SYNTHESIS OF VINYLALLENOLS VIA PALLADIUM-CATALYZED ARYLATION REACTIONS OF (Z)-2,4-ENYNE OXIRANES WITH ORGANOBORONS

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by

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ABSTRACT

SYNTHESIS OF VINYLALLENOLS VIA PALLADIUM-CATALYZED ARYLATION REACTIONS OF (Z)-2,4-ENYNE OXIRANES WITH ORGANOBORONS

Allenes are important functional groups especially in synthetic organic chemistry. Due to their unique reactivity and high level of chirality transfer, allenes can be used as building blocks in the synthesis of complex molecules. In recent decades transition-metal catalyzed synthesis of allenes with organometallic reagents has become attractive method. For the synthesis of functionalized allenes, addition of different nucleophiles with the help of various transition metals to propargylic compounds bearing a leaving group has been mostly used. Transition metals are crucial for these reactions for shifting them from S_N2 to S_N2' for the formation of allenes.

Within the context of this research, a novel palladium-catalyzed arylation reactions of (*Z*)-2,4-enyne oxiranes with organoborons have been investigated. As a result of the 1,5-substitution reaction, aryl-substituted vinylallenes bearing a hydroxyl group on the allylic position (7-aryl-3,5,6-trien-2-ol) were obtained in high yields and diastereoselectivities. We were able to also disclose that Diels-Alder adducts could be obtained with excellent endo and facial selectivities when the vinylallen types of this study were reacted with dienophiles.

ÖZET

(Z)-2,4-ENİN OKSİRANLARIN ORGANOBORONLAR İLE PALADYUM KATALİZLİ ARİLASYON TEPKİMELERİ ÜZERİNDEN VİNİLALLENOLLERİN SENTEZİ

Allenler özellikle sentetik organik kimyada önemli fonksiyonel gruplardır. Benzersiz reaktiviteleri ve yüksek seviyede kiralite transferinden dolayı allenler komplex moleküllerin sentezinde yapıtaşları olarak kullanılabilirler. Son yıllarda, orgonometalik bileşikler ile geçiş metal katalizli allen sentezleri ilgi çekici hale gelmiştir. Fonksiyonlandırılmış allenler, bir ayrılan grup içeren proparjilik bileşiklerine geçiş metallerin yardımıyla çeşitli nükleofillerin katılması ile sentezlenmektedir. Geçiş metalleri bu tür reaksiyonları S_N2 den S_N2' e kaydırarak allen oluşturması açısından çok büyük öneme sahiptir.

Bu çalışma kapsamında, (Z)-2,4-enin oksiran yapılarının organoboronlar ile paladyum katalizli arilasyon tepkimleri üzerine çalışılmıştır. 1,5-yerdeğiştirme reaksiyonu sonucunda aril bağlı ve allilik pozisyonunda hidroksil grubu taşıyan vinilallenler (7-aril-3,5,6-trien-2-ol) yüksek verim ve diastereoseçimli olarak elde edilebilmiştir. Ayrıca bu çalışmada elde edilen vinilallen tipinin dienofiller ile yüksek endo ve fasiyal seçimli olarak Diels-Alder katılma ürünü elde edilebilmiştir.

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ABBREVIATION

Ac	Acetate
ACN	Acetonitrile
aq.	Aqueous
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
BIPHEP	2,2'-Bis(diphenylphosphino)biphenyl
Bn	Benzyl
Bu	n-Butyl
t-Bu	tert-Butyl
Cy	Cyclohexane
dba	Dibenzylideneacetone
DBU	1,8-Diazabicyclo(5.4.0)undec-7-ene
DCM	Dichloromethane
DIBAL-H	Diisobutylaluminium hydride
DMAP	4-Dimethylaminopyridine
DME	1,2-Dimethoxyethane
DMEDA	N,N′-Dimethylethylenediamine
DMF	*N*,*N*-Dimethylformamide
DPEPhos	Bis-[2-(diphenylphosphino)phenyl]ether
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-Bis(diphenylphosphino)ferrocene
dppm	Bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
d.r.	Diastereomeric ratio
Et	Ethyl
eqv.	Equivalent
Et_2O	Diethyl ether
h	hour
i-Pr	Isopropyl
m-CPBA	meta-chloroperoxybenzoic acid
M	Molar

Me	Methyl
mg	Milligrams
min.	Minute
mL	Milliliter
mmol	Millimoles
N.D.	Not determined
neop	Neopentyl glycol ester
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser Spectroscopy
O.N.	Overnight
Ph	Phenyl
Pr	Propyl
rt	Room Temperature
t	Time
t-Bu-Xanthphos	9,9-Dimethyl-4,5-bis(di-tert-butylphosphino)xanthene
TBDMS	tert-Butyldimethylsilyl
THF	Tetrahydrofurane
TMEDA	Tetramethylethylenediamine
Xanthphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene
Xphos	2-Dicyclohexylphosphino-2′,4′,6′ triisopropylbiphenyl

CHAPTER 1

INTRODUCTION

Allenes are important functional groups especially in synthetic organic chemistry. Due to their unique reactivity and high level of chirality transfer, allenes can be used as building blocks in the synthesis of complex molecules. This reactivity and natural chirality of allenes result in the usage of the synthesis of natural and pharmacological compounds (Scheme 1.).

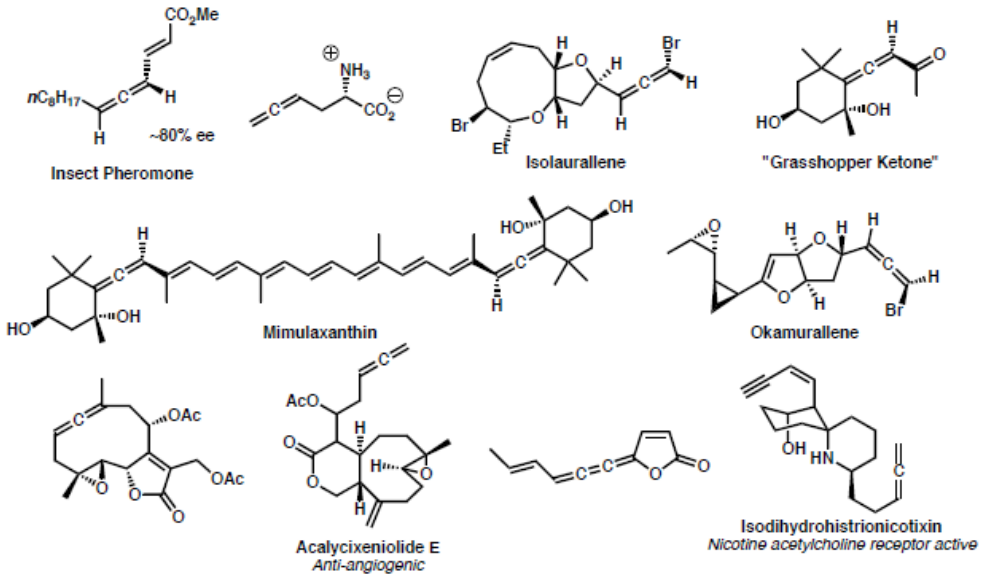

Figure 1.1. Allenic natural products and pharmacologically active allenes.

In last decades transition-metal catalyzed synthesis of allenes with organometallic reagents has become an attractive method. For the synthesis of functionalized allenes, addition of different nucleophiles with the help of various transition metals to propargylic compounds bearing a leaving group has been mostly used. Transition metals are crucial to switch from S_N2 route to S_N2' route for the formation of allenes. Soft and hard nucleophiles are both applicable for S_N2' reactions. Hard nucleophiles like Grignard reagents or alkyl lithiums are used mostly with copper-, iron- and nickel-catalyzed reactions. Palladium, rhodium and iridium are mostly suitable for soft nucleophiles such as organoborons and carbonmonoxide.

Palladium-catalyzed coupling type reactions of propargylic compounds with a leaving group are prominent class of methods for the construction of alkenyl-, alkynyl-, and aryl- or carbonylated allenes. Epoxide rings could also behave as a leaving group in substitution reactions in the pathway of ring opening for allenol derivatives. S_N2''reactions of conjugated enynes are another route for synthesis of alkenylated allenes or vinylallenes. The advantage of this S_N2'' reaction is to enable the construction of functionalized vinylallenes. Vinyl-substituted allenes are valuable compounds because of unique reactivity toward miscellaneous cycloaddition and cyclization reactions.

In light of these informations we have developed a new method for the synthesis of aryl bearing vinylallenols which involves the reaction of enyne oxiranes with organoborons in the presence of a palladium catalyst.

CHAPTER 2

LITERATURE SURVEY

2.1. Synthesis of Allenes via Pd(0)-Catalyzed Reactions of Propargyl Compounds

Propargyl compounds bearing a leaving group are versatile reagents in the synthesis of allene derivatives. In the presence of Pd(0), and a nucleophile 1,3-substitution reaction(SN2') occures to deliver functionalized allenes (Figure 2.1)

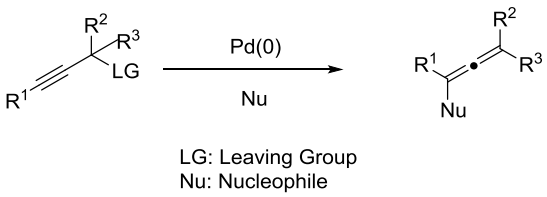

Figure 2.1. Synthesis of Allenes via Pd (0)-Catalyzed Reactions of Propargyl Compounds

Pd (0)-catalyzed reactions of propargyl compounds proceed in two ways; one is the formation of σ-allenylpalladium (**A**) and the other is propargylpalladium (**B**) (Figure 2.2). Reaction pathway changes according to the nucleophile type (Elsevier et al., 1983). After the formation of palladium intermeadiates, the nucleophile inserts into the Pd-LG bond for the target molecule.

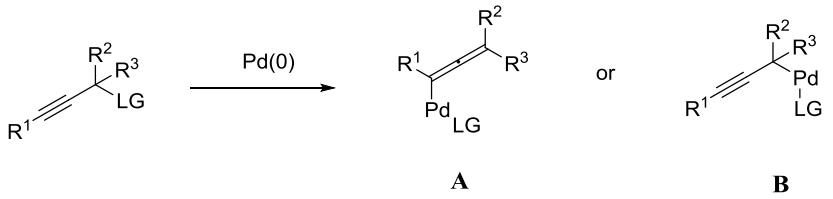

Figure 2.2. Formation of Palladium Intermediates from Propargylic Reagents

Alkenes, alkynes and carbonmonoxide are used widely as nucleophile in 1,3-substitution reactions of propargylic compounds. Beside these nucleophiles forms by transmetallation via main group metals, metal hydrides and organoborons are used (Tsuji, 2004).

In 1986, Tsuji and co-workers revealed that the Pd-catalyzed alkoxycarbonylation reaction of propargyl carbonates resulted in alleneoates. (Tsuji et al., 1986) (Figure 2.3).

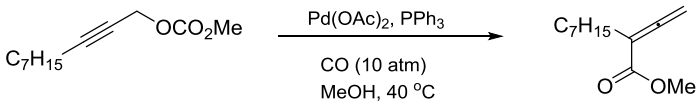

Figure 2.3. Alkoxycarbonylation of Propargyl Carbonates

One of the milestone studies of propargylic compounds is Heck type addition of olefins to form 1,2,4-trienes (vinylallenes). In 1991 Mandai and co-workers reported that Pd-catalyzed reaction of 2-alkynyl carbonates with electron deficient olefins produced vinylallenes in good yields. (Mandai et al., 1991) (Figure 2.4).

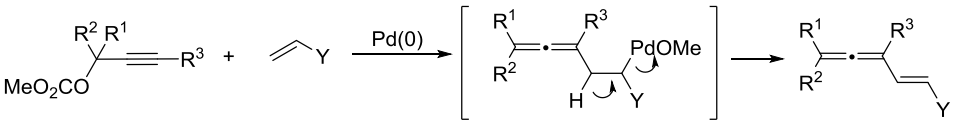

Figure 2.4. Pd-Catalyzed reactions of 2-alkynyl Carbonates with Olefins

In the literature, there are examples where terminal alkynes were used as nucleophiles in the reaction with propargylic compounds. These alkynylation reactions usually were realized in the presence of Cu(I) (Tsuji, 2004) (Figure 2.5).

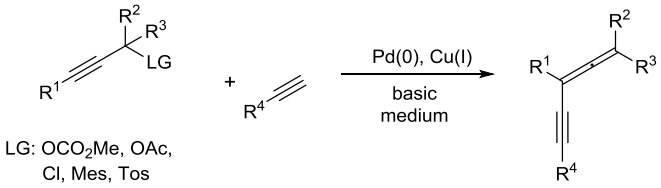

Figure 2.5. Pd(0)-Catalyzed Alkynylation of Propargyl Compounds

Propargylic compounds also react with arylborons in the presence of Pd(0) for the formation of aryl bearing allenes. (Moriya et al., 1994) (Figure 2.6).

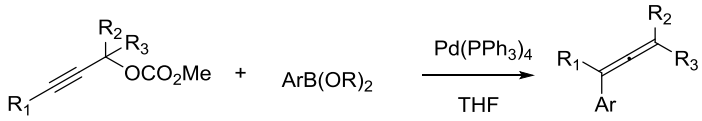

Figure 2.6. Arylation of Propargyl Carbonates

In 2016, Lou et al. have been developed an efficient palladium-catalyzed coupling of propargylic carbonates with organoboranic acids in high yield and chirality transfer. *o*-(Diphenylphosphino) benzaldehyde was choosen as ligand affording allenes under mild reaction conditions (Lou et al., 2016) (Figure 2.7).

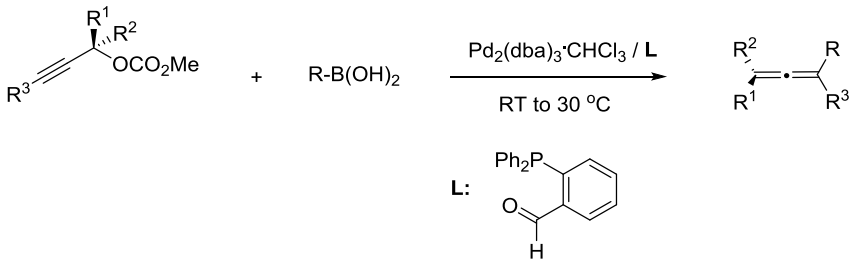

Figure 2.7. Arylation of Propargyl Carbonates in High Chirality Transfer

Besides orgonaborons, alkynes and carbon monoxide, relatively hard nucleophiles like Grignard reagents and organozinc compounds can be used for Pd-catalyzed reactions of propargylic compounds. Luong's group reports the palladium-catalyzed coupling of propargyl chloride with Grignard reagents in moderately good yields (Jeffery-Luong and Linstrumelle, 1980) (Figure 2.8).

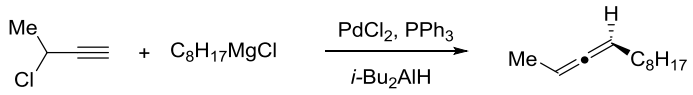

Figure 2.8. Palladium-Catalyzed Coupling of Grignard Reagents with Propargyl Chlorides.

Vermeer et al. reported that *R*-(-)-1-trifluoroacetoxy-1-phenyl-2-propyne when reacted, in proper conditions, with PhZnCl formed allenes in excellent yields. The stereo- and regio-selectivities of the reaction were also superior. The insertion of the palladium at first takes place, and then follows by transmetallation with PhZnCl to form allenyl(phenyl)chloride. The reductive elimination then produces aryl-substituted allenes (Elsevier et al., 1983) (Figure 2.9).

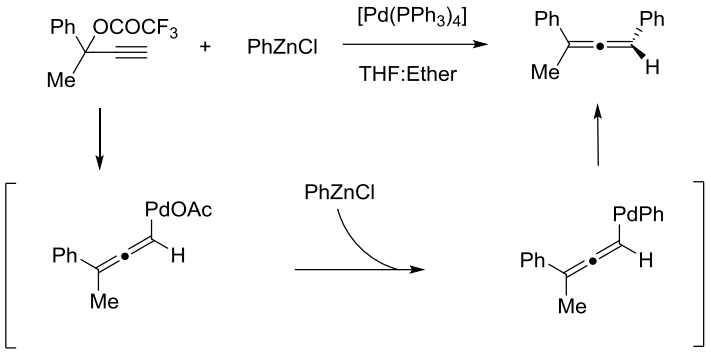

Figure 2.9. Palladium-Catalyzed Addition of Organozinc Compounds to Propargyl Acetates.

In 1997 Piotti and Alper reported that in the existence of CO, an alcohol and Pd(0), propargyl oxiranes generates α-allenol esters via alkoxycarbonylation reaction. The allenyl products having a β-hydroxyl group can further cyclize to geneate an oxygenated five-membered ring (Piotti and Alper, 1997).

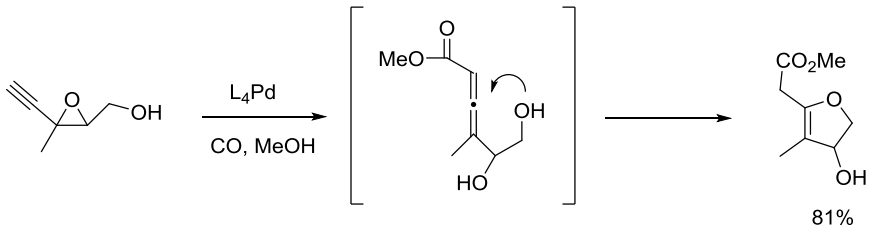

Figure 2.10. Pd(0)-Catalyzed Alkoxycarbonylation of Hydroxyl Functionalized Propargyl Oxiranes

Propargyl oxiranes also give diaseteroselective alkynylation reaction with terminal alkynes in basic medium with the help of Pd(0)/Cu(I) system. An optically active anti-substituted allene could be synthesized (Yoshida et al., 2007) (Figure 2.11)

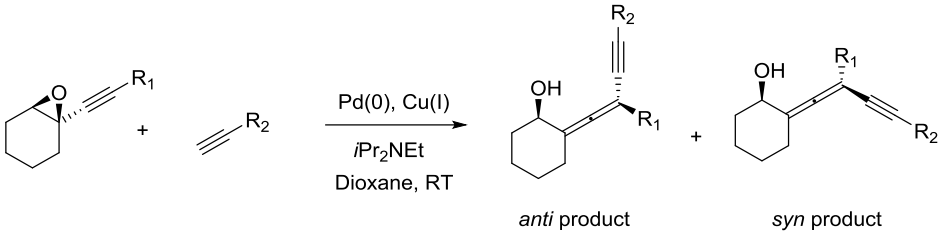

Figure 2.11. Alkynylation of Propargyl Oxirane

The Pd(0)-catalyzed reaction of propargyl oxiranes with arylboronic acids yield α-allenols with *anti*-diastereoselectivity exclusively (Yoshida et al., 2005) (Figure 2.12).

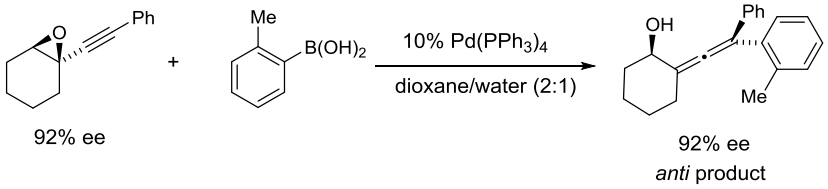

Figure 2.12. Diastereoselective Arylation of Propragyl Oxiranes

2.2. Palladium-Catalyzed Reactions of Allylic Compounds

Beside the propargyl compounds allylic compounds are also reactive towards S_N2' and S_N2 type reactions in the presence of palladium. Allylic compounds react with palladium to undergo cross-coupling with main group organometallic compounds. Substitution usually occurs mainly at less hindered position of allylic terminal (Figure 2.13) (Tsuji, 2000)

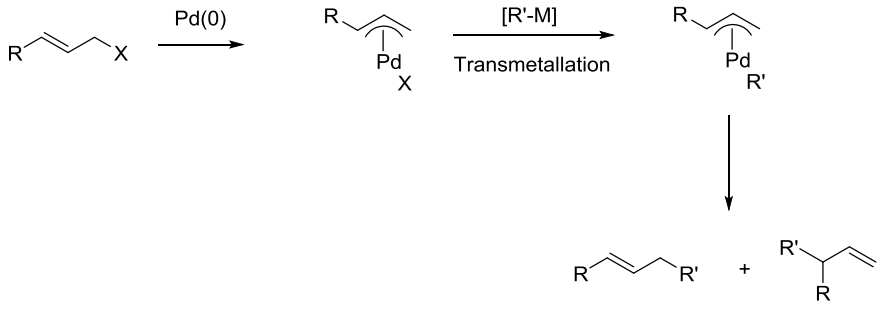

Figure 2.13. Mechanism of Transmetallation of Main Group Metals with π-Allylpalladium.

Murahashi and co-workers (Murahashi et al., 1993) demonstrated that allyl phosphates react with carbon monoxide in the presence of alcohols over a palladium catalyst providing *β,γ*-unsaturated esters in high yields with excellent stereoselectivities (Figure 2.14).

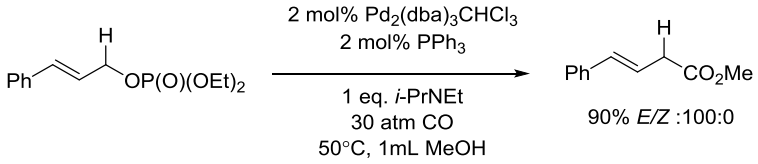

Figure 2.14. Palladium-Catalazed Alkoxycarbonylation of Allyl Phosphates

Enantiospecific 1,4-addition (S_N2') of arylboronic acid to allylic acetates via Pd(II) catalysis was reported by Ohmiya et. al. in 2008 (Figure 2.15).

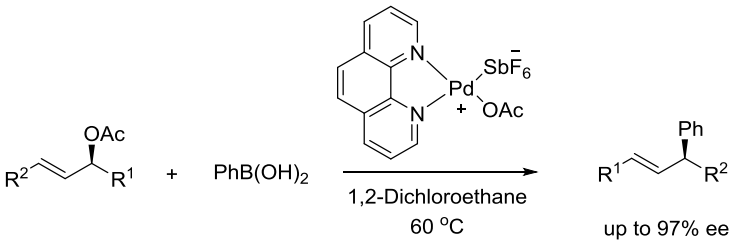

Figure 2.15. S_N2' Type Stereoselective Substitution of Allylic Acetates with Arylboronic Acid

In 2002, a highly regio-selective palladium-catalyzed reaction of allylic bromides with benzyl Grignard reagents was reported by Rosales and co-workers (Figure 2.16). The polyene derivatives were obtained with superior yield and regioselectivity (Rosales et al., 2002).

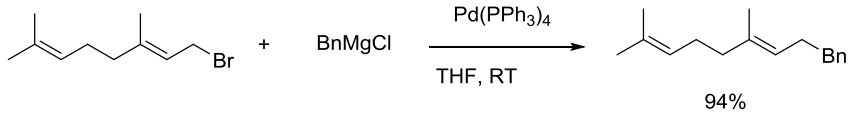

Figure 2.16. Palladium-Catalyzed Synthesis of Polyene Derivatives with Grignard Reagents.

Alkenyloxiranes also afford nucleophilic 1,4- or 1,2-addition products when reacted in the presence of a Pd(0) catalyst. Mostly the 1,4-addition product forms regioselectively with the help of the electronic effect of epoxide oxygen atom (Figure 2.17).

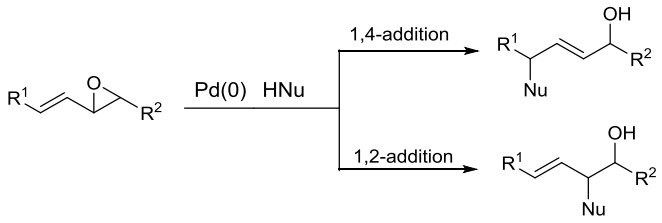

Figure 2.17. 1,4- and 1,2-Addition of Allylic Oxiranes

Regioselective carbonylation of isoprene oxide in the alcohol medium with an added Pd-π-allyl complex under a high pressure of CO atmosphere afforded β, γ-unsaturated δ-hydroxyesters are obtained (Figure 2.18)

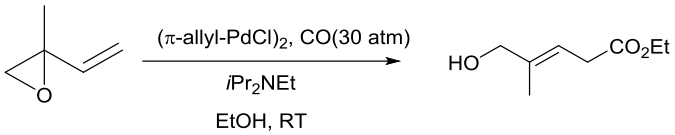

Figure 2.18. Alkoxycarbonylation of Allyl Epoxide

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Palladium-catalyzed coupling reactions of allyl epoxides with organoboronic acids were performed by using a Pd-pincer catalyst. The reactions proceeded under mild conditions, affording arylated allyl alcohols regioselectively (Kjellgren et al., 2005) (Figure 2.19).

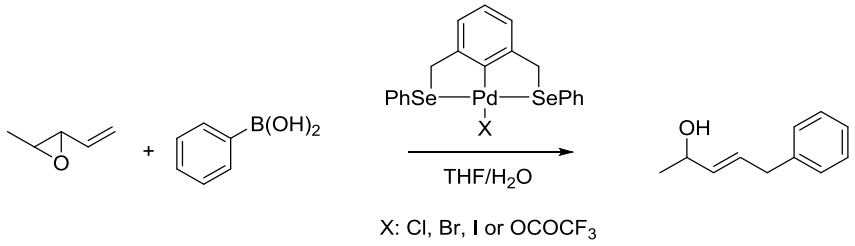


Figure 2.19. Arylation of Allyl Oxiranes

2.3. Palladium(0)-Catalyzed Reactions of Conjugated Enynes

The allylic electrophiles bearings a conjugated alkynyl moiety, shows exceptional performance in nucleophilic reactions.

In 2011 our research group reported that Pd(0)-catalyzed alkoxycarbonylation (Akpınar et al., 2011, Karagöz, et al., 2014) and arylation (Üçüncü et al., 2011) of (*Z*) and (E) configured 2,4-enyne carbonates with arylboronic acids yielded vinylallenes in high yields. Alkoxycarbonylation reaction afforded exclusively (*E*)-configured 2,3,5-trienoates with the intermediacy of the σ- vinylallenyl palladium complex (Figure 2.20).

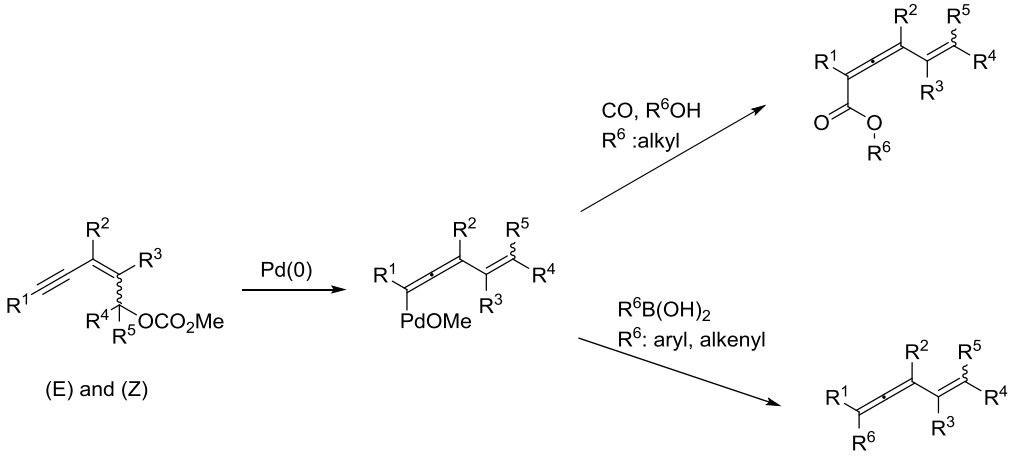


Figure 2.20. Arylation and Alkoxycarbonylation of (E) and (Z)-Configured 2,4-Enyne Carbonates

Our research group also reported Pd(0)-catalyzed alkoxycarbonylation of 2,4-enyne oxiranes.which yielded 7-hydroxy-2,3,5-trienoates in good yields with up to 97:3 diastereomeric ratio (Kuş et al., 2015) (Figure 2.21).

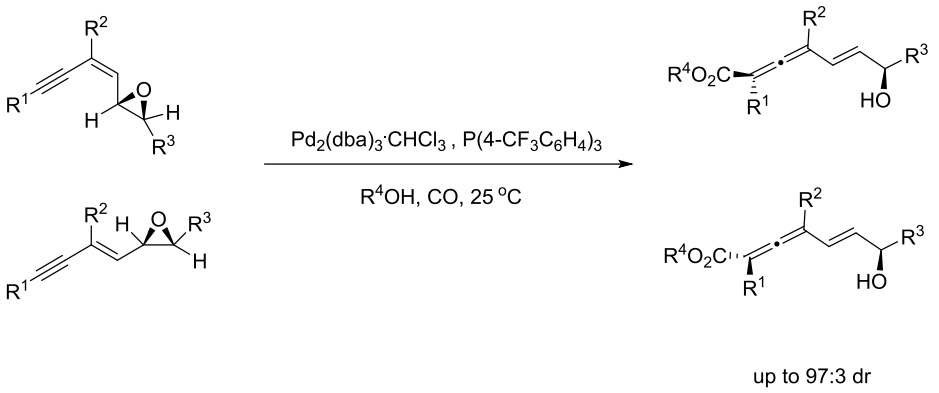


Figure 2.21. Alkoxycarbonylation of 2,4-Enyne Oxiranes

In the light of view of these literature work we decided to investigate Pd(0)-catalyzed arylation of 2,4-enyne oxiranes to result the formation of aryl bearing vinylallenols (Figure 2.22).

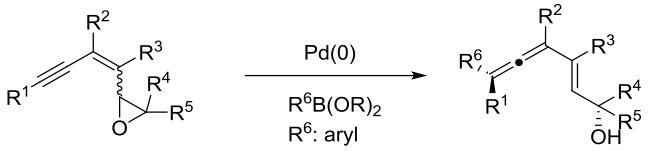


Figure 2.22. Pd(0)-Catalyzed Arylation of 2,4-Enyne Oxiranes

CHAPTER 3

EXPERIMENTAL STUDY

3.1. General Methods

The synthesis of all compounds performed under argon gas. The prepared substrates and products were purified over silica gel by column or flash chromatography with hexane or hexane/ethyl acetate as eluent system. Silica gel material used for the purification of enyne oxirane substrates had a particle size range of 60-200 mesh and treated by NEt_3 before use. It must be noted that the column chromatography of the substrate **1** on an untreated silica gel always resulted in decomposition. All other column purifications were performed on silica gel 60 (35-70 μm). All substrates appeared either colorless or pale yellow oils. The $Pd_2(dba)_3.CHCl_3$ (Ukai, et al. 1974) and $Pd(PPh_3)_4$ (Inorganic Synthesis, Vol. 28, 2009, 107) complexes were synthesized in the laboratory. Yields of crude mixtures and purity of prepared substrates were determined by quantitative ^1H -NMR technique, using *p*-anisaldehyde as the internal standard (Hays and Thompson, 2009). The pure samples were analyzed via: GC-MS (Thermo/ISQ) equipped with Thermo TR-5MS (30 m, 0.25mm ID) column; nuclear magnetic resonance (NMR) spectra were acquired on Varian VnmrJ 400 spectrometer, $CDCl_3$ and C_6D_6 were the solvents used as the NMR solvents and chemical shifts were reported in δ (ppm); a Perkin-Elmer Spectrum 100 was used to achieve infra-red spectra by ATR method with dry samples; high-resolution mass spectral analyses were performed at the Dortmund University of Technology Mass Spectrometry Laboratory on a Thermo Electron system.

DMF was dried by refluxing over CaH_2 overnight, distilled under reduced pressure (20 mmHg, 80 ^oC) and stored over molecular sieve 4Å. DCM was dried over activated molecular sieve 3Å for 48 hours. Toluene was dried over CaH_2 and stored on molecular sieve 3Å. Et_2O and THF were distilled from benzophenone-ketyl under argon prior to use (Armarego and Chai, 2003).

3.2. Synthesis of Substrates

3.2.1. Synthesis of (Z)-1a

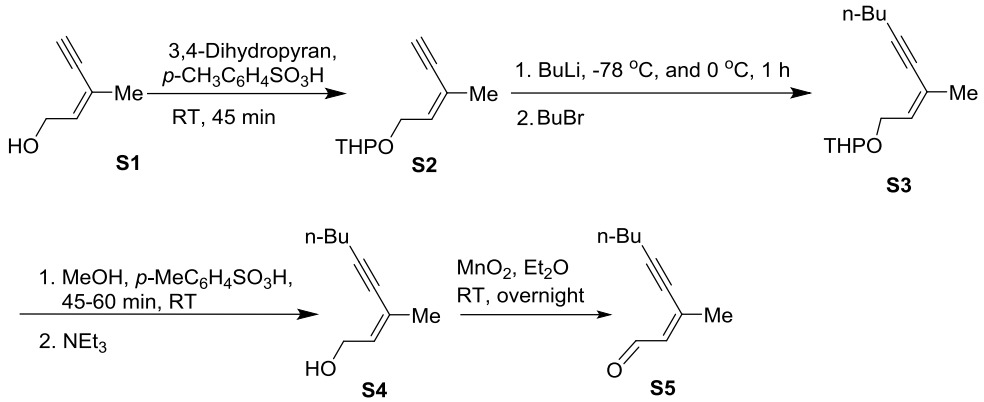


Figure 3.1. Synthesis of enyne aldehyde **S5**

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

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

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

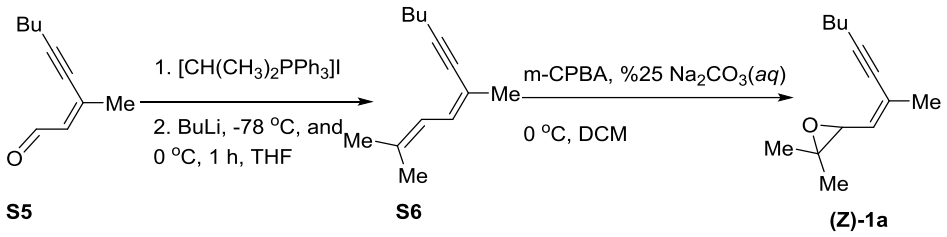


Figure 3.2. Synthesis of **(*Z*)-1a**

A hexane solution of BuLi (4.8 mL, 12 mmol, 2.5 M) was added dropwise to a solution of isopropyl(triphenyl)phosphonium iodide (4.32 g, 10 mmol) in THF (30 mL) at 0 °C, and stirred for further 1 h. The enyne aldehyde **S5** (1.8 g, 12 mmol), was added dropwise to the resulting mixture and stirred for 1 h, at RT. The reaction was quenched by the addition of saturated NH_4Cl(*aq*) solution, and the organic layer was extracted with diethyl ether. The combined extracts were dried over $MgSO_4$, and chromatographed on a silica gel column to obtain pure **S6** (hexane/EtOAc, yield: 1.65 g, 78%), (Ming-Yuan, *et al.* 2004).

To a solution of **S6** (352 mg, 2 mmol) in DCM (30 mL) was added 12 mL solution of Na_2CO_3(*aq*) (25%) followed by 3.4 mmol (587 mg) *m*-chloroperbenzoic acid in portions at 0 ^{0}C. The mixture was stirred at the 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

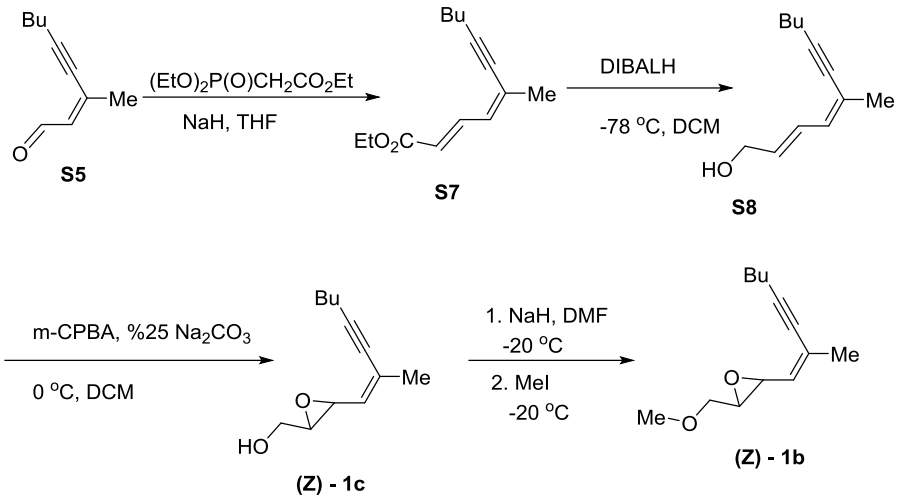


Figure 3.3. Synthesis of **(*Z*)-1b** and **1c**

To a solution of NaH (525 mg, 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 NH_4Cl(*aq*) solution and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give *E/Z* isomers with the isomeric ratio of 95:5. 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 $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to silica gel column chromatography to purify the corresponding **S8** compound (hexane-EtOAc, yield: 2.65 g, 85%), (Kajikawa, *et al.* 2009).

The epoxidation of **S8** (356 mg, 2 mmol) and the 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). The mixture was stirred for 4 h at the same temperature and then the reaction was terminated by the addition of MeOH (5 mL) and brine (5 mL), and extracted with DCM. The combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to column chromatography over NEt_3-pretreated short silica gel column to afford the corresponding alkoxy-substituted enyne oxirane products as colorless oil (*Z*)-**1b** (hexane-EtOAc, yield: 87%), (Caldentey, *et al.* 2011).

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

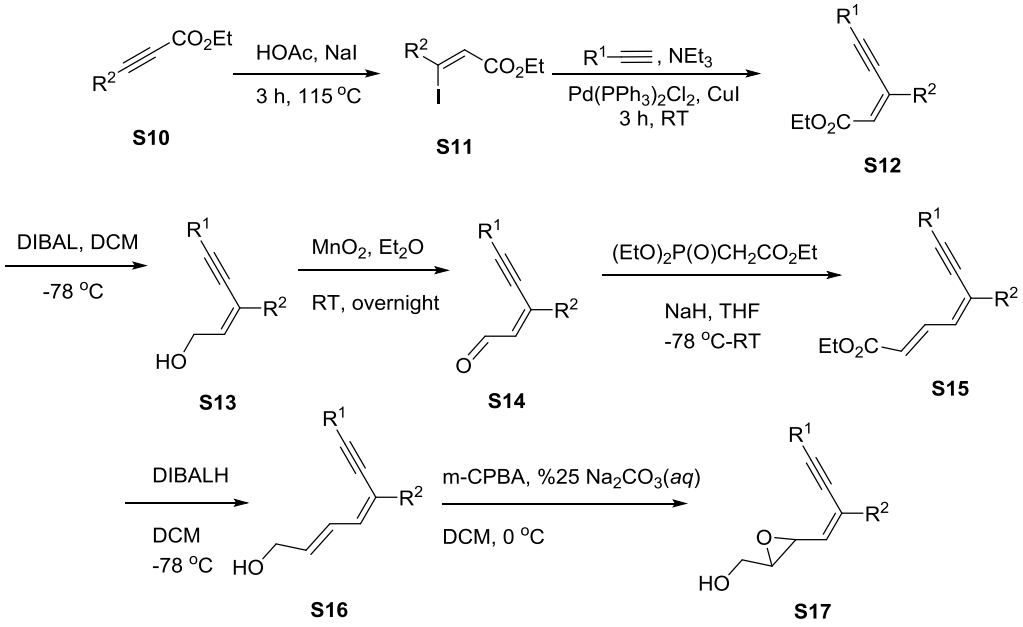


Figure 3.4. Synthesis of **S17**

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

ether (30 mL/mmol of the ester substrate). The washings were combined in a separatory funnel. The phases were separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were treated sequentially with saturated aqueous $NaHCO_3$(*aq*), $Na_2S_2O_3$(*aq*) (1 M), and brine and then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (hexane-EtOAc, yields; R^2= H, 7.6 g, 84%; R^2= Me, 5.97 g, 93%; R^2= t-Bu, 9.6 g, 85%; R^2= Cy, 10.6 g, 86%, R^2= Bu, 9.8 g, 88%;), (Piers, *et al.* 1994). A mixture of **S11** (30 mmol), $PdCl_2(PPh_3)_2$ (210.6 mg, 0.3 mmol, 1% mol of Pd), and CuI (29 mg, 0.15 mmol, 0.5% mol of Cu) in 140 mL of Et_3N was stirred for 10 min at RT under Ar, and then, to this mixture was added a terminal alkyne (36 mmol). The mixture was stirred at RT for 3h. At the end of the reaction, water was added to the resulting mixture and then extracted with Et_2O. The combined organic layers were dried over $MgSO_4$. The solvent was evaporated in vacuo and the product **S12** was purified by column chromatography on silica gel (hexane-EtOAc, yields: R^1= Bu, R^2= H, 4.97 g, 92%; R^1= Ph, R^2= Me, 5.97 g, 93%; R^1= Cy, R^2= Me, 5.94 g, 90%; R^1= *t*-Bu, R^2= Me, 4.95 g, 85%; R^1= Bu, R^2= t-Bu 6.23 g, 88%, R^1= Bu, R^2= Bu 6.30 g, 90%, R^1= Bu, R^2= Cy, 6.21 g, 79%, R^1= H, R^2= Me %90, R^1= TMS, R^2= Me, 4.90 g, 81%).

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 ^oC. After the reaction mixture was stirred for 4 h at the same temperature, 1 M HCl(*aq*) solution was added before extracting with DCM. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to silica gel column chromatography to purify the corresponding **S13** compound (hexane-EtOAc; yields of **S13**: R^1= Bu, R^2= H, 3.14 g, 91%; R^1= Bu, R^2= Cy, 4.89 g, 89%, R^1= Cy, R^2= Me, 3.60 g, 81%; R^1= *t*-Bu, R^2= Me, 3.57 g, 94%; R^1= Bu, R^2= *t*-Bu, 4.2 g, 88%; R^1= Ph, R^2= Me, 3.87 g, 90%, R^1= H, R^2= Me %90, R^1= Bu, R^2= Bu 5.70 g, 78%, R^1= TMS, R^2= Me, 87%), (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 ^oC and the mixture stirred for 1 h, at RT. Subsequently, to

the reaction mixture was added **S14** (6.5-10 mmol) dropwise at -78 °C, and stirred for 1 h, at RT. The reaction was terminated by the addition of saturated NH_4Cl(*aq*) and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to obtain **S15** with *E/Z* isomeric ratios varying in the range of 97:3 to 95:5 (Urabe, *et al.* 1997). The crude mixture was purified on silica gel column (hexane-EtOAc) to obtain **S15** in pure isomeric form (yields of **S15** R^1= Bu, R^2= H, 1.48 g, 72%; R^1= Bu, R^2= Cy, 1.4 g, 68%; R^1= Cy, R^2= Me, 1.97 g, 80%; R^1= *t*-Bu, R^2= Me, 1.80 g, 82%; R^1= Bu, R^2= *t*-Bu, 2.12 g, 81%; R^1= Ph, R^2= Me, 2.04 g, 85%, R^1= Bu, R^2= Bu 5.50 g, 81%, R^1= H, R^2= Me %70, R^1= TMS, R^2= Me, 3.52 g, 90%).

A DIBALH (~3 eq, 1.0 M in cyclohexane) solution was added dropwise to the solution of **S15** in DCM (~6 mL/mmol **S15**) at –78 °C. After the reaction mixture was stirred for 4 h at the same temperature, 1 M HCl(*aq*) solution was added before extracting with DCM. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to silica gel column chromatography to purify the corresponding **S16** compound (hexane-EtOAc; yields of **S16**: R^1= Bu, R^2= H, 1.12 g, 95%; R^1= Bu, R^2= Cy, 1.1 g, 94%; R^1= Cy, R^2= Me, 1.55 g, 95%; R^1= *t*-Bu, R^2= Me, 1.39 g, 95%; R^1= Bu, R^2= *t*-Bu, 1.6 g, 90%; R^1= Bu, R^2= Bu 3.23 g, 71%, R^1= Ph, R^2= Me, 1.6 g, 92%, R^1= H, R^2= Me %85, R^1= TMS, R^2= Me, 2.82 g, 76%), (Kajikawa, *et al.* 2009).

The epoxidation of **S16** (2 mmol) and isolation of the corresponding **S17** products were performed as specified for (*Z*)-**1a** (yields of **S17**: R^1= Bu, R^2= H, 0.19 g, 55%; R^1= Bu, R^2= Cy, 0.26 g, 49%; R^1= Cy, R^2= Me, 0.25 g, 57%; R^1= *t*-Bu, R^2= Me, 0.25 g, 65%; R^1= Bu, R^2= *t*-Bu, 0.24 g, 50%; R^1= Bu, R^2= Bu 1.71 g, 49%, R^1= Ph, R^2= Me, 0.26 g, 60%, R^1= H, R^2= Me %60, R^1= TMS, R^2= Me, 1.52 g, 43%).

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

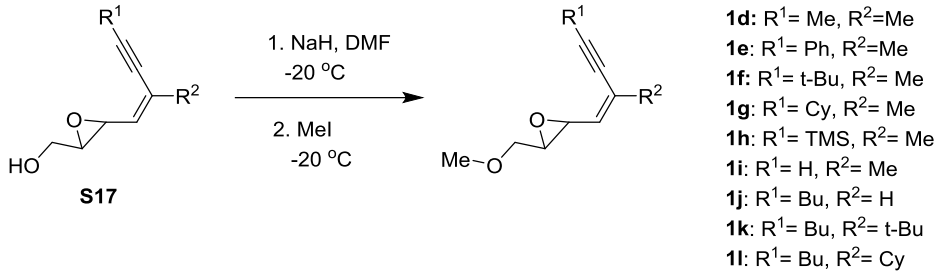


Figure 3.5. Synthesis of **(*Z*)-1d, e, f, g, h, I, j, k, l**

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). The mixture was stirred for 4 h at the same temperature and then the reaction was terminated by the addition of MeOH (5 mL) and brine (5 mL), and extracted with DCM. The combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to column chromatography over NEt_3-pretreated short silica gel column to afford the corresponding alkoxy-substituted enyne oxirane products as colorless oil (hexane-EtOAc, yields: (*Z*)-**1d**, 85%; (*Z*)-**1e**, 84%; (*Z*)-**1f**, 87%; (*Z*)-**1g**, 90%; (*Z*)-**1h**, 90%; (*Z*)-**1i**, 85%; (*Z*)-**1j**, 87%; (*Z*)-**1k**, 83%, (*Z*)-**1l**, 79%,) (Caldentey, *et al.* 2011).

3.2.5. Synthesis of (*Z*)-1m and (*Z*)-1n

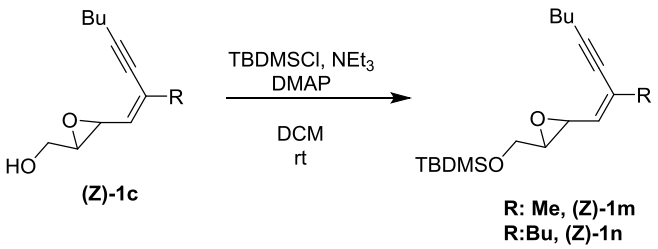


Figure 3.6. Synthesis of **(*Z*)-1m** and **(*Z*)-1n**

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

3.2.6. Synthesis of *(Z)*-1o

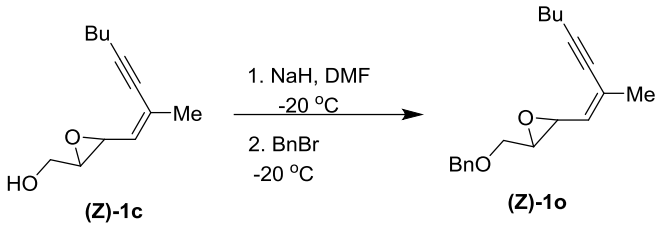


Figure 3.7. Synthesis of **(Z)-1o**

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 (Z)-**1c**) at -20 °C. The mixture was stirred for further 30 min before the addition of methyl iodide (1.2 eq). The mixture was stirred for 4 h at the same temperature and then the reaction was terminated by the addition of MeOH (5 mL) and brine (5 mL), and extracted with DCM. The combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to column chromatography over NEt_3-pretreated short silica gel column to afford the corresponding alkoxy-substituted enyne oxirane products as colorless oil (hexane-EtOAc, yields: (*Z*)-**1o**, 83%).

3.2.7. Synthesis of (*Z*)-1p

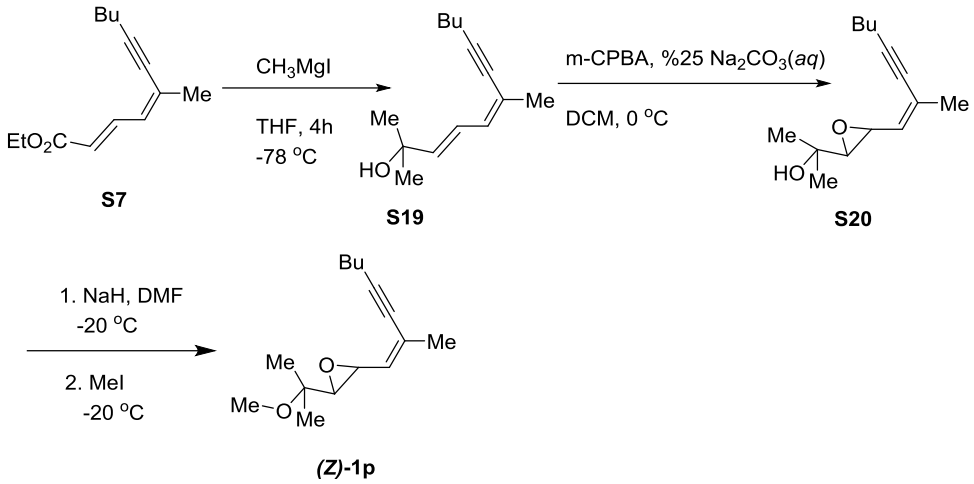


Figure 3.8. Synthesis of **(*Z*)-1p**

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

The epoxidation of **S19** (412 mg, 2 mmol), -and isolation of the product **S20** was performed as specified for **(Z)-1a** (hexane-EtOAc, yield: 0.27 g, 60%).

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

3.2.8. Synthesis of (*Z*)-1r

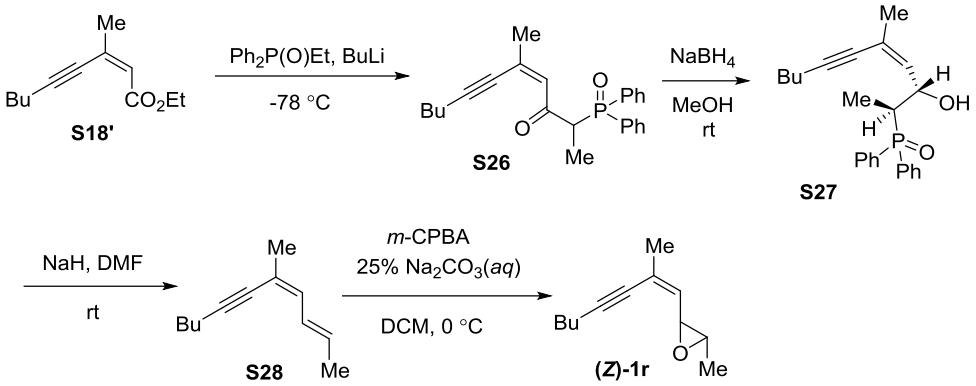


Figure 3.9. Synthesis of **(*Z*)-1r**

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. The saturated NH_4Cl(*aq*) solution was added and subsequently its THF content was removed under reduced pressure. The aqueous residue was diluted with brine (20 mL) and extracted with DCM. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product **S26** was purified by column chromatography on silica gel (hexane-EtOAc, yield: 1.9 g, 25%), (Buss, *et al.* 1985).

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

To a stirred solution of **S27** (1.31 g, 3.45 mmol) in DMF (50 ml) was added NaH (60% dispersion in oil; 138 mg, 3.45 mmol) in one portion at ambient temperature and

stirred for a further 3 h. The reaction was quenched by the addition 25 mL of water and 15 mL of brine and subsequently extracted with Et_2O. The combined extracts were washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product **S28** was purified by column chromatography on silica gel (hexane, yield: 330 mg, 59%), (Buss, *et al.* 1985). The epoxidation of **S28** (162 mg, 1 mmol) and isolation of the product (*Z*)-**1r** was performed (Hexane-EtOAc, yield: 35.6 mg, 20%).

3.2.9. Synthesis of (*Z*)-1s

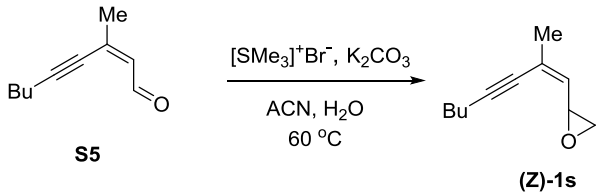


Figure 3.10. Synthesis of **(*Z*)-1s**

A mixture of 3 mmol (471 mg) trimethylsulfonium bromide, 12 mmol (1.65 g) of K_2CO_3 and 0.48 mmol (8.64 mg) H_2O in 5 ml of acetonitrile was stirred for 5 min at 60 ^oC. With vigorous stirring, a solution of 2 mmol (300 mg) **S5** in 3 ml of acetonitrile was added dropwise and stirred for further 2h at 60 ^oC. 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 vacuo. The crude mixture was chromatographed on NEt_3-pretreated short silica gel column which afforded the enyne oxirane (*Z*)-**1s** as a colorless oil (hexane-EtOAc, yield: 82 mg, 25%) (Corey and Chaykovsky, 1965).

3.2.10. Synthesis of (*Z*)-1t

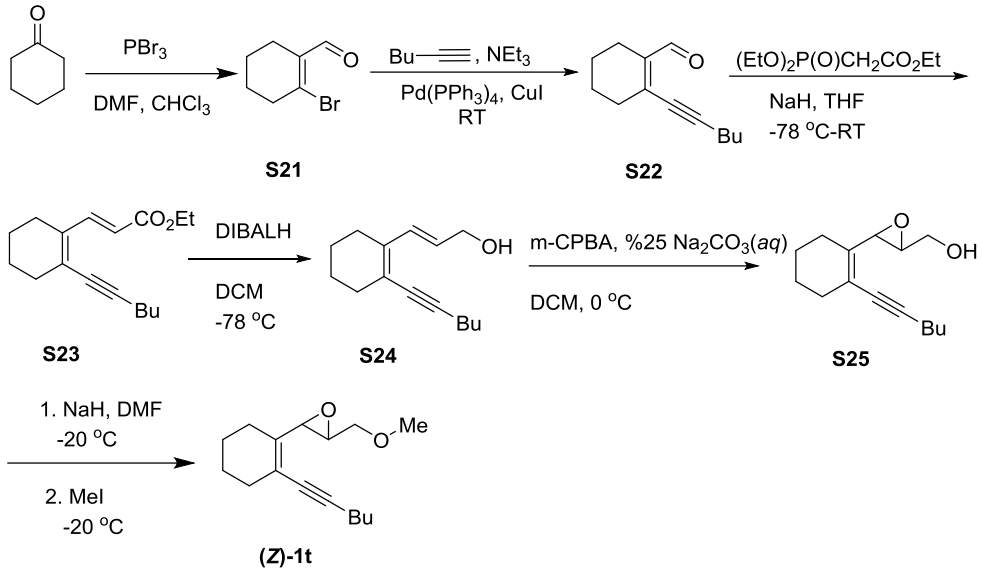


Figure 3.11. Synthesis of **(*Z*)-1t**

PBr_3 (1.4 mL, 13.8 mmol) was added dropwise to a mixture of DMF (1.2 mL, 15.3 mmol) and chloroform (10 mL) at 0 °C and then the resulting mixture was stirred for 1 h. Subsequently, 0.5 g of cyclohexanone (6 mmol) was added dropwise and stirred for 8 h, at RT. The reaction was terminated with water, neutralized with the addition of solid $NaHCO_3$, and extracted with DCM. The extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The purification on short silica gel column provided the compound **S21** (hexane-EtOAc, 0.92 g, 81%), (Lian, *et al.* 2006).

A mixture of **S21** (945 mg, 5 mmol), $Pd(PPh_3)_4$ (123 mg, 0.1 mmol, 2 mol % of Pd), and CuI (21 mg, 0.1 mmol, 2 mmol % of Cu) in 10 mL of Et_3N was stirred for 10 min at RT followed by the addition of 1-hexyne (0.5 g, 6 mmol). After being stirred for 3 h, at RT, water was added and extracted with Et_2O. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain endocyclic enyne aldehyde **S22** (hexane-EtOAc, 0.84 g, 90%), (Lian, *et al.* 2006).

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

3.2.11. Synthesis of (*Z*)-1v

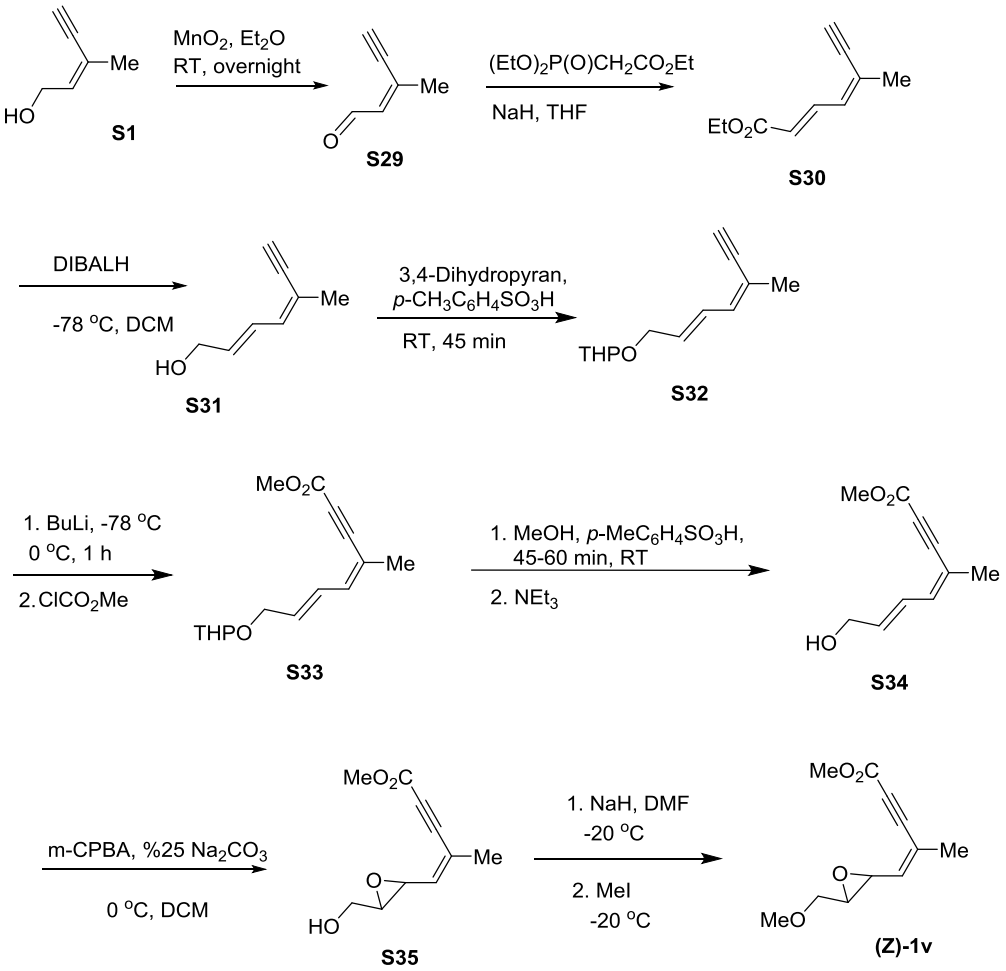


Figure 3.12. Synthesis of **(Z)-1v**

To the solution of **S1** (50 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 (**S29**) was used in the next step (Betzer, *et al.* 1997).

To a solution of NaH (1.1 eq) in THF (2.5 mL/mmol) was added triethyl phosphonoacetate (1.2 eq) at 0 ^oC and the mixture stirred for 1 h, at RT. Subsequently, to the reaction mixture was added **S29** (~50 mmol) dropwise at -78 ^oC, and stirred for 1 h, at RT. The reaction was terminated by the addition of saturated NH_4Cl(*aq*) and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to obtain **S30** with *E/Z* isomeric ratio 95:5 (Urabe, *et al.* 1997). The crude mixture was purified on silica gel column (hexane-EtOAc) to obtain **S30** in pure isomeric form (%74 yield).

A DIBALH (~3 eq, 1.0 M in cyclohexane) solution was added dropwise to the solution of **S30** in DCM (~6 mL/mmol **S30**) at –78 ^oC. After the reaction mixture was stirred for 4 h at the same temperature, 1 M HCl(*aq*) solution was added before extracting with DCM. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was subjected to silica gel column chromatography to purify the corresponding **S31** compound (hexane-EtOAc; yields of **S31** %70).

To the mixture **S31** (1.92 g, 20 mmol) and 3,4-dihydropyran (2.2 mL, 24 mmol) was added *p*-toluenesulfonic acid (44 mg, 0.02 mmol) and then stirred for 45 min at room temperature (RT). Then, the mixture was diluted with 40 mL of dry THF under Ar and cooled to -78 °C. At that temperature, 24 mmol of *n*-BuLi (1.6 M in hexane, 15 mL) was added dropwise via a syringe. After stirring the reaction mixture for 1 h at 0 °C, methyl chloroformate (40 mmol) was added and the mixture was stirred for overnight at room temperature. The reaction was quenched by the addition of saturated NH_4Cl*(aq)* solution and the reaction solution was extracted with Et_2O. The organic phase was washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was used in the following step without any further purification (Betzer, *et al.* 1997).

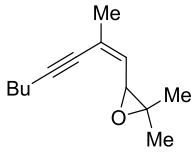
To a solution of the preceding crude compound (**S33**) in methanol (60 mL) *p*-toluenesulfonic acid (1.2 g, 6 mmol) was added and the resulting solution was stirred at RT for 45-60 min. Then, triethylamine was added (1.8 mL), and the solution was concentrated under reduced pressure. The mixture was 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 **S34** (hexane-EtOAc, yield: 2.43 g, 80%), (Ukai, *et al.* 1974).

Further successive synthetic procedures; which involved the epoxidation of **S34** (360 mg, 2 mmol) to **S35** (195 mg, 50% yield), and finally methyl derivatization of hydroxyl group of **S35** (195 mg, 1.0 mmol) to obtain (*Z*)-**1v** (190 mg, 90%) were all conducted as described above.

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

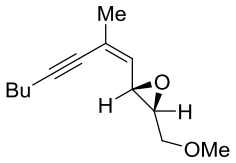
Synthesis of (*E*)-**1b** was performed starting from (*E*)-configured **S1** following the same method employed for the synthesis of (*Z*)-**1b**. Yields: (R^1= Bu, R^2= Me): (*E*)-**S7**, 1.12 g, 79%; (*E*)-**S17**, 0.83 g, 91%; (produced from 4.6 mmol of (*E*)-**S8**), 0.43 g, 47%; (*E*)-**1b** (produced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

3.3. Characterization of Substrates



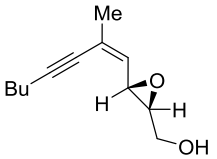
(Z)-**1a**

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



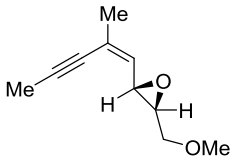
(Z)-**1b**

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



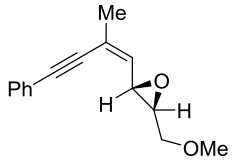
(Z)-**1c**

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



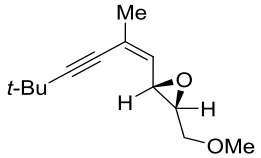
(Z)-**1d**

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



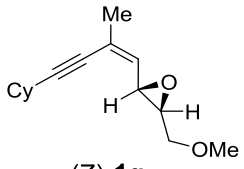
(Z)-**1e**

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



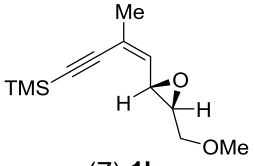
(Z)-**1f**

(*Z*)-1f: ^{1}H NMR (400 MHz, C_6D_6) δ: 5.12 (dd, *J*= 8.5, 1.3 Hz, 1H), 3.95 (dd, *J*= 8.5, 2.3 Hz, 1H), 3.34 (dd, *J*= 11.5, 3.1 Hz, 1H), 3.16 (dd, *J*= 11.5, 5.5 Hz, 1H), 3.09 (s, 3H), 2.90 (ddd, *J*= 5.5, 3.1, 2.3 Hz, 1H), 1.68 (d, *J*= 1.3 Hz, 3H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ: 132.8, 124.5, 103.4, 77.7, 72.4, 58.5, 58.0, 53.7, 30.6, 27.9, 23.4.



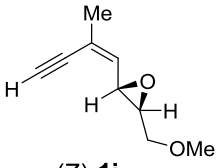
(Z)-**1g**

(*Z*)-1g: ^{1}H NMR (400 MHz, C_6D_6) δ: 5.14 (dq, *J*= 9.0, 1.4 Hz, 1H), 4.01 (dd, *J*= 9.0, 2.0 Hz, 1H), 3.35 (dd, *J*= 11.3, 3.2 Hz, 1H), 3.16 (dd, *J*= 11.3, 5.5 Hz, 1H), 3.09 (s, 3H), 2.91 (ddd, *J*= 5.5, 3.2, 2.0 Hz, 1H), 2.34 (m, 1H), 1.71 (d, *J*= 1.4 Hz, 3H), 1.66-1.03 (m, 10H); ^{13}C NMR (100 MHz, C_6D_6) δ: 132.7, 124.7, 99.5, 79.2, 72.4, 58.5, 58.1, 53.7, 32.5, 32.4, 29.6, 25.7, 24.6, 23.5.



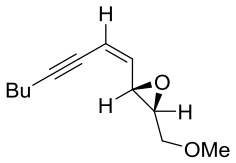
(Z)-**1h**

(*Z*)-1h: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.33 (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), 3.40 (s, 3H), 3.03-3.01 (m, 1H), 1.92 (d, *J*= 0.8 Hz, 3H), 0.02 (s, 9H) ^{13}C NMR: (100 MHz, $CDCl_3$) δ: 133.8, 129.6, 100.2, 95.5, 62.8, 61.4, 60.3, 54.1, 21.9, 0.1.



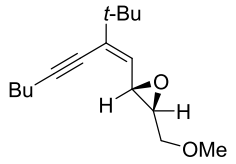
(Z)-**1i**

(*Z*)-1i: ^{1}H NMR (400 MHz, C_6D_6) δ: 5.10 (dq, *J*= 8.9, 1.0 Hz, 1H), 3.84 (dd, *J*= 8.9, 2.0 Hz, 1H), 3.25 (dd, *J*= 11.5, 3.0 Hz, 1H), 3.06-2.99 (m, 1H), 3.05 (s, 3H), 2.83 (ddd, *J*= 5.5, 3.0, 2.0 Hz, 1H), 2.74 (s, 1H), 1.57 (d, *J*= 1.0 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ: 136.0, 122.9, 82.4, 81.5, 72.2, 58.4, 58.0, 53.2, 22.7.



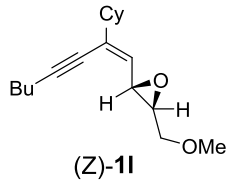
(Z)-**1j**

(*Z*)-1j: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.75 (dtd, *J*= 10.8, 2.4, 0.8 Hz, 1H), 5.44 (dd, *J*= 10.8, 8.8 Hz, 1H), 3.80 (dd, *J*= 8.8, 2.2 Hz, 1H), 3.74 (dd, *J*= 11.2, 2.8 Hz, 1H), 3.44-3.38 (m, 1H), 3.41 (s, 3H), 3.11 (dt, *J*= 5.4, 2.6 Hz, 1H), 2.36 (td, *J*= 6.8, 2.3 Hz, 2H), 1.58-1.41 (m, 4H), 0.92 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2, 115.4, 97.1, 72.3, 59.2, 58.2, 53.3, 50.4, 30.6, 21.9, 19.2, 13.5.



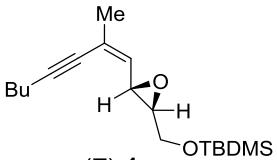
(Z)-**1k**

(*Z*)-1k: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.24 (d, *J*= 8.9 Hz, 1H), 3.81 (dd, *J*= 8.9, 2.4 Hz, 1H), 3.74 (dd, *J*= 11.2, 3.1 Hz, 1H), 3.42-3.38 (m, 1H), 3.41 (s, 3H), 3.10 (ddd, *J*= 5.6, 3.1, 2.4 Hz, 1H), 2.39 (t, *J*= 7.2 Hz, 2H), 1.59-1.41 (m, 4H), 1.11 (s, 9H), 0.93 (t, *J*= 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.2, 127.4, 97.4, 72.7, 59.2, 58.5, 54.7, 36.1, 30.8, 28.9, 21.9, 19.2, 13.6.



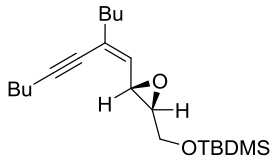
(Z)-**1l**

(*Z*)-1l: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.21 (d, *J*= 8.7 Hz, 1H), 3.77 (dd, *J*= 8.7, 2.4 Hz, 1H), 3.72 (dd, *J*= 11.5, 3.1 Hz, 1H), 3.38 (dd, *J*= 11.5, 5.7 Hz, 1H), 3.40 (s, 3H), 3.07 (dt, *J*= 5.7, 2.4 Hz, 1H), 2.37 (t, *J*= 7.2 Hz, 2H), 2.02-1.97 (m, 1H), 1.76-1.20 (m, 14H), 0.92 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.3, 129.1, 97.0, 76.7, 72.6, 59.2, 58.5, 54.3, 45.4, 31.7, 31.6, 30.8, 29.7, 26.2, 26.0, 22.0, 19.2, 13,6.



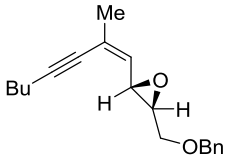
(Z)-**1m**

(*Z*)-1m: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.22 (dd, *J*= 9.1, 1.5 Hz, 1H), 3.86 (dd, *J*= 12.1, 3.2 Hz, 1H), 3.76 (dd, *J*= 9.1, 2.4 Hz, 1H), 3.71 (dd, *J*= 12.1, 4.8 Hz, 1H), 3.00 (ddd, *J*= 4.8, 3.2, 2.4 Hz, 1H), 2.33 (t, *J*= 7.2 Hz, 2H), 1.86 (d, *J*= 1.5 Hz, 3H), 1.56-1.37 (m, 4H), 0.91 (t, *J*= 6.8 Hz, 3H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.9, 125.3, 95.7, 78.7, 63.0, 60.1, 54.3, 30.8, 25.8, 23.8, 22.0, 19.1, 18.3, 13.6, -5.3, -5.4.



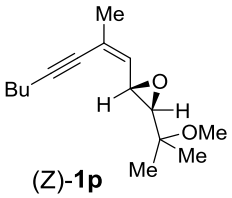
(Z)-**1n**

(*Z*)-1n: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.23 (d, J= 9.4 Hz, 1H), 3.89 (dd, J=12.1, 3.1 Hz, 1H), 3.80 (dd, J= 9.0, 2.3 Hz, 1H), 3.71 (dd, J=11.9, 4.5 Hz, 1H), 3.02 (dt, J=4.8, 2.5 Hz, 1H), 2.35 (t, J=7.0 Hz, 2H), 2.12 (t, J=7.4 Hz, 2H), 1.54-1.38 (m, 6H), 1.35-1.26 (m, 2H), 0.93 (t, J=7.6 Hz, 3H), 0.91 (s, 9H), 0.90 (t, J= 7.4 Hz, 3H), 0.09 (s, 6H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ: 131.2, 130.4, 96.2, 78.0, 63.1, 60.2, 54.3, 37.3, 30.8, 30.2, 25.8, 22.0, 19.2, 18.3, 13.9, 13.6, -5.3.



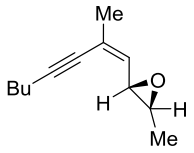
(Z)-**1o**

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



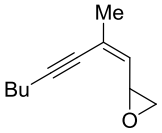
(Z)-**1p**

(*Z*)-1p: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.24 (dd, *J*= 8.9, 1.5 Hz, 1H), 3.69 (dd, *J*= 8.9, 2.3 Hz, 1H), 3.29 (s, 3H), 2.87 (d, *J*= 2.3 Hz, 1H), 2.36 (t, *J*= 6.7 Hz, 2H), 1.87 (d, *J*= 1.5 Hz, 3H), 1.56-1.39 (m, 4H), 1.18 (s, 3H), 1.15 (s, 3H), 0.92 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.2, 125.3, 95.8, 79.0, 74.0, 64.9, 53.4, 50.9, 30.9, 23.9, 22.4, 22.0, 21.1, 19.2, 13.7.



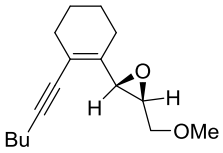
(Z)-**1r**

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



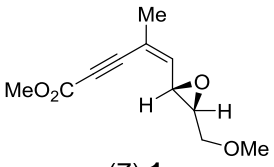
(Z)-**1s**

(*Z*)-1s: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.18 (dd, J=9.0, 1.6 Hz, 1H), 3.84 (ddd, J=9.0, 4.3, 2.7 Hz, 1H), 3.00 (dd, J=5.1, 4.3 Hz, 1H), 2.67 (dd, J=5.1, 2.7 Hz, 1H), 2.36 (t, J=7.2 Hz, 2H), 1.88 (d, J=1.6 Hz, 3H), 1.58-1.50 (m, 2H), 1.48-1.39 (m, 2H), 0.92 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.5, 125.5, 95.7, 78.7, 50.7, 48.7, 30.8, 23.8, 22.0, 19.1, 13.6.



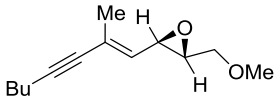
(*Z*)-**1t**

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



(Z)-**1v**

(*Z*)-**1v:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.59 (dq, J= 9.0, 0.8 Hz, 1H), 3.81 (s, 3H), 3.75-3.70 (m, 2H), 3.42 (dd, J=11.6, 6.0 Hz, 1H), 3.41 (s, 3H), 3.14-3.11 (m, 1H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.1, 139.7, 121.7, 84.9, 83.9, 72.2, 59.2, 58.4, 53.5, 52.8, 22.3.



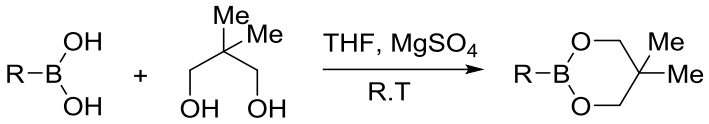
(*E*)-**1b**

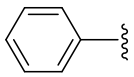
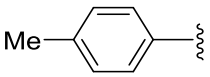
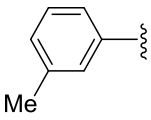
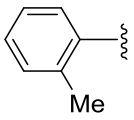
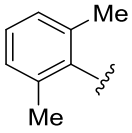
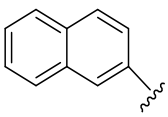
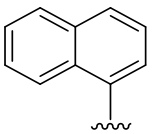
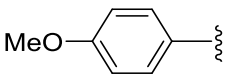
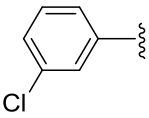
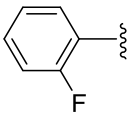
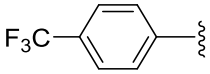
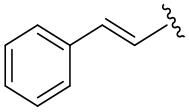
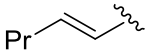
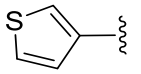
(*E*)-1b: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.35 (dd, *J*= 9.0, 1.0 Hz, 1H), 3.67 (dd, *J*= 11.3, 3.0 Hz, 1H), 3.48 (dd, *J*= 9.0, 2.2 Hz, 1H), 3.44 (dd, *J*= 11.3, 5.1 Hz, 1H), 3.38 (s, 3H), 3.06 (ddd, *J*= 5.1, 3.0, 2.2 Hz, 1H), 2.28 (t, *J*= 6.8 Hz, 2H), 1.93 (d, *J*= 1.0 Hz, 3H), 1.54-1.37 (m, 4H), 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. Synthesis of Organoborons

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

Table 3.1. Synthesis of neopentyl glycol esters

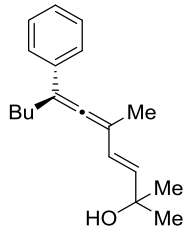


R (yield%)				
				
2a (91%)	**2b** (89%)	**2c** (85%)	**2d** (87%)	**2e** (71%)
				
2f (90%)	**2g** (82%)	**2h** (90%)	**2i** (87%)	**2j** (76%)
				
2k (75%)	**2l** (97%)	**2m** (90%)	**2n** (80%)	

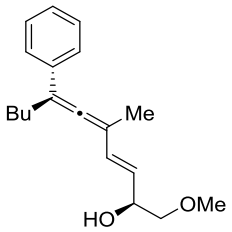
3.5. General Method for Palladium-Catalyzed Reactions of Enyne Oxiranes

The catalyst, the ligand, and the dry solvent (half of the volume necessary for the reaction) were added successively in to the schlenk flask which was dried in oven and cooled under Ar gas and mixture was stirred for 15 min. at 25 ^{o}C. Then, organoboron (3 equivalent), the solution of epoxide compound (0.1 mmol) in dry solvent (other half volume), base and prescribed amount of degassed water was added successively to the schlenk flask and the mixture was stirred in water or oil bath. The reaction was controlled with help of TLC. When the reaction was over, the mixture was concentrated under reduced pressure. The residue was purified using silica gel on column chromatography. In part of the optimization studies the crude product was filtered through a short silica gel column washed with Et_2O and evaporated under reduced atmosphere. The residue was analyzed by ^{1}H NMR using *p*-anisaldehyde as the internal standard.

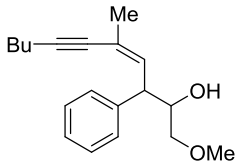
3.6. Characterization of Products



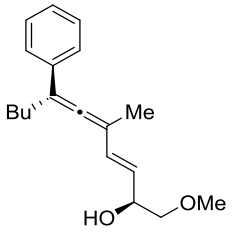
3aa: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.15 (m, 5H), 6.21 (dd, J= 16.0, 2.4 Hz, 1H), 5.74 (dd, J= 15.6, 2.4 Hz, 1H), 2.43 (t, J= 7.6, 2H), 1.89 (s, 3H), 1.51-1.36 (m, 10H), 0.9 (t, J= 8.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.9, 137.2, 136.1, 129.6, 128.3, 126.5, 126.2, 125.4, 120.7, 115.3, 105.1, 102.4, 71.1, 30.0, 29.9, 29.8, 22.4, 15.5, 13.9.; MS (EI, *m/z*): 270 (<5, M^+), 252(6), 195(10), 165(12), 153(15), 141(40), 128(23), 115(35), 91(62), 77(50), 59(100); HRMS (ESI, $C_{19}H_{26}O$ ($(M-H_2O)H)^+$): 253.19508 (calculated); 253.19524 (found). FTIR (ν_{max}/cm^{-1}): 3356, 2923, 1609, 1362, 1142, 974, 763, 692.



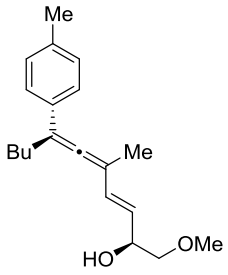
3ba: ^{1}H NMR (400 MHz , C_6D_6): δ 7.43 (dd, J=8.8, 1.6 Hz, 2H), 7.18 (t, J=7.2 Hz, 2H), 7.06 (t, J=8.0 Hz, 1H), 6.55 (dd, J=15.6, 1.6 Hz, 1H), 5.63 (dd, J=16.0, 5.9 Hz, 1H), 4.35-4.31 (m, 1H), 3.14 (dd, A of ABX, JAB = 9.6 Hz, JAX = 3.8 Hz, 1H), 3.11 (dd, B of ABX, JAB = 9.6 Hz, JBX = 8.3 Hz, 1H), 3.01 (s, 3H), 2.40 (t, J=7.2 Hz, 2H), 1.86 (s, 3H), 1.55-1.48 (m, 2H), 1.37-1.28 (m, 2H), 0.86 (t, J=7.6 Hz, 3H, minor), 0.85 (t, J=7.6 Hz, 3H, major). ^{13}C NMR (100 MHz, C_6D_6): δ 208.8, 138.0, 130.4, 129.1, 128.5, 127.3, 127.1, 106.3, 103.4, 77.5, 71.7, 59.0, 30.8, 30.7, 23.1, 15.9, 14.5. MS (EI, *m/z*): 286 (8, M^+), 236(8), 198(15), 169(40), 129(45), 115(52), 91(100), 77(88), 56(84) HRMS (EI) $C_{19}H_{26}O_2$ [$(M+H]^+$, 287.20056 (calculated); 287.20079 (found). FTIR (ν_{max}/cm^{-1})**:** 3426, 2938, 1923, 1455, 1198, 1126, 968, 770, 697. m.p. 46.4-47.8 ºC.



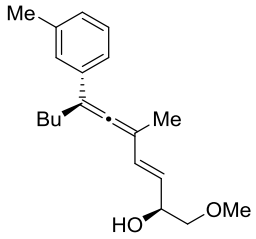
4ba: ^{1}H NMR (400 MHz , $CDCl_3$): δ 7.36-7.21 (M, 5H), 5.74 (d, J= 10.2 Hz, 1H), 4.08 (t, J= 8.4 Hz, 1H), 3.95 (t, J= 9.6 Hz, 1H), 3.54 (dd, J=9.8, 2.7 Hz, 1H), 3.39-3.30 (m, 4H), 2.38 (t, J= 7.2 Hz, 2H), 1.82 (d, J= 1.2 Hz, 3H), 1.55-1.44 (m, 4H), 0.95 (t, J= 7.2 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 134.7, 128.7, 128.3, 126.7, 120.2, 94.9, 79.5, 75.2, 73.0, 59.1, 50.5, 30.9, 23.7, 22.0, 19.2, 13.6.



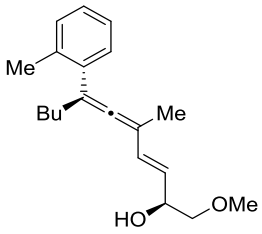
3ba': ^{1}H NMR (400 MHz, C_6D_6): δ 7.46 - 7.40 (m, 2 H), 7.22 - 7.16 (m, 2 H), 7.10 - 7.03 (m, 1 H), 6.55 (dd, *J*=15.8, 1.4 Hz, 1 H), 5.63 (dd, *J*=15.8, 5.9 Hz, 1 H), 4.35 - 4.28 (m, 1 H), 3.15 (dd, A of ABX, JAB = 9.4 Hz, JAX = 4.3 Hz, 1H), 3.08 (dd, B of ABX, JAB = 9.4 Hz, JBX = 7.8 Hz, 1H), 3.00 (d, *J*=0.8 Hz, 3 H, Major), 3.01 (d, *J*=0.8 Hz, 3 H, Minor), 2.39 (t, *J*=7.1 Hz, 2 H, Major), 2.40 (t, *J*=7.1 Hz, 2 H, Minor), 2.19 (br. s, 1 H), 1.86 (s, 3 H), 1.58 - 1.46 (m, 2 H), 1.33 (m, 2 H), 0.86 (t, *J*=7.1 Hz, 3 H, Major), 0.85 (t, *J*=7.1 Hz, 3 H, Minor); ^{13}C NMR (101 MHz, C_6D_6): δ 208.1, 137.2, 129.7, 128.3, 128.2, 126.6, 126.33, 105.6, 102.66, 76.69, 70.91, 58.19, 30.07, 29.99, 22.40, 15.16, 13.8. MS (EI, *m/z*): 286 (<5, M^+), 241(20), 223(25), 199(30), 181(45), 169(100), 91(70), 77(20), 45(50). HRMS (EI) $C_{19}H_{26}O_2$ [$(M+H)^+$, 287.20056 (calculated); 287.20079 (found). FTIR (ν_{max}/cm^{-1})**:** 3428, 2931, 2163, 1925, 1438, 1115, 973, 761, 692.



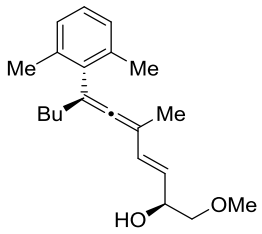
3bb: ^{1}H NMR (400 MHz, C_6D_6): δ 7.41 (d, J=8.2 Hz, 2H), 7.05 (d, J=7.8 Hz, 2H), 6.56 (dd, J=15.8, 1.0 Hz, 1H), 5.63 (dd, J=15.8, 6.1 Hz, 1H), 4.34-4.28 (m, 1H), 3.14 (dd, A of ABX, JAB = 9.4 Hz, JAX = 8.2 Hz, 1H), 3.10 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.5 Hz, 1H), 3.00 (s, 3H, major), 2.98 (s, 3H, minor), 2.43 (t, J=8 Hz, 2H), 2.14 (s, 3H), 1.87 (s, 3H), 1.54 (q, J=8 Hz, 2H), 1.37-1.30 (m, 2H), 0.87 (t, J=7.6 Hz, 3H, minor), 0.86 (t, J=7.6 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 208.6, 136.8, 135.1, 130.7, 129.8, 127.1, 106.2, 103.3, 77.5, 71.7, 58.9, 30.9, 30.6, 23.2, 21.4, 16.0, 14.5. MS (EI, *m/z*): 300 (15, M^+), 282(5), 225(30), 193(30), 155(50), 141(30), 105(20), 91(15), 44(100). HRMS (EI) $C_{20}H_{28}O_2$ [$(M+Na)^+$, 323.19815 (calculated); 323.19834 (found). FTIR (ν_{max}/cm^{-1}): 3444, 2923, 1523, 1441, 1197, 1123, 961, 831, 603.



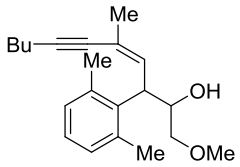
3bc: ^{1}H NMR (400 MHz, C_6D_6): δ 7.36 (s, 1H), 7.31 (d, J=7.8 Hz, 1J), 7.17-7.13 (m, 1H), 6.92 (dt, J=7.4, 0.8 Hz, 1H), 6.58 (dd, J=15.8, 1.4 Hz, 1H), 5.63 (dd, J=16.0, 5.6 Hz, 1H), 4.34-4.30 (m, 1H), 3.13 (dd, A of ABX, JAB = 9.4 Hz, JAX = 7.8 Hz, 1H), 3.10 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.6 Hz, 1H), 3.00 (s, 3H), 2.45 (t, J= 6.4 Hz, 2H, minor), 2.44 (t, J= 6.4 Hz, 2H, major), 2.27 (bs, 1H), 2.14 (s, 3H, major), 2.13 (s, 3H, minor), 1.88 (s, 3H), 1.59-1.51 (m, 2H), 1.40-1.30 (m, 2H), 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 208.8, 138.4, 138.0, 130.6, 129.1, 128.5, 128.2, 127.8, 124.3, 106.4, 103.2, 77.5, 71.7, 58.9, 30.9, 30.8, 23.2, 21.9, 16.0, 14.5. MS (EI, *m/z*): 300 (5, M^+), 237(15), 195(40), 183(85), 143(45), 105(100), 91(40), 77(25), 45(40). HRMS (EI) $C_{20}H_{28}O_2$ [$(M+H)^+$, 301.21621 (calculated); 301.21639 (found). FTIR (ν_{max}/cm^{-1}): 3435, 2922, 1606, 1470, 1258, 1107, 956, 797, 699.



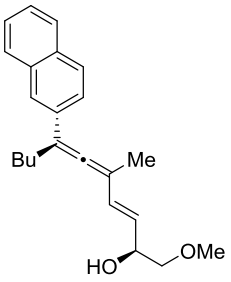
3bd: ^{1}H NMR (400 MHz, C_6D_6): δ 7.26 (d, J=6.7 Hz, 1H), 7.11-7.04 (m, 3H), 6.58 (dd, J=15.6, 1.6 Hz, 1H), 5.54 (dd, J=15.7, 5.9 Hz, 1H), 4.34-4.29 (m, 1H), 3.13 (dd, A of ABX, JAB = 9.4 Hz, JAX = 7.7 Hz, 1H), 3.09 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.7 Hz, 1H), 3.00 (s, 3H, major), 3.00 (s, 3H, minor), 2.35 (s, 3H), 2.33 (td, J=7.2, 2.8 Hz, 2H), 1.8 (s, 3H), 1.50-1.42 (m, 2H), 1.36-1.26 (m, 2H), 0.85 (t, J=7.2 Hz, 3H, minor), 0.84 (t, J=7.2 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 206.9, 138.6, 136.3, 131.2, 130.9, 128.8, 127.9, 127.5, 126.6, 104.9, 100.5, 77.5, 71.6, 58.9, 34.7, 30.7, 23.1, 21.2, 16.0, 14.5. MS (EI, *m/z*): 300 (20, M^+), 282(5), 225(30), 193(30), 155(50), 141(30), 105(20), 91(15), 44(100). HRMS (EI) $C_{20}H_{28}O_2$ [$(M+Na)^+$, 323.19815 (calculated); 323.19835 (found). FTIR (ν_{max}/cm^{-1}): 3413, 2922, 1449, 1190, 1142, 959, 756, 728.



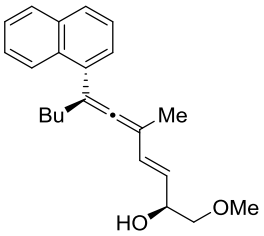
3be: ^{1}H NMR (400 MHz, C_6D_6): δ 7.06-6.96 (m, 3H), 6.65 (d, J=15.6 Hz, 1H, major), 6.63 (d, J=15.6 Hz, 1H, minor), 5.52 (ddd, 15.9, 5.9, 1.8 Hz, 1H), 4.35-4.31 (m, 1H), 3.13 (dd, A of ABX, JAB = 9.2 Hz, JAX = 7.8 Hz, 1H), 3.08 (dd, B of ABX, JAB = 9.2 Hz, JBX = 3.5 Hz, 1H), 3.00 (s, 3H), 2.34 (s, 6H), 2.13-2.07 (m, 2H), 1.77 (s, 3H), 1.55-1.48 (m, 2H), 1.37-1.26 (m, 2H), 0.85 (t, J=7.2 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 204.8, 138.9, 136.0, 130.7, 128.3, 127.7, 127.5, 104.1, 100.8, 77.5, 71.6, 58.9, 34.1, 30.8 (minor), 30.5 (major), 23.3, 20.8, 15.7, 14.6. MS (EI, *m/z*): 314 (50, M^+), 269(60), 197(45), 157(30), 119(55), 45(100). HRMS (EI) $C_{21}H_{30}O_2$ [$(M+H)^+$, 315.23186 (calculated); 315.23200 (found). FTIR (ν_{max}/cm^{-1}): 3421, 2944, 1470, 1386, 1190, 1129, 956, 760.



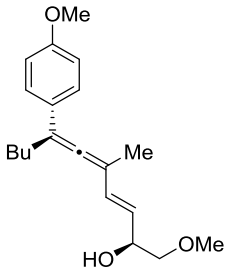
4be: ^{1}H NMR (400 MHz, C_6D_6): δ 7.00-6.96 (m, 3H), 6.35 (d, J=8.2 Hz, 1H), 4.69 (t, J=8.6 Hz, 1H), 4.27-4.22 (m, 1H), 3.18 (dd, J=9.4, 2.8 Hz, 1H), 3.14-3.07 (m, 1H), 2.92 (s, 3H, major), 2.91 (s, 3H, minor), 2.50-2.35 (m, 6H), 2.11 (t, J=6.8 Hz, 2H), 1.87 (d, J=0.8 Hz, 3H), 1.34-1.18 (m, 4H), 0.78 (t, J=7.2 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 139.5, 137.1, 128.3, 126.9, 120.8, 95.2, 81.4, 75.3, 73.1, 58.9, 46.7, 31.4, 24.5, 22.6, 20.0, 14.1. MS (EI, *m/z*): 314 (<5, M^+), 269(15), 239(100), 198(55), 183(85), 169(95), 119(40), 55(40). HRMS (EI) $C_{21}H_{30}O_2$ [$(M+H)^+$, 315.23186 (calculated); 315.23202 (found). FTIR (ν_{max}/cm^{-1}): 3451, 2912, 1460, 1391, 1122, 767.



3bf: ^{1}H NMR (400 MHz, C_6D_6): δ 7.84 (s, 1H), 7.72 (dd, J=8.4, 1.6 Hz, 1H), 7.68-7.60 (m, 3H), 7.26 (quind, J=7.1, 1.6 Hz, 2H), 6.62 (dd, J=15.8, 1.4 Hz, 1H), 5.67 (dd, J=15.7, 5.9 Hz, 1H), 4.37-4.33 (m, 1H), 3.15 (dd, A of ABX, JAB = 9.4 Hz, JAX = 7.8 Hz, 1H), 3.12 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.5 Hz, 1H), 3.01 (s, 3H), 2.52 (t, J=7.6 Hz, 2H), 2.35 (bs, 1H), 1.91 (s, 3H), 1.63-1.56 (m, 2H), 1.38 (sext, J=7.6 Hz, 2H), 0.89 (t, J=7.2 Hz, 3H, minor), 0.89 (t, J=7.2 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 209.6, 135.4, 134.7, 133.5, 130.3, 128.8, 128.7, 126.7, 126.5, 126.3, 124.6, 106.6, 103.8, 77.5, 71.7, 59.0, 30.8, 30.7, 23.2, 16.0, 14.6. MS (EI, *m/z*): 336 (15, M^+), 291(30), 261(30), 219(80), 207(55), 165(45), 141(100), 73(50), 45(60). HRMS (EI) $C_{23}H_{28}O_2$ [$(M+Na)^+$, 359.19815 (calculated); 359.19828 (found). FTIR (ν_{max}/cm^{-1}): 3451, 2950, 1449, 1363, 1122, 959, 863, 825, 747.

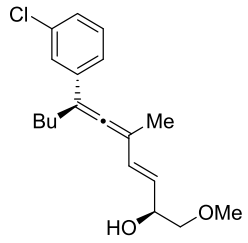


3bg: ^{1}H NMR (400 MHz, C_6D_6): δ 8.39 (d, J=8.6 Hz, 1H), 7.66 (dd, J=8.2, 0.8 Hz, 1H), 7.57 (d, J=8.2 Hz, 1H), 7.41-7.37 (m, 2H), 7.29-7.24 (m, 2H), 6.67 (dd, J=15.8, 1.4 Hz, 1H, major), 6.66 (dd, J=15.8, 1.4 Hz, 1H, minor), 5.54 (dd, J=15.8, 5.7 Hz, 1H), 4.35-4.30 (m, 1H), 3.13 (dd, A of ABX, JAB = 9.4 Hz, JAX = 8.1 Hz, 1H), 3.08 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.7 Hz, 1H), 3.00 (s, 3H, major), 2.99 (s, 3H, minor), 2.47 (td, J=7.5, 1.8 Hz, 2H), 1.84 (s, 3H), 1.52 (quint, J=7.2 Hz, 2H, major), 1.52 (quint, J=7.2 Hz, 2H, minor), 1.33 (sext, J=7.6 Hz, 2H), 0.84 (t, J=7.6 Hz, 3H, minor), 0.83 (t, J=7.6 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 207.3, 135.0, 132.4, 130.8, 129.2, 128.1, 126.6, 126.3, 126.3, 126.3, 126.1, 104.5, 100.7, 77.5, 71.6, 58.9, 35.5, 31.0, 23.1, 16.1, 14.5. MS (EI, *m/z*): 336 (20, M^+), 273(30), 261(55), 229(100), 217(65), 202(80), 165(60), 141(35), 44(95). HRMS (EI) $C_{23}H_{28}O_2$ [$(M+Na)^+$, 359.19815 (calculated); 359.19825 (found). FTIR (ν_{max}/cm^{-1}): 3435, 2922, 1946, 1470, 1206, 1129, 986, 804, 782.

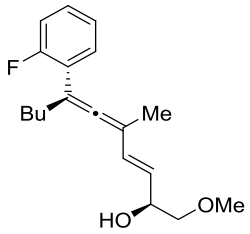


3bh: ^{1}H NMR (400 MHz, C_6D_6): δ 7.38 (d, J=9.2 Hz, 2H), 6.82 (d, J=8.4 Hz, 2H), 6.58 (dd, J= 15.8, 1.4 Hz, 1H), 5.64 (dd, J=15.7, 5.9 Hz, 1H), 4.37-4.32 (m, 1H), 3.33 (s, 3H, major), 3.32 (s, 3H, minor), 3.16 (dd, A of ABX, JAB = 9.4 Hz, JAX = 4.3 Hz, 1H), 3.12 (dd, B of ABX, JAB = 9.4 Hz, JBX = 7.6 Hz, 1H), 3.02 (s, 3H, minor), 3.02 (s, 3H, major), 2.42 (t, J=6.8 Hz, 2H), 1.89 (s, 3H), 1.60-1.51 (m, 2H), 1.40-1.31 (m, 2H), 0.88 (t, J=7.2 Hz, 3H, minor), 0.87 (t, J=7.2 Hz, 3H, major), ^{13}C NMR (101 MHz, C_6D_6): δ 208.4, 130.9, 130.1, 128.2, 128.2, 114.7, 105.9, 103.3, 77.5, 71.7, 59.0, 55.2, 31.0, 30.9, 23.2, 16.1, 14.5. MS (EI, *m/z*): 316 (10, M^+), 259(80), 209(100), 171(95), 121(75), 44(90). HRMS (EI) $C_{20}H_{28}O_3$ [$(M+H)^+$, 317.21112 (calculated); 317.21117 (found). FTIR

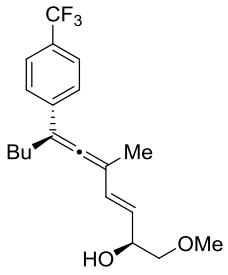
(ν_{max}/cm^{-1})**:** 3444, 2931, 2867, 1925, 1613, 1512, 1454, 1247, 1174, 1120, 1041, 967, 835, 597.



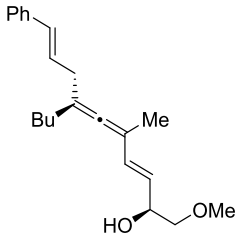
3bi: ^{1}H NMR (400 MHz, C_6D_6): δ 7.53 (t, J=2.0 Hz, 1H), 7.17 (dd, J=1.6, 0.8 Hz, 1H), 7.04 (ddd, J=7.9, 2.1. 1.0 Hz, 1H), 6.87 (t, J=8.0 Hz, 1H, major), 6.86 (t, J=8.0 Hz, 1H, minor), 6.49 (dd, J=15.7, 1.6 Hz, 1H), 5.60 (dd, J=15.7, 5.9 Hz, 1H), 4.32-4.28 (m, 1H), 3.12 (dd, A of ABX, JAB = 9.4 Hz, JAX = 7.7 Hz, 1H), 3.08 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.7 Hz, 1H), 3.00 (s, 3H, minor), 3.00 (s, 3H, major), 2.30 (bs, 1H), 2.22 (t, J=7.6 Hz, 2H), 1.78 (s, 3H), 1.47-1.38 (m, 2H), 1.27 (sext, J= 7.6 Hz, 2H), 0.83 (t, J= 7.2 Hz, 3H, minor), 0.82 (t, J= 7.2 Hz, 3H, minor). ^{13}C NMR (101 MHz, C_6D_6): δ 208.8, 140.2, 135.3, 130.3, 129.7, 129.1, 127.3, 126.9, 125.2 (major), 125.2 (minor), 105.4, 104.0, 77.4, 71.5, 59.0, 30.8 (minor), 30.6 (major), 30.4, 23.0, 15.7, 14.5. MS (EI, *m/z*): 320 (5, M^+), 257(15), 203(45), 165(35), 125(40), 44(100). HRMS (EI) $C_{19}H_{25}FO_2$ [$(M+Na)^+$, 343.14408 (calculated); 343.14387 (found). FTIR (ν_{max}/cm^{-1}): 3406, 2930, 1617, 1480, 1109, 972, 783, 686.



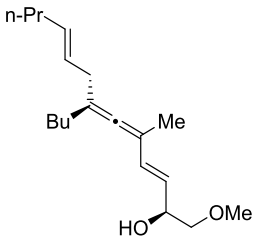
3bj: ^{1}H NMR (400 MHz, C_6D_6): δ 7.25-7.21 (m, 1H), 6.85-6.80 (m, 3H), 6.59 (dd, J=15.8, 1.4 Hz, 1H), 5.59 (dd, J=16, 5.9 Hz, 1H), 4.33-4.29 (m, 1H), 3.13 (dd, A of ABX, JAB = 9.4 Hz, JAX = 8.2 Hz, 1H), 3.09 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.6 Hz, 1H), 3.00 (s, 3H), 2.47 (t, J=7.4 Hz, 2H), 2.30 (bs, 1H), 1.85 (s, 3H), 1.52-1.44 (m, 2H), 1.32 (sext, J=8.0 Hz, 2H), 0.84 (t, J=7.2 Hz, 3H, minor), 0.83 (t, J=7.2 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 209.2, 161.1 (d, J=242 Hz), 130.4 (major), 130.4 (minor), 129.0, 128.9, 128.5, 126.6, 124.6, 116.7 (minor), 116.5 (major), 101.6 (major), 101.4 (minor), 77.4, 71.6, 58.9, 32.8 (major), 32.8 (minor), 30.8, 23.0, 16.0, 14.4. MS (EI, *m/z*): 304 (5, M^+), 259(15), 199(25), 187(60), 133(25), 109(100), 45(35). HRMS (EI) $C_{19}H_{25}FO_2$ [$(M+H)^+$, 305.19113 (calculated); 305.19129 (found). FTIR (ν_{max}/cm^{-1}): 3425, 2923, 1487, 1440, 1196, 1110, 971, 752.



3bk: ^{1}H NMR (400 MHz, C_6D_6): δ 7.37 (d, J=8.2 Hz, 2H), 7.22 (d, J=7.8 Hz, 2H), 6.54 (dd, J=15.7, 1.6 Hz, 1H, major), 6.53 (dd, J=15.7, 1.6 Hz, 1H, minor), 5.64 (dd, J=15.7, 5.5 Hz, 1H, minor), 5.64 (dd, J=15.7, 5.5 Hz, 1H, major), 4.32 (dt, J=3.8, 1.8 Hz, 1H), 3.15 (dd, A of ABX, JAB = 11.8 Hz, JAX = 9.6 Hz, 1H), 3.09 (dd, B of ABX, JAB = 11.8 Hz, JBX = 2.1 Hz, 1H), 3.00 (s, 3H), 2.24 (t, J=7.2 Hz, 2H), 1.82 (s, 3H), 1.48-1.40 (m, 2H), 1.36-1.27 (m, 2H), 0.87 (t, J=7.2 Hz, 3H, minor), 0.88 (t, J=7.2 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 209.3, 141.8, 129.5, 129.2, 129.0, 127.1, 125.9 (q, J=3.8 Hz), 105.5, 104.1, 77.4, 71.5, 59.0, 30.8 (minor), 30.6 (major), 30.4, 23.1, 15.7, 14.5. MS (EI, *m/z*): 354 (<1, M^+), 309(35), 291(30), 267(45), 249(60), 237(90), 159(85), 109(45), 55(40), 45(100). HRMS (EI) $C_{20}H_{25}F_3O_2$ $[(M+H]^+$, 355.1784 (calculated); 355.18810 (found). FTIR (ν_{max}/cm^{-1})**:** 3435, 2941, 2862, 1609, 1326, 1160, 1133, 1071, 833, 612.

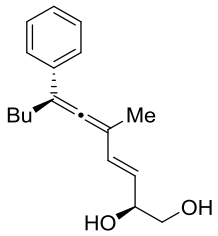


3bl: ^{1}H NMR (400 MHz, C_6D_6): δ 7.27-7.23 (m, 2H), 7.12 (t, J=7.8 Hz, 2H), 7.05-7.02 (m, 1H), 6.83 (d, J=16.4 Hz, 1H, major), 6.81 (d, J=16.4 Hz, 1H, minor), 6.58 (d, J=16.4 Hz, 1H), 6.57 (dd, J=15.8, 0.4 Hz, 1H, major), 6.56 (dd, J=15.8, 0.4 Hz, 1H, minor), 5.64 (ddd, J=16, 5.6, 0.8 Hz, 1H, minor), 5.64 (ddd, J=16, 5.6, 0.8 Hz, 1H, major), 4.36-4.31 (m, 1H), 3.14 (dd, A of ABX, JAB = 9.4 Hz, JAX = 7.7 Hz, 1H), 3.10 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.6 Hz, 1H), 3.00 (s, 3H, minor), 3.00 (s, 3H, major), 2.26 (t, J=7.2 Hz, 2H), 1.86 (s, 3H), 1.57-1.50 (m, 2H), 1.39-1.30 (m, 2H), 0.89 (t, J=7.6 Hz, 3H, minor), 0.88 (t, J=7.6 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 212.4, 138.4, 130.4, 129.2, 127.8, 127.8, 127.0, 106.0, 101.6, 77.4, 71.6, 59.0, 30.6, 29.4, 23.2, 16.1, 14.6. MS (EI, *m/z*): 312(40), 267(35), 223(15), 195(80), 165(60), 115(50), 91(100), 32(60). FTIR (ν_{max}/cm^{-1}): 3435, 2923, 1460, 1142, 957, 753, 693.

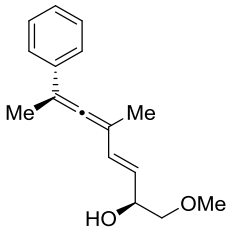


3bm: 1H NMR (400 MHz, C6D6): δ 6.53 (dd, J=15.1, 1.0 Hz, 1H, major), 6.52 (dd, J=15.1, 1.0 Hz, 1H, minor), 6.09 (d, J=16.0 Hz, 1H, major), 6.09 (d, J=16.0 Hz, 1H, minor), 5.65 (dt, J=15.7, 7.0 Hz, 1H), 5.58 (dd, J=15.6, 5.6 Hz, 1H, minor), 5.58 (dd, J=15.6, 5.6 Hz, 1H, major), 4.33-4.29 (m, 1H),), 3.13 (dd, A of ABX, JAB = 9.5 Hz, JAX = 7.8 Hz, 1H), 3.09 (dd, B of ABX, JAB = 9.5 Hz, JBX = 4.0 Hz, 1H), 3.00 (s, 3H, minor), 3.00 (s, 3H, major), 2.20 (t, J=7.2 Hz, 2H), 2.02 (q, J=6.5 Hz, 2H), 1.84 (s, 3H), 1.56-1.48 (m, 2H), 1.39-1.29 (m, 4H), 0.89 (t, J=7.6 Hz, 3H, minor), 0.87 (t, J=7.6 Hz, 3H, major), 0.85 (t, J=7.6 Hz, 3H, major), 0.85 (t, J=7.6 Hz, 3H, minor). 13C NMR (101 MHz, C6D6): δ 210.5, 131.0, 129.6, 128.7, 127.8, 105.3, 101.2, 77.5, 71.6, 58.9, 35.8, 30.7, 29.6, 23.4, 23.3, 16.2, 14.6, 14.3. MS (EI, m/z): 278(10), 233(25), 161(30), 119(45),

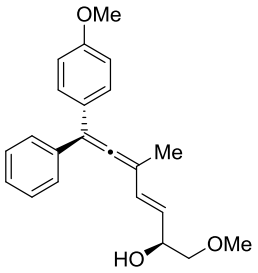
105(100), 93(60), 55(55). HRMS (EI) C19H32O2 [(M+Na]$^+$, 315.23186 (calculated); 315.23202 (found). FTIR (ν_{max}/cm^{-1}): 3442, 2927, 1480, 1261, 1113, 958, 796.



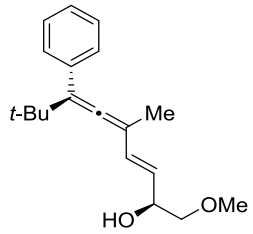
3ca: ^{1}H NMR (400 MHz, C_6D_6): δ 7.45 - 7.42 (m, 2 H), 7.21 - 7.16 (m, 2 H), 7.08-7.04 (m, 1 H), 6.42 (dd, J=15.6, 1.6 Hz, 1H), 5.51 (dd, J= 15.6, 6.4 Hz, 1H, minor), 5.50 (dd, J= 15.6, 6.4 Hz, 1H, major), 4.05-4.02 (m, 1H), 3.40-3.37 (m, 1H), 3.30-3.24 (m, 1H), 2.40 (t, J=7.4 Hz, 2H), 1.82 (d, J= 0.8 Hz, 3H), 1.55-1.48 (m, 2H), 1.38-1.28 (m, 2H), 0.87 (t, J= 7.6 Hz, 3H, minor), 0.86 (t, J= 7.6 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 208.9, 137.9, 130.9, 129.1, 127.4, 127.1, 106.4, 103.3, 73.8, 67.2, 30.8 (minor), 30.8 (major), 30.7, 23.2, 15.9, 14.5. MS (EI, *m/z*): 256(25), 239(27), 112(95), 83(40), 70(75), 57(100), 43(65). HRMS (EI) $C_{18}H_{24}O_2$ [$(M+H)^+$, 273.18491 (calculated); 273.18506 (found). FTIR (ν_{max}/cm^{-1})**:** 3365, 2951, 2920, 2862, 1925, 1597, 1454, 1079, 1031, 967, 750, 698.



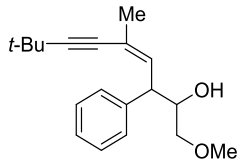
3da: ^{1}H NMR (400 MHz, C_6D_6): δ 7.39 (d, J=8.4 Hz, 2H), 7.16 (t, J=7.6 Hz, 2H), 7.05 (t, J=7.6 Hz, 1H), 6.52 (d, J=15.6 Hz, 1H, minor), 6.51 (d, J=15.6 Hz, 1H, major), 5.63 (ddd, J=15.8, 5.9, 0.8 Hz, 1H), 4.33-4.29 (m, 1H), 3.13 (dd, A of ABX, JAB = 8.7 Hz, JAX = 6.8 Hz, 1H), 3.11 (dd, B of ABX, JAB = 8.7 Hz, JBX = 3.4 Hz, 1H), 3.01 (s, 3H), 2.36 (bs, 1H), 1.98 (s, 3H, minor), 1.97 (s, 3H, major), 1.83 (d, J=0.8 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 208.9, 138.1, 130.4, 129.0, 128.7, 127.3, 126.7, 102.2, 101.0, 77.4, 71.7, 59.0, 17.5, 15.8. MS (EI, *m/z*): 244 (10, M^+), 199(100), 181(35), 166(45), 128(35), 105(20), 91(30), 77(20), 45(25). FTIR (ν_{max}/cm^{-1}): 3432, 2922, 1498, 1449, 1135, 1027, 978, 767, 689, 593.



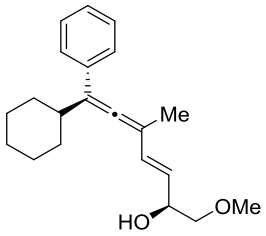
3eh: ^{1}H NMR (400 MHz, C_6D_6): δ 7.52-7.46 (m, 2H), 7.40-7.36 (m, 1H), 7.38 (d, J=8.8 Hz, 1H), 7.18-7.14 (m, 2H), 7.10-7.06 (m, 1H), 6.79-6.75 (m, 1H), 6.77 (d, J=8.4 Hz, 1H), 6.58 (dd, J=15.8, 1.4 Hz, 1H), 5.63 (dd, J=15.7, 5.9 Hz, 1H), 4.30 (q, J=5.6 Hz, 1H), 3.29 (s, 3H, major), 3.29 (s, 3H, minor), 3.11 (dd, A of ABX, JAB = 8.6 Hz, JAX = 5.8 Hz, 1H), 3.08 (dd, B of ABX, JAB = 8.6 Hz, JBX = 2.4 Hz, 1H), 3.00 (s, 3H), 2.31 (bs, 1H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 210.5, 160.0, 138.2, 130.6 (minor), 130.6 (major), 130.0, 129.9, 129.4 (major), 129.4 (minor), 129.2, 129.1, 127.9, 114.7, 110.3, 103.2, 77.4, 71.6, 59.0, 55.2, 16.0. MS (EI, *m/z*): 336 (30, M^+), 291(100), 262(65), 247(40), 183(30), 155(25), 30(25), 45(45). HRMS (EI) $C_{22}H_{24}O_3$ [$(M+H)^+$, 337.17982 (calculated); 337.17992 (found). FTIR (ν_{max}/cm^{-1}): 3432, 2931, 1507, 1267, 1180, 1122, 1036, 978, 834, 767, 700.



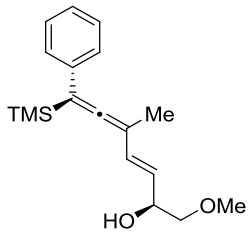
3fa: ^{1}H NMR (400 MHz, C_6D_6): δ 7.30-7.27 (m, 2H), 7.14-7.12 (m, 2H), 7.09-7.05 (m, 1H), 6.59 (dd, J=15.7, 1.2 Hz, 1H, major), 6.57 (dd, J=15.7, 1.2 Hz, 1H, minor), 5.51 (dd, J=16.0, 4.3 Hz, 1H), 4.35-4.31 (m, 1H, major), 4.29-4.25 (m, 1H, minor), 3.13 (dd, A of ABX, JAB = 9.3 Hz, JAX = 8.1 Hz, 1H), 3.08 (dd, B of ABX, JAB = 9.3 Hz, JBX = 3.7 Hz, 1H), 3.00 (s, 3H, major), 2.97 (s, 3H, minor), 2.24 (bs, 1H), 1.77 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 206.1, 138.5, 131.2, 130.2, 128.9, 128.5, 127.7, 127.3, 127.1, 100.9, 77.5, 71.6, 58.9, 35.7, 31.8, 30.5, 16.4. MS (EI, *m/z*): 286 (10, M^+), 241(75), 197(100), 165(35), 141(40), 105(85), 57(95). FTIR (ν_{max}/cm^{-1}): 3422, 2960, 1460, 1199, 1132, 969, 709.



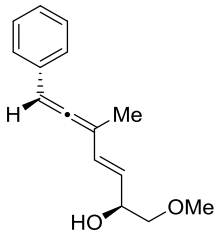
4fa: ^{1}H NMR (400 MHz, C_6D_6): δ 7.40 (d, 7.8 Hz, 2H), 7.20 (d, J=7.6 Hz, 2H), 7.07 (t, J=7.6 Hz, 1H), 6.12 (dd, J=9.6, 1.4 Hz, 1H), 4.26 (dd, J=9.8, 6.0 Hz, 1H), 4.10-4.06 (m, 1H), 3.30 (dd, A of ABX, JAB = 9.4 Hz, JAX = 7.1 Hz, 1H), 3.23 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.4 Hz, 1H), 3.00 (s, 3H), 2.22 (s, 1H), 1.80 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6): δ 143.4, 136.4, 129.1, 128.5, 128.3, 127.0, 121.1, 102.8, 79.7, 75.8, 74.6,59.0, 50.4, 31.6, 28.6, 24.0. MS (EI, *m/z*): 268(5), 212(100), 197(65), 169(65), 155(95), 141(35), 91(55), 41(40). FTIR (ν_{max}/cm^{-1}): 3446, 2910, 1459, 1364, 1117, 1079, 688.



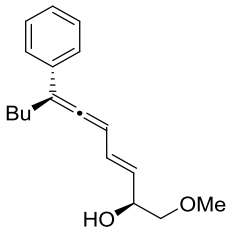
3ga: ^{1}H NMR (400 MHz, C_6D_6): δ 7.43 (d, J=8.2 Hz, 2H), 7.19 (d, J=7.2 Hz, 2H), 7.08-7.04 (m, 1H), 6.57 (d, J=15.7 Hz, 1H, major), 6.56 (d, J=15.7 Hz, 1H, minor), 5.63 (ddd, J=15.7, 5.9, 0.8 Hz, 1H), 4.36-4.32 (m, 1H), 3.15 (dd, A of ABX, JAB = 9.2 Hz, JAX = 7.7 Hz, 1H), 3.11 (dd, B of ABX, JAB = 9.2 Hz, JBX = 3.6 Hz, 1H), 3.01 (s, 3H, major), 2.98 (s, 3H, minor), 1.48-1.41 (m, 1H), 2.34 (bs, 1H), 1.96-1.93 (m, 2H), 1.86 (d, J=0.8 Hz, 3H), 1.72-1.58 (m, 3H), 1.30-1.08 (m, 5H). ^{13}C NMR (101 MHz, C_6D_6): δ 208.6, 137.7, 130.7, 129.1, 128.3, 127.6, 127.3, 112.7, 104.2, 77.5, 71.7, 59.0, 39.3, 33.8, 33.8, 27.3, 27.3, 27.0, 16.1. MS (EI, *m/z*): 312 (10, M^+), 267(70), 181(100), 141(50), 91(80), 45(60). FTIR (ν_{max}/cm^{-1}): 3444, 2923, 2858, 1506, 1458, 1123, 953, 774, 701.



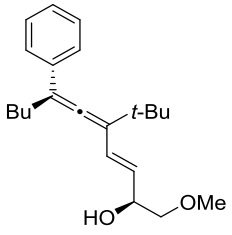
3ha: ^{1}H NMR (400 MHz, C_6D_6): δ 7.41 (d, J=6.8 Hz, 2H, major), 7.41 (d, J=6.8 Hz, 2H, minor), 7.18-7.15 (m, 2H), 7.05 (t, J=6.8 Hz, 1H), 6.56 (dd, J=15.6, 1.6 Hz, 1H, major), 6.54 (dd, J=15.6, 1.6 Hz, 1H, minor), 5.55 (dd, J=15.6, 5.6 Hz, 1H, minor), 5.54 (dd, J=15.6, 5.6 Hz, 1H, major), 4.35-4.31 (m, 1H, major), 4.26-4.21 (m, 1H, minor), 3.13 (dd, A of ABX, JAB = 9.4 Hz, JAX = 8.2 Hz, 1H), 3.09 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.6 Hz, 1H), 3.00 (s, 3H, minor), 3.00 (s, 3H, major), 2.23 (bs, 1H), 1.80 (s, 3H), 0.24 (s, 9H, minor), 0.23 (s, 9H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 212.9, 138.1, 130.1, 129.2, 128.7,127.3 (minor), 127.3 (major), 127.0, 101.3, 97.3, 77.5, 71.7, 58.9, 15.3, 0.6 (minor), 0.2 (major). MS (EI, *m/z*): 302 (M^+), 257(5), 196(10), 140(5), 105(25), 73(100), 45(55). FTIR (ν_{max}/cm^{-1}): 3435, 2934, 1911, 1254, 1134, 845, 698.



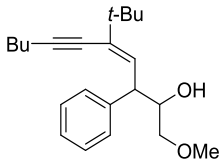
3ia: ^{1}H NMR (400 MHz, C_6D_6): δ 7.23 (d, J=6.8 Hz, 2H), 7.11 (t, J= 7.6 Hz, 2H), 7.01 (t, J=7.2 Hz, 1H), 6.49 (d, J=16.0 Hz, 1H), 6.20 (s, 1H), 5.62 (ddt, J=15.6, 5.6, 1.2 Hz, 1H), 4.28 (bs, 1H. major), 4.16 (bs, 1H, minor), 3.11-3.08 (m, 1H), 3.00 (s, 3H), 3.02-2.90 (m, 1H), 2.16 (bs, 1H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 210.0, 135.4, 129.3, 128.5, 128.3, 127.7, 127.6 (major), 127.6 (minor), 110.7, 104.1, 77.3, 71.6, 59.0, 15.7. MS (EI, *m/z*): 230(15, M^+), 185(100), 165(30), 152(45), 129(60), 115(50), 91(40), 77(30), 45(30). FTIR (ν_{max}/cm^{-1}): 3412, 2929, 1506, 1471, 1118, 966, 753, 683.



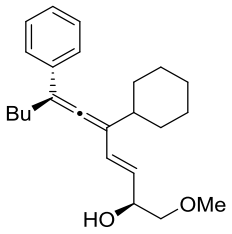
3ja: ^{1}H NMR (400 MHz, C_6D_6): δ 7.44 (d, J=7.0 Hz, 2H), 7.18 (t, J=7.2 Hz, 2H), 7.06 (t, J=7.2 Hz, 1H), 6.37 (ddd, 15.3, 10.6, 1.2 Hz, 1H), 6.16 (dt, 10.6, 2,9 Hz, 1H), 5.61 (dd, 15.5, 5.7 Hz, 1H), 4.27-4.23 (m, 1H), 3.09 (dd, A of ABX, JAB = 9.4 Hz, JAX = 8.1 Hz, 1H), 3.05 (dd, B of ABX, JAB = 9.4 Hz, JBX = 3.6 Hz, 1H), 2.98 (s, 3H), 2.39-2.34 (m, 2H), 2.24 (bs, 1H), 1.52 (quin, J=7.2 Hz, 2H), 1.32 (sext, J=7.6 Hz, 2H), 0.86 (t, J=7.6 Hz, 3H, minor), 0.85 (t, J=7.6 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 209.0, 137.3, 131.6, 129.1, 128.5, 127.5, 127.1, 108.2, 97.6, 77.2, 71.3, 58.9, 30.8, 30.5, 23.2, 14.5. MS (EI, *m/z*): 272 (<5, M^+), 254(5), 227(20), 209(20), 185(65), 167(55), 155(75), 141(70), 129(65), 115(70), 91(100), 77(30), 45(50). FTIR (ν_{max}/cm^{-1}): 3426, 2932, 1450, 1133, 974, 772, 701.



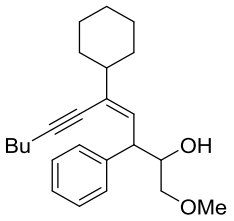
3ka: ^{1}H NMR (400 MHz, C_6D_6): δ 7.52 (d, J=7.6 Hz, 2H), 7.21 (t, J=7.6 Hz, 2H), 7.06 (t, J=8.0 Hz, 1H), 6.42 (dd, J=15.5, 1.4 Hz, 1H), 6.03 (dd, J=15.6, 5.2 Hz, 1H, minor), 6.02 (dd, J=15.6, 5.2 Hz, 1H, major), 4.31 (bs, 1H), 3.04 (dd, A of ABX, JAB = 7.7 Hz, JAX = 7.3 Hz, 1H), 3.01 (dd, B of ABX, JAB = 7.7 Hz, JBX = 1.3 Hz, 1H), 2.94 (s, 3H, minor), 2.93 (s, 3H, major), 2.47-2.42 (m, 2H), 2.24 (bs, 1H), 1.61 (quin, J=7.6 Hz, 2H), 1.56 (s, 3H, minor), 1.55 (s, 3H, major), 1.39-1.33 (m, 2H), 1.19 (s, 9H, minor), 1.19 (s, 9H, major), 0.90 (t, J=7.6 Hz, 3H, minor), 0.89 (t, J=7.6 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 203.0, 138.2, 130.8, 129.2, 128.3, 127.2, 126.4, 125.7, 117.3, 109.3, 77.4, 71.5, 58.8, 34.9, 31.0, 30.8, 30.4 (minor), 30.1 (major), 23.4, 14.6. MS (EI, *m/z*): 309(<5), 253(20), 212(20), 197(65), 155(95), 140(60), 105(40), 91(100), 69(40), 57(95). FTIR (ν_{max}/cm^{-1}): 3421, 2867, 1453, 1379, 1242, 1155, 806, 701.



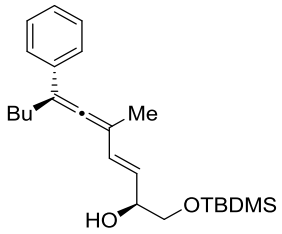
4ka: ^{1}H NMR (400 MHz, C_6D_6): δ 7.44 (d, 7.8 Hz, 2H), 7.20 (d, J=8.0 Hz, 2H), 7.06 (td, J=8.0, 1.2 Hz, 1H), 6.37 (d, J=9.8 Hz, 1H, minor), 6.33 (d, J=9.8 Hz, 1H, major), 4.37 (dd, J=9.6, 5.7 Hz, 1H), 4.17-4.12 (m, 1H), 3.34 (dd, A of ABX, JAB = 9.3 Hz, JAX = 7.3 Hz, 1H), 3.28 (dd, B of ABX, JAB = 9.3 Hz, JBX = 3.6 Hz, 1H), 3.02 (s, 3H), 2.28 (s, 1H), 2.21 (t, J=6.5 Hz, 2H), 1.44-1.31 (m, 4H), 1.22 (s, 9H), 0.82 (t, J=7.6 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 143.6, 136.1, 131.7, 129.1, 129.0, 127.0, 96.5, 79.5, 75.9, 74.6, 59.0, 50.2, 36.5, 32.1 (minor), 31.7 (major), 29.9, 22.6, 19.8, 14.1. MS (EI, *m/z*): 328(<1, M^+), 310(5), 253(25), 197(65), 155(100), 91(40), 57(25). FTIR (ν_{max}/cm^{-1}): 3452, 2958, 2923, 1468, 1354, 1115, 763, 710.



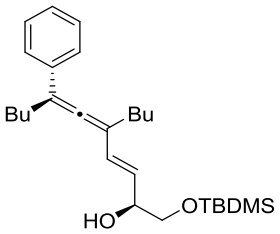
3la: ^{1}H NMR (400 MHz, C_6D_6): δ 7.51 (d, J=7.4 Hz, 2H), 7.20 (t, J=7.6 Hz, 2H), 7.07 (t, J=7.2 Hz, 1H), 6.39 (dd, J=16.0, 1.2 Hz, 1H), 5.86 (dd, J=16.0, 5.9 Hz, 1H), 4.35-4.31 (m, 1H), 3.14 (dd, A of ABX, JAB = 9.5 Hz, JAX = 8.9 Hz, 1H), 3.10 (dd, B of ABX, JAB = 9.5 Hz, JBX = 4.0 Hz, 1H), 2.99 (s, 3H), 2.46-2.42 (m, 2H), 2.29 (bs, 1H), 2.26-2.22 (m, 1H), 2.07-2.04 (m, 2H), 1.71-1.56 (m, 4H), 1.39-1.06 (m, 7H), 0.89 (t, J=7.2 Hz, 3H, minor), 0.88 (t, J=7.2 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 207.1, 138.0, 129.1, 128.9, 128.3, 127.3, 126.7, 114.4, 109.0, 77.5, 71.8, 58.9, 39.3, 33.8, 33.7, 31.1, 30.8, 27.3, 27.3, 27.0, 23.4, 14.5. MS (EI, *m/z*): 336(10), 309(35), 279(45), 207(40), 155(50), 91(100), 55(55), 32(55). FTIR (ν_{max}/cm^{-1}): 3446, 2918, 2846, 1424, 1142, 1000, 777, 683.



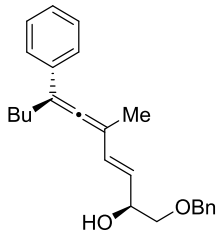
4la: ^{1}H NMR (400 MHz, C_6D_6): δ 7.45 (d, J=7.8 Hz, 2H), 7.20 (t, J=7.8 Hz, 2H), 7.08 (t, J=7.2 Hz, 1H), 6.22 (d, J=9.8 Hz, 1H), 4.34 (dd, J=9.8, 5.5 Hz, 1H), 4.14 (bs, 1H), 3.39-3.25 (m, 2H), 3.04 (s, 3H), 2.21 (t, J=6.4 Hz, 2H), 2.08 (t, J=12.0 Hz, 1H), 1.84 (dd, J=26.4, 12.4 Hz, 2H), 1.71-1.65 (m, 2H), 1.58-1.29 (m, 7H), 1.22-1.08 (m, 3H), 0.82 (t, J=6.8 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 143.6, 132.2, 129.1, 129.0, 128.3, 127.0, 95.9, 79.6, 75.9, 74.6, 59.1, 49.9, 46.4, 33.1, 32.9, 31.7, 27.1, 27.0, 26.8, 22.6, 19.9, 14.1. MS (EI, *m/z*): 336(<5), 279(65), 223(55), 197(60), 155(100), 115(40), 91(85), 55(35). FTIR (ν_{max}/cm^{-1}): 3469, 2940, 1459, 1269, 1089, 876, 697.



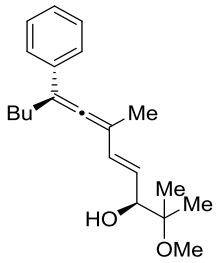
3ma: ^{1}H NMR (400 MHz, C_6D_6): δ 7.44 (d, J=7.6 Hz, 2H), 7.19 (t, J=8.0 Hz, 2H), 7.07 (t, J=7.4 Hz, 1H), 6.59 (dd, J=16.0, 1.2 Hz, 1H, minor), 6.58 (dd, J=16.0, 1.2 Hz, 1H, major), 5.65 (dd, J=15.8, 6.1 Hz, 1H), 4.25 (bs, 1H), 3.53 (dd, A of ABX, JAB = 9.9 Hz, JAX = 7.3 Hz, 1H), 3.43 (dd, B of ABX, JAB = 9.9 Hz, JBX = 3.7 Hz, 1H), 2.39 (t, J=7.6 Hz, 2H), 2.32 (d, J=3.1 Hz, 1H), 1.89 (s, 3H), 1.52 (quin, J=7.6 Hz, 2H), 1.38-1.29 (m, 2H), 0.91 (s, 9H), 0.86 (t, J=7.2 Hz, 3H), 0.01 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6): δ 208.8, 137.9, 134.9, 131.5, 130.6, 129.1, 127.4, 127. 1, 106.3, 103.4, 73.5 (major), 72.4 (minor), 68.2, 30.8, 30.7, 26.4, 23.2, 21.9, 18.8, 16.0, 14.5, -4.9. MS (EI, *m/z*): 386 (<1, M^+), 311(5), 237(30), 195(35), 181(55), 169(30), 105(35), 91(55), 75(100). HRMS (EI) $C_{24}H_{38}O_2Si$ [$(M+H)^+$, 387.27138 (calculated); 387.27155 (found). FTIR (ν_{max}/cm^{-1}): 3426, 2915, 1468, 1318, 1256, 1115, 851, 772, 683.



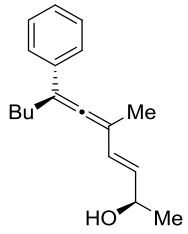
3na: ^{1}H NMR (400 MHz, C_6D_6): δ 7.48 (d, J=8.8 Hz, 2H), 7.20 (t, J=7.6 Hz, 2H), 7.07 (t, J=6.8 Hz, 1H), 6.54 (d, J=15.7 Hz, 1H), 5.80 (ddd, J=15.6, 6.0, 0.4 Hz, 1H), 4.27 (bs, 1H), 3.55 (dd, A of ABX, JAB = 9.8 Hz, JAX = 7.6 Hz, 1H), 3.45 (dd, B of ABX, JAB = 9.8 Hz, JBX = 3.4 Hz, 1H), 2.44 (t, J=7.2 Hz, 2H), 2.29 (t, J=8.0 Hz, 2H), 1.64-1.54 (m, 4H), 1.40-1.29 (m, 4H), 0.91 (s, 9H, major), 0.90 (s, 9H, minor), 0.87 (t, J=7.6 Hz, 3H), 0.85 (t, J=7.6 Hz, 3H), 0.01 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6): δ 208.2, 137.9, 130.2, 129.1, 128.3, 127.4, 126.9, 108.6, 108.0, 73.6, 68.2, 31.0, 30.9, 30.8, 29.8, 26.4, 23.5, 23.3, 18.8, 14.5, 14.5, -4.9. MS (EI, *m/z*): 371(10), 336(5), 315(20), 296(25), 279(25), 212(20), 168(45), 116(60), 91(55), 75(100), 56(95). FTIR (ν_{max}/cm^{-1}): 3437, 2917, 1451, 1272, 1093, 849, 776, 685.



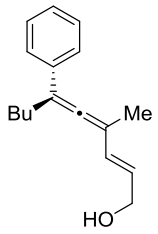
3oa: ^{1}H NMR (400 MHz, C_6D_6): δ 7.44 (d, J=7.8 Hz, 2H), 7.20-7.14 (m, 6H), 7.11-7.05 (m, 2H), 6.57 (d, J= 16.0 hz, 1H), 5.60 (dd, J=15.7, 5.9 Hz, 1H), 4.37-4.34 (m, 1H), 4.24 (s, 2H), 3.28 (dd, A of ABX, J_{AB} = 9.3 Hz, J_{AX} = 7.9 Hz, 1H), 3.21 (dd, B of ABX, J_{AB} = 9.3 Hz, J_{BX} = 3.8 Hz, 1H), 2.39 (t, J=7.2 Hz, 2H), 2.25 (bs, 1H), 1.85 (s, 3H), 1.51 (quin, J=7.4 Hz, 2H), 1.32 (sext, J=7.6 Hz, 2H), 0.86 (t, J=7.2 Hz, 3H, minor), 0.85 (t, J=7.2 Hz, 3H, major). ^{13}C NMR (101 MHz, C_6D_6): δ 208.8, 139.0, 137.9, 130.5, 129.1, 129.0, 128.3, 128.2, 127.4, 127.1, 106.3, 103.4, 75.1, 73.6, 71.8, 30.8, 30.7, 23.2, 15.9, 14.5. MS (EI, *m/z*): 362 (<5, M^+), 320(5), 253(10), 197(20), 181(25), 169(45), 129(20), 91(100), 69(35), 41(40). HRMS (EI) $C_{25}H_{30}O_2$ [$(M+Na)^+$, 385.21380 (calculated); 385.21384 (found). FTIR (ν_{max}/cm^{-1}): 3435, 2915, 1503, 1450, 1142, 983, 763, 674.



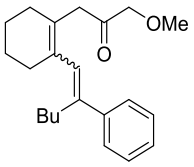
3pa: ^{1}H NMR (400 MHz, C_6D_6): δ 7.44 (d, J=7.2 Hz, 2H, major), 7.43 (d, J=7.2 Hz, 2H, minor), 7.18 (t, J=7.6 Hz, 2H), 7.06 (t, J=7.2 Hz, 1H), 6.59 (d, J=15.6 Hz, 1H, minor), 6.54 (d, J=15.6 Hz, 1H, major), 5.77 (ddd, J=15.7, 6.6, 0.8 Hz, 1H), 4.06 (d, J=6.4 Hz, 1H), 2.92 (s, 3H), 2.55 (bs, 1H), 2.39 (t, J=7.2 Hz, 2H), 1.88 (s, 3H, minor), 1.88 (s, 3H, major), 1.51 (quin, J=7.6 Hz, 2H), 1.32 (sext, J=7.6 Hz, 2H), 1.03 (s, 3H), 0.97 (s, 3H, major), 0.96(s, 3H, minor), 0.86 (t, J=7.6 Hz, 3H, minor), 0.85 (t, J=7.6 Hz, 3H, major). 13C NMR (101 MHz, C_6D_6): δ 208.7, 138.0, 134.9, 131.4, 131.3, 129.1, 127.3, 127.1, 106.2, 103.5, 78.7, 78.0, 72.4, 49.4, 30.8 (major), 30.7 (minor), 23.1, 21.9, 21.1, 19.9, 16.0, 14.5. MS (EI, m/z): 314 (<1, M+), 242(5), 91(5), 115(5), 73(100). FTIR (νmax/cm-1): 3438, 2920, 1480, 1384, 1067, 962, 761, 708.



3ra: ^{1}H NMR (400 MHz, C_6D_6): δ 7.46 (d, J=8.0 Hz, 2H, major), 7.45 (d, J=8.0 Hz, 2H, minor), 7.19 (t, J=7.6 Hz, 2H), 7.07 (t, J=7.2 Hz, 1H), 6.30 (d, J= 15.7 Hz, 1H), 5.59 (ddd, J=15.6, 6.4, 0.8 Hz, 1H), 4.14-4.08 (m, 1H), 2.42 (t, J=7.2 Hz, 2H), 1.85 (d, 0.8 Hz, 3H), 1.54 (quin, J=7.2 Hz, 2H), 1.39-1.30 (m, 2H), 1.13 (d, J=6.4 Hz, 3H, minor), 1.12 (d, J=6.4 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 208.7, 138.0, 134.1, 129.1, 128.3, 127.4, 127.0, 106.2, 103.3, 69.0, 30.9 (minor), 30.8 (major), 30.7, 24.1, 23.2 (minor), 23.2 (major), 16.0, 14.5. MS (EI, *m/z*): 256 (<5, M^+), 238(5), 196(10), 181(15), 169(100), 155(25), 141(25), 129(20), 115(20), 91(25), 77(10), 43(25). FTIR (ν_{max}/cm^{-1}): 3332, 2972, 2920, 1501, 1427, 1089, 982, 782, 708.

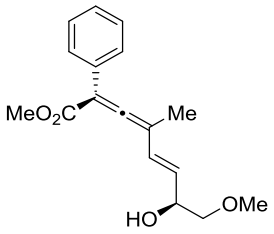


3sa: ^{1}H NMR (400 MHz, C_6D_6): δ 7.45 (d, J=8.0 Hz, 2H), 7.19 (t, J=7.8 Hz, 2H), 7.07 (td, J=7.6, 0.8 Hz, 1H), 6.29 (d, J=15.6 Hz, 1H), 5.59 (dtd, J=15.6, 6.0, 0.8 Hz, 1H), 3.90 (d, J=5.5 Hz, 2H), 2.41 (t, 7.4 Hz, 2H), 1.83 (s, 3H), 1.54 (quin, J=7.4 Hz, 2H), 1.39-1.30 (m, 2H), 0.87 (t, J=7.6 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 208.6, 138.0, 129.7, 129.1, 129.1, 127.4, 127.0, 106.3, 103.4, 63.8, 30.8, 30.7, 23.2, 15.9, 14.5. MS (EI, *m/z*): 242 (<5, M^+), 224(5), 200(15), 169(100), 154(20), 141(25), 128(20), 115(20), 91(30), 41(5). FTIR (ν_{max}/cm^{-1}): 3345, 2912, 1488, 1449, 1305, 978, 689.

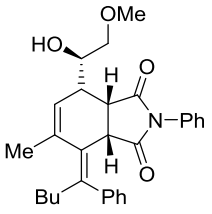


(E)-5ta: ^{1}H NMR (400 MHz, C_6D_6): δ 7.35 (d, J=7.6 Hz, 2H), 7.20-7.16 (m, 2H), 7.11 (d, J=8.0 Hz, 1H), 6.14 (s, 1H), 3.61(d, J=0.8 Hz, 2H), 3.15 (s, 2H), 3.02 (s, 3H), 2.51 (t, J=7.2 Hz, 2H), 2.08 (d, J=9.2 Hz, 4H), 1.58 (bs, 4H), 1.35-1.21 (m, 4H), 0.80 (t, J=6.4 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 206.0, 142.9, 142.5, 133.5, 129.0, 128.7, 128.3, 128.1, 127.2, 78.0, 59.2, 45.3, 39.4, 31.1, 30.7, 30.4, 23.6, 23.4, 22.8, 14.4. MS (EI, *m/z*): 326(10, M^+), 281(25), 238(95), 181(55), 129(30), 91(100), 45(35). FTIR (ν_{max}/cm^{-1}): 2922, 1738, 1440, 1209, 1094, 767, 700.

(Z)-5ta: ^{1}H NMR (400 MHz, C_6D_6): δ 7.31 (d, J=8.0 Hz, 2H), 7.20-7.16 (m, 2H), 7.08-7.03 (m, 1H), 6.12 (s, 1H), 3.67 (d, J=0.8 Hz, 2H), 3.12 (s, 2H), 3.08 (s, 3H), 2.40 (t, J= 7.2 Hz, 2H), 1.96 (bs, 2H), 1.87 (bs, 2H), 1.48-1.36 (m, 4H), 1.38 (s, 4H), 0.82 (t, J= 6.4 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 205.8, 143.1, 142.0, 133.5, 129.5, 128.5, 128.0, 127.7, 78.0, 59.2, 45.2, 39.4, 31.3, 31.0, 30.4, 23.7, 23.4, 22.8, 14.4. MS (EI, *m/z*): 326(20, M^+), 281(25), 238(95), 181(60), 141(35), 91(100), 45(35). FTIR (ν_{max}/cm^{-1}): 2922, 1738, 1440, 1209, 1094, 767, 700.



3va: ^{1}H NMR (400 MHz, C_6D_6): δ 7.75 (d, J=6.4 Hz, 2H), 7.18 (t, J=7.0 Hz, 2H), 7.07 (t, J= 7.8 Hz, 6.46 (dd, J=15.8, 1.2 Hz, 1H, minor), 6.43 (dd, J=15.8, 1.2 Hz, 1H, major), 5.59 (dd, J=16.0, 6.4 Hz, 1H), 4.22 (bs, 1H), 3.41 (s, 3H, minor), 3.40 (s, 3H, major), 3.05-3.00 (m, 2H), 2.99 (s, 3H), 2.25 (bs, 1H), 1.72 (d, J=0.8 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 216.7, 166.5, 139.9, 131.1, 129.4, 129.0, 128.3, 127.0, 105.2, 103.4, 77.1, 71.4, 59.0, 52.2, 15.0; MS (EI, m/z): 288 (2, M+), 256 (3), 211 (5), 183(5), 155 (17), 115 (8), 89 (4), 77 (9), 51 (5), 45 (100); HRMS (ESI): $C_{17}H_{21}O_4$ $(MH)^+$: 289.1434 (calculated), 289.1439 (found). FTIR (νmax/cm^{-1}): 3419, 2922, 2851, 1926, 1716, 1492, 1434, 1369, 1321, 1273, 1195, 1171, 1123, 1062, 1039, 964, 918, 898, 781, 694



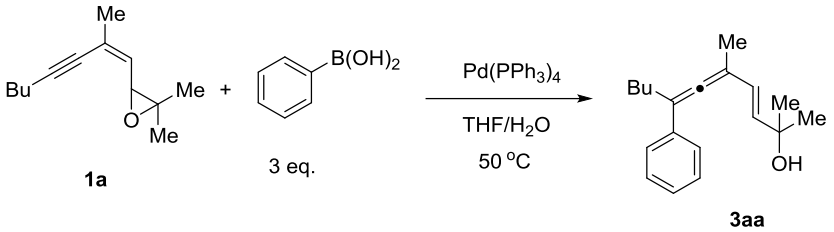
6ba: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42 (m, 3H), 7.37 (t, J=7.6 Hz, 3H), 7.32-7.29 (m, 2H), 7.15 (d, J=7.6 Hz, 2H), 6.00 (d, J=2.4 Hz, 1H), 4.30 (q, J=5.5 Hz, 1H), 3.93 (d, J=8.6 Hz, 1H), 3.64-3.56 (m, 2H), 3.43 (s, 3H, minor), 3.41 (s, 3H, major), 3.14 (dd, J=8.6, 5.9 Hz, 1H), 2.56-2.48 (m, 1H), 2.40-2.33 (m, 2H), 2.06 (t, J=1.6 Hz, 3H), 1.34-1.24 (m, 4H), 0.83 (t, J=7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.8, 177.0, 143.6, 140.8, 138.4, 131.8, 129.1, 128.8, 128.2, 128.2, 127.3, 126.5, 126.0, 74.8, 69.7, 59.1, 47.1, 44.9, 40.0, 36.0, 30.5, 22.9, 22.2, 13.9. MS (EI, *m/z*): 441(90), 385(50), 328(40), 237(20), 207(30), 181(100), 145(90), 91(90), 45(35). FTIR (ν_{max}/cm^{-1}): 2954, 2849, 1724, 1512, 1367, 1209, 1128, 719.

CHAPTER 4

RESULTS AND DISCUSSION

The Pd(0)-catalyzed reaction of enyne oxirane (**1a**) with phenyl boronic acid was initiated by performing the reaction over the catalyst $Pd(PPh_3)_4$ in THF/water mixture at 50 ^oC of reaction temperature to obtain vinylallenols with a phenyl group.

Table 4.1. Effect of Reaction Parameters on the Pd(0)-Catalyzed Arylation of **1a**



Entry	Pd (mol %)	THF/H_2O(ml)	Time(h)	[a]Yield %
1	1	2/1	18	**62**
2	2	2/1	2	**68**
3	3	2/1	1.5	**73**
4	3	2/2	1.5	**72**
5	3	2/0	24	**0**
6	3	4/2	1.5	**71**
7	3	1/0.5	1.5	**58**

[a] NMR yield Reactions were performed with 0.1 mmol of **1a**

Initially, the palladium % loading was investigated for **1a** conversion and the highest yield was obtained with 3% Pd loading (Table 4.1., Entry 3). Then the water content was varied and it was determined that presence of water is needed for the formation of product (Entry 5). The variation of THF/H_2O ratio seems to have no dramatic effect on the product (**3aa**) (Entry 3,4).). The method is applicable at more diluted

medium (Entry 6), whereas a comperetively lower yield was obtained at more concentrated solution. (Entry 7).

After these results, the method was studied with the monosubstituted enyne epoxide **1b** having a disubstituted oxirane ring. When the reaction was performed with phenyl boronic acid, boronic acid ester was formed with the enyne oxirane **1b** (Figure 4.1) as the result of lack of steric hindrence of **1b** compared to **1a**. Beside phenyl boronic acid, formation of boronic acid ester was also observed with potassium phenyl trifluoroborate and phenyl boroxine.

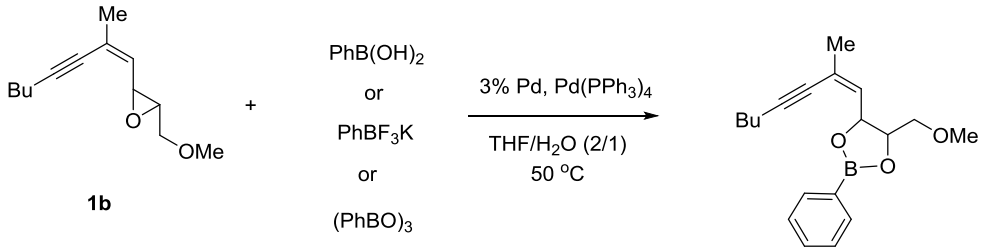
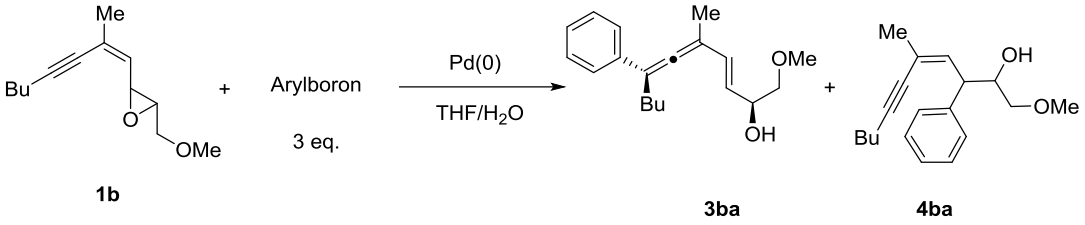


Figure 4.1. Boronic Acid Ester Formation of Enyne Oxirane

Table 4.2. Effect of Reaction Parameters on the Pd(0)-Catalyzed Arylation of **1b**



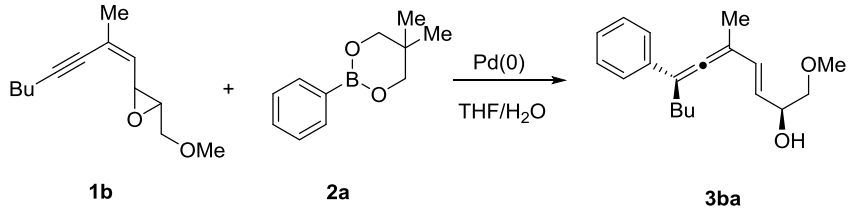
Entry	Arylboron	Catalyst	THF/H_2O(ml)	°C	Time (h)	Yield[a] 3ba (Yield[a] 4ba)	dr
1	$NaBPh_4$	3% Pd, $Pd(PPh_3)_4$	2/1	50	2	**67**	**79:21**
2	$NaBPh_4$	3% Pd, $Pd(PPh_3)_4$	2/0.5	50	1.5	**75**	**83:17**
3	$NaBPh_4$	3% Pd, $Pd(PPh_3)_4$	2/0.25	50	2.5	**40**	-
4	$NaBPh_4$	3% Pd, $Pd(PPh_3)_4$	2/1	RT	4	**23 (49)[b]**	-
5	$NaBPh_4$	3% Pd, $Pd(PPh_3)_4$	2/0.5	RT	4	**31 (33)**	-
6	$NaBPh_4$	2% Pd, $Pd(PPh_3)_4$	2/0.5	50	2	**70**	**82:18**
7	$NaBPh_4$	1% Pd, $Pd(PPh_3)_4$	2/0.5	50	2.5	**65**	**82:18**
8	PhBneo[c]	3% Pd, $Pd(PPh_3)_4$	2/0.5	50	1.5	**78**	**79:21**
9	$NaBPh_4$	3% Pd, $Pd(PPh_3)_4$	1/0.25	50	1.25	**34**	**79:21**
10	$NaBPh_4$	3% Pd, $Pd(PPh_3)_4$	4/1	50	1.5	**68**	**77:23**
11	$NaBPh_4$	3% Pd, $Pd_2(dba)_3CHCl_3$ /PPh_3 (12%)	2/0.5	50	1.5	**72**	**78:22**

Reactions were performed with 0.1 mmol **1b**, [a] NMR yield, [b] Isolated yield, [c] Phenylboronic acid neopenthyl glycol ester.

When the arylboron source was changed to the sodium salt of tetraphenyl borate and phenylboronic acid neopentyl glycol ester, the target product could be obtained in good yields and with moderate diastereoselectivities (Table 4.2.) The decrease of the THF:water ratio from 2/1 to 2/0.5 caused to improve the desired product **3ba** yield some extent (Entries 1 and 2). However a further decrease to 2/0.25 led to decrease the yield dramatically (Entry 3). Interestingly when reaction was performed at room temperature not only **3ba** but also an allylic substitution product **4ba** was formed in moderate yield (Entry 5). The formation of **4ba** seems directly proportional with the water amount added into the reaction medium (Entry 4). Decreasing the Pd loading showed no positive effect on the yield and the diastereoselectivity (Entry 6 and 7). The application of different concentration (lower or higher) was detrimental for the product formation (Entry 9 and 10). When phenylboronic acid neopentyl glycol ester was used instead the yield of **3ba** increased but decrease in diastereomeric ratio (Entry 8). As the Pd(0) source changed to chloroform adduct dibenzylideneacetone (dba) complex of palladium and triphenylphosphine as ligand, both reaction yield and dr ratio decreased relatively (Entry 11). Due to the being air and temperature sensitive of tetrakis(triphenylphosphine) palladium(0) complex and ease of usage of air stable palladium-dba complex especially when ligand change was desired for diasteroselectivity palladium-dba complex was chosen as palladium precursor.

When the reaction was performed with phenylboronic acid neopentyl glycol ester (**2a**) and with the presence of the dba complex of Pd and PPh_3 combination at 50 ^oC, a good yield was obtained with moderate dr level (Table 4.3., Entry 1). While a slight increase of P/Pd ratio from 4/1 to 4.5/1 ratio the dr level somewhat, a decreased of the yield was observed (Entry 2). However, a significantly lower dr level could be provided with the further increase of the ligand to Pd ratio (5/1) (Entry 3). It appears that a better dr level could be provided when the reaction was performed at rt with a P to Pd ratio 4.5/1 (Entry 4). It apparent that $Pd(PPh_3)_4$ catalyst cannot surrogate $Pd_2(dba)_3CHCl_3/PPh_3$ combination as the comparable experiment with the former catalyst afforded the corresponding vinylallene rather in a lower yield and with a lower dr level (Entry 5).

Table 4.3. Pd(0) Precurser and Ligand Effect on Yield and Diastereoselectivity of **3ba**



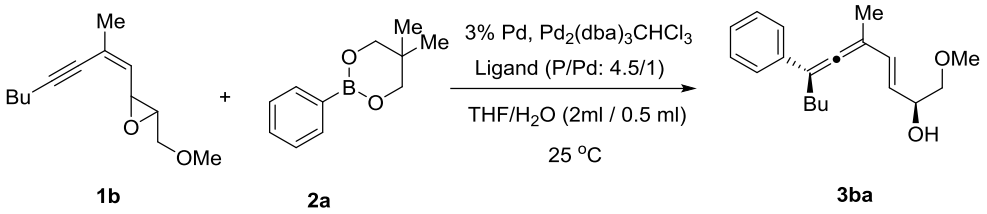
Entry	Catalyst	Ligand	THF/H_2O(ml)	^oC	Time (h)	Yield[a]	dr
1	3% Pd, $Pd_2(dba)_3CHCl_3$	12% PPh_3	2/0.5	50	1	**81**	**70:30**
2	3% Pd, $Pd_2(dba)_3CHCl_3$	13.5% PPh_3	2/0.5	50	1	**73**	**77:23**
3	3% Pd, $Pd_2(dba)_3CHCl_3$	15% PPh_3	2/0.5	50	1	**70**	**58:42**
4	3% Pd, $Pd_2(dba)_3CHCl_3$	13.5% PPh_3	2/0.5	RT	4	**81**	**76:24**
5	3% Pd, $Pd(PPh_3)_4$	-	2/0.5	RT	4	**77**	**73:27**

Reactions were performed with 0.1 mmol **1b** and 3 eq. of **2a**, [a]NMR yield

After the determination optimum conditions related to P to Pd ratio, temperature, THF:water ratio a variety of mono-and bidentate ligands were tested for their efficiency on the catalytic activity of the palladium (Table 4.4). When strongly electron withdrawing -trifluoromethyl- substituted phenyl phosphine ligand was examined, although no stereoselectivity was detected, the percent yield of **3ba** was nearly quantitative with this ligand (Entry 5). With the aim of increasing the diastereomeric selectivity, the lower reaction temperatures 10 ^oC and 0 ^oC tested. Under these conditions the selectivity was improved up to dr level of 84/16 though required longer reaction times for a complete conversion (Entry 6 and 7). Except with tris(2-furyl) phosphine and methyl diphenylphosphine (Entry 8 and10) with other monodentate ligands poor results were attained on the bases of dr level. Air stable tetrafluoroborate salt of trialkylphosphine ligands (tris(tert-butyl) phosphine and tricyclohexyl phosphine) was also examined. In order to liberate the bare forms of trialkylphosphines a basic medium is required (Netherton and Fu, 2001).

Therefore, with these ligands $NaHCO_3$ was present as the base within the reaction medium, with the presence of tricyclohexyl phosphine no product formation was observed (Entry 12). When the base was changed to KF, **3ba** formation was in 78% yield but proceeded with low diastereoselectivity (Entry 13). When the reaction was carried out with bidentate ligands, despite the best selectivity was observed with dppe ligand, reaction time was unaffordable long with this ligand (Entry 22). Then the reaction temperature was raised to 50 ^oC to accelerate the reaction but diastereoselectivity diminished at this temperature (Entry 23). Apparently, no benefit was gained with the presence of the base $NaHCO_3$ with the ligand dppp. (Entry 24). Nevertheless, it was pleasure to find that the beneficial effect of $NaHCO_3$ was noticeable over the activity of Pd/DPEphos catalyst system, providing a complete conversion of the substrate to the desired product being recovered in an excellent yield (96%) with a synthetically meaningful dr level (87:13) within an acceptable period of time (Entry 26). No better result could be obtained when performing the reaction at a sub-room temperature.

Table 4.4. Ligand Effect on Yield and Diastereoselectivity of **3ba**



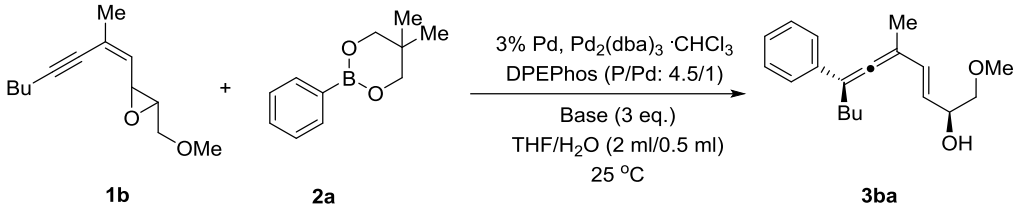
1b **2a** **3ba**

Entry	Ligand	Time (h)	Yield[a]	dr
1	$P(4\text{-}OMeC_6H_4)_3$	19	**72**	**75:25**
2	$P(2\text{-}OMeC_6H_4)_3$	19	**55**	**61:39**
3	$P(2,6\text{-}OMeC_6H_3)_3$	40	**52**	**58:42**
4	$P(2,4,6\text{-}MeC_6H_2)_3$	3	**64**	**75:25**
5	$P(4\text{-}CF_3C_6H_4)_3$	2.5	**99**	**50:50**
6[b]	$P(4\text{-}CF_3C_6H_4)_3$	4	**78**	**80:20**
7[c]	$P(4\text{-}CF_3C_6H_4)_3$	11	**86**	**84:16**
8	Tris (2-furyl) phosphine	15	**65**	**85:15**
9	PPh_2Bn	21	**42**	**77:23**
10	PPh_2Me	23	**70**	**85:15**
11[d]	$[HP(t\text{-}Bu)_3]BF_4$	3.5	**46**	**80:20**
12[d]	$[HPCy_3]BF_4$	72	**-**	**-**
13[e]	$[HPCy_3]BF_4$	5	**78**	**72:28**
14	$AsPh_3$	20	**66**	**82:18**
15	XANTPHOS	5	**43**	**64:36**
16	t-Bu-XANTPHOS	72	**-**	**-**
17[f]	(±)-BINAP	48	**38**	**66:34**
18	BIPHEP	20	**65**	**70:30**
19	dppf	20	**61**	**73:27**
20	dppe	30	**81**	**84:16**
21	dppb	40	**48**	**83:17**
22	dppp	72	**70**	**88:12**
23[g]	dppp	14	**85**	**86:14**
24[d]	dppp	16	**91**	**83:17**
25	DPEPhos	1.5	**92**	**80:20**
26[d]	DPEPhos	3.5	**96**	**87:13**
27[b,d]	DPEPhos	24	**78**	**85:15**

Reactions were performed with 0.1 mmol **1b** and 3 eq. of **2a**, [a]NMR yield, [b]10 °C, [c]0 °C, [d]3 eq. of $NaHCO_3$ was used, [e]3 eq. of KF was used, [f]41% starting material was recovered, [g]50 °C

With DPEPhos as the choice of the ligand in hand, the optimization studies were continued to survey the most suitable base of the method. Among the bases tested, generally the amine bases revealed better results than inorganic bases especially in terms of diastereoselectivity (Table 4.5). The highest yield and diastereoselectivity were obtained with the presence of N,N-diisopropylethyl amine (Entry 10). A heteroaryl 2,2-bipyridyl- was entirely incompetent for the method (Entry 18). $Pd(PPh_3)_4$ was tested once again under the modified conditions. However, no better result was possible with this pre-ligated Pd catalyst (Entry 19). Even CO was evaluated as for its potency as ligand, but failed to show any promotive effect with its presence as the combination of Ar/CO (9/1) under a balloon pressure. In this condition however the yield was moderate, diastereoselectivity was not high (Entry 20). When reaction was performed in air atmosphere the yield was convincing but diastereoselectivity was not (Entry 21).

Table 4.5. Effect of Base on Yield and Diastereoselectivity of **3ba**

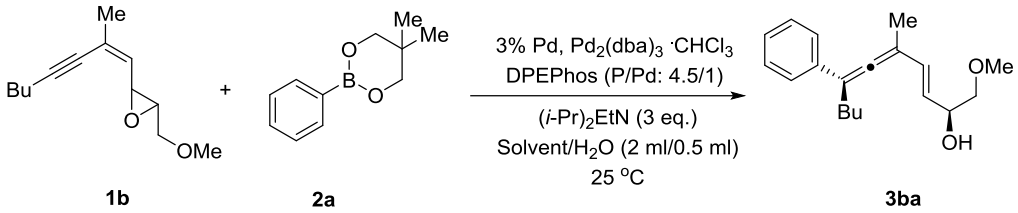


Entry	Base	Time(h)	Yield [a,b]	dr
1	KF	1.5	**81**	**87:13**
2	K_2CO_3	2.5	**88**	**77:23**
3	Cs_2CO_3	7	**93**	**83:17**
4	CsF	4.5	**88**	**87:13**
5	NaOAc	22	**56**	**77:23**
6	KOH	22	**35**	**78:22**
7	Et_3N	5	**90**	**89:11**
8	*n*-Bu_3N	16	**70**	**85:15**
9	*n*-Pr_3N	16	**72**	**86:14**
10	(*i*-Pr)$_2$EtN	2	**90**	**90:10**
11	(*i*-Pr)$_2$NH	22	**77**	**85:15**
12	Cy_2MeN	6	**85**	**87:13**
13	N,N-dimethyl aniline	1	**82**	**78:22**
14	DBU	20	**52**	**69:31**
15	TMEDA	48	**36(49)**	**-**
16	DMEDA	48	**(60)**	**-**
17	2,2-Bipyridyl	96	**26(57)**	**-**
18[c]	(*i*-Pr)$_2$EtN	96	**-**	**-**
19[d]	(*i*-Pr)$_2$EtN	5	**61**	**80:20**
20[e]	(*i*-Pr)$_2$EtN	1.5	**84**	**86:14**
21[f]	(*i*-Pr)$_2$EtN	2	**88**	**84:16**

Reactions were performed with 0.1 mmol **1b** and 3 eq. of **2a**, [a] NMR yield, [b] values in paranthesis are the yield of starting material that recovered, [c] 2,2-Bipyridyl used as ligand, [d] $Pd(PPh_3)_4$ was used as Pd source, [e] reaction was performed under Ar/CO (9/1) atmosphere in balloon pressure, [f] Air atmosphere.

The solvent effect was also evaluated. Besides THF, different ethereal solvents and also polar protic and aprotic solvents were tried (Table 4.6.). Ethereal solvents commonly showed higher yield and selectivity.

Table 4.6. Solvent Effect on Formation of **3ba**



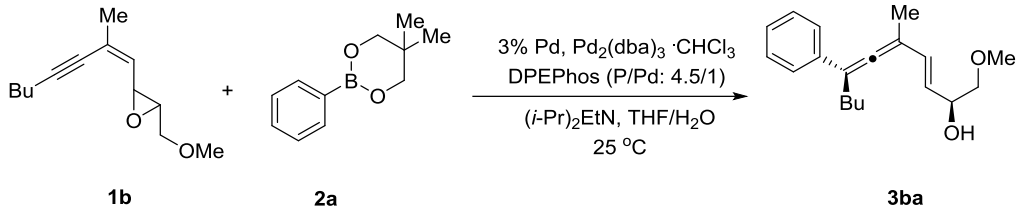
1b **2a** **3ba**

Entry	Solvent	Time(h)	Yield [a]	dr
1	Dioxane	2	**95**	**89:11**
2	DME	2	**91**	**86:14**
3	ACN	20	**67**	**65:35**
4	DMF	20	**74**	**74:26**
5	*i*-PrOH	2	**74**	**81:19**

Reactions were performed with 0.1 mmol **1b** and 3 eq. of **2a**, [a] NMR yield

As the choice of the solvent THF in hand variation of the amounts of components of the reaction, such as base, water and as well as the temperature of reaction medium was assessed (Table 4.7.). The product **3ba** was obtained with a higher dr level as the base amount increases and 4 eq. was decided to be sufficient on in terms of the economy and a satisfactory dr level could be afforded under these conditions (Entry 1-2-3). No improvement could be achieved with variation of water content and concentration of the solution and it must be noted that lessening the water content lowered the reaction rate significantly (Entry 6 and 7). A slight improvement at dr level is possible by reducing the reaction temperature to 10 or 0°C (Entry 8 and 9). Finally, the organoboron content of the reaction mixture could be gratefully lessened to 2 equivalent from 3 equivalent without compromising the product yield the reaction rate (Entry 10).

Table 4.7. Effect of Base Amount, Water Ratio, Concentration and Temperature of **3ba**



1b **2a** **3ba**

Entry	Eq. Of Base	THF/H_2O (ml)	°C	Time(h)	Yield [a]	dr
1	2	2/0.5	25	3	**90**	**90:10**
2	4	2/0.5	25	2	**92**	**91:9**
3	6	2/0.5	25	2	**89**	**92:8**
4	4	2/1	25	4	**71**	**89:11**
5	4	2/0.25	25	16	**78**	**88:12**
6	4	1/0.25	25	1.5	**72**	**88:12**
7	4	4/1	25	3	**95**	**91:9**
8	4	2/0.5	10	4	**91**	**92:8**
9	4	2/0.5	0	9	**85**	**92:8**
10[b]	4	2/0.5	25	2.5	**87**	**91:9**

Reactions were performed with 0.1 mmol **1b** and 3 eq. of **2a**, [a] NMR yield, [b] 2 eq. **2a** was used

After the optimized reaction parameters were determined, the reaction established was verified on the (*E*) configured enyne oxirane (**(*E*)-1b**). It was interesting to find that the method afforded the desired vinylallene product in high yield, but with a quite low dr level (24:76) with a major stereoisomeric form (**3ba'**) that is the diastereomer of **3ba** which is the product of its (*Z*)-configured counterpart (Figure 4.2).

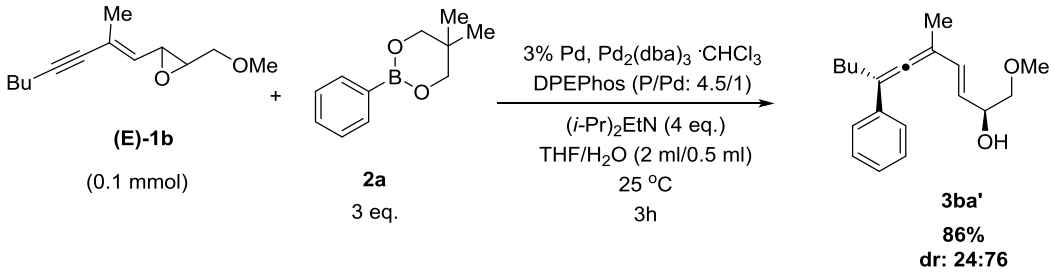
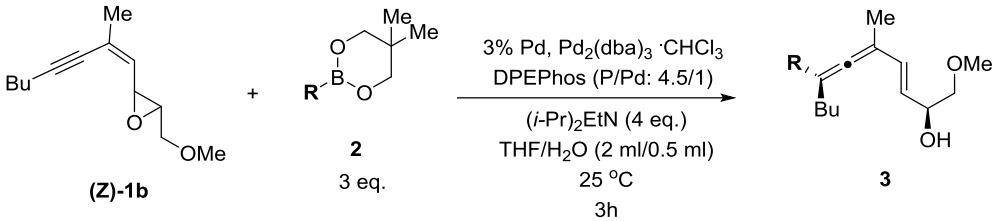


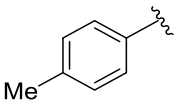
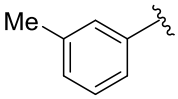
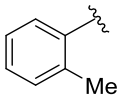
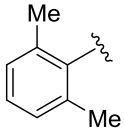
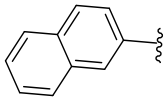
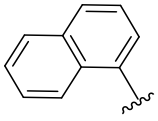
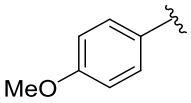
Figure 4.2. Pd(0)-Calayzed Arylation Reaction of **(*E*)-1b**

Having determined that the method is more stereoselective with (Z)-configured enyne oxiranes, next the scope of the method was surveyed for both a number of organoborons and enyne oxirane structures as well.

The scope of the method seems to be astonishingly wide for the location and diversity of functional groups on organoboron structures (Table 4.8).

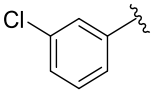
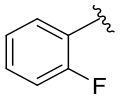
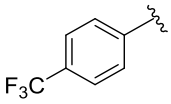
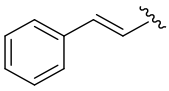
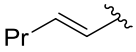
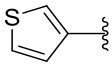
Table 4.8. Pd(0)-Catalyzed Reaction of the (*Z*)-Enyne Oxirane (**(*Z*)-1a**) with Different Organoboronates



Entry	R	Time (h)	Product	Yield %[a]	dr
1	 **2b**	1.5	**3bb**	**93**	**92:8**
2	 **2c**	2	**3bc**	**72**	**90:10**
3	 **2d**	1.5	**3bd**	**87**	**92:8**
4[b]	 **2e**	20	**3be**	**28**	**85:15**
5	 **2f**	2	**3bf**	**88**	**91:9**
6	 **2g**	1.5	**3bg**	**93**	**91:9**
7	 **2h**	1.5	**3bh**	**95**	**91:9**

(cont. on next page)

Table 4.8 (cont.)

8	 **2i**	9	**3bi**	**78**	**90:10**
9	 **2j**	6	**3bj**	**83**	**92:8**
10	 **2k**	12	**3bk**	**81**	**92:8**
11	 **2l**		**3bl**	**73**	**64:36**
12	 **2m**	4	**3bm**	**63**	**85:15**
13[c]	 **2n**	3	**3bn**	**-**	**-**

Reactions were performed with 0.1 mmol **1b** and 3 eq. of **2**, [a]Isolated yields, [b]43% allylic arylated by product was formed. [c] β-hydride elemination byproduct was observed as inseperable mixture of the target product.

Electron-rich arylboronates provided the corresponding arylated vinylallenol products with good to high yields except with the highly sterically hindered 2,6-dimethylphenylboronate (Table 4.8. Entry 4). When 2,6-substituted phenylboronate was used allylic arylated by product (**4be**) (Figure 4.3.) was recovered with 43% isolated yield. It was noticed that the reactions with electron-deficient arylboronates needed longer reaction times for completion, affording the corresponding products in moderate yields but good dr levels. This reactivity difference might be resulted from the less reactivity of the electron poor organoborons toward transmetallation step with the intermediate of π-allyl palladium complex. When alkenylboronate was used both the reaction yield and selectivity decreased (Table 4.8. Entry 11 and 12).

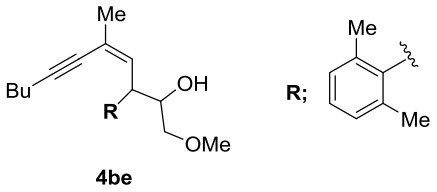


Figure 4.3. Allylic Arylated Product **4be**

Performing the reaction with 3-thienylboronate lead to the formation of a byproduct (Figure 4.4.) formed as a result of β-hydride elemination afterwards formation of a π-allyl-Pd complex with the help of the base in the medium with the ratio 1/4 corresponding to the target vinyallenol . It is considered that the sulfide coordination of palladium probably switched its activity toward elimination rather than transmetallation route.

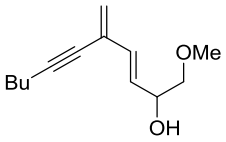


Figure 4.4. *β*-hydride Elemination Product

Next we explored the scope of the method on different substrate type beginning with the enyne oxirane with different substituents (**R[1]**) on the alkynyl carbon. The yields and dr levels of the corresponding products were comparable to that obtained with **1b** when methyl (**3de**) or phenyl (**3eh**) substituted enyne oxiranes were reacted with esters of phenylboronic acid and *p*-methoxyphenylboronic acid, respectively. (Table 4.9., Entry 1 and 2). However, when **R[1]** was substituted with a comparatively bulky cyclohexyl (**3ga**), *t*-butyl (**3fa**) and trimethylsilyl (**3ha**) group, the corresponding desired vinyallene products were obtained in lower yields and their formation was accompanied by the formation of allylic substitution products **4fa**, **4ga** and **4ha** respectively (Entry 3, 4 and 5). To minimize difficulty of migration of π-allyl coordinated palladium to α-allenyl-palladium intermediate, the reactions with bulky susbstituents on alkynyl moiety were also performed with less bulky PPh_3 ligand instead of DPEPhos. No allylic addition product formation was observed with the reaction of **1g** and **1h**. Nevertheless with t-butyl group 5% yield of **4fa** was obtained. The enyne oxiranes with terminal alkyne moiety (R^1 = H, **3ia**) and disubstituted alkenyl moiety (R^2 = H, **3ja**) both afforded the corresponding vinylallene products in moderate yields. The product selectivity is evidently influenced

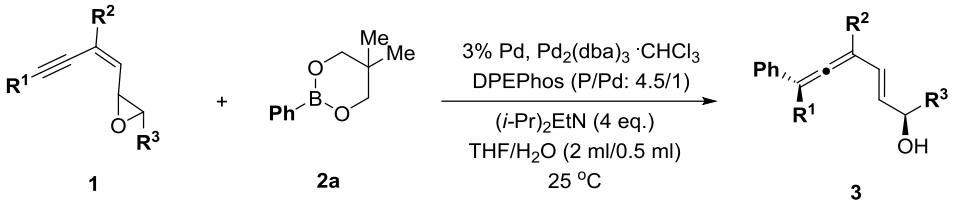
by the size of the alkenyl substituent **R^2**. The presence of cyclohexyl group in **R^2** led the formation of the allylic substituted product **4la** in 16% along with the moderate formation of the vinylallene **3la** (Entry 9). When ligand was changed to PPh_3, formation of **4la** was inhibited. The presence of a highly-encumbered group, such as tert-butyl, at **R^2** caused to cease the formation of an vinyallene product and hence was the allylic arylation product (**4ka**) only to form which was recovered with 62% percent yield at the end of the reaction. As presence of bulky groups in alkynyl moiety, the reaction was performed with PPh_3 ligand instead of DPEPhos when alkenyl moiety was bulky either. Even if reaction was performed in the presence of PPh_3 when **R^2** was t-butyl- **4ka** was still major product, but 16% vinylallenol (**3ka**) product was obtained.

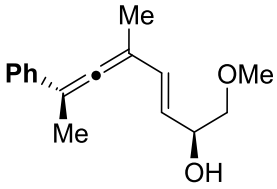
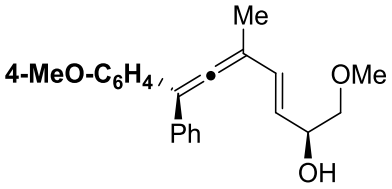
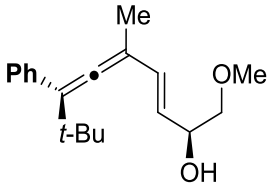
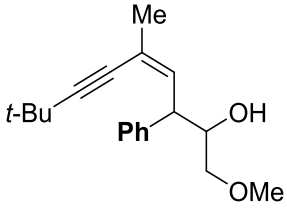
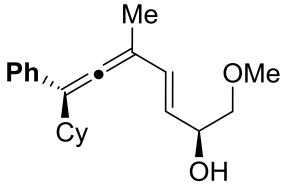
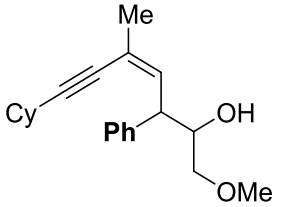
It seems that the method can tolerate various substituent types and organization of substituents (**R^3**) on the epoxide ring moiety. When the pendant oxygen functionality is free hydroxyl group there was some reduction in the corresponding product formation (Entry 10). The presence of this group as benzyloxymethyl group (**3oa**) (Entry 12) or in a silyl protected form (**3ma**) (Entry 11) had no noticible effect on the effectiveness of the method.

While the presence of dimethyl (**1a**) or dimethylmethoxy methyl (**1p**) groups on the oxirane terminus was well tolerated with the proposed methodology and thus the corresponding products were isolated in high yields and dr levels (Entry 13 and 14). The presence of only one methyl substituent (**1r**) on the oxirane terminus, interestingly led the lengthening the reaction period for the complete conversion of the substrate (Entry 15). When there was no substituent on oxirane ring, the desired product **3sa** could also be obtained in a good yield (Entry 16)

.

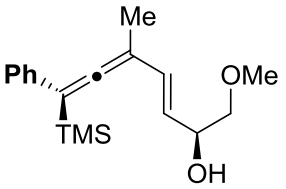
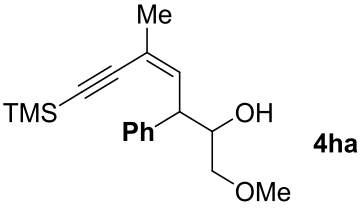
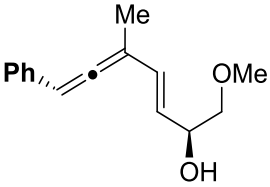
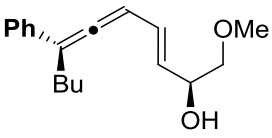
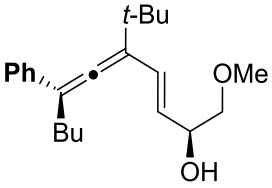
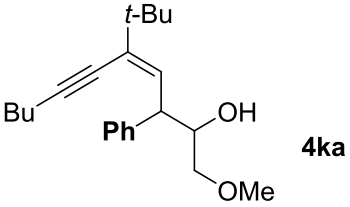
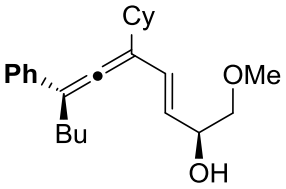
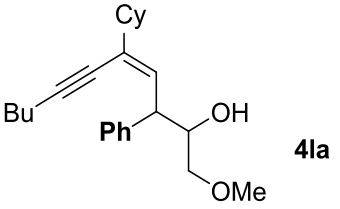
Table 4.9. Arylation of Enyne Oxiranes



Entry	Product		Time (h)	Yield %[a]	dr
1	 **3da**		1	**93**	**92:8**
2	 **3eh**		3	**93**	**91:9**
3	 **3fa**	DPEPhos	16	**68**	**92:8**
		PPh_3	10	**71**	**88:12**
	 **4fa**	DPEPhos	16	**11**	**N.D.[b]**
		PPh_3	10	**5**	**N.D.[b]**
4	 **3ga**	DPEPhos	8	**71**	**92:8**
		PPh_3	5	**73**	**85:15**
	 **4ga**	DPEPhos	8	**9**	**N.D.[b]**
		PPh_3	5	-	-

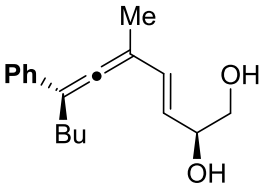
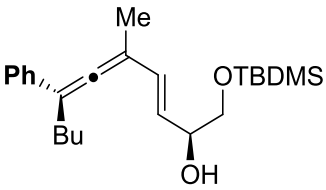
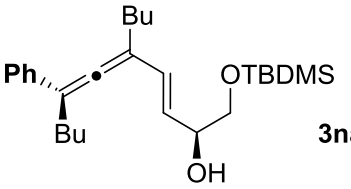
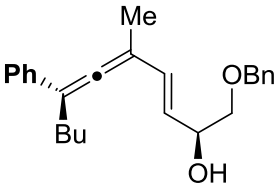
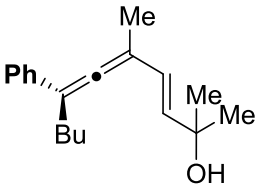
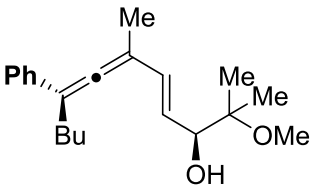
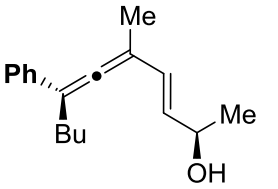
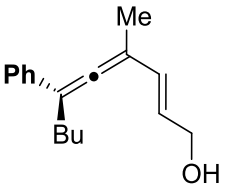
(cont. on next page)

Table 4.9 (cont.)

	 **3ha**	DPEPhos	16	**71**	**91:9**
		PPh_3	8	**77**	**87:13**
5	 **4ha**	DPEPhos	16	**12**	**N.D.[b]**
		PPh_3	8	-	-
6	 **3ia**		1	**74**	**91:9**
7	 **3ja**		4	**67**	**89:11**
	 **3ka**	DPEPhos	8	-	-
		PPh_3	3	**16**	**85:15**
8	 **4ka**	DPEPhos	8	**62**	**83:17**
		PPh_3	3	**61**	**81:19**
	 **3la**	DPEPhos	3	**68**	**88:12**
		PPh_3	2	**72**	**85:15**
9	 **4la**	DPEPhos	3	**16**	**N.D.[b]**
		PPh_3	2	-	-

(cont. on next page)

Table 4.9 (cont.)

10	 **3ca**	1.5	**78**	**91:9**
11	 **3ma**	2	**87**	**92:8**
12	 **3na**	1.5	**88**	**92:9**
13	 **3oa**	2.5	**88**	**90:10**
14	 **3aa**	1.5	**94**	**-**
15	 **3pa**	2	**87**	**92:8**
16	 **3ra**	16	**73**	**91:9**
17	 **3sa**	2	**78**	**-**

Reactions were performed with 0.1 mmol **1** and 3 eq. of **2a**, [a] Isolated yield, [b] Not Determined

An unexpected result has been faced with the substrate having an endocyclic double bond. The reaction resulted in formation of an arylated dienone structure (**5ta**) with 55% percent yield together with an allylic arylation product (**4ta**) was obtained with 10% yield (Figure 4.6.). The expected vinylallene **3ta** should be the precursor the structure **5ta**. As it is formed, successive isomerization and tautomerization of **3ta** should be responsible for the formation of **5ta**.

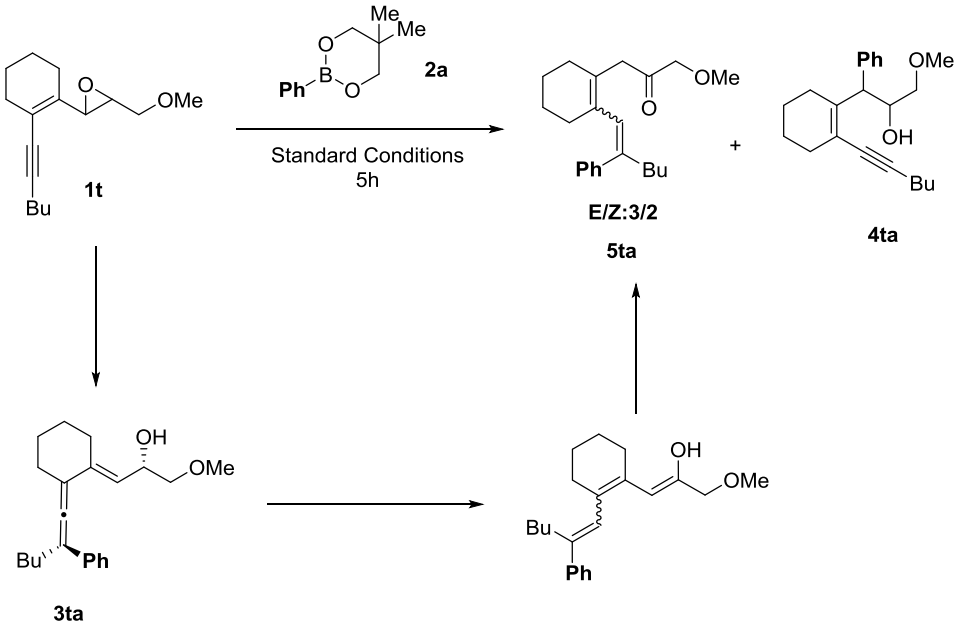


Figure 4.5. Pd-Catalyzed Reaction of the Enyne Substrate (**1s**) Containing an Endocyclic Double Bond with **2a**

To determine which diastereomer is the major one, a reaction with methyl ester group on alkynyl moiety (**1v**) was performed (Figure 4.6). Ester group was chosen because forming arylated vinylallenol is identical with the product of alkoxycarbonylation reaction of enyne epoxide that bears phenyl group on alkynyl moiety which was published in 2015 by Kuş et al. As comparing the 1H NMR spectra of these two products, we can conclude that different diasteromers of the same compound was formed in arylation and alkoxycarbonylation reaction. Kuş et al. also determined the exact structure of compound by X-Ray crystallography.

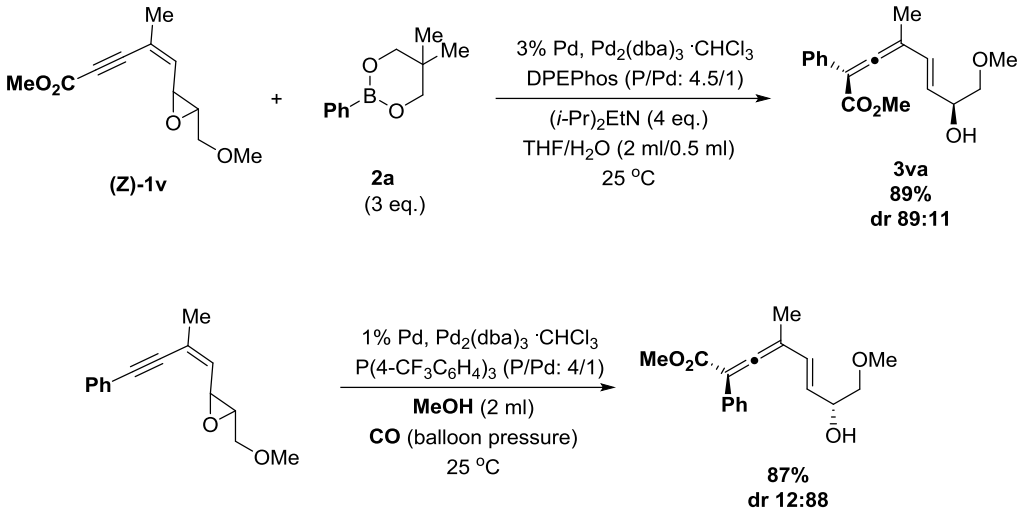


Figure 4.6. Determination of Major Diastereomer

As an application study of vinyl allenol products a Diels-Alder cyclization reaction was conducted between **3ba** with phenyl maleimide which yielded the expected [4+2] cyclization product in 62% percent yield with complete endo and facial selectivities (Figure 4.7). This reaction revealed the importance of vinyl allenols for producing a potential valuable building block for the synthesis of complex molecules.

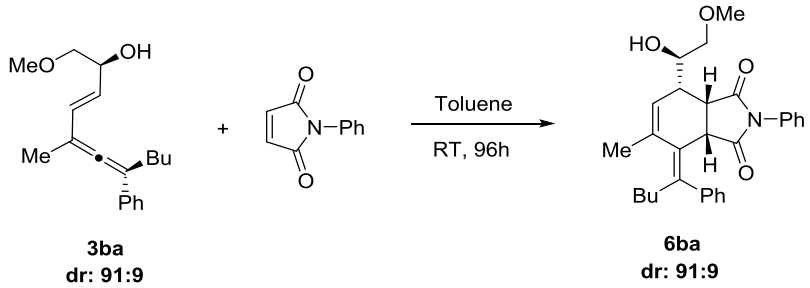


Figure 4.7. Diels-Alder Reaction of 3ba with Phenyl maleimide

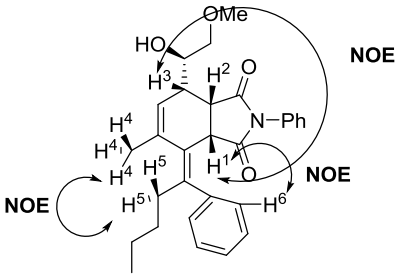


Figure 4.8. NOESY study of 6ba

The relative configuration of the adduct **6ba** was determined through NOESY NMR analysis. The NOESY spectrum showed a relationship between H^1 and H^3, H^1 and H^6, and H^4 and H^5 indicating a structure in consistent with those of previous (Whipple and Kelly, 1988 and Luo et al., 2016).

The mechanisms illustrated in Figure 4.8. is proposed to account for the stereoselective formation of **3**. The reaction cycle should begin with ring-opening by the attack of a palladium complex to **1** in anti-mode leading to formation of π-allylpalladium complexes **A** and **B** respectively. After transmetallation with arylboron intermediates **A'** and **B'** forms. These intermediates additionally undergo a palladium shift to the far alkynyl carbon proceeding mainly with retention to form vinylallenyl palladium complex **C**, respectively. When a bulky group is positioned at $\mathbf{R^1}$ and $\mathbf{R^2}$ it retards the effective migration of the π-allyl coordinated palladium and as a result allylic arylated products form. (Figure 4.9.)This σ-allenylpalladium complex (**C**) undergo reductive elemination to yield **3** stereoselectively.

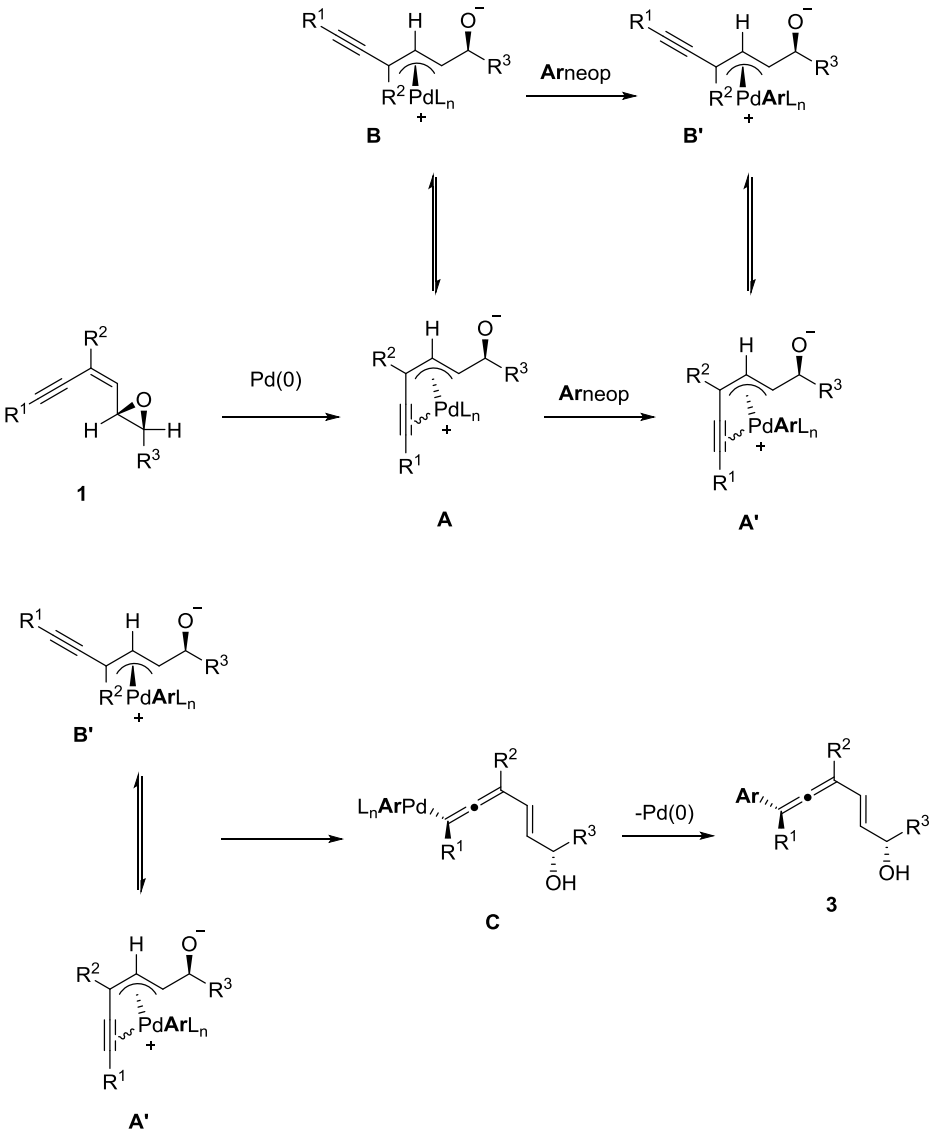


Figure 4.9. Mechanism of Arylation of Conjugated Enyne Oxiranes

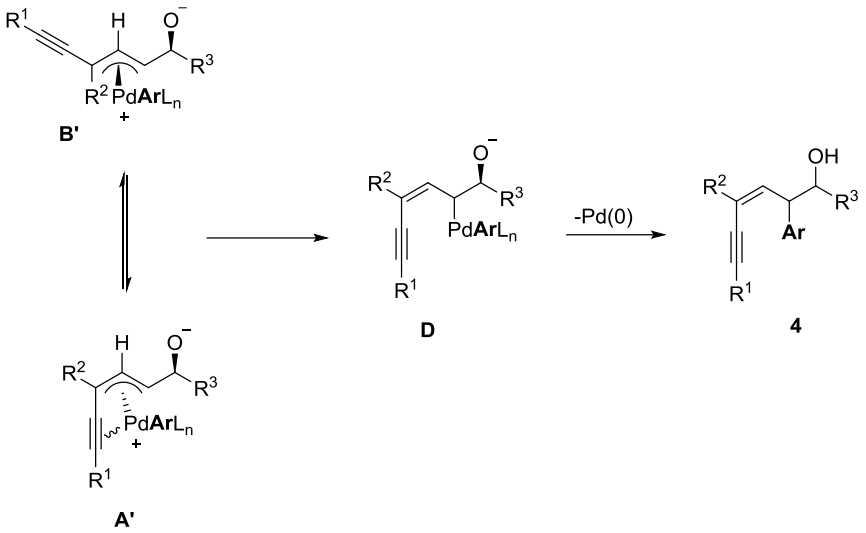


Figure 4.10. Mechanism of Allylic Arylated Products

CHAPTER 5

CONCLUSION

To conclude, a novel palladium-catalyzed diastereoselective arylation reaction of 2,4-enyne oxiranes with organoborons was performed. This palladium catalyzed reactions resulted in the introduction of possibly functionalized group in 1,5-relation with respect to the oxirane group, affording aryl bearing vinylallenol structures. These products are versatile building blocks for valuable target molecules that is proofed by performing Diels-Alder cyclization reaction of synthesized vinylallenol.

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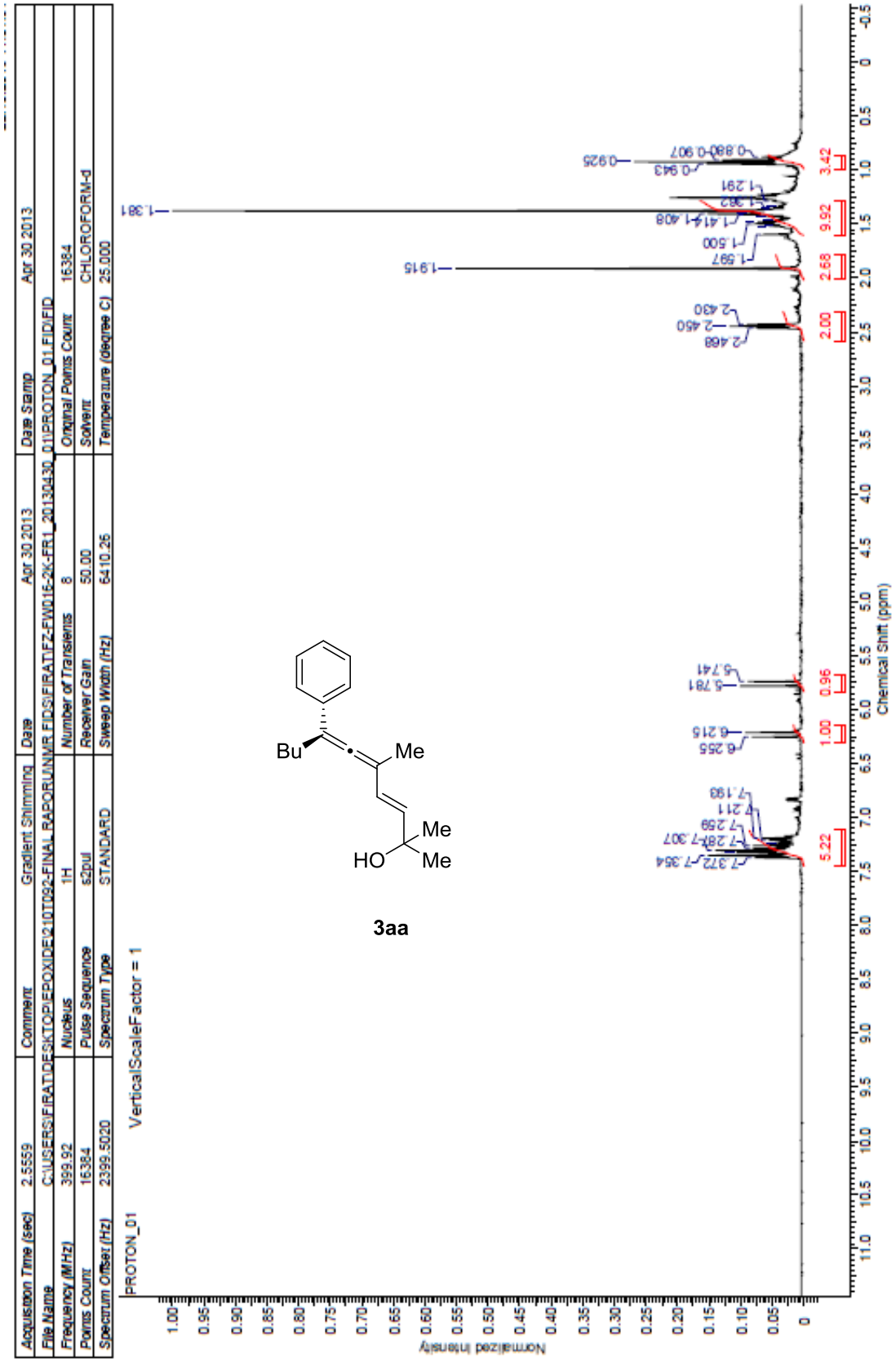
APPENDIX A

^{1}H and ^{13}C NMR SPECTRA of PRODUCTS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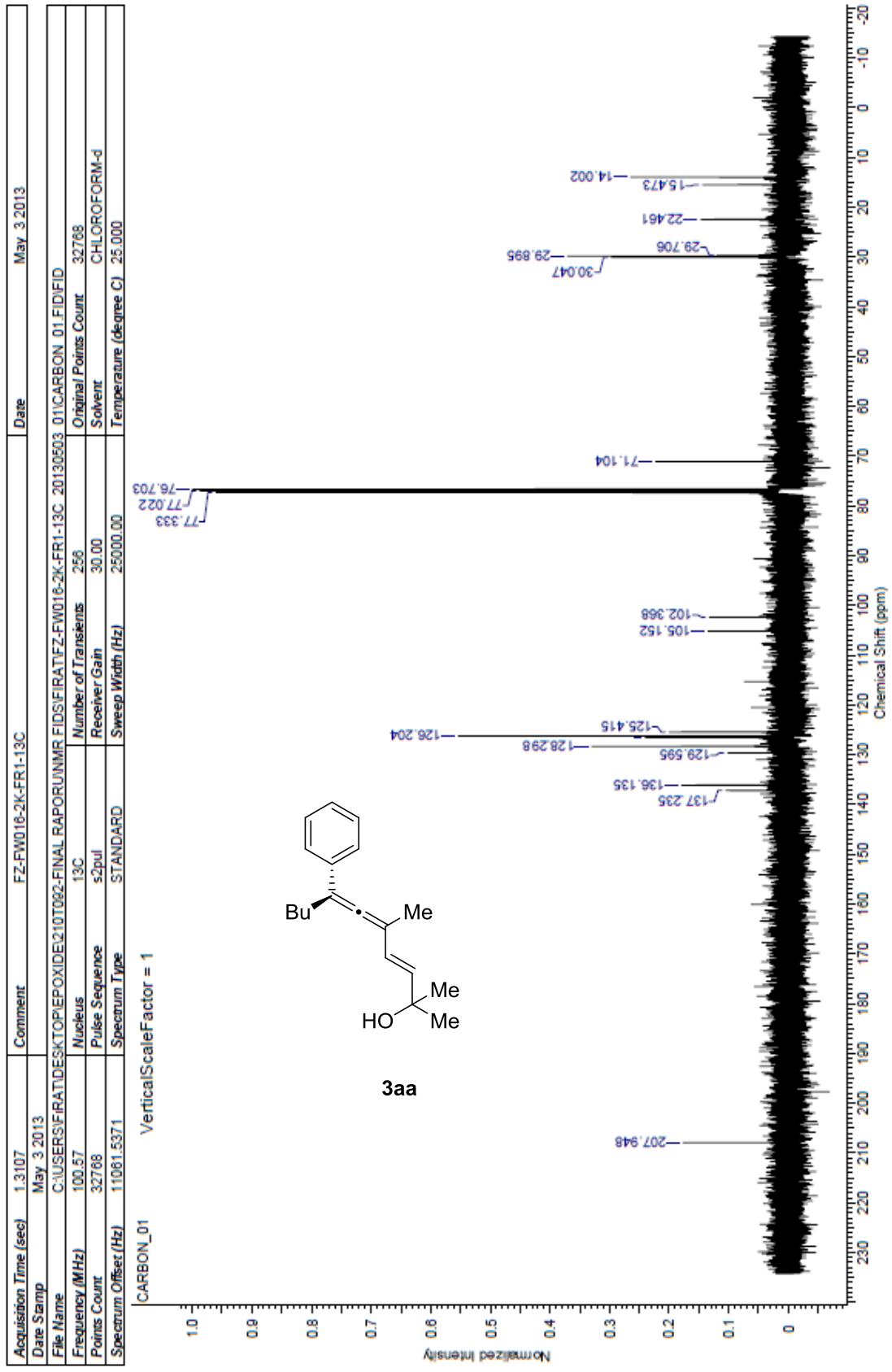
Me
HO
Me
3aa
Normalized Intensity
Chemical Shift (ppm)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Nucleus 13C
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Points Count 32768
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Receiver Gain 30.00
Solvent CHLOROFORM-d
Spectrum Offset (Hz) 11081.5371
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
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136.135
129.595
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71.104
30.047
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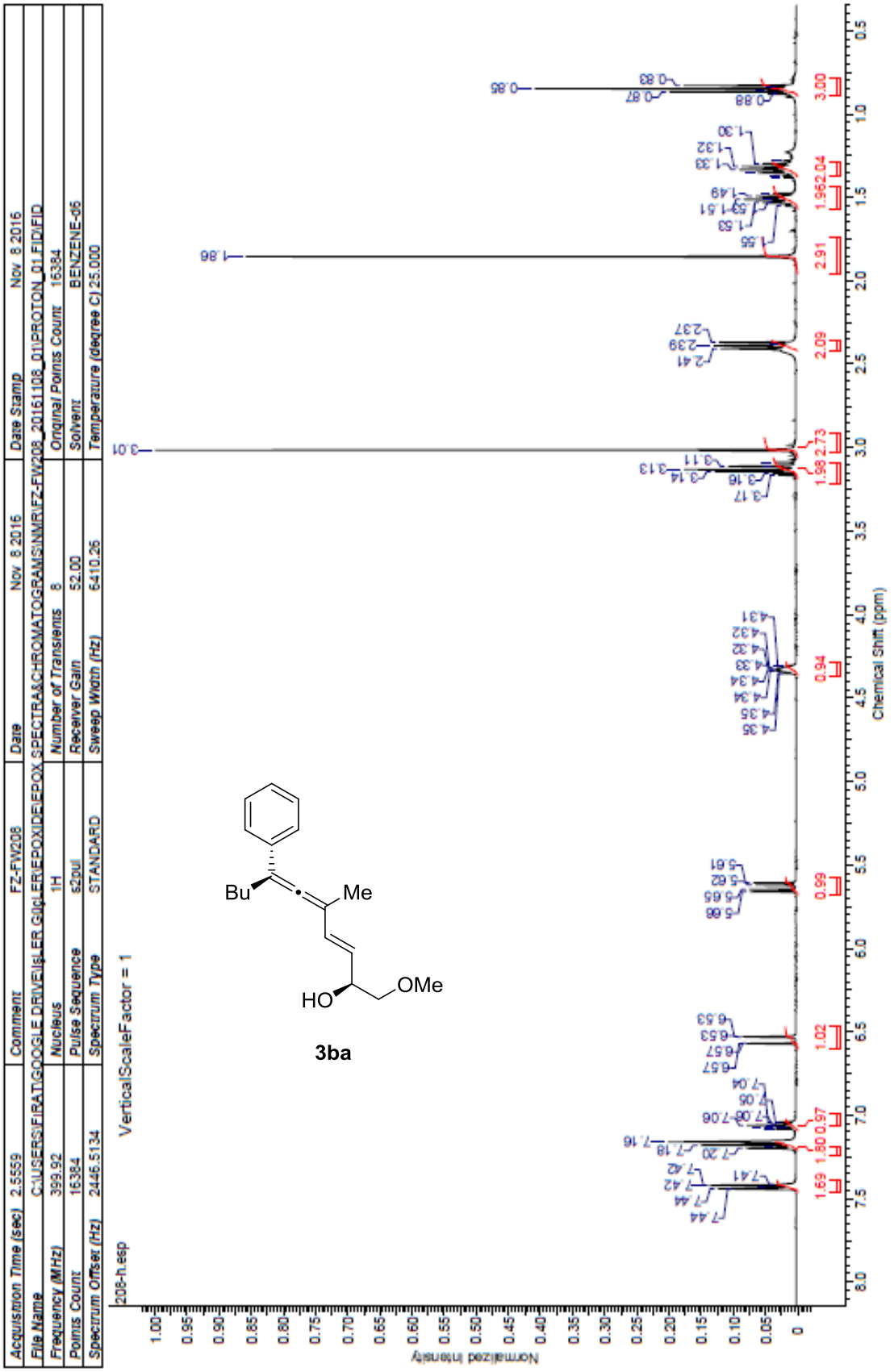
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Points Count 16384
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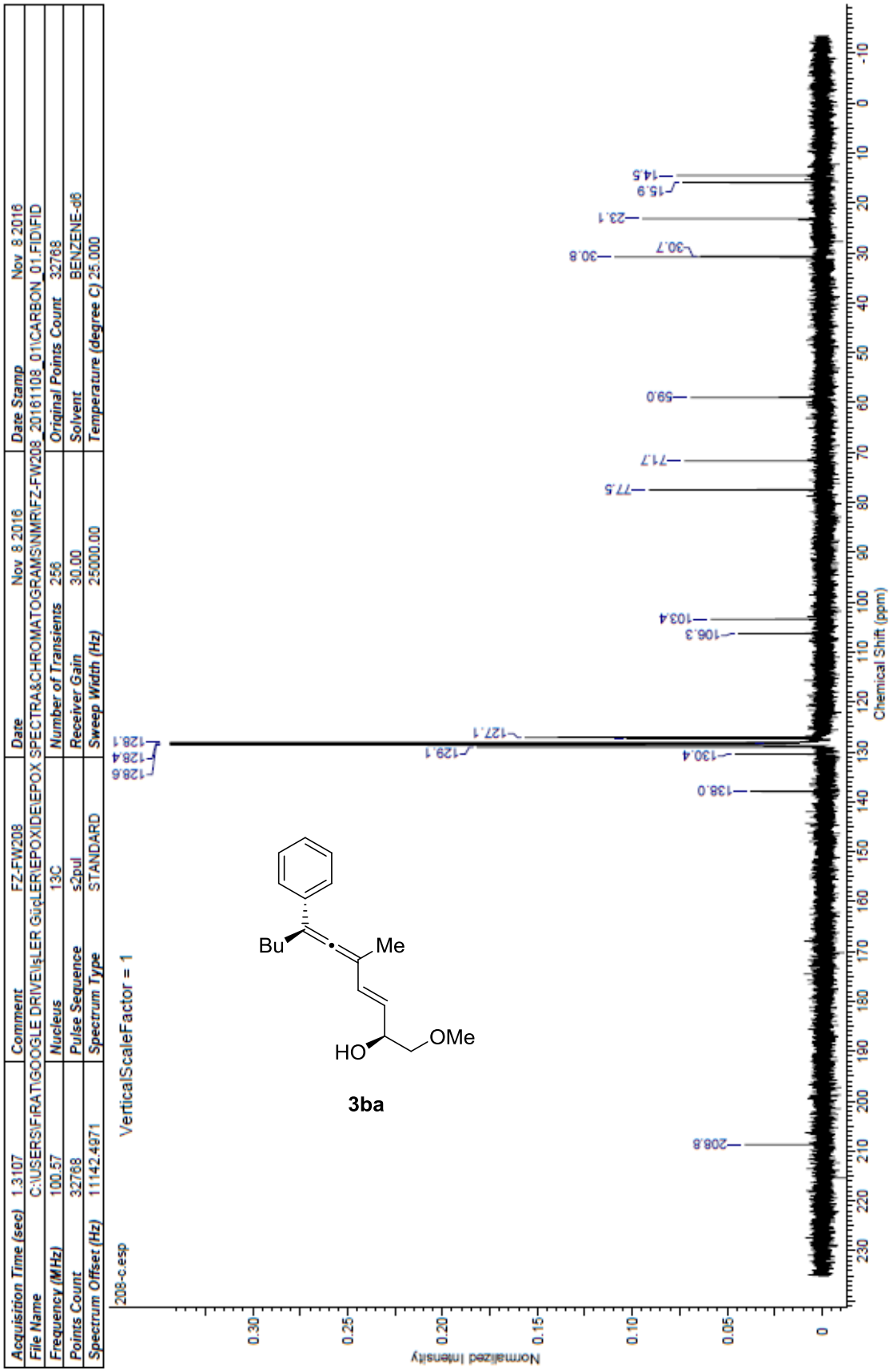
HO
OMe
3ba
Normalized Intensity
Chemical Shift (ppm)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HO
OMe
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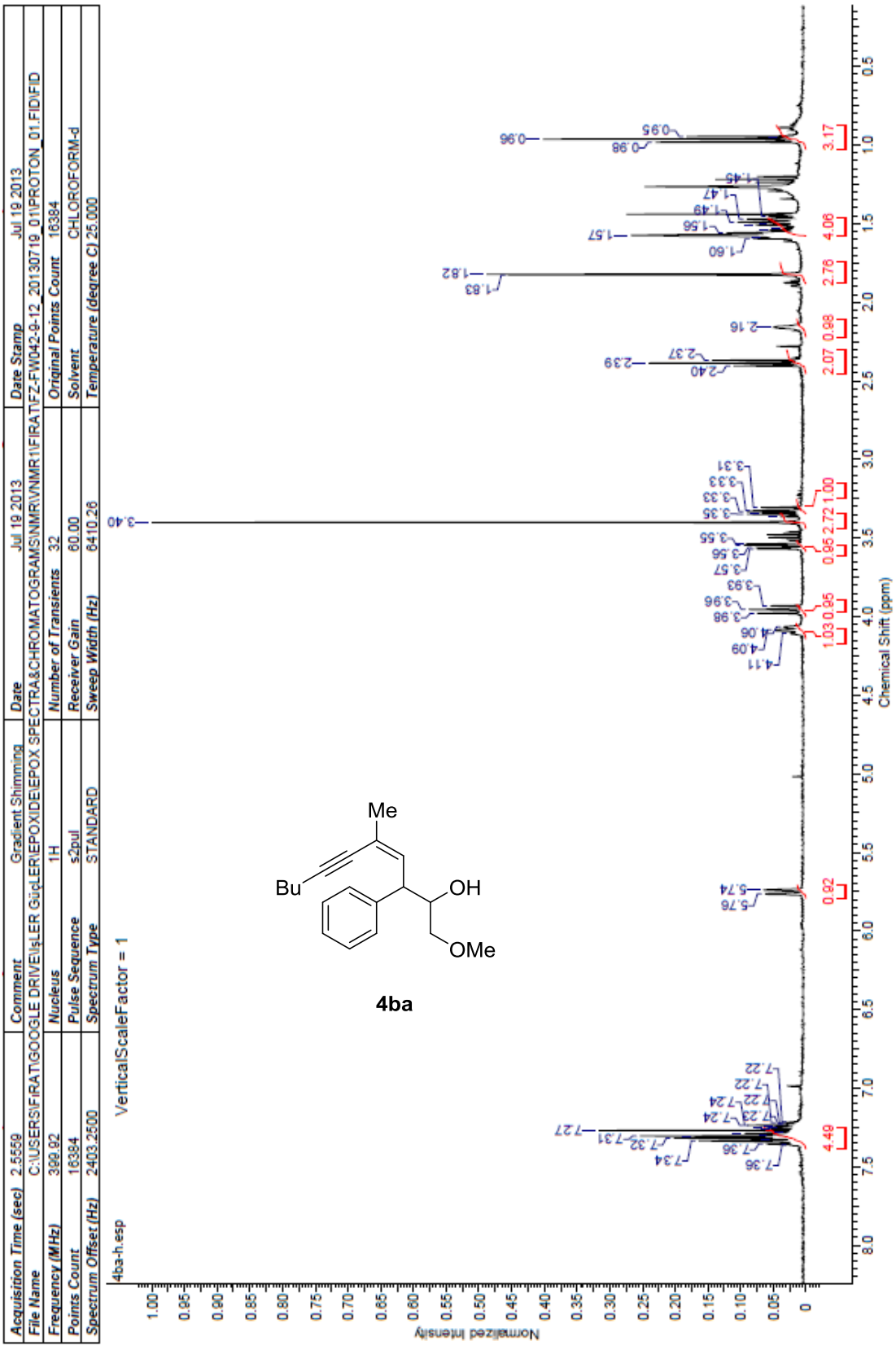
Normalized Intensity
Chemical Shift (ppm)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Receiver Gain 60.00
Solvent CHLOROFORM-d
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Bu
OH
OMe
4ba
Normalized Intensity
Chemical Shift (ppm)

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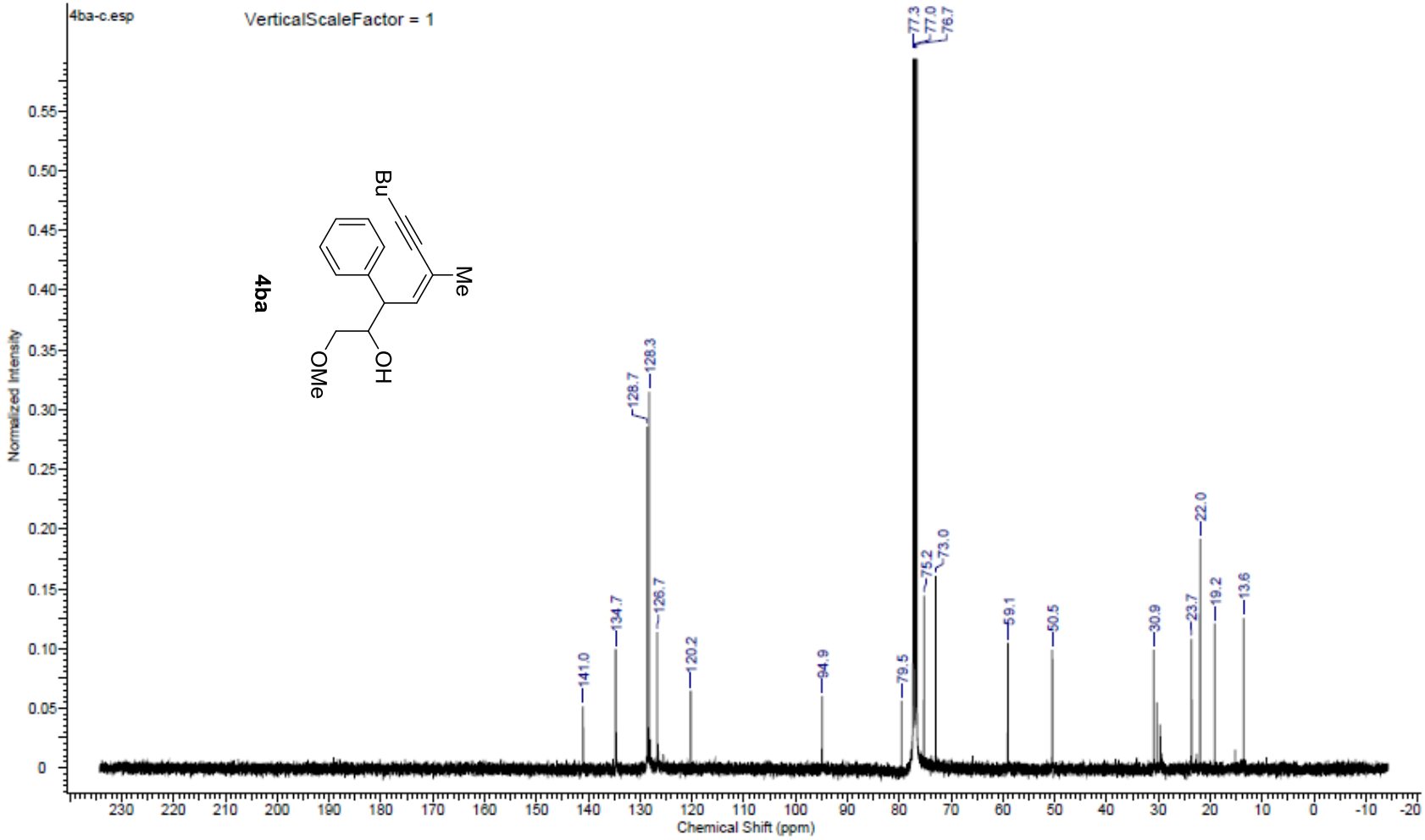

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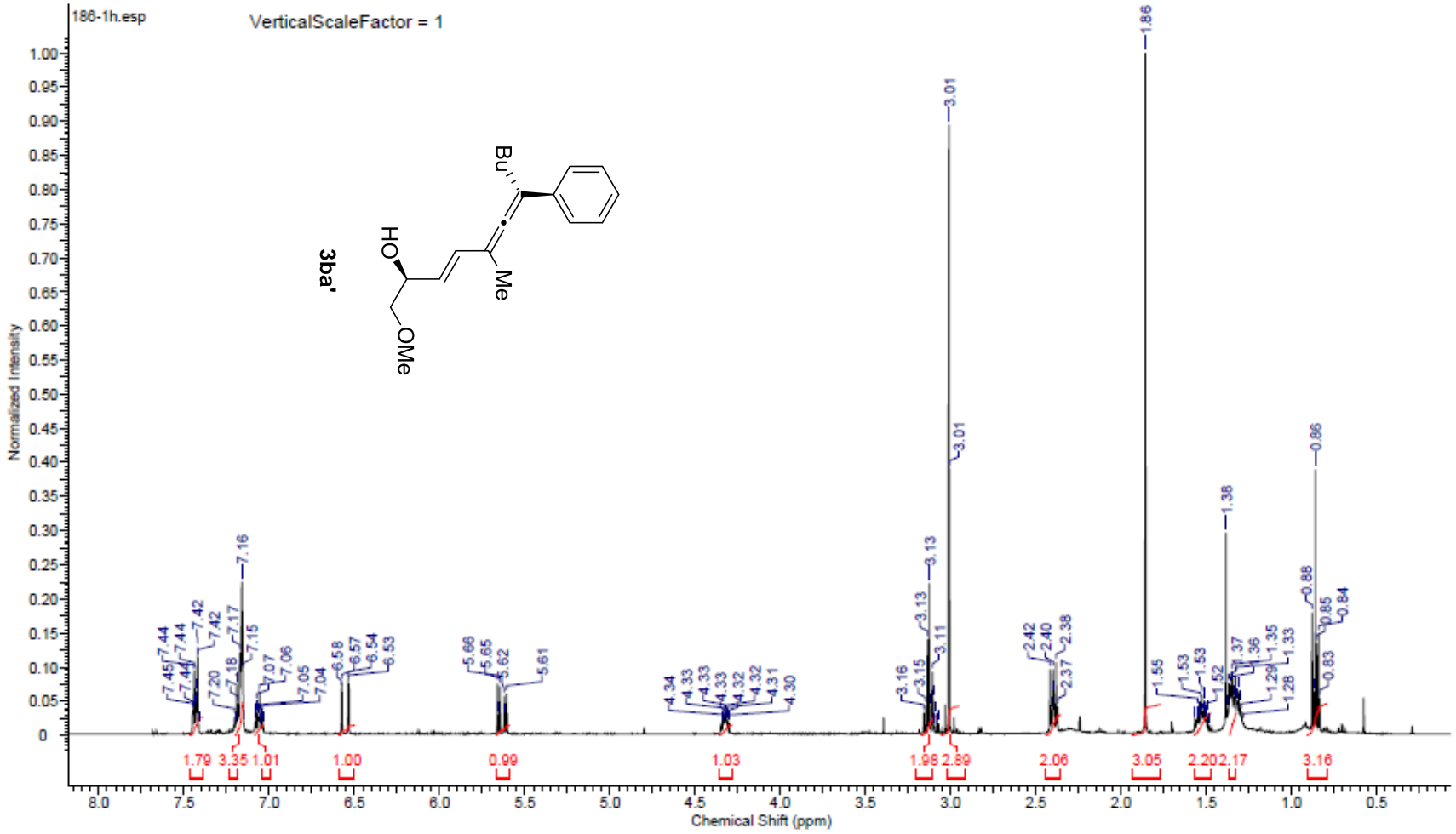

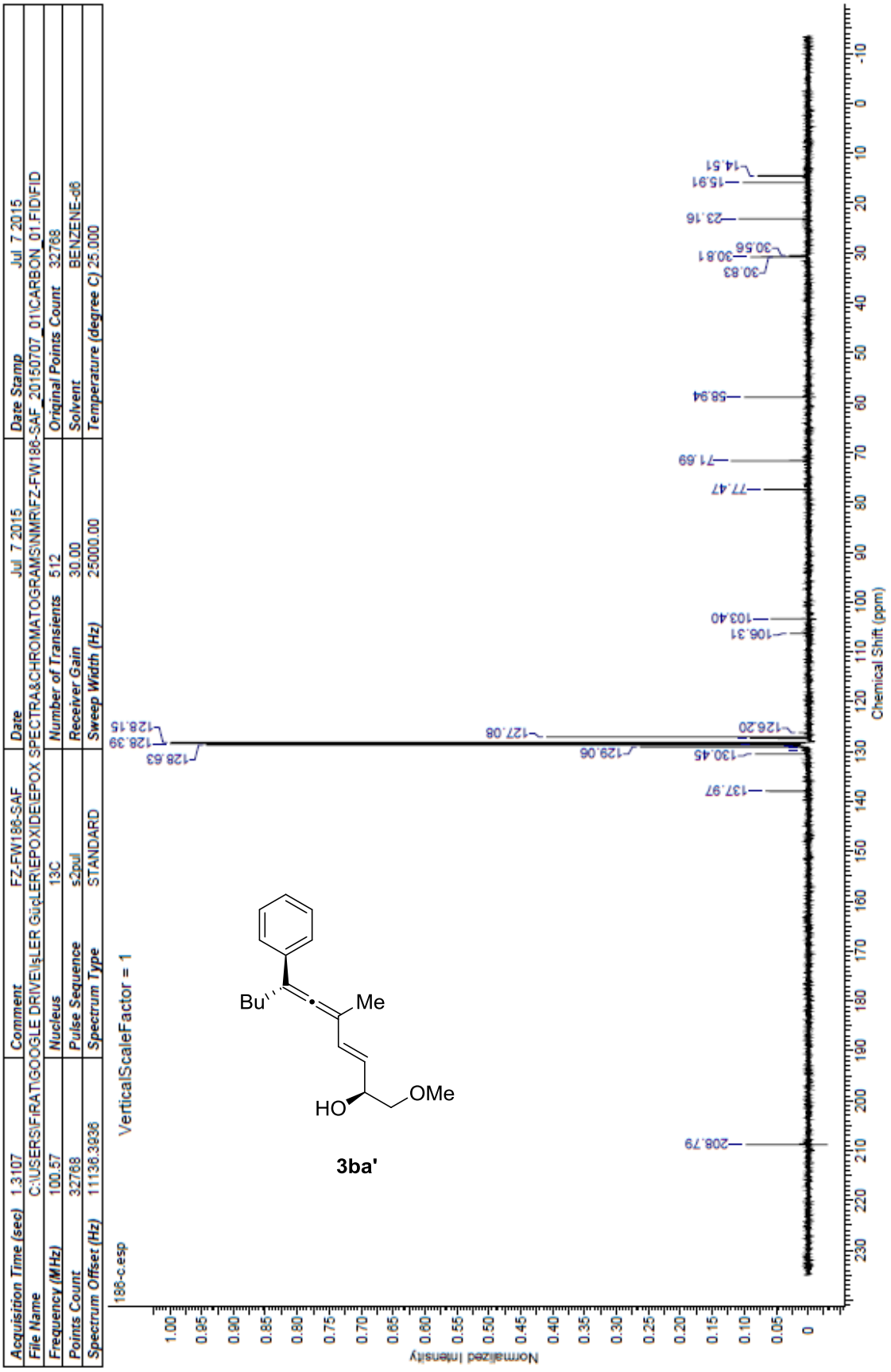
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Solvent BENZENE-d6
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Spectrum Type STANDARD
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Temperature (degree C) 25.000
186-c.esp
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Me
HO
OMe
3ba'
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129.06
128.63
128.39
128.15
127.08
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106.31
103.40
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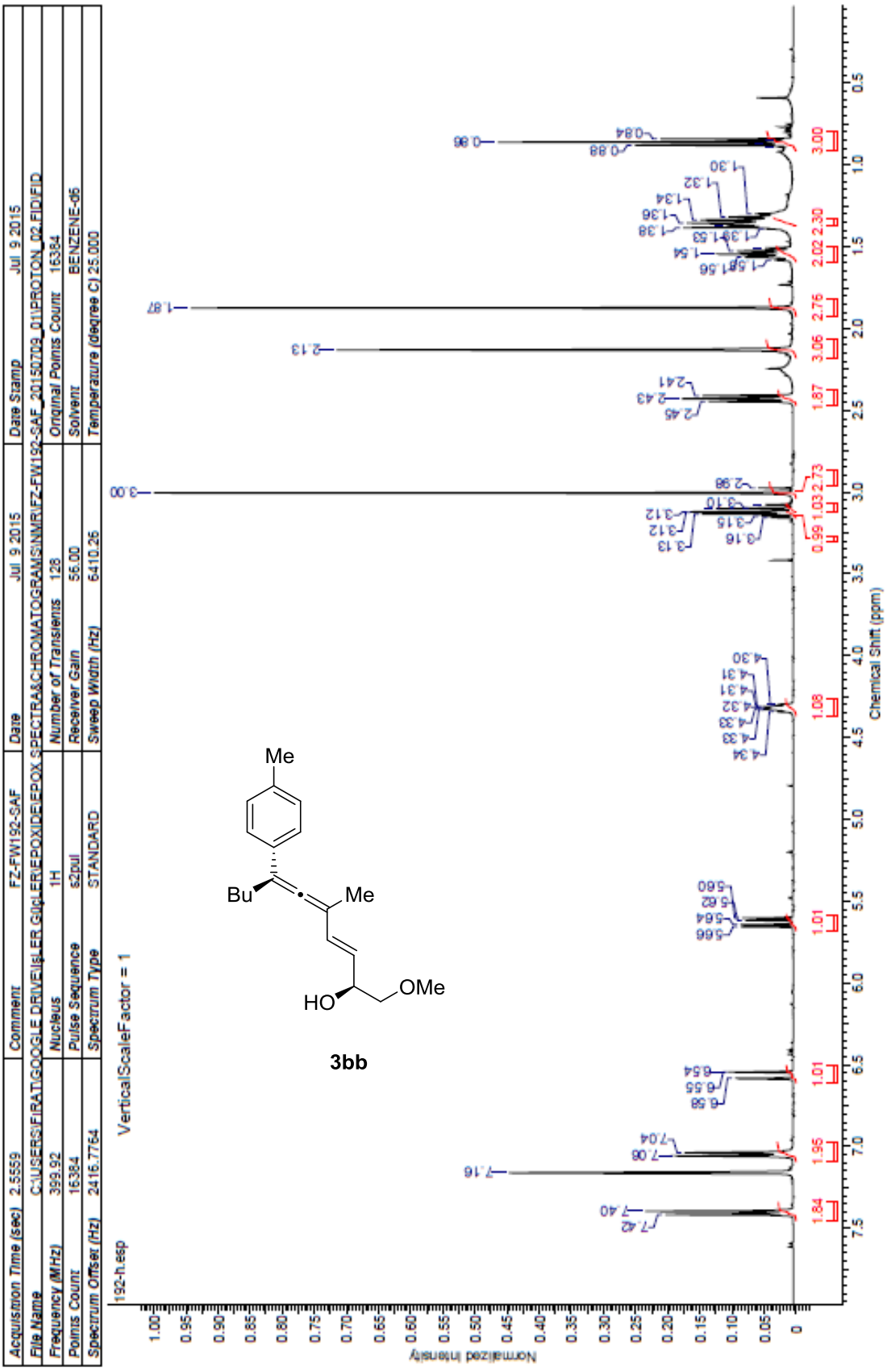
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Solvent BENZENE-d6
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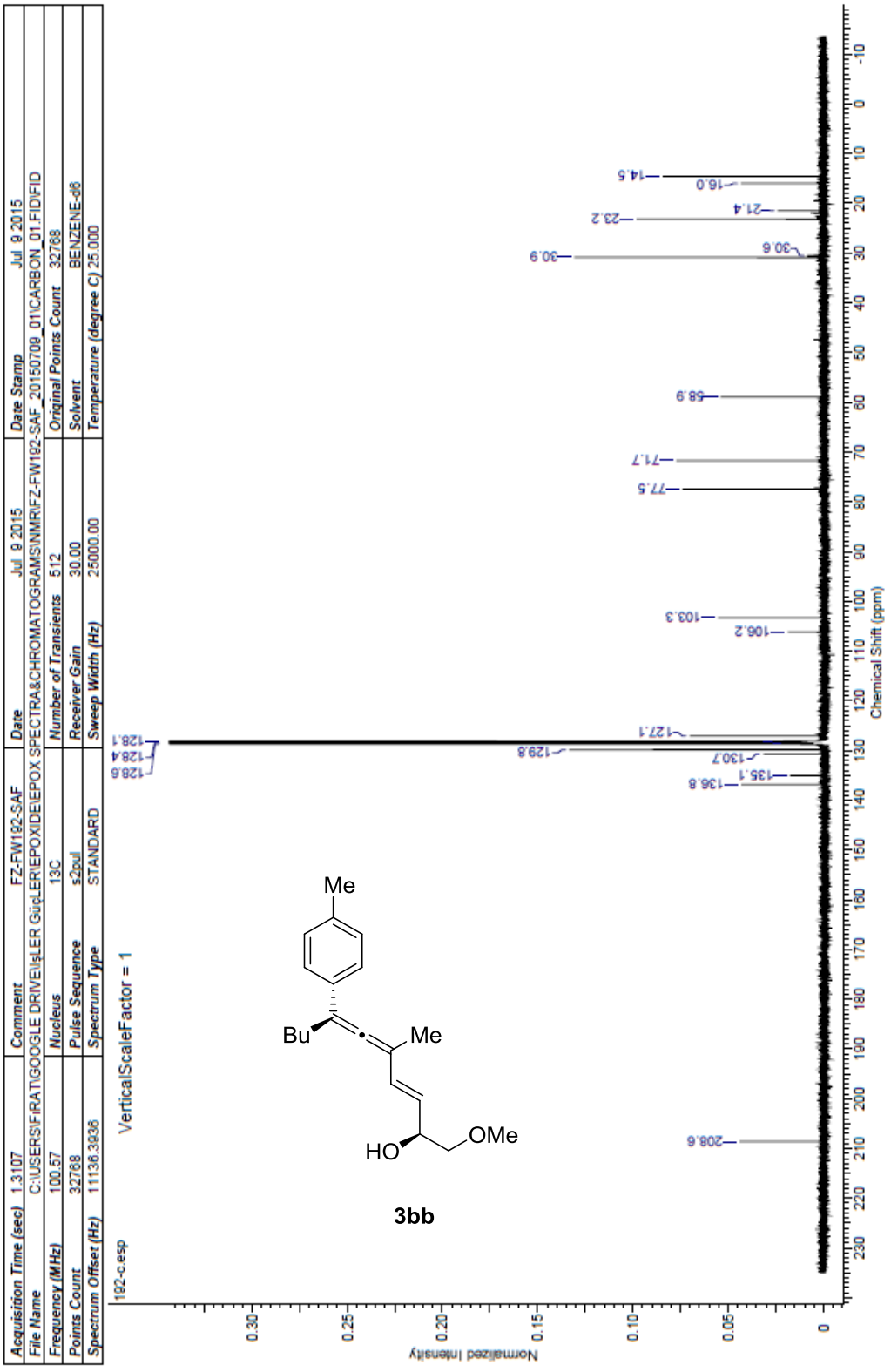
Bu
Me
HO
OMe
3bb
Normalized Intensity
Chemical Shift (ppm)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Points Count 32768
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Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
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130.7
135.1
136.8
208.6
103.2
106.2
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58.9
30.9
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Bu
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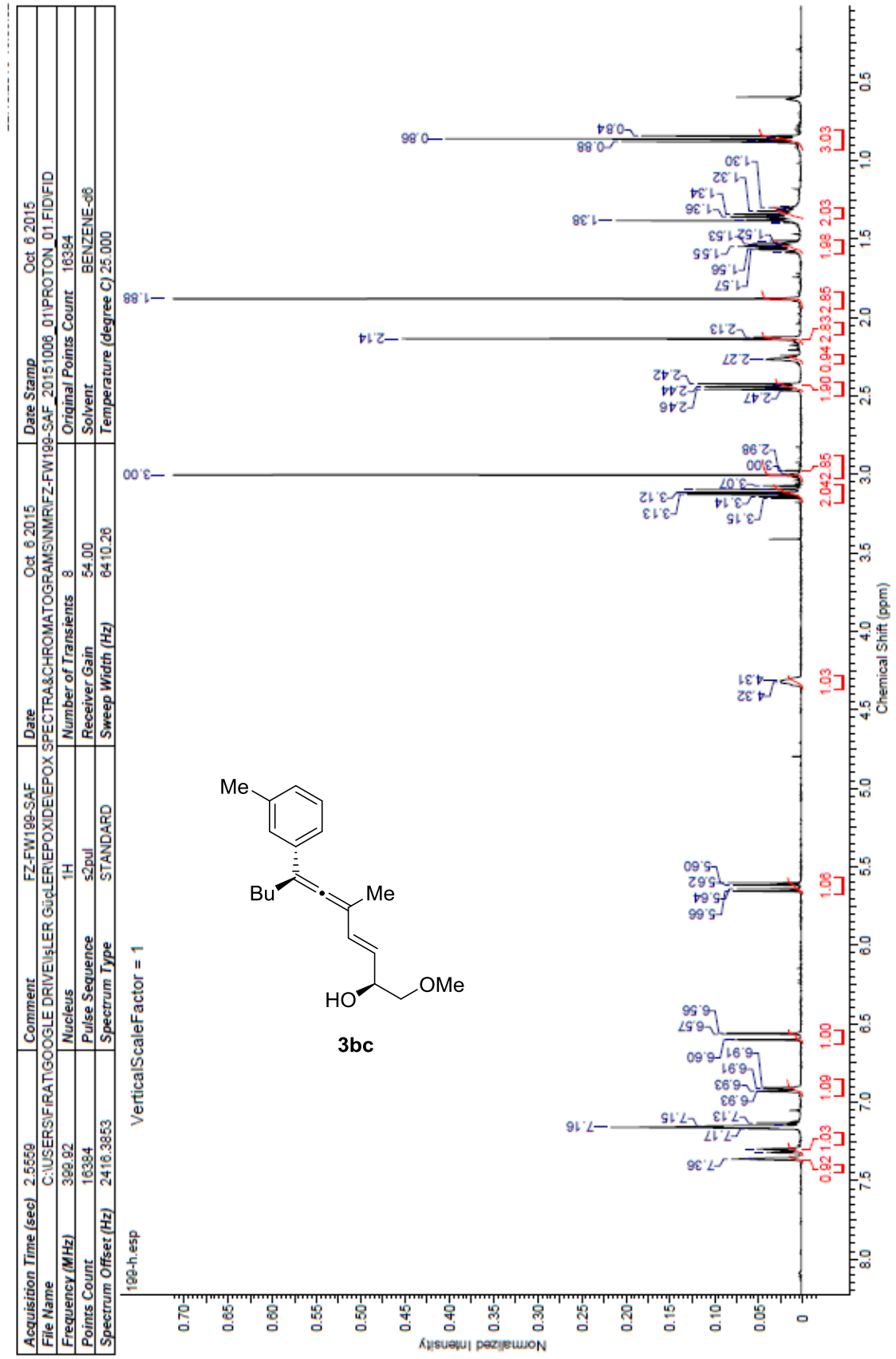
HO
OMe
3bb
Normalized Intensity
Chemical Shift (ppm)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Pulse Sequence s2pul
Spectrum Type STANDARD
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Number of Transients 8
Receiver Gain 54.00
Sweep Width (Hz) 6410.26
Date Stamp Oct 6 2015
Original Points Count 16384
Solvent BENZENE-d6
Temperature (degree C) 25.000
199-h.esp
VerticalScaleFactor = 1
Me
Bu
Me
HO
OMe
3bc
Normalized Intensity
Chemical Shift (ppm)

Acquisition Time (sec)	1.3107	*Comment*	FZ-FW199-SAF	*Date*	Oct 6 2015	*Date Stamp*	Oct 6 2015
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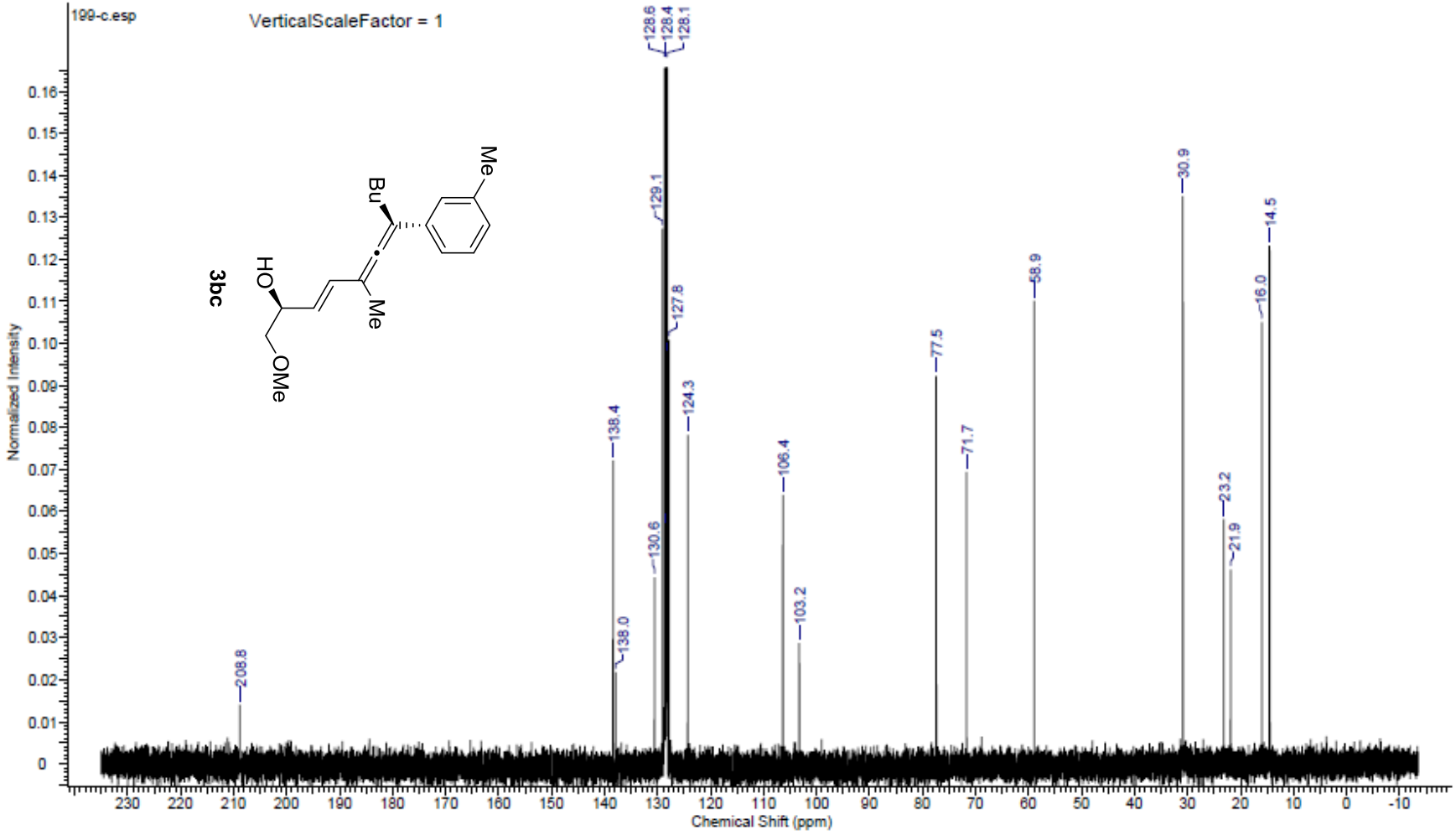

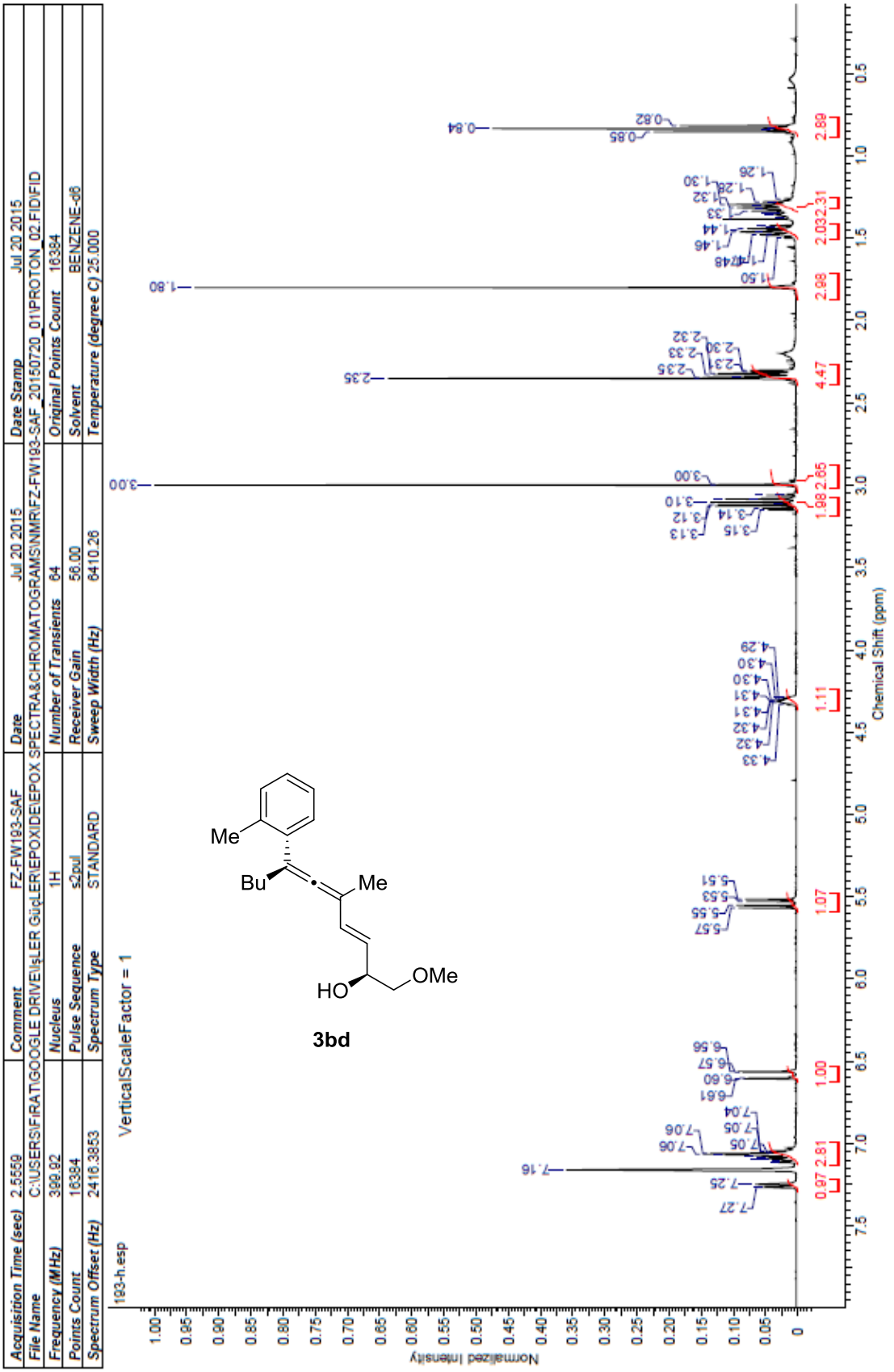
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HO
OMe
3bd
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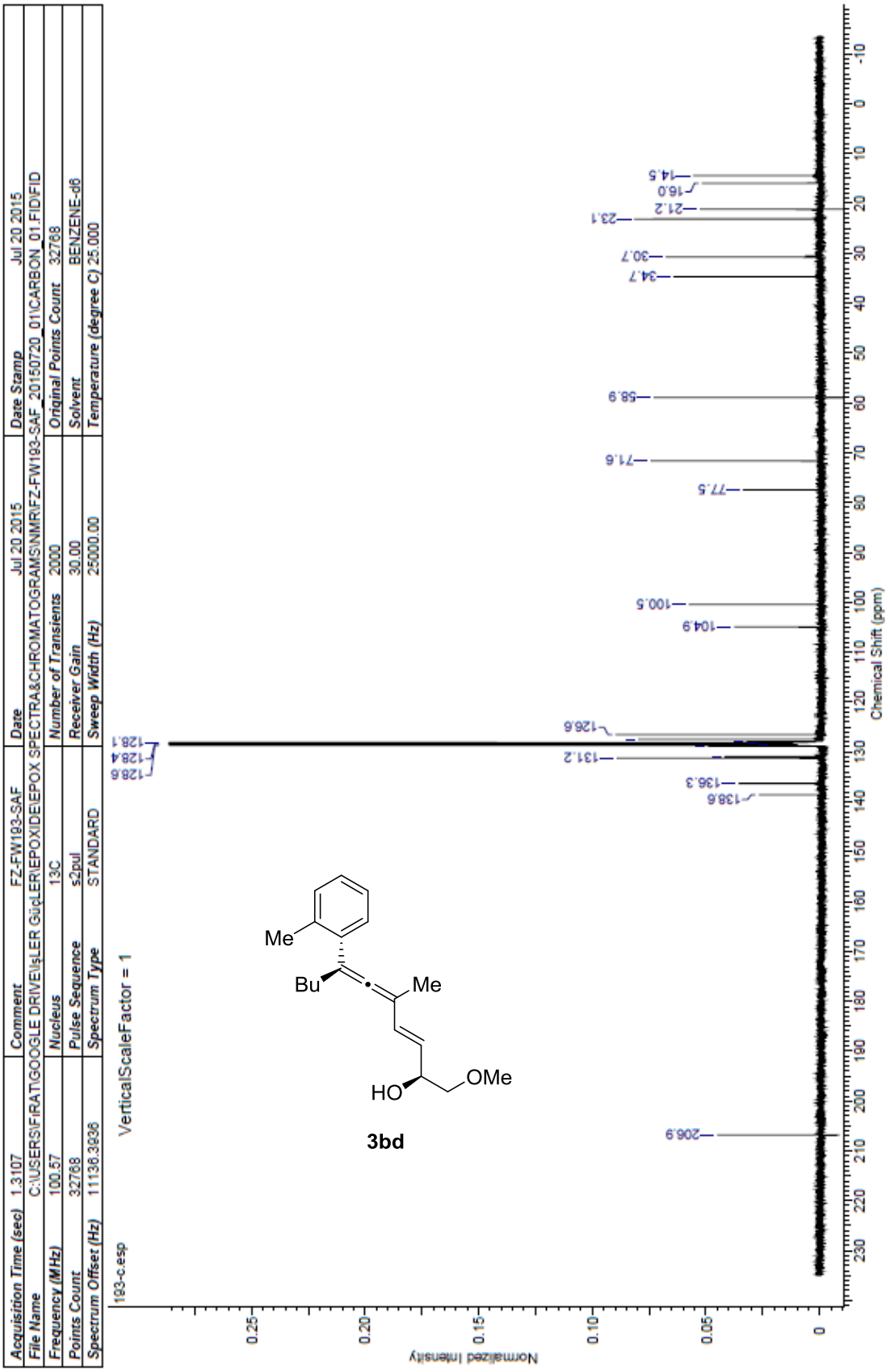
Chemical Shift (ppm)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Points Count 32768
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Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
193-c.esp
VerticalScaleFactor = 1
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Bu
Me
HO
OMe
3bd
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128.4
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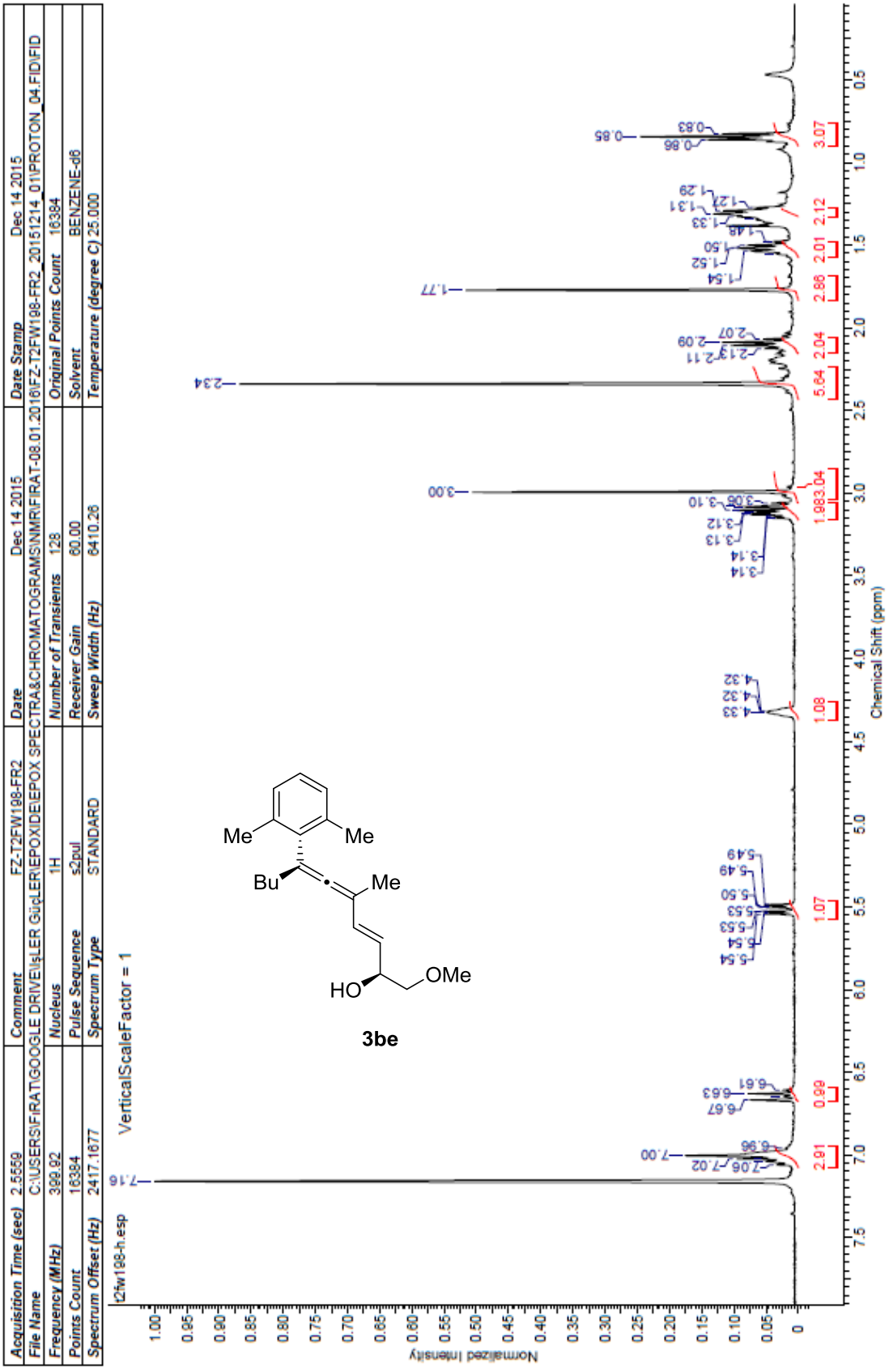
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Sweep Width (Hz) 6410.26
Date Stamp Dec 14 2015
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Solvent BENZENE-d6
Temperature (degree C) 25.000
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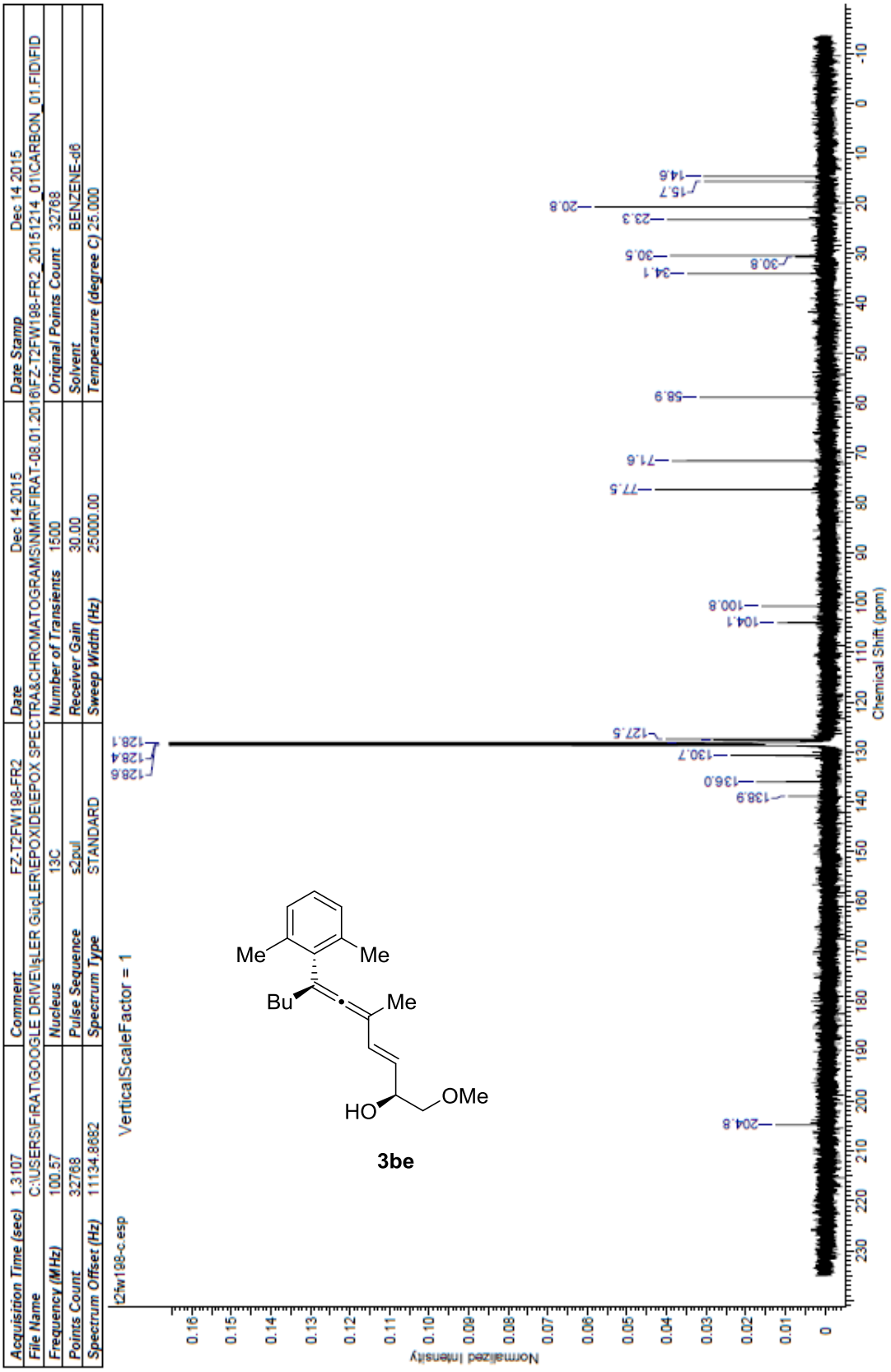
Me
Bu
Me
HO
OMe
3be
Normalized Intensity
Chemical Shift (ppm)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Solvent BENZENE-d6
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130.7
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100.8
104.1
77.5
71.6
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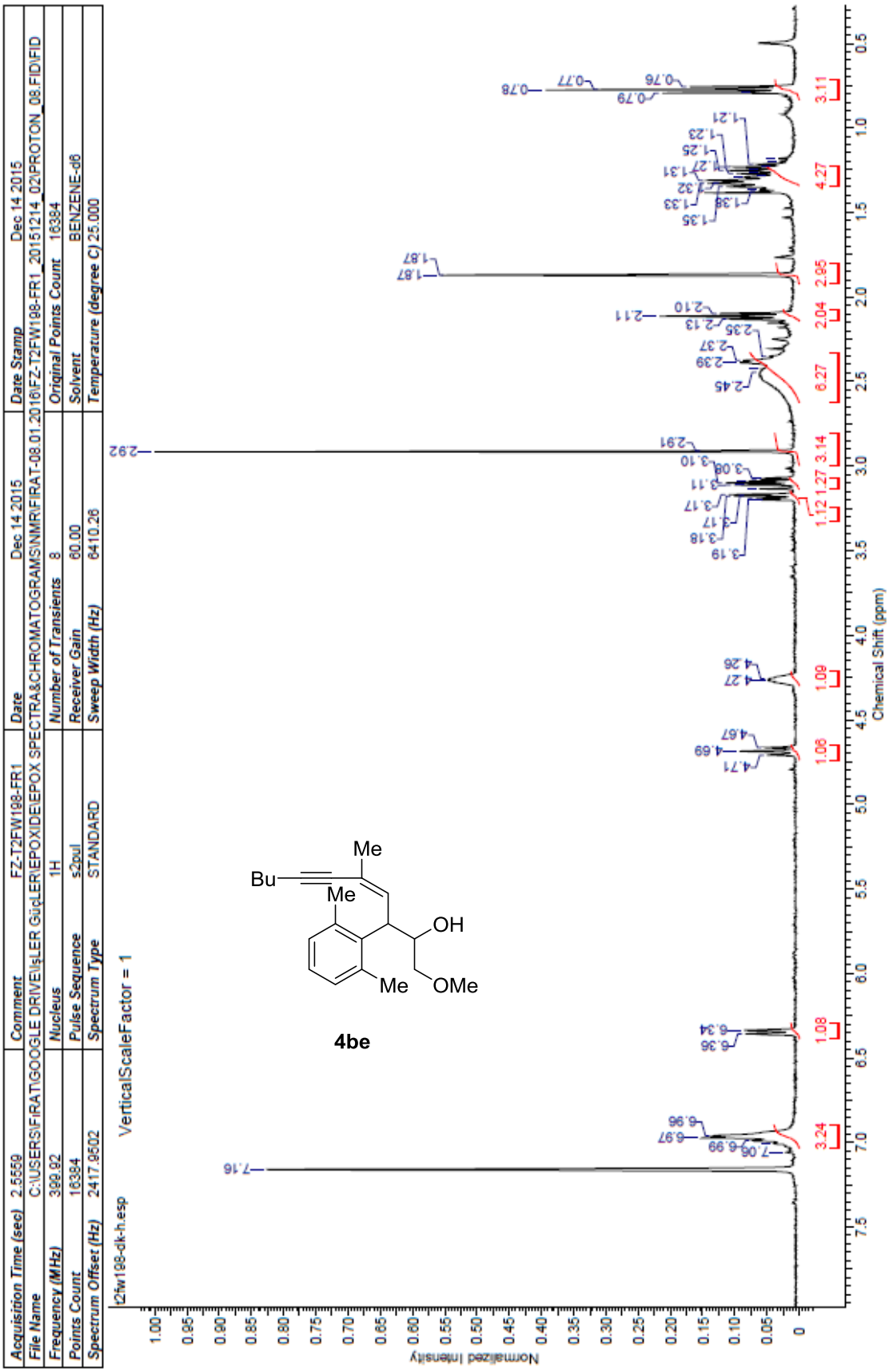
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Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
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Solvent BENZENE-d6
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Spectrum Type STANDARD
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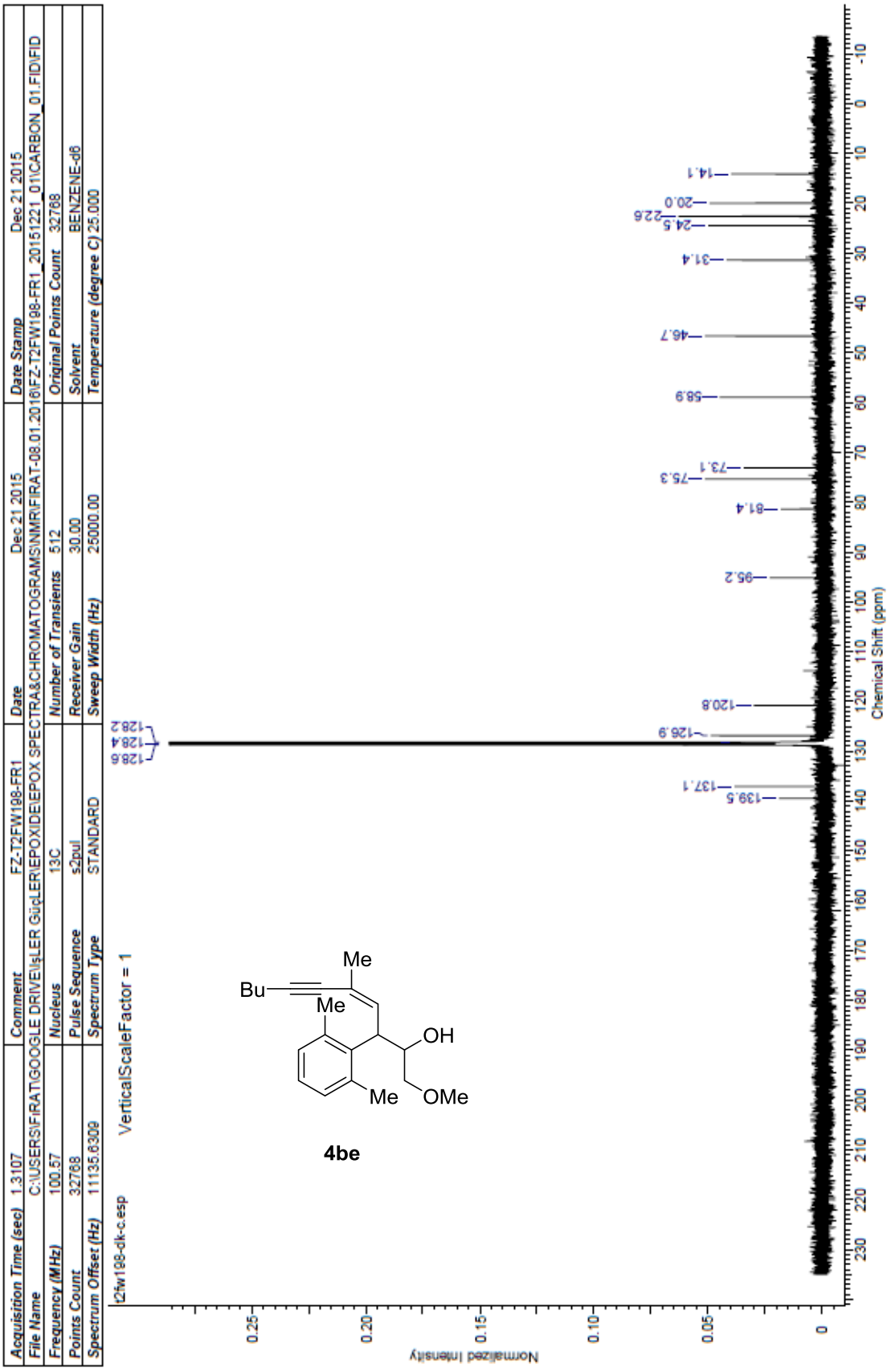
Me
OMe
4be
Normalized Intensity
Chemical Shift (ppm)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Points Count 32768
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Solvent BENZENE-d6
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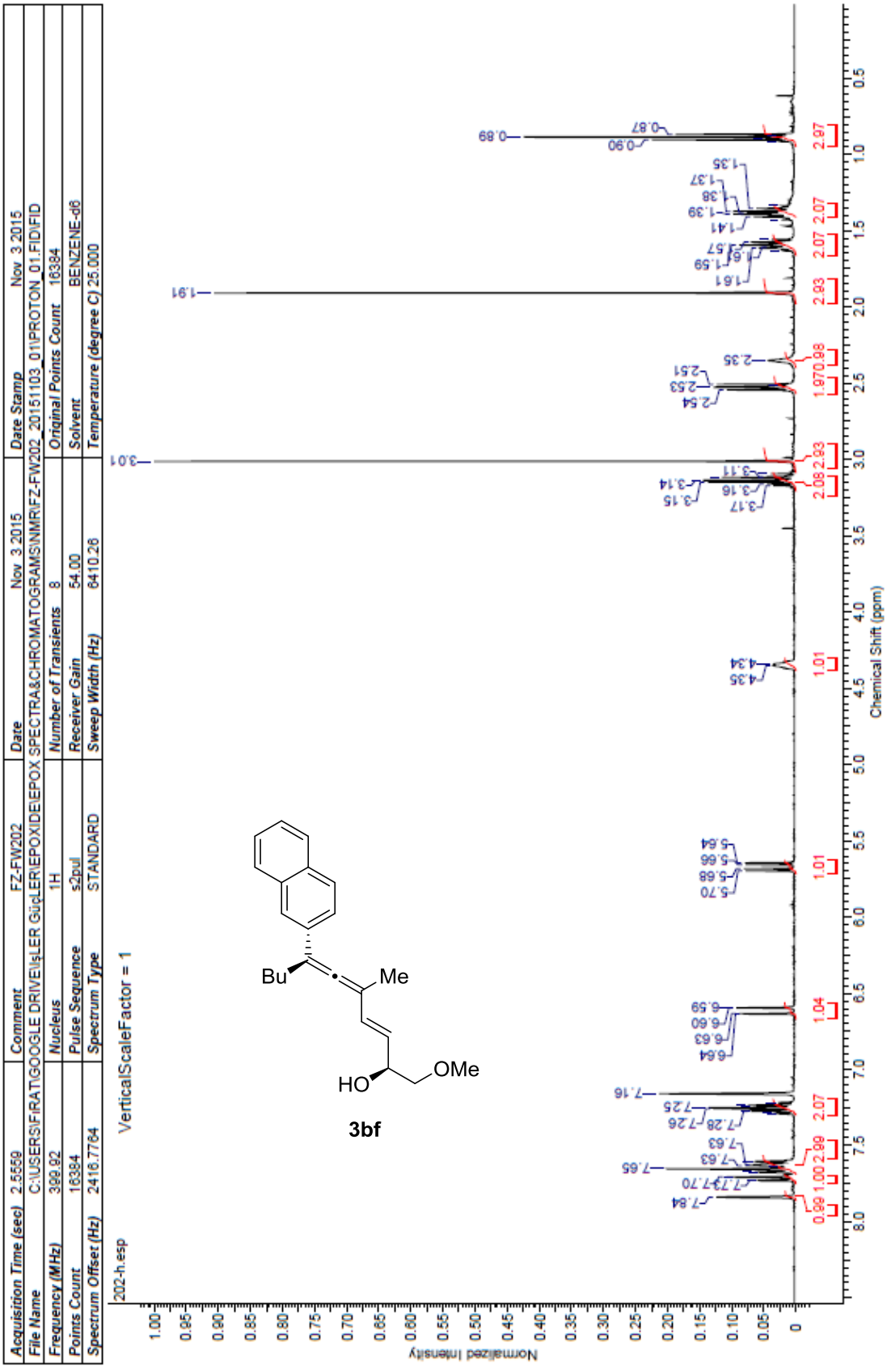
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
t2fw198-dk-c.esp
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
128.6
128.4
128.2
126.9
120.8
139.5
137.1
95.2
81.4
75.3
73.1
58.9
46.7
31.4
24.5
22.6
20.0
14.1
Me
Bu
Me
OH
Me
OMe

4be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Comment FZ-FW202
Date Nov 3 2015
Date Stamp Nov 3 2015
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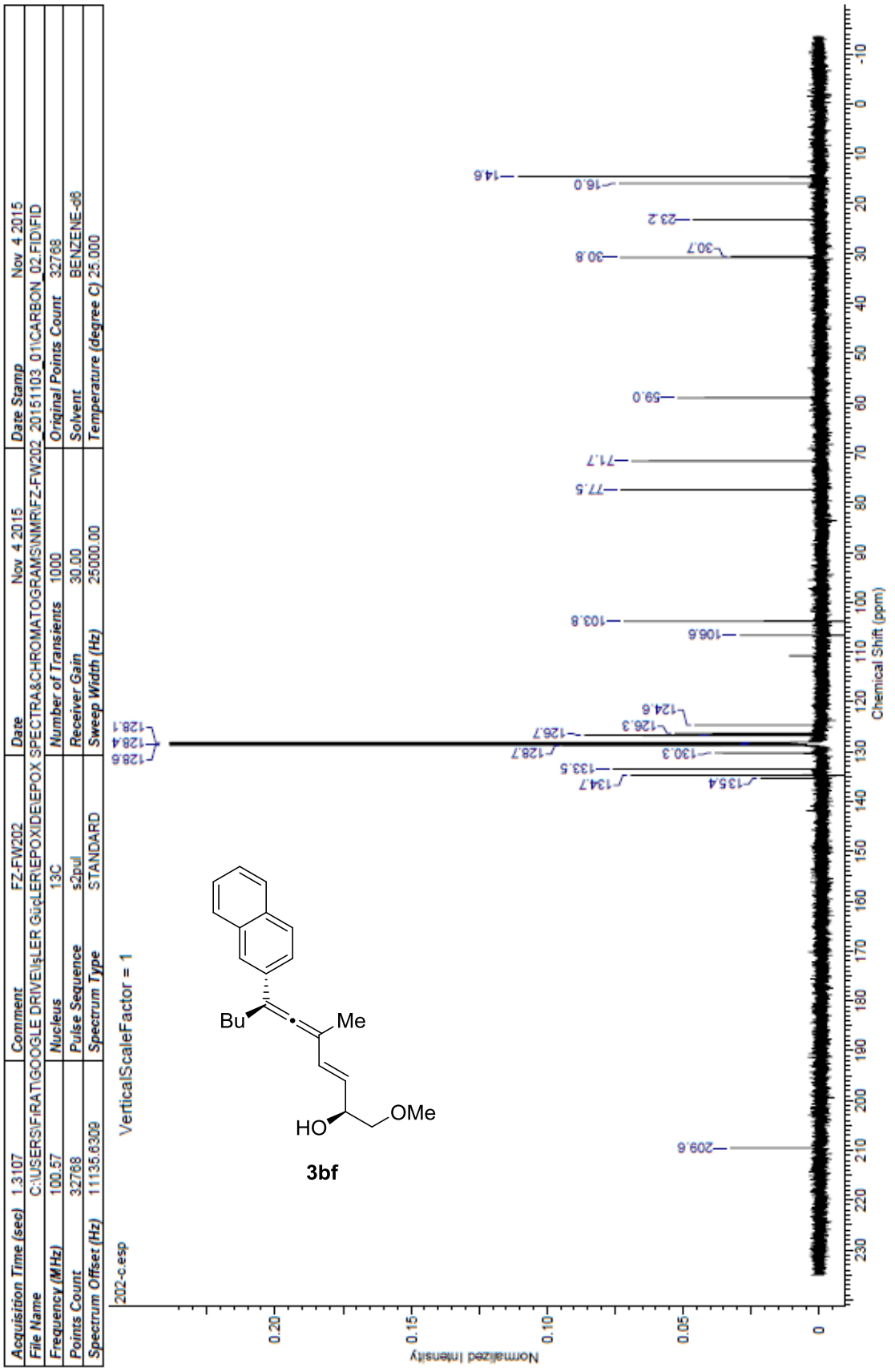
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 54.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2416.7764
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
202-h.esp
VerticalScaleFactor = 1
Bu
Me
HO
OMe
3bf
Normalized Intensity
Chemical Shift (ppm)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Date Nov 4 2015
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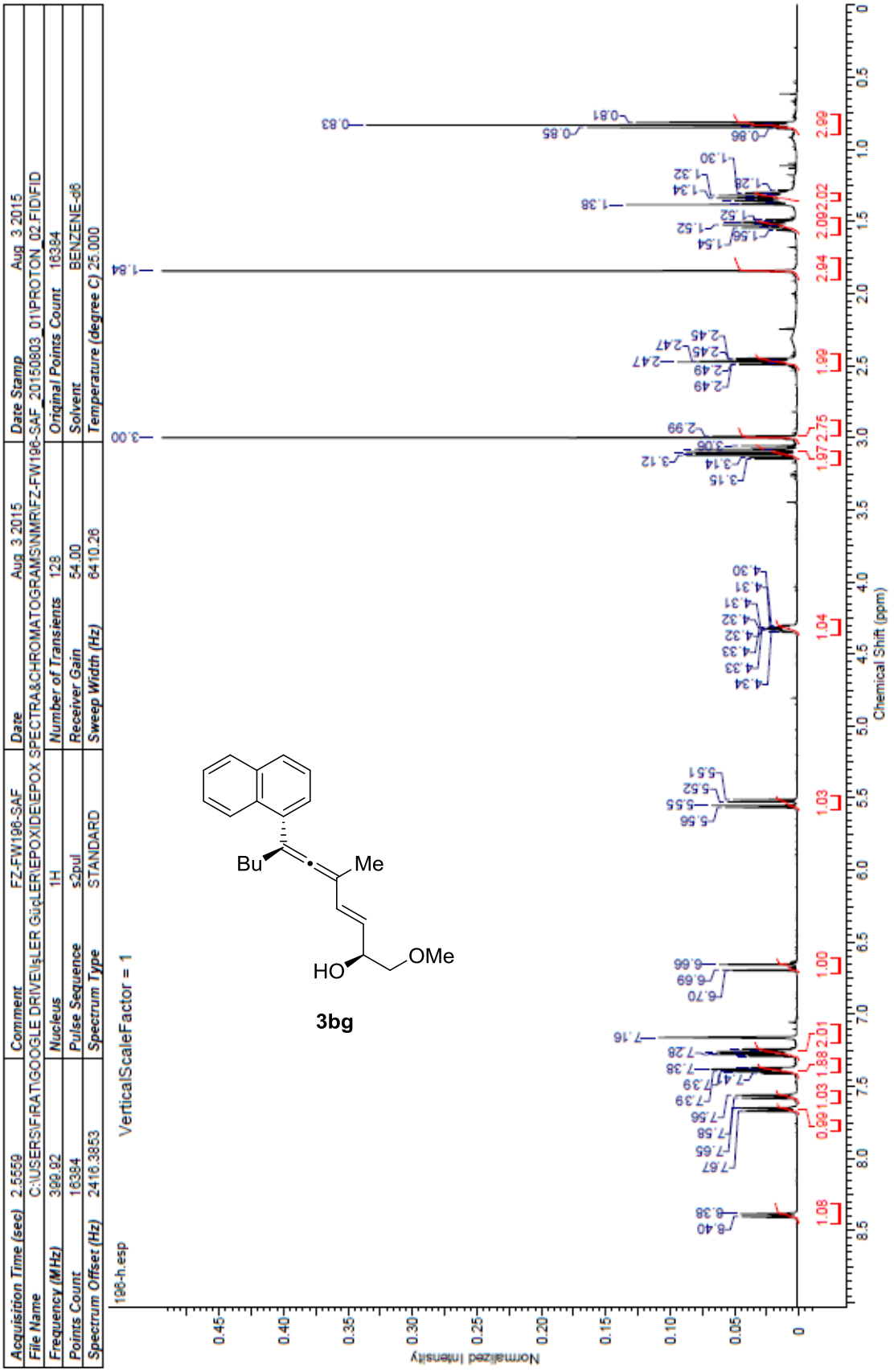
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 1000
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11135.6309
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
202-c.esp
VerticalScaleFactor = 1
Bu
Me
HO
OMe
3bf
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW196-SAF
Date Aug 3 2015
Date Stamp Aug 3 2015
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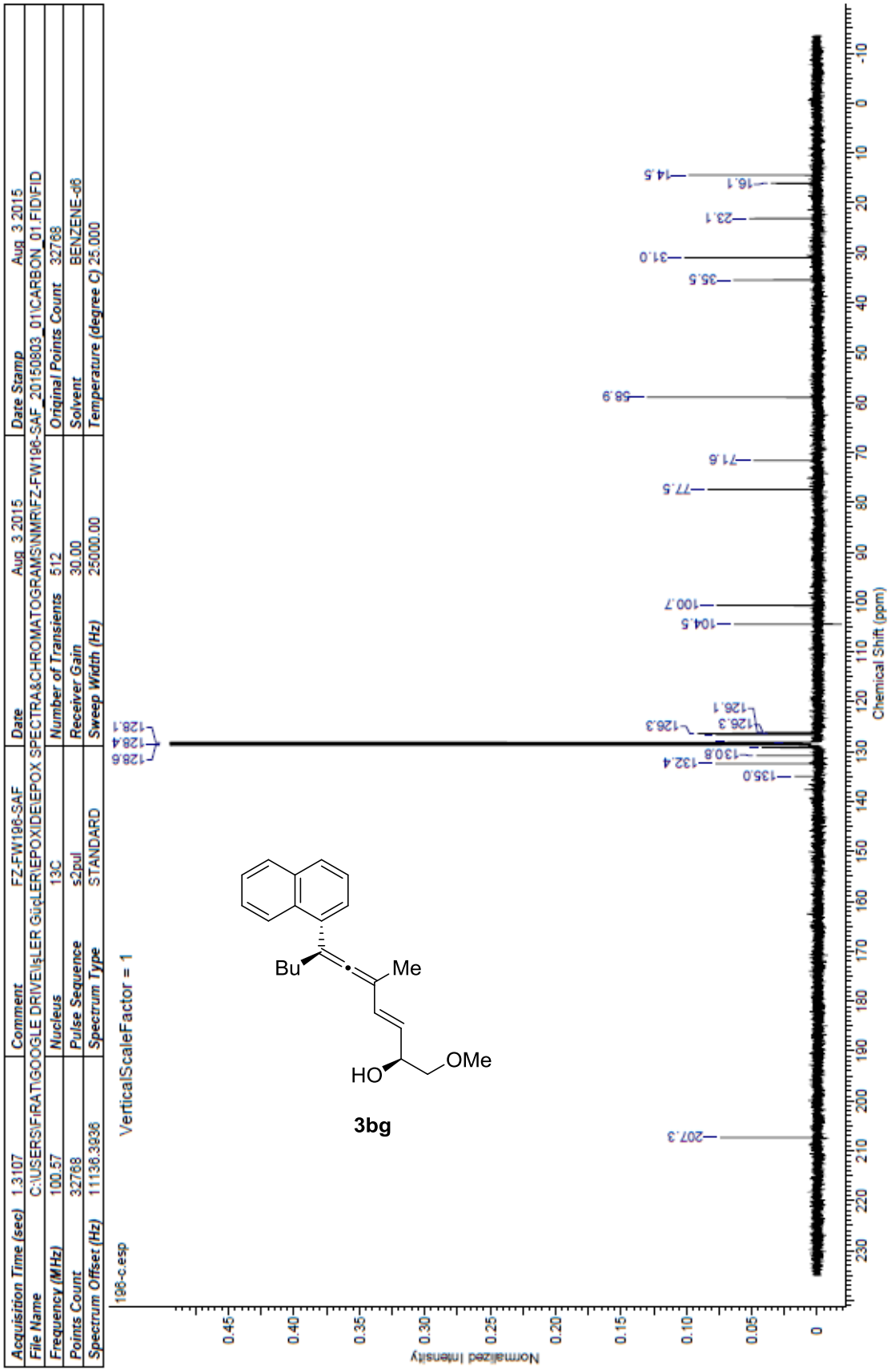
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 128
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 54.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2416.3853
Spectrum Type STANDARD
Sweep Width (Hz) 8410.26
Temperature (degree C) 25.000
196-h.esp
VerticalScaleFactor = 1
Bu
Me
HO
OMe
3bg
Normalized Intensity
Chemical Shift (ppm)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Date Aug 3 2015
Date Stamp Aug 3 2015
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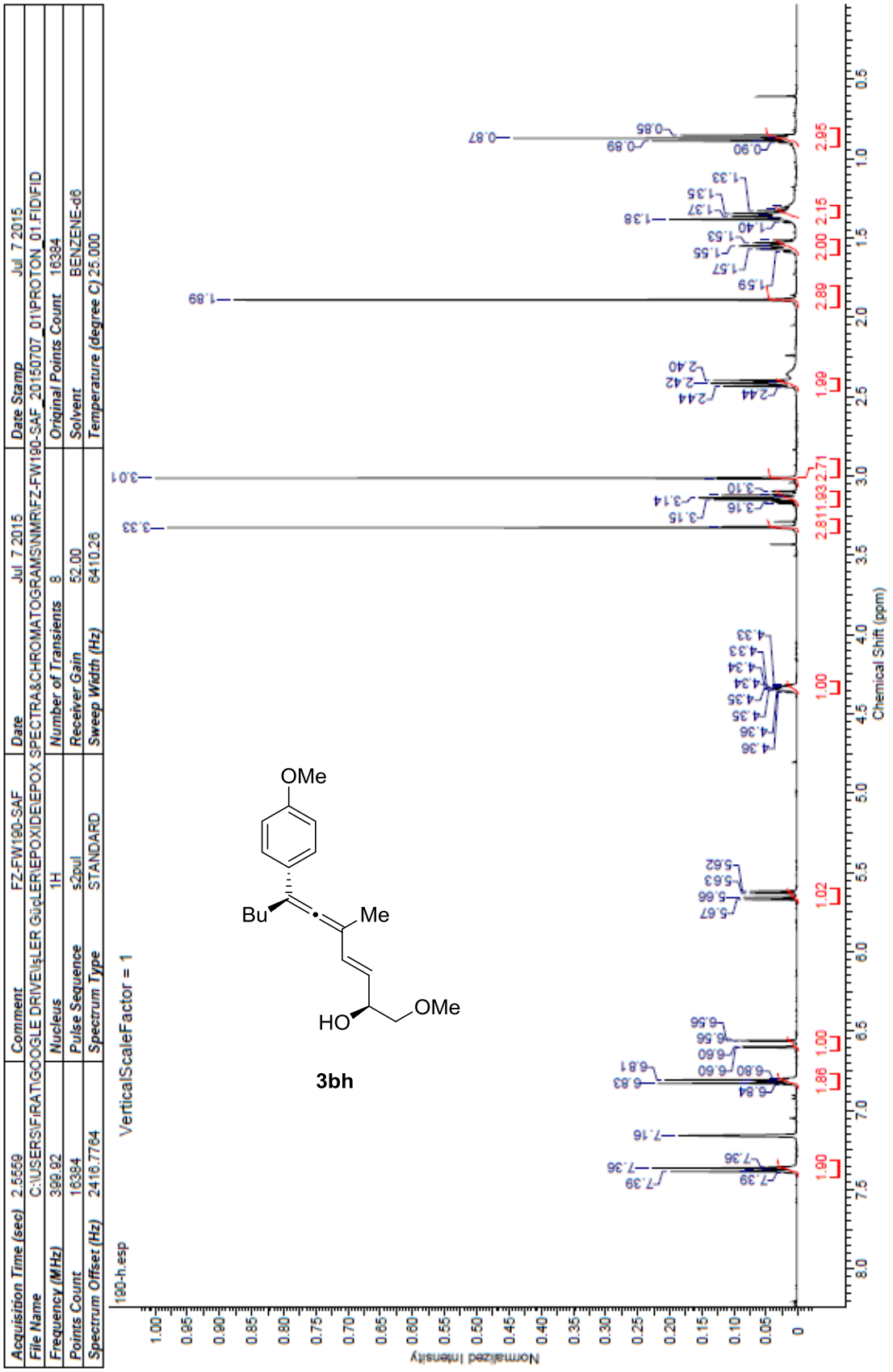
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 512
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
196-c.esp
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
128.6
128.4
128.1
207.3
135.0
132.4
130.8
126.3
126.3
126.1
104.5
100.7
77.5
71.6
58.9
35.5
31.0
23.1
16.1
14.5
Bu
Me
HO
OMe
3bg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Comment FZ-FW190-SAF
Date Jul 7 2015
Date Stamp Jul 7 2015
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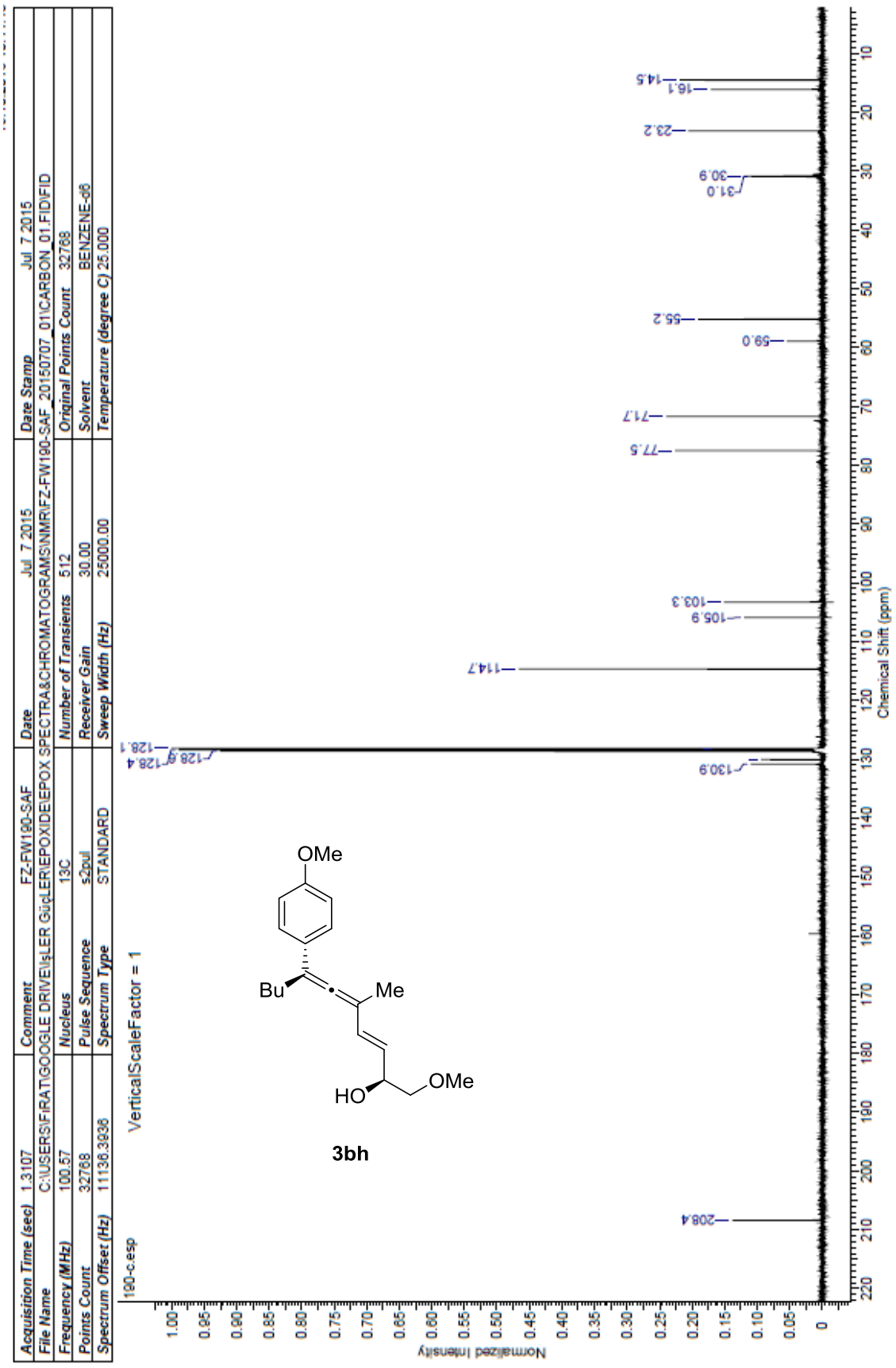
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 52.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2416.7764
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
190-h.esp
VerticalScaleFactor = 1
OMe
Bu
Me
HO
OMe
3bh
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW190-SAF
Date Jul 7 2015
Date Stamp Jul 7 2015
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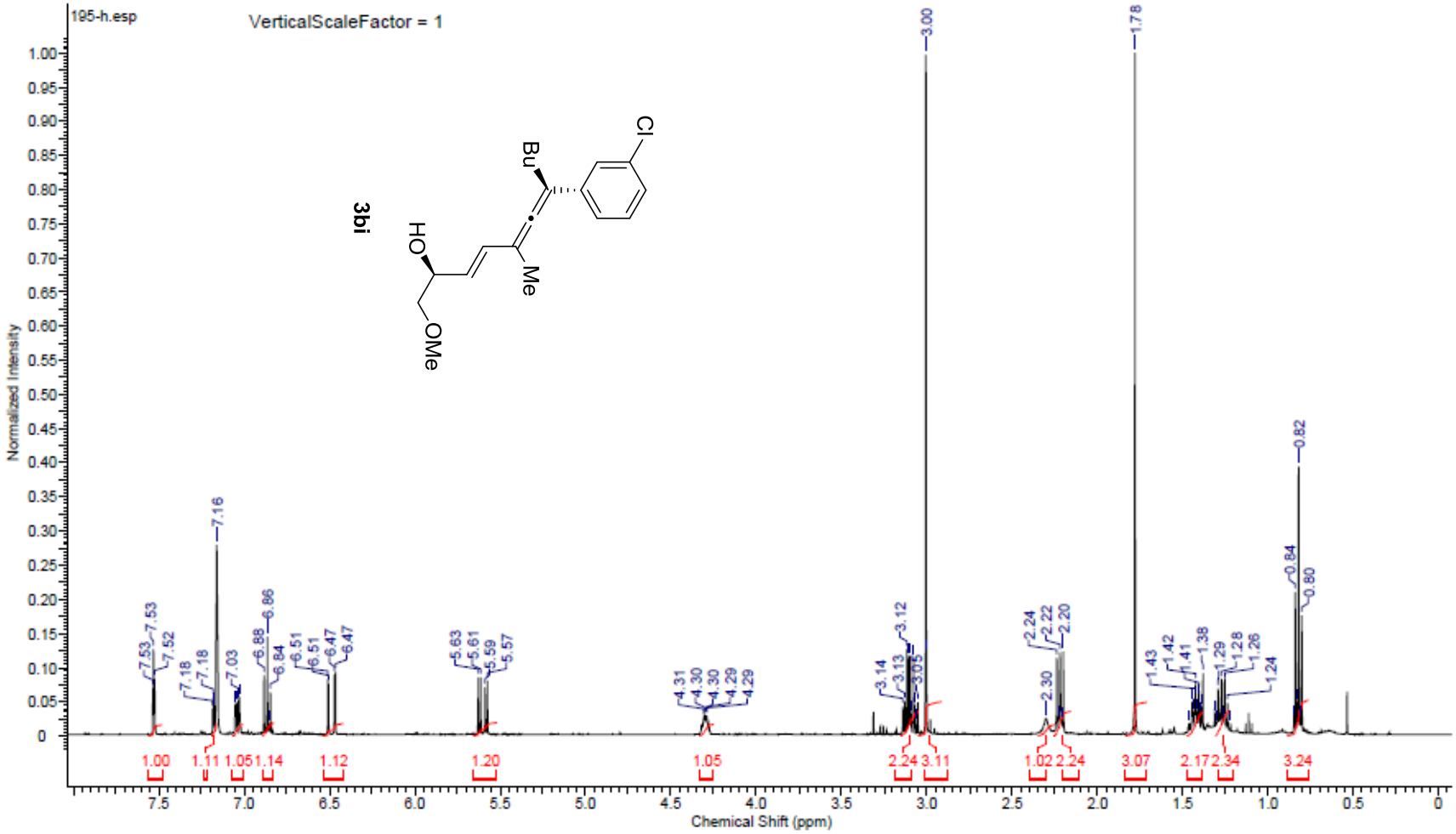
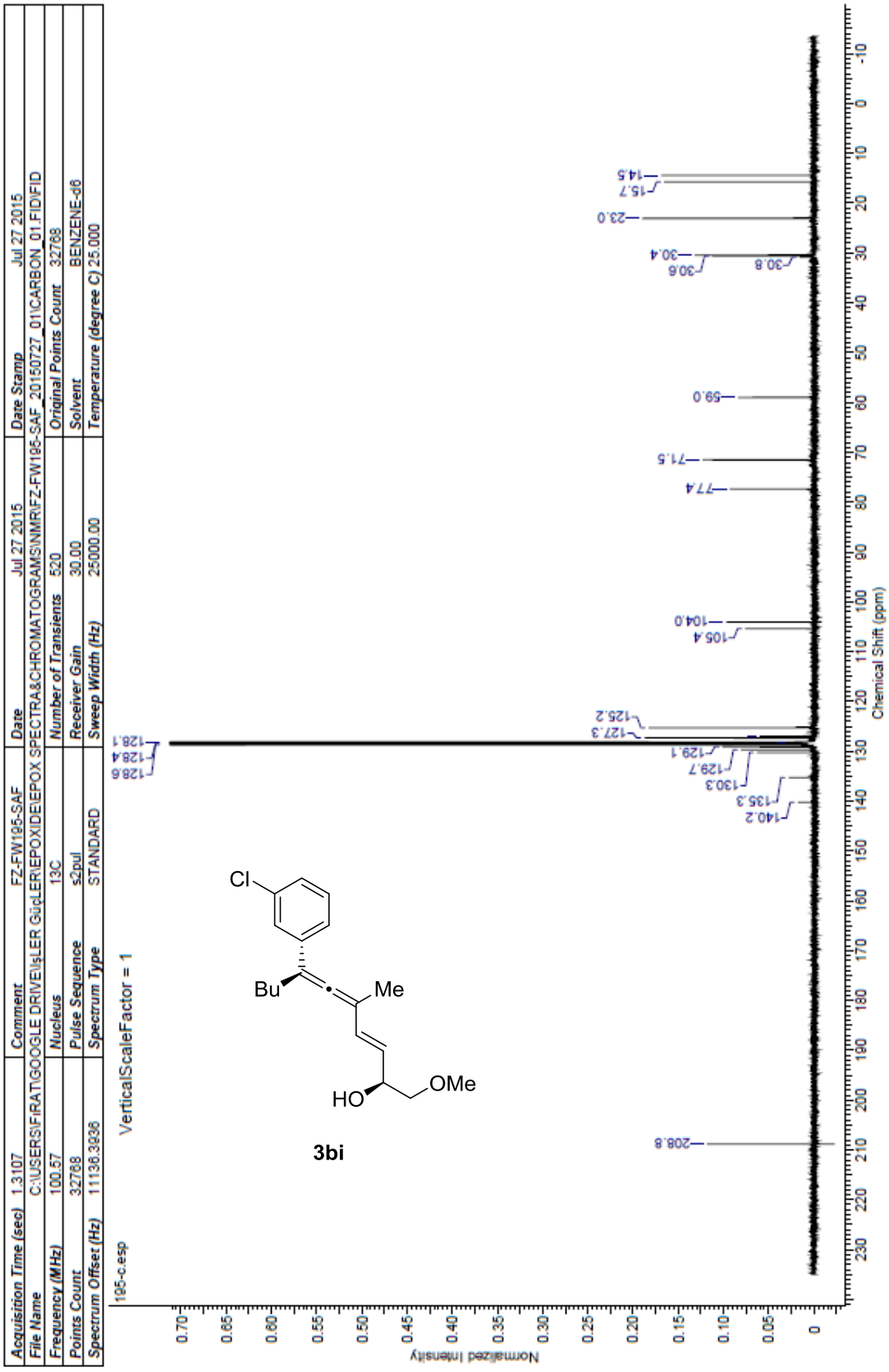
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 512
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
190-c.esp
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
208.4
130.9
128.6
128.4
128.1
114.7
105.9
103.3
77.5
71.7
59.0
55.2
31.0
30.9
23.2
16.1
14.5
OMe
Bu
Me
HO
OMe
3bh

Acquisition Time (sec)	2.5559	*Comment*	FZ-FW195-SAF	*Date*	Jul 27 2015	*Date Stamp*	Jul 27 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IŞLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FZ-FW195-SAF_20150727_01\PROTON_02.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	52.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3853	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

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Date Jul 27 2015
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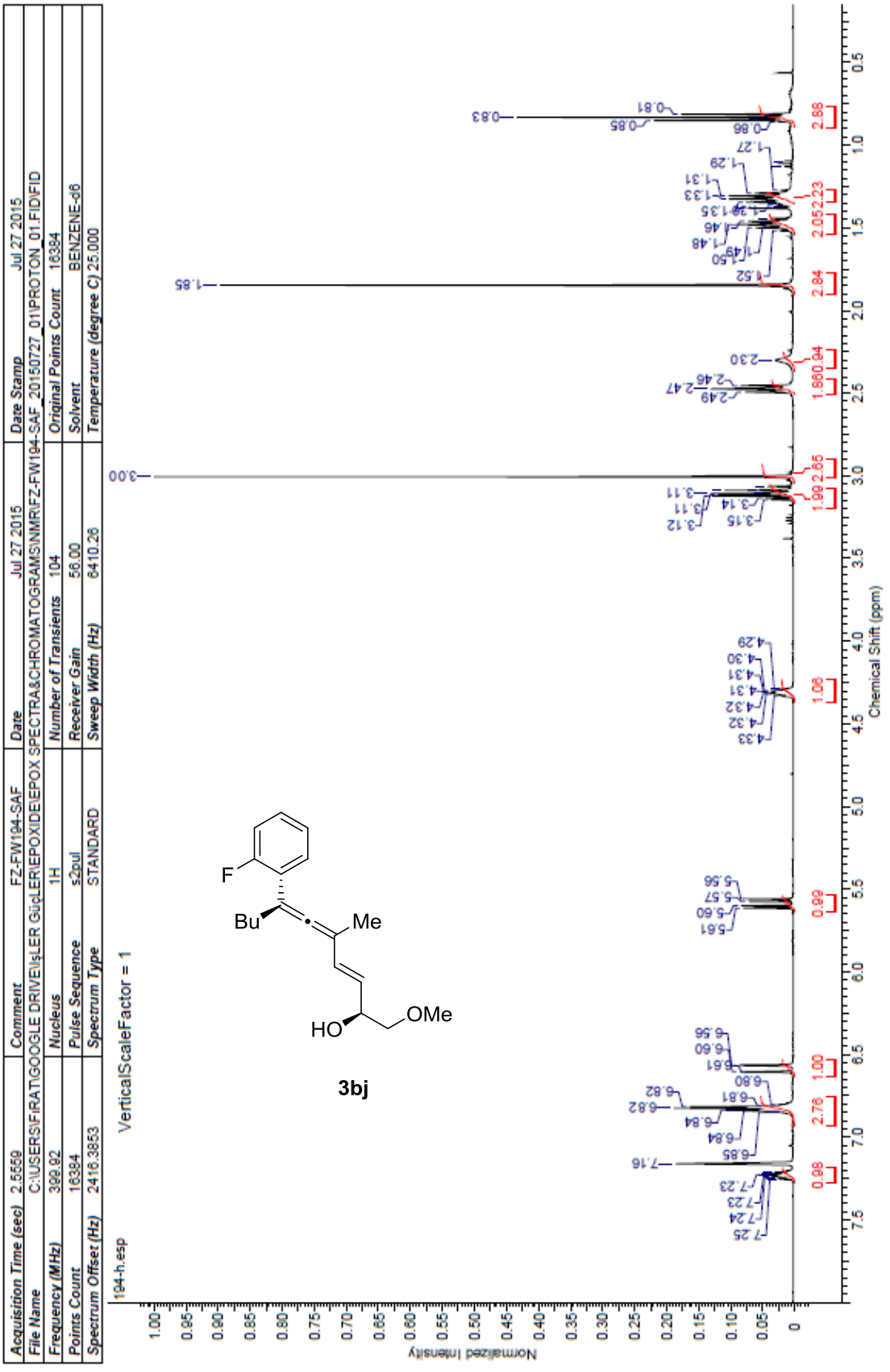
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 520
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
195-c.esp
VerticalScaleFactor = 1
Cl
Bu
Me
HO
OMe
3bi
Normalized Intensity
Chemical Shift (ppm)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FZ-FW194-SAF
Date
Jul 27 2015
Date Stamp
Jul 27 2015
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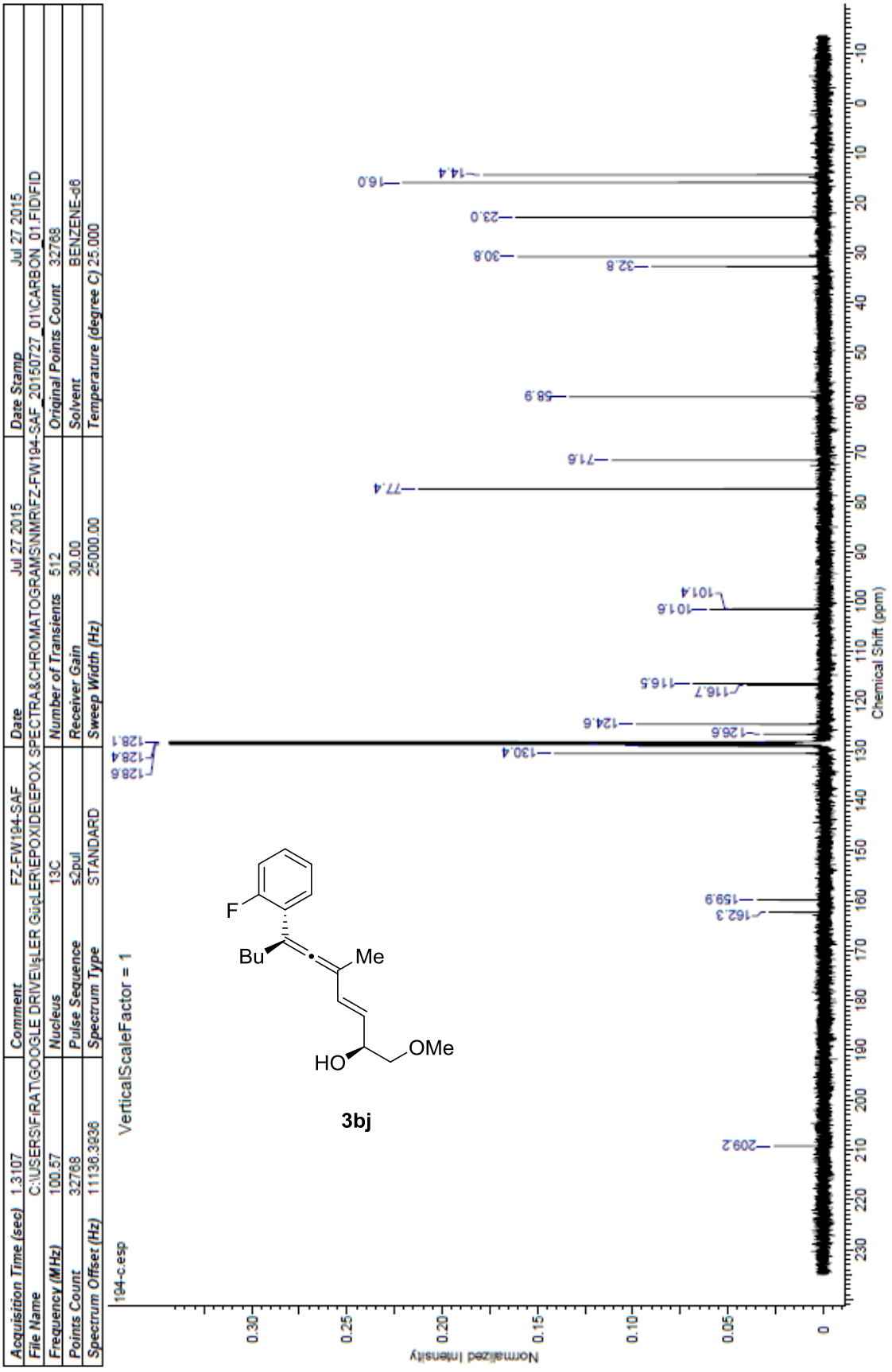
Frequency (MHz) 399.92
Nucleus
1H
Number of Transients 104
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 56.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2416.3853
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
194-h.esp
VerticalScaleFactor = 1
F
Bu
Me
HO
OMe
3bj
Normalized Intensity
Chemical Shift (ppm)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FZ-FW194-SAF
Date
Jul 27 2015
Date Stamp
Jul 27 2015
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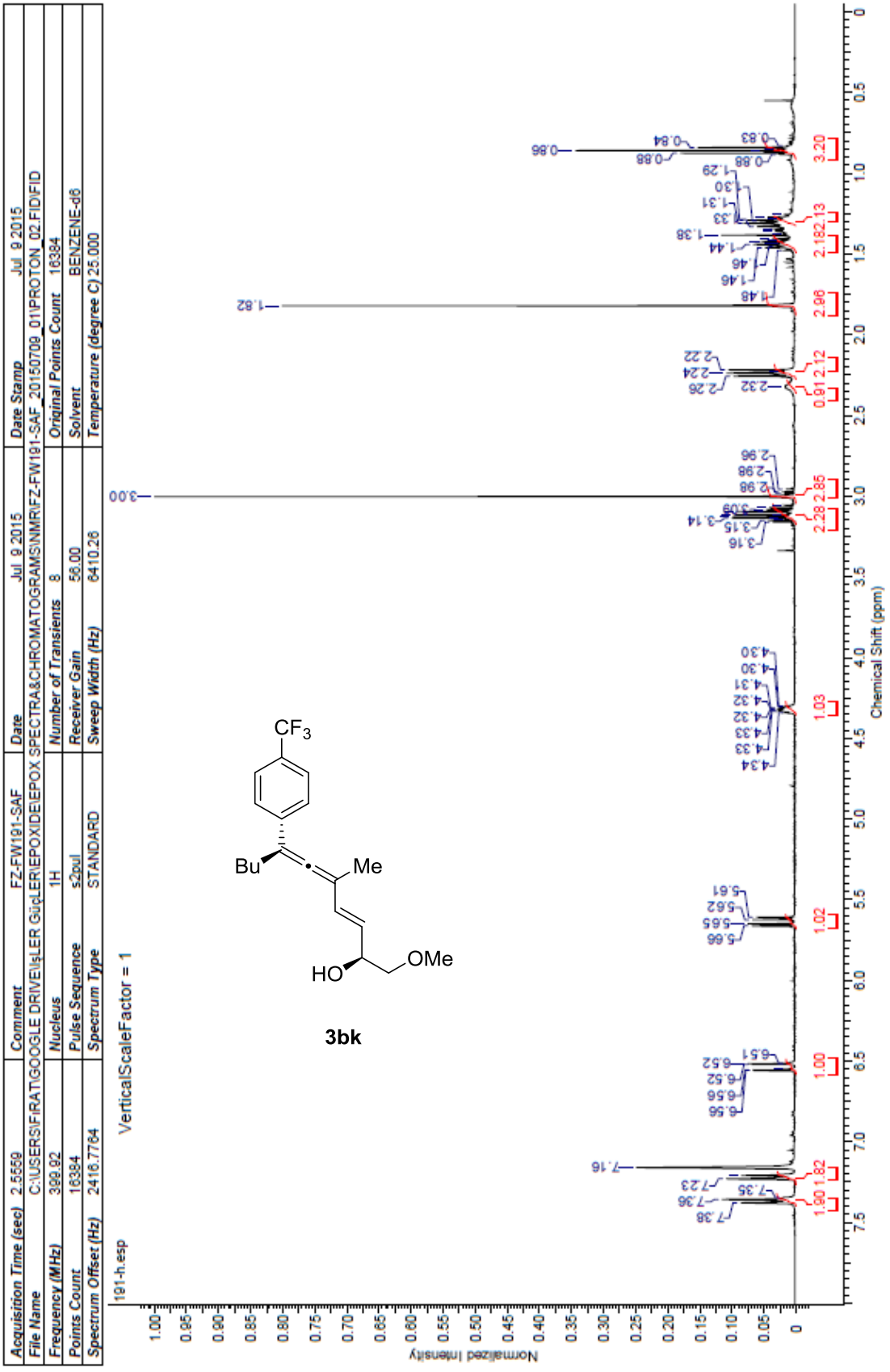
Frequency (MHz) 100.57
Nucleus
13C
Number of Transients 512
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
194-c.esp
VerticalScaleFactor = 1
F
Bu
Me
HO
OMe
3bj
Normalized Intensity
Chemical Shift (ppm)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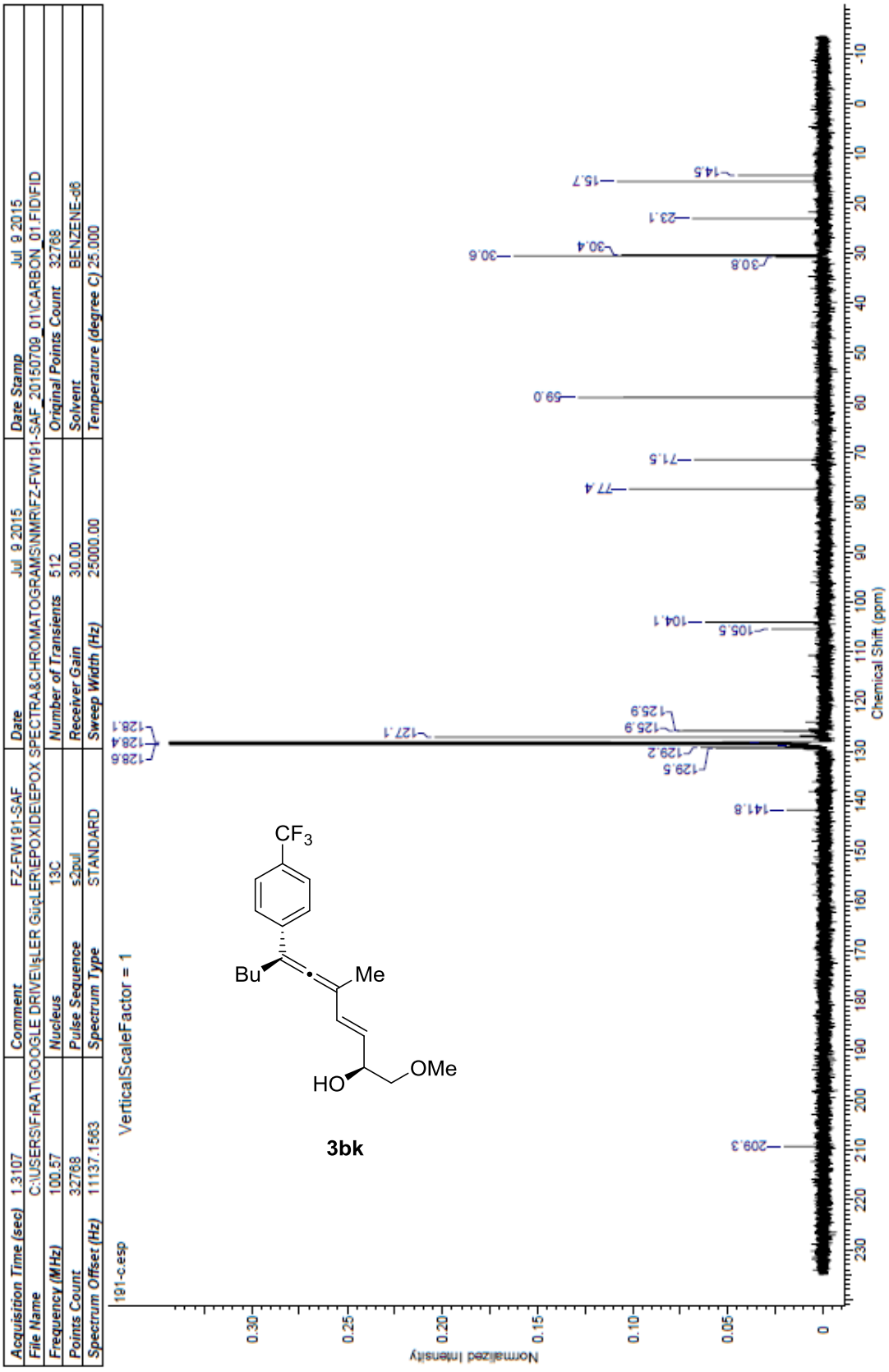
Frequency (MHz) 399.92
Points Count 16384
Spectrum Offset (Hz) 2416.7764
Comment FZ-FW191-SAF
Nucleus 1H
Pulse Sequence s2pul
Spectrum Type STANDARD
Date Jul 9 2015
Number of Transients 8
Receiver Gain 58.00
Sweep Width (Hz) 6410.26
Date Stamp Jul 9 2015
Original Points Count 16384
Solvent BENZENE-d6
Temperature (degree C) 25.000
191-h.esp
VerticalScaleFactor = 1
CF3
Bu
Me
HO
OMe
3bk
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW191-SAF
Date Jul 9 2015
Date Stamp Jul 9 2015
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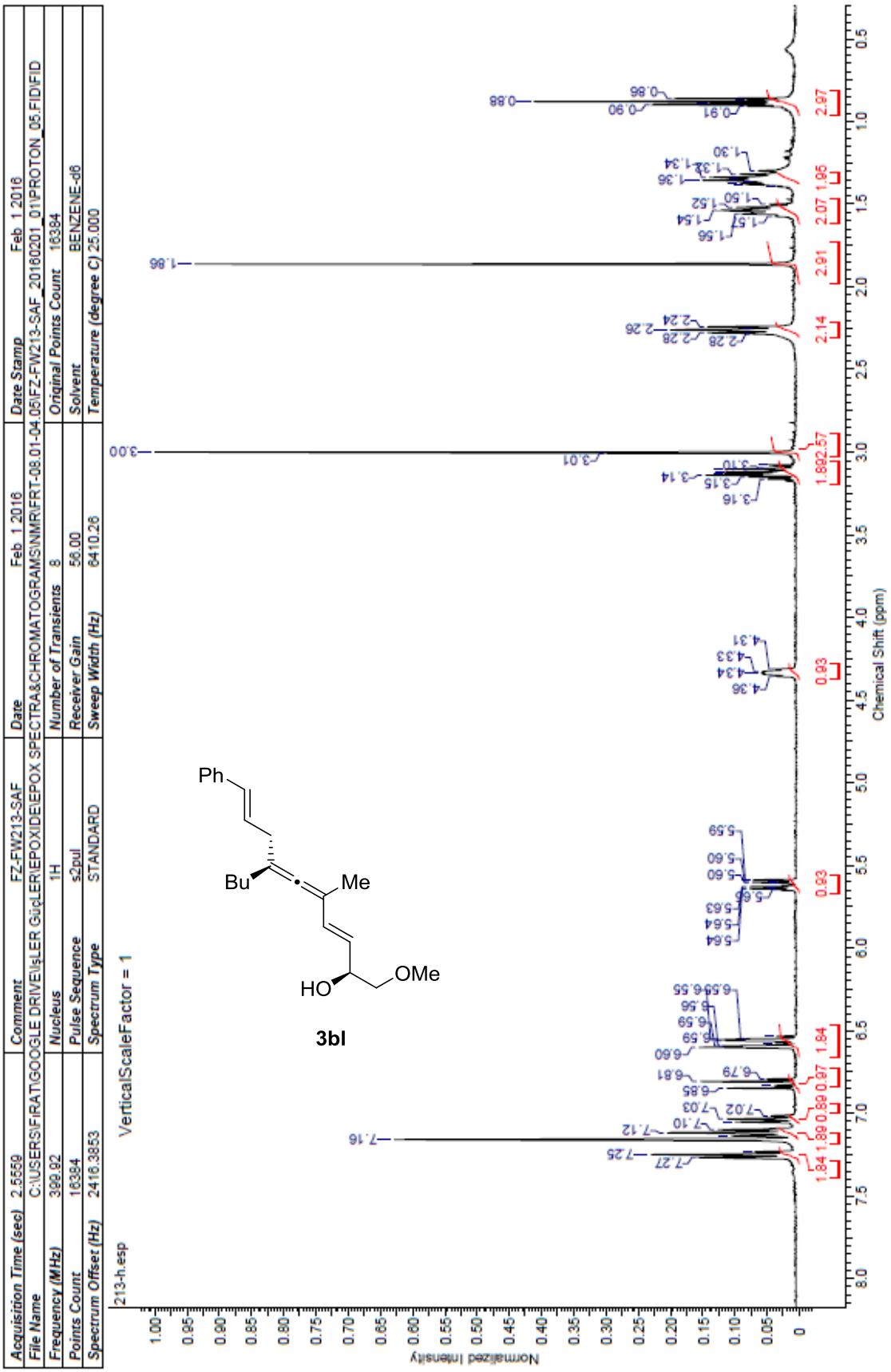
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 512
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11137.1563
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
191-c.esp
VerticalScaleFactor = 1
CF3
Bu
Me
HO
OMe
3bk
Normalized Intensity
Chemical Shift (ppm)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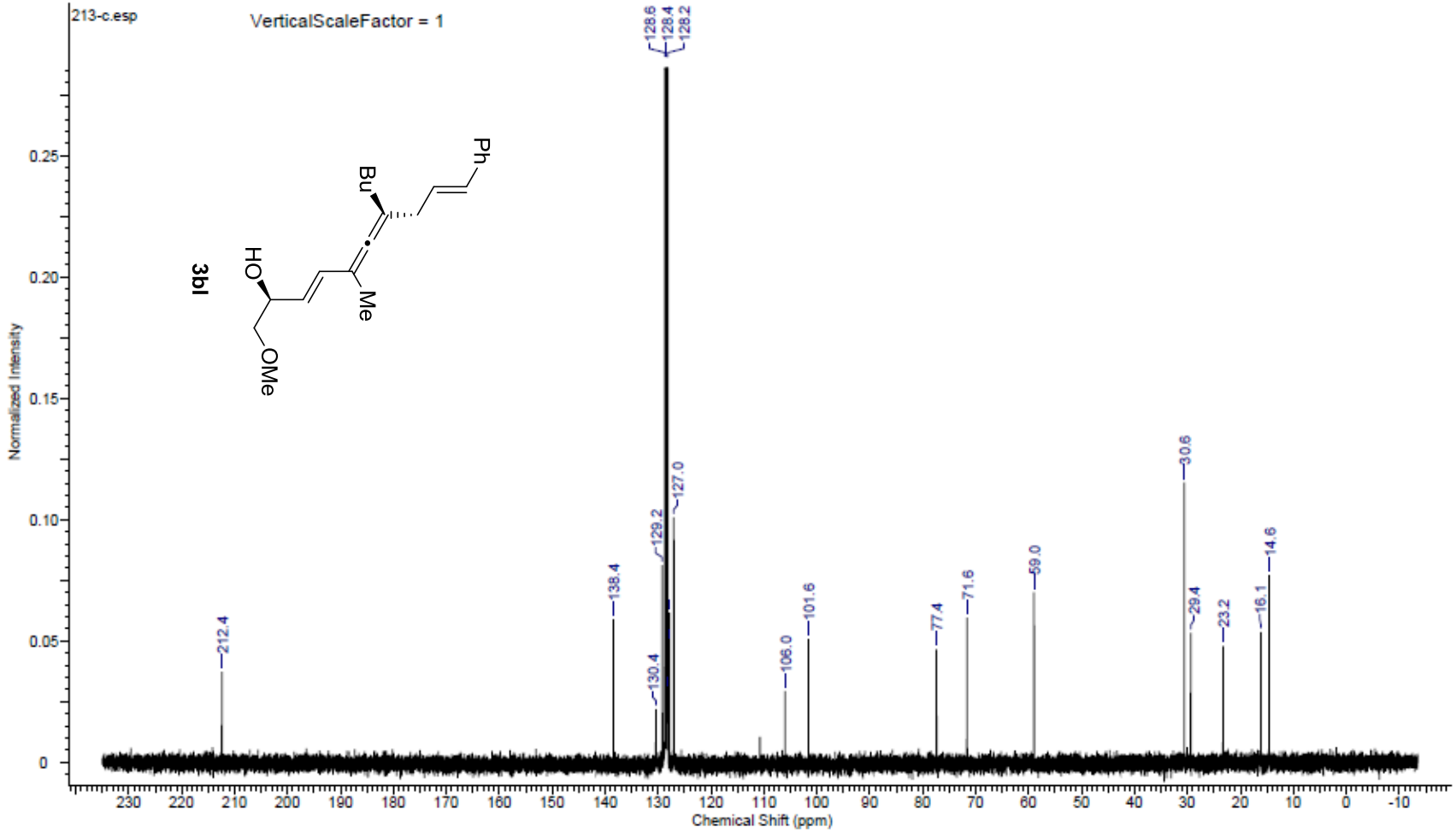
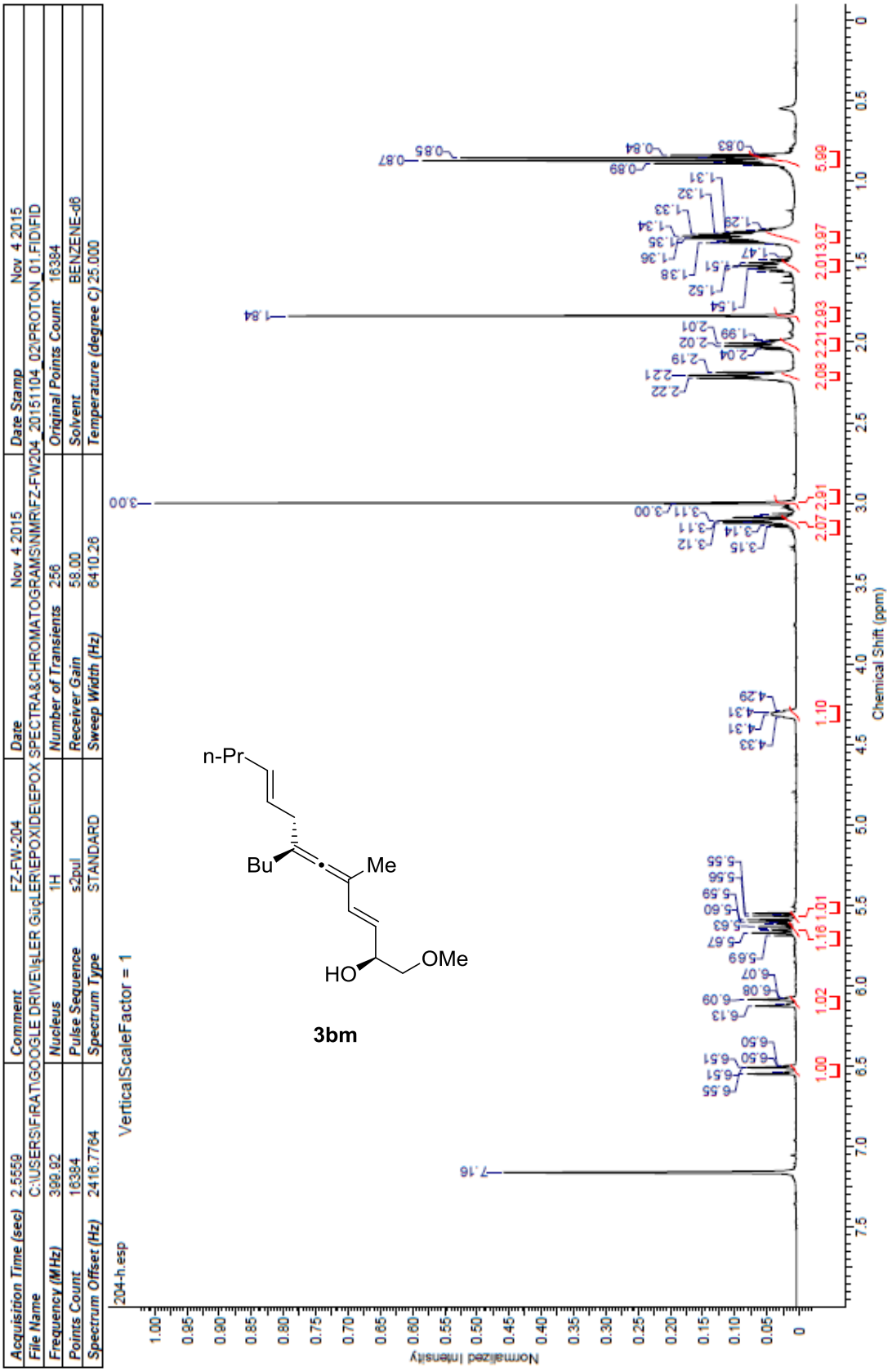
Frequency (MHz) 399.92
Points Count 16384
Spectrum Offset (Hz) 2416.3853
Comment FZ-FW213-SAF
Nucleus 1H
Pulse Sequence s2pul
Spectrum Type STANDARD
Date Feb 1 2016
Number of Transients 8
Receiver Gain 56.00
Sweep Width (Hz) 6410.26
Date Stamp Feb 1 2016
Original Points Count 16384
Solvent BENZENE-d6
Temperature (degree C) 25.000
213-h.esp
VerticalScaleFactor = 1
Ph
Bu
Me
HO
OMe
3bl
Normalized Intensity
Chemical Shift (ppm)

Acquisition Time (sec)	1.3107	*Comment*	FZ-FW213-SAF	*Date*	Feb 1 2016	*Date Stamp*	Feb 1 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IŞLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FRT-08.01-04.05\FZ-FW213-SAF_20160201_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	512	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11135.6309	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

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Comment FZ-FW-204
Date Nov 4 2015
Date Stamp Nov 4 2015
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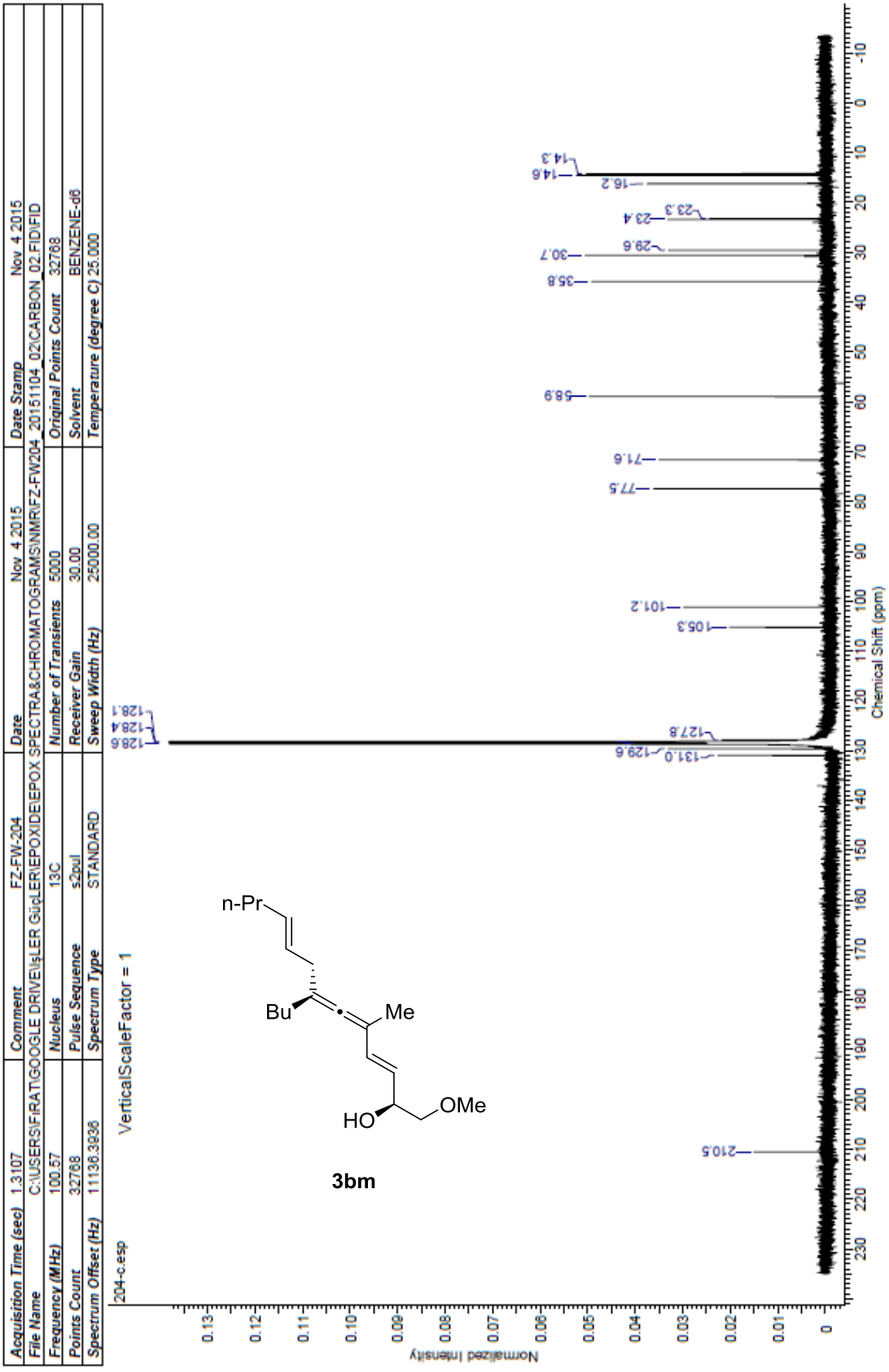
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 256
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 58.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2416.7764
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
204-h.esp
VerticalScaleFactor = 1
n-Pr
Bu
Me
HO
OMe
3bm
Normalized Intensity
Chemical Shift (ppm)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Date Nov 4 2015
Date Stamp Nov 4 2015
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Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 5000
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
204-c.esp
VerticalScaleFactor = 1
n-Pr
Bu
Me
HO
OMe
3bm
Normalized Intensity
Chemical Shift (ppm)
128.6
128.4
128.1
127.8
131.0
129.6
105.3
101.2
77.5
71.6
58.9
35.8
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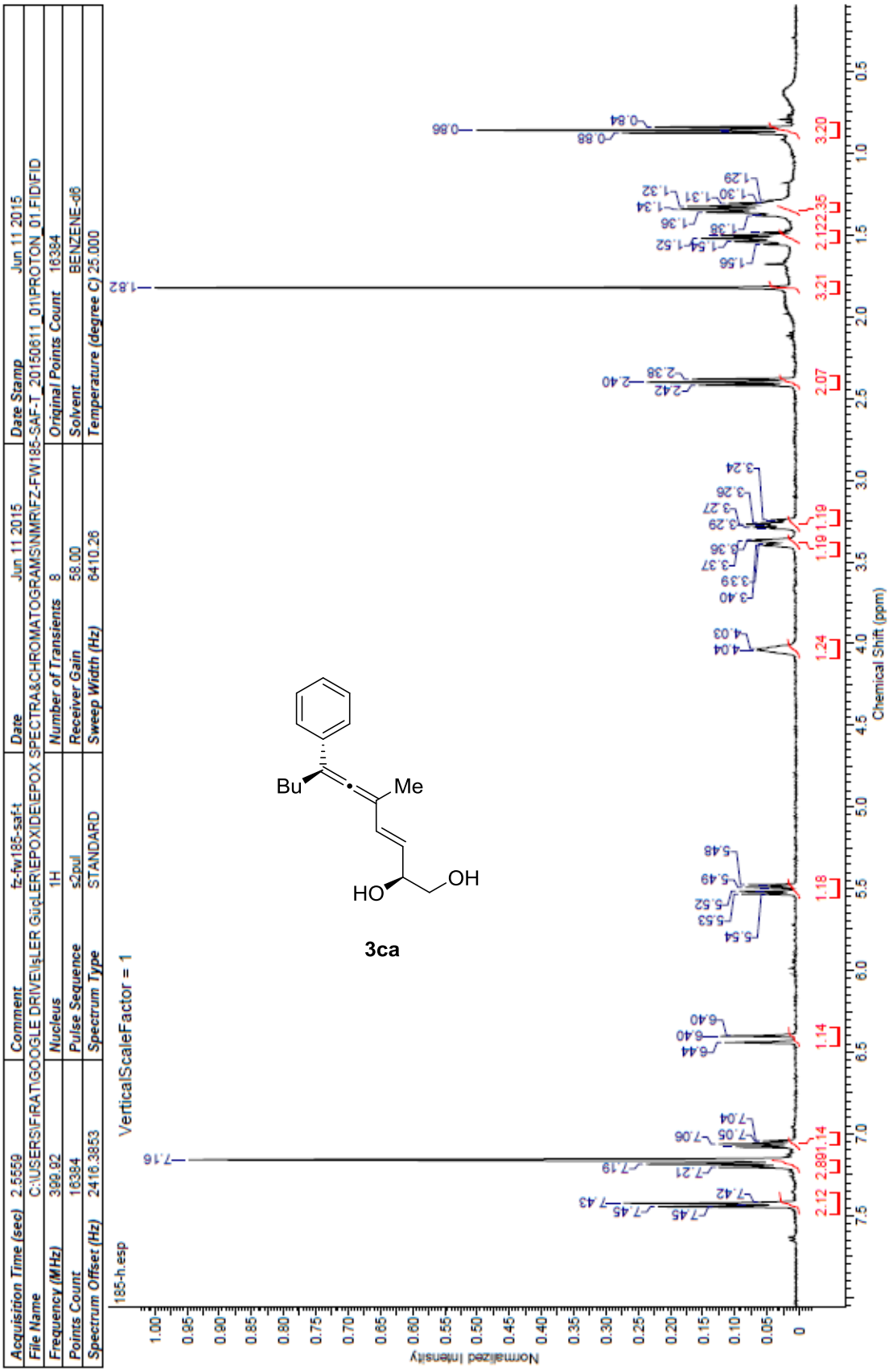
23.4
23.3
16.2
14.6
14.3
210.5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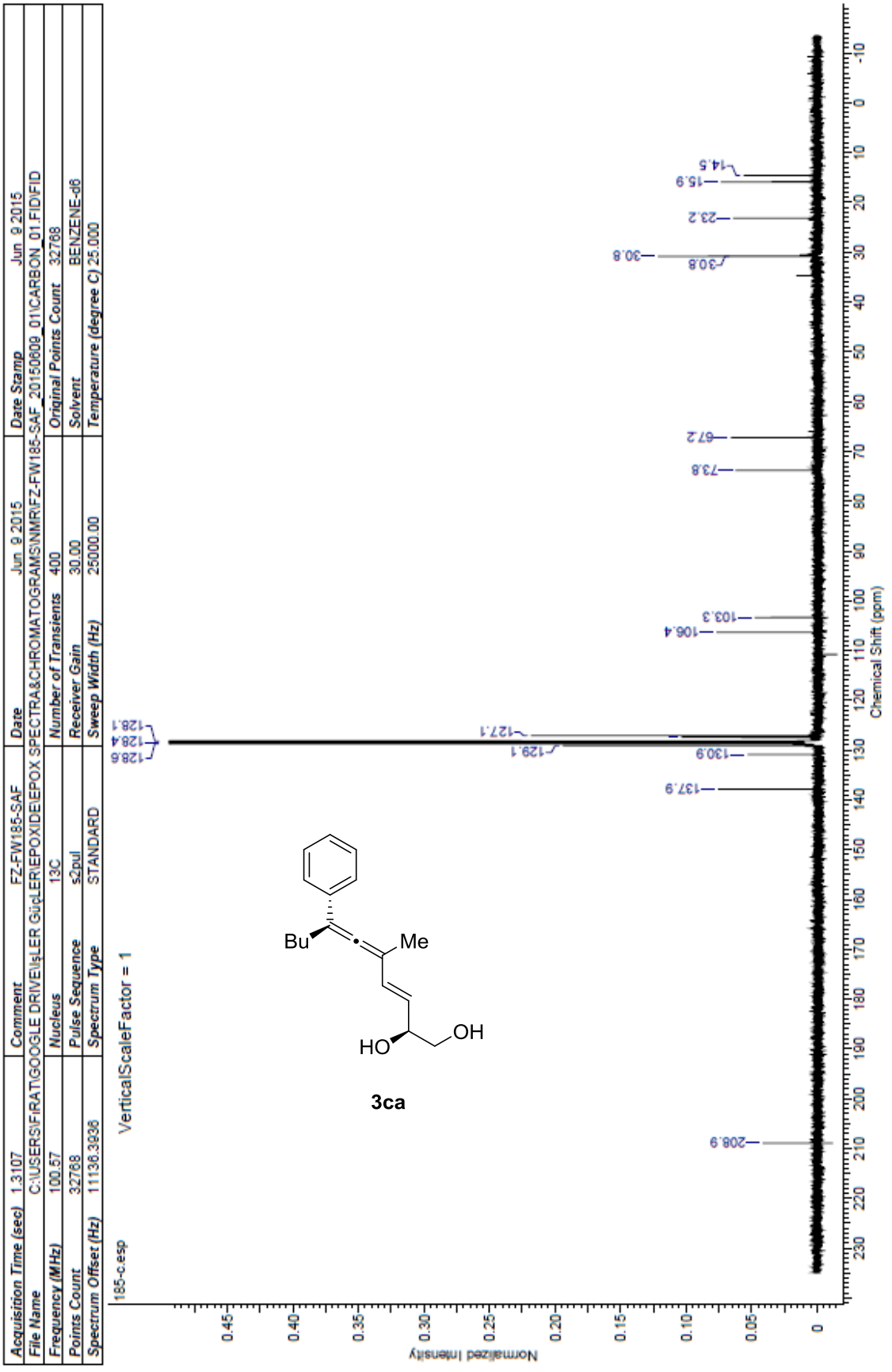
Frequency (MHz) 399.92
Points Count 16384
Spectrum Offset (Hz) 2416.3853
Comment
Nucleus 1H
Pulse Sequence s2pul
Spectrum Type STANDARD
fz-fw185-saf-t
Date Jun 11 2015
Number of Transients 8
Receiver Gain 58.00
Sweep Width (Hz) 6410.26
Date Stamp Jun 11 2015
Original Points Count 16384
Solvent BENZENE-d6
Temperature (degree C) 25.000
185-h.esp
VerticalScaleFactor = 1
Bu
Me
HO
OH
3ca
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW185-SAF
Date Jun 9 2015
Date Stamp Jun 9 2015
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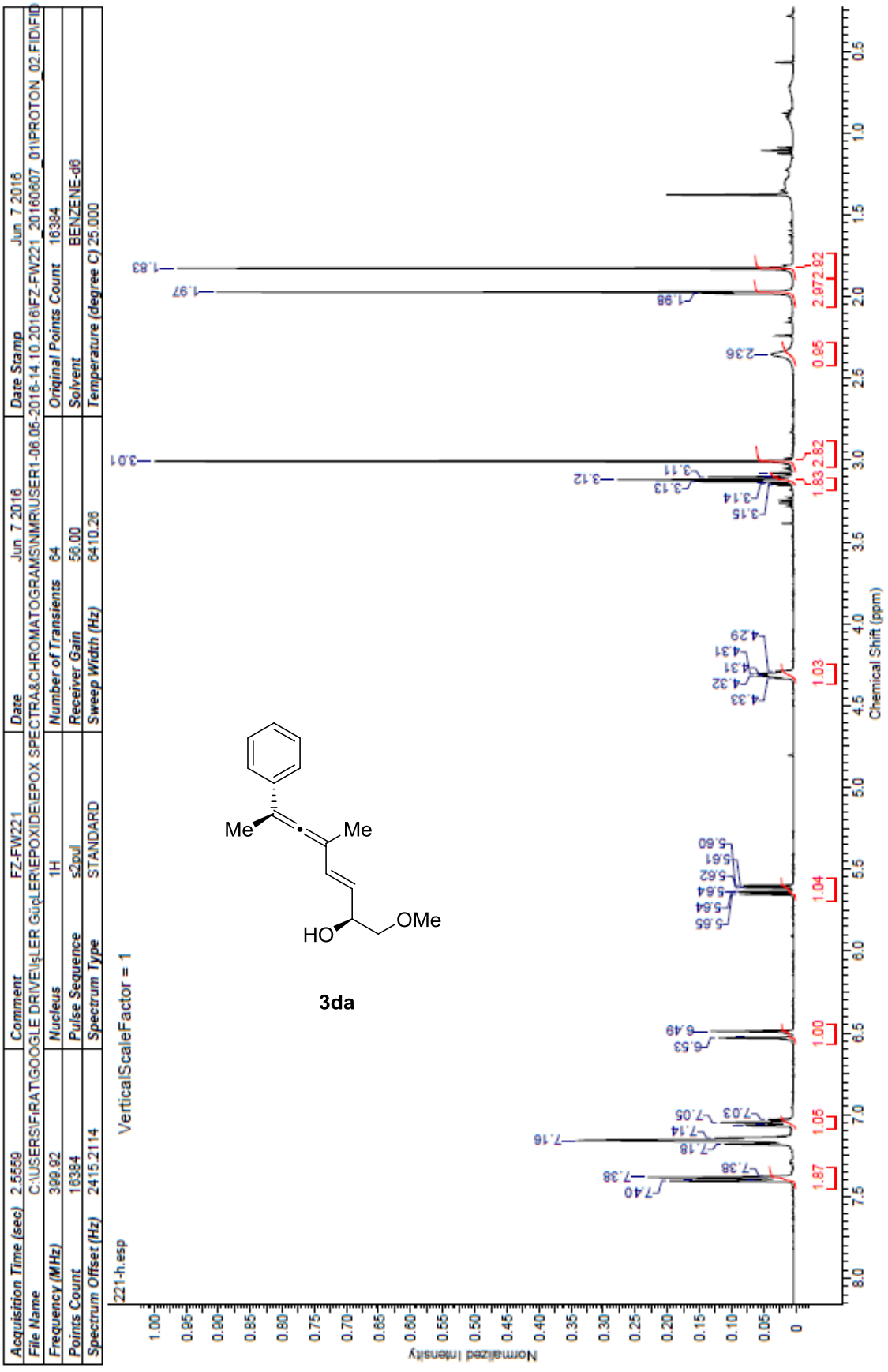
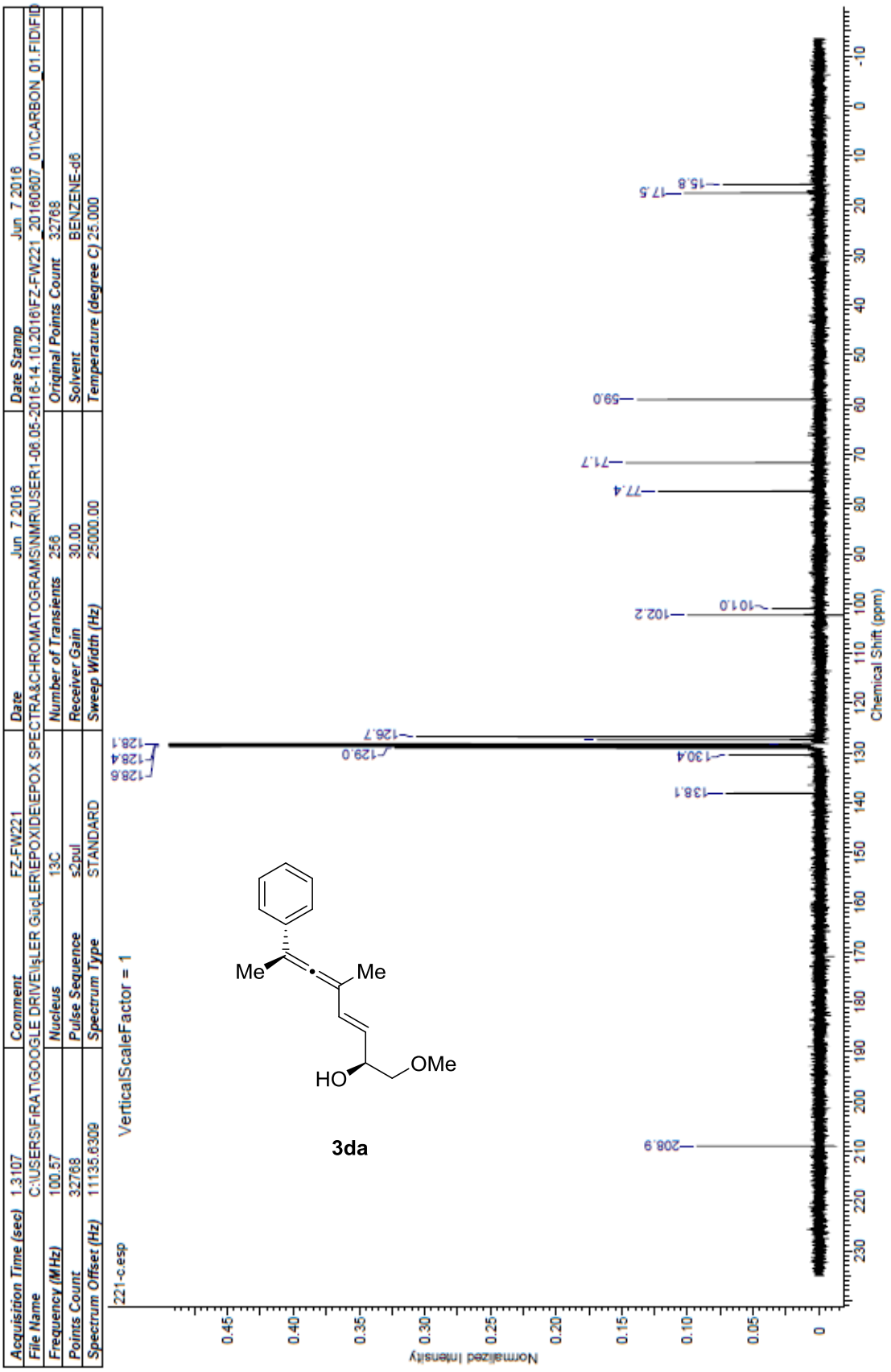
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 400
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
185-c.esp
VerticalScaleFactor = 1
Bu
Me
HO
OH
3ca
208.9
137.9
130.9
129.1
127.1
128.6
128.4
128.1
106.4
103.3
73.8
67.2
30.8
30.8
23.2
15.9
14.5
Normalized Intensity
Chemical Shift (ppm)


Acquisition Time (sec) 2.5559
Comment
Date Jun 7 2016
Date Stamp Jun 7 2016
File Name C:\USERS\FIRAT\GOOGLE DRIVE\ISLER GÜÇLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\USER1-06.05-2016-14.10.2016\FZ-FW221_20160607_01\PROTON_02.FID\FID
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 64
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 58.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2415.2114
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
FZ-FW221
221-h.esp
VerticalScaleFactor = 1
Me
Me
HO
OMe
3da
Normalized Intensity
Chemical Shift (ppm)


Acquisition Time (sec) 1.3107
Comment FZ-FW221
Date Jun 7 2016
Date Stamp Jun 7 2016
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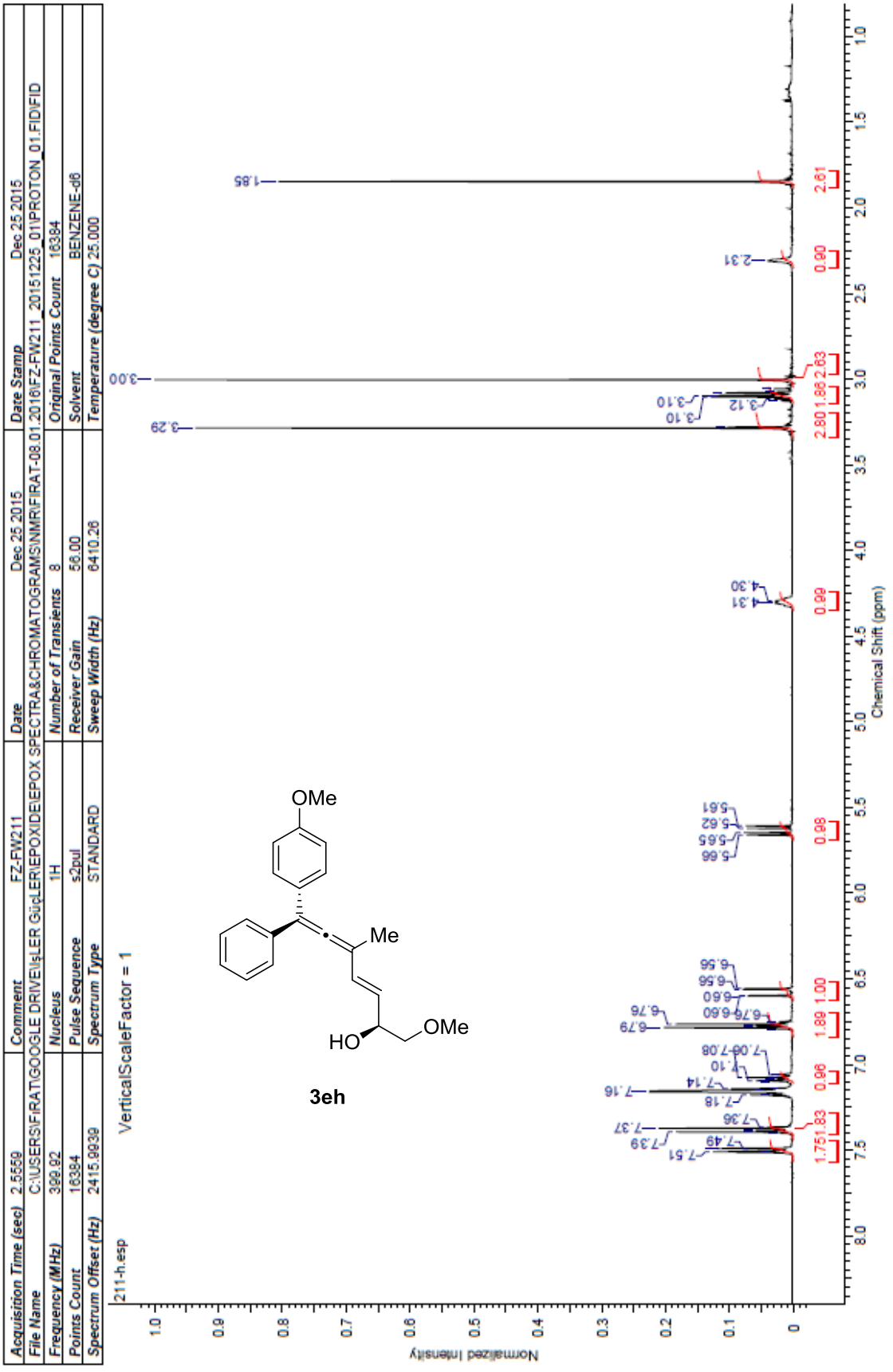
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 256
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11135.6309
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
221-c.esp
VerticalScaleFactor = 1
Me
Me
HO
OMe
3da
208.9
138.1
130.4
129.0
128.7
128.6
128.4
128.1
102.2
101.0
77.4
71.7
59.0
17.5
15.8
Normalized Intensity
Chemical Shift (ppm)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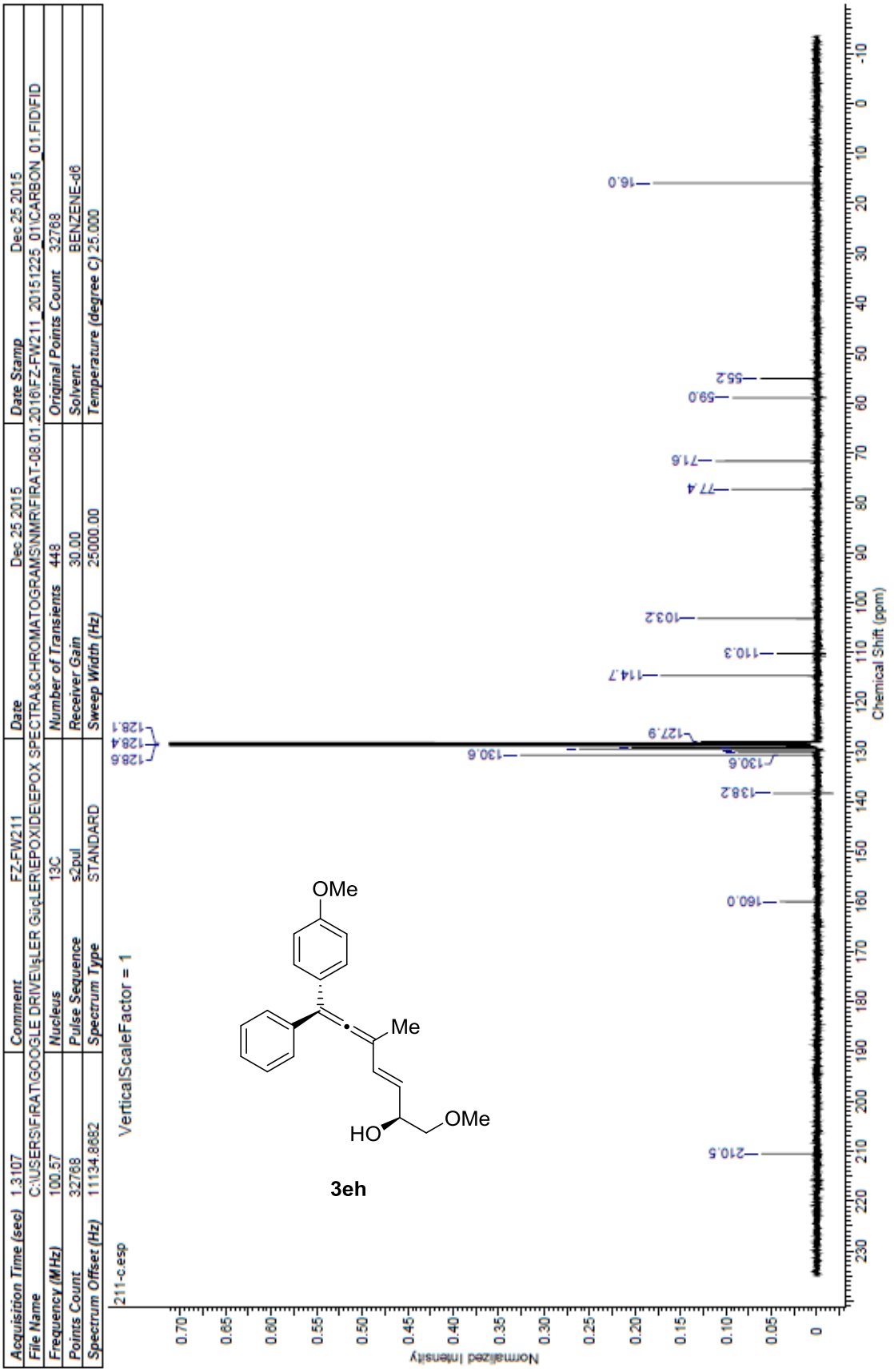
Frequency (MHz) 399.92
Points Count 16384
Spectrum Offset (Hz) 2415.9939
Comment FZ-FW211
Nucleus 1H
Pulse Sequence s2pul
Spectrum Type STANDARD
Date Dec 25 2015
Number of Transients 8
Receiver Gain 56.00
Sweep Width (Hz) 6410.26
Date Stamp Dec 25 2015
Original Points Count 16384
Solvent BENZENE-d6
Temperature (degree C) 25.000
211-h.esp
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
OMe
Me
HO
OMe
3eh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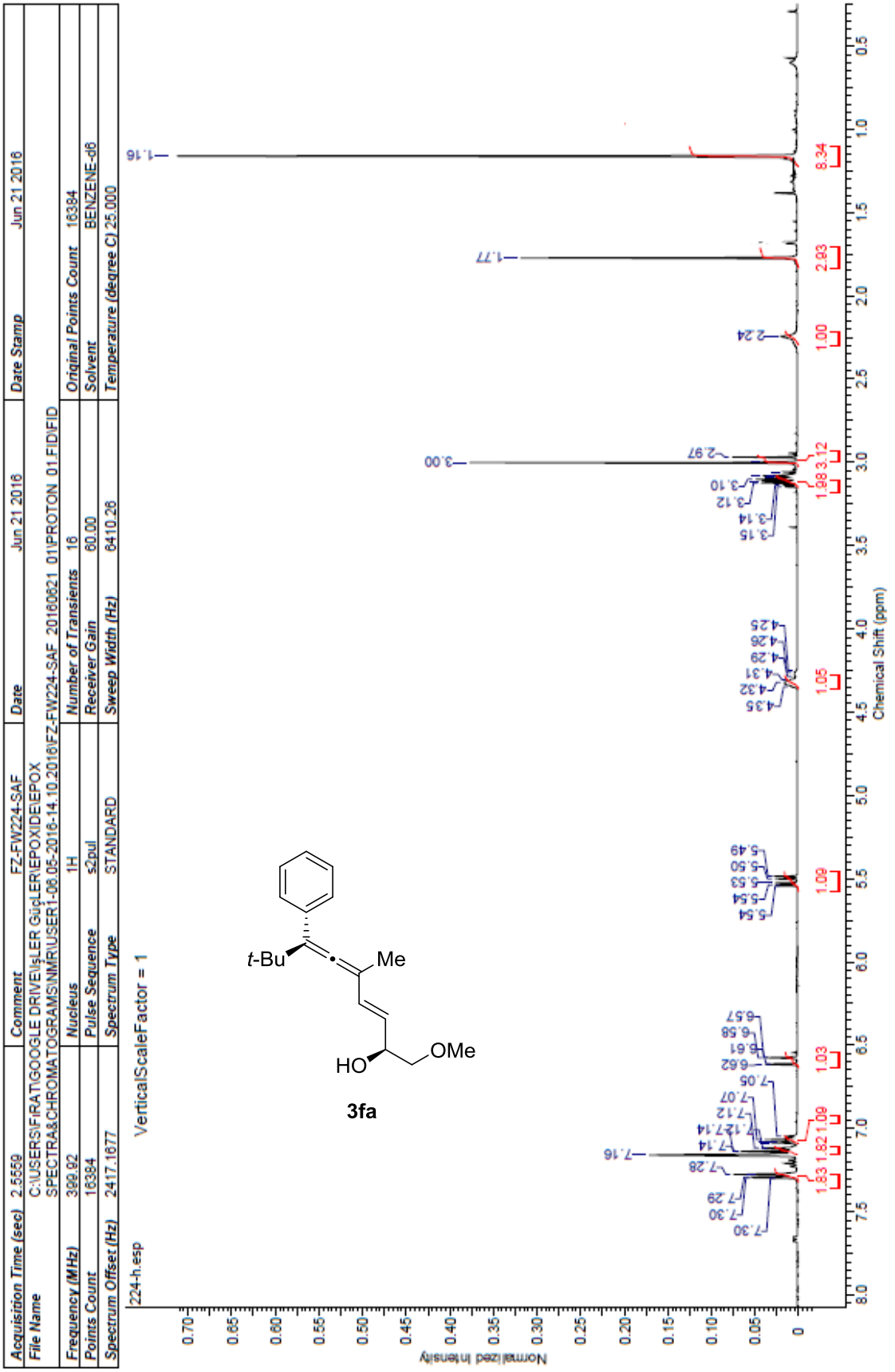
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 448
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11134.8682
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
211-c.esp
VerticalScaleFactor = 1
OMe
Me
HO
OMe
3eh
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW224-SAF
Date Jun 21 2016
Date Stamp Jun 21 2016
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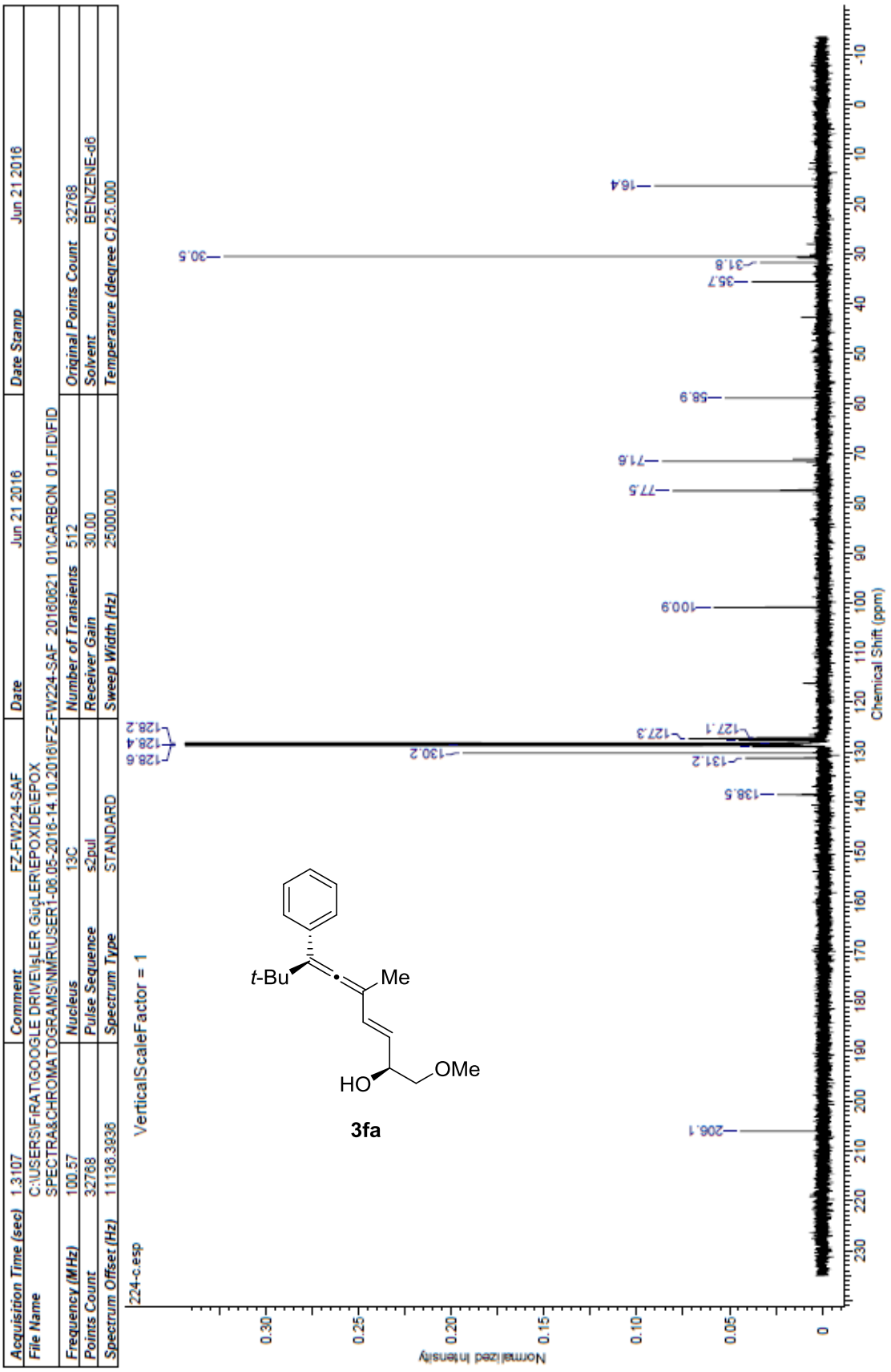
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 16
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 60.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2417.1677
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
224-h.esp
VerticalScaleFactor = 1
t-Bu
Me
HO
OMe
3fa
Normalized Intensity
Chemical Shift (ppm)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Date Stamp Jun 21 2016
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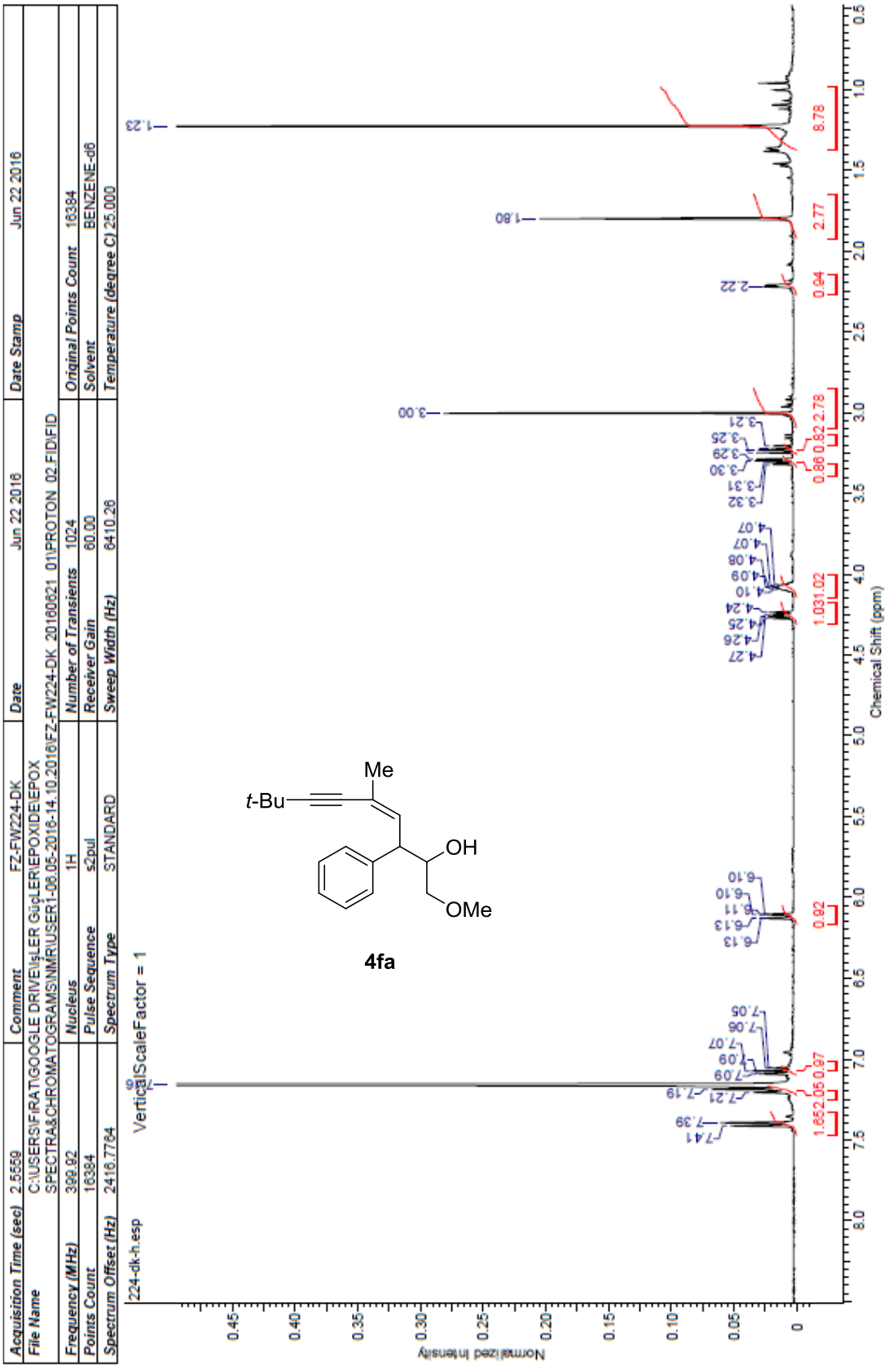
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 512
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
224-c.esp
VerticalScaleFactor = 1
206.1
164
138.5
131.2
130.2
128.6
128.4
128.2
127.3
127.1
100.9
77.5
71.6
58.9
35.7
31.8
30.5
t-Bu
Me
HO
OMe
3fa
Normalized Intensity
Chemical Shift (ppm)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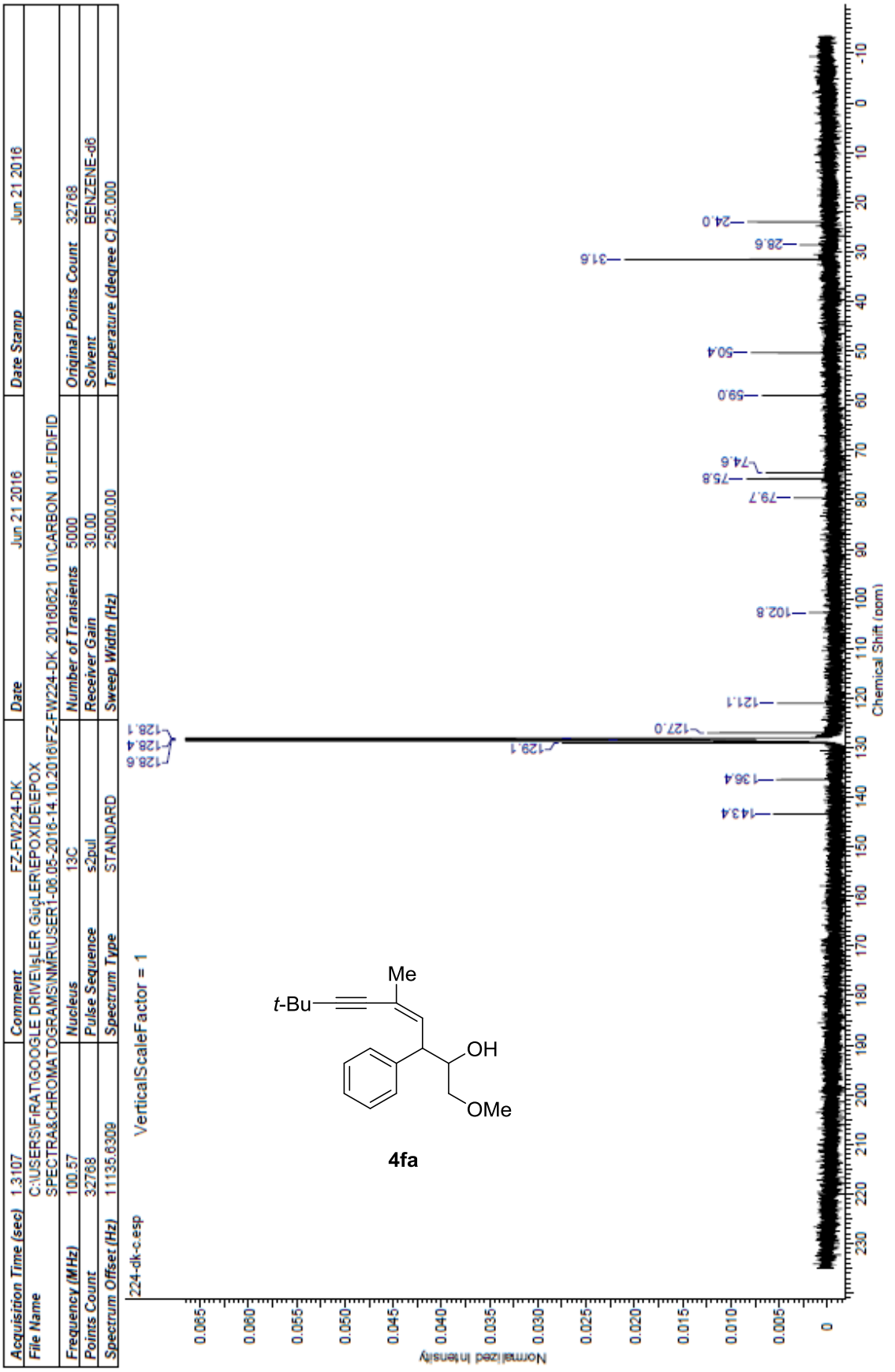
Comment FZ-FW224-DK
Date Jun 22 2016
Date Stamp Jun 22 2016
File Name C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçlER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\USER1-06.05-2016-14.10.2016\FZ-FW224-DK_20160621_01\PROTON_02.FID\FID
Frequency (MHz) 399.92
Nucleus 1H
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 60.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2418.7764
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
224-dk-h.esp
VerticalScaleFactor = 1
Me
t-Bu
OH
OMe
4fa
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW224-DK
Date Jun 21 2016
Date Stamp Jun 21 2016
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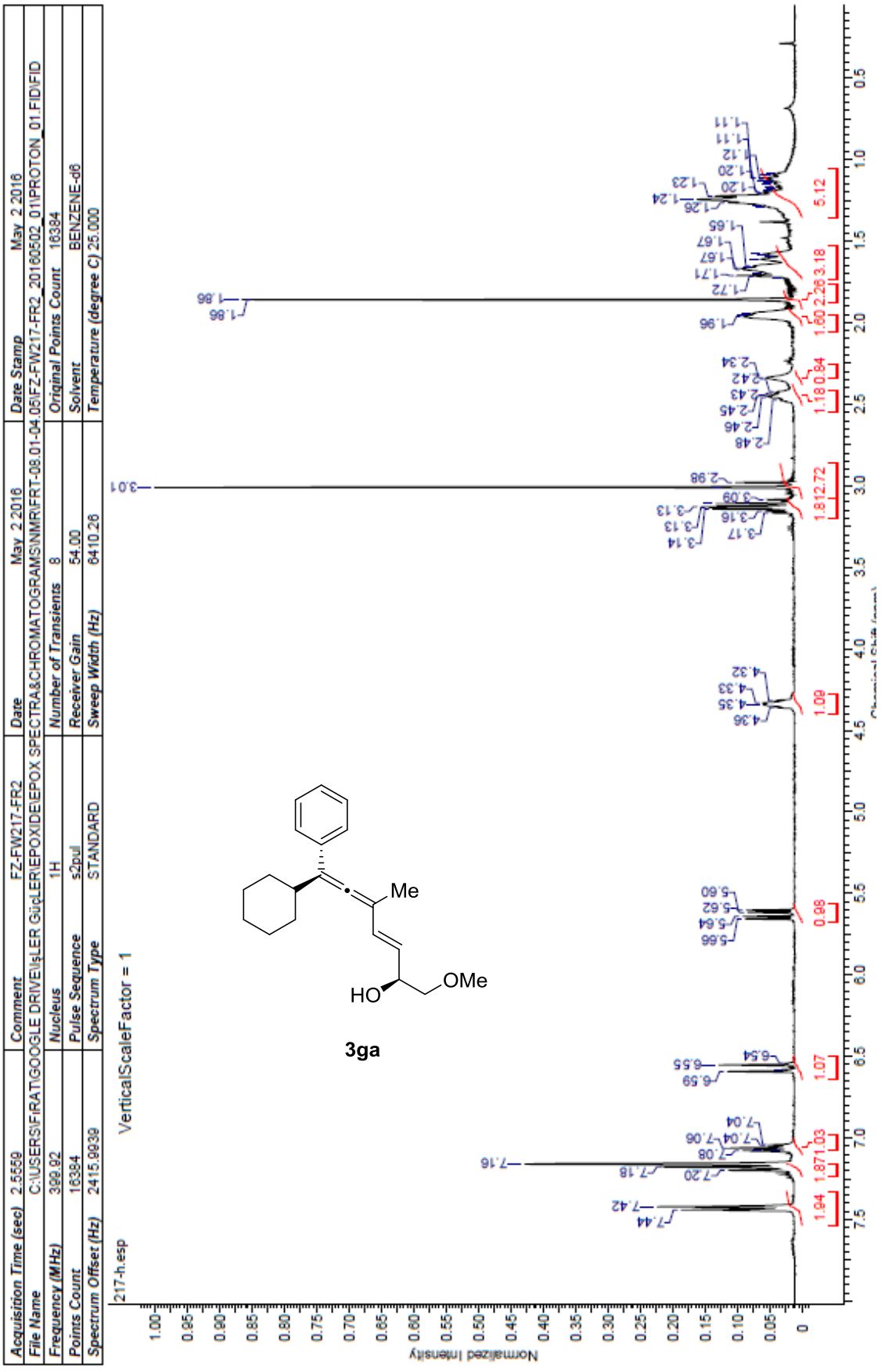
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 5000
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11135.8309
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
224-dk-c.esp
VerticalScaleFactor = 1
Me
t-Bu
OH
OMe
4fa
Normalized Intensity
Chemical Shift (ppm)
128.6
128.4
128.1
129.1
127.0
121.1
102.8
79.7
75.8
74.6
59.0
50.4
31.6
28.6
24.0
136.4
143.4


Acquisition Time (sec) 2.5559
Comment FZ-FW217-FR2
Date May 2 2016
Date Stamp May 2 2016
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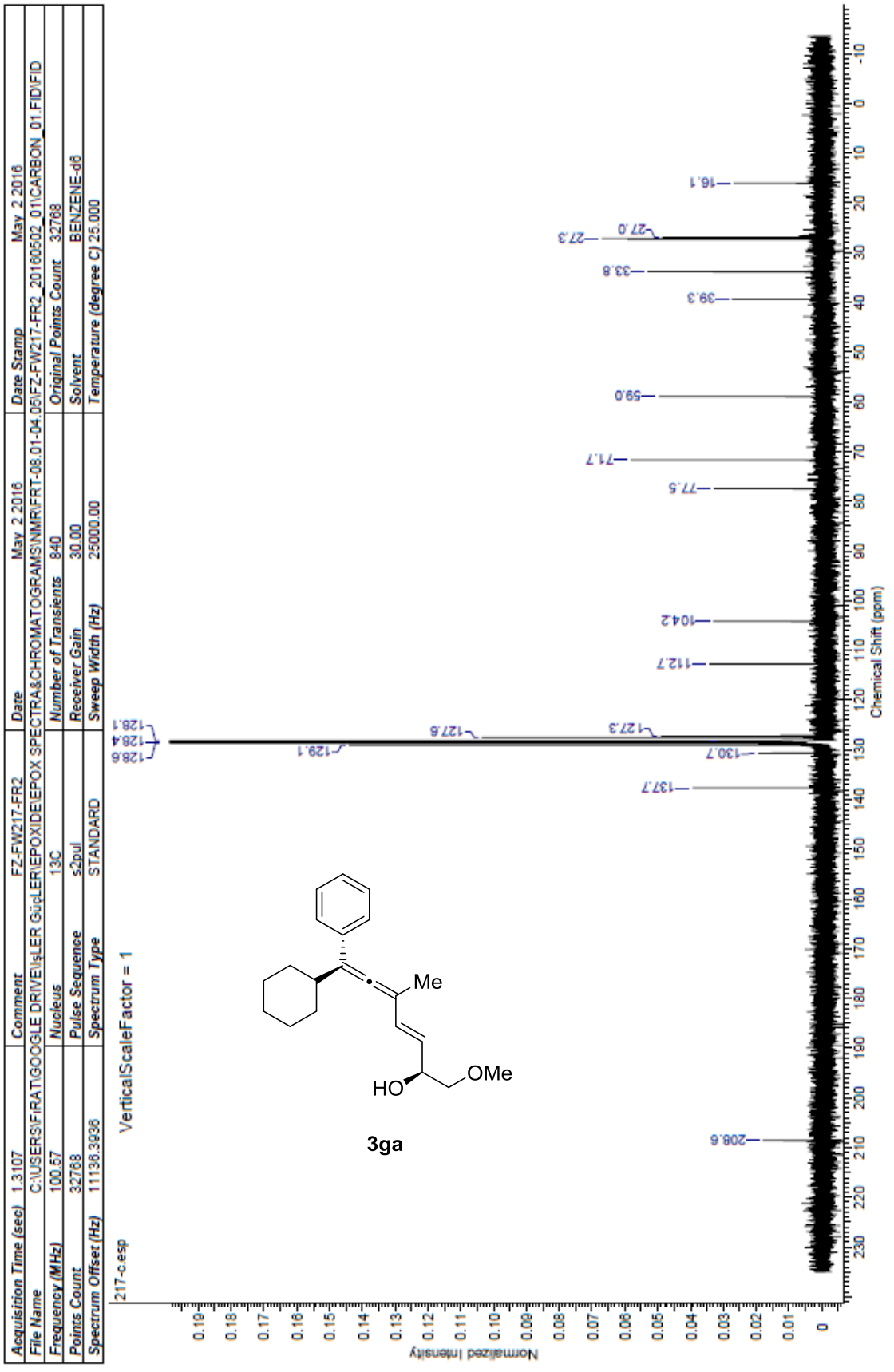
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 54.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2415.9939
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
217-h.esp
VerticalScaleFactor = 1
Me
HO
OMe
3ga
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW217-FR2
Date May 2 2016
Date Stamp May 2 2016
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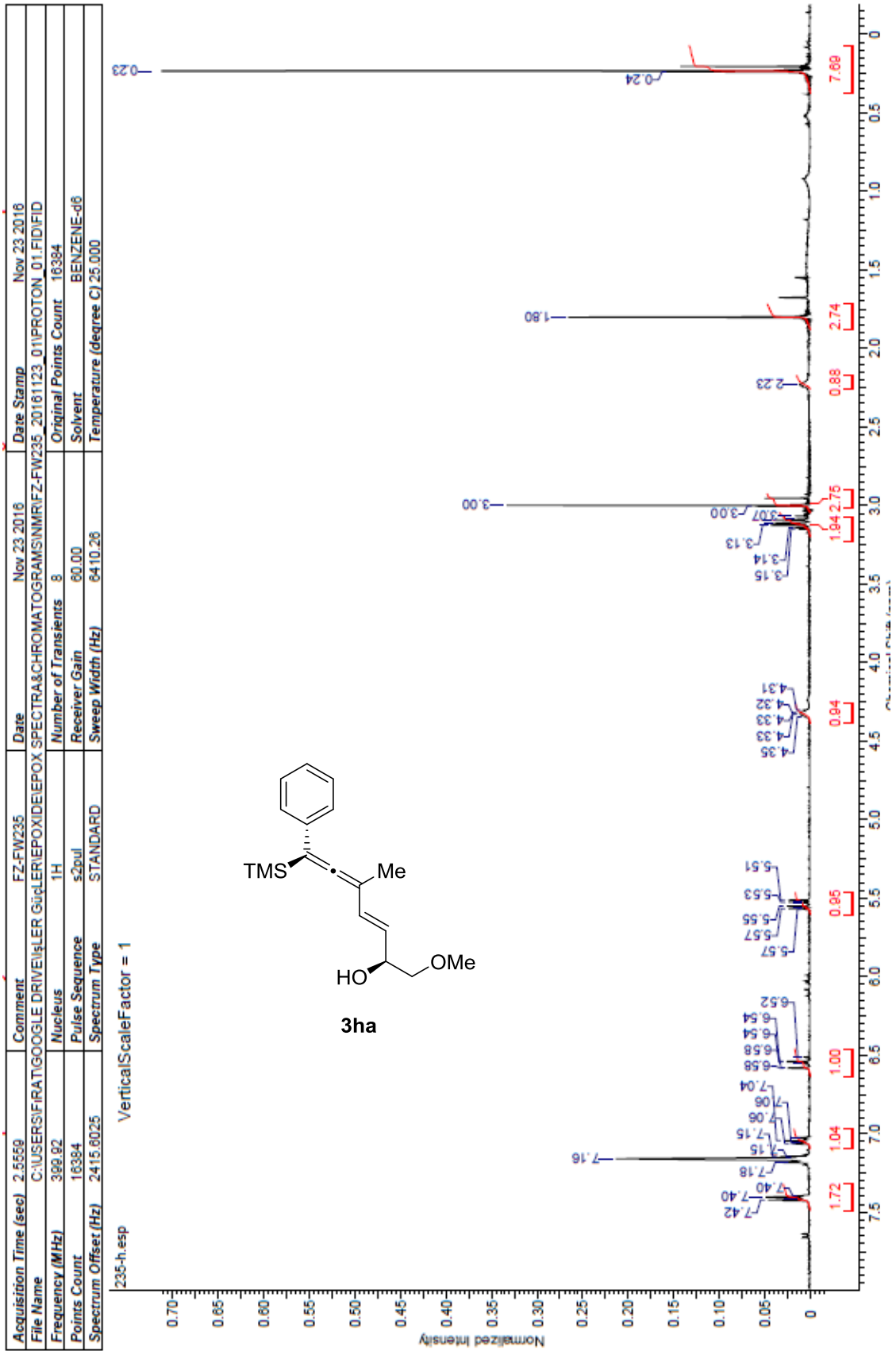
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 840
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
217-c.esp
VerticalScaleFactor = 1
Me
HO
OMe
3ga
Normalized Intensity
Chemical Shift (ppm)
208.6
137.7
130.7
129.1
128.6
128.4
128.1
127.6
127.3
112.7
104.2
77.5
71.7
59.0
39.3
33.8
27.3
27.0
16.1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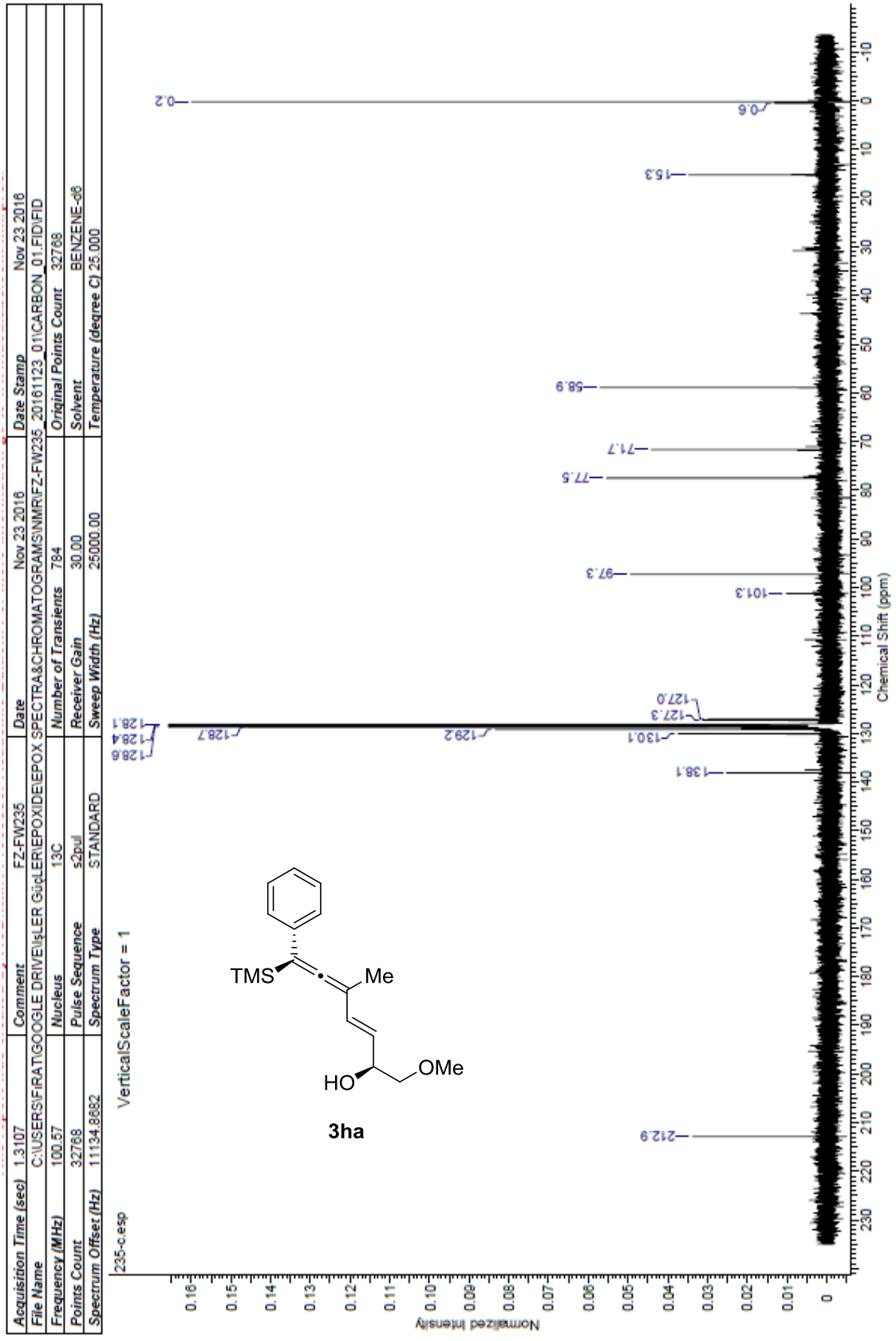
Frequency (MHz) 399.92
Points Count 16384
Spectrum Offset (Hz) 2415.6025
Comment FZ-FW235
Nucleus 1H
Pulse Sequence s2pul
Spectrum Type STANDARD
Date Nov 23 2016
Number of Transients 8
Receiver Gain 60.00
Sweep Width (Hz) 6410.26
Date Stamp Nov 23 2016
Original Points Count 16384
Solvent BENZENE-d6
Temperature (degree C) 25.000
235-h.esp
VerticalScaleFactor = 1
TMS
Me
HO
OMe
3ha
Normalized Intensity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Comment FZ-FW235
Date Nov 23 2016
Date Stamp Nov 23 2016
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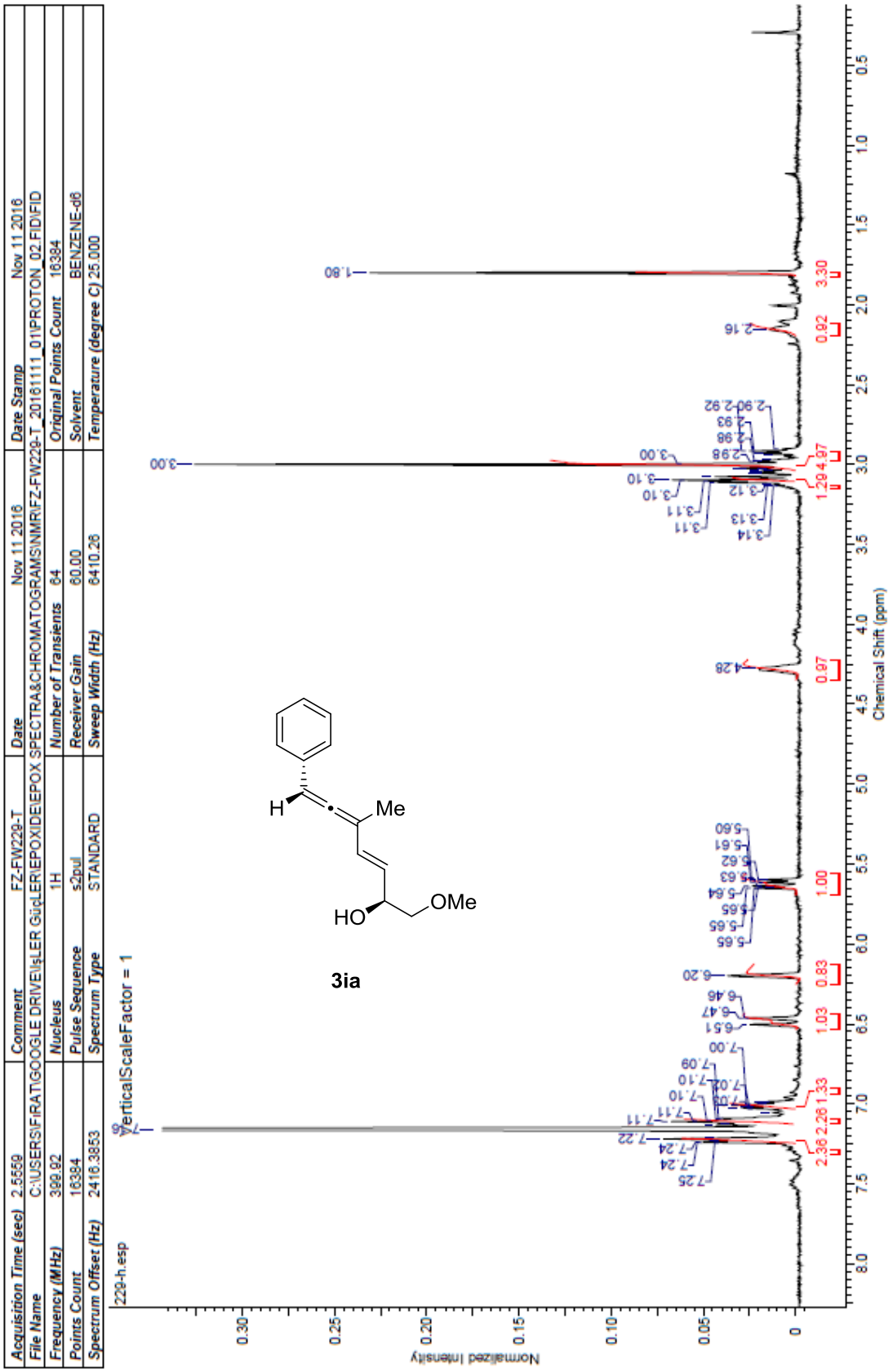
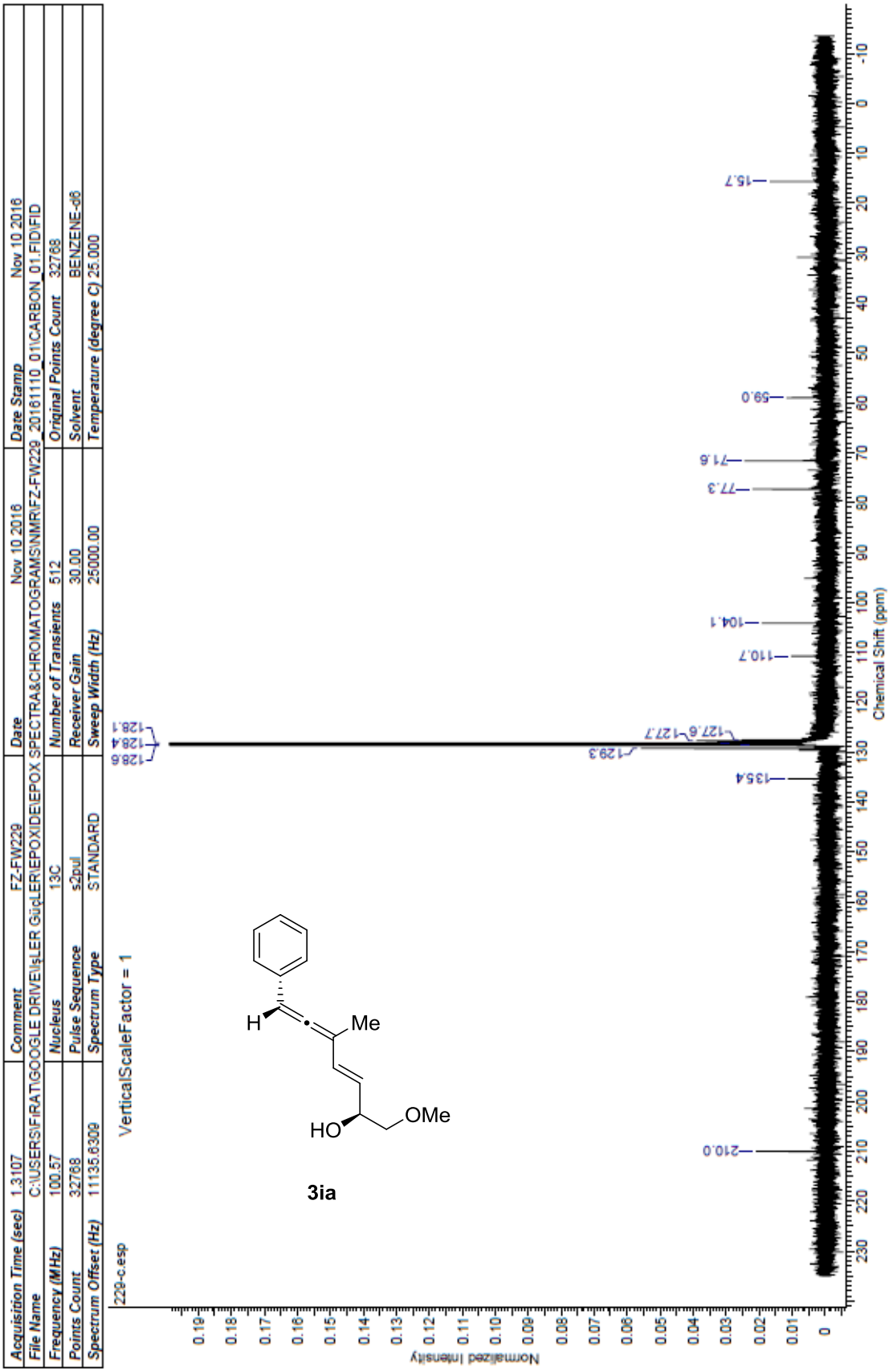
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 784
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11134.8682
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
235-c.esp
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
TMS
Me
HO
OMe
3ha


Acquisition Time (sec) 2.5559
Comment FZ-FW229-T
Date Nov 11 2016
Date Stamp Nov 11 2016
File Name C:\USERS\FIRAT\GOOGLE DRIVE\IsLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FZ-FW229-T_20161111_01\PROTON_02.FID\FID
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 64
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 60.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2416.3853
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
229-h.esp
VerticalScaleFactor = 1
H
Me
HO
OMe
3ia
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW229
Date Nov 10 2016
Date Stamp Nov 10 2016
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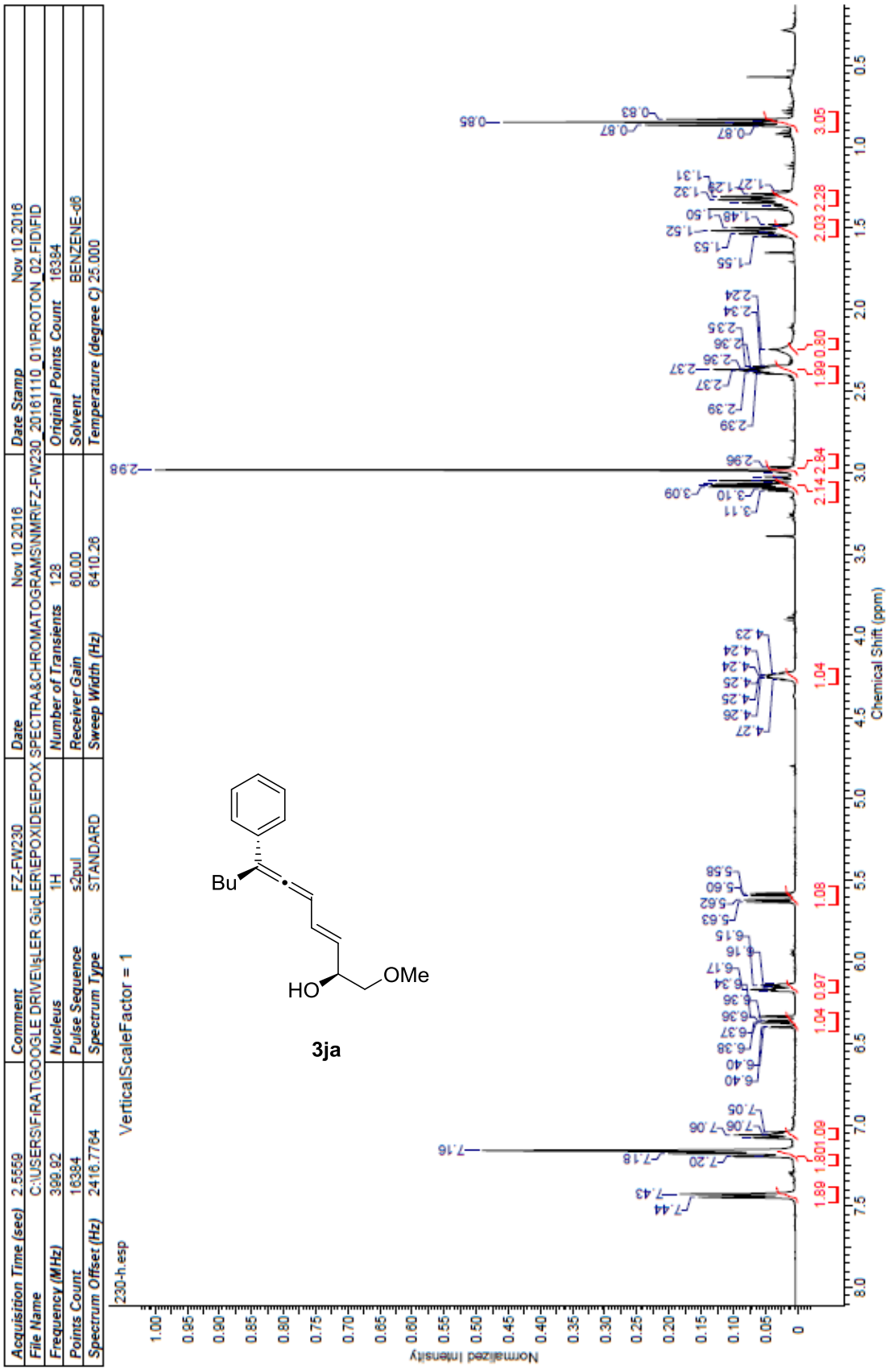
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 512
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11135.6309
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
229-c.esp
VerticalScaleFactor = 1
H
Me
HO
OMe
3ia
Normalized Intensity
Chemical Shift (ppm)
210.0
135.4
129.3
128.6
128.4
128.1
127.6
127.7
110.7
104.1
77.3
71.6
59.0
15.7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Date Nov 10 2016
Date Stamp Nov 10 2016
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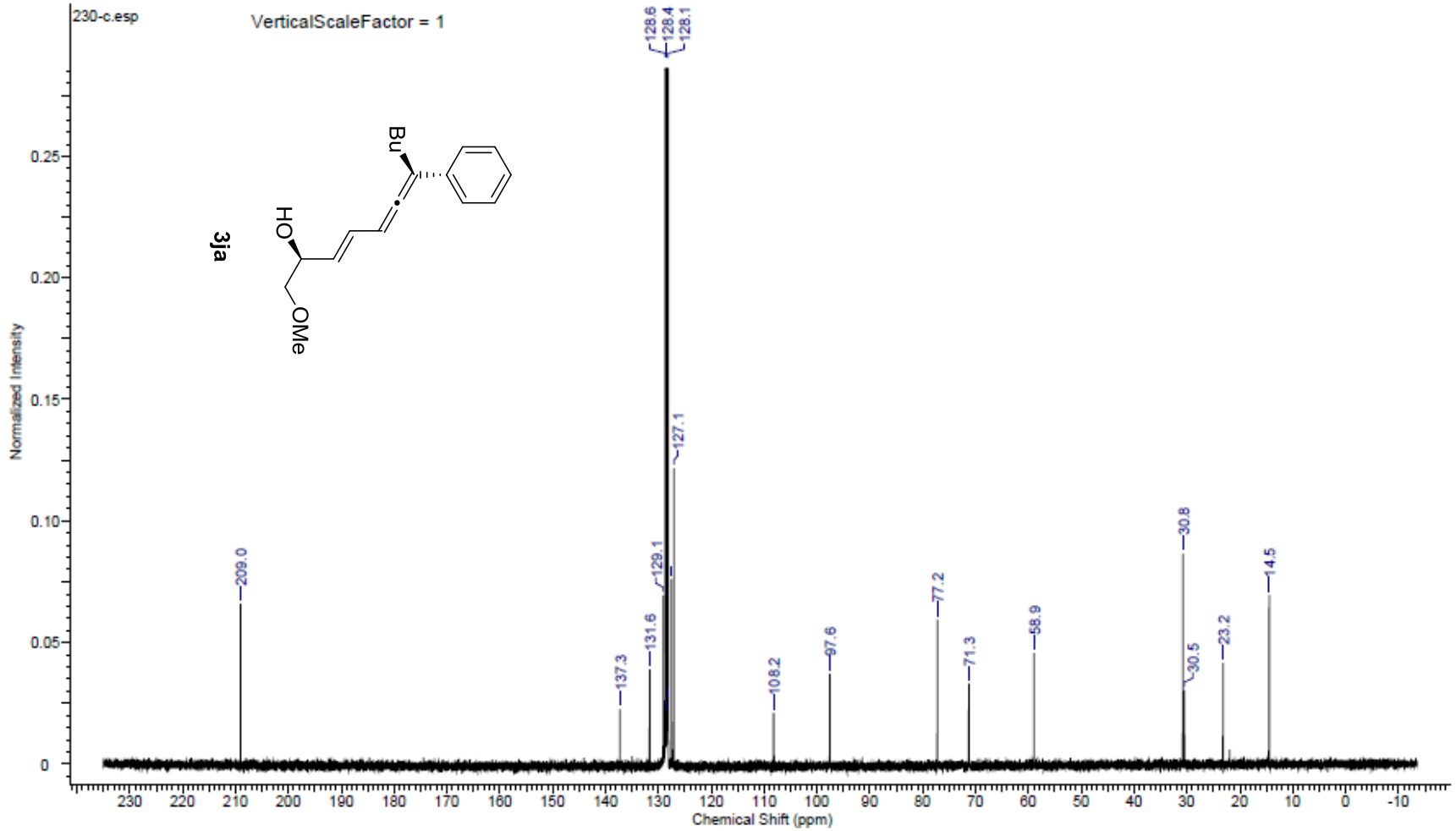
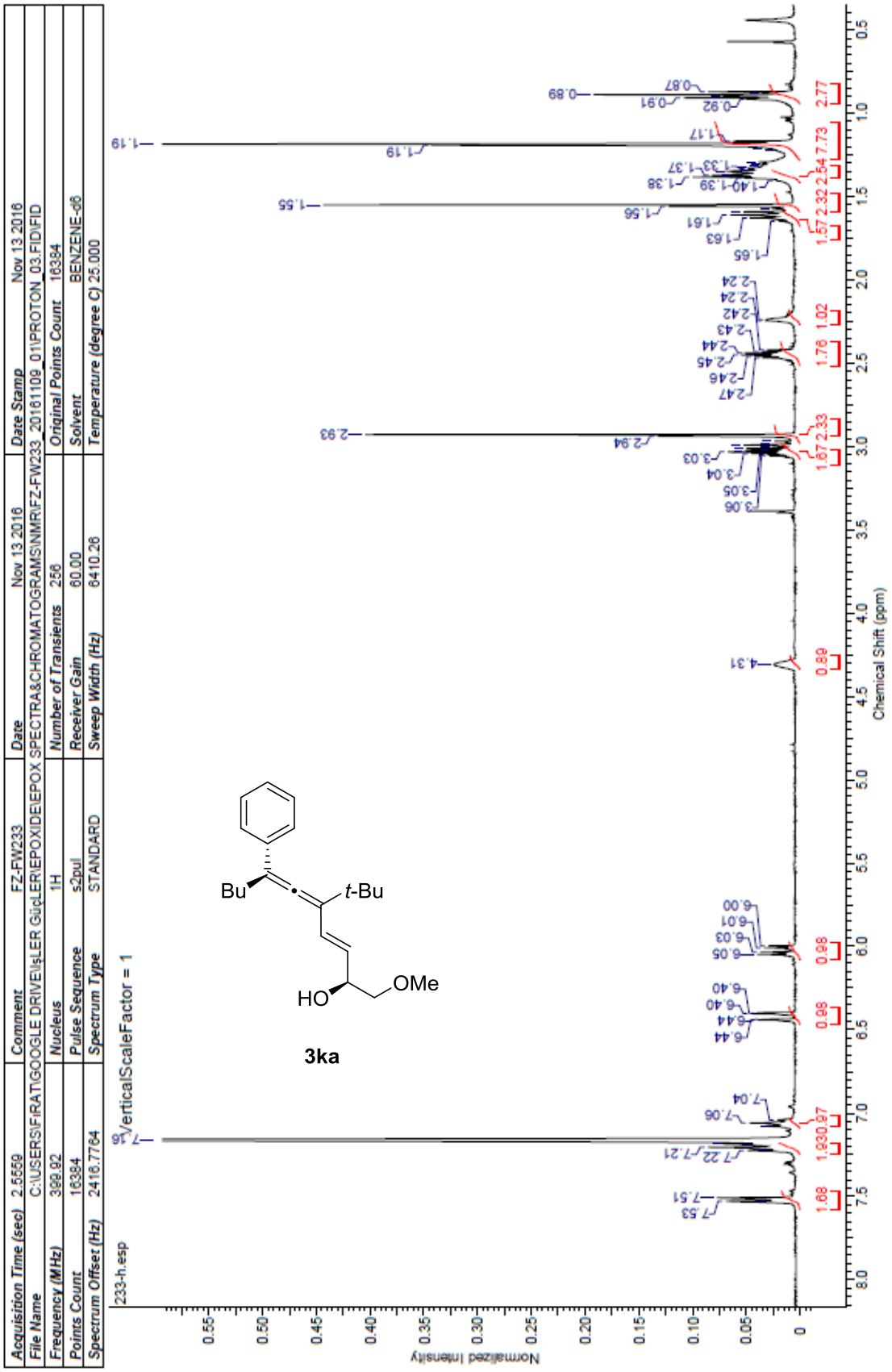
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 128
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 80.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2416.7764
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
230-h.esp
VerticalScaleFactor = 1
Bu
HO
OMe
3ja
Normalized Intensity
Chemical Shift (ppm)

Acquisition Time (sec)	1.3107	*Comment*	FZ-FW230	*Date*	Nov 11 2016	*Date Stamp*	Nov 11 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IŞLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FZ-FW230_20161110_01\CARBON_03.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	2000	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11135.6309	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

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Comment FZ-FW233
Date Nov 13 2016
Date Stamp Nov 13 2016
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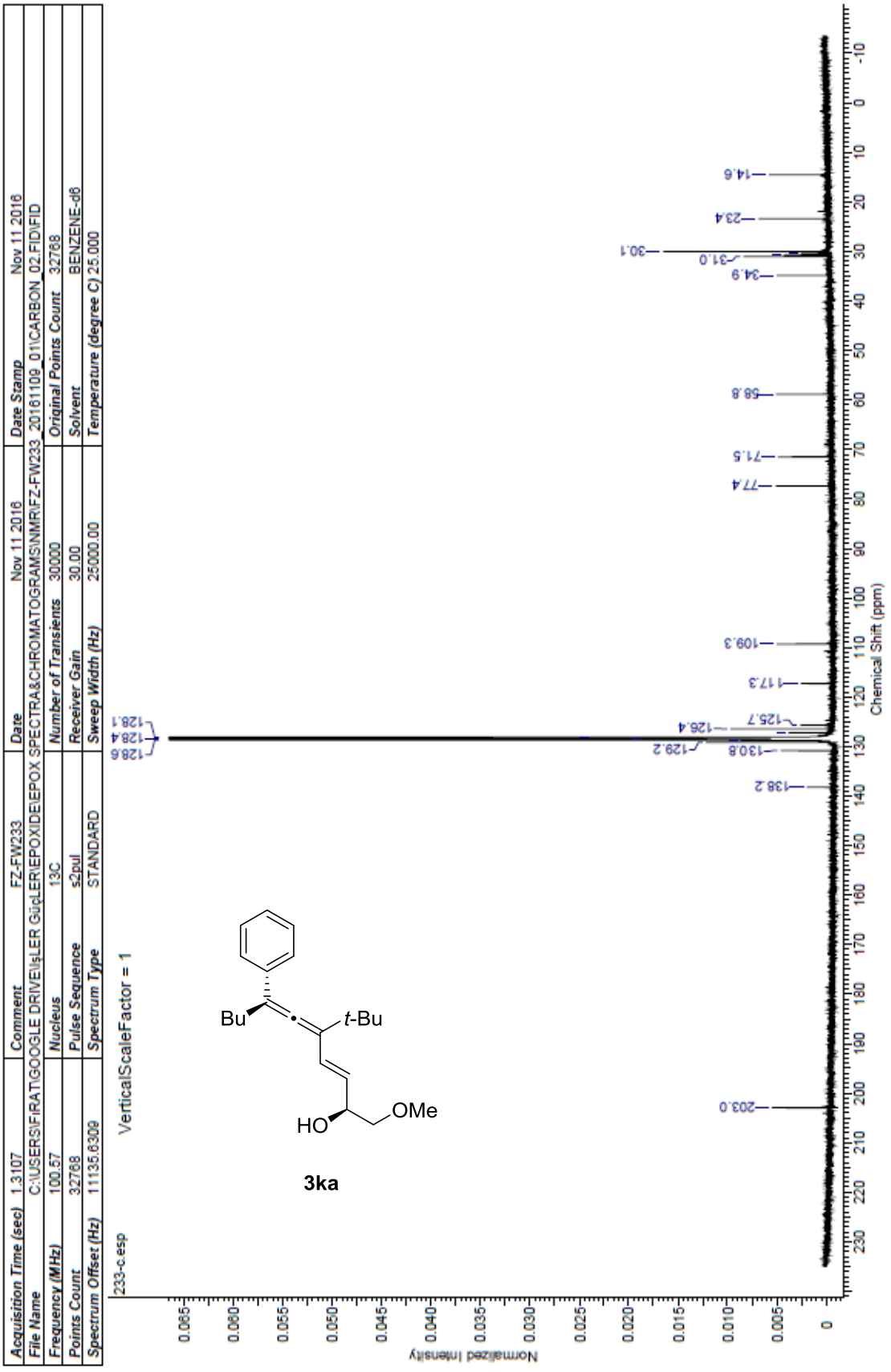
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 256
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 60.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2416.7764
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
233-h.esp
VerticalScaleFactor = 1
Bu
t-Bu
HO
OMe
3ka
Normalized Intensity
Chemical Shift (ppm)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Comment
FZ-FW233
Date
Nov 11 2016
Date Stamp
Nov 11 2016
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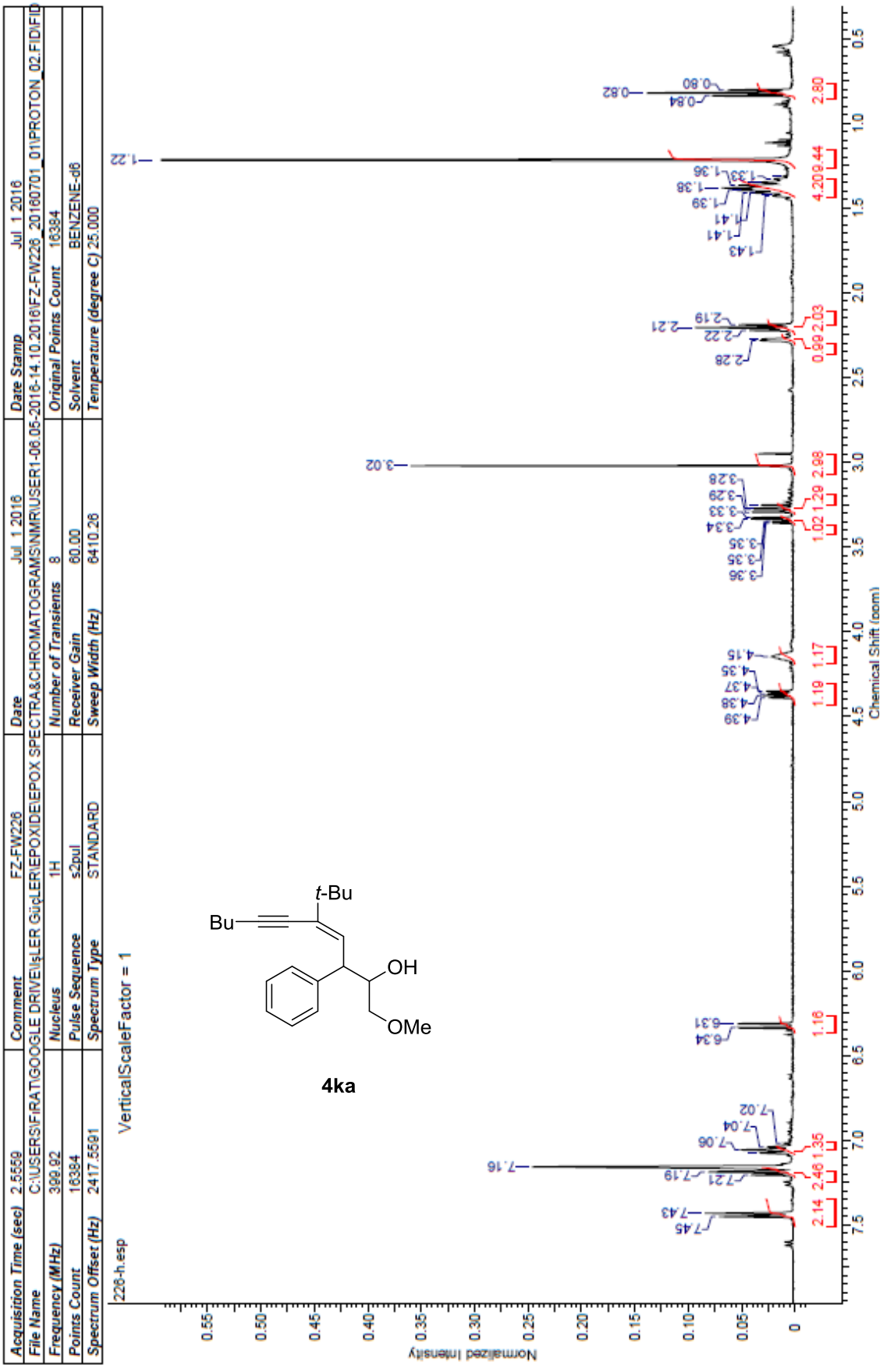
Frequency (MHz) 100.57
Nucleus
13C
Number of Transients 30000
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11135.6309
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
233-c.esp
VerticalScaleFactor = 1
Bu
t-Bu
HO
OMe
3ka
Normalized Intensity
Chemical Shift (ppm)
203.0
138.2
130.8
129.2
128.6
128.4
128.1
125.7
117.3
109.3
77.4
71.5
58.8
34.9
31.0
30.1
23.4
14.6


Acquisition Time (sec) 2.5559
Comment FZ-FW226
Date Jul 1 2016
Date Stamp Jul 1 2016
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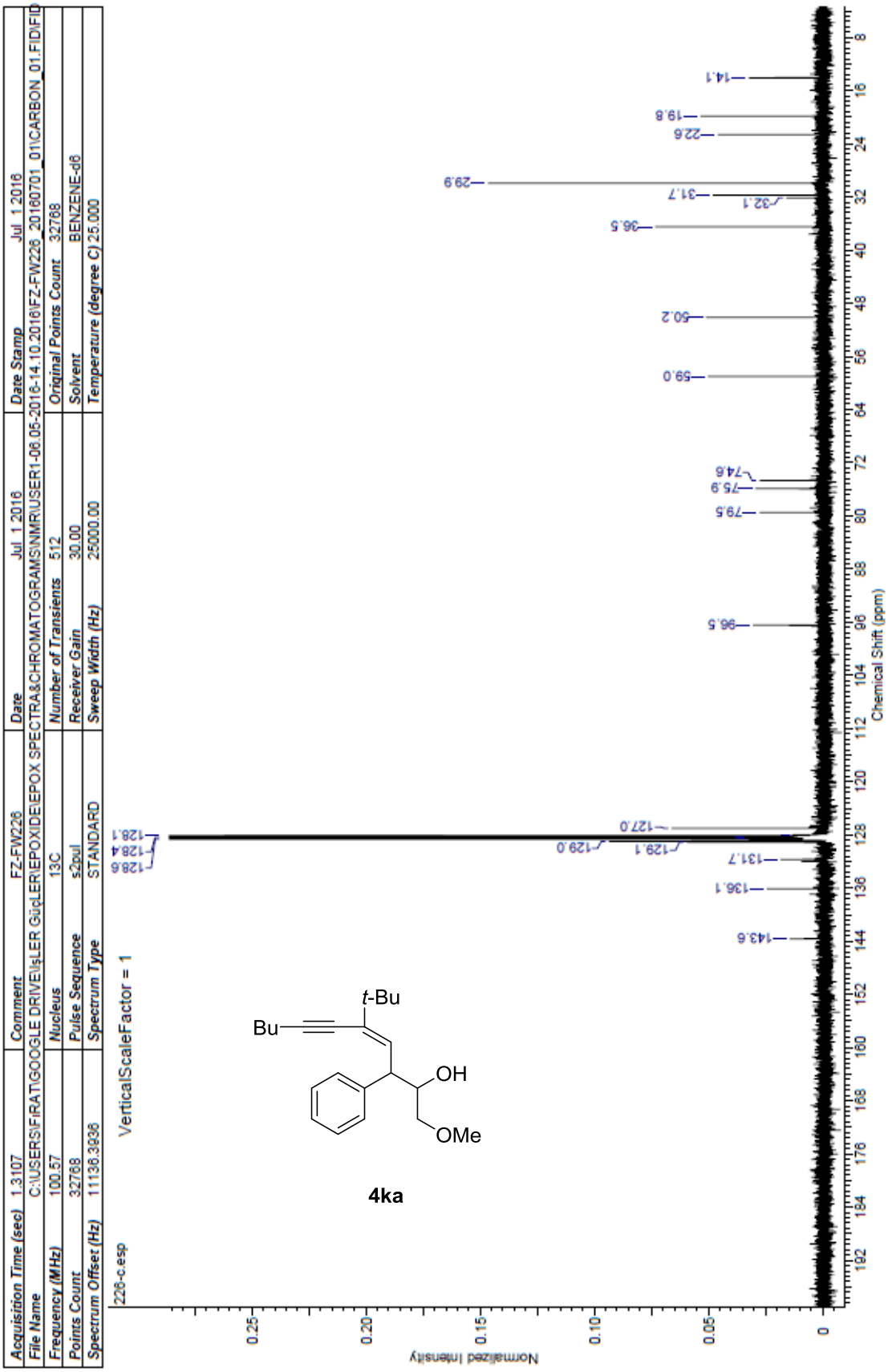
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 60.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2417.5591
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
226-h.esp
VerticalScaleFactor = 1
t-Bu
Bu
OH
OMe
4ka
Normalized Intensity
Chemical Shift (ppm)


Acquisition Time (sec) 1.3107
Comment
FZ-FW226
Date
Jul 1 2016
Date Stamp
Jul 1 2016
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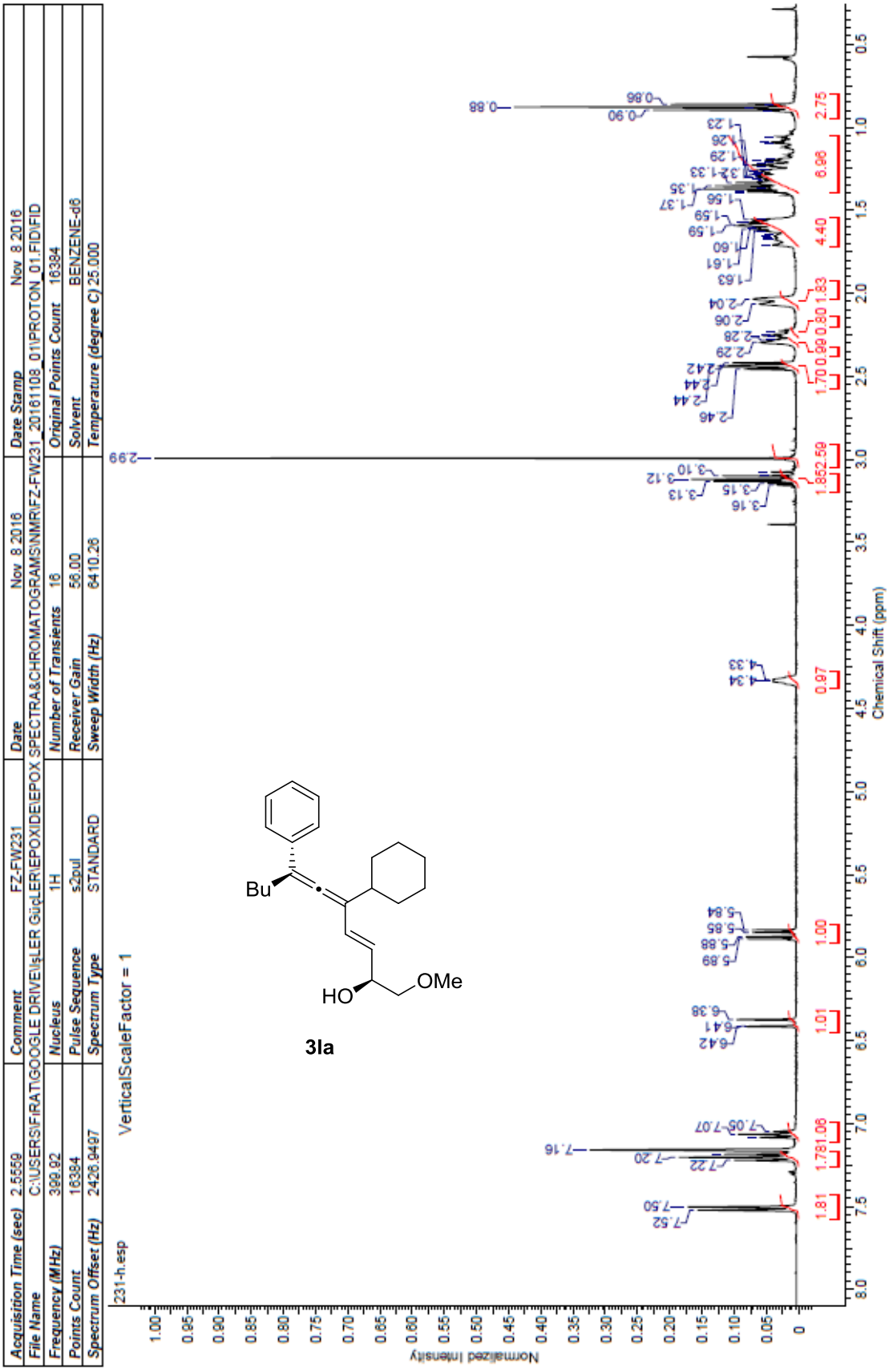
Frequency (MHz) 100.57
Nucleus
13C
Number of Transients 512
Original Points Count 32768
Points Count 32768
Pulse Sequence
s2pul
Receiver Gain 30.00
Solvent
BENZENE-d6
Spectrum Offset (Hz) 11138.3936
Spectrum Type
STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
226-c.esp
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
t-Bu
Bu
OH
OMe
4ka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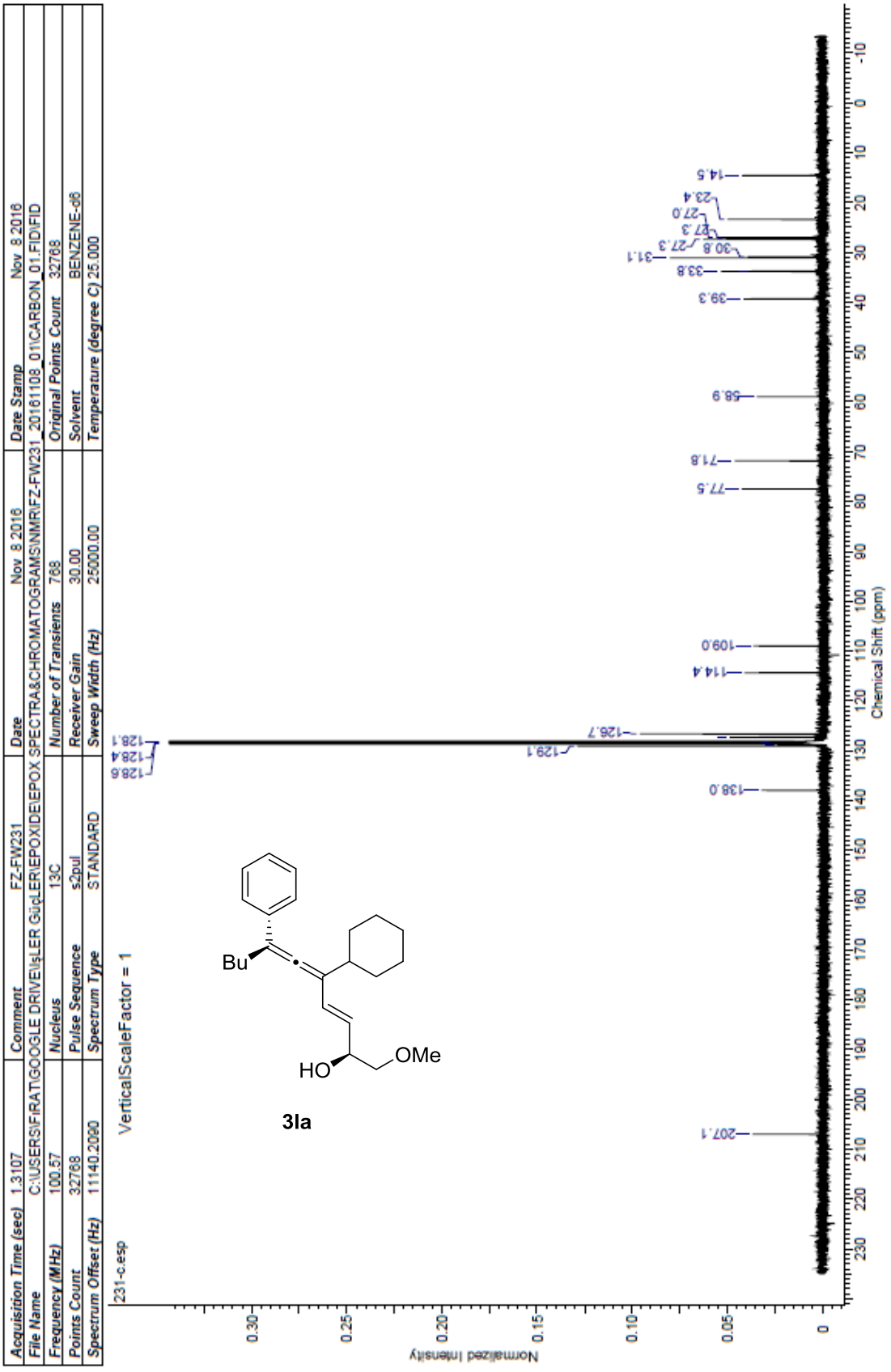
Frequency (MHz) 399.92
Points Count 16384
Spectrum Offset (Hz) 2426.8497
Comment FZ-FW231
Nucleus 1H
Pulse Sequence s2pul
Spectrum Type STANDARD
Date Nov 8 2016
Number of Transients 16
Receiver Gain 58.00
Sweep Width (Hz) 6410.26
Date Stamp Nov 8 2016
Original Points Count 16384
Solvent BENZENE-d6
Temperature (degree C) 25.000
231-h.esp
VerticalScaleFactor = 1
Bu
HO
OMe
3la
Normalized Intensity
Chemical Shift (ppm)


Acquisition Time (sec) 1.3107
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FZ-FW231
Date
Nov 8 2016
Date Stamp
Nov 8 2016
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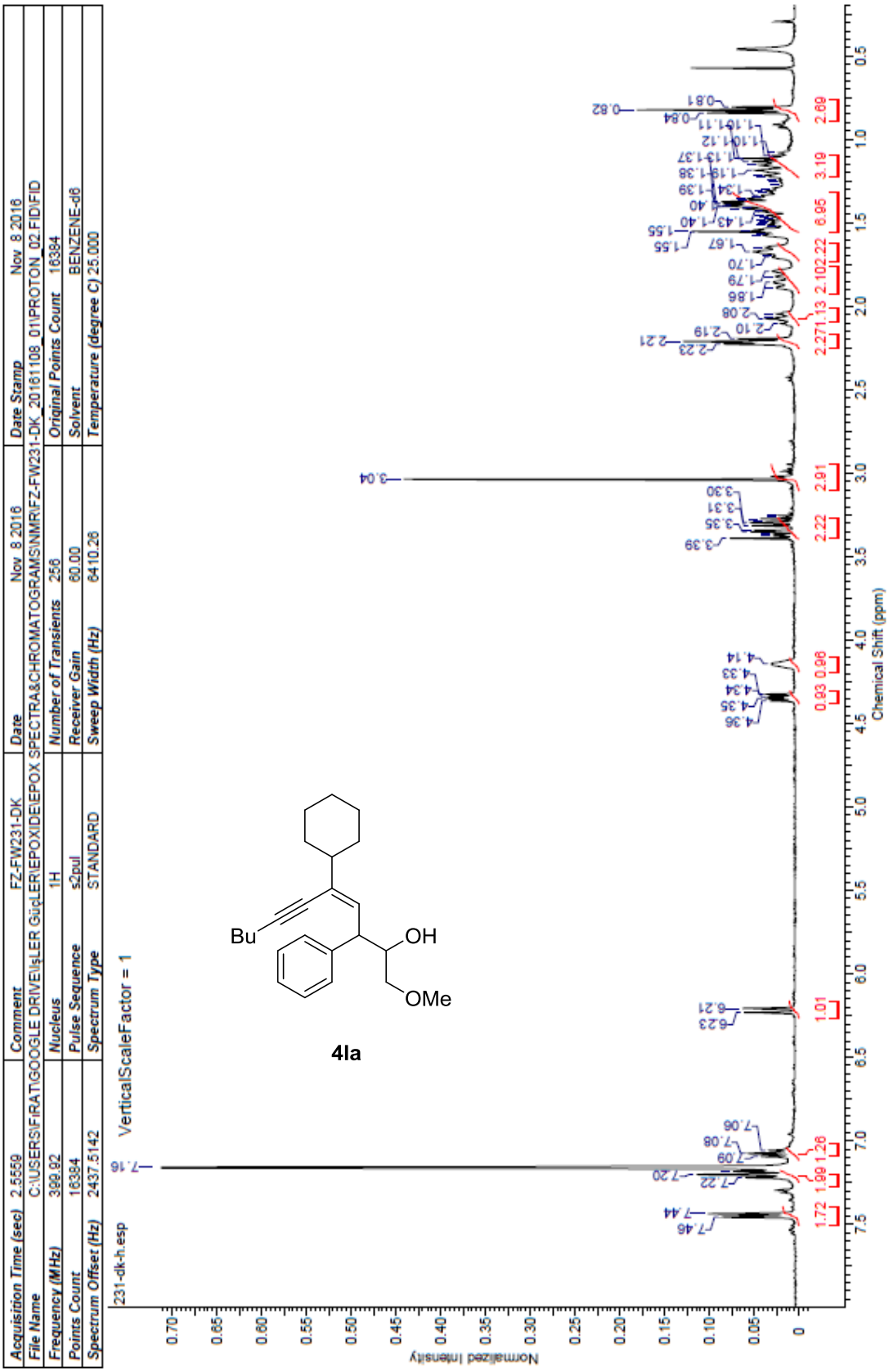
Frequency (MHz) 100.57
Nucleus
13C
Number of Transients 768
Original Points Count 32768
Points Count 32768
Pulse Sequence
s2pul
Receiver Gain 30.00
Solvent
BENZENE-d6
Spectrum Offset (Hz) 11140.2090
Spectrum Type
STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
231-c.esp
VerticalScaleFactor = 1
Bu
HO
OMe
3la
128.6
128.4
128.1
129.1
126.7
138.0
207.1
14.5
23.4
27.0
27.3
27.3
30.8
31.1
33.8
39.3
58.9
71.8
77.5
109.0
114.4
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW231-DK
Date Nov 8 2016
Date Stamp Nov 8 2016
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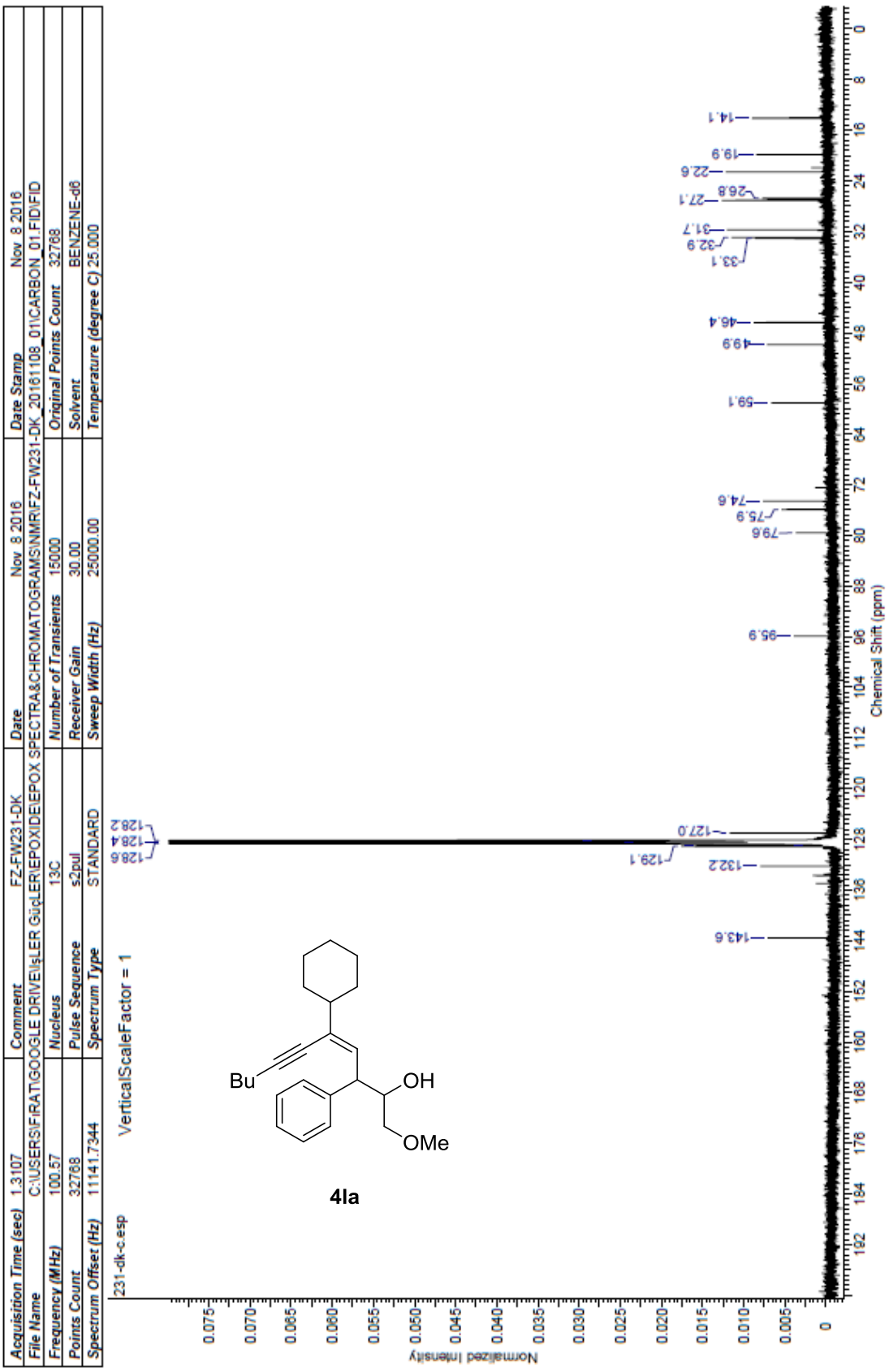
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 256
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 60.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2437.5142
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
231-dk-h.esp
VerticalScaleFactor = 1
Bu
OH
OMe
4la
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW231-DK
Date Nov 8 2016
Date Stamp Nov 8 2016
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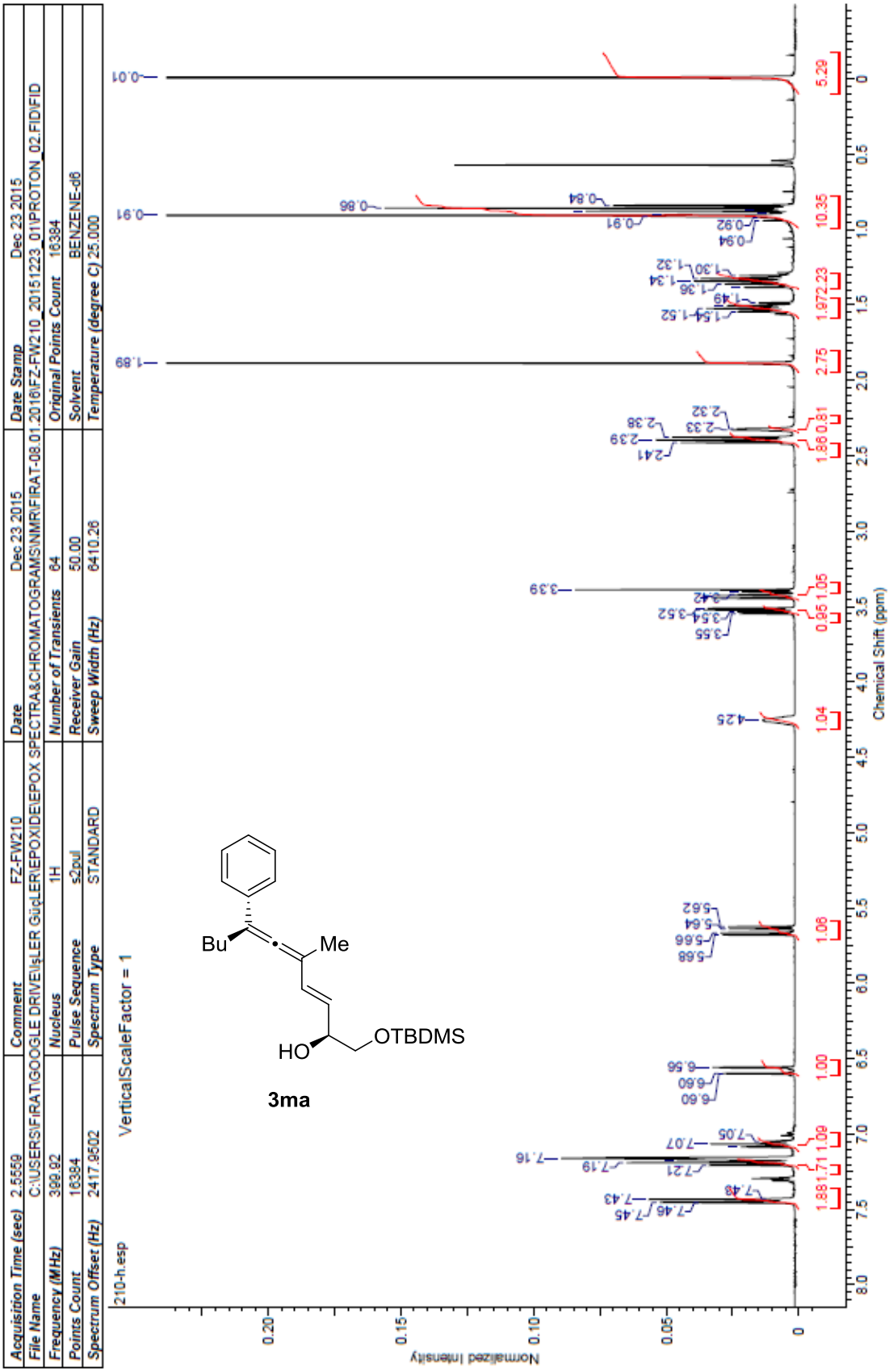
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 15000
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11141.7344
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
231-dk-c.esp
VerticalScaleFactor = 1
Bu
OH
OMe
4la
Normalized Intensity
Chemical Shift (ppm)


Acquisition Time (sec) 2.5559
Comment FZ-FW210
Date Dec 23 2015
Date Stamp Dec 23 2015
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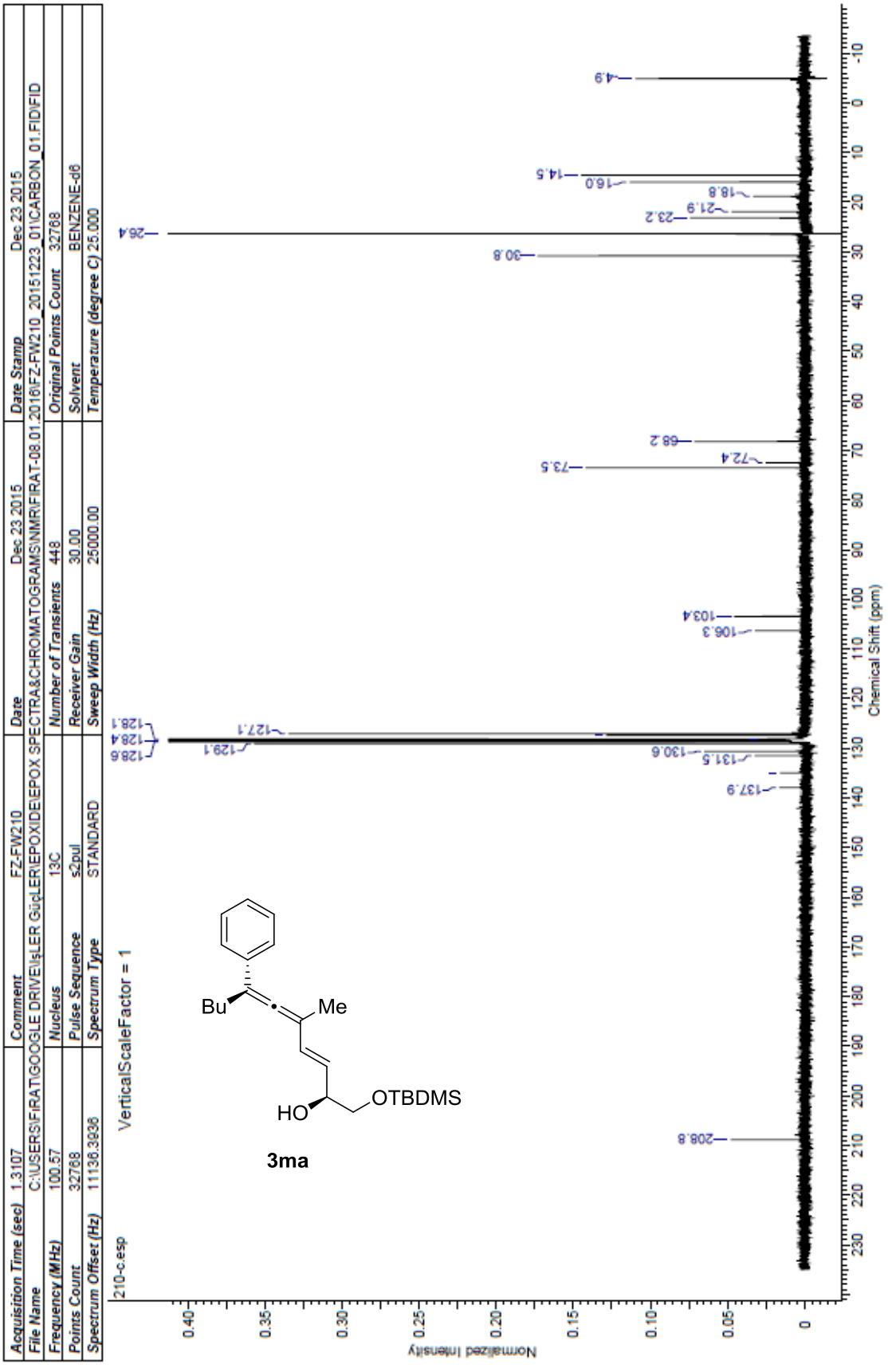
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 64
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 50.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2417.9502
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
210-h.esp
VerticalScaleFactor = 1
Bu
Me
HO
OTBDMS
3ma
Normalized Intensity
Chemical Shift (ppm)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Date Dec 23 2015
Date Stamp Dec 23 2015
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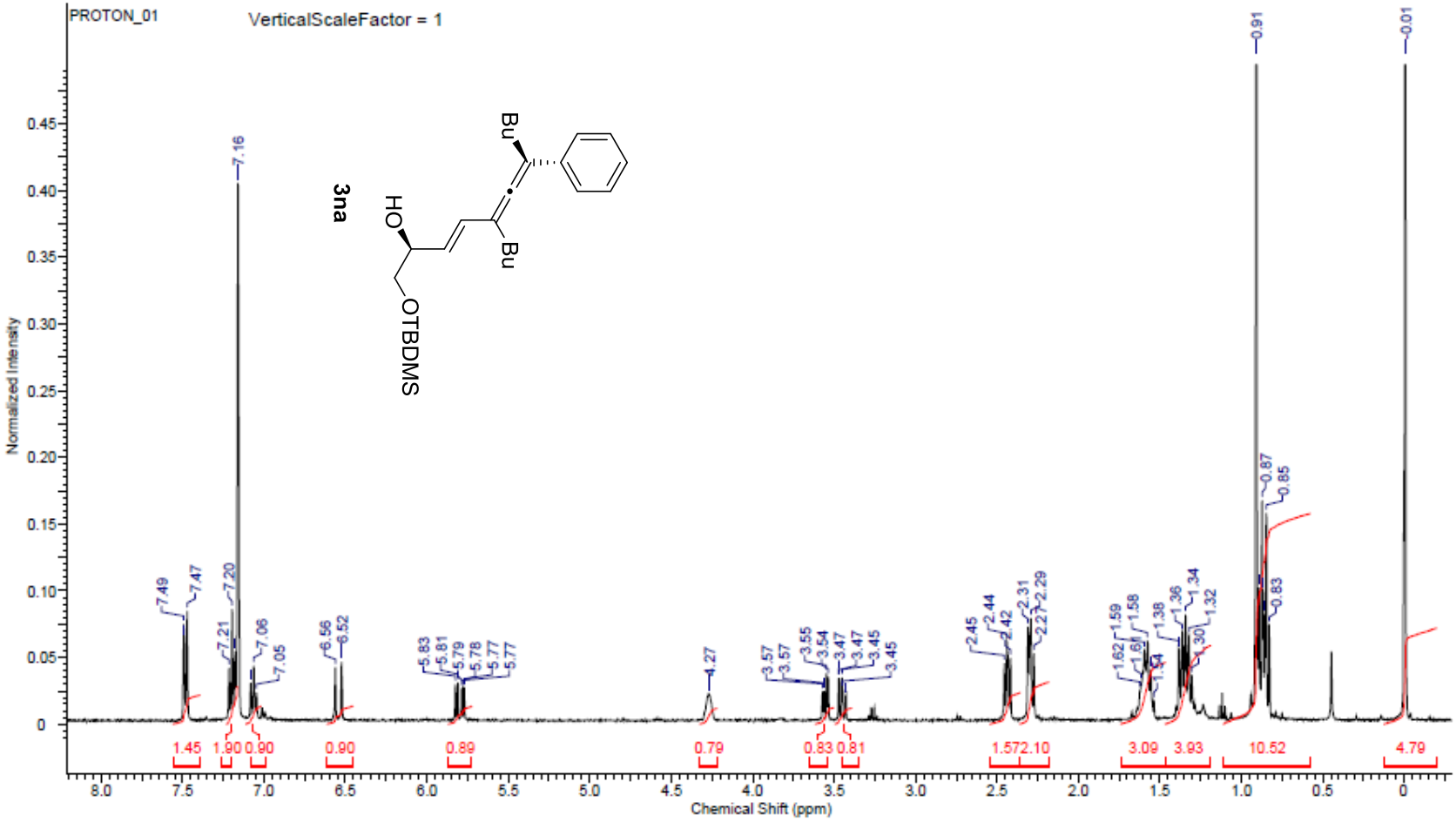
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 448
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
210-c.esp
VerticalScaleFactor = 1
Bu
Me
HO
OTBDMS
3ma
Normalized Intensity
Chemical Shift (ppm)

Acquisition Time (sec)	2.5559	*Comment*	FZ-FW216-2-KOLON-C6D6			*Date*	Feb 22 2016
Date Stamp	Feb 22 2016						
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FRT-08.01-04.05\FZ-FW216-2-KOLON-C6D6_20160222_01\PROTON_01.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2416.3853	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



Acquisition Time (sec)	1.3107	*Comment*	FZ-FW216-2-KOLON-C6D6			*Date*	Feb 22 2016
Date Stamp	Feb 22 2016						
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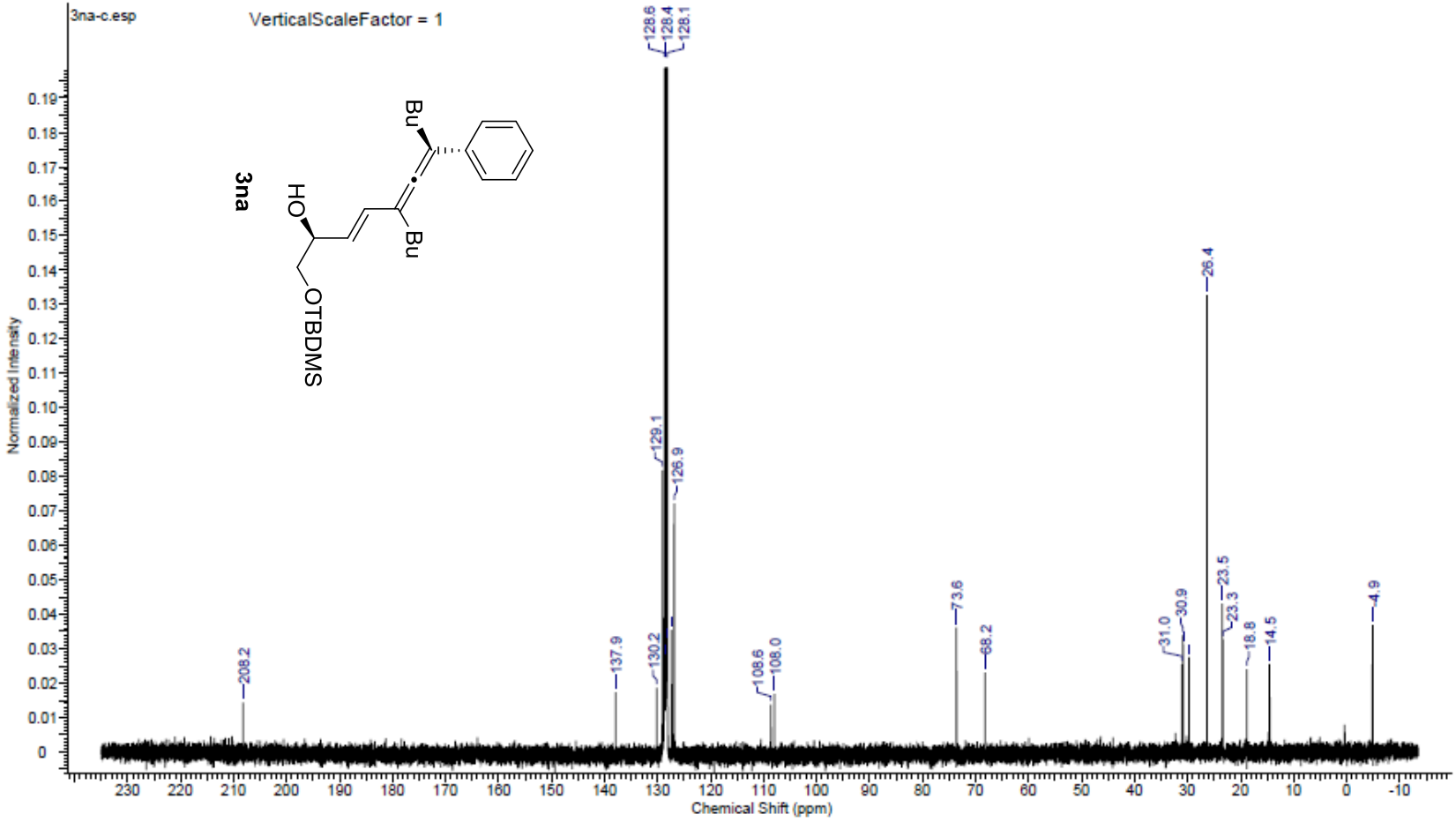
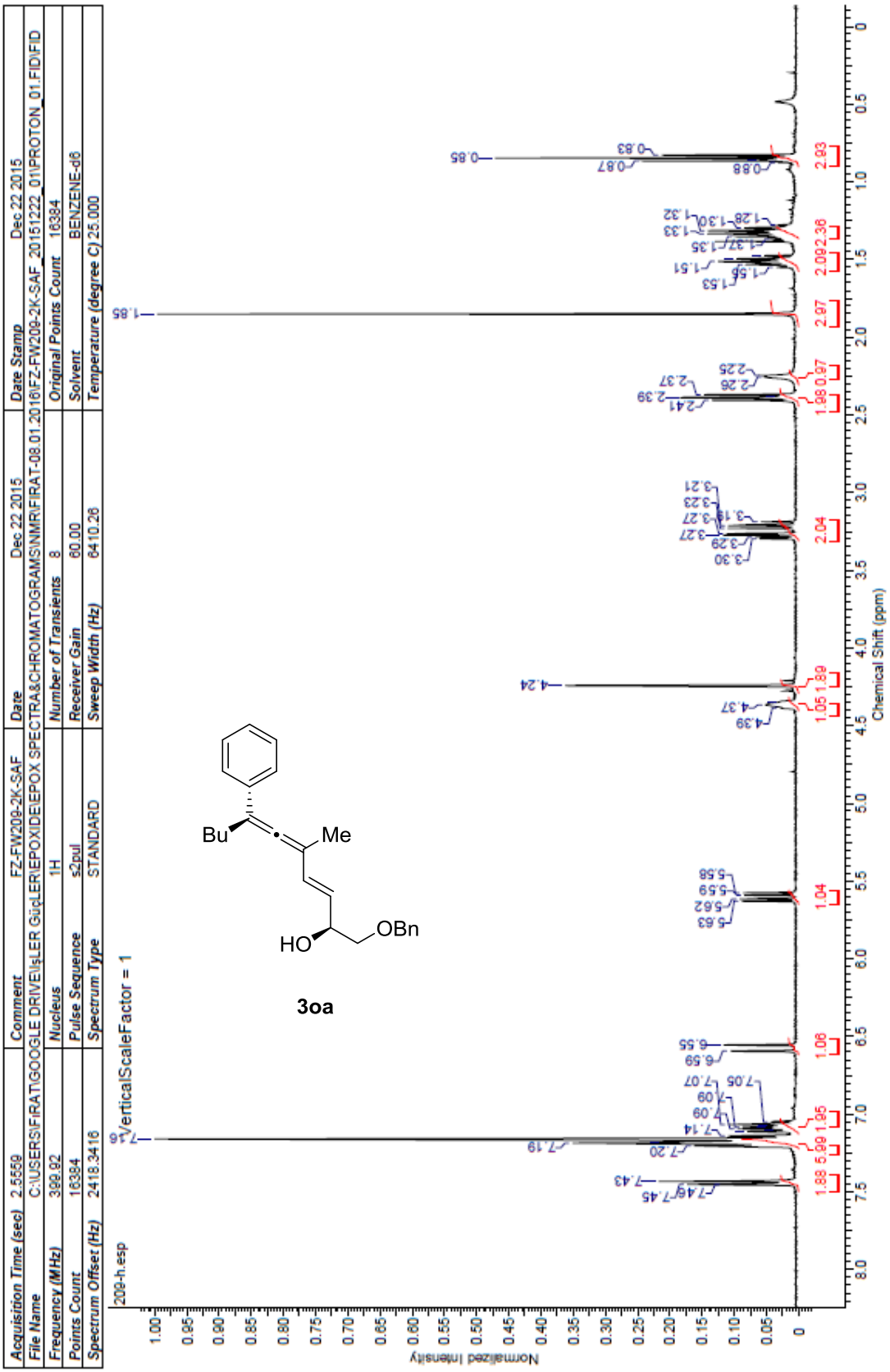
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	1000	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11135.6309	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

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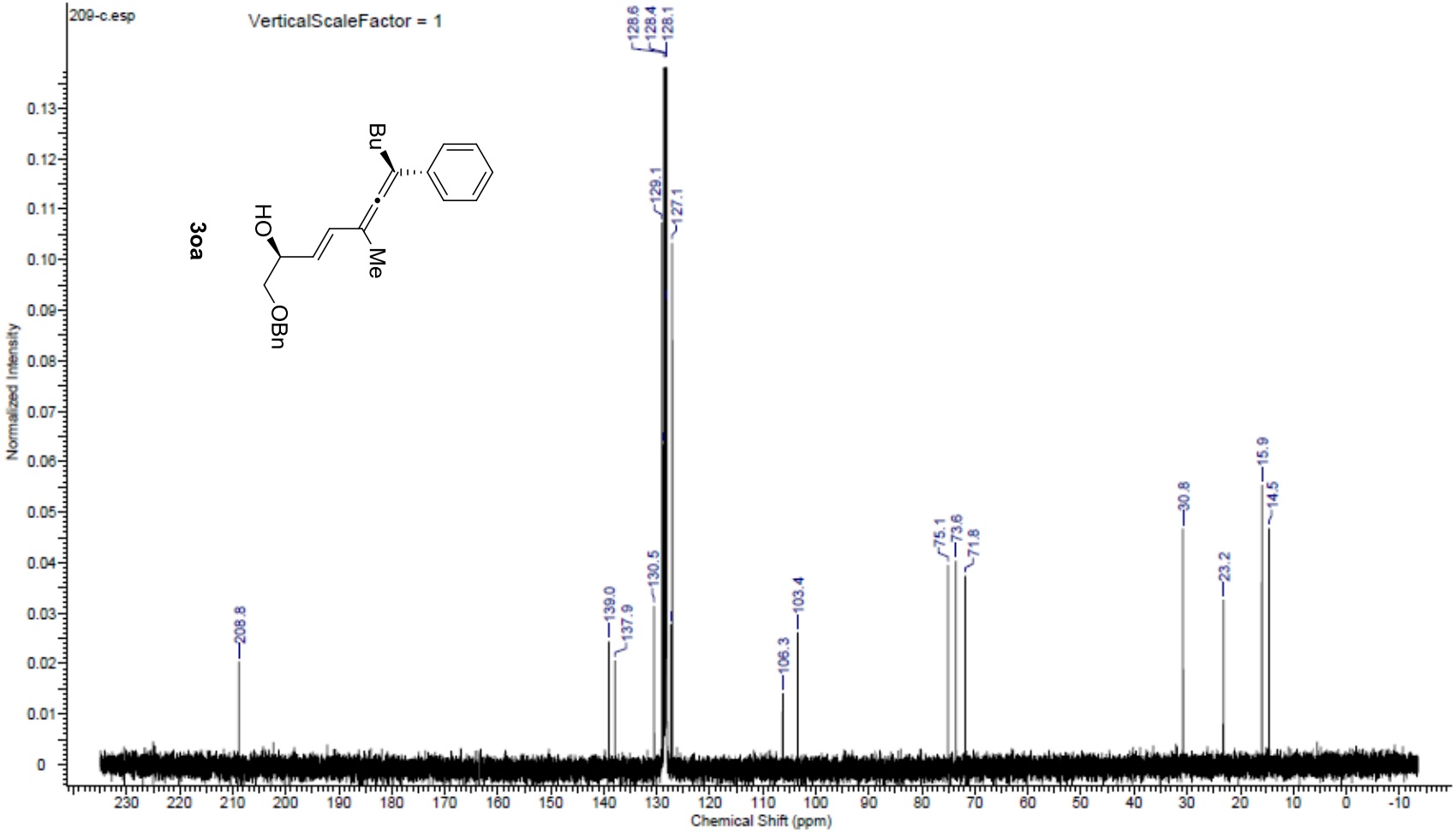
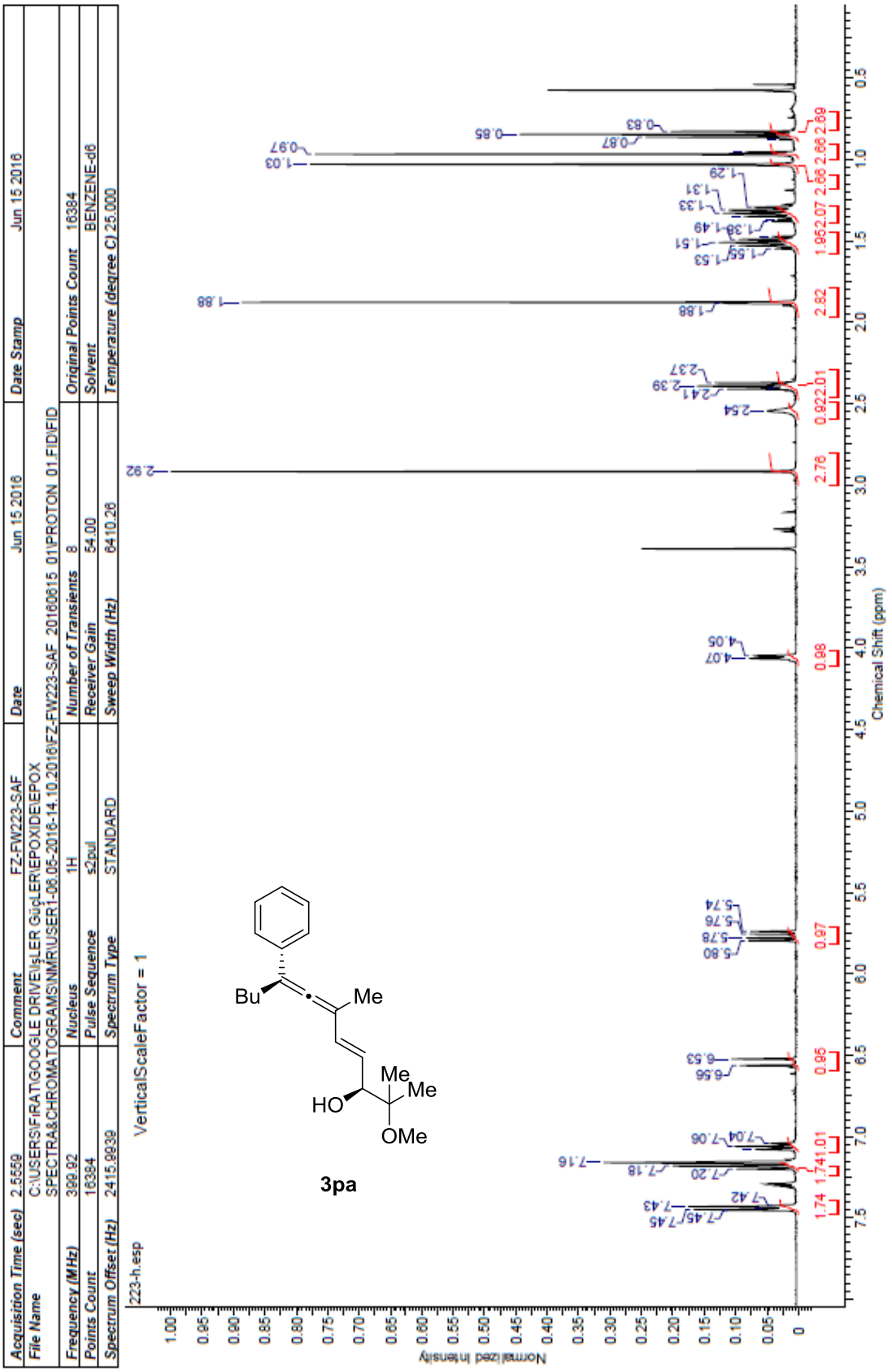
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 60.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2418.3418
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
Comment FZ-FW209-2K-SAF
Date Dec 22 2015
Date Stamp Dec 22 2015
209-h.esp
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
Bu
Me
HO
OBn
3oa

Acquisition Time (sec)	1.3107	*Comment*	FZ-FW209-2K-SAF	*Date*	Dec 22 2015	*Date Stamp*	Dec 22 2015
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IŞLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FIRAT-08.01.2016\FZ-FW209-2K-SAF_20151222_01\CARBON_01.FID\FID						
Frequency (MHz)	100.57	*Nucleus*	13C	*Number of Transients*	1000	*Original Points Count*	32768
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	11134.8682	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	25000.00	*Temperature (degree C)*	25.000

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Date Jun 15 2016
Date Stamp Jun 15 2016
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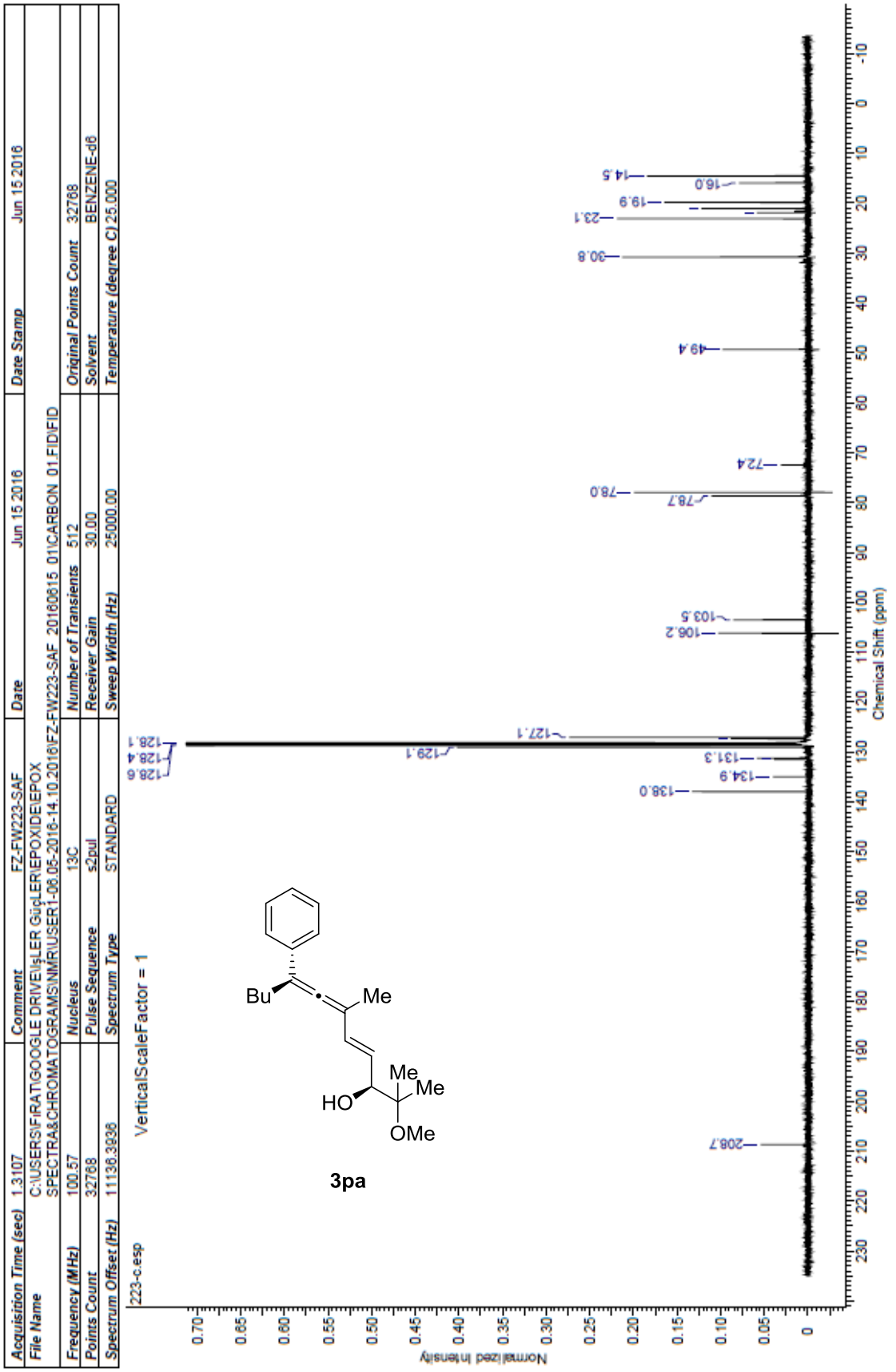
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 54.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2415.9939
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
223-h.esp
VerticalScaleFactor = 1
Bu
Me
Me
Me
HO
OMe
3pa
Normalized Intensity
Chemical Shift (ppm)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Comment FZ-FW223-SAF
Date Jun 15 2016
Date Stamp Jun 15 2016
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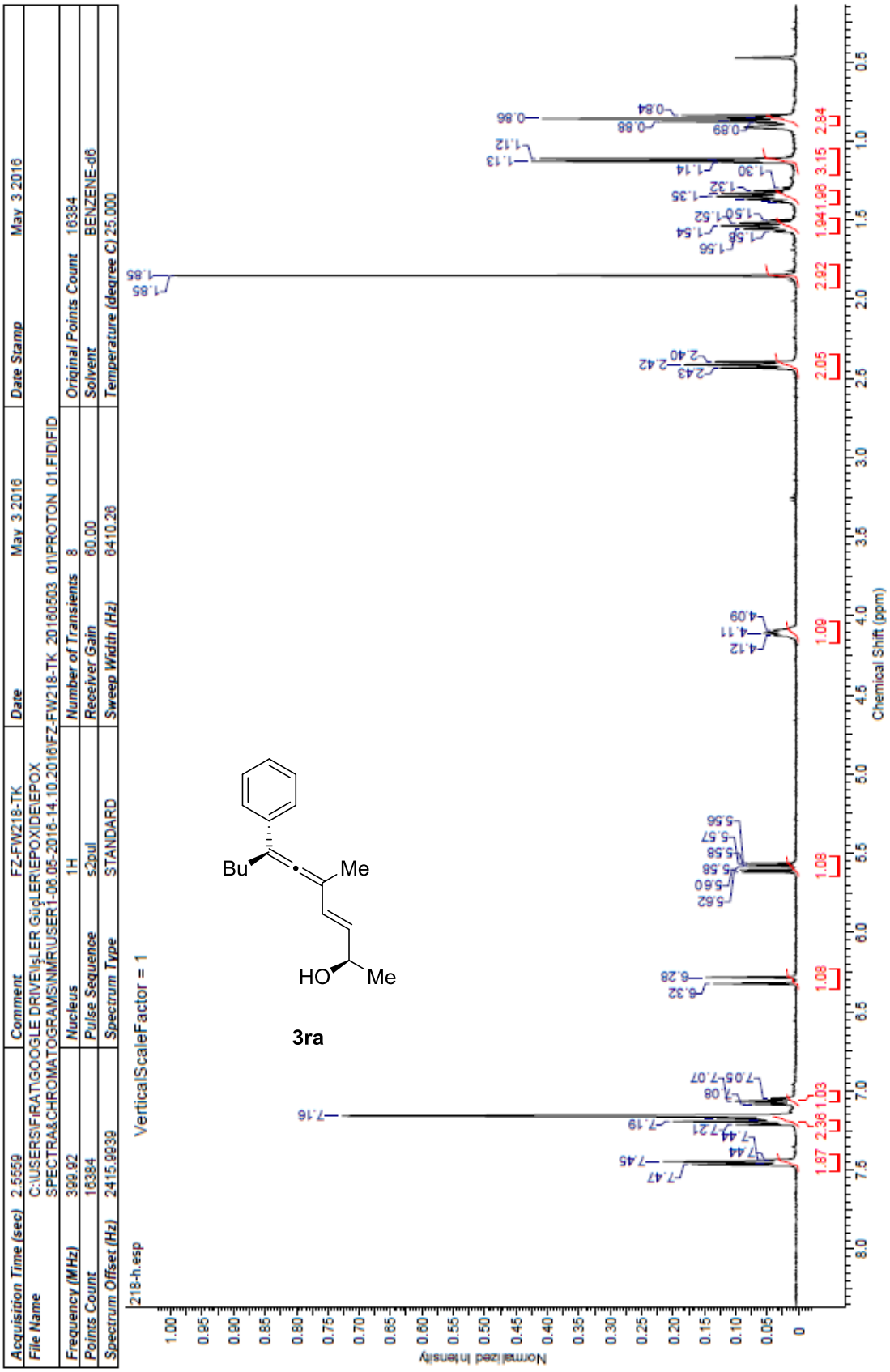
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 512
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
223-c.esp
VerticalScaleFactor = 1
Bu
Me
HO
Me
Me
OMe
3pa
128.6
128.4
128.1
129.1
127.1
138.0
134.9
131.3
106.2
103.5
78.7
78.0
72.4
49.4
30.8
23.1
19.9
16.0
14.5
208.7
Normalized Intensity
Chemical Shift (ppm)


Acquisition Time (sec) 2.5569
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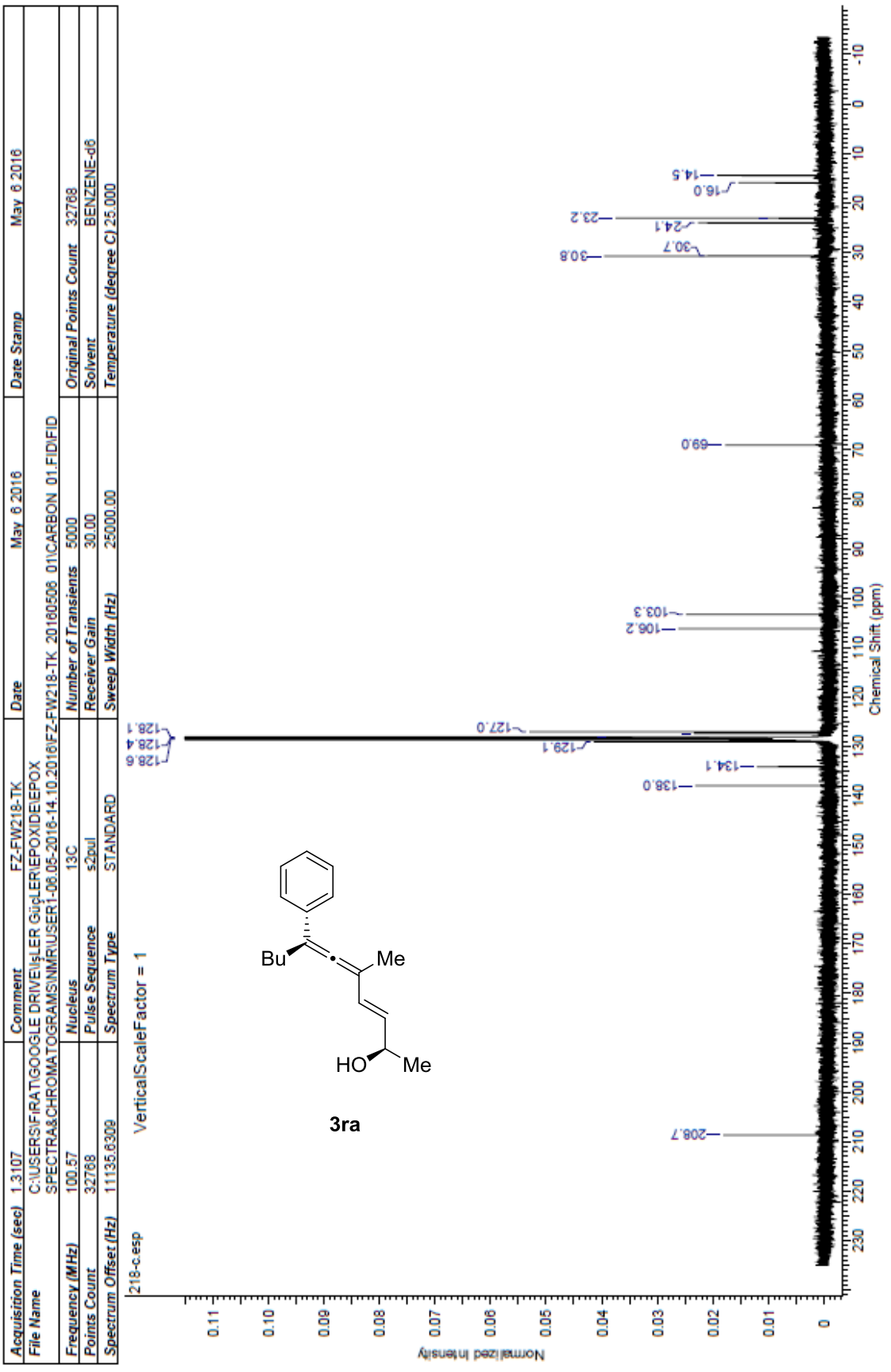
Frequency (MHz) 399.92
Points Count 16384
Spectrum Offset (Hz) 2415.9939
Comment FZ-FW218-TK
Nucleus 1H
Pulse Sequence s2pul
Spectrum Type STANDARD
Date May 3 2016
Number of Transients 8
Receiver Gain 60.00
Sweep Width (Hz) 6410.26
Date Stamp May 3 2016
Original Points Count 16384
Solvent BENZENE-d6
Temperature (degree C) 25.000
218-h.esp
VerticalScaleFactor = 1
Bu
Me
HO
Me
3ra
Normalized Intensity
Chemical Shift (ppm)


Acquisition Time (sec) 1.3107
Comment FZ-FW218-TK
Date May 6 2016
Date Stamp May 6 2016
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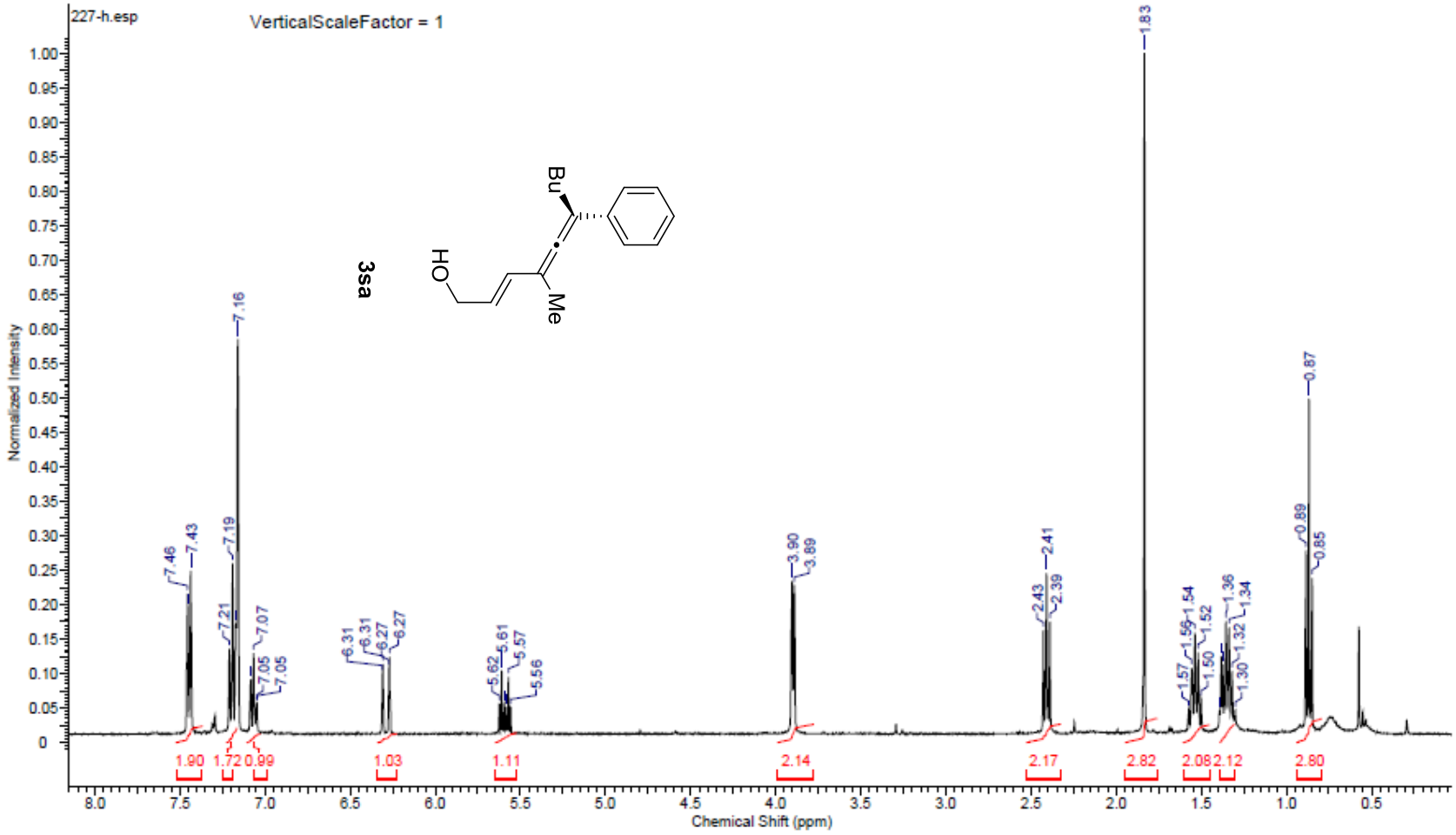
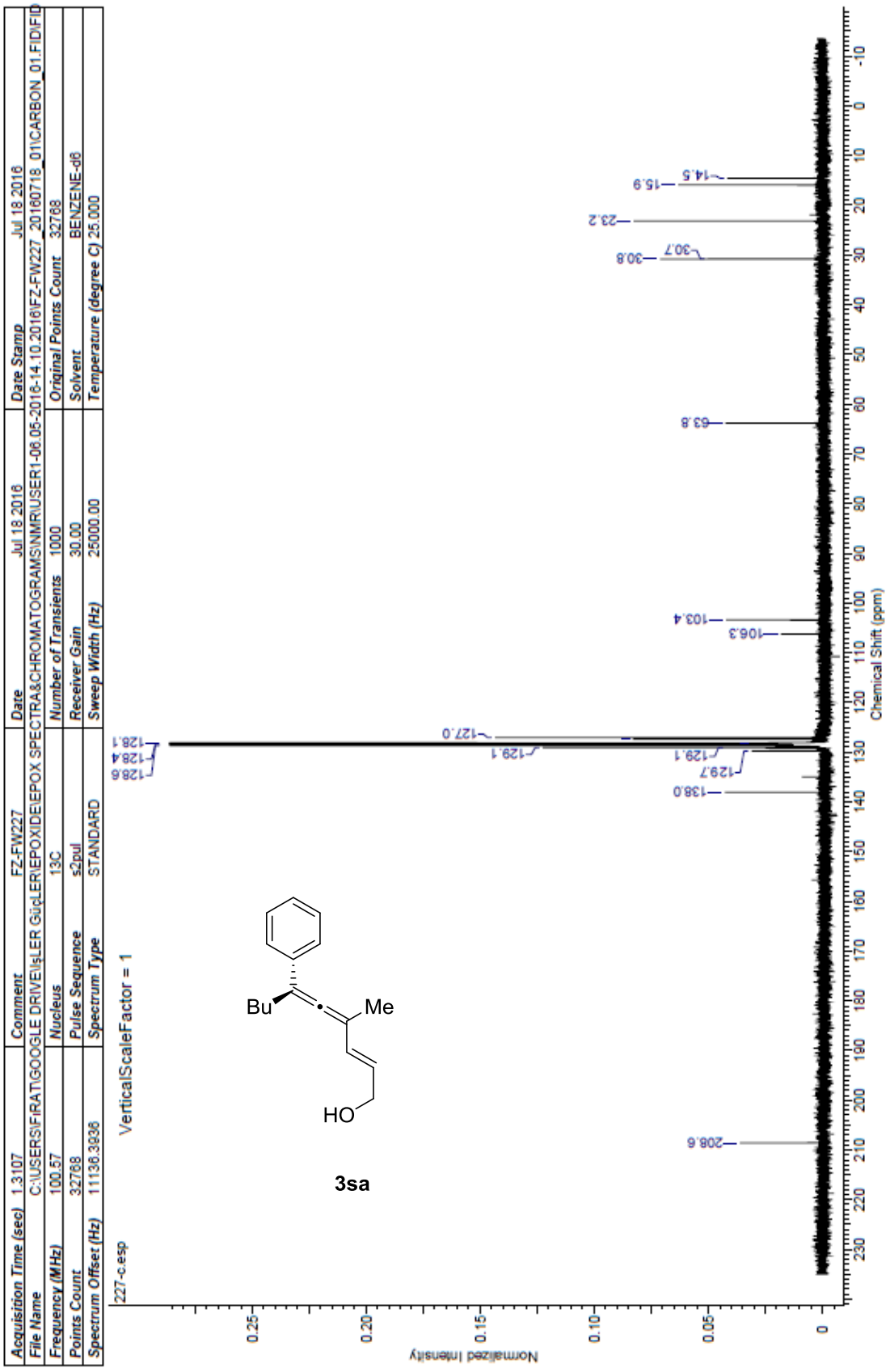
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 5000
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11135.6309
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
218-c.esp
VerticalScaleFactor = 1
Bu
Me
HO
Me
3ra
Normalized Intensity
Chemical Shift (ppm)

Acquisition Time (sec)	2.5559	*Comment*	FZ-FW227	*Date*	Jul 18 2016	*Date Stamp*	Jul 18 2016
File Name	C:\USERS\FIRAT\GOOGLE DRIVE\IŞLER GÜÇLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\USER1-06.05-2016-14.10.2016\FZ-FW227_20160718_01\PROTON_02.FID\FID						
Frequency (MHz)	399.92	*Nucleus*	1H	*Number of Transients*	8	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00	*Solvent*	BENZENE-d6
Spectrum Offset (Hz)	2417.9502	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000

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Comment FZ-FW227
Date Jul 18 2016
Date Stamp Jul 18 2016
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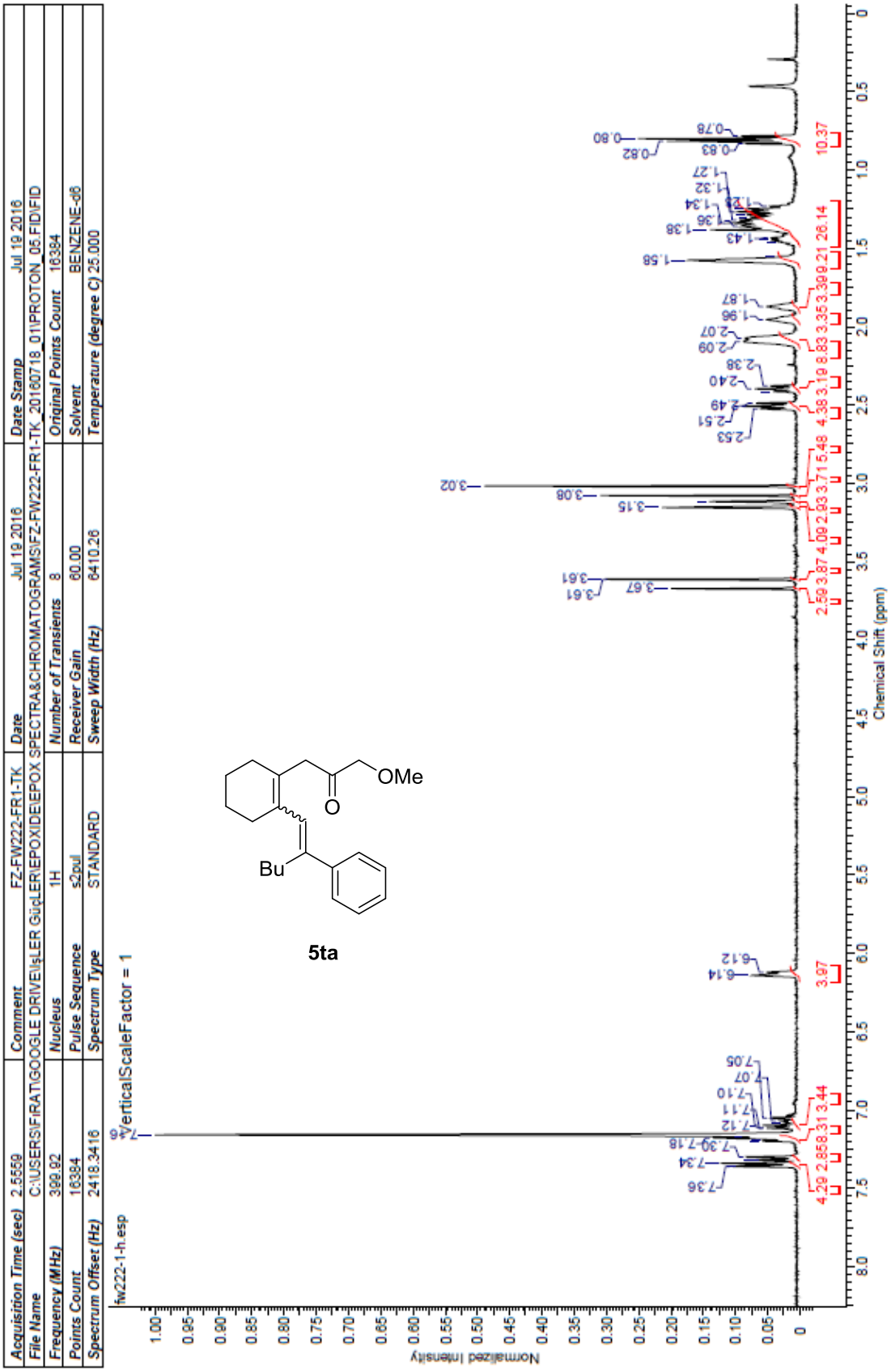
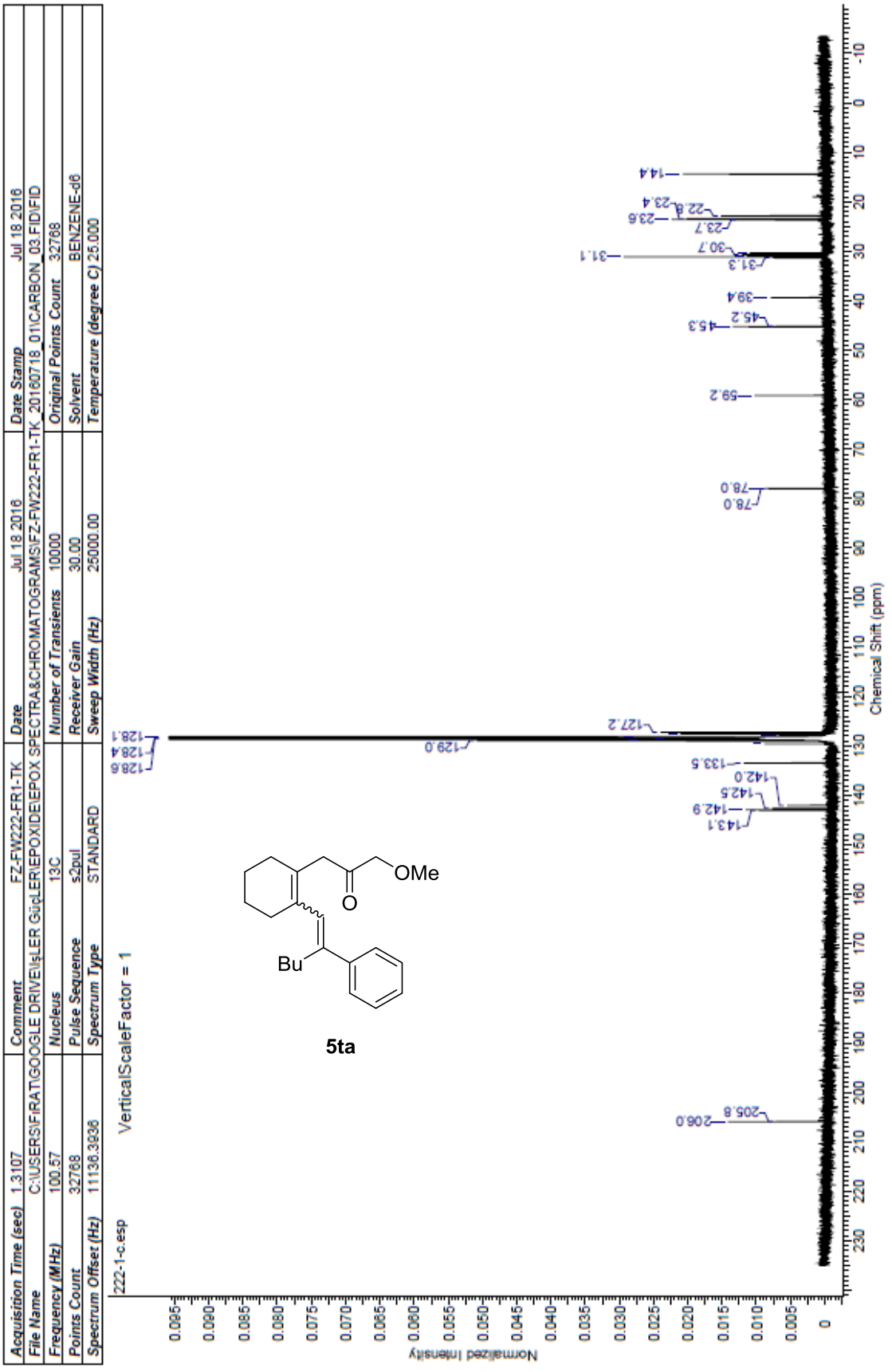
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 1000
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11136.3936
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
227-c.esp
VerticalScaleFactor = 1
Bu
Me
HO
3sa
Normalized Intensity
Chemical Shift (ppm)
208.6
138.0
129.7
129.1
128.6
128.4
128.1
127.0
106.3
103.4
63.8
30.8
30.7
23.2
15.9
14.5


Acquisition Time (sec) 2.5559
Comment FZ-FW222-FR1-TK
Date Jul 19 2016
Date Stamp Jul 19 2016
File Name C:\USERS\FIRAT\GOOGLE DRIVE\IŞLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\FZ-FW222-FR1-TK_20160718_01\PROTON_05.FID\FID
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 60.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2418.3416
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
fw222-1-h.esp
VerticalScaleFactor = 1
OMe
O
Bu
5ta
Normalized Intensity
Chemical Shift (ppm)


Acquisition Time (sec) 1.3107
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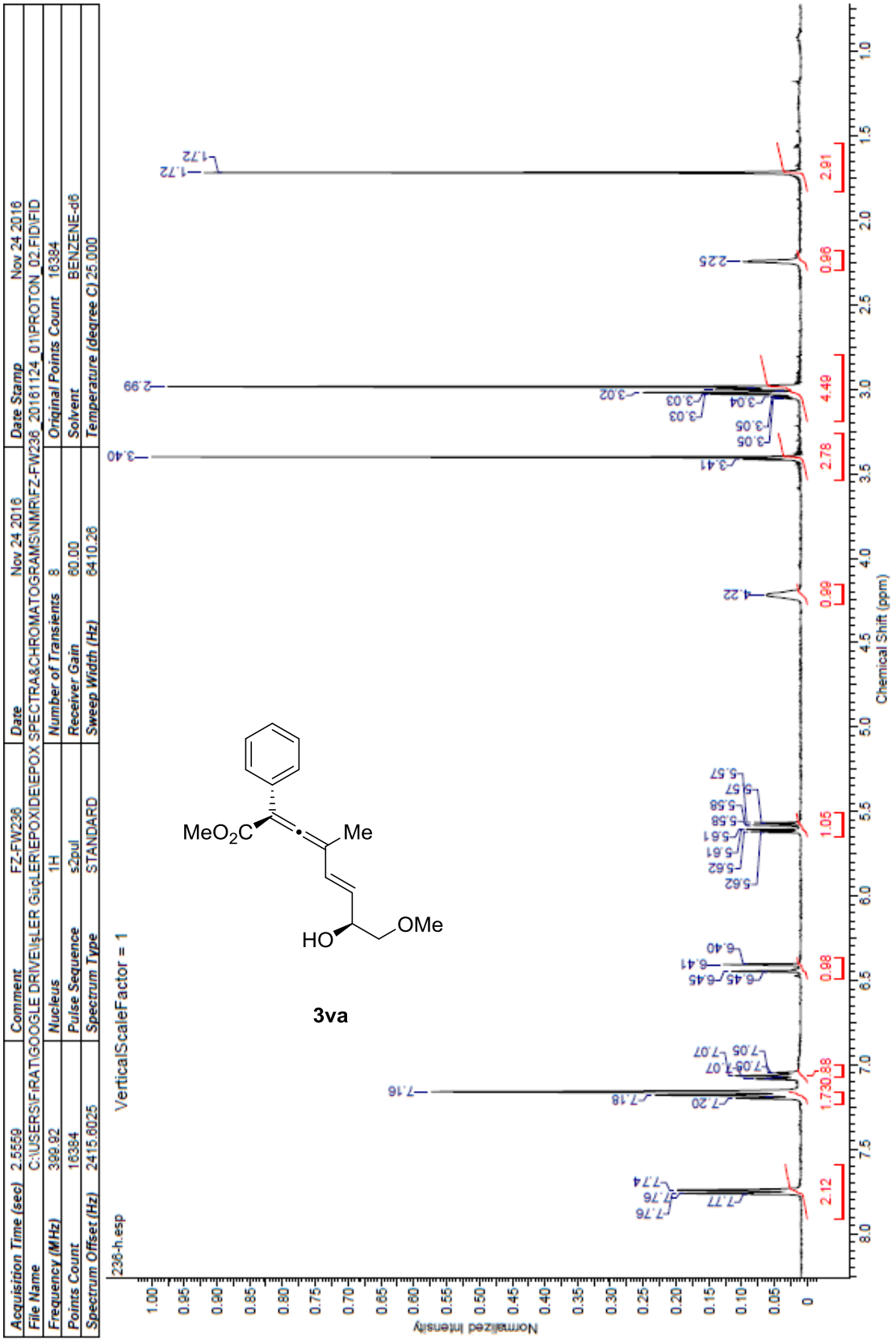
Frequency (MHz) 100.57
Points Count 32768
Spectrum Offset (Hz) 11136.3936
Comment FZ-FW222-FR1-TK
Nucleus 13C
Pulse Sequence s2pul
Spectrum Type STANDARD
Date Jul 18 2016
Number of Transients 10000
Receiver Gain 30.00
Sweep Width (Hz) 25000.00
Date Stamp Jul 18 2016
Original Points Count 32768
Solvent BENZENE-d6
Temperature (degree C) 25.000
222-1-c.esp
VerticalScaleFactor = 1
OMe
O
Bu
5ta
Normalized Intensity
Chemical Shift (ppm)


Acquisition Time (sec) 2.5559
Comment FZ-FW236
Date Nov 24 2016
Date Stamp Nov 24 2016
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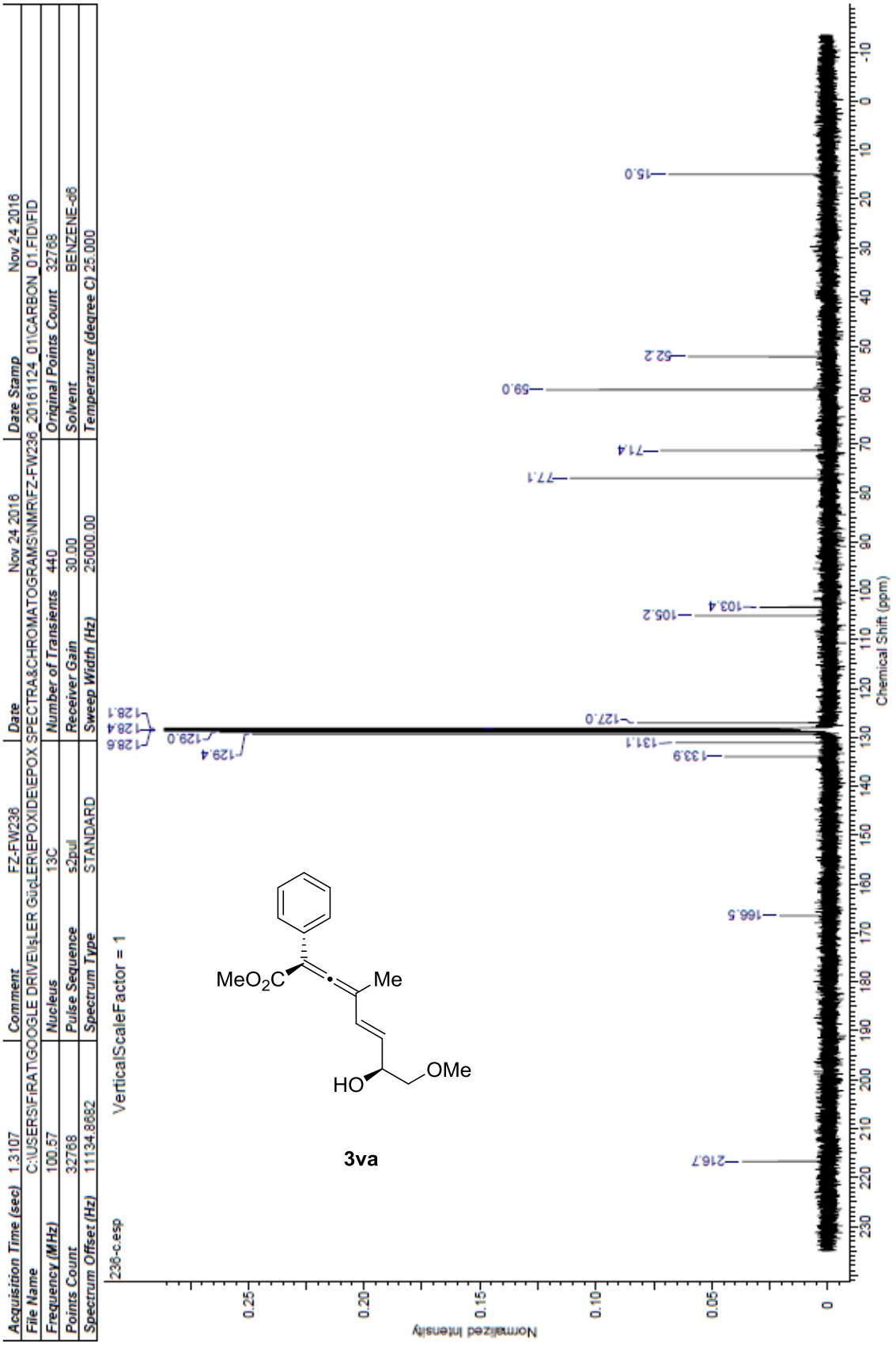
Frequency (MHz) 399.82
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 60.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 2415.6025
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
236-h.esp
VerticalScaleFactor = 1
MeO2C
Me
HO
OMe
3va
Normalized Intensity
Chemical Shift (ppm)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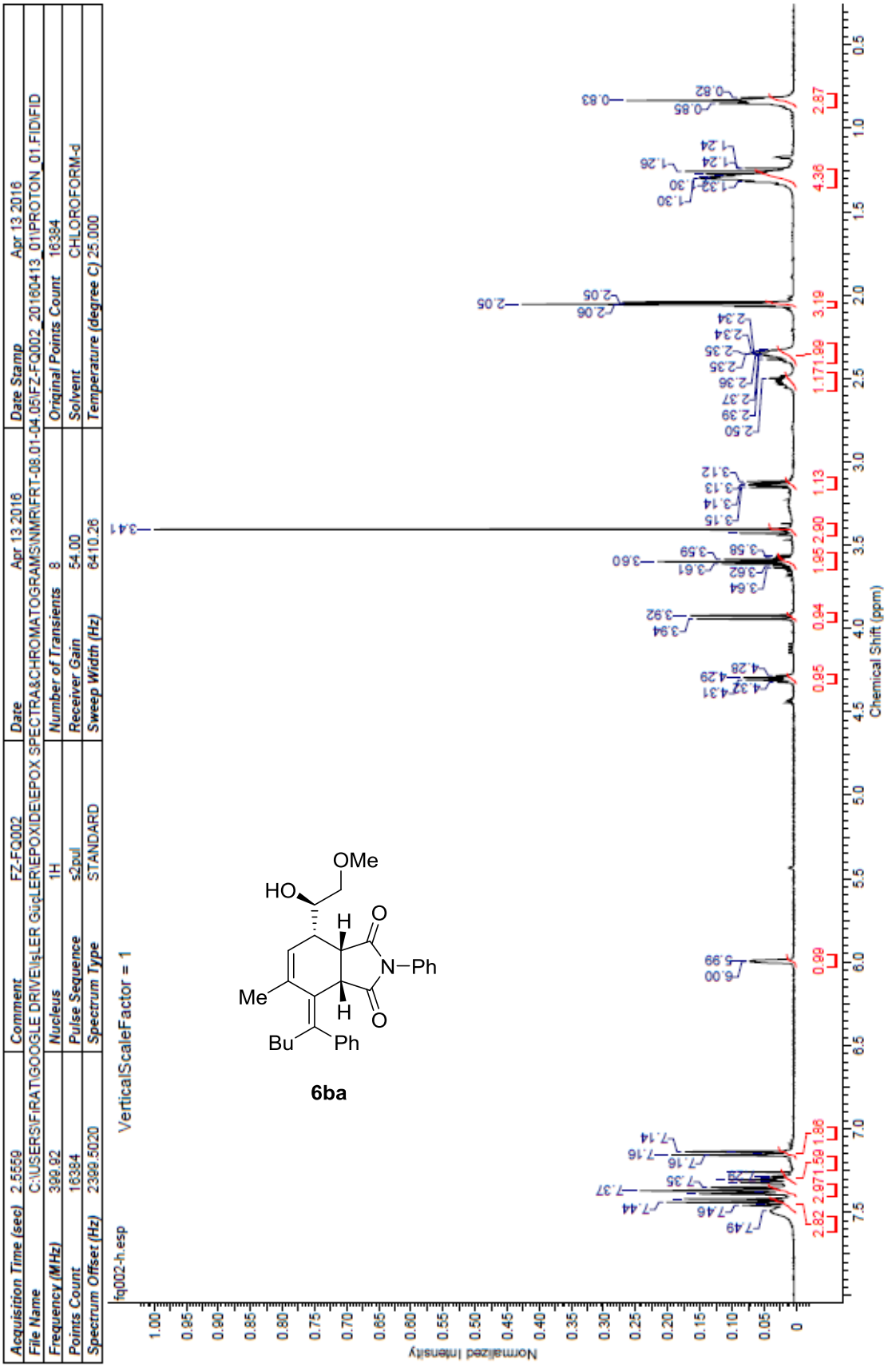
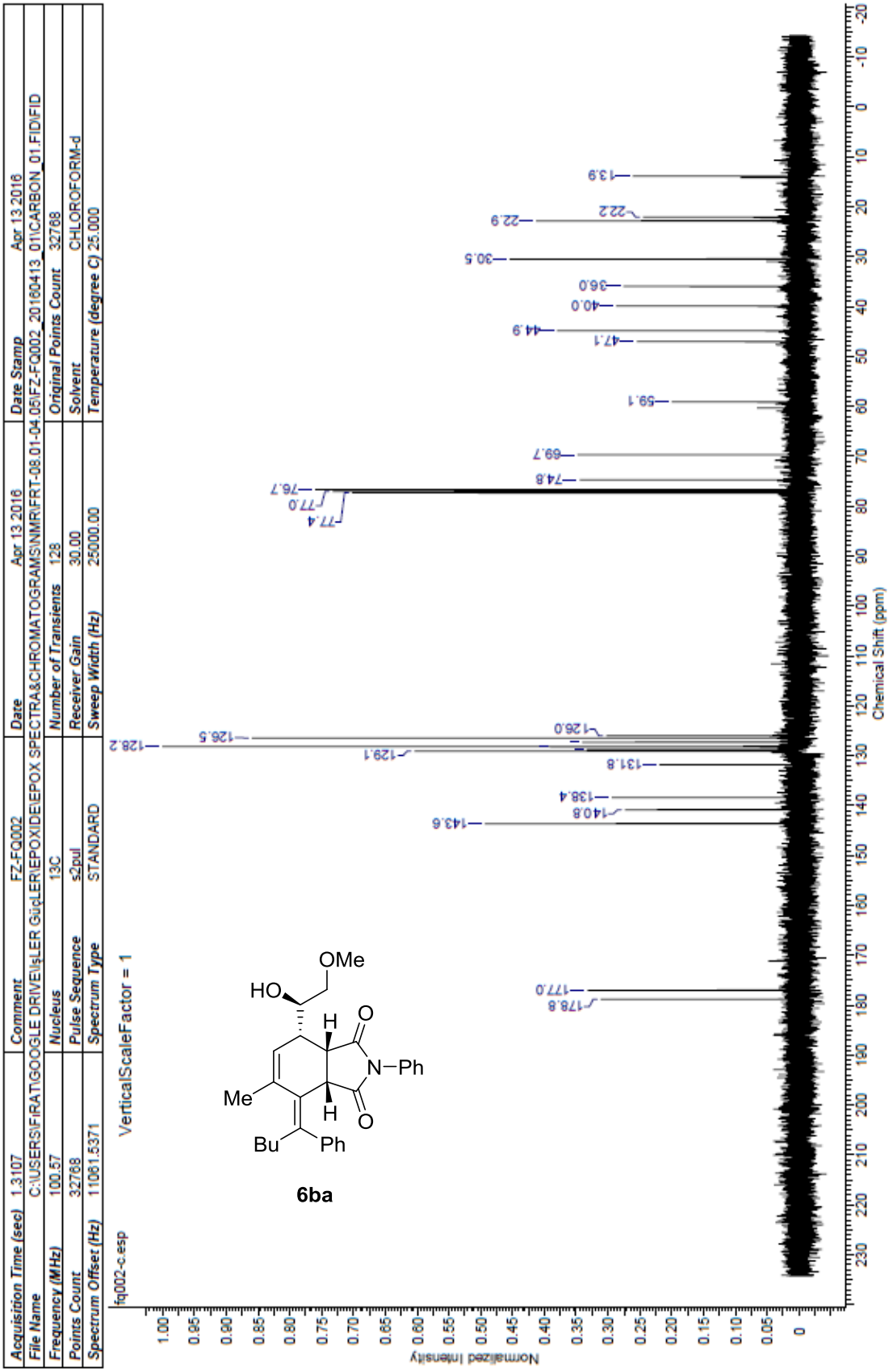
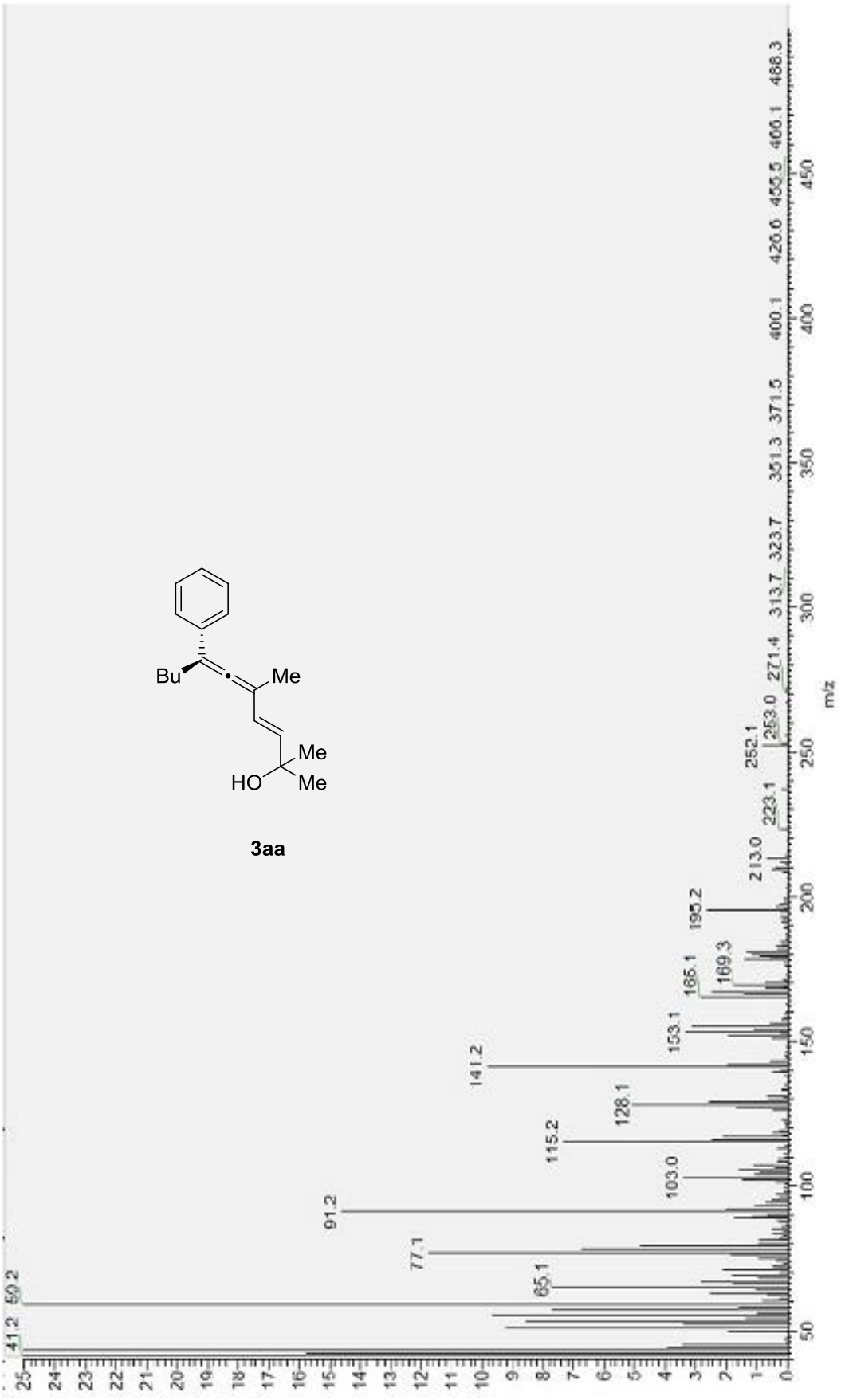
Comment
FZ-FW236
Date
Nov 24 2016
Date Stamp
Nov 24 2016
File Name C:\USERS\FIRAT\GOOGLE DRIVE\IşLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FZ-FW236_20161124_01\CARBON_01.FID\FID
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 440
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent BENZENE-d6
Spectrum Offset (Hz) 11134.8682
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
236-c.esp
VerticalScaleFactor = 1
Normalized Intensity
Chemical Shift (ppm)
216.7
166.5
133.9
131.1
129.4
129.0
128.6
128.4
128.1
127.0
105.2
103.4
77.1
71.4
59.0
52.2
15.0
MeO2C
Me
HO
OMe
3va

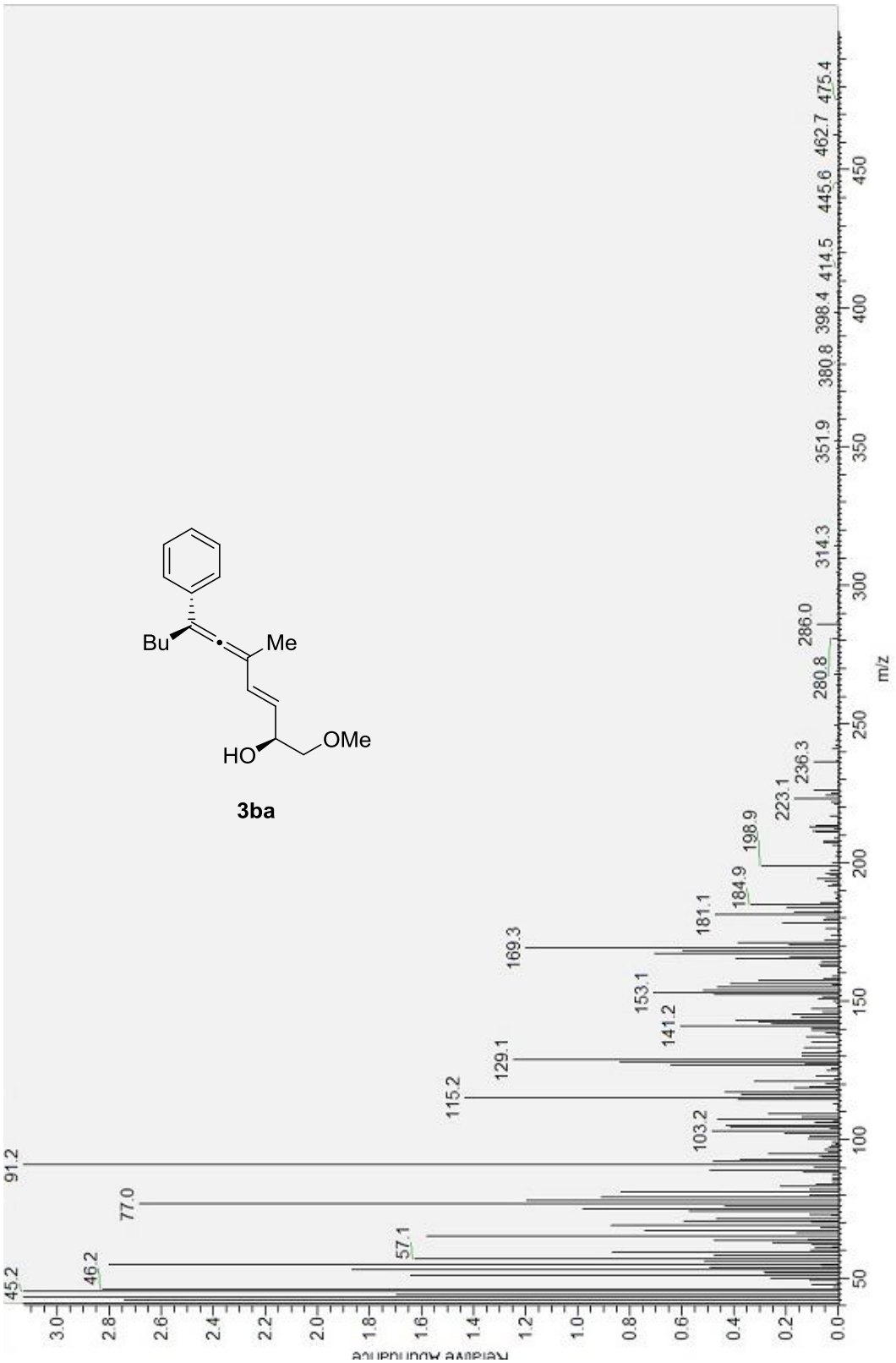

Acquisition Time (sec) 2.5559
Comment
Date Apr 13 2016
Date Stamp Apr 13 2016
File Name C:\USERS\FIRAT\GOOGLE DRIVE\LER GÜRCÜLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FRT-08.01-04.05\FZ-FQ002_20160413_011\PROTON_01.FID\FID
Frequency (MHz) 399.92
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 54.00
Solvent CHLOROFORM-d
Spectrum Offset (Hz) 2399.5020
Spectrum Type STANDARD
Sweep Width (Hz) 6410.26
Temperature (degree C) 25.000
fq002-h.esp
VerticalScaleFactor = 1
OMe
HO
H
O
N–Ph
Me
H
O
Bu
Ph
6ba
Normalized Intensity
Chemical Shift (ppm)

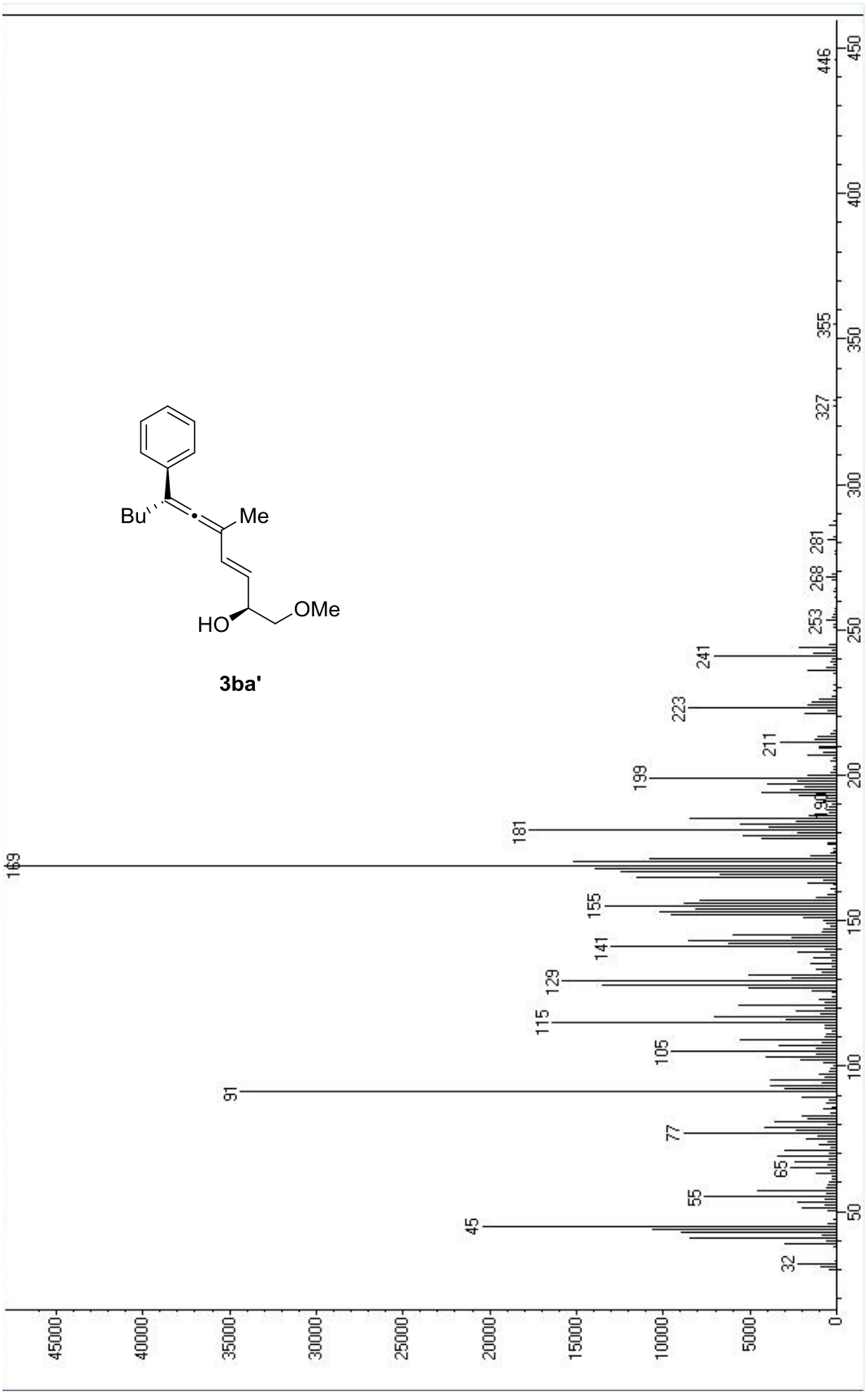

Acquisition Time (sec) 1.3107
Comment FZ-FQ002
Date Apr 13 2016
Date Stamp Apr 13 2016
File Name C:\USERS\FIRAT\GOOGLE DRIVE\ŞLER GüçLER\EPOXIDE\EPOX SPECTRA&CHROMATOGRAMS\NMR\FRT-08.01-04.05\FZ-FQ002_20160413_01\CARBON_01.FID\FID
Frequency (MHz) 100.57
Nucleus 13C
Number of Transients 128
Original Points Count 32768
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent CHLOROFORM-d
Spectrum Offset (Hz) 11081.5371
Spectrum Type STANDARD
Sweep Width (Hz) 25000.00
Temperature (degree C) 25.000
fq002-c.esp
VerticalScaleFactor = 1
OMe
HO
H
O
N–Ph
Me
H
O
Bu
Ph
6ba
178.8
177.0
143.6
140.8
138.4
131.8
129.1
128.5
128.2
126.0
77.4
77.0
76.7
74.8
69.7
59.1
47.1
44.9
40.0
36.0
30.5
22.9
22.2
13.9
Normalized Intensity
Chemical Shift (ppm)

APPENDIX B

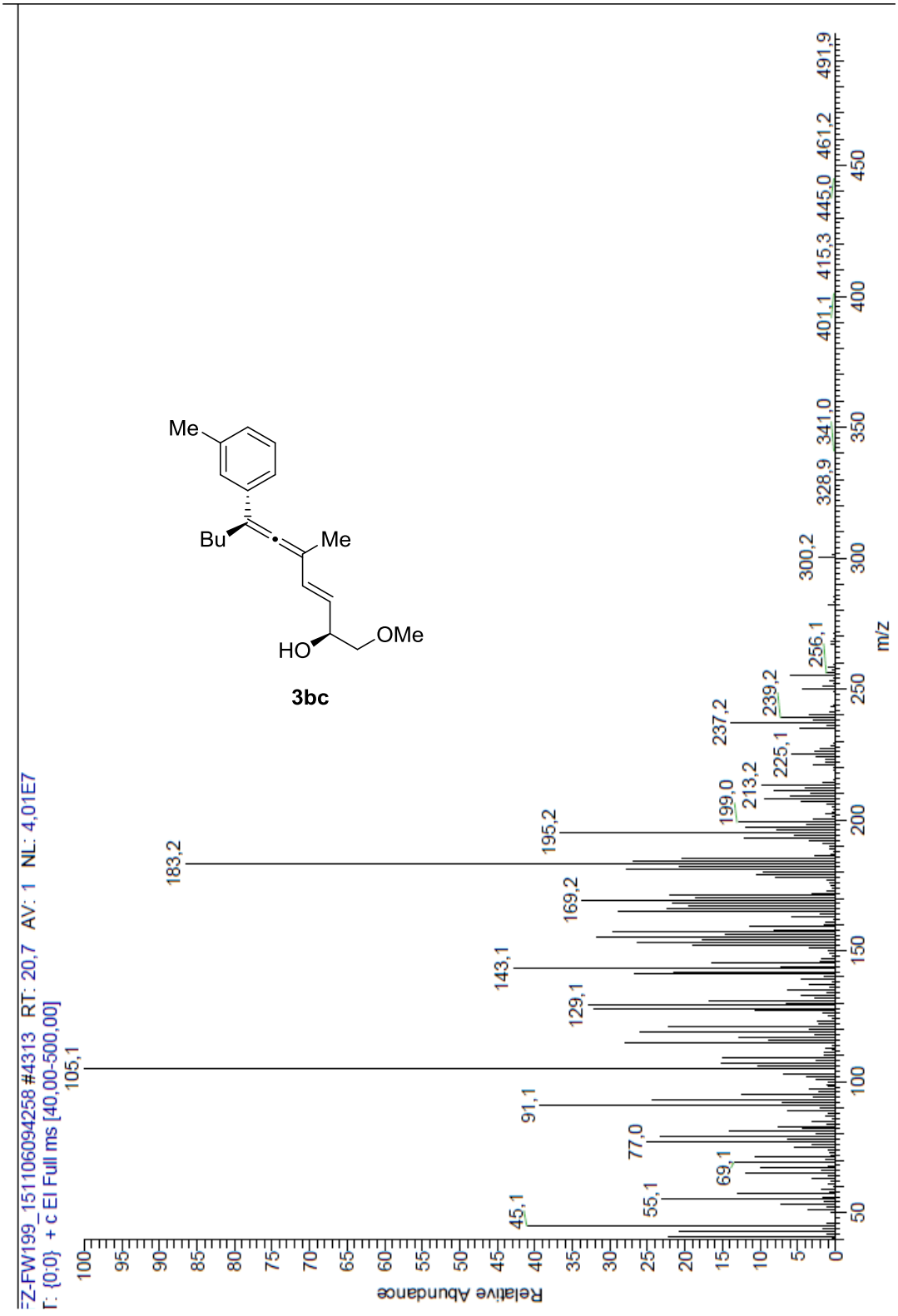
MASS SPECTRA of PRODUCTS

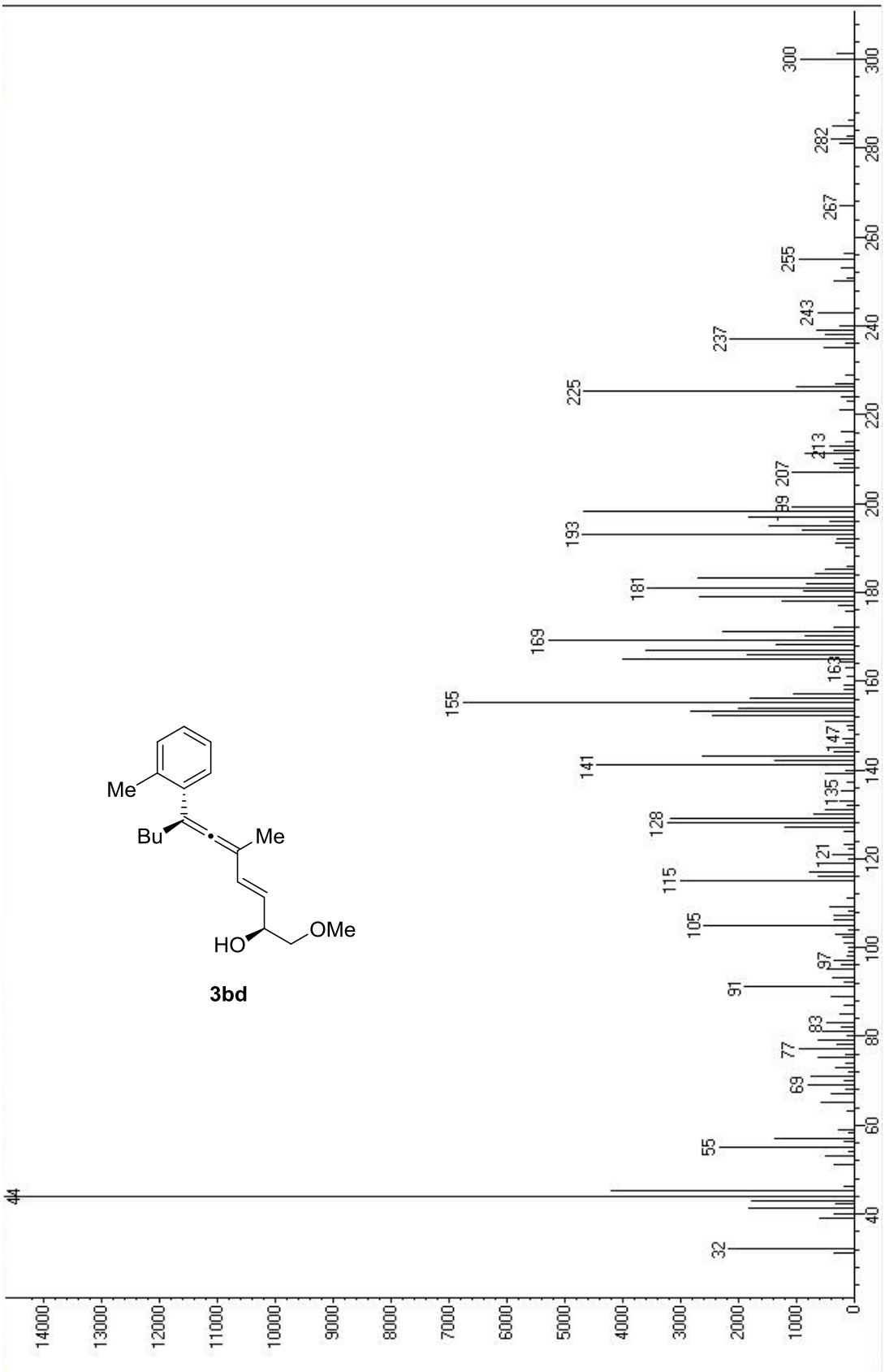

Bu
Me
Me
HO
Me
3aa
m/z
41.2
59.2
65.1
77.1
91.2
103.0
115.2
128.1
141.2
153.1
166.1
169.3
195.2
213.0
223.1
252.1
253.0
271.4
313.7
323.7
351.3
371.5
400.1
426.6
455.5
466.1
488.3

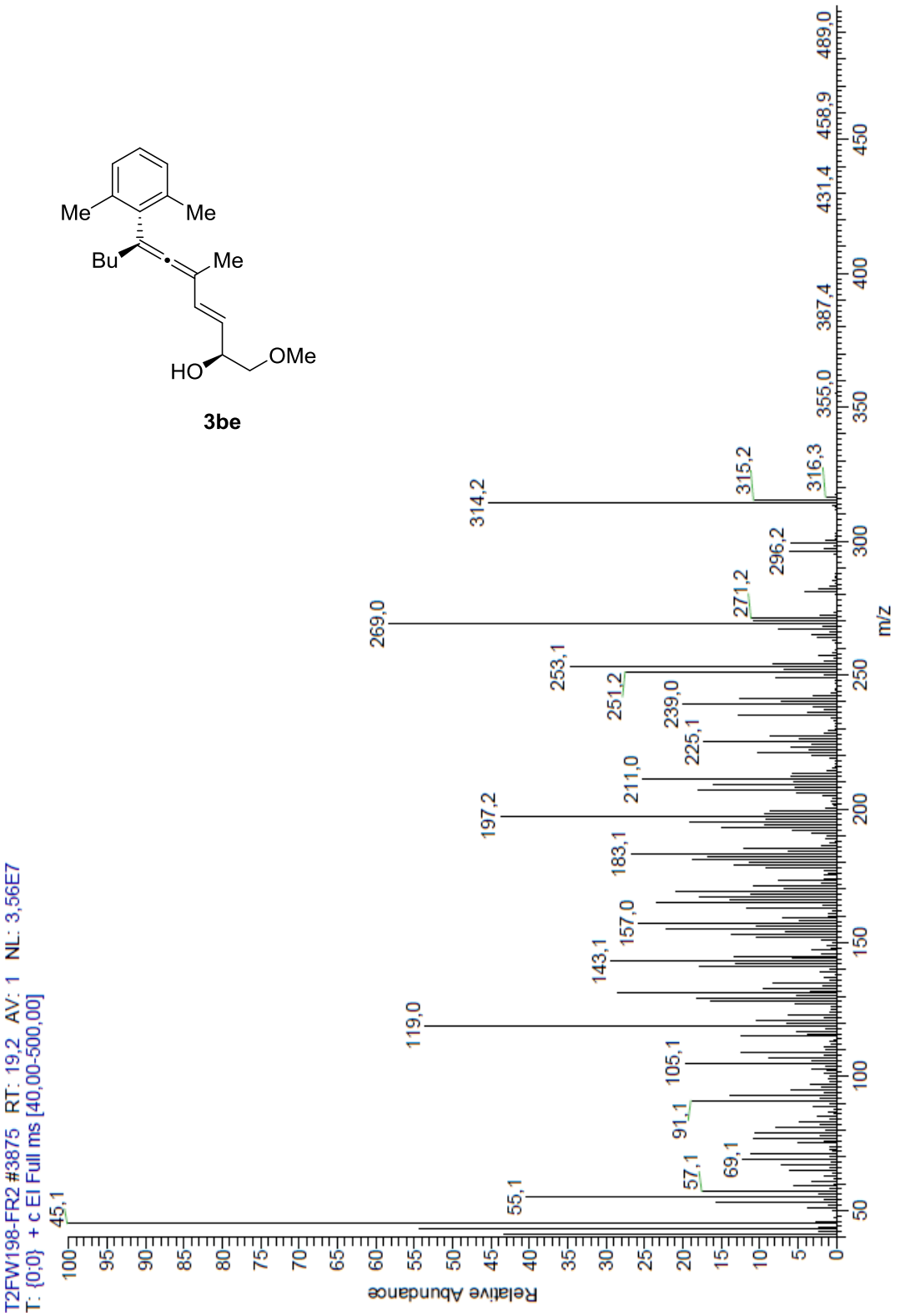

Bu
Me
HO
OMe
3ba
91.2
77.0
46.2
45.2
57.1
115.2
129.1
103.2
169.3
153.1
141.2
181.1
184.9
198.9
223.1
236.3
280.8
286.0
314.3
351.9
380.8
398.4
414.5
445.6
462.7
475.4
m/z

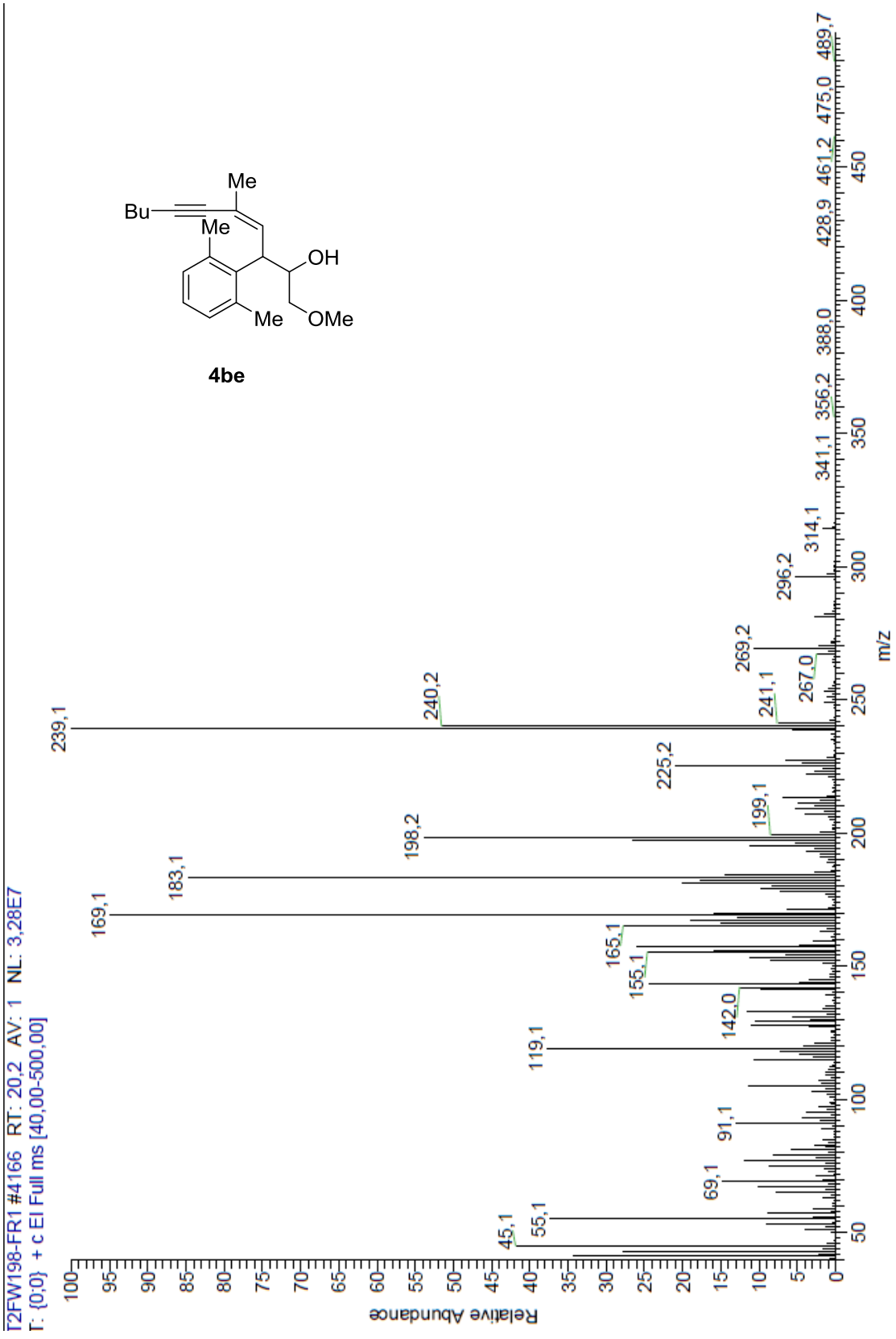

Bu
Me
HO
OMe
3ba'
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
32
45
55
65
77
91
105
115
129
141
155
169
181
199
211
223
241
253
268
281
327
355
446
50
100
150
200
250
300
350
400
450

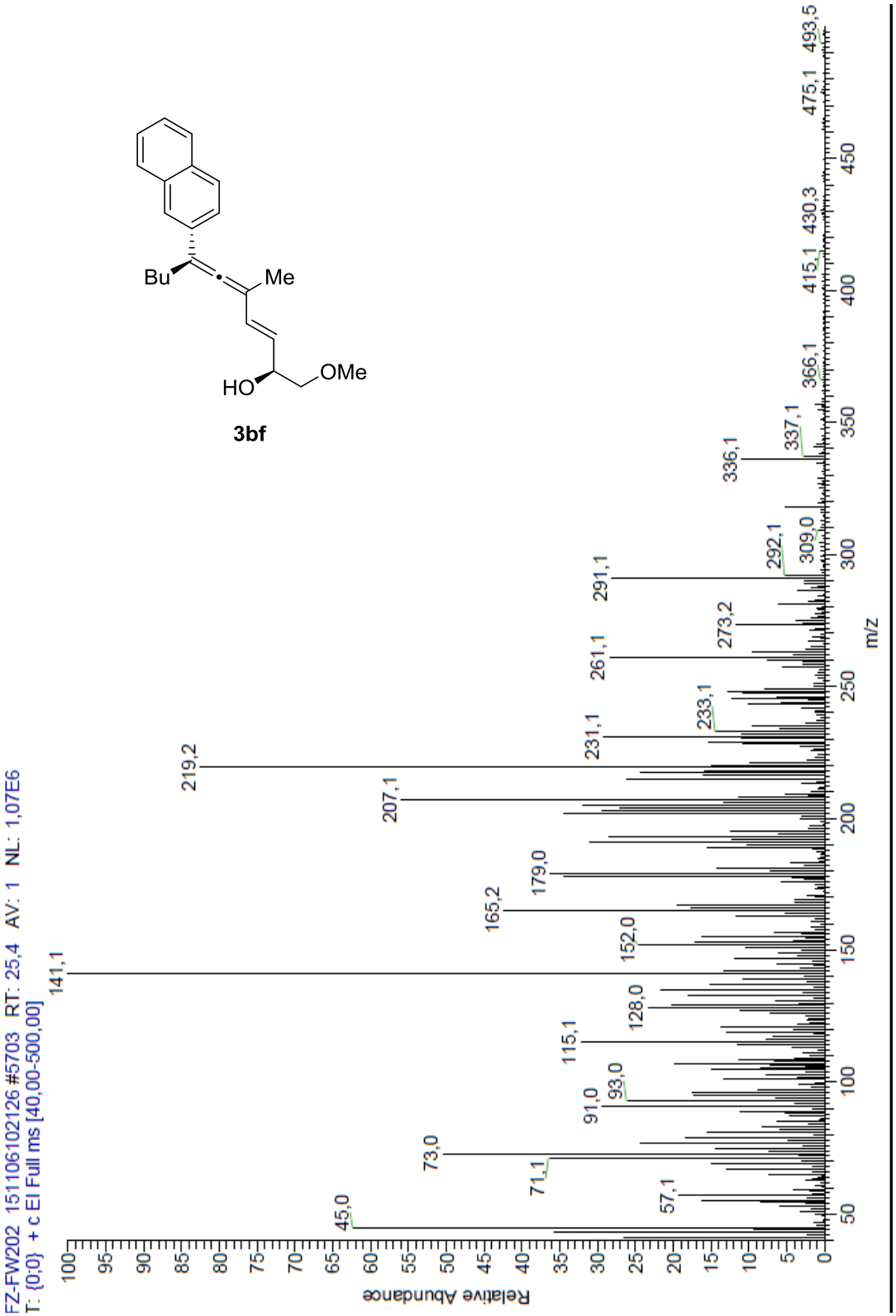
3bb

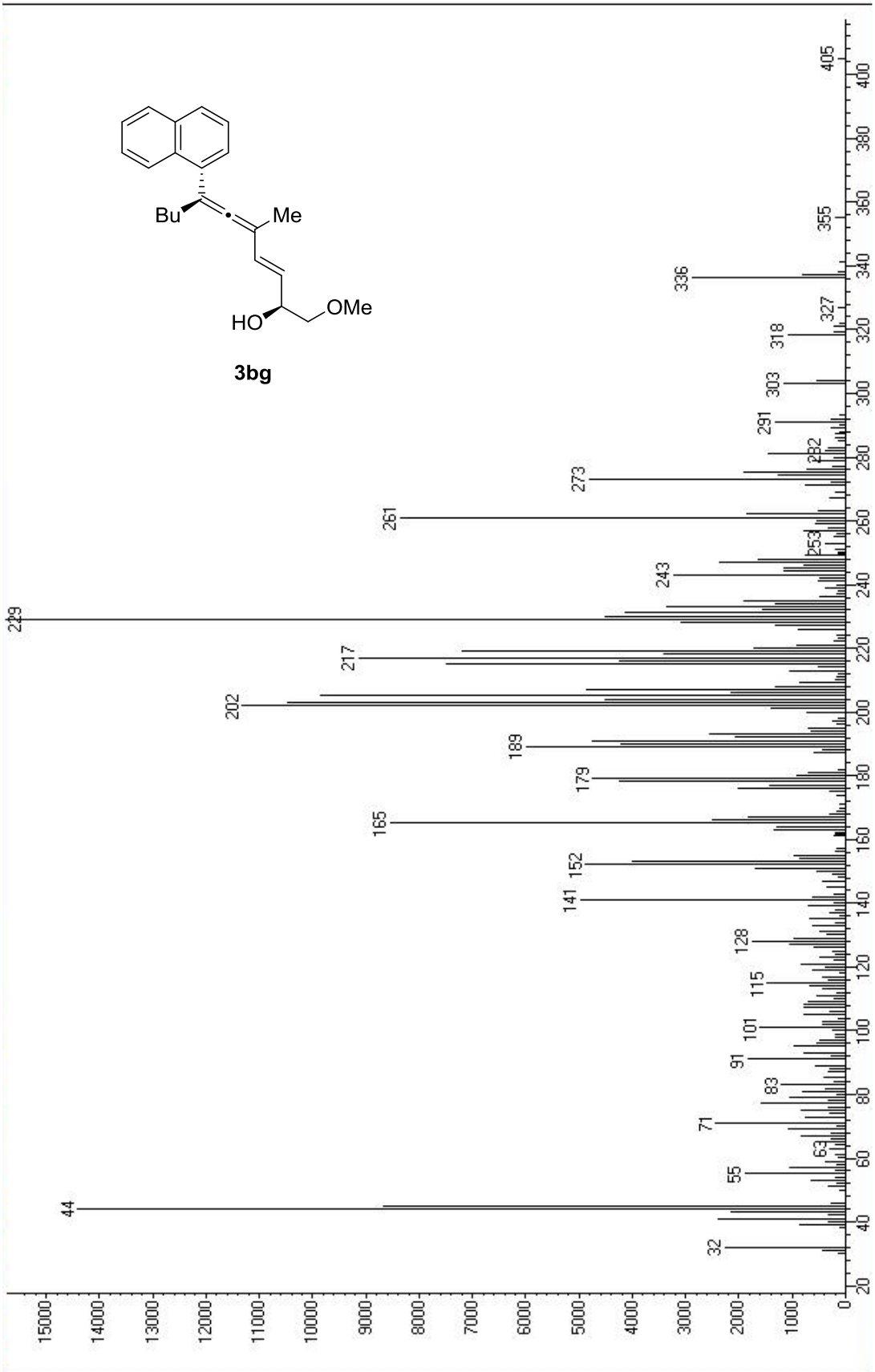

Me
Bu
Me
HO
OMe
3bc
=Z-FW199_151106094258 #4313 RT: 20,7 AV: 1 NL: 4,01E7
Γ: {0;0} + c EI Full ms [40,00-500,00]
Relative Abundance
m/z
105,1
183,2
195,2
169,2
143,1
129,1
91,1
77,0
69,1
55,1
45,1
199,0
213,2
225,1
237,2
239,2
256,1
300,2
328,9
341,0
401,1
415,3
445,0
461,2
491,9

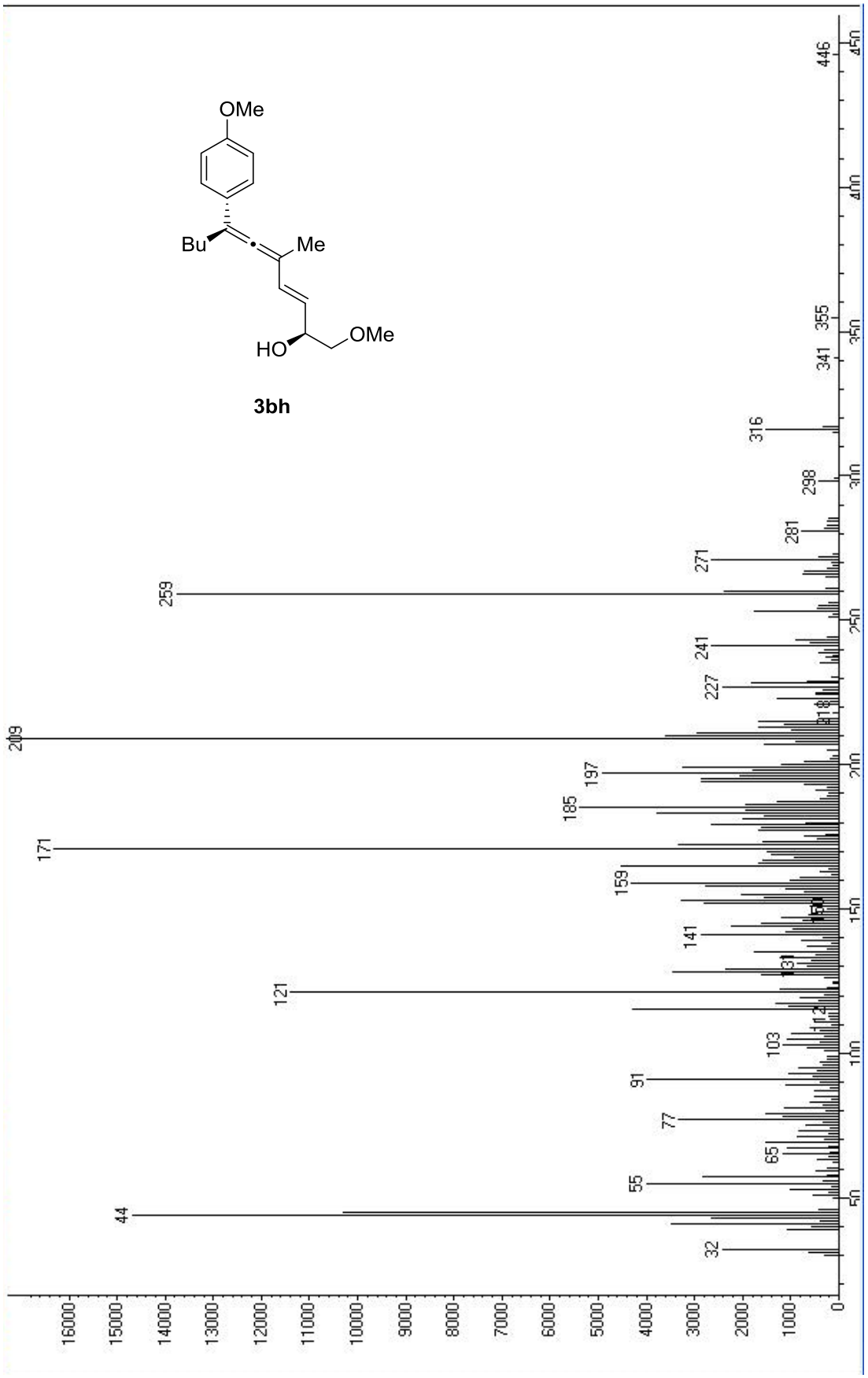

Me
Bu
Me
HO
OMe
3bd

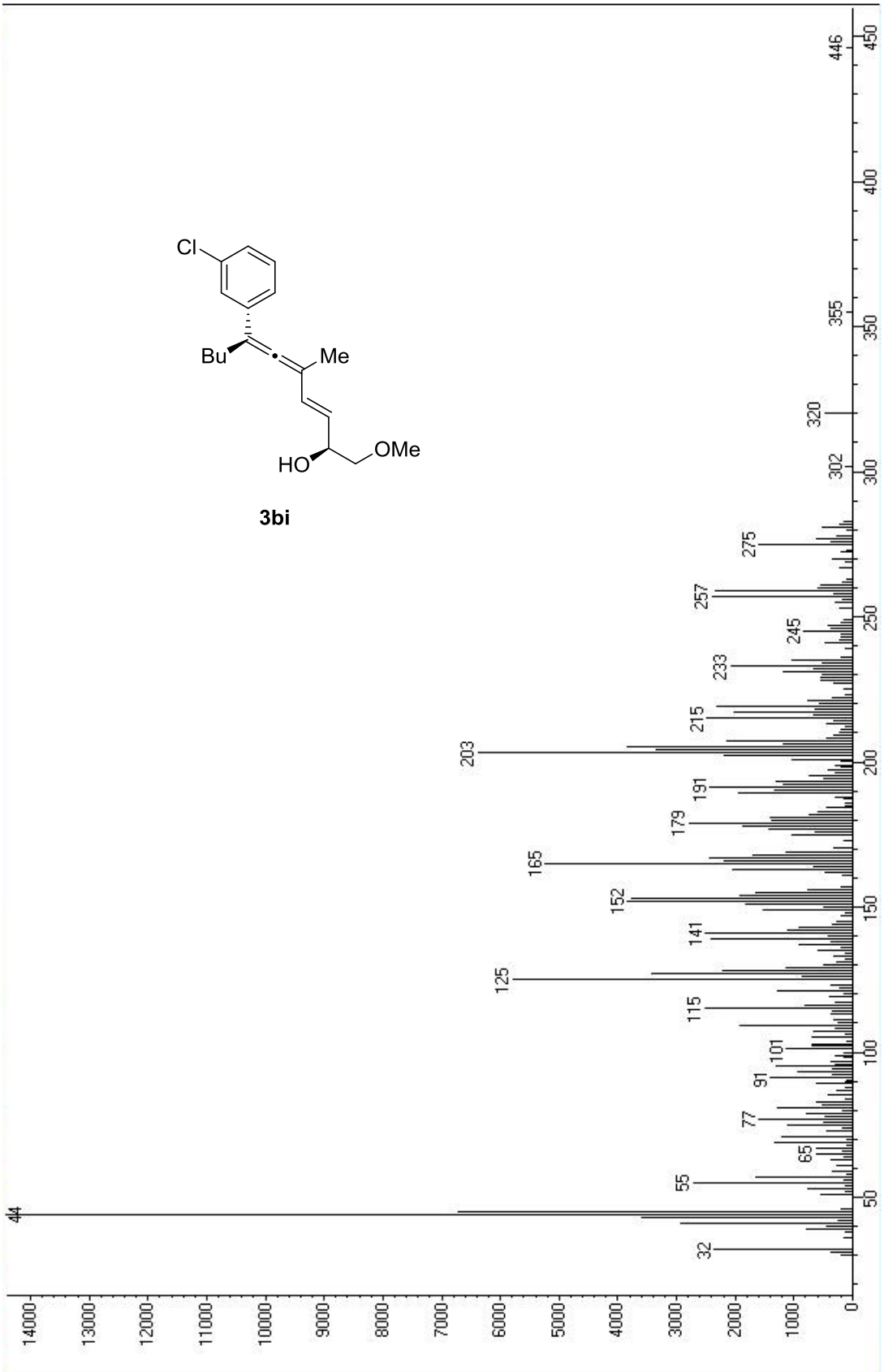

Me
Me
Bu
Me
HO
OMe
3be
T2FW198-FR2 #3875 RT: 19,2 AV: 1 NL: 3,56E7
T: {0;0} + c EI Full ms [40,00-500,00]
Relative Abundance
m/z
45,1
55,1
57,1
69,1
91,1
105,1
119,0
143,1
157,0
183,1
197,2
211,0
225,1
239,0
251,2
253,1
269,0
271,2
296,2
314,2
315,2
316,3

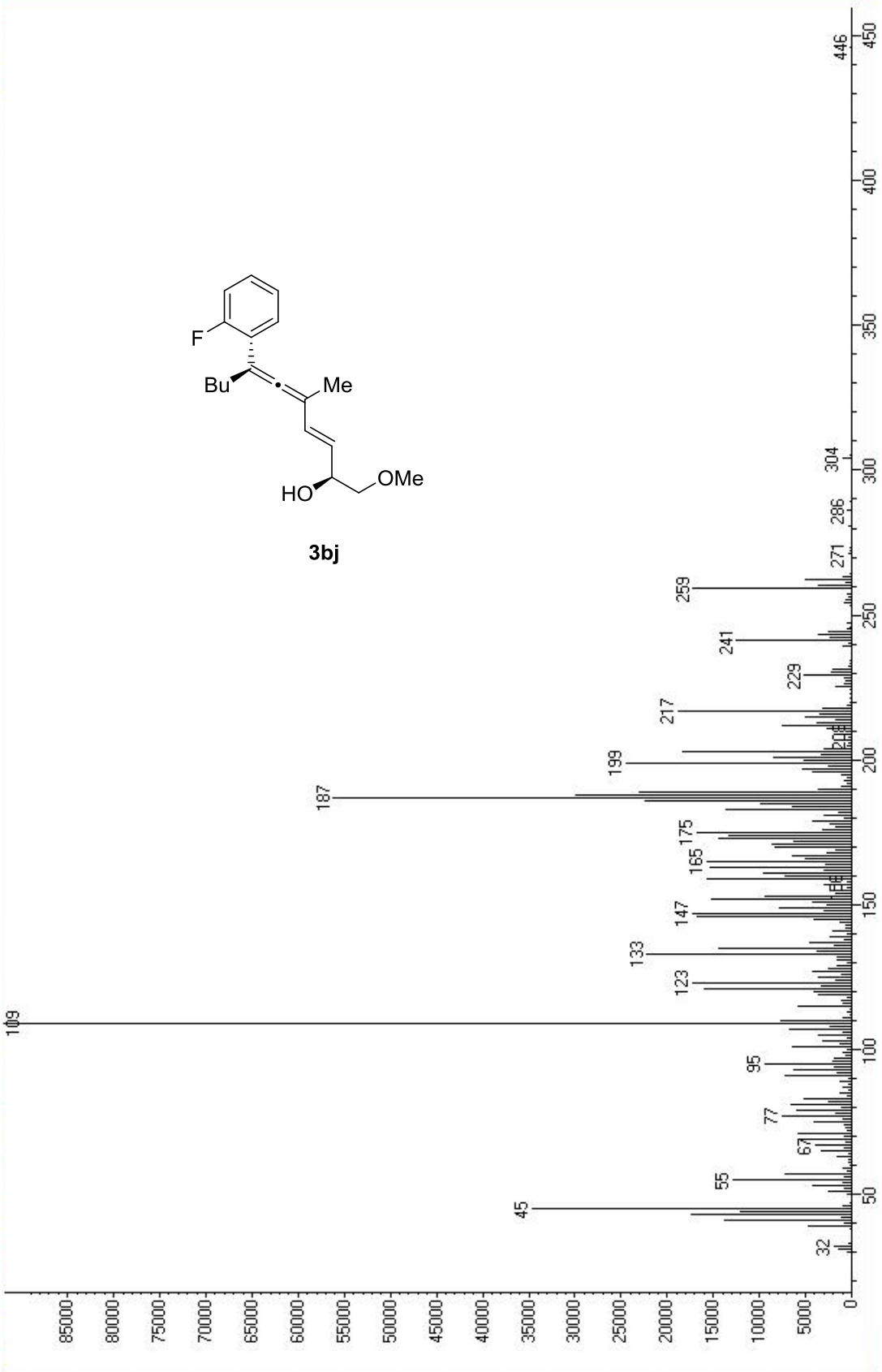

Me
Bu
Me
OH
Me
OMe
4be
T2FW198-FR1 #4166 RT: 20,2 AV: 1 NL: 3,28E7
T: {0;0} + c EI Full ms [40,00-500,00]
Relative Abundance
m/z
239,1
240,2
241,1
267,0
269,2
296,2
314,1
341,1
356,2
388,0
428,9
461,2
475,0
489,7
225,2
198,2
199,1
183,1
169,1
165,1
155,1
142,0
119,1
91,1
69,1
55,1
45,1

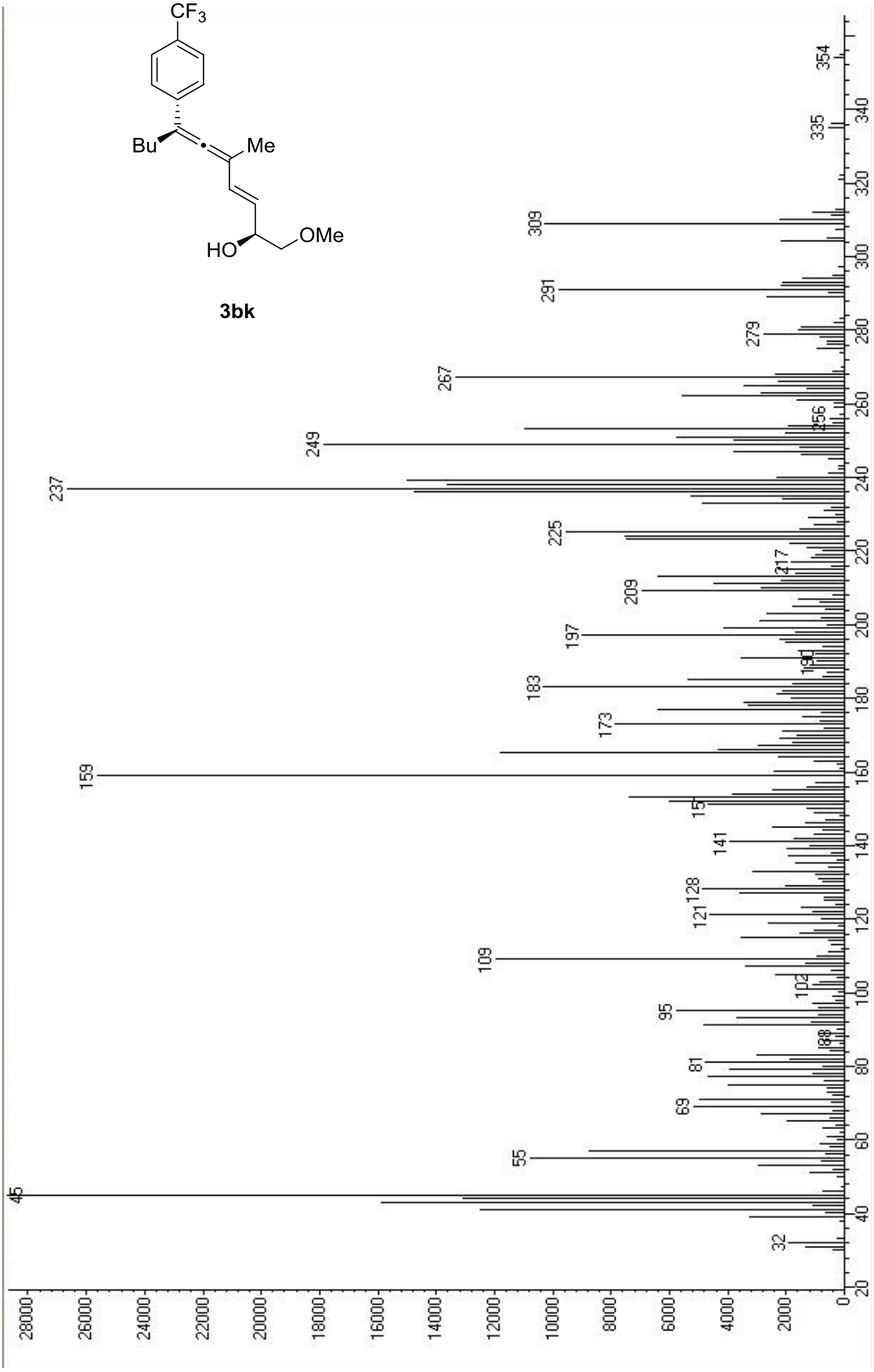

FZ-FW202 151106102126 #5703 RT: 25,4 AV: 1 NL: 1,07E6
T: {0;0} + c EI Full ms [40,00-500,00]
Bu
Me
HO
OMe
3bf
Relative Abundance
m/z
141,1
219,2
207,1
45,0
73,0
71,1
57,1
91,0
93,0
115,1
128,0
152,0
165,2
179,0
231,1
233,1
261,1
273,2
291,1
292,1
309,0
336,1
337,1
366,1
415,1
430,3
475,1
493,5

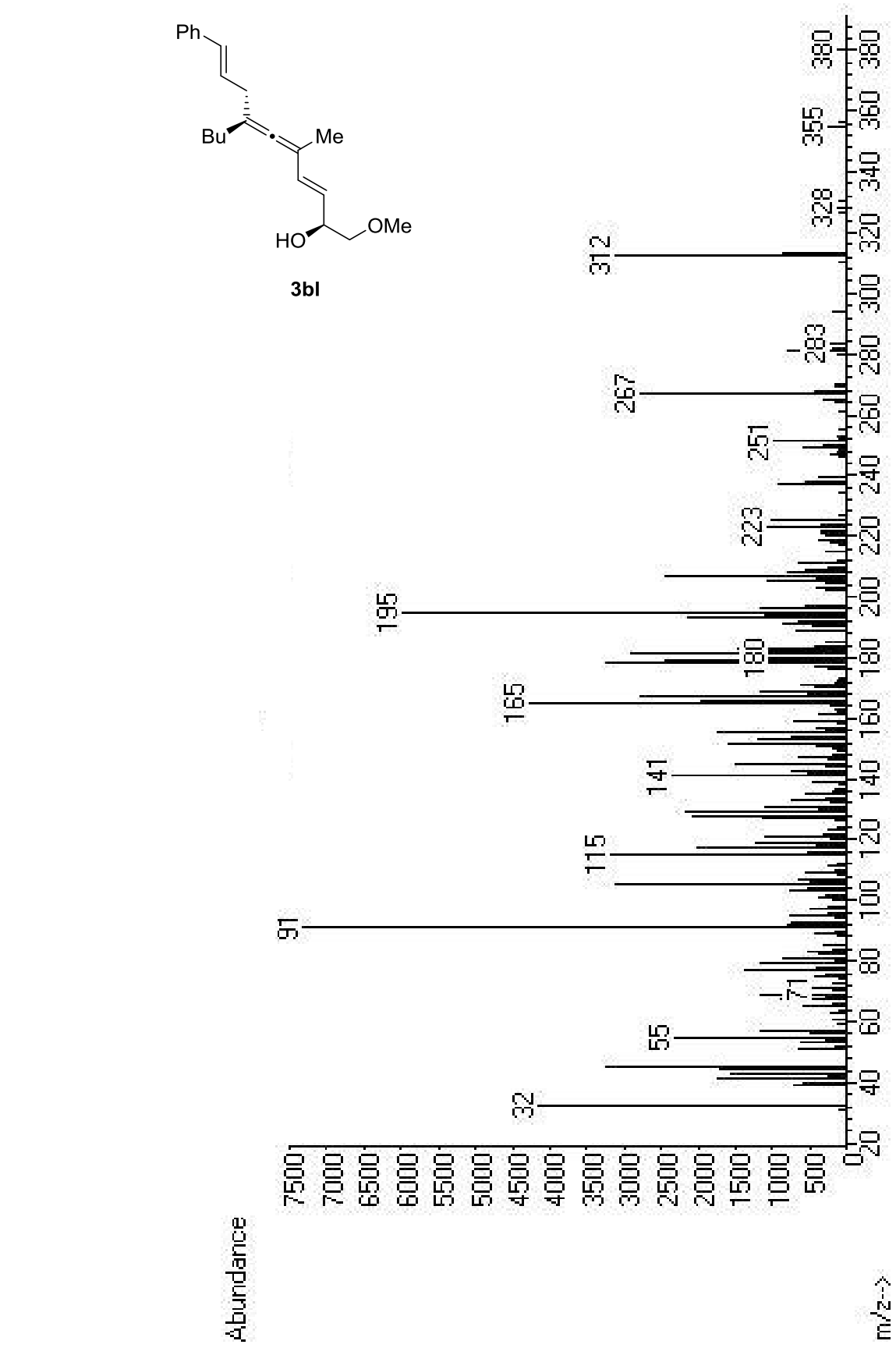

Bu
Me
HO
OMe
3bg

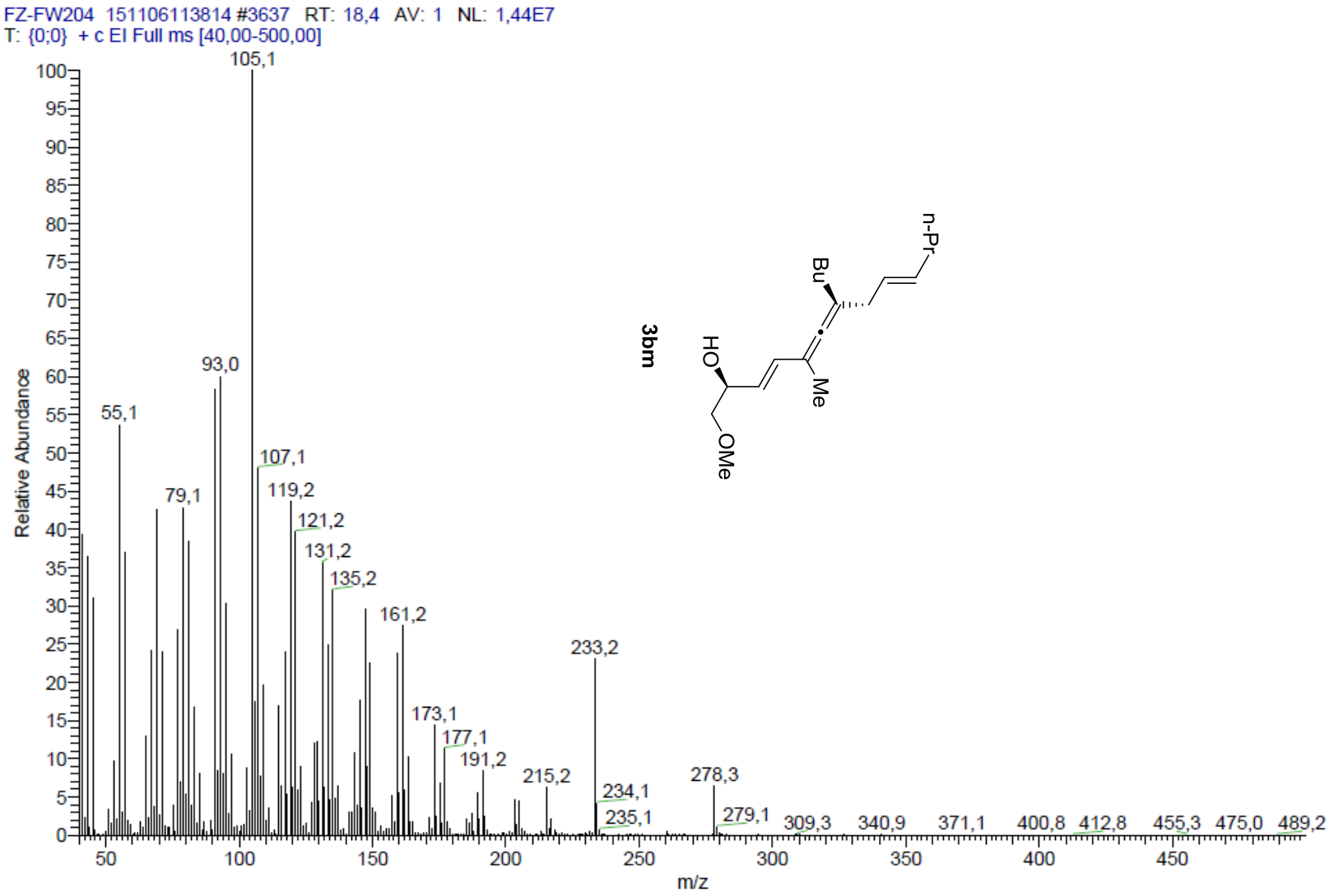

OMe
Bu
Me
OMe
HO
3bh
446
355
341
316
298
281
271
259
241
227
209
197
185
171
159
141
131
121
103
91
77
65
55
44
32
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

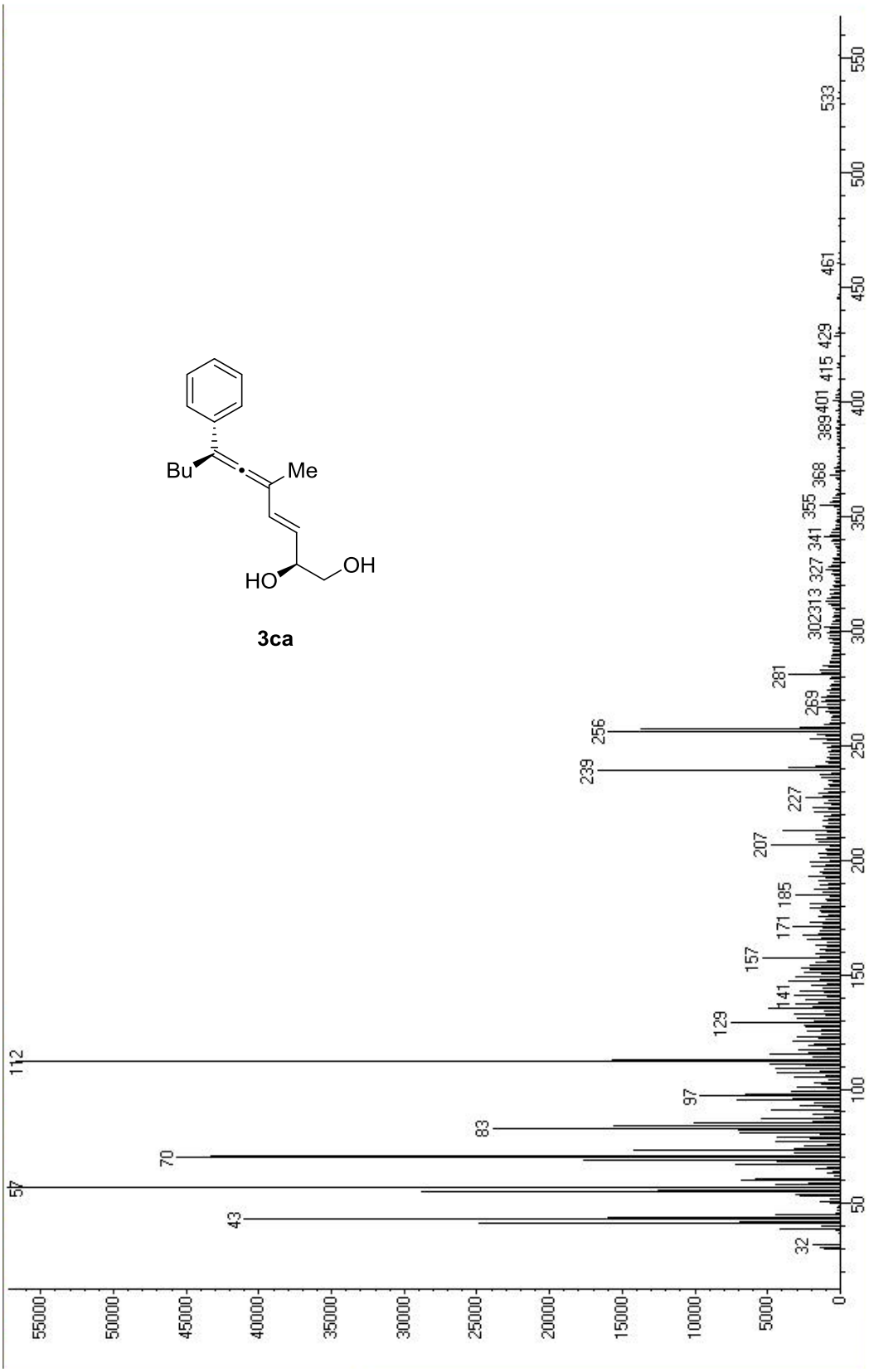

Cl
Bu
Me
HO
OMe
3bi
44
32
55
65
77
91
101
115
125
141
152
165
179
191
203
215
233
245
257
275
302
320
355
446
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000

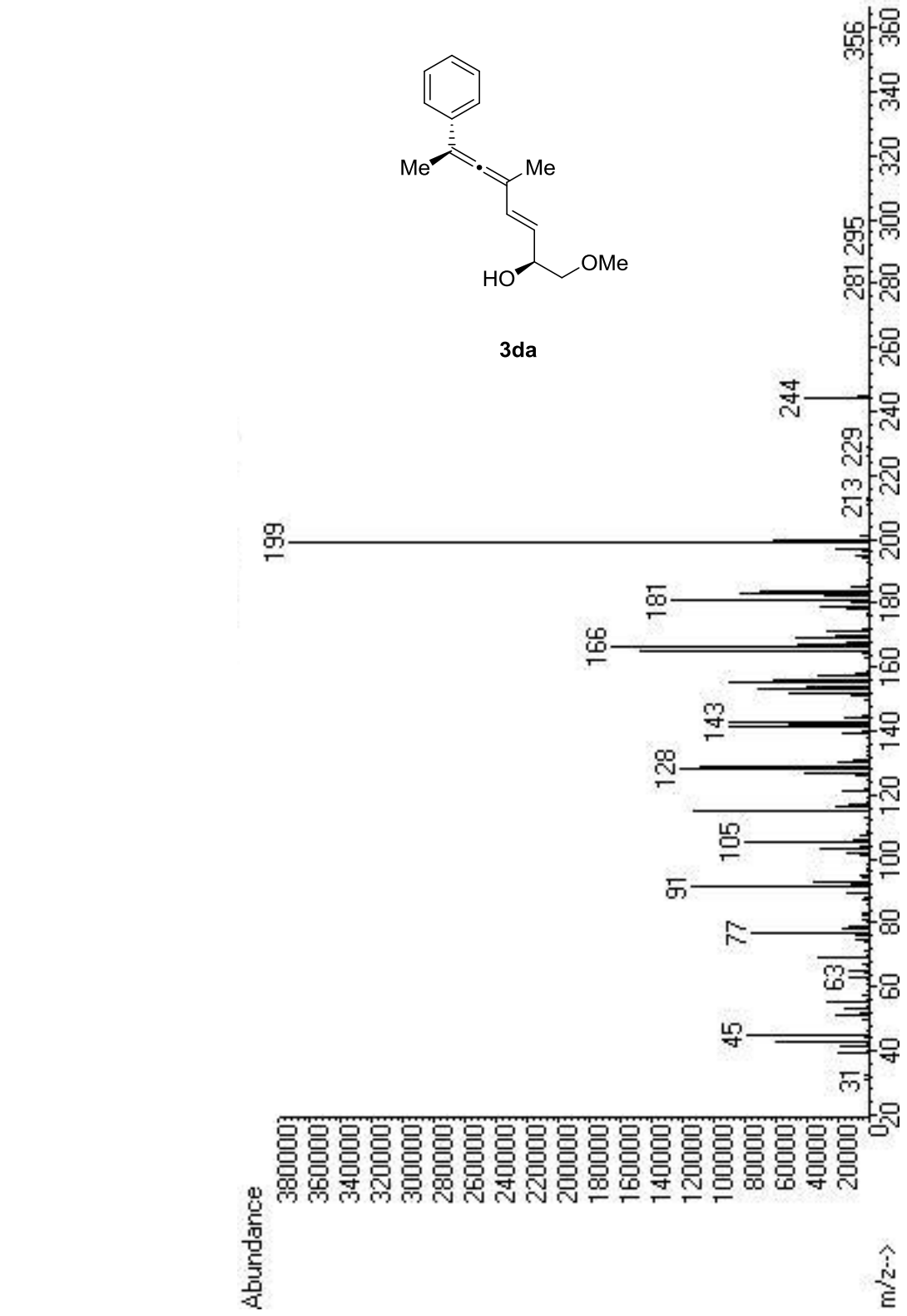

F
Bu
Me
HO
OMe
3bj

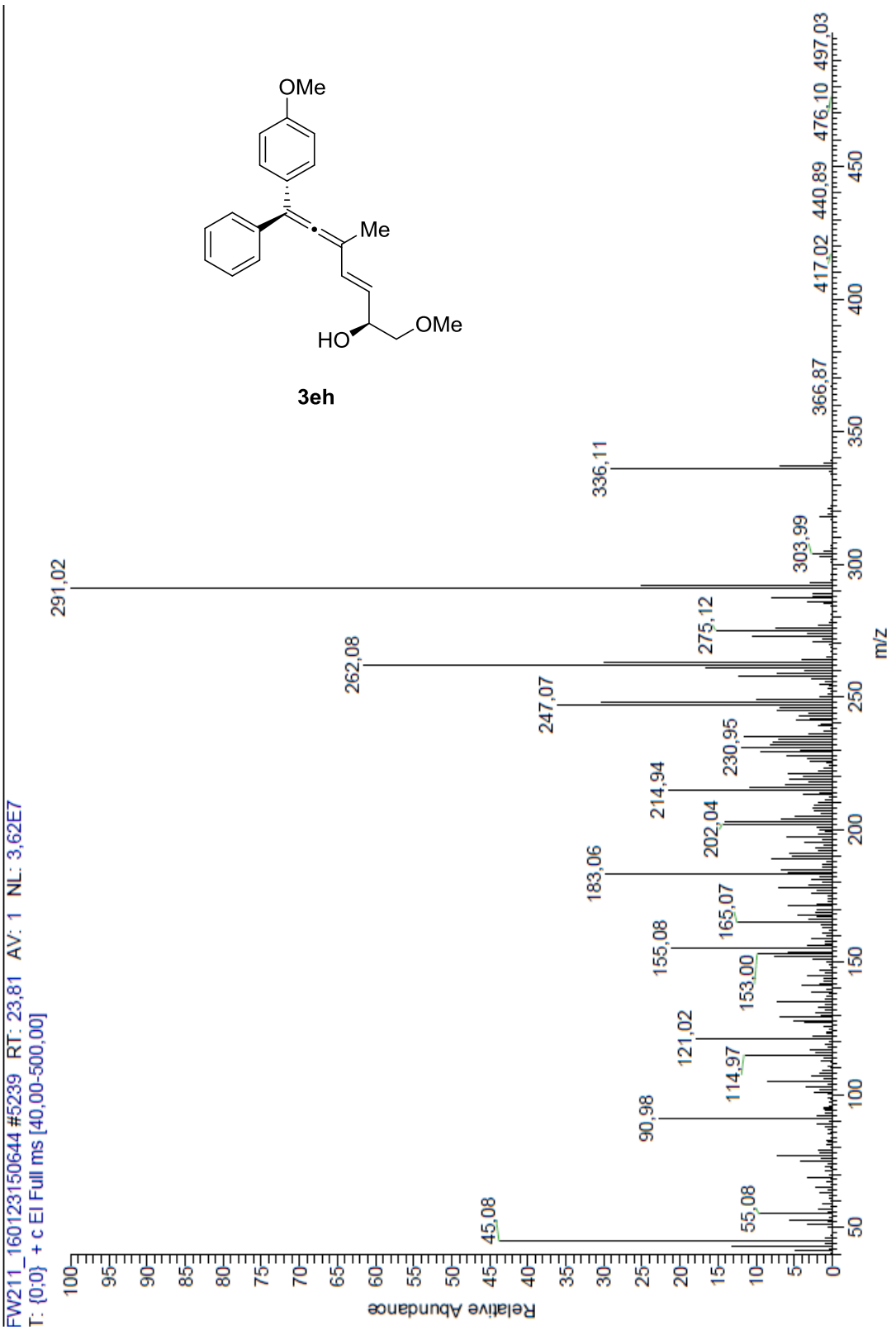

CF3
Bu
Me
HO
OMe
3bk

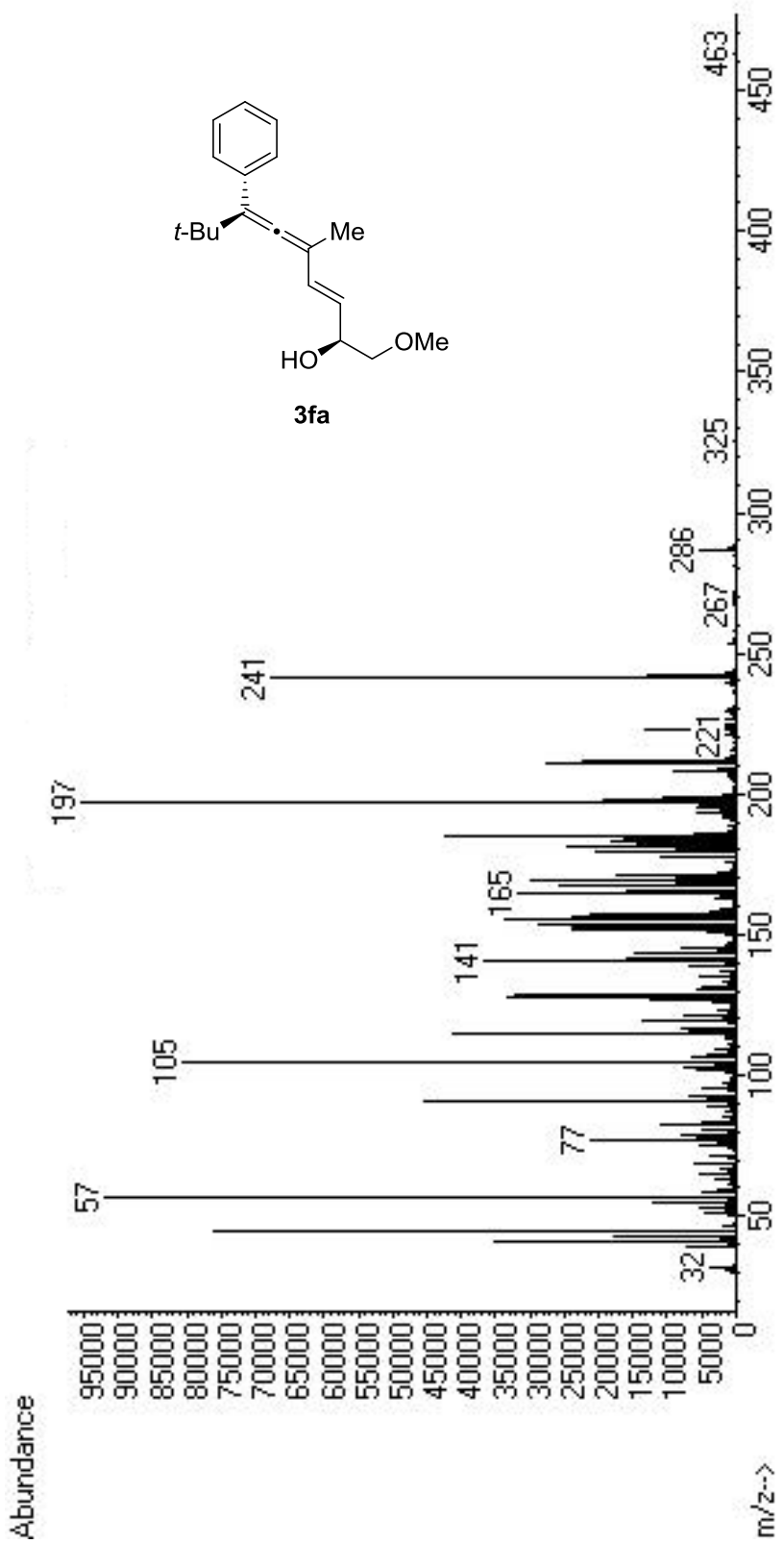

Ph
Bu
Me
HO
OMe
3bl
Abundance
m/z-->
91
195
165
115
141
32
55
71
312
267
223
251
283
328
355
380

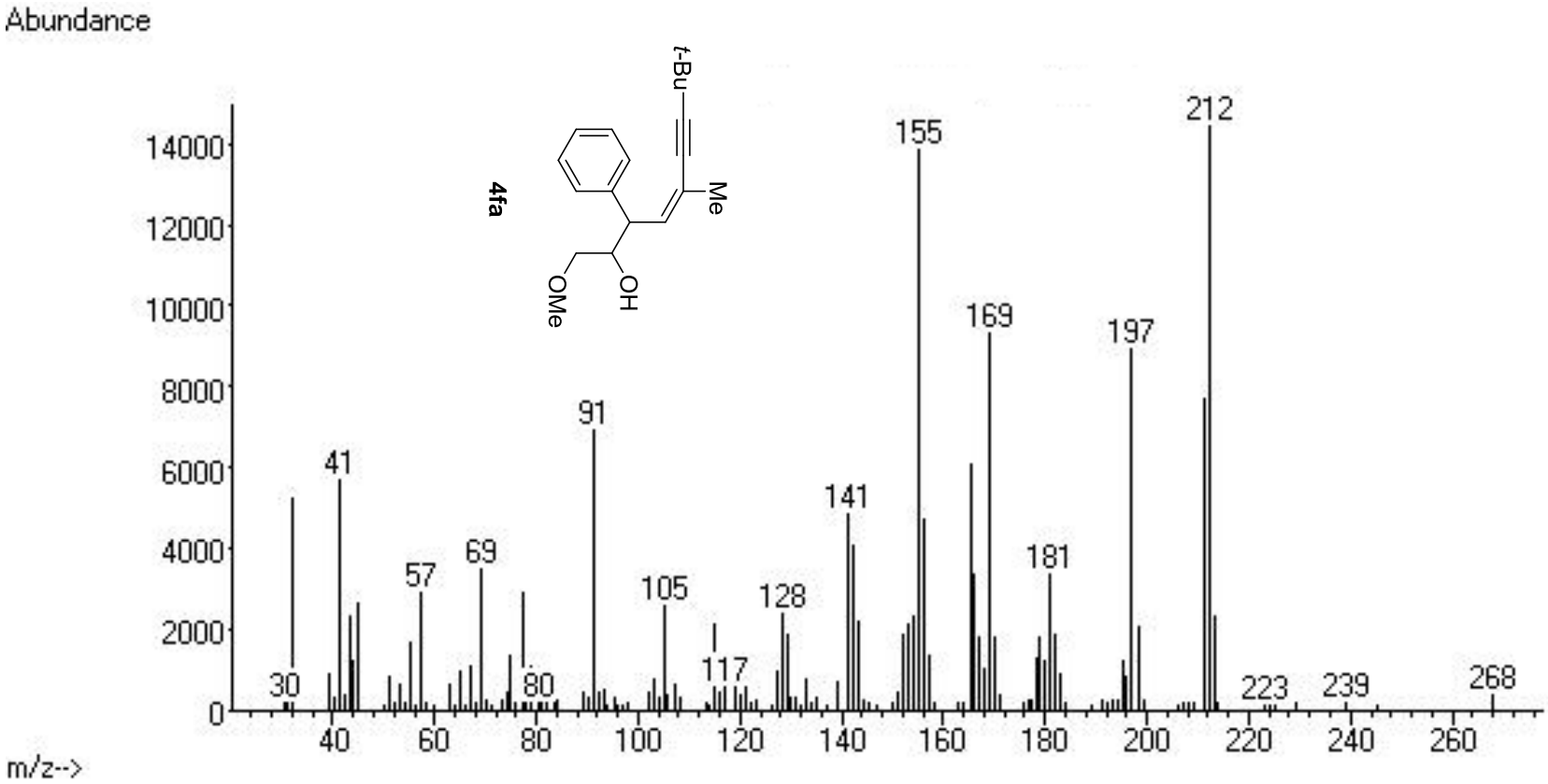

FZ-FW204 151106113814 #3637 RT: 18,4 AV: 1 NL: 1,44E7
T: {0;0} + c EI Full ms [40,00-500,00]
Relative Abundance
m/z
105,1
93,0
55,1
79,1
107,1
119,2
121,2
131,2
135,2
161,2
233,2
173,1
177,1
191,1
215,2
234,1
235,1
278,3
279,1
309,3
340,9
371,1
400,8
412,8
455,3
475,0
489,2
3bm
n-Pr
Bu
Me
HO
OMe


Bu
Me
HO
OH
3ca
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
50
100
150
200
250
300
350
400
450
500
550
32
43
57
70
83
97
112
129
141
157
171
185
207
227
239
256
269
281
302
313
327
341
355
368
389
401
415
429
461
533


Me
Me
HO
OMe
3da
Abundance
m/z-->


OMe
Me
HO
OMe
3eh
FW211_160123150644 #5239 RT: 23,81 AV: 1 NL: 3,62E7
T: {0;0} + c EI Full ms [40,00-500,00]
Relative Abundance
m/z
45,08
55,08
90,98
114,97
121,02
153,00
155,08
165,07
183,06
202,04
214,94
230,95
247,07
262,08
275,12
291,02
303,99
336,11
366,87
417,02
440,89
476,10
497,03

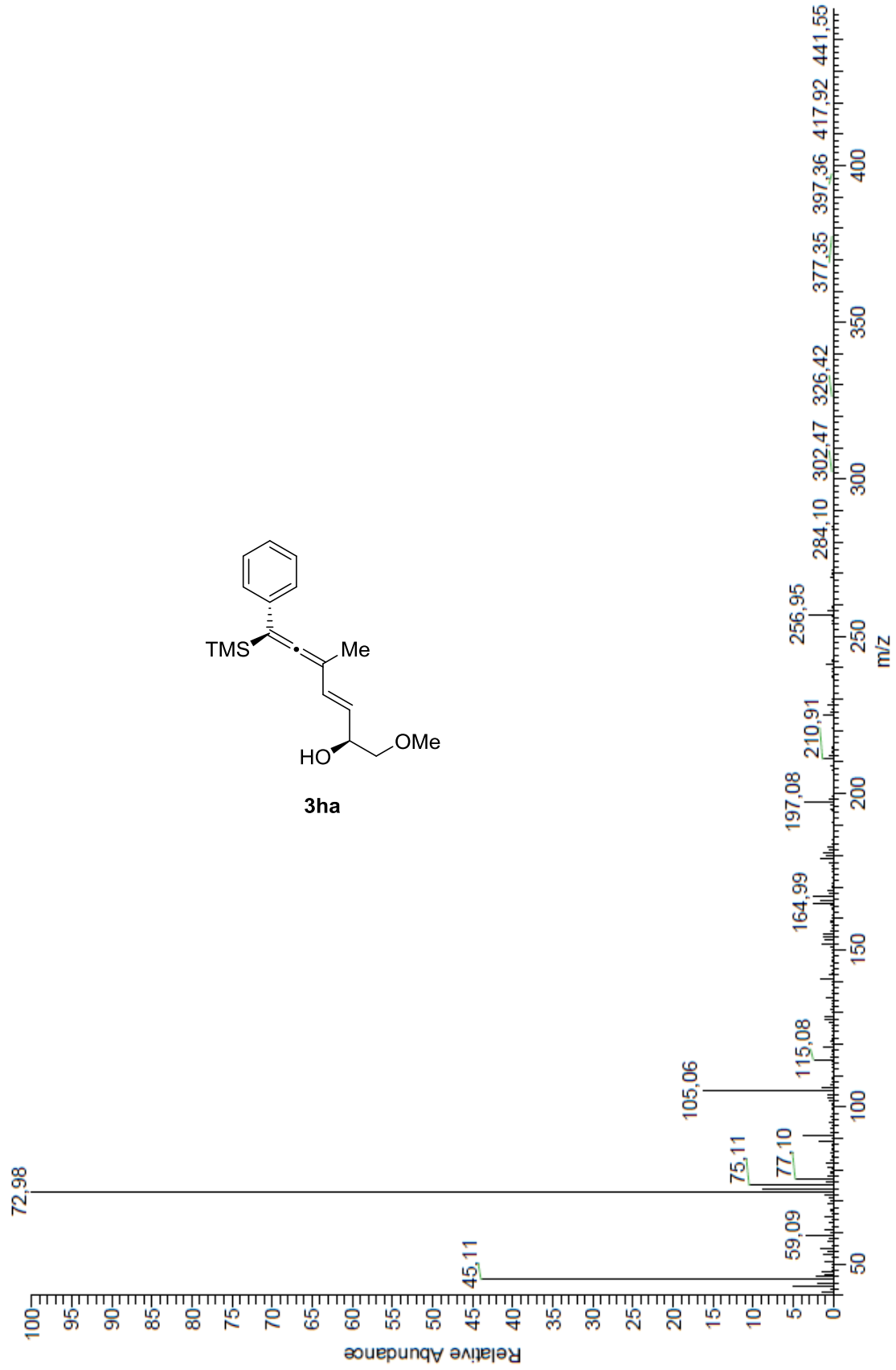

t-Bu
Me
HO
OMe
3fa
Abundance
m/z-->


Abundance
14000
12000
10000
8000
6000
4000
2000
0
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
30
41
57
69
80
91
105
117
128
141
155
169
181
197
212
223
239
268
4fa
t-Bu
Me
OH
OMe

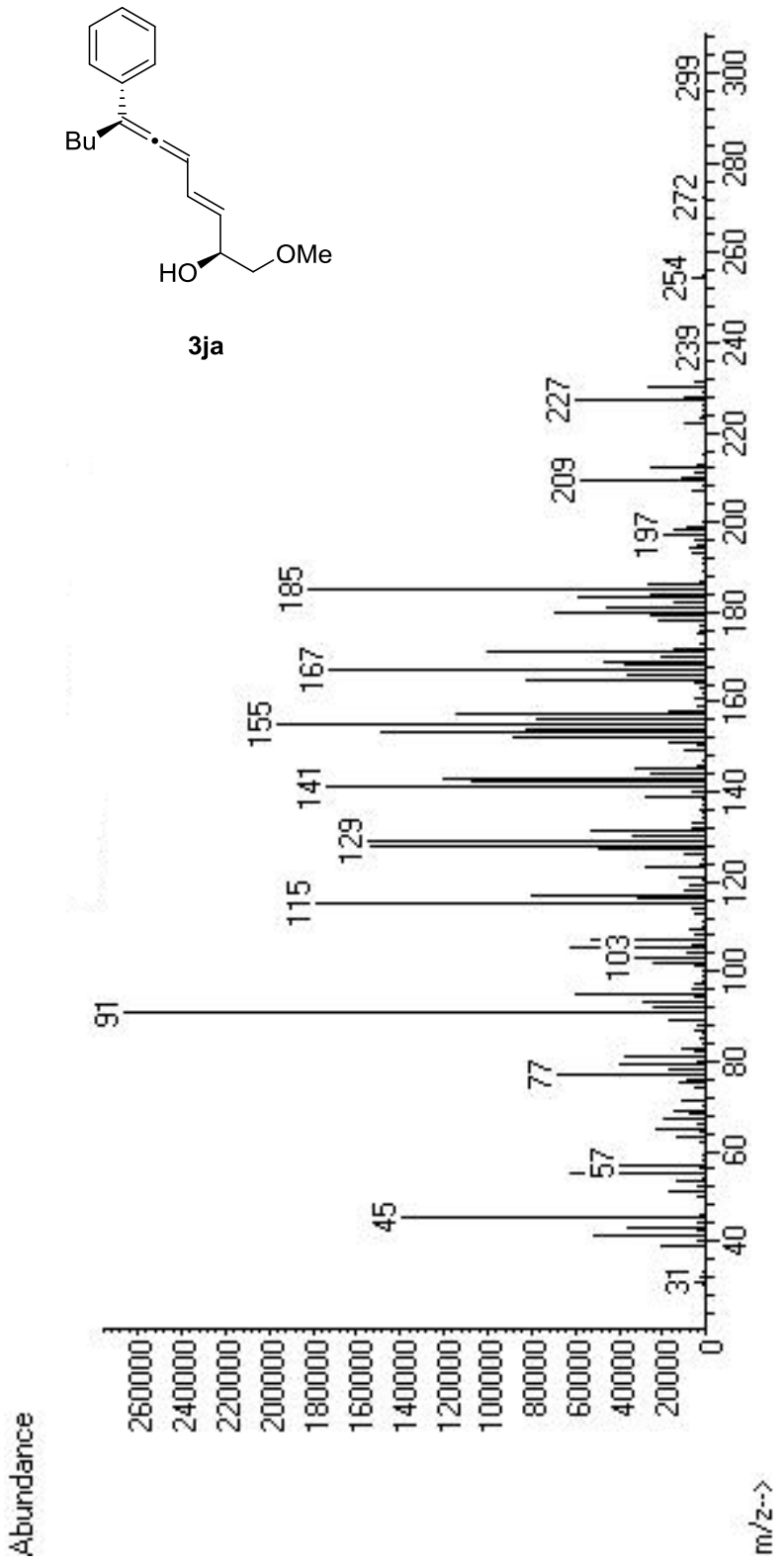
Me
HO
OMe

3ga

Abundance
m/z-->
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
50
100
150
200
250
300
350
400
450
500
550
600
650
45
91
141
181
209
237
267
312
401
460
503
649


TMS
Me
HO
OMe
3ha
Relative Abundance
m/z
72,98
75,11
77,10
105,06
115,08
164,99
197,08
210,91
256,95
284,10
302,47
326,42
377,35
397,36
417,92
441,55
45,11
59,09

H
Me
HO
OMe
3ia
Abundance
m/z-->


Bu
HO
OMe
3ja
Abundance
m/z-->
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
31
40
45
57
60
77
80
91
100
103
115
120
129
140
141
155
160
167
180
185
197
200
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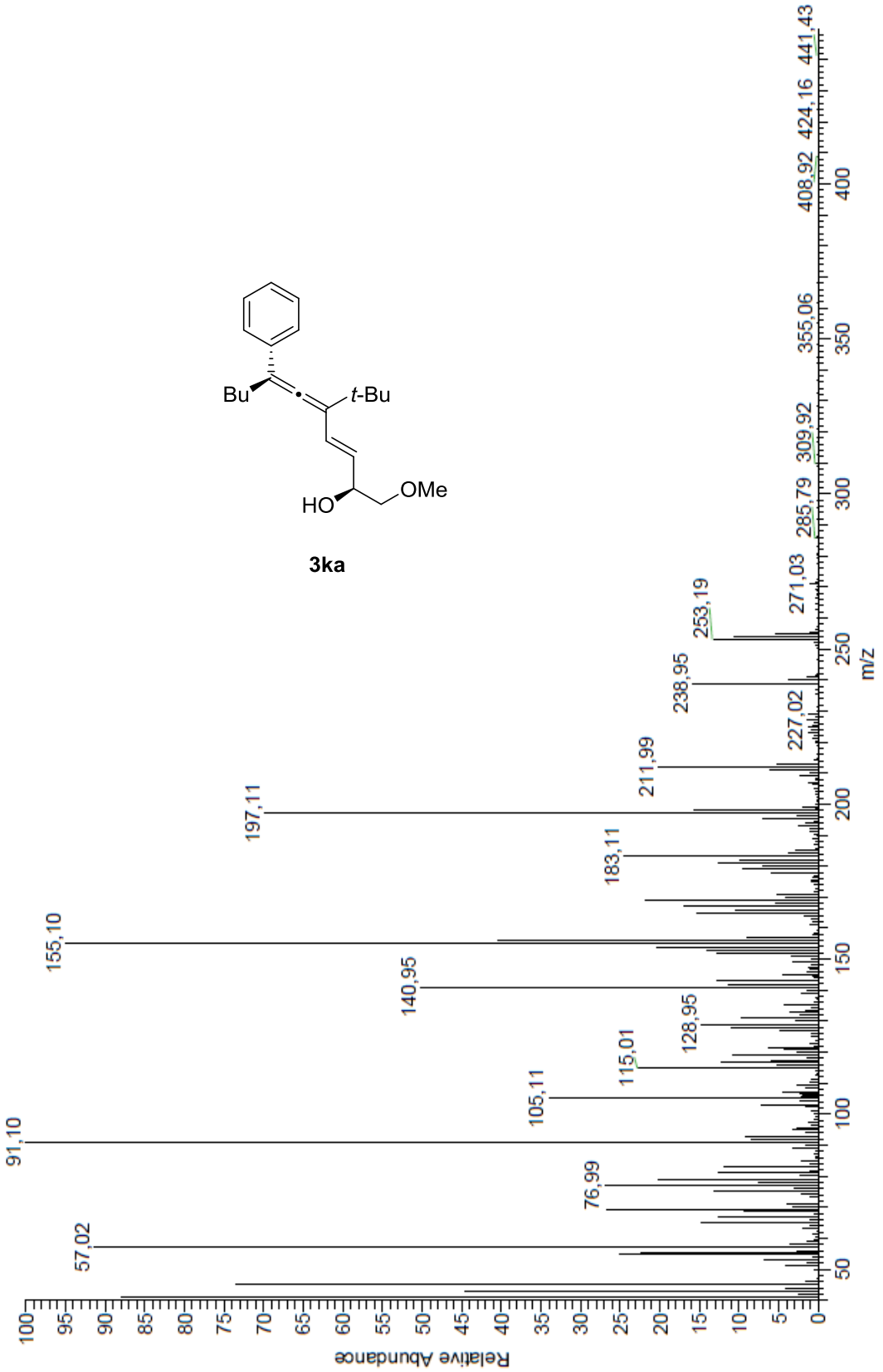
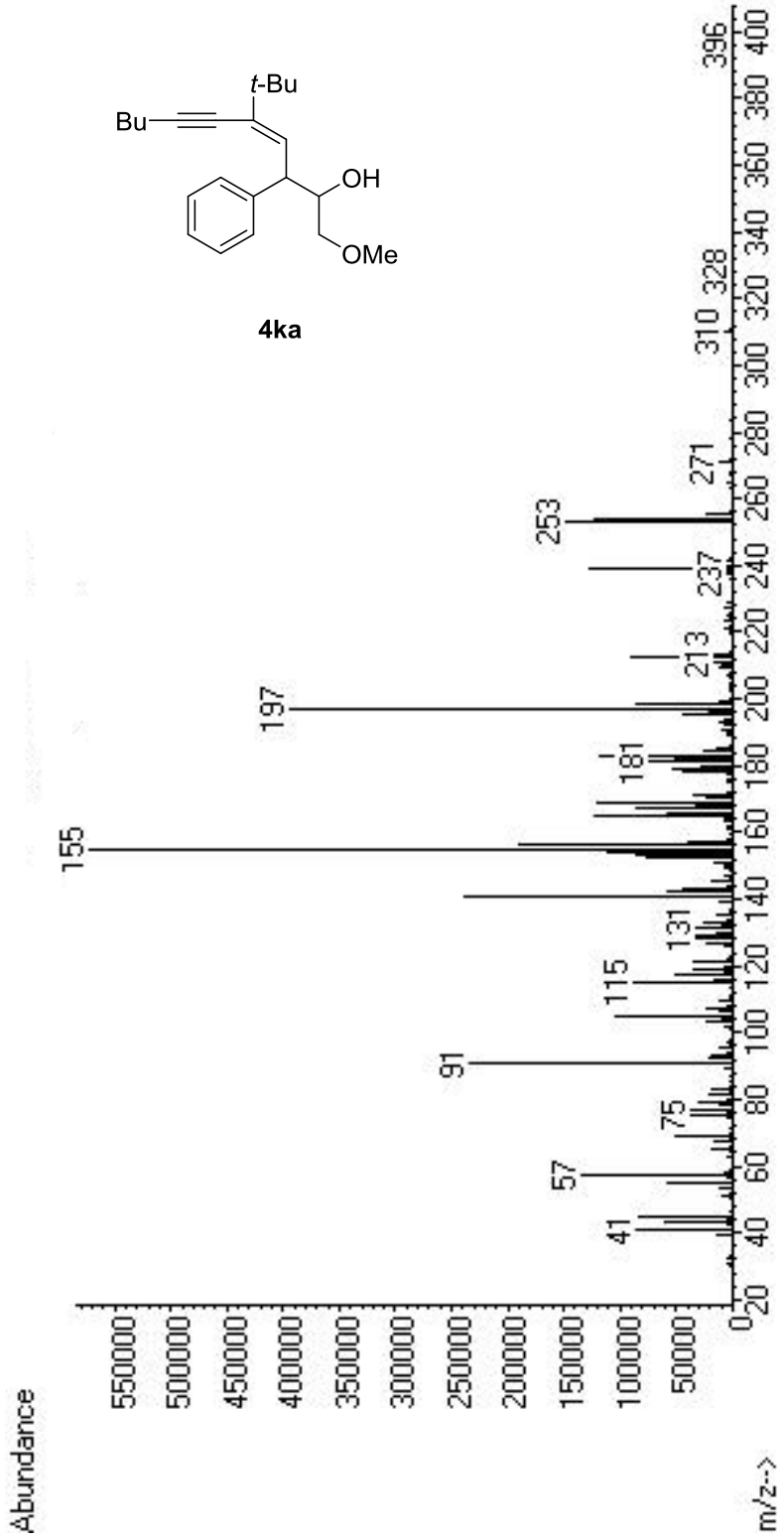
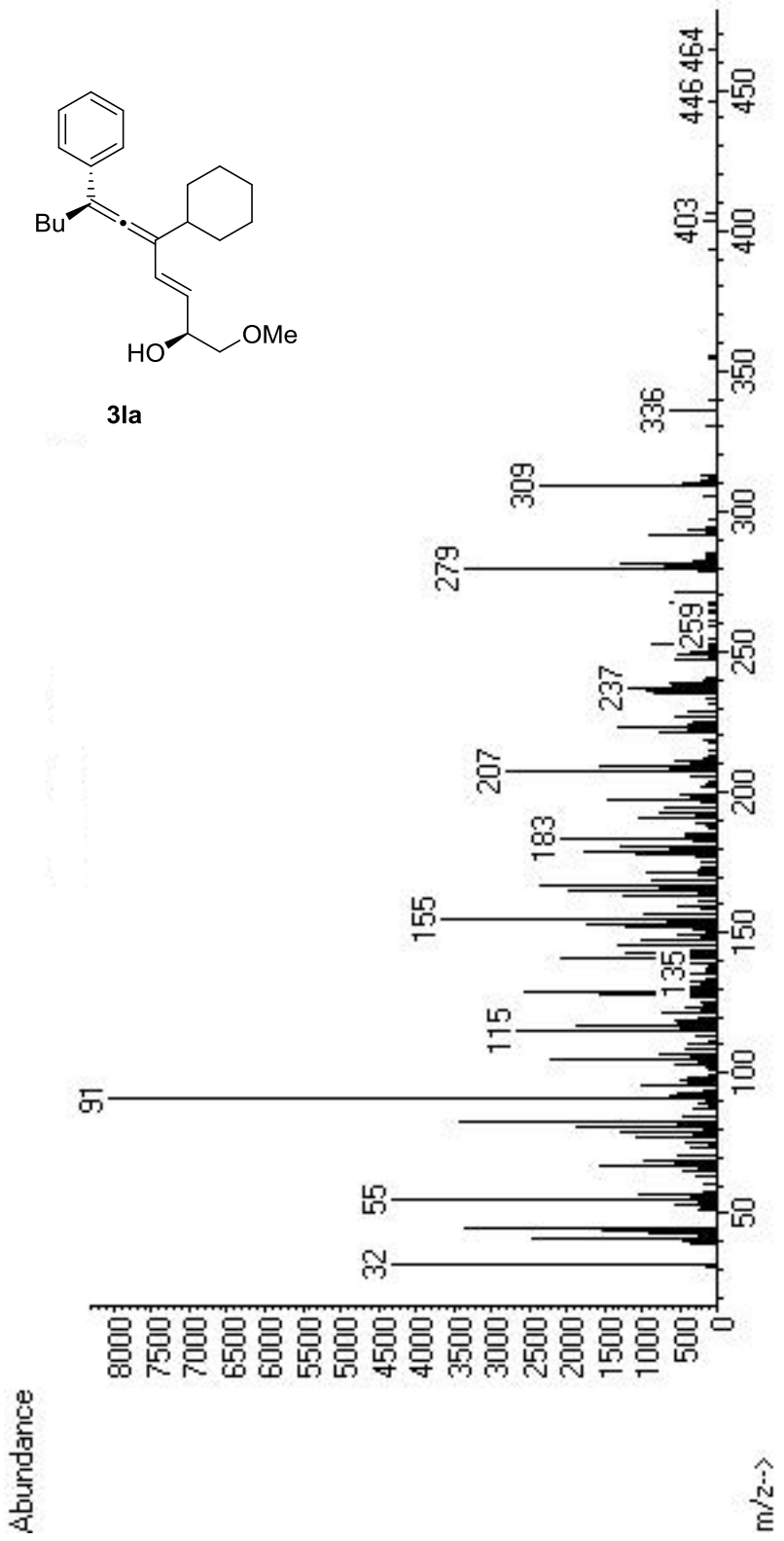
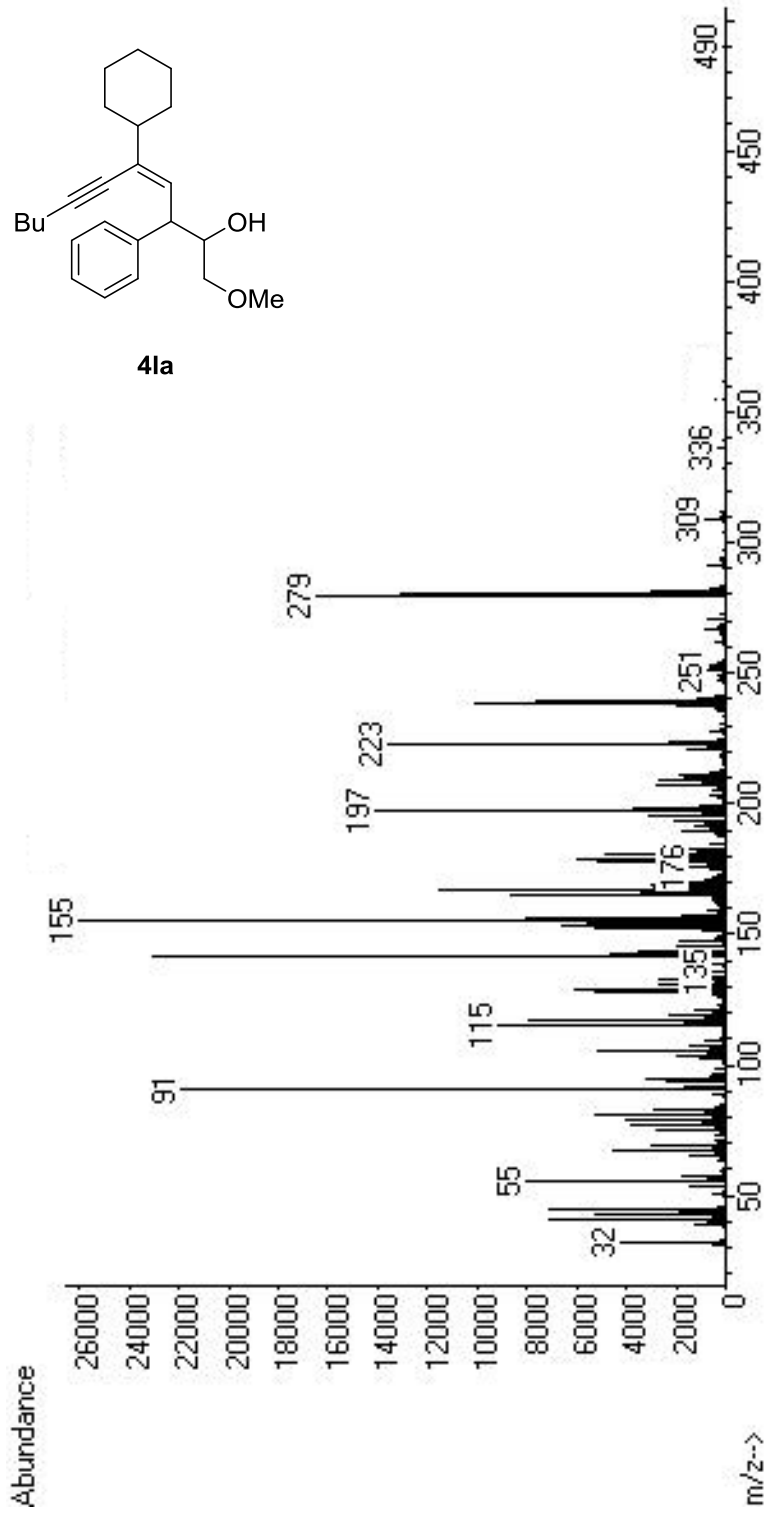
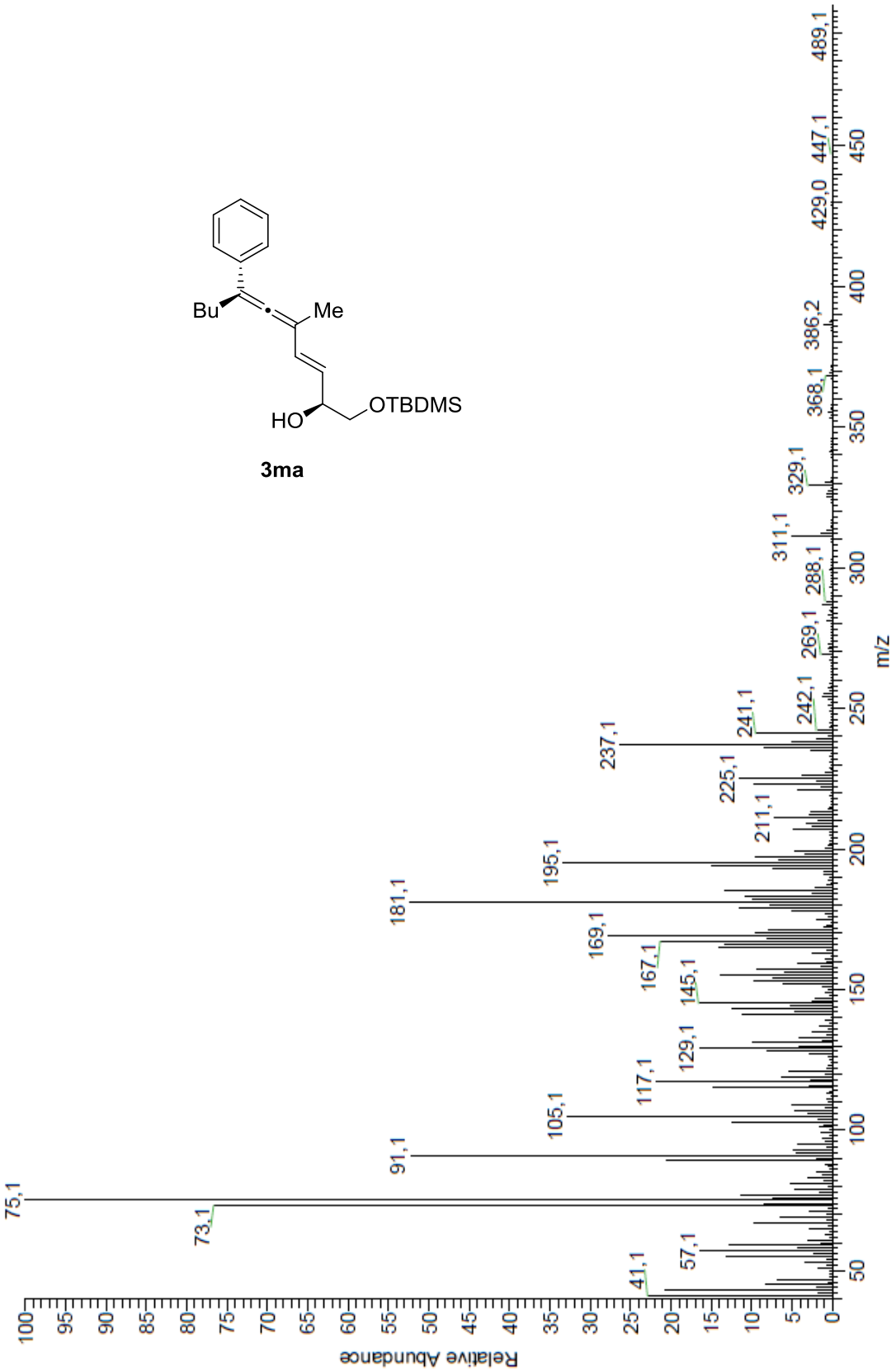
220
227
239
240
254
260
272
280
299
300

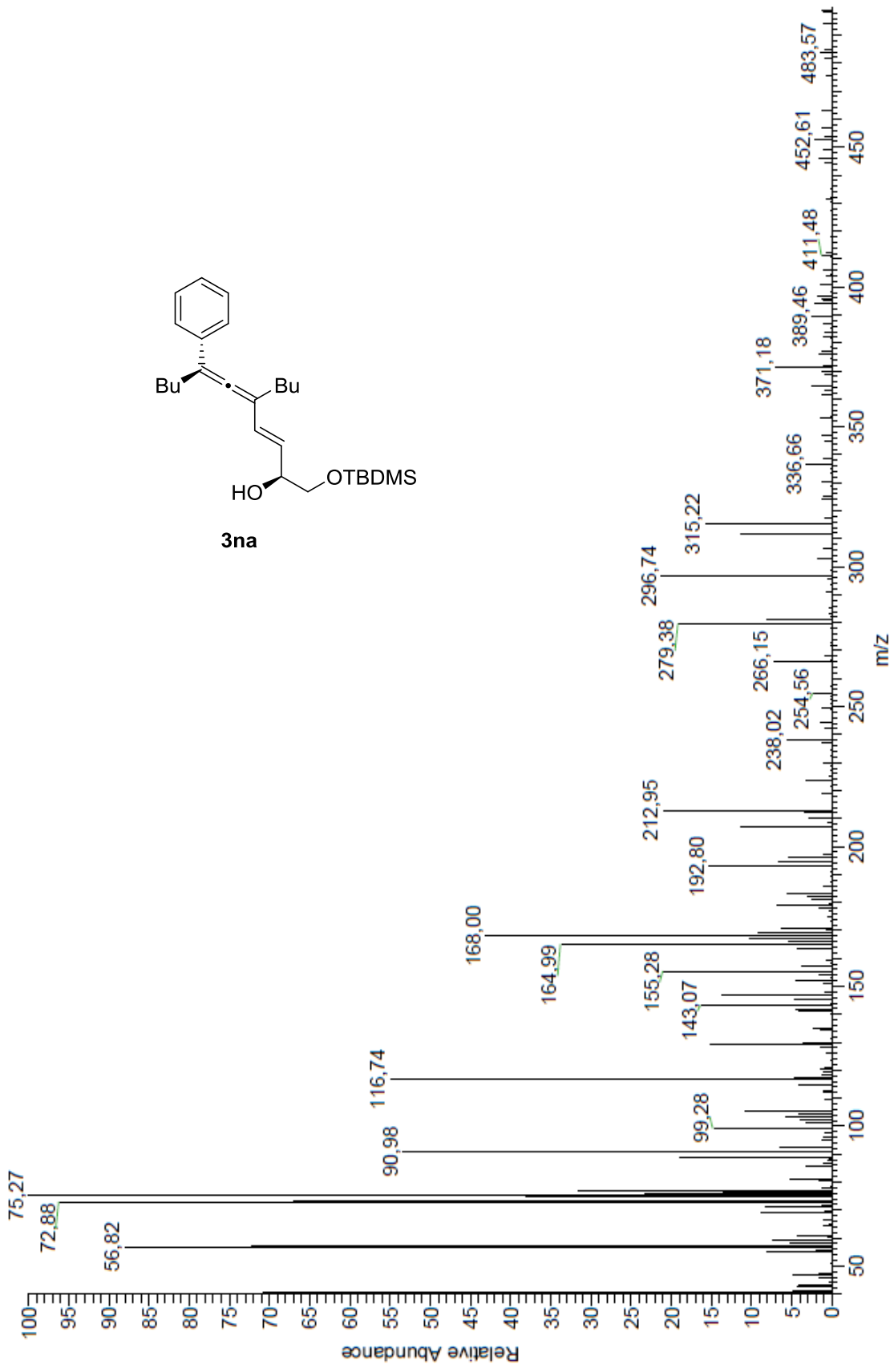

Bu
t-Bu
HO
OMe
3ka
Relative Abundance
m/z
91,10
57,02
155,10
197,11
140,95
183,11
211,99
105,11
115,01
128,95
76,99
238,95
253,19
271,03
227,02
285,79
309,92
355,06
408,92
424,16
441,43

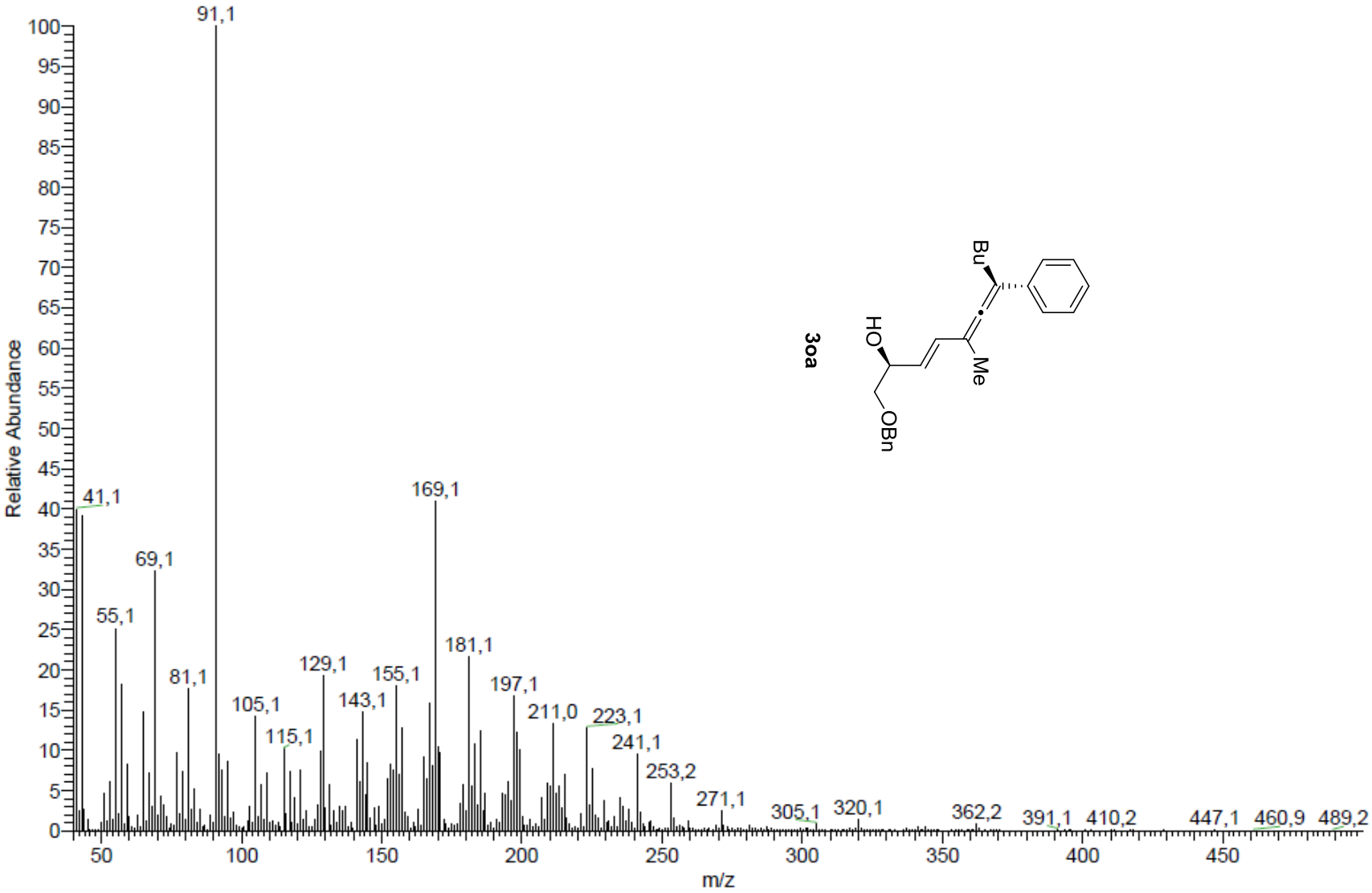

t-Bu
Bu
OH
OMe
4ka
Abundance
m/z-->


Bu
HO
OMe
3la
Abundance
m/z-->


Bu
OH
OMe
4la
Abundance
m/z-->
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
50
100
150
200
250
300
350
400
450
490
32
55
91
115
135
155
176
197
223
251
279
309
336


Bu
Me
HO
OTBDMS
3ma
Relative Abundance
m/z
75,1
73,1
91,1
105,1
117,1
129,1
145,1
167,1
169,1
181,1
195,1
211,1
225,1
237,1
241,1
242,1
269,1
288,1
311,1
329,1
368,1
386,2
429,0
447,1
489,1
41,1
57,1


Bu
Bu
HO
OTBDMS
3na
Relative Abundance
m/z
75,27
72,88
56,82
90,98
116,74
99,28
168,00
164,99
155,28
143,07
212,95
192,80
238,02
254,56
266,15
279,38
296,74
315,22
336,66
371,18
389,46
411,48
452,61
483,57


91,1
Relative Abundance
m/z
41,1
69,1
55,1
81,1
105,1
115,1
129,1
143,1
155,1
169,1
181,1
197,1
211,0
223,1
241,1
253,2
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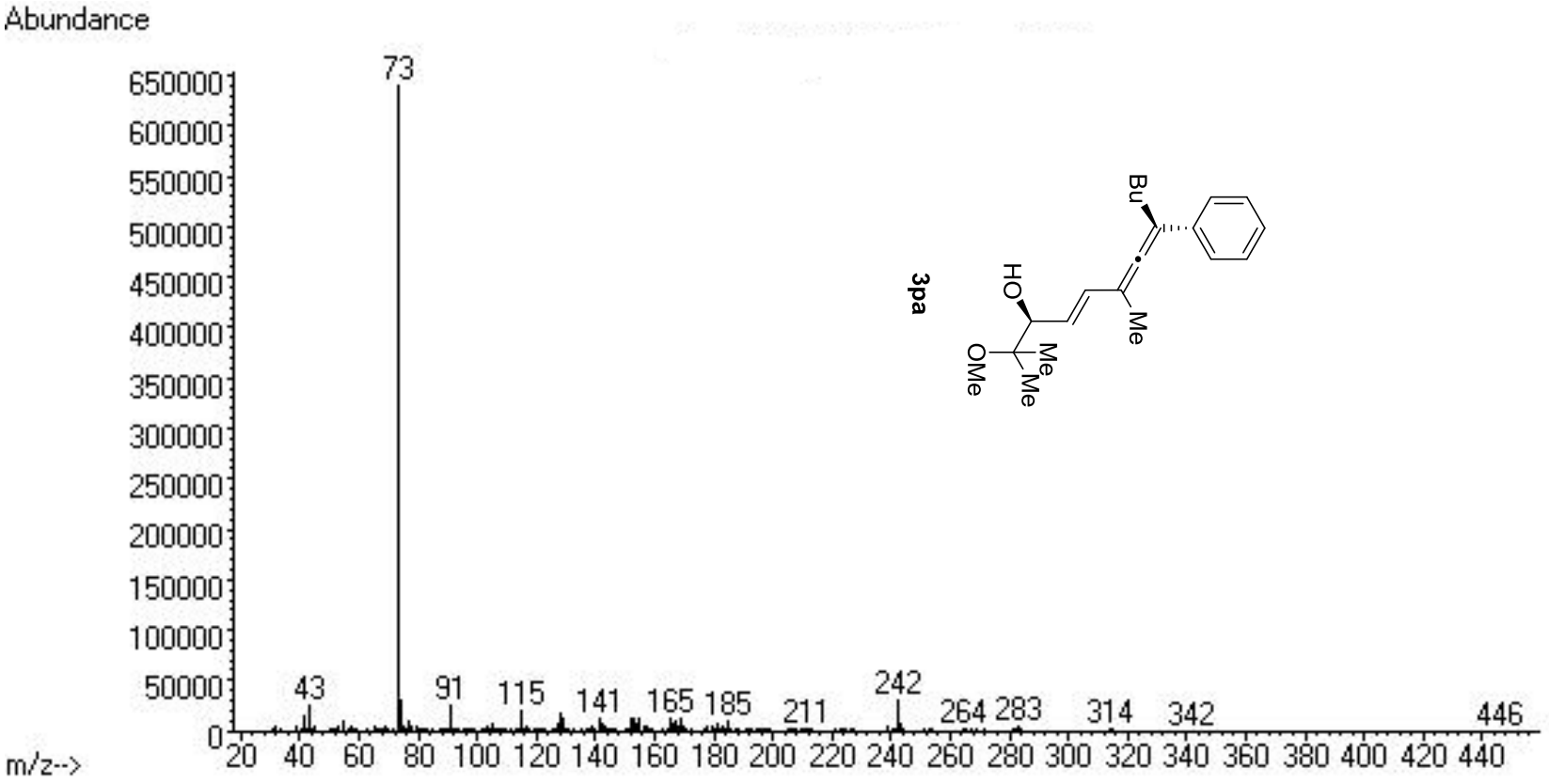
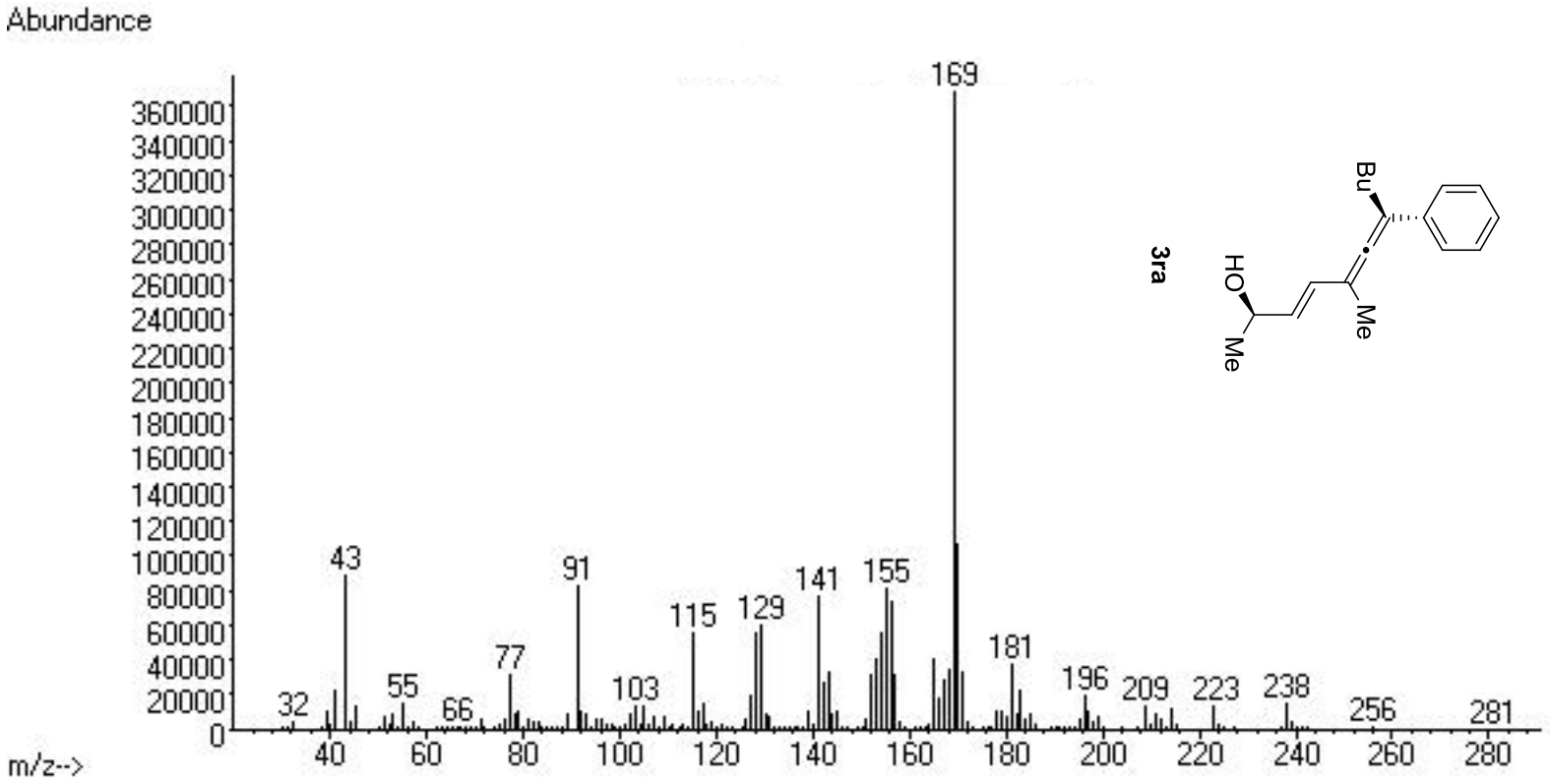
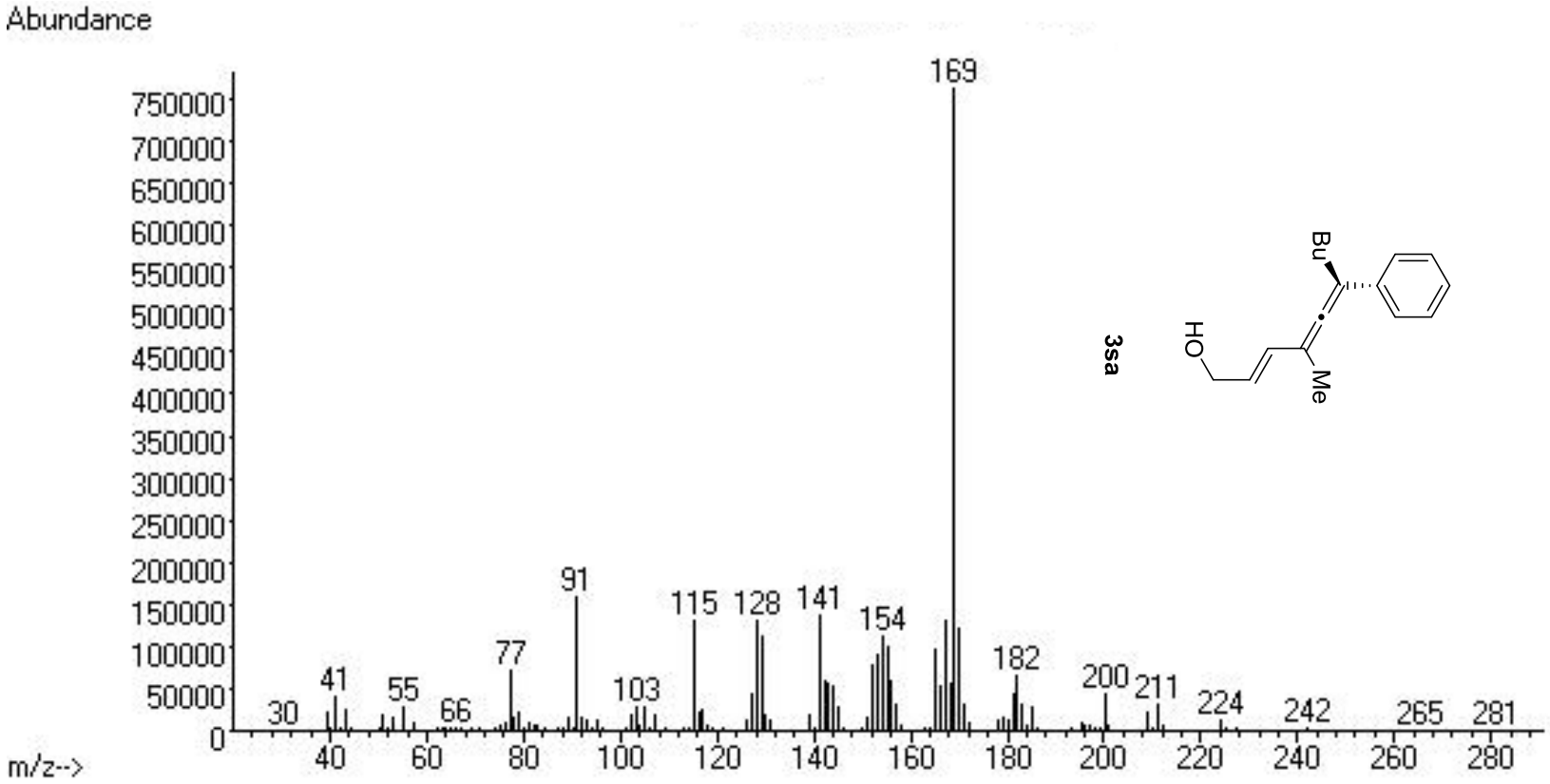
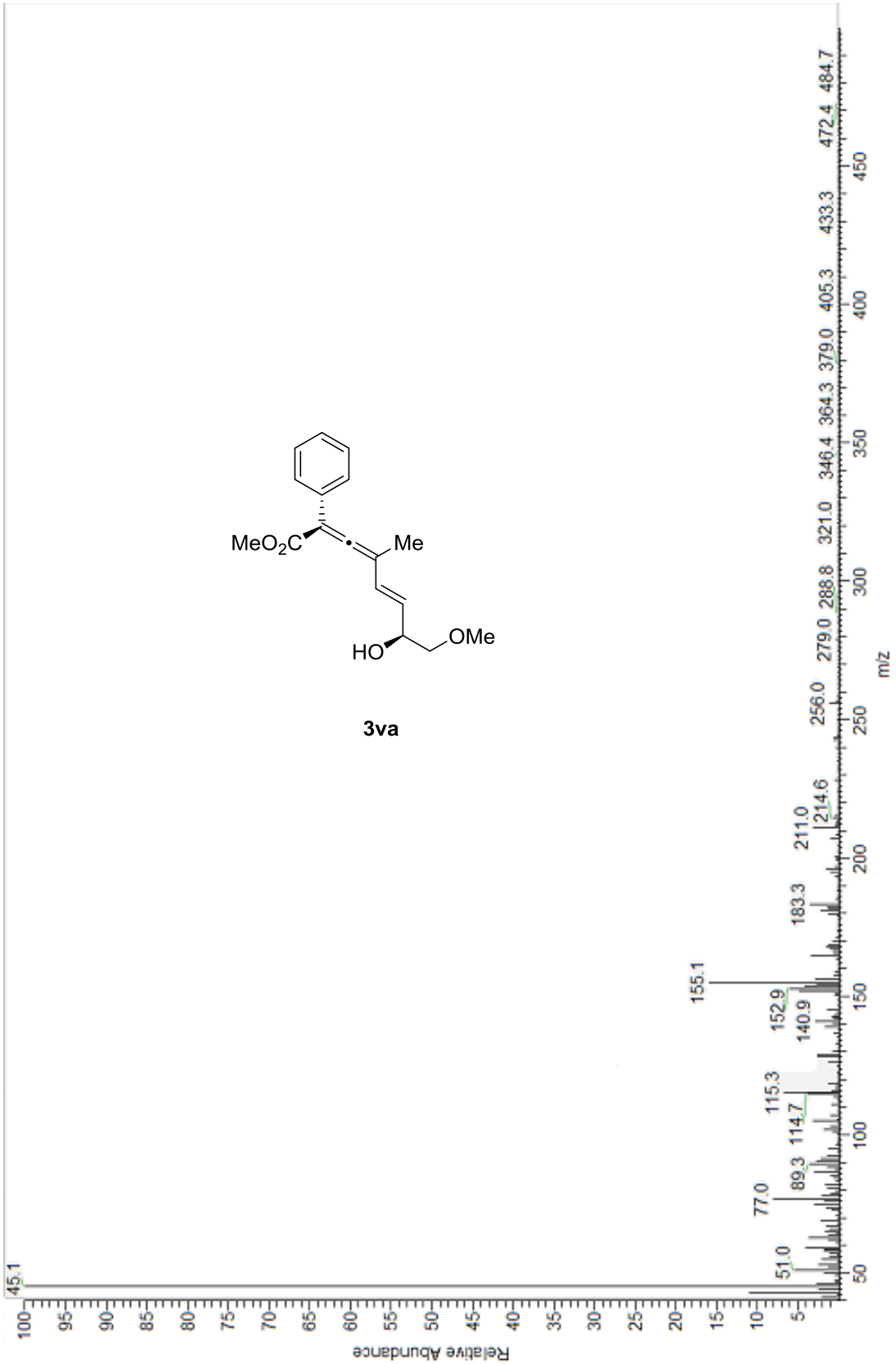
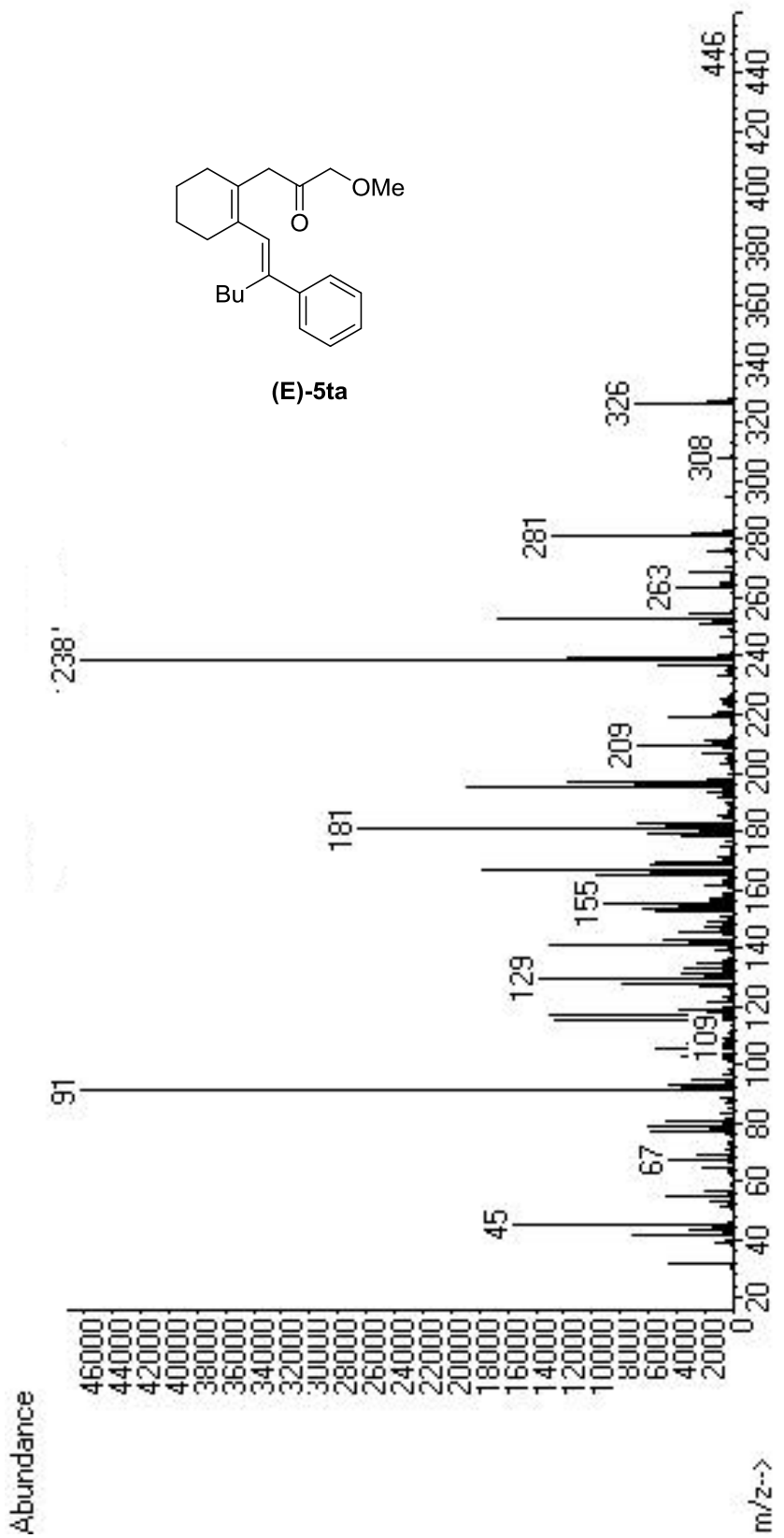
362,2
391,1
410,2
447,1
460,9
489,2
3oa
Bu
HO
Me
OBn

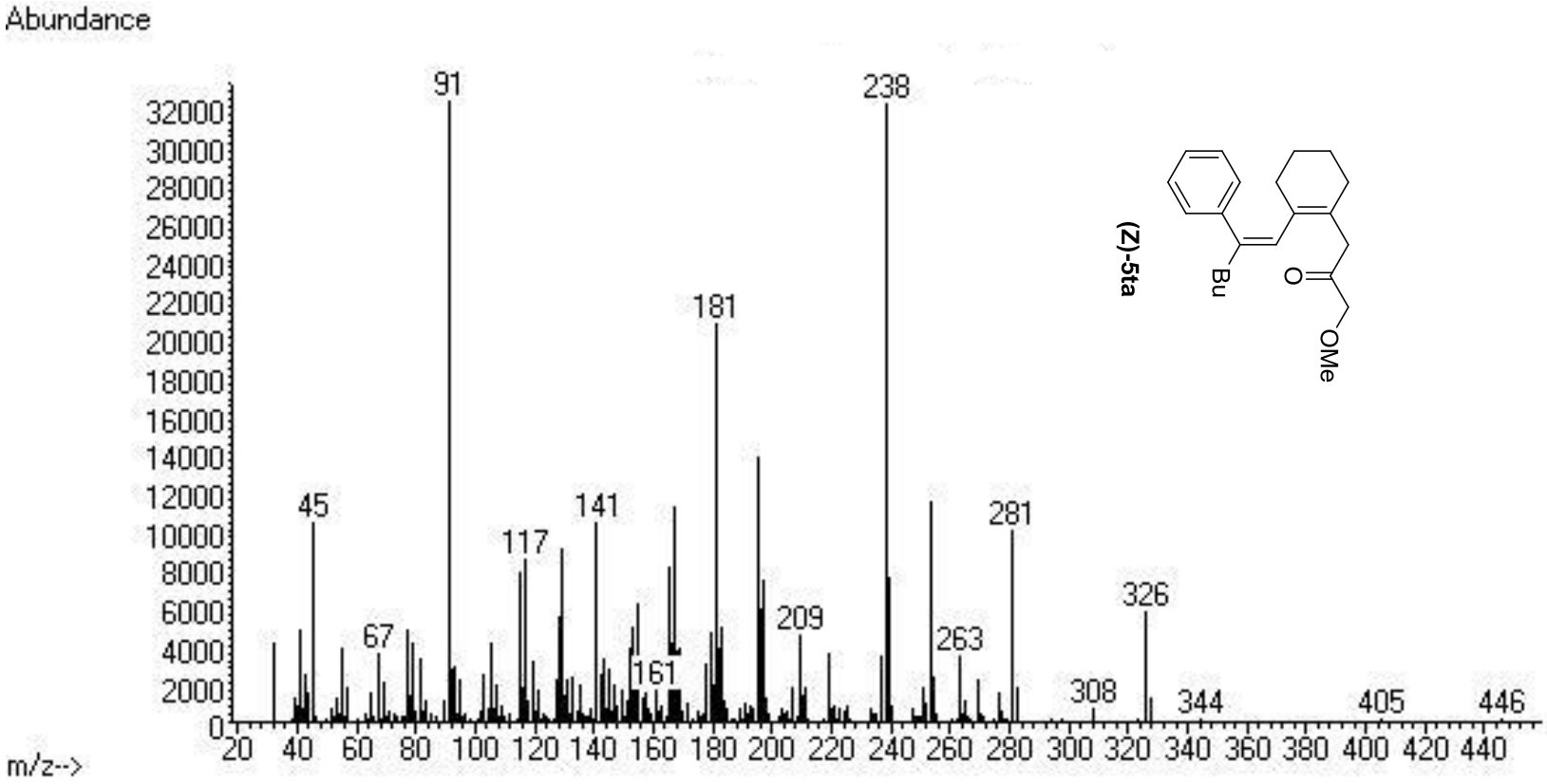

Abundance
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440
73
43
91
115
141
165
185
211
242
264
283
314
342
446
3pa
Bu
HO
Me
OMe
Me
Me

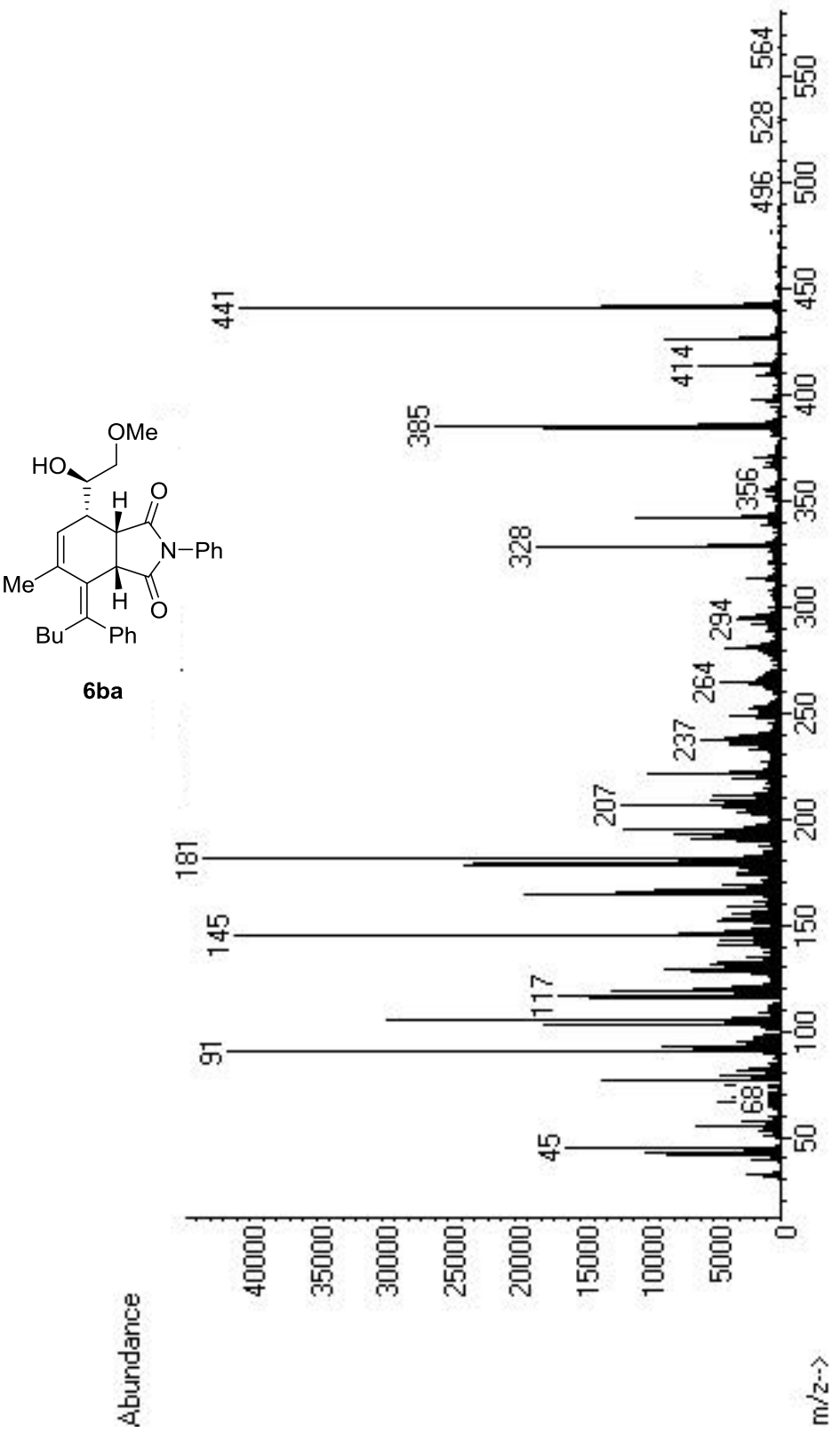

Abundance
m/z-->
169
43
91
141
155
115
129
181
77
103
196
209
223
238
256
281
32
55
66
3ra
Bu
HO
Me
Me


Abundance
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
30
41
55
66
77
91
103
115
128
141
154
169
182
200
211
224
242
265
281
40
60
80
100
120
140
160
180
200
220
240
260
280
3sa
Bu
HO
Me


MeO2C
Me
HO
OMe
3va
Relative Abundance
m/z
45.1
51.0
77.0
89.3
114.7
115.3
140.9
152.9
155.1
183.3
211.0
214.6
256.0
279.0
288.8
321.0
346.4
364.3
379.0
405.3
433.3
472.4
484.7


OMe
O
Bu
(E)-5ta
Abundance
m/z-->
91
238
45
67
109
129
155
181
209
263
281
308
326
446


Abundance
m/z-->
91
238
181
45
141
117
281
326
209
67
263
161
308
344
405
446
(Z)-5ta
Bu
O
OMe


OMe
HO
H
O
N–Ph
Me
H
O
Bu
Ph
6ba
Abundance
m/z-->
40000
35000
30000
25000
20000
15000
10000
5000
0
50
100
150
200
250
300
350
400
450
500
550
564
528
496
441
414
385
356
328
294
264
237
207
181
145
117
91
68
45

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PhD İzmir Institute of Technology 2016
MSc İzmir Institute of Technology 2011
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WORK EXPERIENCE

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2016 – R&D Responsible, TOYO Printing Inks
2008 – 2016 İzmir Institute of Technology, Teaching and Research Assistant
2007 – DYO Inks Chemical Company, Trainee
2006 – Türk Henkel A.Ş. Chemical Company, Trainee

FOREIGN LANGUAGE

English (Advanced)

PUBLISHED ARTICLES

1) Rhodium Catalyzed Alkoxycarbonylative Cyclization Reactions of 1,6 Enynes, ADVANCED SYNTHESIS & CATALYSIS, 353, 897-902, **2011**)

2) Synthesis of α,β-Unsaturated Ketones by Rhodium-Catalyzed Carbonylative Arylation of Internal Alkynes with Arylboronic Acids, SYNLETT, Issue 17, 2587-2592, **2008**)