

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 vinylallenes 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'')-süstitüsyon 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.

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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	<i>N, N</i> -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>i</i> -Pr	<i>Iso</i> -propyl
M	Molar
<i>m</i>	Meta
<i>m</i> -CPBA	<i>meta</i> -Chloroperbenzoic acid
Me	Methyl
mg	Milligrams
min.	Minutes

mL	Milliliters
μm	Micrometer
<i>o</i>	Ortho
<i>p</i>	Para
Ph	Phenyl
RT	Room temperature
t	Time
<i>t</i> -Bu	Tertiary butyl
TBDMS	Tertiary butyldimethylsilyl chloride
THF	Tetrahydrofurane
Ts	<i>para</i> -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.

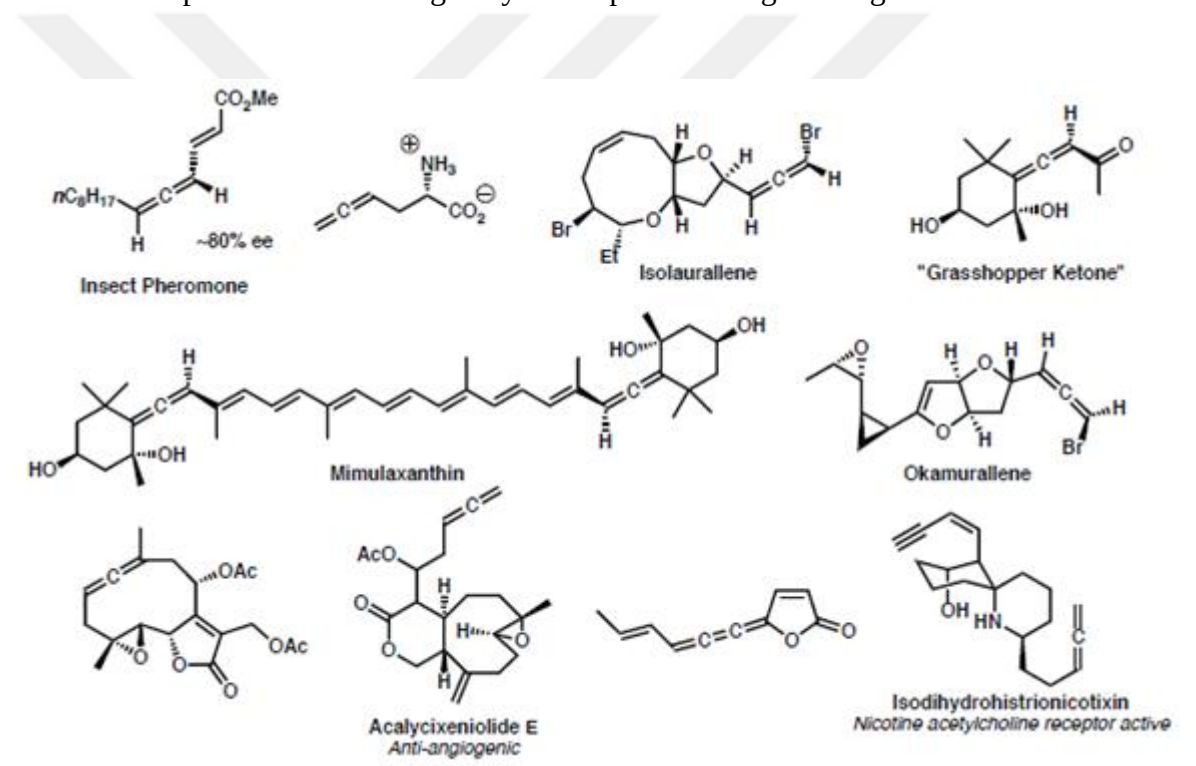


Figure 1.1. Allenic natural products and pharmacologically active allenes.
(Source: Tsuji, et al. 1995)

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-substitution 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.

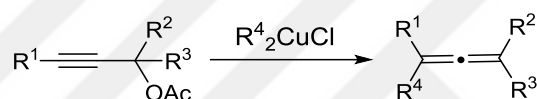


Figure.2.1. 1,3-Substitution method of propargyl acetates with stoichiometric level of organocuprates (Source: Rona, et al. 1968; 1969)

In addition to acetates, benzoate, carbonate, sulphonate, ether, acetal, oxirane, and halide substituted of propargylic 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 stoichiometric reactions of propargyl epoxide compounds with organometals were with dialkyl lithium 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.

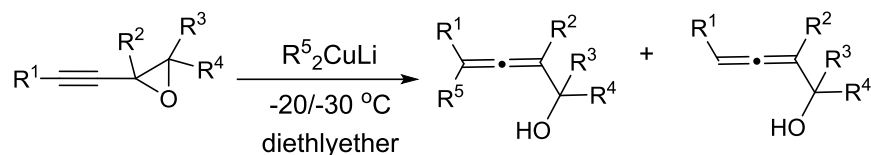


Figure 2.2 Stoichiometric reactions of propargyl epoxides dialkylcopperlithium cuprates
(Source: de Montellano, et al., 1973)

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* $\text{S}_{\text{N}}2'$ mode to afford enantiomerically enriched α -allenol structures (Figure 2.3).

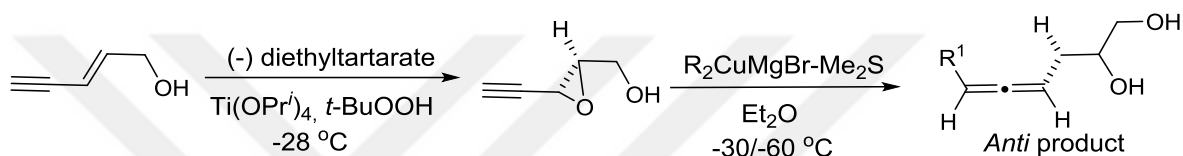


Figure 2.3. The reaction of an enantio-enriched enyne oxirane with organocuprates
(Source: Oehlschlager and Czyzewska, et al. 1983).

The method has been brought to catalytic level firstly by Alexakis and his group (1989; 1991). According to their findings, diastereoselectivity 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).

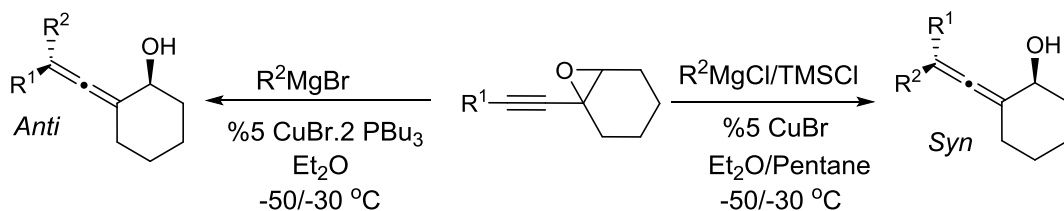


Figure 2.4. CuBr catalyzed reactions of propargylic epoxides and Grignard reagents.
(Source: Alexakis et al. 1989; 1991)

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).

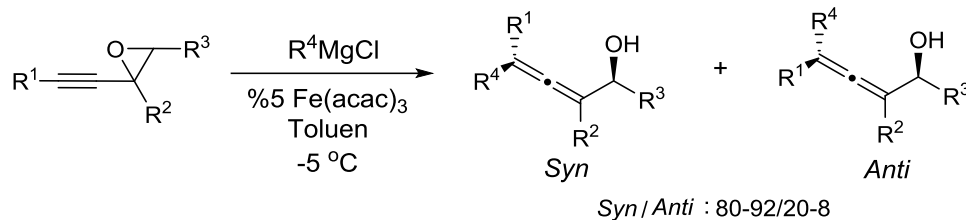


Figure 2.5. Iron catalyzed reactions of propargylic epoxides with Grignard reagents.
(Source: Fürstner, et al. 2003)

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).

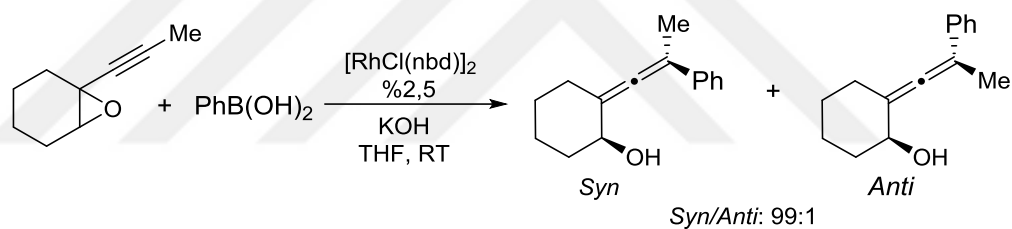


Figure 2.6. The synthesis of arylated allenols with rhodium catalysis via the reaction of propargyl epoxides with arylboronic acids (Source: Miura, et al. 2007)

2.2. Metal-Catalysed S_N2'-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 reagents are "hard" basic reagents, 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).

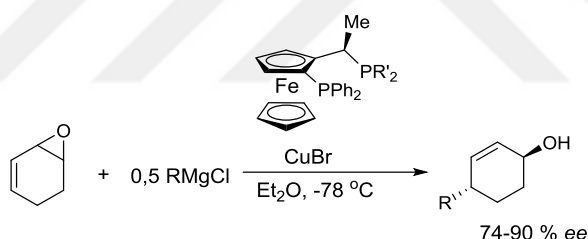


Figure 2.8. The copper catalyzed kinetic resolution of alkenyl oxiranes with Grignard Reagents (Source: Millet and Alexakis, et al. 2007)

2.3. Metal Catalysed Substitution 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'' -nucleophilic 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.

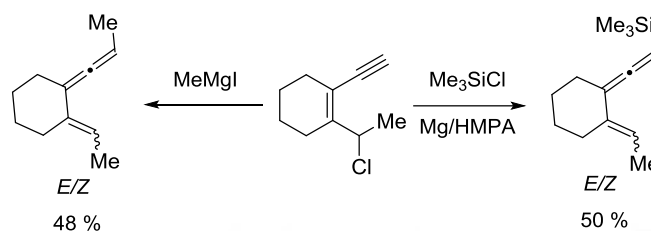


Figure 2.9. 1,5- S_N2'' -nucleophilic substitution reactions of 1-chloro-2-en-4-in compounds with methylmagnesium iodide or trimethylmagnesium chloride (Source: Gore, et al. 1972; Dulcere, et al. 1974; Dulcere, et al. 1981)

Krause and Purpura accomplished a more general method for this purpose. 2,4-enyne acetates underwent 1,5-substitution 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 synthesized enyne acetates (Figure 2.10) (Krause, 2000). The absolute configuration of the products were not reported.

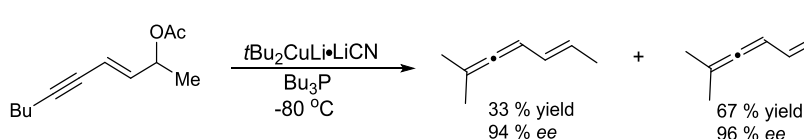


Figure 2.10. 1,5-Substitution reaction (S_N2'') of 1,4-enyne acetates with organolithium cuprates (Source: Krause, et al. 2000)

They also tried this method on two *E*-enyne oxirane substrates by using stoichiometric quantities of $\text{Me}_2\text{CuLi} \cdot \text{LiI}$ or $t\text{-Bu}_2\text{CuLi} \cdot \text{LiCN}$ 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).

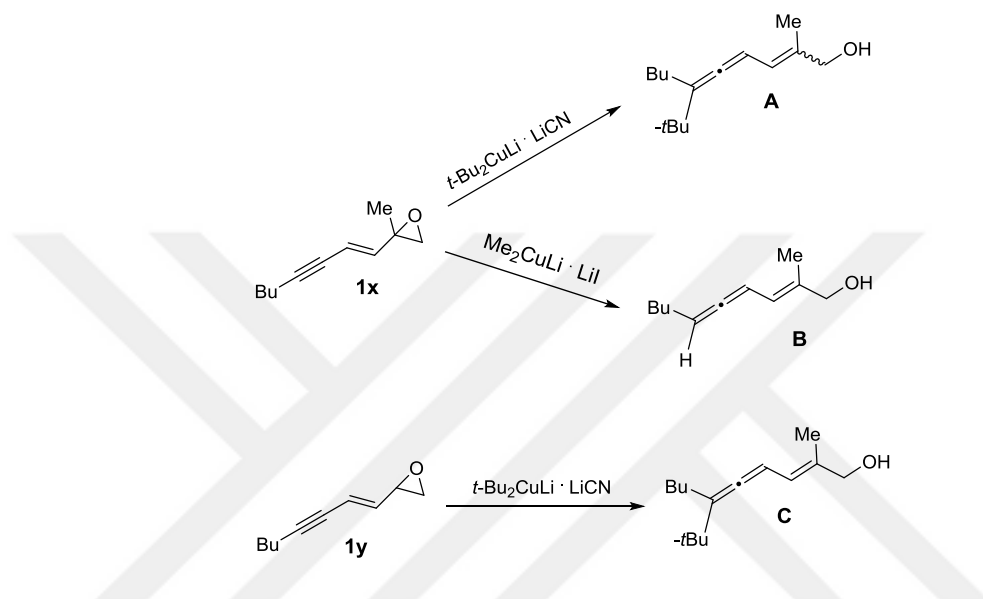


Figure 2.11. The reaction of *E*-enyne oxirane substrates and of Me_2CuLi , LiI or $t\text{-Bu}_2\text{CuLi} \cdot \text{LiCN}$ alkyl cuprates (Source: Krause, et al. 2000)

Our group have conducted palladium- and rhodium-catalyzed 1,5-substitution 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) (Uçuncü, 2011).

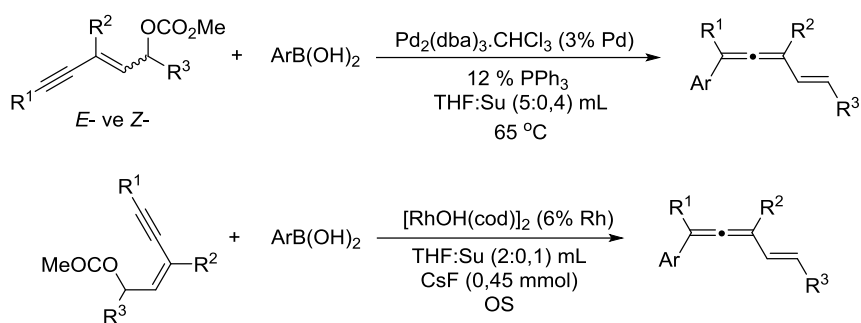


Figure 2.12. Palladium- and rhodium-catalyzed coupling reactions of carbonates and acetates of 2,4-enynols with organoboronic acids (Source: Uçuncü, et al. 2011)

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

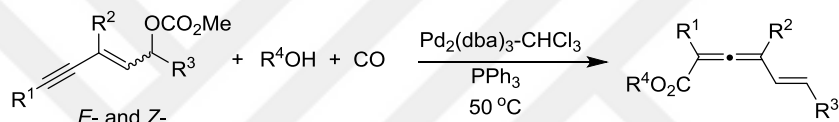


Figure 2.13. Palladium-catalyzed alkoxy carbonylation reactions of enyne carbonates with enyne oxiranes. (Source: Akpınar, et al. 2011)

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.

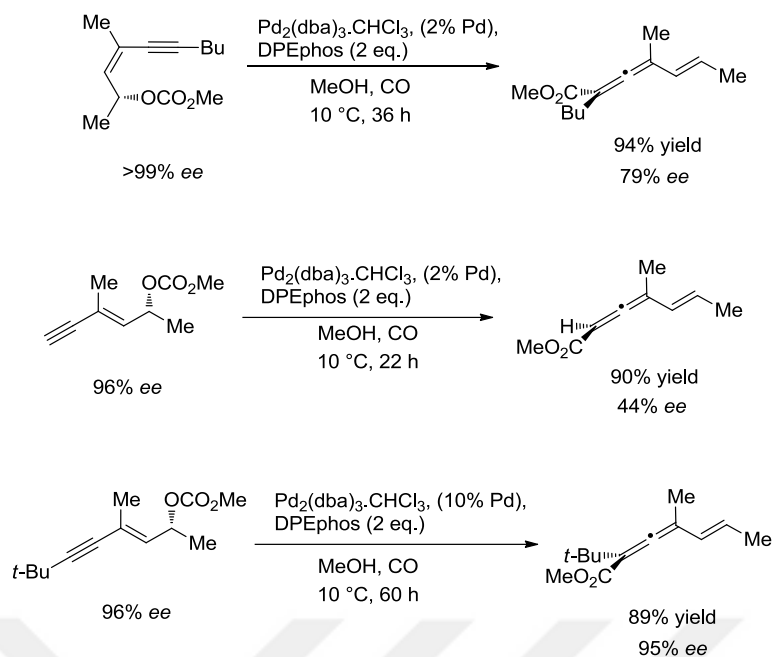


Figure 2.14. Palladium-catalysed alkoxy carbonylation reaction of (*E* and *Z*)-2, 4-enyne carbonates leading to enantio-enriched vinylallene derivatives. (Source: Karagöz, *et al.* 2014)

In a recent study that was conducted in our laboratories, the palladium-catalyzed alkoxy carbonylation 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).

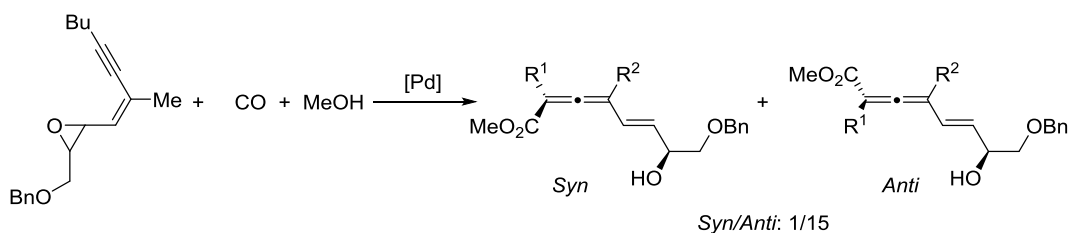


Figure 2.15. Anti-selective palladium catalyzed alkoxy carbonylation reactions (Source: Kuş, *et al.* 2013b).

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)

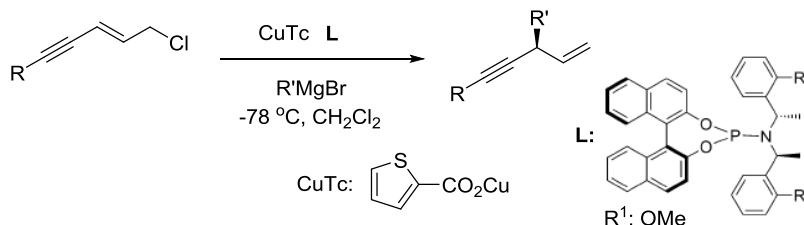


Figure 2.16. Cu(I) catalyzed reactions of enyne chlorides with Grignard reagents (Source: Li and Alexakis, et al. 2012)

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 pheromone 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).

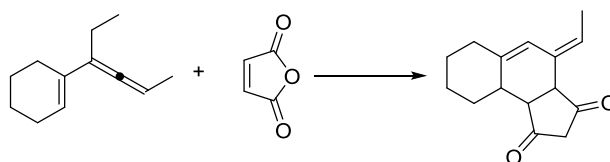


Figure 2.17. Diels Alder reactions in high reactivity and stereo-selectivity
(Source: Spino, et al. 1998)

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

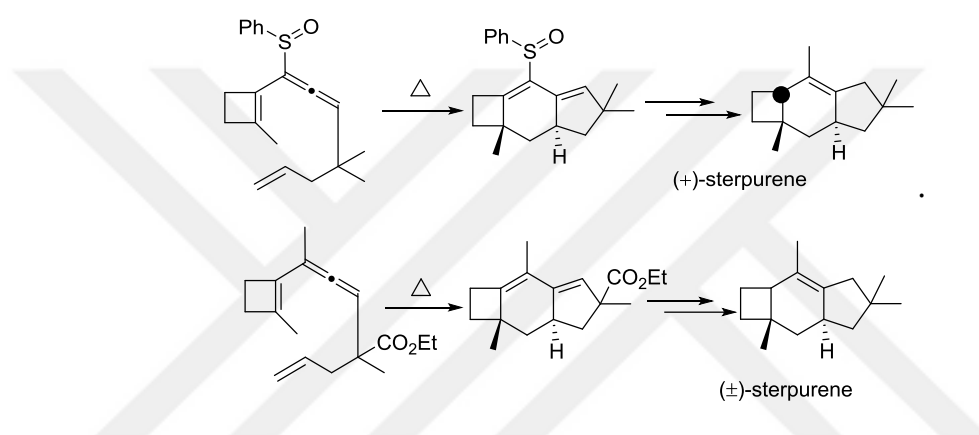


Figure 2.18. The synthesis of optically active sterpurene via intramolecular Diels Alder reaction ([4+2] catenulation) of a vinylallene structure (Source: Gibbs, 1989, Krause, et al. 1993)

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.

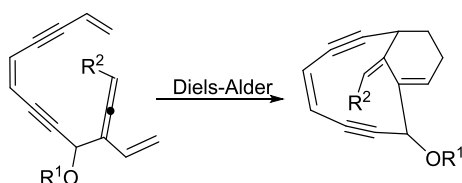


Figure 2.19. Intramolecular Diels Alder reaction of s vinylallene structure in the synthesis of esperamicin A (Source: Schrieber, et al. 1988)

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).

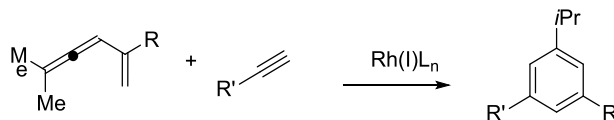


Figure 2.20. Rh(I) catalysis of vinylallenes with terminal alkynes (Source: Murakami, et al. 1988)

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

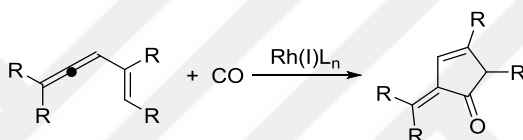


Figure 2.21. Pauson-Khand type reactions (Source: Murakami, et al. 1999a, 199b)

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

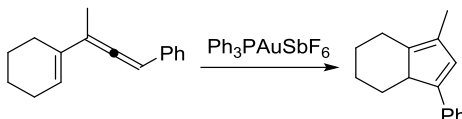


Figure 2.22 Gold-catalyzed cyclization of vinylallenes (Source: Lee, et al. 2007)

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; Lemièrre, 2009).

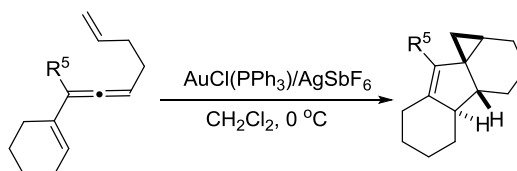


Figure 2.23. Gold-catalysed cycloisomerisation reactions of vinylallenes in high stereo-selectivity (Source: Gandon, et al. 2008; Lemièrre, et al. 2009)

CHAPTER 3

EXPERIMENTAL STUDY

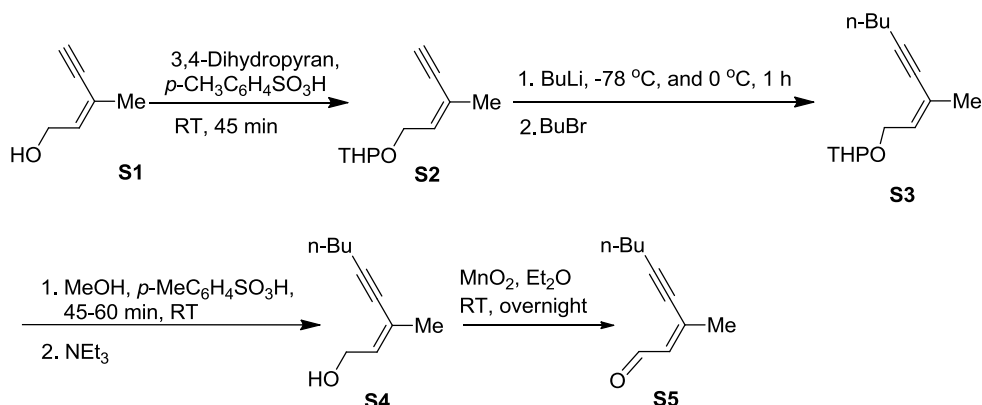
3.1. General Methods of Drying Solvents

DMF, and DCM solvents were all purified by a solvent purification system. Et₂O and THF were distilled from benzophenone-ketyl under argon prior to use. For the iron-catalyzed reactions, THF solvent dried by refluxing over LiAlH₄.

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 NEt₃ 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 Pd₂(dba)₃-CHCl₃ complex was synthesized in the laboratory (Ukai, et al. 1974).

3.2.1. Synthesis of (Z)-1a

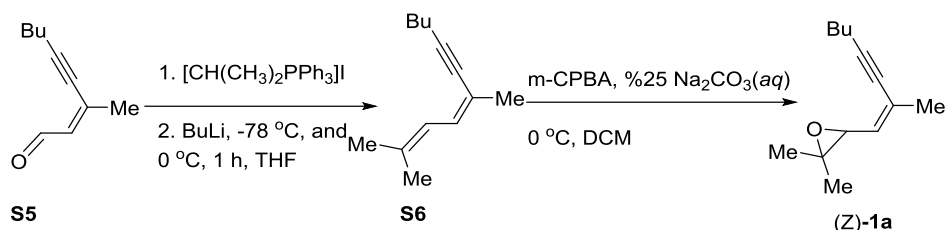


To the mixture of commercially available, (Z)-pent-2-en-4-yn-1-ol (**S1**) (1.92 g, 20 mmol) and 3,4-dihydropyran (2.2 mL, 24 mmol) was added *p*-toluenesulfonic acid (44 mg, 0.02 mmol) and then stirred for 45 min at room temperature (RT). Then, the mixture was diluted with 40 mL of dry THF under Ar and cooled to $-78\text{ }^\circ\text{C}$. 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 $0\text{ }^\circ\text{C}$, 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 $\text{NH}_4\text{Cl}(\text{aq})$ 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 (Betzner, *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

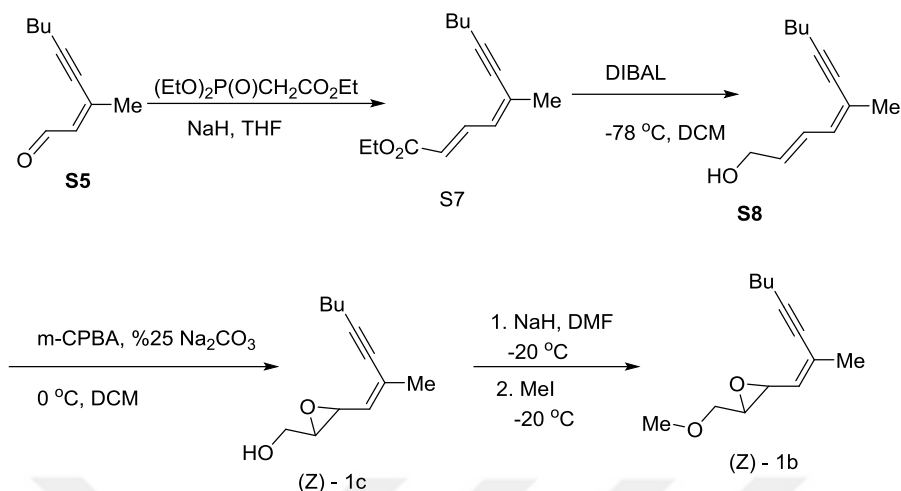
through Celite, the solution was concentrated under reduced pressure. The crude aldehyde (**S5**) was used in the next step (Betzer, *et al.* 1997).



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 $0\text{ }^\circ\text{C}$, 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 $\text{NH}_4\text{Cl}(\text{aq})$ 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 $\text{Na}_2\text{CO}_3(\text{aq})$ (25%) followed by 3.4 mmol (587 mg) *m*-chloroperbenzoic acid dropwise at $0\text{ }^\circ\text{C}$. 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



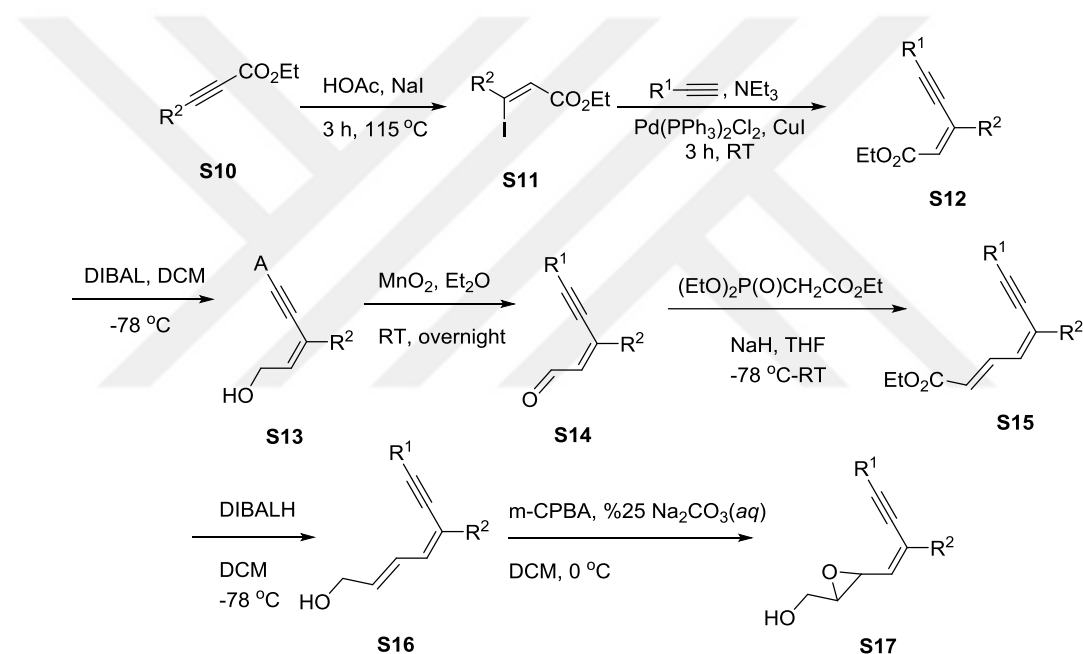
To a solution of NaH (525 g, 22 mmol) in THF (50 mL) was added triethyl phosphonoacetate (4.8 mL, 24 mmol) at 0 °C, and the mixture stirred 1 h, at RT. Subsequently, to the reaction mixture was added **S5** (3 g, 20 mmol) dropwise at -78 °C and stirred for 1 h, at RT. The reaction was terminated by the addition of aqueous NH₄Cl(aq) solution and extracted with Et₂O. The organic layer was dried over MgSO₄, 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 °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 MgSO₄, 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 MgSO₄, filtered, and concentrated under reduced pressure. The crude mixture was subjected to column chromatography over NEt₃-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 alkyne 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 $\text{NaHCO}_3(aq)$, $\text{Na}_2\text{S}_2\text{O}_3(aq)$ (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; $\text{R}^2 = \text{H}$, 7.6 g, 84%; $\text{R}^2 = \text{Me}$, 8.4 g, 87%; $\text{R}^2 = t\text{-Bu}$, 9.6 g, 85%; $\text{R}^2 = \text{Cy}$, 10.6 g, 86%), (Piers, *et al.* 1994). A mixture of **S11** (30 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (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: $\text{R}^1 = \text{Bu}$, $\text{R}^2 = \text{H}$, 4.97 g, 92%; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, 5.97 g, 93%; $\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{Me}$, 5.94 g, 90%; $\text{R}^1 = t\text{-Bu}$, $\text{R}^2 = \text{Me}$, 4.95 g, 85%; $\text{R}^1 = \text{Bu}$, $\text{R}^2 = t\text{-Bu}$, 6.23 g, 88%; $\text{R}^1 = \text{Bu}$, $\text{R}^2 = \text{Cy}$, 6.21 g, 79%; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$ %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 $\text{HCl}(aq)$ 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**: $\text{R}^1 = \text{Bu}$, $\text{R}^2 = \text{H}$, 3.14 g, 91%; $\text{R}^1 = \text{Bu}$, $\text{R}^2 = \text{Cy}$, 4.89 g, 89%; $\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{Me}$, 3.60 g, 81%; $\text{R}^1 = t\text{-Bu}$, $\text{R}^2 = \text{Me}$, 3.57 g, 94%; $\text{R}^1 = \text{Bu}$, $\text{R}^2 = t\text{-Bu}$, 4.2 g, 88%; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, 3.87 g, 90%; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$ %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).

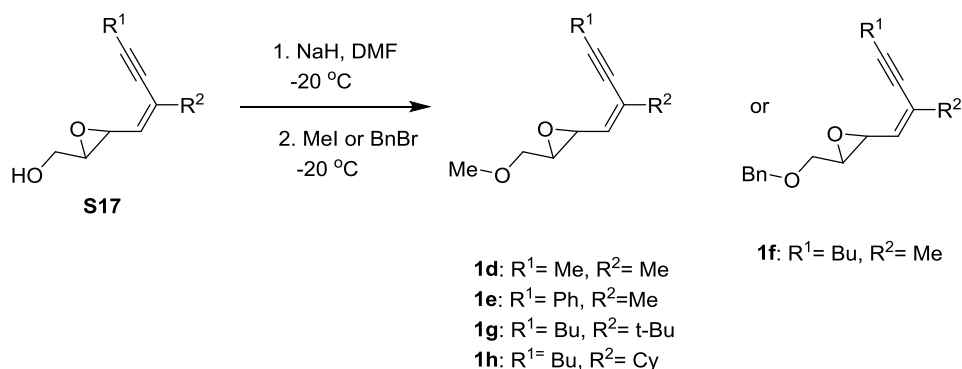
To a solution of NaH (1.1 eq) in THF (2.5 mL/mmol **S14**) was added triethyl phosphonoacetate (1.2 eq) at 0°C and the mixture stirred for 1 h, at RT. Subsequently, to the reaction mixture was added **S14** (6.5-10 mmol) dropwise at -78°C , and stirred for 1 h, at RT. The reaction was terminated by the addition of saturated $\text{NH}_4\text{Cl}(aq)$ 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** R¹= Bu, R²= H, 1.48 g, 72%; R¹= Bu, R²= Cy, 1.4 g, 68%; R¹= Cy, R²= Me, 1.97 g, 80%; R¹= *t*-Bu, R²= Me, 1.80 g, 82%; R¹= Bu, R²= *t*-Bu, 2.12 g, 81%; R¹= Ph, R²= Me, 2.04 g, 85%, R¹= H, R²= 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 MgSO₄, 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**: R¹= Bu, R²= H, 1.12 g, 95%; R¹= Bu, R²= Cy, 1.1 g, 94%; R¹= Cy, R²= Me, 1.55 g, 95%; R¹= *t*-Bu, R²= Me, 1.39 g, 95%; R¹= Bu, R²= *t*-Bu, 1.6 g, 90%; R¹= Ph, R²= Me, 1.6 g, 92%, R¹= H, R²= Me %85), (Kajikawa, *et al.* 2009).

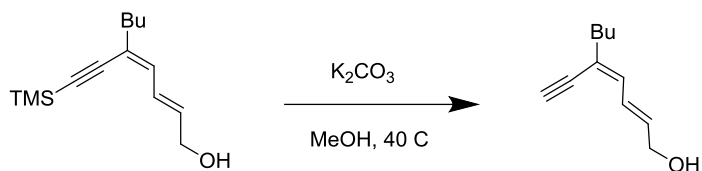
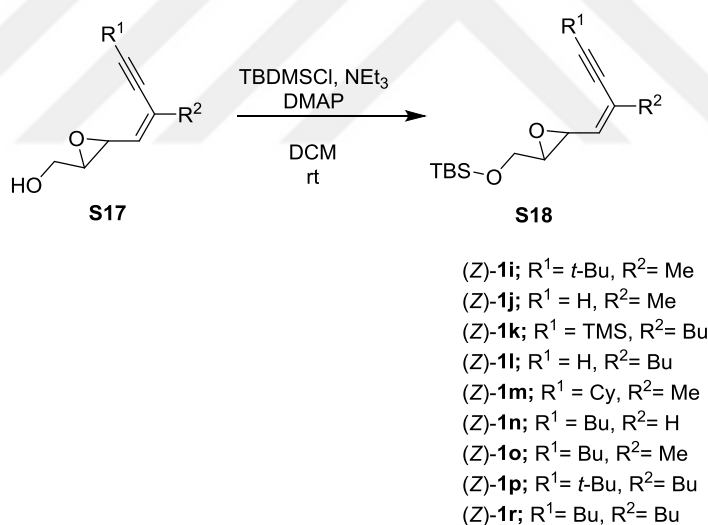
The epoxidation of **S16** (2 mmol) and isolation of the corresponding **S17** products were performed as specified for (Z)-**1a** (yields of **S17**: R¹= Bu, R²= H, 0.19 g, 55%; R¹= Bu, R²= Cy, 0.26 g, 49%; R¹= Cy, R²= Me, 0.25 g, 57%; R¹= *t*-Bu, R²= Me, 0.25 g, 65%; R¹= Bu, R²= *t*-Bu, 0.24 g, 50%; R¹= Ph, R²= Me, 0.26 g, 60%, R¹= H, R²= Me %60).

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



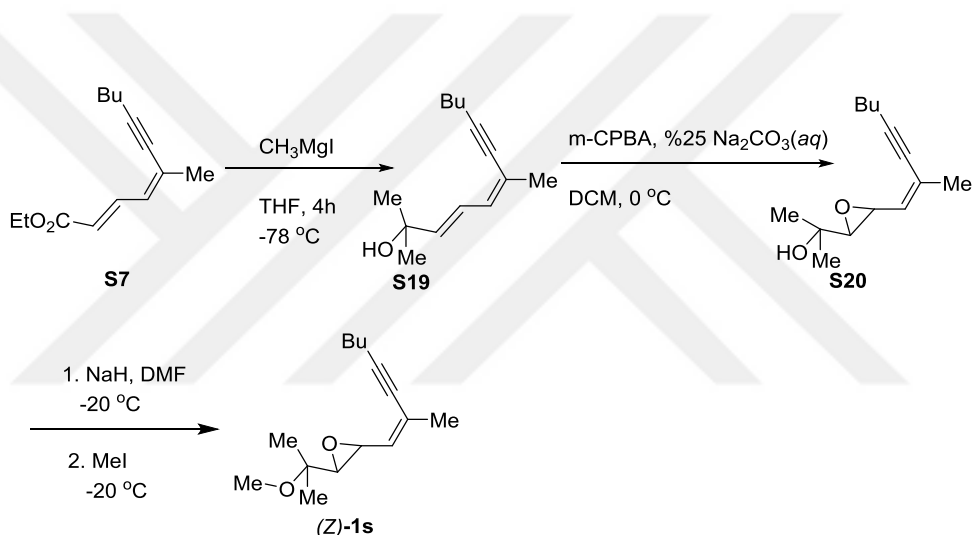
As for the alkylation of the pendant hydroxyl group of **S17**, a suspension of sodium hydride (1.1 eq) in DMF (1 mL) was added to a solution of **S17** (1 mmol) in DMF (1 mL/mmol **S17**) at -20 °C. The mixture was stirred for further 30 min before the addition of methyl iodide (1.2 eq) or benzyl bromide (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 MgSO₄, filtered, and concentrated under reduced pressure. The crude mixture was subjected to column chromatography over NEt₃-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**



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 CH₂Cl₂ (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 MgSO₄, filtered, and evaporated. The residue was chromatographed over NEt₃-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

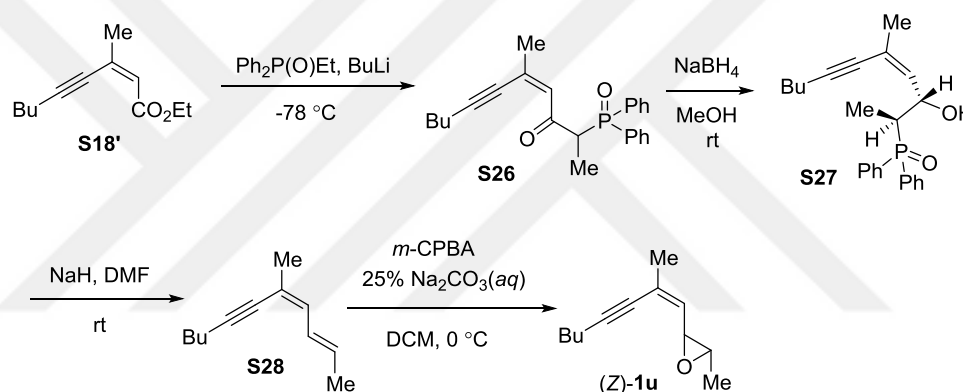


To the dry Et₂O (15 mL) solution of **S7** (1.1 g, 5 mmol) was added an ethereal (15 mL) solution of 2.1 eq. MeMgI (5.25 mL, 10.5 mmol, 2 M) dropwise at $-50\text{ }^\circ\text{C}$, and then the mixture stirred for 6 h at the same temperature. The mixture was allowed to warm to $0\text{ }^\circ\text{C}$ and quenched by the addition of 30 mL of saturated NH₄Cl(aq) solution before extracting with Et₂O. The combined extracts were dried over MgSO₄, filtered, and evaporated. The resulting residue was purified on a silica gel column to afford **S19** (hexane-EtOAc, yield: 0.49 g, 80%).

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 $\text{NH}_4\text{Cl}(\text{aq})$ 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 NaBH₄ (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 NH₄Cl(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 MgSO₄, 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).

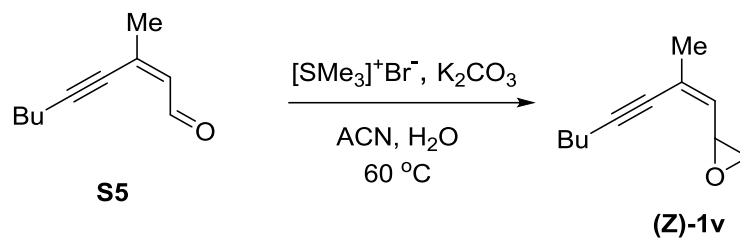
To a stirred solution of **S27** (1.31 g, 3.45 mmol) in DMF (50 ml) was added NaH (60% dispersion in oil; 138 mg, 3.45 mmol) in one portion at ambient temperature and stirred for a further 3 h. The reaction was quenched by the addition 25 mL of water and 15 mL of brine and subsequently extracted with Et₂O. The combined extracts were washed with water, dried over MgSO₄, 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: (R¹= Bu, R²= 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%.

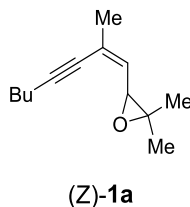
3.2.10. Synthesis of (Z)-1v



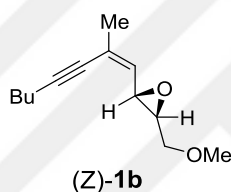
A mixture of 3 mmol (471 mg) trimethylsulfonium bromide, 12 mmol (1.65 g) of K_2CO_3 and 0.48 mmol (8.64 mg) H_2O in 5 ml of acetonitrile was stirred for 5 min at $60\text{ }^\circ\text{C}$. With vigorous stirring, a solution of 2 mmol (300 mg) S5 in 3 ml of acetonitrile was added dropwise and stirred for further 2h at $60\text{ }^\circ\text{C}$. 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

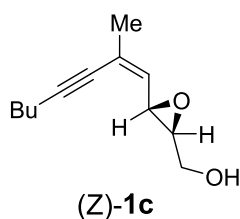
NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm downfield from Me₄Si.



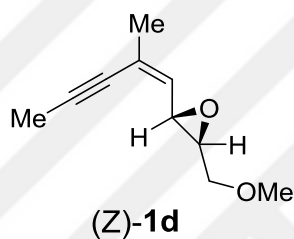
(Z)-1a: ¹H NMR (400 MHz, CDCl₃) δ: 5.38 (dq, *J*= 8.9, 1.5 Hz, 1H), 3.65 (d, *J*= 8.9 Hz, 1H), 2.34 (t, *J*= 6.8 Hz, 2H), 1.87 (s, 3H), 1.56-1.36 (m, 4H), 1.35 (s, 3H), 1.27 (s, 3H), 0.9 (t, *J*= 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 130.7, 125.5, 95.9, 79.1, 62.6, 60.5, 30.9, 24.9, 24.2, 22.1, 19.6, 19.3, 13.7.



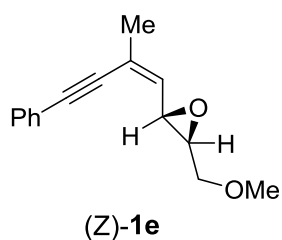
(Z)-1b: ¹H NMR (400 MHz, CDCl₃) δ: 5.23 (dd, *J*= 8.9, 1.2 Hz, 1H), 3.74 (dd, *J*= 8.9, 2.4 Hz, 1H), 3.71 (dd, *J*= 11.6, 3.2 Hz, 1H), 3.40 (dd, *J*= 11.6, 5.7 Hz, 1H), 3.40 (s, 3H), 3.08 (ddd, *J*= 5.7, 3.2, 2.4 Hz, 1H), 2.35 (t, *J*= 7.2 Hz, 2H), 1.87 (d, *J*= 1.2 Hz, 3H), 1.55-1.40 (m, 4H), 0.92 (t, *J*= 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 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.



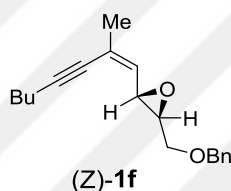
(Z)-1c: ^1H NMR (400 MHz, CDCl_3) δ : 5.25 (dd, J = 9.0, 1.4 Hz, 1H), 3.96 (dd, J = 12.6, 2.3 Hz, 1H), 3.87 (dd, J = 9.0, 2.3 Hz, 1H), 3.68 (dd, J = 12.6, 4.1 Hz, 1H), 3.11-3.09 (m, 1H), 2.36 (t, J = 7.0 Hz, 2H), 1.88 (d, J = 1.4 Hz, 3H), 1.56-1.39 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C { ^1H } NMR (100 MHz, C_6D_6) 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.



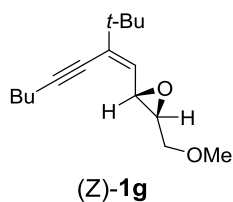
(Z)-1d: ^1H NMR (400 MHz, CDCl_3) δ : 5.23 (d, J =9.0 Hz, 1H), 3.74-3.73 (m, 1H), 3.71 (t, J =4.0 Hz, 1H), 3.41 (s, 3H), 3.40 (dd, J =12.0, 8.0 Hz, 1H), 3.08 (ddd, J =5.7, 3.1, 2.2 Hz, 1H), 2.0 (s, 3H), 1.87 (d, J =1.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 131.6, 125.8, 91.3, 77.8, 72.6, 59.2, 58.4, 54.1, 23.8.



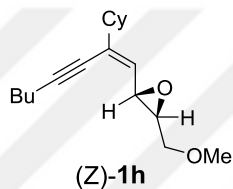
(Z)-1e: ^1H NMR (400 MHz, CDCl_3) δ : 7.46–7.44 (m, 2H), 7.34–7.32 (m, 3H), 5.38 (dq, J = 9.0, 1.5 Hz, 1H), 3.84 (dd, J = 9.0, 2.4 Hz, 1H), 3.74 (dd, J = 11.7, 3.2 Hz, 1H), 3.43 (dd, J = 11.7, 6.0 Hz, 1H), 3.42 (s, 3H), 3.14 (ddd, J = 6.0, 3.2, 2.4 Hz, 1H), 2.00 (d, J = 1.5 Hz, 3H); ^{13}C NMR (100 MHz, 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.



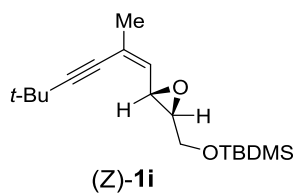
(Z)-1f: ^1H NMR (400 MHz, C_6D_6) δ : 7.24–7.22 (m, 2H), 7.14–7.10 (m, 2H), 7.05 (dt, J = 7.2, 1.6 Hz, 1H), 5.14 (dd, J = 8.9, 1.6 Hz, 1H), 4.35 (d, A of AB, J_{AB} = 12.1 Hz, 1H), 4.31 (d, B of AB, J_{AB} = 12.1 Hz, 1H), 4.01 (dd, J = 8.9, 2.2 Hz, 1H), 3.45 (dd, J = 11.4, 3.0 Hz, 1H), 3.25 (dd, J = 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.



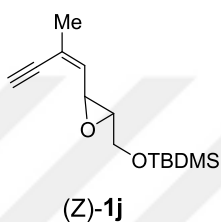
(Z)-1g: ^1H NMR (400 MHz, CDCl_3) δ : 5.24 (d, J = 8.9 Hz, 1H), 3.81 (dd, J = 8.9, 2.4 Hz, 1H), 3.74 (dd, J = 11.2, 3.1 Hz, 1H), 3.42-3.38 (m, 1H), 3.41 (s, 3H), 3.10 (ddd, J = 5.6, 3.1, 2.4 Hz, 1H), 2.39 (t, J = 7.2 Hz, 2H), 1.59-1.41 (m, 4H), 1.11 (s, 9H), 0.93 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 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.



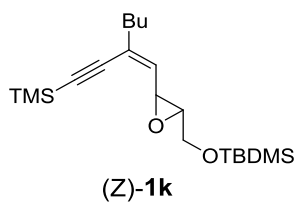
(Z)-1h: ^1H NMR (400 MHz, CDCl_3) δ : 5.21 (d, J = 8.7 Hz, 1H), 3.77 (dd, J = 8.7, 2.4 Hz, 1H), 3.72 (dd, J = 11.5, 3.1 Hz, 1H), 3.38 (dd, J = 11.5, 5.7 Hz, 1H), 3.40 (s, 3H), 3.07 (dt, J = 5.7, 2.4 Hz, 1H), 2.37 (t, J = 7.2 Hz, 2H), 2.02-1.97 (m, 1H), 1.76-1.20 (m, 14H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C 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.



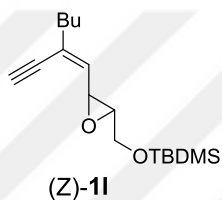
(Z)-1i: ^1H NMR (400 MHz, CDCl_3) δ : 5.21 (d, J = 9.0 Hz, 1H), 3.87 (dd, J = 12.0, 3.2 Hz, 1H), 3.74 (m, 2H), 3.01 (m, 1H), 1.86 (s, 3H), 1.26 (s, 9H), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR: (100 MHz, CDCl_3) δ : 131.6, 125.3, 103.8, 77.1, 62.9, 60.2, 54.3, 31.0, 28.1, 25.9, 23.9, 18.3, -5.3.



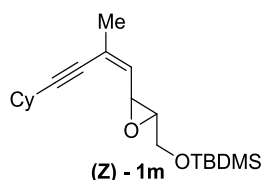
(Z)-1j: ^1H NMR (400 MHz, CDCl_3) δ : 5.41 (dq, J = 8.8, 0.8 Hz, 1H), 3.88 (dd, J =12.1, 3.1 Hz, 1H), 3.80 (dd, J = 9.0, 2.0 Hz, 1H), 3.72 (dd, J = 12.1, 4.7 Hz, 1H), 3.19 (s, 1H), 3.06-3.03 (m, 1H), 1.91 (d, J =1.2 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C NMR: (100 MHz, CDCl_3) δ : 135.4, 123.5, 82.2, 81.7, 62.9, 60.1, 54.0, 25.9, 23.2, 18.3, -5.3.



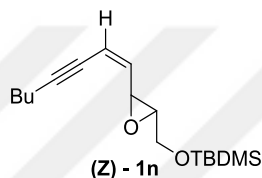
(Z)-1k: ^1H NMR (400 MHz, CDCl_3) δ : 5.32 (dt, $J=9.1, 2.0$ Hz, 1H), 3.88 (dd, $J=12.1, 3.1$ Hz, 1H), 3.81 (dd, $J=9.2, 2.2$ Hz, 1H), 3.75 (dd, $J=11.7, 4.3$ Hz, 1H), 3.03-3.01 (m, 1H), 2.14 (td, $J=7.4, 1.2$ Hz, 2H), 1.53-1.43 (m, 2H), 1.36-1.27 (m, 2H), 0.90 (s, 9H), 0.90 (t, $J=7.6$ Hz, 3H), 0.20 (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: ^1H 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: ^1H 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.

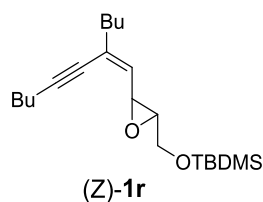


(Z)-1n: ^1H NMR (400MHz, CDCl_3) δ : 5,73 (dtd, $J = 0,8, 2,3, 10,6$ Hz, 1H), 5,45 (dd, $J = 9,0, 11,0$ Hz, 1H), 3,91 (dd, $J = 2,7, 12,1$ Hz, 1H), 3,86 (dd, $J = 1,6, 9,0$ Hz, 1H), 3,74 (dd, $J = 4,3, 11,7$ Hz, 1H), 3,08 - 3,04 (m, 1H), 2,35 (dt, $J = 2,2, 7,1$ Hz, 2H), 1,52 (s, 2H), 1,42 (d, $J = 7,0$ 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.

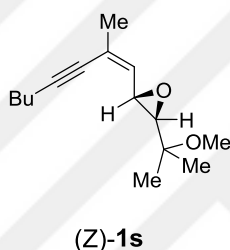


(Z)-1p

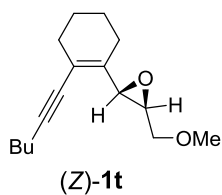
34



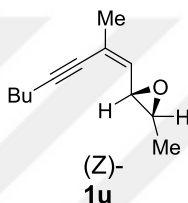
(Z)-1r: ^1H NMR (400 MHz, CDCl_3) δ : 5.23 (d, J = 9.4 Hz, 1H), 3.89 (dd, J =12.1, 3.1 Hz, 1H), 3.80 (dd, J = 9.0, 2.3 Hz, 1H), 3.71 (dd, J =11.9, 4.5 Hz, 1H), 3.02 (dt, J =4.8, 2.5 Hz, 1H), 2.35 (t, J =7.0 Hz, 2H), 2.12 (t, J =7.4 Hz, 2H), 1.54-1.38 (m, 6H), 1.35-1.26 (m, 2H), 0.93 (t, J =7.6 Hz, 3H), 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.



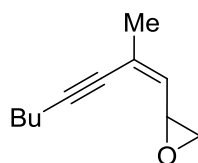
(Z)-1s: ^1H NMR (400 MHz, CDCl_3) δ : 5.24 (dd, J = 8.9, 1.5 Hz, 1H), 3.69 (dd, J = 8.9, 2.3 Hz, 1H), 3.29 (s, 3H), 2.87 (d, J = 2.3 Hz, 1H), 2.36 (t, J = 6.7 Hz, 2H), 1.87 (d, J = 1.5 Hz, 3H), 1.56-1.39 (m, 4H), 1.18 (s, 3H), 1.15 (s, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 132.2, 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: ^1H 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.

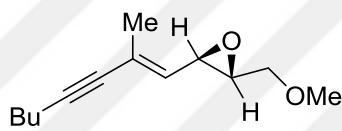


(Z)-1u: ^1H NMR (400 MHz, C_6D_6) δ : 5.16 (dd, J = 8.9, 1.4 Hz, 1H), 3.75 (dd, J = 8.9, 2.1 Hz, 1H), 2.64 (qd, J = 5.4, 2.1 Hz, 1H), 2.08 (t, J = 6.8 Hz, 2H), 1.73 (d, J = 1.4 Hz, 3H), 1.31-1.20 (m, 4H), 1.04 (d, J = 5.2 Hz, 3H), 0.72 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ : 133.7, 123.9,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



(Z)-1v

(Z)-1v: ^1H 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

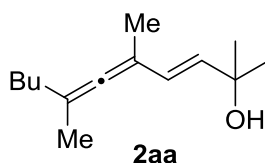
(E)-1b: (400 MHz, CDCl_3) δ : 5.35 (dd, $J= 9.0, 1.0$ Hz, 1H), 3.67 (dd, $J= 11.3, 3.0$ Hz, 1H), 3.48 (dd, $J= 9.0, 2.2$ Hz, 1H), 3.44 (dd, $J= 11.3, 5.1$ Hz, 1H), 3.38 (s, 3H), 3.06 (ddd, $J= 5.1, 3.0, 2.2$ Hz, 1H), 2.28 (t, $J= 6.8$ Hz, 2H), 1.93 (d, $J= 1.0$ Hz, 3H), 1.54-1.37 (m, 4H), 0.90 (t, $J= 7.6$ 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

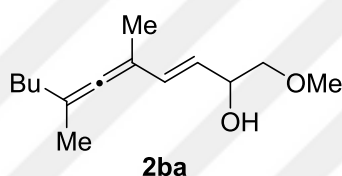
FeCl_2 was weighed into a Schlenck apparatus in glow box, then a gas balloon filled with dry Ar gas (the gas was passed through a P_2O_5 filled glass tube) was attached. THF (2 mL) was added and then stirred for 15 minutes magnetically at a prescribed reaction temperature. The Grignard Reagent was added 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 enynne 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 $\text{NH}_4\text{Cl}_{(\text{aq})}$, 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

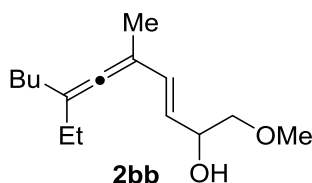
The synthesized alkylation products were analyzed by GC-MS. NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si . Infrared spectra were obtained by ATR method with neat samples. High-resolution mass spectral analyses of new compounds were performed 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.



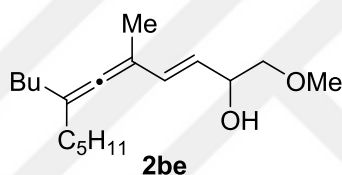
2aa: ^1H NMR (400 MHz, C_6D_6) δ : 6.45 (d, $J=16.0$ Hz, 1H), 5.64 (d, $J=15.6$ Hz, 1H), 1.94 (dt, $J=7.4, 3.6$ Hz, 2H), 1.86 (s, 3H), 1.68 (s, 3H), 1.43 (sextet, $J=7.2$ Hz, 2H), 1.30 (sextet, $J=7.2$ Hz, 2H), 1.19 (s, 6H), 0.94 (bs, 1H), 0.86 (t, $J=7.4$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 204.9, 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3349, 2968, 2934, 2868, 1458, 1367, 1251, 1151, 969, 903.



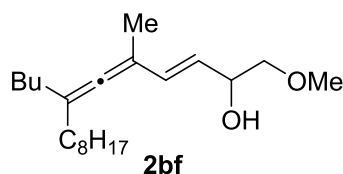
2ba: ^1H NMR (400 MHz, C_6D_6) δ : 6.52 (dd, $J=15.9, 1.2$ Hz, 1H) (Major), 6.51 (dd, $J=15.9, 1.2$ Hz, 1H) (Minor), 5.50 (dd, $J=15.9, 6.0$ Hz, 1H), 4.30 (dddd, $J=7.8, 6.0, 4.0, 1.2$ Hz, 1H), 3.11 (dd, A of ABX, $J_{\text{AB}}=17.4$ Hz, $J_{\text{AX}}=4.0$ Hz, 1H), 3.06 (dd, B of ABX, $J_{\text{AB}}=17.4$ Hz, $J_{\text{BX}}=7.8$ 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(75); FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3471, 2970, 2922, 2853, 1705, 1597, 1480, 1283, 1156, 842, 793, 627.



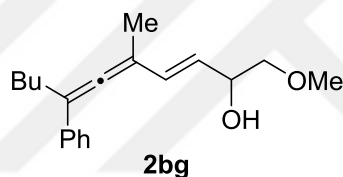
2bb: ^1H NMR (400 MHz, C_6D_6) δ : 6.51 (dd, $J=15.8, 1.2$ Hz, 1H), 5.50 (dd, $J=14.8, 6.0$ Hz, 1H), 4.32-4.24 (m, 1H), 3.13-3.02 (m, 2H), 2.96 (s, 3H), 2.17 (bs, 1H), 1.91-1.83 (m, 4H), 1.80 (s, 3H), 1.43-1.21 (m, 4H), 0.98 (t, $J=7.2$ Hz, 3H) (Major), 0.97 (t, $J=7.6$ Hz, 3H, (Minor)), 0.83 (t, $J=7.6$ 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3441, 2921, 2853, 1460, 1382, 1097, 960, 734, 695



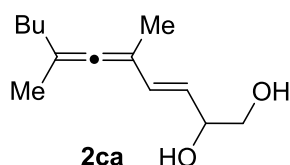
2be: ^1H NMR (400MHz, C_6D_6) δ : 6.57 (dt, $J = 15.8, 1.5$ Hz, 1H), 5.55 (dd, $J = 15.8, 6.1$ Hz, 1H), 4.39 - 4.31 (m, 1H), 3.16 (dd, A of ABX, $\text{JAB} = 9.4$ Hz, $\text{JAX} = 3.5$ Hz, 1H), 3.12 (dd, B of ABX, $\text{JAB} = 9.4$ Hz, $\text{JBX} = 8.3$ Hz, 1H), 3.01 (s, 3H), 2.32 (br. s., 1H), 1.96 (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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3422, 2911, 2853, 1705, 1460, 1264, 1097, 842, 783, 685.



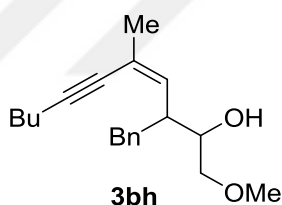
2bf: ^1H NMR (400 MHz, C_6D_6) δ : 6.58 (dt, $J=15.7, 1.76$ Hz, 1H), 5.55 (dd, $J=15.7, 6.06$ Hz, 1H), 4.38 - 4.32 (m, 1H), 3.16 (dd, A of ABX, $J_{\text{AB}} = 9.4$ Hz, $J_{\text{AX}} = 3.6$ Hz, 1H), 3.12 (dd, B of ABX, $J_{\text{AB}} = 9.4$ Hz, $J_{\text{BX}} = 7.9$ Hz, 1H), 3.01 (s, 3H), 2.29 (br. 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3490, 2961, 2931, 2843, 1695, 1617, 1509, 1254, 1097, 1029, 832, 774, 636, 617.



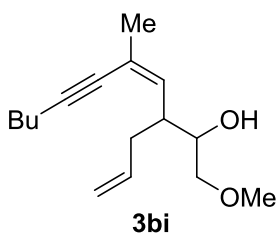
2bg: ^1H NMR (400 MHz, C_6D_6) δ : 7.46 - 7.40 (m, 2H), 7.22 - 7.16 (m, 2H), 7.10 - 7.03 (m, 1H), 6.55 (dd, $J=15.8, 1.4$ Hz, 1H), 5.63 (dd, $J=15.8, 5.9$ Hz, 1H), 4.35 - 4.28 (m, 1H), 3.15 (dd, A of ABX, $J_{\text{AB}} = 9.4$ Hz, $J_{\text{AX}} = 4.3$ Hz, 1H), 3.08 (dd, B of ABX, $J_{\text{AB}} = 9.4$ Hz, $J_{\text{BX}} = 7.8$ 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3433, 2948, 2920, 2855, 1456, 1363, 1195, 1130, 971, 757, 691.



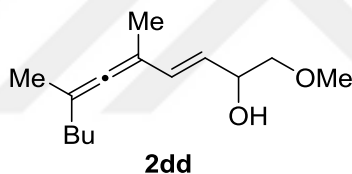
2ca: ^1H NMR (400 MHz, C_6D_6) δ : 6.44 (dd, $J = 1.4, 15.8$ Hz, 1H) (Major), 6.42 (dd, $J = 1.4, 15.8$ Hz, 1H) (Minor), 5.43 (dd, $J = 6.3, 15.7$ Hz, 1H), 4.12 - 4.03 (m, 1H), 3.42 (dd, $J_{AB} = 11.0$ Hz, $J_{AX} = 7.5$ Hz, 1H) (Major), 3.42 (dd, $J_{AB} = 11.0$ Hz, $J_{AX} = 7.5$ Hz, 1H) (Minor), 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3343, 2951, 2921, 2862, 1450, 1372, 1146, 1058, 1029, 960.



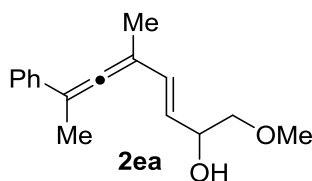
3bh: ^1H NMR (400 MHz, C_6D_6) δ : 7.36 (d, $J=7.0$ Hz, 2H), 7.21 (t, $J=7.4$ Hz, 2H), 7.08 (t, $J=7.40$ Hz, 1H), 5.95 (dd, $J=9.4, 1.2$ Hz, 1H), 3.91 (dt, $J=8.8, 2.8$ Hz, 1H), 3.33 - 3.27 (m, 1H), 3.22 - 3.10 (m, 3H), 2.97 (s, 3H), 2.86 (dd, B of ABX, $J_{AB} = 11.7$ Hz, $J_{BX} = 4.7$ Hz, 1H), 2.29 (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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3402, 2921, 2878, 1500, 1441, 1088, 1039, 960, 754, 695.



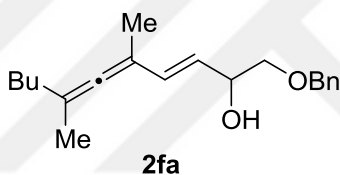
3bi: ^1H NMR (400 MHz, C_6D_6) δ : 5.94 (ddt, $J=17.0, 10.1, 7.1$ Hz, 1H), 5.82 (dd, $J=9.8, 1.4$ Hz, 1H), 5.15 (dq, $J=17.0, 1.3$ Hz, 1H), 5.05 (dt, $J=10.0, 1.3$ Hz, 1H), 3.97 (ddd, $J=7.2, 4.3, 3.3$ Hz, 1H), 3.28 - 3.37 (m, 2H), 3.06 (s, 3H), 3.05 – 2.96 (m, 2H), 2.53 (dt, $J=14.1, 7.1$ Hz, 1H), 2.38 (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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3412, 2931, 2862, 1695, 1607, 1509, 1254, 1156, 1117, 1039, 842, 617.



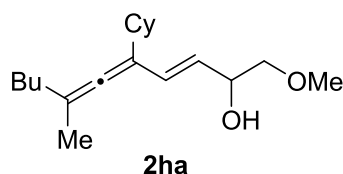
2dd: ^1H NMR (400 MHz, C_6D_6) δ : 6.56 (dd, $J=15.9, 1.4$ Hz, 1H) (Minor), 6.55 (dd, $J = 15.8, 1.4$ Hz, 1H) (Major), 5.54 (dd, $J = 15.9, 6.0$ Hz, 1H), 4.38 - 4.30 (m, 1H), 3.19 - 3.07 (m, 2H), 3.01 (s, 3H) (Major), 3.00 (s, 3H) (Minor), 2.26 (br. s., 1H), 1.91 (t, $J=7.20$ Hz, 2H) (Major), 1.90 (t, $J = 7.2$ 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3432, 2926, 2851, 1450, 1367, 1193, 1127, 961, 612.



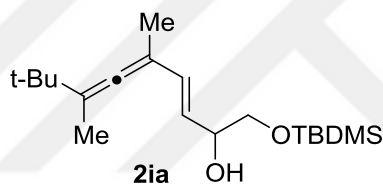
2ea: ^1H NMR (400 MHz, C_6D_6) δ : 7.44 – 7.36 (m, 2H), 7.21 – 7.12 (m, 2H), 7.09 – 7.01 (m, 1H), 6.52 (ddd, $J = 1.4, 4.3, 15.8$ Hz, 1H), 5.63 (dd, $J = 6.1, 15.8$ Hz, 1H), 4.31 (dd, $J = 1.6, 5.5$ Hz, 1H), 3.13 (dd, $J_{AB} = 9.4$ Hz, $J_{AX} = 7.9$ Hz, 1H), 3.10 (dd, $J_{AB} = 9.4$ Hz, $J_{BX} = 3.4$ 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3450, 2926, 2852, 1500, 1450, 1367, 1193, 1127, 1068, 961, 754, 704, 612.



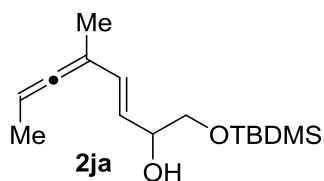
2fa: ^1H NMR (400 MHz, C_6D_6) δ : 7.26 – 7.12 (m, 4H), 7.12 – 7.04 (m, 1H), 6.56 (ddd, $J = 1.4, 4.0, 15.7$ Hz, 1H), 5.52 (ddd, $J = 0.8, 4.0, 16.0$ Hz, 1H), 4.44 – 4.34 (m, 1H), 4.25 (s, 2H), 3.30 (dd, $J_{AB} = 9.3$ Hz, $J_{AX} = 8.0$ Hz, 1H), 3.23 (dd, $J_{AB} = 9.3$ Hz, $J_{BX} = 3.4$ Hz, 1H), 2.31 (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 (101 MHz, 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3427, 2924, 2848, 1946, 1661, 1462, 1358, 1110, 1025, 977, 740, 683.



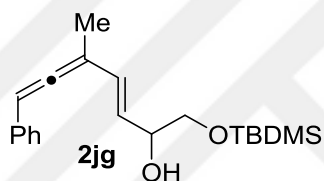
2ha: ^1H NMR (400 MHz, C_6D_6) δ : 6.40 (dd, $J = 1.6, 16.0$ Hz, 1H), 5.77 (dd, $J = 5.9, 16.0$ Hz, 1H), 4.39 - 4.30 (m, 1H), 3.20 - 3.09 (m, 2H), 2.99 (s, 3H), 2.22 - 2.12 (m, 2H), 1.98 - 1.90 (m, 2H), 1.78 - 1.71 (m, 2H), 1.69 (s, 3H), 1.63 - 1.59 (m, 1H), 1.50 - 1.40 (m, 2H), 1.37 - 1.14 (m, 8H), 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3440, 2918, 2860, 1450, 1193, 1127, 969, 894.



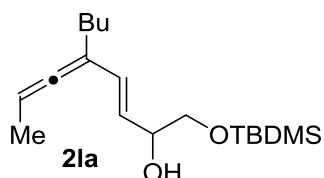
2ia: ^1H NMR (400 MHz, C_6D_6) δ : 6.57 (dd, $J = 1.2, 15.7$ Hz, 1H) (Major), 6.55 (dd, $J = 1.2, 15.7$ Hz, 1H) (Minor), 5.57 (dd, $J = 5.9, 15.7$ Hz, 1H), 4.30 - 4.24 (m, 1H), 3.54 (dd, $J_{\text{AB}} = 10.0$ Hz, $J_{\text{AX}} = 7.3$ Hz, 1H), 3.44 (dd, $J_{\text{AB}} = 10.0$ Hz, $J_{\text{BX}} = 4.1$ 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3440, 2951, 2910, 2852, 1467, 1359, 1251, 1112, 961, 836, 787.



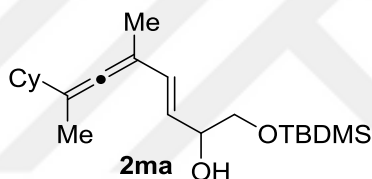
2ja: ^1H NMR (400 MHz, C_6D_6) δ : 6.54 (td, $J = 1.2, 15.7$ Hz, 1H), 5.56 (ddd, $J = 1.4, 6.0, 15.7$ Hz, 1H), 5.16 – 5.05 (m, 1H), 4.31 – 4.18 (m, 1H), 3.52 (dd, $J_{AB} = 9.9$ Hz, $J_{AX} = 7.3$ Hz, 1H), 3.41 (dd, $J_{AB} = 9.9$ Hz, $J_{BX} = 4.1$ Hz, 1H), 1.80 (d, $J = 2.7$ Hz, 3H), 1.52 (d, $J = 7.0$ 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3424, 2934, 2852, 1707, 1467, 1375, 1256, 1110, 824, 762, 670.



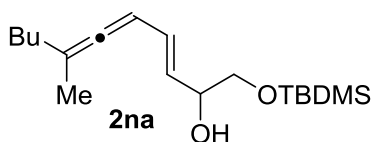
2jg: ^1H NMR (400 MHz, C_6D_6) δ : 7.26 – 7.22 (m, 2H), 7.12 (s, 2H), 7.04 – 6.98 (m, 1H), 6.53 (td, $J = 1.4, 15.7$ Hz, 1H) (Minor), 6.52 (td, $J = 1.4, 15.7$ Hz, 1H) (Major), 6.24 – 6.18 (m, 1H), 5.66 (qdd, $J = 1.2, 5.9, 15.7$ Hz, 1H), 4.26 – 4.19 (m, 1H), 3.51 (dd, $J_{AB} = 9.9$ Hz, $J_{AX} = 7.5$ 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3523, 2926, 2835, 2735, 1682, 1599, 1583, 1516, 1317, 1251, 1151, 1010, 836, 621.



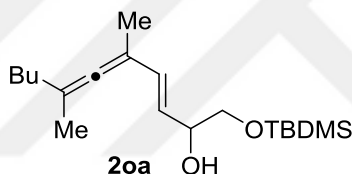
2la: ^1H NMR (400 MHz, C_6D_6) δ : 6.49 (d, $J = 16.0$ Hz, 1H), 5.70 (dd, $J = 7.0$, 11.7 Hz, 1H), 5.24 - 5.13 (m, 1H), 4.77 - 4.74 (m, 1H) (Minor), 4.31 - 4.21 (m, 1H) (Major), 3.50 (dd, $J_{AB} = 10.0$ Hz, $J_{AX} = 7.5$ Hz, 1H), 3.40 (dd, $J_{AB} = 10.0$ Hz, $J_{BX} = 4.7$ Hz, 1H), 2.16 (dd, $J = 3.5$, 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3432, 2951, 2934, 2860, 1707, 1475, 1359, 1251, 1102, 836, 770.



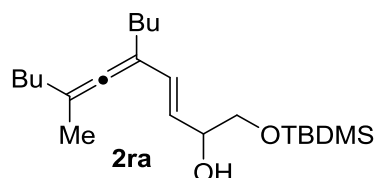
2ma: ^1H NMR (400 MHz, C_6D_6) δ : 6.58 (ddd, $J = 1.2$, 3.1, 16.0 Hz, 1H), 5.57 (ddd, $J = 0.8$, 5.9, 15.7 Hz, 1H), 4.34 - 4.23 (m, 1H), 3.54 (dd, $J_{AB} = 8.7$ Hz, $J_{AX} = 5.4$ Hz, 1H), 3.45 (dd, $J_{AB} = 8.7$ Hz, $J_{BX} = 0.5$ Hz, 1H), 2.35 (dd, $J = 2.0$, 12.5 Hz, 1H), 1.86 (d, $J = 0.8$ Hz, 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 ($<1\text{M}^+$), 275(5), 201(20), 187(15), 159(20), 145(25), 119(65), 105(55), 75(100), 67(40), 55(50); FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3424, 2943, 2860, 1450, 1384, 1259, 1118, 977, 845, 787, 670.



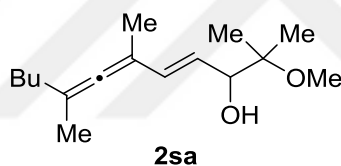
2na: ^1H NMR (400 MHz, C_6D_6) δ : 6.40 (ddd, $J = 1.2, 10.6, 15.3$ Hz, 1H), 5.88 (qd, $J = 2.7, 10.6$ Hz, 1H), 5.56 (dd, $J = 5.9, 15.3$ Hz, 1H), 4.24 – 4.14 (m, 1H), 3.48 (dd, $J_{\text{AB}} = 9.8$ Hz, $J_{\text{AX}} = 7.5$ Hz, 1H), 3.38 (dd, $J_{\text{AB}} = 9.8$ Hz, $J_{\text{BX}} = 3.9$ Hz, 1H), 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3433, 2958, 2929, 2861, 1454, 1357, 1260, 1124, 959, 833, 765.



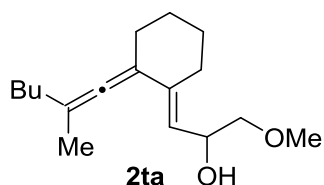
2oa: ^1H NMR (400 MHz, C_6D_6) δ : ppm 6.59 (dd, $J=15.8, 1.4$ Hz, 1H), 5.57 (dd, $J=15.8, 6.1$ Hz, 1H), 4.31 – 4.24 (m, 1H), 3.54 (dd, $J_{\text{AB}} = 9.8$ Hz, $J_{\text{AX}} = 7.5$ Hz, 1H), 3.43 (dd, $J_{\text{AB}} = 9.8$ Hz, $J_{\text{BX}} = 3.9$ Hz, 1H), 1.95 – 1.88 (m, 2H), 1.86 (s, 3H), 1.65 (s, 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3430, 2942, 2854, 1454, 1366, 1246, 1103, 972, 863, 786.



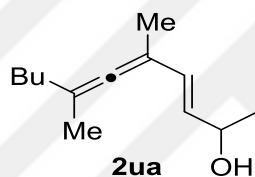
2ra: ^1H NMR (400 MHz, C_6D_6) δ : 6.52 (dd, $J = 1.2, 15.7$ Hz, 1H), 5.69 (dd, $J = 6.3, 16.0$ Hz, 1H), 4.32 – 4.23 (m, 1H), 3.56 (dd, $J_{AB} = 9.8$ Hz, $J_{AX} = 7.5$ Hz, 1H), 3.46 (dd, $J_{AB} = 9.8$ Hz, $J_{BX} = 4.3$ Hz, 1H), 2.22 (t, $J = 7.4$ Hz, 2H), 1.94 (t, $J = 6.7$ Hz, 2H), 1.68(s, 3H) (Major) – 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3432, 2960, 2934, 2851, 1467, 1367, 1259, 1110, 969, 836, 787, 679



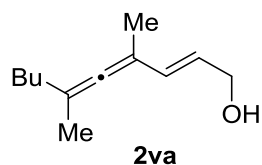
2sa: ^1H NMR (400 MHz, C_6D_6) δ : 6.58 (d, $J=15.6$ Hz, 1H), 5.68 (dd, $J = 6.7, 15.7$ Hz, 1H) (Minor), 5.67 (dd, $J = 6.7, 15.7$ Hz, 1H) (Major), 4.08 (d, $J = 6.8$ Hz, 1H), 2.91 (s, 3H), 2.51-2.49 (m, 1H), 1.94-1.89 (m, 2H), 1.86 (s, 3H), 1.65 (s, 3 H)(Major), 1.63 (s, 3H) (Minor), 1.40 (quint, $J=7.2$ 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3449, 2960, 2926, 2868, 1475, 1367, 1151, 1068, 961, 737, 621.



2ta: ^1H 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3440, 2926, 2843, 1748, 1657, 1442, 1209, 1127, 1077, 969, 903, 621.



2ua: ^1H 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 (dq, $J=1.0, 6.3$ 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3500, 2951, 2872, 1695, 1597, 1519, 1264, 1166, 1029, 832, 774, 607.



2va: ^1H 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): 3324, 2960, 2934, 2876, 1442, 1359, 1094, 1002, 969.

CHAPTER 4

RESULTS AND DISCUSSION

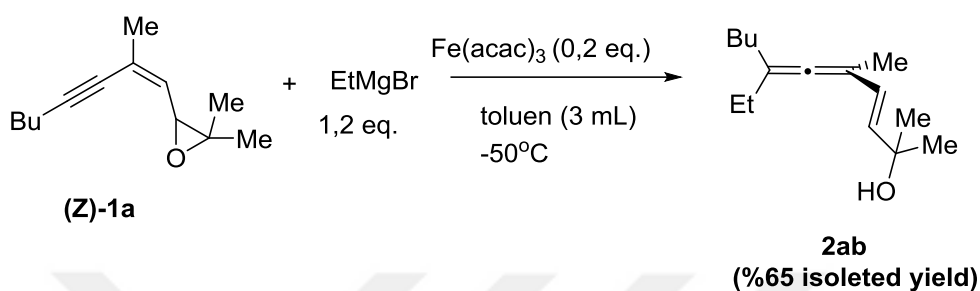
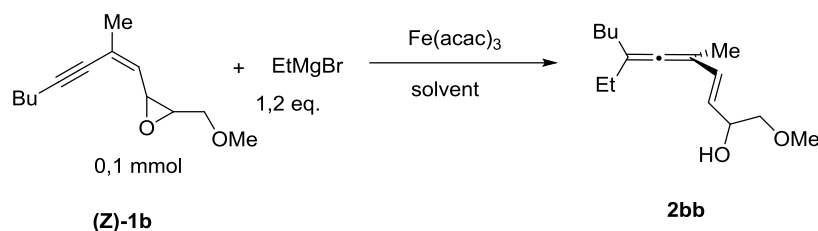


Figure 4.1. 1,5-(SN_2'') reaction of Z-1a reagent with iron-catalyzed Grignard reagent

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. The 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 diastereomeric 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



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 ₂ O	direct	-50	1.5:1	78 ^b
7	0.2	Et ₂ O	direct	-50	1.6:1	70
8	1.0	Et ₂ O	Syringe pump (15 min.)	-50	1.5:1	67
9	1.0	Et ₂ O	Syringe pump (15 min.)	-50	1.5:1	64
10	1.0	Et ₂ O	direct	-80	2.2:1	70
11	0.2	Et ₂ O	direct	-80	not detected	39
12	0.2	Et ₂ O	Syringe pump (15 min.)	-80	not detected	40
13	1.0	Et ₂ O	direct	-20	1:1	48
14	-	Et ₂ O	direct	-50	-	-

^a It is detected by using ¹H-NMR method and benzaldehyde internal standard compound.

^b Isolated yield.

^c Diastereoselectivity ratio was determined by ¹H NMR.

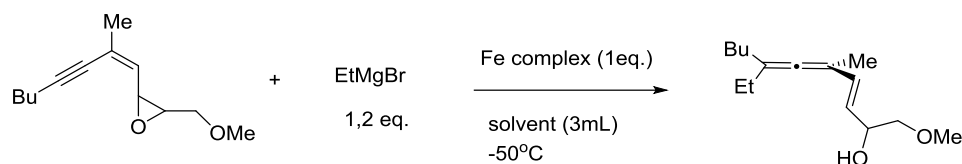
Instead of the formation of vinylallene after the reaction performed with (Z)-1b, a complex mixture was observed to form under the reaction conditions that is executed with (Z)-1a. Even increasing the iron complex loading from 0.2 equivalent to 1.0 and

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 °C. The yield of this reaction where iron complex was 1.0 equivalent was comparable to that performed at -50 °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 °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 ₂ O	-	0
2	FeCl ₂	THF	1:1	81
3	FeBr ₂	Et ₂ O	not detected	15
4	FeBr ₂	THF	1:1	44
5	FeCl ₃	THF	-	0
6	Fe(OTf) ₃	Et ₂ O	-	0
7 ^c	FeCl ₂	THF	1:1	20

^a Detected by using ¹H-NMR method and benzaldehyde internal standard compound.

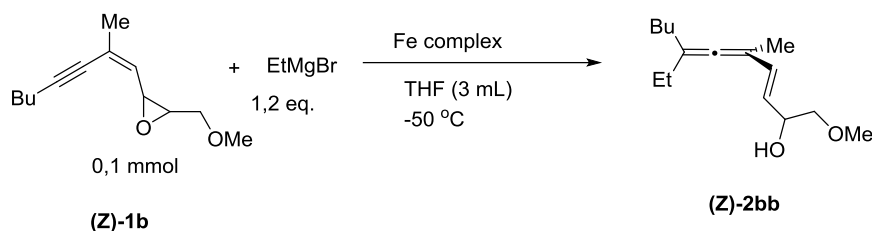
^b Diastereoselectivity ratio was determined by ¹H NMR.

^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 FeCl₂ in Et₂O (No:1). This may be due to insufficient solubility of FeCl₂ in Et₂O. FeCl₂ 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 stereo-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



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'-bipyridine (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 ¹H-NMR method and benzaldehyde internal standard compound.

^b Diastereoselectivity ratio was determined by ¹H NMR.

^c Equivalents were given based on iron complex.

In the reactions of (Z)-1b reagent with FeCl₂ 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 organocopper² or Grignard⁹ 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 FeCl₂-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 % FeCl₂ 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 enlarged (Figure:4.1).

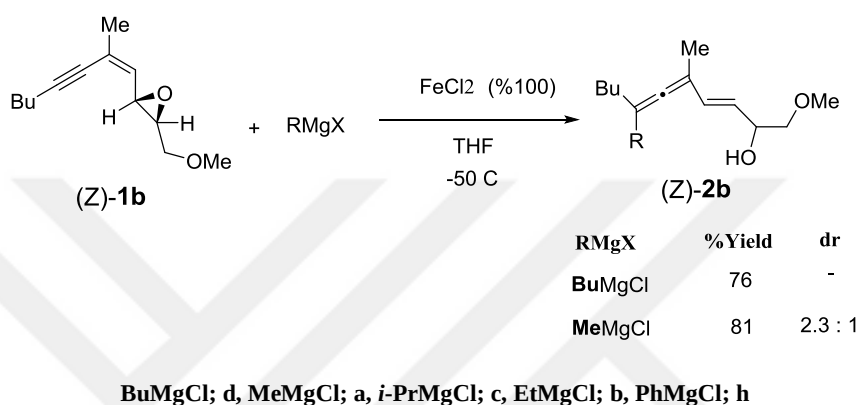


Figure.4.2 Reaction of (Z)-**1b** with different Grignard reagent

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)

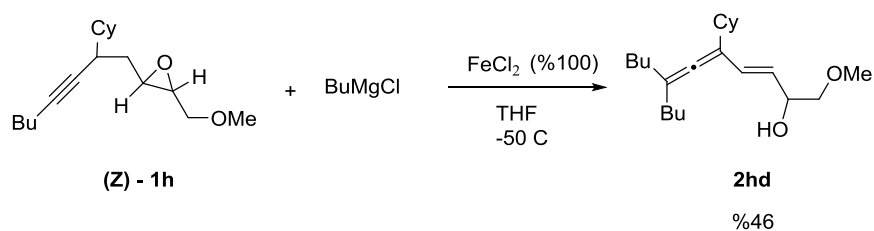
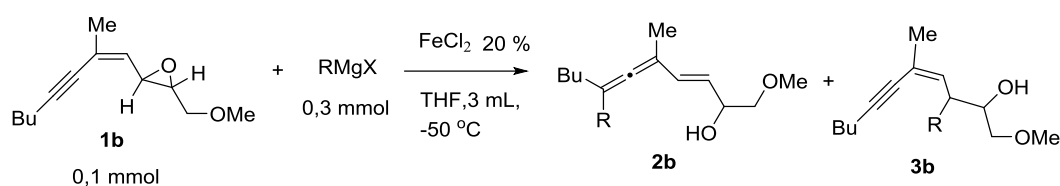


Figure.4.3 Presence of a cyclohexyl group on the alkenyl carbon reaction with BuMgCl

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), $\text{S}_{\text{N}}2$ products were the only structures that recovered at the end of the reactions. It is thought that $\text{S}_{\text{N}}2$ 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	MeMgI	82 (1.7: 1)	-	55min.
2	EtMgCl	75 (1: 1)	-	65min.
3	n-C ₅ H ₁₁ MgCl	83 (1.8: 1) ^b	-	120min.
4	n-C ₈ H 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.

^ad.r.: diastereomeric ratio. ^bd r: determined by HPLC. ^cC: 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).

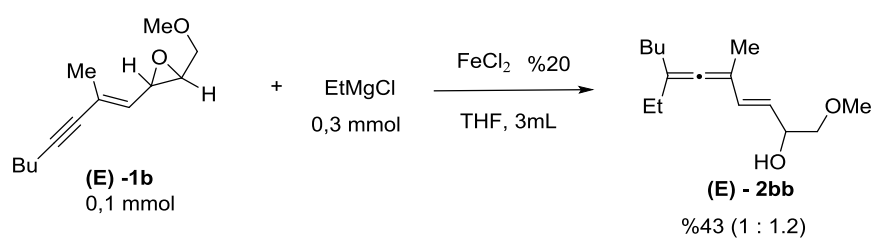


Figure.4.4 The reactions of enyn oxirane (*E*)-1b with EtMgCl

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 R₃ 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 R¹ position reaction result as similar as butyl group in R¹ 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 R¹ position and thus the vinylallene compound (**2ma**) could be obtained at the yield of 81% (No 5).

Increasing the size of R¹ 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 benefited by the reactions with (CH₃)₂CHMgCl and PhMgCl, low yields being obtained with these reactions.

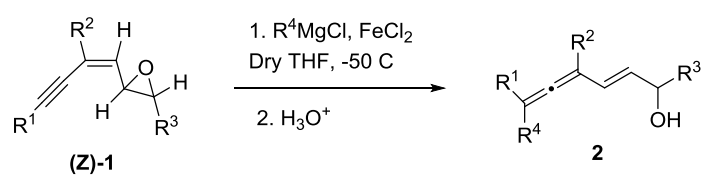
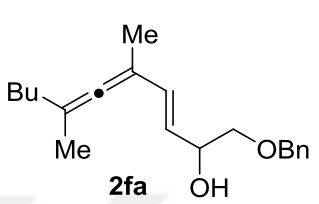
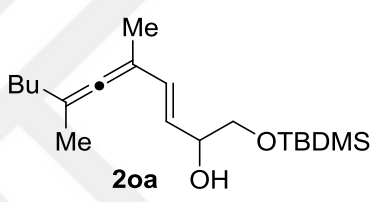
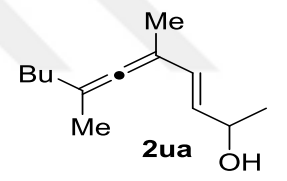
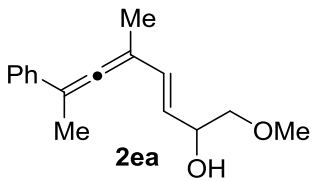
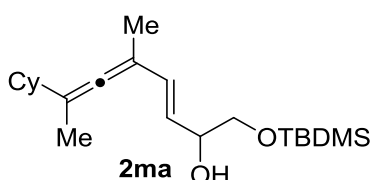
The method was also successfully applicable for those enyne oxiranes containing only disubstituted alkenyl group (**1n**) or for that when R₂ is butyl (**1r** and **1l**). (No: 12-14). On the other hand, when R² group was cyclohexyl, reaction yield obtained in a low level 55%. (No 16). Reaction conditions effected negatively when R² group was bulky.

The presence of the bulky Me₃Si 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)

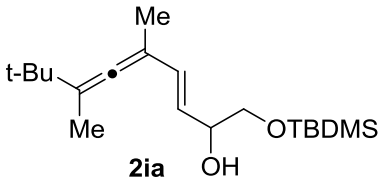
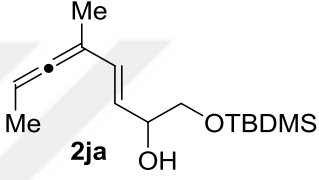
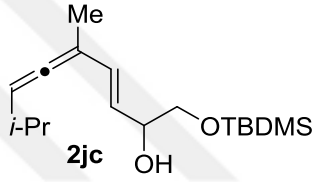
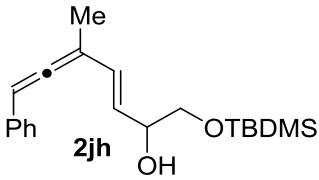
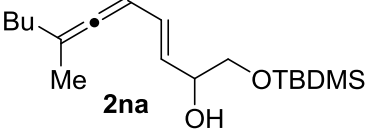


Table 4.5. Fe-catalysed Reactions of enyne oxirane with Grignard Reagents.

 (Z)-1 2						
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

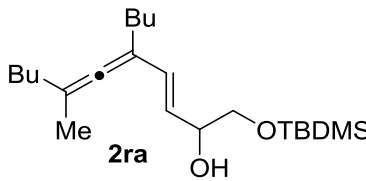
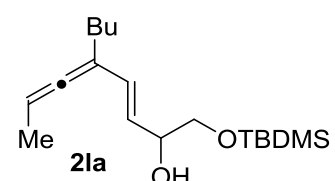
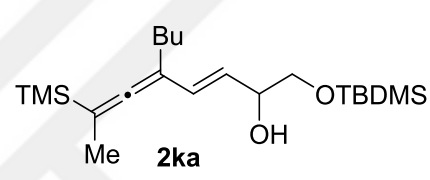
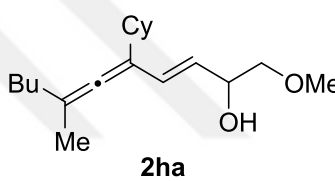
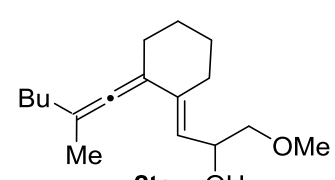
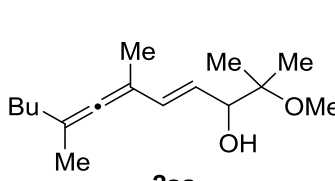
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Table 4.5 (cont.)

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>i</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

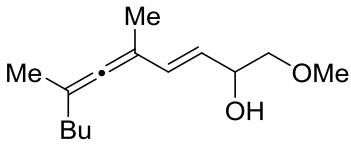
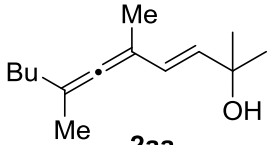
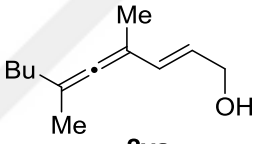
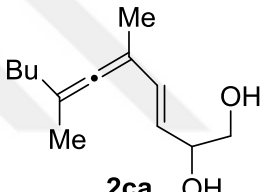
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Table 4.5 (cont.)

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

(cont. on next page)

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.

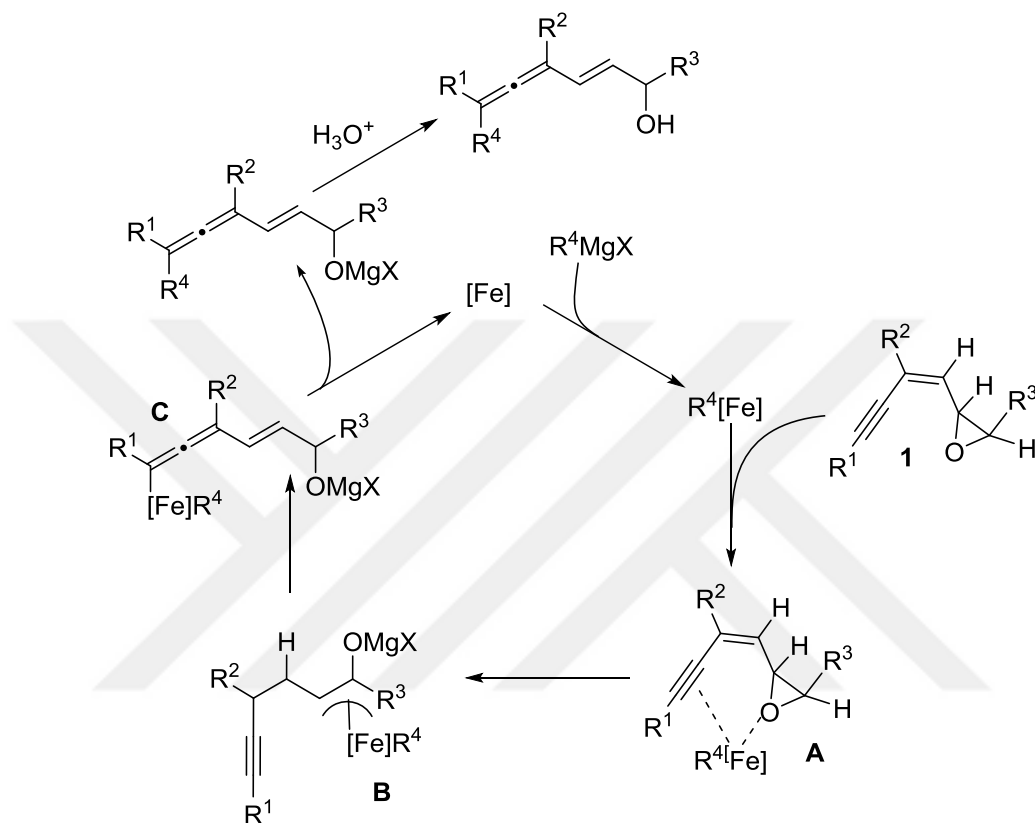


Figure.4.5 Presence of a cyclohexyl group on the alkenyl carbon reaction with BuMgCl

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

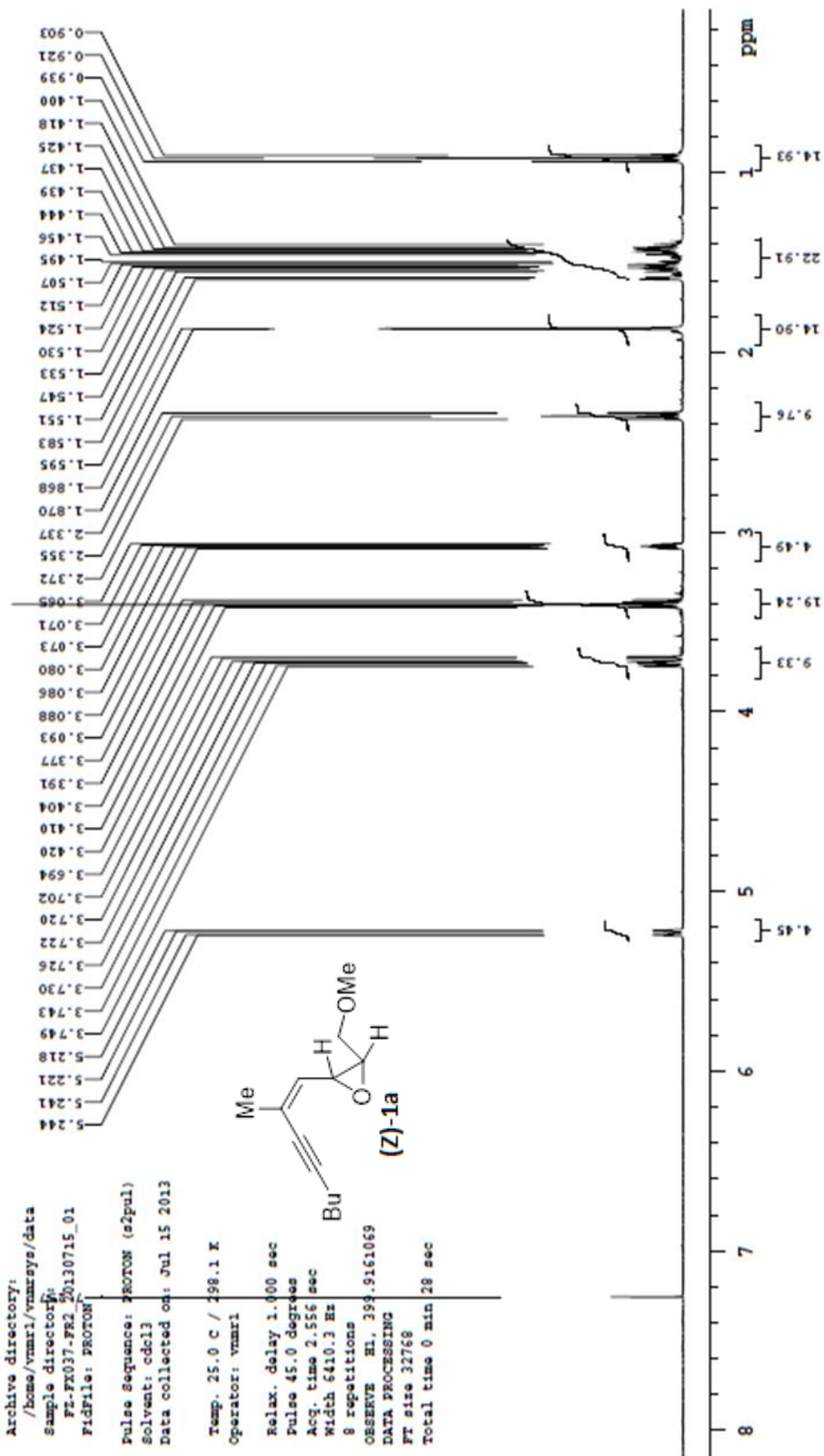
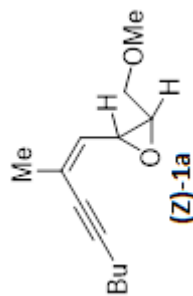
^1H AND ^{13}C SPECTRUM OF REACTANTS



Gradient Shimming

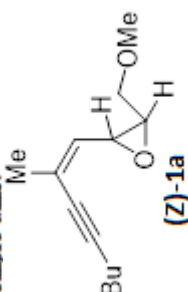


Sample Name:
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Data Collected on:
vnmrs400-vnmrs400
Archive directory:
/home/vnmr1/vnmrsys/data
Sample directory:
F2-FX037-FR2_20130715_01
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jul 15 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.00 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 640.3 Hz
8 repetitions
OBSERVE H1, 399.9161069
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec



PZ-FX049-13C

Sample Name:



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, 399.91065 MHz

Power 46 dB

continuously on

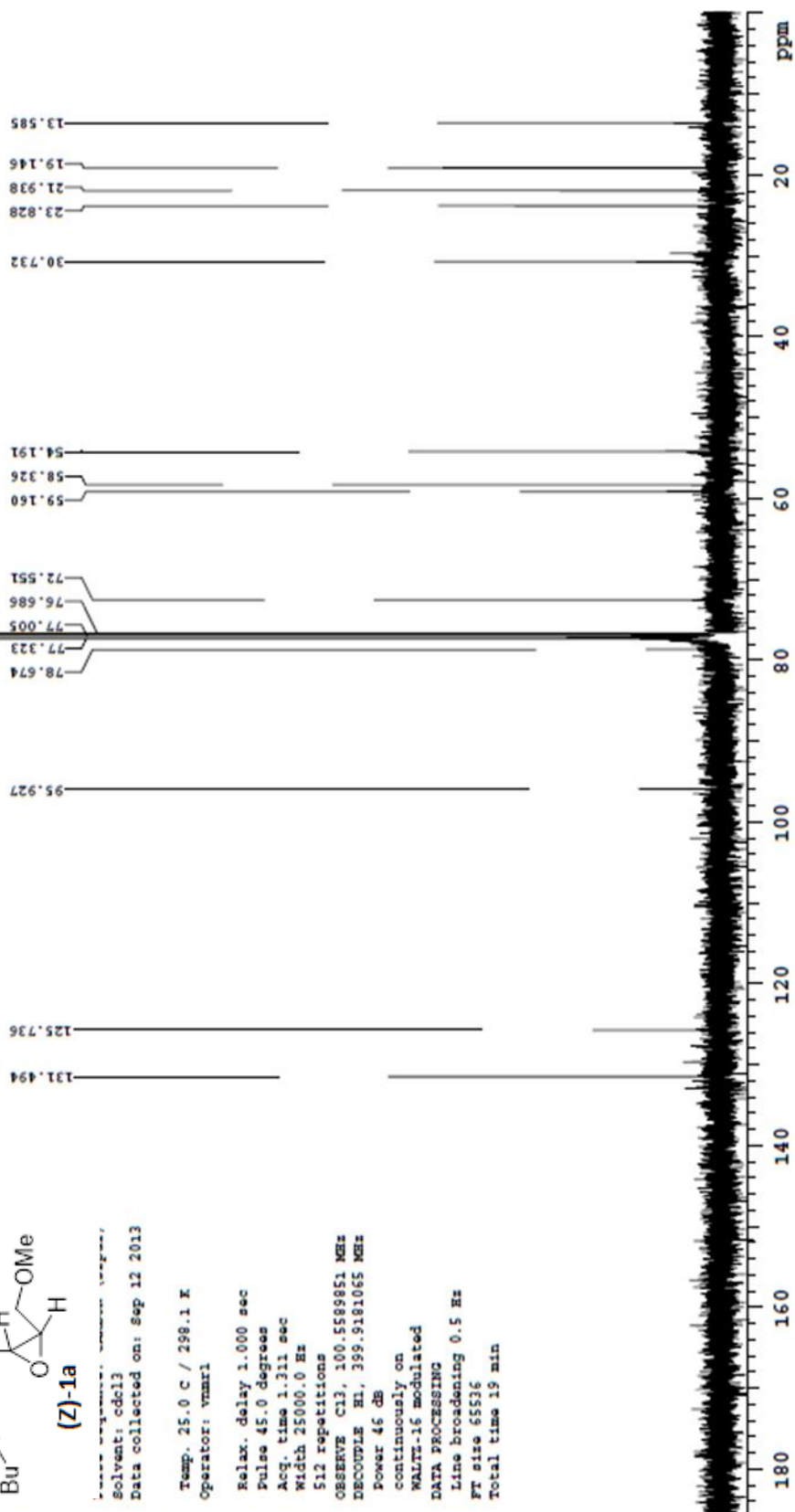
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

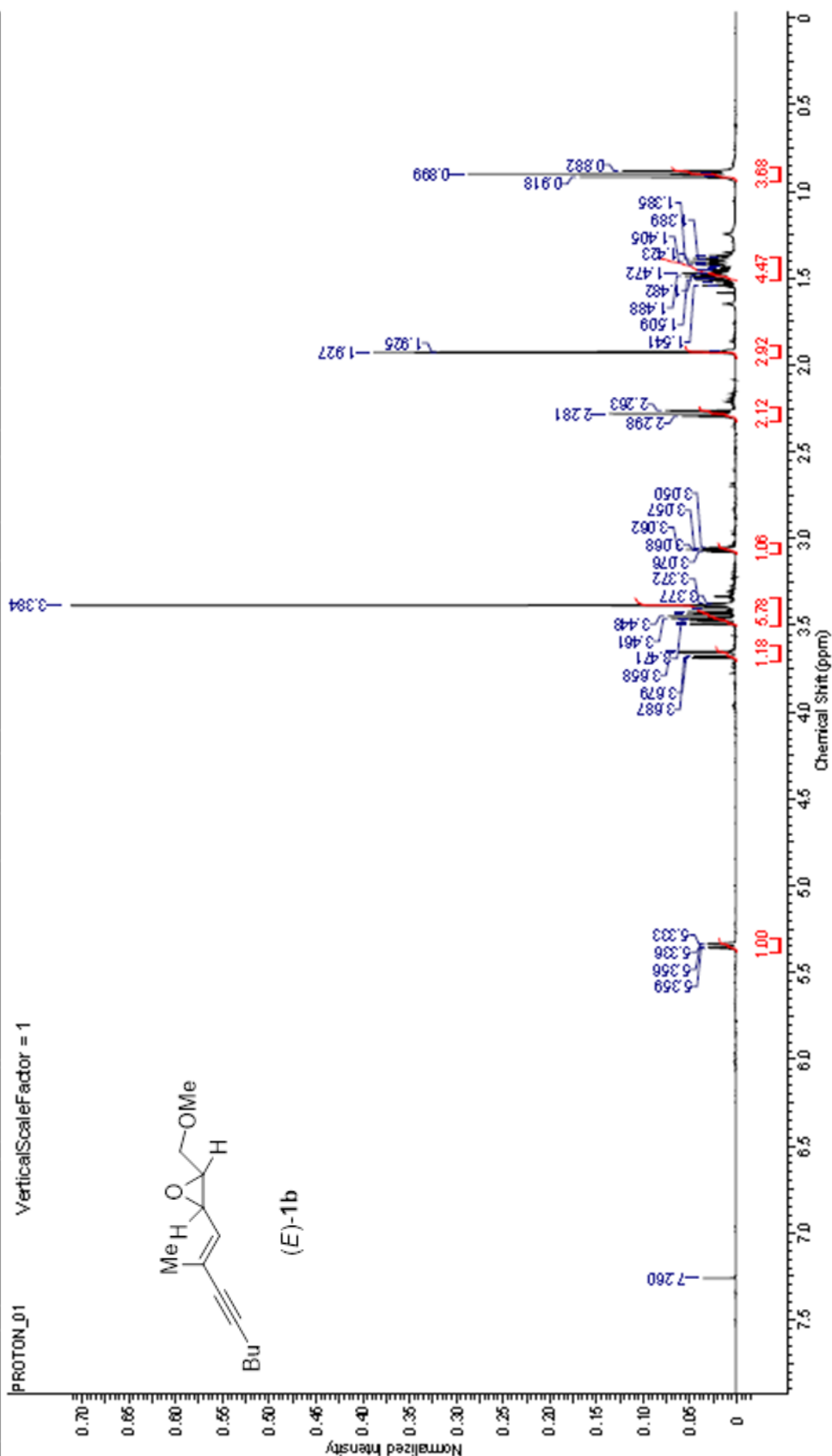
FT size 65536

Total time 19 min



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Date Stamp	Dec 19 2013	File Name	C:\USERS\FIRAT\BESKTOP\MELHMHK-1812\0ME 20131219_01\PROTON_01.FID\AQ	Original Points Count	16394
Frequency (MHz)	399.92	Nucleus	¹ H	Solvent	CHLOROFORM-d
Points Count	16394	Pulse Sequence	s2pul	Temperature (degree C)	25.000
Spectrum Offset (Hz)	2399.5020	Spectrum Type	STANDARD		

Vertical Scale Factor = 1



NR-18120ME

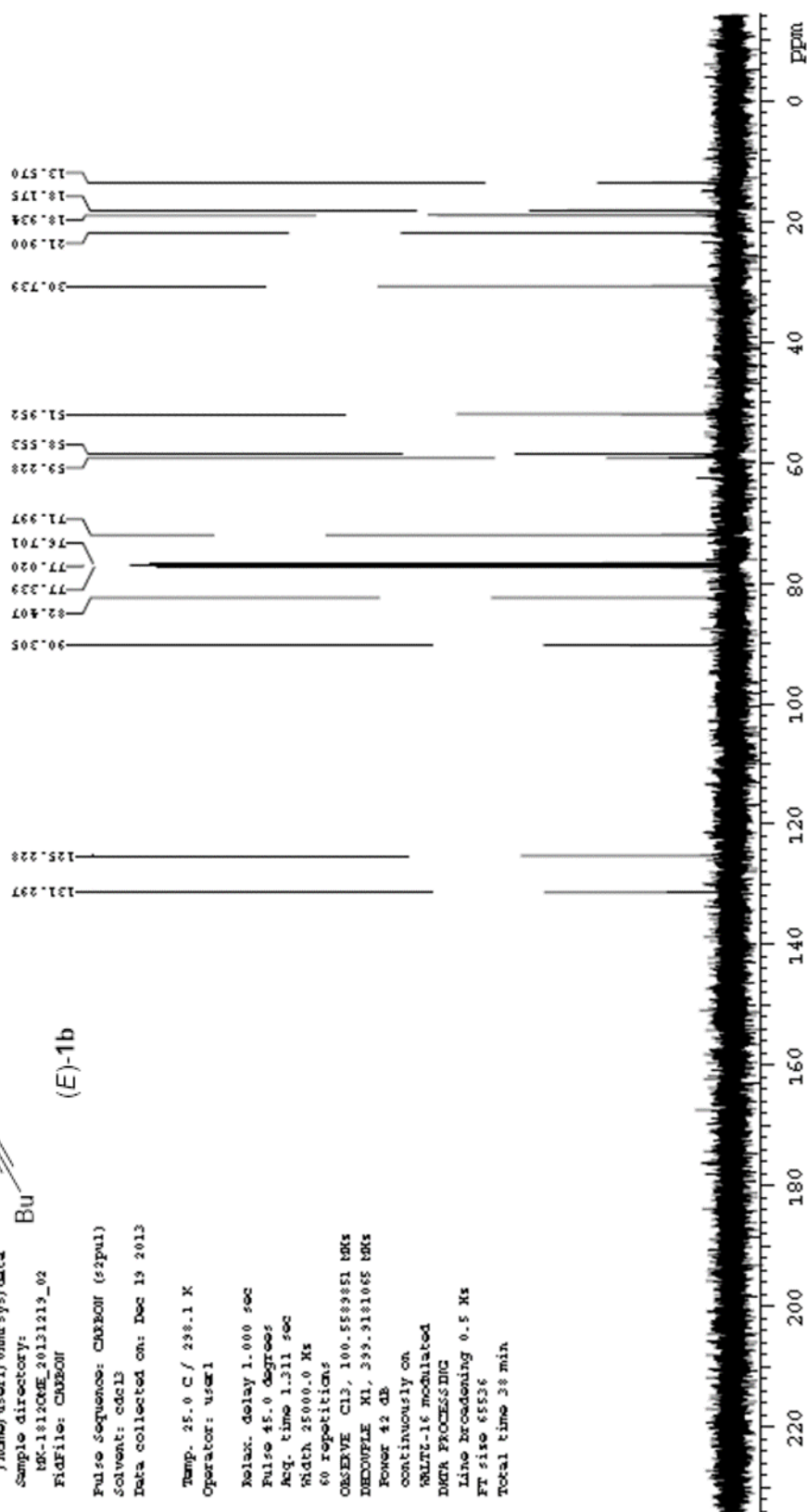
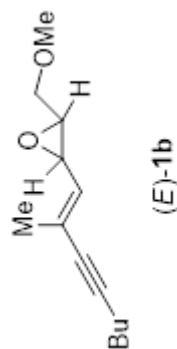
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NR-18120ME
Data Collected on:
vnmr5400-vnmr5400
Archive directory:
/home/user1/vnmr5400/data
Sample directory:
NR-18120ME_20131219_02
FidFile: C00000

Pulse Sequence: C00000 (s2pul)
Solvent: cdcl3
Data collected on: Dec 19 2013

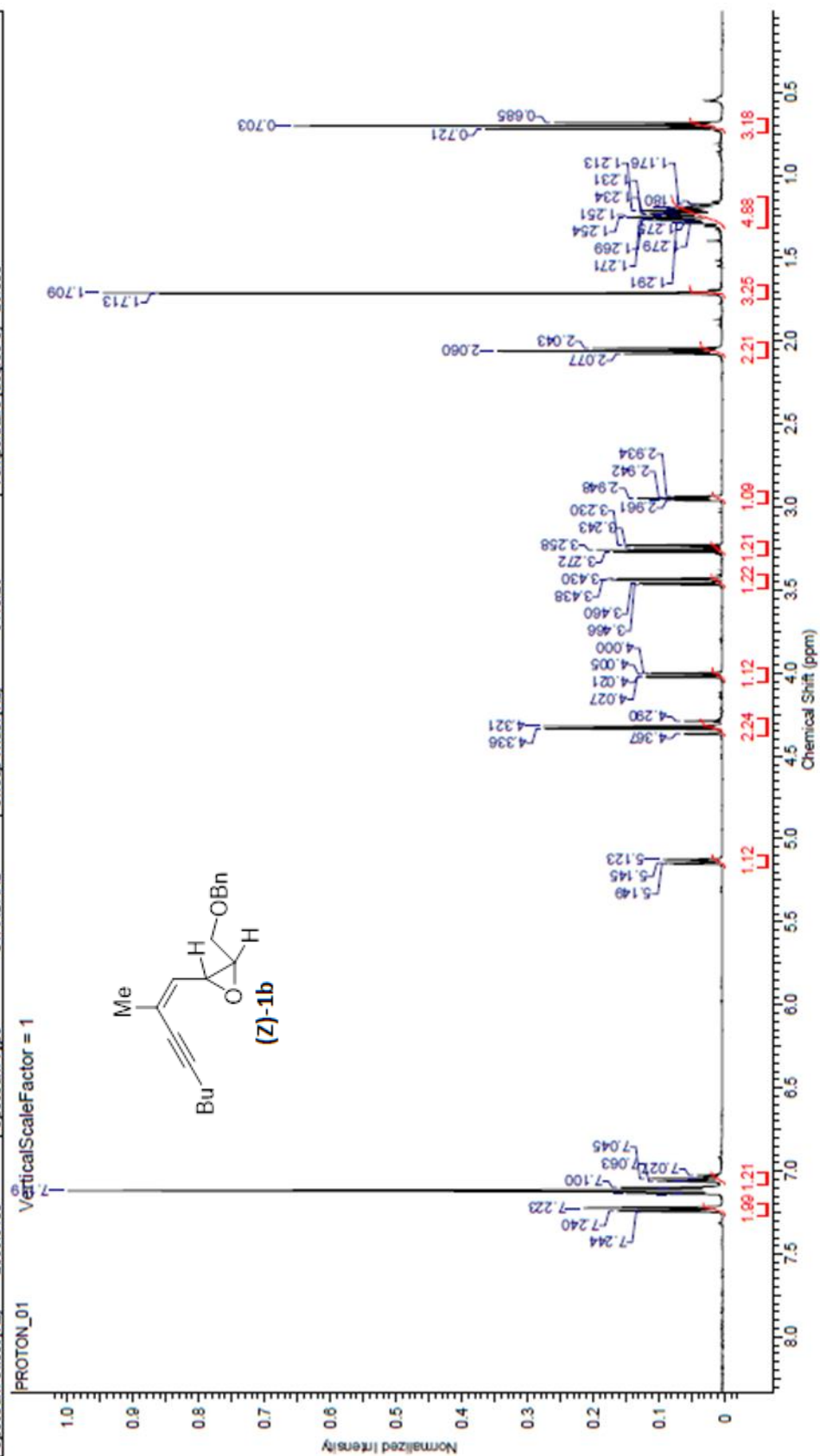
Temp. 25.0 C / 298.1 K
Operator: user1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
60 repetitions

OBSERVE C13, 100.550051 MHz
DECOUPLE X1, 399.3101045 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min



Acquisition Time (sec)	2.5559	Comment	MK-OBN-EPO-TEK	Date	Feb 25 2013
Date Stamp	Feb 25 2013	File Name	C:\USERS\FRATIDESK\TOP\EPOXIDE\210T092-FINAL RAPORUN\MR		
Frequency (MHz)	399.92	Nucleus	¹ H	Original Points Count	16384
Points Count	16384	Pulse Sequence	s2pul	Solvent	BENZENE-d6
Spectrum Offset (Hz)	2399.5100	Spectrum Type	STANDARD	Temperature (degree C)	25.000



MX-OTBS-REACT

Sample Name:

MX-OTBS-REACT

Data Collected on:

vmars400-vmars400

Archive directory:

/home/user1/vmarsys/data

Sample directory:

MX-OTBS-REACT_20140930_01

FidFile: PROTON_01

Pulse Sequence: PROTON (zgpg30)

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

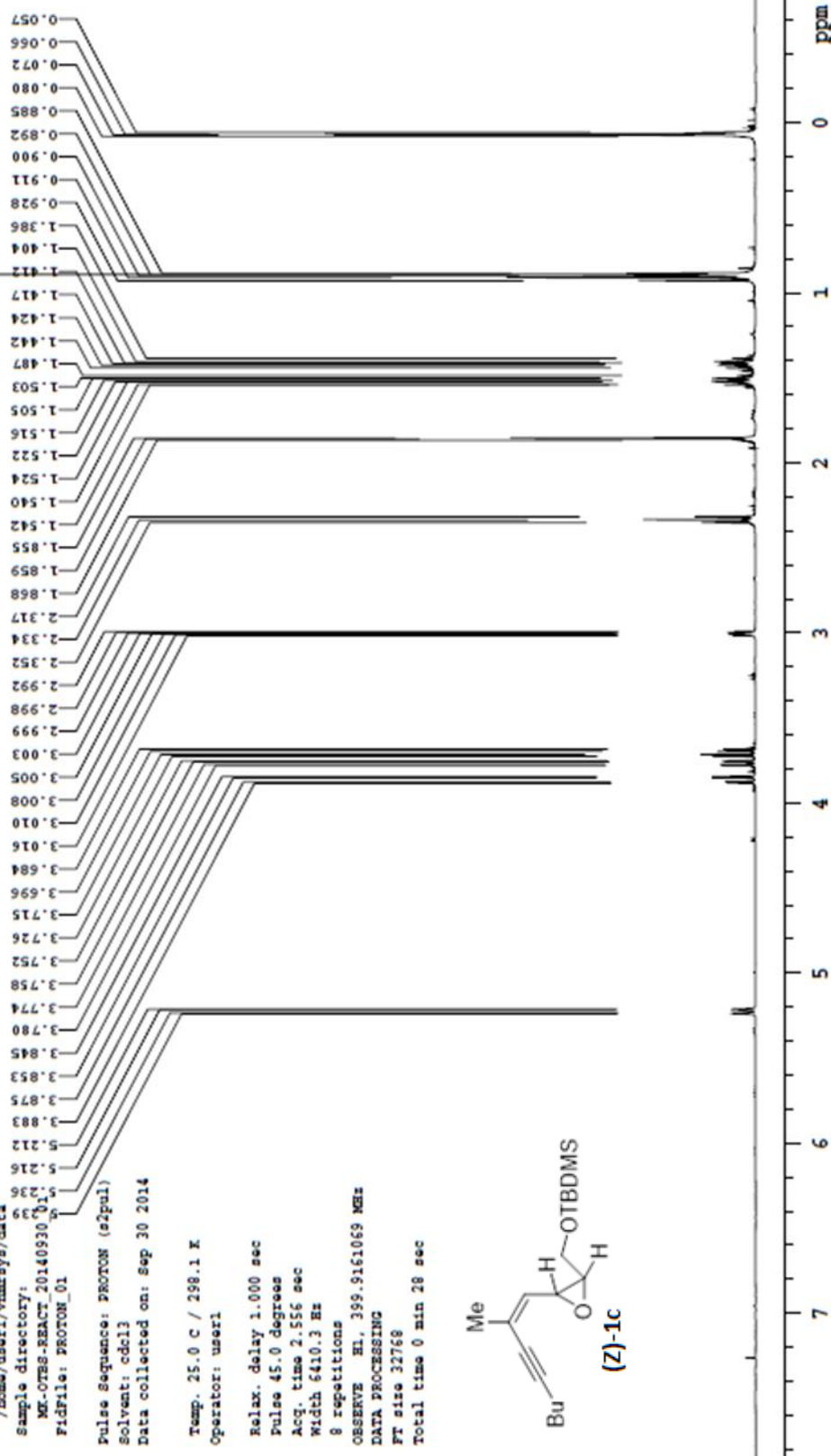
8 repetitions

OBSERVE H1, 399.9161069 MHz

DATA PROCESSING

FT size 32768

Total time 0 min 28 sec



MX-OTBS-REACT

Sample Name:

MX-OTBS-REACT

Data Collected on:

vmars400-vmars400

Archive directory:

/home/user1/vmars400

Sample directory:

MX-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 CH3, 100.5589851 MHz

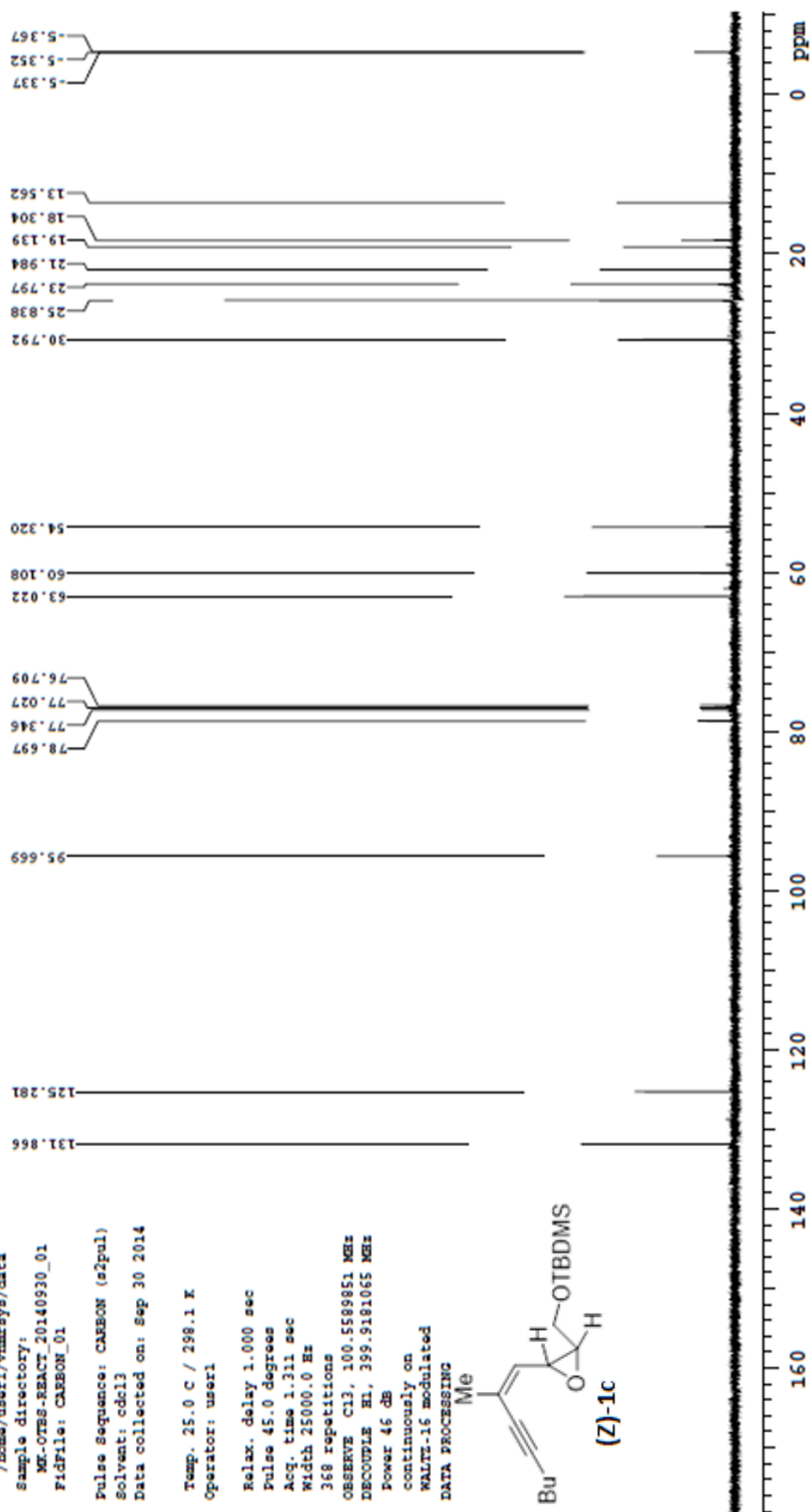
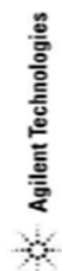
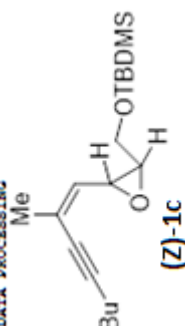
DECOUPLE H1, 399.5181065 MHz

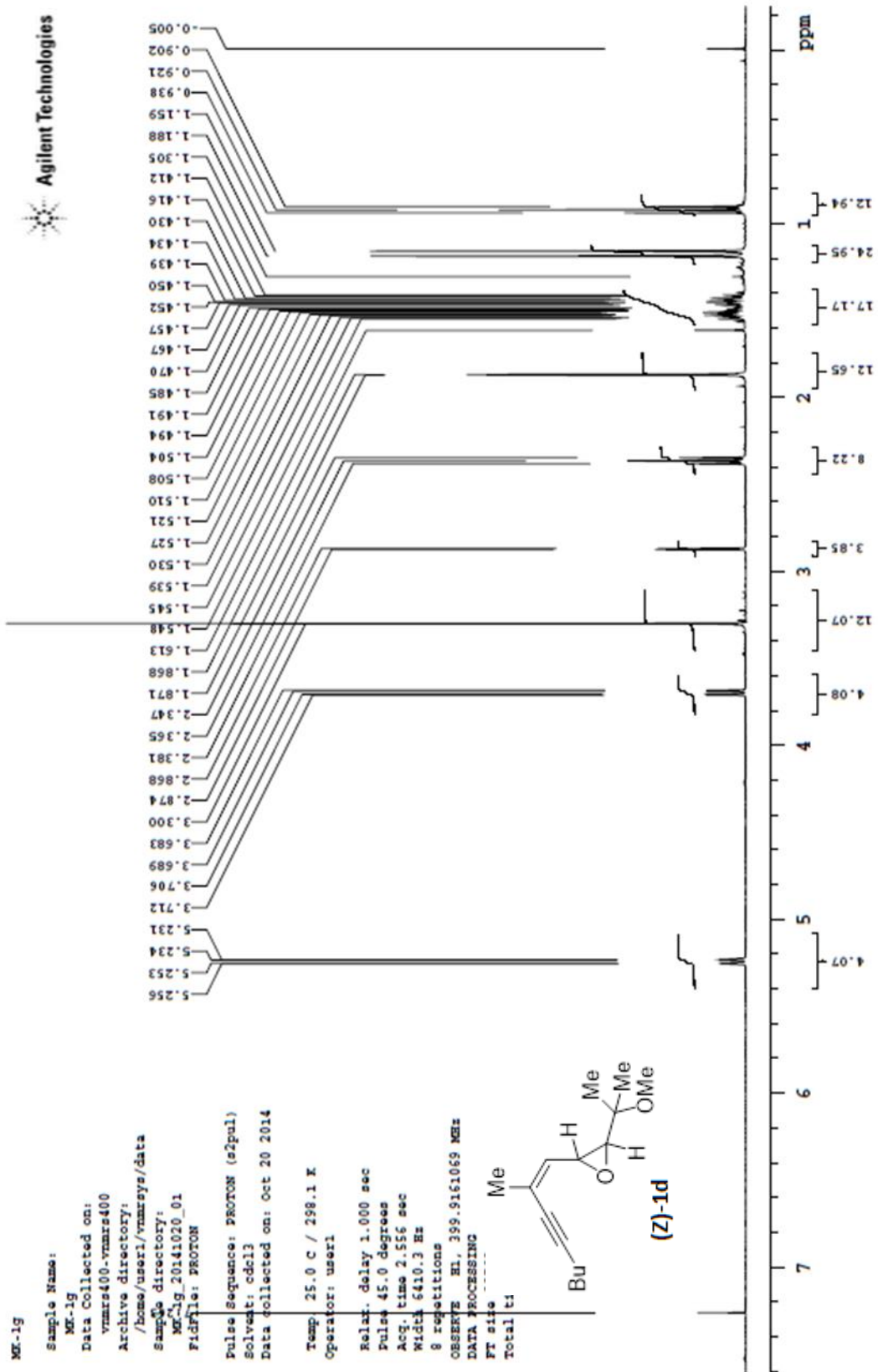
Power 46 dB

continuously on

WALTZ-16 MODULATED

DATA PROCESSING





MR-1g

Sample Name:

MR-1g

Data Collected on:

vmars400-vmars400

Archive directory:

/home/user1/vmarsys/data

Sample directory:

MR-1g_20141010_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

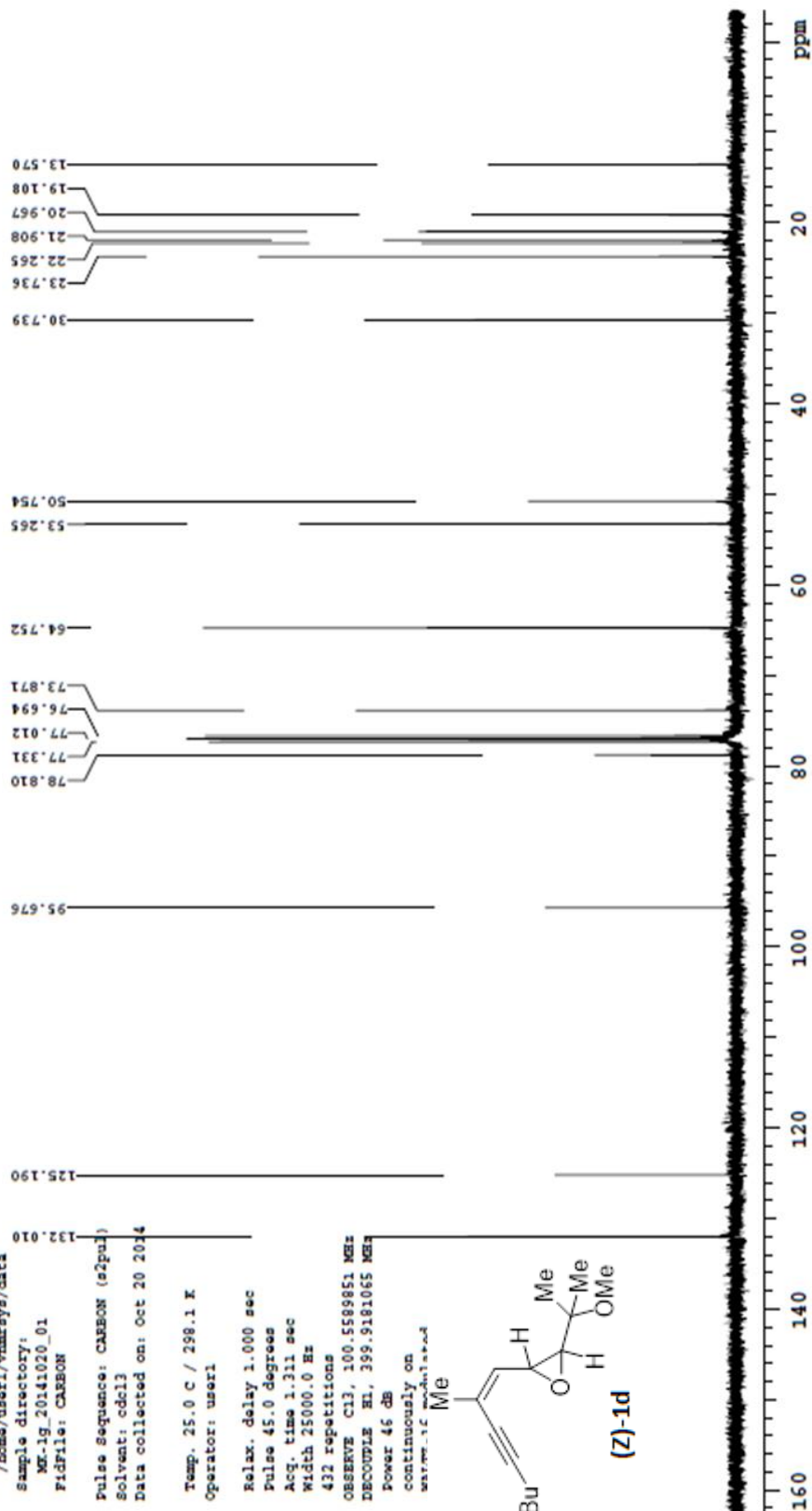
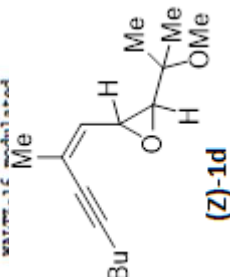
OBSERVE CH3, 100.559851 MHz

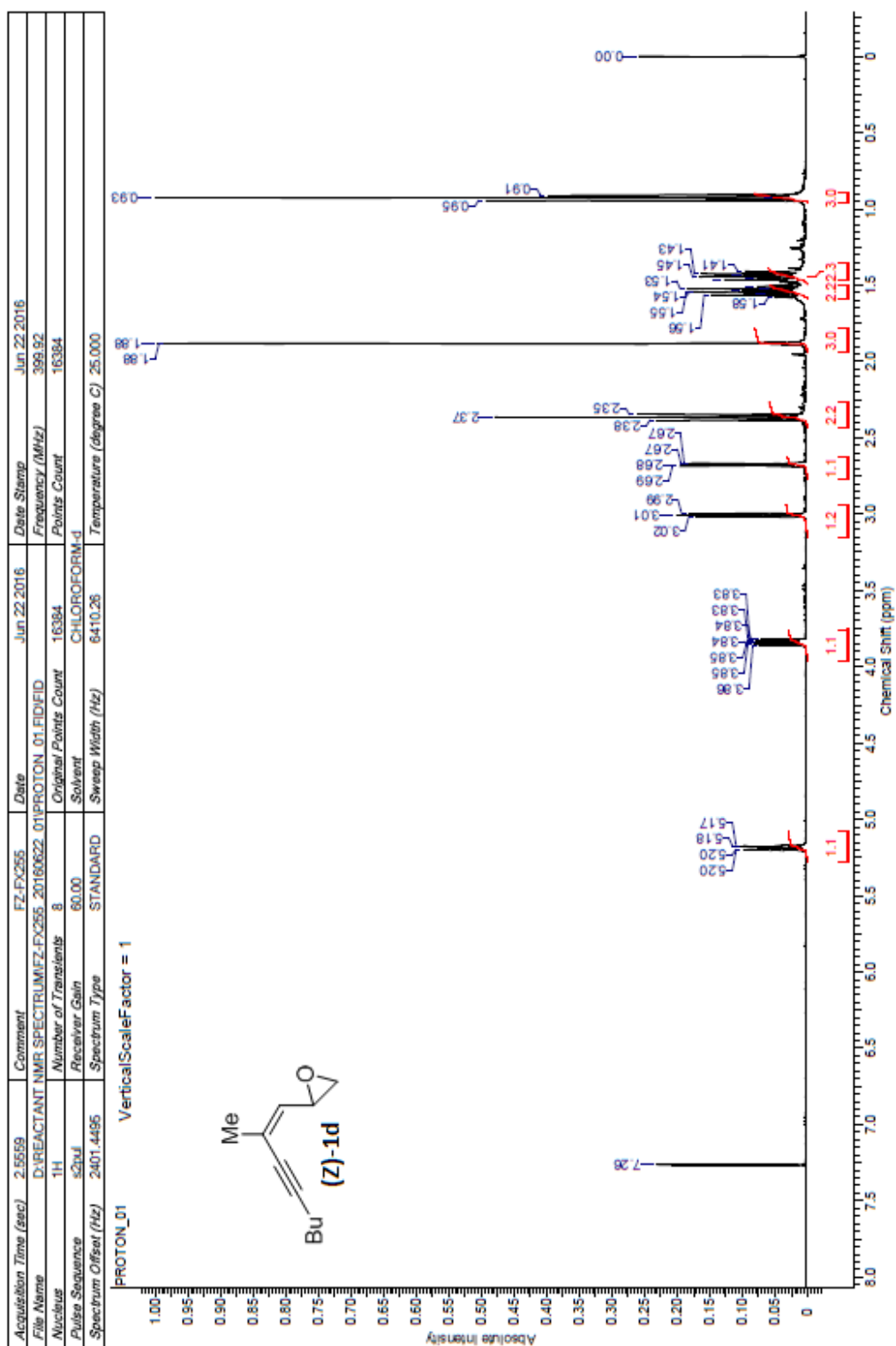
DECOUPLE H1, 399.9181065 MHz

Power 46 dB

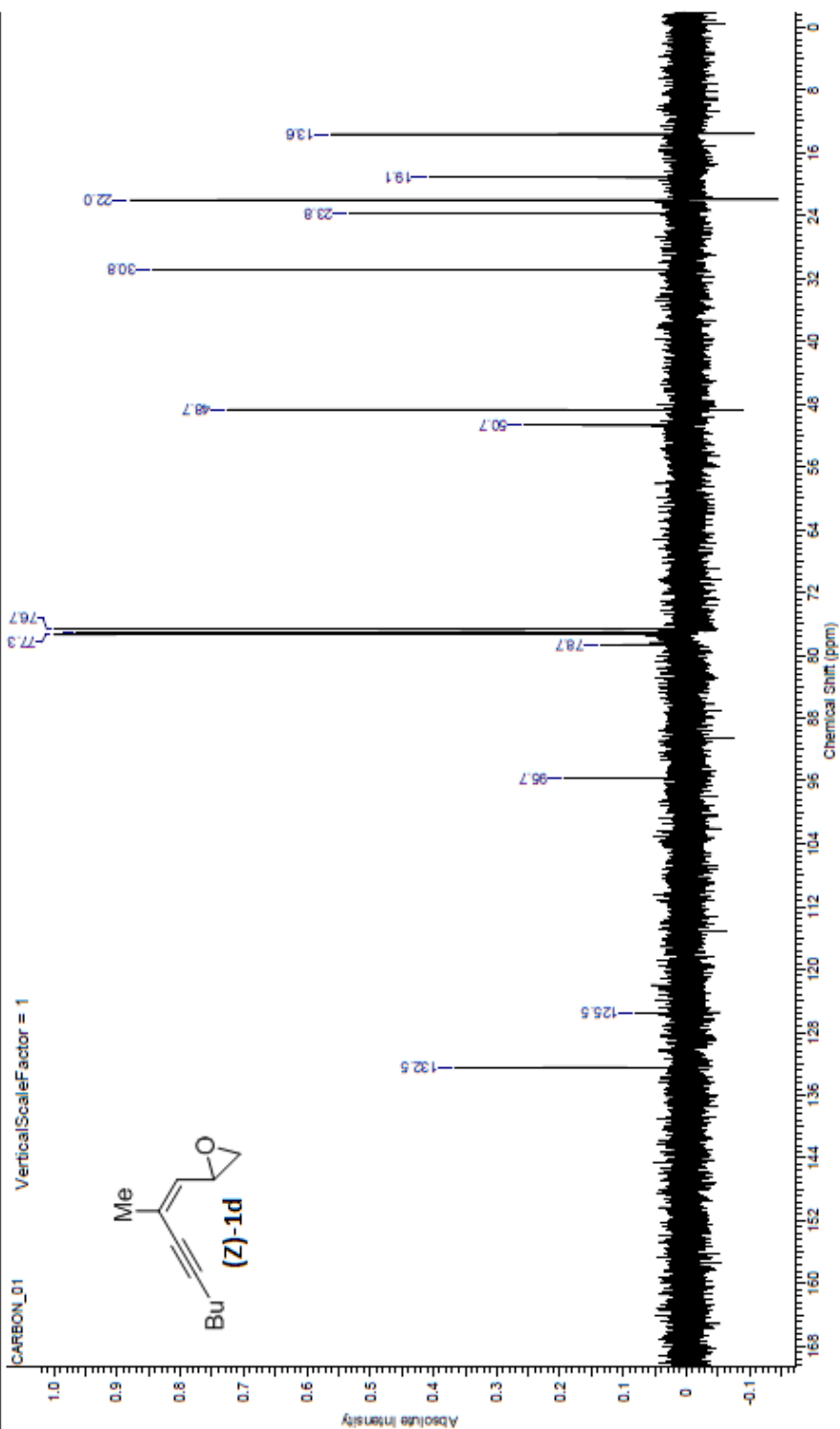
continuously on

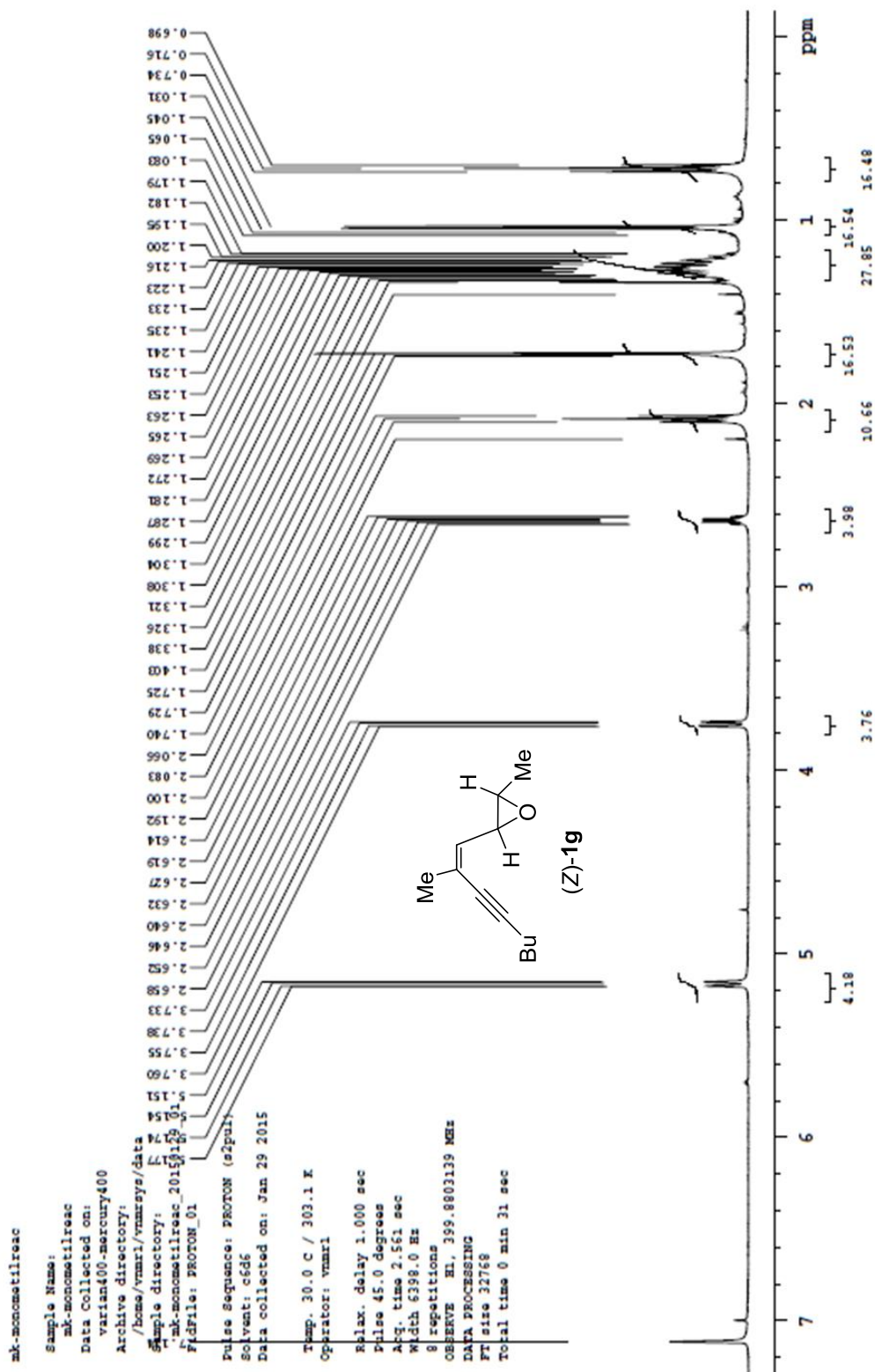
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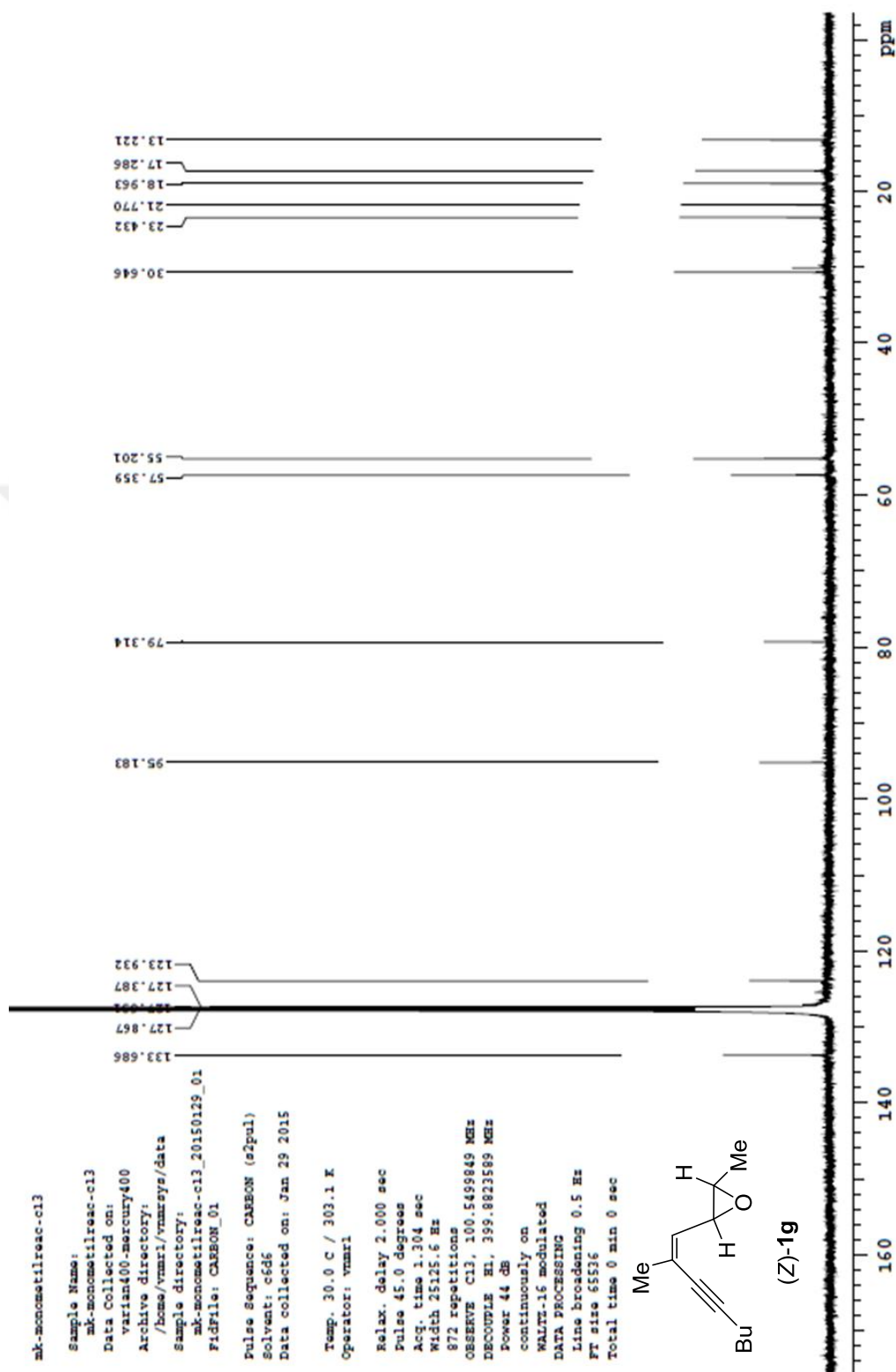




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Nucleus	¹³ C	Number of Transients	256	Original Points Count	32768	Points Count	32768
Pulse Sequence	zgpg30	Receiver Gain	30.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	11061.5371	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000

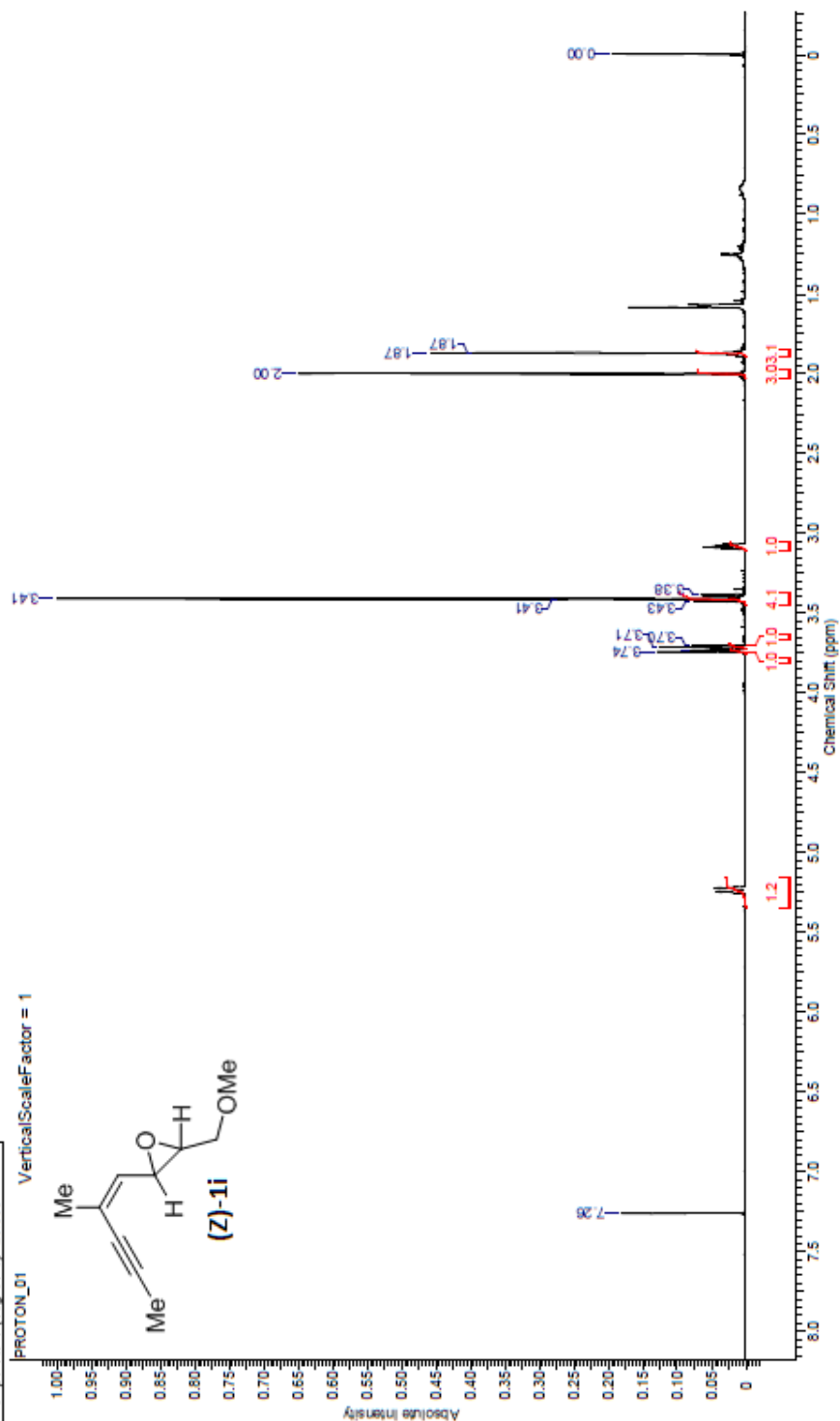




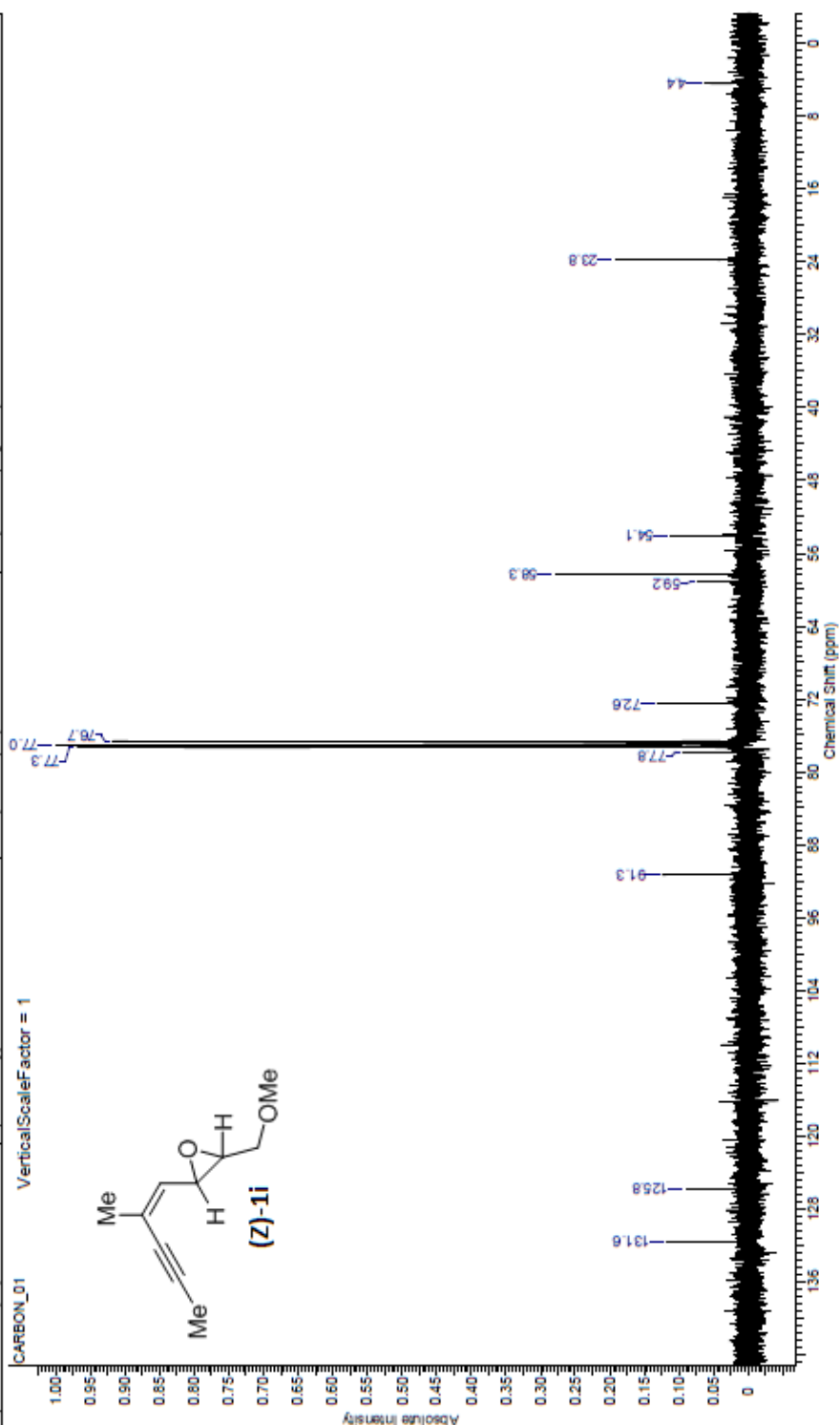


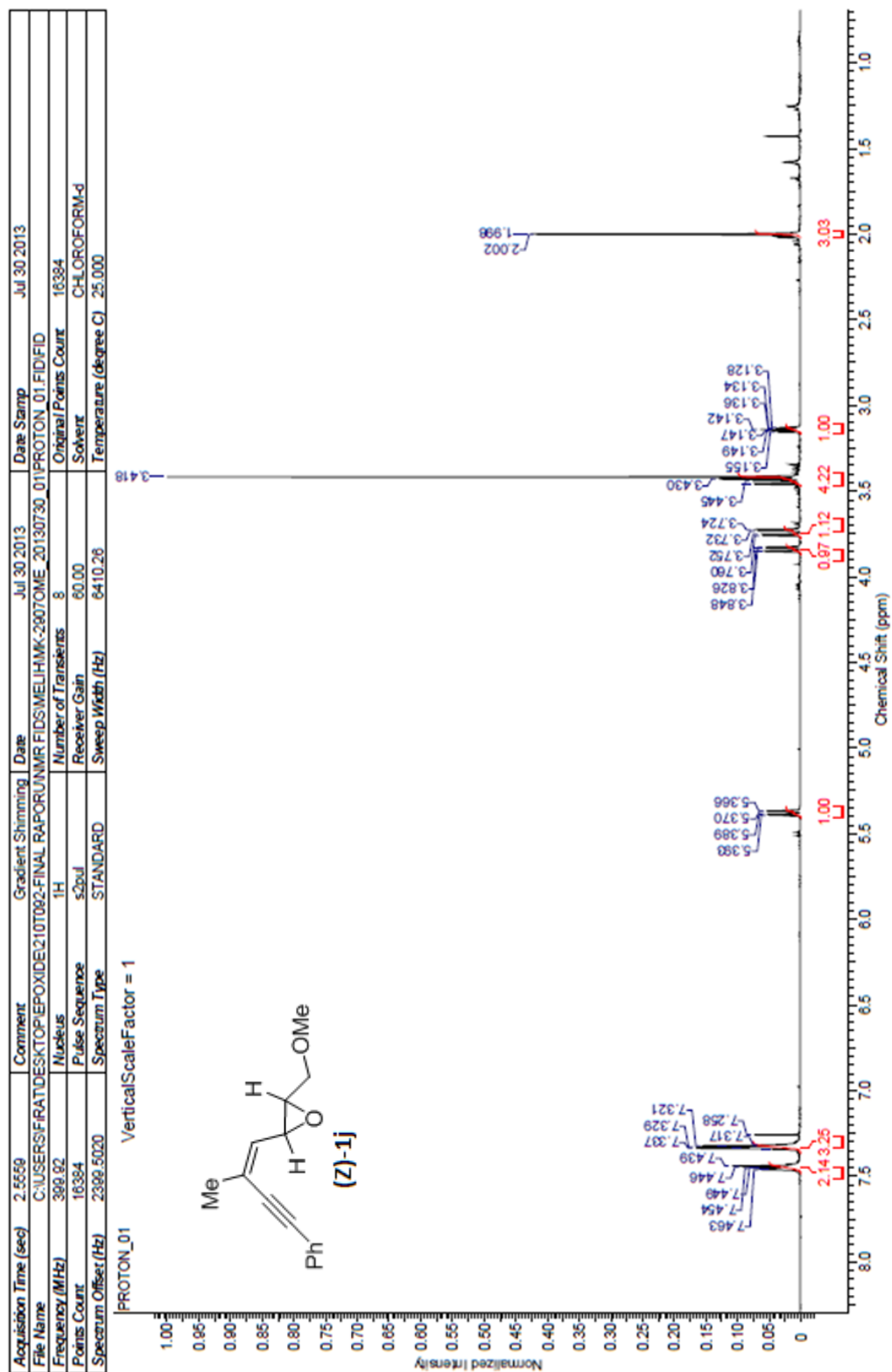
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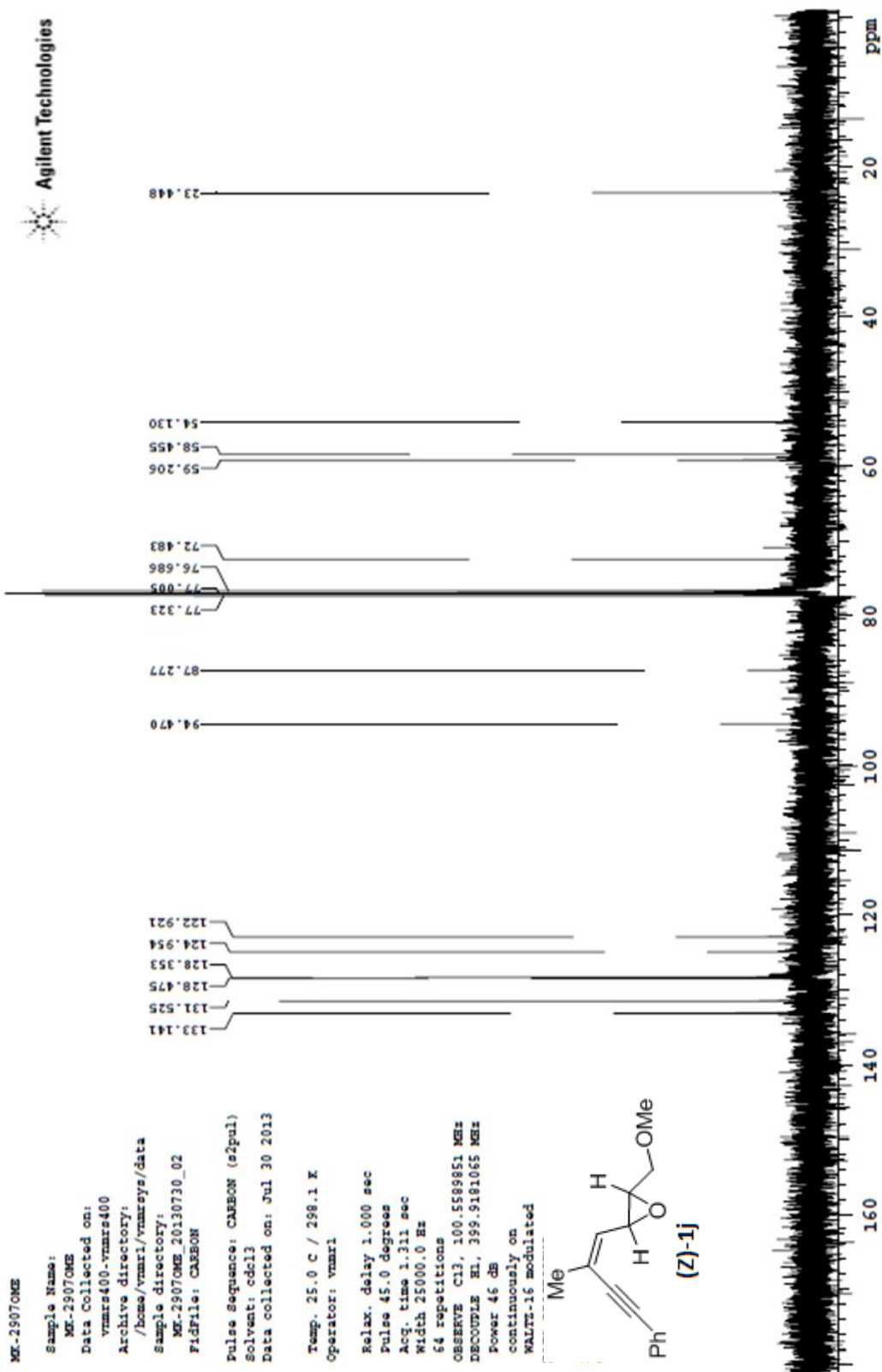
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Number of Transients	8	Original Points Count	16384	Points Count	16384	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26
Solvent	CHLOROFORM-d			Spectrum Offset (Hz)	2399.5020				
Temperature (degree C)	25.000								



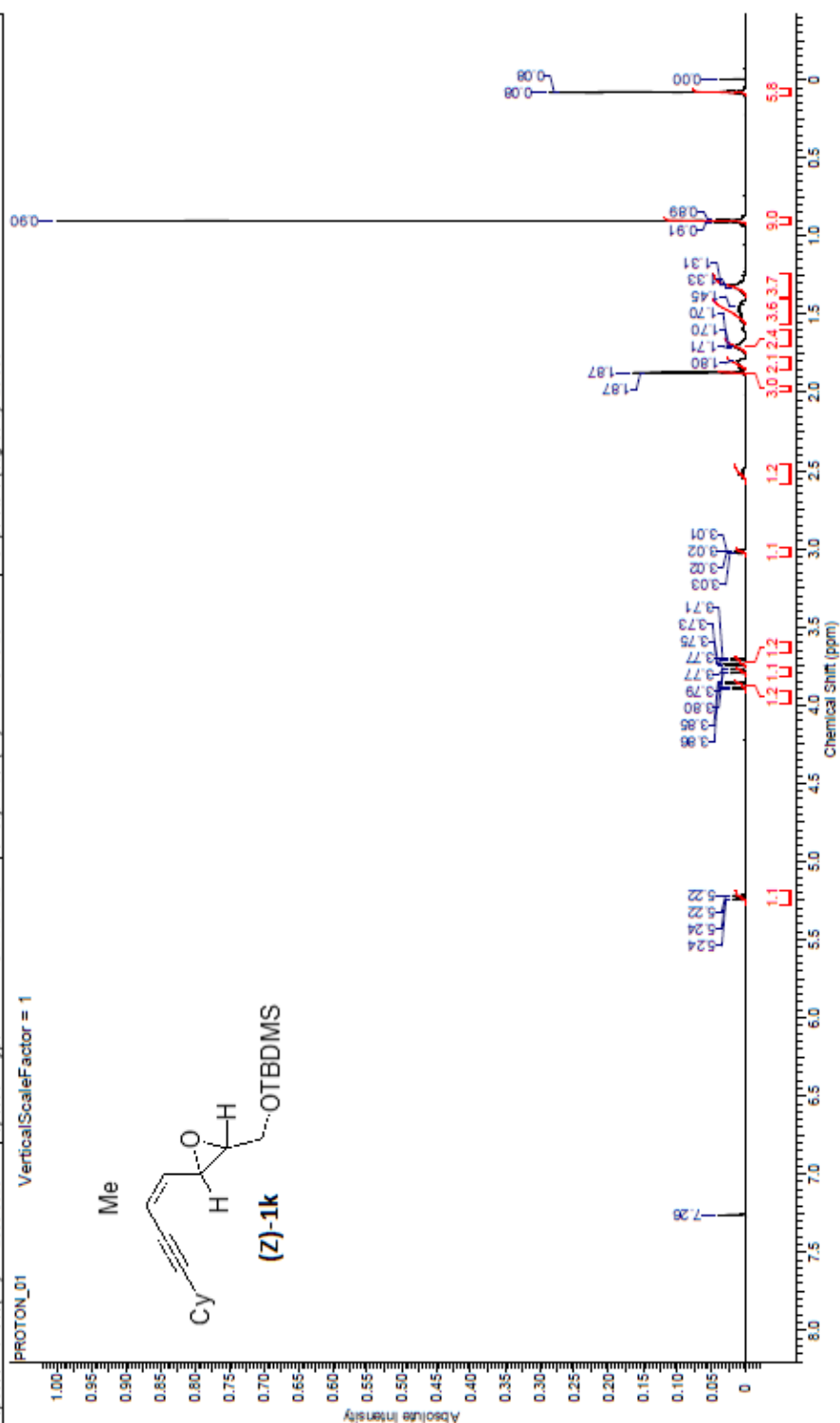
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Nucleus	¹³ C	Number of Transients	512	Original Points Count	32768	Points Count	32768
Pulse Sequence	s2hul	Receiver Gain	30.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	11061.5371	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000



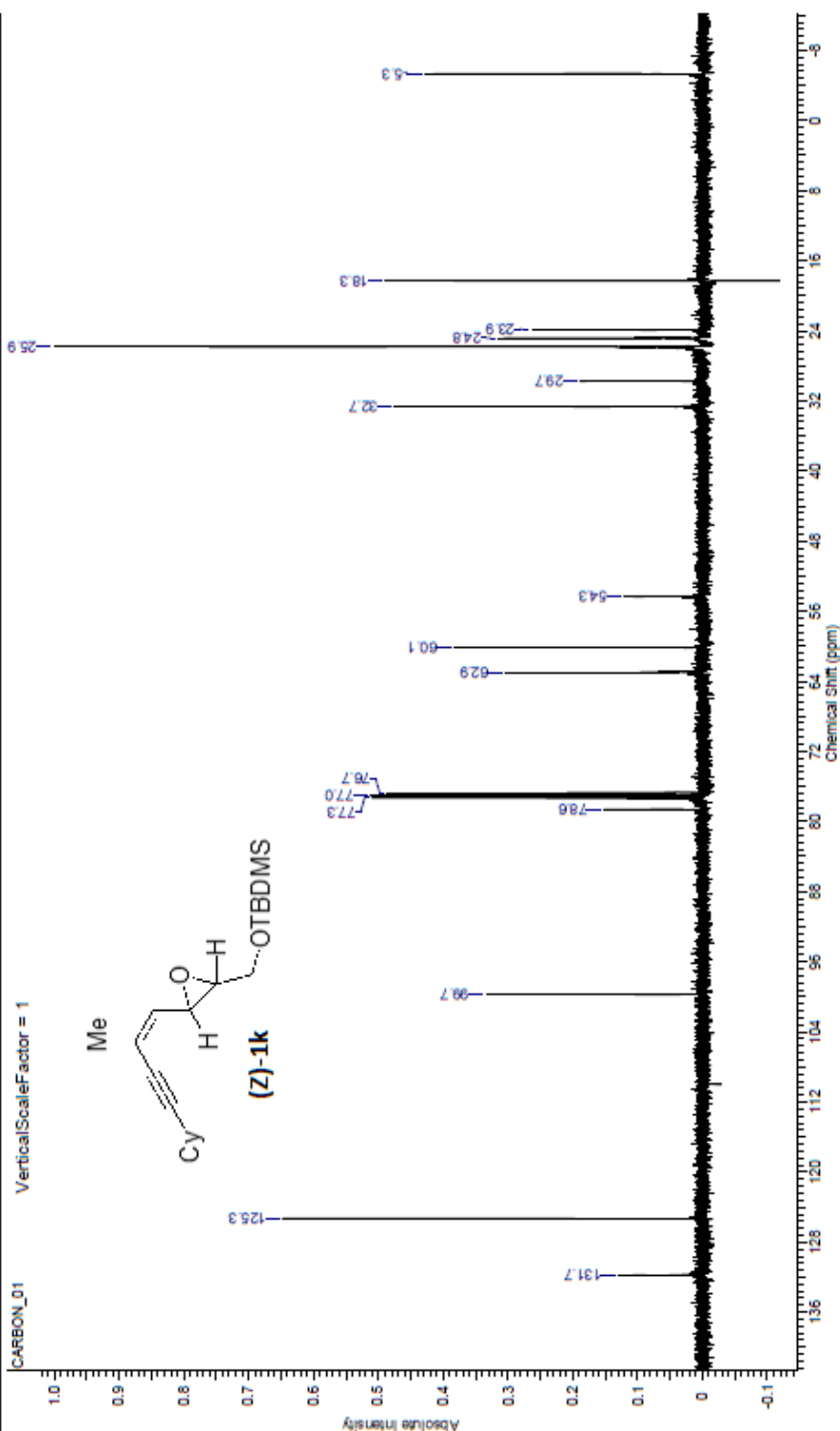




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Nucleus	1H	Number of Transients	8	Points Count
Pulse Sequence	s2pul	Receiver Gain	58.00	16384
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		Sweep Width (Hz)	6410.26	Temperature (degree C)
				25.000

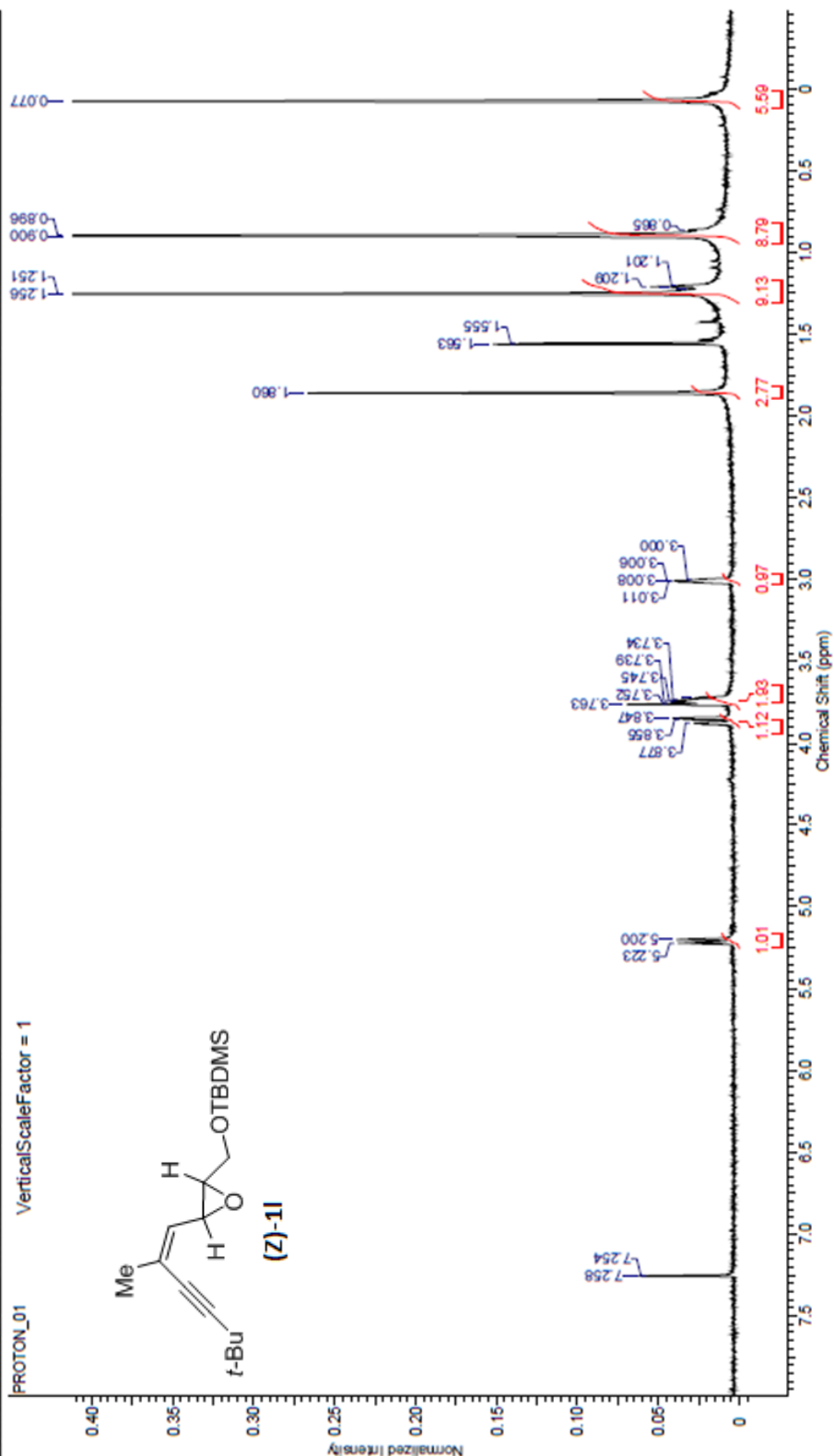


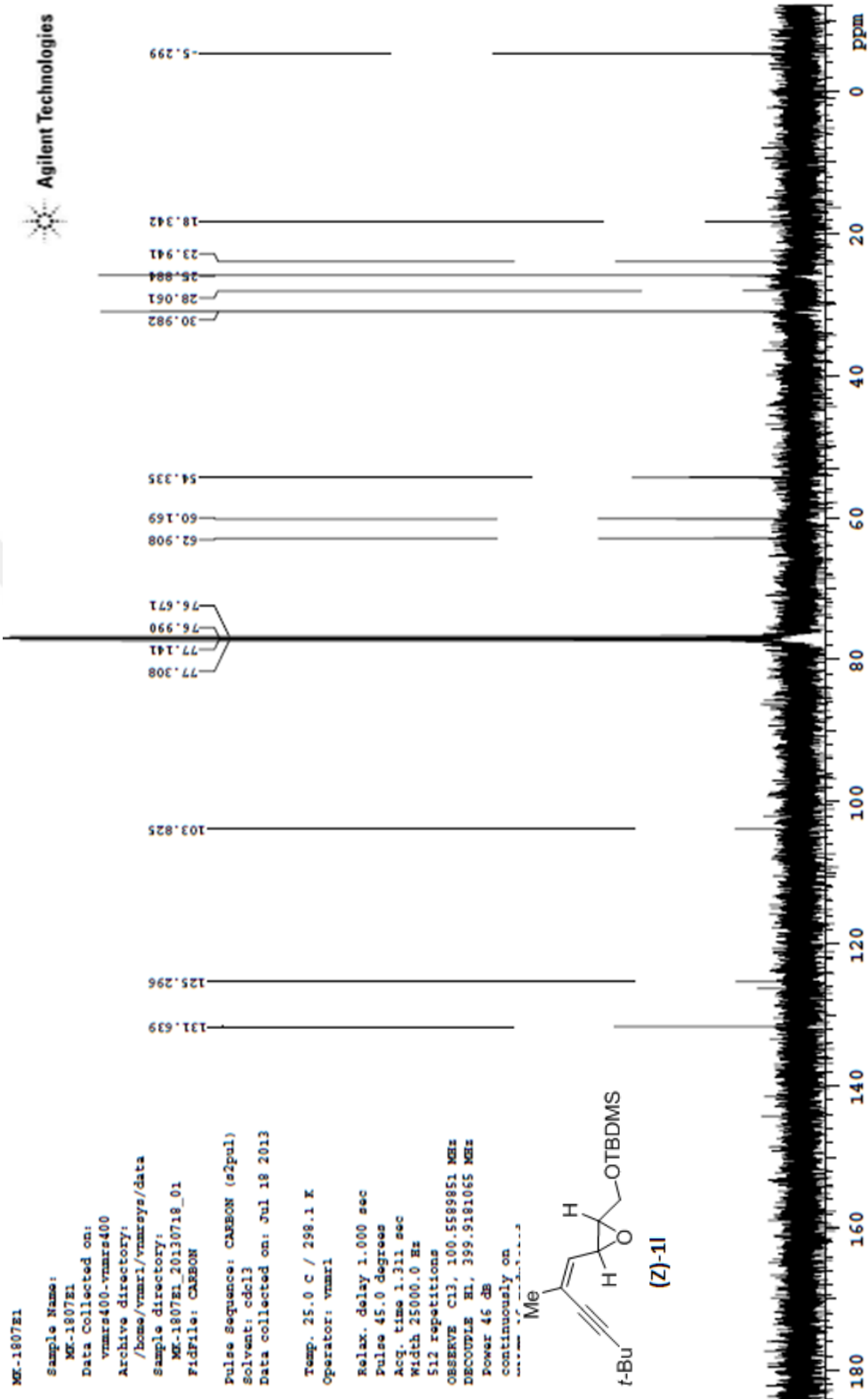
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Nucleus	¹³ C	Number of Transients	256	Original Points Count	32768	Points Count	32768
Pulse Sequence	zgpg30	Receiver Gain	30.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	11061.5371	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000



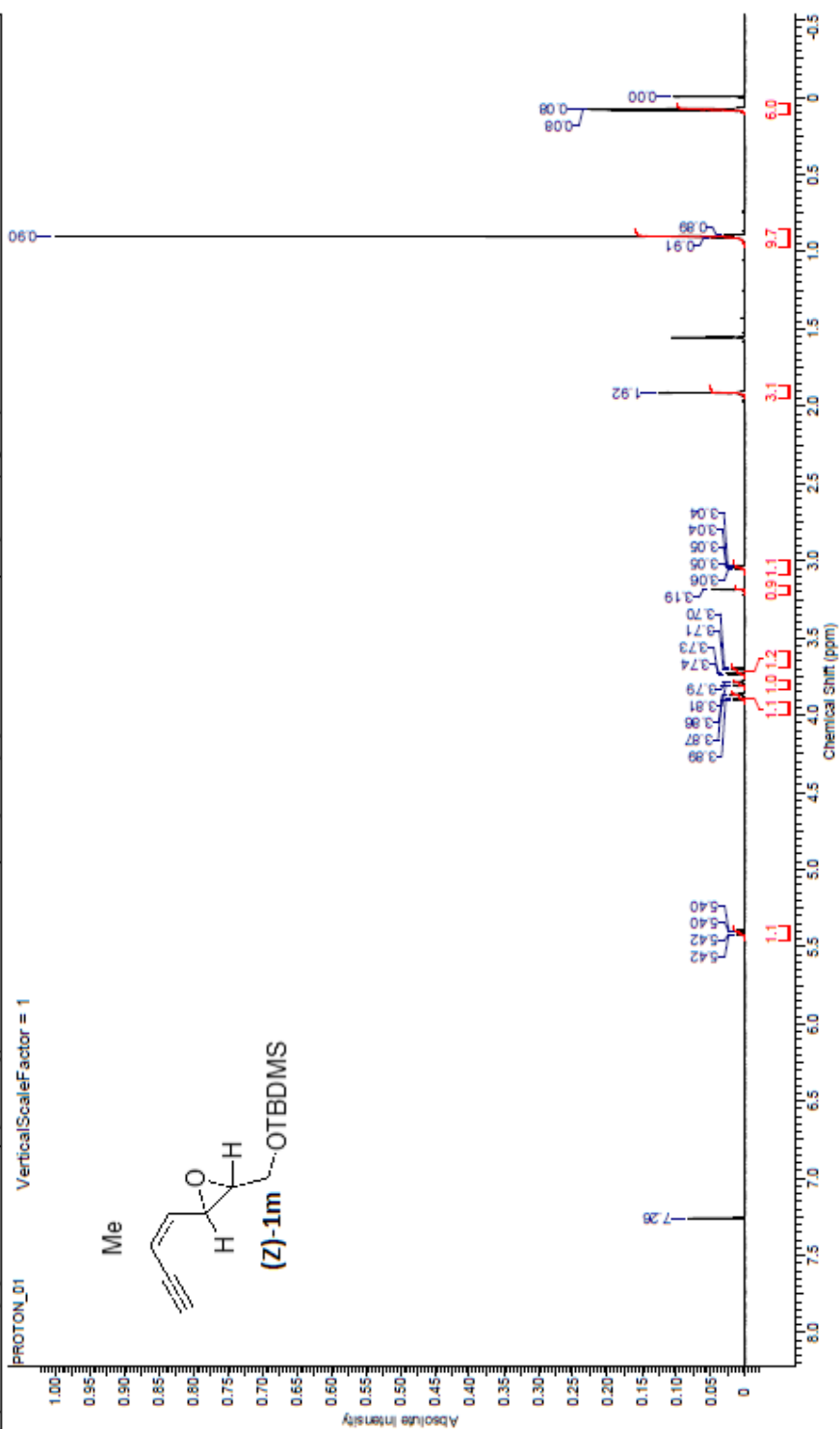
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Frequency (MHz)	399.82	Nucleus	¹ H	Number of Transients	8	Original Points Count	18394
Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	60.00	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	2389.5020	Spectrum Type	STANDARD	Sweep Width (Hz)	8410.26	Temperature (degree C)	25.000

VerticalScaleFactor = 1

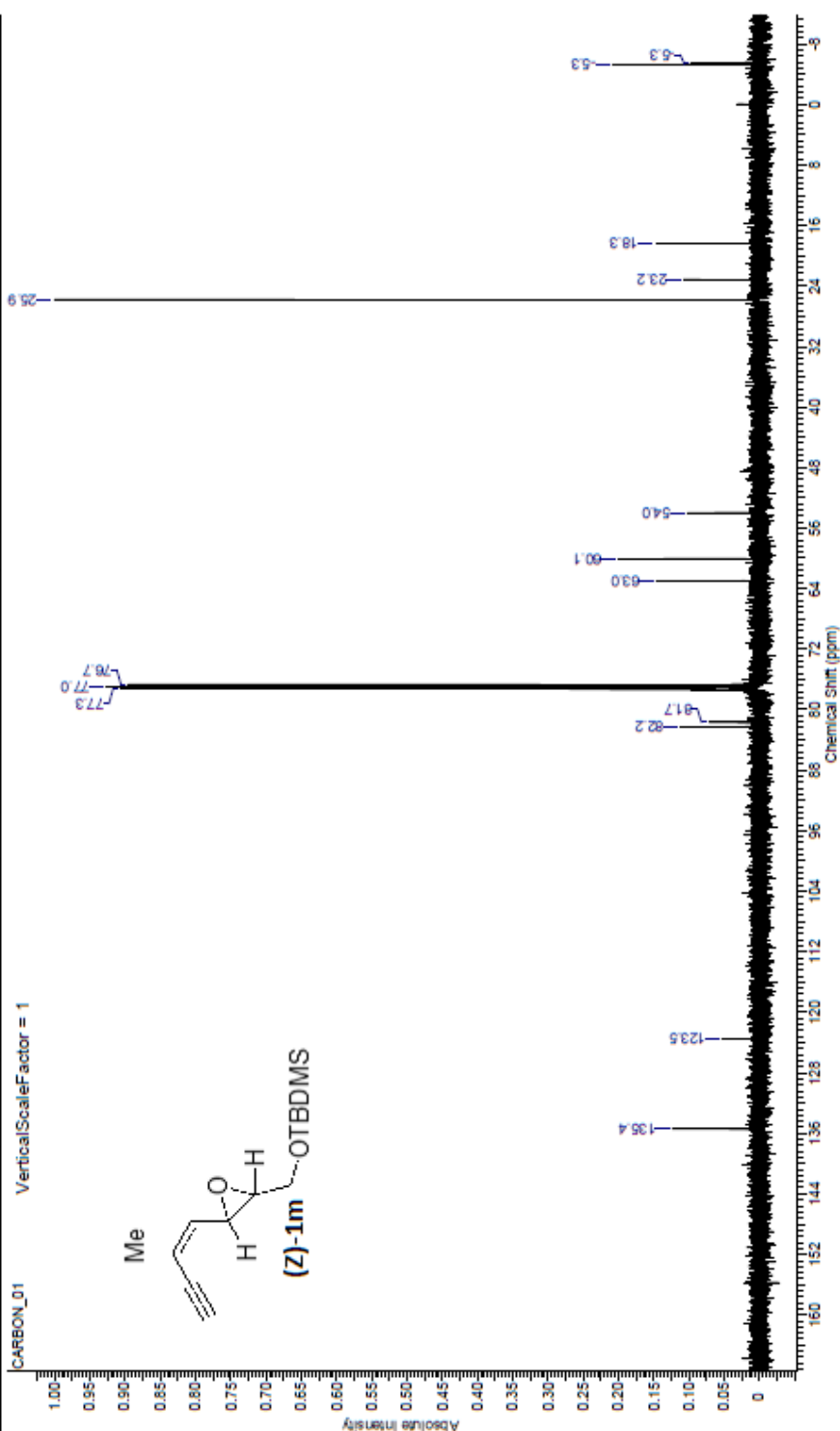




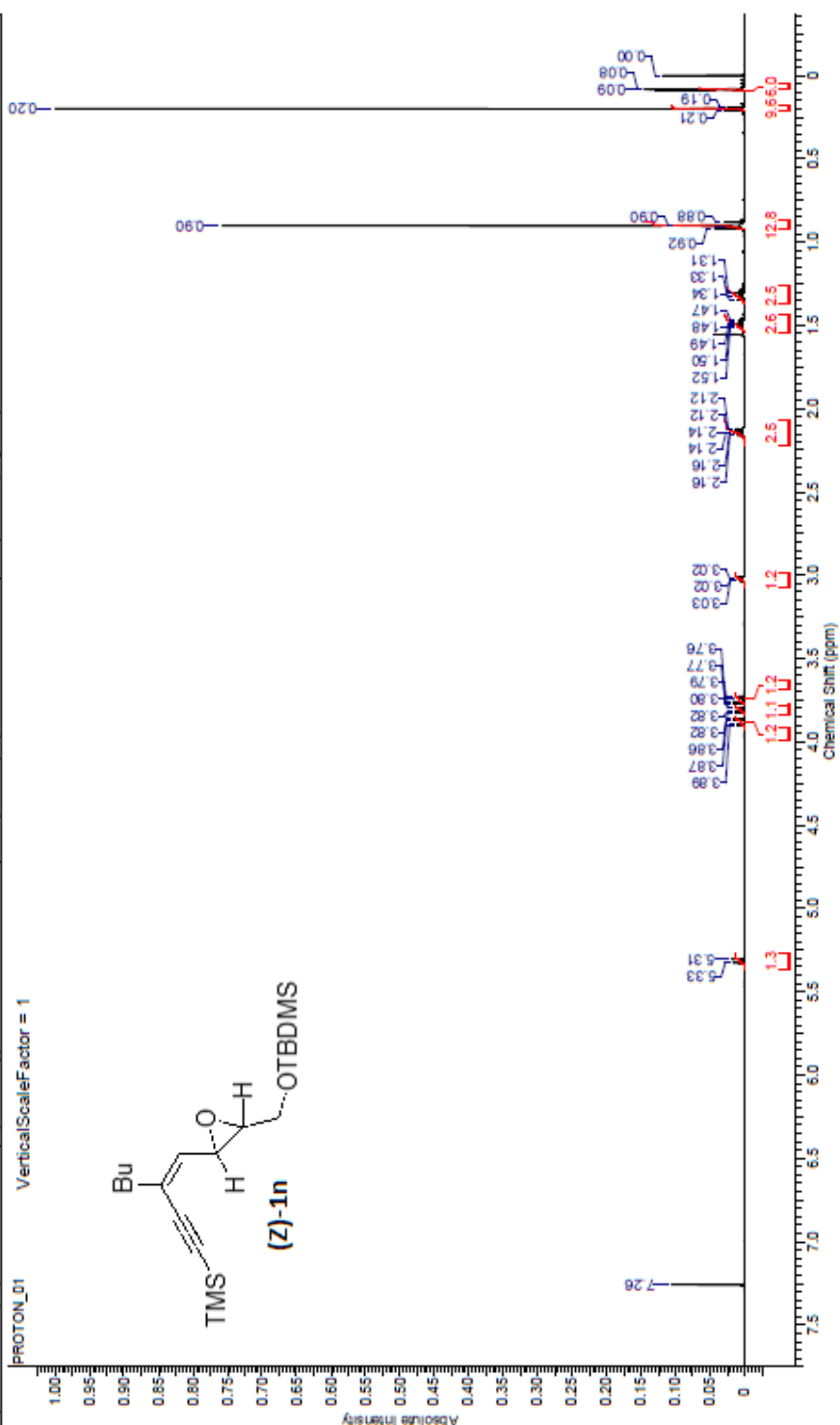
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Nucleus	¹ H	Number of Transients	8	Original Points Count	16384	Points Count	16384
Pulse Sequence	s2h1	Receiver Gain	60.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	2399.5020	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



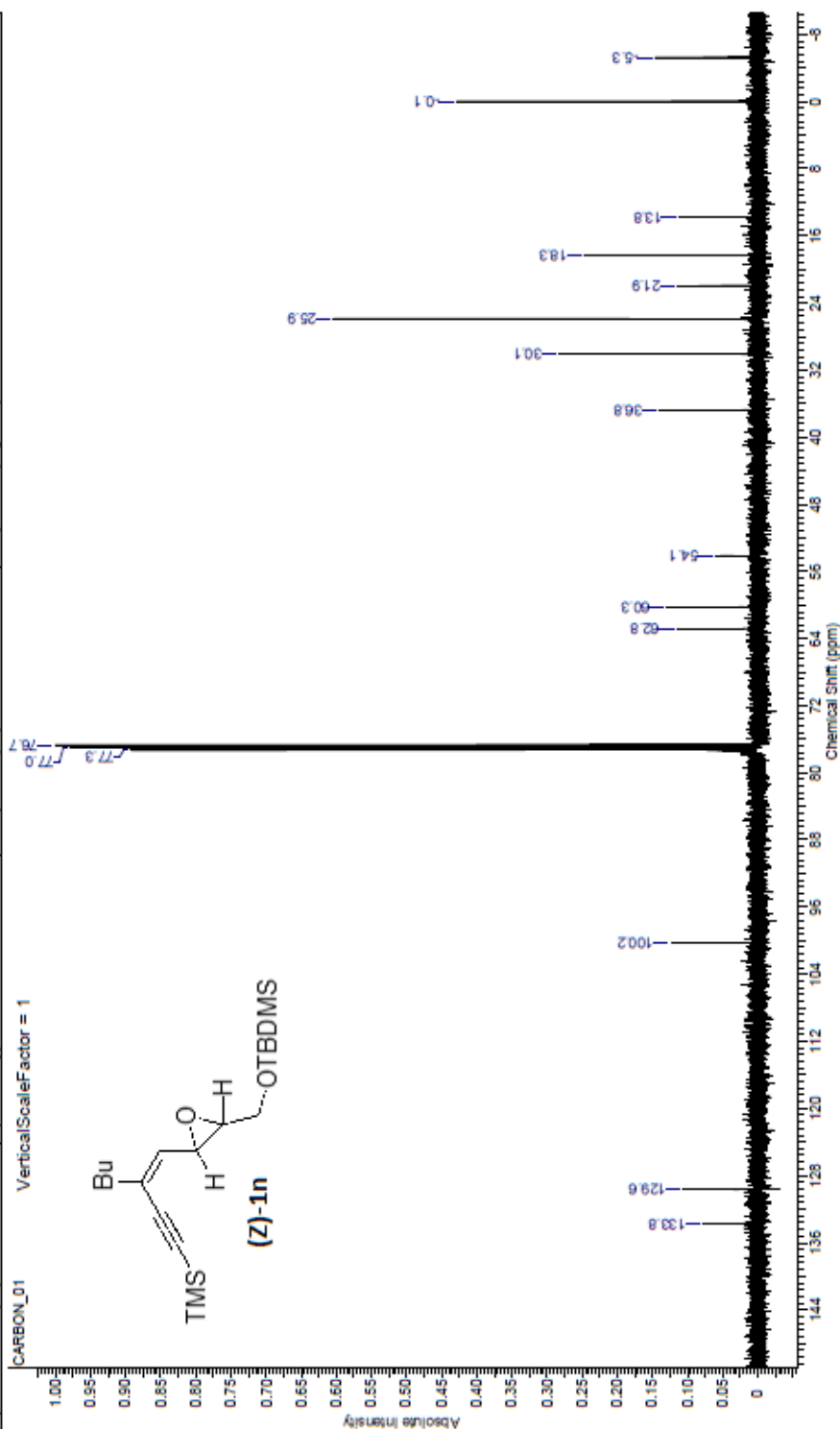
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Nucleus	¹³ C	Number of Transients	1000	Original Points Count	32768	Points Count	32768
Pulse Sequence	s2h1	Receiver Gain	30.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	11061.5371	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000



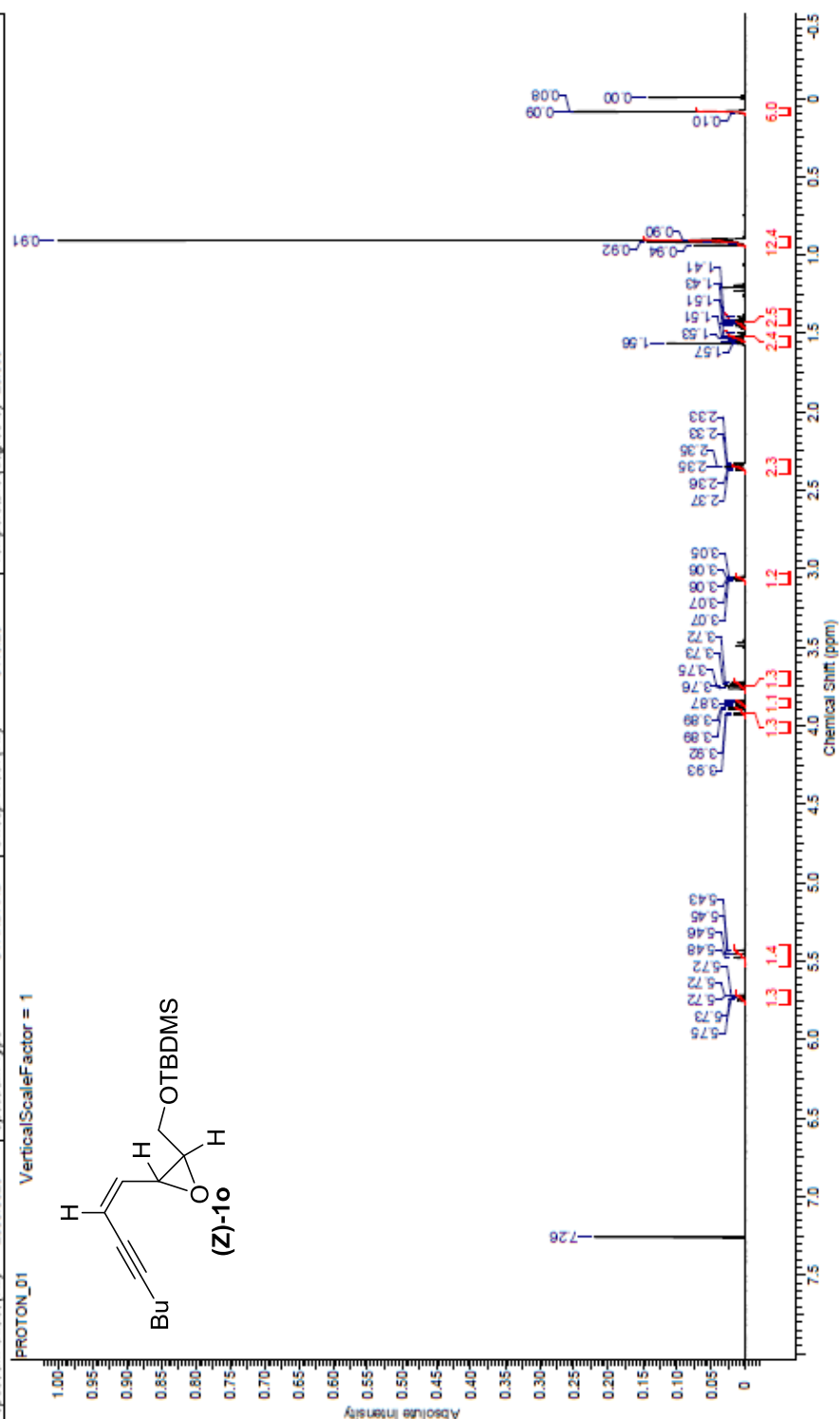
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Nucleus	¹ H	Number of Transients	8	Original Points Count	16384	Points Count	16384
Pulse Sequence	s2h1	Receiver Gain	60.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	2399.5020	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



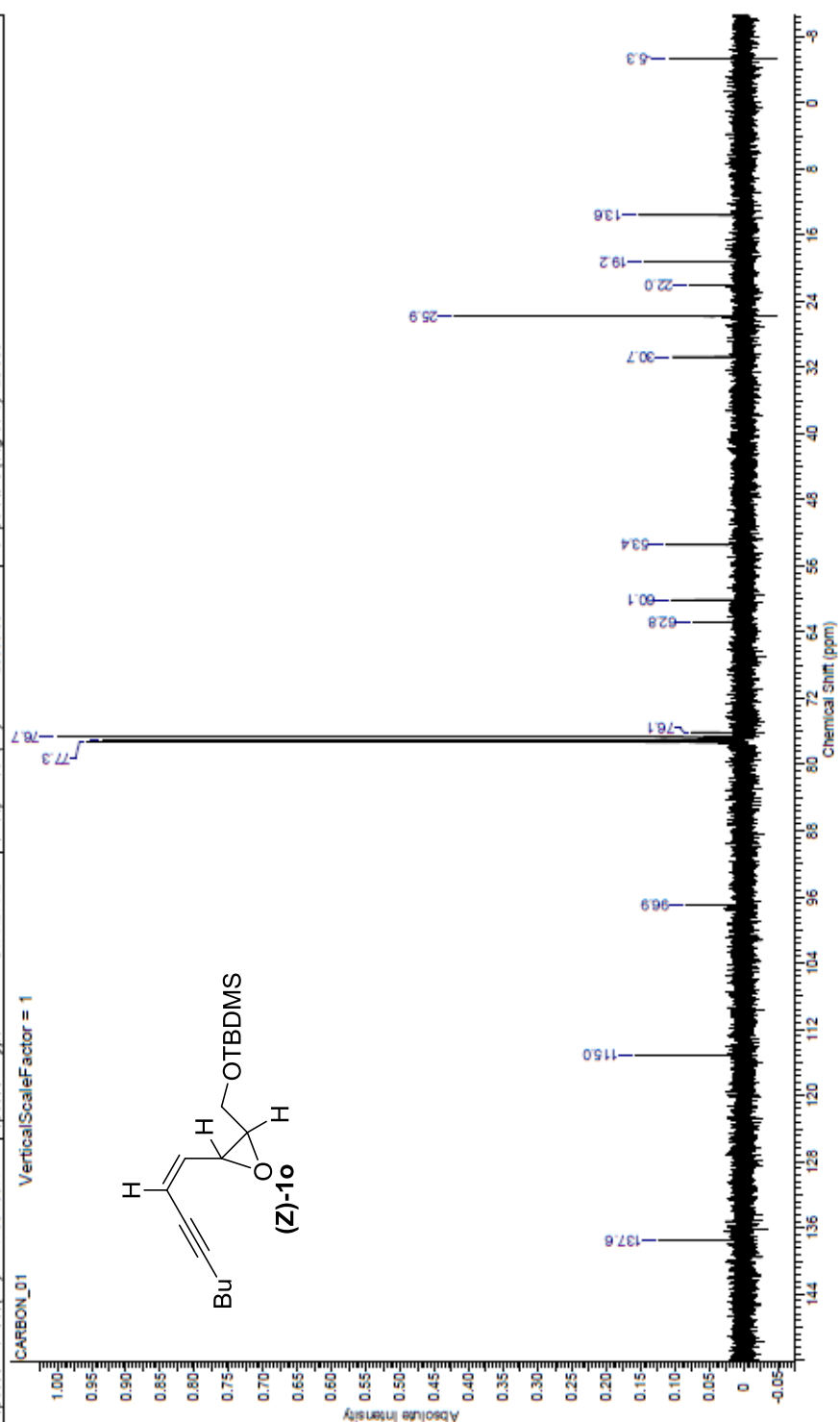
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Nucleus	13C	Number of Transients	1000	Solvent	CHLOROFORM-d	Temperature (degree C)	25.000
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Spectrum Offset (Hz)	11061.5371	Spectrum Type	STANDARD				



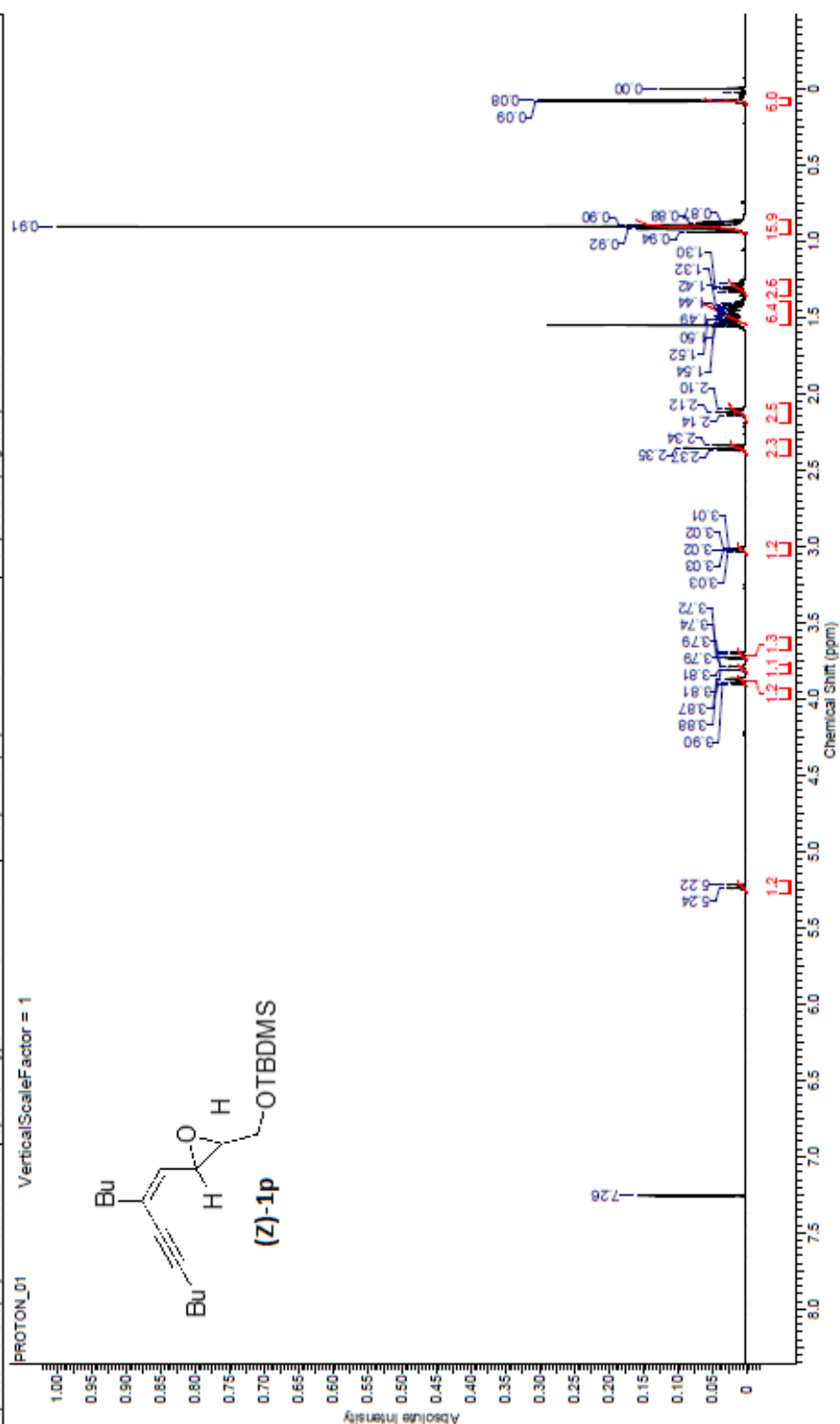
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1H		Number of Transients 8	Original Points Count 16384	Points Count 16394
Pulse Sequence	s2qul	Receiver Gain 60.00	Solvent CHLOROFORM-d	
Spectrum Offset (Hz)	2399.5020	STANDARD	Sweep Width (Hz) 6410.26	Temperature (degree C) 25.000



Acquisition Time (sec)	1:31:07	Comment	F2-FX-215	Date	Mar 16 2016	Date Stamp	Mar 16 2016
File Name	D:\REACTANT NMR SPECTRUM\F2-FX-215_20160316_01\CARBON_01.FID\FID						
Nucleus	13C	Number of Transients	512	Original Points Count	32768	Frequency (MHz)	100.57
Pulse Sequence	s2pul	Receiver Gain	30.00	Solvent	CHLOROFORM-d	Points Count	32768
Spectrum Offset (Hz)	11061.5371	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degrees C)	25.000



Acquisition Time (sec)	Comment	Date	Date Stamp
2.5559	F2-FX199	Feb-18-2016	Feb 18 2016
File Name	D:\REACTANT NMR SPECTRUM\F2-FX199_20160218_01\PROTON_01\FID\FID		Frequency (MHz)
Nucleus	1H		399.92
		Original Points Count	16384
Pulse Sequence	s2nu1	Solvent	CHLOROFORM-d
		Receiver Gain	60.00
Spectrum Offset (Hz)	2399.5020	Spectrum Type	STANDARD
		Sweep Width (Hz)	6410.26
		Temperature (degree C)	25.000





MY-CHROME

Sample Name:

MY-CHROME

Data Collected on:

vmars400-vmars400

Archive directory:

/home/user1/vmarsys/data

Sample directory:

MY-CHROME 20141230_01

File: 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 640.3 Hz

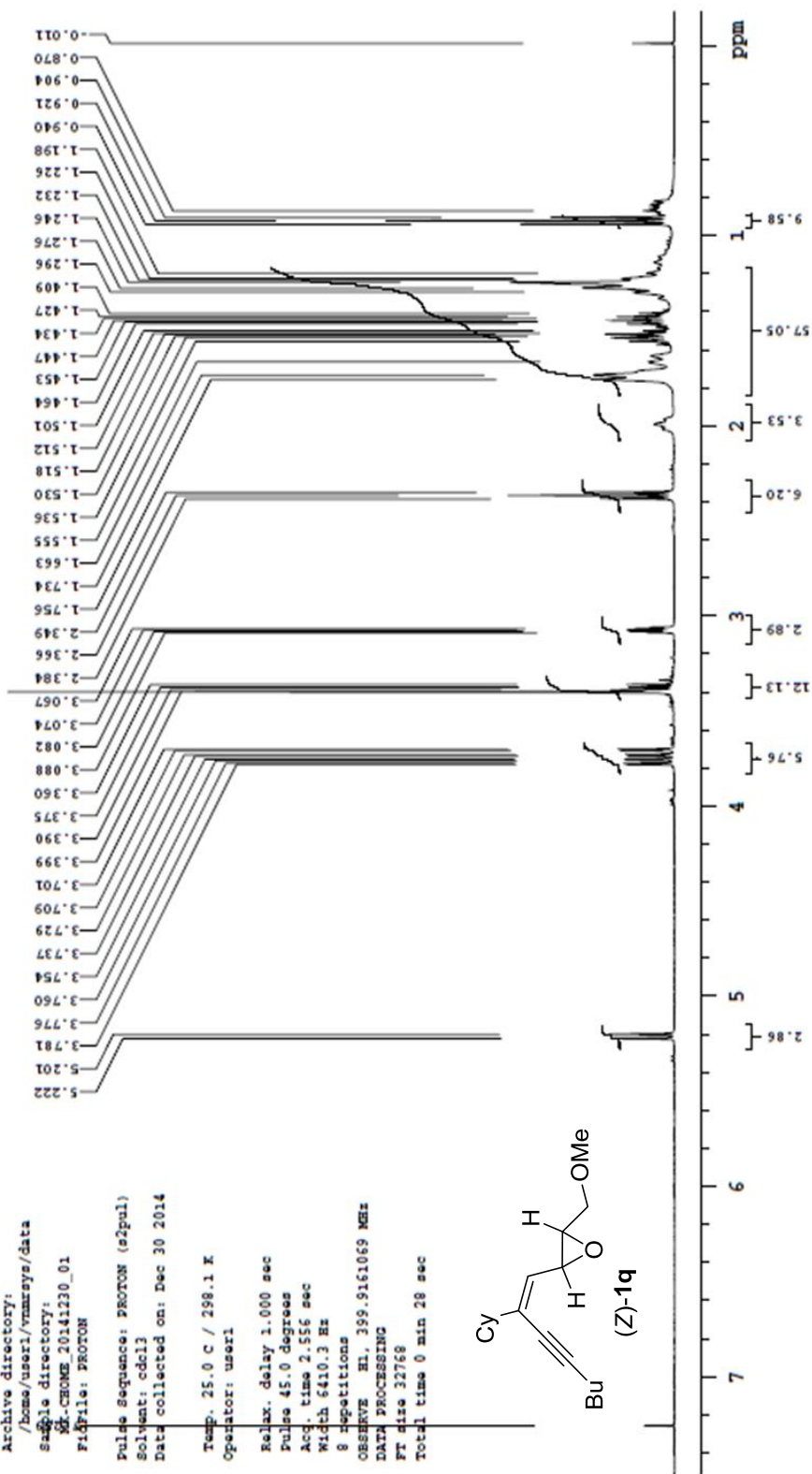
8 Repetitions

OBSERVE H1, 399.916169 MHz

DATA PROCESSING

FI size 32768

Total time 0 min 28 sec



MY-CHROME

Agilent Technologies

Sample Name:

MY-CHROME

Data Collected on:

vmrs400-vmrs400

Archive directory:

/home/user1/vmrs400/data

Sample directory:

MY-CHROME_20141230_01

FidFile: CARBON

Pulse Sequence: CARBON (zgpg3)

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, 100.558951 MHz

DECOUPLE H1, 399.918165 MHz

Power 46 dB

continuously on

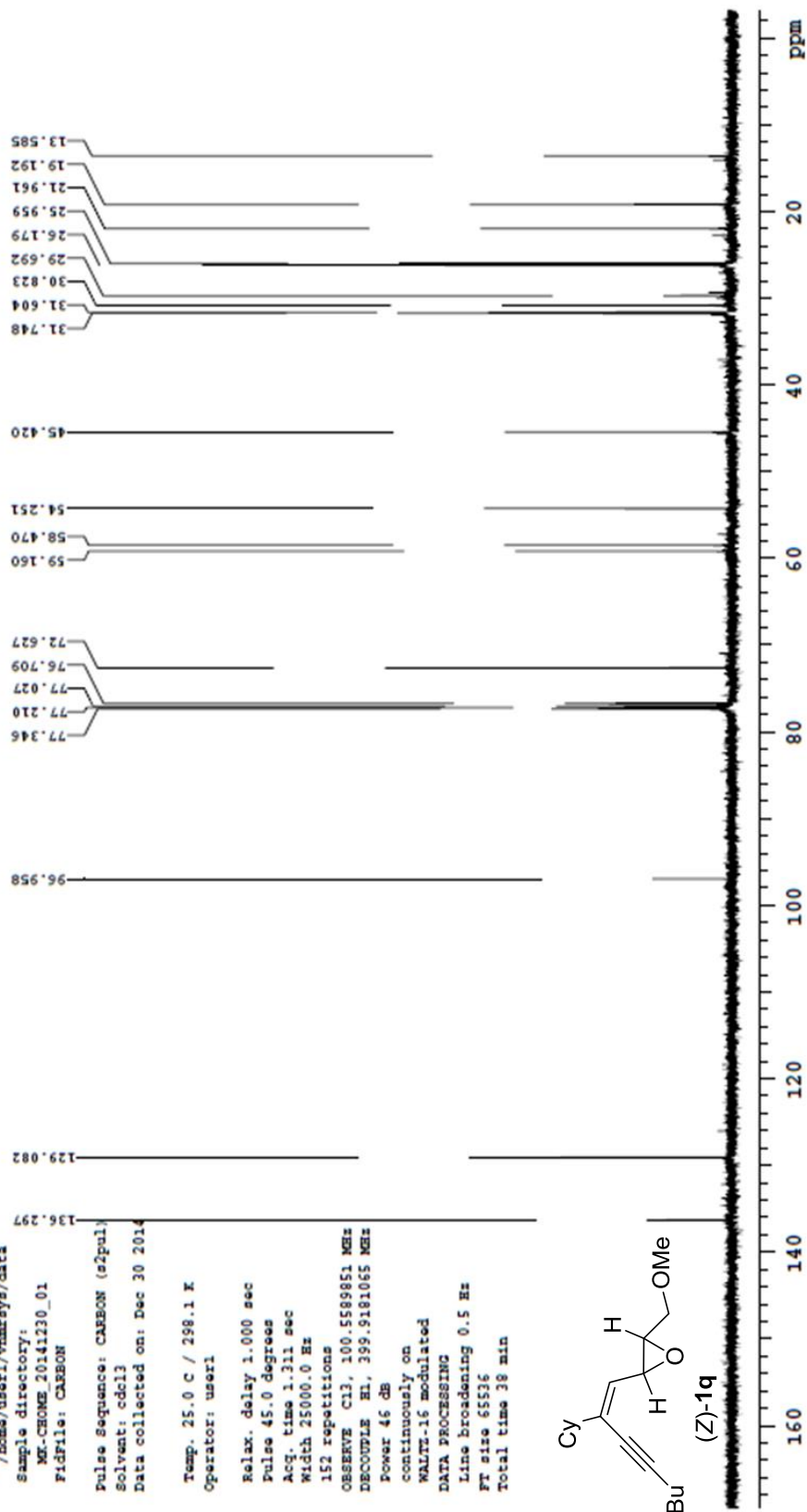
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

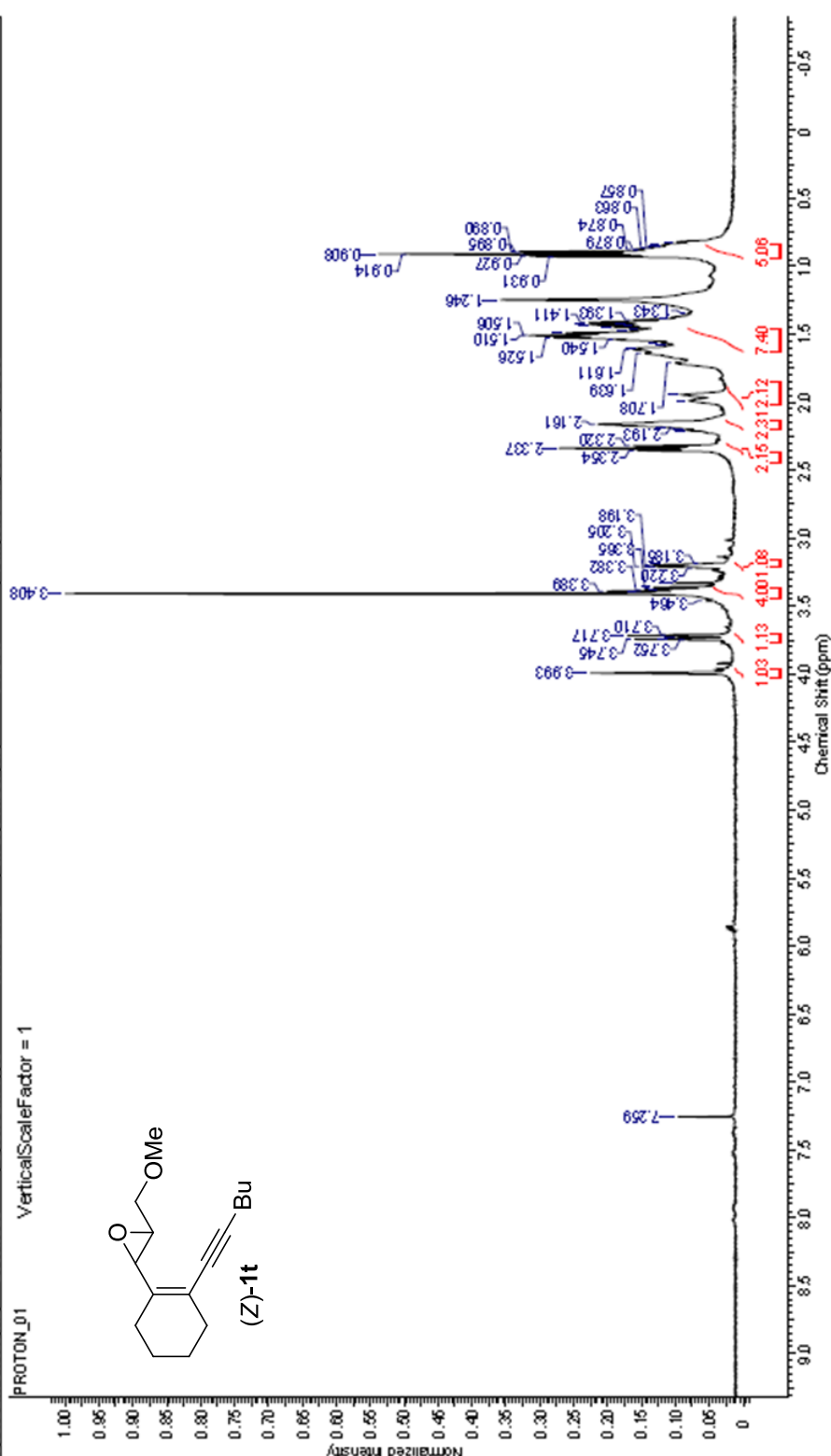
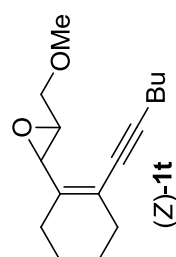
FT size 65536

Total time 38 min



Acquisition Time (sec)	2.5569	Comment	Gradient Shimming	Date	Oct 25 2013
Date Stamp	Oct 25 2013	File Name	CAUSERSVIRATODES1TOPMELJHMK26101_20131025_01PROTON_01.FID.FID		
Frequency (MHz)	399.92	Nucleus	¹ H	Original Points Count	16384
Points Count	16384	Pulse Sequence	s2pul	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5020	Spectrum Type	STANDARD	Temperature (degree C)	25.000

PROTON_01 VerticalScaleFactor = 1

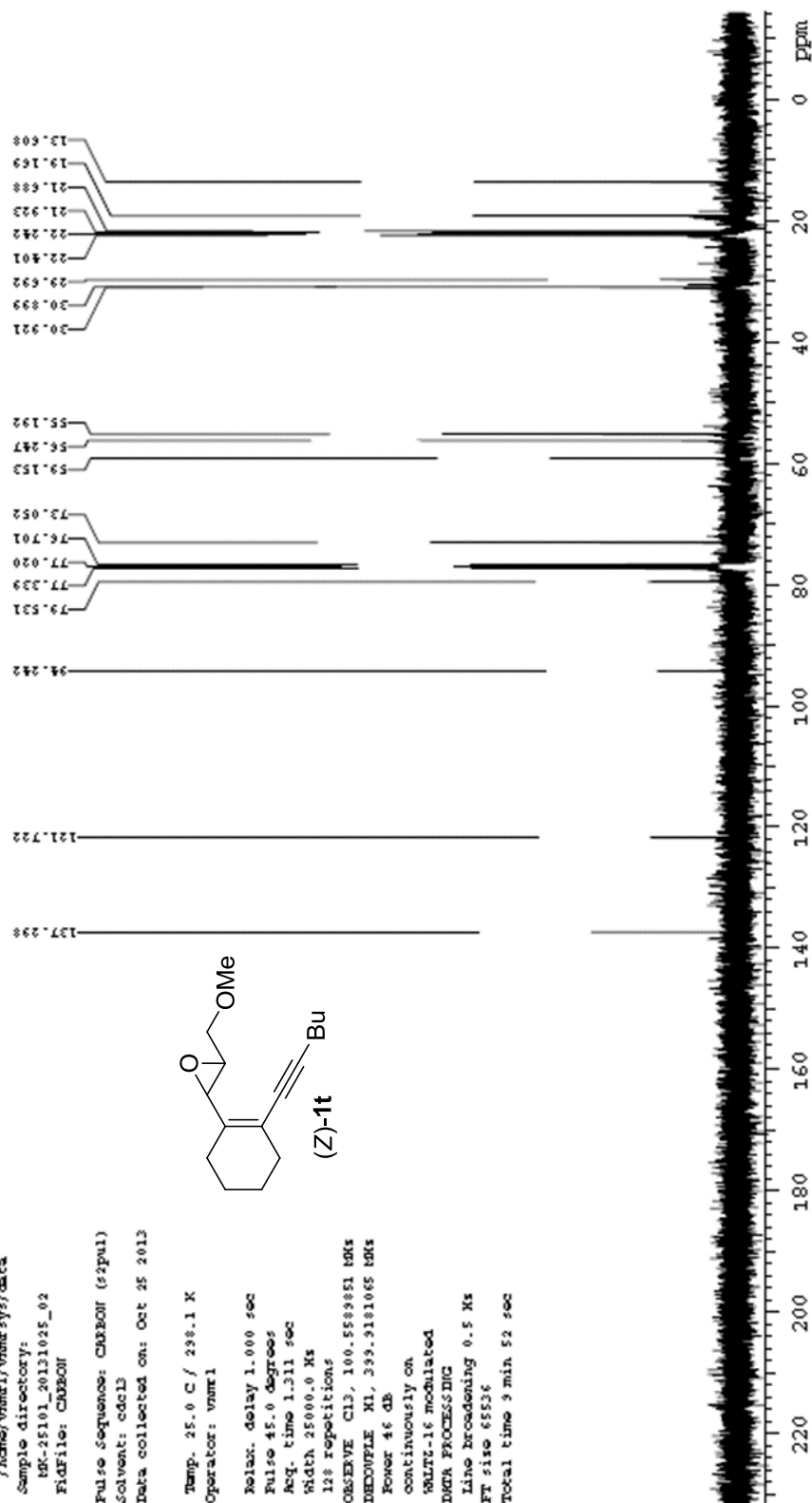
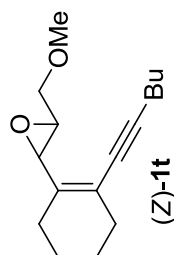


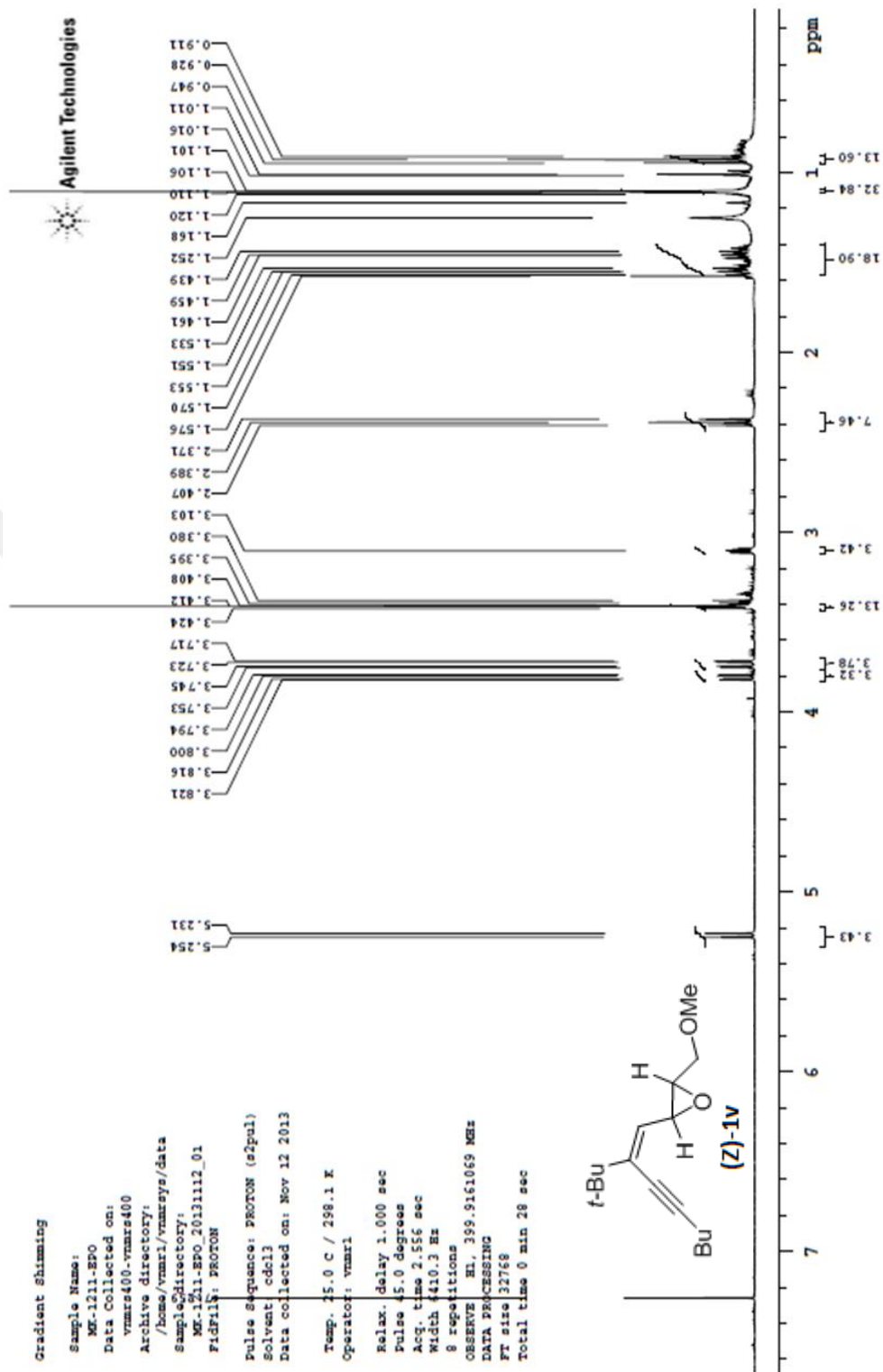
NR-25101

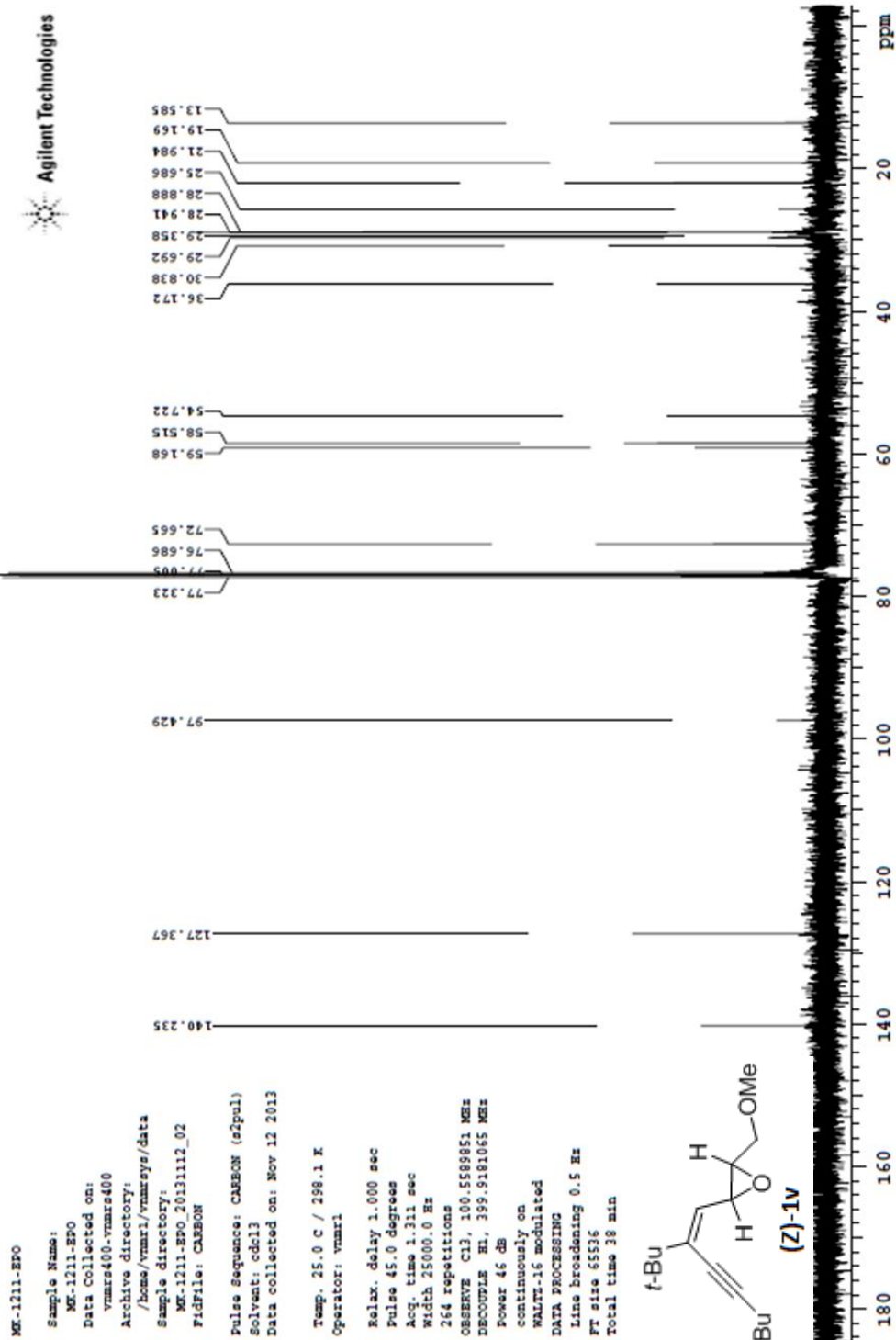
Sample Name:
NR-25101
Data Collected on:
vnmr5400-vnmr5400
Archive directory:
/home/vnmr1/vnmr5400/data
Sample directory:
NR-25101_20131025_02
FidFile: CH2OH

Pulse Sequence: CH2OH (zgpg30)
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 CH3, 100.5589851 MHz
DECOUPLE X1, 339.3181065 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







MT-1a

Sample Name:

MT-1a

Data Collected on:

vmrs400-vmrs400

Archive directory:

/home/user1/vmrs400/data

Sample directory:

MT-1a.20141021_01

File:

PRON

Pulse Sequence: PRON (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

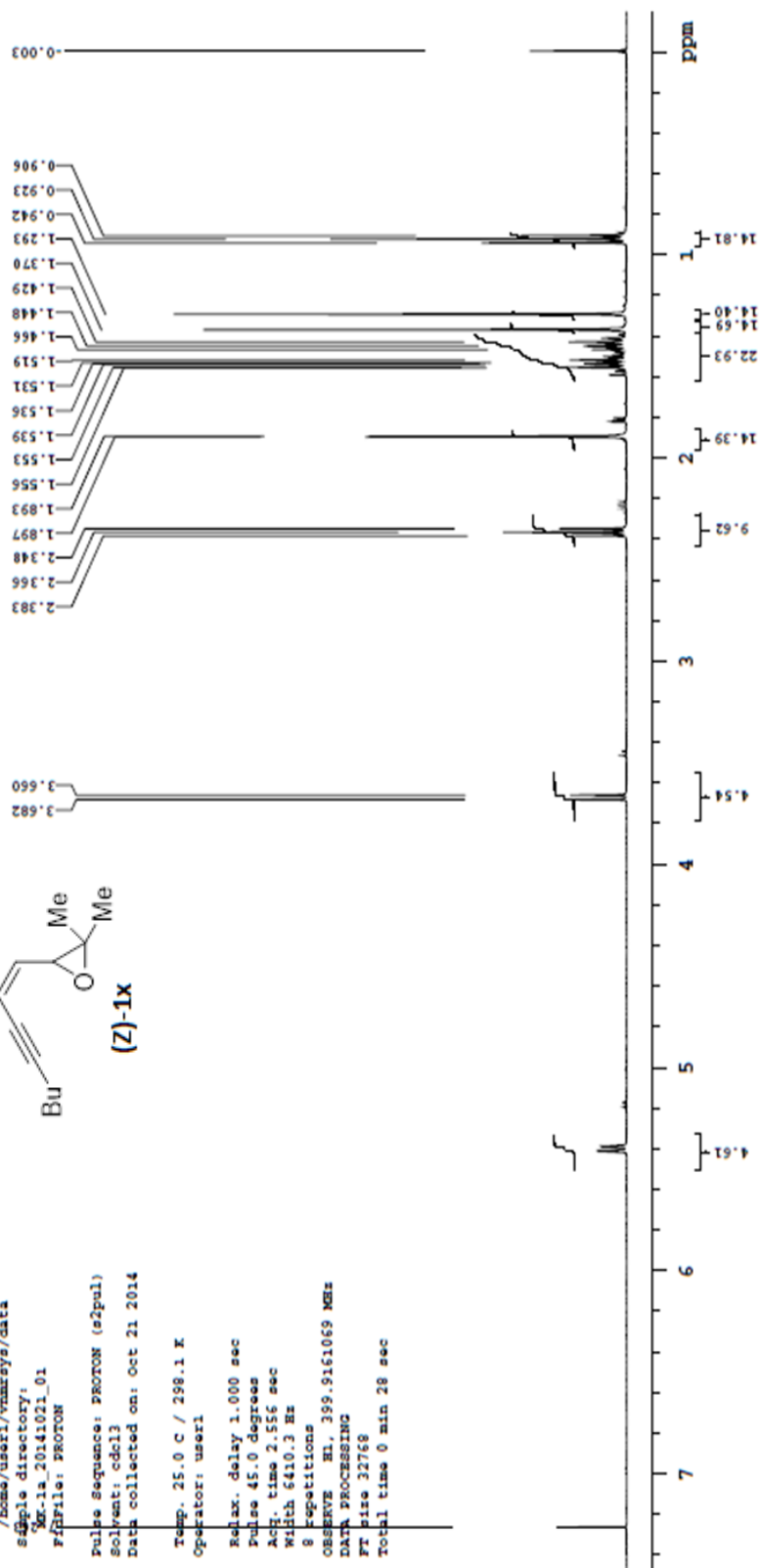
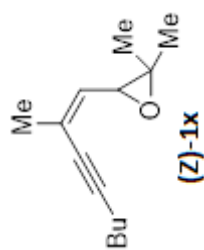
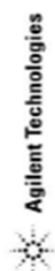
8 Repetitions

OBSERVE HI, 399.9161069 MHz

DATA PROCESSING

FT size 32768

Total time 0 min 28 sec



ME-1a

Sample Name:

ME-1a

Data Collected on:

vmars400-vmars400

Archive directory:

/home/user1/vmarsys/data

Sample directory:

ME-1a_20141021_01

FidFile: CARBON

Pulse Sequence: CARBON (zgpg3)

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 CH3, 100.558951 MHz

DECOUPLE H1, 399.518105 MHz

Power 46 dB

continuously on

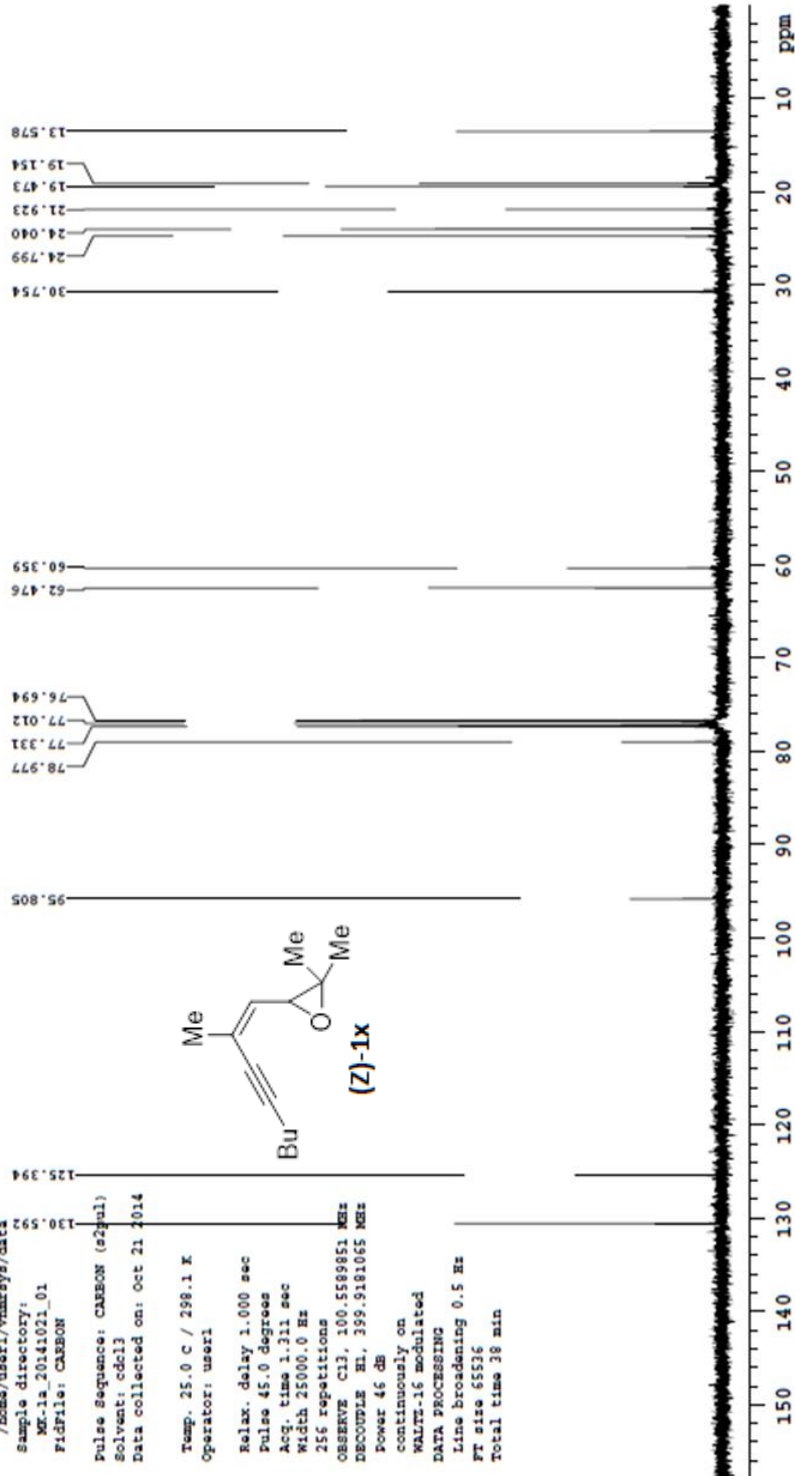
WALTZ-16 modulated

DATA PROCESSING

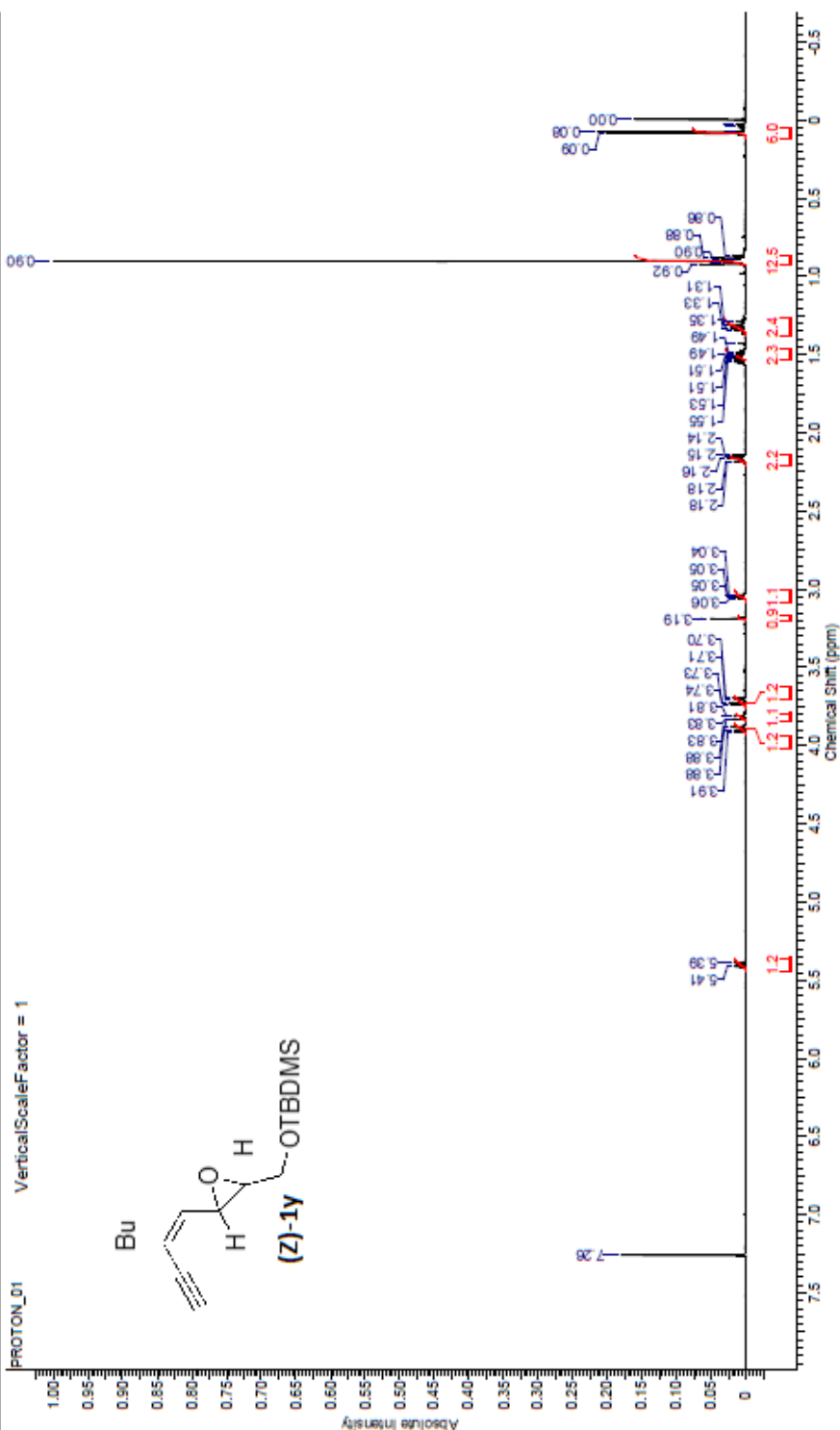
Line broadening 0.5 Hz

FT size 65536

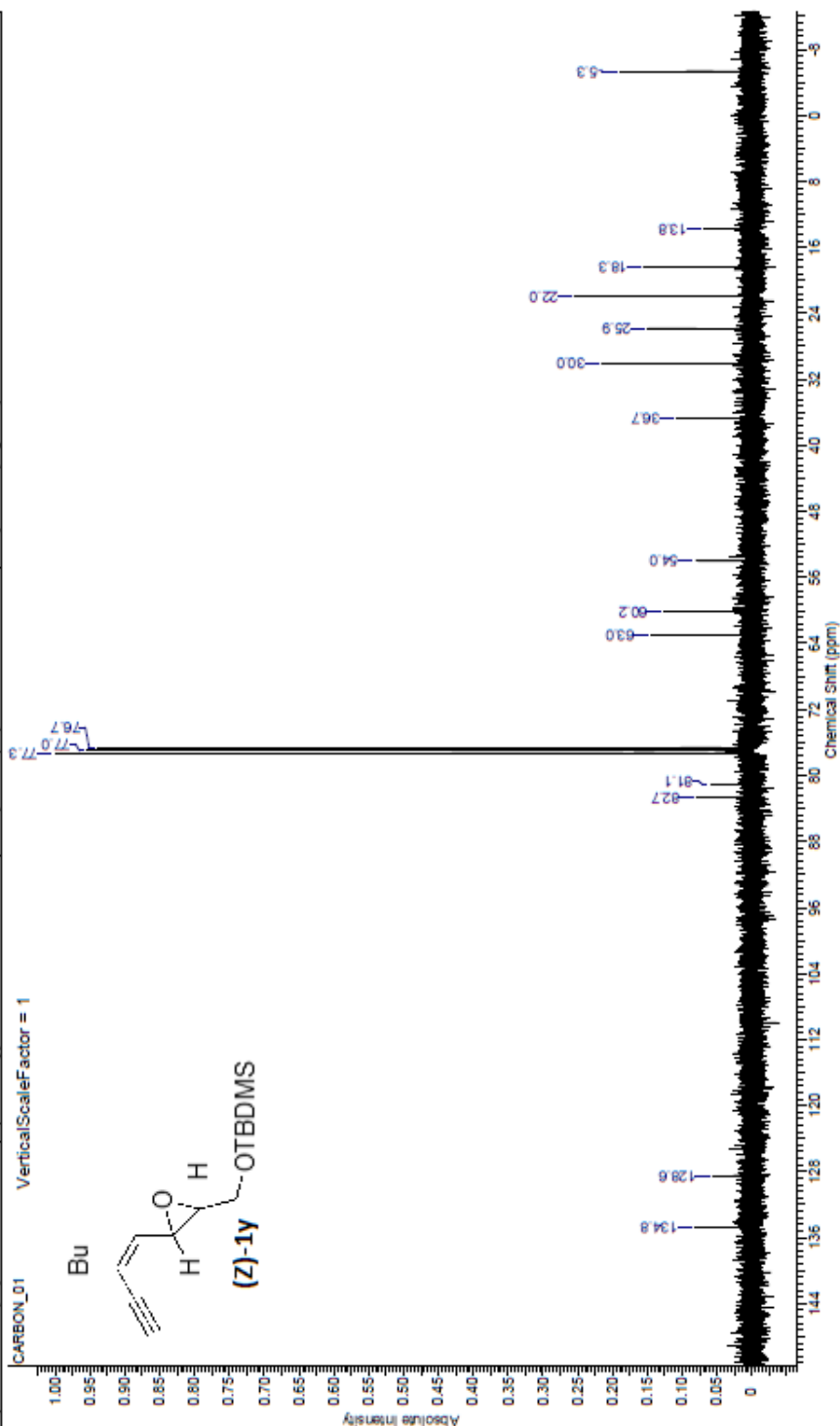
Total time 38 min



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	¹ H	Number of Transients	8	Original Points Count	16384	Points Count	16384
Pulse Sequence	s2h1	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-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	¹³ C	Number of Transients	512	Original Points Count	32768	Points Count	32768
Pulse Sequence	sCh1	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



FZ-FX077

Agilent Technologies



Sample Name:

FZ-FX077

Data Collected on:

vmrs400-vmrs400

Archive directory:

/home/vmrs/vmrs400/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: vmrs1

Relax: delay 1.000 sec

Pulse: 45.0 degrees

Acq. time 2.556 sec

Width 6410.3 Hz

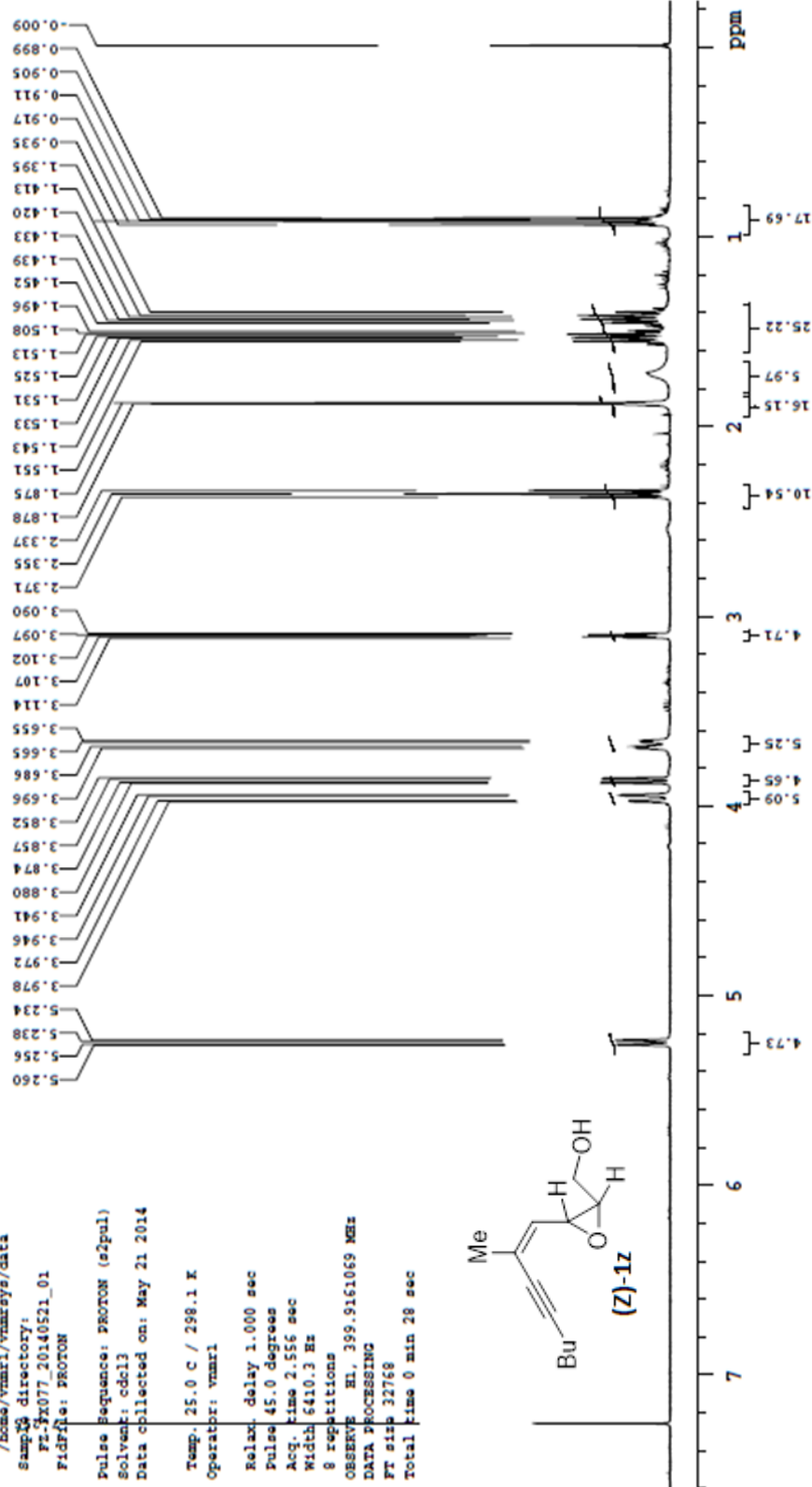
8 repetitions

OBSERVE RL 399.9161069 MHz

DATA PROCESSING

FT size 32768

Total time 0 min 28 sec



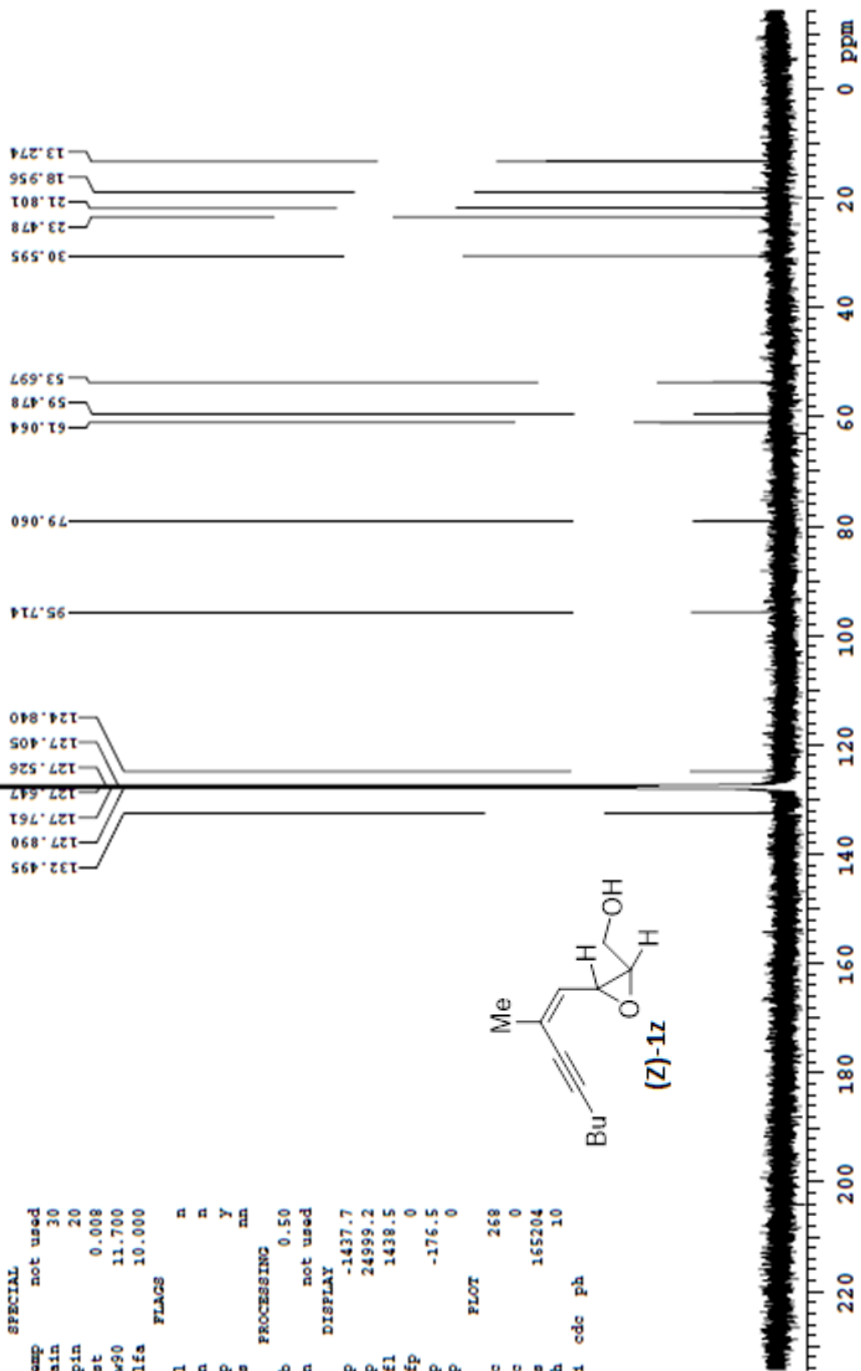
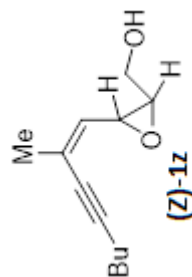
ME-05-11-12-SAP-T

exp41 CARBON

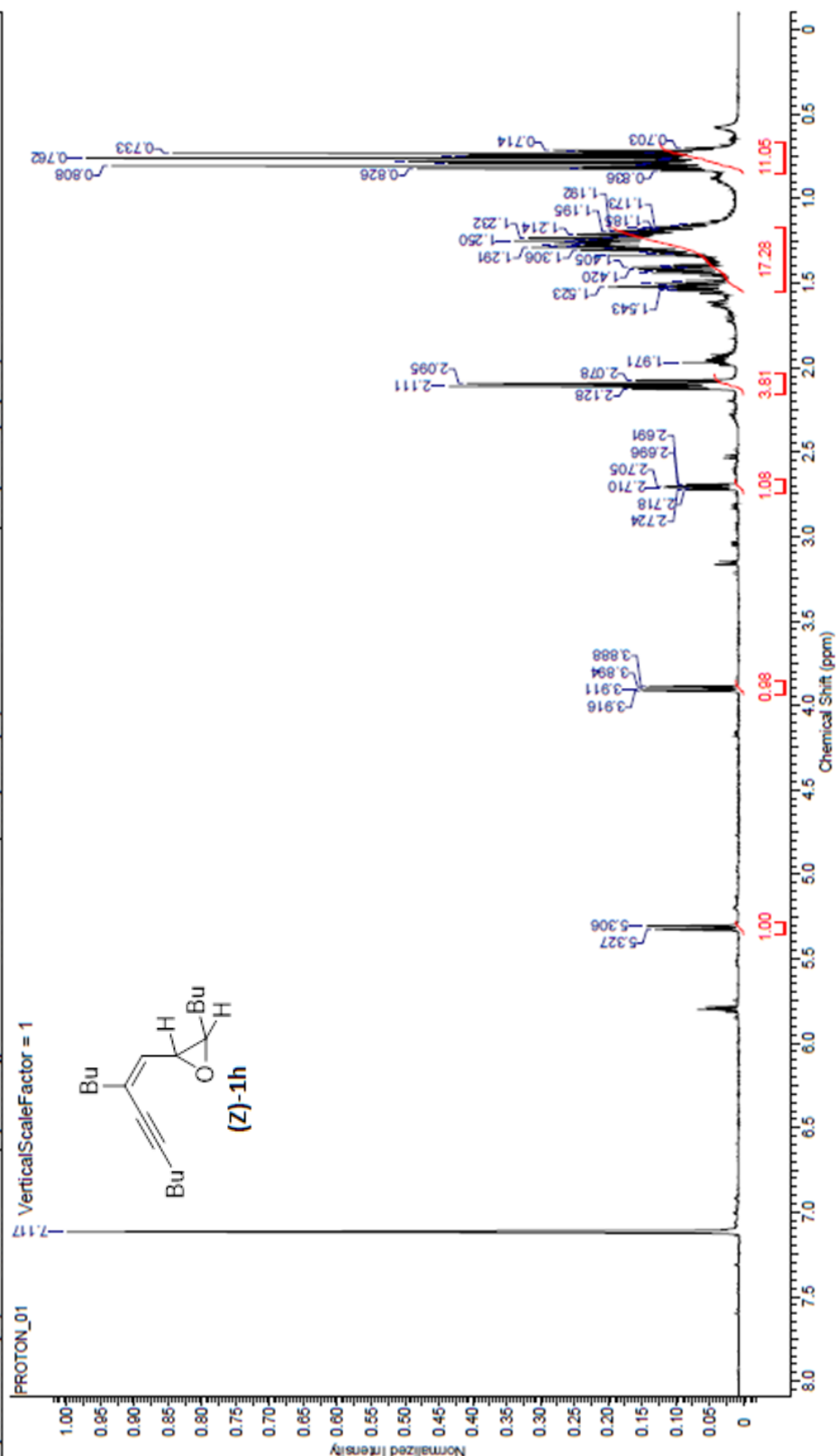
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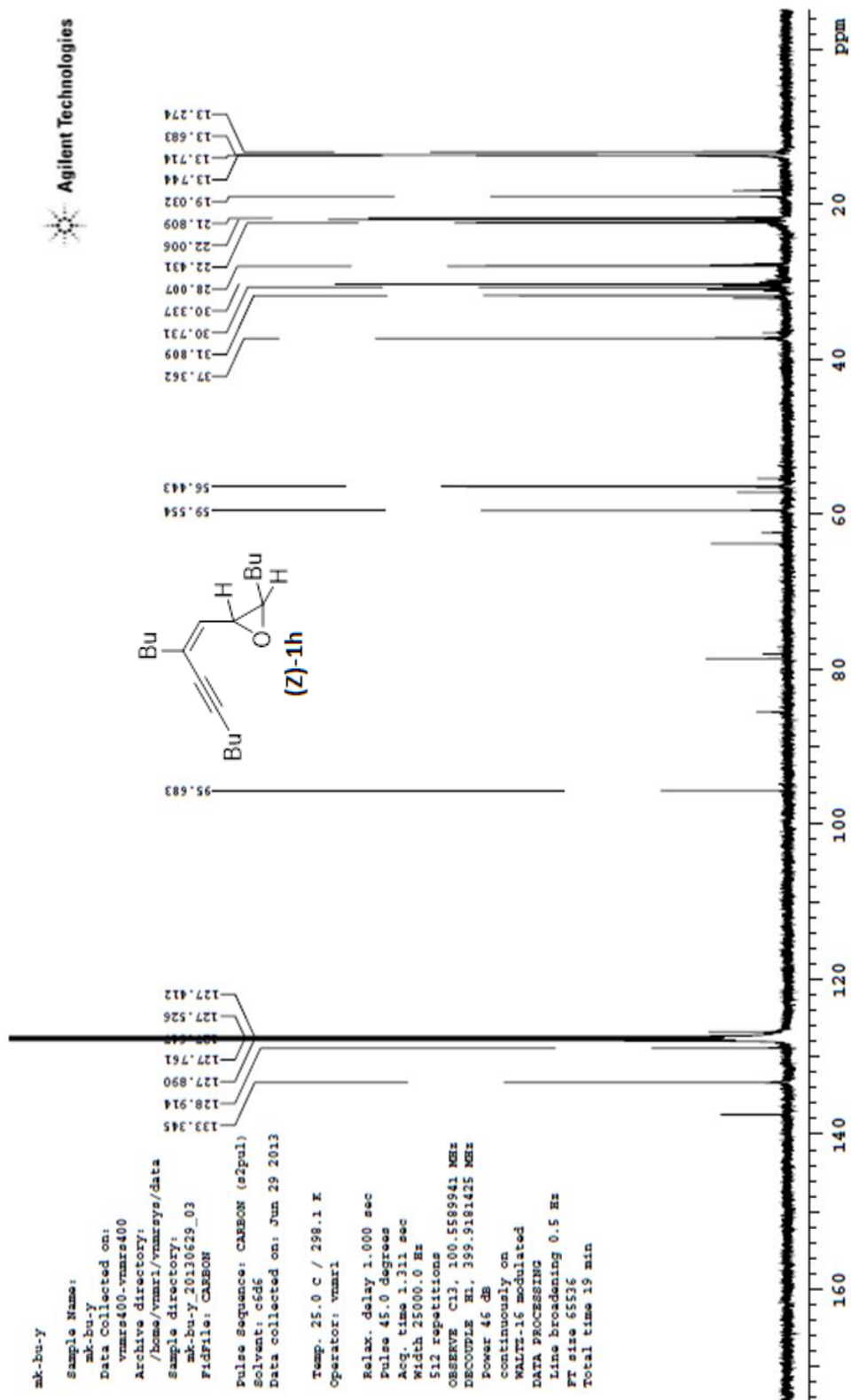
SAMPLE          PRESATURATION
date Nov 5 2012 satmode n
solvent cfd6 wet
file /home/vmri/v- SPECIAL
mrsize/data/LEVENT- temp not used
ANTOX/MELIE/MELIE- gain 30
/ME-05-11-12-SAP-T- spin 20
_20121105_02/CARBO- hst 0.008
N 01.fid pw90 11.700
ACQUISITION alfa 10.000
sw 25000.0
at 1.311 11
np 65536 in n
fb 17000 dp y
bs 64 hs
dl 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 rf1 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
decave w vs 165204
dpr 46 th 10
dmf 10101 ai cdc ph

```



Acquisition Time (sec)	2.5559	Comment	mk-bu-y	Date	Jun 29 2013	Date Stamp	Jun 29 2013
File Name	C:\USERS\FIRAT\DESKTOP\EPPOXIDE\210T02-FINAL RAPOR\NMR FIDS\MELI-HMK-BU-Y_20130629_02\PROTON_01.FID\FID						
Frequency (MHz)	300.02	Nucleus	¹ H	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



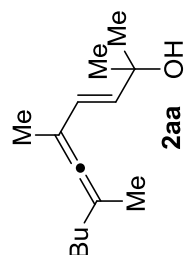
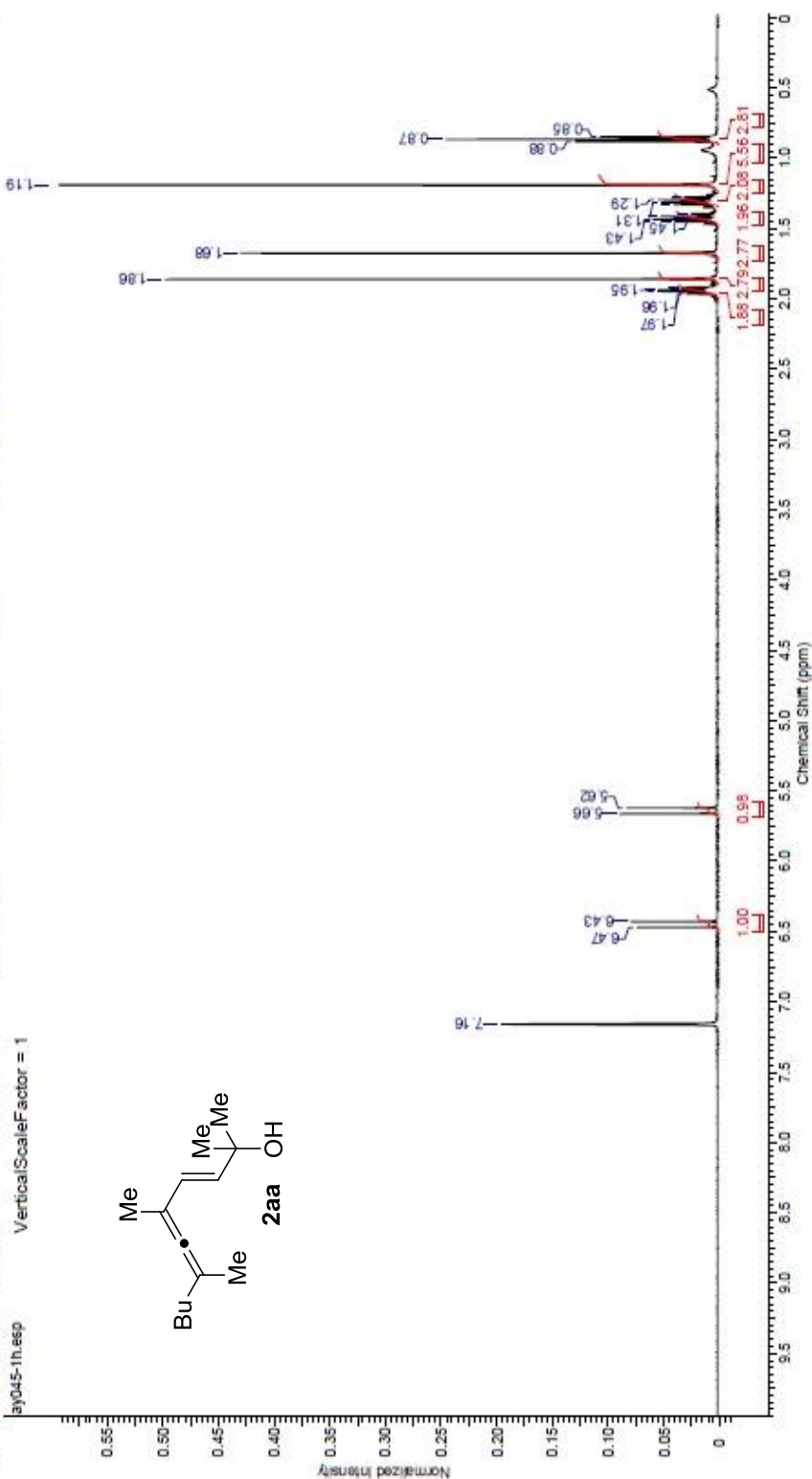


APPENDIX B

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

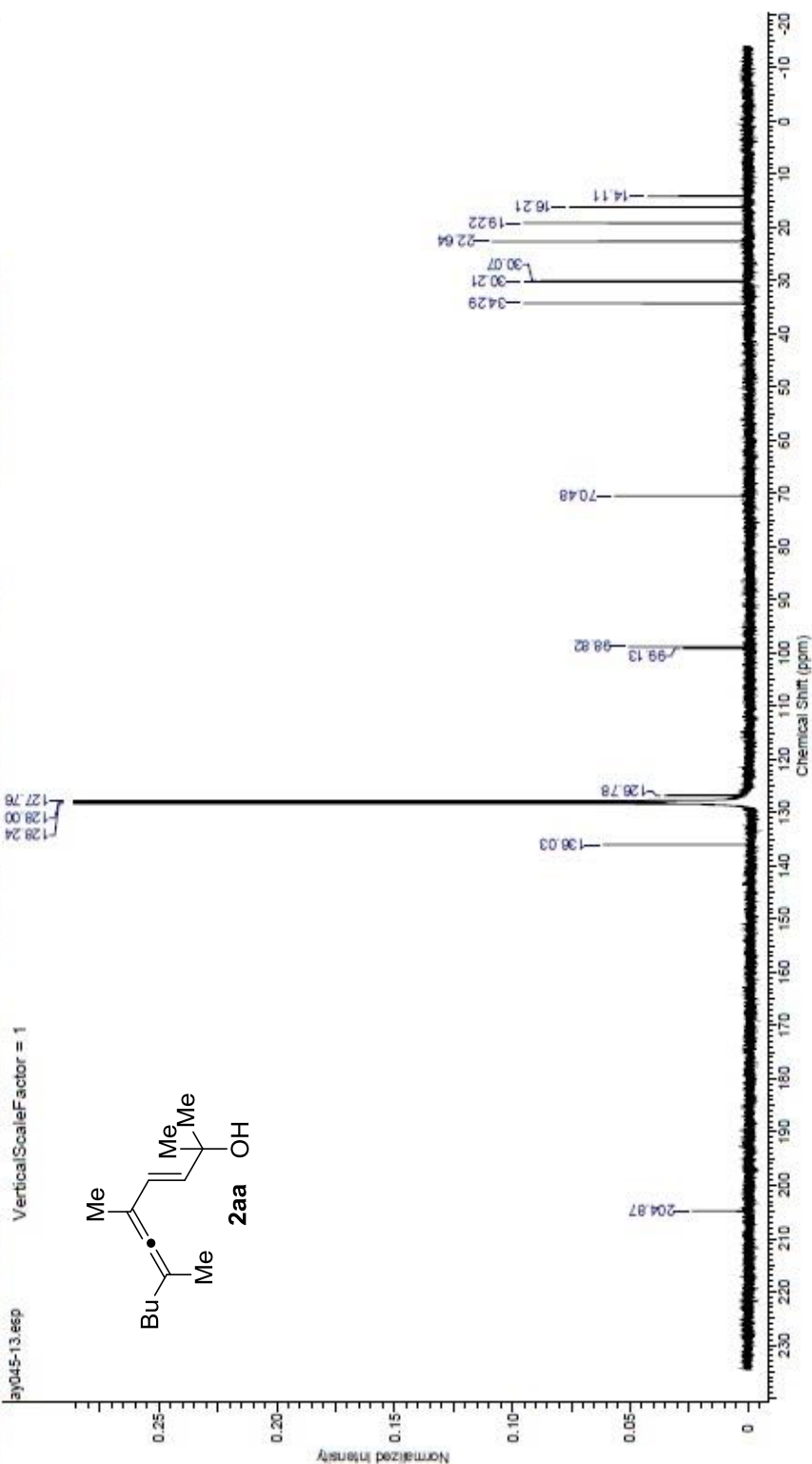


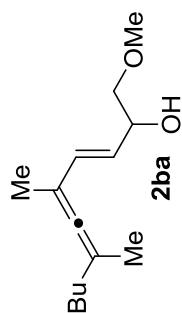
Acquisition Time (sec)	2.5559	Comment	AA-AY-045Y	Date	Jun 30 2016	Date Stamp	Jun 30 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\GLR GUERREPOXIDE\VER FF G0X GUARING\ARINC\AA-AY-045Y_20160530_011PROTON_01.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	8	Original Points Count	16384
Points Count	16384	Pulse Sequence	s2ou	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



28.07.2016 14:16:27

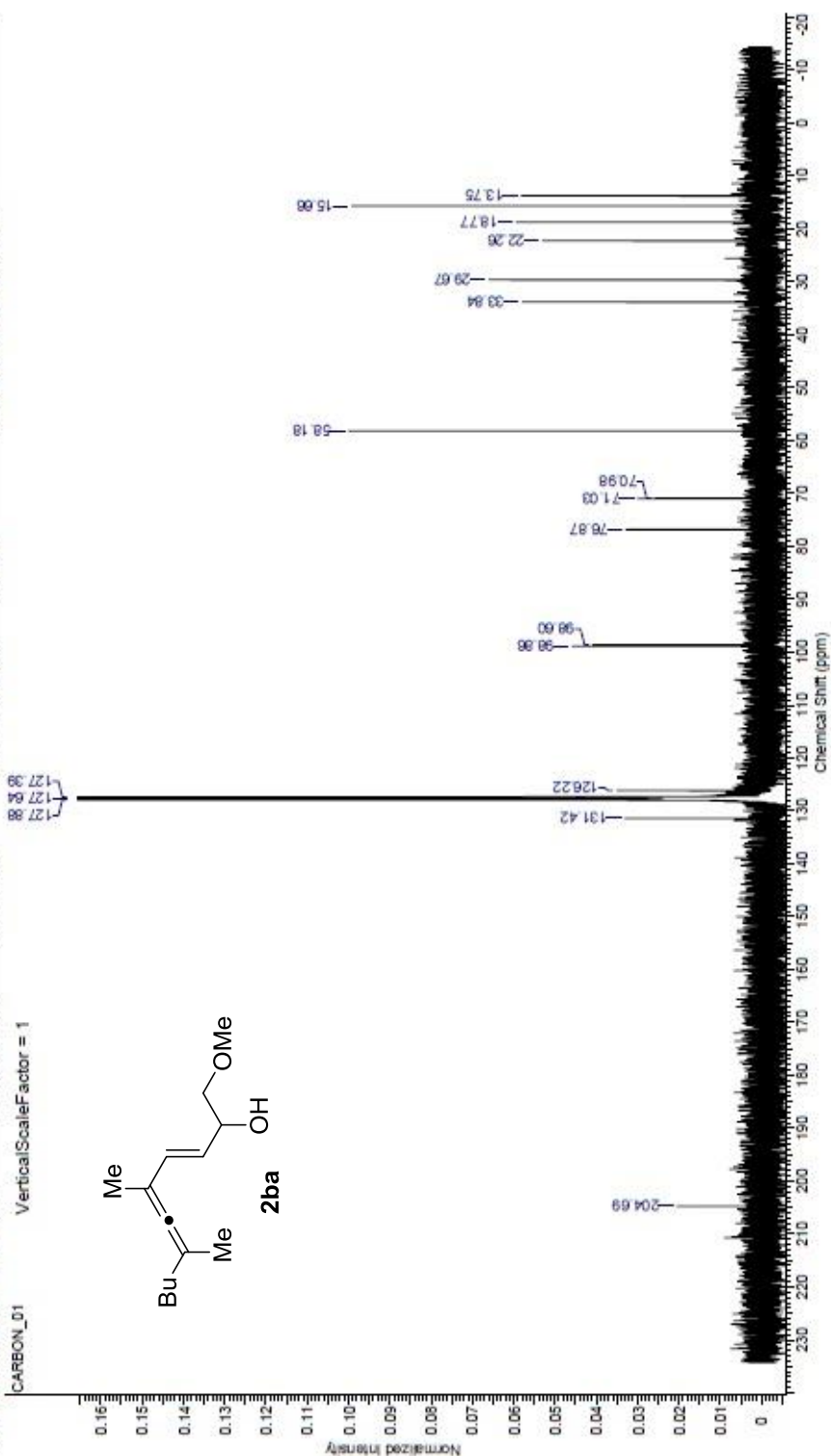
Acquisition Time (sec)	1.3107	Comment	AA-AY-Q454	Date	Jun 30 2016	Date Stamp	Jun 30 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\JULIUS GIGLER\POXIDE\VER FE GSK CUIARIN\ACIARIN\DATA\BIN\AA-AY-Q454_20160630_01\CARBON_03.FID\FID						
Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	2000	Original 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





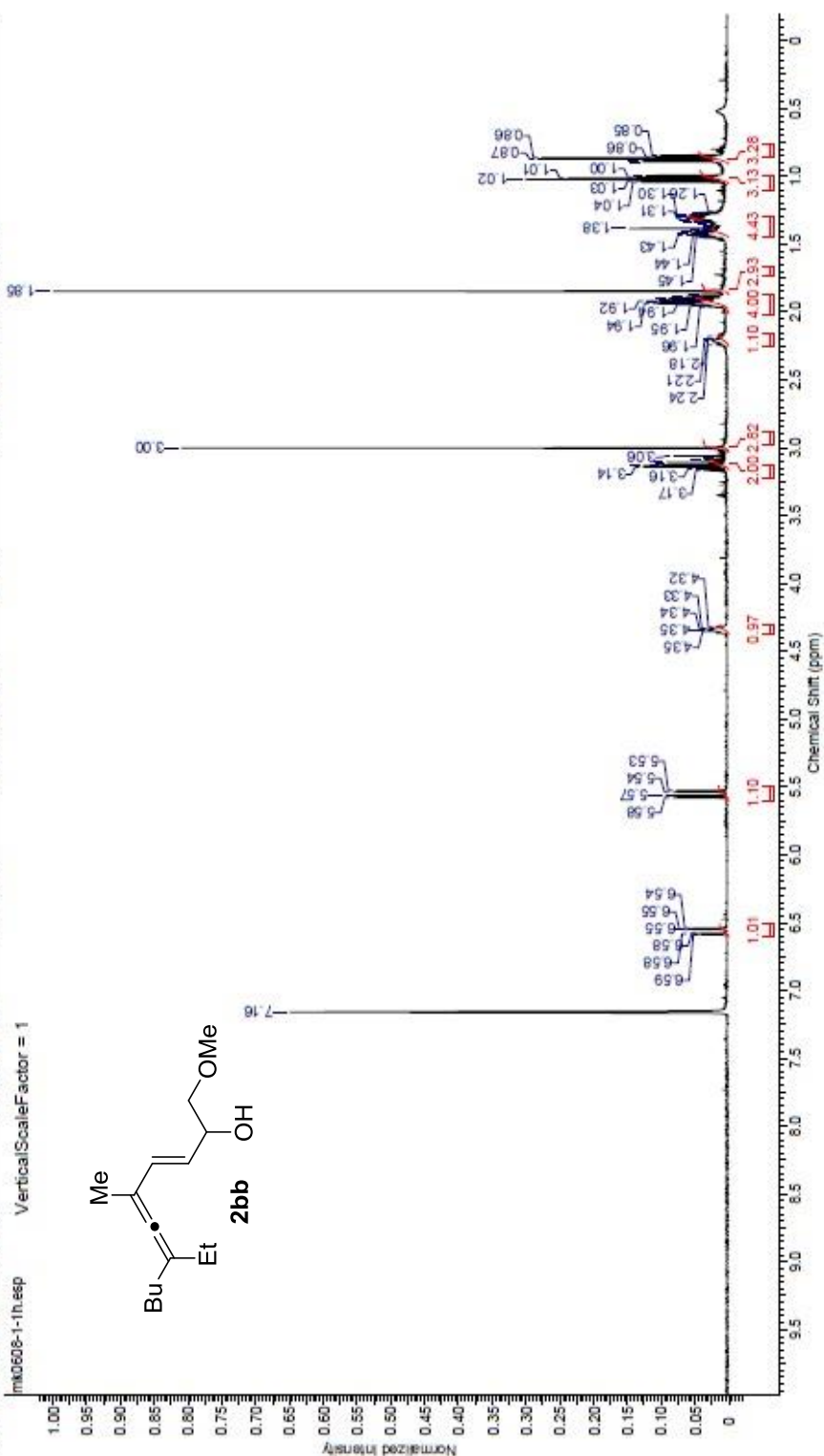
26.07.2016 21:06:27

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\USERS\FIRAT\GOOGLE DRIVE\ESKILER\MELI\HMK-0708-1-TKR-C_20150813_01\CARBON_01.FID\FID					Original Points Count	32768
Frequency (MHz)	100.57	Nucleus	13C	Number of Transients	512	Solvent	BENZENE-d6
Points Count	32768	Pulse Sequence	s20ul	Receiver Gain	30.00	Temperature (degree C)	25.000
Spectrum Offset (Hz)	11061.4873	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00		

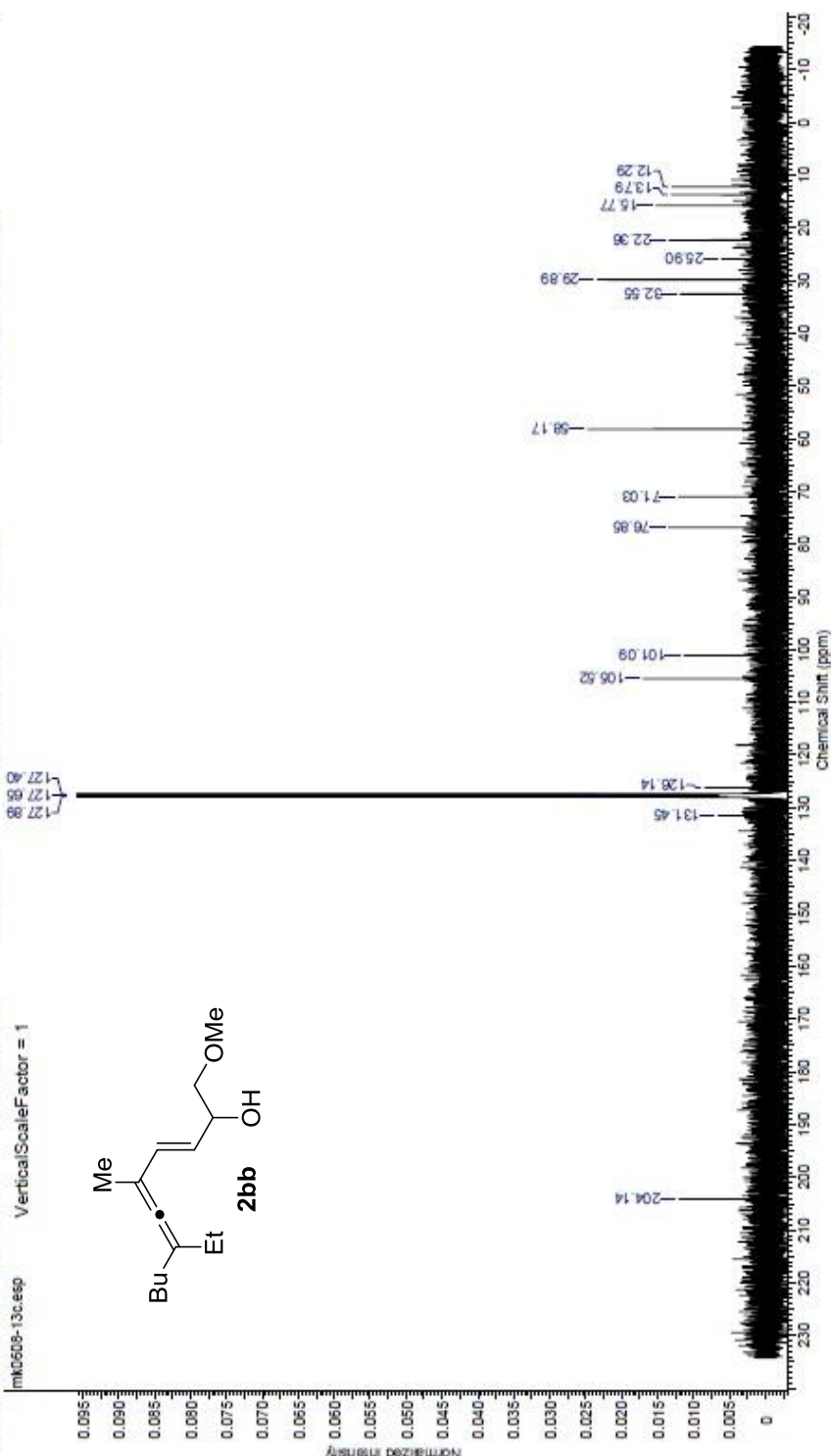


28.07.2016 11:31:12

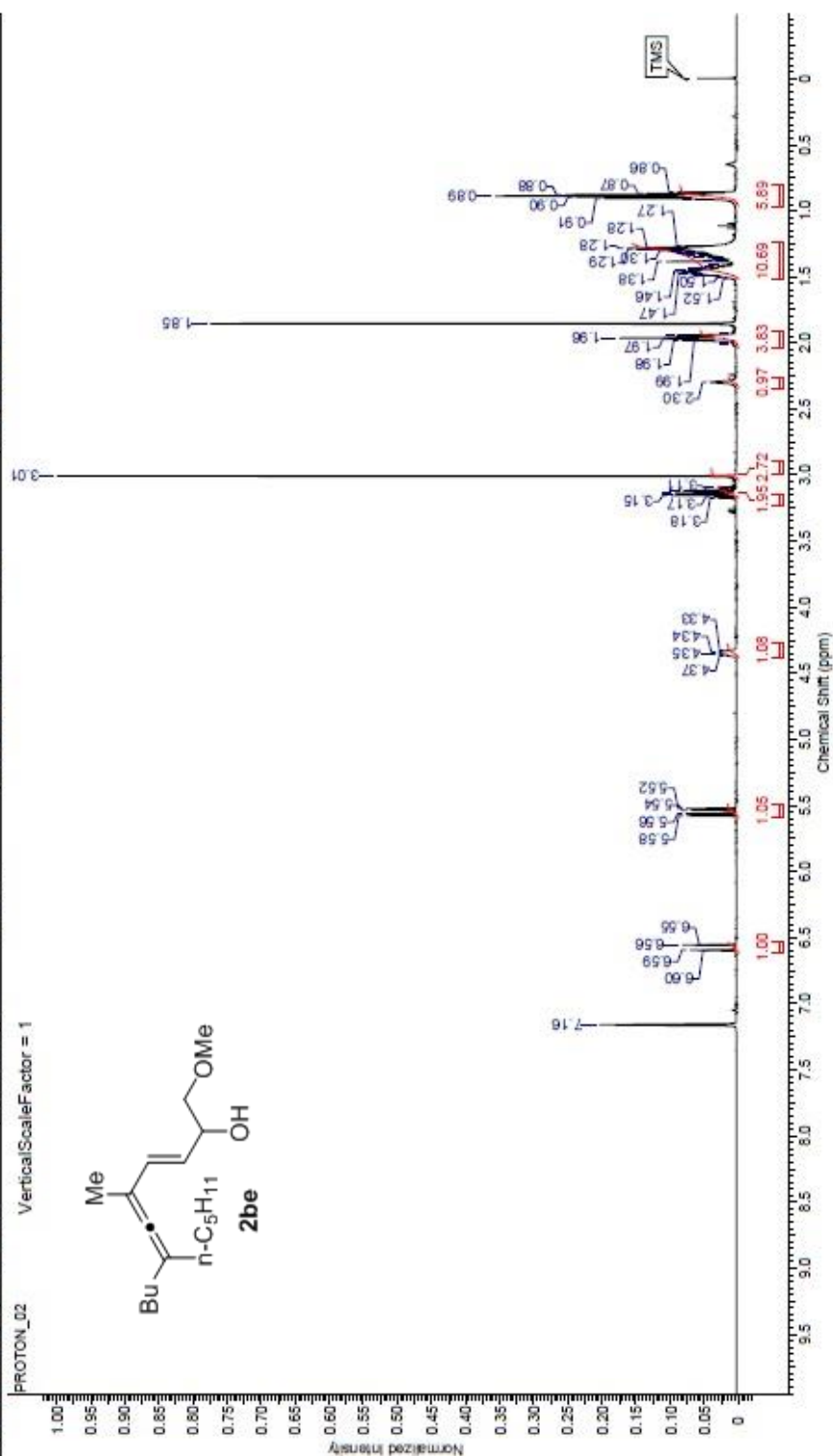
Acquisition Time (sec)	2.5559	Comment	MK-2704-1-C5D6	Date	May 26 2015	Date Stamp	May 26 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\1518\ER.GUCLER\POXIDE\VER FE G3K CUARIN\20150526_011\PROTON_01.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	8	Original Points Count	16384
Points Count	16384	Pulse Sequence	zgpg30	Receiver Gain	60.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	2416.3853	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



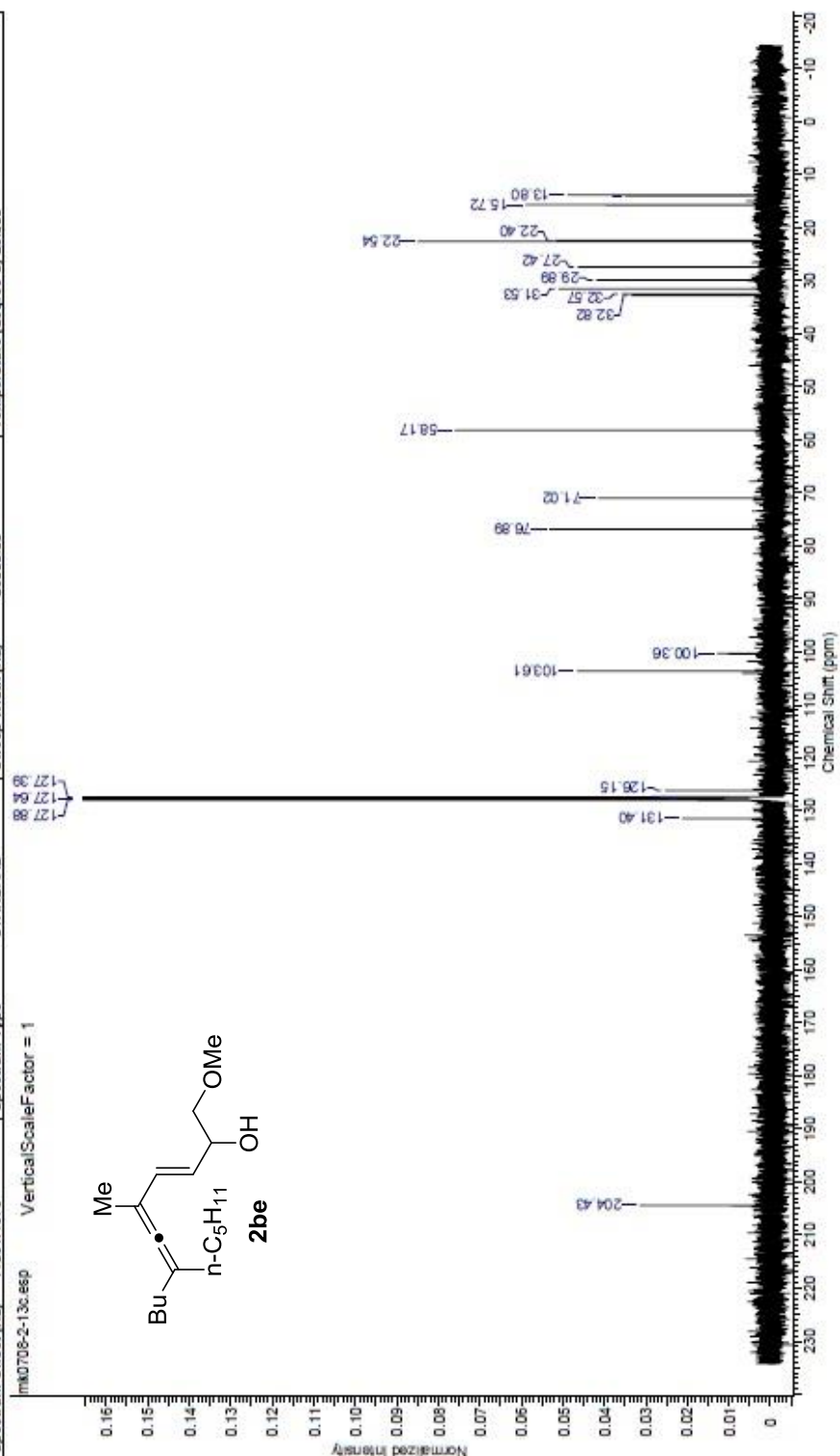
Acquisition Time (sec)	1.3107	Comment	MK-2704-1-56D6	Date	May 26 2015	Date Stamp	May 26 2015
File Name	C:\USERS\FIRST\GOOGLE DRIVE\JLIER GULPERPOXIDE\VER FE 60K QUARING\ABING DATA\EMIR ES\KILIRME						DMCARBON_01.FID.FID
Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	512	Original Points Count	32768
Points Count	32768	Pulse Sequence	s2bul	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



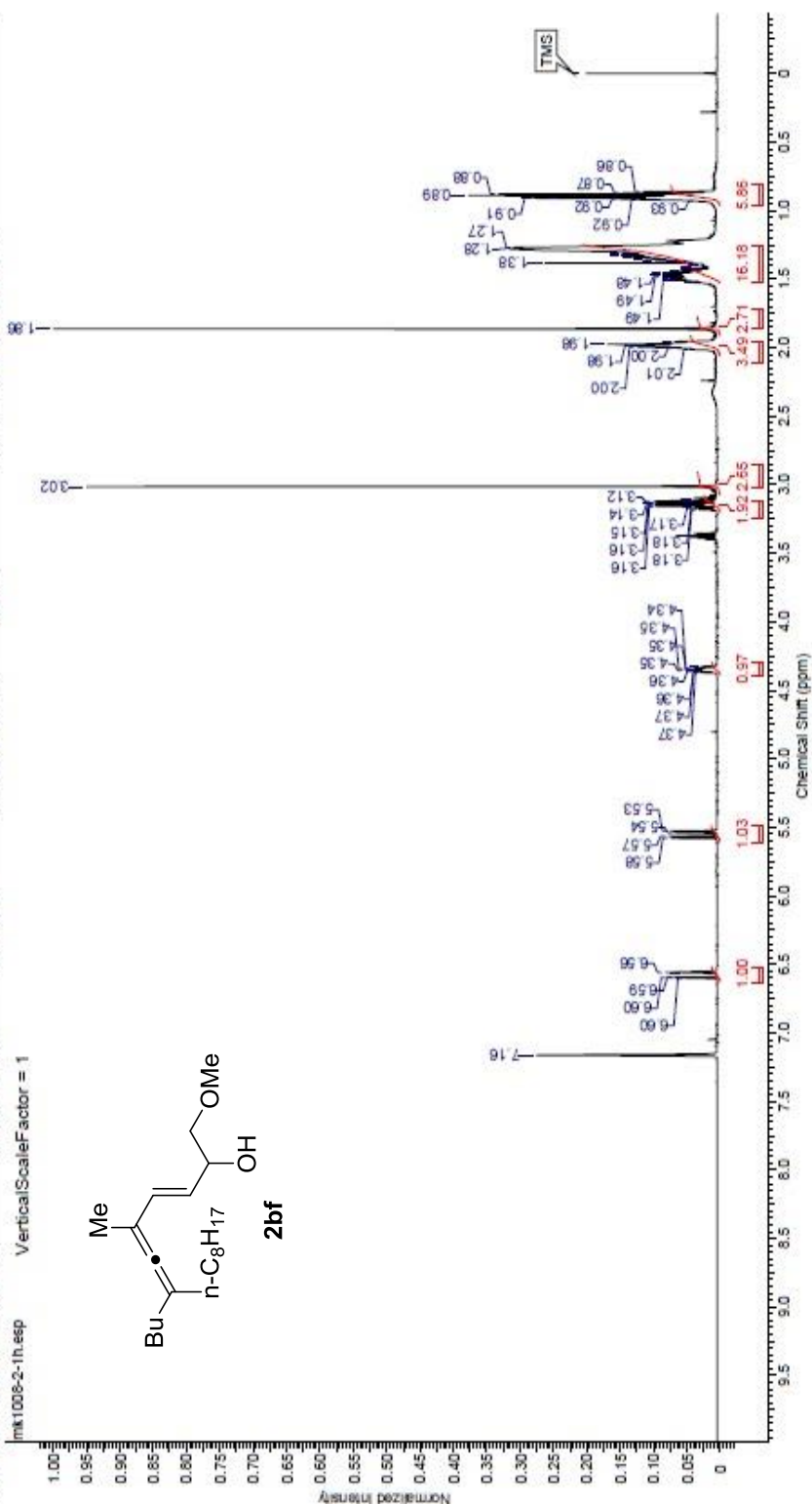
File Name	Acquisition Time (sec)	Comment	MR-0708-2-TKR	Date	Aug 13 2015	Date Stamp	Aug 13 2015
C:\USERS\FIRAT\GOOGLE DRIVE\USLER GUPLER\EPIDEXYER FE GKK CU\AVINGS\ARINC DATA\EMIR ESKILER\MR1	2.5559						
Frequency (MHz)	393.92	Nucleus	1H				
Points Count	16384	Pulse Sequence	s2pul				
Spectrum Offset (Hz)	2416.7032	Spectrum Type	STANDARD				
Sweep Width (Hz)	54.00	Receiver Gain	54.00				
Temperature (degrees C)	25.000	Number of Transients	8				
		Original Points Count	16384				
		Solvent	BEHNZENE-d6				

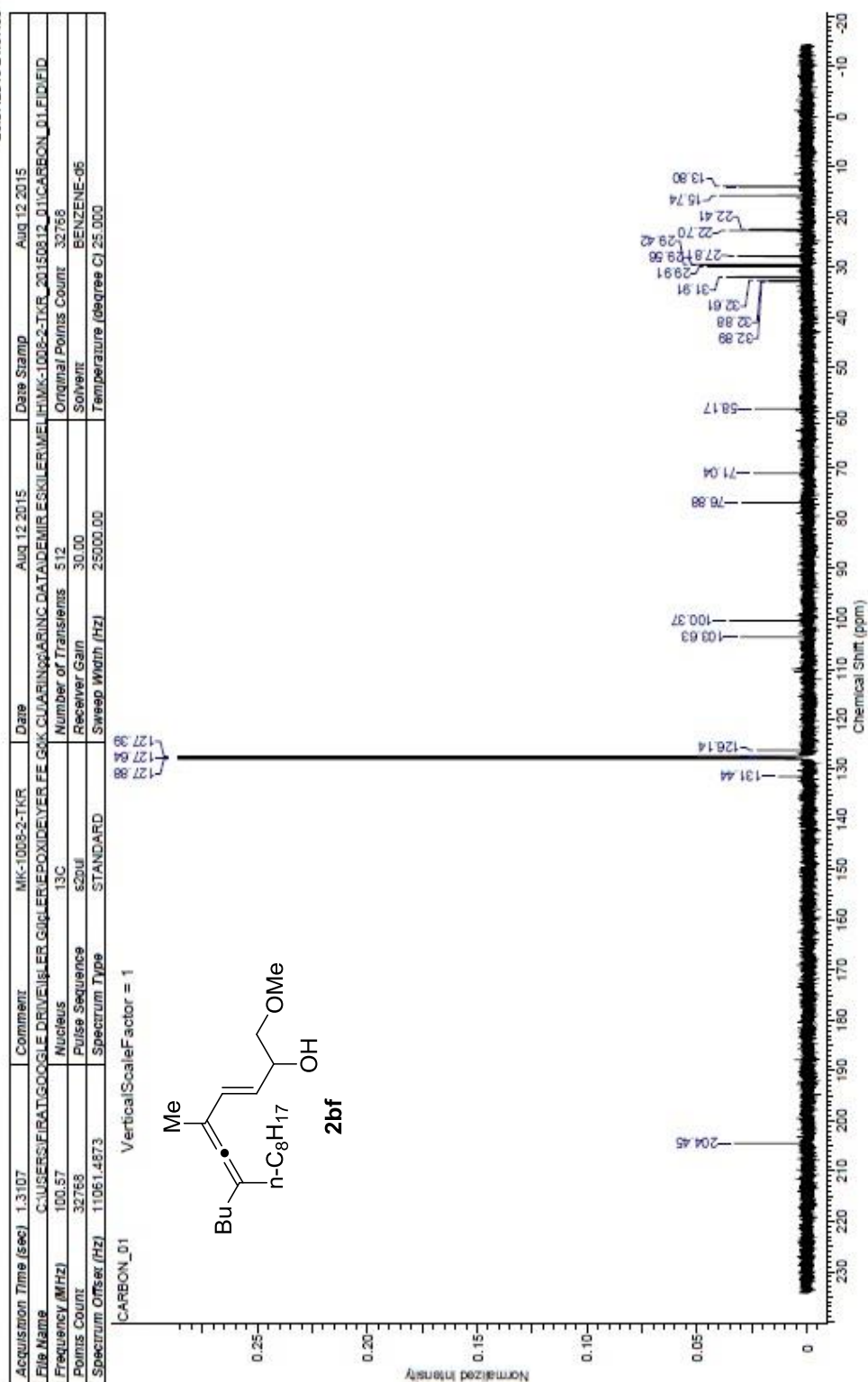


File Name	Acquisition Time (sec)	Comment	Date	Date Stamp
CHUSERSFRATGOOGLE DRIVE\UGLER GÜLER\POXIDEXYER FE GAK CUARING\BARING DATA\MIR ES\KILIR MEL HMK-3708-2-TKR-C-20150813_01\CARBON_02.FID.FID	1.3107	MIK-0708-2-TKR-C	Aug 13 2015	
Frequency (MHz)	100.57	Nucleus 13C	Number of Transients 512	Original Points Count 32768
Points Count	32768	Pulse Sequence s2pul	Receiver Gain 30.00	Solvent BENZENE-d6
Spectrum Offset (Hz)	11061.4873	Spectrum Type STANDARD	Sweep Width (Hz) 25000.00	Temperature (degree C) 25.000

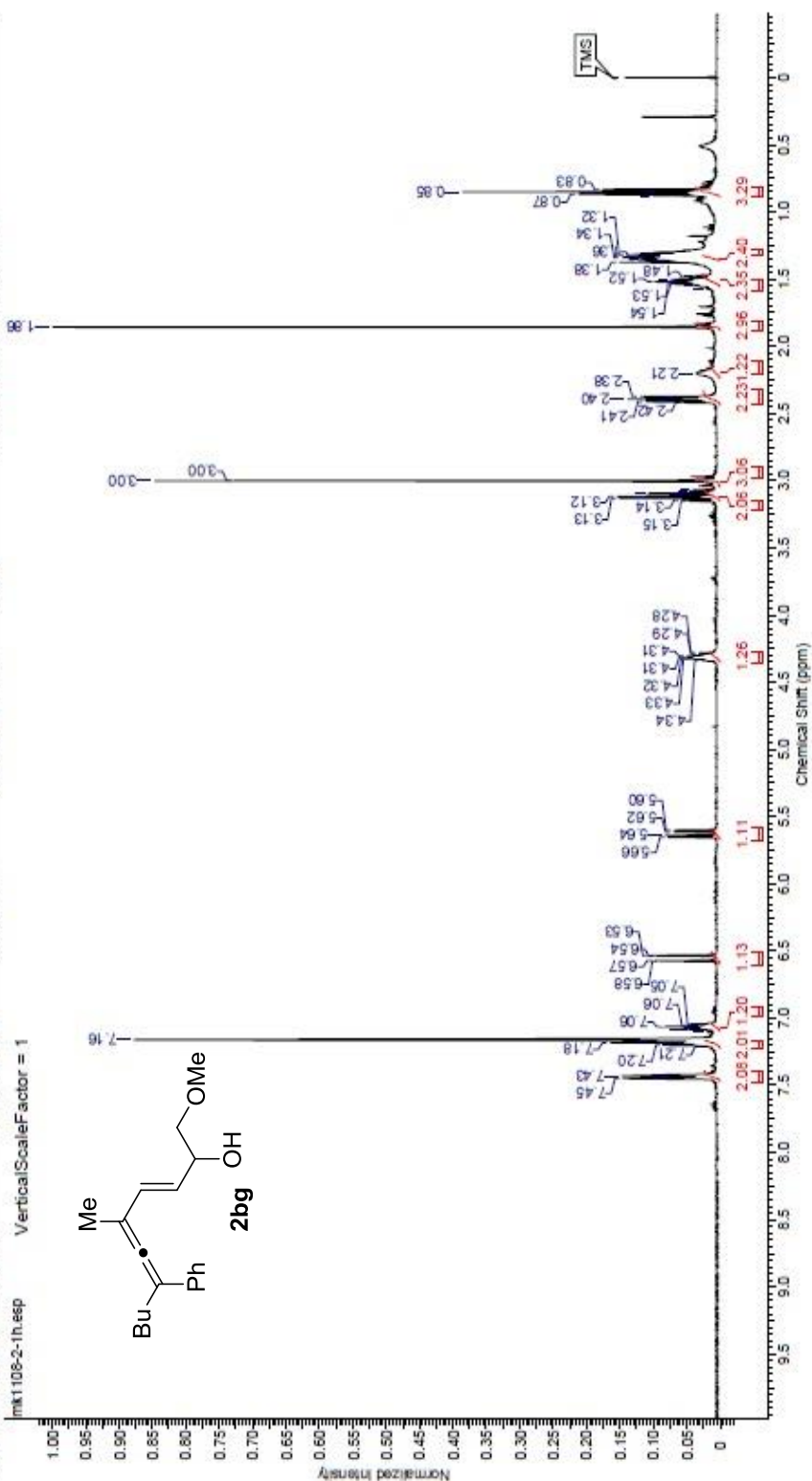


Acquisition Time (sec)	2.5559	Comment	MK-1008-2-TKR	Date	Aug 11 2015	Date Stamp	Aug 11 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\USERS\FIRAT\GOOGLE DRIVE\ESKILER\MK-1008-2-TKR_20150811_011PROTON_D2.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	32	Original Points Count	16384
Points Count	16384	Pulse Sequence	zgpg30	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



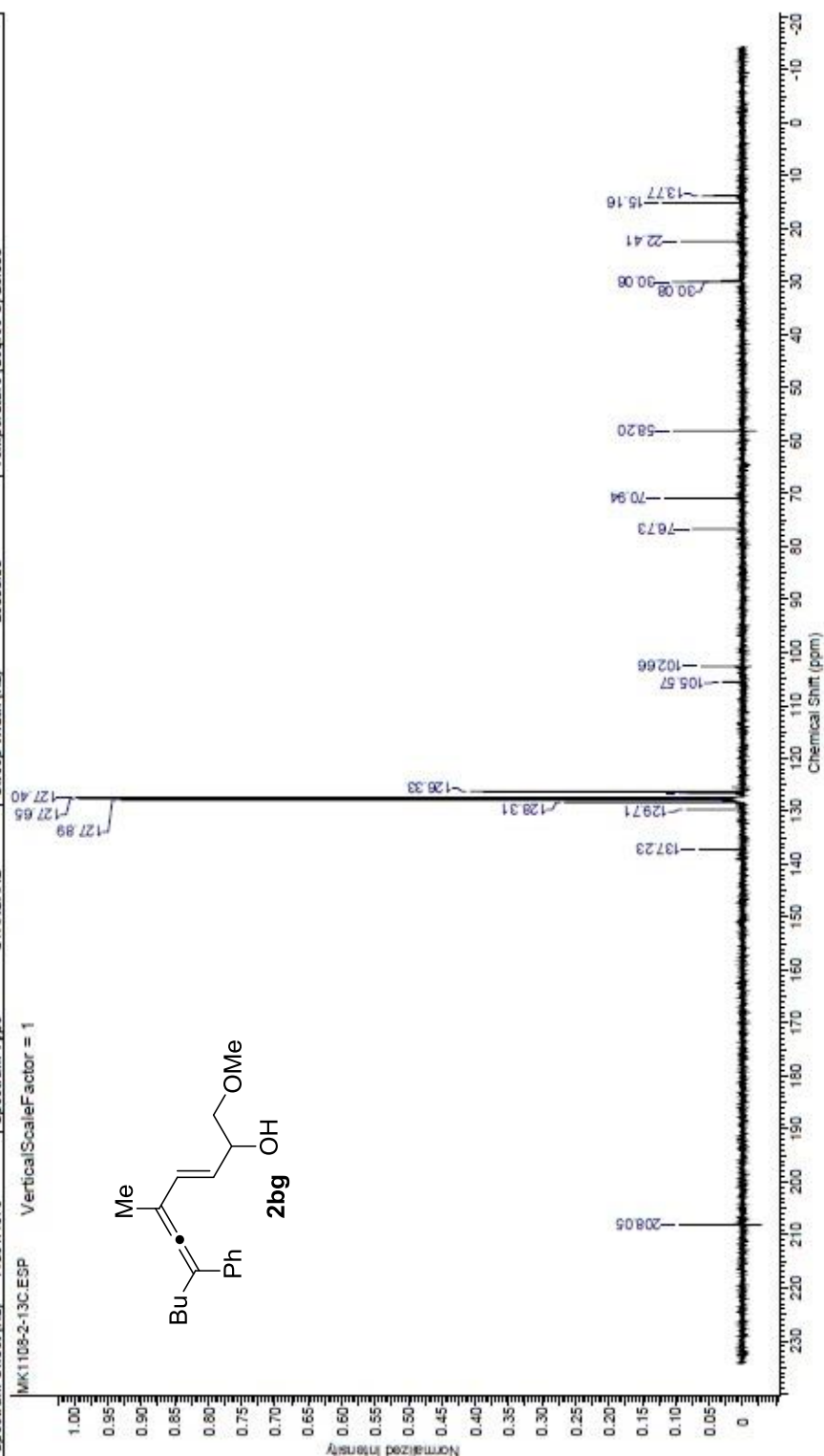


File Name	Acquisition Time (sec)	Comment	MK-1108-2A-TKR	Date	Date Stamp
C:\USERS\FIRAT\GOOGLE DRIVE\ELI\GUP\ERPOXID\YERLE GKK CUARIN\GAPINIC.DAT	2.5559			Aug 14 2015	Aug 14 2015
Frequency (MHz)	399.92	Nucleus	1H		HHMK-1108-2A-TKR_20150814_OUPROTON_00.FID.FID
Points Count	16384	Pulse Sequence	s2pul	Number of Transients	16384
Spectrum Offset (Hz)	2416.3181	Spectrum Type	STANDARD	Receiver Gain	Solvent
				60.00	BENZENE-d6
				6410.26	Temperature (degree C) 25.000



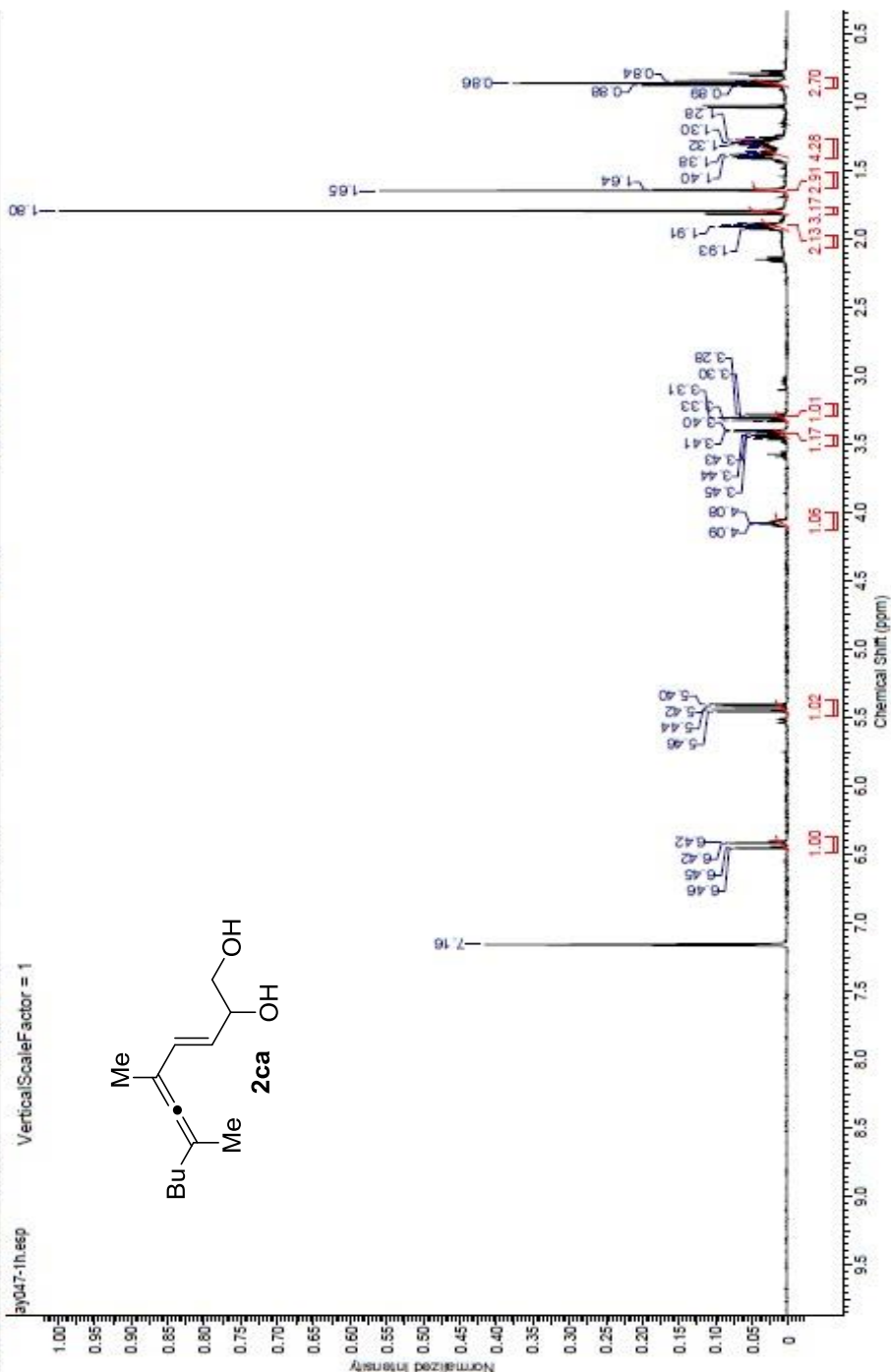
28.07.2016 17:11:22

Acquisition Time (sec)	1.3107	Comment	F2-FW186-SAF	Date	Jul 7 2015	Date Stamp	Jul 7 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\JELER GUGLER\POXIDE\POX SPECTRA&CHROMATOGRAMS\NMR\F2-FW186-SAF_20150707_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	512	Original Points Count	32768
Points Count	32768	Pulse Sequence	zgpg30	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



28.07.2016 14:48:54

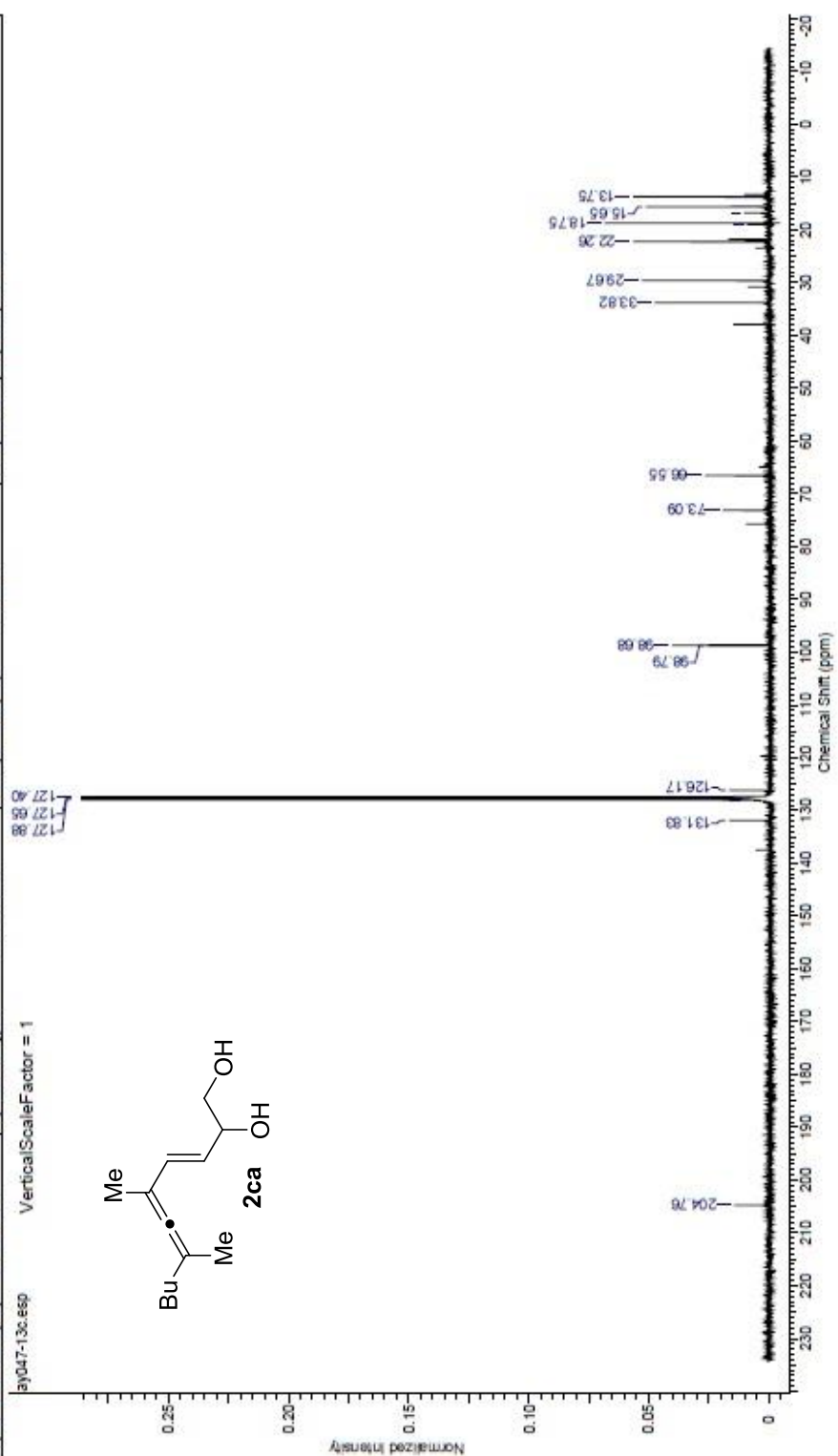
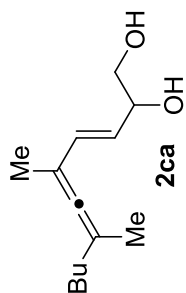
Acquisition Time (sec)	2.5559	Comment	AA-AY-047	Date	Jul 20 2016	Date Stamp	Jul 20 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\GLYCOLERPOXIDE\VER FE GSK CUJING\NMR\DATA\AA-AY-047_20160720_01\FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	8	Original Points Count	16384
Points Count	16384	Pulse Sequence	sgzui	Receiver Gain	60.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	2417.5502	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



Acquisition Time (sec)	1.3107	Comment	AA-AY-047	Date	Jul 21 2016	Date Stamp	Jul 21 2016
File Name	C:\USERS\FRAT\GOOGLE DRIVE\UGER GUINER\POXIDEX\VEYER FE GKK CUARING\JCARING DATA\INCAA-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	s2nuF	Receiver Gain	30.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	110611.4673	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000

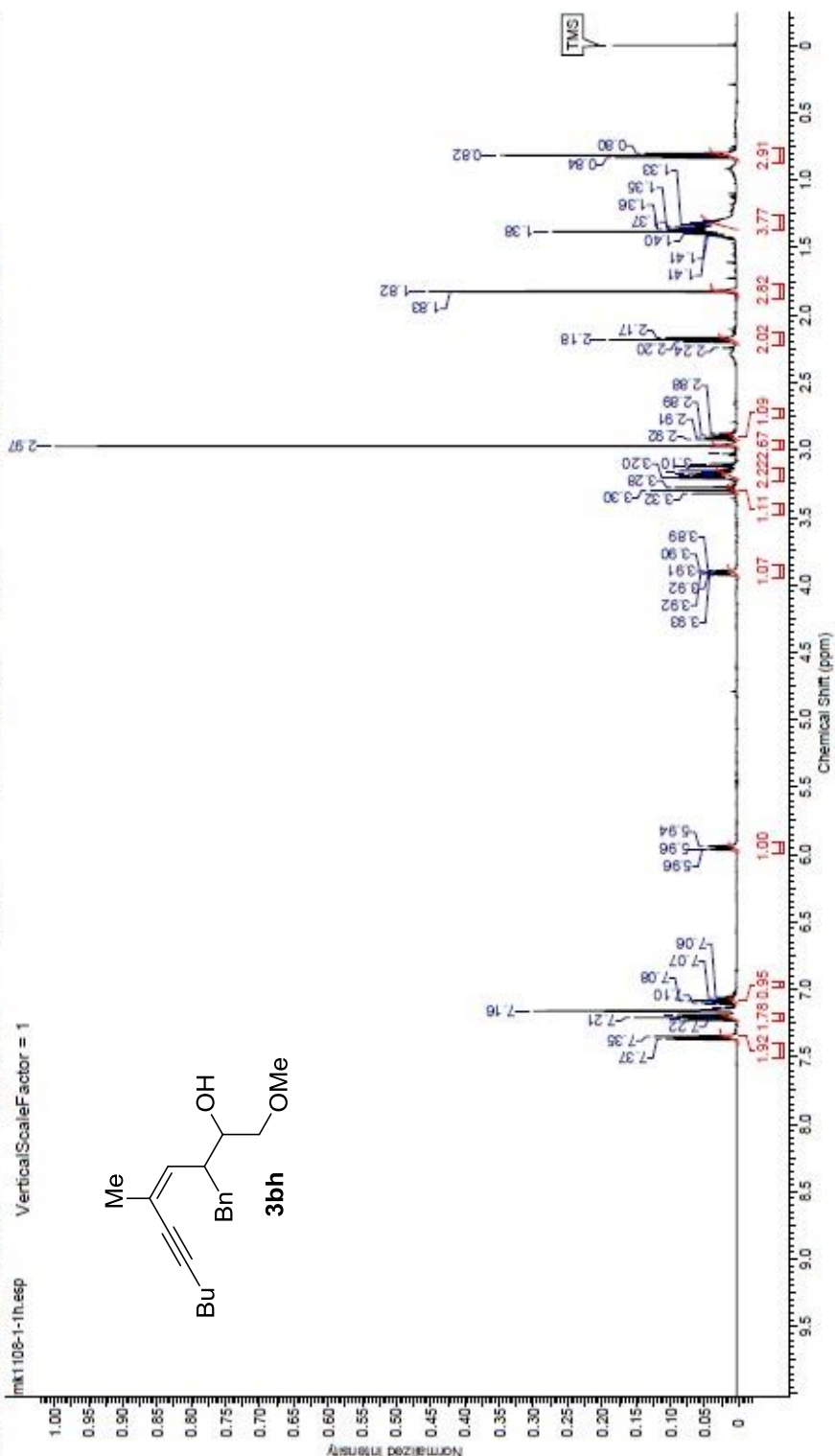
ay047-13c.esp

VerticalScaleFactor = 1



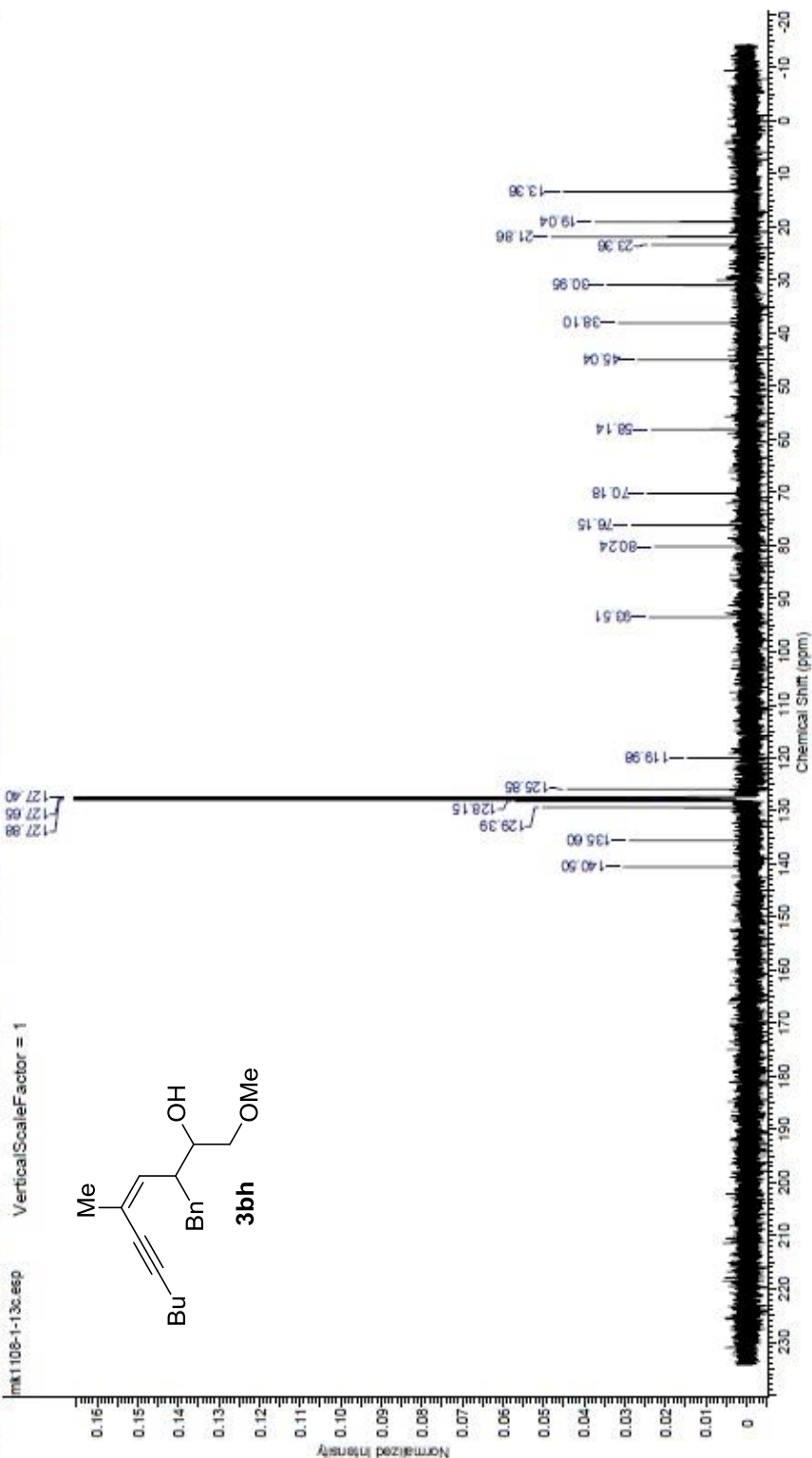
26.07.2016 22:15:49

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\GLR\POXIDE\VER FE GSK CUARING\MARINC DATA\EMIS ES\KILME\1108-1-1_20150811_011\PROTON_01.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	32	Original Points Count	16384
Points Count	16384	Pulse Sequence	zgpg30	Receiver Gain	58.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	2416.7052	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



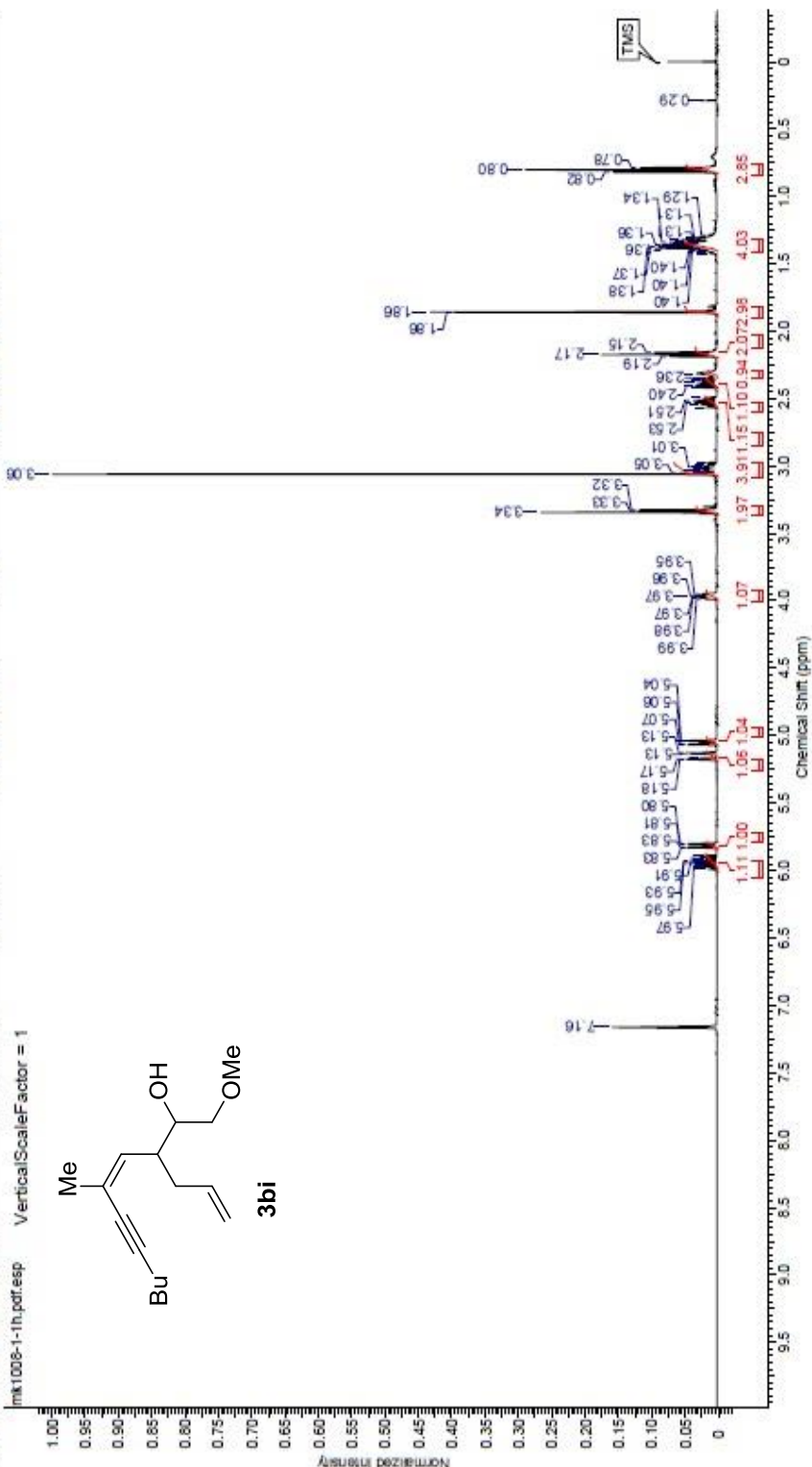
26.07.2016 22:15:22

Acquisition Time (sec)	1.3107	Comment	MI-0811-1-1	Date	Aug 12 2015	Date Stamp	Aug 12 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\JELER GÜLER\POXIDE\VER FE GAK CUARING\ACARINC.DAT\DEMIR ESKILER\MIHMK-0811-1-1_20150812_01.FID\FID						
Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	512	Original Points Count	32768
Points Count	32768	Pulse Sequence	zgpg30	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

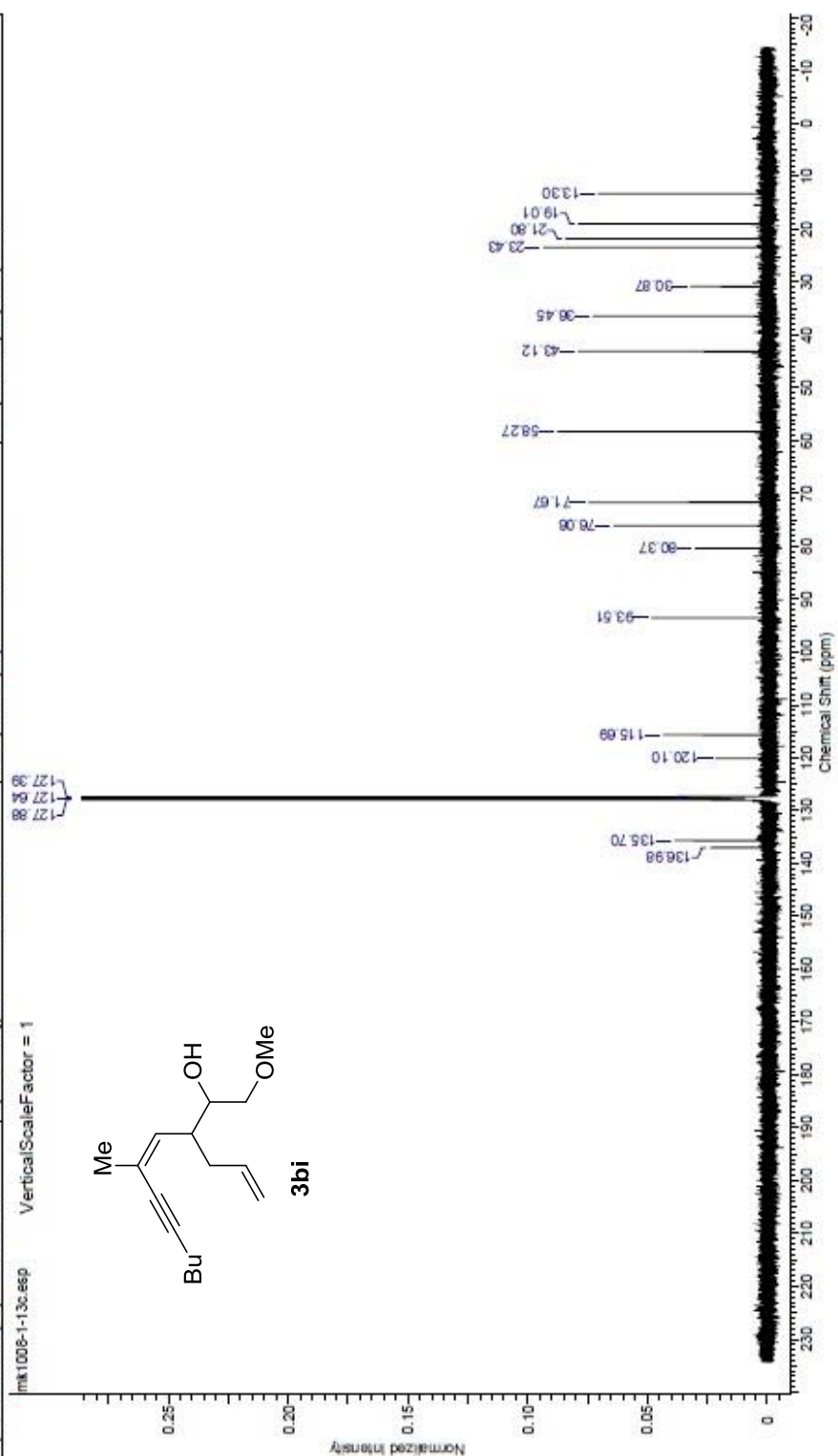


26.07.2016 22:23:33

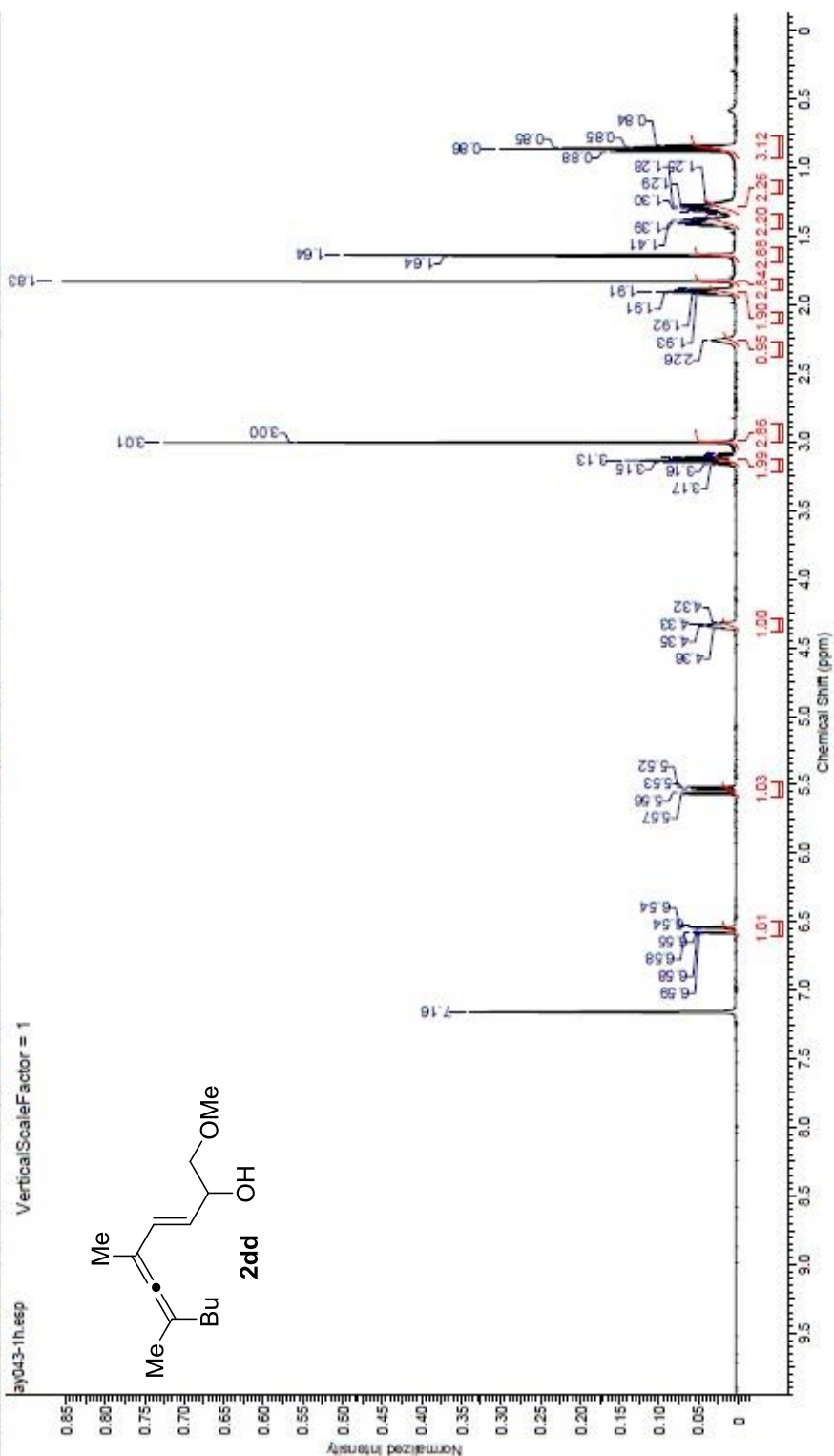
Acquisition Time (sec)	2.5559	Comment	MK-1008-1ALLY	Date	Aug 10 2015	Date Stamp	Aug 10 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\GLR\GUGLER\POXIDE\VER FE GSK QUARING\ACRINC.DAT\ADEMIR\ESKILER\ME	Nucleus	¹ H	Number of Transients	8	Original Points Count	16384
Frequency (MHz)	399.92	Pulse Sequence	s2pul	Receiver Gain	54.00	Solvent	BENZENE-d6
Points Count	16384	Spectrum Type	STANDARD	Sweep Width (Hz)	5410.25	Temperature (degree C)	25.000
Spectrum Offset (Hz)	2417.4919						



File Name	Acquisition Time (sec)	Comment	Date	Aug 10 2015	Date Stamp	Aug 10 2015
CHLUSERSFRATGOOGLE DRIVE\UGLER GUINER\POXIDE\VERFE GAK CUARINO\CARBON DATA\ENR\ESKILER\MEL-HMK-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	s2ou1	Receiver Gain	30.00	Solvent BENZENE-d6
Spectrum Offset (Hz)	110611.4673	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C) 25.000

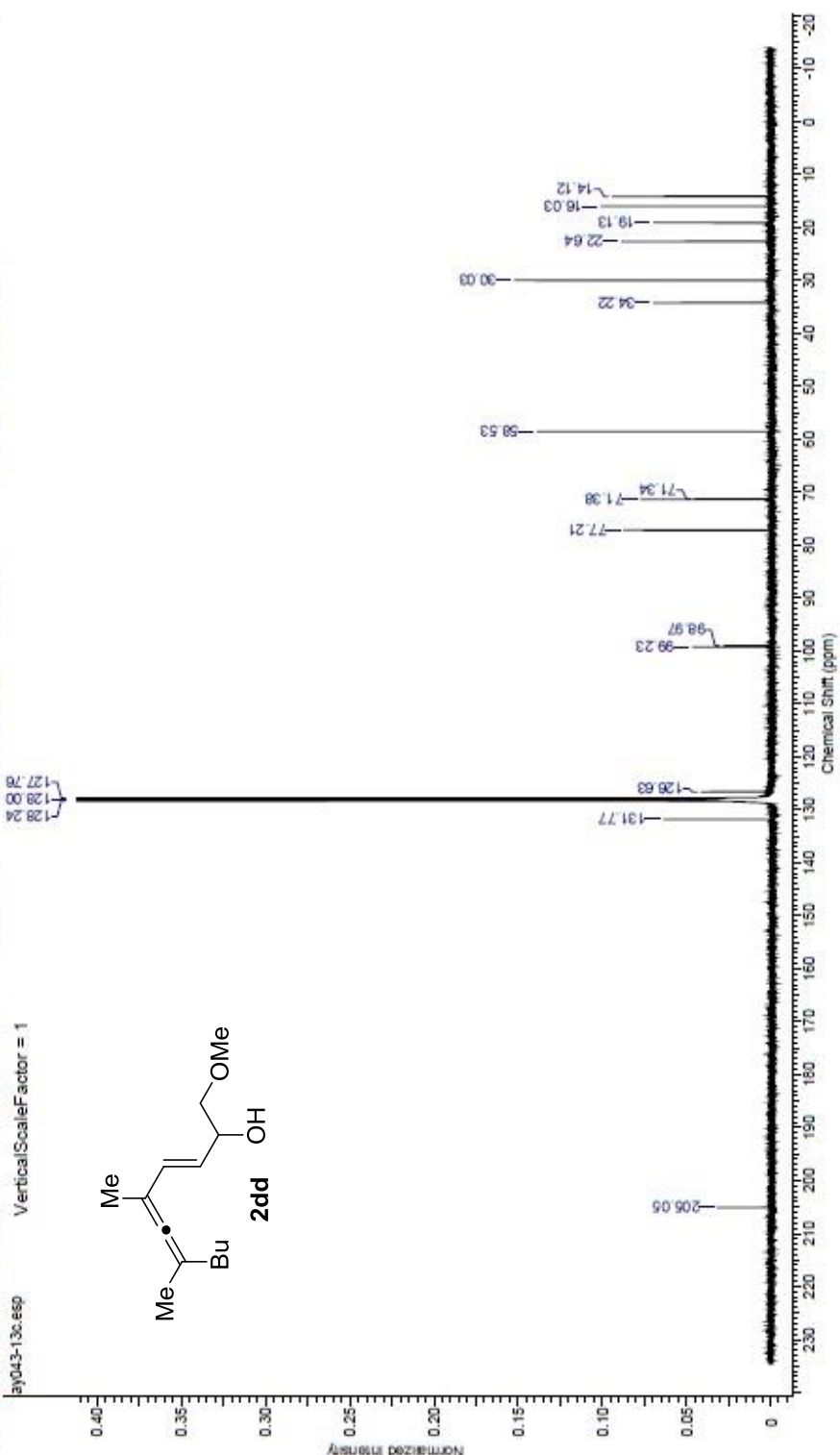


Acquisition Time (sec)	2.5559	Comment	AA-AY-043	Date	Jun 8 2016	Date Stamp	Jun 8 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\ELER GUGLER\POXIDEYER FE GAK CUARING\ACRINC DATA\BIN\AA-AY-043_20160608_01\PROTON.D1 FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	8	Original Points Count	16384
Points Count	16384	Pulse Sequence	g22ul	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



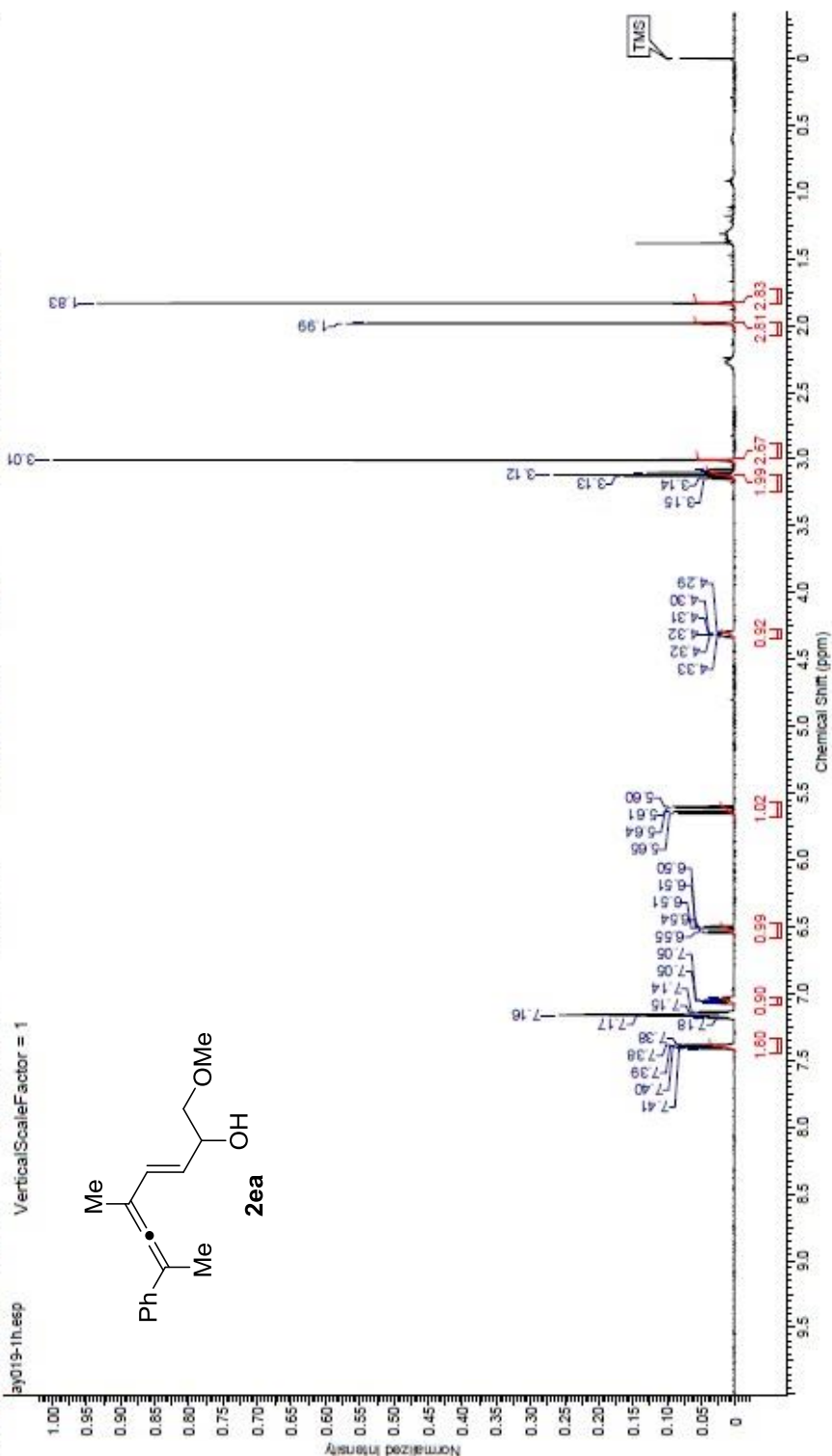
28.07.2016 14:01:53

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\UGLER GIGLER\POXIDE\VER FE 30K CUARING\GARING DATA\AA-AY-043_20160608_01\CARBON_02.FID\FID						
Frequency (MHz)	100.67	Nucleus	¹³ C	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



26.07.2016 22:35:53

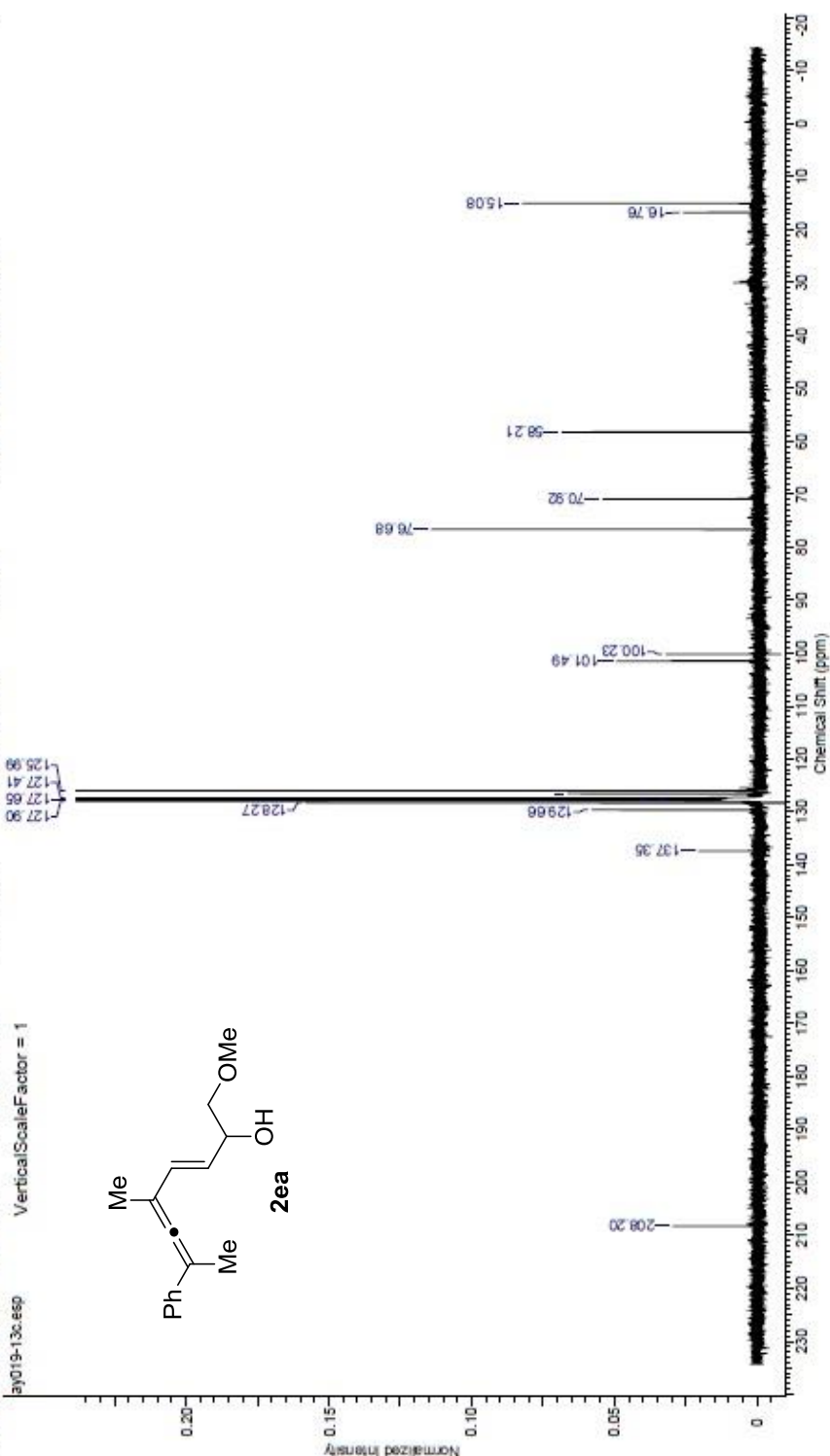
Acquisition Time (sec)	2.5559	Comment	AA-AY-019-1S	Date	Jan 7 2016	Date Stamp	Jan 7 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\1S\ER-GUCLER\POXIDE\VER FE G3K CUARIN\SPARINC.DAT\AVRINCAA-AY-019-1S_20160107_01.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	5	Original Points Count	16384
Points Count	16384	Pulse Sequence	zgpg30	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



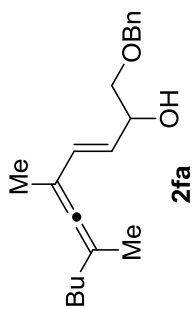
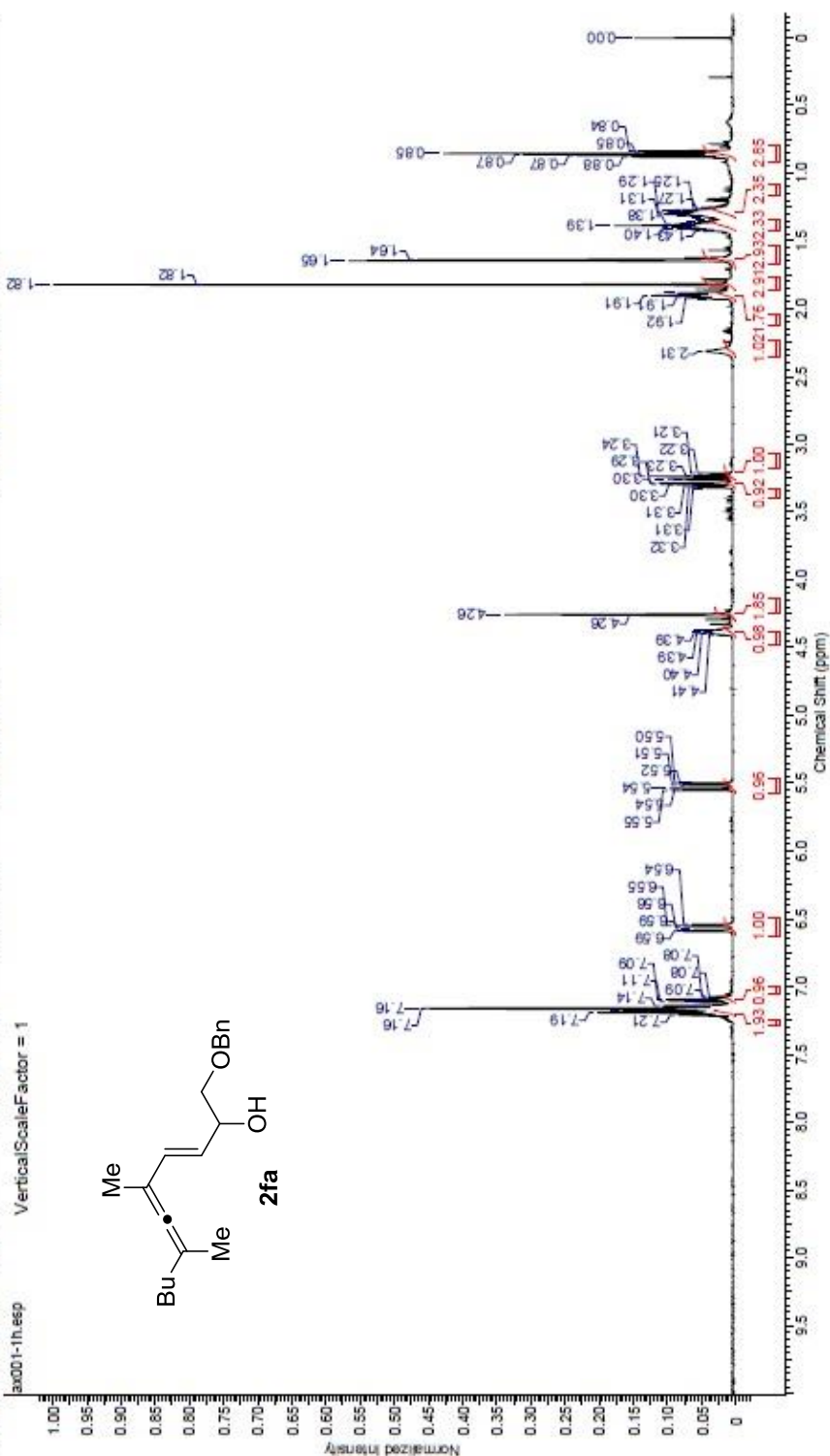
26.07.2016 22:37:06

Acquisition Time (sec)	1.3107	Comment	AA-AY-019-TS	Date	Jan 7 2016	Date Stamp	Jan 7 2016
File Name	C:\USERS\FIBAT\GOOGLE_DRIVE\ELER\GUGLER\POXIDE\VER EE GAK CUARING\CARBON-AA-AY-019-TS_20160107_02\CARBON_01.FID\FID						
Frequency (MHz)	100.67	Nucleus	¹³ C			Original Points Count	32768
Points Count	32768	Pulse Sequence	62pul			Solvent	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	Spectrum Type	STANDARD			Temperature (degree C)	25.000

VerticalScaleFactor = 1

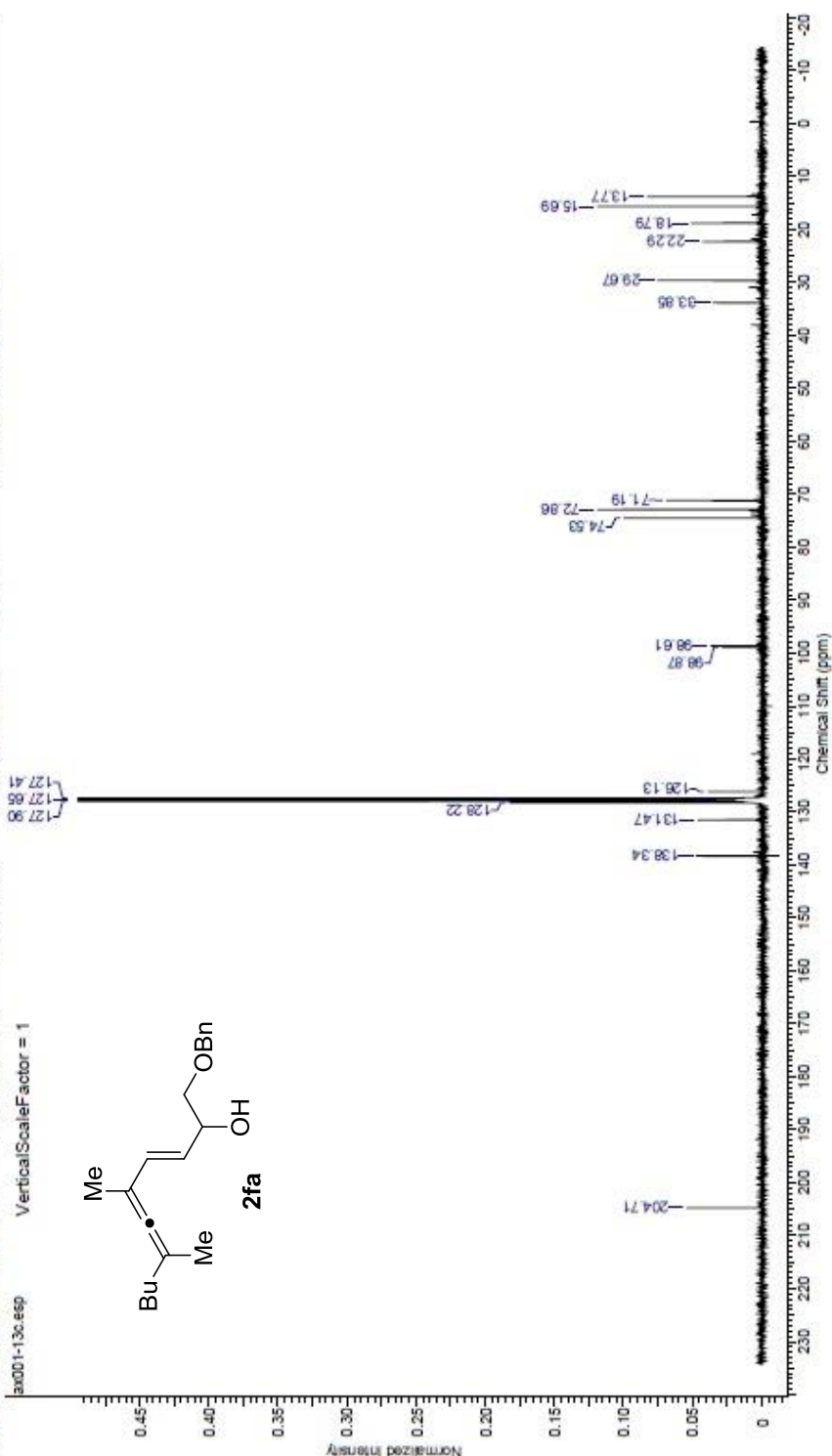


File Name	Acquisition Time (sec)	Comment	Date	Date Stamp	
C:\USERS\FIRAT\GOOGLE DRIVE\UGL\GLUGLER\POXIDE\VEYER FE G6X C\UARIING\JARING DATA\HIN\CAA-AX-301B_20151026_01\PROTON_01\FID\FID	2.5559	AA-AX-301B	Oct 26 2015	Oct 26 2015	
Frequency (MHz)	399.92	Nucleus	Number of Transients	8	Original Points Count
Points Count	15384	Pulse Sequence	Receiver Gain	54.00	Solvent
Spectrum Offset (Hz)	2418.3416	Spectrum Type	Temperature (degrees C)	25.000	BENZENE-d6

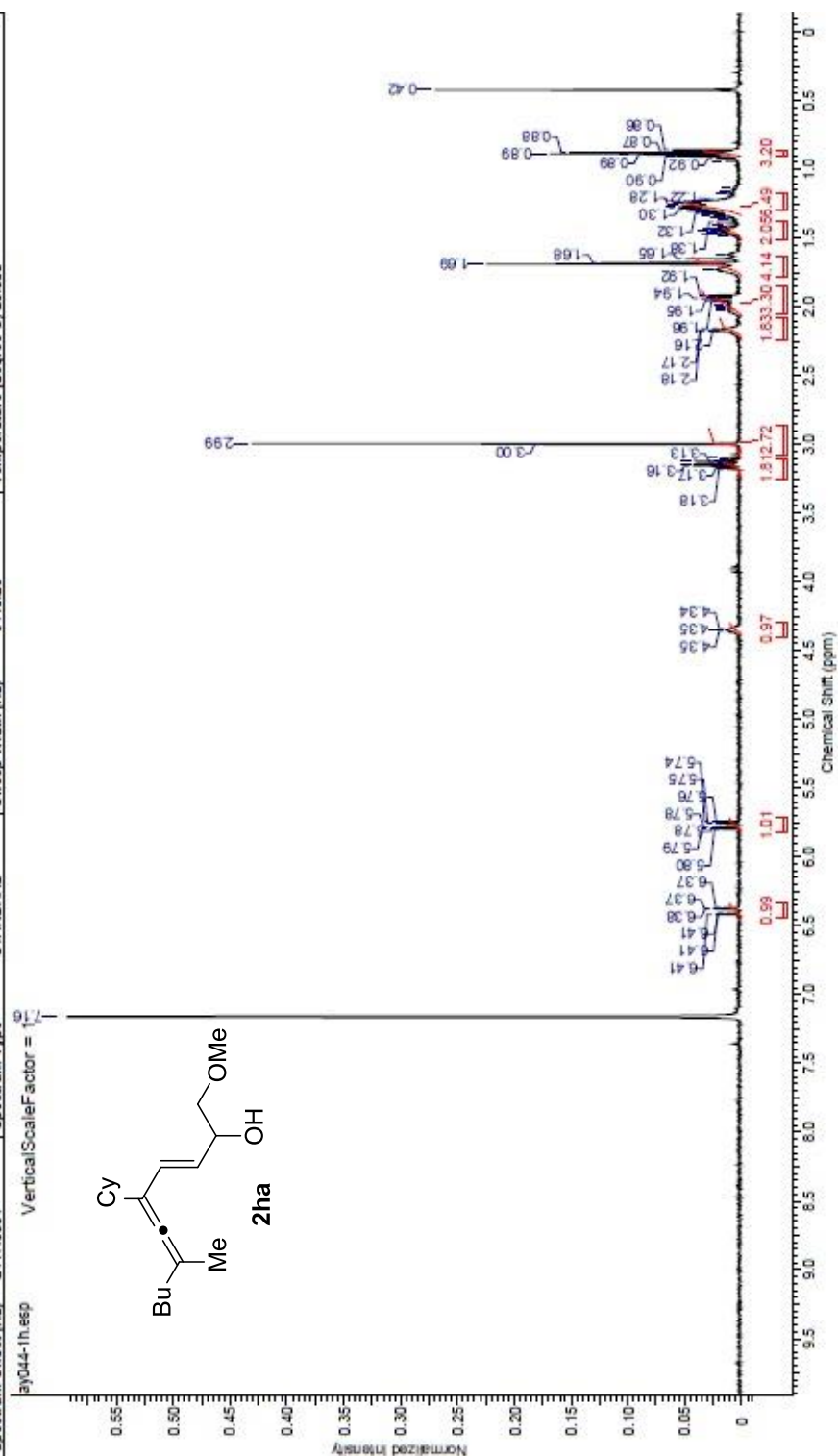


28.07.2016 16:16:16

Acquisition Time (sec)	1.3107	Comment	AA-AX-014Y	Date	Feb 23 2016	Date Stamp	Feb 23 2016
File Name	C:\USERS\FIRST\GOOGLE DRIVE\FILES\GUILIEREPOXIDE\VER FE 60K CUARING\ABRINC.DAT\ABRINC-AA-AX-014Y_20160223_011CARBON_Q2.FID\FID						
Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	5000	Original Points Count	32768
Points Count	32768	Pulse Sequence	zgpg30	Receiver Gain	30.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000

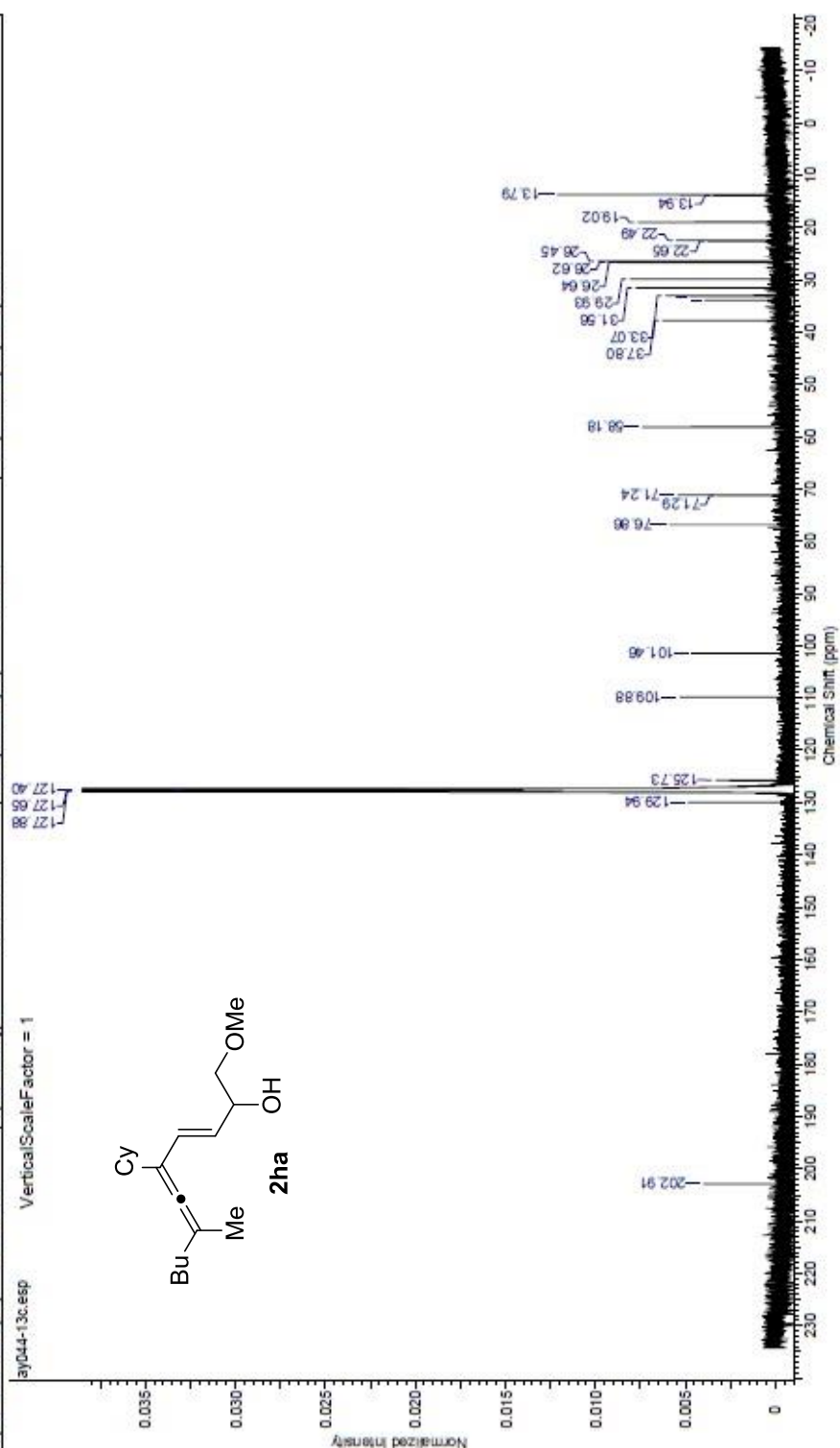


Acquisition Time (sec)	Comment	Date	Jul 1 2016	Date Stamp	Jul 1 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\UGLER\GLP\EROD\OXYDE\VER FF G&K\CUARINGS\ARINC\DATA\ARINC\AA-AY-0445_20160701_01\FID\FID				
Frequency (MHz)	393.92	Nucleus	1H	Number of Transients	8
Poisns Count	16384	Pulse Sequence	s2pul	Receiver Gain	50.00
Spectrum Offset (Hz)	2417.5591	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26
				Temperature (degrees C)	25.0000
				Solvent	BENZENE-d6
				Original Points Count	16384



28.07.2016 14:39:34

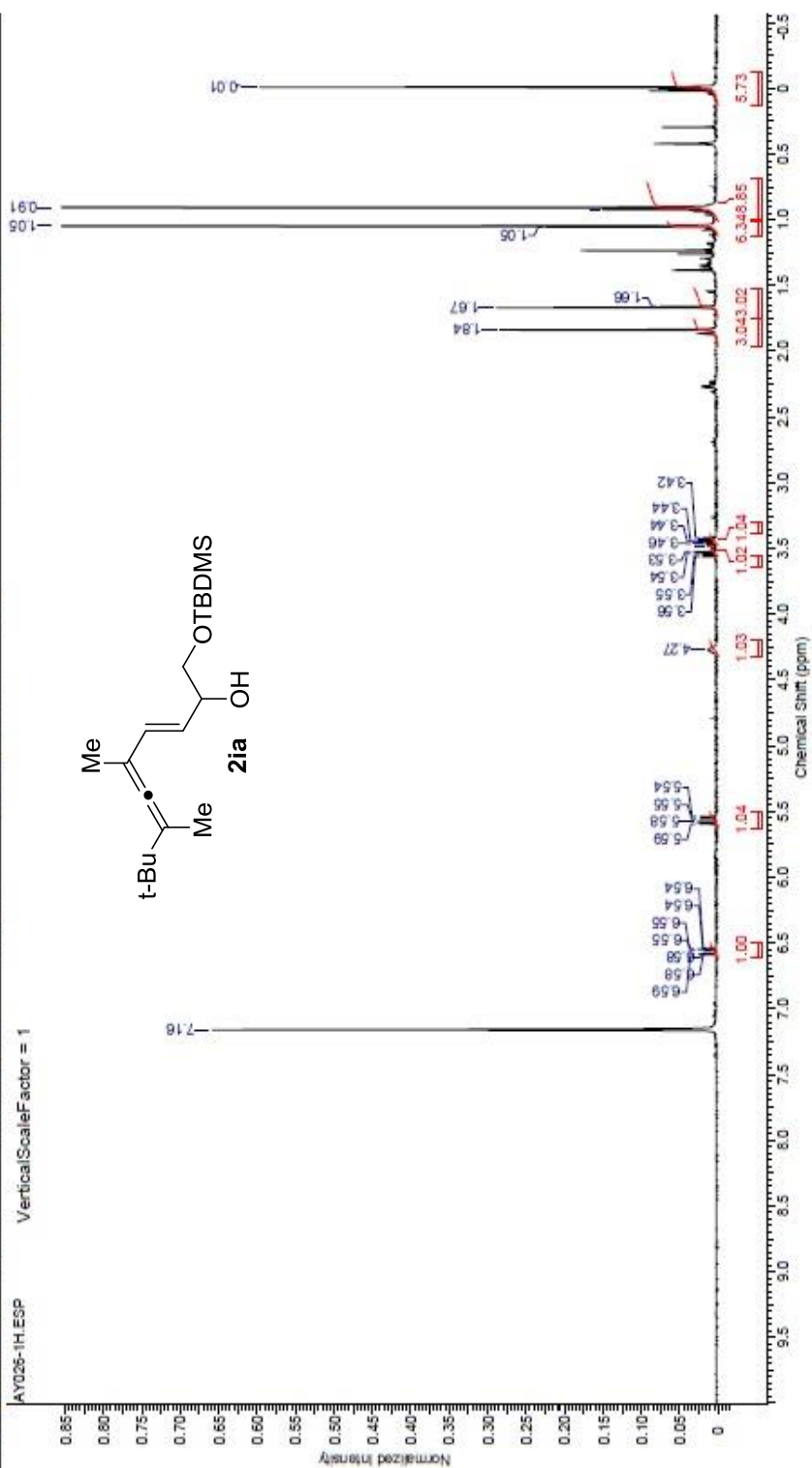
Acquisition Time (sec)	1.3107	Comment	A4-AY-044S	Date	Jul 2 2016	Date Stamp	Jul 2 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\JELER GIGLER\POXIDE\VER FE GOK CUARING\BARINC DATA\NMR\A4-AY-044S_20160701_011\CARBON_04.FID.FID						
Frequency (MHz)	100.67	Nucleus	¹³ C	Number of Transients	20000	Original Points Count	32768
Points Count	32768	Pulse Sequence	s2bui	Receiver Gain	30.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000



Acquisition Time (sec)	2.5559	Comment	Date	Jan 27 2016	Date Stamp	Jan 27 2016
File Name	C:\USERS\FRAT\GOOGLE DRIVE\UGLER GUPFER\POXI\VERFF GKK CUARING\JARING DATA\NINCAA-AY-005_20160127_01\PROTON_01.FID.FID					
Frequency (MHz)	359.92	Nucleus	1H	Number of Transients	16	Original Points Count 15384
Points Count	15384	Pulse Sequence	sZpol	Receiver Gain	50.00	Solvent BENZENE-d6
Spectrum Offset (Hz)	2416.7764	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C) 25.0000

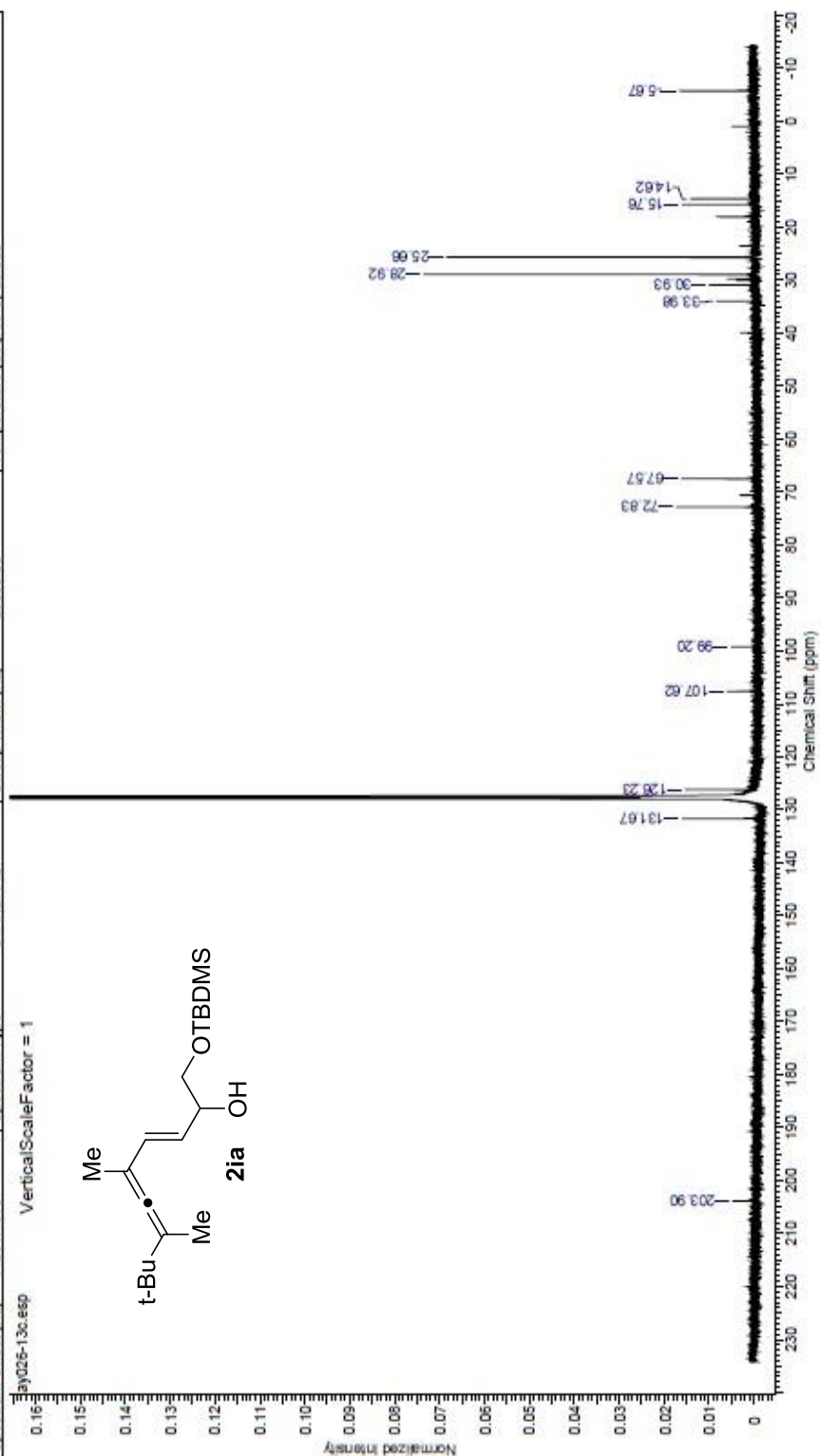
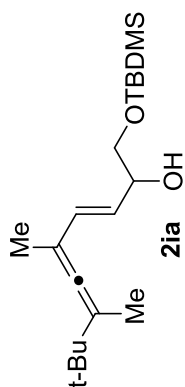
AY026-1H.ESP

VerticalScaleFactor = 1



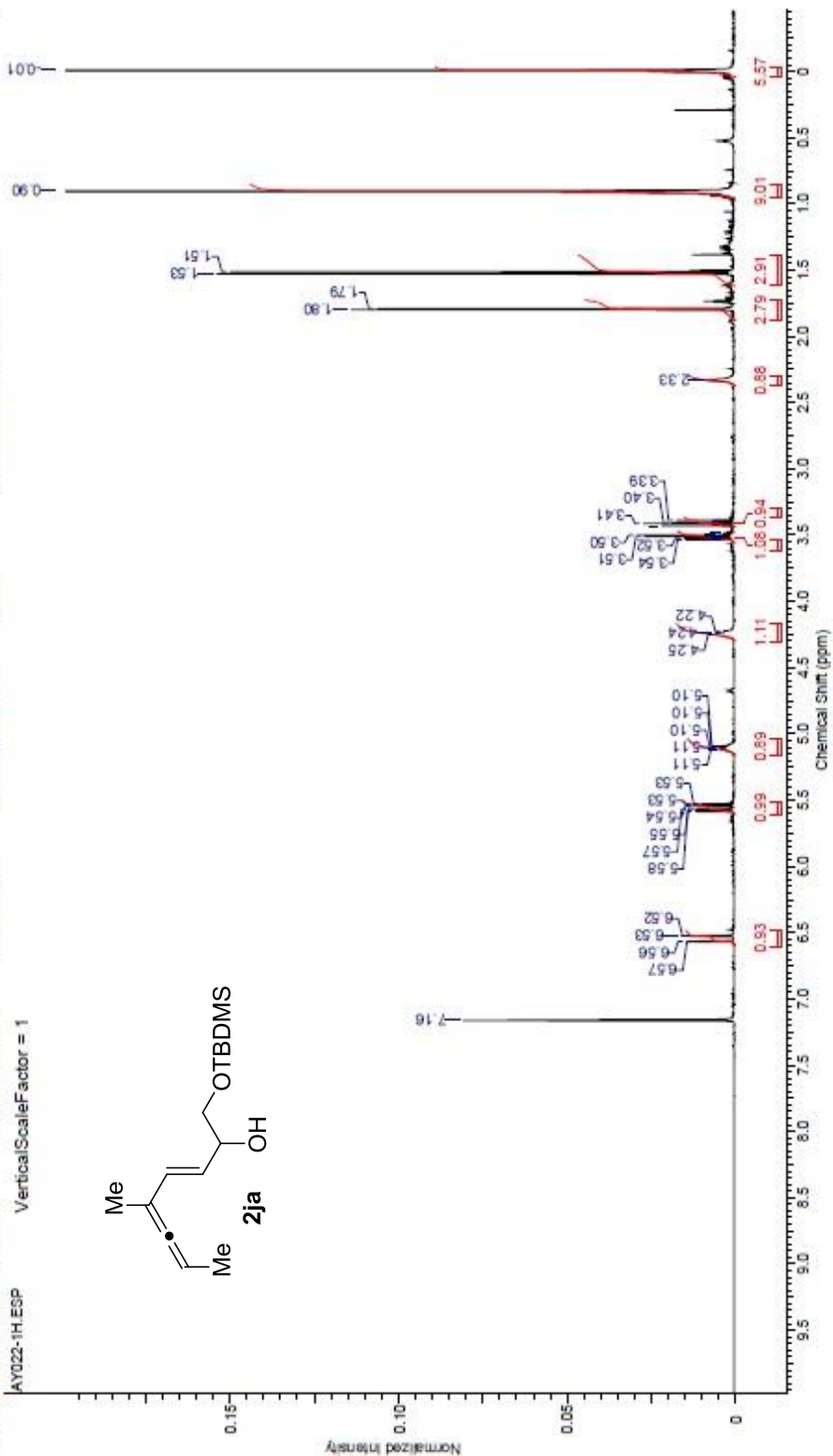
Acquisition Time (sec)	Comment	Date	Feb 8 2016	Date Stamp	Feb 8 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\FIRAT\GPR\EXPERIMENT\GPR_FIRAT_02\CARBON_02_FID.FID				
Frequency (MHz)	100.57	Nucleus	13C	Original Points Count	32768
Points Count	32768	Pulse Sequence	s2pul	Receiver Gain	30.00
Spectrum Offset (Hz)	11051.4873	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00
				Temperature (degree C)	25.000

VerticalScaleFactor = 1

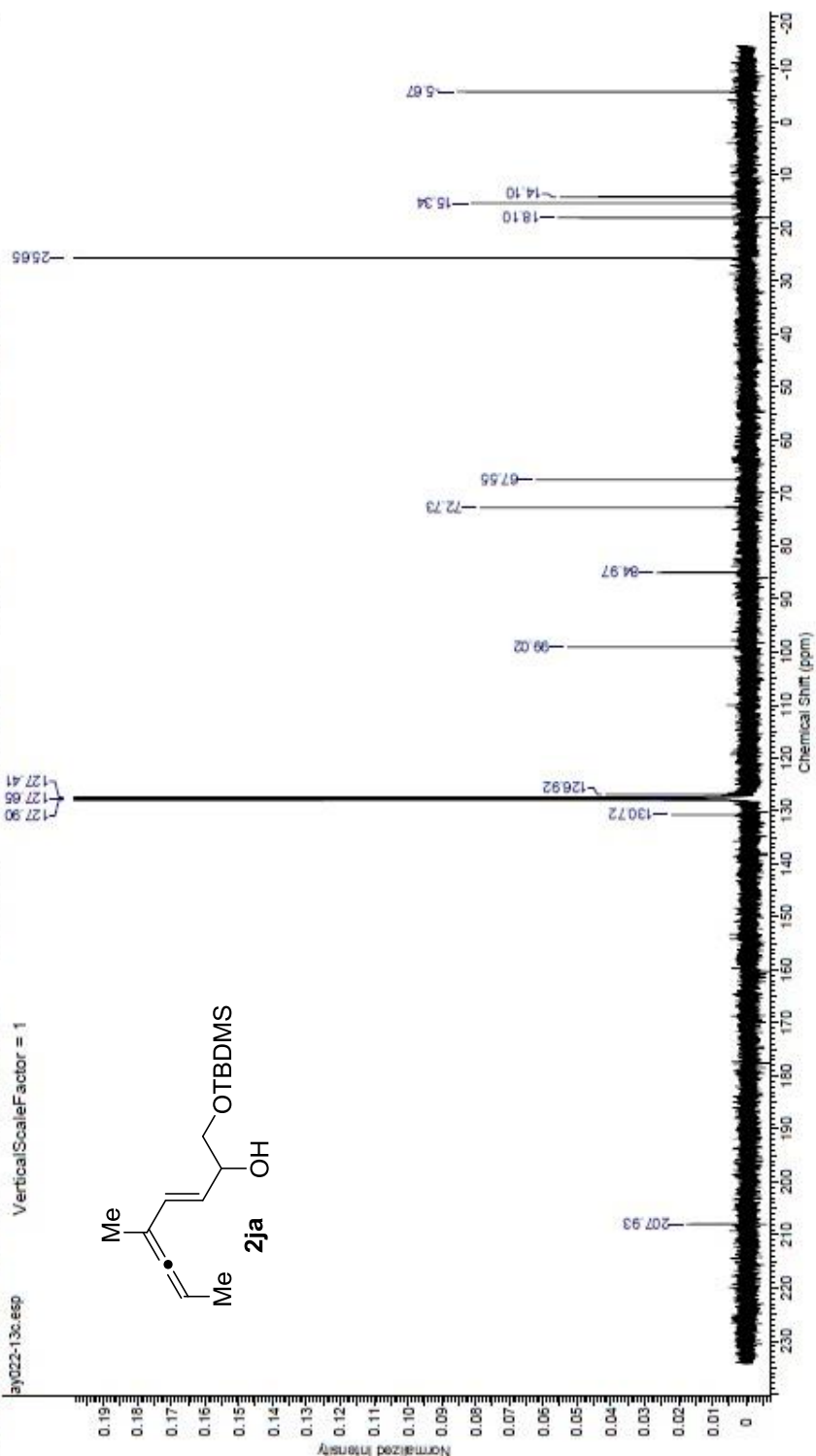


28.07.2016 15:59:05

Acquisition Time (sec)	2.5555	Comment	AA-AY-022-T	Date	Jan 8 2016	Date Stamp	Jan 8 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\JELER GUGLER\POXIDELVER FF GSK CUJARI\20160108_01\PROTON_01\FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	8	Original Points Count	15384
Points Count	15384	Pulse Sequence	s20ul	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

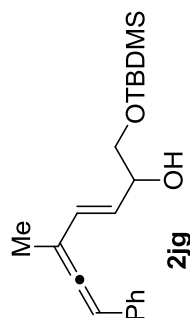
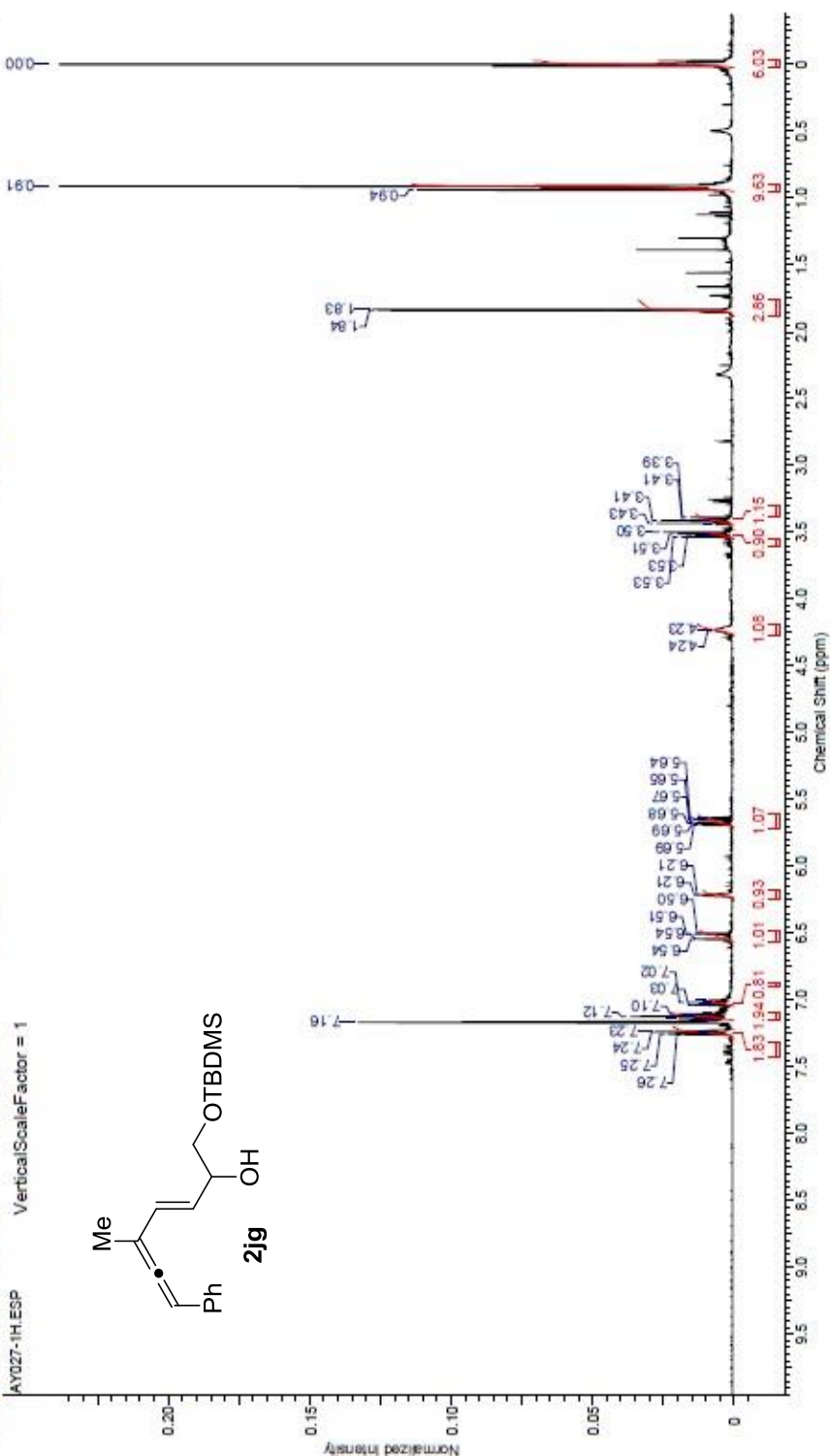


Acquisition Time (sec)	1.3107	Comment	A4-AY-022-T	Date	Jan 8 2016	Date Stamp	Jan 8 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\GLER\POXIDE\VER FE GAK CUARING\CARINC DATA\BINCAA-AY-022-T_20160108_01.FID\FID						
Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	512	Original Points Count	32768
Points Count	32768	Pulse Sequence	sgpul	Receiver Gain	30.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	11061.4573	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000



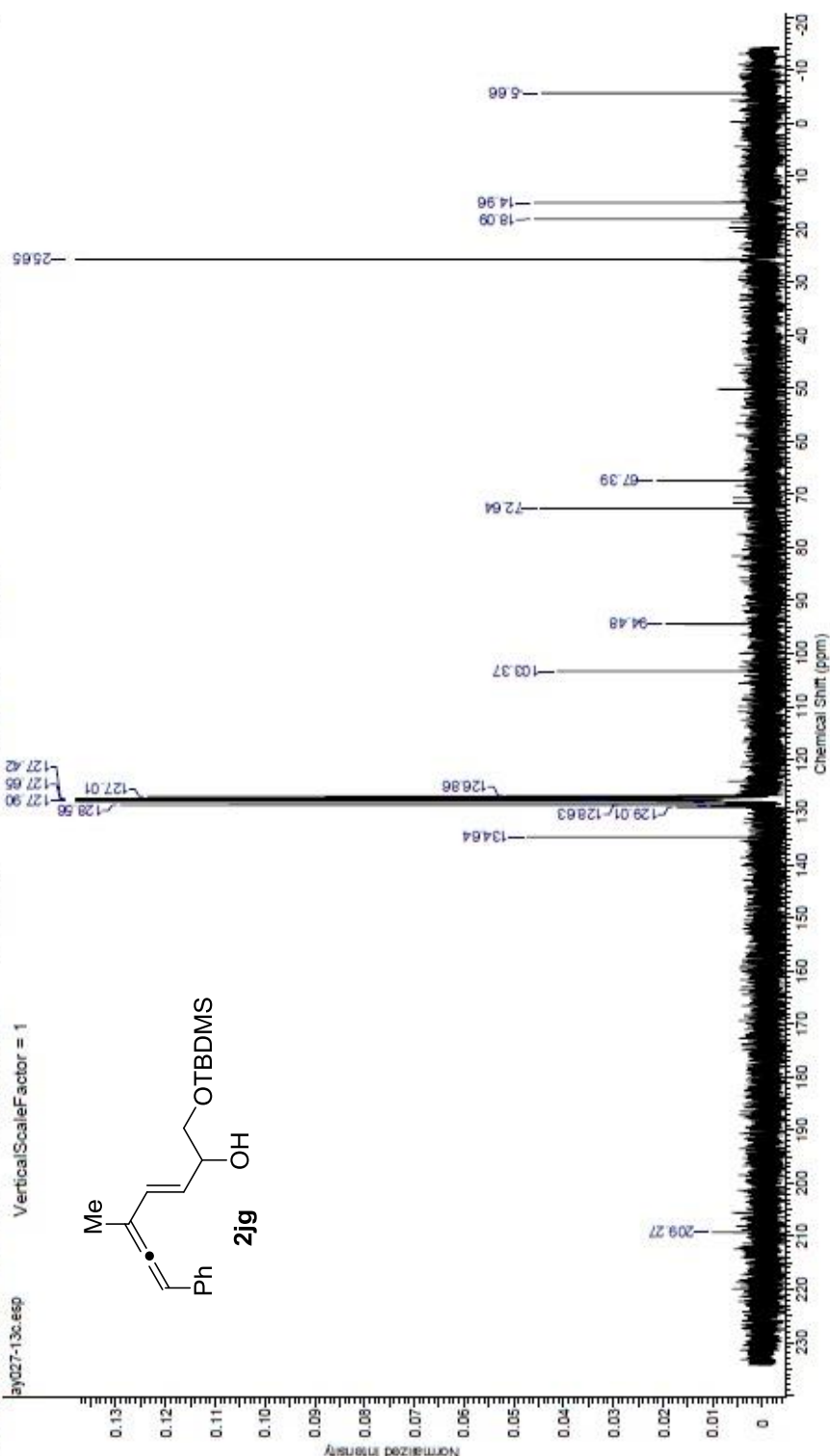
28.07.2016 15:59:55

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\BILGULER\POXIDE\VER FE GSK CUARING\DATA\BIN\AA-AY-027_20160201_01\PROTON.D1.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	8	Original Points Count	16384
Points Count	16384	Pulse Sequence	s2nu1	Receiver Gain	56.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	2418.6658	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



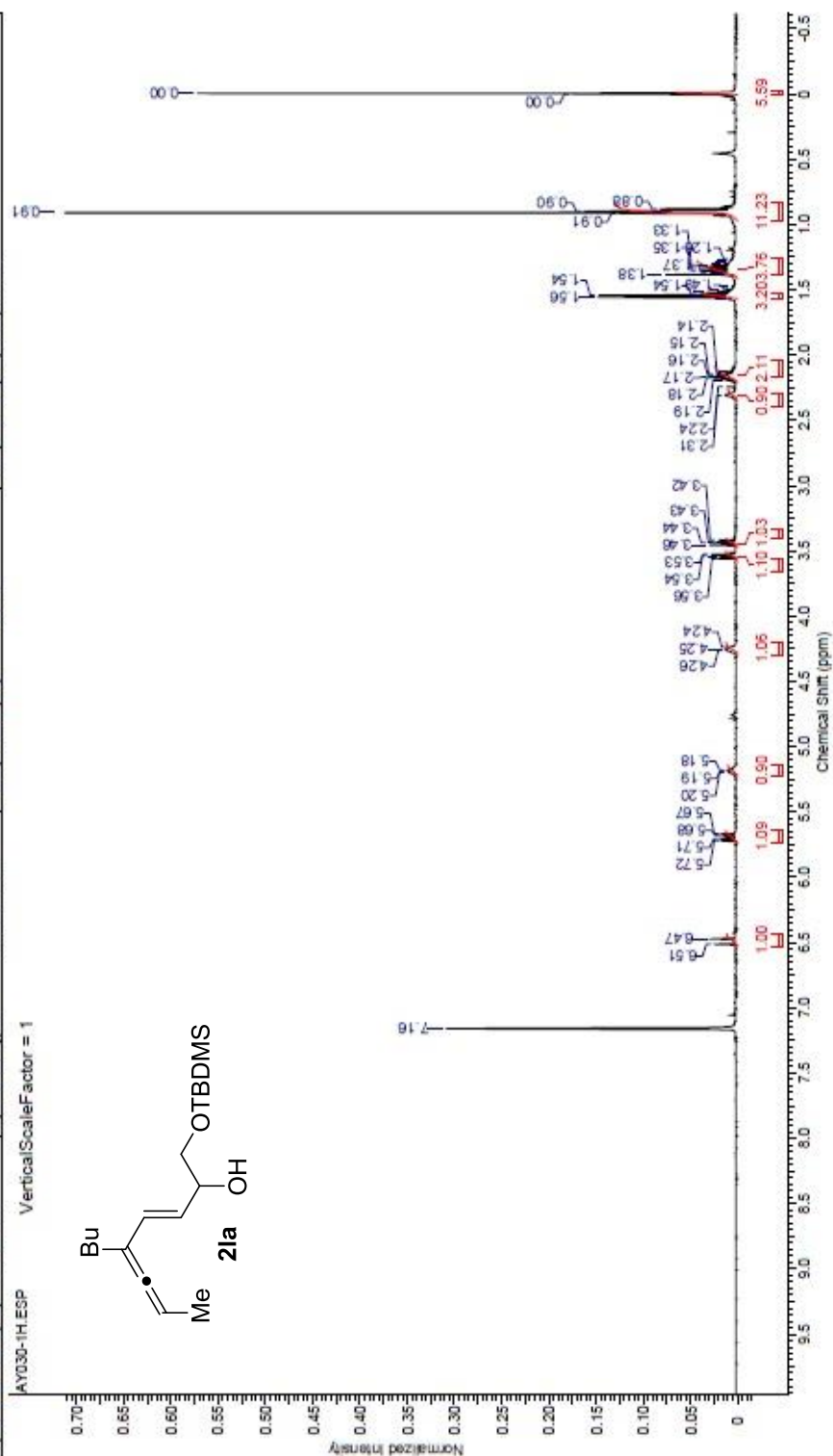
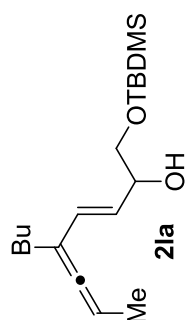
26.07.2016 23:02:43

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\JSLER\GLICLEREPOXIDE\VER FE 030K CUARIN\027C.D1\CARBON.D1.FID\FID						
Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	512	Original Points Count	32768
Points Count	32768	Pulse Sequence	szbul	Receiver Gain	30.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	11061.4873	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000



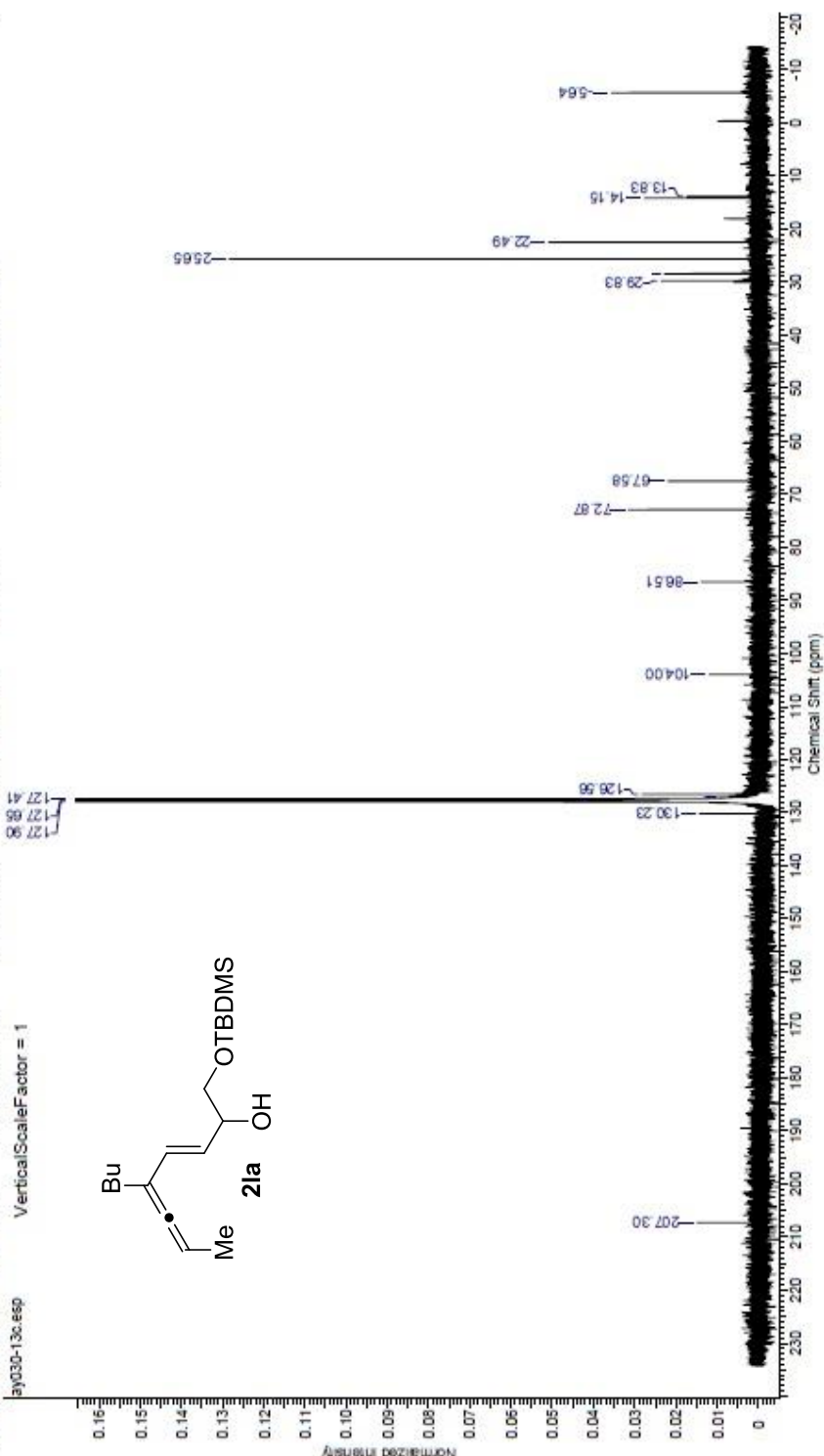
Acquisition Time (sec)	2.5559	Comment	AA-AV-030T	Date	Feb 26 2016	Date Stamp	Feb 26 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\UGLER GUPLER\POXI\DEYER FE GKK CUARING\JARC DATA\NCAA-AV-030T_20160226_01\FID\FID.FID						
Frequency (MHz)	399.92	Nucleus	1H	Number of Transients	8	Original Points Count	16384
Points Count	16384	Pulse Sequence	s2ou1	Receiver Gain	50.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	Spectrum Type	STANDARD	Sweep Width (Hz)	5410.26	Temperature (degree C)	25.000

VerticalScaleFactor = 1

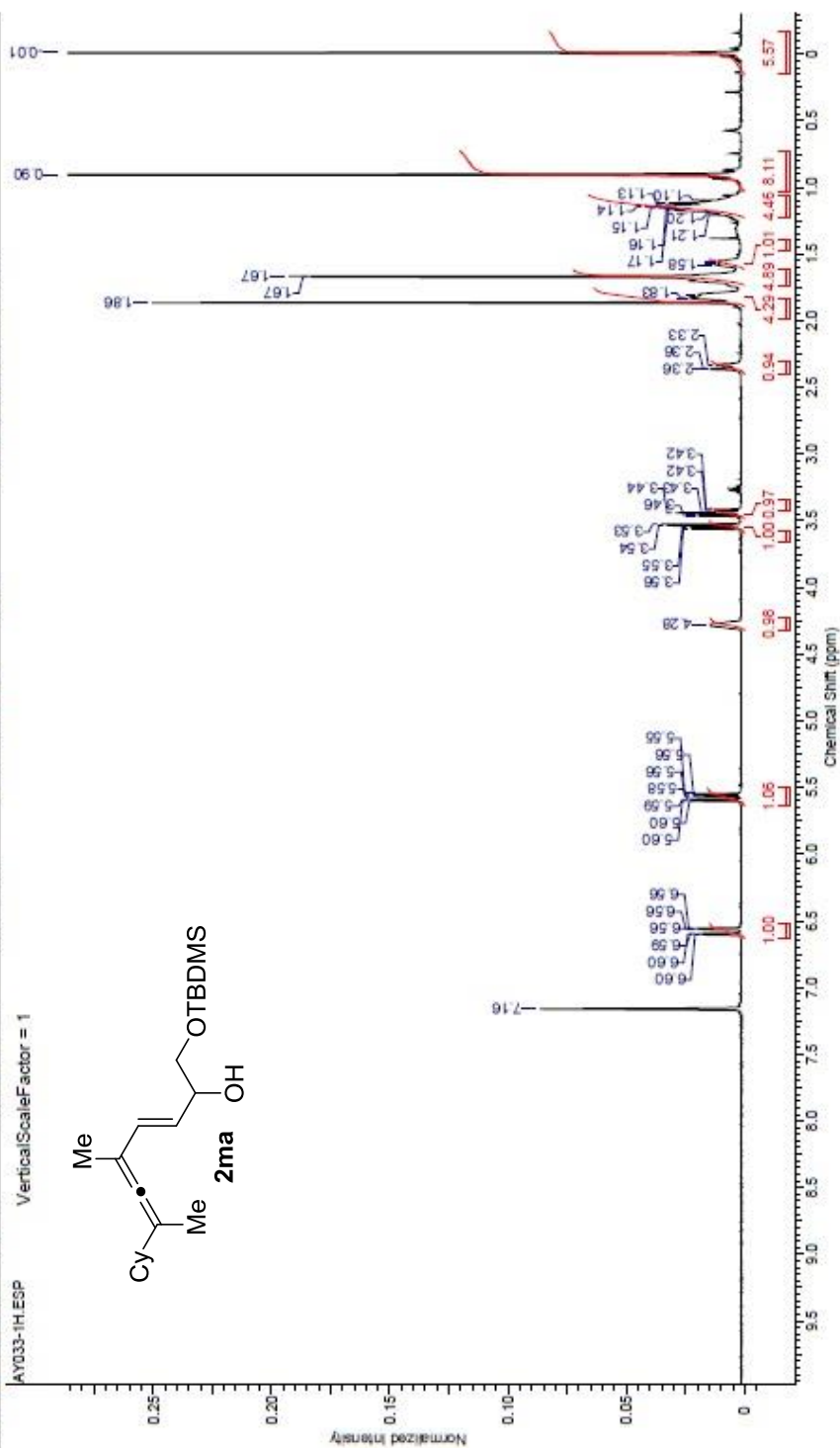


Acquisition Time (sec)	1.3107	Comment	AA-AY-030T	Date	Feb 26 2016	Date Stamp	Feb 26 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\JELER GUGLER\POXIDE\VER FE 58K GUARING\ABING DATA\ABING\AA-AY-030T_20160226_01UCARBON_01.FID\FID						
Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	1000	Original Points Count	32768
Points Count	32768	Pulse Sequence	zgpg30	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

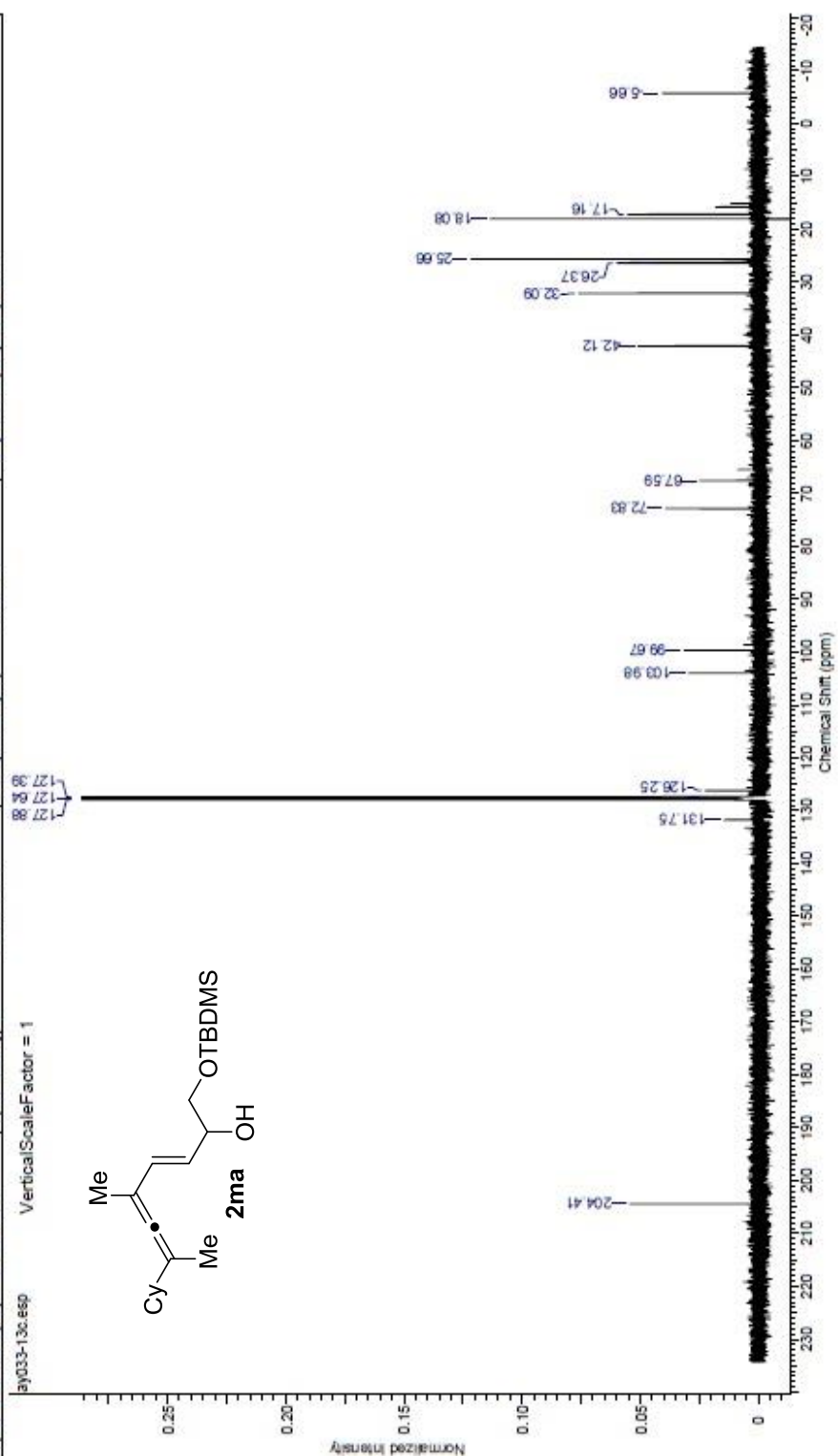
Vertical Scale Factor = 1



File Name	Acquisition Time (sec)	Comment	Date	Date Stamp
C:\USERS\FRAT\GOOGLE DRIVE\UGL\ERPOXIDE\VER FE GKK CUARING\JARING DATA\RINGC\AA-AY-033T_20160331_01\PROTON_02.FID	2.5559	AA-AY-033T	Mar 31 2016	Mar 31 2016
Frequency (MHz)	399.92	Nucleus 1H	Number of Transients 8	Original Points Count 16384
Points Count	16384	Pulse Sequence	Receiver Gain 54.00	Solvent BENZENE-d6
Spectrum Offset (Hz)	2415.7764	STANDARD	Sweep Width (Hz) 6410.26	Temperature (degree C) 25.000

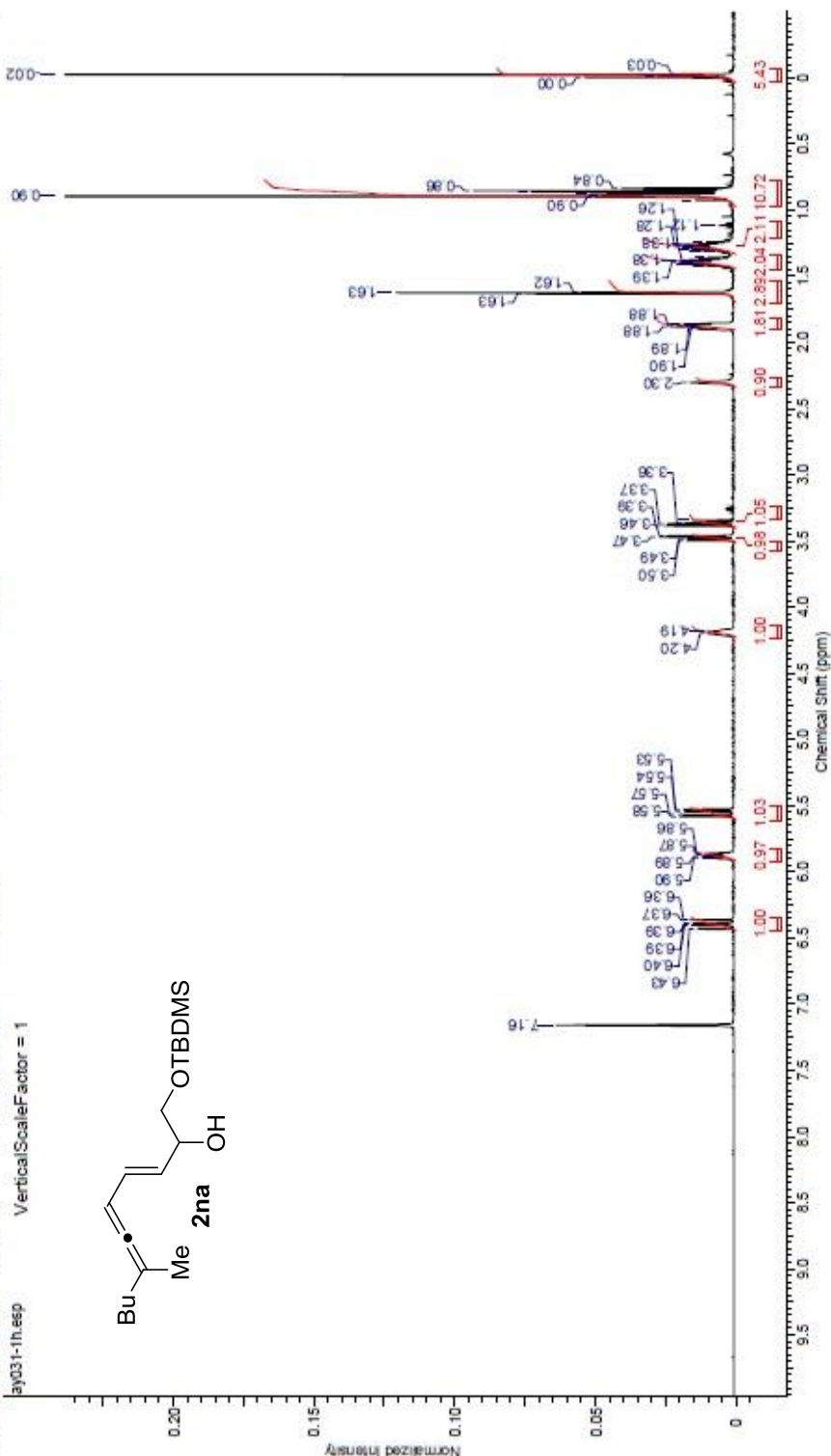


File Name	Acquisition Time (sec)	Comment	Date	Date Stamp	
CUSESFRATGOOGLE DRIVE\UGLER GUGLEROXIDE\VEFF G&K CUARING\LABING DATA\BINCAA-AY-033C_20160422_DUCARBON_01.FID.FID	1.3107	AA-AY-033C	Apr 22 2016	Apr 22 2016	
Frequency (MHz)	100.57	Nucleus	13C	Number of Transients	512
Points Count	32768	Pulse Sequence	szpul	Receiver Gain	30.00
Spectrum Offset (Hz)	11061.4573	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00
				Temperature (degree C)	25.000
				Solvent	BENZENE-d6
				Original Points Count	32768



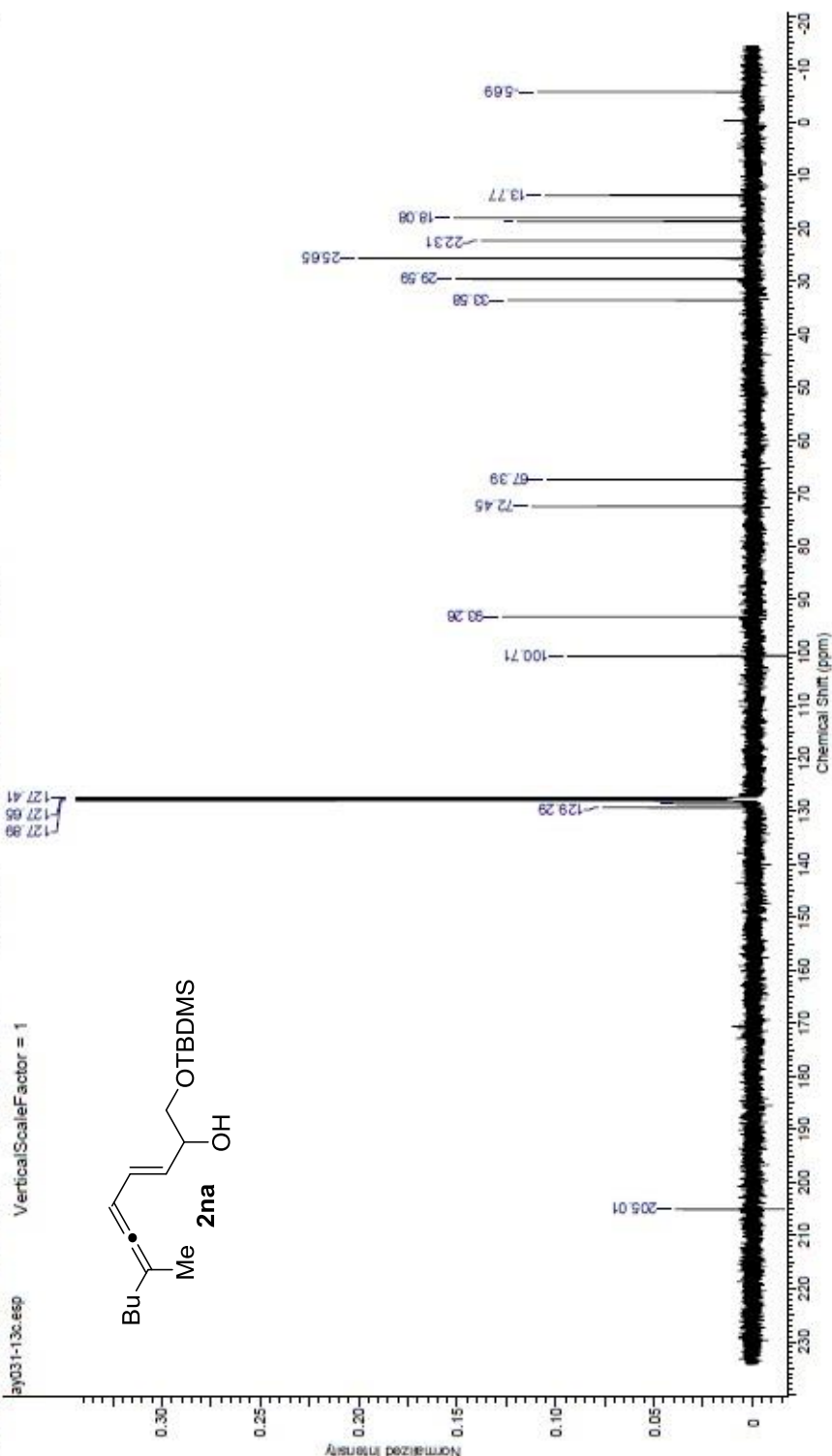
29.07.2016 11:27:19

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\1518\ER-GUCLER\POXIDE\VER FE 60K CUARIN\SPICARINC.DAT\AVRINCAA-AY-031_20160318_01.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	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

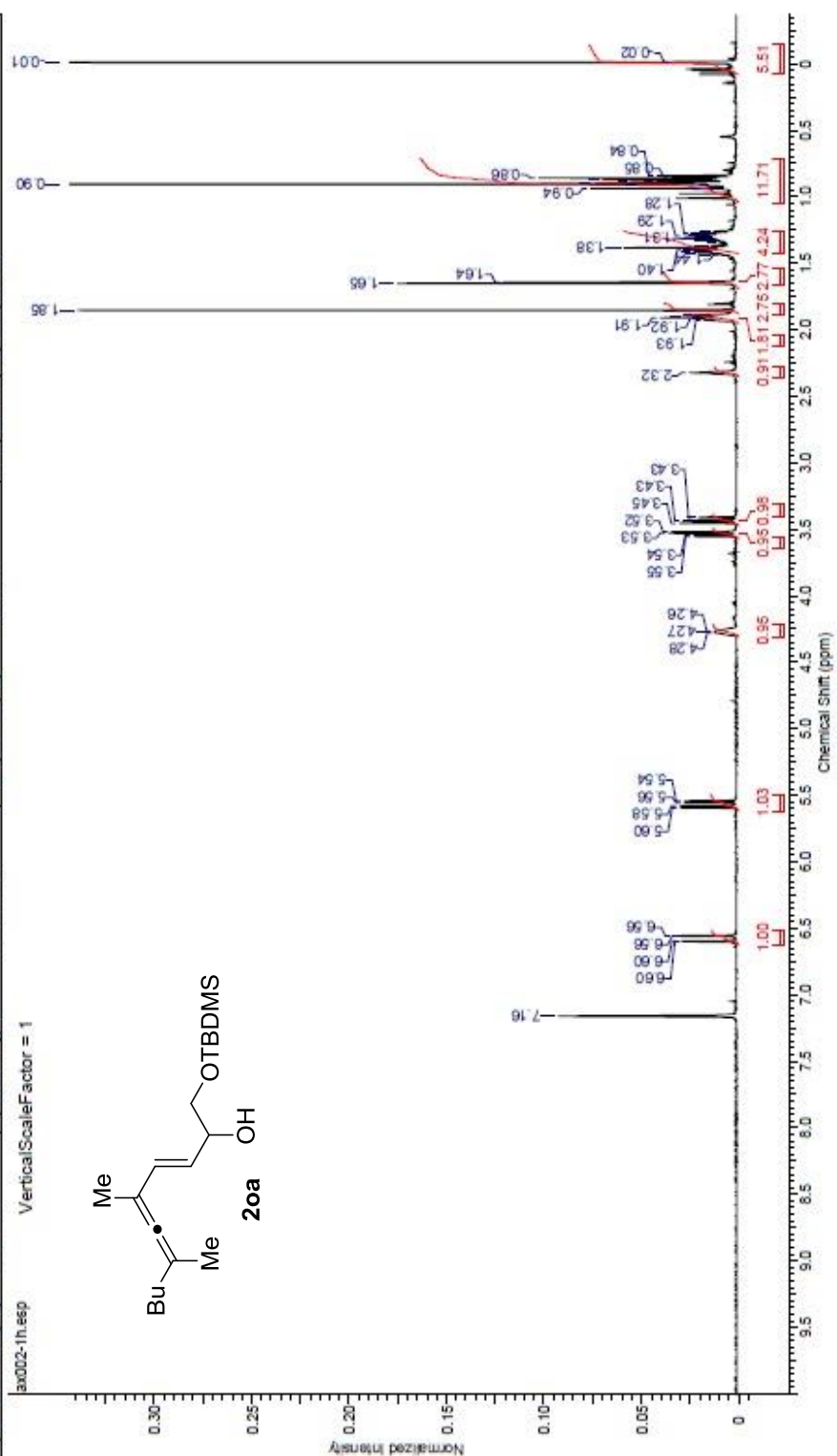


29.07.2016 11:30:38

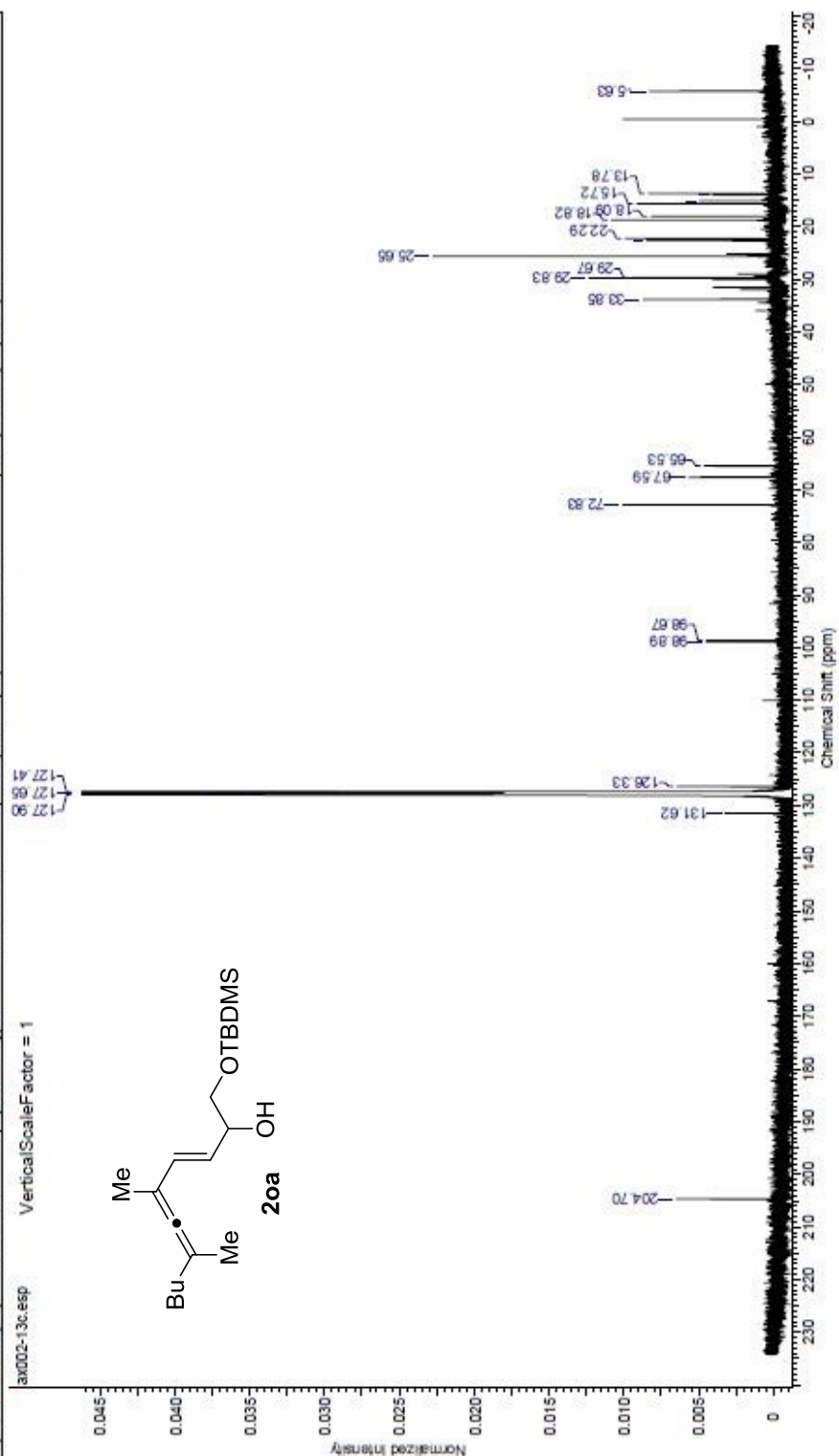
Acquisition Time (sec)	1.3107	Comment	AA-AY-031	Date	Mar 15 2016	Date Stamp	Mar 15 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\ISLER\GUGLER\POXIDE\VER FE 60K CUARIN\92\ARINC.DAT\AVRINCAA-AY-031_20160315_01\CARBON13.FID\FID					Original Points Count	32768
Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	256	Solvent	BENZENE-d6
Points Count	32768	Pulse Sequence	g2ou1	Receiver Gain	30.00	Temperature (degree C)	25.000
Spectrum Offset (Hz)	11051.4873	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00		



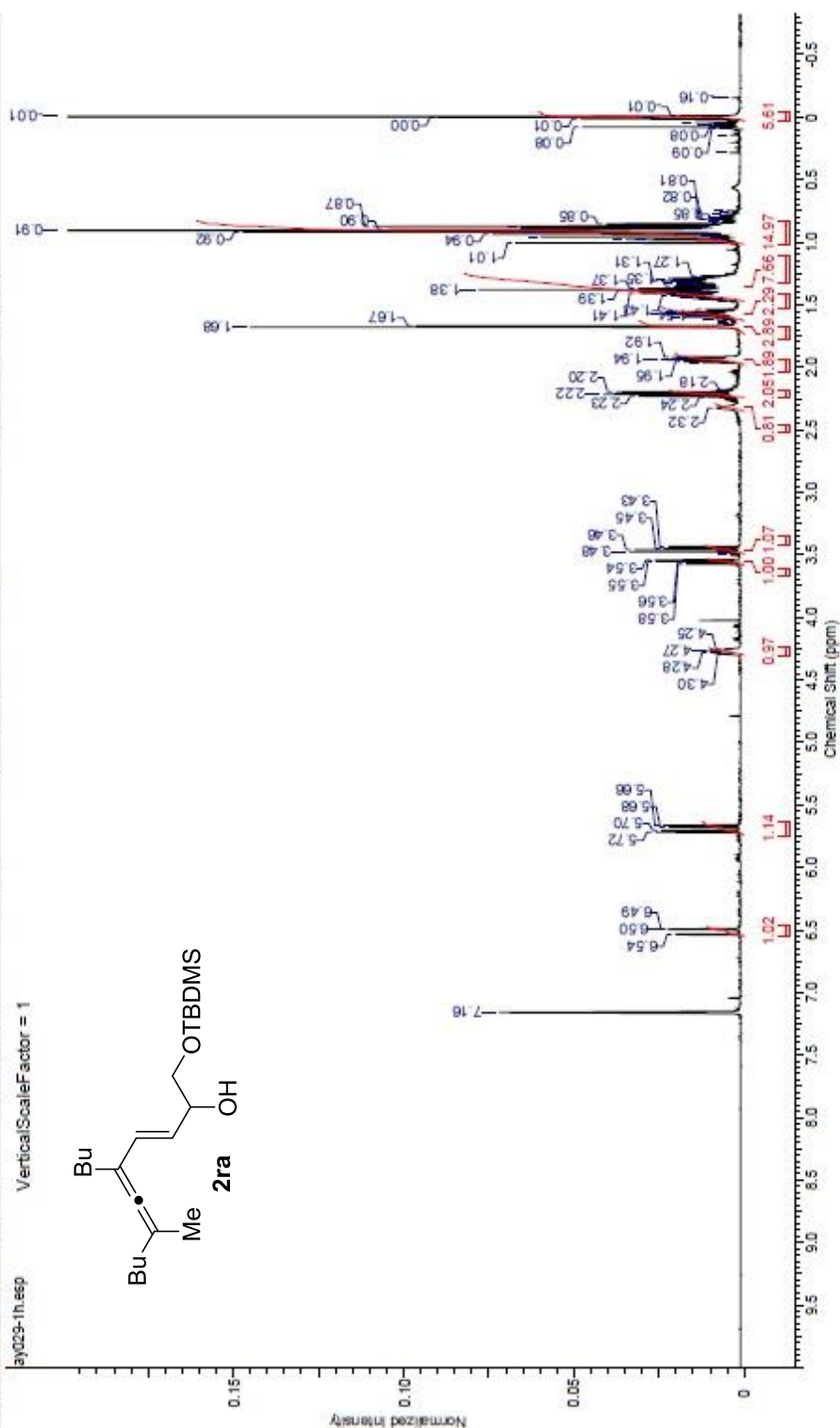
Acquisition Time (sec)	2.5559	Comment	AA-AX-002T2	Date	Oct 27 2015	Date Stamp	Oct 27 2015
File Name	C:\USERS\FRATIGOLE\DRIVE\UGLER\GUPLEX\OXYNEVER FE GKK QUABING\JARC DATA\NINCAA-AX-002T2_20151027_00\PROTON.D1.FID\FID						
Frequency (MHz)	399.92	Nucleus	1H			Original Points Count	16384
Points Count	16384	Pulse Sequence	szpul			Receiver Gain	52.00
Spectrum Offset (Hz)	2416.7764	Spectrum Type	STANDARD			Sweep Width (Hz)	6410.26
						Temperature (degree C)	25.000



Acquisition Time (sec)	1.3107	Comment	AA-AX-002Y	Date	Feb 22 2016	Date Stamp	Feb 22 2016
File Name	CHUSERSFRATGOOGLE DRIVE\UGLER GUPLER\POXI\VER FE GKK QUARING\JARING DATA\NINCAA-AX-002Y_20160222.D	Nucleus	13C	Number of Transients	20000	Original Points Count	32768
Frequency (MHz)	100.57	Pulse Sequence	32pul	Receiver Gain	30.00	Solvent	BENZENE-d6
Points Count	32768	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.0000
Spectrum Offset (Hz)	11061.4873						

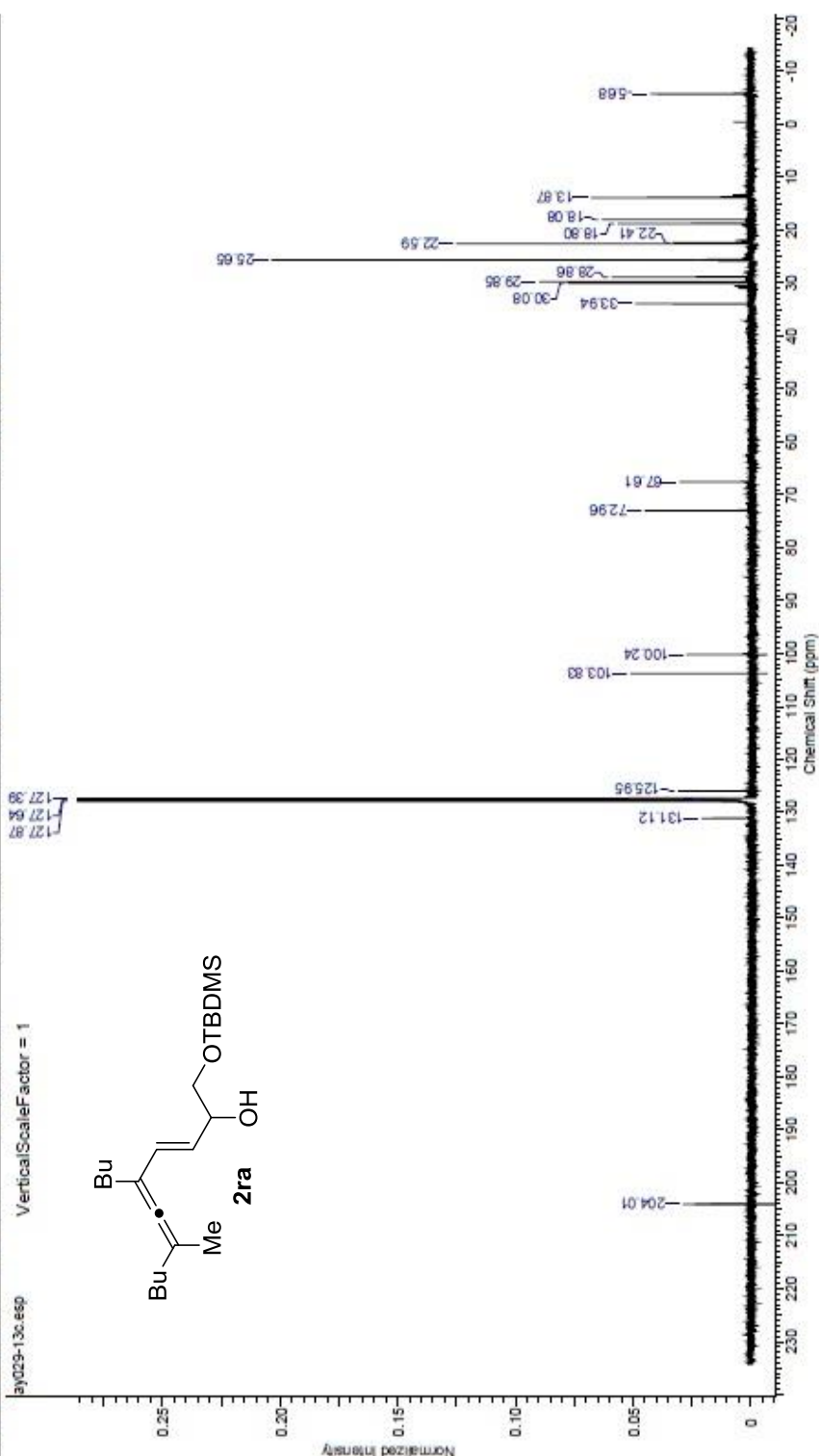


Acquisition Time (sec)	Comment	Date	Date Stamp
2.5559	AA-AY-029	Feb 19 2016	Feb 19 2016
File Name C:\USERS\FRAT\GOOGLE DRIVE\UGLER\GLUGLER\POXIDEX\VER FE GKK CU\ARING\ARING DATA\RING-AA-AY-029_20160219_01\PROTON_01\FID\FID			
Frequency (MHz)	Nucleus	Number of Transients	Original Points Count
399.92	1H	8	15394
Points Count	Pulse Sequence	Receiver Gain	Solvent
16384	s2pul	50.00	BENZENE-d6
Spectrum Offset (Hz)	Spectrum Type	Sweep Width (Hz)	Temperature (degrees C)
2416.7764	STANDARD	6410.26	Temperature (degrees C) 25.000



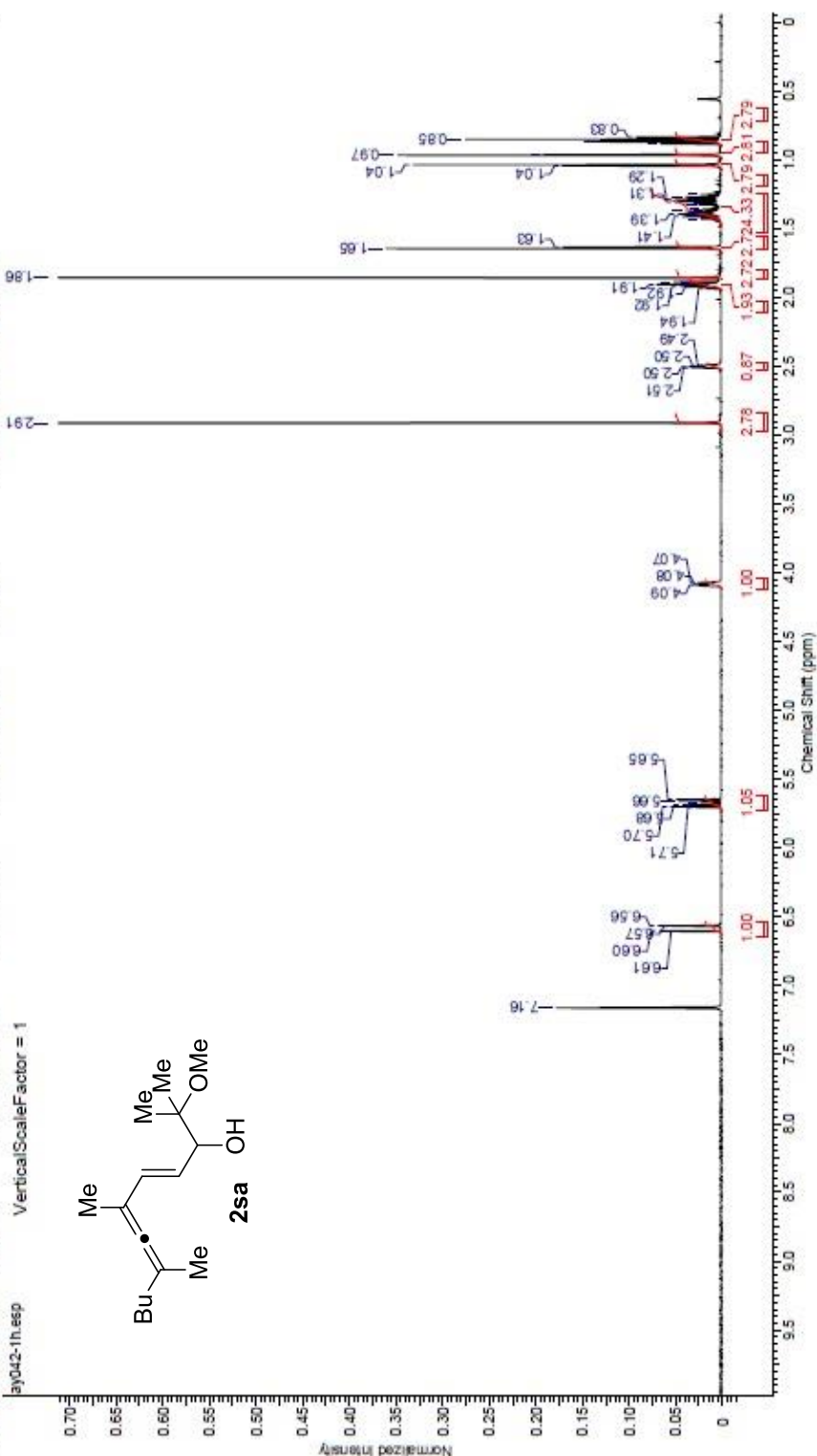
28.07.2016 13:23:24

Acquisition Time (sec)	1.3107	Comment	AA-AY-029	Date	Feb 19 2016	Date Stamp	Feb 19 2016
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Frequency (MHz)	100.57	Nucleus	¹³ C	Number of Transients	2000	Original Points Count	32768
Points Count	32768	Pulse Sequence	s2oul	Receiver Gain	30.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	11051.4873	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00	Temperature (degree C)	25.000



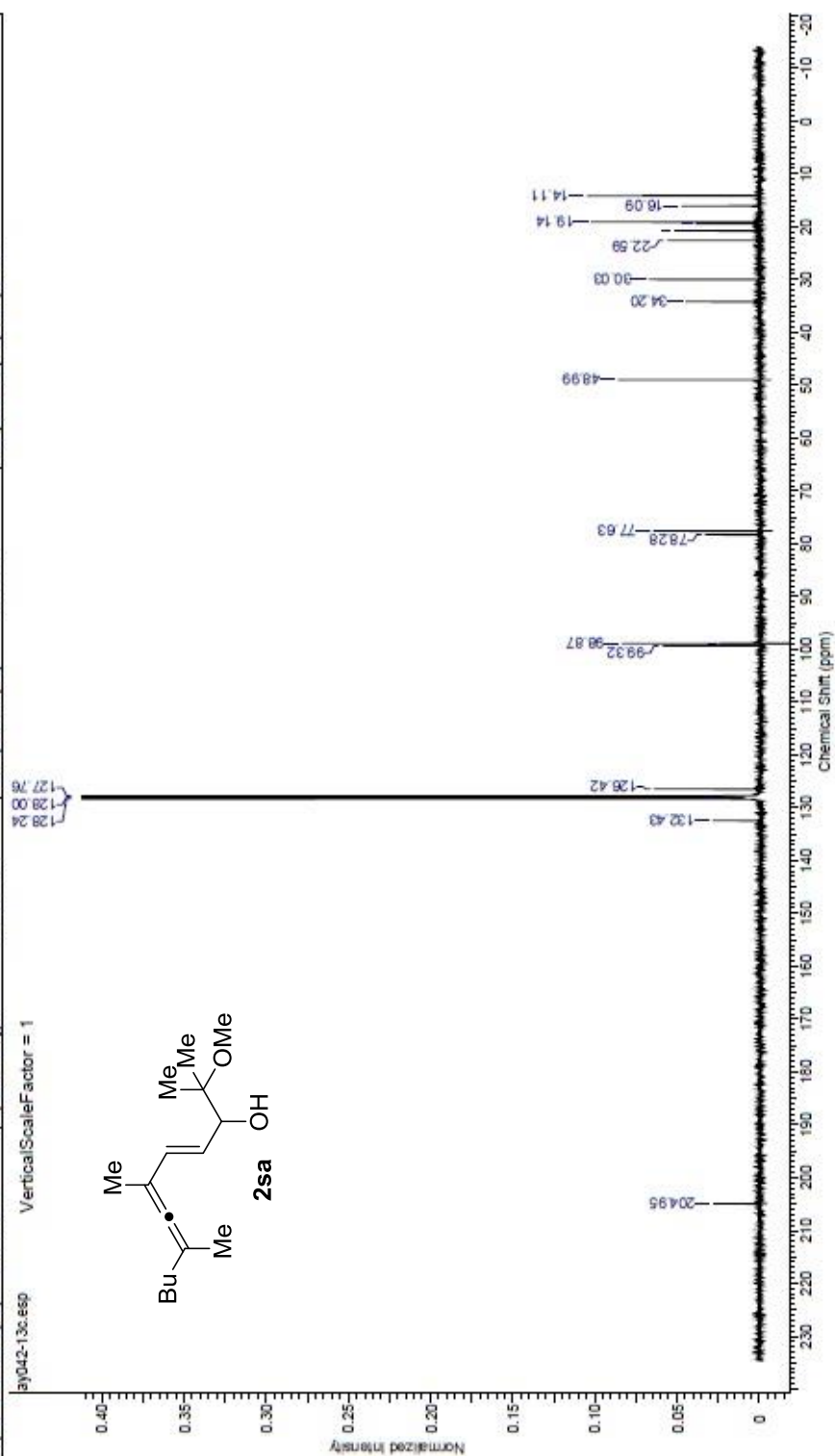
28.07.2016 13:47:42

Acquisition Time (sec)	2.5559	Comment	AA-AY-Q42TKR	Date	Jun 15 2016	Date Stamp	Jun 15 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\JELER GAZK CUARINOC\ARINC.DAT\AY-Q42TKR_20160615_011PROTON_01.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	8	Original Points Count	16384
Points Count	16384	Pulse Sequence	zgpg30	Receiver Gain	60.00	Solvent	BENZENE-d6
Spectrum Offset (Hz)	2416.7764	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	25.000



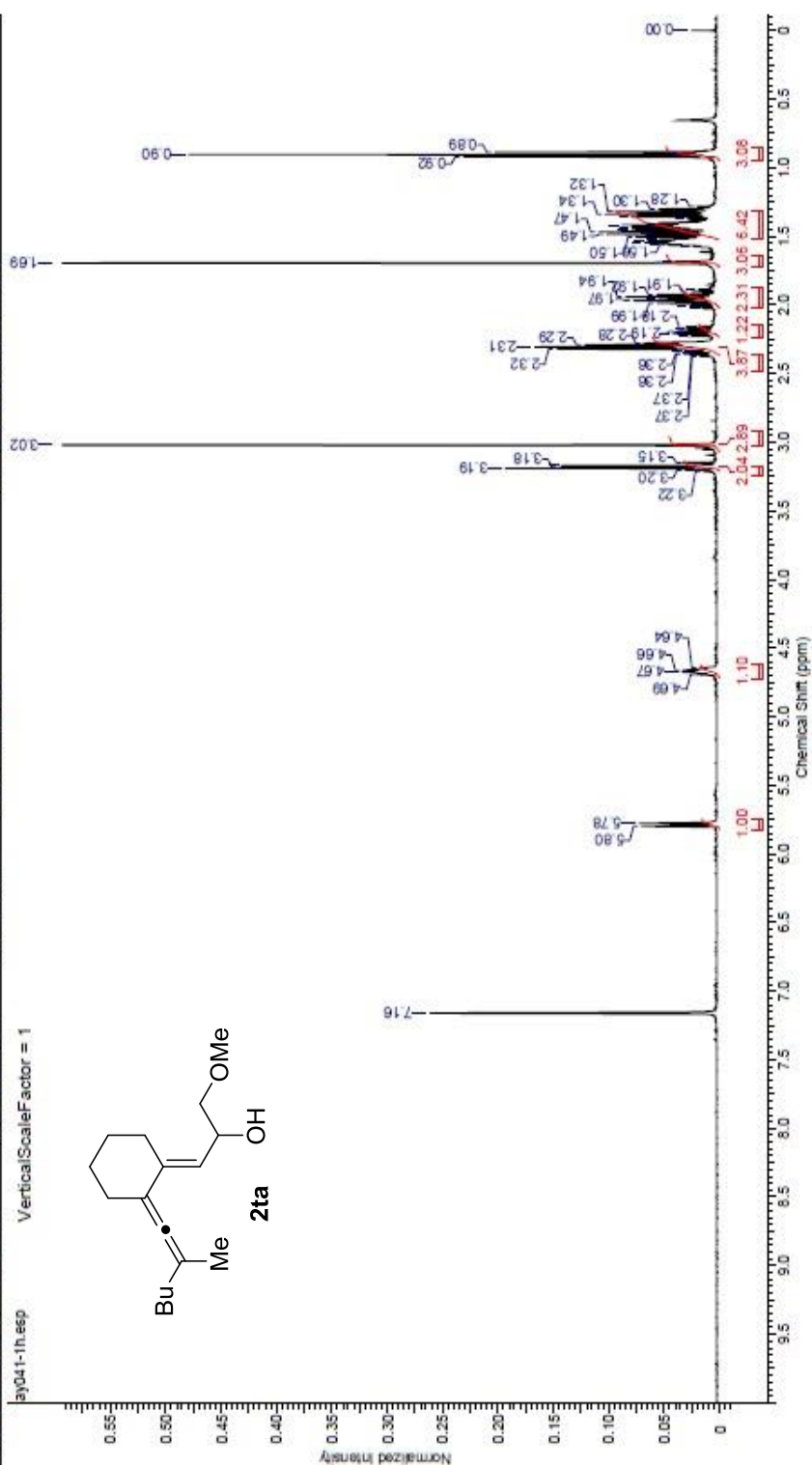
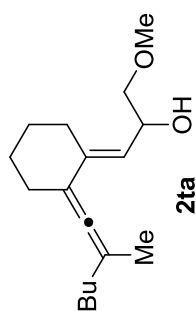
Acquisition Time (sec)	1.3107	Comment	AA-AY-042TKR	Date	Jun 15 2016	Date Stamp	Jun 15 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\UGLER GUPLER\POXI\DEYER FE GKK CU\ARING\ARINC DATA\ARINC\AA-AY-042TKR_20160615_01\CARBON_03.FID\FID						
Frequency (MHz)	100.57	Nucleus	13C			Number of Transients	5000
Points Count	32768	Pulse Sequence	s2bul			Receiver Gain	30.00
Spectrum Offset (Hz)	11037.1699	Spectrum Type	STANDARD			Sweep Width (Hz)	25000.00
						Temperature (degree C)	25.000

VerticalScaleFactor = 1



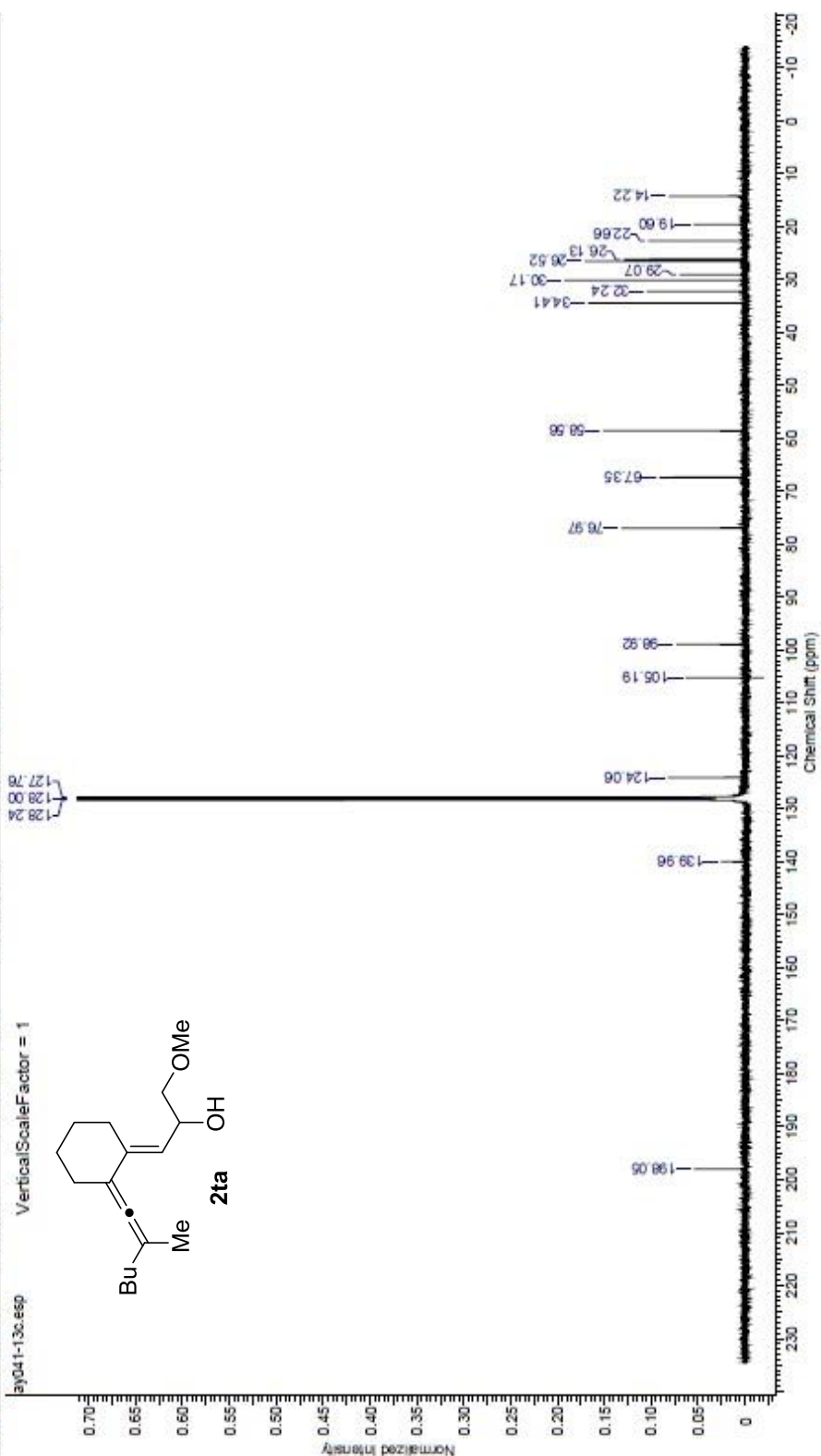
Acquisition Time (sec)	2.5559	Comment	AA-VY-041-T	Date	Jun. 6 2016	Date Stamp	Jun. 6 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\UGLER GUPLER\POXI\DEYER FE GKK CUARINGS\JARC DATA\JARC-AA-VY-041-T_20160606_01.FID\FID						
Frequency (MHz)	399.92	Nucleus	1H				
Points Count	16384	Pulse Sequence	s2ouf				
Spectrum Offset (Hz)	2416.7764	Spectrum Type	STANDARD				
		Receiver Gain	58.00				
		Sweep Width (Hz)	6410.26				
		Temperature (degree C)	25.000				
		Original Points Count	16384				
		Solvent	BENZENE-d6				

VerticalScaleFactor = 1



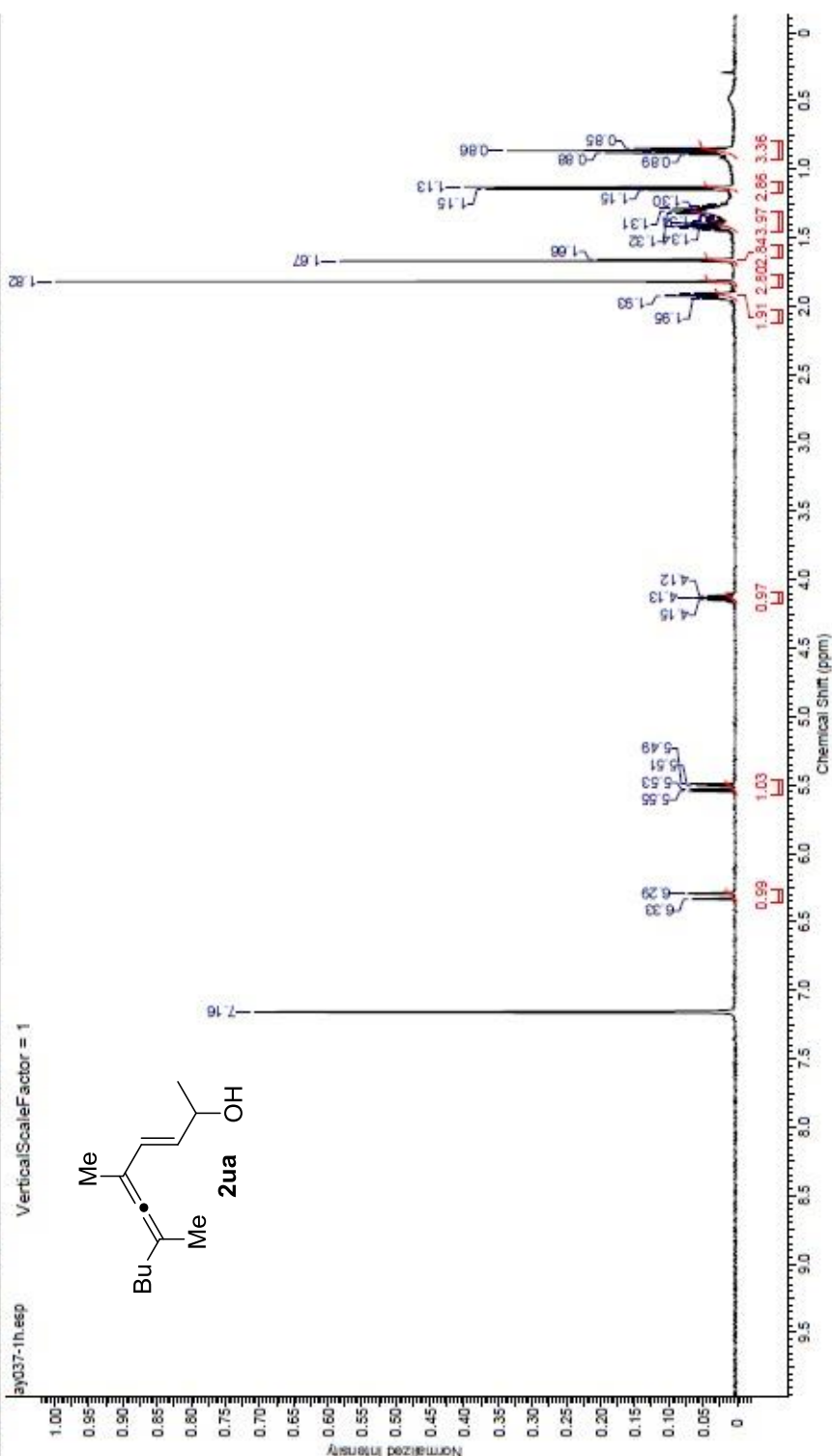
28.07.2016 13:41:41

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\ELER GUCLER\PEOXIDE\VER.FE GAK CUJABING\ABING DATA\BIN\AA-AY-041-T_20160606_01\CARBON_01.FID.FID						
Frequency (MHz)	100.57	Nucleus	¹³ C	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



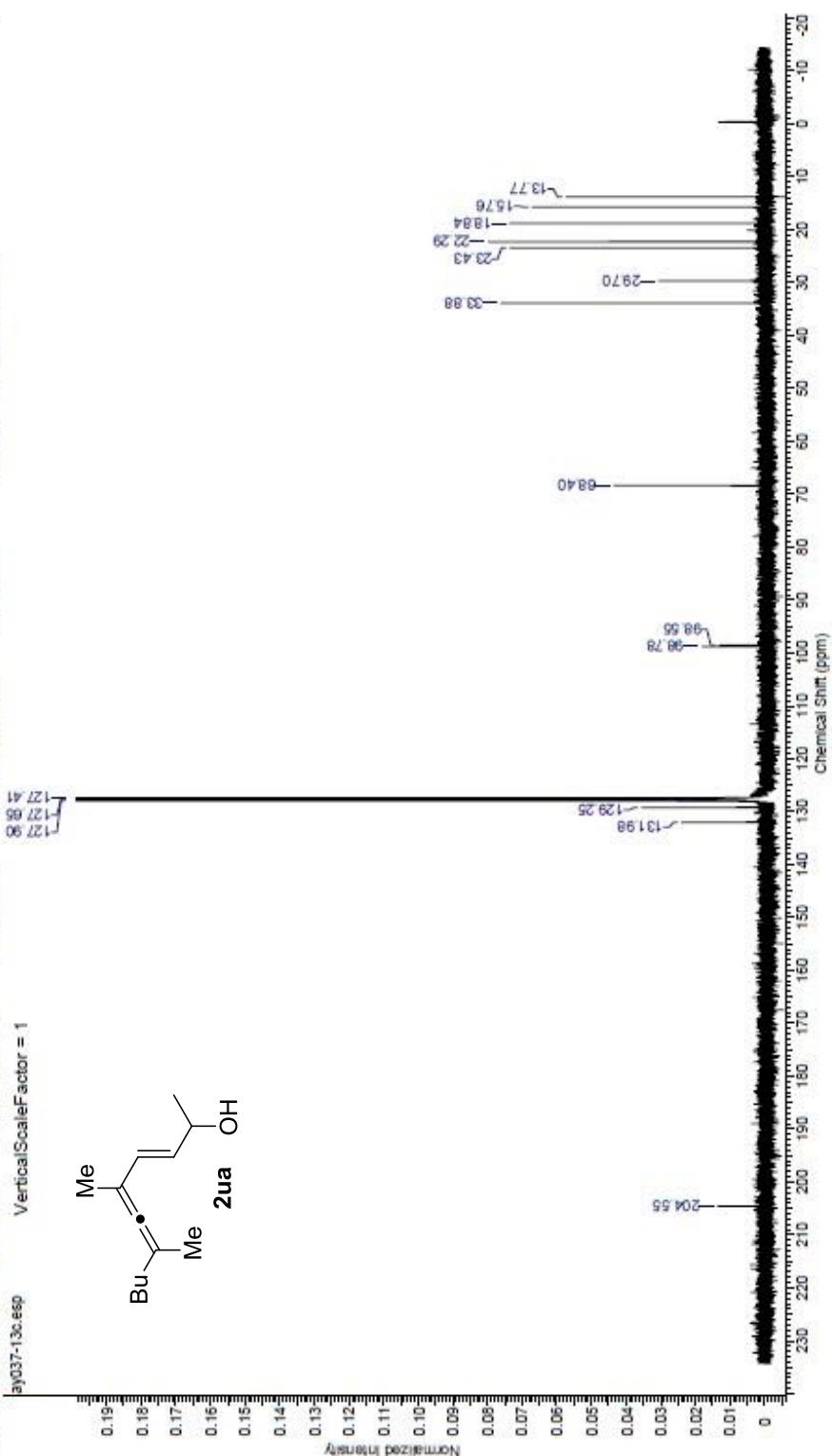
28.07.2016 15:01:55

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\ISLER\GUGLER\POXIDE\VER FE 63K CUARIN\20160614_011\PROTON_01.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	8	Original Points Count	16384
Points Count	16384	Pulse Sequence	zgpg30	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



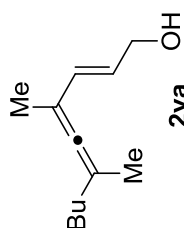
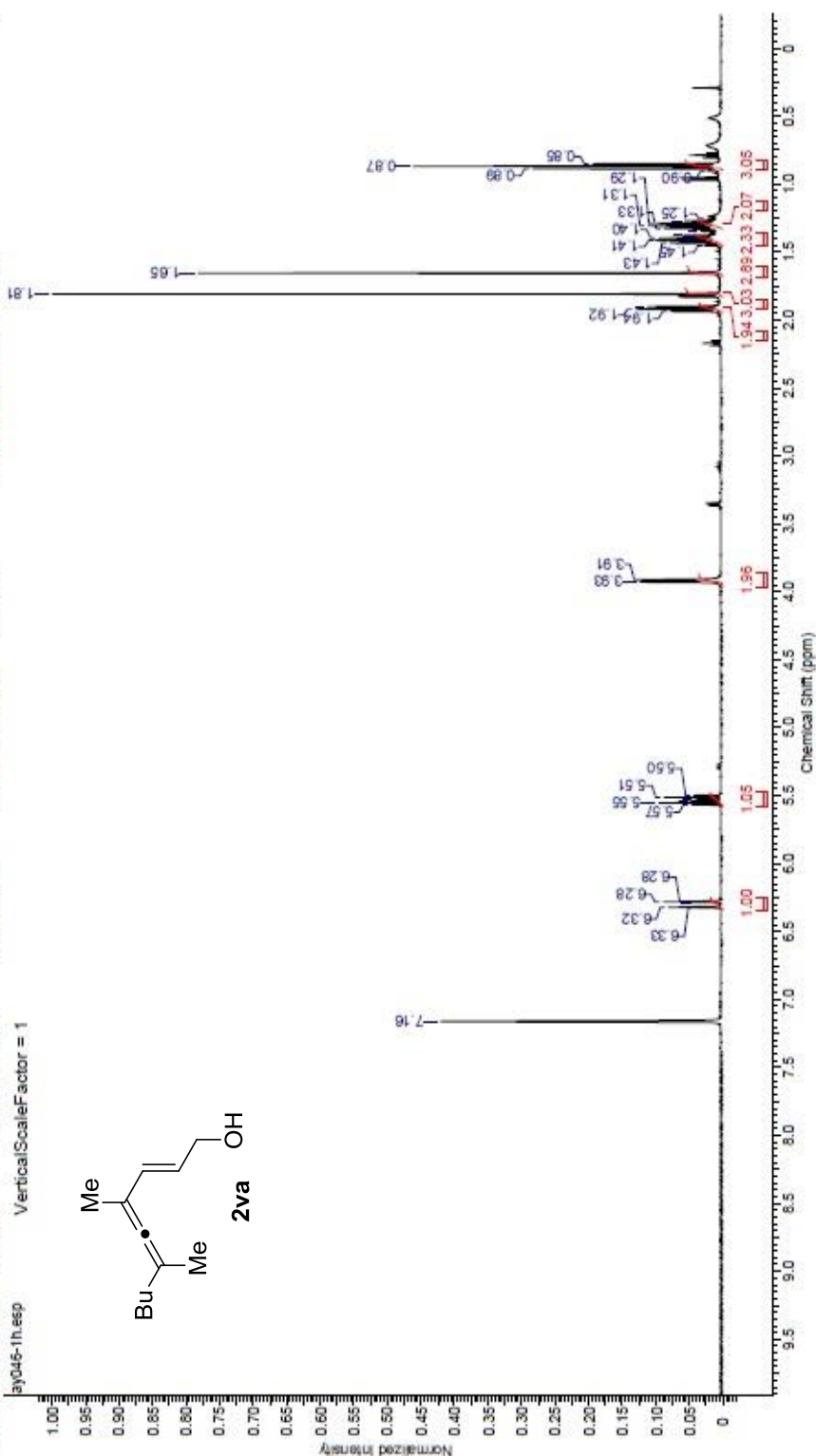
28.07.2016 15:04:10

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\UGLER GUGLER\POXIDE\VER FE GOK CUARING\GARING DATA\ARINC\AA-AY-034-2_20160411_DICARBON_03.FID.FID						
Frequency (MHz)	100.57	Nucleus	¹³ C	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



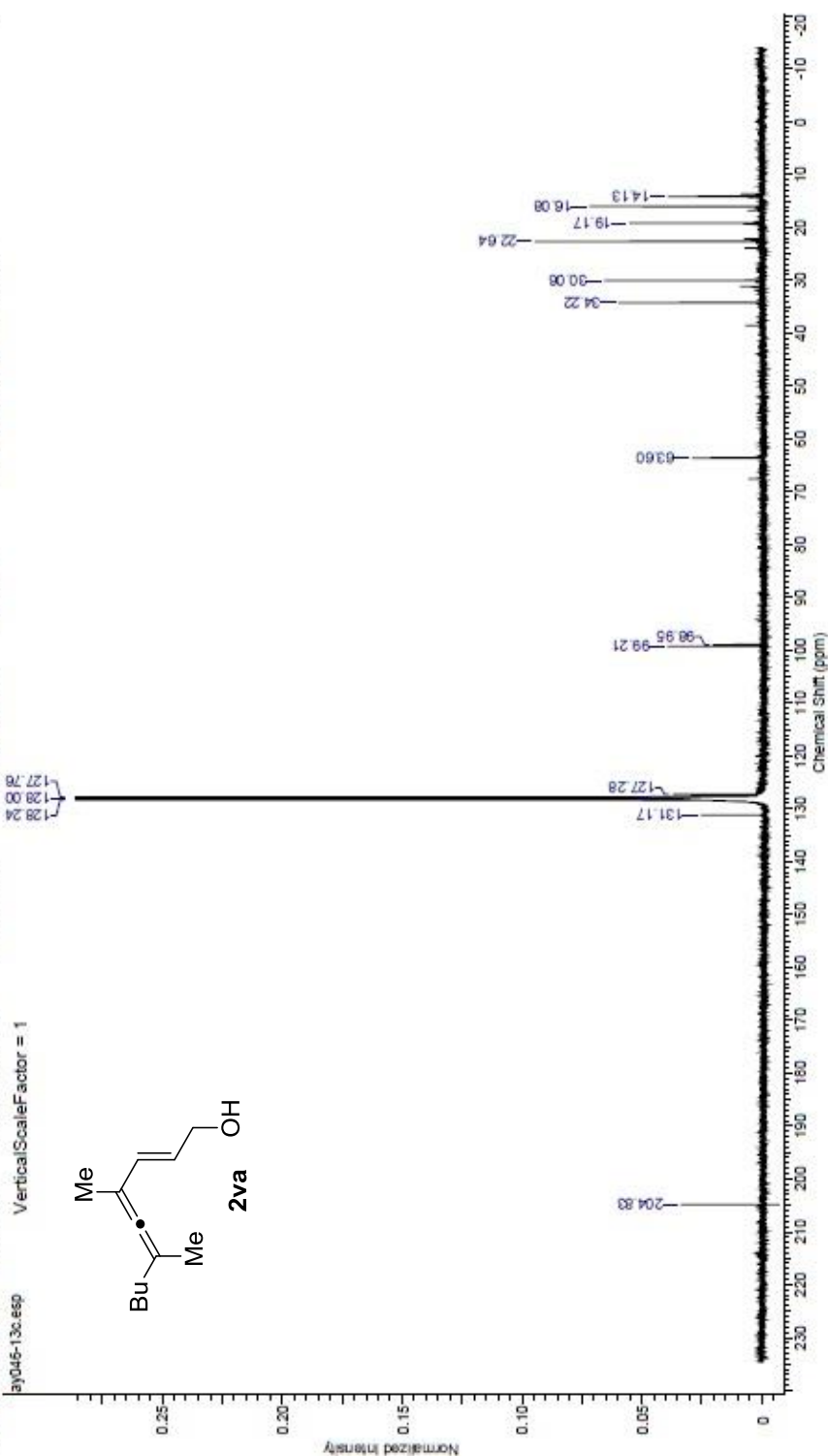
28.07.2016 14:20:36

Acquisition Time (sec)	2.5559	Comment	AA-AY-045-2	Date	Jun 24 2016	Date Stamp	Jun 24 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\JELER GIGLER\POXIDE\VER FE G0K CUARIN\28JARINC DATA\AIRC\AA-AY-045-2_20160624_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	Nucleus	¹ H	Number of Transients	8	Original Points Count	16384
Points Count	16384	Pulse Sequence	zgpg30	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



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\JER GUILLERIEPOXIDE\VER FE 04K CUJARING\CARINC.DAT\AVERINCA-AY-046-2_20160624_03.FID\FID					Original Points Count	32768
Frequency (MHz)	100.67	Nucleus	13C	Number of Transients	5000	Solvent	BENZENE-d6
Points Count	32768	Pulse Sequence	62pul	Receiver Gain	30.00	Temperature (degree C)	25.000
Spectrum Offset (Hz)	11097.9336	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00		



APPENDIX C

MASS SPECTRUM OF PRODUCTS



