SYNTHESIS OF ALLYL ALCOHOLS BY PALLADIUM-CATALYZED 1,3-SUBSTITUTION REACTIONS OF ALKENYL EPOXIDES WITH ORGANOBORONS

A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

in Chemistry

by
Erman KIBRIS

July 2016
İZMİR

We approve the thesis of **Erman KIBRIS**

Examining Committee Members:

Prof. Dr. Levent ARTOK
Department of Chemistry, İzmir Institute of Technology

Prof. Dr. Canan VARLIKLI
Department of Photonics, İzmir Institute of Technology

Prof. Dr. Stephen Thomas ASTLEY
Department of Chemistry, Ege University

27 July 2016

Prof. Dr. Levent ARTOK
Supervisor, Department of Chemistry
İzmir Institute of Technology

Prof. Dr. Ahmet Emin EROĞLU
Head of Department of Chemistry

Prof. Dr. R. Bilge KARAÇALI
Dean of the Graduate School of
Engineering and Sciences

ABBREVIATIONS

Ac	Acetate
aq.	Aqueous
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
Bn	Benzyl
Bu	n-Butyl
t-Bu	tert-Butyl
Cy	Cyclohexane
dba	Dibenzylideneacetone
DCM	Dichloromethane
DIBAL-H	Diisobutylaluminium hydride
DMAP	4-Dimethylaminopyridine
DME	1,2-Dimethoxyethane
DMF	*N*,*N*-Dimethylformamide
DPEPhos	Bis-[2-(diphenylphosphino)phenyl]ether
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	Bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
d.r.	Diastereomeric ratio
Et	Ethyl
eqv.	Equivalent
Et_2O	Diethyl ether
h	hour
m-CPBA	meta-chloroperoxybenzoic acid
M	Molar
Me	Methyl
mg	Miligrams
min.	Minute
mL	Mililiter
mmol	Milimoles
N.D.	Not determined

neop	Neopentyl glycol ester
NMR	Nuclear magnetic resonance
O.N.	Overnight
Ph	Phenyl
Pr	Propyl
rt	Room Temperature
t	Time
i-Pr	iso-Propyl
SIPr	1,3-bis(2,6-di-i-propylphenyl) imidazol-2-ylidene
TBDMS	tert-Butyldimethylsilyl
THF	Tetrahydrofurane
Xanthphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene
Xphos	2-Dicyclohexylphosphino-2′,4′,6′ triisopropylbiphenyl

ACKNOWLEDGEMENTS

There are many people to thank firstly, I am heartily thankful to my supervisor Prof. Dr. Levent Artok for his patient guidance, encouragement and excellent advice not only throughout this study but also in my life. This thesis could not have been written without his astute guidance.

It was honor to study with him. Also I would like to thank all old and new members of İYTE organic research group, Doğan Taç, Fırat Ziyanak and İsmet Arınç Aytaç.

Special thanks to Prof. Dr. Canan Varlıklı and Assist. Prof. Dr. Stephen Asthey participating as committee member and for reviewing my work. I would like to thank to the TUBITAK (114Z228) for the financial support to this project.

I am deeply and forever indebted to my parents for their love, support and encouragement throughout my entire life especially Melike Sayar.

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ABSTRACT

SYNTESIS OF ALLYL ALCOHOLS BY PALLADIUM-CATALYZED 1,3-SUBSTITUTION REACTIONS OF ALKENYL EPOXIDES WITH ORGANOBORONS

1,3-Substitution reactions of allylic compounds having a good leaving group is a prominent method in Organic Chemistry for the synthesis of new allylic reagents with an exchanged functional group. These reactions usually require the use of metal catalysts and one of the most challenging aspects for these applications is the regio- and stereo-selectivity of the process for a wide range of substrate types. Other compounds such as vinyl epoxides are also acceptable for substitution reactions.

An important advantage of using these reagents is that opening of the oxirane ring during the substitution process lead to the generation of a hydroxyl group and as a result affords allyl alcohols which are important intermediaries in organic syntheses.

An example of regio-selective metal-catalyzed reactions of vinyl epoxides having a terminal alkenyl group with environmentally benign organoborons was reported in the literature. However, no such success could be achieved with vinyl epoxides with an internal alkenyl group. Therefore, within the context of this method internal vinyl epoxides were successfully subjected to 1,3-substitution reactions with organoborons which yielded arylated allyl alcohols in both a regio- and stereo-selective manner. The method is applicable under quite mild conditions where a palladium-$AsPh_3$ combination is used to activate the process.

ÖZET

ALKENİL EPOKSİTLERİN ORGANOBORLAR İLE PALADYUM KATALİZLİ 1,3-SÜBSTİTÜSYON TEPKİMELERİ ARACILIĞI İLE ALLİL ALKOLLERİN SENTEZİ

Kolay bir terkeden gruba sahip allilik bileşiklerin 1,3-sübstitüsyon tepkimeleri farklı bir fonksiyonel gruba sahip yeni allilik bileşiklerin sentezi organik kimyada önemli bir tepkime tipidir. Bu tip tepkimeler çoğunlukla bir metal katalizörü ile gerçekleştirilmektedir. Bu amaçla uygulanan yöntemlerin uygulamasında en önemli zorluk tepkimlerin yeterli mertebede regio ve stereo seçimli olarak geniş bir sübstrat yelpazesini içerecek şekilde gerçekleştirmektir.

Sübstitüsyon tepkimelerine uygun bir allilik bileşikte vinil epoksitlerdir. Bu yapıların kullanımında önemli bir avantaj epoksit oksijenin tepkime sonunda yalnızca bir bağının kopması sonucu hidroksil grubuna dönüşerek organik sentezlerde önemli bir ara yapı olan allil alkollerin oluşmasıdır.

Literatürde terminal alkenil gruba sahip vinil epoksitlerin çevre dostu organoborlar ile metal katalizli tepkimelerinin regio- ve stereo seçimli olarak gerçekleştiği rapor edilmiştir. Ancak aynı başarı iç alkenil gruba sahip yapılar için sağlanamamıştır. Bu nedenle bu tez çalışması kapsamında iç alkenil gruplu vinil epoksitlerin organoboronlar ile regio ve stereo seçimli olarak 1,3-sübstitüsyon tarzında arillenmesi başarılmıştır. Yöntem bir paladyum katalizörü ve $AsPh_3$ ligandının kullanıldığı ılıman koşullar gerektirmektedir.

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CHAPTER 1

INTRODUCTION

The studies about transition-metal-catalyzed reactions with various organometallic reagents have been an increasingly attractive method in recent years. The alkenyl or aryl addition to unsaturated compounds which have at least one leaving group is a well-known procedure. These compounds give generally S_N2 type reaction with a nucleophile in the absence of transition metals. However, the transition metals can change this orientation and the reactions may occur in the S_N2' manner.

The hard nucleophiles are used generally with copper- or nickel-catalyzed reactions over unsaturated compounds in order to shift the selectivity toward S_N2' type reaction. However, the usage of these nucleophiles such as grignard reagents, organolithium, and organozinc compounds have some restrictions, since they are highly air and moisture sensitive.

On the other hand, the organoboron compounds are highly stable to moisture and easy-to-handle without special precautions. These advantages have increased the popularity of organoborons day by day. In 1979, the palladium catalyzed cross-coupling reaction with derivatives of organoboronic acids known as the Suzuki reaction was published by Suzuki and Miyaura (Miyaura, Yamada, and Suzuki 1979). In a short interval, a variety of organoboron compounds began to be used on different types of coupling and substitution reactions over transition metals. Generally, the 1,3- selective substitution of propargylic compounds is performed to produce allenyl compounds (Moriya, Miyaura and A. 1994). And also in 2011, the palladium catalyzed S_N2''-selective reaction with boronic acids was first performed on 2-en-4-yne carbonate structures (Üçüncü et al. 2011).

Inspired of these information, in contrast to large number of reports about allylic alkylations, there are only a few allylic arylation reactions over the alkenyl compounds in the literature. In these works, the hard reaction conditions were required because the air sensitive compounds like grignard reagents and organozinc compounds were used as the nucleophile. Therefore, we performed palladium(0)- catalyzed 1,3-selective allylic

arylation reaction on vinyl oxiranes to provide arylated allyl alcohols under mild conditions.

CHAPTER 2

LITERATURE WORKS

2.1.Transition- Metal-Catalyzed Allylic Arylation Reaction of Allylic Compounds

The alkenyl compounds play an important role in organic synthesis. 1,3 Substitution reaction is a useful method for the formation of allylic reagents with a variety of functional groups. In literature, there are vast number of studies on highly efficient allylic alkylation reactions on vinyl compounds. But there are a few works about the allylic arylation reaction on alkenyl compounds and the regio selectivity of these reactions were not effectiveness.

In 1994, Bäckvall reported highly regio-selective Cu-catalyzed S_N2'-type arylation with Grignard reagents. In the absence of the catalyst the selectivity shifted in the favor of S_N2 pathway, the ratio of S_N2:S_N2' being 91:9 in this case (Figure 2.1).(Bäckvall, Persson, and Bombrun 1994)

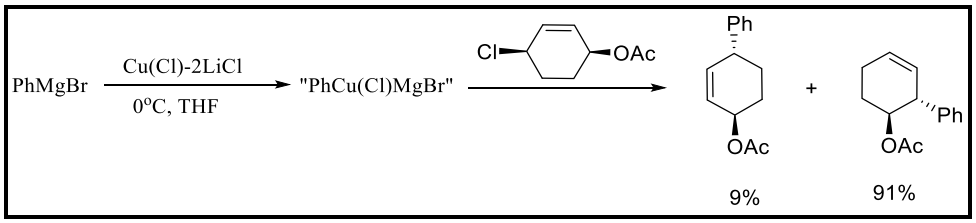


Figure 2.1.Cu(I)-catalyzed arylation reaction of an alkenyl chloride with a Grignard Reagent (Source: Bäckvall, Persson, and Bombrun 1994).

After this invention on cyclic alkenyl compounds, Kacprzynski reported the copper catalyzed arylation on silyl substituted alkenyl phosphorous esters with arylzinc reagents. To achieve the enantio- and regio-selective process, it was assisted from the use of N-heterocyclic carbine (NHC) ligands (Figure 2.2).(Kacprzynski et al. 2007)

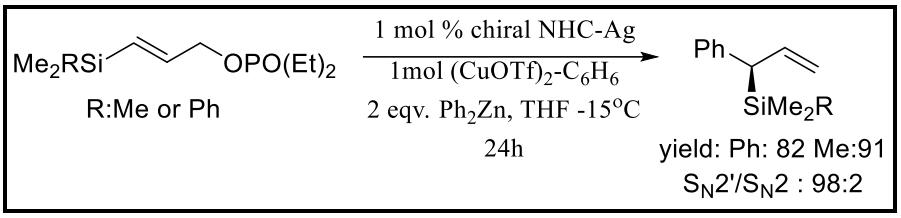


Figure 2.2.Copper-catalyzed arylation reaction of silyl substituted alkenyl phosphono esters (Source:Kacprzynski et al. 2007).

An assymmetric method on allylic arylation of non-cyclic allyl halide compounds were introduced by Selim (Selim, Yamada, and Tomioka 2008). This work shows that the copper-catalyzed stereo-selective arylation reaction can be applied the non-cyclic allyl compounds with moderate regioselectivities. Interestingly, however, all the improvements of the regio-selectivity always resulted in a reduced enantio-selectivity (Figure 2.3).

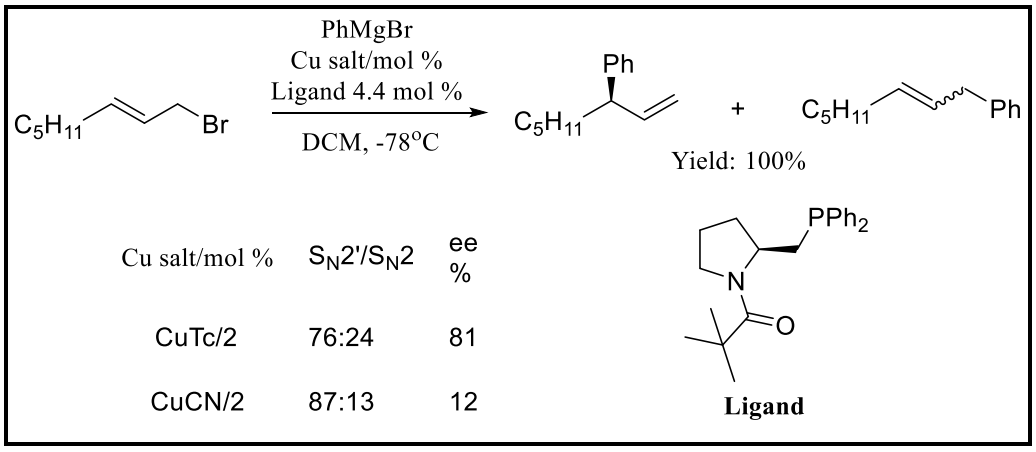


Figure 2.3.Copper catalyzed reaction of a non-cyclic allyl bromide with phenyl grignard reagent (Source:Selim, Yamada, and Tomioka 2008).

Selim also published another paper about stereo- and regio-selective reactions of phenyl substituted allyl compounds after 1 year. They achieved the asymmetric arylation with NHC based copper catalyst at high regio- and enantio-selectivities (Figure 2.4) (Selim et al. 2009).

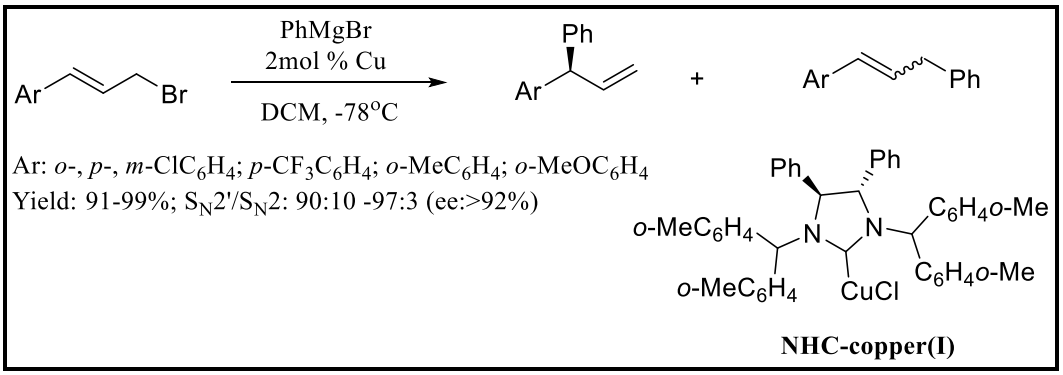


Figure 2.4. NHC-Copper(I) catalyzed reaction of phenyl substituted alkenyl compound (Source: Selim et al. 2009).

Enantio-selective iridium-catalyzed allylic arylation reaction was applied on the aryl substituted allyl compounds having a carbonate group as a leaving group by Polet (Polet et al. 2009). Though this method afforded the molecules in high ee percentages, the regio-selectivities were exceedingly poor (Figure 2.5).

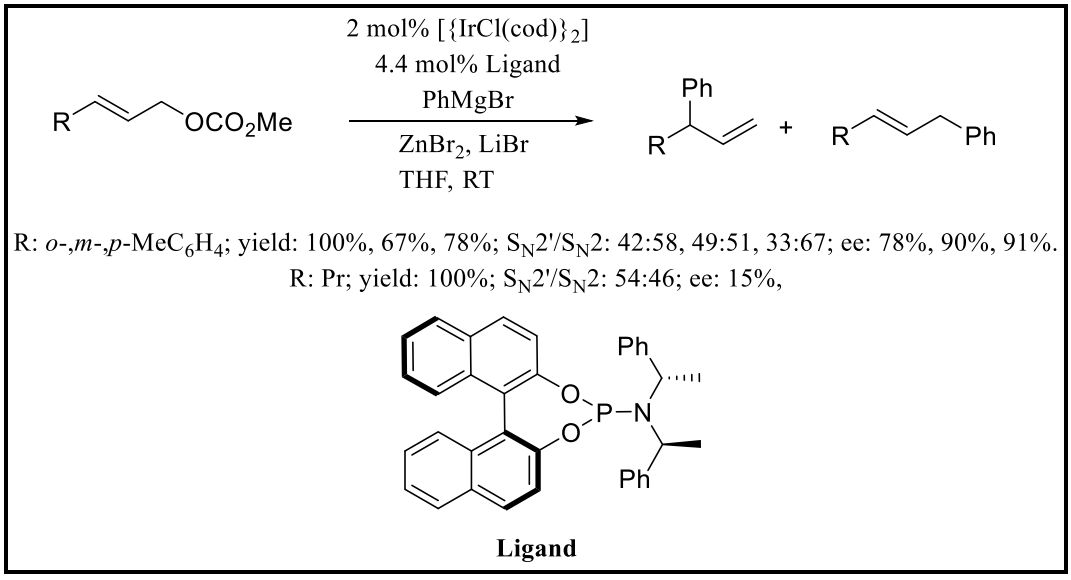


Figure 2.5.Iridium-catalyzed allylic arylation (Source: Polet et al. 2009).

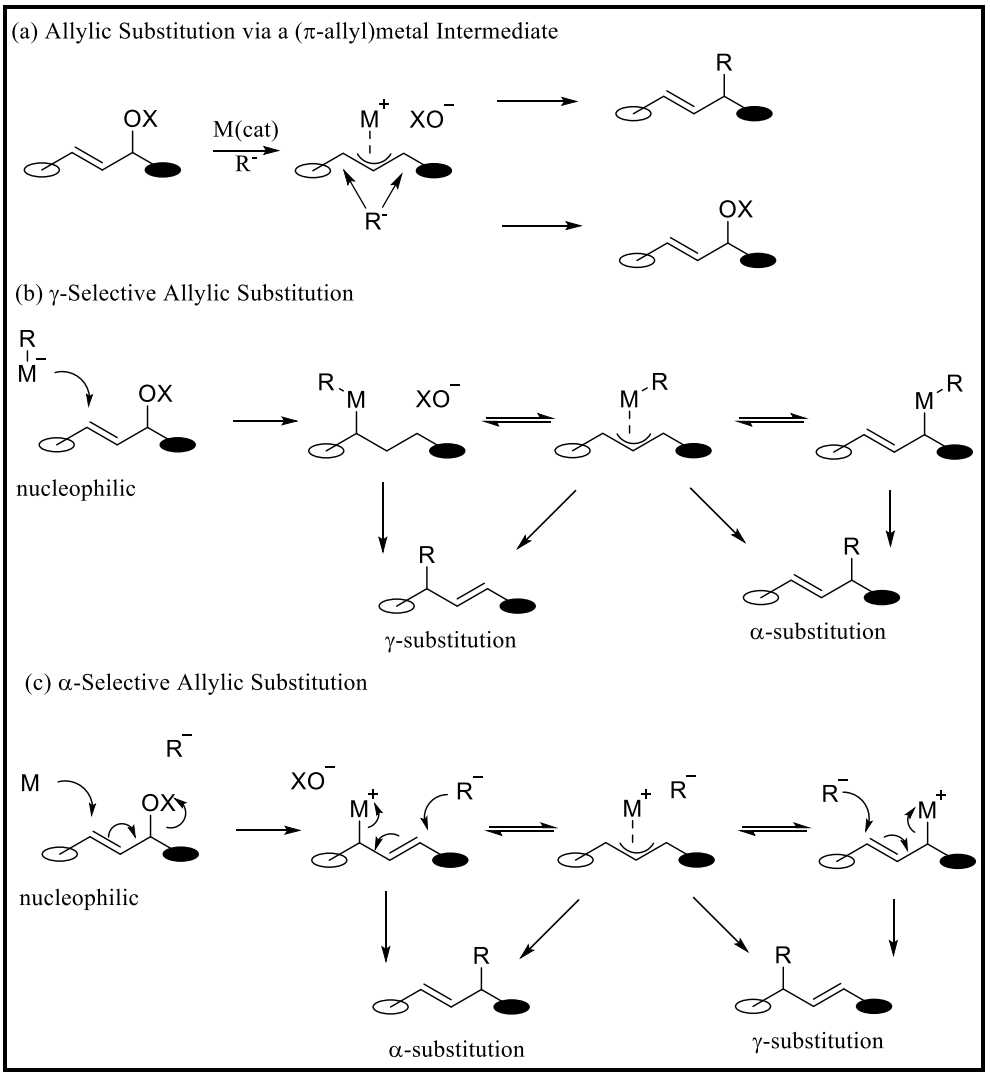


Figure 2.6.Metal-Mediated Allylic Substitution
(Source: Ohmiya, Yokokawa, and Sawamura 2010)

Before the Ohmiya paper, there is three type of metal-mediated allylic substitutions mechanisms (Figure 2.6). First one is the allylic substitution involving a (π-allyl) metal intermediate. However, in this mechanism, the regioselectivity is highly dependent on the electronic and/or steric substituent effects of compounds (Trost and Crawley 2003). In second example mechanism, the formal S_N2' attack of the organometallic nucleophile which are generally monoalkyl heterocuprate reagents produces a (σ-allyl) metal species via oxitative addition the result of the reductive elimination, the C-C bond at the γ-position was formed. But in some examples of these type mechanism, the significant S_N2 product was formed (Yoshikai, Zhang, and Nakamura 2008). In the last example, (σ-allyl) metal complexes was formed after strongly nucleophilic translation metal complex attacked the allylic substrates. The

complex underwent a second allylic displacement with a carbon nucleophile. After reductive elimination of metal complexes, the α or γ selective substitution products were occurred.

Hirohisa et al. reported Pd(II)-catalyzed arylation of allylic acetates with arylboronic acids in 2010 (Ohmiya et al. 2010). Their method was highly γ-selective (Figure 2.7), (Figure 2.8). They proposed a plausible mechanism to account for this high selectivity as is outlined in Figure 2.8., The reaction starts with the formation of cationic mono(acetoxo)-palladium(II) complex **A** which is the product of the 1,10-phenthroline-ligated $Pd(OAc)_2$ and $AgSbF_6$. The complex A involves with transmetallation with arylboronic acid to afford the complex B. In next step, B interact with the allylic acetate which is shown with C. Then, this interaction undergoes regio-selective C-C double bond insertion into the aryl-Pd bond (carbopalladation) in order to form a metallacyclic alkylpalladium (II) complex D. Finally, β-acetoxy elimination occur and the phenyl substituted product is formed. They also noted that the attempts to use a pinacolato ester instead of boronic acid resulted in no reaction.

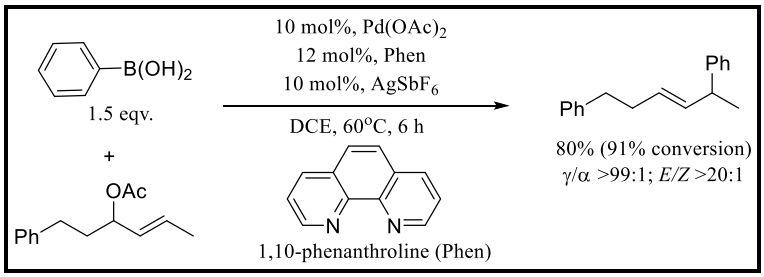


Figure 2.7.Palladium-catalyzed reaction of allylic acetates with arylboronic acids (Source: Ohmiya et al. 2010)

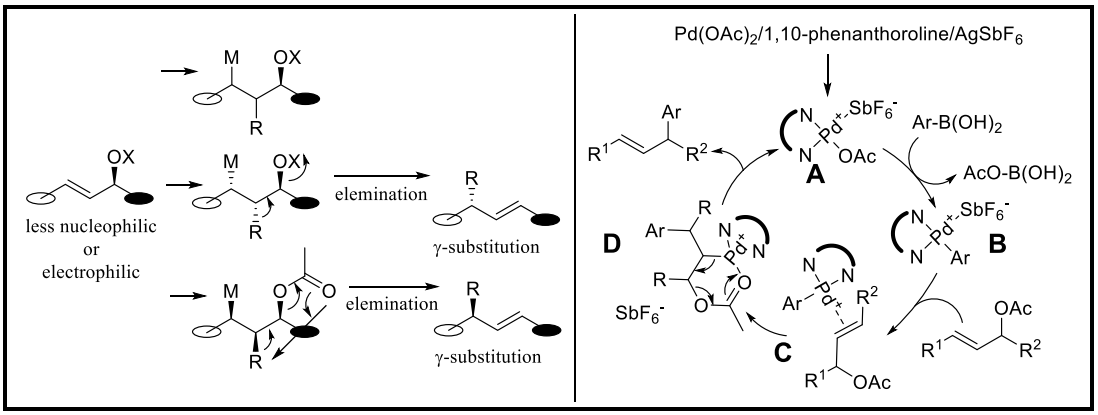


Figure 2.8.Scenarios for new type of γ-selective allylic substitution & proposed mechanism for the reaction (Source: Ohmiya et al. 2010)

In 2010, Whittaker report the copper-catalyzed 1,3-selective substitution of allylic chlorides with arylboronic esters (Whittaker, Rucker, and Lalic 2010). The use of aryl boronic acid pinacol ester in the copper(I)-catalyzed reaction provided higher regio-selectivity as compared to those used hard nucleophiles, such as phenylmagnesium halides and arylzinc compounds. This reaction was applied with NHC-ligand and the regio-selectivity was well up to 99% for 18 examples (Figure 2.9).

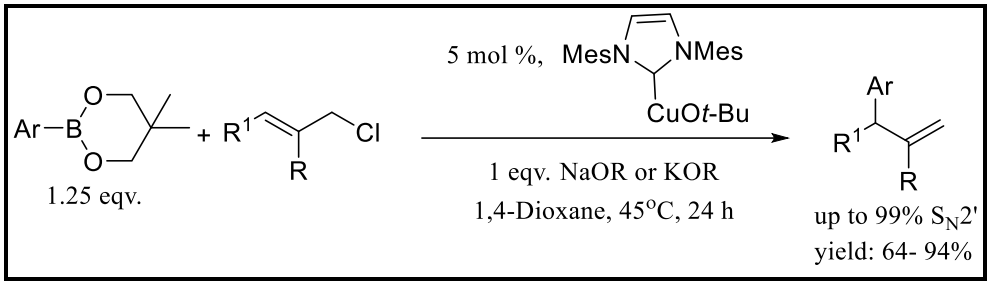


Figure 2.9.Copper catalyzed 1,3-selective substitution of allylic chlorides with aryl boronic esters (Source: Whittaker, Rucker, and Lalic 2010).

Allyl phosphono esters could be arylated with arylboronic esters over CuCl/asymmetric NHC ligand with excellent stereo- and region-selectivities (Figure 2.10) (Takeda et al. 2014).

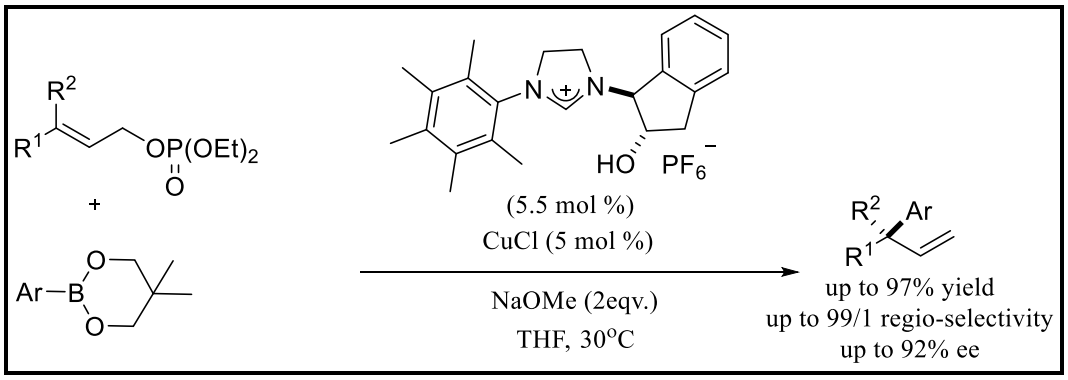


Figure 2.10.Copper-catalyzed asymmetric allylic substitution of allyl phosphates with aryl boronates (Source: Takeda et al. 2014).

2.2.Metal-Catalyzed Reactions of Vinyl Oxiranes with Grignard Reagents

In 2005, Ueki reported the reaction of *gem*-difluorianted vinyl oxiranes with mono alkylcopper reagents (Ueki et al. 2005). In this report, they tried catalytic reaction on the fluorinated vinyl oxiranes but only 43% of reactant was consumed and the regio selectivity of reaction was poor. On the other hand, the non-catalytic trial on this substrate provided good regio selectivity for the S_N2-product and yield (Figure 2.11). When they used the non-fluorinated compound, the regio selectivity of reaction changed to S_N2'-product.

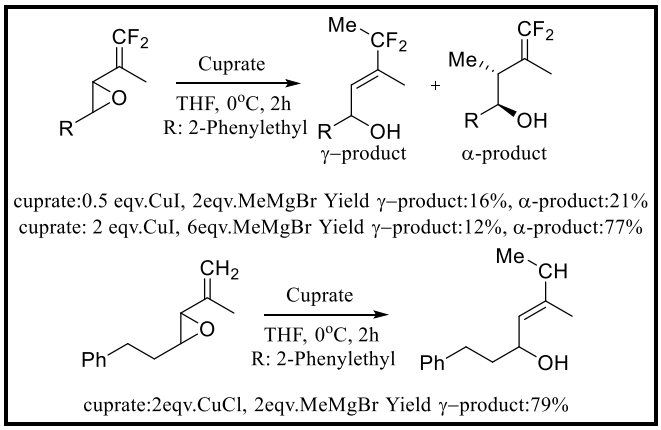


Figure 2.11.The Reaction of alkenyl oxiranes with grignard reagents
(Source: Ueki et al. 2005)

In 2007, the copper catalyzed kinetic resolution of 1,3-cyclohexadiene monoepoxide with grignard reagents leading to good yields, excellent regio selectivity and good enantiomeric excesses was published by Millet and Alexakis (Millet and Alexakis 2007). But this chiral ferrocenyl-based diphosphine ligand performance provided only 61% ee and moderate regio-selectivity for *i*-PrMgCl as used for derivative of secondary grignard reagents (Figure 2.12).

After one year, Millet and Alexakis was published another method for copper catalyzed the kinetic resolution of 1,3-cyclohexadiene monoepoxide with grignard reagents(Millet and Alexakis 2008). This method show that SimplePhos ligand is able to perform the kinetic resolution of racemic cyclic vinyloxirane with good regio- and stereo-selectivities and from low to good yields. And also this reaction condition increased the

stereo-selectivity of secondary grignard reagents like *i*-PrMgCl on the S_N2' product (Figure 2.13).

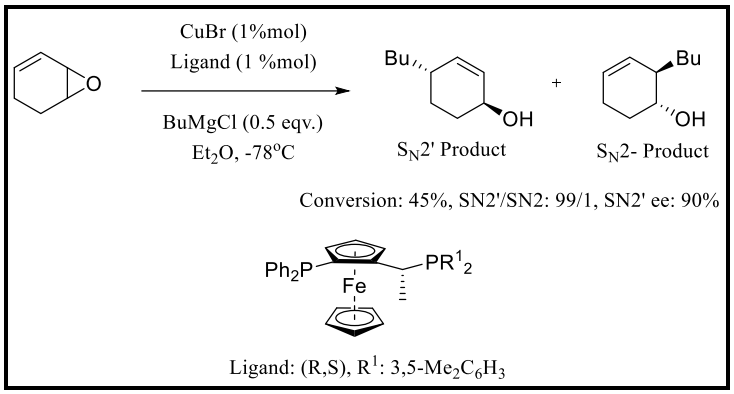
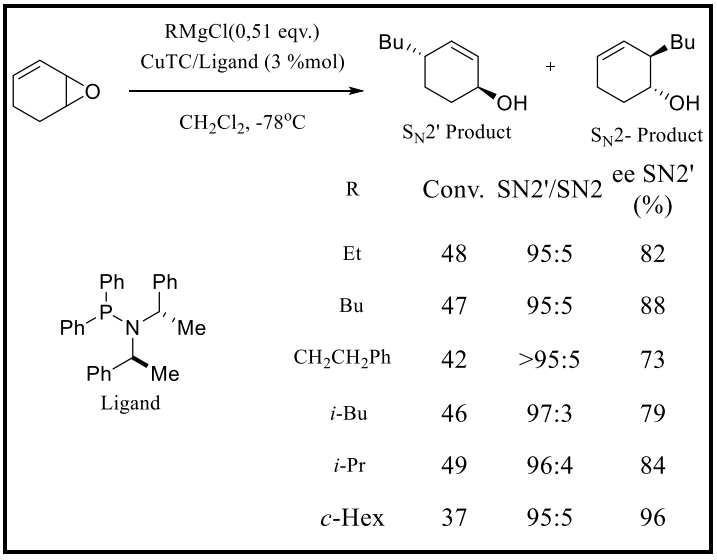


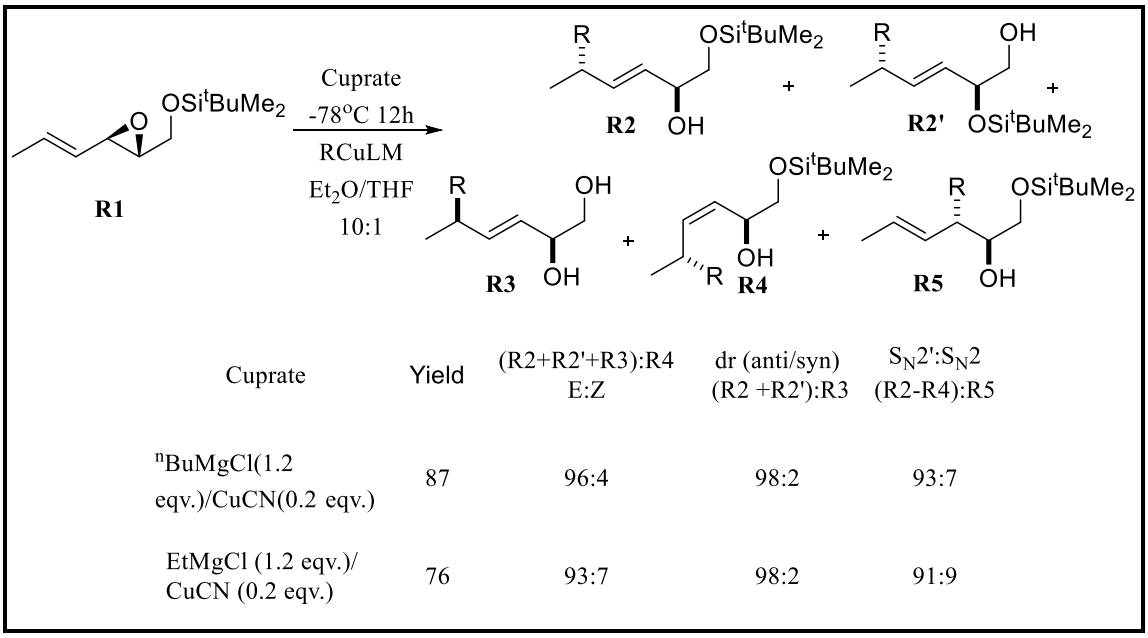
Figure 2.12.Copper catalyzed kinetic resolution of 1,3-Cyclohexadiene monoepoxide with grignard reagents (Source: Millet and Alexakis 2007)



R	Conv.	SN2'/SN2	ee SN2' (%)
Et	48	95:5	82
Bu	47	95:5	88
CH_2CH_2Ph	42	>95:5	73
i-Bu	46	97:3	79
i-Pr	49	96:4	84
c-Hex	37	95:5	96

Figure 2.13.SimplePhos as efficient ligand for the copper-catalyzed kinetic resolution of cyclic vinyloxiranes with grignard reagents (Source: Millet and Alexakis 2008)

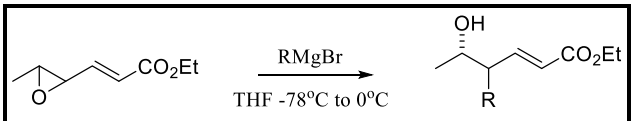
In 2012, Dieter published the copper catalyzed reaction of silyllated-vinyloxirane (Dieter, Huang, and Guo 2012). They showed that the cupper catalyzed reactions with alkyl grignard reagents were S_N2' product which were *E* isomers. These reactions also are highly stereo-selective (Figure 2.14).



Cuprate	Yield	(R2+R2'+R3):R4 E:Z	dr (anti/syn) (R2 +R2'):R3	$S_N2':S_N2$ (R2-R4):R5
^{n}BuMgCl(1.2 eqv.)/CuCN(0.2 eqv.)	87	96:4	98:2	93:7
EtMgCl (1.2 eqv.)/ CuCN (0.2 eqv.)	76	93:7	98:2	91:9

Figure 2.14.Copper-mediated reactions of trans-1-(tert-Butyldimethylsilyloxy)-2,3-epoxy-4-hexene (Source: Dieter, Huang, and Guo 2012)

In 2010, the iron-catalyzed regio selective reaction of γ,δ-epoxy-α,β-unsaturated esters with grignard reagents was published by Hata (Hata et al. 2010). Result of the reaction, only one regio isomer was occurred at good yield with alkyl grignard reagent and at moderate yield with phenyl grignard and methoxy substituted phenyl grignard reagent (Figure 2.15).



R	$FeCl_2$ (Mol%)	Yield %
Ph	12	60
o-$MeOC_6H$	10	57
Me	11	81

Figure 2.15The iron-catalyzed reaction of vinyl oxirane (Source: Hata et al. 2010)

2.3.Metal-Catalyzed Reactions of Vinyl Oxiranes with Organoborons

The regio-and stereo-selective substitution reactions of vinyl oxiranes can be a good strategy for the synthesis allyl alcohols.

In 2009, Tortosa reported that 1,4-diol compounds can be obtained via the copper-catalyzed successive borylation and oxidation reactions of vinyl oxiranes (Figure 2.16) (Tortosa 2011).

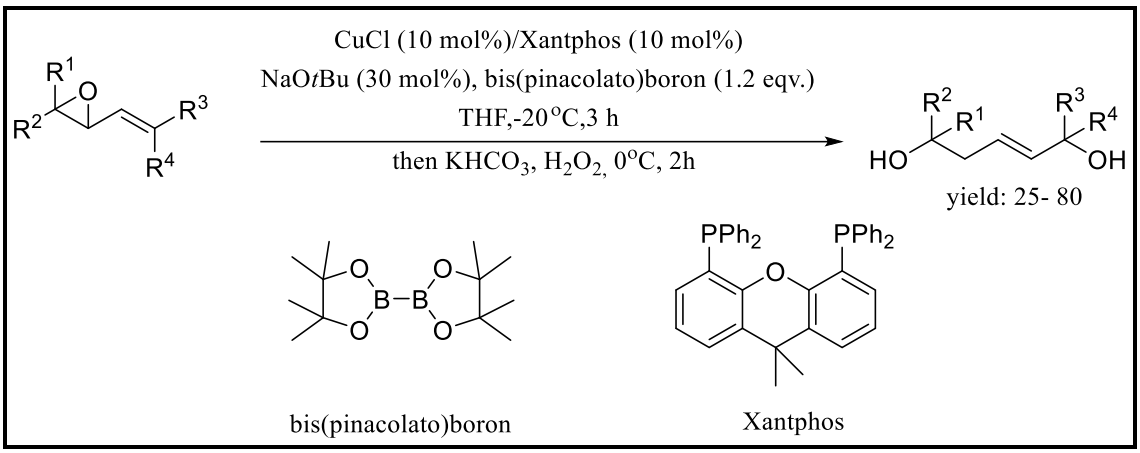


Figure 2.16.A Cu-catalyzed borylation and oxidation sequence leading to 1,4-diol compounds (Source: Tortosa 2011).

A Nickel-catalyzed borylative ring opening reaction of vinyl epoxides with was published by Crotti ref. Accordingly, a regio-selective borylative ring opening takes place catalytically (Figure 2.17) and this follows by addition onto an aldehyde to yield a diol compound.

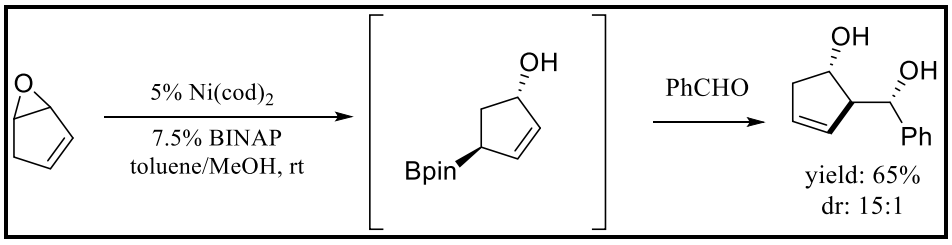
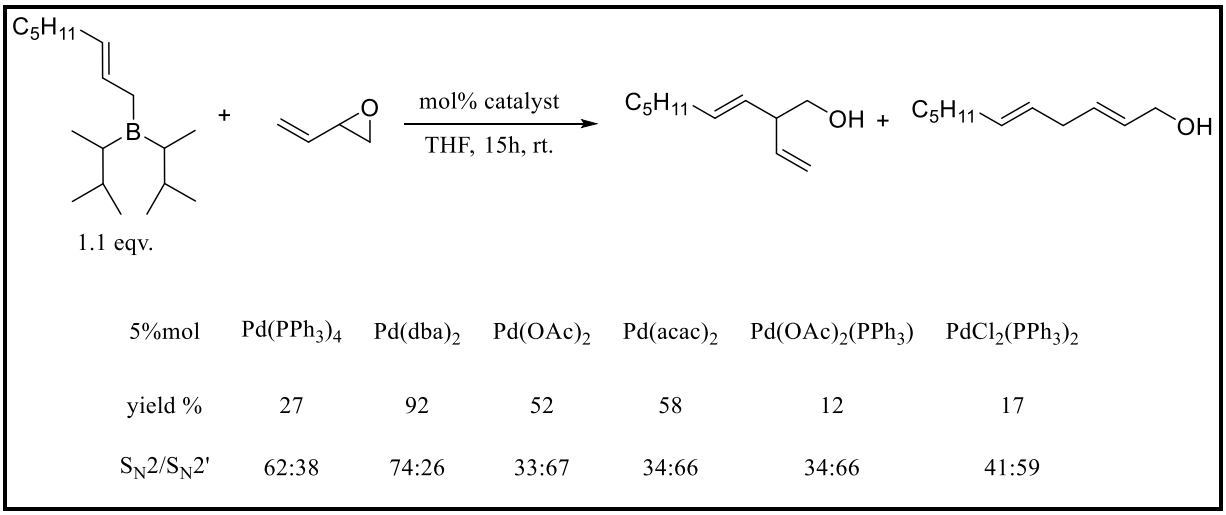


Figure 2.17. Nickel-catalyzed borylative ring opening reaction of vinyl epoxides (Source: Crotti et al. 2009)

The pd-catalyzed reaction of vinyl oxiranes with alkenylborons is reported in 1982 by Miyaura. In their studies 3,4-epoxy-1-butane was the only vinyl epoxide

compound that was tested and no sufficient regio-selectivity could be provided with this substrate (Figure 2.18).



5%mol	$Pd(PPh_3)_4$	$Pd(dba)_2$	$Pd(OAc)_2$	$Pd(acac)_2$	$Pd(OAc)_2(PPh_3)$	$PdCl_2(PPh_3)_2$
yield %	27	92	52	58	12	17
S_N2/S_N2'	62:38	74:26	33:67	34:66	34:66	41:59

Figure 2.18.Pd-catalyzed reaction of *(E)*-hexenylbis(1,2-dimethylpropyl) borane with 3,4-epoxy-1-butene (Miyaura, Tanebe and Suginome 1982).

A Pd-pincer complex-catalyzed method on alkenylation and arylation of terminal vinyl epoxides with organoborons was developed by Kjellgren. The linear allyl alcohols were produced with high regio-selectivity (Figure 2.19). But, when this method was applied on a cyclic structure epoxide, the regio-selectivity was decreased to 1,3-/1,2-ratio of 2:1 (Kjellgren et al. 2005).

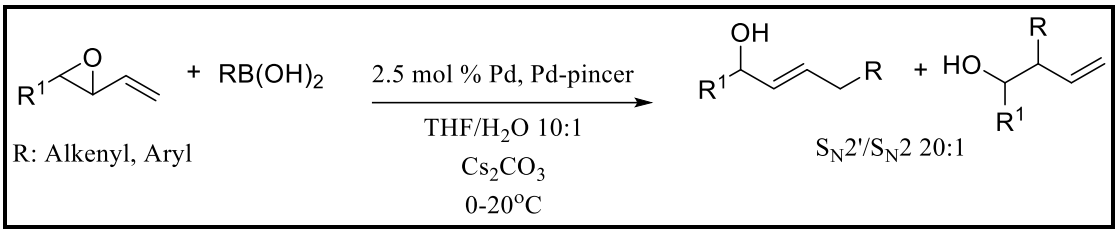


Figure 2.19.Pincer complex catalyzed cross-coupling reaction of vinyl epoxides with boronic acids (Source: Kjellgren et al. 2005).

CHAPTER 3

EXPERIMENTAL STUDY

3.4. General

Tetrahydrofuran (THF), diethyl ether (Et_2O) and 1,4 –dioxane solvents were distilled from benzophenone-ketyl under argon prior to use. Dichloromethane (DCM) and toluene were dried using molecular sieve 4A. Dimethylformamide (DMF) was purified by reflux over calcium hydride (5 w/v) under inert gas overnight and stored on molecular sieve 4A. Dimethoxyethane (DME) was dried by storing over the metallic sodium wire. Acetonitrile stirred with P_2O_5 **(5%** w/v) for 24h and then it was refluxed under inert gas overnight, then it was distillated.

The palladium complexes of $Pd_2(dba)_3{\cdot}CHCl_3$ (Ukai, et al. 1974), $Pd_2(dba)_3$ (Zalesskiy and Ananikov 2012), and $[PdCl(C_3H_5)]_2$ (Dent, Long and Wilkinson 1964) were synthesized in the laboratory.

3.5. Synthesis of Substrates

3.5.1. Synthesis of Vinyl Oxiranes

The syntheses of all compounds were performed under argon gas and the column chromatography purification of the synthesized compounds was applied on the silica gel 60 (35−70 μm).

Triethyl phosphonoacetate (4.8mL, 24 mmol) was added drop by drop to the solution of NaH (525 mg, 22 mmol) in 50 mL THF and the mixture was stirred for 1 hour at room temperature. After that, the reaction mixture was cooled to –78^{o}C and *trans*-aldehyde (~20 mmol) was added slowly and stirred for 1 hour. The reaction was terminated by the addition of saturated NH_4Cl and extracted with Et_2O. The organic layer

was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to obtain **S2**. The residue was used in following step without any further purification.

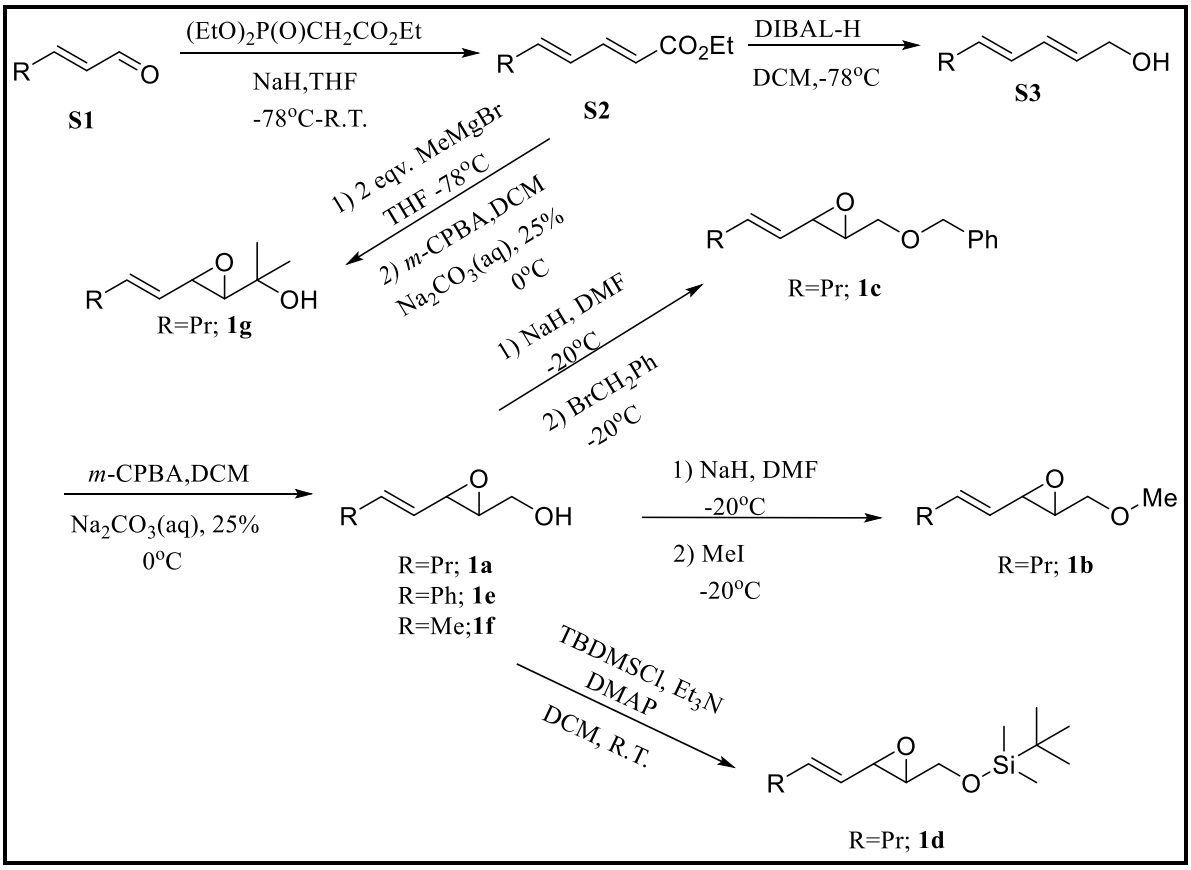


Figure 3.1. Synthesis of Alkenyl Oxiranes

At –78 °C, the DIBAL-H (~30 mmol, 1.0 M in DCM) solution was added dropwise to the solution of **S2** in DCM (80 mL). The reaction mixture was stirred for 3 hours and then the reaction was neutralized with 1 M HCl(aq) solution and extracted with DCM. The combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel 60 (hexane/ ethyl acetate as the eluent) gave the diene compounds **S3** (yield: R: Pr, 1.64 g, 65%; R, Ph, 1.92 g, 60%, R, Me, 1.08 g, 55%).

To a mixture of **S3** (~3 mmol) in DCM (50 mL) and 16 mL solution of Na_2CO_3 (25%) was added 5.1 mmol (880 mg) of *m*-CPBA dropwise at 0 °C under Argon. The mixture was controlled with TLC until the reactant was consumed completely. At the end of the process, the mixture was extracted with DCM, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was chromatographed on NEt_3-treated silica gel column (hexane/ ethyl acetate as the eluent)

which afforded the vinyl oxiranes (yield: **1a**, 234,2 mg, 55%; **1e**, 306,2 mg, 58%, **1f**, 110 mg 30%).

1mL of 2 M solution of vinyl epoxide alcohol (**1a** or **1b**) in DMF was added on the suspension of NaH (2.2 mmol) in DMF (1 mL) at -20 °C. The mixture was stirred until all NaH solids were dissolved before the addition of methyl iodide (2.4 mmol) or benzyl bromide (2.4 mmol). The mixture was stirred for 4 h at the same temperature, and then the reaction was terminated by the addition of MeOH (5 mL) and brine (5 mL) and extracted with DCM. The combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to column chromatography over NEt_3-treated silica gel column (eluent: hexane-EtOAc) to produce compound **1b** or **1c** or **1f** (yield, **1b**: 278 mg, 90% ,**1e**: 200 mg, 96%, **1c**: 334 mg, 77%).

A mixture of **1a** (285 mg, 2 mmol), Et_3N (0.36 mL, 2.6 mmol), *t*-butyldimethylsilyl chloride (400 mg, 2.6 mmol), and 4-dimethylaminopyridine (DMAP) (30 mg, 0.24 mmol) in DCM (30 mL) was stirred at room temperature for 1 h and then, the mixture was extracted with water and the water phase washed with DCM. The organic solution was dried with $MgSO_4$, filtered, and evaporated. The residue was chromatographed over NEt_3-treated silica gel column to afford silylated vinyl oxirane compound **1d** (hexane-EtOAc as an eluent, yield, **1d**: 500 mg, 97%).

At –78°C, the 3.5 mL of 3 M MeMgBr in THF was added drop by drop to 5 mmol of **S2** solution in 15 mL THF. After the addition, the reaction mixture was heated slowly to rt and then stirred for 30 min. The saturated NH_4Cl(aq) solution (10 mL) was added in the mixture and then extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was used in following step without any further purification. To the mixture of dienol obtained (∼5 mmol) in DCM (70 mL) and 25 mL solution of Na_2CO_3 (25%) was added 7 mmol (1.2 g) of *m*-CPBA dropwise at 0 °C under Argon. The mixture was controlled with TLC until the reactant was consumed completely. At the end of the process, the mixture was extracted with DCM, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was chromatographed on NEt_3-treated silica gel column (hexane/ ethyl acetate as the eluent) which afforded the vinyl oxirane (yield: 1g, 485 mg ,57%) (Kus and Artok 2015).

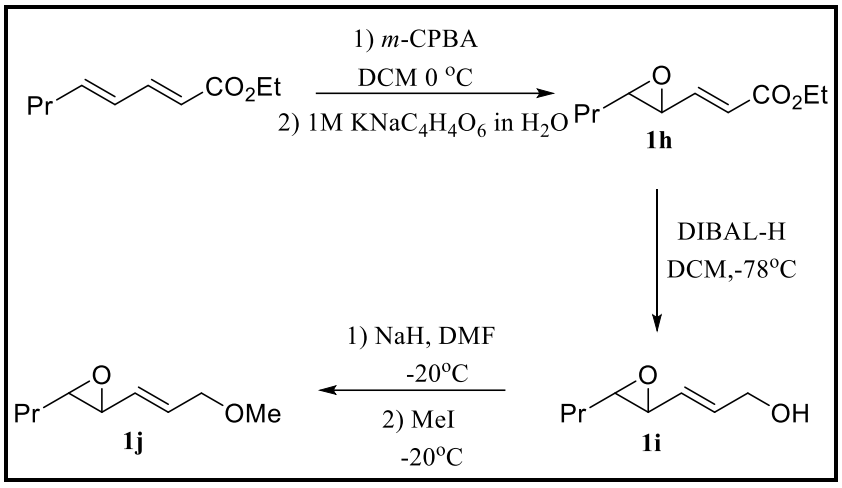


Figure 3.2 Epoxidation of ethyl (2*E*,4*E*)-octa-2,4-dienoate to synthesis **1h**

To the DCM solution (15 mL) of ethyl-(*2E,4E*)-octa-2,4-dienoate (840 mg, 5mmol) was added *m*-CPBA (1.7 g 6 mmol) in one portion at 0 °C and stirred for 2 h. The crude solution was extracted with a saturated solution of Na_2CO_3(aq) and DCM, successively, and dried with $MgSO_4$, filtered, and evaporated under reduced pressure. The substrate was purified using silica gel column (hexane-EtOAc as an eluent, yield, **1h**, 698 mg, 76%) (Dieter, Huang, and Guo 2012).

To a solution of **1j** (920 mg, 5 mmol) in DCM (9.0 mL), was added DIBAL-H (11.0 mL of a 1.0 M solution in DCM, 5.2 mmol) dropwise at-78 ºC and stirred for 30 min. Then, MeOH (4.5 mL) was added and the mixture was warmed to ambient temperature. Then, an aqueous sodium potassium tartrate (1.0 M) solution (Rochelle's salt, 15 mL) was added and the mixture was stirred at rt for 1 h. The aqueous phase was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to provide allylic alcohol **1i**. The substrate **1i** was purified using silica gel column (hexane-EtOAc as the eluent, yield, **1i**, 575 mg, 80%) (Tortosa 2011). The above-mentioned methylation process was applied for synthesis **1j** with the level of 90% yield.

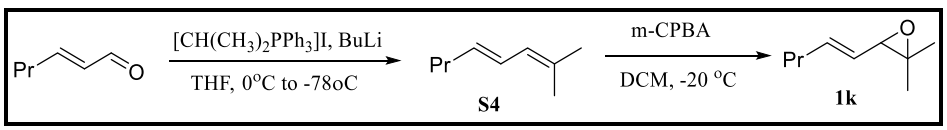


Figure 3.3 Synthesis of *(E)*-2,2-dimethyl-3-(pent-1-en-1-yl) oxirane **1k**

A hexane solution of BuLi (4.8 mL, 12 mmol, 2.5 M) was added dropwise to a solution of isopropyl(triphenyl)-phosphonium iodide (4.32 g, 10 mmol) in THF (30 mL) at 0 °C and stirred for further 1 h. The *trans*-2-hexenal (1.1 mL, 10 mmol) was added slowly in the mixture at -78 °C. The reaction mixture was stirred until α,β unsaturated aldehyde was consumed as judged by TLC. After that, the reaction was neutralized and extracted with saturated NH_4Cl solution and Et_2O, successively. The combined extracts were dried over $MgSO_4$, filtered, and separated from the solvent by reduced pressure at 0 °C. After purification over the silica gel column the pure dialkyl substituted diene compound **S4** was obtained (hexane-EtOAc as the eluent, yield, 920 mg, 74%).

To the suspension of *m*-CPBA (7.5 mmol) in 30 mL DCM was added drop by drop in to 0.1 M the diene compound (**S4**) solution in 50 mL DCM at -20 °C. After the solution was stirred for 2 h, the extraction process was applied with water and DCM. After that the organic layer was dried with $MgSO_4$, and concentrated under reduced pressure at 25 °C. Using silica gel column (hexane-EtOAc as the eluent), the pure vinyl oxirane **1k** was obtained The regio-selectivity of the oxirane (*(E)*-2,2-dimethyl-3-(pent-1-en-1-yl)oxirane/2-(2-methylprop-1-en-1-yl)-3-propyloxirane) was determined to be 9.6:1 (yield, **1k**: 365 mg 52%) (Kuş et al., 2015).

1,3-Cyclohexadiene (1mL, 10 mmol), 50mL DCM, and 16 mL 25% Na_2CO_3(aq) was added into a flask in sequence. After this mixture was cooled to 0 °C, 2 g *m*-CPBA was added and the reaction was controlled with help of TLC. After reactant was consumed, the solution was extracted with DCM, dried with $MgSO_4$, and filtered over a short silica gel column. The solvent was removed under reduced pressure at 0 °C and the cyclic epoxide **1l** was recovered in pure form (yield, 430 mg, 45%). (Ramesh, et al. 1992).

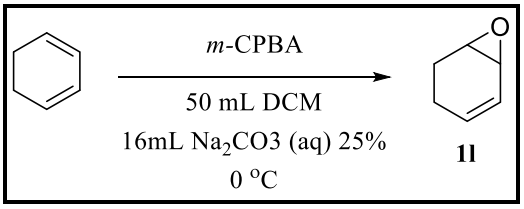


Figure 3.4 The synthesis of 3,4-epoxycyclohexene 1l.

To a solution of hex-1-yne (2.05 g, 25.0 mmol) in hexanes (15 mL) at 0 °C was added diisobutylaluminum hydride (1 M in DCM, 25 mL, 25.0 mmol). The solution was warmed to 40 °C and stirred for 16 h. Volatile components were then evaporated, and the

residue was dissolved in THF (50 mL) and cooled to 0 °C. CuCl (2.25 g, 27.5 mmol) was then added in portions over 10 min, and the suspension allowed to warm to room temperature and stir for 4 h. The black suspension was then poured onto a stirred mixture of H_2SO_4 (5%, 100 mL) and Et_2O (100 mL), the phases were separated, and the aqueous layer further extracted with Et_2O. The substrate (5E,7E)-dodeca-5,7-diene was purified using silica gel column (hexane as the eluent, yield 1,6 g, 79%)(Farthing and Koc 1998). After that, the epoxidation process was applied and the substrate **1m** was obtained.

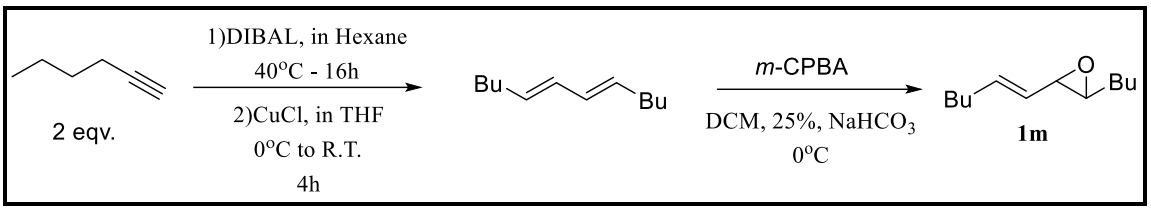


Figure 3.5The synthesis of (E)-2-butyl-3-(hex-1-en-1-yl)oxirane

3.5.2.Characterization of Alkenyl Oxiranes

The synthesized reactants were analyzed by GC-MS and the NMR spectra were recorded on a 400 MHz spectrometer.

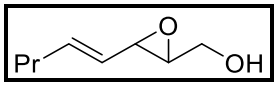


Figure 3.6. *(E)*-(3-(pent-1-en-1-yl) oxiran-2-yl) methanol

1a: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5,96 (td, J = 6,7, 15,5 Hz, 1H), 5,20 (tdd, J = 1,4, 8,3, 15,5 Hz, 1H), 3,94 (d, J = 12,5 Hz, 1H), 3,73–3,63 (m, 1H), 3,38 (dd, J = 2,3, 8,2 Hz, 1H), 3,08 (td, J = 2,3, 3,9 Hz, 1H), 2,06 (q, J = 6,7 Hz, 2H), 1,42 (sex, J = 7,4 Hz, 2H), 0,91 (t, J = 7,4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 137,7, 126,4, 61,3, 59,9, 55,9, 34,4, 22,0, 13,6. MS (EI, *m/z*): 111(22), 99(24), 83(78), 69(98), 55(100).

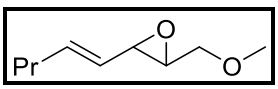


Figure 3.7. *(E)*-2-(methoxymethyl)-3-(pent-1-en-1-yl) oxirane

1b: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5,94 (td, J = 6,7, 15,5 Hz, 1H), 5,18 (dd, J = 8,2, 15,7 Hz, 1H), 3,66 (dd, J = 3,1, 11,3 Hz, 1H), 3,44–3,41 (m, 1H), 3,40 (s, 3H), 3,24 (dd, J = 2,0, 8,2 Hz, 1H), 3,05 (td, J = 2,7, 5,5 Hz, 1H), 2,05 (q, J = 7,0 Hz, 1H), 1,41 (sxt, J = 7,4 Hz, 2H), 0,91 (t, J = 7,4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ: 137,5, 126,7, 72,4, 59,2, 58,4, 56,1, 34,4, 22,0, 13,6. MS (EI, m/z): 123(4), 113(34), 83(24), 81(38), 71(40), 58(80), 45(100).

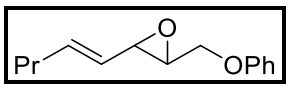


Figure 3.8. *(E)*-2-(pent-1-en-1-yl)-3-(phenoxymethyl) oxirane

1c: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7,40 – 7,26 (m, 5H), 5,93 (td, *J* = 6,9, 15,5 Hz, 1H), 5,17 (dd, *J* = 8,4, 15,5 Hz, 1H), 4,60 (d, J_{AB} = 11,7, Hz 1H), 4,56 (dd, J_{AB} = 11,7 Hz, 1H), 3,75 (dd, J_{AB} = 11,3 Hz, J_{AX} = 5,5 Hz, 1H), 3,51 (dd, J_{AB} = 11,3 Hz, J_{BX} = 3,1 Hz, 1H), 3,25 (dd, *J* = 2,3, 8,2 Hz, 1H), 3,10 (td, *J* = 2,6, 5.4 Hz, 1H), 2,04 (q, *J* = 6,7 Hz, 2H), 1,41 (sxt, *J* = 7,4 Hz, 2H), 0,90 (t, *J* = 7,2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 137,8, 137,6, 128,4, 127,8, 127,8, 126,7, 73,3, 70,0, 58,7, 56,2, 34,4, 22,0, 13,7. MS (EI, m/z) 232 (1>, M^+), 126 (11), 111(2), 107 (8), 91 (100), 83 (41), 68 (5), 65 (12), 55 (25), 41 (15).

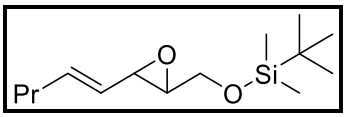


Figure 3.9. *(E)-tert*-butyldimethyl((3-(pent-1-en-1-yl) oxiran-2-yl) methoxy) silane

1d: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5,92 (td, *J* = 6,7, 15,5 Hz, 1H), 5,19 (tdd, *J* = 1,6, 8,3, 15,6 Hz, 1H), 3,85 (dd, J_{AB} = 11,9 Hz, J_{AX} = 4,5 Hz, 1H), 3,70 (dd, J_{AB} = 11,9 Hz, J_{BX} = 3,3 Hz, 1H), 2,99 (ddd, *J* = 1,6, 2,6, 3,6 Hz, 1H), 2,08 – 2,00 (m, *J* = 1,4, 8,0 Hz, 2H), 1,41 (sxt, *J* = 7,4 Hz, 2H), 0,89 (s, 9 H), 0,90 (t, *J* = 7,4 Hz, 3H), 0,07 (d, *J* = 3,1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 137,1, 126,9, 63,2, 60,3, 56,3, 34,4, 25,9, 22,1, 13,6, -5,3. MS (EI, m/z) 256 (1>, M+), 199 (24), 185 (2), 169 (8), 157 (9), 143 (23), 129 (13), 117 (14), 113 (22), 107 (16), 101 (33), 89 (18), 83 (22), 79 (15), 75 (99), 59 (38), 55 (100), 41 (33).

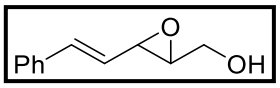


Figure 3.10. *(E)*-(3-styryloxiran-2-yl) methanol

1e: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7,42 – 7,36 (m, 2H), 7,35 – 7,30 (m, 2H), 7,29 – 7,26 (m, 1H), 6,81 (d, *J* = 16,0 Hz, 1H), 5,94 (dd, *J* = 8,0, 15,8 Hz, 1H), 4,06 – 3,97 (m, 1H), 3,81 – 3,70 (m, 1H), 3,60 (dd, *J* = 2,2, 8,0 Hz, 1H), 3,21 (td, *J* = 2,3, 3,9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 135,9, 135,0, 128,7, 128,2, 126,5, 125,7, 61,1, 60,4, 55,9. MS (EI, m/z) 176 (12, M+), 145 (22), 127 (16), 117 (100), 115 (60), 91 (31), 77 (10), 65 (12), 51 (12).

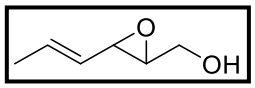


Figure 3.11. *(E)*-(3-(prop-1-en-1-yl) oxiran-2-yl) methanol

1f: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.96 (qd, *J* = 7.0, 14.9 Hz, 1 H), 5.22 (qdd, *J* = 1.6, 8.2, 15.3 Hz, 1 H), 3.93 (dd, *J* = 2.2, 12.7 Hz, 1 H), 3.66 (dd, *J* = 3.7, 12.7 Hz, 1 H), 3.37 (dd, *J* = 2.2, 8.4 Hz, 1 H), 3.09 - 3.04 (m, 1 H), 1.74 (td, *J* = 1.6, 6.7 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 132.5, 127.6, 61.3, 59.9, 55.8, 17.9.

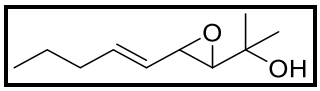


Figure 3.12.*(E)*-2-(3-(pent-1-en-1-yl) oxiran-2-yl) propan-2-ol

1g: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.90 (td, *J* = 7.1, 15.2 Hz, 1 H), 5.33 (ddd, *J* = 1.6, 7.8, 15.3 Hz, 1 H), 3.17 (d, *J* = 8.2 Hz, 1 H), 2.06 (q, *J* = 7.0 Hz, 2 H), 1.77 (d, *J* = 19.6 Hz, 1 H), 1.42 (qd, *J* = 7.4, 14.7 Hz, 2 H), 1.34 (s, 3 H), 1.28 (s, 3 H), 0.91 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 137.5, 125.2, 110.0, 64.4, 60.0, 34.6, 24.6, 22.2, 18.9, 13.6.

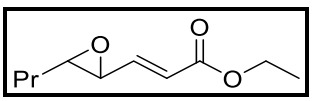


Figure 3.13. Ethyl *(E)*-3-(3-propyloxiran-2-yl) acrylate

1h: ^{1}H NMR (400 MHz , $CDCl_3$) δ = 6.68 (dd, *J* = 7.0, 15.7 Hz, 1 H), 6.12 (d, *J* = 15.7 Hz, 1 H), 4.20 (q, *J* = 7.0 Hz, 2 H), 3.20 (dd, *J* = 1.6, 7.0 Hz, 1 H), 2.89 (dt, *J* = 2.2, 5.6 Hz, 1 H), 1.68 - 1.38 (m, 4 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.00 - 0.94 (m, 3 H). 13C NMR (101MHz , $CDCl_3$) δ = 165.7, 144.8, 123.5, 61.3, 60.5, 56.3, 33.9, 19.1, 14.2, 13.8.

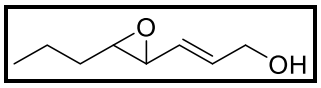


Figure 3.14.*(E)*-3-(3-propyloxiran-2-yl) prop-2-en-1-ol

1i: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.06 (td, *J* = 5.5, 15.7 Hz, 1 H), 5.48 (tdd, *J* = 1.9, 7.8, 15.5 Hz, 1 H), 4.17 (dd, *J* = 1.4, 5.3 Hz, 2 H), 3.12 (dd, *J* = 2.3, 7.8 Hz, 1 H), 2.84 (dt, *J* = 2.0, 5.5 Hz, 1 H), 1.63 - 1.41 (m, 4 H), 0.99-0.92 (m, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 133.9, 129.0, 62.7, 60.4, 57.9, 34.0, 19.2, 13.9.

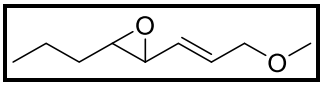


Figure 3.15. *(E)*-2-(3-methoxyprop-1-en-1-yl)-3-propyloxirane

1j: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.96 (td, *J* = 5.6, 15.8 Hz, 1 H), 5.47 (tdd, *J* = 1.4, 7.8, 15.6 Hz, 1 H), 3.93 (dd, *J* = 1.6, 5.9 Hz, 2 H), 3.34 (s, 3 H), 3.11 (dd, *J* = 2.3, 7.8 Hz, 1 H), 2.83 (dt, *J* = 2.3, 5.5 Hz, 1 H), 1.60 - 1.41 (m, 4 H), 0.95 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 131.2, 130.5, 72.1, 60.3, 58.1, 57.9, 34.0, 19.2, 13.9.

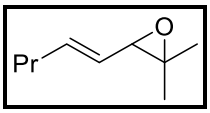


Figure 3.16. *(E)*-2,2-dimethyl-3-(pent-1-en-1-yl) oxirane

1k: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.90 (td, *J* = 7.0, 15.7 Hz, 1 H), 5.31 (dd, *J* = 7.8, 15.7 Hz, 1 H), 3.17 (d, *J* = 7.8 Hz, 1 H), 2.07 (q, *J* = 7.0 Hz, 2 H), 1.42 (sxt, *J* = 7.4 Hz, 2 H), 1.34 (s, 3 H), 1.28 (s, 3 H), 0.91 (t, *J* = 7.0 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 137.5, 125.2, 64.4, 60.0, 34.6, 24.6, 22.2, 18.9, 13.6.

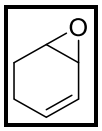


Figure 3.17. 7-Oxabicyclo [4.1.0] hept-2-ene

1l: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.07 - 5.81 (m, 2 H), 3.51 (td, *J* = 1.4, 2.7 Hz, 1 H), 3.24 (dt, *J* = 1.8, 4.0 Hz, 1 H), 2.31 - 2.17 (m, 1 H), 2.13 - 1.99 (m, 2 H), 1.68 - 1.57 (m, 1 H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 133.1, 123.1, 55.2, 47.1, 20.8, 20.6.

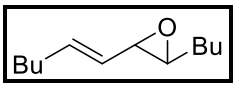
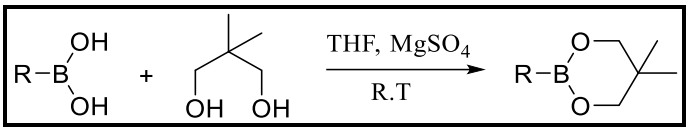


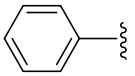
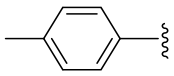
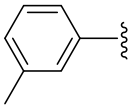
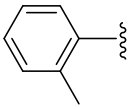
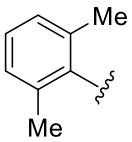
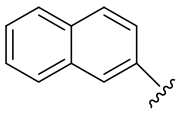
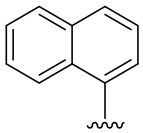
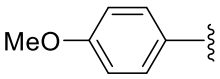
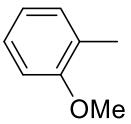
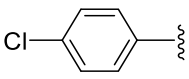
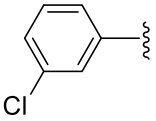
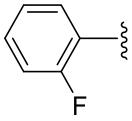
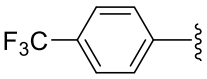
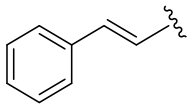
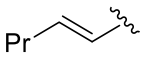
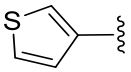
Figure 3.18(E)-2-butyl-3-(hex-1-en-1-yl)oxirane

1m: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.89 (td, *J* = 7.0, 14.5 Hz, 1 H), 5.16 (ddd, *J* = 1.2, 8.0, 15.5 Hz, 1 H), 3.05 (d, *J* = 8.2 Hz, 1 H), 2.80 (t, *J* = 5.5 Hz, 1 H), 2.05 (q, *J* = 6.9 Hz, 2 H), 1.59 - 1.23 (m, 10 H), 0.89 (q, *J* = 7.4 Hz, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.6, 127.5, 60.4, 58.8, 32.0, 31.7, 31.0, 28.0, 22.5, 22.2, 14.0, 13.9.

3.5.3.Synthesis of Organoborons

Table 3.1.Synthesis of neopentyl glycol esters



R (yield%)				
				
2a (91%)	**2b** (89%)	**2c** (85%)	**2d** (87%)	**2e** (71%)
				
2f (90%)	**2g** (82%)	**2h** (90%)	**2i** (92%)	**2j** (92%)
				
2k (87%)	**2l** (76%)	**2m** (75%)	**2n** (97%)	**2o** (90%)
				
		2p (80%)		

Under Ar gas and at rt, to the dry THF (15 mL) solution of organoboronic acid (10 mmol) was added $MgSO_4$ (14 mmol, 1.7 g). Then, 2,2 dimethyl propan-1,3-diol (11 mmol, 1.2 g) was added to the mixture and stirred overnight. The crude mixture was concentrated under reduced pressure and boronic acid neopentyl glycol ester derivative was purified on silica gel column (hexane-EtOAc as an eluent) (Matthew et al. 2014). The yields are given in Table 3.1.

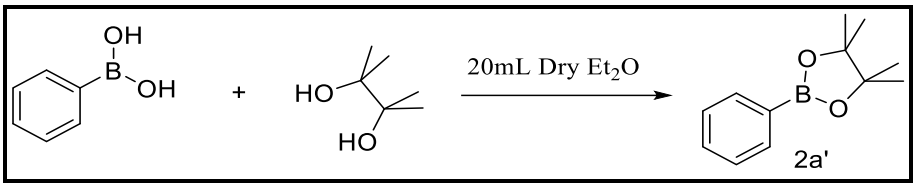


Figure 3.19. Synthesis of phenyl boronic acid pinacol ester

Phenylboronic acid (610 mg, 5 mmol) and 2,3-dimethyl-2,3-butandiol (590 mg, 5 mmol) in 20 mL of diethyl ether were stirred overnight at rt. The crude mixture was concentrated under reduced pressure and phenylboronic acid pinacol ester (2a') was obtained after chromatographed on silica gel column (hexane-EtOAc as an eluent). (Morandi, et al. 2005).

3.5.4.Characterization of Organoborons

The synthesized boronic acid ester derivatives were analyzed by NMR spectra recorded on a 400 MHz spectrometer.

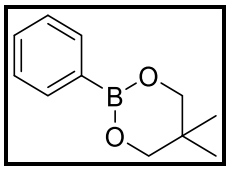


Figure 3.20. 5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane

2a: ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.80 (d, J = 7.0 Hz,2H),7.46-7.39 (m, 1H),7.38-7.32 (m, 2H),3.77 (d, J = 0.8 Hz, 4H),1.02 (s, 6H).

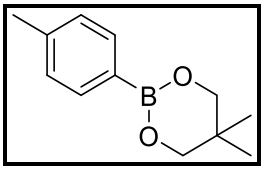


Figure 3.21. 5,5-Dimethyl-2-(p-tolyl)-1,3,2-dioxaborinane

2b: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 3.77 (s, 4H), 2.37 (s, 3H), 1.03 (s, 6H).

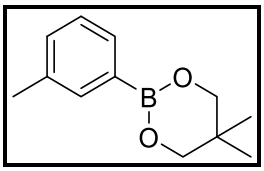


Figure 3.22. 5,5-Dimethyl-2-(o-tolyl)-1,3,2-dioxaborinane

2c: 1H NMR (400 MHz, CDCl3) δ: 7.24-7.62 (4H, m), 3.77 (4H, s), 2.35 (3H, s), 1.02 (6H, s),

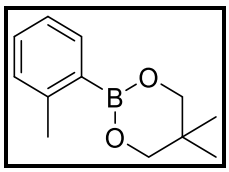


Figure 3.23. 5,5-Dimethyl-2-(m-tolyl)-1,3,2-dioxaborinane

2d: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 - 7.69 (m, 1 H), 7.31 - 7.25 (m, 1 H), 7.19 - 7.11 (m, 2 H), 3.78 (s, 4 H), 2.52 (s, 3 H), 1.04 (s, 6 H).

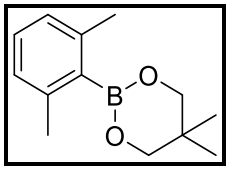


Figure 3.24. 2-(2,6-Dimethylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane

2e: ^{1}H NMR (400MHz, CDCl3) δ = 7.10 (t, *J* = 7.0 Hz, 1 H), 6.94 (d, *J* = 7.4 Hz, 2 H), 3.89 - 3.70 (m, 4 H), 2.39 (s, 6 H), 1.22 - 1.00 (m, 6 H).

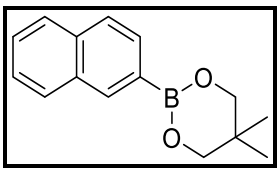


Figure 3.25. 5,5-Dimethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborinane

2f: ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.35 (s, 1 H), 7.80-7.89 (m, 4 H), 7.44-7.51 (m, 2 H), 3.84 (s, 4H), 1.06 (s, 6H).

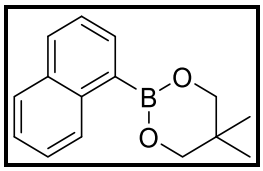


Figure 3.26. 5,5-Dimethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborinane

2g: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.0 (dd, J = 8.4, 1.2 Hz, 1H), 8.08 (dd, J = 6.9, 1.4 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.86 (dd, J = 8.1, 1.5 Hz, 1H), 7.59-7.42 (m, 3H), 3.91 (s, 4H), 1.11 (s, 6H).

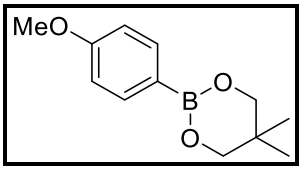


Figure 3.27. 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane

2h: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 4H), 1.02 (s, 6H).

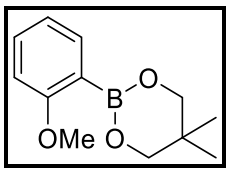


Figure 3.28. 2-(2-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane

2i: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 7.4 Hz, 1 H), 7.36 (t, J = 7.8 Hz, 1 H), 6.94 (t, J = 7.4 Hz, 1 H), 6.86 (d, J = 8.2 Hz, 1 H), 3.84 (s, 3 H), 3.79 (s, 4 H), 1.04 (s, 6 H).

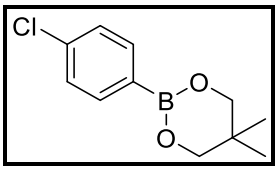


Figure 3.29. 2-(4-Chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane

2j: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 – 7.67 (m, 2 H), 7.35 – 7.29 (m, 2 H), 3.76 (s, 4H), 1.02 (s, 6H).

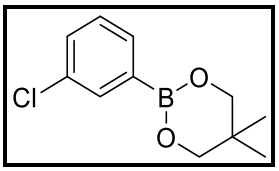


Figure 3.30. 2-(3-Chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane

2k: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.66 (d, 1H), 7.39 (m, 1H), 7.27 (t, 1H), 3.78 (s, 4H), 1.03 (s, 6H).

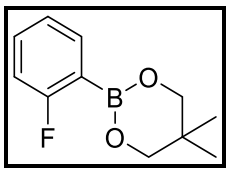


Figure 3.31. 2-(2-Fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane

2l: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 - 7.69 (m, 1 H), 7.43 - 7.35 (m, 1 H), 7.12 (t, *J* = 7.4 Hz, 1 H), 7.00 (t, *J* = 8.6 Hz, 1 H), 3.80 (s, 4 H), 1.12 - 0.99 (m, 6 H).

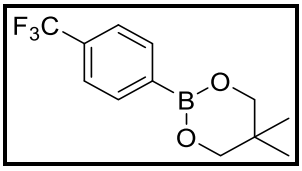


Figure 3.32. 5,5-Dimethyl-2-(4-(trifluoromethyl) phenyl)-1,3,2-dioxaborinane

2m: ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.91 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 3.79 (s, 4H), 1.03 (s, 6H).

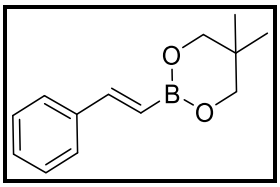


Figure 3.33. *(E)*-5,5-Dimethyl-2-styryl-1,3,2-dioxaborinane

2n: ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.48 (d, *J* = 7.2 Hz, 2H), 7.40-7.16 (m, 4H), 6.11 (d, *J* = 18.3 Hz, 1H), 3.69 (s, 4H), 1.00 (s, 6H).

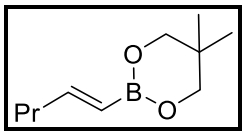


Figure 3.34. *(E)*-5,5-Dimethyl-2-(pent-1-en-1-yl)-1,3,2-dioxaborinane

2o: ^{1}H NMR (400MHz, $CDCl_3$) δ: 6.60 - 6.46 (m, 1 H), 5.34 (d, J = 17.6 Hz, 1 H), 3.63 (s, 4 H), 2.11 (dq, J = 1.6, 6.7 Hz, 2 H), 1.43 (sxt, J = 7.4 Hz, 2 H), 0.97 (s, 7 H), 0.90 (t, J = 7.2 Hz, 3 H).

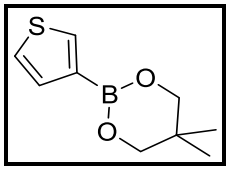


Figure 3.35. 5,5-Dimethyl-2-(thiophen-3-yl)-1,3,2-dioxaborinane

2p: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (dd, J = 2.6, 0.8 Hz, 1H), 7.38 (dd, J = 4.8, 0.9 Hz, 1H), 7.31 (dd, J = 4.8, 2.7 Hz, 1H), 3.75 (s, 4H), 1.02 (s, 6H).

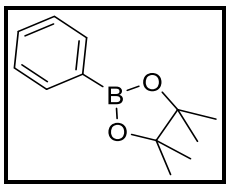


Figure 3.36. 4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane

2a': ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 – 7.86 (m, 2 H), 7.46 (tt, J = 7.40, 1,60 Hz, 1H) 7.37 (t. J = 7,80 Hz, 2H), 1.35 (s, 12H).

3.6.General Method for Palladium-Catalyzed Reactions of Vinyl Oxiranes

Successively, catalyst, ligand, and dry solvent (half of the volume necessary for the reaction) were added in to the schlenk flask which was dried in oven and cooled under Ar gas. The mixture was stirred for 30 min. at 25 ^{o}C. After that successively, organoboron, base, and the solution of epoxide compound in dry solvent (other half volume) and

prescribed amount of degassed water was added to the schlenk flask and the mixture was stirred in water or oil bath. The reaction was controlled with help of TLC. When the reaction process was judged to be complete, the mixture was concentrated under reduced pressure. It must be noted based on our experience that the color of the reaction solution usually turned from yellow to dark brown when the reaction cycle is halted. The residue was purified using silica gel on column chromatography and the alcohol product was obtained. In part of the optimization studies the crude was filtered through a short silica gel column (height 10 cm and width 2 cm), washed with Et_2O and evaporated under reduced atmosphere. The residue was analyzed by ^{1}H NMR using *p*-anisaldehyde as the internal standard.

The synthesized products were analyzed by GC and GC-MS. NMR spectra in $CDCl_3$ or C_6D_6 were recorded on a 400 MHz spectrometer.

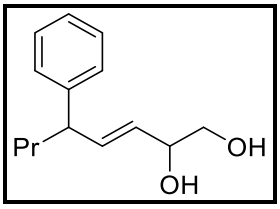


Figure 3.37. *(E)*-5-Phenyloct-3-ene-1,2-diol

3aa: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 –7.26 (m, 2H), 7.22–7.13 (m, 3H), 5.91 (dd, J = 7.8, 15.7 Hz, 1H), 5.46 (dd, J = 6.5, 15.7 Hz, 1H), 4.20 (dt, J = 3.5, 6.5 Hz, 1H), 3.61 (dd, J = 3.5, 11.3 Hz, 1H), 3.49 – 3.42 (m, 1H), 3.26 (q, J = 7.4 Hz, 1H), 2.16 (br, s, 2H), 1.68 (q, J = 7.4 Hz, 2H), 1.31–1.20 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.3, 137.6, 128.5, 127.8, 127.5, 126.2, 73.0, 66.5, 48.3, 37.9, 20.6, 14.0, ^{1}H NMR (400 MHz, C_6DC_6) δ: 7.20–7.16 (m, 2 H), 7.12–7.02 (m, 3 H), 5.81 (ddd, J = 1.4, 7.8, 15.5 Hz, 1H) (major), 5.78 (ddd, J = 1.4, 7.8, 15.5 Hz, 1H) (minor), 5.34 (ddd, J = 15.5, 6.6, 1.2 Hz, 1H) (major), 5.31 (ddd, J = 15.5, 6.6, 1.2 Hz, 1H) (minor), 3.99–3.93 (m, 1H), 3.36 (dd, J_{AB} = 11.2 Hz, J_{AX} = 7.7 Hz, 1H), 3.35 (dd, J_{AB} = 11.2 Hz, J_{BX} = 3.6 Hz, 1H), 3.11 (q, J = 8.6 Hz, 1H), 2.27–1.92 (m, 2H), 1.57 (q, J = 7.7 Hz, 2H), 1.25–1.14 (m, 2H), 0.83 (t, J=7.2 Hz, 3H), ^{13}C NMR (101 MHz, C_6D_6) δ: 144.5, 136.3, 128.4, 128.4, 127.5, 126.1, 72.7, 66.5, 48.4, 37.9, 20.6, 13.8, MS (EI, m/z): 220 (M^+, 1), 202 (2), 189 (56), 171 (23), 134 (12), 129 (57), 115 (33), 91 (100), 77 (8). FTIR (ν_{max}/cm^{-1}): 3398, 2925, 1724, 1601, 1453, 1343, 1030, 879, 700.

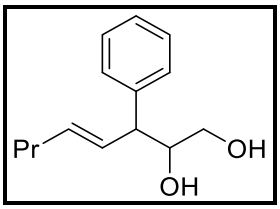


Figure 3.38. *(E)*-3-Phenyloct-4-ene-1,2-diol

4aa: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35–7.28 (m, 2 H), 7.25–7.18 (m, 3 H), 5.72 (dd, JAB = 15.3 Hz, JAX = 8.0 Hz, 1H), 5.66 (dd, JAB = 15.3 Hz, JBX = 5.9 Hz, 1H), 3.84 (ddd, J = 2.9, 5.9, 8.6 Hz, 1H), 3.52 (dd, J = 2.9, 11.5 Hz, 1H), 3.39–3.31 (m, 2H), 2.05 (q, J = 7.2 Hz, 2H), 1.40 (sex, J = 7.2 Hz, 2H), 0.89 (t, J = 7.2 Hz, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ: 134.8, 129.5, 128.8, 128.6, 127.8, 126.8, 74.3, 64.2, 52.7, 34.7, 22.4, 13.7, ^{1}H NMR (400 MHz, C_6DC_6) δ: 7.15–6.94 (m, 5H), 5.68 (dd, J = 8.6, 15.5 Hz, 1H), 5.42 (td, J = 6.7, 15.5 Hz, 1H), 3.68 (ddd, J = 3.1, 6.7, 7.9 Hz, 1H), 3.40 (dd, J = 3.1, 11.3 Hz, 1H), 3.28 (dd, J = 6.5, 11.3 Hz, 2H), 1.85 (q, J = 7.2 Hz, 2H), 1.22 (sex, J = 7.2 Hz, 2H), 0.79 (t, J = 7.2 Hz, 3H), 13C NMR (101 MHz, C_6D_6) δ: 141.8, 133.4, 130.1, 128.5, 128.0, 126.4, 74.4, 64.3, 52.4, 34.6, 22.4, 13.4, MS (EI, m/z): 220 (M+, 29), 205 (100), 145 (11), 105 (9), 91 (5). FTIR (ν_{max}/cm^{-1}): 3393, 2925, 1724, 1601, 1453, 1343, 1030, 879, 700.

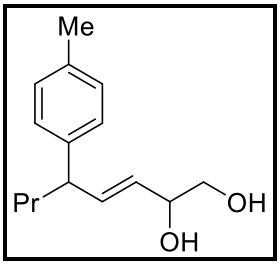


Figure 3.39. *(E)*-5-(*p*-Tolyl) oct-3-ene-1,2-diol

3ab: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 – 7.08 (m, 2H), 7.08 – 7.02 (m, 2H), 5.89 (ddd, *J* = 1.2, 7.8, 15.7 Hz, 1H), 5.43 (ddd, *J* = 1.0, 6.4, 15.4 Hz, 1H), 4.22 – 4.13 (m, 1H), 3.58 (dd, J_{AB} = 11.3 Hz, J_{AX} = 7.5 Hz, 1H), 3.43 (dd, J_{AB} = 11.3 Hz, J_{BX} = 3.5 Hz, 1H), 3.22 (q, *J* = 7.4 Hz, 1H), 2.60 (br, s., 2H), 2.32 (s, 3H), 1.66 (q, *J* = 7.7 Hz, 2H), 1.35 – 1.18 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.3, 137.7, 135.7, 129.2, 127.6, 127.4, 73.0, 66.5, 47.9, 37.9, 21.0, 20.7, 14.0, ^{1}H NMR (400 MHz, C_6DC_6) δ = 7.09 – 6.98 (m, 4H), 5.91 (ddd, *J* = 1.2, 7.7, 15.4 Hz, 1H), 5.43 (ddd,

J = 1.2, 6.0, 15.6 Hz, 1H), 4.19 – 4.09 (m, 1H), 3.54 – 3.31 (br, s., 2H), 3.48 (dd, J_{AB} = 11.1 Hz, J_{AX} = 8.1 Hz, 1H), 3.39 (dd, J_{AB} = 11.1 Hz, J_{BX} = 2.8 Hz, 1H), 3.17 (q, *J* = 7.4 Hz, 1H), 2.15 (s, 3H), 1.64 (q, *J* = 7.6 Hz, 2H), 1.34 – 1.16 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H), ^{13}C NMR (101 MHz, C_6D_6) δ = 141.5, 136.7, 135.2, 1291., 128.1, 127.5, 72.9, 66.7, 48.0, 38.1, 20.7, 20.6, 13.9, MS (EI, m/z) 234 (4, M^+), 204 (3), 185 (39), 160 (5), 147 (14), 143 (100), 131 (38), 105 (98), 91 (25), 77 (10), 55 (15), 41 (18). FTIR (ν_{max}/cm^{-1}): 3362, 2924, 2870 1513, 1457, 1378, 1075, 1021, 971, 874, 812, 721.

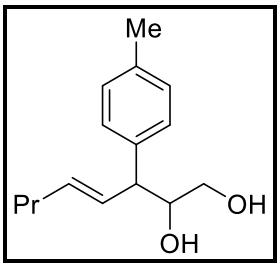


Figure 3.40. *(E)*-3-(*p*-Tolyl) oct-4-ene-1,2-diol

4ab: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 - 7.05 (m, 4 H), 5.75 - 5.60 (m, 2 H), 3.81 (ddd, J = 3.1, 6.1, 8.8 Hz, 1 H), 3.50 (d, J = 3.1 Hz, 1 H), 3.36 (dd, J = 6.3, 11.3 Hz, 1 H), 3.30 (t, J = 8.2 Hz, 1 H), 2.32 (s, 3 H), 2.07 - 2.00 (m, 2 H), 1.65 - 1.51 (m, 2 H), 1.40 (qd, J = 7.1, 14.6 Hz, 2 H), 0.88 (t, J = 7.4 Hz, 3 H), MS (EI, m/z) 234 (1>, M^+), 174(45), 143 (6), 131 (100), 118 (14), 91 (23), 77 (58), 61 (79), 43 (58). FTIR (ν_{max}/cm^{-1}): 3385, 2924, 2856, 1514, 1457, 1378, 1261, 1075, 1022, 878, 721.

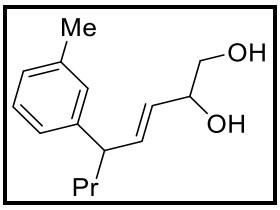


Figure 3.41.*(E)*-5-(*m*-Tolyl) oct-3-ene-1,2-diol

3ac: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (t, *J* = 8.6 Hz, 1H), 7.03 - 6.90 (m, 3 H), 5.88 (ddd, *J* = 1.2, 8.0, 15.5 Hz, 1H), 5.43 (ddd, *J* = 1.0, 6.3, 15.5 Hz, 1 H), 4.22 - 4.11 (m, 1 H), 3.57 (dd, *J* = 3.3, 11.2 Hz, 1H), 3.41 (dd, *J* = 7.6, 11.2 Hz, 1 H), 3.20 (q, *J* = 7.4 Hz, 1 H), 2.67 (br. s., 2H), 2.32 (s, 3H), 1.65 (q, *J* = 7.6 Hz, 2H), 1.31 - 1.20 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.4, 138.0, 137.6, 128.3,

128.3, 127.7, 126.9, 124.5, 73.0, 66.5, 48.3, 38.0, 21.5, 20.7, 14.0. ^{1}H NMR (400MHz , C_6D_6) δ = 7.14 - 7.11 (m, 2 H), 7.05 - 7.02 (m, 2 H), 5.74 (ddd, *J* = 1.6, 7.6, 15.5 Hz, 1 H), 5.29 (ddd, *J* = 1.2, 5.9, 15.7 Hz, 1 H), 3.96 - 3.90 (m, 1 H), 3.40 (q, *J* = 7.4 Hz, 1 H), 3.32 (dd, J_{AB} = 11.0 Hz, J_{AX} = 7.9 Hz, 1H), 3.21 (dd, J_{AB} = 11.0 Hz, J_{BX} = 3.5 Hz, 1H), 2.24 (s, 3H) (Minor) 2.17 (s, 3 H) (Major), 1.94 (br. s, 2 H), 1.59 (q, *J* = 7.7 Hz, 2 H), 1.28 - 1.13 (m, 2 H), 0.83 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (101MHz, C_6D_6) δ = 142.4, 135.9, 130.3, 128.4, 126.4, 126.3, 125.9, 72.7, 66.5, 43.4, 37.5, 20.6, 19.4, 13.9.), MS (EI, m/z) 234 (2, M^+), 216(1), 203(44), 185(63), 173(5), 143 (100), 131 (40), 105 (95), 91 (29), 77 (10), 55 (10), 41 (10). FTIR (ν_{max}/cm^{-1}): 3368, 2925, 2870, 1606, 1458, 1378, 1075, 1030, 971, 876, 704.

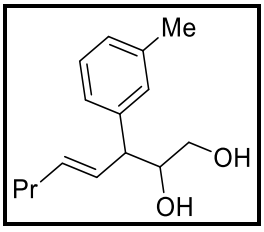


Figure 3.42. *(E)*-3-(*m*-Tolyl) oct-4-ene-1,2-diol

4ac: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 - 7.17 (m, 1 H), 7.08 - 6.95 (m, 3 H), 5.78 - 5.60 (m, 2 H), 3.83 (ddd, *J* = 2.9, 6.1, 8.6 Hz, 1 H), 3.52 (dd, *J* = 3.1, 11.3 Hz, 1 H), 3.36 (dd, *J* = 6.3, 11.3 Hz, 1 H), 3.29 (t, *J* = 8.4 Hz, 1 H), 2.33 (s, 3 H), 2.23 (br. s., 0 H), 2.04 (q, *J* = 5.9 Hz, 2 H), 1.94 (br. s., 1 H), 1.41 (sxt, *J* = 7.8 Hz, 2 H), 0.89 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.0, 134.7, 129.6, 128.6, 128.5, 127.5, 124.8, 74.3, 64.2, 52.7, 34.7, 29.7, 22.4, 21.5, 13.7. MS (EI, m/z) 216(<1), 203(46), 159(7), 145(7), 115 (14), 105 (22), 91 (15), 77 (6), 55 (4), 43 (4). FTIR (ν_{max}/cm^{-1}): 3385, 2923, 2854, 1606, 1460, 1378, 1076, 1038, 970, 877, 783, 705.

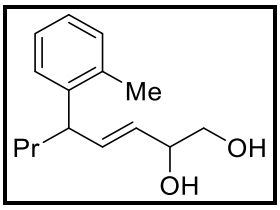


Figure 3.43. *(E)*-5-(*o*-Tolyl) oct-3-ene-1,2-diol

3ad: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 – 7.06 (m, 4H), 5.86 (ddd, *J* = 1.2, 7.5, 15.6 Hz, 1H), 5.42 (ddd, *J* = 1.2, 6.5, 15.5 Hz, 1H), 4.23 – 4.16 (m, 1H), 3.60 (dd, J_{AB} = 11.2 Hz, J_{AX} = 7.5 Hz, 1H), 3.52 (q, *J* = 7.6 Hz, 1H), 3.45 (dd, J_{AB} = 11.2 Hz, J_{BX} = 3.5 Hz, 1H), 2.31 (s, 3H), 1.76 – 1.59 (m, 2H), 1.40 – 1.16 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.2, 137.2, 135.7, 130.4, 127.8, 126.3, 126.2, 125.9, 73.0, 66.5, 43.3, 37.5, 20.7, 19.6, 14.1, ^{1}H NMR (400 MHz, C_6D_6) δ = 7.18 – 7.07 (m, 2H), 7.06 – 6.98 (m, 2H), 5.80 (ddd, *J* = 1.6, 7.6, 15.5 Hz, 1H), 5.34 (ddd, *J* = 1.2, 6.1, 15.5 Hz, 1H), 4.08 – 4.01 (m, 2H), 3.43 (q, *J* = 7.0, 1H), 3.41 (dd, J_{AB} = 13.4 Hz, J_{AX} = 6.9 Hz, 1H), 3.31 (dd, J_{AB} = 13.4 Hz, J_{AX} = 4.4 Hz, 1H), 2.92 (br, s, 2H), 2.18 (s, 3H), 1.61 (q, *J* = 7.6 Hz, 2H), 1.30 – 1.18 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, C_6D_6) δ = 142.5, 136.0, 135.6, 130.4, 128.4, 126.5, 126.4, 125.9, 72.9, 66.7, 43.5, 37.6, 20.7, 19.5, 14.0, MS (EI, m/z) 234 (4, M+), 203 (45), 191 (8), 185 (66), 143 (100), 173 (4), 147 (13), 143 (100), 105 (90), 91 (32), 77 (10), 55 (10), 41 (10). FTIR (ν_{max}/cm^{-1}): 3364, 2926, 2870, 1460, 1378, 1074, 972, 874, 756, 726.

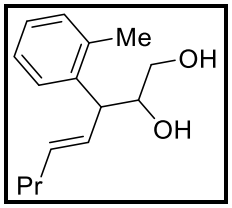


Figure 3.44. *(E)*-3-(*o*-Tolyl) oct-4-ene-1,2-diol

4ad: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 - 7.08 (m, 4H), 5.70 - 5.58 (m, 2H), 3.96 - 3.85 (m, 1H), 3.64 - 3.58 (m, 1 H), 3.55 (d, *J* = 11.0 Hz, 1 H), 3.38 - 3.27 (m, 1H), 2.34 (s, 3 H), 2.08 - 1.99 (m, 2H), 1.39 (sxt, *J* = 7.3 Hz, 2 H), 0.88 (t, *J* = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.4, 135.9, 134.8, 130.7, 129.8, 126.7, 126.3, 126.3, 74.1, 64.0, 47.6, 34.6, 22.4, 19.8, 13.7, MS (EI, m/z) 234 (1>, M+), 174 (47), 159 (5), 145 (6), 131 (100), 119 (11), 115 (13), 105 (22), 91 (17), 77 (5), 65 (2), 55 (3), 43 (3). FTIR (ν_{max}/cm^{-1}): 3364, 2922, 2853, 1660, 1463, 1377, 969, 755, 724.

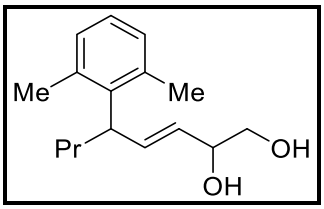


Figure 3.45. *(E)*-5-(2,6-Dimethylphenyl) oct-3-ene-1,2-diol

3ae: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.04 - 6.92 (m, 3H), 6.06 (dd, *J* = 5.1, 15.7 Hz, 1H), 5.35 (ddd, *J* = 2.0, 6.6, 15.7 Hz, 1H), 4.22 (dt, *J* = 3.7, 6.9 Hz, 1 H), 3.85 (q, *J* = 7.4 Hz, 1H), 3.61 (dd, *J* = 3.5, 11.3 Hz, 1H), 3.45 (dd, *J* = 7.6, 11.2 Hz, 1 H), 2.35 - 2.26 (m, 6H), 1.88 - 1.73 (m, 2H), 1.33 (s, 1 H), 1.24 - 1.12 (m, 1H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{1}H NMR (400MHz ,C_6D_6) δ = 7.03 - 6.91 (m, 3 H), 5.91 (ddd, *J* = 1.4, 5.1, 15.8 Hz, 1 H), 5.25 (ddd, *J* = 2.0, 6.2, 15.7 Hz, 1 H), 3.97 - 3.88 (m, 1 H), 3.75 (q, *J* = 6.3 Hz, 1 H), 3.29 (dd, *J* = 3.5, 11.0 Hz, 1 H), 3.16 (dd, *J* = 7.6, 10.8 Hz, 1 H), 2.22 (s, 6 H), 1.69 (q, *J* = 7.8 Hz, 3 H), 1.27 - 1.07 (m, 2 H), 0.81 (t, *J* = 7.4 Hz, 3 H). MS (EI, m/z) 248 (4, M+), 247 (5), 220 (28), 205 (70), 177 (26), 170 (18), 161 (17),.133 (32), 105 (26), 91 (18), 57 (92), 41 (100). FTIR (ν_{max}/cm^{-1}): 3368, 2923, 2854, 1465, 1378, 1075, 973, 874, 767.

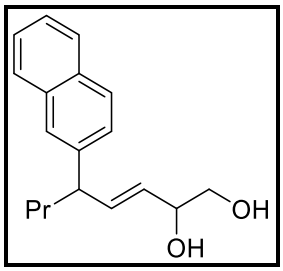


Figure 3.46. *(E)*-5-(Naphthalen-2-yl) oct-3-ene-1,2-diol

3af: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 – 7.74 (m, 3H), 7.60 (s, 1H), 7.52 – 7.39 (m, 2H), 7.31 (dd, *J* = 1.8, 8.4 Hz, 1H), 5.98 (ddd, *J* = 1.2, 7.4, 15.7 Hz, 1H), 5.48 (ddd, *J* = 1.2, 6.3, 15.7 Hz, 1H), 4.23 – 4.14 (m, 1H), 3.58 (dd, J_{AB} = 11.2 Hz, J_{AX} = 7.5 Hz, 1H), 3.43 (dd, J_{AB} = 11.2 Hz, J_{BX} = 3.5 Hz, 1H), 3.42 (q, *J* = 7.4 Hz, 1H), 2.54 (d, *J* = 8.6 Hz, 1 H), 1.78 (q, *J* = 7.6 Hz, 1H), 1.37 – 1.18 (m, 2H), 0.91 (q, *J* = 7.2 Hz, 2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.7, 137.4, 133.6, 132.2, 128.1, 128.1, 127.6, 127.6, 126.1, 126.0, 125.9, 125.4, 73.0, 66.5, 48.4, 37.7, 20.7, 14.0, ^{1}H NMR (400 MHz, C_6D_6) δ = 7.66 (dd, *J* = 8.2, 17.6 Hz, 3H), 7.56 (s, 1H), 7.31 – 7.22 (m, 3H), 5.95 (ddd, *J* = 1.2,

7.5, 15.6 Hz, 1H), 5.44 (ddd, J = 1.0, 6.0, 15.4 Hz, 1H), 4.13 (m, 1H), 3.47 (dd, J_{AB} = 11.3 Hz, J_{AX} = 8.1 Hz, 1H), 3.38 (dd, J_{AB} = 11.3 Hz, J_{BX} = 3.2 Hz, 1H), 3.29 (q, J = 7.3 Hz, 1H), 1.72 – 1.63 (m, 2H), 1.34 – 1.13 (m, 3H), 0.85 (t, J = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, C_6D_6) δ = 142.0, 136.2, 133.9, 132.5, 128.6, 128.1, 127.6, 126.2, 126.0, 125.8, 125.2, 72.9, 66.6, 48.5, 37.8, 20.7, 13.9, MS (EI, m/z) 270 (36, M^+), 239 (18), 221 (42), 209 (10), 195 (10), 179 (100), 167 (54), 152 (20), 141 (56), 128 (19), 115 (10), 55 (4), 41 (4), 31 (4). FTIR (ν_{max}/cm^{-1}): 3365, 2927, 2870, 1600, 1457, 1377, 1260, 1024, 815, 746.

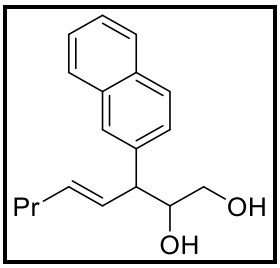


Figure 3.47. *(E)*-3-(Naphthalen-2-yl) oct-4-ene-1,2-diol

4af: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 – 7.75 (m, 3H), 7.66 (d, J = 1.6 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.35 (dd, J = 1.6, 8.6 Hz, 1 H), 5.82 (tdd, J = 1.2, 8.6, 15.3 Hz, 1H), 5.71 (td, J = 6.3, 15.3 Hz, 1H), 3.97 (ddd, J = 2.9, 6.0, 8.7 Hz, 1H), 3.55 (dd, J_{AB} = 11.4 Hz, J_{AX} = 6.3 Hz, 1H), 3.53 (t, J = 8.6 Hz, 1 H), 3.40 (dd, J_{AB} = 11.4 Hz, J_{BX} = 3.1 Hz, 1H), 2.06 (q, J = 7.7 Hz, 2H), 1.41 (qd, J = 7.4, 14.7 Hz, 2H), 0.89 (t, J = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.6, 135.0, 133.6, 130.6, 129.4, 128.5, 127.6, 127.6, 126.4, 126.2, 126.1, 125.7, 74.3, 64.2, 52.7, 34.7, 22.4, 13.7, MS (EI, m/z) 270 (1, M^+), 253 (1), 236 (1), 210 (54), 193 (6), 178 (20), 167 (100), 152 (20), 141 (22), 128 (15), 115 (13), 81 (6), 44 (8), 32 (10). FTIR (ν_{max}/cm^{-1}): 3385, 2924, 2854, 1724, 1600, 1463, 1377, 1260, 1075, 971, 816, 746.

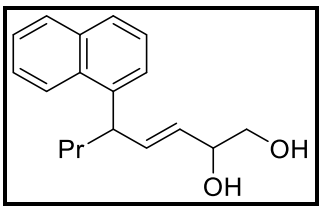


Figure 3.48. *(E)*-5-(Naphthalen-1-yl) oct-3-ene-1,2-diol

3ag: ^{1}H NMR (400 MHz, C_6D_6) δ = 8.08 (d, *J* = 8.6 Hz, 1H), 7.67 (dd, *J* = 1.0, 7.6 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.40 – 7.22 (m, 3H), 7.16 (s, 1H), 5.96 (dd, *J* = 7.4, 15.3 Hz, 1H), 5.43 (dd, *J* = 5.7, 15.5 Hz, 1H), 4.07 (m, 1H), 4.02 (q, *J* = 7.8, 1H), 3.44 – 3.36 (m, 1H), 3.35 – 3.14 (m, 3H), 1.84 – 1.66 (m, 2H), 1.38 – 1.15 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, C_6D_6) δ = 140.7, 135.9, 134.3, 131.9, 129.0, 128.8, 126.7, 125.6, 125.6, 125.3, 124.1, 123.4, 72.9, 66.6, 42.7, 37.7, 20.9, 14.0, MS (EI, m/z) 270 (25), 239 (13), 221 (35), 179 (100), 167 (88), 165 (96), 152 (53), 141 (78), 41 (56). FTIR (ν_{max}/cm^{-1}): 3361, 2928, 2870, 1596, 1509, 1457, 1365, 1074, 1027, 972, 875, 777.

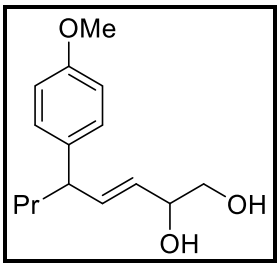


Figure 3.49. *(E)*-5-(4-Methoxyphenyl) oct-3-ene-1,2-diol

3ah: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 – 7.03 (m, 2H), 6.88 – 6.79 (m, 2H), 5.88 (ddd, *J* = 1.2, 7.6, 15.5 Hz, 1H), 5.42 (ddd, *J* = 1.2, 6.4, 15.6 Hz, 1H), 4.23 – 4.15 (m, *J* = 3.5 Hz, 1H), 3.78 (s, 3H), 3.59 (dd, J_{AB} = 11.3 Hz, J_{AX} = 7.9 Hz, 1H), 3.36 (dd, J_{AB} = 11.3 Hz, J_{BX} = 3.5 Hz, 1H), 3.21 (q, *J* = 7.4 Hz, 1H), 2.31 (br, s, 2H), 1.72 – 1.56 (m, 2H), 1.32 – 1.15 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.9, 137.9, 136.3, 128.4, 127.5, 113.8, 73.0, 66.5, 55.2, 47.4, 38.0, 20.6, 14.0, ^{1}H NMR (400 MHz, C_6D_6) δ = 7.06 – 6.99 (m, 2H), 6.86 – 6.79 (m, 2H), 5.86 (dd, *J* = 7.6, 15.5 Hz, 1H), 5.38 (dd, *J* = 6.1, 15.5 Hz, 1H), 4.08 – 4.01 (m, 1H), 3.42 (dd, J_{AB} = 10.7 Hz, J_{AX} = 7.5 Hz, 1H), 3.35 (s, 3H), 3.32 (dd, J_{AB} = 10.7 Hz, J_{BX} = 3.5 Hz, 1H), 3.13 (q, *J* = 7.4 Hz, 1 H), 2.45 (br, s, 2 H), 1.60 (q, *J* = 7.6 Hz, 2H), 1.33 – 1.15 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, C_6D_6) δ = 158.3, 136.9, 136.4, 128.5, 128.0, 113.9, 72.8, 66.6, 54.4, 47.5, 38.1, 20.7, 13.9, MS (EI, m/z) 250 (16, M^+), 232 (3), 219 (5), 207 (35), 201 (24), 189 (10), 176 (6), 171 (8), 159 (100), 147 (38), 135 (10), 128 (7), 121 (54), 115 (17), 77 (10), 65 (5), 55 (7), 41 (7), 31 (7).

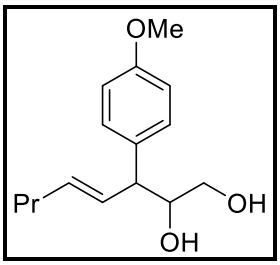


Figure 3.50. *(E)*-3-(4-Methoxyphenyl) oct-4-ene-1,2-diol

4ah: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 – 7.10 (m, 2H), 6.89 – 6.82 (m, 2H), 5.69 (dd, J_{AB} = 15.3 Hz, J_{AX} = 8.1 Hz, 1H), 5.64 (dd, J_{AB} = 15.3 Hz, J_{BX} = 5.2 Hz, 1H), 3.79 (s, 3H), 3.83 – 3.75 (m, 1H), 3.52 (dd, J_{AB} = 11.4 Hz, J_{AX} = 6.5 Hz, 1H), 3.36 (dd, J_{AB} = 11.4 Hz, J_{BX} = 2.9 Hz, 1H), 3.30 (t, *J* = 8.2 Hz, 1 H), 2.04 (q, *J* = 7.2, 2H), 1.40 (sxt, *J* = 6.7 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.04 – 6.99 (m, 2H), 6.78 – 6.73 (m, 2H), 5.68 (tdd, *J* = 1.5, 8.8, 15.3 Hz, 1H), 5.44 (td, *J* = 7.0, 15.3 Hz, 1H), 3.71 – 3.65 (m, 1H), 3.46 (dd, *J* = 3.1, 11.3 Hz, 1H), 3.36 – 3.26 (m, 2H), 3.30 (s, 3H), 1.87 (q, *J* = 6.7 Hz, 2H), 1.24 (sxt, *J* = 7.4 Hz, 2H), 0.80 (t, *J* = 7.0 Hz, 3H).

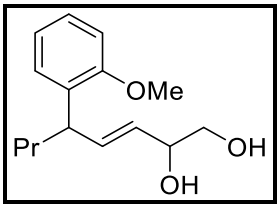


Figure 3.51. *(E)*-5-(2-Methoxyphenyl) oct-3-ene-1,2-diol

3ai: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 - 7.10 (m, 2 H), 6.91 (dt, *J* = 1.2, 7.4 Hz, 1 H), 6.85 (dd, *J* = 0.8, 8.2 Hz, 1 H), 5.95 (ddd, *J* = 1.2, 7.8, 15.7 Hz, 1 H), 5.46 (ddd, *J* = 1.2, 6.5, 15.5 Hz, 1 H), 4.24 - 4.16 (m, 1 H), 3.81 (s, 3 H), 3.75 (q, *J* = 7.8 Hz, 1 H), 3.65 - 3.55 (m, 1 H), 3.53 - 3.41 (m, 1 H), 1.97 (br. s., 1 H), 1.88 (br. s., 1 H), 1.67 (q, *J* = 7.6 Hz, 2 H), 1.33 - 1.19 (m, 2 H), 0.88 (t, *J* = 7.4 Hz, 3 H). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.20 - 7.13 (m, 1 H), 7.07 (dt, *J* = 2.0, 7.8 Hz, 1 H), 6.91 (t, *J* = 7.4 Hz, 1 H), 6.57 (d, *J* = 8.2 Hz, 1 H), 5.93 (dd, *J* = 7.8, 15.7 Hz, 1 H), 5.44 (dd, *J* = 6.1, 15.5 Hz, 1 H), 3.98 - 3.89 (m, 2 H), 3.32 (s, 3 H), 3.32 (dd, J_{AB} = 10.7 Hz, J_{AX} = 7.3 Hz, 1H), 3.22 (dd, J_{AB} = 10.7 Hz, J_{BX} = 3.3 Hz, 1H), 3.22 (dd, *J* = 7.0, 11.3 Hz, 1 H), 1.70 (qd, *J* = 6.6, 9.3 Hz, 2 H), 1.42 - 1.20 (m, 2 H), 0.88 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (101 MHz, C_6D_6) δ = 157.0, 136.0, 132.9, 128.5, 126.9, 120.7, 110.6, 72.8, 66.5, 54.6, 54.6, 40.8, 37.2, 20.8, 13.9. MS

(EI, m/z) 250 (5, M^+), 219 (12), 201 (31), 159 (62), 121 (100), 91 (61), 77 (22), 43 (63), 41 (76). FTIR (ν_{max}/cm^{-1}): 3372, 2925, 1491, 1240, 1029, 874, 752.

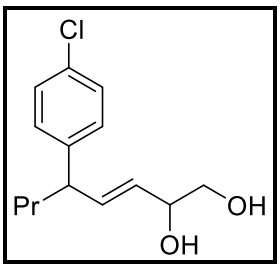


Figure 3.52. *(E)*-5-(4-Chlorophenyl) oct-3-ene-1,2-diol

3aj: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.18 (m, 2H), 7.13 – 7.03 (m, 2H), 5.86 (ddd, *J* = 1.2, 7.6, 15.5 Hz, 1H), 5.42 (ddd, *J* = 1.2, 6.3, 15.7 Hz, 1H), 4.23 – 4.15 (m, 1H), 3.59 (dd, J_{AB} = 11.3 Hz, J_{AX} = 8.1 Hz, 1H), 3.43 (dd, J_{AB} = 11.3 Hz, J_{BX} = 3.3 Hz, 1H), 3.23 (q, *J* = 7.4 Hz, 1 H), 2.48 (br, s., 2H), 1.72 – 1.56 (m, 2H), 1.33 – 1.12 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.8, 136.9, 131.8, 128.9, 128.6, 128.2, 72.9, 66.5, 47.6, 37.8, 20.5, 13.9. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.19 – 7.11 (m, 2H), 6.86 – 6.77 (m, 2H), 5.77 (ddd, *J* = 1.2, 7.8, 15.7 Hz, 1H), 5.34 (ddd, *J* = 1.0, 5.9, 15.5 Hz, 1H), 4.12 (m, 1H), 3.47 (dd, J_{AB} = 11.2 Hz, J_{AX} = 7.9 Hz, 1H), 3.36 (dd, J_{AB} = 11.2 Hz, J_{BX} = 3.1 Hz, 1H), 3.01 (q, *J* = 7.4 Hz, 1H), 1.56 – 1.40 (m, 2H), 1.24 – 1.04 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, C_6D_6) δ = 142.9, 135.8, 131.8, 128.9, 128.5, 128.5, 72.8, 66.6, 47.6, 37.7, 20.5, 13.8. MS (EI, m/z) 254 (4, M^+), 236 (1), 223 (72), 218 (1), 205 (22), 193 (5), 179 (8), 163 (42), 151 (30), 139 (18), 125 (100), 115 (42), 103 (6), 89 (6), 77 (6), 57 (14), 41 (8), 31 (8). FTIR (ν_{max}/cm^{-1}): 3363, 2926, 2870, 1491, 1365, 1090, 1014, 821, 719.

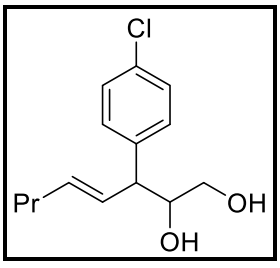


Figure 3.53. *(E)*-3-(4-Chlorophenyl) oct-4-ene-1,2-diol

4aj: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.26 (m, 2H), 7.18 – 7.12 (m, 2H), 5.67 (dd, J_{AB} = 15.6 Hz, J_{AX} = 15.6 Hz, 1H), 5.64 (dd, J_{AB} = 15.6 Hz, J_{AX} = 6.9 Hz, 1H), 3.80 (ddd, *J* = 3.1, 6.0, 8.5 Hz, 1 H), 3.53 (dd, J_{AB} = 11.4 Hz, J_{AX} = 6.1Hz, 1H), 3.48 (q, *J* = 7.0 Hz, 1 H), 3.34 (dd, J_{AB} = 11.4 Hz, J_{BX} = 2.9 Hz, 1H), 3.37 – 3.31 (m, 2H), 2.08 – 2.00 (m, 2H), 1.40 (sxt, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). MS (EI, m/z) 223 (1), 194 (54), 177 (1), 159 (16).151 (100), 138 (24), 125 (42), 115 (40), 99 (3), 91 (6), 77 (7), 61 (10), 55 (8), 43 (8). FTIR (ν_{max}/cm^{-1}): 3361, 2922, 2853, 1463, 1377, 1074, 774.

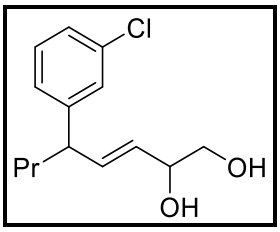


Figure 3.54. *(E)*-5-(3-Chlorophenyl) oct-3-ene-1,2-diol

3ak: ^{1}H NMR (400 MHz, C_6D_6) δ = 7.23 - 7.12 (m, 2 H), 7.08 - 7.02 (m, 1 H), 6.91 - 6.79 (m, 2 H), 5.73 (tdd, *J* = 1.2, 7.8, 16.0 Hz, 1 H), 5.33 (ddd, *J* = 1.2, 5.9, 15.3 Hz, 1 H), 4.09 - 4.00 (m, 1 H), 3.42 (ddd, *J* = 0.8, 3.1, 11.0 Hz, 1 H), 3.31 (dt, *J* = 1.2, 9.6 Hz, 1 H), 3.19-3.66 (br. s, 2 H), 2.99 (q, *J* = 7.4 Hz, 1 H), 1.46 (q, *J* = 7.4 Hz, 2 H), 1.24 - 1.02 (m, 2 H), 0.79 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (101 MHz, C_6D_6) δ = 146.9, 135.4, 134.3, 129.7, 128.9, 127.7, 126.3, 125.7, 72.7, 66.5, 48.1, 37.6, 20.5, 13.7. MS (EI, m/z) 254 (1>, M^+), 223 (23), 205 (7), 167 (20), 125 (70), 115 (100), 103 (19), 89 (6), 77 (36), 57 (58), 43 (60), 41 (90). FTIR (ν_{max}/cm^{-1}): 3354, 2926, 2871, 1595, 1571, 1077, 1028, 971, 874, 782, 696.

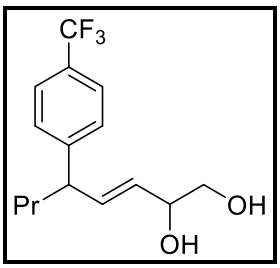


Figure 3.55. *(E)*-5-(4-(Trifluoromethyl) phenyl) oct-3-ene-1,2-diol

3am: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 5.89 (ddd, *J* = 1.4, 7.7, 15.6 Hz, 1H), 5.47 (ddd, *J* = 1.2, 6.3, 15.7 Hz, 1H), 4.24

– 4.17 (m, 1H), 3.61 (dd, J_{AB} = 11.1 Hz, J_{AX} = 7.7 Hz, 1H), 3.45 (dd, J_{AB} = 11.1 Hz, J_{BX} = 3.3 Hz, 1H), 3.33 (q, J = 7.6 Hz, 1 H), 2.28 (br, s, 2H), 1.76 – 1.61 (m, 2H), 1.35 – 1.12 (m, 2H), 0.88 (t, J = 7.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.4, 148.4, 136.4, 128.6, 128.4, 127.9, 125.4, 72.8, 66.5, 48.2, 37.7, 20.6, 13.9.^{1}H NMR (400 MHz, C_6D_6) δ = 7.38 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 7.4 Hz, 2H), 5.78 – 5.67 (m, 1H), 5.36 – 5.26 (m, 1H), 4.10 – 3.98 (m, 1H), 3.46 – 3.36 (m, 1H), 3.34 – 3.25 (m, 1 H), 3.02 (q, J = 7.4 Hz, 1H), 1.45 (td, J = 7.5, 15.5 Hz, 2H), 1.20 – 0.99 (m, 2H), 0.80 (t, J = 7.4 Hz, 3H), ^{13}C NMR (101 MHz, C_6D_6) δ = 148.6, 135.2, 129.0, 128.9, 127.8, 125.3, 123.4, 72.6, 66.5, 48.1, 37.6, 20.5, 13.7. MS (EI, m/z) 269 (11), 257 (100), 237 (11), 213 (7), 201 (43), 181 (18), 165 (10), 159 (71), 145 (12), 127 (12), 115 (12), 95 (1), 87 (10), 71 (5), 57 (30), 43 (10), 31 (8). FTIR (ν_{max}/cm^{-1}): 3381, 2926, 1324, 1120, 1067, 972, 835.

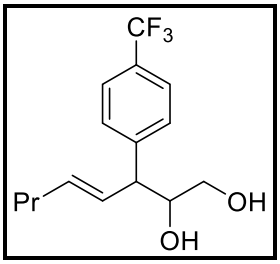


Figure 3.56. *(E)*-3-(4-(Trifluoromethyl) phenyl) oct-4-ene-1,2-diol

4am: ^{1}H NMR (400 MHz, C_6D_6) δ = 7.32 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 5.56 (tdd, J = 1.5, 8.8, 15.3 Hz, 1H), 5.35 (td, J = 6.7, 15.5 Hz, 1H), 3.51 (dt, J = 3.5, 6.8 Hz, 1H), 3.25 (dd, J_{AB} = 10.8 Hz, J_{AX} = 6.9 Hz, 1H), 3.18 (t, J = 8.2 Hz, 1H), 3.11 (dd, J_{AB} = 10.8 Hz, J_{BX} = 2.5 Hz, 1H), 1.85 (dq, J = 1.6, 6.7 Hz, 2H), 1.23 (q, J = 7.4 Hz, 2H), 0.80 (t, J = 7.4 Hz, 3H). MS (EI, m/z) 228 (70), 208 (65), 185 (100), 172 (93), 165 (35), 159 (54), 145 (11), 129 (20), 103 (4), 91 (6), 69 (12), 61 (54), 55 (18), 43 (20), 31 (6). FTIR (ν_{max}/cm^{-1}): 3388, 2925, 2854, 1464, 1326, 1125, 1068, 836.

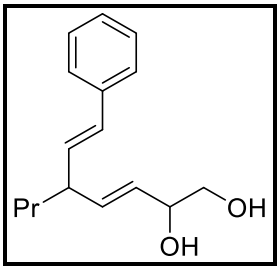


Figure 3.57. *(E)*-5-(*(E)*-Styryl) oct-3-ene-1,2-diol

3an: ^{1}H NMR (400 MHz, C_6D_6) δ = 7.33 – 7.24 (m, 2H), 7.20 – 7.11 (m, 2H), 7.09 – 7.01 (m, 1H), 6.45 (d, *J* = 16.0 Hz, 1H) (minor), 6.36 (d, *J* = 16.0 Hz, 1H) (major), 6.19 (dd, *J* = 7.8, 16.0 Hz, 1H) (minor), 6.05 (dd, *J* = 7.8, 16.0 Hz, 1H) (major), 5.75 (ddd, *J* = 1.2, 7.4, 15.7 Hz, 1H), 5.48 (ddd, *J* = 1.2, 6.0, 15.6 Hz, 1H), 4.29 – 4.16 (m, 1H), 3.57 (dd, J_{AB} = 11.3 Hz, J_{AX} = 8.1 Hz, 1H), 3.46 (dd, J_{AB} = 11.3 Hz, J_{BX} = 3.2 Hz, 1H), 2.78 (quin, *J* = 7.3 Hz, 1H), 1.45 – 1.36 (m, 2H), 1.36 – 1.24 (m, 2H), 0.89 (t, *J* = 6.7 Hz, 3H) (major), 0.86 (t, *J* = 6.7 Hz, 3H) (minor), ^{13}C NMR (101 MHz, C_6D_6) δ = 135.2, 132.9, 129.8, 128.6, 128.4, 127.0, 126.3, 126.2, 73.0, 66.7, 45.7, 37.1, 20.4, 13.9, MS (EI, m/z) 228 (2), 215 (6), 197 (10), 185 (78), 167 (18), 155 (30), 143 (65), 129 (60), 115 (50), 107 (20), 91 (100), 77 (15), 55 (10), 43 (10). FTIR (ν_{max}/cm^{-1}): 3378, 2924, 2852, 1464, 1260, 1092, 1025, 799.

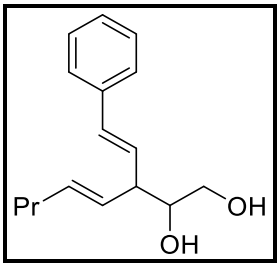


Figure 3.58. *(E)*-3-(*(E)*-Styryl) oct-4-ene-1,2-diol

4an: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 7.28 (m, 4H), 7.26 – 7.20 (m, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 8.2, 16.0 Hz, 1H), 5.66 (td, *J* = 6.7, 15.3 Hz, 1H), 5.50 (dd, *J* = 8.6, 15.3 Hz, 1H), 3.76 (d, *J* = 11.3 Hz, 1H), 3.67 (t, *J* = 8.6 Hz, 1H), 3.64 – 3.57 (m, 1H), 3.04 (q, *J* = 7.8 Hz, 1H), 2.07 (q, *J* = 7.0 Hz, 2H), 1.43 (sxt, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 137.0, 134.6, 131.8, 128.6, 128.5, 128.2, 127.4, 126.2, 110.0, 73.7, 64.5, 50.1, 34.8, 22.4, 13.7. MS (EI, m/z) 246 (1, M^+), 215 (2), 185 (72), 165 (4), 155 (10), 143 (95), 129 (66), 115 (42), 105 (12), 91 (100), 77 (12), 65 (8), 55 (10), 43 (10), 31 (4).

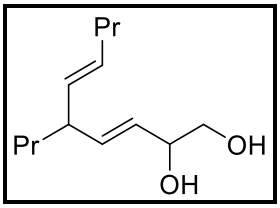


Figure 3.59. (3*E*,6*E*)-5-Propyldeca-3,6-diene-1,2-diol

3ao: ^{1}H NMR (400 MHz, C_6D_6) δ = 5.67 (ddd, *J* = 1.2, 7.4, 14.5 Hz, 1H), 5.43 (q, *J* = 6.3 Hz, 1 H), 5.39 (t, *J* = 6.3 Hz, 1H), 5.30 (dd, *J* = 7.8, 15.7 Hz, 1H), 4.15 – 4.06 (m, 1H), 3.48 (dd, J_{AB} = 11.0 Hz, J_{AX} = 7.9 Hz, 1H), 3.37 (dd, J_{AB} = 11.0 Hz, J_{BX} = 3.5 Hz, 1H), 3.17 (q, *J* = 7.4 Hz, 1H), 2.65 (td, *J* = 6.8, 13.7 Hz, 1H), 2.55 (br, s, 2H), 1.96 (q, *J* = 6.8 Hz, 2H), 1.42 – 1.25 (m, 6H), 0.98 – 0.81 (m, 6H), ^{13}C NMR (101MHz, C_6D_6) δ = 136.1, 133.1, 130.0, 128.1, 73.0, 66.7, 45.3, 37.3, 34.7, 22.7, 20.4, 13.9, 13.5. MS (EI, m/z) 195 (1), 181 (26), 151 (27), 107 (29), 95 (38), 91 (22), 81 (43), 67 (79), 55 (66), 43 (79), 41 (100). FTIR (ν_{max}/cm^{-1}): 3368, 2926, 2871, 1458, 1378, 1074, 1029, 970, 874.

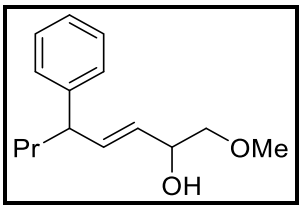


Figure 3.60. *(E)*-1-Methoxy-5-phenyloct-3-en-2-ol

3ba: ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.32–7.26 (m, 2H), 7.22–7.14 (m, 3H), 5.92 (dd, *J* = 7.8, 15.7 Hz, 1H), 5.44 (dd, *J* = 6.3, 15.7 Hz, 1H), 4.32–4.24 (m, 1H), 3.41–3.36 (m, 1H), 3.38 (s, 3H), 3.29–3.21 (m, 2 H), 2.37 (br, s., 1H), 1.68 (q, *J* = 7.4 Hz, 2H), 1.31–1.22 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 144.5, 137.2, 128.4, 127.6, 127.6, 126.1, 76.7, 71.1, 59.0, 48.3, 38.0, 20.6, 14.0. ^{1}H NMR (400 MHz, C_6DC_6) *δ*: 7.21–7.16 (m, 2 H), 7.13–7.01 (m, 3 H), 5.93 (ddd, *J* = 1.4, 7.8, 15.5 Hz, 1H) (major), 5.92 (ddd, *J* = 1.4, 7.8, 15.5 Hz, 1H) (minor), 5.45 (ddd, *J* = 0.8, 6.3, 15.3 Hz, 1H), 4.22 (m, 1H), 3.16 (q, *J* = 7.8 Hz, 1H), 3.08 (dd, J_{AB} = 8.6 Hz, J_{AX} = 6.2 Hz, 1H), 3.10 (dd, J_{AB} = 8.6 Hz, J_{BX} = 2.4 Hz, 1H), 3.00 (s, 3H) (minor), 2.99 (s, 3 H) (major), 2.29 (br, s., 1H), 1.60 (q, *J* = 7.5 Hz, 2H), 1.28–1.17 (m, 2H), 0.83 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (101 MHz, C_6D_6) *δ*: 144.7, 136.1, 128.4, 128.4, 127.6, 126.0, 76.8, 70.7, 58.2, 48.5, 38.1, 20.6, 13.8. MS (EI, m/z): 234 (M^+, 1), 216 (1), 189 (54), 171 (29).145 (15), 134 (24), 129 (44), 115 (32), 105 (20), 101 (18), 91 (100), 77 (7), 69 (6), 57 (13), 45 (26). FTIR (ν_{max}/cm^{-1}): 3435, 2926,1601, 1452, 1120, 969, 699, 614.

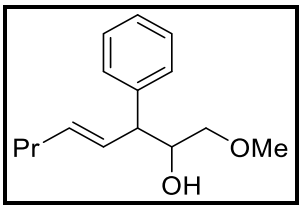


Figure 3.61. *(E)*-1-Methoxy-3-phenyloct-4-en-2-ol

4ba: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.28 (m, 3H), 7.25–7.19 (m, 2H), 5.76 (dd, J = 9.8, 15.3 Hz, 1H), 5.61 (td, J = 6.6, 15.3 Hz, 1H), 3.98–3.91 (m, 1H), 3.36 (t, J = 8.2 Hz, 1H), 3.33–3.26 (m, 4 H), 3.14 (dd, J = 6.8, 9.6 Hz, 1H), 2.04 (q, J = 7.0 Hz, 2H), 1.39 (sex, J = 7.2 Hz, 2H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.8, 134.0, 129.4, 128.6, 127.9, 126.6, 74.5, 73.2, 59.0, 52.4, 34.7, 22.4, 13.7. ^{1}H NMR (400 MHz, C_6DC_6) δ: 7.22- 7.03 (m, 5H), 5.94 (dd, J = 8.4, 15.4 Hz, 1H) (major), 5.68 (dd, J = 8.4, 15.4 Hz, 1H) (minor), 5.48 (td, J = 7.0, 15.4 Hz, 1H), 4.04 (m, 1H) (minor), 3.99 (m, 1H) (major), 3.43 (t, J = 7.6 Hz, 1H), 3.18 (dd, J_{AB} = 9.4 Hz, J_{AX} = 7.1 Hz, 1H), 3.10 (dd, J_{AB} = 9.4 Hz, J_{BX} = 3.4 Hz, 1H), 3.03 (s, 3H) (minor), 2.97 (s, 3 H) (major), 2.25 (br, s., 1H), 1.93 (q, J = 7.2 Hz, 2H), 1.28 (qd, J = 7.2, 14.6 Hz, 2H), 0.82 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ: 142.5, 132.7, 130.3, 128.4, 128.2, 126.3, 74.8, 73.2, 58.2, 52.2, 34.7, 22.4, 13.4. MS (EI, m/z): 217 (48), 199 (5), 185 (15), 173 (26), 159 (34), 119 (52), 113 (7), 104 (100), 91 (11), 81 (8), 67 (7), 53 (10), 45 (20). FTIR (ν_{max}/cm^{-1}): 3447, 2923,2852, 1733, 1454, 1123, 971, 700.

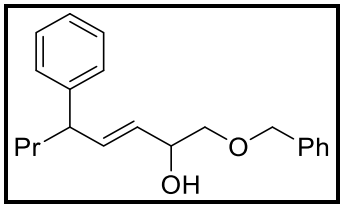


Figure 3.62. *(E)*-1-(Benzyloxy)-5-phenyloct-3-en-2-ol

3ca: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.27 (m, 7H), 7.25 – 7.16 (m, 3H), 5.94 (dd, J = 7.8, 15.7 Hz, 1H), 5.47 (dd, J = 6.5, 15.5 Hz, 1H), 4.57 (s, 2H), 4.38 – 4.30 (m, 1H), 3.51 (dd, J_{AB} = 9.5 Hz, J_{AX} = 8.2 Hz, 1H), 3.37 (dd, J_{AB} = 9.5 Hz, J_{BX} = 3.5 Hz, 1H), 3.28 (q, J = 7.2 Hz, 1H), 2.55 (br, s., 1H), 1.70 (q, J = 7.4 Hz, 2H), 1.40 – 1.17 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101MHz, $CDCl_3$) δ = 144.5, 137.9, 137.2, 128.5, 128.4, 127.8, 127.8, 127.7, 127.6, 126.2, 74.3, 73.3, 71.3, 48.4, 38.0, 20.7, 14.1. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.21 – 7.12 (m, 6H), 7.12 – 7.03 (m, 4H), 5.93 (ddd, J = 1.2, 7.8, 15.7 Hz, 1H), 5.45 (ddd, J = 1.2, 5.9, 15.7 Hz, 1H), 4.29 – 4.24 (m, 1H), 4.22 (s, 2H), 3.23 (dd, J_{AB} = 9.4 Hz, J_{AX} = 8.1 Hz, 1H), 3.19 (dd, J_{AB} = 9.4 Hz, J_{BX} = 3.6 Hz, 1H), 3.15 (q, J = 7.4 Hz, 1 H), 2.39 (br, s., 1H), 1.59 (q, J = 7.6 Hz, 2H), 1.31 – 1.12 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ = 144.7, 138.3, 136.0, 128.5, 128.4,

128.2, 127.6, 127.5, 126.0, 74.5, 72.8, 70.9, 48.5, 38.1, 20.7, 13.8, MS (EI, m/z) 310 (1>, M^+), 189 (14), 177 (15), 133 (22), 91 (100). FTIR (ν_{max}/cm^{-1}): 3436, 2925, 2857, 1453, 1103, 970, 698.

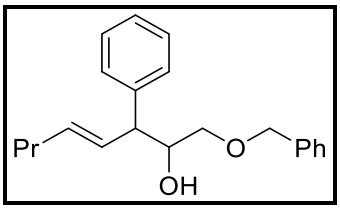


Figure 3.63. *(E)*-1-(Benzyloxy)-3-phenyloct-4-en-2-ol

4ca: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.27 (m, 8H), 7.25 – 7.17 (m, 2H), 5.77 (dd, *J* = 9.0, 15.3 Hz, 1H), 5.58 (td, *J* = 6.8, 15.3 Hz, 1H), 4.49 (d, J_{AB} = 11.9 Hz, 1 H), 4.45 (d, J_{AB} = 11.9 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.45 – 3.37 (m, 2H), 3.27 (dd, *J* = 6.7, 9.8 Hz, 1H), 2.03 (dq, *J* = 1.2, 7.0 Hz, 2H), 1.38 (qd, *J* = 7.4, 14.7 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.9, 138.0, 133.9, 129.5, 128.6, 128.4, 128.0, 127.7, 127.7, 126.6, 73.3, 73.3, 72.2, 52.3, 34.7, 22.5, 13.7, ^{1}H NMR (400MHz, C_6D_6) δ = 7.22 – 7.12 (m, 8H), 7.11 – 7.02 (m, 2H), 5.92 (tdd, *J* = 1.4, 8.4, 15.4 Hz, 1H), 5.46 (dtd, *J* = 1.2, 6.7, 15.7 Hz, 1H), 4.21 (d, J_{AB} = 11.7 Hz, 1H), 4.18 (d, J_{AB} = 11.7 Hz, 1H), 4.01 (dt, *J* = 3.5, 6.7 Hz, 1H), 3.46 (t, *J* = 7.6 Hz, 1H), 3.33 (dd, J_{AB} = 9.7 Hz, J_{AX} = 6.5 Hz, 1H), 3.24 (dd, J_{AB} = 9.7 Hz, J_{BX} = 3.7 Hz, 1H), 2.22 (br, s., 1H), 1.92 (dq, *J* = 1.2, 7.0 Hz, 2H), 1.27 (qd, *J* = 7.2, 14.8 Hz, 2H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ = 142.5, 138.5, 132.8, 130.2, 128.4, 128.3, 128.2, 126.3, 73.4, 72.9, 72.5, 52.2, 34.7, 22.4, 13.4. MS (EI, m/z) 310 (1>, M^+), 160 (60), 159 (53), 117 (100), 104 (27), 91 (99). FTIR (ν_{max}/cm^{-1}): 3453, 2924, 2857, 1453, 1364, 1260, 1099, 734, 698.

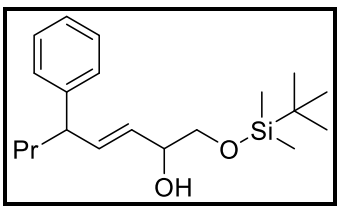


Figure 3.64.*(E)*-1-((*tert*-Butyldimethylsilyl) oxy)-5-phenyloct-3-en-2-ol

3da: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 5.91 (dd, *J* = 7.8, 15.7 Hz, 1H), 5.42 (dd, *J* = 6.5, 15.5 Hz, 1H), 4.18 – 4.09 (m, 1H), 3.60

(dd, J_{AB} = 9.9 Hz, J_{AX} = 7.6 Hz, 1H), 3.41 (dd, J_{AB} = 9.9 Hz, J_{BX} = 3.7 Hz, 1H), 3.26 (q, *J* = 7.6 Hz, 1H), 1.69 (dq, *J* = 2.7, 6.7 Hz, 2H), 1.39 – 1.14 (m, 2H), 0.90 (s, 6H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.5, 137.2, 128.4, 127.8, 127.6, 126.1, 72.7, 67.2, 48.4, 38.0, 25.9, 20.7, 18.3, 14.0, -5.3, -5.4. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.21 – 7.14 (m, 2H), 7.13 – 7.02 (m, 3H), 5.96 (ddd, *J* = 1.4, 7.8, 15.5 Hz, 1H), 5.48 (ddd, *J* = 1.2, 5.9, 15.3 Hz, 1H), 4.19 – 4.11 (m, 1H), 3.47 (dd, J_{AB} = 10.0 Hz, J_{AX} = 7.1 Hz, 1H), 3.38 (dd, J_{AB} = 10.0 Hz, J_{BX} = 3.8 Hz, 1H), 3.18 (q, J = 7.4 Hz, 1H), 2.39 – 2.29 (bs., 1H), 1.62 (q, *J* = 7.6 Hz, 2H), 1.23 (sptd, *J* = 7.0, 28.6 Hz, 2H), 0.89 (s, 9H), 0.83 (t, *J* = 7.4 Hz, 3H), -0.04 (d, *J* = 1.6 Hz, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ = 136.2, 128.7, 128.4, 127.6, 126.0, 72.5, 67.5, 48.6, 38.1, 25.7, 20.7, 18.1, 13.8, -5.7, -5.7. MS (EI, m/z) 275 (5), 186 (11), 185 (50), 159 (27), 143 (78), 129 (64), 117 (41), 91 (90), 75 (100), 73 (82). FTIR (ν_{max}/cm^{-1}): 3453, 2926, 2855, 1463, 1108, 836, 777, 699.

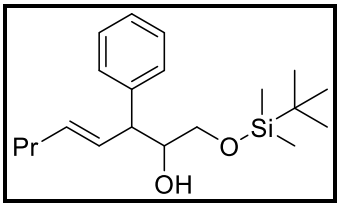


Figure 3.65. *(E)*-1-((*tert*-Butyldimethylsilyl) oxy)-3-phenyloct-4-en-2-ol

4da: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 5.79 (dd, *J* = 8.6, 15.3 Hz, 1H), 5.53 (td, *J* = 6.7, 15.3 Hz, 1H), 3.85 (spt, *J* = 3.5 Hz, 1H), 3.48 (dd, *J* = 3.5, 10.2 Hz, 1H), 3.34 (dd, *J* = 7.0, 9.8 Hz, 2H), 2.02 (q, *J* = 7.3 Hz, 2H), 1.38 (sxt, *J* = 7.4 Hz, 2H), 0.97 – 0.76 (m, 12H), -0.01 (s, 6H), ^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.1, 133.2, 129.8, 128.5, 128.0, 126.5, 74.6, 65.0, 51.8, 34.8, 30.3, 25.9, 22.5, 18.2, 13.7, 1.0, -5.4, -5.4. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.21 – 7.27 (m, 2H), 7.13 – 7.20 (m, 2H), 7.07 (d, *J* = 7.4 Hz, 1H), 5.97 (ddt, *J* = 15.3, 8.3, 1.5 Hz, 1H), 5.51 (dt, *J* = 15.3, 6.8 Hz, 1H), 3.86 – 3.93 (m, 1H), 3.55 (dd, J_{AB} = 10.1 Hz, J_{AX} = 6.5 Hz, 1H), 3.48 (t, *J* = 7.6 Hz, 1H), 3.44 (dd, J_{AB} = 10.1 Hz, J_{BX} = 3.7 Hz, 1H), 1.94 (q, *J*=6.7 Hz, 4H), 1.28 (sxt, *J* = 7.4 Hz, 4H), 0.92 (s, 9H), 0.82 (t, *J* = 7.4 Hz, 3H), -0.02 ppm (d, *J* = 1.6 Hz, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ = 142.6, 132.7, 130.4, 128.4, 128.3, 126.3, 74.6, 65.3, 51.9, 34.7, 25.7, 22.5, 18.1, 13.5, 1.0, -5.7, -5.7, MS (EI, m/z) 277 (5), 117 (72), 105 (70), 103 (32), 75 (100), 73 (62). FTIR (ν_{max}/cm^{-1}): 3483, 2927, 2857, 1463, 1256, 1116, 835, 777, 700.

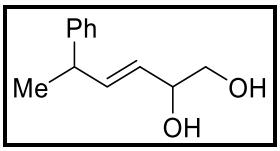


Figure 3.66. *(E)*-5-Phenylhex-3-ene-1,2-diol

3fa: ^{1}H NMR (400MHz, C_6D_6) δ = 7.21 - 7.14 (m, 2 H), 7.11 - 7.03 (m, 3 H), 5.79 (ddd, *J* = 1.6, 6.8, 15.5 Hz, 1 H), 5.31 (ddd, *J* = 1.4, 6.1, 15.7 Hz, 1 H), 3.95 - 3.87 (m, 1 H), 3.36 - 3.30 (m, 1 H), 3.29 - 3.17 (m, 2 H), 1.21 (d, *J* = 7.0 Hz, 4 H). ^{13}C NMR (101MHz, C_6D_6) δ = 145.9, 137.6, 128.9, 127.6, 126.6, 73.1, 66.9, 42.5, 21.4. MS (EI, m/z): 192 (M^+, 1>), 174 (10), 161 (22), 143 (100), 128 (32), 115 (31), 105 (27), 91 (55), 77 (40), 55 (26), 43 (23).

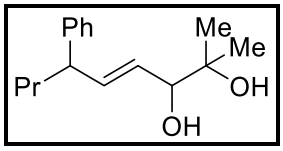


Figure 3.67. *(E)*-2-Methyl-6-phenylnon-4-ene-2,3-diol

3ga: ^{1}H NMR (400 MHz, C_6D_6) δ = 7.22 - 7.15 (m, 2 H), 7.13 - 7.03 (m, 3 H), 5.80 (ddd, *J* = 1.2, 7.8, 15.7 Hz, 1 H), 5.51 (ddd, *J* = 1.2, 7.0, 15.7 Hz, 1 H), 3.77 (dd, *J* = 1.0, 6.8 Hz, 1 H), 3.17 (q, *J* = 7.7 Hz, 1 H), 2.42 (br. s, 2 H), 1.61 (q, *J* = 7.6 Hz, 2 H), 1.32 - 1.16 (m, 2 H), 1.10 (d, *J* = 1.2 Hz, 6 H), 0.84 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (101 MHz, C_6D_6) δ = 144.7, 137.0, 128.6, 128.4, 127.5, 126.0, 79.2, 72.5, 48.4, 37.9, 26.2, 23.5, 20.7, 13.8. MS (EI, m/z): 231 (1>), 214 (1>), 145 (2), 133 (6), 129 (6), 115 (19), 91 (20), 77 (2), 59 (100), 43 (17). FTIR (ν_{max}/cm^{-1}): 3401, 2928, 2871, 1453, 1164, 972, 699.

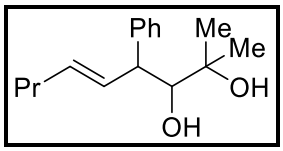


Figure 3.68.*(E)*-2-methyl-4-phenylnon-5-ene-2,3-diol

4ga: ^{1}H NMR (400MHz, $CDCl_3$) δ = 7.34 - 7.24 (m, 4 H), 7.24 - 7.17 (m, 1 H), 5.81 (dd, *J* = 9.4, 15.3 Hz, 1 H), 5.62 (td, *J* = 6.7, 15.6 Hz, 1 H), 3.68 (d, *J* = 5.5 Hz, 1 H),

3.49 (dd, *J* = 5.9, 9.4 Hz, 1 H), 2.30 (br. s., 1 H), 2.16 (br. s., 1 H), 2.03 (q, *J* = 6.9 Hz, 2 H), 1.39 (sxt, *J* = 7.4 Hz, 2 H), 1.22 - 1.19 (m, 3 H), 1.08 - 1.02 (m, 3 H), 0.88 (t, *J* = 7.2 Hz, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.2, 134.5, 130.0, 128.7, 127.9, 126.5, 79.7, 51.7, 34.7, 29.7, 27.1, 25.3, 22.4, 13.7. MS (EI, m/z): 248 (M^+, 1>), 160 (36), 117 (41).104 (22), 91 (21), 77 (7), 71 (10), 59 (100), 43 (37). FTIR (ν_{max}/cm^{-1}): 3422, 2926, 2858, 1453, 1378, 1160, 973, 700.

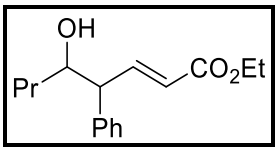


Figure 3.69. Ethyl-*(E)*-5-hydroxy-4-phenyloct-2-enoate

4ha: ^{1}H NMR (400 MHz, C_6D_6) δ = 7.55 (ddd, *J* = 1.4, 8.8, 15.7 Hz, 1 H), 7.12 - 6.95 (m, 5 H), 5.96 (d, *J* = 15.7 Hz, 1 H), 4.02 (q, *J* = 7.3 Hz, 2 H), 3.57 (br. s., 1 H), 3.21 - 3.11 (m, 1 H), 1.48 - 1.30 (m, 2 H), 1.24 - 1.13 (m, 3 H), 0.96 (t, *J* = 7.0 Hz, 3 H), 0.73 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (101MHz, C_6D_6) δ = 148.4, 140.7, 128.6, 128.2, 126.7, 123.3, 73.7, 59.8, 55.6, 37.1, 18.8, 13.9, 13.6. FTIR (ν_{max}/cm^{-1}): 3476, 2926, 2873, 1739, 1465, 1380, 1221, 1139, 701.

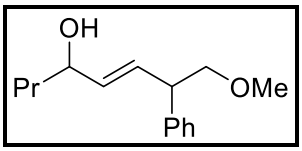


Figure 3.70.*(E)*-8-methoxy-7-phenyloct-5-en-4-ol

3ja: ^{1}H NMR (400 MHz, C_6D_6) δ = 7.22 - 7.12 (m, 4 H), 7.11 - 7.02 (m, 1 H), 5.85 (ddd, *J* = 1.2, 7.4, 15.7 Hz, 1 H), 5.54 (ddd, *J* = 1.2, 6.7, 15.7 Hz, 1 H), 3.97 (q, *J* = 5.5 Hz, 2 H), 3.57 (q, *J* = 6.3 Hz, 2 H), 3.46 (dd, J_{AB} = 9.2 Hz, J_{AX} = 7.5 Hz, 1H), 3.42 (dd, J_{AB} = 9.2 Hz, J_{BX} = 6.6 Hz, 1H), 3.05 (s, 3 H), 1.53 - 1.26 (m, 4 H), 0.83 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.2, 135.4, 131.0, 128.4, 128.1, 126.5, 76.5, 72.2, 58.2, 48.5, 39.6, 18.8, 13.9. MS (EI, m/z) 172 (6), 130 (31), 129 (16), 115 (10), 91 (17), 77 (6), 71 (44), 45 (100), 43 (57), 41 (34). FTIR (ν_{max}/cm^{-1}): 3422, 2928, 2971, 1453, 1111, 968, 699.

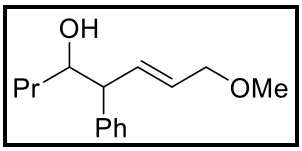


Figure 3.71. *(E)*-8-Methoxy-5-phenyloct-6-en-4-ol

4ja: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 - 7.28 (m, 2 H), 7.25 - 7.17 (m, 3 H), 6.03 (ddd, *J* = 0.8, 9.0, 15.7 Hz, 1 H), 5.70 (td, *J* = 5.9, 15.3 Hz, 1 H), 3.93 (d, *J* = 5.9 Hz, 2 H), 3.81 (q, *J* = 7.0 Hz, 1 H), 3.36 - 3.24 (m, 1 H), 3.31 (s, 3 H), 1.54 - 1.47 (m, 1 H), 1.37 - 1.28 (m, 3 H), 0.85 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.8, 133.1, 129.7, 128.7, 128.0, 126.6, 74.0, 72.8, 57.9, 55.9, 36.7, 18.9, 14.0.

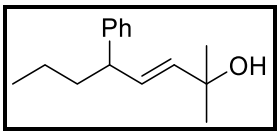


Figure 3.72. *(E)*-2-Methyl-5-phenyloct-3-en-2-ol

3ka: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 - 7.25 (m, 2 H), 7.22 - 7.13 (m, 3 H), 5.75 (dd, *J* = 7.4, 15.3 Hz, 1 H), 5.61 (d, *J* = 15.7 Hz, 1 H), 3.22 (q, *J* = 7.7 Hz, 1 H), 1.66 (q, *J* = 7.6 Hz, 2 H), 1.35 - 1.14 (m, 2 H), 1.29 (d, *J* = 3.1 Hz, 6 H) 0.88 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.0, 137.5, 130.9, 128.4, 127.5, 126.0, 70.7, 48.1, 38.2, 29.9, 29.8, 20.7, 14.0. MS (EI, m/z) 218 (1>, M^+), 175 (4), 157 (6), 149 (12), 115 (10), 91 (14), 77 (7), 71 (8), 59 (19), 43 (100). FTIR (ν_{max}/cm^{-1}): 3368, 2959, 2927, 2871, 1453, 1149, 970, 910, 760, 698.

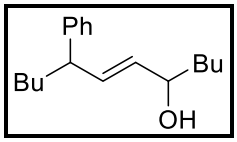


Figure 3.73(E)-8-phenyldodec-6-en-5-ol

3ma: ^{1}H NMR (400 MHz, C_6D_6) δ = 7.23 - 7.11 (m, 5 H), 7.10 - 7.04 (m, 1 H), 5.72 (dd, *J* = 7.6, 15.5 Hz, 1 H), 5.45 (dd, *J* = 6.5, 15.5 Hz, 1 H), 3.88 (q, *J* = 5.9 Hz, 1 H), 3.16 (q, *J* = 7.4 Hz, 1 H), 1.66 (q, *J* = 7.3 Hz, 2 H), 1.49 - 1.13 (m, 10 H), 0.87 - 0.81 (m, 6 H). ^{13}C NMR (101 MHz, C_6D_6) δ = 144.9, 134.2, 133.3, 128.4, 127.5, 126.0, 72.2, 48.6, 37.2, 35.6, 29.8, 27.6, 22.7, 22.6, 13.9, 13.8. MS (EI, m/z) 203 (2), 185 (3), 145 (6),

118 (18), 91 (42), 85 (40), 57 (62), 41 (100). FTIR (ν_{max}/cm^{-1}): 3420, 2928, 2975, 1445, 1098, 967, 704.

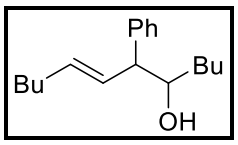


Figure 3.74(E)-6-phenyldodec-7-en-5-ol

4ma: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 - 7.27 (m, 2 H), 7.24 - 7.16 (m, 3 H), 5.76 - 5.57 (m, 2 H), 3.78 - 3.67 (m, 1 H), 3.18 (t, *J* = 8.0 Hz, 1 H), 2.06 (q, *J* = 6.7 Hz, 2 H), 1.84 (br. s., 1 H), 1.49 - 1.17 (m, 10 H), 0.86 (td, *J* = 7.0, 15.7 Hz, 6 H). ^{13}C NMR (101MHz, $CDCl_3$) δ = 142.4, 134.7, 129.5, 128.6, 127.9, 126.4, 74.0, 56.4, 34.0, 32.3, 31.5, 27.9, 22.6, 22.2, 14.0, 13.9.

CHAPTER 4

RESULTS AND DISCUSSION

In this study, the Pd-catalyzed 1,3-substitution reactions of alkenyl oxiranes with organoborons were studied. For this purpose, the optimization conditions were thoroughly examined

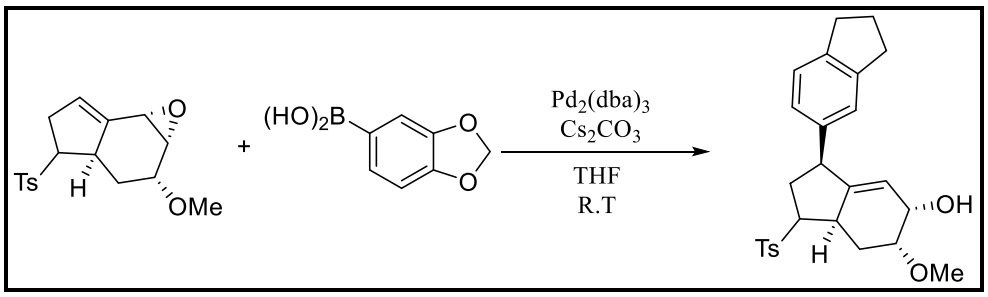


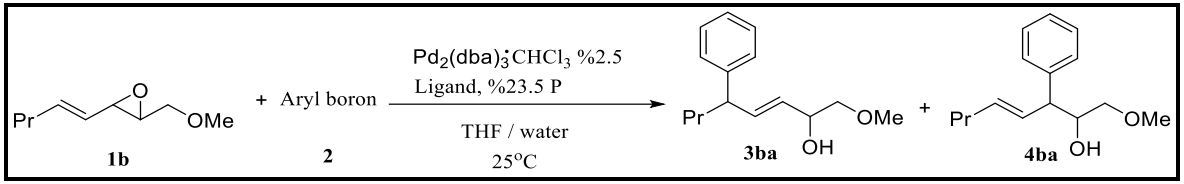
Figure 4.1. A method for the synthesis of montabuphine
(Source: Guan et al. 2012)

It was recently disclosed that as one of the synthesis step that was applied in synthesis of a biologically active compound, Pd-catalyzed coupling of an organoboronic acid with a cyclic vinyl epoxide proceeded stereo- and regio-selectively to give a 1,3-substituted major product (Figure 4.1). Hence, we have preferred to perform our first trial over the conditions reported therein for an acyclic vinyl epoxide compound **1b**, that is with phenyl boronic acid, using $Pd_2(dba)_3{\cdot}CHCl_3$ as the Pd-complex, Cs_2CO_3 as a base, in dried THF, and 25 °C. The result was rather disappointing in fact, proceeded with poor regio- and diastereo-selectivity. (Table 4.1, No 1). However, it should be noted that the regio-isomers could be isolated from each other by silica gel column chromatography. In the same conditions, the usage of $NaBPh_4$ as a boron source decreased the regio-selectivity further (Table 4.1, No 2). While the reaction with phenyl boroxine $(PhBO)_3$ resulted in low yields, with $KPhBF_3$ the reactant was recovered as unreacted (Table 4.1, No 3 and 4). The use of phenyl boronic acid neopentyl glycol ester (Phneop) improved the regio-selectivity of the products in favor of 1,3-substitution product, however, diastereo-selectivity was significantly diminished. (Table 4.1, No 5). No significant improvement for the selectivity was observed with the use of an organic base ($(i\text{-Pr})_2NEt$)

(Table 4.1, No 6). It was intriguing to observe however that the existence of water in the reaction mixture drastically improved the stereoselectivity and also caused the shift of this selectivity in favor of other diastereomeric structure. However, this improvement was accompanied by a decrease in regio-isomeric ratio (Table 4.1, No 7). With phenylboronic acid, the reaction gave nearly a similar result (Table 4.1, No 8).

The presence of a bidentate phosphine ligand DPEPhos could not further improve the process (Table 4.1, No 9-13).

Table 4.1. The Effect of conditions on reaction of vinyl epoxide (**1b**) with phenylboron compounds[a]



No	Ligand	Aryl Boron (eqv.)	THF/H_2O (mL)	Base (eqv.)	t, hour(s)	%**3b** (dr)[b]	%**4b** (dr)[b]
1	-	$PhB(OH)_2$ (2)	2.5:0	Cs_2CO_3 (2)	0.83	55 (1:4,7)	29 (7:1)
2	-	$NaBPh_4$ (2)	2.5:0	Cs_2CO_3 (2)	0.83	55 (N.D.)	45 (N.D.)
3	-	$(PhBO)_3$ (2)	2.5:0	Cs_2CO_3 (2)	O.N.	30 (N.D.)	(N.D.)
4	-	$PhBF_3K$ (2)	2.5:0	Cs_2CO_3 (2)	O.N.	-	-
5	-	PhBneop (2)	2.5:0	Cs_2CO_3 (2)	21	82 (3:1)	13 (3:1)
6	-	PhBneop (2)	2.5:0	(*i*-Pr)$_2$NEt (4)	<1	65 (6,6:1)	16 (1,1:1)
7	-	PhBneop (3)	2.0.5	(*i*-Pr)$_2$NEt (4)	0.25	53 (1:20)	22 (35:1)
8	-	$PhB(OH)_2$ (3)	2.0.5	(*i*-Pr)$_2$NEt (4)	0.33	53 (1:15)	31 (8:1)
9	DPEPhos	PhBneop (3)	2.0.5	(*i*-Pr)$_2$NEt (4)	8<>24	62 (1:18)	26 (34:1)
10	DPEPhos	$PhB(OH)_2$ (3)	2.0.5	(*i*-Pr)$_2$NEt (4)	7.5	58 (1:29)	22 (23:1)
11	DPEPhos	PhBneop (3)	2.0:0	(*i*-Pr)$_2$NEt (4)	24	-	-
12	DPEPhos	PhBneop (3)	2:0.5	Cs_2CO_3 (2)	O.N.	56 (1:30)	21 (>40:1)
13	DPEPhos	PhBneop (3)	2:0.5	$N(Et)_3$ (2)	7	61 (1:32)	20 (>40:1)

[a]O.N.: Overnight. [b] Determined by ^1H NMR using C_6D_6 solvent and N.D.: Not determined.

It was suprising for us to find that the vinyl oxirane **1a** with an unprotected pendant hydroxyl group afforded much better regio-selectivity in the presence of DPEphos ligand and organic base as compared to its unprotected form **1b**, producing **3a** and **4a** in 69% and 6% isolated yields, respectively. The compound containing oxygen group might have affect the activity of the metal as a result of coordination of free hydroxyl group with the palladium core.

In the next stage of the optimization studies, the ligand activity was surveyed. It should be noted that since the tedious column isolation work-up is highly time consuming, the ^{1}H NMR technique has been the usual preferred technique for the quantitative analysis of the crude products for fast screening of the optimum conditions. However, this technique allowed us only the determination of the **3aa** product accurately and the accurate analysis of the 4aa product has not been possible since its related proton signals were overlapped with those of other reagents existing within the mixture

The variation of DPEPhos amount had no remarkable influence on the reaction selectivity (Table 4.2, No 2 and 3) and therefore, the ratio of P/Pd was kept nearly 4:1 for the next experiments.

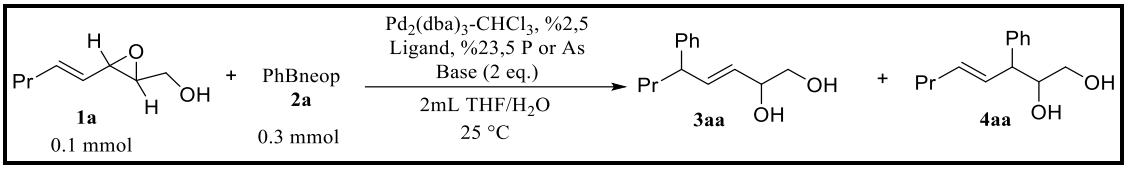
However, it should be noted that no further improvements have been possible by use of any of mono- or bidentate phosphine ligands tested for this study. The bidentate ligands xantphos, dppb, and significant number of electron rich and poor ligands resulted in intricate mixture. No conversion would be possible with the use of dppp and P(2-$MeOC_6H_4)_3$ ligands. On the other hand, among the other ligands tested only dppf ligand afforded a comparable result with respect to that which was obtained with DPEphos.

At last part of optimization of ligands, several non-phosphorous ligands were examined. The product **3a** formation was lowered significantly with the use of 2,2'-bipyridyl , whereas relatively moderate product formation has been possible with the use of an N-heterocyclic carbene precursor (1,3-bis(2,6-di-*i*-propylphenyl)imidazol-2-ylidene) (Table 4.2, No 25 and 26) On the other hand it has been delightful to find that the best selectivity could be obtained with the presence of $AsPh_3$ within the reaction medium, which produced **3aa** and **4aa** in 78% and 6% isolated yields, respectively in the presence of NEt_3 base (Table 4.2, No 27). A comparative result was obtained with (*i*-$Pr)_2NH$ base (No 33), with its use **3aa** and **4aa** formations being 79% and 10%, respectively.

It is apparent that the method is quite component to the number of other organic and inorganic bases. The variation of the base type had modest influence on the activity

of the system. (Table 4.2, No 28-34). However, a relatively lower yield was obtained without presence of any base and also without any ligands the reaction was obtained at 30% isolated yield. (Table 4.2, No 35 and No 36).

Table 4.2.Effect of the ligand on pd-catalyzed reaction of alkenyl epoxide (**1a**) with PhBneop



No	Ligand	Base	t, hour(s)	%**3a**[a] (dr)	%**4a**
1	DPEPhos	$N(Et)_3$	3	77-69[b] (30:1)	6 [b]
2	DPEPhos[c]	$N(Et)_3$	1	66	N.D.
3	DPEPhos[d]	$N(Et)_3$	1	71	N.D.
4	Xanthphos	$N(Et)_3$	3	Complex	
5	*t*-Bu-Xantphos	$N(Et)_3$	1	63	N.D.
6	dppe	$N(Et)_3$	5 days	44	N.D.
7	dppp	$N(Et)_3$	20	-	-
8	dppb	$N(Et)_3$	1	Complex	
9	dppf	$N(Et)_3$	2	77	N.D.
10	±BINAP	$N(Et)_3$	20	22	N.D.
11	PPh_3	$N(Et)_3$	1.5	Complex	
12	$Pd(PPh_3)_4$	$N(Et)_3$	2.5	Complex	
13	$P(4\text{-}MeOC_6H_4)_3$	$N(Et)_3$	2.5	Complex	
14	$P(2\text{-}MeOC_6H_4)_3$	$N(Et)_3$	20	-	-
15	P $(4\text{-}CF_3)$ C_6H_4	$N(Et)_3$	2.5	Complex	
16	$Ph(2\text{-furyl})_3$	$N(Et)_3$	1.5	Complex	
17	$[(t\text{-}Bu)_3PH]BF_4$	$N(Et)_3$	4.5	56	N.D.
18	$[Cy_3PH]BF_4$	$N(Et)_3$	8	69	N.D.
19	$P(Bu)_3$	$N(Et)_3$	1.5	44	N.D.

(cont. on next page)

Table 4.2 (cont.)

19	$P(Bu)_3$	$N(Et)_3$	1.5	44	N.D.
20	$P(Ph_2Bn)_3$	$N(Et)_3$	20	49	N.D.
21	$P(Ph_2Me)_3$	$N(Et)_3$	20	32	N.D.
22	Xphos	$N(Et)_3$	3 days	57	N.D.
23	$P(OBu)_3$	$N(Et)_3$	1.75	62	N.D.
24	$P(OPh)_3$	$N(Et)_3$	3 days	54	N.D.
25	2,2'-Bipyridyl	$N(Et)_3$	5 days	38	N.D.
26	SIPr	$N(Et)_3$	1	68	N.D.
27	**Ph_3As**	**$N(Et)_3$**	**2.5**	**84-78[b]**	**6[b]**
28	Ph_3As	K_3PO_4	3	80	N.D.
29	Ph_3As	Cs_2CO_3	2.75	83	N.D.
30	Ph_3As	K_2CO_3	3.5	78	N.D.
31	Ph_3As	KF	3.5	80	N.D.
32	Ph_3As	KOH	1.5	82	N.D.
33	**Ph_3As**	**$(i\text{-Pr})_2NH$**	**2**	**84-79[b]**	**10[b]**
34	Ph_3As	$(i\text{-Pr})_2NEt$	4	82	N.D.
35	Ph_3As	-	3	72	N.D.
36	-	$(i\text{-Pr})_2NEt$	1.5	33-30[b]	N.D.

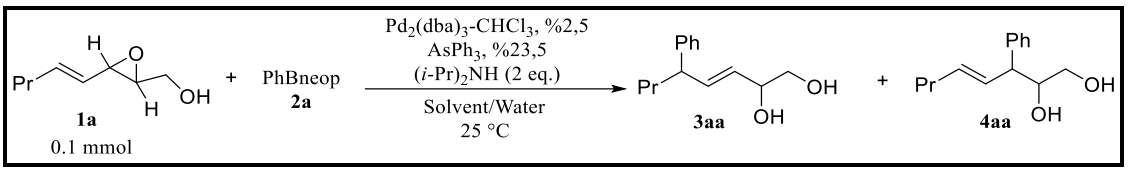
[a]Determined by internal standard using *p*-anisaldehyde by ^{1}H-NMR. [b]Isolated yield [c]%10 P. [d]%15 P

Reducing the reaction concentration to the half or doubling it caused a decrease of the reaction yield (Table 4.3, No 1 and 2). While the ratio of water in the reaction mixture directly affected the reaction time, the NMR yield of these reactions were not affected significantly (Table 4.3, No 3and 4). According to all results obtained so far, for 0.1 mmol reactant, the available solvent system was set to be 2 mL THF/0.5 mL H_2O.

The various organic solvents were tested (Table 4.3, No 5-12) and among the solvents tried, only was acetone that led to the formation of a comparable yield, albeit the reaction rate was highly diminished and took 2 days for a complete conversion (Table 4.3, No 9). The lower yields were obtained with the use of other solvents, such as DMF, isopropanol, DCM, dioxane, DME, toluene, and acetonitrile.

At 50°C, the reaction rate was relatively accelerated, but the NMR yield was slightly lowered to 78% (Table 4.3, No 13). On the other hand, at 10°C the reaction rate was reasonably decelerated though the reaction yield did not change (Table 4.3, No 14). It is obvious that doubling the reaction scale was tolerated by the method (Table 4.3, No 15). The less usage of PhBneop than 3 eqv. caused a decrease of the yield (Table 4.3, No 16 and 17).

Table 4.3. Optimization of solvent system of pd-catalyzed reaction with PhBneop



No	Solvent	Solvent/H_2O (mL)	PhBneop (eqv.)	T °C	t, hour(s)	%3aa[a]	%4aa
1	THF	4/1	3	25	5.5	66	N.D.[f]
2	THF	1/0.25	3	25	2.5	58	N.D.
3	THF	2/0.25	3	25	5	80	N.D.
4	THF	2/1	3	25	2.25	82	N.D.
5	DCM	2/0.5	3	25	5.2	36	N.D.
6	Toluene	2/0.5	3	25	5.2	50	N.D.
7	DMF	2/0.5	3	25	O.N.	65	N.D.
8	Isopropanol	2/0.4	3	25	O.N.	74	N.D.
9[c]	Acetone	2/0.4	3	25	2 days	82	N.D.
10[c]	1.4-Dioxane	2/0.5	3	25	5.5	73	N.D.
11	Acetonitrile	2/0.5	3	25	O.N.	48[e]	N.D.
12	DME[g]	2/0.5	3	25	O.N.	76	N.D.
13	THF	2/0.5	3	50	<1	78	N.D.
14	THF	2/0.5	3	10	O.N.	83	N.D.
15[d]	THF	4/1	3	25	3	83-76[b]	12[b]
16[d]	THF	4/1	2	25	3.5	70	N.D.
17[d]	THF	4/1	1.5	25	5	51	N.D.

[a]Determined by ^{1}H-NMR using *p*-anisaldehyde as the internal standard. [b]Isolated yield. [c]Not dried solvents. [d] 0.2 mmol reactant. [e]Reactant was not consumed completely. [f]N. D.: Not determined. [g]The base is NEt_3.

An another type of organoboron ester, the pinacol ester of phenylboronic acid was also reacted with alkenyl oxirane **1a**. The reaction kinetic was slowed by this change and the desired product was obtained with lower yield as 71% (Figure 2.2).

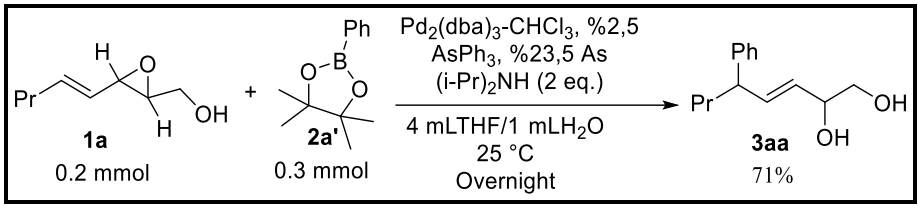
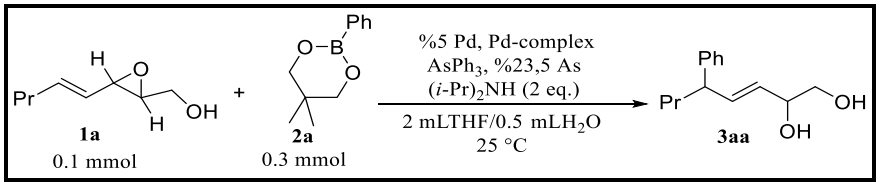


Figure 4.2.The reaction of alkenyl oxirane with pinacol ester of phenylboronic acid

In the arylation reactions, catalytic effects of some of pd complexes were also examined and it was observed that palladium acetate and π-allyl palladium chloride dimer which are Pd(II)-complexes were not effective as compared to Pd (0)-complexes. These catalysts slowed the reaction for a full conversion of the reactant and the lover yields were gained (Table 4.4, No 1 and 2). Non-solvent coordinated $Pd_2(dba)_3$ complex showed a lower catalytic activity than $Pd_2(dba)_3 \cdot CHCl_3$ (Table 4.4, No 3 and Table 4.2, No 27).

Table 4.4. Arylation reactions of the vinyl epoxide **1a** with various Pd-catalysts



No	Pd	T, hour(s)	% **3aa**[a]
1	$Pd(OAc)_2$	2 days	66
2	$[PdCl(C_3H_5)]_2$	2 days	51
3	$Pd_2(dba)_3$	O. N.	77

[a]Determined by ^{1}H-NMR using *p*-anisaldehyde as the internal standard.

The table 4.5 includes the results of arylation reaction of the vinyl epoxide **1a** with various RBneop reagents. The method was effectively applicable to electron-rich arylborons (Table 4.5, No 1-3 and 7-8) and 2-napthylboron reagent (Table 4.5, No 5 and 6). The desired product **3a** was formed with these organoborons at high yields and diastereomeric ratios. Although the *ortho*-substituted methyl, methoxy and 1-napthyl organoborons substrates which are relatively sterically hindered reagents (Table 4.5, No

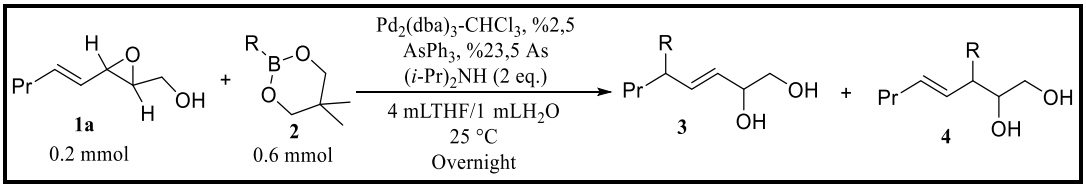
2,6 and 8) slowed down the reaction rate, their performance from the point of allylic substitution yield was more or less comparable to other isomers.

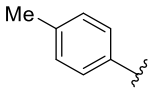
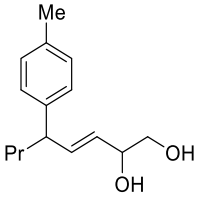
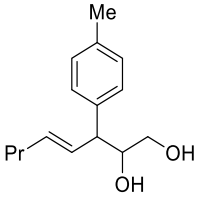
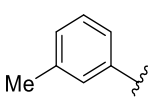
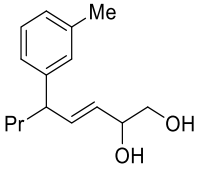
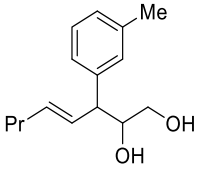
It was noticed that the organoborons having electron-withdrawing groups showed a weak performance in the reaction. Longer reaction periods are required for complete conversion of the vinyl epoxide with these reagents and moderate yields were recovered with *p*- and *m*- substituted ones (Table 4.5, No 9, 10 and 12). A low yield was obtained with a *o*-substituted electron poor organoboron reagent **2m** (Table 4.5), No 11). This reactivity difference might be resulted from in the less reactivity of the electron poor organoborons toward transmetallation step with the intermediate of π-allyl palladium complex.

The reaction with an alkenyl boron derivative containing a phenyl group resulted in the formation of product at 80% yield and with relatively lower 10:1 diastereomeric ratio (Table 4.5, No 13). On the other hand, alkenyl boron compound containing propyl group showed lower activity and the product **3ap** was formed at 30% yield (Table 4.5, No 14).

During a reaction with thiophenylboron ester **2r** palladium black formation was observed in first hour of the reaction and as a result the vinyl epoxide was recovered as it is. (Table 4.5, No 15).

Table 4.5.Reaction of vinyl epoxide 1a with various neopentyl glycol esters



No	Boron ester, **2**	Time, h	Product, **3**	**3**% (dr)	Product, **4**	**4**%
1	 **2b**	1.75	 **3ab**	76 (>20)	 **4ab**	6
2	 **2c**	1.67	 **3ac**	75 (>20)	 **4ac**	2

(cont. on next page)

Table 4.5 (cont.)

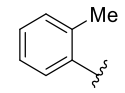
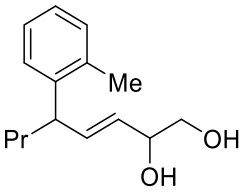
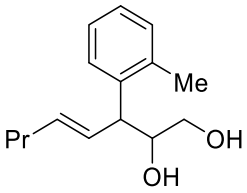
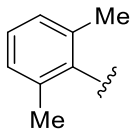
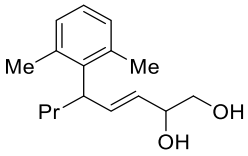
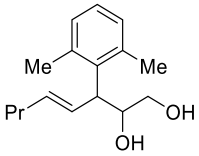
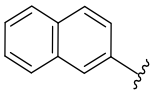
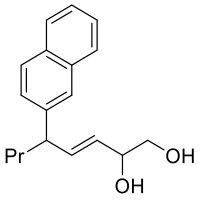
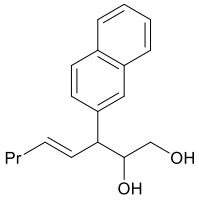
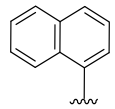
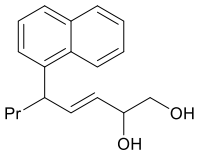
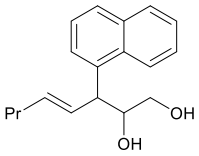
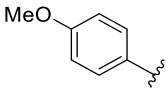
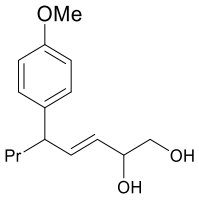
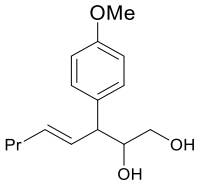
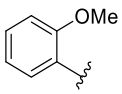
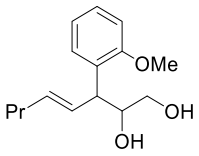
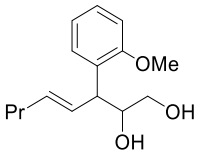
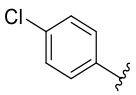
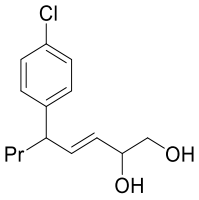
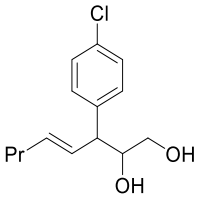
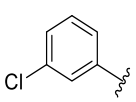
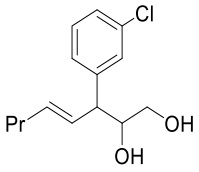
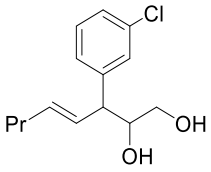
3	 **2d**	O. N.	 **3ad**	79 (9:1)	 **4ad**	-
4	 **2e**	O.N.	 **3ae**	12[x] (>20)	 **4ae**	-
5	 **2f**	3.75	 **3af**	74 (>20)	 **4af**	10
6	 **2g**	O. N.	 **3ag**	75 (>20)	 **4ag**	7
7	 **2h**	1.5	 **3ah**	80 (>20)	 **4ah**	8
8	 **2i**	O. N.	 **3ai**	78 (>20)	 **4ai**	4[x]
9	 **2j**	O. N.	 **3aj**	56 (>20)	 **4aj**	2
10	 **2k**	O. N.	 **3ak**	53 (>20)	 **4ak**	-

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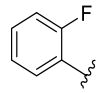
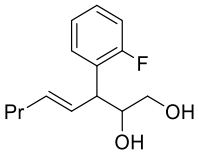
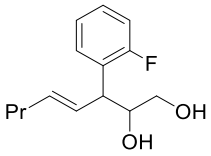
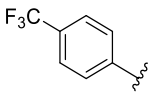
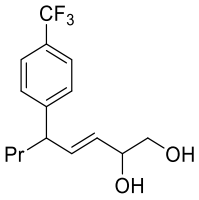
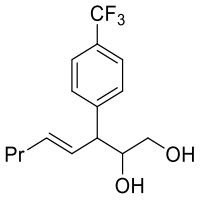
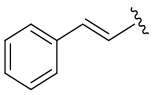
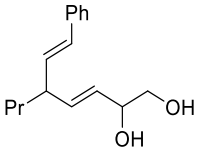
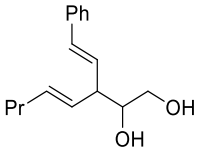
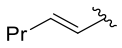
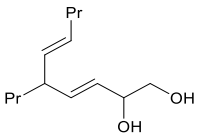
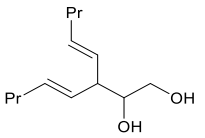
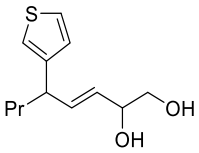
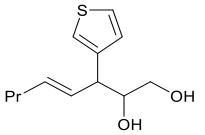
Table 4.5 (cont.)

11	 **2m**	4 days	 **3am**	23 (>20)	 **4am**	-
12	 **2n**	O. N.	 **3an**	51 (>20)	 **4an**	5
13	 **2o**	2	 **3ao**	80 (10:1)	 **4ao**	7
14	 **2p**	O. N.	 **3ap**	30 (>20)	 **4ap**	<1
15	 **2r**	O. N.	 **3ar**	-	 **4ar**	-

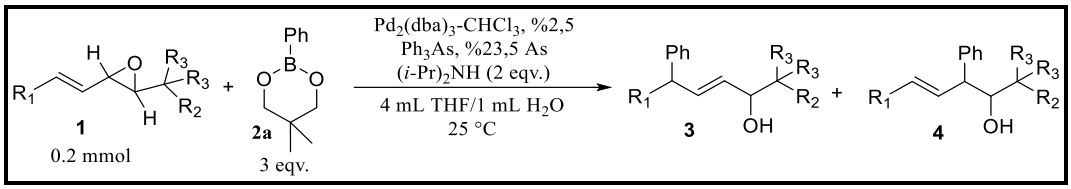
O. N.: Overnight. N. D.: Not determined. Dr: Diastereomeric ratio.

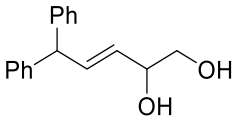
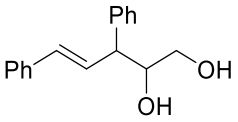
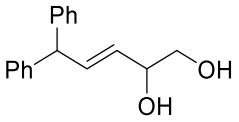
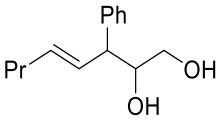
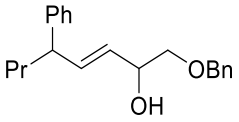
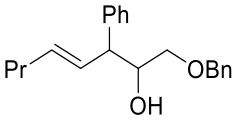
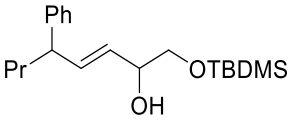
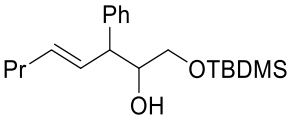
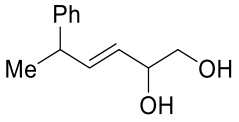
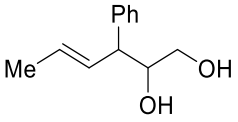
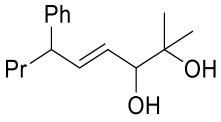
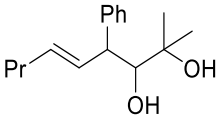
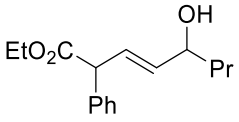
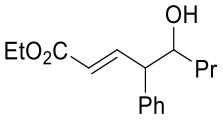
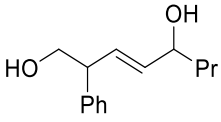
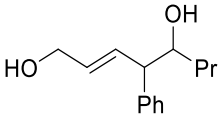
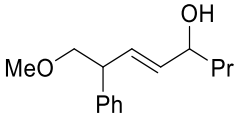
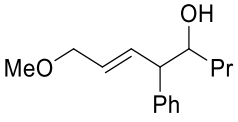
Next, the substrate scope of the method was also surveyed over various alkenyl oxiranes. The use of vinyl epoxide with phenyl group attached to the far alkenyl carbon as the reactant in the reaction resulted in a complex mixture. Although the desired product **3ea** compound could not be isolated, the simple substitution product **4ea** was determined to be 30% yield by NMR technique (Table 4.6, No 1). The reaction with DPEphos ligand of **1e** also did not alter the reaction fate at all (Table 4.6, No 2).

When the hydroxyl group was protected by methyl (**1c**) and silyl (**1d**) groups, the ratio of regio-selectivities of reactions were decreased (Table 4.6, No 3 and 4). It was possible that the coordination of the oxygen containing group which was next to the oxirane ring with the Pd-metal somehow influences the regio-selectivity on the reaction. The reaction's efficiency was not affected with by the presence of a methyl group at R_1 and at R_3. Therefore, the yields of these reactions were obtained at high level (Table 4.6, No 5 and 6).

The reactant having an ester group at R_1 led to only the formation of the simple substitution product **4ha** exclusively (Table 4.6, No 7). While the presence of a hydroxyl group within R1 lowered the regio-selectivity of the process the methyl protection of this group even further worsened the selectivity and lower total yields were obtained (Table 4.6, No 8 and 9).

Table 4.6. The pd-catalyzed reaction of various alkenyl epoxides with PhBneop



No	t, h	Product **3** (yield%)	Product **4** (yield%)
1	O.N.	 **3ea** (N.D.)	 **4ea** (30%)[a]
2[b]	O.N.	 **3ea** (3%)	 **4ea** (12%)[a]
3	7	 **3ca** (66%)	 **4ca** (25%)
4	5.3	 **3da** (65%)	 **4da** (18%)
5	1.5	 **3fa** (84%)[a]	 **4fa** (-)
6	4.7	 **3ga** (79%)	 **4ga** (10%)
7	2 days	 **3ha** (-)	 **4ha** (51%)
8	6	 **3ia** (51%)[a]	 **4ia** (25%)[a]
9	10	 **3ja** (22%)	 **4ja** (10%)

[a]Determined by ^{1}H-NMR using *p*-anisaldehyde as the internal standard.[b] The reaction was performed using DPEPhos ligand (22.5 P).

In Figure 4.3, with the oxirane having fully alkyl groups, the reaction was resulted in 65% isolated yield after overnight reaction period. And in figure 4.5, the reaction of mono alkyl substituted oxiranes gave 44% isolated yield for **3ma** and 16% isolated yield for **4ma** product.

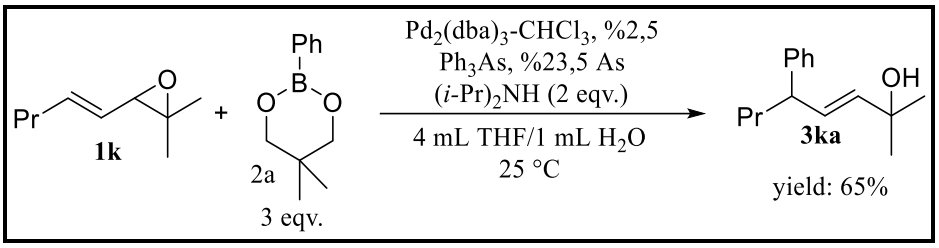


Figure 4.3. Syntesis of *(E)*-2-methyl-5-phenyloct-3-en-2-ol

The reaction also was tried on a cyclic structure. Conversely, the reaction with 3,4-epoxycyclohexene was complete in 1 hour, but a complex mixture was obtained instead of the desired arylated product.

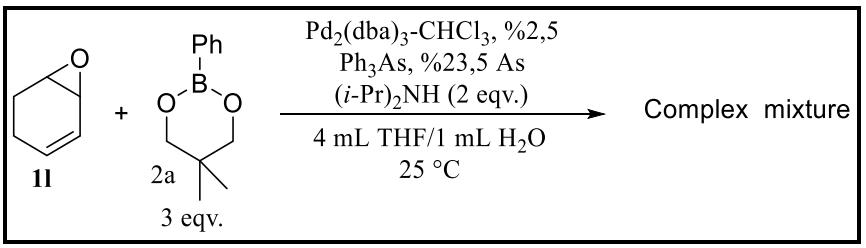


Figure 4.4. The reaction of 3,4-epoxy cyclohexene

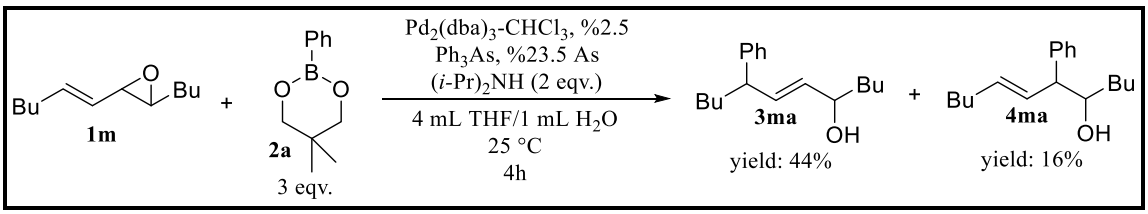


Figure 4.5 The reaction of (E)-2-butyl-3-(hex-1-en-1-yl)oxirane

CHAPTER 5

CONCLUSION

As a consequence, a new 1,3-substitution selective arylation reaction of vinyl oxiranes was performed with aryl or alkenyl neopentyl glycol boron esters in the presence of triphenyl arsine ligated tris(dibenzylideneacetone)dipalladium (0) chloroform adduct. The products were obtained with highly diastereomeric ratios

The advantages of reaction are the applicability at room temperature, the use of various stable boron esters in aqueous medium.

REFERENCES

Bäckvall, J.-E., E.S.M. Persson, and A. Bombrun. 1994. “Regiocontrol in Copper-Catalyzed Cross Coupling of Allylic Chlorides with Aryl Grignard Reagents.” *J. Org. Chem.* 59 (15): 4126–30.

Crotti, Stefano, Ferruccio Bertolini, Franco Macchia, and Mauro Pineschi. 2009. “Nickel-Catalyzed Borylative Ring Opening of Vinyl Epoxides and Aziridines.” *Organic Letters* 11 (16): 3762–65. doi:10.1021/ol901429g.

Dieter, R. Karl, Yaxin Huang, and Fenghai Guo. 2012. “Regio- and Stereoselectivity in the Reactions of Organometallic Reagents with an Electron-Deficient and an Electron-Rich Vinyloxirane: Applications for Sequential Bis-Allylic Substitution Reactions in the Generation of Vicinal Stereogenic Centers.” *Journal of Organic Chemistry* 77 (11): 4949–67. doi:10.1021/jo300304n.

Farthing, Christopher N, and Pavel Koc. 1998. “The Stereochemical Dichotomy in Palladium (0) - and Nickel (0) -Catalyzed Allylic Substitution” 7863 (0): 6661–72.

Guan, Yifu, Hongbin Zhang, Chengxue Pan, Jia Wang, Rong Huang, and Qilin Li. 2012. “Flexible Synthesis of Montanine-like Alkaloids: Revisiting the Structure of Montabuphine.” *Organic & Biomolecular Chemistry* 10 (19): 3812–14. doi:10.1039/c2ob25374g.

Hata, Takeshi, Rie Bannai, Mamoru Otsuki, and Hirokazu Urabe. 2010. “Iron-Catalyzed Regio- and Stereoselective Substitution of Γ,δ-Epoxy-A,β-Unsaturated Esters and Amides with Grignard Reagents.” *Organic Letters* 12 (5): 1012–14. doi:10.1021/ol100022w.

Kacprzynski, Monica A., Tricia L. May, Stephanie A. Kazane, and Amir H. Hoveyda. 2007. “Enantioselective Synthesis of Allylsilanes Bearing Tertiary and Quaternary Si-Substituted Carbons through Cu-Catalyzed Allylic Alkylations with Alkylzinc and Arylzinc Reagents.” *Angewandte Chemie - International Edition* 46 (24): 4554–58. doi:10.1002/anie.200700841.

Kjellgren, Johan, Juhanes Aydin, Olov A. Wallner, Irina V. Saltanova, and Kálmán J. Szabó. 2005. “Palladium Pincer Complex Catalyzed Cross-Coupling of Vinyl Epoxides and Aziridines with Organoboronic Acids.” *Chemistry - A European Journal* 11 (18): 5260–68. doi:10.1002/chem.200500270.

Kus, Melih, and Levent Artok. 2015. “Palladium-Catalyzed Alkoxycarbonylation of Conjugated Enyne Oxiranes: A Diastereoselective Method for the Synthesis of 7 -Hydroxy-2,3,5-Trienoates.” doi:10.1021/acs.joc.5b00382.

Matthew, S C, B W Glasspoole, P Eisenberger, and C M Crudden. 2014. “Synthesis of

Enantiomerically Enriched Triarylmethanes by Enantiospecific Suzuki-Miyaura Cross-Coupling Reactions." *J Am Chem Soc* 136 (16): 5828–31. doi:10.1021/ja412159g.

Millet, Renaud, and Alexandre Alexakis. 2007. "Copper-Catalyzed Kinetic Resolution of 1,3-Cyclohexadiene Monoepoxide with Grignard Reagents." *Synlett*, no. 3: 435–38. doi:10.1055/s-2007-967945.

———. 2008. "SimplePhos as Efficient Ligand for the Copper-Catalyzed Kinetic Resolution of Cyclic Vinyloxiranes with Grignard Reagents." *Synlett* 2008 (12): 1797–1800. doi:10.1055/s-2008-1077901.

Miyaura, Norio, Kinji Yamada, and Akira Suzuki. 1979. "A New Stereospecific Cross-Coupling by the Palladium-Catalyzed Reaction of 1-Alkenylboranes with 1-Alkenyl or 1-Alkynyl Halides." *Tetrahedron Letters* 20 (36): 3437–40. doi:10.1016/S0040-4039(01)95429-2.

Ohmiya, Hirohisa, Natsumi Yokokawa, and Masaya Sawamura. 2010. "Copper-Catalyzed ??-Selective and Stereospecific Allyl-Aryl Coupling between (Z)-Acyclic and Cyclic Allylic Phosphates and Arylboronates." *Organic Letters* 12 (10): 2438–40. doi:10.1021/ol100841y.

Polet, Damien, Xavier Rathgeb, Caroline A Falciola, Jean Baptiste Langlois, Samir El Hajjaji, and Alexandre Alexakis. 2009. "Enantioselective Iridium-Catalyzed Allylic Arylation." *Chemistry - A European Journal* 15 (5): 1205–16. doi:10.1002/chem.200801879.

Selim, Khalid B, Yasumasa Matsumoto, Ken-ichi Yamada, and Kiyoshi Tomioka. 2009. "Efficient Chiral N-Heterocyclic Carbene / Copper (I) -Catalyzed Asymmetric Allylic Arylation with Aryl Grignard Reagents ** Zuschriften" 2 (I): 8889–91. doi:10.1002/ange.200904676.

Selim, Khalid B, Ken-ichi Yamada, and Kiyoshi Tomioka. 2008. "Copper-Catalyzed Asymmetric Allylic Substitution with Aryl and Ethyl Grignard Reagents." *Chemical Communications (Cambridge, England)*, no. 41: 5140–42. doi:10.1039/b809140d.

Takeda, Momotaro, Keishi Takatsu, Ryo Shintani, and Tamio Hayashi. 2014. "Synthesis of Quaternary Carbon Stereocenters by Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Arylboronates."

Tortosa, Mariola. 2011. "Synthesis of Syn and Anti 1,4-Diols by Copper-Catalyzed Boration of Allylic Epoxides." *Angewandte Chemie - International Edition* 50 (17): 3950–53. doi:10.1002/anie.201100613.

Trost, Barry M., and Matthew L. Crawley. 2003. "Asymmetric Transition-Metal-Catalyzed Allylic Alkylations: Applications in Total Synthesis." *Chemical Reviews* 103 (8): 2921–43. doi:10.1021/cr020027w.

Ueki, Hisanori, Takashi Chiba, Takashi Yamazaki, and Tomoya Kitazume. 2005. “Highly Regio- and Stereocontrolled SN2′ Reactions of Gem-Difluorinated Vinyloxiranes with Monoalkylcopper Reagents.” *Tetrahedron* 61 (47): 11141–47. doi:10.1016/j.tet.2005.09.018.

Üçüncü, Muhammed, Erman Karakuş, Melih Kuş, Gürkan Eray Akpinar, Özge Aksin-Artok, Norbert Krause, Sila Karaca, Nuran Elmaci, and Levent Artok. 2011. “Rhodium- and Palladium-Catalyzed 1,5-Substitution Reactions of 2-En-4-Yne Acetates and Carbonates with Organoboronic Acids.” *Journal of Organic Chemistry* 76 (15): 5959–71. doi:10.1021/jo200201r.

Whittaker, Aaron M, Richard P Rucker, and Gojko Lalic. 2010. “Catalytic SN2???-Selective Substitution of Allylic Chlorides with Arylboronic Esters.” *Organic Letters* 12 (14): 3216–18. doi:10.1021/ol101171v.

Yoshikai, Naohiko, Song Lin Zhang, and Eiichi Nakamura. 2008. “Origin of the Regio- and Stereoselectivity of Allylic Substitution of Organocopper Reagents.” *Journal of the American Chemical Society* 130 (39): 12862–63. doi:10.1021/ja804682r.

APPENDIX A

^{1}H NMR AND ^{13}CNMR SPECTRUMS OF REACTANTS

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Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
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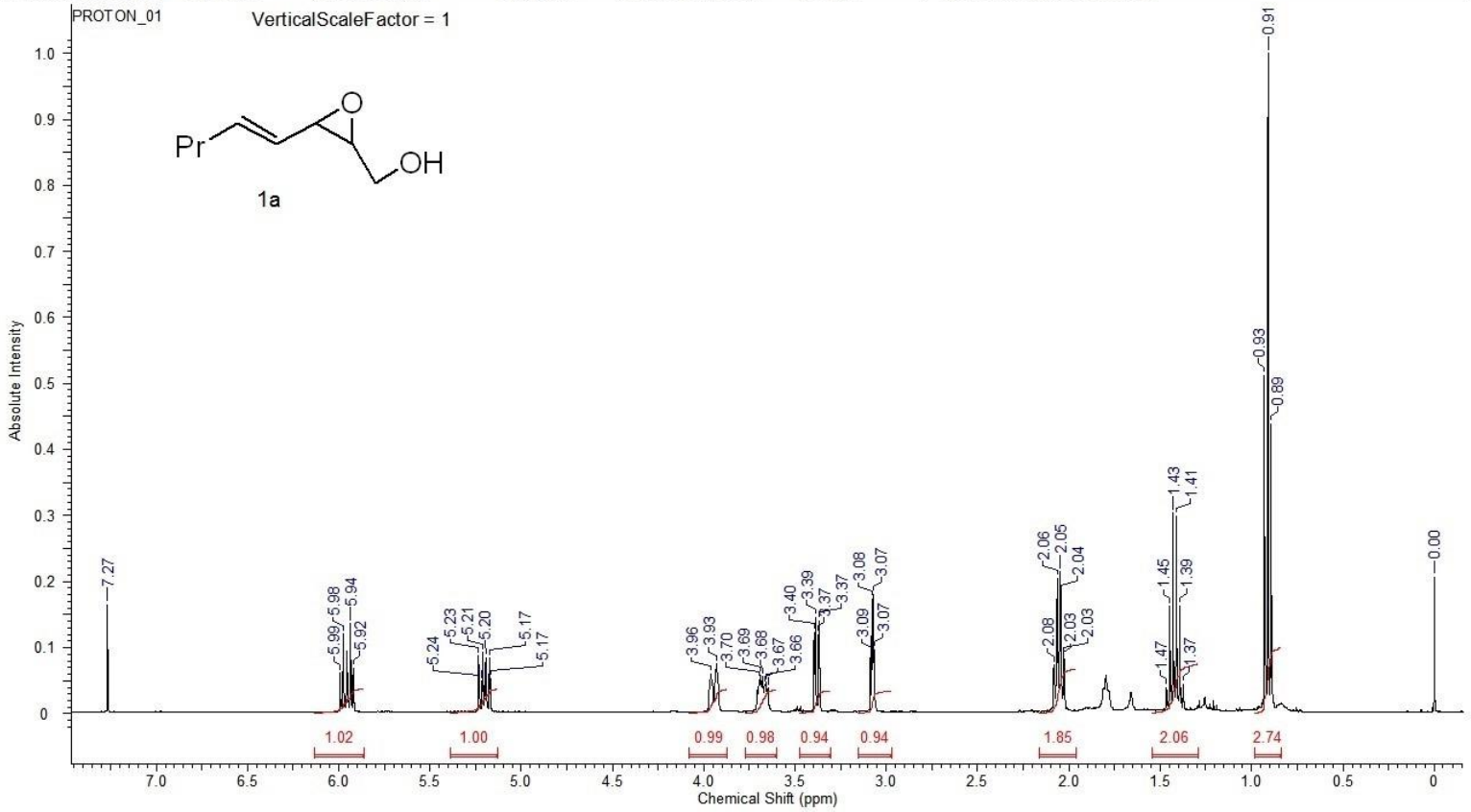

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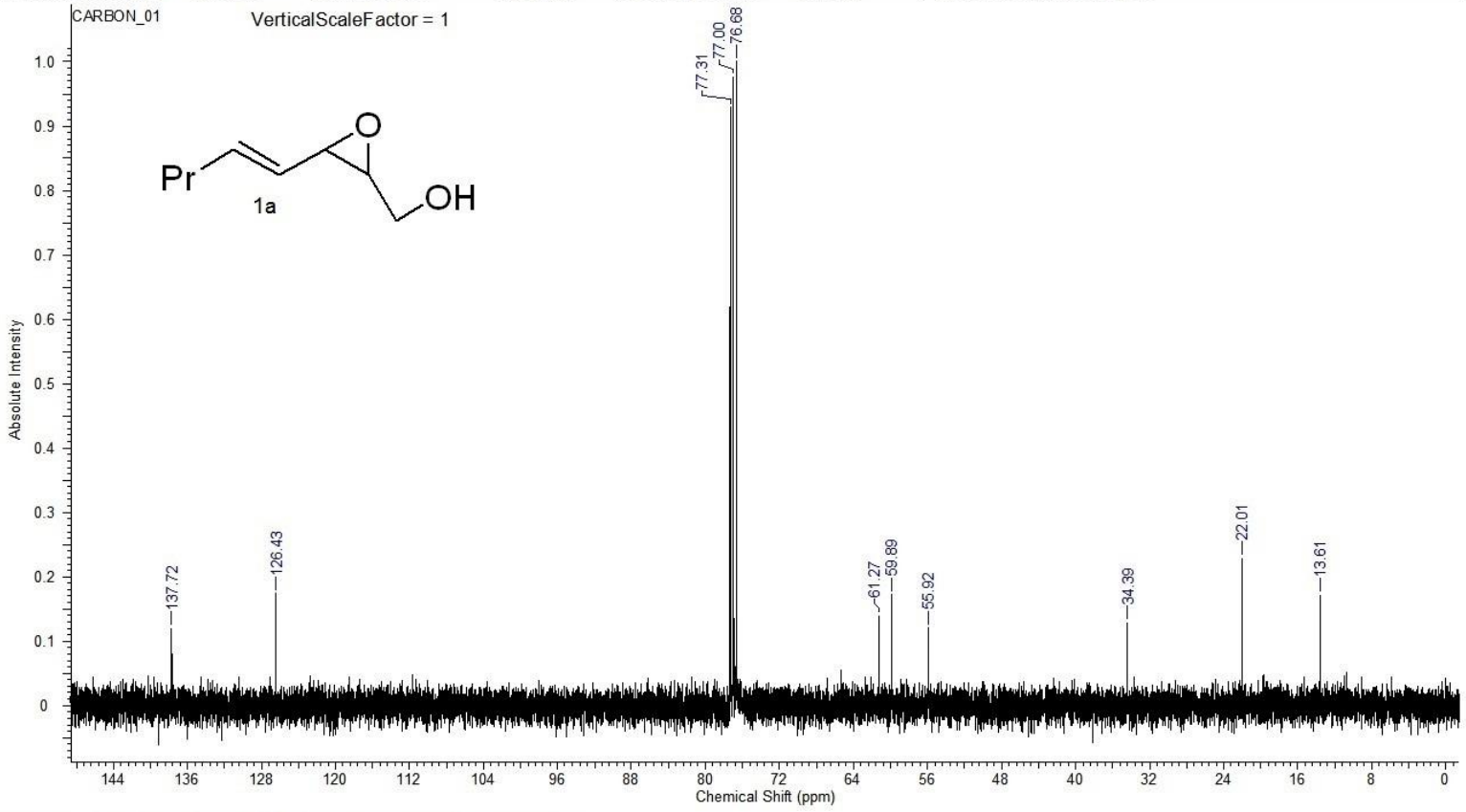

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1b

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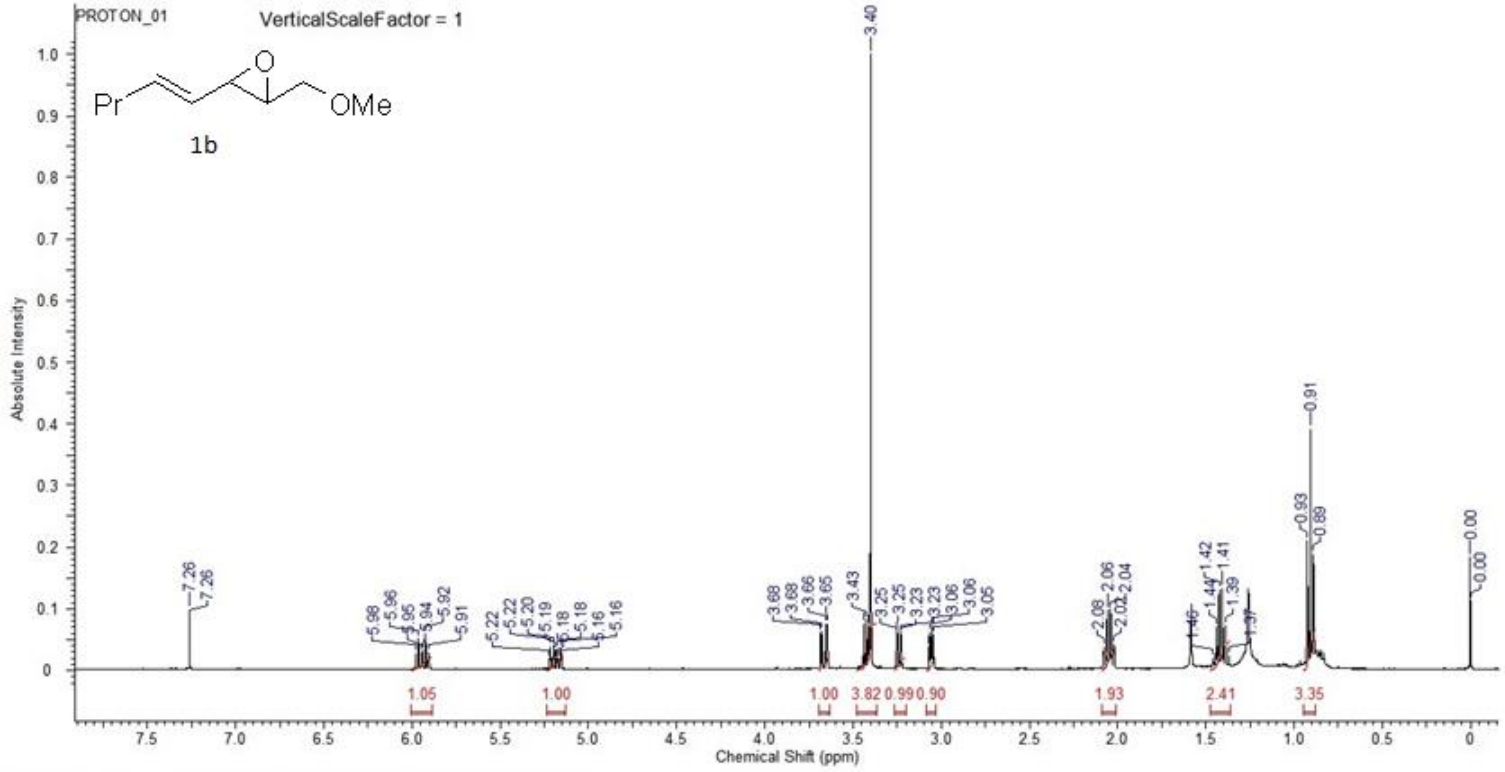
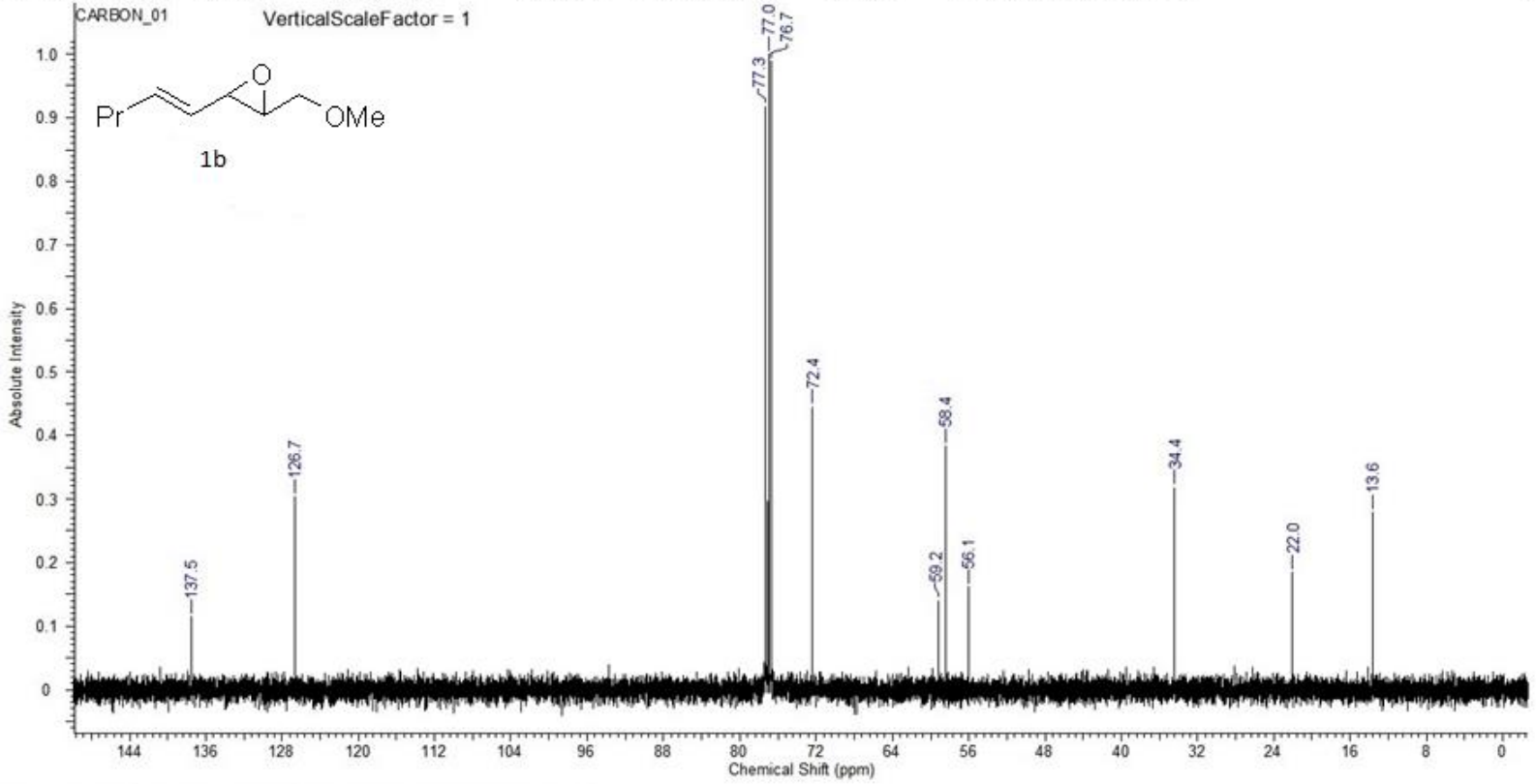
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2400.6670	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



C:\Users\Erman\Desktop\ERMAN\ERM-STZ-ENEPO-OME_20150804_01\PROTON_01

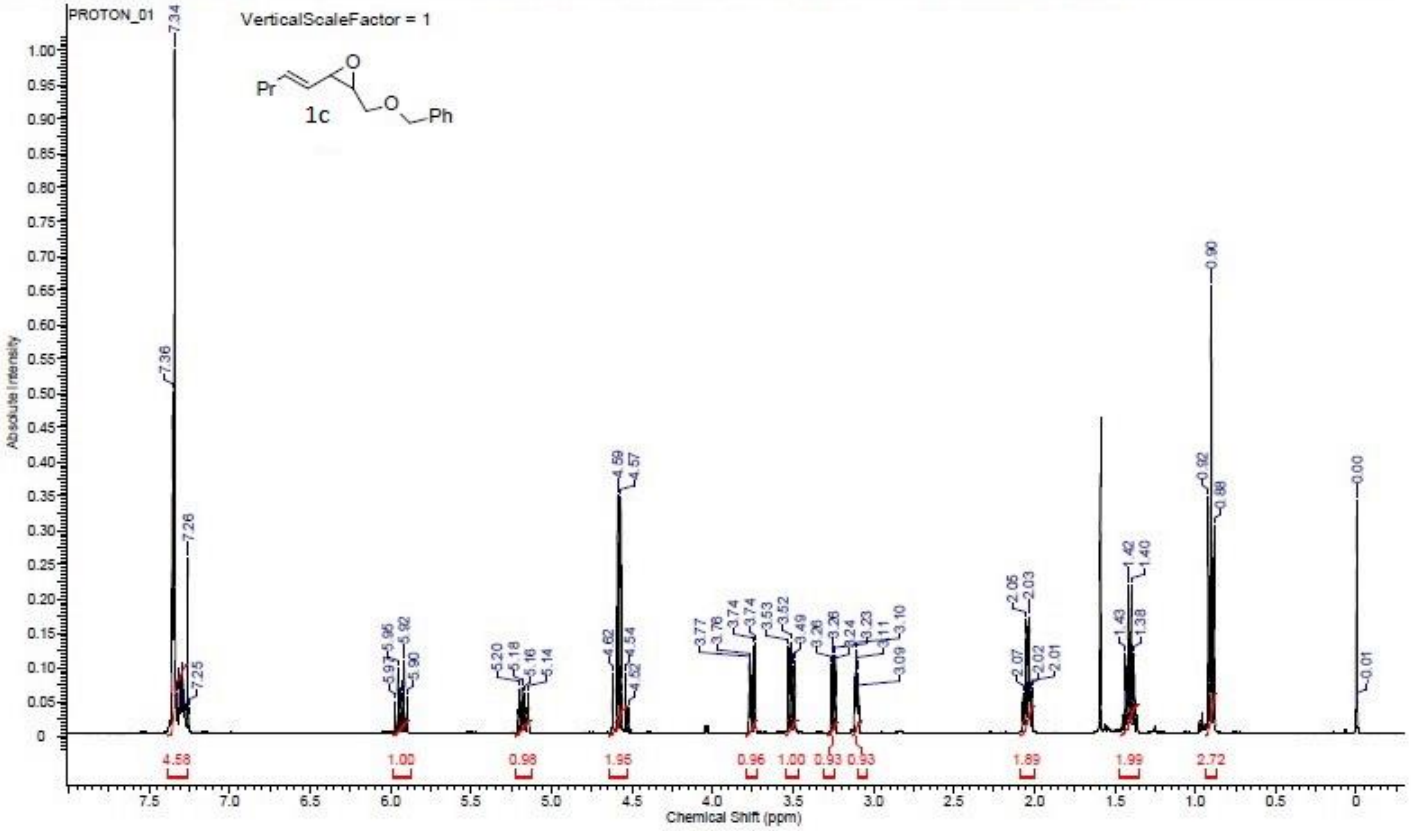
12.10.2015 13:21:26
1b

Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEPO-OME			*Date*	Mar 16 2015
Date Stamp	Mar 16 2015	*File Name*	C:\Users\Erman\Desktop\ERMAN\ERM-ENEPO-OME_20150316_01\CARBON_01.fid\fid				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

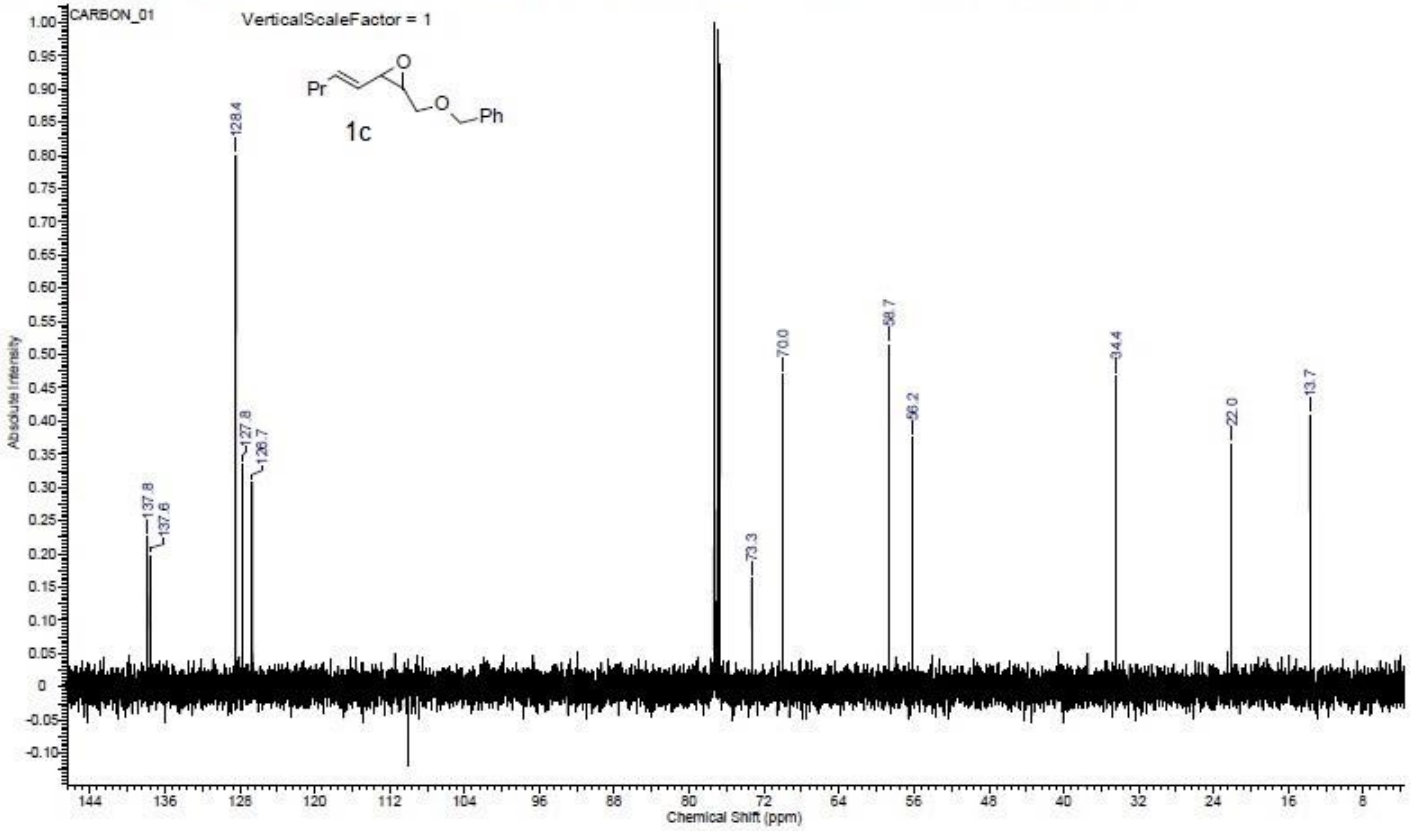


C:\Users\Erman\Desktop\ERMAN\ERM-ENEPO-OME_20150316_01\CARBON_01

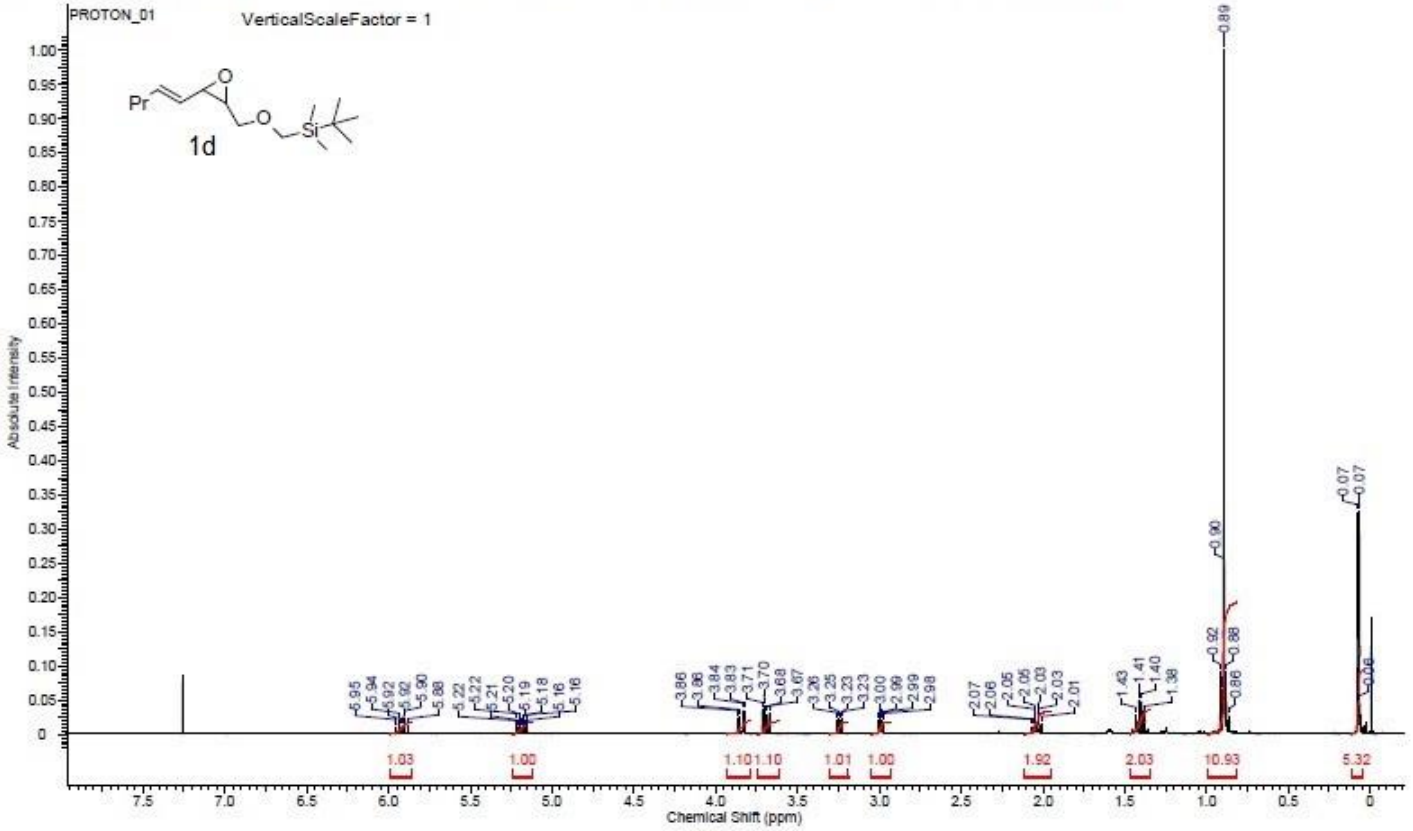
Acquisition Time (sec)	2.5559	*Comment*	ERM-STZ-PR-ENEP-OBN			*Date*	Jan 4 2016
Date Stamp	Jan 4 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-STZ-PR-ENEP-OBN_20160104_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



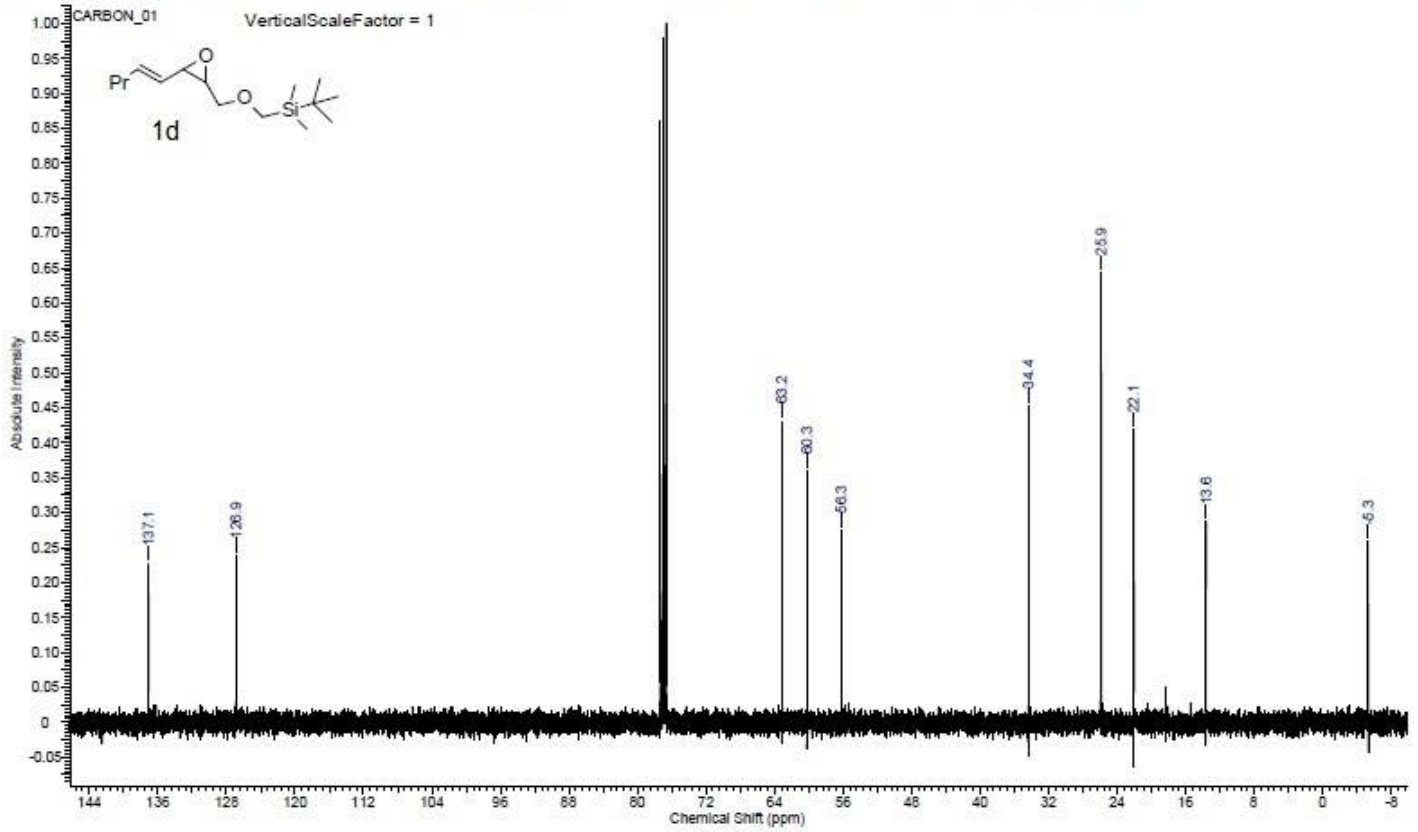
Acquisition Time (sec)	1.3107	*Comment*	ERM-STZ-PR-ENEP-OBN			*Date*	Jan 4 2016
Date Stamp	Jan 4 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-STZ-PR-ENEP-OBN_20160104_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



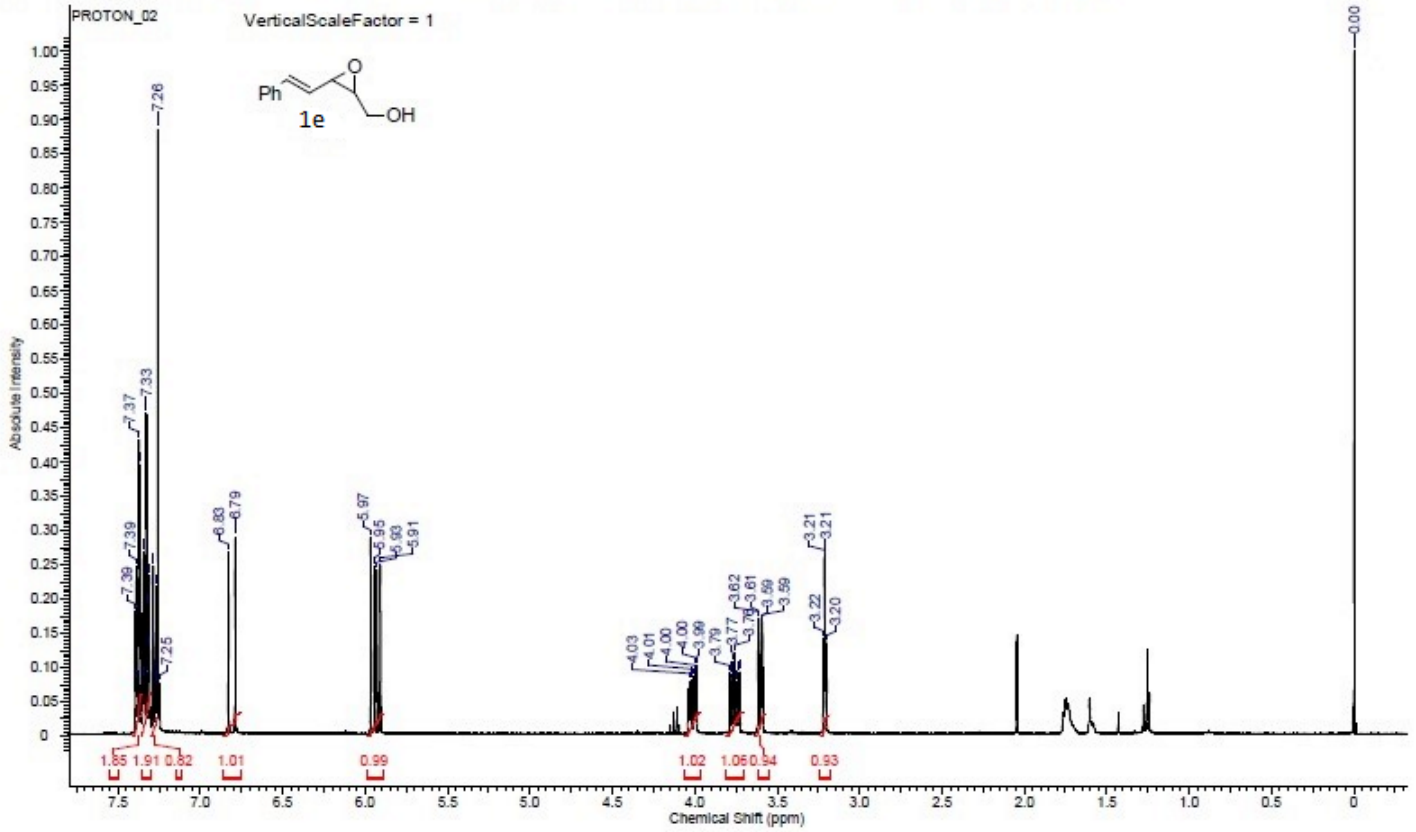
Acquisition Time (sec)	2.5559	*Comment*	ERM-STZ-PR-OTDMBS			*Date*	Dec 18 2015
Date Stamp	Dec 18 2015	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-STZ-PR-OTDMBS_20151218_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



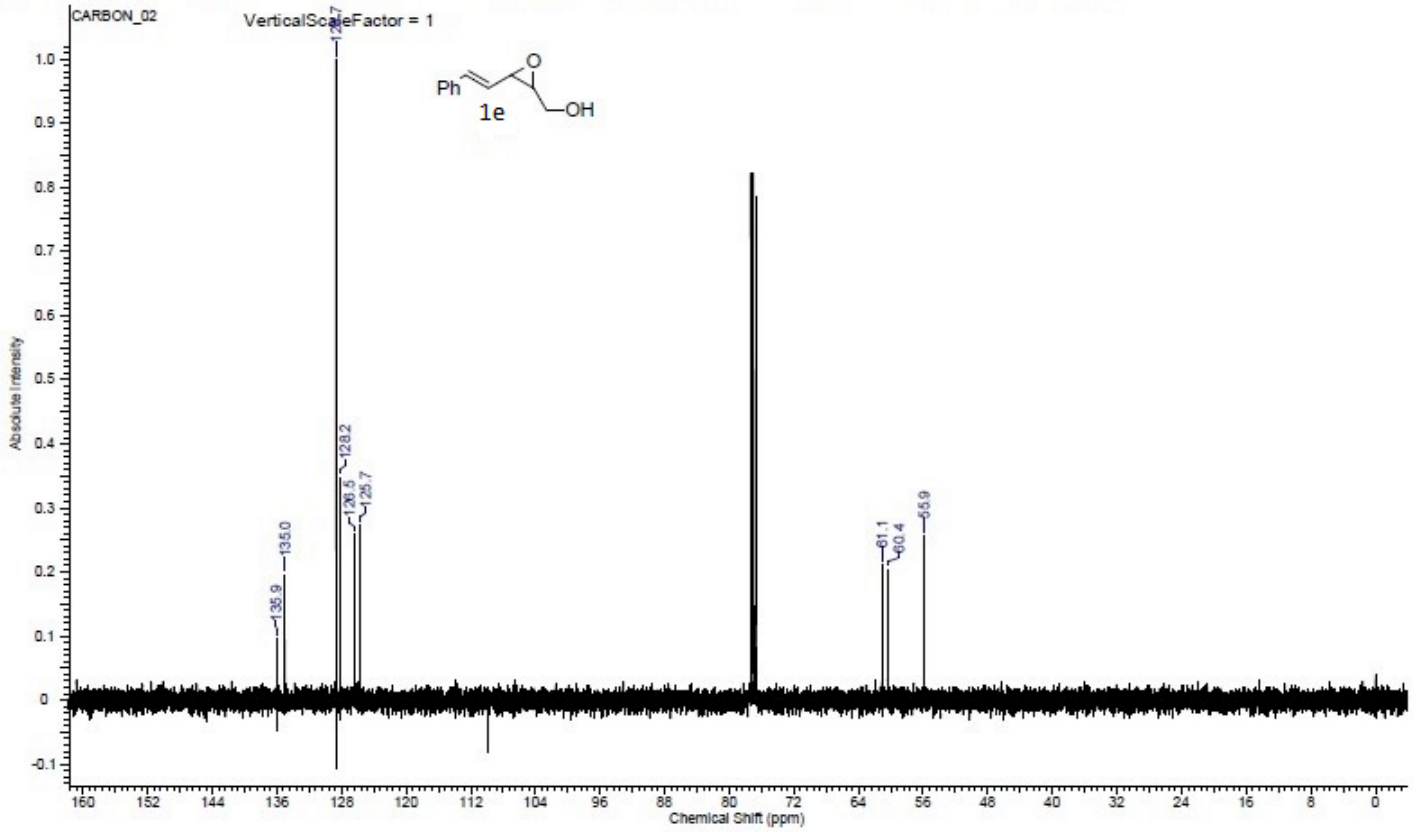
Acquisition Time (sec)	1.3107	*Comment*	ERM-STZ-PR-OTDMBS			*Date*	Dec 18 2015
Date Stamp	Dec 18 2015	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-STZ-PR-OTDMBS_20151218_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



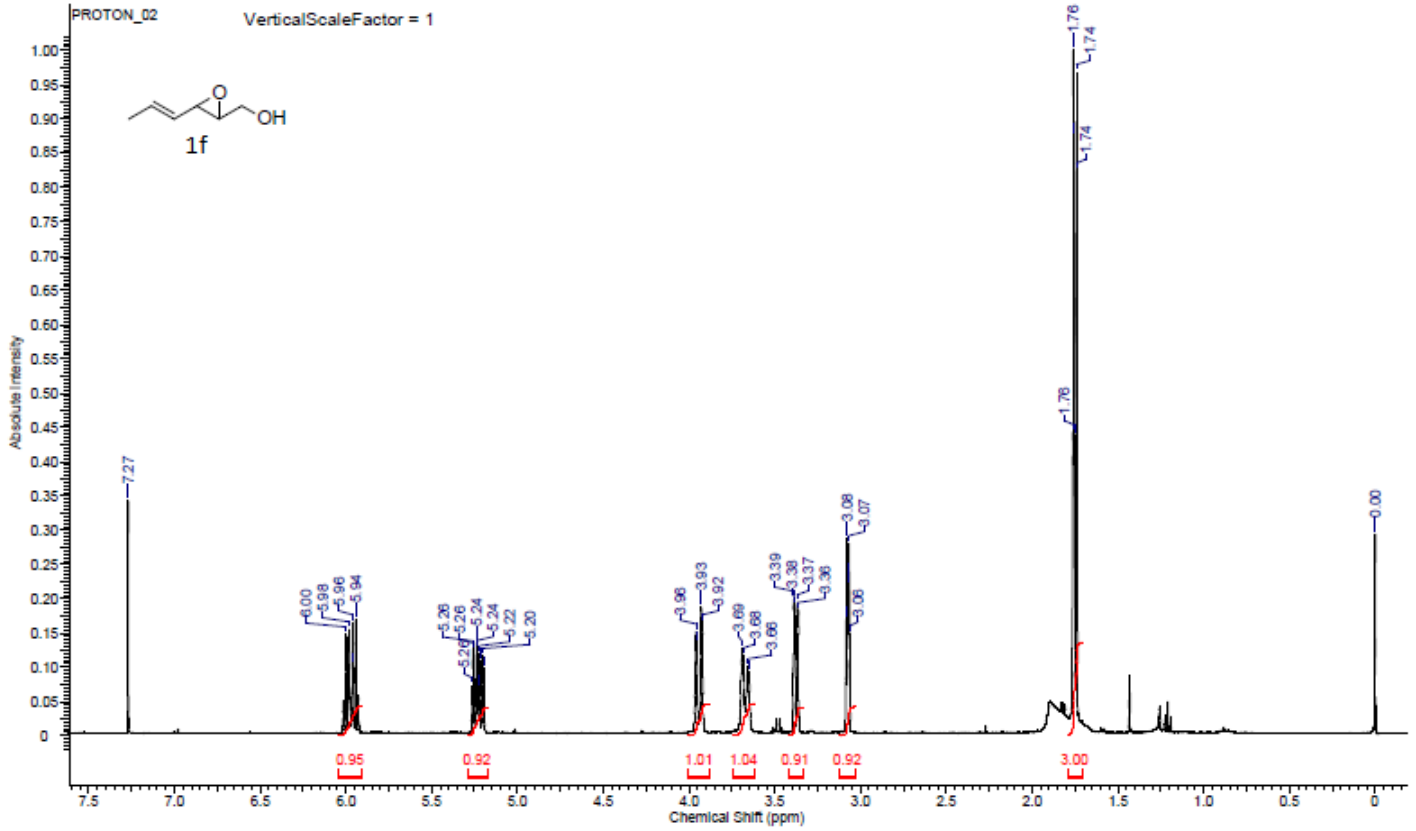
Acquisition Time (sec)	2.5559	*Comment*	ERM-PH-ENEP-OH			*Date*	Jan 18 2016
Date Stamp	Jan 18 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-PH-ENEP-OH_20160118_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



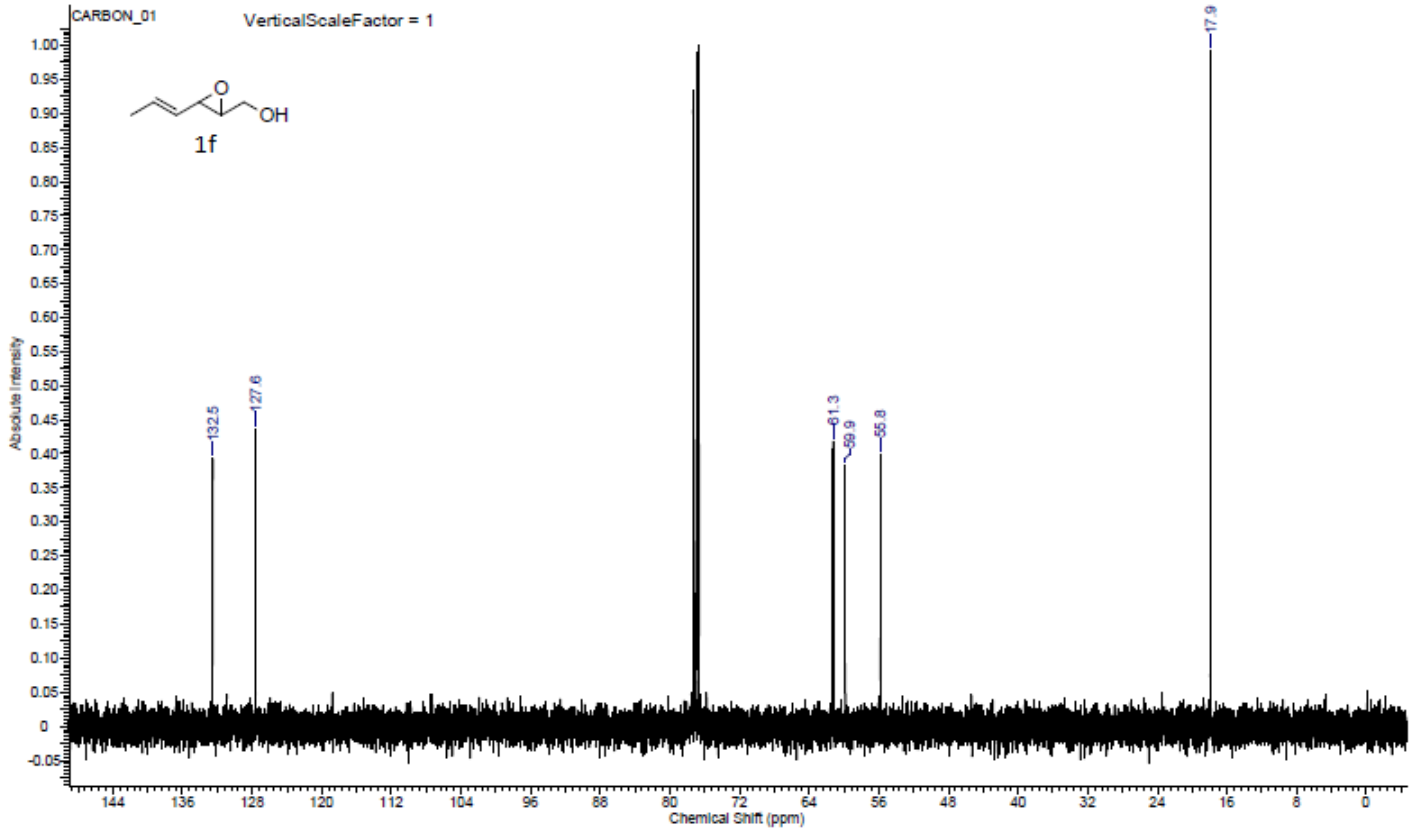
Acquisition Time (sec)	1.3107	*Comment*	ERM-PH-ENEP-OH			*Date*	Jan 18 2016
Date Stamp	Jan 18 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-PH-ENEP-OH_20160118_01\CARBON_02.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



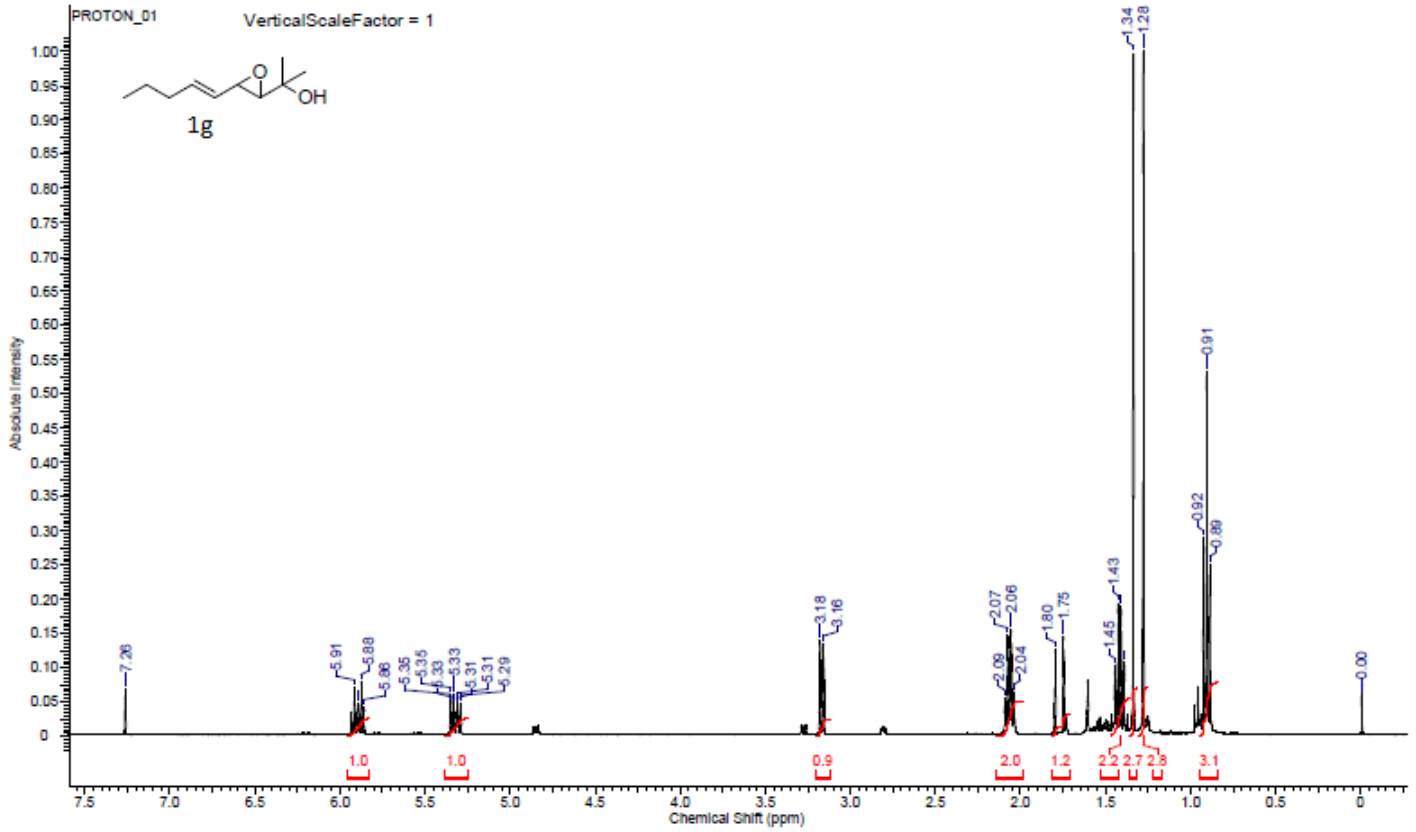
Acquisition Time (sec)	2.5559	*Comment*	ERM-STZ-ME-ENEP-OH			*Date*	May 31 2016
Date Stamp	May 31 2016	*File Name*	F:\UNTITLED FOLDER\ERM-STZ-ME-ENEP-OH_20160531_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2403.0146	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



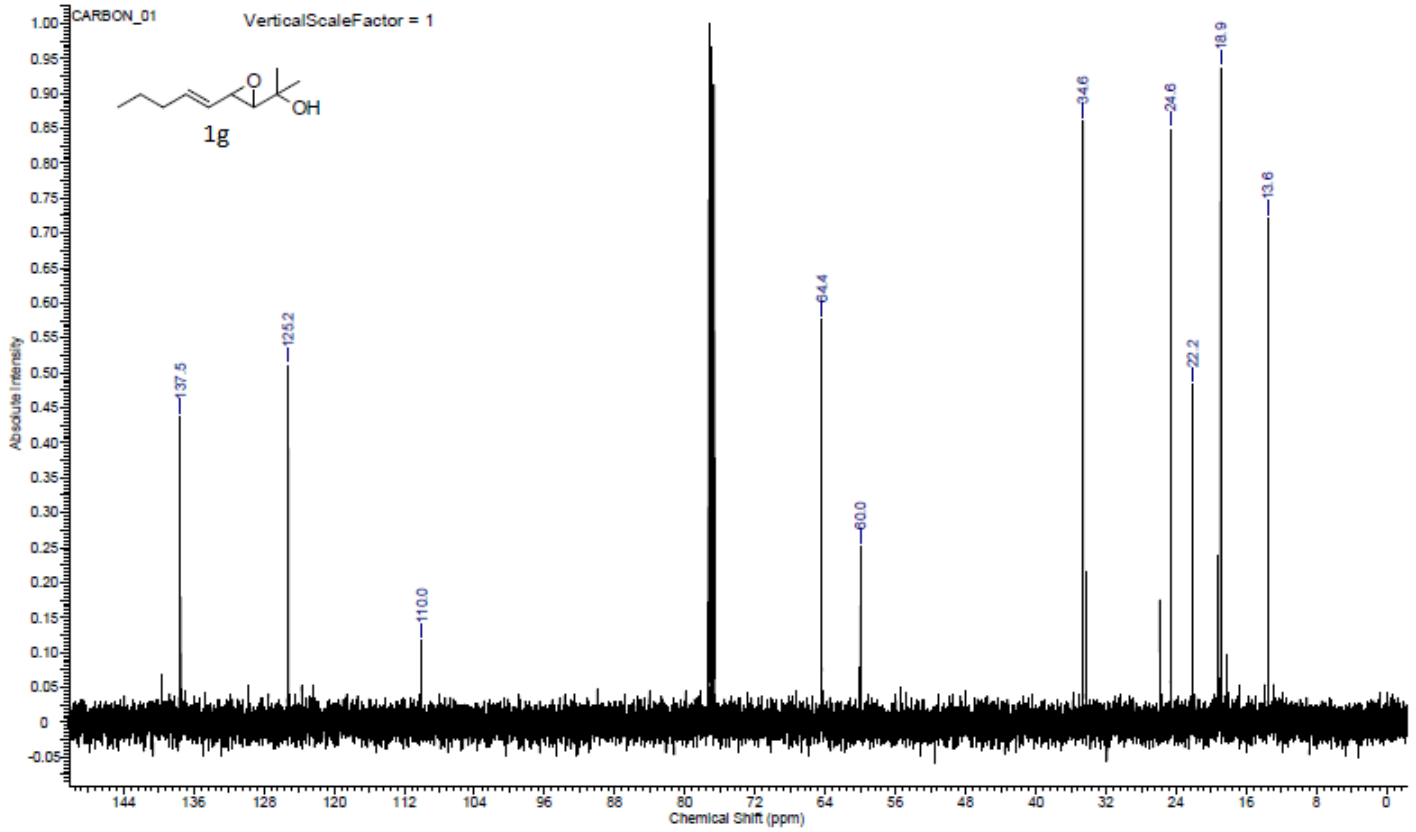
Acquisition Time (sec)	1.3107	*Comment*	ERM-STZ-ME-ENEP-OH			*Date*	May 31 2016
Date Stamp	May 31 2016	*File Name*	F:\UNTITLED FOLDER\ERM-STZ-ME-ENEP-OH_20160531_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



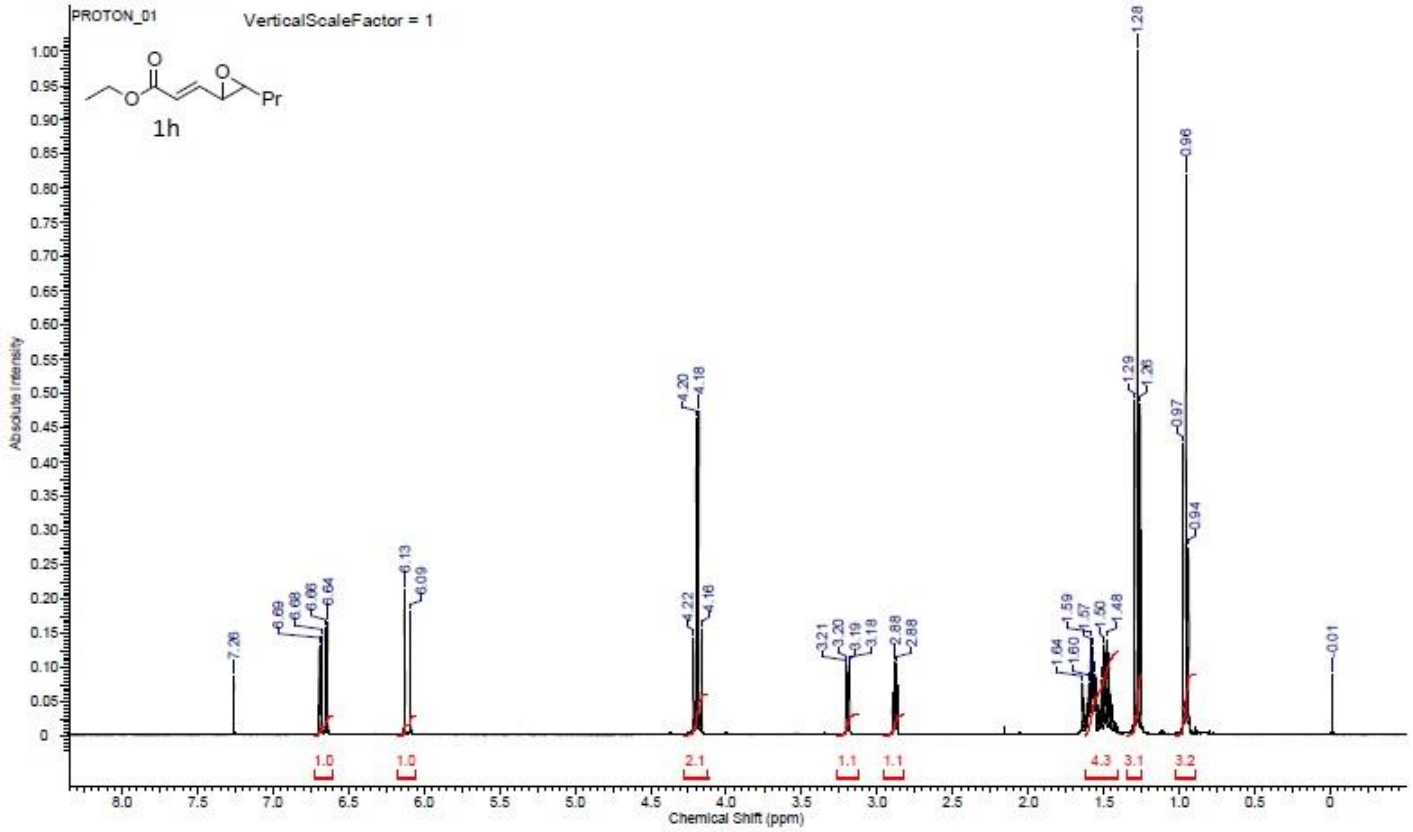
Acquisition Time (sec)	2.5559	*Comment*	erm-stz-pr-enepo-dime			*Date*	Jun 1 2016
Date Stamp	Jun 1 2016	*File Name*	F:\UNTITLED FOLDER\ERM-STZ-PR-ENEPO-DIME_20160601_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



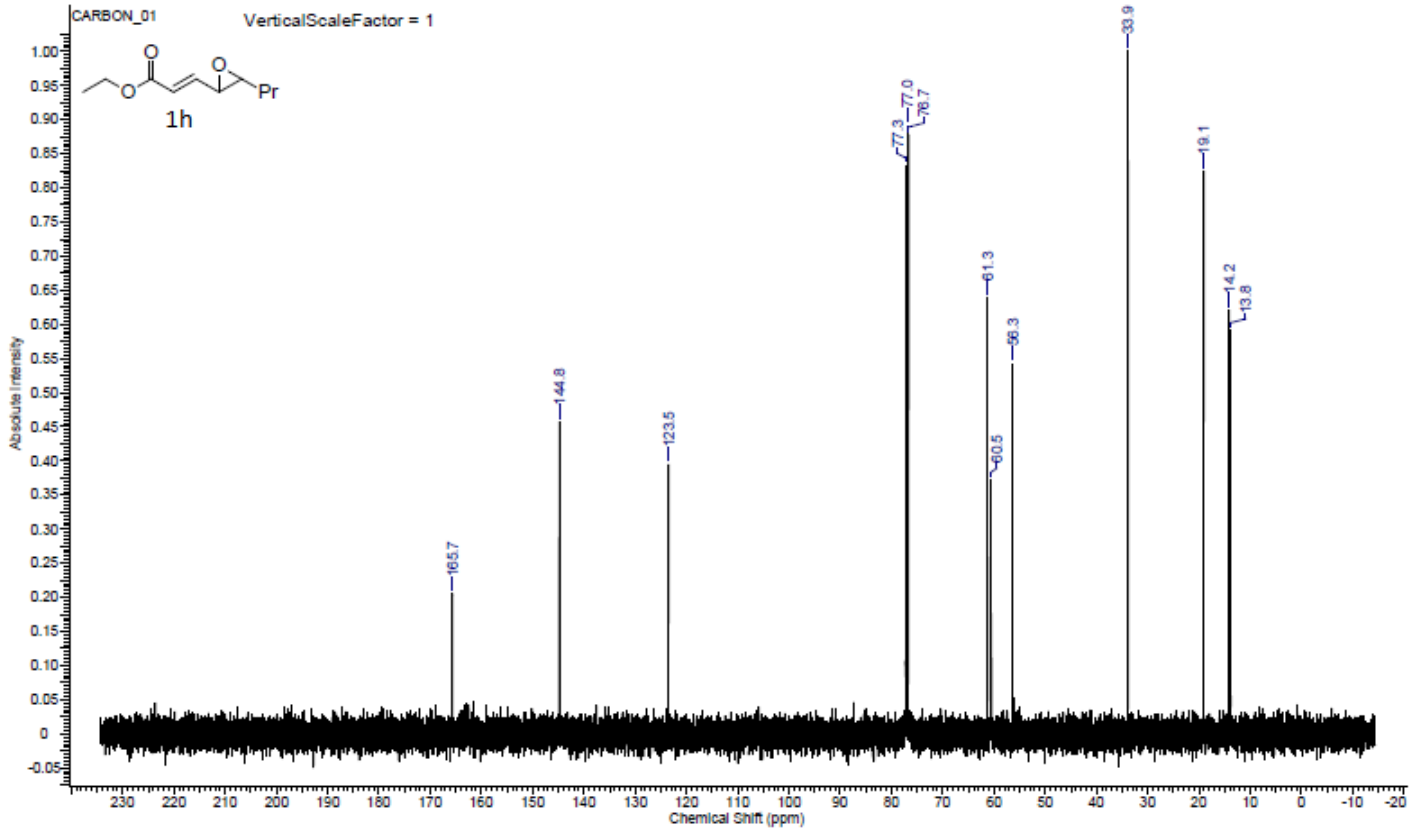
Acquisition Time (sec)	1.3107	*Comment*	erm-stz-pr-enepo-dime			*Date*	Jun 1 2016
Date Stamp	Jun 1 2016	*File Name*	F:\UNTITLED FOLDER\ERM-STZ-PR-ENEPO-DIME_20160601_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



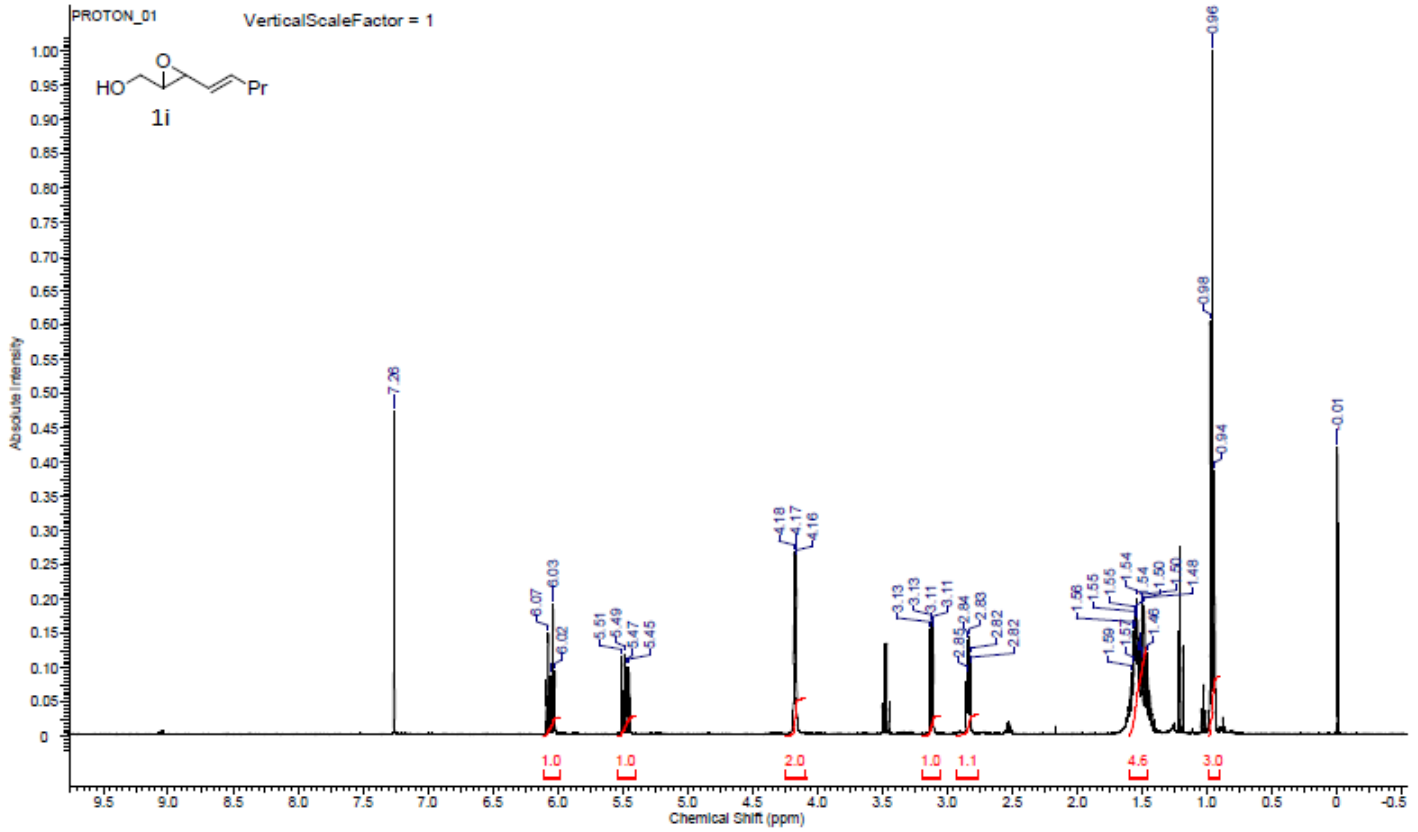
Acquisition Time (sec)	2.5559	*Comment*	YB-30-reactant			*Date*	Aug 18 2016	*Date Stamp*	Aug 18 2016
File Name	D:\YB-30-REACTANT_20160818_01\PROTON_01.FID\FID					*Frequency (MHz)*	399.92	*Nucleus*	1H
Number of Transients	16	*Original Points Count*	16384	*Points Count*	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	54.00
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	2400.0332	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26
Temperature (degree C)	25.000								



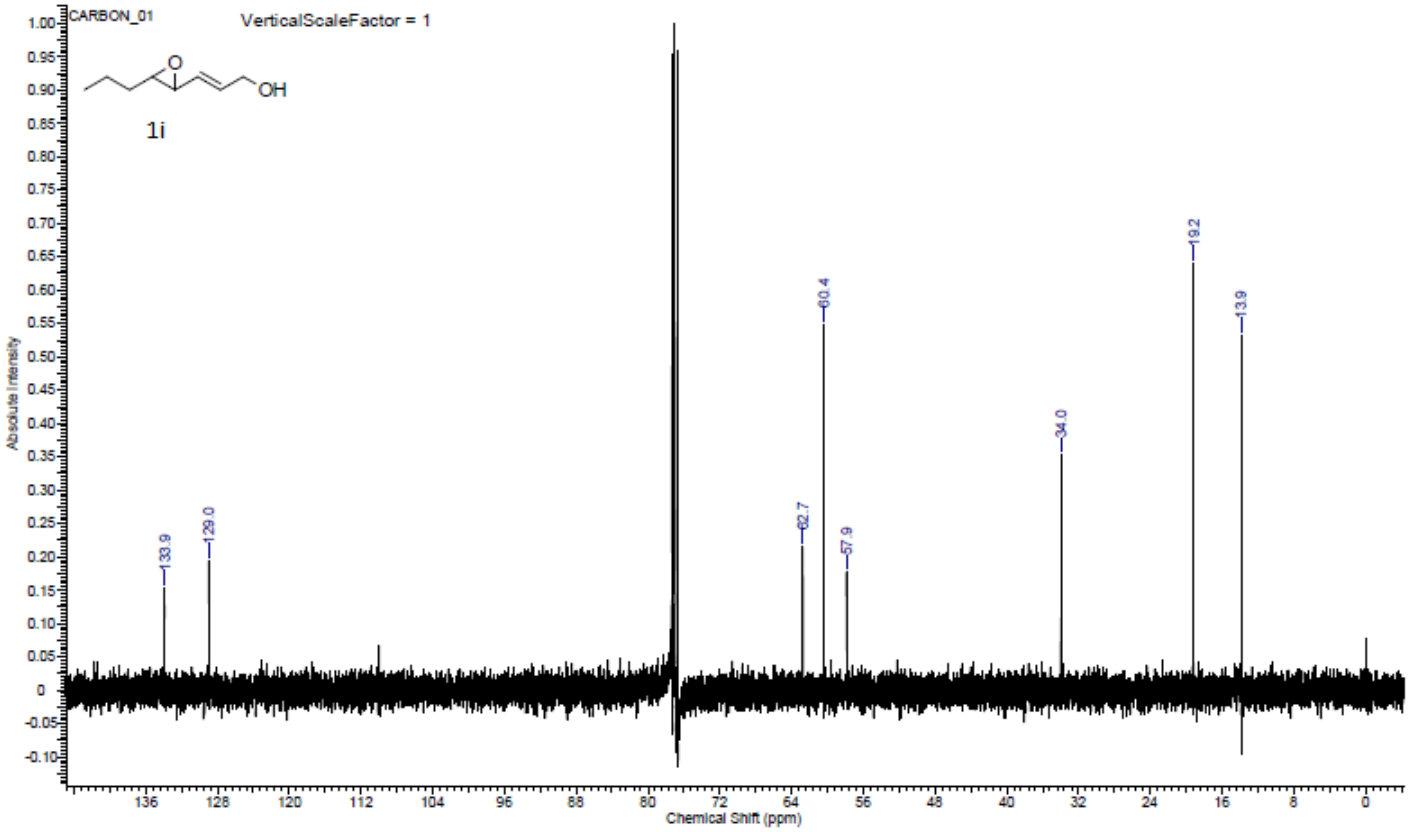
Acquisition Time (sec)	1.3107	*Comment*	YB-030-reactnt			*Date*	Aug 17 2016	*Date Stamp*	Aug 17 2016
File Name	D:\YB-030-REACTNT_20160817_01\CARBON_01.FID\FID					*Frequency (MHz)*	100.57	*Nucleus*	13C
Number of Transients	256	*Original Points Count*	32768	*Points Count*	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00
Temperature (degree C)	25.000								



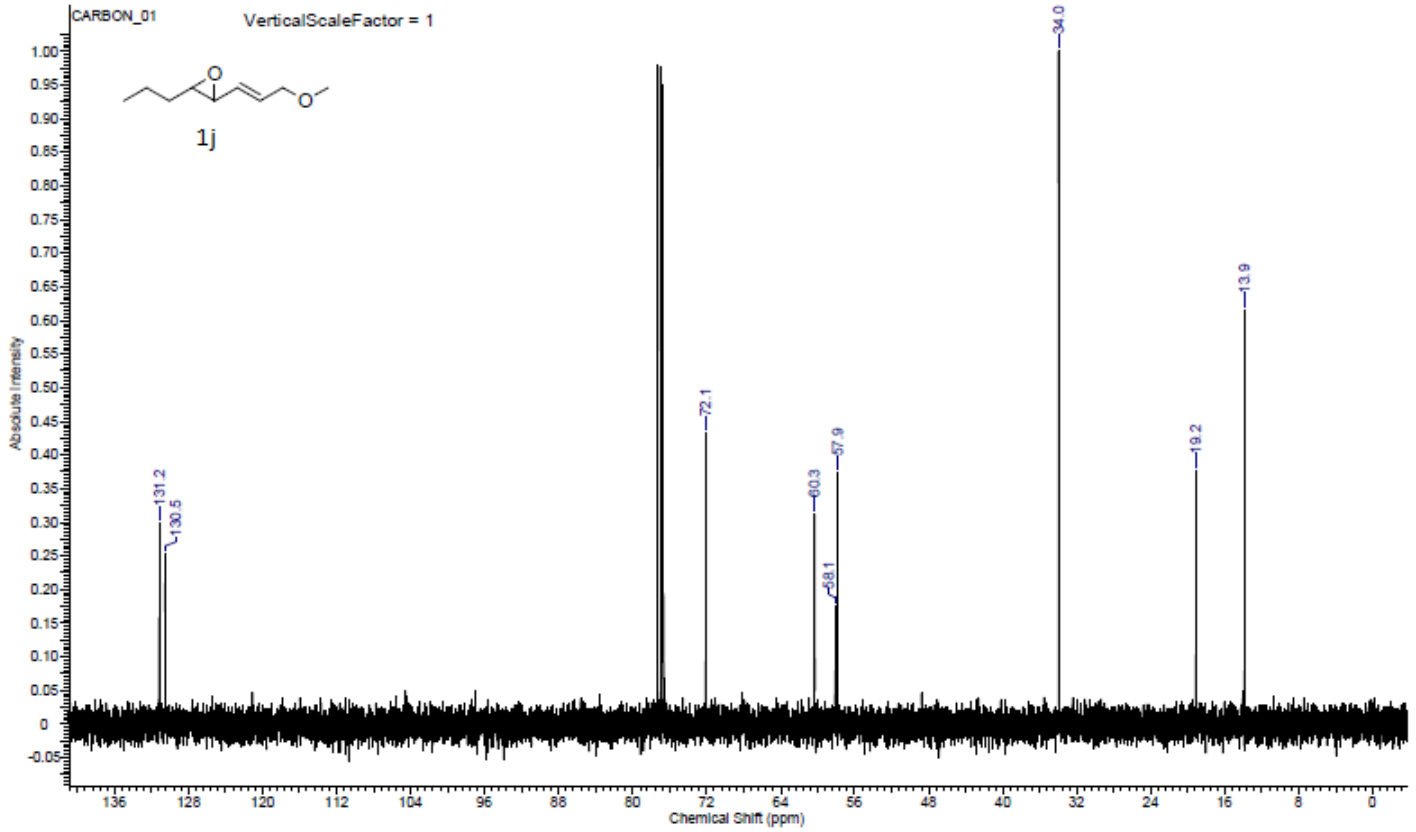
Acquisition Time (sec)	2.5559	*Comment*	erm-stz-ohch2eneppr-tmz			*Date*	Jun 15 2016
Date Stamp	Jun 15 2016	*File Name*	C:\USERS\ERMAN\DESKTOP\WET\ERM-STZ-OHCH2ENEPPR-TMZ_20160615_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



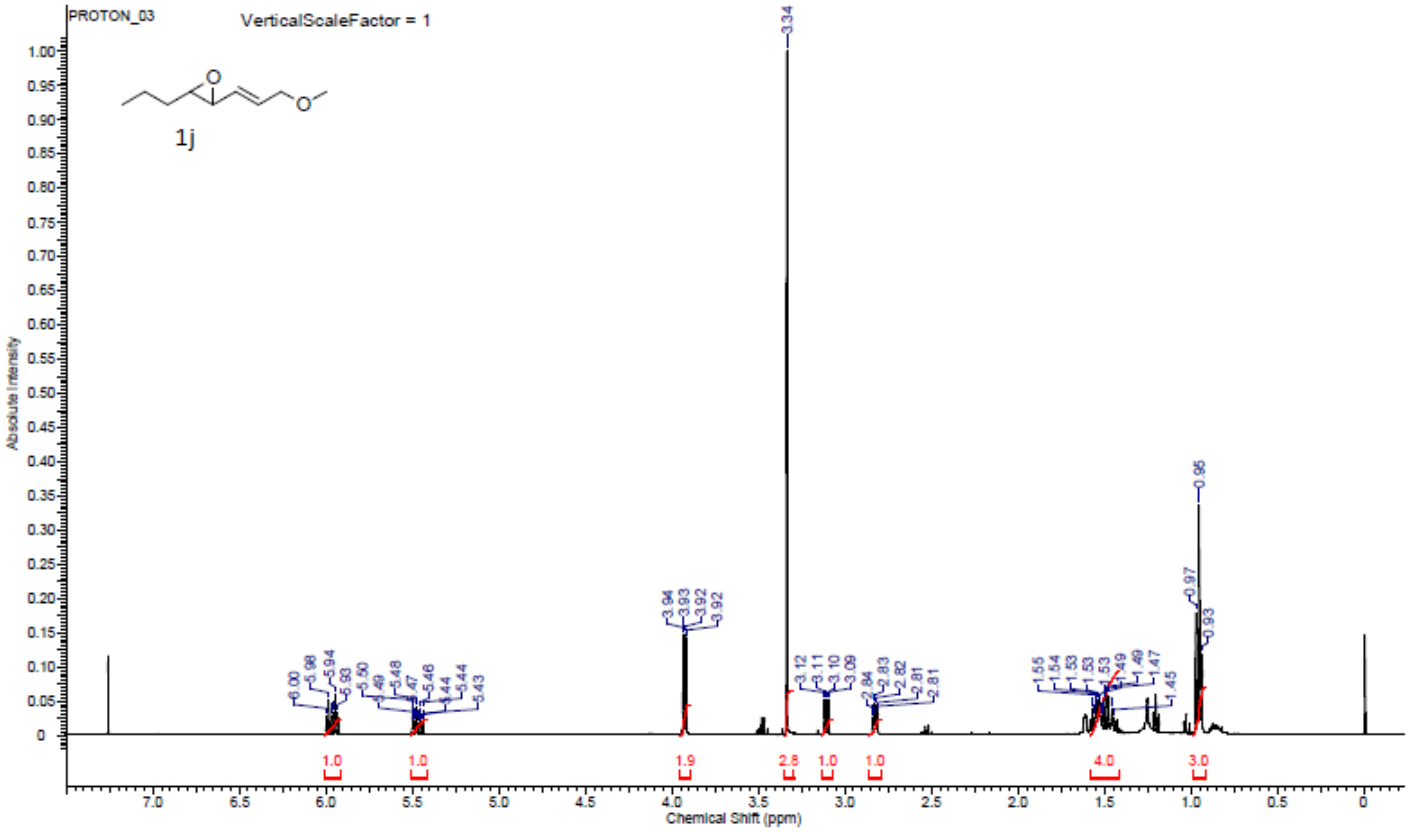
Acquisition Time (sec)	1.3107	*Comment*	erm-stz-ohch2eneppr-tmz			*Date*	Jun 15 2016
Date Stamp	Jun 15 2016	*File Name*	F:\WET\ERM-STZ-OHCH2ENEPPR-TMZ_20160615_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



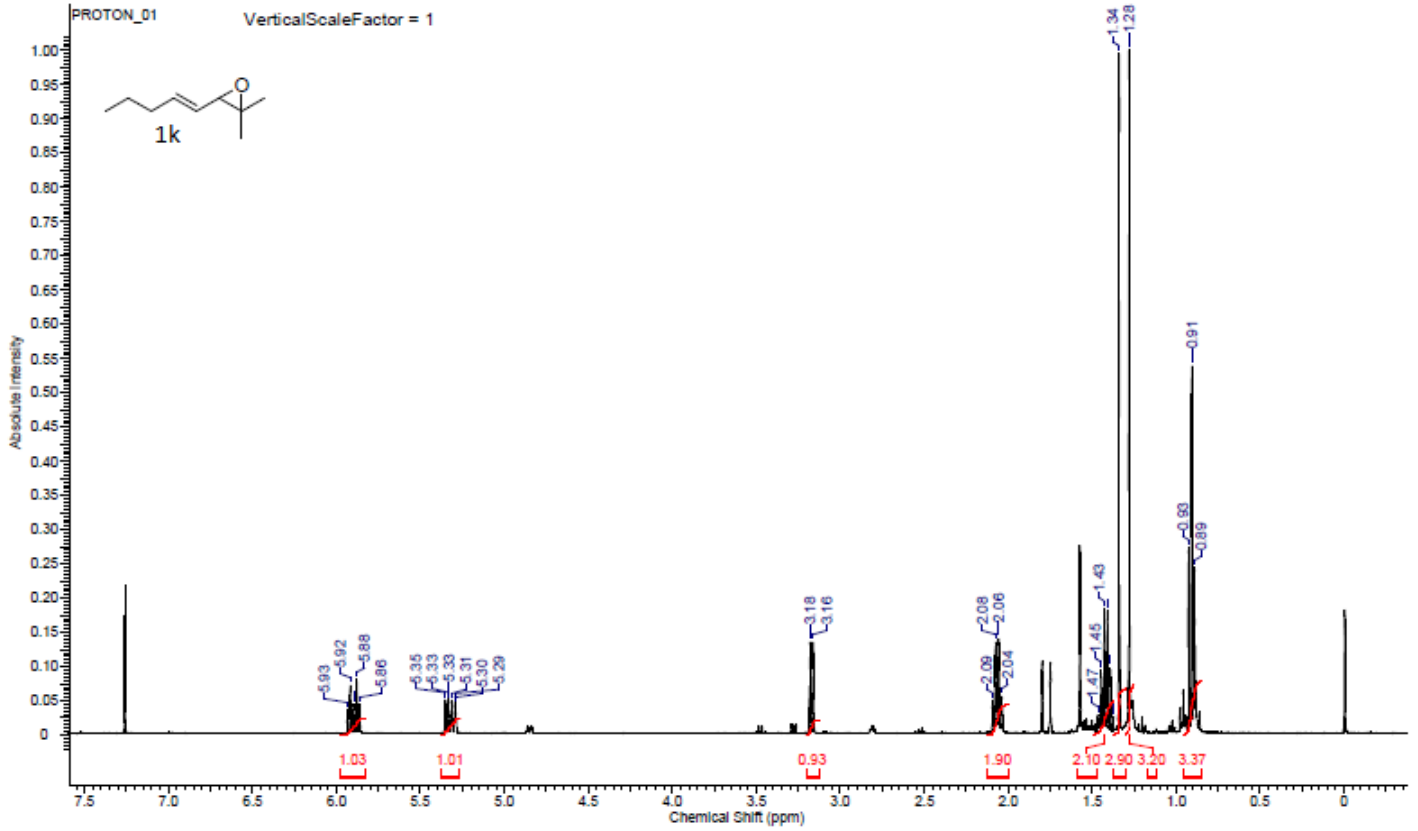
Acquisition Time (sec)	1.3107	*Comment*	ERM-STZ-MeOENEPPR			*Date*	Jun 17 2016
Date Stamp	Jun 17 2016	*File Name*	F:\WET\ERM-STZ-MEOENEPPR_20160617_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



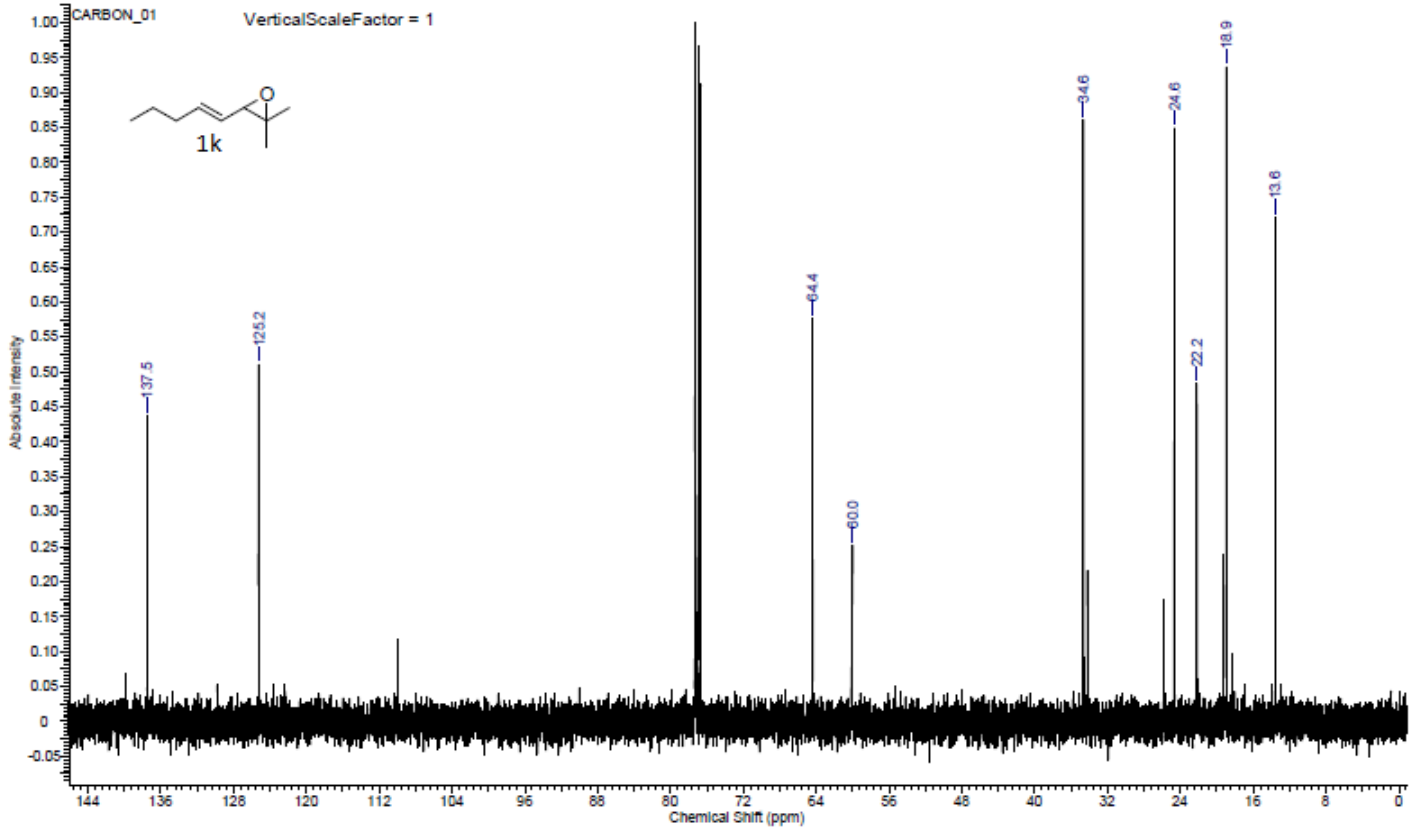
Acquisition Time (sec)	2.5559	*Comment*	ERM-STZ-MeOENEPPR			*Date*	Jun 17 2016
Date Stamp	Jun 17 2016	*File Name*	F:\WET\ERM-STZ-MEOENEPPR_20160617_01\PROTON_03.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



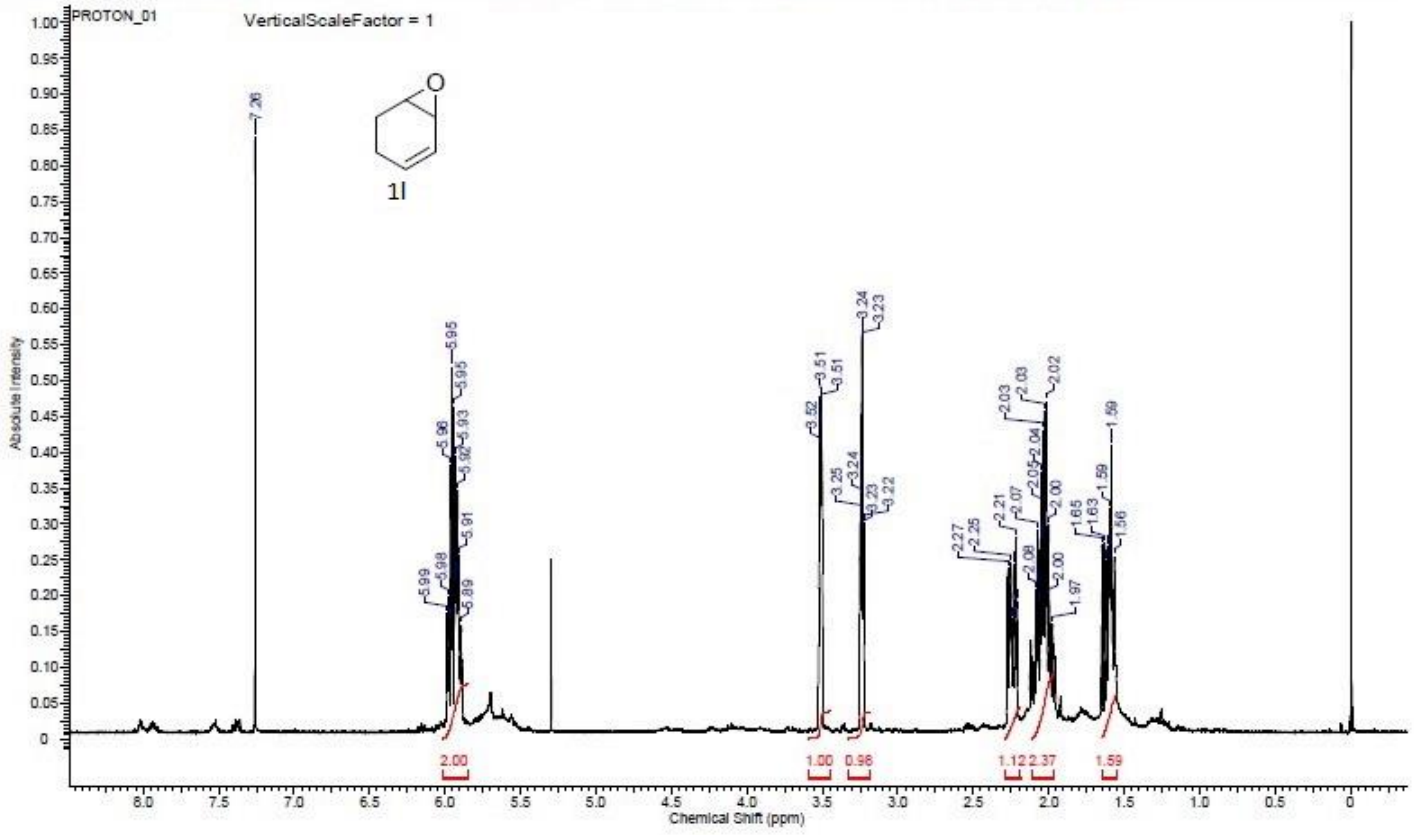
Acquisition Time (sec)	2.5559	*Comment*	ERM-STZ-PR-ENEPO-DIME-2			*Date*	Jun 10 2016
Date Stamp	Jun 10 2016	*File Name*	F:\WET\ERM-STZ-PR-ENEPO-DIME-2_20160610_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



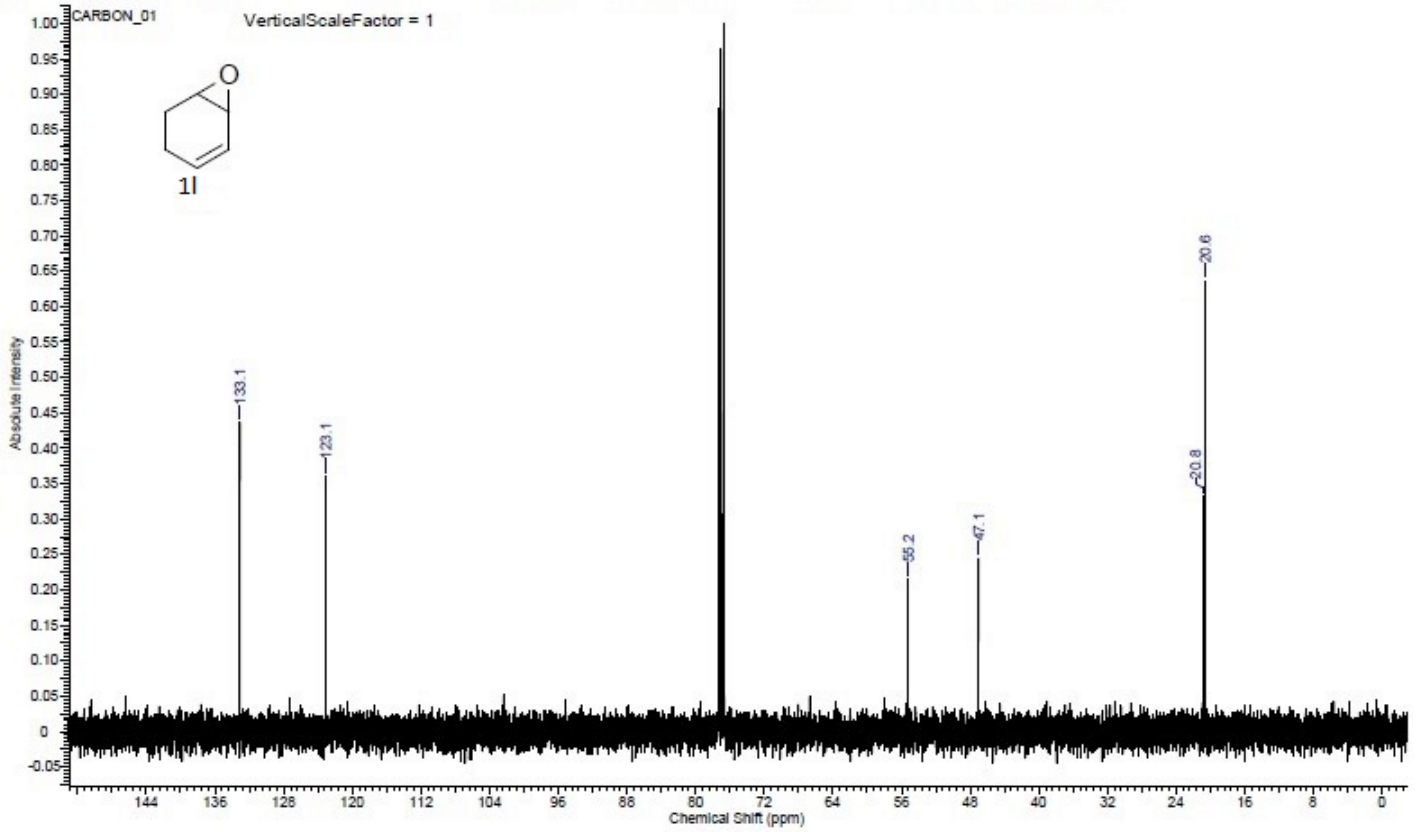
Acquisition Time (sec)	1.3107	*Comment*	erm-stz-pr-enepo-dime			*Date*	Jun 1 2016
Date Stamp	Jun 1 2016	*File Name*	F:\WET\ERM-STZ-PR-ENEPO-DIME_20160601_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



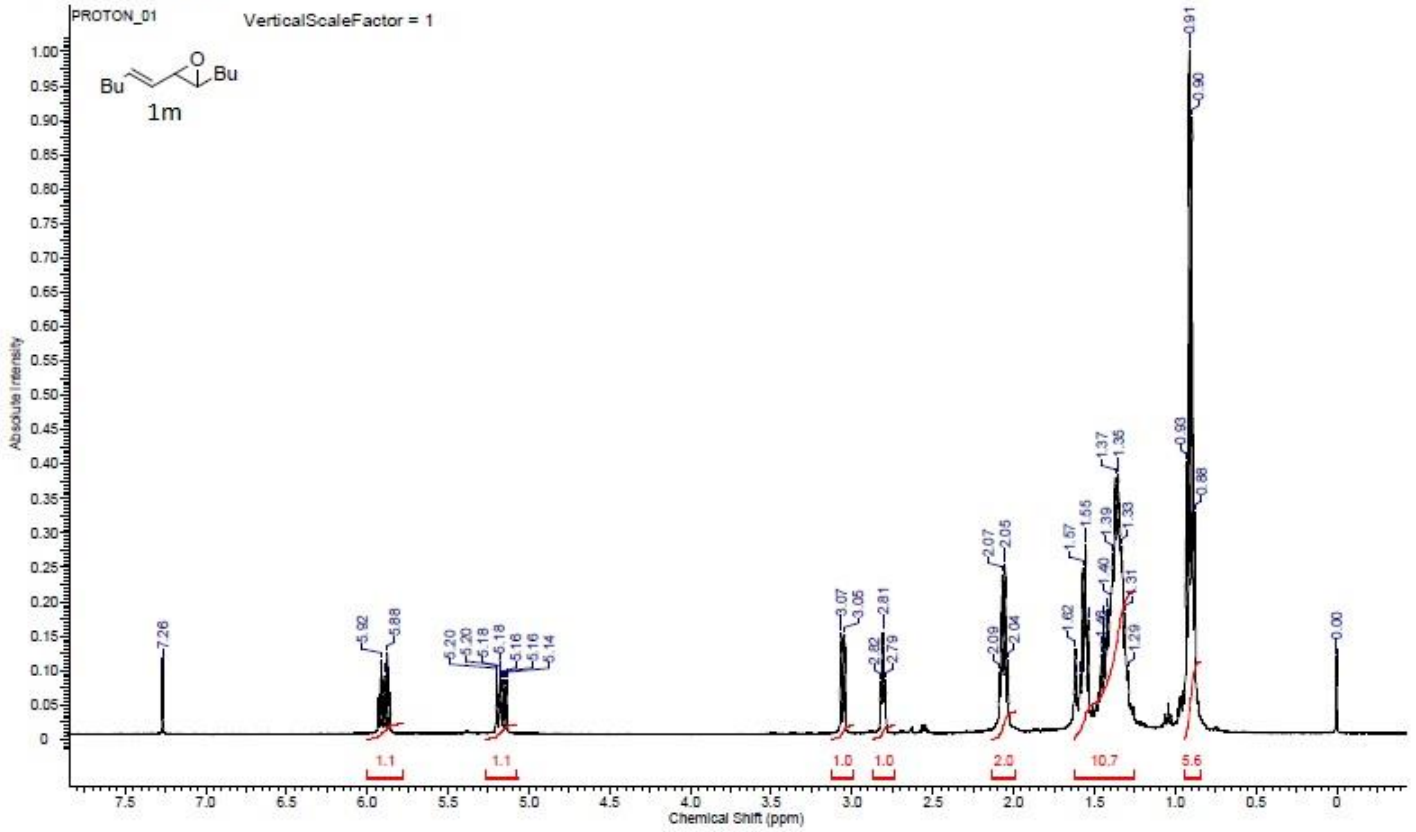
Acquisition Time (sec)	2.5559	*Comment*	ERM-STZ-CYCEPO			*Date*	Feb 1 2016
Date Stamp	Feb 1 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-STZ-CYCEPO_20160201_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



Acquisition Time (sec)	1.3107	*Comment*	ERM-STZ-CYCEPO			*Date*	Feb 1 2016
Date Stamp	Feb 1 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-STZ-CYCEPO_20160201_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-STZ-BUENEPBU			*Date*	Jul 19 2016	*Date Stamp*	Jul 19 2016
File Name	F:\ERM-STZ-BUENEPBU_20160719_01\PROTON_01.FID\FID					*Frequency (MHz)*	399.92	*Nucleus*	1H
Number of Transients	8	*Original Points Count*	16384	*Points Count*	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	2403.4060	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26
Temperature (degree C)	25.000								



Acquisition Time (sec)	1.3107	*Comment*	ERM-STZ-BUENEPBU			*Date*	Jul 19 2016
Date Stamp	Jul 19 2016	*File Name*	F:\ERM-STZ-BUENEPBU_20160719_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
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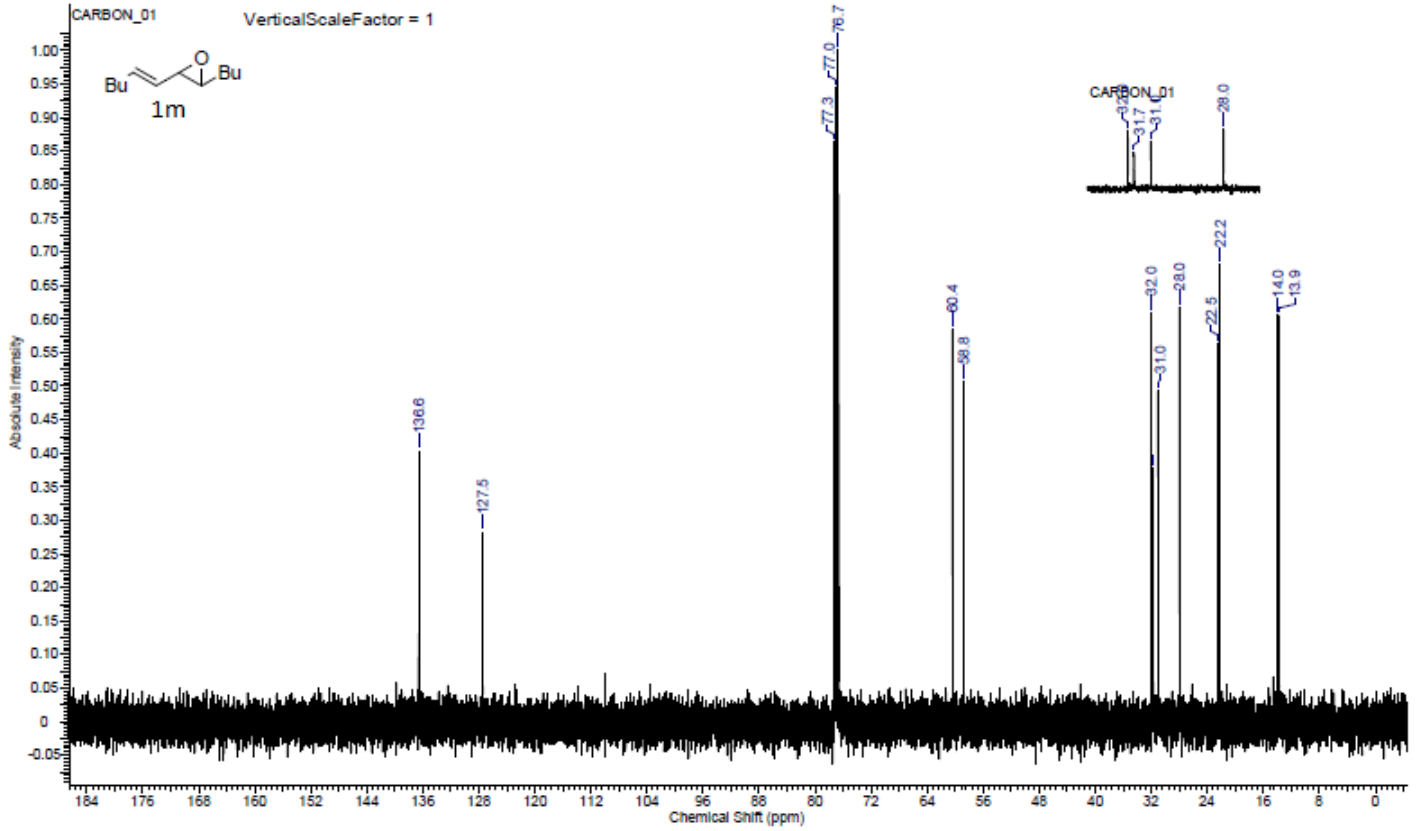

APPENDIX B

^{1}H NMR AND ^{13}CNMR SPECTRUMS OF PRODUCTS

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

10.10.2015 04:47:06

Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-138-1_3			*Date*	Sep 4 2015
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Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	54.00	*Solvent*	CHLOROFORM-d
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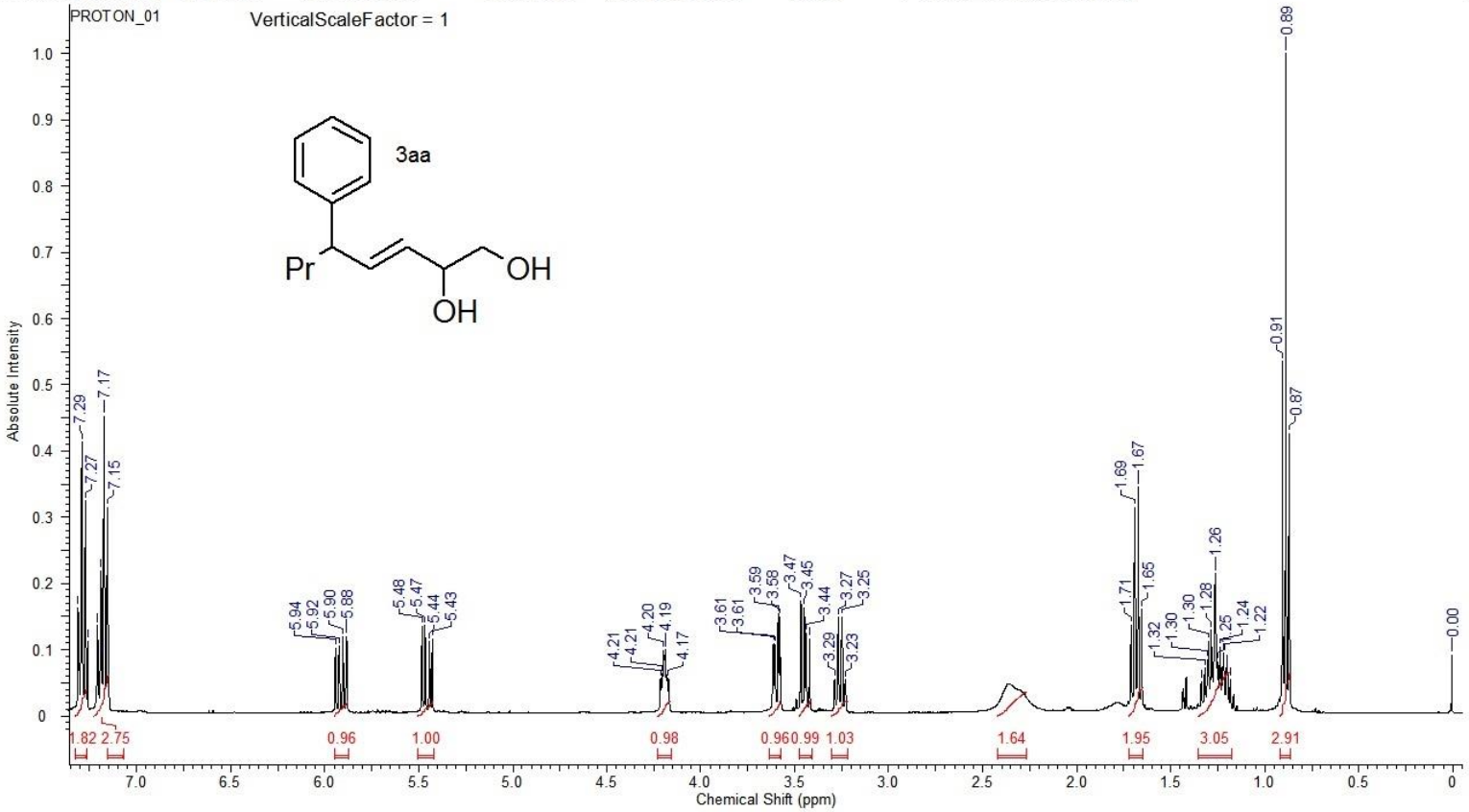

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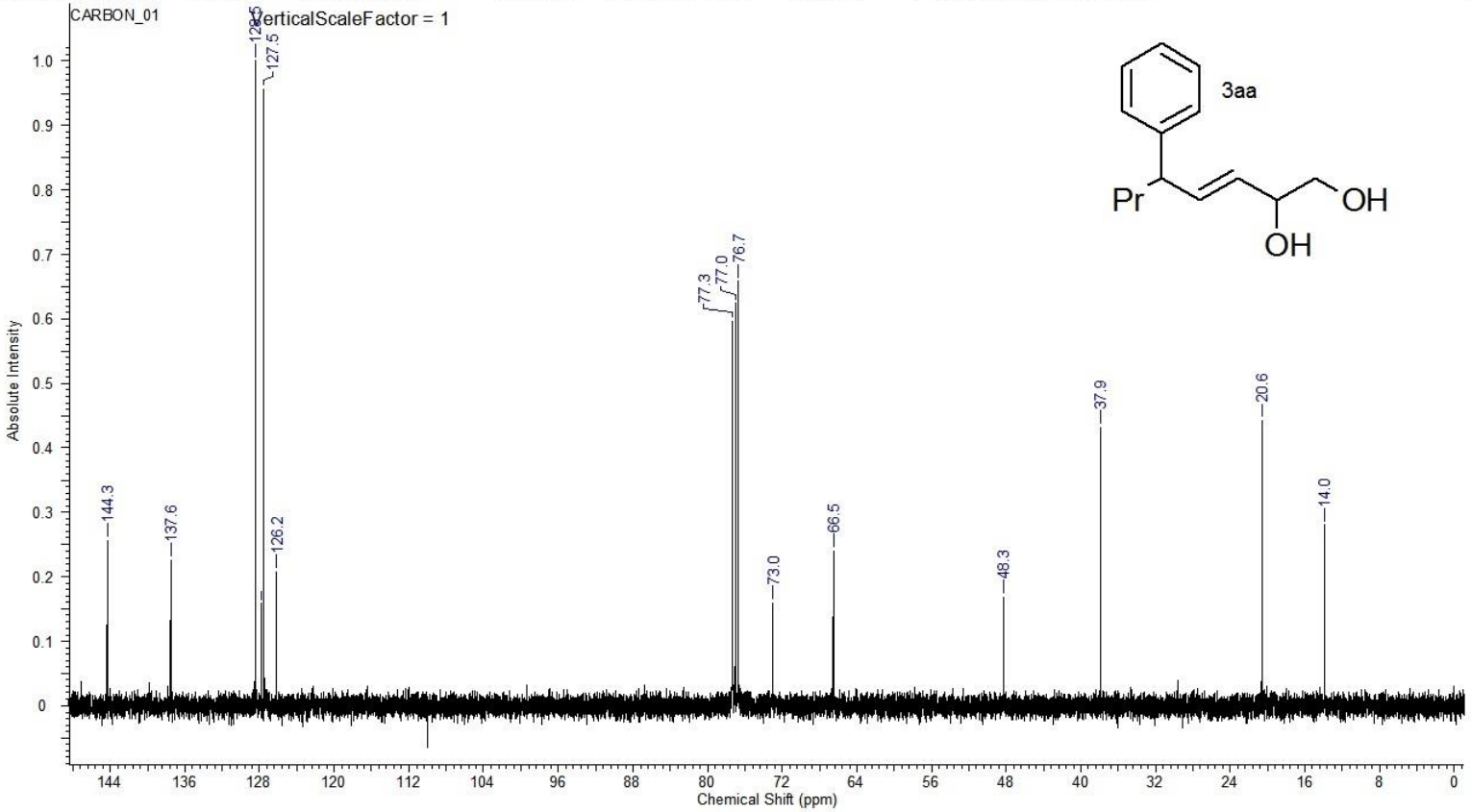
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

10.10.2015 04:43:12

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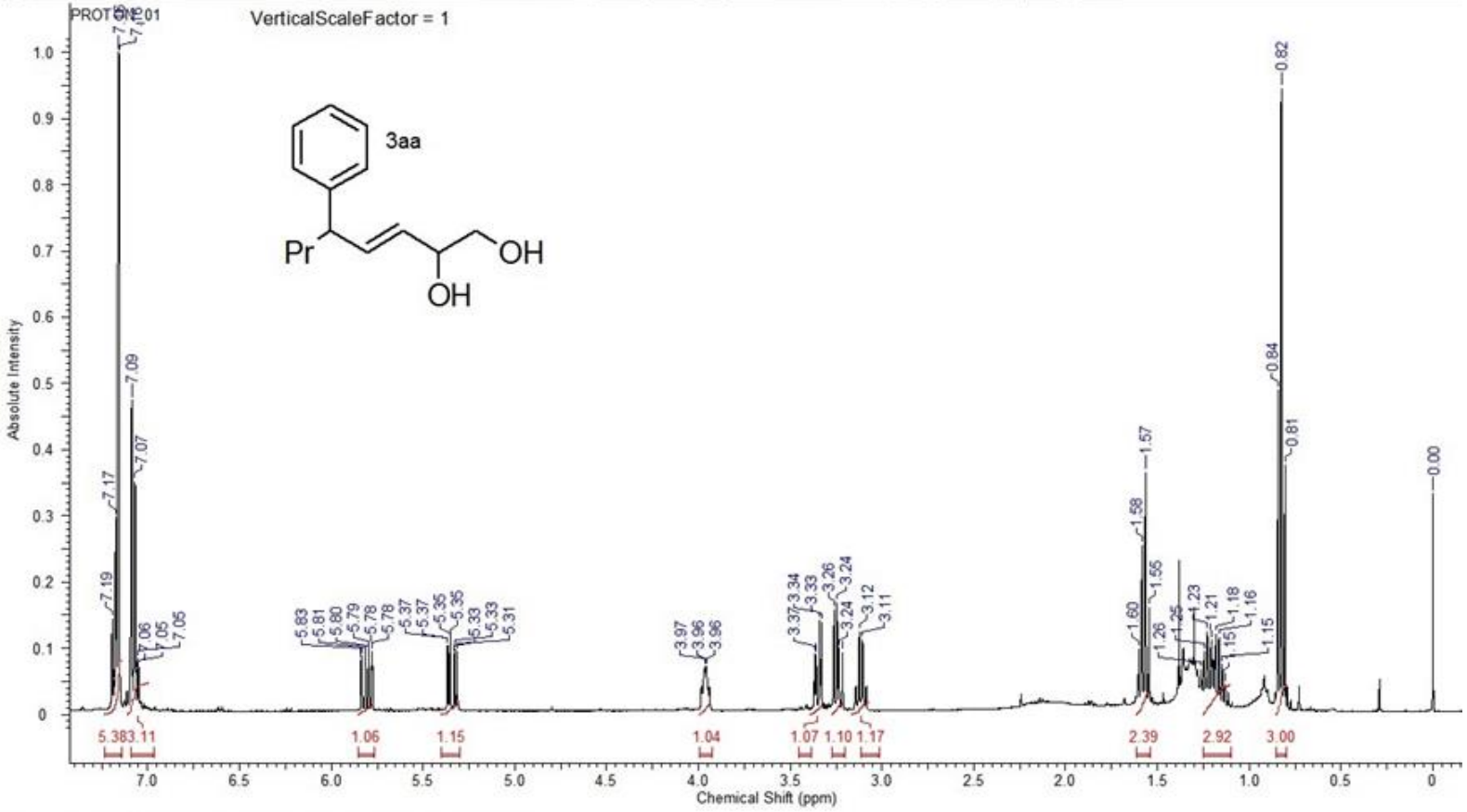
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	58.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2415.9268	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

10.10.2015 04:12:51

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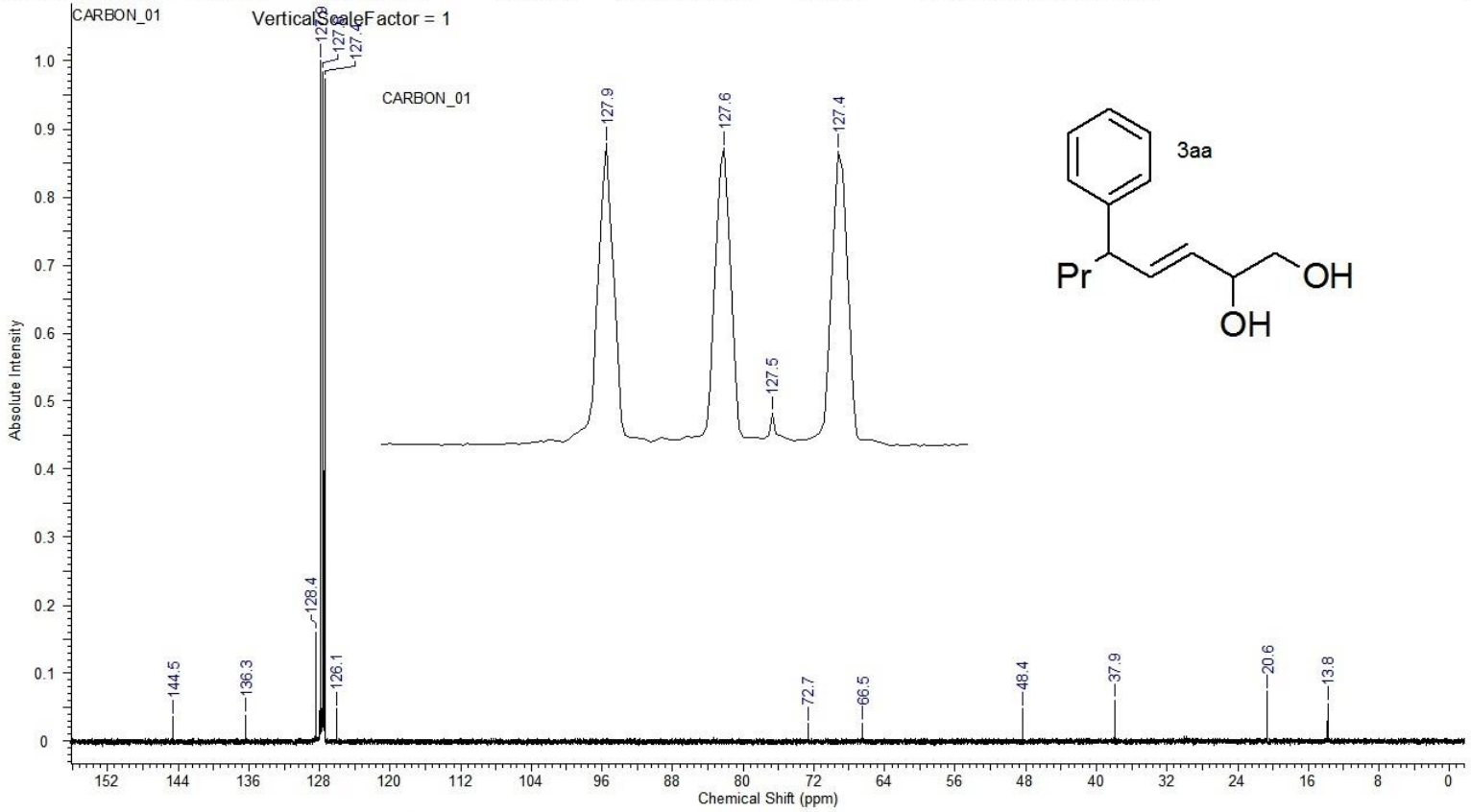
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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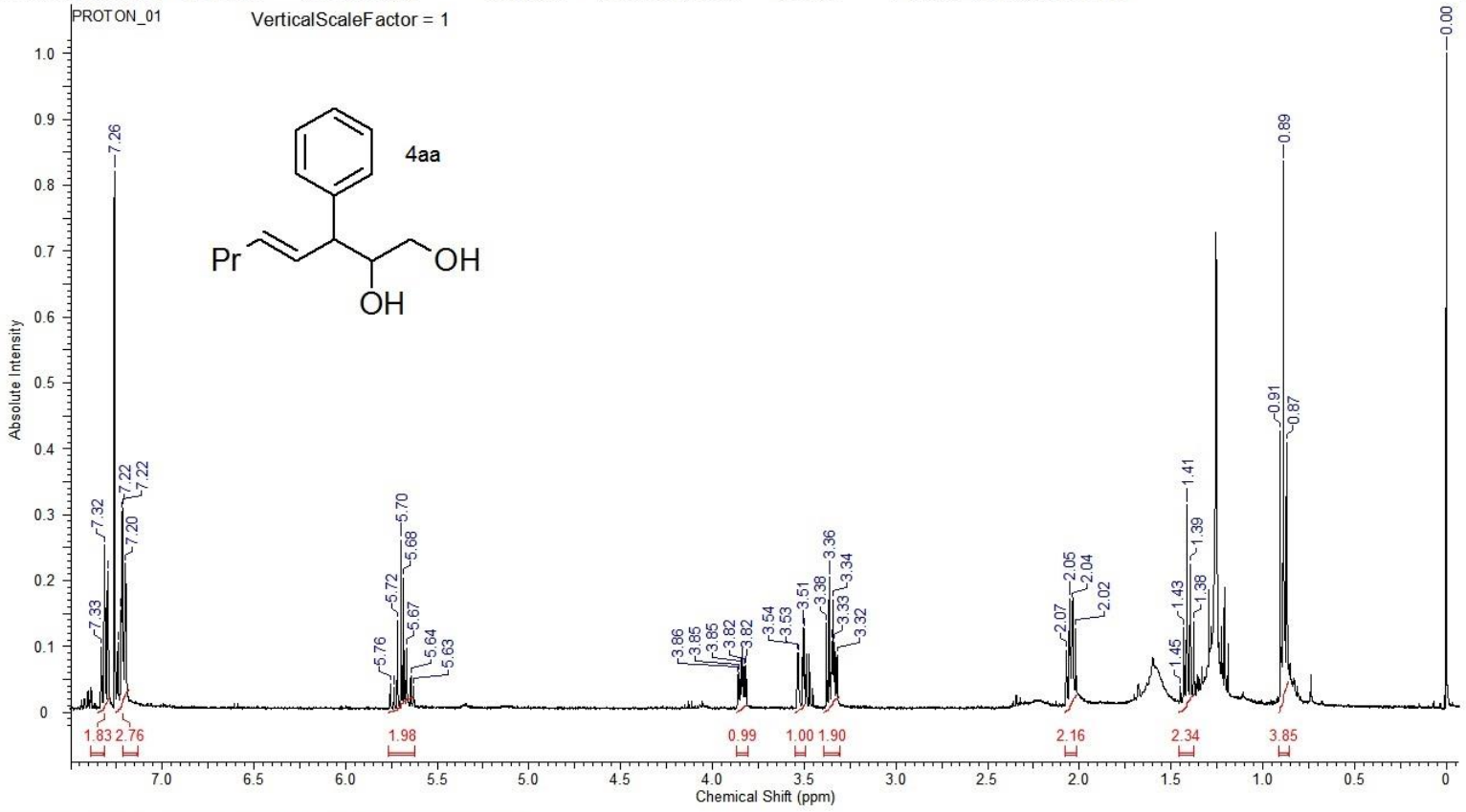
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
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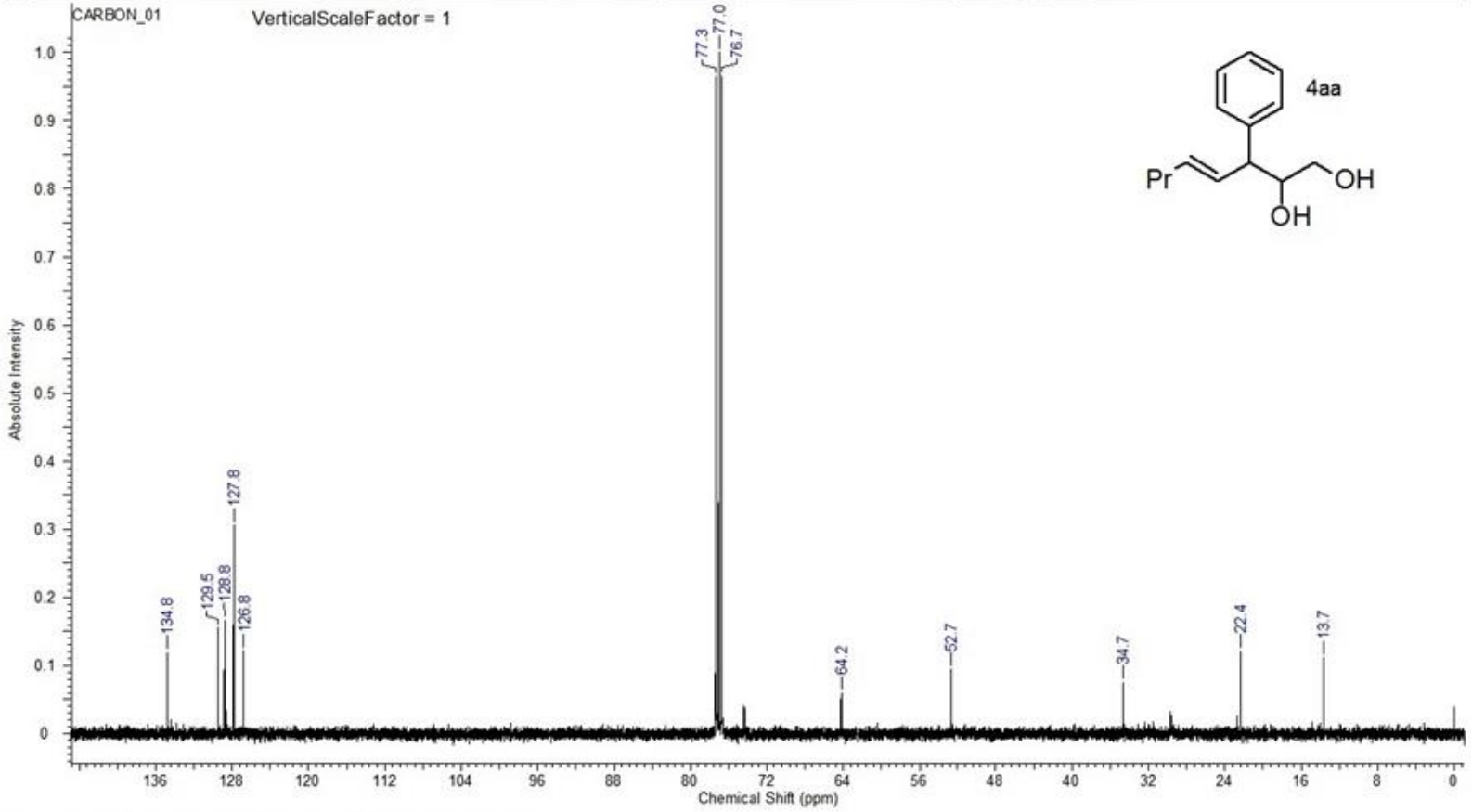

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This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
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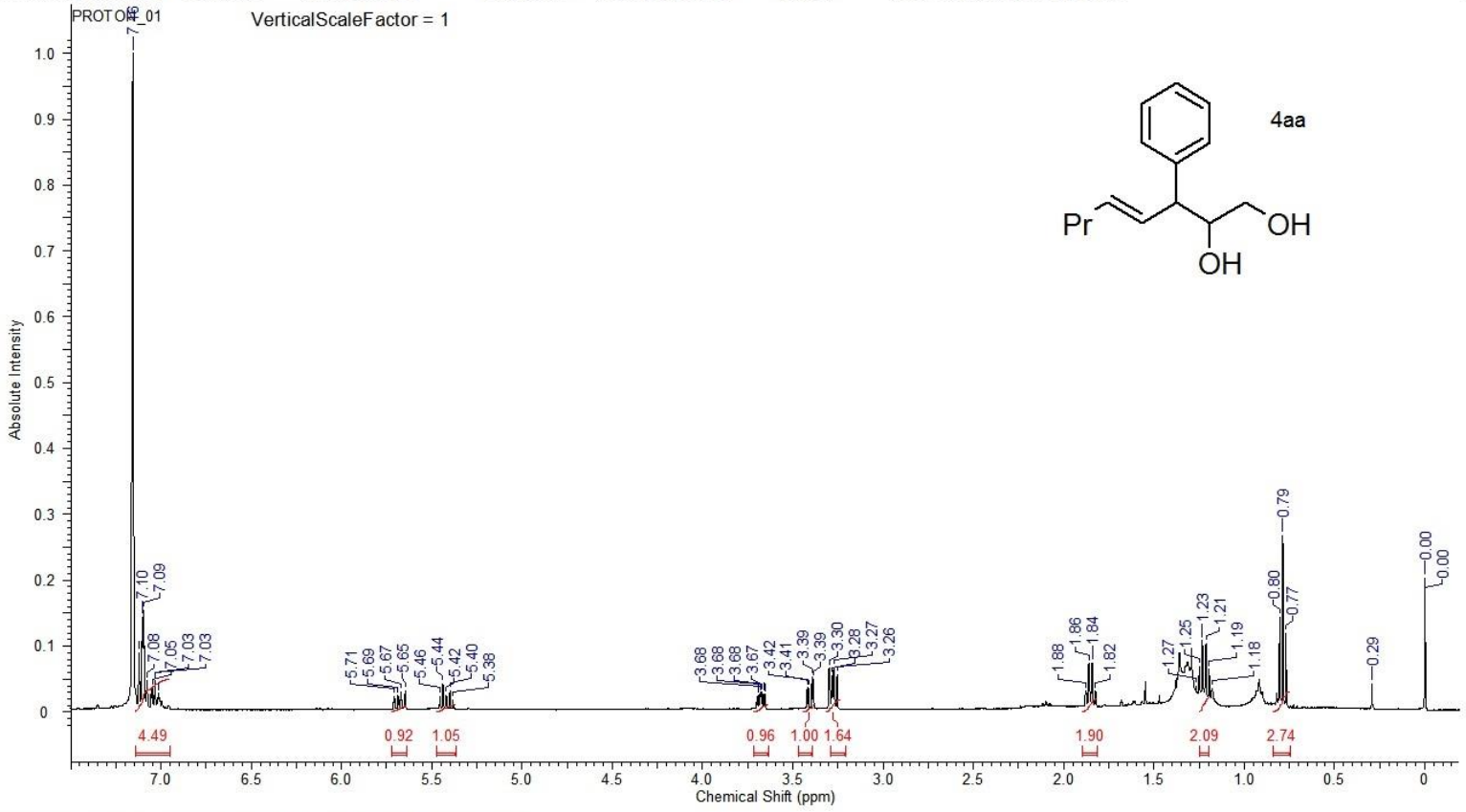

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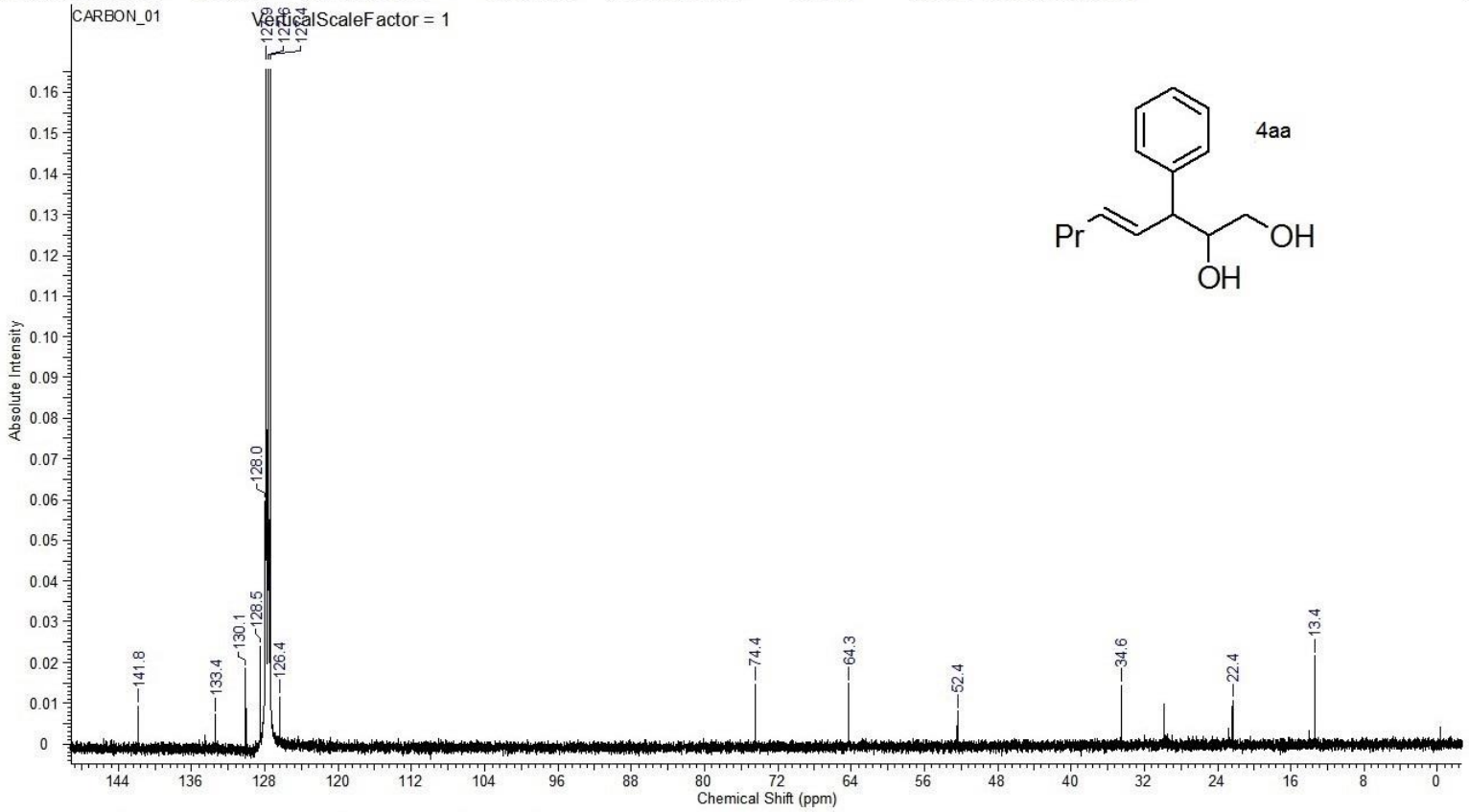

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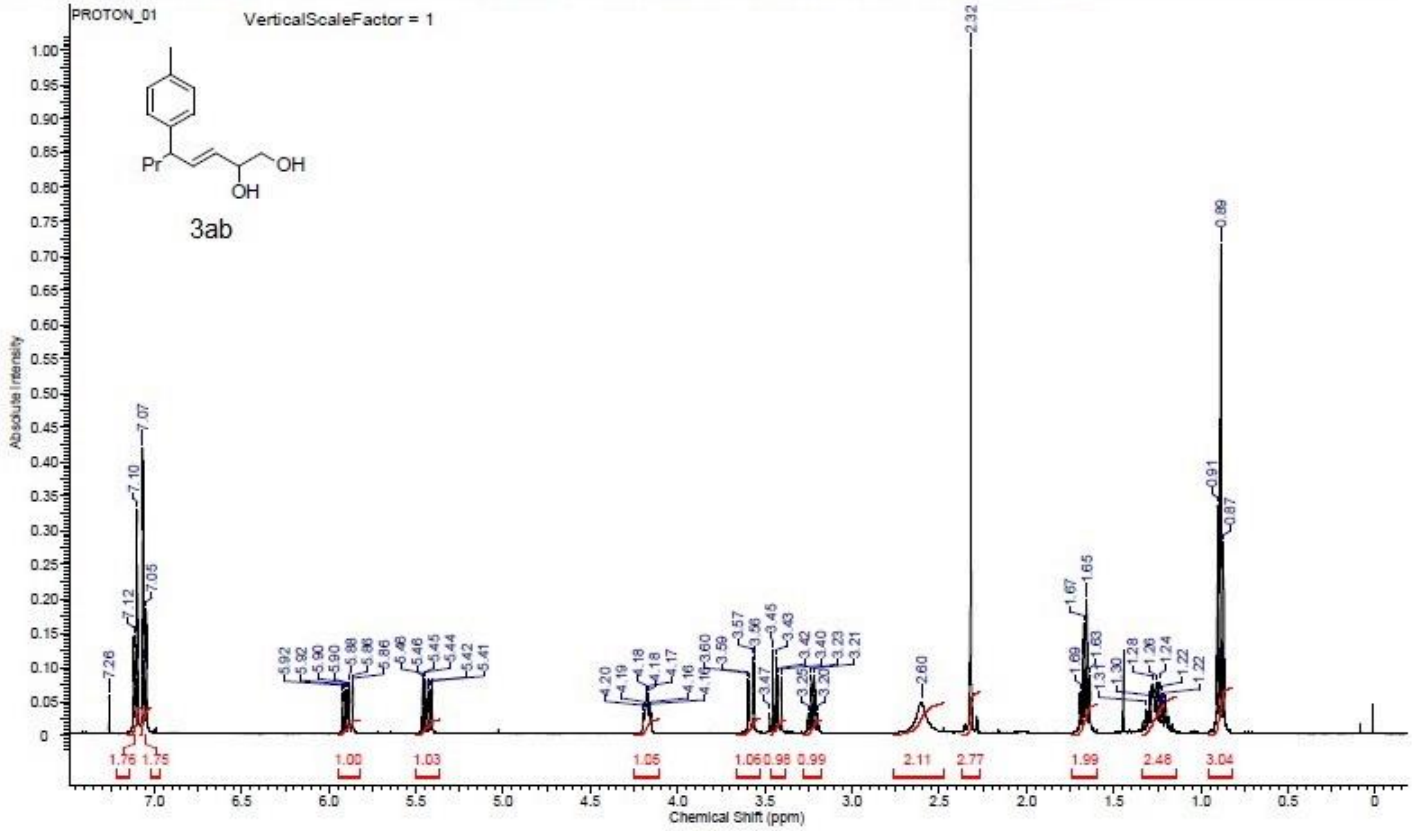
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	50.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
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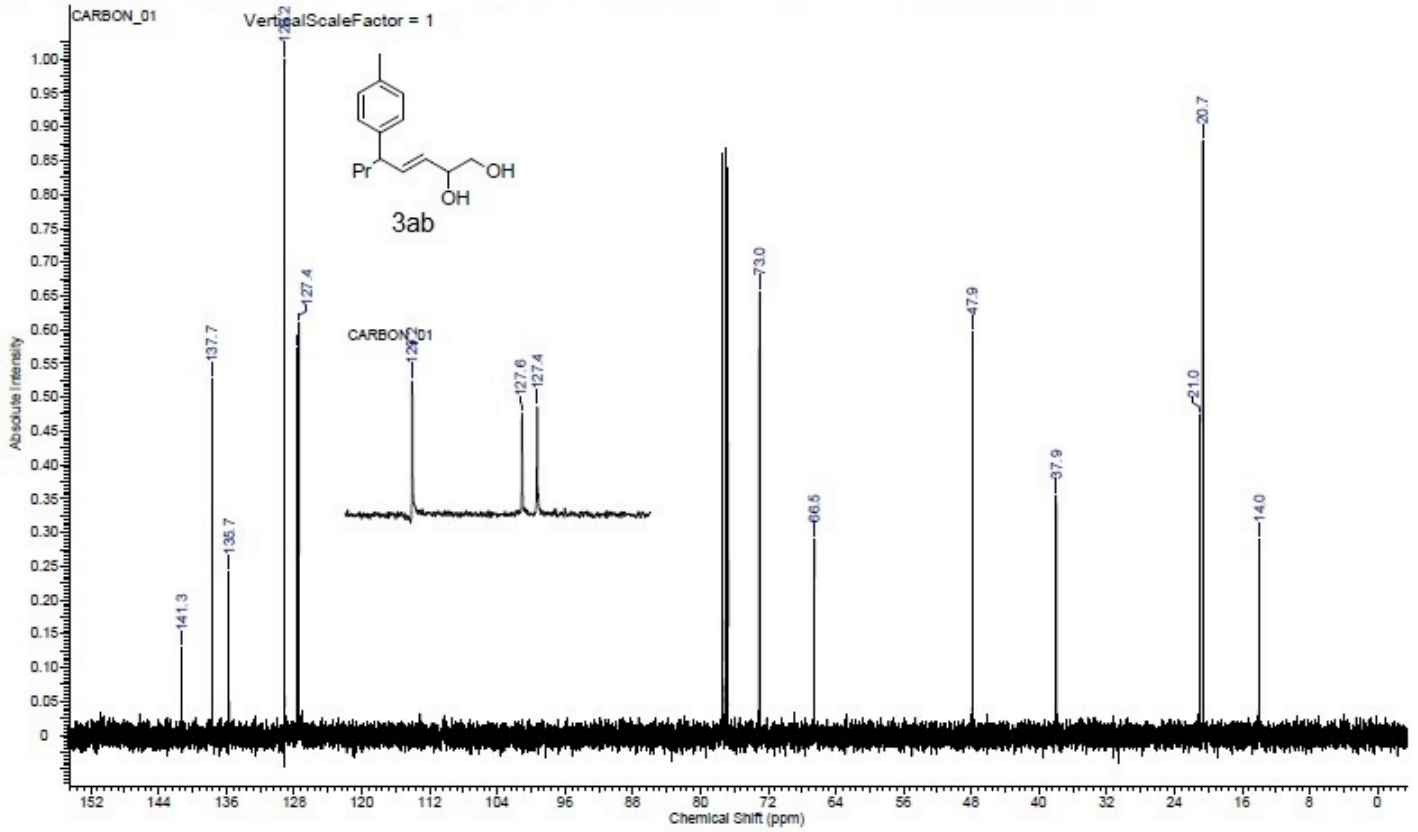

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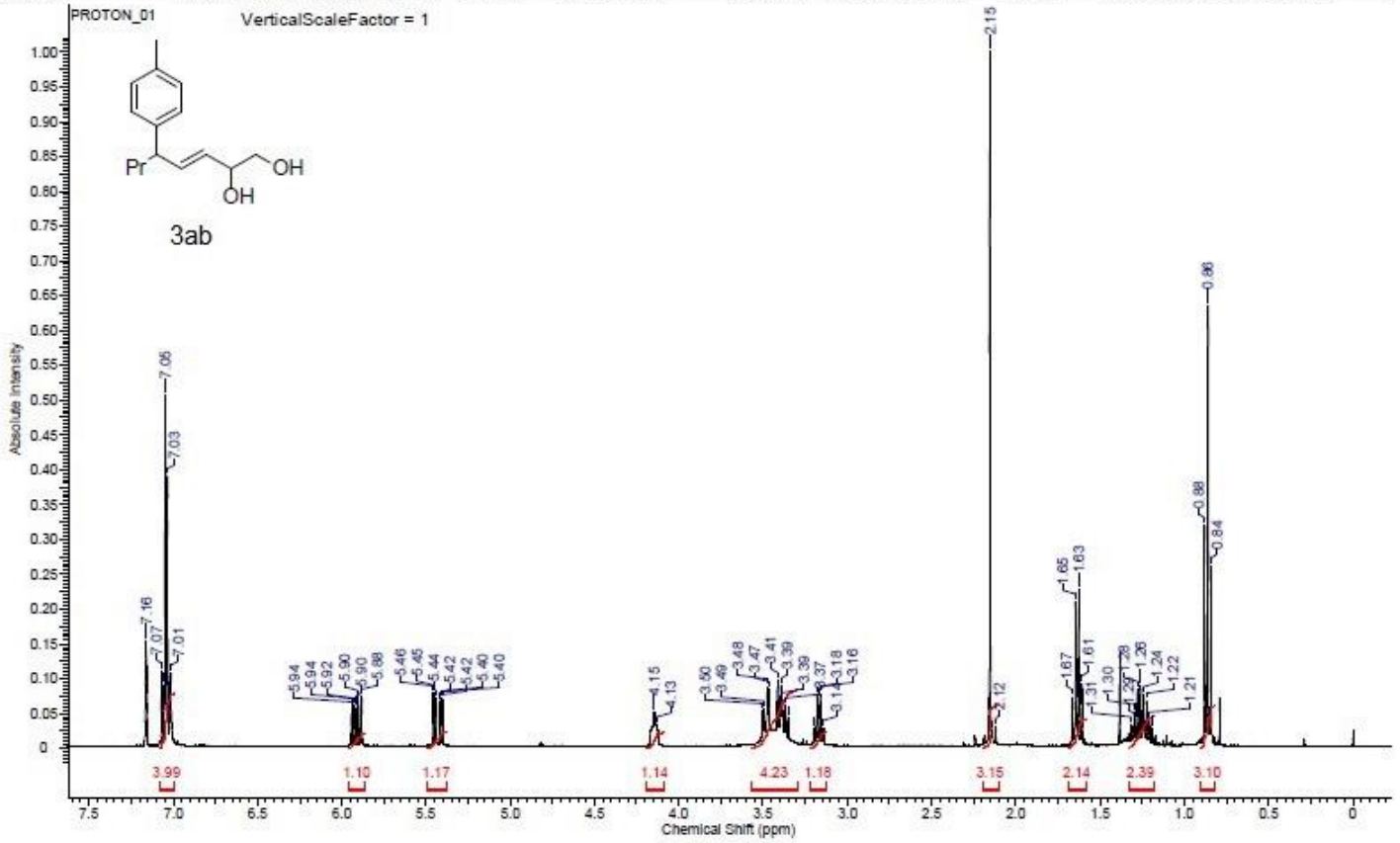

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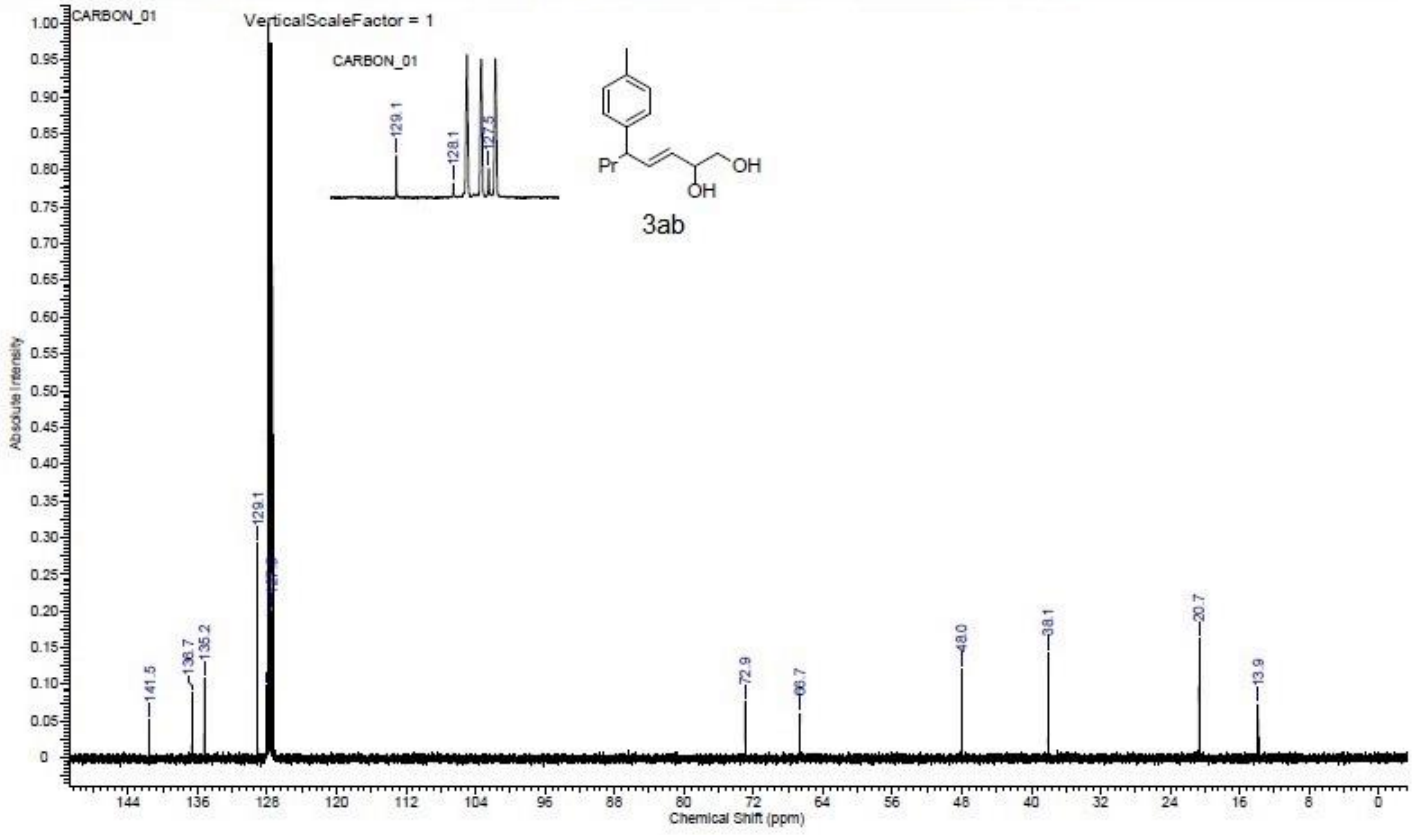
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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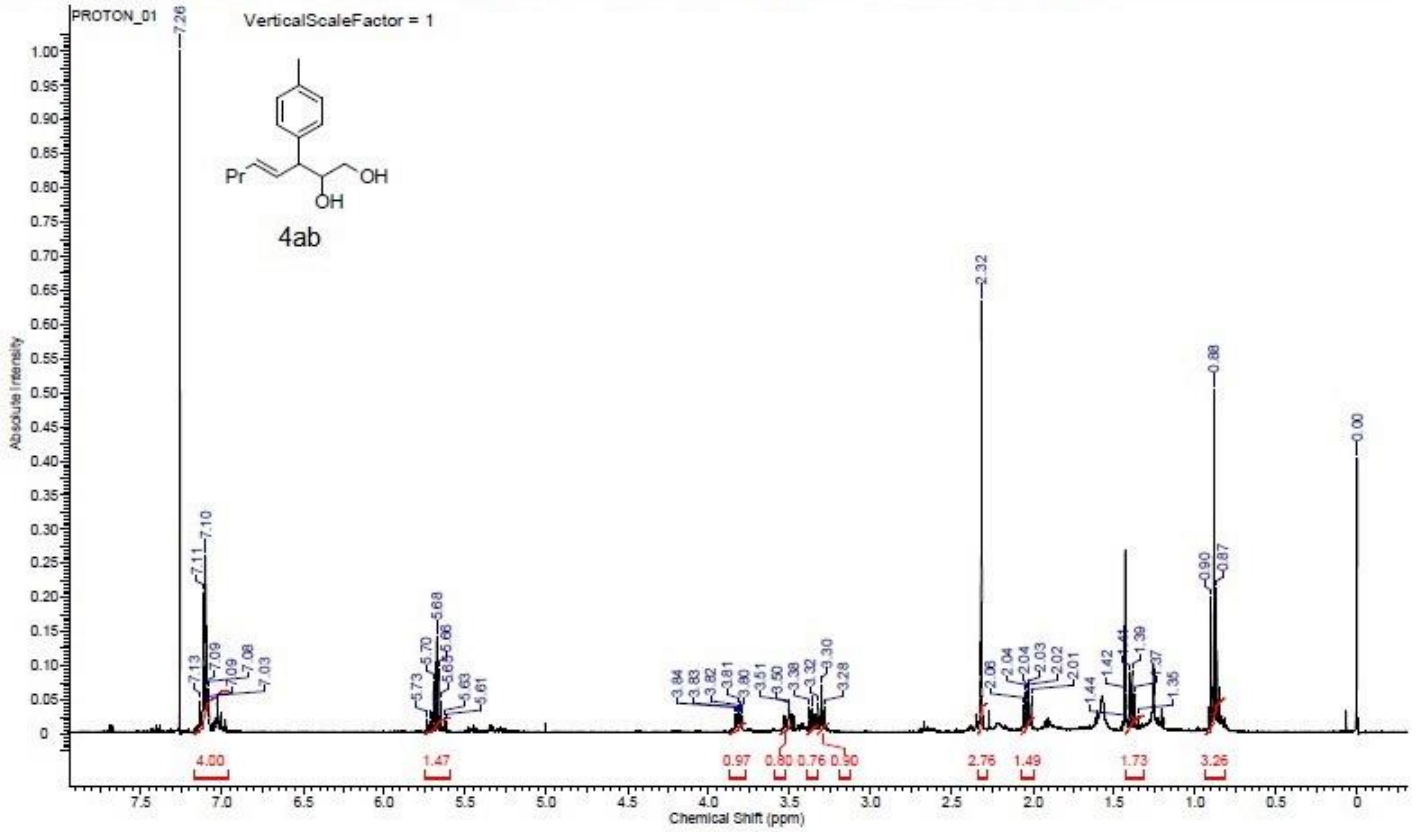
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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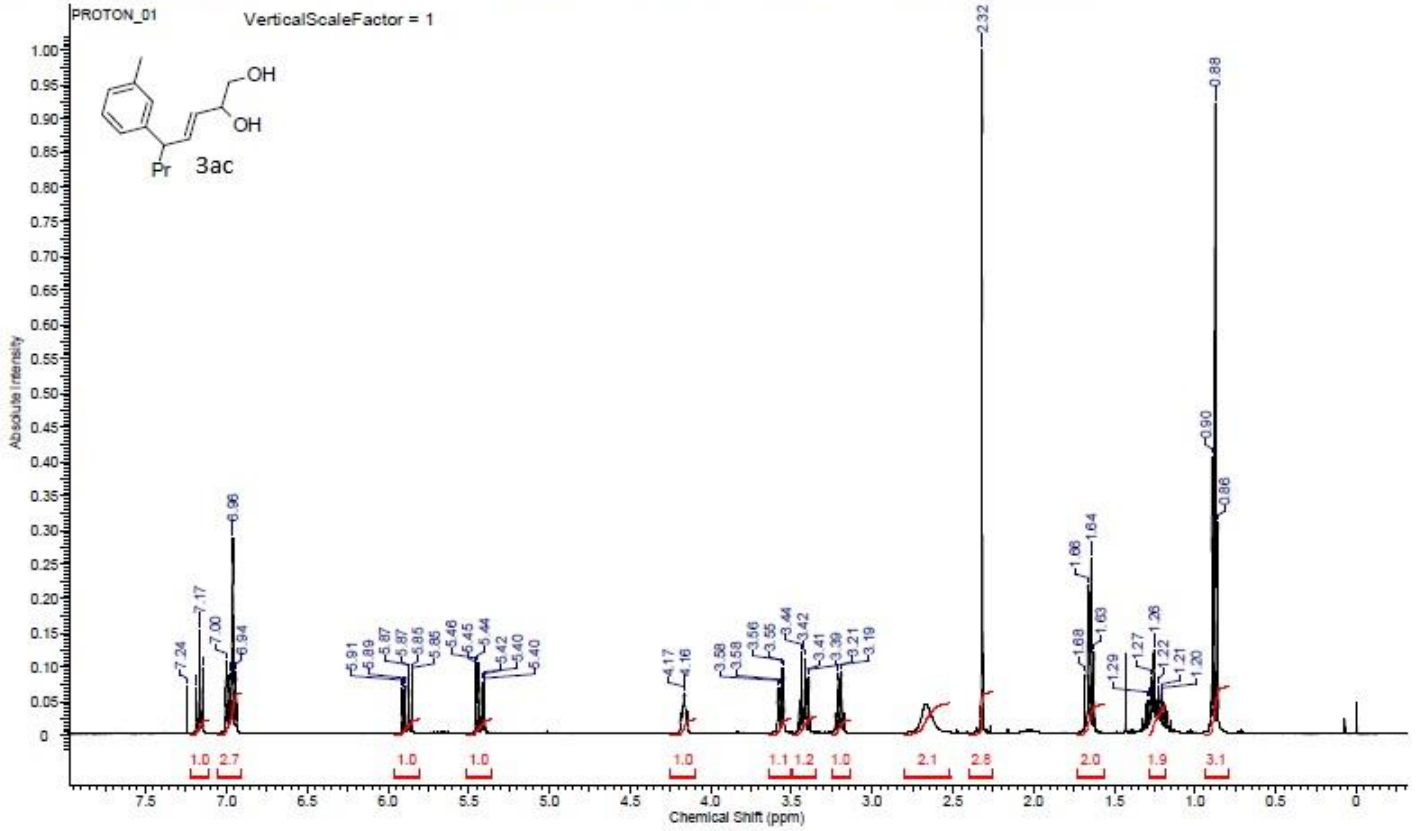

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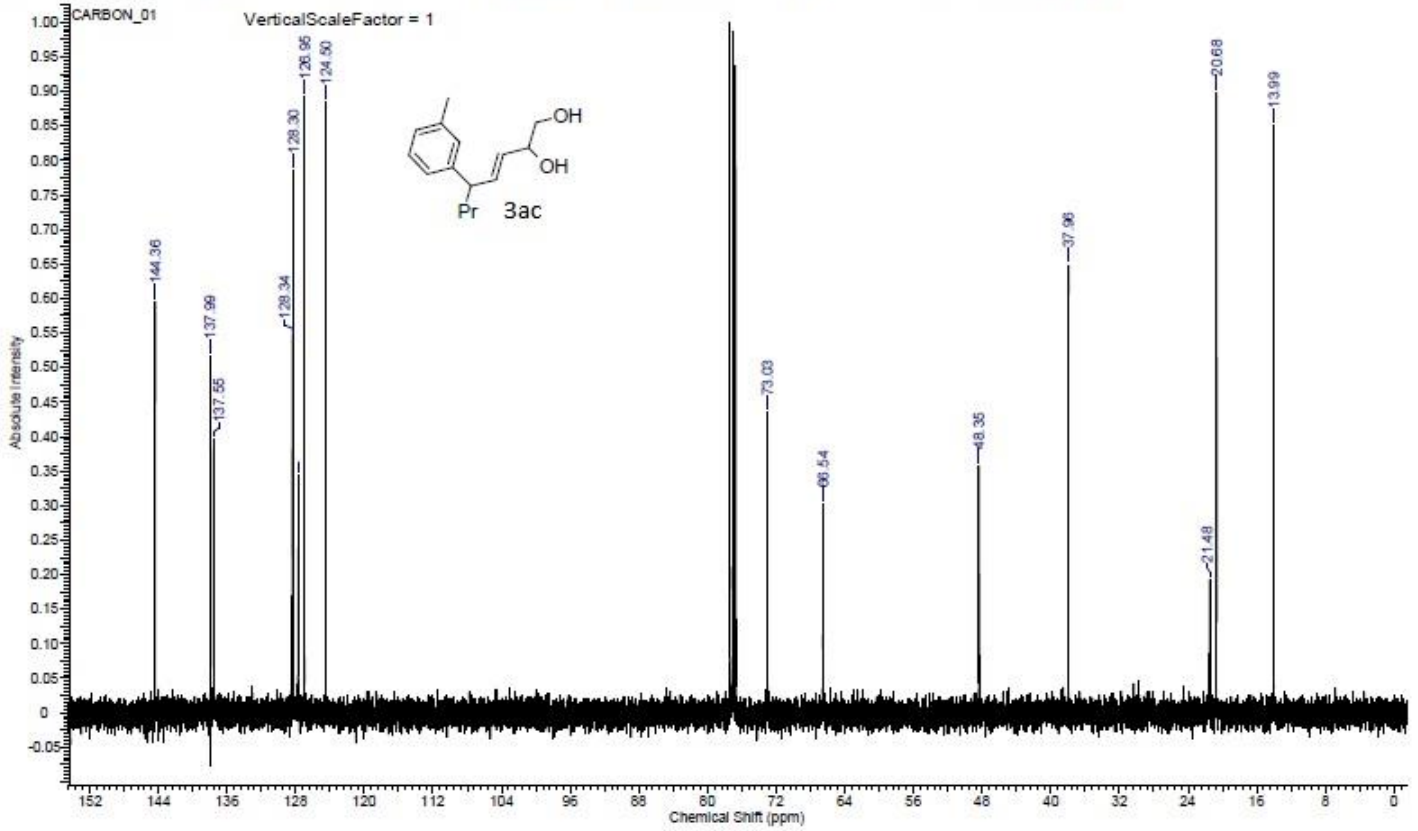
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	50.00	*Solvent*	BENZENE-d6
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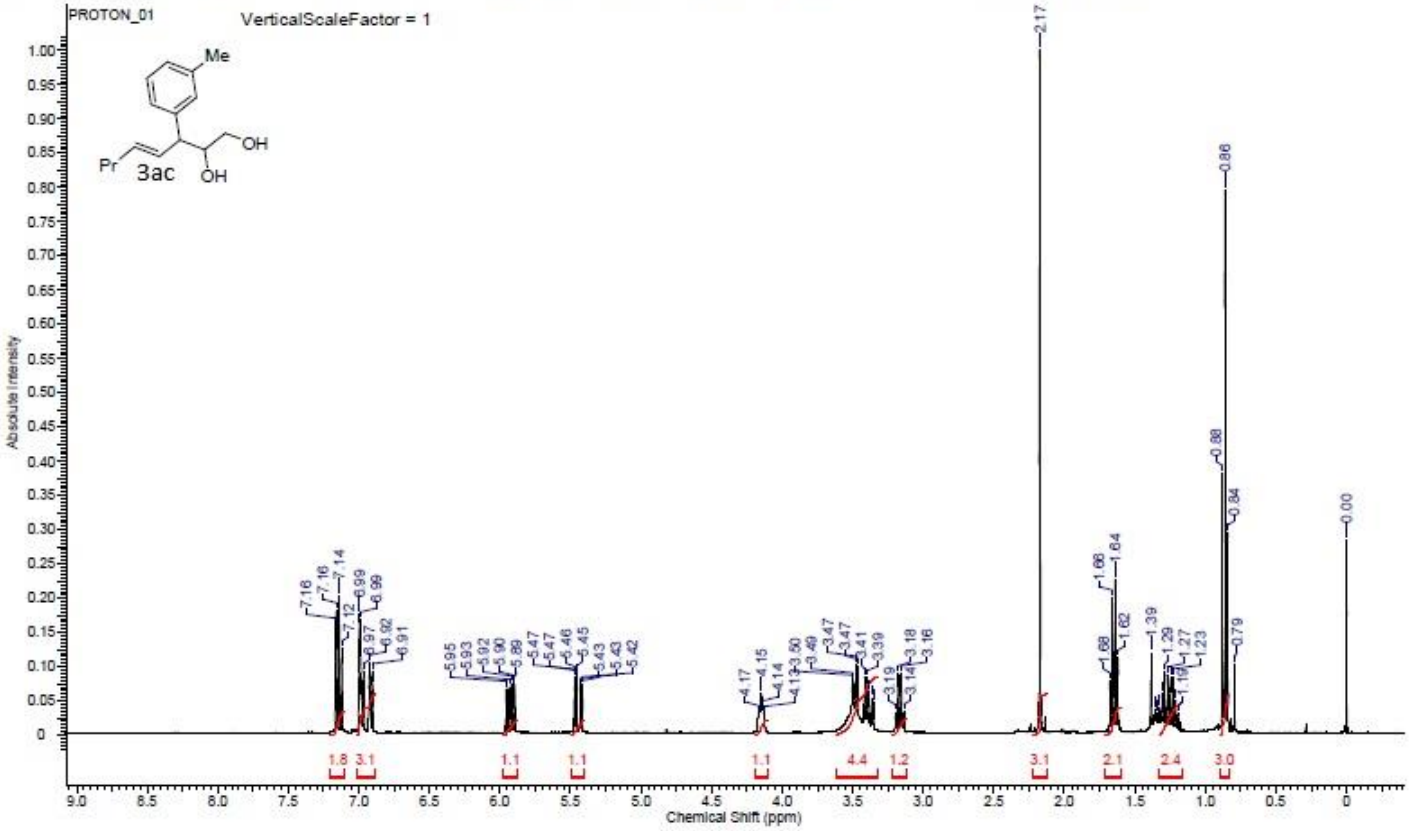

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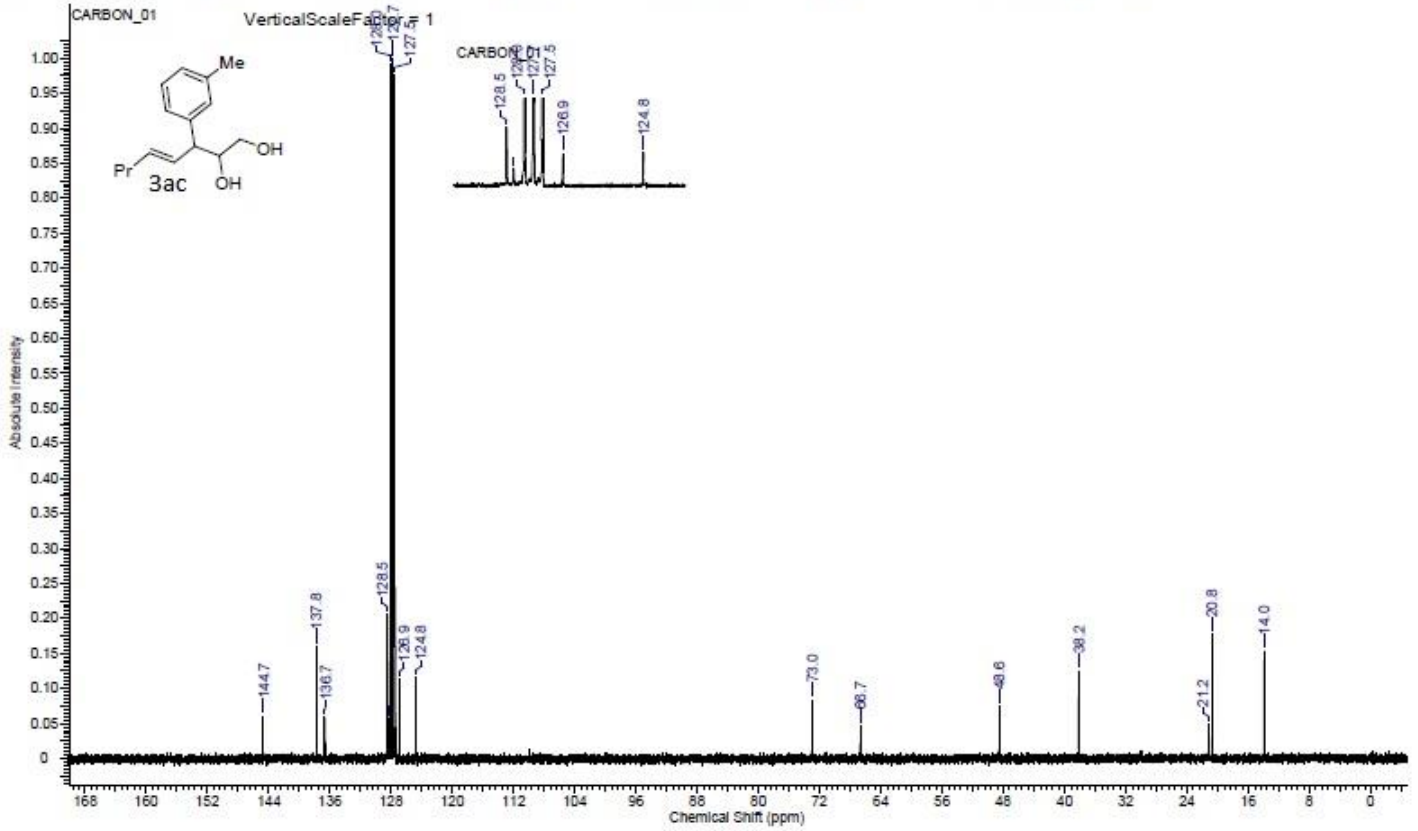
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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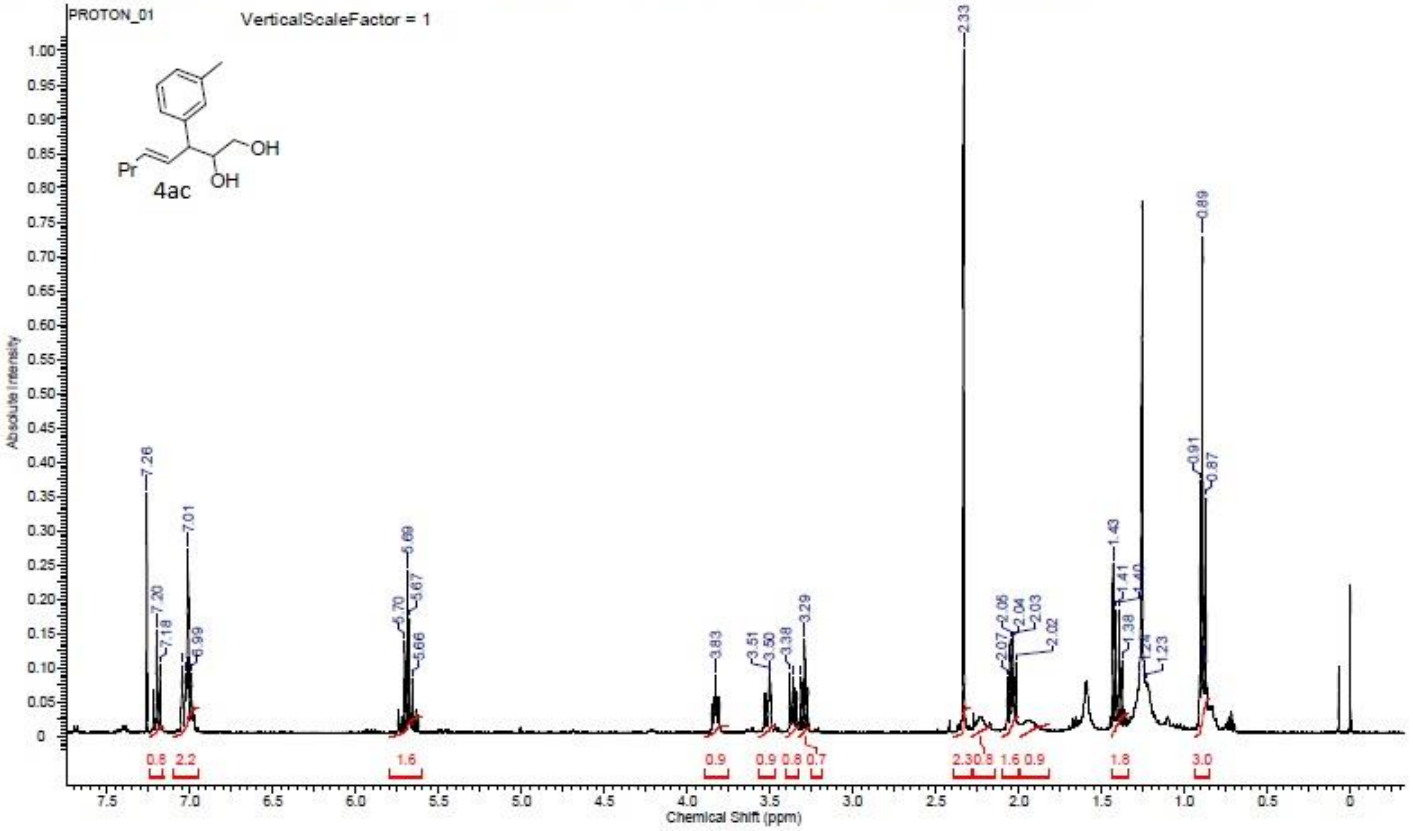
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
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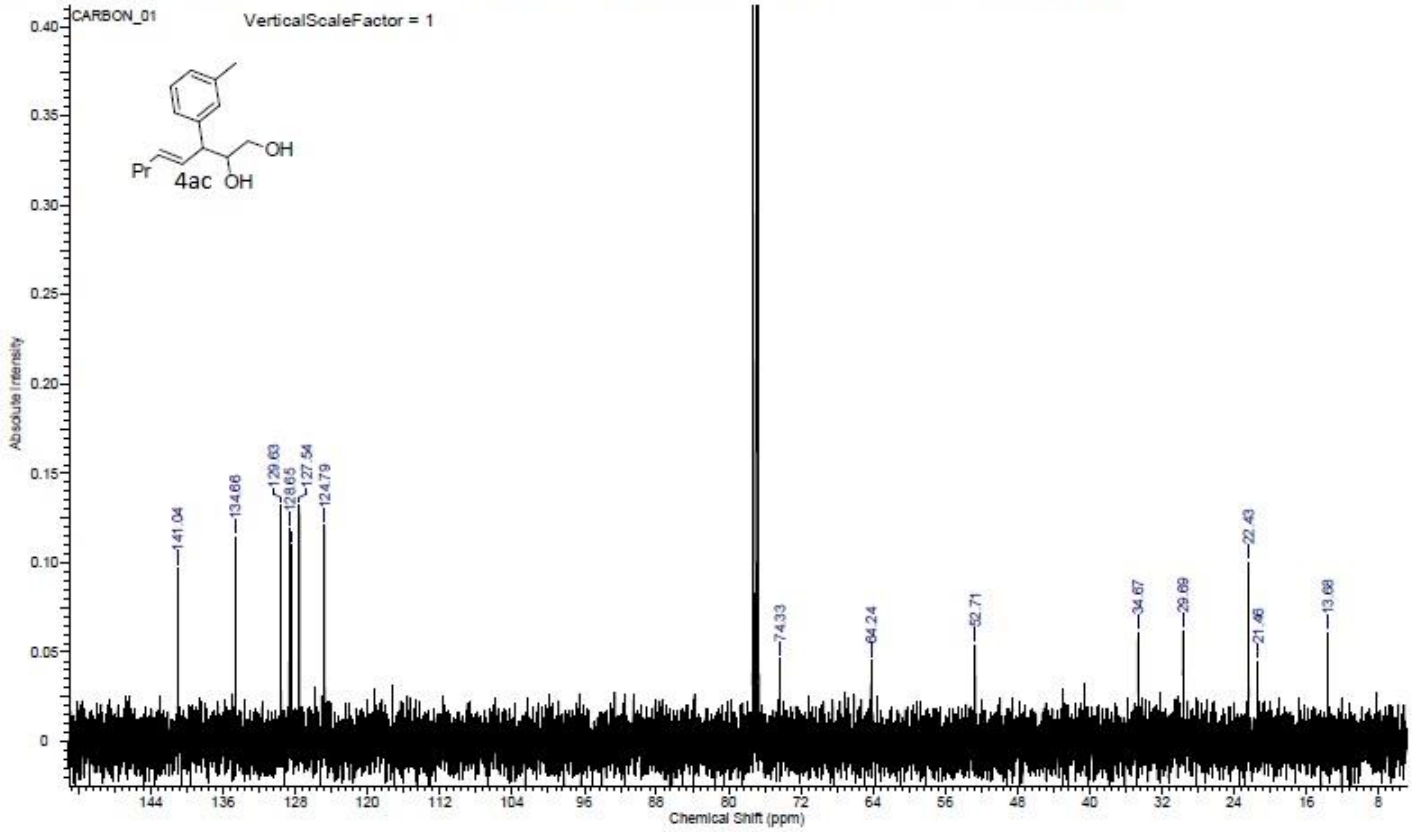

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Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
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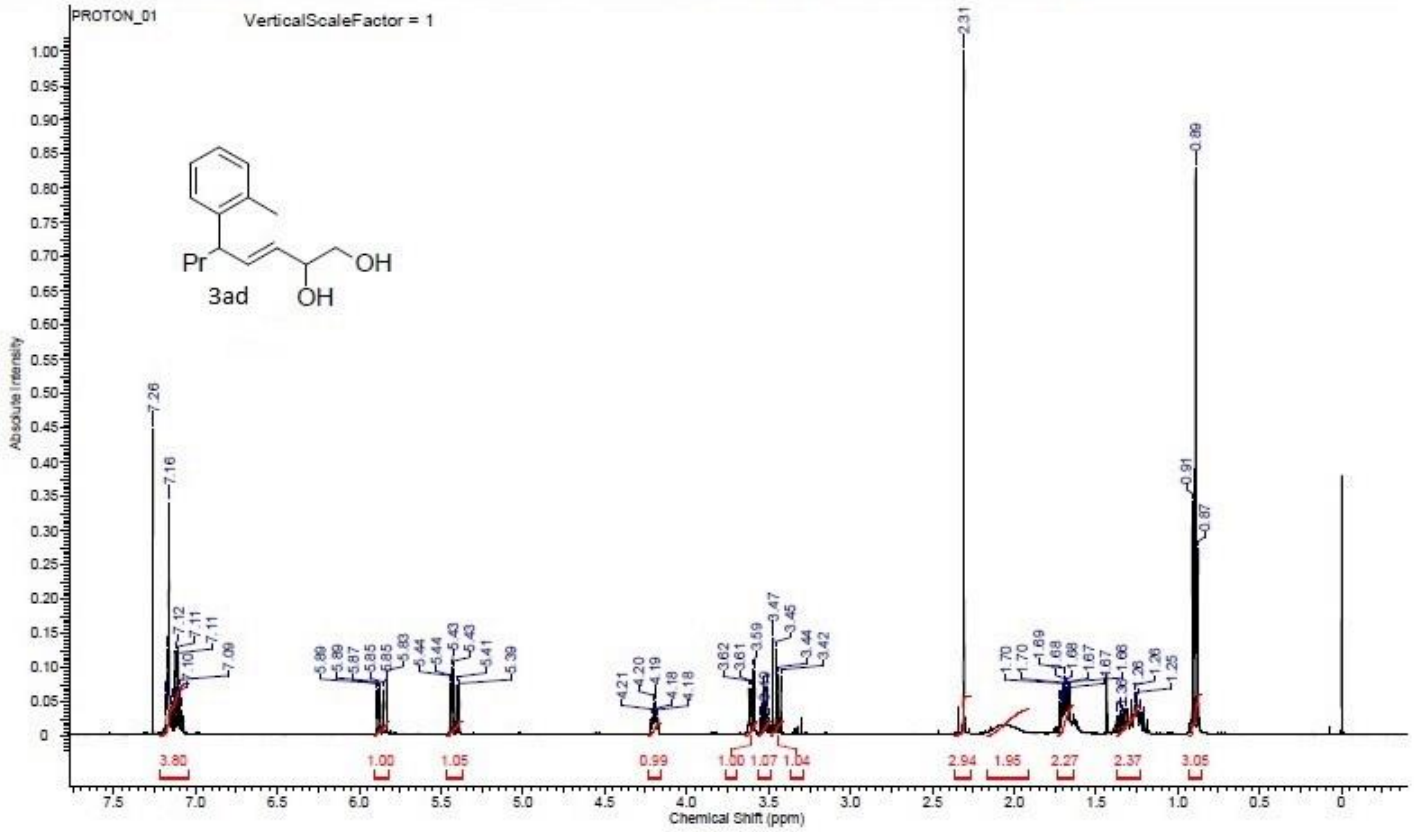
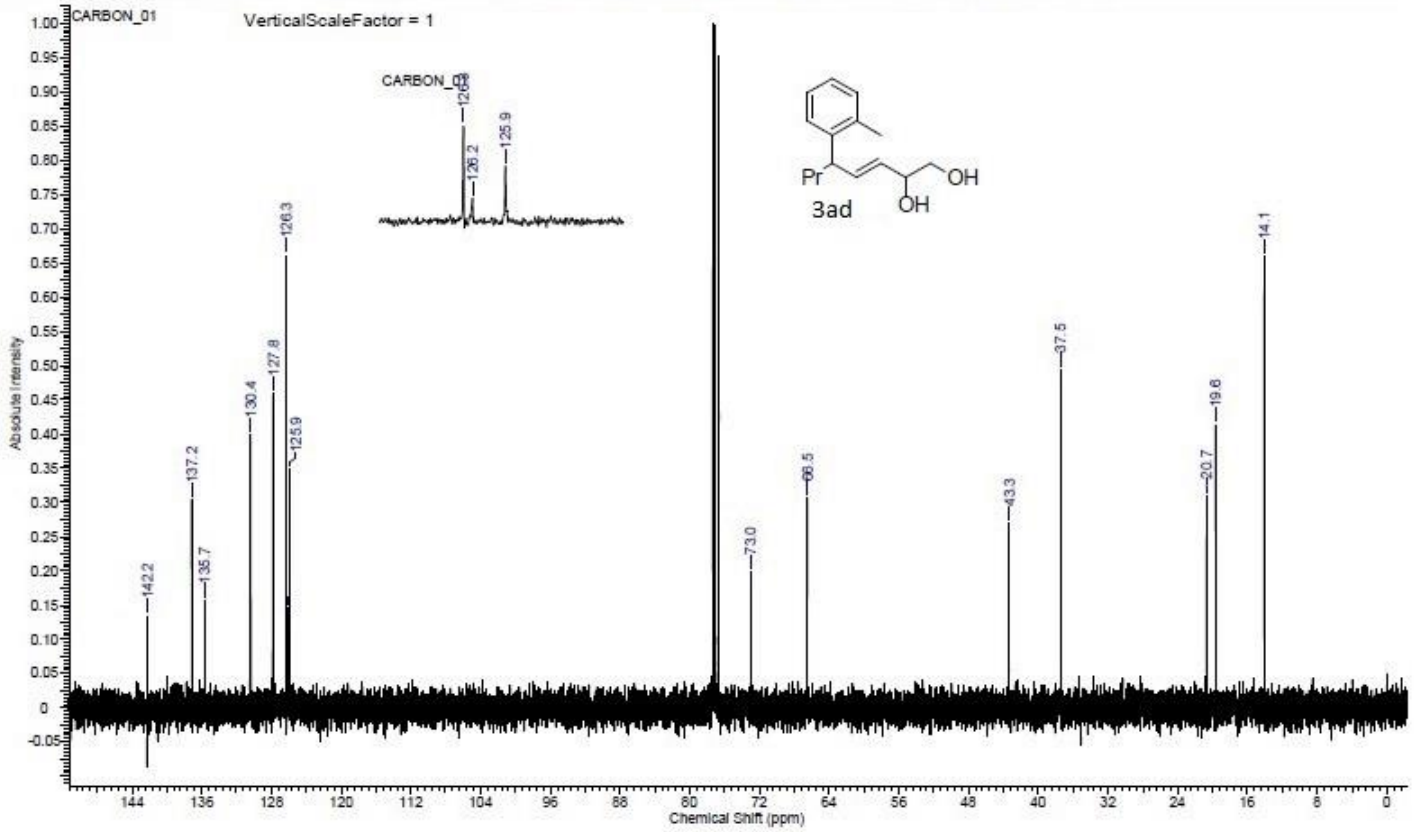
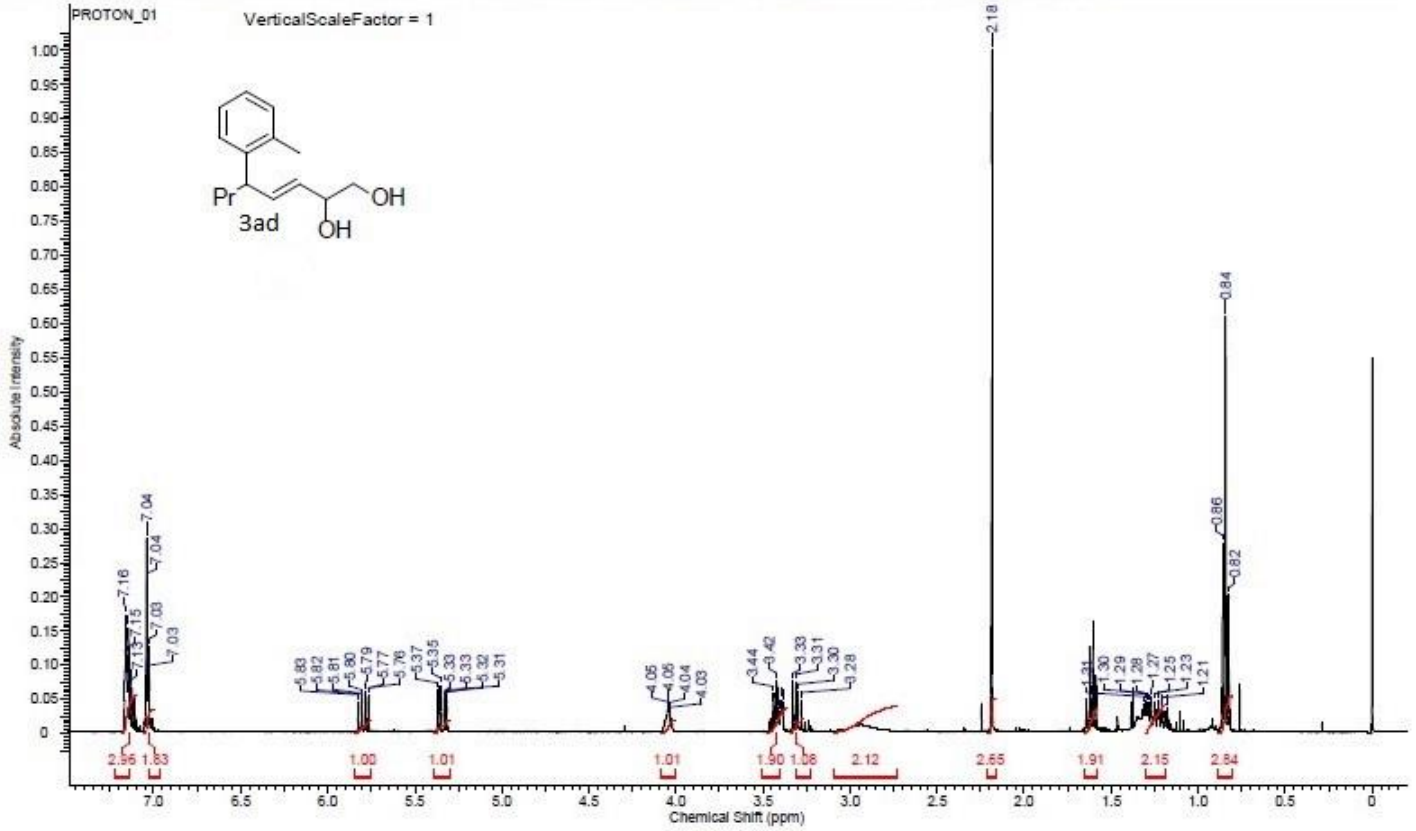


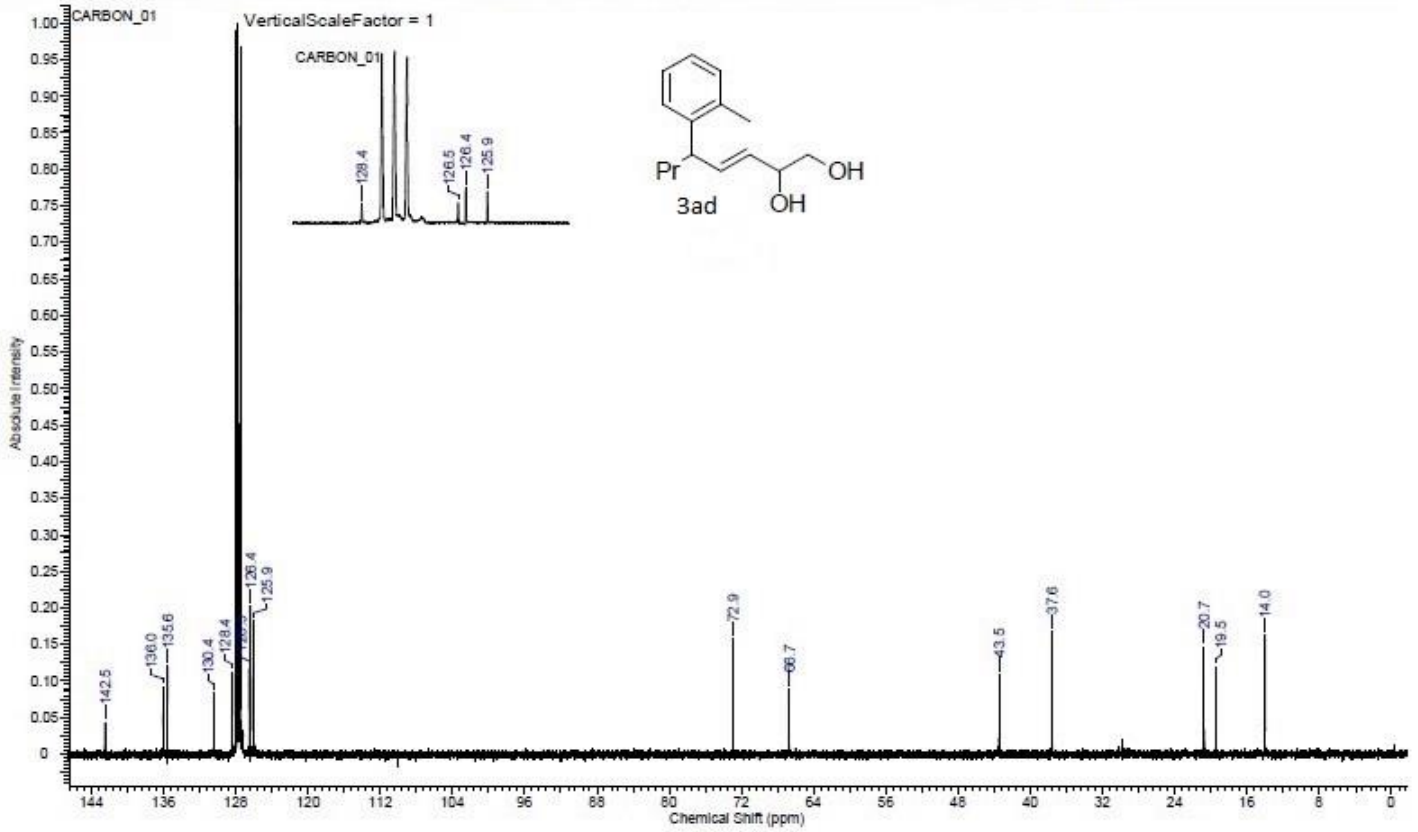
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-193-1_3-CDCL3			*Date*	Mar 30 2016
Date Stamp	Mar 30 2016	*File Name*	D:\YENI NMR\ERM-ENEP-193-1_3-CDCL3_20160330_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



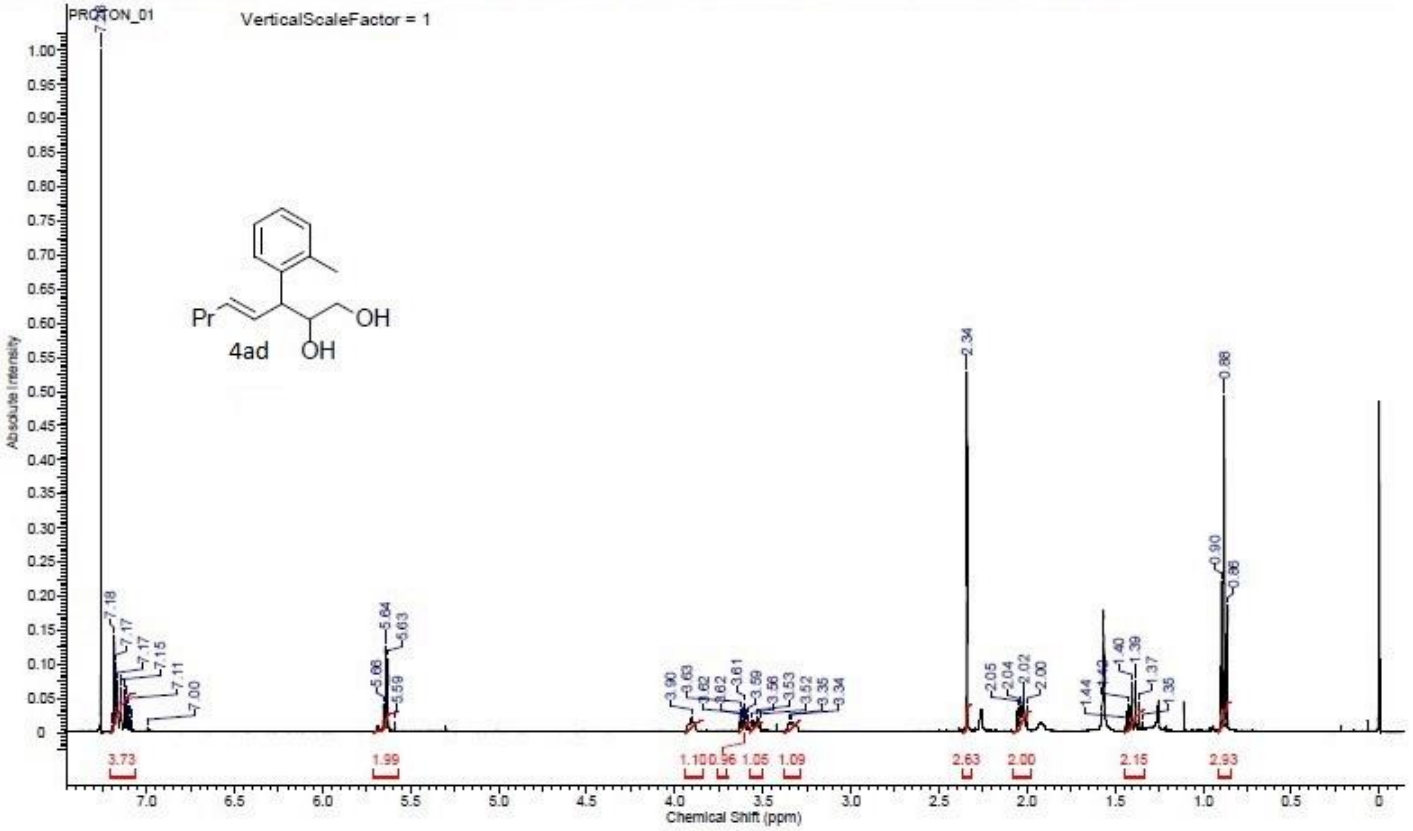
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-193-1_3			*Date*	Feb 11 2016
Date Stamp	Feb 11 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-193-1_3_20160211_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	50.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2380.7119	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



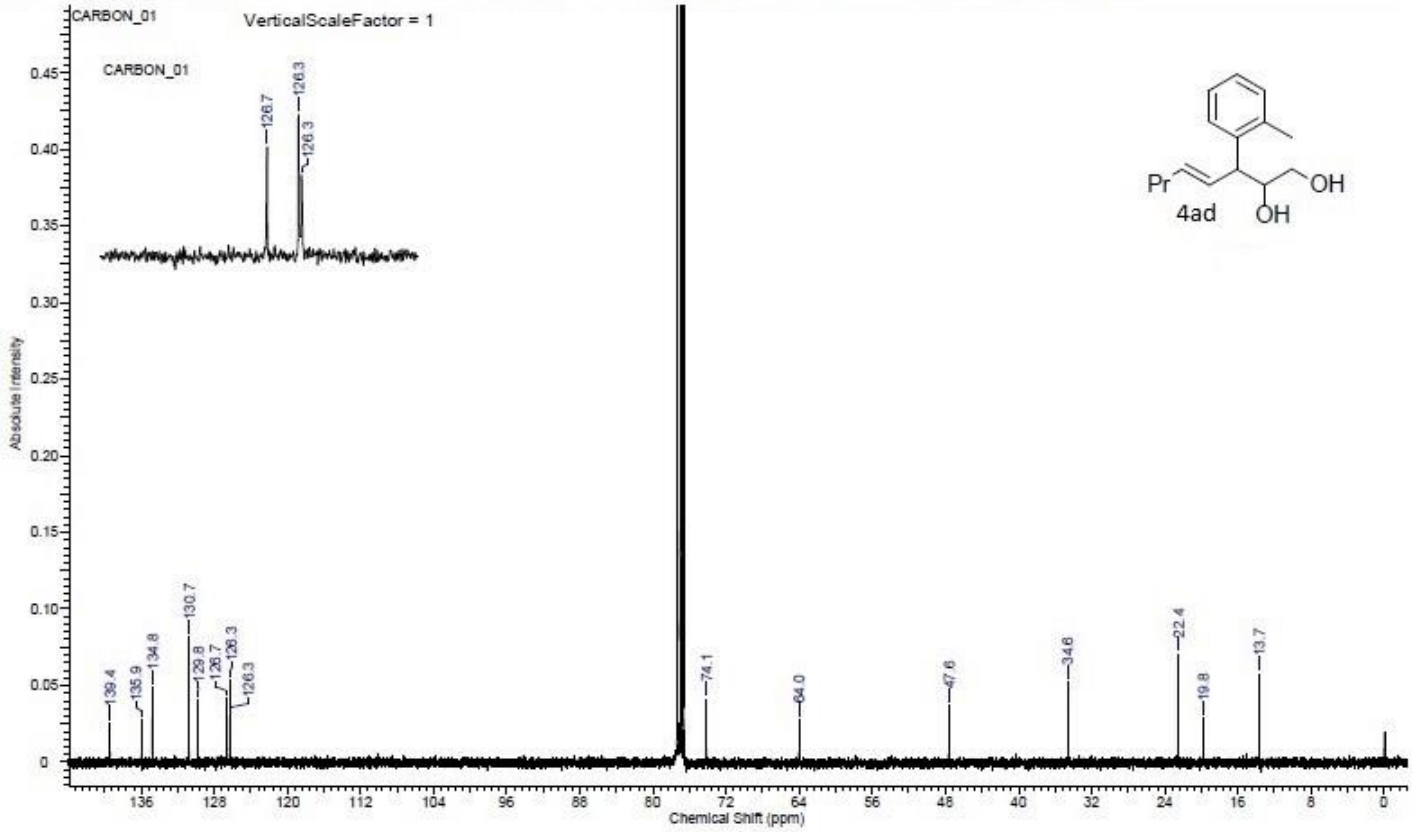
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-193-1_3			*Date*	Feb 12 2016
Date Stamp	Feb 12 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-193-1_3_20160211_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



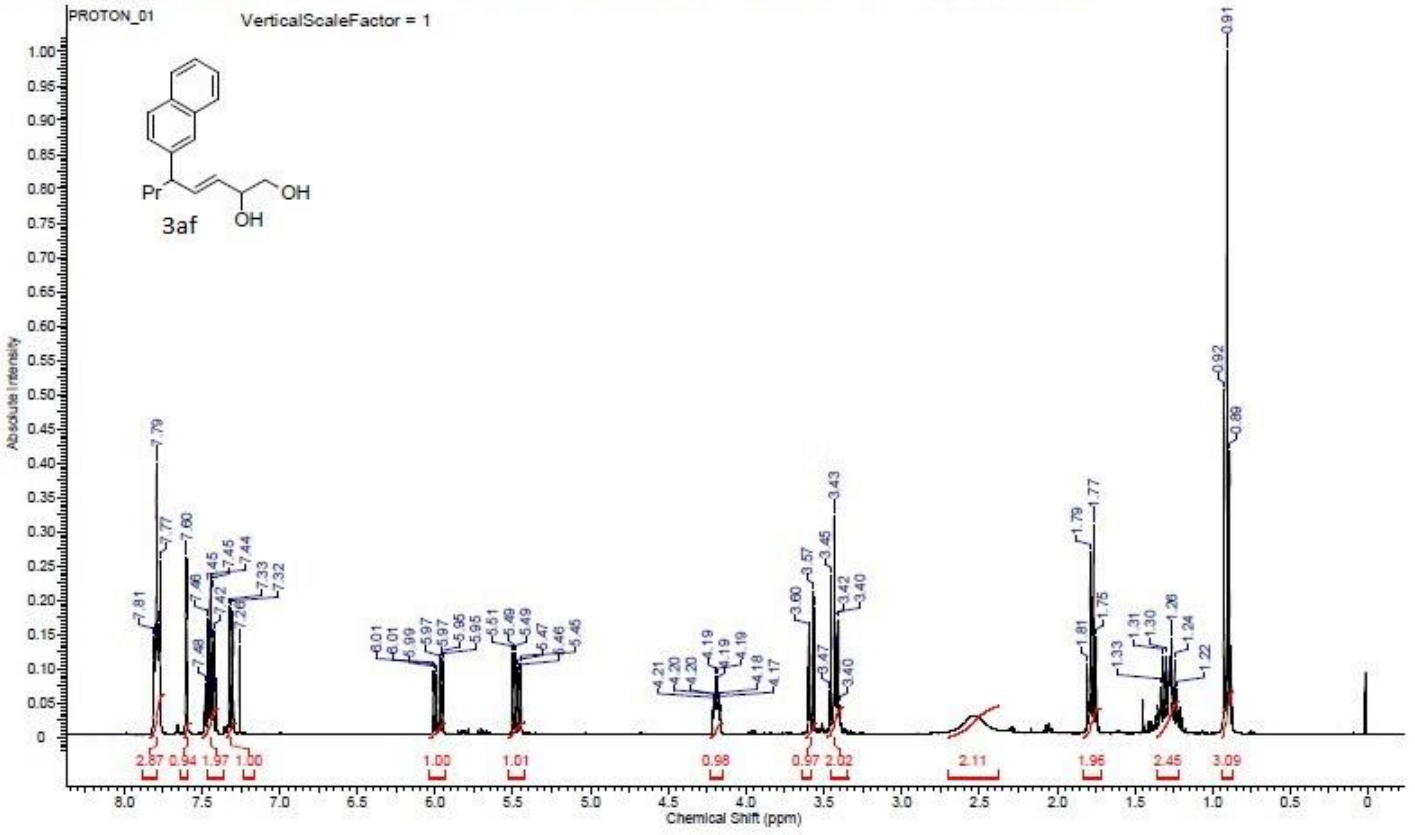
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-193-1_1			*Date*	Feb 12 2016
Date Stamp	Feb 12 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-193-1_1_20160212_02\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



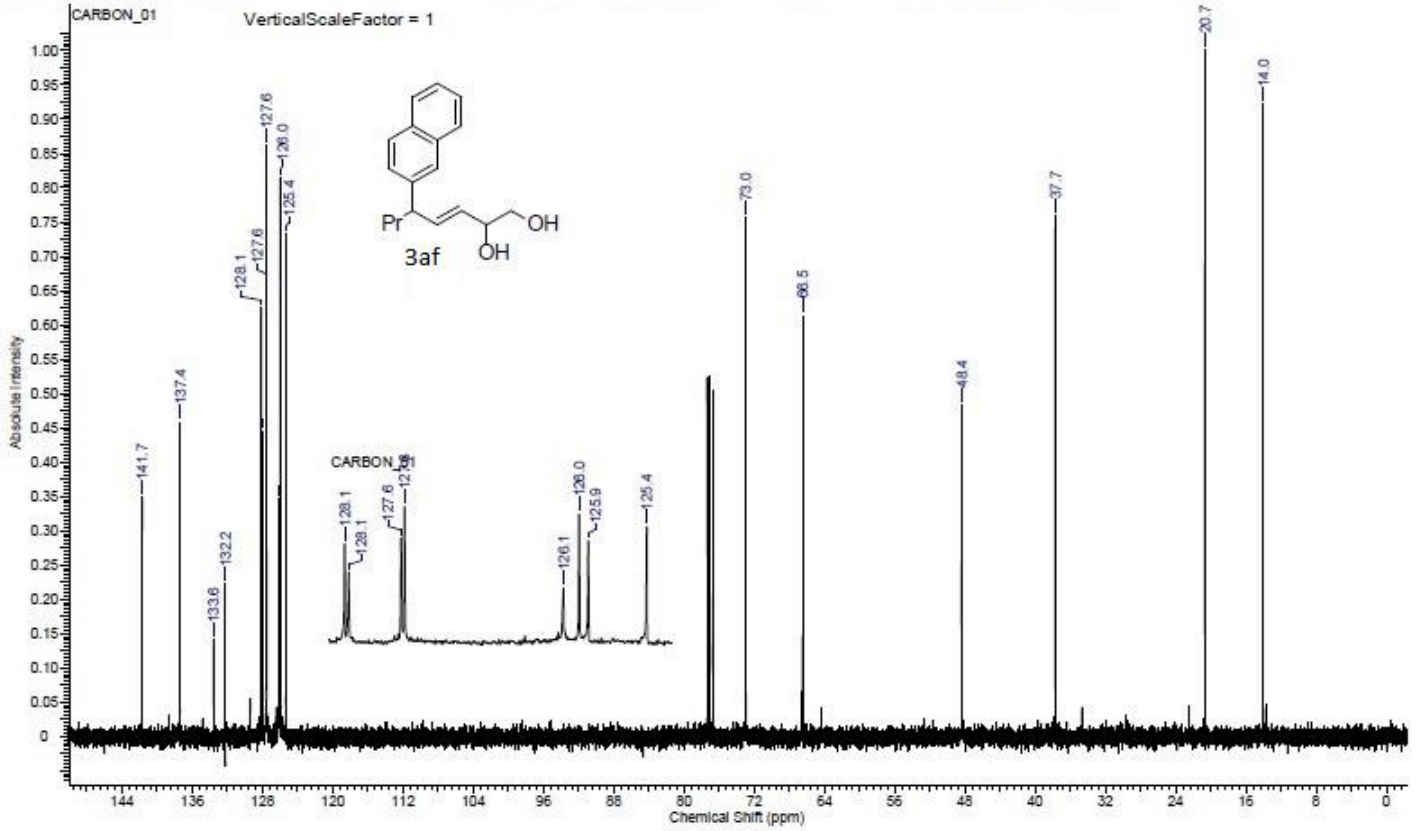
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-193-1_1			*Date*	Feb 12 2016
Date Stamp	Feb 12 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-193-1_1_20160212_02\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	5000	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



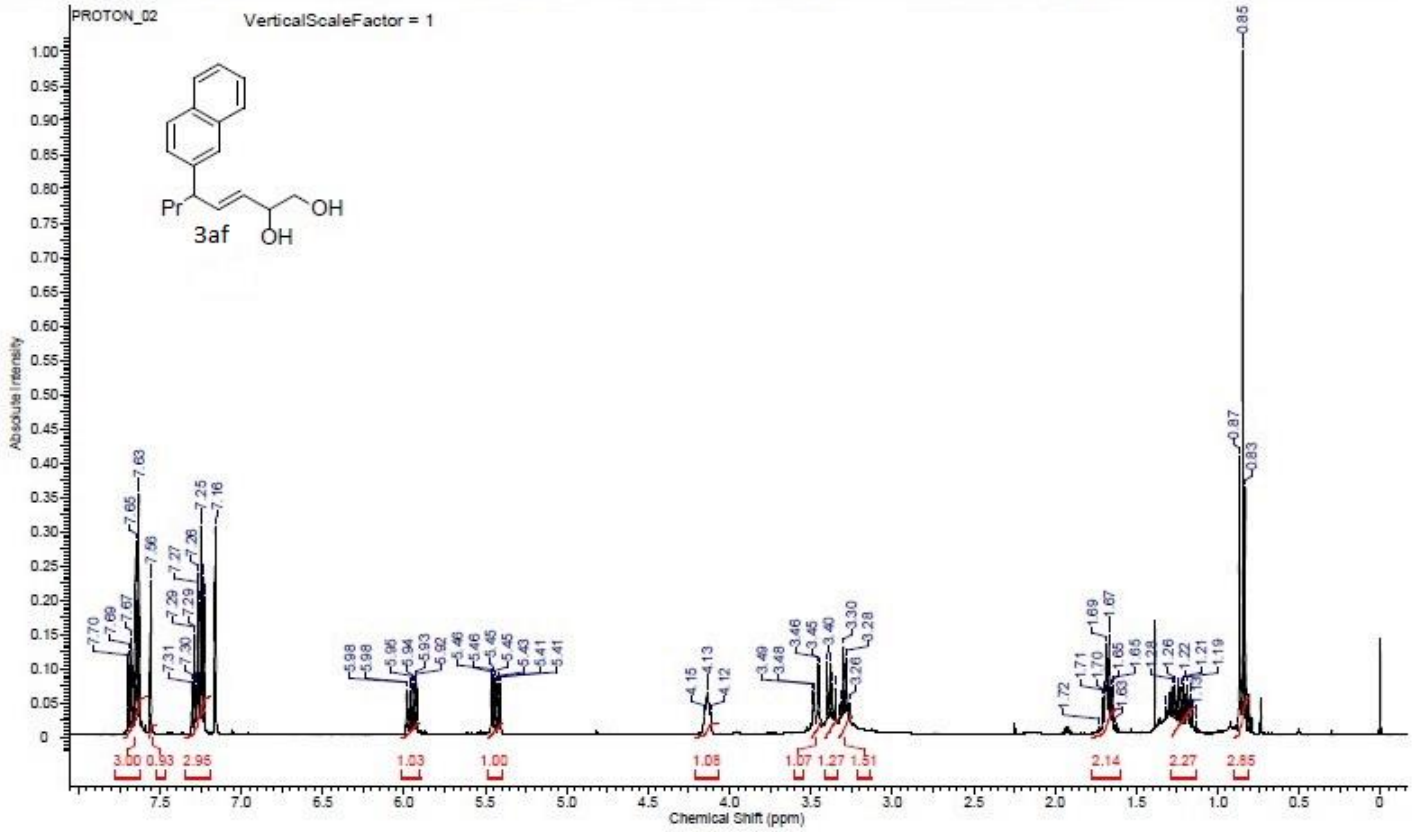
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-200-1_3-CDCL3			*Date*	Mar 30 2016
Date Stamp	Mar 30 2016	*File Name*	D:\YENI NMR\ERM-ENEP-200-1_3-CDCL3_20160330_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	54.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



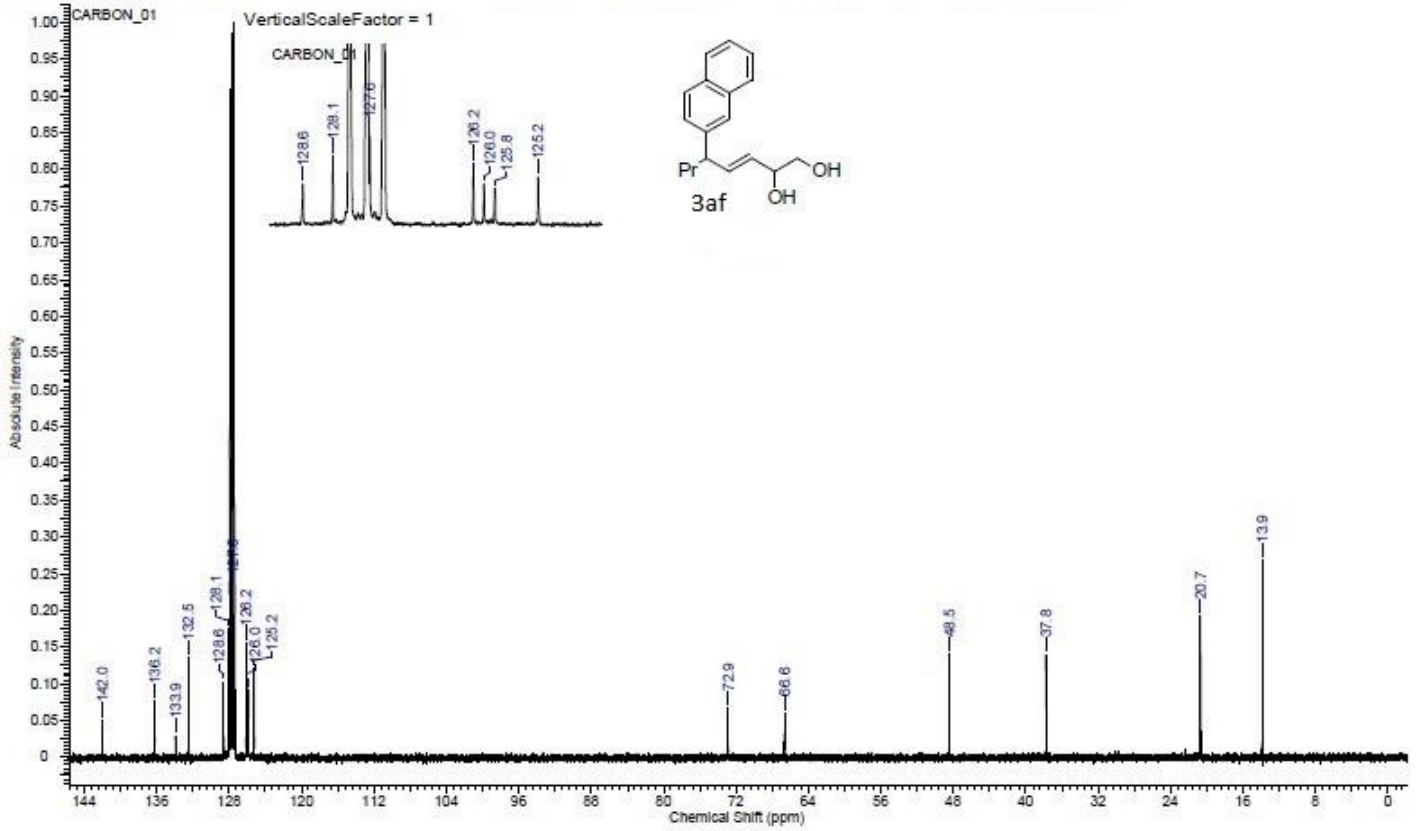
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-200-1_3-CDCL3			*Date*	Mar 30 2016
Date Stamp	Mar 30 2016	*File Name*	D:\YENI NMR\ERM-ENEP-200-1_3-CDCL3_20160330_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



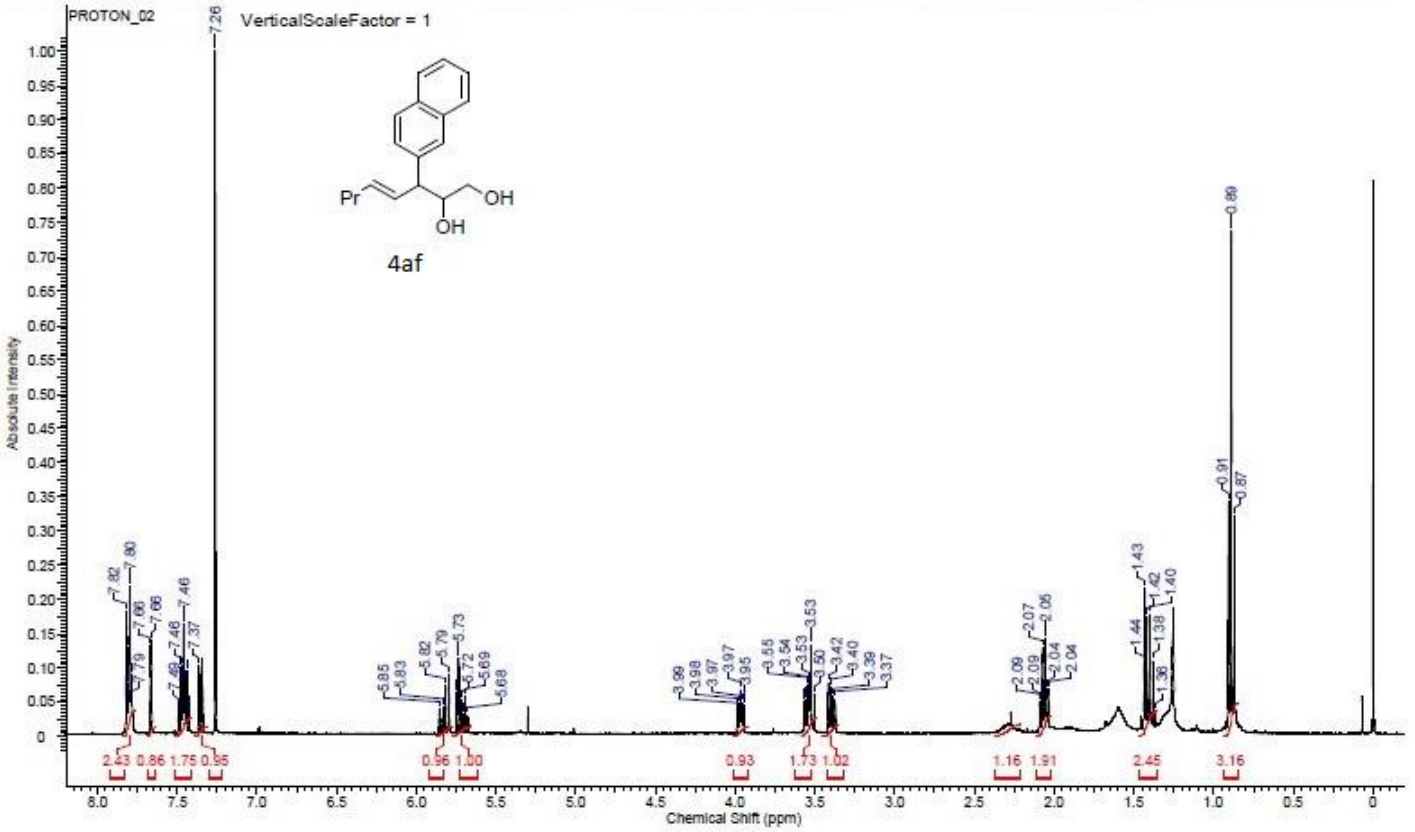
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-200-1_3			*Date*	Feb 24 2016
Date Stamp	Feb 24 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-200-1_3_20160224_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	64	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	52.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7092	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



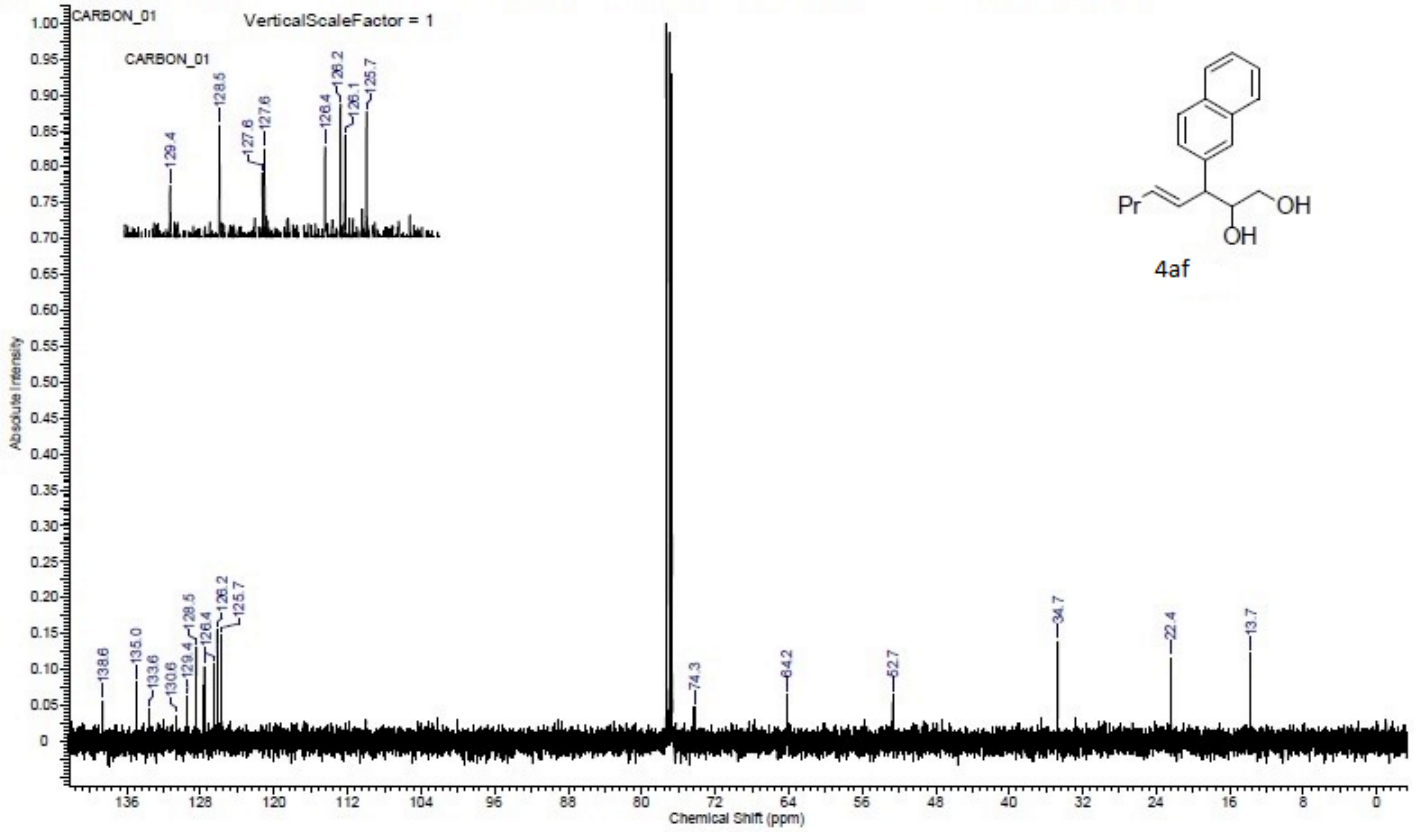
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-200-1_3			*Date*	Feb 24 2016
Date Stamp	Feb 24 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-200-1_3_20160224_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



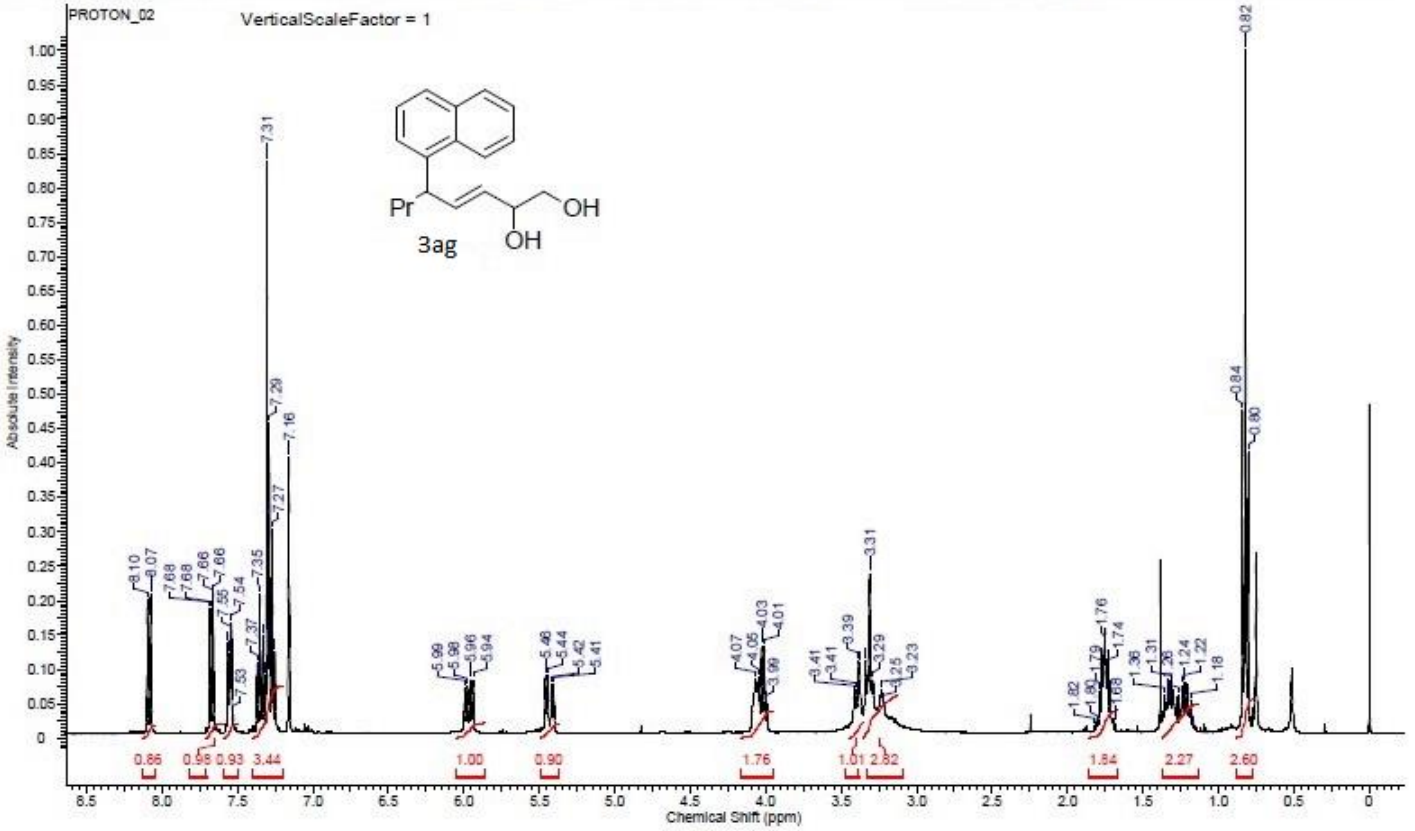
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-200-1_1-DOGRU			*Date*	Feb 24 2016
Date Stamp	Feb 24 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-200-1_1-DOGRU_20160224_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



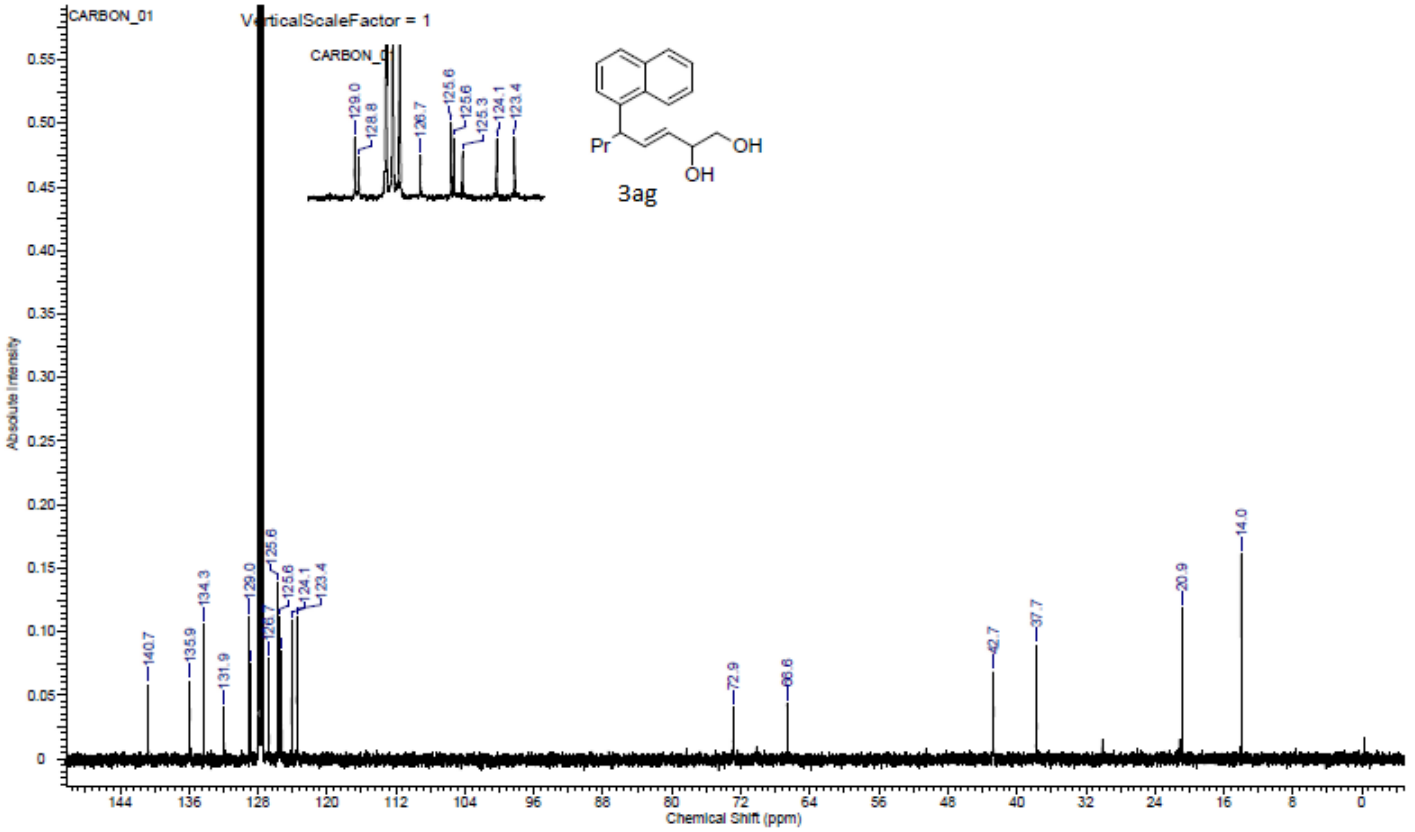
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-200-1_1-DOGRU			*Date*	Feb 24 2016
Date Stamp	Feb 24 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-200-1_1-DOGRU_20160224_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	500	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



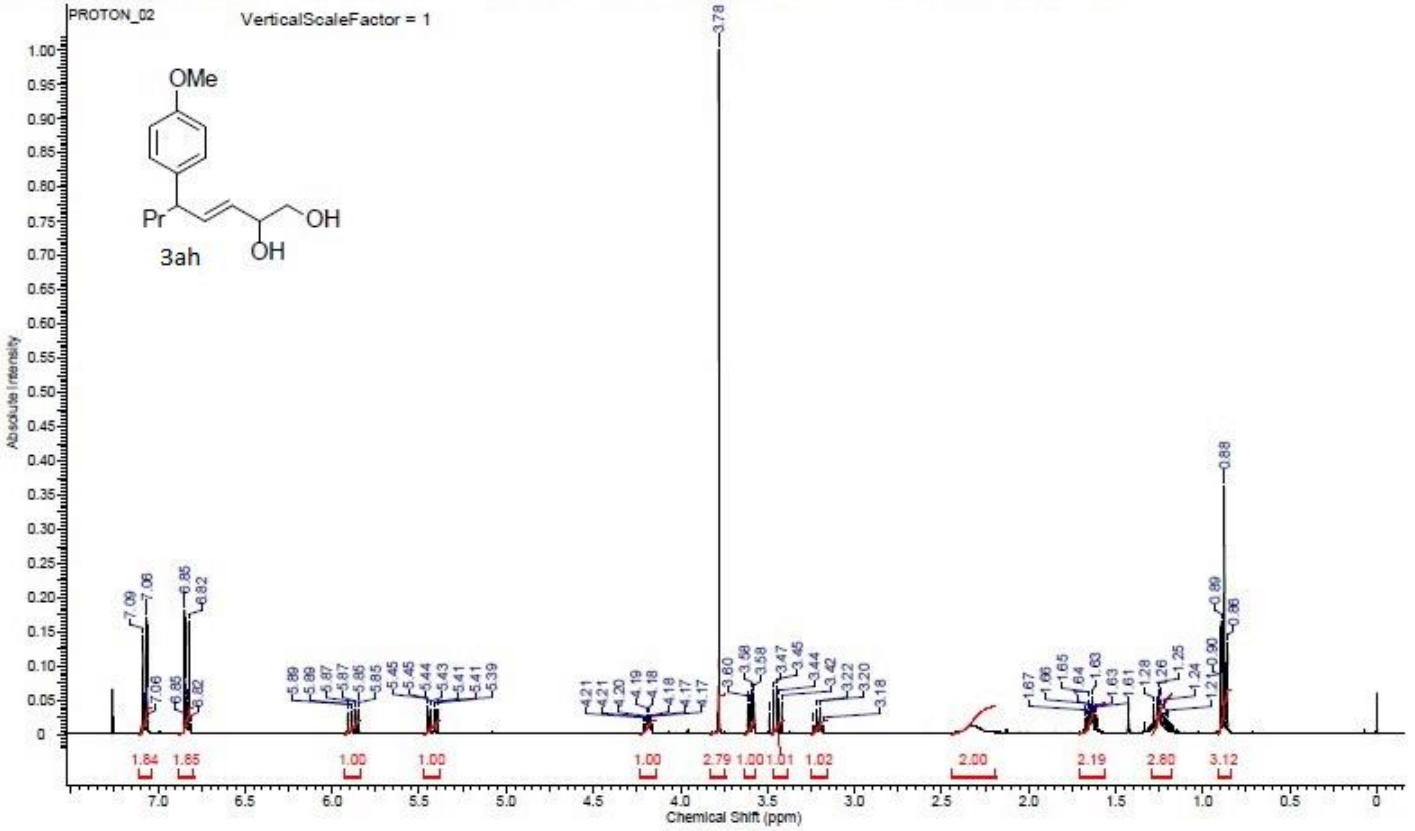
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-203-1_3			*Date*	Feb 29 2016
Date Stamp	Feb 29 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-203-1_3_20160229_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	52.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3181	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



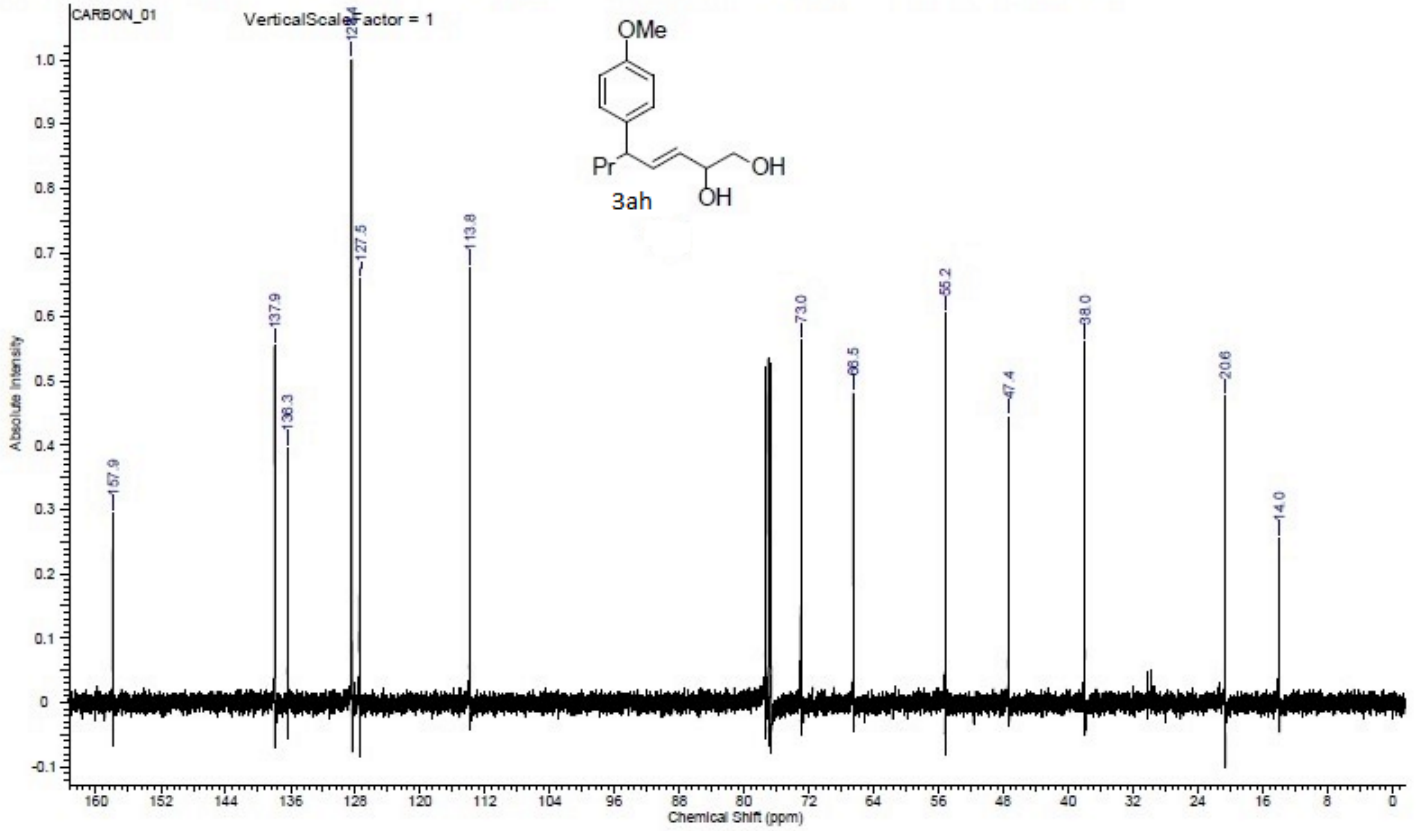
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-203-1_3			*Date*	Feb 29 2016
Date Stamp	Feb 29 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-203-1_3_20160229_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



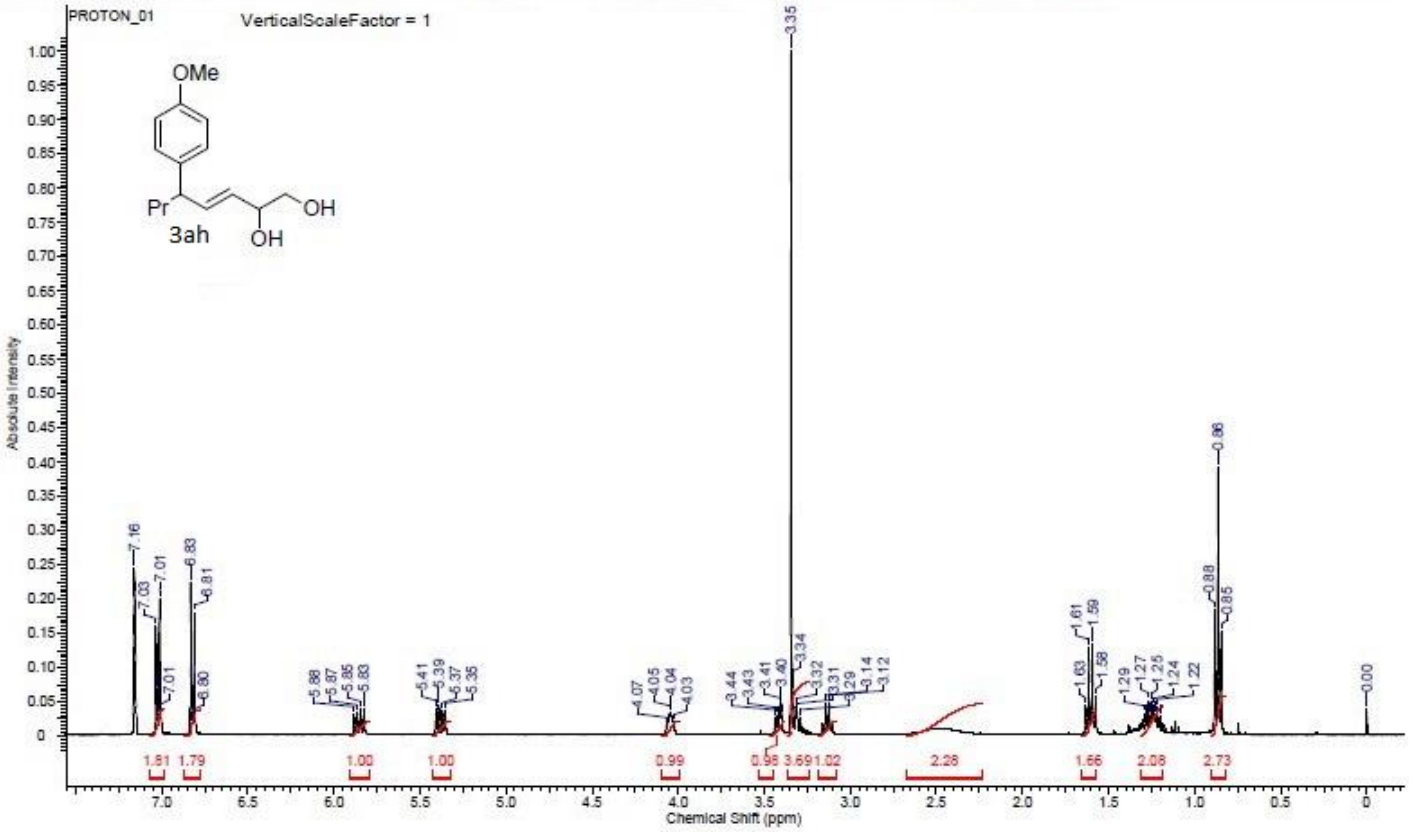
Acquisition Time (sec)	2.5559	*Comment*	erm-enep-191-1_3			*Date*	Feb 10 2016
Date Stamp	Feb 10 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-191-1_3_20160210_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	54.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



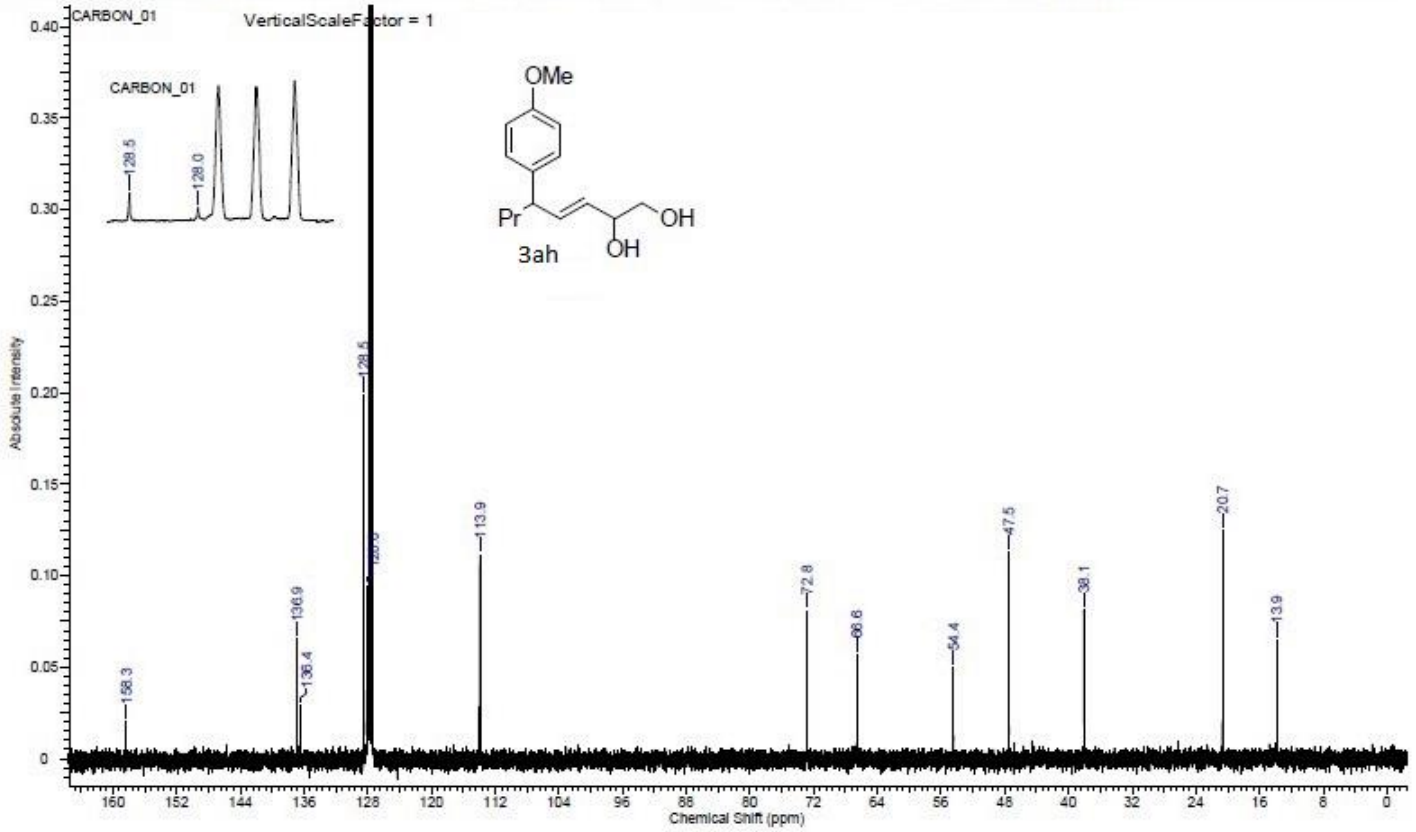
Acquisition Time (sec)	1.3107	*Comment*	erm-enep-191-1_3			*Date*	Feb 10 2016
Date Stamp	Feb 10 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-191-1_3_20160210_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



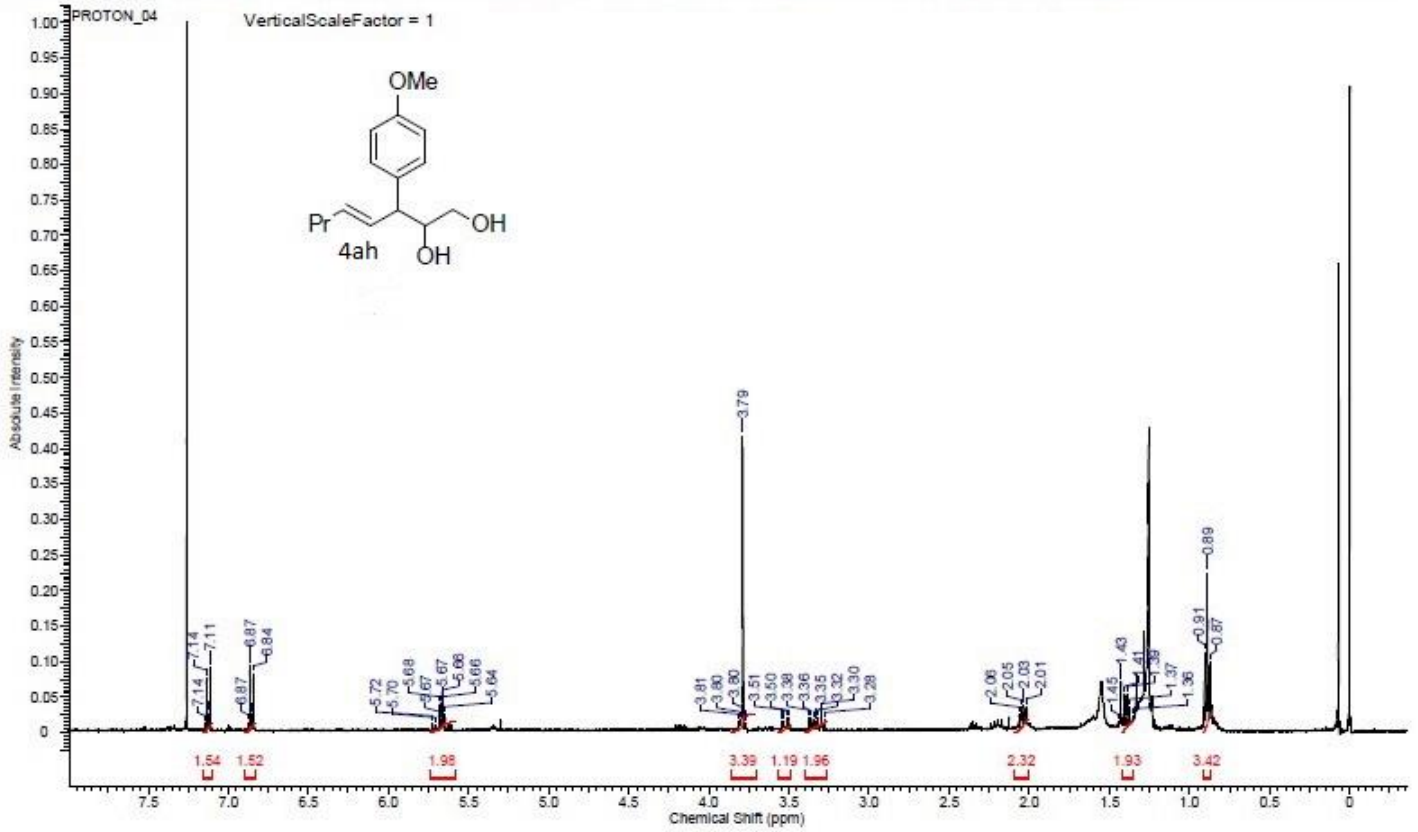
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-191-1_3			*Date*	Feb 2 2016
Date Stamp	Feb 2 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-191-1_3_20160202_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	56.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3181	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



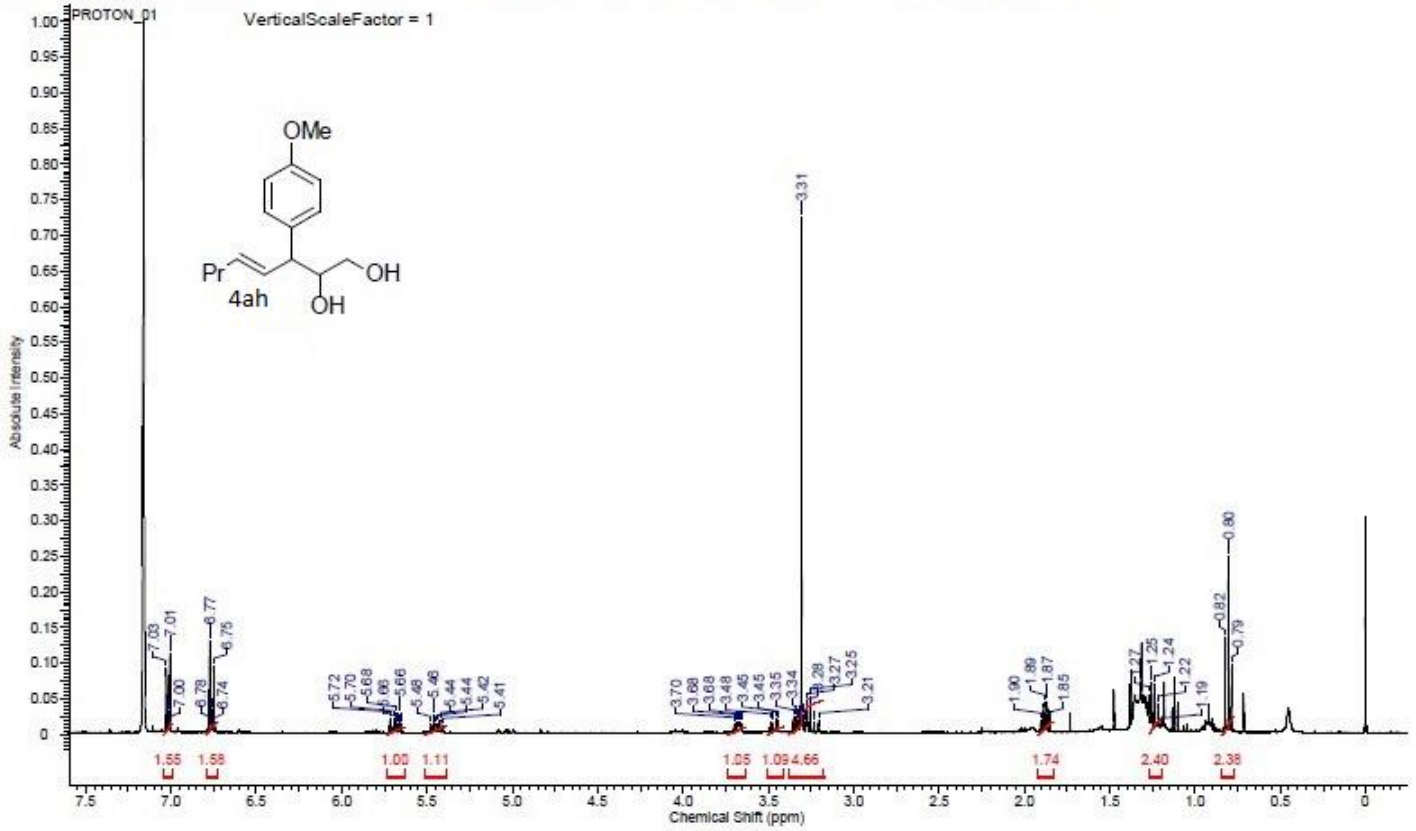
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-191-1_3			*Date*	Feb 2 2016
Date Stamp	Feb 2 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-191-1_3_20160202_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



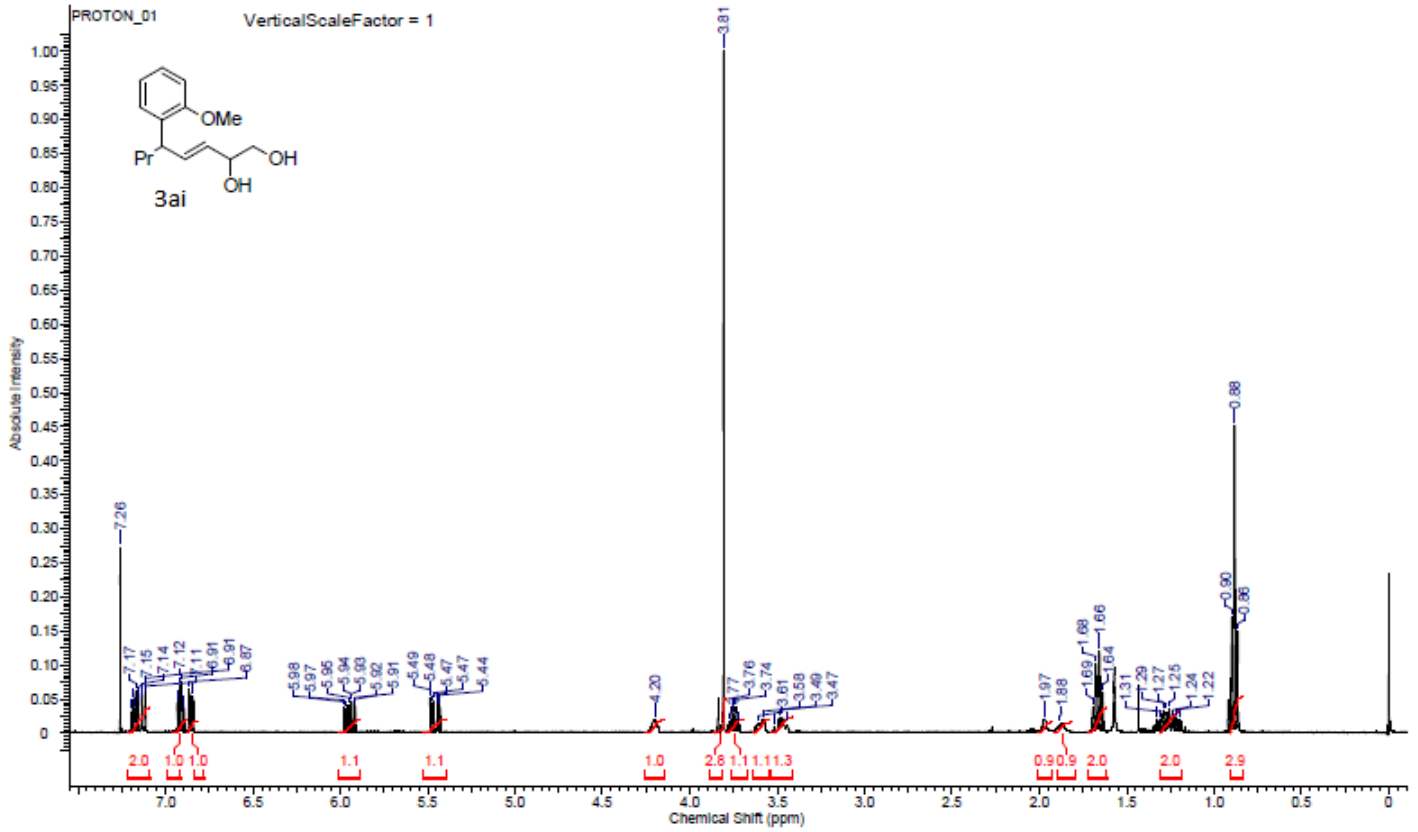
Acquisition Time (sec)	2.5559	*Comment*	erm-enep-191-1_1			*Date*	Feb 10 2016
Date Stamp	Feb 10 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-191-1_1_20160210_01\PROTON_04.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-191-1_1			*Date*	Feb 2 2016
Date Stamp	Feb 2 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-191-1_1_20160202_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

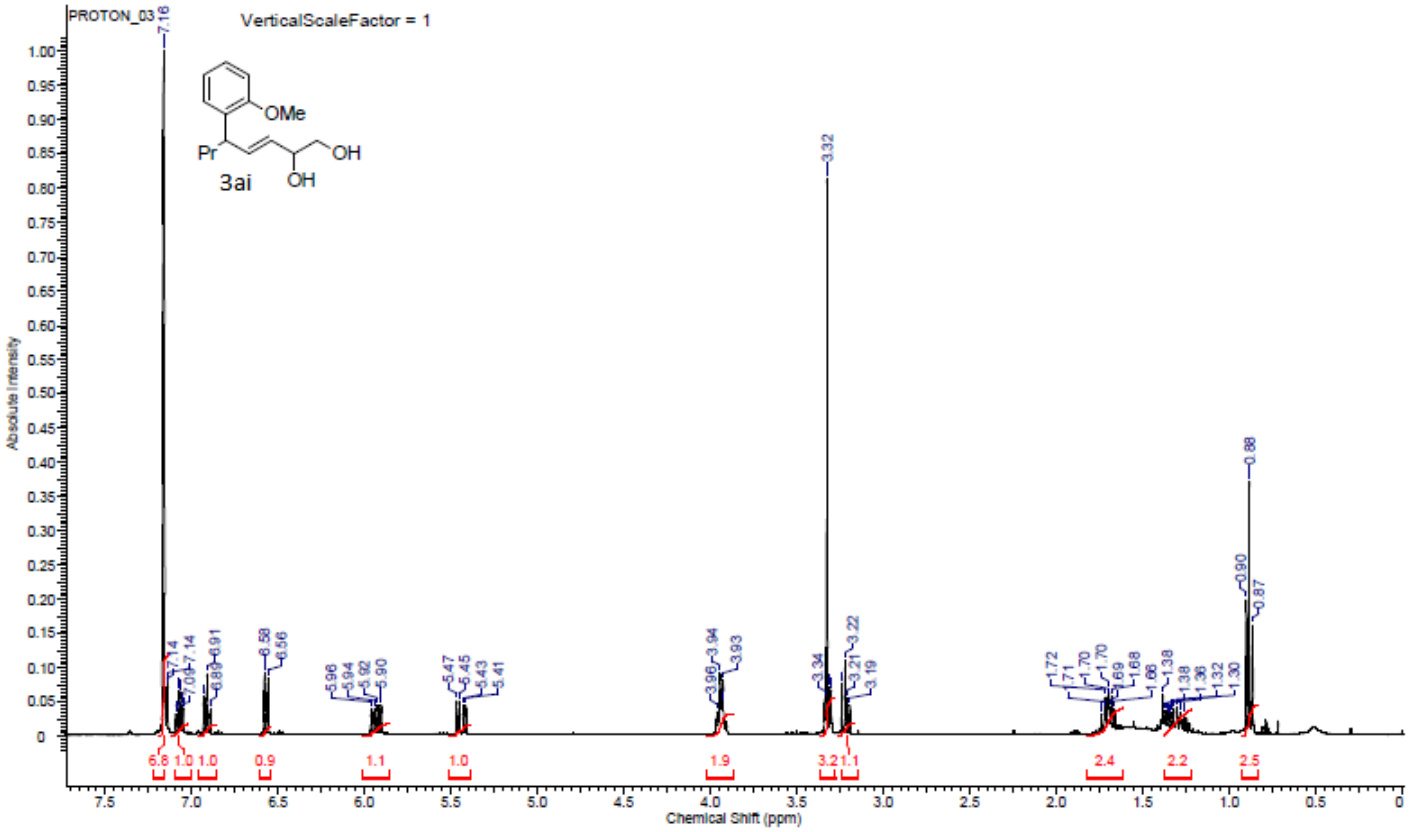


Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-210-1_3-CDCL3			*Date*	Apr 22 2016
Date Stamp	Apr 22 2016	*File Name*	F:\UNTITLED FOLDER\ERM-ENEP-210-1_3-CDCL3_20160422_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

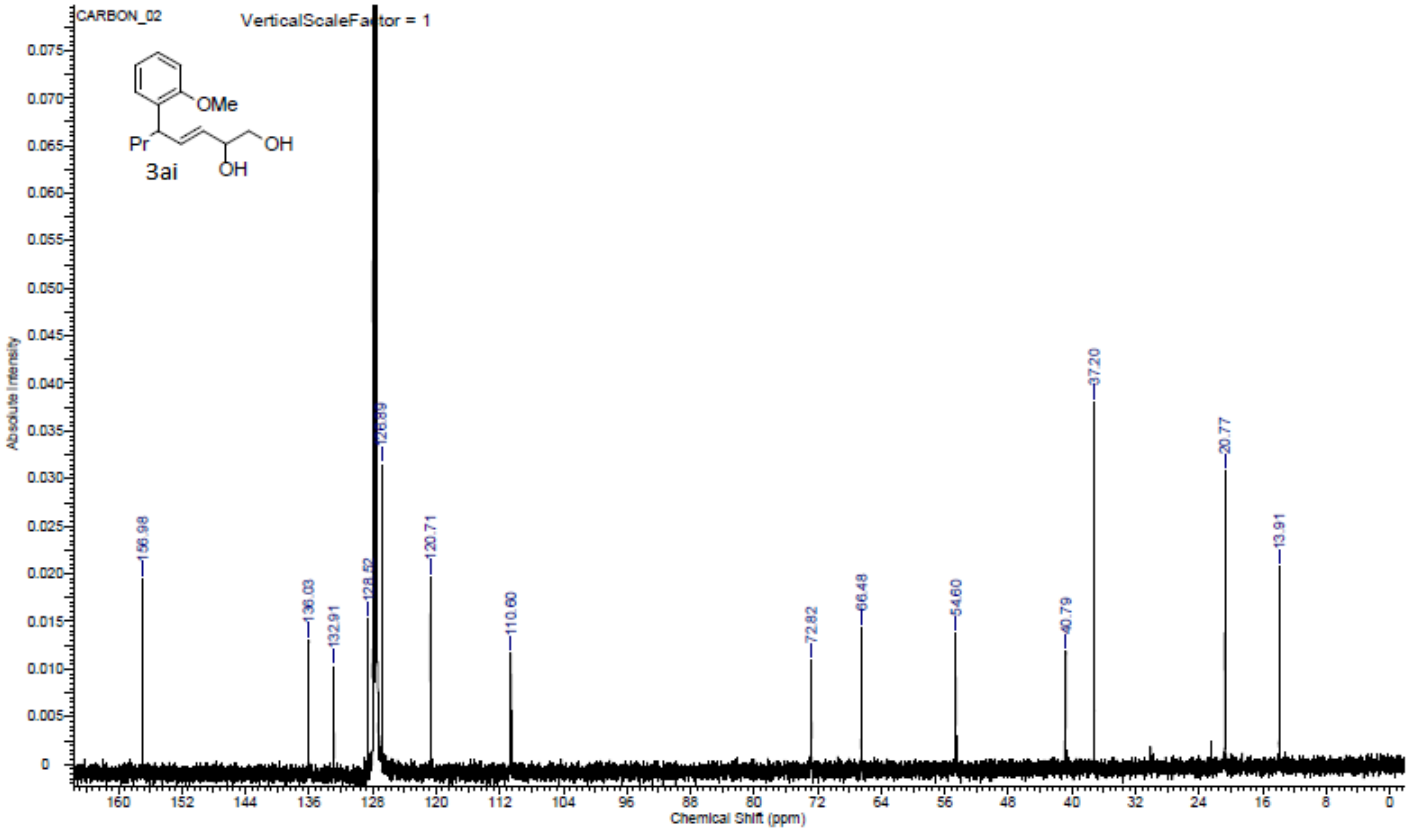


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

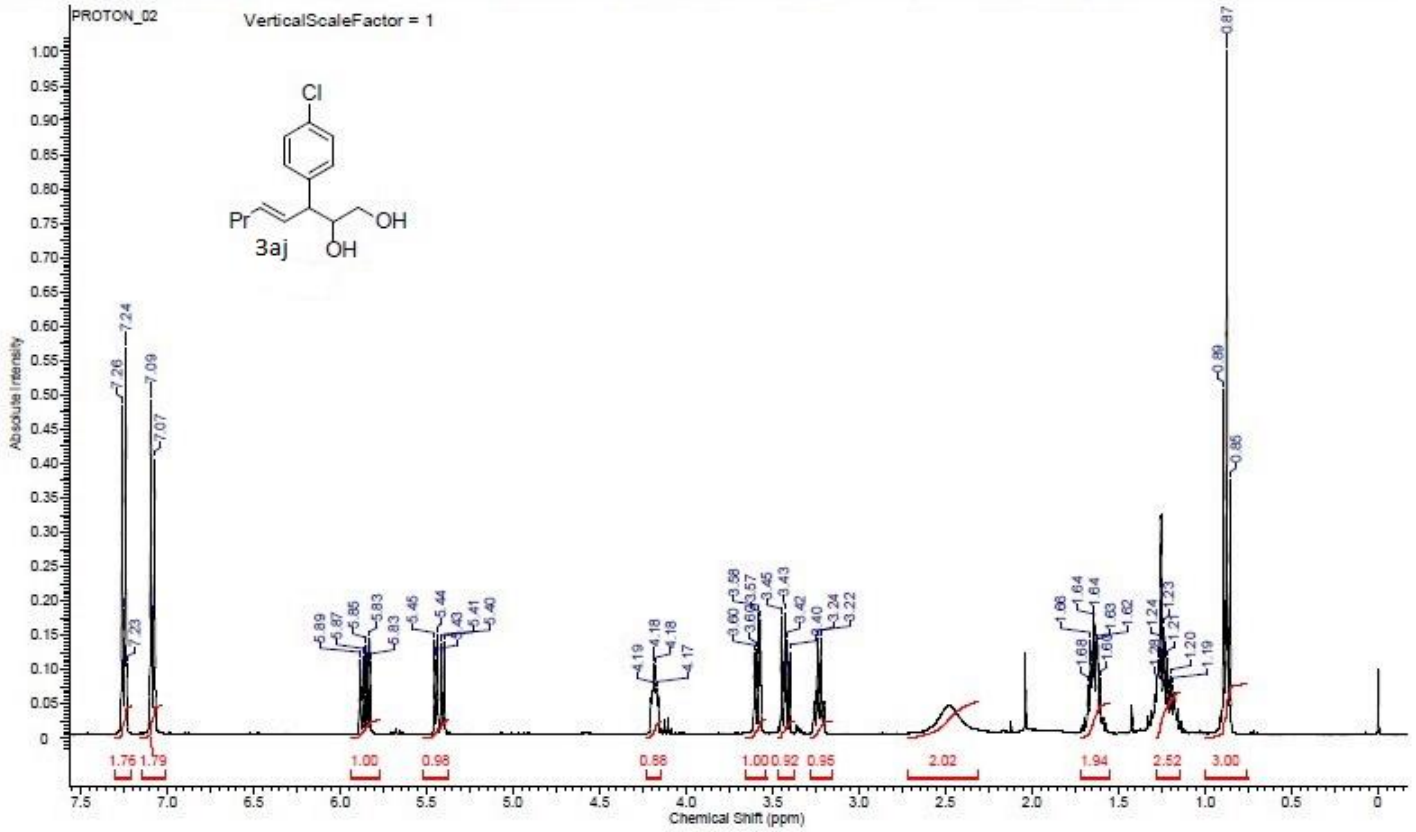
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-210-1_3-BNZ			*Date*	Apr 25 2016
Date Stamp	Apr 25 2016	*File Name*	C:\USERS\ERMAN\DESKTOP\UNTITLED FOLDER\ERM-ENEP-210-1_3-BNZ_20160425_01\PROTON_03.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	64	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3853	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



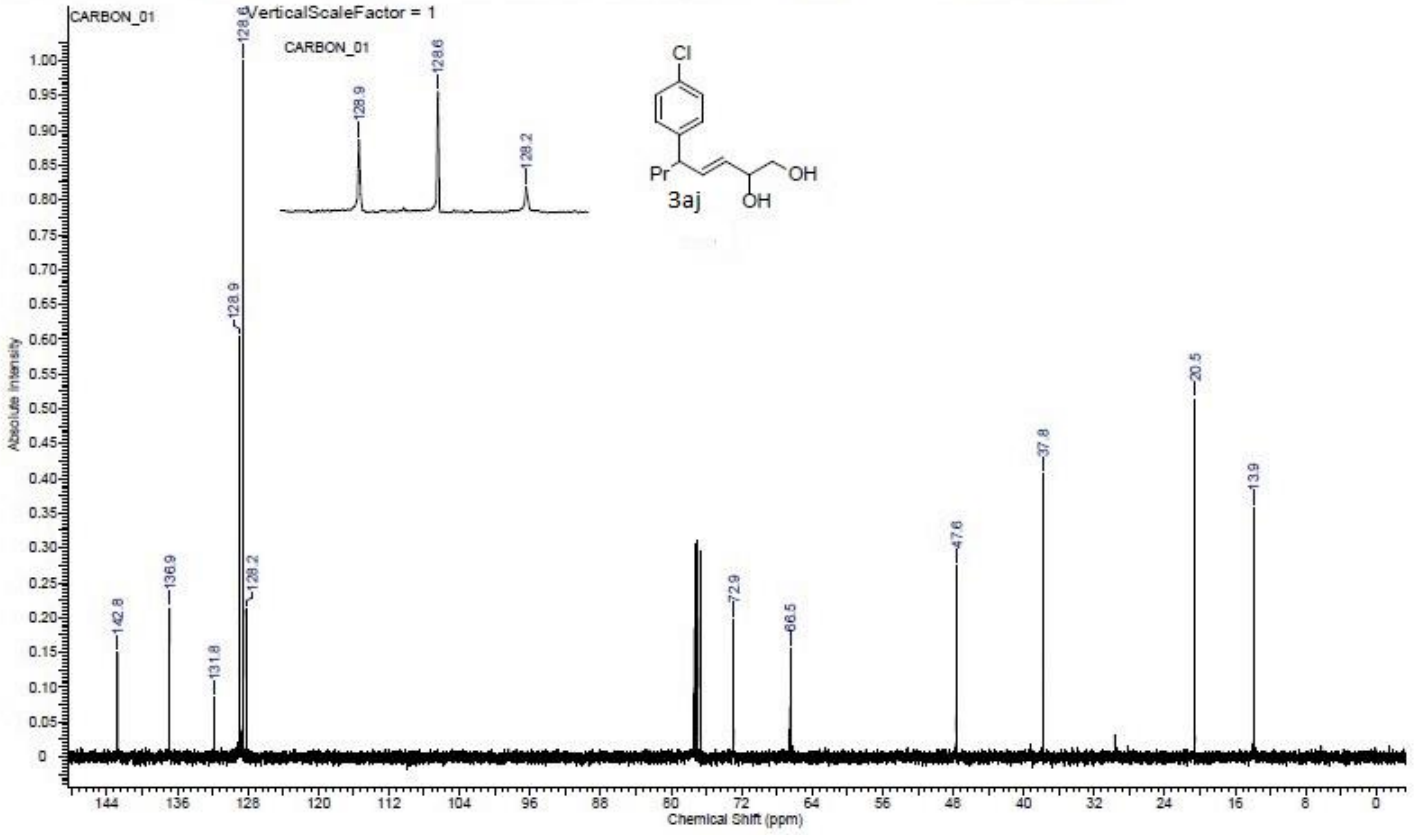
Acquisition Time (sec)	1.3107	*Comment*	erm-enep-210-1_3-bnz			*Date*	Apr 27 2016
Date Stamp	Apr 27 2016	*File Name*	C:\USERS\ERMAN\DESKTOP\UNTITLED FOLDER\ERM-ENEP-210-1_3-BNZ_20160426_01\CARBON_02.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	12000	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



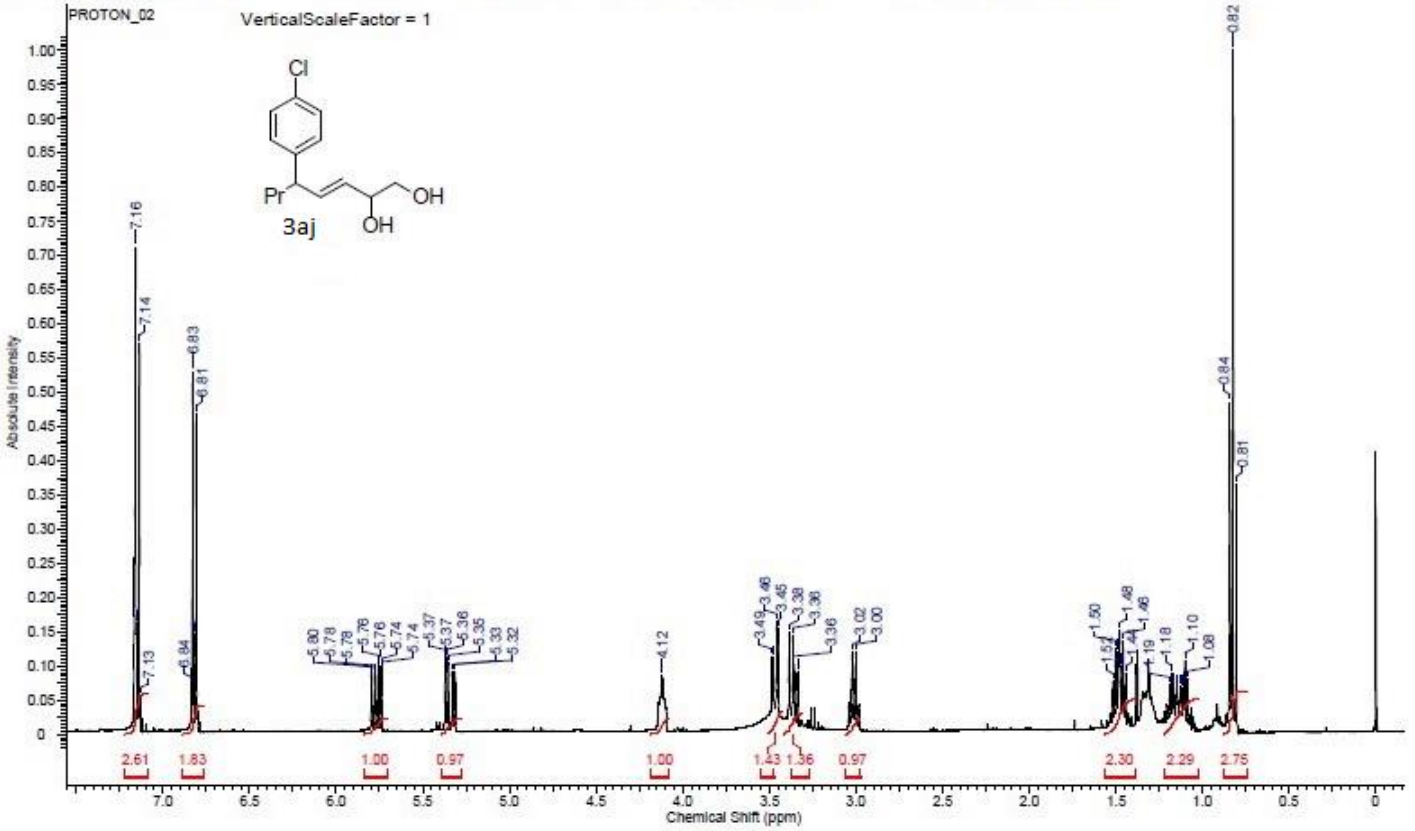
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-195-1_3			*Date*	Feb 15 2016
Date Stamp	Feb 15 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-195-1_3_20160215_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	52.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



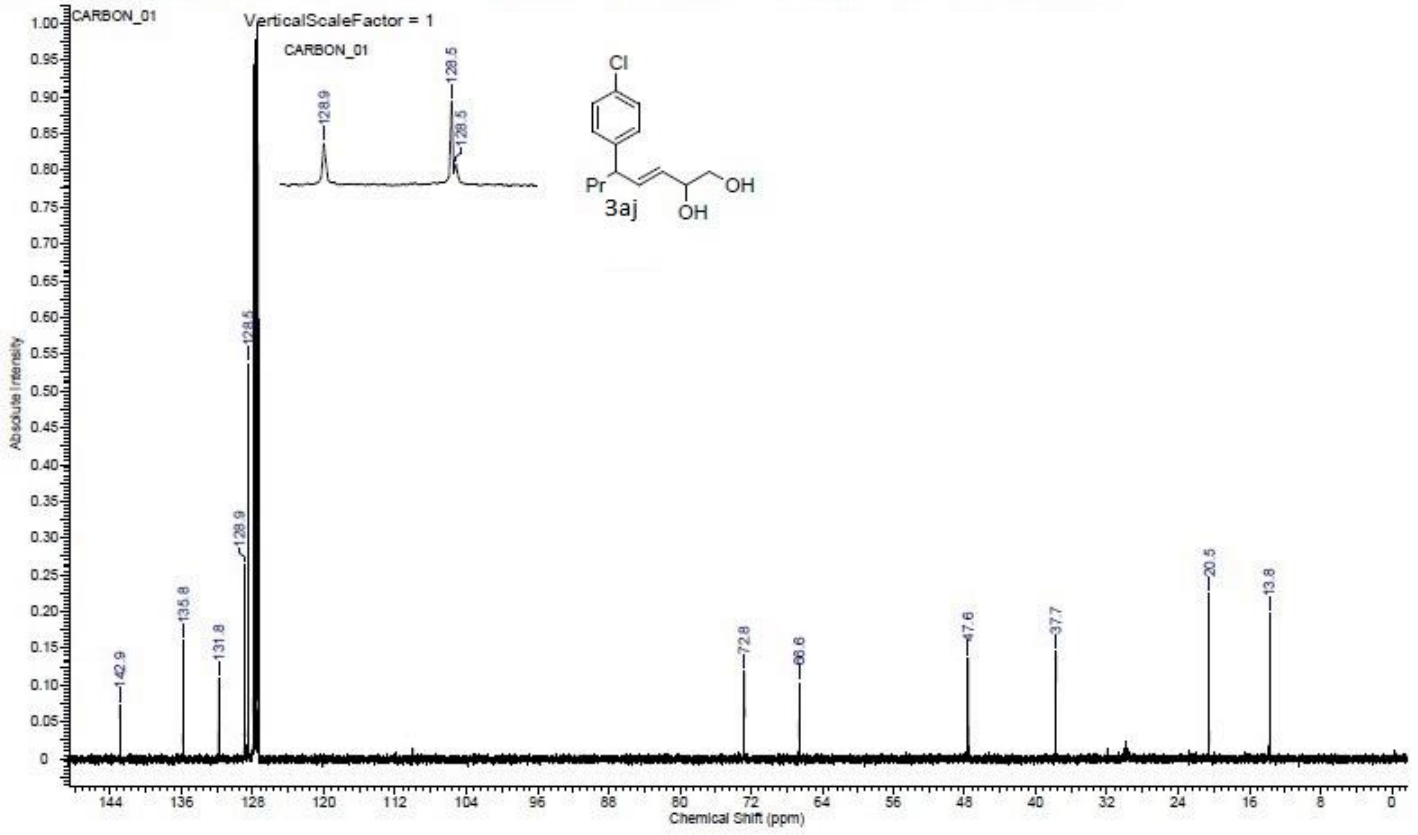
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-195-1_3			*Date*	Feb 15 2016
Date Stamp	Feb 15 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-195-1_3_20160215_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



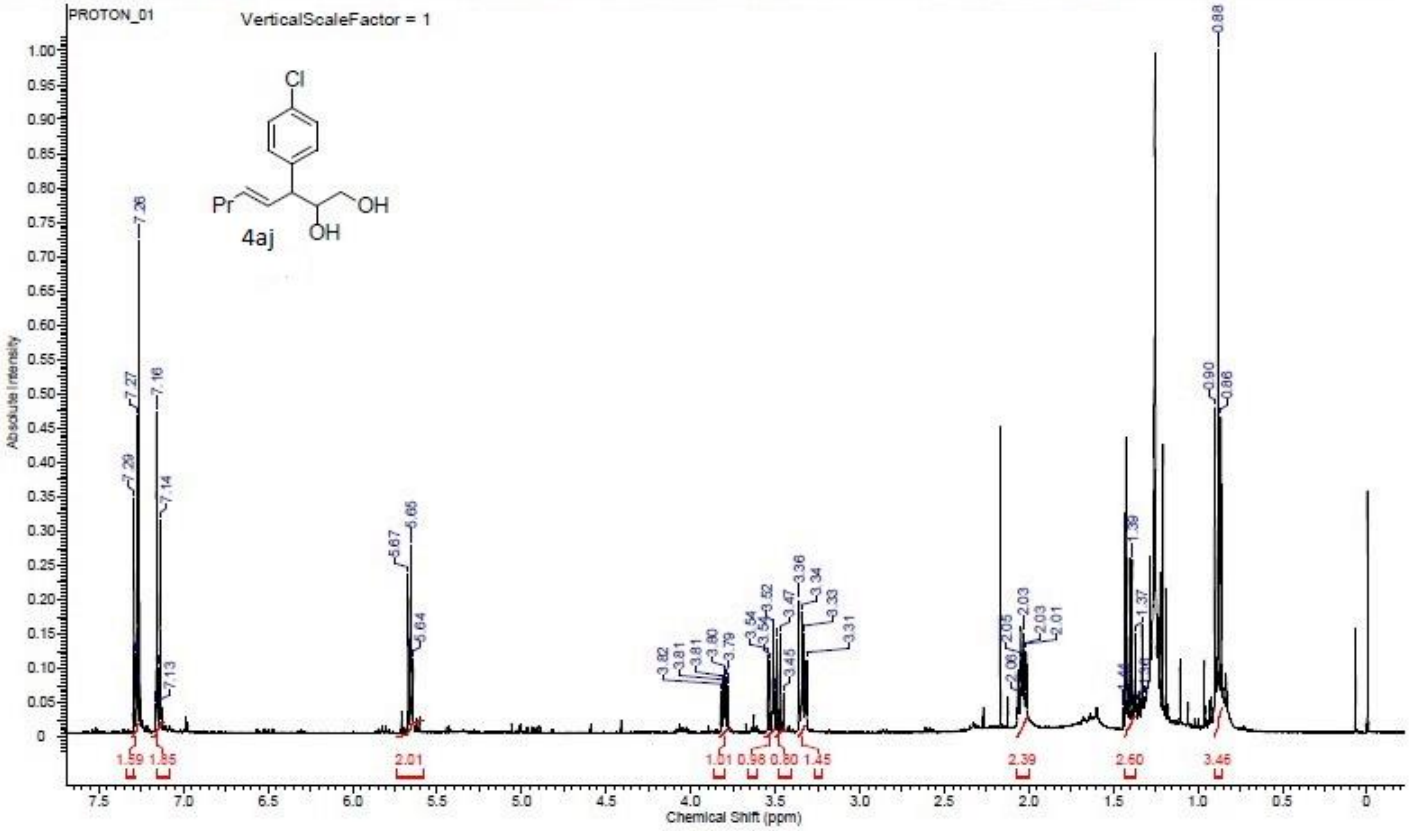
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-195-1_3			*Date*	Feb 12 2016
Date Stamp	Feb 12 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-195-1_3_20160212_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	50.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.1006	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



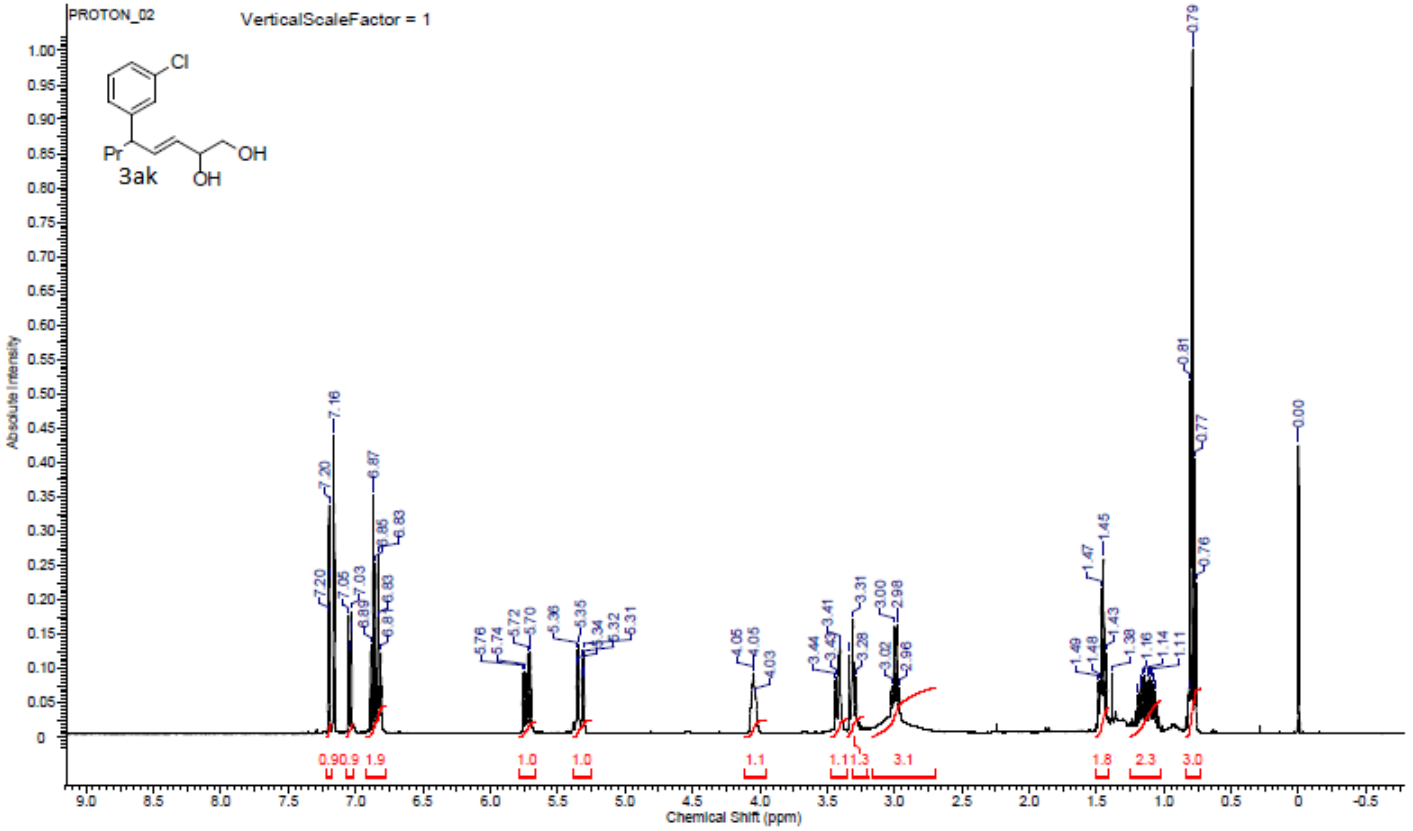
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-195-1_3			*Date*	Feb 12 2016
Date Stamp	Feb 12 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-195-1_3_20160212_02\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-195-1-1			*Date*	Feb 16 2016
Date Stamp	Feb 16 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-195-1-1_20160216_01\PROTON_01.FID/FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

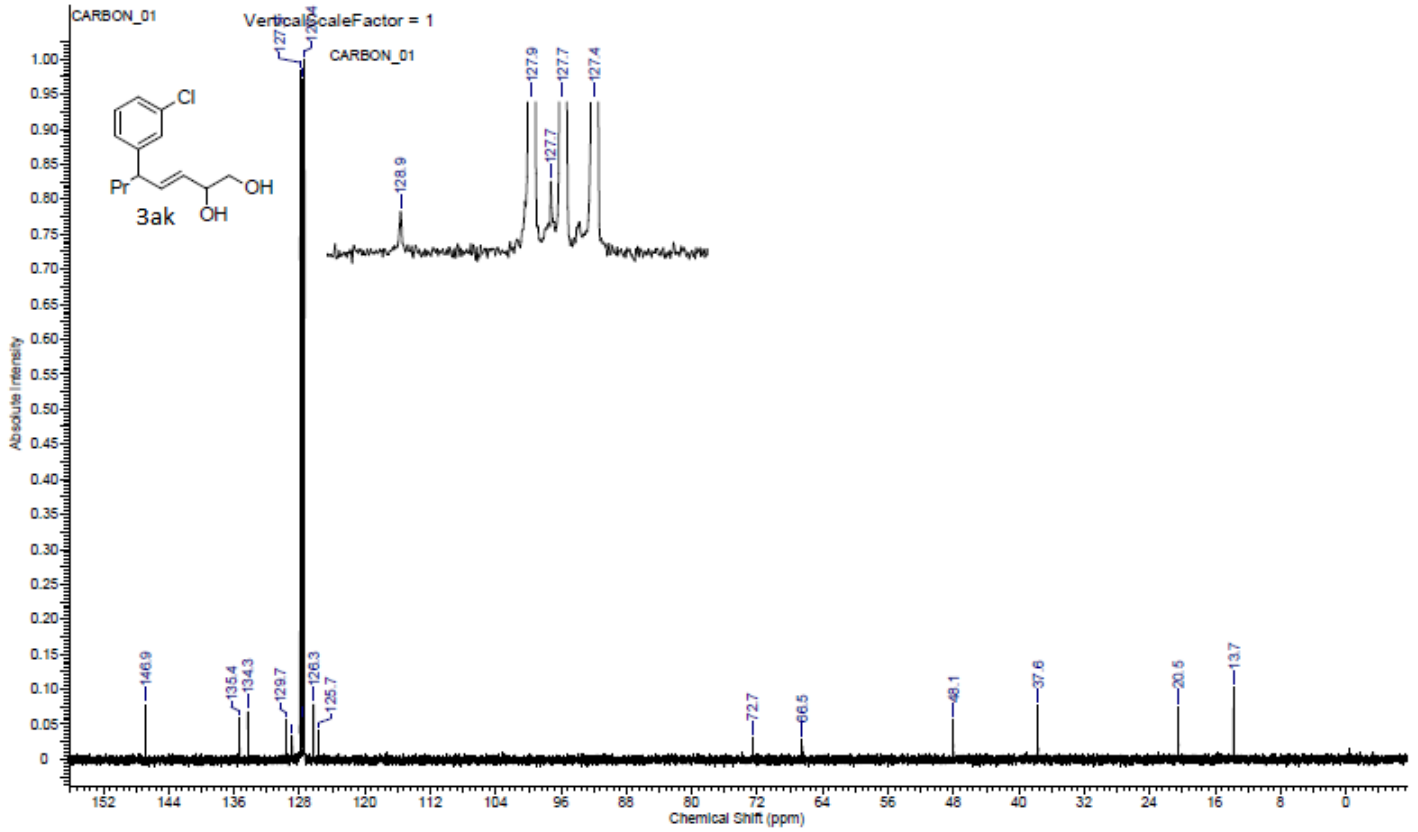


Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-213-1_3-BNZ			*Date*	May 4 2016
Date Stamp	May 4 2016	*File Name*	C:\USERS\ERMAN\DESKTOP\UNTITLED FOLDER\ERM-ENEP-213-1_3-BNZ_20160504_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	54.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3181	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

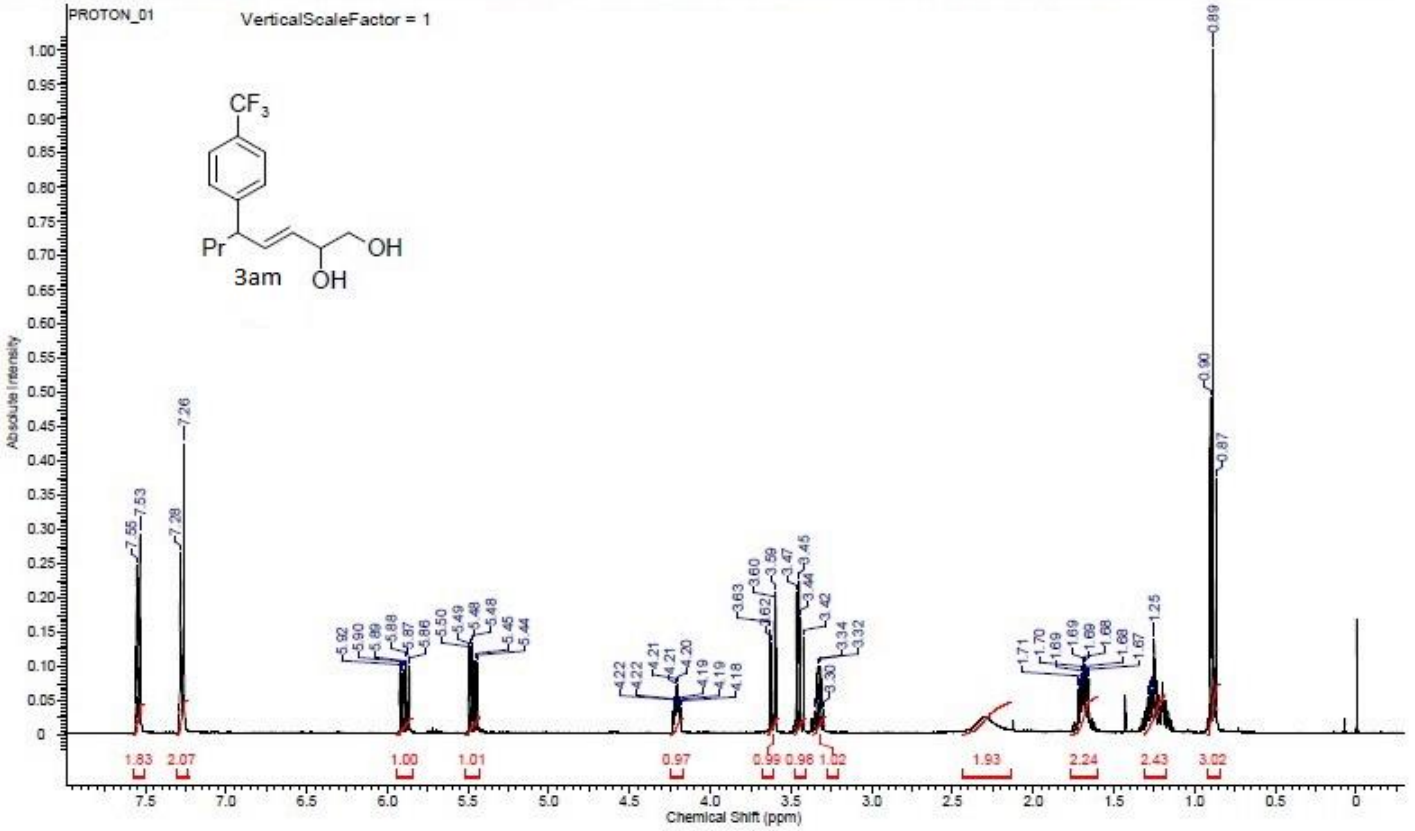


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

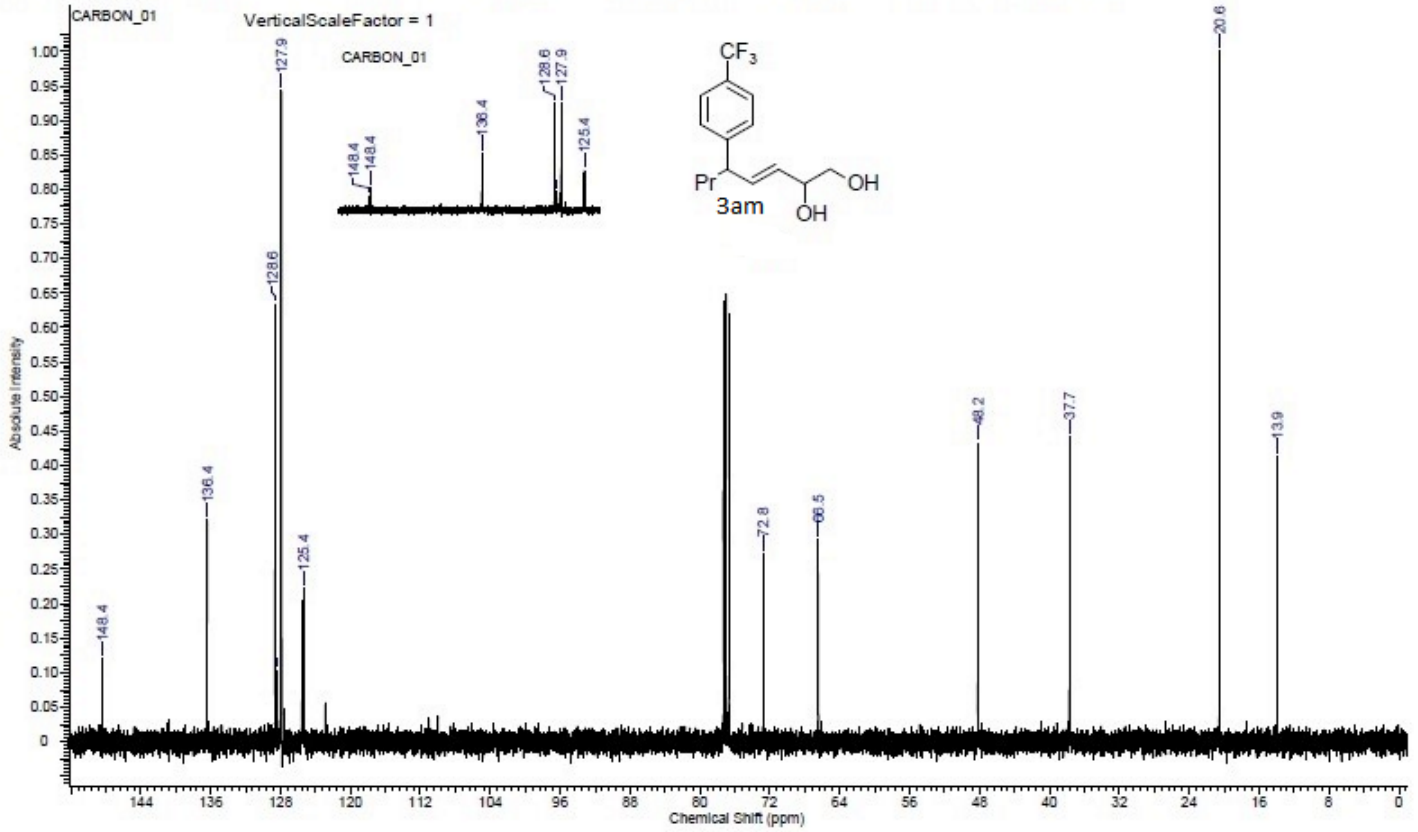
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-213-1_3-BNZ			*Date*	May 4 2016
Date Stamp	May 4 2016	*File Name*	C:\USERS\ERMAN\DESKTOP\UNTITLED FOLDER\ERM-ENEP-213-1_3-BNZ_20160504_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



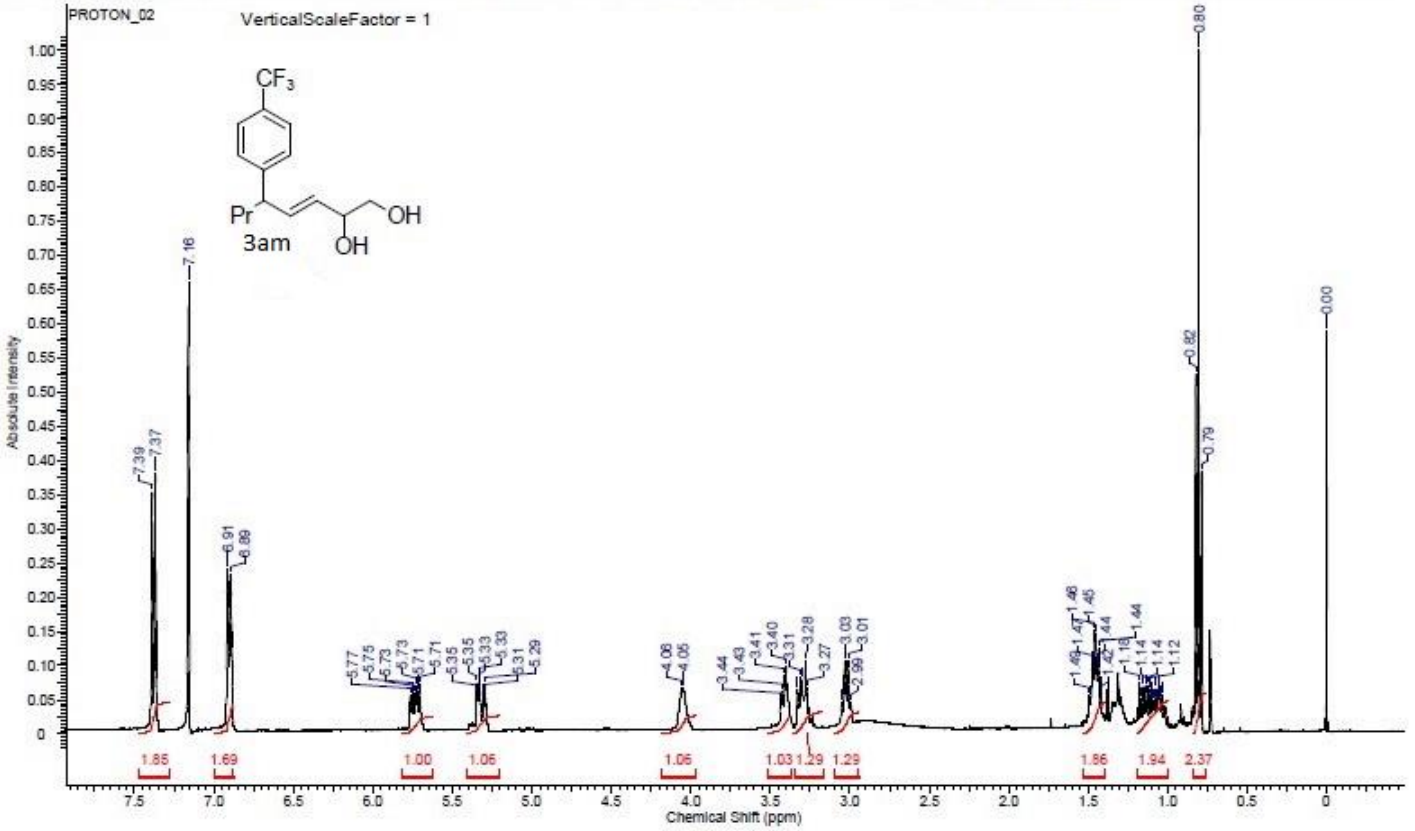
Acquisition Time (sec)	2.5559	*Comment*	erm-enep-192-1_3			*Date*	Feb 10 2016
Date Stamp	Feb 10 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-192-1_3_20160210_02\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	56.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



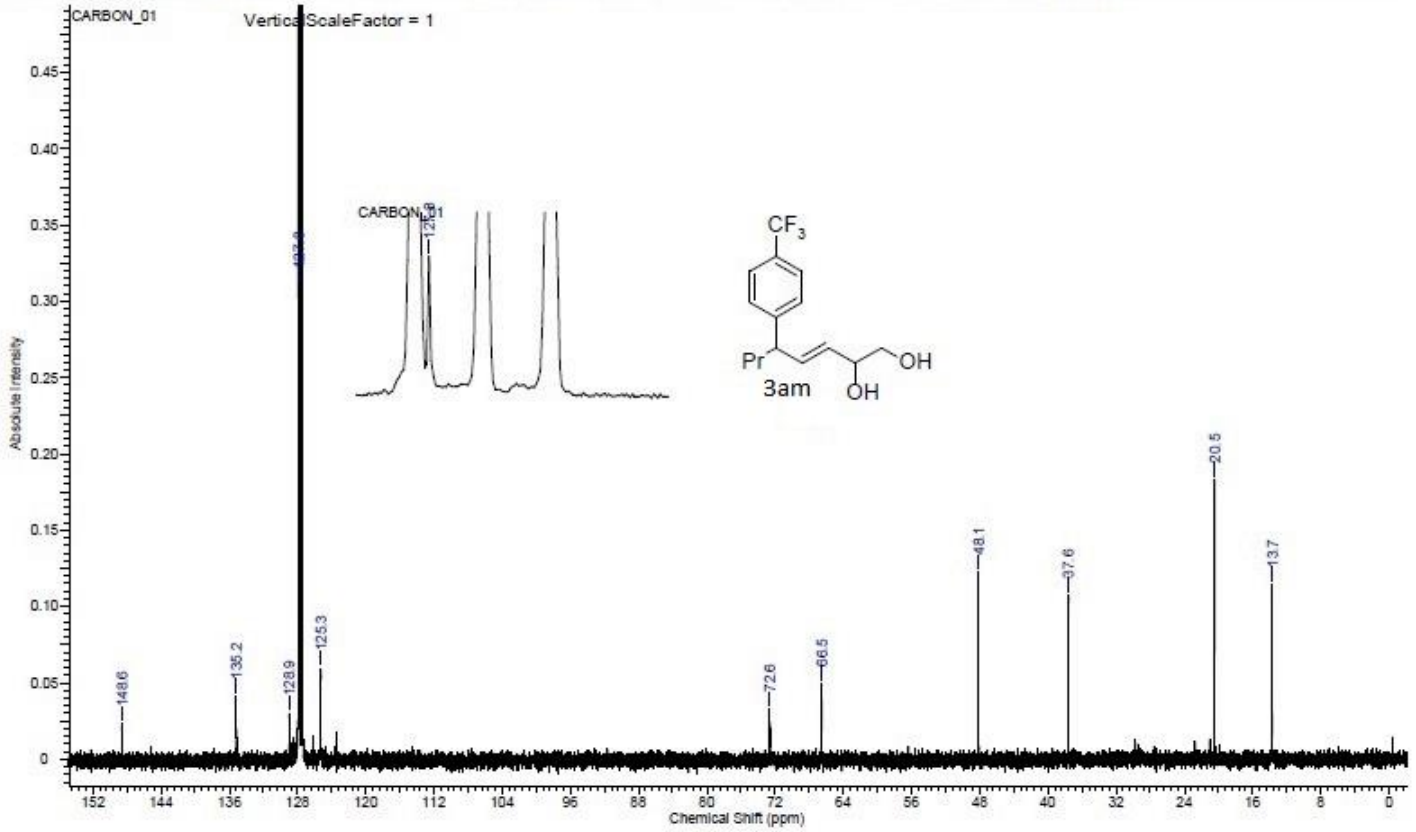
Acquisition Time (sec)	1.3107	*Comment*	erm-enep-192-1_3			*Date*	Feb 10 2016
Date Stamp	Feb 10 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-192-1_3_20160210_02\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



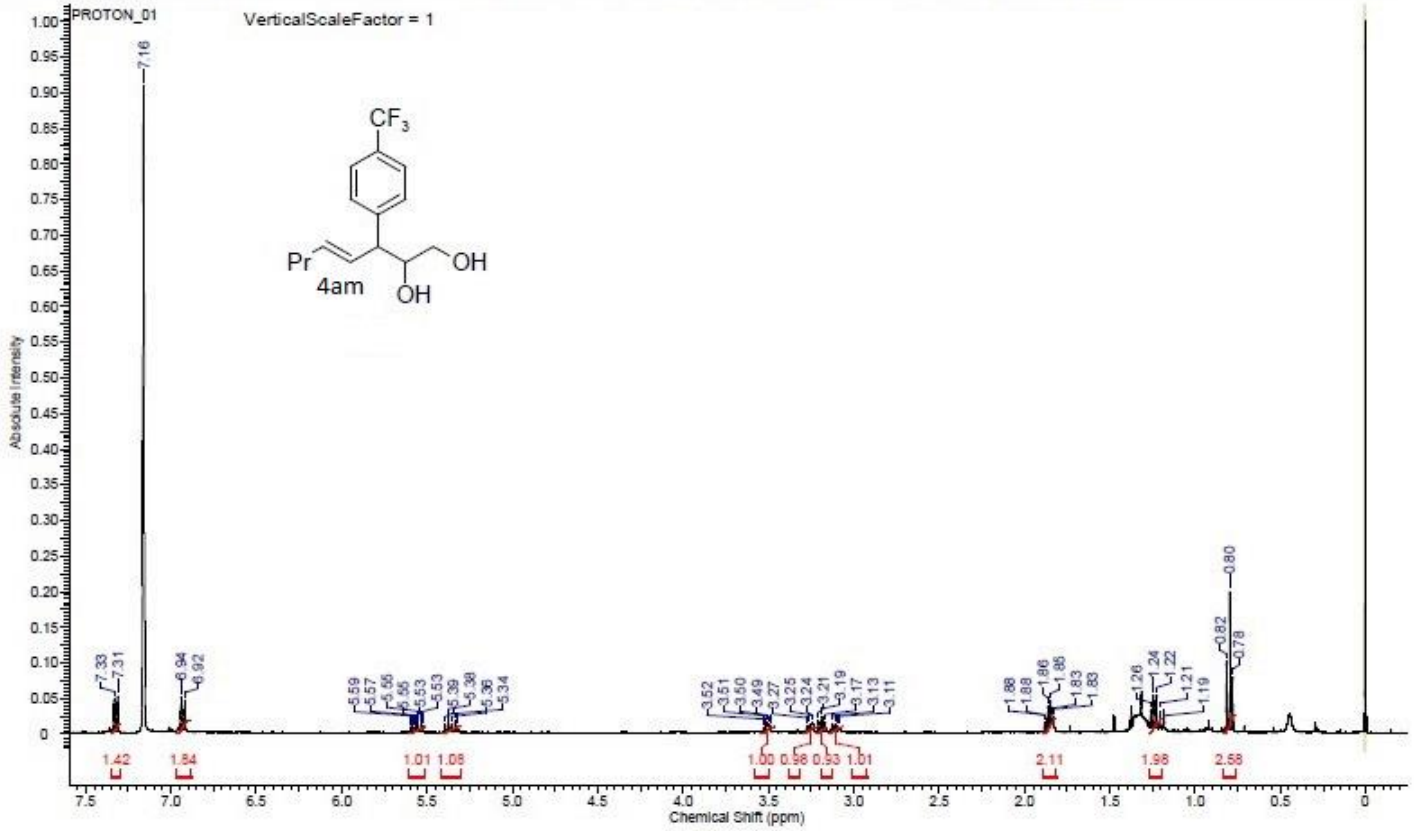
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-192-1_3			*Date*	Feb 2 2016
Date Stamp	Feb 2 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-192-1_3_20160202_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	16	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	54.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3181	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



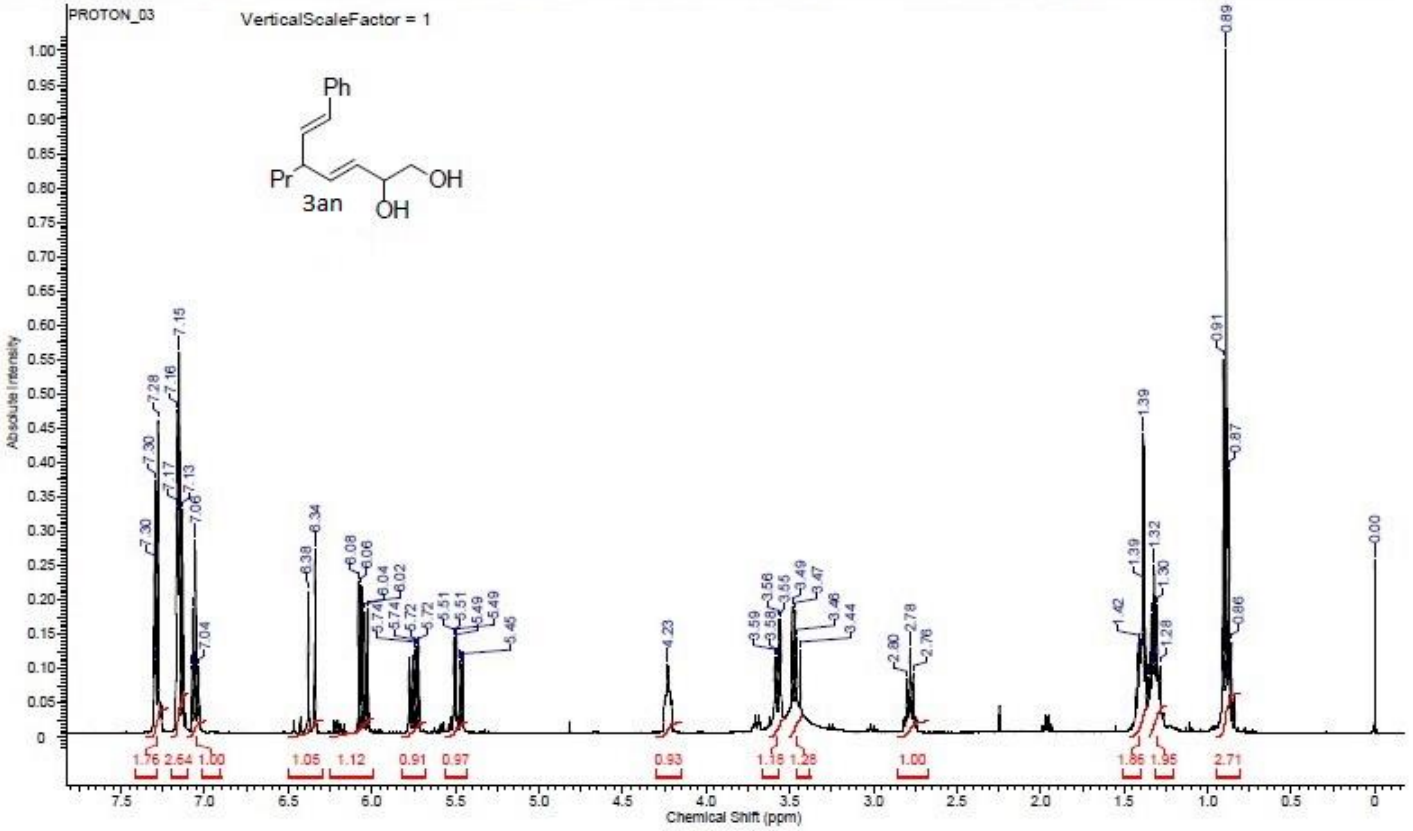
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-192-1_3			*Date*	Feb 2 2016
Date Stamp	Feb 2 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-192-1_3_20160202_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



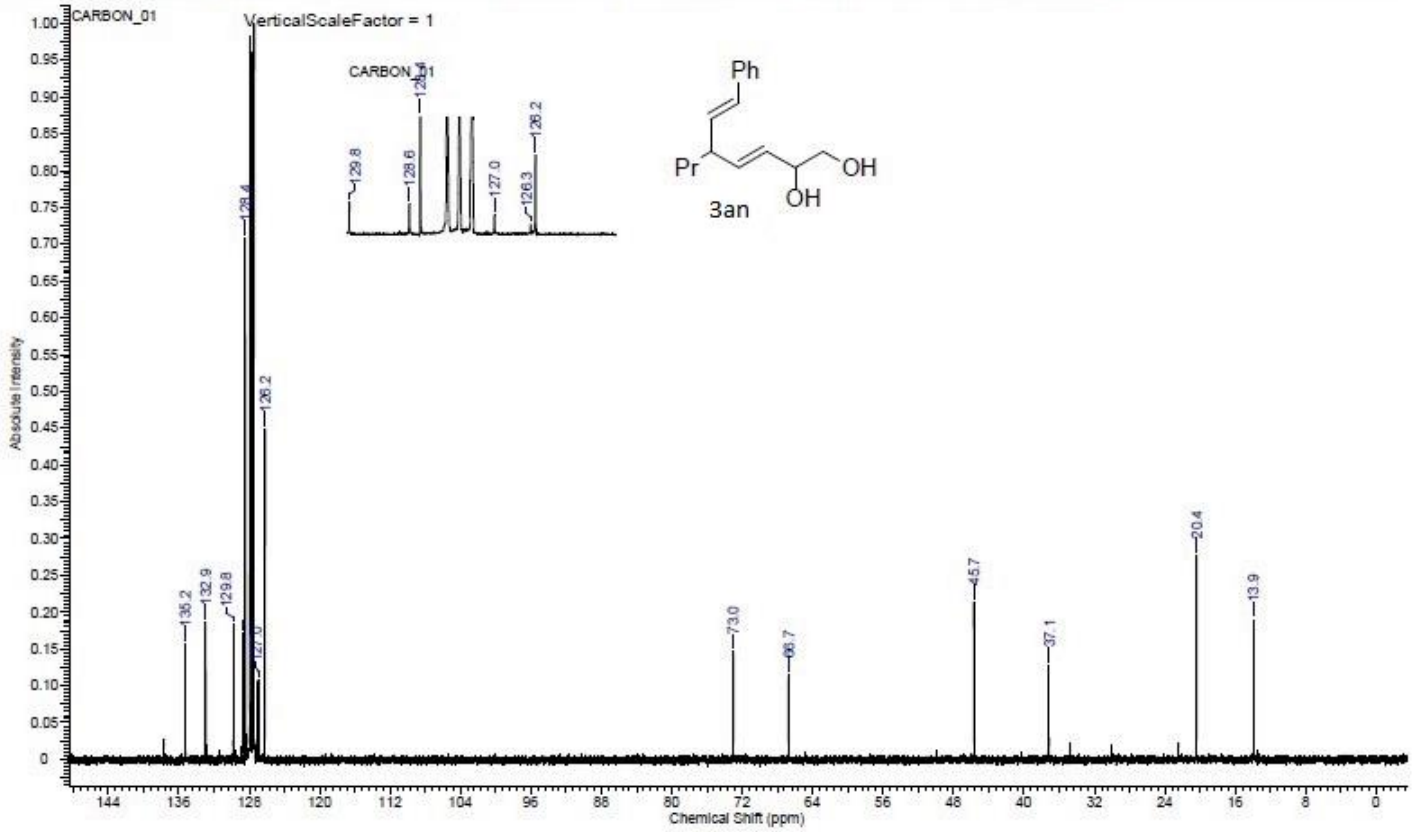
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-192-1_1			*Date*	Feb 2 2016
Date Stamp	Feb 2 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-192-1_1_20160202_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



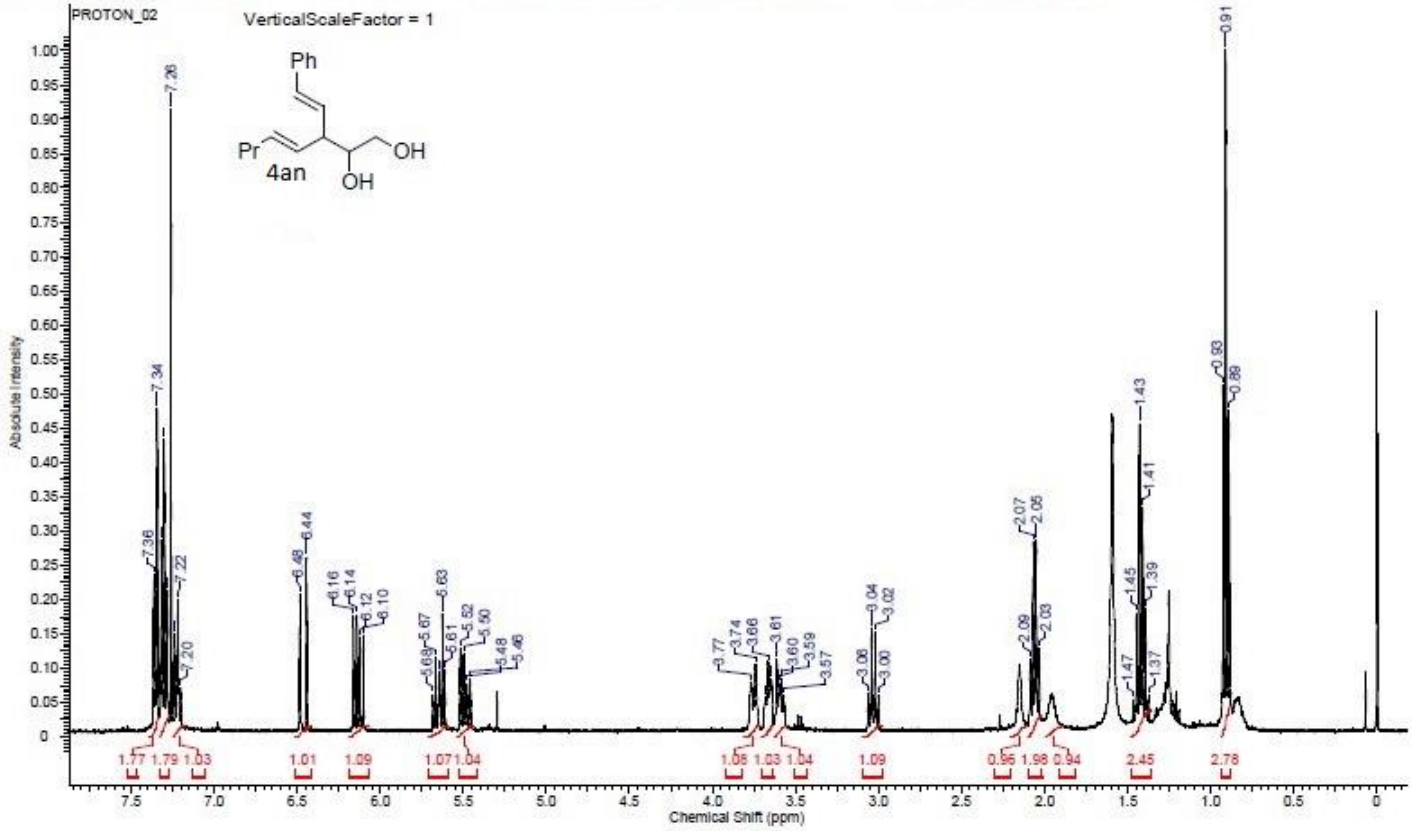
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-202-1_3			*Date*	Feb 26 2016
Date Stamp	Feb 26 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-202-1_3_20160226_01\PROTON_03.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	50.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.4919	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



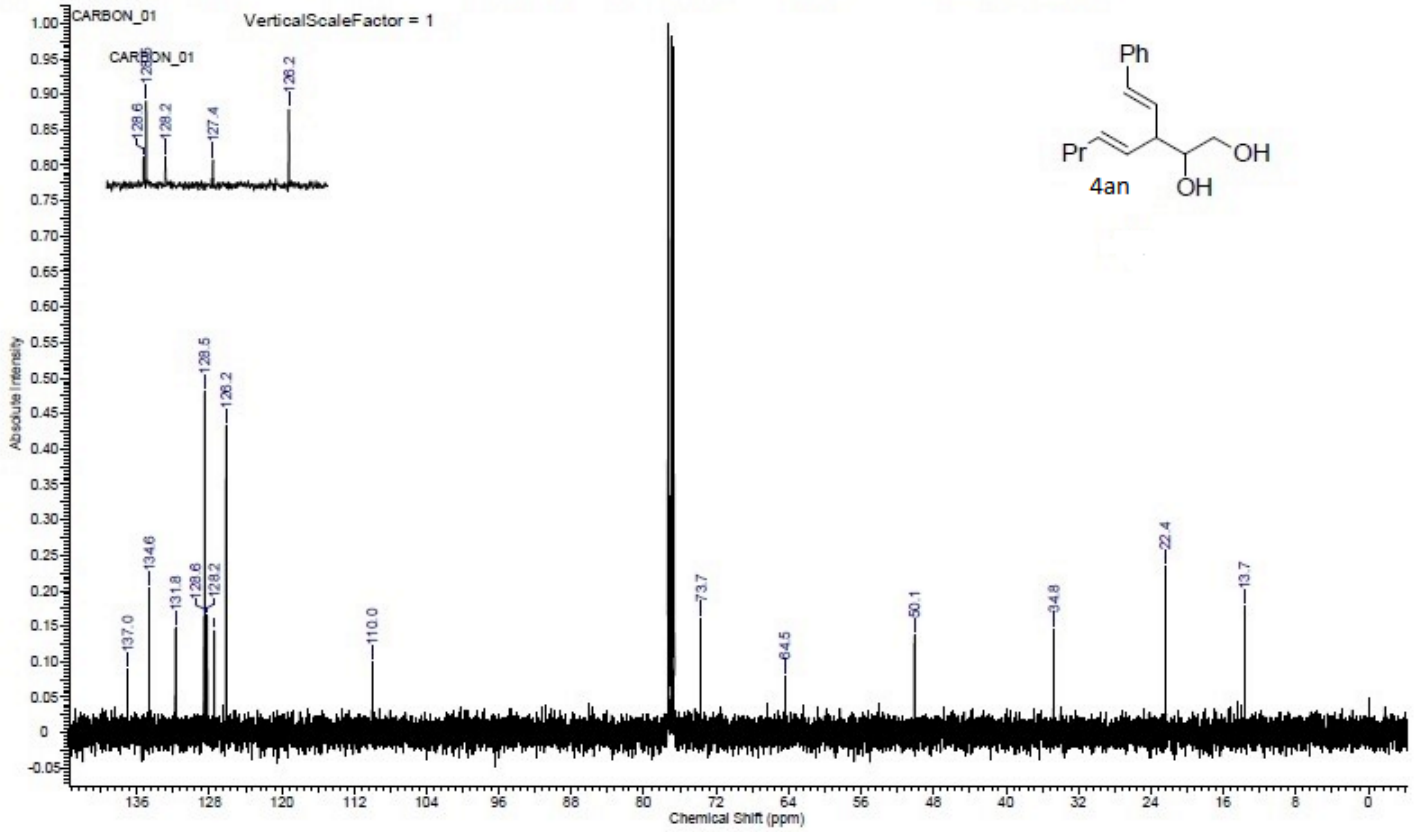
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-202-1_3			*Date*	Feb 26 2016
Date Stamp	Feb 26 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-202-1_3_20160226_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



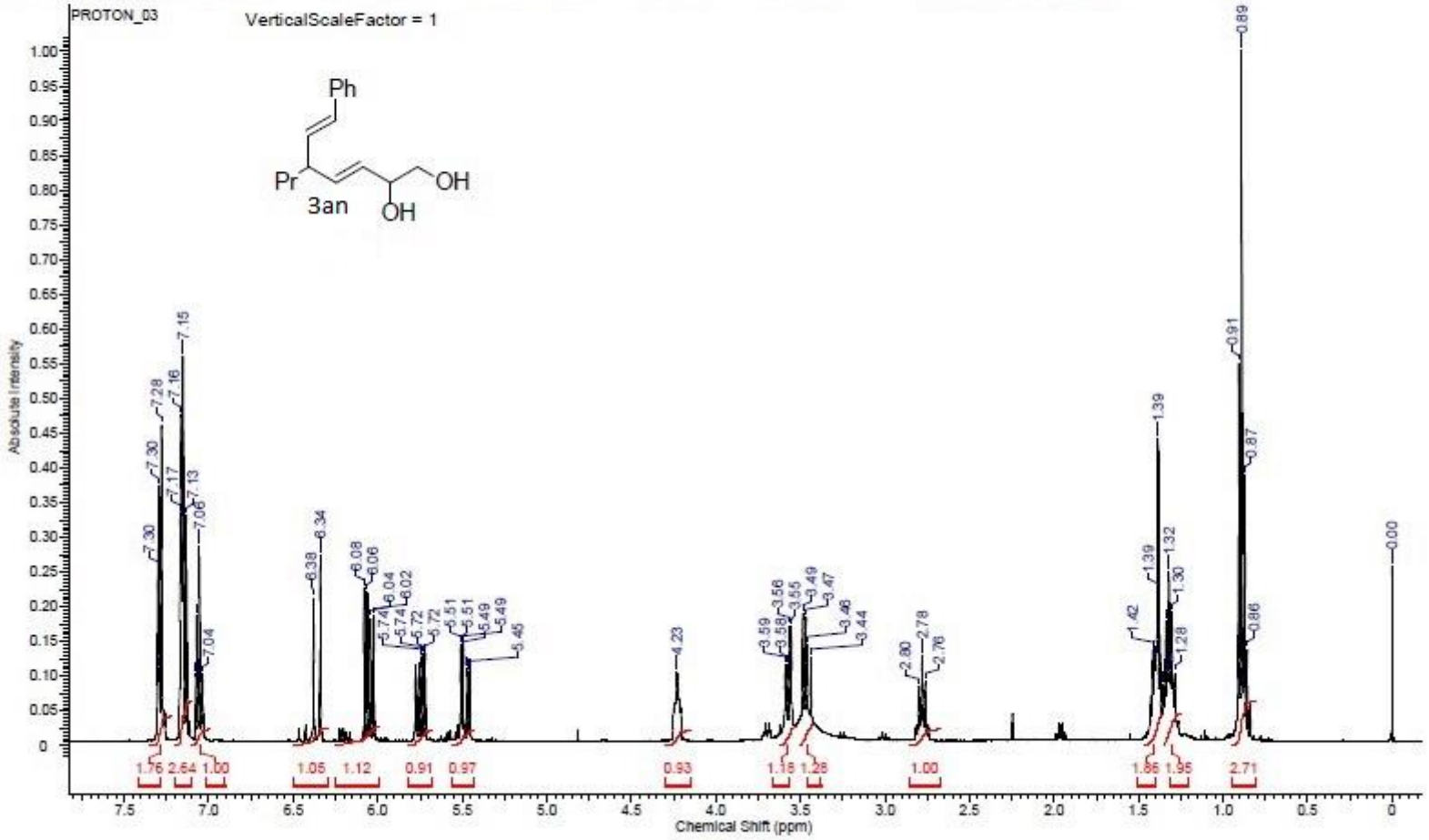
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-202-1_1			*Date*	Feb 26 2016
Date Stamp	Feb 26 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-202-1_1_20160226_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



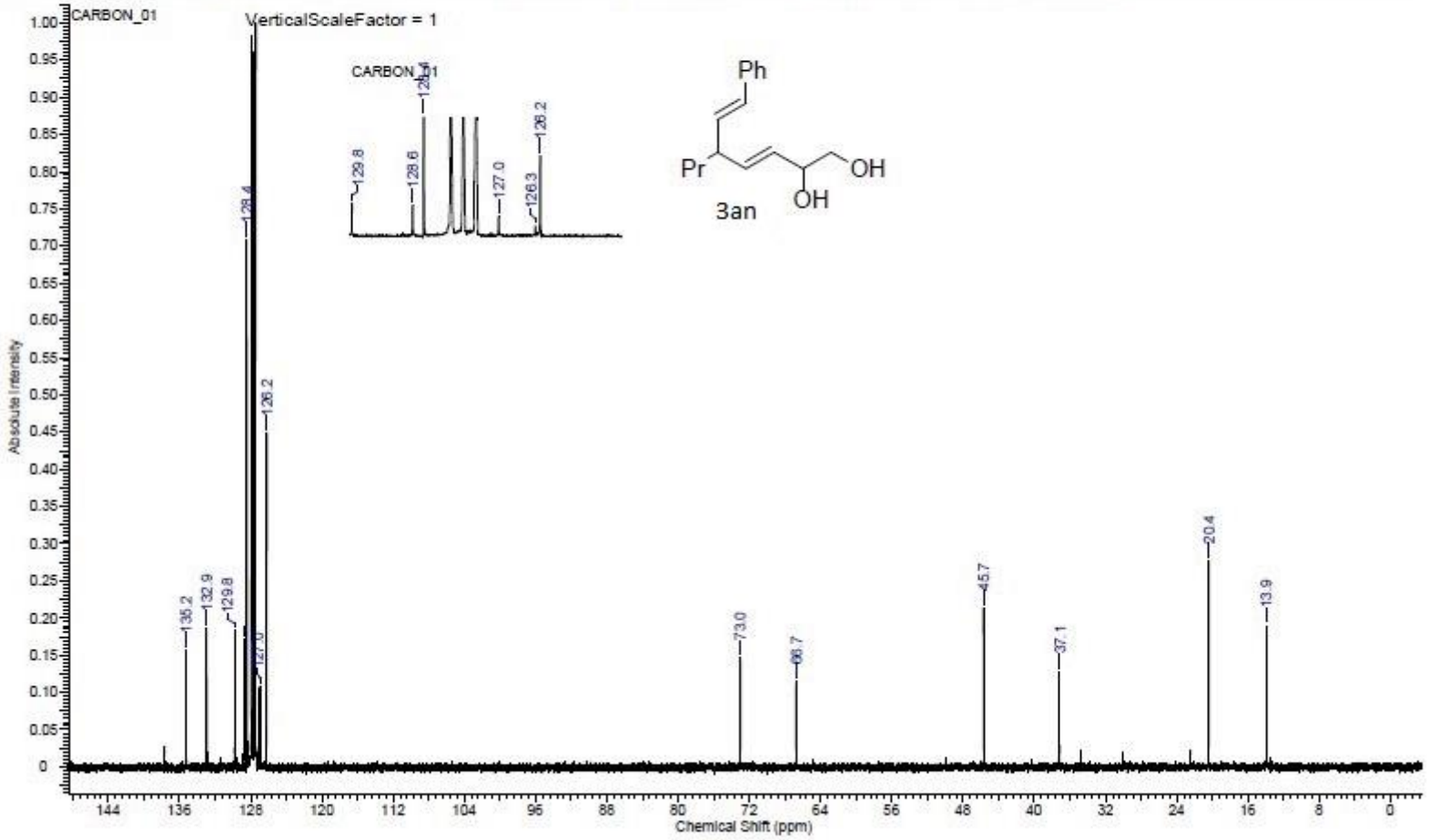
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-202-1_1			*Date*	Feb 26 2016
Date Stamp	Feb 26 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-202-1_1_20160226_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	400	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



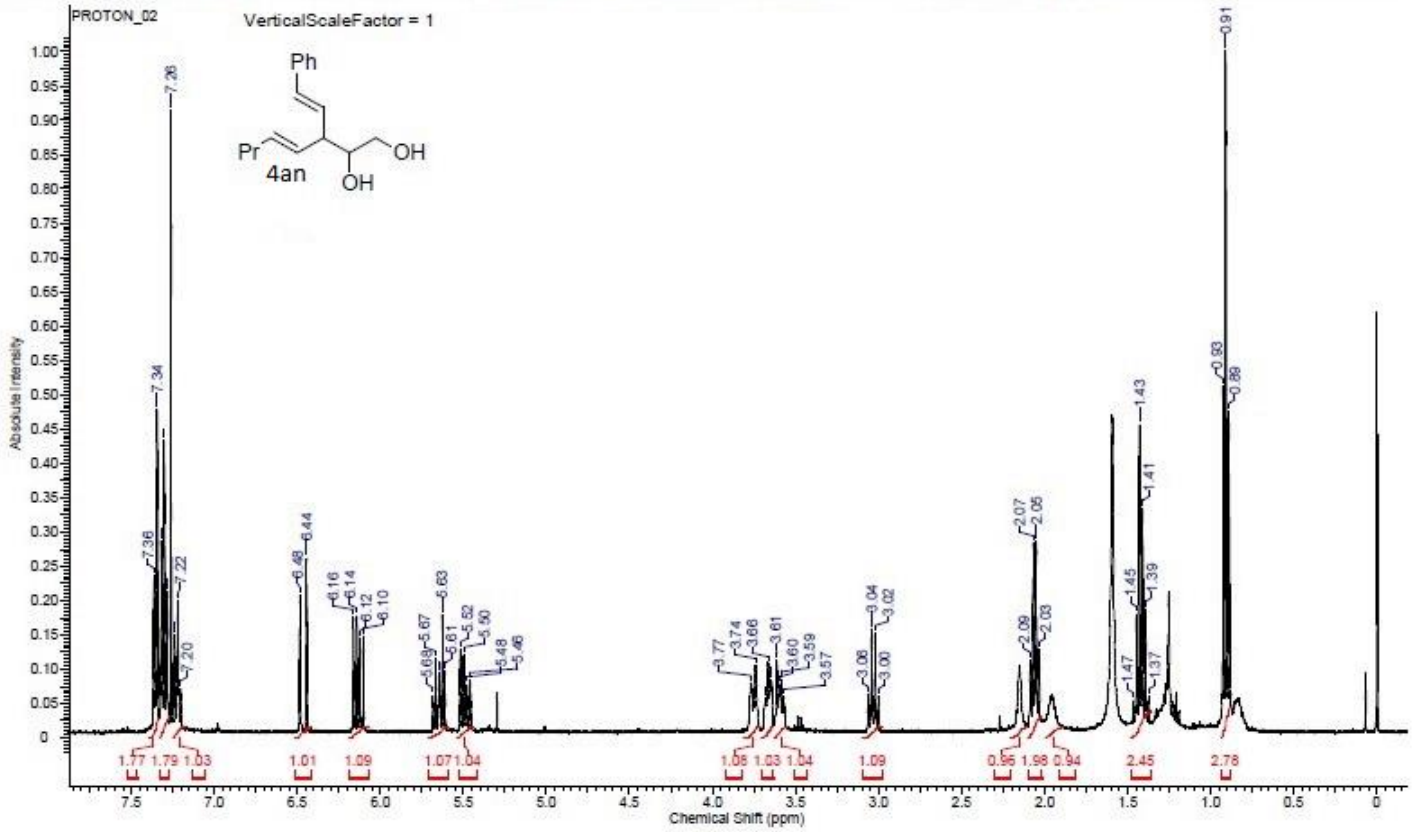
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-202-1_3			*Date*	Feb 26 2016
Date Stamp	Feb 26 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-202-1_3_20160226_01\PROTON_03.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	50.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.4919	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



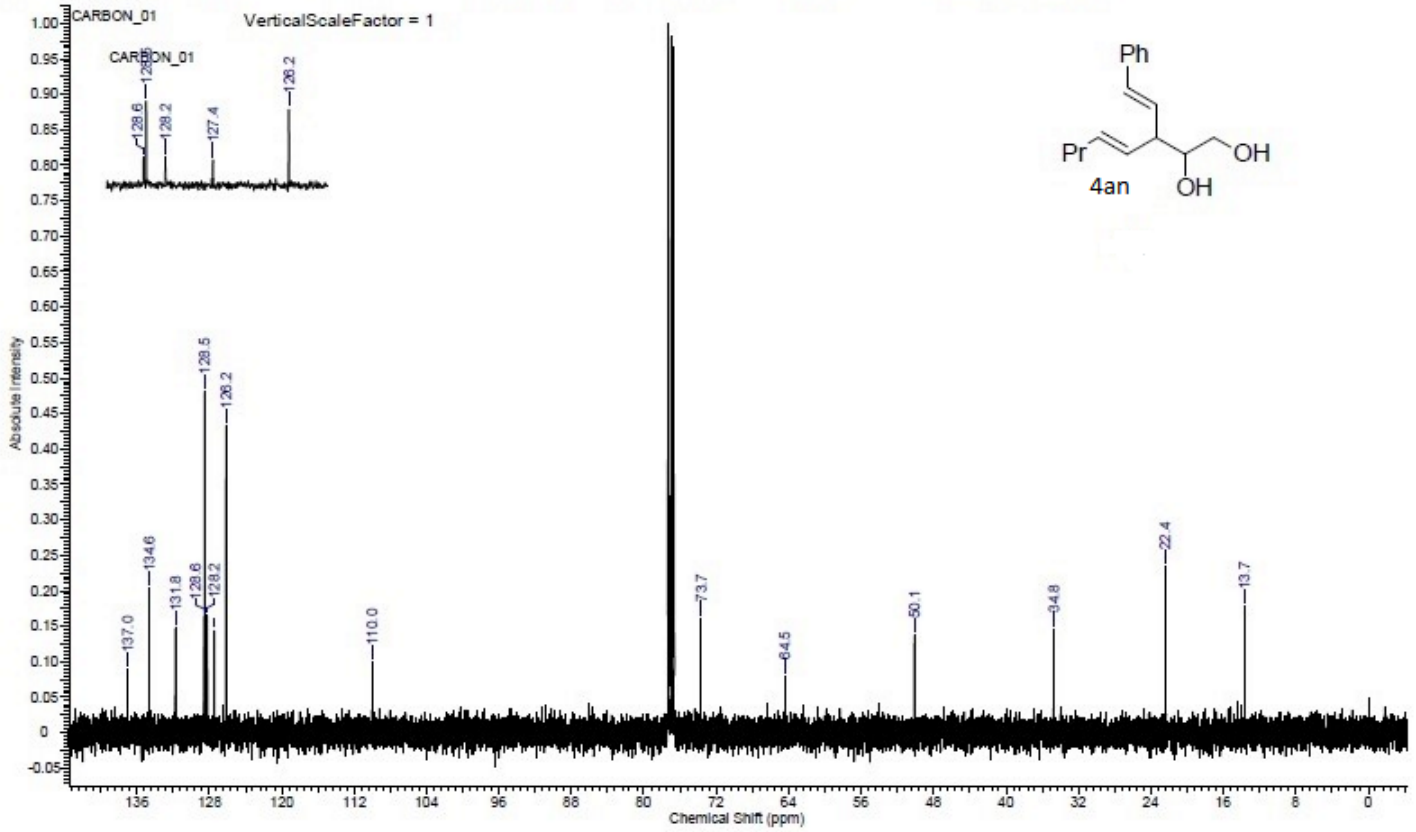
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-202-1_3			*Date*	Feb 26 2016
Date Stamp	Feb 26 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-202-1_3_20160226_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



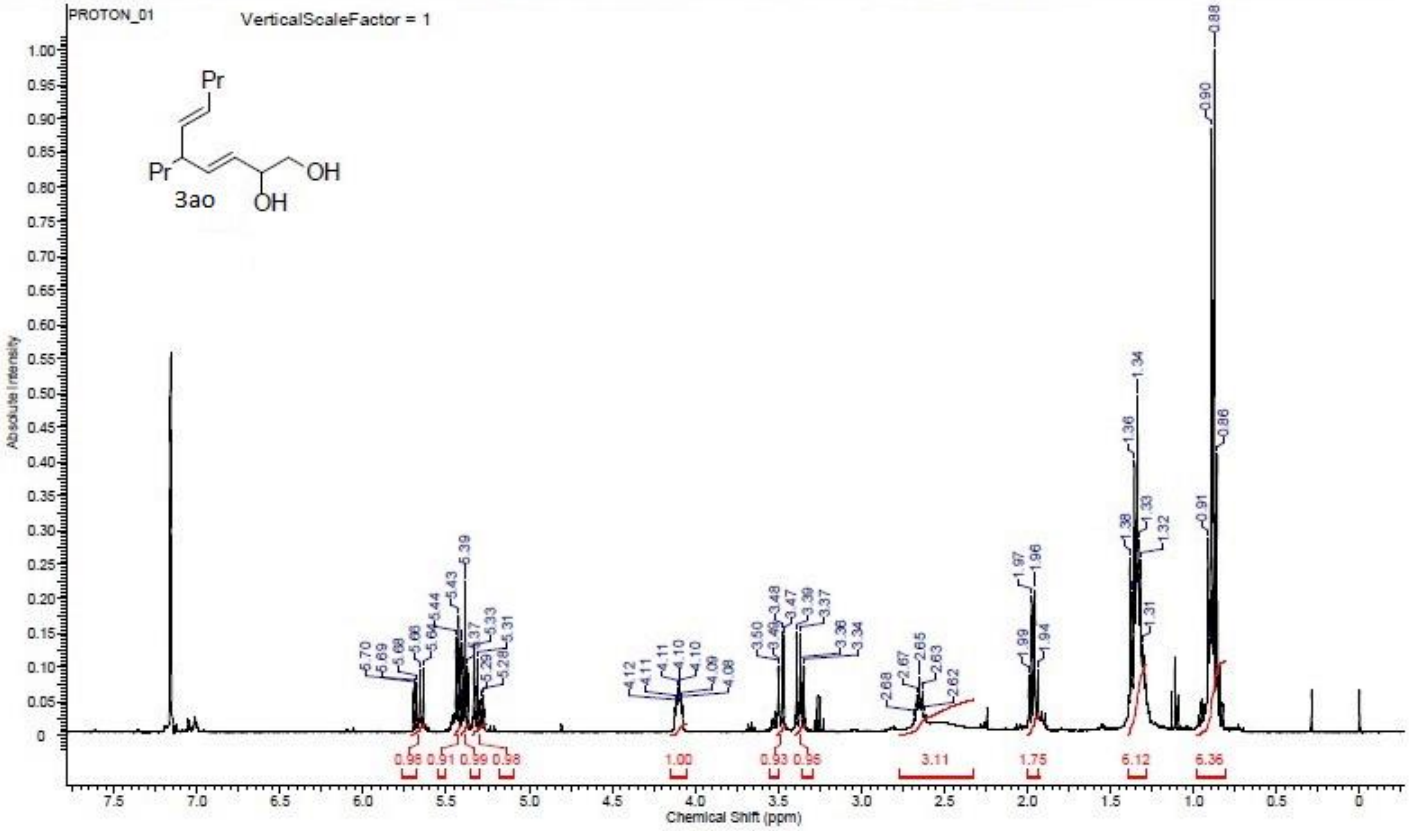
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-202-1_1			*Date*	Feb 26 2016
Date Stamp	Feb 26 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-202-1_1_20160226_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



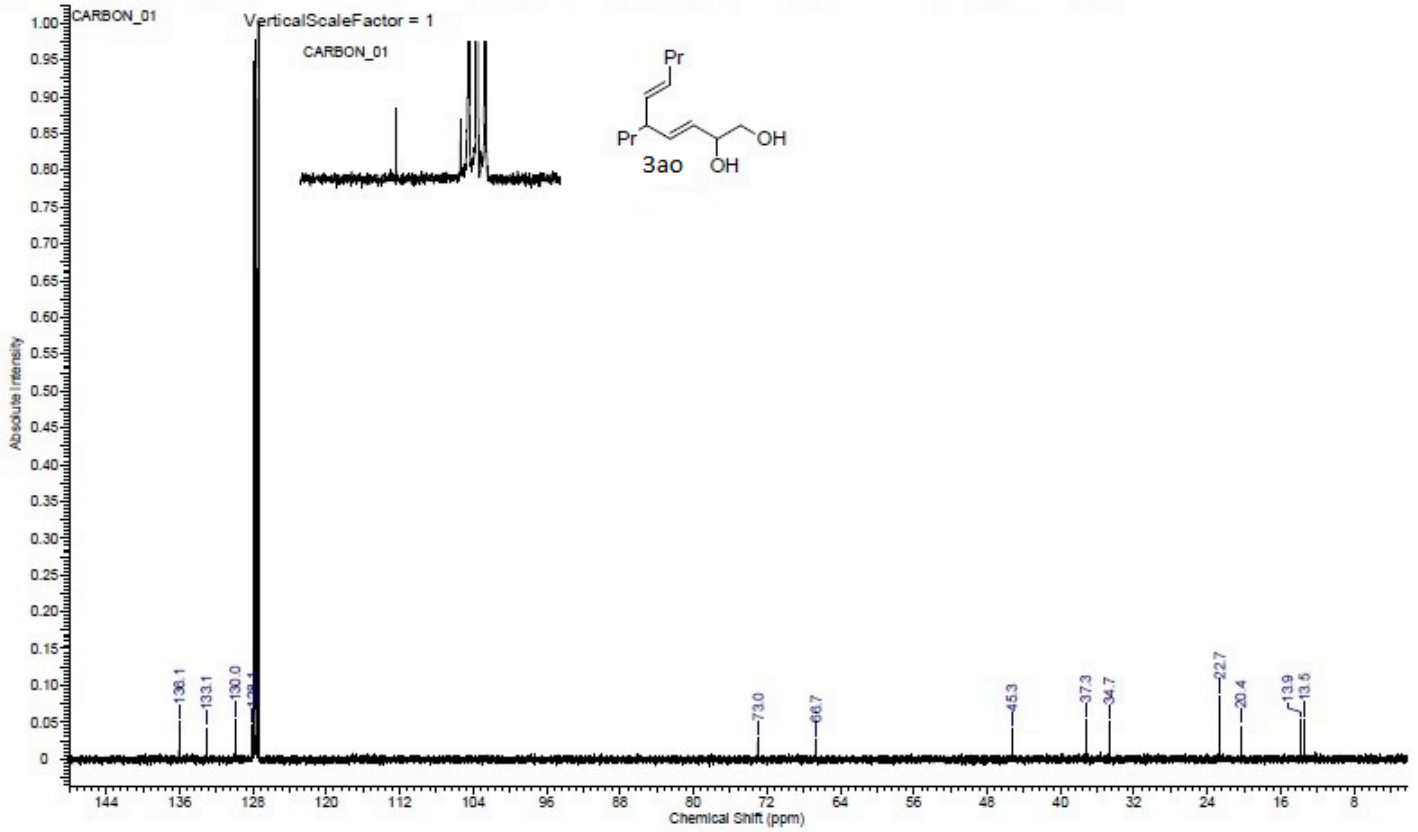
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-202-1_1			*Date*	Feb 26 2016
Date Stamp	Feb 26 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-202-1_1_20160226_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	400	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-204-TKR-1-3			*Date*	Apr 5 2016
Date Stamp	Apr 5 2016	*File Name*	D:\NMRYEN12\ERM-ENEP-204-TKR-1-3_20160405_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	58.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7092	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-204-TKR-1-3			*Date*	Apr 6 2016
Date Stamp	Apr 6 2016	*File Name*	C:\USERS\ERMAN\DESKTOP\EFE\ERM-ENEP-204-TKR-1-3_20160405_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	400	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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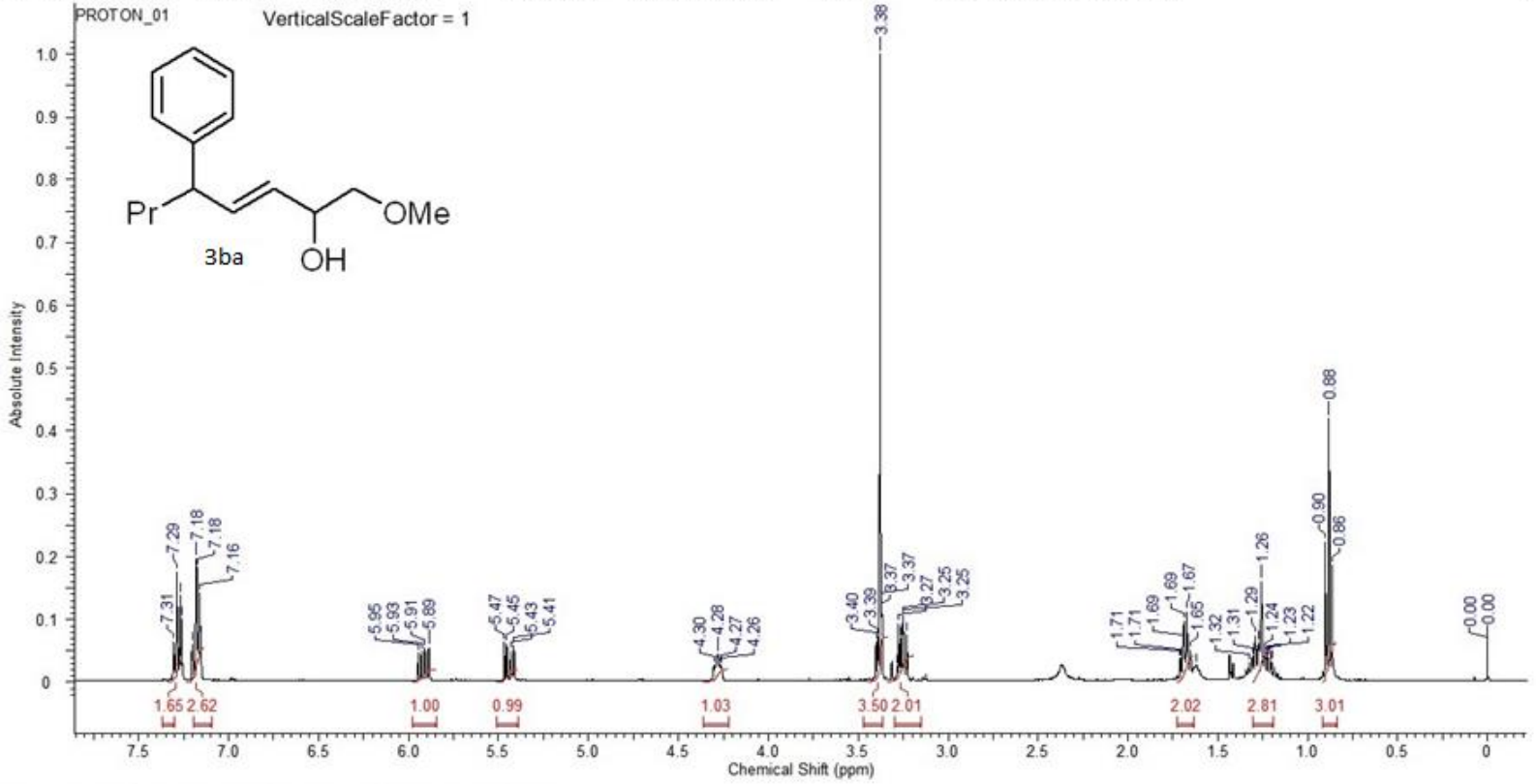
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-114-1_3			*Date*	Oct 6 2015
Date Stamp	Oct 6 2015	*File Name*	C:\Users\Erman\Desktop\123\ERM-ENEP-114-1_3_20151006_01\PROTON_01.fid\fid				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	56.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2398.7107	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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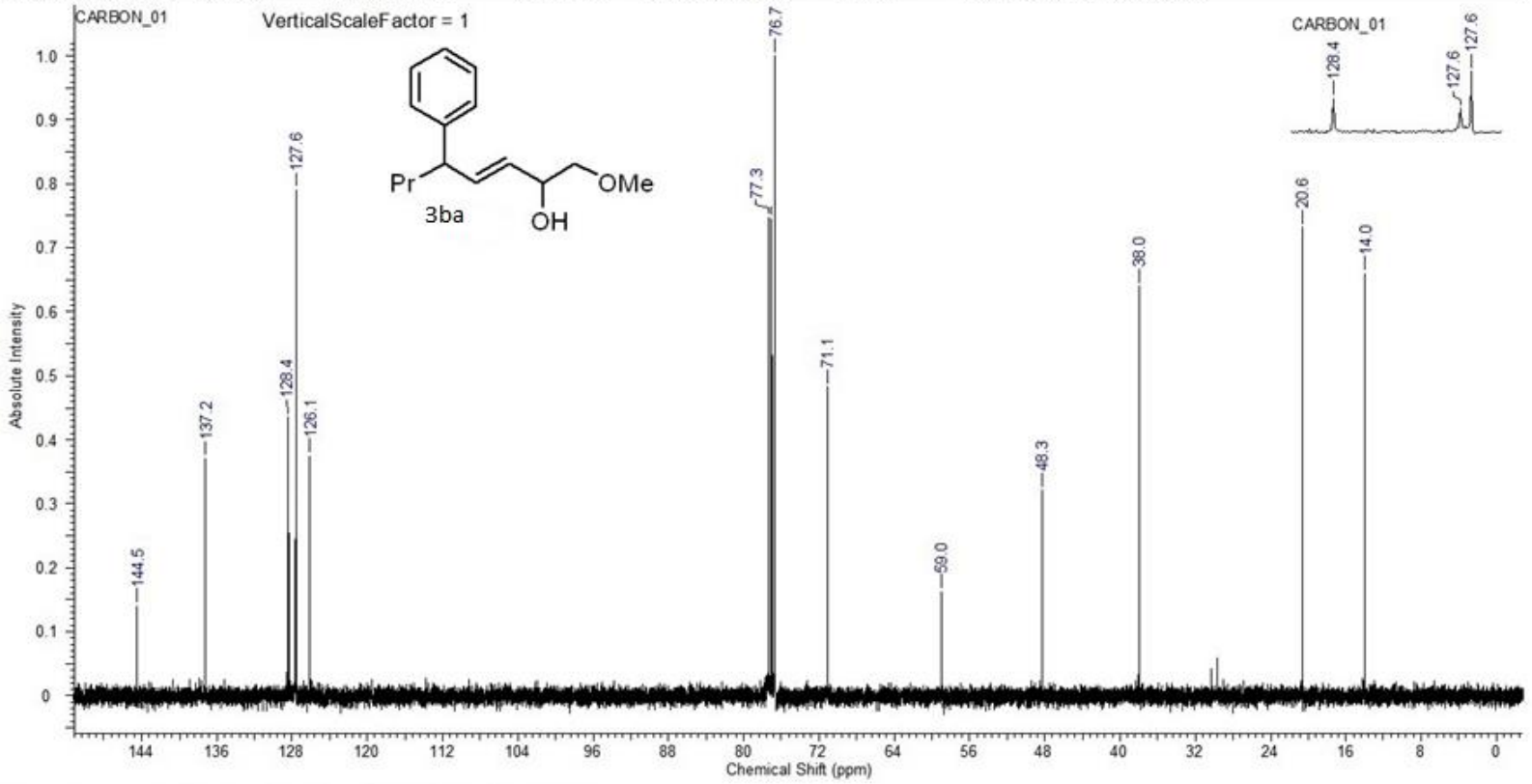
12.10.2015 20:32:45
3ba

Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-114-C-CDCL3			*Date*	Oct 7 2015
Date Stamp	Oct 7 2015	*File Name*	C:\Users\Erman\Desktop\123\ERM-ENEP-114-C-CDCL3_20151007_01\CARBON_01.fid\fid				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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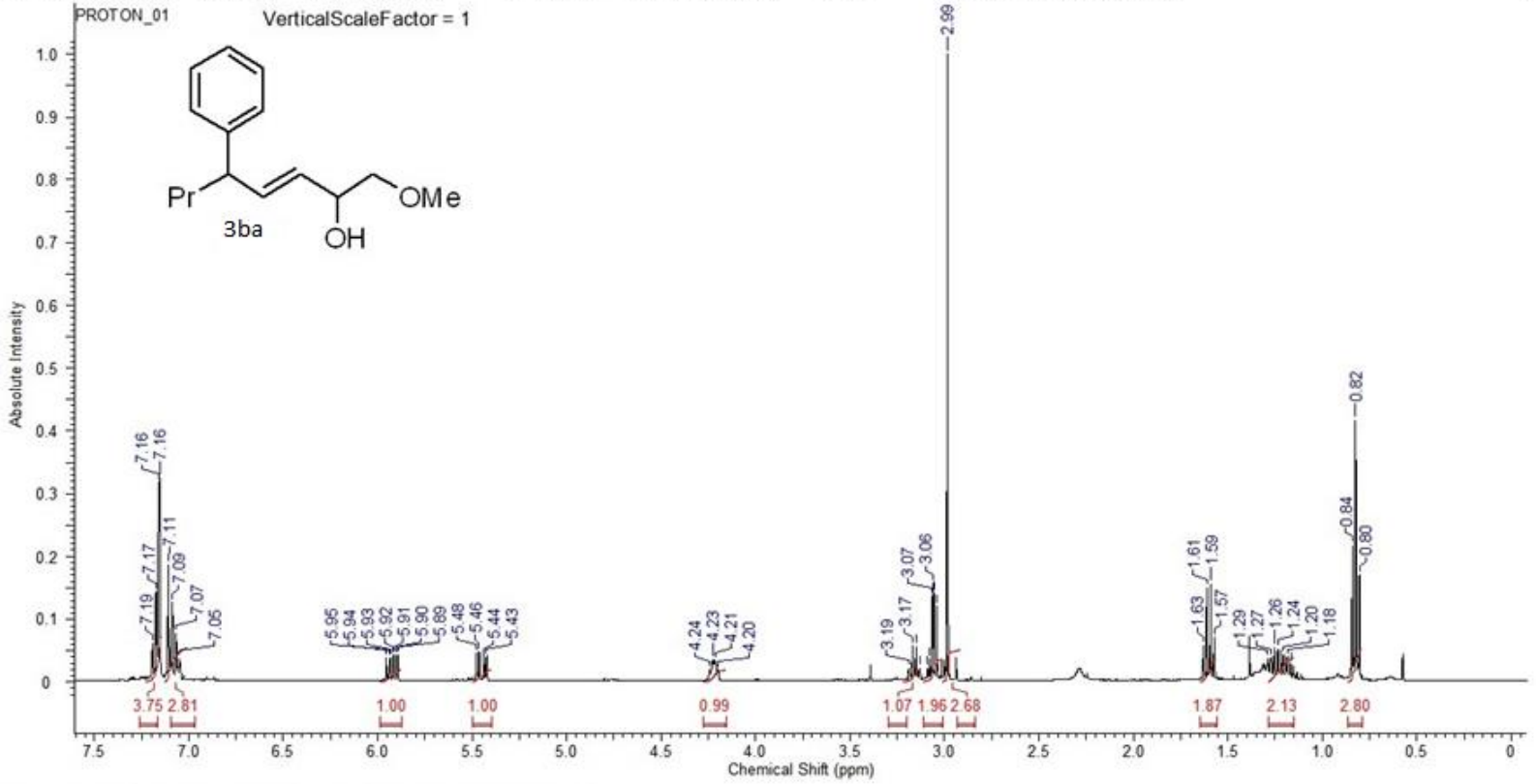
12.10.2015 20:38:54
3ba

Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-81-1_3			*Date*	Apr 28 2015
Date Stamp	Apr 28 2015	*File Name*	C:\Users\Erman\Desktop\ERMAN\ERM-ENEP-81-1_3_20150428_01\PROTON_01.fid\fid				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	56.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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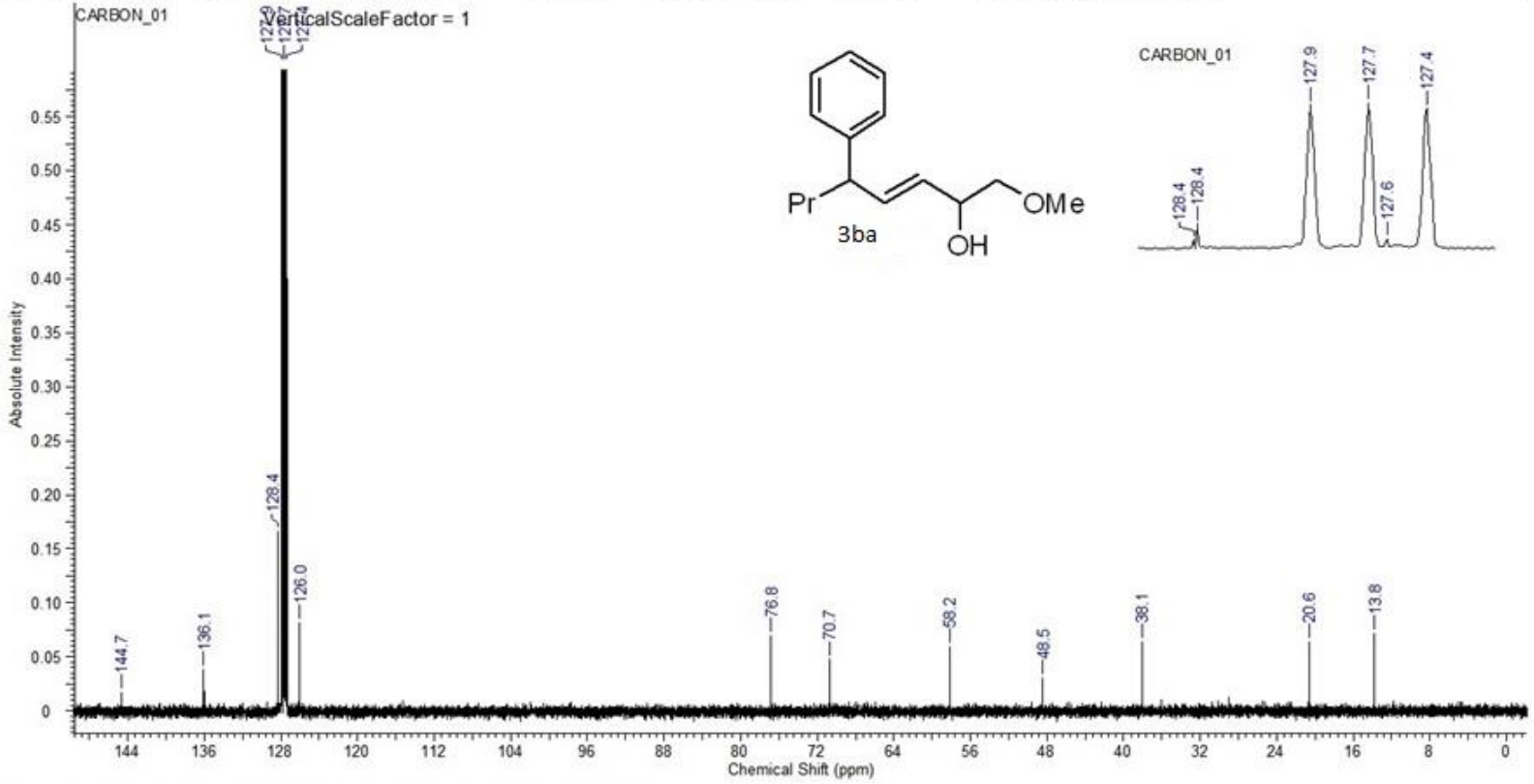
12.10.2015 20:45:39
3ba

Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-75-1_3-CABONE			*Date*	Apr 21 2015
Date Stamp	Apr 21 2015	*File Name*	C:\Users\Erman\Desktop\ERMAN\ERM-ENEP-75-1_3-CABONE_20150421_01\CARBON_01.fid\fid				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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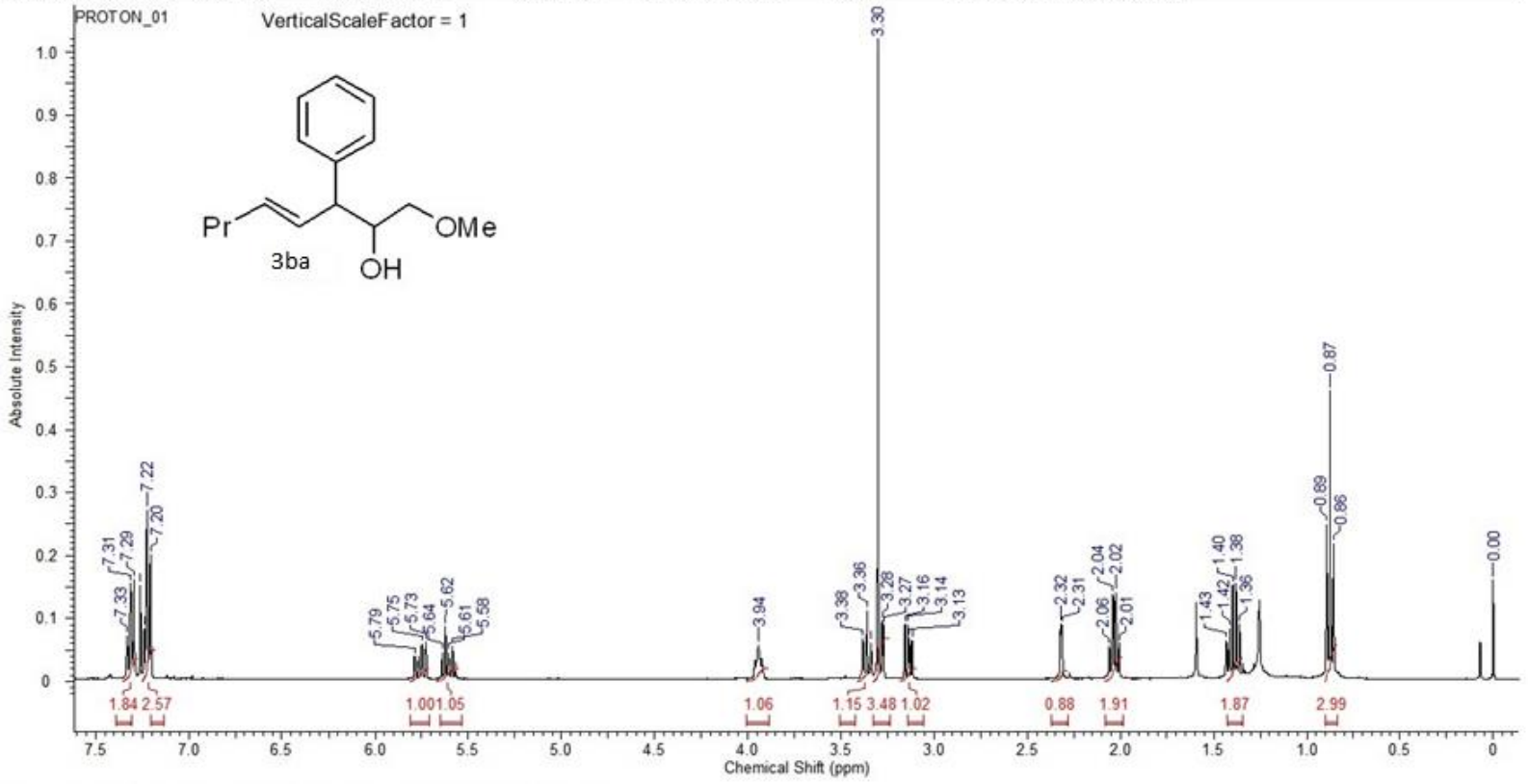
12.10.2015 16:18:39
4ba

Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-54-1_1sub			*Date*	Mar 21 2015
Date Stamp	Mar 21 2015	*File Name*	C:\Users\Erman\Desktop\ERMAN\ERM-ENEP-54-1_1sub_20150321_01\PROTON_01.fid\fid				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	58.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.8845	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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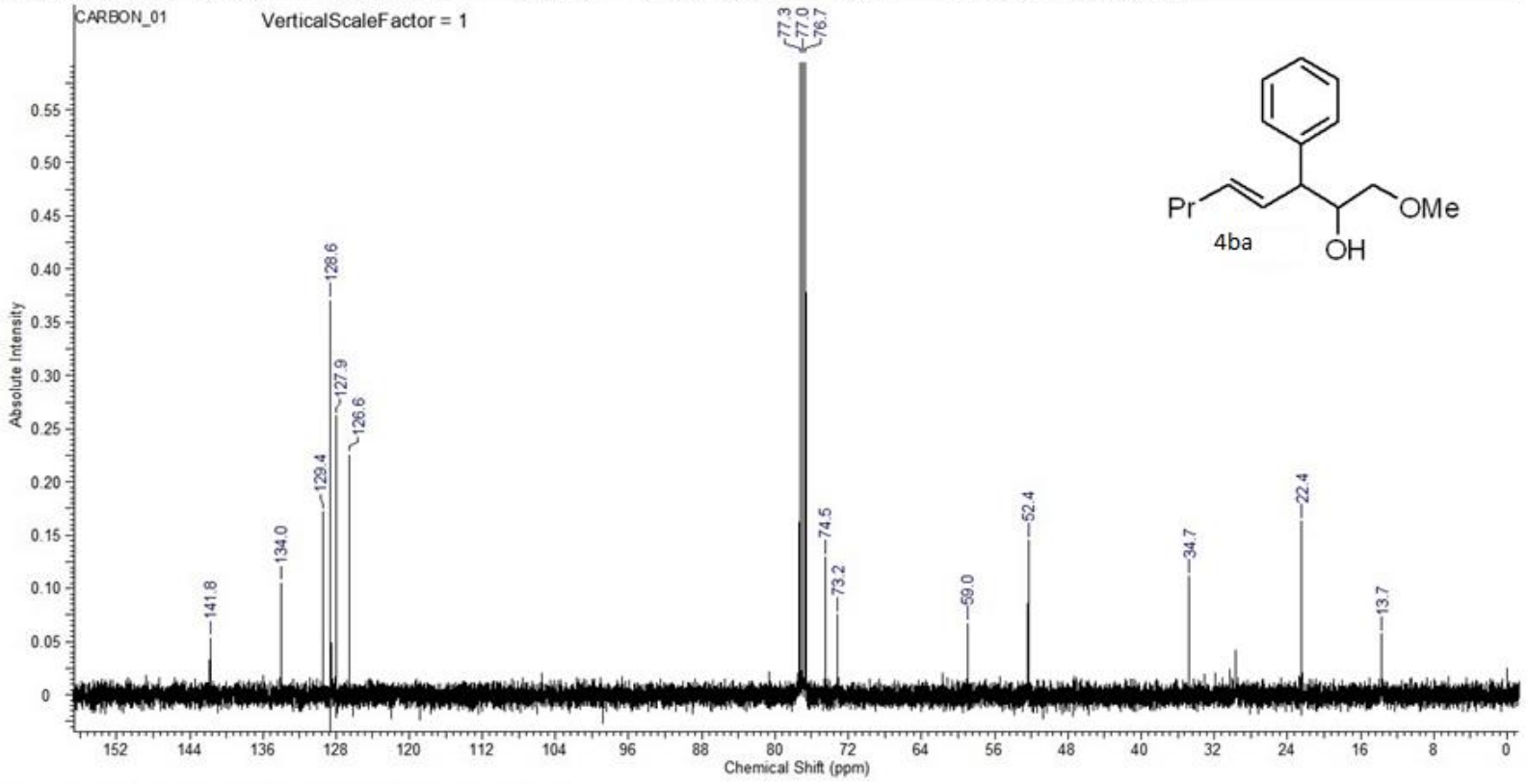
12.10.2015 16:53:00
4ba

Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-114-1_1-C			*Date*	Oct 6 2015
Date Stamp	Oct 6 2015	*File Name*	C:\Users\Erman\Desktop\123\ERM-ENEP-114-1_1-C_20151006_01\CARBON_01.fid\fid				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	1500	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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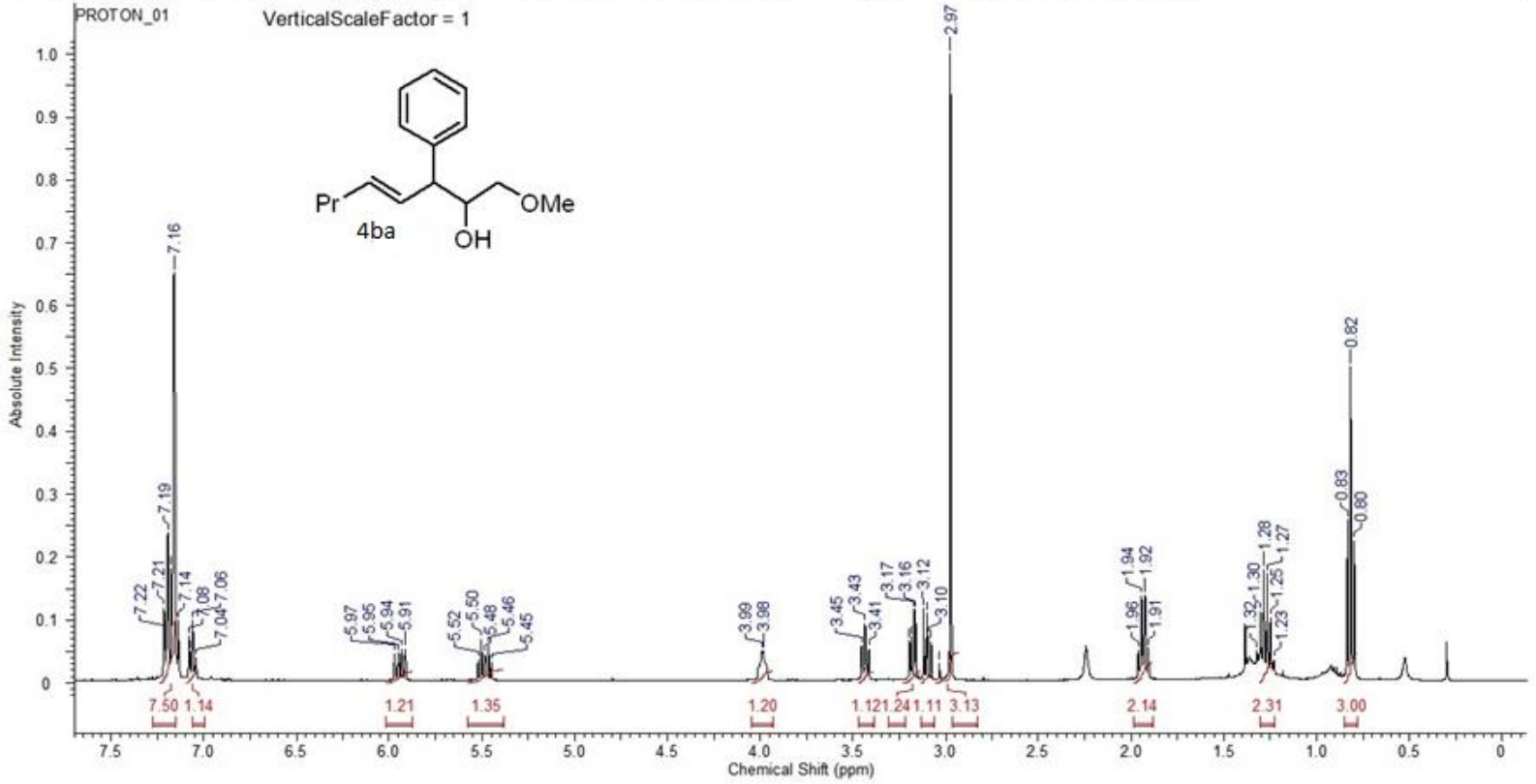
12.10.2015 16:12:57
4ba

Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-54-1_1subC6D6			*Date*	Mar 24 2015
Date Stamp	Mar 24 2015	*File Name*	C:\Users\Erman\Desktop\ERMAN\ERM-ENEP-54-1_1subC6D6_20150324_01\PROTON_01.fid\fid				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	56.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.1677	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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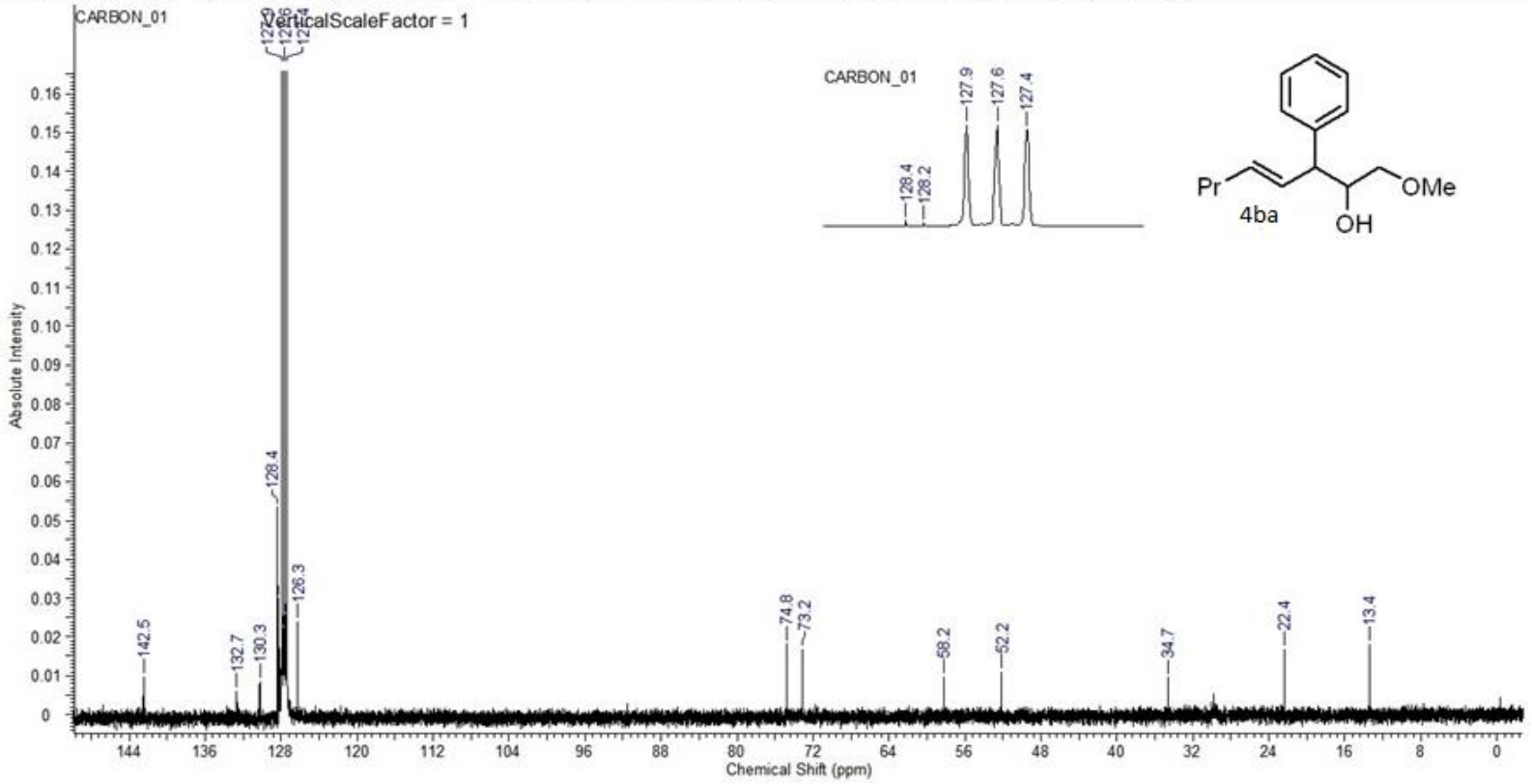
12.10.2015 16:57:03
4ba

Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-114-1_1-BNZ			*Date*	Oct 8 2015
Date Stamp	Oct 8 2015	*File Name*	C:\Users\Erman\Desktop\123\ERM-ENEP-114-1_1-BNZ_20151008_03\CARBON_01.fid\fid				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	2000	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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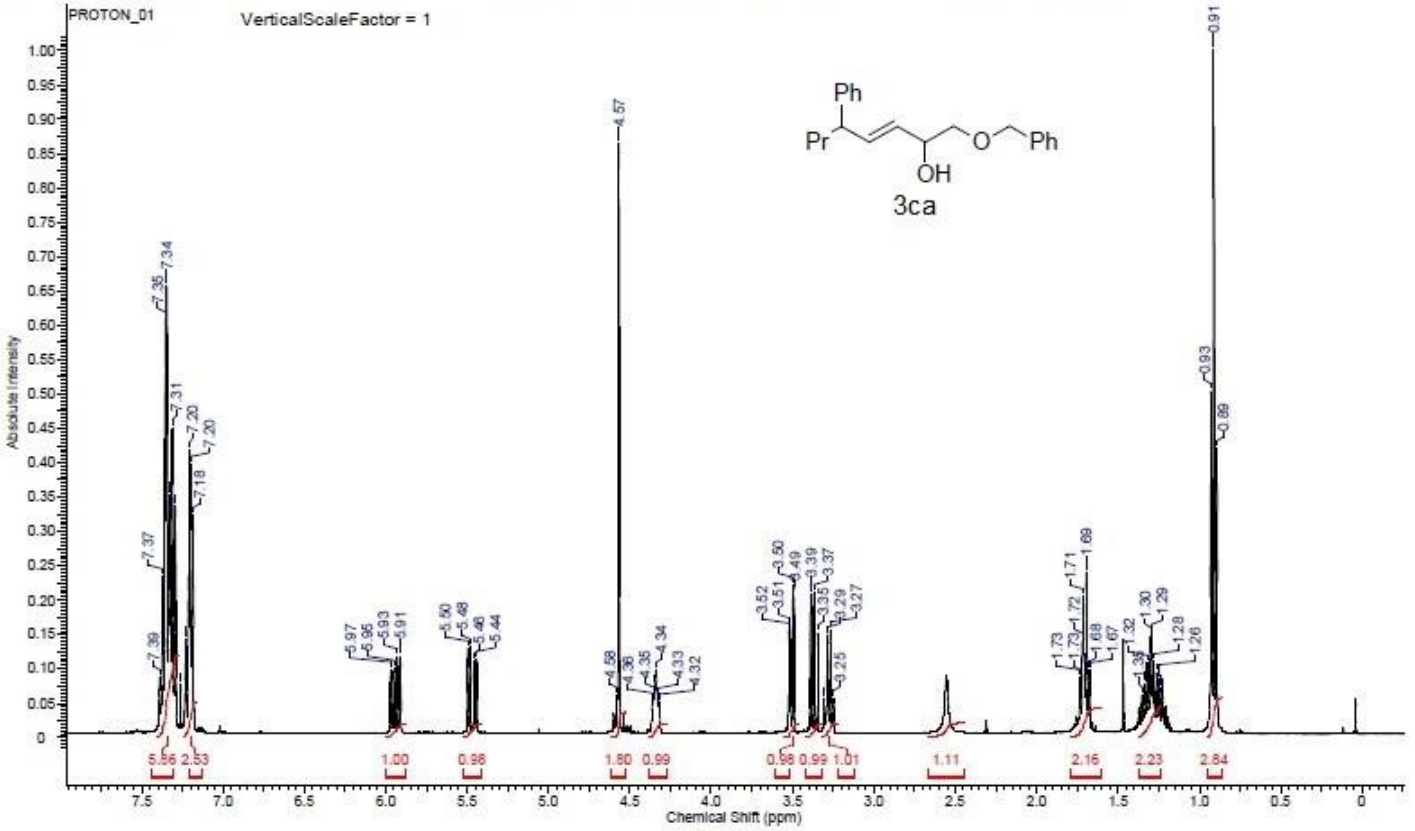
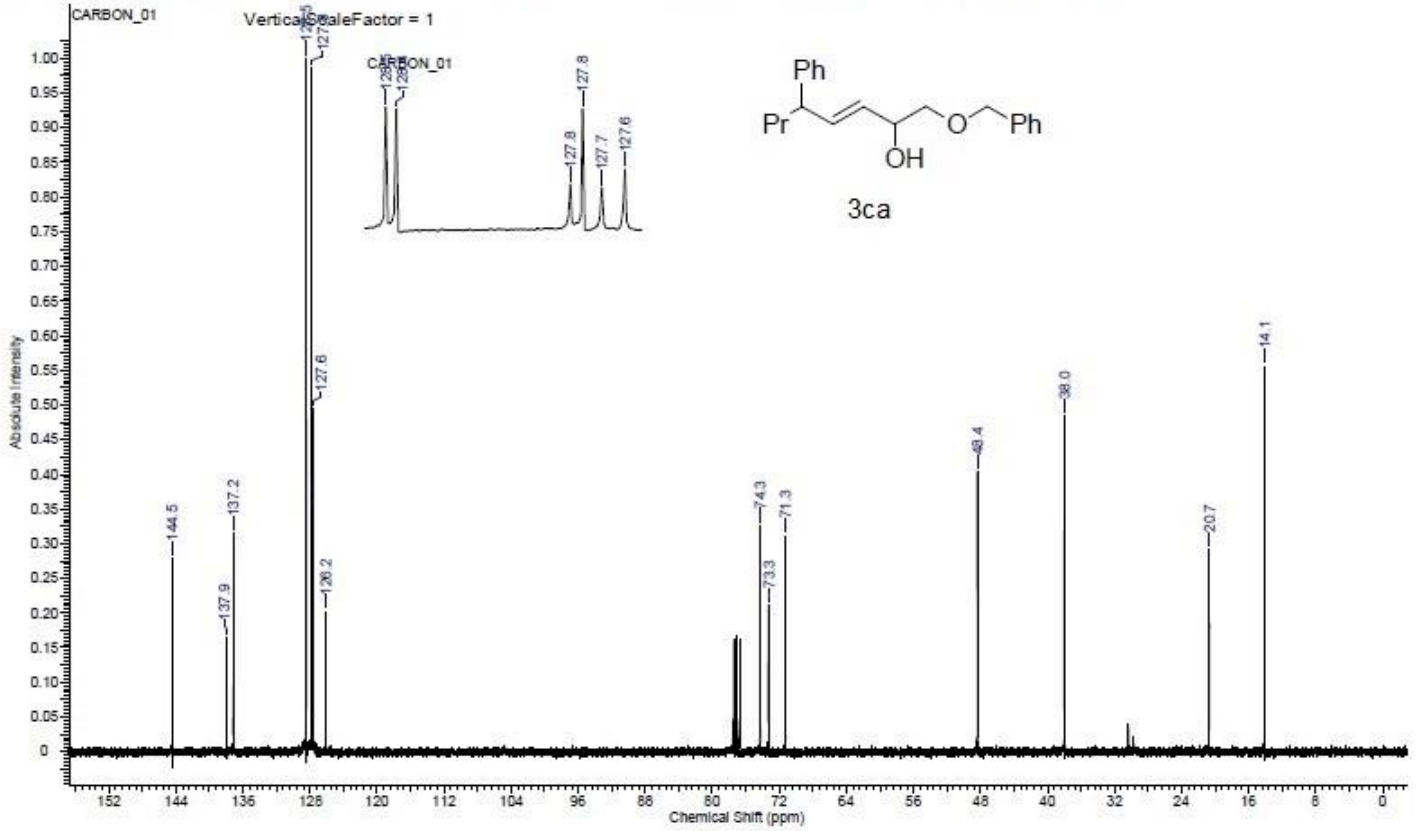
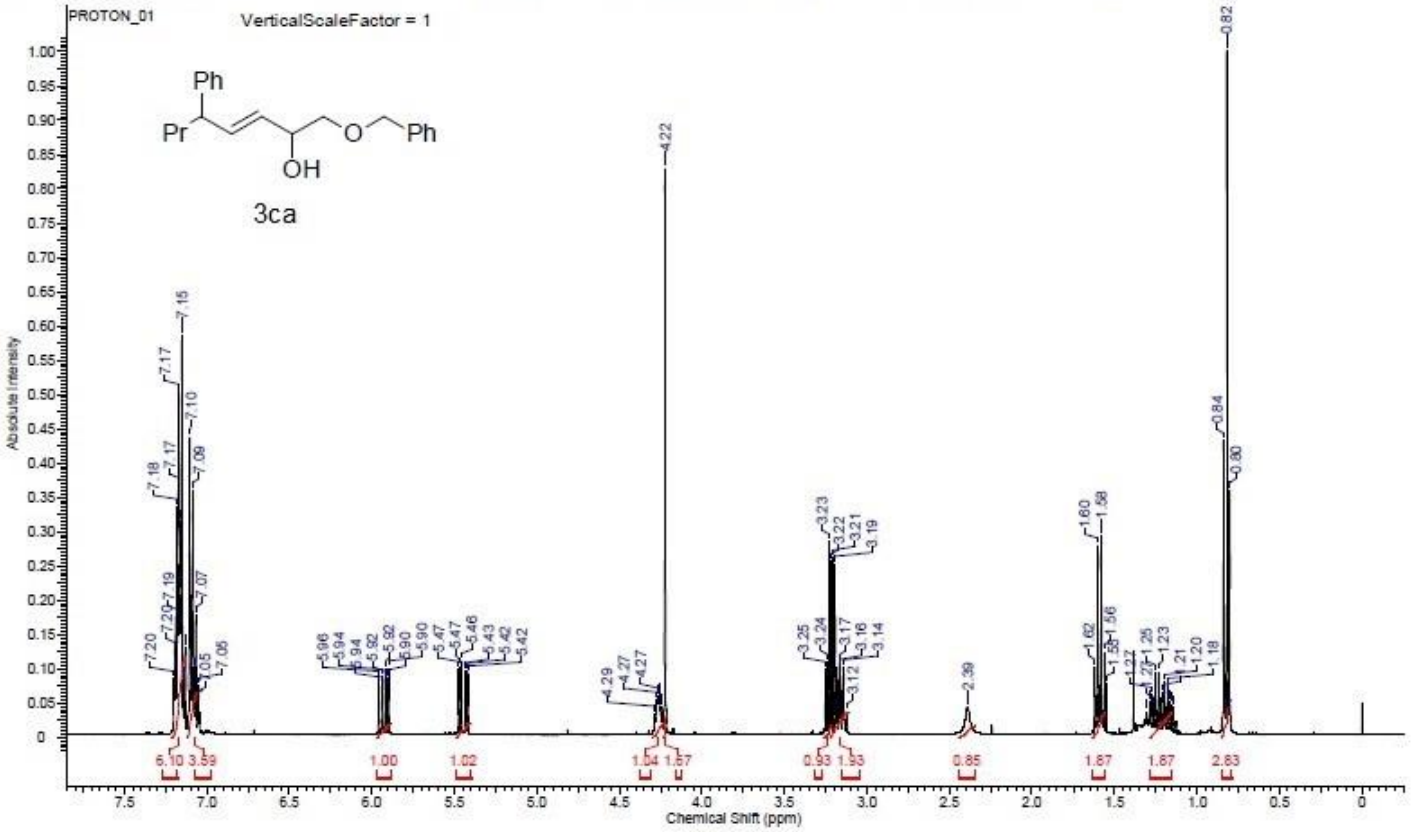
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-185-1_3			*Date*	Jan 19 2016
Date Stamp	Jan 19 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-185-1_3_20160119_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	46.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



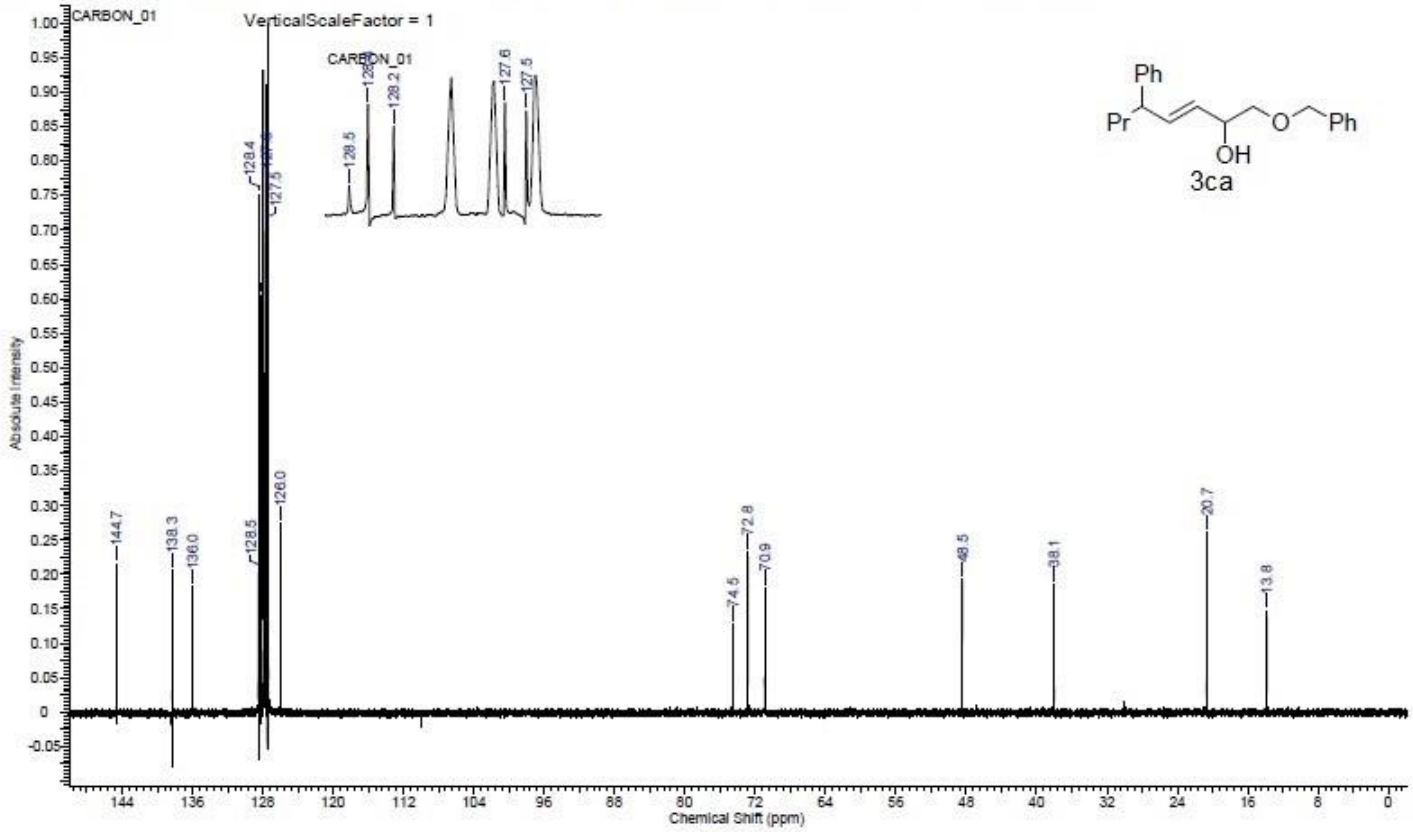
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-185-1_3			*Date*	Jan 19 2016
Date Stamp	Jan 19 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-185-1_3_20160119_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



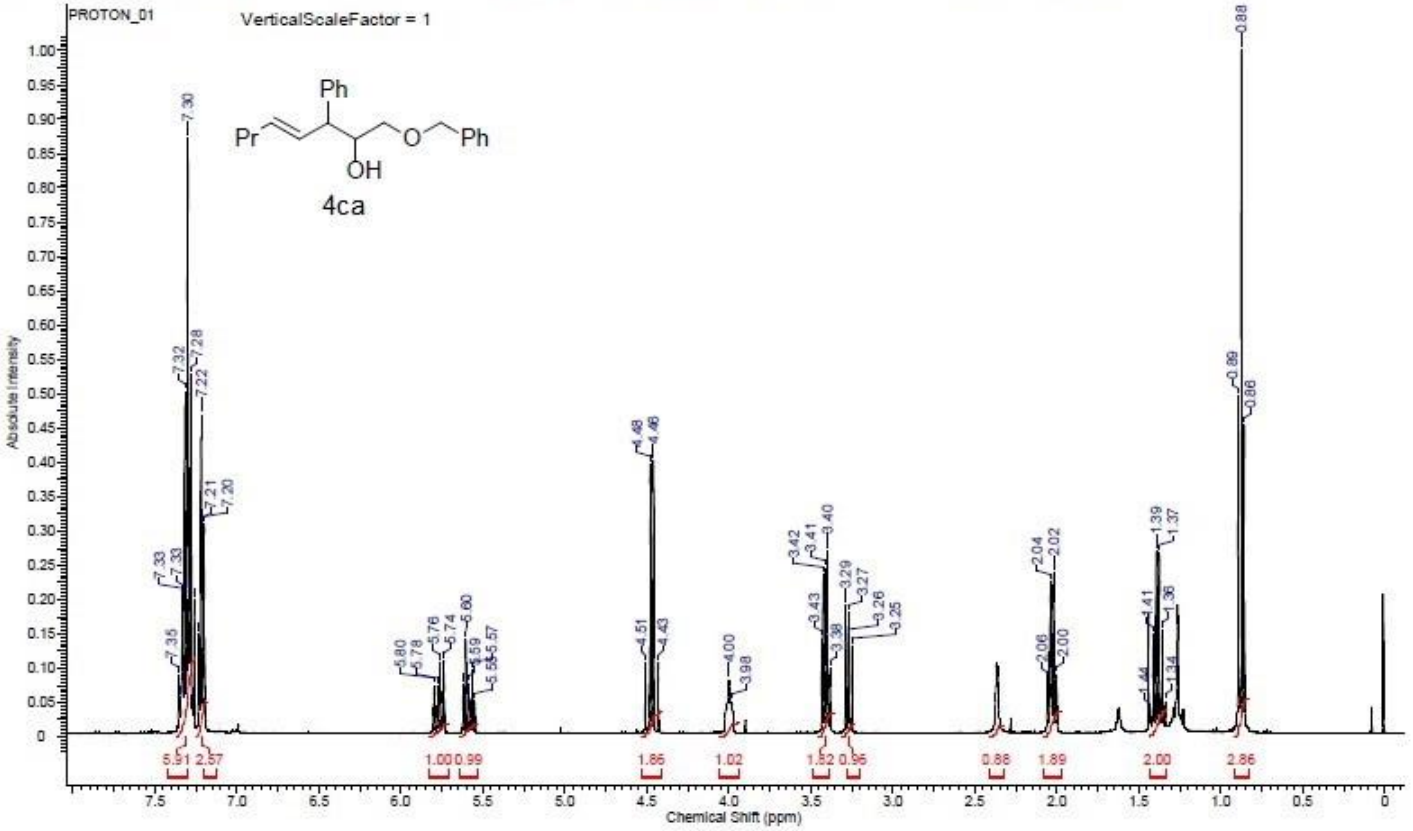
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-185-1_3			*Date*	Jan 8 2016
Date Stamp	Jan 8 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-185-1_3_20160108_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	52.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7092	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



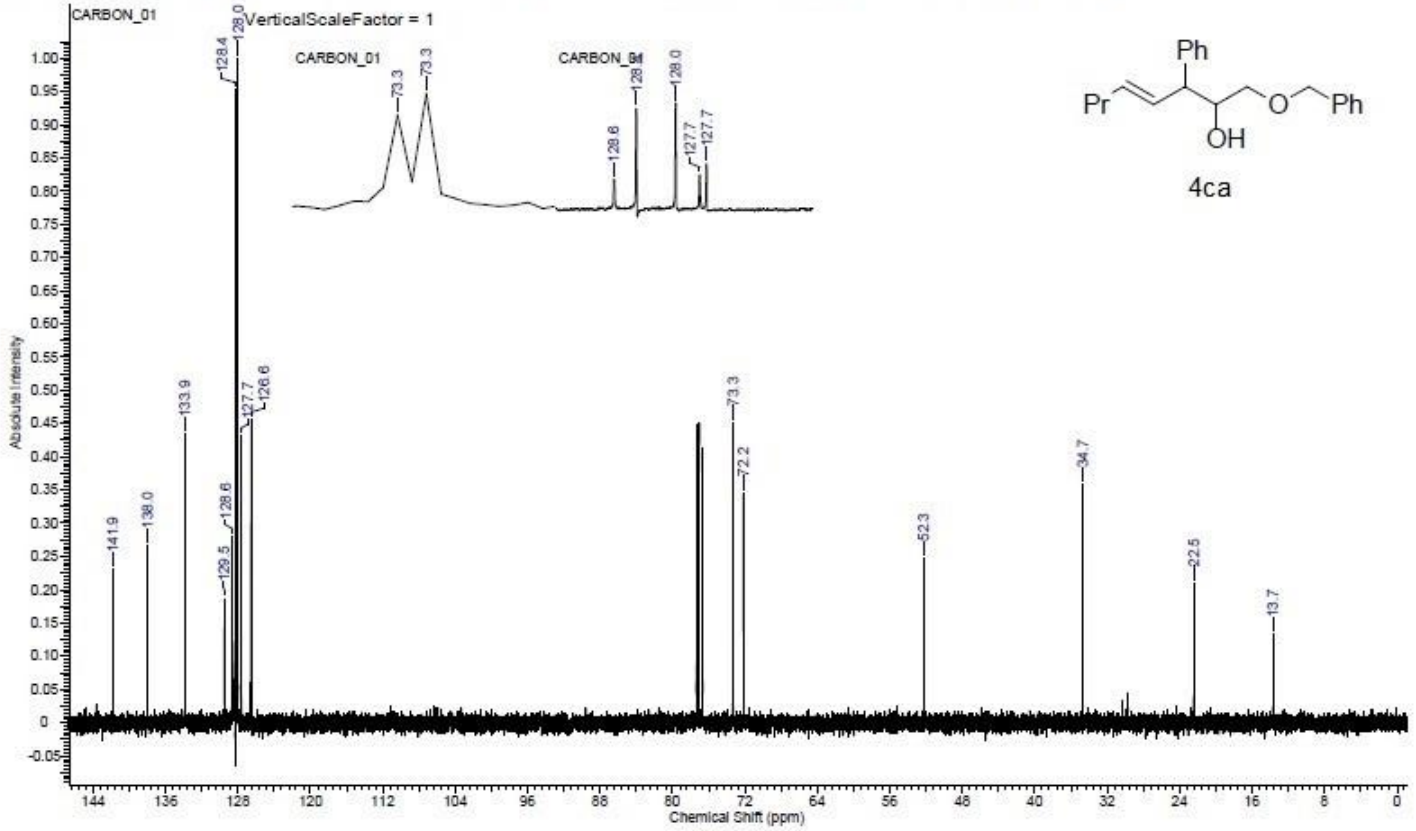
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-185-1_3			*Date*	Jan 11 2016
Date Stamp	Jan 11 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-185-1_3_20160108_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



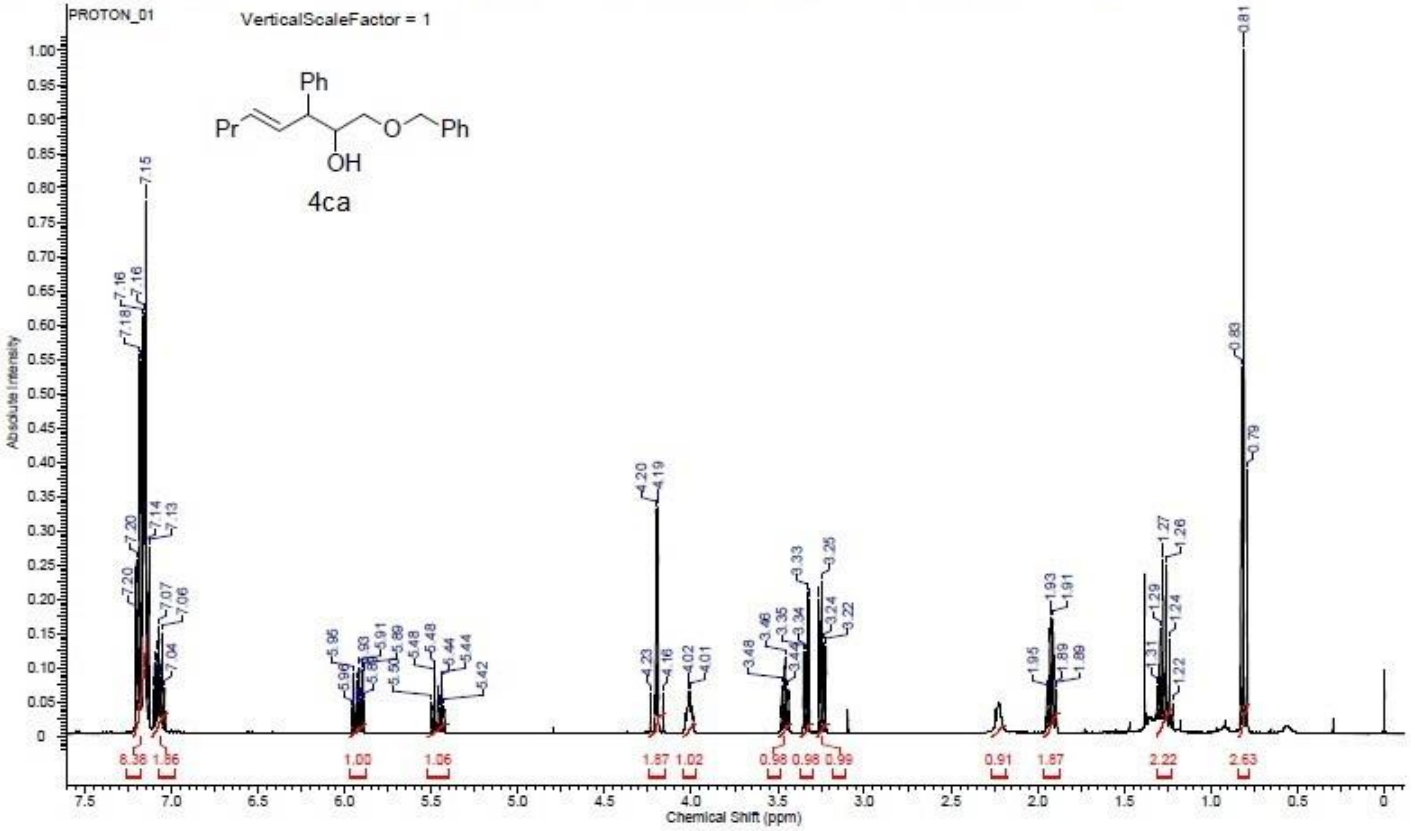
Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-185-1_1			*Date*	Jan 19 2016
Date Stamp	Jan 19 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-185-1_1_20160119_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	56.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-185-1_1			*Date*	Jan 19 2016
Date Stamp	Jan 19 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-185-1_1_20160119_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-185-1_1			*Date*	Jan 8 2016
Date Stamp	Jan 8 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-185-1_1_20160108_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	58.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2415.9268	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-185-1_1			*Date*	Jan 11 2016
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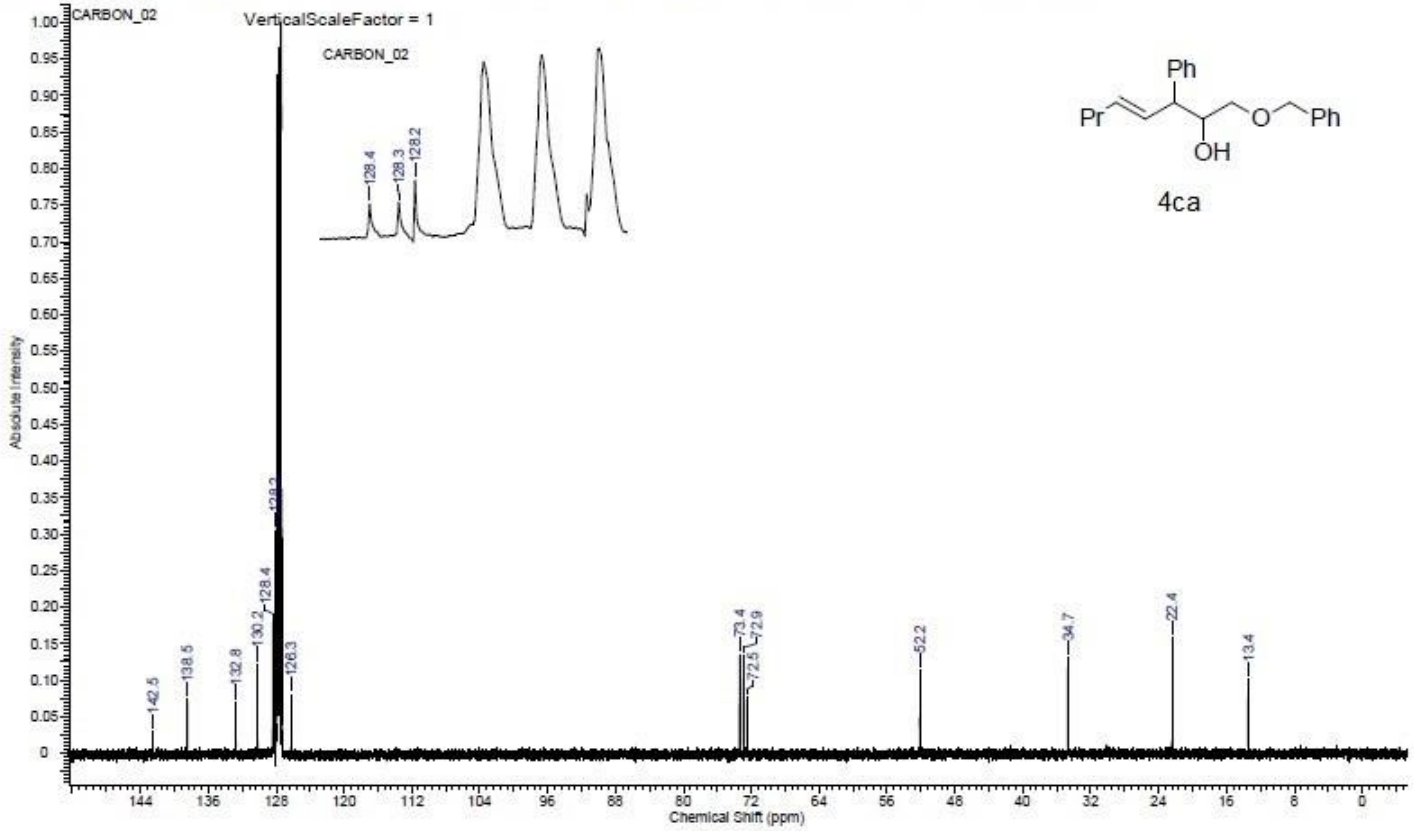
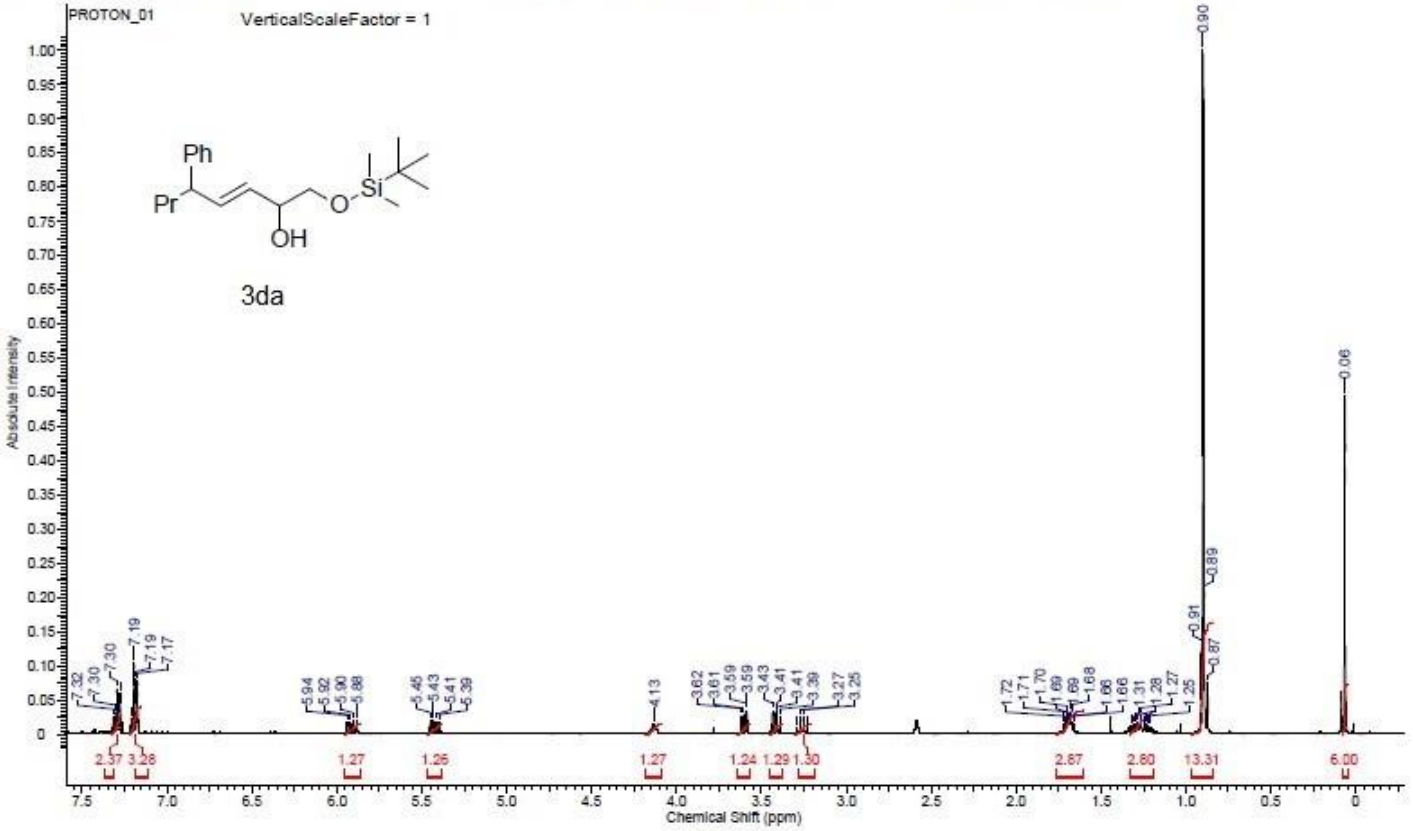
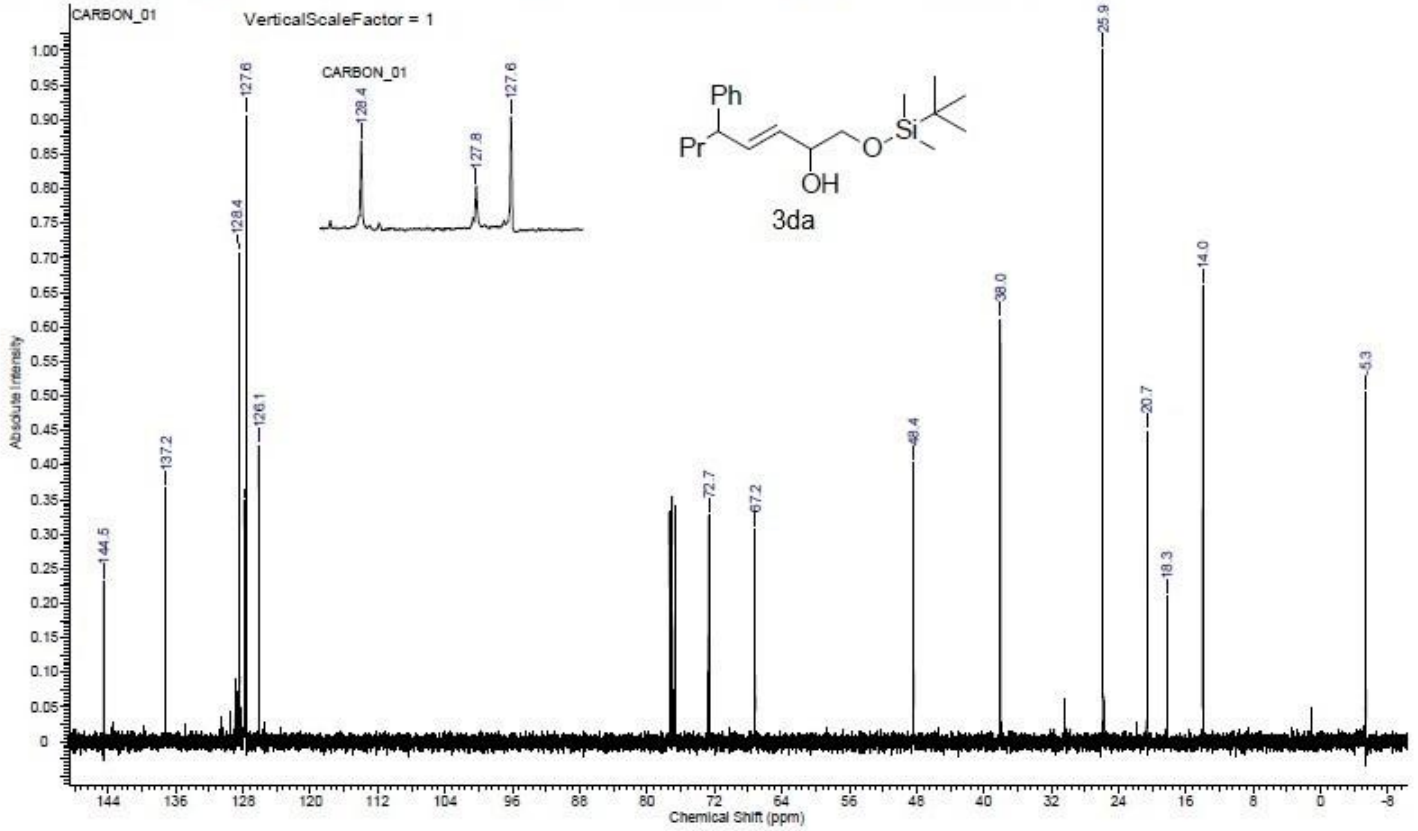
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-184-1_3			*Date*	Jan 21 2016
Date Stamp	Jan 21 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-184-1_3_20160121_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	48.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-184-1_3			*Date*	Jan 21 2016
Date Stamp	Jan 21 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-184-1_3-13C_20160121_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	160	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-184-1_3			*Date*	Jan 18 2016
Date Stamp	Jan 18 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-184-1_3_20160118_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	48.00	*Solvent*	BENZENE-d6
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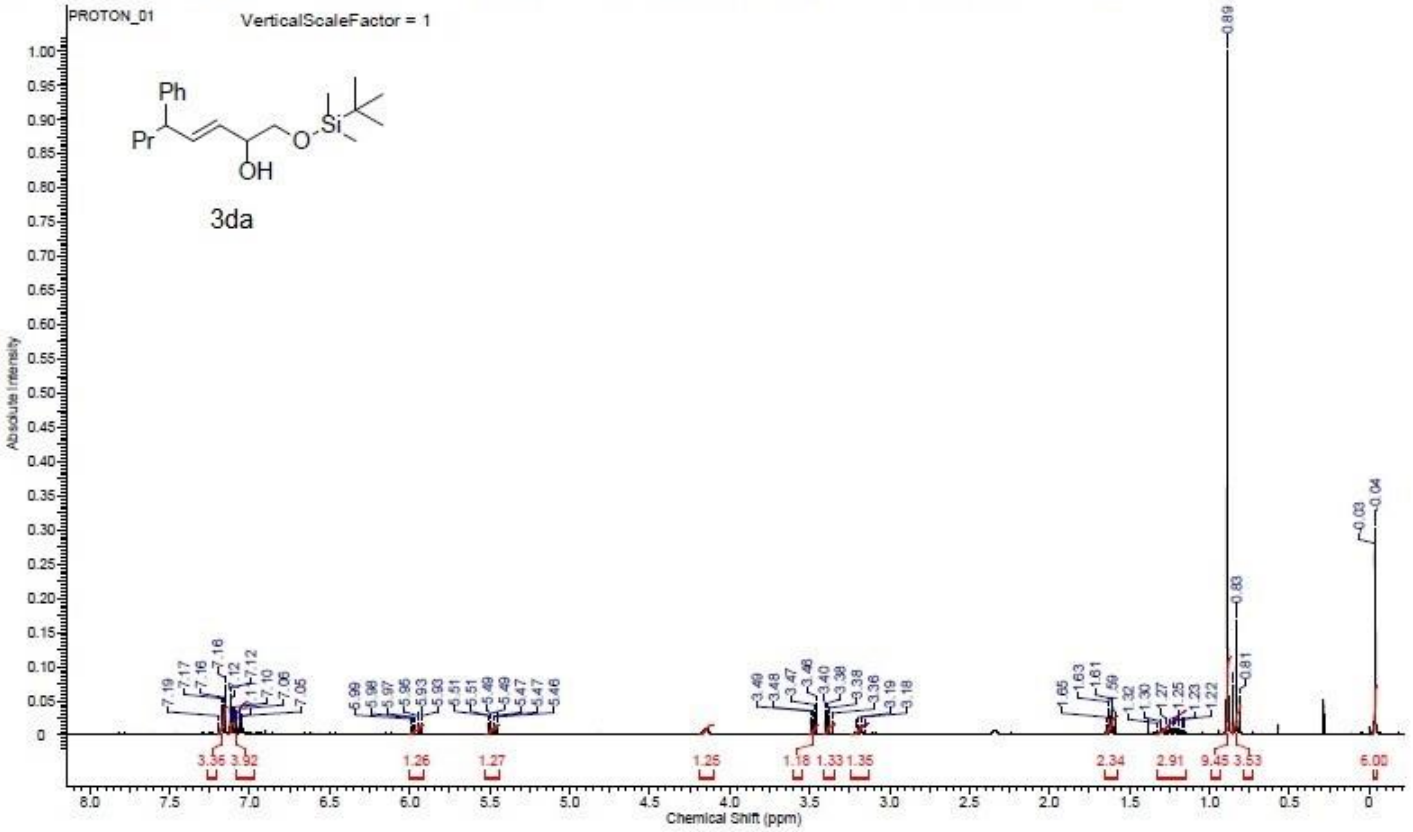
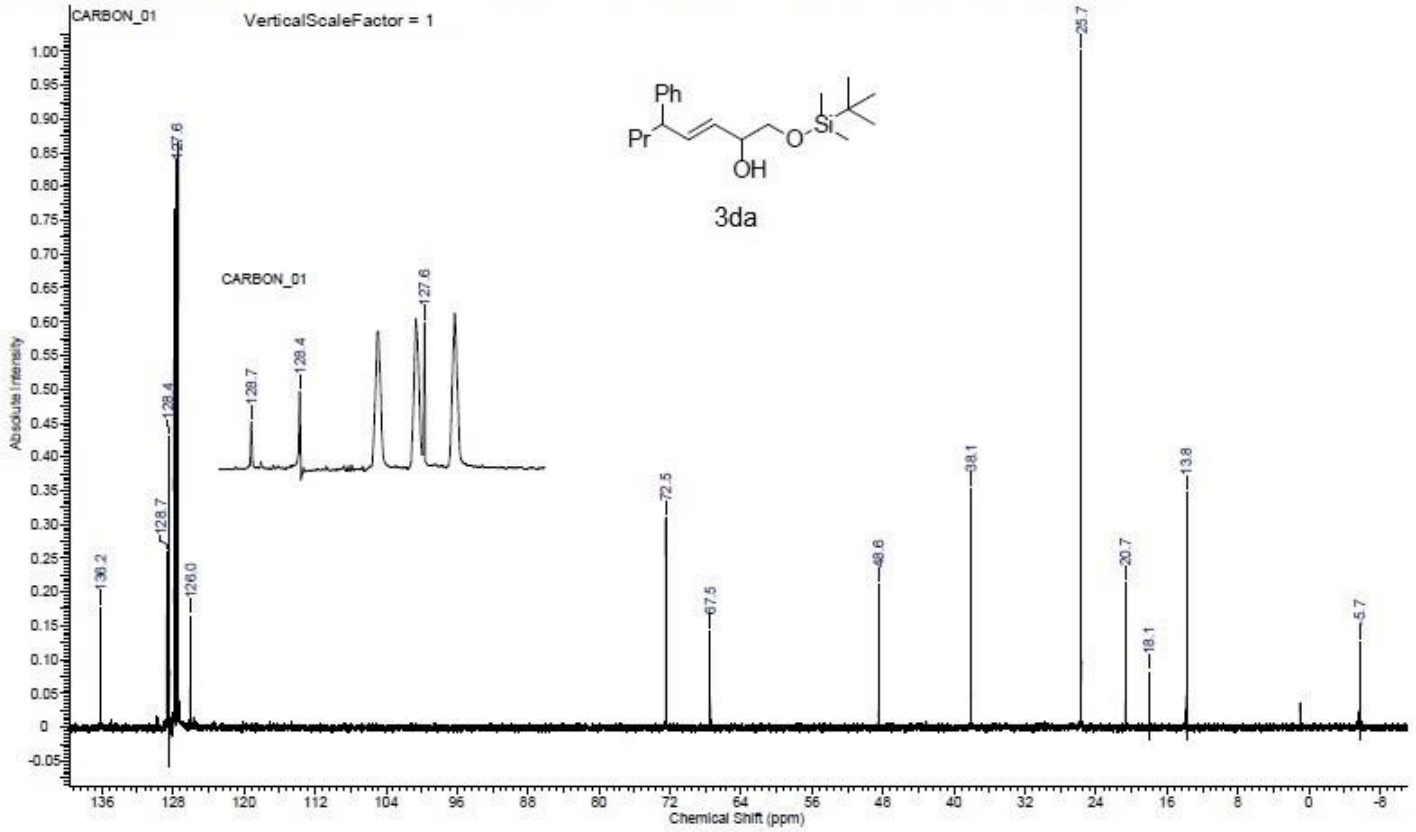
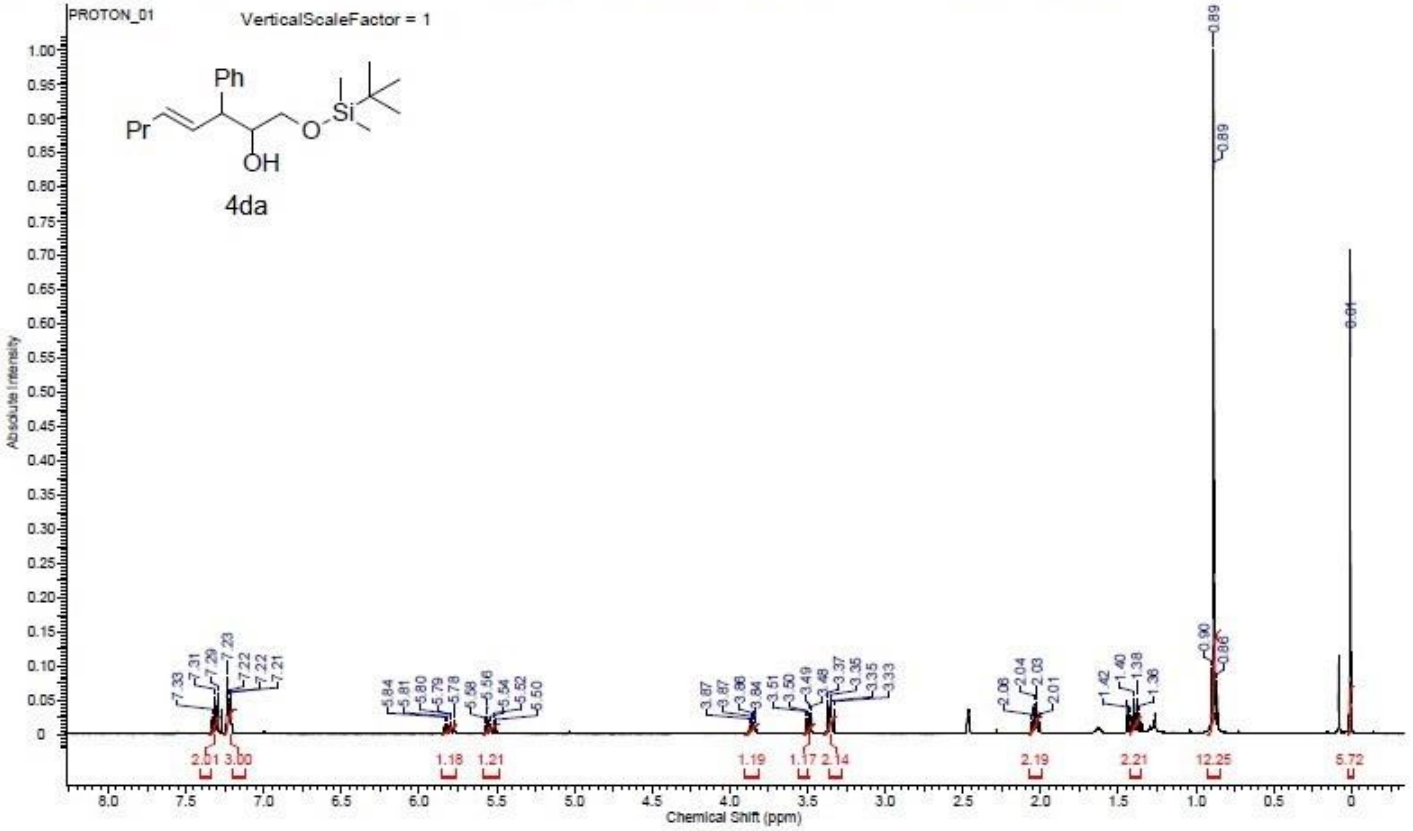


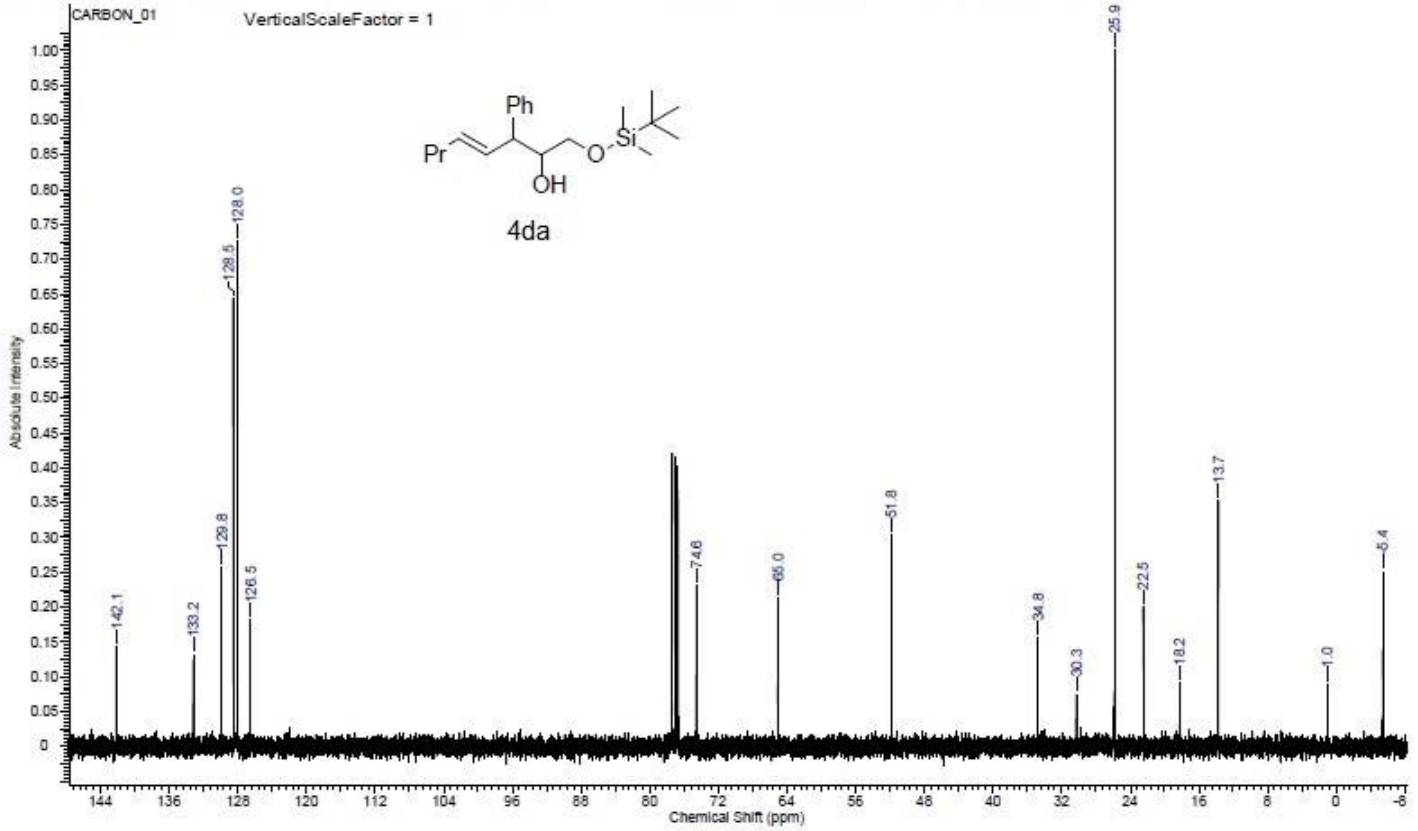
Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-184-1_3			*Date*	Jan 18 2016
Date Stamp	Jan 18 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-184-1_3_20160118_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-184-1_1			*Date*	Jan 21 2016
Date Stamp	Jan 21 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-184-1_1_20160121_01\PROTON_01.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	56.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2404.0322	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



Acquisition Time (sec)	1.3107	*Comment*	ERM-ENEP-184-1_1			*Date*	Jan 21 2016
Date Stamp	Jan 21 2016	*File Name*	C:\USERS\ERMAN\GOOGLE DRIVE\ERMAN\ERM-ENEP-184-1_1_20160121_01\CARBON_01.FID\FID				
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-184-1_1			*Date*	Jan 18 2016
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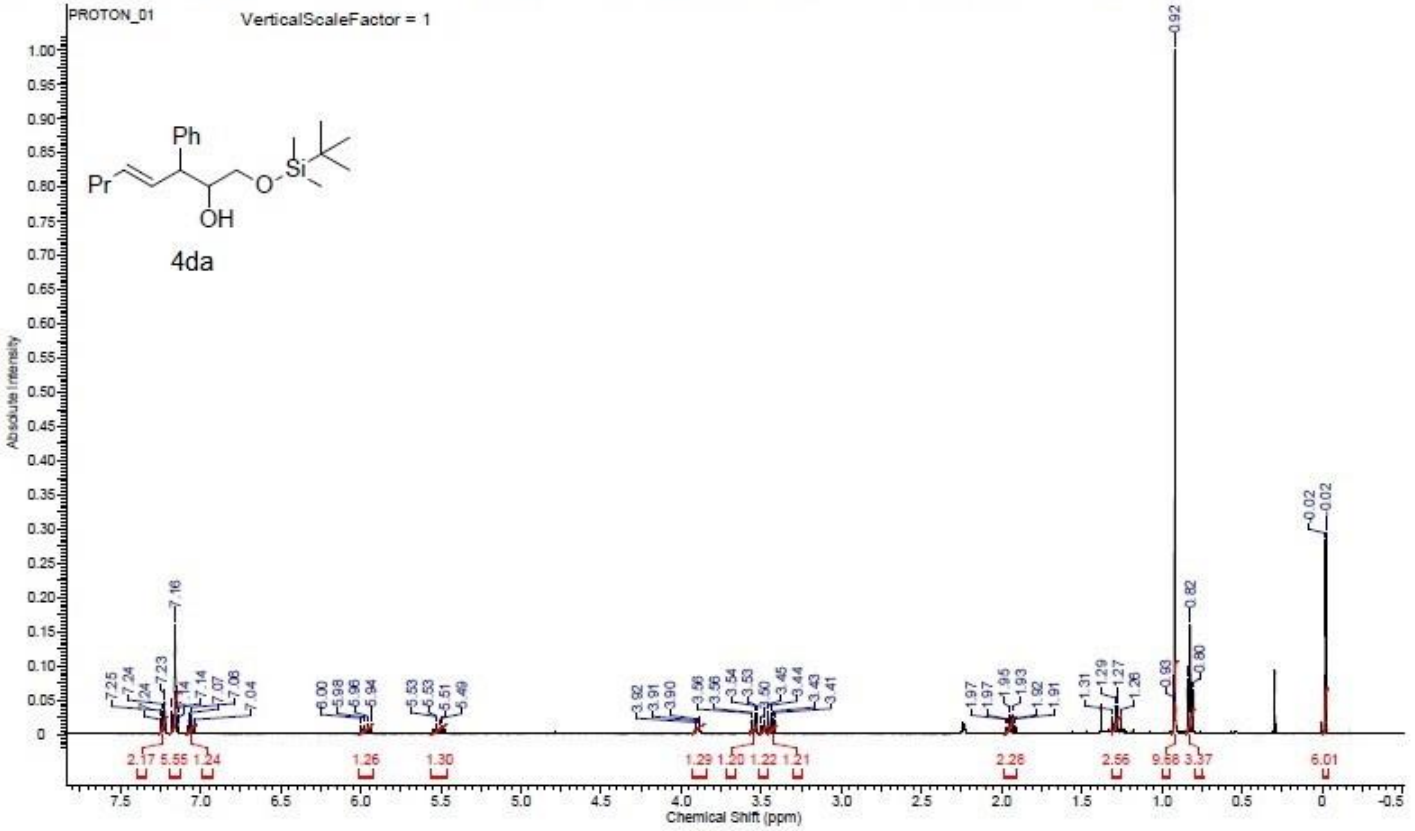
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	58.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3853	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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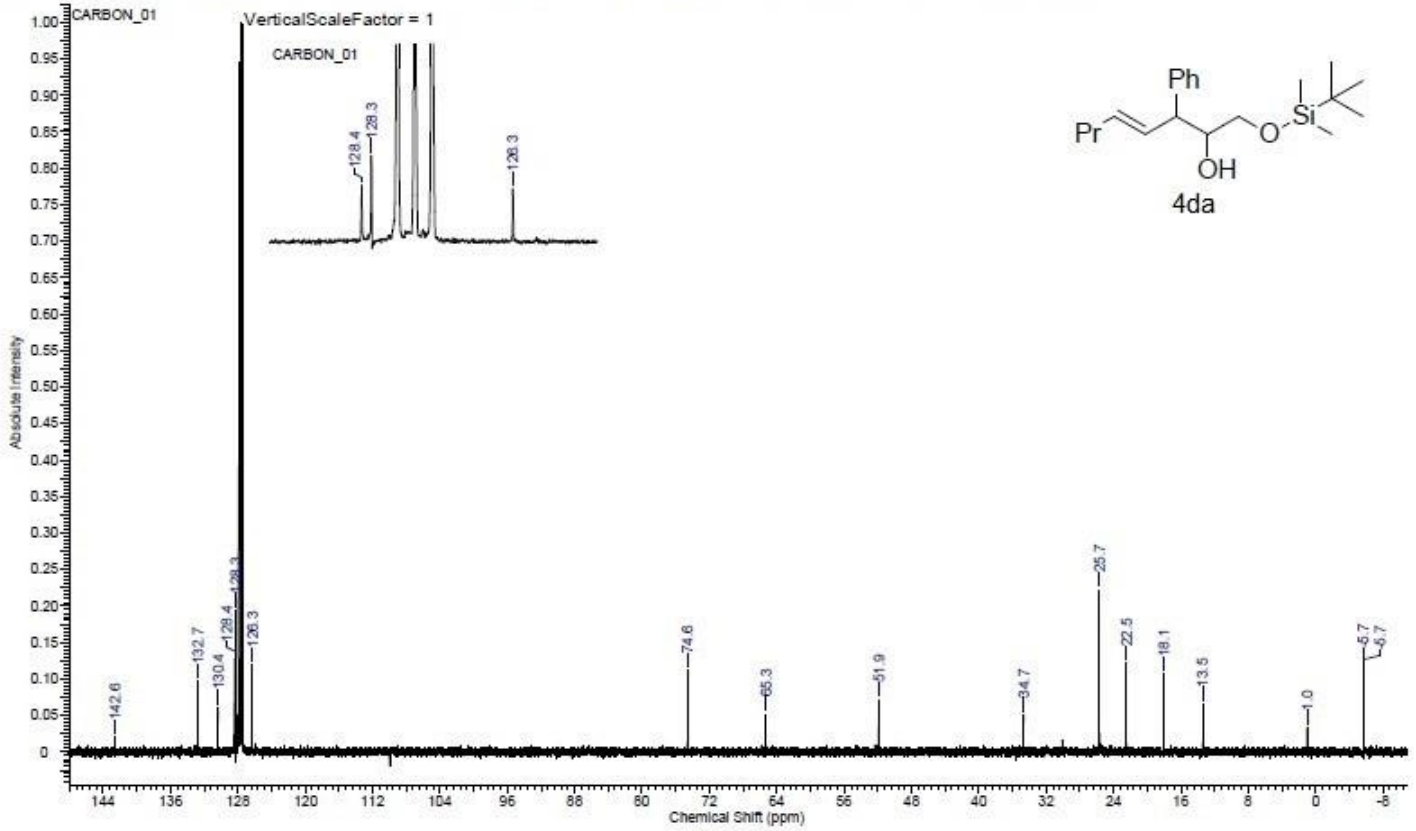
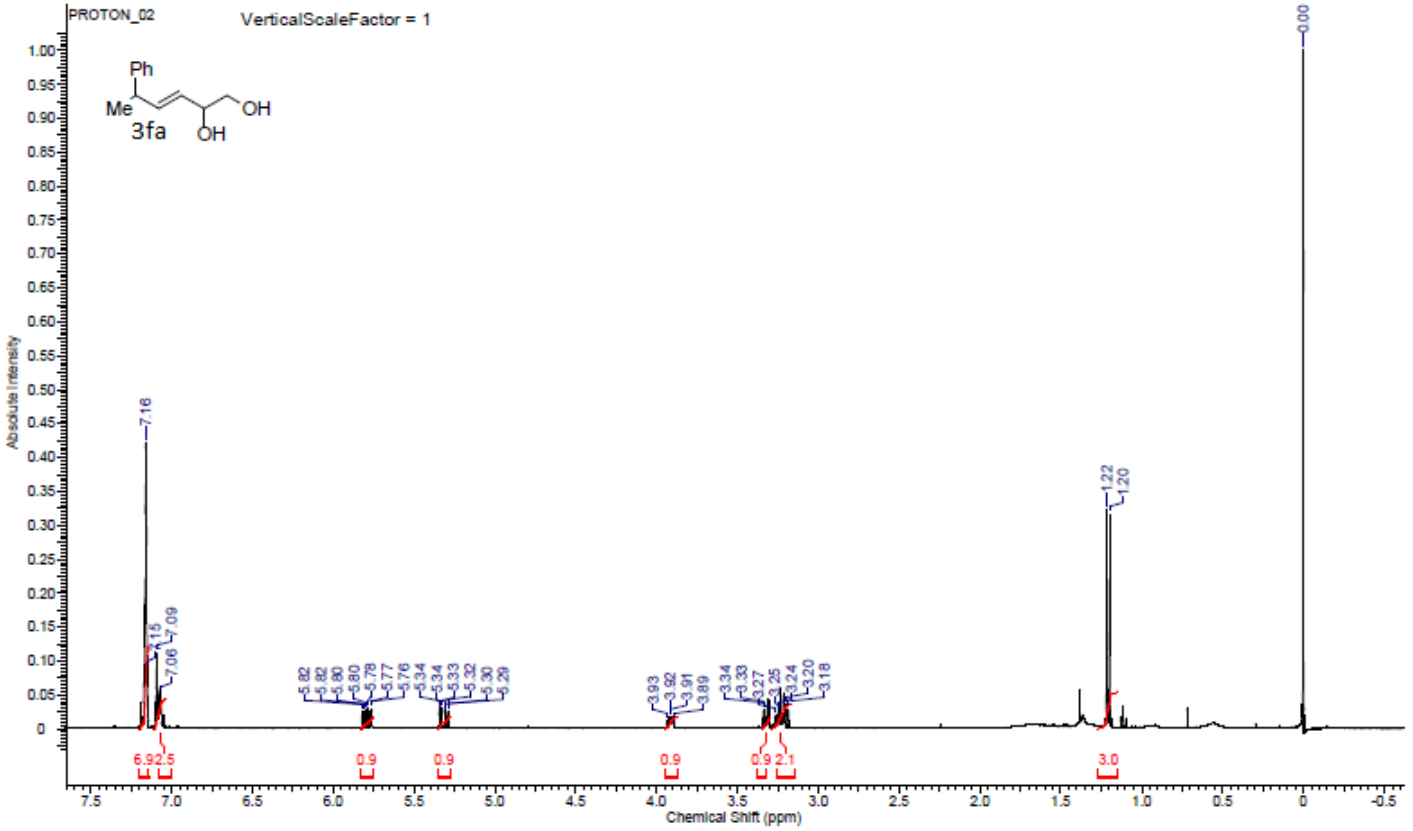
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-215-1_3-BNZ			*Date*	Jun 7 2016
Date Stamp	Jun 7 2016	*File Name*	C:\USERS\ERMAN\DESKTOP\WET\ERM-ENEP-215-1_3-BNZ_20160607_01\PROTON_02.FID\FID				
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3181	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	700	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
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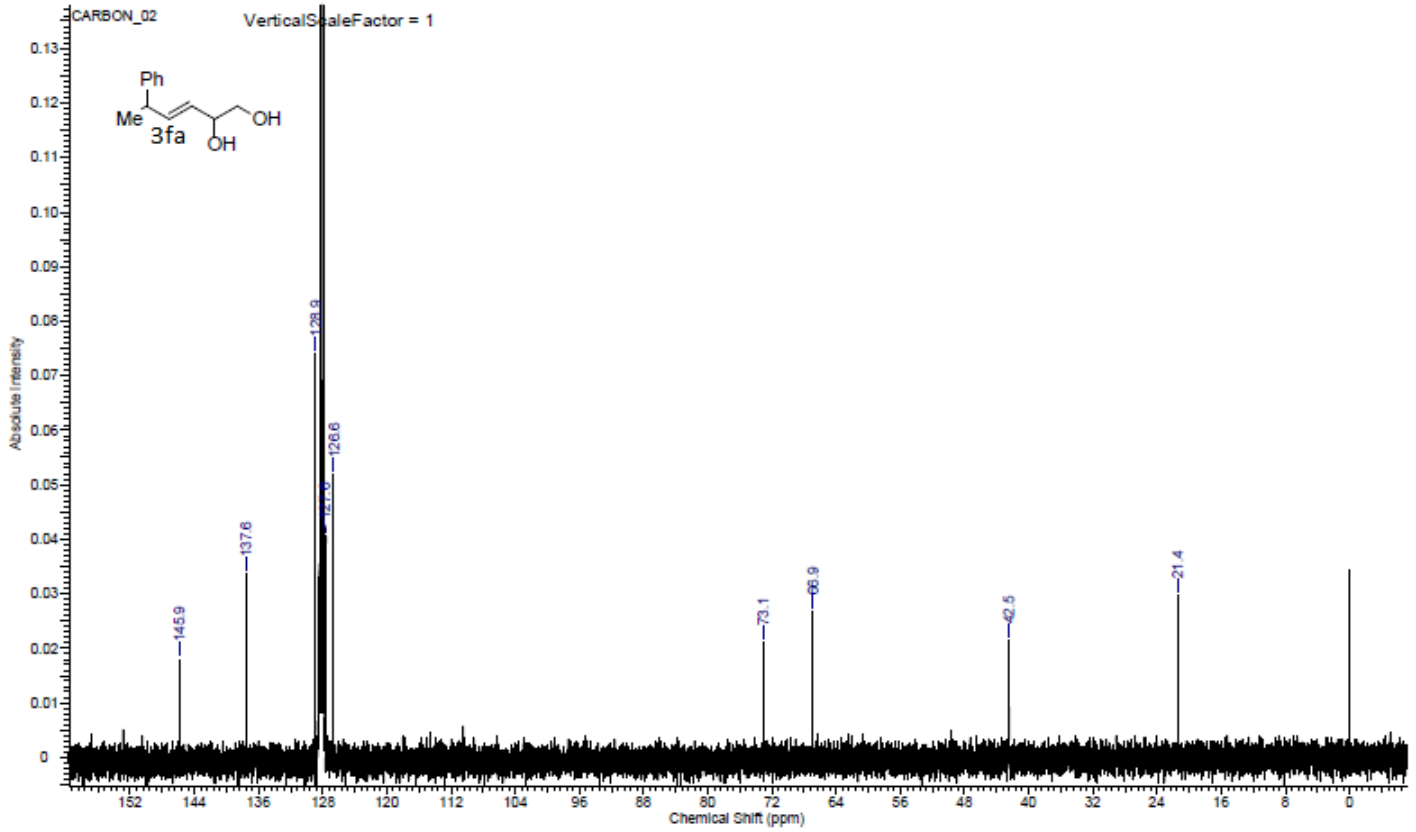

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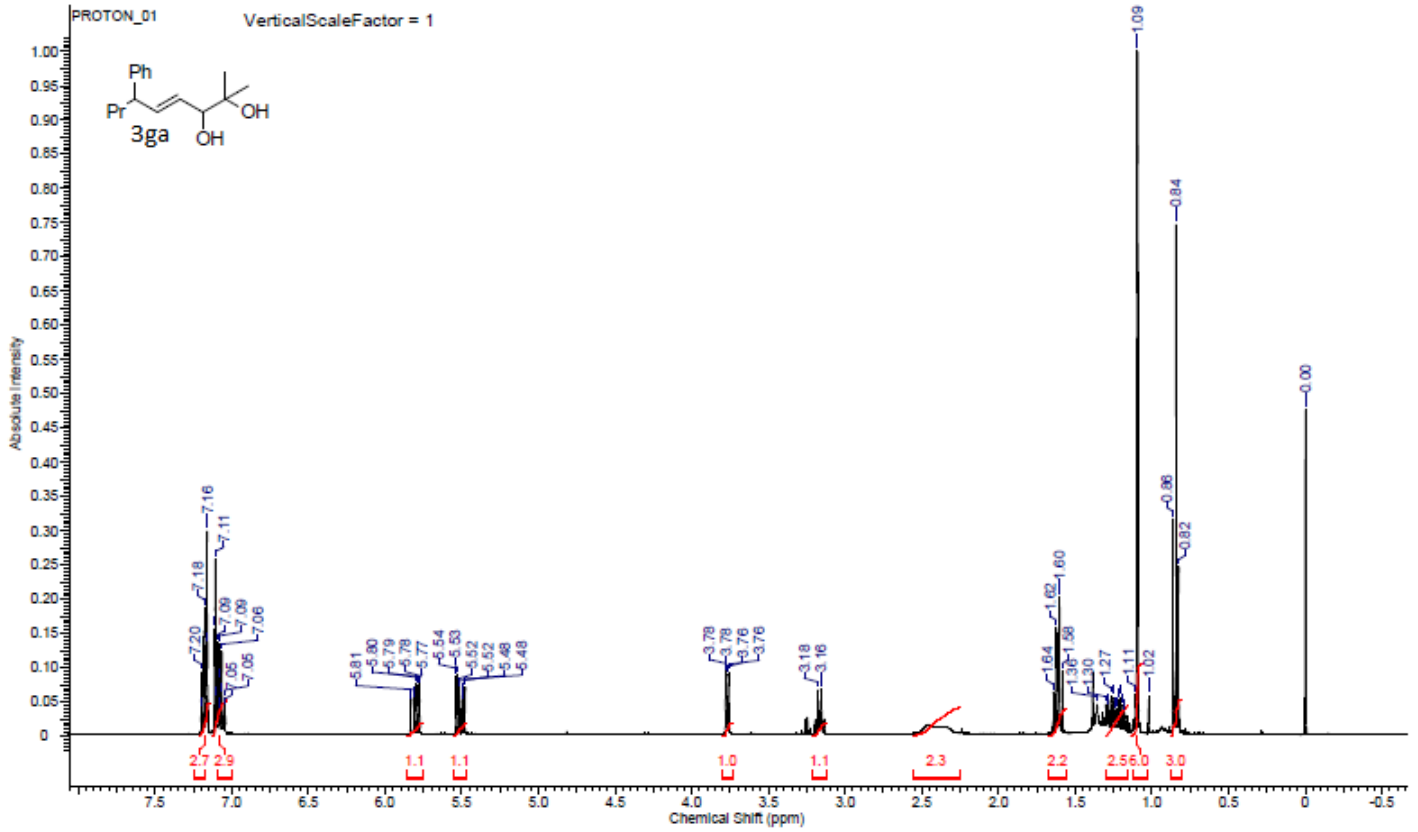
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	52.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.4919	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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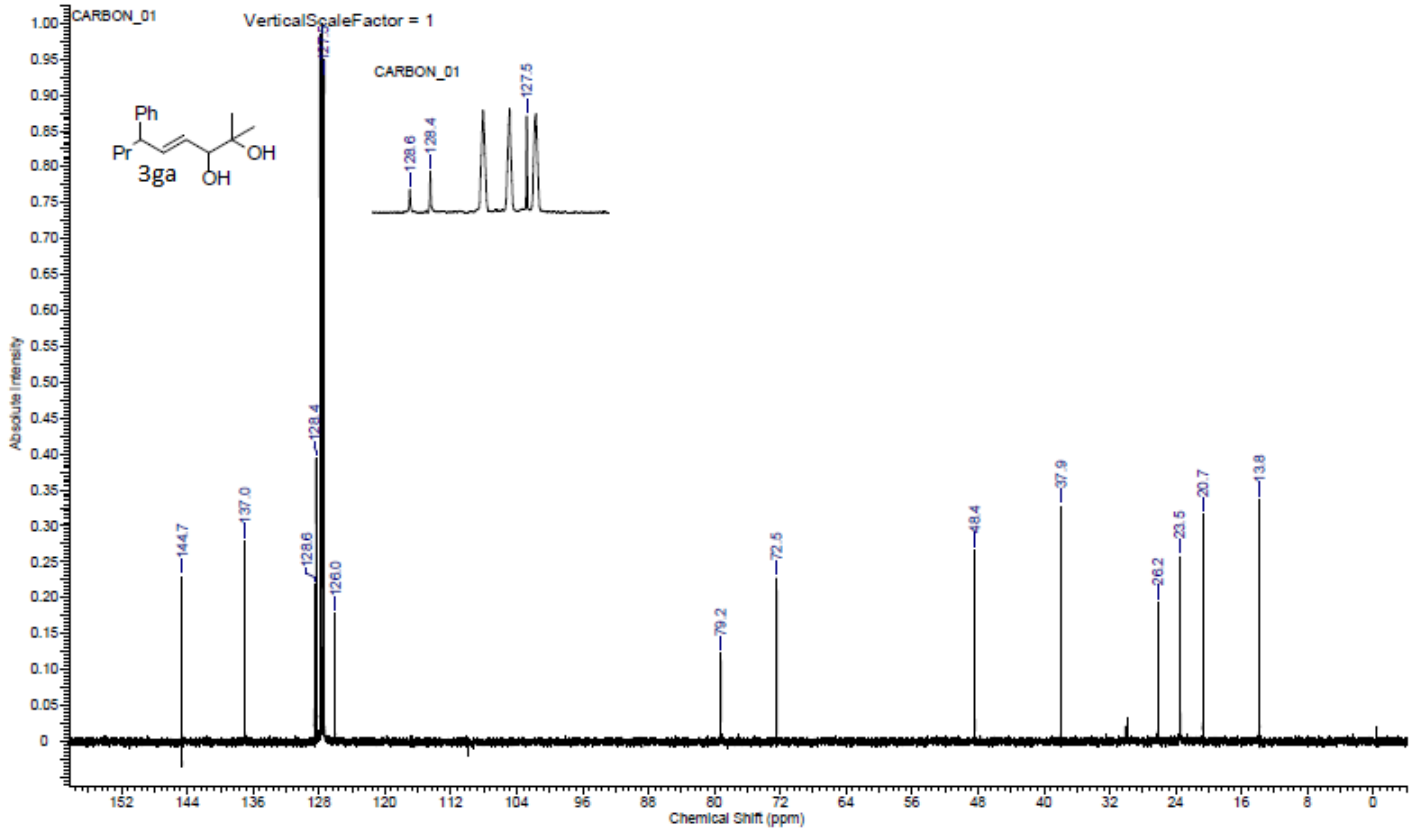
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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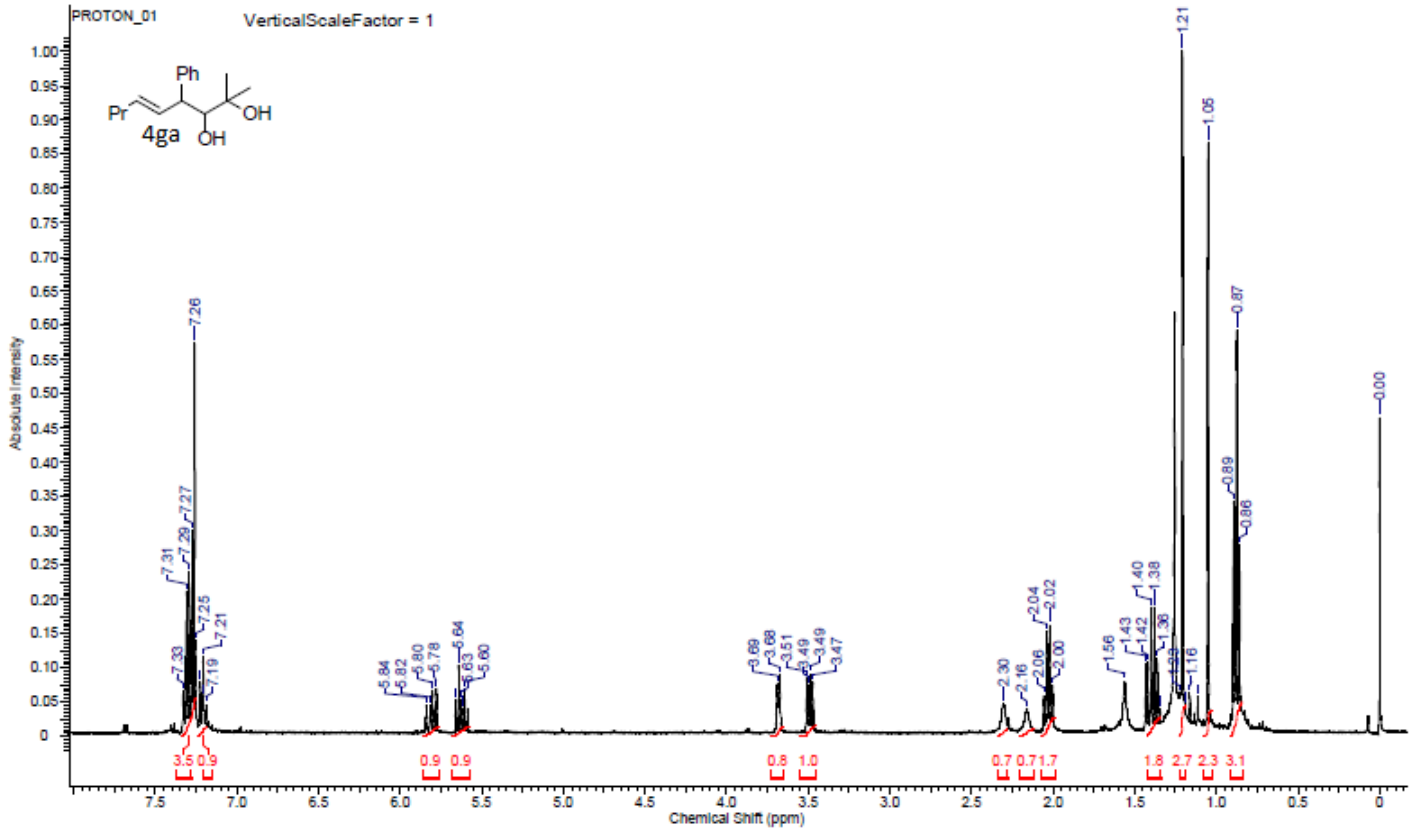
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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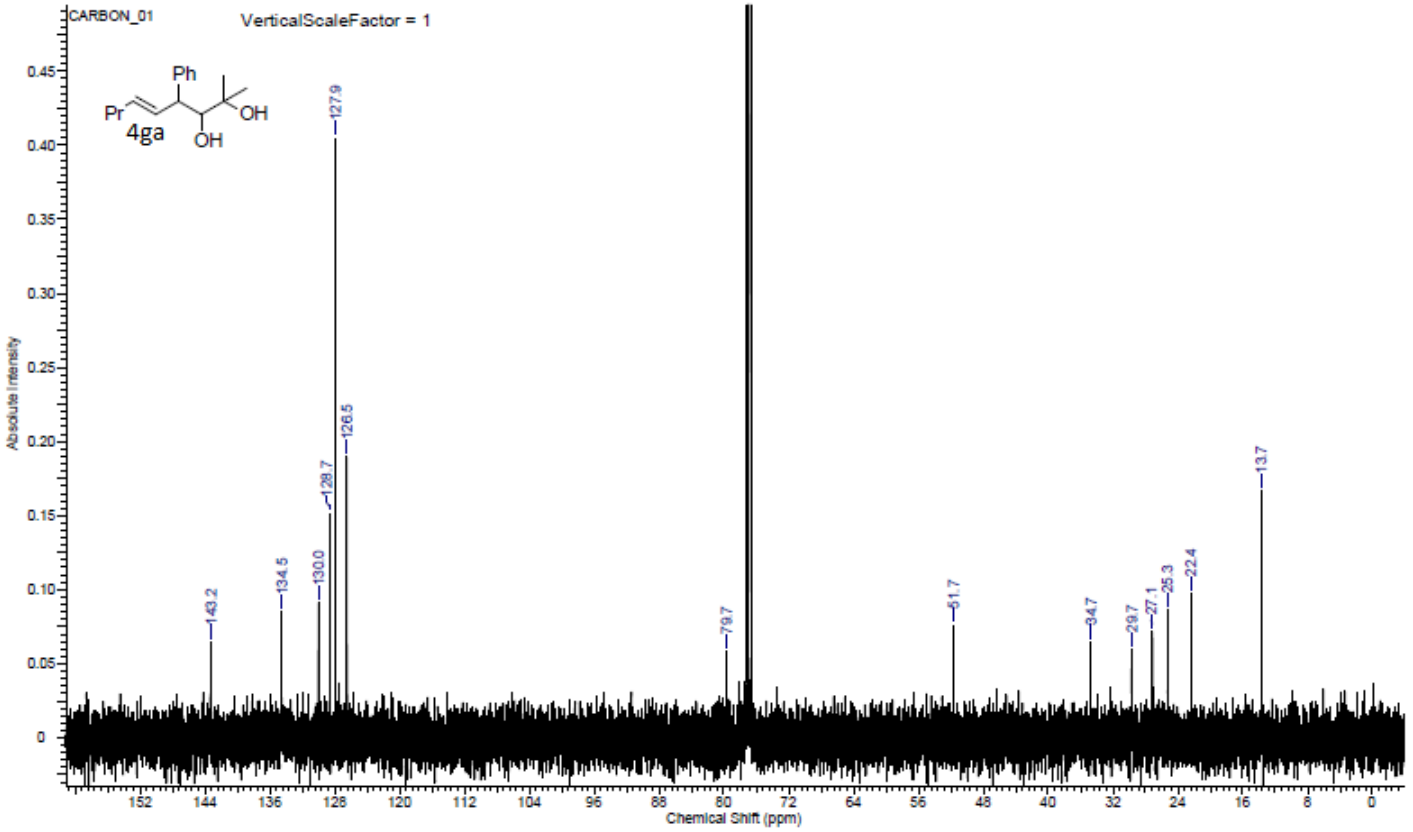
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



Acquisition Time (sec)	2.5559	*Comment*	ERM-ENEP-214-1_3			*Date*	May 26 2016
Date Stamp	May 26 2016	*File Name*	C:\USERS\ERMAN\DESKTOP\WET\ERM-ENEP-214-1_3_20160526_01\PROTON_02.FID\FID				
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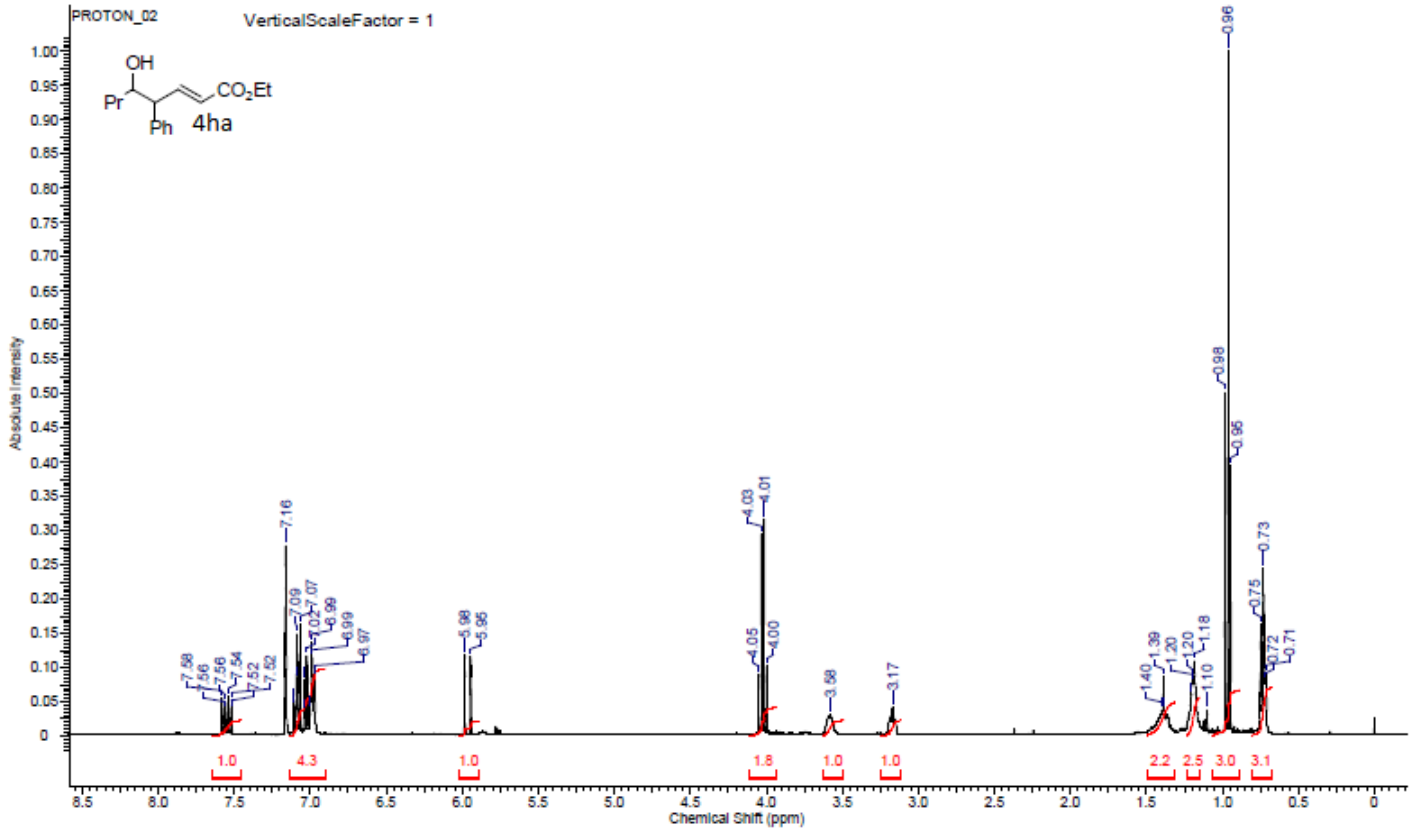
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.1006	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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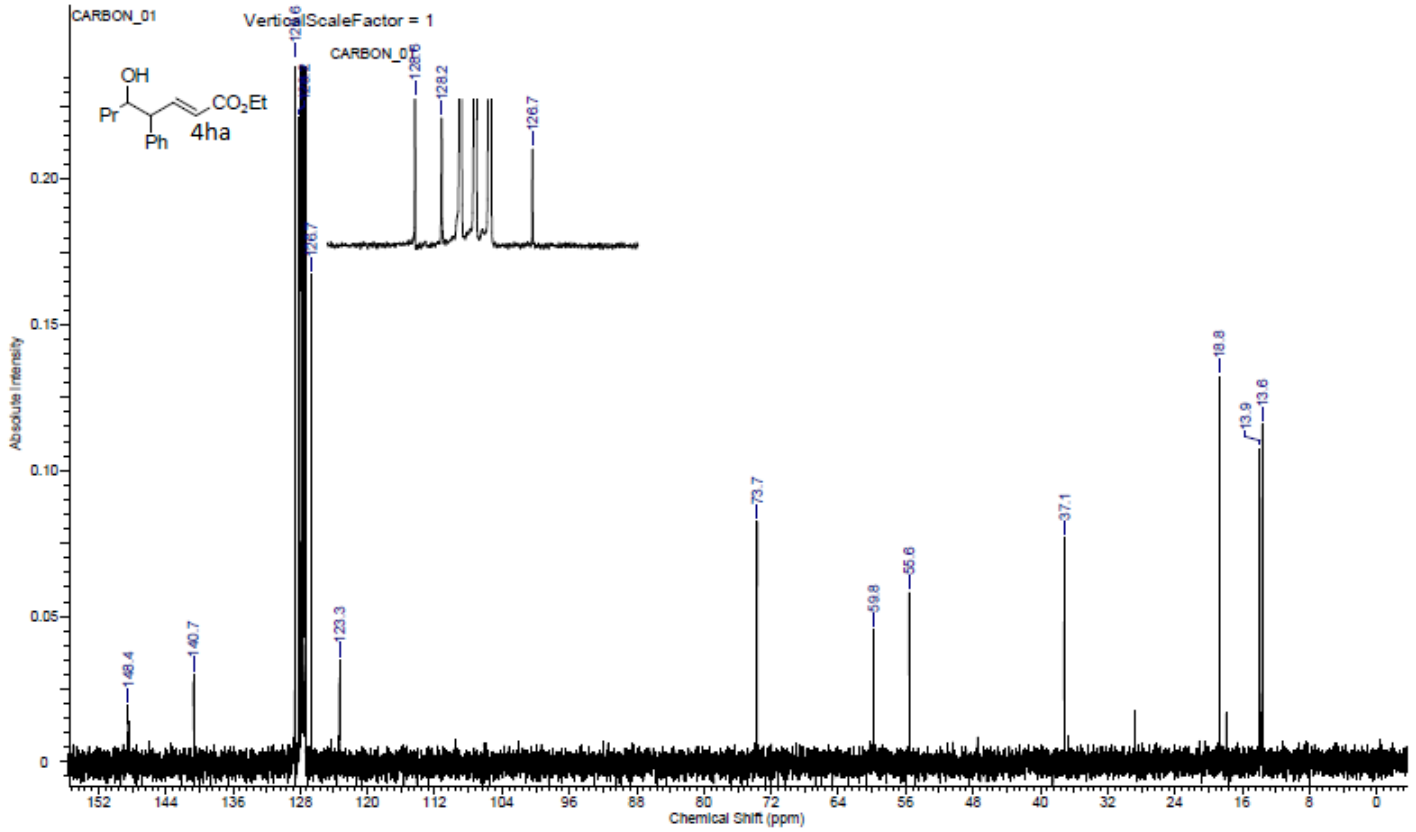
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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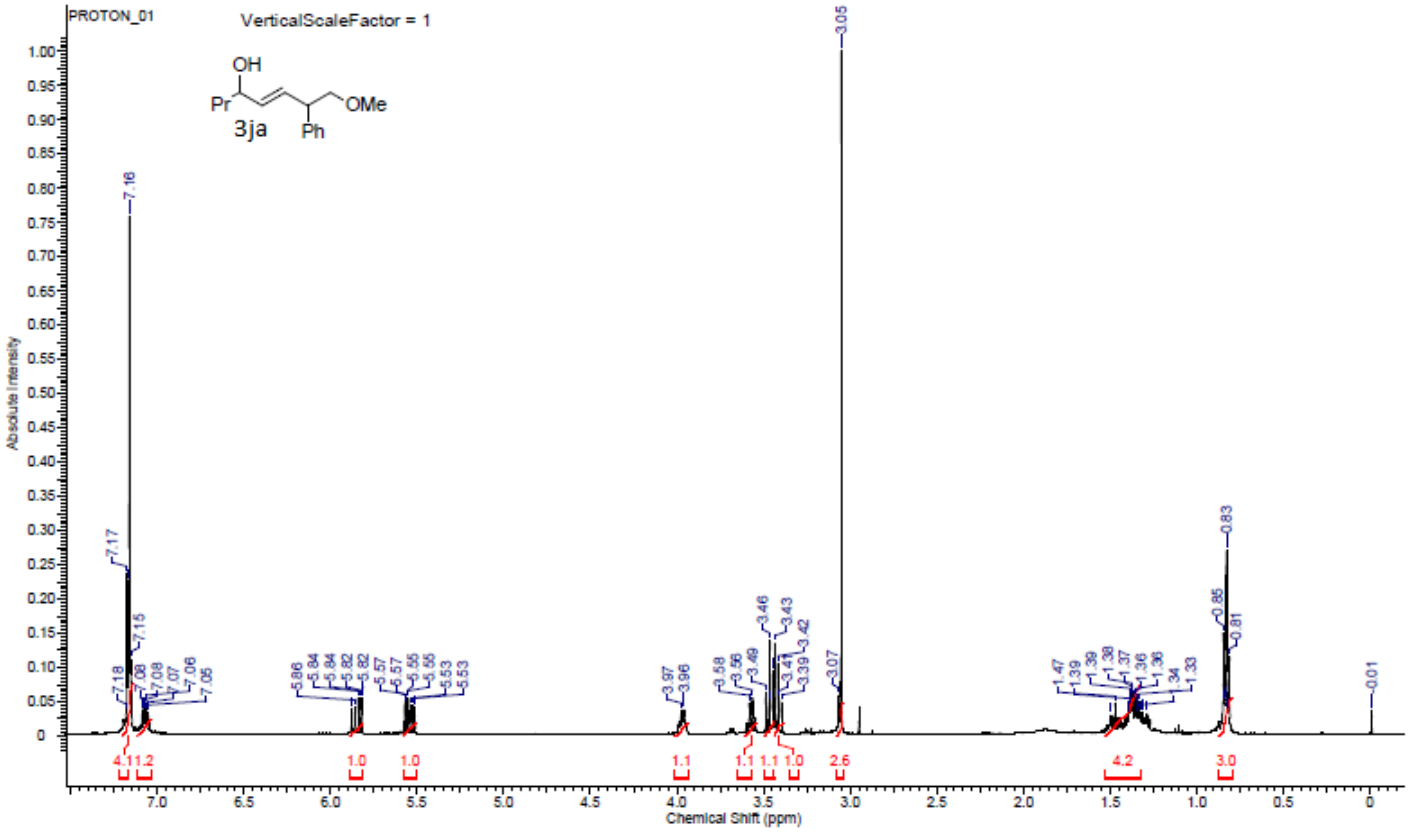
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	52.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2378.0400	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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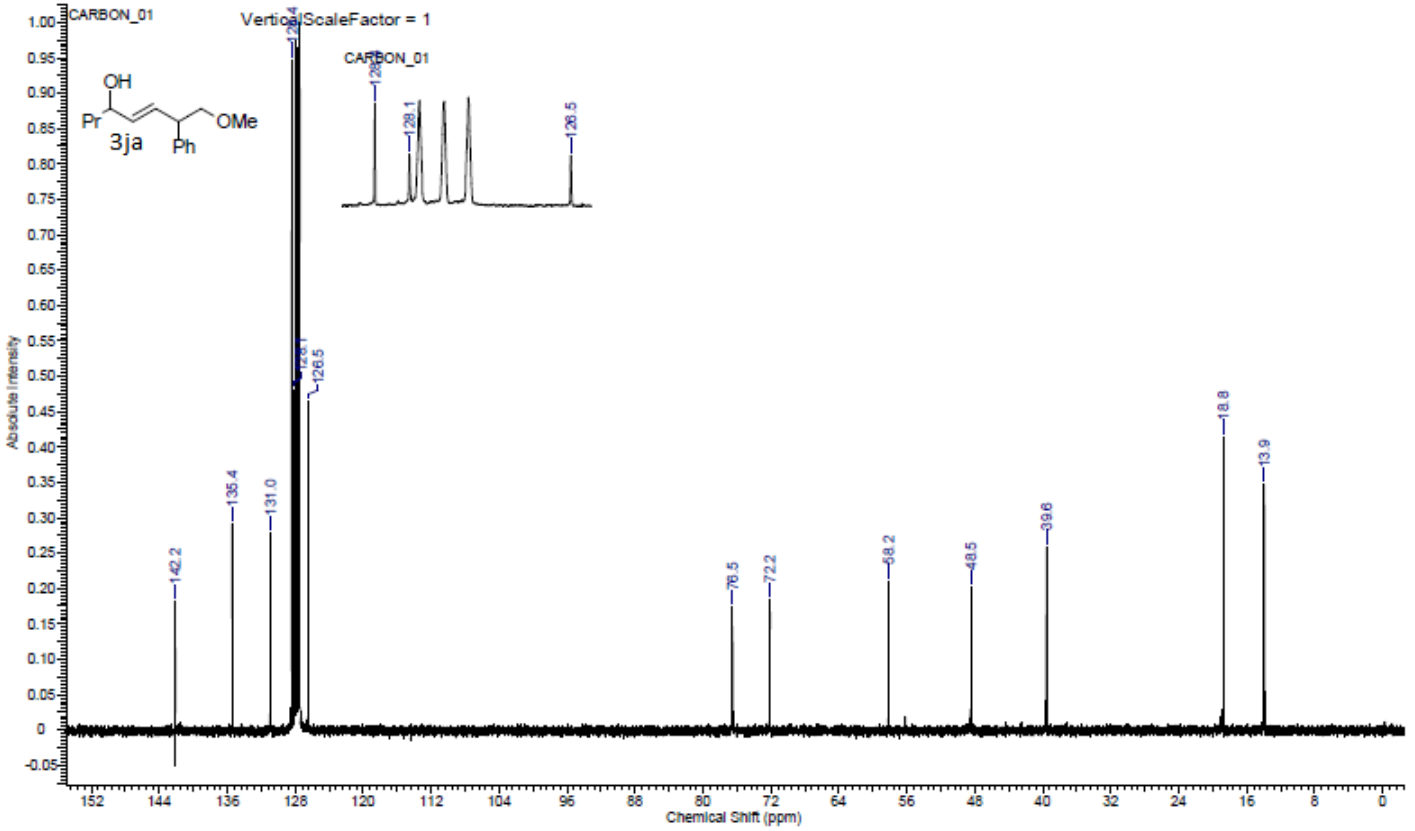
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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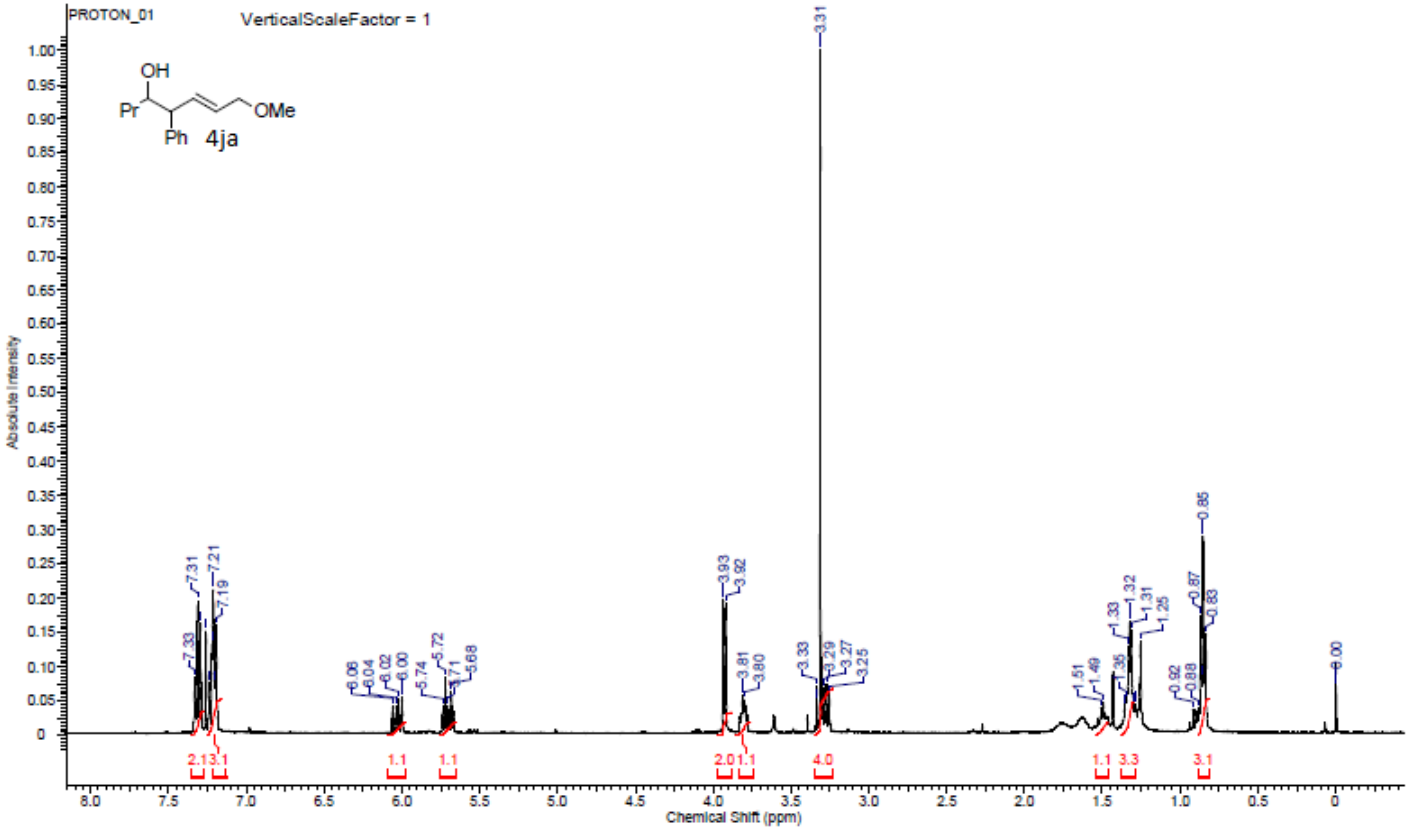
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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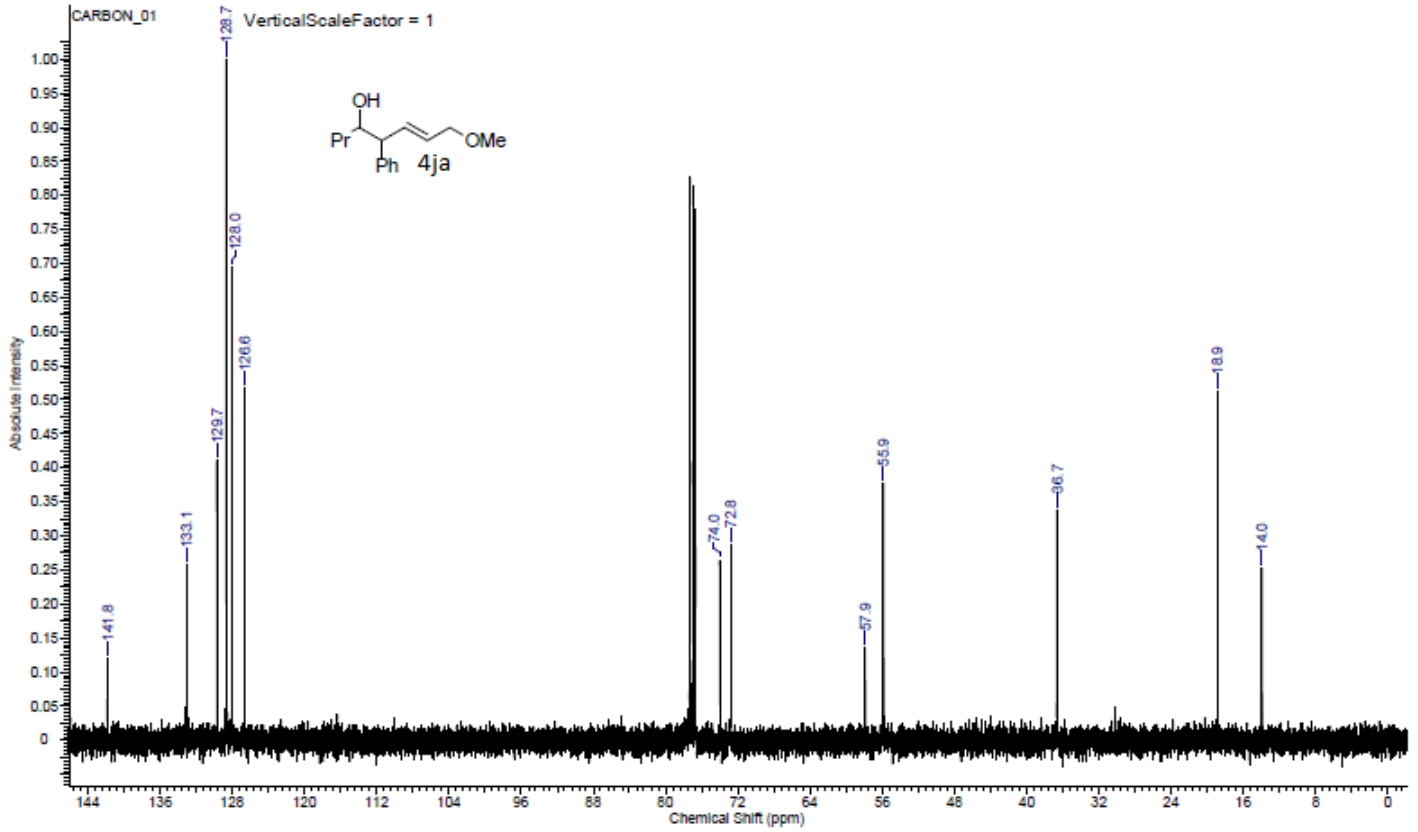
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	50.00	*Solvent*	CHLOROFORM-d
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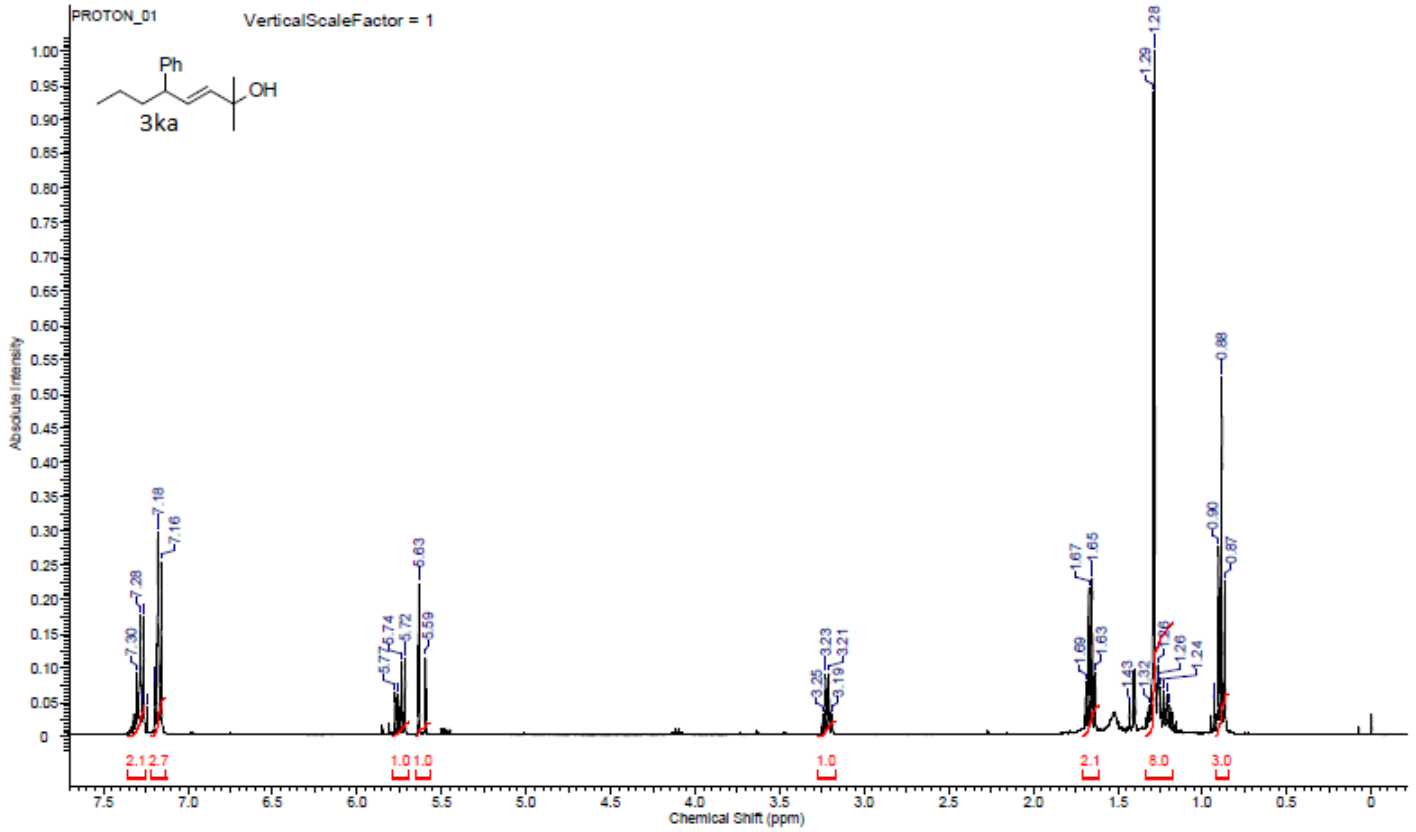

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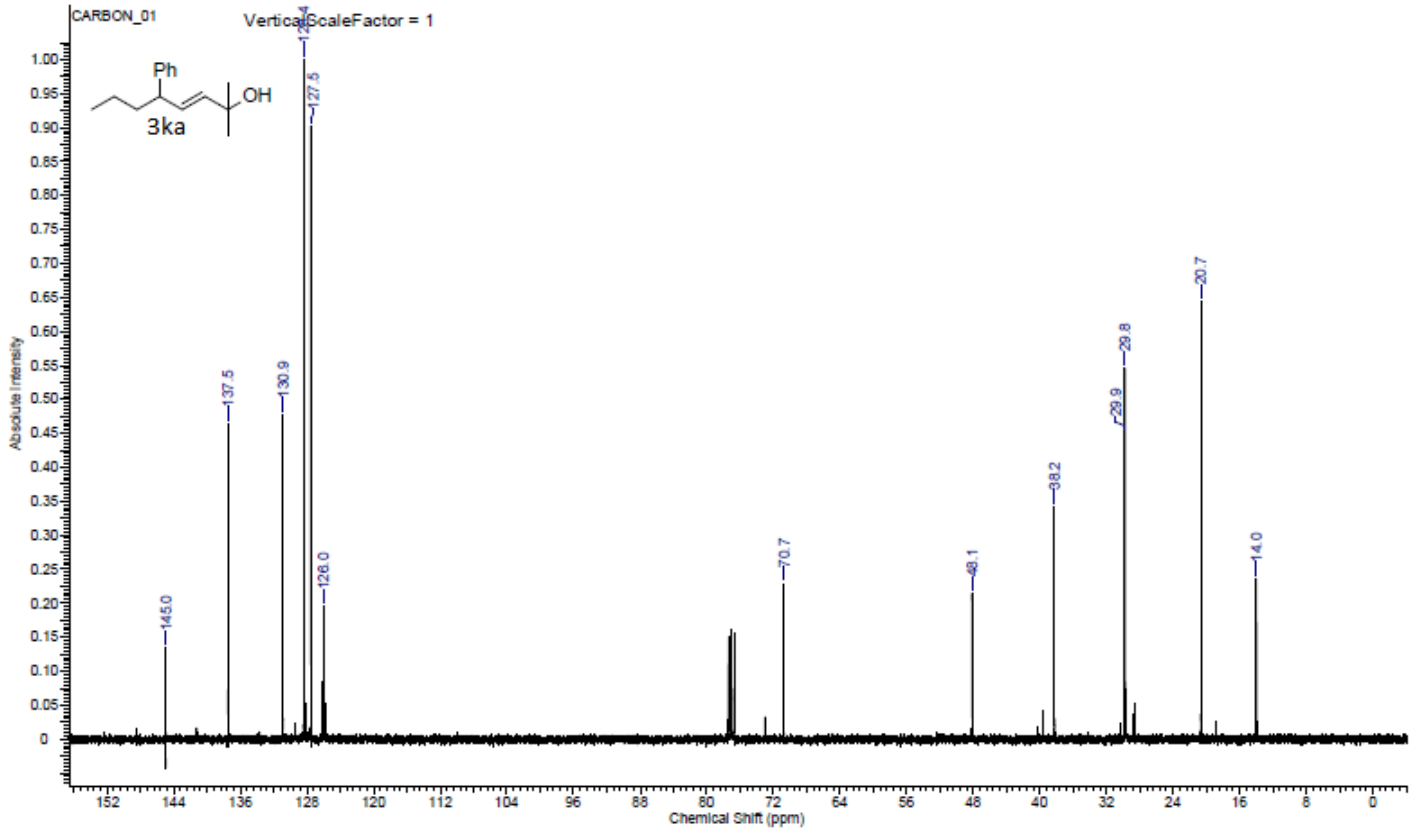
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	256	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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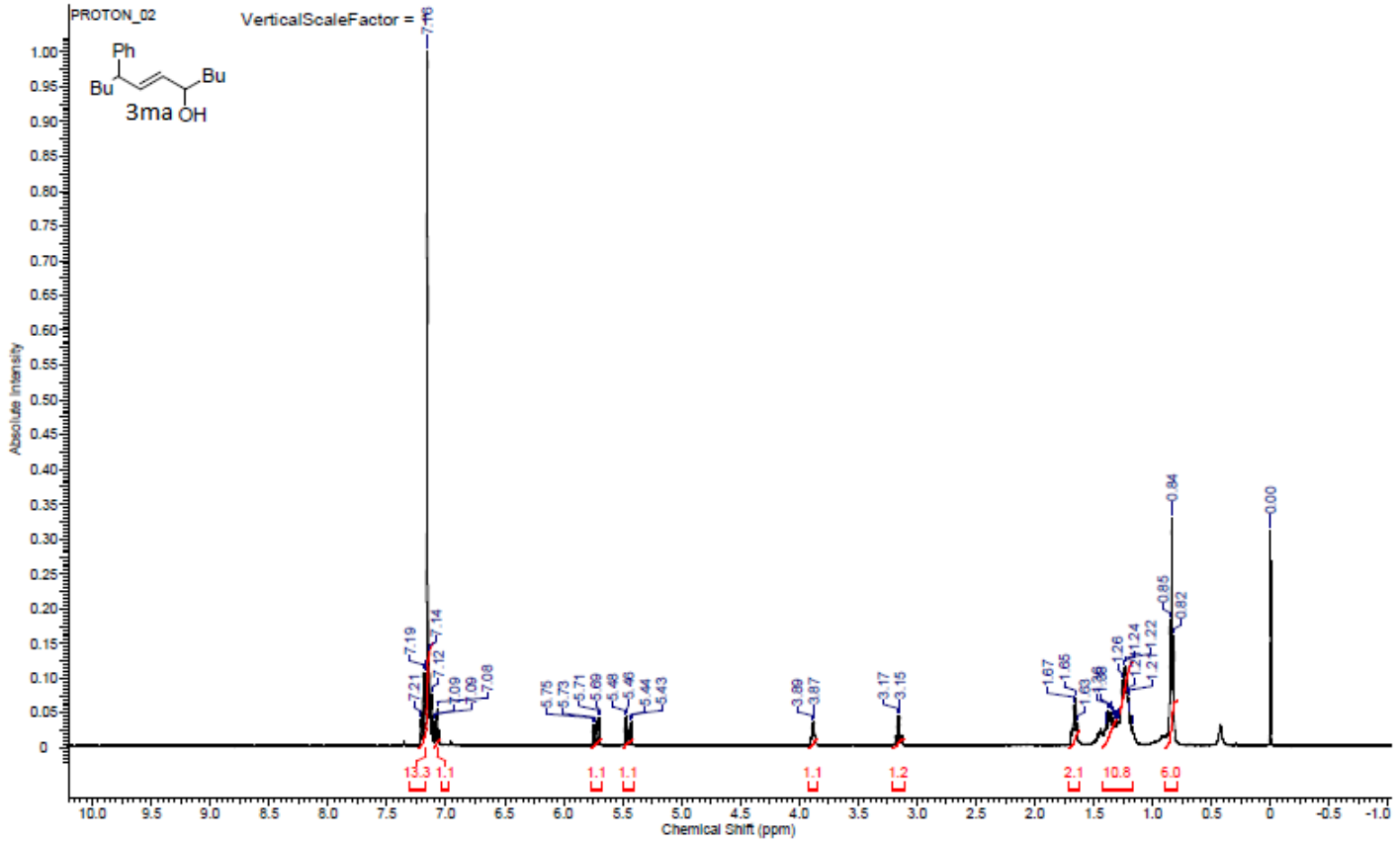
Number of Transients	8	*Original Points Count*	16384	*Points Count*	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00
Solvent	BENZENE-d6	*Spectrum Offset (Hz)*	2417.1006	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



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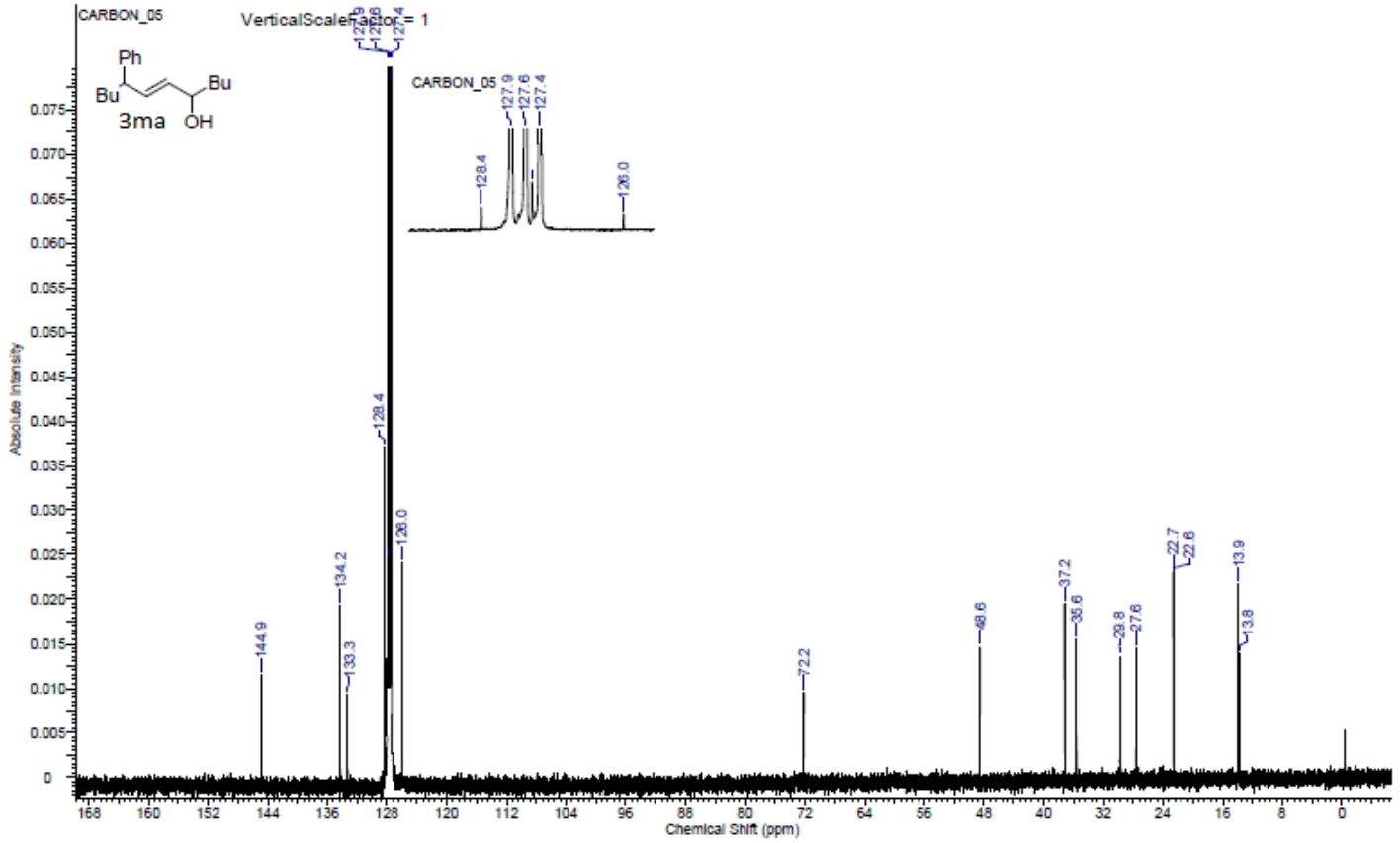

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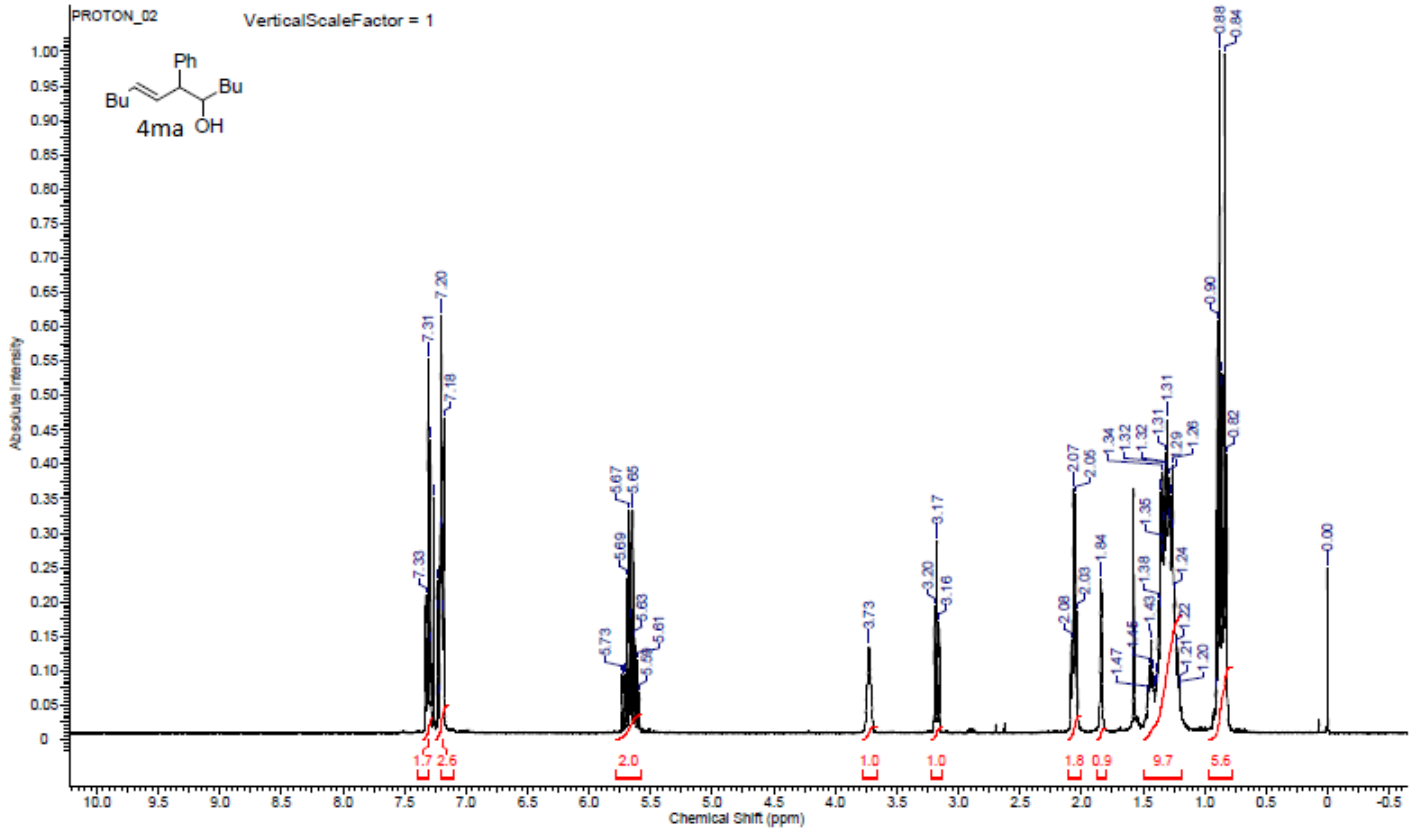
Number of Transients	8	*Original Points Count*	16384	*Points Count*	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26
Temperature (degree C)	25.000								



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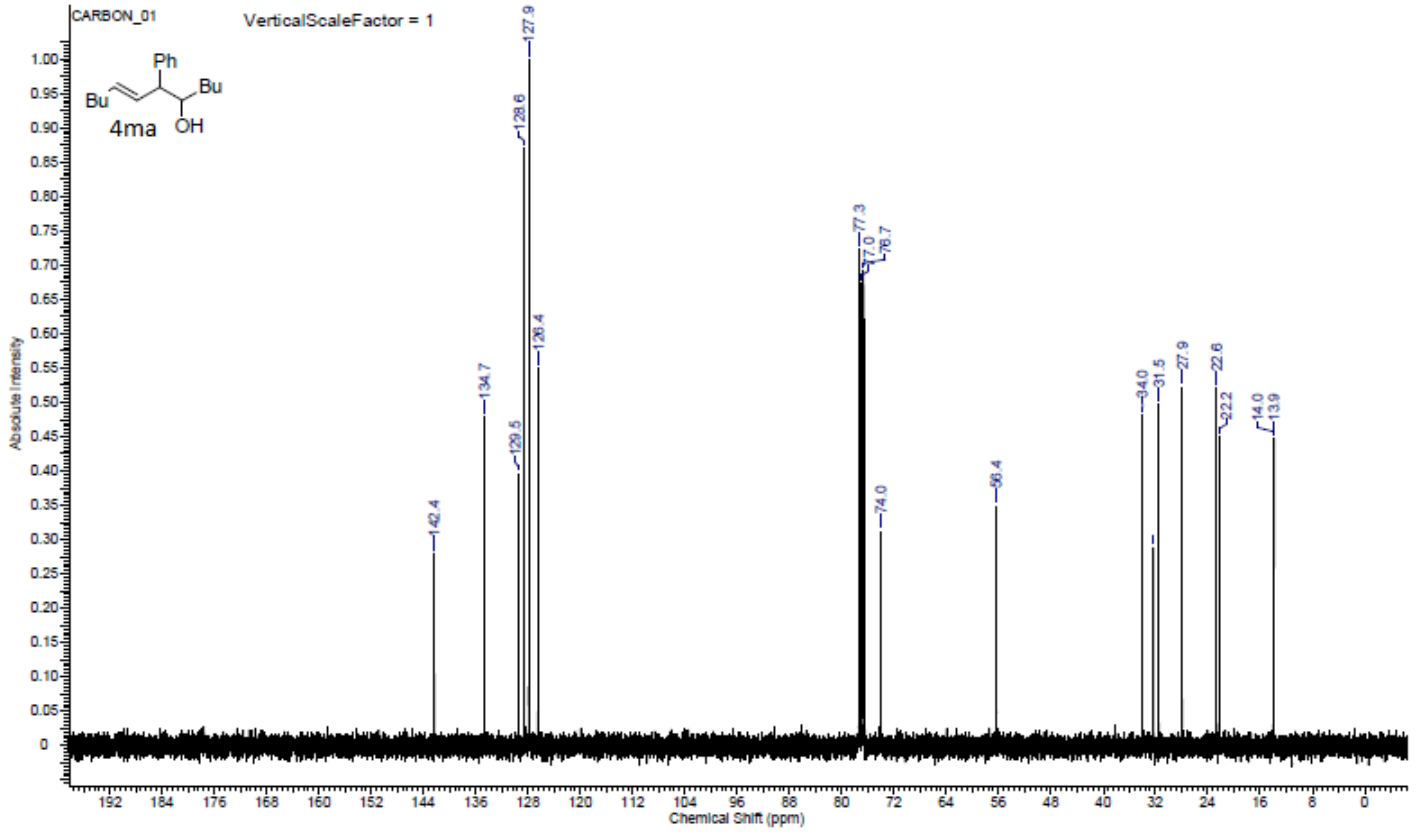
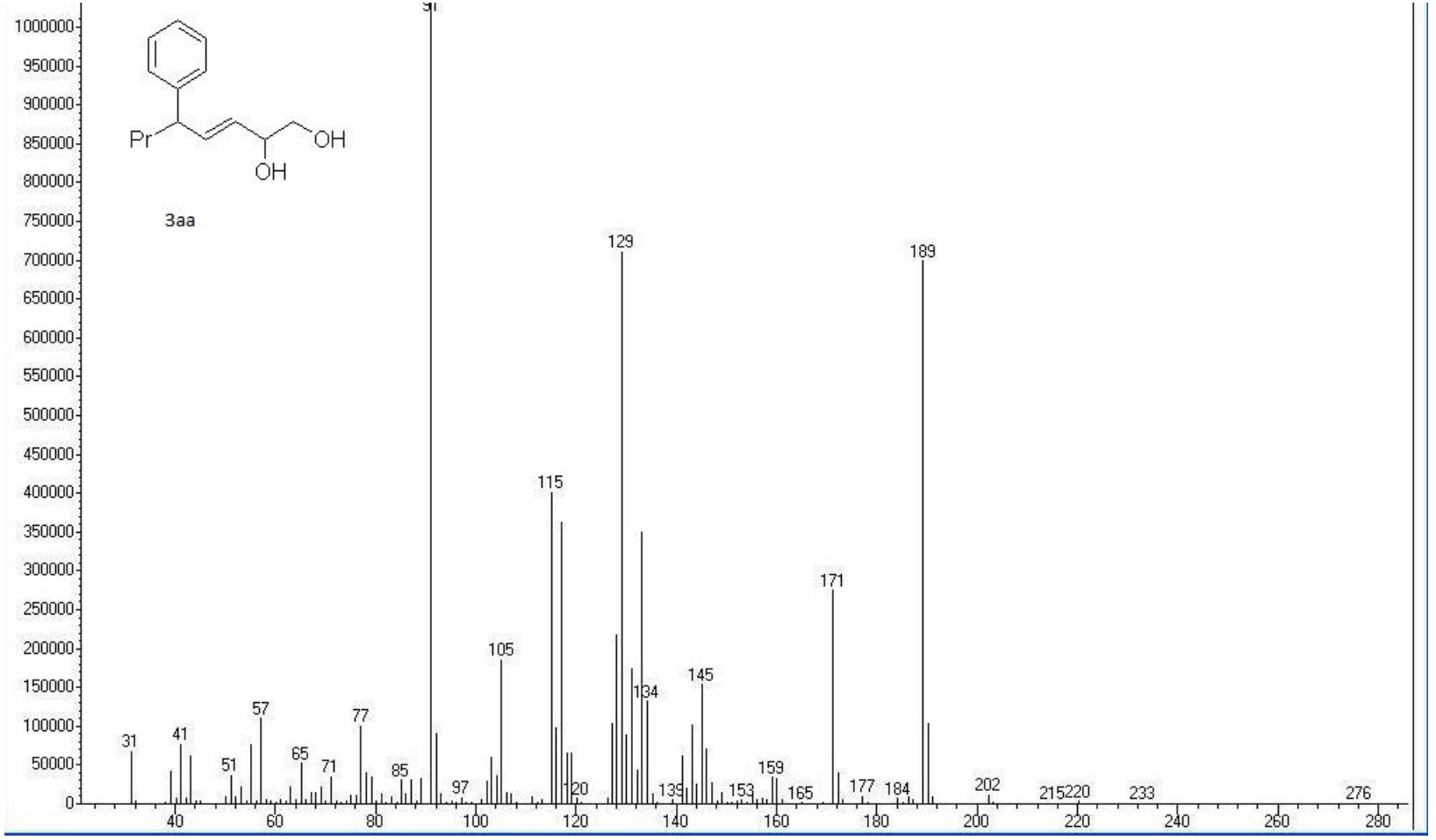
File Name	F:\ERM-ENEP-224-1_1_20160718_01\CARBON_01.FID\FID					*Frequency (MHz)*	100.57	*Nucleus*	13C
Number of Transients	512	*Original Points Count*	32768	*Points Count*	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	11061.5371	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00
Temperature (degree C)	25.000								



APPENDIX C

MASS SPECTRUMS OF PRODUCTS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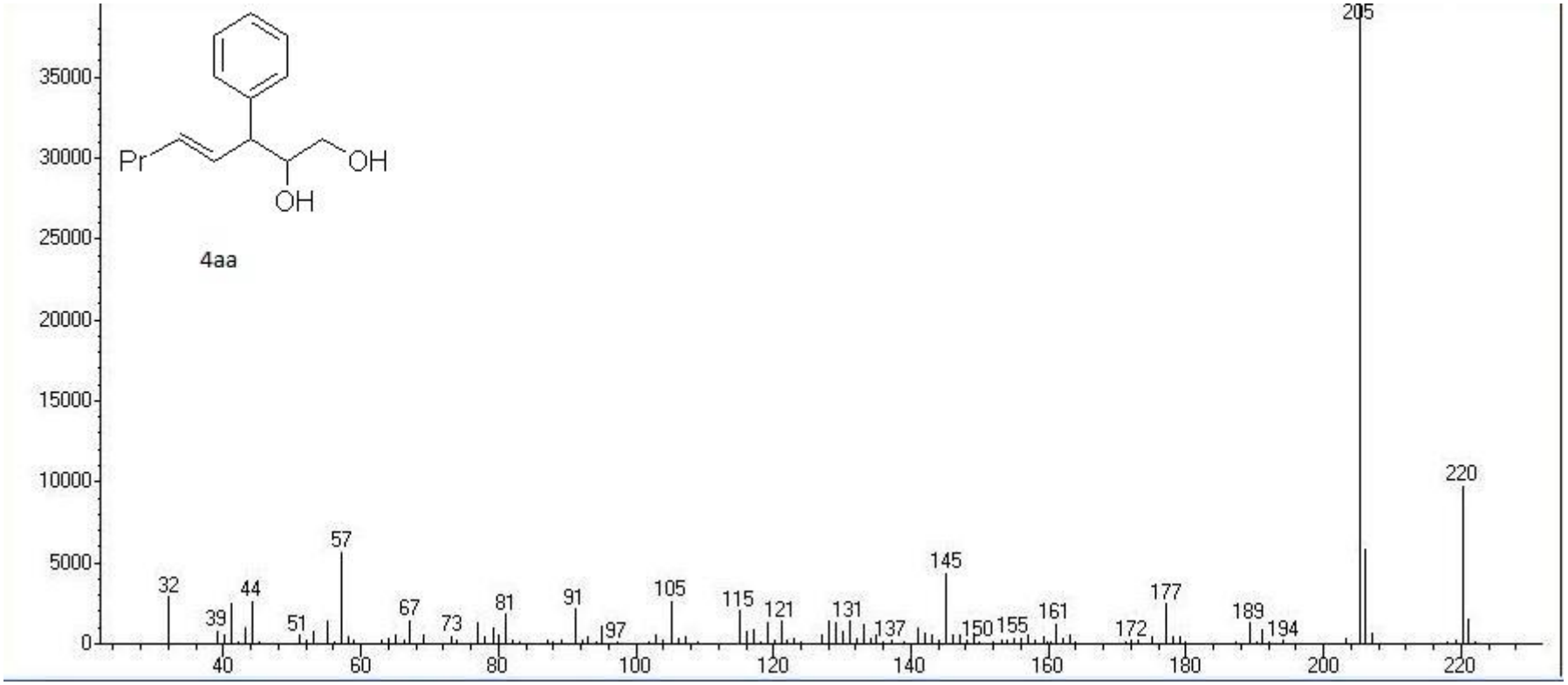
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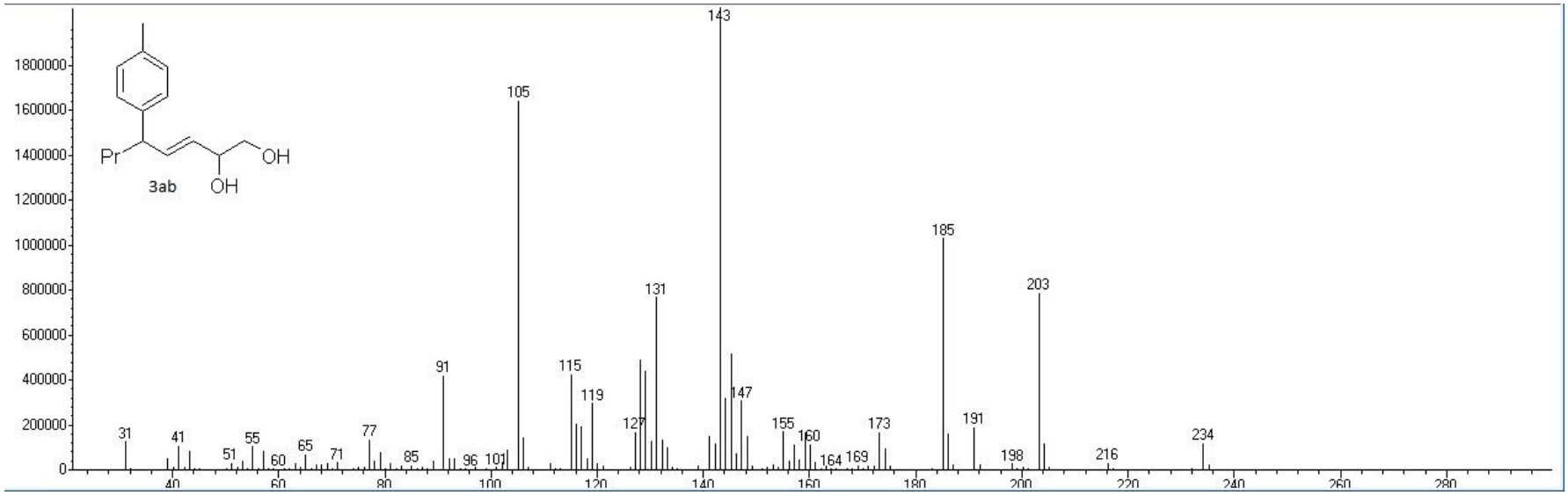
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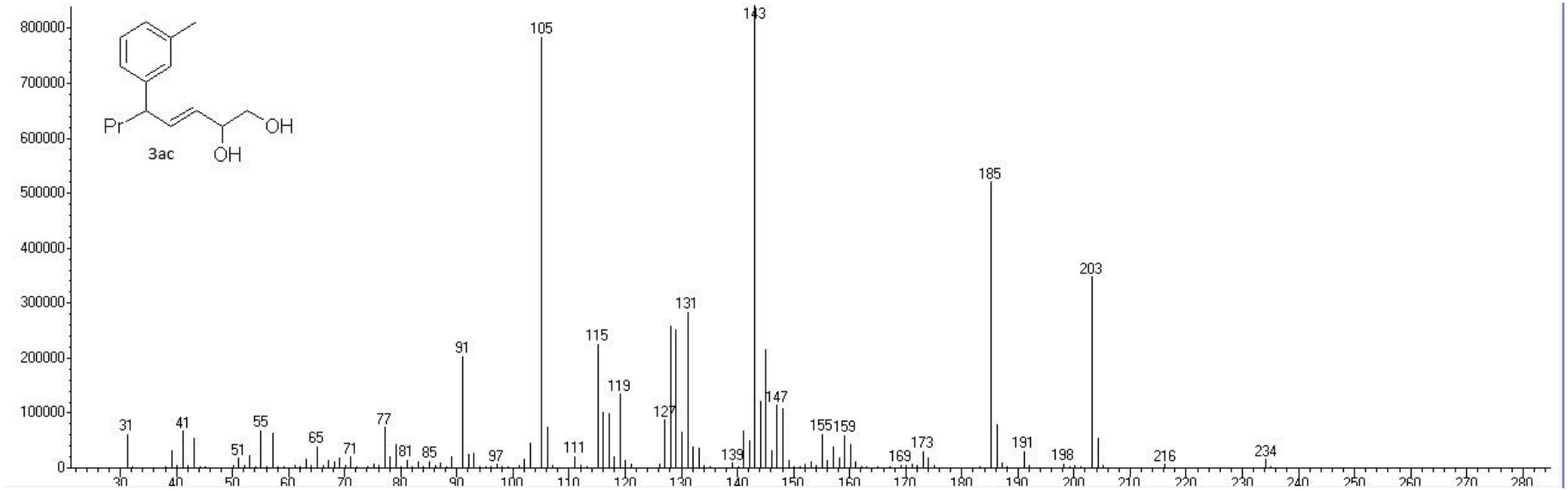
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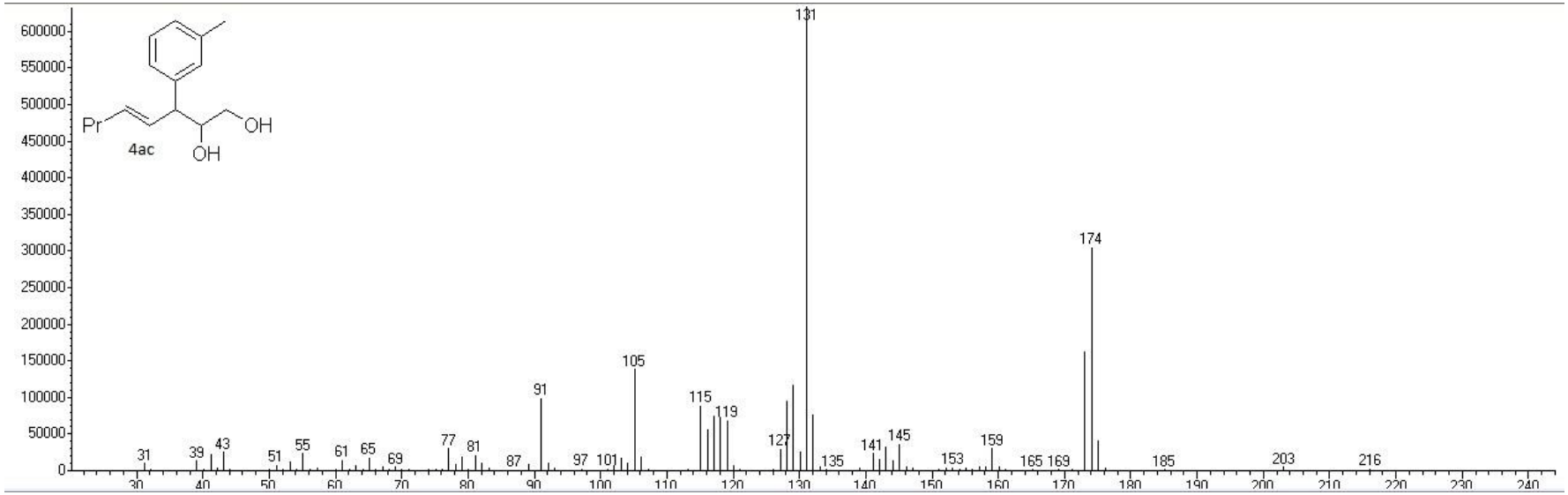
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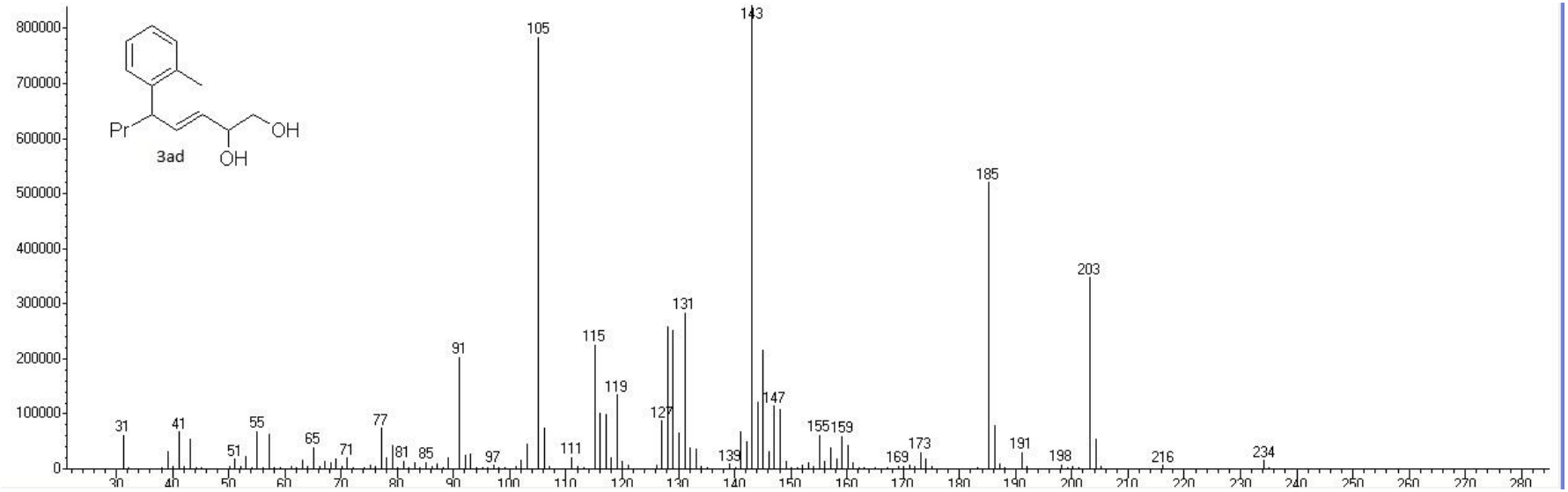
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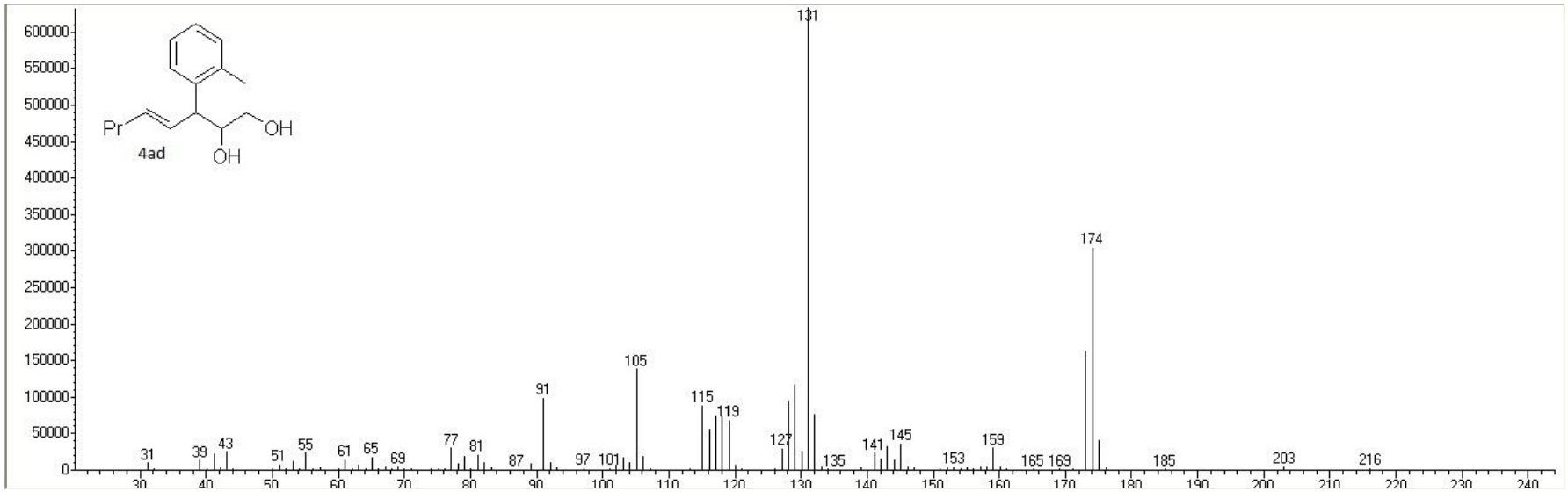
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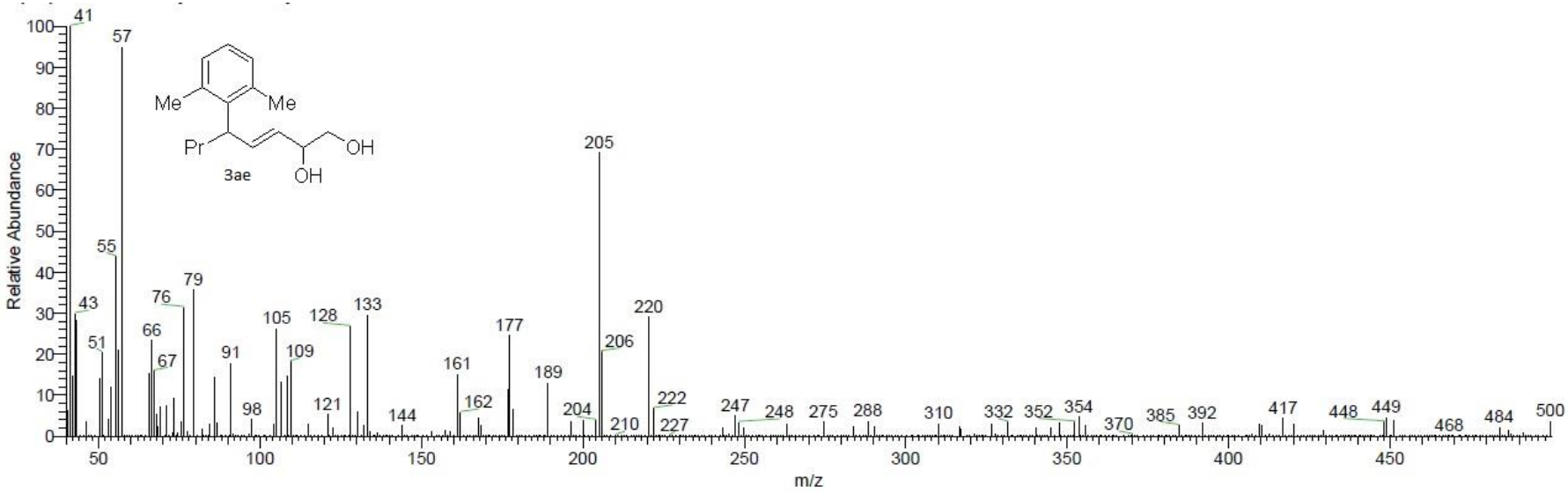
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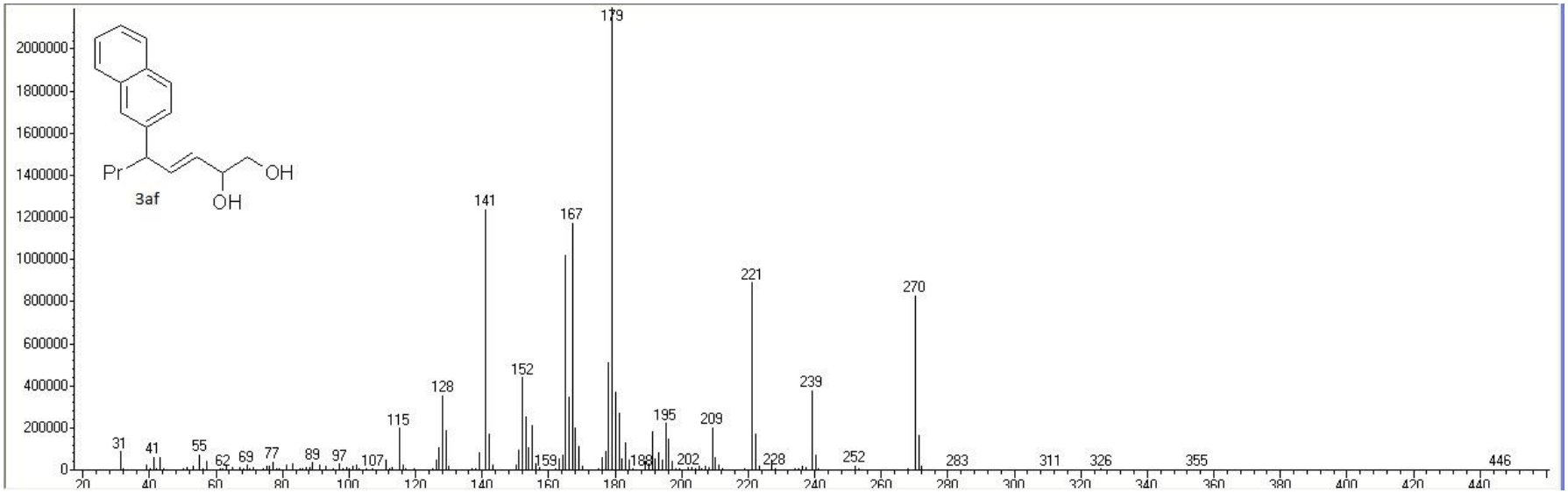
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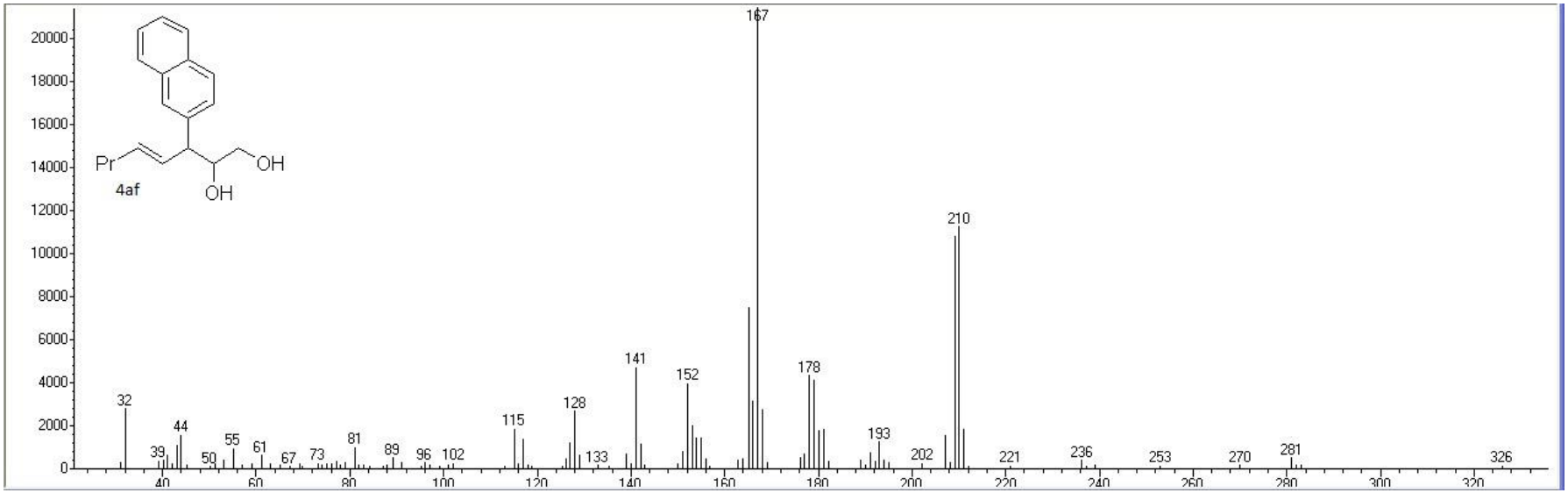
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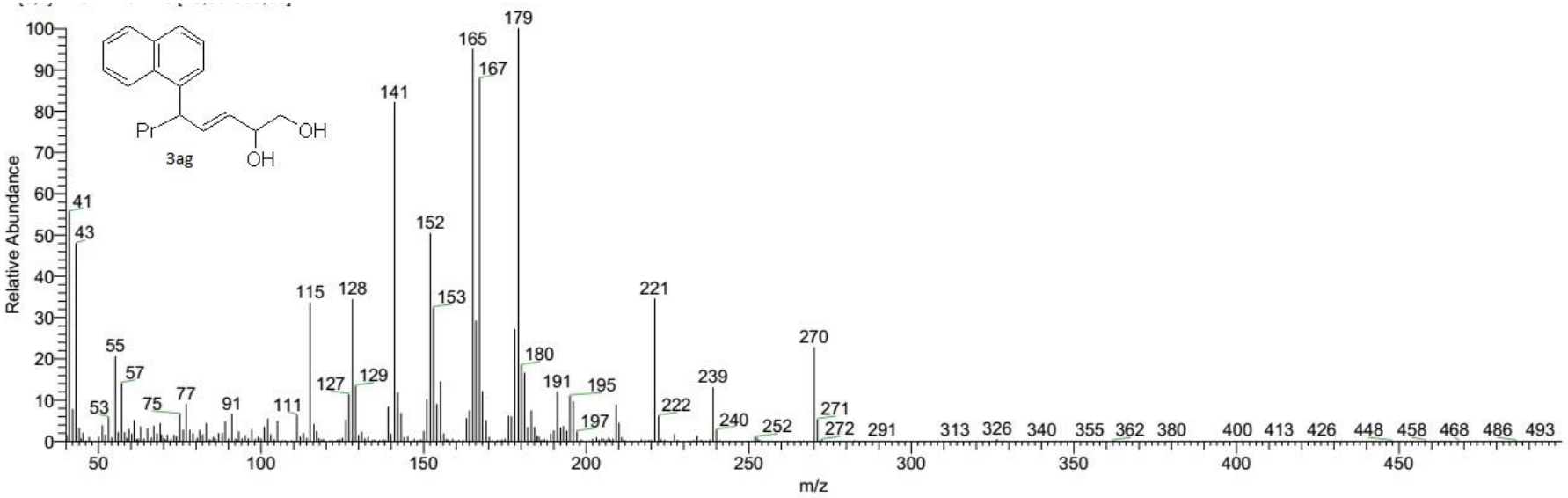
Relative Abundance
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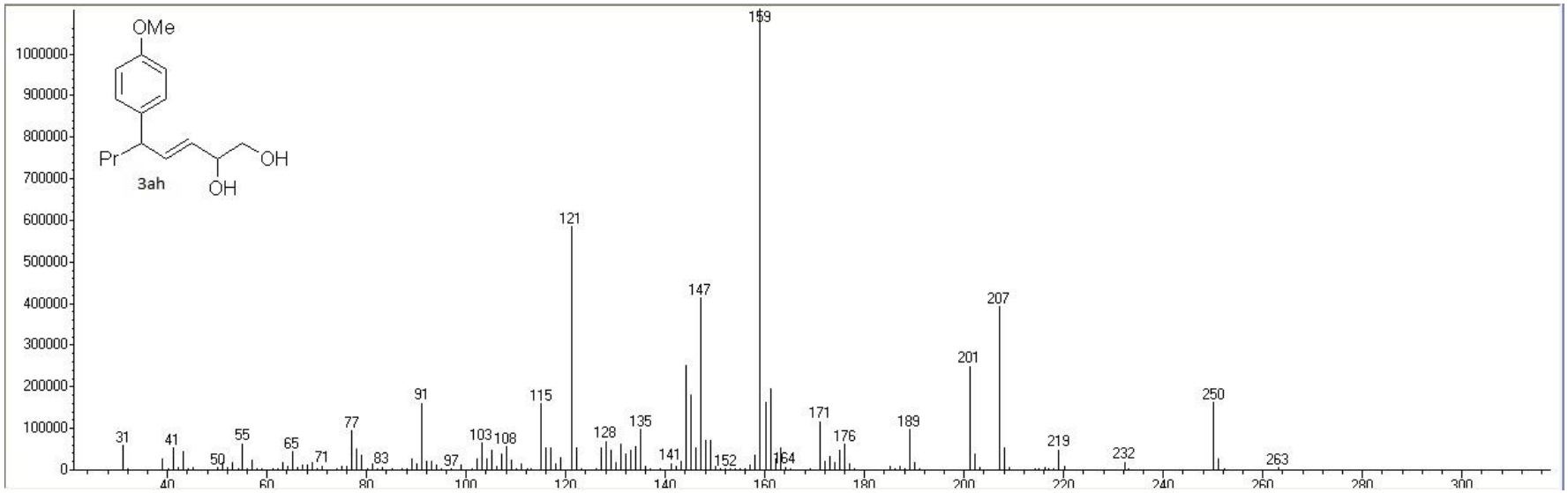
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OH
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152
164
176
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800000
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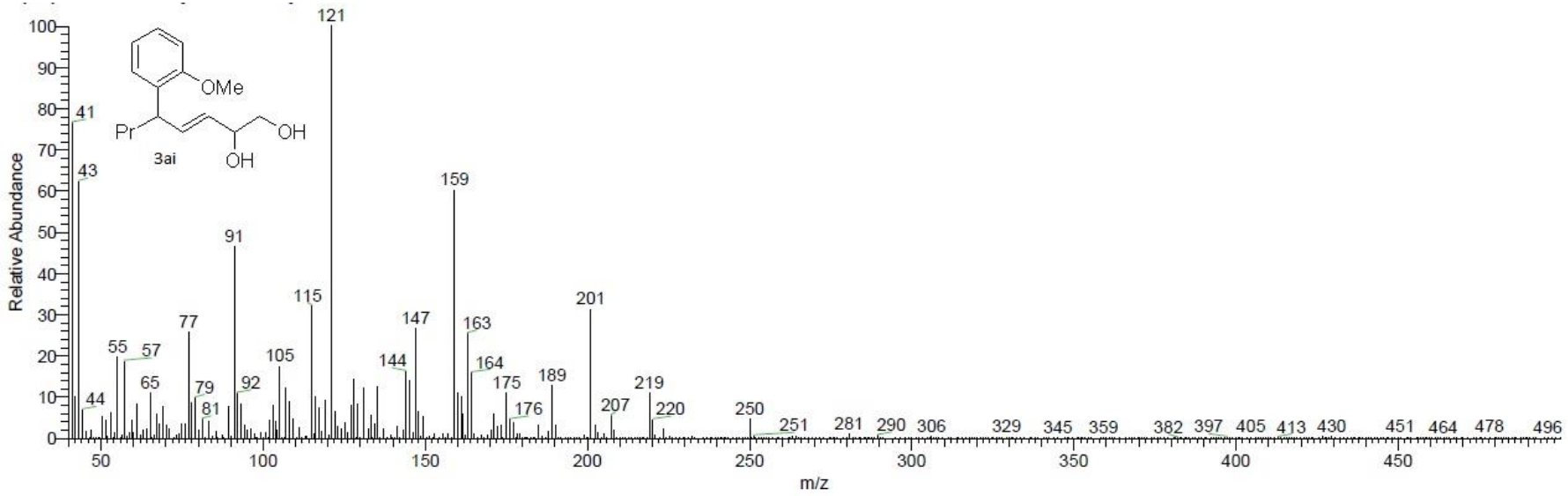
Relative Abundance
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Pr
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OH
3ai
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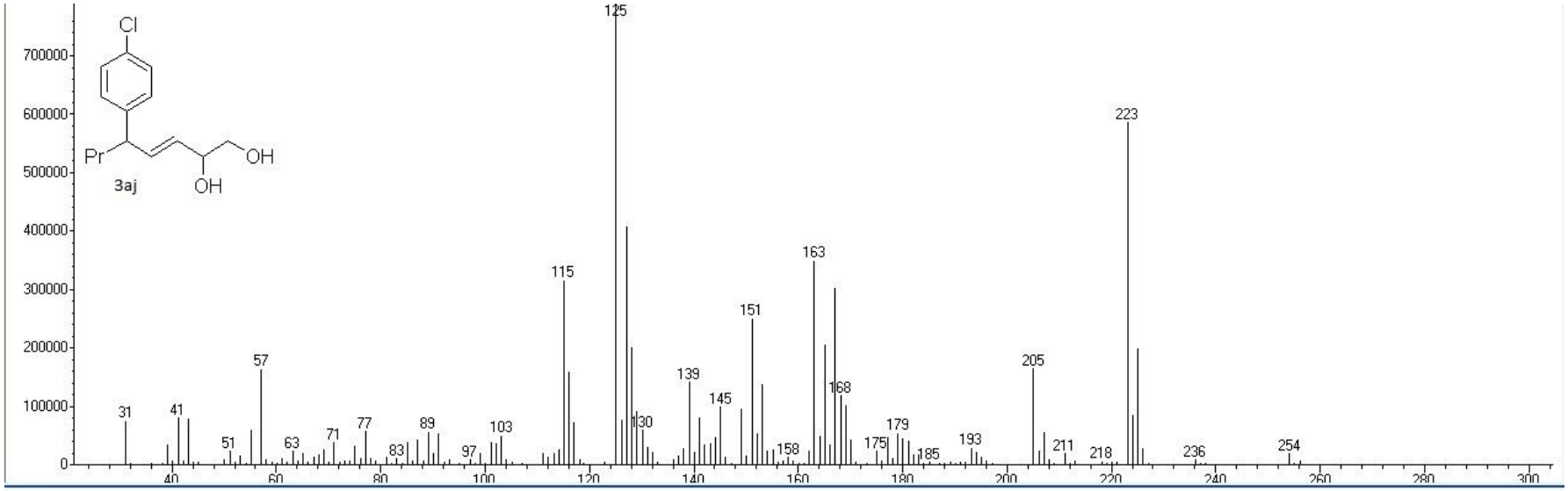
Cl
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OH
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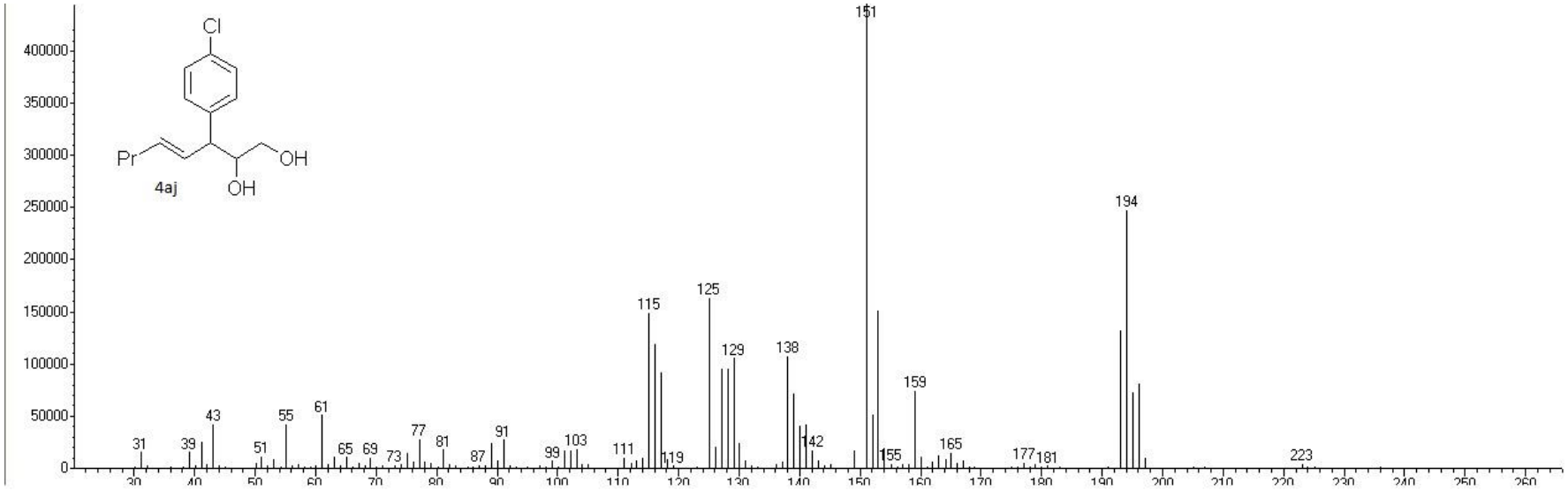
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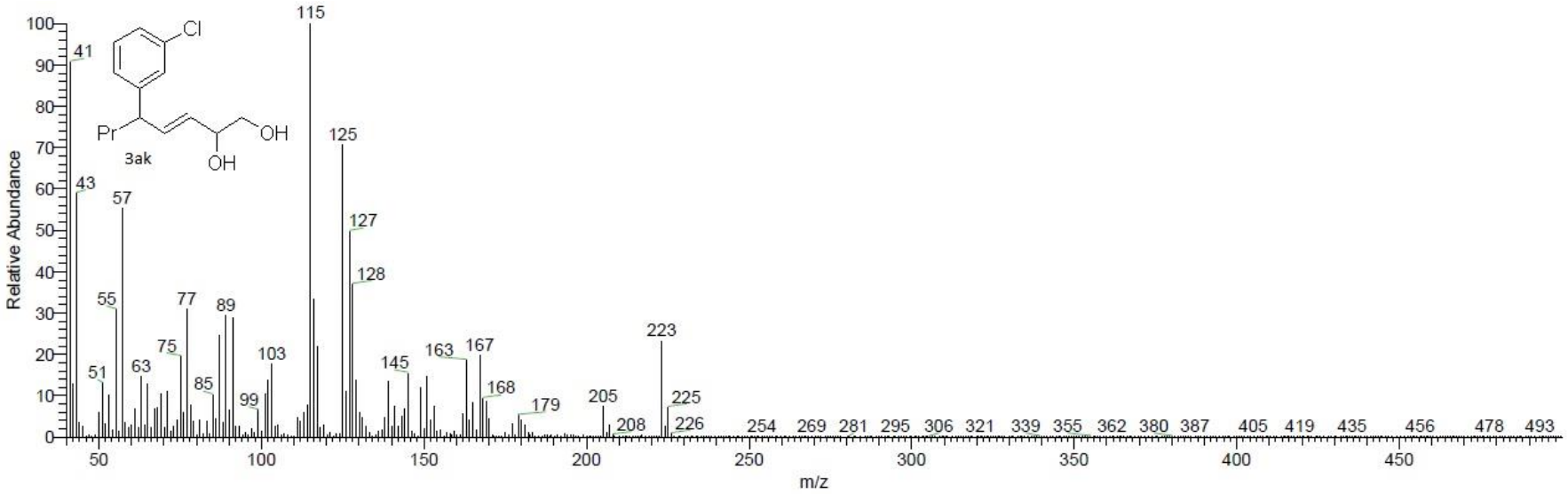
Relative Abundance
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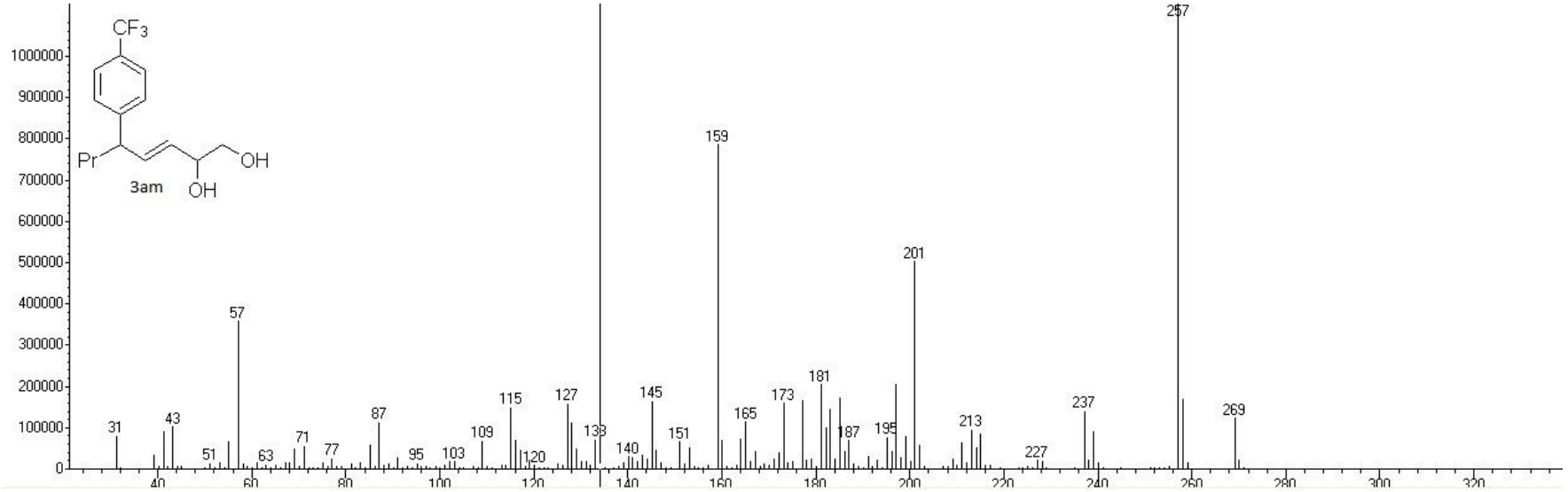
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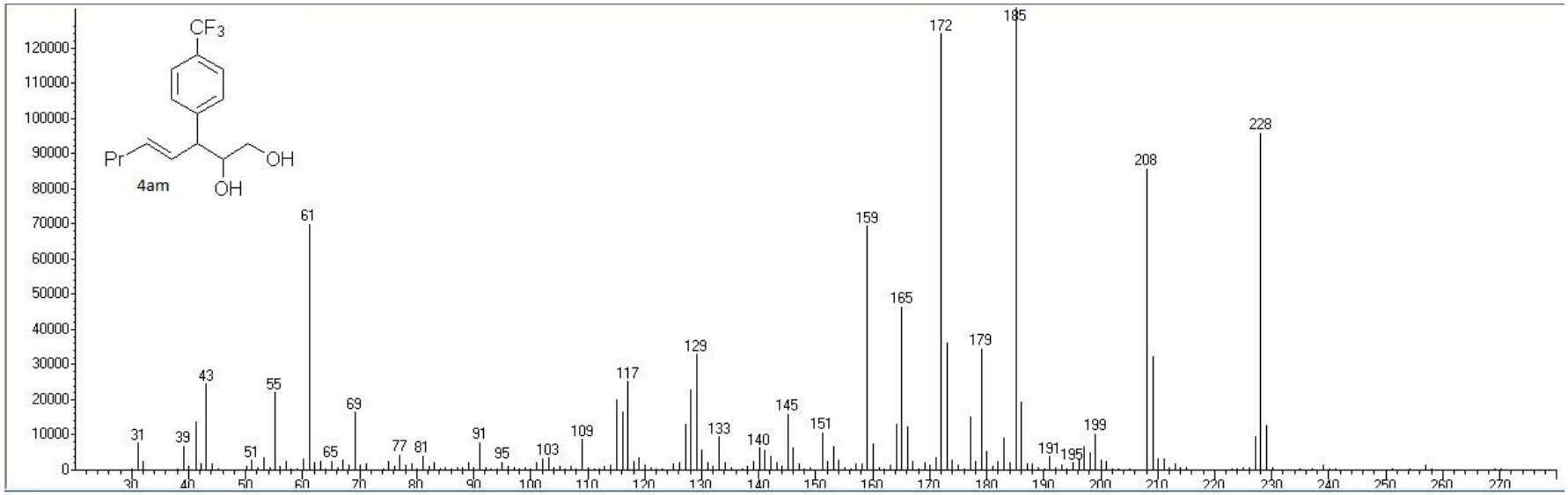
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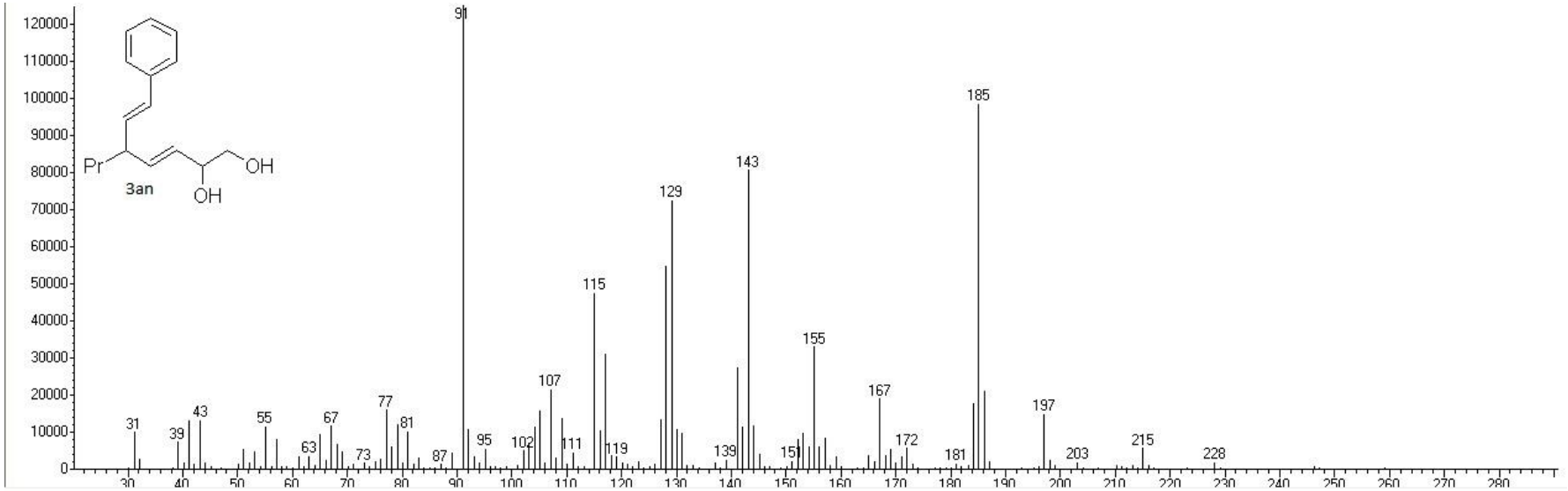
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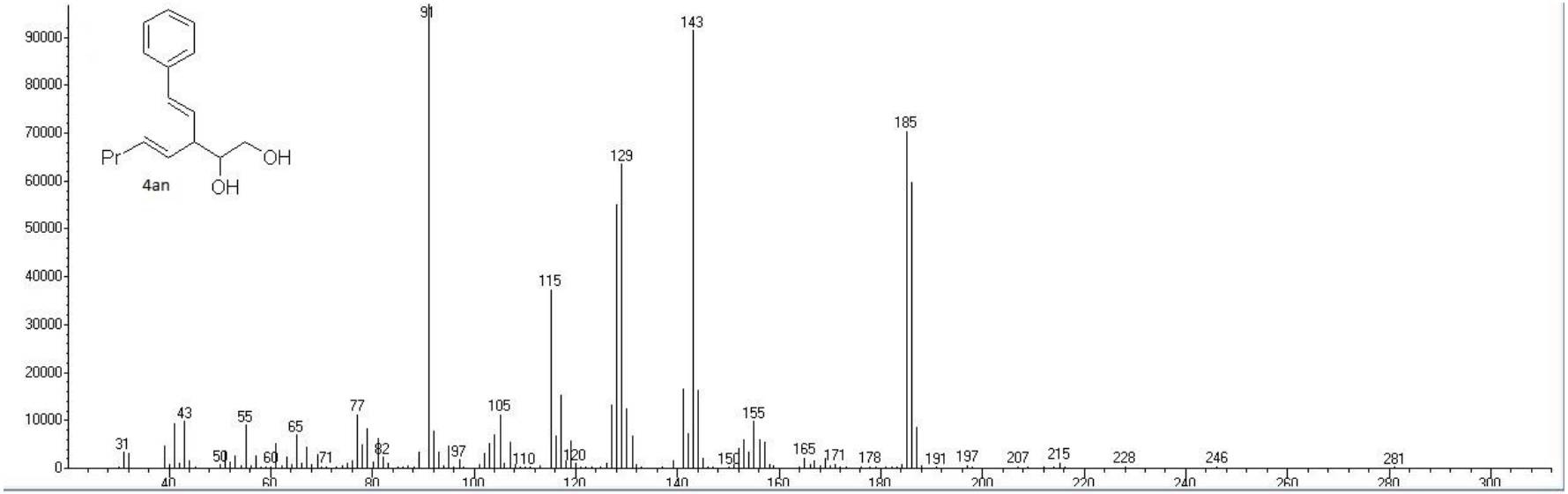
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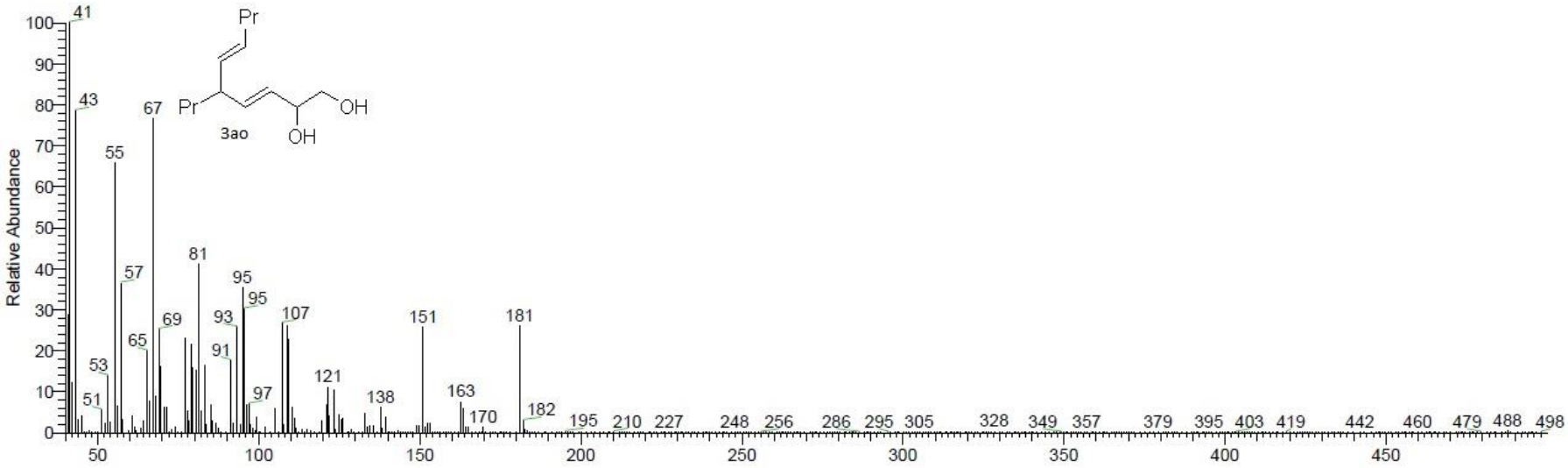
Relative Abundance
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Pr
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OH
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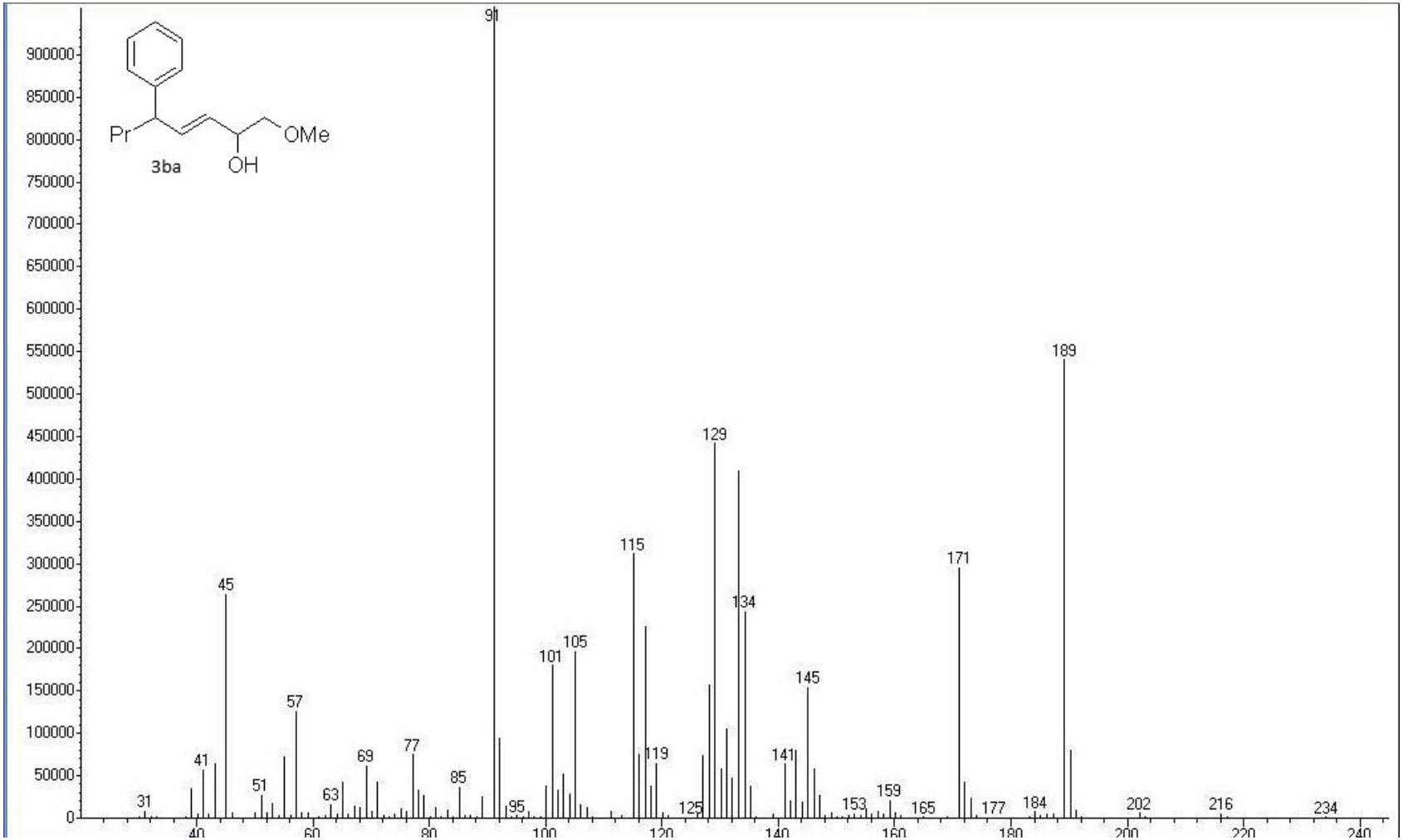
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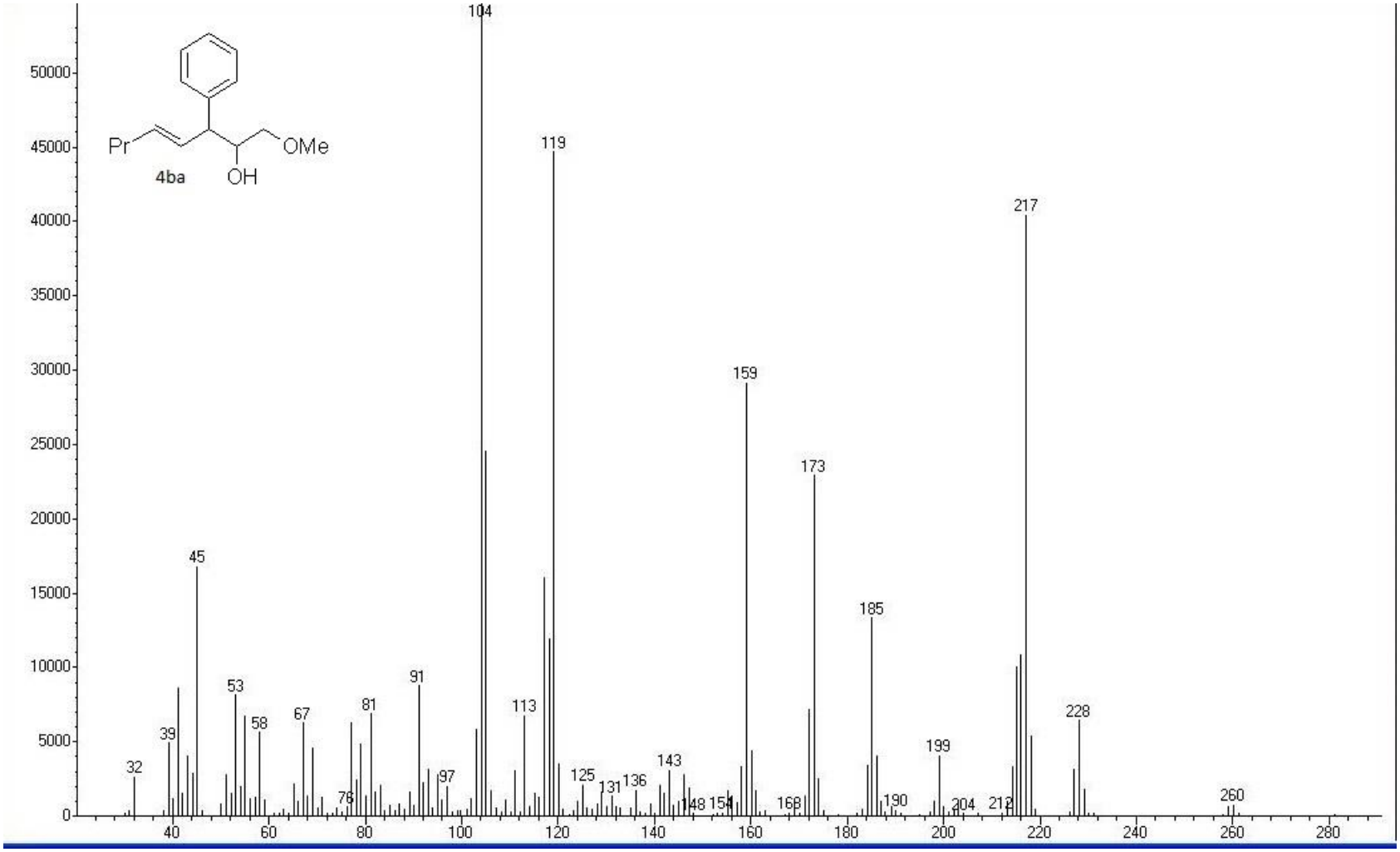
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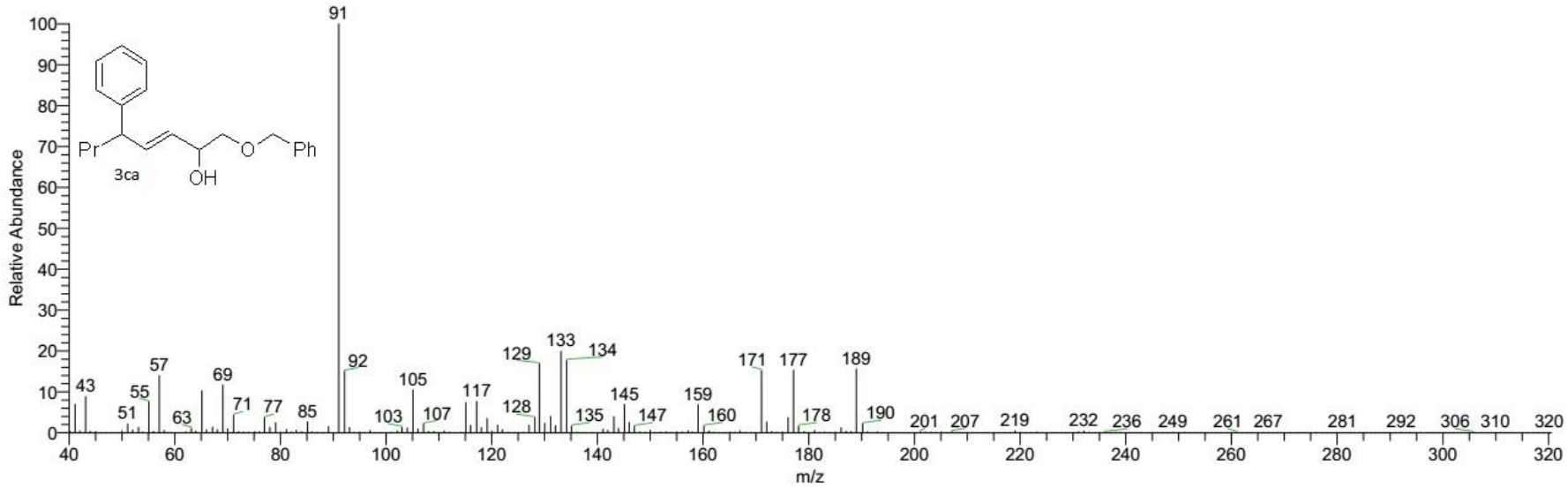
Relative Abundance
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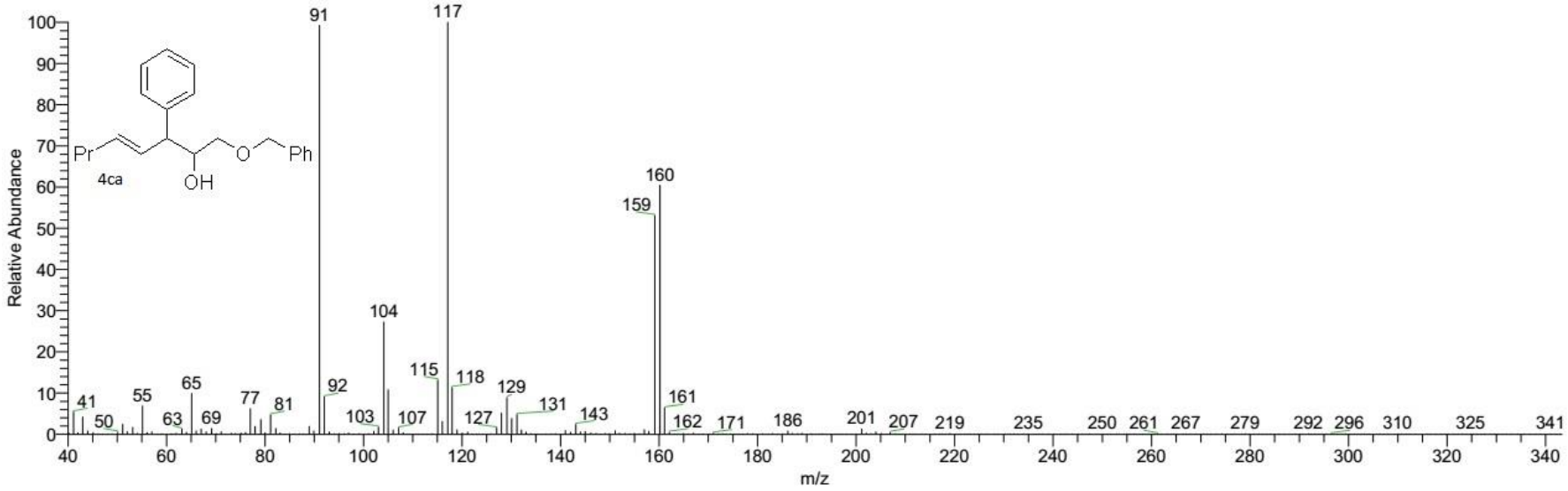
Relative Abundance
m/z
Pr
Ph
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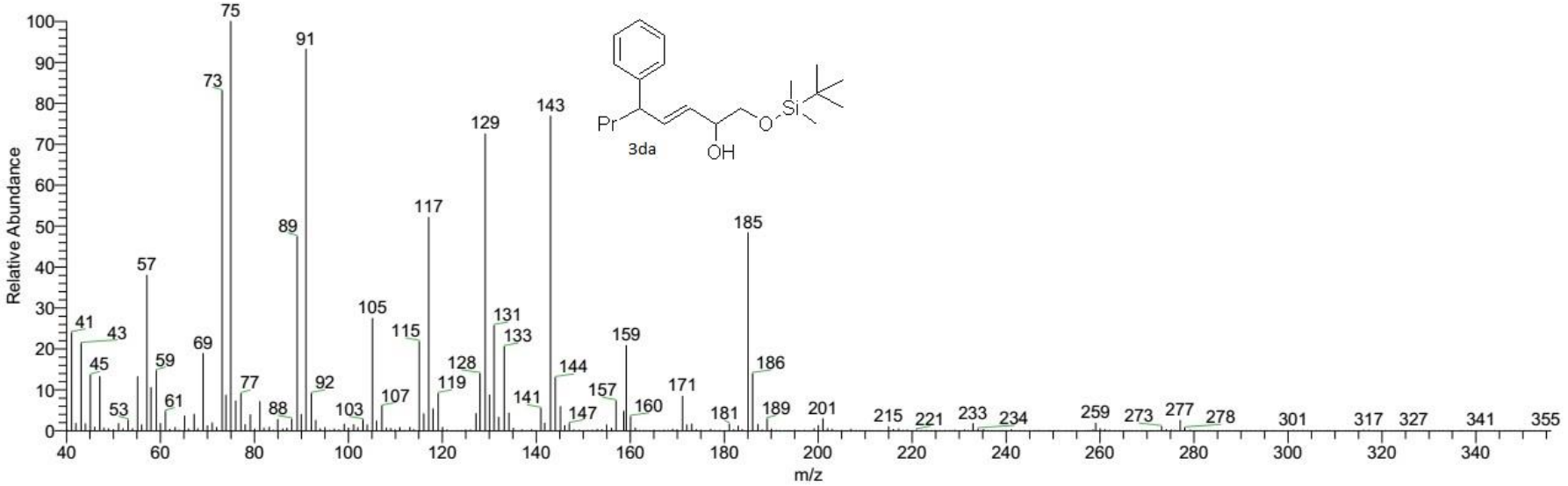
Relative Abundance
m/z
Pr
OH
O
Si
3da
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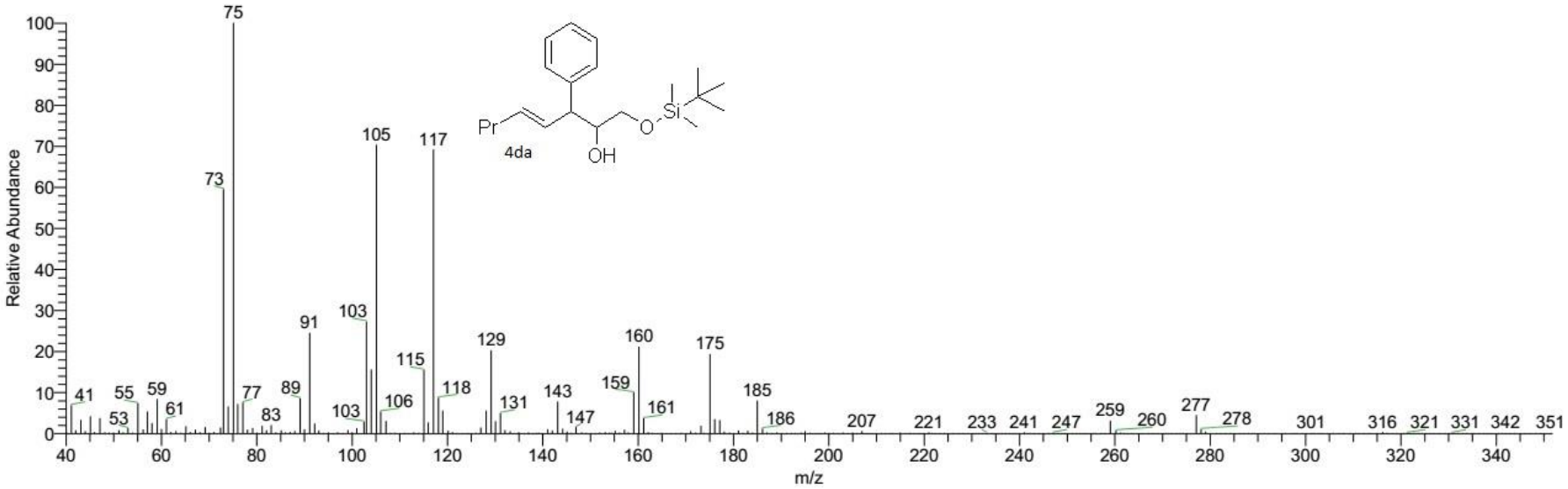
Relative Abundance
m/z
Pr
4da
OH
O
Si
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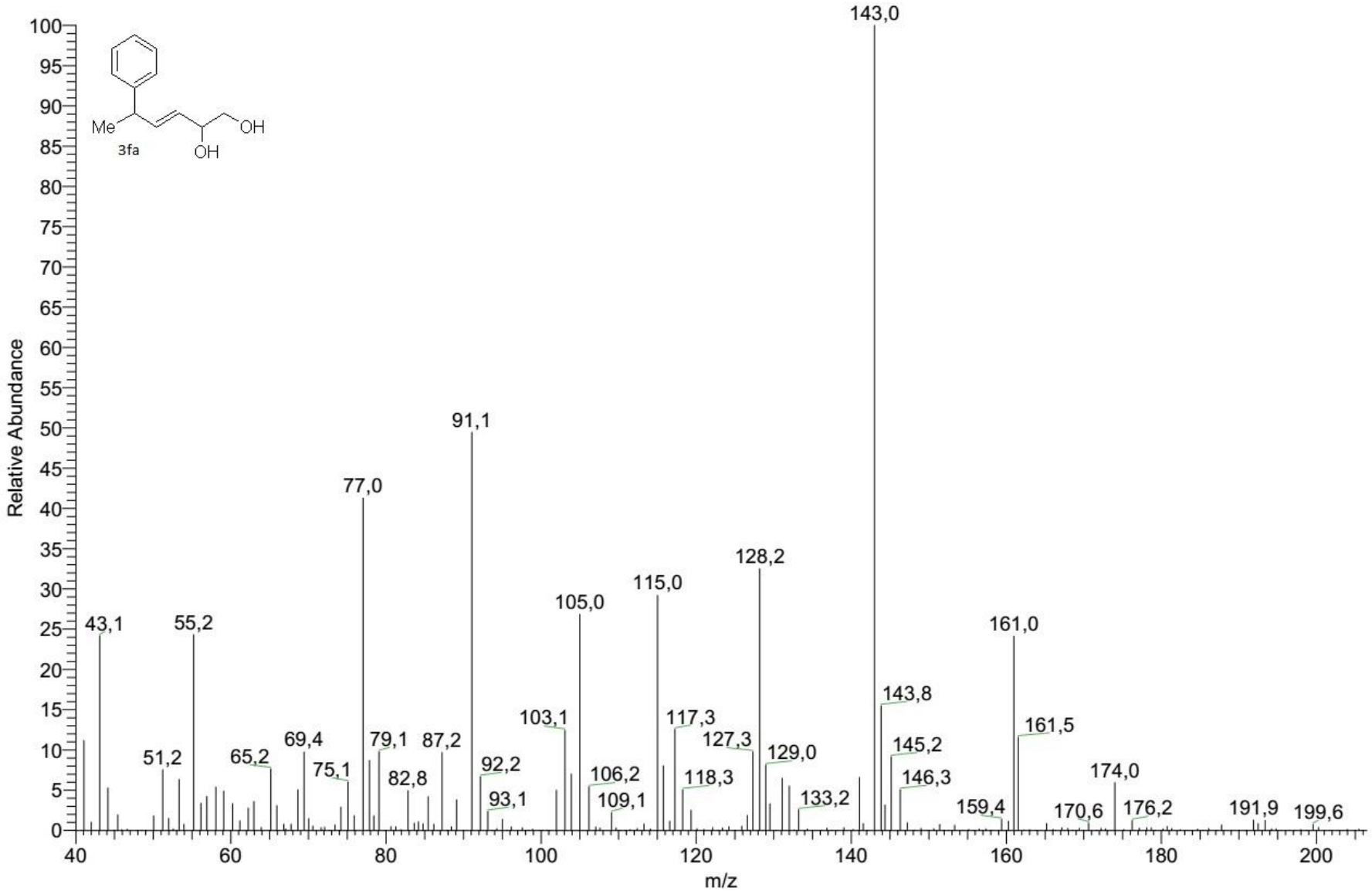
Me
OH
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3fa
Relative Abundance
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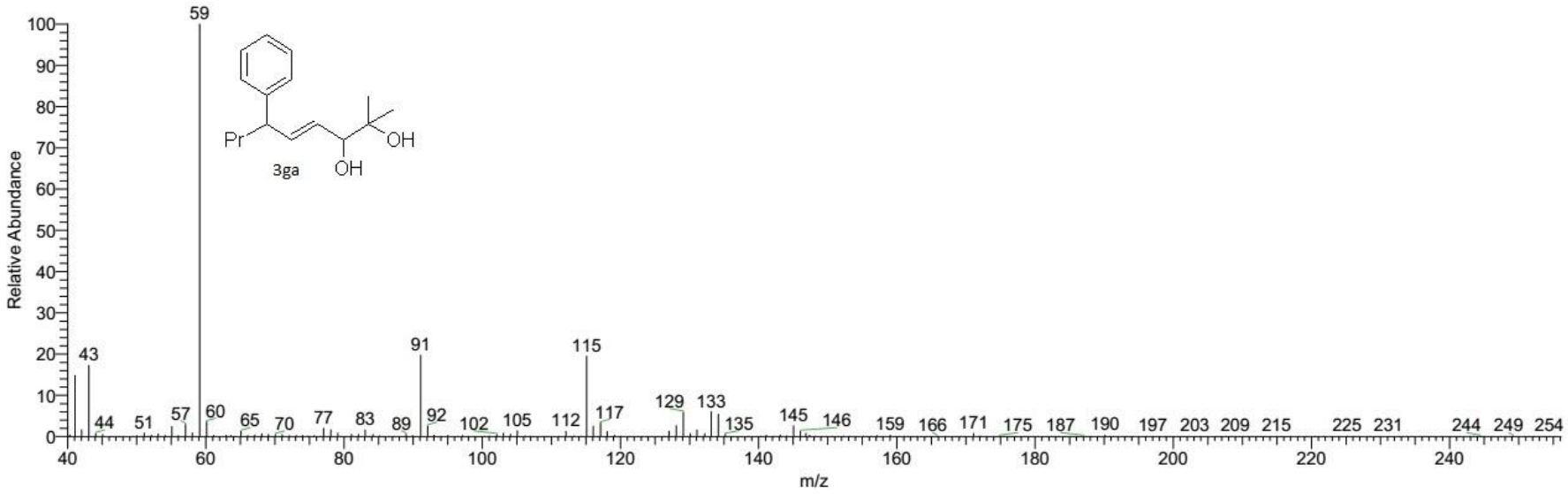
59
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OH
Relative Abundance
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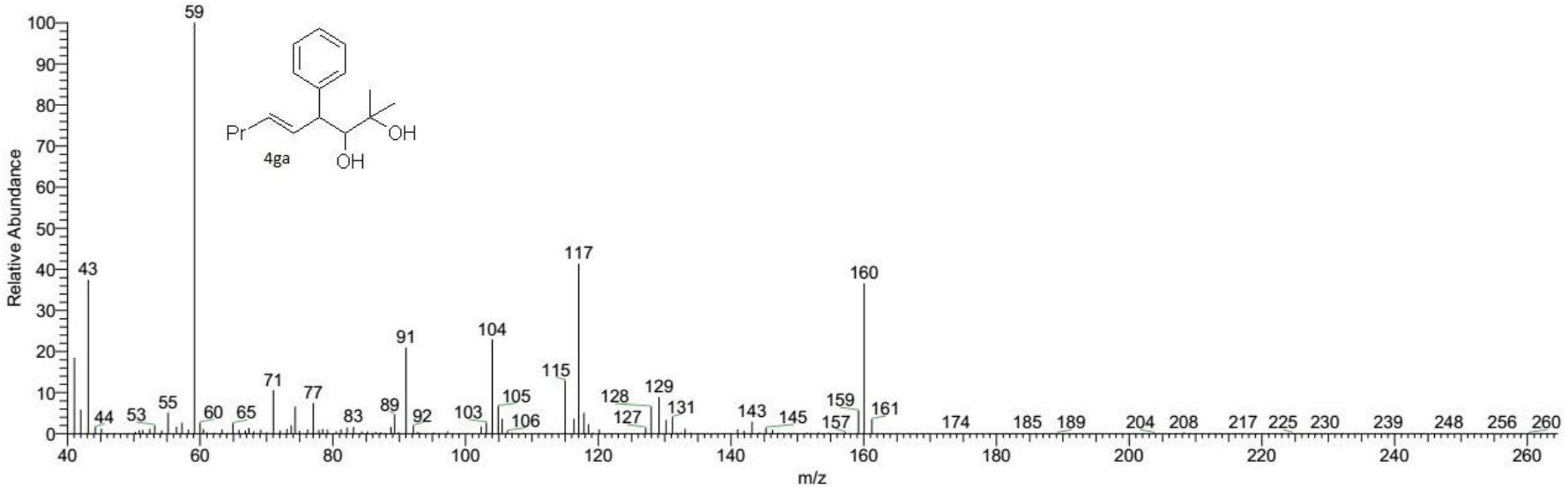
Relative Abundance
m/z
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OH
OH
4ga
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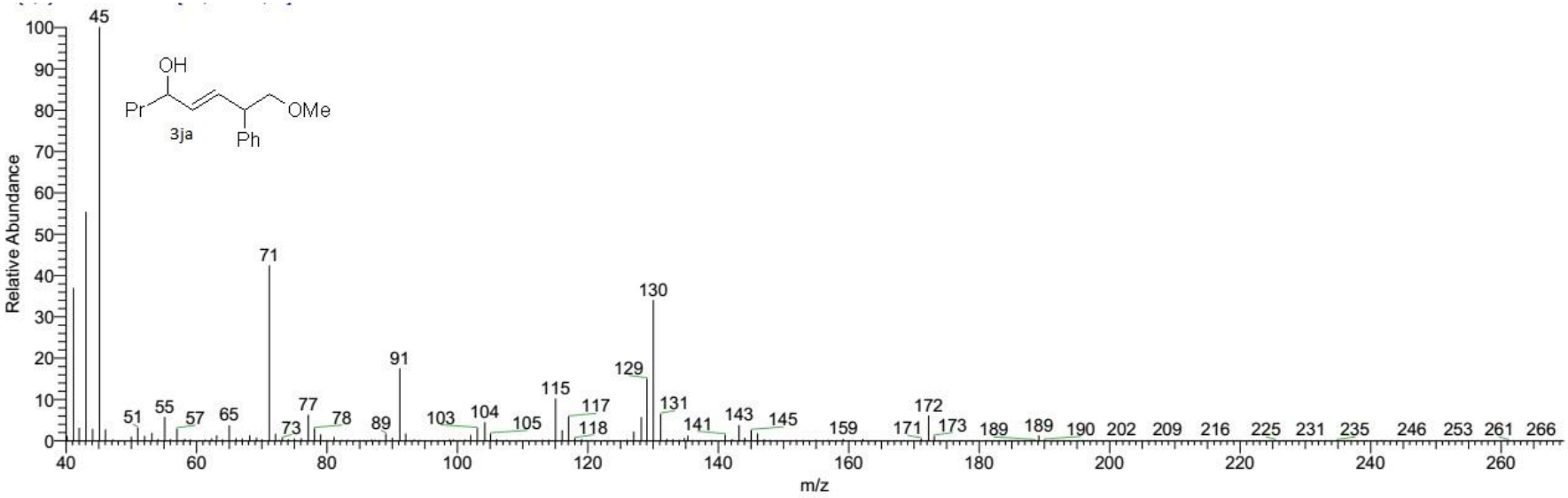
OH
Pr
OMe
Ph
3ja
Relative Abundance
m/z
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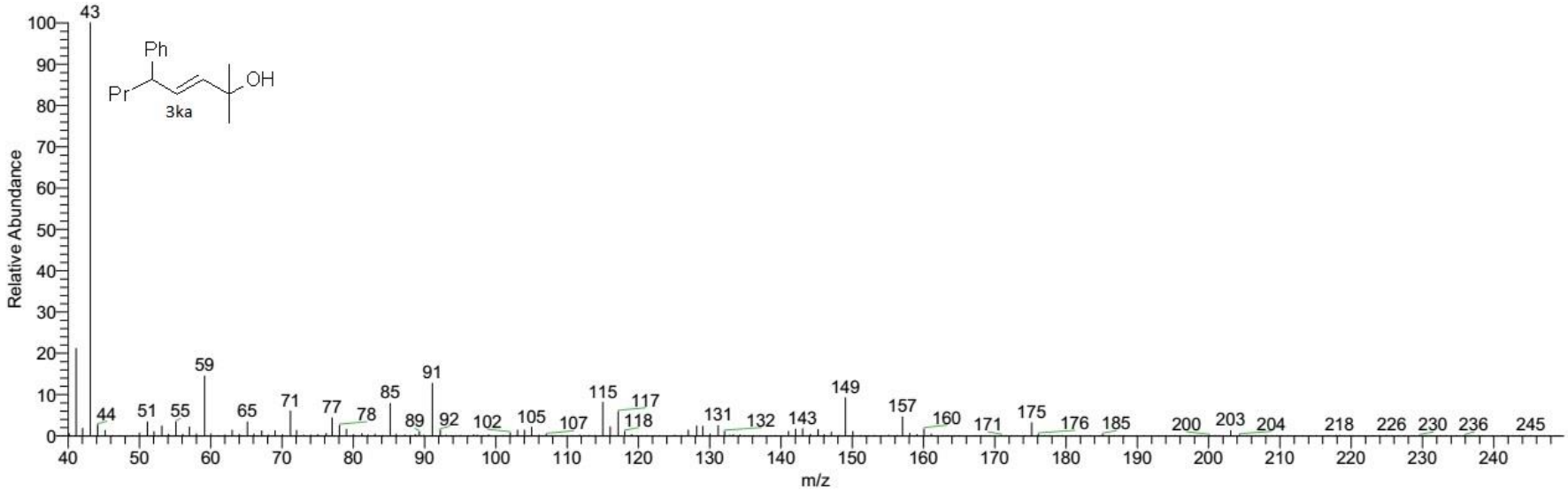
Ph
Pr
OH
3ka
Relative Abundance
m/z
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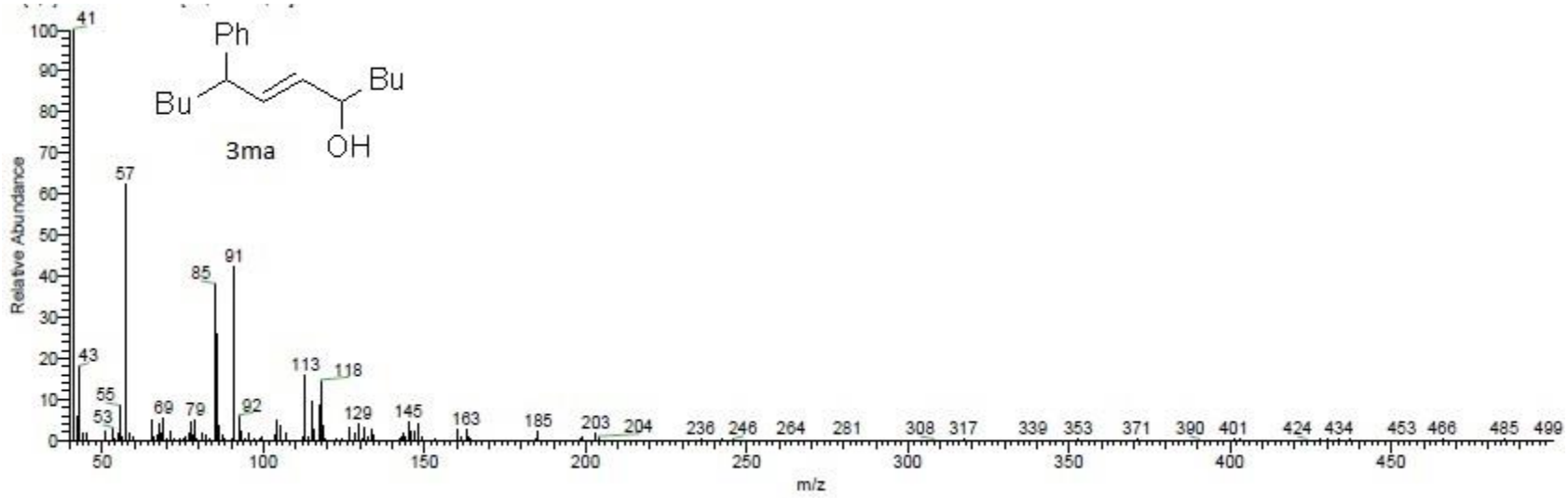
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Relative Abundance
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