COUPLING REACTIONS OF ENYNE OXIRANS WITH GRIGNARD REAGENTS

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ABSTRACT

COUPLING REACTIONS OF ENYNE OXIRANS WITH GRIGNARD REAGENTS

Laboratory-synthesized (Z)-2,4-Enyne oxiranes were subjected iron-catalyzed reactions with Grignard reagents. The reactions afforded majorly *E*-configured vinylallenes with a hydroxyl group on the allylic carbon as the 1,5-(S_N2'')-substitution products. However, in some case, along with the desired vinyllallenes products, 1,1- (S_N2) and 1,3-substitution (S_N2') by-products were also recovered. Diastereo-selectivity of the method is strictly reliant on the syn/anti mode of the alkylation process. This study provides a new methodology for the synthesis of vinylallenes which are potential building blocks of biological active molecules.

ÖZET

ENİN OKSİRANLARIN GRİGNARD REAKTİFLERİ İLE KENETLENME TEPKİMELERİ

Laboratuvarda sentezlenen (*Z*)-2,4-enin oksiran bileşiklerinin Grignard reaktifleri ile demir katalizli tepkimeleri gerçekleştirilmiştir. Bu tepkimeler ana ürün olarak 1,5-(S_N2”)-sübstitüsyon ürünü olan *E*-konfigürasyona sahip allilik pozisyonunda hidroksil grubu bulunan vinilallen ürünleri vermektedir. 1,1-(S_N2) ve 1,3-(S_N2) ürünleri de bazı reaktiflerin tepkimelerinde oluşabilmektedir. Tepkimenin diastereo seçimliliği alkilasyonun yalnızca *syn* ya da *anti* modunda gerçekleşmesine bağlıdır. Bu çalışma, biyolojik olarak aktif moleküllerin çeşitli yapı taşları olabilecek vinylallen sentezi için yeni bir yöntem sunmaktadır.

TABLE OF CONTENTS

APPENDICES

LIST OF FIGURES

LIST OF TABLES

<u>Figure</u> **<u>Page</u>**

LIST OF SYMBOLS AND ABBRAVIATIONS

Ac	Acetate
aq.	Aqueous
Ar	Aryl
Bu	Butyl
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthalene
BIPHEP	2,2'-bis(diphenylphosphino)-1,1’-biphenyl
Bn	Benzyl
Cy	Cyclohexyl
dba	Dibenzylideneacetone
DCM	Dichloromethane
DIBALH	Diisobutylaluminum hydride
DMAP	4-Dimethylaminopyridine
DMF	*N, N*-Dimethylformamide
dppb	1,4-Bis(diphenylphosphino) butane
dppe	1,2-Bis(diphenylphosphino) ethane
dppf	1,1′-Bis(diphenylphosphino) ferrocene
dpph	1,6-Bis(diphenylphosphino) hexane
DPEphos	Bis[(2-diphenylphosphino) phenyl] ether
d.r.	Diastereomeric ratio
Et	Ethyl
etc.	and other things
equiv.	Equivalent
g	Grams
h.	Hour(s)
i-Pr	*Iso*-propyl
M	Molar
m	Meta
m-CPBA	*meta*-Chloroperbenzoic acid
Me	Methyl
mg	Milligrams
min.	Minutes

mL	Milliliters
μm	Micrometer
o	Ortho
p	Para
Ph	Phenyl
RT	Room temperature
t	Time
t-Bu	Tertiary butyl
TBDMS	Tertiary butyldimethylsilyl chloride
THF	Tetrahydrofurane
Ts	*para*-Toluenesulfonyl
Xantphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene

CHAPTER 1

INTRODUCTION

Allenes are among the crucial functional groups in synthetic organic chemistry. (Figure 1.1). Allenes can be used as elements for the syntheses of vast number of complex molecules due to their unique reactivities and high level of axial to center chirality transfer that they can undergo in the course various transformations. Also, the presence of large number of allene motifs in the nature in enantio-pure form make them particularly attractive for production of biologically active pharmacological reagents.

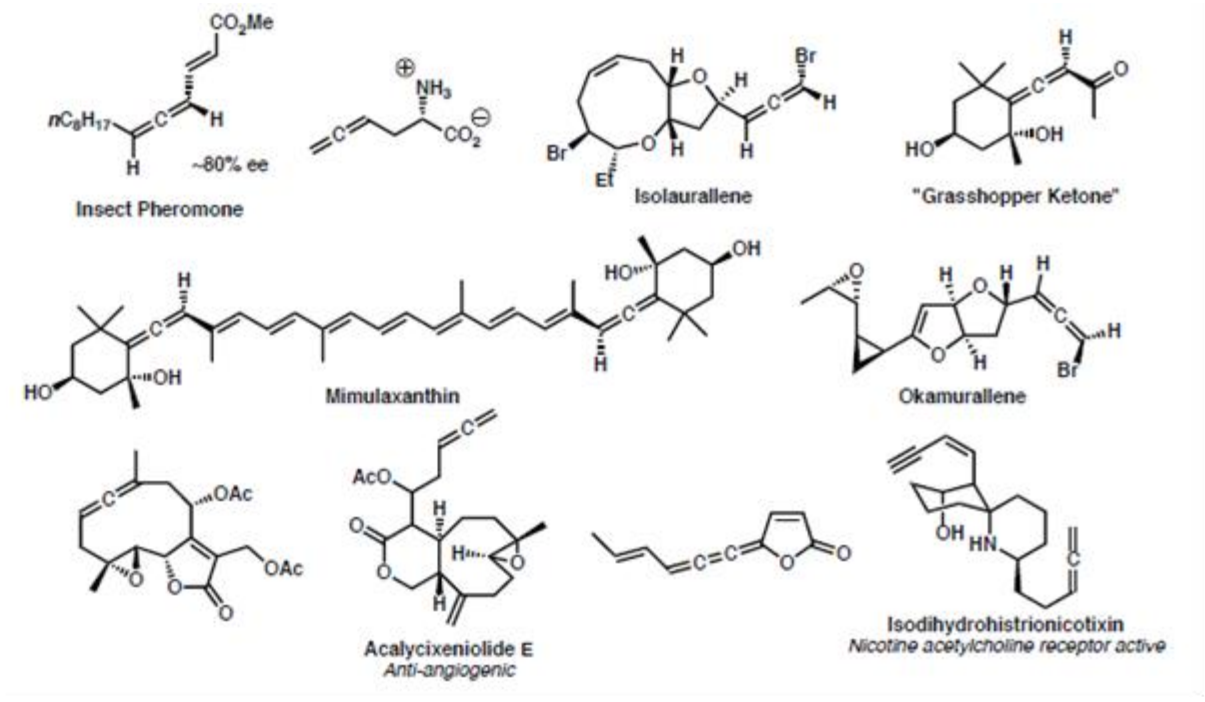


Figure 1.1. Allenic natural products and pharmacologically active allenes.
(Source: Tsuji, et al. 1995)

In last decades, the transition metal-catalyzed formation of allenes have become popular method and Cu, Rh, Pd, and Fe were the mostly used metals for this purpose.

While acetate, carbonate, phosphate, and halides of propargyl compounds have been generally used substrate types in S_N2' (1,3-substitution) type reactions that lead to the allene structures, there are only a scarce number of S_N2'' (1,5-substitution) type application applied in the synthesis of multi substituted allenic structures.

In this context, we, first time, accomplished that the reactions of the conjugated enyne oxiranes with Grignard Reagents in the presence of an iron catalysis afforded vinylallene structures with a hydroxyl group on the allylic position.

CHAPTER 2

LITERATURE WORK

2.1. Metal-Catalysed S_N2'-Type Reactions of Propargyl Epoxides

The reaction of propargyl acetates with stoichiometric level organocuprates was the first 1, 3-substition of method established in synthesis of allenes in 1968 (Rona, 1968; 1969) (Figure. 2.1.). Later on, this technique was further improved and had a wide range of usage.

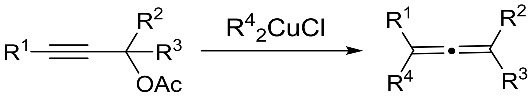


Figure.2.1. 1,3-Substition method of propargyl acetates with stoichiometric level of organocuprates (Source: Rona, et al. 1968; 1969)

In addition to acetates, benzoate, carbonate, sulphonate, ether, acetal, oxirane, and halide substituted of propargyllic reagents were also successfully used. (Alexakis, 1999; Hoffmann-Roder, 2004; Ma, 2004).

Especially the reactions of propargylic epoxide compounds have held great importance. Because these oxirane species create a hydroxyl group upon conjugate addition, which is an important reactive functional group, alongside allenyl moieties. The first stochiometric reactions of propargyl epoxide compounds with organometals were with dialkyllithium cuprate compounds which were carried out by de Montellano (1973). In these reactions, each case however, the reductively formed tri-substituted α-allenol products accompanied the formation of the desired alkylated tetra-substituted alkylated α-allenol products, (Figure 2.2). In this study the stereo-selectivity of the method was not determined.

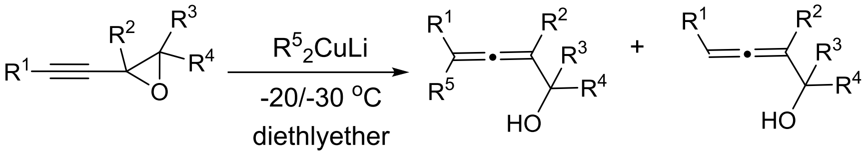


Figure 2.2 Stoichiometric reactions of propargyl epoxides dialkyllithium cuprates (Source: de Montellano, et al., 1973)

However, Oehlschlager and Czyzewska (1983) established in their studies that an enantio-enriched propargyl epoxide with a terminal alkynyl group reacts with organocuprates in the presence of Me_2S in mainly *anti* S_N2' mode to afford enantiomerically enriched α-allenol structures (Figure 2.3).

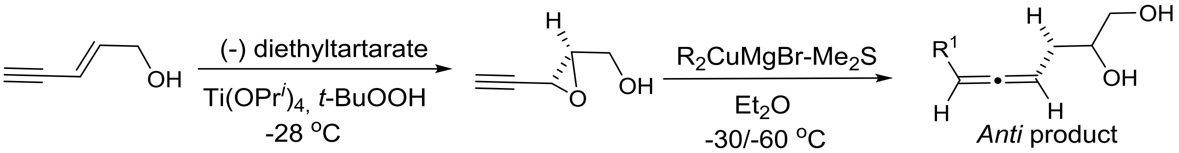


Figure 2.3. The reaction of an enantio-enriched enyne oxirane with organocuprates (Source: Oehlschlager and Czyzewska, et al. 1983).

The method has been brought to catalytic level firstly by Alexakis and his group (1989; 1991). According to their findings, diasteroselectivity of allenol products resulting from CuBr catalyzed reactions of propargylic epoxides and Grignard reagents varies in respect to the ligand and other additive materials present in the reaction medium (Figure 2.4).

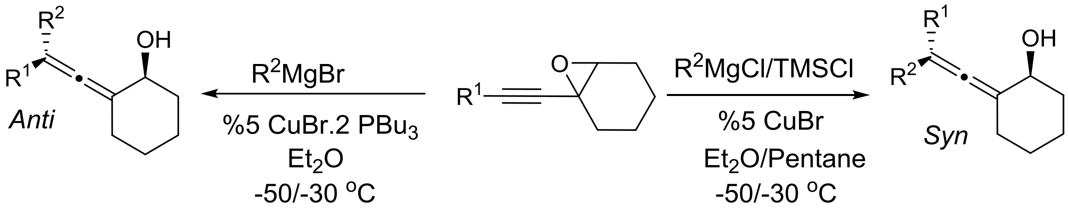


Figure 2.4. CuBr catalyzed reactions of propargylic epoxides and Grigrnard reagents. (Source: Alexakis et al. 1989; 1991)

Fürstner and coworkers found that the reaction can be catalyzed by an iron compound (2003). The *syn*/*anti* ratios of reaction vary between 80/20-90/10 range (Figure 2.5).

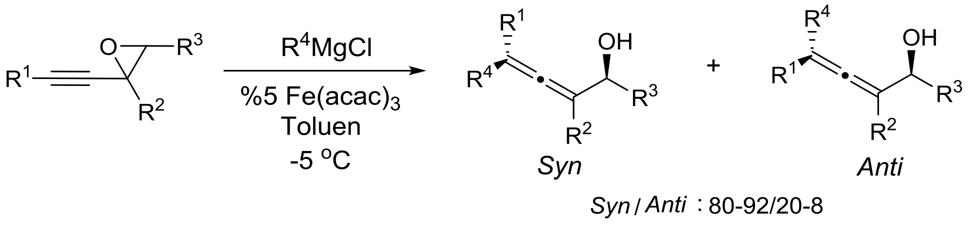


Figure 2.5. Iron catalyzed reactions of propargylic epoxides with Grignard reagents. (Source: Fürstner, et al. 2003)

The synthesis of arylated allenols with rhodium catalysis, via reaction of propargyl epoxides with arylboronic acid was made possible. The reaction happened mostly at *syn* mode (Miura, 2007) (Figure 2.6).

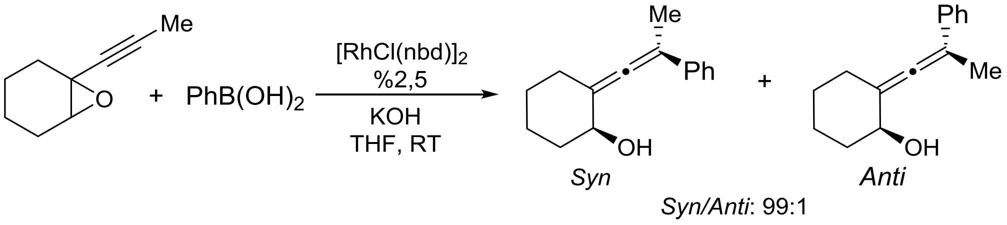


Figure 2.6. The synthesis of arylated allenols with rhodium catalysis via the reaction of propargyl epoxides with arylboronic acids (Source: Miura, et al. 2007)

2.2. Metal-Catalysed SN2’-Type Reactions of Allyl Epoxides

There are not many studies carried out on allyl epoxides S_N2' reactions with Grignard Reagents (Falciola, 2008). The main reason for this would be that the as the Grignard reactives are "hard" basic reactives, they are very prone to $S_N2$reactions (Hyoung, 2008) (Figure 2.7).

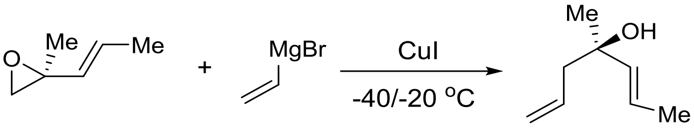


Figure 2.7. S_N2' reactions allyl epoxides and Grignard Reagents (Source:Hyoung, et al. 2008)

However, Millet and Alexakis were able to conduct a copper-catalyzed kinetic resolution of cyclic alkenyl oxiranes with the help of a chiral ferrocene ligand (2007) (Figure 2.8).

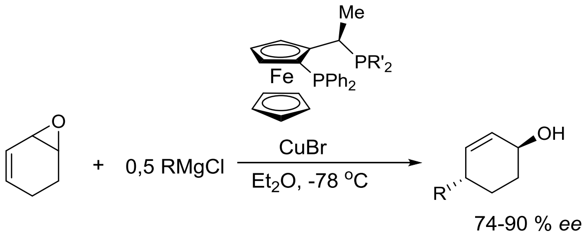


Figure 2.8. The copper catalyzed kinetic resolution of alkenyl oxiranes with Grignard Reagents (Source: Millet and Alexakis, et al. 2007)

2.3. Metal Catalysed Substition Reactions of 2,4-Enyne Reagents

As mentioned above, the metal catalyzed reactions of the propargylic reagents create allenic structures through the S_N2' (1,3-substitution) reaction, whereas the allylic products can be obtained from S_N2' reactions of allylic reagents. As the 2,4-Enyne structure in fact has a leaving group on the allylic position, it would be reasonable to expect to observe S_N2 or S_N2' reactions.

Goré and Dulcere conducted 1,5-S_N2''-nucleophylic substitution reactions of 1-chloro-2-en-4-in compounds with methylmagnesium iodide or trimethylmagnesium chloride compounds in a non-catalyzed environment. Reactions created vinylallenes with a *E* and isomeric mixture (Figure 2.9) (Gore, 1972; Dulcere, 1974; Dulcere, 1981). However, this method is not very general and desired vinylallenes could not be obtained from all other Grignard Reagents.

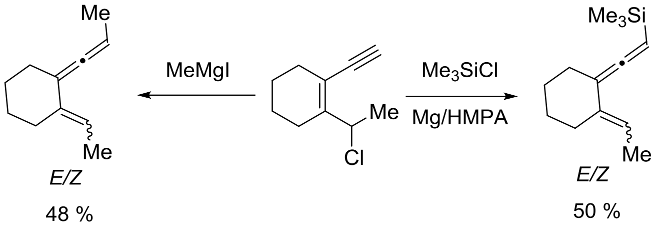


Figure 2.9. 1,5-SN2''-nucleophylic substitution reactions of 1-chloro-2-en-4-in compounds with methylmagnesium iodide or trimethylmagnesium chloride (Source: Gore, et al. 1972; Dulcere, et al. 1974; Dulcere, et al. 1981)

Krause and Purpura accomplished a more general method for this purpose. 2,4-enyne acetates underwent 1,5-substition reactions (S_N2'') with organolithium cuprates and thus yielded the corresponding alkylated vinylallene products (1999). The reactions proceeded with low diastereo-selectivity, yielding the products as the *E*/Z configurational mixtures, nevertheless, the high levels of center-to-axis enantiomeric transfer could be achieved with enantio-purely synthetized enyne acetates (Figure 2.10) (Krause, 2000) The absolute configuration of the products were not reported.

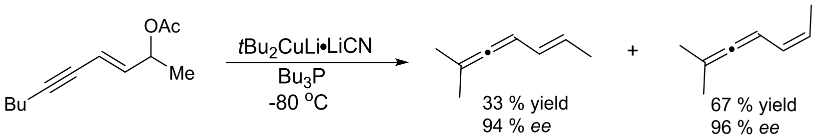


Figure 2.10. 1,5-Substition reaction (SN2'') of 1,4-enyne acetates with organolithium cuprates (Source: Krause, et al. 2000)

They also tried this method on two *E*-enyne oxirane substrates by using stochiometric quantities of Me_2CuLi LiI or *t*-Bu_2CuLi LiCN alkyl cuprates. The reaction of both enyne oxiranes with *t*-butylcuprate allow the production the corresponding alkylated vinylallenes, one of which being obtained in the form of E/Z mixture. However, using with the methylcuprate nucleophilic reagent resulted in only the formation of a non-alkylated reductive vinylallene product (Figure 2.11).

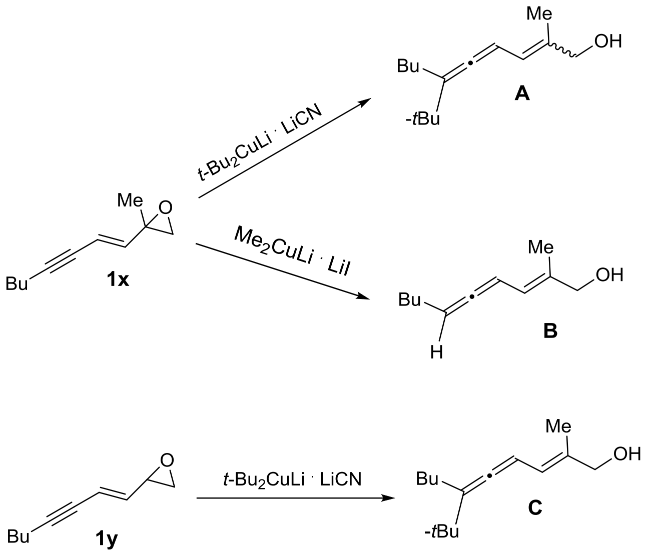


Figure 2.11. The reaction of *E*-enyne oxirane substrates and of Me_2CuLi**,** LiI or t-Bu_2CuLi,·LiCN alkyl cuprates (Source: Krause, et al. 2000)

Our group have conducted palladium- and rhodium-catalyzed 1,5-substition reactions of enyne carbonate and enyne acetate structures, respectively, with arylboronic acids. Whereas both *E*- and *Z*-enyne carbonate structures were eligible reagents for palladium-catalyzed method which yielded the desired arylated vinylallene products with exclusively *E*-configuration, it’s the rhodium-catalyzed version was only applicable to the *Z*-configured enyne acetates (Figure 2.12) (Uçüncü, 2011).

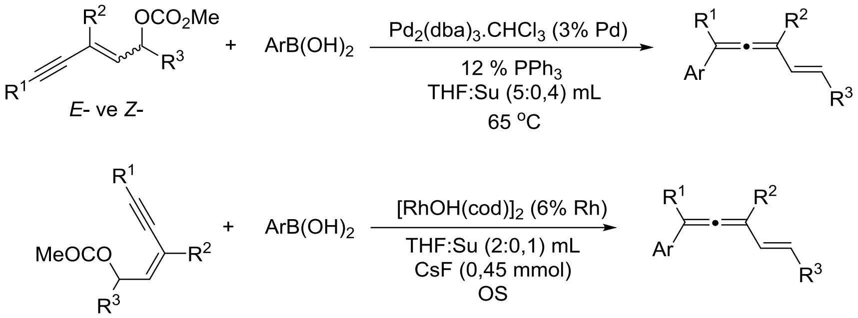


Figure 2.12. Palladium- and rhodium-catalyzed coupling reactions of carbonates and acetates of 2,4-enynols with organoboronic acids (Source: Uçüncü, et al. 2011)

Vinylallene esters could be obtained via palladium-catalyzed alkoxycarbonylation reactions of enyne oxiranes (Figure 2.13) (Akpınar, 2011).

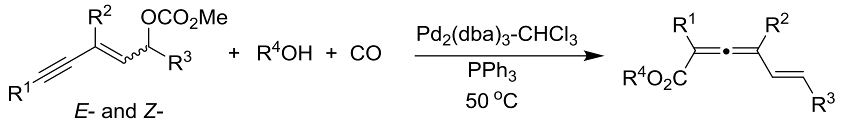


Figure 2.13. Palladium-catalyzed alkoxycarbonylation reactions of enyne carbonates with enyne oxiranes. (Source: Akpınar, et al. 2011)

The reaction conditions were also applied to an enantio-enriched (*Z*)-2, 4-enyne carbonates. It was found that the reaction proceeded with complete racemization. But after tuning the reaction parameters, moderate to good transfer of chirality was observed depending on the olefin geometry and substituents on the alkyne moiety.

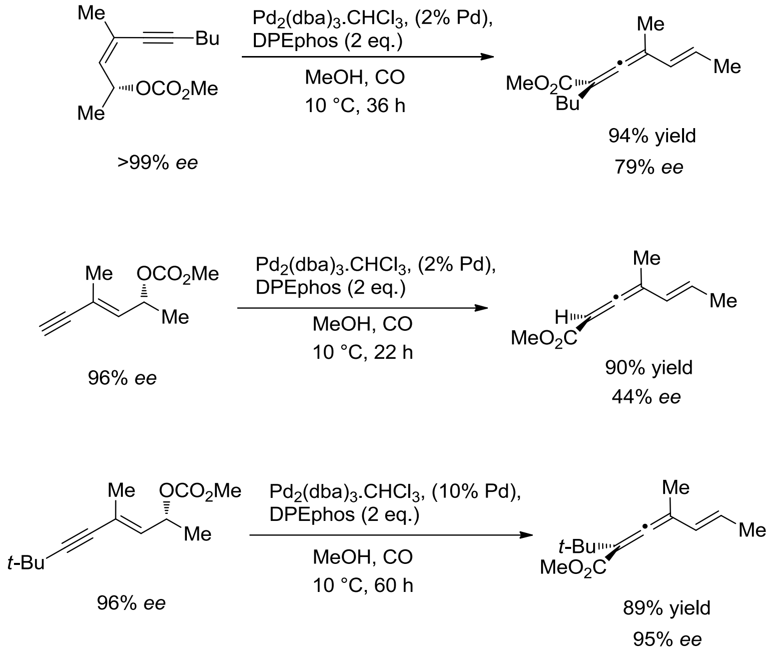


Figure 2.14. Palladium-catalysed alkoxycarbonylation reaction of (*E* and *Z*)-2, 4-enyne carbonates leading to enantio-enriched vinylallene derivatives. (Source: Karagöz, *et al*. 2014)

In a recent study that was conducted in our laboratories, the palladium-catalyzed alkoxycarbonylation reactions of enyne oxiranes proceeded with high stereo-selectivity and yielded 7-Hydroxy-2,3,5-trienoates chiefly in *Anti*-mode. (Figure 2.17). (Kuş, 2013b).

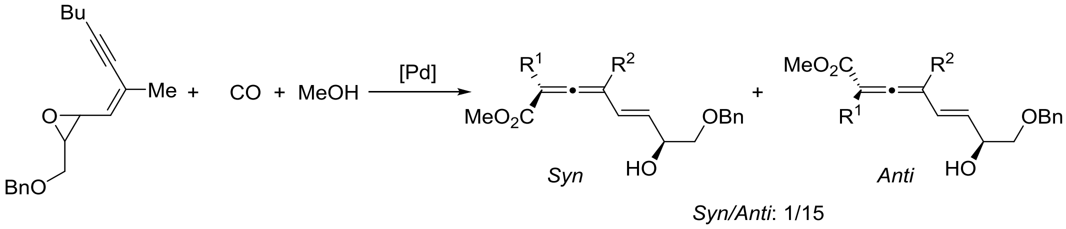


Figure 2.15. Anti-selective palladium catalyzed alkoxycarbonylation reactions (Source: Kuş, et al. 2013b).

On contrary to the general trends with conjugated enyne systems, Li and Alexakis (2012) have found that the Cu(I) catalyzed reactions of primary enyne chlorides with Grignard reagents underwent 1,3-S_N2'reaction. (Figure 2.18)

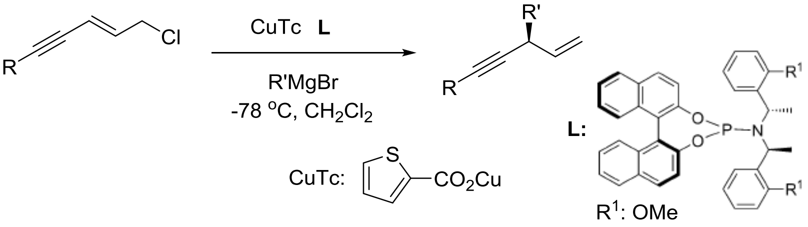


Figure 2.16. Cu(I) catalyzed reactions of enyne chlorides with Grignard reagents (Source: Li and Alexakis, et al. 2012)

2.4. Vinylallenes as Reactive Compounds

More than 150 types of allene and cumulene compounds from natural sources have been identified. Most of these compounds are enantiomerically pure and have biological activity (Krause, 2004a; 2004b; Hoffmann-Röder, 2004). There are significant number of natural compounds containing an alkenyl structure conjugated to allenyl sites, the most typical of these structures being the methyl (*R*, *E*) -(-)-tetradeca-2,4,5-trienoate (**7**) compound which is a pheromene isolated from bean weevil (*Acanthoscelides obtectus*).

The importance of allenic structures cannot be constricted to their biological activities. The unique reactivity of these structures makes their usage in the synthesis of complex structures possible. For example, in Diels Alder reactions they have high reactivity and stereo-selectivity (Figure 2.19) (Spino, 1998).

Their ability to transfer their axial chirality to cyclo-entrainment products makes asymmetric cyclic synthesis possible (Reich, 1988; Koop, 1996; Gibbs, 1989). Also, their tendency to adopt *s-cis* conformation in conformational balance makes their structures highly reactive (Reich, 1988; Koop, 1996; Bond, 1990).

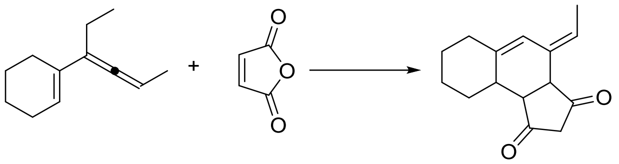


Figure 2.17. Diels Alder reactions in high reactivity and stereo-selectivity (Source: Spino, et al. 1998)

Sterpurene compound, which is a fungal metabolite, were synthesized enantiopurely (Gibbs, 1989) (Figure 2.20) and racemically by intramolecular Diels Adler reaction ([4+2] catenulation) with vinylallenes (Krause, 1993) (Figure 2.20)

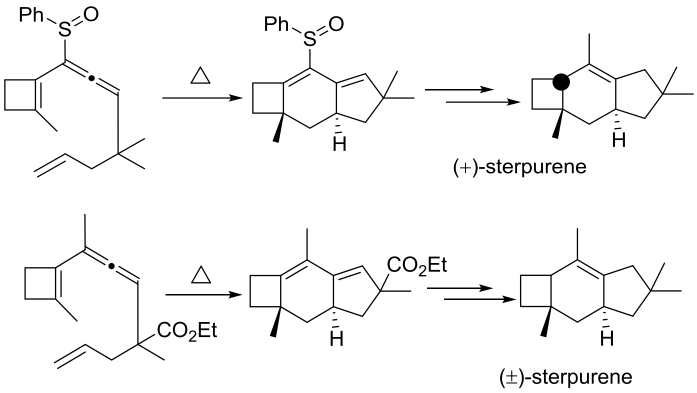


Figure 2.18. The synthesis of optically active sterpurene via intramolecular Diels Adler reaction ([4+2] catenulation) of a vinylallene structure (Source: Gibbs, 1989, Krause, et al. 1993)

The intramolecular Diels Alder reaction of vinylallenes have been used to synthesize a biogenetical intermediary structure called esperamicin A (Figure 2.21) (Schrieber, 1988). The ability to transfer chirality of allenic structure is especially important for this transformation.

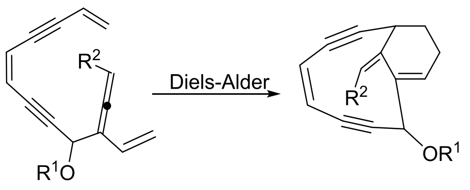


Figure 2.19. Intramolecular Diels Alder reaction of s vinylallene structure in the synthesis of esperamicin A (Source: Schreiber, et al. 1988)

Vinylallenes can be helpful in various catalytic intramolecular cyclization reactions, as well. Rh(I) catalysis of vinylallenes with terminal alkynes have created *tri*-substituted benzenes (Figure 2.22) (Murakami, 1988).

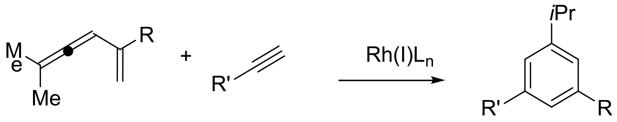


Figure 2.20. Rh(I) catalysis of vinylallenes with terminal alkynes
(Source: Murakami, et al. 1988)

Pauson-Khand type reactions also can be conducted with vinylallenes (Figure 2.23) (Murakami, 1999a, 199b).

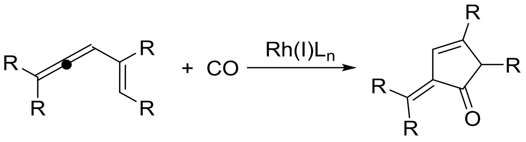


Figure 2.21. Pauson-Khand type reactions (Source: Murakami, et al. 1999a, 199b)

It has been established that the vinylallenes form into cyclopentadiene derivatives as result of gold-catalyzed cyclization (Figure 2.24) (Lee, 2007).

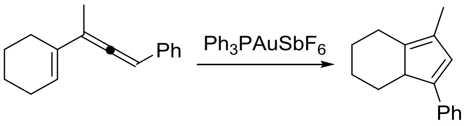


Figure 2.22 Gold-catalyzed cyclization of vinylallenes (Source: Lee, et al. 2007)

One French group synthesized polycyclic structures with high stereo-selectivity by gold catalyzed cycloisomerisation reactions of vinylallenes with a tethered alkenyl group (Figure 2.25) (Gandon, 2008; Lemiere, 2009).

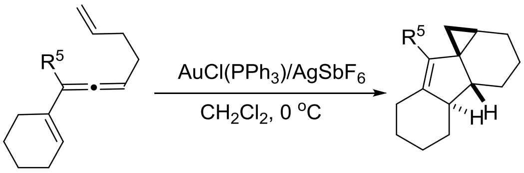


Figure 2.23. Gold-catalysed cycloisomerisation reactions of vinylallenes in high stereo-selectivity (Source: Gandon, et al. 2008; Lemiere, et al. 2009)

CHAPTER 3

EXPERIMENTAL STUDY

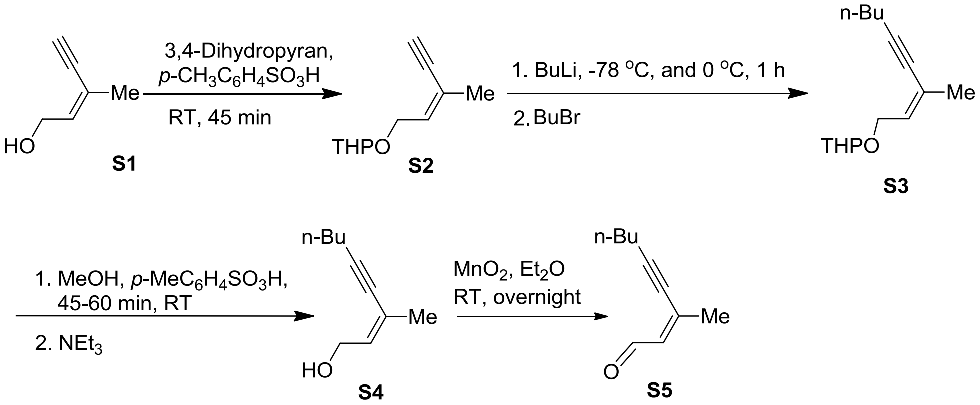
3.1. General Methods of Drying Solvents

DMF, and DCM solvents were all purified by a solvent purification system. Et_2O and THF were distilled from benzophenone-ketyl under argon prior to use. For the iron-catalyzed reactions, THF solvent dried by refluxing over $LiAlH_4$.

3.2. Synthesis of Substrates

Syntheses of all enyne oxirane starting materials (**1**) were performed under Ar gas and purification of all synthesized molecules was performed by column chromatography on silica gel. Silica gel material used for the purification of enyne oxirane substrates had a particle size range of 60-200 mesh and treated by NEt_3 before use. It must be noted that the column chromatography of the substrate **1** on an untreated silica gel always resulted in decomposition. All other column purifications were performed on silica gel 60 (35-70 μm). All substrates appeared either colorless or pale yellow oils. The $Pd_2(dba)_3$-$CHCl_3$ complex was synthesized in the laboratory (Ukai, et al. 1974).

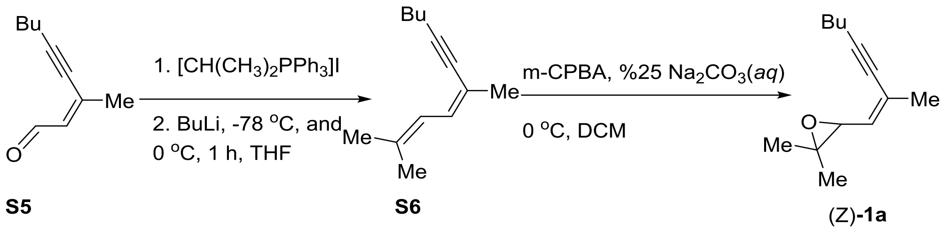
3.2.1. Synthesis of (Z)-1a



To the mixture of commercially available, (Z)-pent-2-en-4-yn-1-ol (**S1**) (1.92 g, 20 mmol) and 3,4-dihydropyran (2.2 mL, 24 mmol) was added *p*-toluenesulfonic acid (44 mg, 0.02 mmol) and then stirred for 45 min at room temperature (RT). Then, the mixture was diluted with 40 mL of dry THF under Ar and cooled to -78 °C. At that temperature, 24 mmol of BuLi (1.6 M in hexane, 15 mL) was added dropwise via a syringe. After stirring the reaction mixture for 1 h at 0 °C, butyl bromide (4.3 mL, 40 mmol) was added and the mixture was stirred for 5 days at reflux. The reaction was quenched by the addition of saturated NH_4Cl*(aq)* solution and the reaction solution was extracted with Et_2O. The organic phase was washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was used in the following step without any other purification (Betzer, *et al.* 1997).

To a solution of the preceding crude compound (**S3**) in methanol (60 mL) *p*-toluenesulfonic acid (1.2 g, 6 mmol) was added and the resulting solution was stirred at RT for 45-60 min. Then, triethylamine was added (1.8 mL), and the solution was concentrated under reduced pressure. The mixture was taken into DCM and washed with water. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel gave the enynol **S4** (hexane-EtOAc, yield: 2.43 g, 80%), (Ukai, *et al.* 1974).

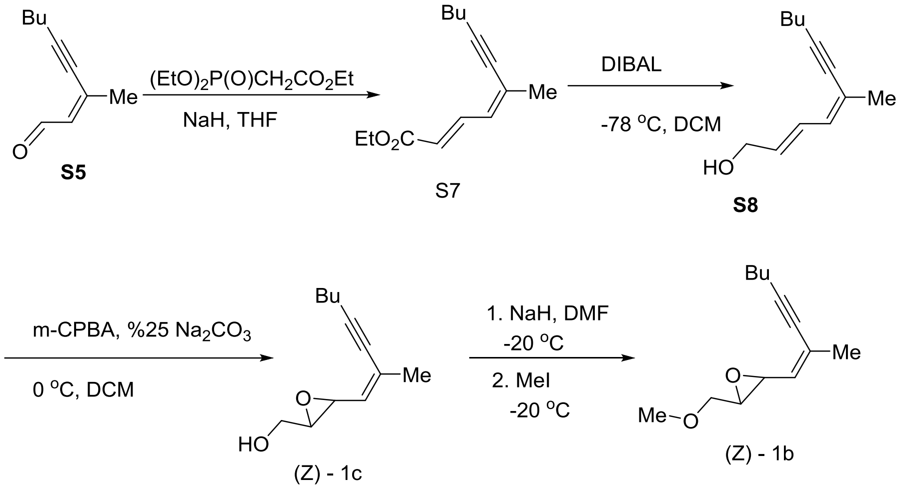
To the solution of **S4** (≈17 mmol) in 60 mL of dry diethyl ether, activated MnO_2 (30 g, 0.3 mol) was added, and the mixture was stirred overnight at RT. After filtration through Celite, the solution was concentrated under reduced pressure. The crude aldehyde (**S5**) was used in the next step (Betzer, *et al.* 1997).



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 enyne aldehyde **S5** (1.8 g, 12 mmol), was added dropwise to the resulting mixture and stirred for 1 h, at RT. The reaction was quenched by the addition of saturated NH_4Cl(*aq*) solution, and the organic layer was extracted with diethyl ether. The combined extracts were dried over $MgSO_4$, and chromatographed on a silica gel column to obtain pure **S3a** (hexane/EtOAc, yield: 1.65 g, 78%), (Ming-Yuan, *et al.* 2004).

To a solution of **S6** (352 mg, 2 mmol) in DCM (30 mL) was added 12 mL solution of Na_2CO_3(*aq*) (25%) followed by 3.4 mmol (587 mg) *m*-chloroperbenzoic acid dropwise at 0 ^{0}C. The mixture was stirred at same temperature and monitored with TLC until the reactant was consumed completely. At the end of the epoxidation 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-pretreated short silica gel column which afforded the enyne oxirane (*Z*)-**1a** as a colorless oil (hexane-EtOAc, yield: 269 mg, 70%).

3.2.2. Synthesis of (Z)-1b and 1c



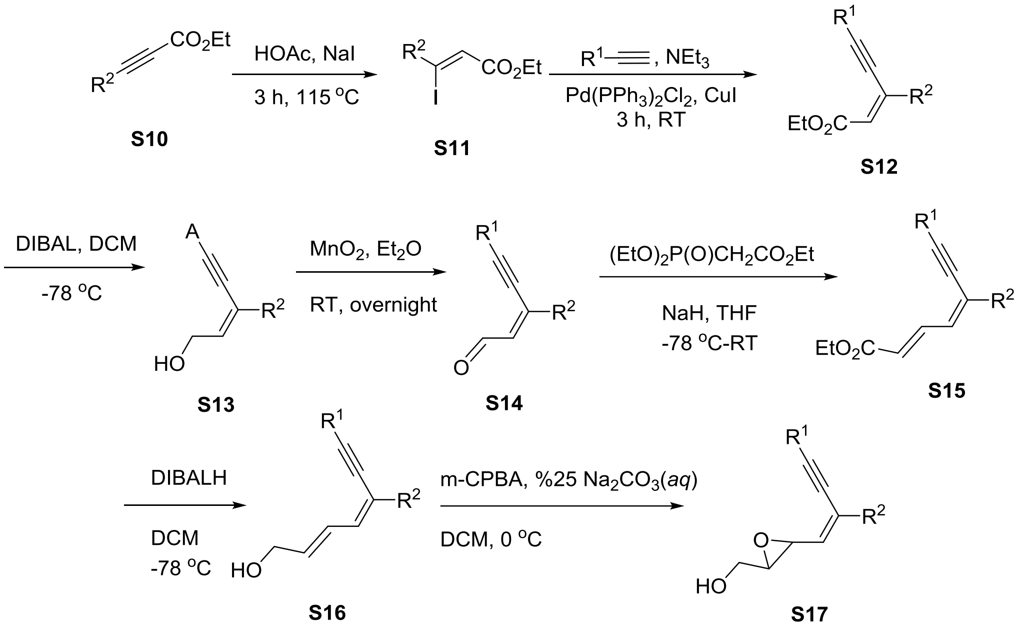
To a solution of NaH (525 g, 22 mmol) in THF (50 mL) was added triethyl phosphonoacetate (4.8 mL, 24 mmol) at 0 ^{o}C, and the mixture stirred 1 h, at RT. Subsequently, to the reaction mixture was added **S5** (3 g, 20 mmol) dropwise at -78 ^{o}C and stirred for 1 h, at RT. The reaction was terminated by the addition of aqueous NH_4Cl(*aq*) solution and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give *E/Z* isomer 95:5 isomeric ratios. The crude mixture was purified on silica gel column to obtain **S7** in pure isomeric form (hexane-EtOAc, yield: 3.17 g, 72%), (Urabe, *et al.* 1997).

A DIBALH (44 mL, 44 mmol, 1.0 M in cyclohexane) solution was added dropwise to the solution of **S7** (3.85 g, 17.5 mmol) in DCM (120 mL) at –78 ^{o}C. After the reaction mixture was stirred for 4 h at the same temperature, 1 M HCl(*aq*) solution was added before extracting with DCM. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to silica gel column chromatography to purify the corresponding **S8** compound (hexane-EtOAc, yield: 2.65 g, 85%), (Kajikawa, *et al.* 2009).

The epoxidation of **S8** (356 mg, 2 mmol) and isolation of the product **(Z)-1c** was performed as specified for (*Z*)**-1a** (hexane-EtOAc, yield: 233 mg, 60%). As for the alkylation of the pendant hydroxyl group of **(Z)-1c**, a suspension of sodium hydride (1.1 eq) in DMF (1 mL) was added to a solution of **(Z)-1c** (1 mmol) in DMF (1 mL/mmol) at -20 °C. The mixture was stirred for further 30 min before the addition of methyl iodide

(1.2 eq) or benzyl bromide (1.2 eq). 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-pretreated short silica gel column to afford the corresponding alkoxy-substituted enyne oxirane products as colorless oil (*Z*)-**1b** (hexane-EtOAc, yield: 87%), (Caldentey, *et al.* 2011).

3.2.3 Synthesis of hydroxyl tethered (Z)-2,4-enyne oxiranes



To a solution of alkynoic ester **S10** (40 mmol) and acetic acid (240 mmol, 13.8 mL or 512 mmol, 20.8 mL when **S10** is ethyl 4, 4-dimethylpent-2-ynoate and ethyl 3-cyclohexylpropiolate) was added sodium iodide (9.6 g, 64 mmol or 19.2 g, 128 mmol when **S17** is ethyl 4, 4-dimethylpent-2-ynoate and ethyl 3-cyclohexylpropiolate) and stirred for 3 h at 115 °C. After completion of the reaction, the brown mixture was transferred while hot to a separatory funnel containing water (10 mL/mmol of the ester substrate). The reaction flask was washed with a mixture of water (5 mL) and diethyl ether (30 mL/mmol of the ester substrate). The washings were combined in a separatory funnel. The phases were separated and the aqueous phase was extracted with diethyl ether.

The combined organic phases were treated sequentially with saturated aqueous $NaHCO_3$(*aq*), $Na_2S_2O_3$(*aq*) (1 M), and brine and then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (hexane-EtOAc, yields; R^2= H, 7.6 g, 84%; R^2= Me, 8.4 g, 87%; R^2= t-Bu, 9.6 g, 85%; R^2= Cy, 10.6 g, 86%), (Piers, *et al.* 1994). A mixture of **S11** (30 mmol), $PdCl_2(PPh_3)_2$ (210.6 mg, 0.3 mmol, 1% mol of Pd), and CuI (29 mg, 0.15 mmol, 0.5% mol of Cu) in 140 mL of Et_3N was stirred for 10 min at RT under Ar, and then, to this mixture was added a terminal alkyne (36 mmol). The mixture was stirred at RT for 3h. At the end of the reaction, water was added to the resulting mixture and then extracted with Et_2O. The combined organic layers were dried over $MgSO_4$. The solvent was evaporated in vacuo and the product **S12** was purified by column chromatography on silica gel (hexane-EtOAc, yields: R^1= Bu, R^2= H, 4.97 g, 92%; R^1= Ph, R^2= Me, 5.97 g, 93%; R^1= Cy, R^2= Me, 5.94 g, 90%; R^1= *t*-Bu, R^2= Me, 4.95 g, 85%; R^1= Bu, R^2= t-Bu 6.23 g, 88%, R^1= Bu, R^2= Cy, 6.21 g, 79%, R^1= H, R^2= Me %90).

A DIBALH (~3 eq, 1.0 M in cyclohexane) solution was added dropwise to the solution of **S12** in DCM (~6 mL/mmol **S12**) at –78 °C. After the reaction mixture was stirred for 4 h at the same temperature, 1 M HCl(*aq*) solution was added before extracting with DCM. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to silica gel column chromatography to purify the corresponding **S13** compound (hexane-EtOAc; yields of **S13**: R^1= Bu, R^2= H, 3.14 g, 91%; R^1= Bu, R^2= Cy, 4.89 g, 89%, R^1= Cy, R^2= Me, 3.60 g, 81%; R^1= *t*-Bu, R^2= Me, 3.57 g, 94%; R^1= Bu, R^2= *t*-Bu, 4.2 g, 88%; R^1= Ph, R^2= Me, 3.87 g, 90%, R^1= H, R^2= Me %90), (Kajikawa, *et al.* 2009).

To the solution of **S13** (≈20 mmol) in 70 mL of dry diethyl ether, activated MnO_2 (35.1 g, 0.35 mol) was added, and the mixture was stirred overnight at RT. After filtration through Celite, the solution was concentrated under reduced pressure. The crude aldehyde (**S20**) was used in the next step (Betzer, *et al.* 1997).

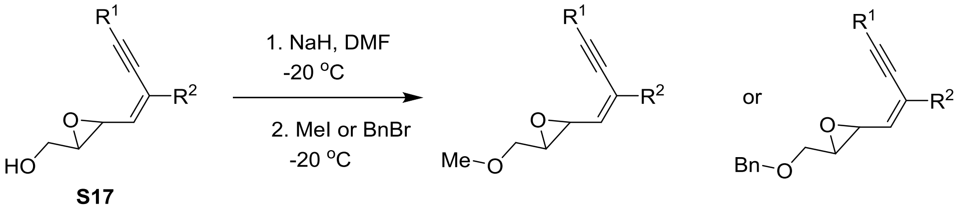
To a solution of NaH (1.1 eq) in THF (2.5 mL/mmol **S14**) was added triethyl phosphonoacetate (1.2 eq) at 0 °C and the mixture stirred for 1 h, at RT. Subsequently, to the reaction mixture was added **S14** (6.5-10 mmol) dropwise at -78 °C, and stirred for 1 h, at RT. The reaction was terminated by the addition of saturated NH_4Cl(*aq*) and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to obtain **S15** with *E/Z* isomeric ratios varying in the range of 97:3

to 95:5 (Urabe, *et al.* 1997). The crude mixture was purified on silica gel column (hexane-EtOAc) to obtain **S15** in pure isomeric form (yields of **S15** R^1= Bu, R^2= H, 1.48 g, 72%; R^1= Bu, R^2= Cy, 1.4 g, 68%; R^1= Cy, R^2= Me, 1.97 g, 80%; R^1= *t*-Bu, R^2= Me, 1.80 g, 82%; R^1= Bu, R^2= *t*-Bu, 2.12 g, 81%; R^1= Ph, R^2= Me, 2.04 g, 85%, R^1= H, R^2= Me %70).

A DIBALH (~3 eq, 1.0 M in cyclohexane) solution was added dropwise to the solution of **S15** in DCM (~6 mL/mmol **S15**) at –78 °C. After the reaction mixture was stirred for 4 h at the same temperature, 1 M HCl(*aq*) solution was added before extracting with DCM. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to silica gel column chromatography to purify the corresponding **S16** compound (hexane-EtOAc; yields of **S16**: R^1= Bu, R^2= H, 1.12 g, 95%; R^1= Bu, R^2= Cy, 1.1 g, 94%; R^1= Cy, R^2= Me, 1.55 g, 95%; R^1= *t*-Bu, R^2= Me, 1.39 g, 95%; R^1= Bu, R^2= *t*-Bu, 1.6 g, 90%; R^1= Ph, R^2= Me, 1.6 g, 92%, R^1= H, R^2= Me %85), (Kajikawa, *et al.* 2009).

The epoxidation of **S16** (2 mmol) and isolation of the corresponding **S17** products were performed as specified for (*Z*)-**1a** (yields of **S17**: R^1= Bu, R^2= H, 0.19 g, 55%; R^1= Bu, R^2= Cy, 0.26 g, 49%; R^1= Cy, R^2= Me, 0.25 g, 57%; R^1= *t*-Bu, R^2= Me, 0.25 g, 65%; R^1= Bu, R^2= *t*-Bu, 0.24 g, 50%; R^1= Ph, R^2= Me, 0.26 g, 60%, R^1= H, R^2= Me %60).

3.2.4. Synthesis of (Z)-1d, e, f, g, h

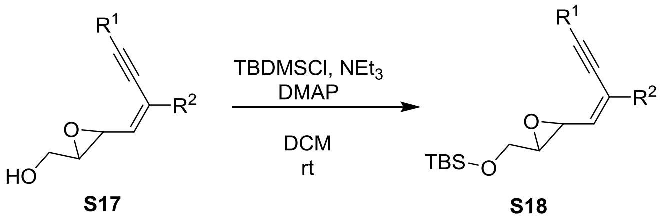


1d: R^1= Me, R^2= Me
1e: R^1= Ph, R^2=Me
1g: R^1= Bu, R^2= t-Bu
1h: $R^{1=}$ Bu, R^2= Cy

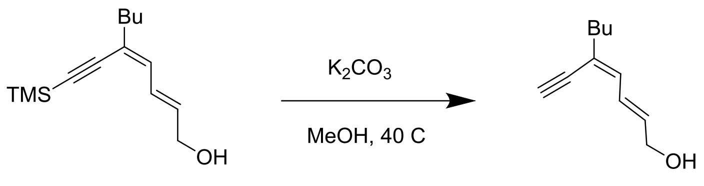
1f: R^1= Bu, R^2= Me

As for the alkylation of the pendant hydroxyl group of **S17**, a suspension of sodium hydride (1.1 eq) in DMF (1 mL) was added to a solution of **S17** (1 mmol) in DMF (1 mL/mmol **S17**) at -20 °C. The mixture was stirred for further 30 min before the addition of methyl iodide (1.2 eq) or benzyl bromide (1.2 eq). 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-pretreated short silica gel column to afford the corresponding alkoxy-substituted enyne oxirane products as colorless oil (hexane-EtOAc, yields: (*Z*)-**1d**, 85%; (Z)-**1e**, %84; (*Z*)-**1f**, 83%; (*Z*)-**1g**, 87%; (*Z*)-**1h**, 83%), (Caldentey, *et al.* 2011).

3.2.5. Synthesis of (Z)-1i, j, k, l, m, n, o, p, r

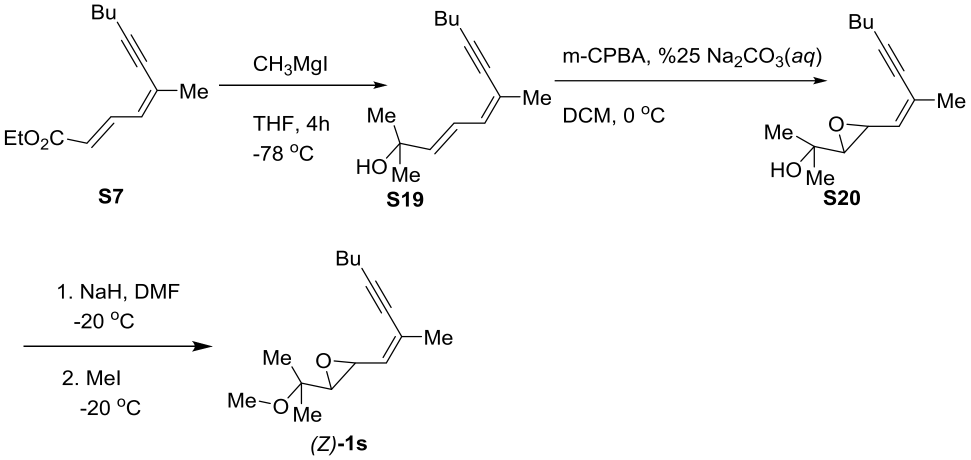


(*Z*)-**1i;** R^1= *t*-Bu, R^2= Me
(*Z*)-**1j;** R^1 = H, R^2= Me
(*Z*)-**1k;** R^1 = TMS, R^2= Bu
(*Z*)-**1l;** R^1 = H, R^2= Bu
(*Z*)-**1m;** R^1 = Cy, R^2= Me
(*Z*)-**1n;** R^1 = Bu, R^2= H
(*Z*)-**1o;** R^1= Bu, R^2= Me
(*Z*)-**1p;** R^1= *t*-Bu, R^2= Bu
(*Z*)-**1r;** R^1= Bu, R^2= Bu



A pendant hydroxyl group of **S17** (0.9 – 0.12 mmol), *t*-butyldimethylsilyl chloride (0.2 g, 1.3 mmol), and 4-dimethylaminopyridine (DMAP) (15 mg, 0.12 mmol) in CH_2Cl_2 (12 mL) was stirred at RT for 24 h. Then, the reaction was terminated by water and the content of the reaction flask was extracted with DCM. The organic solution was dried with $MgSO_4$, filtered, and evaporated. The residue was chromatographed over NEt_3-pretreated short silica gel column to afford silylated enyne oxiranes as a colorless oil (hexane-EtOAc, yields: (*Z*)-**1i**, 70%; (*Z*)-**1j,** 83%; (Z)-**1k**, 86%; (Z)-**1l**, 73%, (Z)-**1m**, 78%, (Z)-**1n**, 80%, (*Z*)-**1o**, 79%, (Z)-**1p**, 72%, (*Z*)-**1r**, 74%. (Schmidt, *et al.* 2002).

3.2.6. Synthesis of (Z)-1s

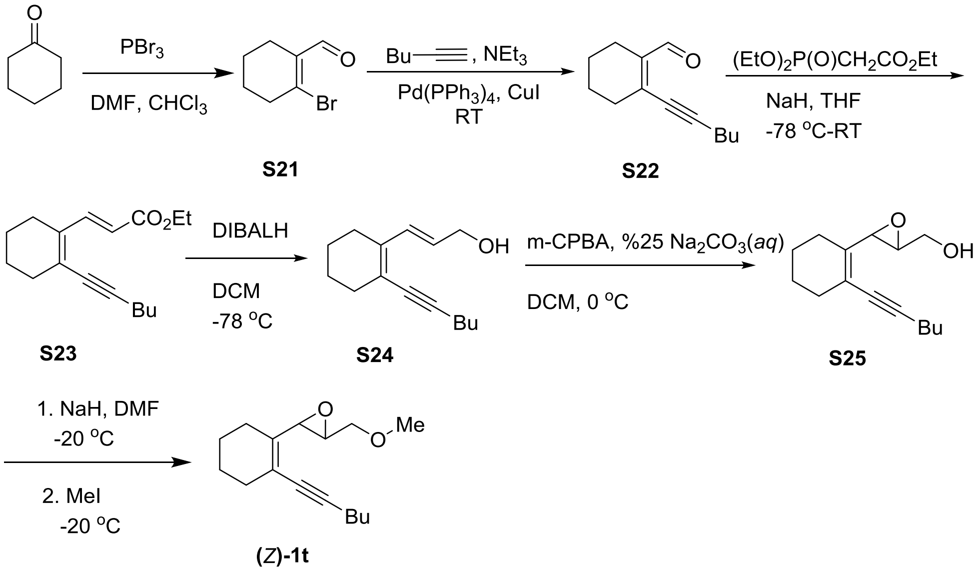


To the dry Et_2O (15 mL) solution of **S7** (1.1 g, 5 mmol) was added an ethereal (15 mL) solution of 2.1 eq. MeMgI (5.25 mL, 10.5 mmol, 2 M) dropwise at -50 °C, and then the mixture stirred for 6 h at the same temperature. The mixture was allowed to warm to 0 °C and quenched by the addition of 30 mL of saturated NH_4Cl(*aq*) solution before extracting with Et_2O. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The resulting residue was purified on a silica gel column to afford **S19** (hexane-EtOAc, yield: 0.49 g, 80%).

The epoxidation of **S19** (412 mg, 2 mmol), and isolation of the product **S20** was performed (hexane-EtOAc, yield: 0.27 g, 60%).

The hydroxyl group of **S20** (222 mg, 1.0 mmol) was methylated as described above furnishing the enyne oxirane (*Z*)-**1s** in 90% yield (0.21 g).

3.2.7. Synthesis of (Z)-1t

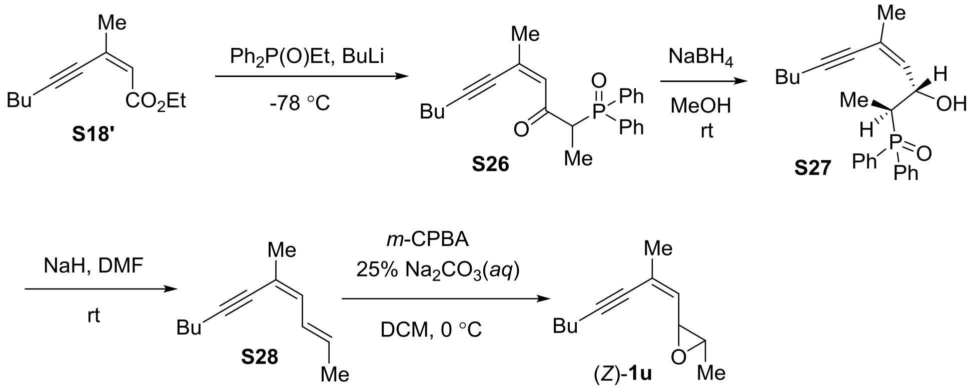


PBr$_3$ (1.4 mL, 13.8 mmol) was added dropwise to a mixture of DMF (1.2 mL, 15.3 mmol) and chloroform (10 mL) at 0 °C and then the resulting mixture was stirred for 1 h. Subsequently, 0.5 g of cyclohexanone (6 mmol) was added dropwise and stirred for 8 h, at RT. The reaction was terminated with water, neutralized with the addition of solid NaHCO$_3$, and extracted with DCM. The extract was washed with brine, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The purification on short silica gel column provided the compound **S21** (hexane-EtOAc, 0.92 g, 81%), (Lian, *et al.* 2006).

A mixture of **S21** (945 mg, 5 mmol), Pd(PPh$_3$)$_4$ (123 mg, 0.1 mmol, 2 mol % of Pd), and CuI (21 mg, 0.1 mmol, 2 mmol % of Cu) in 10 mL of Et$_3$N was stirred for 10 min at RT followed by the addition of 1-hexyne (0.5 g, 6 mmol). After being stirred for 3 h, at RT, water was added and extracted with Et$_2$O. The combined organic phases were dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain endocyclic enyne aldehyde **S22** (hexane-EtOAc, 0.84 g, 90%), (Lian, *et al.* 2006).

The conversion of **S22** (840 mg, 4.42 mmol) to dienyne ester **S23** was performed by HWE reaction as described above (hexane-EtOAc, 0.96 g, 84%). Further successive synthetic procedures; which involved the reduction of the ester **S23** (960 mg, 3.7 mmol) to the enyne alcohol **S24** (730 mg, 91% yield), the epoxidation of **S24** (436 mg, 2 mmol) to **S25** (260 mg, 55% yield), and finally methyl derivatization of hydroxyl group of **S25** (260 mg, 1.1 mmol) to obtain (*Z*)-**1t** (0.22 g, 90%) were all conducted as described above.

3.2.8. Synthesis of (Z)-1u



To a stirred solution of diphenylethylphosphine oxide (4.6 g, 20 mmol) in dry THF (70 mL) was added BuLi (2.5 M in hexane, 8.8 mL, 22 mmol) dropwise at 0 °C and stirred for a further 30 min. The solution was cooled to -78 °C and then the dienyne ester **S18'** (3.88 g, 20 mmol) was added dropwise. The solution was allowed to warm to ambient temperature and subsequently stirred overnight. Saturated NH_4Cl(*aq*) solution was added and subsequently its THF content was removed under reduced pressure. The aqueous residue was diluted with brine (20 mL) and extracted with DCM. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product **S26** was purified by column chromatography on silica gel (hexane-EtOAc, yield: 1.9 g, 25%), (Buss, *et al.* 1985).

To a stirred solution of **S26** (1.9 g, 5 mmol) in ethanol (50 mL) was added $NaBH_4$ (189 mg, 5 mmol) in one portion and stirred for a further 8h at ambient temperature. The reaction afforded **S27** enriched in *threo* form. Saturated NH_4Cl(*aq*) (15 mL) was added and subsequently its ethanol content was removed under reduced pressure. The aqueous mixture was diluted with brine (20 mL), extracted with DCM. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product **S27** was isolated in pure *threo* form by column chromatography on silica gel (hexane-EtOAc, yield: 1.31 g, 69%), (Buss, *et al.* 1985).

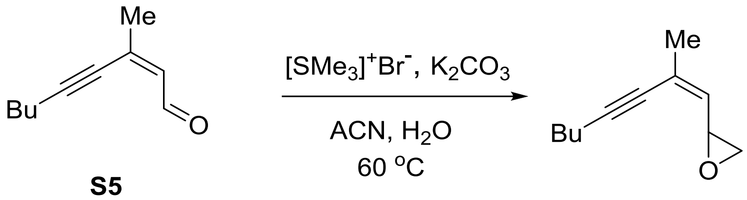
To a stirred solution of **S27** (1.31 g, 3.45 mmol) in DMF (50 ml) was added NaH (60% dispersion in oil; 138 mg, 3.45 mmol) in one portion at ambient temperature and stirred for a further 3 h. The reaction was quenched by the addition 25 mL of water and 15 mL of brine and subsequently extracted with Et_2O. The combined extracts were washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product **S28** was purified by column chromatography on silica gel (hexane, yield: 330 mg, 59%), (Buss, *et al.* 1985).

The epoxidation of **S28** (162 mg, 1 mmol) and isolation of the product (*Z*)-**1u** was performed (Hexane-EtOAc, yield: 35.6 mg, 20%).

3.2.9. Synthesis of (*E*)-1b

Synthesis of (*E*)-**1b** was performed starting from (*E*)-configured **S1** following the same method employed for the synthesis of (*Z*)-**1b**. Yields: (R^1= Bu, R^2= Me): (*E*)-**S7**, 1.12 g, 79%; (*E*)-**S17**, 0.83 g, 91%; (produced from 4.6 mmol of (*E*)-**S8**), 0.43 g, 47%; (*E*)-**1b** (produced from 2.2 mmol of (*E*)-**S17**), 0.40 g, 88%.

3.2.10. Synthesis of (Z)-1v



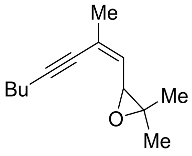
S5

(Z)-1v

A mixture of 3 mmol (471 mg) trimethylsulfonium bromide, 12 mmol (1.65 g) of K_2CO_3 and 0.48 mmol (8.64 mg) H_2O in 5 ml of acetonitrile was stirred for 5 min at 60 oC. With vigorous stirring, a solution of 2 mmol (300 mg) S5 in 3 ml of acetonitrile was added dropwise and stirred for further 2h at 60 ^{o}C. After cooling to room temperature, the mixture was filtered and 50 ml of Et_2O was added to filtrate and filtered again. After washing of filtrate with pentane, solvent was removed in vacuum. The crude mixture was chromatographed on NEt_3-pretreated short silica gel column which afforded the enyne oxirane (Z)-**1v** as a colorless oil (hexane-EtOAc, yield: 82 mg, 25%) (Purpura and Krause, 1999).

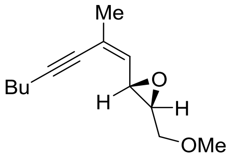
3.3. Characterization of Reactants

NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si.



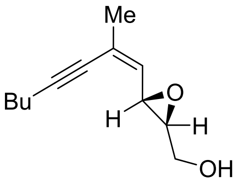
(Z)-**1a**

(*Z*)-**1a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.38 (dq, *J*= 8.9, 1.5 Hz, 1H), 3.65 (d, *J*= 8.9 Hz, 1H), 2.34 (t, *J*= 6.8 Hz, 2H), 1.87 (s, 3H), 1.56-1.36 (m, 4H), 1.35 (s, 3H), 1.27 (s, 3H), 0.9 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 130.7, 125.5, 95.9, 79.1, 62.6, 60.5, 30.9, 24.9, 24.2, 22.1, 19.6, 19.3, 13.7.



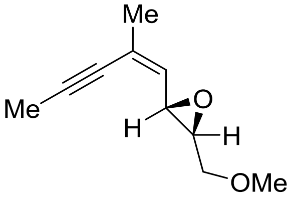
(Z)-**1b**

(*Z*)-**1b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.23 (dd, *J*= 8.9, 1.2 Hz, 1H), 3.74 (dd, *J*= 8.9, 2.4 Hz, 1H), 3.71 (dd, *J*= 11.6, 3.2 Hz, 1H), 3.40 (dd, *J*= 11.6, 5.7 Hz, 1H), 3.40 (s, 3H), 3.08 (ddd, *J*= 5.7, 3.2, 2.4 Hz, 1H), 2.35 (t, *J*= 7.2 Hz, 2H), 1.87 (d, *J*= 1.2 Hz, 3H), 1.55-1.40 (m, 4H), 0.92 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.5, 125.7, 95.9, 78.7, 72.5, 59.2, 58.3, 54.2, 30.7, 23.8, 21.9, 19.1, 13.6.



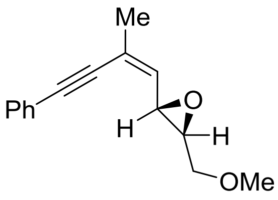
(Z)-**1c**

(Z)-**1c**: 1H NMR (400 MHz, CDCl3) δ: 5.25 (dd, J= 9.0, 1.4 Hz, 1H), 3.96 (dd, J= 12.6, 2.3 Hz, 1H), 3.87 (dd, J= 9.0, 2.3 Hz, 1H), 3.68 (dd, J= 12.6, 4.1 Hz, 1H), 3.11-3.09 (m, 1H), 2.36 (t, J= 7.0 Hz, 2H), 1.88 (d, J= 1.4 Hz, 3H), 1.56-1.39 (m, 4H), 0.92 (t, J= 7.2 Hz, 3H); 13C{1H} NMR (100 MHz, C6D6) δ: 132.5, 124.8, 95.7, 79.1, 61.1, 59.5, 53.7, 30.6, 23.5, 21.8, 19.0, 13.3.



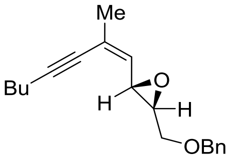
(Z)-**1d**

(Z)-**1d**: 1H NMR (400 MHz, CDCl3) δ: 5.23 (d, J=9.0 Hz, 1H), 3.74-3.73 (m, 1H), 3.71 (t, J=4.0 Hz, 1H), 3.41 (s, 3H), 3.40 (dd, J=12.0, 8.0 Hz, 1H), 3.08 (ddd, J=5.7, 3.1, 2.2 Hz, 1H), 2.0 (s, 3H), 1.87 (d, J=1.6 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 131.6, 125.8, 91.3, 77.8, 72.6, 59.2, 58.4, 54.1, 23.8.



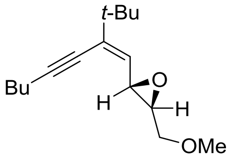
(Z)-**1e**

(*Z*)-**1e:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.44 (m, 2H), 7.34-7.32 (m, 3H), 5.38 (dq, *J*= 9.0, 1.5 Hz, 1H), 3.84 (dd, *J*= 9.0, 2.4 Hz, 1H), 3.74 (dd, *J*= 11.7, 3.2 Hz, 1H), 3.43 (dd, *J*= 11.7, 6.0 Hz, 1H), 3.42 (s, 3H) 3.14 (ddd, *J*= 6.0, 3.2, 2.4 Hz, 1H), 2.00 (d, *J*= 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.1, 131.5, 128.5, 128.3, 124.9,122.9, 94.5, 87.3, 72.5, 59.2, 58.5, 54.1, 23.4.



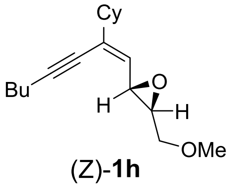
(Z)-**1f**

(Z)-**1f:** ^{1}H NMR (400 MHz, C_6D_6) δ: 7.24−7.22 (m, 2H), 7.14− 7.10 (m, 2H), 7.05 (dt, J = 7.2, 1.6 Hz, 1H), 5.14 (dd, J = 8.9, 1.6 Hz, 1H), 4.35 (d, A of AB, J_{AB} = 12.1 Hz, 1H), 4.31 (d, B of AB, J_{AB} = 12.1 Hz, 1H), 4.01 (dd, J = 8.9, 2.2 Hz, 1H), 3.45 (dd, J = 11.4, 3.0 Hz, 1H), 3.25 (dd, J = 11.4, 5.5 Hz, 1H), 2.95 (ddd, J = 5.5, 3.0, 2.2 Hz, 1H), 2.06 (t, J = 6.8 Hz, 2H), 1.71 (d, J = 1.6 Hz, 3H), 1.29−1.16 (m, 4H), 0.7 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ: 138.5, 132.8, 128.2, 127.4, 127.3, 124.8, 95.5, 79.1, 72.8, 70.0, 58.2, 53.8, 30.6, 23.5, 21.8, 18.9, 13.3.



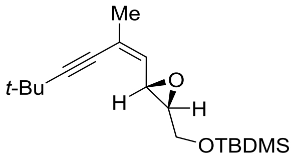
(Z)-**1g**

(*Z*)-**1g:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.24 (d, *J*= 8.9 Hz, 1H), 3.81 (dd, *J*= 8.9, 2.4 Hz, 1H), 3.74 (dd, *J*= 11.2, 3.1 Hz, 1H), 3.42-3.38 (m, 1H), 3.41 (s, 3H), 3.10 (ddd, *J*= 5.6, 3.1, 2.4 Hz, 1H), 2.39 (t, *J*= 7.2 Hz, 2H), 1.59-1.41 (m, 4H), 1.11 (s, 9H), 0.93 (t, *J*= 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 140.2, 127.4, 97.4, 72.7, 59.2, 58.5, 54.7, 36.1, 30.8, 28.9, 21.9, 19.2, 13.6.



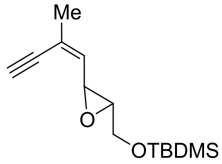
(Z)-**1h**

(*Z*)-**1h:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.21 (d, *J*= 8.7 Hz, 1H), 3.77 (dd, *J*= 8.7, 2.4 Hz, 1H), 3.72 (dd, *J*= 11.5, 3.1 Hz, 1H), 3.38 (dd, *J*= 11.5, 5.7 Hz, 1H), 3.40 (s, 3H), 3.07 (dt, *J*= 5.7, 2.4 Hz, 1H), 2.37 (t, *J*= 7.2 Hz, 2H), 2.02-1.97 (m, 1H), 1.76-1.20 (m, 14H), 0.92 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 136.3, 129.1, 97.0, 76.7, 72.6, 59.2, 58.5, 54.3, 45.4, 31.7, 31.6, 30.8, 29.7, 26.2, 26.0, 22.0, 19.2, 13,6.



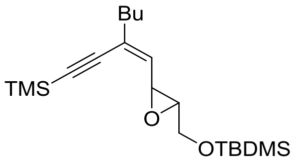
(Z)-**1i**

(*Z*)-**1i:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.21 (d, *J*= 9.0 Hz, 1H), 3.87 (dd, *J*= 12.0, 3.2 Hz, 1H), 3.74 (m, 2H), 3.01 (m, 1H), 1.86 (s, 3H), 1.26 (s, 9H), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR: (100 MHz, CDCl$_3$) δ: 131.6, 125.3, 103.8, 77.1, 62.9, 60.2, 54.3, 31.0, 28.1, 25.9, 23.9, 18.3, -5,3.



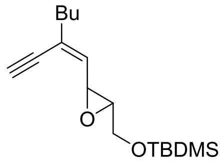
(Z)-**1j**

(*Z*)-**1j:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.41 (dq, J= 8.8, 0.8 Hz, 1H), 3.88 (dd, J=12.1, 3.1 Hz, 1H), 3.80 (dd, J= 9.0, 2.0 Hz, 1H), 3.72 (dd, J= 12.1, 4.7 Hz, 1H), 3.19 (s, 1H), 3.06-3.03 (m, 1H), 1.91 (d, J=1.2 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C NMR: (100 MHz, CDCl$_3$) δ: 135.4, 123.5, 82.2, 81.7, 62.9, 60.1, 54.0, 25.9, 23.2, 18.3, -5.3.



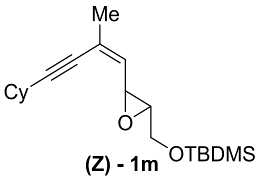
(Z)-**1k**

(*Z*)-**1k:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.32 (dt, J=9.1, 2.0 Hz, 1H), 3.88 (dd, J=12.1, 3.1 Hz, 1H), 3.81 (dd, J=9.2, 2.2 Hz, 1H), 3.75 (dd, J= 11.7, 4.3 Hz, 1H), 3.03-3.01 (m, 1H), 2.14 (td, J= 7.4, 1.2 Hz, 2H), 1.53-1.43 (m, 2H), 1.36-1.27 (m, 2H), 0.90 (s, 9H), 0.90 (t, J=7.6 Hz, 3H), 0.20 (s, 9H), 0.09 (s, 6H). ^{13}C NMR: (100 MHz, CDCl$_3$) δ: 133.8, 129.6, 100.2, 62.8, 60.3, 54.1, 36.8, 30.1, 25.9, 21.9, 18.3, 13.8, 0.1, -5.3.



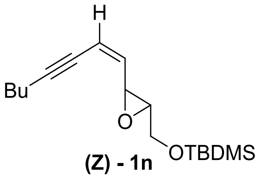
(Z)-**1l**

(*Z*)-**1l:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.40 (d, J=9.4 Hz, 1H), 3.90 (dd, J=12.1, 3.1 Hz, 1H), 3.82 (dd, J=9.0, 2.0 Hz, 1H), 3.72 (dd, J= 12.0, 4.5 Hz, 1H), 3.19 (d, 0.8 Hz, 1H), 3.06-3.04 (m, 1H), 2.16 (t, J=7.8 Hz, 2H), 1.55-1.47 (m, 2H), 1.37-1.27 (m, 2H), 0.90 (s, 9H), 0.90 (t, J=7.6 Hz, 3H), 0.08 (s, 6H). ^{13}C NMR: (100 MHz, CDCl$_3$) δ: 134.8, 128.6, 82.7, 81.1, 63.0, 60.2, 54.0, 36.7, 30.0, 25.9, 22.0, 18.3, 13.8, -5.3.



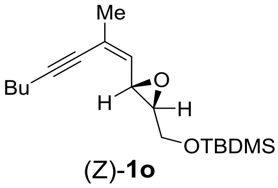
(Z) - 1m

(*Z*)-**1m:**^{1}H NMR (400 MHz, $CDCl_3$) δ: 5,23 (dd, J = 1,6, 9,0 Hz, 1 H), 3,88 (dd, J = 3,1, 12,1 Hz, 1 H), 3,79 (dd, J = 2,2, 9,2 Hz, 1 H), 3,73 (dd, J = 4,5, 11,9 Hz, 1 H), 3,02 (s, 1 H), 2,57 - 2,48 (m, 1 H), 1,88 (d, J = 1,6 Hz, 3 H), 1,86 - 1,78 (m, 2 H), 1,76 - 1,65 (m, 2 H), 1,56 - 1,43 (m, 3 H), 1,32 (br, s, 3 H), 0,91 (s, 9 H), 0,08 (d, J = 1,6 Hz, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 131,7, 125,3, 99,7, 78,6, 62,9, 62,9, 60,1, 54,3, 32,7, 29,7, 25,9, 24,8, 23,9, 18,3, -5,3, -5,3.



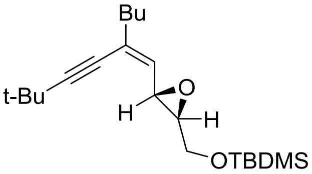
(Z) - 1n

(*Z*)-**1n:** ^{1}H NMR (400MHz, $CDCl_3$) δ: 5,73 (dtd, J = 0,8, 2,3, 10,6 Hz, 1H), 5,45 (dd, J = 9,0, 11,0 Hz, 1H), 3,91 (dd, J = 2,7, 12,1 Hz, 1H), 3,86 (dd, J = 1,6, 9,0 Hz, 1H), 3,74 (dd, J = 4,3, 11,7 Hz, 1H), 3,08 - 3,04 (m, 1H), 2,35 (dt, J = 2,2, 7,1 Hz, 2H), 1,52 (s, 2H), 1,42 (d, J = 7,0 Hz, 2H), 0,92 (t, J = 7,2 Hz, 3H), 0,91 (s, 9 H), 0,09 (d, J = 2,3 Hz, 6H). ^{13}C NMR (101 MHz $CDCl_3$) δ: 137,6, 115,0, 96,9, 76,1, 62,8, 60,1, 53,4, 30,7, 25,9, 22,0, 19,2, 13,6, -5,3, -5,3.



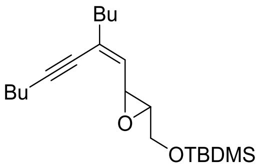
(Z)-**1o**

(*Z*)-**1o:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.22 (dd, *J*= 9.1, 1.5 Hz, 1H), 3.86 (dd, *J*= 12.1, 3.2 Hz, 1H), 3.76 (dd, *J*= 9.1, 2.4 Hz, 1H), 3.71 (dd, *J*= 12.1, 4.8 Hz, 1H), 3.00 (ddd, *J*= 4.8, 3.2, 2.4 Hz, 1H), 2.33 (t, *J*= 7.2 Hz, 2H), 1.86 (d, *J*= 1.5 Hz, 3H), 1.56-1.37 (m, 4H), 0.91 (t, *J*= 6.8 Hz, 3H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 131.9, 125.3, 95.7, 78.7, 63.0, 60.1, 54.3, 30.8, 25.8, 23.8, 22.0, 19.1, 18.3, 13.6, -5.3, -5.4.



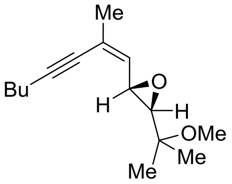
(Z)-**1p**

(*Z*)-**1p:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.21 (d, *J*= 9.0 Hz, 1H), 3.87 (dd, *J*= 12.0, 3.2 Hz, 1H), 3.74 (m, 2H), 3.01 (m, 1H), 1.86 (s, 3H), 1.26 (s, 9H), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ: 131.6, 125.3, 103.8, 77.1, 62.9, 60.2, 54.3, 31.0, 28.1, 25.9, 23.9, 18.3, -5,3.



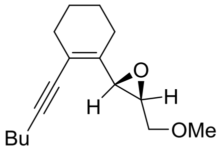
(Z)-**1r**

(*Z*)-**1r:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.23 (d, J= 9.4 Hz, 1H), 3.89 (dd, J=12.1, 3.1 Hz, 1H), 3.80 (dd, J= 9.0, 2.3 Hz, 1H), 3.71 (dd, J=11.9, 4.5 Hz, 1H), 3.02 (dt, J=4.8, 2.5 Hz, 1H), 2.35 (t, J=7.0 Hz, 2H), 2.12 (t, J=7.4 Hz, 2H), 1.54-1.38 (m, 6H), 1.35-1.26 (m, 2H), 0.93 (t, J=7.6 Hz, 3H), 0.91 (s, 9H), 0.90 (t, J= 7.4 Hz, 3H), 0.09 (s, 6H). ^{13}C NMR: (100 MHz, CDCl$_3$) δ: 131.2, 130.4, 96.2, 78.0, 63.1, 60.2, 54.3, 37.3, 30.8, 30.2, 25.8, 22.0, 19.2, 18.3, 13.9, 13.6, -5.3.



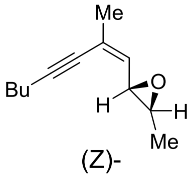
(Z)-**1s**

(*Z*)-**1s:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.24 (dd, *J*= 8.9, 1.5 Hz, 1H), 3.69 (dd, *J*= 8.9, 2.3 Hz, 1H), 3.29 (s, 3H), 2.87 (d, *J*= 2.3 Hz, 1H), 2.36 (t, *J*= 6.7 Hz, 2H), 1.87 (d, *J*= 1.5 Hz, 3H), 1.56-1.39 (m, 4H), 1.18 (s, 3H), 1.15 (s, 3H), 0.92 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 132.2, 125.3, 95.8, 79.0, 74.0, 64.9, 53.4, 50.9, 30.9, 23.9, 22.4, 22.0, 21.1, 19.2, 13.7.



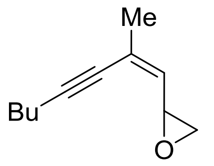
(*Z*)-**1t**

(*Z*)-**1t:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.00-3.97 (m, 1H), 3.73 (dt, *J*= 11.2, 2.8 Hz, 1H), 3.45-3.30 (m, 4H), 3.20 (sext, *J*= 2.8 Hz, 1H), 2.34 (t, *J*= 6.8 Hz, 2H), 2.21-2.10 (m, 2H), 2.02-1.91 (m, 2H), 1.79-1.32 (m, 6H), 0.98-0.79 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3, 121.7, 94.2, 79.5, 73.1, 59.2, 56.2, 55.2, 30.9, 30.8, 22.4, 22.2, 21.9, 21.7, 19.2, 13.6.



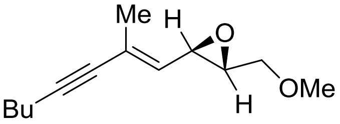
(Z)-
1u

(*Z*)-**1u:** ^{1}H NMR (400 MHz, C_6D_6) δ: 5.16 (dd, *J*= 8.9, 1.4 Hz, 1H), 3.75 (dd, *J*= 8.9, 2.1 Hz, 1H), 2.64 (qd, *J*= 5.4, 2.1 Hz, 1H), 2.08 (t, *J*= 6.8 Hz, 2H), 1.73 (d, *J*= 1.4 Hz, 3H), 1.31-1.20 (m, 4H), 1.04 (d, *J*= 5.2 Hz, 3H), 0.72 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ: 133.7, 123.9, 95.2, 79.3, 57.4, 55.2, 30.6, 23.4, 21.8, 19.0, 17.3, 13.2.



(Z)-**1v**

(*Z*)-**1v:** ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.18 (dd, J=9.0, 1.6 Hz, 1H), 3.84 (ddd, J=9.0, 4.3, 2.7 Hz, 1H), 3.00 (dd, J=5.1, 4.3 Hz, 1H), 2.67 (dd, J=5.1, 2.7 Hz, 1H), 2.36 (t, J=7.2 Hz, 2H), 1.88 (d, J=1.6 Hz, 3H), 1.58-1.50 (m, 2H), 1.48-1.39 (m, 2H), 0.92 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 132.5, 125.5, 95.7, 78.7, 50.7, 48.7, 30.8, 23.8, 22.0, 19.1, 13.6.



(*E*)-**1b**

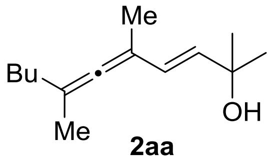
(*E*)-**1b:** (400 MHz, CDCl$_3$) δ: 5.35 (dd, *J*= 9.0, 1.0 Hz, 1H), 3.67 (dd, *J*= 11.3, 3.0 Hz, 1H), 3.48 (dd, *J*= 9.0, 2.2 Hz, 1H), 3.44 (dd, *J*= 11.3, 5.1 Hz, 1H), 3.38 (s, 3H), 3.06 (ddd, *J*= 5.1, 3.0, 2.2 Hz, 1H), 2.28 (t, *J*= 6.8 Hz, 2H), 1.93 (d, *J*= 1.0 Hz, 3H), 1.54-1.37 (m, 4H), 0.90 (t, *J*= 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 131.3, 125.2, 90.3, 82.4, 80.0, 59.2, 58.6, 51.9, 30.7, 21.9, 18.9, 18.2, 13.6.

3.4. General Procedure for Iron Catalysed with Grignard Reagents Reactions

$FeCl_2$ was weighed into a Schlenck apparatus in glow box, then a gas balloon filled with dry Ar gas (the gas was passed through a P_2O_5 filled glass tube) was attached. THF (2 mL) was added and then stirred for 15 minutes magnetically at a prescribed reaction temperature. The Grignard Reagent was added drop by drop and the reaction mixture was stirred approximately 15 minutes before the addition of the substrate. The reaction was initiated by the addition of the enynye oxirane drop-wise in 1 mL of THF When the reaction progress is complete as judged by TLC analysis, the excess Grignard was neutralized with saturated $NH_4Cl_{(aq)}$, extracted with diethyl ether and dried over $MgSO_4$. The solvent content was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the product as a pale-yellow oil.

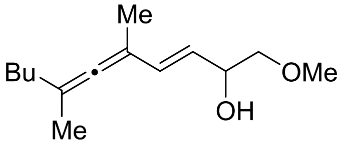
3.5. Characterization of Products

The synthesized alkylation products were analyzed by GC-MS. NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si. Infrared spectra were obtained by ATR method with neat samples. High-resolution mass spectral analyses of new compounds were performed using EI-High Resolution Double Focusing Magnetic Sector (ionization mode: 70 eV, emission current: 1 mA, source temperature: 160 °C, resolution: 10,000 (10% valley definition)) and ESI-LTQ Orbitrap (source voltage: +3.8 kV, capillary voltage: 41 V, capillary temperature: 275 °C, tube lens voltage: 140 V, system resolution: 60,000 (10% valley definition)). The coupling constants of olefinic protons and NOE studies confirmed (*E*)-configured structures. ^1H NMR analyses of vinylallene products, were performed in C_6D_6. With this solvent, the ^1H NMR signals of diastereomers were resolved adequately, allowing to determine diastereomeric ratios smoothly. In contrast, when using $CDCl_3$ solvent, diastereomeric signals were all overlapped.



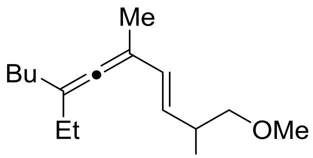
2aa

2aa: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.45 (d, J=16.0 Hz, 1H), 5.64 (d, J= 15.6 Hz, 1H), 1.94 (dt, J= 7.4, 3.6 Hz, 2H), 1.86 (s, 3H), 1,68 (s, 3H), 1.43 (sextet, J= 7.2 Hz, 2H), 1.30 (sextet, J=7.2 Hz, 2H), 1.19 (s, 6H), 0.94 (bs, 1H), 0.86 (t, J=7.4 Hz, 3H) ; ^{13}C NMR (101 MHz, C_6D_6) δ: 204.9, 136.0, 126.8, 99.1, 98.8, 70.5, 34.3, 30.2, 30.2, 30.1, 22.6, 19.2, 16.2, 14.1; MS (EI, m/z): 208 (<5, M$^+$), 166(15), 123(35), 107(80), 93(75), 59(70), 43(100); FTIR (ν_{max}/cm^{-1}): 3349, 2968, 2934, 2868, 1458, 1367, 1251, 1151, 969, 903.



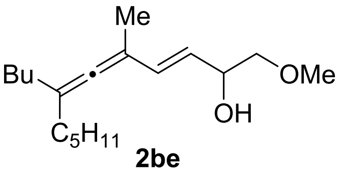
2ba

2ba: ^{1}H NMR (400 MHz,C_6D_6) δ: 6.52 (dd, J = 15.9, 1.2 Hz, 1H) (Major), 6.51 (dd, J = 15.9, 1.2 Hz, 1H) (Minor), 5.50 (dd, J = 15.9, 6.0 Hz, 1H), 4.30 (dddd, J = 7.8, 6.0, 4.0, 1.2 Hz, 1H), 3.11 (dd, A of ABX, J_{AB} = 17.4 Hz, J_{AX} = 4.0 Hz, 1H), 3.06 (dd, B of ABX, J_{AB} = 17.4 Hz, J_{BX} = 7.8 Hz, 1H), 2.96 (s, 3H) (Major), 2.97 (s, 3H) (Minor), 2.02 (bs, 1H), 1.86 (t, J = 7.2 Hz, 2H), 1.79 (s, 3H), 1.60 (s, 3H) (Major), 1.59 (s, 3H) (Minor), 1.41-1.20 (m, 4H), 0.81 (t, J = 7.2 Hz, 3H) (Major), 0.82 (t, J = 7.2 Hz, 3H) (Minor); ^{13}C NMR (101 MHz ,C_6D_6) δ: 204.8, 131.4, 126.3 (Minor), 126.2 (Major), 98.9, 98.6, 76.9 (Minor), 76.8 (Major), 71.0 (Major) 71.0 (Minor), 58.2, 33.9, 29.7, 22.3, 18.8, 15.8, 13.8; MS (EI, *m/z*): 224 (<1, M$^+$), 179(20), 137(50), 123(65), 107(100), 95(80), 81(50), 67(55), 43(759; FTIR (ν_{max}/cm^{-1}): 3471, 2970, 2922, 2853, 1705, 1597, 1480, 1283, 1156, 842, 793, 627.



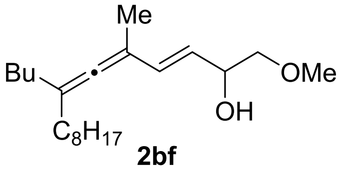
2bb

2bb: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.51 (dd, J=15.8, 1.2 Hz, 1H), 5.50 (dd, J=14.8, 6.0 Hz, 1H), 4.32-4.24 (m, 1H), 3.13-3.02 (m, 2H), 2.96 (s, 3H), 2.17 (bs, 1H), 1.91-1.83 (m, 4H), 1.80 (s, 3H), 1.43-1.21 (m, 4H), 0.98 (t, J=7.2 Hz, 3H) (Major), 0.97 (t, J=7.6 Hz, 3H, (Minor)), 0.83 (t, J=7.6 Hz, 3H) (Minor), 0.82 (t, J=7.6 Hz, 3H) (Major); ^{13}C NMR (101 MHz ,C_6D_6) δ: 204.2, 131.5, 126.1, 105.8, 101.1, 76.9, 71.1, 58.2, 32.6, 29.9, 25.9, 22.4(Minor), 22.4 (Major) 15.8, 13.8, 12.3 ; MS (EI, *m/z*): 238 (<5, M$^+$), 220(5), 193(45), 175(25), 151(45), 133(40), 121(90), 109(100), 91(60), 55(50), 45(55); FTIR (ν_{max}/cm^{-1}): 3441, 2921, 2853, 1460, 1382, 1097, 960, 734, 695



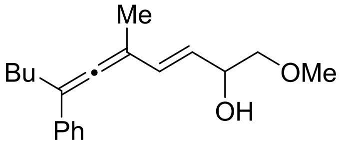
2be

2be: ^{1}H NMR (400MHz, C_6D_6) δ: 6.57 (dt, J = 15.8, 1.5 Hz, 1H), 5.55 (dd, J = 15.8, 6.1 Hz, 1H), 4.39 - 4.31 (m, 1H), 3.16 (dd, A of ABX, JAB = 9.4 Hz, JAX = 3.5 Hz, 1H), 3.12 (dd, B of ABX, JAB = 9.4 Hz, JBX = 8.3 Hz, 1H), 3.01 (s, 3H), 2.32 (br. s., 1H), 1.96 (t, J = 7.6 Hz, 4H), 1.85 (s, 3H), 1.53 - 1.40 (m, 4H), 1.38 - 1.23 (m, 6H), 0.89 (dquin, J = 7.6, 3.6, 3.6, 3.6, 3.6 Hz, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ: 204.4, 131.4, 126.2, 103.6, 100.4, 76.9, 71.0, 58.2, 32.8 (Major), 32.8 (Minor), 32.6 (Minor), 32.6 (Major), 31.5 (Major), 31.5 (Minor) 29.9, 27.4, 22.5, 22.4, 15.7, 14.0, 13.8; MS (EI, *m/z*): 280 (<5, M$^+$), 235(30), 205(15), 179(30), 149(60), 119(359, 109(95), 93(95), 81(75), 55(80), 43(100); FTIR (ν_{max}/cm^{-1}): 3422, 2911, 2853, 1705, 1460, 1264, 1097, 842, 783, 685.



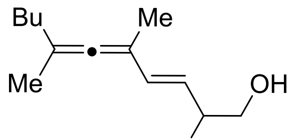
2bf

2bf: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.58 (dt, *J*=15.7, 1.76 Hz, 1H), 5.55 (dd, *J*=15.7, 6.06 Hz, 1H), 4.38 - 4.32 (m, 1H), 3.16 (dd, A of ABX, J_{AB} = 9.4 Hz, J_{AX} = 3.6 Hz, 1H), 3.12 (dd, B of ABX, J_{AB} = 9.4 Hz, J_{BX} = 7.9 Hz, 1H), 3.01 (s, 3H), 2.29 (br. s., 1H), 1.95 - 2.02 (m, 4H), 1.86 (s, 3H), 1.54 - 1.23 (m, 16H) 0.94 - 0.86 (m, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ: 204.5, 131.4, 126.1, 103.6, 100.4, 76.9, 71.0 (Major), 71.0 (Minor), 58.2, 32.9 (Minor), 32.9 (Major), 32.6 (Major), 32.6 (Minor), 31.9, 29.9, 29.6, 29.4, 29.4, 27.8, 22.7, 22.4, 15.7, 14.0, 13.8; MS (EI, *m/z*): 322 (5, M^+), 277(40), 247(20), 205(30), 179(559, 149(100), 109(80), 93(85), 57(95); FTIR (ν_{max}/cm^{-1}): 3490, 2961, 2931, 2843, 1695, 1617, 1509, 1254, 1097, 1029, 832, 774, 636, 617.



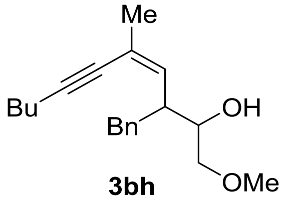
2bg

2bg: ^{1}H NMR (400 MHz, C_6D_6) δ: 7.46 - 7.40 (m, 2H), 7.22 - 7.16 (m, 2H), 7.10 - 7.03 (m, 1H), 6.55 (dd, *J*=15.8, 1.4 Hz, 1H), 5.63 (dd, *J*=15.8, 5.9 Hz, 1H), 4.35 - 4.28 (m, 1H), 3.15 (dd, A of ABX, JAB = 9.4 Hz, JAX = 4.3 Hz, 1H), 3.08 (dd, B of ABX, JAB = 9.4 Hz, JBX = 7.8 Hz, 1H), 3.00 (d, *J*=0.8 Hz, 3H) (Major), 3.01 (d, *J*=0.8 Hz, 3H) (Minor), 2.39 (t, *J*=7.1 Hz, 2H) (Major), 2.40 (t, *J*=7.1 Hz, 2H) (Minor), 2.19 (br. s, 1H), 1.86 (s, 3H), 1.58 - 1.46 (m, 2H), 1.33 (m, 2H), 0.85 (t, *J*=7.1 Hz, 3H) (Major), 0.86 (t, *J*=7.1 Hz, 3H) (Minor); ^{13}C NMR (101MHz , C_6D_6) δ: 208.1, 137.2, 129.7, 128.3 (Minor), 128.3 (Major), 126.6 (Minor), 126.6 (Major), 126.3, 105.6, 102.6, 76.7, 70.9 (Major), 70.9 (Minor) 58.2, 30.1 (Minor), 30.1 (Major), 30.0 (Major), 30.0 (Minor), 22.4(Major), 22.4 (Minor), 15.16, 13.8; MS (EI, *m/z*): 286 (20, M^+), 241(20), 225(30), 181(45), 169(100), 129(40), 91(75), 45(95); FTIR (ν_{max}/cm^{-1}): 3433, 2948, 2920, 2855, 1456, 1363, 1195, 1130, 971, 757, 691.



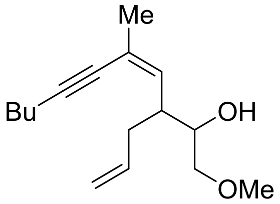
2ca

2ca: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.44 (dd, J = 1.4, 15.8 Hz, 1H) (Major), 6.42 (dd, J = 1.4, 15.8 Hz, 1H) (Minor), 5.43 (dd, J = 6.3, 15.7 Hz, 1H), 4.12 - 4.03 (m, 1H), 3,42 (dd, J_{AB} = 11,0 Hz, J_{AX} = 7,5 Hz, 1H) (Major), 3,42 (dd, J_{AB} = 11,0 Hz, J_{AX} = 7,5 Hz, 1H) (Minor), 3,32 (dd, J_{AB} = 11,0 Hz, J_{BX} = 3,9 Hz, 1H) (Minor), 3,31 (dd, J_{AB} = 11,0 Hz, J_{BX} = 3,9 Hz, 1H) (Major), 1.94 - 1.88 (m, 2H), 1.80 (s, 3H), 1.65 (s, 1H) (Major), 1.64 (s, 1H) (Minor), 1.46 - 1.23 (m, 7H), 0.87 (t, J = 7.2 Hz, 3H) (Minor), 0.86 (t, J = 7.2 Hz, 3H) (Major); ^{13}C NMR (101 MHz , C_6D_6) δ: 204.8, 131.8, 126.2, 98.8, 98.7, 73.2 (Minor), 73.1 (Major), 66.6, 33.9 (Minor), 33.8 (Major), 29.7 (Minor), 29.7 (Major), 22.3 (Minor), 22.3 (Major), 18.8, 15.6, 13.8 ; MS (EI, m/z): 210 (<5, M^+), 167(5), 137(15), 107(100), 91(40), 77(35), 67(40), 43(45); FTIR (ν_{max}/cm^{-1}): 3343, 2951, 2921, 2862, 1450, 1372, 1146, 1058, 1029, 960.



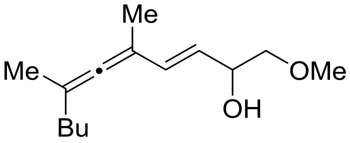
3bh

3bh: ^{1}H NMR (400 MHz, C_6D_6) δ: 7.36 (d, J=7.0 Hz, 2H), 7.21 (t, J=7.4 Hz, 2H), 7.08 (t, J=7.40 Hz, 1H), 5.95 (dd, J=9.4, 1.2 Hz, 1H), 3.91 (dt, J=8.8, 2.8 Hz, 1H), 3.33 - 3.27 (m, 1H), 3.22 - 3.10 (m, 3H), 2.97 (s, 3H), 2.86 (dd, B of ABX, J_{AB} = 11.7 Hz, J_{BX} = 4.7 Hz, 1H), 2.29 (br. s., 1 H), 2.18 (t, J=7.0 Hz, 2H), 1.83 (d, J=1.6 Hz, 3H), 1.43 - 1.28 (m, 4H), 0.82 (t, J=7.0 Hz, 3H); ^{13}C NMR (101 MHz , C_6D_6) δ: 140.5, 135.6, 129.4, 128.2, 125.9, 120.0, 93.5, 80.2, 76.2, 70.2, 58.1, 45.0, 38.1, 31.0, 23.4, 21.9, 19.0, 13.4; MS (EI, *m/z*): 255(5), 184(55), 135(30), 105(25), 93(100), 45(75); FTIR (ν_{max}/cm^{-1}): 3402, 2921, 2878, 1500, 1441, 1088, 1039, 960, 754, 695.



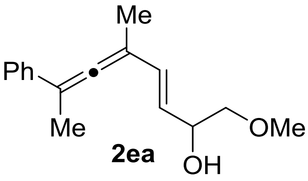
3bi

3bi: ^{1}H NMR (400 MHz, C_6D_6) δ: 5.94 (ddt, *J*=17.0, 10.1, 7.1 Hz, 1H), 5.82 (dd, *J*=9.8, 1.4 Hz, 1H), 5.15 (dq, *J*=17.0, 1.3 Hz, 1H), 5.05 (dt, *J*=10.0, 1.3 Hz, 1H), 3.97 (ddd, *J*=7.2, 4.3, 3.3 Hz, 1H), 3.28 - 3.37 (m, 2H), 3.06 (s, 3H), 3.05 – 2.96 (m, 2H), 2.53 (dt, J=14.1, 7.1 Hz, 1H), 2.38 (dt, J=14.1, 7.1 Hz, 1H), 2.31 (br. s., 1H), 2.17 (t, J=6.9 Hz, 2H), 1.86 (d, J=1.4 Hz, 3H), 1.44 - 1.27 (m, 4H), 0.80 (t, J=6.9 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ: 137.0 , 135.7, 120.1, 115.7, 93.5, 80.4, 76.1, 71.7, 58.3, 43.1, 36.4, 30.9, 23.4, 21.8, 19.0, 13.3 ; MS (EI, *m/z*): 232(<5), 208(10), 158(10), 121(20), 119(30), 105(35), 93(100), 45(75); FTIR (ν_{max}/cm^{-1}): 3412, 2931, 2862, 1695, 1607, 1509, 1254, 1156, 1117, 1039, 842, 617.



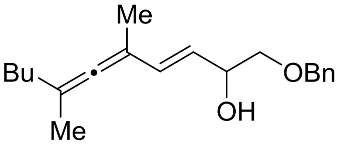
2dd

2dd: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.56 (dd, *J*=15.9, 1.4 Hz, 1H) (Minor), 6.55 (dd, *J* = 15.8, 1.4 Hz, 1H) (Major), 5.54 (dd, J = 15.9, 6.0 Hz, 1H), 4.38 - 4.30 (m, 1H) 3.19 - 3.07 (m, 2H), 3.01 (s, 3H) (Major), 3.00 (s, 3H) (Minor), 2.26 (br. s., 1H), 1.91 (t, *J*=7.20 Hz, 2H) (Major), 1.90 (t, J = 7.2 Hz, 2H) (Minor), 1.83 (s, 3H), 1.64 (s, 3H) (Minor), 1.64 (s, 3H) (Major), 1.46 - 1.35 (m, 2H) 1.35 - 1.22 (m, 2H) 0.86 (t, *J*=7.4 Hz, 3H) (Major), 0.85 (t, *J*=7.4 Hz, 3H) (Minor); ^{13}C NMR (101 MHz, C_6D_6) δ: 205.0, 131.8, 126.6 (Major), 126.6 (Minor), 99.2, 99.0, 77.2, 71.4 (Major), 71.3 (Minor) 58.5, 34.2 (Major), 34.2 (Minor), 30.0, 22.6, 19.1, 16.0, 14.1; MS (EI, m/z): 224 (<1, M^+), 179(15), 162(20), 137(40), 123(60), 107(100), 95(80), 77(50), 55(75), 45(95); FTIR (ν_{max}/cm^{-1}): 3432, 2926, 2851, 1450, 1367, 1193, 1127, 961, 612.



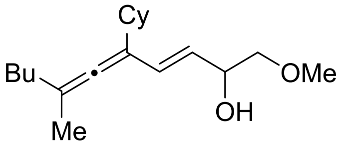
2ea

2ea: ^{1}H NMR (400 MHz, C_6D_6) δ: 7.44 – 7.36 (m, 2H), 7.21 – 7.12 (m, 2H), 7.09 – 7.01 (m, 1H), 6.52 (ddd, *J* = 1.4, 4.3, 15.8 Hz, 1H), 5.63 (dd, *J* = 6.1, 15.8 Hz, 1H), 4.31 (dd, *J* = 1.6, 5.5 Hz, 1H), 3.13 (dd, J_{AB} = 9.4 Hz, J_{AX} = 7.9 Hz, 1H), 3.10 (dd, J_{AB} = 9.4 Hz, J_{BX} = 3.4 Hz, 1H), 3.01 (s, 3H), 2.33 – 2.22 (br, s, 1H), 1.98 (s, 3H) (Major), 1.98 (s, 3H) (Minor), 1.83 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ: 208.2, 137.3, 129.7, 128.3 (Minor), 128.3 (Major), 126.6 (Minor), 126.6 (Major), 126.0, 101.5, 100.2, 76.7, 70.9 (Major), 70.9 (Minor), 58.2, 16.8 (Major), 16.7 (Minor), 15.1; MS (EI, *m/z*): 244 (25, M^{+}), 199(100), 181(55), 166(60), 143(30), 129(35), 91(30), 77(25), 43(80); FTIR (ν_{max}/cm^{-1}): 3450, 2926, 2852, 1500, 1450, 1367, 1193, 1127, 1068, 961, 754, 704, 612.



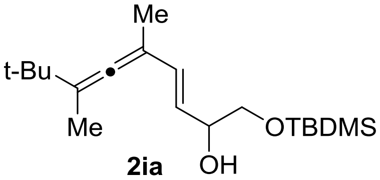
2fa

2fa: ^{1}H NMR (400 MHz ,C_6D_6) δ: 7.26 – 7.12 (m, 4H), 7.12 – 7.04 (m, 1H), 6.56 (ddd, *J* = 1.4, 4.0, 15.7 Hz, 1H), 5.52 (ddd, *J*= 0.8, 4.0, 16.0 1H), 4.44 – 4.34 (m, 1H), 4.25 (s, 2H), 3.30 (dd, J_{AB} = 9.3 Hz, J_{AX} = 8.0 Hz, 1H), 3.23 (dd, J_{AB} = 9.3 Hz, J_{BX} = 3.4 Hz, 1H), 2.31 (br. s., 1H), 1.82 (s, 3H), 1.64 (d, *J* = 3.1 Hz 3H), 1.45 – 1.34 (m, 2H), 1.34 – 1.22 (m, 2H), 0.86 (t, *J* = 12 Hz, 3H) (Minor), 0.85 (t, *J* = 12 Hz, 3H) (Major); ^{13}C NMR (101MHz , C_6D_6) δ: 204.7, 138.3, 131.5 (Major), 131.5 (Minor), 128.2, 127.5, 126.2 (Minor), 126.1 (Major), 98.9, 98.6, 74.5, 72.9, 71.2 (Minor), 71.2, 33.9 (Minor), 33.9 (Major), 29.7, 22.3, 18.8, 15.7, 13.8; MS (EI, *m/z*): 300 (<1, M^{+}), 282(<5), 123(10), 107(20), 91(100), 79(18), 65(20); FTIR (ν_{max}/cm^{-1}): 3427, 2924, 2848, 1946, 1661, 1462, 1358, 1110, 1025, 977, 740, 683.



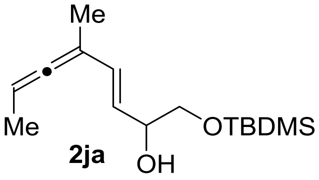
2ha

2ha: ^{1}H NMR (400 MHz ,C_6D_6) δ: 6.40 (dd, *J* = 1.6, 16.0 Hz, 1H), 5.77 (dd, *J* = 5.9, 16.0 Hz, 1H), 4.39 - 4.30 (m, 1H), 3.20 - 3.09 (m, 2H), 2.99 (s, 3H), 2.22 - 2.12 (m, 2H), 1.98 - 1.90 (m, 2H), 1.78 - 1.71 (m, 2H), 1.69 (s, 3H), 1.63 - 1.59 (m, 1H), 1.50 - 1.40 (m, 2H), 1.37 - 1.14 (m, 8H), 0.91 - 0.84 (m, 3H); ^{13}C NMR (101 MHz , C_6D_6) δ: 202.9, 129.9, 125.8 (Minor), 125.7, 109.9, 101.5, 76.9, 71.3 (Minor), 71.2, 58.2, 37.8, 34.0, 33.2 (Minor), 33.2 (Major), 33.1, 31.6, 29.9, 26.7 (Minor), 26.6 (Major), 26.5, 22.7 (Minor), 22.5 (Major), 19.0, 13.9 (Minor), 13.8 (Major); MS (EI, m/z): 292 (<1, M^+), 217(10), 175(10), 147(5), 105(15), 83(25), 54(15), 45(100) ; FTIR (ν_{max}/cm^{-1}): 3440, 2918, 2860, 1450, 1193, 1127, 969, 894.



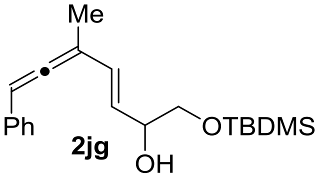
2ia

2ia: ^{1}H NMR (400 MHz,C_6D_6) δ: 6.57 (dd, *J* = 1.2, 15.7 Hz, 1H) (Major), 6.55 (dd, *J* = 1.2, 15.7 Hz, 1H) (Minor), 5.57 (dd, *J* = 5.9, 15.7 Hz, 1H), 4.30 – 4.24 (m, 1H), 3.54 (dd, J_{AB} = 10.0 Hz, J_{AX} = 7.3 Hz, 1H), 3.44 (dd, J_{AB} = 10.0 Hz, J_{BX} = 4.1 Hz, 1H), 1.87 (s, 3H) (Minor), 1.84 (s, 3H) (Major), 1.67 (s, 3H) (Major), 1.66 (s, 3H) (Minor), 1.05 (s, 6H), 0.91 (s, 9H), -0.01 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ: 203.9, 131.7, 126.2, 107.6, 99.2, 72.8, 67.6, 34.0, 30.9, 28.9, 25.7, 15.8, 14.6, -5.6 (Minor), -5,7 (Major); MS (EI, *m/z*): 306(2), 281(15), 248(15), 207(25), 178(10), 118(30), 74(60), 59(100) ; FTIR (ν_{max}/cm^{-1}): 3440, 2951, 2910, 2852, 1467, 1359, 1251, 1112, 961, 836, 787.



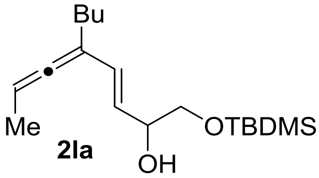
2ja

2ja: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.54 (td, *J* = 1.2, 15.7 Hz, 1H), 5.56 (ddd, *J* = 1.4, 6.0, 15.7 Hz, 1H), 5.16 – 5.05 (m, 1H), 4.31 – 4.18 (m, 1H), 3.52 (dd, J_{AB} = 9.9 Hz, J_{AX} = 7.3 Hz, 1H), 3.41 (dd, J_{AB} = 9.9 Hz, J_{BX} = 4.1 Hz, 1H), 1.80 (d, *J* = 2.7 Hz, 3H), 1.52 (d, *J* = 7.0 Hz, 3H) (Major), 1.52 (d, *J* = 7.0 Hz, 3H) (Minor), 0.90 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ: 207.9, 130.7, 126.9, 99.0, 85.0, 72.7, 67.5, 25.7, 18.1, 15.3, 14.1, -5.6 (Minor), -5.7 (Major); MS (EI, *m/z*): 268 (<1, M^+), 211(10), 193(5), 119(40), 105(30), 91(20), 75(100), 43(15); FTIR (ν_{max}/cm^{-1}): 3424, 2934, 2852, 1707, 1467, 1375, 1256, 1110, 824, 762, 670.



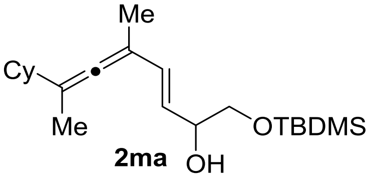
2jg

2jg: ^{1}H NMR (400 MHz, C_6D_6) δ: 7.26 – 7.22 (m, 2H), 7.12 (s, 2H), 7.04 – 6.98 (m, 1H), 6.53 (td, *J* = 1.4, 15.7 Hz, 1H) (Minor), 6.52 (td, *J* = 1.4, 15.7 Hz, 1H) (Major), 6.24 – 6.18 (m, 1H), 5.66 (qdd, *J* = 1.2, 5.9, 15.7 Hz, 1H), 4.26 – 4.19 (m, 1H), 3.51 (dd, J_{AB} = 9.9 Hz, J_{AX} = 7.5 Hz, 1H), 3.41 (dd, J_{AB} = 9.9 Hz, J_{BX} = 4.3 Hz, 1H), 2.35 – 2.26 (br. s, 1H), 1.84 (d, *J* = 2.7 Hz, 3H) (Minor), 1.83 (d, *J* = 2.7 Hz, 3H) (Major), 0.91 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ: 209.3, 134.6, 128.6 (Minor), 128.6 (Major), 127.0, 126.9, 103.4, 94.5, 81.6, 72.6, 67.4, 25.6, 18.1, 15.0, -5.6 (Minor), -5.7 (Major) ; MS (EI, *m/z*): 330 (<1, M^+), 312(5), 273(10), 181(50), 156(65), 141(55), 105(35), 75(100), 59(15); FTIR (ν_{max}/cm^{-1}): 3523, 2926, 2835, 2735, 1682, 1599, 1583, 1516, 1317, 1251, 1151, 1010, 836, 621.



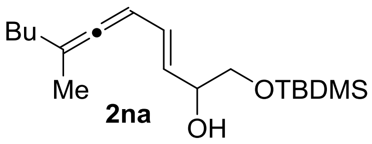
2la

2la: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.49 (d, J = 16.0 Hz, 1H), 5.70 (dd, J = 7.0, 11.7 Hz, 1H), 5.24 - 5.13 (m, 1H), 4.77 - 4.74 (m, 1H) (Minor), 4.31 - 4.21 (m, 1H) (Major), 3.50 (dd, J_{AB} = 10.0 Hz, J_{AX} = 7.5 Hz, 1H), 3.40 (dd, J_{AB} = 10.0 Hz, J_{BX} = 4.7 Hz, 1H), 2.16 (dd, J = 3.5, 7.8 Hz, 2H), 1.55 (d, J = 7.0 Hz, 3H), 1.54 (quin, J = 6,7 Hz, 2H), 1.35 (sxt, J = 7.2 Hz, 2H), 0.96 - 0.84 (m, 12H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ: 207.3, 130.2, 126.6, 104.0, 86.5, 72.9, 67.6, 29.8, 28.4, 25.7, 22.5, 14.1, 13.8, -5.6 (Major), -5.7 (Minor); MS (EI, m/z): 253(5), 161(10), 119(20), 105(40), 91(25), 75(100), 57(50); FTIR (ν_{max}/cm^{-1}): 3432, 2951, 2934, 2860, 1707, 1475, 1359, 1251, 1102, 836, 770.



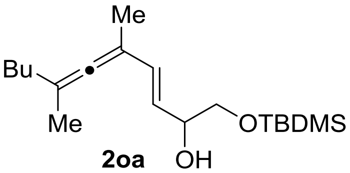
2ma

2ma: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.58 (ddd, J = 1.2, 3.1, 16.0 Hz, 1H), 5.57 (ddd, J = 0.8, 5.9, 15.7 Hz, 1H), 4.34 – 4.23 (m, 1H), 3.54 (dd, J_{AB} = 8.7 Hz, J_{AX} = 5.4 Hz, 1H), 3.45 (dd, JAB = 8.7 Hz, J_{BX} = 0.5 Hz, 1H), 2.35 (dd, J = 2.0, 12.5 Hz, 1H), 1.86 (d, J = 0.8 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.75 – 1.62 (m, 5H), 1.61 – 1.51 (m, 1H), 1.27 – 1.04 (m, 5H), 0.95 – 0.86 (m, 9H), -0.01 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ: 204.4, 131.8 (Major), 131.7 (Minor), 126.3, 104.0, 99.7, 72.9 (Minor), 72.8 (Major), 67.6, 42.1 (Major), 42.1 (Minor), 32.1 (Major), 32.1 (Minor), 26.4 (Minor), 26.4 (Major), 26.3 (Minor), 26.3 (Major), 25.7, 18.1, 17.2, -5.6 (Minor), -5.7 (Major) ; MS (EI, *m/z*): 350 (<1M$^+$), 275(5), 201(20), 187(15), 159(20), 145(25), 119(65), 105(55), 75(100), 67(40), 55(50); FTIR (ν_{max}/cm^{-1}): 3424, 2943, 2860, 1450, 1384, 1259, 1118, 977, 845, 787, 670.



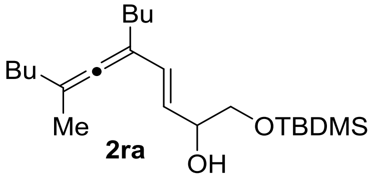
2na

2na: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.40 (ddd, J = 1.2, 10.6, 15.3 Hz, 1H), 5.88 (qd, J = 2.7, 10.6 Hz, 1H), 5.56 (dd, J = 5.9, 15.3 Hz, 1H), 4.24 – 4.14 (m, 1H), 3.48 (dd, J_{AB} = 9.8 Hz, J_{AX} = 7.5 Hz, 1H), 3.38 (dd, J_{AB} = 9.8 Hz, J_{BX} = 3.9 Hz, 1H), 2.35 – 2.26 (br, s, 1H), 1.88 (s, 2H), 1.68 – 1.56 (m, 3H), 1.45 – 1.34 (m, 2H), 1.33 – 1.21 (m, 2H), 0.90 (s, 9H), 0.86 (t, J = 8 Hz, 3H) (Major), 0.86 (t, J = 8 Hz, 3H) (Minor), -0.02 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ: 205.0 (Major), 205.0 (Minor), 129.3 (Major), 129.3 (Minor), 128.6 (Major), 128.6 (Minor) 100.7, 93.3, 72.4, 67.4, 33.6, 29.6, 25.7, 22.3, 18.7, 18.1, 13.8, -5.7 (Minor), -5.7 (Major) ; MS (EI, *m/z*): 310 (<1, M$^+$), 253 (5), 211(5), 161(20), 119(35), 105(70), 91(40), 75(100), 55(35); FTIR (ν_{max}/cm^{-1}): 3433, 2958, 2929, 2861, 1454, 1357, 1260, 1124, 959, 833, 765.



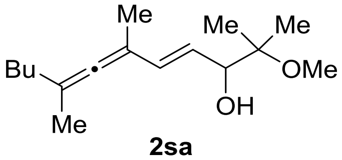
2oa

2oa: ^{1}H NMR (400 MHz, C_6D_6) δ: ppm 6.59 (dd, *J*=15.8, 1.4 Hz, 1H), 5.57 (dd, *J*=15.8, 6.1 Hz, 1H), 4.31 – 4.24 (m, 1H), 3.54 (dd, J_{AB} = 9.8 Hz, J_{AX} = 7.5 Hz, 1H), 3.43 (dd, J_{AB} = 9.8 Hz, J_{BX} = 3.9 Hz, 1H), 1.95 – 1.88 (m, 2H), 1.86 (s, 3H), 1.65 (s, 3H) (Major), 1.65 (s, 3H) (Minor), 1.46 – 1.23 (m, 4H), 0.91 (s, 12H), 0.86 (t, *J*=7.4 Hz, 3H), -0.01 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ: 204.7, 131.6, 126.3, 98.9, 98.7, 72.8 (Minor), 72.8 (Major), 67.6, 65.5, 33.9, 29.8, 29.7, 25.7, 22.7 (Major), 22.3 (Minor), 18.8, 18.1, 15.7(Major), 15.2 (Minor), 14.0 (Minor), 13.8 (Major), -5.6 (Minor), -5.7 (Major); MS (EI, *m/z*): 324 (<1, M$^+$), 267(10), 225(5), 175(35), 133(55), 119(65), 105(65), 75(100), 55(70); FTIR (ν_{max}/cm^{-1}): 3430, 2942, 2854, 1454, 1366, 1246, 1103, 972, 863, 786.



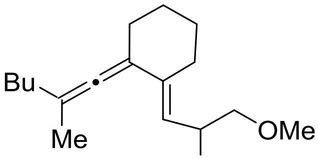
2ra

2ra: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.52 (dd, *J* = 1.2, 15.7 Hz, 1H), 5.69 (dd, *J* = 6.3, 16.0 Hz, 1H), 4.32 – 4.23 (m, 1H), 3.56 (dd, J_{AB} = 9.8 Hz, J_{AX} = 7.5 Hz, 1H), 3.46 (dd, J_{AB} = 9.8 Hz, J_{BX} = 4.3 Hz, 1H), 2.22 (t, *J* = 7.4 Hz, 2H), 1.94 (t, *J* = 6.7 Hz, 2H), 1.68(s, 3H) (Major) – 1.67 (s, 3H) (Minor), 1.58 (quin, *J* = 7.4 Hz, 2H), 1.48 – 1.24 (m, 6 H), 0.99 – 0.82 (m, 15H), 0.03 - -0.05 (m, 6H); ^{13}C NMR (101 MHz , C_6D_6) δ: 204.0, 131.1 (Major), 131.1 (Minor) 125.9, 103.8, 100.2, 73.0 (Minor), 73.0 (Major), 67.6, 33.9, 30.1, 29.8, 28.9, 25.7, 22.6, 22.4, 18.8, 18.1, 13.9, 13.8, -5.6 (Minor), -5.7 (Major); MS (EI, *m/z*): 366 (<1, M^+), 348(2), 309(5), 267(5), 217(15), 175(10), 161(15), 119(30), 105(40), 91(30), 75(100), 57(45) ; FTIR (ν_{max}/cm^{-1}): 3432, 2960, 2934, 2851, 1467, 1367, 1259, 1110, 969, 836, 787, 679



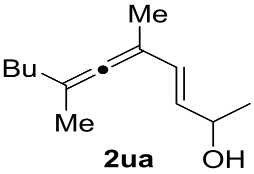
2sa

2sa: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.58 (d, J=15.6 Hz, 1H), 5.68 (dd, J = 6.7, 15.7 Hz, 1H) (Minor), 5.67 (dd, J = 6.7, 15.7 Hz, 1H) (Major), 4.08 (d, J= 6.8 Hz, 1H), 2.91 (s, 3H), 2.51-2.49 (m, 1H), 1.94-1.89 (m, 2H), 1.86 (s, 3H), 1.65 (s, 3 H)(Major), 1.63 (s, 3H) (Minor), 1.40 (quint, J=7.2 Hz, 2H), 1.29(quint, J=7.2 Hz, 2H), 1.04-1.03 (m, 3H), 0.97 (s, 3H), 0.87 (t, J = 7.4 Hz, 3H) (Minor), 0.85 (t, J = 7.4 Hz, 3H) (Major); ^{13}C NMR (101 MHz, C_6D_6) δ: 205.0, 132.5 (Minor), 132.4 (Major), 126.5 (Minor), 126.4 (Major), 99.3, 98.9 (Minor), 98.9 (Major), 78.4 (Minor), 78.3 (Major), 77.6 (Major), 77.6 (Minor), 49.0, 34.3 (Minor), 34.2 (Major), 30.0, 22.6 (Minor), 22.6 (Major), 20.8, 19.4 (Major), 19.4 (Minor), 19.1, 16.1 (Minor), 16.1 (Major), 14.1; MS (EI, m/z): 252 (<1, M^+), 220(5), 180(10), 73(100), 43(10); FTIR (ν_{max}/cm^{-1}): 3449, 2960, 2926, 2868, 1475, 1367, 1151, 1068, 961, 737, 621.



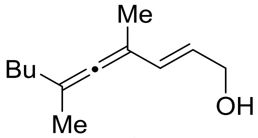
2ta

2ta: ^{1}H NMR (400 MHz, C_6D_6) δ: 5.79 (d, J=8.0 Hz, 1H), 4.67 (q, J= 6.0 Hz, 1H), 3.20-3.17 (m, 2H), 3.03 (s, 3H)(Major), 3.02 (s, 3H)(Minor), 2.37-2.28 (m, 4H), 2.22-2.16 (m, 1H), 2.02-1.85 (m, 2H), 1.69 (s, 3H) (Major), 1.68 (s, 3H) (Minor), 1.57-1.40 (m, 6H), 1.32 (sextet, J=7.2 Hz, 2H), 0.90 (t, J= 7.2 Hz, 3H) (Major), 0.89 (t, J= 7.2 Hz, 3H) (Minor); ^{13}C NMR (101 MHz, C_6D_6) δ: 198.0, 140.0, 124.1, 105.2, 98.9, 77.0, 67.4, 58.6, 34.4, 32.2, 30.2, 29.1, 26.5, 26.1, 22.7, 19.6, 14.2; MS (EI, m/z): 264 (20, M$^+$), 219(20), 189(25), 147(50), 105(80), 91(75), 55(65), 45(100); FTIR (ν_{max}/cm^{-1}): 3440, 2926, 2843, 1748, 1657, 1442, 1209, 1127, 1077, 969, 903, 621.



2ua

2ua: ^{1}H NMR (400 MHz, C_6D_6) δ: 6.31 (dd, J = 1.6, 15.7 Hz, 1H) (Major), 6.31 (dd, J = 1.6, 15.7 Hz, 1H) (Minor), 5.52 (dd, J = 6.3, 15.7 Hz, 1H) (Major), 5.52 (dd, J = 6.3, 15.7 Hz, 1H) (Minor), 4.14 (dquin, J = 1.0, 6.3 Hz, 1H), 1.97 – 1.88 (m, 2H), 1.82 (s, 3H), 1.67 (s, 3H) (Major), 1.67 (s, 3H) (Minor), 1.47 – 1.37 (m, 2H), 1.36 – 1.24 (m, 2H), 1.15 (d, J = 6,7 Hz, 3H) (Minor), 1.14 (d, J = 6.7 Hz, 3H) (Major), 0.87 (t, J = 7.2 Hz, 3H) (Minor), 0.86 (t, J = 7.2 Hz, 3H) (Major); ^{13}C NMR (101 MHz, C_6D_6) δ: 204.5, 132.0 (Major), 132.0 (Minor), 129.2 (Major), 129.2 (Minor), 98.8, 98.6, 68.4, 33.9 (Major), 33.9 (Minor), 29.7, 23.4, 22.3, 18.8, 15.8, 13.8 (Major), 13.8 (Minor); MS (EI, m/z): 194 (<1, M$^+$), 152(5), 107(60), 91(25), 79(20), 67(20), 43(100); FTIR (ν_{max}/cm^{-1}): 3500, 2951, 2872, 1695, 1597, 1519, 1264, 1166, 1029, 832, 774, 607.

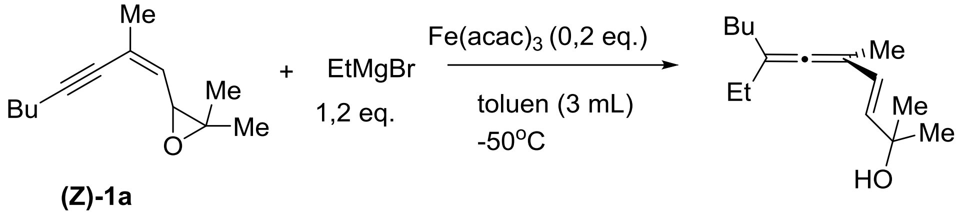


2va

2va: ^{1}H NMR (400MHz, C_6D_6) δ: 6.30 (d, J=16.0 Hz, 1H), 5.53 (dt, J=16.0, 5.6 Hz, 1H), 3.92 (d, J=5.2 Hz, 2H), 1.92 (t, J=7.2 Hz, 2H), 1.81 (s, 3H), 1.66 (s, 3H), 1.41 (sextet, J=7.2 Hz, 2H), 1.30 (sextet, J=7.2 Hz, 2H), 0.87 (t, J=7.2 Hz, 3H), 0.72 (s, 1H); ^{13}C NMR (101MHz, C_6D_6) δ: 204.8, 131.2, 127.3, 99.2, 99.0, 63.6, 34.2, 30.1, 22.6, 19.2, 16.1, 14.1; MS (EI, m/z): 180 (<1, M^{+}), 149(5), 138(10), 107(100), 91(35), 79(30), 55(30), 41(70); FTIR (ν_{max}/cm^{-1}): 3324, 2960, 2934, 2876, 1442, 1359, 1094, 1002, 969.

CHAPTER 4

RESULTS AND DISCUSSION



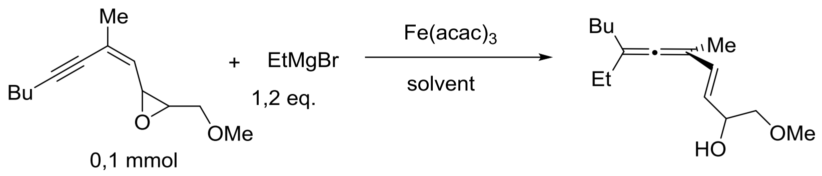
(Z)-1a

2ab
(%65 isoleted yield)

Figure 4.1. 1,5-(SN_2’’) reaction of Z-1a reagent with iron-catalyzed Grignard reagent

The reaction of Z-configured enyne oxirane **(Z)-1a** compound with 1.2 equivalent EtMgBr in the presence of 0.2 equivalent $Fe(acac)_3$ was performed in 3 mL toluene, at -50 °C. Th desired ethyl bonded vinylallene **2ab** product was obtained in 65% isolated yield. Afterwards, the optimization studies were conducted using **(Z)-1b** compound in order to be able to track diasterемeric selectivity of the method.

Table 4.1. Iron-catalysed 1,5-(S_N2'') reaction of enyne oxirane (Z)-1b reagent with Grignard reagent: optimization study



(Z)-1b

2bb

No	**% Fe(acac)₃ (Eq.)**	**Solvent (3 mL)**	**Type of Addition (Duration)**	**Temperature (°C)**	**dr[c]**	**Yield[a] (%)**
1	0.2	toluene	Syringe pump (15 min.)	-50	-	0
2	0.2	toluene	Syringe pump (15 min.)	-50	-	0
3	1.0	toluene	Syringe pump (15 min.)	-50	-	0
4	1.0	THF	direct	-50	1:1	55
5	1.0	DCM	direct	-50	1.2:1	54
6	1.0	Et_2O	direct	-50	1.5:1	78[b]
7	0.2	Et_2O	direct	-50	1.6:1	70
8	1.0	Et_2O	Syringe pump (15 min.)	-50	1.5:1	67
9	1.0	Et_2O	Syringe pump (15 min.)	-50	1.5:1	64
10	1.0	Et_2O	direct	-80	2.2:1	70
11	0.2	Et_2O	direct	-80	not detected	39
12	0.2	Et_2O	Syringe pump (15 min.)	-80	not detected	40
13	1.0	Et_2O	direct	-20	1:1	48
14	-	Et_2O	direct	-50	-	-

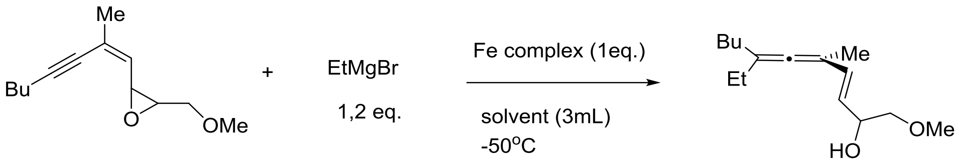
[a] It is detected by using ^{1}H-NMR method and benzaldehyde internal standard compound.
[b] Isolated yield.
[c] Diastereoselectivity ratio was determined by ^{1}H NMR.

Instead of the formation of vinylallene after the reaction performed with (Z)-**1b**, a complex mixture was observed to form under the reaction conditions that is executed with (Z)-**1a**. Even increasing the iron complex loading from 0.2 equivalent to 1.0 and adding the Grignard reagent slowly within the test reaction medium by syringe pump at different durations did not change the results (Table, 4.1, No: 1-3). However, the desired vinylallene product **2bb** was obtained in 55% yield but with low diastereomeric ratio (dr) when iron complex was 1.0 equivalent and THF was used as solvent in place of toluene (No:4). Using DCM as solvent did not improve the reaction; therefore, a similar yield and dr were obtained. On the other hand, when diethyl ether was used as solvent, the vinylallene product was obtained in 78% isolated yield and 1.5:1 dr (No:6) on contrary to the experiments conducted using DCM and THF. Even though slow addition of Grignard reagent or decreasing iron complex to 0.2 equivalents did not affect stereo-selectivity significantly, a slightly lower yield was obtained.

The reaction of (Z)-**1b** compound with EtMgBr was performed at -80 ^{o}C. The yield of this reaction where iron complex was 1.0 equivalent was comparable to that performed at -50 ^{o}C; however, a slight increase of dr (2.2:1) was observed (No: 10). Since decreasing iron loading to 0.2 equivalent and slow addition of Grignard reagent led to complex, the vinylallene formation was observed in a significantly low yield (No:11-12). At a more moderate reaction temperature (-20 ^{o}C), a rather low yield and selectivity were observed (No: 13). Only S_N2 type reaction (No:14) in the absence of iron.

The effect of different iron complexes on product yield and diastereoselectivity was also studied after determination of optimum temperature.

Table 4.2. Effect of different iron catalysts on S_N2'' reaction of (Z)-1b reagent with Grignard reagent



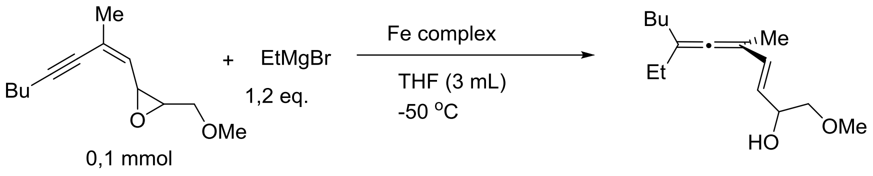
No	Fe complex (1 equivalent)	Solvent (3 mL)	dr[b]	Yield[a] (%)
1	$FeCl_2$	Et_2O	-	0
2	$FeCl_2$	THF	1:1	81
3	$FeBr_2$	Et_2O	not detected	15
4	$FeBr_2$	THF	1:1	44
5	$FeCl_3$	THF	-	0
6	$Fe(OTf)_3$	Et_2O	-	0
7[c]	$FeCl_2$	THF	1:1	20

[a] Detected by using ^{1}H-NMR method and benzaldehyde internal standard compound.
[b] Diastereoselectivity ratio was determined by ^{1}H NMR.
[c] Performed at -80 °C.

A complex product mixture was formed, and the corresponding vinylallene product could not be detected at the reaction of Z-**1b** compound in the presence of 1 equivalent of $FeCl_2$ in Et_2O (No:1). This may be due to insufficient solubility of $FeCl_2$ in Et_2O. $FeCl_2$ compound is well soluble in THF and thus the vinylallenes were usually obtained in high yields, however, the stereo-selectivity of the process was not so satisfactory (No: 2). Reducing the temperature to -80 °C did not affect the steeo-selectivity but decreased the yield significantly (No: 7). The vinylallene product was observed in very low yields or not detected at all even though (Z)-**1b** reagent was fully consumed with the presence of other iron resources used (No: 5-6).

The effect of a number of ligands was also studied on the reaction.

Table 4.3. Effect of ligands on the iron-catalyzed reaction of (Z)-1b with Grignard reagent



(Z)-1b

(Z)-2bb

No	**Iron complex (Eq.)**	**Ligand (Eq.)** [c]	**dr**[b]	**Yield**[a] **(%)**
1	$FeCl_2$ (1.0)	Dppe (4.0)	1.6:1	49
2	$FeCl_2$ (1.0)	Dppb (4.0)	1.5:1	47
3[d]	$FeCl_2$ (1.0)	Xantphos (4.0)	1:1	42
4	$Fe(acac)_3$ (1.0)	triphenylphosphine (4,0)	1.6:1	68
5	$Fe(acac)_3$ (0.5)	1,10- phenanthroline (2.0)	1.3:1	58
6	$Fe(acac)_3$ (0.5)	2,2'-biprydine (4.0)	1.4:1	52
7	$Fe(acac)_3$ (0.5)	TMEDA (4.0)	1.2:1	67

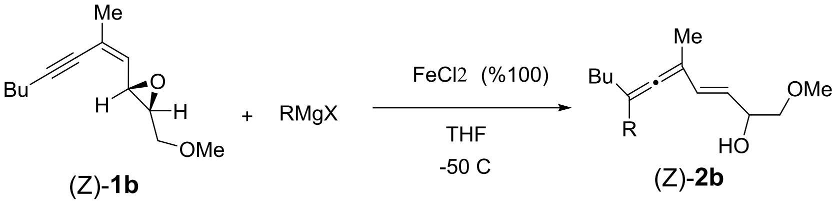
[a] It is detected by using ^{1}H-NMR method and benzaldehyde internal standard compound.
[b] Diastereoselectivity ratio was determined by ^{1}H NMR.
[c] Equivalents were given based on iron complex.

In the reactions of (Z)-**1b** reagent with $FeCl_2$ or $Fe(acac)_3$, variety of iron complexes in the presence of mono- or bidentate phosphorous or nitrogen ligands in THF, there appeared a quite decrease at catalytic activity of the iron catalyst (No: 1-7).

It was determined by previous studies that the reactions of these reagents with organocopper[2] or Grignard[9] compounds gave (*E*) and (*Z*) isomeric mixtures of vinylallenes. However, (*E*) configured products were only the isomeric type formed by the method developed by us.

Previously, S_N2” reactions of the enyne acetate structures with organocuprates were established. Yet, due to the negative effect of copper on biological systems, its use in stoichiometric amounts is not preferred in industrial applications, whereas, the use of iron compounds as catalysts a preferable choice because it is environmental benign and low in cost.

A different mode of preparation of the reaction medium was also tried; the substrate **1b** was gently added within the reaction medium containing $FeCl_2$-Grignard mixture via an automatic syringe. by this approach, the enyne oxirane **1b** was converted to the corresponding vinylallene product at the yield of 81% when reacted with MeMgCl over the 1 eq of % $FeCl_2$ and the yields were 76% and 51%, when the Grignard Reagents are BuMgCl and *i*-PrMgCl, respectively. It must be noted that the diastereoselectivity decreased as the size of Grignard-alkyl group enlargened (Figure:4.1).



RMgX	%Yield	dr
BuMgCl	76	-
MeMgCl	81	2.3 : 1

BuMgCl; d, MeMgCl; a, *i*-PrMgCl; c, EtMgCl; b, PhMgCl; h

Figure.4.2 Reaction of (Z)-**1b** with different Grignard reagent

With the presence of a cyclohexyl group on the alkenyl carbon which is proximal to the alkynyl moiety (**1h**), the reaction partially slowed down and hence just 46% of the vinylallene product could be isolated. (Figure:4.2)

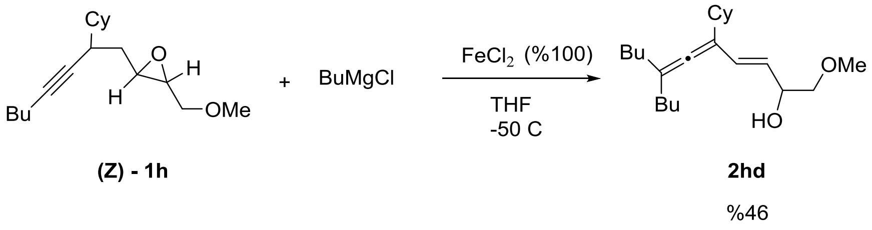
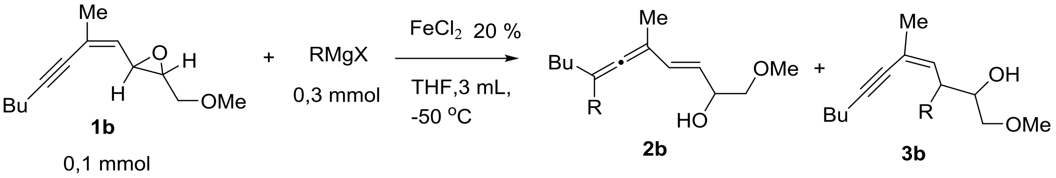


Figure.4.3 Presence of a cyclohexyl group on the alkenyl carbon reaction with BuMgCl

Activity of enyne oxirane (**1b**) with various Grignard reagents in the presence of a catalytic amount of $FeCl_2$ (20%) was investigated (Table 4.4). The substitution reactions of Grignard reagents with a primer alkyl group was completed in relatively short times, typically within 30 min., then provided (No 1-4) the vinylallene products containing a hydroxyl group positioned on the allylic carbon in usually high yields (**2b**). With PhMgCl the enyne oxirane **1b** formed in a low yield and it took relatively longer reaction period to achieve the complete conversion of the enyne substrate (No 5). The iron-catalyzed reactions allyl- and benzyl magnesium chlorides (BnMgCl) (No 6-8), S_N2 products were the only structures that recovered at the end of the reactions. It is thought that S_N2 reactions occurred no-catalytically since the product **3b** can also be produced in the absence of the iron compound (No 7).

Table 4.4. The reactions of enyne oxirane (Z)-1b with various Grignard Reagents.



No	RMg	%2b (d.r.)[a]	%3b	Time
1	MeMgl	82 (1.7: 1)	-	55min.
2	EtMgCl	75 (1: 1)	-	65min.
3	n-C_5H_{11}MgCl	83 (1.8: 1)[b]	-	120min.
4	n-C_8H_{17}MgCl	92 (1.2: 1)[b]	-	130min.
5	PhMgCl	35 (2.2: 1)	-	105min.
6	AllylMgCl	-	87	100min.
7[c]	AllylMgCl	-	80	110min.
8	BnMgCl	-	53	120min.

[a]d.r.: diastereomerical ratio. [b].d r: determined by HPLC. [c]C: Catalyst-free

It was also found that the (*E*)-configured enyne oxiranes are not so suitable substrates for the method because the reaction of (*E*)-**1b** with EtMgCl did not proceed so cleanly and therefore yielded the vinylallene (*E*)-**2bb** in a low yield (43%) owing to the formation of accompanying unidentified by-products. (Figure: 4.3).

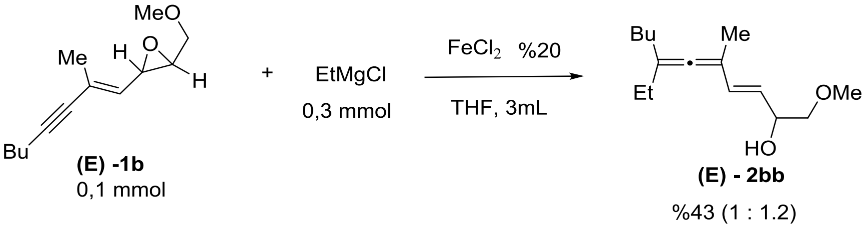


Figure.4.4 The reactions of enyn oxirane (E)-**1b** with EtMgCl

It was realized that the enyne oxirane can also successfully be used with a pendant hydroxyl group as benzyl or silyl protected forms. These reagents reacted with MeMgCl to give rise 72% and 74% corresponding vinylallene yields, respectively. (Table 4.5, No 1,2).

The Enyne oxirane having a methyl group in the R_3 instead of a protected carbinol group could transform into the product **2ua** with a 3.1:1 dr vinylallene structure in high yield (No 3). When dimethyl-bearing epoxide ring was examined, vinylallen product was obtained in good yield of 83%. (No 20). Furthermore, epoxide ring was unsubstituted, reaction realized in moderately good yield 67%. (No 21)

2dd methyl group in R^1 position reaction result as similar as butyl group in R^1 position. (No 19). The reaction with the enyne oxirane containing a phenyl group on the alkynyl carbon was sluggish and required a level of catalyst loading, typically 60%, to afford a modest yield of the vinylallene product, which is also accompanied by intricate mixture of unidentified by-products. (No 4).

The method was able to tolerate the bulkier cyclohexyl group in R^1 position and thus the vinylallene compound (**2ma**) could be obtained at the yield of 81% (No 5).

Increasing the size of R^1 to highly bulky *t*-butyl group was highly inferior to the reactivity of the substrate (**1i**) toward 1,5-nucleophilic substitution reaction. With the presence of 0.5 eq. of the corresponding product was obtained only in 30% yield and a further increase of the catalyst loading to 1 eq increased the yield only to 42% (No 6 and 7).

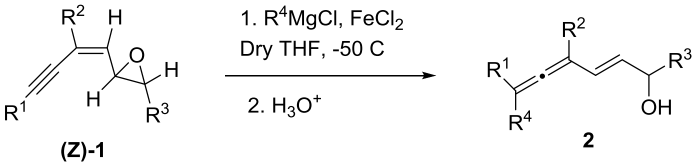
Although It is well known that terminal alkynes are actively susceptible to deprotonation in by Grignard reagents We have found that S_N''-type reaction can also successfully carried out with the enyne oxirane having a terminal alkynyl group (**1j**). Moreover, the good dr (5.7:1) was afforded by this reagent when reacted with MeMgCl contained medium. However, this substrate having a smallest substituent on the distal alkynyl carbon (H) could not be beneficiated by the reactions with $(CH_3)_2CHMgCl$ and PhMgCl, low yields being obtained with these reactions.

The method was also successfully applicable for those enyne oxiranes containing only disubstituted alkenyl group (**1n**) or for that when R_2 is butyl (**1r** and **1l**). (No: 12-14). On the other hand, when R^2 group was cyclohexyl, reaction yield obtained in a low level 55%. (No 16). Reaction conditions effected negatively when R^2 group was bulky.

The presence of the bulky Me_3Si on the alkynyl carbon made the the substrate completely inert to the made. With this substrate, no product formation was observed and the substrate was recovered completely unreacted (No 15).

When substrate **1t** having endocyclic double bond gave good yield was 81%. Moreover, excellent dr was afforded by this reagent. (dr:20,3/1) (No 17)

Table 4.5. Fe-catlysed Reactions of enyne oxirane with Grignard Reagents.



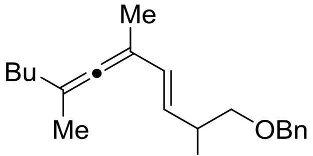
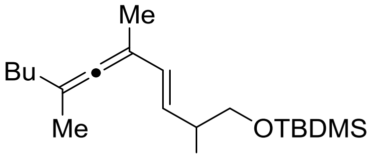
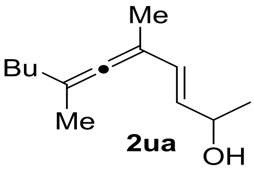
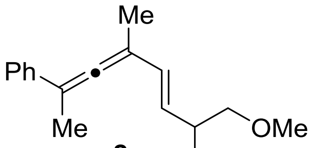
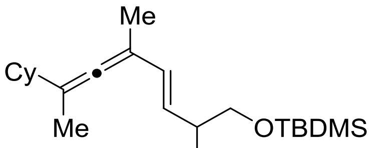
No	R^4	% Fe	% Yield	dr[a]	time	Product
1	Me	20	72	1.9/1	50min.	 **2fa**
2	Me	20	74	1.7/1	45min.	 **2oa**
3	Me	20	71	3.5/1	55min.	 **2ua**
4	Me	60	63	1.2/1	65min.	 **2ea**
5	Me	20	81	1.1/1[c].	80min.	 **2ma**

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Table 4.5 (cont.)

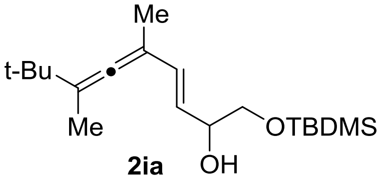
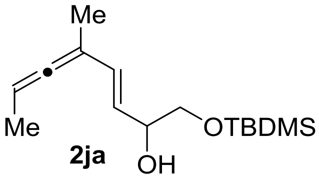
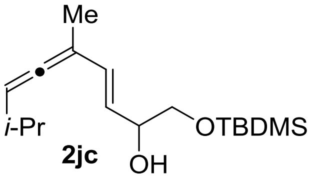
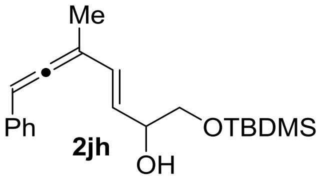
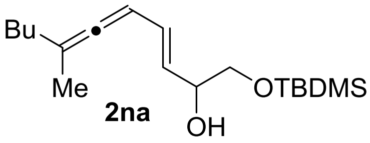
6	Me	50	30	3.7/1	75min.	 **2ia**
7	Me	100	42	3.7/1	65min.	**2ia**
8	Me	20	83	5.7/1	40min.	 **2ja**
9	*i*-Pr	100	18	3.5/1 [c]	75min.	 **2jc**
10	Ph	20	26	2.5/1	55min.	 **2jh**
11	Ph	100	48	2.7/1	50min	**2jh**
12	Me	20	85	1.3/1	60min.	 **2na**

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Table 4.5 (cont.)

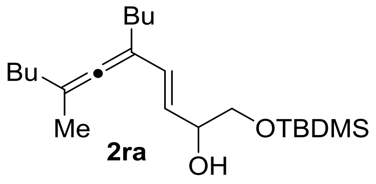
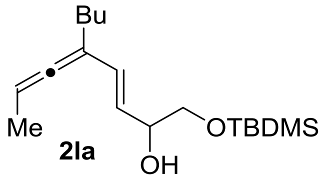
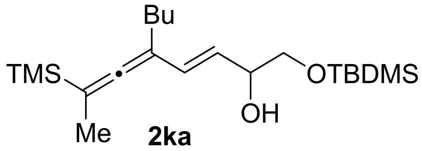
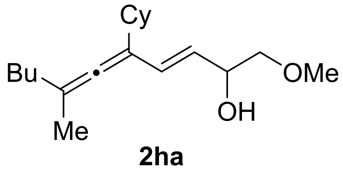
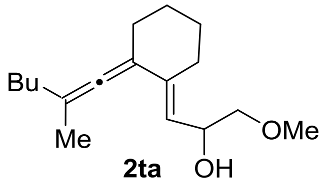
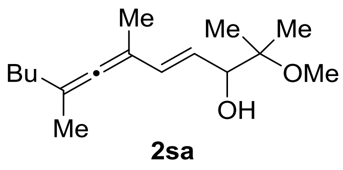
13	Me	20	78	1.5/1	.70min.	 **2ra**
14	Me	20	81	3,5/1	45min.	 **2la**
15	Me	100	N.D.[b]	N.D.[b]	O. N	 **2ka**
16	Me	100	55	N.D.[b]	75min.	 **2ha**
17	Me	20	81	20,3/1	55min.	 **2ta**
18	Me	20	89	2,5/1	50min.	 **2sa**

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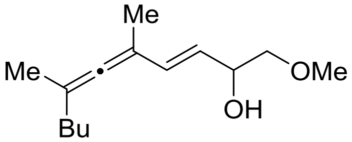
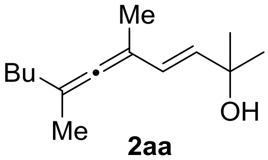
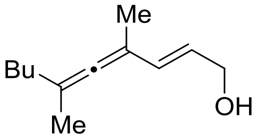
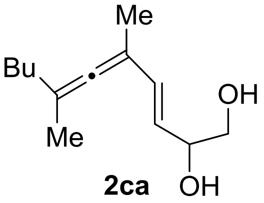
Table 4.5 (cont.)

19	Bu	20	75	1/1,2	55min.	 **2dd**
20	Me	20	83		50min.	 **2aa**
21	Me	20	67		45min.	 **2va**
22	Me	20	61	2.73/1	120min.	 **2ca**

[a] dr.: diastereomeric ratio. [b] N.D.: not determined.[c] determined by HPLC

Reactions probably begin with the formation of the organoiron structure by transmetallation of the Grignard reagent with iron (Figure 4.4). The epoxidation oxidative association of this reactive organometalline can form the π-allyliron (B) intermediate structure. The coordination of the organoiron's substrate with the triple bond (A) may have activated this step. (E) -conjugate enine oxirane is not possible in this way. (E) -1a can result from this difference in product yield at lower yields. In the next step, the migration of iron to distant alkynyl carbon and the rearrangement of π electrons will form the vinylallenyl iron structure (C). The fact that the R1 and R2 groups are too large in size will limit this migration and the metallicity of the alkynyl carbon which is compatible with the experimental data. The reaction is terminated by a reductive addition step to give the vinylated product having a hydroxyl group in the allylic group and the iron catalyst will be converted to the re-active form and will participate in the next reaction cycle. It is yet to bring an explanation of the stereo chemistry of the reaction. For this, the main stereochemical structure of the products needs to be determined.

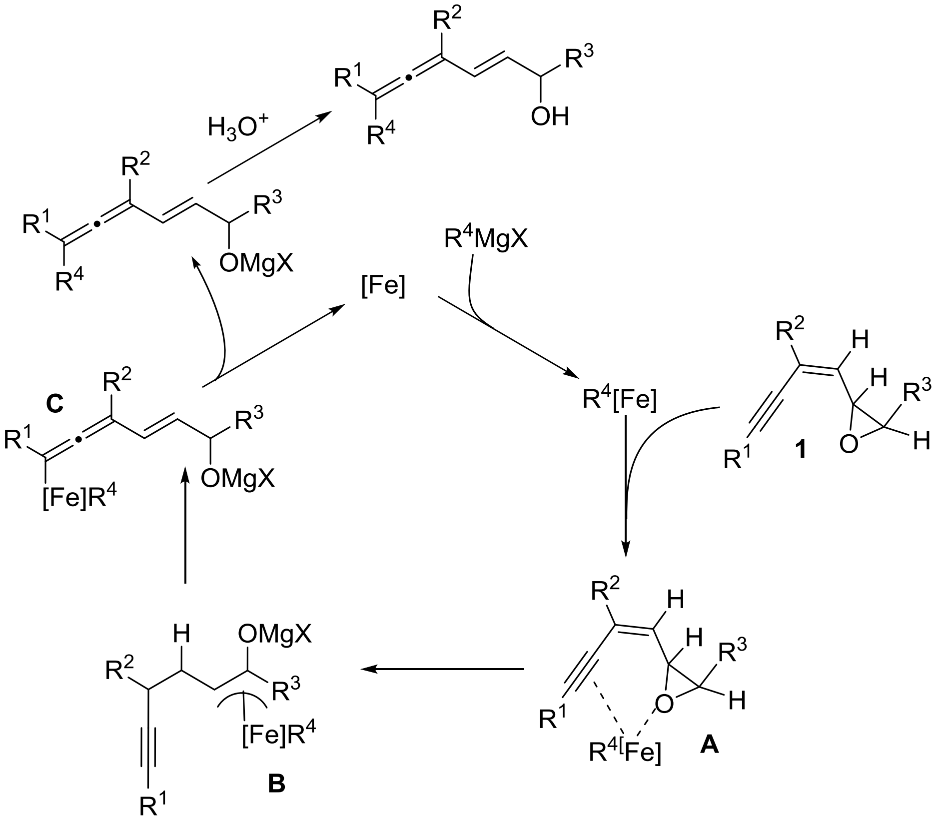


Figure.4.5 Presence of a cyclohexyl group on the alkenyl carbon reaction with BuMgCl

CHAPTER 5

CONCLUSION

In this study 1, 5-(S_N2'') substitution reactions were realized with 2,4-enyn oxirane compounds synthesized in laboratory and Grignard reagents over an iron-catalyst.

The occurrence of other potential 1,1- substitution (S_N2) and 1,3 – substitution (S_N2') reactions pathways has been minimized over an iron-catalyst. At the end of this reaction; (*i*)- a new carbon-carbon bond formed; (*ii*)-led to form a conjugate vinylallene structure because of the rearrangement of π-electrons; and (*iii*)-opening of the epoxide ring led the formation of a hydroxyl group on the allylic positioned.

In summary within the scope of this project, the first detailed iron-catalyzed reactions of enyne compounds that have an epoxide group with Grignard reagents has been presented

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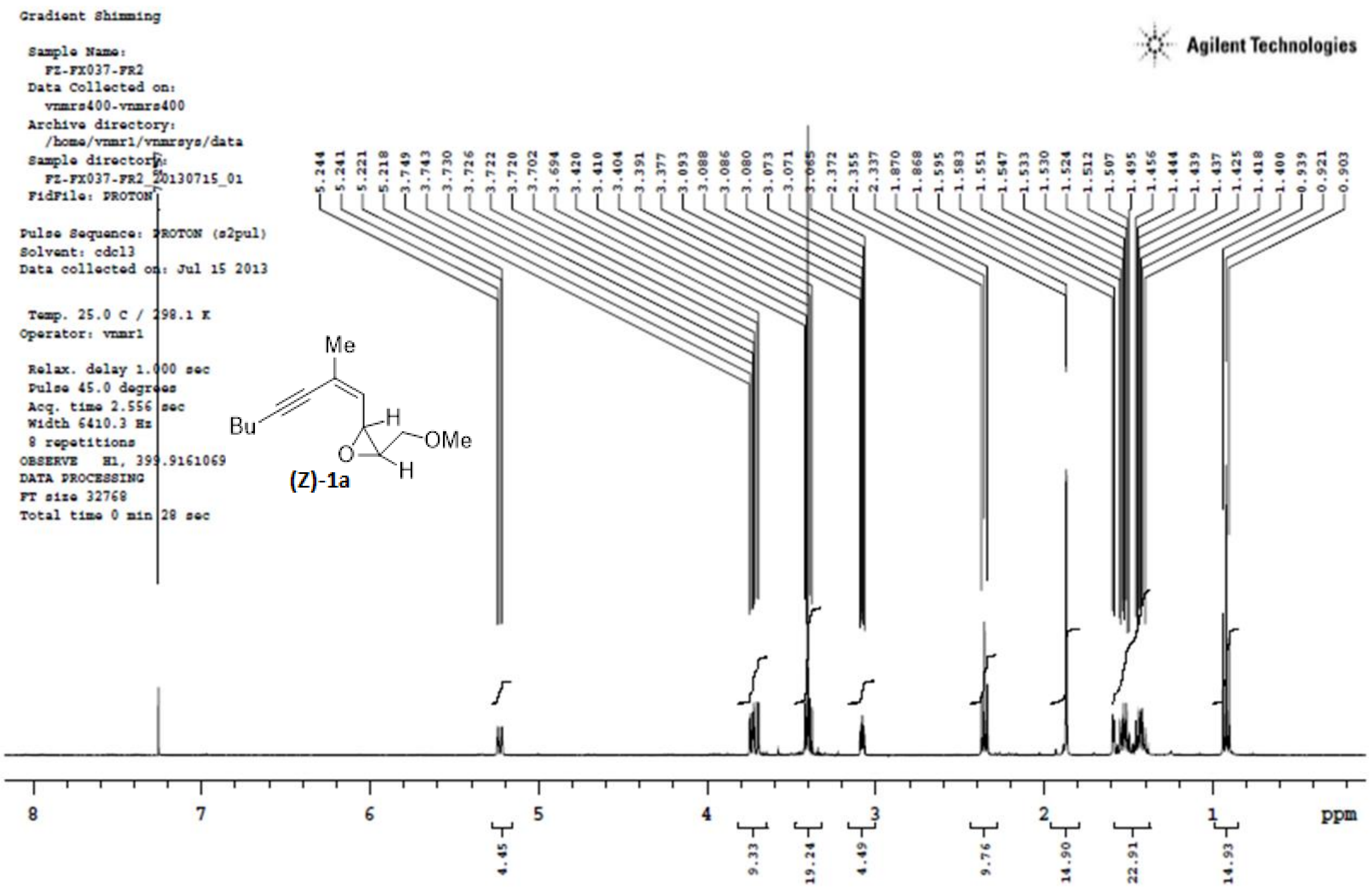
APPENDIX A

^{1}H AND ^{13}C SPECTRUM OF REACTANTS



Gradient Shimming

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Sample directory:
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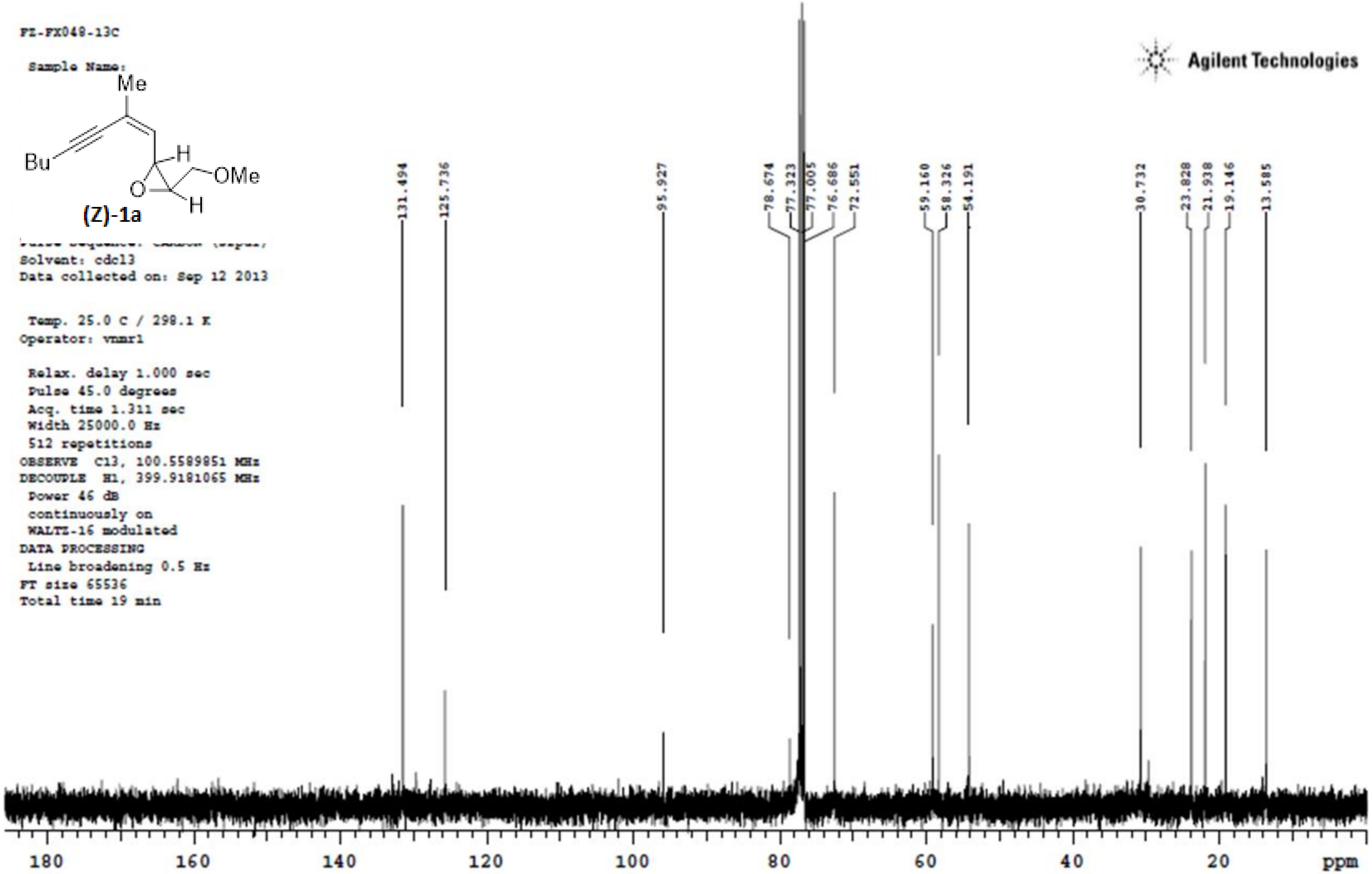
FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jul 15 2013

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.9161069
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec

(Z)-1a



FZ-FX048-13C

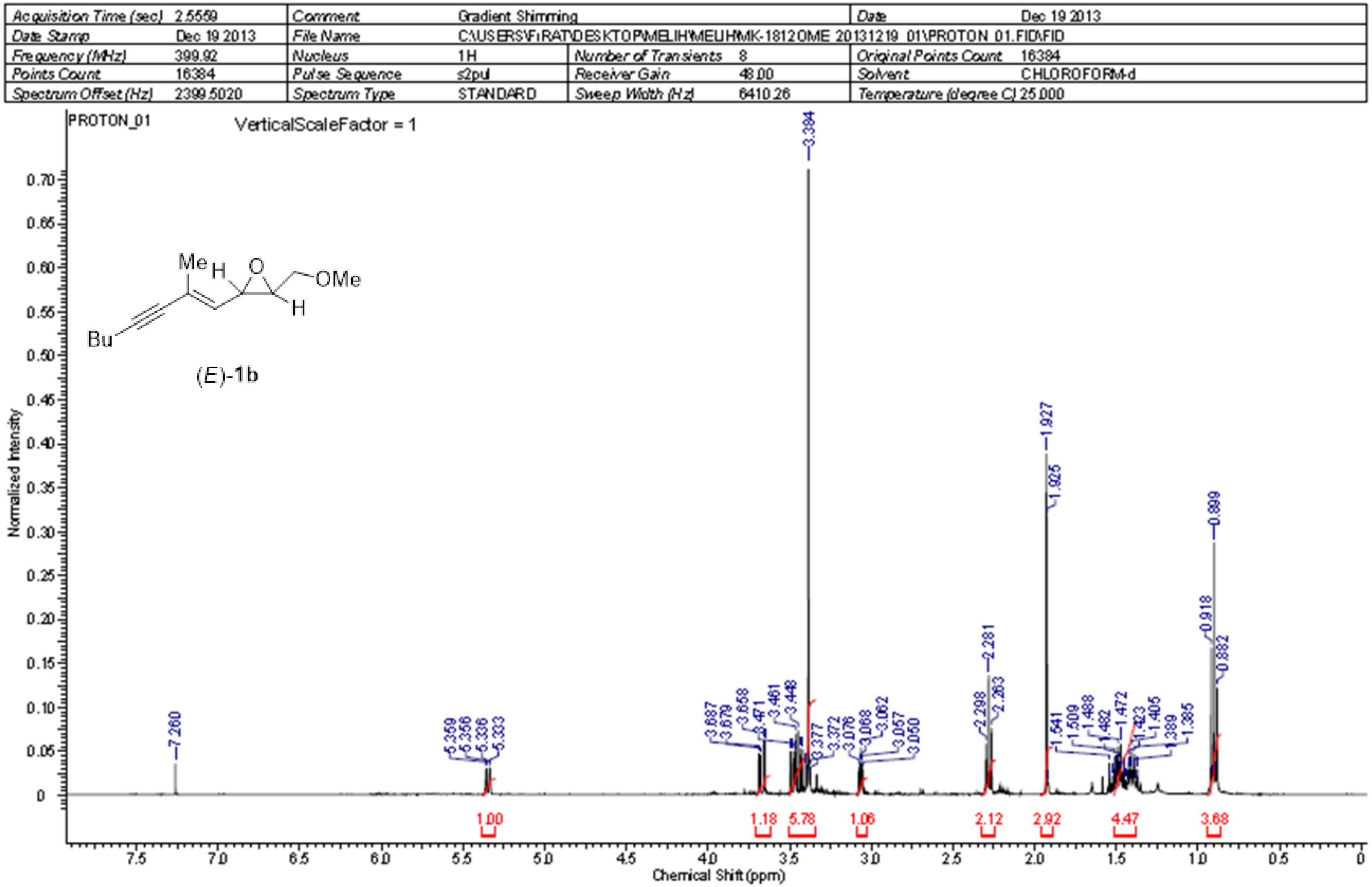
Sample Name:

(Z)-1a

[illegible]
Solvent: cdcl3
Data collected on: Sep 12 2013

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.5589851 MHz
DECOUPLE H1, 399.9181065 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min



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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*	48.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

(*E*)-**1b**

```
MK-1812OME

 Sample Name:
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 Data Collected on:
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 Archive directory:
   /home/user1/vnmrsys/data
 Sample directory:
   MK-1812OME_20131219_02
 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 19 2013

 Temp. 25.0 C / 298.1 K
Operator: user1

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 60 repetitions
OBSERVE  C13, 100.5589851 MHz
DECOUPLE  H1, 399.9181065 MHz
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 continuously on
 WALTZ-16 modulated
DATA PROCESSING
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FT size 65536
Total time 38 min
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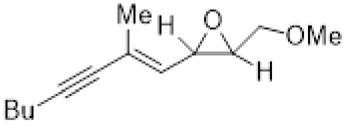
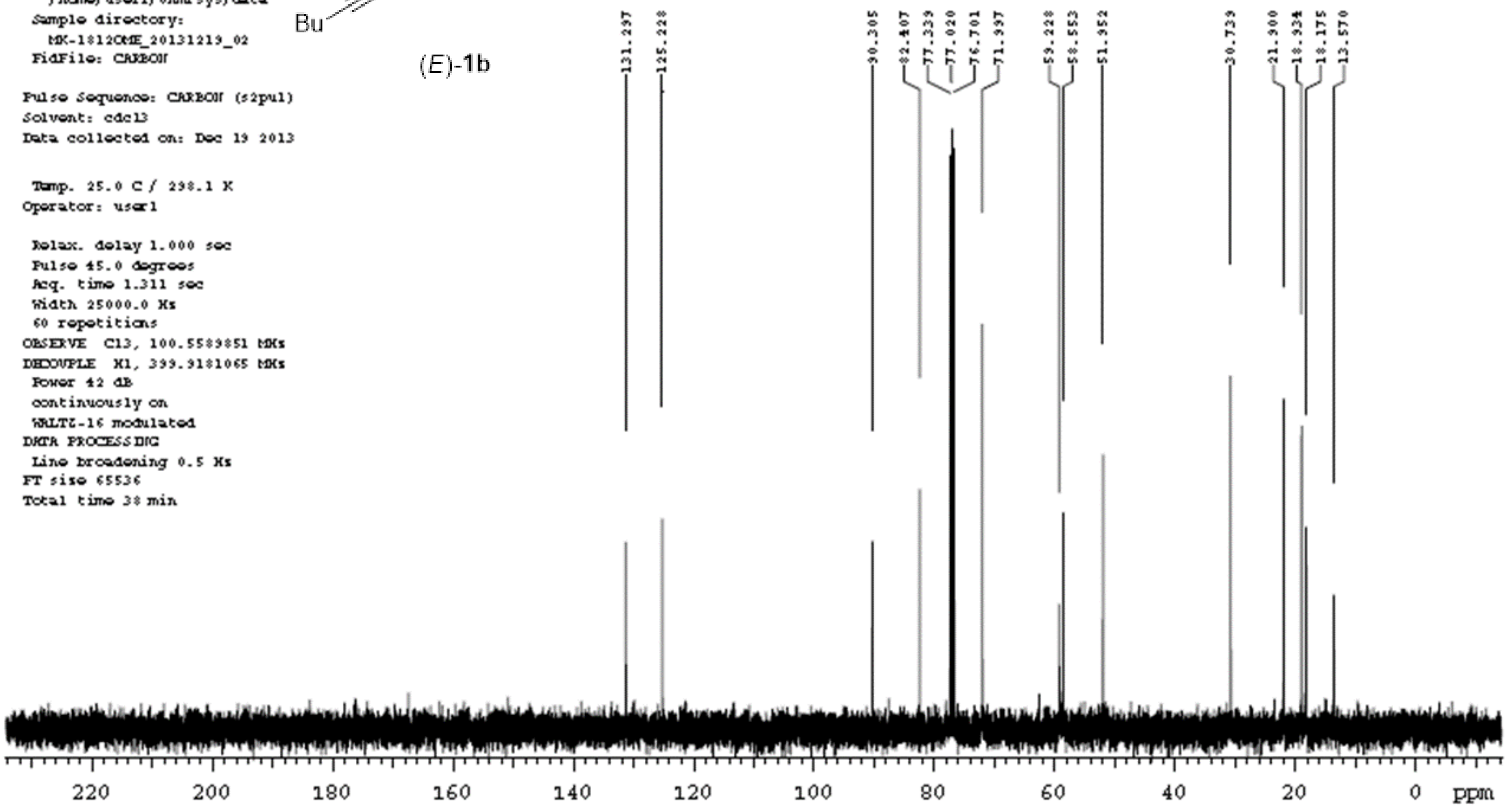


(*E*)-**1b**

Agilent Technologies



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Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	48.00	Solvent	BENZENE-d6
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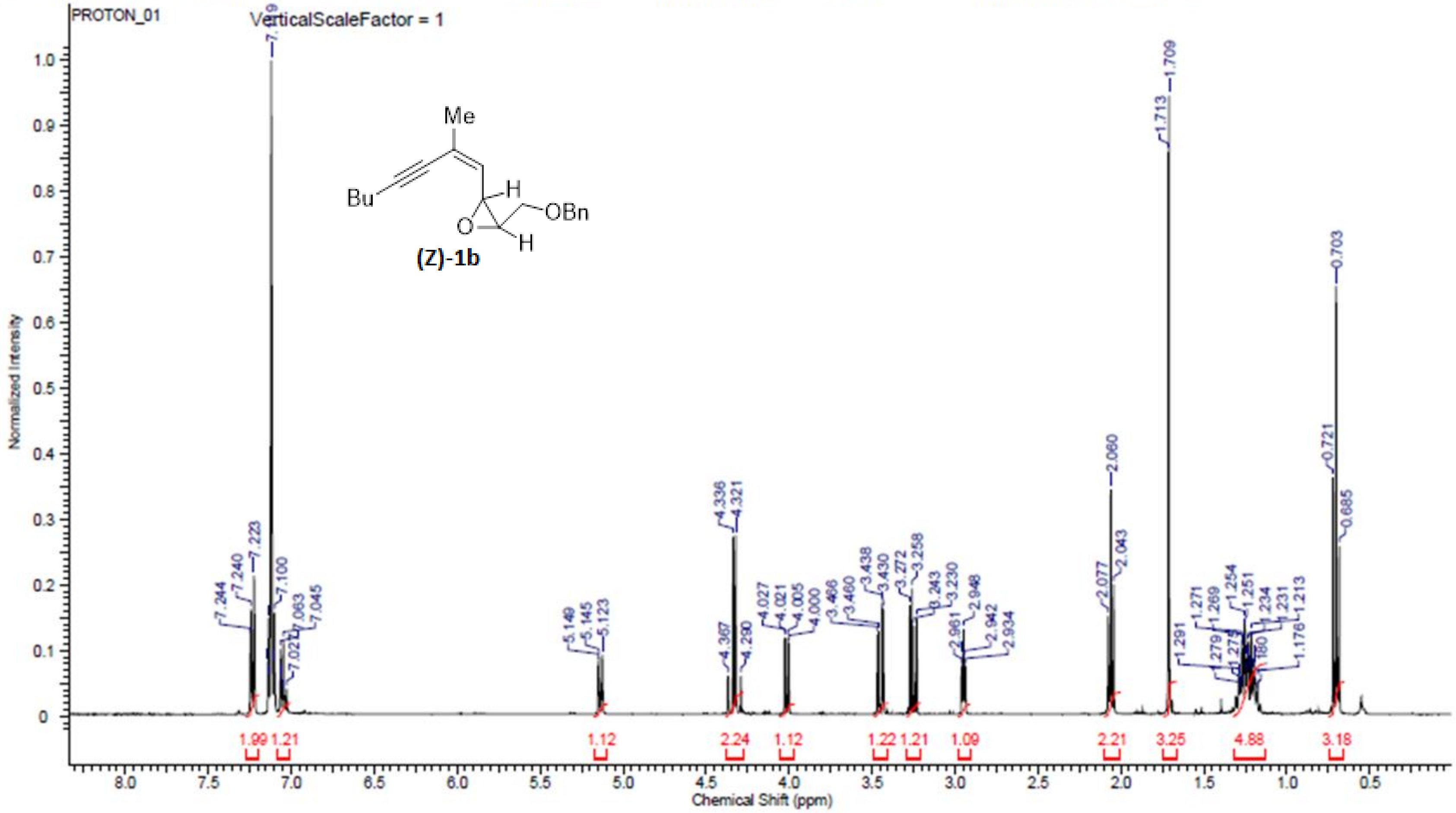

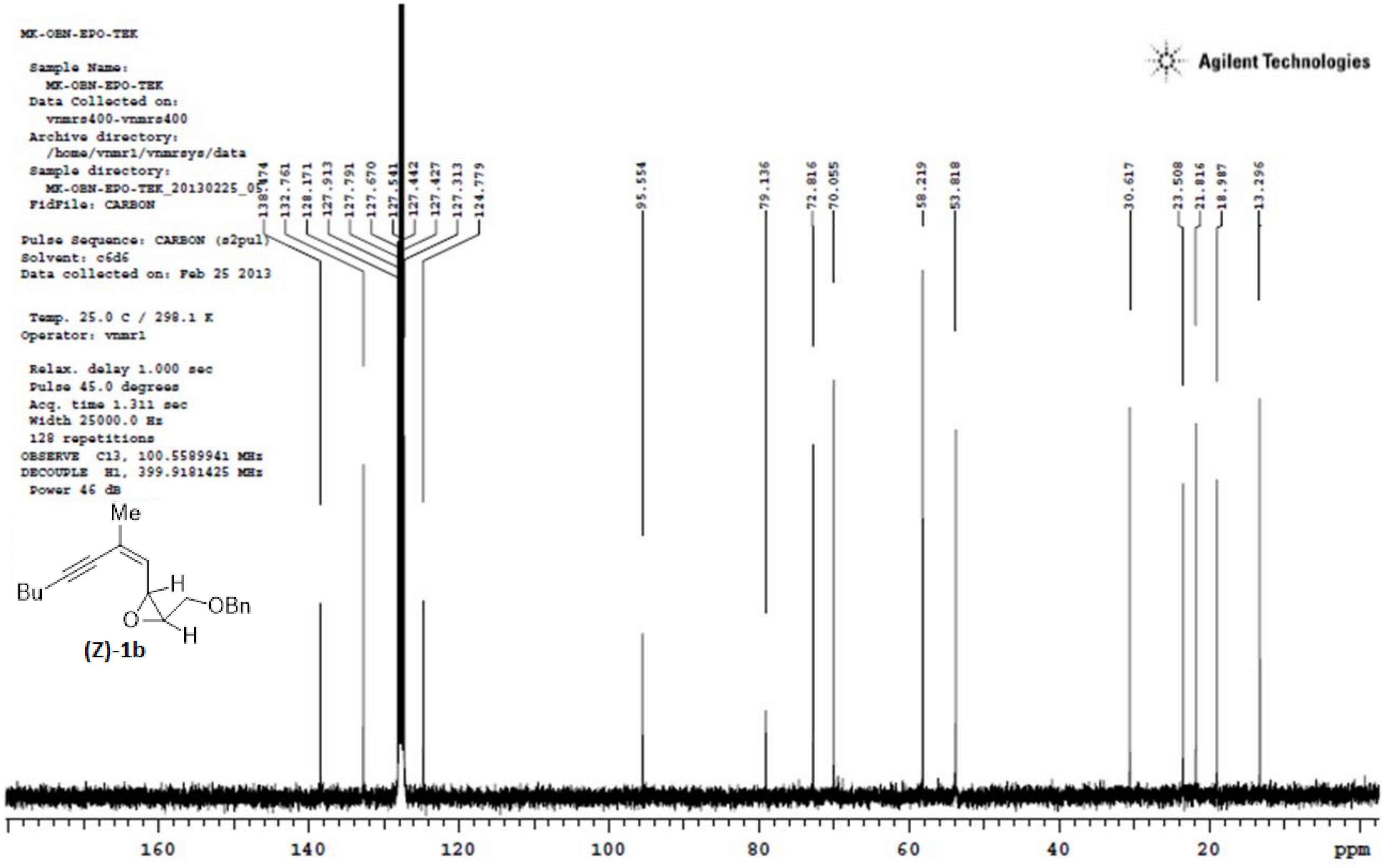

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   MK-OBN-EPO-TEK_20130225_05
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Pulse Sequence: CARBON (s2pul)
Solvent: c6d6
Data collected on: Feb 25 2013

 Temp. 25.0 C / 298.1 K
Operator: vnmr1

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 128 repetitions
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DECOUPLE  H1, 399.9181425 MHz
 Power 46 dB
```
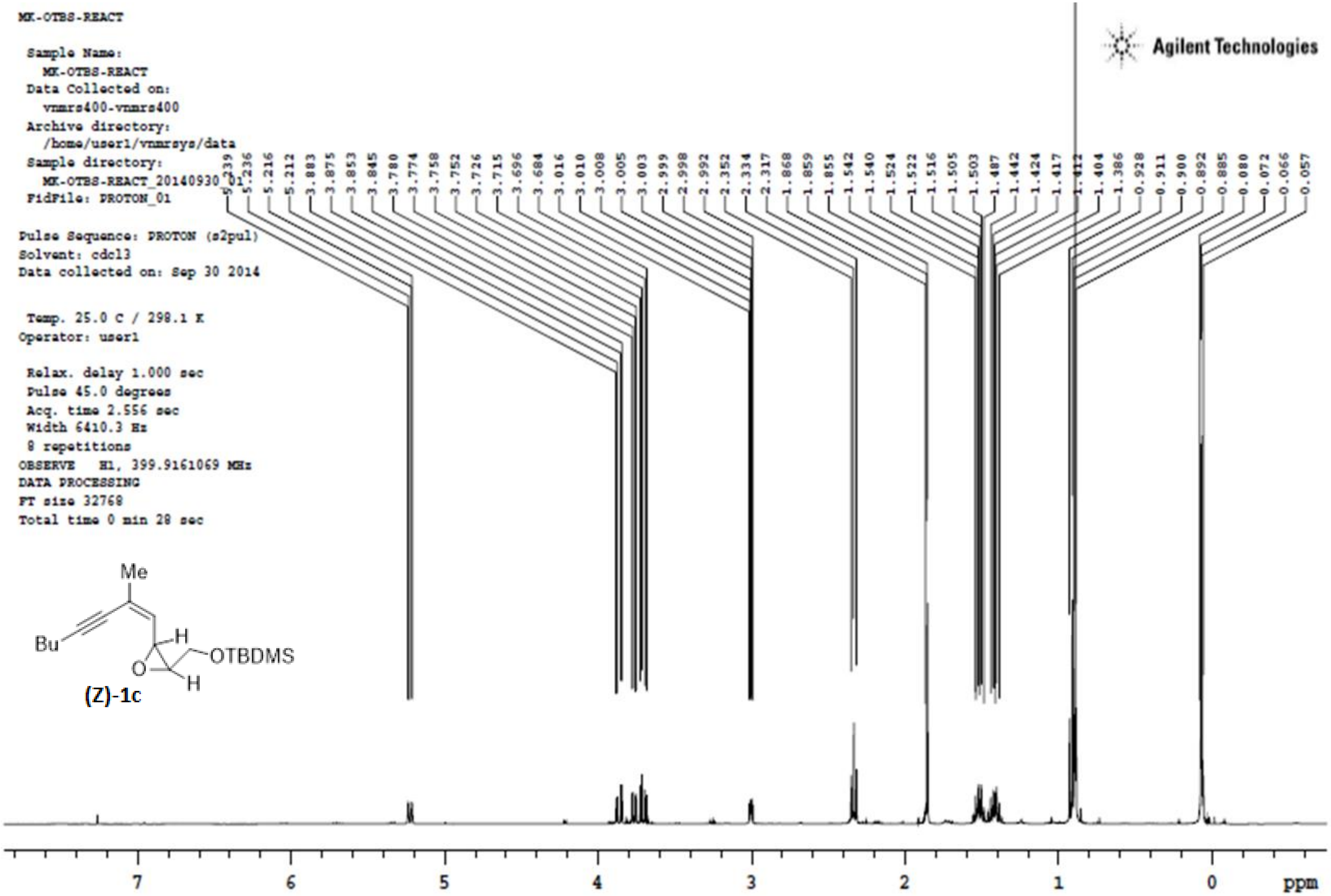

(Z)-1b



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 Sample directory:
   MK-OTBS-REACT_20140930_01
 FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 30 2014

 Temp. 25.0 C / 298.1 K
Operator: user1

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
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OBSERVE   H1, 399.9161069 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
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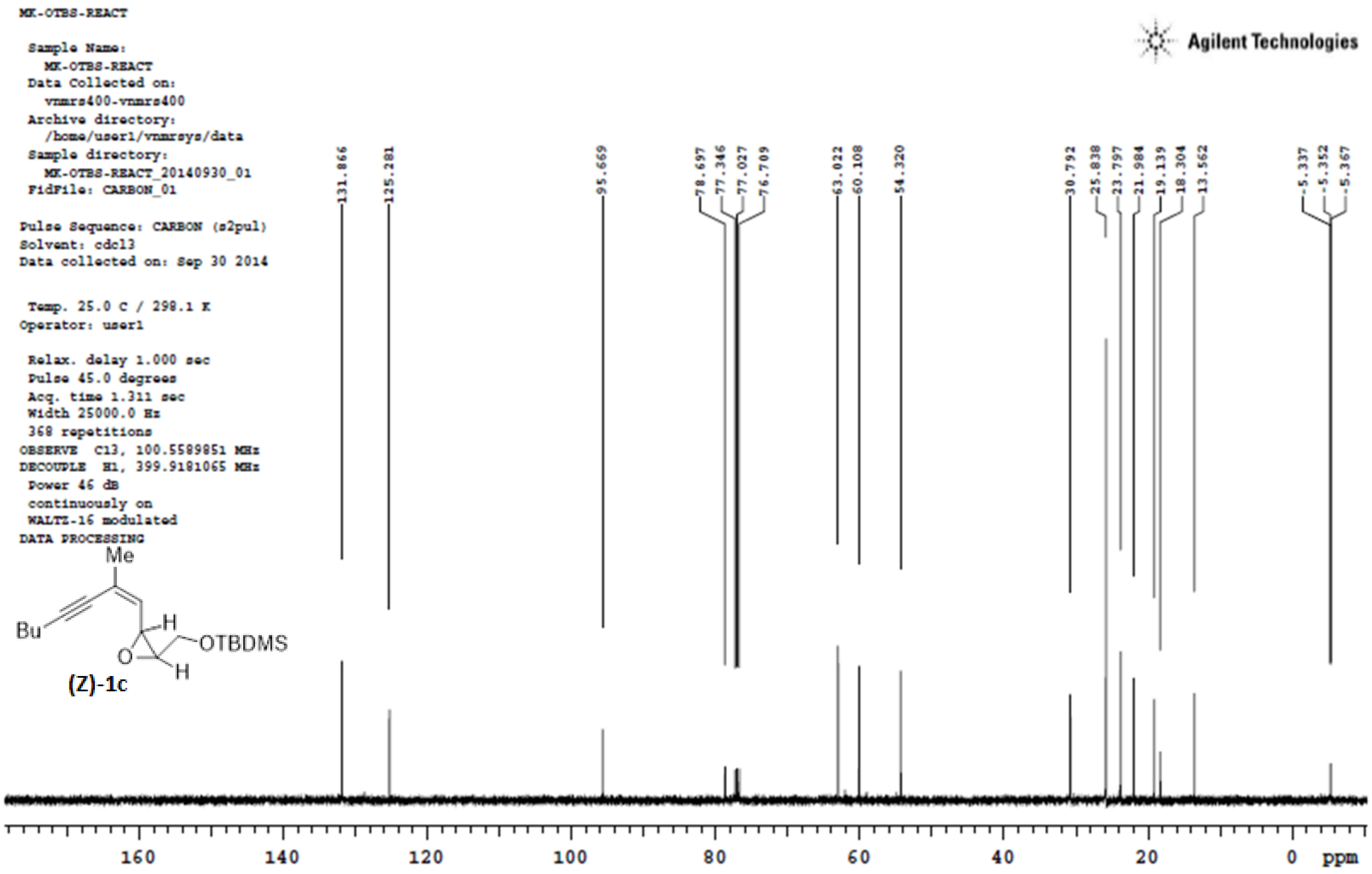
(Z)-1c



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Archive directory:
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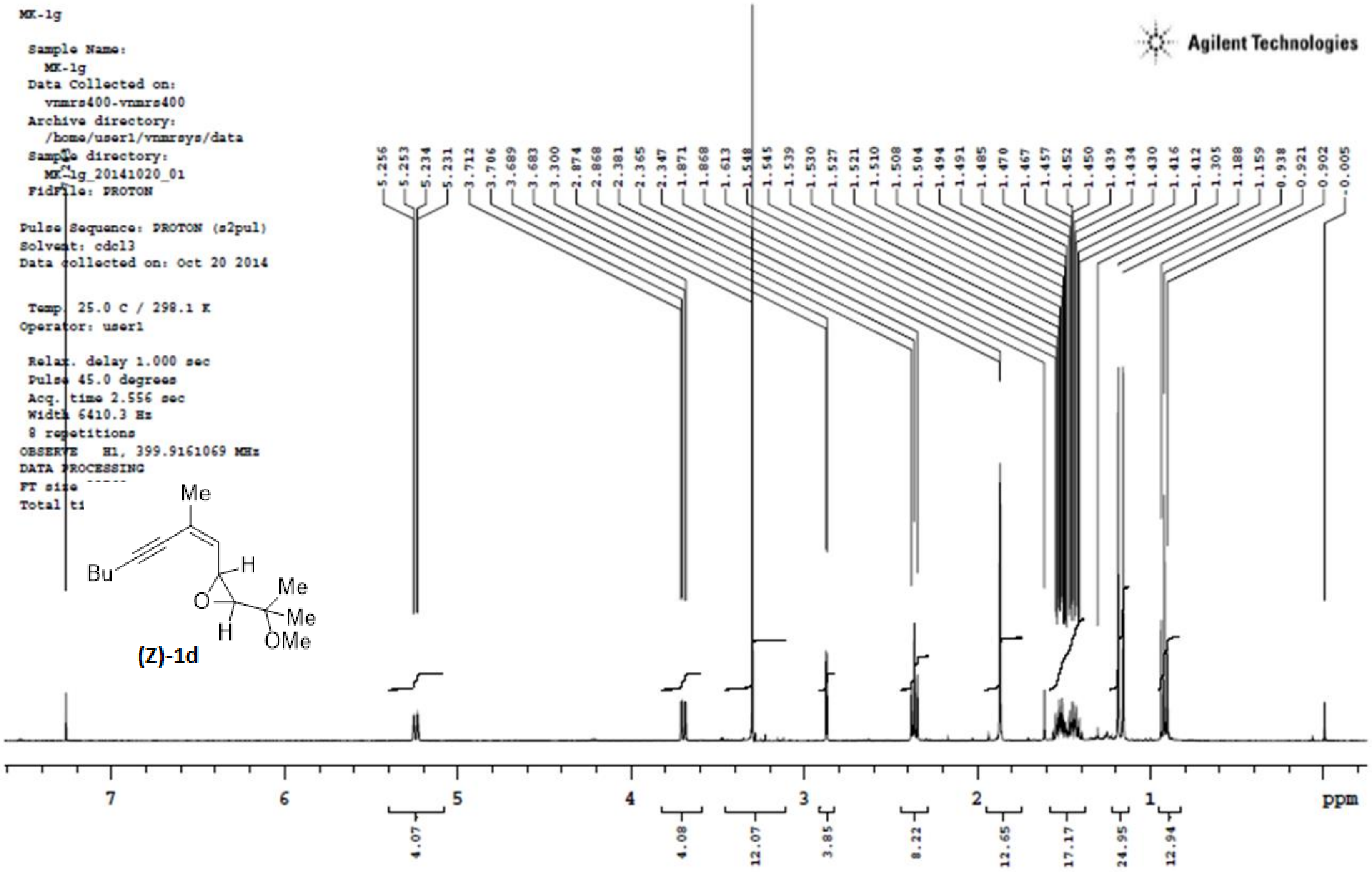
Sample directory:
MK-OTBS-REACT_20140930_01
FidFile: CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 30 2014

Temp. 25.0 C / 298.1 K
Operator: user1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
368 repetitions
OBSERVE C13, 100.5589851 MHz
DECOUPLE H1, 399.9181065 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING

(Z)-1c



MK-1g

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Sample directory:
MK-1g_20141020_01
FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 20 2014

Temp. 25.0 C / 298.1 K
Operator: user1

Relax. delay 1.000 sec
Pulse 45.0 degrees
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Width 6410.3 Hz
8 repetitions
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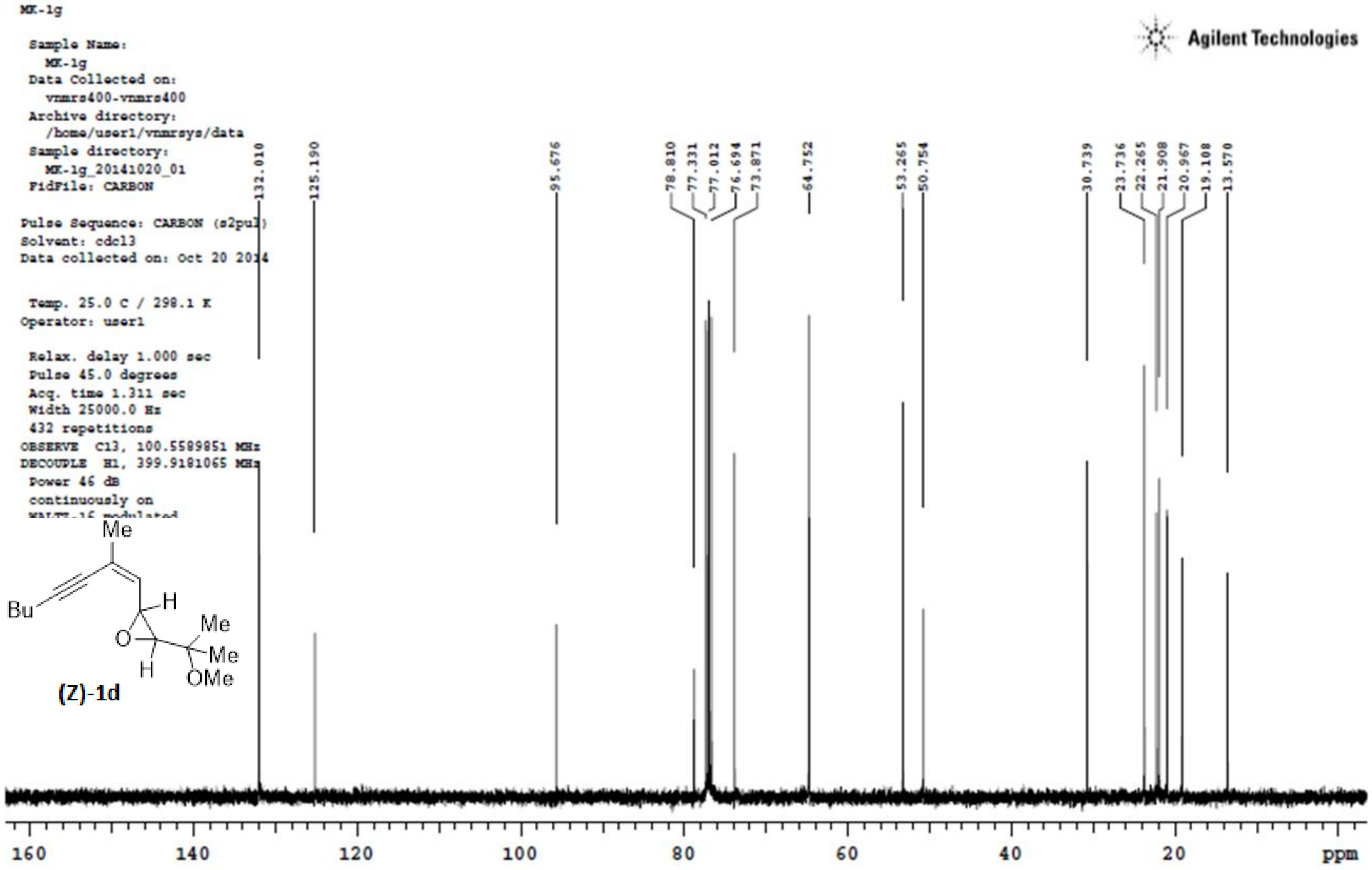
DATA PROCESSING
FT size
Total ti

(Z)-1d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MX-1g_20141020_01
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 20 2014

Temp. 25.0 C / 298.1 K
Operator: user1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
432 repetitions
OBSERVE C13, 100.5589851 MHz
DECOUPLE H1, 399.9181065 MHz
Power 46 dB
continuously on
WALTZ-16 modulated

(Z)-1d

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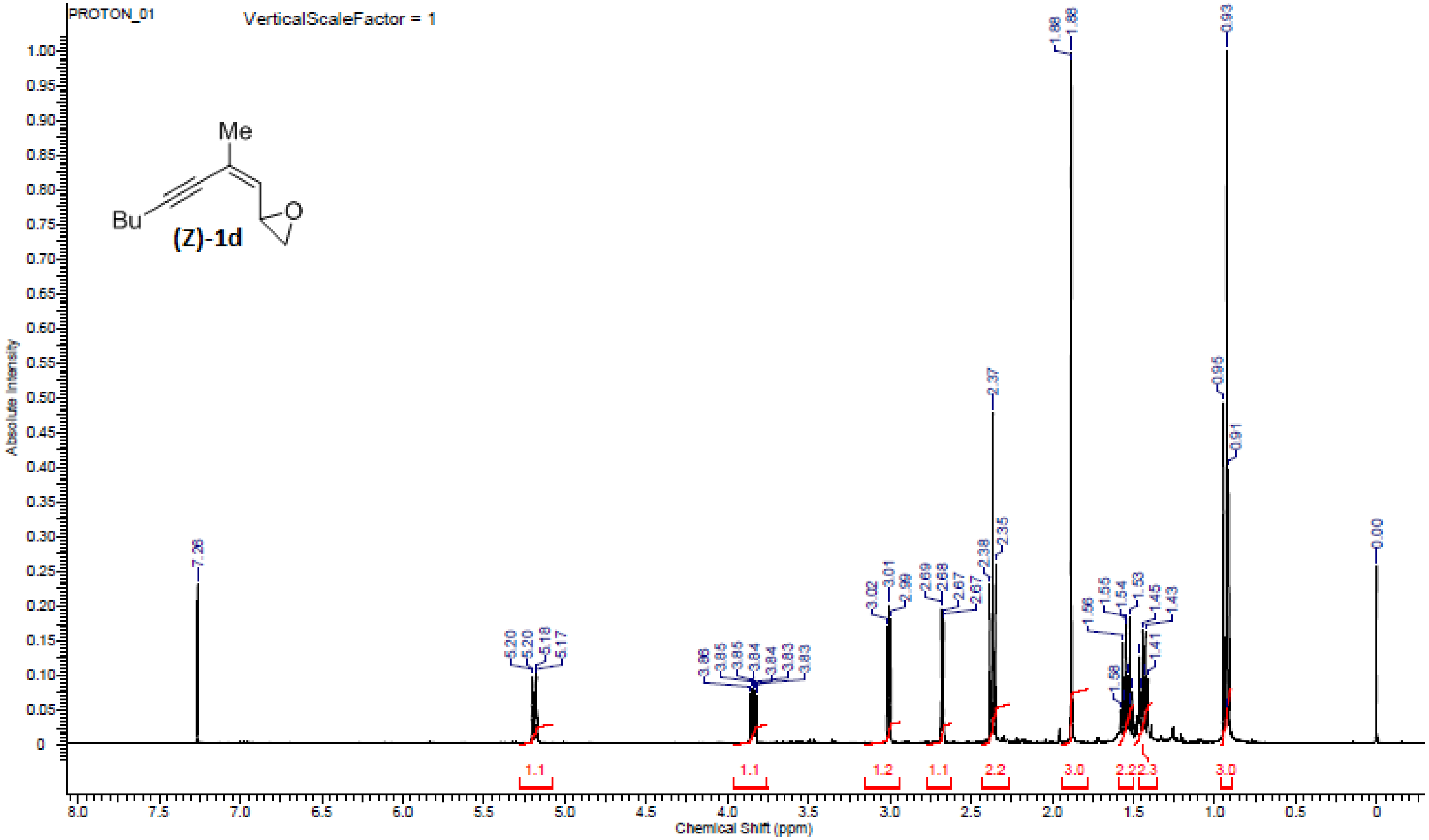

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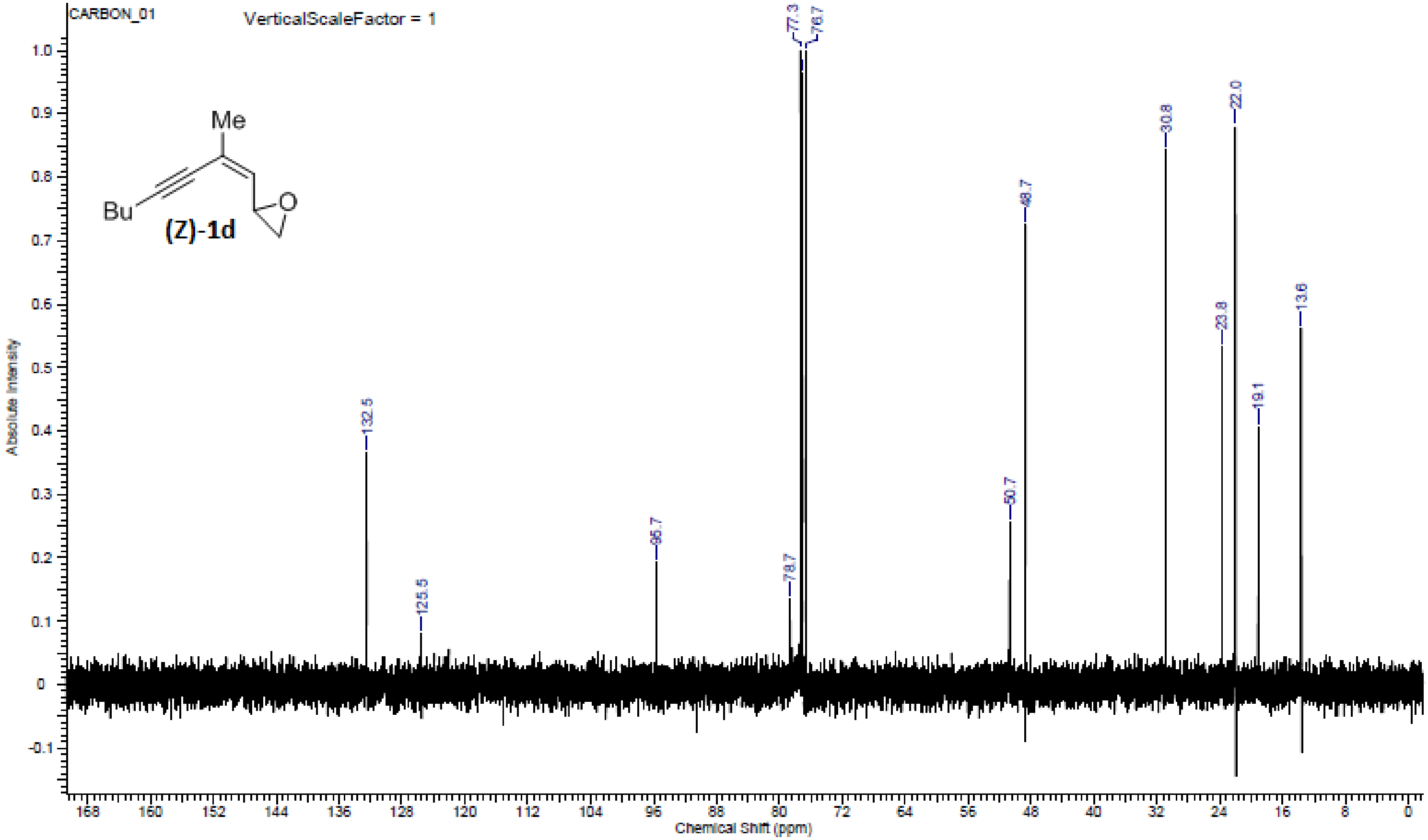

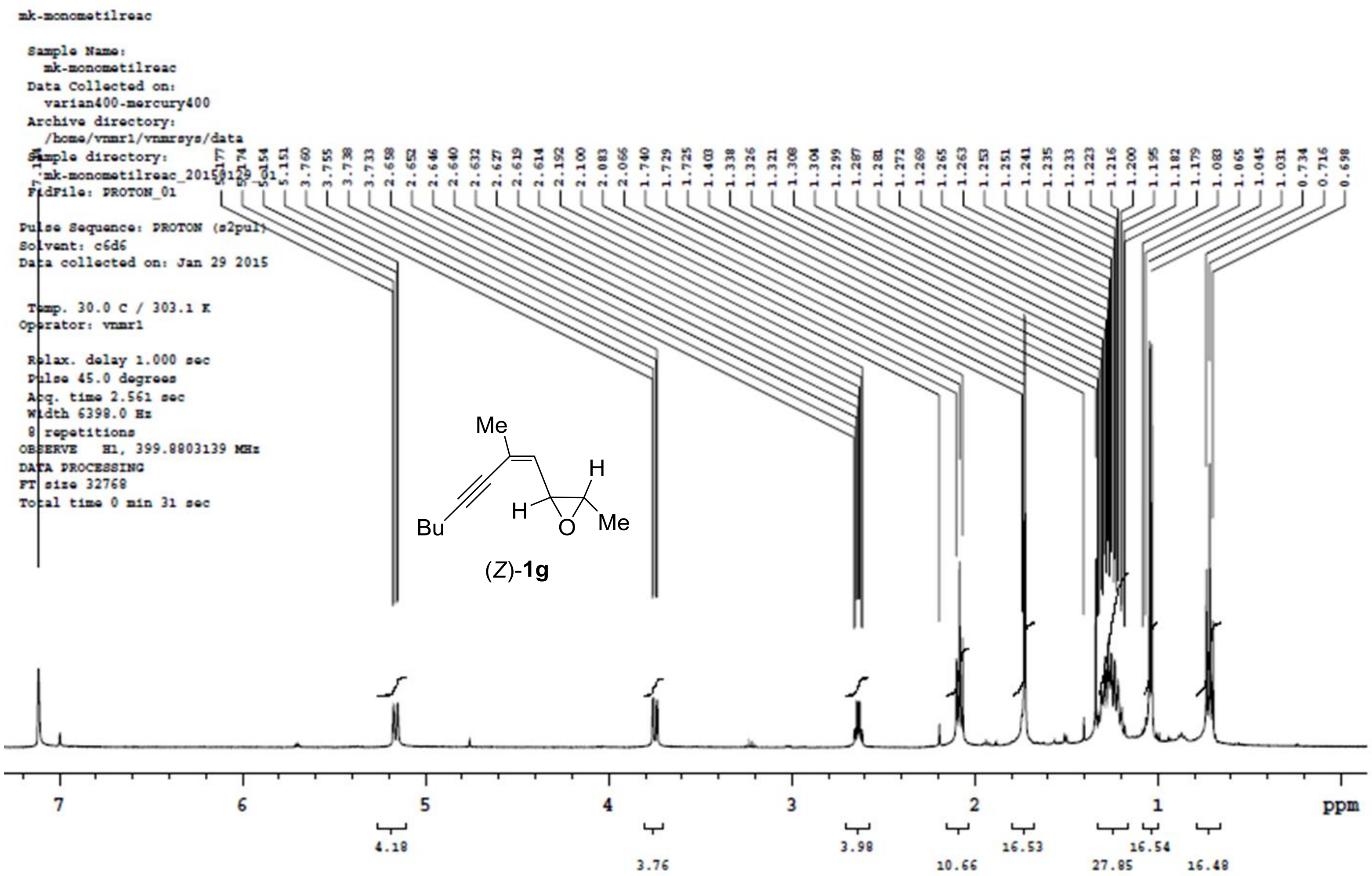
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Pulse Sequence: PROTON (s2pul)
Solvent: c6d6
Data collected on: Jan 29 2015
Temp. 30.0 C / 303.1 K
Operator: vnmr1
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Pulse 45.0 degrees
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Width 6398.0 Hz
8 repetitions
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DATA PROCESSING
FT size 32768
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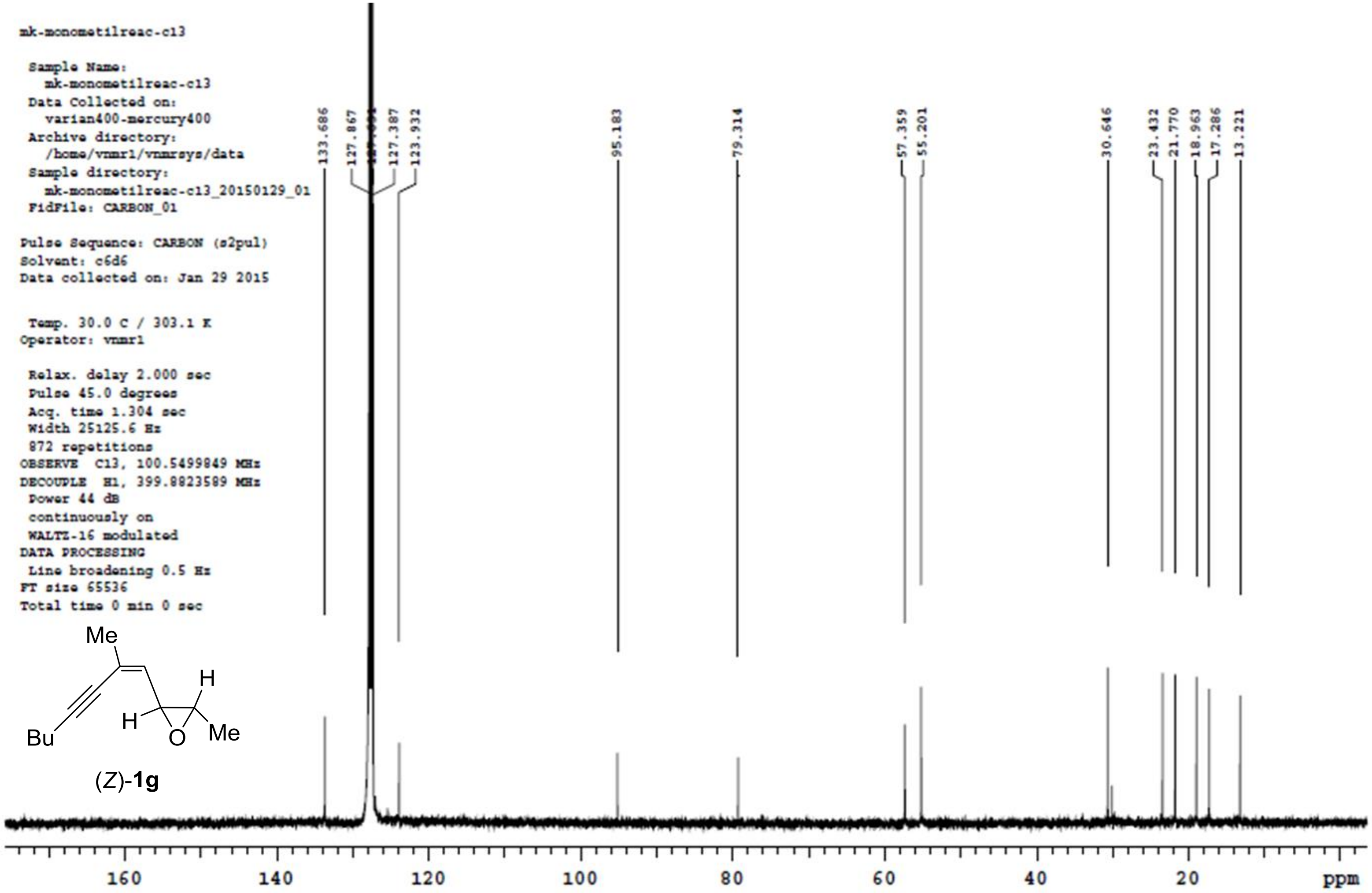
(*Z*)-**1g**



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 FidFile: CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: c6d6
Data collected on: Jan 29 2015

 Temp. 30.0 C / 303.1 K
Operator: vnmr1

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 Acq. time 1.304 sec
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 872 repetitions
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DECOUPLE  H1, 399.8823589 MHz
 Power 44 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
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(*Z*)-**1g**

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

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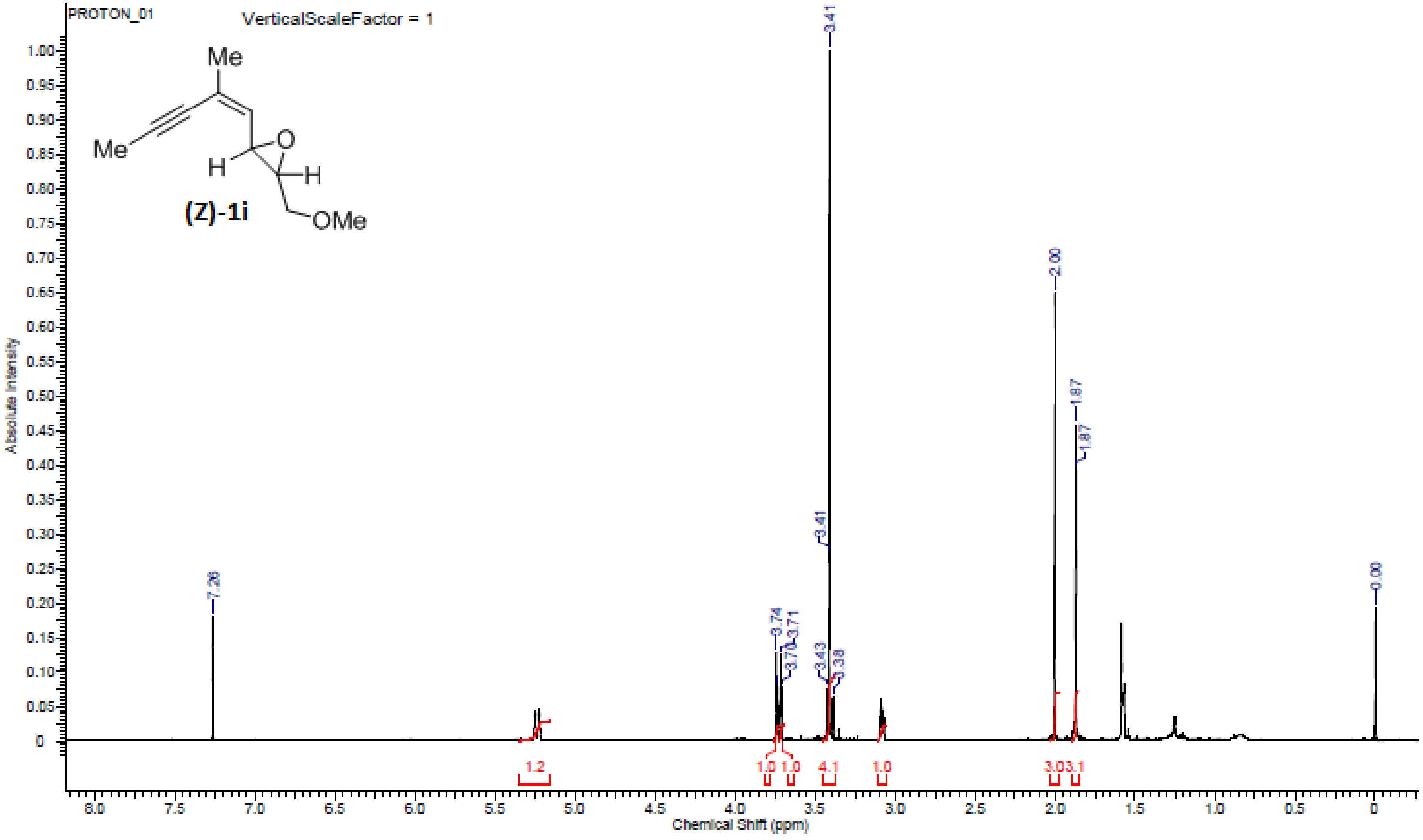

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Pulse Sequence	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d		
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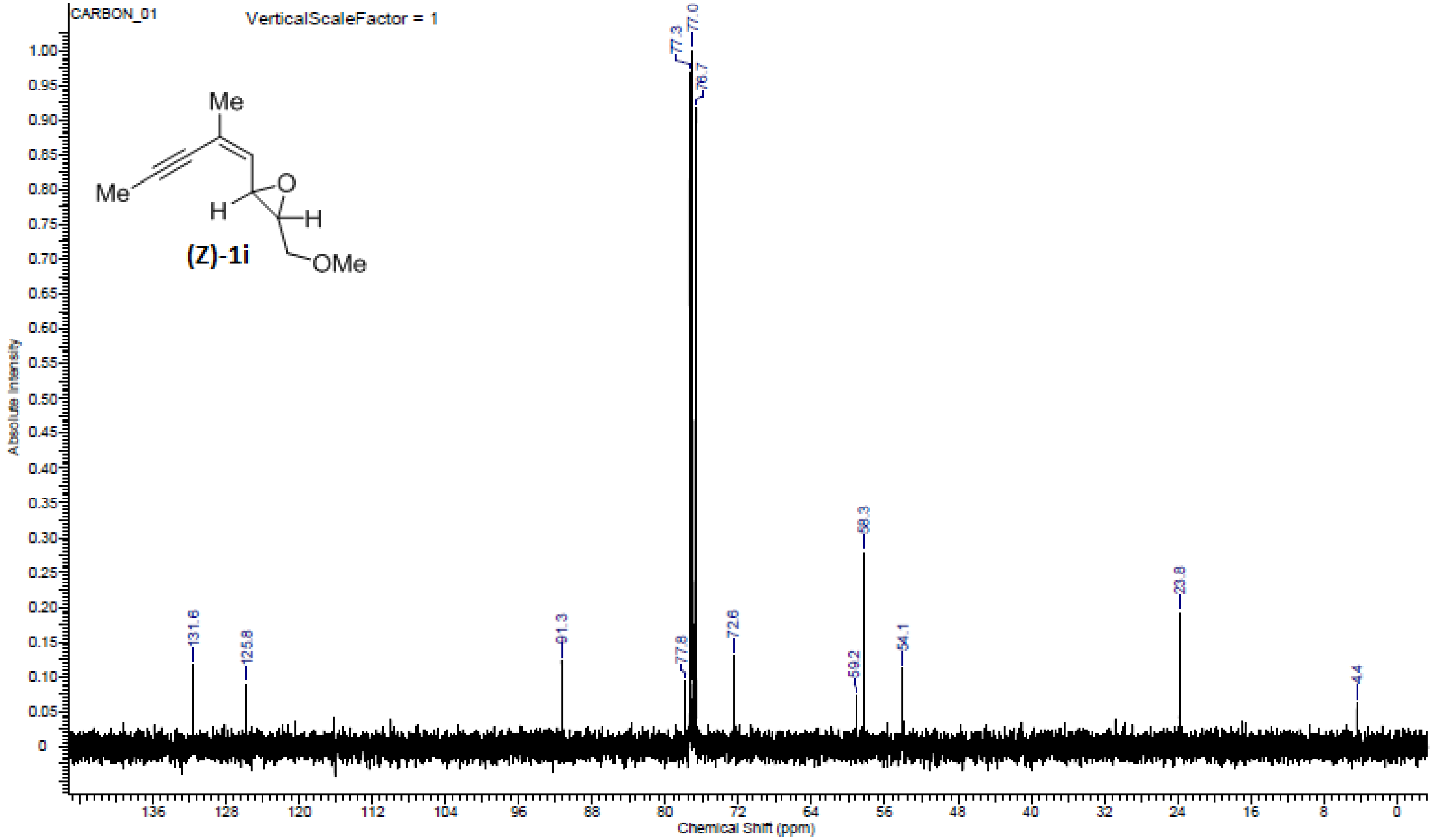

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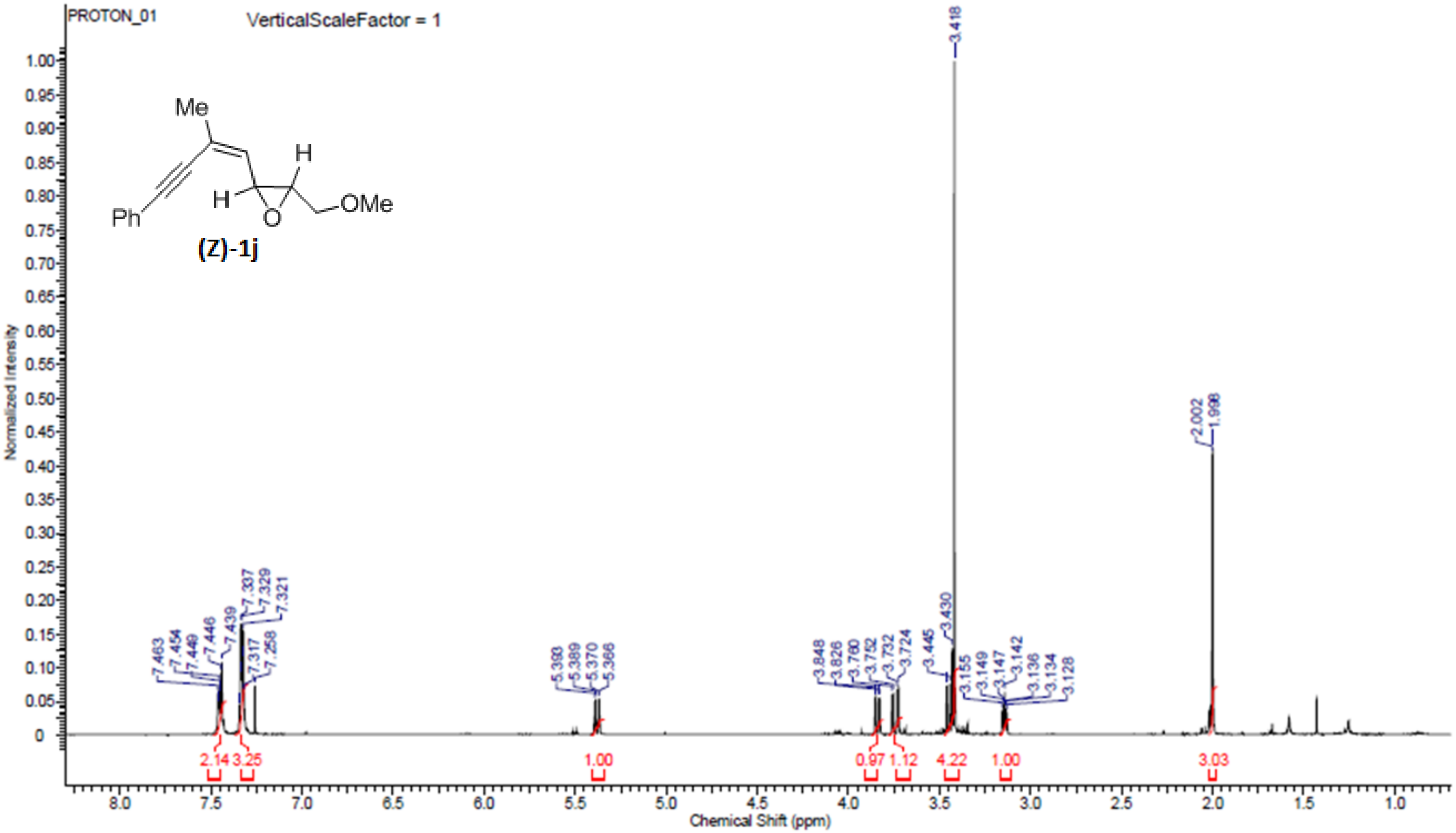
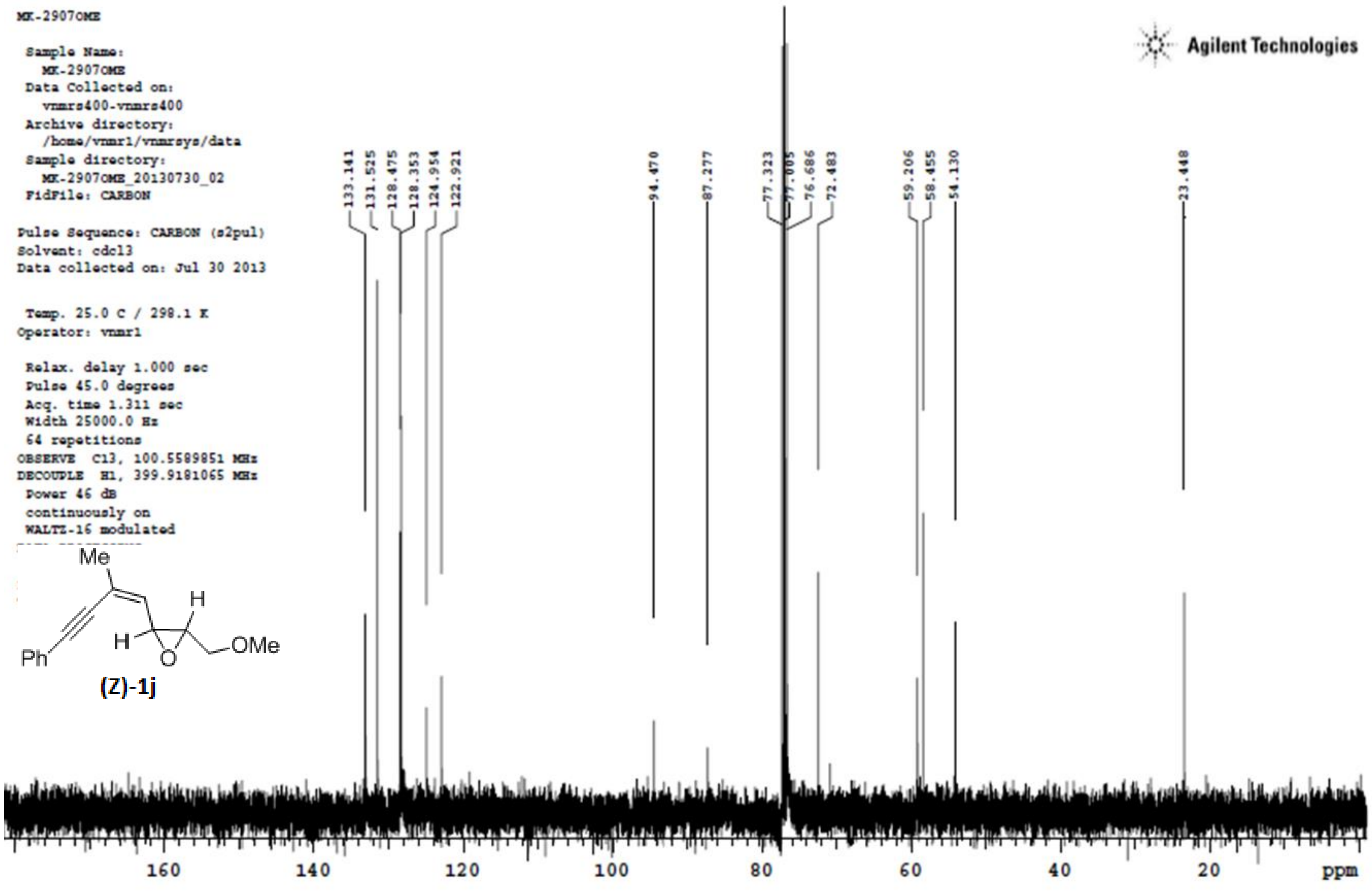
Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	60.00	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



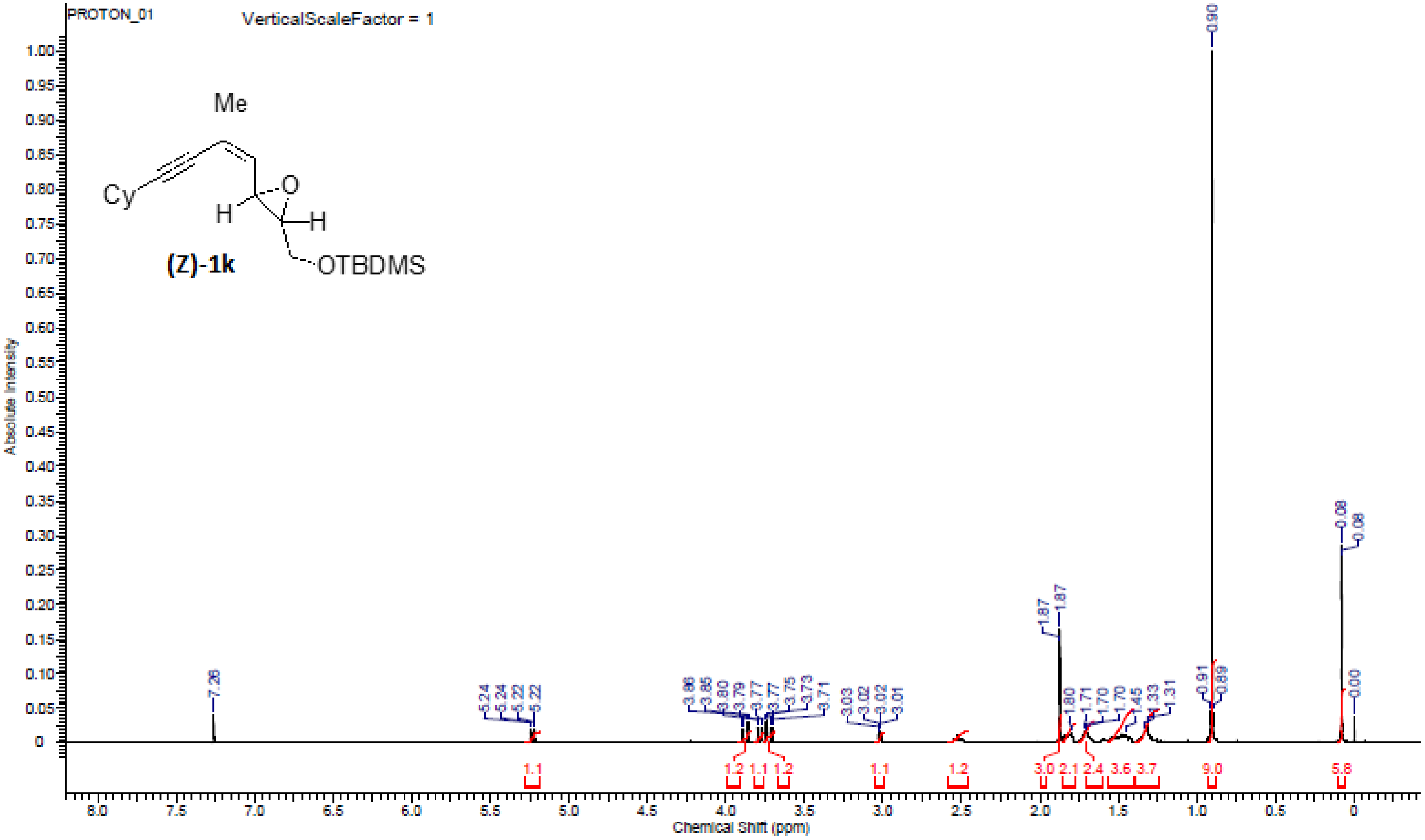


```
MK-2907OME

 Sample Name:
   MK-2907OME
 Data Collected on:
   vnmrs400-vnmrs400
 Archive directory:
   /home/vnmr1/vnmrsys/data
 Sample directory:
   MK-2907OME_20130730_02
 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 30 2013

 Temp. 25.0 C / 298.1 K
Operator: vnmr1

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 64 repetitions
OBSERVE  C13, 100.5589851 MHz
DECOUPLE  H1, 399.9181065 MHz
 Power 46 dB
 continuously on
 WALTZ-16 modulated
```

(Z)-1j

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

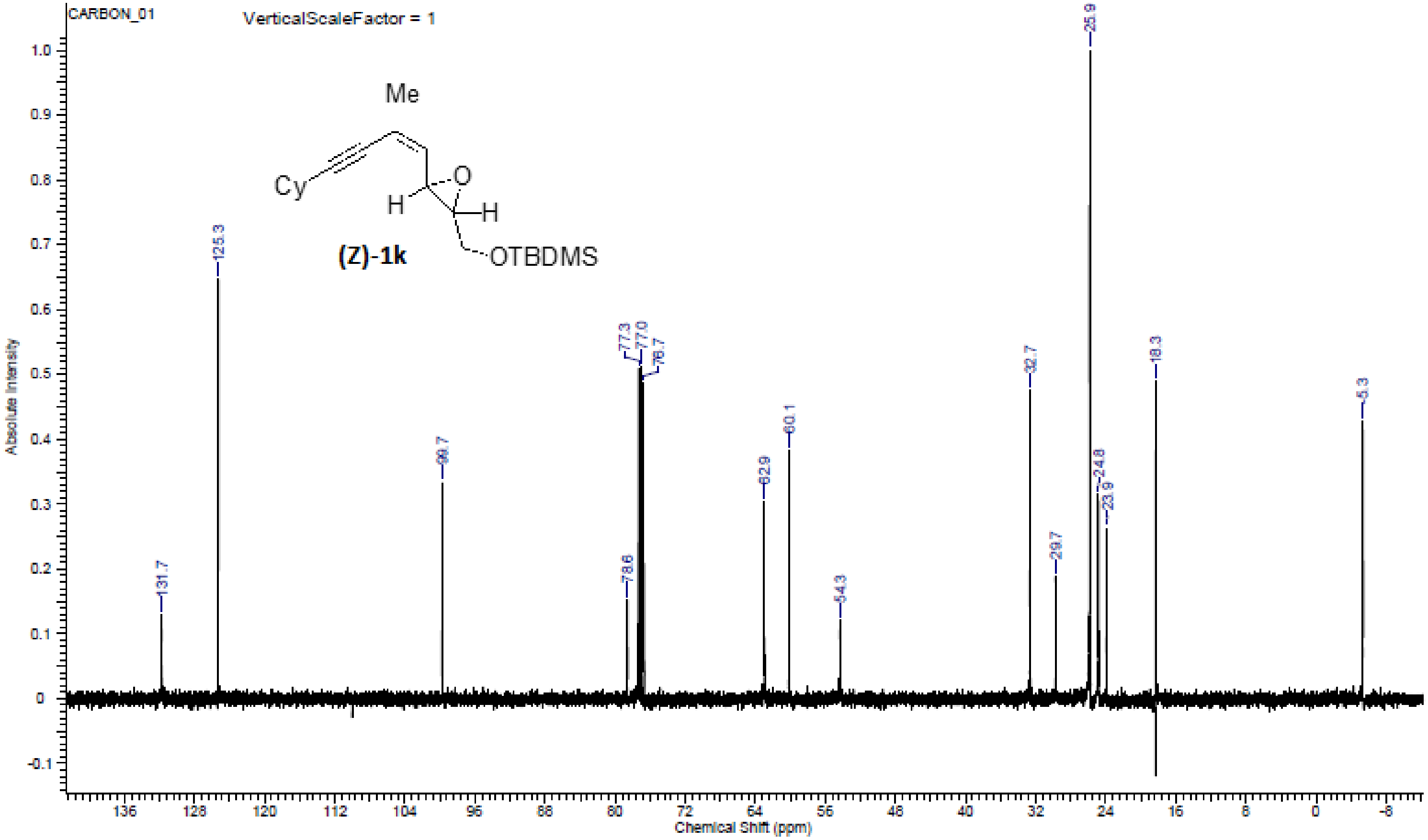
Acquisition Time (sec)	2.5559	*Comment*	FZ-FX-218	*Date*	Apr 25 2016	*Date Stamp*	Apr 25 2016
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX-218_20160425_01\PROTON_01.FID\FID					*Frequency (MHz)*	399.92
Nucleus	1H	*Number of Transients*	8	*Original Points Count*	16384	*Points Count*	16384
Pulse Sequence	s2pul	*Receiver Gain*	58.00	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	2399.5020	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

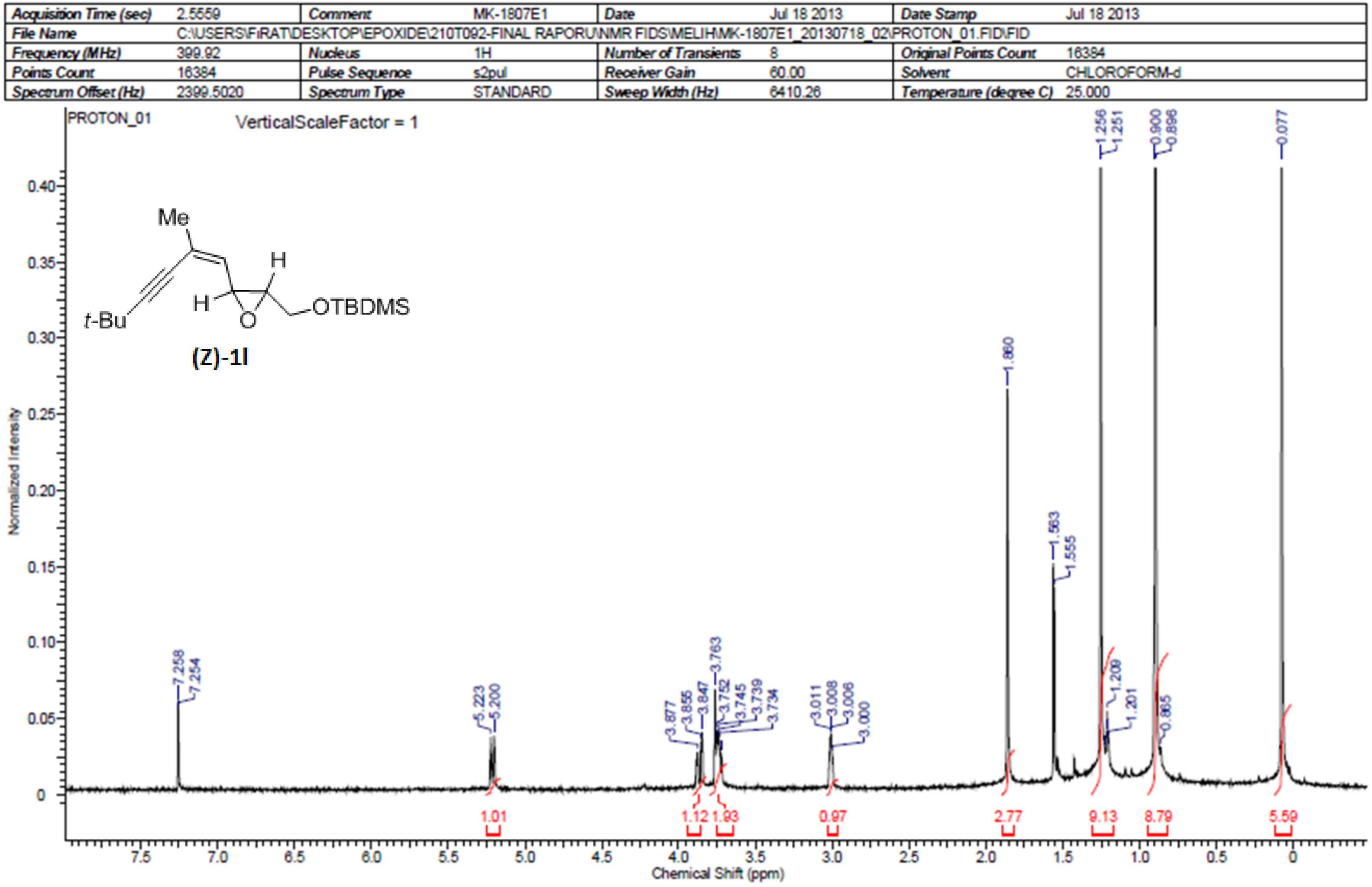


(Z)-1k

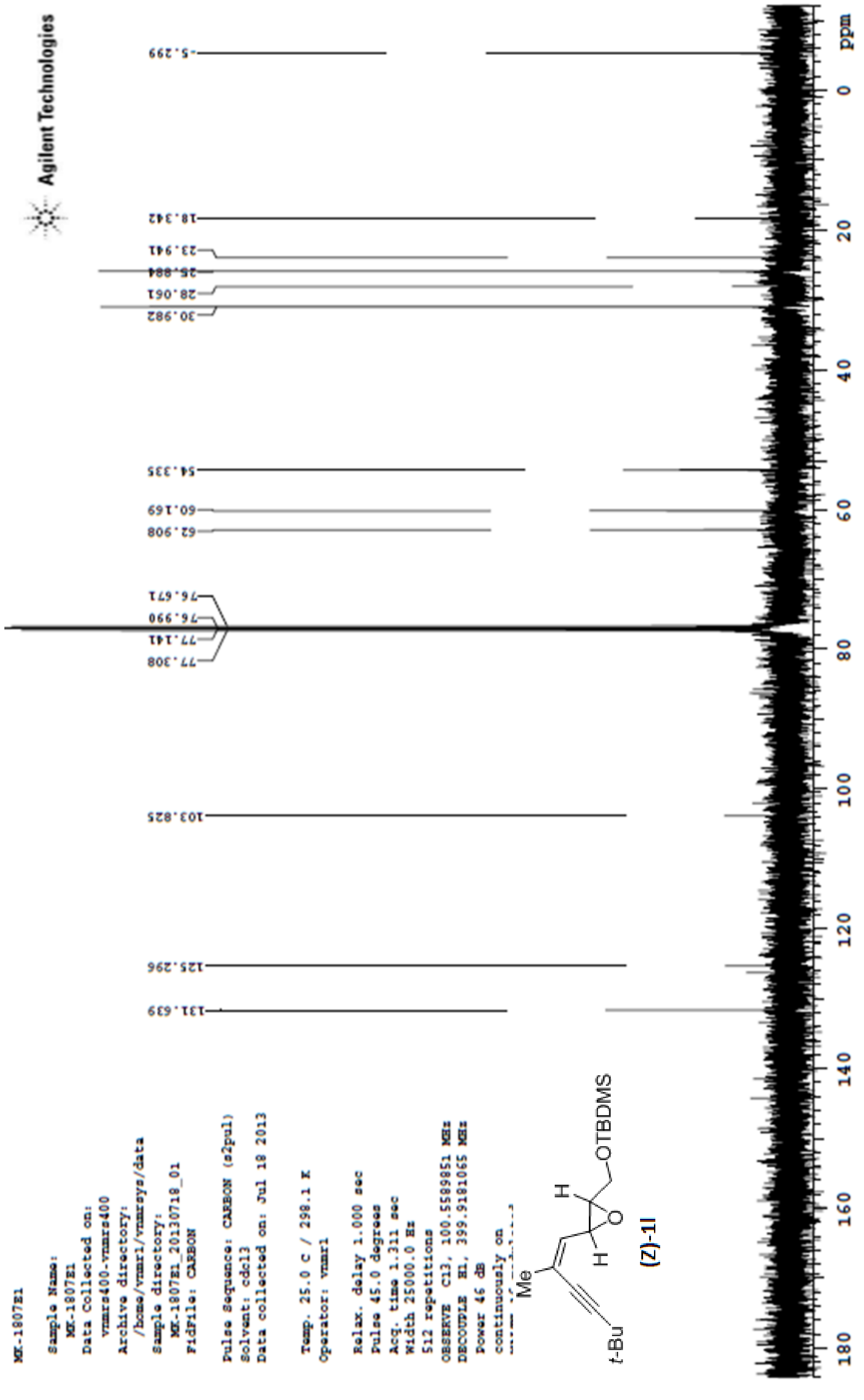
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.3107	*Comment*	FZ-R1CYH-C	*Date*	Apr 22 2016	*Date Stamp*	Apr 22 2016
File Name	D:\REACTANT NMR SPECTRUM\FZ-R1CYH-C_20160422_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**	MK-1807E1	**Date**	Jul 18 2013	**Date Stamp**	Jul 18 2013
File Name	C:\USERS\FIRAT\DESKTOP\EPOXIDE\210T092-FINAL RAPORU\NMR FIDS\MELIH\MK-1807E1_20130718_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**	60.00	**Solvent**	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	6410.26	**Temperature (degree C)**	25.000



(Z)-1l

MK-1807E1

Sample Name:
MK-1807E1
Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/vnmr1/vnmrsys/data
Sample directory:
MK-1807E1_20130718_01
FidFile: CARBON

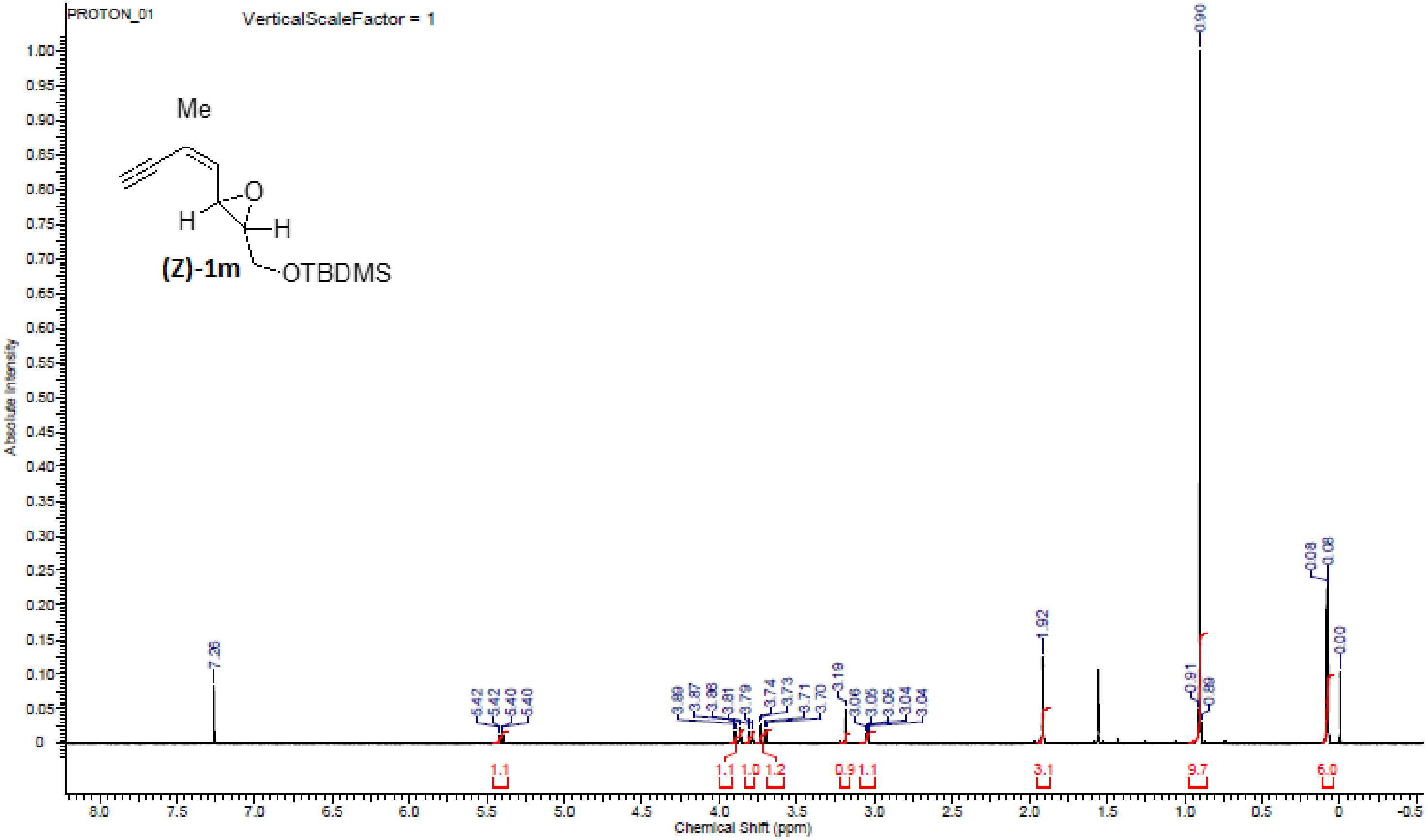
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 18 2013

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.5589851 MHz
DECOUPLE H1, 399.9181065 MHz
Power 46 dB
continuously on

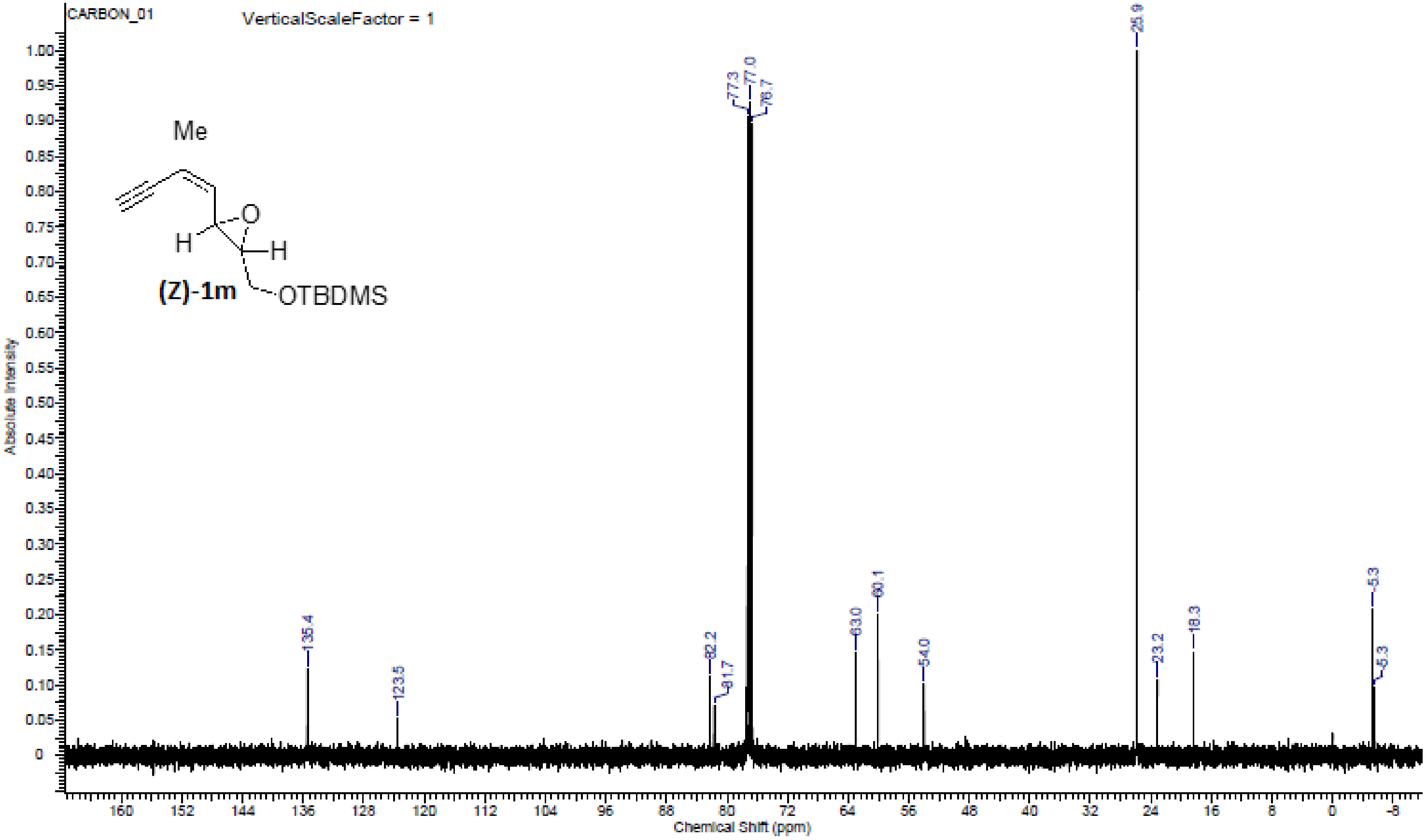
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	2.5559	*Comment*	FZ-FX171	*Date*	Dec 28 2015	*Date Stamp*	Dec 28 2015
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX171_20151228_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



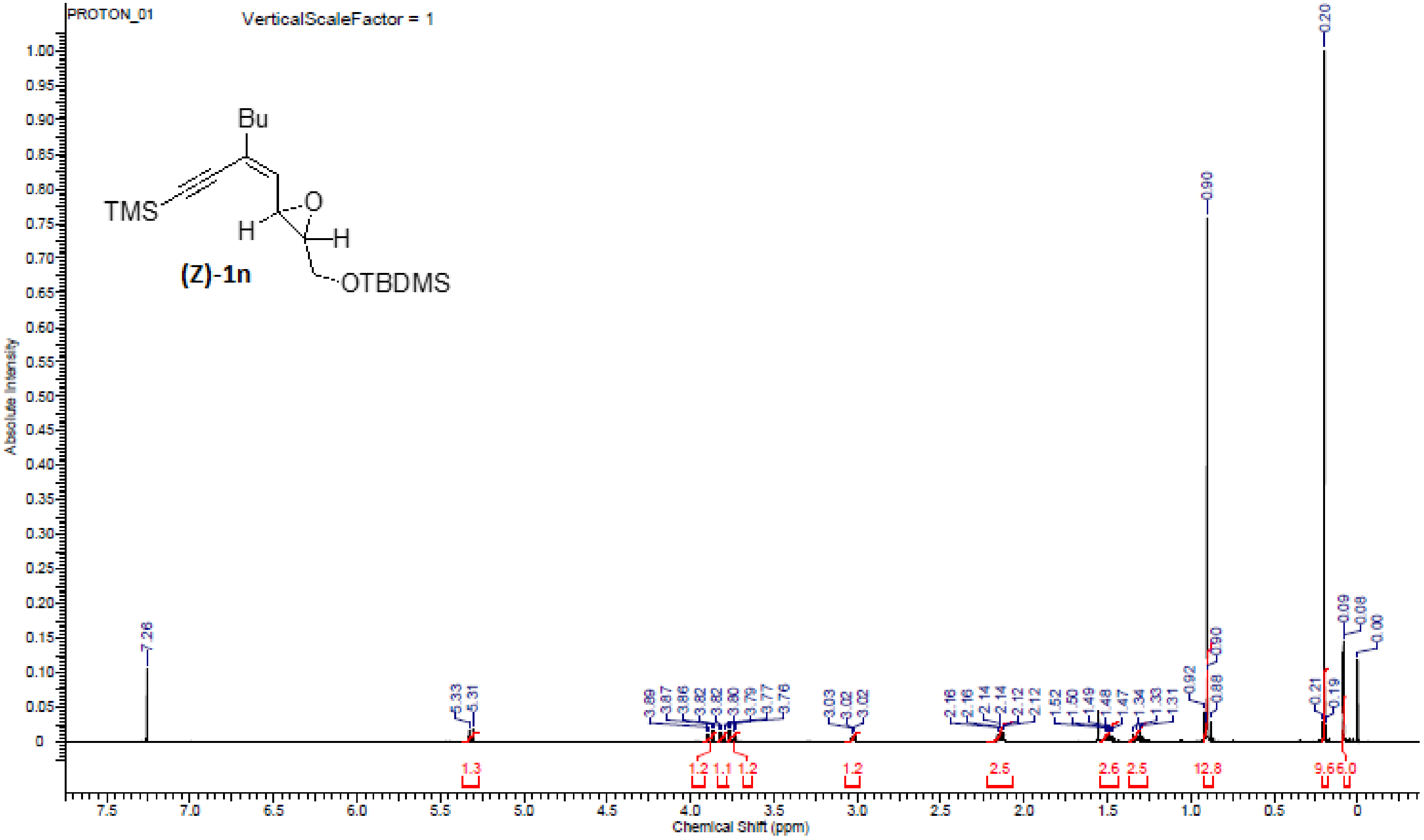
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.3107	*Comment*	FZ-FX171	*Date*	Dec 28 2015	*Date Stamp*	Dec 28 2015
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX171_20151228_01\CARBON_01.FID\FID					*Frequency (MHz)*	100.57
Nucleus	13C	*Number of Transients*	1000	*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



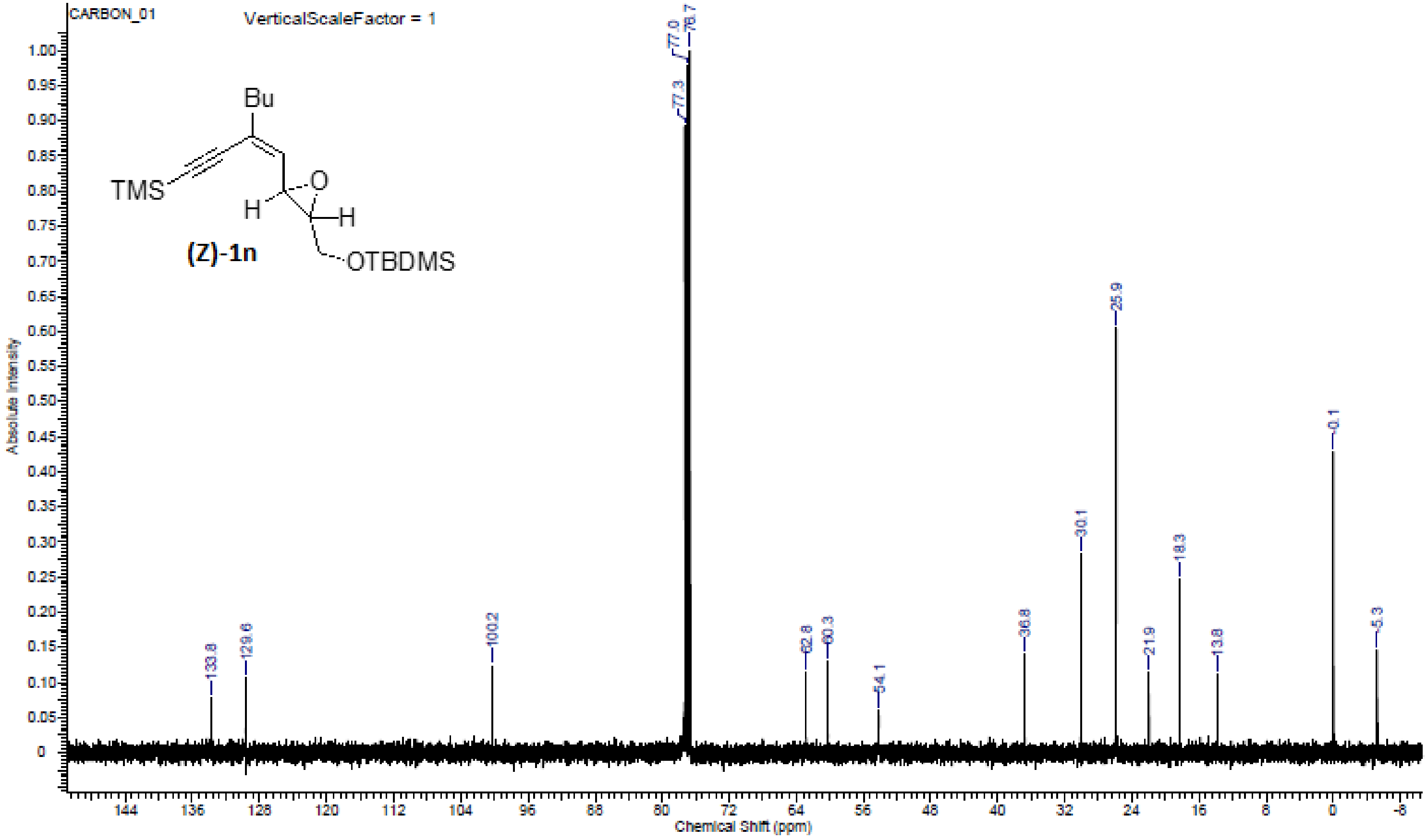
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	2.5559	*Comment*	FZ-FX194	*Date*	Feb 16 2016	*Date Stamp*	Feb 16 2016
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX194_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



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

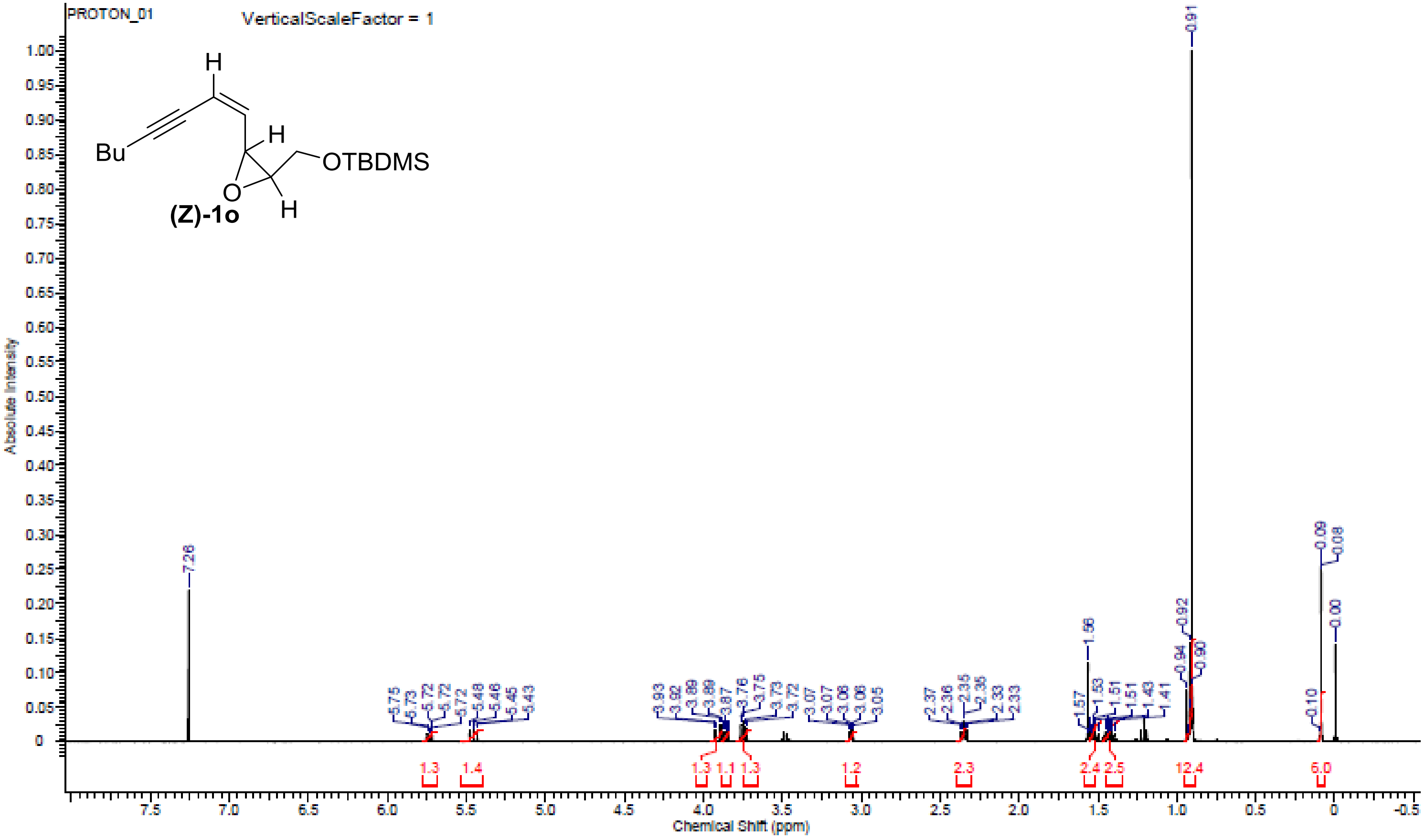
Acquisition Time (sec)	1.3107	*Comment*	FZ-FX194	*Date*	Feb 16 2016	*Date Stamp*	Feb 16 2016
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX194_20160216_01\CARBON_01.FID\FID					*Frequency (MHz)*	100.57
Nucleus	13C	*Number of Transients*	1000	*Original Points Count*	32768	*Points Count*	32768
Pulse Sequence	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



(Z)-1n

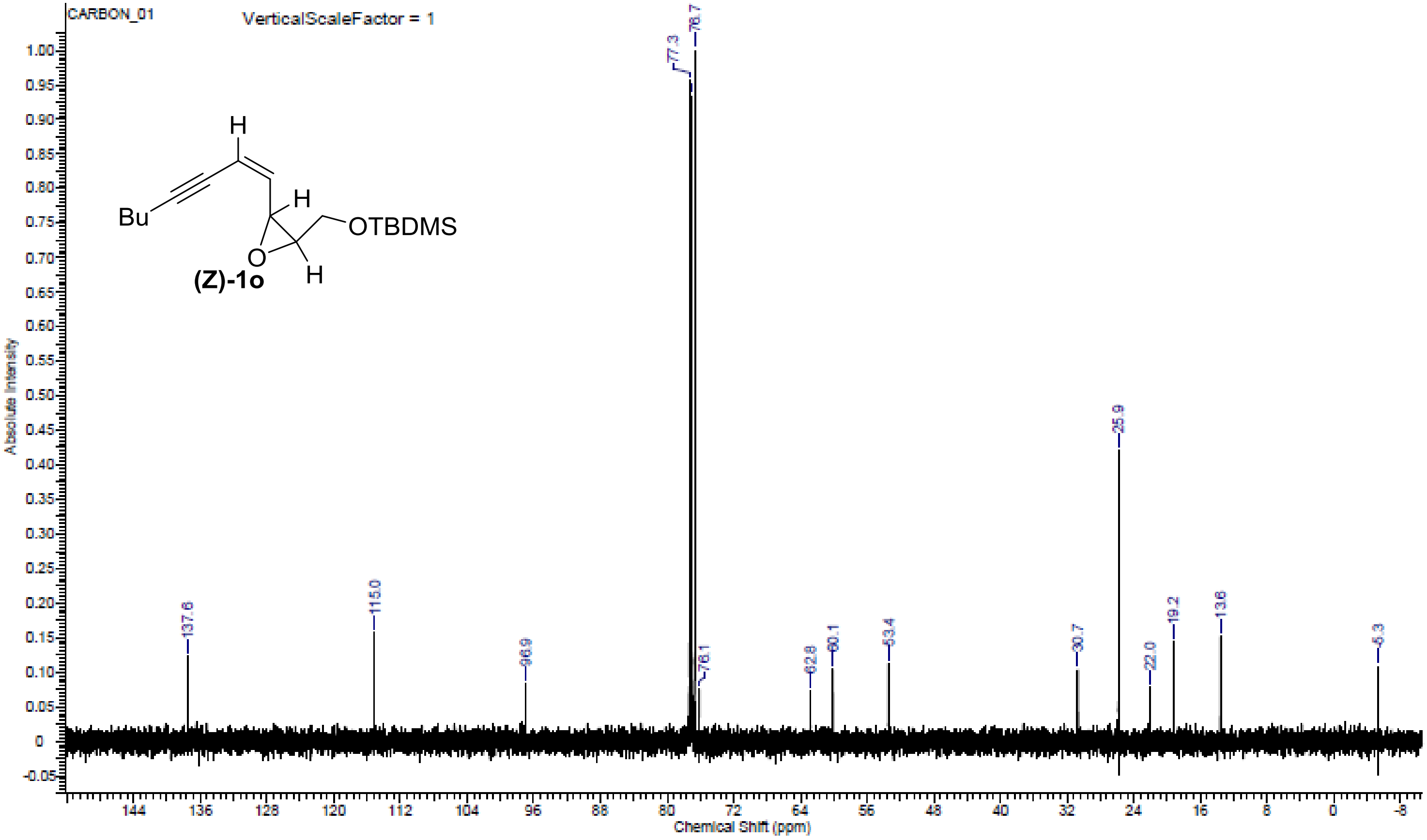
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	2.5559	*Comment*	FZ-FX-215	*Date*	Mar 16 2016	*Date Stamp*	Mar 16 2016
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX-215_20160316_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



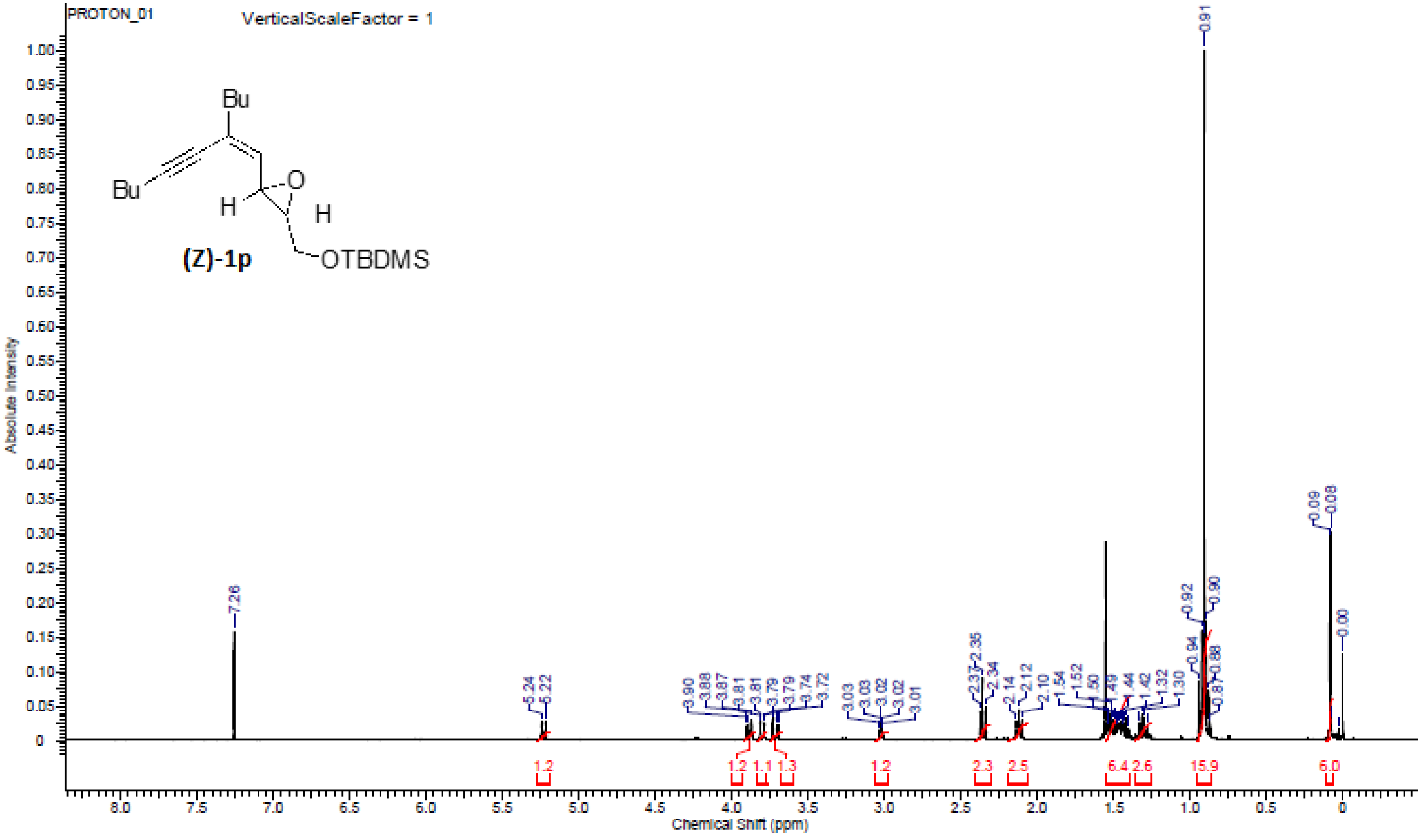
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.3107	*Comment*	FZ-FX-215	*Date*	Mar 16 2016	*Date Stamp*	Mar 16 2016
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX-215_20160316_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

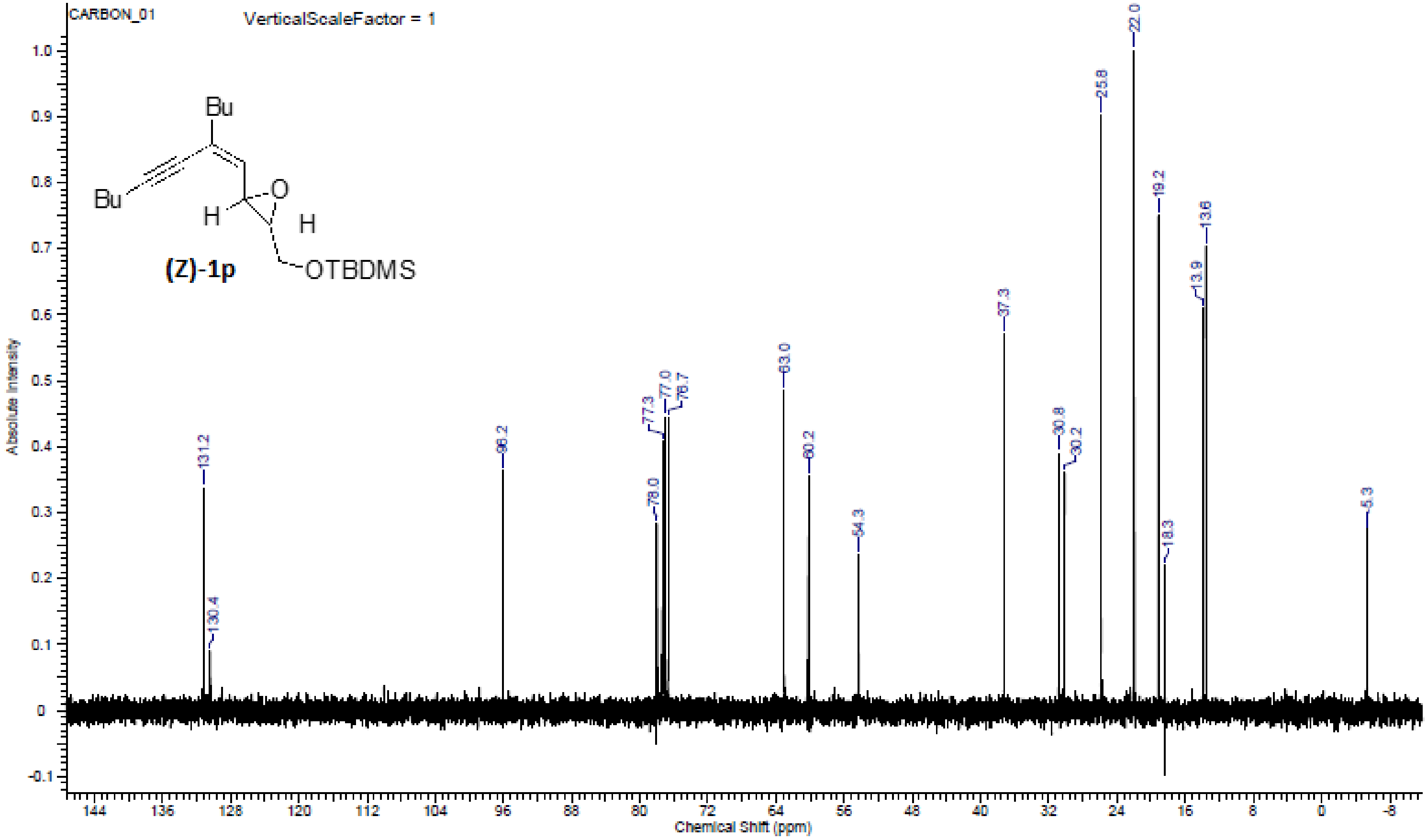


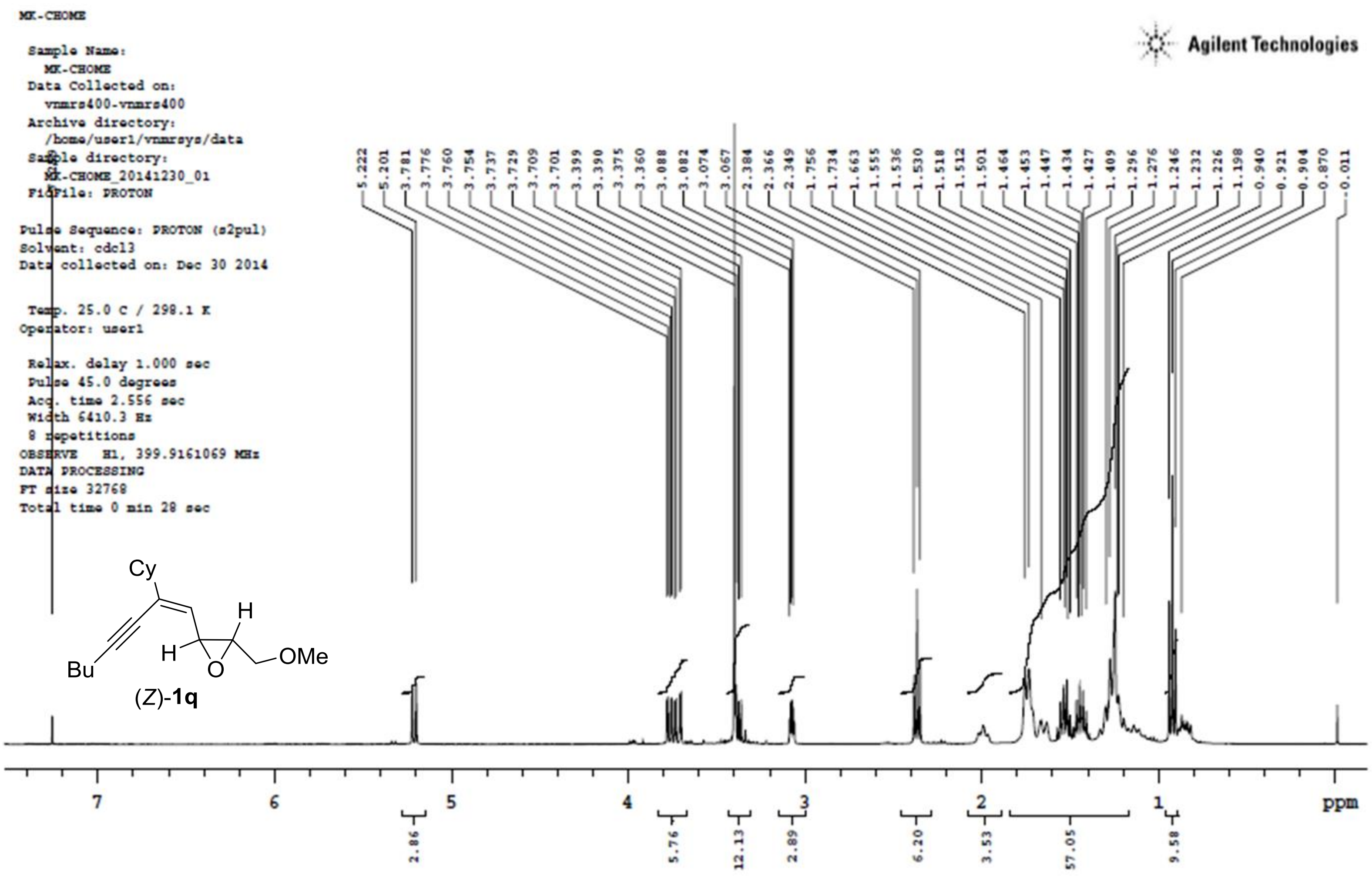
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	2.5559	*Comment*	FZ-FX199	*Date*	Feb 18 2016	*Date Stamp*	Feb 18 2016
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX199_20160218_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*	FZ-FX199-13C	*Date*	Feb 25 2016	*Date Stamp*	Feb 25 2016
File Name	D:\FIRAT HOCA DATA\FIRAT\FZ-FX199-13C_20160225_01\CARBON_01.FID\FID					*Frequency (MHz)*	100.57
Nucleus	13C	*Number of Transients*	32	*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





MK-CHOME

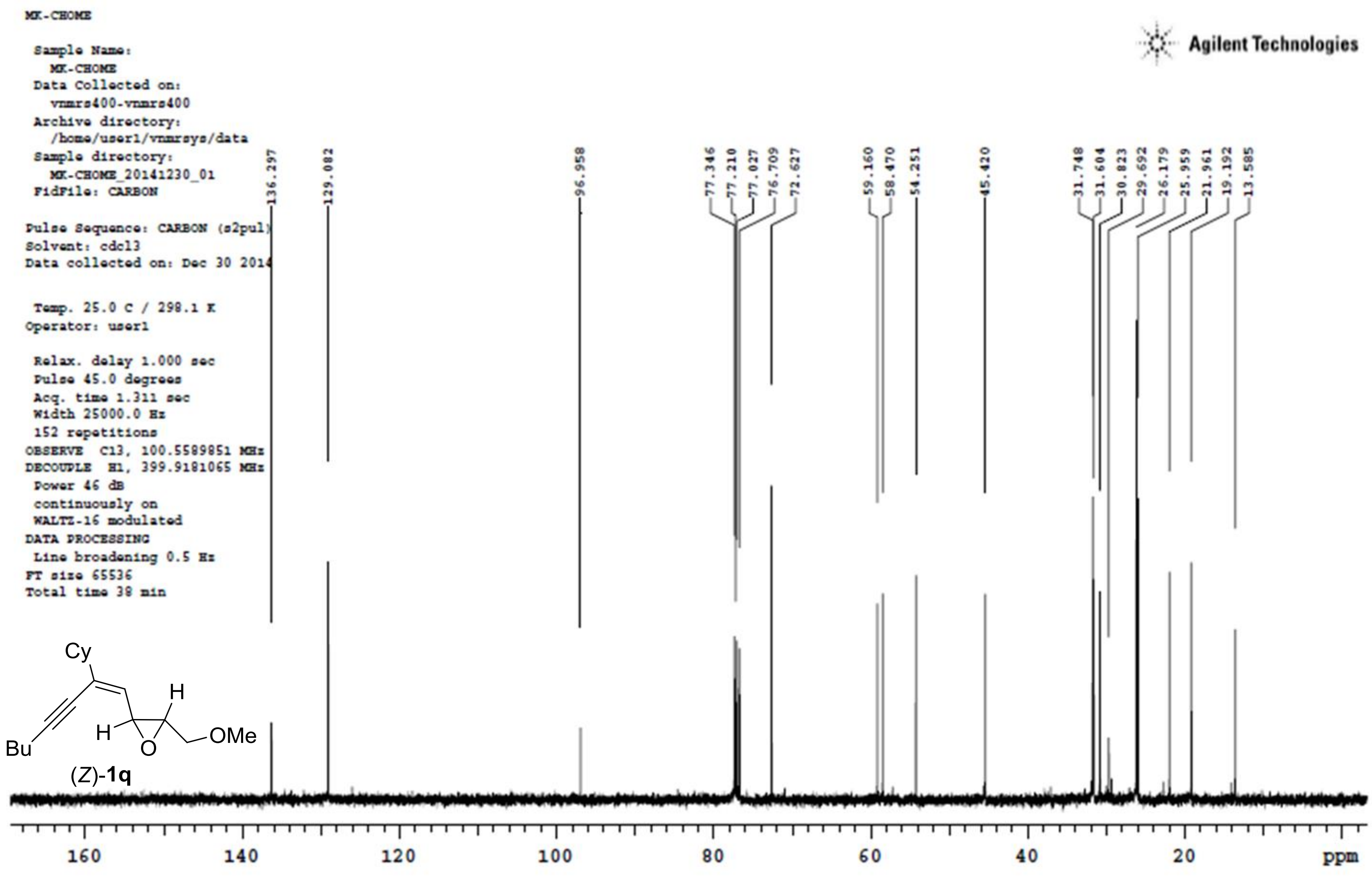
Sample Name:
MK-CHOME
Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/user1/vnmrsys/data
Sample directory:
MK-CHOME_20141230_01
FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 30 2014

Temp. 25.0 C / 298.1 K
Operator: user1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.9161069 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec

(Z)-1q



MK-CHOME

Sample Name:
MK-CHOME
Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/user1/vnmrsys/data
Sample directory:
MK-CHOME_20141230_01
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 30 2014

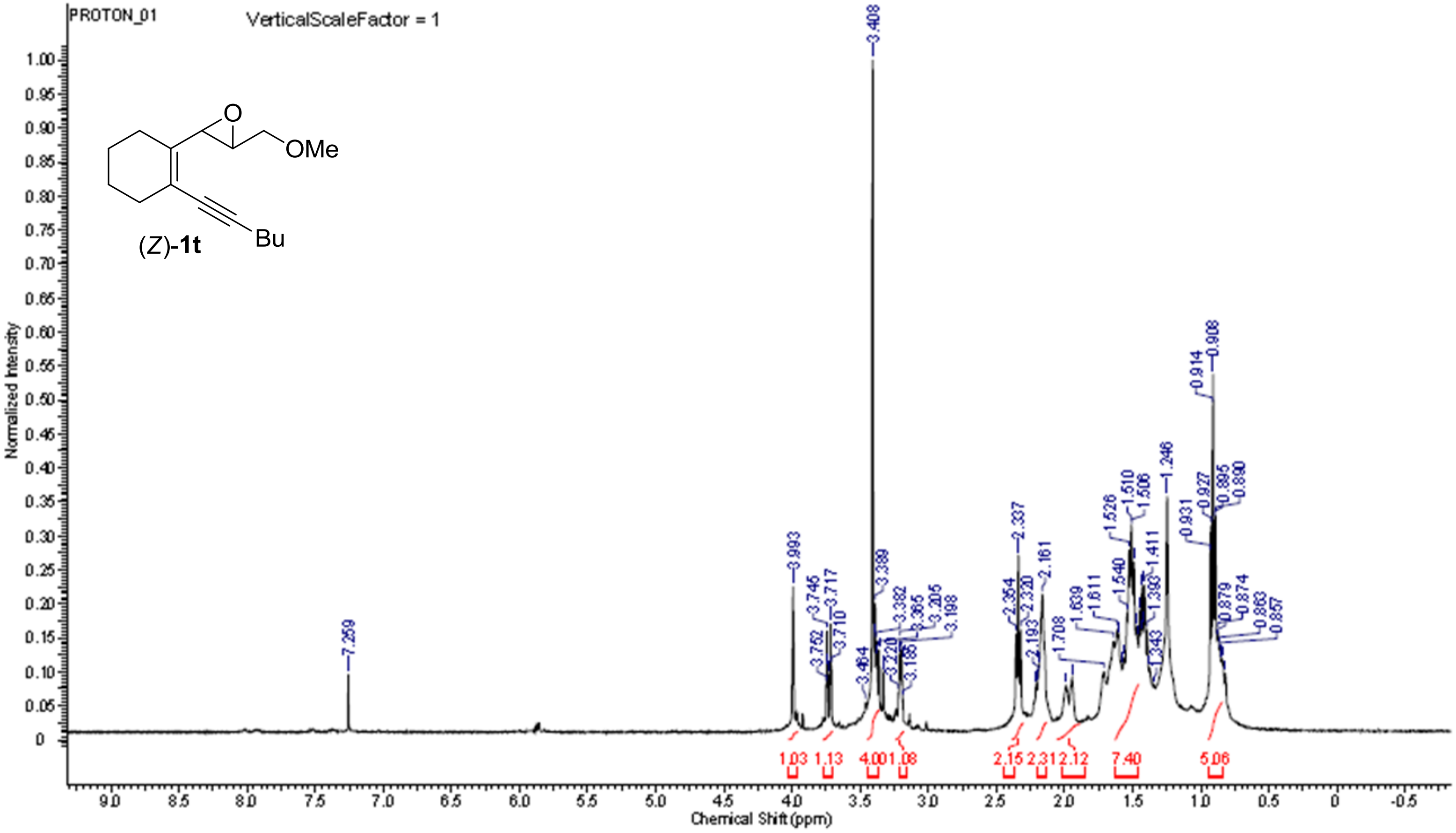
Temp. 25.0 C / 298.1 K
Operator: user1

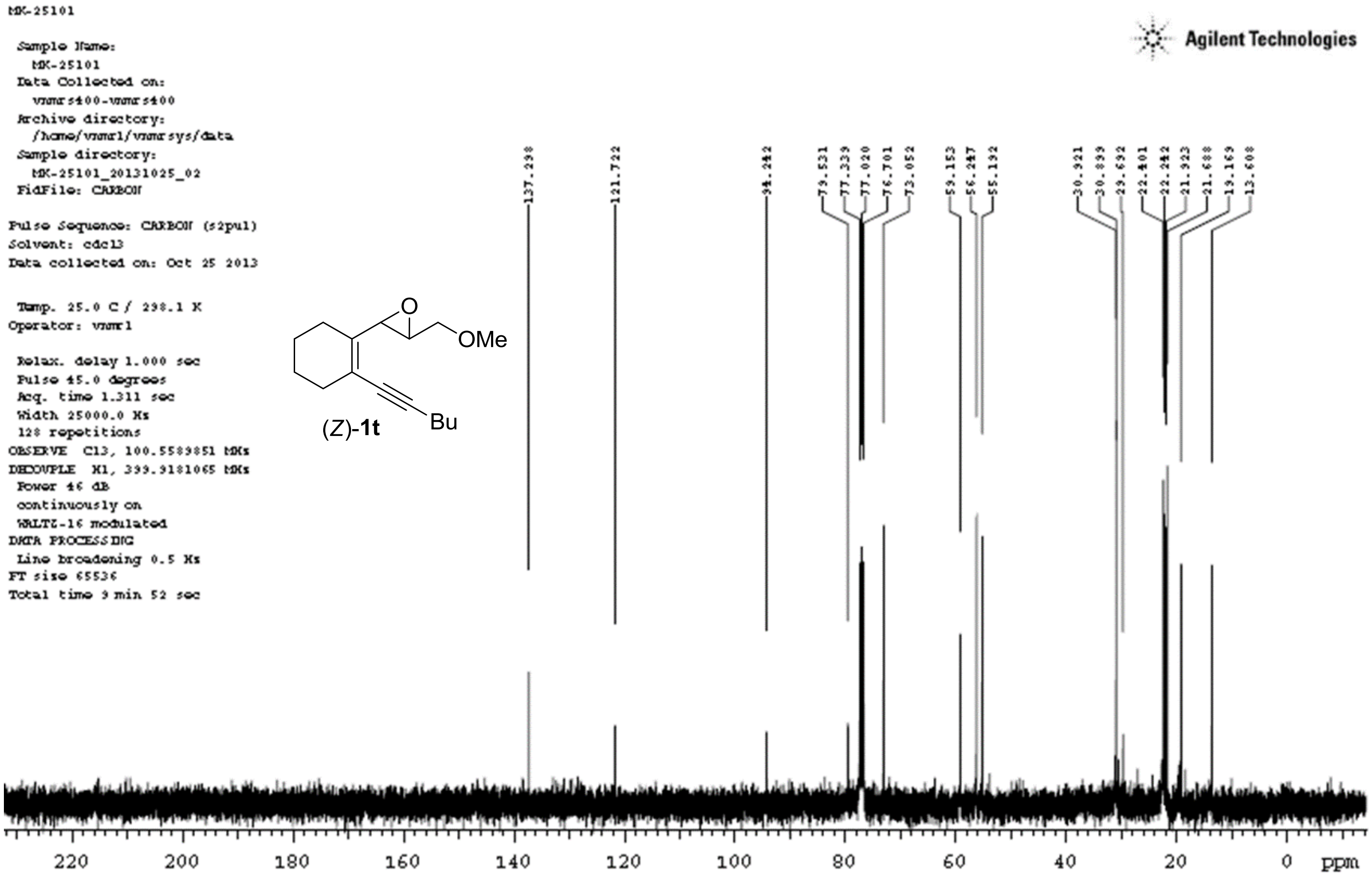
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
152 repetitions
OBSERVE C13, 100.5589851 MHz
DECOUPLE H1, 399.9181065 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min

(*Z*)-**1q**

07.08.2014 14:06:53

Acquisition Time (sec)	2.5559	Comment	Gradient Shimming			Date	Oct 25 2013
Date Stamp	Oct 25 2013	File Name	C:\USERS\FIRAT\DESKTOP\MELIH\MK-25101_20131025_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	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000





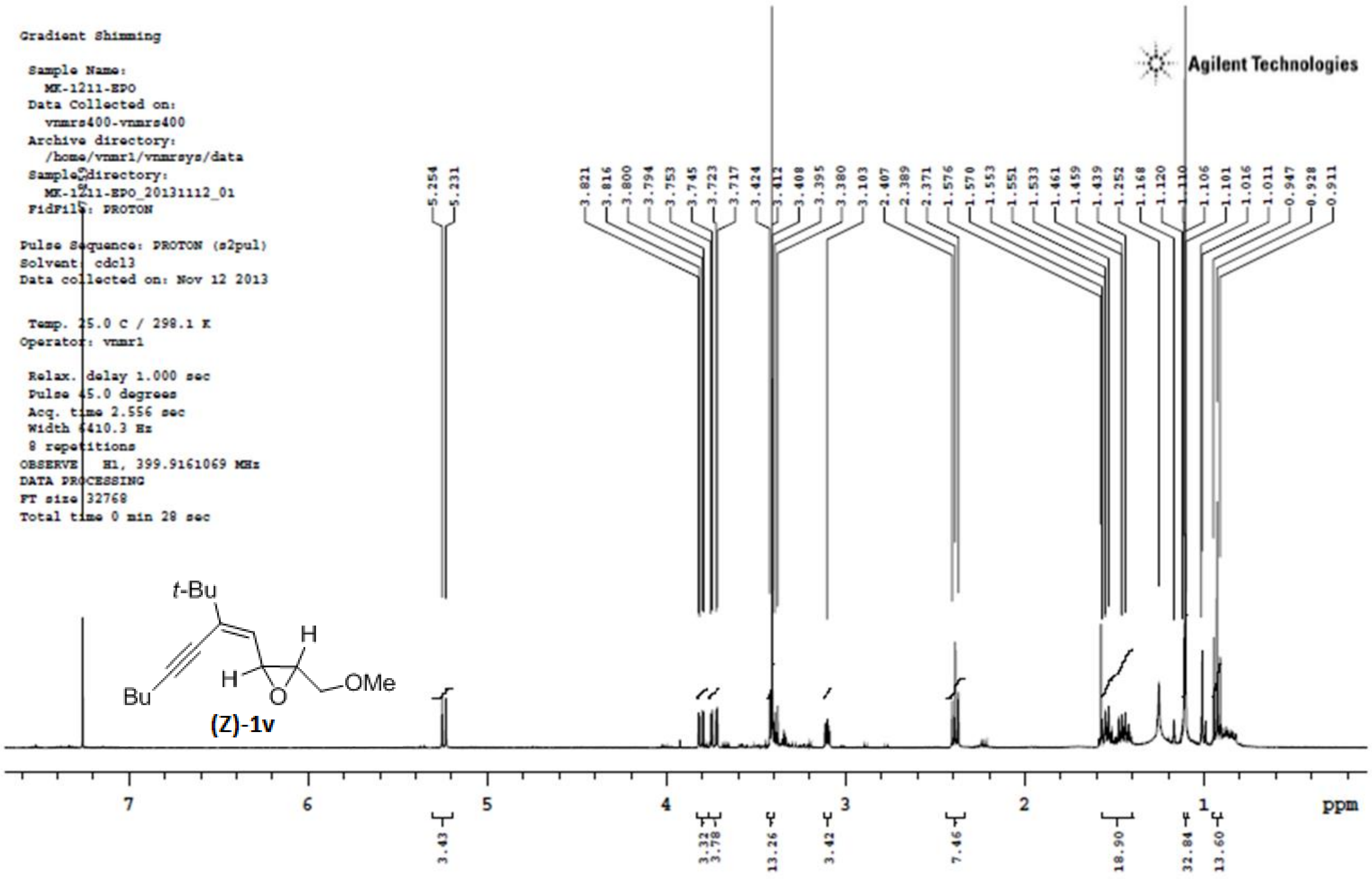
MK-25101

Sample Name:
MK-25101
Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/vnmr1/vnmrsys/data
Sample directory:
MK-25101_20131025_02
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 25 2013

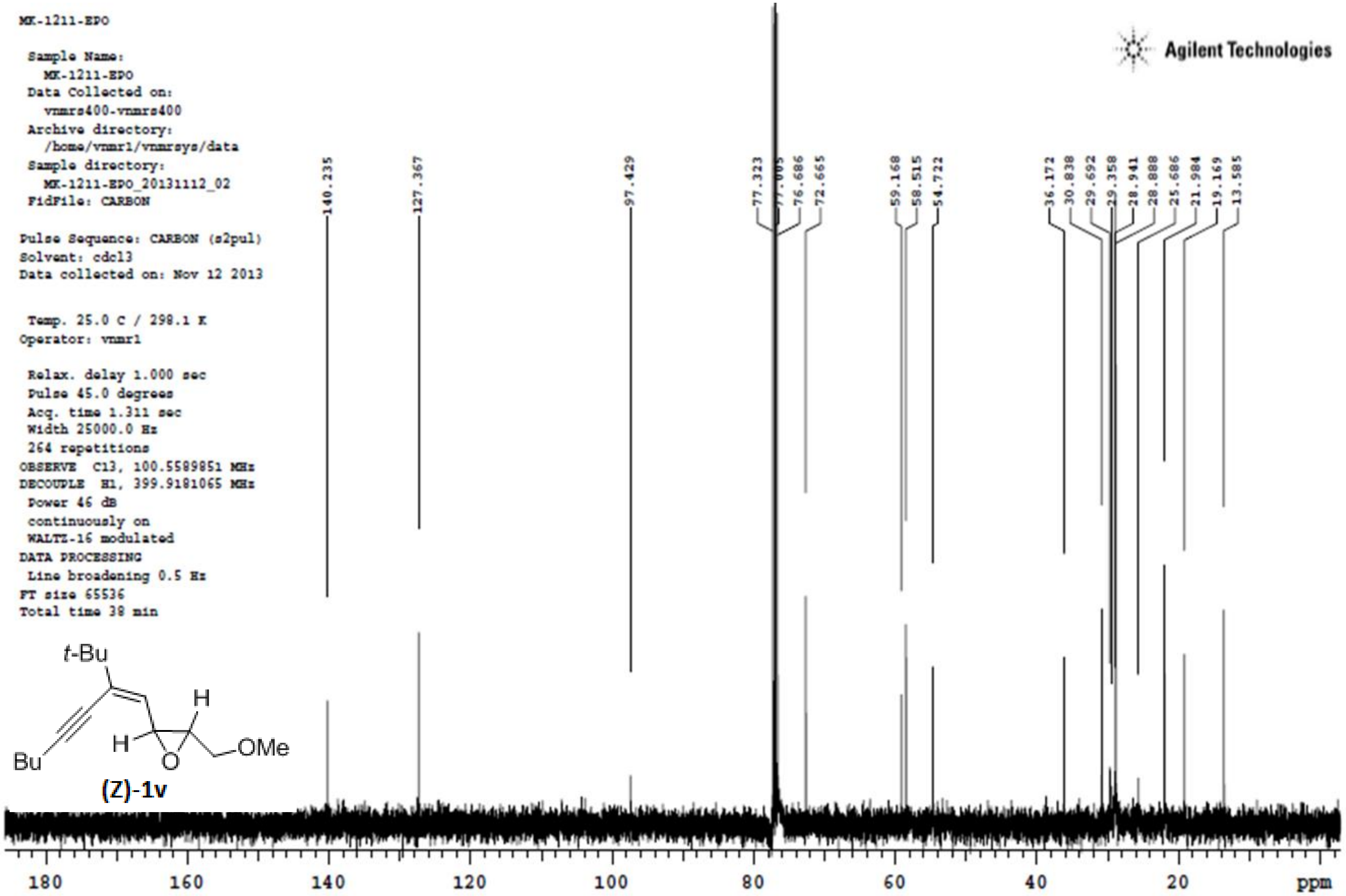
Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
128 repetitions
OBSERVE C13, 100.5589851 MHz
DECOUPLE H1, 399.9181065 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min 52 sec



```
Gradient Shimming

 Sample Name:
   MK-1211-EPO
 Data Collected on:
   vnmrs400-vnmrs400
 Archive directory:
   /home/vnmr1/vnmrsys/data
 Sample directory:
   MK-1211-EPO_20131112_01
 FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 12 2013

 Temp. 25.0 C / 298.1 K
Operator: vnmr1

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 8 repetitions
OBSERVE   H1, 399.9161069 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
```

(Z)-1v



MK-1211-EPO

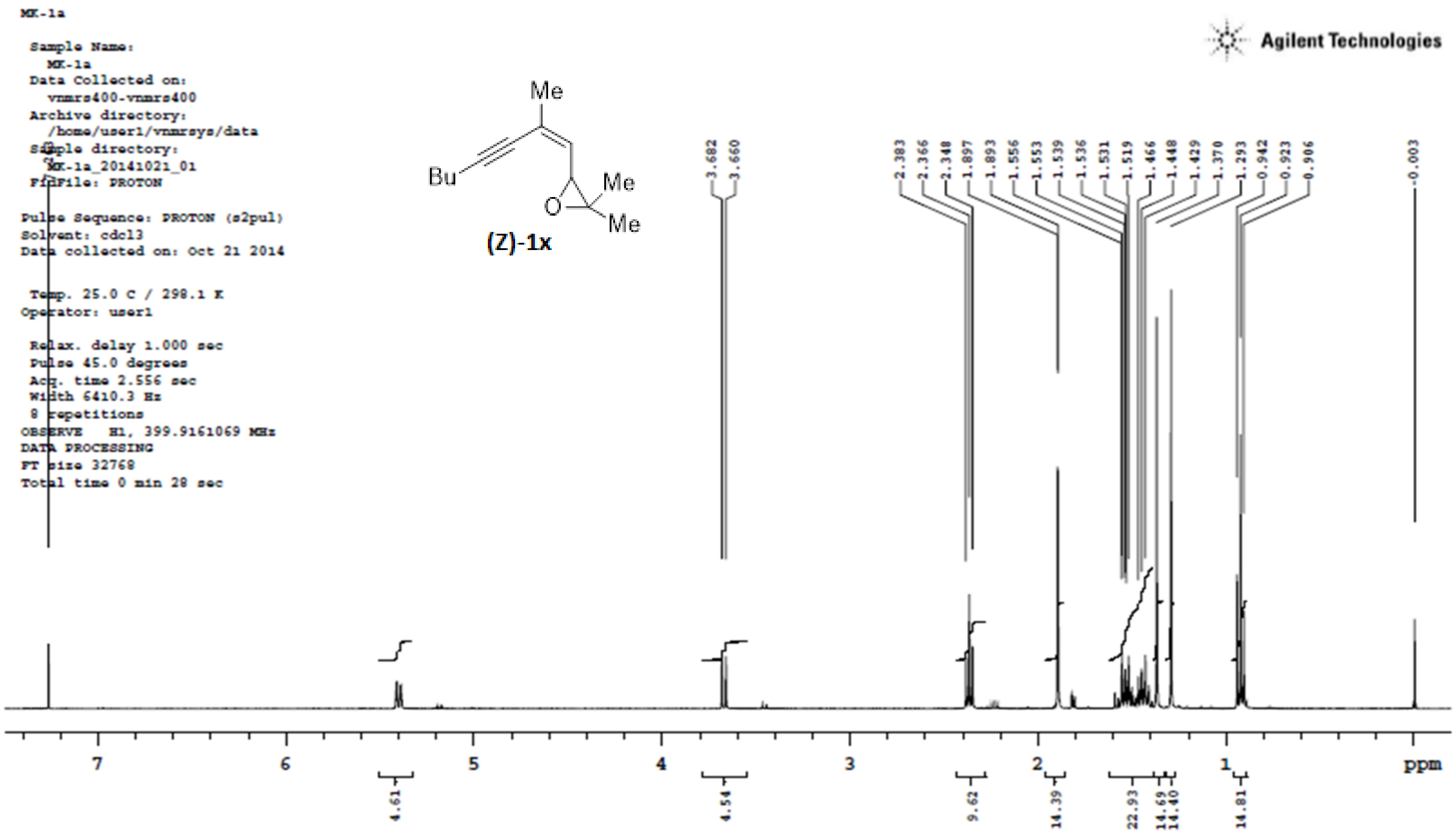
Sample Name:
MK-1211-EPO
Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/vnmr1/vnmrsys/data
Sample directory:
MK-1211-EPO_20131112_02
FidFile: CARBON

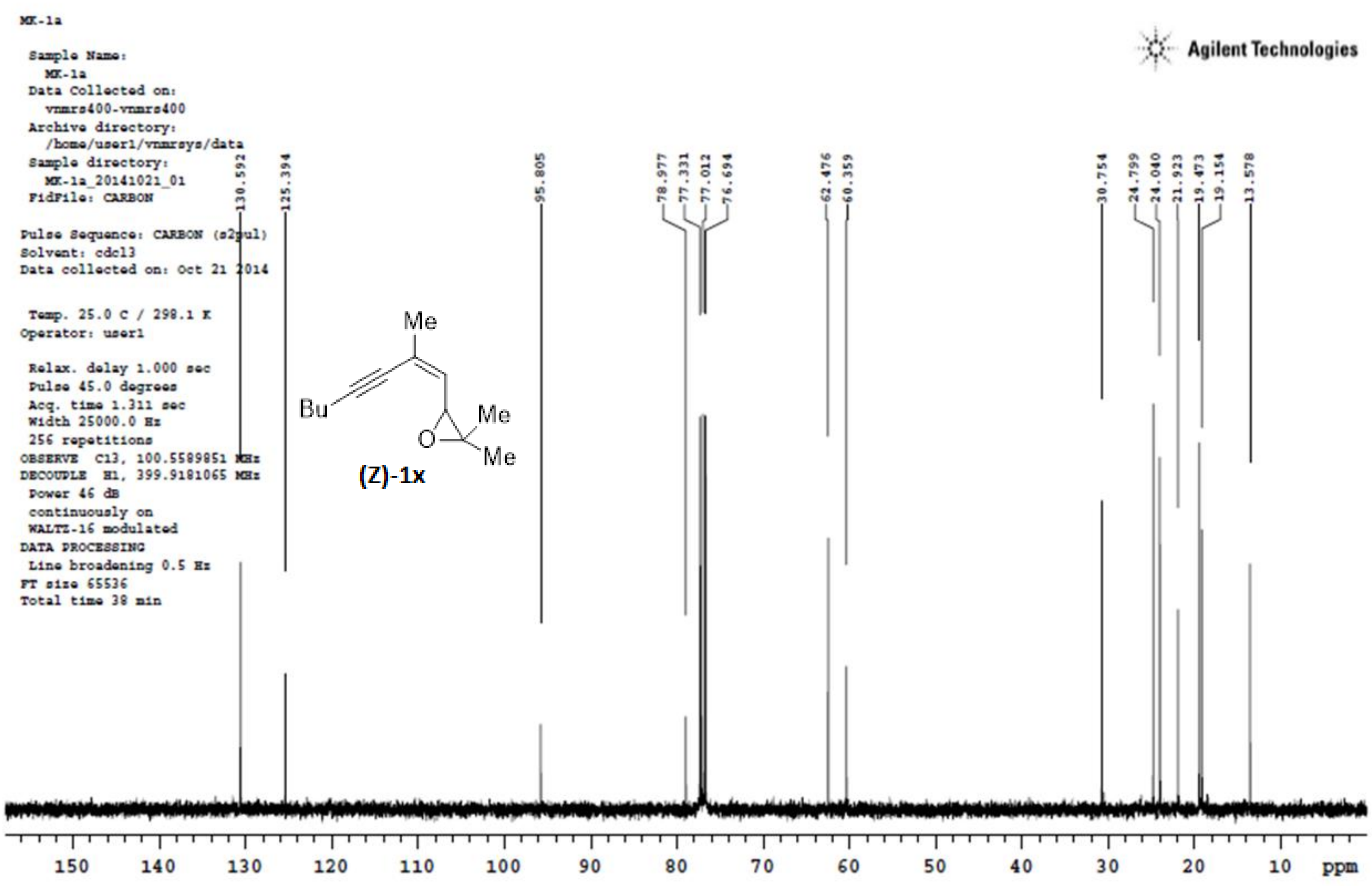
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 12 2013

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
264 repetitions
OBSERVE C13, 100.5589851 MHz
DECOUPLE H1, 399.9181065 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min

(Z)-1v


(Z)-1x
MK-1a
Sample Name:
MK-1a
Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/user1/vnmrsys/data
Sample directory:
MK-1a_20141021_01
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 21 2014
Temp. 25.0 C / 298.1 K
Operator: user1
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.9161069 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
Agilent Technologies
Me
Bu
O
Me
Me
3.682
3.660
2.383
2.366
2.348
1.897
1.893
1.556
1.553
1.539
1.536
1.531
1.519
1.466
1.448
1.429
1.370
1.293
0.942
0.923
0.906
-0.003
7
6
5
4
3
2
1
ppm
4.61
4.54
9.62
14.39
22.93
14.69
14.40
14.81


MX-1a

Sample Name:
MX-1a
Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/user1/vnmrsys/data
Sample directory:
MX-1a_20141021_01
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 21 2014

Temp. 25.0 C / 298.1 K
Operator: user1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
256 repetitions
OBSERVE C13, 100.5589851 MHz
DECOUPLE H1, 399.9181065 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min

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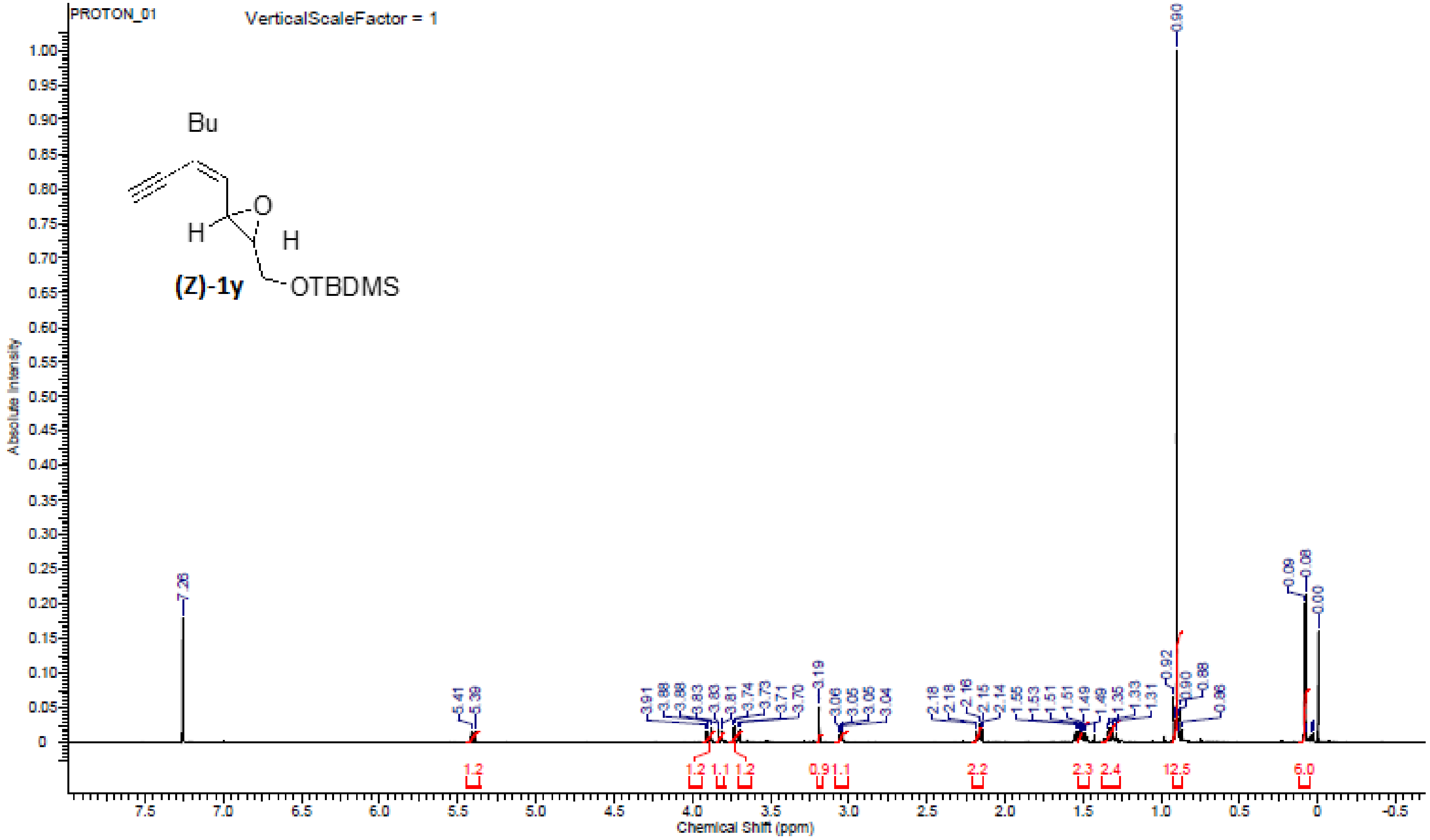
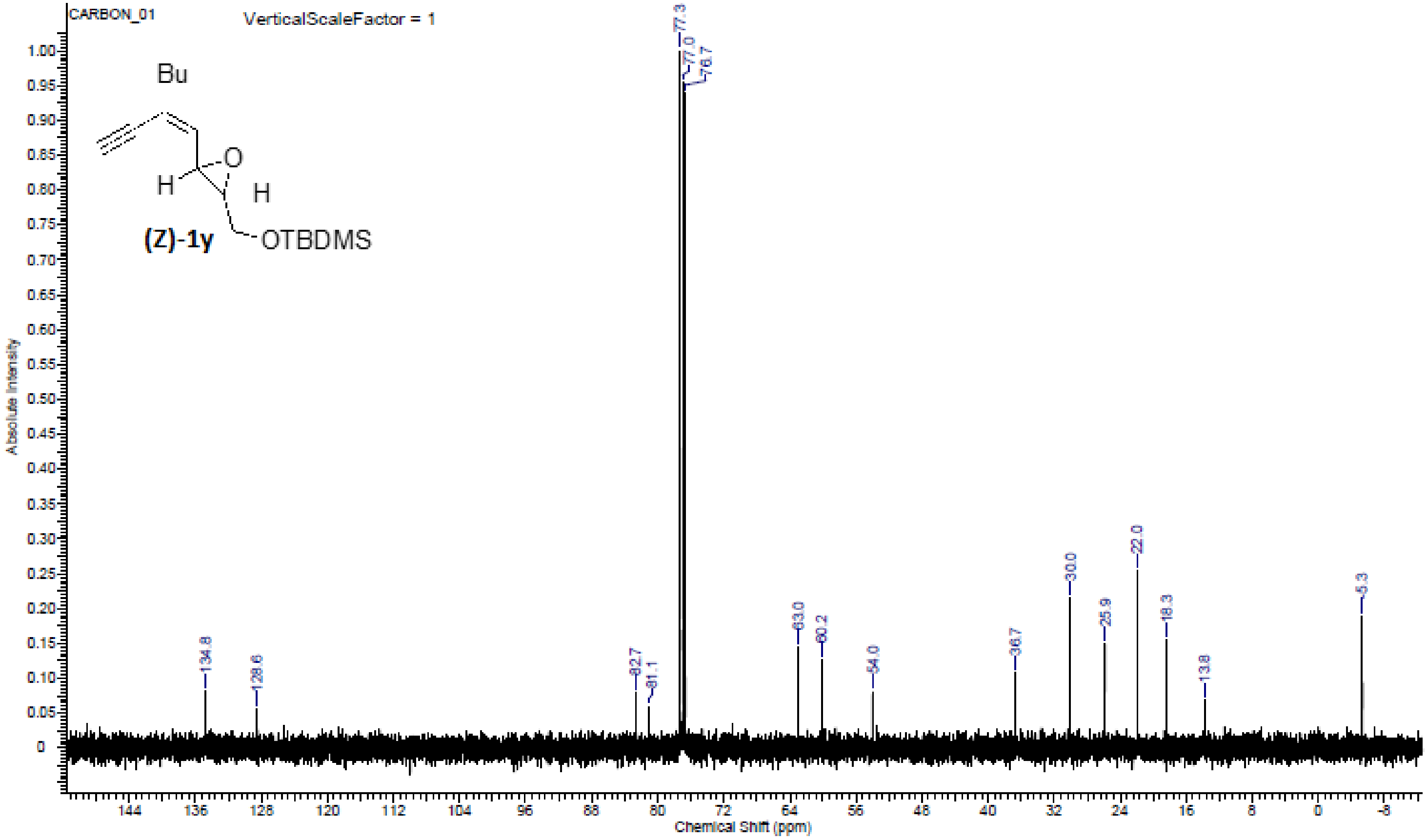
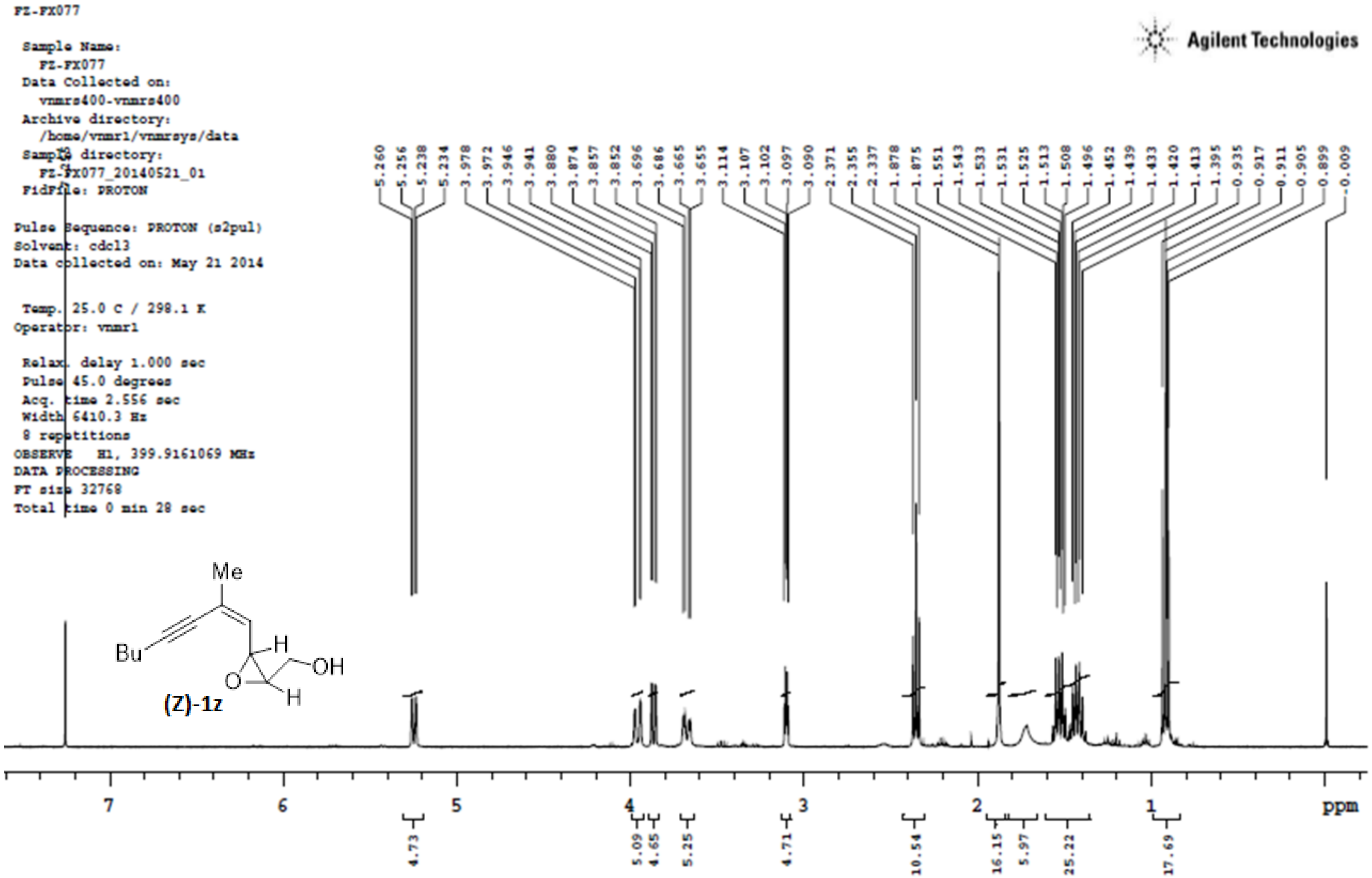
Acquisition Time (sec)	2.5559	*Comment*	FZ-FX202	*Date*	Feb 25 2016	*Date Stamp*	Feb 25 2016
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX202_20160225_01\PROTON_01.FID\FID					*Frequency (MHz)*	399.92
Nucleus	1H	*Number of Transients*	8	*Original Points Count*	16384	*Points Count*	16384
Pulse Sequence	s2pul	*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)	1.3107	*Comment*	FZ-FX202	*Date*	Feb 25 2016	*Date Stamp*	Feb 25 2016
File Name	D:\REACTANT NMR SPECTRUM\FZ-FX202_20160225_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


(Z)-1y



FZ-FX077

Sample Name:
FZ-FX077
Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/vnmr1/vnmrsys/data
Sample directory:
FZ-FX077_20140521_01
FidFile: PROTON

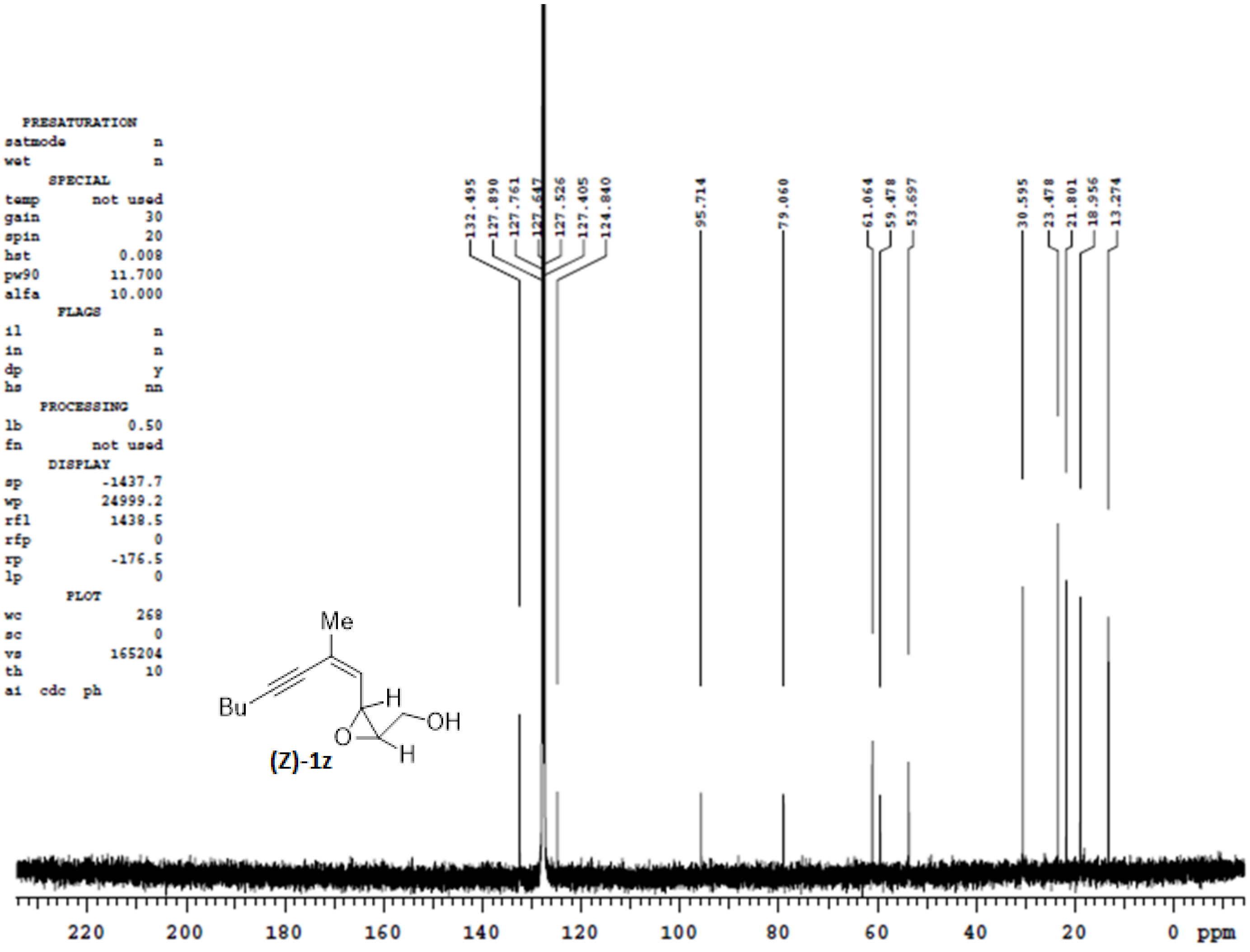
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2014

Temp. 25.0 C / 298.1 K
Operator: vnmr1

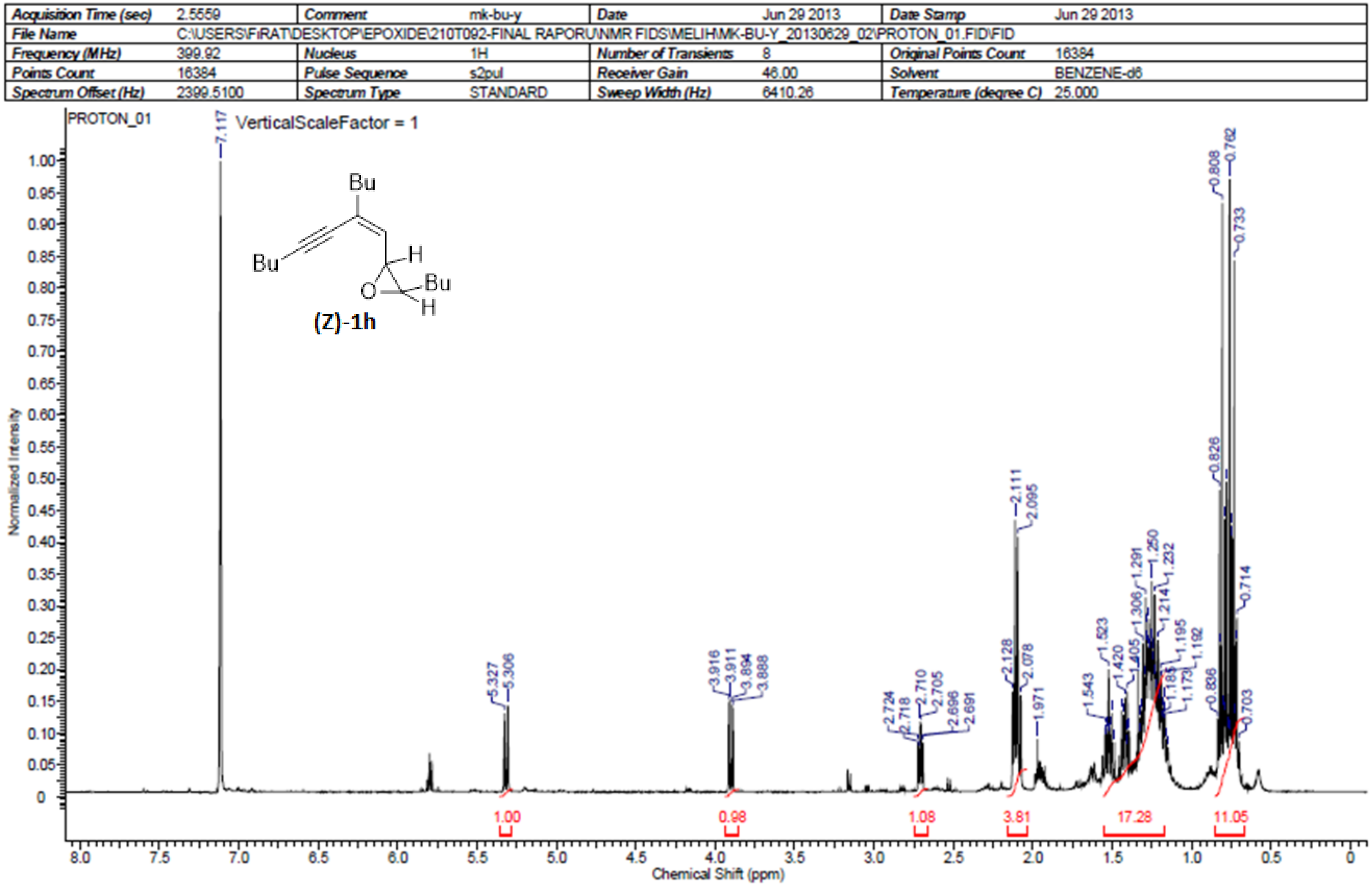
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.9161069 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec

(Z)-1z

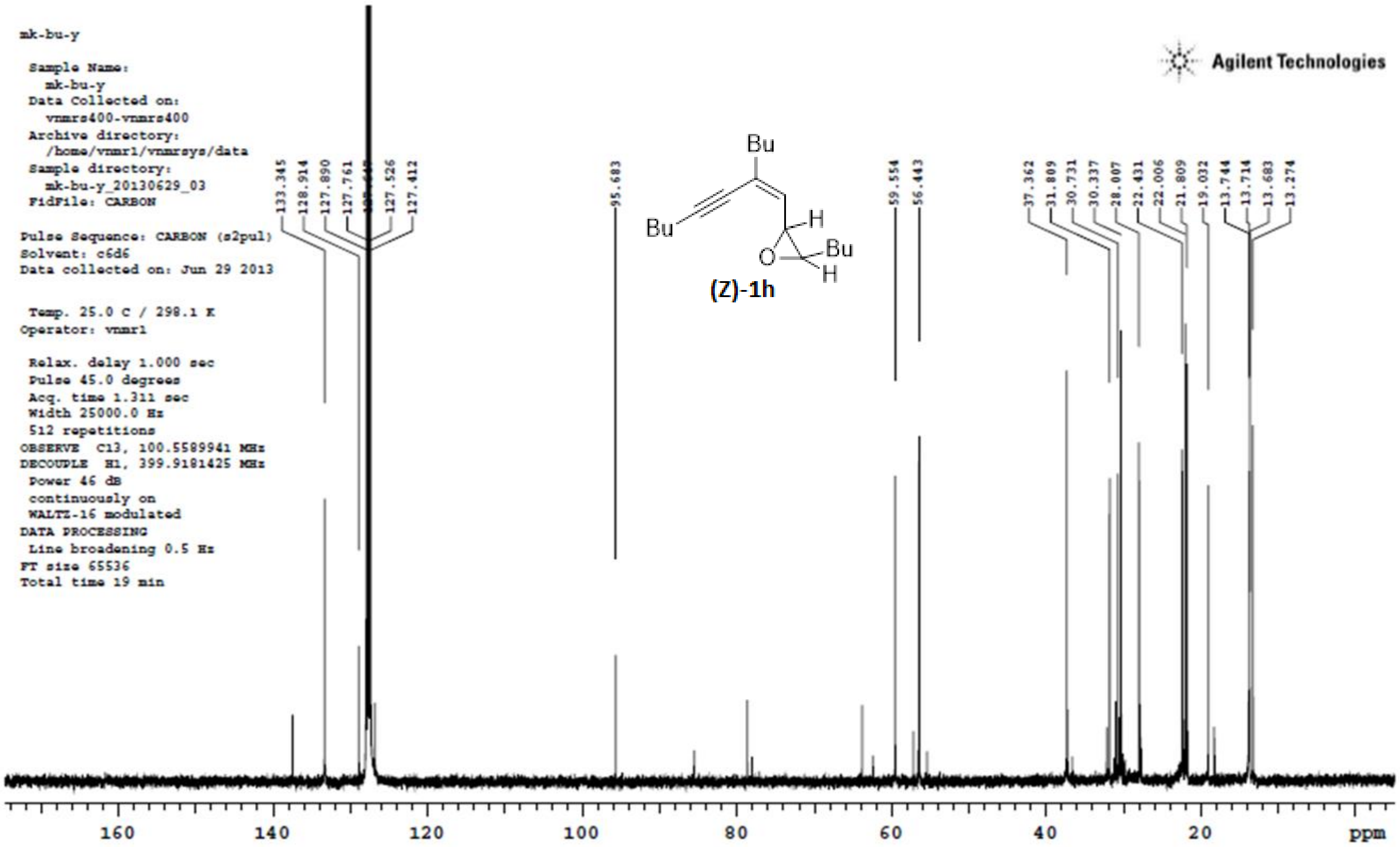
```
MK-05-11-12-SAF-T

exp41  CARBON

      SAMPLE             PRESATURATION
date   Nov  5 2012  satmode              n
solvent        c6d6  wet                  n
file /home/vnmr1/v~        SPECIAL
nmrsys/data/LEVENT~ temp         not used
 ARTOK/MELIH/MELIH~ gain               30
/MK-05-11-12-SAF-T~ spin               20
_20121105_02/CARBO~ hst             0.008
          N_01.fid  pw90           11.700
   ACQUISITION      alfa           10.000
sw          25000.0          FLAGS
at            1.311  il                 n
np            65536  in                 n
fb            17000  dp                 y
bs               64  hs                nn
d1            1.000       PROCESSING
nt             1000  lb              0.50
ct             1000  fn          not used
   TRANSMITTER             DISPLAY
tn              C13  sp           -1437.7
sfrq        100.570  wp           24999.2
tof          1531.2  rfl           1438.5
tpwr             54  rfp                0
pw            5.850  rp            -176.5
    DECOUPLER        lp                 0
dn               H1          PLOT
dof               0  wc               268
dm              yyy  sc                 0
decwave           w  vs            165204
dpwr             46  th                10
dmf           10101  ai  cdc  ph
```



(Z)-1z



Acquisition Time (sec)	2.5559	Comment	mk-bu-y	Date	Jun 29 2013	Date Stamp	Jun 29 2013
File Name	C:\USERS\FIRAT\DESKTOP\EPOXIDE\210T092-FINAL RAPORU\NMR FIDS\MELIH\MK-BU-Y_20130629_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	46.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	2399.5100	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



(Z)-1h

mk-bu-y

Sample Name:
mk-bu-y
Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/vnmr1/vnmrsys/data
Sample directory:
mk-bu-y_20130629_03
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: c6d6
Data collected on: Jun 29 2013

Temp. 25.0 C / 298.1 K
Operator: vnmr1

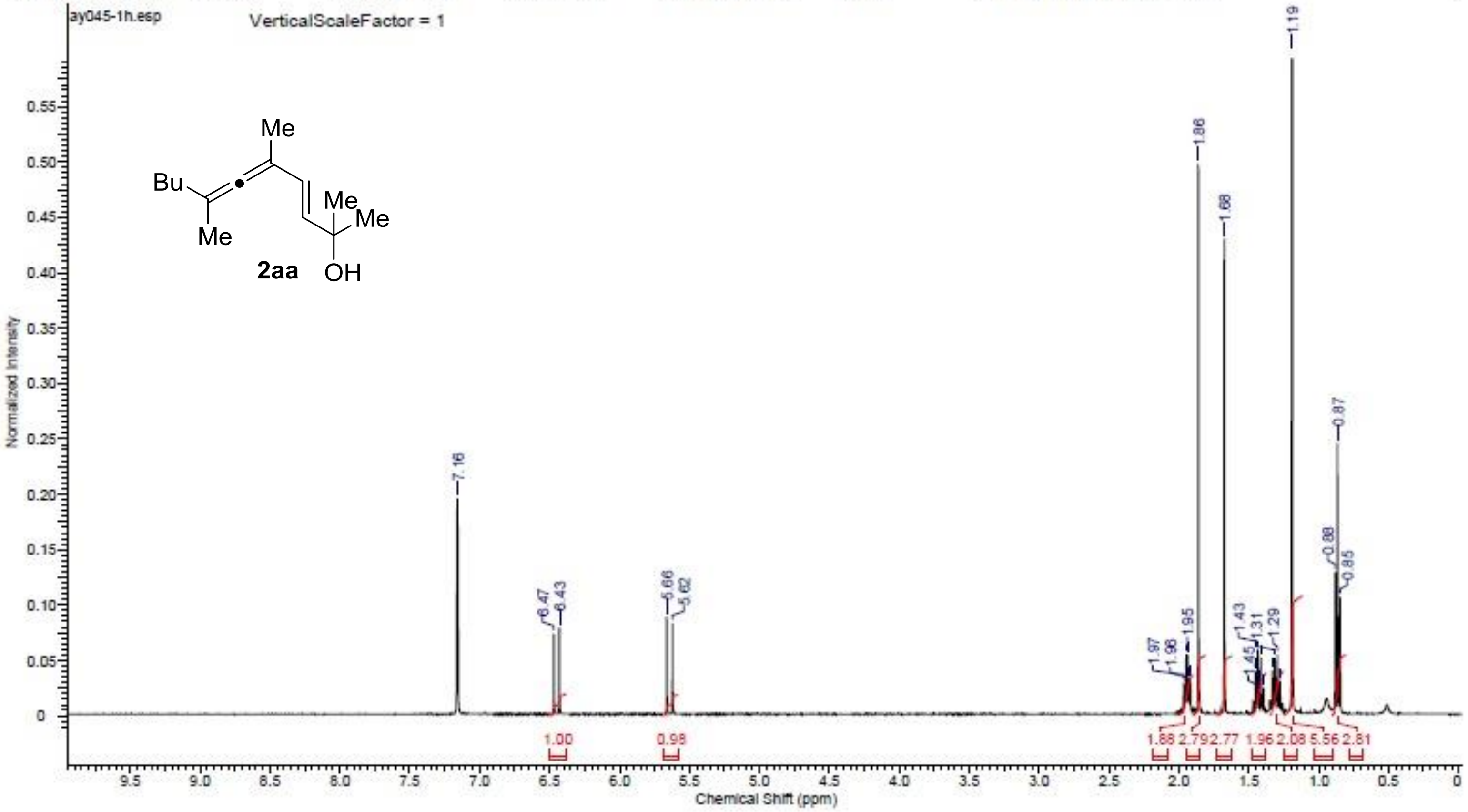
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.5589941 MHz
DECOUPLE H1, 399.9181425 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min

APPENDIX B

^{1}H AND ^{13}C SPECTRUM OF PRODUCTS

28.07.2016 14:04:42

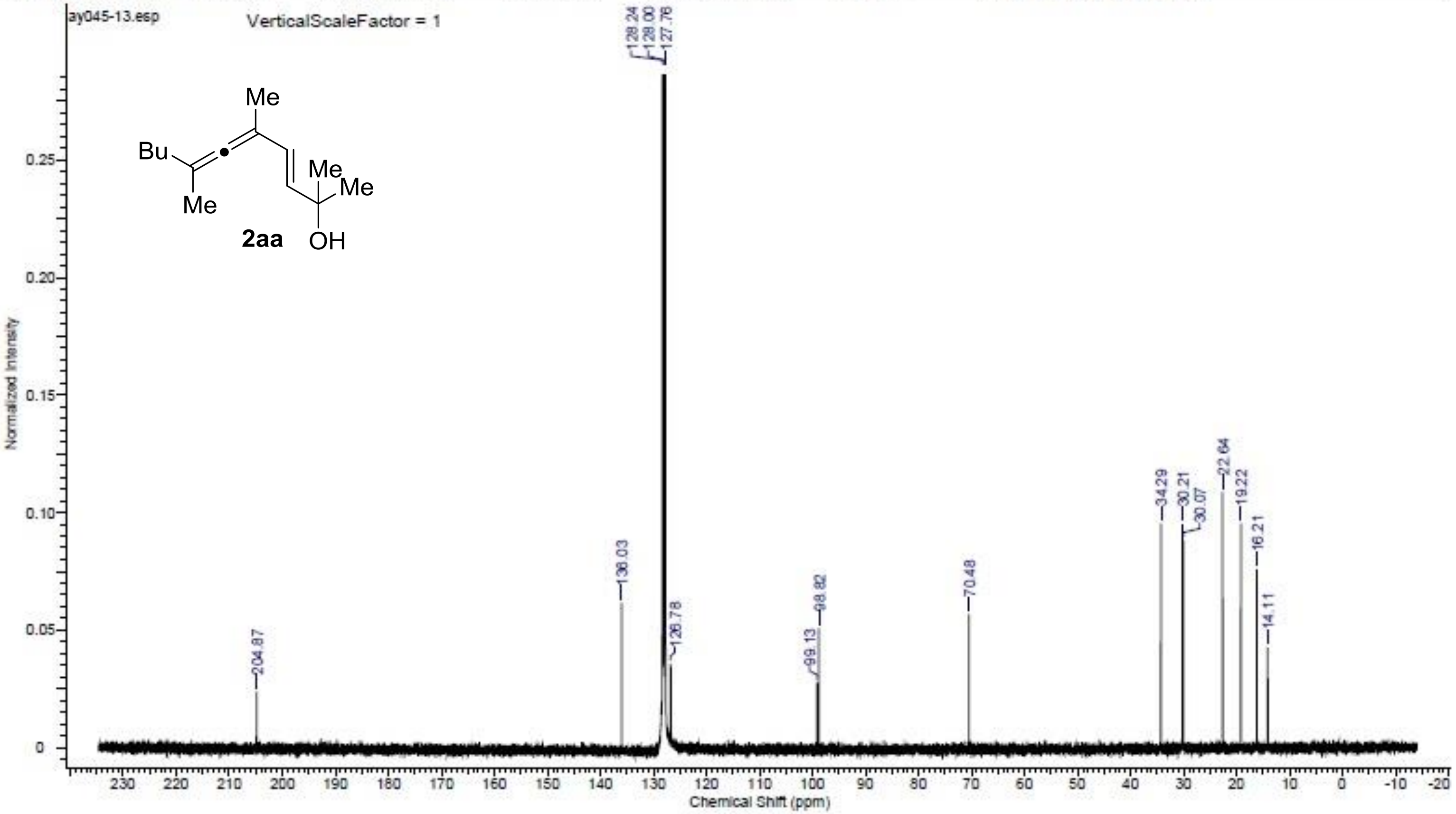
Acquisition Time (sec)	2.5559	*Comment*	AA-AY-045Y	*Date*	Jun 30 2016	*Date Stamp*	Jun 30 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-045Y_20160630_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.5591	*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/

28.07.2016 14:16:27

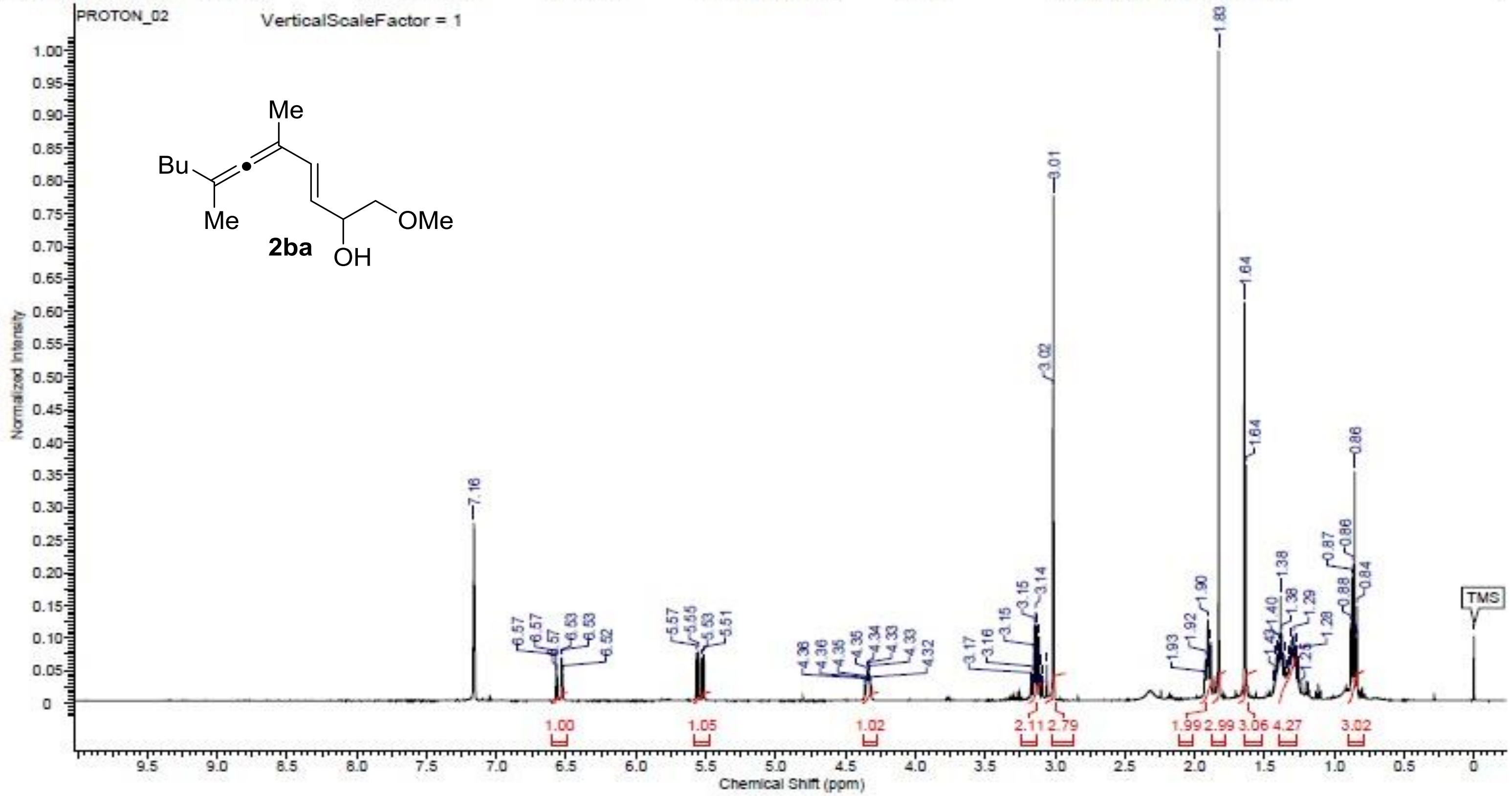
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-0454	*Date*	Jun 30 2016	*Date Stamp*	Jun 30 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-0454_20160630_01\CARBON_03.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	2000	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11097.1709	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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

26.07.2016 21:03:51

Acquisition Time (sec)	2.5559	*Comment*	MK-0708-1-TKR	*Date*	Aug 13 2015	*Date Stamp*	Aug 13 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-0708-1-TKR_20150813_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*	BENZENE-d6
Spectrum Offset (Hz)	2417.1006	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

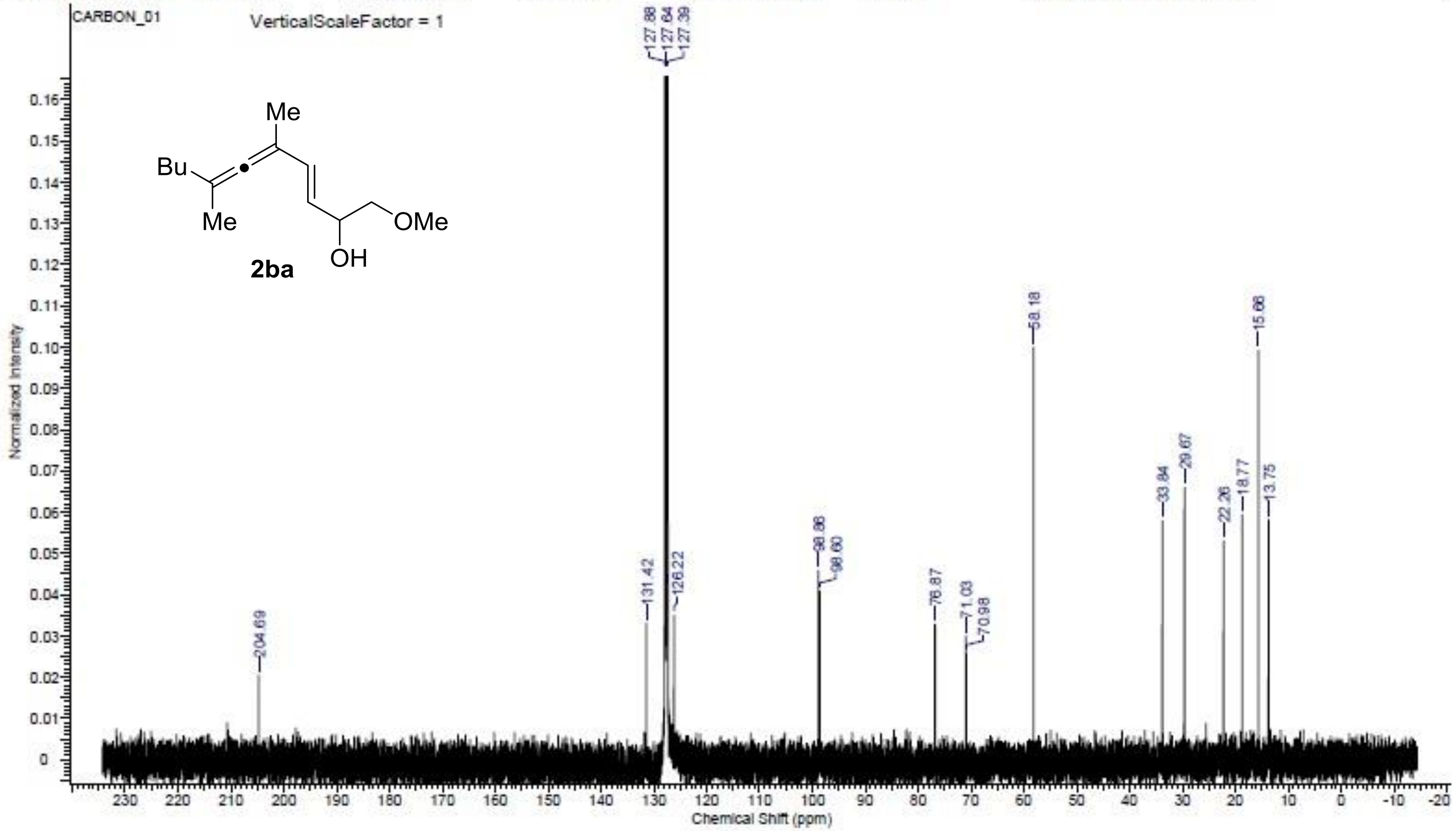


2ba

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

26.07.2016 21:06:27

Acquisition Time (sec)	1.3107	*Comment*	MK-0708-1-TKR-C	*Date*	Aug 13 2015	*Date Stamp*	Aug 13 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-0708-1-TKR-C_20150813_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*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

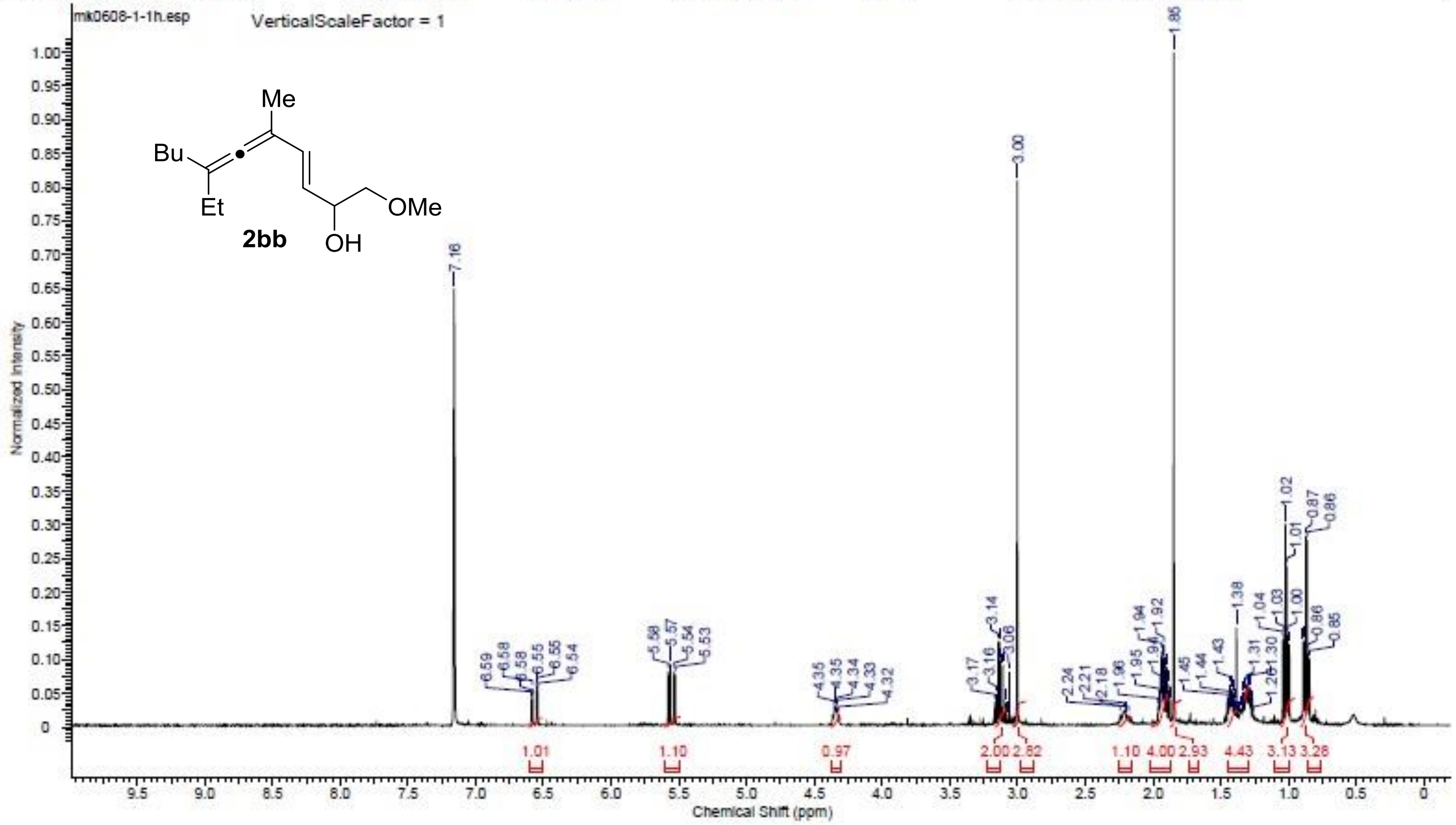


2ba

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

28.07.2016 11:31:12

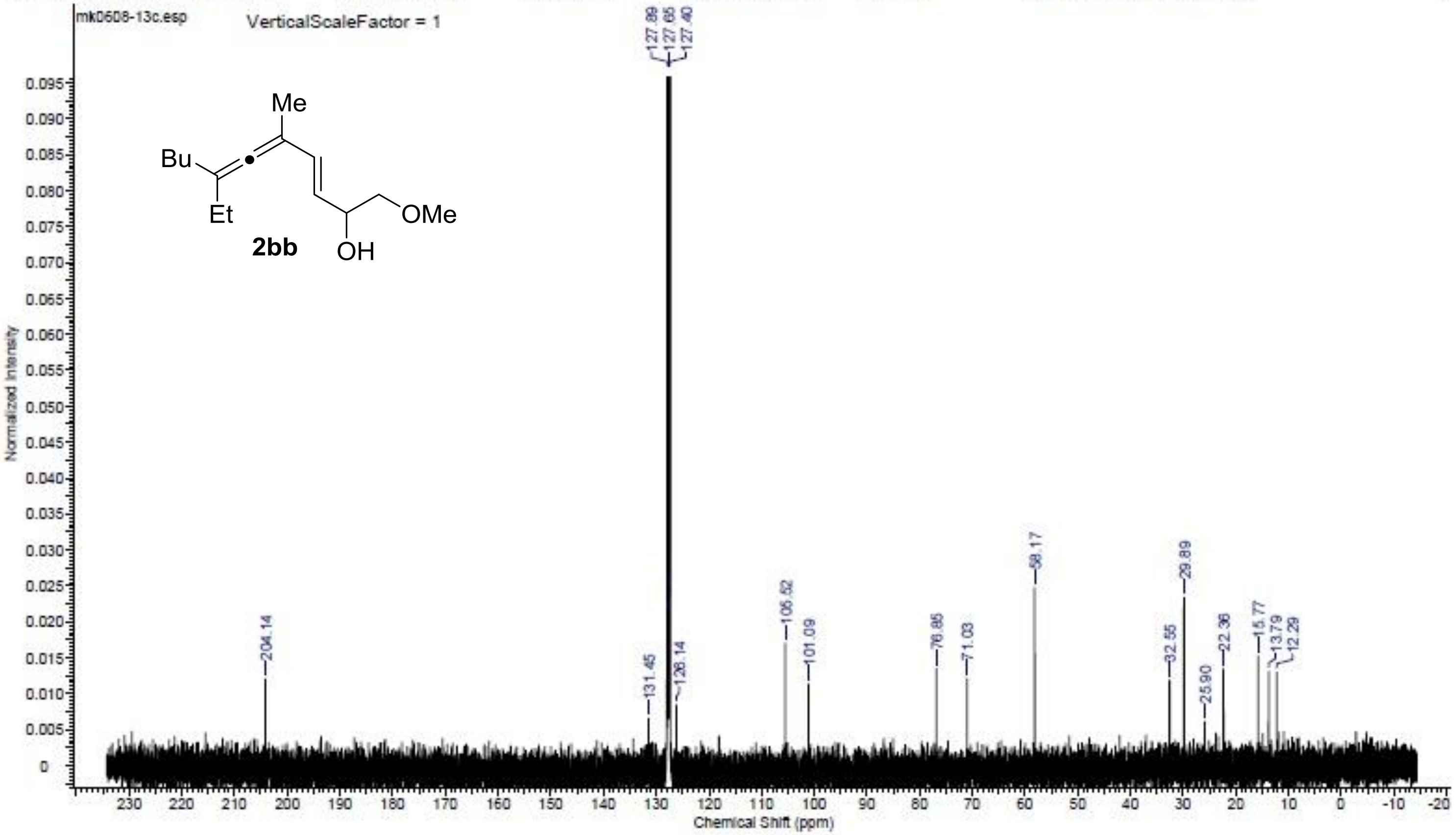
Acquisition Time (sec)	2.5559	*Comment*	MK-2704-1-C6D6	*Date*	May 26 2015	*Date Stamp*	May 26 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GÖK CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-2704-1-C6D6_20150526_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3853	*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/

28.07.2016 11:59:32

Acquisition Time (sec)	1.3107	*Comment*	MK-2704-1-C6D6	*Date*	May 26 2015	*Date Stamp*	May 26 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-2704-1-C6D6_20150526_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*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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26.07.2016 21:15:14

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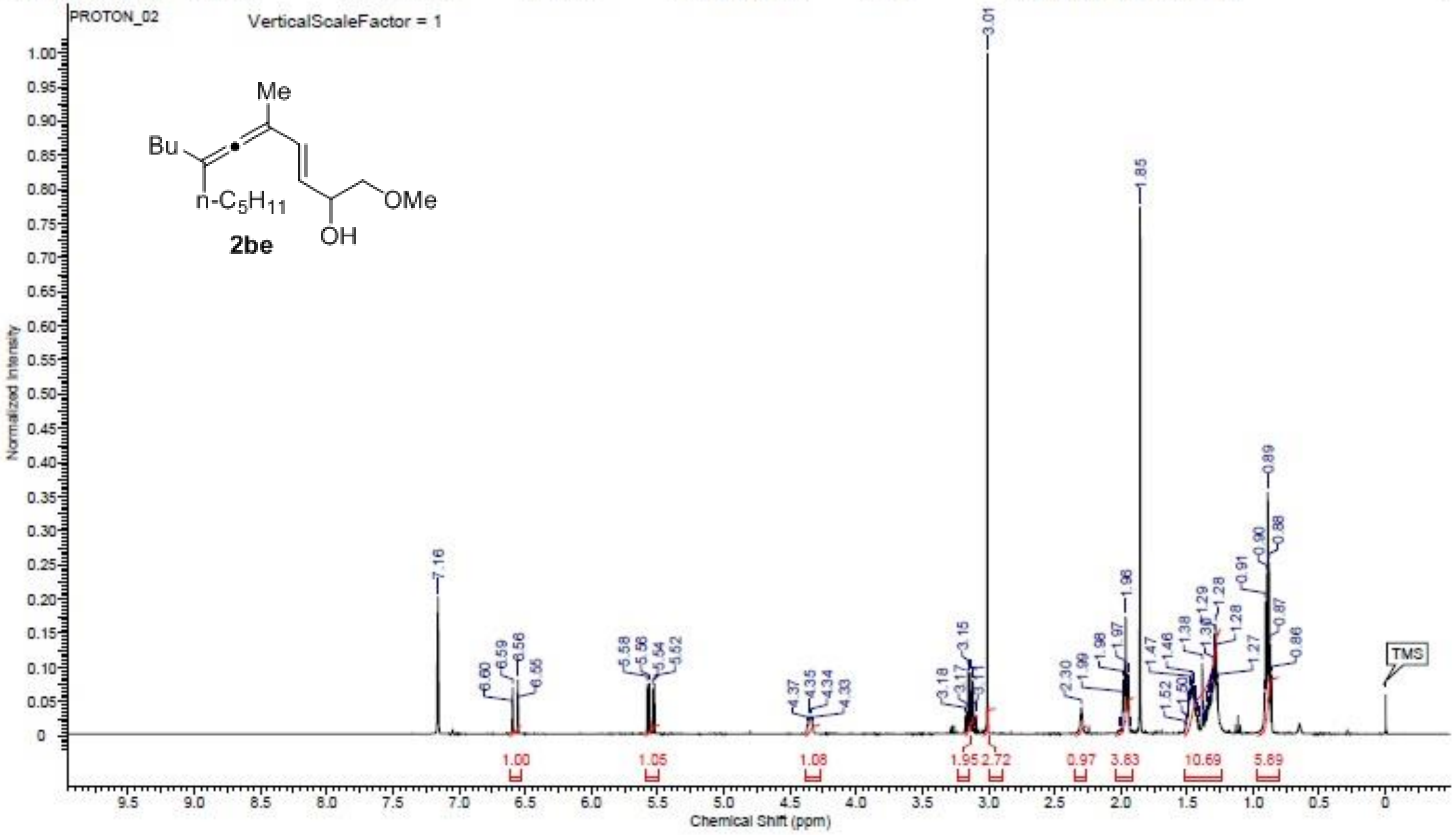
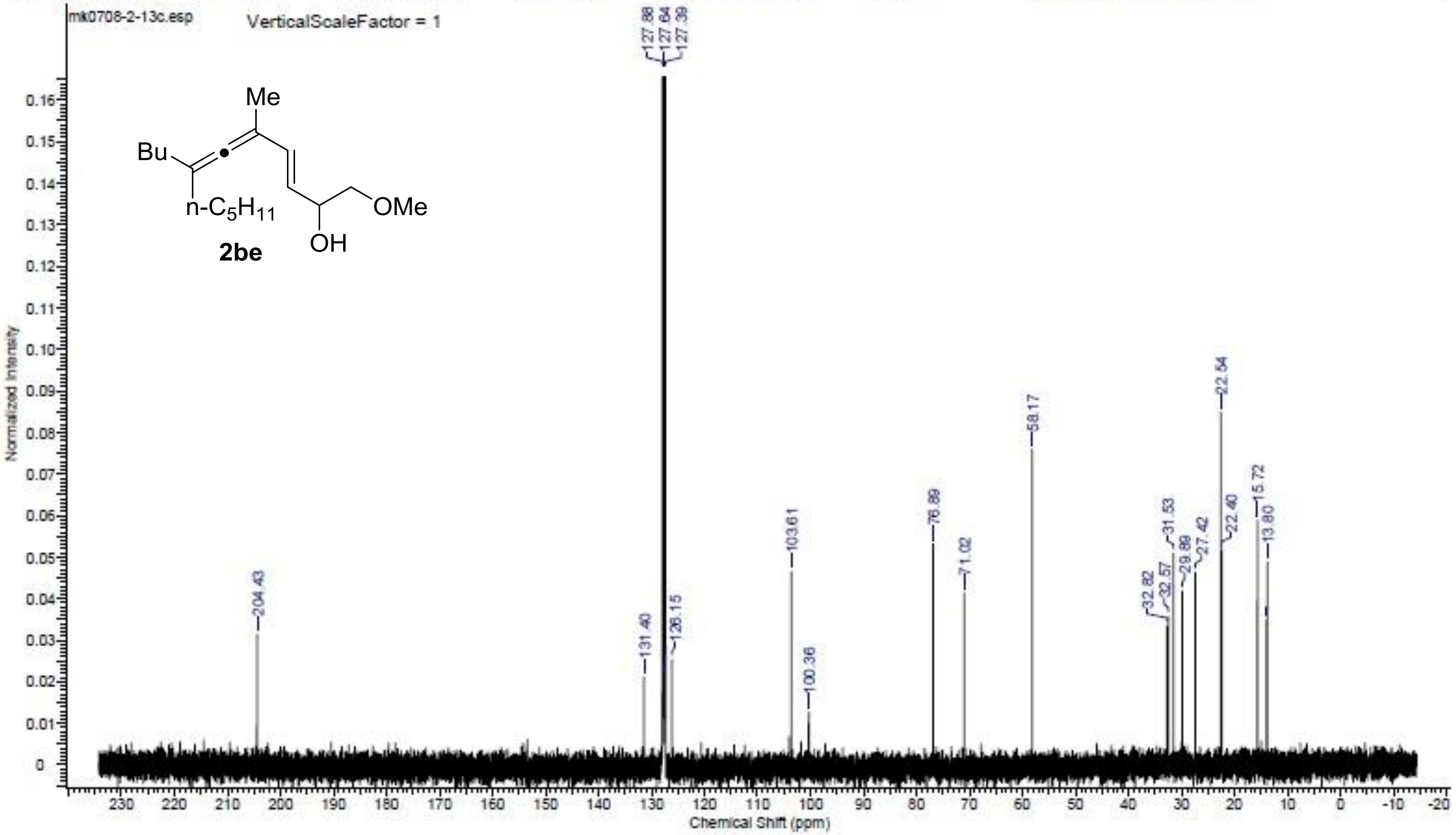
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-0708-2-TKR_20150813_01\PROTON_02.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	54.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7092	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000


2be

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

26.07.2016 21:17:36

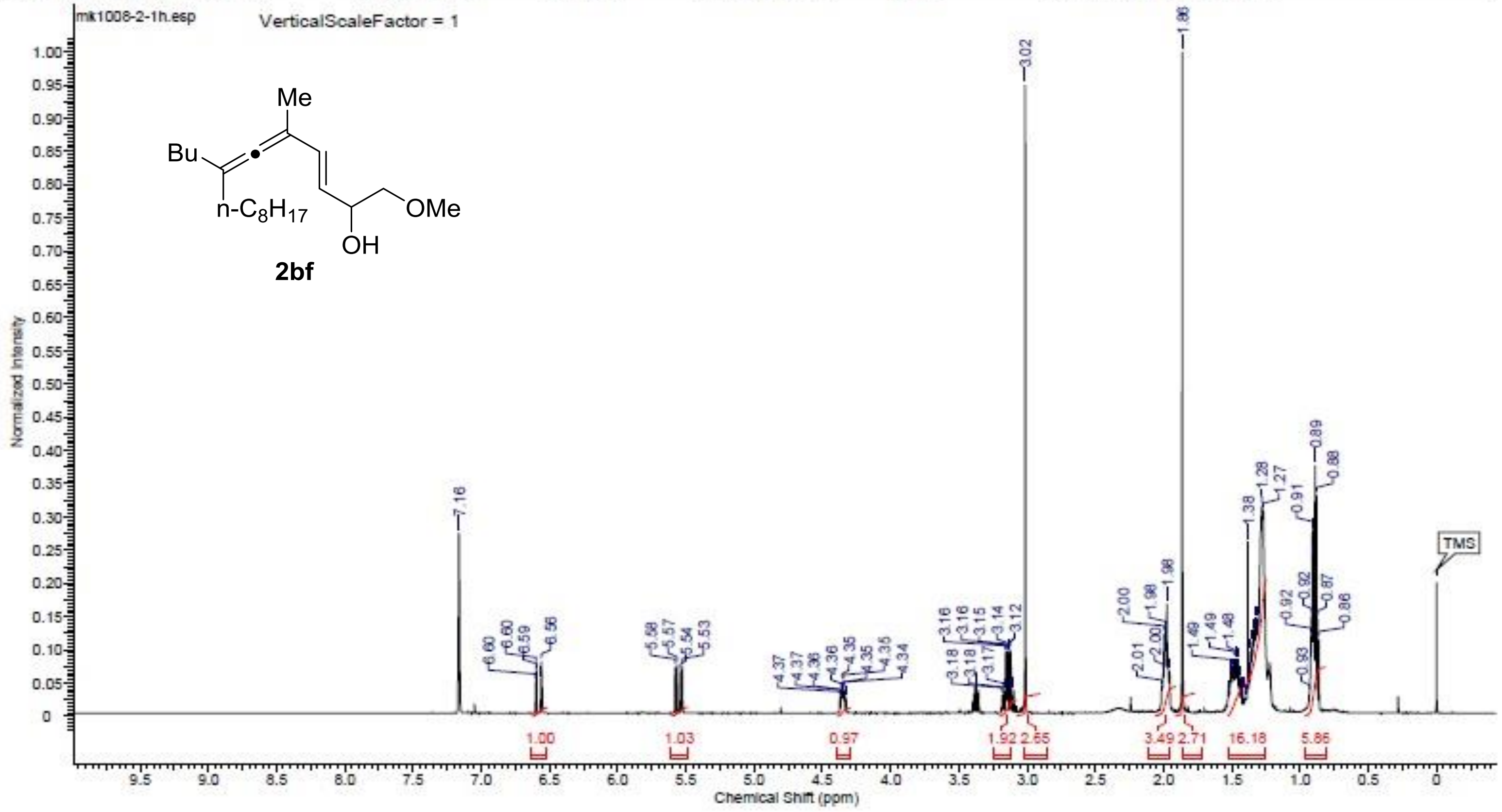
Acquisition Time (sec)	1.3107	*Comment*	MK-0708-2-TKR-C	*Date*	Aug 13 2015	*Date Stamp*	Aug 13 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-0708-2-TKR-C_20150813_01\CARBON_02.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



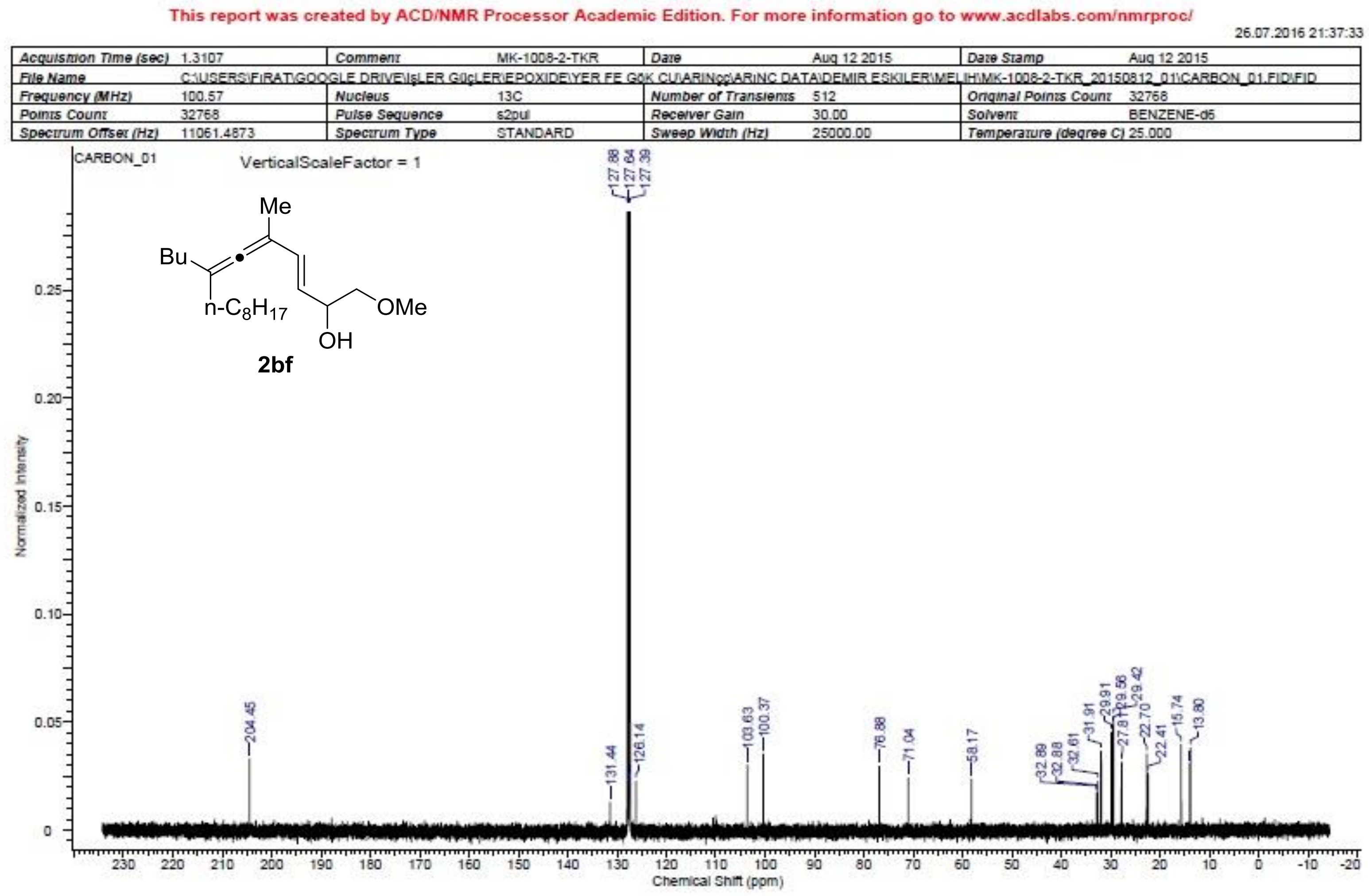
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

26.07.2016 21:30:03

Acquisition Time (sec)	2.5559	*Comment*	MK-1008-2-TKR	*Date*	Aug 11 2015	*Date Stamp*	Aug 11 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-1008-2-TKR_20150811_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)	2417.1006	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



2bf



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

26.07.2016 21:37:33

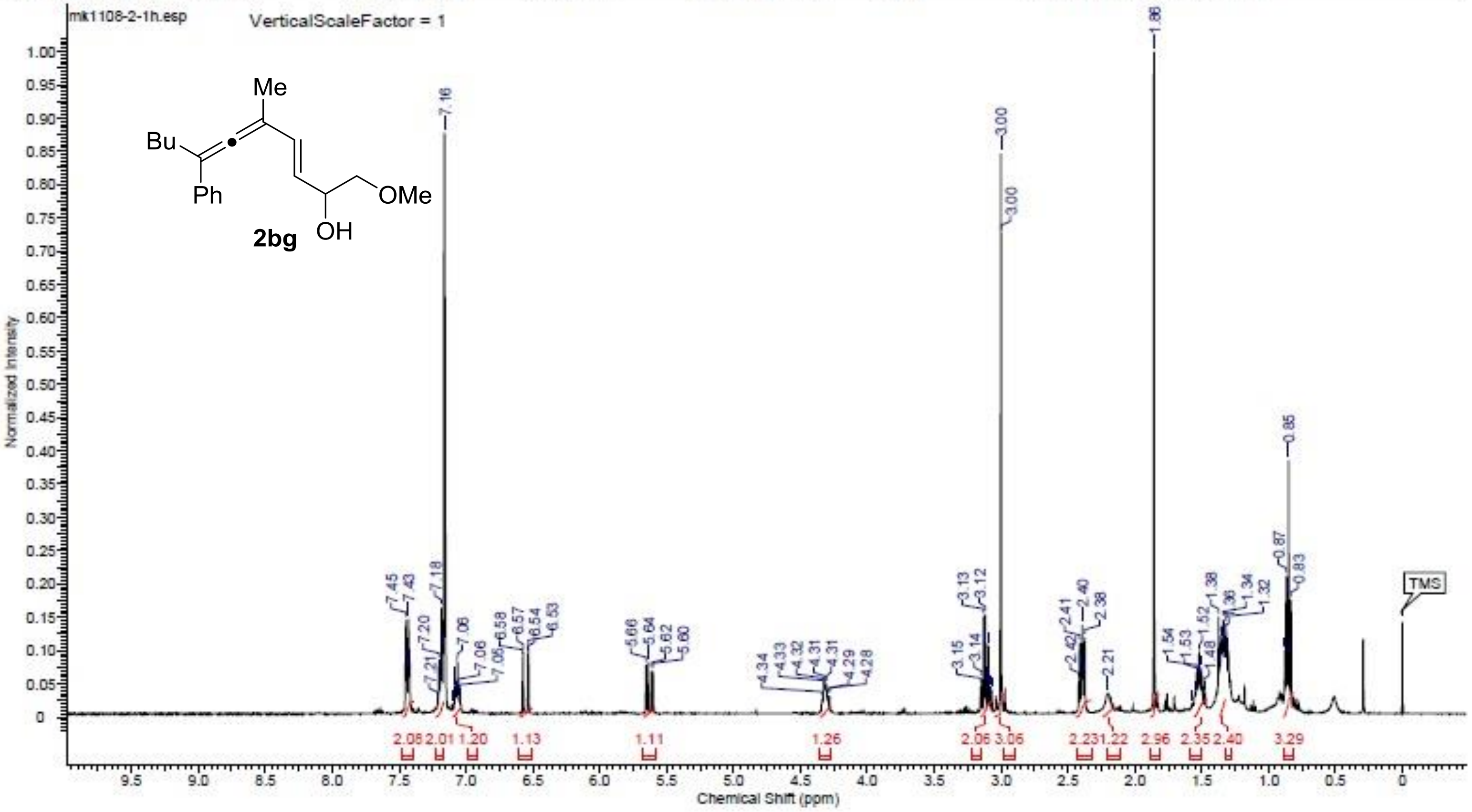
Acquisition Time (sec)	1.3107	Comment	MK-1008-2-TKR	Date	Aug 12 2015	Date Stamp	Aug 12 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-1008-2-TKR_20150812_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	Nucleus	13C	Number of Transients	512	Original Points Count	32768
Points Count	32768	Pulse Sequence	s2pul	Receiver Gain	30.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000

2bf

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

26.07.2016 22:02:42

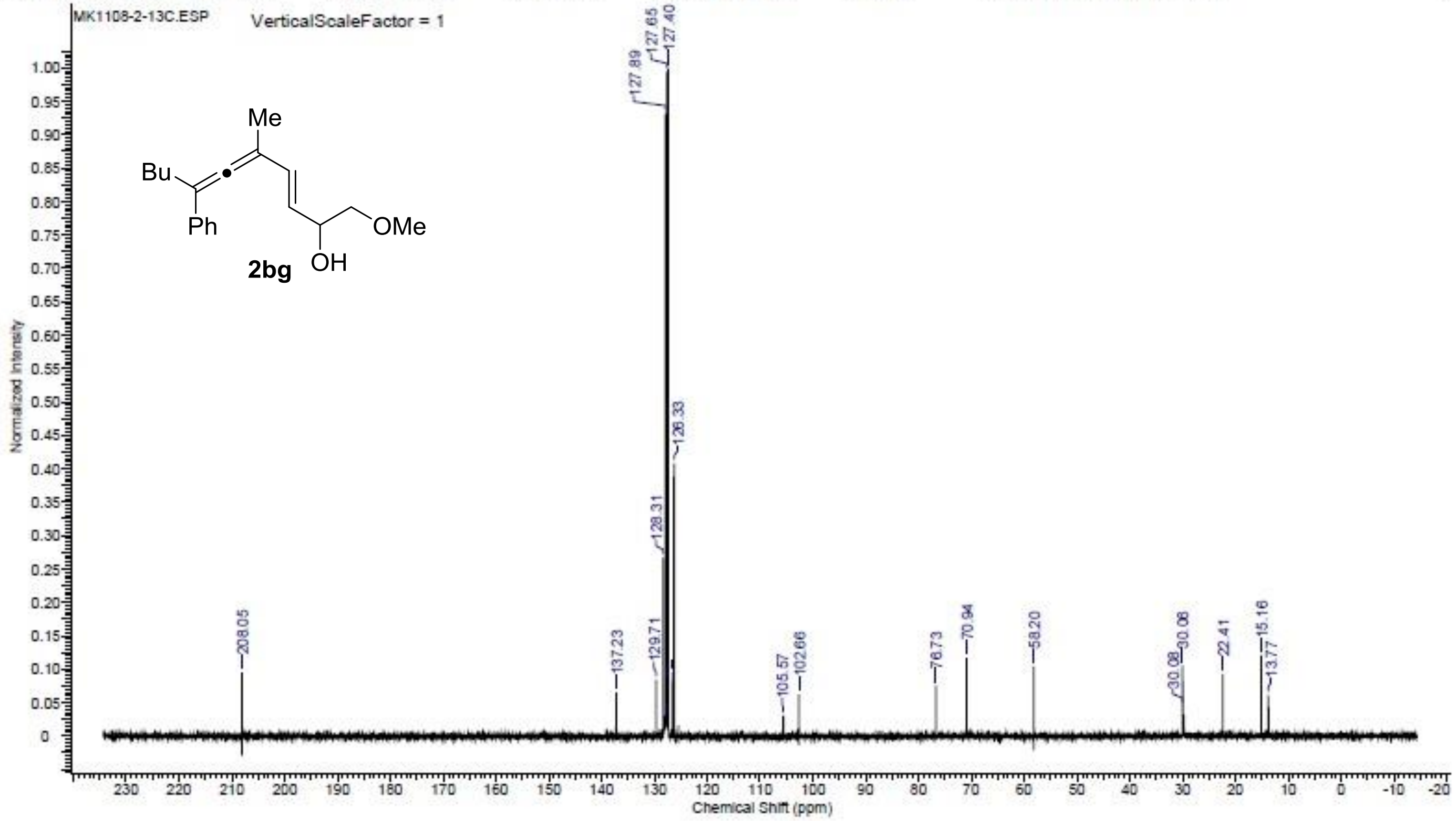
Acquisition Time (sec)	2.5559	*Comment*	MK-1108-2A-TKR	*Date*	Aug 14 2015	*Date Stamp*	Aug 14 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-1108-2A-TKR_20150814_01\PROTON_02.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	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/

28.07.2016 17:11:22

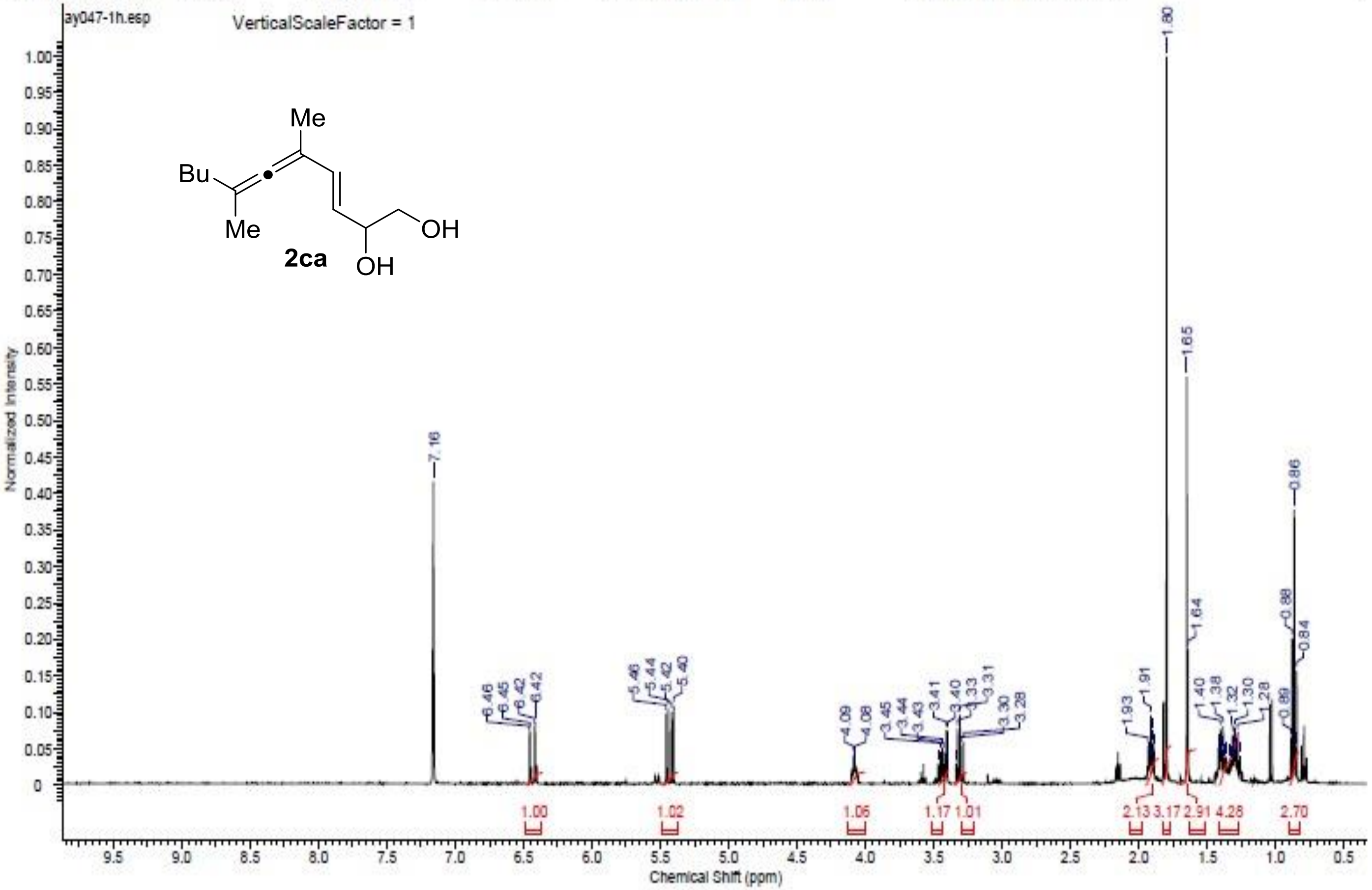
Acquisition Time (sec)	1.3107	*Comment*	FZ-FW186-SAF	*Date*	Jul 7 2015	*Date Stamp*	Jul 7 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FZ-FW186-SAF_20150707_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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

28.07.2016 14:48:54

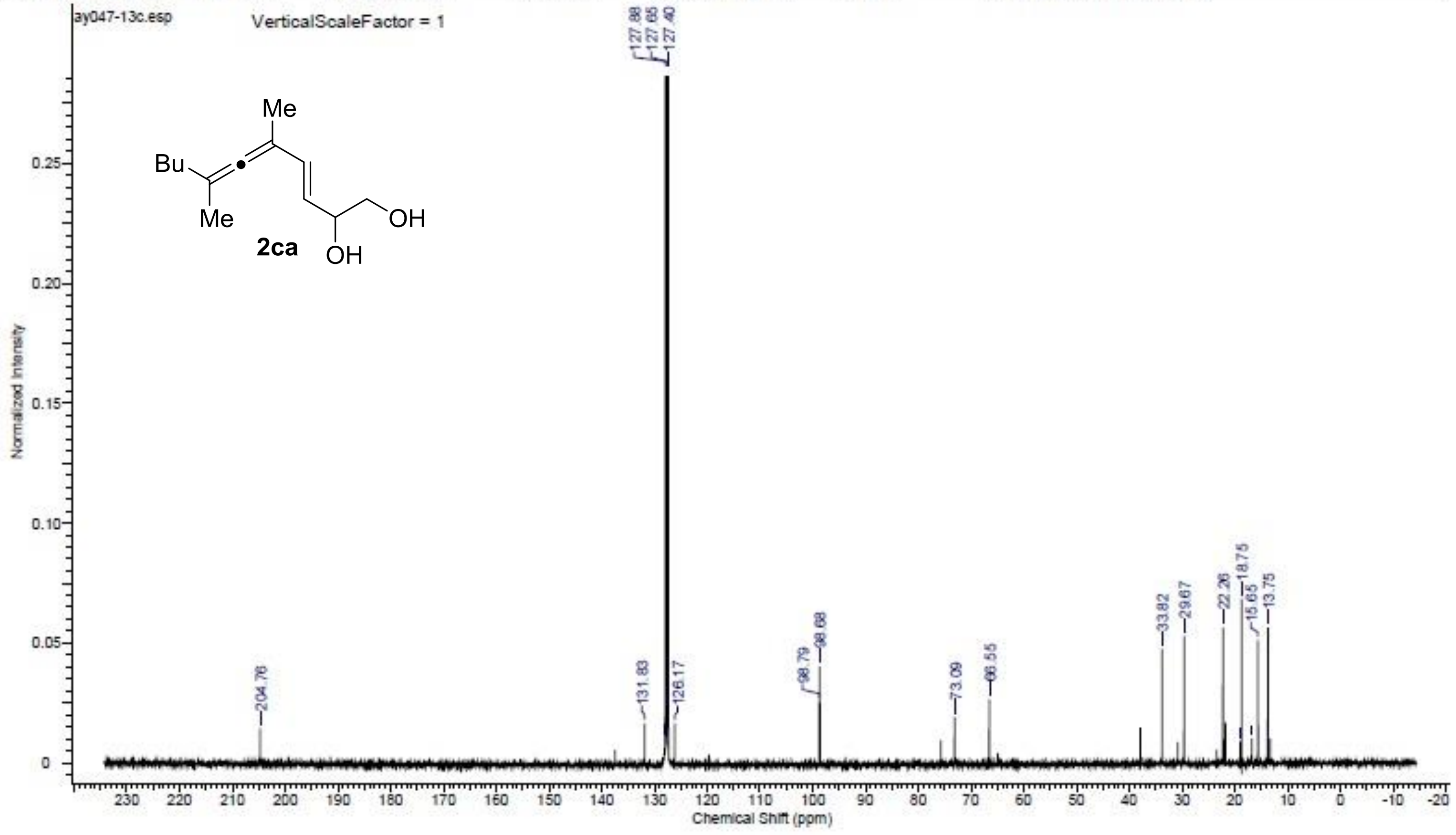
Acquisition Time (sec)	2.5559	*Comment*	AA-AY-047	*Date*	Jul 20 2016	*Date Stamp*	Jul 20 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\ARINC\AA-AY-047_20160720_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.9502	*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/

28.07.2016 14:54:58

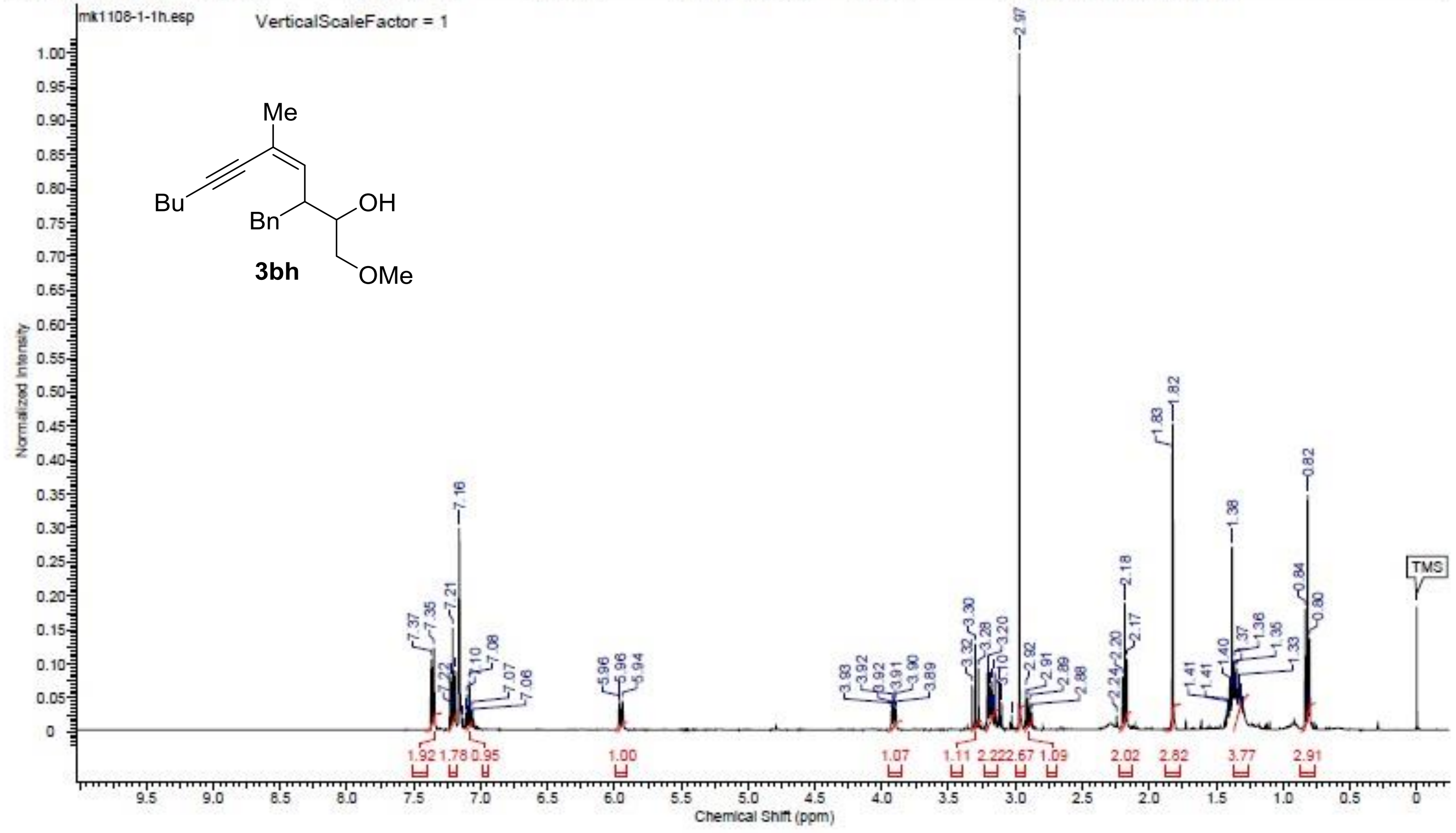
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-047	*Date*	Jul 21 2016	*Date Stamp*	Jul 21 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-047_20160721_02\CARBON_04.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	10000	*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



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

26.07.2016 22:15:49

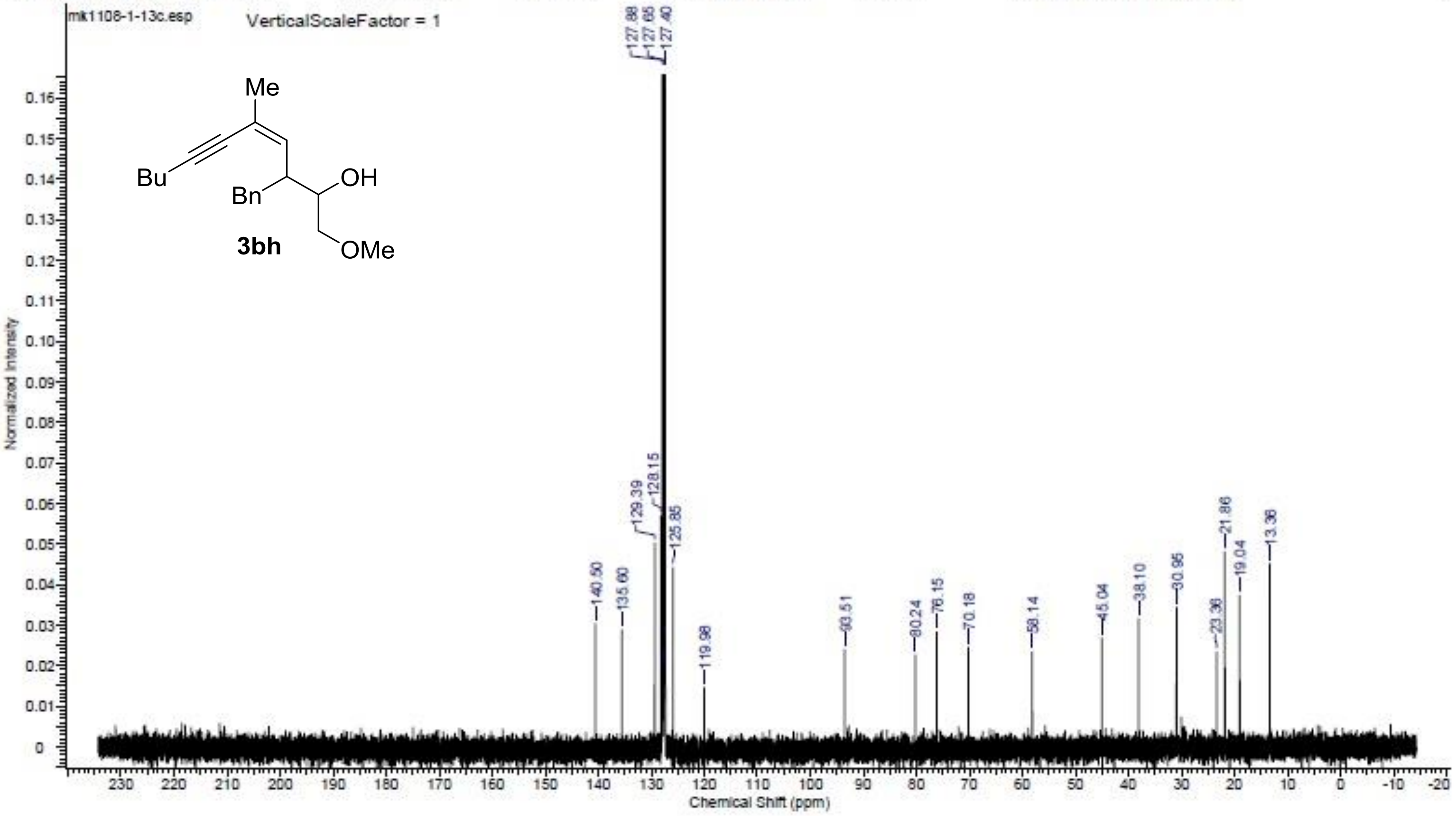
Acquisition Time (sec)	2.5559	*Comment*	MK-1108-1-1	*Date*	Aug 11 2015	*Date Stamp*	Aug 11 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-1108-1-1_20150811_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	32	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	58.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7092	*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/

26.07.2016 22:15:22

Acquisition Time (sec)	1.3107	*Comment*	MK-0811-1-1	*Date*	Aug 12 2015	*Date Stamp*	Aug 12 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-0811-1-1_20150812_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*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

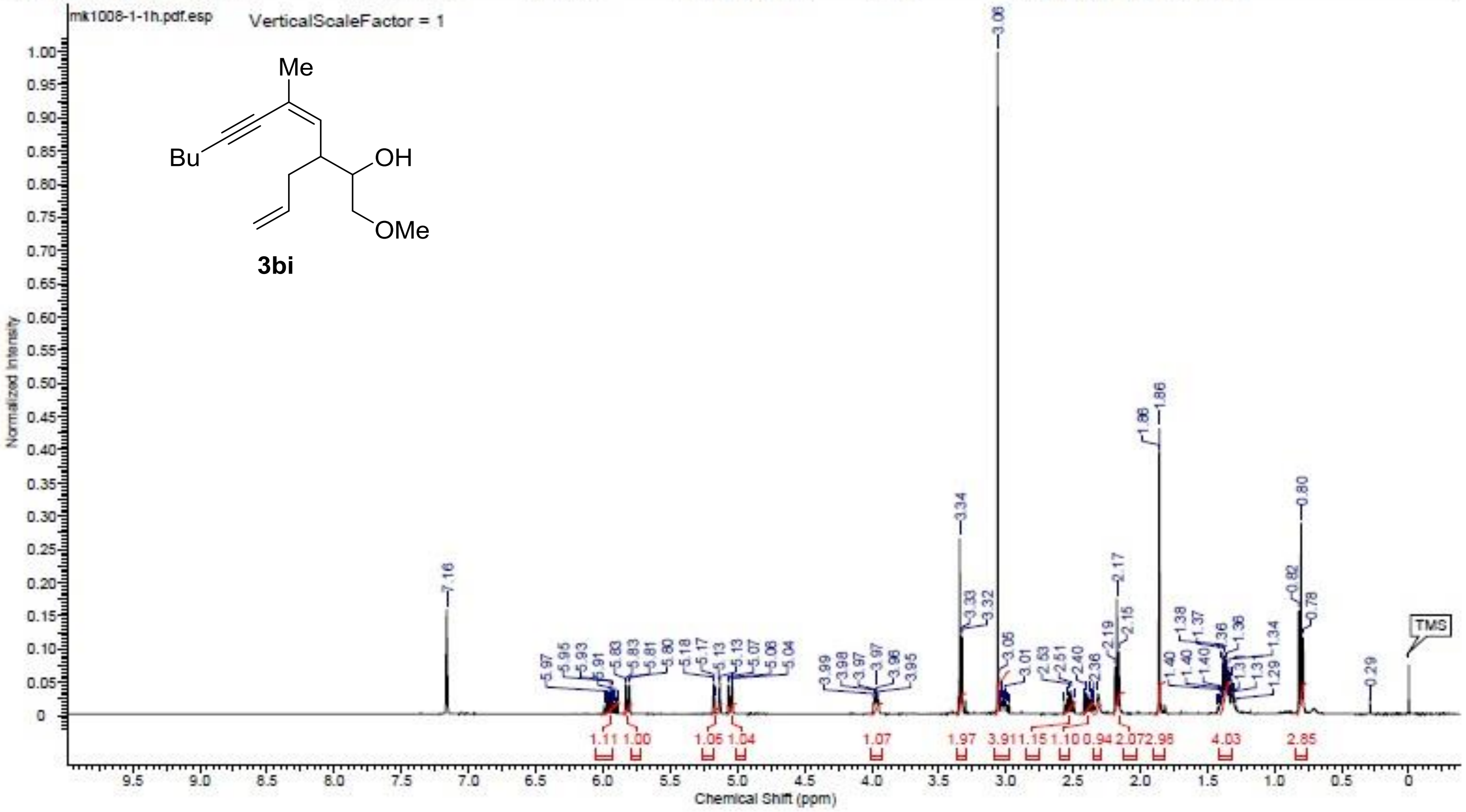


3bh

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

26.07.2016 22:23:33

Acquisition Time (sec)	2.5559	*Comment*	MK-1008-1ALLY	*Date*	Aug 10 2015	*Date Stamp*	Aug 10 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-1008-1ALLY_20150810_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*	BENZENE-d6
Spectrum Offset (Hz)	2417.4919	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

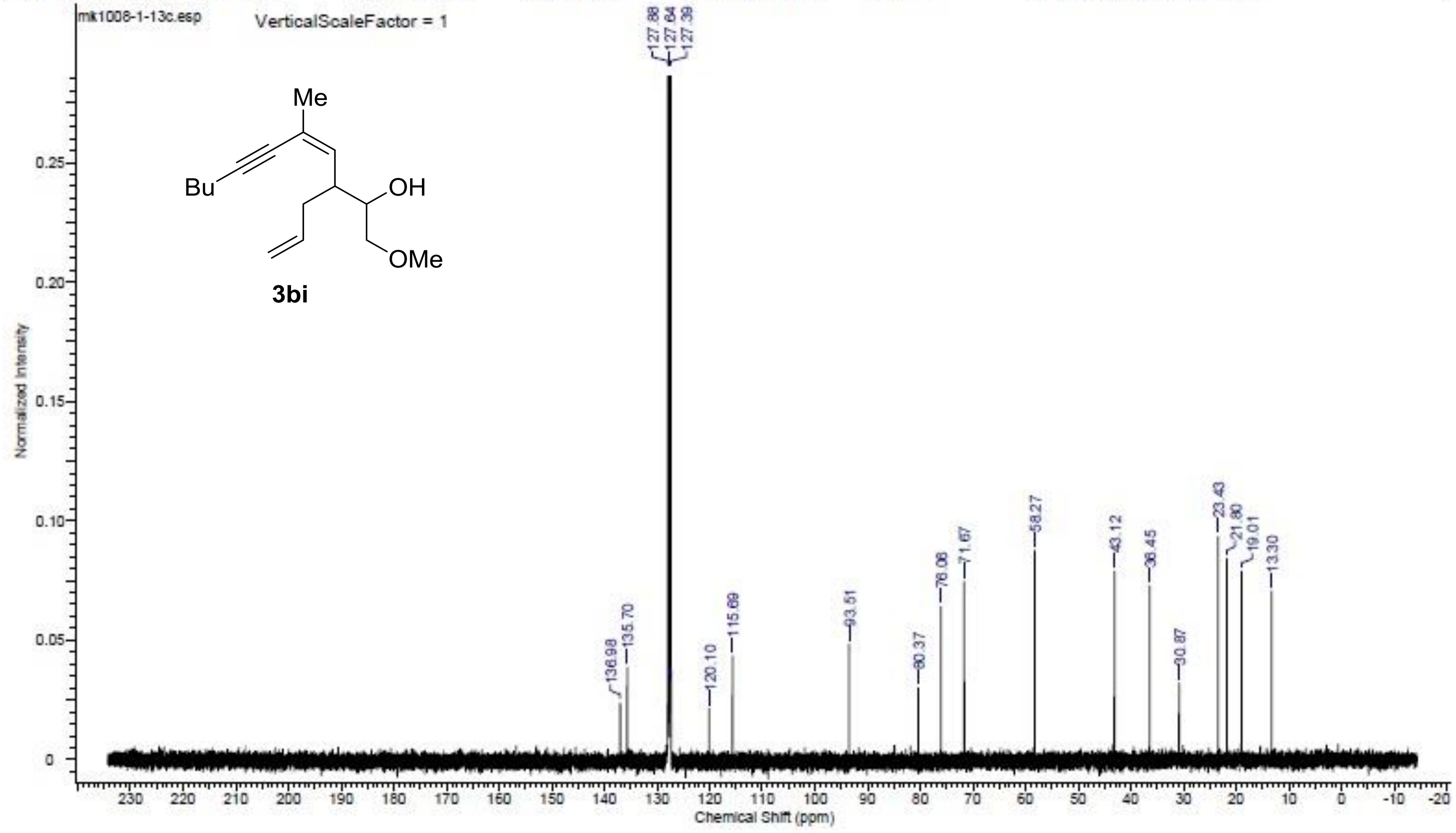


3bi

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

26.07.2016 22:25:47

Acquisition Time (sec)	1.3107	*Comment*	MK-1008-1ALLY	*Date*	Aug 10 2015	*Date Stamp*	Aug 10 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\DEMIR ESKILER\MELIH\MK-1008-1ALLY_20150810_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*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

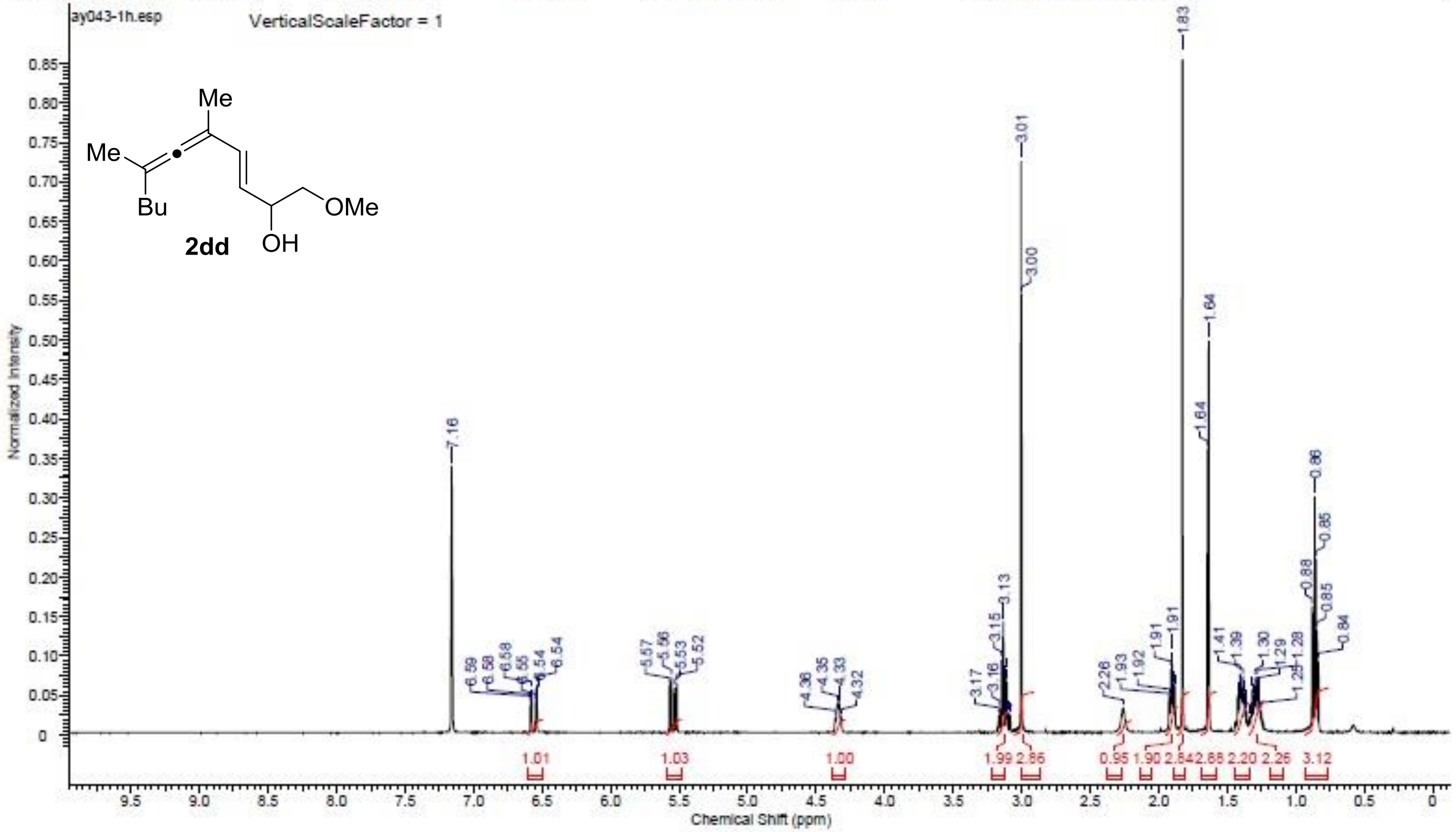


3bi

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

28.07.2016 13:56:51

Acquisition Time (sec)	2.5559	*Comment*	AA-AY-043	*Date*	Jun 8 2016	*Date Stamp*	Jun 8 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\ARINC\AA-AY-043_20160608_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*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

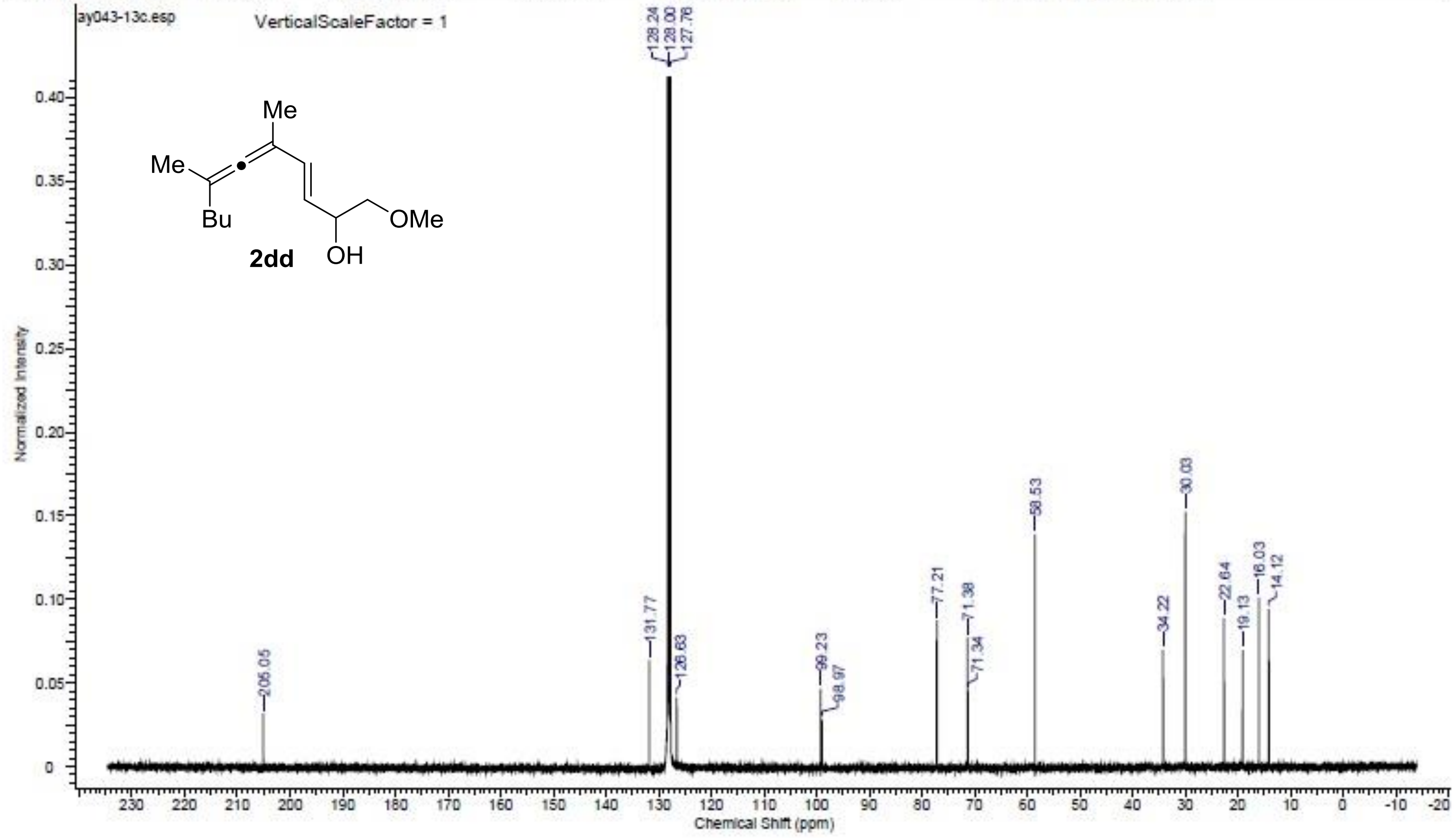


2dd

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

28.07.2016 14:01:53

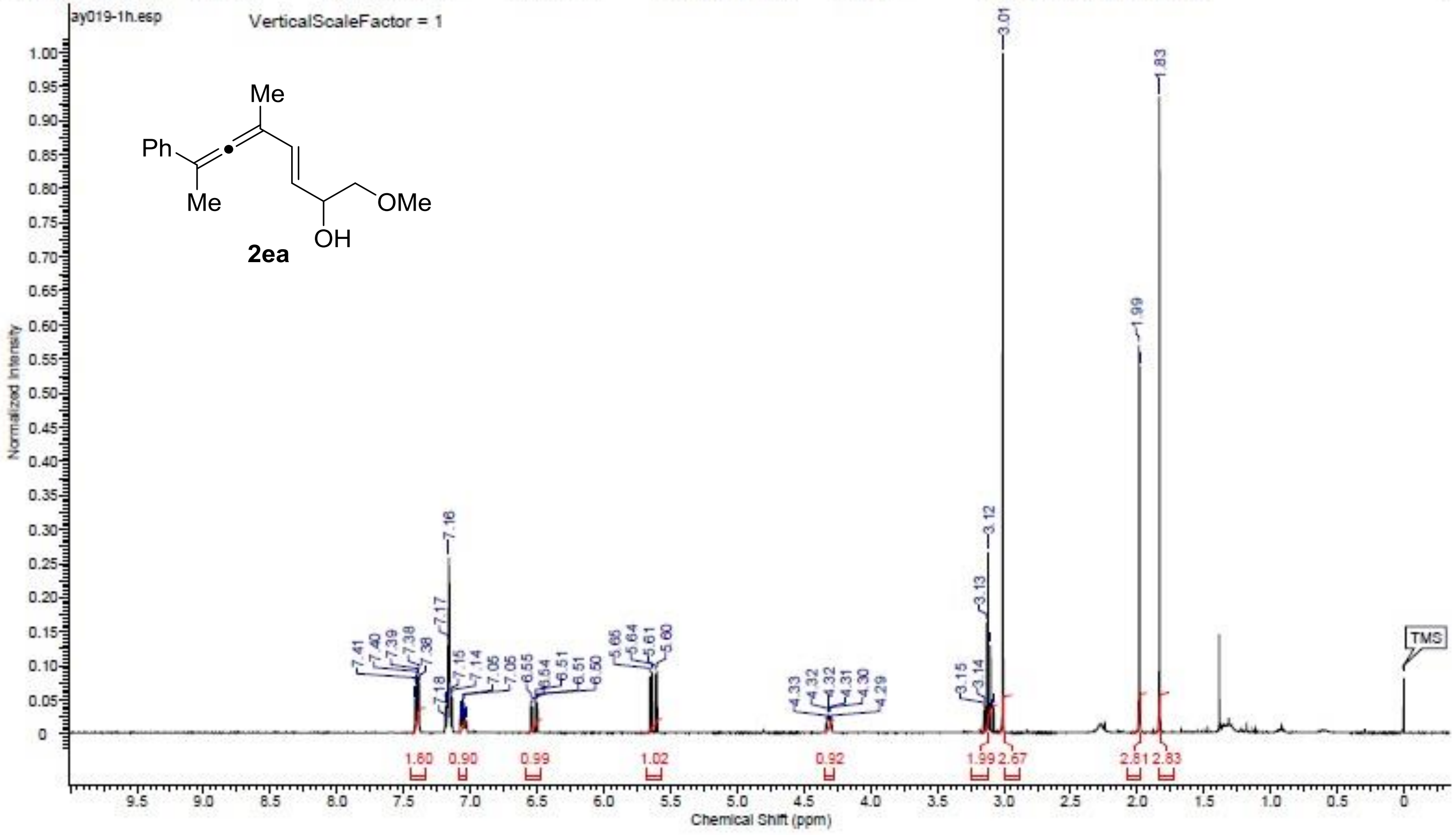
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-043	*Date*	Jun 8 2016	*Date Stamp*	Jun 8 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-043_20160608_01\CARBON_02.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	2000	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11097.1709	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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

26.07.2016 22:35:53

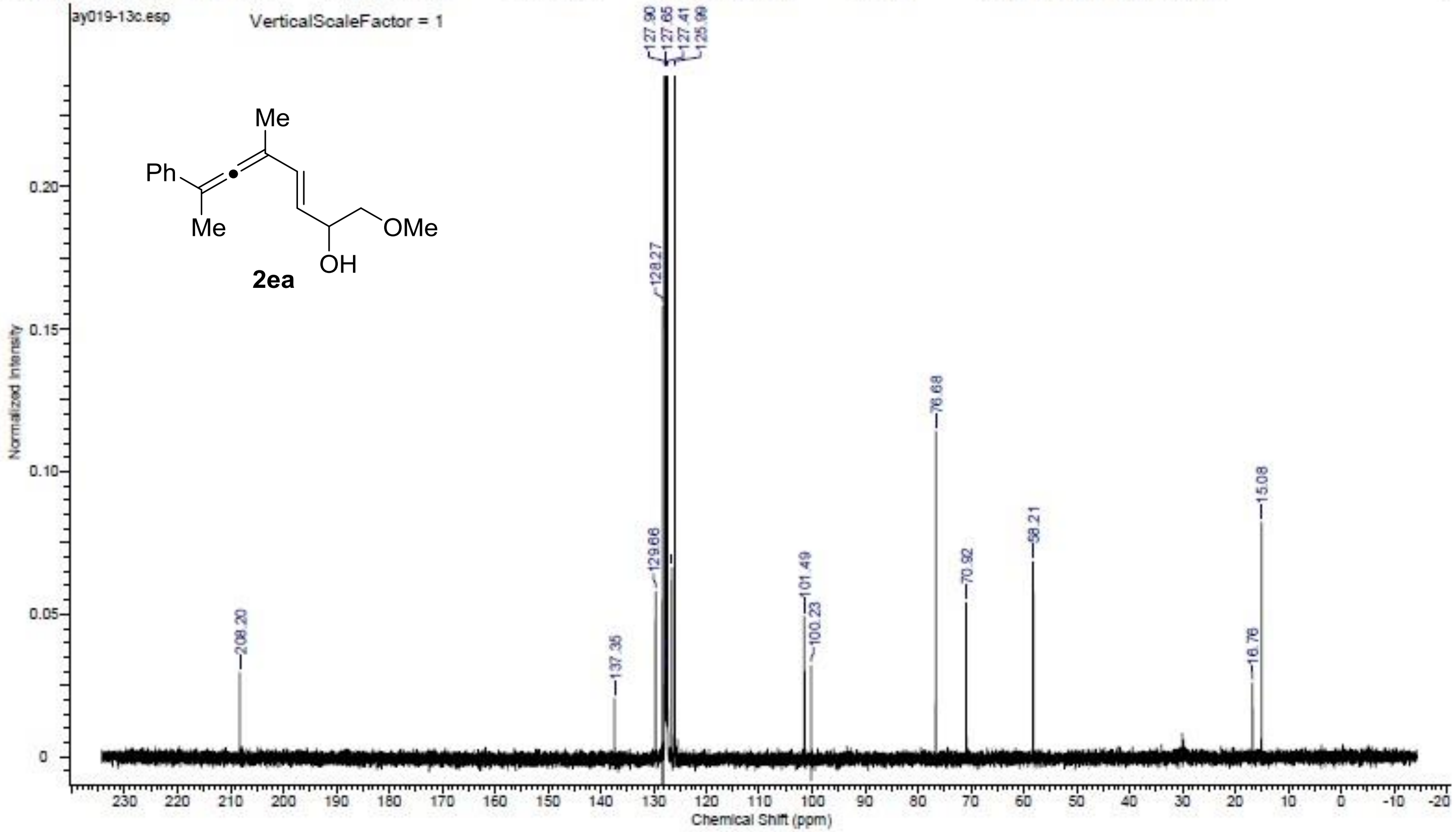
Acquisition Time (sec)	2.5559	*Comment*	AA-AY-019-IS	*Date*	Jan 7 2016	*Date Stamp*	Jan 7 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-019-TS_20160107_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*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



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

26.07.2016 22:37:06

Acquisition Time (sec)	1.3107	Comment	AA-AY-019-TS	Date	Jan 7 2016	Date Stamp	Jan 7 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-019-TS_20160107_02\CARBON_01.FID\FID						
Frequency (MHz)	100.57	Nucleus	13C	Number of Transients	1000	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

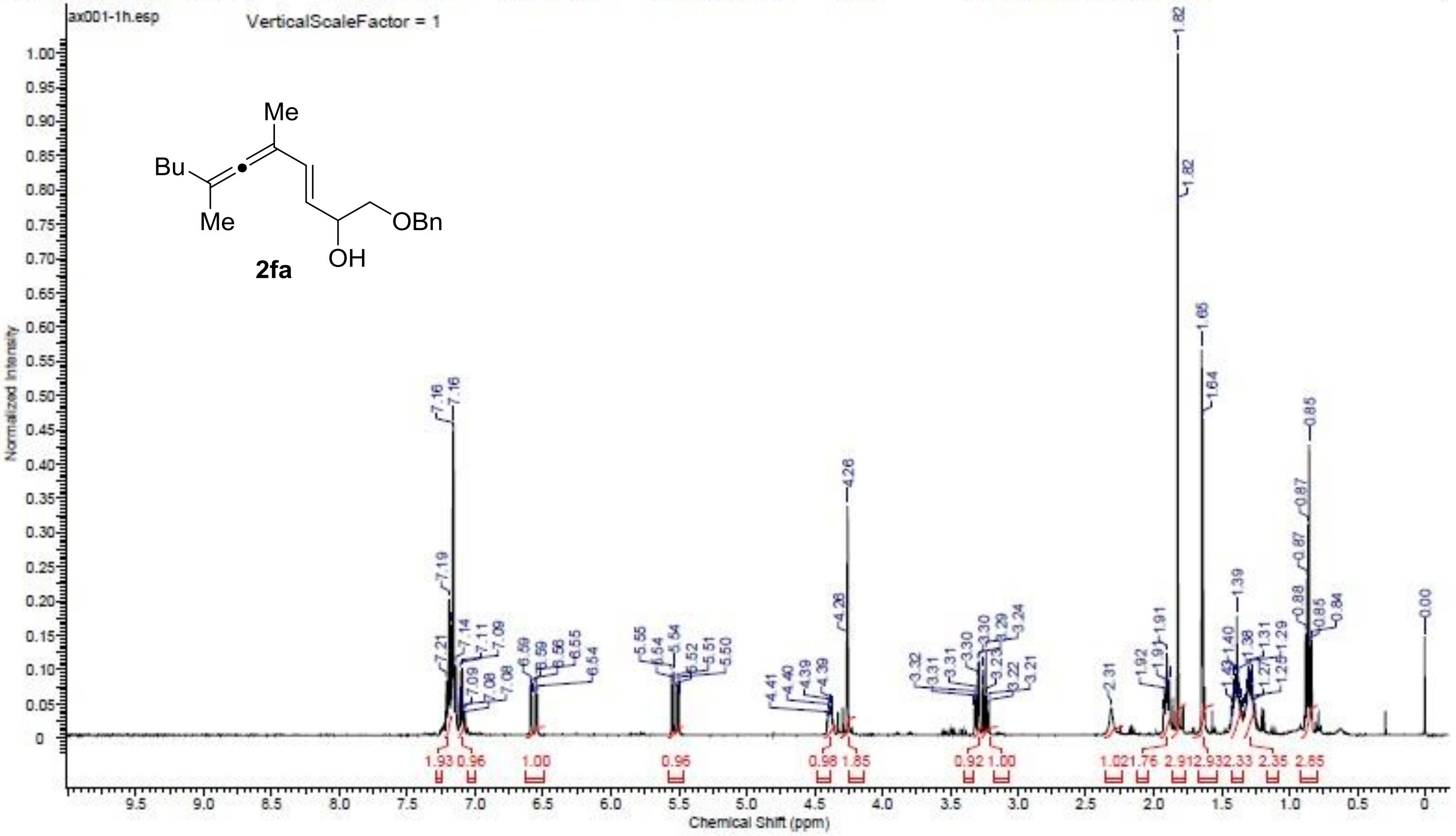


2ea

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

28.07.2016 16:13:23

Acquisition Time (sec)	2.5559	*Comment*	AA-AX-001B	*Date*	Oct 26 2015	*Date Stamp*	Oct 26 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\ARINC\AA-AX-001B_20151026_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*	BENZENE-d6
Spectrum Offset (Hz)	2418.3416	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

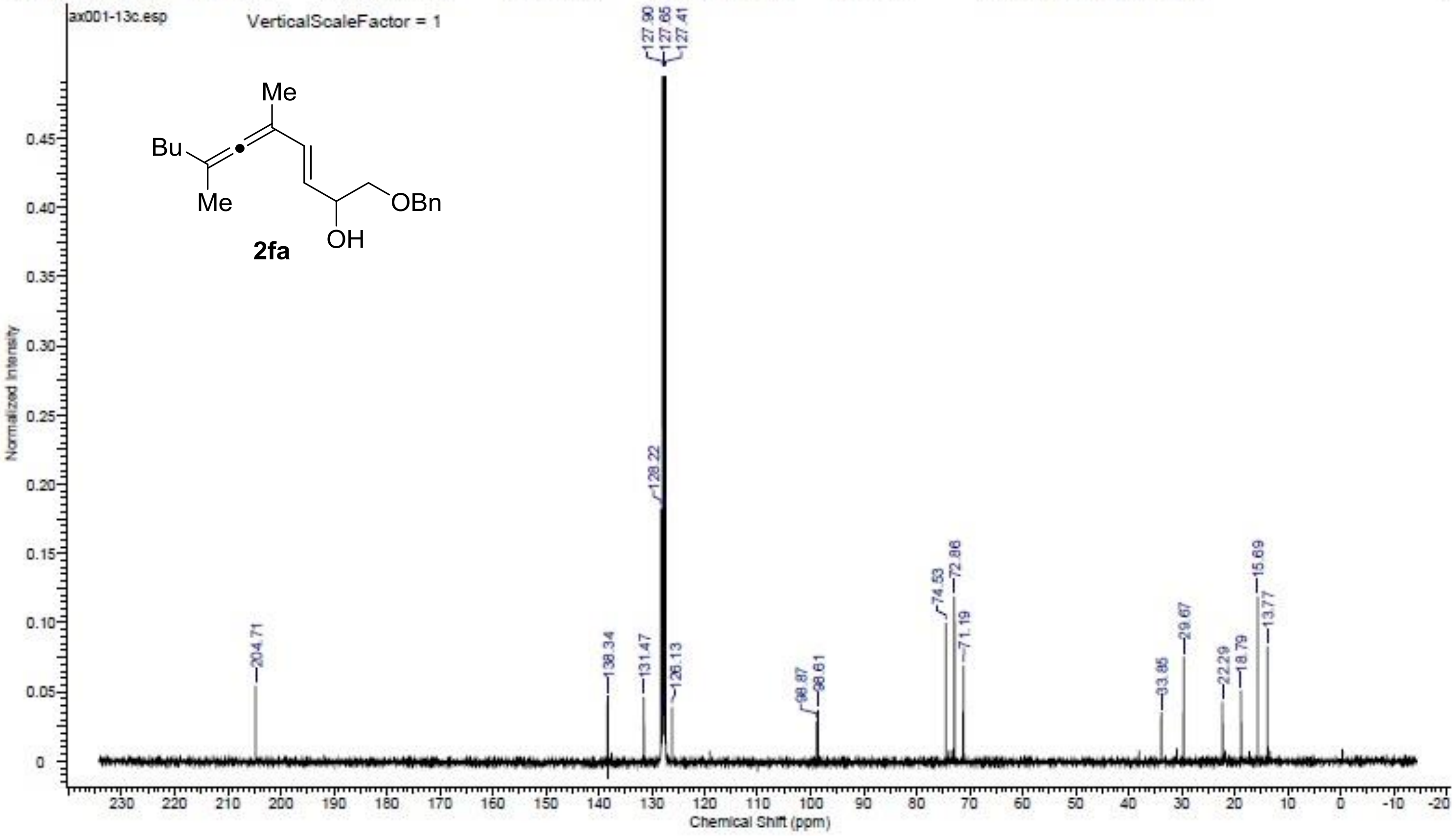


142

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

28.07.2016 16:16:16

Acquisition Time (sec)	1.3107	*Comment*	AA-AX-014Y	*Date*	Feb 23 2016	*Date Stamp*	Feb 23 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AX-014Y_20160223_01\CARBON_02.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*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

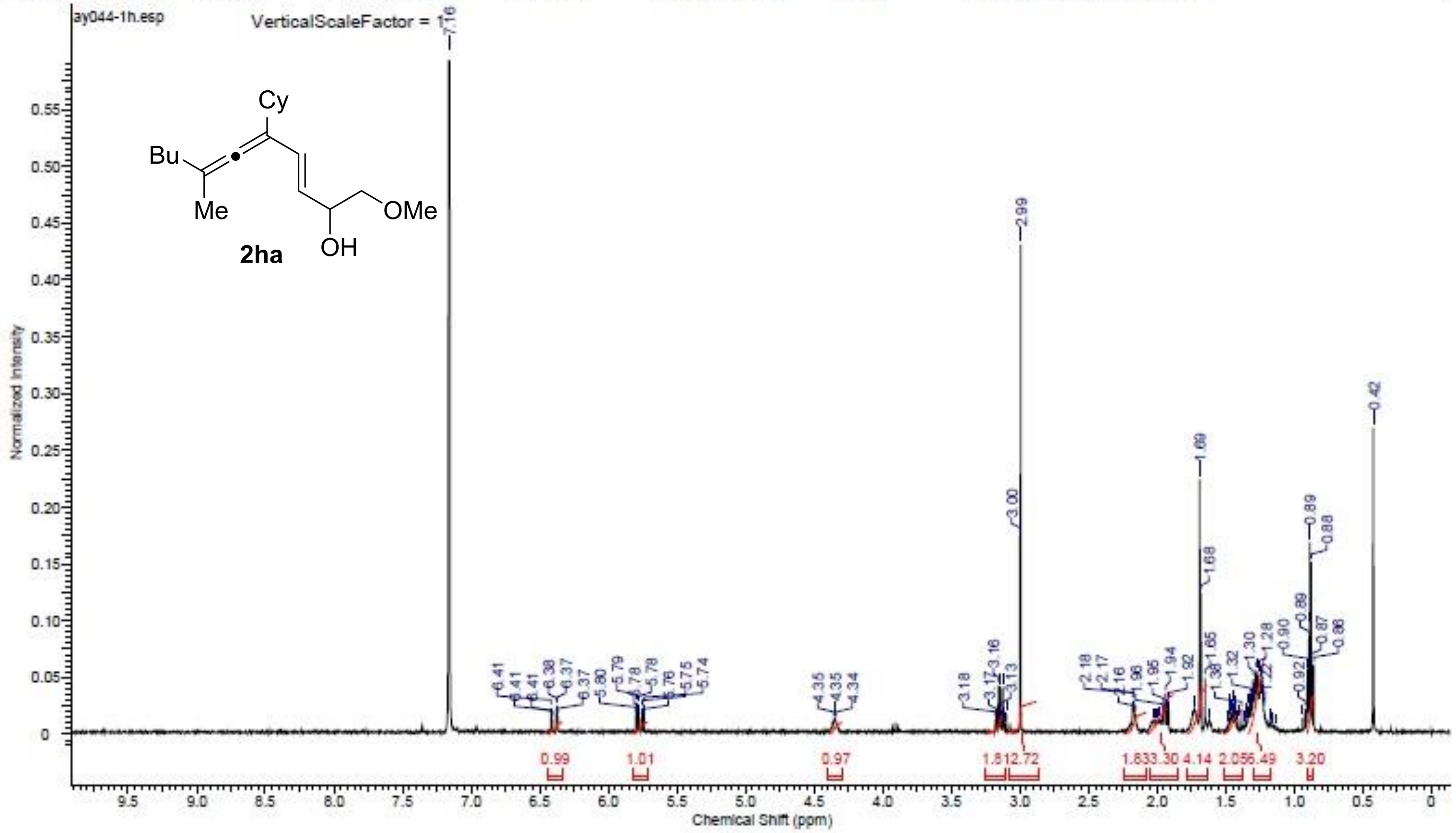


2fa

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

28.07.2016 14:32:17

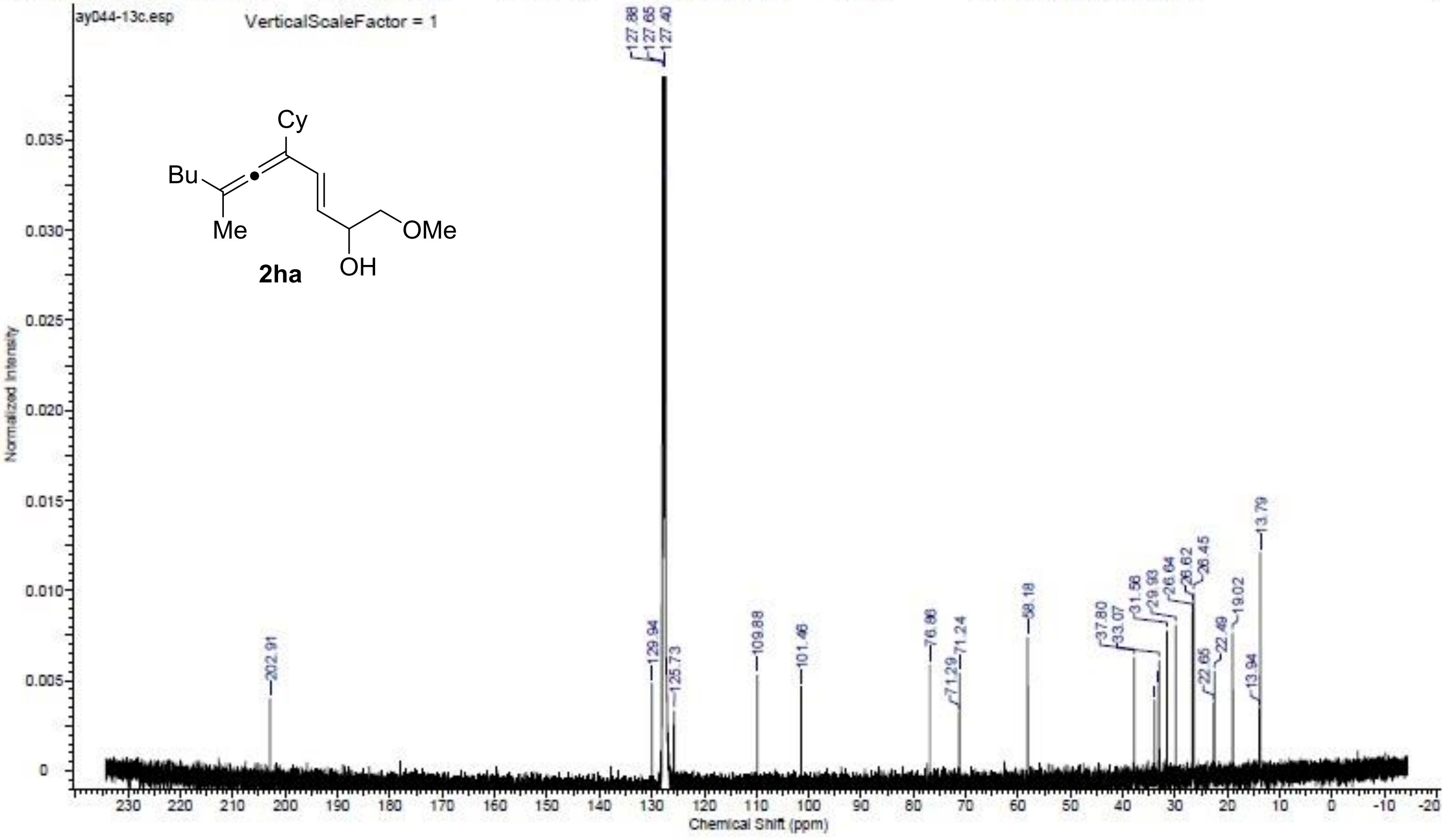
Acquisition Time (sec)	2.5559	*Comment*	AA-AY-044S	*Date*	Jul 1 2016	*Date Stamp*	Jul 1 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-044S_20160701_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.5591	*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/

28.07.2016 14:39:34

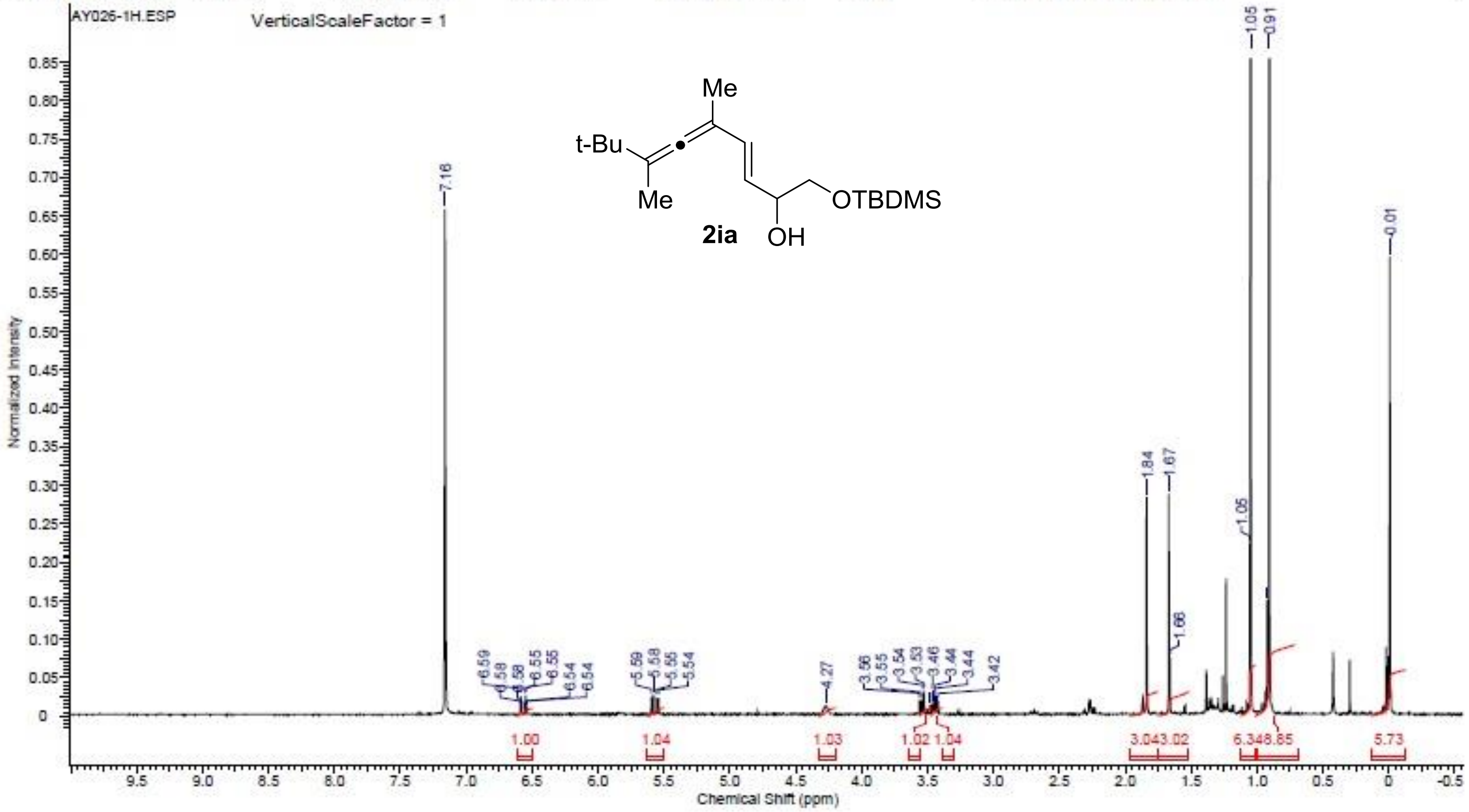
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-044S	*Date*	Jul 2 2016	*Date Stamp*	Jul 2 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\ARINC\AA-AY-044S_20160701_01\CARBON_04.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	20000	*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



2ha

28.07.2016 16:00:45

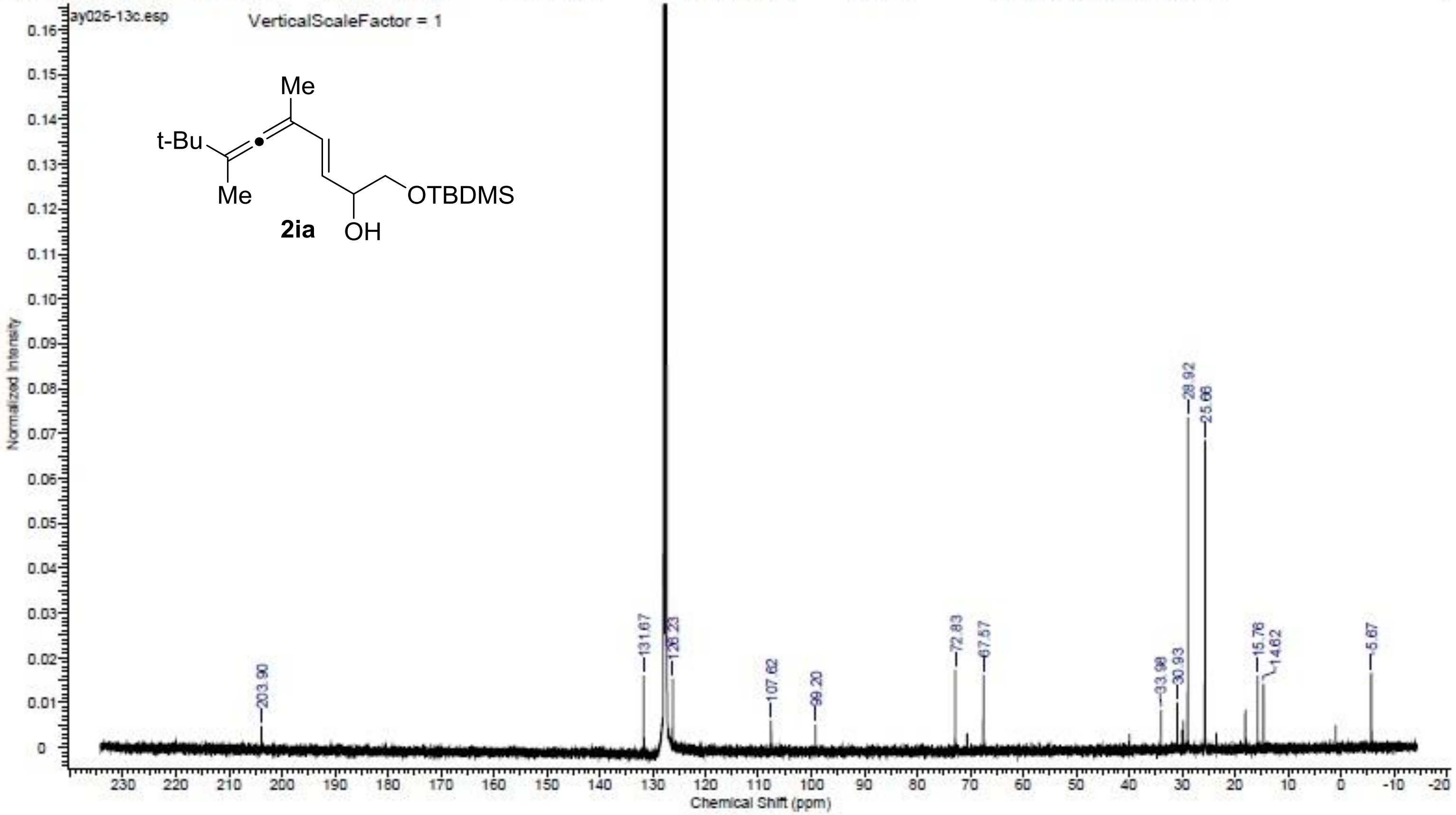
Acquisition Time (sec)	2.5559	*Comment*	AA-AY-026	*Date*	Jan 27 2016	*Date Stamp*	Jan 27 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\ARINC\AA-AY-026_20160127_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	16	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*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/

26.07.2016 23:14:24

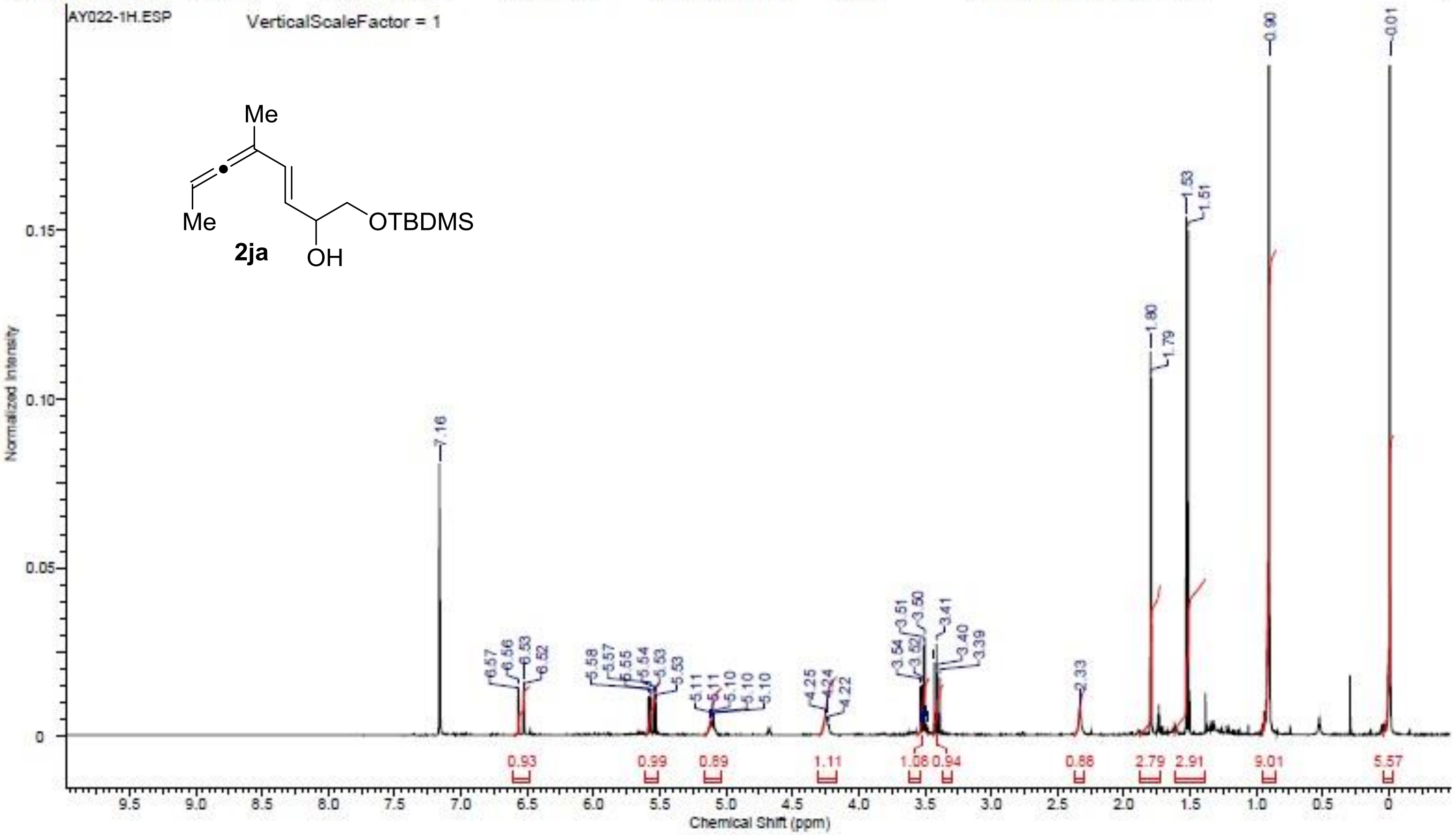
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-026CA	*Date*	Feb 8 2016	*Date Stamp*	Feb 8 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-026CA_20160208_01\CARBON_02.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	10000	*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



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

28.07.2016 15:59:05

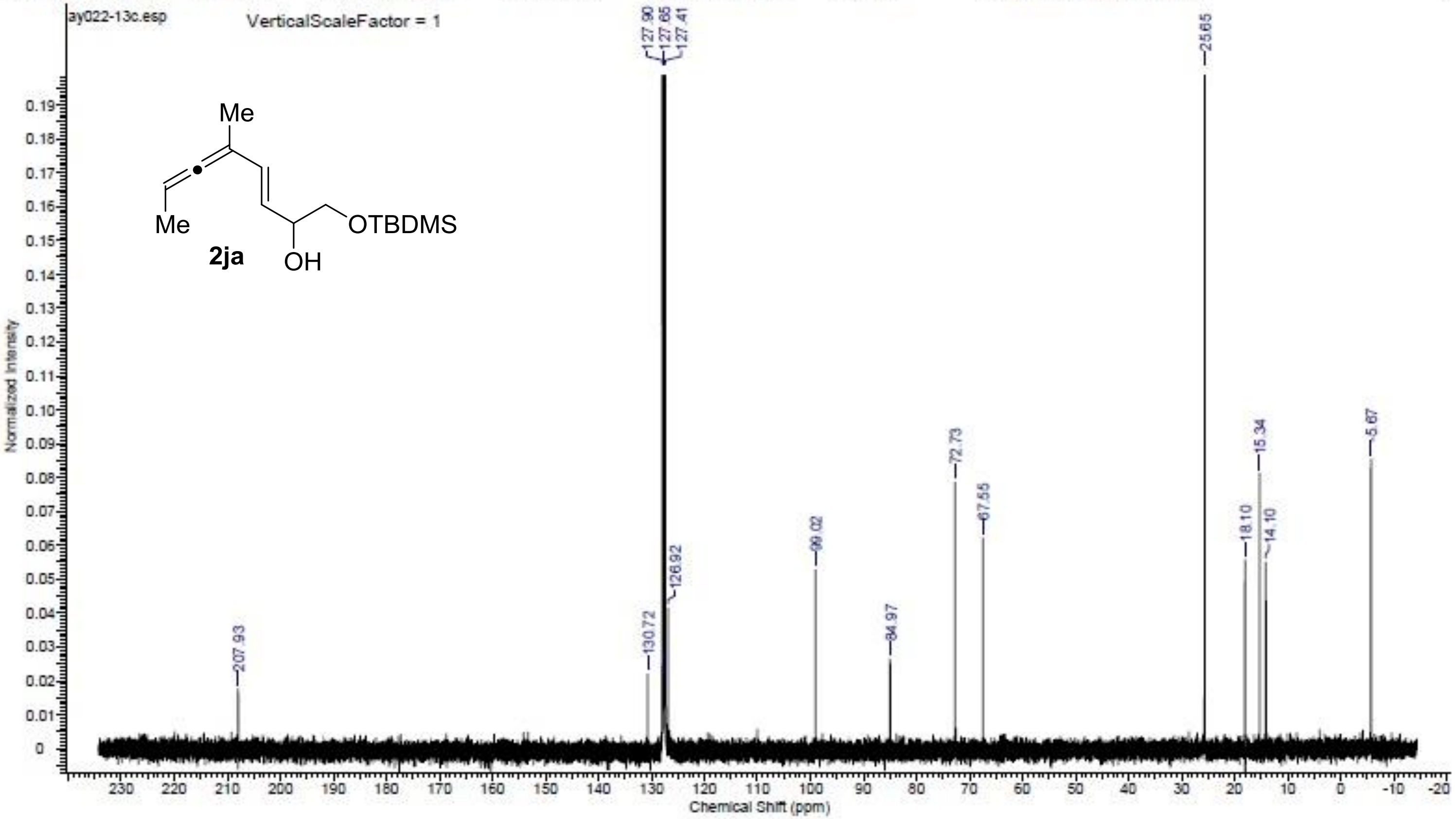
Acquisition Time (sec)	2.5559	*Comment*	AA-AY-022-T	*Date*	Jan 8 2016	*Date Stamp*	Jan 8 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\ARINC\AA-AY-022-T_20160108_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	58.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

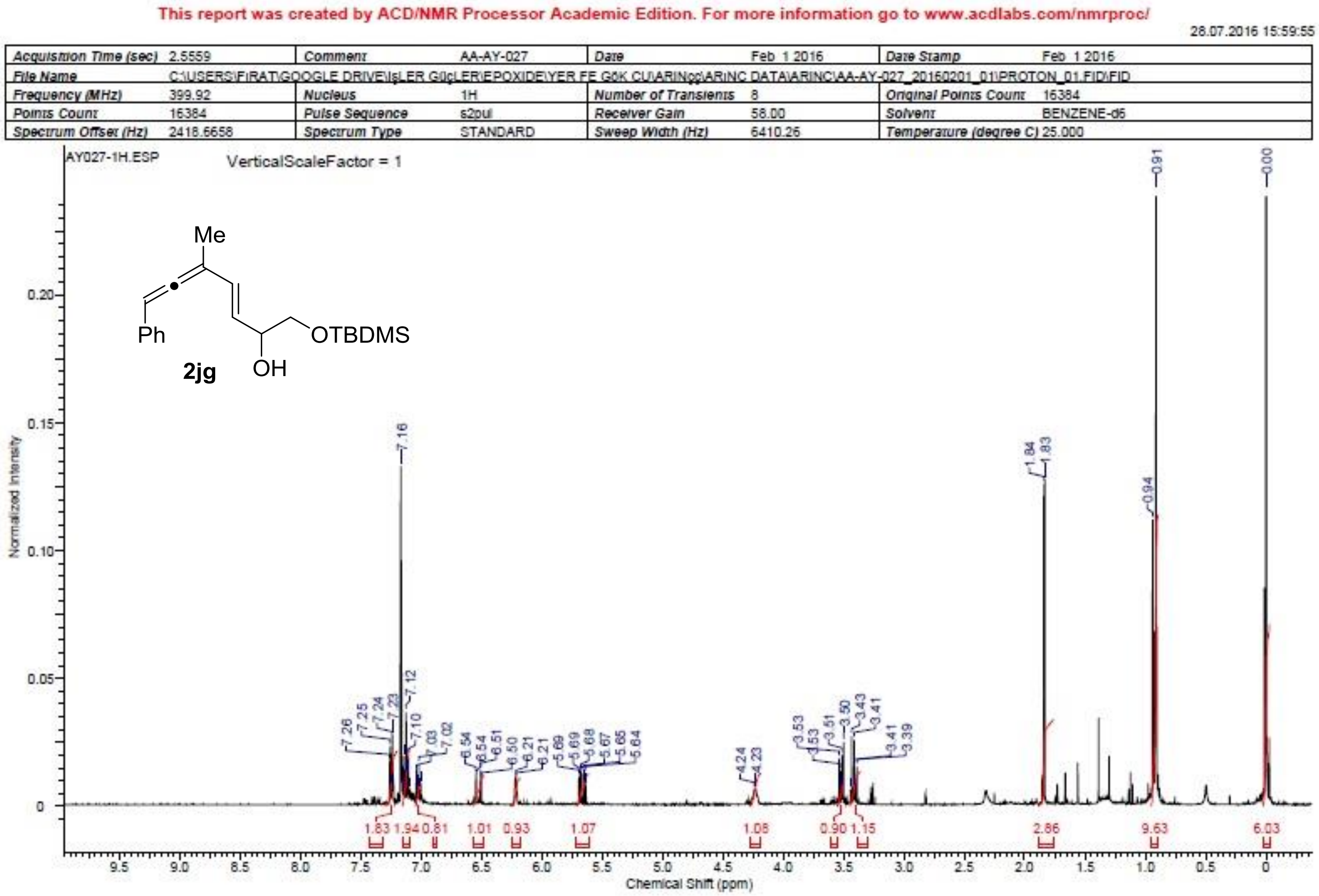


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

26.07.2016 22:50:21

Acquisition Time (sec)	1.3107	*Comment*	AA-AY-022-T	*Date*	Jan 8 2016	*Date Stamp*	Jan 8 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-022-T_20160108_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*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000





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

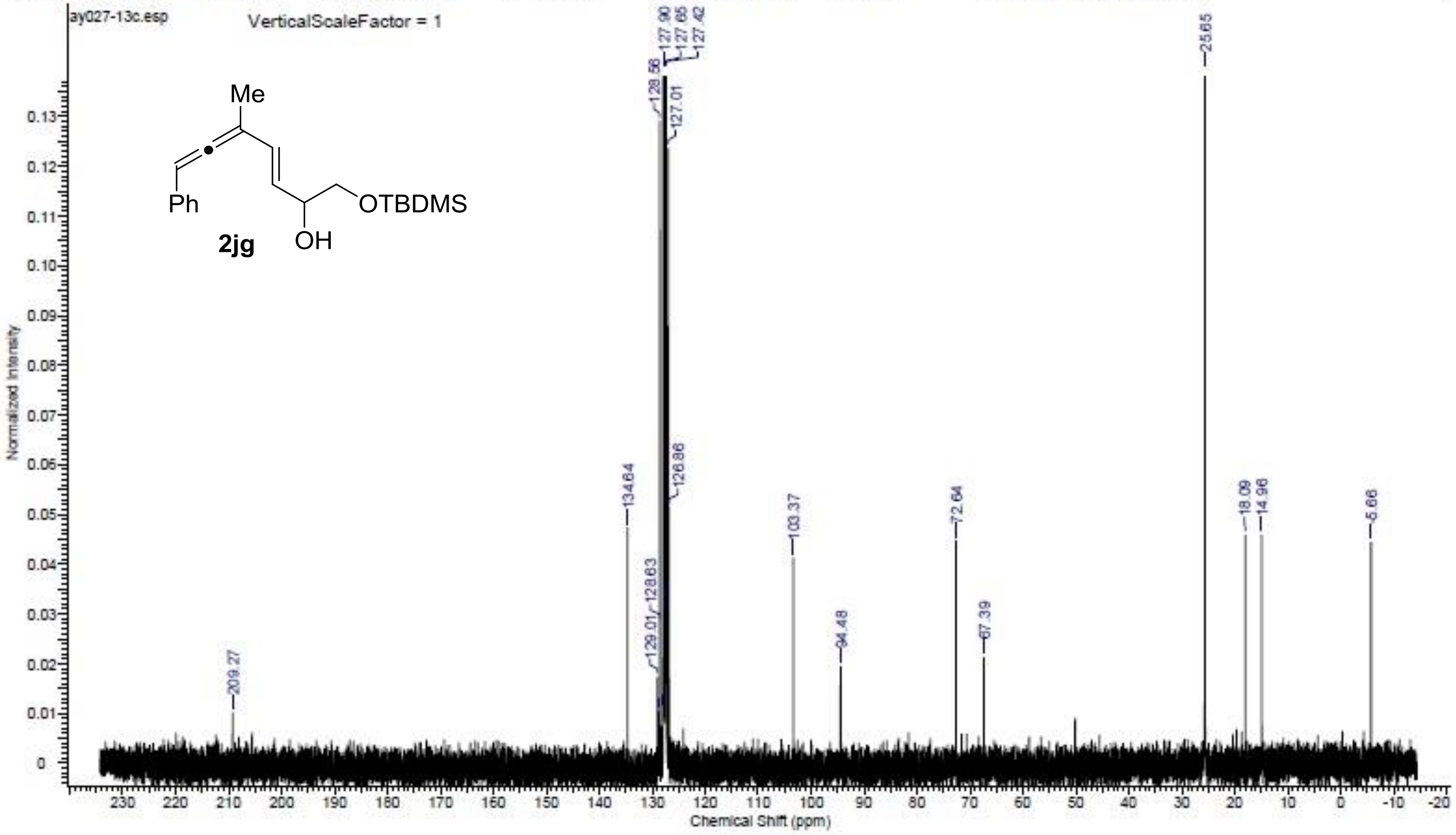
28.07.2016 15:59:55

Acquisition Time (sec)	2.5559	Comment	AA-AY-027	Date	Feb 1 2016	Date Stamp	Feb 1 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-027_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	58.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	2418.6658	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/

26.07.2016 23:02:43

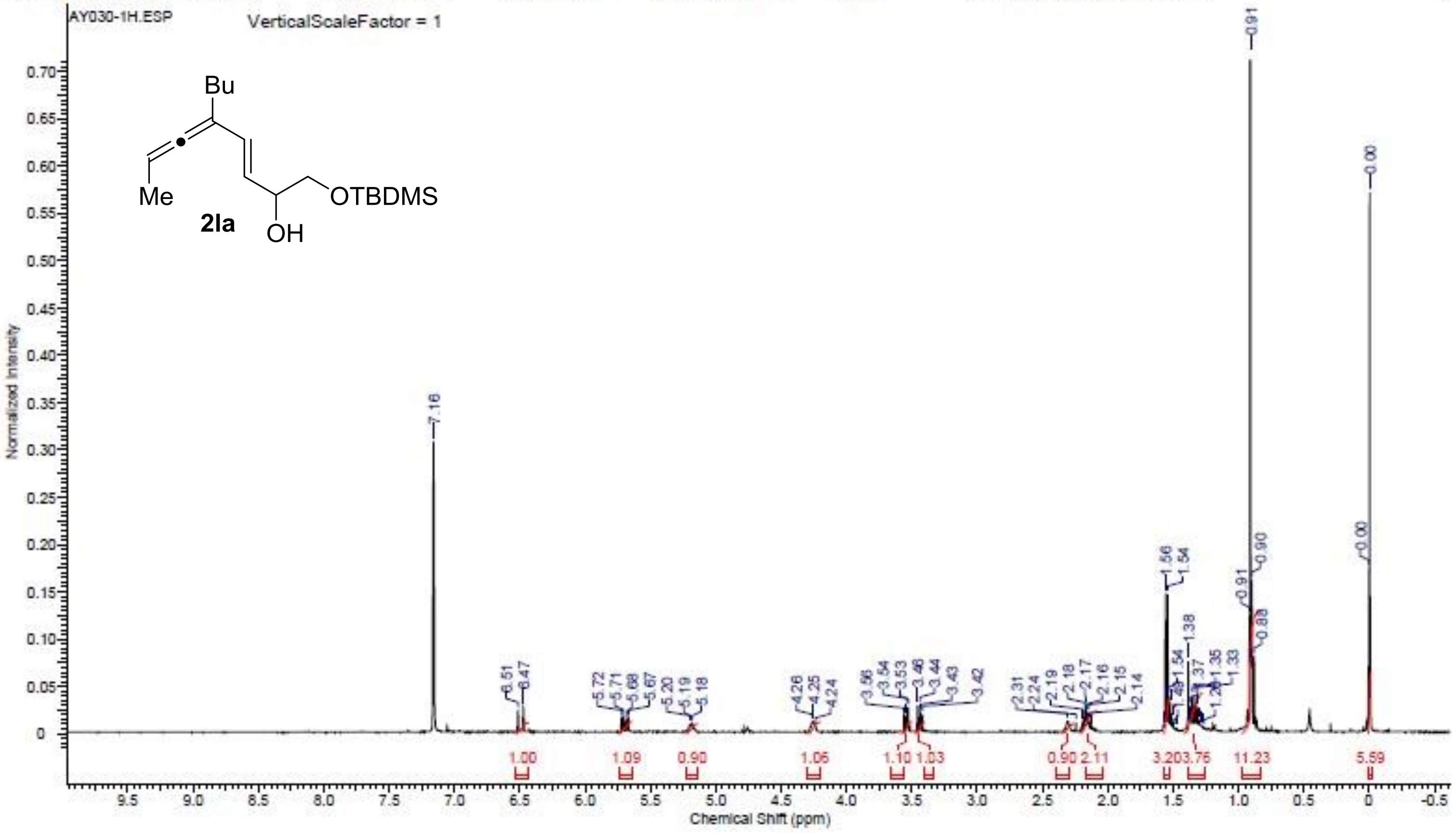
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-027C	*Date*	Feb 2 2016	*Date Stamp*	Feb 2 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-027C_20160202_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

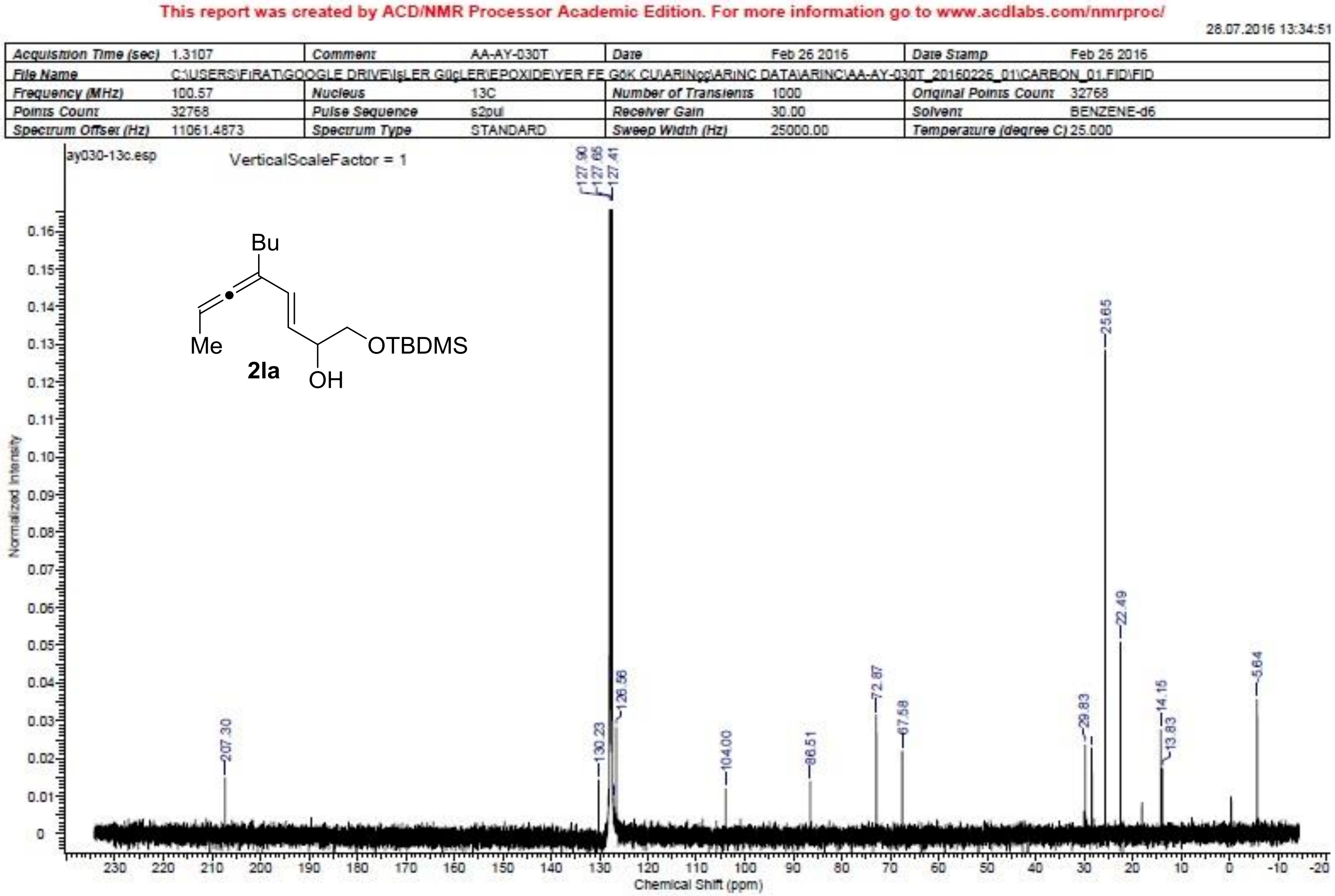


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

28.07.2016 16:02:35

Acquisition Time (sec)	2.5559	*Comment*	AA-AY-030T	*Date*	Feb 26 2016	*Date Stamp*	Feb 26 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FF G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-030T_20160225_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*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*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/

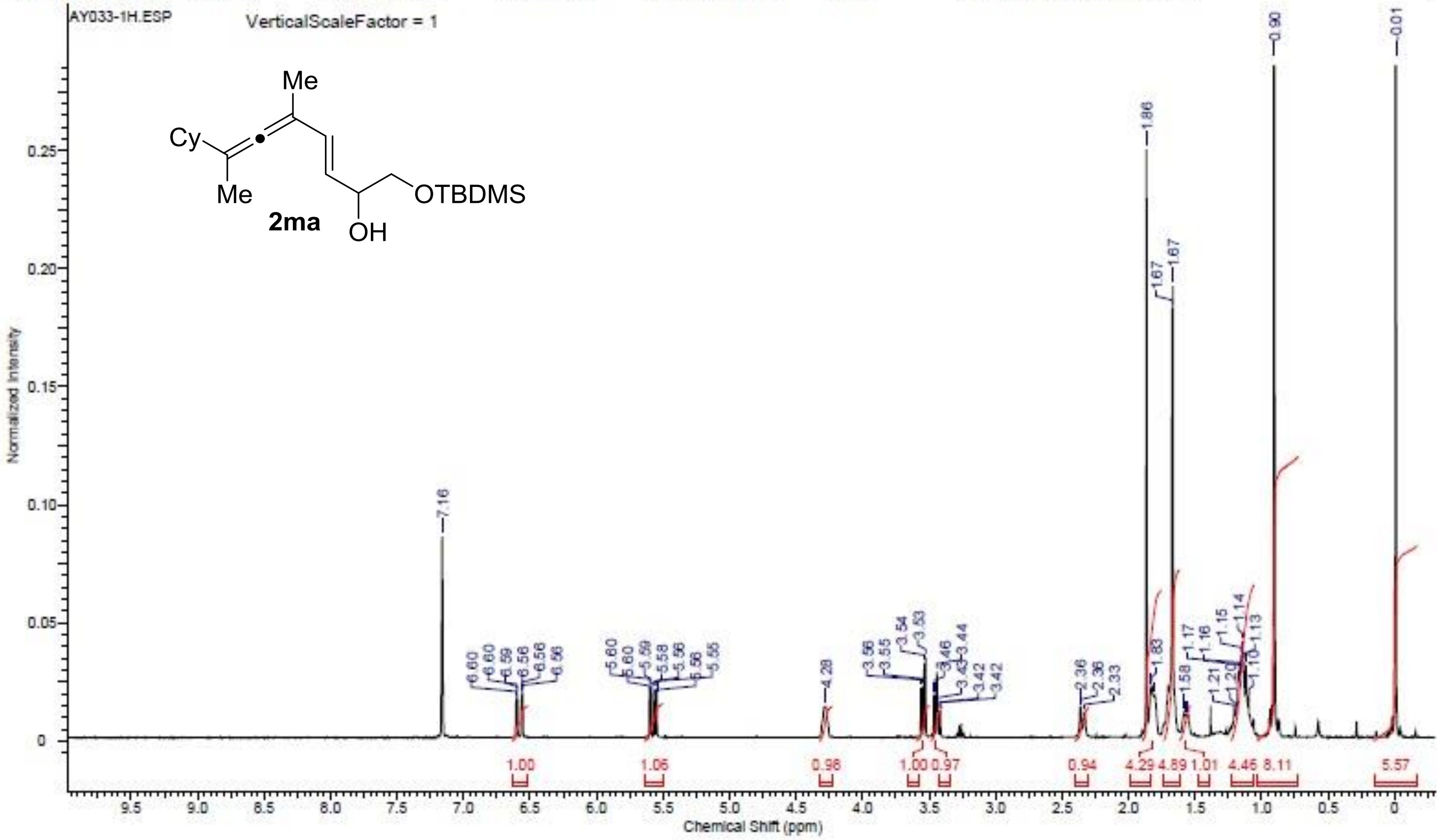
28.07.2016 13:34:51

Acquisition Time (sec)	1.3107	*Comment*	AA-AY-030T	*Date*	Feb 26 2016	*Date Stamp*	Feb 26 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\ARINC\AA-AY-030T_20160225_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	1000	*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

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

28.07.2016 15:55:49

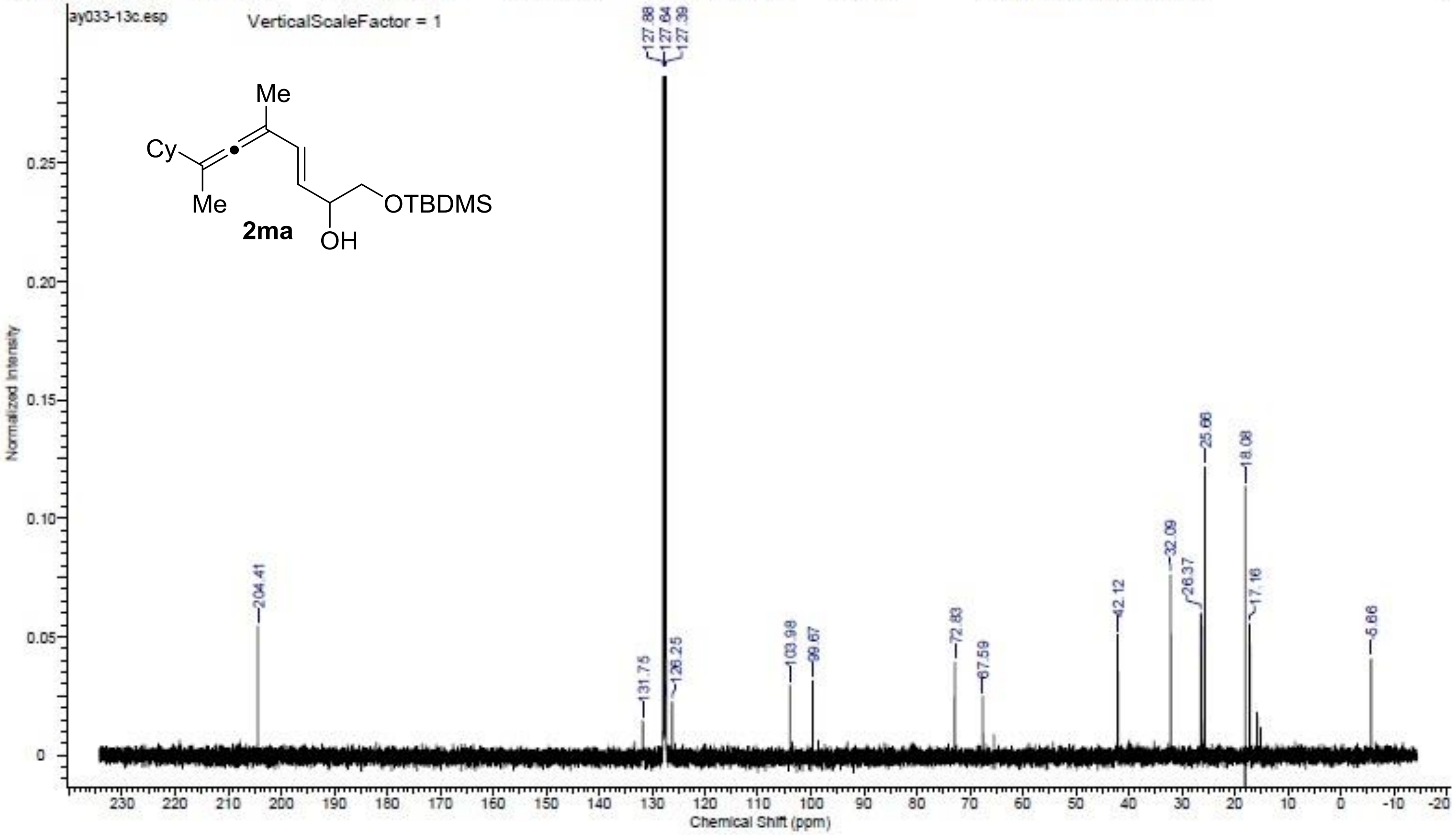
Acquisition Time (sec)	2.5559	*Comment*	AA-AY-033T	*Date*	Mar 31 2016	*Date Stamp*	Mar 31 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-033T_20160331_01\PROTON_02.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	54.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*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/

26.07.2016 23:39:28

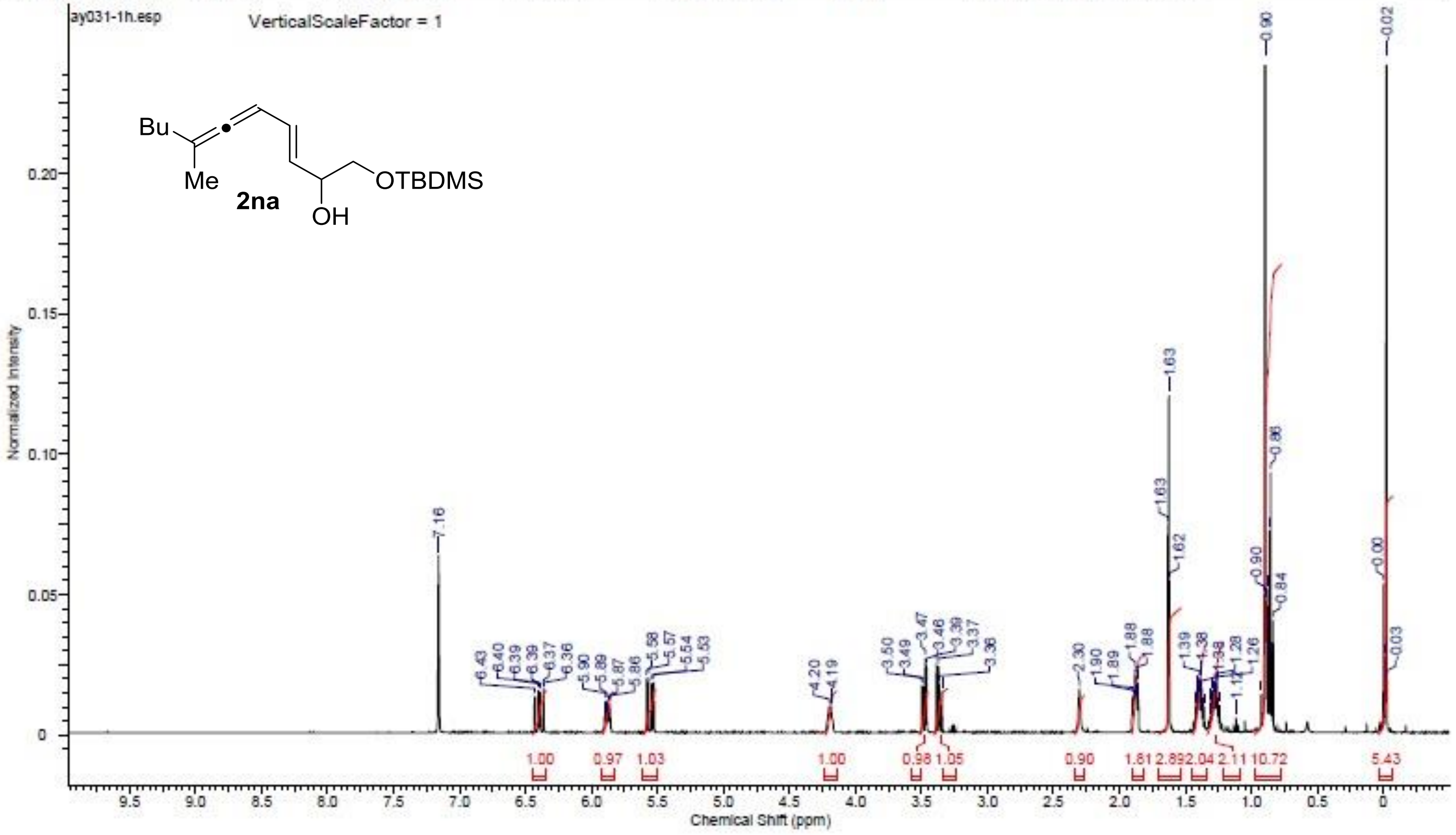
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-033C	*Date*	Apr 22 2016	*Date Stamp*	Apr 22 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-033C_20160422_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

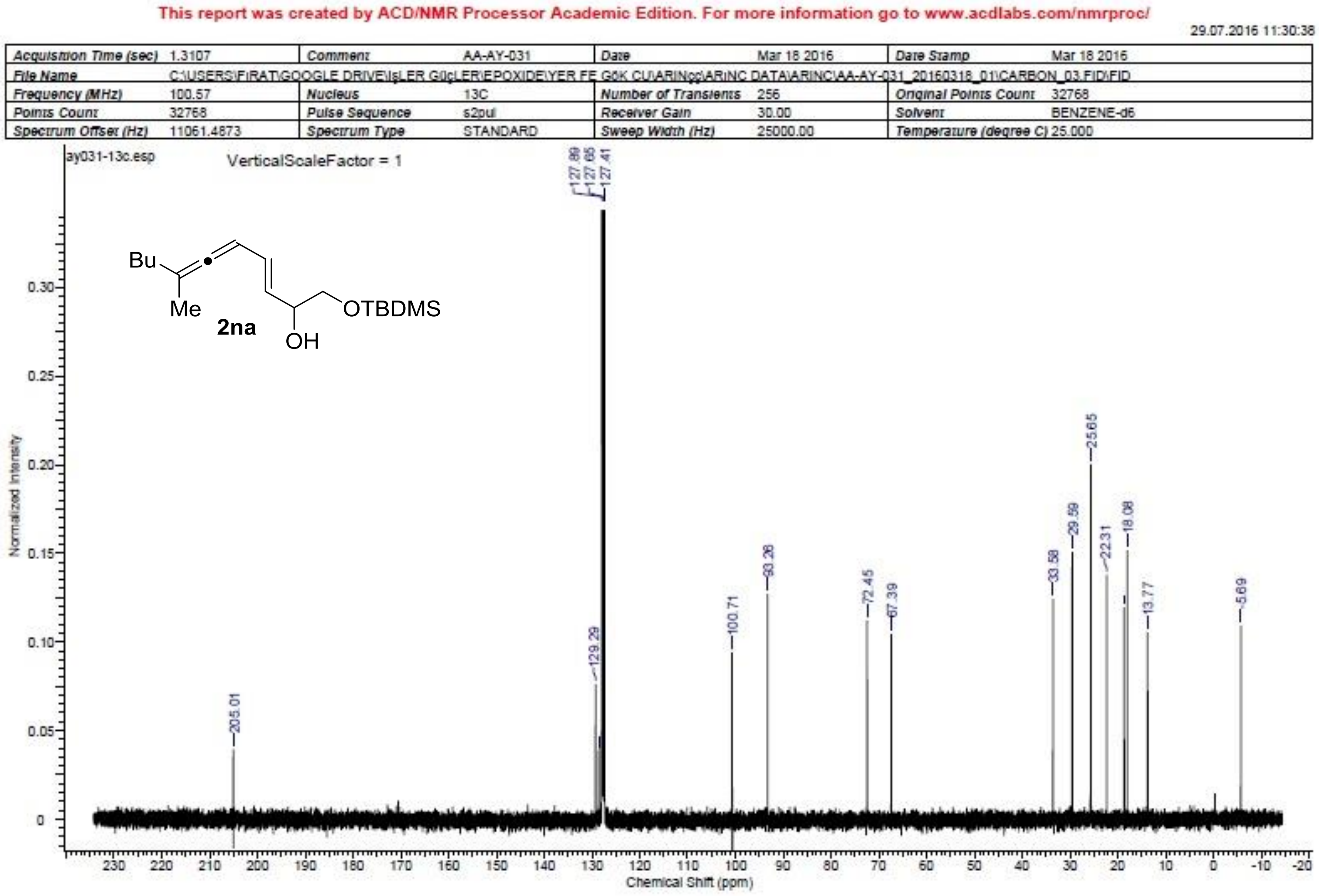


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

29.07.2016 11:27:19

Acquisition Time (sec)	2.5559	*Comment*	AA-AY-031	*Date*	Mar 18 2016	*Date Stamp*	Mar 18 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-031_20160318_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*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*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/

29.07.2016 11:30:36

Acquisition Time (sec)	1.3107	*Comment*	AA-AY-031	*Date*	Mar 18 2016	*Date Stamp*	Mar 18 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-031_20160318_01\CARBON_03.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

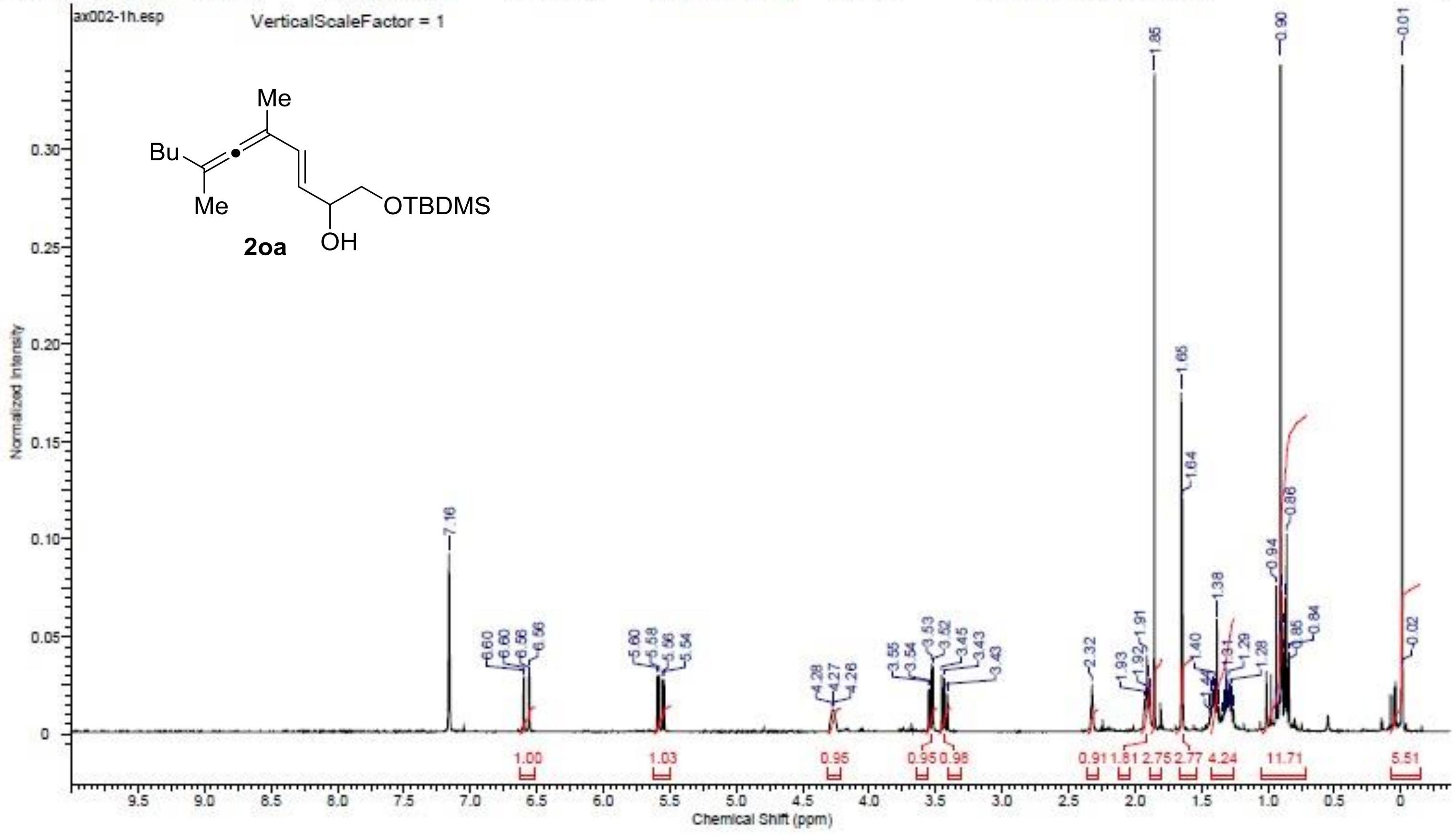
ay031-13c.esp

VerticalScaleFactor = 1

2na

28.07.2016 16:21:40

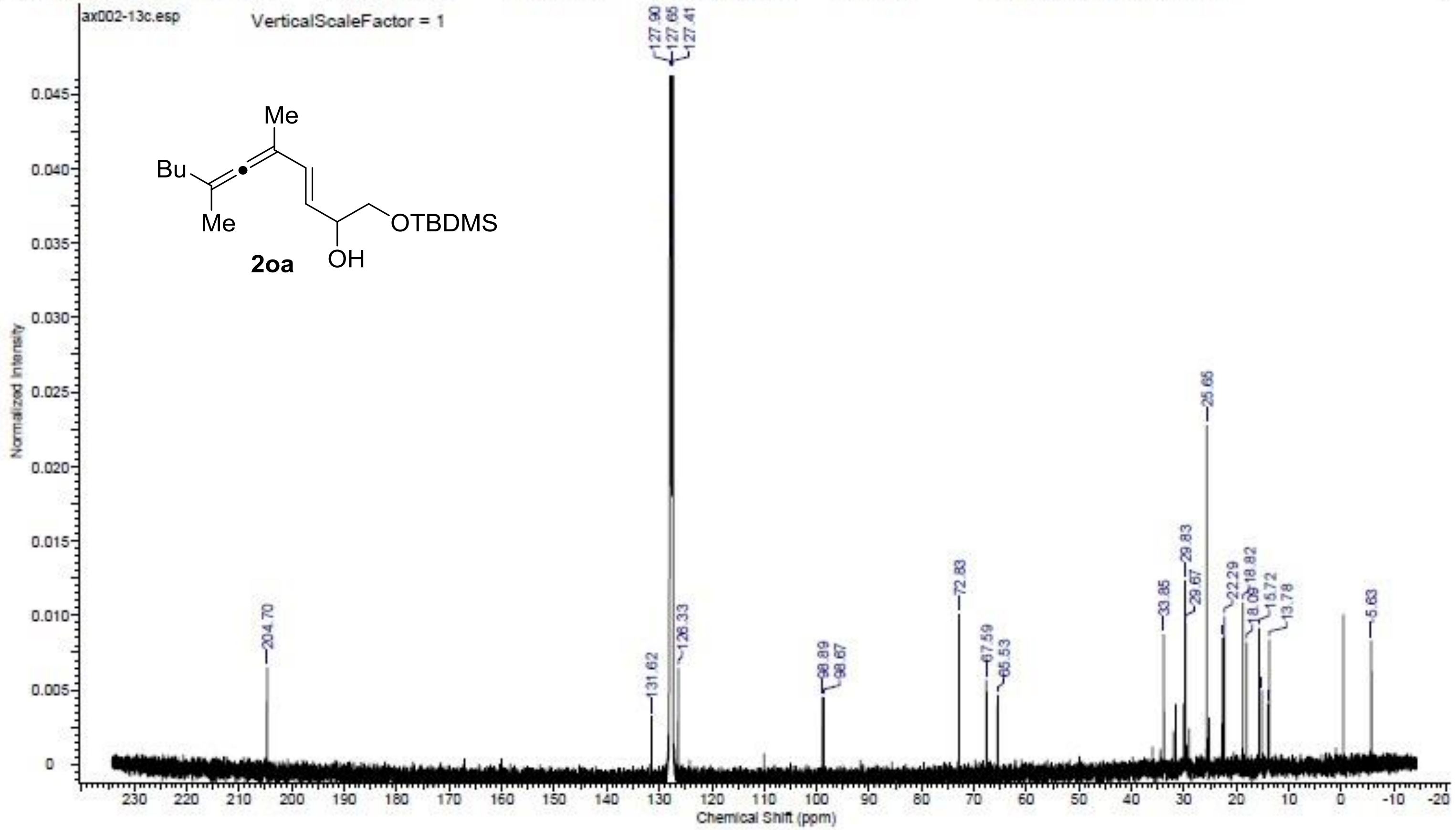
Acquisition Time (sec)	2.5559	*Comment*	AA-AAX-002T2	*Date*	Oct 27 2015	*Date Stamp*	Oct 27 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AAX-002T2_20151027_02\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	52.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*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/

28.07.2016 16:28:26

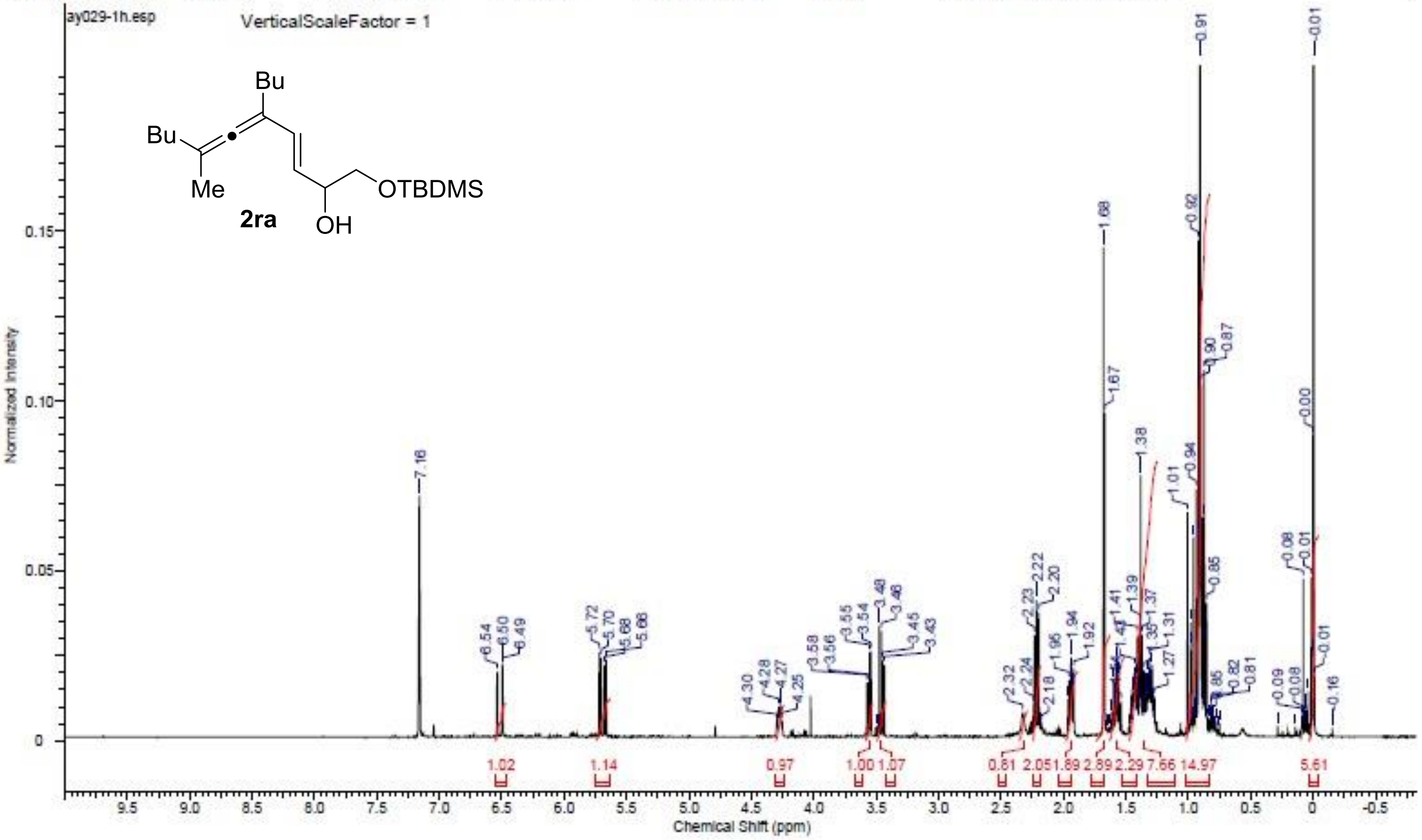
Acquisition Time (sec)	1.3107	*Comment*	AA-AX-002Y	*Date*	Feb 22 2016	*Date Stamp*	Feb 22 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AX-002Y_20160222_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	20000	*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

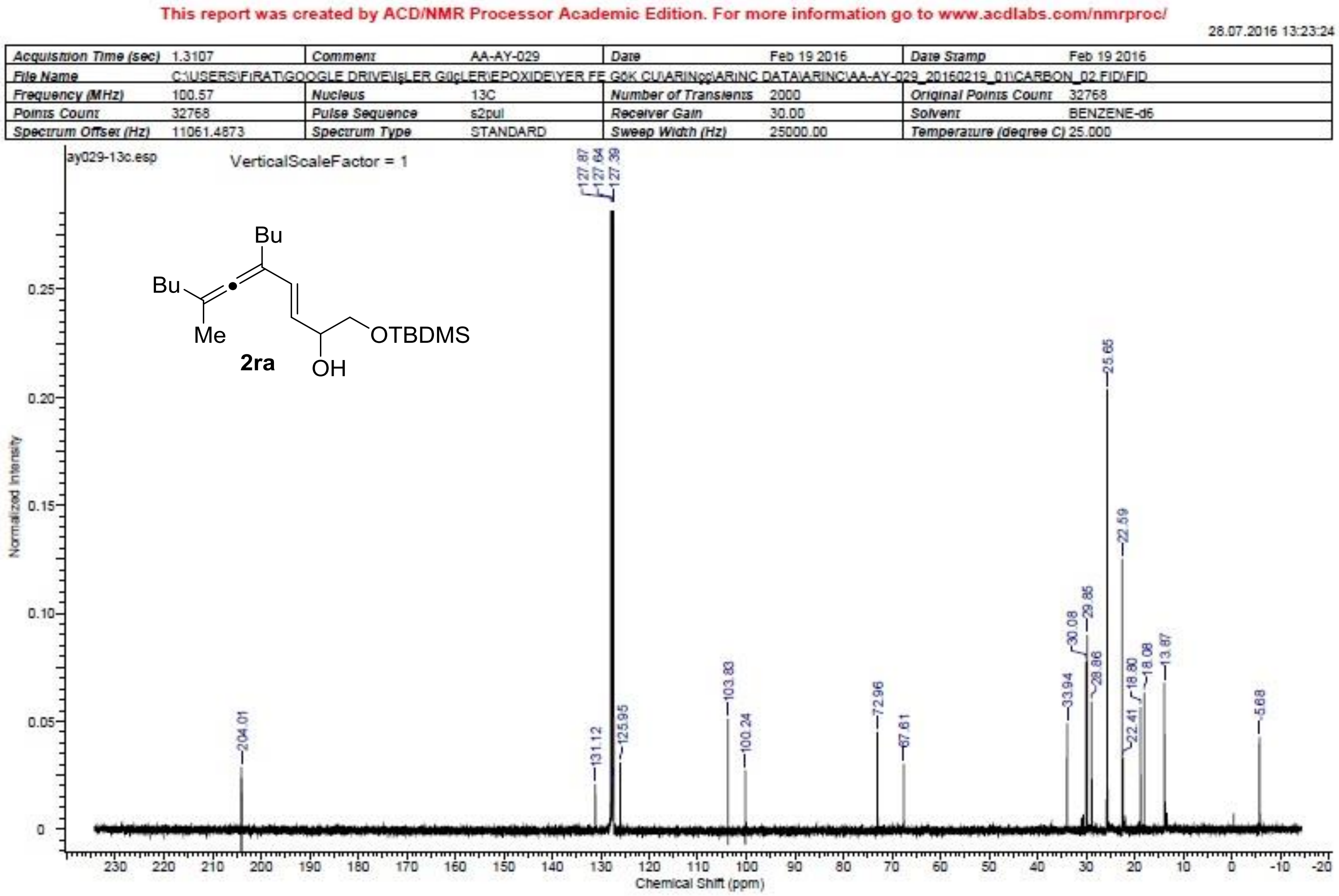


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

28.07.2016 13:21:15

Acquisition Time (sec)	2.5559	*Comment*	AA-AY-029	*Date*	Feb 19 2016	*Date Stamp*	Feb 19 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-029_20160219_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)	2416.7764	*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/

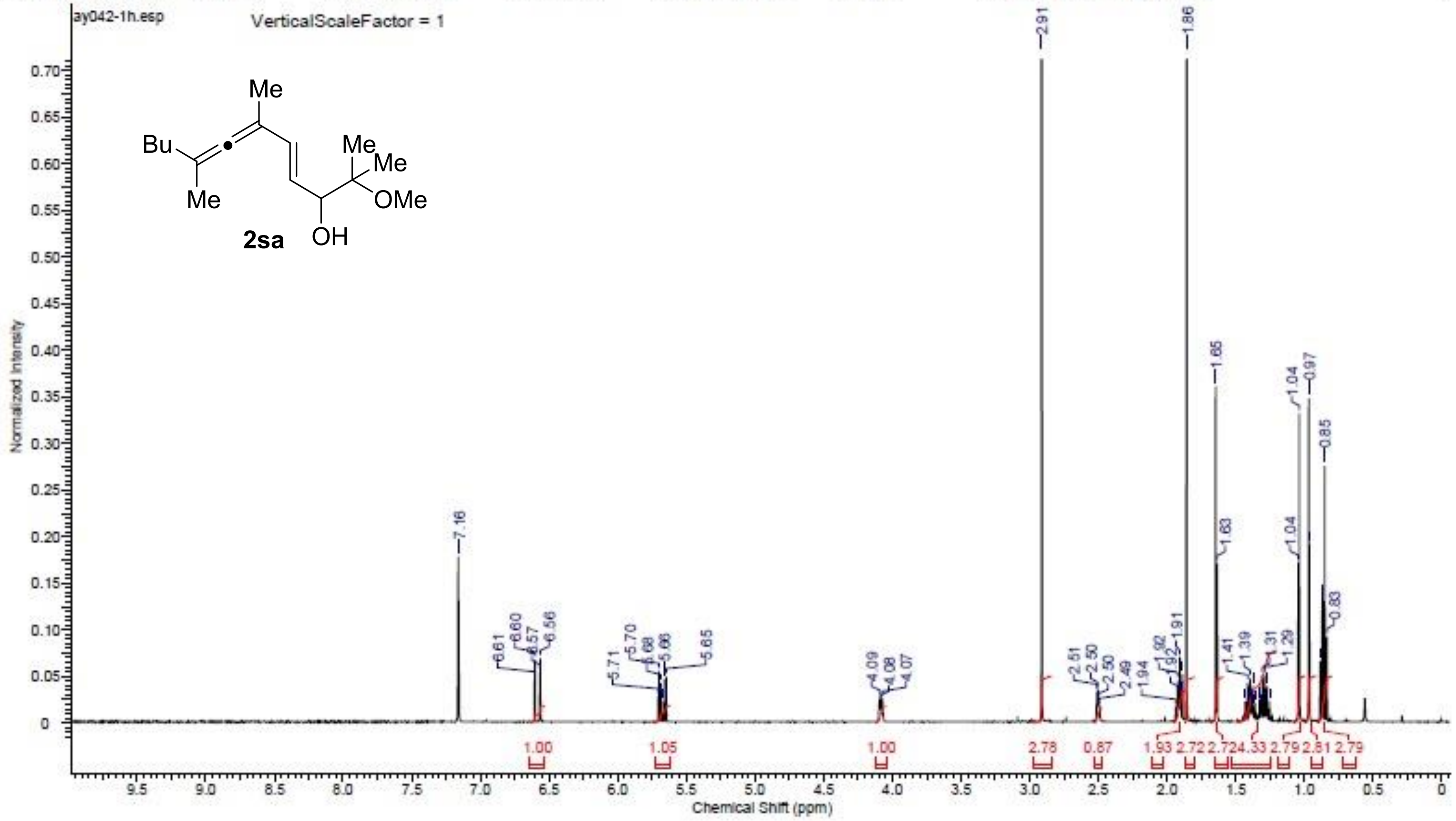
28.07.2016 13:23:24

Acquisition Time (sec)	1.3107	*Comment*	AA-AY-029	*Date*	Feb 19 2016	*Date Stamp*	Feb 19 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\ARINC\AA-AY-029_20160219_01\CARBON_02.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

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

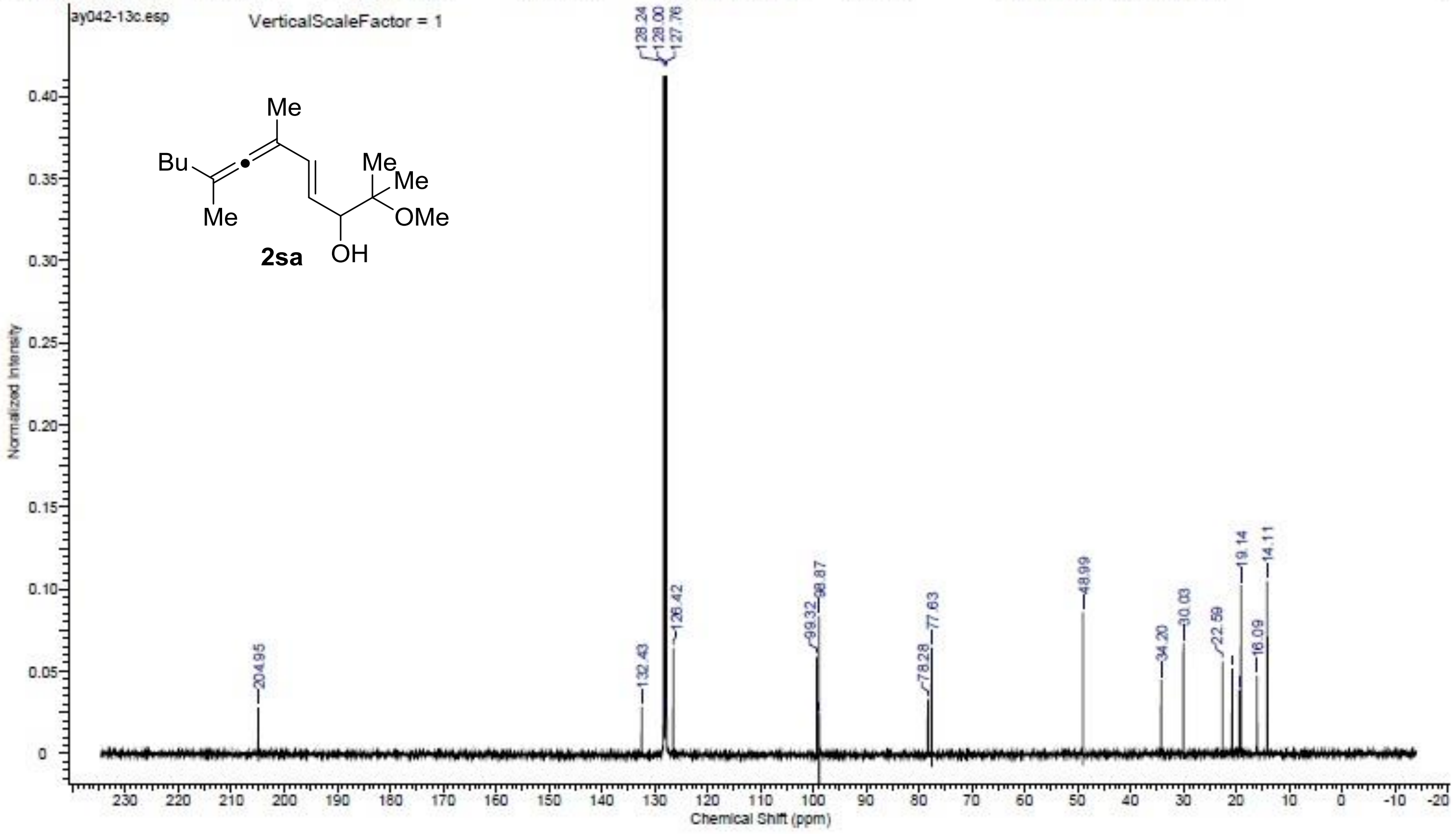
28.07.2016 13:47:42

Acquisition Time (sec)	2.5559	Comment	AA-AY-042TKR	Date	Jun 15 2016	Date Stamp	Jun 15 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-042TKR_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	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



28.07.2016 13:50:03

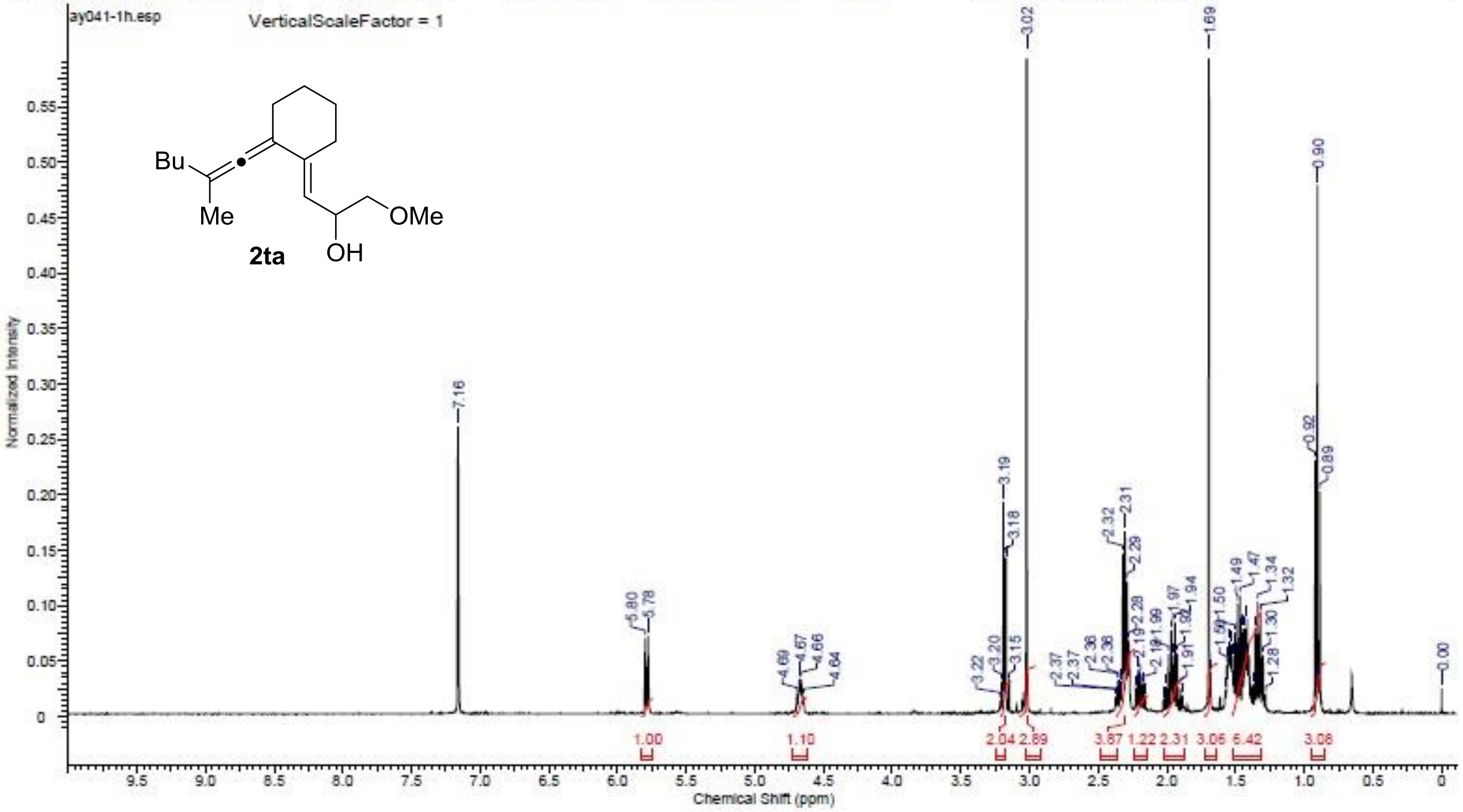
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-042TKR	*Date*	Jun 15 2016	*Date Stamp*	Jun 15 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE GöK CU\ARINçç\ARINC DATA\ARINC\AA-AY-042TKR_20160615_01\CARBON_03.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	5000	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11097.1699	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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

28.07.2016 13:39:42

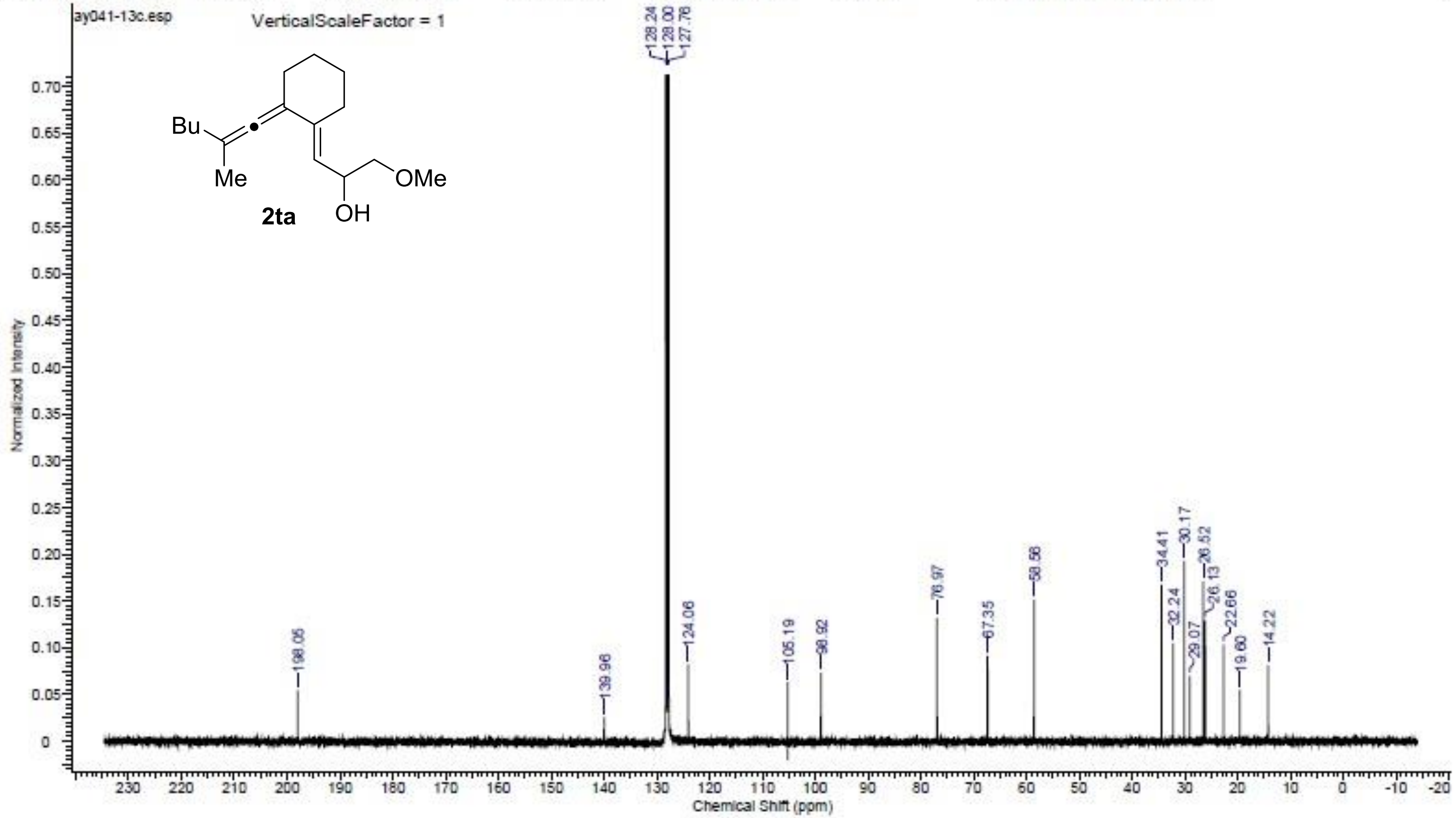
Acquisition Time (sec)	2.5559	*Comment*	AA-AY-041-T	*Date*	Jun 6 2016	*Date Stamp*	Jun 6 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-041-T_20160606_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	58.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*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/

28.07.2016 13:41:41

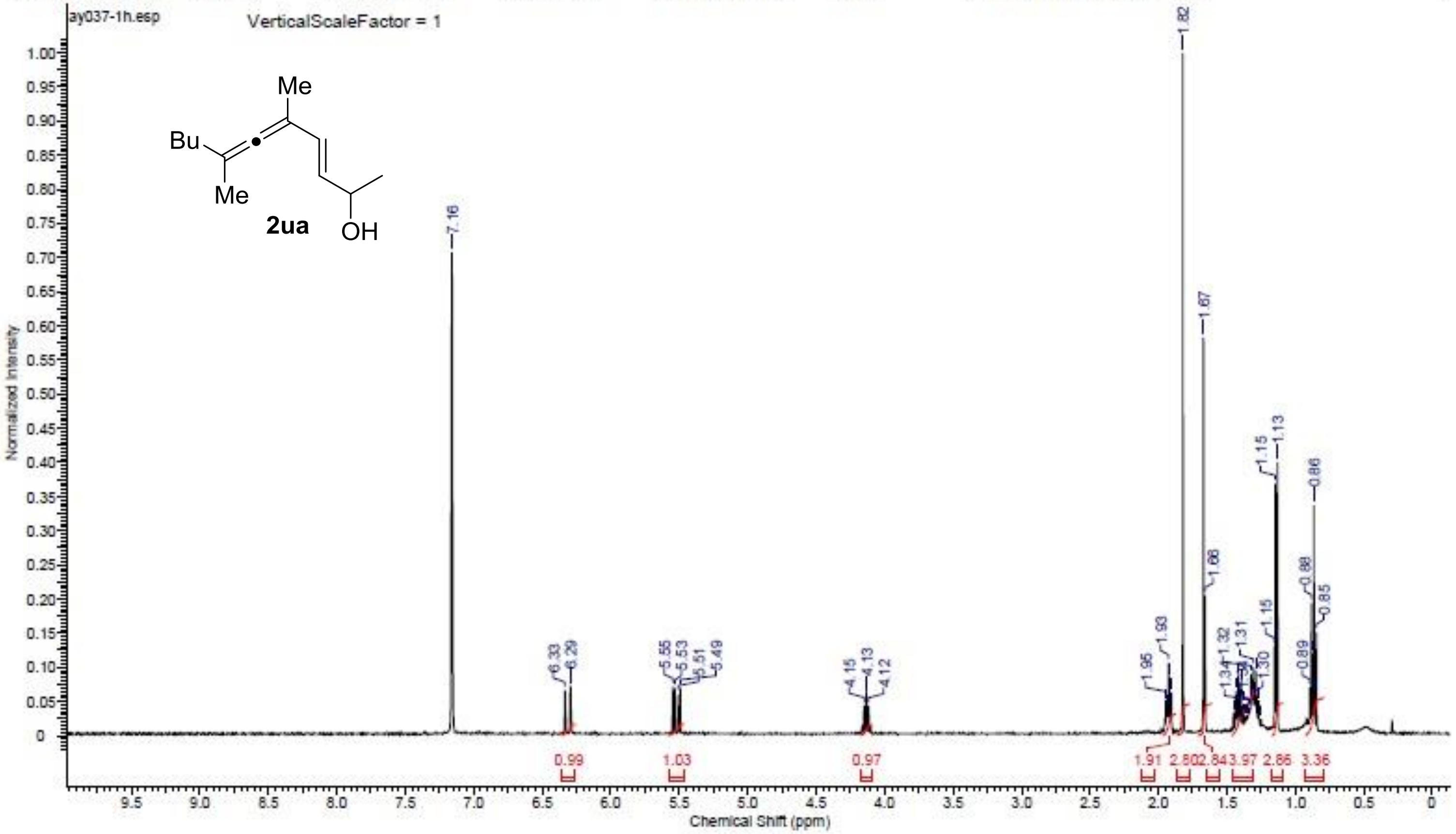
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-041-T	*Date*	Jun 6 2016	*Date Stamp*	Jun 6 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-041-T_20160606_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11097.1709	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000



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

28.07.2016 15:01:55

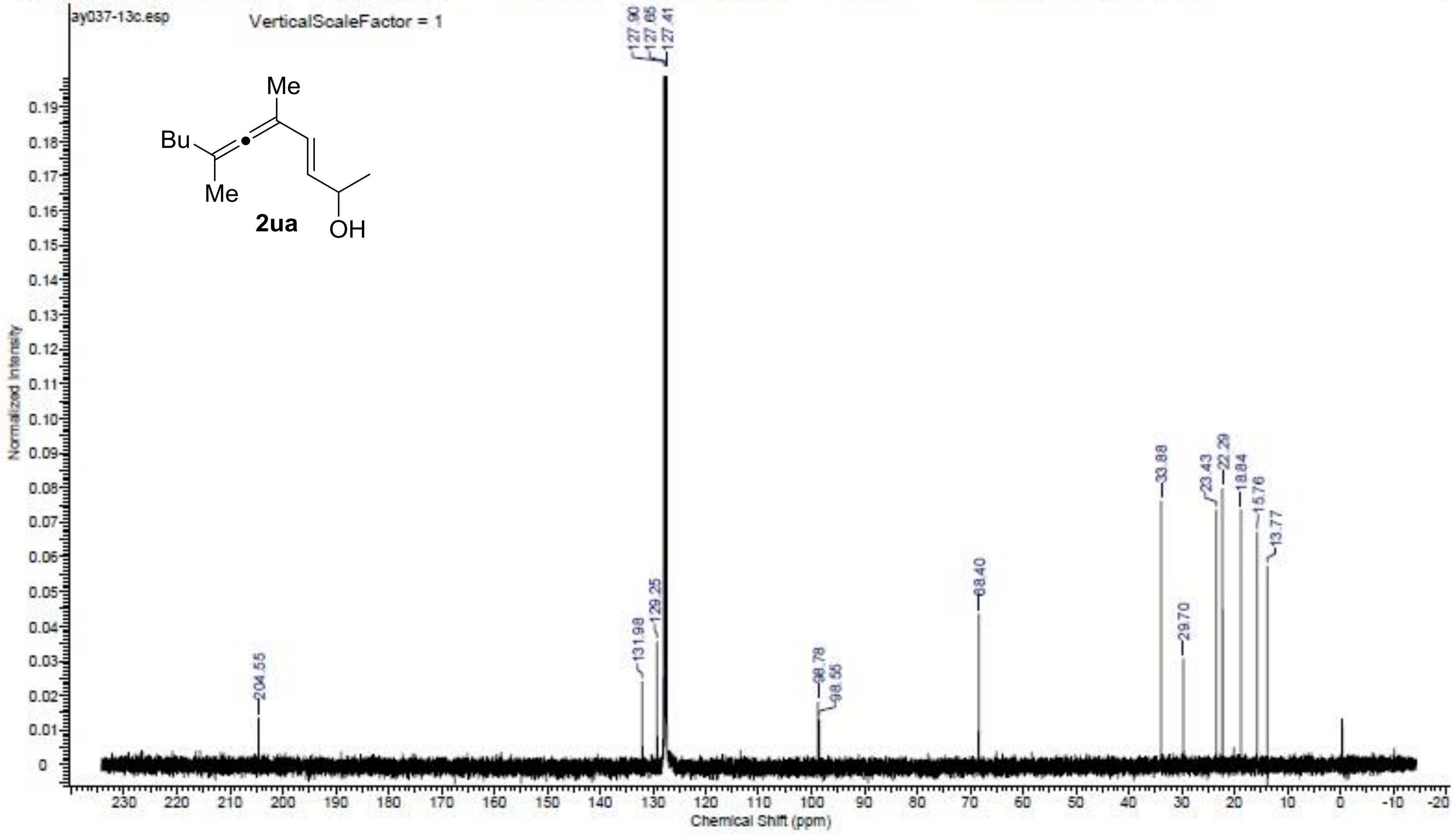
Acquisition Time (sec)	2.5559	*Comment*	AA-AY-037T	*Date*	Jun 14 2016	*Date Stamp*	Jun 14 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-037T_20160614_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	*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/

28.07.2016 15:04:10

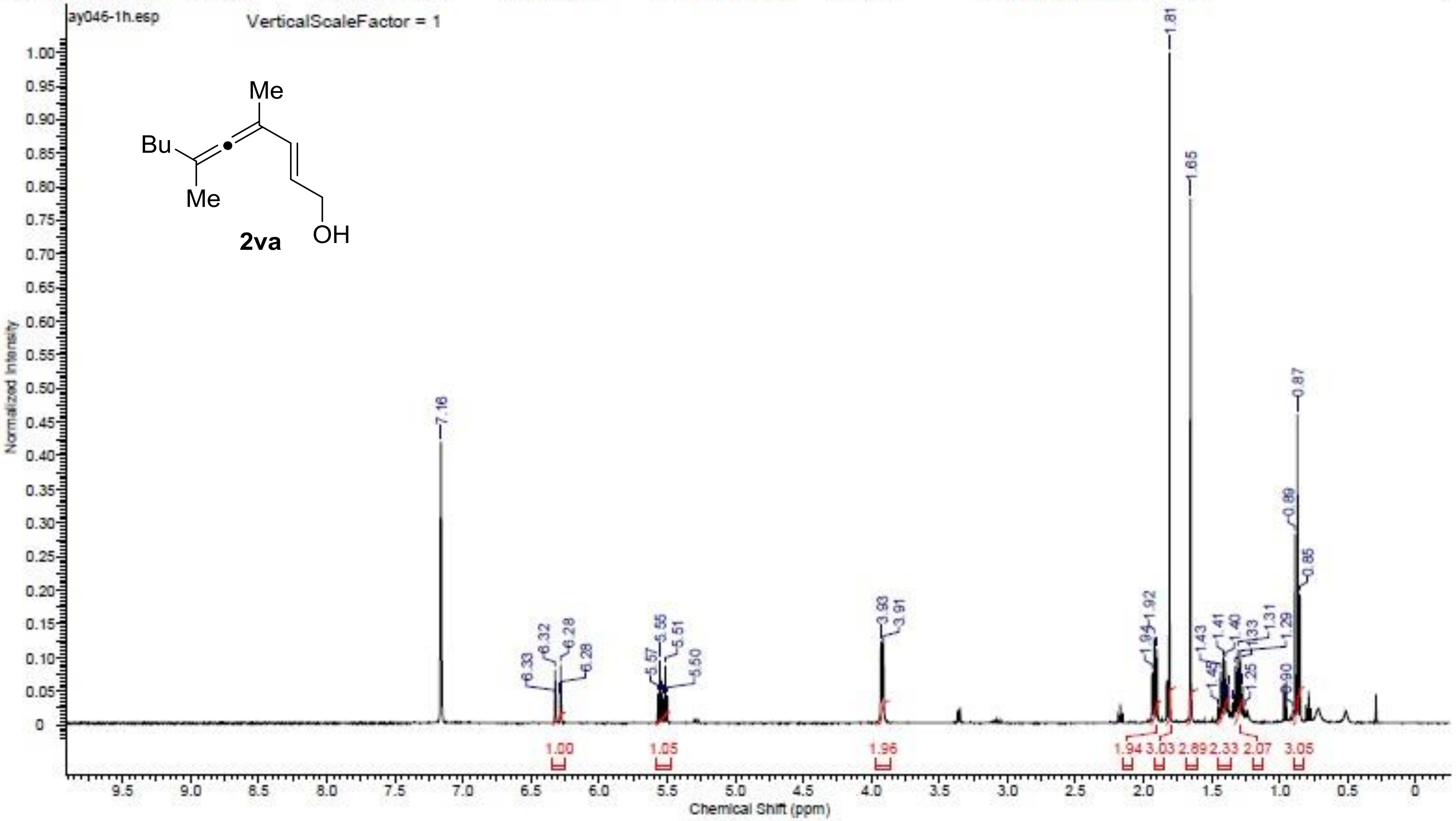
Acquisition Time (sec)	1.3107	*Comment*	AA-AY-034-2	*Date*	Apr 12 2016	*Date Stamp*	Apr 12 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G0K CU\ARINçç\ARINC DATA\ARINC\AA-AY-034-2_20160411_01\CARBON_03.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	1000	*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



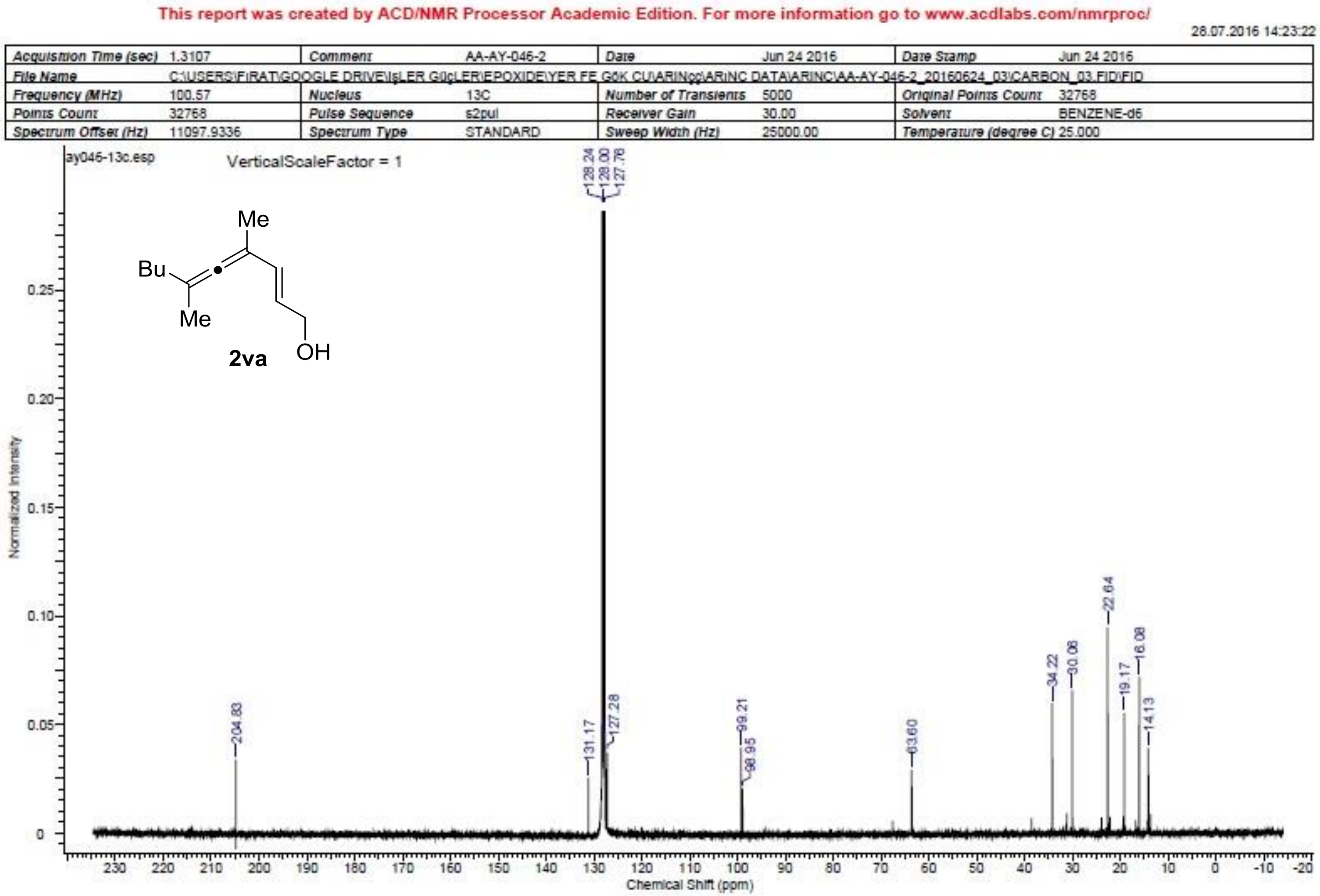
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

28.07.2016 14:20:36

Acquisition Time (sec)	2.5559	*Comment*	AA-AY-046-2	*Date*	Jun 24 2016	*Date Stamp*	Jun 24 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-046-2_20160624_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*	BENZENE-d6
Spectrum Offset (Hz)	2417.5591	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



2va



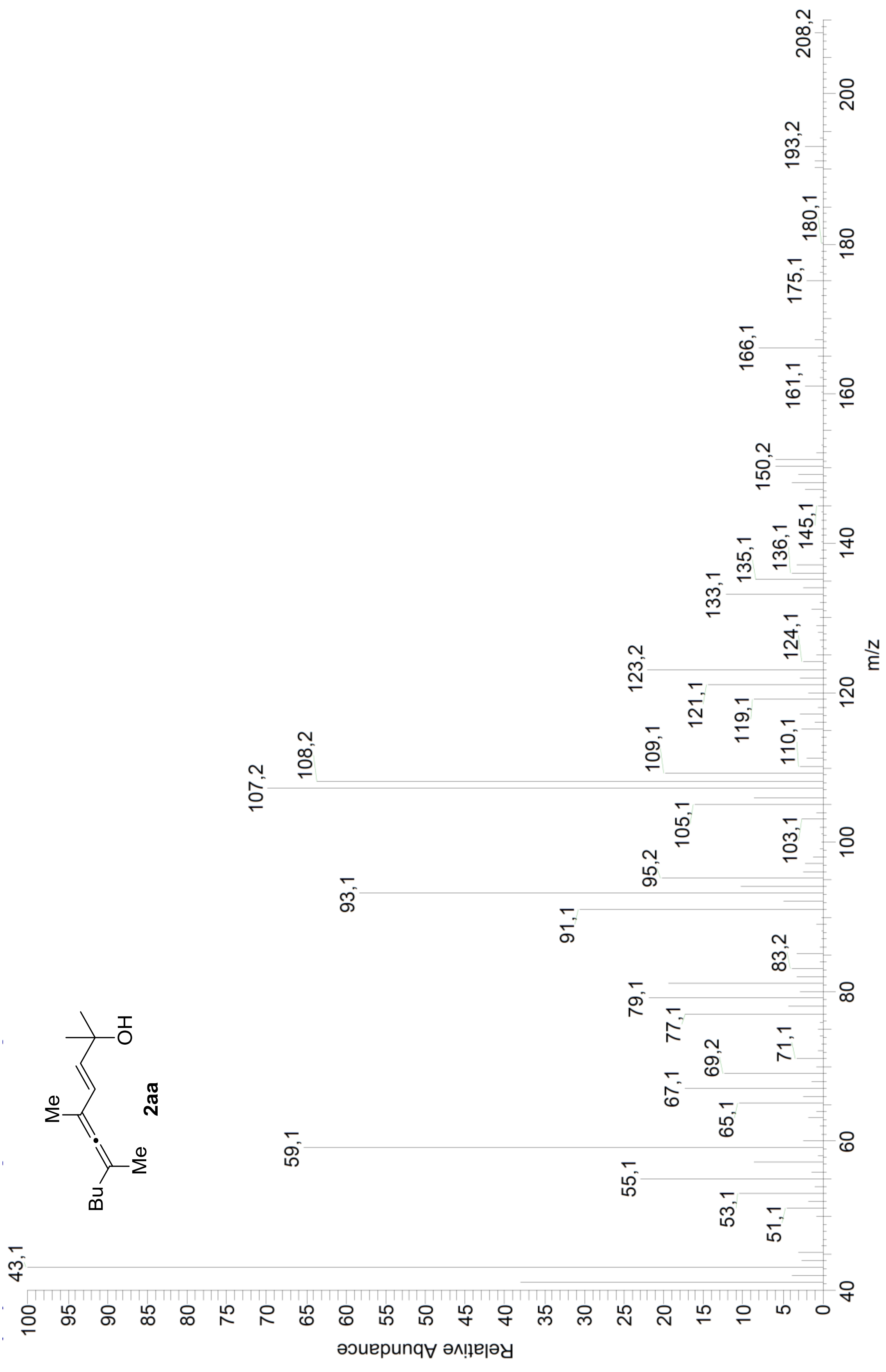
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

28.07.2016 14:23:22

Acquisition Time (sec)	1.3107	*Comment*	AA-AY-046-2	*Date*	Jun 24 2016	*Date Stamp*	Jun 24 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\YER FE G6K CU\ARINçç\ARINC DATA\ARINC\AA-AY-046-2_20160624_03\CARBON_03.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*	BENZENE-d6
Spectrum Offset (Hz)	11097.9336	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

APPENDIX C

MASS SPECTRUM OF PODUCTS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Me
Me
OH
2aa
Relative Abundance
m/z
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53,1
55,1
59,1
65,1
67,1
69,2
71,1
77,1
79,1
83,2
91,1
93,1
95,2
103,1
105,1
107,2
108,2
109,1
110,1
119,1
121,1
123,2
124,1
133,1
135,1
136,1
145,1
150,2
161,1
166,1
175,1
180,1
193,2
208,2
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
40
60
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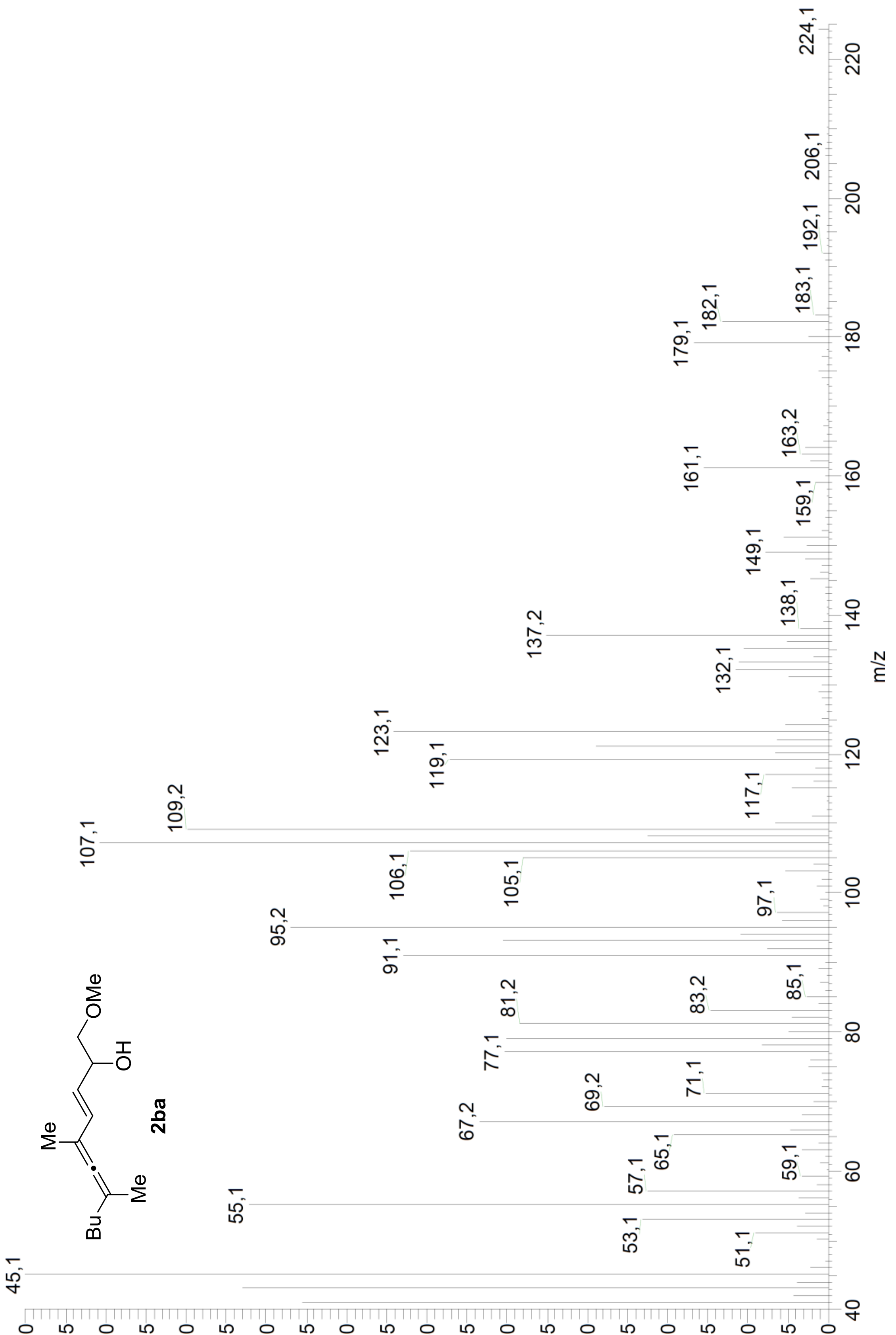
100
120
140
160
180
200


2ba
Bu
Me
Me
OH
OMe
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
40
60
80
100
120
140
160
180
200
220
45,1
51,1
53,1
55,1
57,1
59,1
65,1
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71,1
77,1
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83,2
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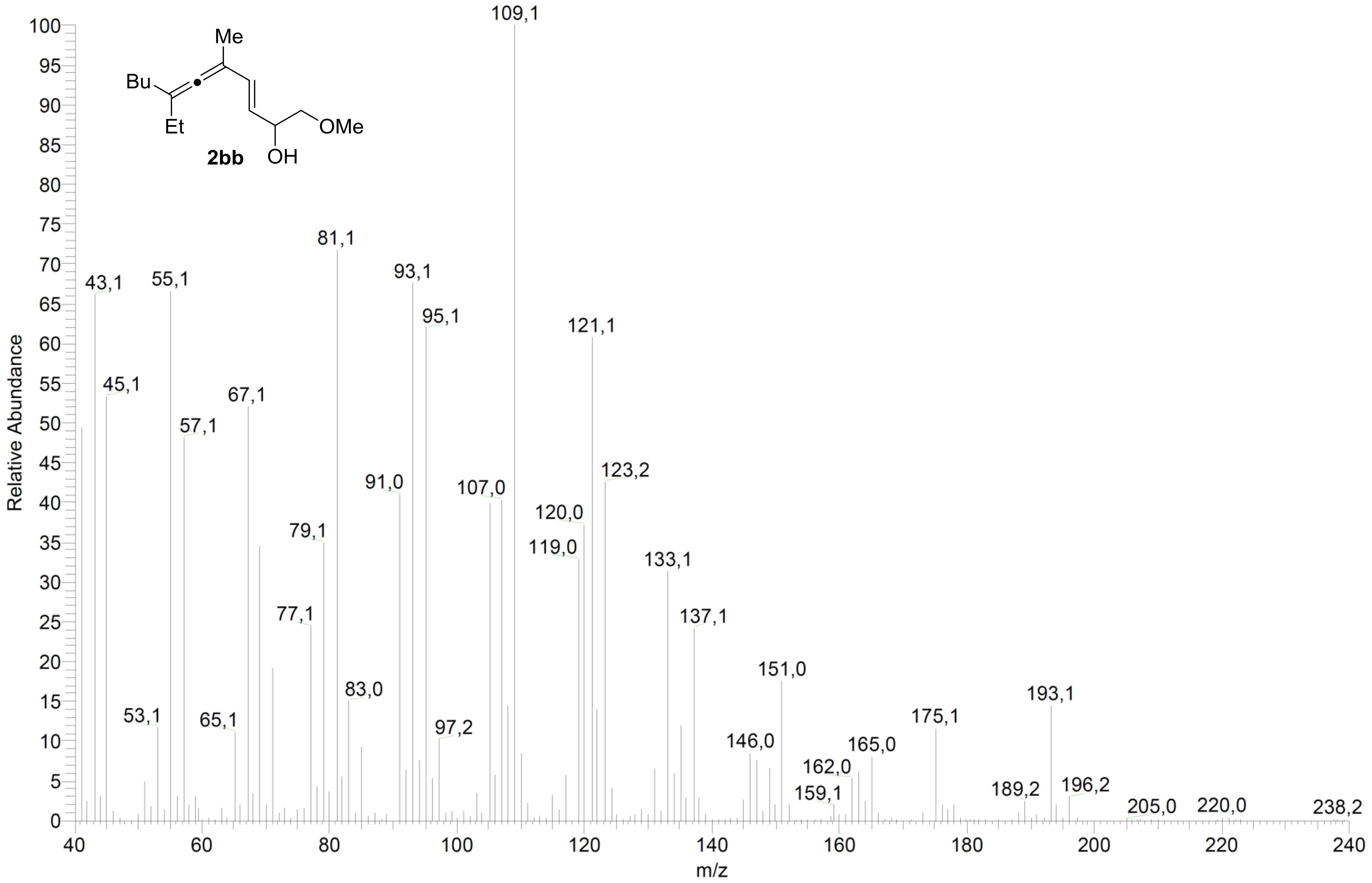
224,1


2bb

Bu
Me
Et
OMe
OH
Relative Abundance
m/z
100
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90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
40
60
80
100
120
140
160
180
200
220
240
109,1
81,1
93,1
43,1
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67,1
57,1
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137,1
151,0
83,0
193,1
175,1
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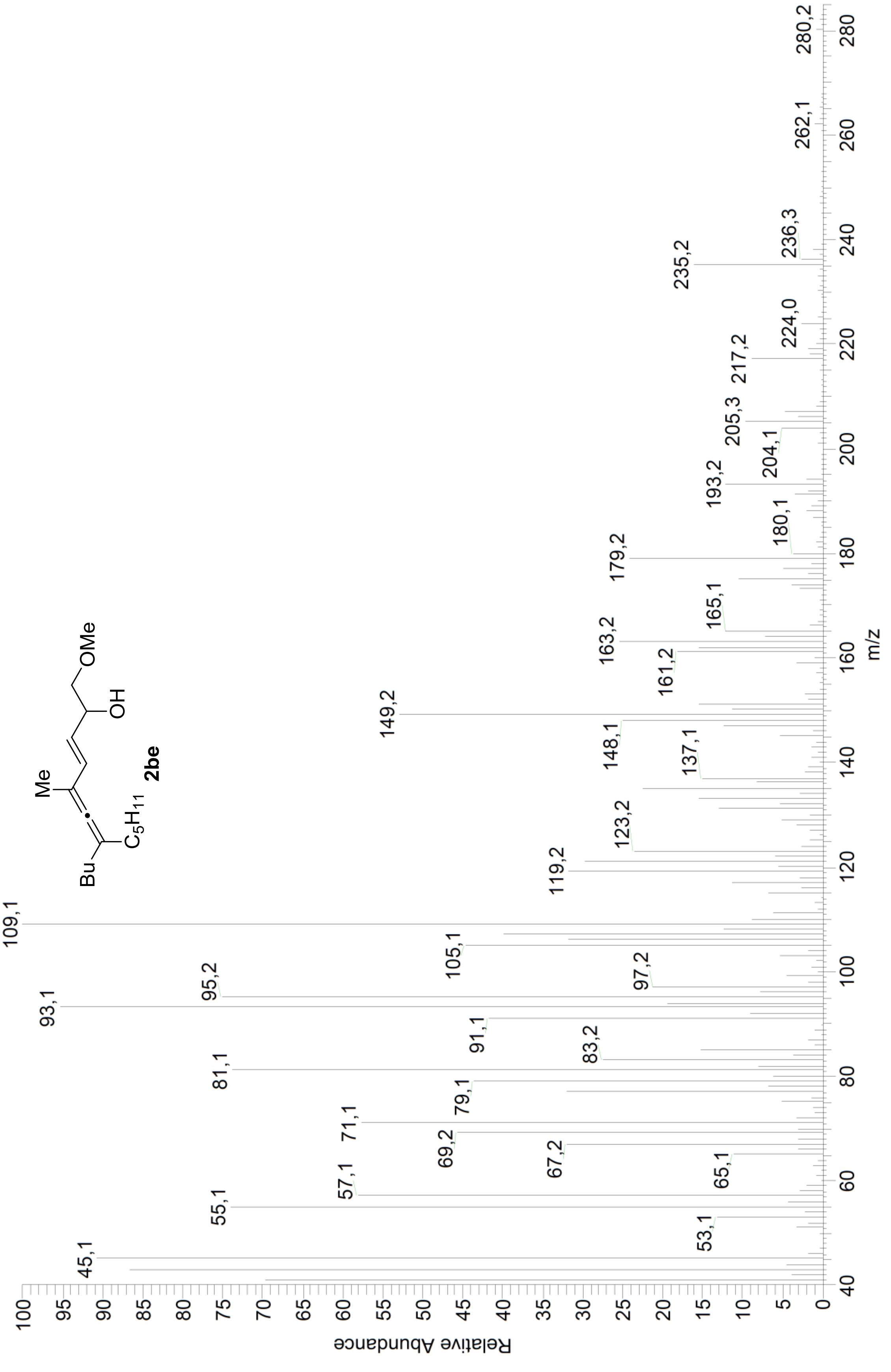
238,2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OMe
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83,2
91,1
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105,1
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179,2
180,1
193,2
204,1
205,3
217,2
224,0
235,2
236,3
262,1
280,2
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
m/z
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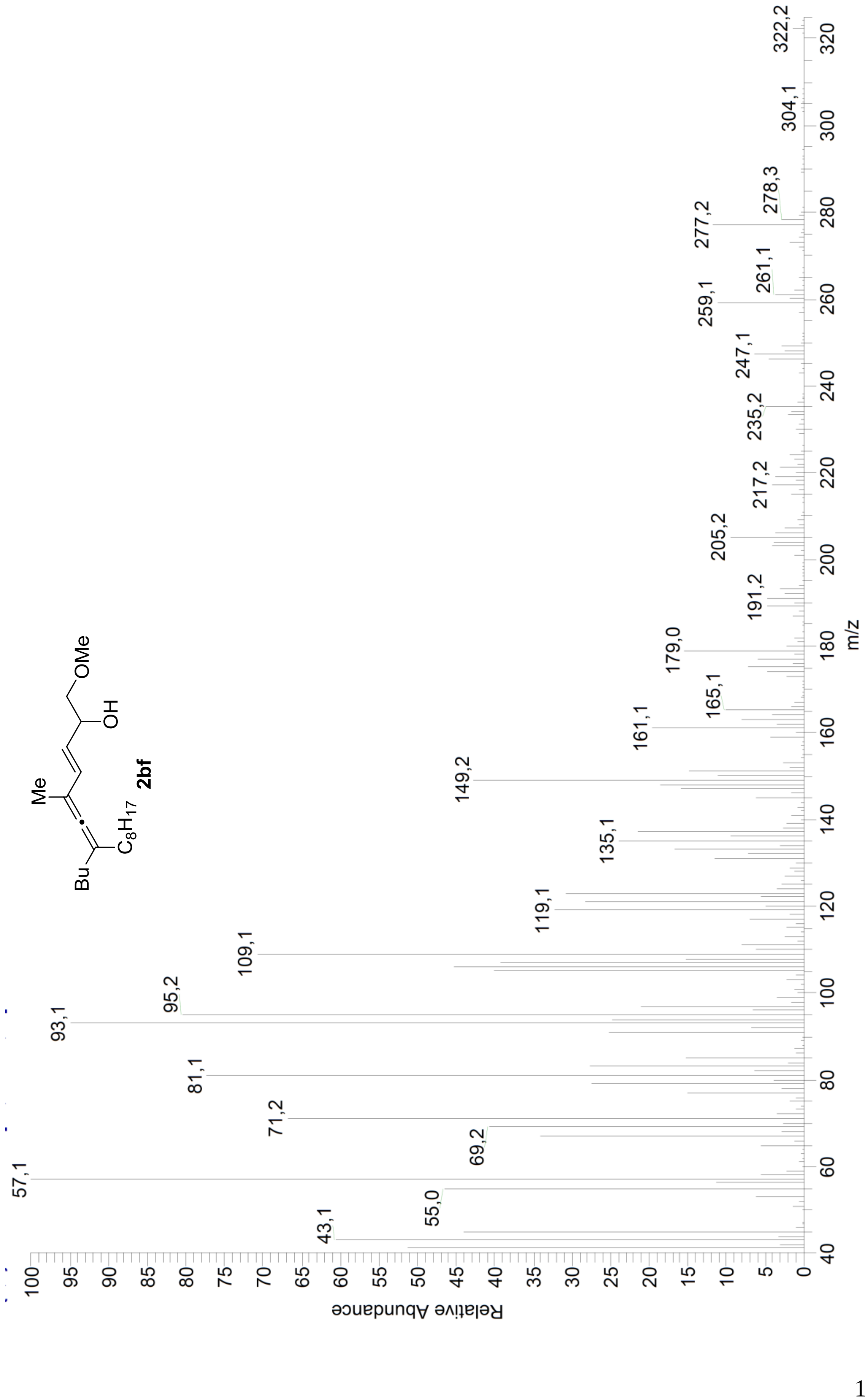
180
200
220
240
260
280


Relative Abundance
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95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
m/z
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
43,1
55,0
57,1
69,2
71,2
81,1
93,1
95,2
109,1
119,1
135,1
149,2
161,1
165,1
179,0
191,2
205,2
217,2
235,2
247,1
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277,2
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304,1
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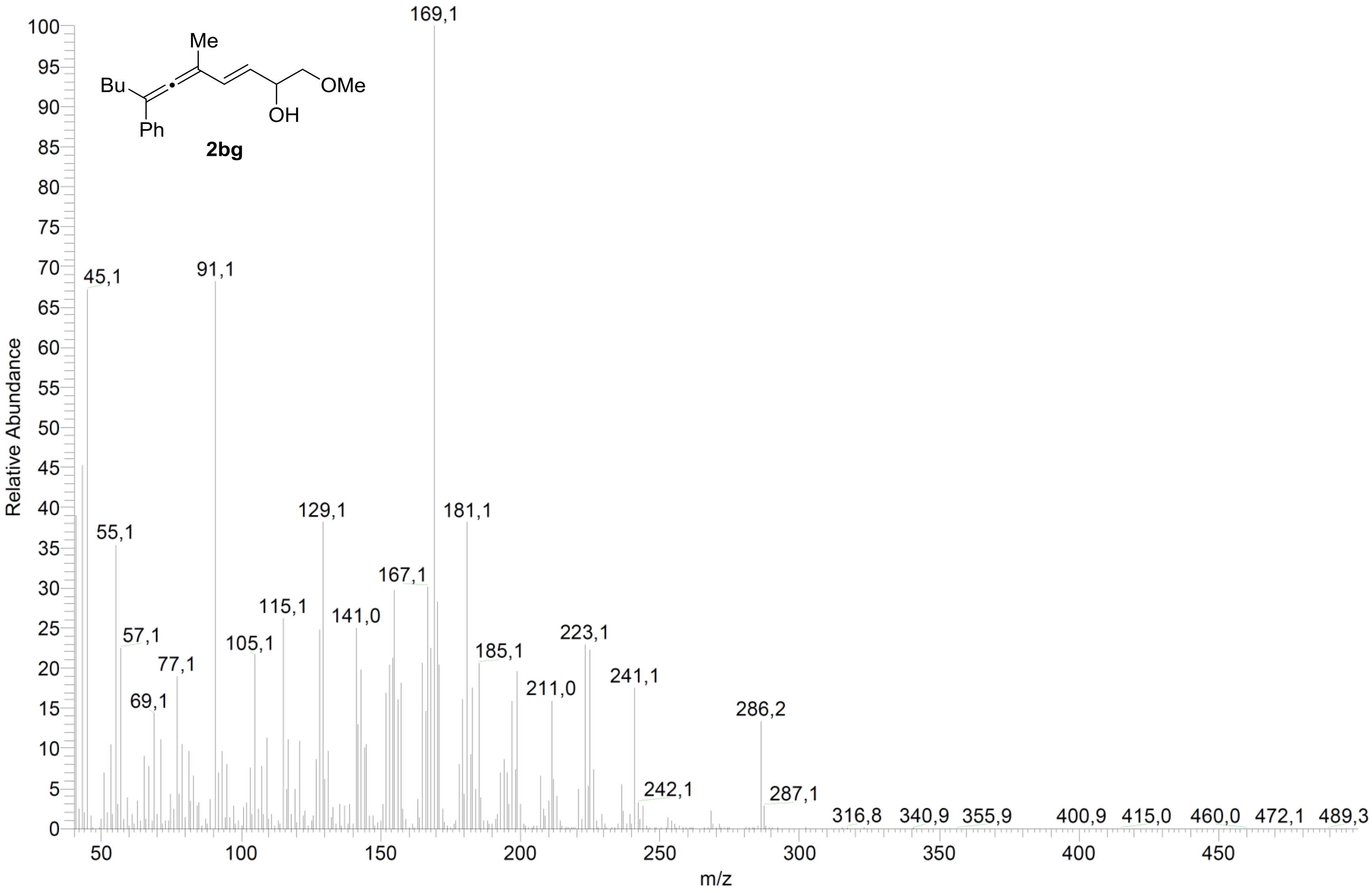
Bu
C_8H_{17}
OH
OMe
2bf


2bg
Bu
Ph
Me
OH
OMe
Relative Abundance
m/z
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15
20
25
30
35
40
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200
250
300
350
400
450
169,1
45,1
91,1
129,1
181,1
55,1
167,1
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241,1
211,0
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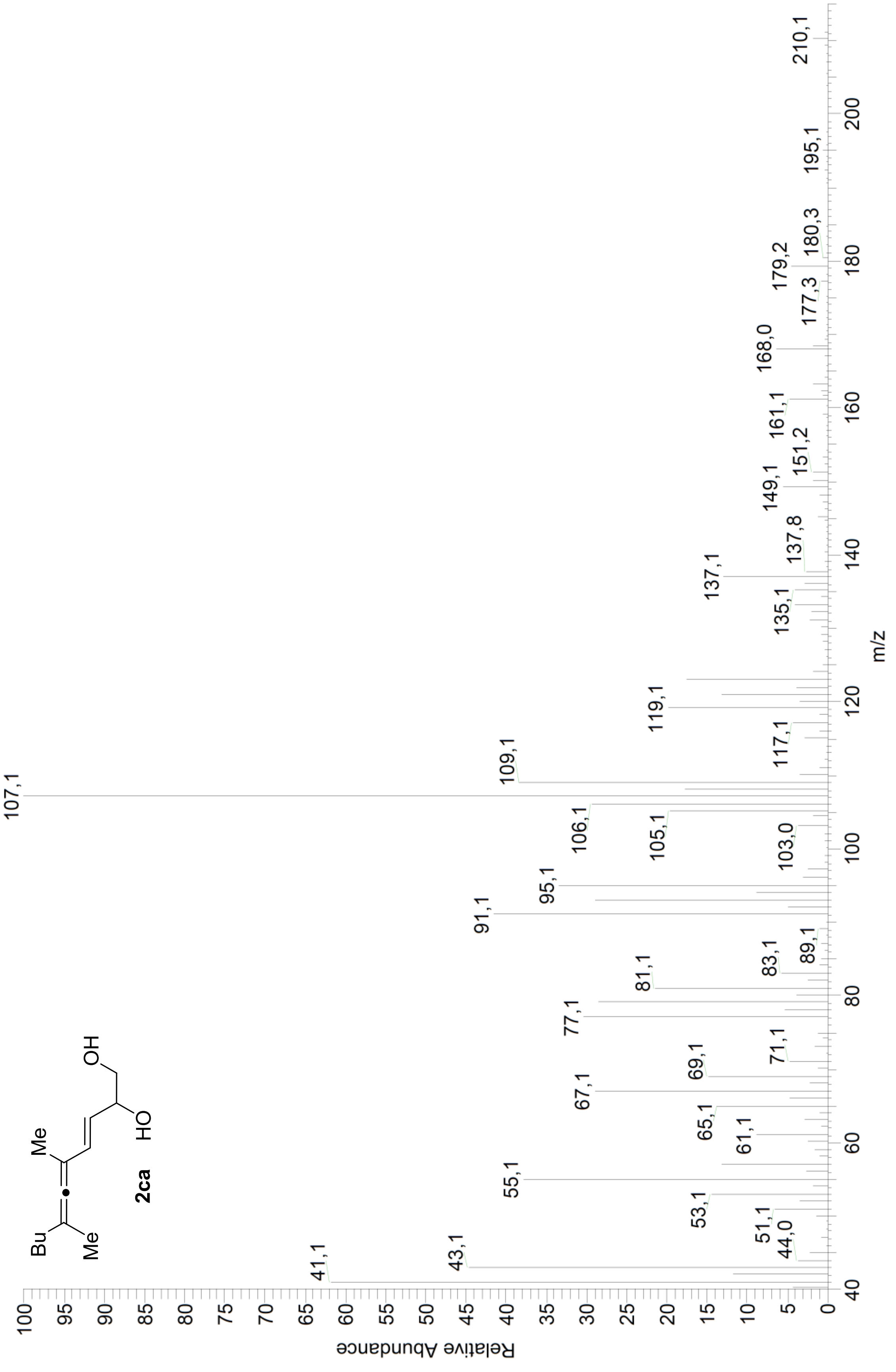
2ca
Bu
Me
Me
HO
OH
Relative Abundance
m/z
100
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90
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70
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50
45
40
35
30
25
20
15
10
5
0
40
60
80
100
120
140
160
180
200
41,1
43,1
44,0
51,1
53,1
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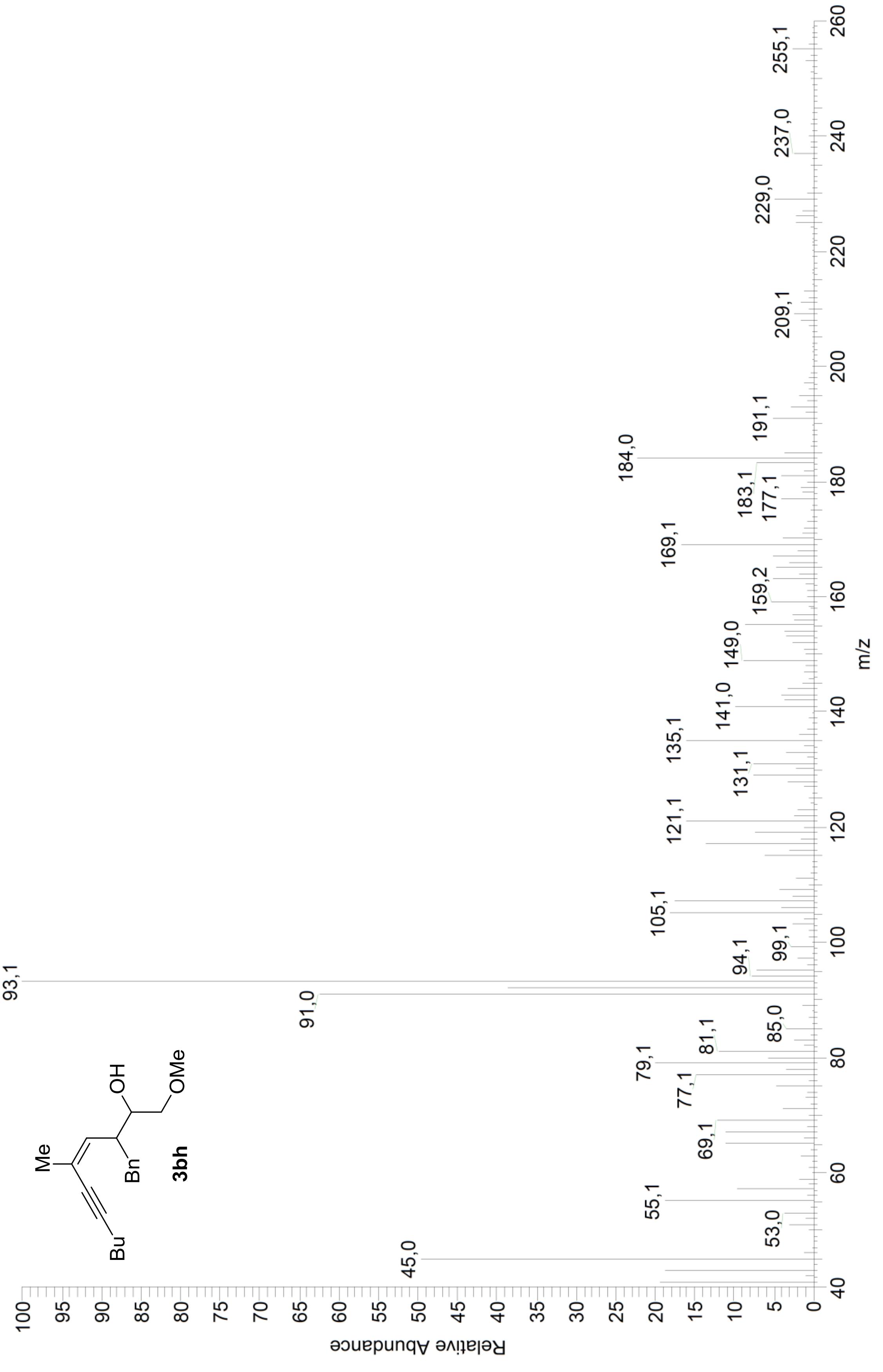
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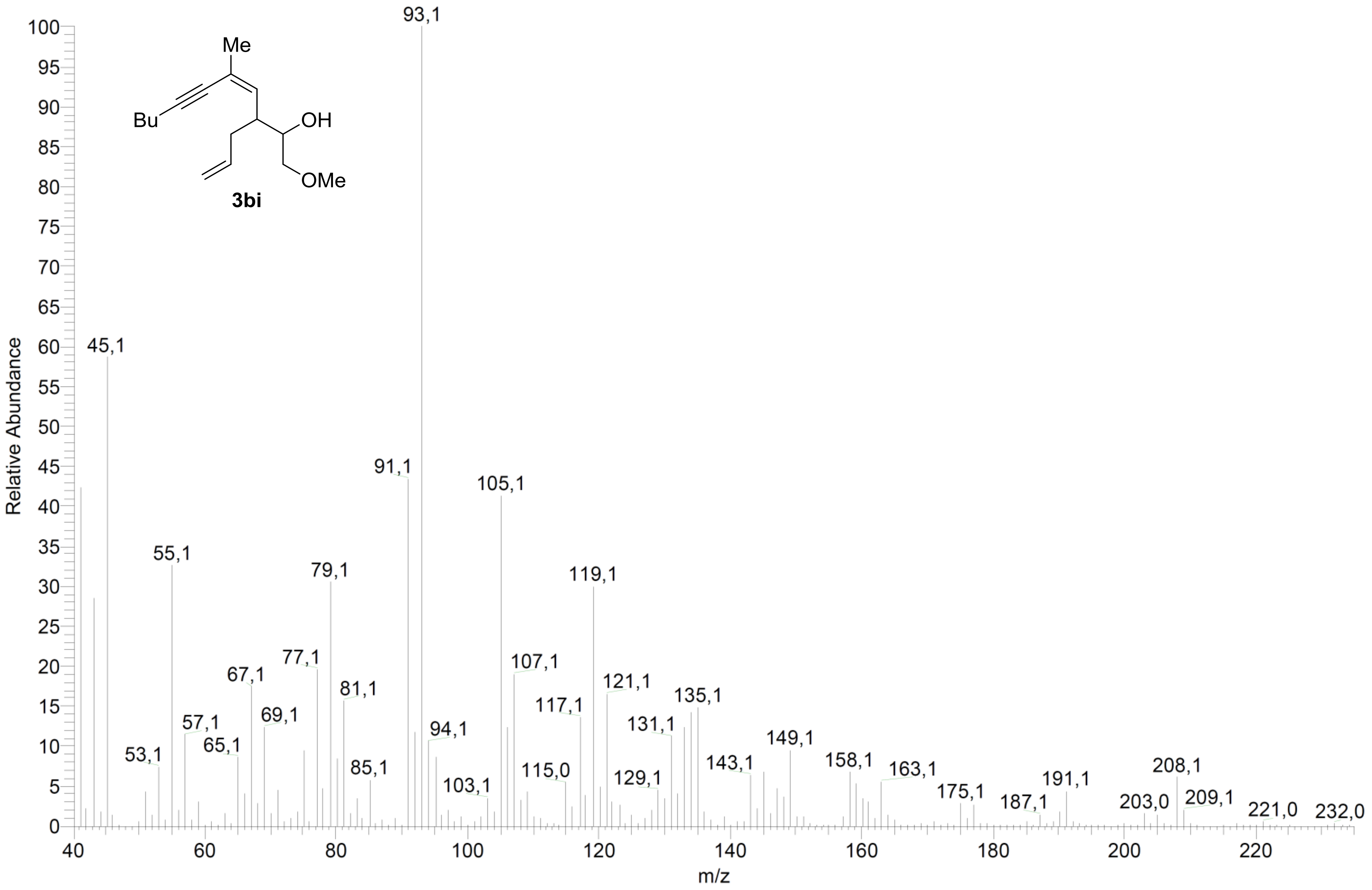

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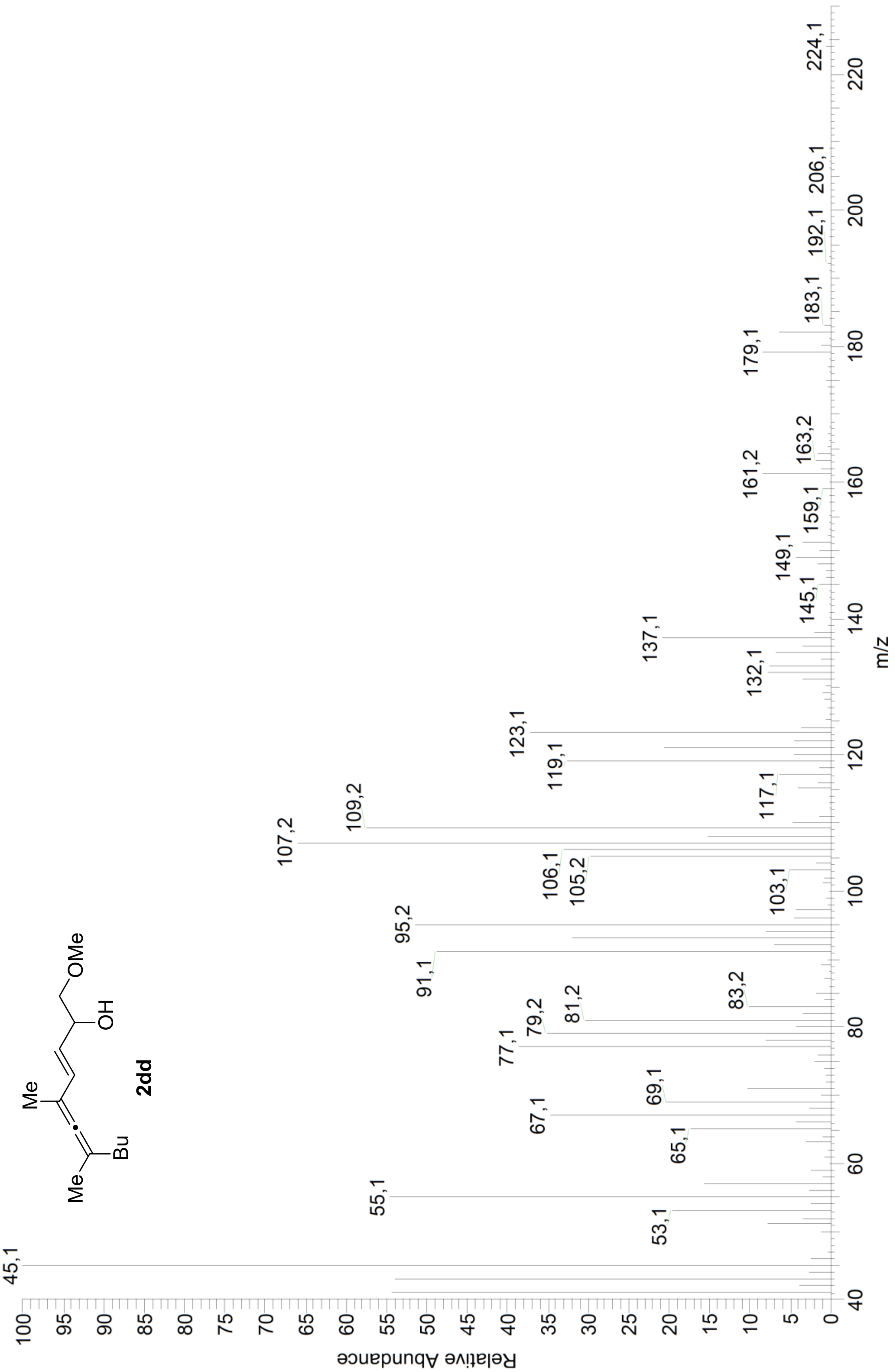
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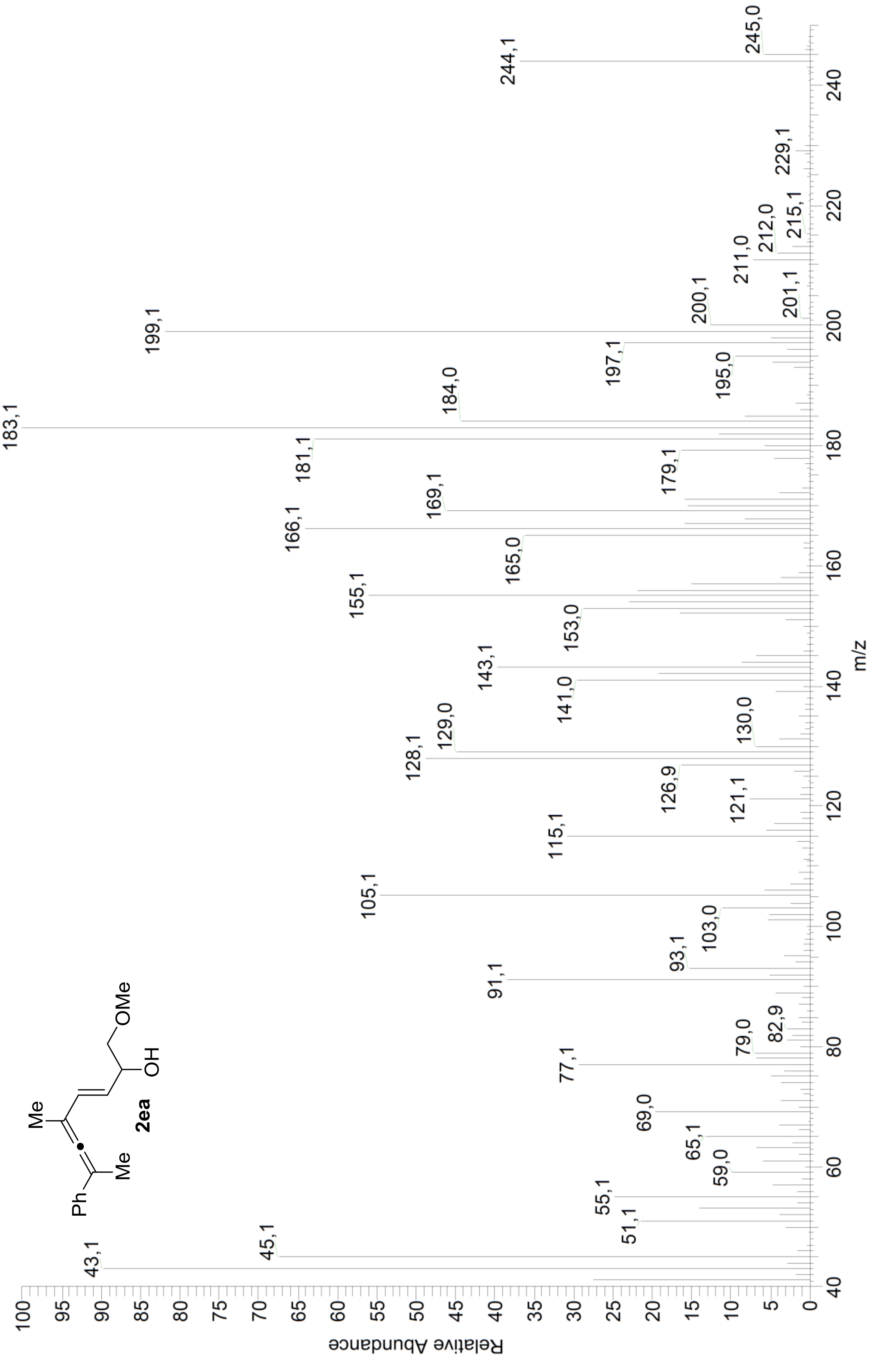
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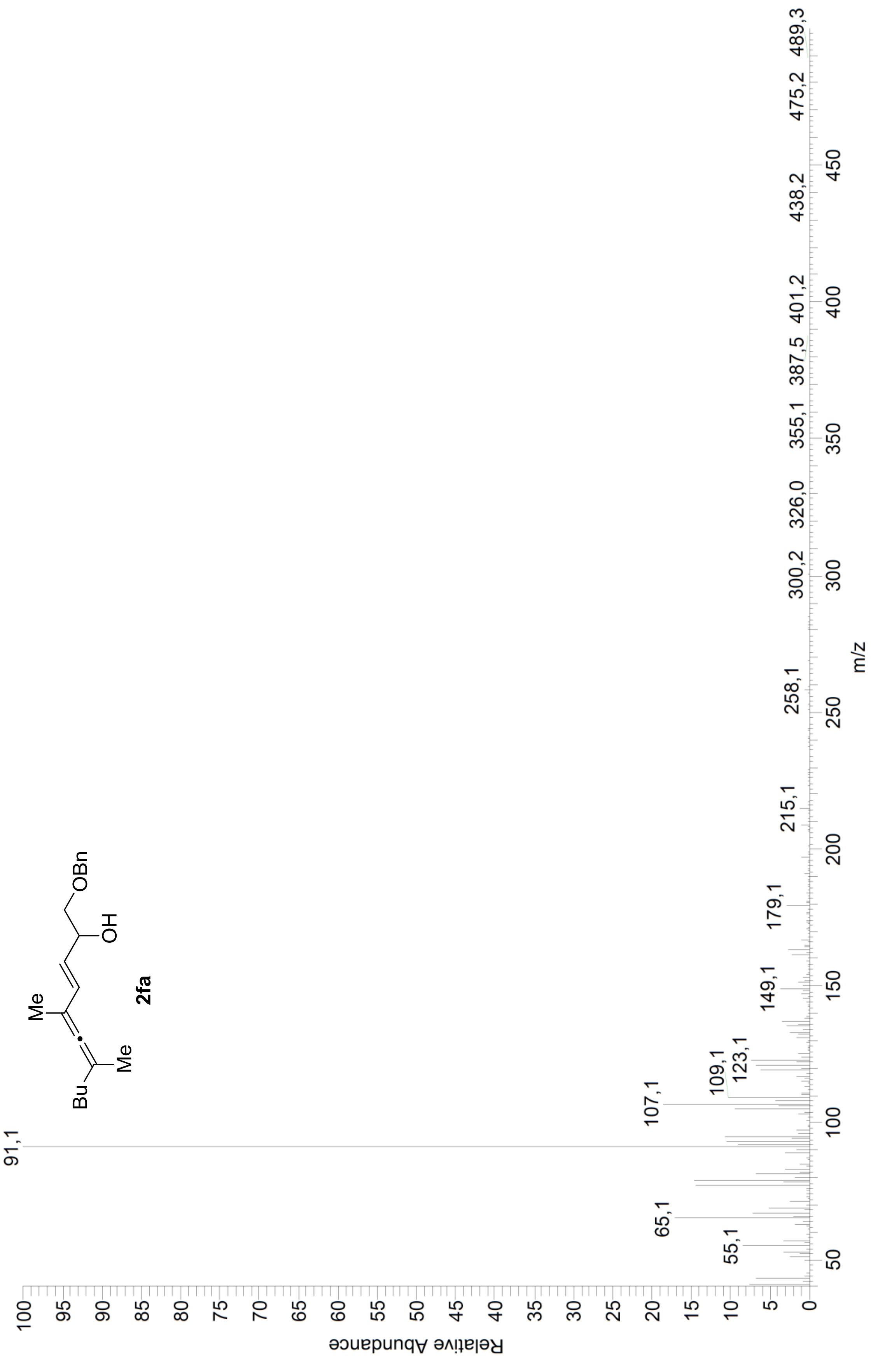
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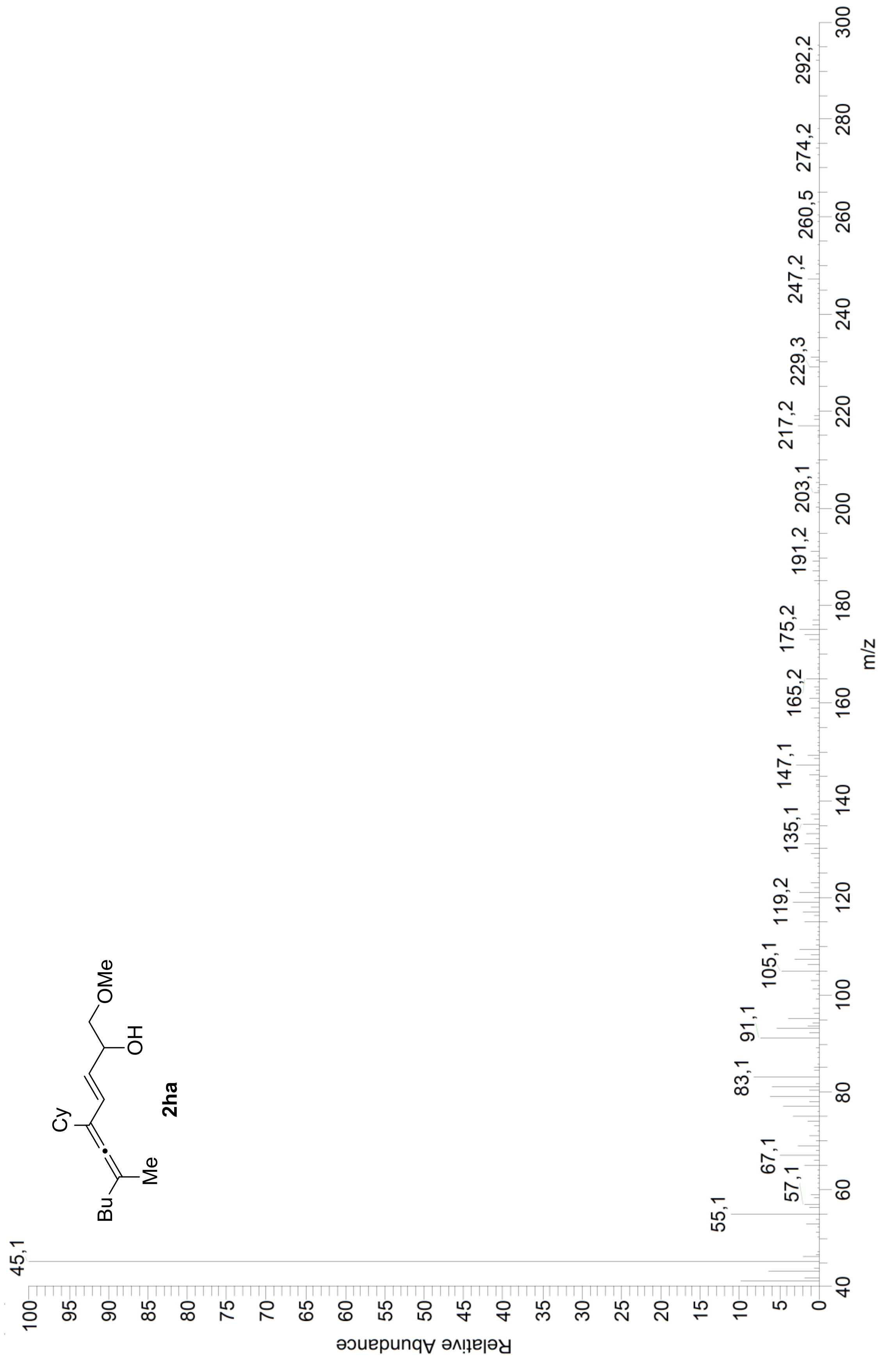
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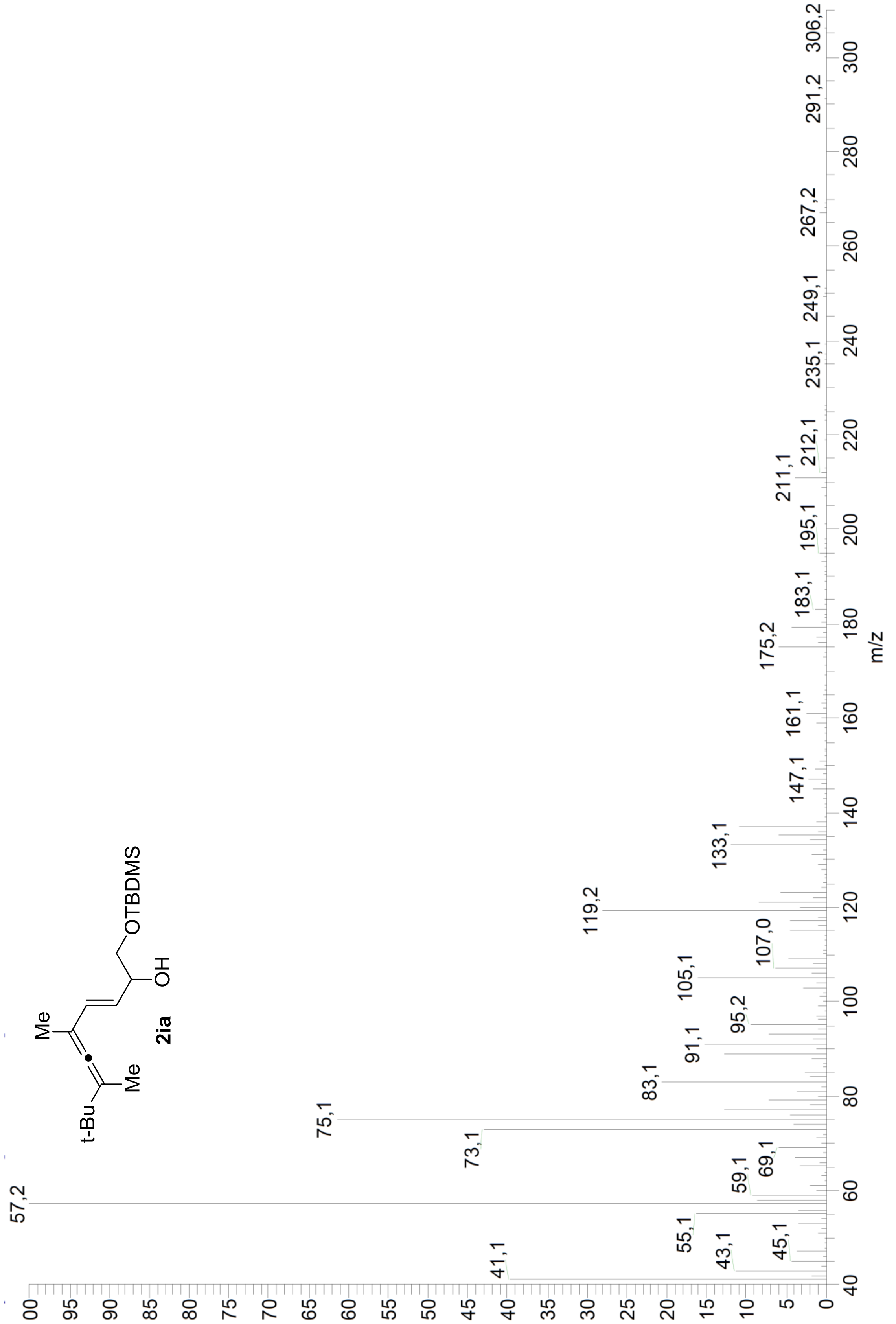
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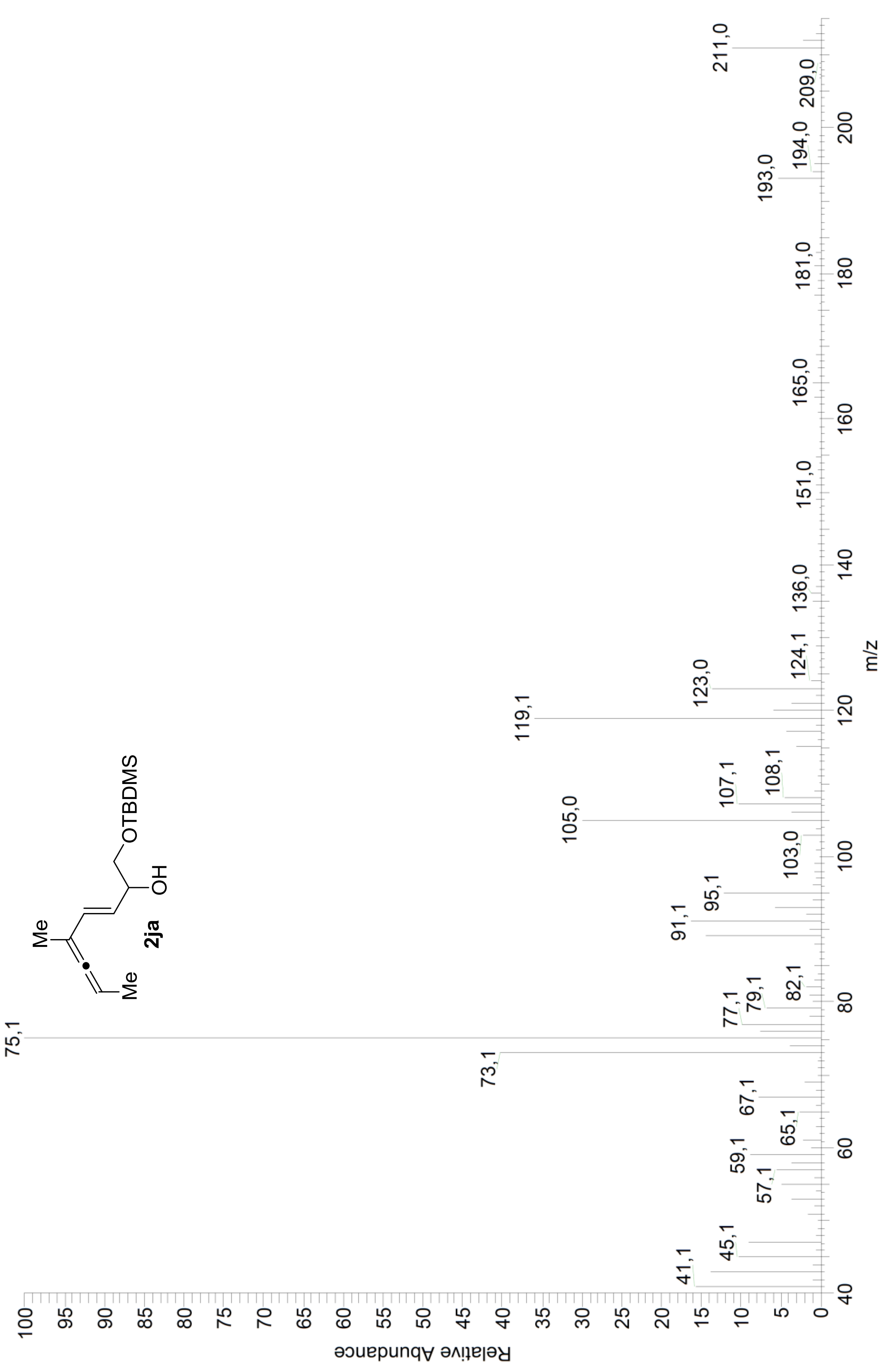
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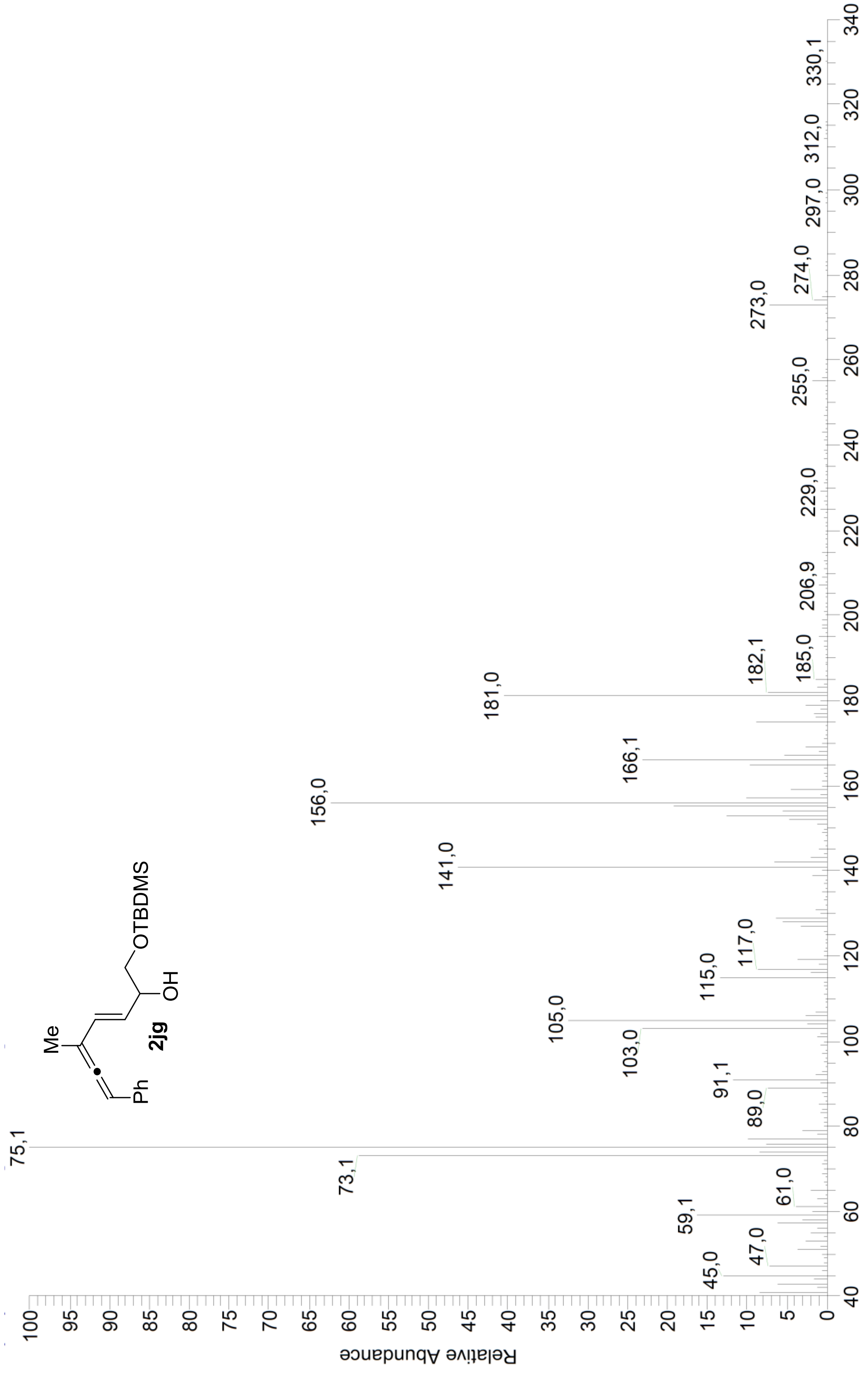

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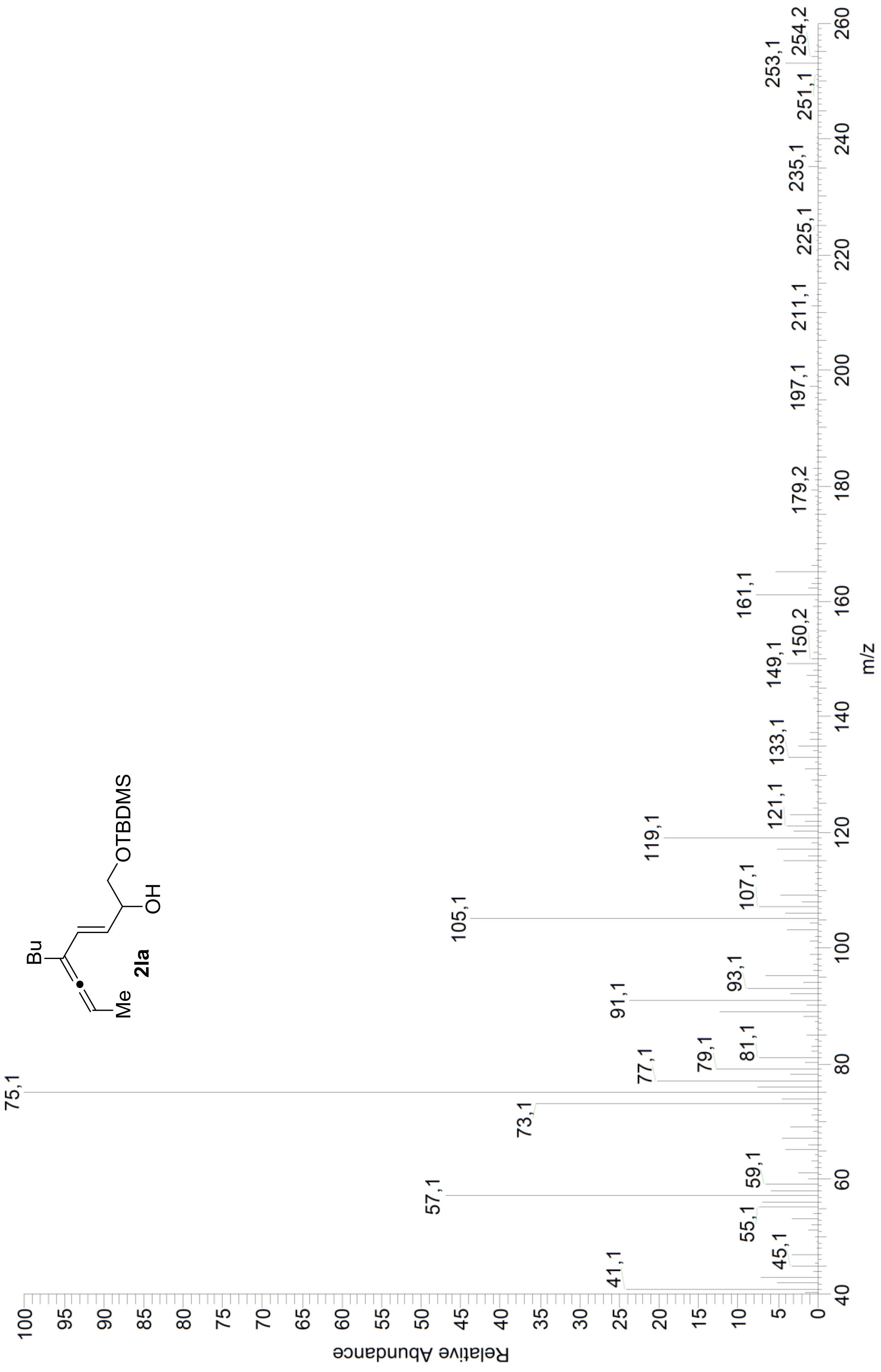
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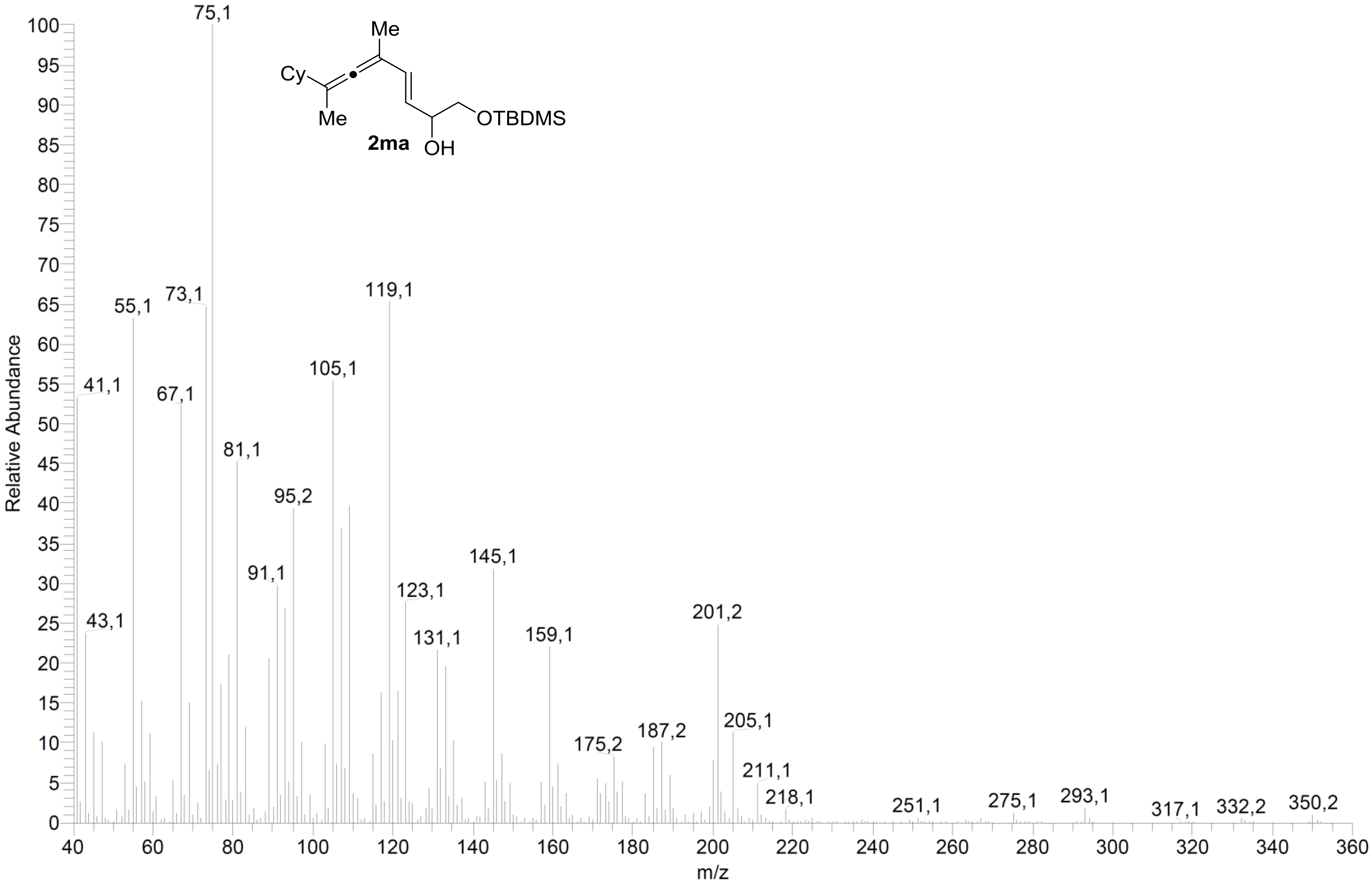
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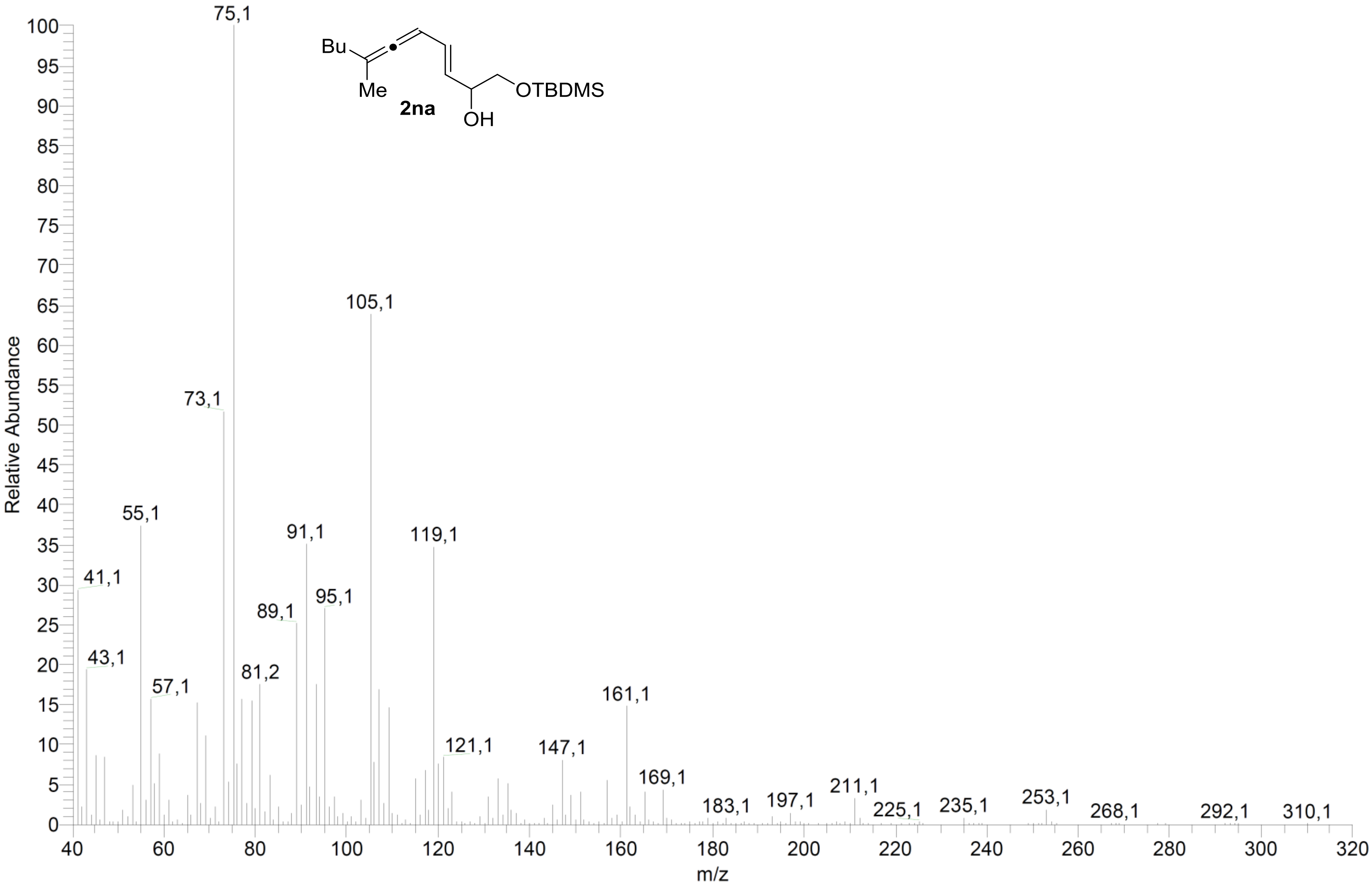
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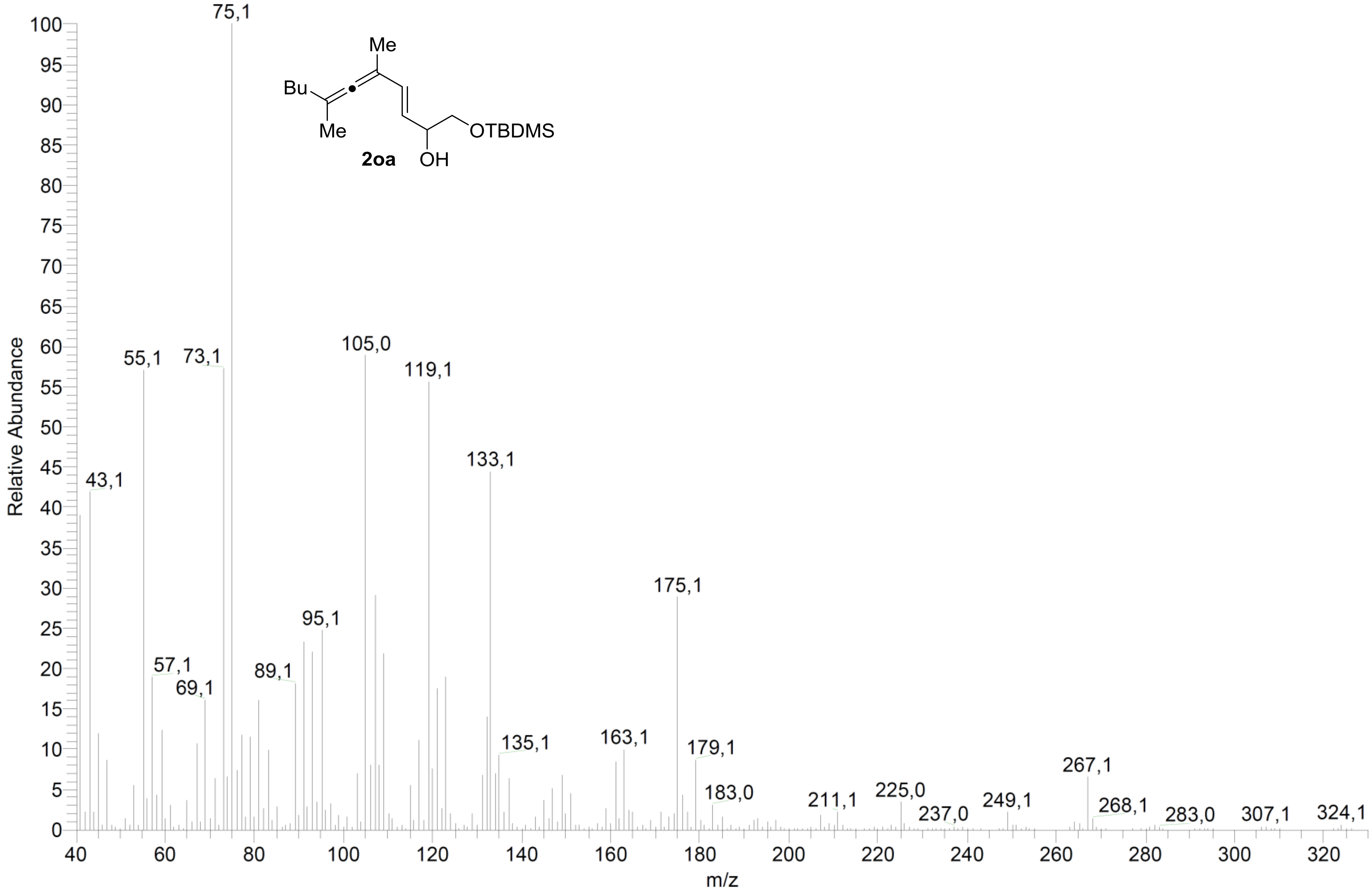
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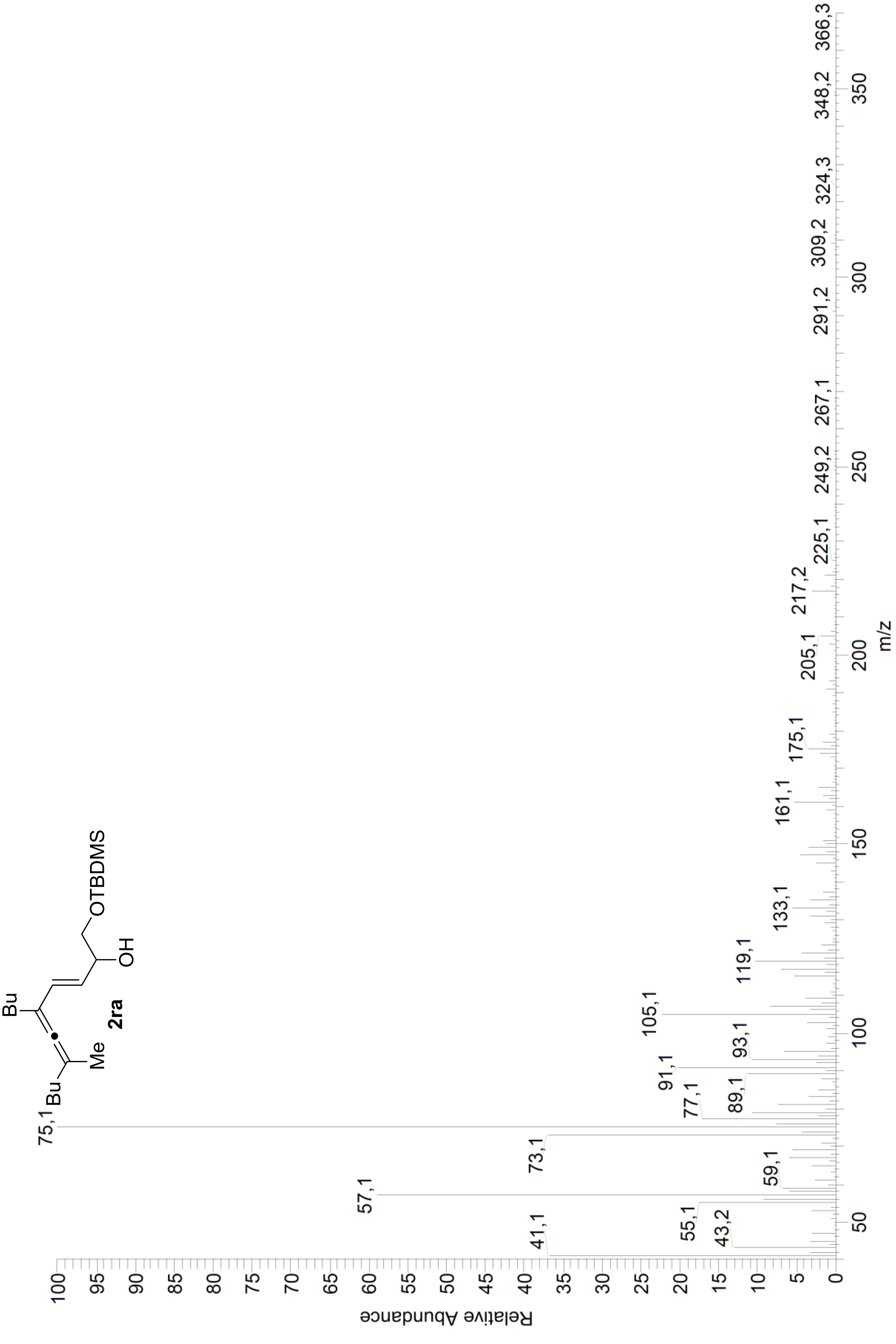

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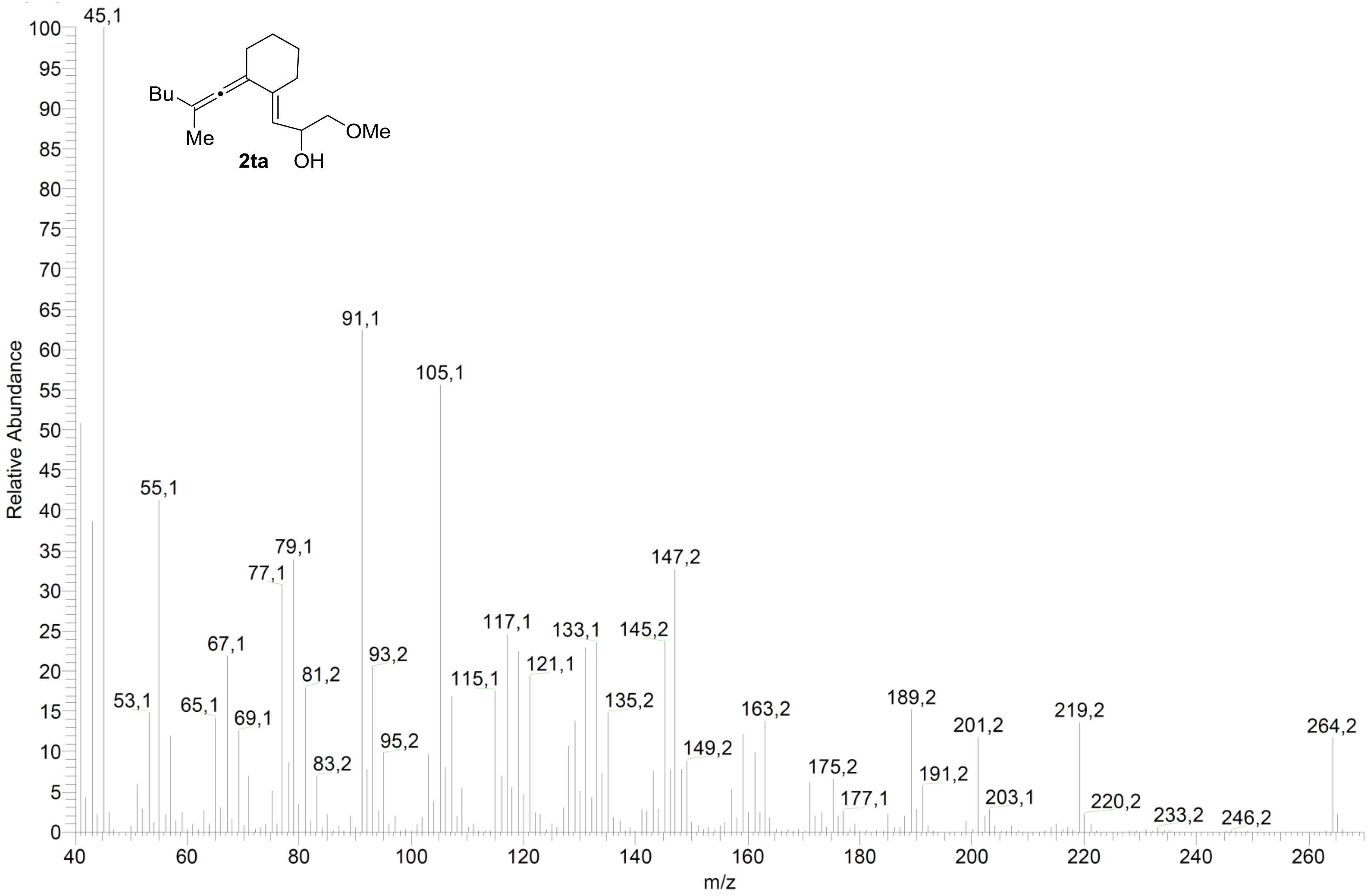
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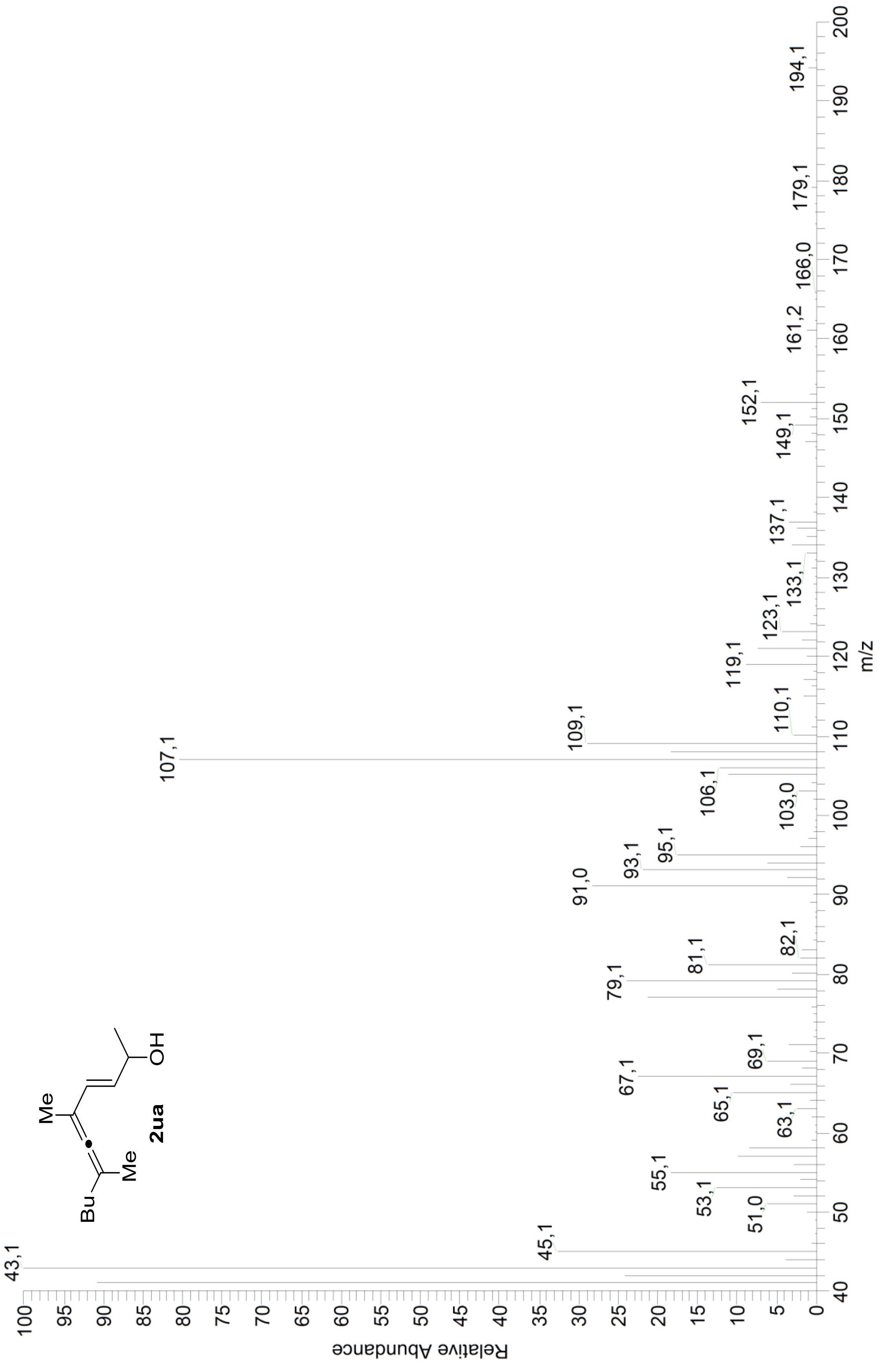
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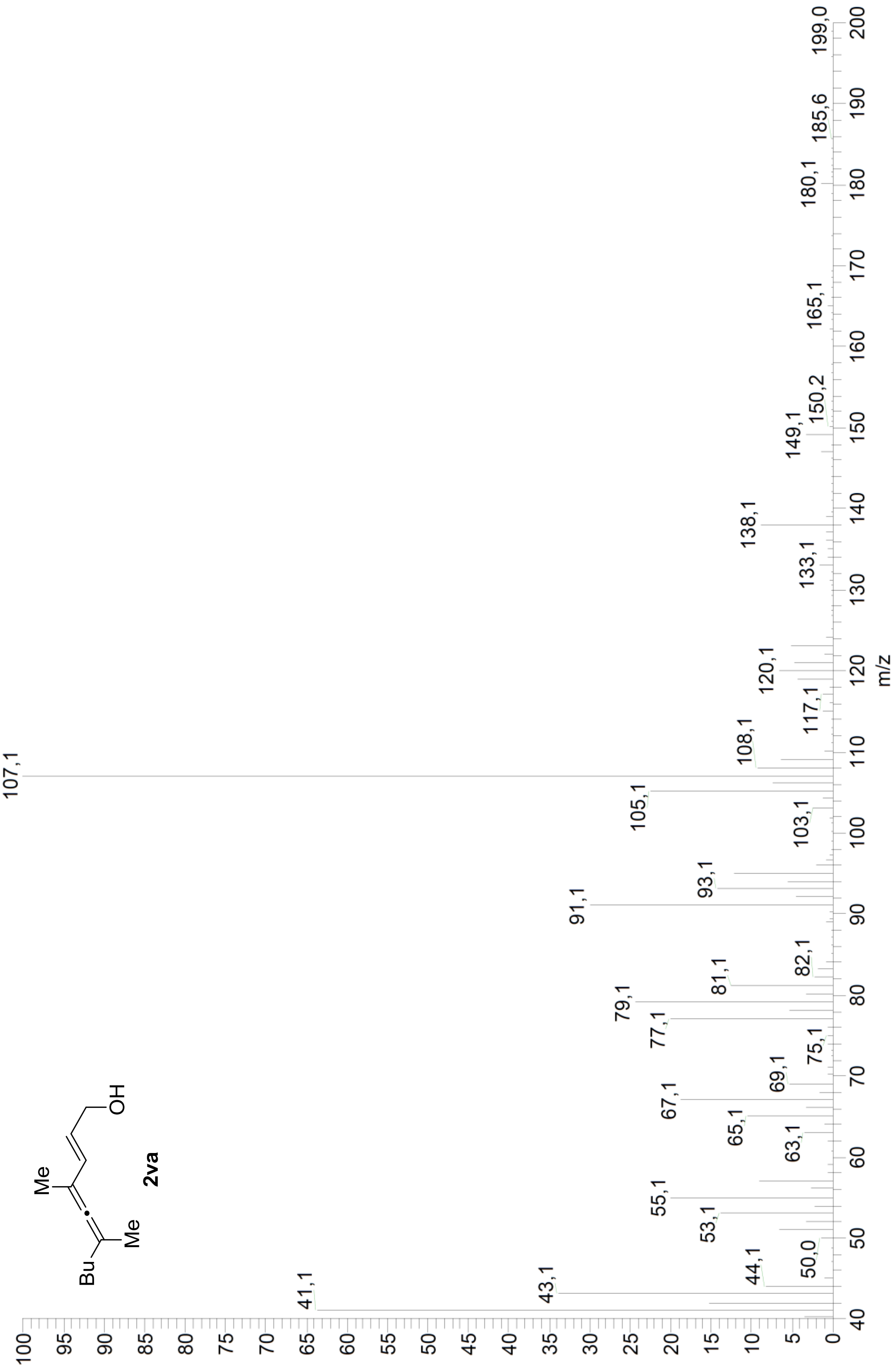

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