 2979 (w), 2935 (w), 2870 (w), 1715 (w), 1372 (m), 1116 (m), 1077 (m), 1052 (m), 967 (w), 947 (w), 778 (m) cm^{-1}. HRMS (DART+) for $C_{22}H_{28}BO_4$ $[M+H]^+$: Calc'd: 367.2075, found: 367.2074.



S7

6b,9a-dimethyl-8-(4-methylpentyl)-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (S7).

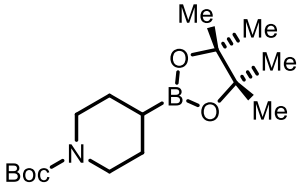
The reaction was prepared according to **Method 4** with 4-methylpent-1-ene (1.26 g, 15 mmol, 1.0 equiv.), triethylsilane (1.85 g, 15.9 mmol, 1.06 equiv.), and trichloroborane (1M in hexanes, 16.95 mL, 16.95 mmol, 1.13 equiv.), and Et_2O:H_2O (1:1, 40.0 mL), and then KHF_2 (4.92 g, 63.0 mmol, 4.2 equiv.), and H_2O (1 mL) to afford the trifluoro-isohexyl-potassio-boron intermediate. To a portion of this intermediate was then added 1,2-dimethylacenaphthylene-1,2-diol (353.8 mg, 3.0 mmol, 1.0 equiv.), iron trichloride (13.4 mg, 0.083 mmol, 5 mol %), imidazole, (337.3 mg, 4.95 mmol, 3.0 equiv.), and MeCN:H_2O (1:1, 8.3 mL). The product was then purified by silica gel chromatography (50% ether in hexanes) to afford a white solid. (469 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.61-7.57 (m, 2H), 7.55 (d, *J* = 6.9 Hz, 2H), 1.77 (s, 6H), 1.43 (dq, *J* = 13.3, 6.7 Hz, 1H), 1.33 (p, *J* = 7.8 Hz, 2H), 1.08-1.03 (m, 2H), 0.77 (d, *J* = 6.6 Hz, 6H), 0.70 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 134.8, 131.5, 128.6, 125.3, 119.5, 91.7, 41.9, 27.8, 22.7, 22.2, 21.8. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. IR (neat) ν_{max} 3044 (w), 2952 (m), 2930 (m), 2867 (w), 1499 (w), 1373 (m), 1306 (m), 1263 (m), 1238 (m), 1116 (s), 1078 (s), 825 (m), 777 (m), 744 (m) cm^{-1}. HRMS (DART+) for $C_{20}H_{26}BO_2$ $[M+H]^+$: Calc'd: 309.2020, found: 309.2025



S8

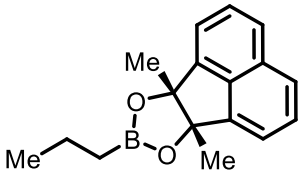
8-cyclopentyl-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (S8).

The reaction was performed according to **Method 1** with cyclopentylboronic acid (400 mg, 3.51 mmol, 1.0 equiv), 1,2-dimethylacenaphthylene-1,2-diol (752.1 mg, 3.51 mmol, 1.0 equiv.), iron trichloride (28.5 mg, 0.176 mmol, 5 mol %), imidazole (717 mg, 10.5 mmol, 3.0 equiv.), and MeCN (17.6 mL). The product was then purified by concentrating the crude mixture, dissolving in dichloromethane, and passing through a fritted funnel of silica gel to afford a white solid. (952 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.5 Hz, 2H), 7.55 (d, J = 6.9 Hz, 2H), 1.76 (s, 6H), 1.72-1.63 (m, 2H), 1.54-1.49 (m, 2H), 1.47-1.32 (m, 4H), 1.11 (p, J = 9.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 134.8, 131.4, 128.5, 125.2, 119.5, 91.6, 28.7, 26.9, 22.2. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. IR (neat) ν_{max} 3045 (w), 2983 (w), 2950 (w), 2863 (w), 1370 (m), 1304 (m), 1211 (m), 1114 (m), 1073 (m), 882 (m), 644 (w) cm^{-1}. HRMS (DART+) for $C_{19}H_{22}BO_2$ $[M+H]^+$: Calc'd: 293.1707, found: 293.1707.



***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate.**

Title compound was prepared according to the literature procedure.[8] Spectral data matches the literature data.[8]



S9

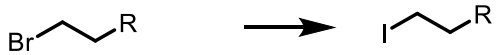
6b,9a-dimethyl-8-propyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (S9).

Title compound was prepared from **Method 1** with commercially available *n*-propylboronic acid. The crude product was purified using silica gel chromatography (1% EtOAc/Hexanes, stained in CAM) to afford a white solid (84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.60 (dd, J = 8.1, 6.9 Hz, 2H), 7.55 (d, J = 6.5 Hz, 2H), 1.78

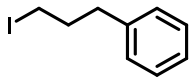
(s, 6H), 1.38 (h, J = 7.5 Hz, 2H), 0.84 (t, J = 7.4 Hz, 3H), 0.73 (t, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 134.8, 131.5, 128.6, 125.3, 119.5, 91.7, 22.3, 17.5, 17.0. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.87. IR (neat) ν_{max} 3044 (w), 2955 (w), 2930 (w), 2870 (w), 1498 (w), 1458 (w), 1405 (w), 1371 (s), 1324 (m), 1305 (s), 1267 (m), 1211 (m), 1174 (m), 1117 (s), 1079 (s), 968 (m), 903 (w), 883 (w), 826 (s), 779 (s), 728 (w) cm^{-1}. HRMS (DART+) for $C_{17}H_{20}BO_2$ $[M+H]^+$: Calc'd: 267.1551, found: 267.1548.

3.5.2.2 *Procedures for the Preparation of Alkyl Iodides*

A. General Procedure for the Preparation of Alkyl Iodides from Alkyl Bromides.

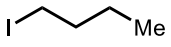


To a solution of alkyl bromide (1.0 equiv.) in acetone (1.5M), sodium iodide (2.0 equiv.) was added. The mixture was stirred at room temperature for 16 h. Solvent was removed under reduced pressure, then EtOAc (20 mL) and water (15 mL) are added to the residue. It was extracted with EtOAc 3 times. Next, the organic layer was washed with $Na_2S_2O_3$ (sat. aq.) solution, then brine, then dried over Na_2SO_4. The crude residue was purified by silica gel column (1-5% EtOAc/hexanes) followed by distillation if it was possible without decomposition of the alkyl iodide.



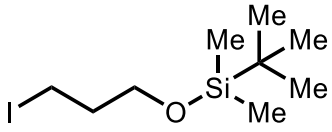
(3-iodopropyl)benzene

The title compound was prepared according to **general procedure** with (3-bromopropyl)benzene (95% yield). Spectral data were in accordance with literature report.[9] The title compound was distilled prior to use to yield colorless oil.



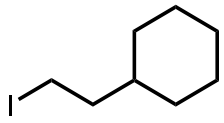
1-Iodobutane.

The title compound was prepared according to the procedure reported in the literature.[10] All spectral data were in accordance with the literature.[10]



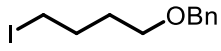
tert-butyl(3-iodopropoxy)dimethylsilane.

The title compound was prepared according to the procedure reported in the literature.[11] All spectral data were in accordance with the literature.[11]



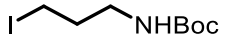
(2-iodoethyl)cyclohexane.

The title compound was prepared according to the procedure reported in the literature.[12] All spectral data were in accordance with the literature.[12]



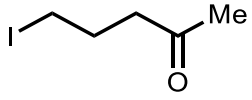
((4-iodobutoxy)methyl)benzene

The title compound was prepared according to the literature procedure.[13] All spectral data were in accord with the literature.[13]



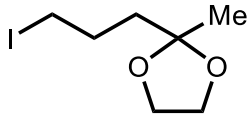
***tert*-butyl (3-iodopropyl)carbamate.**

The title compound was prepared according to the **general procedure** with corresponding *tert*-butyl (3-bromopropyl)carbamate (75% yield). All spectral data were in accord with the literature.[14]



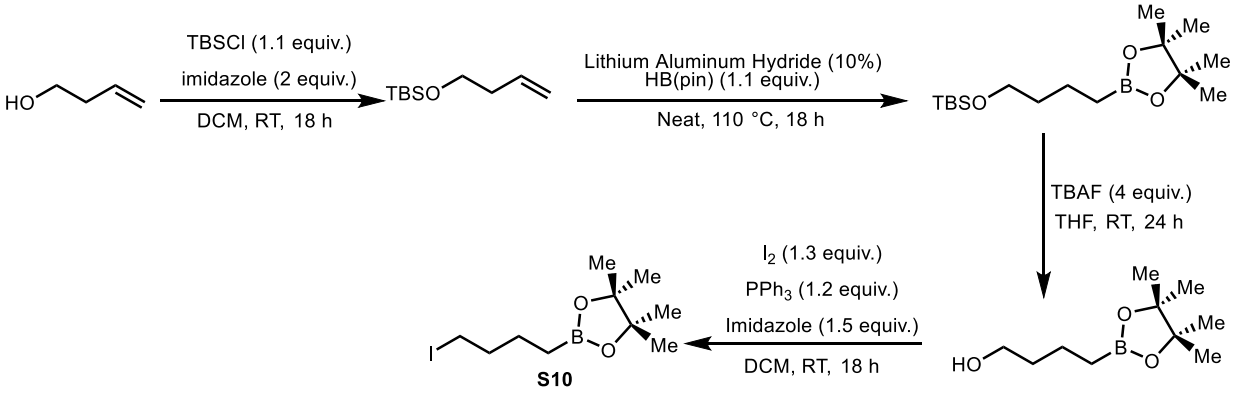
5-iodopentan-2-one.

The title compound was prepared according to the procedure reported in the literature.[15] All spectral data were in accordance with the literature.[15]



2-(3-iodopropyl)-2-methyl-1,3-dioxolane.

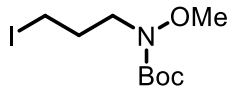
The title compound was prepared according to the procedure reported in the literature.[16] All spectral data were in accordance with the literature.[16]



4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-ol (S10).

The synthesis of but-3-enoxy-tert-butyl-dimethyl-silane was conducted through methods described in the literature.[17] The synthesis of tert-butyl-dimethyl-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy]silane was prepared in accordance with the literature.[6] In a two dram vial with a stir bar was added lithium aluminum hydride (38.0 mg, 0.536 mmol, 10 mol %), but-3-enoxy-tert-butyl-dimethyl-silane (1.00 g, 5.37 mmol, 1.0 equiv.), and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.856 mL, 5.90 mmol, 1.1 equiv), and stirred at 110 °C in oil bath for 24 hours. The crude material was then filtered through a silica gel plug using dichloromethane, and concentrated under reduced pressure. The crude material was purified via silica gel chromatography (5% EtOAc in hexanes) to afford the product as a colorless liquid (1.24 g, 3.94 mmol, 74%). Then to a round bottom flask was added tert-butyl-dimethyl-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy]silane (940 mg, 2.99 mmol, 1.0 equiv.) followed by tetrabutyl ammonium fluoride (1M in THF, 12 mL, 12 mmol, 4.0 equiv.), and allowed to stir at room temperature for 24 hours. Water was then added to the reaction, and the aqueous layer was extracted three times using EtOAc, dried with sodium sulfate, and then concentrated under reduced pressure. The crude material was then purified via silica gel chromatography (40% Et_2O in pentane), to afford a colorless liquid (374 mg, 1.87 mmol, 63%). Then, to a round bottom flask was added

triphenylphosphine (588 mg, 2.24 mmol, 1.2 equiv.), followed by dichloromethane (3.7 mL), followed by iodine (588 mg, 2.43 mmol, 1.3 equiv.). 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-ol was then added to a round bottom flask (374 mg, 0.187 mmol, 1.0 equiv) at 0 °C, and allowed to warm to room temperature and stirred for 18 hours. The reaction was then filtered by vacuum filtration and concentrated under reduced pressure. To the filtrate was added saturated sodium thiosulfate, and the solution was extracted three times with a solution of 20% EtOAc in hexanes. The organic layers are then dried with sodium sulfate, and concentrated under reduced pressure. The crude material was then purified via silica gel chromatography (40% diethyl ether in hexanes) to afford a light brown liquid (350 mg, 1.13 mmol, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18 (t, J = 7.1 Hz, 2H), 1.84 (p, J = 7.2 Hz, 2H), 1.51 (dt, J = 15.3, 7.7 Hz, 2H), 1.24 (s, 12H), 0.79 (t, J = 7.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.2, 36.3, 30.5, 25.2, 25.0, 6.9. ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.8. IR (neat) ν_{max} 2977 (s), 2928 (s), 2856 (m), 1460 (w), 1407 (m), 1379 (s), 1322 (s), 1241 (m), 1200 (m), 1145 (s), 968 (m), 846 (m), 724 (w), 672 (w), 601 (w), 571 (w), 551 (w), 538 (w) cm^{-1}. HRMS (DART+) for $C_{10}H_{21}BO_4I$ $[M+H]^+$: Calc'd: 311.0674, found: 311.0671.

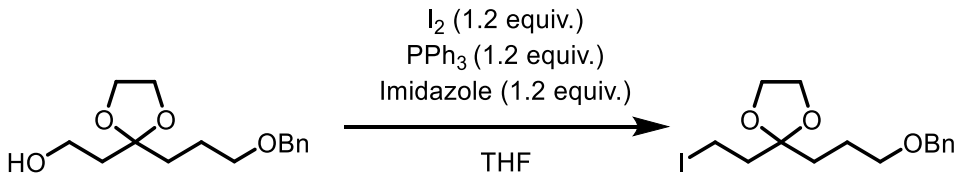


S11

***tert*-butyl (3-iodopropyl)(methoxy)carbamate (S11).**

Sodium hydride (90% purity, 186.6 mg, 7.00 mmol, 1.03 equiv.) was placed into an oven dried round bottom flask with a stir bar, inside glovebox, which was sealed with rubber septum, then brought outside of glovebox. DMF (10.0 mL) was added while under nitrogen atmosphere and *tert*-butyl N-methoxycarbamate[18] (1.00 g, 6.79 mmol, 1.0 equiv.) in 3.0 mL DMF was slowly added at 0 °C. The mixture was allowed to stir for 1 hour at room temperature. Then 1,3-dibromopropane (5.49 g, 27.2 mmol, 2.76 mL, 4.0 equiv.) was added in one portion. The mixture was left to stir overnight at room temperature under nitrogen atmosphere. It was first diluted with EtOAc (100 mL), then water (25 mL) was carefully added. Organic compound was extracted with EtOAc, washed with water, brine, and dried over Na_2SO_4. Solvents were removed to afford pale yellow oil. Which was purified by silica gel chromatography (5-10% EtOAc/Hexanes), which was then treated with NaI (2.00 g, 13.4 mmol, 2.0 equiv.) in 10 mL of acetone. It was allowed to stir overnight at room temperature, open to air. $Na_2S_2O_3$ (aq. sat.) was added to quench excess iodide, then organic compound was extracted with EtOAc. Title compound was purified using silica gel chromatography (10% EtOAc/Hexanes) to yield pale yellow oil (1.57g, 73% over two steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.53 (t, J = 6.7 Hz, 2H), 3.20 (t, J = 6.9 Hz, 2H), 2.13 (p, J = 6.8 Hz, 2H), 1.50 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 81.7, 62.4, 49.5, 31.4, 28.5, 3.0. IR (neat) ν_{max} 2976 (m), 2933 (w), 2161 (w), 1701 (s), 1476 (w), 1435 (w), 1392 (m), 1367 (s), 1288 (w), 1236 (m), 1154 (s), 1085 (m), 1016

(w), 977 (w), 855 (w), 765 (w) cm^{-1}. HRMS (DART+) for $C_9H_{19}NO_3I$ $[M+H]^+$: Calc'd: 316.0404, found: 316.0473.



S12

2-(3-(benzyloxy)propyl)-2-(2-iodoethyl)-1,3-dioxolane (S12).

To a 100 mL round-bottom flask, equipped with a magnetic stir bar, 2-(2-(3-(benzyloxy)propyl)-1,3-dioxolan-2-yl)ethan-1-ol[19] (1.45 g, 5.44 mmol, 1.0 equiv.), I_2 (1.66 g, 6.53 mmol, 1.2 equiv.), Imidazole (0.444 g, 6.53 mmol, 1.2 equiv), PPh_3 (1.71g, 6.53 mmol, 1.2 equiv) were added and dissolved in THF (10.0 mL). The mixture was allowed to stir at room temperature overnight. It was then diluted with EtOAc, quenched with $Na_2S_2O_3$ (aq. sat.) solution, extracted with EtOAc three times. It was washed with brine, and dried with Na_2SO_4. Solvents were removed under reduced pressure to give a solid residue. Crude material was purified by silica gel chromatography (5% EtOAc/Hexanes, $KMnO_4$ stain) to yield a pale yellow oil (1.87 g, 91% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.33 (m, 4H), 7.29-7.26 (m, 1H), 4.50 (s, 2H), 3.94 (s, 4H), 3.47 (m, 2H), 3.16-3.13 (m, 2H), 2.29-2.26 (m, 2H), 1.69-1.67 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 128.5, 127.8, 127.7, 111.5, 73.0, 70.3, 65.3, 42.8, 33.9, 24.2, -2.1. IR (neat) ν_{max} 3028 (w), 2956 (s), 2879 (s), 2358 (w), 1495 (w), 1453 (m), 1360 (m), 1207 (m), 1100 (s), 1028 (m), 949 (m), 858 (w), 737 (m), 698 (m) cm^{-1}. HRMS (DART+) for $C_{15}H_{22}O_3I$ $[M+H]^+$: Calc'd: 377.0608, found: 377.0602.

3.5.2.3 *General Procedure for the Conjunctive Cross-Coupling*

A. General Procedure A (using vinyl boronic ester, and alkyl organolithium reagents)

Inside the glovebox, an oven-dried 2 dram vial equipped with a stir bar was charged with 6b,9a-dimethyl-8-vinyl-acenaphthyleno[1,2-*d*][1,3,2]dioxaborole (vinylB(mac)), (55.0 mg, 0.22 mmol, 1.1 equiv). The boronic ester was dissolved in 0.5 mL Et_2O, capped with septum, taped, and was removed from the glovebox. The vial was placed under positive pressure of N_2, cooled to 0 °C in ice bath, then the organolithium reagent (0.2 mmol, 1.0 equiv) was added dropwise over about 5 min. After the addition was complete, the vial was removed from the ice bath and allowed to stir for 5 minutes at room temperature. Then the solvent was carefully removed under reduced pressure while not being exposed to air, and put under vacuum for 15 min.

Inside the glovebox, to another oven-dried 2 dram vial equipped with a stir bar, catalyst stock solution was prepared. It was charged with (TMEDA)Ni(*o*-tol)Cl (6.0 mg, 0.020 mmol, 10 mol %) and (*S,S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %). Subsequently, it was suspended in 0.2 mL of THF and was allowed to stir for 5 min. Then 0.4 mL of DMSO was added, and was allowed to stir for 5 min, or until it was completely dissolved.

After the first vial was under vacuum for 15 min, the vial was filled with nitrogen, then brought into the glovebox. 0.9 mL of THF was added to the vial containing boron ate complex. Iodide electrophile (0.24 mmol, 1.2 equiv) was added, then, 0.6 mL of nickel catalyst complex stock solution was added slowly. The vial was sealed with polypropylene cap, taped, and brought outside the glovebox and was allowed to stir for 18-24h at room temperature. Reaction mixture is then diluted with ether, and 0.5mL of H_2O is added (for removal of DMSO). Crude product can be obtained after filtering through a silica gel plug with ether.

B. General Procedure B (using alkyl boronic esters, and vinyllithium in THF)

Inside the glovebox, an oven-dried 2 dram vial equipped with a stir bar was charged with alkyl B(mac) (0.22 mmol, 1.1 equiv). It was dissolved in 0.5mL THF, capped with septum, taped, and was brought outside the glovebox with vinyl lithium solution in syringe pierced through the septum. Vial was placed under positive pressure of N_2, cooled to 0 °C in ice bath, then the vinyllithium in THF (0.2 mmol, 1.0 equiv) was added dropwise over about 5 min. After the addition was complete, the vial was removed from the ice bath and allowed to stir for 5 min at room temperature.

Inside the glovebox, to another oven-dried 2 dram vial equipped with a stir bar, catalyst stock solution was prepared. It was charged with (TMEDA)Ni(*o*-tol)Cl (6.0 mg, 0.020 mmol, 10 mol %) and (*S,S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %). Subsequently, it was suspended in 0.2 mL of THF and was allowed to stir for 5 min. Then 0.4 mL of DMSO was added, and was allowed to stir for 5 min, or until it was completely dissolved.

The vial was taped over the top of septum, then brought into the glovebox. More THF was added until a total of 0.9 mL of THF was added to the vial containing boron ate complex, including THF contained in vinyl lithium solution. Iodide electrophile (0.24 mmol, 1.2 equiv) was added, then, 0.6 mL of nickel catalyst complex solution was added slowly. The vial was sealed with polypropylene cap, taped, and brought outside the glovebox and was allowed to stir for 18-24h at room temperature. Reaction mixture is then diluted with ether, and 0.5mL of H_2O is added (for removal of DMSO). Crude product can be obtained after filtering through a silica gel plug with ether.

Preparation of vinyllithium in THF:

Vinyllithium in THF was prepared according to the previous report[20], using tetravinyltin (1.0 equiv.), and *n*-butyllithium solution in hexanes (2.0 equiv.). It was stored in freezer of the argon-filled glovebox and warmed up to room temperature prior to use.

Titration method used for vinyllithium in THF, or other organolithium reagents:

First, an oven dried 2-dram vial, equipped with a magnetic stir bar, was sealed with septum cap, and was allowed to cool to room temperature under vacuum. To the vial, an accutately weighed amount of 2,6-di-*tert*-butyl-4-methylphenol (BHT) (ca. 100.0 mg) is added, with 1,10-phenanthroline (ca. 2.0 mg) as the endpoint indicator for the titration. The vial is then sealed with septum cap, atmosphere exchanged with nitrogen three times, then dissolved in 2mL of anhydrous THF. While under nitrogen atmosphere, the vial is placed in ice bath and cooled to 0 ºC, and titrated with organolithium reagent (usually in a 1.00mL syringe), until dark purple color persists. Total amount of volume used to reach endpoint is used for calculation of reagent concentration. This process is performed twice for accuracy.

Considerations regarding General Procedure A vs. B, reaction temperatures, and their reaction times:

If either **General Procedure A** and **B** are considered, reactions using **Procedure A** (vinylB(mac) and organolithium) results in a slightly faster reaction than **Procedure B** (for **2a**, full conversion (by ^{11}B NMR) by **Procedure A** is in 15 h, and by **Procedure B** it is in

20 h). As shown in the optimization table, conducting the reaction at 60 ºC (in oil bath), results in 10-15% lower yield, but without loss in enantiomeric ratio. For **2a**, the reaction is completed in about 4 hours.

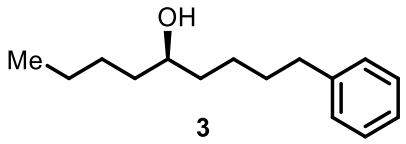
C. General Method for Oxidation of Boronic Ester Products: (Oxidation Procedure)

Note: Where appropriate, boronic ester products were oxidized. In these cases, the procedure listed below was used employed. Prior to oxidation, boronic ester products were purified by silica gel chromatography such that it only contains product (or may contain inseparable alkylB(mac), and vinylB(mac)). The initial purification was often required to avoid carrying over the inseparable impurities during the purification of secondary alcohols.

The purified boronic ester product (which may or may not contain alkylB(mac) or vinylB(mac) as impurities) was diluted with tetrahydrofuran (1 mL). The crude mixture was cooled to 0 ºC and 3M NaOH (1 mL) and 30% H_2O_2 (1 mL) were added dropwise. The reaction mixture was allowed to warm to room temperature, and was allowed to stir at room temperature for 3 hours. The reaction mixture was cooled to 0 ºC and $Na_2S_2O_3$ (aq. sat., 1 mL) was added dropwise (while monitoring temperature of the flask). After warming to room temperature the aqueous layer was extracted with ethyl acetate (3 x 7 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure, and subsequently purified via silica gel column chromatography to provide the desired products.

3.5.2.4 *Characterization of the Conjunctive Cross Coupling Products and Analysis of Stereochemistry*

^{11}B NMR spectra were recorded on a Varian Gemini-500 (160 MHz), with external standard ($BF_3 \cdot Et_2O$): 0.0 ppm. If the value is not specified, the ^{11}B chemical shifts for the compounds are 35-36 ppm.



3

(*R*)-1-phenylnonan-5-ol (3).

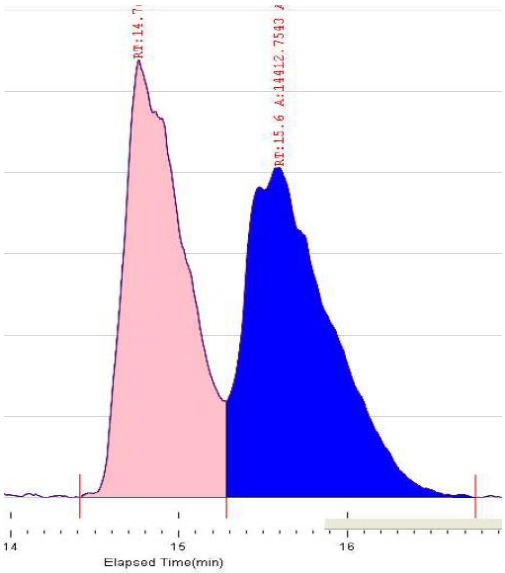
The reaction was performed according to the **General Procedure A** with vinylB(mac) (55.0 mg, 0.22 mmol, 1.1 equiv.), *n*-butyllithium (2.5 M in hexane, 0.08 mL, 0.2 mmol, 1.0 equiv.), and (3-iodopropyl)benzene (59.1 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). Boronic ester was purified prior to oxidation using 1% EtOAc in Hexanes. Crude boronic ester was then subjected to **Oxidation Procedure**. The crude alcohol was purified by silica gel column chromatography (3% EtOAc in hexanes, stained with CAM) to afford a colorless oil (30.0 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.20-7.16 (m, 3H), 3.61-3.56 (m, 1H), 2.63 (t, J = 7.7 Hz, 2H), 1.70-1.59 (m, 2H), 1.52-1.26 (m, 11H), 0.91 (t, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.8, 128.5, 128.4, 125.8, 72.1, 37.5, 37.4, 36.1, 31.7, 28.0, 25.5, 22.9, 14.2. IR (neat) ν_{max} 3346 (br, w), 3063 (w), 3026 (w), 2929 (s), 2857 (m), 1604 (w), 1496 (m), 1454 (m), 1378 (w), 1126 (w), 1058 (w), 1030 (w), 1002 (w), 901 (w), 746 (m), 698 (s) cm^{-1}. HRMS (DART) for $C_{16}H_{25}O_2$ $[M+H]^+$: Calc'd: 249.1849, found: 249.1840. $[\alpha]_D^{20}$: -2.382 (c = 0.850, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

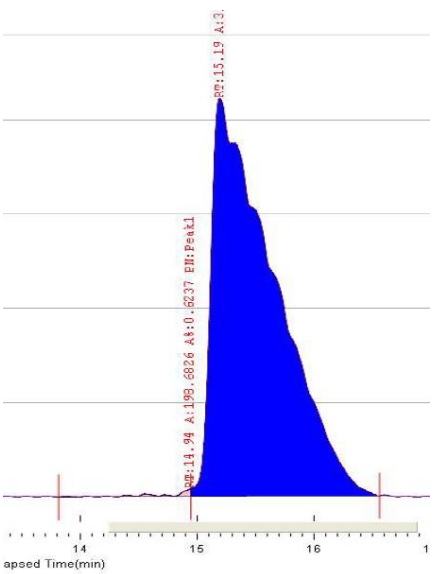
Racemic material was prepared by reaction of 5-phenylpentanal[21] and *n*-BuLi in THF at -78°C. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel OD-RH, 2% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (R)-1-phenylnonan-5-ol.

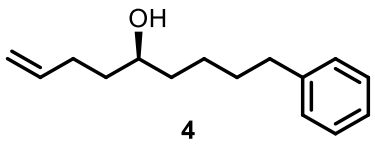
Racemic Material Standard Conditions



Peak No	% Area	Area	RT (min)
1	48.3089	13469.7353	14.76
2	51.6911	14412.7543	15.6
Total:	100	27882.4896	



Peak No	% Area	Area	RT (min)
1	0.6237	198.6826	14.94
2	99.3763	31656.556	15.19
Total:	100	31855.2386	



4

(*S*)-9-phenylnon-1-en-5-ol (4).

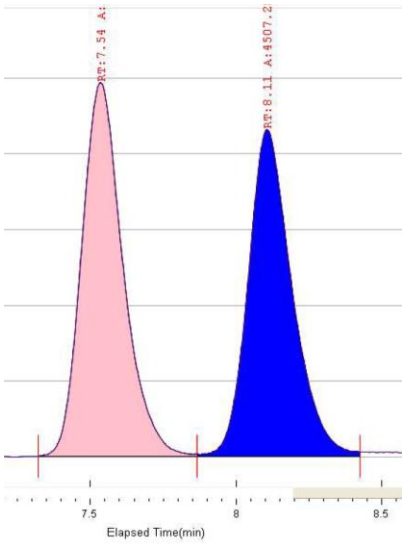
The reaction was performed according to the **General Procedure B** with 8-(but-3-en-1-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (61.2 mg, 0.22mmol, 1.1 equiv.), vinyllithium (1.45 M in THF, 0.137 mL, 0.2 mmol, 1.0 equiv.), and (3-iodopropyl)benzene (59.1 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). Boronic ester was purified prior to oxidation using 1% EtOAc in Hexanes. Crude boronic ester was then subjected to **Oxidation Procedure**. The crude alcohol was purified by silica gel column chromatography (5% EtOAc in hexanes, stained with CAM) to afford a colorless oil (24.0 mg, 55% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.19-7.18 (m, 3H), 5.88-5.81 (m, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 4.98 (d, *J* = 9.9 Hz, 1H), 3.65-3.60 (m, 1H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.24-2.17 (m, 1H), 2.17-2.10 (m, 1H), 1.71-1.60 (m, 2H), 1.49-1.37 (m, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 138.7, 128.5, 128.4, 125.8, 114.9, 71.5, 37.5, 36.6, 36.1, 31.6, 30.2, 25.4. IR (neat) ν_{max} 3340 (br, w), 3063 (w), 3026 (w), 2930 (s), 2856 (m), 1640 (w), 1604 (w), 1496 (w), 1453 (m), 1062 (w), 1030 (w), 995 (w), 909 (m), 746 (m), 698 (s), 646 (w) cm^{-1}. HRMS (DART+) for $C_{15}H_{21}$ $[M+H-H_2O]^+$: Calc'd: 201.1638, found: 201.1634. $[\alpha]_D^{20}$: -2.167 (c = 0.830, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

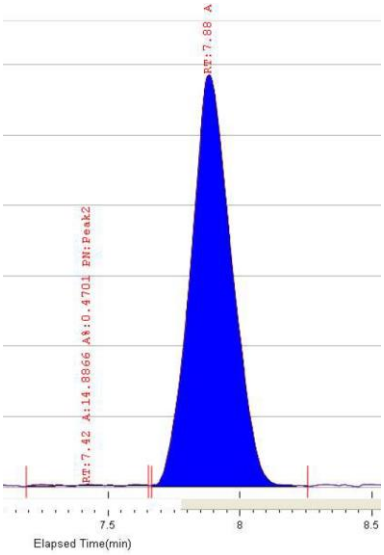
Chiral SFC (Chiracel AD-H, 7% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (S)-9-phenylnon-1-en-5-ol.

Racemic Material

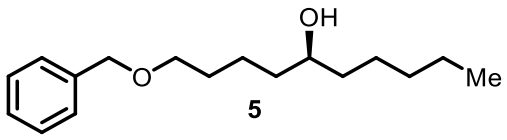


Peak No	% Area	Area	RT (min)
1	51.8232	4848.4241	7.54
2	48.1768	4507.282	8.11
Total:	100	9355.7061	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.4701	14.8866	7.42
2	99.5299	3152.0328	7.88
Total:	100	3166.9194	



5

(*S*)-1-(benzyloxy)decan-5-ol (5).

The reaction was performed according to the **General Procedure B** using 8-(4-(benzyloxy)butyl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (85.0 mg, 0.22 mmol, 1.1 equiv.), vinyllithium (1.52 M in THF, 0.131 mL, 0.2 mmol, 1.0 equiv.), 1-iodobutane (44.2 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). Boronic ester was purified prior to oxidation using 1% EtOAc in Hexanes. Crude boronic ester was then subjected to **Oxidation Procedure**. The crude alcohol was purified by silica gel column chromatography (5% EtOAc in hexanes, stained with CAM) to afford a colorless oil (31.7 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.32 (m, 4H), 7.29-7.26 (m, 1H), 4.51 (s, 2H), 3.61-3.56 (m, 1H), 3.48 (t, *J* = 6.5 Hz, 2H), 1.70-1.59 (m, 2H), 1.54-1.26 (m, 13H), 0.90 (t, *J* =

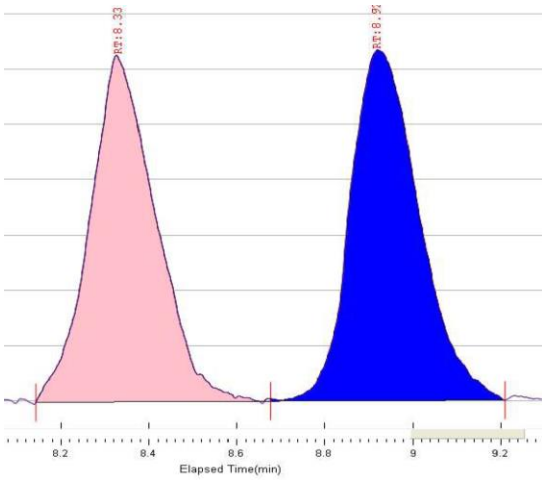
6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 128.5, 127.8, 127.6, 73.0, 72.0, 70.4, 37.6, 37.3, 32.0, 29.9, 25.5, 22.8, 22.5, 14.2. IR (neat) ν_{max} 3403 (br, w), 3030 (w), 2928 (s), 2857 (s), 2359 (w), 1496 (w), 1454 (m), 1363 (m), 1260 (w), 1204 (w), 1101 (s), 1028 (m), 908 (w), 805 (w), 734 (s), 697 (s), 614 (w) cm^{-1}. HRMS (DART+) for $C_{17}H_{29}O_2$ $[M+H]^+$: Calc'd: 265.2162, found: 265.2159. $[\alpha]_D^{20}$: -0.230 (c = 0.870, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

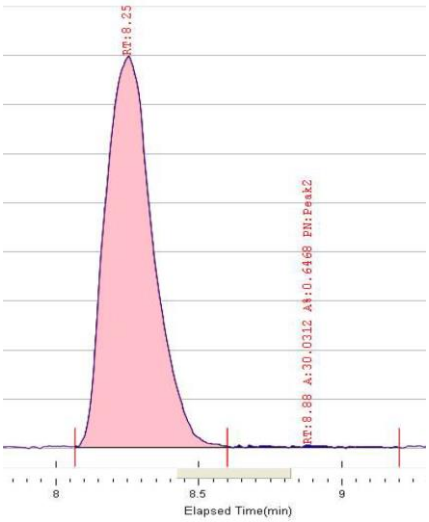
Chiral SFC (Chiracel OD-H, 7% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (S)-1-(benzyloxy)decan-5-ol.

Racemic Material

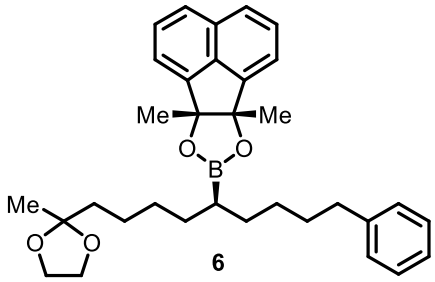


Peak No	% Area	Area	RT (min)
1	48.5806	1302.1548	8.33
2	51.4194	1378.2463	8.92
Total:	100	2680.4011	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	99.3532	4612.8672	8.25
2	0.6468	30.0312	8.88
Total:	100	4642.8984	



6

6b,9a-dimethyl-8-((*S*)-1-(2-methyl-1,3-dioxolan-2-yl)-9-phenylnonan-5-yl)-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (6).

The reaction was performed according to the **General Procedure B** with 6b,9a-dimethyl-8-[4-(2-methyl-1,3-dioxolan-2-yl)butyl]acenaphthyleno[1,2-d][1,3,2]dioxaborole (80.6

mg, 0.22 mmol, 1.1 equiv.), vinylithium (1.63 M in THF, 0.123 mL, 0.2 mmol, 1.0 equiv.), (3-iodopropyl)benzene (59.1 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude product was then purified by silica gel chromatography (20-45% dichloromethane in hexanes, stained in CAM) to afford a clear oil (53.3 mg, 52%).

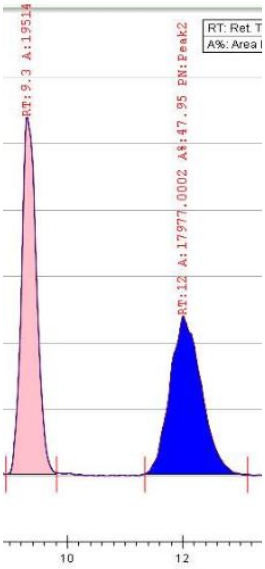
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 6.9 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 3.93-3.81 (m, 4H), 2.36 (m, 2H), 1.73 (s, 6H), 1.46-1.37 (m, 4H), 1.36-1.18 (m, 9H), 1.14-0.98 (m, 4H), 0.95-0.86 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 143.0, 134.7, 131.4, 128.5 (2), 128.2, 125.6, 125.3, 119.5, 110.3, 91.6, 64.7, 39.1, 35.9, 31.6, 31.3, 31.2, 29.4, 28.8, 24.4, 23.8, 23.6 (br), 22.1 (2). IR (neat) ν_{max} 3025 (w), 2980 (w), 2928 (s), 2856 (m), 2361 (w), 2014 (w), 1740 (w), 1454 (m), 1380 (m), 1308 (m), 1214 (m), 1117 (s), 1079 (s), 805 (m) cm^{-1}. HRMS (DART+) for $C_{33}H_{42}BO_4$ $[M+H]^+$: Calc'd: 513.3171, found: 513.3169. $[\alpha]_D^{20}$: -1.560 (c = 0.500, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

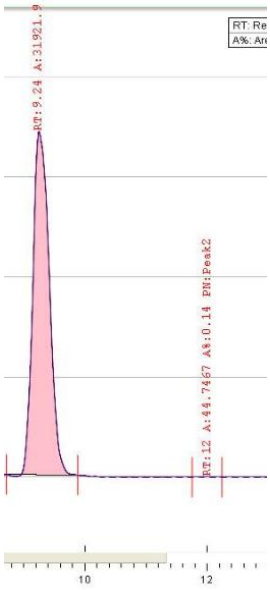
Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel OJ-H, 8% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of 6b,9a-dimethyl-8-((S)-1-(2-methyl-1,3-dioxolan-2-yl)-9-phenylnonan-5-yl)-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole.

Racemic Material

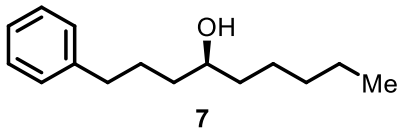


Standard Conditions



Peak Info			
Peak No	% Area	Area	RT (min)
1	52.05	19514.1072	9.3
2	47.95	17977.0002	12
Total:	100	37491.1074	

Peak Info			
Peak No	% Area	Area	RT (min)
1	99.86	31921.9619	9.24
2	0.14	44.7467	12
Total:	100	31966.7086	



7

(*S*)-1-phenylnonan-4-ol (7).

The reaction was performed according to **General Procedure B** with phenylpropylB(mac) (75.3mg, 0.22 mmol, 1.1 equiv.), vinylithium (1.45 M in THF, 0.138 mL, 0.2 mmol, 1.0 equiv.), 1-iodobutane (44.2 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). Boronic ester was purified prior to oxidation using 1% EtOAc in Hexanes. Crude boronic ester was then subjected to **Oxidation Procedure**. The crude alcohol was then purified by silica gel chromatography (2-3% EtOAc in hexanes, stained in CAM) to afford a clear oil (27.3 mg, 62%).

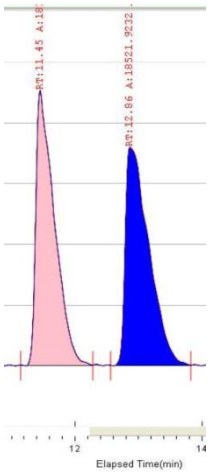
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.20-7.16 (m, 3H), 3.64-3.59 (m, 1H), 2.69-2.59 (m, 2H), 1.83-1.74 (m, 1H), 1.71-1.61 (m, 1H), 1.55-1.37 (m, 5H), 1.36-1.22 (m, 5H), 0.89 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 128.5, 128.4, 125.8, 72.0, 37.6, 37.2, 36.1, 32.0, 27.6, 25.4, 22.8, 14.2. IR (neat) ν_{max} 3347 (br), 3026 (s), 2929 (s), 2858 (s), 2359 (w), 2182 (w), 1454 (m), 748 (m), 698 (m) cm^{-1}. HRMS (DART+) for $C_{15}H_{28}NO$ $[M+NH_4]^+$: Calc'd: 238.2165, found: 238.2163. $[\alpha]_D^{20}$: 0.914 (c = 0.500 $CHCl_3$, l=50 mm).

Analysis of Stereochemistry:

A stereoisomer mixture was prepared by the synthesis of racemic product. To a 2-dram vial equipped with a stir bar was added (3-iodopropyl)benzene (128 mg, 0.520 mmol, 1 equiv), followed by Et_2O : pentane (2:3, 2 mL: 3 mL, 0.1 M). Then the vial was flushed with nitrogen and cooled down to -78 °C. *tert*-butyllithium (1.14 mmol, 73.18 mg, 2.2 equiv) was then added dropwise over five minutes. The reaction was then brought to room temperature and allowed to stir for one hour. The mixture was then cooled down to -78 °C and hexanal (104 mg, 1.04 mmol, 2 equiv) was added and allowed to stir at -78 °C for 3 hours, and then warmed to room temperature and stirred for an additional 18 hours. The mixture was then quenched with water, followed by extraction of the aqueous layer three times with ethyl acetate. The organic layers were then dried with sodium sulfate and concentrated under reduced pressure. The crude material was then purified via silica gel chromatography (4% EtOAc in hexanes) to yield a colorless oil (0.281 mmol, 62 mg, 54%). Absolute stereochemistry was assigned via analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel ODR-H, 3% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (S)-1-phenylnonan-4-ol.

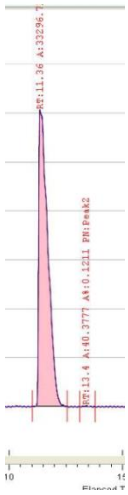
Racemic Material



Peak Info

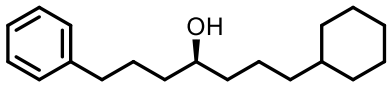
Peak No	% Area	Area	RT (min)
1	49.7954	18370.9779	11.45
2	50.2046	18521.9232	12.86
Total:	100	36892.9011	

Standard Conditions



Peak Info

Peak No	% Area	Area	RT (min)
1	99.8789	33296.7199	11.36
2	0.1211	40.3777	13.4
Total:	100	33337.0976	



8

(*S*)-1-cyclohexyl-7-phenylheptan-4-ol (8).

The reaction was performed according to the **General Procedure B** with phenylpropylB(mac) (75.3 mg, 0.22 mmol, 1.1 equiv.), vinylithium (1.45 M in THF, 0.138 mL, 0.2 mmol, 1.0 equiv.), 2-iodoethylcyclohexane (57.2 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL, 0.13M). Crude boronic ester was then subjected to **Oxidation Procedure**. The crude alcohol was then purified by silica gel chromatography (2% EtOAc in hexanes, stained in CAM) to afford a clear oil (34.0 mg, 62%).

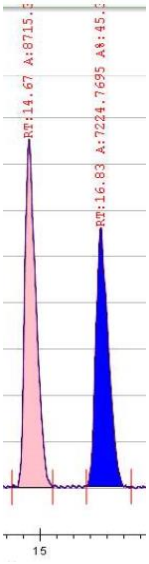
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.25 (m, 3H), 7.20-7.16 (m, 2H), 3.65-3.58 (m, 1H), 2.69-2.58 (m, 2H), 1.84-1.73 (m, 1H), 1.72-1.60 (m, 6H), 1.55-1.34 (m, 5H), 1.34-1.23 (m, 3H), 1.23-1.08 (m, 5H), 0.91-0.80 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 128.5, 128.4, 125.8, 72.0, 37.9, 37.8, 37.6, 37.2, 36.1, 33.6, 33.5, 27.6, 26.9, 26.6, 23.0. IR (neat) ν_{max} 3463 (br), 2920 (s), 2850 (m), 2360 (m), 2335 (m), 1453 (w), 744 (w) cm^{-1}. HRMS (DART+) for $C_{19}H_{34}NO$ $[M+NH_4]^+$: Calc'd: 292.2635, found: 292.2632. $[\alpha]_D^{20}$: 0.400 (c = 0.500, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol %) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

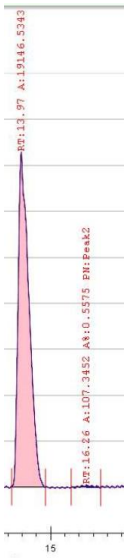
Chiral SFC (Chiracel OJ-H, 8% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (S)-1-cyclohexyl-7-phenylheptan-4-ol.

Racemic Material

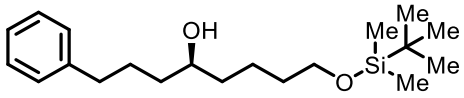


Peak Info			
Peak No	% Area	Area	RT (min)
1	54.6756	8715.3673	14.67
2	45.3244	7224.7695	16.83
Total:	100	15940.1368	

Standard Conditions



Peak Info			
Peak No	% Area	Area	RT (min)
1	99.4425	19146.5343	13.97
2	0.5575	107.3452	16.26
Total:	100	19253.8795	



9

(*R*)-8-((tert-butyldimethylsilyl)oxy)-1-phenyloctan-4-ol (9).
The reaction was performed according to **General Procedure B** with phenylpropylB(mac) (75.3 mg, 0.22 mmol, 1.1 equiv.), vinylithium (1.45 M in THF, 0.138 mL, 0.2 mmol, 1.0 equiv.), *tert*-butyl-(3-iodopropoxy)-dimethyl-silane (72.1 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). Crude boronic ester was then subjected to **Oxidation Procedure**. The crude product was then purified by silica gel chromatography (2-3% EtOAc in hexanes, stained in CAM) to afford a clear oil (39.7 mg, 59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.25 (m, 3H), 7.20-7.16 (m, 2H), 3.65-3.59 (m, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.66-2.60 (m, 2H), 1.83-1.74 (m, 1H), 1.71-1.62 (m, 1H) 1.56-1.33 (m, 8H), 0.89 (s, 10H), 0.05 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 128.5,

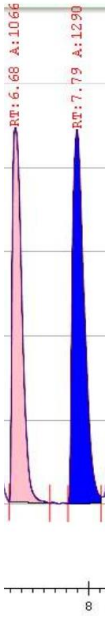
128.4, 125.9, 71.9, 63.2, 37.3, 37.1, 36.1, 32.9, 27.6, 26.1, 22.1, 18.5, -5.1. IR (neat) ν_{max} 3374 (br), 3026 (s), 2929 (s), 2857 (s), 1471 (m), 1255 (m), 1098 (s), 836 (s), 775 (s) cm^{-1}. HRMS (DART+) for $C_{20}H_{37}O_2Si$ $[M+H]^+$: Calc'd: 337.2557, found: 337.2543. $[\alpha]_D^{20}$: 1.400 (c = 0.500, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol %) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel OJ-H, 3% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (R)-8-((tert-butyldimethylsilyl)oxy)-1-phenyloctan-4-ol.

Racemic Matieral



Peak Info			
Peak No	% Area	Area	RT (min)
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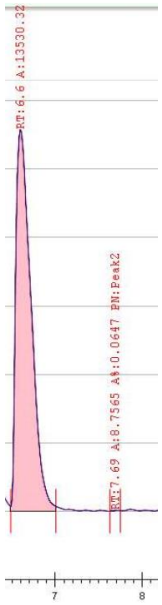
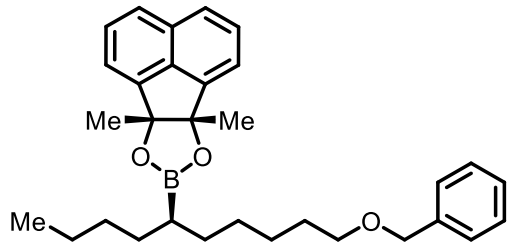
2	54.7497	12906.6862	7.79
Total:	100	23573.9666	

Standard Conditions



Peak Info			
Peak No	% Area	Area	RT (min)
1	99.9353	13530.3274	6.6
2	0.0647	8.7565	7.69
Total:	100	13539.0839	



10

8-((*R*)-10-(benzyloxy)decan-5-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (10).

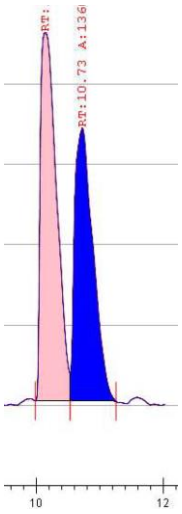
The reaction was performed according to the **General Procedure B** with *n*-butylB(mac) (61.6 mg, 0.22 mmol, 1.1 equiv.), vinyllithium (1.51 M in THF, 0.131 mL, 0.2 mmol, 1.0 equiv.), ((4-iodobutoxy)methyl)benzene (69.6 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude boronic ester was purified by silica gel column chromatography (5% EtOAc in hexanes, stained with CAM) to afford a colorless oil (51.2 mg, 55% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.59-7.56 (m, 2H), 7.53 (d, *J* = 6.5 Hz, 2H), 7.34-7.32 (m, 4H), 7.27-7.26 (m, 1H), 4.44 (s, 2H), 3.29 (t, *J* = 6.8 Hz, 2H), 1.75 (s, 6H), 1.44-1.38 (m, 2H), 1.32-1.24 (m, 4H), 1.17-0.99 (m, 8H), 0.92-0.87 (m, 1H), 0.69 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 138.9, 134.7, 131.4, 128.5, 128.4, 127.7, 127.5, 125.2, 119.5, 91.6, 72.9, 70.6, 31.4, 31.3, 31.0, 29.7, 29.0, 26.3, 23.7 (br), 22.9, 22.2, 14.1. ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.9. IR (neat) ν_{max} 3031 (w), 2925 (m), 2853 (m), 1497 (w), 1454 (m), 1380 (m), 1306 (m), 1252 (m), 1230 (m), 1213 (m), 1174 (m), 1115 (s), 1077 (s), 1028 (m), 968 (m), 885 (m), 825 (s), 777 (s), 733 (m), 696 (m), 612 (w) cm^{-1} HRMS (DART+) for $C_{31}H_{40}BO_3[M+H]^+$: Calc'd: 471.3065, found: 471.3076. $[\alpha]_D^{20}$: -0.471 (c = 0.425, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel OJ-H, 4% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of 8-((R)-10-(benzyloxy)decan-5-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole.

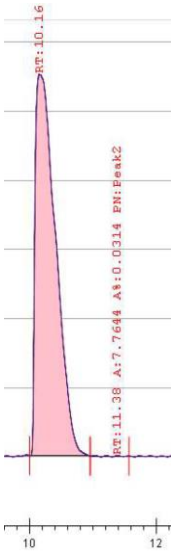
Racemic Material



Peak Info

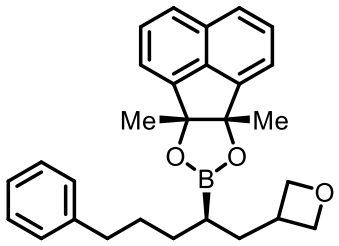
Peak No	% Area	Area	RT (min)
1	54.3517	16199.1162	10.15
2	45.6483	13605.1598	10.73
Total:	100	29804.276	

Standard Conditions



Peak Info

Peak No	% Area	Area	RT (min)
1	99.9686	24693.0679	10.16
2	0.0314	7.7644	11.38
Total:	100	24700.8323	



11

6b,9a-dimethyl-8-((*R*)-1-(oxetan-3-yl)-5-phenylpentan-2-yl)-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (11).

The reaction was performed according to the **General Procedure B** with phenylpropylB(mac) (75.3 mg, 0.22 mmol, 1.1 equiv.), vinyllithium (1.51 M in THF, 0.131 mL, 0.2 mmol, 1.0 equiv.), 3-iodooxetane (44.2 mg, 0.24mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude boronic ester was purified by silica gel column chromatography (10% EtOAc in hexanes, stained with CAM) to afford a colorless oil (37.2 mg, 44% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.60 (ddd, *J* = 8.0, 6.9, 3.4 Hz, 2H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.23-7.20 (m, 2H), 7.16-7.13 (m, 1H), 7.00 – 6.91 (m, 2H), 4.54 (dd, *J* = 7.8, 5.8 Hz, 1H), 4.40 (dd, *J* = 7.8, 5.8 Hz, 1H), 4.19 (t, *J* = 6.2 Hz, 1H), 4.09 (t, *J* = 6.2 Hz, 1H), 2.79 (hept, *J* = 7.4 Hz, 1H), 2.48-2.39 (m, 2H), 1.76 (s, 6H), 1.71-1.25 (m, 6H), 0.93-0.87 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.7 (2), 142.6, 134.6, 131.4, 128.6, 128.3 (2), 125.6, 125.5, 119.6, 119.5, 91.9, 78.1, 78.0, 36.1, 35.6, 35.1, 31.2, 30.8, 22.2, 22.1. Due to the quadrupolar nature of boron,

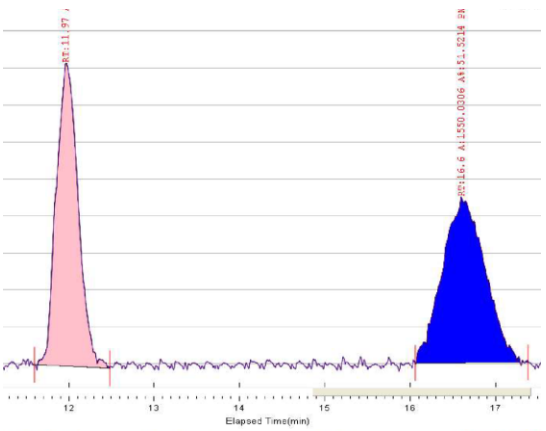
the carbon adjacent to boron was not detectable. IR (neat) ν_{max} 3025 (w), 2929 (s), 2859 (s), 1602 (w), 1496 (m), 1454 (m), 1383 (s), 1314 (s), 1262 (m), 1213 (m), 1175 (m), 1116 (s), 1078 (s), 1031 (w), 977 (m), 886 (w), 845 (s), 826 (w), 805 (w), 779 (s), 749 (m), 700 (m), 684 (w) cm^{-1}. HRMS (DART+) for $C_{28}H_{32}BO_3$ $[M+H]^+$: Calc'd: 427.3439, found: 427.2431. $[\alpha]_D^{20}$: -0.200 (c = 1.00, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

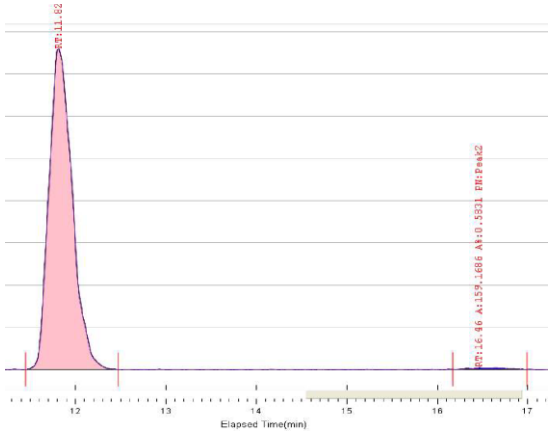
Chiral SFC (Chiracel OJ-H, 6% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of 6b,9a-dimethyl-8-((R)-1-(oxetan-3-yl)-5-phenylpentan-2-yl)-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole.

Racemic Material

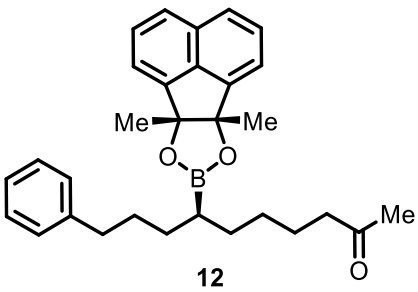


Peak No	% Area	Area	RT (min)
1	48.4786	1458.4893	11.97
2	51.5214	1550.0306	16.6
Total:	100	3008.5199	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	99.4169	27136.1817	11.82
2	0.5831	159.1686	16.46
Total:	100	27295.3503	



12

(7*S*)-7-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborol-8-yl)-10-phenyldecan-2-one (12).

The reaction was performed according to the **General Procedure B** with phenylpropylB(mac) (75.3 mg, 0.22 mmol, 1.1 equiv.), vinylithium (1.45 M in THF, 0.138 mL, 0.2 mmol, 1.0 equiv.), 5-iodopentan-2-one (50.9 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude product was then purified by silica gel chromatography (6% EtOAc in hexanes, stained in CAM) to afford a clear oil (20.0 mg, 22%).

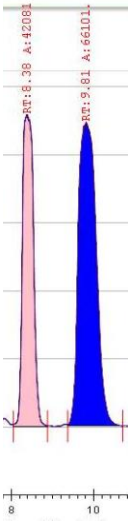
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.59 (ddd, *J* = 8.1, 7.0, 2.3 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H), 6.93 (d, *J* = 7.0 Hz, 2H), 2.45-2.37 (m, 2H), 2.17 (td, *J* = 7.9, 2.3 Hz, 2H), 2.04 (s, 3H), 1.76 (s, 6H), 1.43-1.20 (m, 8H), 1.12-0.99 (m, 2H), 0.99-0.93 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.4, 145.0 (2), 142.9, 134.7, 131.5, 128.6, 128.4, 128.2, 125.5, 125.3, 119.5, 91.7, 43.8, 36.1, 31.1, 31.0, 30.9, 29.9, 28.6, 24.1, 22.2. Due to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. IR (neat) ν_{max} 3026 (w), 2972 (w), 2926 (m), 2852 (w), 2361 (w), 2195 (w), 1974 (w), 1715 (m), 1382 (m), 1308 (m), 1117 (w), 1079 (w), 826 (m), 780 (m) cm^{-1}. HRMS (DART+) for $C_{30}H_{36}BO_3$ $[M+H]^+$: Calc'd: 455.2752, found: 455.2763. $[\alpha]_D^{20}$: 0.540 (c = 0.370, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel OJ-H, 7% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (7S)-7-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)-10-phenyldecan-2-one:

Racemic Material



Peak Info

Peak No	% Area	Area	RT (min)
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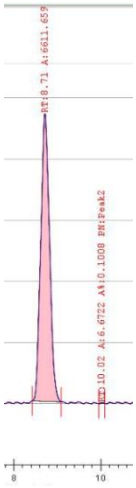
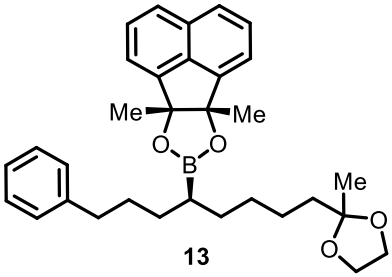
2	61.1016	66101.6519	9.81
Total:	100	108183.1241	

Standard Conditions



Peak Info

Peak No	% Area	Area	RT (min)
1	99.8992	6611.659	8.71
2	0.1008	6.6722	10.02
Total:	100	6618.3312	



13

6b,9a-dimethyl-8-((*S*)-8-(2-methyl-1,3-dioxolan-2-yl)-1-phenyloctan-4-yl)-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (13).

The reaction was performed according to the **General Procedure B** with phenylpropylB(mac) (75.3 mg, 0.22 mmol, 1.1 equiv.), vinylithium (1.45 M in THF, 0.138 mL, 0.2 mmol, 1.0 equiv.), 2-(3-iodopropyl)-2-methyl-1,3-dioxolane (61.5 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude product was then purified by silica gel chromatography (7% EtOAc in hexanes, stained in CAM) to afford a clear oil (56.1 mg, 56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.58 (ddd, *J* = 8.1, 7.0, 3.0 Hz, 2H), 7.54 (dd, *J* = 6.9, 2.1 Hz, 2H) 7.18 (t, *J* = 7.4 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.0 Hz, 2H), 3.92-3.84 (m, 4H), 2.44-2.35 (m, 2H), 1.75 (s, 6H), 1.48-1.41 (m, 2H), 1.38-1.29 (m, 5H), 1.29-1.20 (m, 5H), 1.15-1.02 (m, 3H), 0.99-0.93 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0 (2), 142.9, 134.7, 131.4, 128.5, 128.3, 128.2, 125.5, 125.3, 119.5, 110.3, 91.7, 91.6, 64.6, 39.1, 36.1, 31.3, 31.1, 30.9, 29.4, 24.4, 23.8, 22.2, 22.1. Due

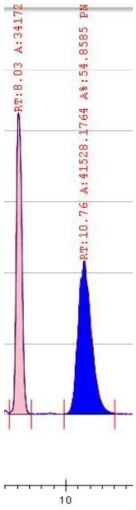
to the quadrupolar nature of boron, the carbon adjacent to boron was not detectable. IR (neat) ν_{max} 3444 (br), 3026 (w), 3026 (w), 2933 (m), 2858 (m), 2365 (w), 1714 (w), 1461 (s), 1380 (s), 1309 (m), 1079 (s), 989 (s), 780 (m) cm^{-1}. HRMS (DART+) for $C_{32}H_{40}BO_4$ $[M+H]^+$: Calc'd: 449.3014, found: 499.3033. $[\alpha]_D^{20}$: 0.514 (c = 0.500, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel OJ-H, 8% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of 6b,9a-dimethyl-8-((S)-8-(2-methyl-1,3-dioxolan-2-yl)-1-phenyloctan-4-yl)-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole.

Racemic Material



Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
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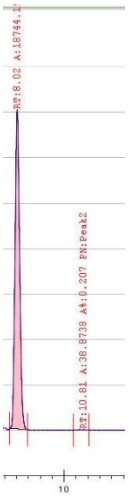
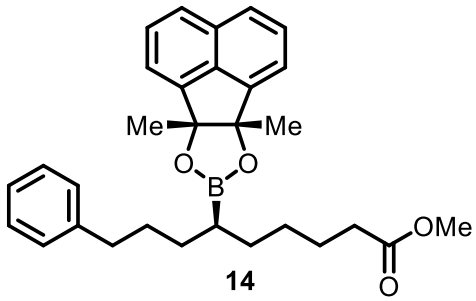
2	54.8585	41528.1764	10.76
Total:	100	75700.5293	

Standard Conditions



Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	99.793	18744.1989	8.02
2	0.207	38.8738	10.81
Total:	100	18783.0727	



14

methyl (6*S*)-6-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborol-8-yl)-9-phenylnonanoate (14).

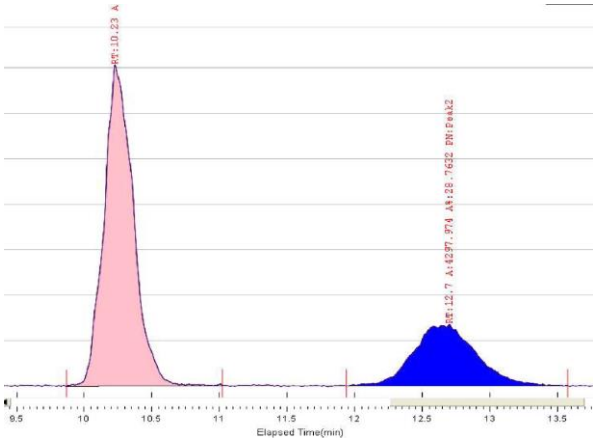
The reaction was performed according to the **General Procedure B** with phenylpropylB(mac) (75.3 mg, 0.22 mmol, 1.1 equiv.), vinyllithium (1.51 M in THF, 0.131mL, 0.2mmol, 1.0 equiv.), and methyl 4-iodobutanoate (54.7 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S,S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude boronic ester was purified by silica gel column chromatography (5% EtOAc in hexanes, stained with CAM) to afford a colorless oil (56.1 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.62-7.58 (m, 2H), 7.57-7.55 (m, 2H), 7.22-7.19 (m, 2H), 7.15-7.12 (m, 1H), 6.94-6.92 (m, 2H), 3.64 (s, 3H), 2.47-2.37 (m, 2H), 2.13 (t, *J* = 7.9 Hz, 2H), 1.78 (s, 6H), 1.53-1.45 (m, 2H), 1.41-1.27 (m, 6H), 1.19-1.06 (m, 2H), 1.03-0.95 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 145.0 (2), 142.8, 134.7, 131.4, 128.5, 128.3, 128.2, 125.5, 125.3, 119.5, 91.7, 51.5, 36.1, 34.1, 31.0, 30.9, 30.8, 28.6, 25.2, 23.4 (br), 22.1 (2). IR (neat) ν_{max} 3025 (w), 2928 (m), 2854 (m), 1738 (s), 1602 (w), 1497 (w), 1454 (m), 1435 (m), 1413 (m), 1382 (m), 1308 (m), 1262 (m), 1213 (m), 1174 (m), 1117 (s), 1078 (m), 968 (w), 885 (w), 826 (m), 779 (m), 750 (m), 700 (m) cm^{-1}. HRMS (DART+) for $C_{30}H_{36}BO_4$ $[M+H]^+$: Calc'd: 471.2701, found: 471.2706. $[\alpha]_D^{20}$: +1.571 (c = 1.00, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

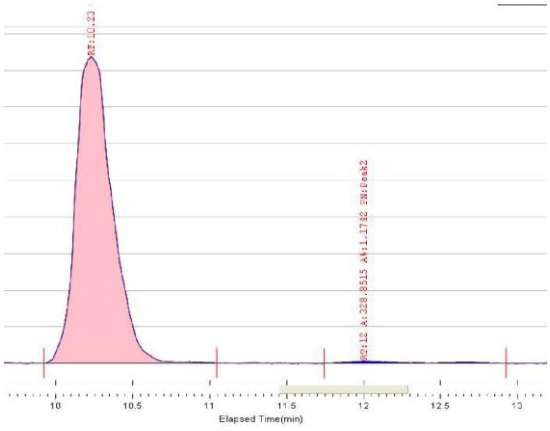
Chiral SFC (Chiracel OJ-H, 6% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of methyl (6S)-6-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)-9-phenylnonanoate.

Racemic Material

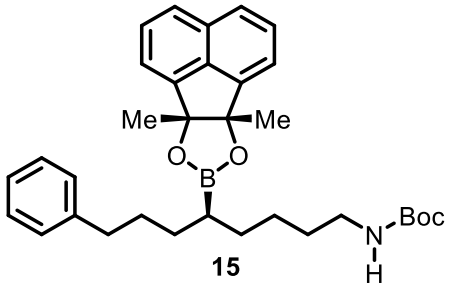


Peak Info			
Peak No	% Area	Area	RT (min)
1	71.2368	10644.6379	10.23
2	28.7632	4297.974	12.7
Total:	100	14942.6119	

Standard Conditions



Peak Info			
Peak No	% Area	Area	RT (min)
1	98.8258	27677.3806	10.23
2	1.1742	328.8515	12
Total:	100	28006.2321	



15

***tert*-butyl ((5*R*)-5-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborol-8-yl)-8-phenyloctyl)carbamate (15).**

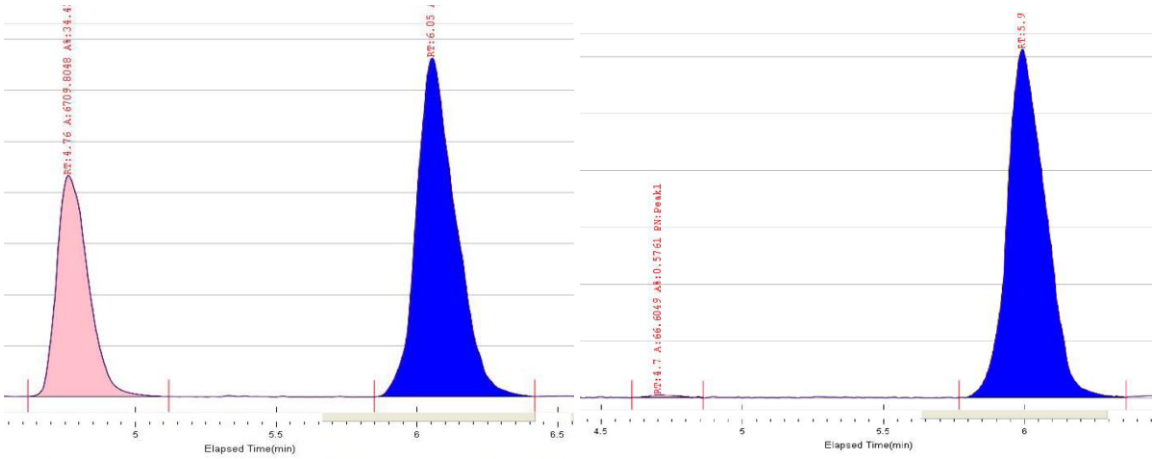
The reaction was performed according to the **General Procedure B** with phenylpropylB(mac) (75.3 mg, 0.22 mmol, 1.1 equiv.), vinyllithium (1.51 M in THF, 0.131mL, 0.2mmol, 1.0 equiv.), and *tert*-butyl N-(3-iodopropyl)carbamate (68.4 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude boronic ester was purified by silica gel column chromatography (10% EtOAc in hexanes, stained with CAM) to afford a colorless oil (63.3 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.60 (ddd, *J* = 8.1, 6.8, 1.8 Hz, 2H), 7.55 (d, *J* = 6.9 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.3 Hz, 2H), 4.34-4.11 (br s, 1H), 2.99-2.79 (m, 2H), 2.48-2.36 (m, 2H), 1.77 (s, 6H), 1.46 (s, 9H), 1.41-1.23 (m, 8H), 1.17-1.03 (m, 2H), 1.01-0.93 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 144.9, 142.8, 134.7, 131.4, 128.6, 128.3, 128.2, 125.5, 125.3, 119.5, 119.5, 91.7, 79.0, 40.5, 36.1, 31.1, 30.9, 30.8, 30.0, 28.6, 26.2, 23.6 (br), 22.1. IR (neat) ν_{max} 3360 (br, w), 3025 (w), 2975 (m), 2928 (m), 2856 (m), 1713 (s), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1307 (m), 1249 (m), 1174 (s), 1117 (s), 1078 (m), 1041 (w), 968 (w), 886 (w), 826 (m), 779 (m), 749 (w), 699 (m), 683 (w), 668 (w) cm^{-1}. HRMS (DART+) for $C_{33}H_{43}BNO_4$ $[M+H]^+$: Calc'd: 528.3280, found: 528.3286. $[\alpha]_D^{20}$: +0.057 (c = 1.00, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

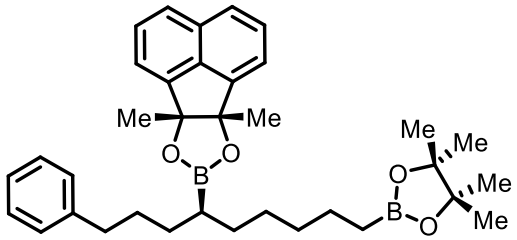
Chiral SFC (Chiracel AD-H, 12% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of tert-butyl ((5R)-5-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)-8-phenyloctyl)carbamate.

Racemic Material Standard Conditions



Peak No	% Area	Area	RT (min)
1	34.4373	6709.8048	4.76
2	65.5627	12774.3288	6.05
Total:	100	19484.1336	

Peak No	% Area	Area	RT (min)
1	0.5761	66.6049	4.7
2	99.4239	11494.9649	5.99
Total:	100	11561.5698	



16

6b,9a-dimethyl-8-((*S*)-1-phenyl-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonan-4-yl) 6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (16).

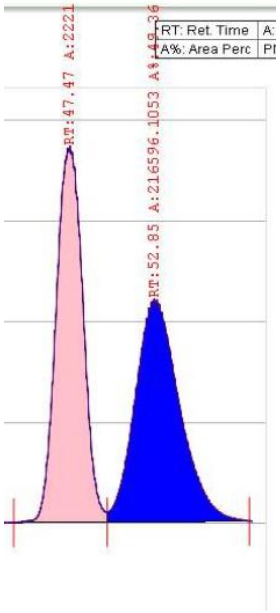
The reaction was performed according to **General Procedure B** with phenylpropylB(mac) (75.3 mg, 0.22 mmol, 1.1 equiv.), vinylithium (1.63 M in THF, 0.123mL, 0.2 mmol, 1.0 equiv.), 2-(4-iodobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (74.4 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude boronic ester was then purified by silica gel chromatography (30-60% dichloromethane in hexanes, stained in CAM) to afford a clear oil (60.8 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2H), 7.58 (tdd, J=8.1, 2.1, 1.0 Hz, 2H), 7.55-7.52 (m, 2H), 7.17 (t, J = 7.7 Hz, 2H), 7.11 (t, J = 6.7 Hz, 1H) 6.89 (d, J = 8.0 Hz, 2H), 2.44-2.32 (m, 2H), 1.75 (s, 6H), 1.37-1.29 (m, 5H), 1.24 (s, 14H), 1.18-1.05 (m, 5H), 0.99-0.91 (m, 1H), 0.65 (t, J = 7.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 145.0, 142.9, 134.7, 131.4, 128.5, 128.3, 128.2, 125.4, 125.3, 119.5, 91.6, 82.9, 36.1, 32.7, 31.3, 31.1, 30.9, 28.9, 25.0, 24.0, 23.6 (br), 22.2 (2), 11.2 (br). IR (neat) ν_{max} 3025 (w), 2977 (m), 2925 (s), 2855 (m), 2361 (w), 2235 (w), 1379 (s), 1310 (s), 1146 (m), 1079 (m), 847 (m), 825 (m), 805 (m), 536 (m) cm^{-1}. HRMS (DART+) for $C_{35}H_{47}B_2O_4$ $[M+H]^+$: Calc'd: 553.3655, found: 553.3681. $[\alpha]_D^{20}$: -0.743 (c = 0.500, $CHCl_3$, l=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

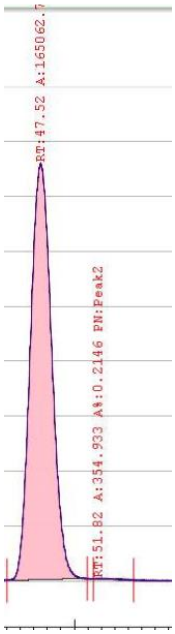
Chiral SFC (Chiracel OJ-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of 6b,9a-dimethyl-8-((S)-1-phenyl-9-(4,4,5,5 tetramethyl-1,3,2-dioxaborolan-2-yl)nonan-4-yl) 6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole.

Racemic Material

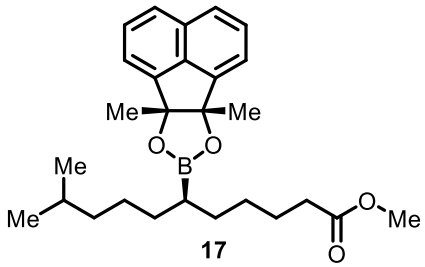


Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	50.6336	222156.2969	47.47
2	49.3664	216596.1053	52.85
Total:	100	438752.4022	

Standard Conditions



Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	99.7854	165062.7596	47.52
2	0.2146	354.933	51.82
Total:	100	165417.6926	



17

methyl (6*S*)-6-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)-10-methylundecanoate (17).

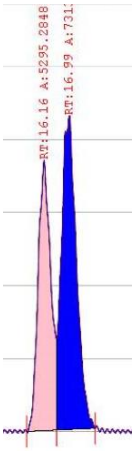
The reaction was performed according to general procedure **General Procedure B** with 8-isohexyl-6b,9a-dimethyl-acenaphthyleno[1,2-d][1,3,2]dioxaborole (67.8 mg, 0.22 mmol, 1.1 equiv.), vinylithium (1.63 M in THF, 0.123 mL, 0.2 mmol, 1.0 equiv.), methyl 4-

iodobutanoate (54.7 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude product was then purified by silica gel chromatography (6% EtOAc in hexanes, stained in CAM) to afford a clear oil (47.1 mg, 54%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 6.8 Hz, 2H), 3.62 (s, 3H), 2.11 (t, *J* = 7.5 Hz, 2H), 1.76 (s, 6H), 1.46 (p, *J* = 7.8 Hz, 2H), 1.37-1.18 (m, 5H), 1.18-0.87 (m, 7H), 0.66 (dd, *J* = 8.7, 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 145.0, 134.7, 131.5, 128.5, 125.3, 119.5, 91.6, 51.5, 39.1, 34.1, 31.6, 31.0, 28.7, 27.8, 26.8, 25.2, 23.7 (br), 22.6, 22.5, 22.1. IR (neat) ν_{max} 2951 (s), 2925 (s), 2854 (m), 2360 (w), 2335 (w), 2181 (w), 1978 (w), 1740 (s), 1382 (m), 1308 (m), 1117 (s), 1079 (m), 826 (m), 779 (m) cm^{-1}. HRMS (DART+) for $C_{27}H_{38}BO_4$ $[M+H]^+$: Calc'd: 437.2858, found: 437.2874. $[\alpha]_D^{20}$: 0.550° (c = 0.500, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:
Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel AD-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of methyl (6S)-6-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)-10-methylundecanoate.

Racemic Material



Peak Info			
Peak No	% Area	Area	RT (min)
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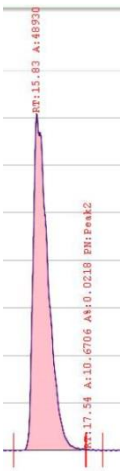
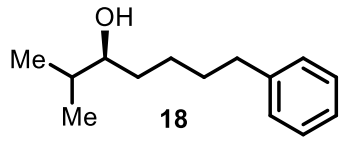
2	58.0022	7313.2115	16.99
Total:	100	12608.4963	

Standard Conditions



Peak Info			
Peak No	% Area	Area	RT (min)
1	99.9782	48930.2524	15.83
2	0.0218	10.6706	17.54
Total:	100	48940.923	



(*S*)-2-methyl-7-phenylheptan-3-ol (18).

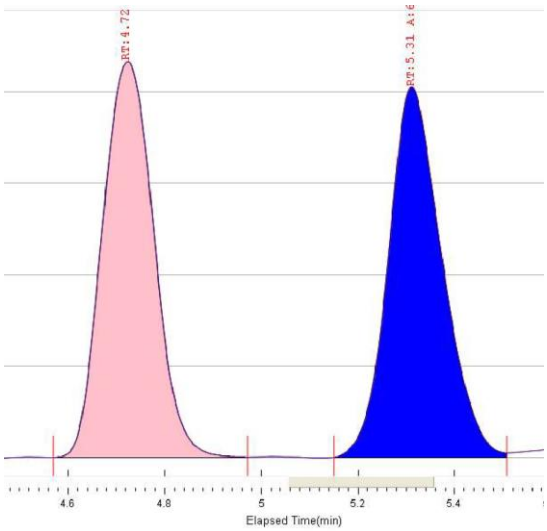
The reaction was performed according to the **General Procedure A** with vinylB(pin) (33.9 mg, 0.22 mmol, 1.1 equiv.), isopropyllithium (0.643 M in pentane, 0.31 mL, 0.2 mmol, 1.0 equiv.), and (3-iodopropyl)benzene (59.1 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). Boronic ester was purified prior to oxidation using 1% EtOAc in Hexanes. Crude boronic ester was then subjected to **Oxidation Procedure**. The crude alcohol was purified by silica gel column chromatography (3% EtOAc in hexanes, stained with CAM) to afford a colorless oil (21.2 mg, 51% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.18-7.16 (m, 3H), 3.37-3.33 (m, 1H), 2.66-2.59 (m, 2H), 1.71-1.59 (m, 3H), 1.56-1.46 (m, 2H), 1.44-1.34 (m, 2H), 1.30 (br s, 1H), 0.90 (t, J = 6.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.8, 128.5, 128.4, 125.8, 76.8, 36.1, 34.1, 33.6, 31.7, 25.9, 19.0, 17.2. IR (neat) ν_{max} 3026 (w), 3363 (br, w), 3063 (w), 3026 (w), 2932 (s), 2857 (m), 1604 (w), 1496 (m), 1463 (m), 1453 (m), 1385 (w), 1367 (w), 1130 (w), 1056 (w), 1030 (w), 983 (m), 875 (w), 746 (m), 698 (s), 568 (w) cm^{-1}. HRMS (DART+) for $C_{14}H_{26}NO$ $[M+NH_4]^+$: Calc'd: 224.2009, found: 224.2007. $[\alpha]_D^{20}$: -18.618 (c = 0.830, $CHCl_3$, l=50 mm).

Analysis of Stereochemistry:

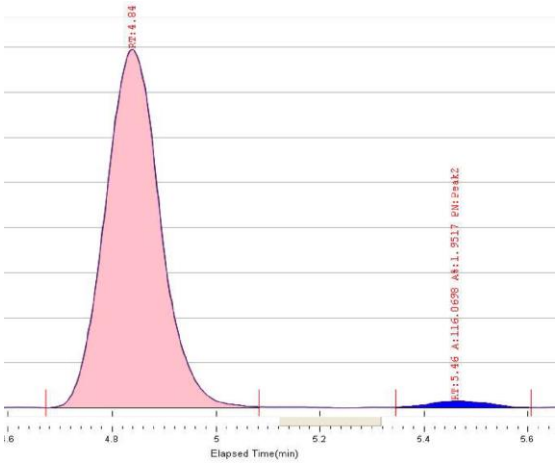
Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the general procedure A with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel OD-RH, 4% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (S)-2-methyl-7-phenylheptan-3-ol.

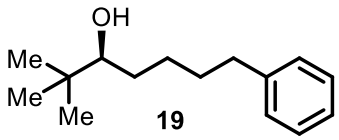
Racemic Material Standard Conditions



Peak No	% Area	Area	RT (min)
1	50.6181	6382.3954	4.72
2	49.3819	6226.5221	5.31
Total:	100	12608.9175	



Peak No	% Area	Area	RT (min)
1	98.0483	5831.0083	4.84
2	1.9517	116.0698	5.46
Total:	100	5947.0781	



19

(*S*)-2,2-dimethyl-7-phenylheptan-3-ol (19).

The reaction was performed according to the **General Procedure A** with vinylB(pin) (33.9 mg, 0.22 mmol, 1.1 equiv.), *tert*-butyllithium (1.70 M in pentane, 0.118 mL, 0.2 mmol, 1.0 equiv.), and (3-iodopropyl)benzene (59.1 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The reaction was also run at 45 °C, in an oil bath. Boronic ester was purified prior to oxidation using 1% EtOAc in Hexanes. Crude boronic ester was then subjected to **Oxidation Procedure**. The crude alcohol was purified by silica gel column chromatography (20-50% DCM in hexanes, stained with CAM) to afford a colorless oil (11.0 mg, 25% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 3.18 (d, J = 10.5 Hz, 1H), 2.67-2.59 (m, 2H), 1.72-1.24 (m, 7H), 0.89 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 128.6, 128.4, 125.8, 80.0, 36.2, 35.1, 31.7, 31.5, 26.9, 25.8. IR (neat) ν_{max} 3404 (br, w), 3063 (w), 3026 (w), 2936 (s), 2858 (s), 1604 (w), 1496 (m), 1478 (m), 1464 (m), 1454 (m), 1392 (m), 1363 (m), 1328 (w), 1084 (m), 1030 (w), 995 (m), 908 (w), 746 (m), 698 (s) cm^{-1}. HRMS (DART) for $C_{15}H_{23}$ $[M+H-H_2O]^+$: Calc'd: 203.1794, found: 203.1786. $[\alpha]_D^{20}$: -28.323 (c = 0.475, $CHCl_3$, l=50 mm).

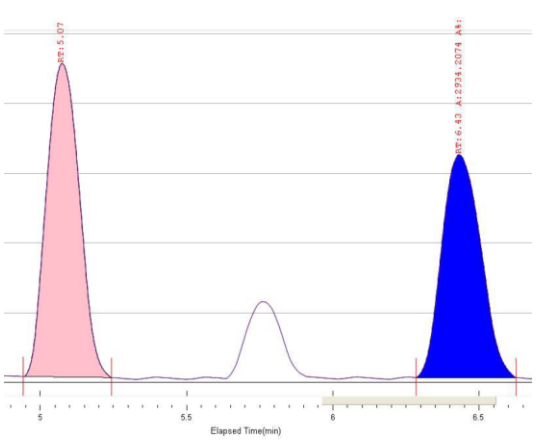
Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure A** with (*R*,*R*)-Ph-Pybox (12 mol%)

as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

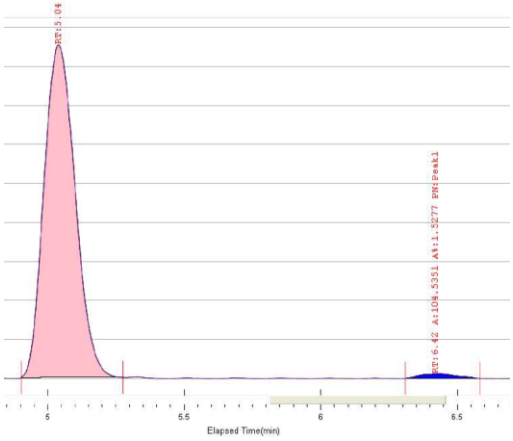
Chiral SFC (Chiracel OD-RH, 3% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (S)-2,2-dimethyl-7-phenylheptan-3-ol.

Racemic Material

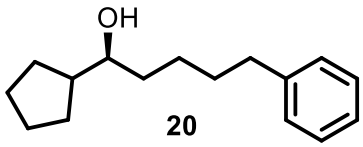


Peak No	% Area	Area	RT (min)
1	54.3763	3497.1215	5.07
2	45.6237	2934.2074	6.43
Total:	100	6431.3289	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	98.4723	6738.2473	5.04
2	1.5277	104.5351	6.42
Total:	100	6842.7824	



20

(*S*)-1-cyclopentyl-5-phenylpentan-1-ol (20).

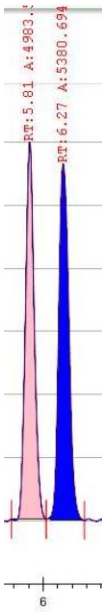
The reaction was performed according to the **General Procedure B,** with 8-cyclopentyl-6b,9a-dimethyl-acenaphthyleno[1,2-d][1,3,2]dioxaborole (64.3 mg, 0.22 mmol, 1.1 equiv.), vinylithium (1.63 M in THF, 0.123 mL, 0.2 mmol, 1.0 equiv.), (3-iodopropyl)benzene (59.1 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). Crude boronic ester was then subjected to **Oxidation Procedure**. The crude alcohol was then purified by silica gel chromatography (2-3% EtOAc in hexanes, stained in CAM) to afford a clear oil (21.8 mg, 47%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.24 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 2H), 3.43-3.36 (m, 1H), 2.63 (t, *J* = 6.6Hz, 2H), 1.91-1.81 (m, 1H), 1.81-1.73 (m, 1H), 1.71-1.58 (m, 4H), 1.58-1.49 (s, 4H), 1.45-1.36 (m, 2H), 1.36-1.28 (m, 2H), 1.24-1.14 (m, 1H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 128.5, 128.4, 125.8, 76.0, 46.5, 36.2, 36.1, 31.7, 29.3, 28.6, 25.9, 25.7, 25.6. IR (neat) ν_{max} 3376 (br), 2935 (s), 2859 (s), 2361 (w), 1453 (m), 1051 (w), 746 (w), 698 (w) cm^{-1}. HRMS (DART) for $C_{16}H_{28}NO$ $[M+NH_4]^+$: Calc'd: 250.2165, found: 250.2168. $[\alpha]_D^{20}$: -6.998 (c = 0.500, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

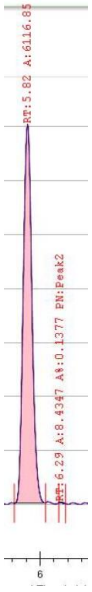
Chiral SFC (Chiracel ODR-H, 6% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (S)-1-cyclopentyl-5-phenylpentan-1-ol.

Racemic Material

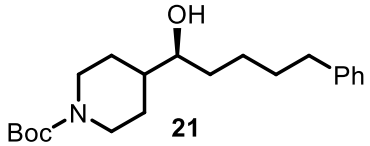


Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	48.084	4983.5287	5.81
2	51.916	5380.6944	6.27
Total:	100	10364.2231	

Standard Procedures



Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	99.8623	6116.8591	5.82
2	0.1377	8.4347	6.29
Total:	100	6125.2938	



21

***tert*-butyl (*S*)-4-(1-hydroxy-5-phenylpentyl)piperidine-1-carboxylate (21).**

The reaction was performed according to the **General Procedure B** with *tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (68.5 mg, 0.22 mmol, 1.1 equiv.), vinyllithium (1.52 M in THF, 0.131 mL, 0.2 mmol, 1.0 equiv.), (3-iodopropyl)benzene (59.1 mg, 0.24 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). Boronic ester was purified prior to oxidation using 1% EtOAc in Hexanes. Crude boronic ester was then subjected to **Oxidation Procedure**. The crude

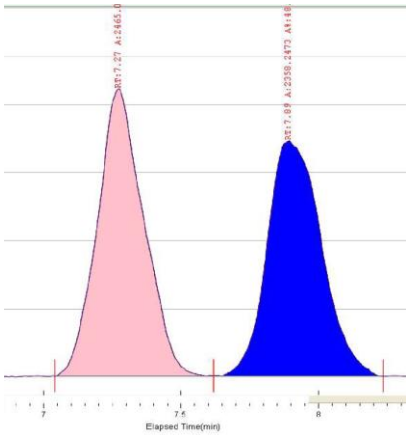
alcohol was purified by silica gel column chromatography (1:4:5 EtOAc/DCM/hexanes, stained with CAM) to afford a colorless oil (36.8 mg, 53% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 4.14 (br s, 2H), 3.37 (m, 1H), 2.78-2.50 (m, 2H), 2.62 (t, J = 7.6 Hz, 2H), 1.79-1.72 (m, 1H) 1.69-1.17 (m, 11H), 1.45 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 142.6, 128.5, 128.4, 125.8, 79.4, 75.2, 44.0 (br), 42.2, 36.0, 34.1, 31.6, 28.6, 28.4 (br), 27.3 (br), 25.6. IR (neat) ν_{max} 3456 (br, w), 2931 (m), 2856 (m), 2361 (w), 1693 (s), 1671 (s), 1496 (w), 1452 (m), 1427 (s), 1366 (m), 1280 (m), 1235 (m), 1169 (s), 1076 (m), 1003 (w), 976 (w), 942 (w), 867 (w), 748 (w), 699 (m) cm^{-1}. HRMS (DART+) for $C_{21}H_{34}NO_3$ $[M+H]^+$: Calc'd: 348.2533 , found: 348.2525. $[\alpha]_D^{20}$: -7.369 (c = 1.00, $CHCl_3$, l=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol%) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel OD-RH, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of tert-butyl (S)-4-(1-hydroxy-5-phenylpentyl)piperidine-1-carboxylate.

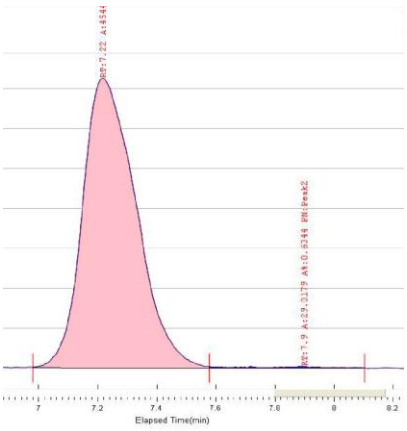
Racemic Material



Peak Info

Peak No	% Area	Area	RT (min)
1	51.1074	2465.0775	7.27
2	48.8926	2358.2473	7.89
Total:	100	4823.3248	

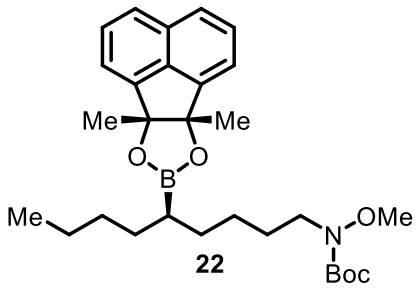
Standard Conditions



Peak Info

Peak No	% Area	Area	RT (min)
1	99.3656	4544.9881	7.22
2	0.6344	29.0179	7.9
Total:	100	4574.006	

3.5.2.5 *Procedures and Characterization of Compounds for the Synthesis of (R)-(-)-N-Boc-Coniine and tert-butyl (R)-2-butylpiperidine-1-carboxylate.*



22

***tert*-butyl ((5*R*)-5-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborol-8-yl)nonyl)(methoxy)carbamate (22).**

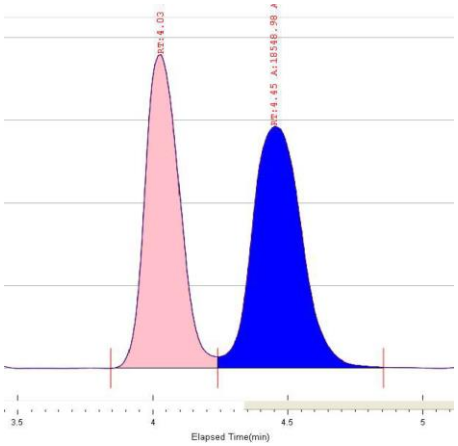
The reaction was performed according to the **General Procedure A** with vinylB(mac) (55.0 mg, 0.22 mmol, 1.1 equiv.), *n*-butyllithium (2.5 M in hexanes, 0.08 mL, 0.20 mmol, 1.0 equiv.), *tert*-butyl N-(3-iodopropyl)-N-methoxy-carbamate (75.6 mg, 0.24mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude boronic ester was purified by silica gel column chromatography (3% EtOAc in hexanes, stained with CAM) to afford a colorless oil (61.4 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.58 (t, J = 7.5 Hz, 2H), 7.53 (d, J = 6.9 Hz, 2H), 3.59 (s, 3H), 3.27-3.17 (m, 2H), 1.76 (s, 6H), 1.47 (s, 9H), 1.48-1.40 (m, 2H), 1.38-1.23 (m, 4H), 1.18-0.97 (m, 6H), 0.91 (p, J = 7.6 Hz, 1H), 0.68 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 145.0, 134.7, 131.4, 128.5, 125.2, 119.5, 91.6, 81.0, 62.3, 49.2, 31.3, 30.9 (2), 28.5, 27.4, 26.3, 23.7 (br), 22.9, 22.2, 14.0. IR (neat) ν_{max} 2974 (m), 2929 (s), 2857 (m), 1703 (s), 1498 (w), 1458 (m), 1435 (m), 1382 (s), 1367 (s), 1307 (s), 1262 (m), 1233 (m), 1174 (s), 1159 (s), 1117 (s), 1079 (s), 995 (w), 968 (w), 886 (w), 859 (w), 826 (m), 778 (m), 684 (w), 668 (w) cm^{-1}. HRMS (DART+) for $C_{29}H_{46}BN_2O_5$ $[M+NH_4]^+$: Calc'd: 513.3494, found: 513.3488. $[\alpha]_D^{20}$: -1.171 (c = 1.00, $CHCl_3$, l=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure A** with (*R*,*R*)-Ph-Pybox (12 mol %) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

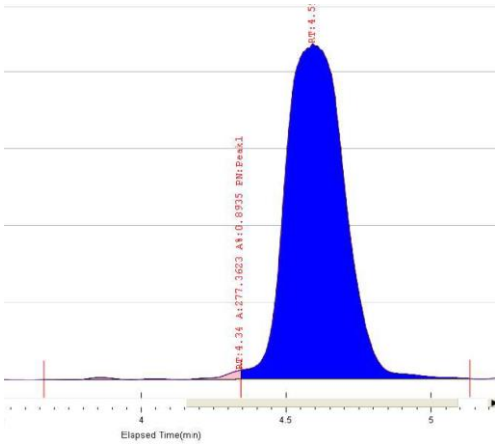
Chiral SFC (Chiracel OJ-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of tert-butyl ((5R)-5-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)nonyl)(methoxy)carbamate.

Racemic Material

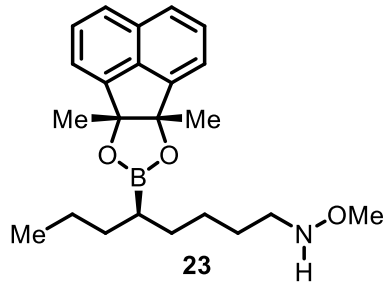


Peak No	% Area	Area	RT (min)
1	47.5345	16805.6482	4.03
2	52.4655	18548.98	4.45
Total:	100	35354.6282	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.8935	277.3623	4.34
2	99.1065	30763.4155	4.59
Total:	100	31040.7778	



23

***N*-((5*R*)-5-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborol-8-yl)octyl)-O-methylhydroxylamine (23).**

The reaction was performed according to the **General Procedure B** with propylB(mac) (58.6 mg, 0.22 mmol, 1.1 equiv.), vinyllithium (1.51 M in hexanes, 0.131 mL, 0.2 mmol, 1.0 equiv.), *tert*-butyl N-(3-iodopropyl)-N-methoxy-carbamate (75.6 mg, 0.24mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (6.0 mg, 0.020 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (8.9 mg, 0.024 mmol, 12 mol %), in 3:1 THF:DMSO (1.5 mL). The crude boronic ester was purified by silica gel column chromatography (3% EtOAc in hexanes, stained with CAM), which was then treated with TFA (0.08 mL, 1.0 mmol, 8.6 equiv.) in DCM (0.6 mL, [substrate] = 0.2 M) for 4 hours at room temperature.

The title compound was purified by silica gel column chromatography (10% EtOAc in hexanes, stained with CAM) to afford a pale yellow oil (44.9 mg, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H), 7.59 (t, J = 7.5 Hz, 2H), 7.54 (d, J = 6.9 Hz, 2H), 5.07 (br s, 1H), 3.47 (s, 3H), 2.68 (t, J = 7.1 Hz, 1H), 1.76 (s, 6H), 1.36-1.01 (m, 10H), 0.94 (p, J = 8.2 Hz, 2H), 0.76 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0,

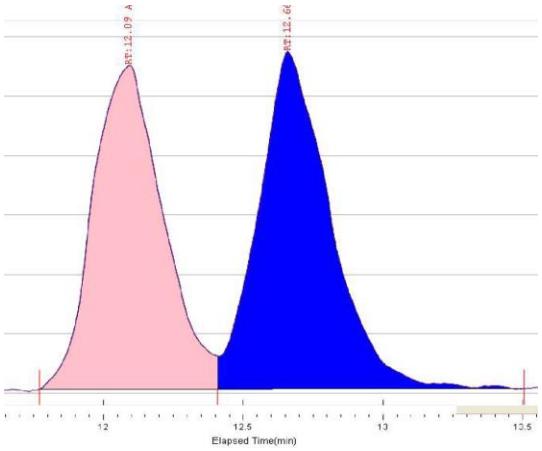
134.7, 131.4, 128.5, 125.3, 119.5 (2), 91.6 (2), 61.8, 51.8, 33.5, 31.1, 27.4, 26.6, 23.5 (br), 22.2 (3), 14.4. IR (neat) ν_{max} 3044 (w), 2930 (s), 2856 (m), 1498 (w), 1460 (m), 1435 (m), 1411 (m), 1381 (s), 1349 (m), 1307 (s), 1263 (m), 1213 (m), 1174 (m), 1117 (s), 1079 (s), 967 (w), 889 (w), 826 (s), 805 (w), 779 (s), 683 (w), 668 (w) cm^{-1}. HRMS (DART+) for $C_{23}H_{33}BNO_3$ $[M+H]^+$: Calc'd: 382.2548, found: 382.2547. $[\alpha]_D^{20}$: -1.057 (c = 1.00, $CHCl_3$, *l*=50 mm).

Analysis of Stereochemistry:

Racemic material was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure B** with (*R*,*R*)-Ph-Pybox (12 mol %) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

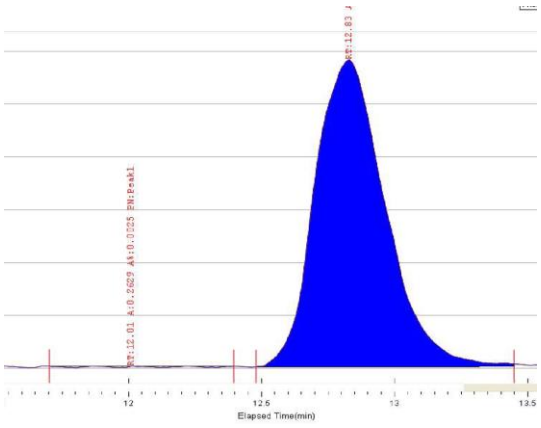
Chiral SFC (Chiracel OD-H, 4% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of N-((5R)-5-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)octyl)-O-methylhydroxylamine.

Racemic Material

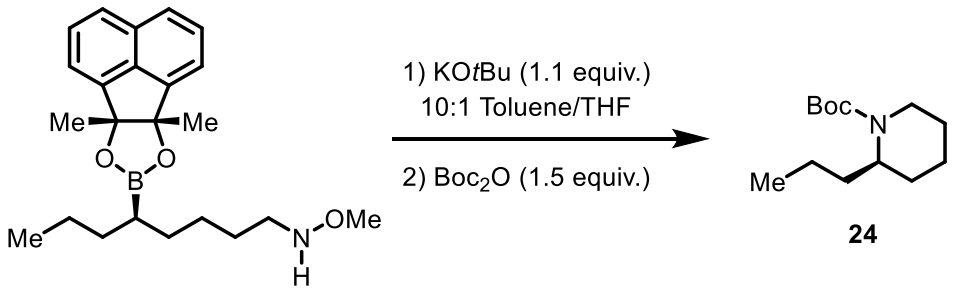


Peak No	% Area	Area	RT (min)
1	48.3602	4744.0661	12.09
2	51.6398	5065.7834	12.66
Total:	100	9809.8495	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.0025	0.2629	12.01
2	99.9975	10649.3867	12.83
Total:	100	10649.6496	



24

(6*R*)-*N*-(*tert*-Butoxycarbonyl)-6-propylpiperidine (24). (*R*)-(-)-N-Boc-Coniine.

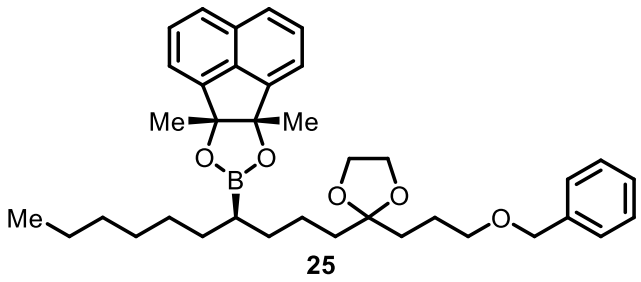
Following the **Amination Procedure,** with KOtBu (6.2 mg, 0.055 mmol, 1.1 equiv.) *N*-((5*R*)-5-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborol-8-yl)octyl)-O-methylhydroxylamine (19.1 mg, 0.05 mmol, 1.0 equiv.) in 10:1 toluene/THF (1.1 mL), the crude product was purified by silica gel chromatography (5% EtOAc/Hexanes, stained in $KMnO_4$ or Ninhydrin). Title compound was isolated as a colorless, clear oil (10.4 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.20 (br s, 1H), 3.96 (br d, *J* = 8.2 Hz, 1H), 2.74 (t, *J* = 13.0 Hz, 1H), 1.63-1.20 (m, 10H), 1.45 (s, 9H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3, 79.1, 50.3 (br), 38.8 (br), 32.1, 29.9, 28.7, 25.9, 19.6, 19.2, 14.2. IR (neat) ν_{max} 2930 (m), 2864 (w), 1687 (s), 1454 (m), 1415 (m), 1390 (m), 1364 (m), 1341 (m), 1317 (w), 1244 (m), 1170 (m), 1144 (s), 1074 (m), 1018 (m), 960 (w), 925 (w), 876 (w), 815 (w), 767 (m), 660 (w), 579 (w), 534 (w) cm^{-1}. HRMS (DART+) for $C_{13}H_{26}NO_2$ $[M+H]^+$: Calc'd: 228.1958, found: 228.1953. $[\alpha]_D^{20}$: –29.650 (c = 0.500, $CHCl_3$, *l*=50 mm).

Absolute stereochemistry was determined by comparison of optical rotation to the literature (Measured: $[\alpha]_D^{20}$: –29.650 (c = 0.500, $CHCl_3$, *l*=50 mm). Literature: $[\alpha]_D^{20}$: -25.6 (c = 0.6, $CHCl_3$) [22a], $[\alpha]_D^{26}$: –28.1 (c = 1.0,$CHCl_3$)[22b]) and the absolute stereochemistry was assigned to be (6*R*)-*N*-(*tert*-Butoxycarbonyl)-6-propylpiperidine, or (*R*)-(-)-N-Boc-Coniine.

Method for Intramolecular Amination of Boronic Ester Product: ***(Amination Procedure)***

Inside the glovebox, to an oven-dried 2-dram vial, KO*t*Bu (0.055 mmol, 1.1 equiv) was added. It was then sealed with septum, taped, and brought outside the glovebox. While under positive nitrogen atmosphere, 0.1mL of THF was added. Then, aminoboronic ester (0.05 mmol, 1 equiv) in toluene was added (1.0mL, 0.05M). It was heated to 110 ºC in an oil bath and allowed to stir for 16 h. Then after allowing the reaction mixture to return to room temperature, Boc_2O (0.188M in THF, 0.4 mL, 0.075 mmol, 1.5 equiv) was added and allowed to stir for 3 h. Then water was added and it was extracted three times with EtOAc. Crude product was purified by silica gel chromatography and stained with Ninhydrin.

3.5.2.6 *Procedures and Characterization of Compounds for the Synthesis of (-)-indolizidine 209D.*



25

8-((*R*)-1-(2-(3-(benzyloxy)propyl)-1,3-dioxolan-2-yl)decan-4-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (25).

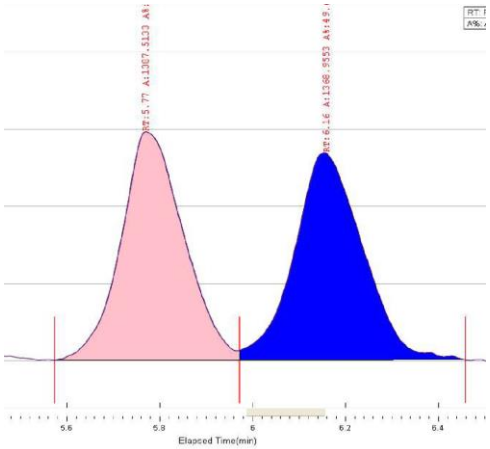
The reaction was performed according to the **General Procedure A,** with vinylB(mac) (165.1 mg, 0.66 mmol, 1.1 equiv.), *n*-hexyllithium (2.14 M in hexanes, 0.28 mL, 0.6 mmol, 1.0 equiv.), 2-(3-(benzyloxy)propyl)-2-(2-iodoethyl)-1,3-dioxolane (270.9 mg, 0.72 mmol, 1.2 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (18.0 mg, 0.060 mmol, 10 mol %), and (*S*,*S*)-Ph-Pybox (26.6 mg, 0.072 mmol, 12 mol %), in 3:1 THF:DMSO (4.5 mL). The reaction was conducted for a longer time of 48 h. The crude boronic ester was purified by silica gel column chromatography (10% EtOAc in hexanes, CAM stain) to afford a colorless oil (210.4 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.58-7.55 (m, 4H), 7.36-7.35 (m, 4H), 7.29-7.28 (m, 1H), 4.52 (s, 2H), 3.83-3.75 (m, 4H), 3.45 (t, J = 6.5 Hz, 2H), 1.77 (s, 6H), 1.69-1.60 (m, 2H), 1.59-1.53 (m, 2H), 1.52-1.44 (m, 2H), 1.39-1.25 (m, 4H), 1.25-1.16 (m, 2H), 1.16-1.00 (m, 8H), 0.94 (p, J = 7.6 Hz, 1H), 0.81 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0 (2), 138.8, 134.7, 131.4, 128.5, 128.4, 127.7, 127.5, 125.2, 119.5, 111.6, 91.6, 72.8, 70.6, 65.0, 37.5, 33.6, 31.8, 31.6, 31.3, 29.4, 29.0, 24.2, 23.7 (br), 23.4, 22.5, 22.2, 14.2. ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.8. IR (neat) ν_{max} 3032 (w), 2924 (s), 2854 (s), 2158 (w), 1497 (w), 1455 (w), 1380 (s), 1307 (s), 1263 (m), 1212 (m), 1174 (m), 1116 (s), 1077 (s), 947 (w), 887 (w), 825 (s), 806 (w), 778 (s), 736 (m), 698 (m), 554 (w) cm^{-1}. HRMS (DART+) for $C_{37}H_{50}BO_5$ $[M+H]^+$: Calc'd: 585.3746, found: 585.3746. $[\alpha]_D^{20}$: -3.285 (c = 1.00, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

The product was treated with 3M NaOH (1.0 mL) and H_2O_2 (1.0 mL) to afford corresponding secondary alcohol. Racemic compound was prepared by mixing the other enantiomer prepared from running a second reaction according to the **General Procedure A** with (*R*,*R*)-Ph-Pybox (12 mol %) as the ligand instead of (*S*,*S*)-Ph-Pybox. Absolute stereochemistry was assigned by analogy (see product **(*R*)-(-)-N-Boc-Coniine**, **(-)-indolizidine 209D**).

Chiral SFC (Chiracel OD-RH, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (R)-1-(2-(3-(benzyloxy)propyl)-1,3-dioxolan-2-yl)decan-4-ol.

Racemic Material



Peak Info			
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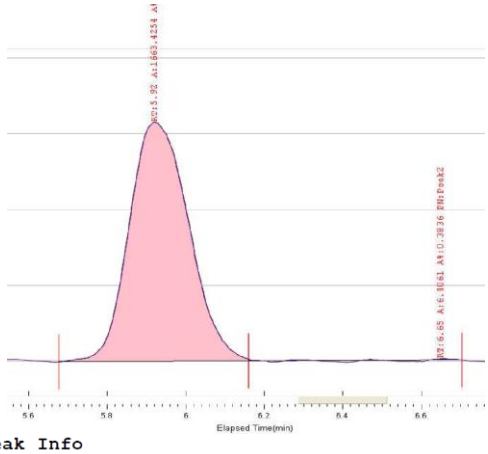
2	49.6634	1368.9553	6.16
Total:	100	2756.4686	

Standard Conditions



Peak Info			
Peak No	% Area	Area	RT (min)
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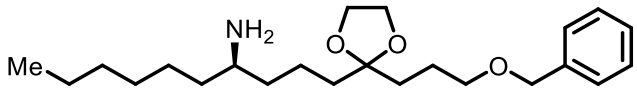
2	0.3836	6.4061	6.65
Total:	100	1669.8315	

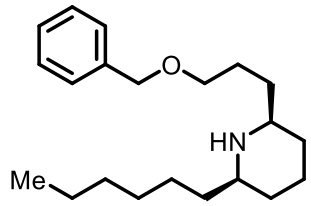


26

(*R*)-1-(2-(3-(benzyloxy)propyl)-1,3-dioxolan-2-yl)decan-4-amine (26).

The title compound was synthesized using slightly modified literature procedure.[23] To an oven-dried 2-dram vial, 8-((*R*)-1-(2-(3-(benzyloxy)propyl)-1,3-dioxolan-2-yl)decan-4-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (200.0 mg, 0.34 mmol, 1.0 equiv.) was transferred. Then it was brought into the glovebox, charged with a stir bar, dissolved in Toluene (2.0 mL). Then, $MeONH_2$ (1.77 M in THF, 0.29 mL, 0.51 mmol, 1.5 equiv.) was added. Subsequently, KOtBu (57.6 mg or 0.51 mmol, 1.5 equiv.) was added, sealed with septum and brought outside the glovebox and was stirred at 80 °C in oil bath for 16 h. It was allowed to cool to room temperature, then H_2O (2 mL) was added. After letting it stir for 5 min, crude mixture was extracted with EtOAc (15 mL x 3). Solvents were removed under reduced pressure and the compound was purified by silica gel chromatography (5% MeOH/1% Et_3N/EtOAc, stained in ninhydrin) to afford pale yellow oil (116.0 mg, 90% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.33 (m, 4H), 7.28-7.26 (m, 1H), 4.50 (s, 2H), 3.92 (s, 4H), 3.50-3.45 (m, 2H), 2.71-2.63 (m, 1H), 1.72-1.66 (m, 4H), 1.63-1.58 (m, 2H), 1.49-1.21 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 128.5, 127.7, 127.6, 111.7, 72.9, 70.6, 65.1, 51.3, 38.5, 38.2, 37.5, 33.8, 32.0, 29.6, 26.3, 24.4, 22.8, 20.6, 14.2. IR (neat) ν_{max} 2925 (s), 2855 (s), 2006 (w), 1958 (w), 1584 (w, br), 1496 (w), 1455 (m), 1361 (m), 1310 (w), 1206 (w), 1100 (s), 1074 (s), 1029 (m), 947 (m), 816 (w), 736 (m), 698 (m), 613 (w), 575 (w), 564 (w), 547 (w) cm^{-1}.

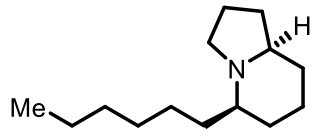
HRMS (DART+) for $C_{23}H_{40}NO_3$ $[M+H]^+$: Calc'd: 378.3003, found: 378.3006. $[\alpha]_D^{20}$: +1.118 (c = 1.00, $CHCl_3$, *l* = 50 mm).



27

(2*R*,6*R*)-2-(3-(benzyloxy)propyl)-6-hexylpiperidine (27).

To a 20 mL scintillation vial equipped with a stir bar, (*R*)-1-(2-(3-(benzyloxy)propyl)-1,3-dioxolan-2-yl)decan-4-amine (37.0mg , 0.098mmol) was transferred. 1.0 mL of 1 N HCl and 1.0 mL of THF was added and it was allowed to stir at room temperature for 16 h. Afterwards, the mixture was neutralized with $NaHCO_3$ (aq. sat.) and extracted with Et_2O three times. Solvents were removed and MeOH (1.5 mL) was added. Then Pd/C (10%) (10.4 mg) was added then sealed with a rubber septum. The atmosphere was exchanged with H_2 and was allowed to stir vigorously for 3 h. After exchanging the atmosphere with N_2, it was filtered through a short pad of celite with methanol. The crude mixture was purified by silica gel chromatography (Et_2O, stain with $KMnO_4$) to afford the title compound as pale yellow oil (26.7 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, 4H), 7.30-7.25 (m, 1H), 4.50 (s, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.50-2.42 (m, 2H), 1.80-1.73 (m, 1H), 1.69-1.60 (m, 4H), 1.50-1.38 (m, 2H), 1.37-1.21 (m, 12H), 1.06-0.96 (m, 2H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 128.4, 127.7, 127.6, 73.0, 70.6, 57.3, 57.0, 37.6, 34.1, 32.8, 32.7, 31.9, 29.6, 26.4, 26.0, 24.9, 22.7, 14.2. IR (neat) ν_{max} 3030 (w), 2926 (s), 2854 (s), 2176 (w), 1961 (w, br), 1496 (w), 1454 (m), 1361 (w), 1331 (w), 1204 (w), 1102 (m), 1028 (w), 733 (m), 697 (m), 579 (w), 555 (w), 547 (w), 532 (w) cm^{-1}. HRMS (DART+) for $C_{21}H_{36}NO$ $[M+H]^+$: Calc'd: 318.2791, found: 318.2804. $[\alpha]_D^{20}$: +1.600 (c = 0.500, $CHCl_3$, *l* = 50 mm).

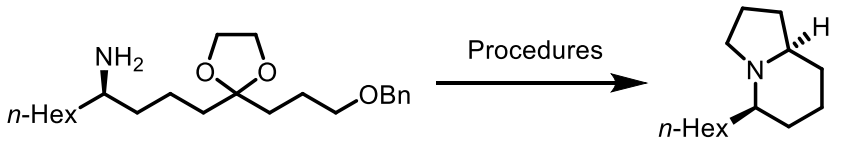


28

(5*R*,8a*R*)-5-hexyloctahydroindolizine (28). (-)-indolizidine 209D

Title compound was prepared from following literature procedure[24] with (2*R*,6*R*)-2-(3-(benzyloxy)propyl)-6-hexylpiperidine (26.5 mg, 0.083 mmol, 1.0 equiv.). The title compound was purified using silica gel chromatography (10-20% Et_2O/hexanes, $KMnO_4$ stain). Spectral data matches the literature.[24] (-)-indolizidine 209D was isolated as yellow oil (14.0 mg, 80% yield).

Title compound can be also be prepared from (R)-1-(2-(3-(benzyloxy)propyl)-1,3-dioxolan-2-yl)decan-4-amine, without intermediate purifications, using following procedure:

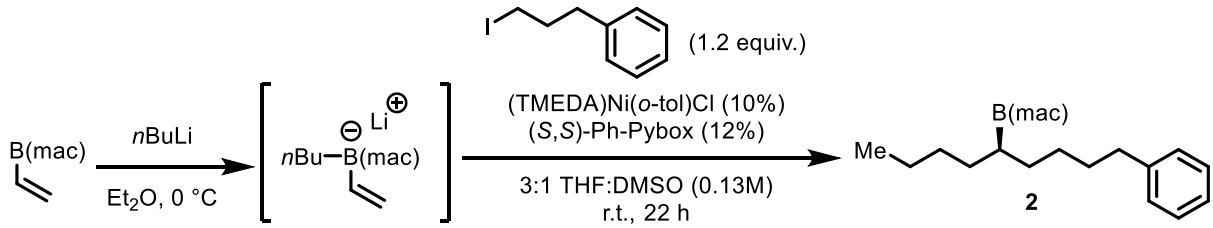


28

To a 20 mL scintillation vial equipped with a stir bar, (*R*)-1-(2-(3-(benzyloxy)propyl)-1,3-dioxolan-2-yl)decan-4-amine (22.7 mg, 0.072 mmol, 1.0 equiv.) was transferred. 1.0 mL of 1 N HCl and 1.0 mL of THF was added and it was allowed to stir at room temperature for 16 h. Then, the mixture was neutralized with $NaHCO_3$ (aq. sat.) and extracted with Et_2O three times. Solvents were removed and MeOH (1.2 mL, 0.062M) was added. Pd/C (10%) (7.7 mg, 0.007 mmol, 10 mol %) was added then sealed with a rubber septum. The atmosphere was exchanged with H_2 and was allowed to stir vigorously for 3 h. After 3 h, 6 N HCl (0.02 mL, 0.12 mmol, 2.0 equiv.) was added and allowed to stir for another 16 h. After exchanging the atmosphere with N_2, it was filtered through a short pad of celite with MeOH. Solvents were removed under reduced pressure. Then to an oven-dried 2-dram vial, crude mixture was transferred, dissolved in 0.6mL of DCM and $SOCl_2$ (0.02 mL, 0.275 mmol, 3.8 equiv.) was added. It was refluxed for 1 h in an oil bath, then excess $SOCl_2$ was removed under reduced pressure. Crude residue was dissolved in DCM (0.6 mL) and K_2CO_3 (86.6 mg, 0.626 mmol, 8.7 equiv.) was added. It was allowed to stir for 16 h at room temperature. Crude mixture was filtered through a short pad of silica gel with Et_2O. The title compound was purified using silica gel chromatography (10-20% Et_2O/Hexanes). (10.0 mg, 66% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.26 (td, *J* = 8.8, 2.2 Hz, 1H), 1.96 (q, *J* = 8.9 Hz, 1H), 1.91-1.69 (m, 8H), 1.69-1.59 (m, 2H), 1.43-1.26 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 65.2, 64.1, 51.7, 34.8, 32.0, 31.2, 31.0, 30.7, 29.9, 26.0, 24.9, 22.8, 20.6, 14.3. IR (neat) ν_{max} 3691 (w), 2929 (s), 2857 (m), 2780 (m), 2710 (w), 2358 (w), 2248 (w), 2217 (w), 2201 (w), 2175 (w), 2141 (w), 2128 (w), 2028 (w), 2015 (w), 1990 (w), 1964 (w), 1457 (m), 1380 (m), 1332 (w), 1228 (w), 1173 (w), 1128 (m), 1054 (w), 809 (w), 615 (w), 589 (m) cm^{-1}. HRMS (DART+) for $C_{14}H_{28}N$ $[M+H]^+$: Calc'd: 210.2216, found: 210.2208. $[\alpha]_D^{20}$: -69.399 (c = 0.545, $CHCl_3$, *l* = 50 mm).

Absolute stereochemistry was determined by comparison of optical rotation to the literature (Measured: $[\alpha]_D^{20}$: -69.399 (c = 0.545, $CHCl_3$, *l* = 50 mm). Literature: $[\alpha]_D^{20}$: -66.5 (c = 1.0, $CHCl_3$).[25a] $[\alpha]_D^{20}$: -80.4 (c = 1.0, CH_2Cl_2).[25b]) and the absolute stereochemistry was assigned to be (5*R*,8a*R*)-5-hexyloctahydroindolizine. (-)-indolizidine 209D.

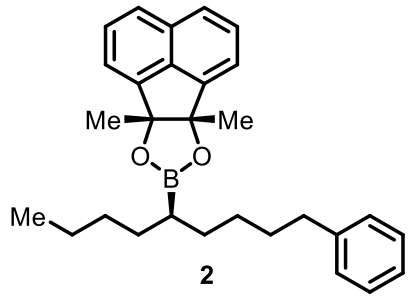
3.5.2.7 *Procedure for the Gram-Scale Reaction*



Inside the glovebox, an oven-dried 100mL round-bottom flask equipped with a magnetic stir bar was charged with vinylB(mac) (1.56 g, 6.26 mmol, 1.1 equiv). It was dissolved in 15.0 mL Et_2O, capped with septum, taped, and was brought outside the glovebox. The flask was placed under positive pressure of N_2, cooled to 0 °C in ice bath, then *n*-butyllithium (2.50 M in hexanes, 2.28 mL, 5.68 mmol, 1.0 equiv) was added dropwise over about 10 min. After the addition was complete, the vial was removed from the ice bath and allowed to stir for 5 minutes at room temperature. Then the solvent was carefully removed under reduced pressure without exposure to air, and put under vacuum for 15 min.

Inside the glovebox, to an oven-dried 20 mL scintillation vial, equipped with a magnetic stir bar, catalyst stock solution was prepared. It was charged with (TMEDA)Ni(*o*-tol)Cl (171.5 mg, 0.569 mmol, 10 mol %), and (*S,S*)-Ph-Pybox (251.5 mg, 0.683 mmol, 12 mol %). Subsequently, it was suspended in 5.7 mL of THF and was allowed to stir for 5 min. Then 11.4 mL of DMSO was added, and was allowed to stir for 10 min, or until it was completely dissolved.

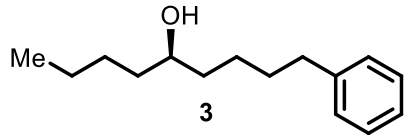
After the flask containing boron ate complex was under vacuum for 15 min, the flask was back filled with nitrogen, then brought into the glovebox. 20.0 mL of THF was added to the flask containing boron ate complex. (3-iodopropyl)benzene (1.68 g, 6.83 mmol, 1.2 equiv) was added, then, all of nickel catalyst complex stock solution (17.1 mL) was added slowly. The vial and syringe containing the catalyst complex was rinsed with additional 5.7 mL of THF. The flask was sealed with septum, taped, and brought outside the glovebox and was allowed to stir for 22 h at room temperature. Reaction mixture is then diluted with ether, and 5.0 mL of H_2O is added (for removal of DMSO). After filtering through a short pad of silica gel with ether, and removal of solvent under reduced pressure the crude mixture was obtained. Then title compound was then purified by silica gel chromatography (10-20% DCM/Hexanes, or 1-2% EtOAc/Hexanes) to afford a clear colorless oil (1.57 g, 65% yield).



2

(6b*R*,9a*S*)-6b,9a-dimethyl-8-((*R*)-1-phenylnonan-5-yl)-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole (2).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 6.9 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 2H), 2.44-2.34 (m, 2H), 1.76 (s, 6H), 1.50-1.40 (m, 2H), 1.39-1.25 (m, 4H), 1.18-1.06 (m, 6H), 1.06-0.99 (m, 1H), 0.71 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 143.0, 134.7, 131.4, 128.5 (2), 128.3, 125.6, 125.2, 119.5, 91.6, 35.9, 31.7, 31.4, 31.3, 31.1, 28.8, 23.7 (br), 22.9, 22.1 (2), 14.1. ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.2. IR (neat) ν_{max} 3026 (w), 2953 (m), 2926 (s), 2855 (m), 1604 (w), 1496 (w), 1455 (m), 1410 (w), 1380 (m), 1348 (m), 1307 (s), 1263 (m), 1233 (m), 1214 (m), 1174 (m), 1117 (s), 1079 (s), 1031 (w), 968 (w), 885 (w), 825 (m), 806 (w), 780 (s), 748 (w), 699 (m), 682 (w), 587 (w), 567 (w), 534 (w) cm^{-1}. HRMS (DART+) for $C_{29}H_{36}BO_2$ $[M+H]^+$: Calc'd: 427.2803, found: 427.2811. $[\alpha]_D^{20}$: -5.028 (c = 1.00, $CHCl_3$, *l* = 50 mm).



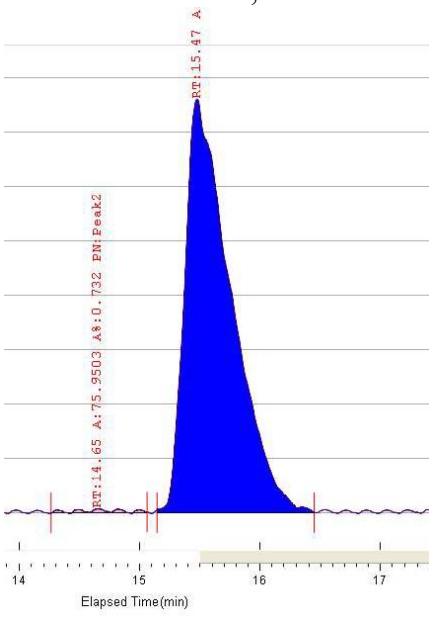
3

(*R*)-1-phenylnonan-5-ol (3).

In order to assess the enantioselectivity of the gram scale reaction, the title compound was obtained by following the **Oxidation Procedure** with (6b*R*,9a*S*)-6b,9a-dimethyl-8-((*R*)-1-phenylnonan-5-yl)-6b,9a-dihydroacenaphtho[1,2-*d*][1,3,2]dioxaborole that was isolated from the gram scale reaction.

Chiral SFC (Chiracel OD-RH, 2% IPA, 3 mL/min, 100 bar, 35 °C, 210-289 nm) – analysis of (R)-1-phenylnonan-5-ol. See Compound 3 for characterization data and racemic SFC trace.

Standard Conditions, Gram-Scale.



Peak Info

Peak No	% Area	Area	RT (min)
1	0.732	75.9503	14.65
2	99.268	10300.2842	15.47
Total:	100	10376.2345	

3.5.3 References

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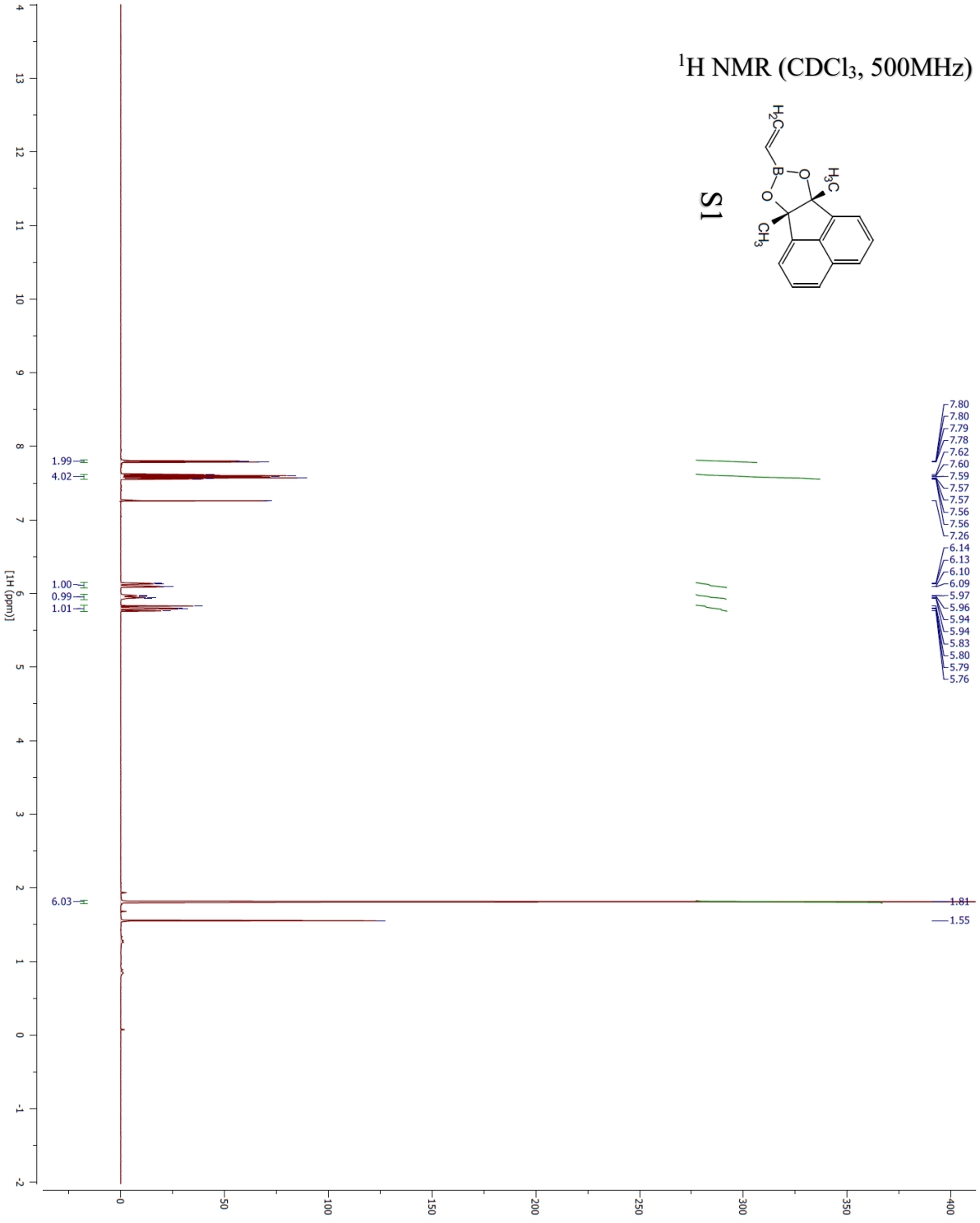
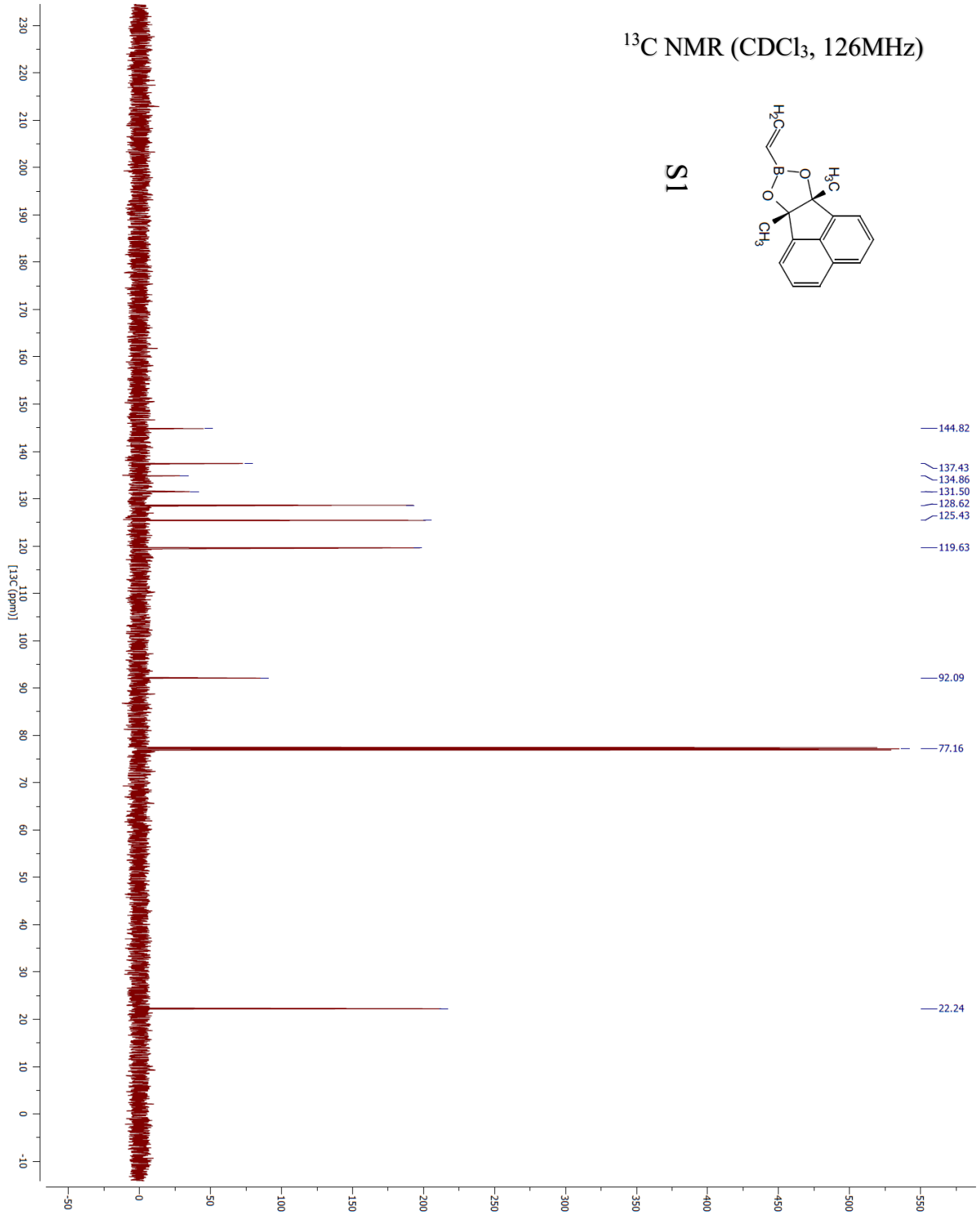
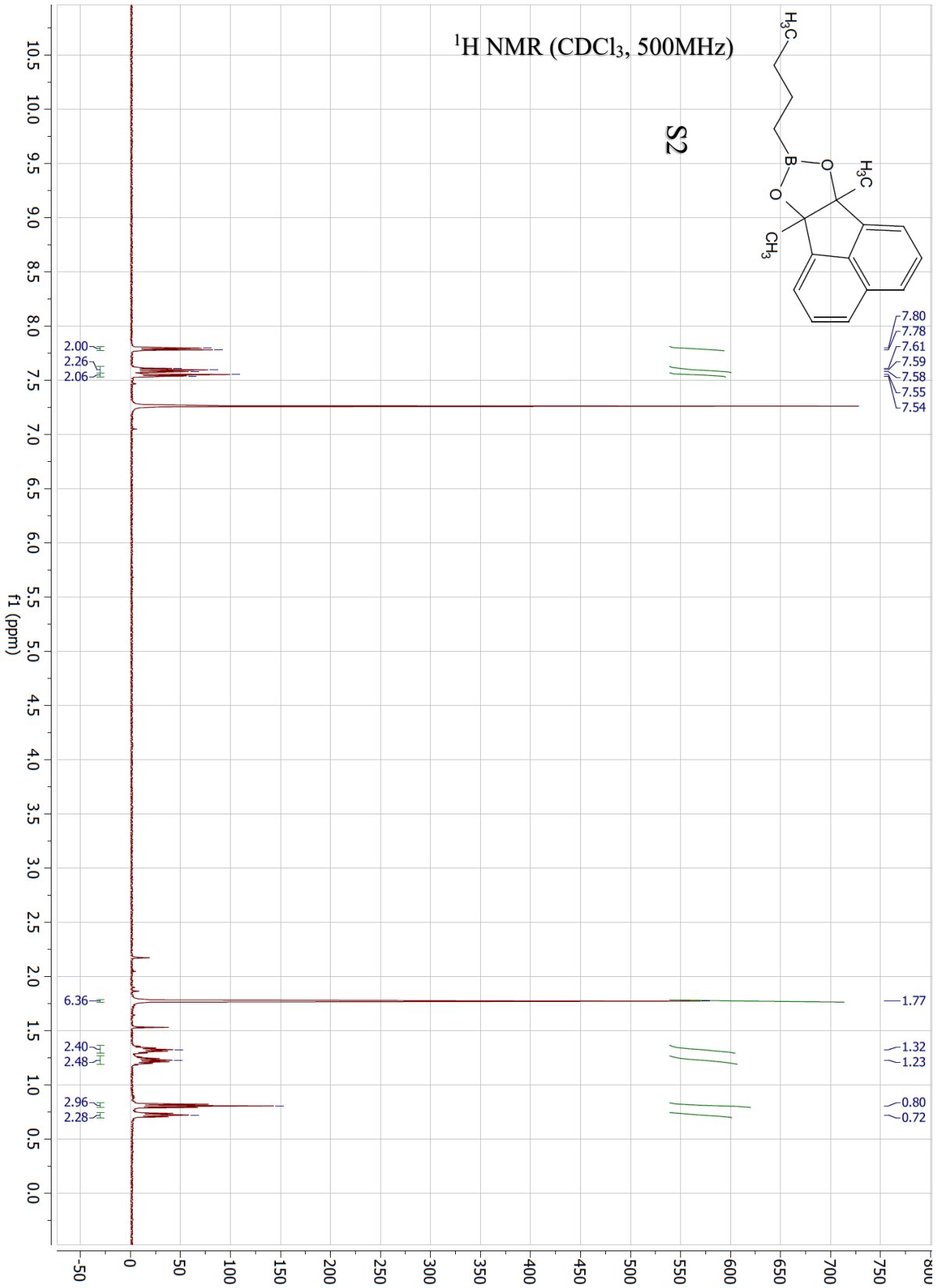
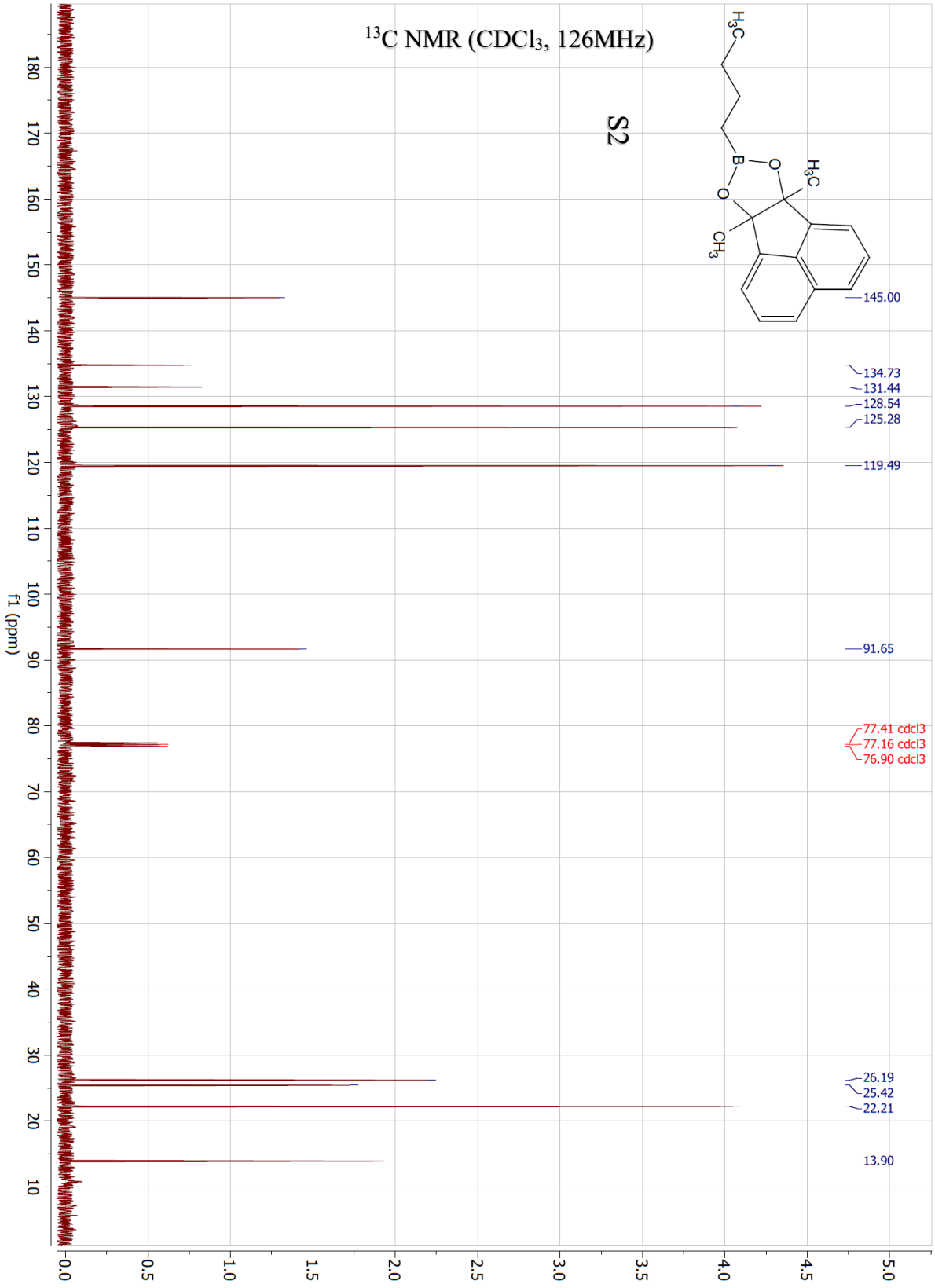
25. (a) Yu, Robert T.; Lee, E. E.; Malik, G.; Rovis, T. *Angew. Chem. Int. Ed.* **2009**, *48*, 2379. (b) Polniaszek, R. P.; Belmont, S. E. *J. Org. Chem.* **1990**, *55*, 4688.

3.5.4 Spectral Data




^{13}C NMR ($CDCl_3$, 126MHz)
S1
144.82
137.43
134.86
131.50
128.62
125.43
119.63
92.09
77.16
22.24
[13C (ppm)]


^{1}H NMR ($CDCl_3$, 500MHz)
S2
H_3C
B
O
O
H_3C
CH_3
7.80
7.78
7.61
7.59
7.58
7.55
7.54
2.00
2.26
2.06
6.36
1.77
2.40
2.48
1.32
1.23
2.96
2.28
0.80
0.72
f1 (ppm)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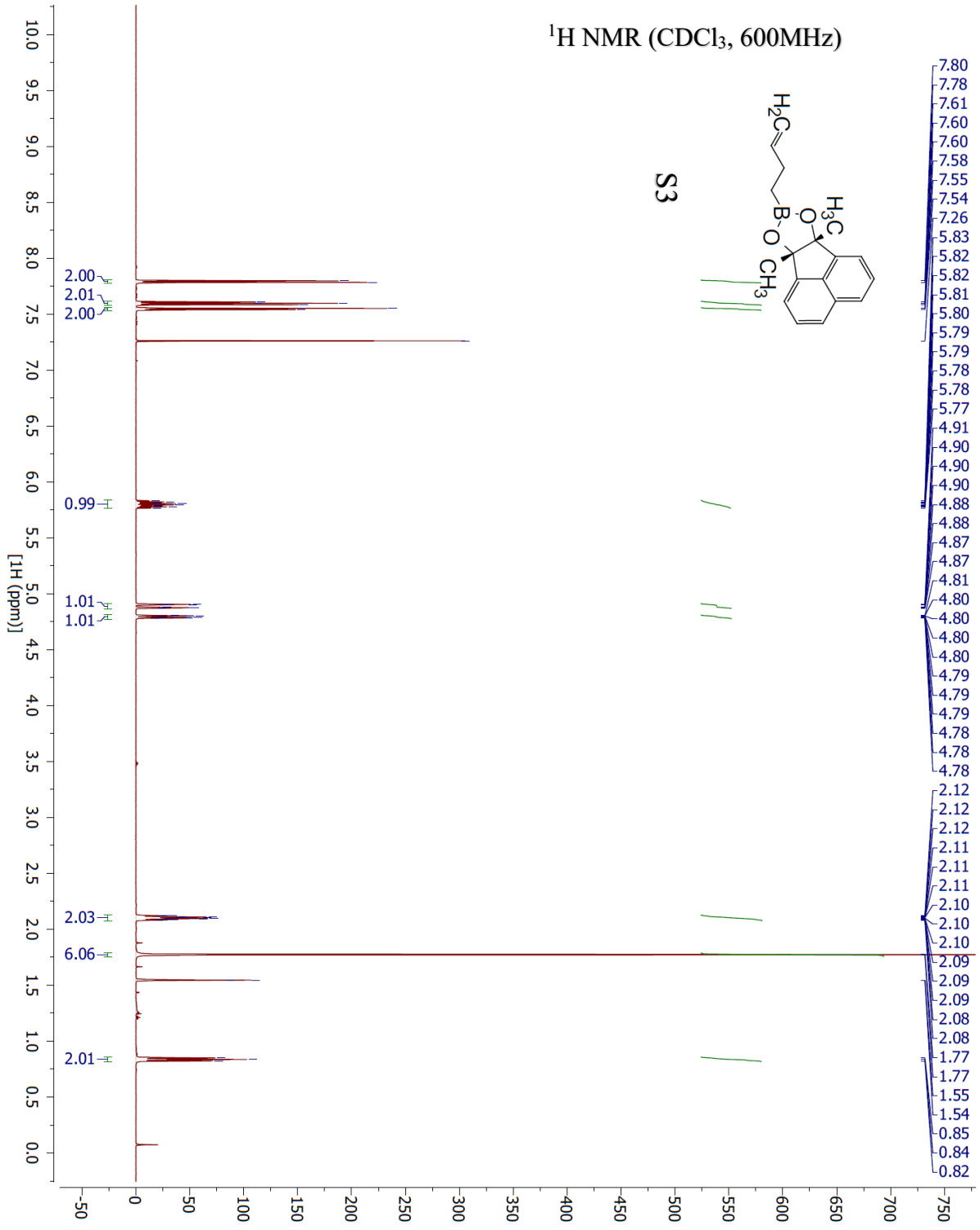
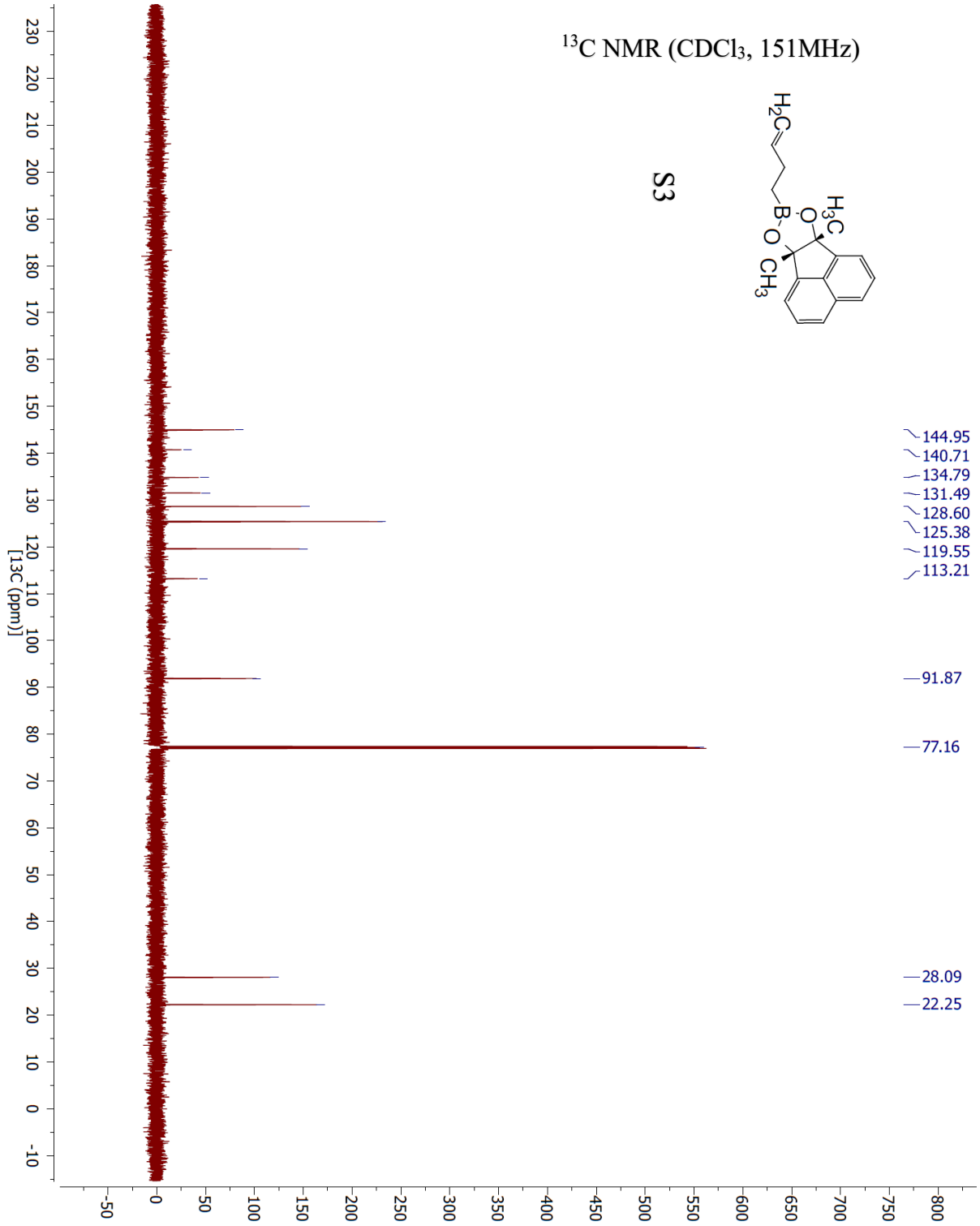
S2
H_3C
B
O
O
H_3C
CH_3
145.00
134.73
131.44
128.54
125.28
119.49
91.65
77.41 cdcl3
77.16 cdcl3
76.90 cdcl3
26.19
25.42
22.21
13.90
f1 (ppm)


^{1}H NMR ($CDCl_3$, 600MHz)
S3
[1H (ppm)]
2.00
2.01
2.00
0.99
1.01
1.01
2.03
6.06
2.01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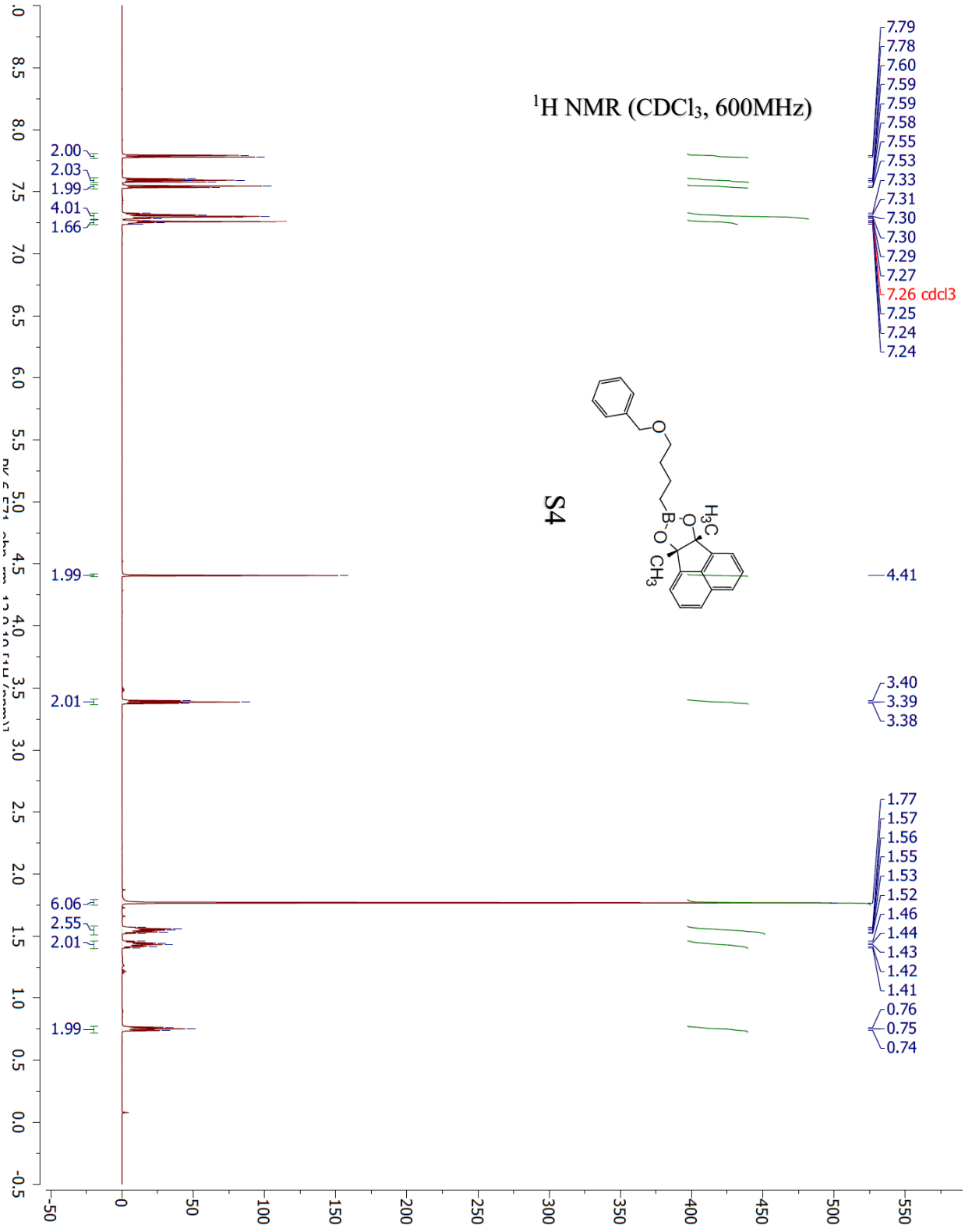
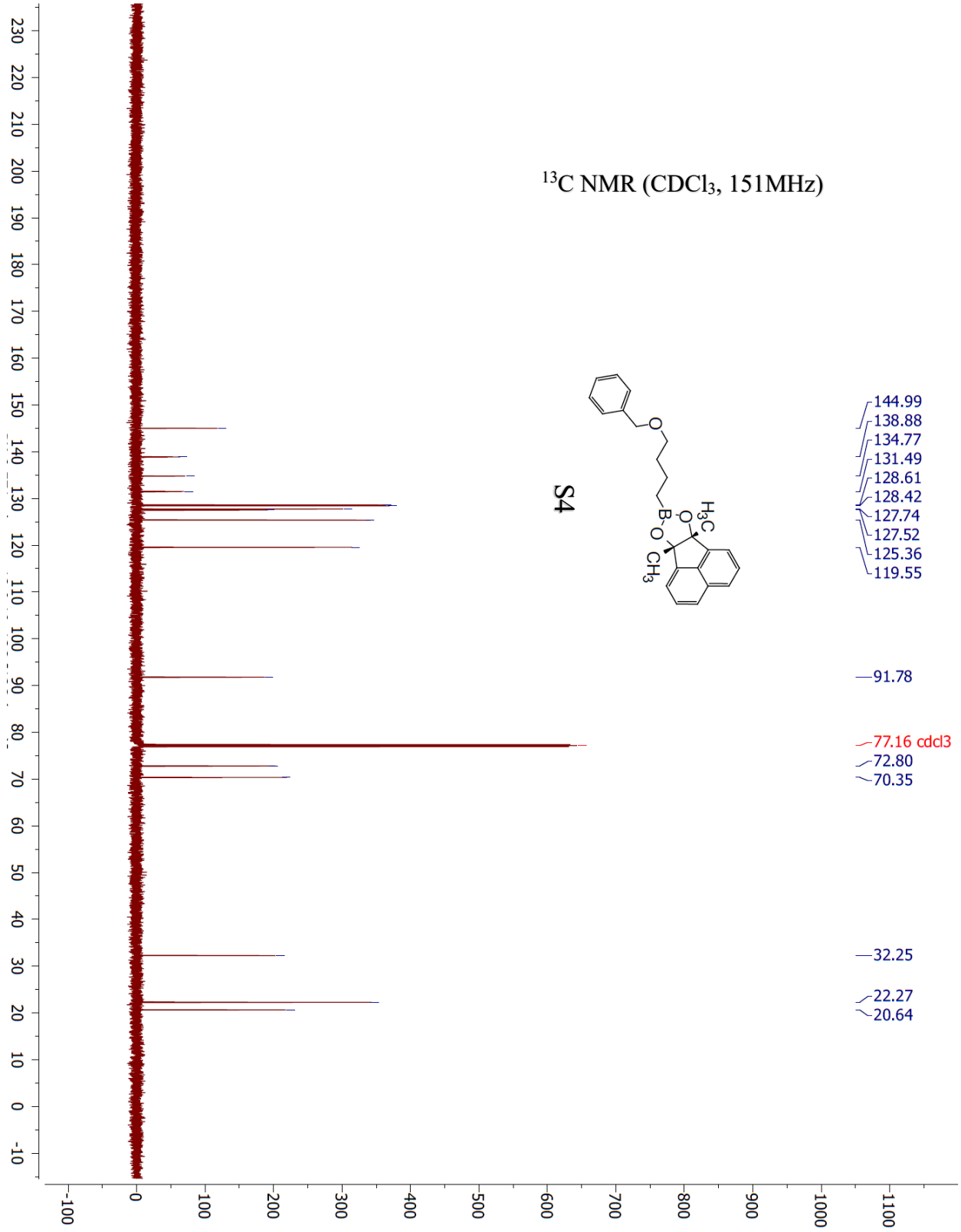
S3
144.95
140.71
134.79
131.49
128.60
125.38
119.55
113.21
91.87
77.16
28.09
22.25
[13C (ppm)]


^{1}H NMR ($CDCl_3$, 600MHz)
S4
7.79
7.78
7.60
7.59
7.59
7.58
7.55
7.53
7.33
7.31
7.30
7.30
7.29
7.27
7.26 cdcl3
7.25
7.24
7.24
2.00
2.03
1.99
4.01
1.66
1.99
4.41
2.01
3.40
3.39
3.38
1.77
1.57
1.56
1.55
1.53
1.52
1.46
1.44
1.43
1.42
1.41
6.06
2.55
2.01
1.99
0.76
0.75
0.74
O
O
B
O
H_3C
CH_3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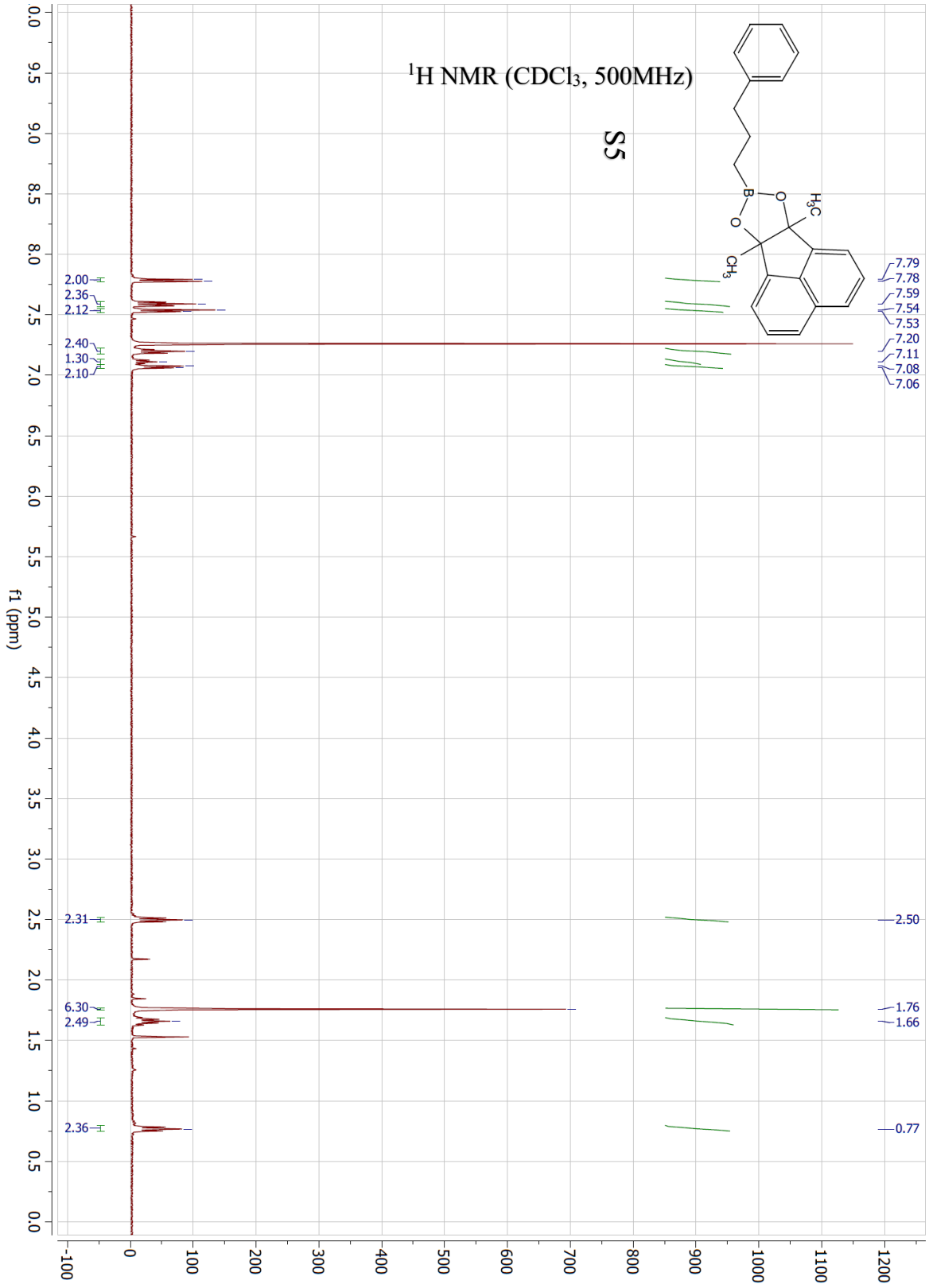
S4
144.99
138.88
134.77
131.49
128.61
128.42
127.74
127.52
125.36
119.55
91.78
77.16 cdcl3
72.80
70.35
32.25
22.27
20.64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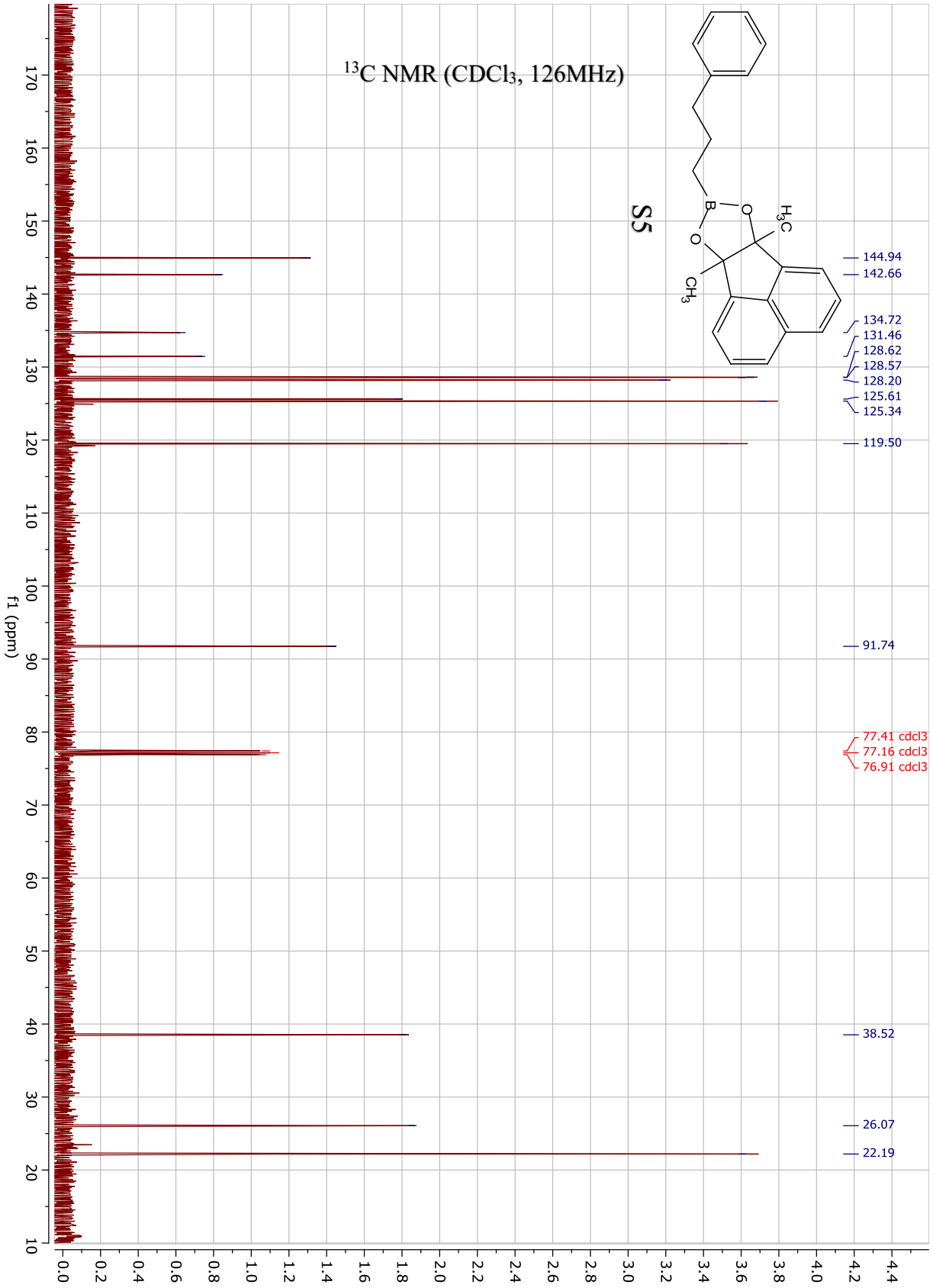
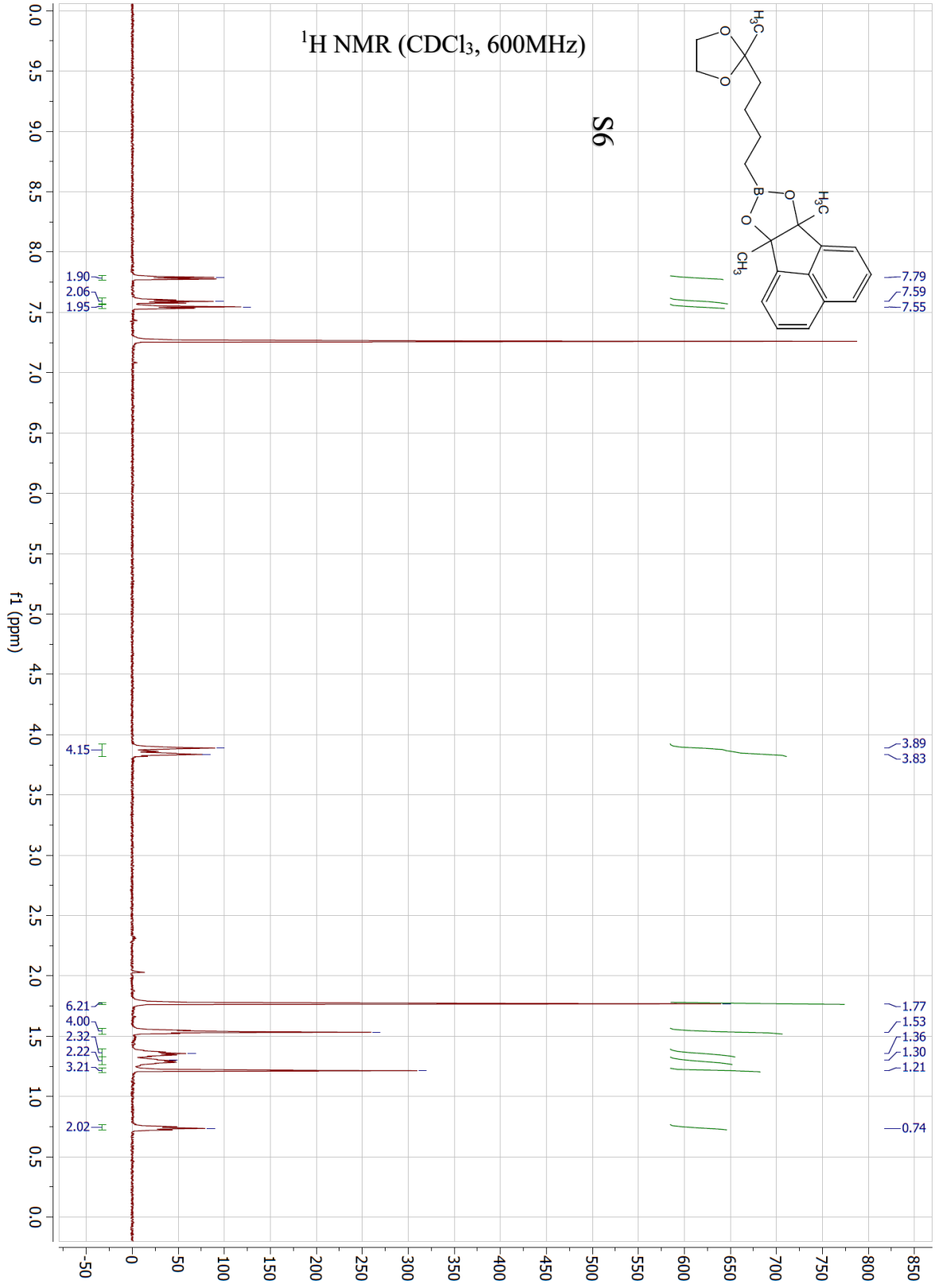
S5
f1 (ppm)
2.00
2.36
2.12
2.40
1.30
2.10
2.31
6.30
2.49
2.36
7.79
7.78
7.59
7.54
7.53
7.20
7.11
7.08
7.06
2.50
1.76
1.66
0.77


^{13}C NMR ($CDCl_3$, 126MHz)
S5
144.94
142.66
134.72
131.46
128.62
128.57
128.20
125.61
125.34
119.50
91.74
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
38.52
26.07
22.19
f1 (ppm)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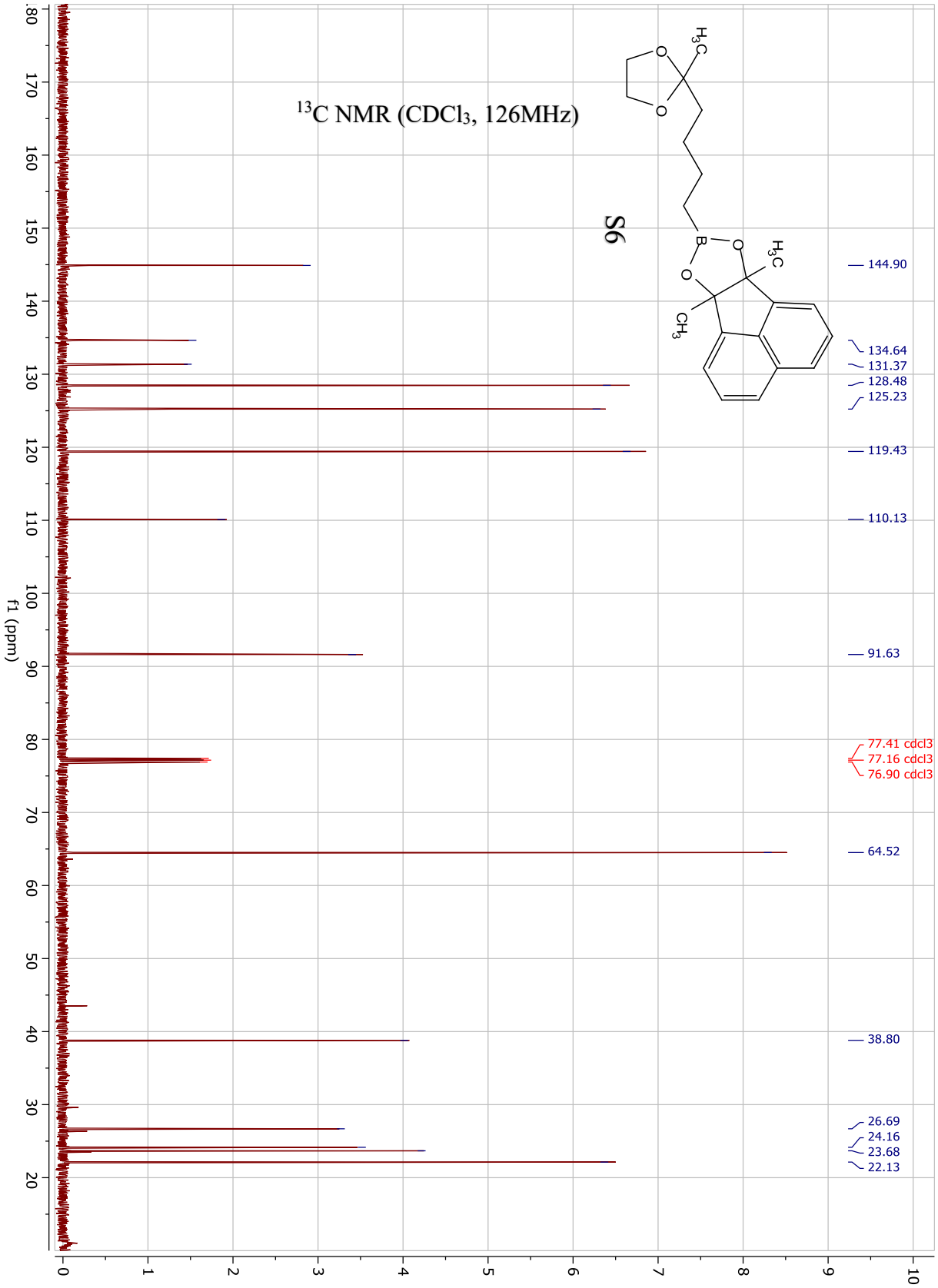
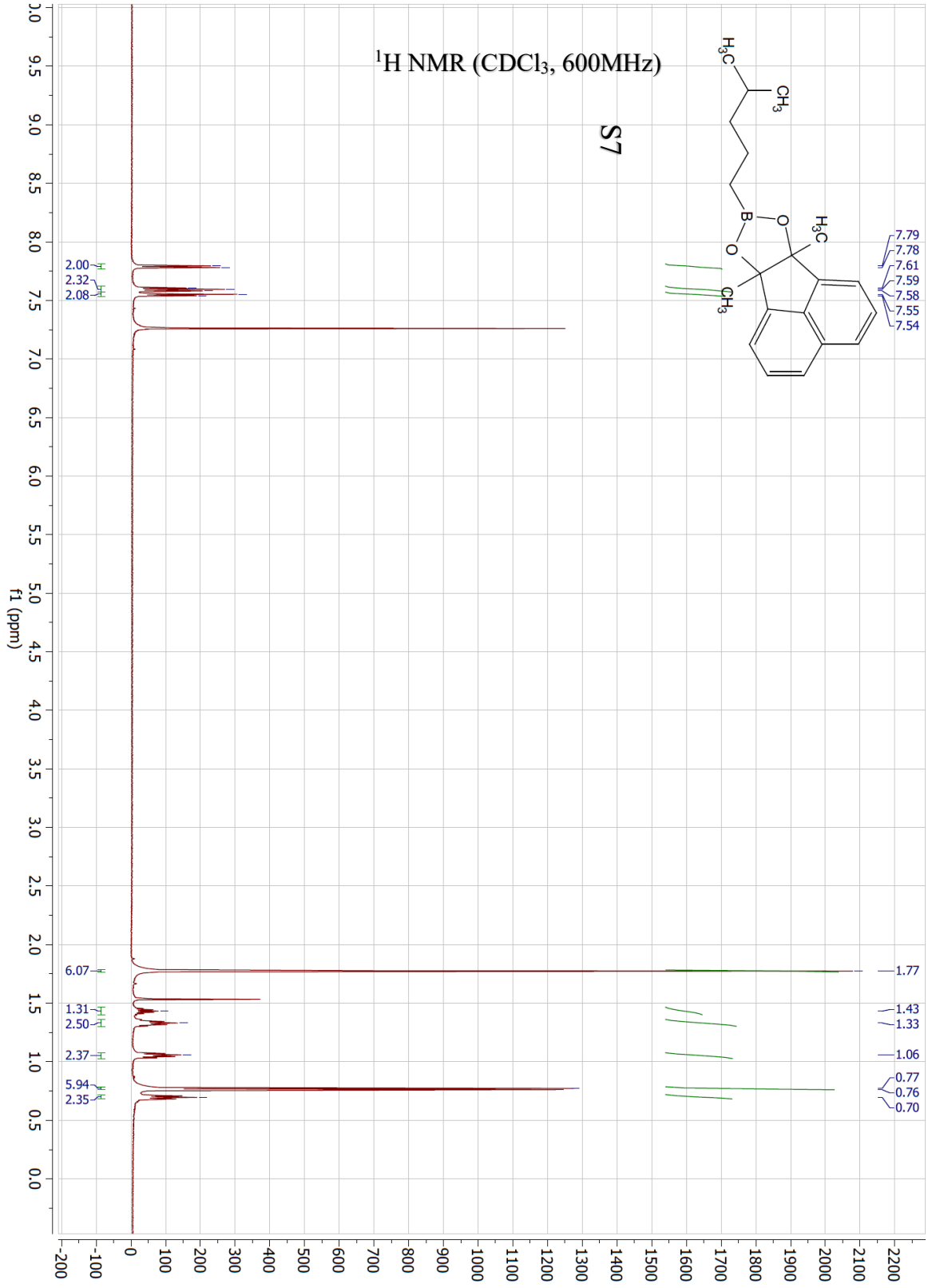
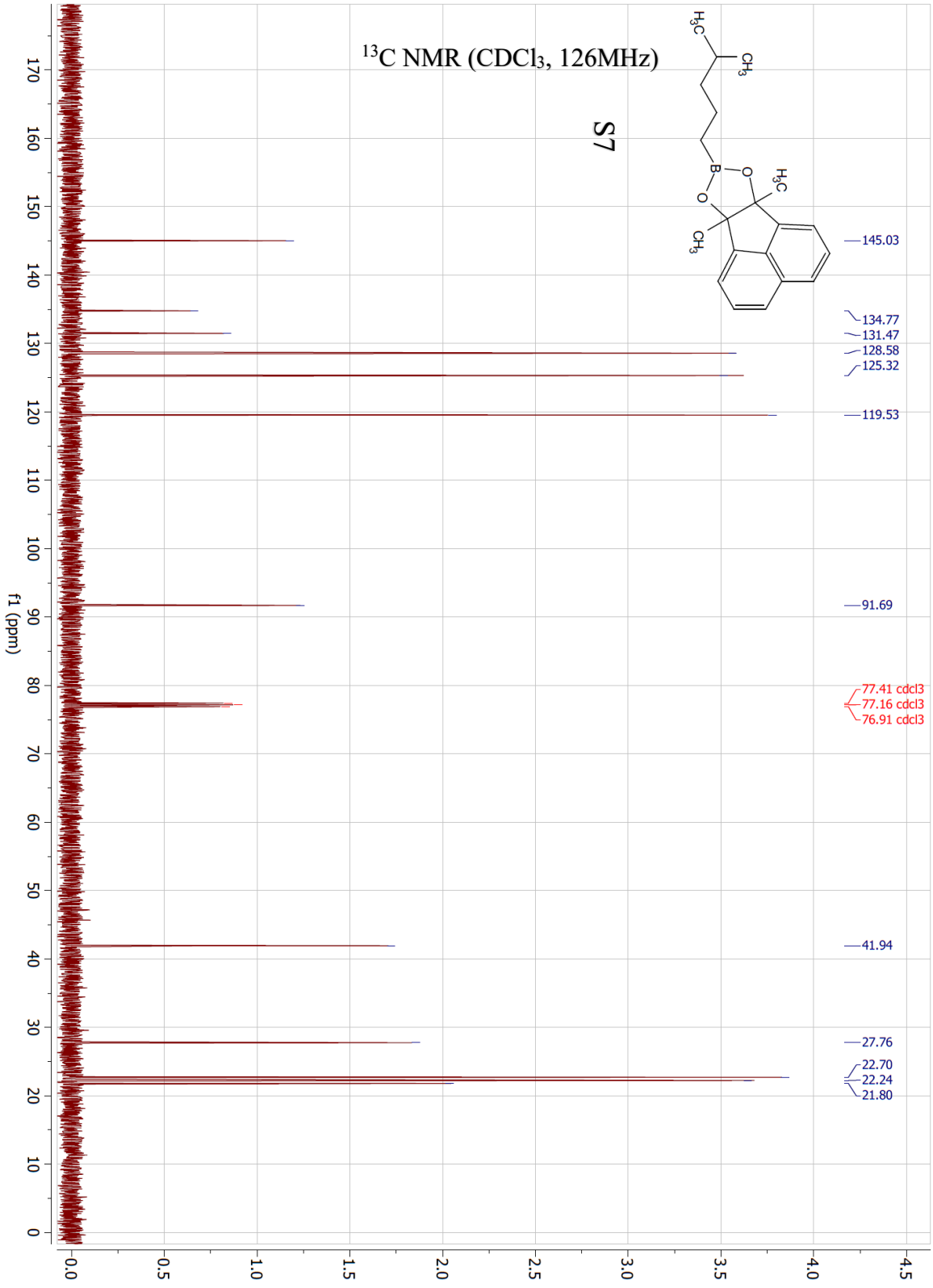
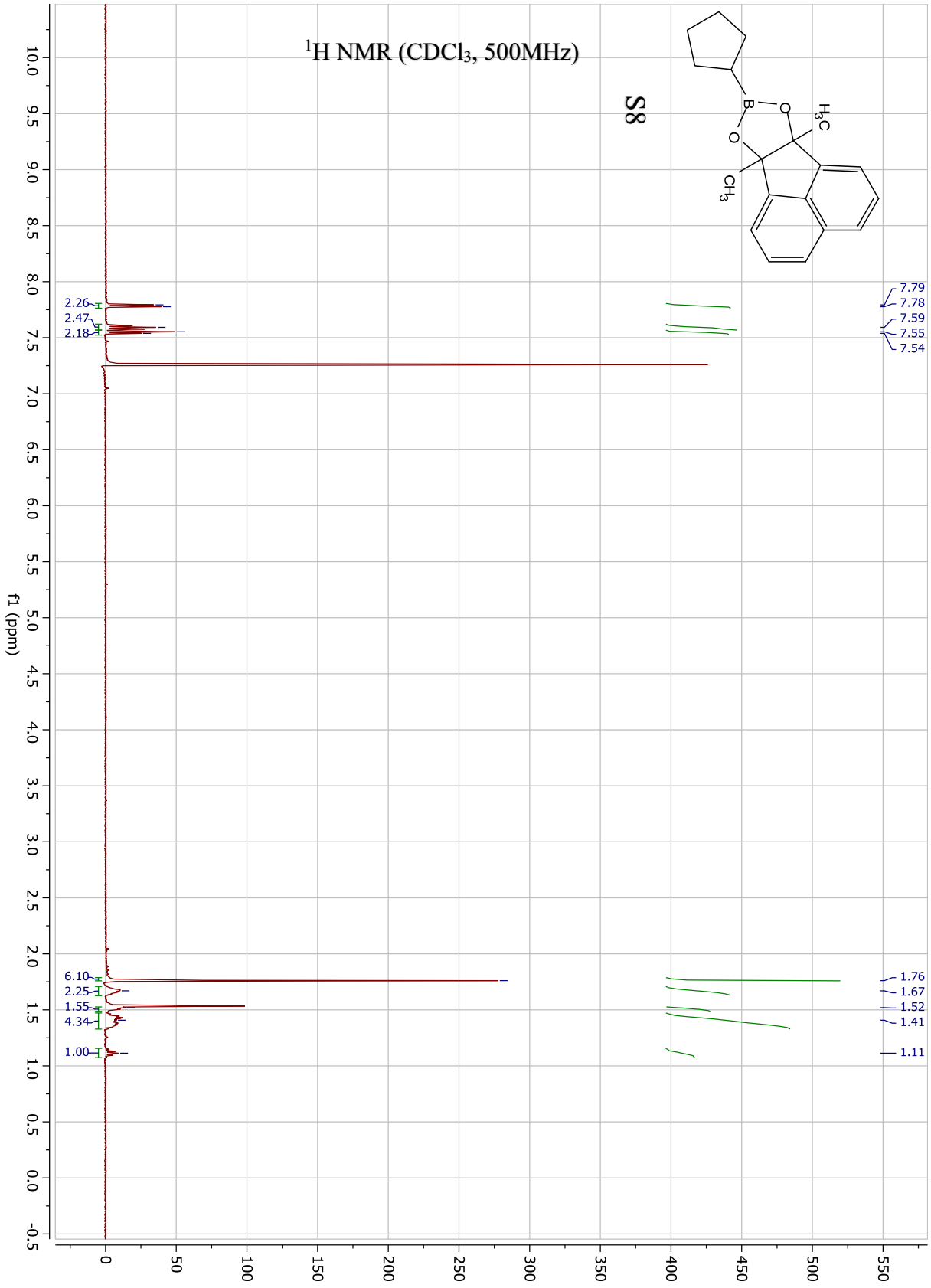
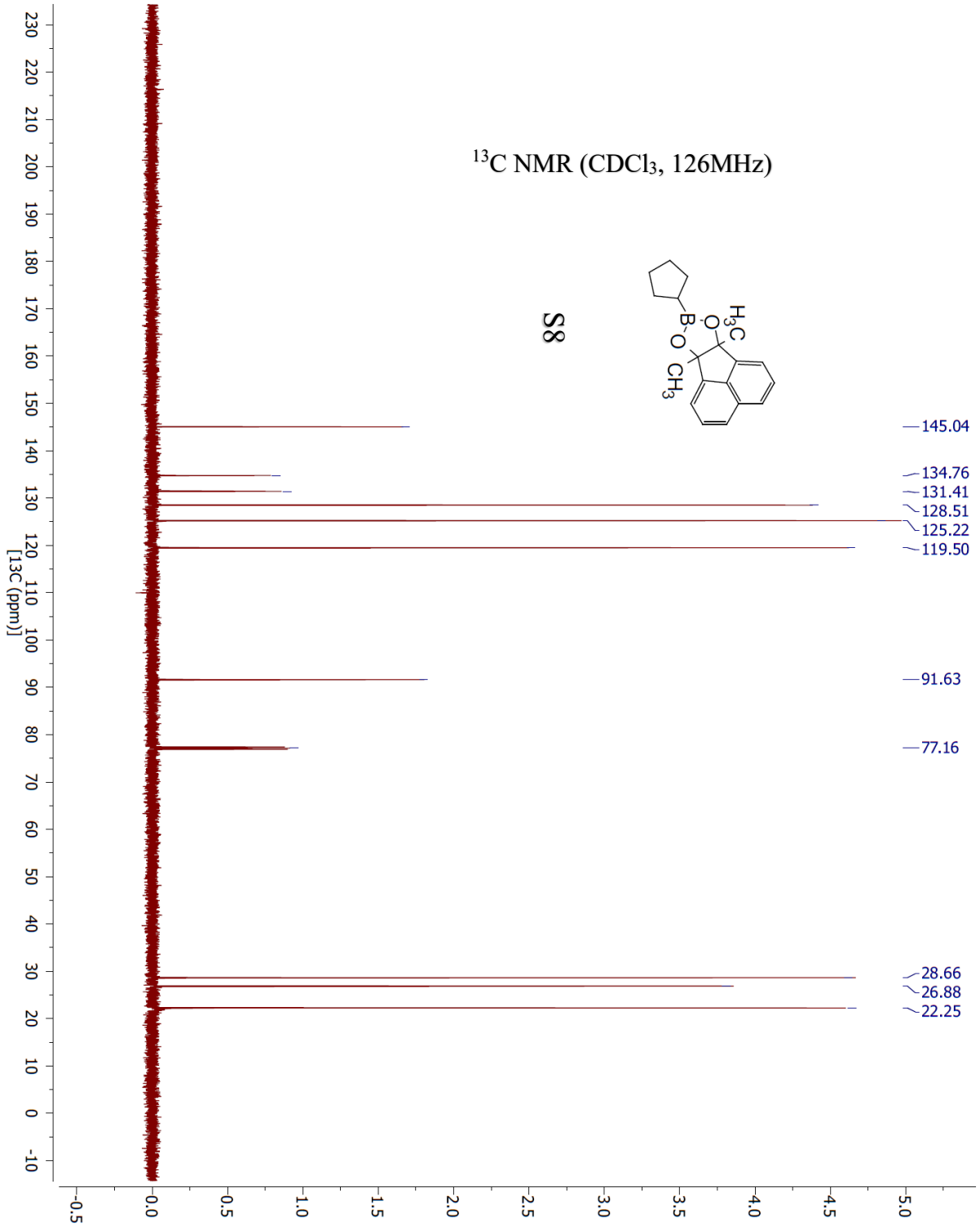
S6
f1 (ppm)
1.90
2.06
1.95
4.15
6.21
4.00
2.32
2.22
3.21
2.02
7.79
7.59
7.55
3.89
3.83
1.77
1.53
1.36
1.30
1.21
0.74


^{13}C NMR ($CDCl_3$, 126MHz)
S6
144.90
134.64
131.37
128.48
125.23
119.43
110.13
91.63
77.41 cdcl3
77.16 cdcl3
76.90 cdcl3
64.52
38.80
26.69
24.16
23.68
22.13
f1 (ppm)


^{1}H NMR ($CDCl_3$, 600MHz)
S7
f1 (ppm)
2.00
2.32
2.08
6.07
1.31
2.50
2.37
5.94
2.35
7.79
7.78
7.61
7.59
7.58
7.55
7.54
1.77
1.43
1.33
1.06
0.77
0.76
0.70


^{13}C NMR ($CDCl_3$, 126MHz)
S7
145.03
134.77
131.47
128.58
125.32
119.53
91.69
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
41.94
27.76
22.70
22.24
21.80
f1 (ppm)


^{1}H NMR ($CDCl_3$, 500MHz)
S8
B
O
O
H_3C
CH_3
2.26
2.47
2.18
6.10
2.25
1.55
4.34
1.00
7.79
7.78
7.59
7.55
7.54
1.76
1.67
1.52
1.41
1.11
f1 (ppm)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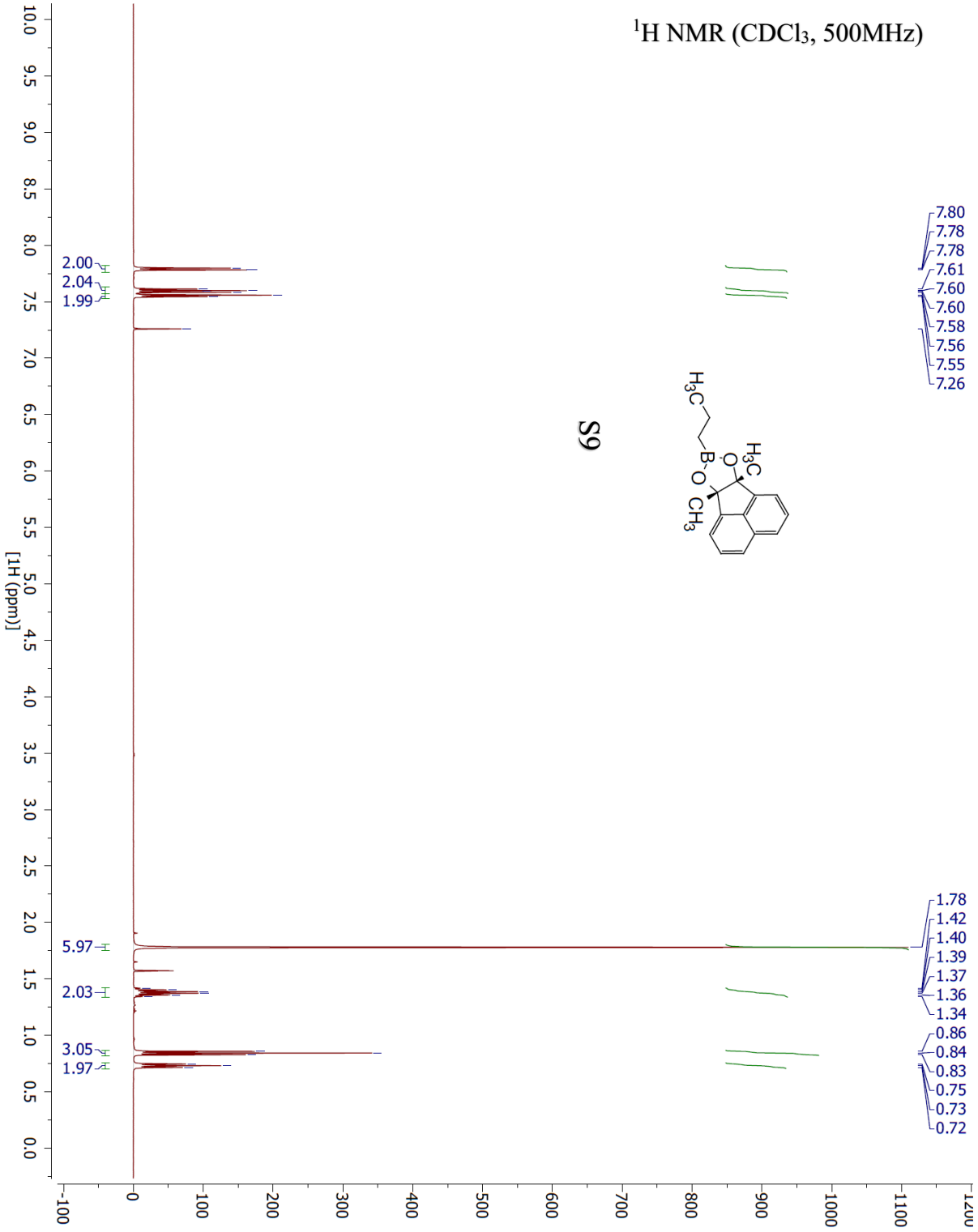
S8
145.04
134.76
131.41
128.51
125.22
119.50
91.63
77.16
28.66
26.88
22.25
[13C (ppm)]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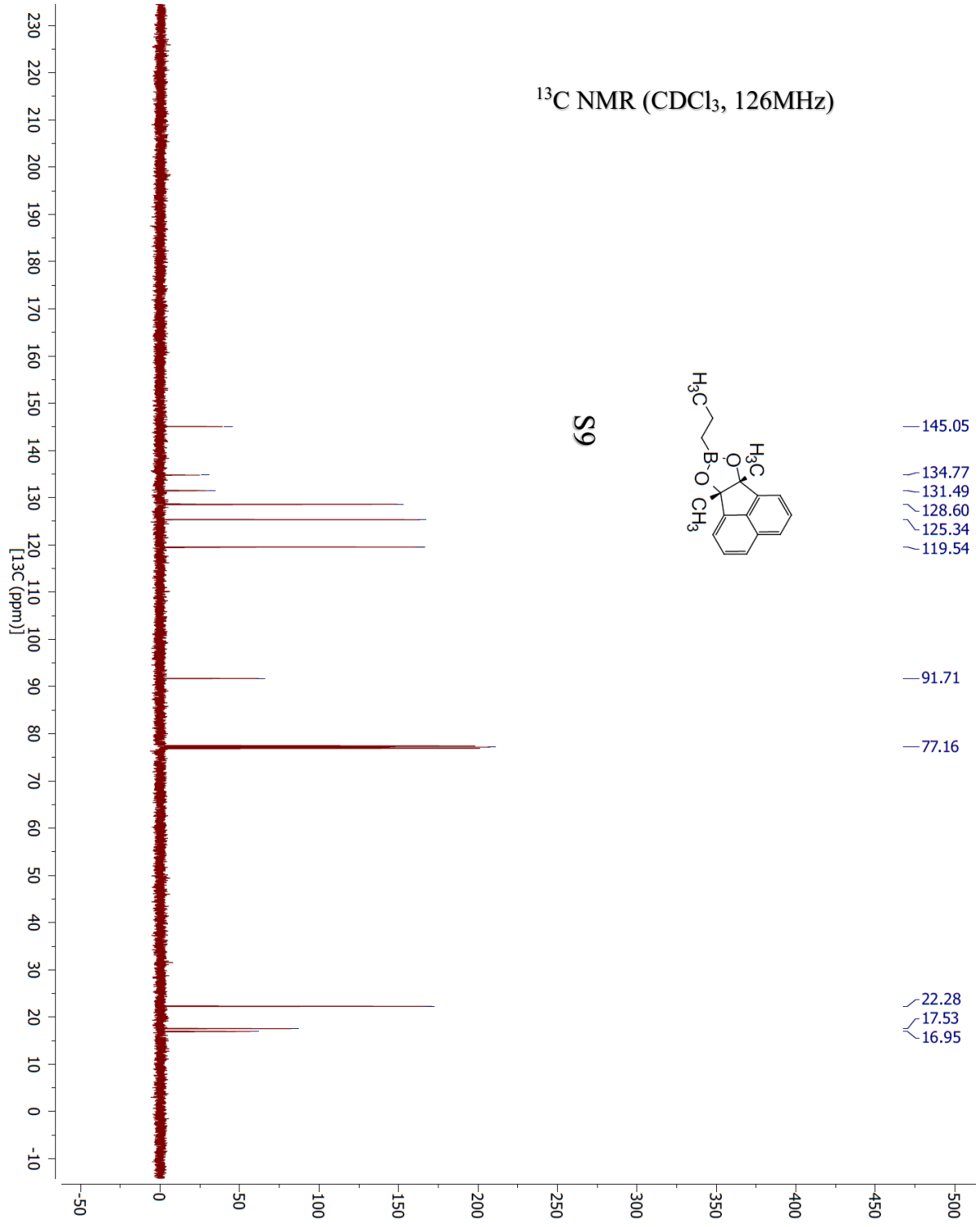
S9
7.80
7.78
7.78
7.61
7.60
7.60
7.58
7.56
7.55
7.26
1.78
1.42
1.40
1.39
1.37
1.36
1.34
0.86
0.84
0.83
0.75
0.73
0.72
2.00
2.04
1.99
5.97
2.03
3.05
1.97
[1H (ppm)]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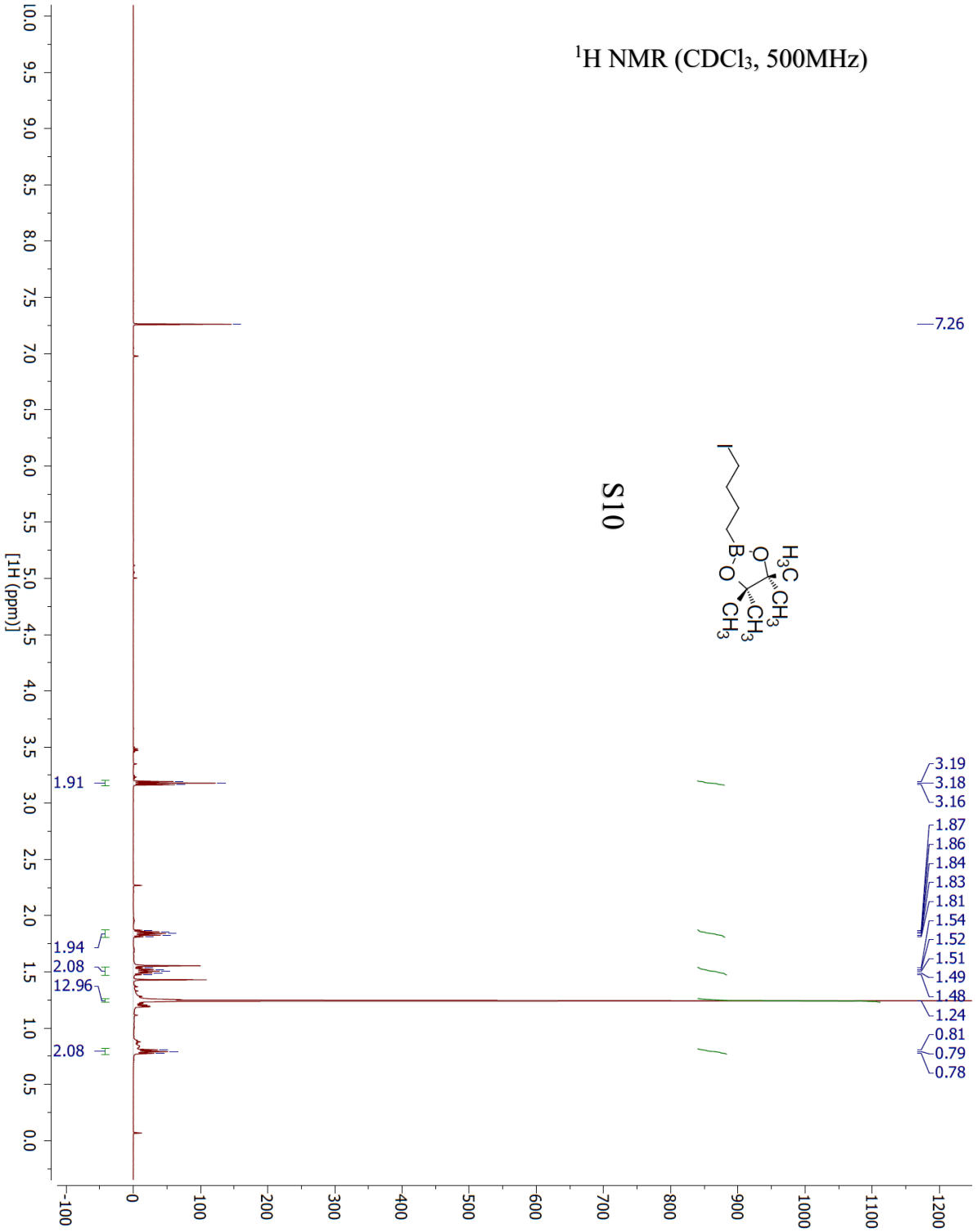
S9
145.05
134.77
131.49
128.60
125.34
119.54
91.71
77.16
22.28
17.53
16.95
[13C (ppm)]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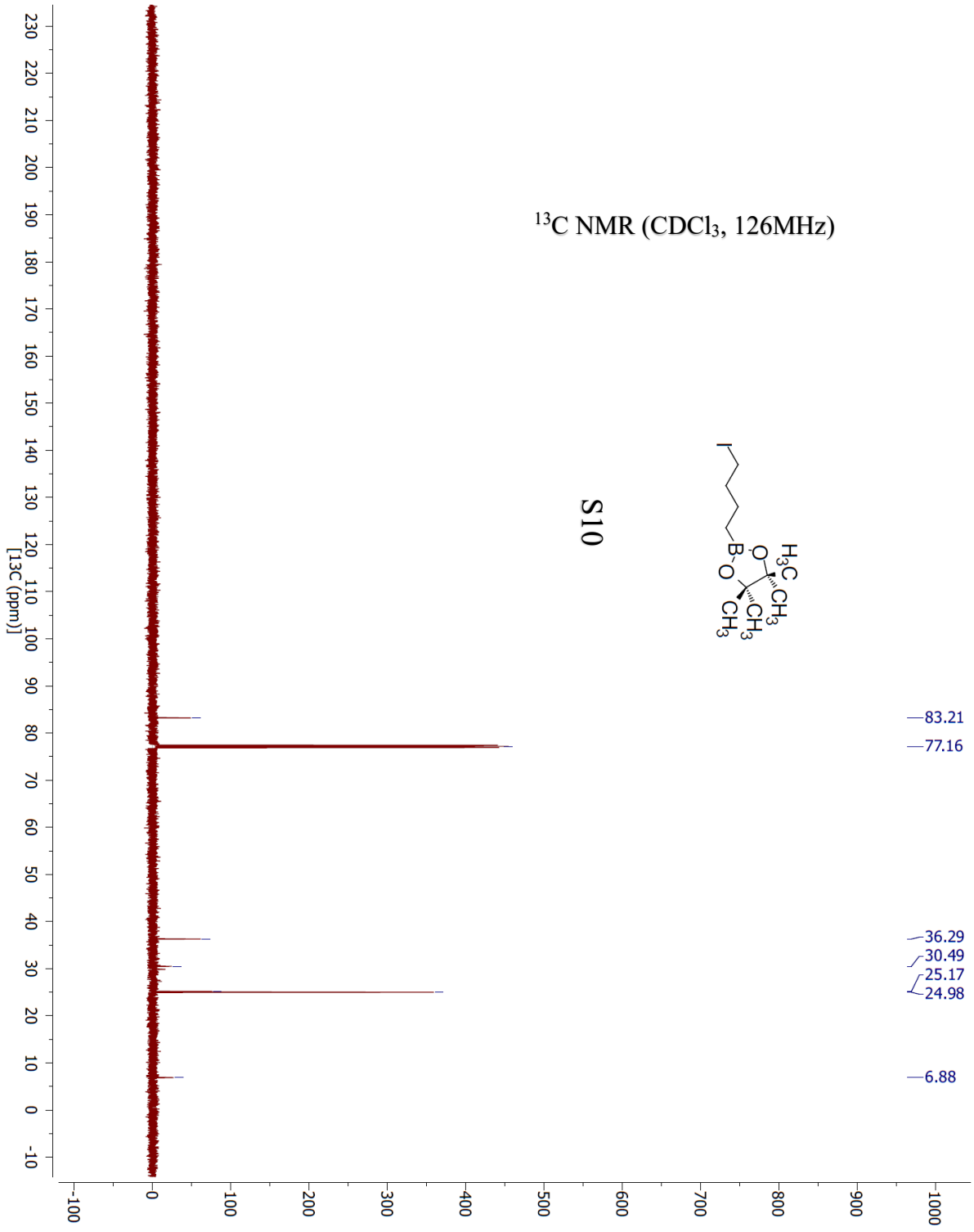
S10
[1H (ppm)]
7.26
3.19
3.18
3.16
1.87
1.86
1.84
1.83
1.81
1.54
1.52
1.51
1.49
1.48
1.24
0.81
0.79
0.78
1.91
1.94
2.08
12.96
2.08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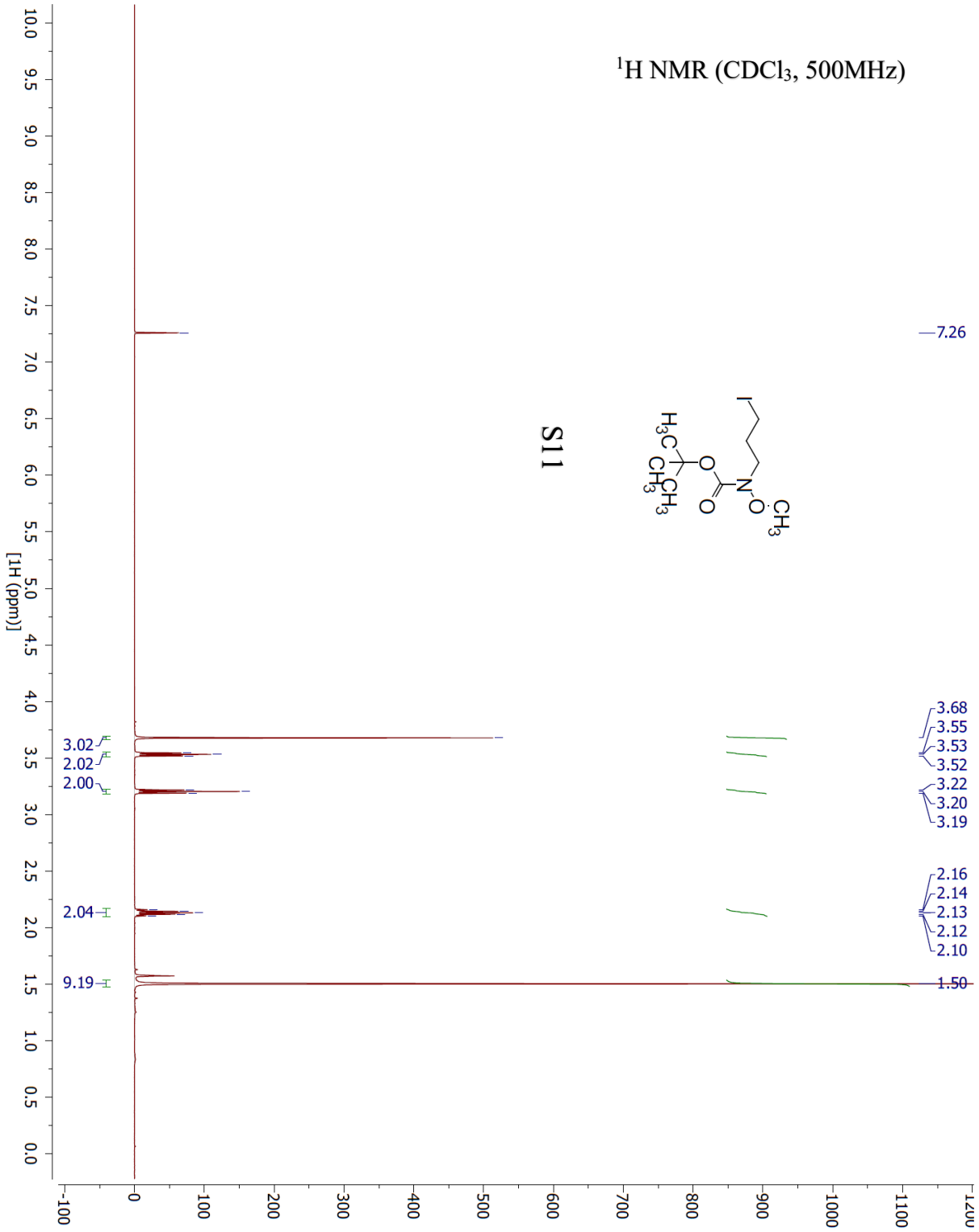
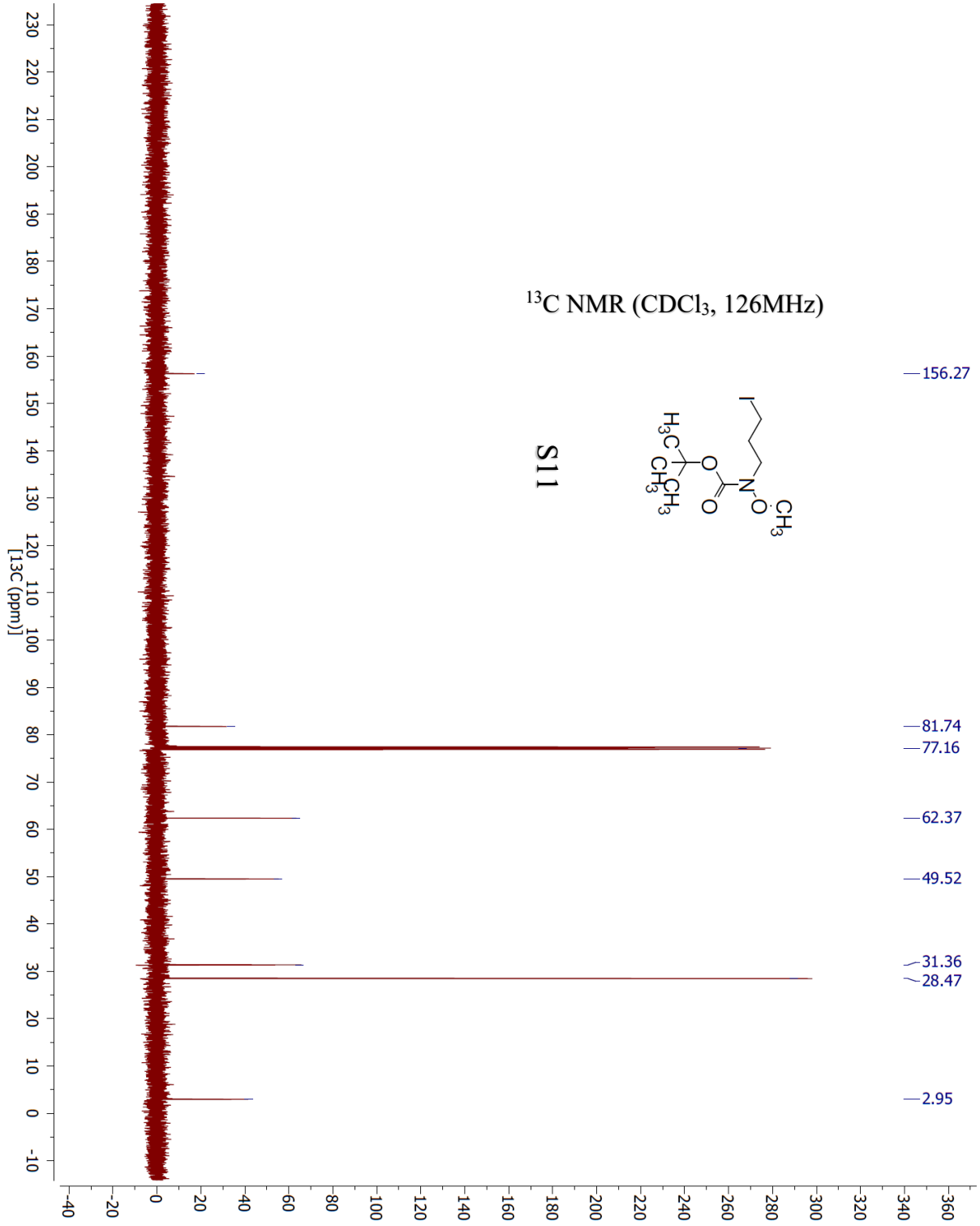
83.21
77.16
36.29
30.49
25.17
24.98
6.88


^{1}H NMR ($CDCl_3$, 500MHz)
S11
7.26
3.68
3.55
3.53
3.52
3.22
3.20
3.19
2.16
2.14
2.13
2.12
2.10
1.50
3.02
2.02
2.00
2.04
9.19
[1H (ppm)]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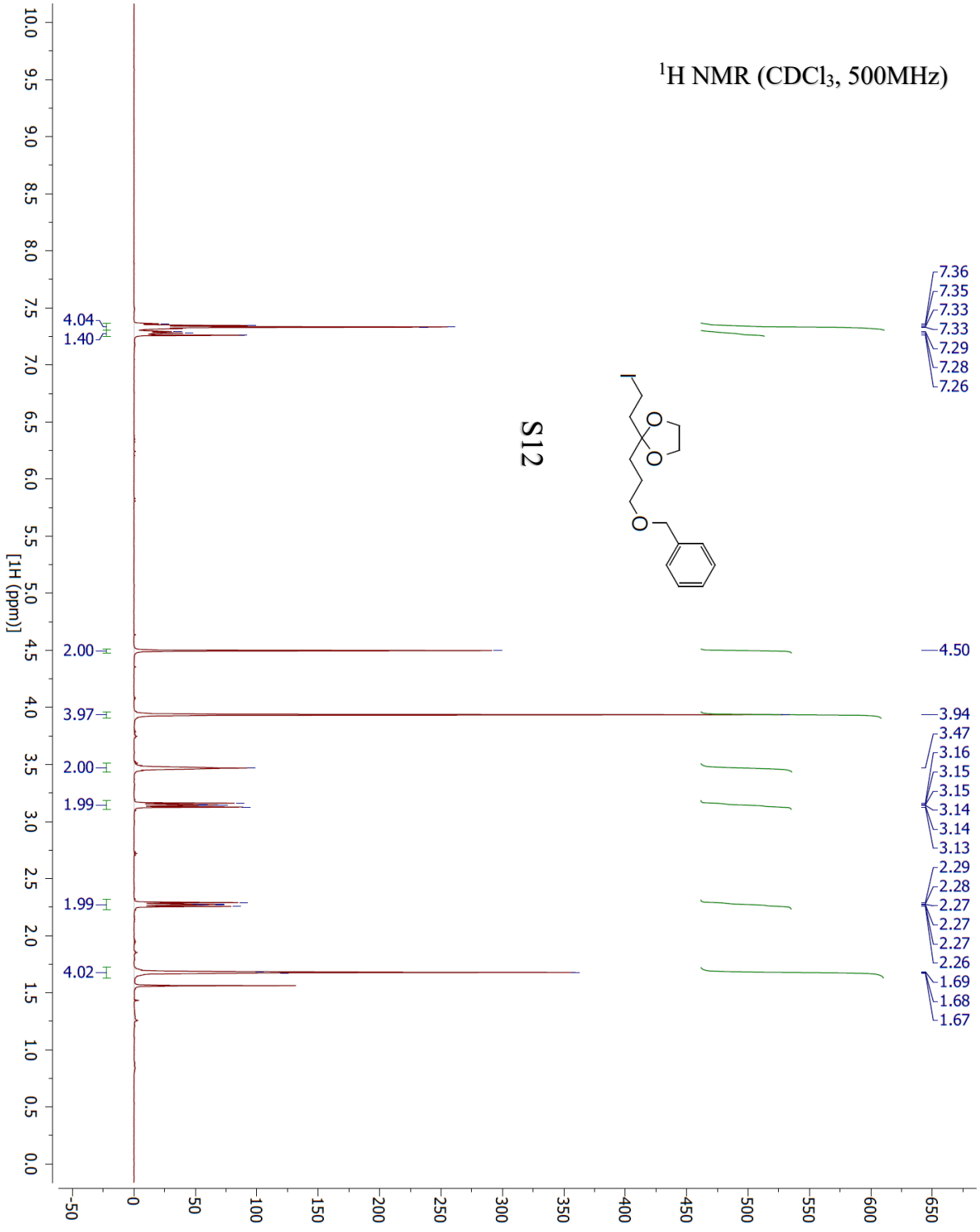
S11
156.27
81.74
77.16
62.37
49.52
31.36
28.47
2.95
[13C (ppm)]


^{1}H NMR ($CDCl_3$, 500MHz)
S12
[1H (ppm)]
4.04
1.40
2.00
3.97
2.00
1.99
1.99
4.02
7.36
7.35
7.33
7.33
7.29
7.28
7.26
4.50
3.94
3.47
3.16
3.15
3.15
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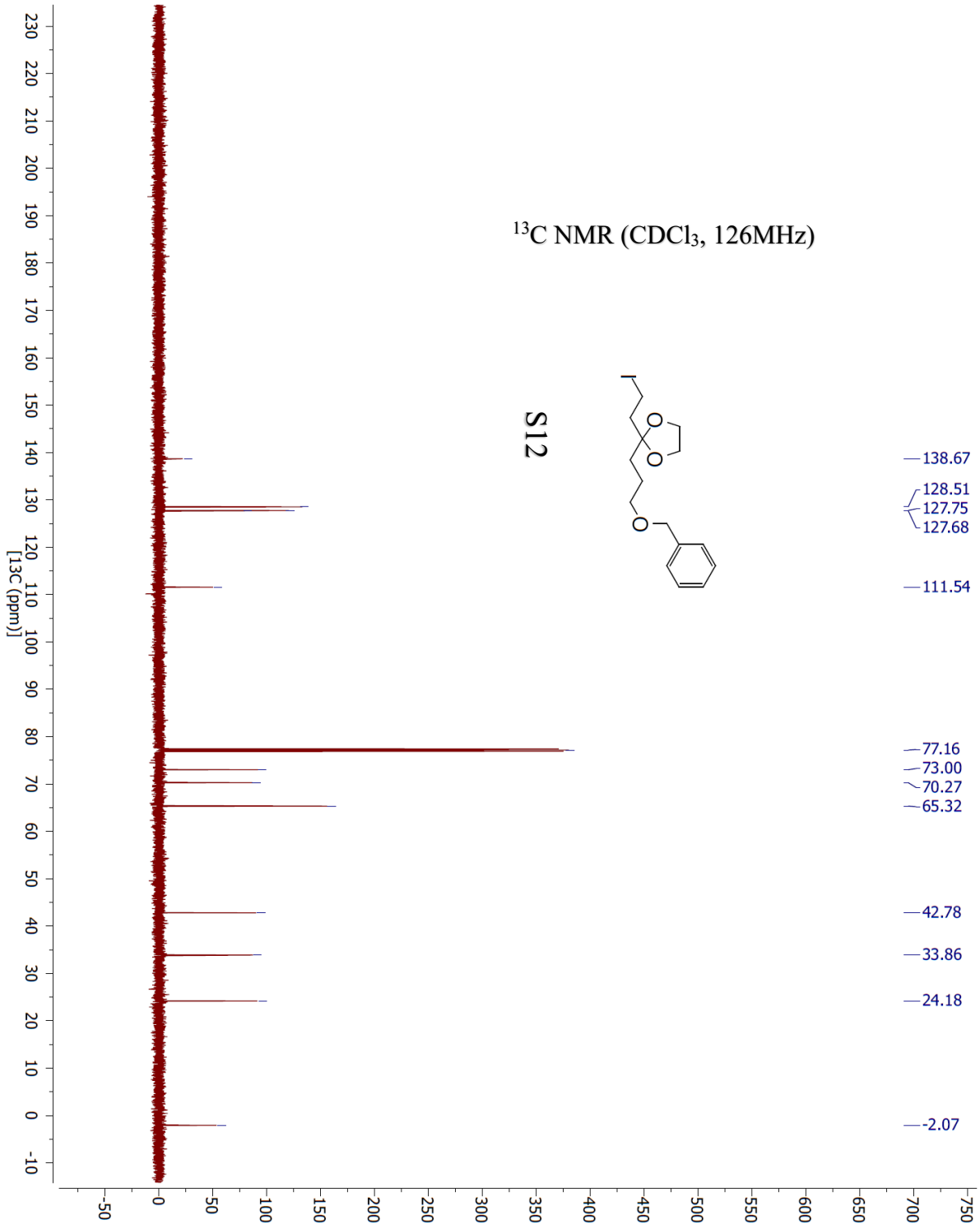
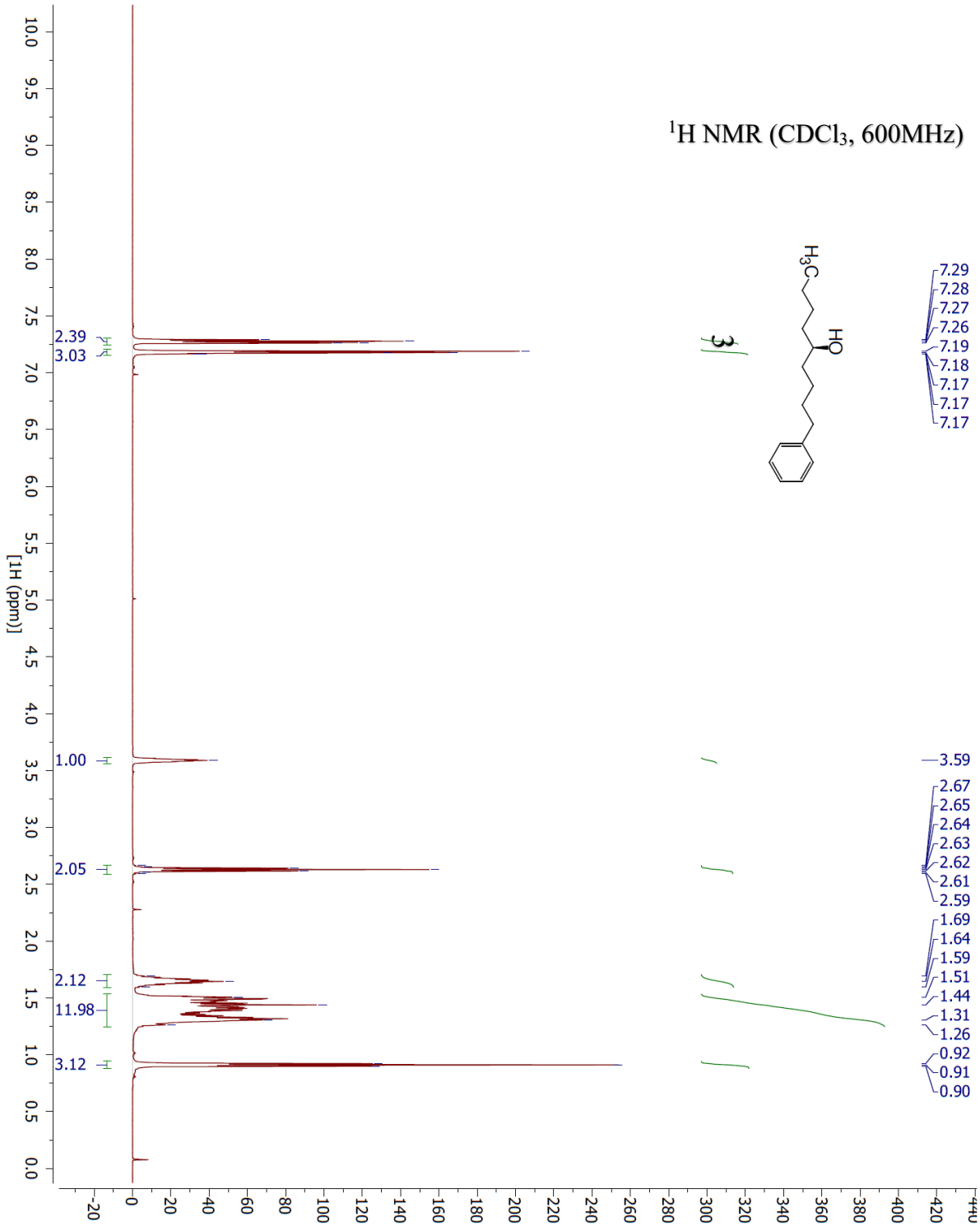
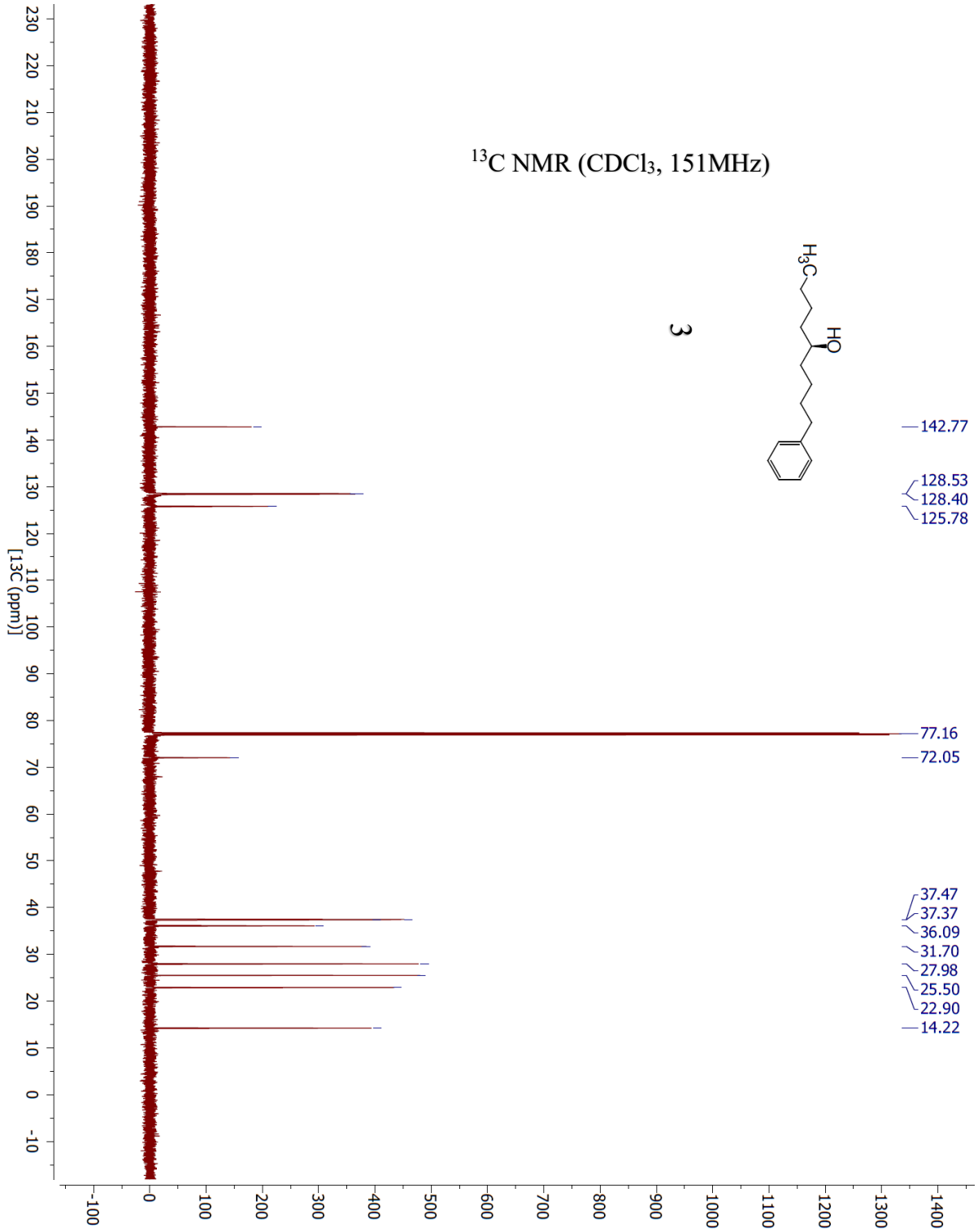
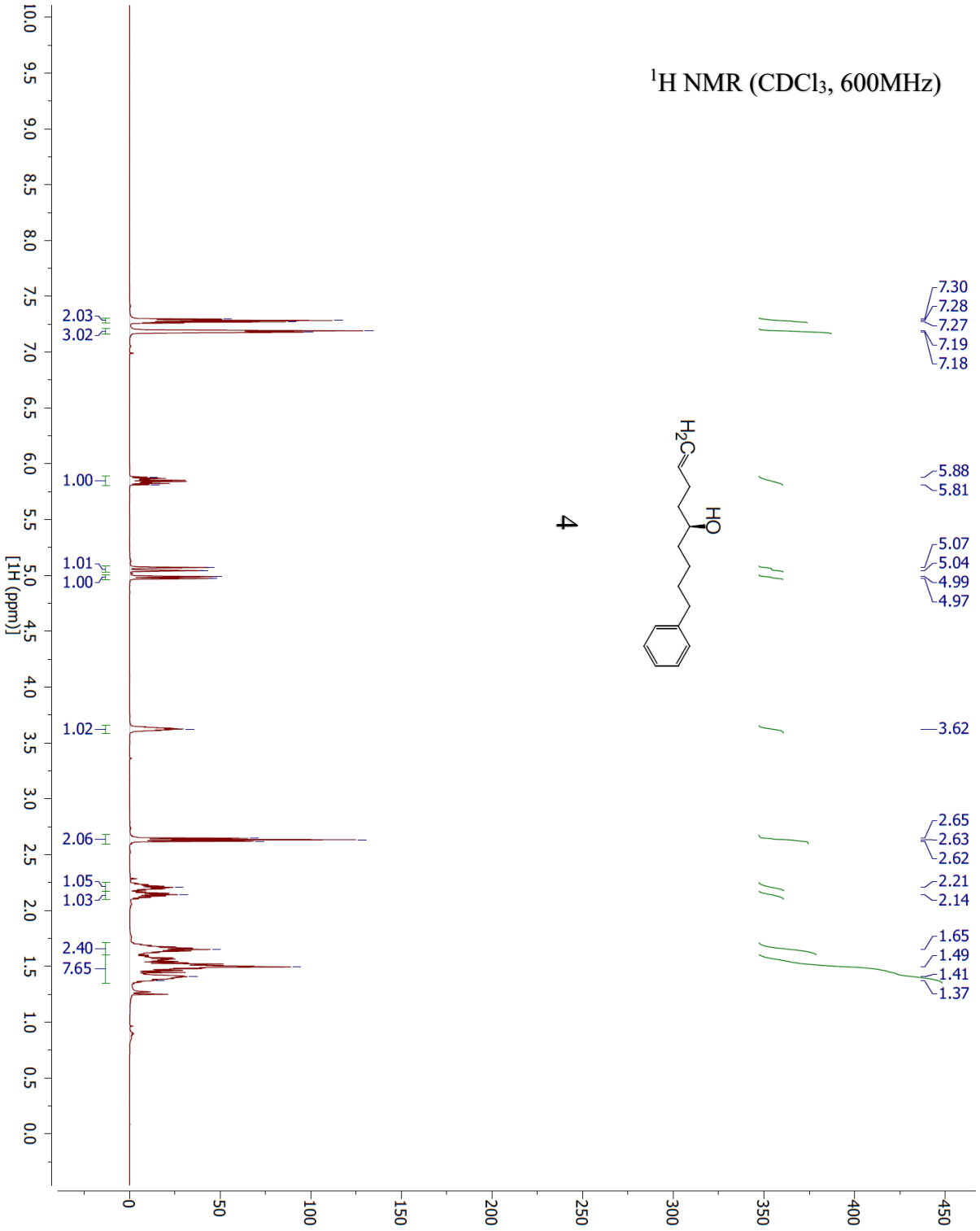
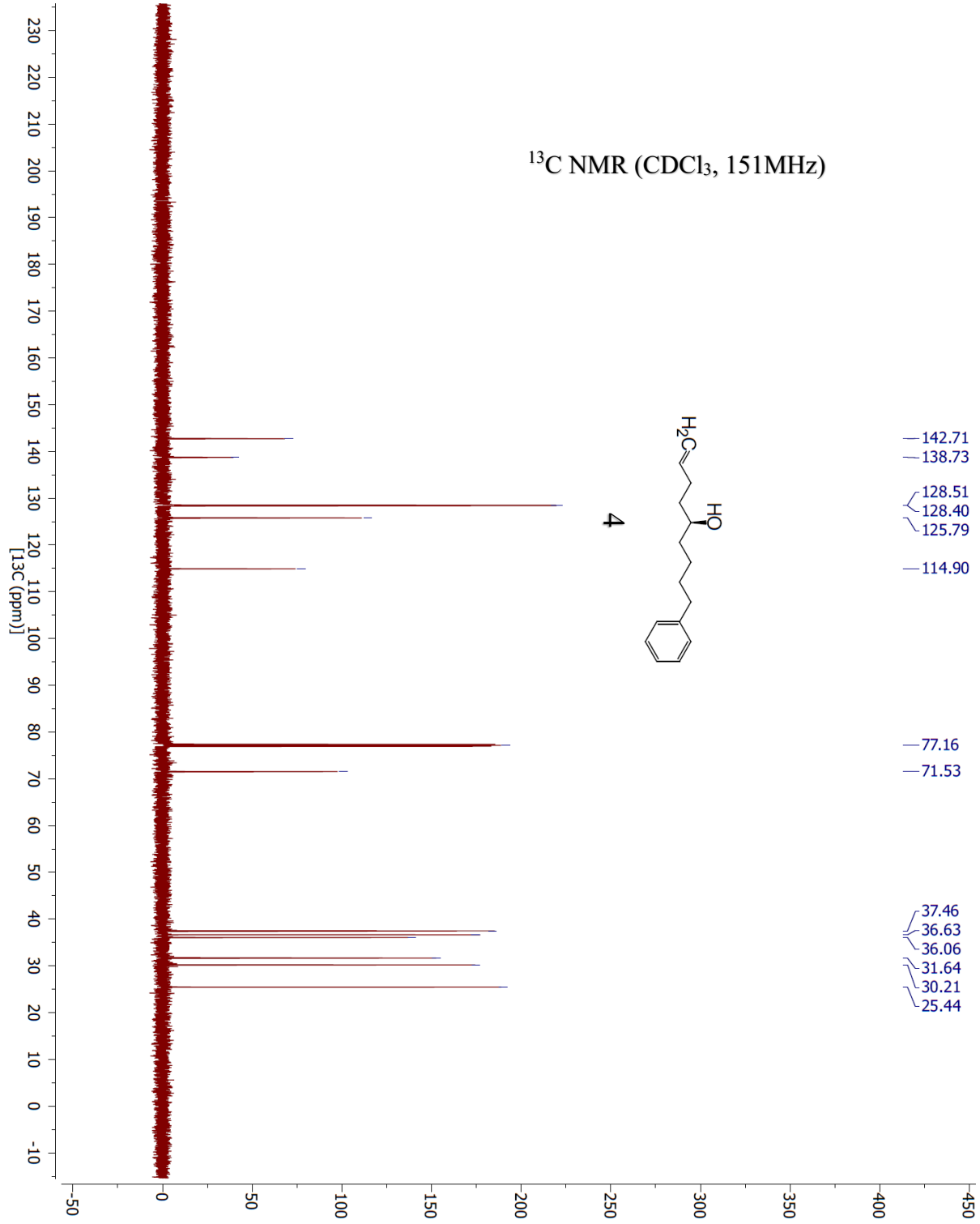
2.27
2.27
2.26
1.69
1.68
1.67

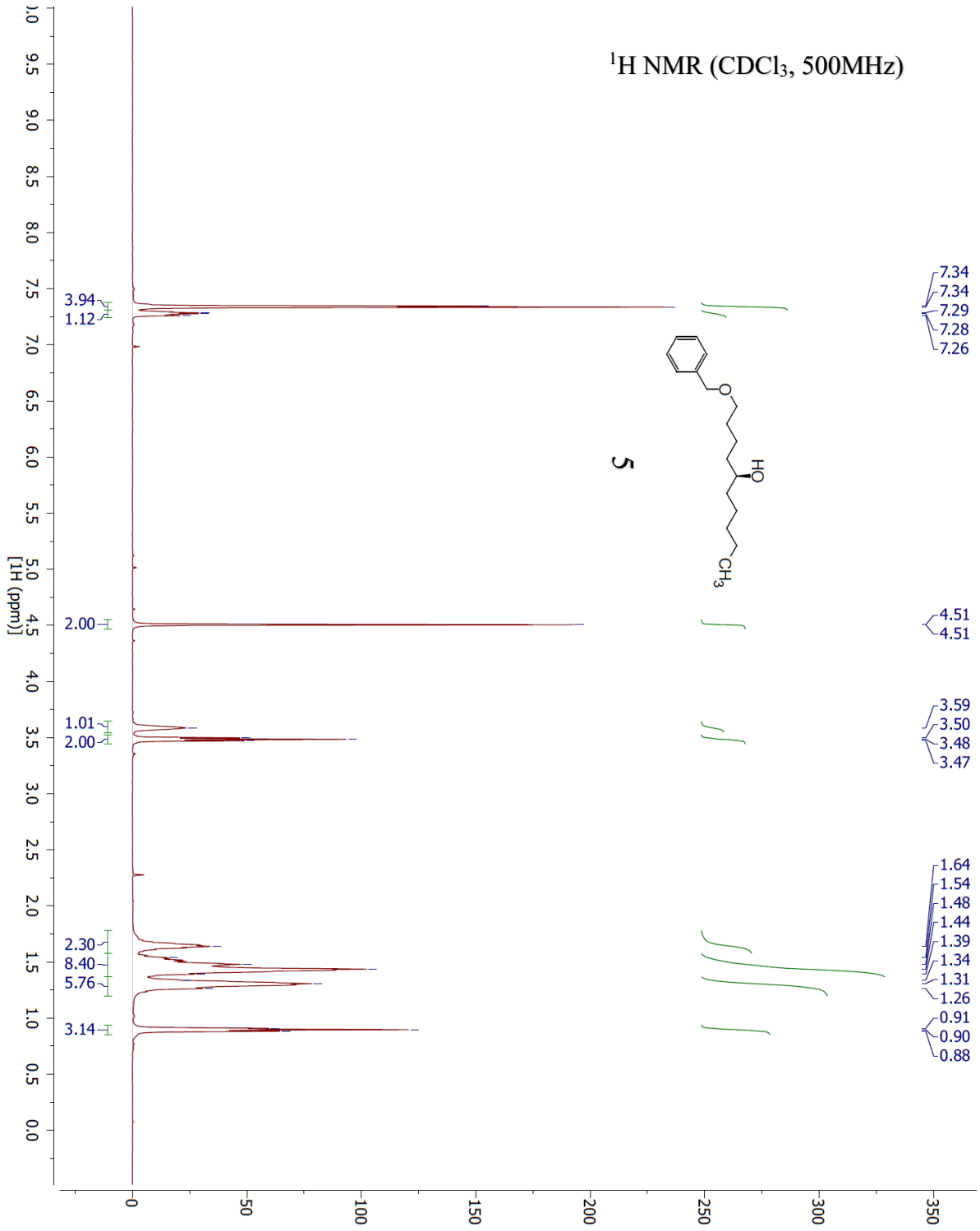

^{13}C NMR (CDCl$_3$, 126MHz)
S12
138.67
128.51
127.75
127.68
111.54
77.16
73.00
70.27
65.32
42.78
33.86
24.18
-2.07
[13C (ppm)]

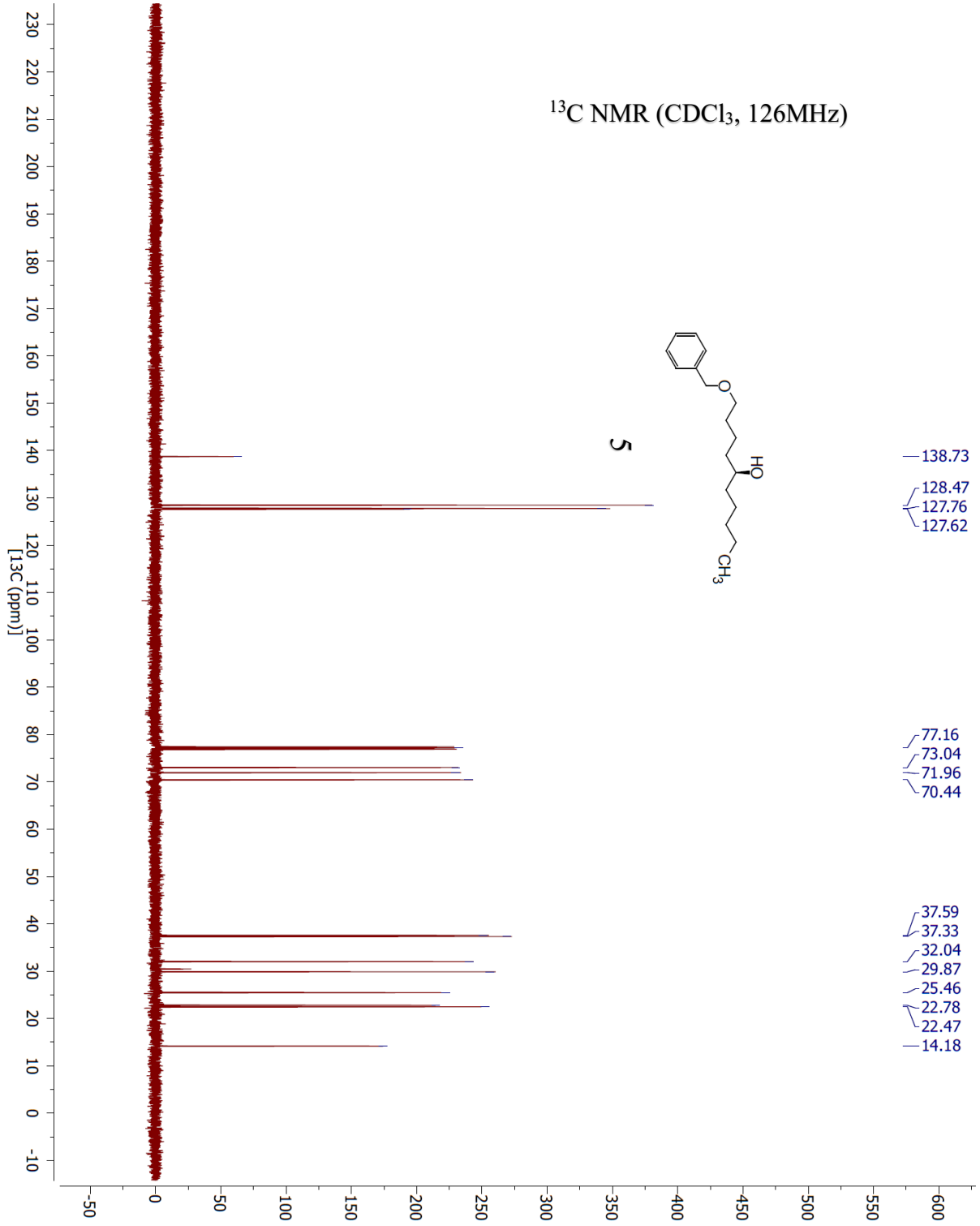

^{1}H NMR ($CDCl_3$, 600MHz)
H_3C
HO
3
7.29
7.28
7.27
7.26
7.19
7.18
7.17
7.17
7.17
3.59
2.67
2.65
2.64
2.63
2.62
2.61
2.59
1.69
1.64
1.59
1.51
1.44
1.31
1.26
0.92
0.91
0.90
2.39
3.03
1.00
2.05
2.12
11.98
3.12
[1H (ppm)]

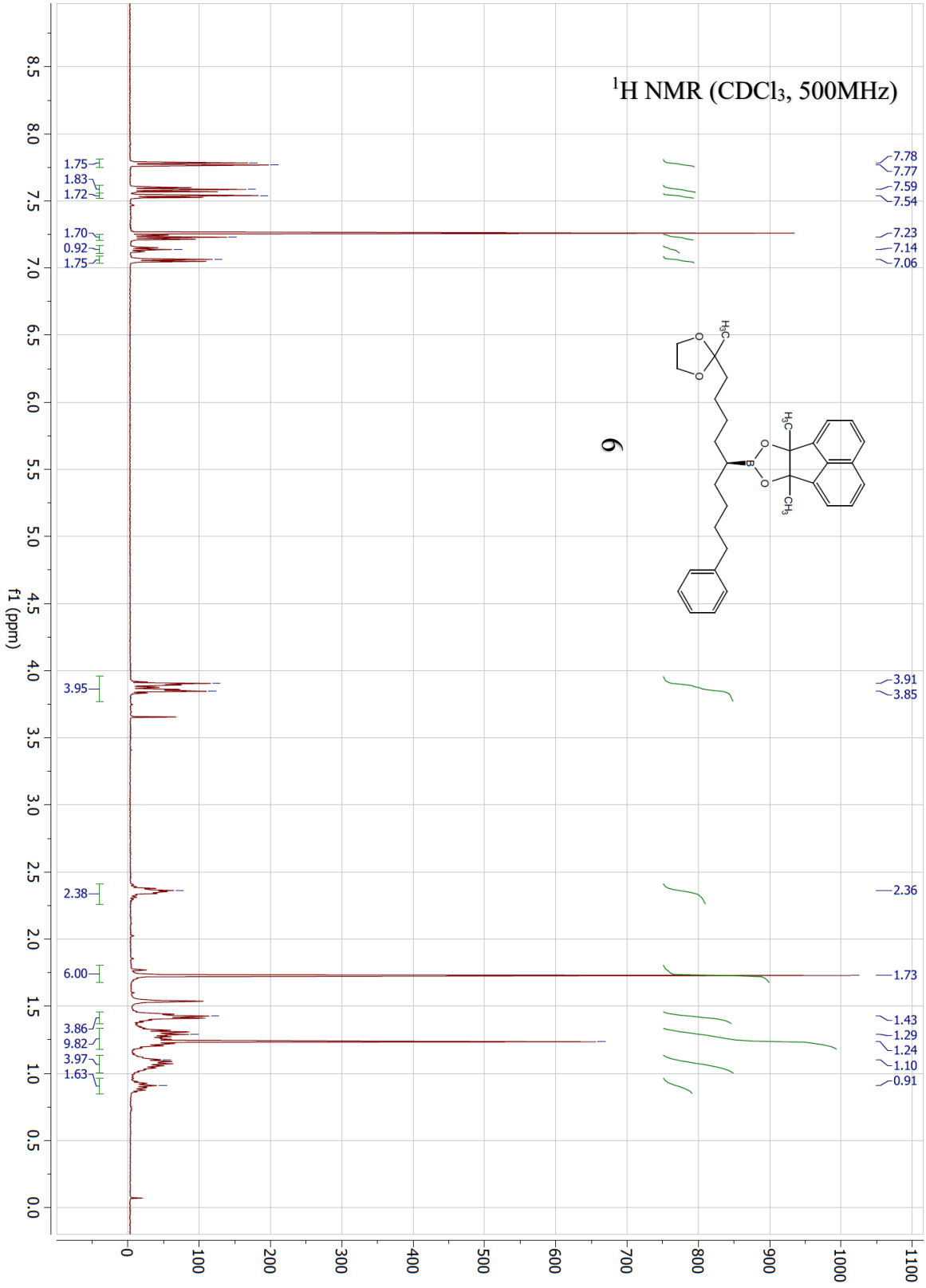

^{13}C NMR (CDCl$_3$, 151MHz)
3
H$_3$C
HO
142.77
128.53
128.40
125.78
77.16
72.05
37.47
37.37
36.09
31.70
27.98
25.50
22.90
14.22
[13C (ppm)]

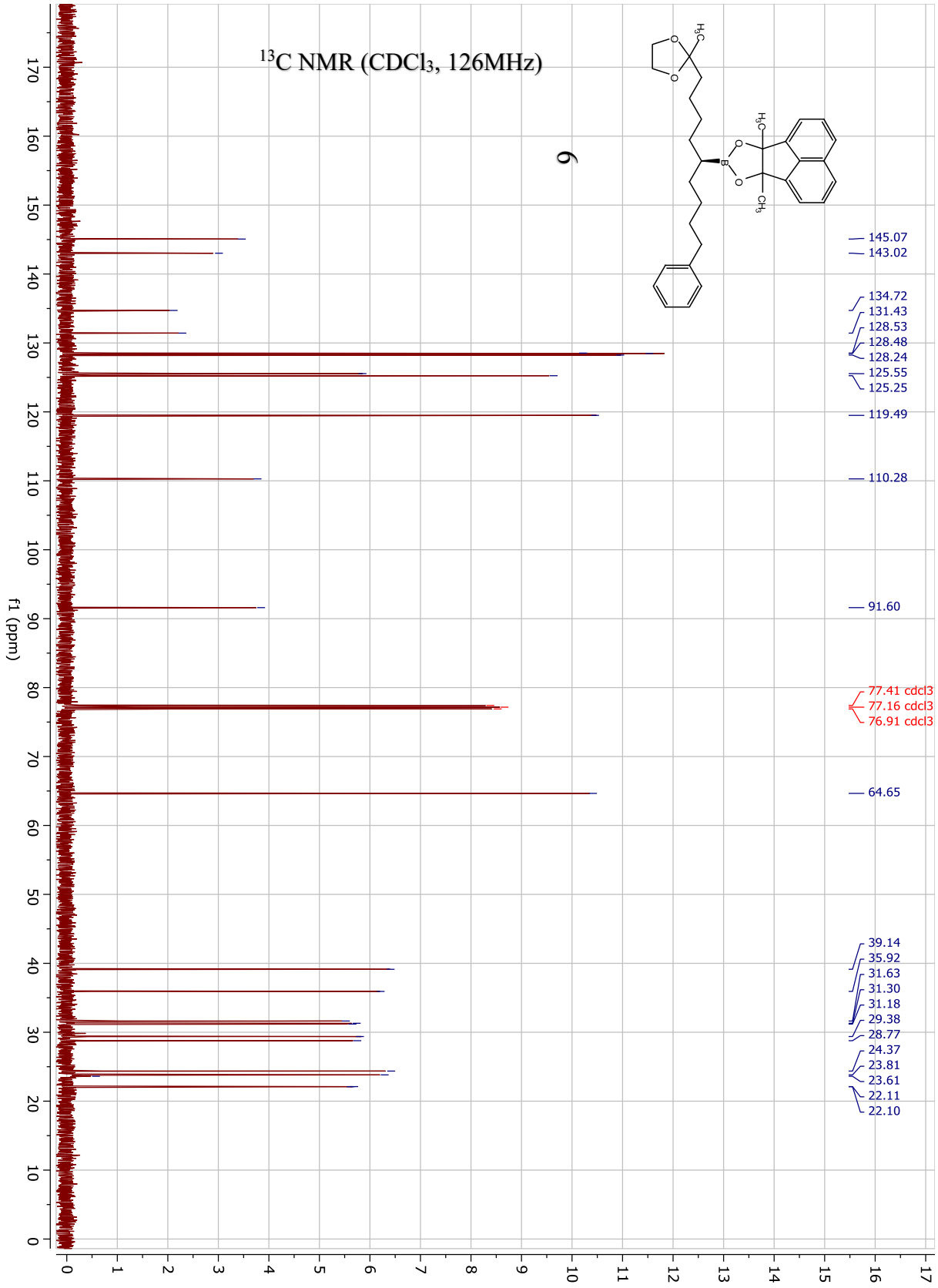

^{1}H NMR ($CDCl_3$, 600MHz)
4
H_2C
HO
[1H (ppm)]
2.03
3.02
1.00
1.01
1.00
1.02
2.06
1.05
1.03
2.40
7.65
7.30
7.28
7.27
7.19
7.18
5.88
5.81
5.07
5.04
4.99
4.97
3.62
2.65
2.63
2.62
2.21
2.14
1.65
1.49
1.41
1.37

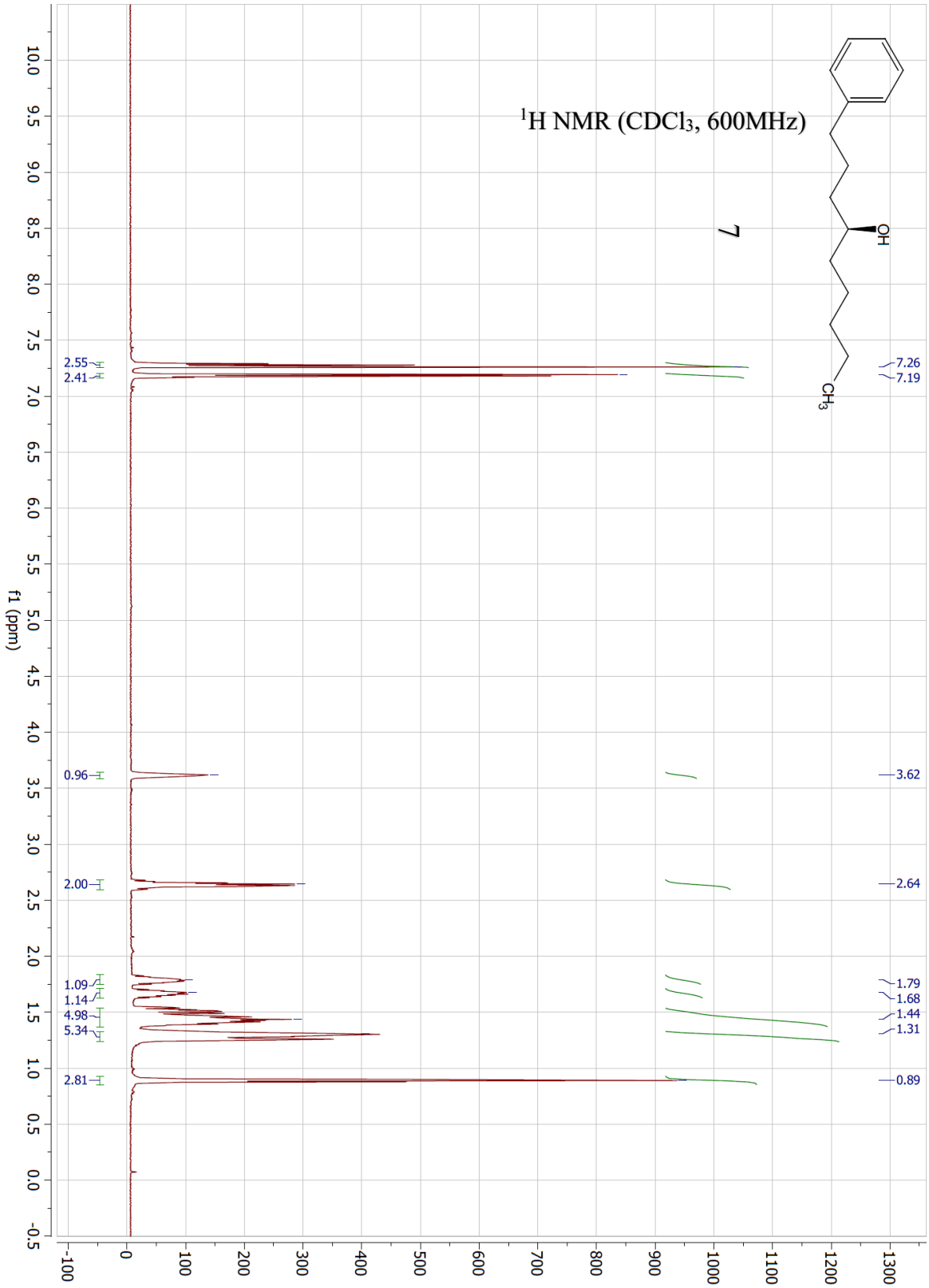

^{13}C NMR (CDCl$_3$, 151MHz)
4
H$_2$C
HO
142.71
138.73
128.51
128.40
125.79
114.90
77.16
71.53
37.46
36.63
36.06
31.64
30.21
25.44
[13C (ppm)]

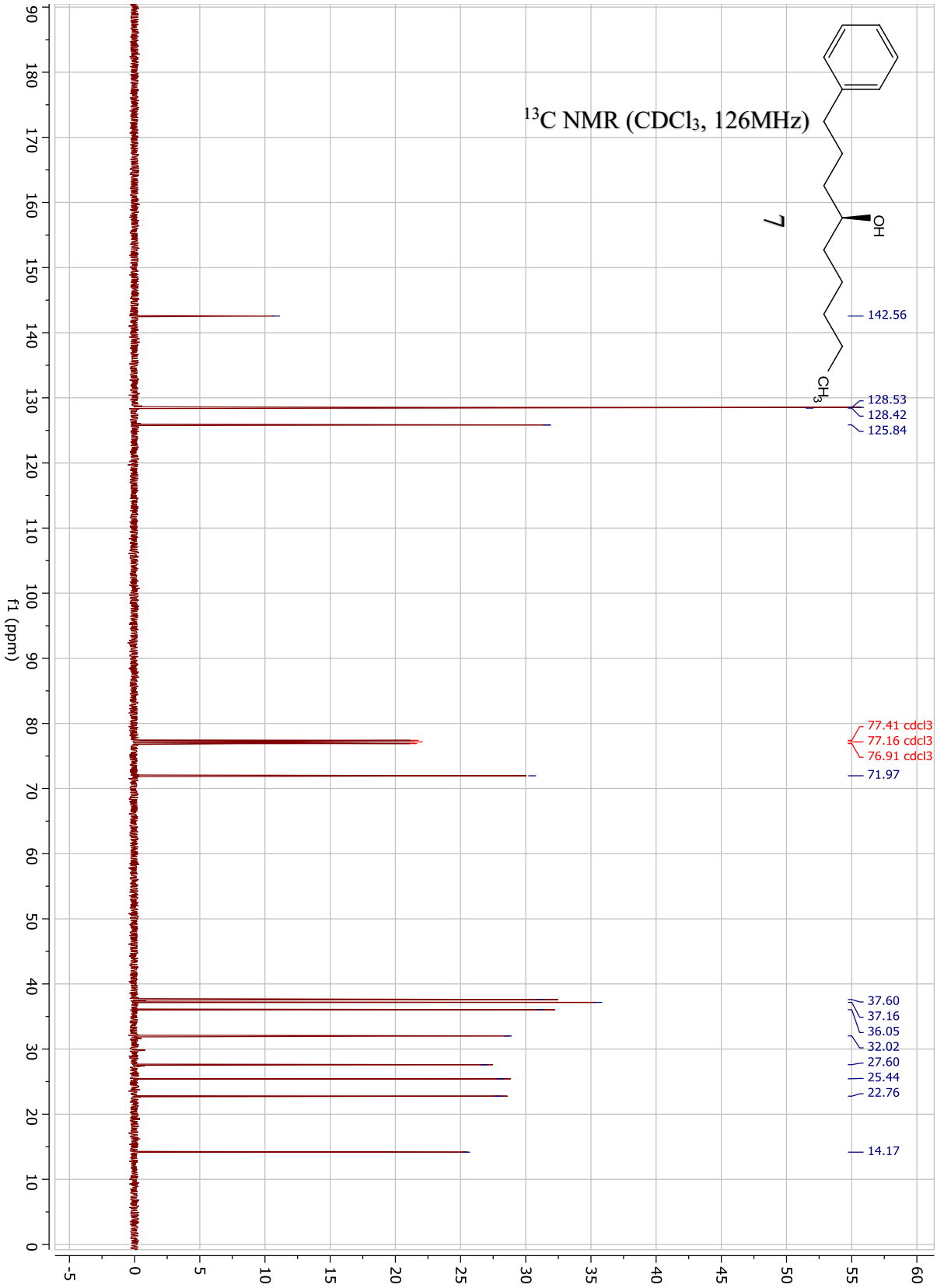

^{1}H NMR ($CDCl_3$, 500MHz)
5
HO
CH_3
[1H (ppm)]
3.94
1.12
2.00
1.01
2.00
2.30
8.40
5.76
3.14
7.34
7.34
7.29
7.28
7.26
4.51
4.51
3.59
3.50
3.48
3.47
1.64
1.54
1.48
1.44
1.39
1.34
1.31
1.26
0.91
0.90
0.88

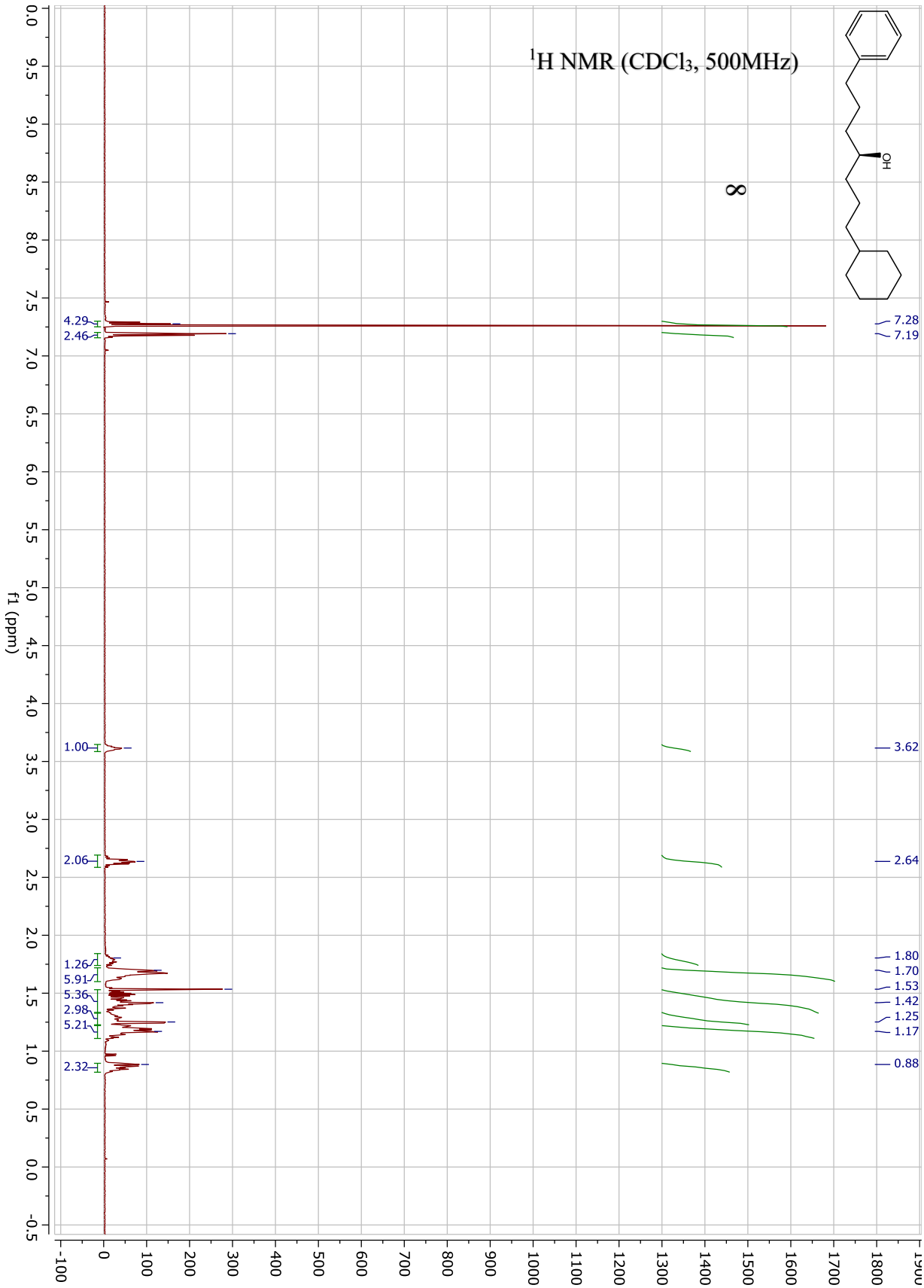

^{13}C NMR ($CDCl_3$, 126MHz)
5
O
HO
CH_3
138.73
128.47
127.76
127.62
77.16
73.04
71.96
70.44
37.59
37.33
32.04
29.87
25.46
22.78
22.47
14.18
[13C (ppm)]

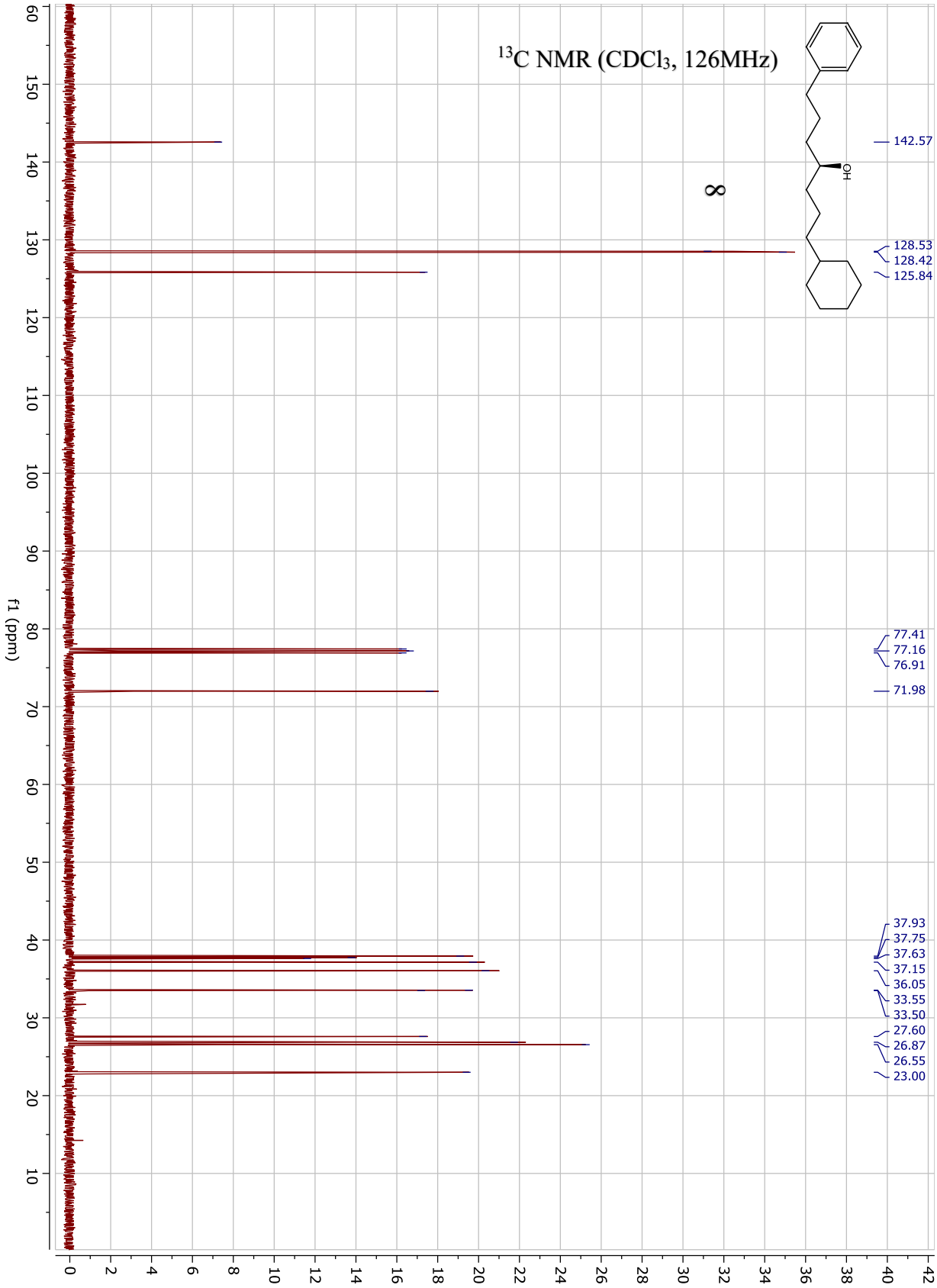

^{1}H NMR ($CDCl_3$, 500MHz)
6
f1 (ppm)
1.75
1.83
1.72
1.70
0.92
1.75
3.95
2.38
6.00
3.86
9.82
3.97
1.63
7.78
7.77
7.59
7.54
7.23
7.14
7.06
3.91
3.85
2.36
1.73
1.43
1.29
1.24
1.10
0.91

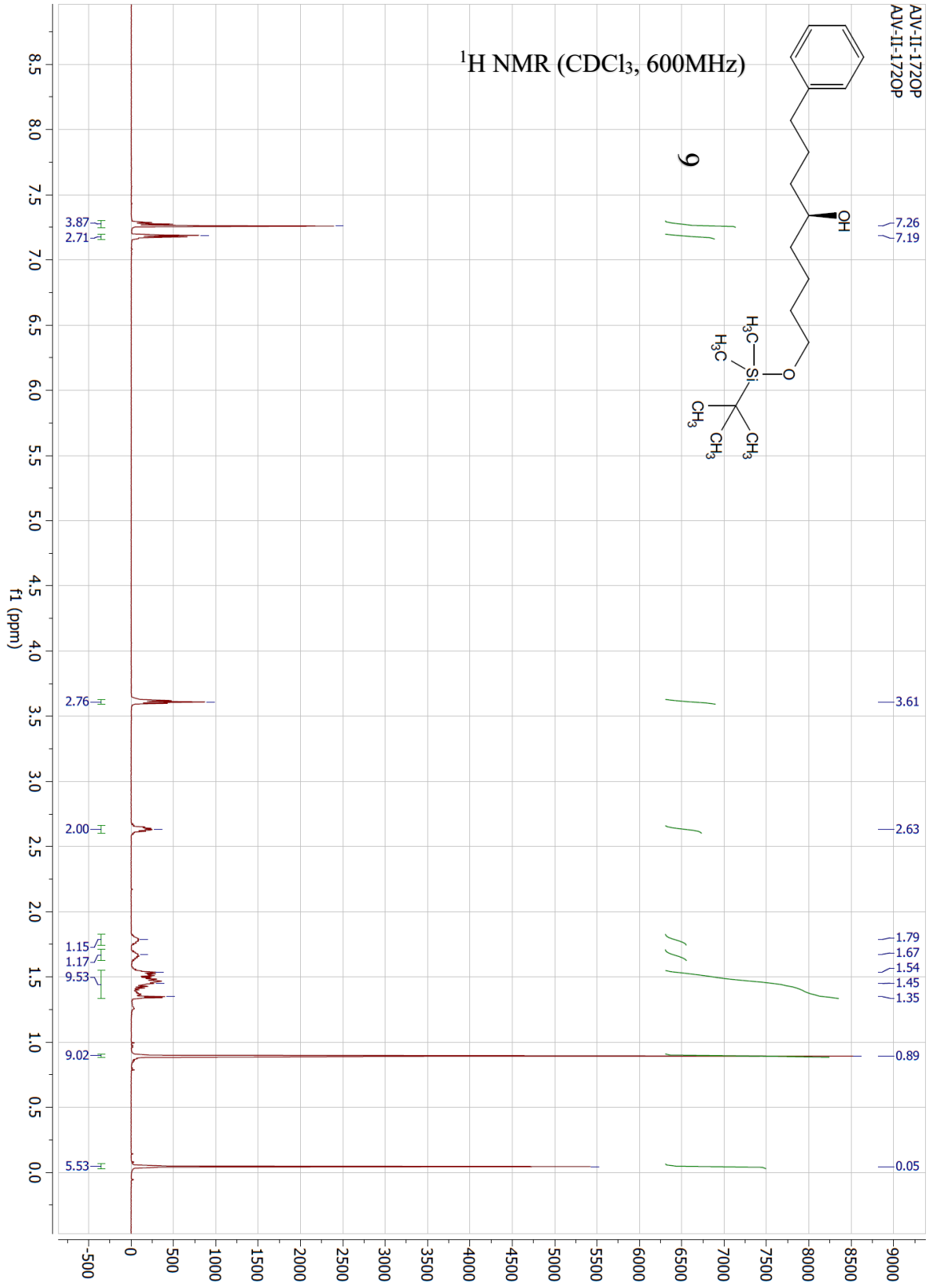

^{13}C NMR ($CDCl_3$, 126MHz)
6
145.07
143.02
134.72
131.43
128.53
128.48
128.24
125.55
125.25
119.49
110.28
91.60
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
64.65
39.14
35.92
31.63
31.30
31.18
29.38
28.77
24.37
23.81
23.61
22.11
22.10
f1 (ppm)

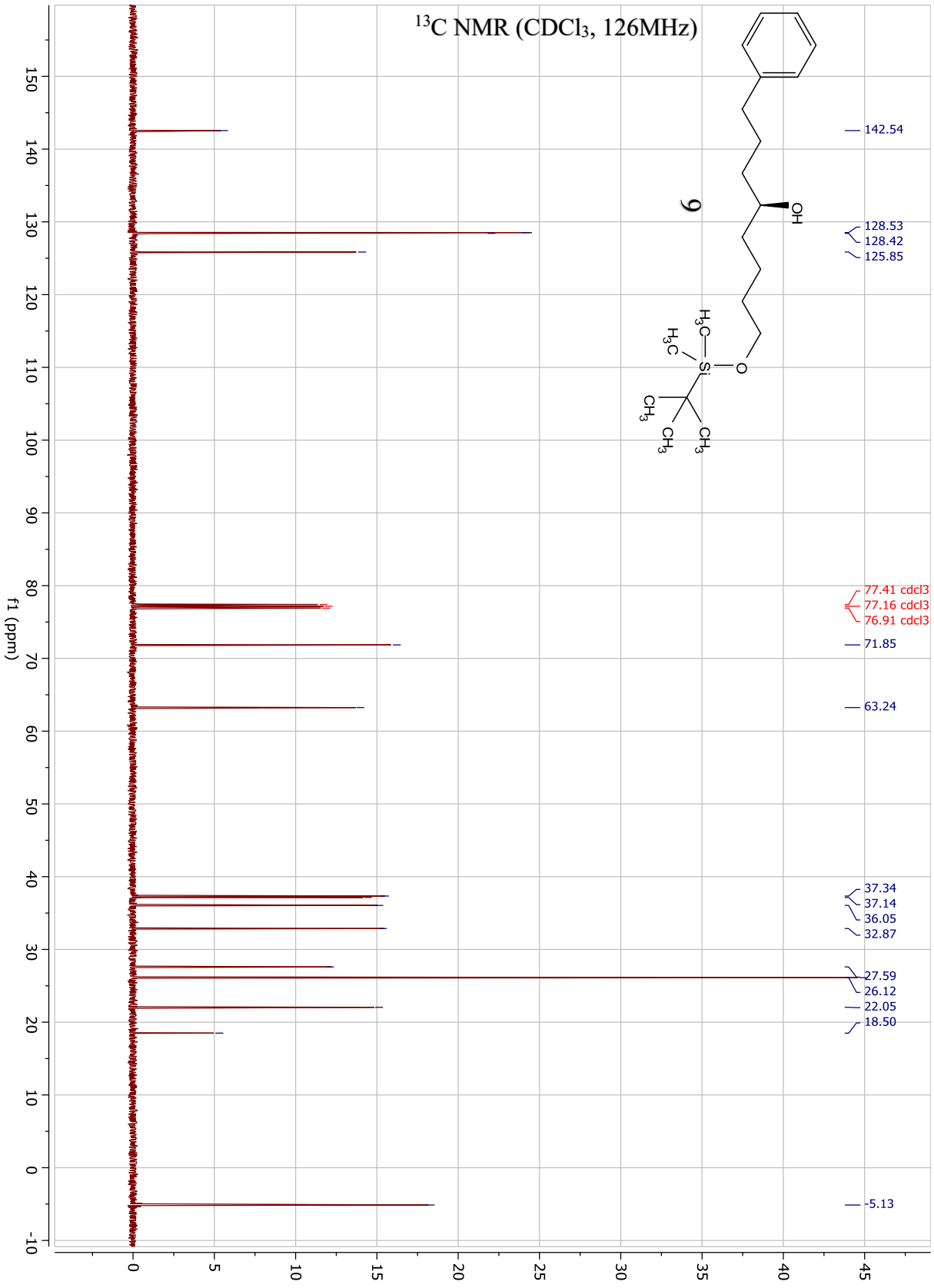

^{1}H NMR ($CDCl_3$, 600MHz)
7
OH
CH_3
f1 (ppm)
2.55
2.41
0.96
2.00
1.09
1.14
4.98
5.34
2.81
7.26
7.19
3.62
2.64
1.79
1.68
1.44
1.31
0.89

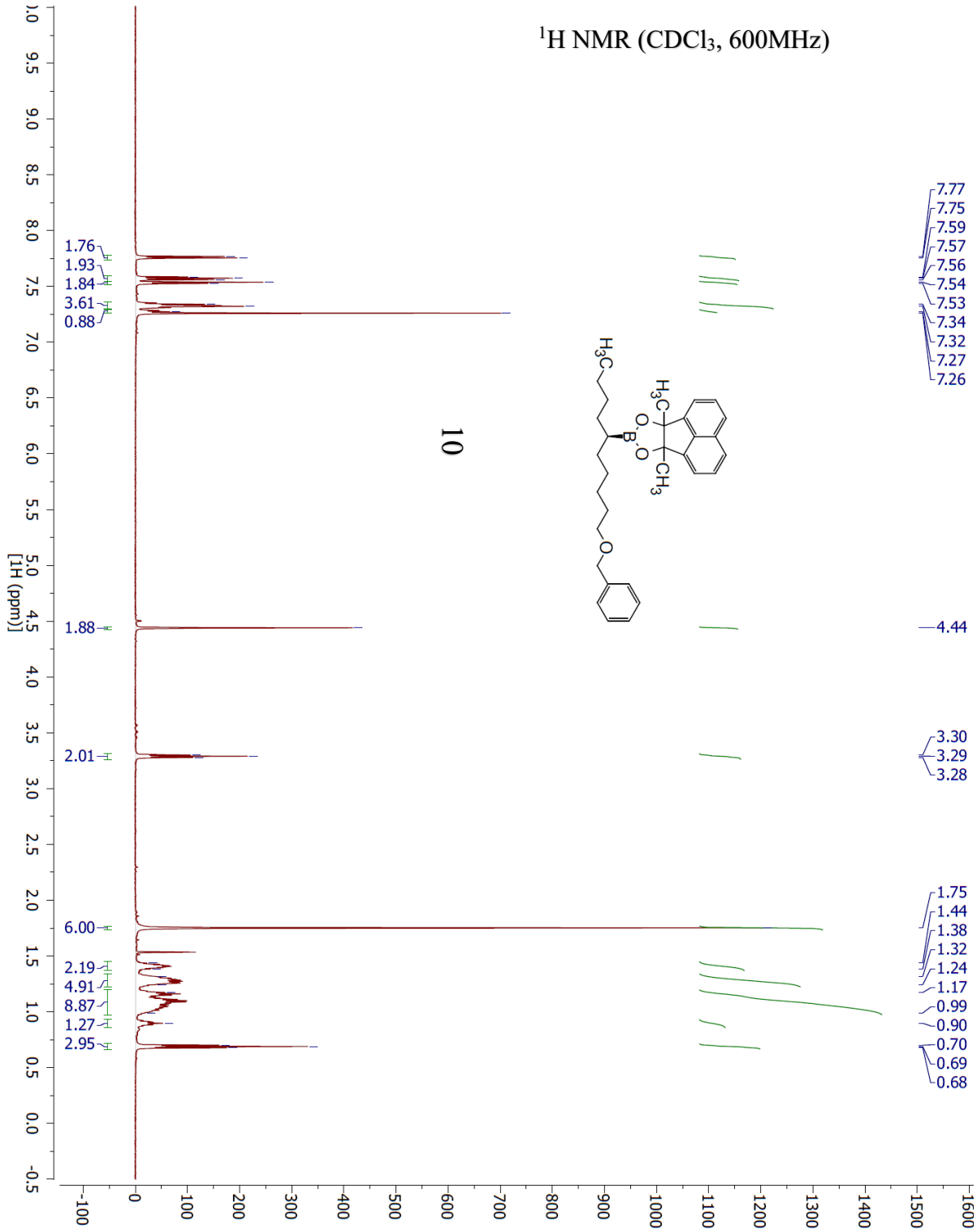

^{13}C NMR ($CDCl_3$, 126MHz)
7
OH
CH_3
142.56
128.53
128.42
125.84
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
71.97
37.60
37.16
36.05
32.02
27.60
25.44
22.76
14.17
f1 (ppm)

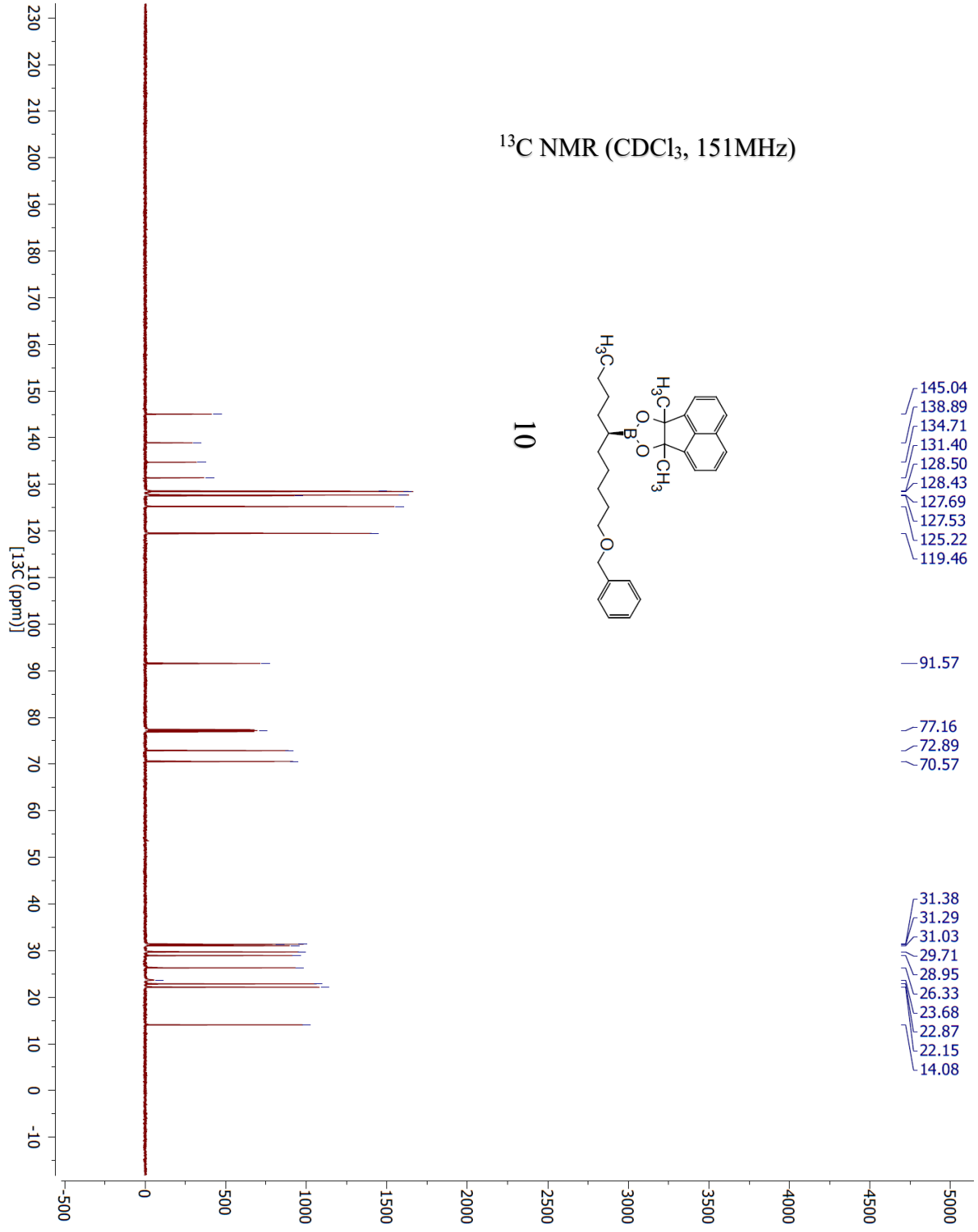

^{1}H NMR ($CDCl_3$, 500MHz)
8
OH
4.29
2.46
1.00
2.06
1.26
5.91
5.36
2.98
5.21
2.32
7.28
7.19
3.62
2.64
1.80
1.70
1.53
1.42
1.25
1.17
0.88
f1 (ppm)

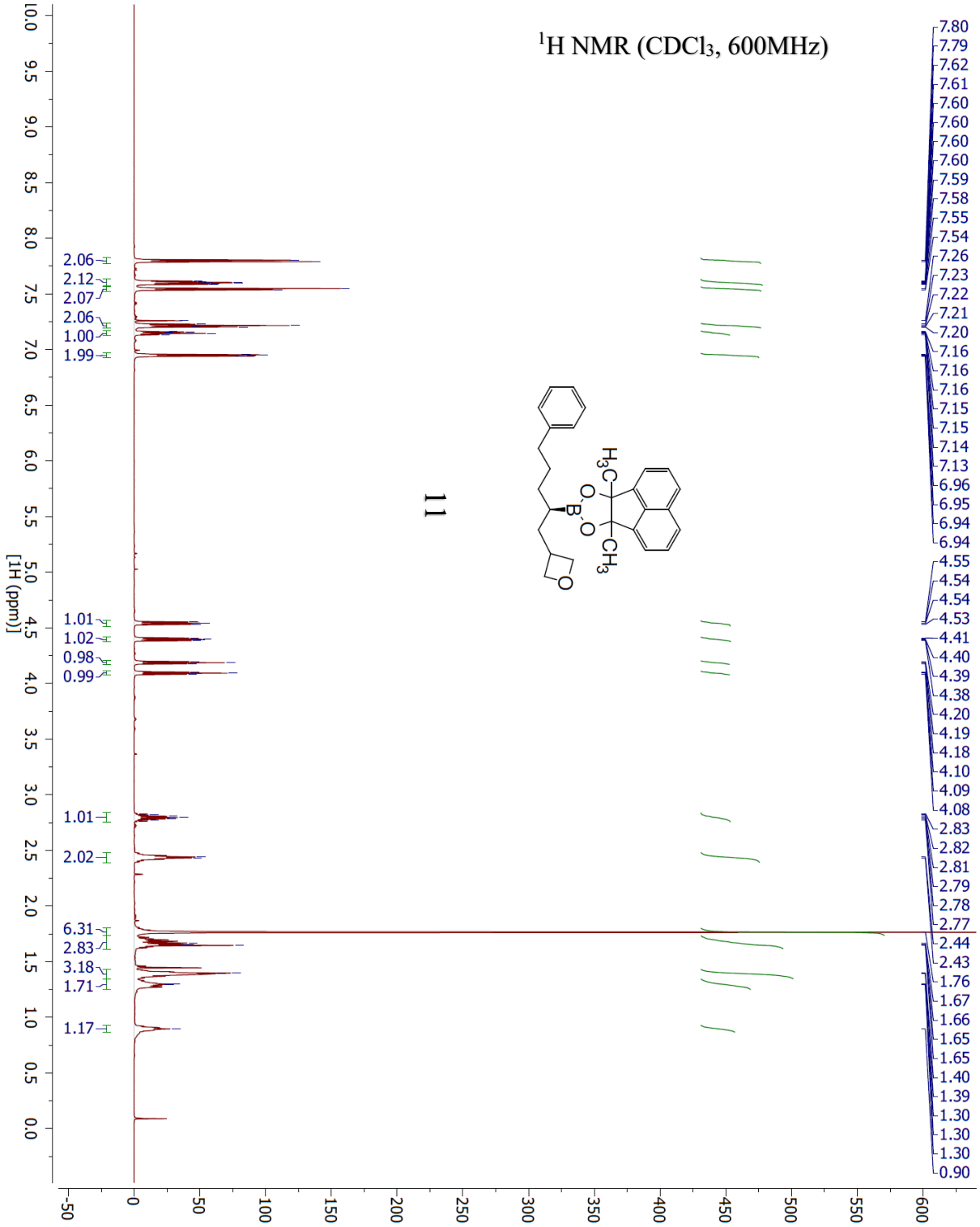

^{13}C NMR ($CDCl_3$, 126MHz)
8
OH
142.57
128.53
128.42
125.84
77.41
77.16
76.91
71.98
37.93
37.75
37.63
37.15
36.05
33.55
33.50
27.60
26.87
26.55
23.00
f1 (ppm)

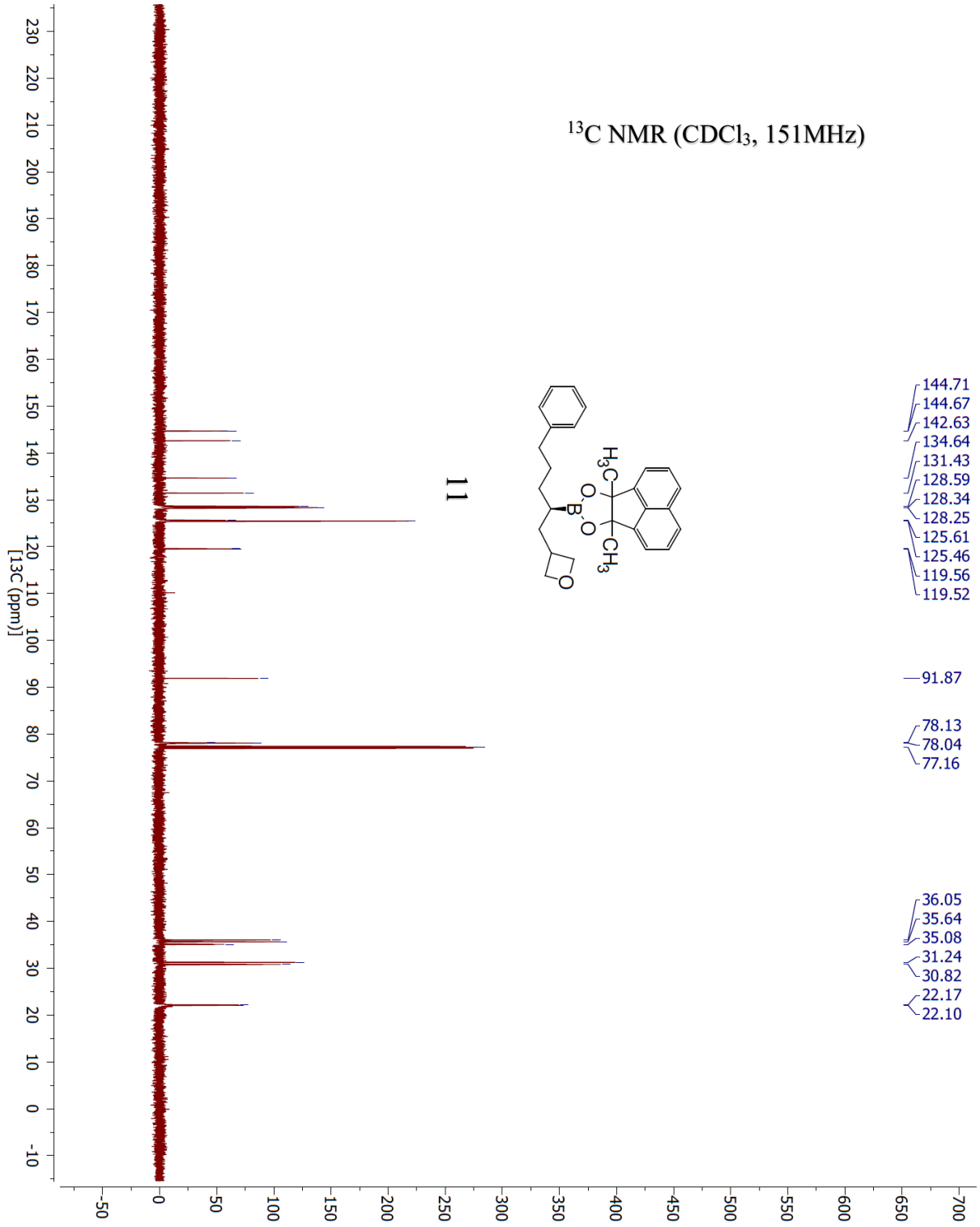

AJV-II-172OP
AJV-II-172OP
^{1}H NMR ($CDCl_3$, 600MHz)
9
OH
H_3C
H_3C
Si
O
CH_3
CH_3
CH_3
3.87
2.71
2.76
2.00
1.15
1.17
9.53
9.02
5.53
7.26
7.19
3.61
2.63
1.79
1.67
1.54
1.45
1.35
0.89
0.05
f1 (ppm)

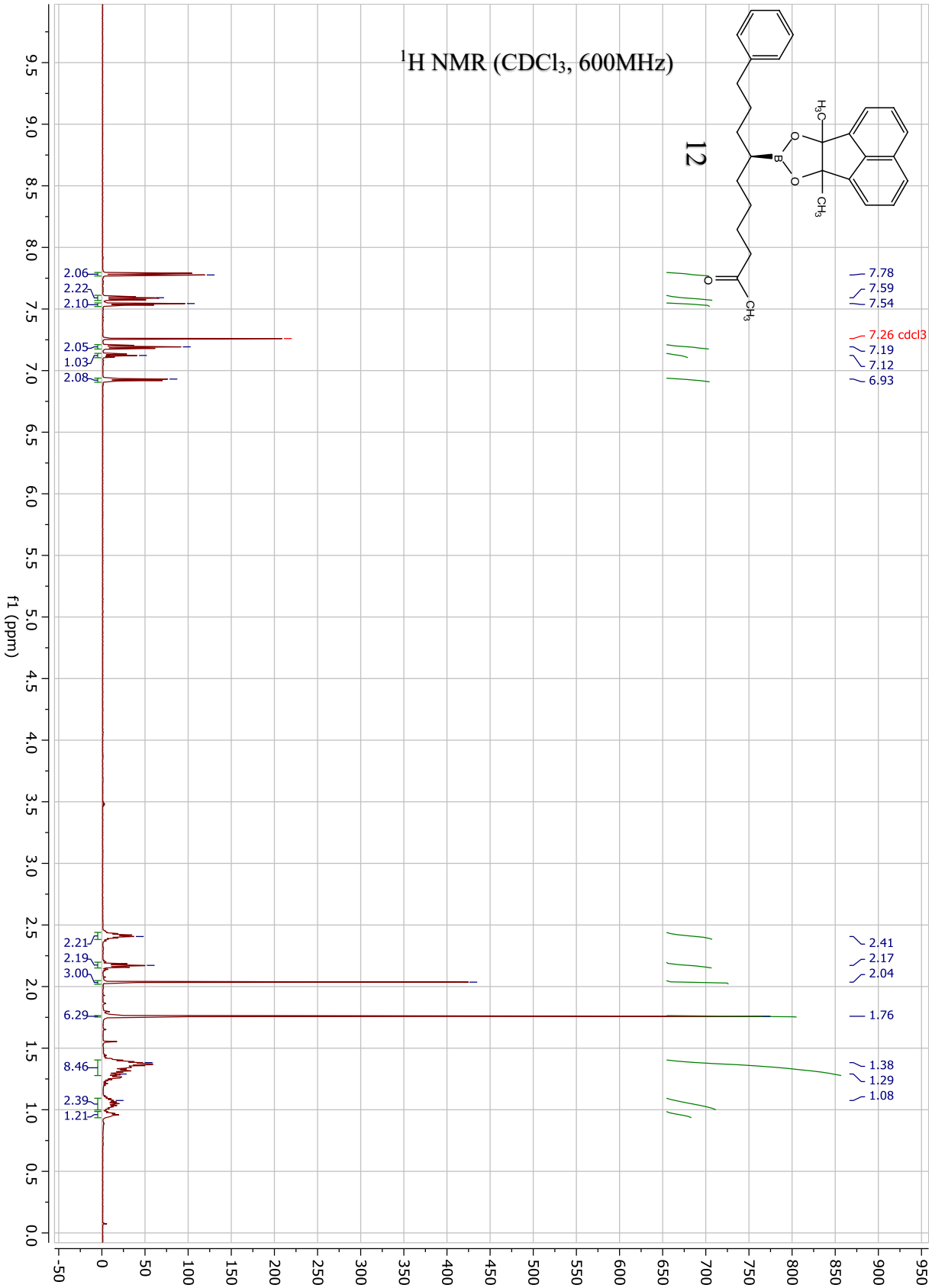

^{13}C NMR ($CDCl_3$, 126MHz)
9
OH
H_3C
H_3C
Si
O
CH_3
CH_3
CH_3
142.54
128.53
128.42
125.85
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
71.85
63.24
37.34
37.14
36.05
32.87
27.59
26.12
22.05
18.50
-5.13
f1 (ppm)

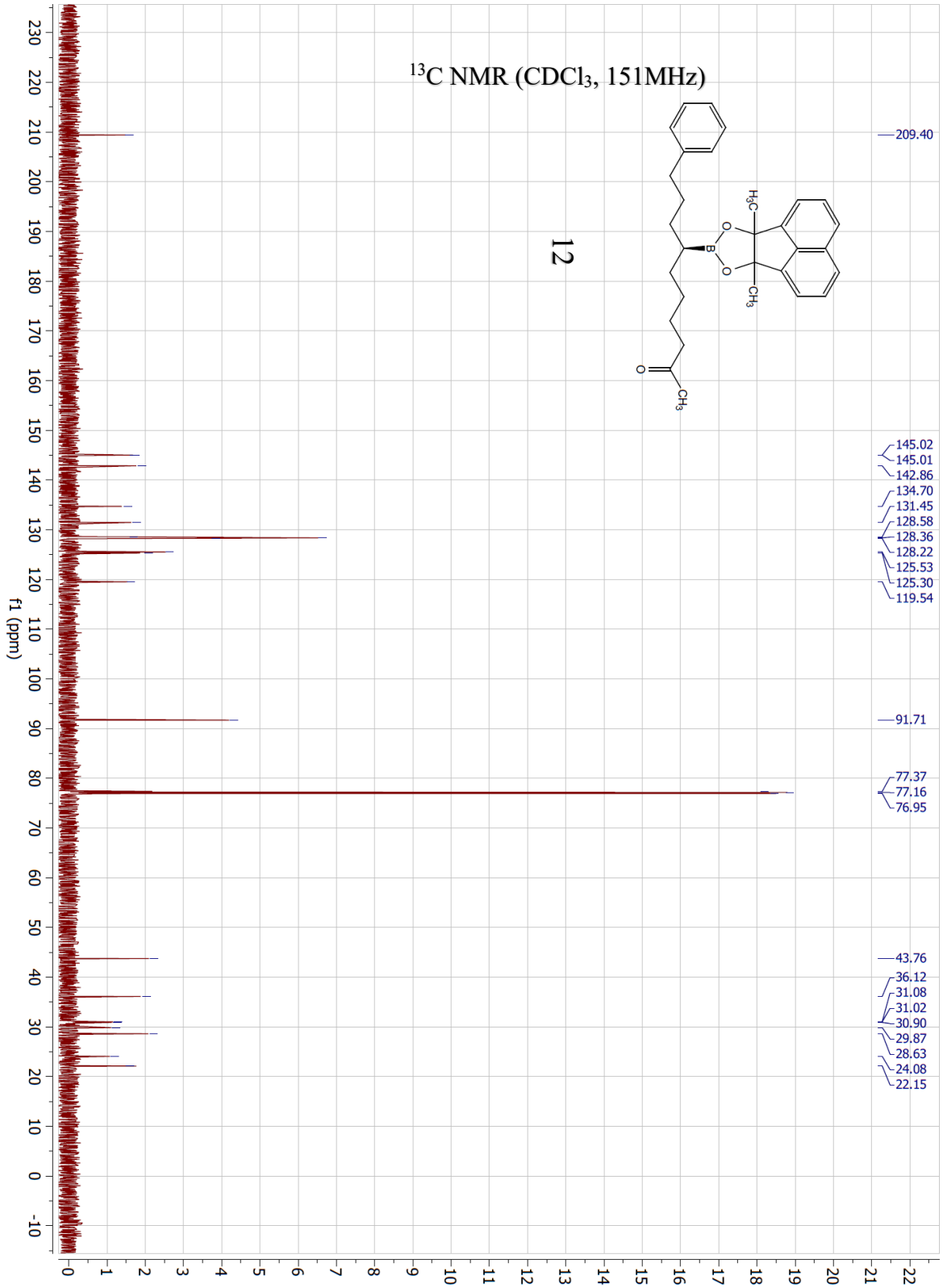

^{1}H NMR ($CDCl_3$, 600MHz)
10
[1H (ppm)]
1.76
1.93
1.84
3.61
0.88
1.88
2.01
6.00
2.19
4.91
8.87
1.27
2.95
7.77
7.75
7.59
7.57
7.56
7.54
7.53
7.34
7.32
7.27
7.26
4.44
3.30
3.29
3.28
1.75
1.44
1.38
1.32
1.24
1.17
0.99
0.90
0.70
0.69
0.68

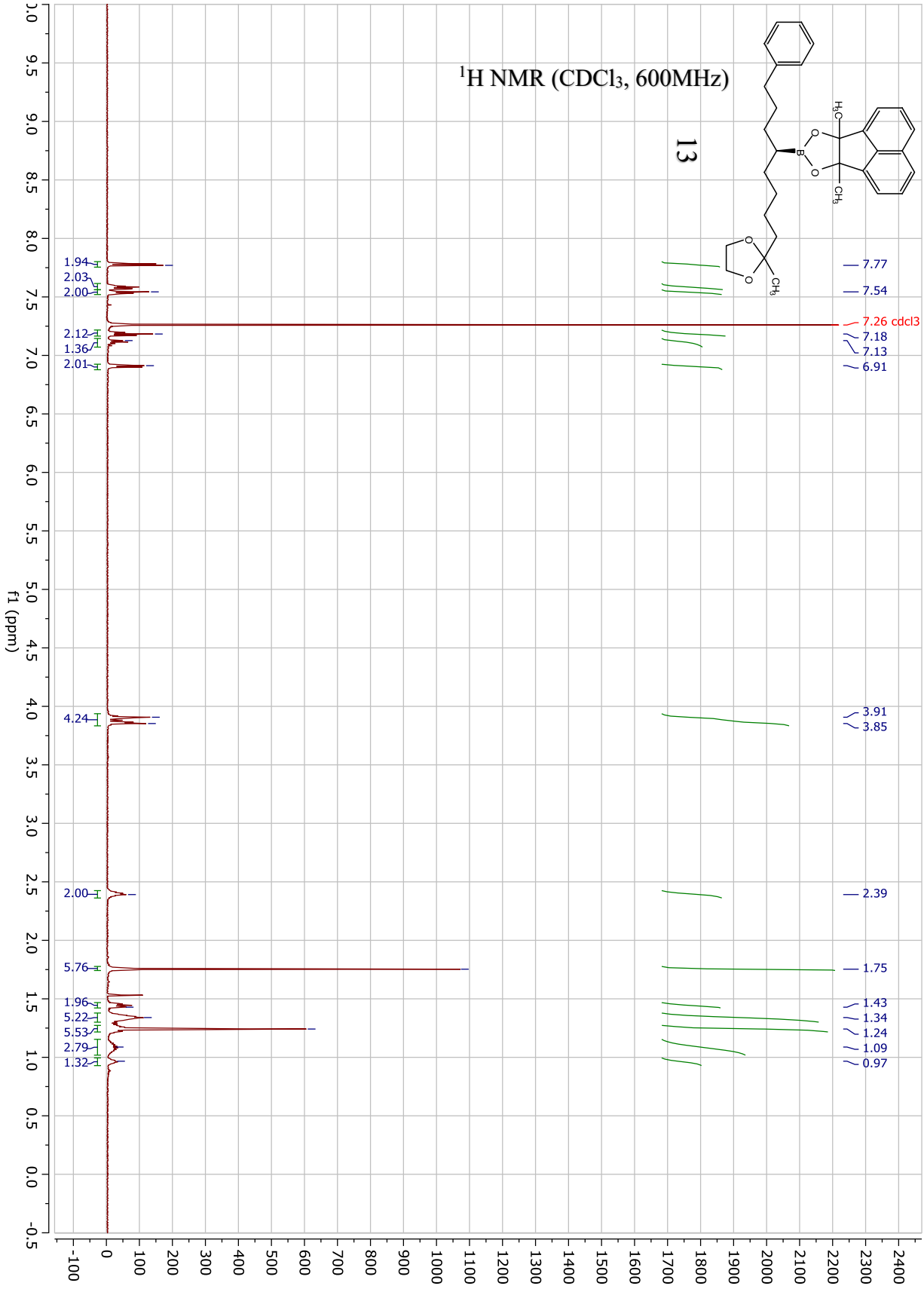

^{13}C NMR ($CDCl_3$, 151MHz)
10
145.04
138.89
134.71
131.40
128.50
128.43
127.69
127.53
125.22
119.46
91.57
77.16
72.89
70.57
31.38
31.29
31.03
29.71
28.95
26.33
23.68
22.87
22.15
14.08
[13C (ppm)]

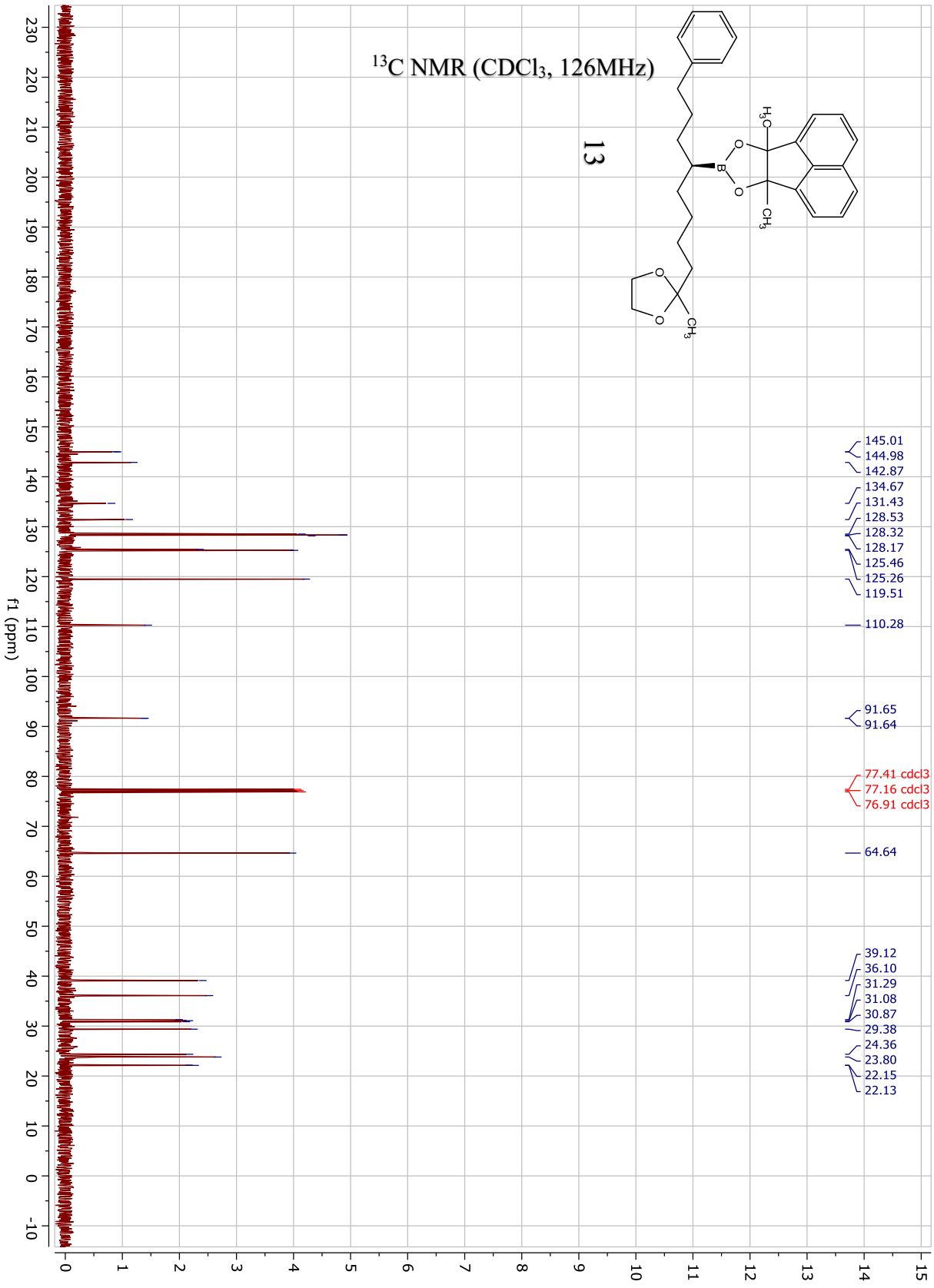

^{1}H NMR ($CDCl_3$, 600MHz)
11
[1H (ppm)]
2.06
2.12
2.07
2.06
1.00
1.99
1.01
1.02
0.98
0.99
1.01
2.02
6.31
2.83
3.18
1.71
1.17
7.80
7.79
7.62
7.61
7.60
7.60
7.60
7.60
7.59
7.58
7.55
7.54
7.26
7.23
7.22
7.21
7.20
7.16
7.16
7.16
7.15
7.15
7.14
7.13
6.96
6.95
6.94
6.94
4.55
4.54
4.54
4.53
4.41
4.40
4.39
4.38
4.20
4.19
4.18
4.10
4.09
4.08
2.83
2.82
2.81
2.79
2.78
2.77
2.44
2.43
1.76
1.67
1.66
1.65
1.65
1.40
1.39
1.30
1.30
1.30
0.90

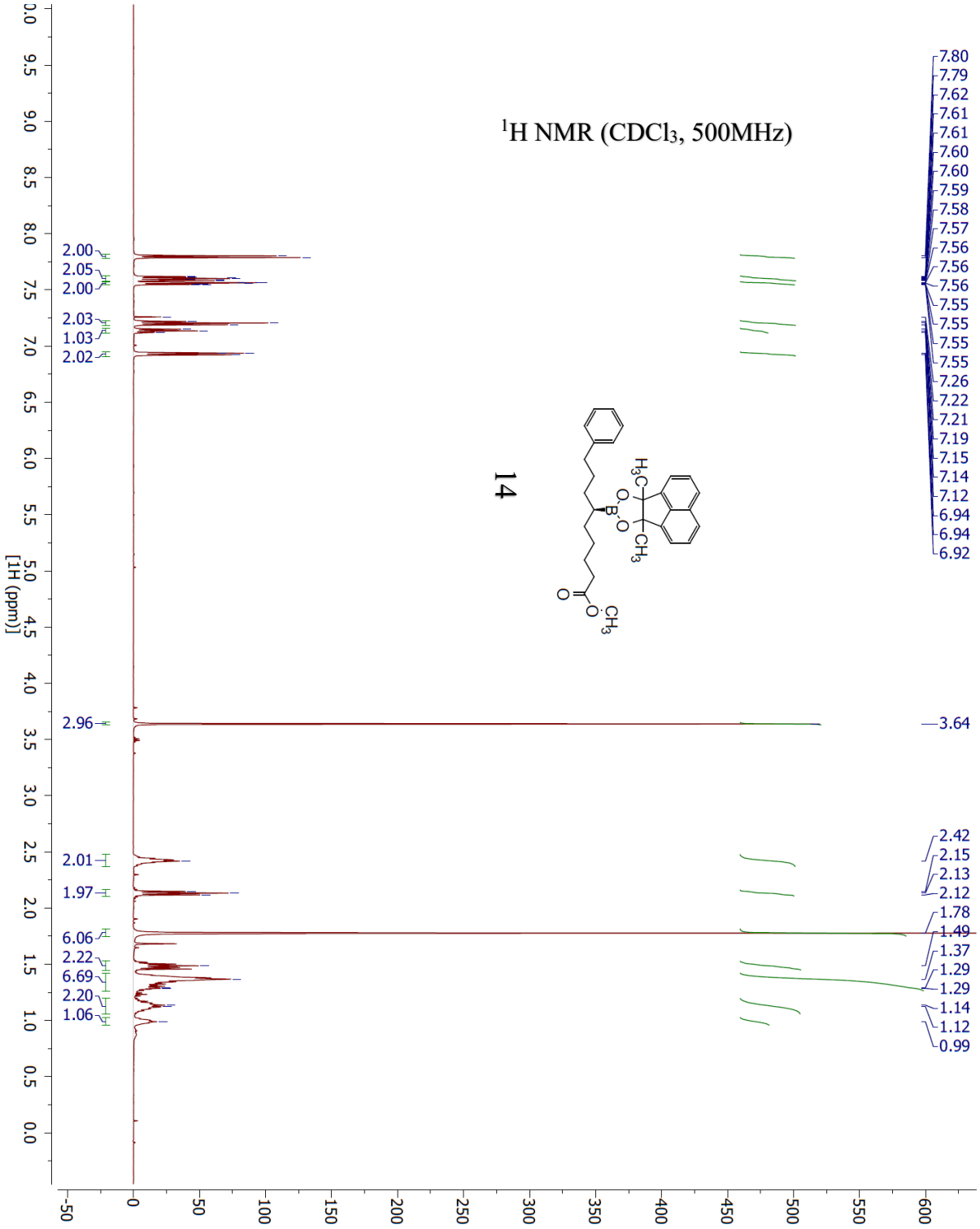

^{13}C NMR (CDCl$_3$, 151MHz)
11
144.71
144.67
142.63
134.64
131.43
128.59
128.34
128.25
125.61
125.46
119.56
119.52
91.87
78.13
78.04
77.16
36.05
35.64
35.08
31.24
30.82
22.17
22.10
[13C (ppm)]

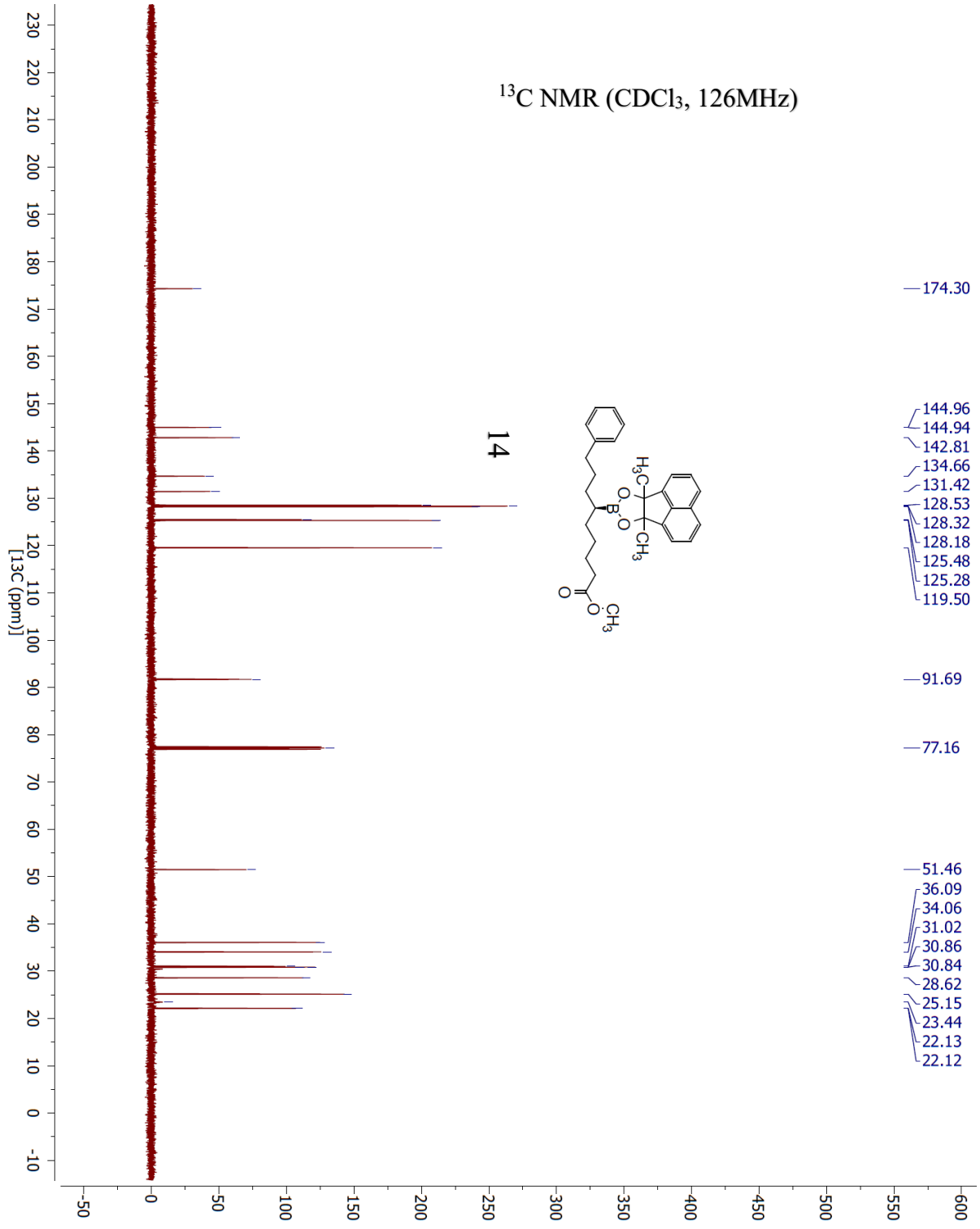

^{1}H NMR (CDCl$_3$, 600MHz)
12
f1 (ppm)
2.06
2.22
2.10
2.05
1.03
2.08
2.21
2.19
3.00
6.29
8.46
2.39
1.21
7.78
7.59
7.54
7.26 cdcl3
7.19
7.12
6.93
2.41
2.17
2.04
1.76
1.38
1.29
1.08

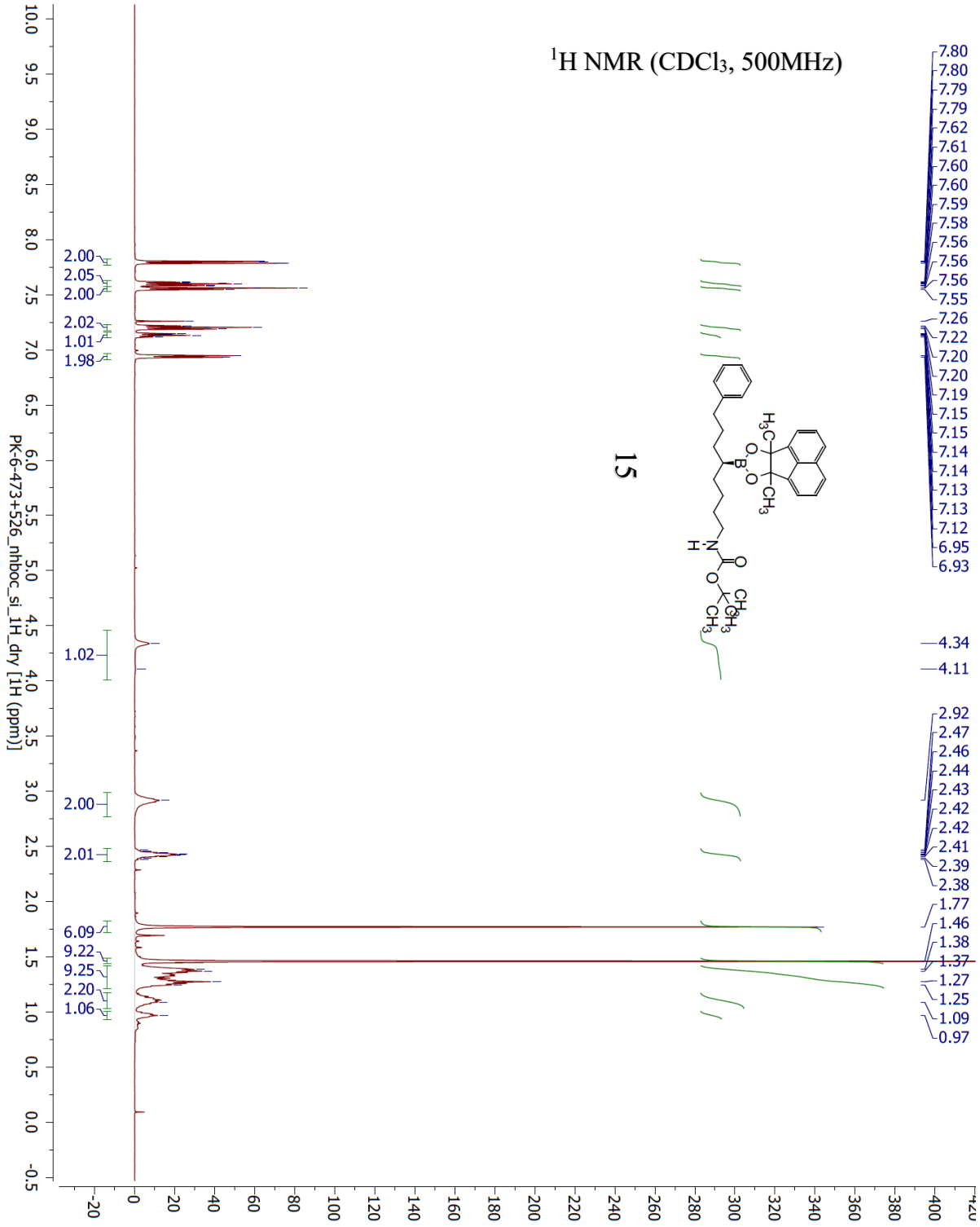

^{13}C NMR ($CDCl_3$, 151MHz)
12
209.40
145.02
145.01
142.86
134.70
131.45
128.58
128.36
128.22
125.53
125.30
119.54
91.71
77.37
77.16
76.95
43.76
36.12
31.08
31.02
30.90
29.87
28.63
24.08
22.15
f1 (ppm)

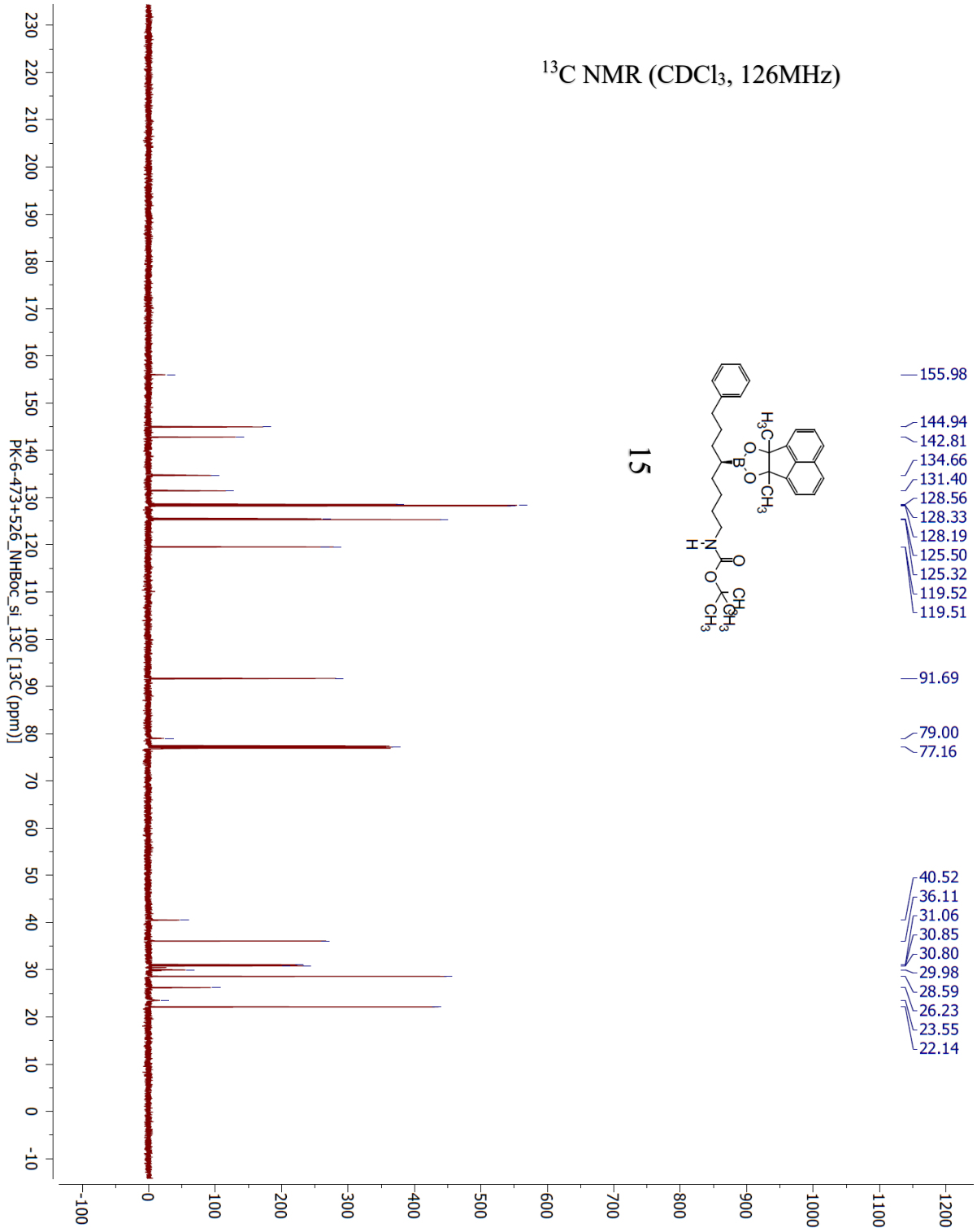

^{1}H NMR ($CDCl_3$, 600MHz)
13
f1 (ppm)
1.94
2.03
2.00
2.12
1.36
2.01
4.24
2.00
5.76
1.96
5.22
5.53
2.79
1.32
7.77
7.54
7.26 cdcl3
7.18
7.13
6.91
3.91
3.85
2.39
1.75
1.43
1.34
1.24
1.09
0.97

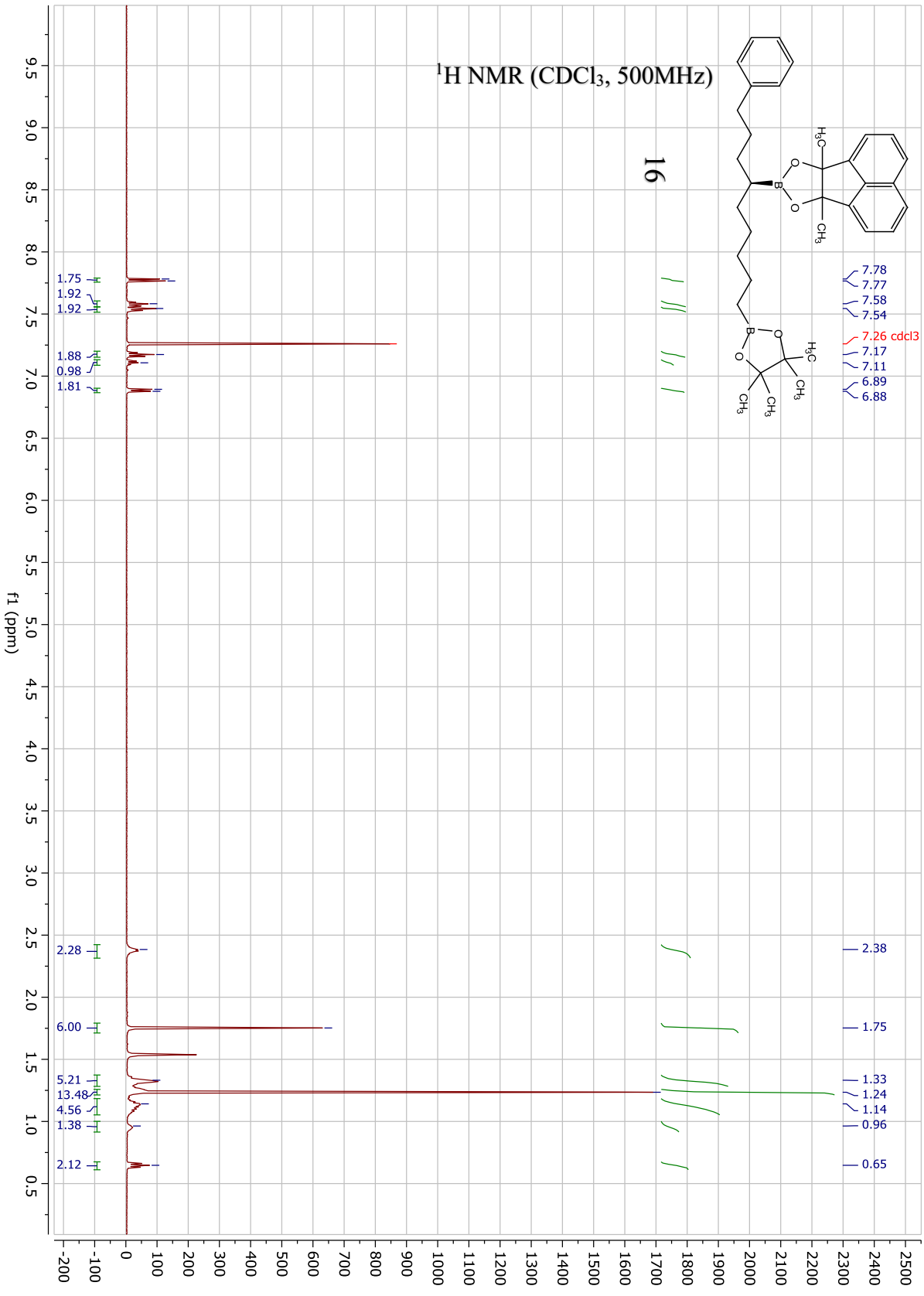

^{13}C NMR ($CDCl_3$, 126MHz)
13
145.01
144.98
142.87
134.67
131.43
128.53
128.32
128.17
125.46
125.26
119.51
110.28
91.65
91.64
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
64.64
39.12
36.10
31.29
31.08
30.87
29.38
24.36
23.80
22.15
22.13
f1 (ppm)

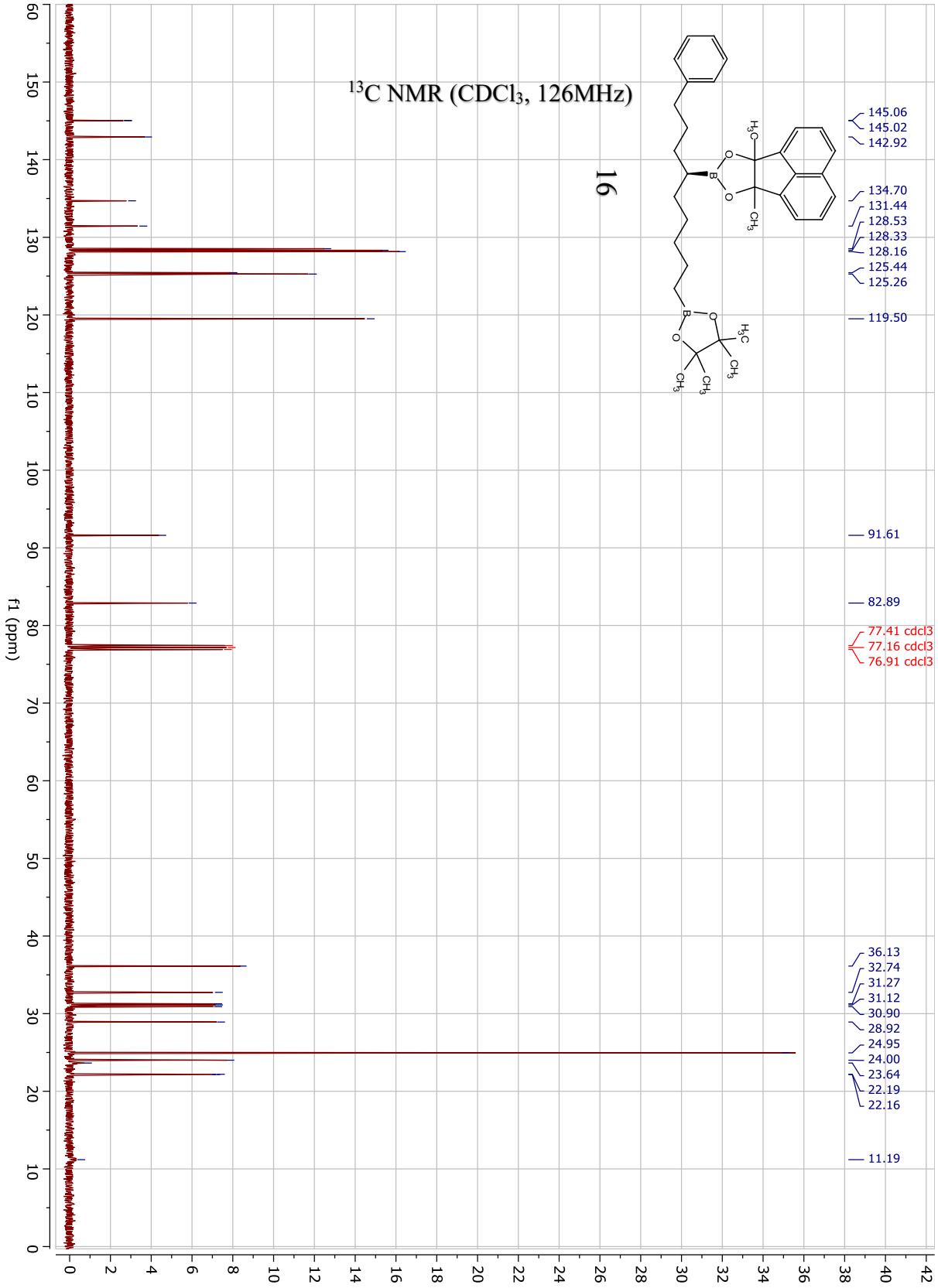

^{1}H NMR ($CDCl_3$, 500MHz)
14
[1H (ppm)]
2.00
2.05
2.00
2.03
1.03
2.02
2.96
2.01
1.97
6.06
2.22
6.69
2.20
1.06
7.80
7.79
7.62
7.61
7.61
7.60
7.60
7.59
7.58
7.57
7.56
7.56
7.56
7.55
7.55
7.55
7.55
7.26
7.22
7.21
7.19
7.15
7.14
7.12
6.94
6.94
6.92
3.64
2.42
2.15
2.13
2.12
1.78
1.49
1.37
1.29
1.29
1.14
1.12
0.99

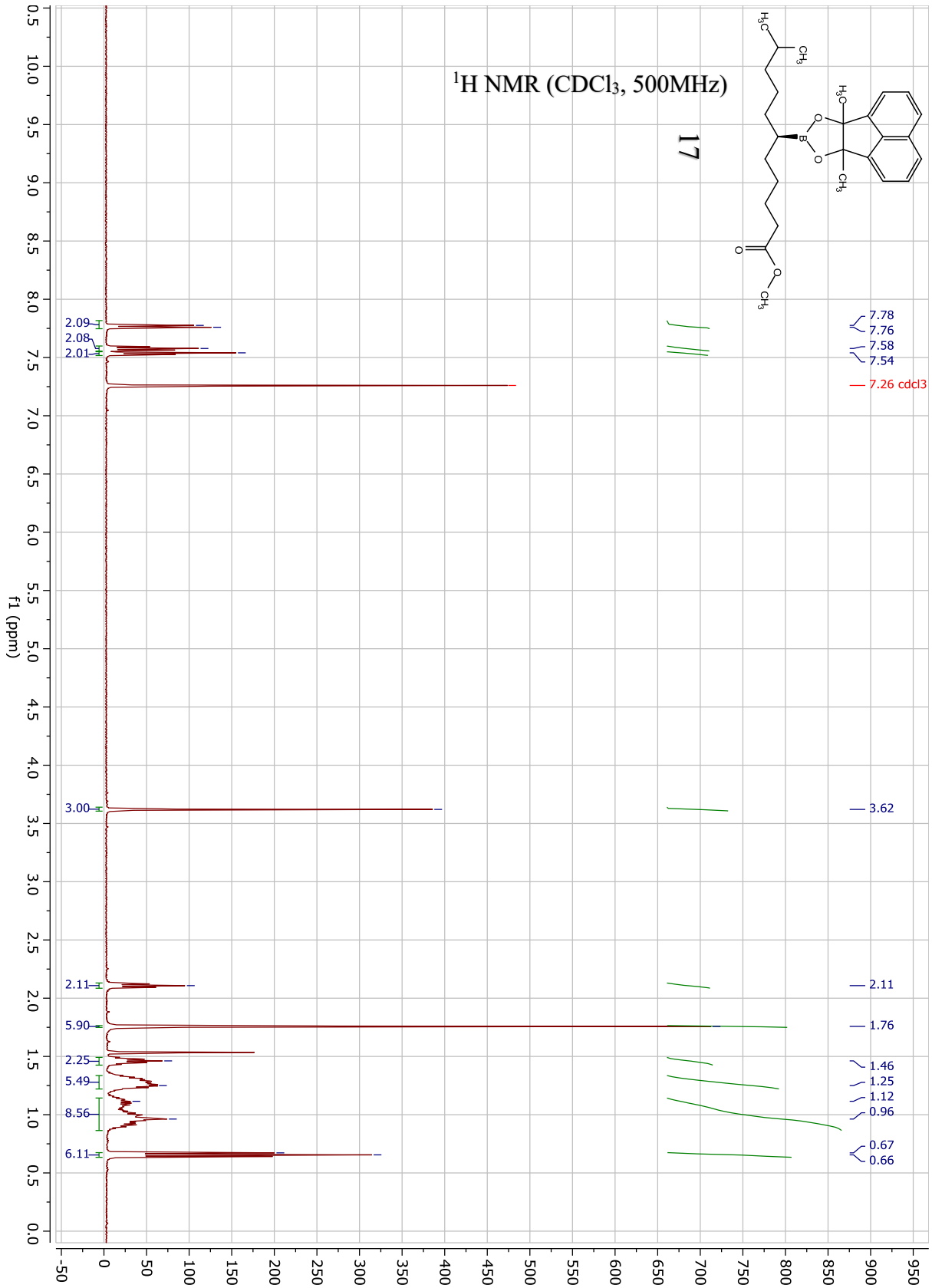

^{13}C NMR (CDCl$_3$, 126MHz)
14
174.30
144.96
144.94
142.81
134.66
131.42
128.53
128.32
128.18
125.48
125.28
119.50
91.69
77.16
51.46
36.09
34.06
31.02
30.86
30.84
28.62
25.15
23.44
22.13
22.12
[13C (ppm)]

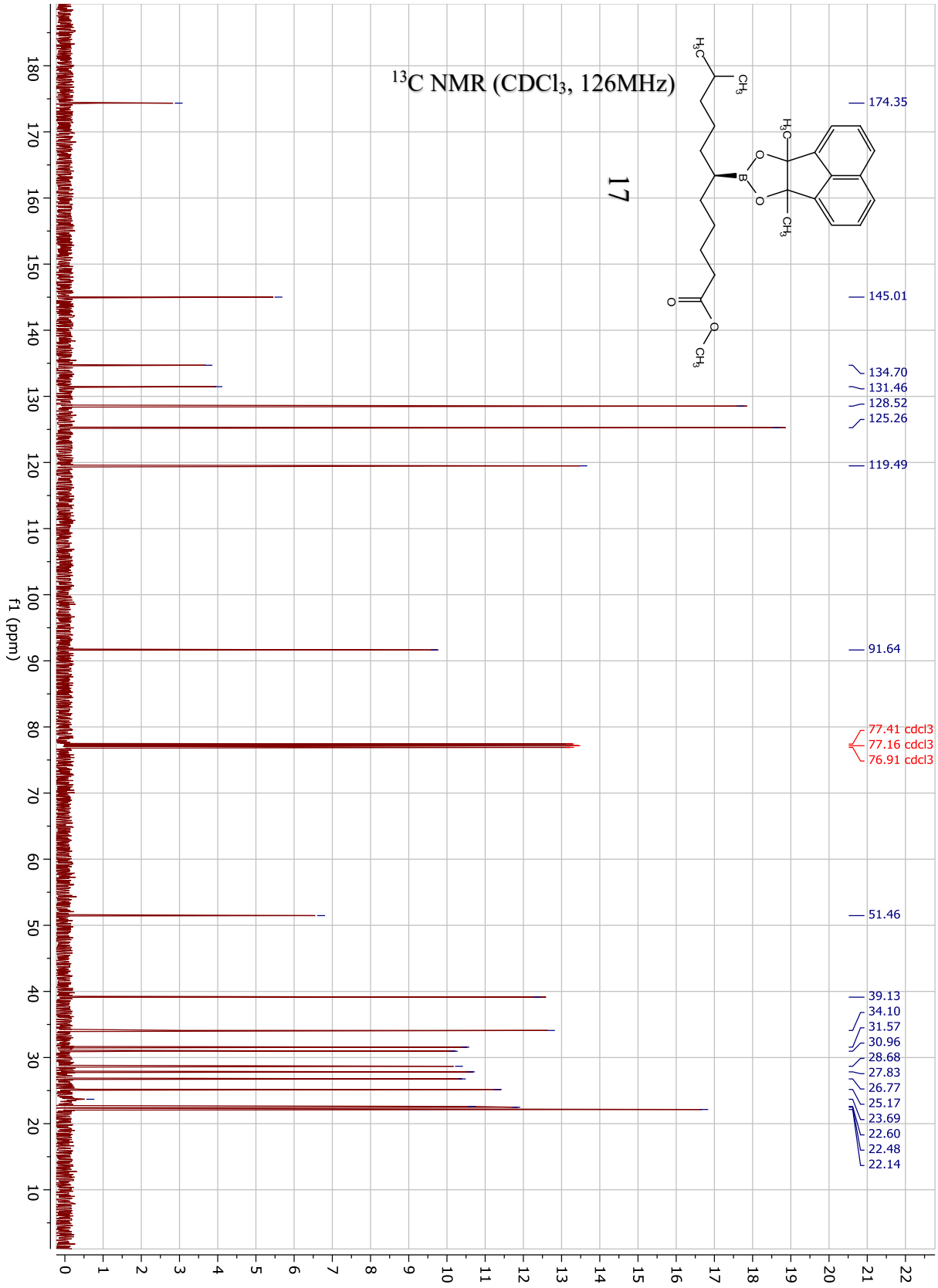

^{1}H NMR ($CDCl_3$, 500MHz)
15
PK-6-473+526_nhboc_si_1H_dry [1H (ppm)]

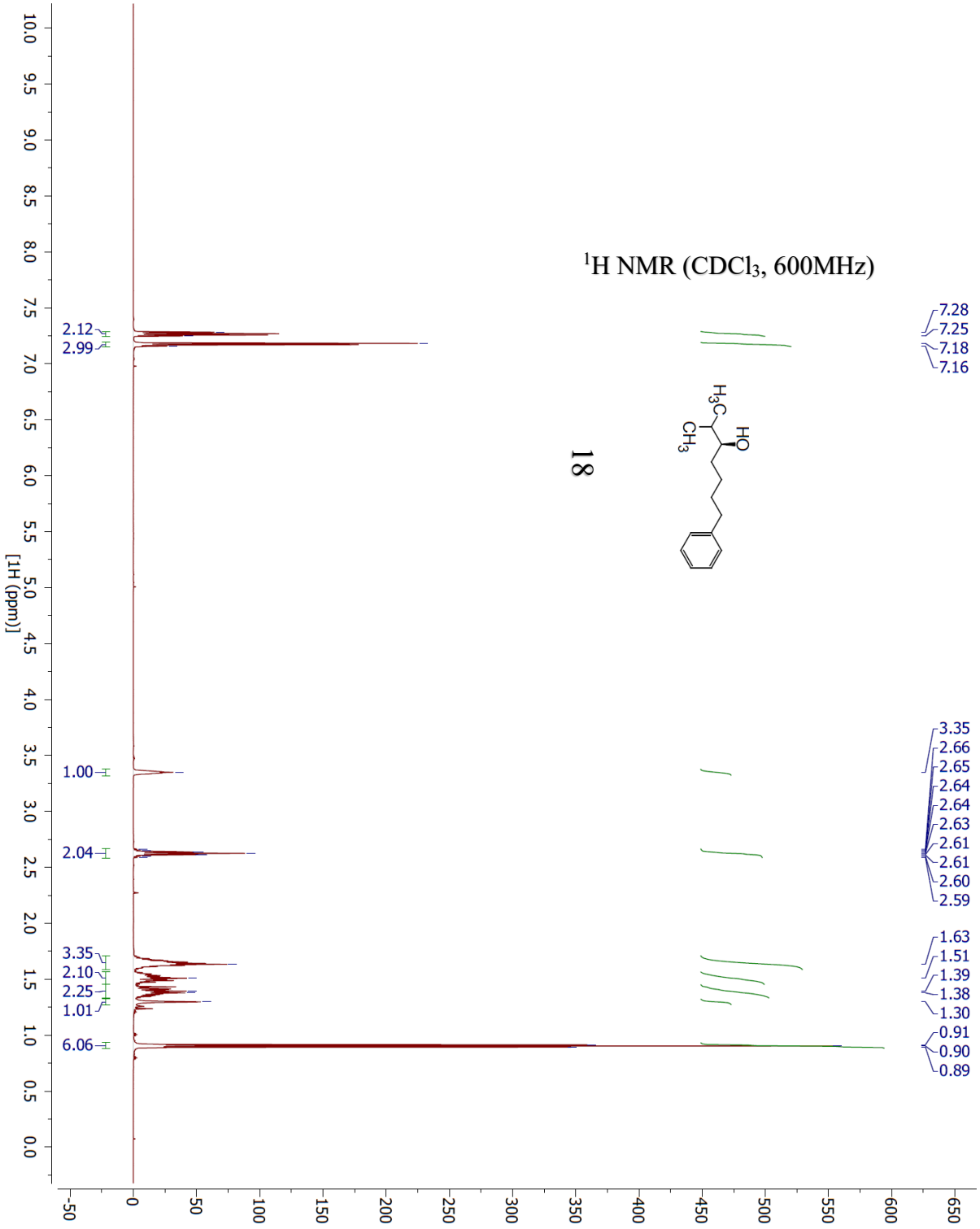

^{13}C NMR ($CDCl_3$, 126MHz)
15
155.98
144.94
142.81
134.66
131.40
128.56
128.33
128.19
125.50
125.32
119.52
119.51
91.69
79.00
77.16
40.52
36.11
31.06
30.85
30.80
29.98
28.59
26.23
23.55
22.14
PK-6-473+526_NHBoc_si_13C [13C (ppm)]

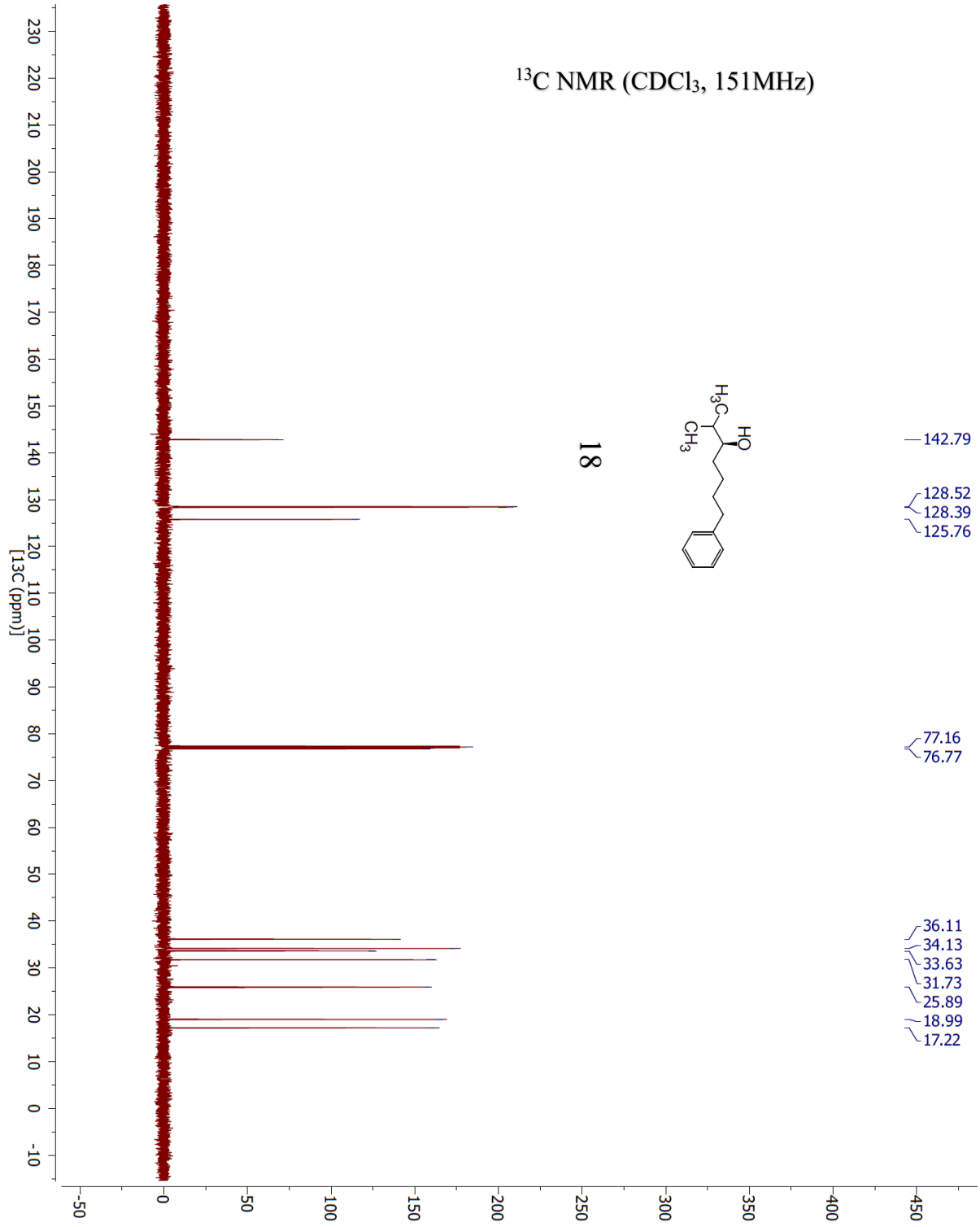

^{1}H NMR ($CDCl_3$, 500MHz)
16
f1 (ppm)
1.75
1.92
1.92
1.88
0.98
1.81
2.28
6.00
5.21
13.48
4.56
1.38
2.12
7.78
7.77
7.58
7.54
7.26 cdcl3
7.17
7.11
6.89
6.88
2.38
1.75
1.33
1.24
1.14
0.96
0.65

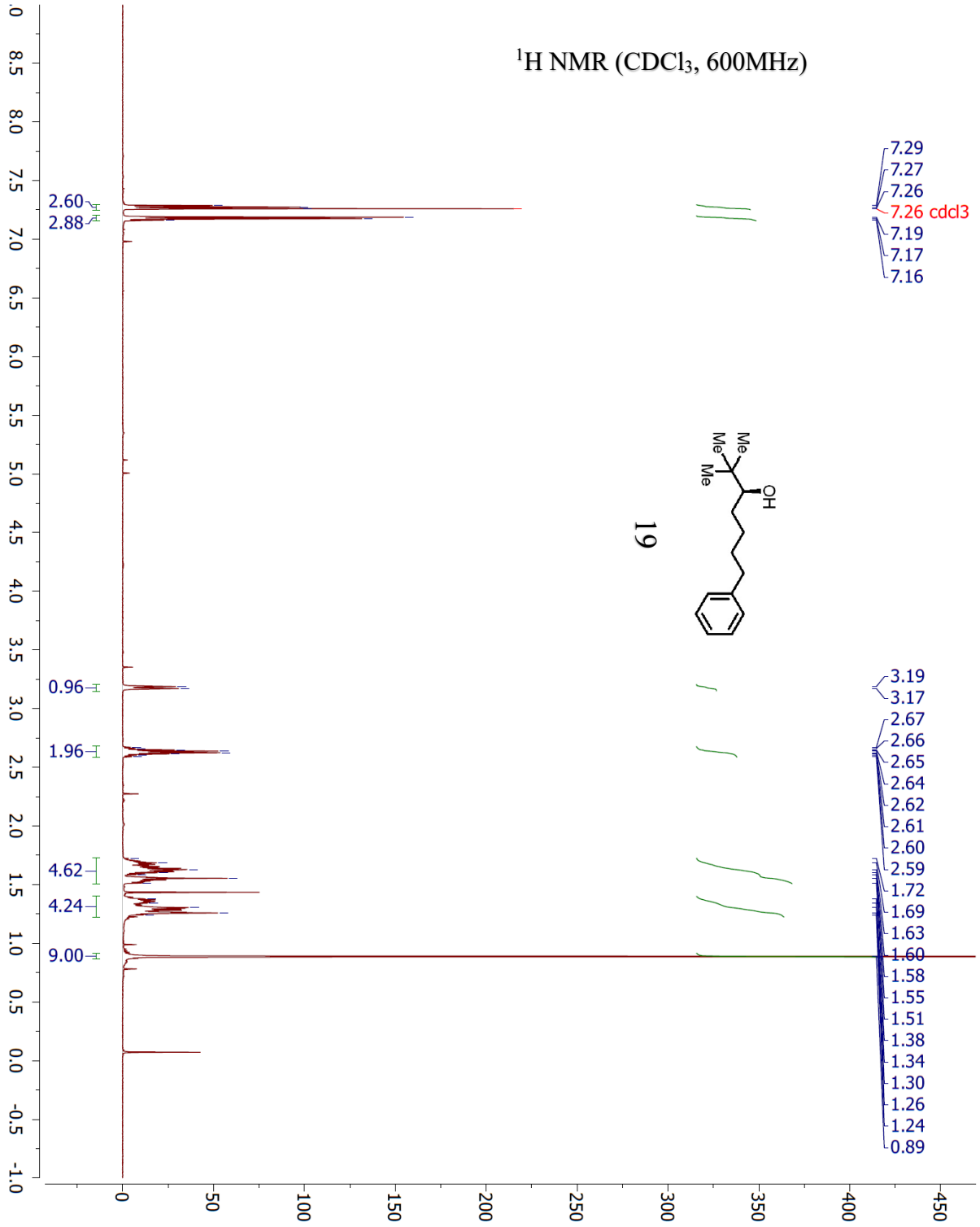

^{13}C NMR ($CDCl_3$, 126MHz)
16
145.06
145.02
142.92
134.70
131.44
128.53
128.33
128.16
125.44
125.26
119.50
91.61
82.89
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
36.13
32.74
31.27
31.12
30.90
28.92
24.95
24.00
23.64
22.19
22.16
11.19
f1 (ppm)

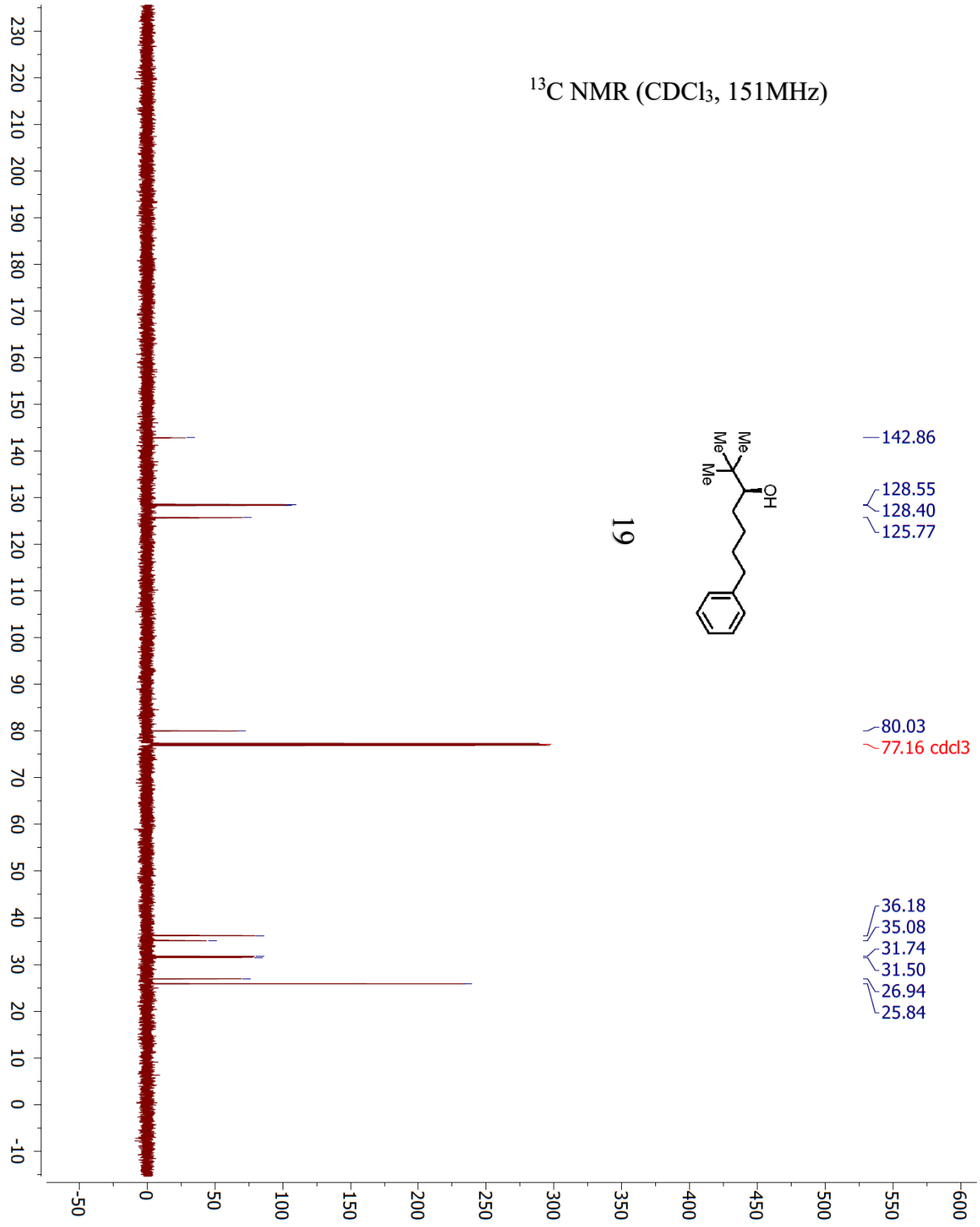

^{1}H NMR ($CDCl_3$, 500MHz)
17
f1 (ppm)
2.09
2.08
2.01
3.00
2.11
5.90
2.25
5.49
8.56
6.11
7.78
7.76
7.58
7.54
7.26 cdcl3
3.62
2.11
1.76
1.46
1.25
1.12
0.96
0.67
0.66

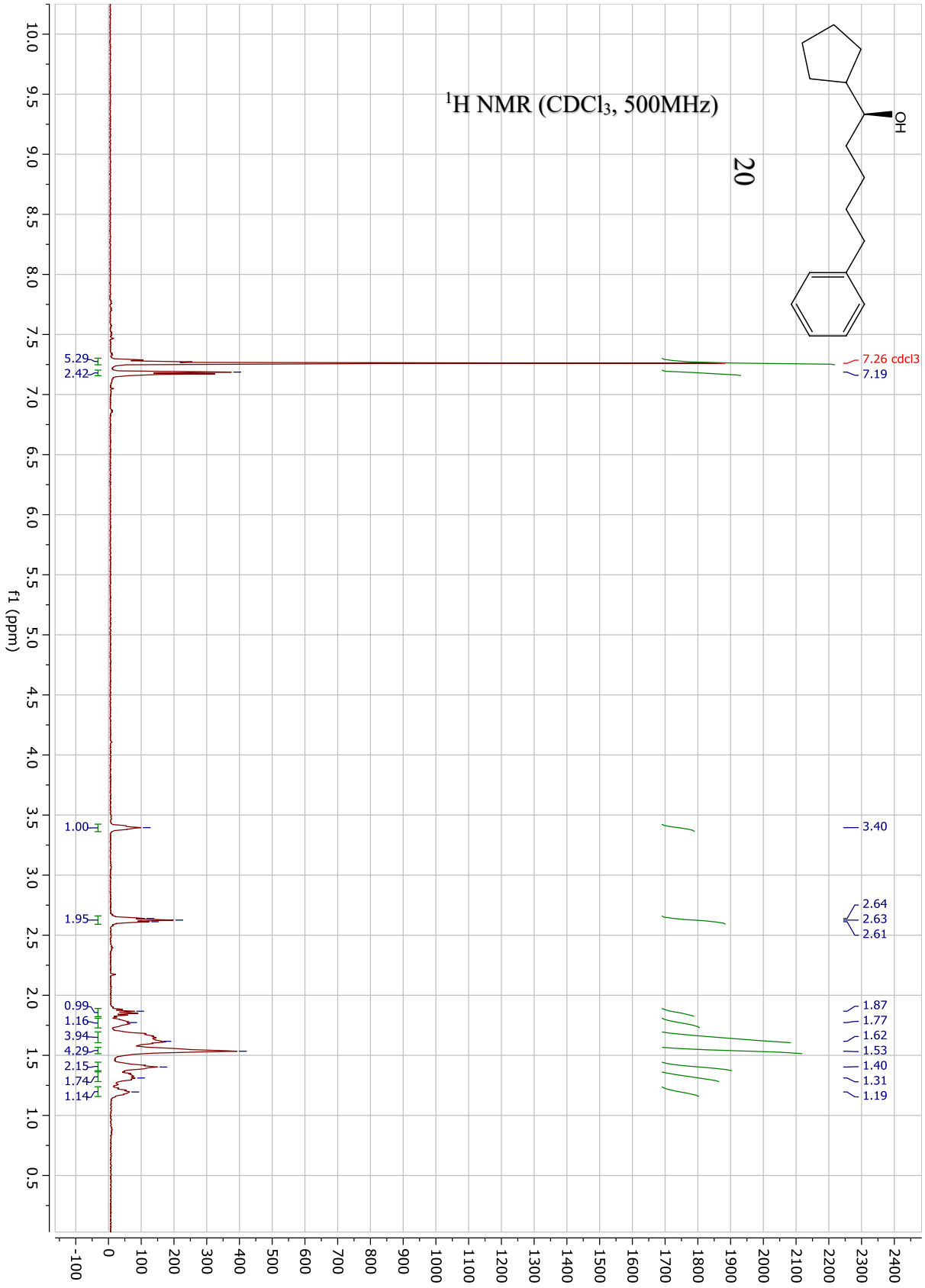

^{13}C NMR ($CDCl_3$, 126MHz)
17
174.35
145.01
134.70
131.46
128.52
125.26
119.49
91.64
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
51.46
39.13
34.10
31.57
30.96
28.68
27.83
26.77
25.17
23.69
22.60
22.48
22.14
f1 (ppm)

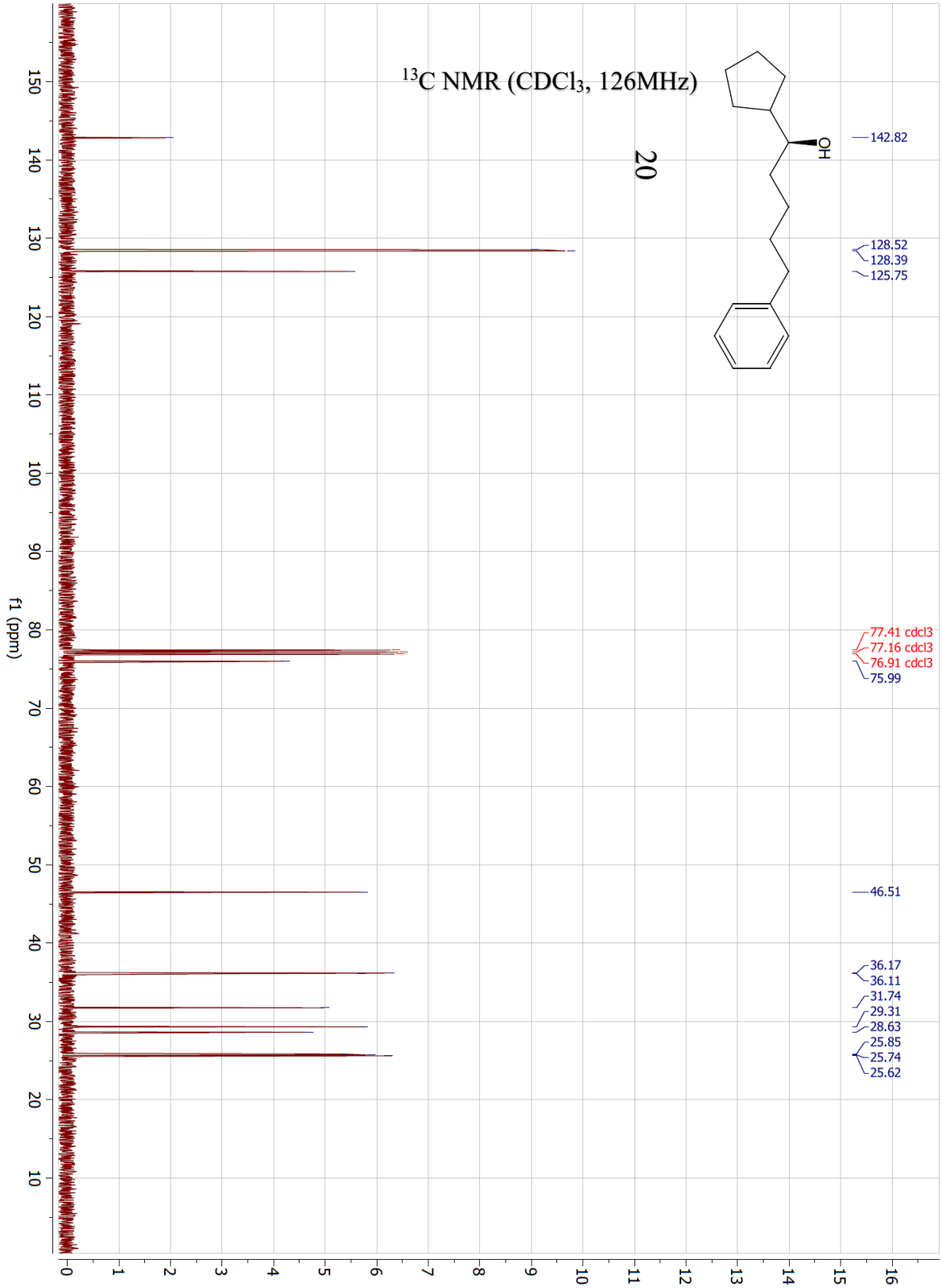

^{1}H NMR ($CDCl_3$, 600MHz)
18
[1H (ppm)]
2.12
2.99
1.00
2.04
3.35
2.10
2.25
1.01
6.06
7.28
7.25
7.18
7.16
3.35
2.66
2.65
2.64
2.64
2.63
2.61
2.61
2.60
2.59
1.63
1.51
1.39
1.38
1.30
0.91
0.90
0.89

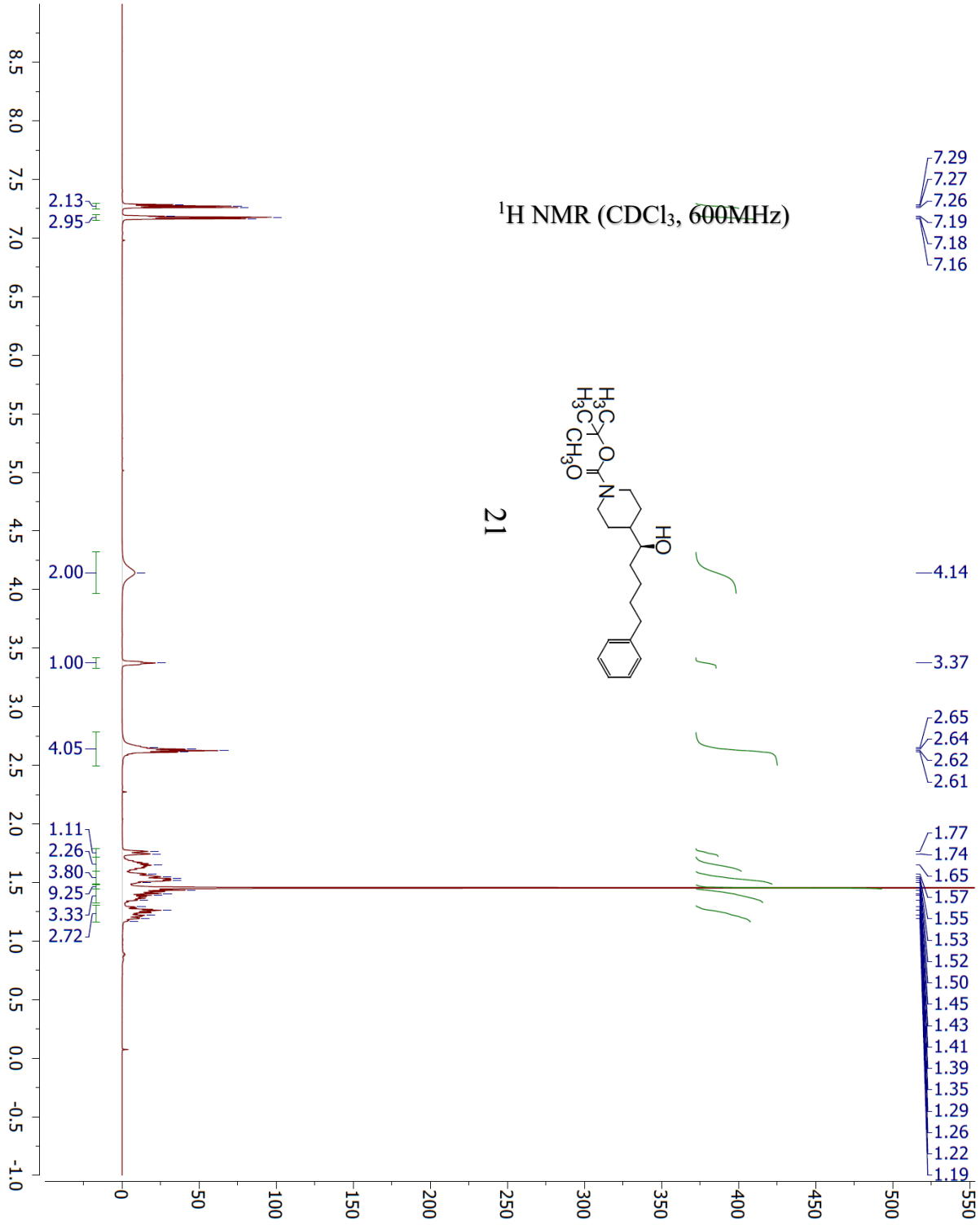

^{13}C NMR ($CDCl_3$, 151MHz)
18
142.79
128.52
128.39
125.76
77.16
76.77
36.11
34.13
33.63
31.73
25.89
18.99
17.22
[13C (ppm)]

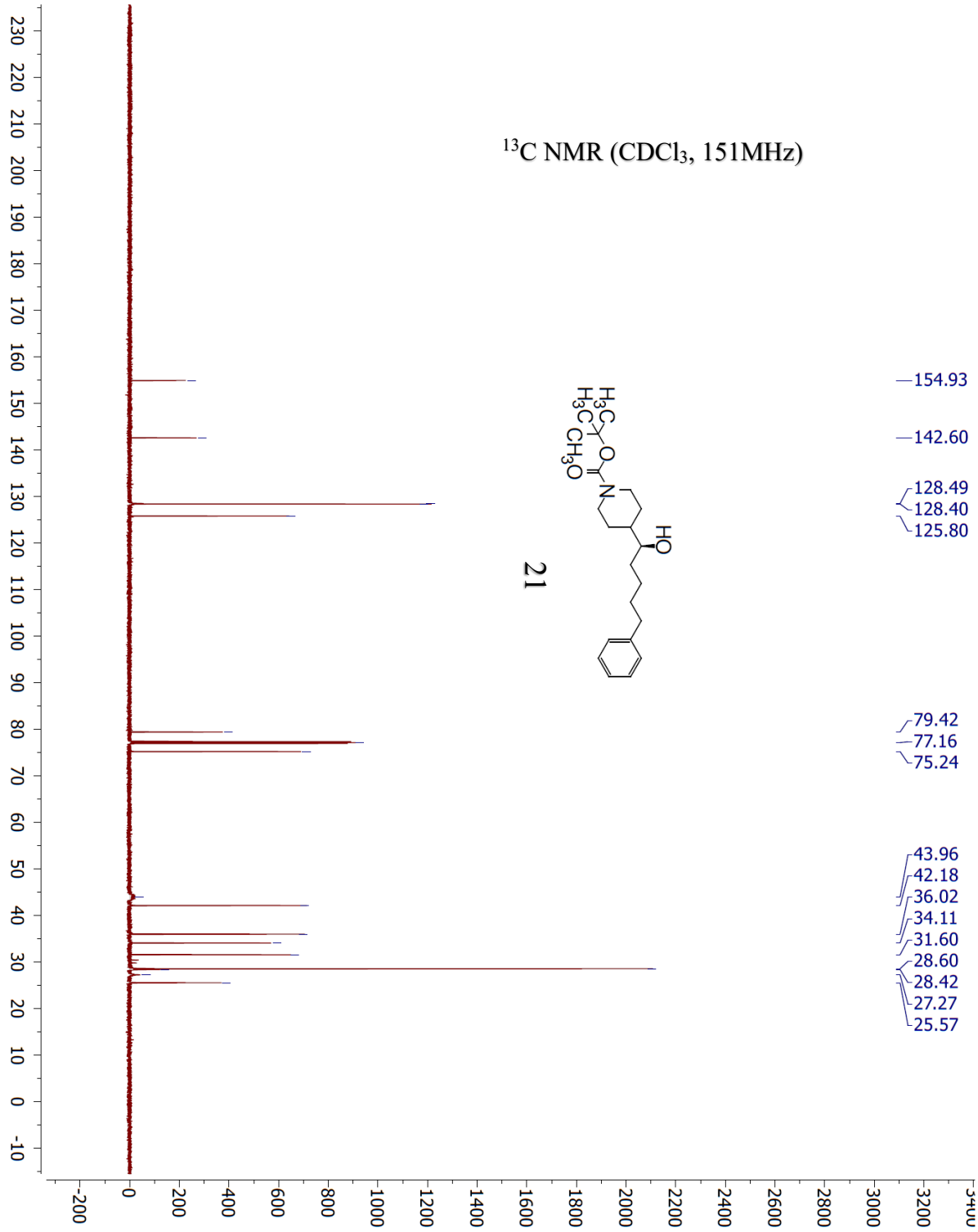

^{1}H NMR ($CDCl_3$, 600MHz)
19
Me
Me
Me
OH
2.60
2.88
0.96
1.96
4.62
4.24
9.00
7.29
7.27
7.26
7.26 cdcl3
7.19
7.17
7.16
3.19
3.17
2.67
2.66
2.65
2.64
2.62
2.61
2.60
2.59
1.72
1.69
1.63
1.60
1.58
1.55
1.51
1.38
1.34
1.30
1.26
1.24
0.89

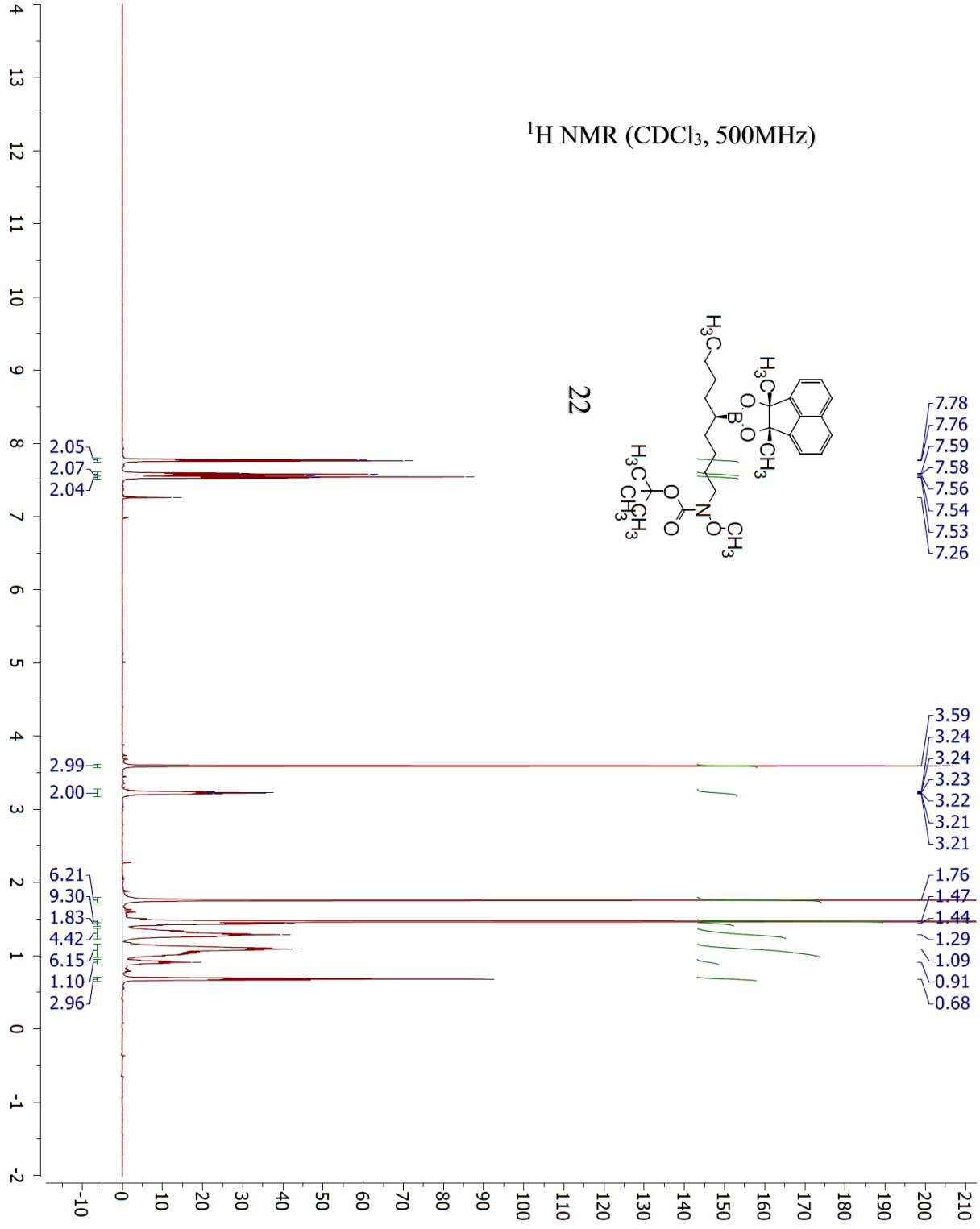

^{13}C NMR (CDCl$_3$, 151MHz)
19
142.86
128.55
128.40
125.77
80.03
77.16 cdcl3
36.18
35.08
31.74
31.50
26.94
25.84
Me
Me
Me
OH

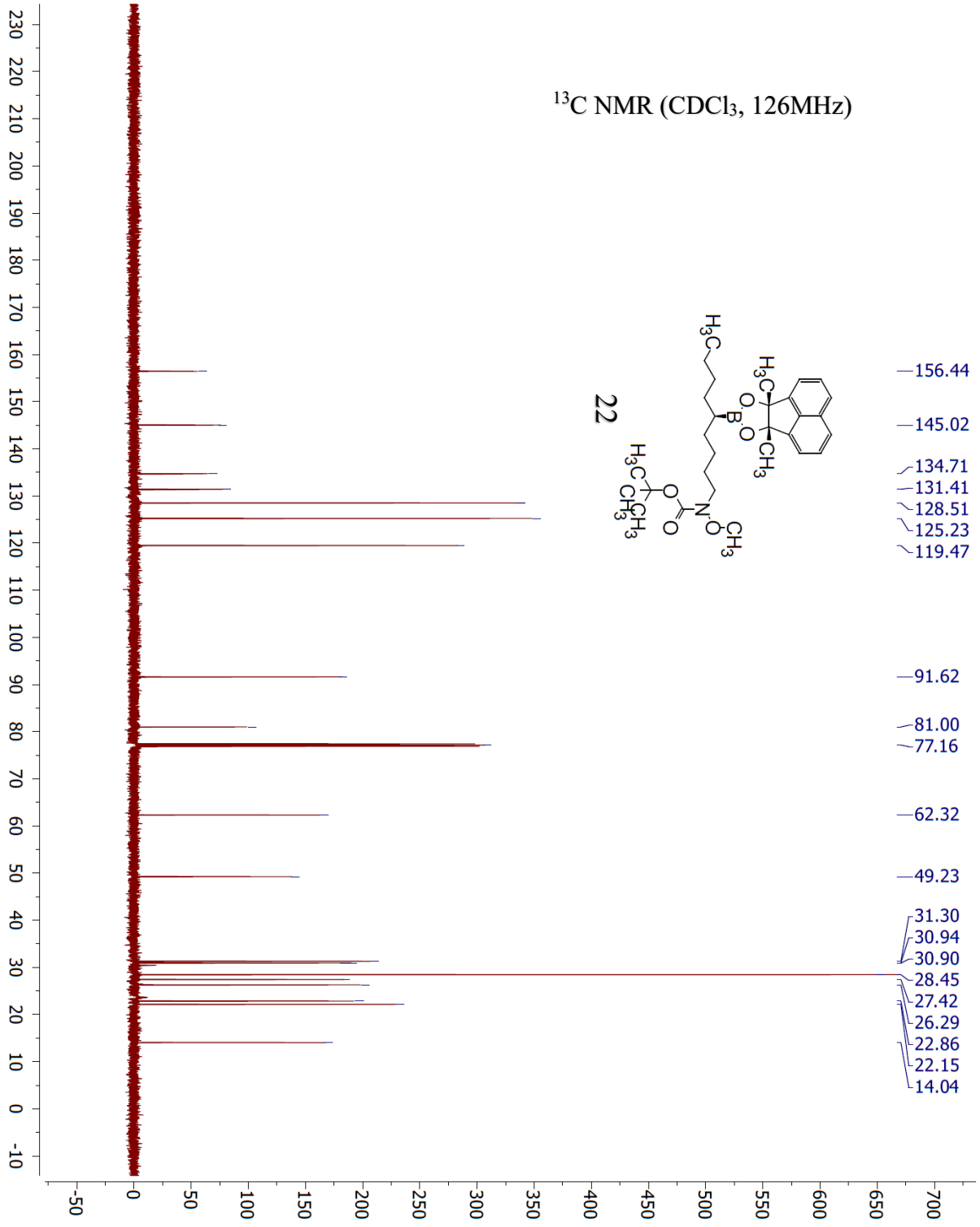

^{1}H NMR ($CDCl_3$, 500MHz)
20
OH
f1 (ppm)
5.29
2.42
1.00
1.95
0.99
1.16
3.94
4.29
2.15
1.74
1.14
7.26 cdcl3
7.19
3.40
2.64
2.63
2.61
1.87
1.77
1.62
1.53
1.40
1.31
1.19

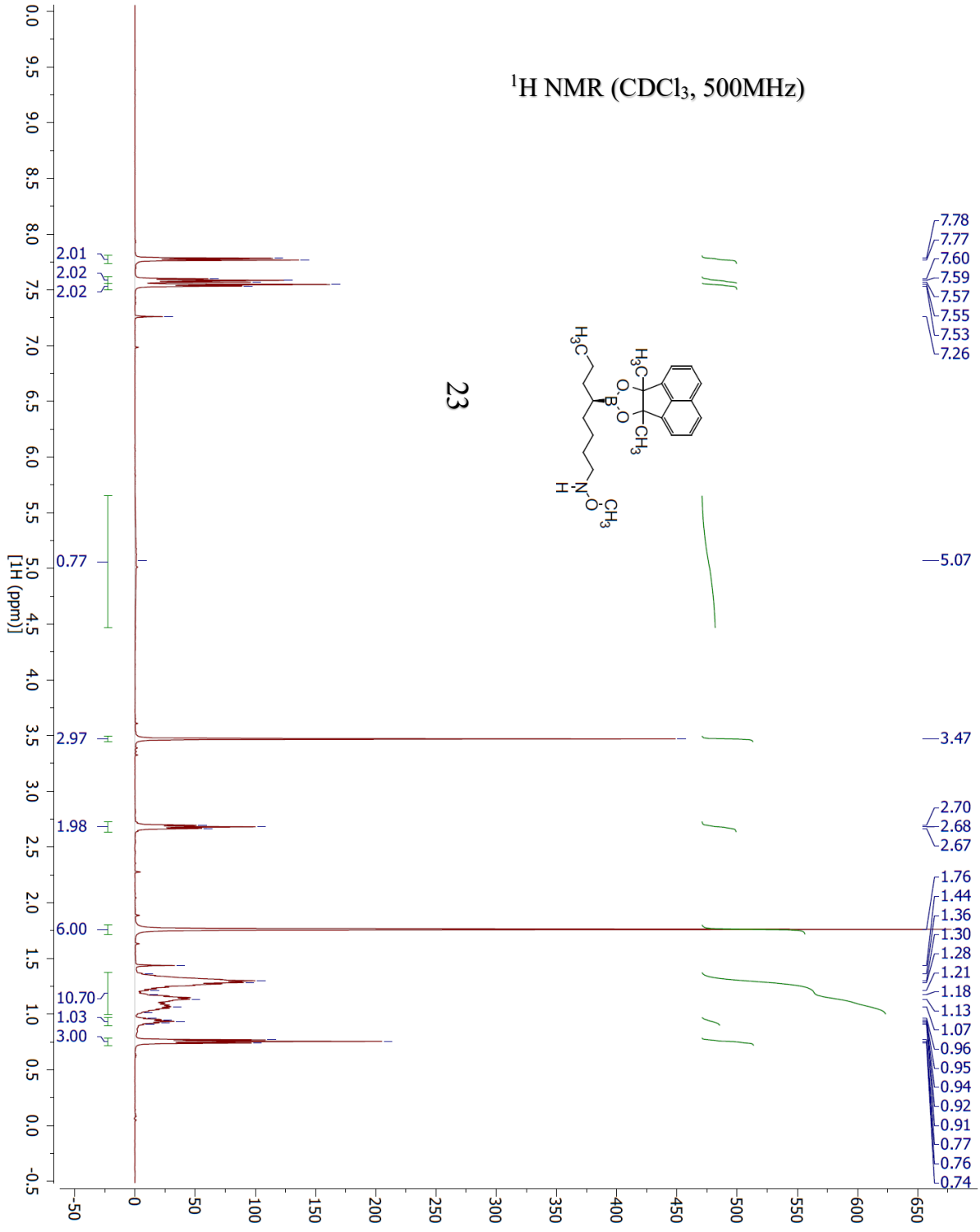

^{13}C NMR ($CDCl_3$, 126MHz)
20
OH
142.82
128.52
128.39
125.75
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
75.99
46.51
36.17
36.11
31.74
29.31
28.63
25.85
25.74
25.62
f1 (ppm)

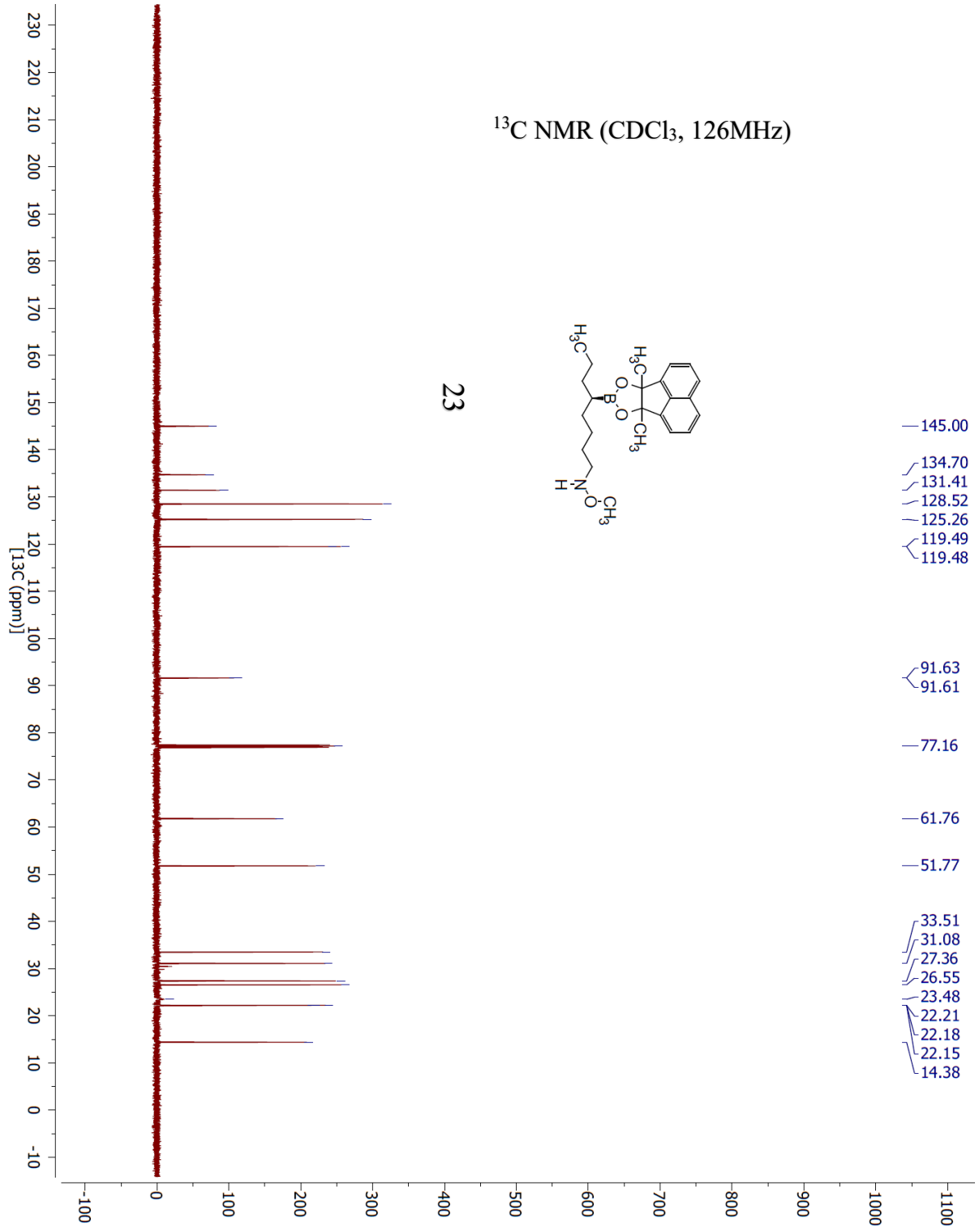

^{1}H NMR ($CDCl_3$, 600MHz)
21
2.13
2.95
2.00
1.00
4.05
1.11
2.26
3.80
9.25
3.33
2.72
7.29
7.27
7.26
7.19
7.18
7.16
4.14
3.37
2.65
2.64
2.62
2.61
1.77
1.74
1.65
1.57
1.55
1.53
1.52
1.50
1.45
1.43
1.41
1.39
1.35
1.29
1.26
1.22
1.19

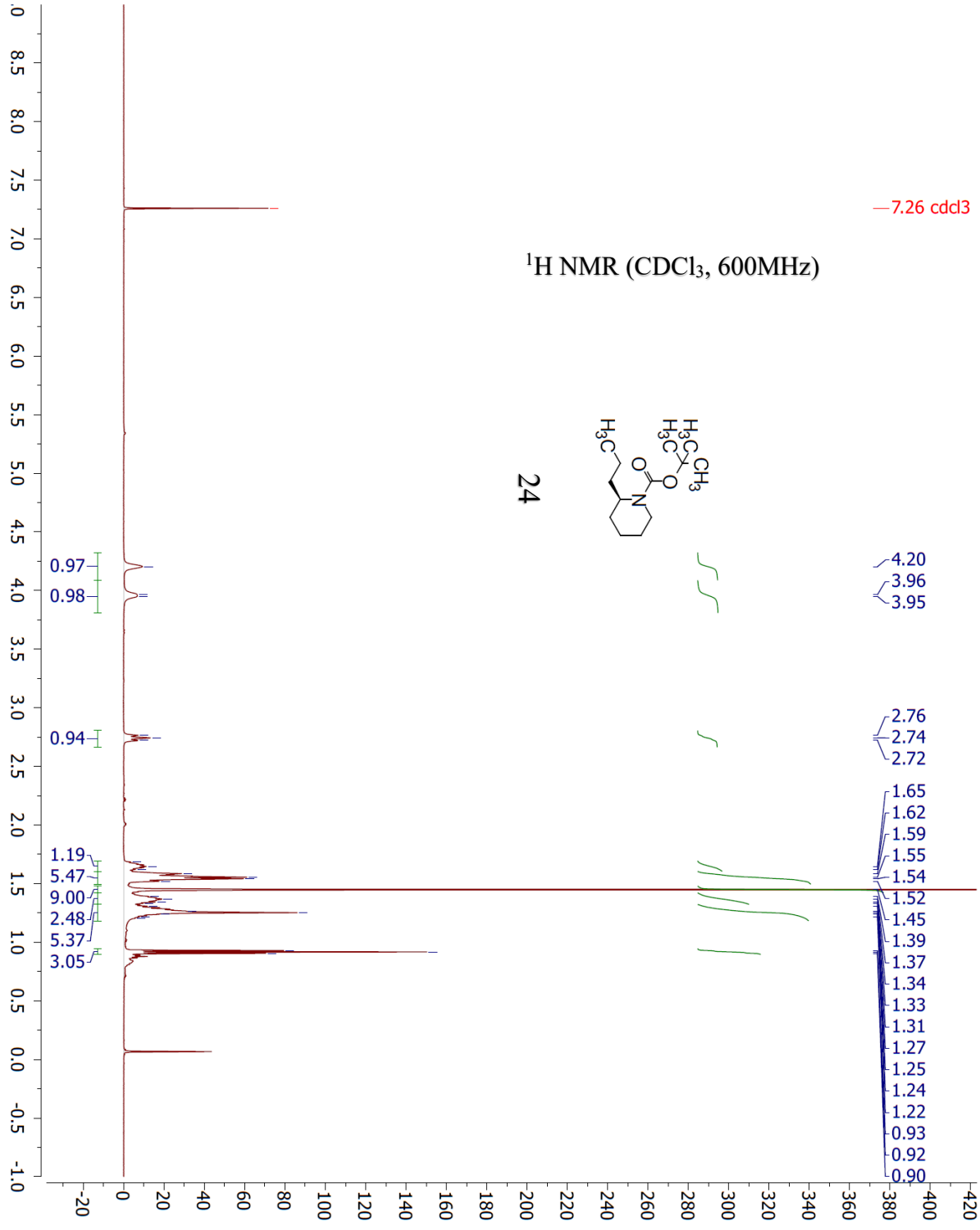

^{13}C NMR ($CDCl_3$, 151MHz)
21
154.93
142.60
128.49
128.40
125.80
79.42
77.16
75.24
43.96
42.18
36.02
34.11
31.60
28.60
28.42
27.27
25.57

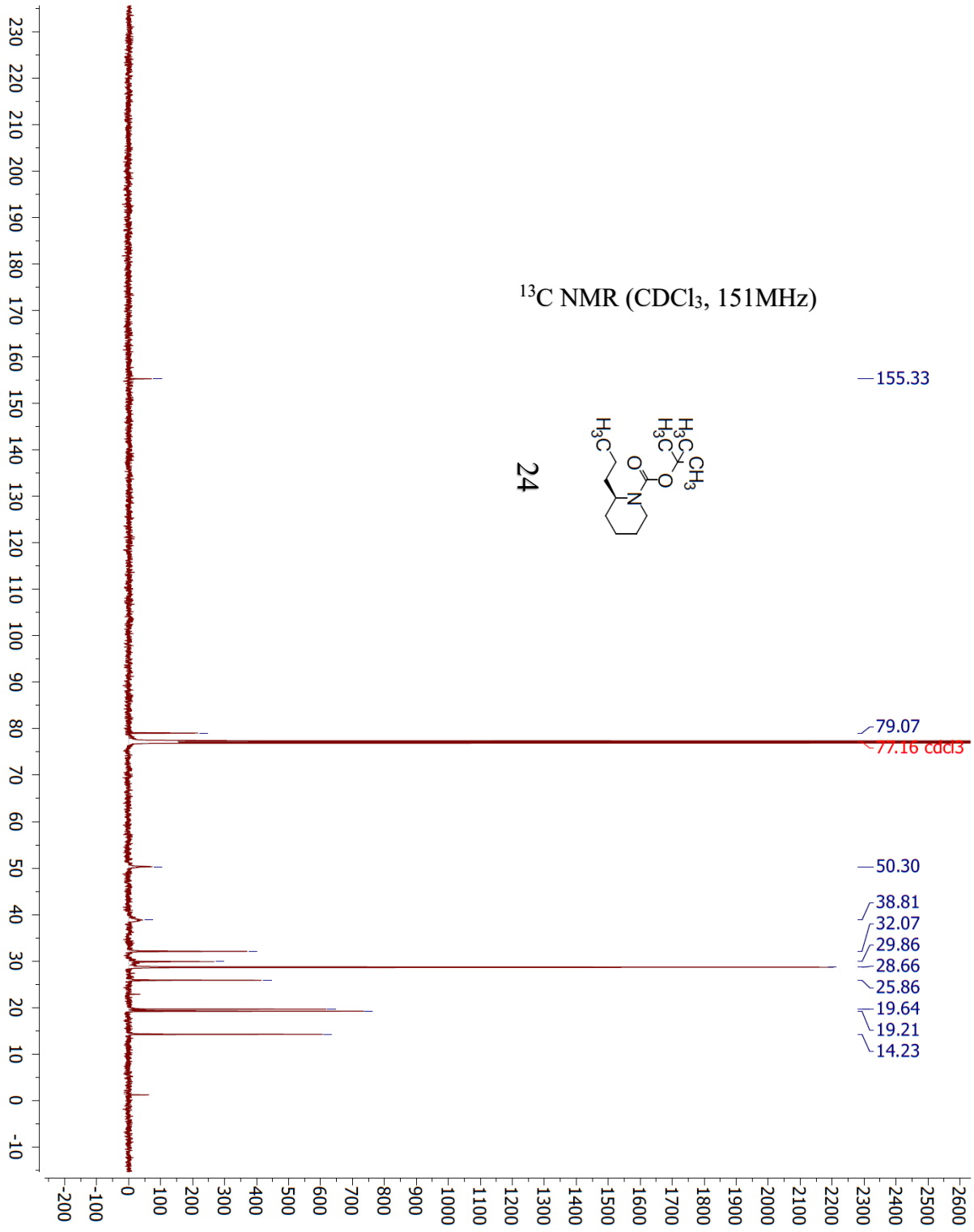

^{1}H NMR ($CDCl_3$, 500MHz)
22
7.78
7.76
7.59
7.58
7.56
7.54
7.53
7.26
3.59
3.24
3.24
3.23
3.22
3.21
3.21
1.76
1.47
1.44
1.29
1.09
0.91
0.68
2.05
2.07
2.04
2.99
2.00
6.21
9.30
1.83
4.42
6.15
1.10
2.96

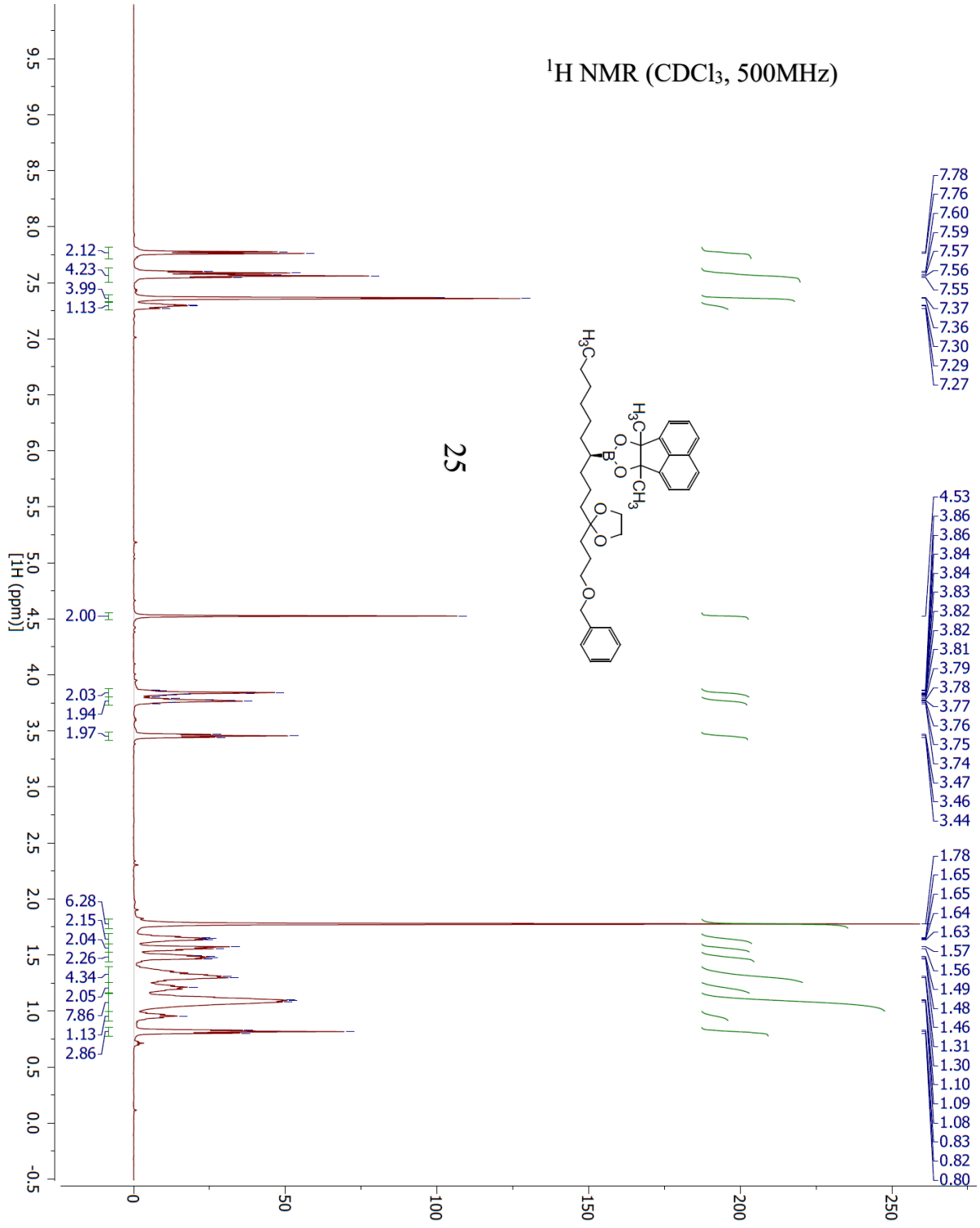

^{13}C NMR ($CDCl_3$, 126MHz)
22
156.44
145.02
134.71
131.41
128.51
125.23
119.47
91.62
81.00
77.16
62.32
49.23
31.30
30.94
30.90
28.45
27.42
26.29
22.86
22.15
14.04

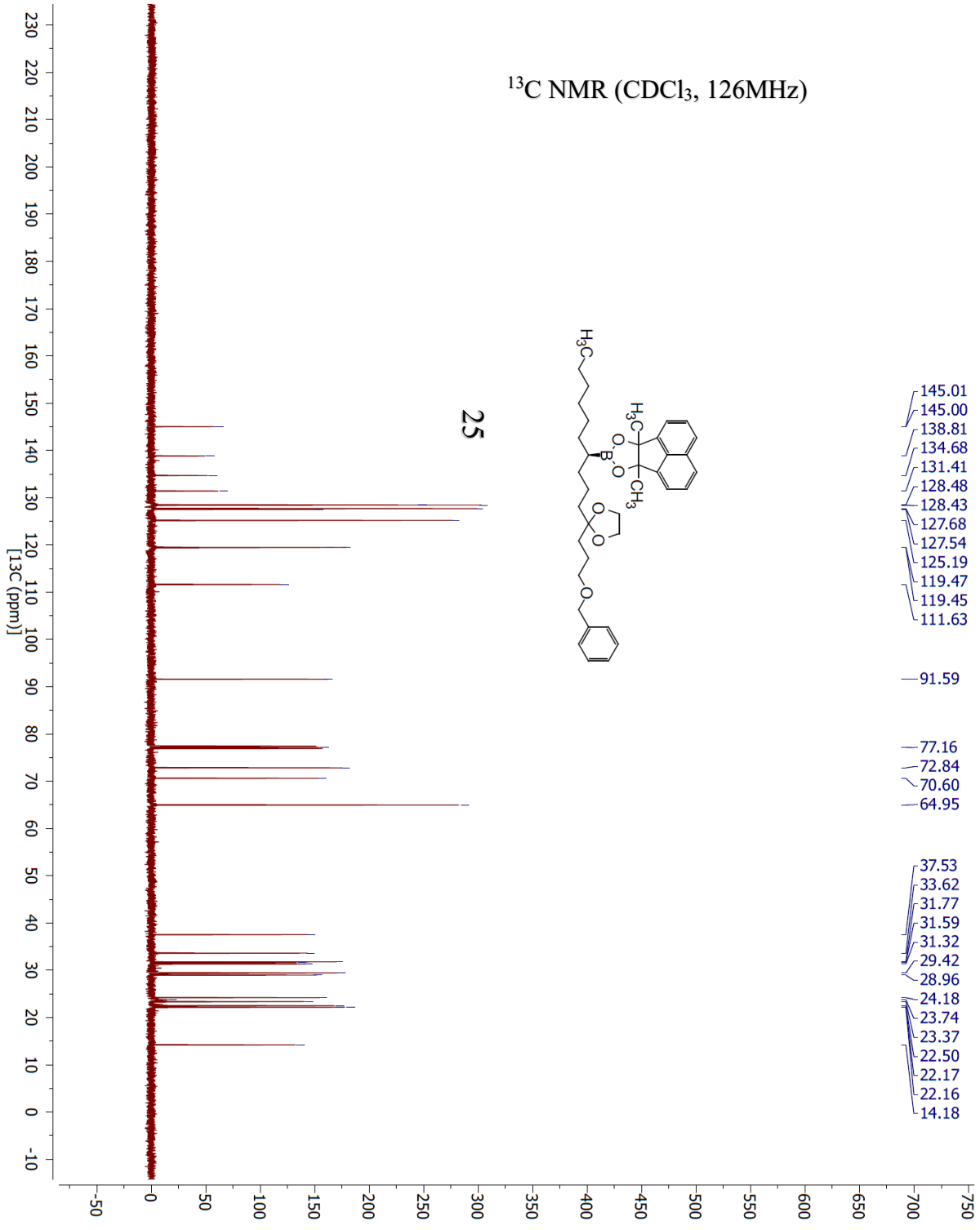

^{1}H NMR ($CDCl_3$, 500MHz)
23
[1H (ppm)]
2.01
2.02
2.02
0.77
2.97
1.98
6.00
10.70
1.03
3.00
7.78
7.77
7.60
7.59
7.57
7.55
7.53
7.26
5.07
3.47
2.70
2.68
2.67
1.76
1.44
1.36
1.30
1.28
1.21
1.18
1.13
1.07
0.96
0.95
0.94
0.92
0.91
0.77
0.76
0.74

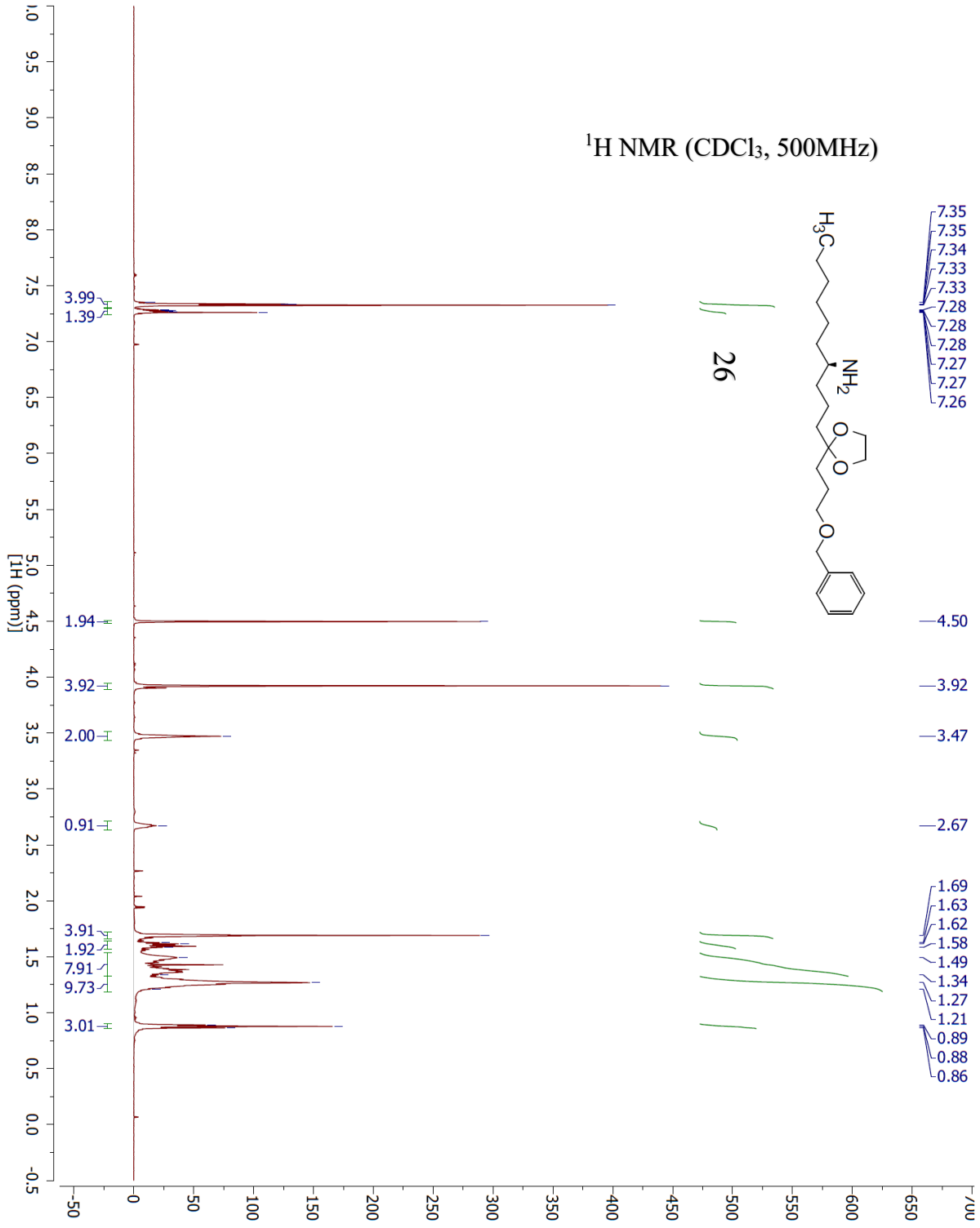

^{13}C NMR (CDCl$_3$, 126MHz)
23
145.00
134.70
131.41
128.52
125.26
119.49
119.48
91.63
91.61
77.16
61.76
51.77
33.51
31.08
27.36
26.55
23.48
22.21
22.18
22.15
14.38
[13C (ppm)]

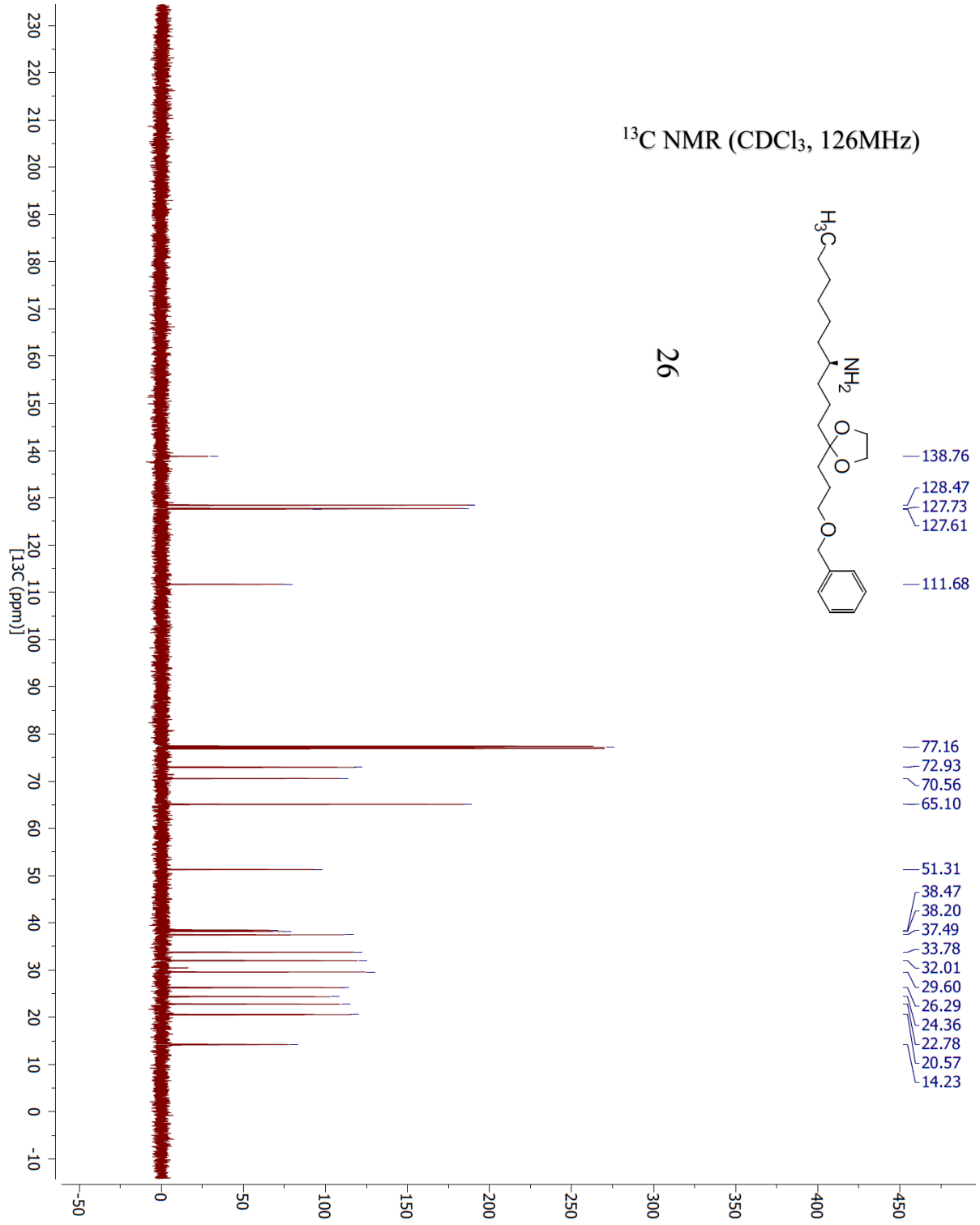

7.26 cdcl3
^{1}H NMR ($CDCl_3$, 600MHz)
24
0.97
0.98
0.94
1.19
5.47
9.00
2.48
5.37
3.05
4.20
3.96
3.95
2.76
2.74
2.72
1.65
1.62
1.59
1.55
1.54
1.52
1.45
1.39
1.37
1.34
1.33
1.31
1.27
1.25
1.24
1.22
0.93
0.92
0.90

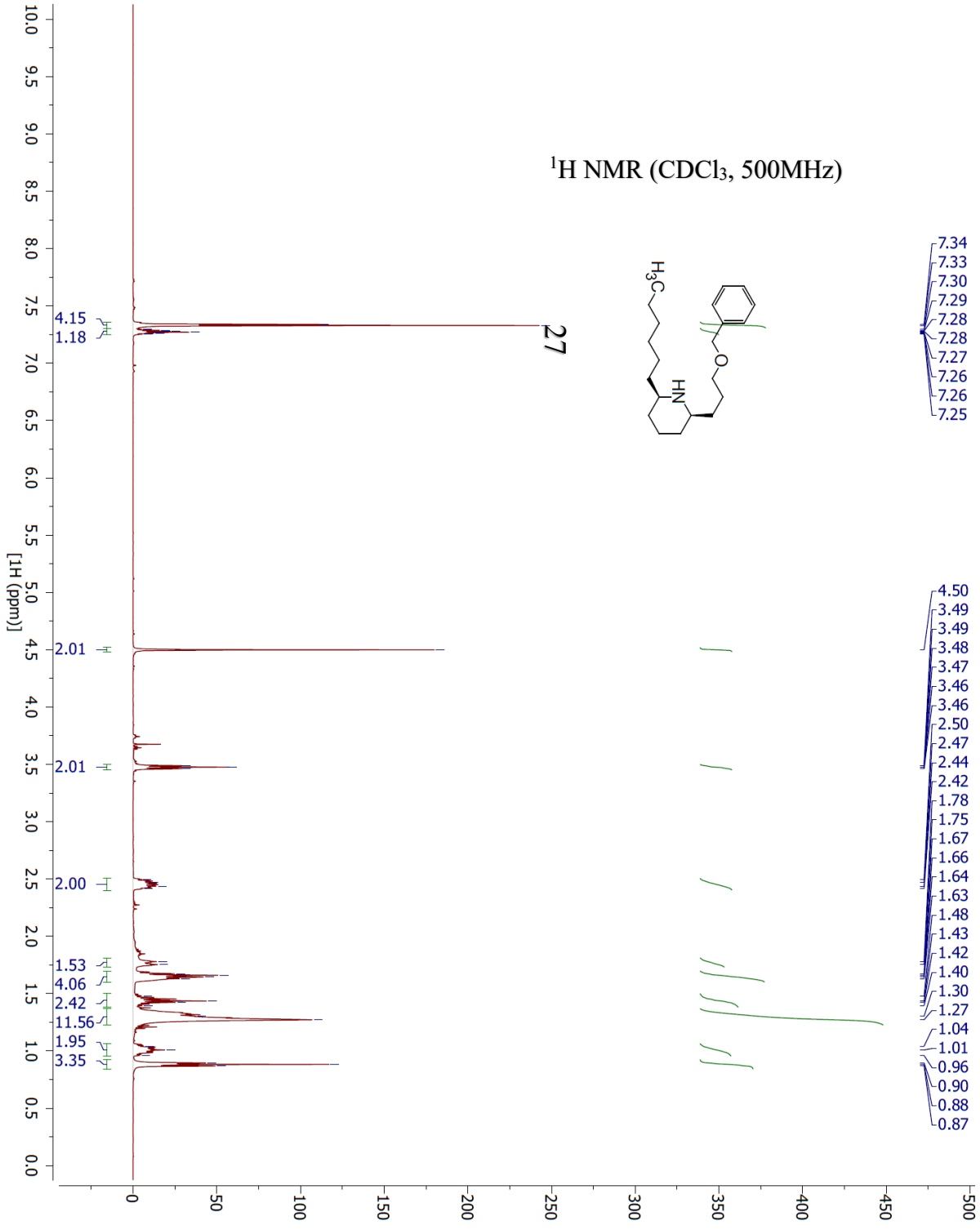

^{13}C NMR ($CDCl_3$, 151MHz)
24
155.33
79.07
77.16 cdcl3
50.30
38.81
32.07
29.86
28.66
25.86
19.64
19.21
14.23

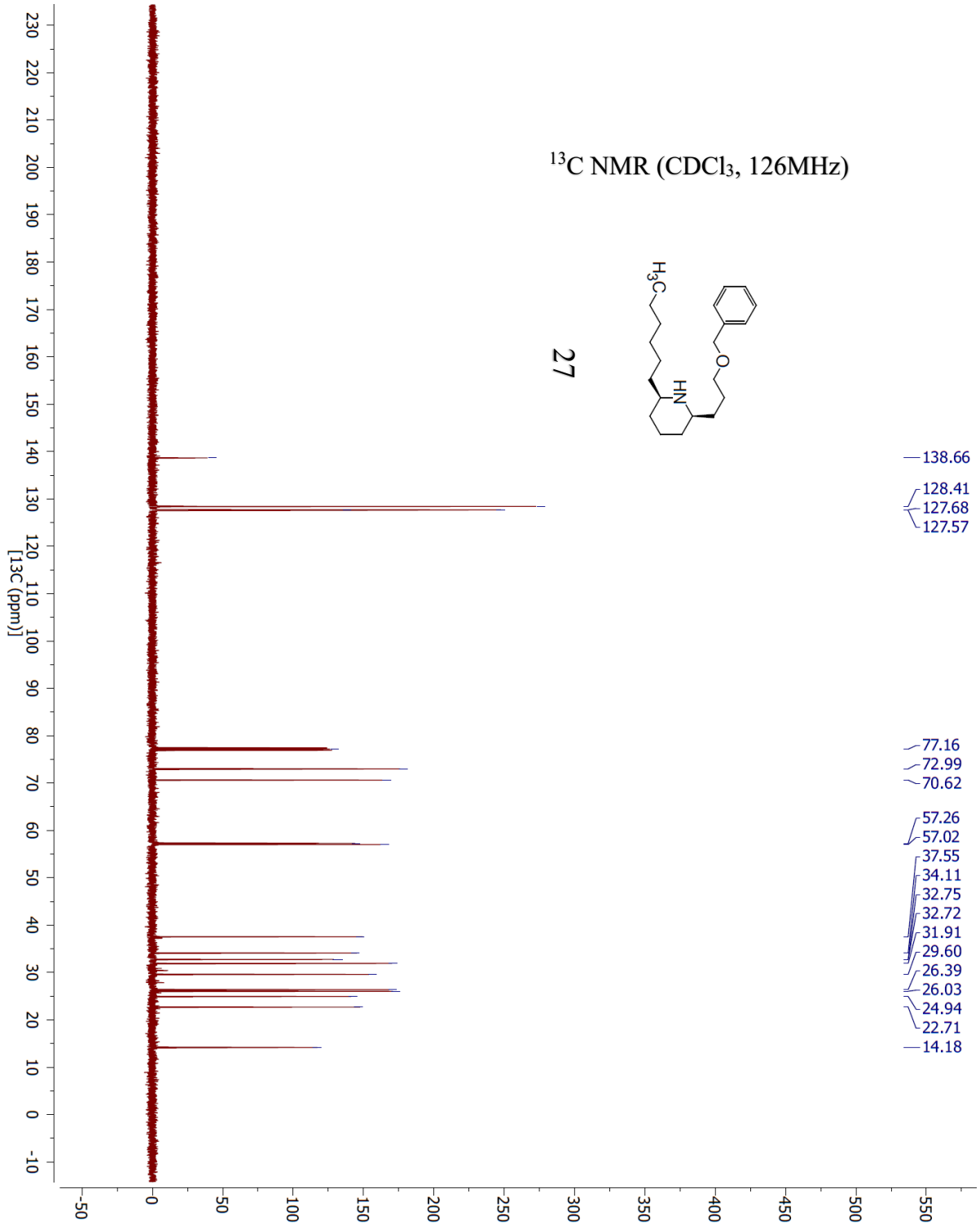

^{1}H NMR ($CDCl_3$, 500MHz)
25
[1H (ppm)]
2.12
4.23
3.99
1.13
2.00
2.03
1.94
1.97
6.28
2.15
2.04
2.26
4.34
2.05
7.86
1.13
2.86
7.78
7.76
7.60
7.59
7.57
7.56
7.55
7.37
7.36
7.30
7.29
7.27
4.53
3.86
3.86
3.84
3.84
3.83
3.82
3.82
3.81
3.79
3.78
3.77
3.76
3.75
3.74
3.47
3.46
3.44
1.78
1.65
1.65
1.64
1.63
1.57
1.56
1.49
1.48
1.46
1.31
1.30
1.10
1.09
1.08
0.83
0.82
0.80

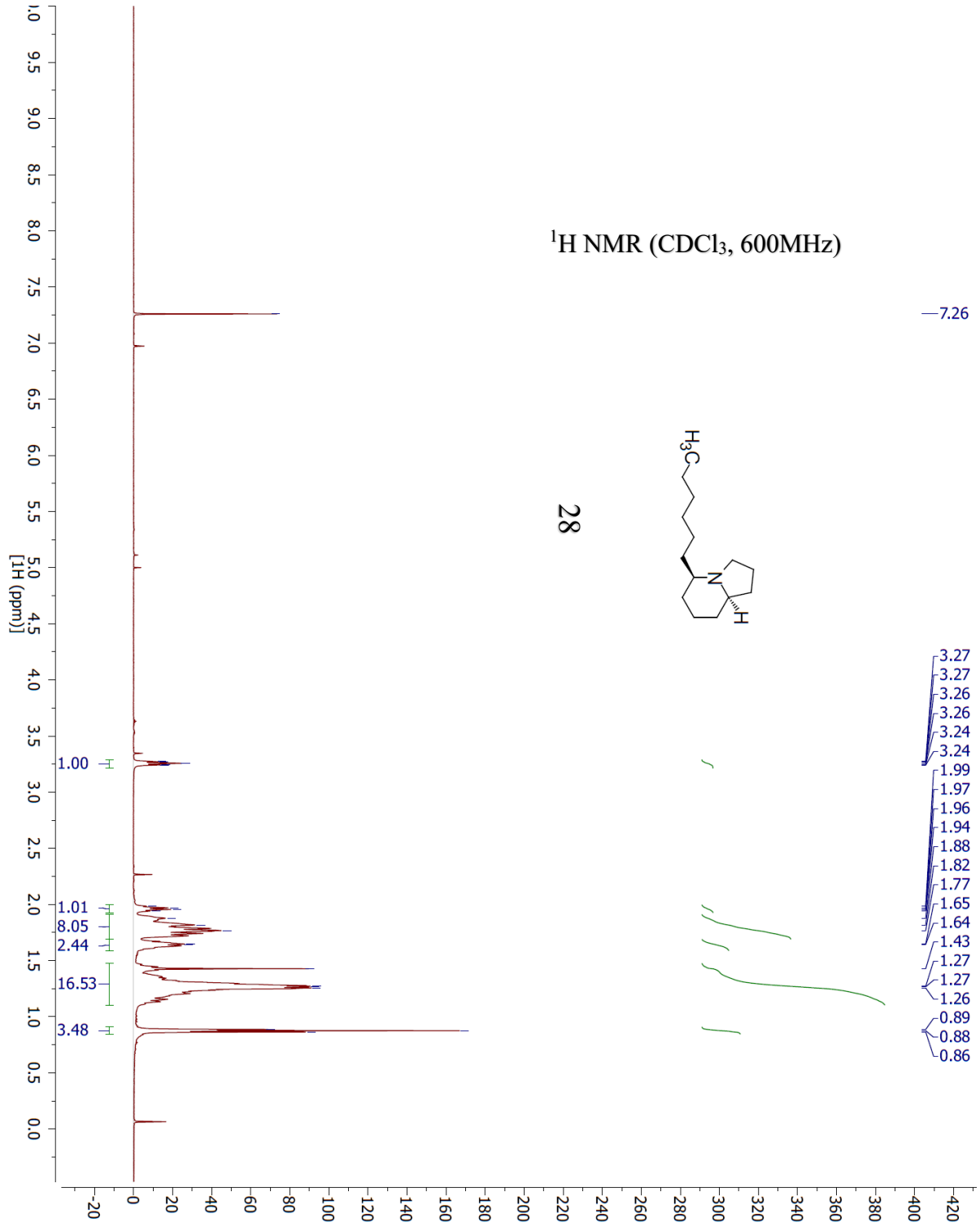

^{13}C NMR ($CDCl_3$, 126MHz)
25
145.01
145.00
138.81
134.68
131.41
128.48
128.43
127.68
127.54
125.19
119.47
119.45
111.63
91.59
77.16
72.84
70.60
64.95
37.53
33.62
31.77
31.59
31.32
29.42
28.96
24.18
23.74
23.37
22.50
22.17
22.16
14.18
[13C (ppm)]

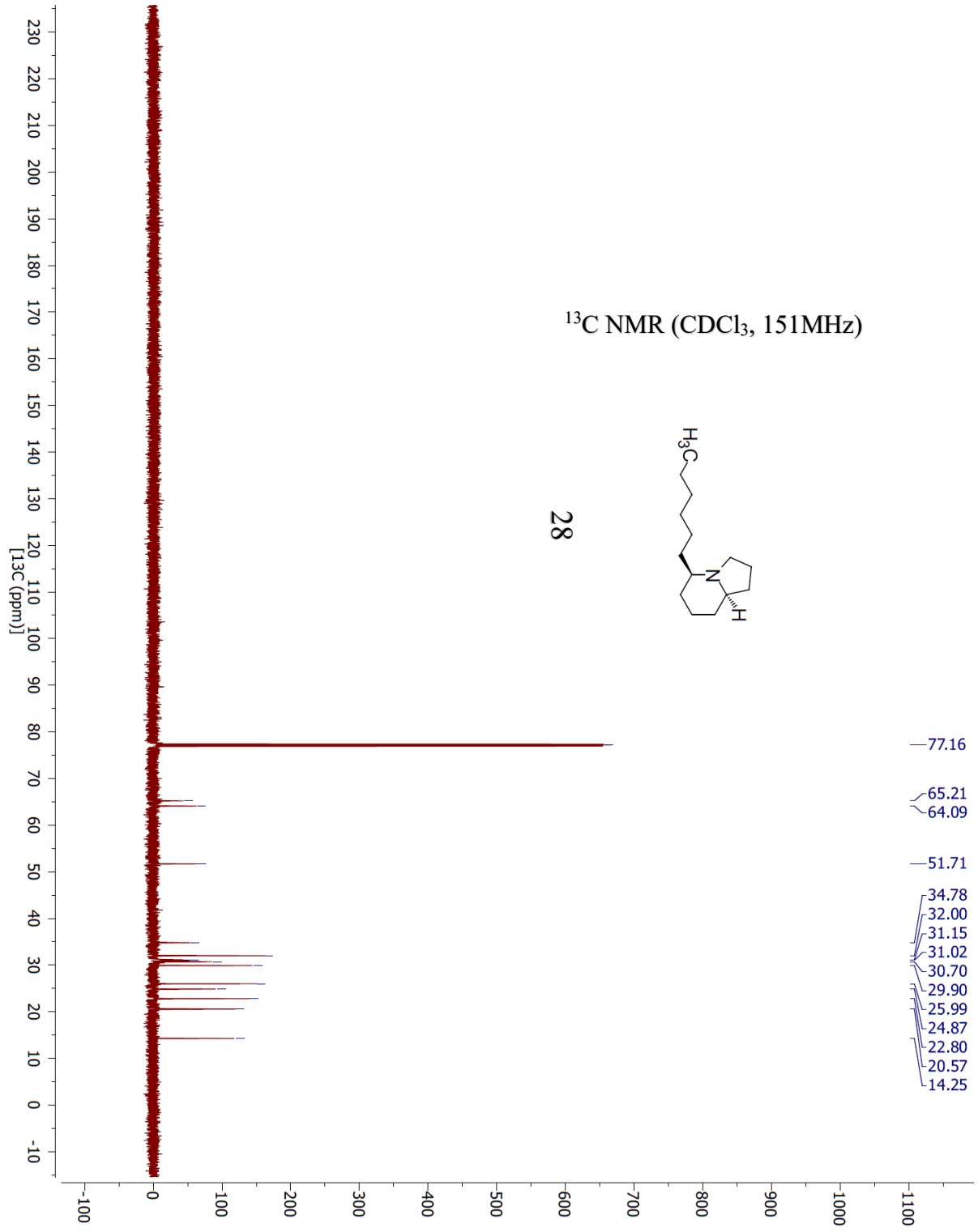

^{1}H NMR ($CDCl_3$, 500MHz)
26
[1H (ppm)]
3.99
1.39
1.94
3.92
2.00
0.91
3.91
1.92
7.91
9.73
3.01
7.35
7.35
7.34
7.33
7.33
7.28
7.28
7.28
7.27
7.27
7.26
4.50
3.92
3.47
2.67
1.69
1.63
1.62
1.58
1.49
1.34
1.27
1.21
0.89
0.88
0.86

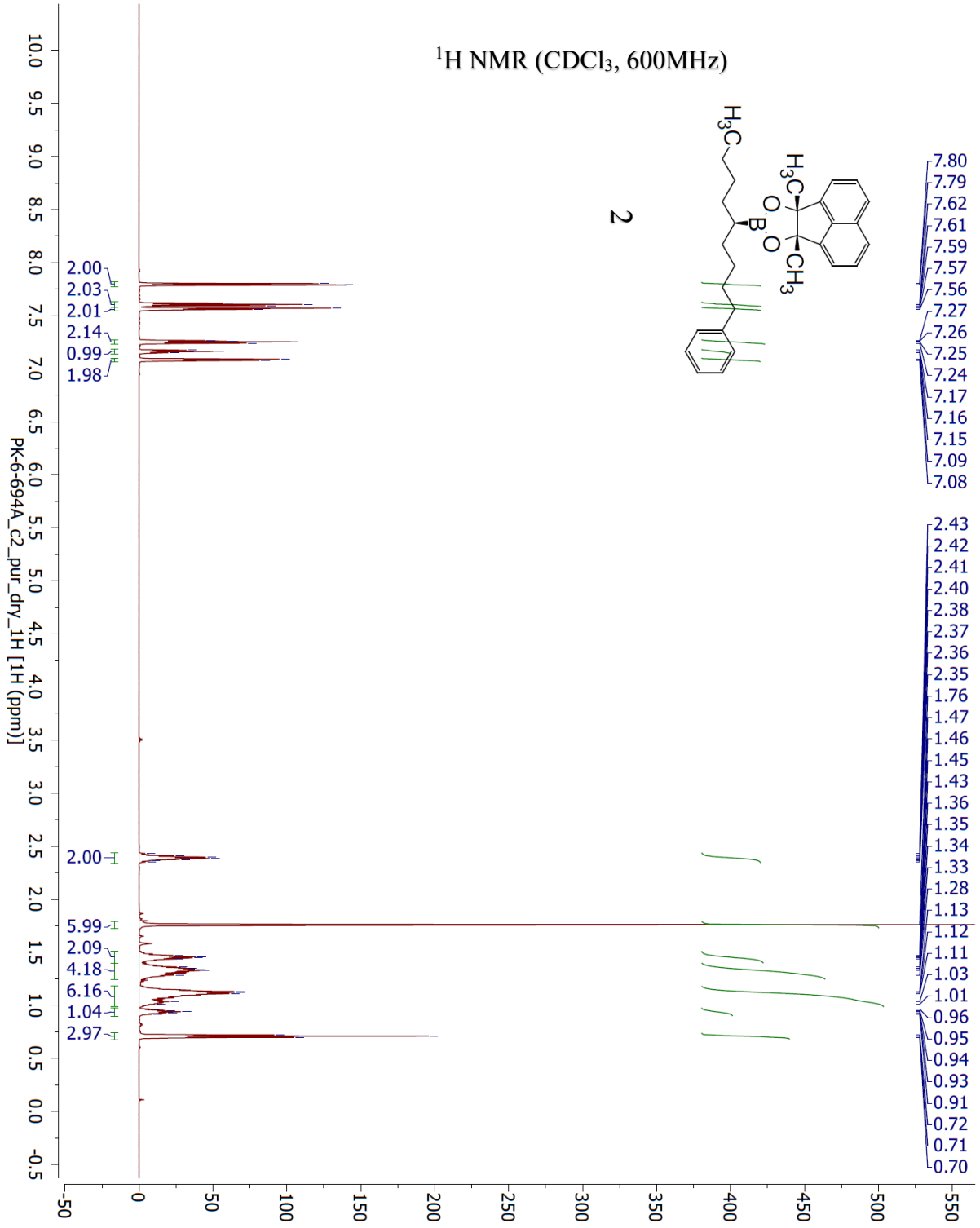

^{13}C NMR ($CDCl_3$, 126MHz)
26
H_3C
NH_2
O
O
O
138.76
128.47
127.73
127.61
111.68
77.16
72.93
70.56
65.10
51.31
38.47
38.20
37.49
33.78
32.01
29.60
26.29
24.36
22.78
20.57
14.23
[13C (ppm)]

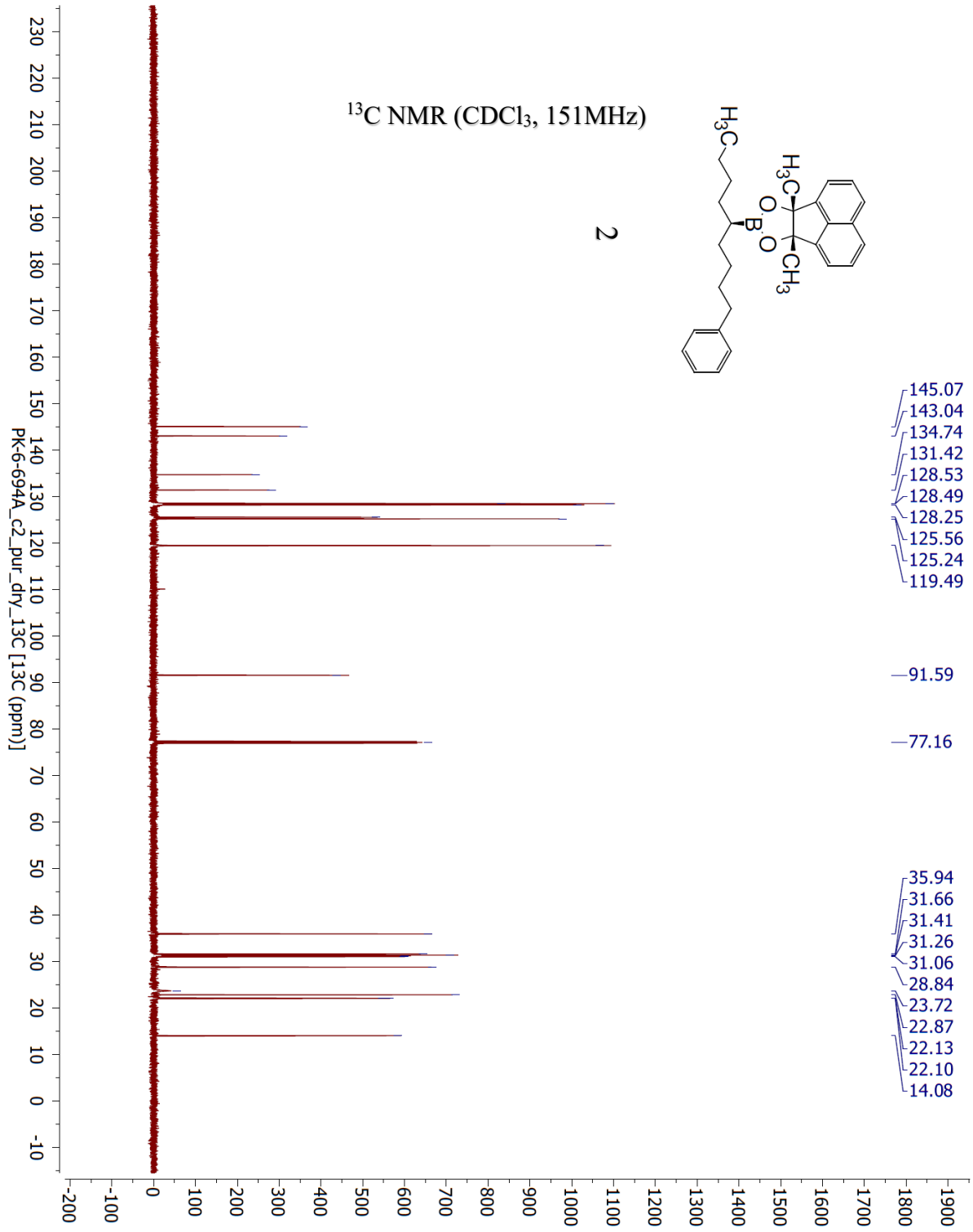

^{1}H NMR ($CDCl_3$, 500MHz)
27
H_3C
HN
O
[1H (ppm)]
4.15
1.18
2.01
2.01
2.00
1.53
4.06
2.42
11.56
1.95
3.35
7.34
7.33
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
4.50
3.49
3.49
3.48
3.47
3.46
3.46
2.50
2.47
2.44
2.42
1.78
1.75
1.67
1.66
1.64
1.63
1.48
1.43
1.42
1.40
1.30
1.27
1.04
1.01
0.96
0.90
0.88
0.87


^{13}C NMR (CDCl$_3$, 126MHz)
27
H$_3$C
HN
O
138.66
128.41
127.68
127.57
77.16
72.99
70.62
57.26
57.02
37.55
34.11
32.75
32.72
31.91
29.60
26.39
26.03
24.94
22.71
14.18
[13C (ppm)]


^{1}H NMR ($CDCl_3$, 600MHz)
28
H_3C
N
H
7.26
3.27
3.27
3.26
3.26
3.24
3.24
1.99
1.97
1.96
1.94
1.88
1.82
1.77
1.65
1.64
1.43
1.27
1.27
1.26
0.89
0.88
0.86
1.00
1.01
8.05
2.44
16.53
3.48
[1H (ppm)]


^{13}C NMR (CDCl$_3$, 151MHz)
28
H3C
N
H
77.16
65.21
64.09
51.71
34.78
32.00
31.15
31.02
30.70
29.90
25.99
24.87
22.80
20.57
14.25
[13C (ppm)]


^{1}H NMR ($CDCl_3$, 600MHz)
2
PK-6-694A_c2_pur_dry_1H [1H (ppm)]


^{13}C NMR ($CDCl_3$, 151MHz)
2
145.07
143.04
134.74
131.42
128.53
128.49
128.25
125.56
125.24
119.49
91.59
77.16
35.94
31.66
31.41
31.26
31.06
28.84
23.72
22.87
22.13
22.10
14.08
PK-6-694A_c2_pur_dry_13C [13C (ppm)]