# PALLADIUM CATALYZED ALKOXYCARBONYLATION REACTIONS OF 2-EN-4-YNE CARBONATES

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**by**
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**İZMİR**

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# ABSTRACT


## PALLADIUM CATALYZED ALKOXYCARBONYLATION REACTIONS OF 2-EN-4-YNE CARBONATES

Homogeneous catalysis relaying on transition metal complexes has led to innovation in organic chemistry. Palladium complexes are the most versatile and used extensively in organic synthesis.

One type of these reactions is the carbonylation reactions with palladium complexes in the presence of alcohol and carbon monoxide. Extensive studies have been carried out on palladium-catalyzed carbonylation reactions of allylic and propargylic compounds. Alkynes containing a leaving group in propargylic position undergo alkoxycarbonylation reactions through the involvement of an σ-allenylpalladium as an intermediate to produce allenic esters. On the other hand, allylic compounds usually leads to β,γ-unsaturated esters through the involvement of a π-allylpalladium complex, when subjected to alkoxycarbonylation processes.

With the high reactivity of allyl carbonates and propargyl carbonates in mind toward P(0)-catalyzed reactions, we attemped the palladium catalyzed alkoxycarbonylation reaction of *Z*- or *E*-configured 2,4-enyne carbonates leading to vinylallene ester structures. The reactions involved 1,5-type substitution and proceeded through formation of σ-vinylallenylpalladium species.

# ÖZET

## 2-EN-4-İN KARBONATLARIN PALADYUM-KATALİZLİ ALKOKSİKARBONİLASYON TEPKİMELERİ

Son yıllarda, geçiş metal kompleksleri organik sentezlerde yoğun olarak kullanılmaya başlanmıştır. Paladyum kompleksleri geniş bir kullanım alanına sahiptir.

Bu reaksiyonlardan bir tanesi alkol ve karbonmonoksit içeren ortamda paladyum kompleksleri ile yapılan alkoksikarbonilasyon tepkimeleridir. Paladyum katalizörlü allilik ve propargilik bileşiklerin karbonilasyon tepkimeleri ile ilgili yoğun çalışmalar literaturde mevcuttur.

Ayrılan grup içeren alkinlerden allen ester oluşumu σ-allenilpaladyum oluşumu yolu ile devam etmektedir. Allilik bileşiklerde ise genellikle π-allenilpaladyum komplekslerinin oluşumu β,γ-doymamış esterlerin sentezinde anahtar basamaktır.

Bu çalışmada, allilik ve propargilik karbonatların yüksek reaktiviteleri göz önünde bulundurularak, çeşitli *Z*- ve E-enin karbonat yapıları ile paladyum katalizörlü alkoksikarbonilasyon tepkimeleri gerçekleştirilerek vinilallen ester yapılarının oluşumu amaçlanmıştır. Tepkimeler 1,5-sübstitüsyon tepkimesi olup, σ-vinylallenylpalladium yapıları üzerinden yürümektedir.

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# CHAPTER 1

# INTRODUCTION

Catalytic carbonylation reaction of unsaturated compounds have been known since 1953 by the pioneering work of Reppe. Since then, the transiton metal catalyzed carbonylation reaction has become important tool for the synthesis of biologycally active α,β-unsaturated carbonyl compounds.

The synthesis of allenes is of current interest due to their high and unique reactivities demonstrated in organic synthesis and the transition metal-catalyzed methods for the synthesis of allenes are know well established. Allenes are present in many natural products and biologically active compounds. They are also important intermediates in organic synthesis.

Over the years, the use of organometallics, such as organozinc, organocopper, organolithium, organoindium reagents for the synthesis of allenes is highly developed.

Reactions of propargyl halides, carbonates, acetates, mesylates, and phosphates with hard and soft carbon nucleophiles can give allenyl derivatives.

Palladium-catalyzed carbonylation reaction of unsaturated compounds has become more useful method for the synthesis of carbonyl compounds. Palladium-catalyzed carbonylation reaction of propargylic compounds are very useful tools for the synthesis of allene structures. Alkynes containing a leaving group in the propargylic position are frequently used as substrates for the reactions catalyzed by Pd(0) complexes.

Several useful methods, mainly based on the reactions of organometallic reagents with suitably functionalized propargyl derivatives have been reported for the development of vinylallenes synthesis, which bear a conjugated vinyl functionalty. Vinyl allenes are useful and unique precursor in organic synthesis.

# CHAPTER 2

# LITERATURE WORK

## 2.1. Palladium-Catalyzed Alkoxycarbonylation of Alkynes

Palladium-catalyzed alkoxycarbonylation reactions of alkynes leads to formation of linear and branched α,β-unsaturated carboxylic acids derivatives in the presence of an alcohol. The linear and branched product ratio depends on the catalytic system (Figure 2.1).

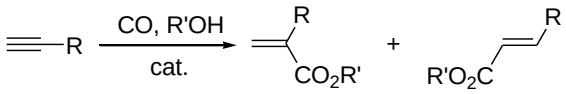



Figure 2.1. Alkoxycarbonylation of alkynes with Pd catalyst

In 1998, Scrivanti *et al.* reported two possible mechanisms for the alkoxycarbonylation reactions of terminal alkynes. First mechanism involves addition of in-situ formed Pd-$CO_2$R species onto triple bond, leading to an (alkoxycarbonyl)palladium complex, after which carboalkoxy moity migrates from the carbon atom of 1-alkyne and finally protonation of vinyl intermediate results in the formation of the desired product (Figure 2.2).

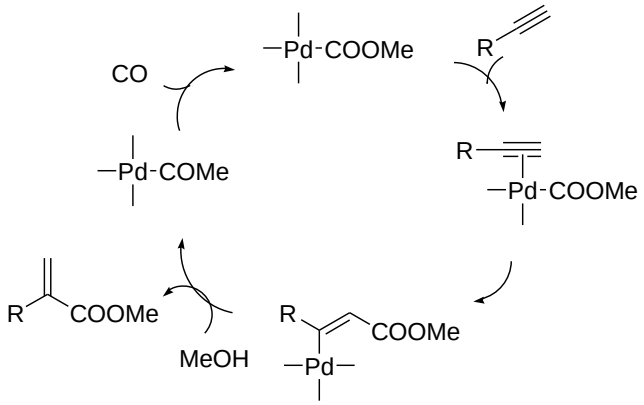



Figure 2.2. The mechanism of alkoxycarbonylation of alkynes which ivolves (alkoxycarbonyl) palladium intermediates (Source: Scrivanti *et al*. 1998)

The second mechanism essentially involves the formation of a (σ-vinyl)palladium complex by the insertion of the alkyne into a Pd-H bond, CO inserts into the Pd-C bond and the following alcoholysis yields the expected ester. Hydride regenerates at the end of this pathway (Figure 2.3).

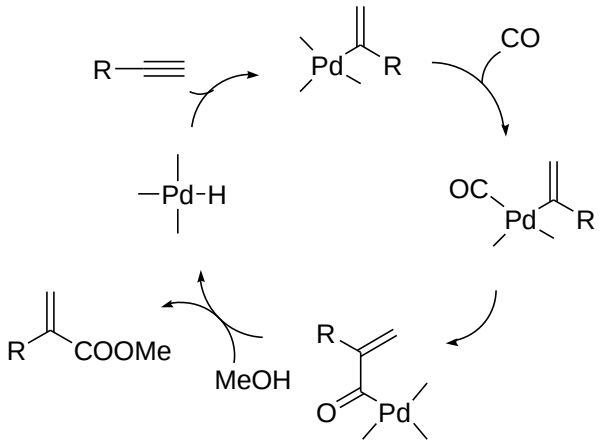



Figure 2.3. The mechanism of alkoxycarbonylation of alkynes which involves a hydride formation (Source: Scrivanti *et al*. 1998)

## 2.1.1. Palladium(0)-Catalyzed Reactions of Propargyl Compounds

Propargylic compounds can undergo several types of transformations with palladium catalysts that yield allene, alkene, alkyne, and enyne derivatives.

Reactions of propargyl coumponds promoted by Pd(0)-catalysts proceed by the formation of either a σ-allenylpalladium or a propargylpalladium as intermediates (Figure 2.4) (Elsevier *et al*. 1983, 1986).

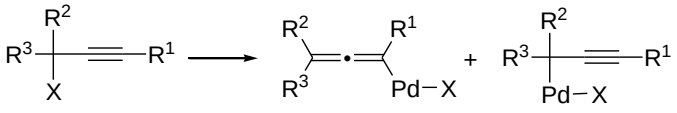



Figure 2.4. Pd(0)-catalyzed reaction of propargyl compounds

Mainly, σ-allenylpalladium intermediates undergo three type of reactions (Tsuji *et al*. 1995):

1-Insertion of unsaturated bonds to σ-bonds.

2-Transmetallation of the σ-allenylpalladium complex with main group metals or metal hydrides.

3-Nucleophilic attack to the central sp carbon of the alkenyl system in σ-allenylpalladium (Figure 2.5).

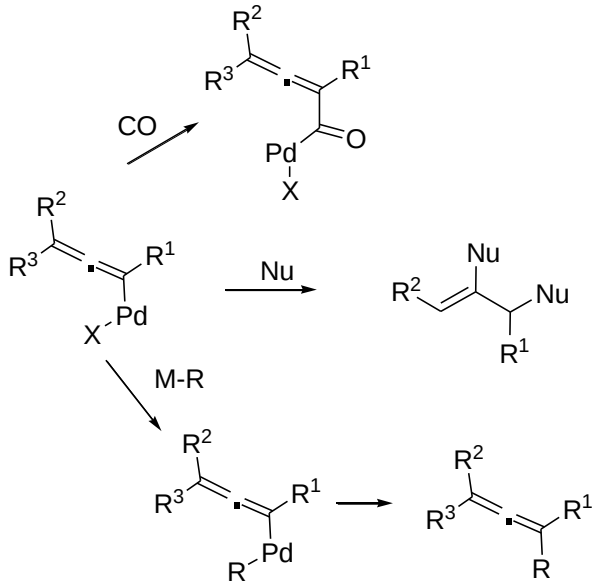
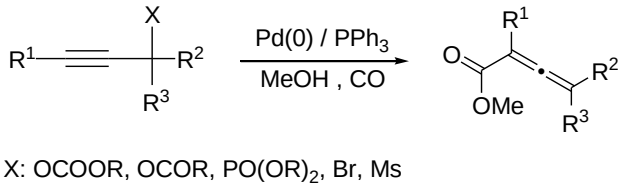



Figure 2.5. Reactions of σ-allenylpalladium intermediates

## 2.1.2. Carbonylation Reactions of Propargylic Compounds Containing a Leaving Group

Propargyl compounds undergo mono- and dicarbonylations depending on the reaction conditions. (Figure 2.6) (Tsuji *et al*. 1993). Alkynes containing a leaving group in the propargylic position are frequently used as substrates for the reactions catalyzed by Pd(0) complexes. The key step of these reactions is the formation of σ-allenylpalladium(II) intermediates (Tsuji *et al*. 1987). Such intermediates can react with a nuchleophile at the central carbon atom of the allene moiety. Furthermore, olefins or CO can insert into the Pd-C bond of σ-allenylpalladium(II) intermediates. Depending on this properties of the σ-allenylpalladium(II) intermediates, various type of reactions of propargylic compounds have been reported.




X: OCOOR, OCOR, $PO(OR)_2$, Br, Ms

Figure 2.6. Pd(0)-catalyzed alkoxycarbonylation of propargyl compounds

In 1986, Tsuji and co-workers reported first palladium-catalyzed carbonylation reaction of propargyl carbonates to yield 2,3-dienyl carboxylates. The desired products were obtained in good yields when the reactions were performed in the presence of methanol (Figure 2.7).

They reported that the corresponding allenic ester forms in low yield when the reactant was a terminal methyl propargyl carbonate. The yield of the method increases when using a $C_7H_{15}$ substituted propargyl carbonate as a reactant. Furthermore, a tertiary propargylic carbonate with a terminal triple bond gave the corresponding allenyl ester with excellent yield.

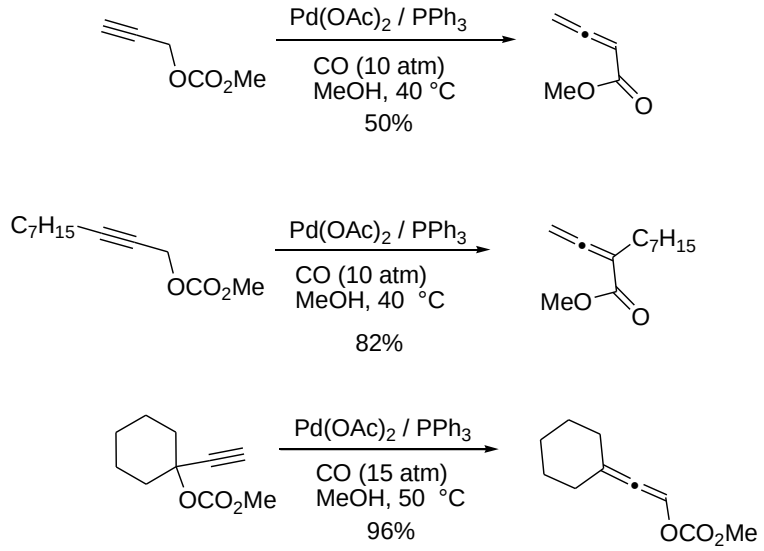



Figure 2.7. Alkoxycarbonylation of propargyl carbonates with $Pd(OAc)_2$ / phosphine , ligand system (Source: Tsuji *et al*. 1986)

According to the their proposed mechanism, initially the propargylic carbonate undergoes oxidative addition with Pd(0) species, which follows by decarboxylation to lead to an (allenyl)-palladium alkoxide complex. Then, CO coordinates to the complex

and inserts into the palladium-carbon bond. 2,3-Dienyl carboxylate is produced after reductive elimination of this intermediate (Figure 2.8).

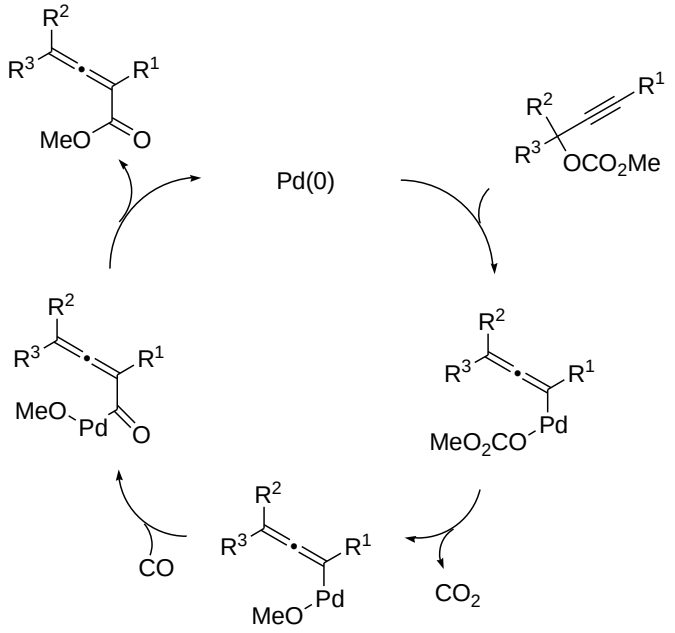



Figure 2.8. Pd-catalyzed carbonylation mechanism of propargylic carbonates

## 2.2. Transition Metal-Catalyzed Carbonylation of Alkenes

Transition metal-catalyzed reactions of alkenes are a significant process for organic synthesis. Carbonylation reactions of alkenes leads to the formation of saturated carbonyl compounds such as carboxylic acids, anhydrides, esters, amides, and *etc* (Chaudhari *et al*. 2005). Palladium-catalyzed reactions of various allylic compounds via the formation of a π-allylpalladium complex offer many synthetically useful methods. In this process, the desired product can be formed in the presence carbon monoxide and a nucleophile such as alcohol, water, or hydrogen. The type of reaction that will take place will be depended on the nuchleophile type used. If the nuchleophile is alcohol, the process is referred to as an alkoxycarbonylation (Figure 2.9) (Beller *et al*. 2009).

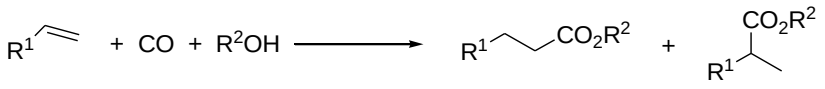



Figure 2.9. Alkoxycarbonylation reactions of alkenes

Two types of mechanisms for the palladium-catalyzed alkoxycarbonylation reactions of alkenes are suggested. (Claver *et al*. 2001)

A Pd-alkyl intermediate forms via the insertion of the alkene into the Pd-hydride bond, then CO inserts into the metal-alkyl bond and gives the acyl-palladium intermediates. Alcohol acts as a nucleophile and gives the desired product (Figure 2.10)

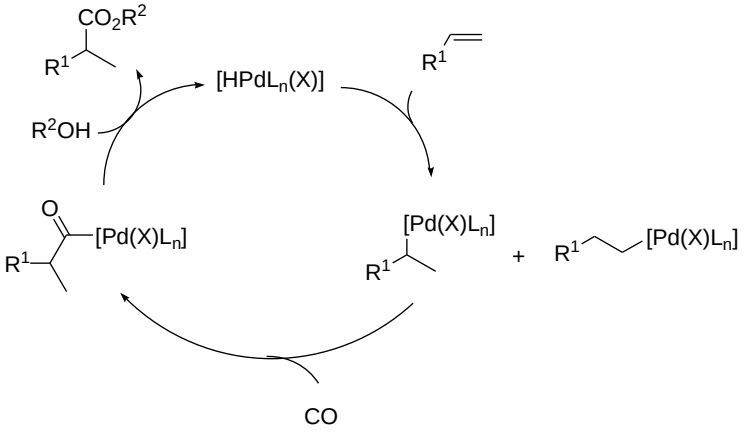



Figure 2.10. The mechanism of palladium-catalyzed alkoxycarbonylation of alkenes which involves acyl-palladium intermediates

According to the other proposed mechanism, a Pd-alkoxycarbonyl intermediate form via the insertion of the alkene into the Pd-C bond, then alcoholysis of the intermediate gives the desired ester and alkoxymetal complex. CO inserts into the Pd-OR bond and palladium-alkoxycarbonyl complex is recycled (Figure 2.11)

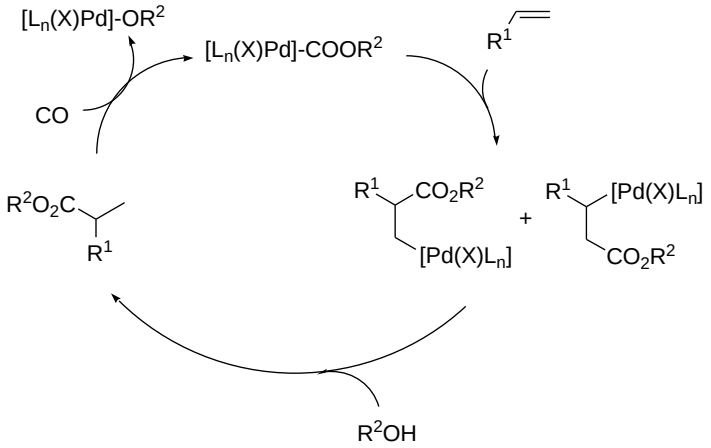



Figure 2.11. The mechanism of palladium-catalyzed alkoxycarbonylation of alkenes which involves Pd-alkoxycarbonyl intermediates

Reaction of alkenes with CO and alcohols lead to the formation of carboxylic acid esters. Allylic esters such as carbonates, acetates and phosphates are widely used for this process.

## 2.2.1. Carbonylation Reactions of Allyl Compounds

In 1984, Tsuji and his co-workers reported first palladium-catalyzed carbonylation reactions of allyl-alkyl carbonates, undergoing a smooth decarboxylation-carbonylation reactions to afford β,γ -unsaturated esters at 50 ºC under atmospheric or low pressure of carbon monoxide and neutral conditions in the presence of palladium-phosphine complexes as catalysts (Figure 2.12).

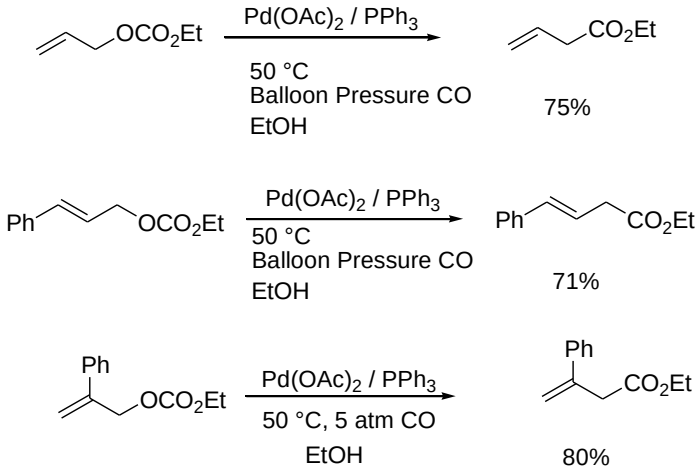



Figure 2.12. Alkoxycarbonylation of allyl alkyl carbonates with $Pd(OAc)_2$ / phosphine ligand system

According to their proposed mechanism, initially a π-allylpalladium alkoxide intermediate forms by the oxidative addition of palladium with the allyl carbonate. There are two possible reaction pathways for the insertion of CO: (1) the insertion of carbon monoxide into the π-allylpalladium bond followed by the formation of 3-butenoylpalladium complex, or (2) the insertion into the palladium alkoxide bond to give a (carboxy)(π-allyl)palladium complex. Finally, β,γ-unsaturated esters were formed by reductive elimination (Figure 2.13). At the same time Pd(0) species is regenerated.

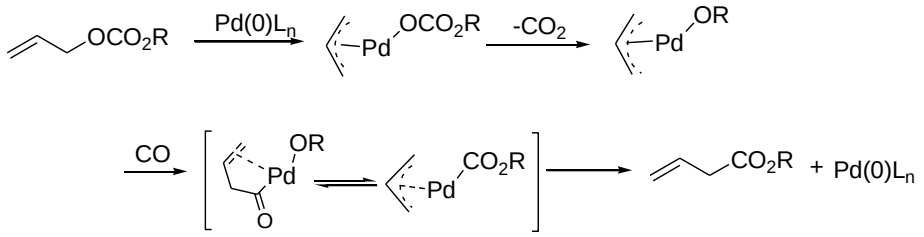



Figure 2.13. Alkoxycarbonylation mechanism of allyl-alkyl carbonates

In 1993, the palladium-catalyzed alkoxycarbonylation of allyl phosphates and allyl acetates were reported by Murahashi and his co-workers The method was highly efficient to give β,γ-unsaturated esters when the carbonylation was carried out with the allyl phosphates in the presence of 0.5 mol 2% of $Pd_2(dba)_3CHCl_3$, 2 mol 2% of $PPh_3$, and 1 equiv. of *i*-$Pr_2NEt$ in ethanol (Figure 2.14). The carbonylation took place on the least substituted allylic position and proceeded with the inversion of the configuration.

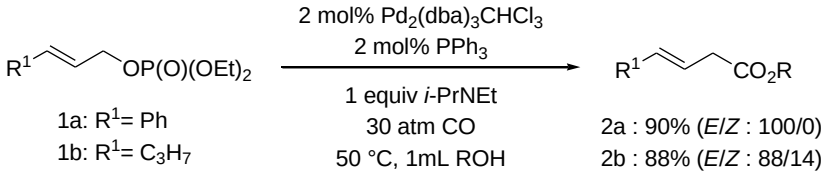



Figure 2.14. Palladium-catalyzed alkoxycarbonylation of allyl phosphates

The palladium-catayzed carbonylation reaction of allyl acetates proceed by the oxidative addition of allyl acetate to palladium(0) complexes to give a π-allylpalladium acetate complex followed by the insertion of CO into the π-allylpalladium bromide complex (Murahashi *et al*. 1993), (Figure 2.15). Sodium bromide was used as a cocatayst due to the ligand exchanging properties with acetate and it accelarates the carbonylation reaction (Figure 2.16).

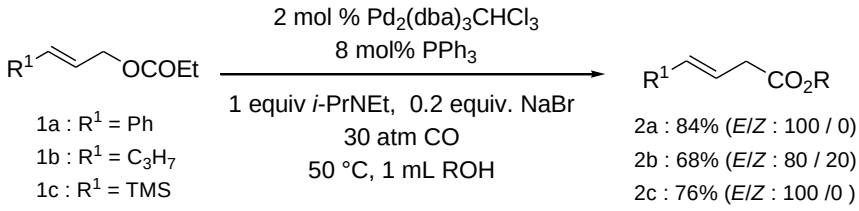



Figure 2.15. Palladium-catalyzed carbonylation of allyl acetates

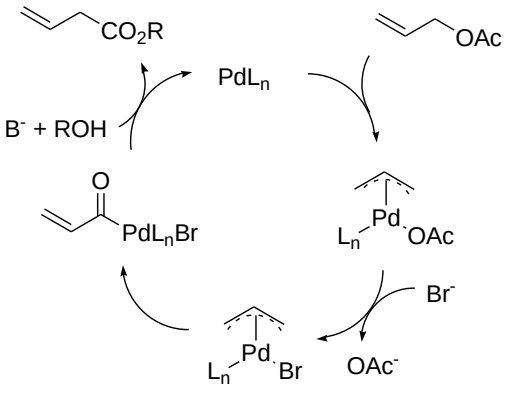



Figure 2.16. Pd-catalyzed carbonylation mechanism of allyl acetates

## 2.3. Synthesis of Vinylallenes

### 2.3.1. Synthesis of Vinylallenes with Grignard Reagents

In 1972, Gore and coworkers reported the reaction of 5-chloropent-3-en-1-ynes with MeMgI in the presence of ether at reflux temperature (Figure 2.17)

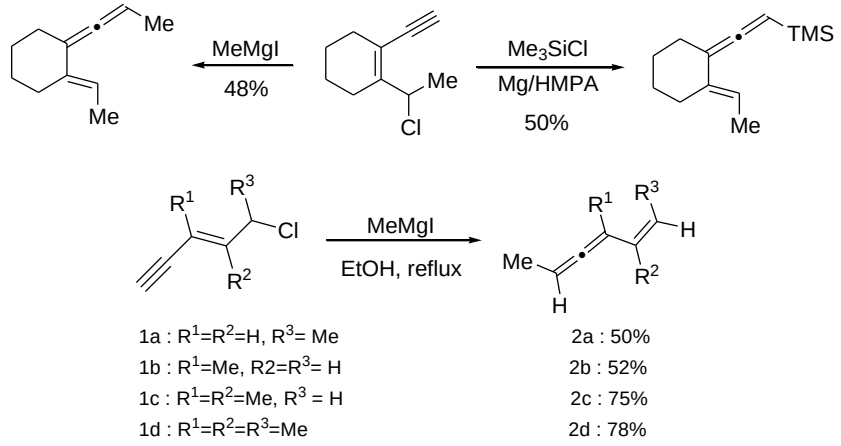
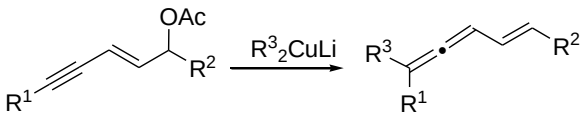



Figure 2.17. The reaction of chloro-enynes with grignard reagents.

Treatment of electrophiles with the Grignard reagents for the formation of vinylallene is a very limited process. The method is not suitable for other Grignard reagent so the only exception is the generation of silylallene from chloroenyne and trimethyl silylmagnesium chloride.

## 2.3.2. Synthesis of Vinylallenes with Organocopper Reagents

In 1999, Krause and coworkers reported a new methodology for the formation of vinylallene by 1,5-($S_N''$)-substitution of enyne acetates with lithium dialkylcuprates. The resulting vinylallenes were usually obtained as mixtures of the *E* and *Z* isomers (Figure 2.18).




| | |
|---|---|
| $R^1$=$R^2$=Me, $R^3$=Bu | 90% (*E*:*Z* = 67:33) |
| $R^1$=$R^2$=Me, $R^3$=*t*-Bu | 93% (*E*:*Z* = 25:75) |
| $R^1$=$Me_3Si$, $R^2$=*t*-Bu, $R^3$=Me | 96% (*E*:*Z* = 40:60) |
| $R^1$=Bu, $R^2$=*t*-Bu, $R^3$=Me | 92% (*E*:*Z* > 99:1) |

Figure 2.18. 1,5-($S_N2''$)-Substitution reactions of enyne acetates with lithium dialkylcuprates

Analogous 1,5-substitutions can also be carried out with enyne oxiranes, which are transformed into the synthetically useful hydroxy-substituted vinylallenes. These transformations can be performed under copper catalysis conditions, by simultaneous addition of the organolithium compound and the substrate with catalytic amounts of the cuprate (Figure 2.19).

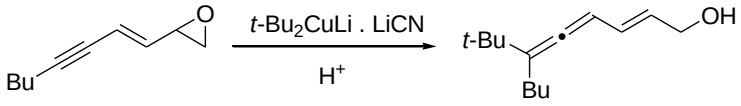



Figure 2.19. The 1,5-substitution reaction of enyne oxiranes

## 2.3.3. Synthesis of Vinylallenes by Wittig-Horner Reactions

In 2005, Takahashi and his coworkers reported that the Wittig-Horner reaction of 1-lithio-1,3-dienyl phosphine oxide with aldehyde afforded stereodefined vinyl allenes in high yield (Figure 2.20).

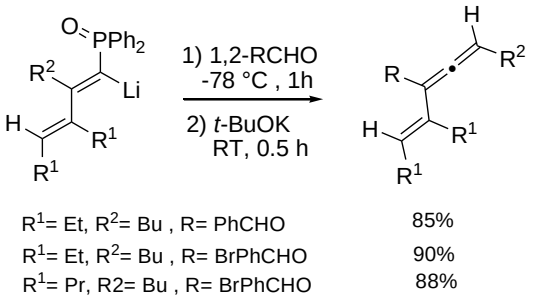



Figure 2.20. Wittig-Horner reaction of 1-lithio-1,3-dienyl phosphine oxide

## 2.3.4. Palladium-Catalyzed Synthesis of Methyl (*R*,*E*)-(-)-Tetradeca-2,4,5-trienoate

In 2005, Hayashi and his coworkers developed an efficient method for the preparation of the sex attractant of the male dried beetle, which is a naturally occurring allene, methyl (*R*,*E*)-tetradeca-2,4,5-trienoate by the palladium-catalyzed reaction of 1-hydro-carbonyl-2-bromo-1,3-buradienes (Figure 2.21.).

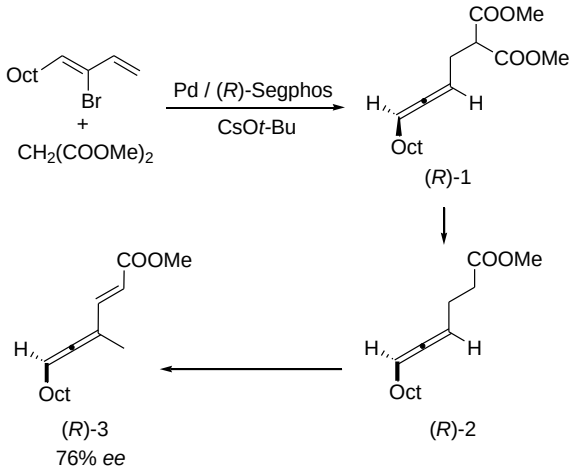



Figure 2.21. Total synthesis of methyl (*R*,*E*)-(-)-tetradeca-2,4,5-trienoate

The optically active allene (*R*)-1 formed by the Pd-catalyzed asymmetric reaction using dimethylmalonate as a pronucleophile followed by the removing of one of the methoxycarbonyl group afforded the (*R*)-2. Finally the reaction of (*R*)-2 with LDA, PhSeBr then $NaIO_4$ in THF results in the formation of (*R*)-3 in 76% enantiomeric excess.

# CHAPTER 3

# EXPERIMENTAL STUDY

## 3.1. General Procedures for Drying the Solvents

Tetrahydrofuran (THF) and dichloromethane (DCM) solvents were all purified by a solvent purification system (MBRAUN SPS-800). $Et_2O$ was distilled from benzophenone-ketyl under argon prior to use. Methanol and ethanol were dried over Mg turnings in the presence of iodine and stored on 3Å molecular sieves under Argon. 1-Propanol and 2-propanol were dried first by stirring over anhydrous CaO and then refluxing over Mg turnings in the presence of iodine. 1-Butanol was dried first by stirring over anhydrous $MgSO_4$ and then refluxed over Mg turnings in the presence of iodine.

## 3.2. Synthesis of Substrates

### 3.2.1. Synthesis of *Z*- and *E*-Enyne Carbonates *Z*-1a, *Z*-1b, *Z*-1i, *Z*-1j, *Z*-1k, and *E*- 1b, *E*-1a, *E*-1*j*, *E*-1*i*

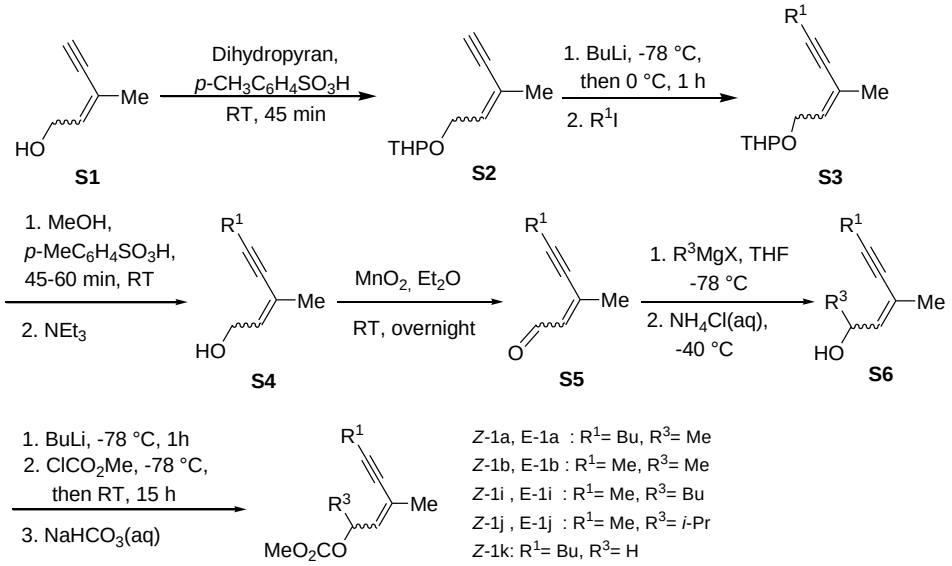



Figure 3.1. Synthesis of *Z*- and E-Enyne Carbonates ***Z*-1a**, ***Z*-1b**, ***Z*-1i**, ***Z*-1j**, ***Z*-1k**, and ***E*-1b, *E*-1a, *E*-1*j*, E-1*i***

To the mixture of commercially available, (*Z*)- or *(E)*-pent-2-en-4-yn-1-ol (**S1**) (1.6 g, 20 mmol) and 3,4-dihydropyran (2.2 mL) was added *p*-toluenesulfonic acid (44 mg, 0.02 mmol) and then stirred for 45 min at room temperature. Then, the mixture was diluted with 40 mL of dry THF under argon and cooled to -78 °C. At that temperature, a 24 mmol hexane solution of BuLi (1.6 M, 15 mL) was added dropwise via a syringe. After stirring the reaction mixture for 1 h at 0 °C, 2.5 mL of alkyl iodide (≈40 mmol) was added dropwise. The mixture was stirred overnight at room temperature when the alkyl halide used was MeI, or 2 days at 50 °C when BuI was used. 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 MgSO4, filtered, and concentrated under reduced pressure. The residue was used in the following step without any other purification. (Ange *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 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 dichloromethane and washed with water. The combined extracts were washed with brine, dried over MgSO4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (hexane/ethyl acetate as the eluent) gave the enynol *Z*-S4 (yields: $R^1$= Me, 86%; Bu, 80%). (Krause *et al.* 1999)

To the solution of (**S4**) (≈17 mmol) in 66 mL of dry diethyl ether, 30 g of activated $MnO_2$ was added, and the mixture was stirred overnight at room temperature. After filtration through Celite, the solution was concentrated under reduced pressure. The crude aldehyde (**S5**) was used in the next step. (Ange *et al.* 1997)

The crude aldehyde (**S5**) was dissolved in 36 mL of anhydrous THF and treated at -78 °C with 1.2 equivalent ethereal solution of $R^3MgX$ (1.6-2.0 M, X stands for iodine in the case of methylation, and bromine for the others) under Ar. At the end of the addition of the Grignard reagent, the mixture was warmed with stirring to -40 °C at nearly 2 h and then, hydrolyzed by the addition of 30 mL of a saturated $NH_4Cl$ solution. After extraction with diethyl ether, the combined organic layers were washed with water, dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and the crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate, yields: ***Z*-S5**; $R^1$= Bu, $R^3$= Me, 65%; $R^1$= Me, $R^3$=Bu, 80%; $R^1$= Me, $R^3$= *i*-Pr, 40%, **E-S5**; $R^1$=Bu , $R^3$=*i*-Pr, 60%; $R^3$= Bu, 70%, $R^1$= Me, 65%.

(*E*)-hept-3-en-5-yn-2-ol which was used in preparation of (*E*)-hept-3-en-5-yn-2-yl methyl carbonate (***E*-1l**) was synthesized according to a reported method. (Krause *et al.* 1999)

The preparation of carbonates from the synthesized enynols (**S6**) was performed via a prescribed method. (Tsuji *et al.* 1994). The products were purified by column chromatography on silica gel (hexane/ethyl acetate/$NEt_3$ (0.5 vol. %)). Enyne carbonate ***Z*-1k** was further subjected to Kugelrohr distillation, (yields: ***Z*-1a**, ***E*-1a,** 55%; ***Z*-1b**, 45%.; ***Z*-1i**, 50%; ***Z*-1j,** 50%; ***Z*-1k**, 58%; ***E*-1l**, 60%, ***E*-1a**,50%, ***E*-1b**, 55%, ***E*-1j**, %60, ***E*-1i**, %50.)

## 3.2.2. Synthesis of *Z*-Enyne Carbonates *Z*-1c-*Z*-1h

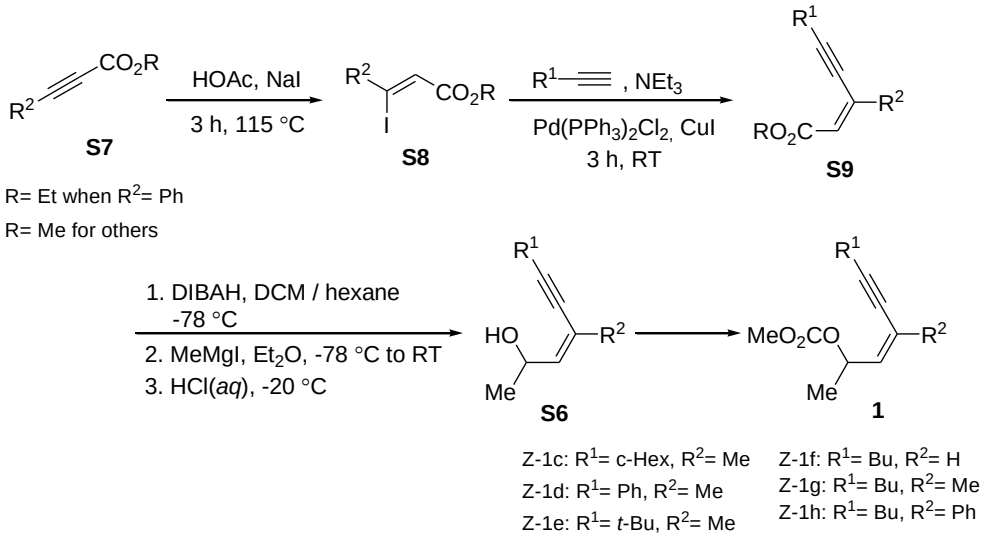



Figure 3.2. Synthesis of *Z*-Enyne Carbonates ***Z*-1c-*Z*-1h**

To a solution of alkynoic ester (**S7)** (≈40 mmol) and acetic acid (240 mmol, 13.8 mL) (512 mmol, 20.8 mL when (**S7)** is ethyl 3-phenylpropiolate was added sodium iodide (9.6 g, 64 mmol) (19.2 g, 128 mmol when (**S7)** is ethyl 3-phenylpropiolate) 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 sodium bicarbonate, aqueous sodium thiosulfate (1 M), and brine and then were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (hexane/ethyl acetate, yields, (**S8)**: $R^2$= H, 84%, Me, 87%; Bu, 84%; Ph, 93%) (Piers *et al.* 1988)

A mixture of (**S8)** (≈35 mmol), $PdCl_2(PPh_3)_2$ (210.6 mg, 0.3 mmol), and CuI (33 mg, 0.17 mmol), in 140 mL of $Et_3N$ was stirred for 10 min at room temperature under Ar, and then, to this mixture was added a terminal alkyne (38 mmol). The mixture was stirred at room temperature 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 (**S9**) was purified by column chromatography on silica gel (hexane/ethyl acetate, yields: $R^1$= Bu, $R^2$= H, 92%; $R^1$= Ph, $R^2$= Me, 93%; $R^1$= *c*-Hex, $R^2$= Me, 90%; $R^1$= *t*-Bu, $R^2$= Me, 85%; $R^1$= Bu, $R^2$= Bu, 92; $R^1$= Bu, $R^2$= Ph, 82) (Takevohi *et al.* 2000)

A dry, three-necked, round-bottomed 250-mL flask equipped with an internal thermometer, a rubber septum, and an Ar gas inlet, was charged with ≈31 mmol of (**S9)** and 63 mL of anhydrous dichloromethane. The stirred solution was cooled to -78 °C and 31 mL of a 1 M solution of diisobutylaluminum hydride in hexane was added dropwise with a syringe at such a rate that the temperature would not exceed -75 °C. After stirring for 30 min at -78 °C, 17 mL $Et_2O$ solution of a MeMgI (34 mmol, 2.0 M) was added dropwise at -78 °C with a syringe. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature. The mixture was hydrolyzed at -20 °C by dropwise addition of 63 mL of a 1 M aqueous solution of hydrochloric acid, followed by addition of 81 mL of ether. The organic layer was separated, the aqueous layer was extracted with ether, and the combined extracts were dried over $MgSO_4$. The solvent was evaporated in vacuo. The product was purified by column chromatography on silica gel (hexane/ethyl acetate; yields: $R^1$= Bu, $R^2$= H, 65%; $R^1$= Ph, $R^2$= Me, 55%; $R^1$= *c*-Hex, $R^2$= Me, 48%; $R^1$= *t*-Bu, $R^2$= Me, 60%; $R^1$= Bu, $R^2$= Bu, 44%; $R^1$= Bu, $R^2$= Ph, 40%) (Normant *et al.* 1998)

The preparation of carbonates from the synthesized enynols was performed via a prescribed method (Tsuji *et al.* 1994) The products were purified on silica gel (hexane/ethyl acetate/$NEt_3$ (0.5 vol.%)). Enyne carbonate ***Z*-1h** was further subjected to Kugelrohr distillation (yields: ***Z*-1c**, 55%; ***Z*-1b**, 45%.; ***Z*-1c**, 48%; ***Z*-1d**, 55%; ***Z*-1e**, 50%; ***Z*-1f**, 65%; ***Z*-1g**, 44%, ***Z*-1h**, 40%).

### 3.2.3. Synthesis of Methyl (R,Z)-4-methylhept-3-en-5-yn-2-yl carbonate [(*R,Z*)-1b]

Sharpless's kinetic resolution method was employed for the preparation of *(R,Z)*-4-methylhept-3-en-5-yn-2-ol. Accordingly, 22.9 mmol of $Ti(OiPr)_4$, and 27.5 mmol of L-(+)-diisopropyl tartrate, were dissolved in 200 mL of dry DCM and cooled to -20 °C. To this mixture, dry DCM solution of 22.9 mmol of racemic mixture of (*Z*)-4-methylhept-3-en-5-yn-2-ol was added and then stirred for 30 min at -20 °C. Then, 45.8 mmol of *t*-butyl hydroperoxide (4 M in toluene) was added and left in a freezer (-20 °C) for 13.5 h. After completion, a pre-cooled (0 °C) 37 mL aqueous solution of 42.4 mmol $FeSO_4$ and 68.7 mmol tartaric acid mixture was added to the reaction mixture with small portions while stirring at -20 °C. The mixture was slowly warmed to room temperature over 1 h, and then extracted with DCM. The DCM solution was concentrated by evaporation and 103 mL of $Et_2O$ was added. The ethereal solution was cooled to 0 °C, and 109 mL of aqueous NaOH was added and stirred at this temperature for 1.5 h. Extraction with ether, drying with MgSO4, and following column chromatography on silica gel using hexane/ethyl acetate eluent yielded the isolated product at 45%. Enantiomeric purity was determined as 94.5% *ee* by GC method using a Hydodex-beta-3P column (25 m, 0.25 mm ID). $[\alpha]_D^{22}$= -1.9° (*c*= 1.0, $CHCl_3$). Its hydroxyl group was modified to carbonate as described above. $[\alpha]_D^{22}$= -1.2° (*c*= 0.2, in $CHCl_3$). Specific Rotation was determined according to Equation 3.1.

$$[\alpha]_D^T = \frac{\text{Observed Rotation, } (\alpha)}{\text{Path length, l (dm) * Concentration of Sample, c (g/ml)}} \qquad (3.1)$$

## 3.3. Characterization of Reactants

The synthesized reactants were analyzed by GC and GC-MS (HP 6890/5973N) and isolated by column chromatography using a hexane-ethyl acetate eluent. High-resolution mass spectral analyses were performed at the Dortmund University of Technology Mass Spectrometry Laboratory on a Thermo Electron system. NMR spectra were recorded on a Varian VnmrJ 400 spectrometer, a Varian Mercury AS 400, or a Bruker DRX 400 spectrometer. Infrared spectra were obtained using a Perkin–Elmer Spectrum 100 by ATR method with neat samples. Optical rotations were measured on a Rudolph Autopol I polarimeter.

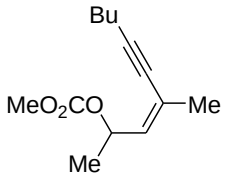



Figure 3.3. Methyl (*Z*)-4-methyldec-3-en-5-yn-2-yl carbonate

***Z*-1a**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 6.05 (dq, *J*= 8.4, 2.4 Hz 1H), 5.55 (dq, *J*= 8.4, 1.2 Hz, 1H), 3.34 (s, 3H), 2.12 (t, *J*= 6.8 Hz, 2H), 1.71 (d, *J*= 1.2 Hz, 3H), 1.41-1.26 (m, 4H), 1.34 (d, *J*= 6.0 Hz, 3H), 0.80 (t, *J*= 7.2 Hz, 3H); $^{13}$C NMR: (101 MHz, $C_6D_6$): δ: 155.7, 135.0, 122.3, 96.7, 79.1, 74.1, 54.0, 31.0, 23.5, 22.2, 20.5, 19.4, 13.7; FT-IR ($\nu_{max}$/cm$^{-1}$): 2980, 2932, 1744, 1441, 1257, 1152, 1100, 1040, 941, 865, 791; MS (EI, *m/z*): 224 (7, $M^+$), 209 (2), 182 (7), 165 (100),149 (55), 133 (21), 123 (25), 115 (5), 105 (58), 91 (88), 77 (42); HRMS: (EI, *m/z*, $M^+$): 224.1407 (calculated), 224.1403 (found).

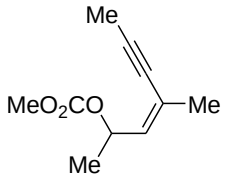



Figure 3.4. Methyl (*Z*)-4-methylhept-3-en-5-yn-2-yl carbonate

***Z*-1b**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 5.99 (dq, *J*= 8.4, 6.8 Hz, 1H), 5.54 (d, *J*= 8.8 Hz, 1H), 3.35 (s, 3H), 1.68 (d, *J*= 1.2 Hz, 3H), 1.57 (s, 3H), 1.32 (d, *J*= 6.4 Hz, 3H); $^{13}$C NMR (101 MHz, C6D6) δ: 155.7, 135.0, 122.2, 92.1, 78.2, 74.1, 54.0, 23.4, 20.5, 4.0; FT-IR ($\nu_{max}$/cm$^{-1}$): 2981, 1744, 1441, 1256, 1028, 941, 791; MS (EI, *m/z*): 182 (4, $M^+$), 167 (8), 123 (100), 107 (45), 91 (97), 77 (34), 65 (24); HRMS (EI, *m/z*, $M^+$): 182.0937 (calculated), 182.0934 (found).

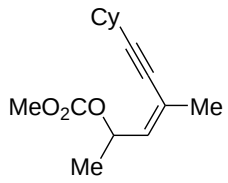



Figure 3.5. (*Z*)-6-cyclohexyl-4-methylhex-3-en-5-yn-2-yl methyl carbonate

***Z*-1c**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.56-5.67 (m, 2H), 3.75 (s, 3H), 2.48-2.58 (m, 1H), 1.86-1.79 (m, 2H), 1.83 (s, 3H), 1.66-1.74 (m, 2H), 1.43-1.53 (m, 3H), 1.30-1.37 (m, 3H), 1.35 (d, *J*= 5.6 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ: 155.3, 134.3, 122.3, 100.7, 78.5, 74.5, 54.7, 32.9, 30.9, 29.9, 26.1, 25.0, 23.7, 20.3; FT-IR ($\nu_{max}$/cm$^{-1}$): 2931, 2855, 2218, 1746, 1442, 1258, 1153, 1034, 942, 792; MS (EI, m/z): 250 (1, $M^+$), 191 (24), 174 (55), 159 (29), 145 (24), 131 (71), 117 (68), 105 (51), 91 (100), 77 (36); HRMS (EI, *m/z*, $M^+$): 250.1564 (calculated), 250.1557 (found).

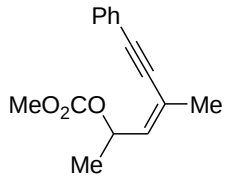



Figure 3.6. Methyl (*Z*)-4-methyl-6-phenylhex-3-en-5-yn-2-yl carbonate

***Z*-1d**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 7.48-7.54 (m, 2H), 6.93-6.99 (m, 3H), 6.13 (dq, *J*= 8.4, 6.4 Hz, 1H), 5.59 (dq, *J*= 8.4, 1.6 Hz, 1H), 3.34 (s, 3H), 1.73 (d, *J*= 1.2 Hz, 3H), 1.32 (d, *J*= 6.0 Hz, 3H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 155.7, 136.5, 132.0, 128.64, 128.60, 123.6, 121.9, 95.7, 87.8, 73.8, 54.1, 23.0, 20.4; FT-IR ($\nu_{max}$/cm$^{-1}$): 2979, 2956, 1744, 1441, 1259, 1035, 941, 755, 690; MS (EI, *m/z*): 244 (3, $M^+$), 185 (62), 167 (100), 152 (90), 141 (24), 128 (26), 115 (28), 102 (11), 91 (13), 77 (14); HRMS (EI, *m/z*, $M^+$): 244.1094 (calculated), 244.1091 (found).

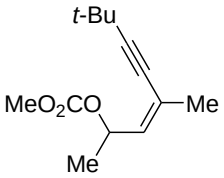



Figure 3.7. Methyl (*Z*)-4,7,7-trimethyloct-3-en-5-yn-2-yl carbonate

***Z*-1e**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 6.08-6.01 (dq, *J*= 8.4, 6.4 Hz, 1H), 5.53 (dq, *J*= 8.4, 1.6 Hz, 1H), 3.35 (s, 3H), 1.68 (d, *J*= 1.2 Hz, 3H), 1.33 (d, *J*= 6.4 Hz, 3H), 1.22 (s, 9H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 155.8, 135.1, 122.4, 104.6, 77.8, 73.9, 54.0, 31.0, 28.3, 23.3, 20.3; FT-IR ($\nu_{max}$/cm$^{-1}$): 2971, 2931, 2869, 1748, 1442, 1263, 1038; MS (EI, *m/z*): 224 (2, $M^+$), 165 (47), 148 (40), 133 (100), 123 (11), 117 (25), 105 (88), 91 (78),77 (33); HRMS (EI, *m/z*, $M^+$): 224.1407 (calculated), 224.1397 (found).

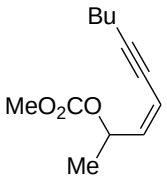



Figure 3.8. (*Z*)-dec-3-en-5-yn-2-yl methyl carbonate

***Z*-1f**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 6.0-6.10 (m, 1H), 5.67(dd, $J_{AB}$= 10.8, 8.0 Hz, 1H), 5.44 (ddq, *J*=10.2, 6.4, 1.2 Hz, 1H), 3.32 (s, 3H), 2.09 (td, *J*= 6.8, 2.4 Hz, 2H), 1.27-1.35 (m, 4H), 1.31 (d, *J*= 6.0 Hz, 3H), 0.78 (t, *J*= 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 155.6, 140.2, 112.1, 97.7, 76.6, 73.2, 54.1, 30.9, 22.2, 20.2, 19.4, 13.7; FT-IR ($\nu_{max}$/cm$^{-1}$): 2959, 2935, 2874, 1747, 1442, 1258, 1034, 942, 792; MS (EI, *m/z*): 210 (2, $M^+$), 195 (1), 168 (7), 151 (80), 135 (31), 119 (15), 109 (33), 91 (100), 77 (46); HRMS: (EI, *m/z*, $M^+$): 210.1250 (calculated), 210.1250 (found).

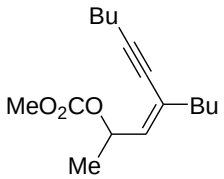



Figure 3.9. (*Z*)-4-butyldec-3-en-5-yn-2-yl methyl carbonate

***Z*-1g**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 6.12 (dq, *J*= 8.4, 6.4 Hz, 1H), 5.65 (d, *J*= 8.4 Hz, 1H), 3.34 (s, 3H), 2.14 (t, *J*= 6.8 Hz, 2H), 2.07 (t, *J*= 7.6 Hz, 2H), 1.52 (quint, *J*= 7.6 Hz, 2H), 1.40 (d, *J*= 6.4 Hz, 3H), 1.29-1.38 (m, 4H), 1.23 (sext, *J*= 7.6 Hz, 2H), 0.83 (t, *J*= 7.4 Hz, 3H), 0.80 (t, *J*= 7.0 Hz, 3H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 155.7, 134.5, 127.1, 97.2, 78.4, 74.2, 54.0, 37.4, 31.1, 30.7, 22.4, 22.2, 20.6, 19.4, 14.1, 13.7; FT-IR ($\nu_{max}$/cm$^{-1}$): 2957, 2932, 2861, 1746, 1441, 1258, 1035, 942, 791; MS (EI, *m/z*): 266(<1, $M^+$), 207 (21), 190 (28), 161 (30), 148 (17), 133 (47), 119 (48), 105 (100), 91 (95), 77 (30); HRMS (EI, *m/z*, $M^+$): 266.1877 (calculated), 266.1868 (found).

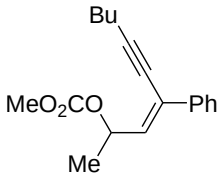



Figure 3.10. Methyl (*Z*)-4-phenyldec-3-en-5-yn-2-yl carbonate

***Z*-1h**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 7.61 (d, *J*= 6.4 Hz, 1H), 7.04-7.17 (m, 3H), 6.31 (d, $J_{AB}$= 8.4 Hz, 1H), 6.24 (dq, $J_{AB}$= 8.0, 6.4 Hz, 1H), 3.37 (s. 3H), 2.18 (t, *J*= 7.2 Hz, 2H), 1.43 (d, *J*= 6.4 Hz, 3H), 1.28-1.40 (m, 4H), 0.80 (t, *J*= 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 155.7, 138.0, 134.6, 128.6, 128.4, 126.8, 126.4, 99.3, 77.3, 74.5, 54.1, 31.0, 22.3, 20.4, 19.5, 13.7; FT-IR ($\nu_{max}$/cm$^{-1}$): 3027, 2956, 2931, 2872, 1744, 1441, 1258, 1034, 942, 791, 762, 693; MS (EI, *m/z*): 286 (7, $M^+$), 227 (70), 211 (56), 195 (22), 185 (31), 167 (100), 153 (82), 141 (44), 128 (37), 115 (42), 105 (10), 91 (27), 77 (21), HRMS (EI, *m/z*, $M^+$): 286.1564 (calculated), 286.1561 (found).

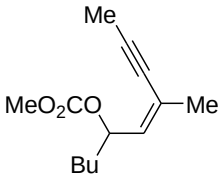



Figure 3.11. Methyl (*Z*)-7-methyldec-6-en-8-yn-5-yl carbonate

***Z*-1i**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 5.99 (dt, *J*= 8.8, 6.8 Hz, 1H), 5.56 (dq, *J*= 8.4, 1.2 Hz, 1H), 3.36 (s, 3H), 1.77-1.89 (m, 1H), 1.73 (d, *J*= 1.6 Hz, 3H), 1.61-1.68 (m, 1H), 1.59 (s, 3H), 1.33-1.47 (m, 2H), 1.25 (sext, *J*= 7.2 Hz, 2H), 0.82 (t, *J*= 7.6 Hz, 3H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 155.9, 134.1, 123.0, 91.8, 78.5, 77.6, 54.0, 34.8, 27.4, 23.6, 22.9, 14.1, 4.1; FT-IR ($\nu_{max}$/cm$^{-1}$): 2956, 2920, 2861, 1745, 1441, 1257, 935, 791;

MS (EI, *m/z*): 224 (3, $M^+$), 209 (2), 165 (100), 149 (18), 133 (11), 123 (28), 108 (30), 91 (71), 85 (7), 77 (42); HRMS (EI, *m/z*, $M^+$): 224.1407 (calculated), 224.1398 (found).

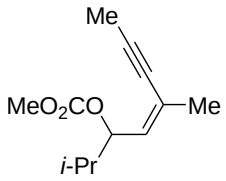



Figure 3.12. Methyl (*Z*)-2,5-dimethyloct-4-en-6-yn-3-yl carbonate

***Z*-1j**: $^1$H NMR (400 MHz, $C_6D_6$) δ: 5.83 (dd, $J_{AB}$= 8.8, 6.4 Hz, 1H), 5.56 (dd, $J_{AB}$= 9.2, 0.8 Hz, 1H), 3.35 (s, 3H), 2.01 (octet, *J*= 6.8 Hz, 1H), 1.73 (d, *J*= 1.2 Hz, 3H), 1.59 (s, 3H), 1.00 (d, *J*= 6.4 Hz, 3H), 0.96 (d, *J*= 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 156.0, 132.1, 124.1, 91.7, 81.8, 78.7, 54.1, 33.1, 23.8, 18.2, 18.0, 4.1; FT-IR ($\nu_{max}$/cm$^{-1}$): 2963, 2921, 2241, 1748, 1638, 1441, 1369, 1324, 1256, 1206, 1139, 1101, 1055, 1030, 1000, 965, 952,935, 917, 855, 791; MS (EI, *m/z*): 210 (< 1, $M^+$), 195 (<1), 167 (38), 151 (38), 134 (28), 119 (100), 108 (22), 91 (66), 77 (13); HRMS (EI, *m/z*, $M^+$): 210.1251 (calculated), 210.1261 (found).

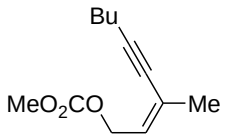



Figure 3.13. Methyl (*Z*)-3-methylnon-2-en-4-ynyl carbonate

***Z*-1k**: $^1$H NMR (400 MHz, $CDCl_3$) δ: 5.72 (dt, *J*= 6.8, 1.2 Hz, 1H), 4.81 (d, *J*= 7.2 Hz, 1H), 3.78 (s, 3H), 2.34 (t, *J*= 7.2 Hz, 2H), 1.87 (d, *J*= 0.8 Hz, 3H), 1.53 (quint, *J*= 7.2 Hz, 2H), 1.42 (sext, *J*= 7.2 Hz, 2H), 0.92 (t, *J*= 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ: 155.9, 128.0, 124.9, 96.9, 78.3, 66.7, 54.9, 30.9, 23.8, 22.1, 19.3, 13.7; FT-IR ($\nu_{max}$/cm$^{-1}$): 2958, 2934, 2906, 1748, 1442, 944, 792; MS (EI, *m/z*): 210 (5, $M^+$), 168 (16), 151 (46), 135 (39), 119 (13), 105 (29), 91 (100), 77 (55); HRMS (EI, *m/z*, $M^+$): 210.1250 (calculated), 210.1251 (found).

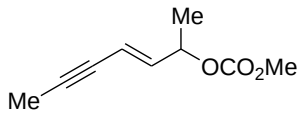



Figure 3.14. (*E*)-hept-3-en-5-yn-2-yl methyl carbonate

***E*-1l**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 5.99 (dd, *J*= 16.0, 6.4 Hz, 1H), 5.71 (d, *J*= 16.0, 1.2 Hz, 1H), 5.18 (quint, *J*= 6.6 Hz, 1 H), 3.765 (s, 3H), 1.98 (d, *J*= 2.0 Hz, 3H), 1.37 (d, *J*= 6.4 Hz, 3H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 155.1, 139.7, 122.9, 74.5, 54.8, 20.2, 4.4; FT-IR ($\nu_{max}$/cm$^{-1}$): 2984, 2957, 2918, 2854, 1743, 1441, 1255, 1036, 941, 871, 790; MS (EI, *m/z*): 168 (3, $M^+$), 153 (3), 136 (2), 109 (100), 91 (79), 77 (37).

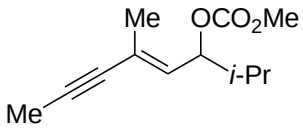



Figure 3.15. Methyl (E)-2,5-dimethyloct-4-en-6-yn-3-yl carbonate

***E*-1j**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.63 (d, $J_{AB}$= 9.6 Hz, 1H), 5.07 (dd, $J_{AB}$= 9.8, 7.0 Hz, 1H), 3.75 (s, 3H), 1.93 (s, 3H), 1.89 (d, *J*= 1.2 Hz, 3H), 0.95 (d, *J*= 6.8 Hz, 3H), 0.90 (d, *J*= 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ: 155.6, 131.5, 124.0, 85.0, 81.9, 79.6, 54.8, 32.5, 18.5, 18.3, 17.9, 4.3 ; FT-IR ($\nu_{max}$/cm$^{-1}$): 2960, 2920, 2868, 2222, 1743, 1639, 1441, 1369, 1322, 1254, 1144, 1094, 1044, 965, 934, 874, 791

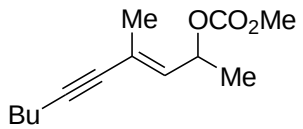



Figure 3.16. Methyl (E)-4-methyldec-3-en-5-yn-2-yl carbonate

***E*-1a**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.67 (d, *J*= 8.8 Hz 1H), 5.48 (dq, *J*= 8.9, 6.5 Hz, 1H), 3.75 (s, 3H), 2.29 (t, *J*= 7.0 Hz, 2H), 1.88 (s, 3H), 1.49 (q, *J*= 7.1 Hz ,2H), 1.41 (q, J= 7.4 Hz, 2H), 1.34 (d, *J*= 6.4 Hz, 3H), 0.91 (t, *J*= 7.2 Hz, 3H); $^{13}$C NMR: (101 MHz, $CDCl_3$): δ: 155.3, 134.0, 122.5, 90.0, 83.0, 77.2, 71.7, 55.0, 31.0, 22.1, 20.0, 19.1, 18.3, 14.0; FT-IR ($\nu_{max}$/cm$^{-1}$): 2958, 2933, 2873, 2217, 1743, 1638, 1441, 1378, 1326, 1257, 1154, 1106, 1036, 939, 904, 865, 791.

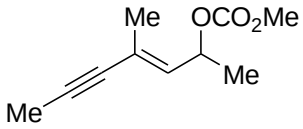



Figure 3.17. Methyl (E)-4-methylhept-3-en-5-yn-2-yl carbonate

***E*-1b**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.99 (d, *J*= 9.2 Hz, 1H), 5.43 (dq, *J*= 9.2, 6.4 Hz, 1H), 3.75 (s, 3H), 1.92 (s, 3H), 1.87 (d, J= 1.2 Hz, 3H), 1.33 (d, *J*= 6.4 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ: 155.3, 134.0, 122.4, 85.0, 82.0, 72.0, 55.0, 20.5, 18.2, 4.3 ; FT-IR ($\nu_{max}$/cm$^{-1}$): 2977, 2957, 2915, 2853, 2227, 1742, 1639, 1584, 1441, 1378, 1327, 1255, 1154, 1101, 1034, 966, 898, 864, 791

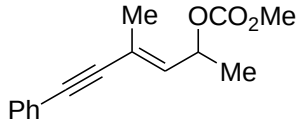



Figure 3.18. Methyl (E)-4-methyl-6-phenylhex-3-en-5-yn-2-yl carbonate

***E*-1d**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.44 (m, 2H), 7.29, 7.31(m, 3H), 5.87 (dd, *J*= 8.8, 1.2 Hz, 1H), 5.50 (dq, *J*= 8.8, 6.5 Hz, 1H), 3.77 (s, 3H), 2.00 (d, *J*= 1.2 Hz, 3H), 1.39 (d, *J*= 6.4 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ:155.3, 135.5, 132.0, 128.4, 123.3, 121.2, 91.3, 88.5, 72.0, 55.0, 20.4, 18.0 ; FT-IR ($\nu_{max}$/cm$^{-1}$): 2956, 2982, 2925, 2853, 1741, 1635, 1597, 1489, 1441, 1378, 1328, 1255, 1181, 1141, 1036, 942, 866, 791.

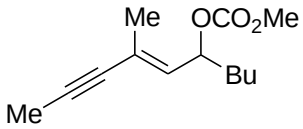



Figure 3.19. Methyl (E)-7-methyldec-6-en-8-yn-5-yl carbonate

***E*-1i**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.62 (d, *J*= 9.2, 1H), 5.26-5.32 (m, 1H), 3.75 (s, 3H), 1.93 (s, 1H), 1.88 (d, *J*= 1.2 Hz, 3H), 1.68-1.77 (m, 1H), 1.49-1.58 (s, 1H), 1.37-1.24 (m, 4H), 0.88 (t, *J*= 6.6 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ: 155.4, 133.1, 123.2, 85.0, 82.0, 75.2, 55.0, 34.2, 27.1, 23.0, 18.4, 14.1, 4.3 ; FT-IR ($\nu_{max}$/cm$^{-1}$): 2957, 2930, 2862, 2222, 1743, 1638, 1441, 1380, 1321, 1259, 1152, 1091, 1036, 933, 879, 866, 791.

## 3.4. General Procedure for Carbonylation Reactions

The substrate, a palladium compound, triphenylphosphine, and an alcohol were added, successively to a Schlenck apparatus with a condenser that is attached to an Ar line. A CO balloon was fixed to the reaction vessel and then, the mixture was stirred magnetically in a preheated oil bath. The course of the reaction was followed by TLC and GC analyzes. At the end of the reaction, the solvent was evaporated and the residue was purified by column chromatography on silica gel (hexane:EtOAc), affording the product. The product, **3ha** was further subjected to Kugelrohr distillation. The all vinylallene products appeared as colorless oil and coupling constants of olefinic protons and NOE studies confirm *E*-configured structures.

A mixture of enyne, catalyst and solvent was added into glass insert which was then placed into a stainless-steel reactor. Reactor was evacuated and purged with sufficient CO twice. Then reactor was pressurized with sufficient CO and the mixture was stirred magnetically in a pre-heated oil bath for 16 h. After cooling reactor, the reaction mixture was recovered with diethylether

## 3.5. Characterization of Products

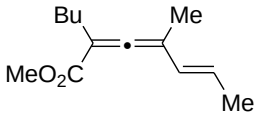



Figure 3.20. (*E*)-methyl 2-butyl-4-methylhepta-2,3,5-trienoate

**3aa**: $^{1}$H NMR (400 MHz, $CDCl_3$): 5.98 (dq, *J*= 15.6, 1.6 Hz, 1H), 5.67 (dq, *J*= 15.2, 6.8 Hz, 1H), 3.70 (s, 3H), 2.24 (t, *J*= 7.2 Hz, 2H), 1.86 (s, 3H), 1.79 (dd, *J*= 6.8, 1.6 Hz, 3H), 1.27-1.43 (m, 4H), 0.89 (t, *J*= 7.2 Hz, 3H); $^{13}$C NMR: (100 MHz, $CDCl_3$) δ: 212.8, 168.0, 127.0, 126.3, 103.9, 100.7, 52.1, 30.3, 28.8, 22.3, 18.5, 15.0, 14.0; FT-IR($\nu_{max}$/cm$^{-1}$): 2955, 2929, 2873, 2860, 1941, 1713, 1262, 1014, 960, MS (EI, *m/z*): 208 (8, $M^+$), 193 (2), 179 (8), 165 (17), 151 (46), 135 (18), 119 (22), 107 (100), 91 (66), 77 (26); HRMS: (ESI, *m/z*, $(M+H)^+$): 209.1536 (calculated), 209.1536 (found).

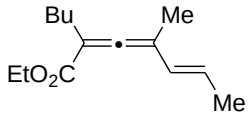



Figure 3.21. (*E*)-ethyl 2-butyl-4-methylhepta-2,3,5-trienoate

**3ab**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.98 (dq, *J*= 15.6, 1.6 Hz, 1H), 5.66 (dq, *J*= 15.6, 6.8 Hz, 1H), 4.16 (dt, *J*= 6.8, 1.2 Hz, 2H), 2.23 (t, *J*= 7.4 Hz, 2H), 1.86 (s, 3H), 1.79 (dd, *J*= 6.8, 1.6 Hz, 3H), 1.28-1.43 (m, 4H), 1.24 (t, *J*=7.2 Hz, 3H), 0.88 (t, *J*= 7.0, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 212.8,167.5, 127.2, 126.0, 103.8, 100.0, 60.8, 30.4, 28.8, 22.3, 18.5, 15.0, 14.43, 14.03; FT-IR ($\nu_{max}$/cm$^{-1}$): 2957, 2929, 2872, 2860, 1940, 1762, 1708, 1445, 1367, 1259, 1239, 1130, 960; MS (EI, *m/z*): 222 (7, $M^+$), 193 (9), 180 (9), 165 (18), 149 (46), 137 (18), 119 (15), 107 (100), 91 (71), 77 (36); HRMS: (ESI, *m/z*, $(M+H)^+$): 223.1693 (calculated), 223.1692 (found).

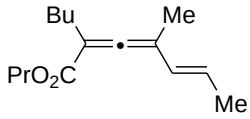



Figure 3.22. (*E*)-propyl 2-butyl-4-methylhepta-2,3,5-trienoate

**3ac**: $^{1}$H NMR: (400 MHz, $CDCl_3$): 5.91 (dq, *J*= 15.6, 1.6 Hz, 1H), 5.59 (dq, *J*= 6.7, 15.8 Hz, 1H), 3.99 (td, *J*= 6.8, 2.4 Hz, 2H), 2.17 (t, *J*= 7.2 Hz, 2H), 1.79 (s, 3H), 1.73 (dd, *J*= 6.6, 1.4 Hz, 3H), 1.57 (sext, *J*= 7.0 Hz, 2H), 1.22-1.37 (m, 4H), 0.85 (t, *J*= 7.2 Hz, 3H), 0.82 (t, *J*= 7.2 Hz, 3H); $^{13}$C NMR: (100 MHz, $CDCl_3$) δ:212.8, 167.6, 127.2, 126.0, 103.8, 100.0, 66.3, 30.4, 28.7, 22.3, 22.2, 18.5, 14.9, 14.0, 10.5; FT-IR ($\nu_{max}$/cm$^{-1}$): 2959, 2929, 2875, 2859, 1941, 1709, 1458, 1260, 960; MS (EI, *m/z*): 236 (8, $M^+$), 207 (5), 194 (7), 177 (7), 165 (10), 149 (45), 137 (29), 121 (15), 107 (100), 91 (65), 77 (34); HRMS: (EI, *m/z*, $M^+$): 236.1771 (calculated), 236.1764 (found).

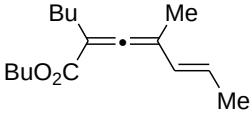



Figure 3.23. (*E*)-butyl 2-butyl-4-methylhepta-2,3,5-trienoate

**3ad**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 6.05 (dq, *J*= 15.6, 1.6 Hz, 1H), 5.44 (dq, *J*= 15.6, 6.8 Hz, 1H), 4.08 (t, *J*= 6.8 Hz, 2H), 2.47 (t, *J*= 7.4 Hz, 2H), 1.77 (s, 3H), 1.56

(dd, *J*= 6.4, 0.8 Hz, 3H), 1.52 (quint, *J*= 7.2 Hz, 2H), 1.42 (quint, *J*= 7.2 Hz, 2H), 1.32 (sext, *J*= 7.4 Hz, 2H), 1.18 (sext, *J*= 7.4 Hz, 2H), 0.85 (t, *J*=7.4 Hz, 3H), 0.73 (t, *J*= 7.4 Hz, 3H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 213.0, 167.1, 125.9, 103.9, 100.6, 64.7, 31.1, 30.9, 29.4, 22.6, 19.5, 18.3, 15.0, 14.1, 13.8; FT-IR ($\nu_{max}$/cm$^{-1}$): 2958, 2932, 2873,1941, 1710, 1458, 1378, 1239, 1119, 960; MS (EI, *m/z*): 250 (3, $M^+$), 165 (13), 149 (50), 137 (35), 121 (12), 107 (100), 91 (44), 77 (20); HRMS (EI, *m/z*, $M^+$): 250.1927 (calculated), 250.1934 (found).

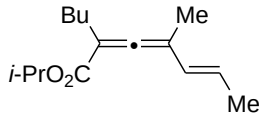



Figure 3.24. (*E*)-propyl 2-butyl-4-methylhepta-2,3,5-trienoate

**3ae**: $^1$H NMR (400 MHz, $CDCl_3$): 5.98 (dq, *J*= 16.0, 1.6 Hz, 1H), 5.65 (dq, *J*= 15.8, 6.6 Hz, 1H), 5.00 (hept, *J*= 6.2 Hz, 1H), 2.22 (t, *J*= 7.4 Hz, 2H), 1.85 (s,3H), 1.79 (dd, *J*= 6.8, 1.6, Hz, 3H), 1.28-1.42 (m, 4H), 1.22 (d, *J*= 6.4 Hz, 6H), 0.86 (t, *J*= 7.2 Hz, 3H); $^{13}$C NMR: (100 MHz, $CDCl_3$) δ: 212.8, 167.1, 127.3, 125.8, 103.8, 100.5, 68.1, 30.4, 28.8, 22.3, 22.0, 18.5, 14.9, 14.1; FT-IR ($\nu_{max}$/cm$^{-1}$): 2979, 2958, 2930, 2860, 1941, 1706, 1466, 1373, 1261, 1241, 1107, 1067, 960; MS (EI, *m/z*): 236 (9, $M^+$), 194 (24), 177 (10), 165 (22), 149 (79), 137 (44), 121 (19), 107 (100), 91 (66), 77 (30); HRMS (EI, *m/z*, $M^+$): 236.1771 (calculated), 236.1762 (found).

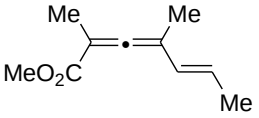



Figure 3.25. (*E*)-methyl 2,4-dimethylhepta-2,3,5-trienoate

**3ba**: $^1$H NMR (400 MHz, $CDCl_3$) δ: 5.98 (dq, *J*= 16.0, 1.6 Hz, 1H), 5.67 (dq, *J*= 15.6, 6.8 Hz, 1H), 3.70 (s, 3H), 1.87 (s, 3H), 1.85 (s, 3H), 1.79 (dd, *J*= 6.8, 1.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 212.9, 168.3, 127.0, 126.5, 102.8, 94.6, 52.2, 18.5, 15.7, 15.0; FT-IR ($\nu_{max}$/cm$^{-1}$): 2989, 2952, 2929, 2857, 1943, 1713, 1436, 1268, 1119, 1037, 960, 920, 759; MS (EI, *m/z*): 166 (53, $M^+$), 151 (50), 138 (14), 123 (40), 107 (34), 107 (34), 95 (22), 91 (100), 79 (32), 77 (28); HRMS (ESI, *m/z*, $(M+H)^+$): 167.1067 (calculated), 167.1065 (found). The enantiomers of this product was separated on an IC

column with hexane:2-propanol= 99:1, flow= 1 mL/min. Retention times 6.9, 7.3 minutes.

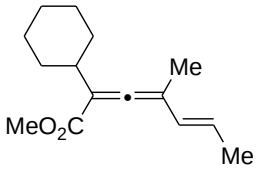



Figure 3.26. (*E*)-methyl 2-cyclohexyl-4-methylhepta-2,3,5-trienoate

**3ca**: $^{1}$H-NMR (500 MHz, $C_6D_6$) δ: 6.06 (dq, *J*= 15.5, 1.5 Hz, 1H) 5.44 (dq, *J*= 15.5, 7.0 Hz, 1H), 3.42 (s, 3H), 2.73 (tt, *J*= 11.5, 3.5 Hz, 1H), 1.98-2.08 (m, 2H), 1.76 (s, 3H), 1.63-1.69 (m, 2H), 1.56 (dd, *J*= 7.0, 1.5 Hz, 3H), 1.03-1.35 (m, 6H); $^{13}$C NMR: (126 MHz, $C_6D_6$) δ: 212.7, 167.2, 125.9, 106.2, 105.1, 51.5, 38.1, 33.4, 33.3, 26.79, 26.77, 26.5, 18.3, 15.19; FT-IR ($\nu_{max}$/cm$^{-1}$): 2925, 2852, 1935, 1714, 1448, 1253, 1228, 960; MS (EI, *m/z*): 234 (50, $M^+$), 205 (61), 175 (60), 165 (33), 159 (30), 152 (36), 133 (65), 119 (87), 105 (76), 91 (100), 77 (47); HRMS (EI, *m/z*, $M^+$): 234.1614 (calculated), 234.1616 (found).

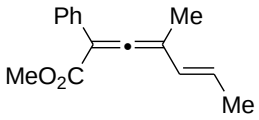



Figure 3.27. (*E*)-methyl 4-methyl-2-phenylhepta-2,3,5-trienoate

**3da**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.51 (m, 2H), 7.31-7.38 (m, 2H), 7.23-7.29 (m, 1H), 6.10 (dq, $J_{AB}$= 15.6 (AB), 1.6 Hz, 1H), 5.80 (dq, $J_{AB}$= 15.6, 6.8 Hz, 1H), 3.81 (s, 3H), 2.00 (s, 3H), 1.84 (dd, *J*= 6.8, 1.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ: 215.2, 166.7, 133.5, 128.6, 128.3, 127.7, 127.6, 126.1, 105.2, 102.3, 52.4, 18.6, 14.9; FT-IR ($\nu_{max}$/cm$^{-1}$): 3057, 3027, 2950, 1928, 1717, 1434, 1380, 1282, 1258, 1196, 1173, 1023, 960, 780, 746, 694, 661; MS (EI, *m/z*): 228 (100, $M^+$), 213 (44), 200 (51), 185 (67), 169 (61), 154 (90), 141 (48), 128 (49), 115 (39), 102 (12), 91 (27), 77 (22), HRMS (EI, *m/z*, $M^+$): 228.1145 (calculated), 228.1142 (found).

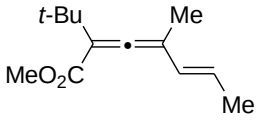


Figure 2.28. (*E*)-methyl 2-*tert*-butyl-4-methylhepta-2,3,5-trienoate

**3ea**: $^{1}$H-NMR (400 MHz, $C_6D_6$) δ: 6.04 (dq, *J*= 15.6, 1.6 Hz, 1H), 5.41 (dq, *J*= 15.6, 6.6 Hz, 1H), 3.37 (s, 3H), 1.73 (s, 3H), 1.55 (dd, *J*= 6.6, 1.6 Hz, 3H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 212.0, 166.5, 127.8, 109.0,104.0, 51.3, 34.6, 29.8, 18.3, 15.1; FT-IR ($\nu_{max}$/cm$^{-1}$): 2992, 2957, 2867, 1935, 1716, 1434, 1362, 1257, 1224, 1060, 1030, 1007, 960, 925, 778; MS (EI, *m/z*): 208 (41, $M^+$), 193 (11), 165 (10), 152 (100), 137 (11), 124 (15), 119 (28), 105 (23), 91 (43), 77 (17); HRMS (EI, *m/z*, $M^+$): 208.1458 (calculated), 208.1453 (found).

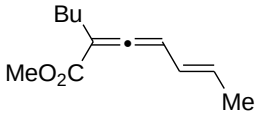



Figure 3.29. (*E*)-methyl 2-butylhepta-2,3,5-trienoate

**3fa**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 6.15 (dt, $J_{AB}$= 9.6, 2.8 Hz, 1H), 5.86 (ddq, $J_{AB}$= 15.2, 10.4, 1.6 Hz, 1H), 5.75 (dq, $J_{AB}$= 15.6, 6.8 Hz, 1H), 3.71 (s, 3H), 2.20-2.29 (m, 2H), 1.77 (dd, *J*= 6.8, 1.2 Hz, 3H); $^{13}$C-NMR (100MHz, $CDCl_3$) δ: 212.8, 167.6, 130.3, 124.0, 101.7, 97.7, 52.3, 30.2, 28.6, 22.3, 18.4, 14.0; FT-IR ($\nu_{max}$/cm$^{-1}$): 2956, 2931, 2861, 1940, 1715, 1435, 1262, 1241, 1119, 962; MS (EI, *m/z*): 194 (10, $M^+$), 165 (22), 152 (65), 137 (48), 123 (19), 105 (30), 93 (100), 77 (52); HRMS (EI, *m/z*, $M^+$): 194.1301 (calculated), 194.1309 (found).

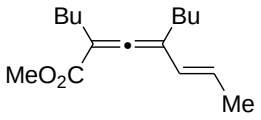



Figure 3.30. Methyl 2-butyl-4-((*E*)-prop-1-enyl)octa-2,3-dienoate

**3ga**: $^{1}$H NMR (400 MHz, $C_6D_6$) δ: 5.98 (dq, $J_{AB}$= 15.6, 1.6 Hz, 1H), 5.57 (dq, *J*= 15.6, 6.8 Hz, 1H), 3.43 (s, 3H), 2.50 (td, *J*= 7.2, 5.2 Hz, 2H), 2.15 (td, *J*= 7.2, 4.0 Hz, 2H), 1.57 (dd, *J*= 6.8, 1.6 Hz, 3H), 1.49-1.60 (m, 4H), 1.27-1.40 (m, 4H), 0.864 (t, *J*= 7.2 Hz, 3H), 0.858 (t, *J*= 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $C_6D_6$) δ: 212.8, 167.6, 127.2, 125.8, 109.0, 101.7, 51.6, 31.0, 30.2, 29.5, 29.0, 22.8, 22.7, 18.5, 14.1; FT-IR ($\nu_{max}$/cm$^{-1}$): 2956, 2930, 2873, 2860, 1938, 1715, 1456, 1435, 1263, 1132, 961; MS (EI, *m/z*): 250 (7), 221 (25), 207 (34), 191 (69), 179 (28), 165 (43), 151 (87), 133 (41), 119

(55), 107 (85), 91 (100), 77 (48); HRMS (EI, *m/z*, $M^+$): 250.1927 (calculated), 250.1923 (found).

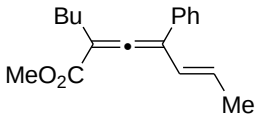



Figure 3.31. (*E*)-methyl 2-butyl-4-phenylhepta-2,3,5-trienoate

**3ha**: $^1$H NMR (400 MHz, $C_6D_6$) δ : 7.46-7.50 (m, 2H), 7.13-7.19 (m, 2H), 7.03-7.09 (m, 1H), 6.10 (dq, $J_{AB}$= 15.6, 1.6 Hz, 1H), 5.90 (dq, $J_{AB}$= 15.2, 6.4 Hz, 1H), 3.40 (s, 3H), 2.43-2.58 (m, 2H), 1.57 (dd, *J*= 7.4, 1.6 Hz, 3H), 1.21-1.32 (m, 4 H), 0.79 (t, *J*= 7.6 Hz, 3H); $^{13}$C NMR: (101 MHz, $C_6D_6$) δ: 211.3, 165.2, 133.6, 126.9, 126.2, 125.9, 124.7,123.6, 109.7, 101.0, 49.8, 28.8, 27.6, 20.7, 16.4, 12.0; FT-IR($\nu_{max}$/cm$^{-1}$): 3025, 2955, 2928, 2872, 1932, 1714, 1434, 1259, 761, 694; MS (EI, *m/z*): 270 (38), 227 (20), 148 (100), 165 (47), 155 (57), 141 (34), 129 (26), 115 (20), 105 (9), 91 (25), 77 (11); HRMS (EI, *m/z*, $M^+$): 270.1614 (calculated), 270.1614 (found).

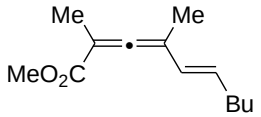



Figure 3.32. (*E*)-methyl 2,4-dimethyldeca-2,3,5-trienoate

**3ia**: $^1$H NMR (400 MHz, $CDCl_3$) δ: 5.96 (dt, *J*= 15.6, 1.4 Hz, 1H), 5.66 (dt, *J*= 15.6, 6.8 Hz, 1H), 3.71 (s, 3H), 2.12 (dq, *J*= 6.8, 1.6 Hz, 2H), 1.87 (s, 3H), 1.86 (s, 3H), 1.28-1.43 (m, 4H), 0.90 (t, *J*= 7.4 Hz, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 213.1, 168.3, 132.0, 125.6, 102.9, 94.6, 52.2, 32.8, 31.6, 22.4, 15.7, 15.0, 14.1; FT-IR($\nu_{max}$/cm$^{-1}$): 2989, 2955, 2927, 2872, 1943, 1715, 1435, 1269, 1119, 962, 760; MS (EI, *m/z*): 208 (<1, $M^+$), 166 (12), 151 (100), 123 (58), 109 (36), 91 (17), 81 (32); HRMS: (ESI, *m/z*, $(M+H)^+$): 209.1536 (calculated), 209.1533 (found).

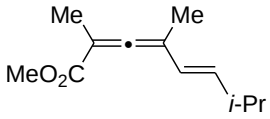



Figure 3.33. (*E*)-methyl 2,4,7-trimethylocta-2,3,5-trienoate

**3ja**: $^{1}$H NMR (400 MHz, $C_6D_6$): δ: 6.06 (dd, *J*= 15.6, 1.2 Hz, 1H), 5.50 (dd, *J*= 15.6, 7.0, Hz, 1H), 3.38 (s, 3H), 2.13-2.24 (m, 1H), 1.98 (s, 3H), 1.75 (s, 3H), 0.89 (d, *J*= 6.8 Hz, 6H); $^{13}$C NMR: (101 MHz, $C_6D_6$): δ: 213.4, 167.7, 138.3, 123.8, 103.0, 95.1, 51.7, 31.8, 22.5, 15.8, 15.0; FT-IR ($\nu_{max}$/cm$^{-1}$): 2958, 2928, 2869, 1944, 1716, 1436, 1269, 1237, 1119, 1043, 965, 760; MS (EI, *m/z*): 194 (35, $M^+$), 179 (36), 163 (9), 152 (56), 147 (26), 135 (85), 119 (100), 105 (69), 91 (83), 77 (47); HRMS (EI, *m/z*, $M^+$): 194.1301 (calculated), 194.1296 (found).

# CHAPTER 4

# RESULTS AND DISCUSSION

In this study, we attempted the Pd(0)-catalyzed carbonylation reactions of *Z*- and E-enyne carbonates aiming at the formation of vinylallenyl ester structures in the presence of alcohol and carbon monoxide.(Artok *et al*. 2011) According to NMR analyses, *E*-configured vinylallenyl esters were achieved in high yields (Figure 4.1).

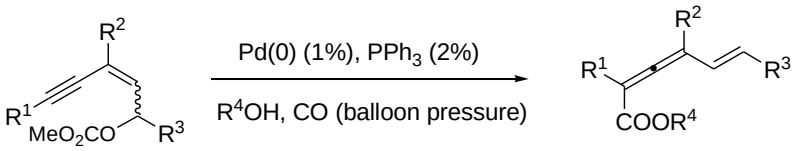
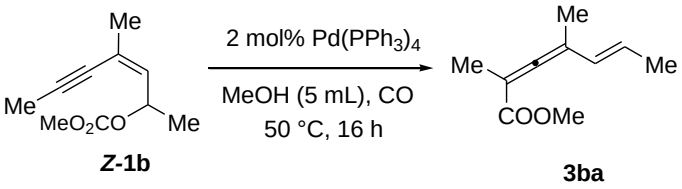



Figure 4.1. Pd(0)-catalyzed alkoxycarbonylation of *Z*- or E-enyne carbonates

During the optimization studies, the reaction temperature, the CO pressure, the catalyst type, ligand type and ligand-catalyst ratio were investigated.

As a preliminary investigation, *Z*-configured enyne carbonate ***Z*-1b** was used and methanol was used as alcohol for the investigation of the effect CO pressure. $Pd(PPh_3)_4$ (2 mol%) used as a catalyst and temperature of the reaction was fixed at 50 ºC during the 16 h of the reaction time (Table 4.1, Entry 1). The results revealed that the the attachment of rubber balloon filled with CO provided sufficient pressure for the method. The application of higher CO pressures did not show any significant effects on the reaction yields (Table 4.1, Entries 2-3).

Table 4.1. Effect of CO pressure on Pd(0)-catalyzed alkoxycarbonylation reaction of ***Z*-1b**



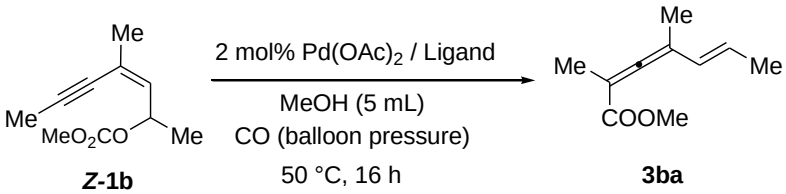

***Z*-1b** **3ba**

| Entry | $P_{CO}$ [atm] | Yield [%][a] |
|---|---|---|
| 1 | 10 | 87 |
| 2 | 5 | 82 |
| 3 | Balloon | 85 |

[a] Isolated yields

The effect of various types of phosphine ligands was also investigated in the presence of 2 mol% $Pd(OAc)_2$ at 50 ºC in methanol (Table 4.2).

Table 4.2. Effect of ligands on Pd(0)-catalyzed alkoxycarbonylation reaction of ***Z*-1b**




***Z*-1b** **3ba**

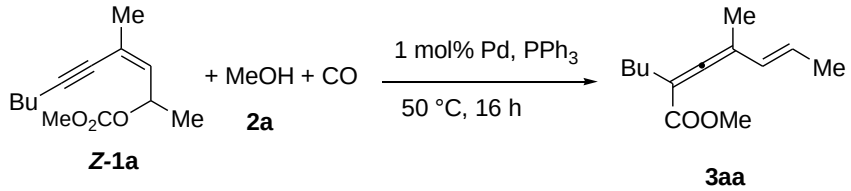
| Entry | Ligand | Ligand % | NMR Yield (%)[a] |
|---|---|---|---|
| 1 | $PPh_3$ | 8 | 67 |
| 2 | $PPh_3$ | 4 | 76 |
| 3 | Xantphos | 4 | 75 |
| 4 | $CH_3(Ph)_2P$ | 12 | 39 |
| 5 | $(4\text{-}CF_3C_6H_4)_3P$ | 4 | 58 |
| 6 | Dppe | 4 | 0 |
| 7 | Dppp | 4 | trace |
| 8 | Dppb | 4 | trace |
| 9 | Dppf | 4 | 22 |
| 10 | BIHEP | 4 | trace |
| 11 | — | — | 0 |

[a] Determined by 1H-NMR using dimethyl sulfoxide as an internal standard

The results indicated that triphenylphosphine and xantphos appears be to the most effective ligands for the alkoxycarbonylation reaction of ***Z*-1b** (Table 4.2, Entries 1-2 and 3). The $CH_3(Ph)_2P$ and $(4\text{-}CF_3C_6H_4)_3P$ showed lower reactivity than $PPh_3$ (Table 4.2, Entries 4-5). The other phosphine derivatives such as Dppe, Dppb, Dbbf and

Bihep proved ineffective **3aa**. (Table 4.2, Entries 6-7-8-9-10-11). As a continuation of optimization process, the effect of various Palladium complex derivatives and the ligand-Pd ratio were investigated. $PPh_3$ was choice of the ligand for the further studies because of its lower cost.

Table 4.3. Effect of the nature of the catalyst and catalyst/ligand ratio on Pd(0)-catalyzed alkoxycarbonylation reaction of ***Z*-1a**[a]



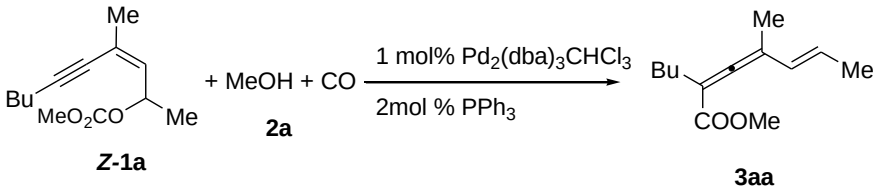

| Entry | Pd | $PPh_3$ (%) | yield (%)[b] |
|---|---|---|---|
| 1 | $Pd(PPh_3)_4$ | - | 85 |
| 2 | $Pd_2(dba)_3CHCl_3$ | 4 | 74 |
| 3 | $Pd(OAc)_2$ | 4 | 67 |
| 4 | $Pd_2(dba)_3CHCl_3$ | 2 | 90 |
| 5 | $Pd(OAc)_2$ | 2 | 83 |
| 6 | $Pd(OAc)_2$ | 1 | 76 |
| 7 | $Pd(PPh_3)_2Cl_2$ | - | 0 |

[a] **1a**: 0.3 mmol, MeOH: 5 mL, CO: balloon pressure.
[b] Determined by $^1$H-NMR using dimethyl sulfoxide as an internal standard.

The reaction of the (*Z*)-2-en-4-yne ***Z*-1a** with MeOH at 50 ºC under just a balloon pressure of CO in the presence of 1 mol% $Pd(PPh_3)_4$ yielded exclusively the related *E*-configured vinylallenylester molecule **3aa** with high yield (Table 4.3, Entry 1). Separate addition of a $PPh_3$ ligand and palladium in the form of $Pd_2(dba)_3CHCl_3$ or $Pd(OAc)_2$ with a respective ligand to palladium ratio of 4/1 afforded lower yields (Tablo 4.3, Entries 2-3). Nevertheless, lowering the ligand to Pd ratio to 2/1 provided the optimal catalyst activity (Tablo 4.3, Entries 4-6).

The effects of temperature were also investigated. The conversion of ***Z*-1a** achieved to complete conversion just within 4-5 h at 50 ºC temperature (Table 4.4, Entry 1). However, the conversion of ***Z*-1a** could not proceed to completion when performing the reaction at room temperature even at a prolonged reaction times (Table 4.4, Entry 2).

Table 4.4. Effect of Temperature on Pd(0)-catalyzed alkoxycarbonylation reaction of ***Z*-1a**[a]

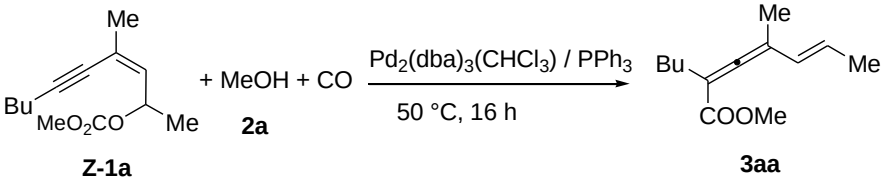



| Entry | T($^0$C) | Yield [%][b] |
|---|---|---|
| 1[c] | 50 | 90 |
| 2[d] | RT | 74(22[e]) |

[a] 1a: 0.3 mmol, MeOH: 5 mL, CO: balloon pressure. [b] Determined by $^1$H-NMR using dimethyl sulfoxide as an internal standard. .[c] (4-5) h.[d] 48 h [e] Unreacted reactant.

Further investigations indicated that increasing the amount of catalysts decreased the formation of vinylallenylester **3aa**. When the amount of catalyst increased from 1 mol% to 2 mol%, with respect to the reactant, the yield of **3aa** decreased slightly from 89% to 85% (Table 4.5, Entries 1-2).

Table 4.5. Effect of the amount of the catalyst on Pd(0)-catalyzed alkoxycarbonylation reaction of ***Z*-1a**



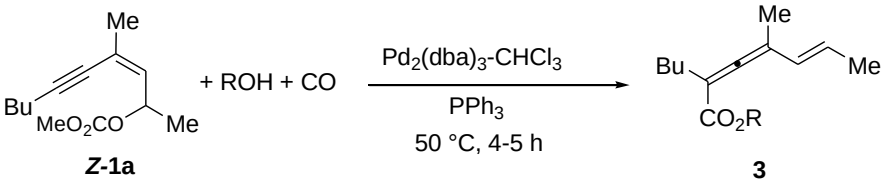

| Entry | Pd% | Yield [%][d] |
|---|---|---|
| 1 | 1[b] | 89 |
| 2 | 2[c] | 85 |

[a] 1a: 0.3 mmol, MeOH: 5 mL, CO: balloon pressure , [b] % 2 mol $PPh_3$ , [c] % 4 mol $PPh_3$, [d] NMR Yield.

The carbonylative reaction of ***Z*-1a** with MeOH, EtOH, or primary saturated $C_3$ and $C_4$ alcohols, under the optimal reaction conditions, that is at 50 ºC, a balloon pressure of CO, in 5 mL of alcohol, used in combination with $Pd_2(dba)_3CHCl_3$ (1 mol%)/$PPh_3$ (2 mol%) gave rise to the corresponding 2,3,5-trienoate products (**3aa-3ad**)

just within 4-5 h in the range of 85-91% isolated yields (Table 4.6, Entries 1-4). A high yield of 2,3,5-trienoate product **3ae** could also be obtained with a bulky alcohol, *i*-propyl alcohol, albeit at a prolonged reaction time (16 h) (Tablo 4.6, Entry 5). In contrast *t*-butyl alcohol appears to be unsuitable because the enyne ***Z*-1a** was recovered as unreacted when it was carbonylated in *t*-butyl alcohol (Tablo 4.6, Entry 6).

Table 4.6. Pd(0)-catalyzed alkoxycarbonylative reaction of ***Z*-1a** with various alcohols[a]




***Z*-1a** **3**

| Entry | ROH | Isolated yield (%) |
|---|---|---|
| 1 | MeOH | 90 (**3aa**) |
| 2 | EtOH | 85 (**3ab**) |
| 3 | PrOH | 91 (**3ac**) |
| 4 | BuOH | 85 (**3ad**) |
| 5 | *i*-PrOH | 91 (**3ae**)[b] |
| 6 | *t*-BuOH | 0 (**3af**) |

[a] 1a: 0.3 mmol, ROH: 5 mL, CO: balloon pressure, 1 mol% Pd, 2 mol% $PPh_3$. [b] 16 h.

The scope of the carbonylation method was surveyed for a range of *Z*-2-en-4-yne carbonates. The method is fully suitable for enynes bearing a methyl, secondary alkyl group, cyclohexyl, or phenyl group on the alkynyl moiety ($R^1$) thereby providing the corresponding 2,3,5-trienoate products **3ba-3da** in high yields when carbonylated in methanol for 4 h under the established conditions (Table 4.7, Entries 1-3).

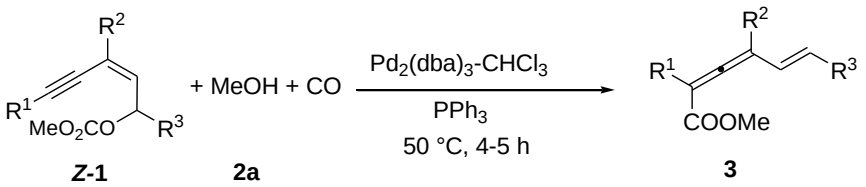
The presence of a highly bulky *t*-butyl group on the alkynyl terminus, however, required a relatively longer reaction period (20 h) for complete conversion and gave rise to the product **3ea** in a moderate yield (64%) (Table 4.7, Entry 4). The methodology also tolerated well the enyne carbonates of which the $R^2$ position is occupied by a H, butyl, or phenyl group, affording the desired products **3fa-3ha** in around 80-82% yields (Table 4.7, Entries 5-7).

It appears that the enyne reactivity is more severely influenced by the size of the $R^3$ group. Varying the $R^3$ group from methyl to butyl reduced the reactivity of the

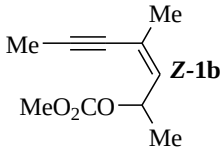
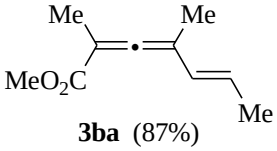
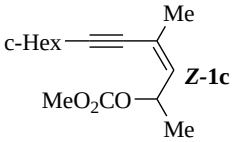
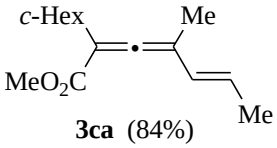
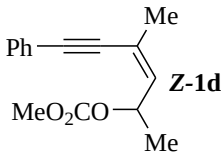
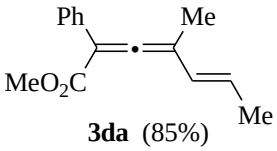
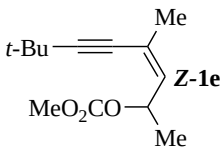
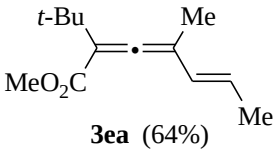
enyne carbonate remarkably; it took nearly 16 h for complete conversion of ***Z*-1i** and to produce the corresponding vinylallenyl ester **3ia** at the yield 81% (Table 4.7, Entry 8). An even more drastic effect could be observed with the substrate in which $R^3$ was the isopropyl group; the reaction of ***Z*-1j** was highly sluggish and its conversion was incomplete when the reaction temperature employed was 50 ºC (Table 4.7, Entry 9). Nevertheless, elevation of the reaction temperature to 65 ºC shortened the reaction period for the complete conversion of ***Z*-1j** to give the product **3ja** in the yield of 71%.

The methoxycarbonylation of an enyne carbonate of a primary alcohol ***Z*-1k** interestingly resulted in the formation of non-separable mixture of ester funtionalized 2-en-4-yne **4ka** by-product and the desired vinylallene product **3ka** (Table 4.7, Entry 10).

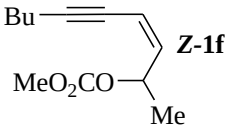
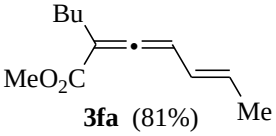
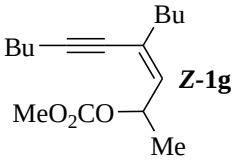
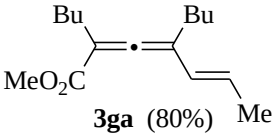
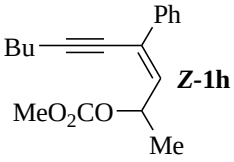
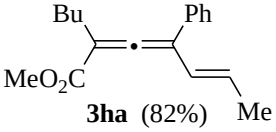
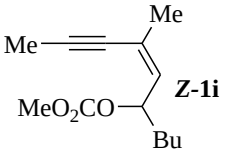
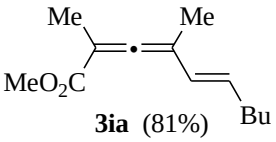
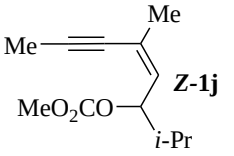
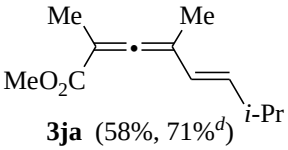
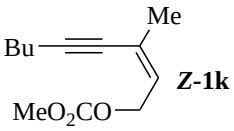
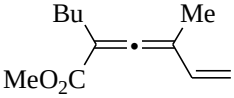
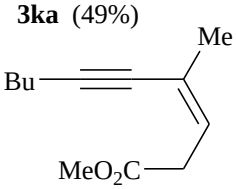
Table 4.7. Pd(0)-catalyzed alkoxycarbonylation reactions of various *Z*-enyne carbonates




***Z*-1** **2a** **3**

| Entry | Enyne carbonate | Time (h) | Product (yield)[b] |
|---|---|---|---|
| 1 |  ***Z*-1b** | 4 |  **3ba** (87%) |
| 2 |  ***Z*-1c** | 4 |  **3ca** (84%) |
| 3 |  ***Z*-1d** | 4 |  **3da** (85%) |
| 4 |  ***Z*-1e** | 20 |  **3ea** (64%) |

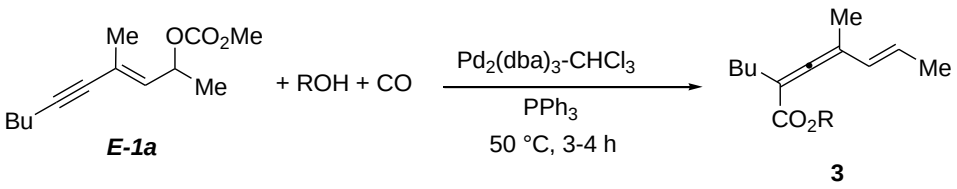
**(Cont. on next page)**

| | | | |
|---|---|---|---|
| 5 |  ***Z*-1f** | 4 |  **3fa** (81%) |
| 6 |  ***Z*-1g** | 4 |  **3ga** (80%) |
| 7 |  ***Z*-1h** | 2 |  **3ha** (82%) |
| 8 |  ***Z*-1i** | 16 |  **3ia** (81%) |
| 9 |  ***Z*-1j** | 22[c]<br>8[d] |  **3ja** (58%, 71%[d]) |
| 10 |  ***Z*-1k** | 24[c] |  **3ka** (49%) +  **4ka** (33%) |

[a] 1a: 0.3 mmol, MeOH: 5 mL, CO: balloon pressure, 1 mol% Pd, 2 mol% $PPh_3$. [b] Isolated yield.
[c] Incomplete conversion. [d] 65 °C.

As a continuation process, the methodology surveyed for the *E*-2-en-4-yne carbonates. The method is suitable for the *E*-configured enyne carbonate in the presence of MeOH, EtOH, primary saturated $C_3$ and $C_4$ alcohols, under the optimal reaction conditions, to produce the corresponding vinylallenyl ester **3aa-3ad** just within 3-4 h in the range of 80-91% isolated yields (Table 4.8, Entries 1-4). A low yield of 2,3,5-trienoate product **3ae** could also be obtained with i-propyl alcohol at the yield (67%) (Table 4.8, Entry 5).

Table 4.8. Pd(0)-catalyzed alkoxycarbonylative reaction of ***E*-1a** with various alcohols[a]




| Entry | ROH | Isolated yield (%) |
|---|---|---|
| 1 | MeOH | 88 (**3aa**) |
| 2 | EtOH | 81 (**3ab**) |
| 3 | PrOH | 91 (**3ac**) |
| 4 | BuOH | 80 (**3ad**) |
| 5 | *i*-PrOH | 67 (**3ae**)[b] |

[a] 1a: 0.3 mmol, ROH: 5 mL, CO: balloon pressure, 1 mol% Pd, 2 mol% $PPh_3$. [b] 6 h.

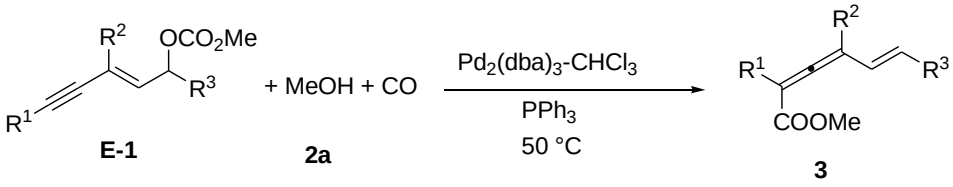
*E*-configured enyne carbonate ***E*-1l** led to a complex mixture (containing only small amounts of the desired vinylallenes) when subjected to the Pd(0)-catalyzed methoxycarbonylation reaction as determined by $^1$H-NMR analysis (Table 4.9, Entry 1).

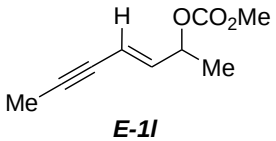
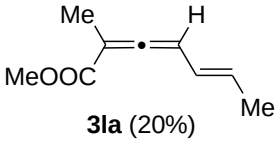
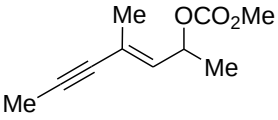
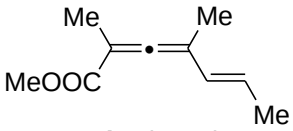
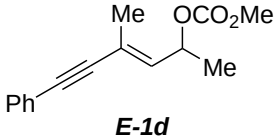
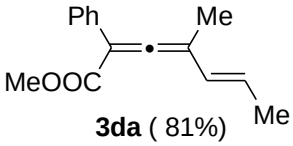
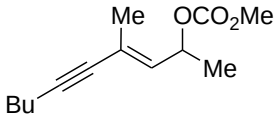
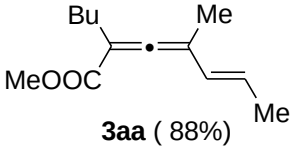
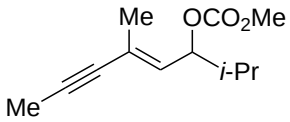
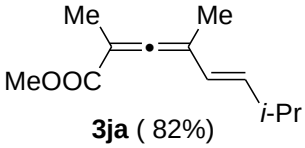
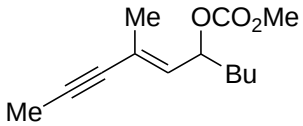
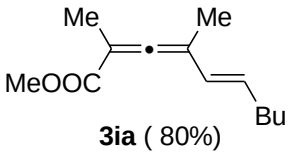
Varying the $R^2$ group from H to methyl increased the reactivity of the enyne carbonate; it took nearly 5h for the complete conversion of ***E*-1b** and to produce the corresponding vinylallenyl ester **3ba** in moderate yield (66%) (Table 4.9, Entry 2).

The method is fully suitable for enynes bearing a butyl and phenyl group on the alkynyl moiety ($R^1$) thereby providing the corresponding 2,3,5-trienoate products **3da - 3aa** in high yields when carbonylated in methanol for 4 h under the established conditions (Table 4.9, Entries 3-4).

The method is also tolerated the enyne carbonates of which the $R^3$ position is occupied by a butyl or isopropyl group, affording the desired products **3ja-3ia** in high yield (Table 4.9, Entries 5-6).

Table 4.9. Pd(0)-catalyzed alkoxycarbonylation reactions of various *E*-enyne carbonates




| Entry | Enyne carbonate | Time (h) | Product (yield)[b] |
|---|---|---|---|
| 1 |  ***E-1l*** | 16[c] |  **3la** (20%) |
| 2 |  ***E-1b*** | 5 |  **3ba** ( 66%) |
| 3 |  ***E-1d*** | 4 |  **3da** ( 81%) |
| 4 |  ***E-1a*** | 4 |  **3aa** ( 88%) |
| 5 |  ***E-1j*** | 4 |  **3ja** ( 82%) |
| 6 |  ***E-1i*** | 6 |  **3ia** ( 80%) |

[a] 1 0.3 mmol, MeOH: 5 mL, CO: balloon pressure, 1 mol% Pd, 2 mol% $PPh_3$. [b] Isolated yield.
[c] Nmr Yield. [d] 65 °C.

As analogy to the Pd(0)-catalyzed reactions of propargylic reagents, the Pd(0)-catalyzed alkoxycarbonylation of *Z*- or E-enyne carbonates should involve the

formation of a σ-allenylpalladium(II) complex (C) by elimination of the leaving group and double bond migration (Figure 4.3).

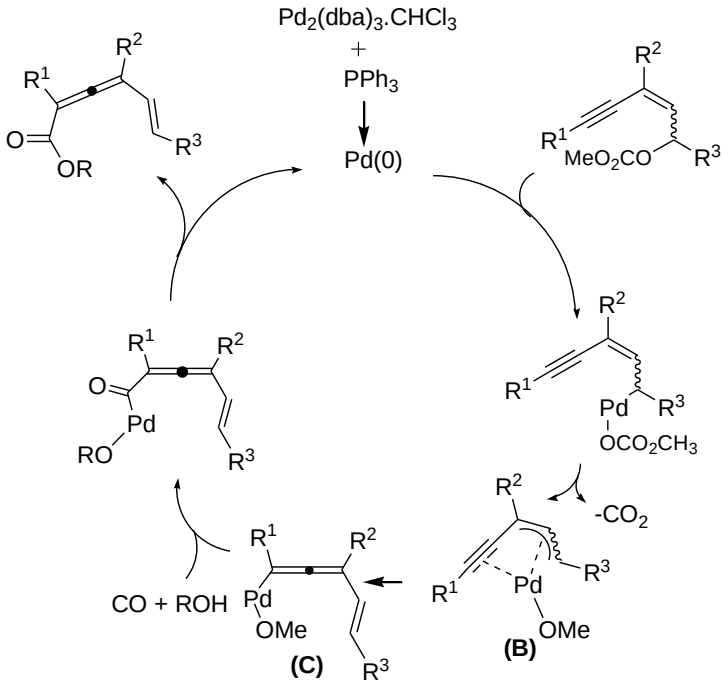



Figure 4.3. Reaction mechanism of alkoxycarbonylation of *Z*- or E-Enyne carbonate

The formation of the σ-allenylpalladium intermediate from propargylic reagents has been based on two unverified paths: (1) the oxidative addition of Pd(0) species and the subsequent shift of Pd to the far alkynyl carbon, or (2) via $S_N2'$ substitution by the attack of the Pd(0) species to the alkynyl carbon. Also for our case, it is uncertain whether the oxidative pathway or 1,5-$S_N2''$ type Pd(0)-substitution is responsible for the formation of the vinylallenypalladium (C) intermediate. Nonetheless, the marked effect on reactivity observed here for the Z-enyne carbonates with respect to the size of their allylic co-substituent ($R^3$) may imply the former. It should also be noted that the formation of (*Z*)-methyl 4-methyldec-3-en-5-ynoate **4ka** from the methoxy carbonylation of **Z-1k** can be ascribed to an allyl palladium(II) intermediate.

The reaction cycle should finalize by the reaction of the intermediate **C** with CO and alcohol to generate the product **3** and a catalytically active Pd(0) species.

Center-to-axis chirality transfer selectivity was demonstrated with the our established method; the respective methoxycarbonylation of a enantiomerically enriched enyne car-bonate **(*R*,*Z*)-1b** (94.5% *ee*) led to the product with 7% *ee*. The application of

higher CO pressure or balloon pressure at room temperature did not show significant effect on chirality transfer. ( Figure 4.4).

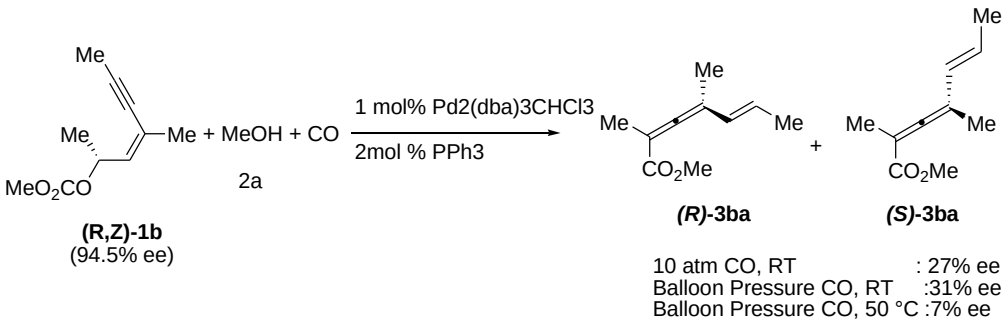



Figure 4.4. Pd(0)-catalyzed alkoxycarbonylation reaction of **(*R*,*Z*)-1b**.

# CHAPTER 5

# CONCLUSION

As a consequence, in this study we developed a new synthetic method for the formation of vinylalleneyl ester structures.

With the high reactivity of allyl carbonates and propargyl carbonates in mind, we attempted the Pd(0)-catalyzed carbonylation of *Z*-or *E*-2-en-4-yne carbonates in an alcohol medium lead to high yields of vinylallenyl esters. *Z*-or E-conjugated enyne reagents with a leaving group in the allylic position seem to reveal similar characteristic reactivities toward transition metal catalyzed reactions with respect to the propargylic reagents. Dual coordination of palladium with both alkynyl moiety and carbonate leaving group is a driving force for the process.

Vinylallenes are useful and unique precursors or intermediates in organic synthesis. Vinylallenes show high reactivity and stereoselectivity due to their axial chirality. They transfer chirality to a new stereocenter in many reactions. According to these crucial importances of vinylallene structures, this study could be extended to synthesize enantioenriched vinylallene derivatives to produce natural products and biologycally active compounds.

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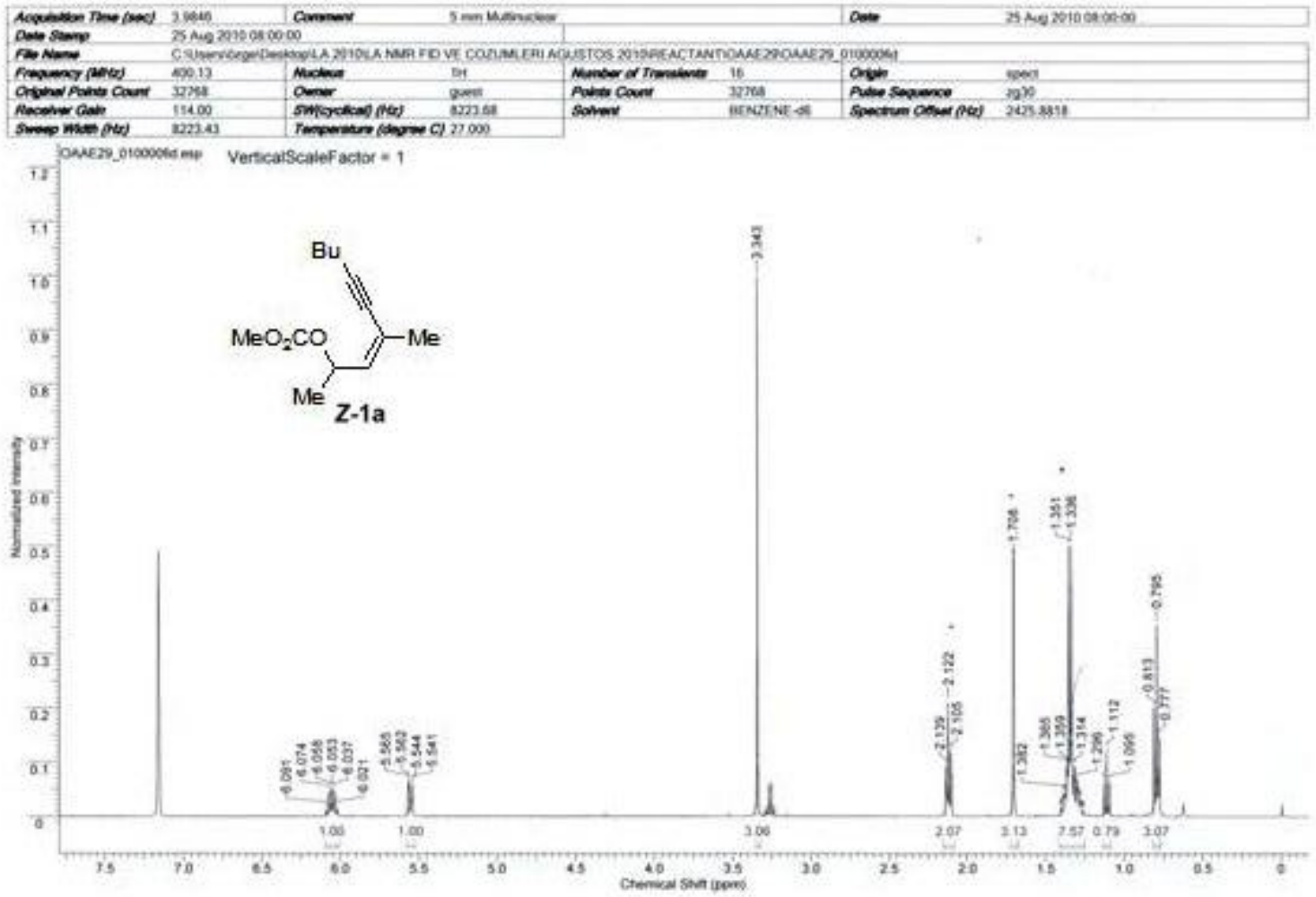
# APPENDIX A

## $^{1}$H NMR and$^{13}$ CNMR SPECTRUMS OF REACTANTS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Nucleus 1H
Number of Transients 16
Origin spect
Original Points Count 32768
Owner guest
Points Count 32768
Pulse Sequence zg30
Receiver Gain 114.00
SW(cyclical) (Hz) 8223.68
Solvent BENZENE-d6
Spectrum Offset (Hz) 2425.8818
Sweep Width (Hz) 8223.43
Temperature (degree C) 27.000
OAAE29_0100006d.esp
VerticalScaleFactor = 1
Bu
MeO2CO
Me
Me
Z-1a
Normalized Intensity
Chemical Shift (ppm)
6.091
6.074
6.056
6.053
6.037
6.021
5.565
5.563
5.544
5.541
3.343
2.129
2.122
2.105
1.708
1.382
1.365
1.359
1.351
1.336
1.314
1.299
1.112
1.095
0.813
0.795
0.777
1.00
1.00
3.06
2.07
3.13
7.57
0.79
3.07

| | | | | | | | |
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| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zgpg30 |
| Receiver Gain | 4096.00 | SW(cyclical) (Hz) | 31847.13 | Solvent | BENZENE-d6 | Spectrum Offset (Hz) | 12694.1426 |
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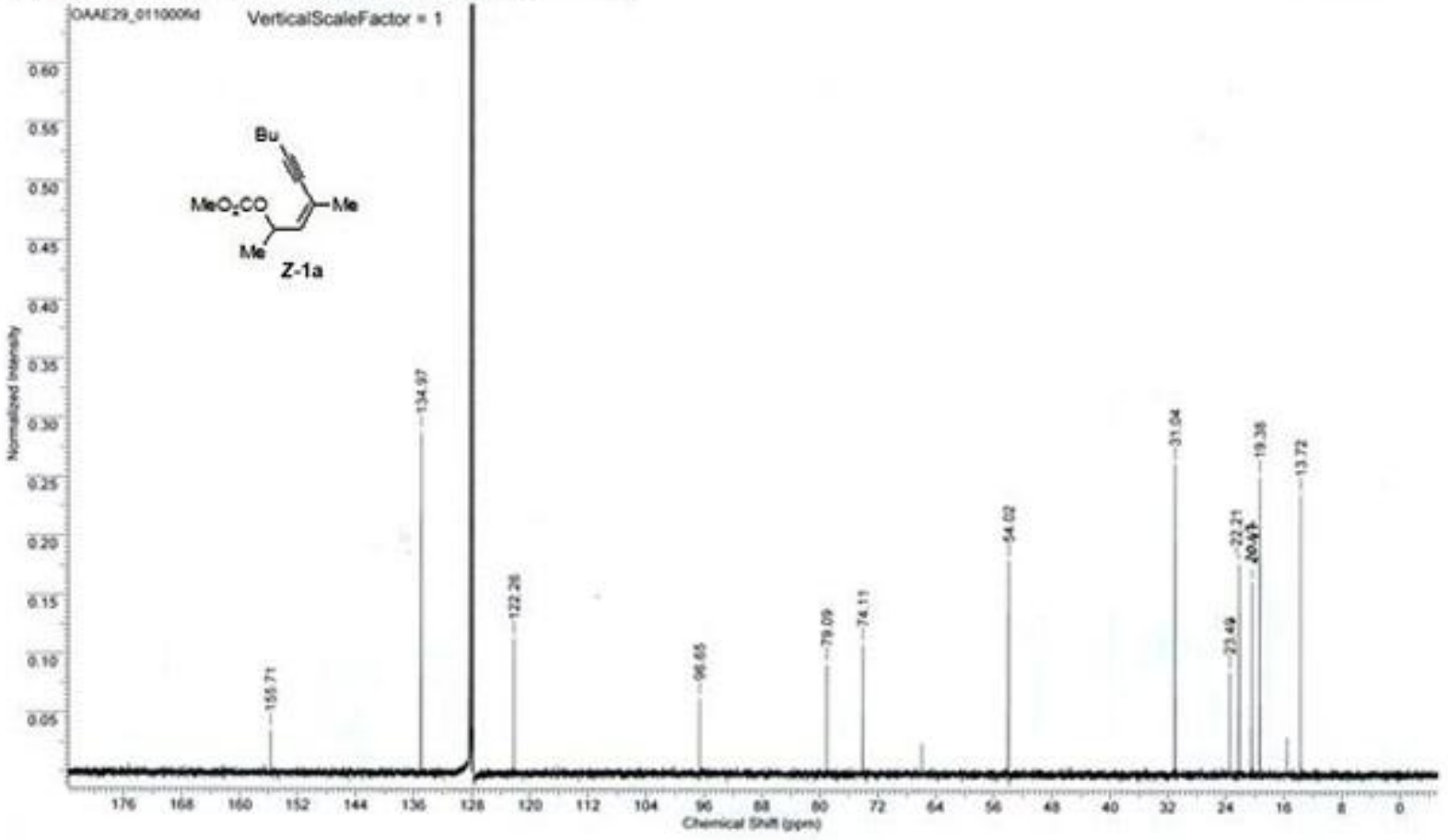

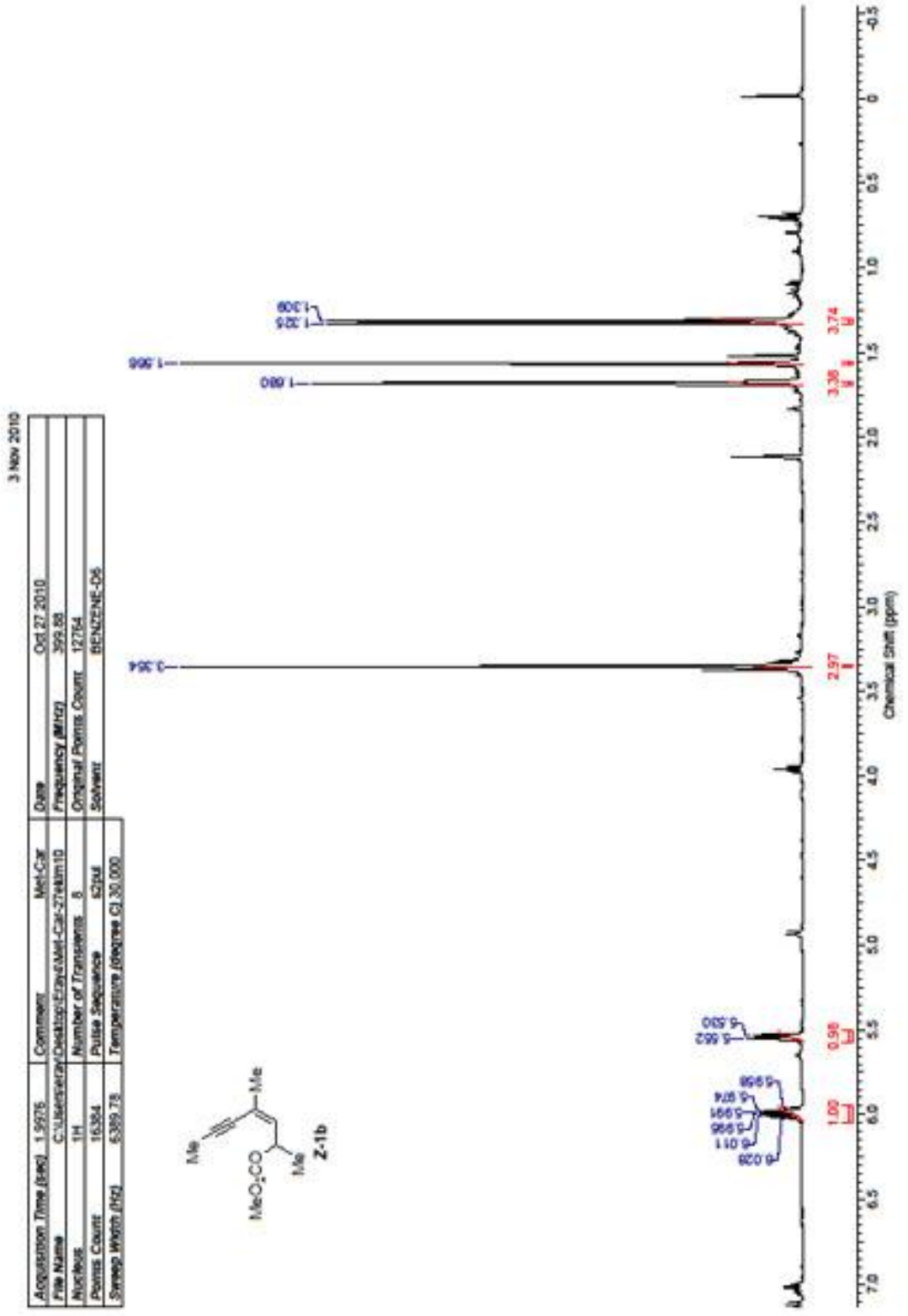
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Comment Mel-Cat
Date Oct 27 2010
Frequency (MHz) 399.88
Number of Transients 8
Pulse Sequence s2pul
Temperature (degree C) 30.000
Original Points Count 12764
Solvent BENZENE-D6
Me
MeO2CO
Me
Me
Z-1b
3.364
1.880
1.308
1.325
6.662
6.500
6.028
6.011
5.996
5.991
5.974
5.958
2.97
3.36
3.74
0.98
1.00
Chemical Shift (ppm)

3 Nov 2010

| | | | | | |
|---|---|---|---|---|---|
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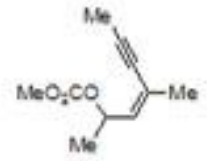


Z-1b

21 Oct 2010

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| Original Points Count | 12764 | Points Count | 16384 | Pulse Sequence | s2pul |
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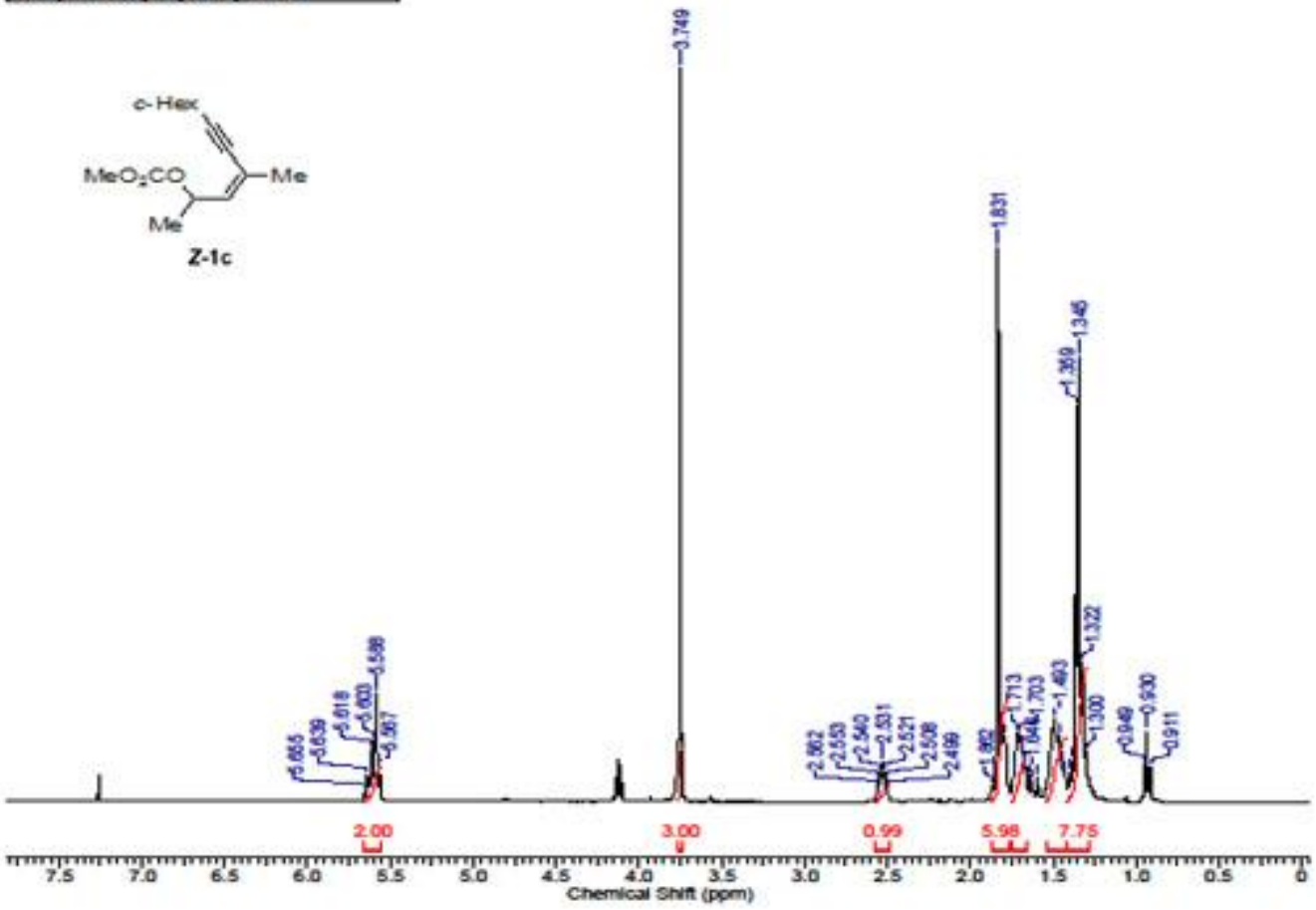

21 Oct 2010

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| Original Points Count | 30135 | Points Count | 32768 | Pulse Sequence | s2pul |
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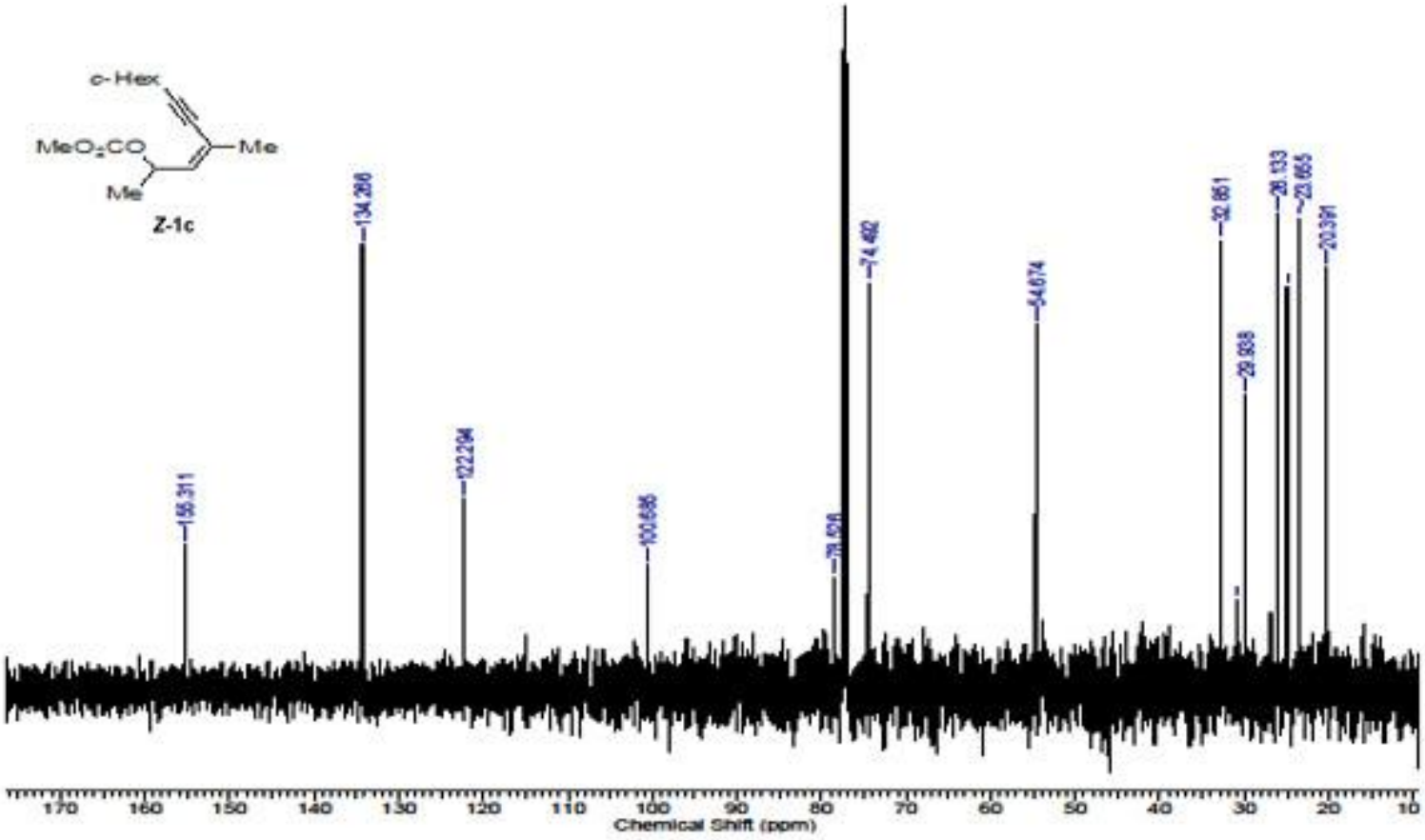
| Temperature (degree C) | 30.000 | | | | |



22 Oct 2010

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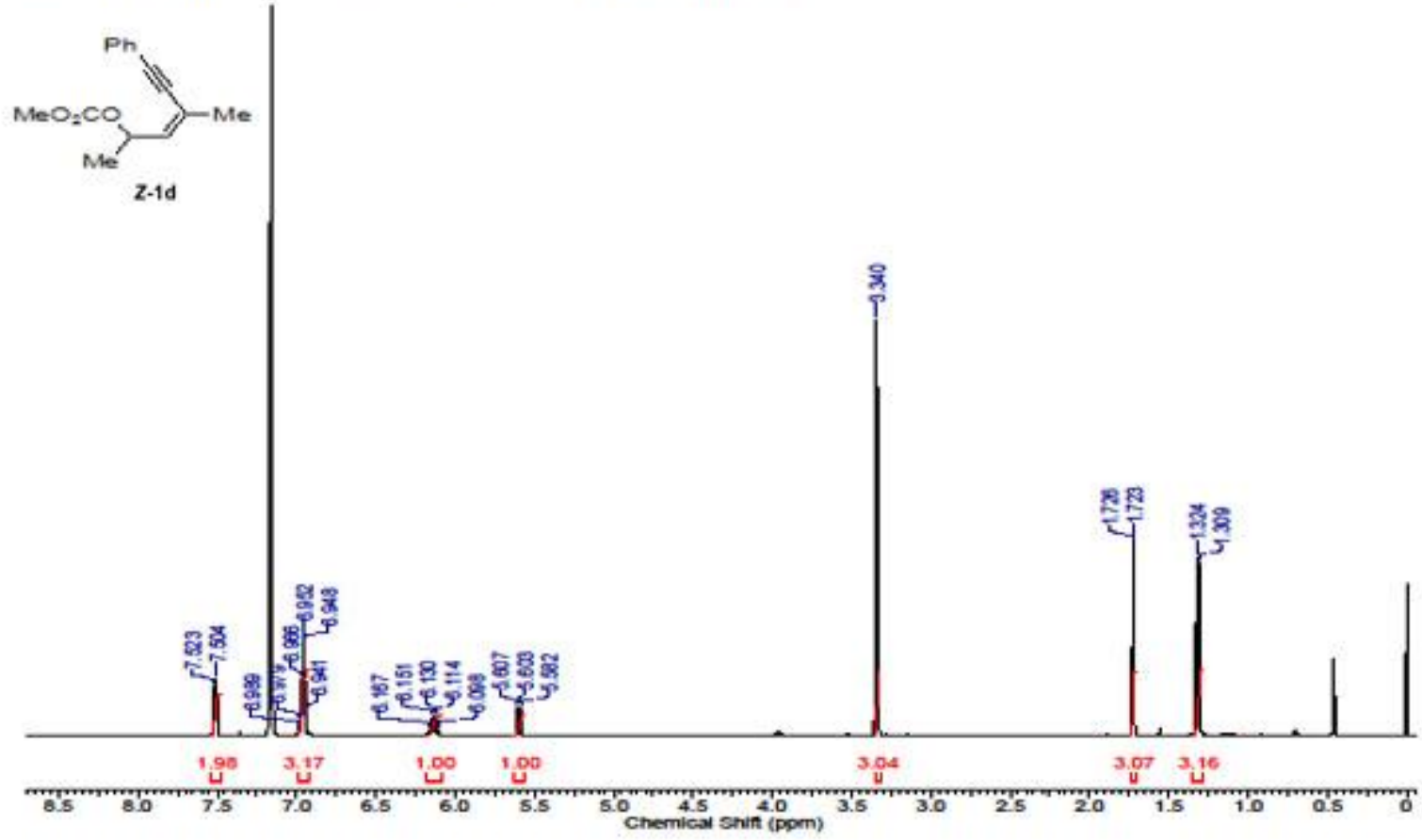
| *Origin* | spect | *Original Points Count* | 32768 | *Owner* | guest |
| *Points Count* | 32768 | *Pulse Sequence* | zg30 | *Solvent* | BENZENE-O6 |
| *Sweep Width (Hz)* | 8223.43 | *Temperature (degree C)* | 27.000 | | |



22 Oct 2010

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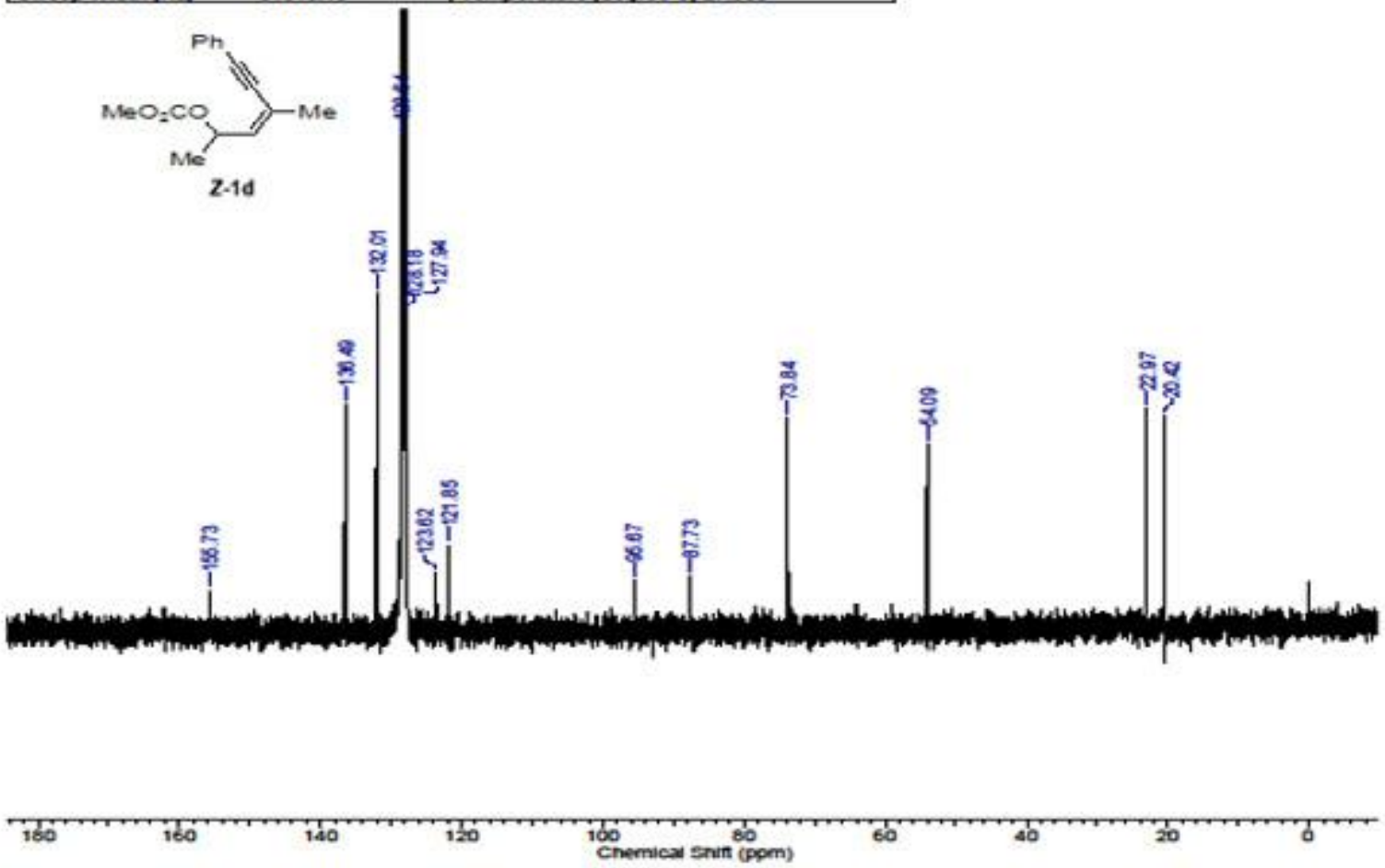

1 Nov 2010

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| *Points Count* | 32768 | *Pulse Sequence* | zg30 | *Solvent* | BENZENE-D6 |
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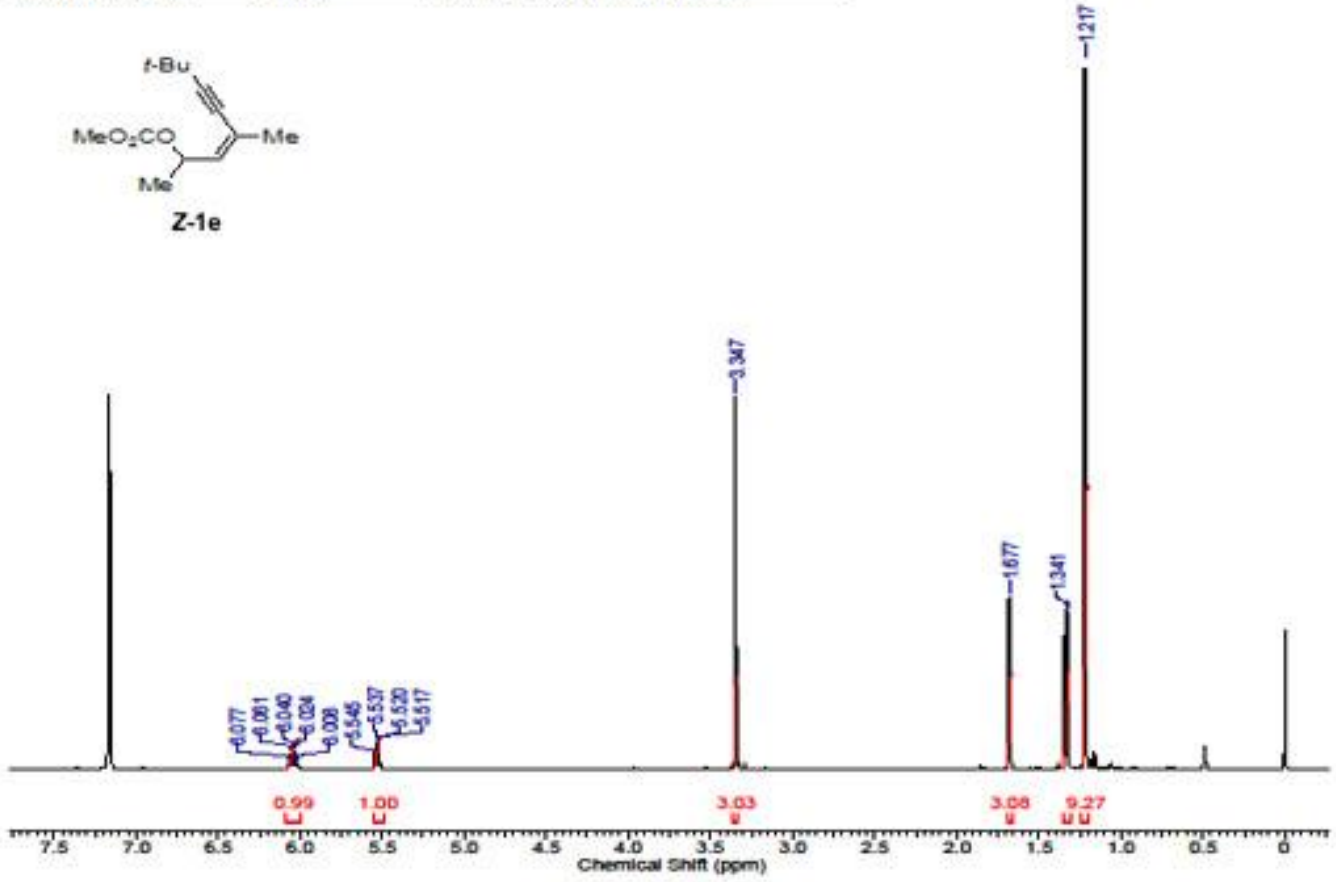

1 Nov 2010

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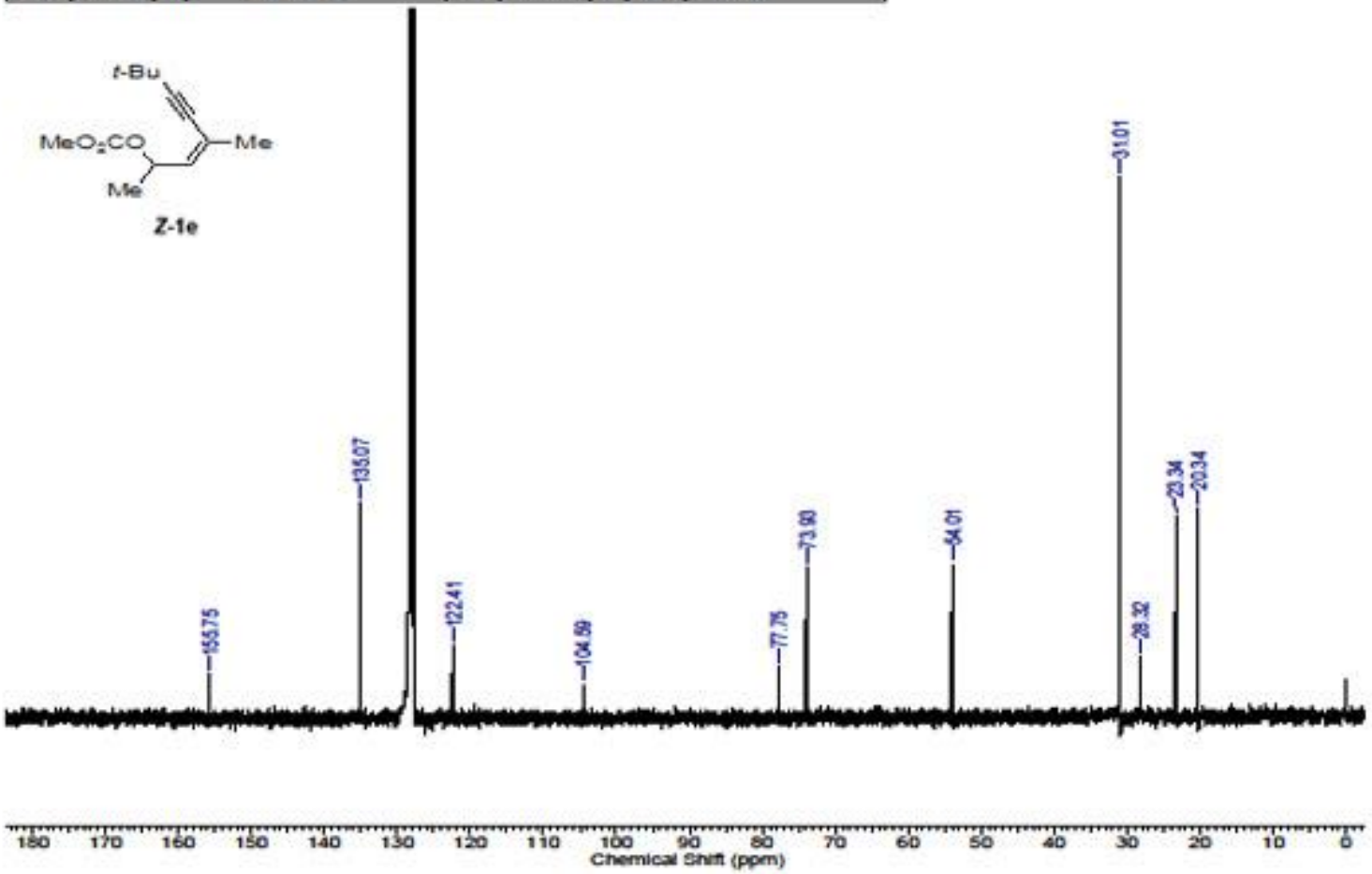

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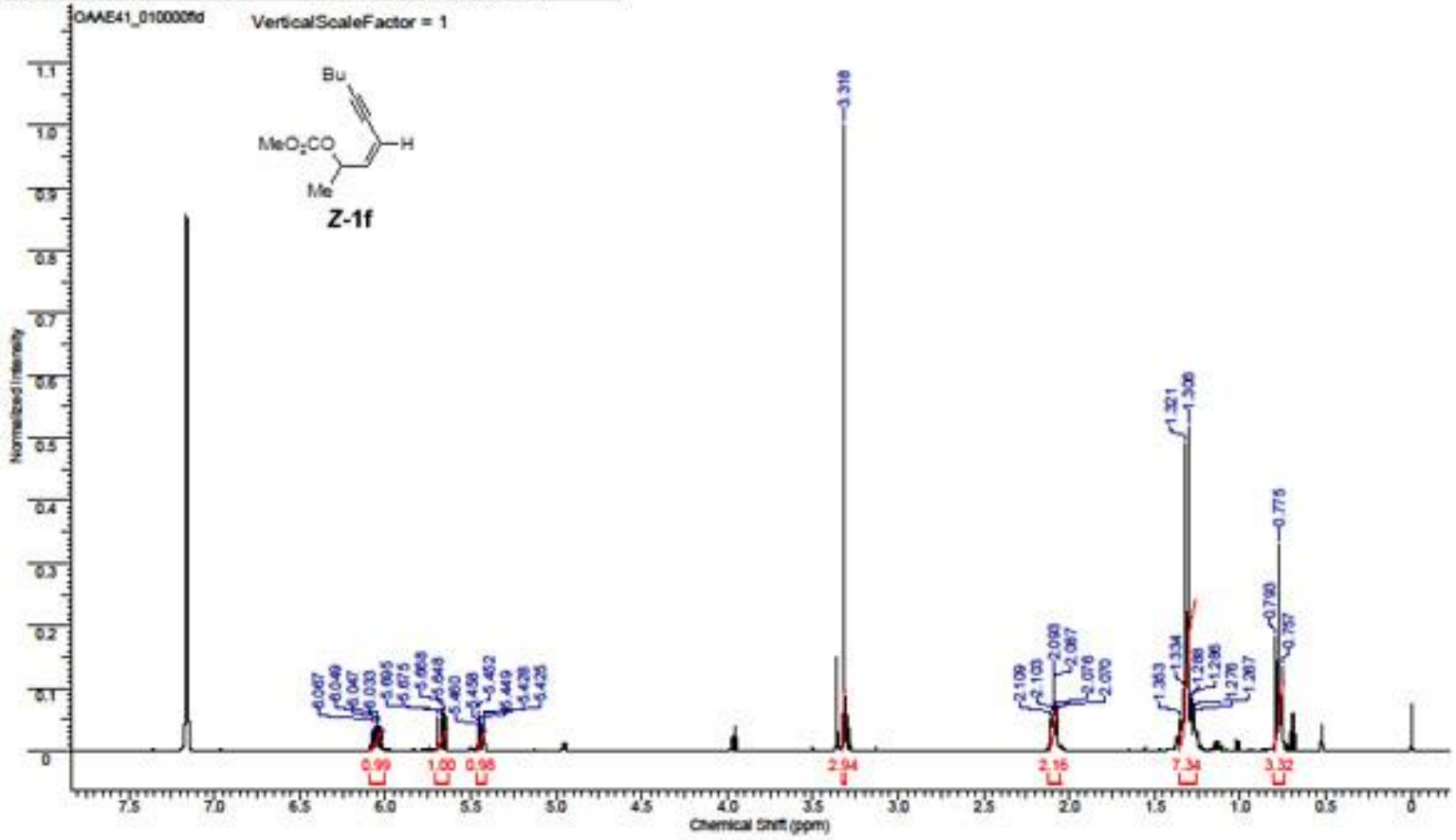

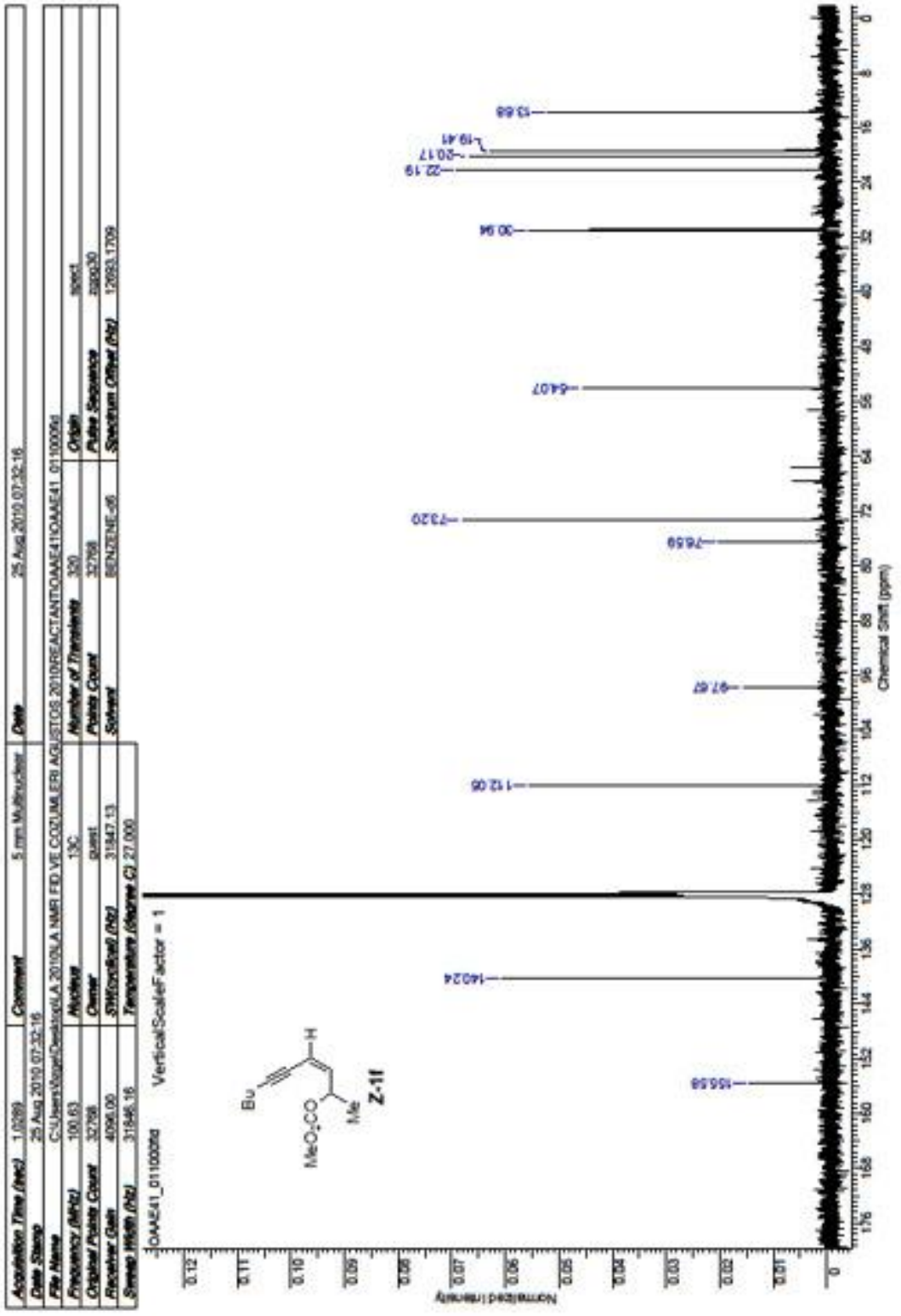
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Nucleus 13C
Number of Transients 320
Origin spect
Original Points Count 32768
Owner guest
Points Count 32768
Pulse Sequence zgpg30
Receiver Gain 4096.00
SW(cycles/s) (Hz) 31847.13
Solvent BENZENE-d6
Spectrum Offset (Hz) 12693.1709
Sweep Width (Hz) 31846.16
Temperature (degree C) 27.000
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VerticalScaleFactor = 1
Bu
H
MeO2CO
Me
Z-11f
Normalized Intensity
Chemical Shift (ppm)
155.58
140.24
112.05
97.67
76.59
73.20
54.07
30.94
22.19
20.17
19.47
13.69

| | | | | | | | |
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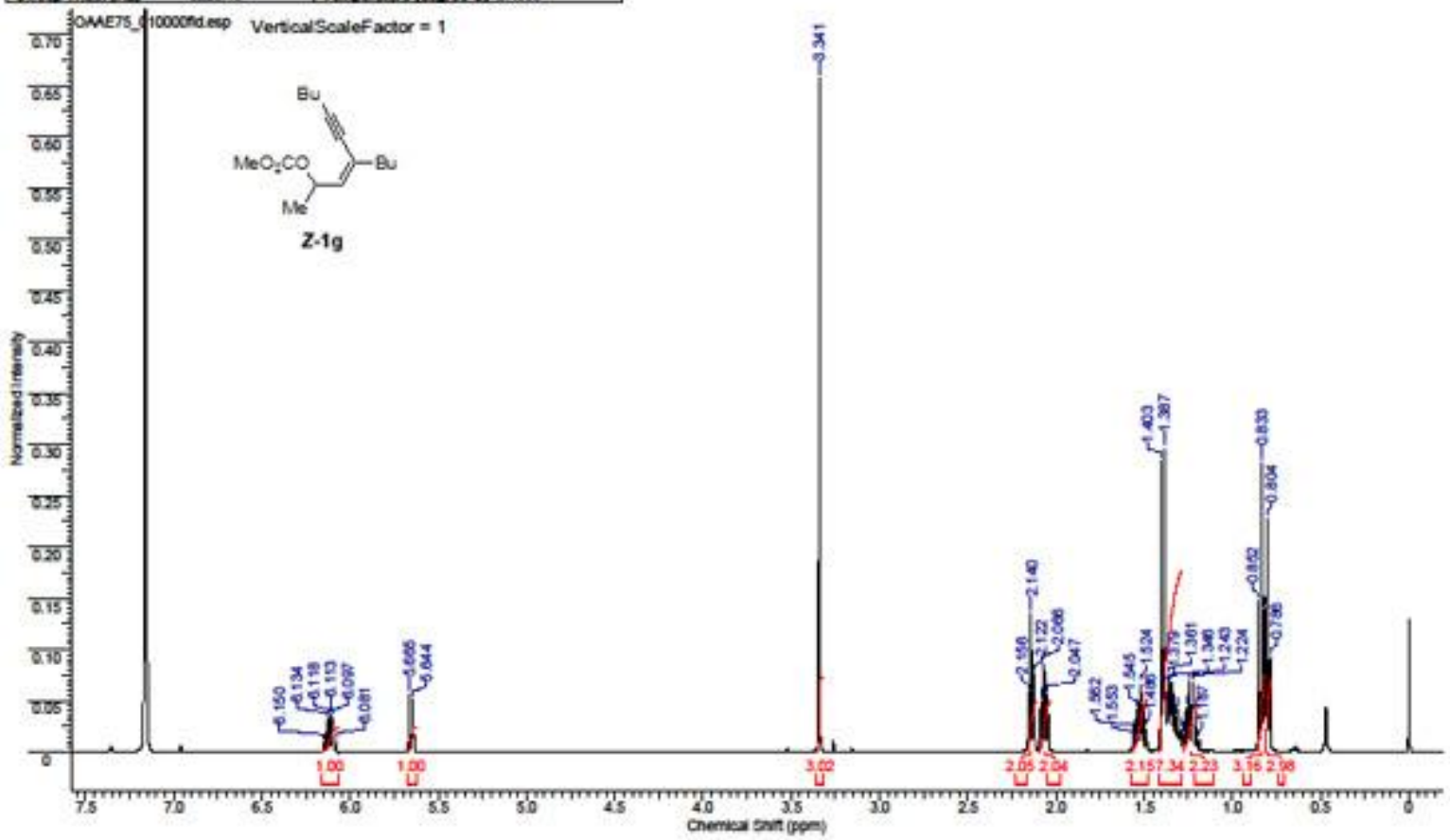
| ***Original Points Count*** | 32768 | ***Owner*** | guest | ***Points Count*** | 32768 | ***Pulse Sequence*** | zg30 |
| ***Receiver Gain*** | 228.10 | ***SW(cyclical) (Hz)*** | 8223.68 | ***Solvent*** | BENZENE-d6 | ***Spectrum Offset (Hz)*** | 2425.8818 |
| ***Sweep Width (Hz)*** | 8223.43 | ***Temperature (degree C)*** | 27.000 | | | | |



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| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zgpg30 |
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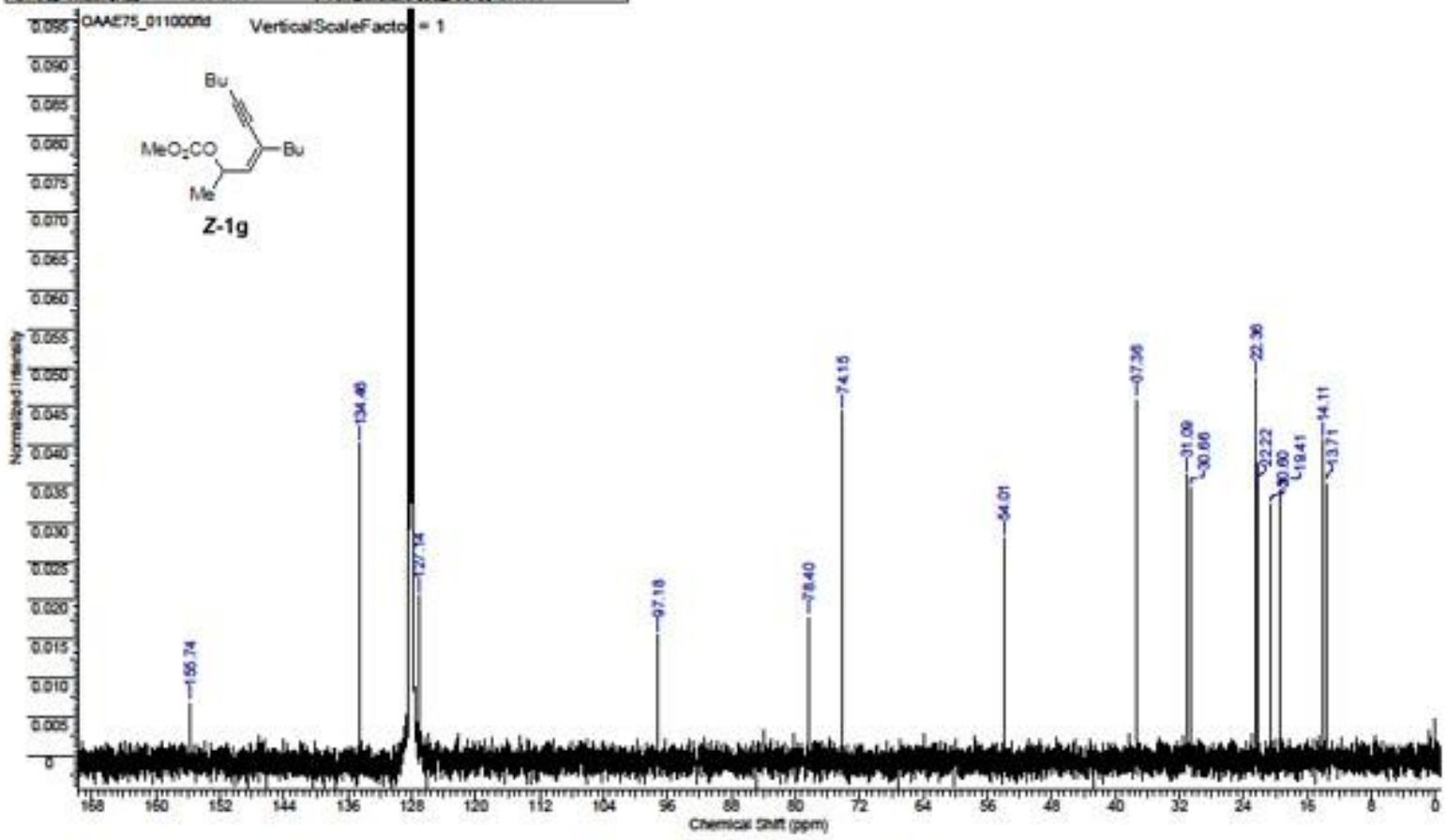

3 Nov 2010

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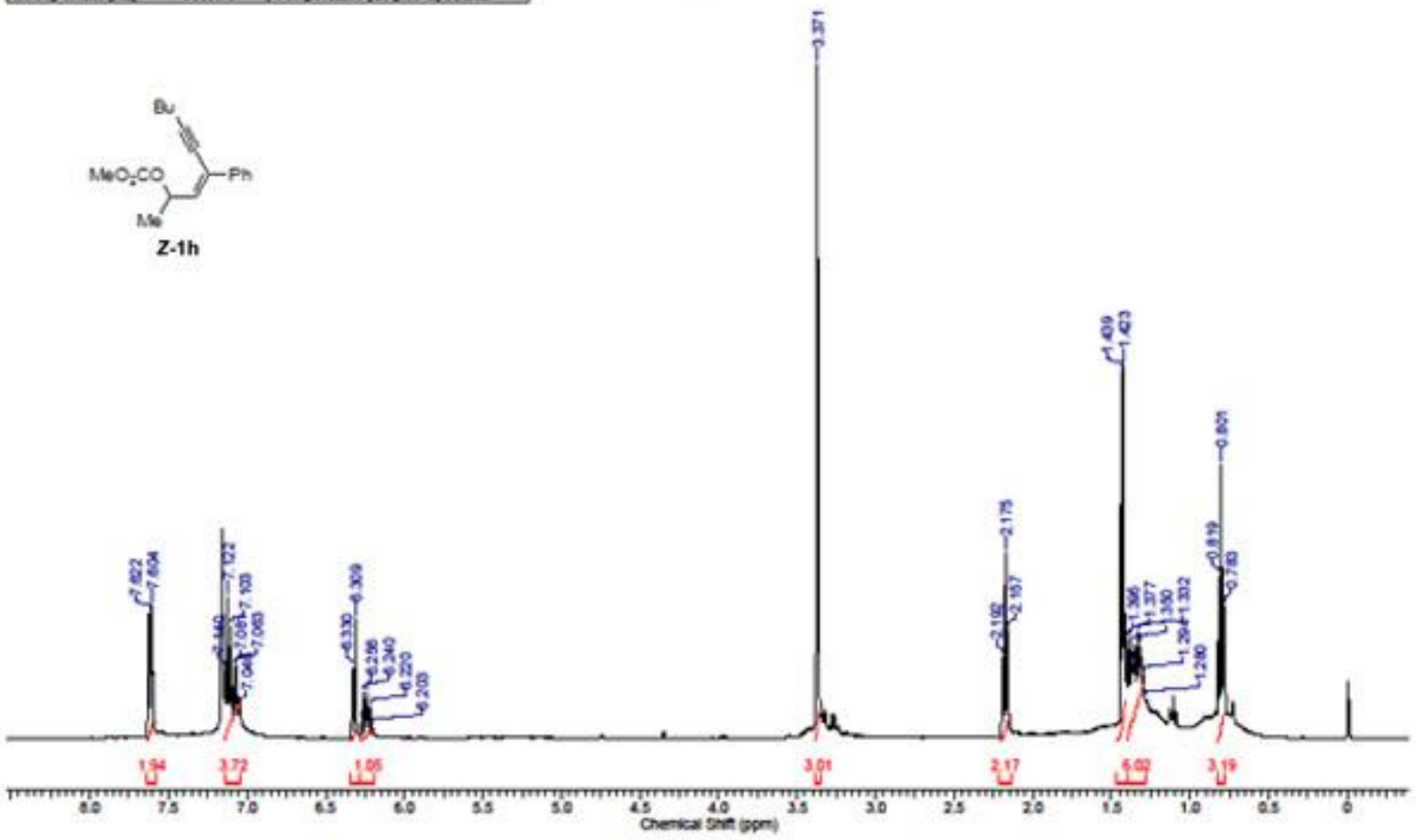
|---|---|---|---|---|---|
| Acquisition Time (sec) | 1.9976 | Comment | AE121 | Date | Oct 27 2010 |
| File Name | C:\Users\eray\Desktop\Eray\AE121-27ekim10 | | | Frequency (MHz) | 399.88 |
| Nucleus | 1H | Number of Transients | 8 | Original Points Count | 12764 |
| Points Count | 16384 | Pulse Sequence | s2pul | Solvent | BENZENE-D6 |
| Sweep Width (Hz) | 6389.78 | Temperature (degree C) | 30.000 | | |



3 Nov 2010

| | | | | | |
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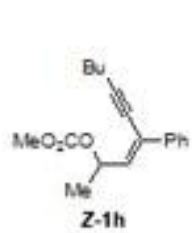
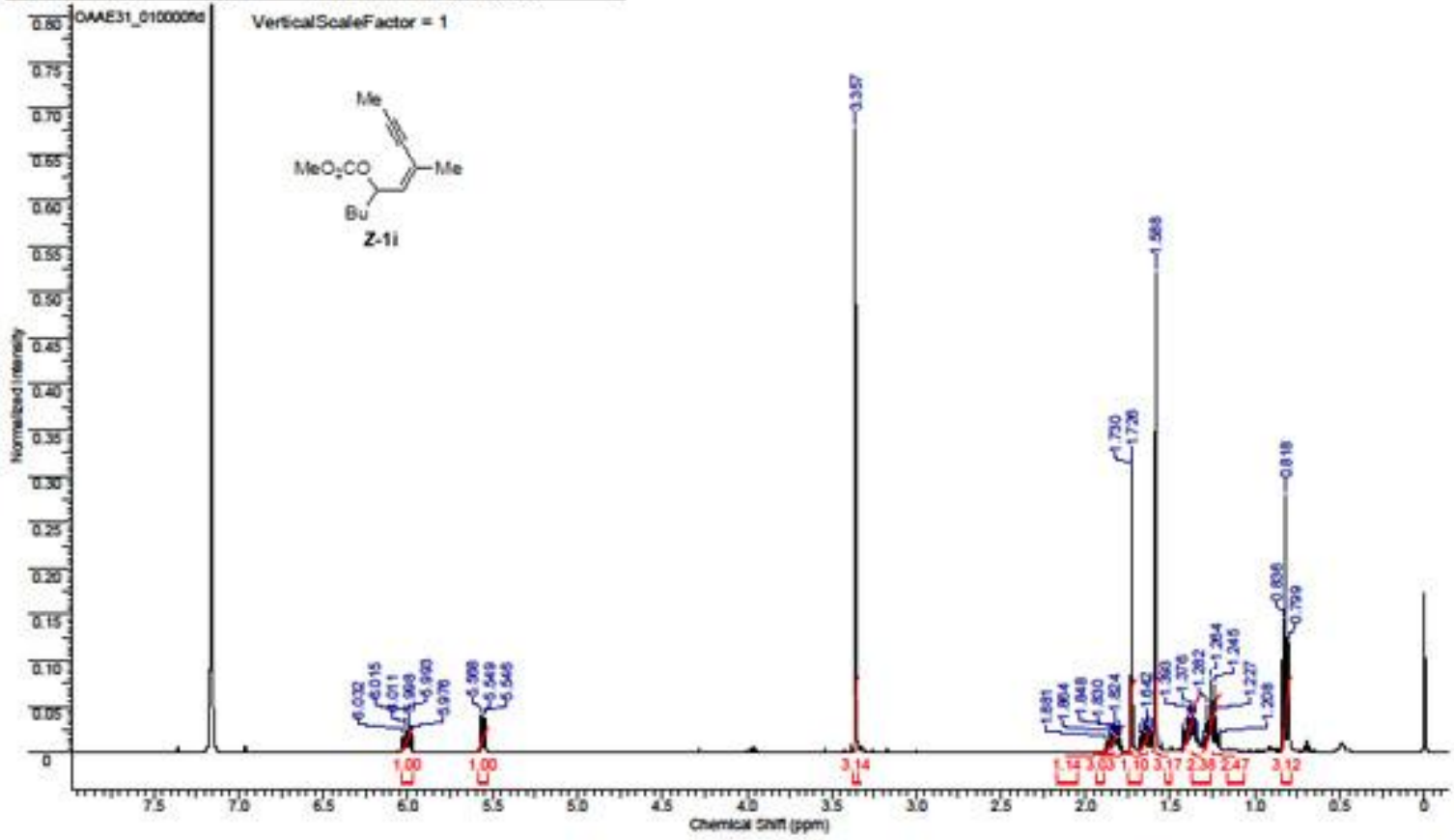
| *Acquisition Time (sec)* | 1.1994 | *Comment* | AE121 | *Date* | Oct 27 2010 |
| *File Name* | C:\Users\ercay\Desktop\Eray\AE121-27ekim10 | | | *Frequency (MHz)* | 100.56 |
| *Nucleus* | 13C | *Number of Transients* | 1000 | *Original Points Count* | 30135 |
| *Points Count* | 32768 | *Pulse Sequence* | s2pul | *Solvent* | BENZENE-D6 |
| *Sweep Width (Hz)* | 25125.63 | *Temperature (degree C)* | 30.000 | | |

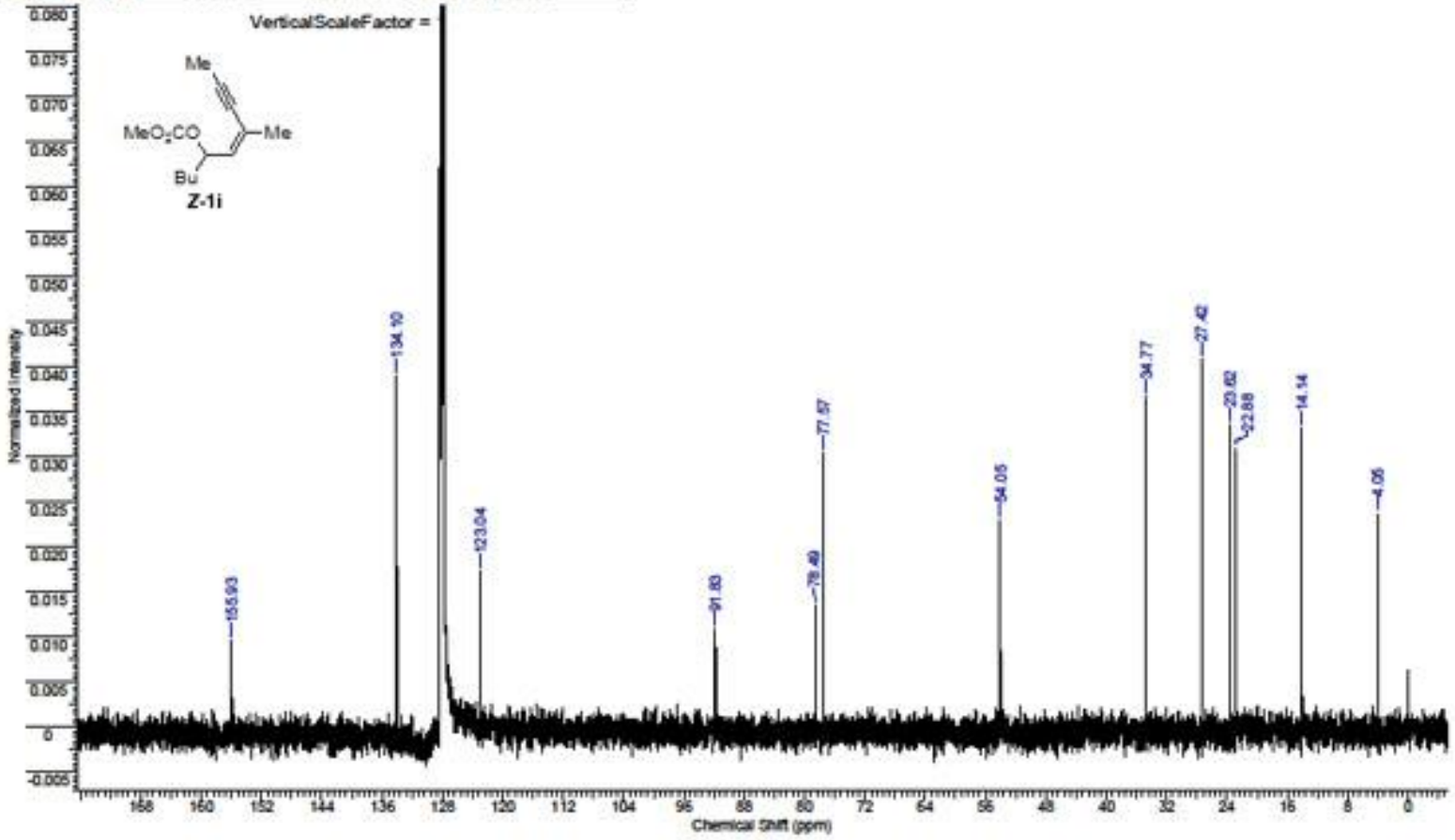



**Z-1h**

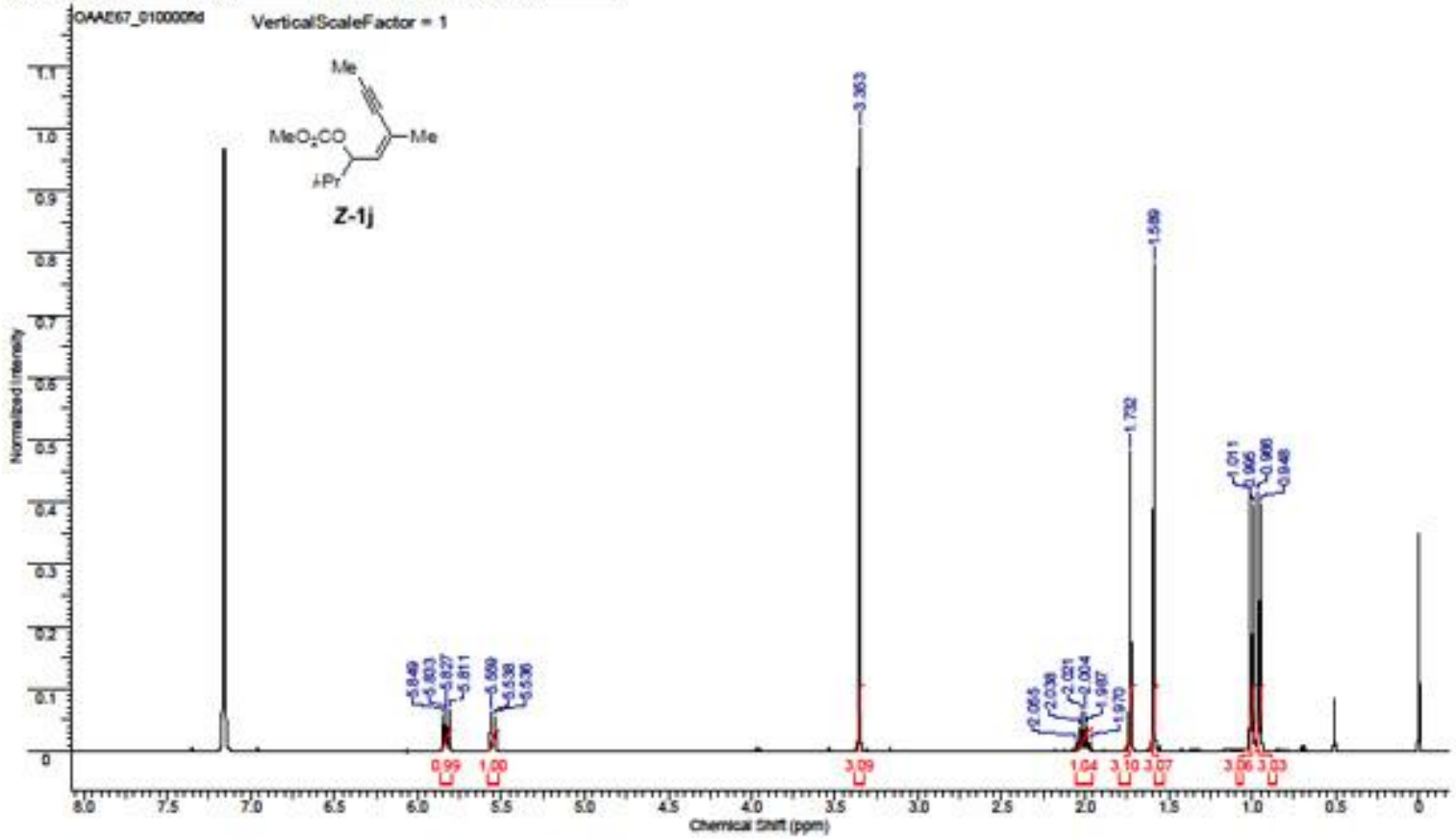
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Acquisition Time (sec) | 3.9846 | Comment | 5 mm Multinuclear | | | Date | 25 Aug 2010 07:38:40 |
| Date Stamp | 25 Aug 2010 07:38:40 | | | | | | |
| File Name | C:\Users\Ozge\Desktop\LA 2010\LA NMR FID VE COZUMLERI AGUSTOS 2010\REACTANT\OAAE31\OAAE31_0100005fid | | | | | | |
| Frequency (MHz) | 400.13 | Nucleus | 1H | Number of Transients | 16 | Origin | spect |
| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zg30 |
| Receiver Gain | 228.10 | SW(cycles) (Hz) | 8223.68 | Solvent | BENZENE-d6 | Spectrum Offset (Hz) | 2425.8818 |
| Sweep Width (Hz) | 8223.43 | Temperature (degree C) | 27.000 | | | | |



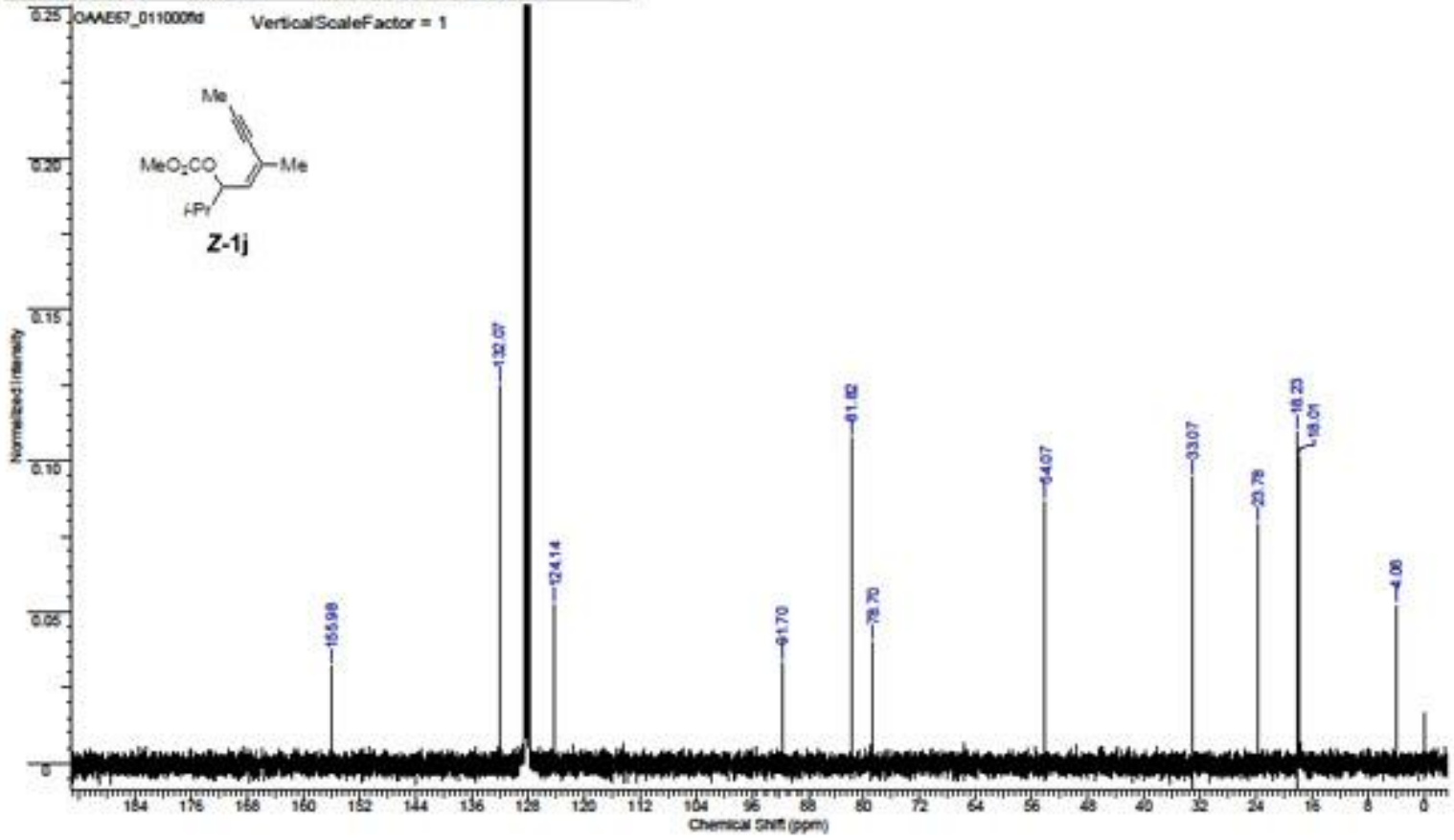
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Acquisition Time (sec) | 1.0289 | Comment | 5 mm Multinuclear | Date | 25 Aug 2010 07:51:28 | | |
| Date Stamp | 25 Aug 2010 07:51:28 | | | | | | |
| File Name | C:\Users\Ozge\Desktop\LA 2010\LA NMR FID VE COZUMLERI AGUSTOS 2010\REACTANT\OAAE3T\OAAE31_011000\fid | | | | | | |
| Frequency (MHz) | 100.63 | Nucleus | 13C | Number of Transients | 320 | Origin | spect |
| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zgpg30 |
| Receiver Gain | 4096.00 | SW(cyclical) (Hz) | 31847.13 | Solvent | BENZENE-d6 | Spectrum Offset (Hz) | 12693.1709 |
| Sweep Width (Hz) | 31846.16 | Temperature (degree C) | 27.000 | | | | |



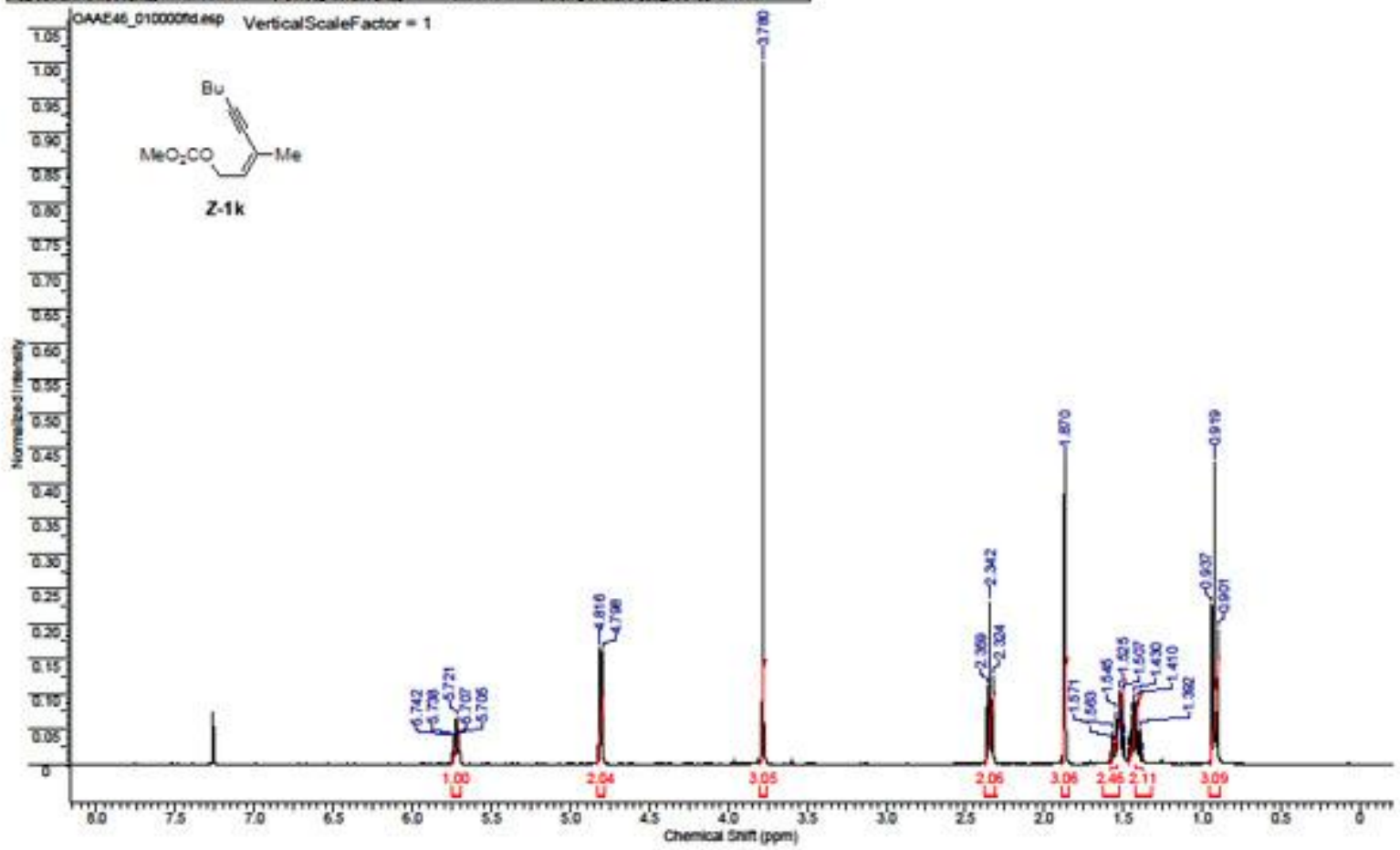
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 3.9846 | ***Comment*** | 5 mm Multinuclear | | | ***Date*** | 24 Aug 2010 10:52:48 |
| ***Date Stamp*** | 24 Aug 2010 10:52:48 | | | | | | |
| ***File Name*** | C:\Users\Ilgaz\Desktop\LA 2010\LA NMR FID VE COZUMLERI AGUSTOS 2010\REACTANT\OAAE67\OAAE67_01000005d | | | | | | |
| ***Frequency (MHz)*** | 400.13 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Origin*** | spect |
| ***Original Points Count*** | 32768 | ***Owner*** | guest | ***Points Count*** | 32768 | ***Pulse Sequence*** | zg30 |
| ***Receiver Gain*** | 203.20 | ***SW(cyclical) (Hz)*** | 8223.68 | ***Solvent*** | BENZENE-d6 | ***Spectrum Offset (Hz)*** | 2425.8818 |
| ***Sweep Width (Hz)*** | 8223.43 | ***Temperature (degree C)*** | 27.000 | | | | |

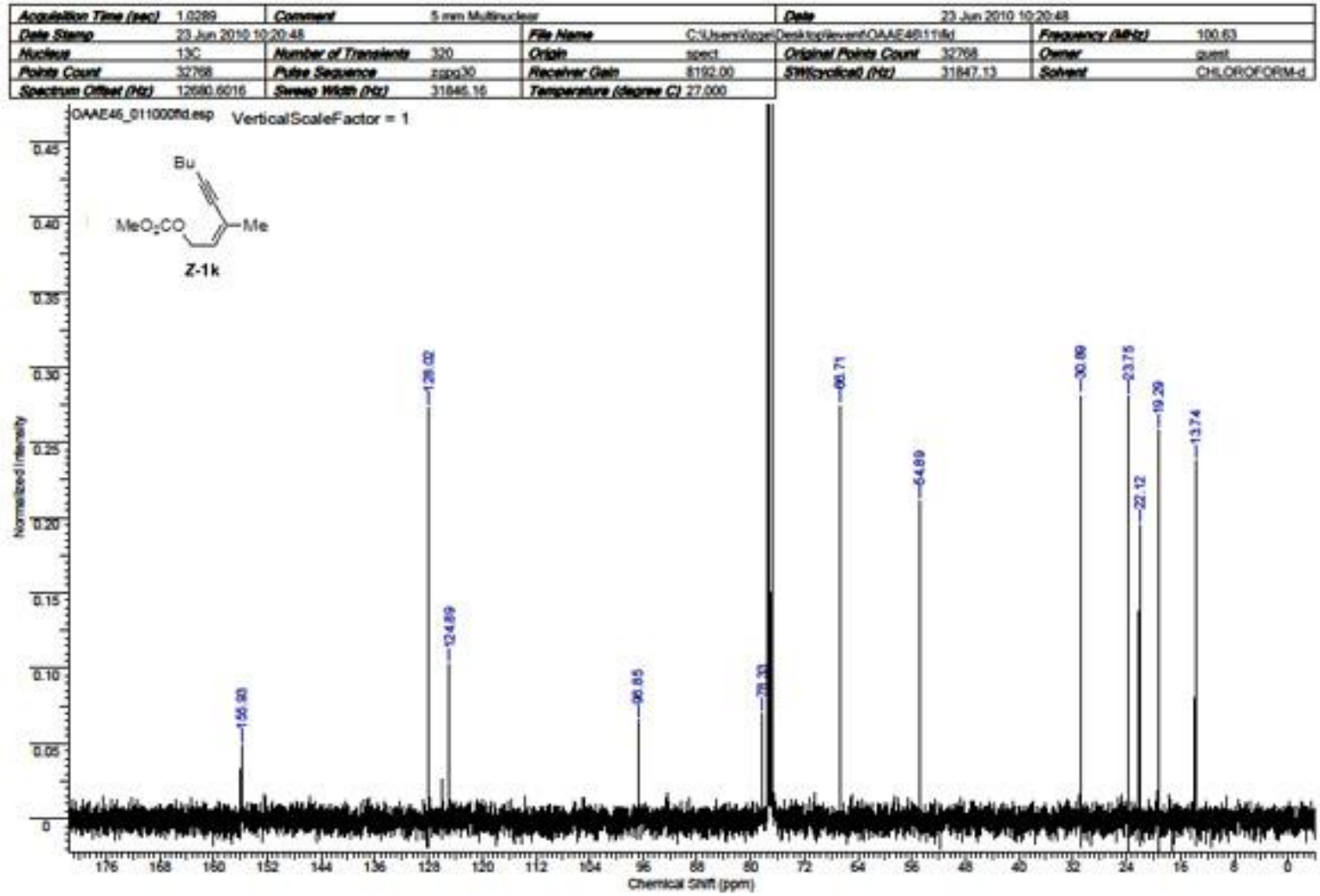


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Acquisition Time (sec) | 1.0289 | Comment | 5 mm Multinuclear | Date | 24 Aug 2010 11:05:36 | | |
| Date Stamp | 24 Aug 2010 11:05:36 | | | | | | |
| File Name | C:\Users\Ozge\Desktop\LA 2010\LA NMR FID VE COZUMLERI AGUSTOS 2010\REACTANT\OAAE67\OAAE67_011000fid | | | | | | |
| Frequency (MHz) | 100.63 | Nucleus | 13C | Number of Transients | 320 | Origin | spect |
| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zgpg30 |
| Receiver Gain | 4096.00 | SW(cycles) (Hz) | 31847.13 | Solvent | BENZENE-d6 | Spectrum Offset (Hz) | 12693.1709 |
| Sweep Width (Hz) | 31846.16 | Temperature (degree C) | 27.000 | | | | |

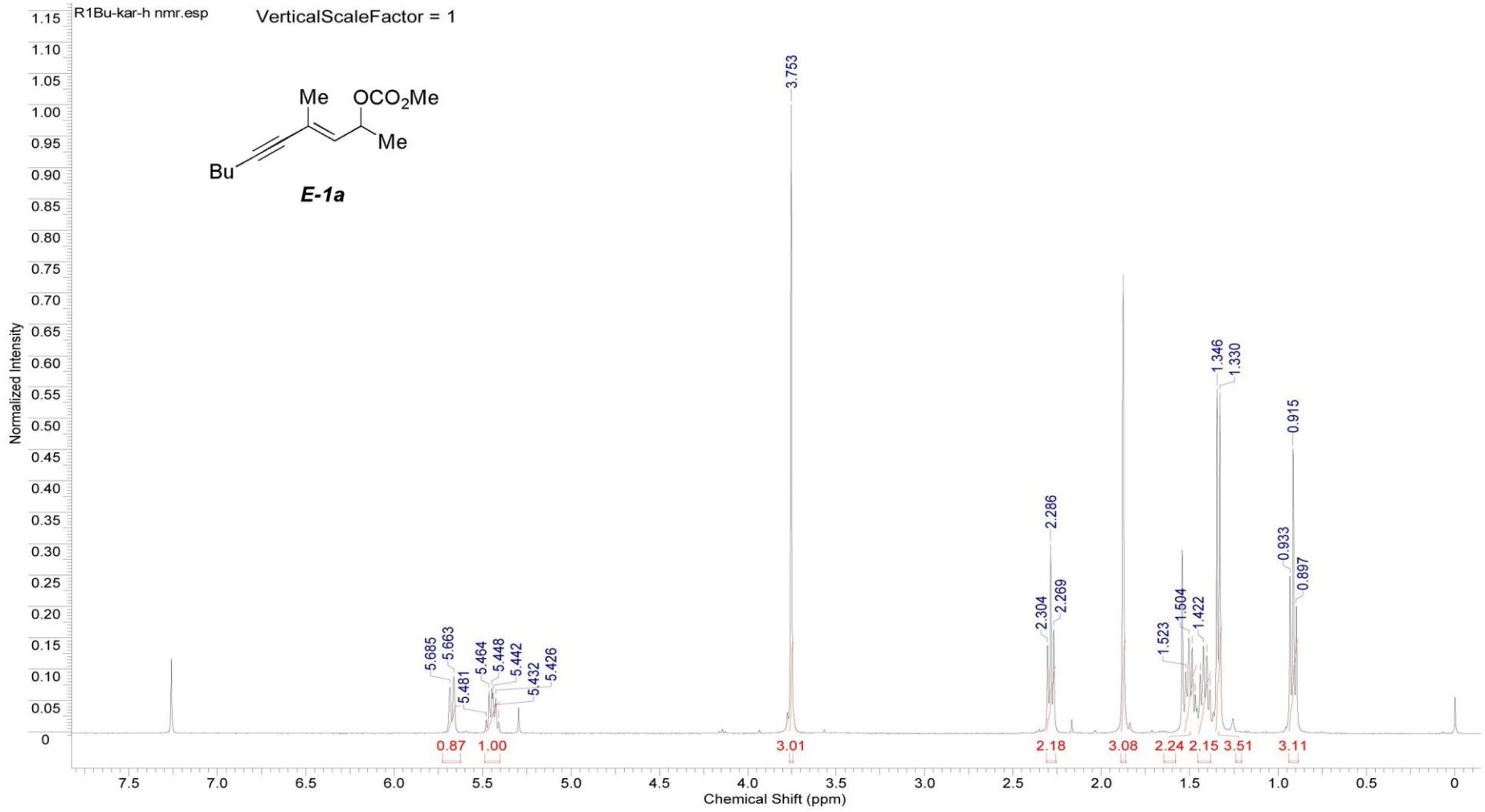


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Acquisition Time (sec) | 3.9846 | Comment | 5 mm Multinuclear | | | Date | 23 Jun 2010 10:08:00 |
| Date Stamp | 23 Jun 2010 10:08:00 | | | File Name | C:\Users\Edgar\Desktop\levent\OAAE46\10\fid | Frequency (MHz) | 400.13 |
| Nucleus | 1H | Number of Transients | 16 | Origin | spect | Original Points Count | 32768 |
| Points Count | 32768 | Pulse Sequence | zg30 | Receiver Gain | 322.50 | SW(cyclical) (Hz) | 8223.68 |
| Spectrum Offset (Hz) | 2461.3779 | Sweep Width (Hz) | 8223.43 | Temperature (degree C) | 27.000 | Owner | guest |
| | | | | | | Solvent | CHLOROFORM-d |

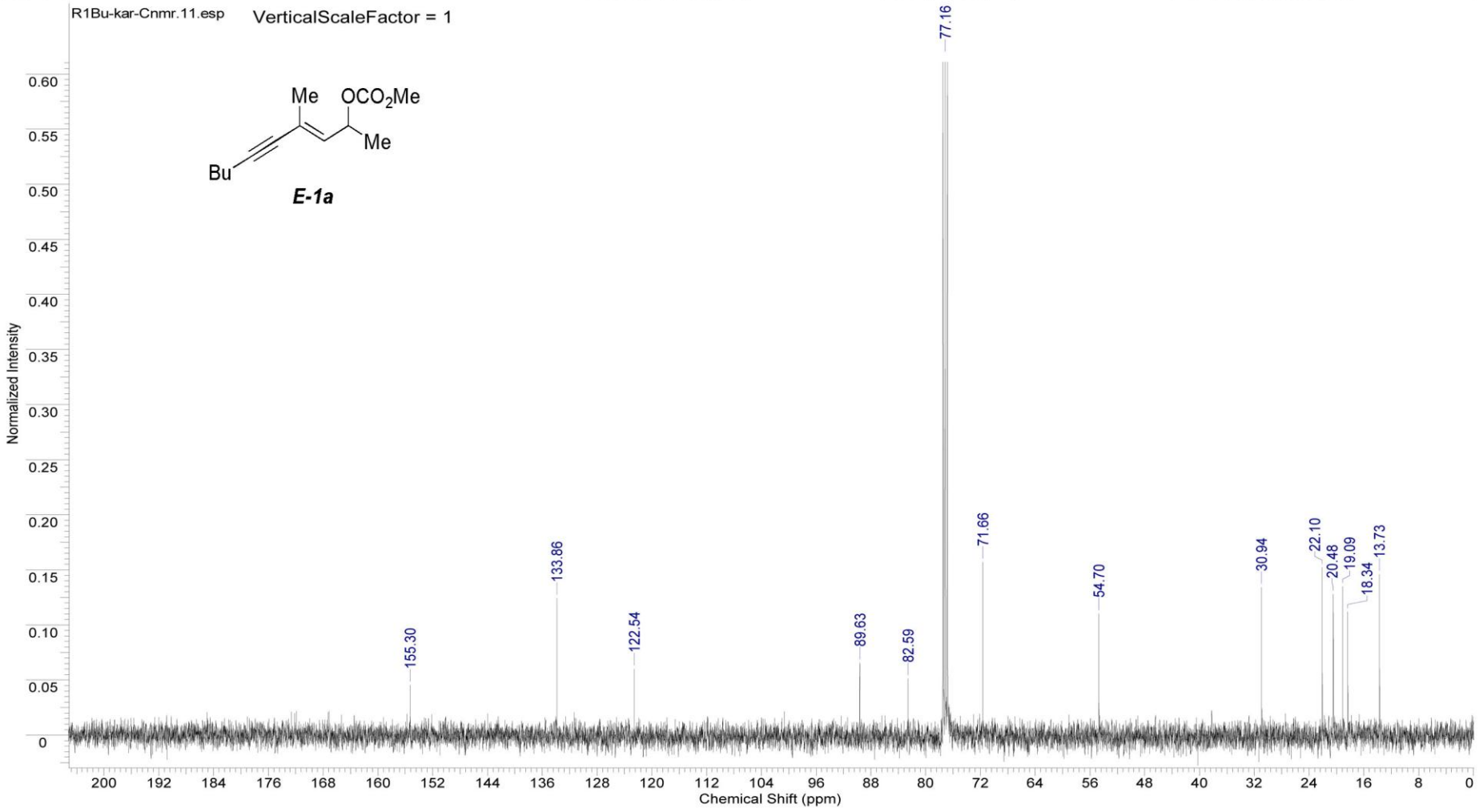



Acquisition Time (sec) 1.0289
Comment 5 mm Multinuclear
Date 23 Jun 2010 10:20:48
Date Stamp 23 Jun 2010 10:20:48
File Name C:\Users\Gigel\Desktop\levent\OAAE46\11\fid
Frequency (MHz) 100.63
Nucleus 13C
Number of Transients 320
Origin spect
Original Points Count 32768
Owner guest
Points Count 32768
Pulse Sequence zgpg30
Receiver Gain 8192.00
SW(cycles) (Hz) 31847.13
Solvent CHLOROFORM-d
Spectrum Offset (Hz) 12680.6016
Sweep Width (Hz) 31846.16
Temperature (degree C) 27.000
OAAE46_011000fid.esp
VerticalScaleFactor = 1
Bu
MeO2CO
Me
Z-1k
Normalized Intensity
Chemical Shift (ppm)
155.93
128.02
124.89
96.85
78.33
66.71
64.89
30.89
23.75
22.12
19.29
13.74

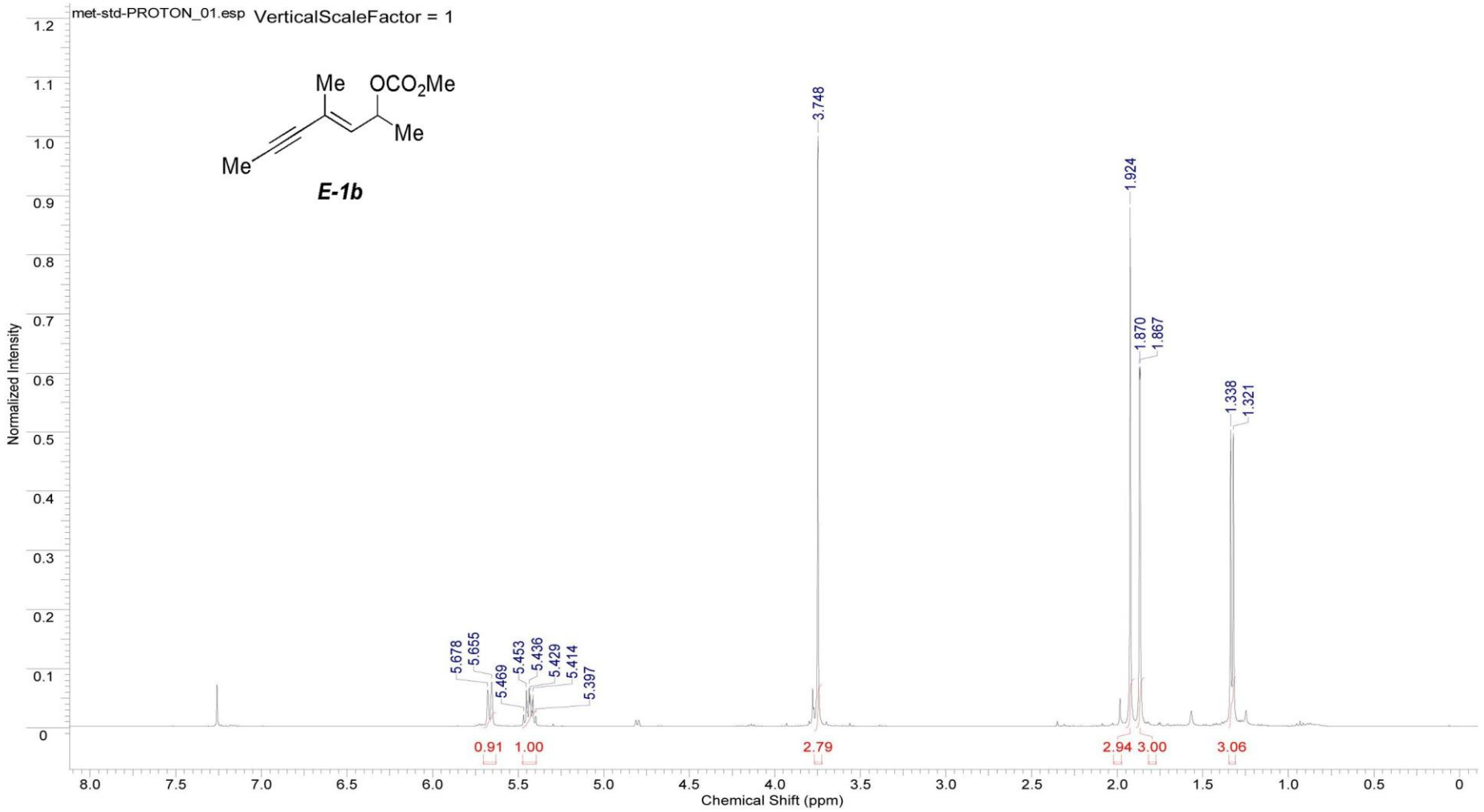
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 1.9976 | *Comment* | R1Bu-kar | *Date* | Apr 1 2011 | | | | |
| *File Name* | C:\Users\eray\Desktop\son nmrler e-kar\r1bu\R1Bu-kar-1nisan11 | | | | | *Frequency (MHz)* | 399.88 | *Nucleus* | 1H |
| *Number of Transients* | 8 | *Original Points Count* | 12764 | *Points Count* | 16384 | *Pulse Sequence* | s2pul | *Solvent* | CHLOROFORM-d |
| *Spectrum Offset (Hz)* | 2400.0662 | *Sweep Width (Hz)* | 6389.78 | *Temperature (degree C)* | 30.000 | | | | |



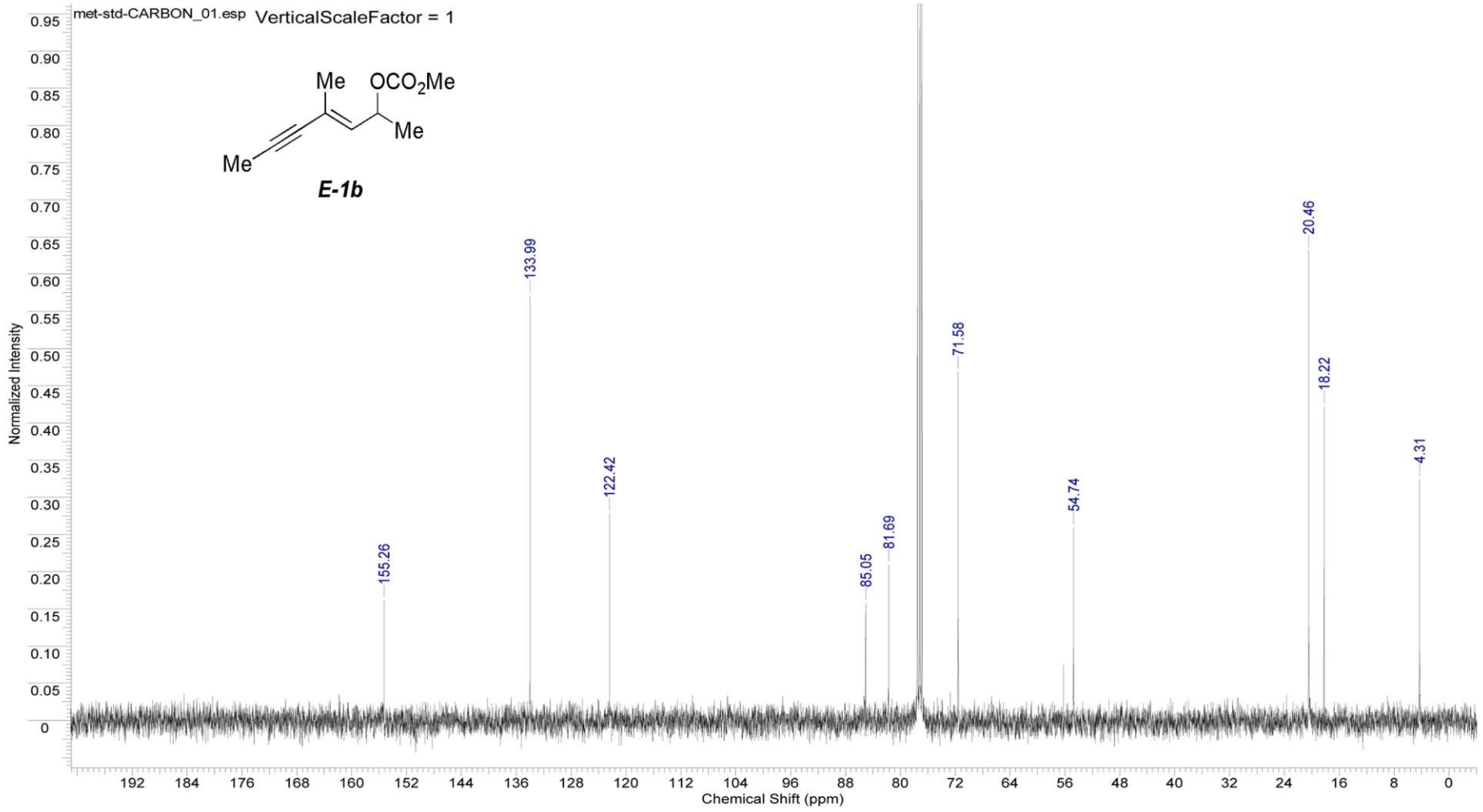
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 1.1994 | ***Comment*** | R1Bu-kar | ***Date*** | Apr 1 2011 | | | | |
| ***File Name*** | C:\Users\eray\Desktop\son nmrler e-kar\r1bu\R1Bu-kar-1nisan11 | | | | | ***Frequency (MHz)*** | 100.56 | ***Nucleus*** | 13C |
| ***Number of Transients*** | 2000 | ***Original Points Count*** | 30135 | ***Points Count*** | 32768 | ***Pulse Sequence*** | s2pul | | |
| ***Solvent*** | CHLOROFORM-d | | | ***Spectrum Offset (Hz)*** | 11055.3701 | ***Sweep Width (Hz)*** | 25125.63 | ***Temperature (degree C)*** | 30.000 |



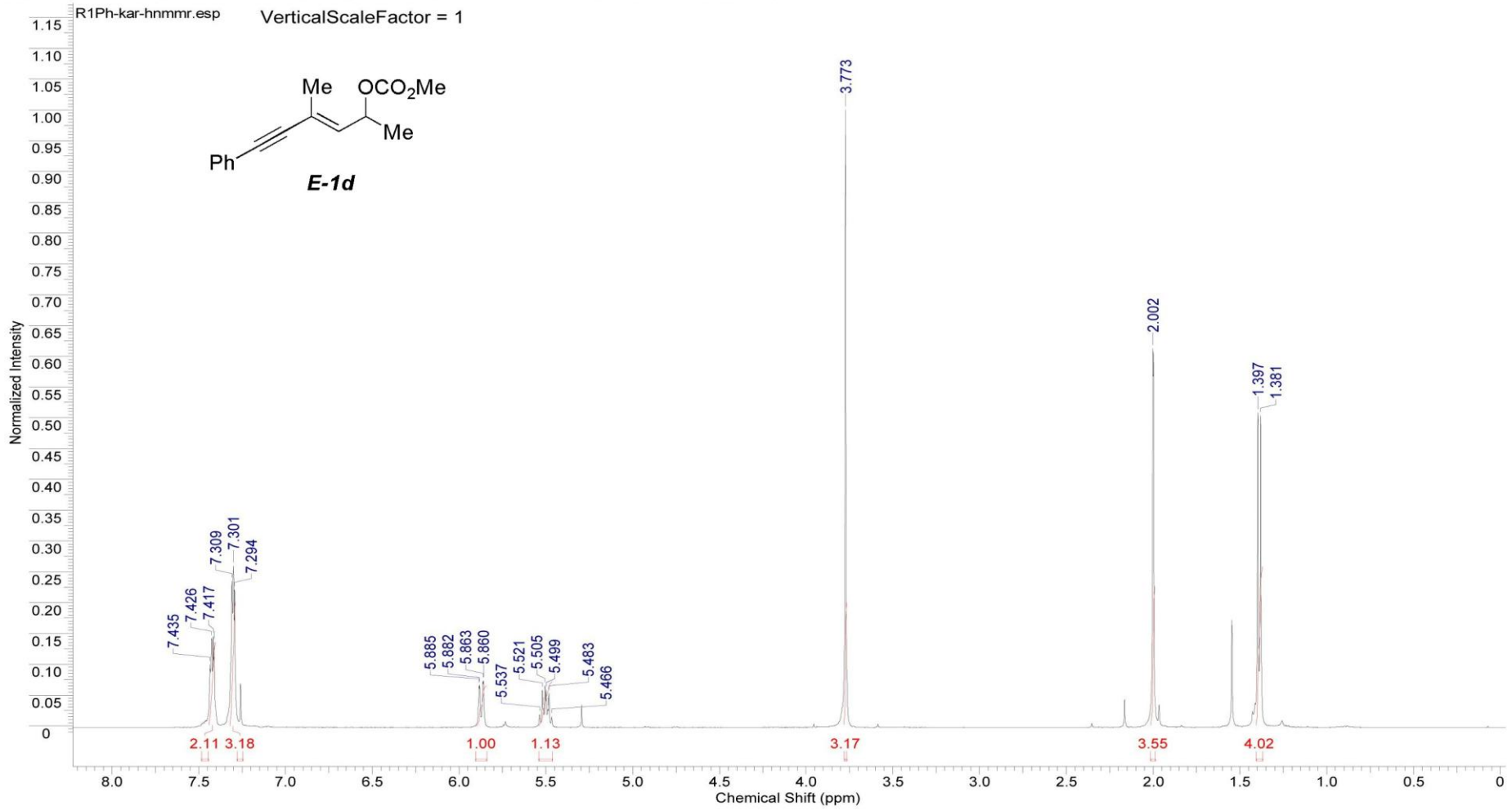
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 2.5559 | *Comment* | GEA-AE-151 | *Date* | Mar 1 2011 | *File Name* | F:\GEA-AE-151-met-std_01Mar2011\PROTON_01 | | |
| *Frequency (MHz)* | 399.52 | *Nucleus* | 1H | *Number of Transients* | 8 | *Original Points Count* | 16384 | *Points Count* | 16384 |
| *Pulse Sequence* | s2pul | *Solvent* | CHLOROFORM-d | | | *Spectrum Offset (Hz)* | 2397.1353 | *Sweep Width (Hz)* | 6410.26 |
| *Temperature (degree C)* | 22.000 | | | | | | | | |



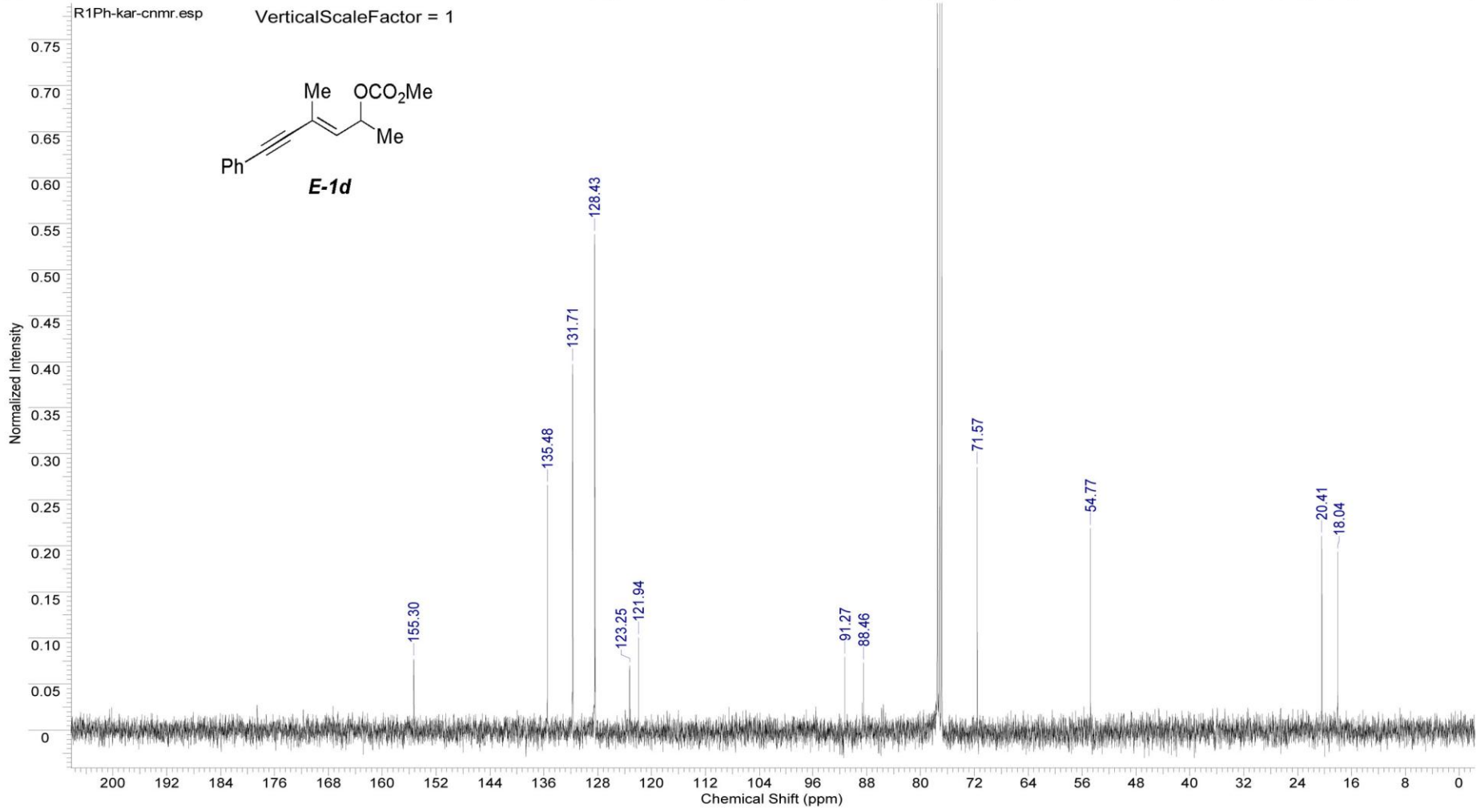
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 1.2845 | *Comment* | GEA-AE-151 | *Date* | Mar 1 2011 | *File Name* | F:\GEA-AE-151-met-std_01Mar2011\CARBON_01 | | |
| *Frequency (MHz)* | 100.47 | *Nucleus* | 13C | *Number of Transients* | 256 | *Original Points Count* | 32768 | *Points Count* | 32768 |
| *Pulse Sequence* | s2pul | *Solvent* | CHLOROFORM-d | | | *Spectrum Offset (Hz)* | 11066.1650 | *Sweep Width (Hz)* | 25510.20 |
| *Temperature (degree C)* | 22.000 | | | | | | | | |



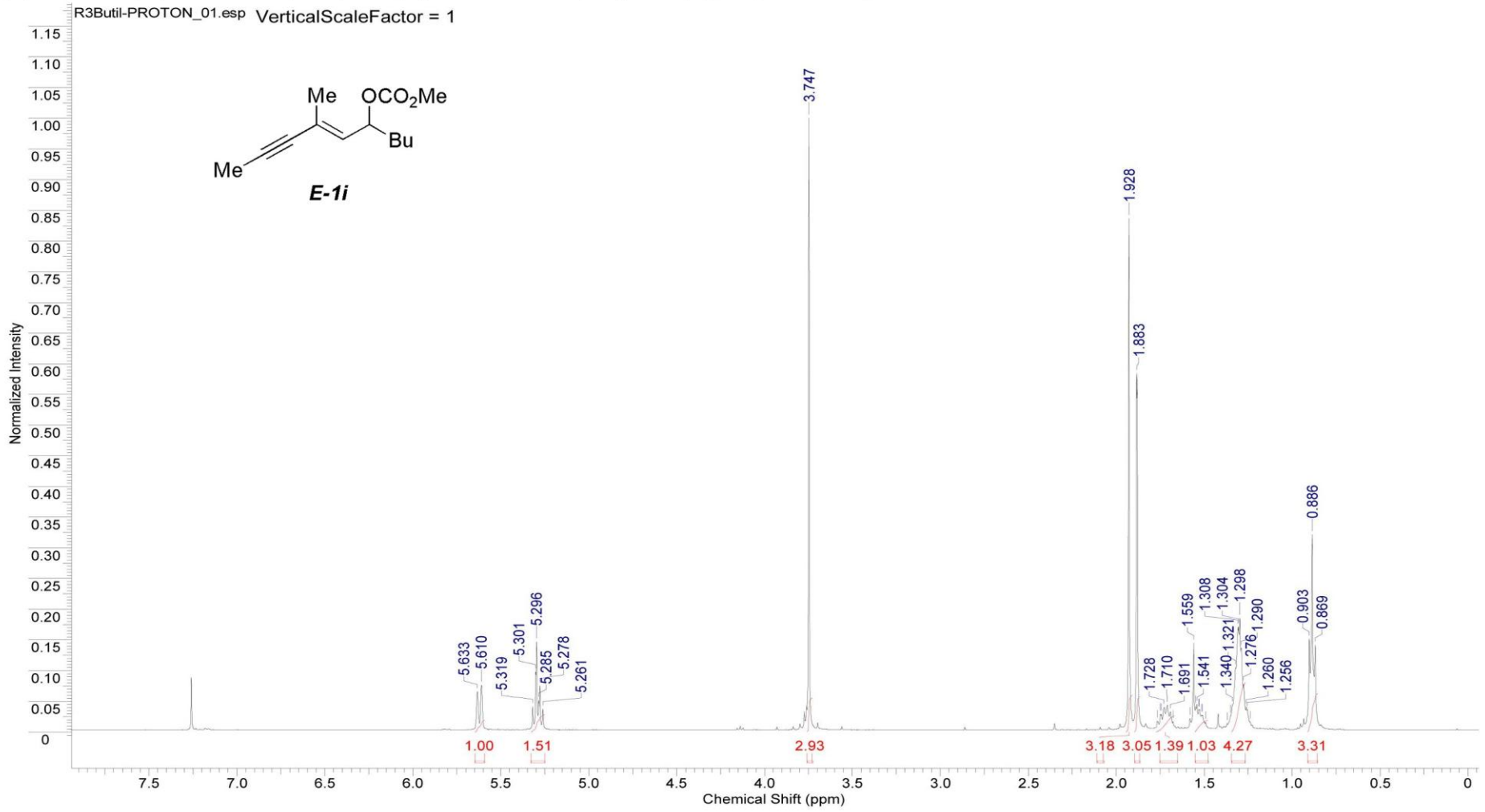
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 1.9976 | *Comment* | R1Ph-KAR | *Date* | Apr 1 2011 | | | | |
| *File Name* | C:\Users\eray\Desktop\son nmrler e-kar\r1ph\R1Ph-kar-1nisan11 | | | | | *Frequency (MHz)* | 399.88 | *Nucleus* | 1H |
| *Number of Transients* | 8 | *Original Points Count* | 12764 | *Points Count* | 16384 | *Pulse Sequence* | s2pul | *Solvent* | CHLOROFORM-d |
| *Spectrum Offset (Hz)* | 2399.2761 | *Sweep Width (Hz)* | 6389.78 | *Temperature (degree C)* | 30.000 | | | | |



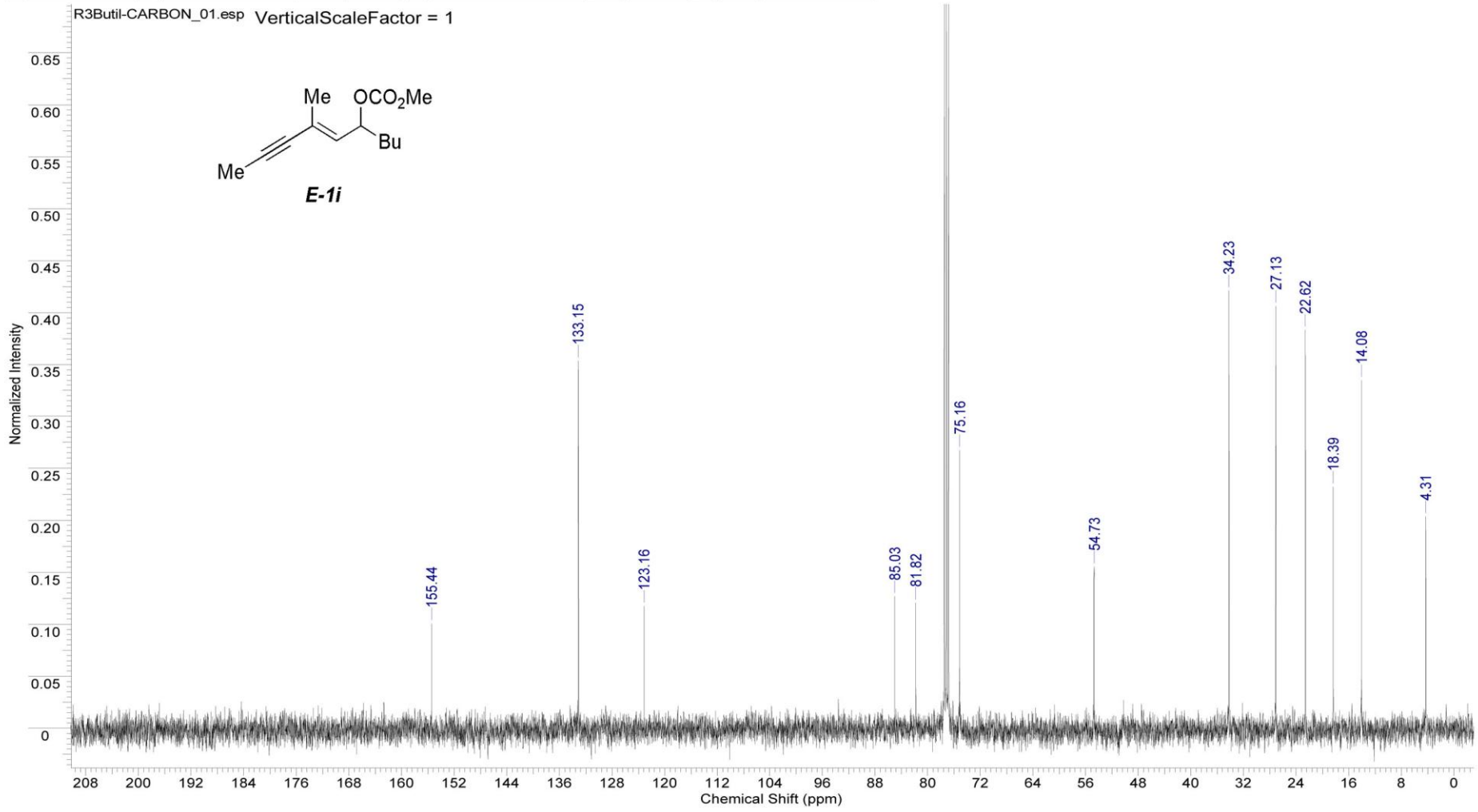
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 1.1994 | *Comment* | R1Ph-KAR | *Date* | Apr 1 2011 | | | | |
| *File Name* | C:\Users\eray\Desktop\son nmrler e-kar\r1ph\R1Ph-kar-1nisan11 | | | | | *Frequency (MHz)* | 100.56 | *Nucleus* | 13C |
| *Number of Transients* | 2000 | *Original Points Count* | 30135 | *Points Count* | 32768 | *Pulse Sequence* | s2pul | | |
| *Solvent* | CHLOROFORM-d | | | *Spectrum Offset (Hz)* | 11054.6035 | *Sweep Width (Hz)* | 25125.63 | *Temperature (degree C)* | 30.000 |



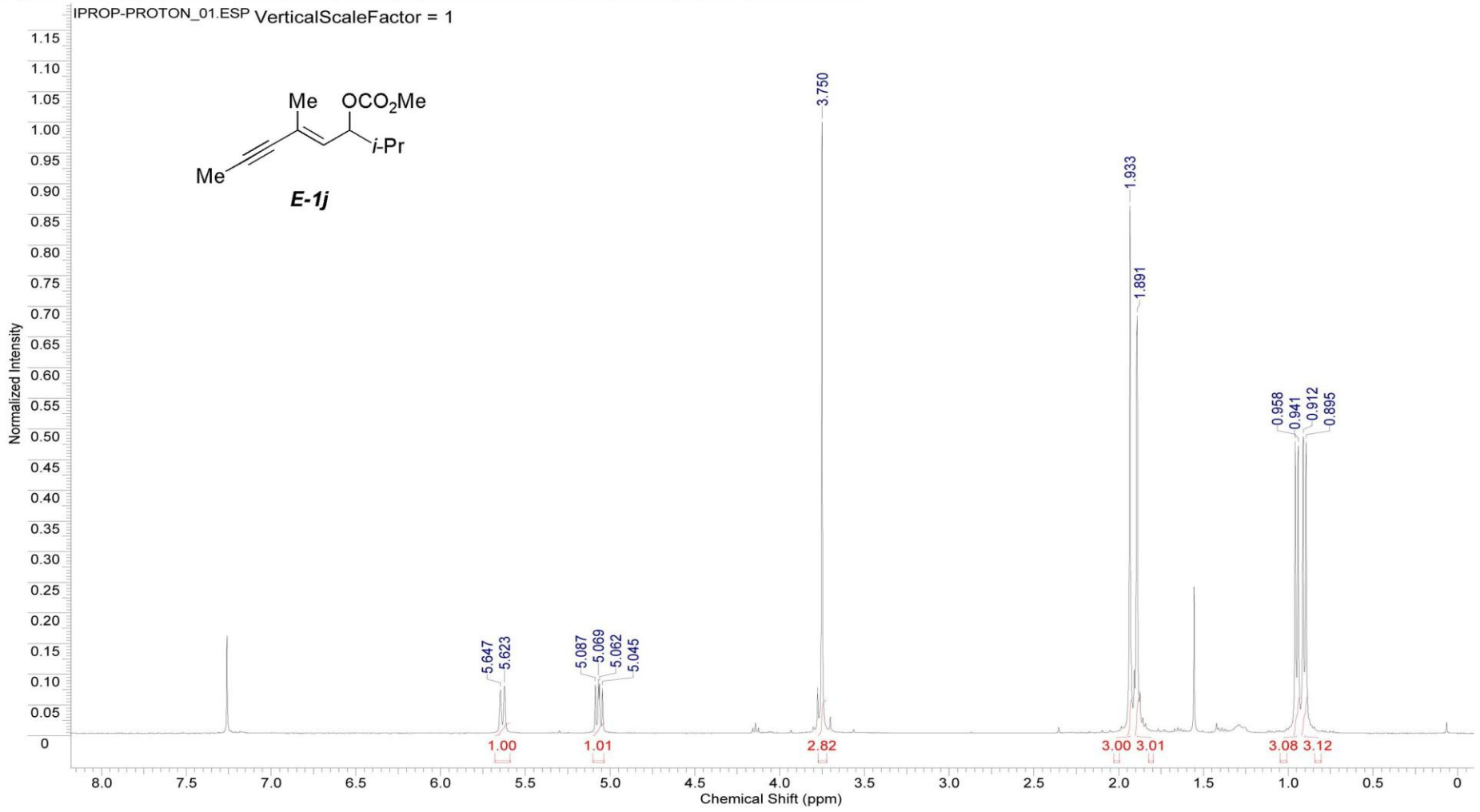
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 2.5559 | *Comment* | MU-R3-BU-KAR | | | *Date* | Mar 24 2011 | | |
| *File Name* | F:\nmr-son\MU-R3-BU-KAR_24Mar2011\PROTON_01 | | | *Frequency (MHz)* | 399.52 | *Nucleus* | 1H | *Number of Transients* | 8 |
| *Original Points Count* | 16384 | *Points Count* | 16384 | *Pulse Sequence* | s2pul | *Solvent* | CHLOROFORM-d | | |
| *Spectrum Offset (Hz)* | 2397.1353 | *Sweep Width (Hz)* | 6410.26 | *Temperature (degree C)* | 20.000 | | | | |



| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 1.2845 | ***Comment*** | MU-R3-BU-KAR | | | ***Date*** | Mar 24 2011 | | |
| ***File Name*** | F:\nmr-son\MU-R3-BU-KAR_24Mar2011\CARBON_01 | | | ***Frequency (MHz)*** | 100.47 | ***Nucleus*** | 13C | ***Number of Transients*** | 512 |
| ***Original Points Count*** | 32768 | ***Points Count*** | 32768 | ***Pulse Sequence*** | s2pul | ***Solvent*** | CHLOROFORM-d | | |
| ***Spectrum Offset (Hz)*** | 11066.1650 | ***Sweep Width (Hz)*** | 25510.20 | ***Temperature (degree C)*** | 20.000 | | | | |

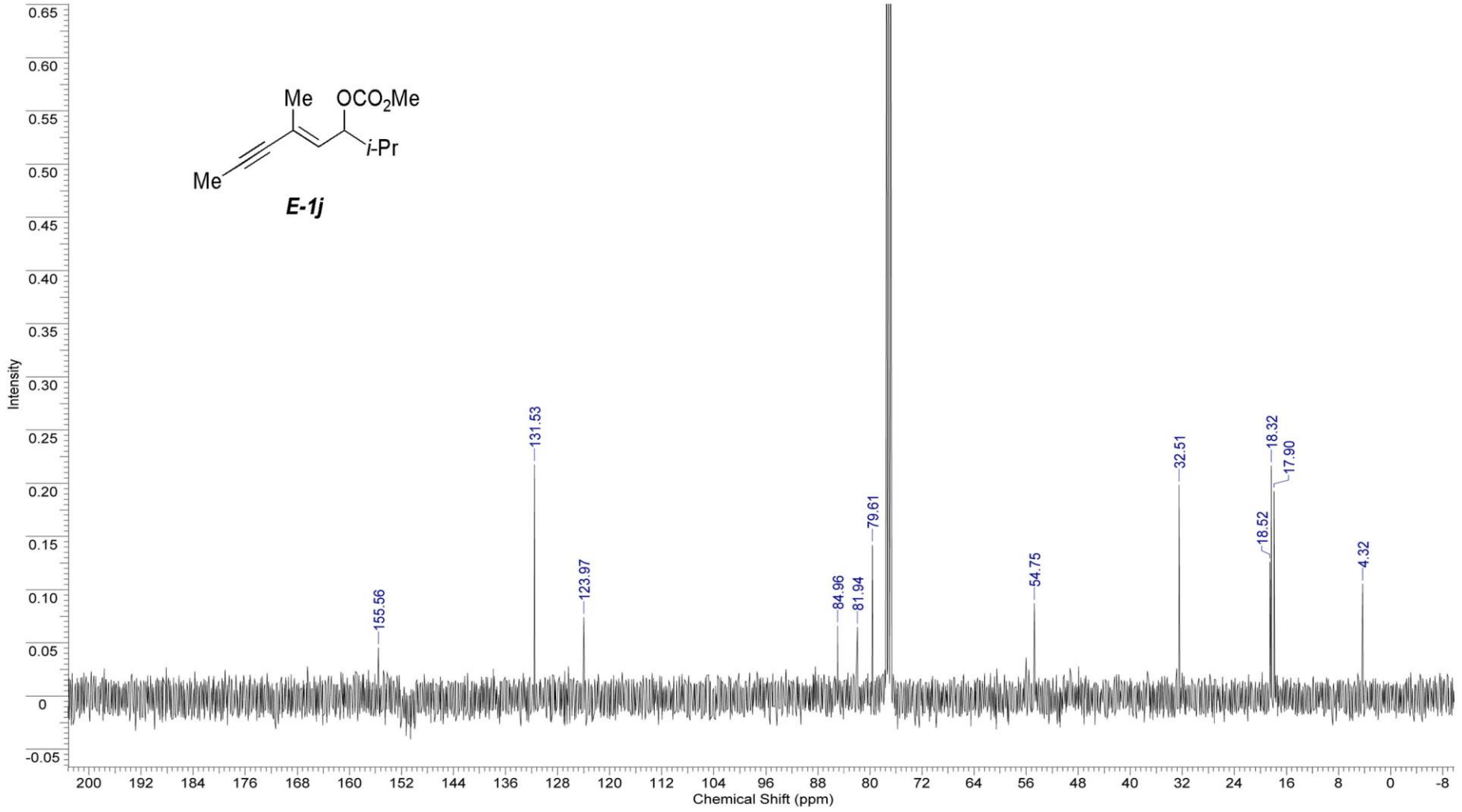


| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 2.5559 | ***Comment*** | MU-IZO-KAR | | | ***Date*** | Mar 24 2011 | | |
| ***File Name*** | F:\nmr-son\MU-IZO-KAR_24Mar2011\PROTON_01 | | | ***Frequency (MHz)*** | 399.52 | ***Nucleus*** | 1H | ***Number of Transients*** | 8 |
| ***Original Points Count*** | 16384 | ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Solvent*** | CHLOROFORM-d | | |
| ***Spectrum Offset (Hz)*** | 2397.5632 | ***Sweep Width (Hz)*** | 6410.26 | ***Temperature (degree C)*** | 20.000 | | | | |

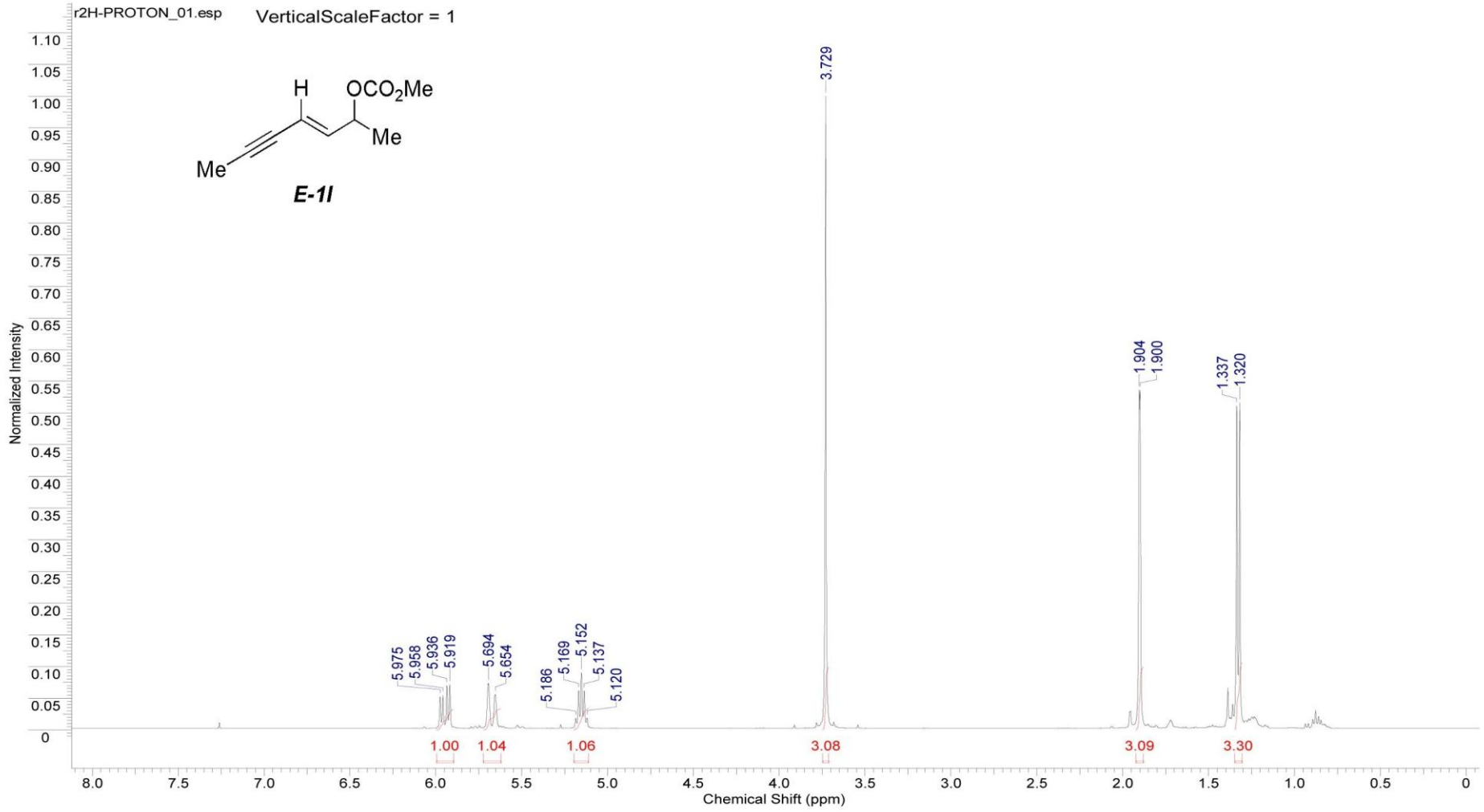


2 Apr 2011

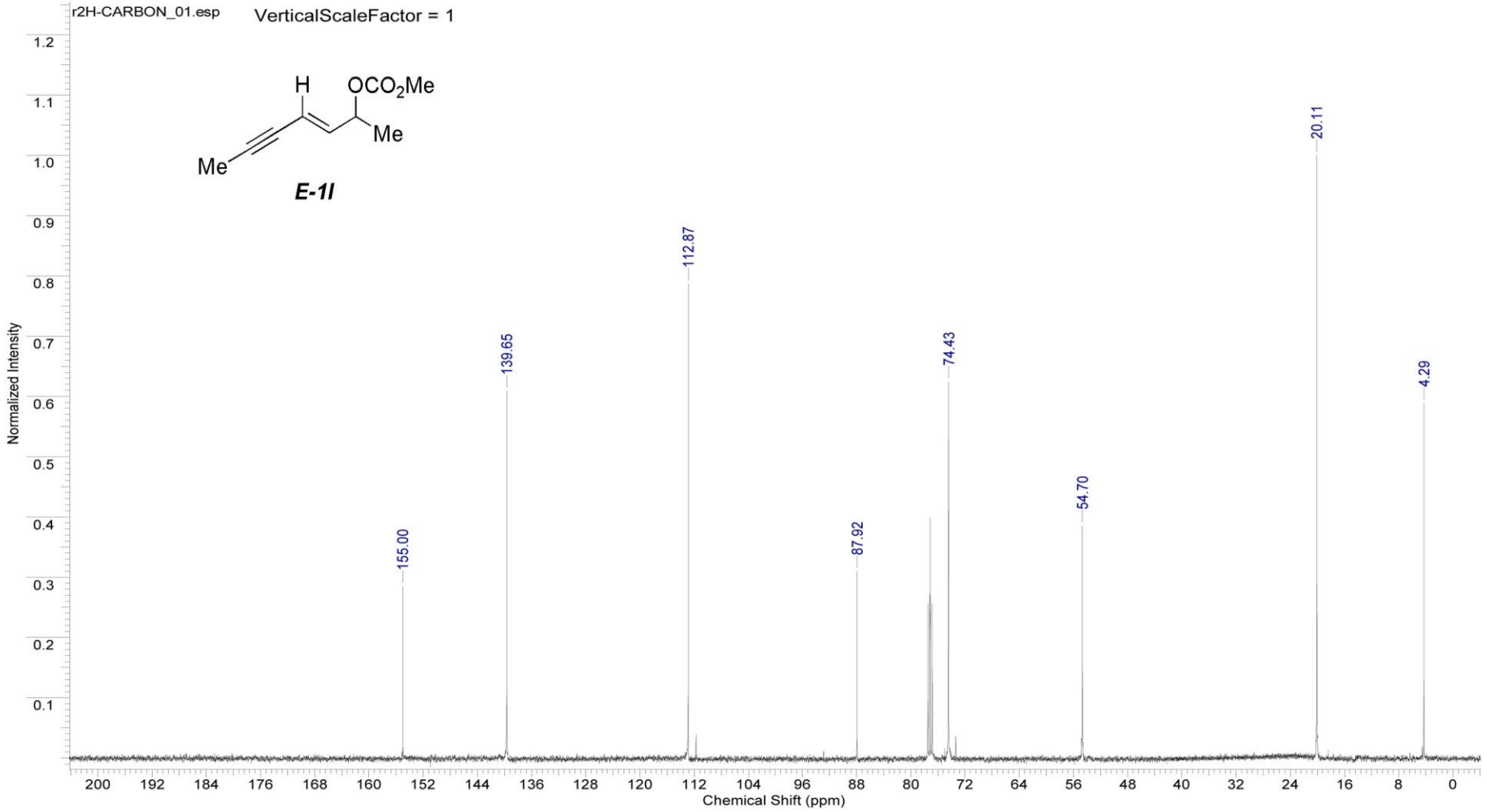
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 1.2845 | ***Comment*** | MU-IZO-KAR | ***Date*** | Mar 24 2011 | ***File Name*** | F:\nmr-son\MU-IZO-KAR_24Mar2011\CARBON_01 | | |
| ***Frequency (MHz)*** | 100.47 | ***Nucleus*** | 13C | ***Number of Transients*** | 512 | ***Original Points Count*** | 32768 | ***Points Count*** | 32768 |
| ***Pulse Sequence*** | s2pul | ***Solvent*** | CHLOROFORM-D | | | ***Sweep Width (Hz)*** | 25510.20 | ***Temperature (degree C)*** | 20.000 |



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 2.5559 | *Comment* | MU-E-ENYNE | | | *Date* | Dec 20 2010 | |
| *File Name* | F:\MU-E-ENYNE_20Dec2010\PROTON_01 | | | *Frequency (MHz)* | 399.52 | *Nucleus* | 1H | *Number of Transients* 8 |
| *Original Points Count* | 16384 | *Points Count* | 16384 | *Pulse Sequence* | s2pul | *Solvent* | CHLOROFORM-d | |
| *Spectrum Offset (Hz)* | 2397.1353 | *Sweep Width (Hz)* | 6410.26 | *Temperature (degree C)* | 20.000 | | | |

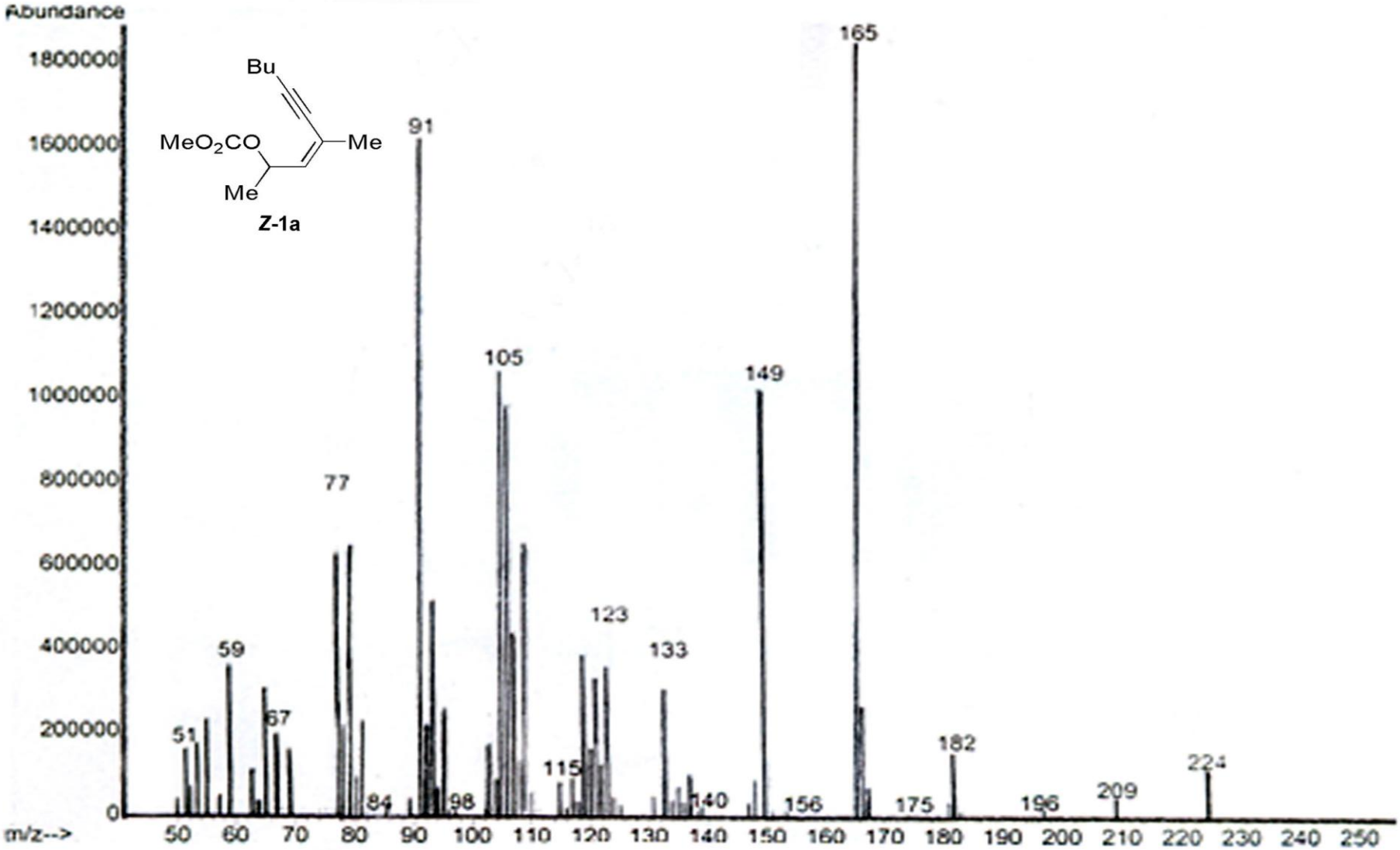


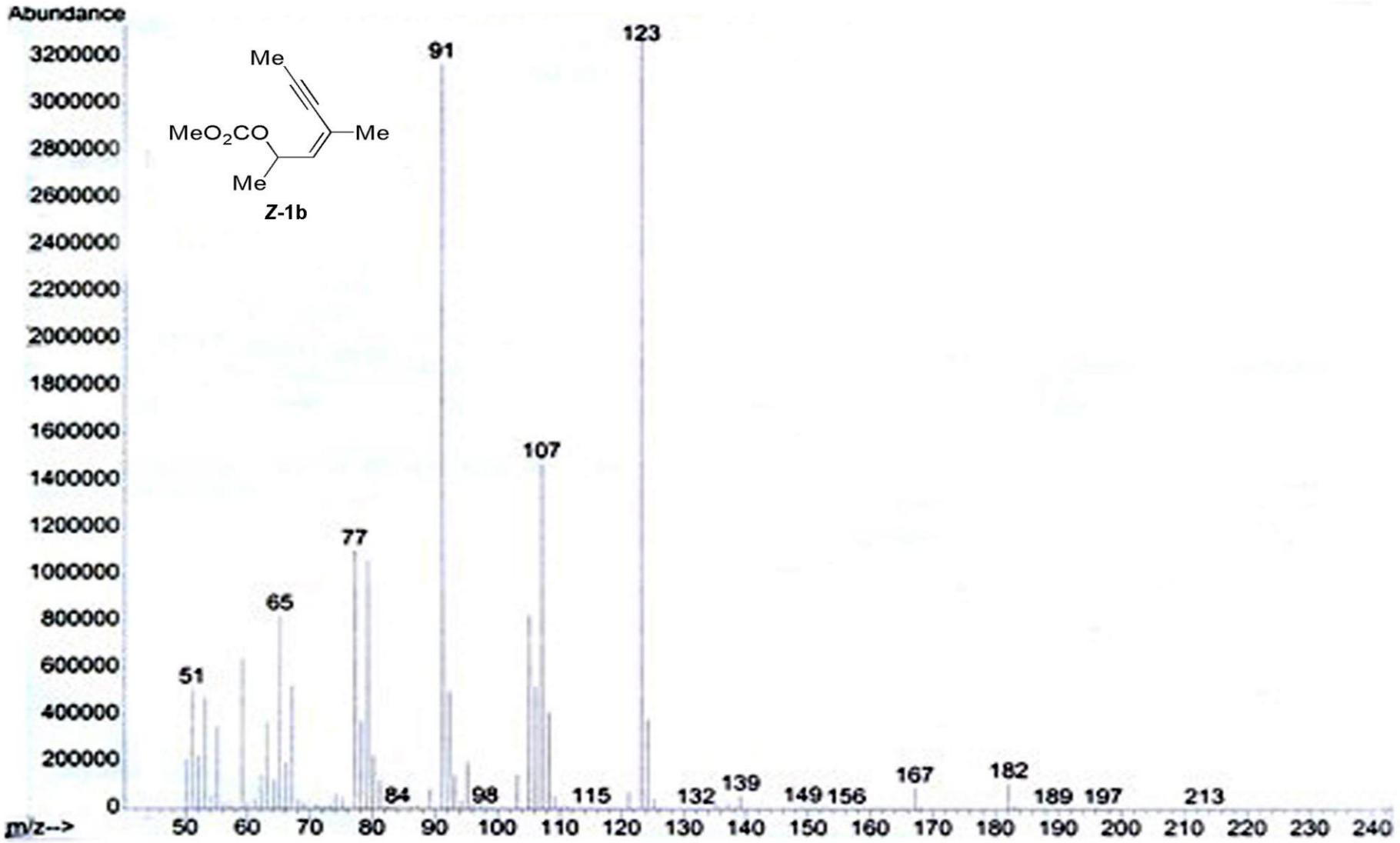
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 1.2845 | *Comment* | MU-E-ENYNE | | | *Date* | Dec 20 2010 | | |
| *File Name* | F:\MU-E-ENYNE_20Dec2010\CARBON_01 | | | *Frequency (MHz)* | 100.47 | *Nucleus* | 13C | *Number of Transients* | 256 |
| *Original Points Count* | 32768 | *Points Count* | 32768 | *Pulse Sequence* | s2pul | *Solvent* | CHLOROFORM-d | | |
| *Spectrum Offset (Hz)* | 11061.4941 | *Sweep Width (Hz)* | 25510.20 | *Temperature (degree C)* | 20.000 | | | | |

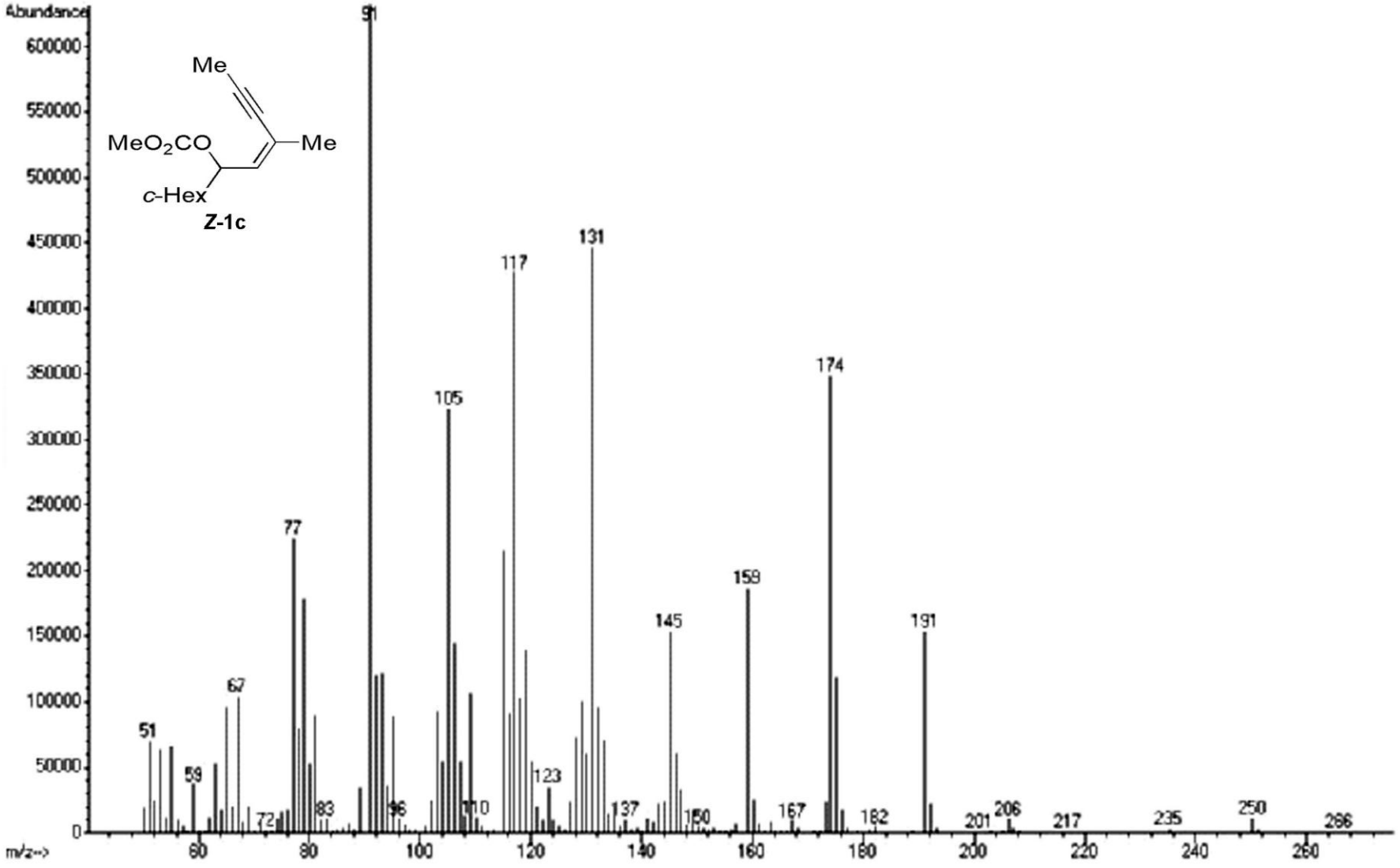


# APPENDIX B

# MASS SPECTRUMS OF REACTANTS


Abundance
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
m/z-->
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250
Bu
MeO2CO
Me
Me
Z-1a
165
91
105
149
77
123
133
59
51
67
84
98
115
140
156
175
182
196
209
224


Abundance
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
m/z-->
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240
91
123
107
77
65
51
84
98
115
132
139
149
156
167
182
189
197
213
Me
MeO2CO
Me
Me
Z-1b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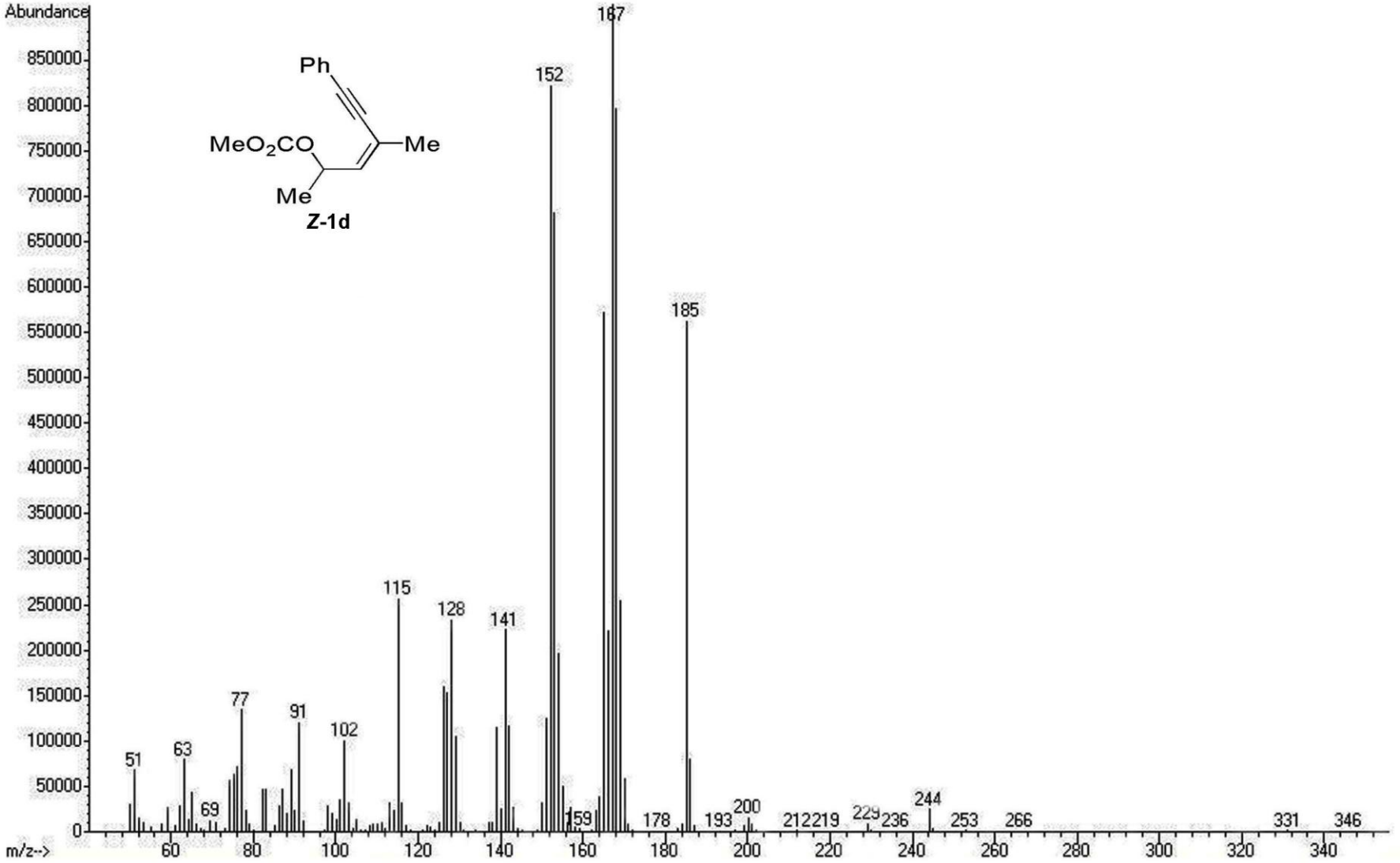
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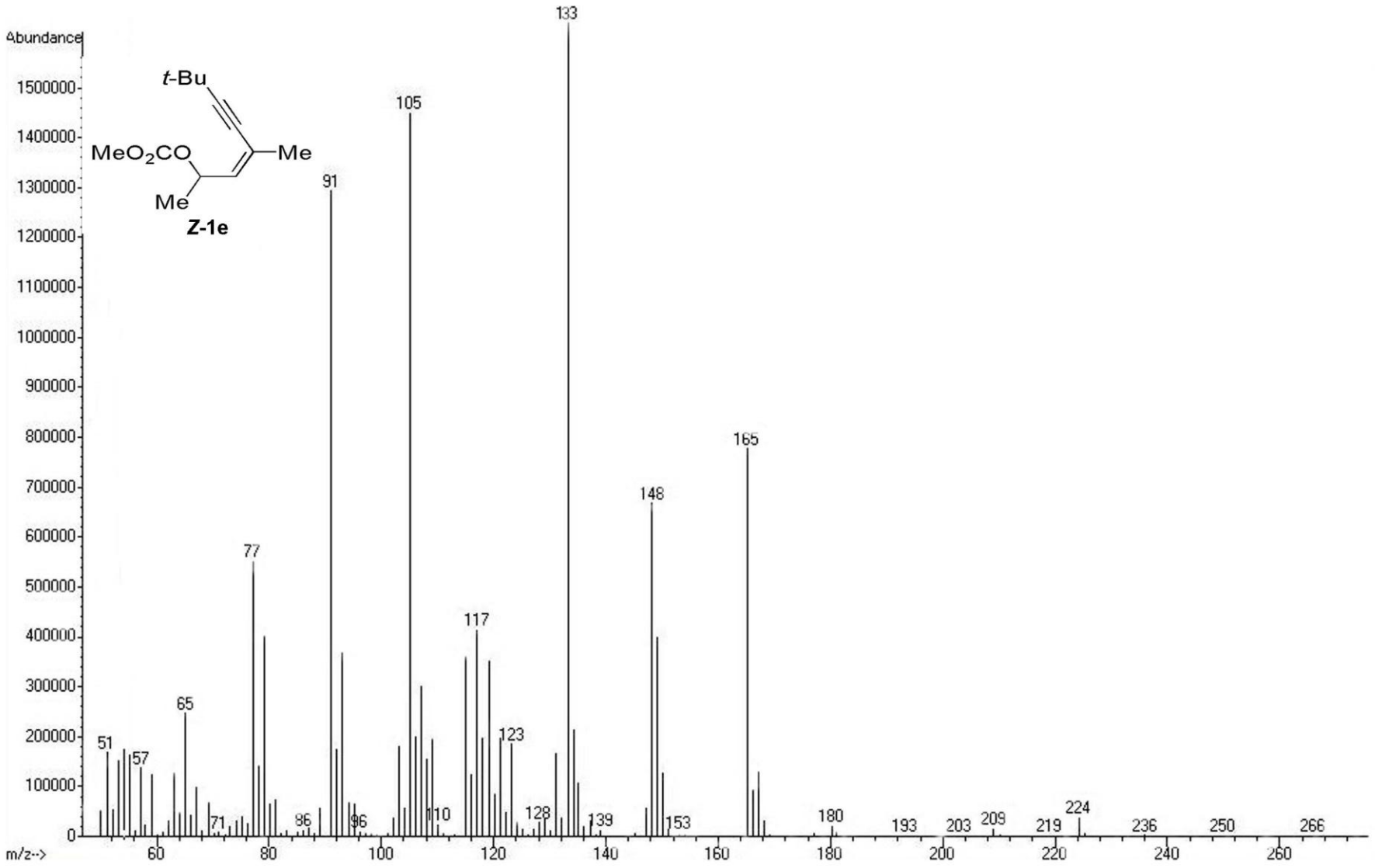
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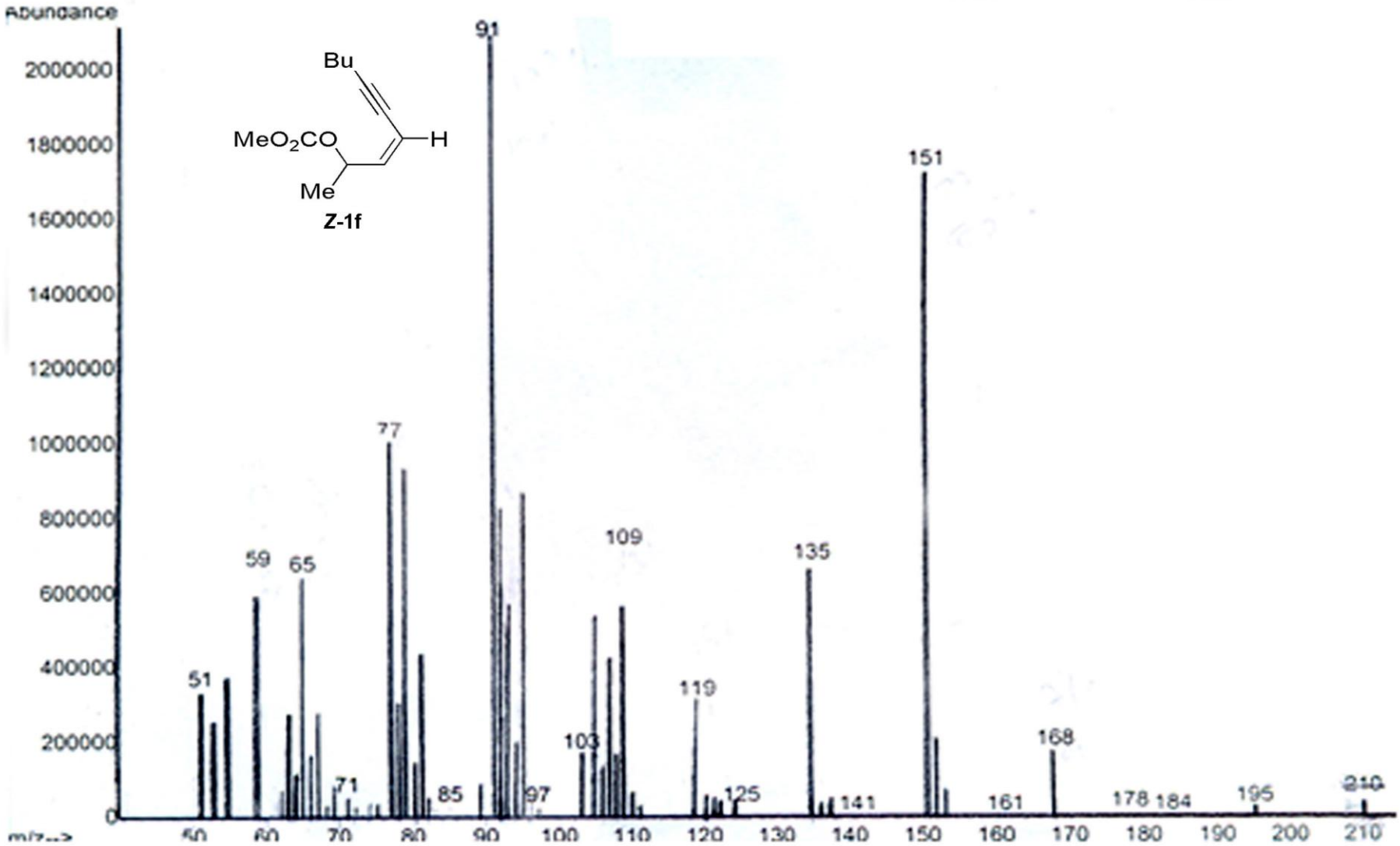
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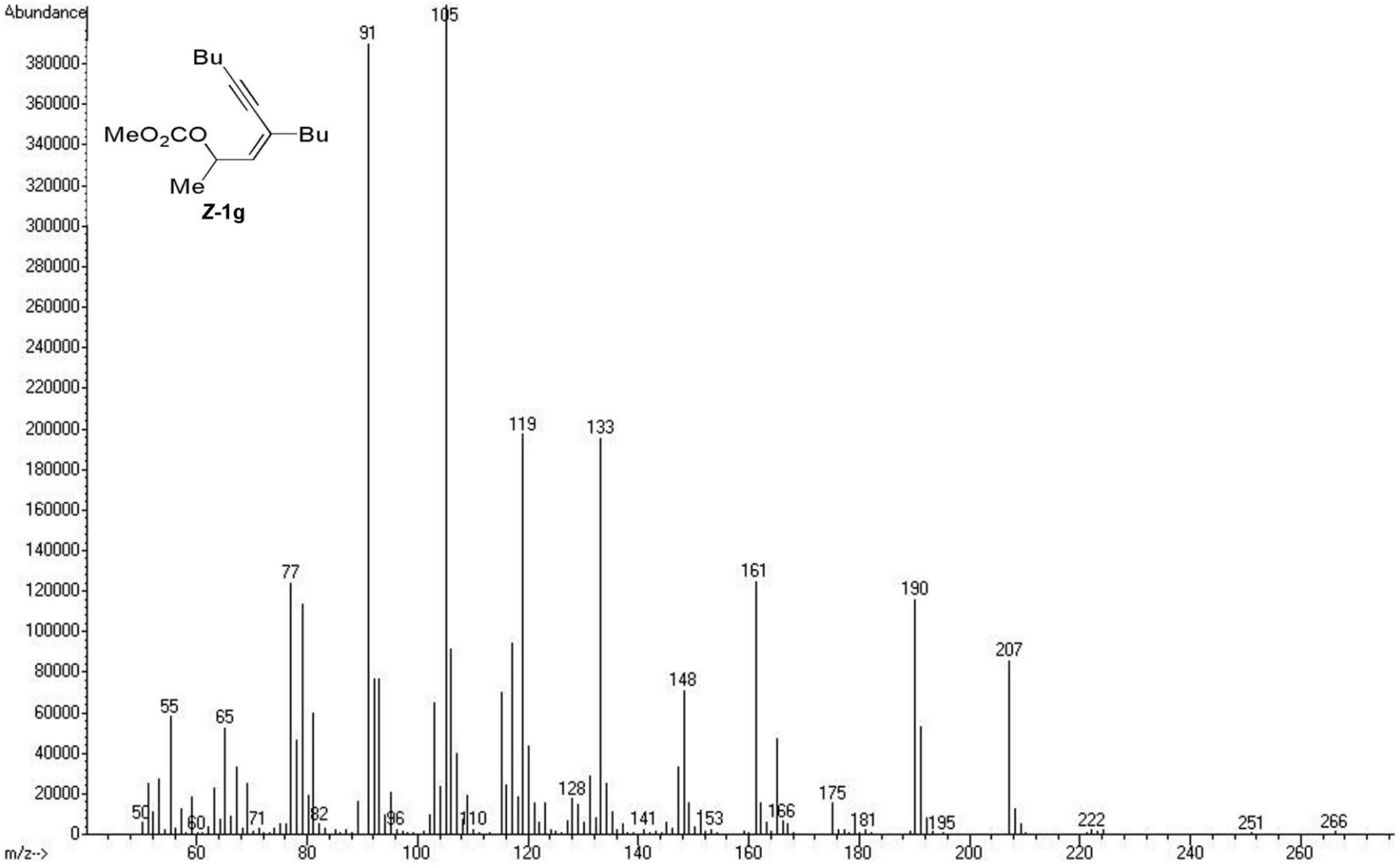
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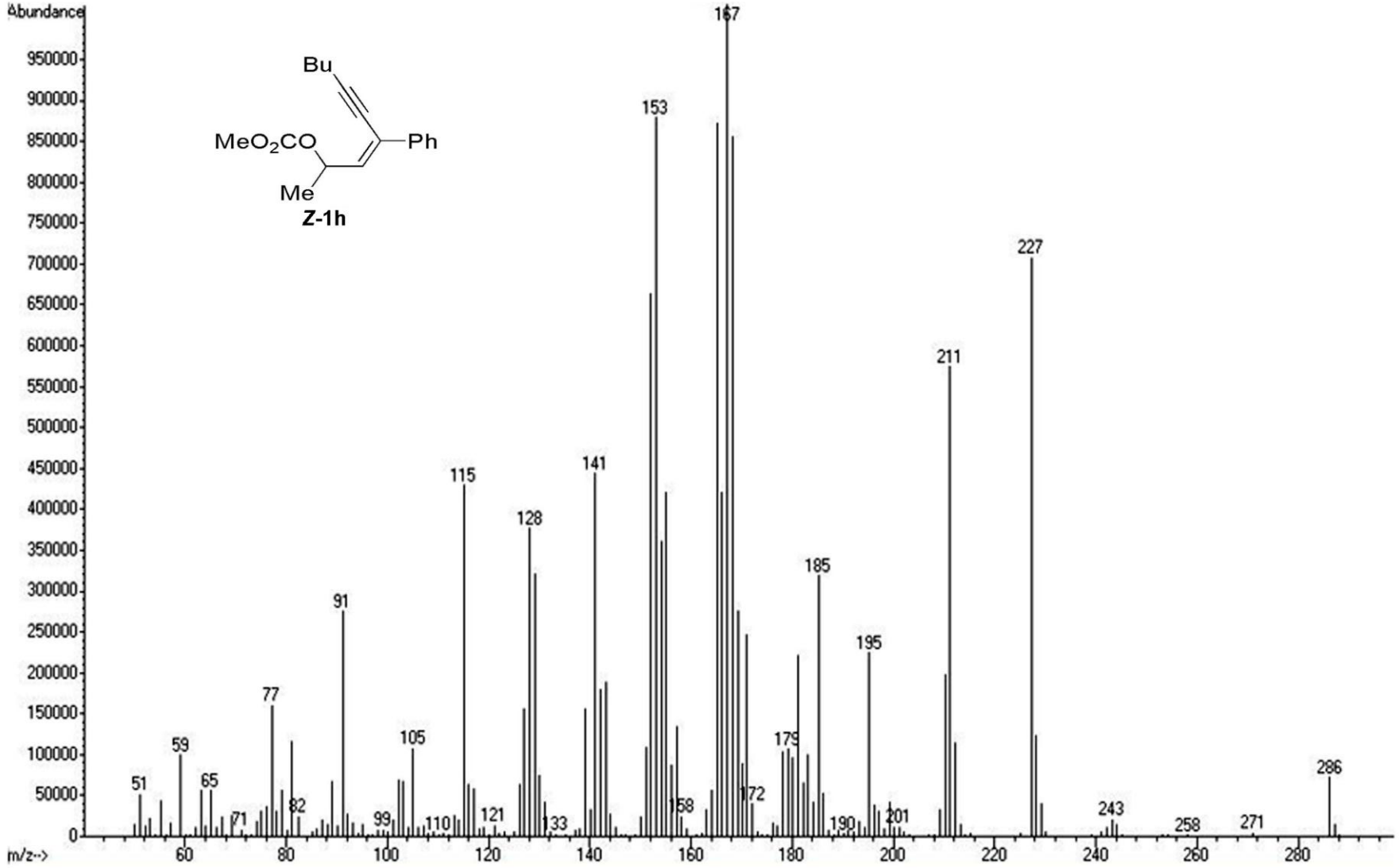
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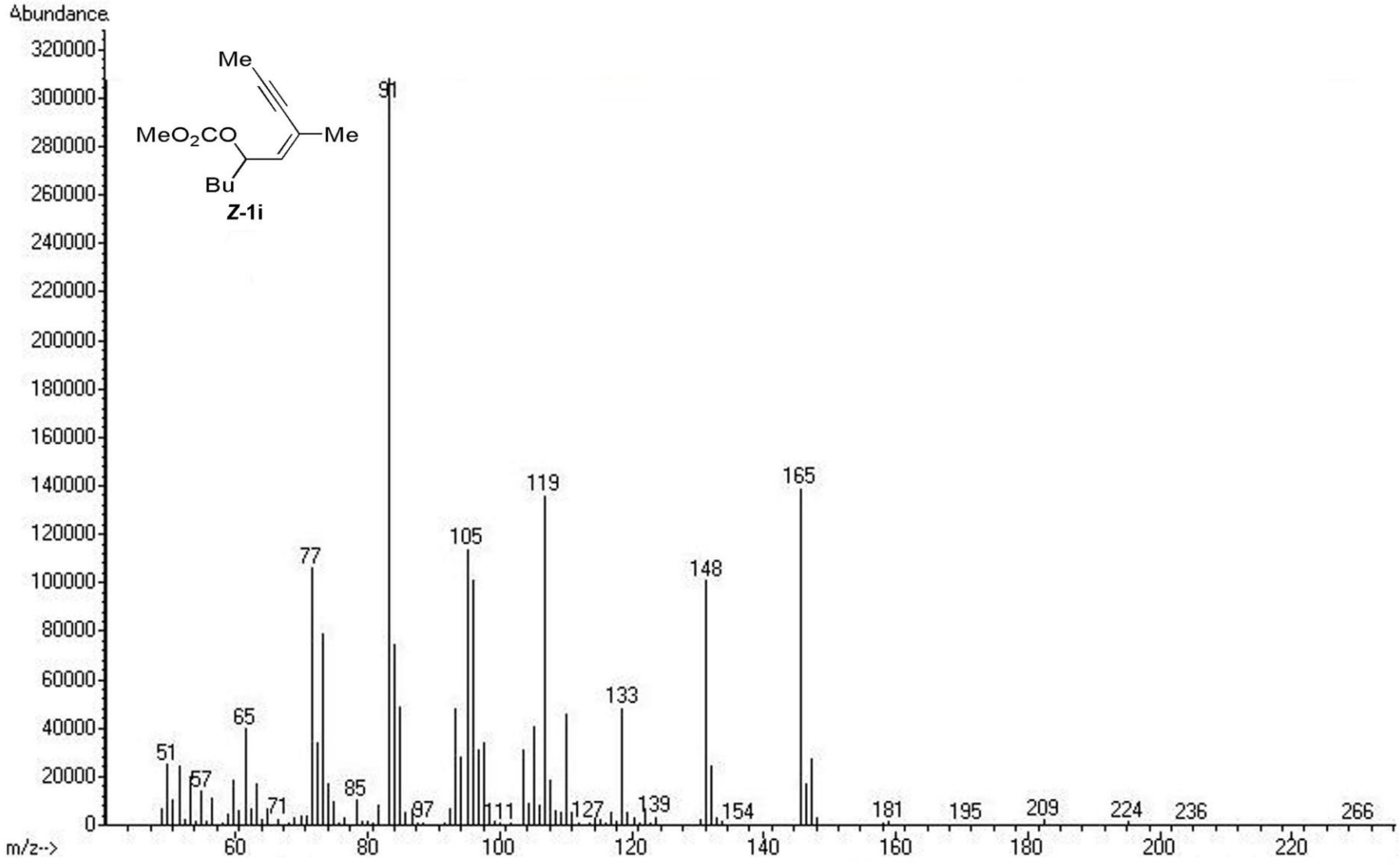
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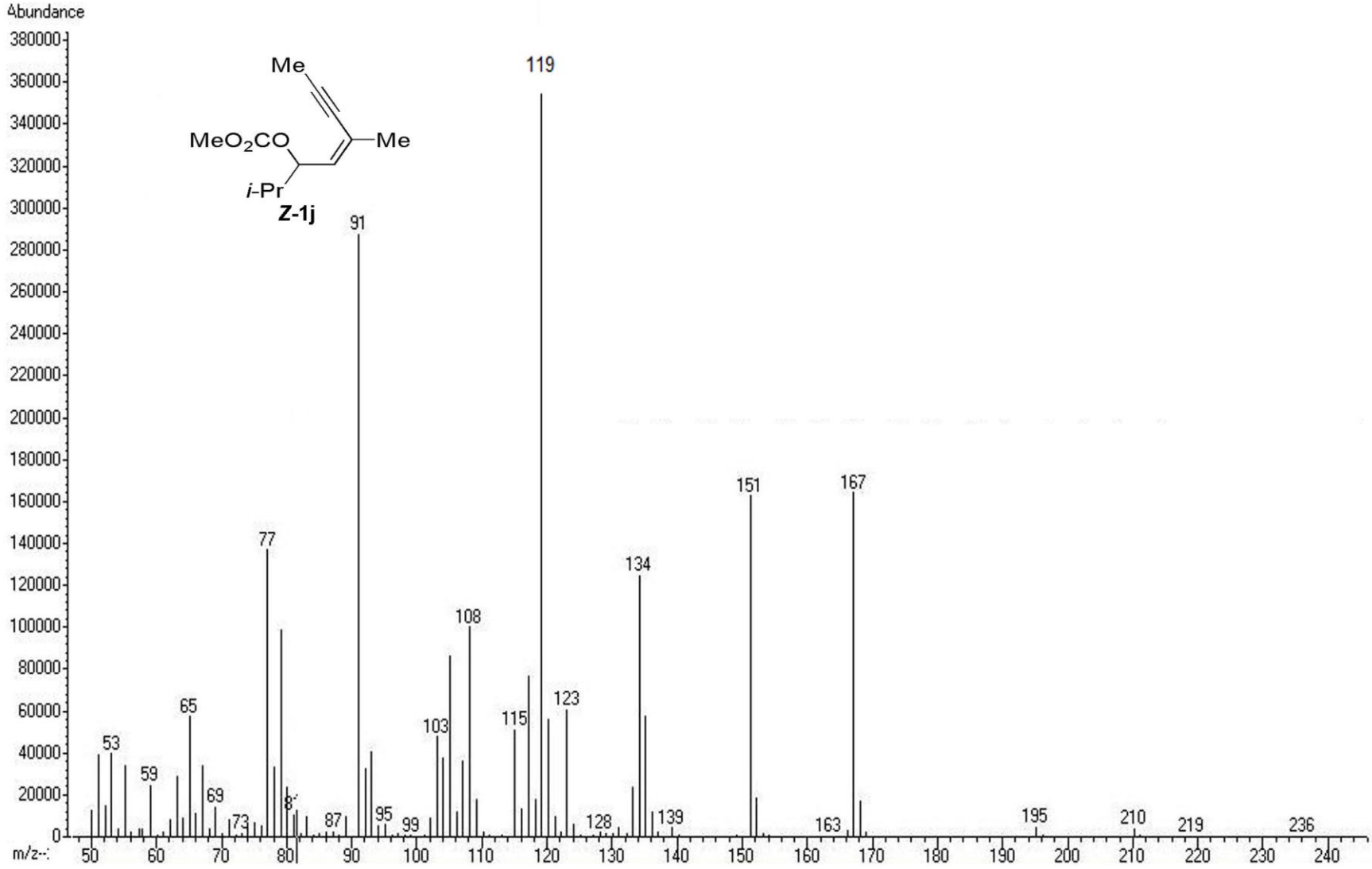
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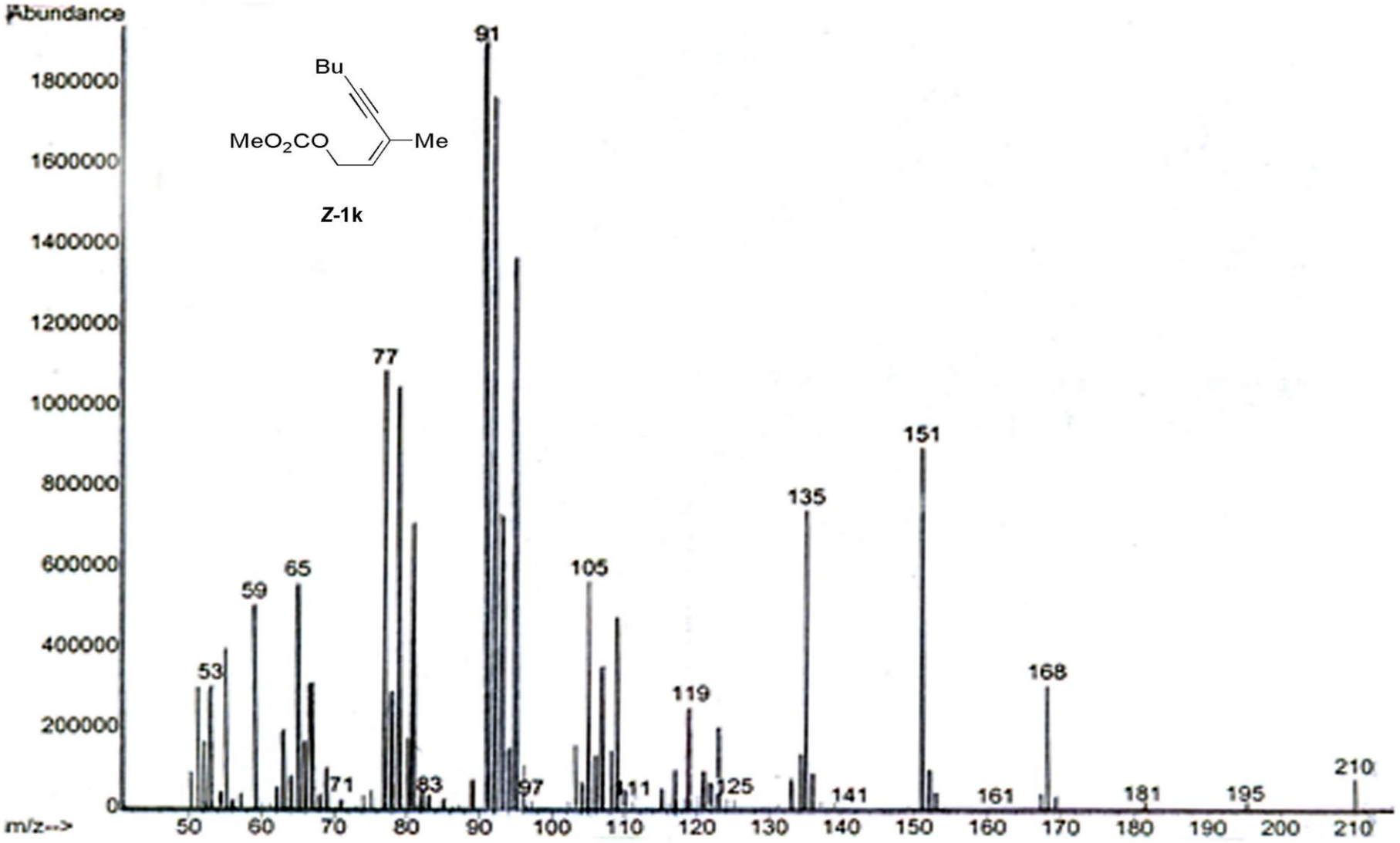
m/z--: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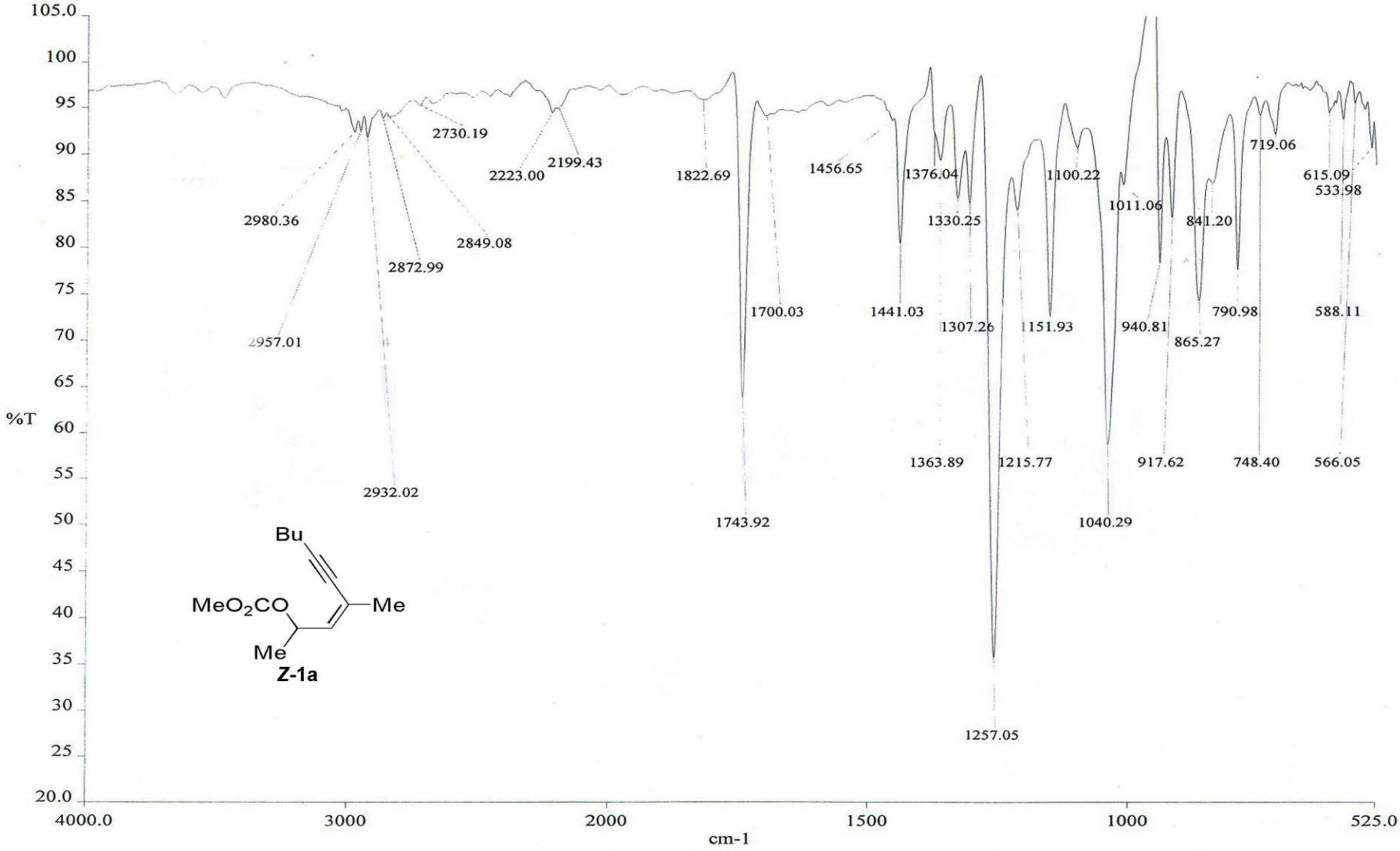
MeO2CO
Me
Z-1k

# APPENDIX C

# FTIR SPECTRUMS OF REACTANTS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2730.19
2223.00
2199.43
1822.69
1700.03
1743.92
1456.65
1441.03
1376.04
1330.25
1307.26
1363.89
1257.05
1215.77
1100.22
1151.93
1040.29
1011.06
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917.62
865.27
841.20
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719.06
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566.05
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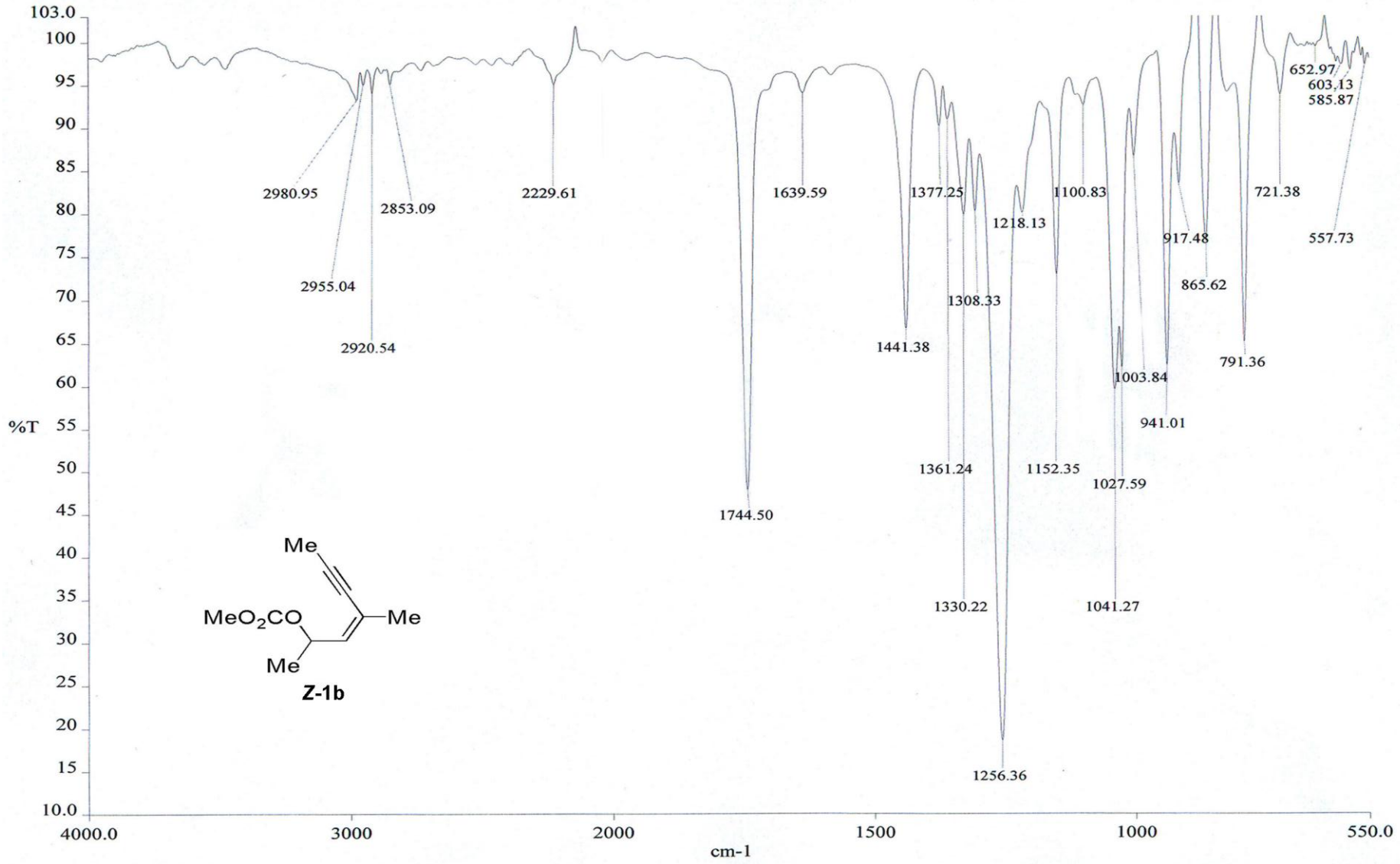
Me
Me
Z-1a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2000
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550.0
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1639.59
1441.38
1377.25
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1330.22
1308.33
1256.36
1218.13
1152.35
1100.83
1041.27
1027.59
1003.84
941.01
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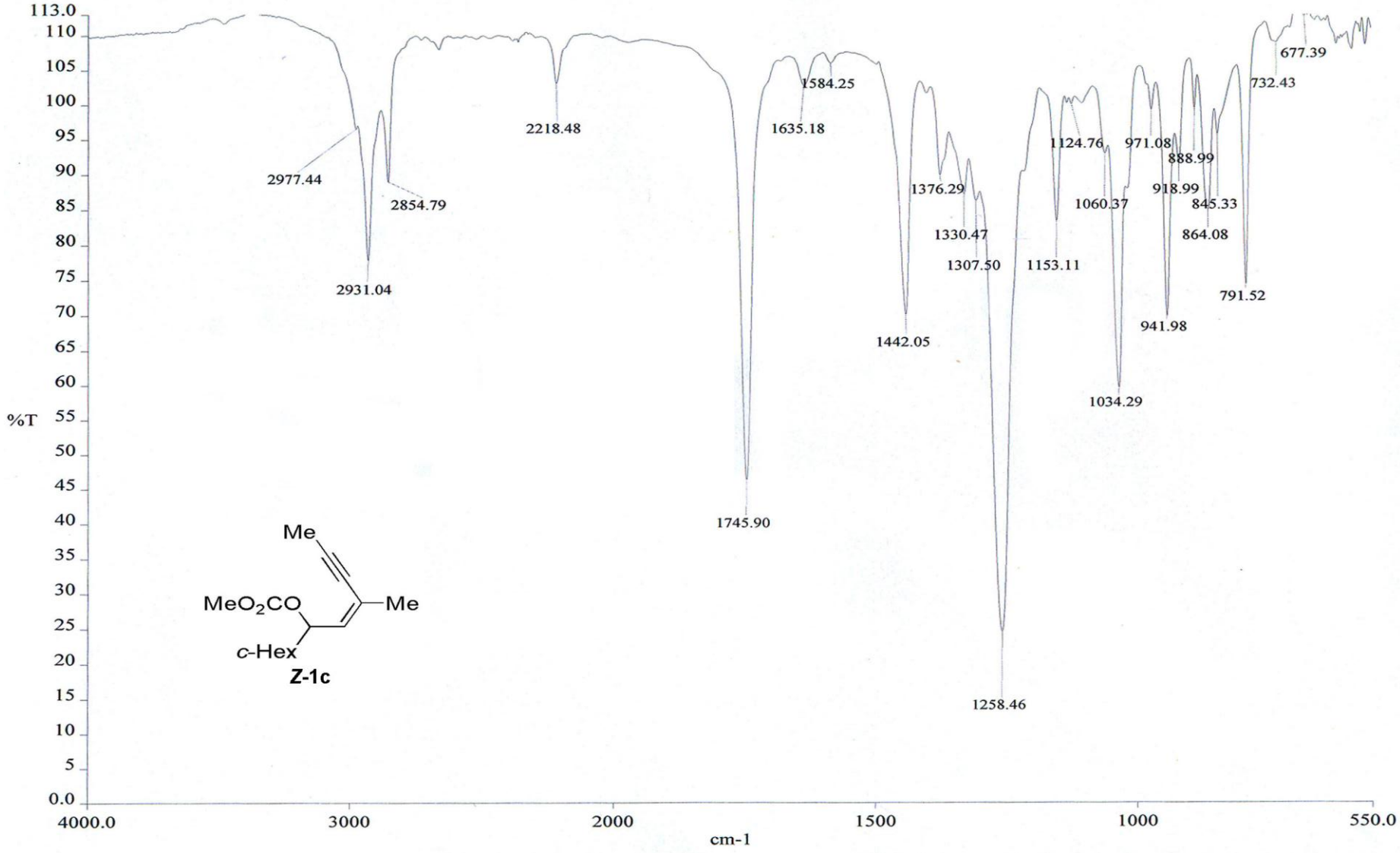
Me
Z-1b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10
5
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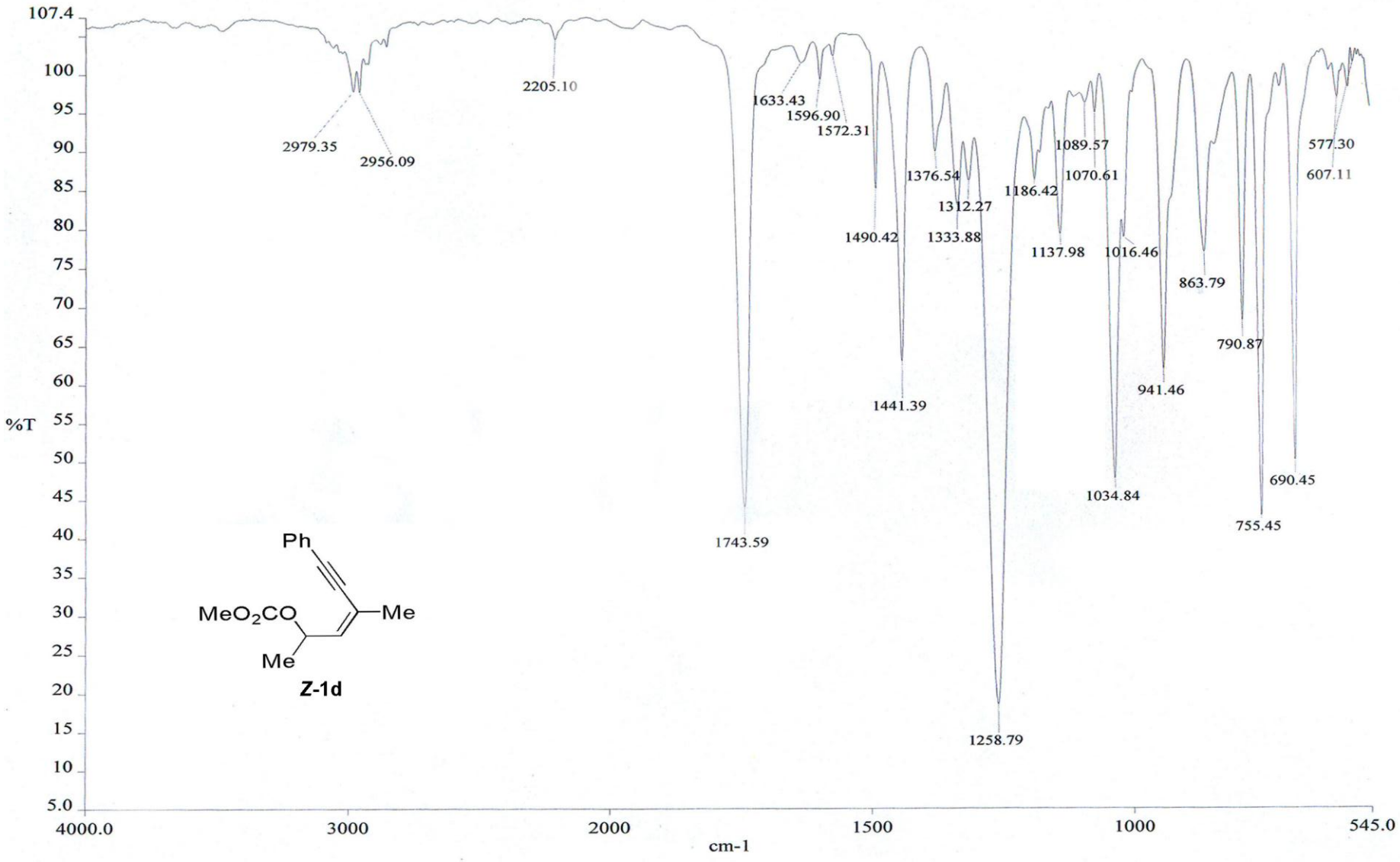
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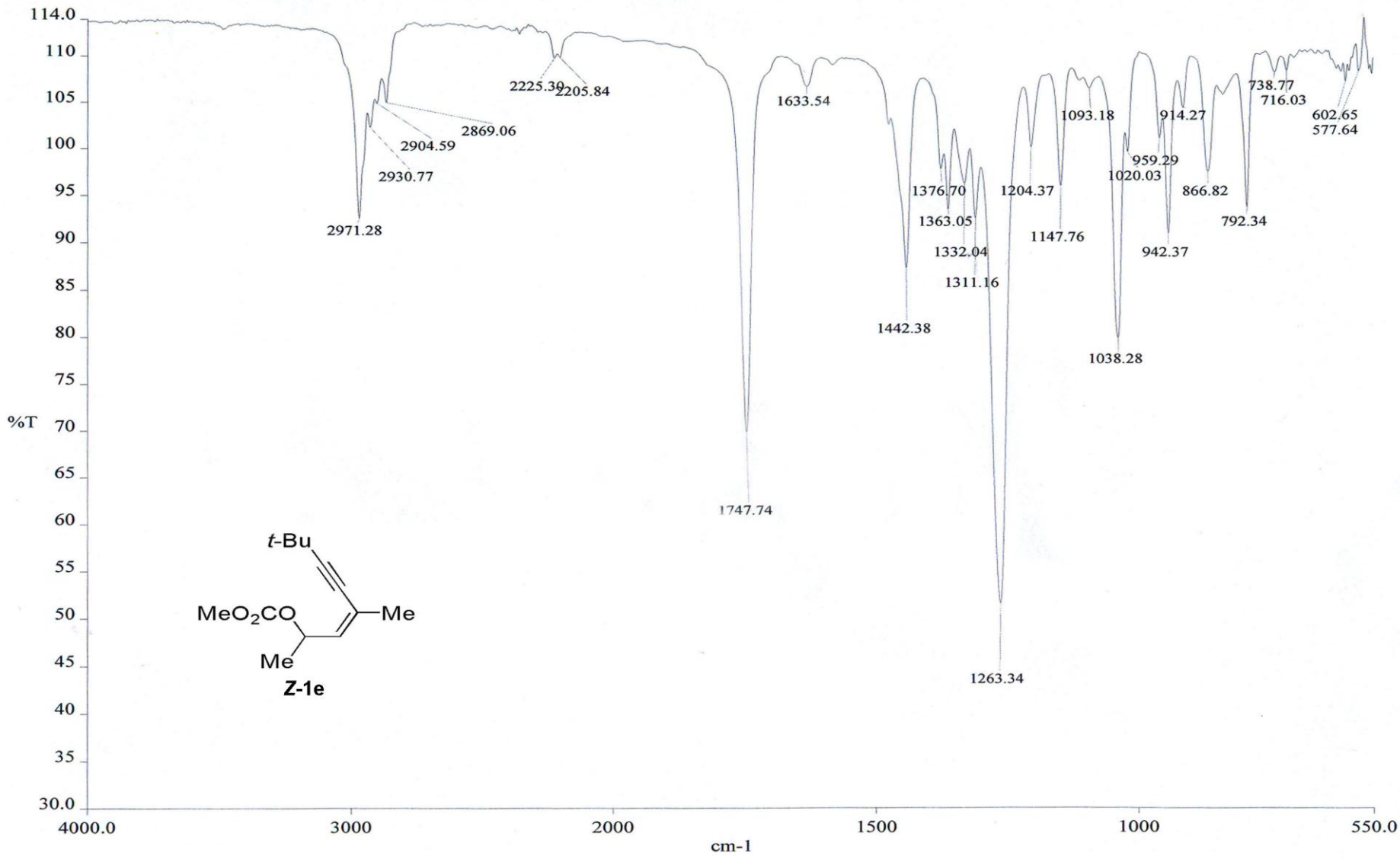
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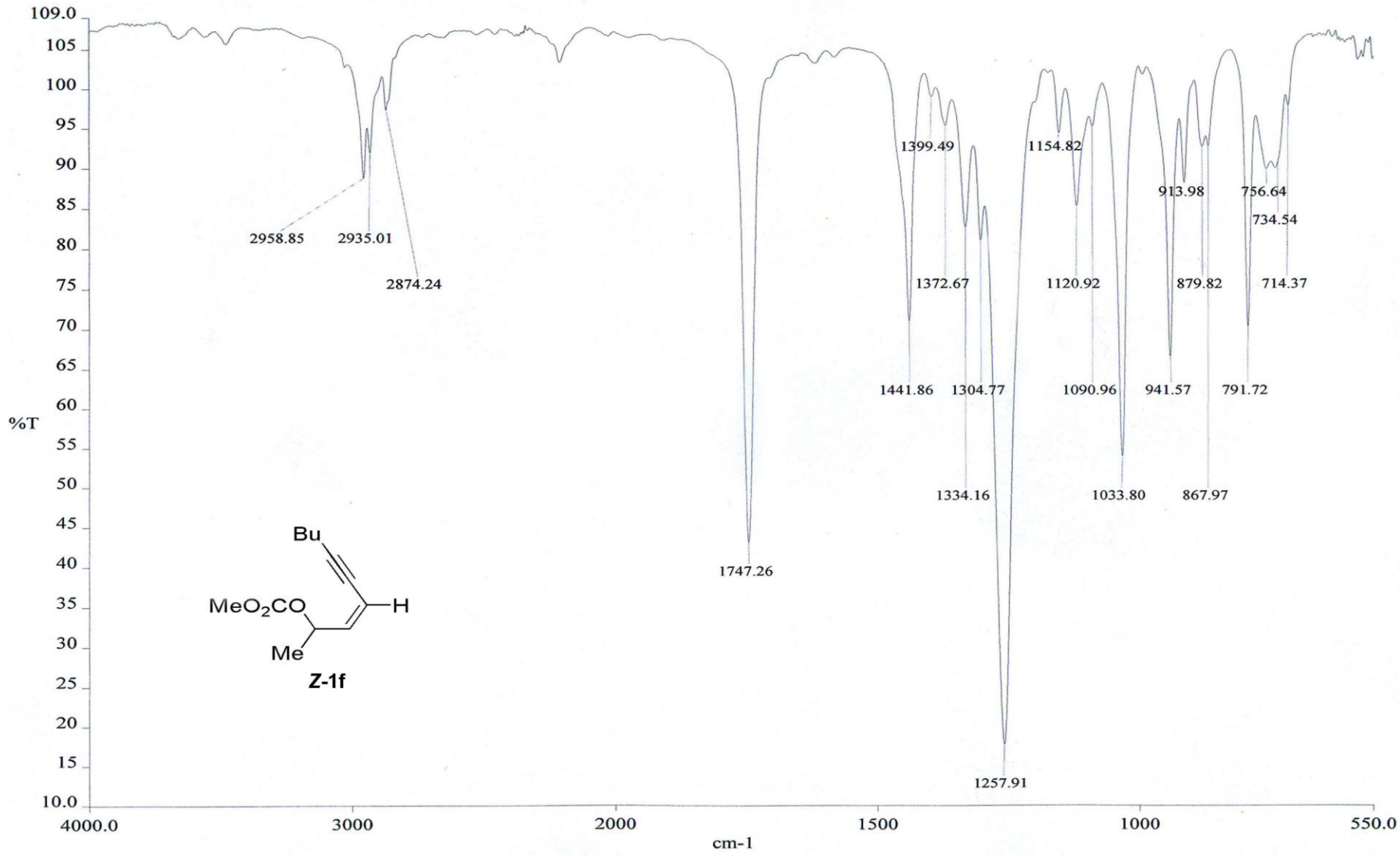
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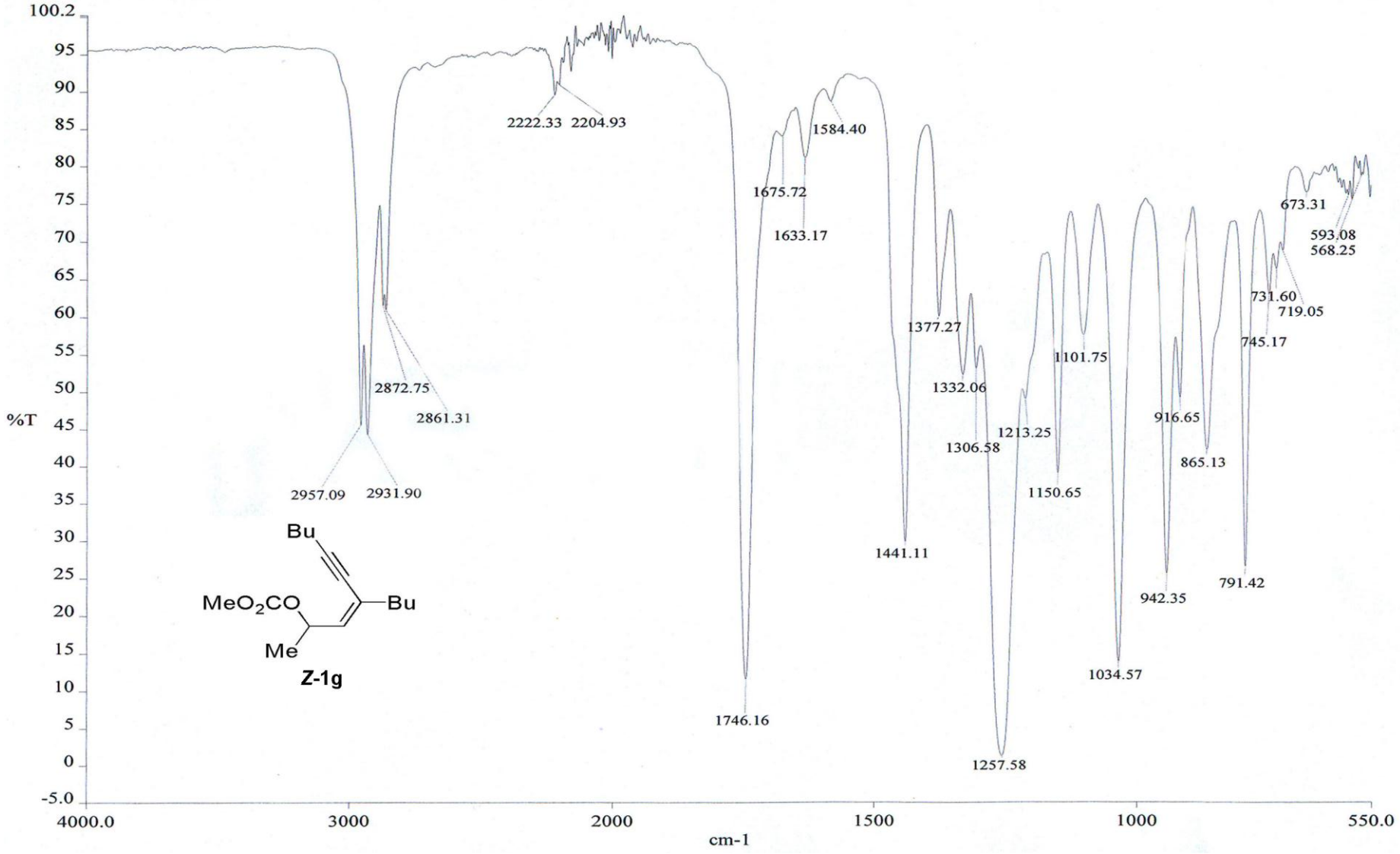
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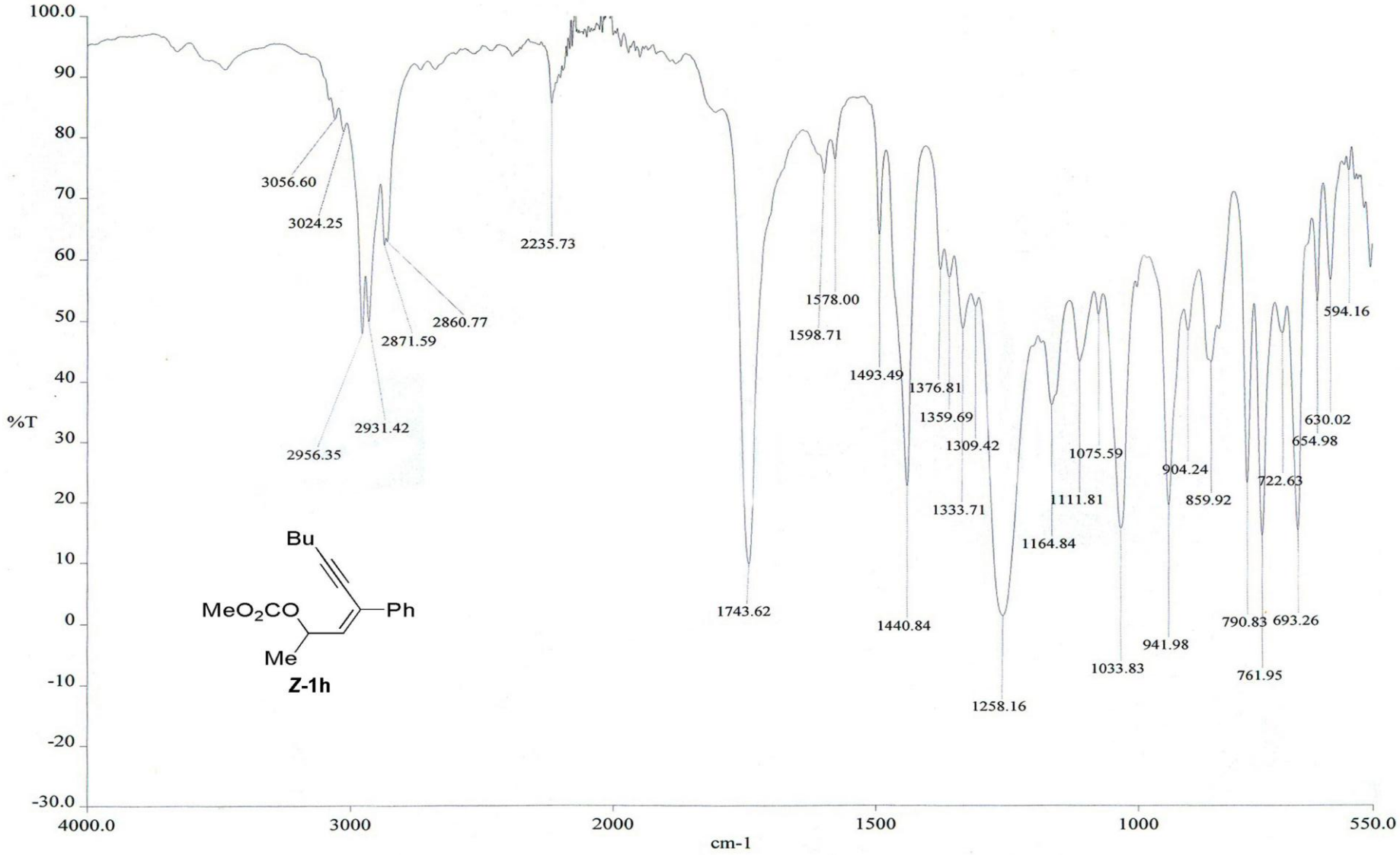
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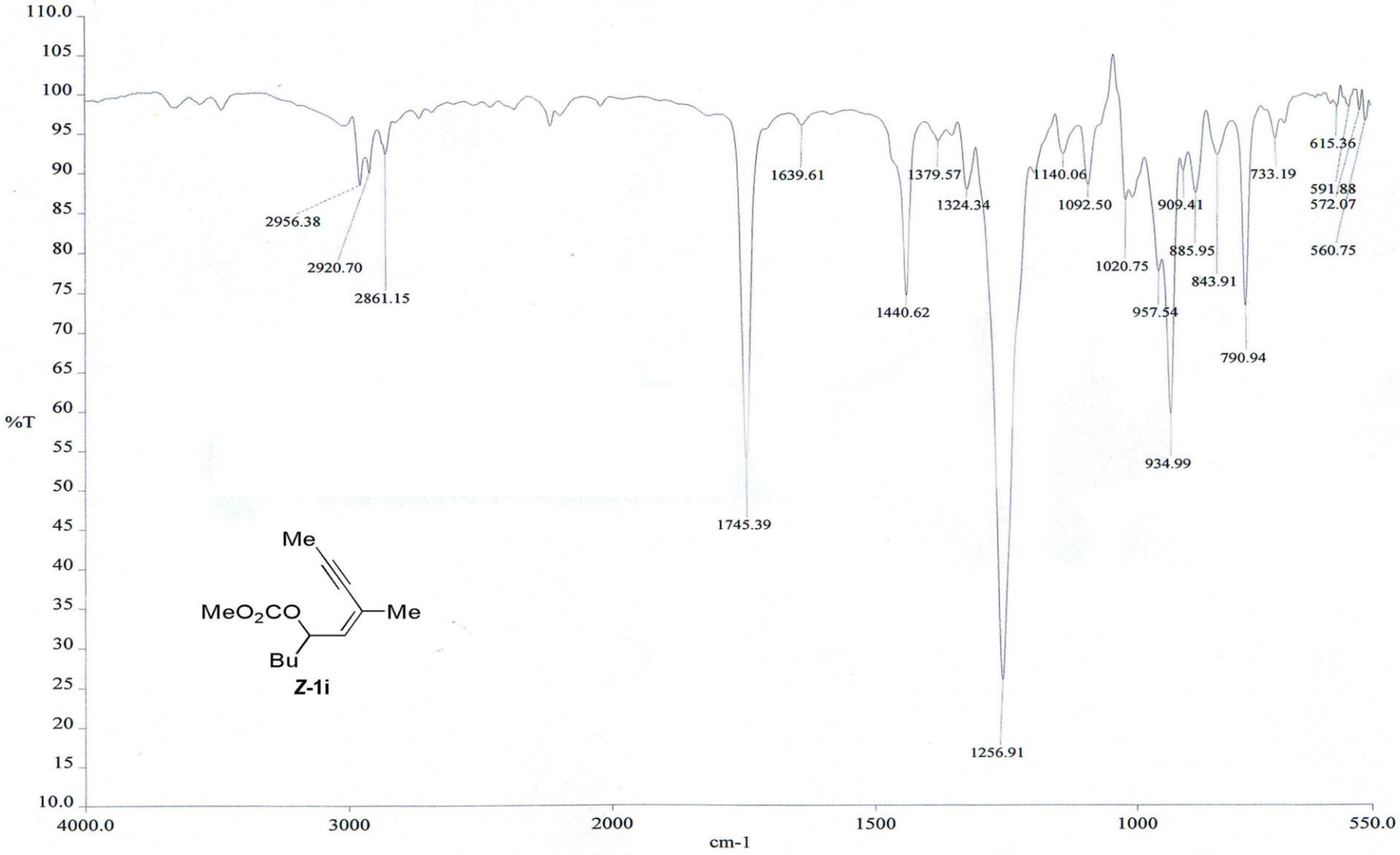
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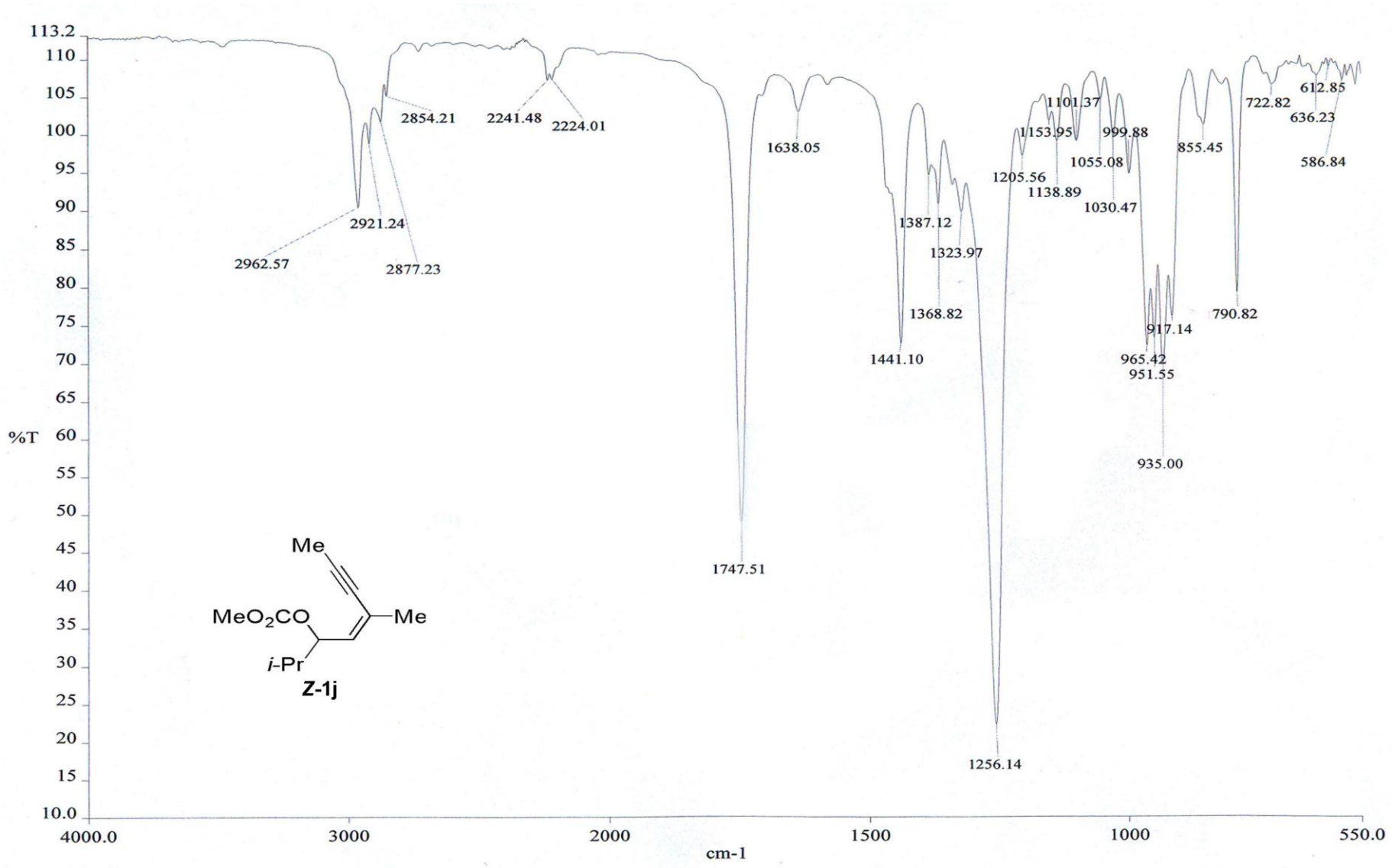
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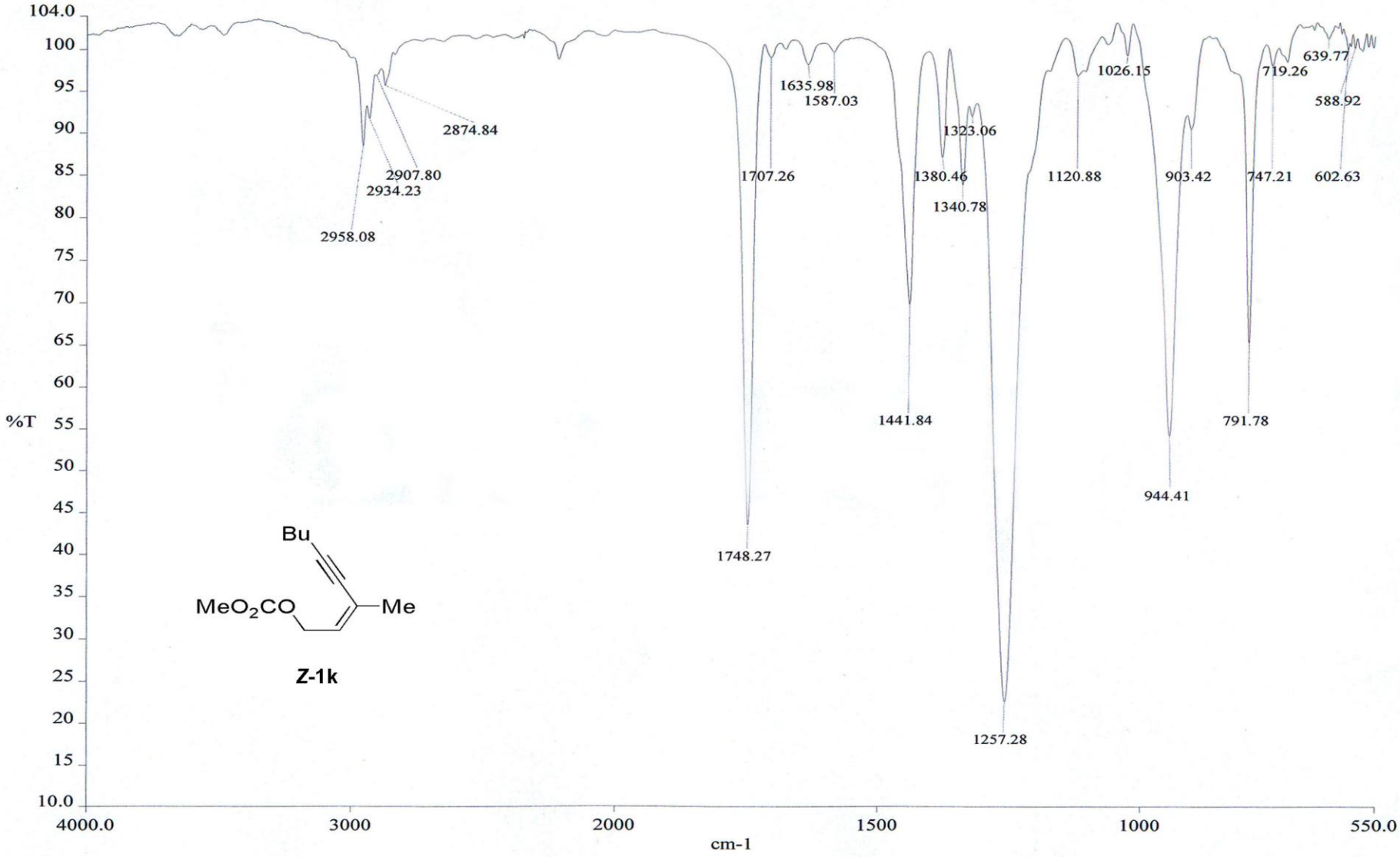
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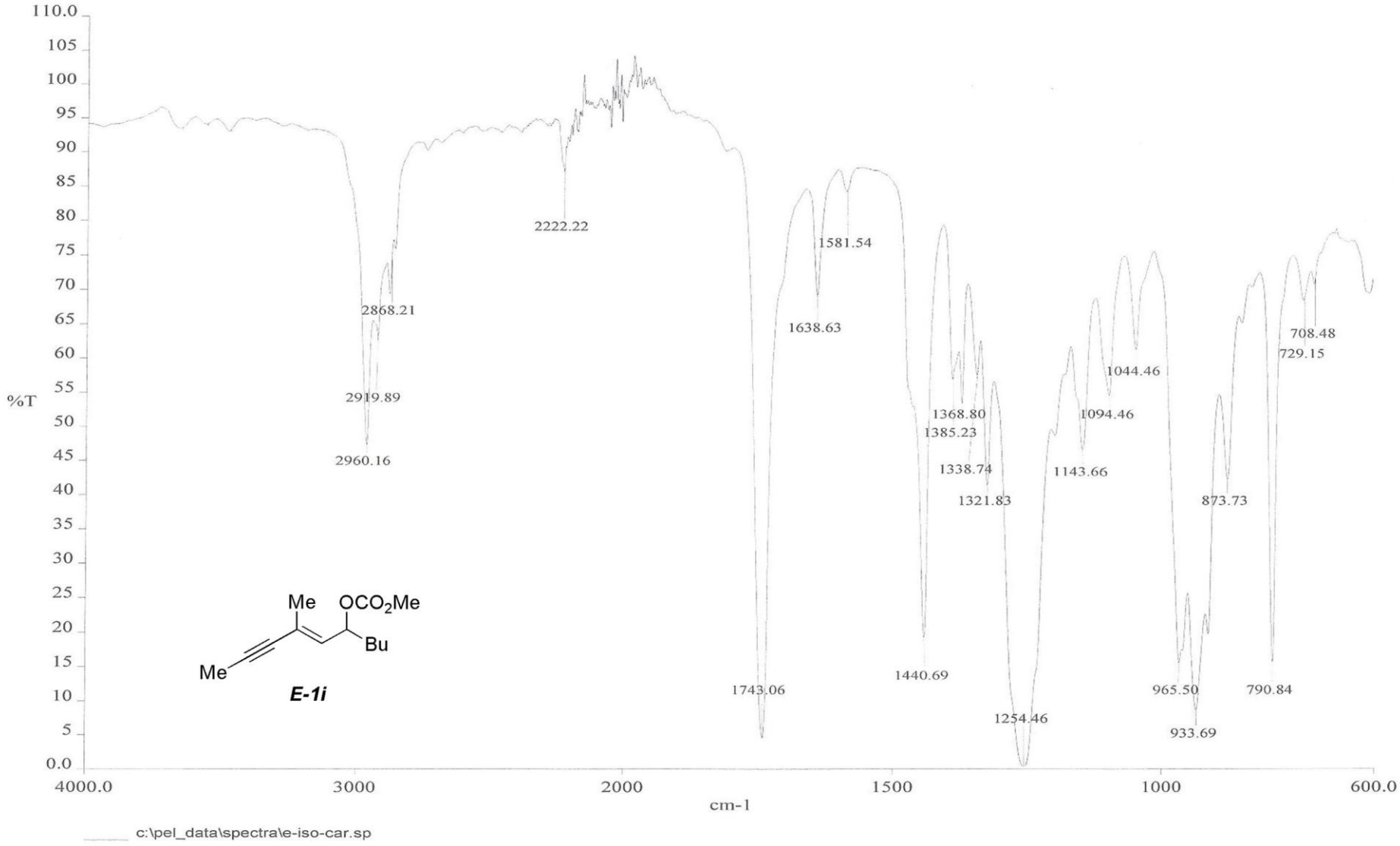
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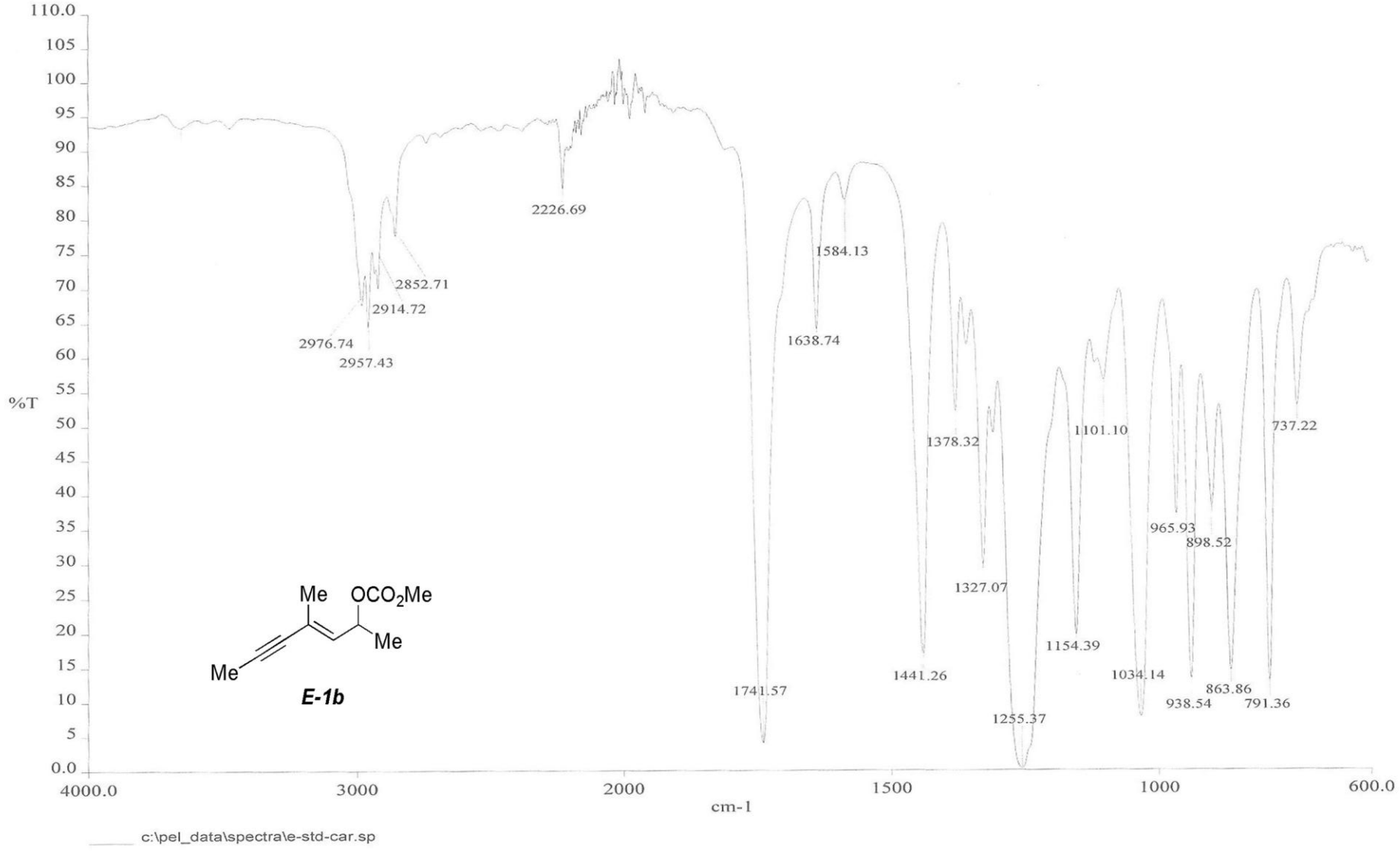
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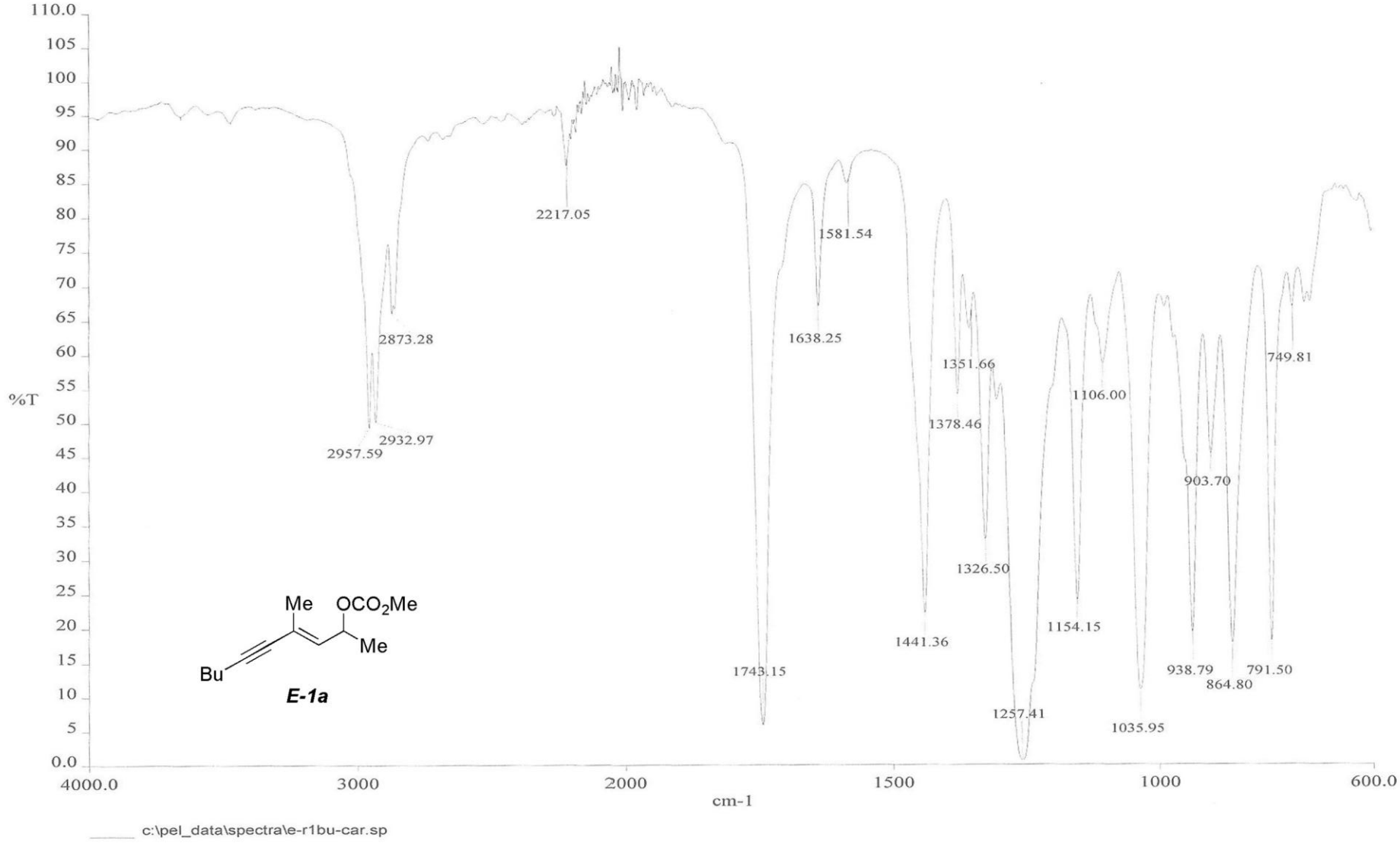
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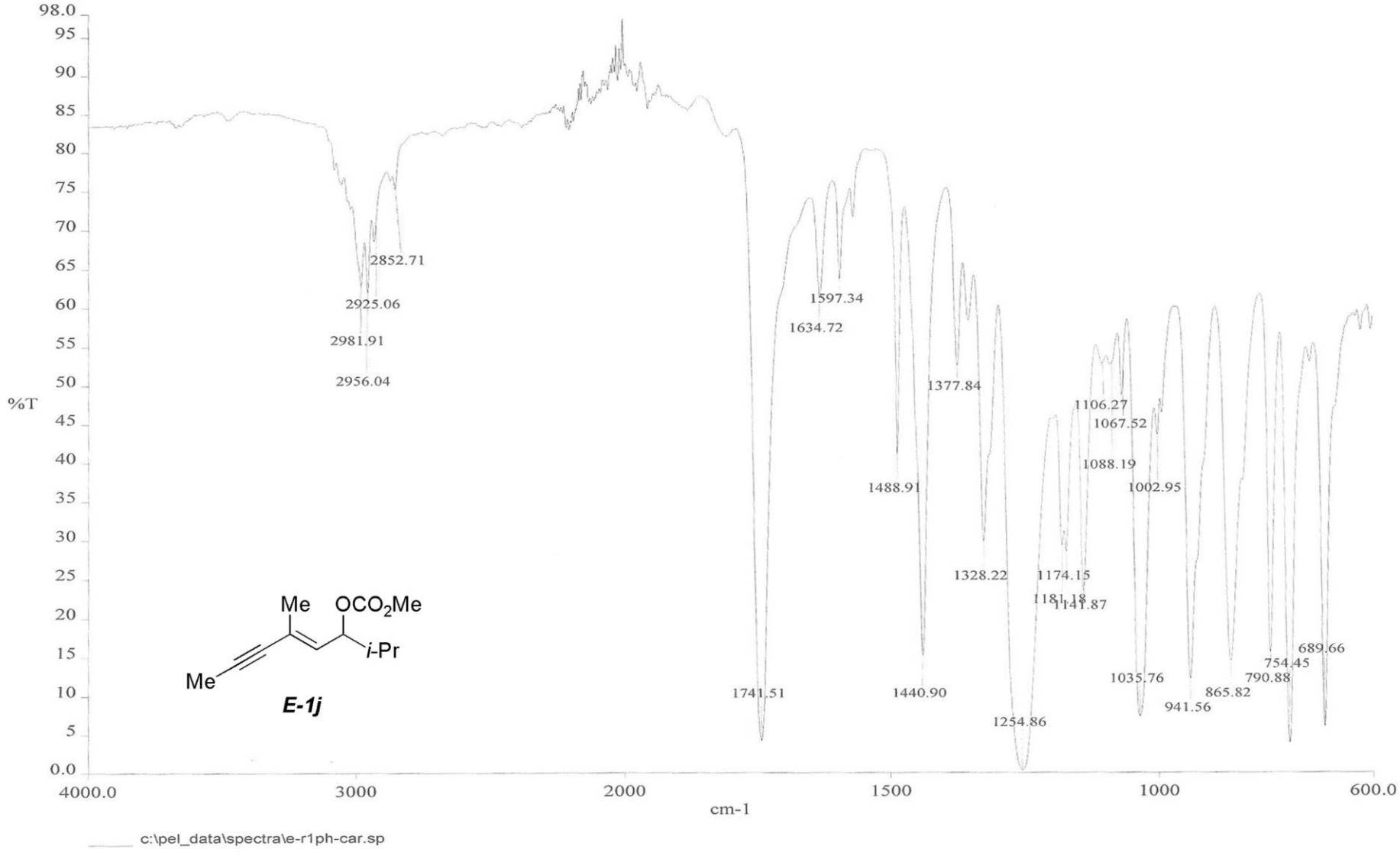
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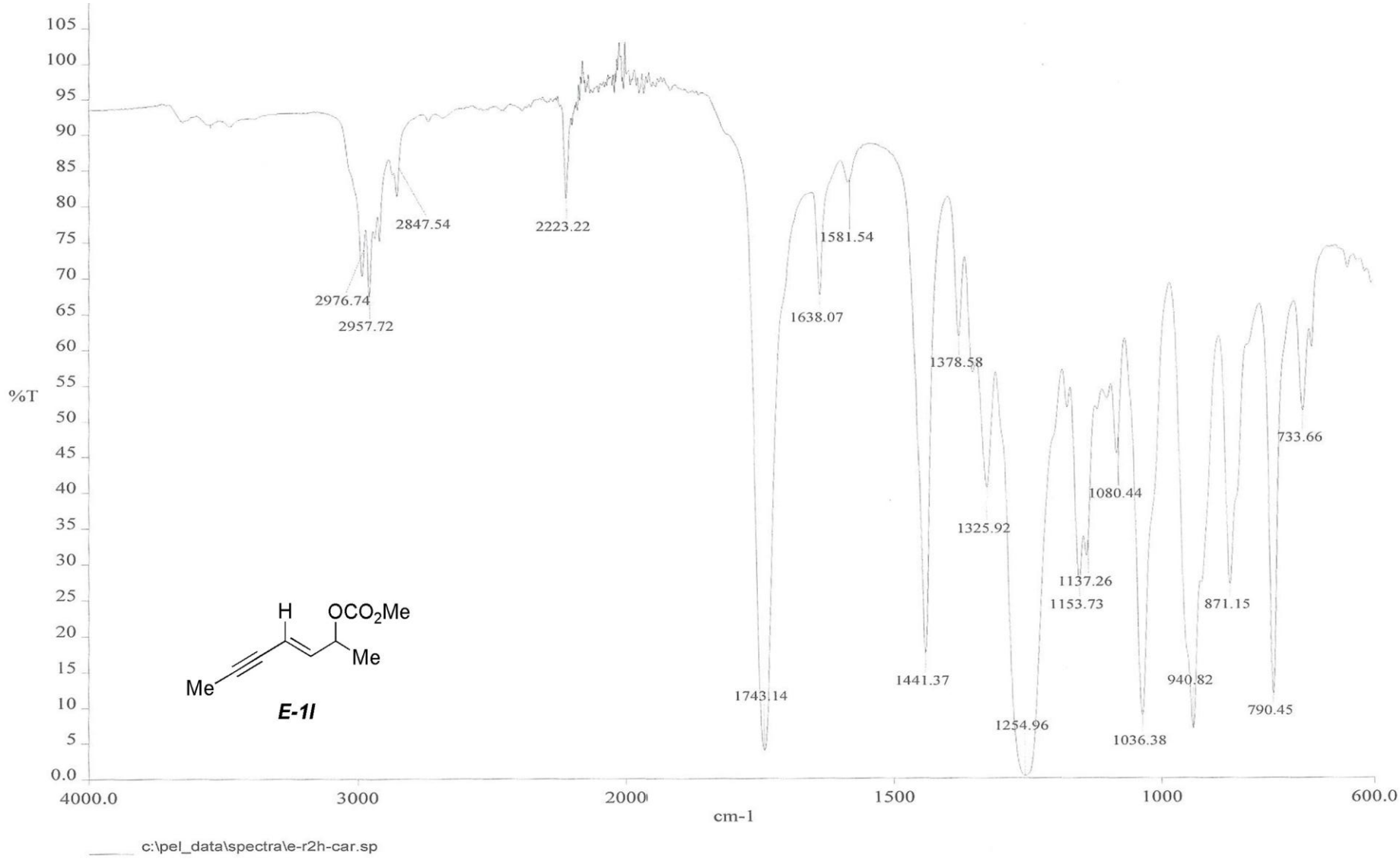
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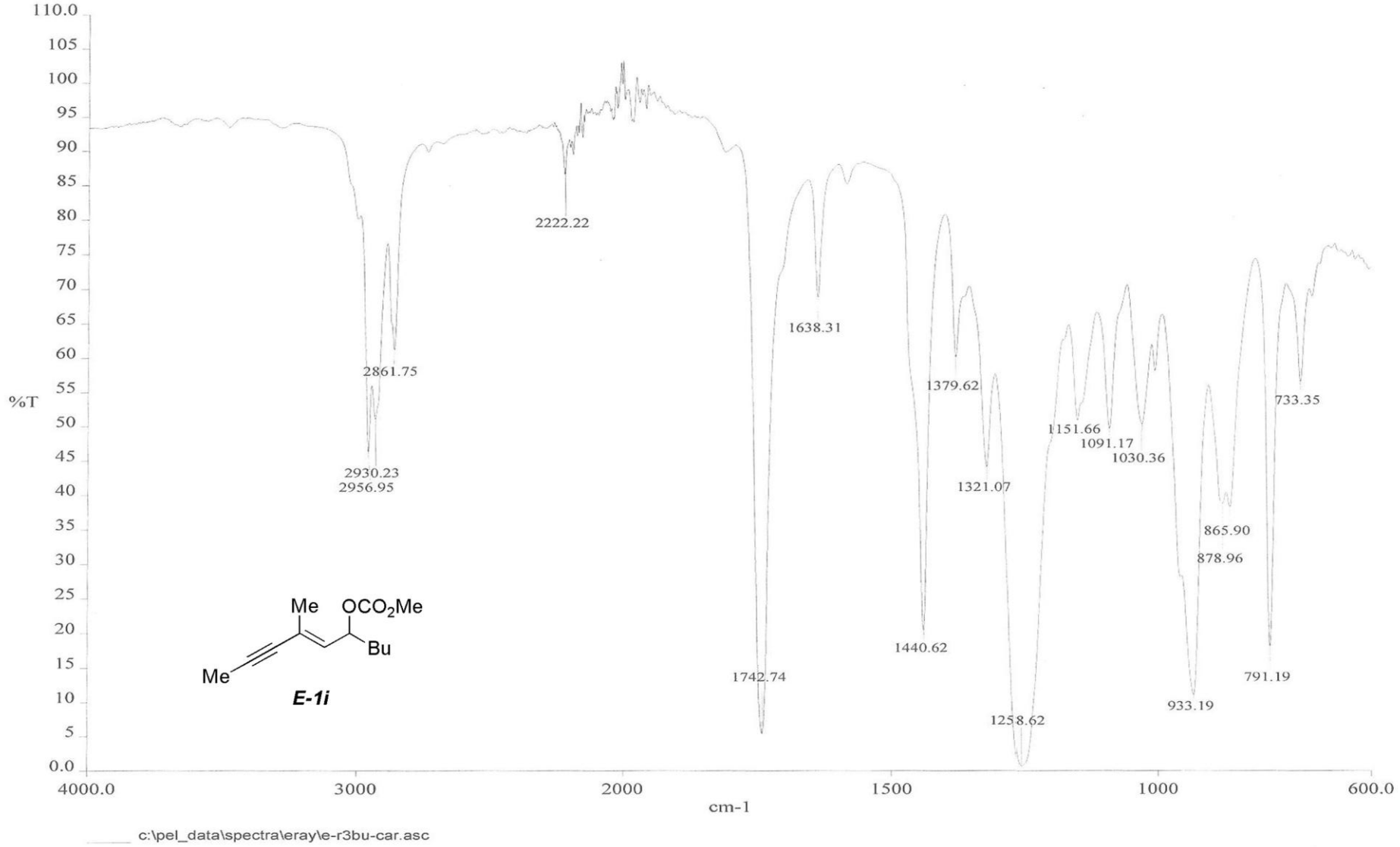
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# APPENDIX D

# $^{1}$H NMR and $^{13}$CNMR SPECTRUMS OF PRODUCTS

| | | | | | | | |
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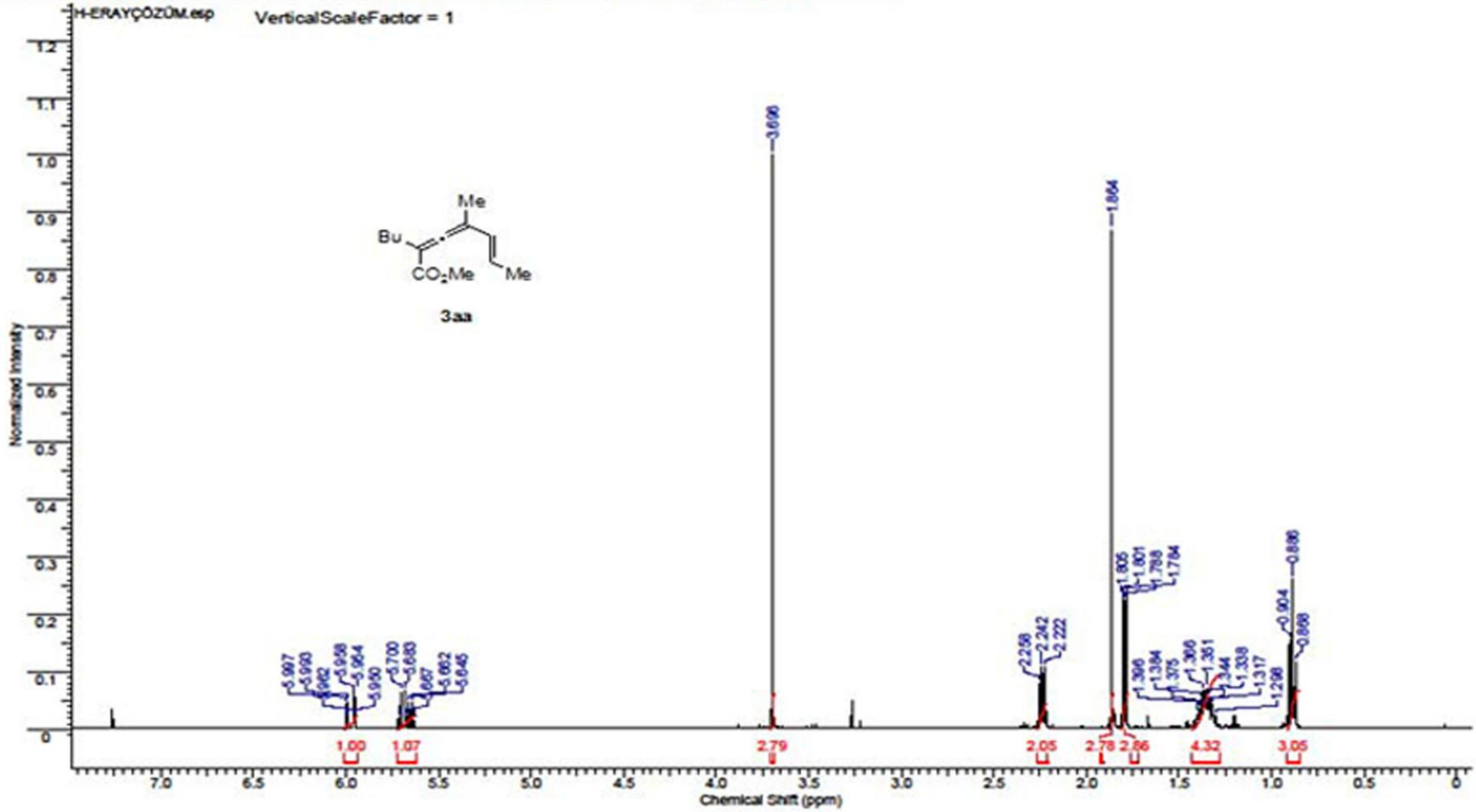
| Acquisition Time (sec) | 2.5559 | Date | Apr 10 2010 | File Name | C:\Users\eray\Desktop\ISIN-NMR\MU-CO35-KOLON_10Apr2010\PROTON_01 | | |
| Frequency (MHz) | 399.52 | Nucleus | 1H | Number of Transients | 8 | Original Points Count | 16384 |
| Points Count | 16384 | Pulse Sequence | s2pul | Solvent | CHLOROFORM-d | | |
| Spectrum Offset (Hz) | 2397.1353 | Sweep Width (Hz) | 6410.26 | Temperature (degree C) | 25.000 | | |



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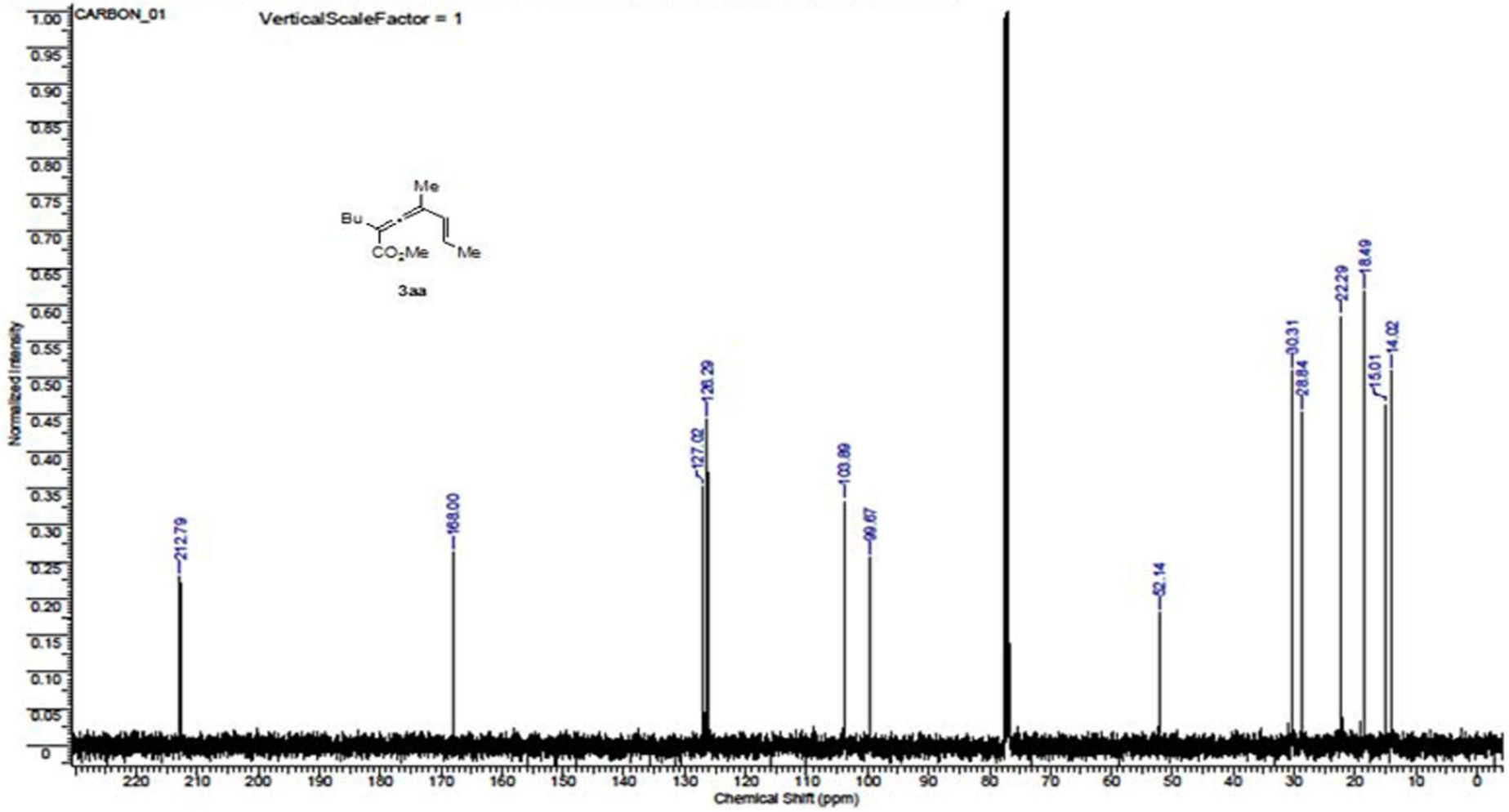
| File Name | C:\Users\Vizge\Desktop\ERAY-ACD Ç\KACAKLAR\CO35\MU-CO35-KOLON_10Apr2010\CARBON_01 | | | | | Frequency (MHz) | 100.47 |
| Nucleus | 13C | Number of Transients | 256 | Original Points Count | 32768 | Points Count | 32768 |
| Pulse Sequence | s2pul | Receiver Gain | 60.00 | Solvent | CHLOROFORM-d | | |
| Spectrum Offset (Hz) | 11065.3867 | Sweep Width (Hz) | 25510.20 | Temperature (degree C) | 25.000 | | |



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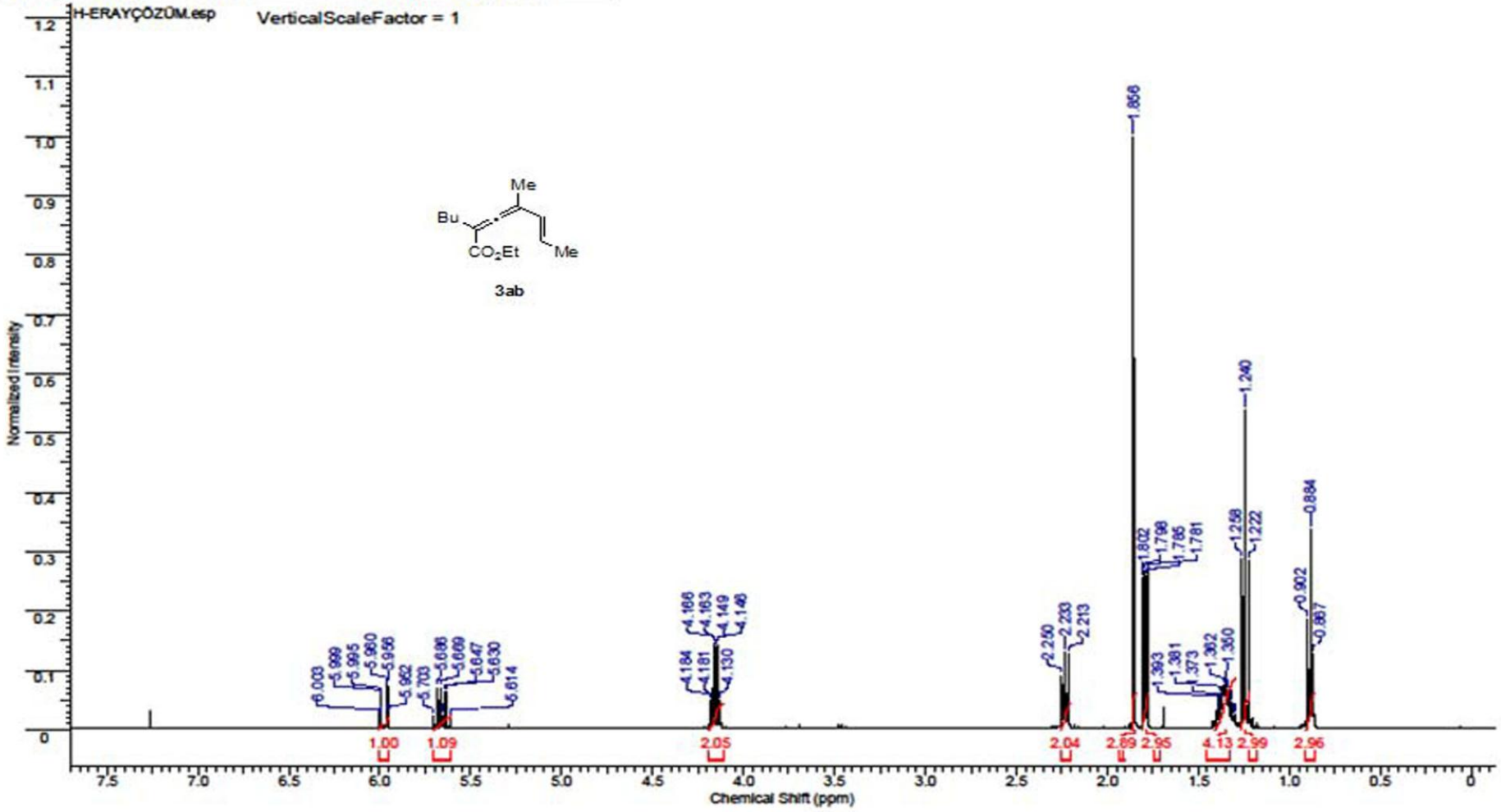
| Nucleus | 1H | Number of Transients | 8 | Original Points Count | 16384 | Points Count | 16384 |
| Pulse Sequence | s2pul | Solvent | CHLOROFORM-d | | | Spectrum Offset (Hz) | 2397.1353 |
| Sweep Width (Hz) | 6410.26 | Temperature (degree C) | 25.000 | | | | |



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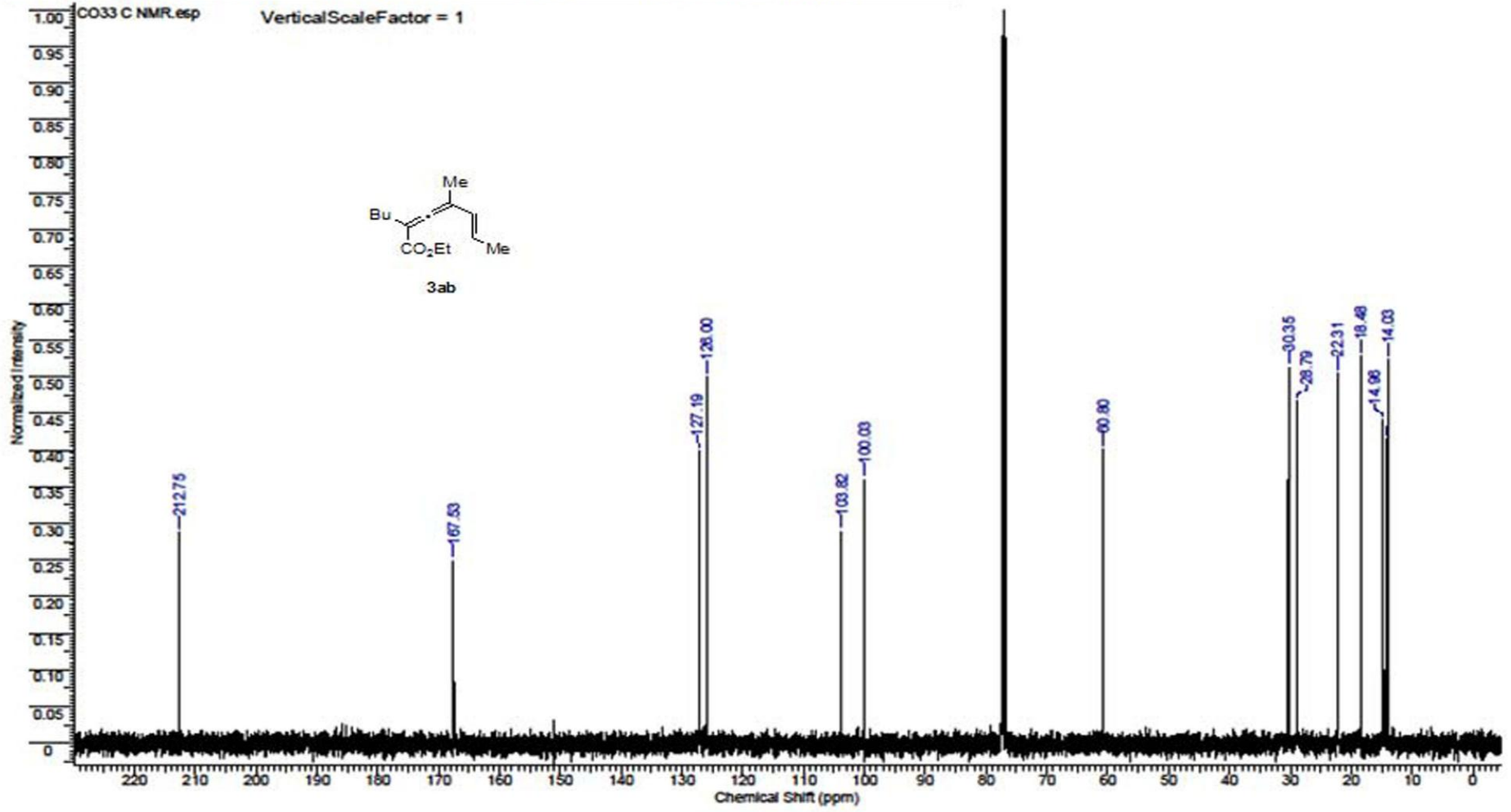
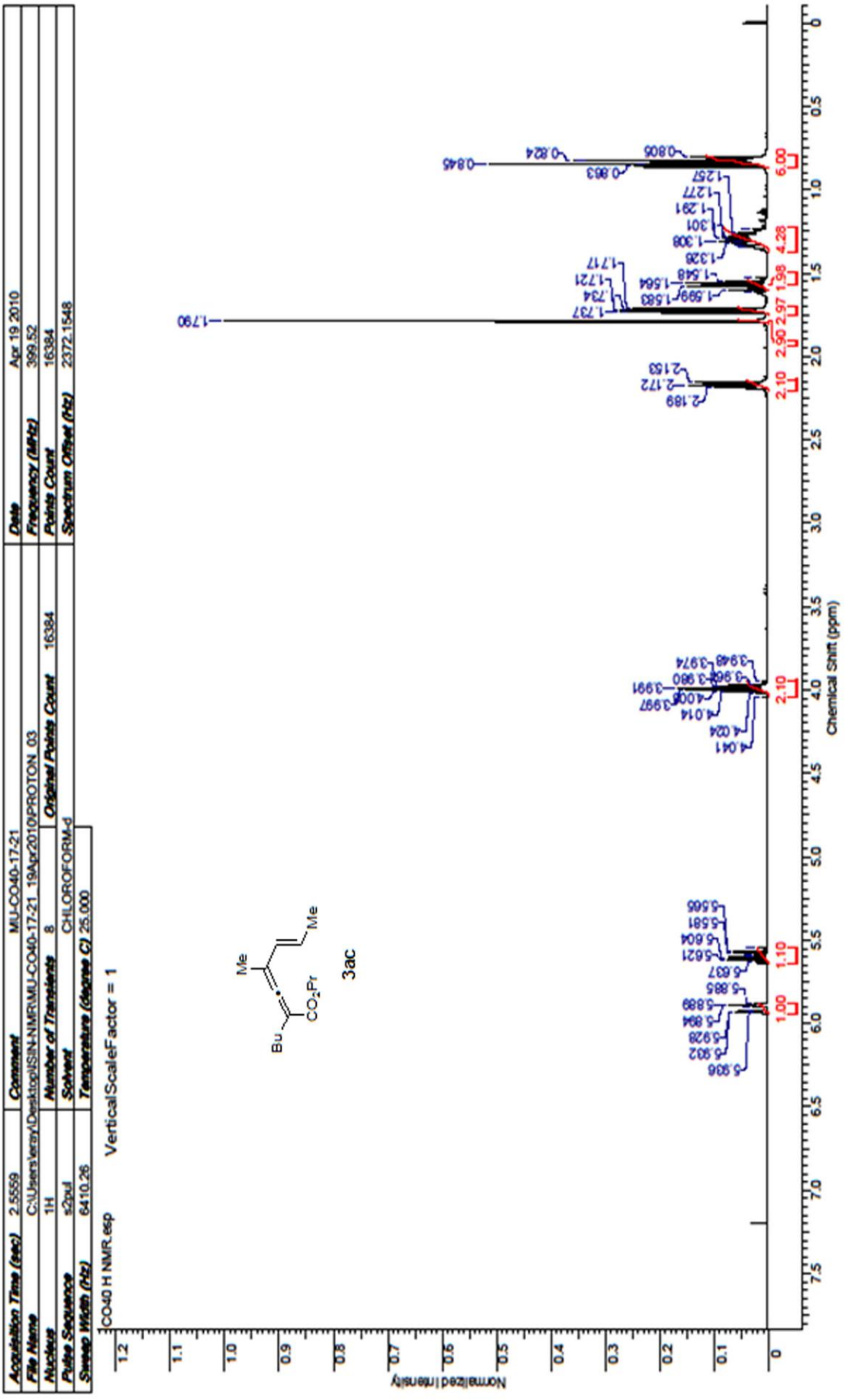
| File Name | C:\Users\Vzgel\Desktop\ERAY-ACD ÇIKACAKLAR\CO33\MU-CO33-KOLON_10Apr2010\CARBON_01 | | | | | Frequency (MHz) | 100.47 |
| Nucleus | 13C | Number of Transients | 256 | Original Points Count | 32768 | Points Count | 32768 |
| Pulse Sequence | s2pul | Receiver Gain | 60.00 | Solvent | CHLOROFORM-d | | |
| Spectrum Offset (Hz) | 11065.3867 | Sweep Width (Hz) | 25510.20 | Temperature (degree C) | 25.000 | | |

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Date Apr 19 2010
File Name C:\Users\vinny\Desktop\SIN-NMR\MU-CO40-17-21_19Apr2010\PROTON_03
Frequency (MHz) 399.52
Nucleus 1H
Number of Transients 8
Original Points Count 16384
Points Count 16384
Pulse Sequence s2pul
Solvent CHLOROFORM-d
Spectrum Offset (Hz) 2372.1548
Sweep Width (hz) 6410.26
Temperature (degree C) 25.000
CO40 H NMR.esp
VerticalScaleFactor = 1
Me
Me
CO2Pr
Bu
3ac
Normalized Intensity
Chemical Shift (ppm)

| | | | | | | | |
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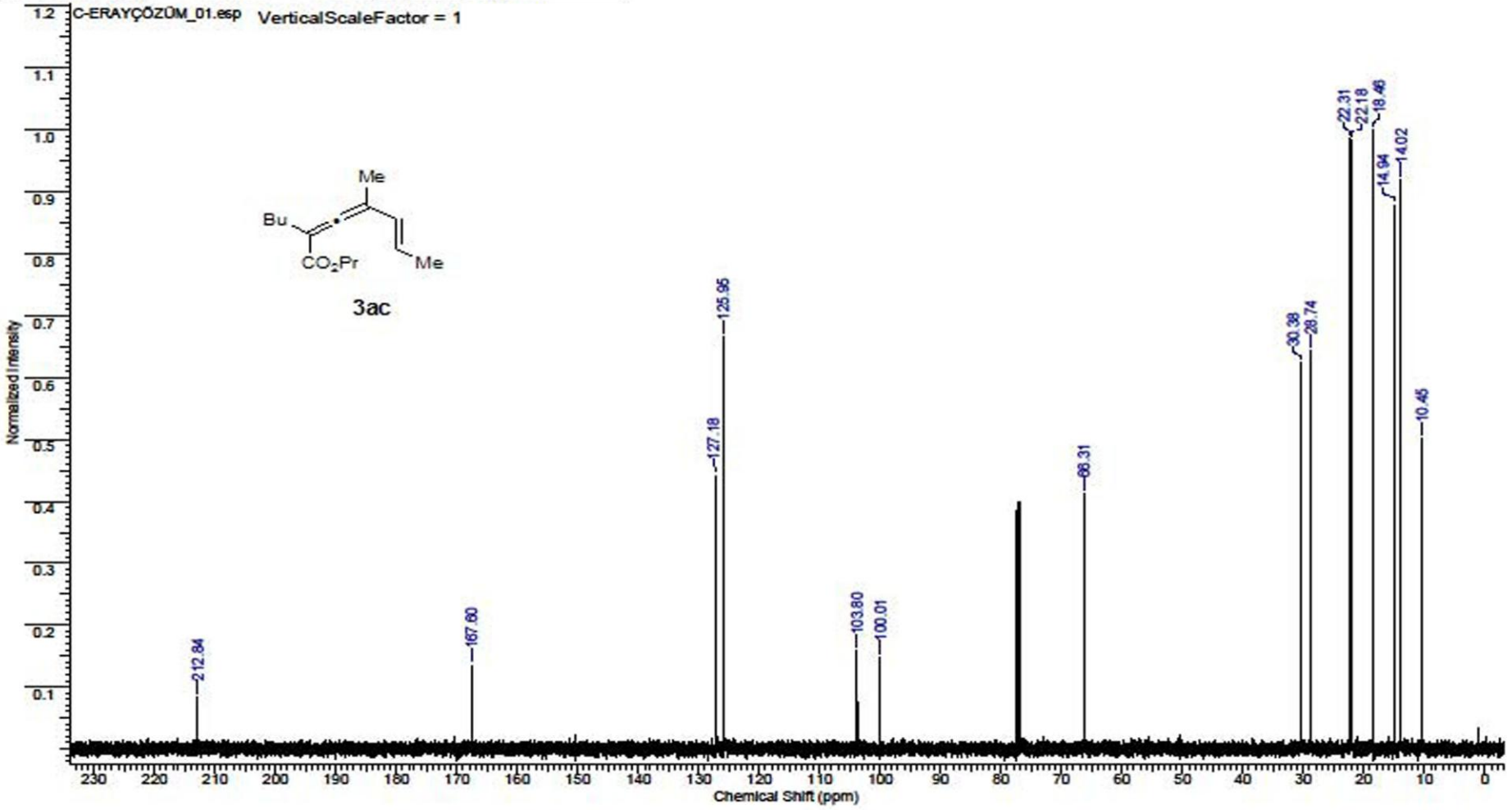
| ***Nucleus*** | 13C | ***Number of Transients*** | 256 | ***Original Points Count*** | 32768 | ***Points Count*** | 32768 |
| ***Pulse Sequence*** | s2pul | ***Solvent*** | CHLOROFORM-d | | | ***Spectrum Offset (Hz)*** | 11066.1650 |
| ***Sweep Width (Hz)*** | 25510.20 | ***Temperature (degree C)*** | 25.000 | | | | |



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| *Number of Transients* | 8 | *Original Points Count* | 12764 | *Points Count* | 16384 | *Pulse Sequence* | s2pul | *Receiver Gain* | 10.00 |
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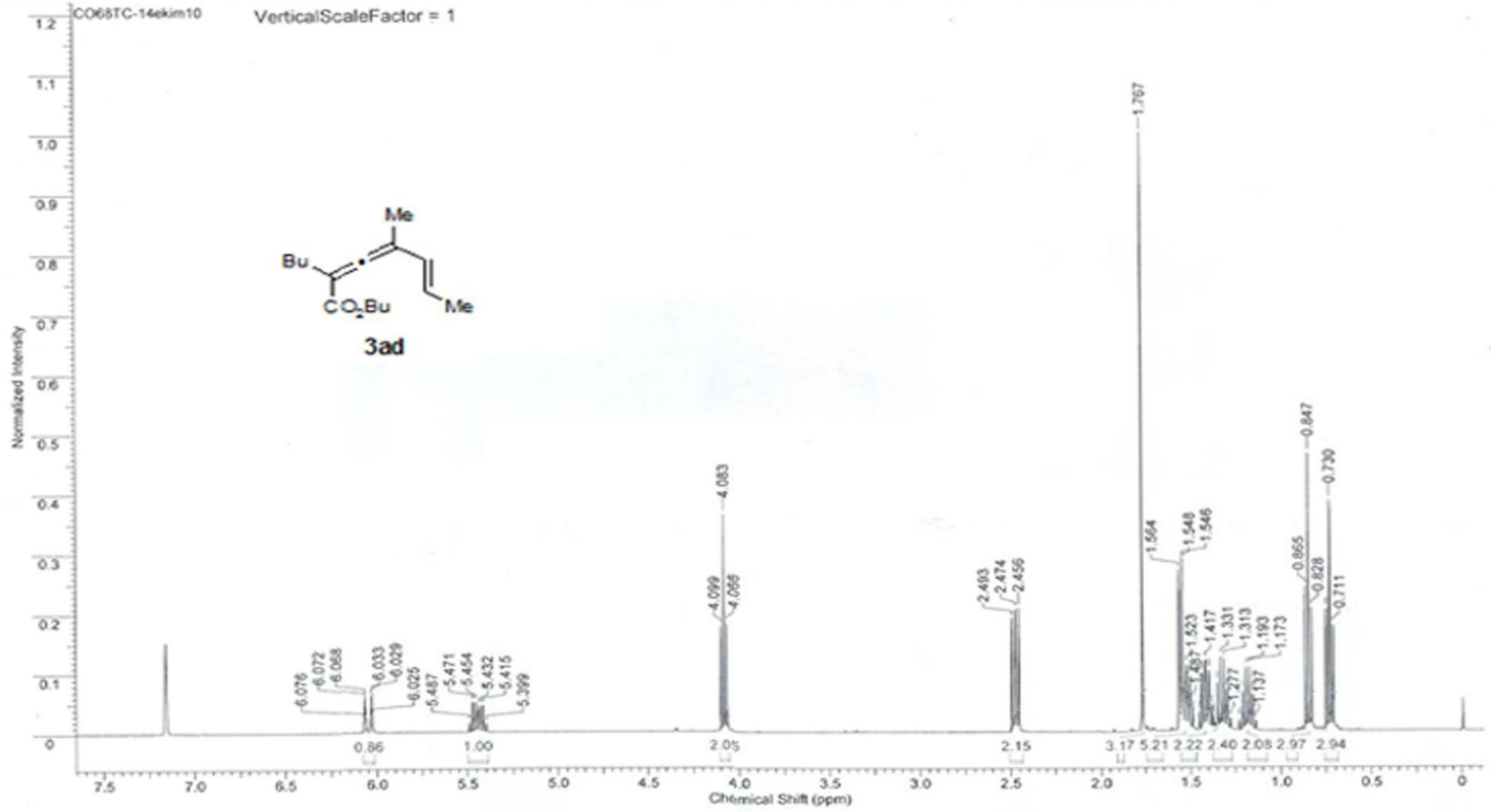

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| *Number of Transients* | 231 | *Original Points Count* | 30135 | *Points Count* | 32768 | *Pulse Sequence* | s2pul | *Receiver Gain* | 26.00 |
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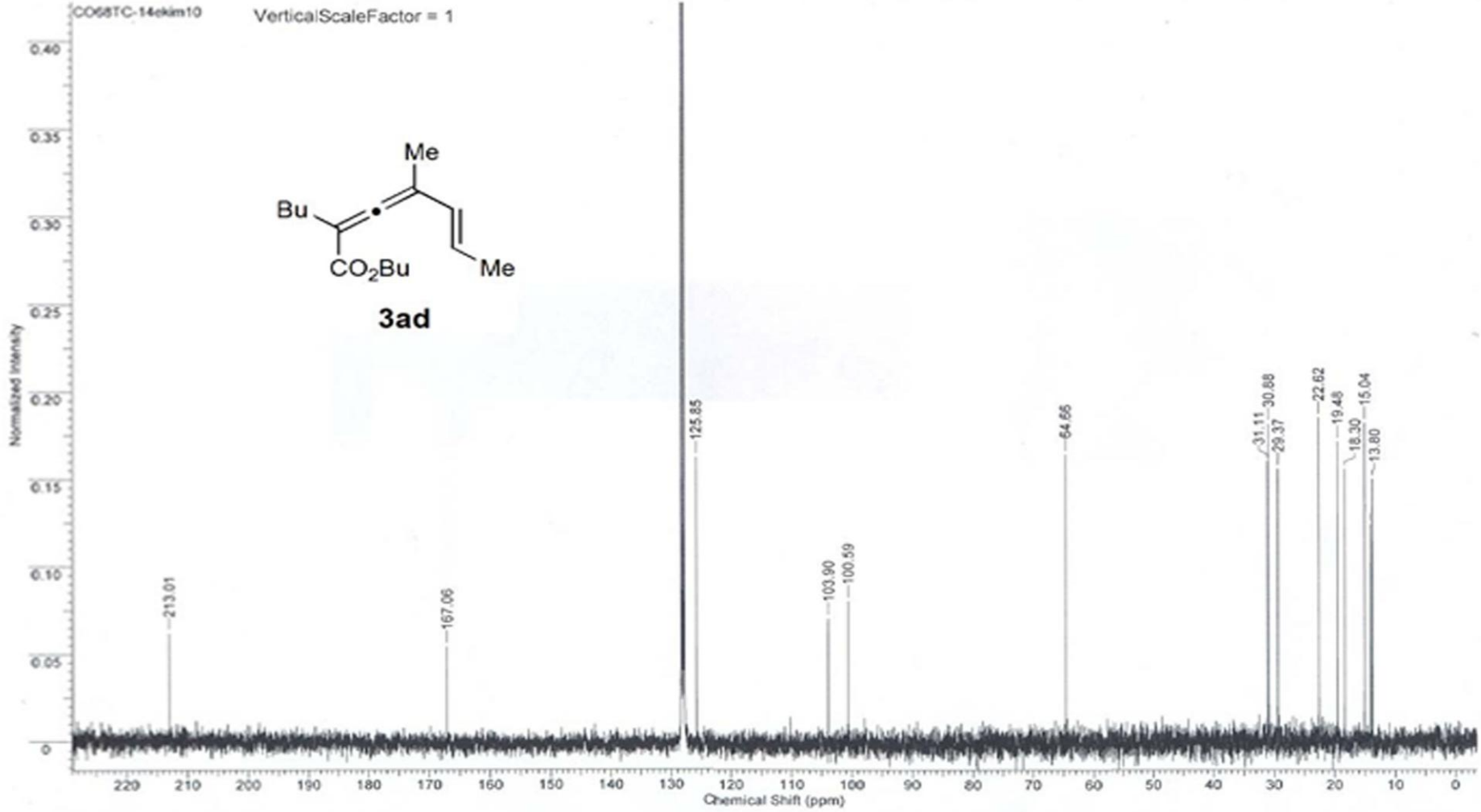

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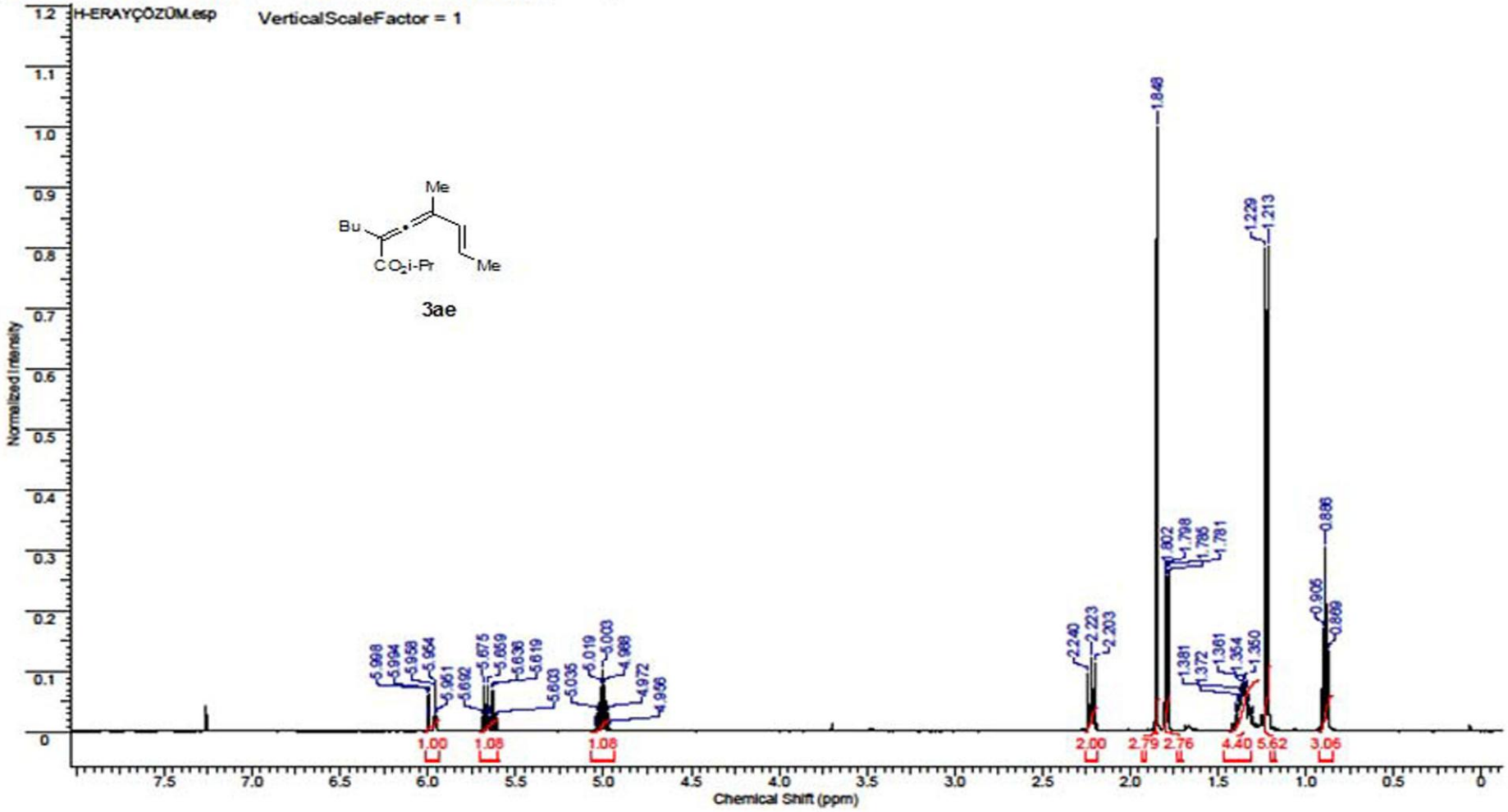
| Nucleus | 1H | Number of Transients | 8 | Original Points Count | 16384 | Points Count | 16384 |
| Pulse Sequence | s2pul | Solvent | CHLOROFORM-d | | | Spectrum Offset (Hz) | 2397.1353 |
| Sweep Width (Hz) | 6410.26 | Temperature (degree C) | 25.000 | | | | |



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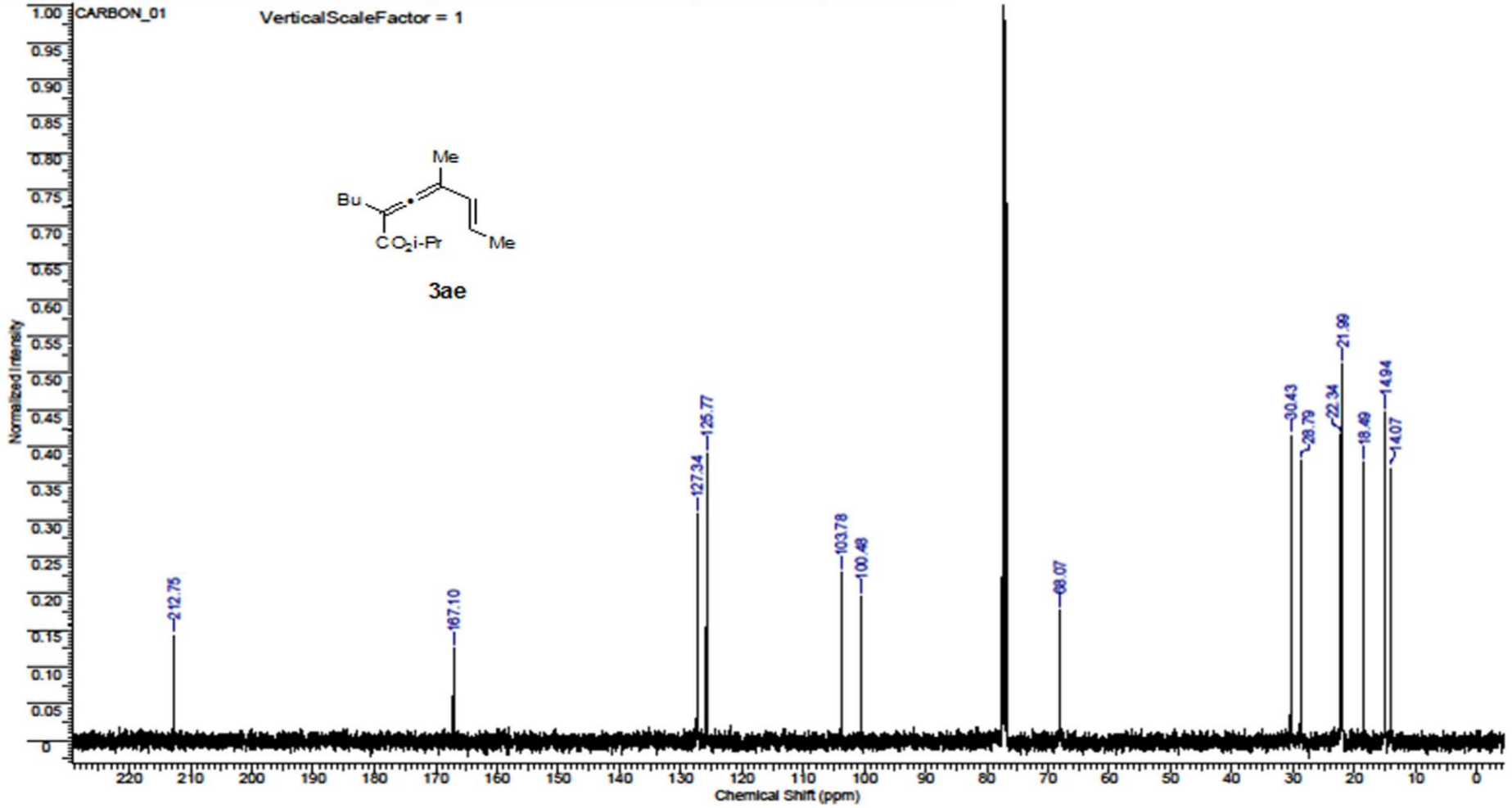
| **Nucleus** | 13C | **Number of Transients** | 512 | **Original Points Count** | 32768 | **Points Count** | 32768 |
| **Pulse Sequence** | s2pul | **Receiver Gain** | 60.00 | **Solvent** | CHLOROFORM-d | | |
| **Spectrum Offset (Hz)** | 11066.9434 | **Sweep Width (Hz)** | 25510.20 | **Temperature (degree C)** | 25.000 | | |



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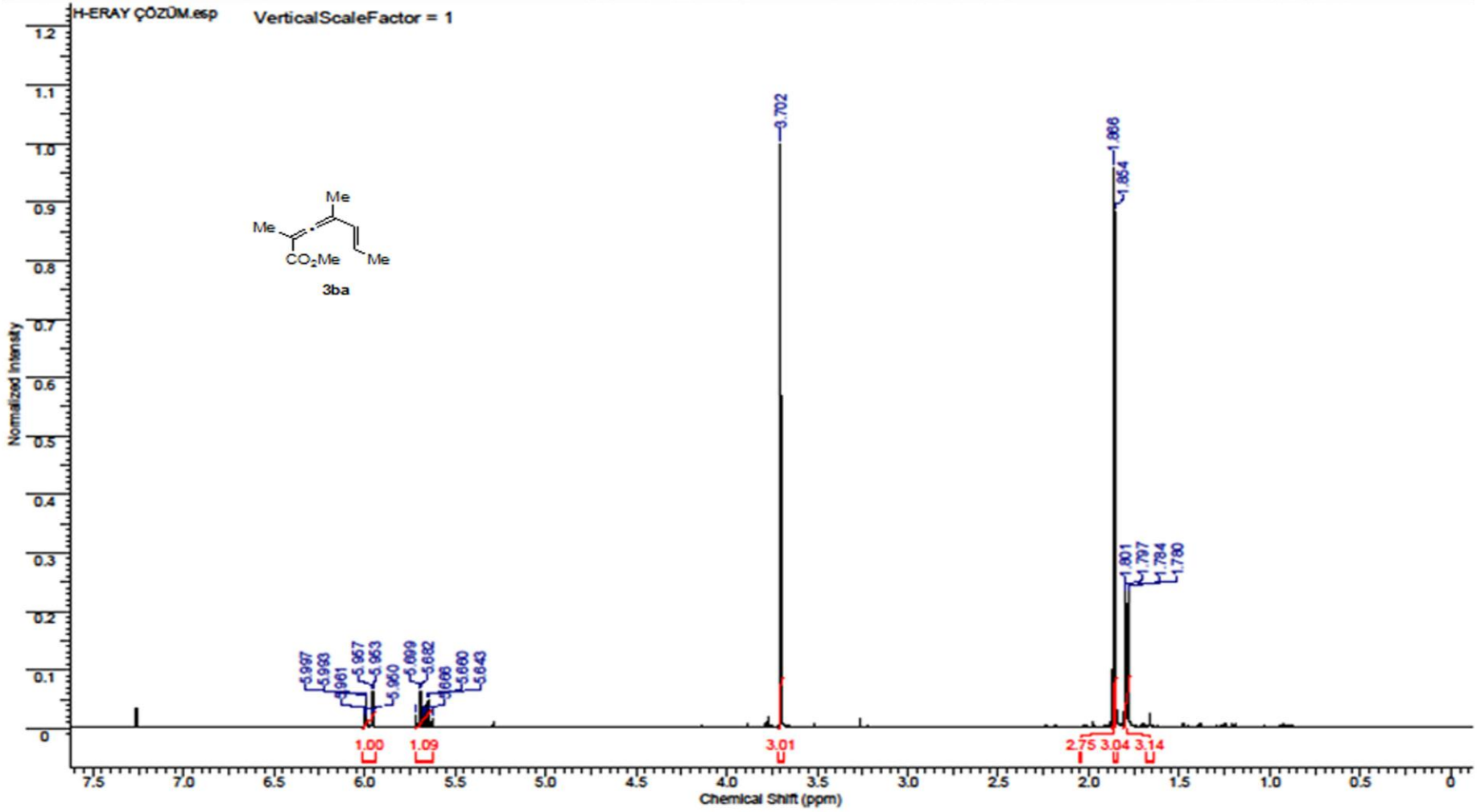
| **Number of Transients** | 8 | **Original Points Count** | 16384 | **Points Count** | 16384 | **Pulse Sequence** | s2pul | |
| **Solvent** | CHLOROFORM-d | | | **Spectrum Offset (Hz)** | 2397.1353 | **Sweep Width (Hz)** | 6410.26 | **Temperature (degree C)** 25.000 |



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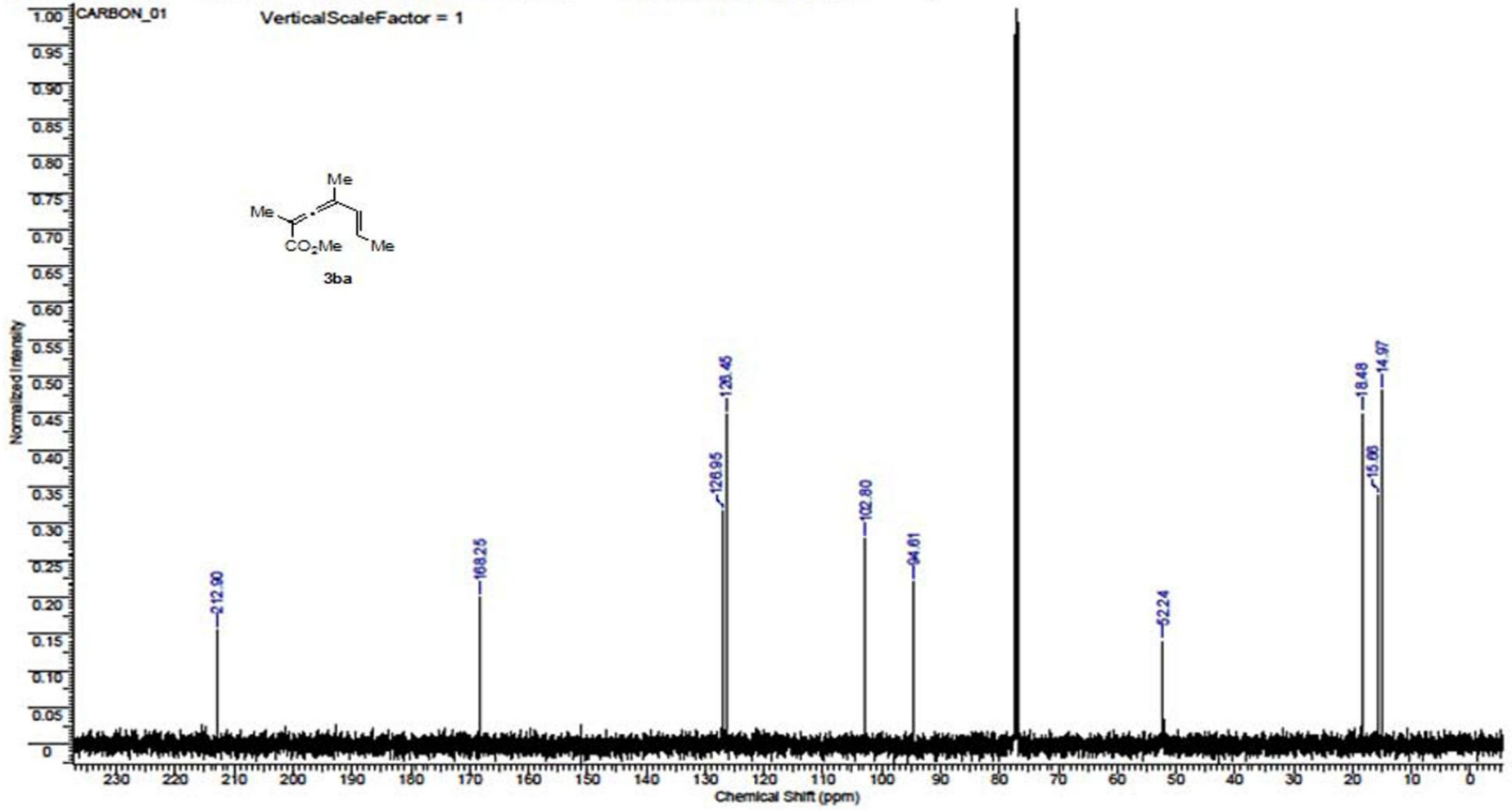
| Date Stamp | Apr 9 2010 | File Name | C:\Users\Vozgel\Desktop\ERAY-ACD CIKACAKLAR\CO30\NMR-CO30\CARBON_01 | | | | |
| Frequency (MHz) | 100.47 | Nucleus | 13C | Number of Transients | 256 | Original Points Count | 32768 |
| Points Count | 32768 | Pulse Sequence | s2pul | Receiver Gain | 60.00 | Solvent | CHLOROFORM-d |
| Spectrum Offset (Hz) | 11065.3867 | Sweep Width (Hz) | 25510.20 | Temperature (degree C) | 25.000 | | |



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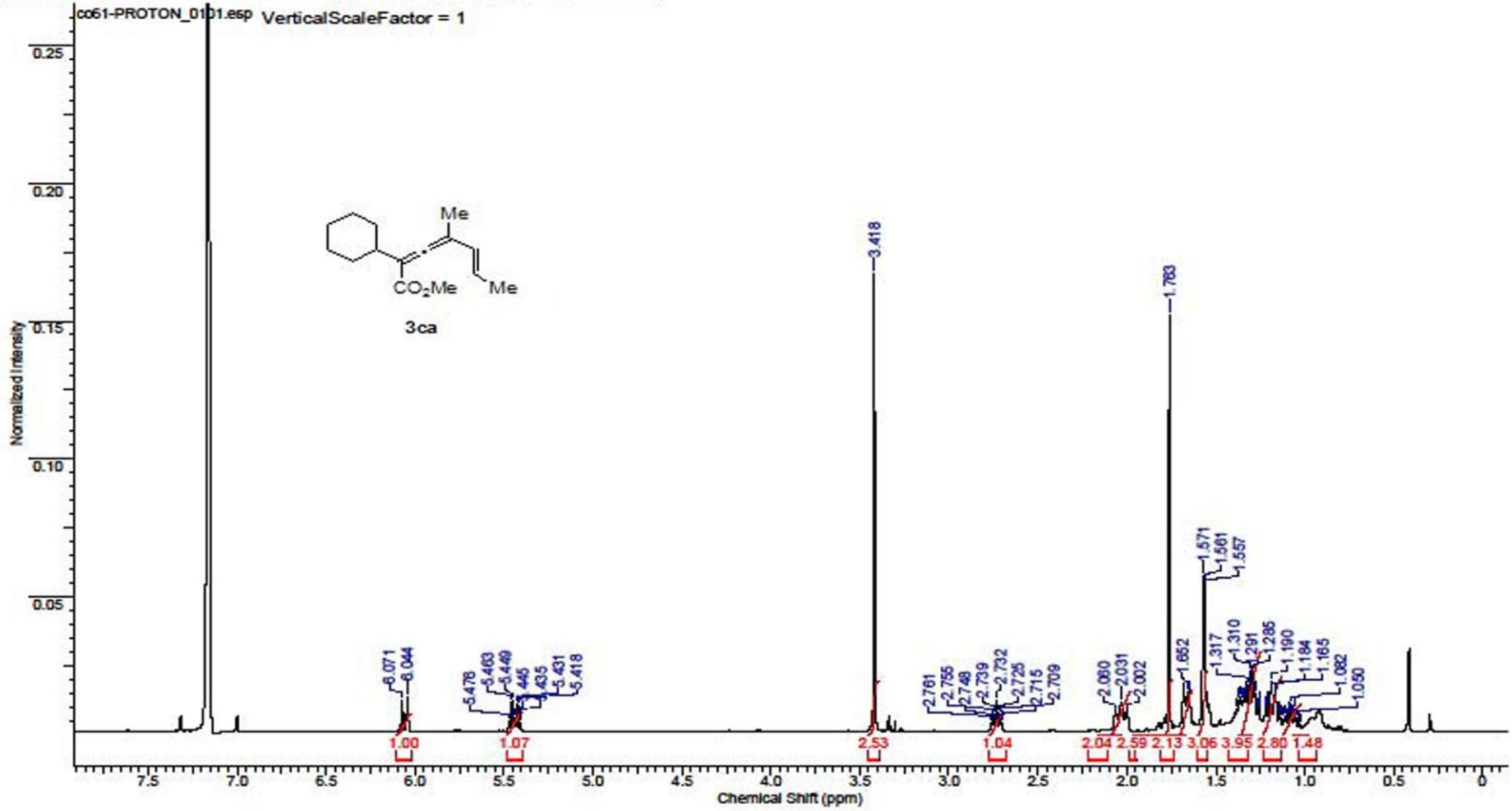
| *Frequency (MHz)* | 499.79 | *Nucleus* | 1H | *Number of Transients* | 128 | *Original Points Count* | 45061 |
| *Points Count* | 65536 | *Pulse Sequence* | s2pul | *Solvent* | BENZENE-d6 | *Spectrum Offset (Hz)* | 4514.2905 |
| *Sweep Width (Hz)* | 11001.10 | *Temperature (degree C)* | 27.000 | | | | |



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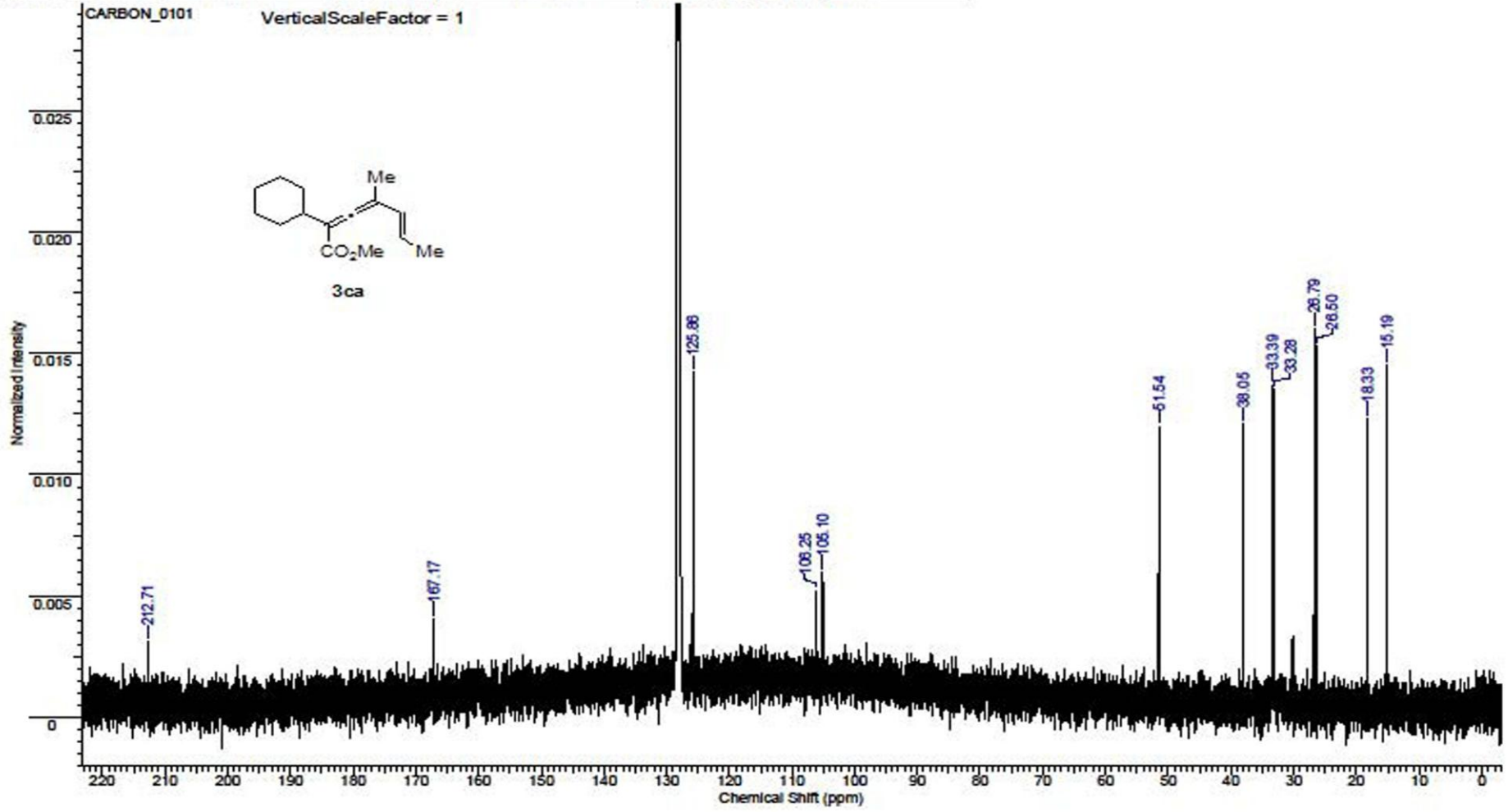
| **File Name** | C:\Users\özge\Desktop\LA 2010\LA NMR FID VE COZUMLERI AGUSTOS 2010\ERAY\OACO61C01\CARBON_0101 | | | | | | |
| **Frequency (MHz)** | 125.69 | **Nucleus** | 13C | **Number of Transients** | 5000 | **Original Points Count** | 41185 |
| **Points Count** | 65536 | **Pulse Sequence** | s2pul | **Receiver Gain** | 60.00 | **Solvent** | BENZENE-d6 |
| **Spectrum Offset (Hz)** | 13875.3359 | **Sweep Width (Hz)** | 31446.54 | **Temperature (degree C)** | 27.000 | | |



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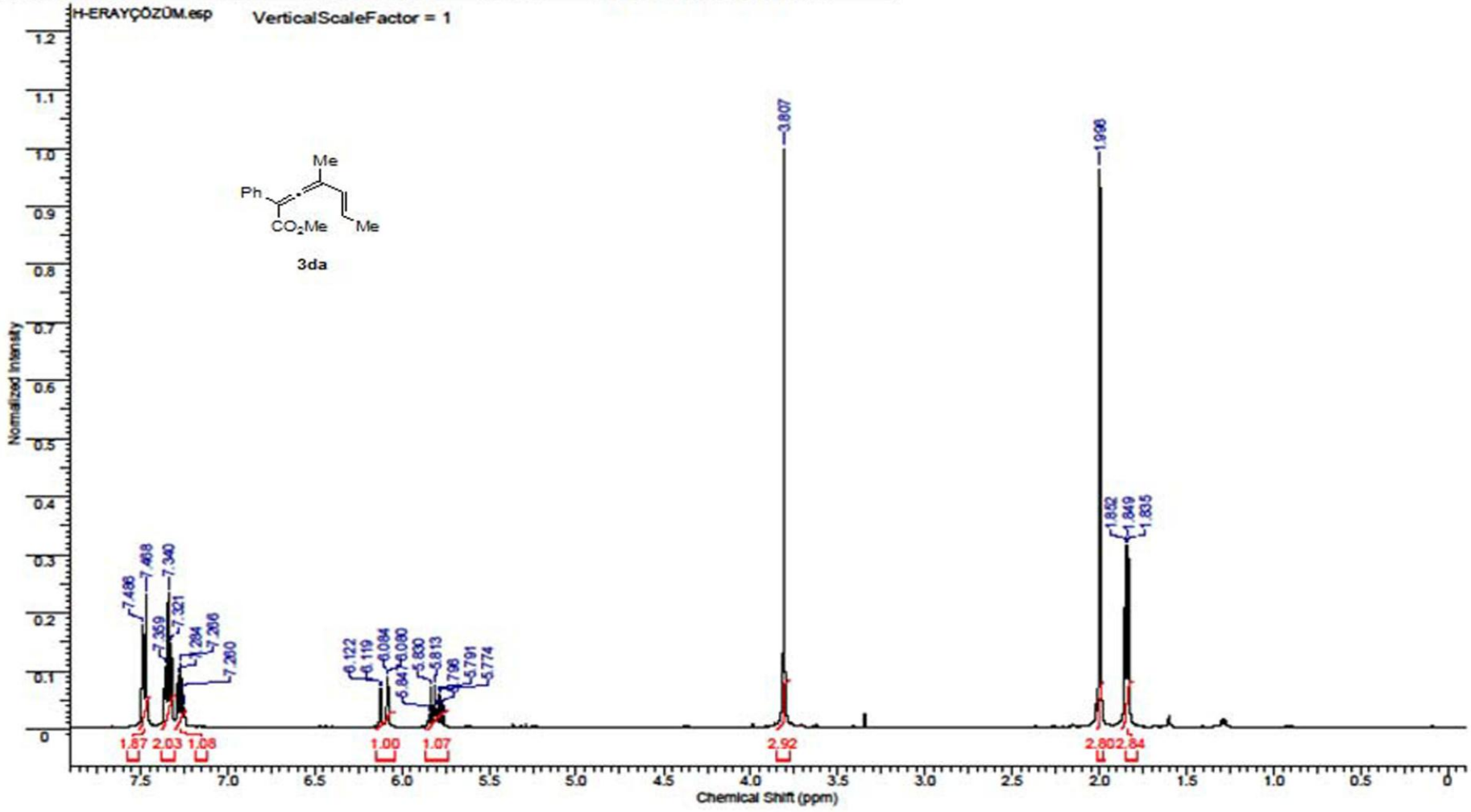
| Frequency (MHz) | 399.52 | Nucleus | 1H | Number of Transients | 8 | Original Points Count | 16384 |
| Points Count | 16384 | Pulse Sequence | s2pul | Solvent | CHLOROFORM-d | | |
| Spectrum Offset (Hz) | 2398.3457 | Sweep Width (Hz) | 6410.26 | Temperature (degree C) | 25.000 | | |



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| Frequency (MHz) | 100.47 | Nucleus | 13C | Number of Transients | 256 | Original Points Count | 32768 |
| Points Count | 32768 | Pulse Sequence | s2pul | Solvent | CHLOROFORM-d | | |
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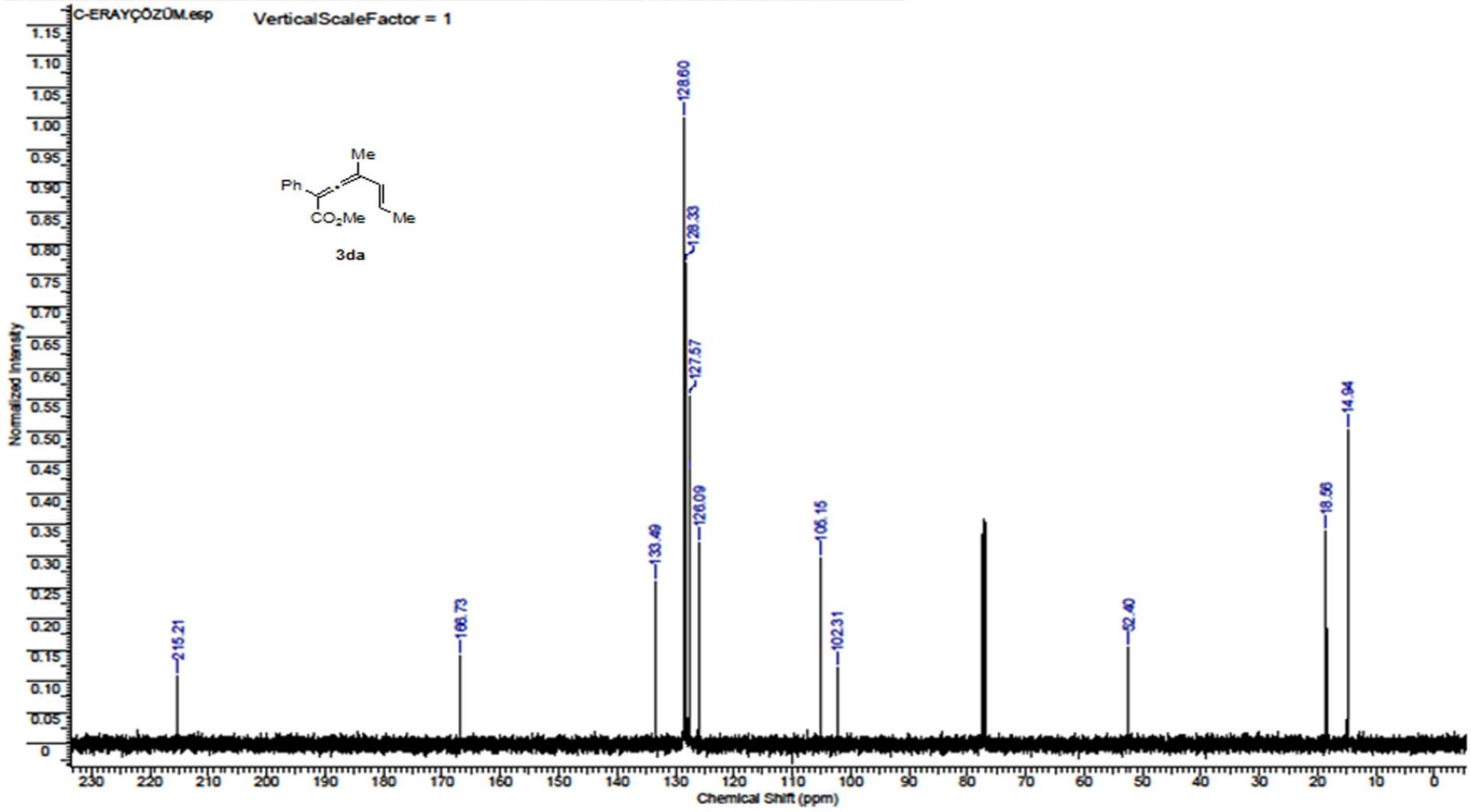

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| ***Date Stamp*** | 24 Aug 2010 03:52:32 | | | | | | |
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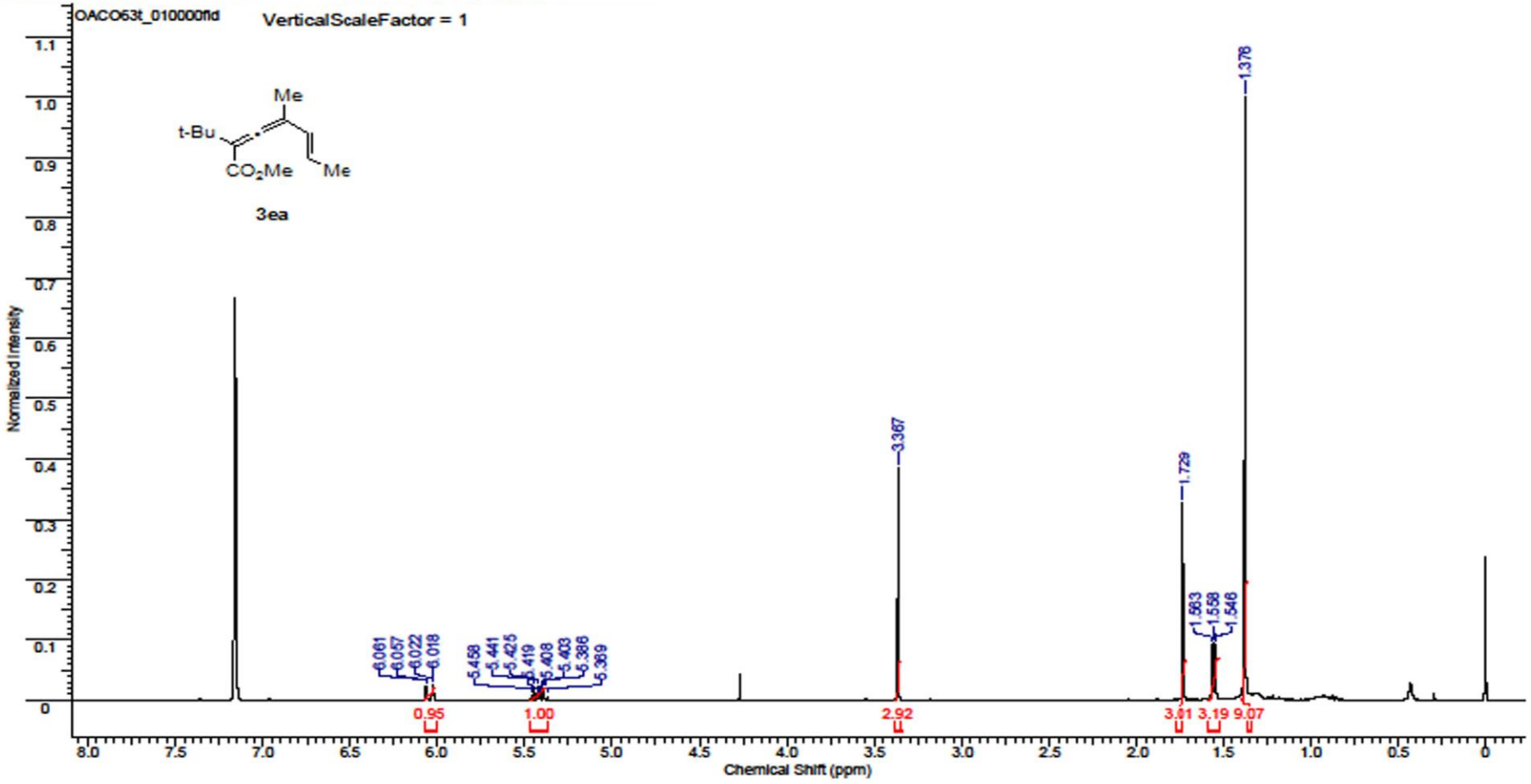
| ***Frequency (MHz)*** | 400.13 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Origin*** | spect |
| ***Original Points Count*** | 32768 | ***Owner*** | guest | ***Points Count*** | 32768 | ***Pulse Sequence*** | zg30 |
| ***Receiver Gain*** | 456.10 | ***SW(cyclical) (Hz)*** | 8223.68 | ***Solvent*** | BENZENE-d6 | ***Spectrum Offset (Hz)*** | 2425.8818 |
| ***Sweep Width (Hz)*** | 8223.43 | ***Temperature (degree C)*** | 27.000 | | | | |



| | | | | | | | |
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| ***Acquisition Time (sec)*** | 3.9846 | ***Comment*** | 5 mm Multinuclear | | | ***Date*** | 24 Aug 2010 03:52:32 |
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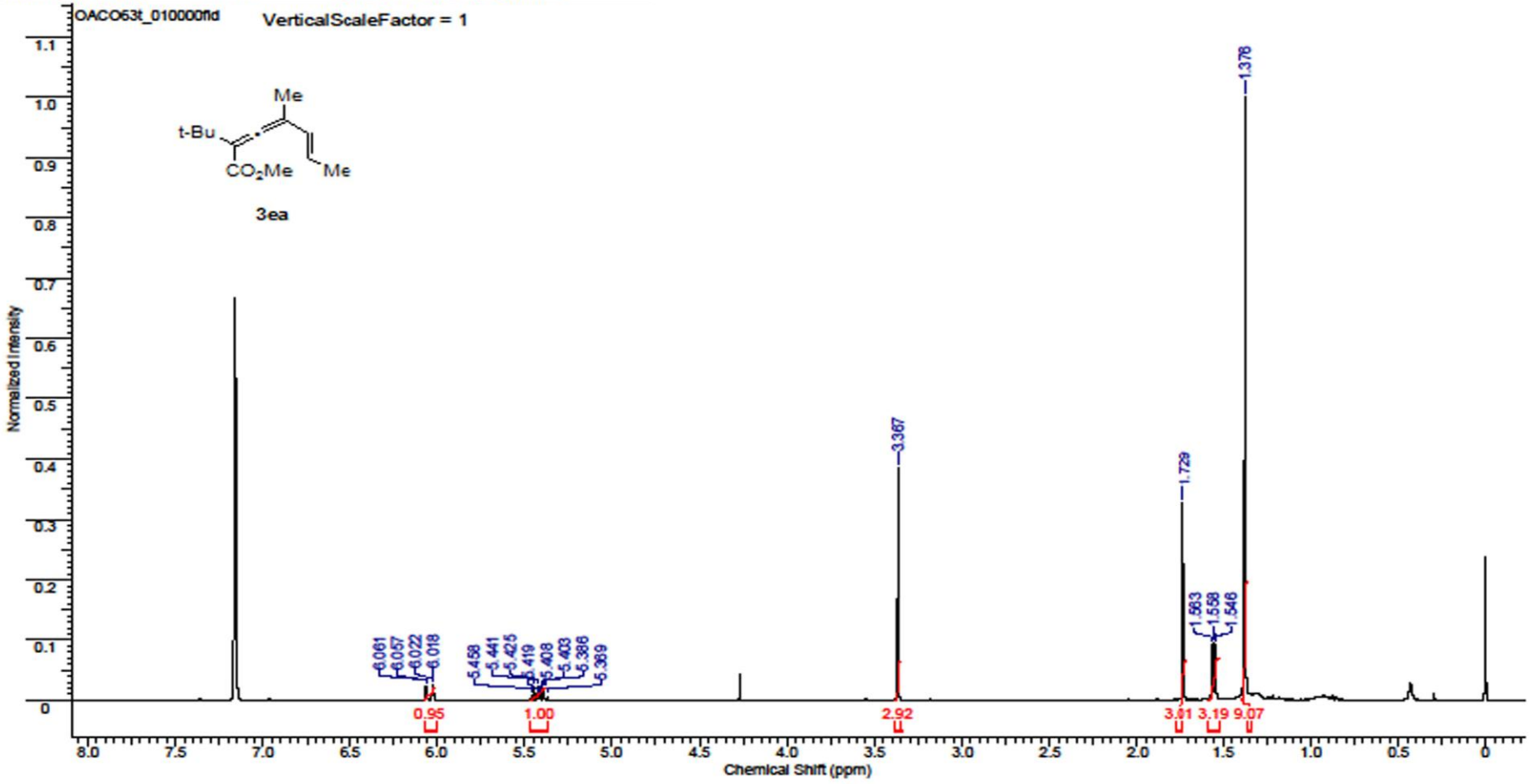
| ***Frequency (MHz)*** | 400.13 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Origin*** | spect |
| ***Original Points Count*** | 32768 | ***Owner*** | guest | ***Points Count*** | 32768 | ***Pulse Sequence*** | zg30 |
| ***Receiver Gain*** | 456.10 | ***SW(cyclical) (Hz)*** | 8223.68 | ***Solvent*** | BENZENE-d6 | ***Spectrum Offset (Hz)*** | 2425.8818 |
| ***Sweep Width (Hz)*** | 8223.43 | ***Temperature (degree C)*** | 27.000 | | | | |



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| Frequency (MHz) | 100.63 | Nucleus | 13C | Number of Transients | 1024 | Origin | spect |
| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zgpg30 |
| Receiver Gain | 4096.00 | SW(cyclical) (Hz) | 31847.13 | Solvent | BENZENE-d6 | Spectrum Offset (Hz) | 12693.1709 |
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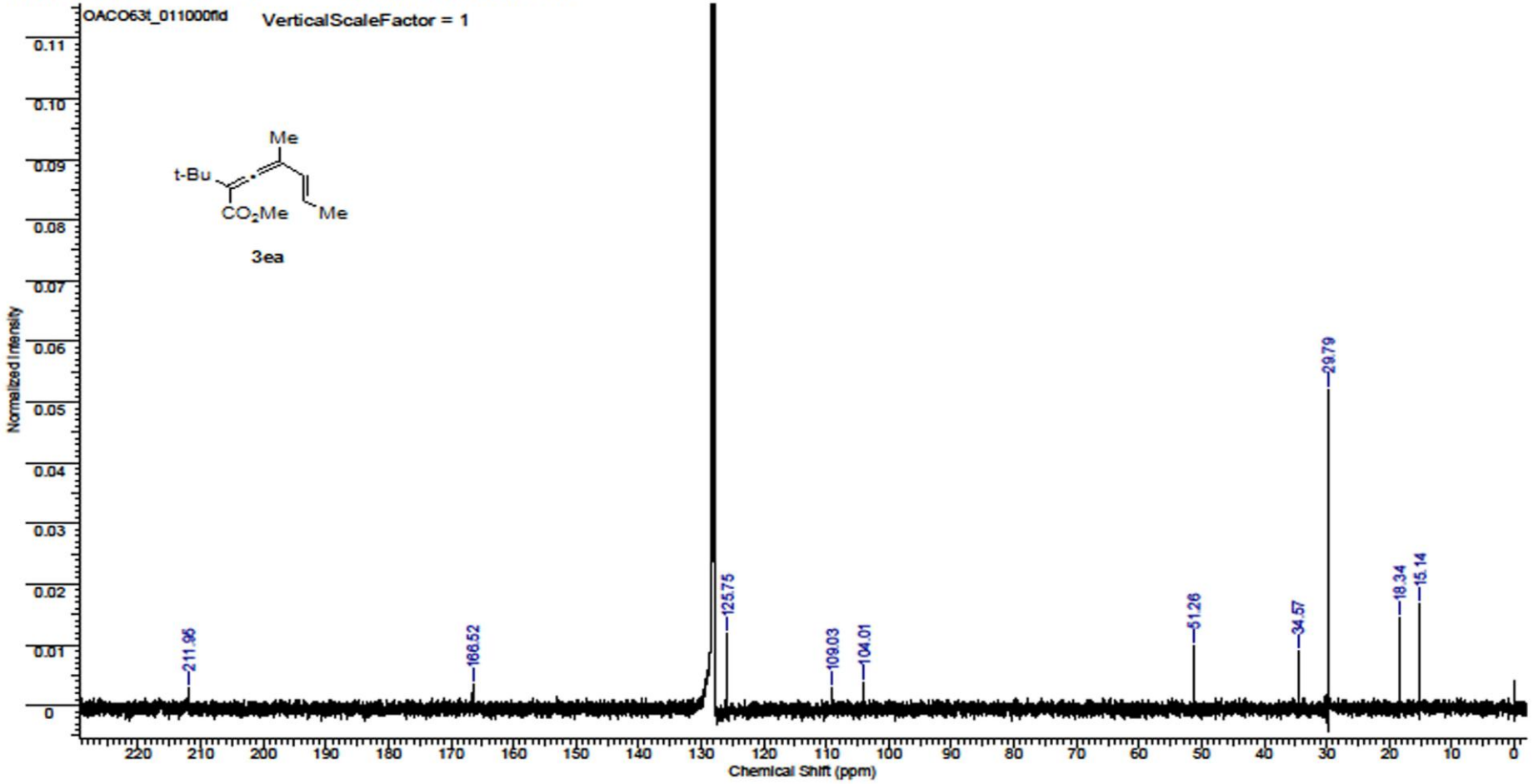

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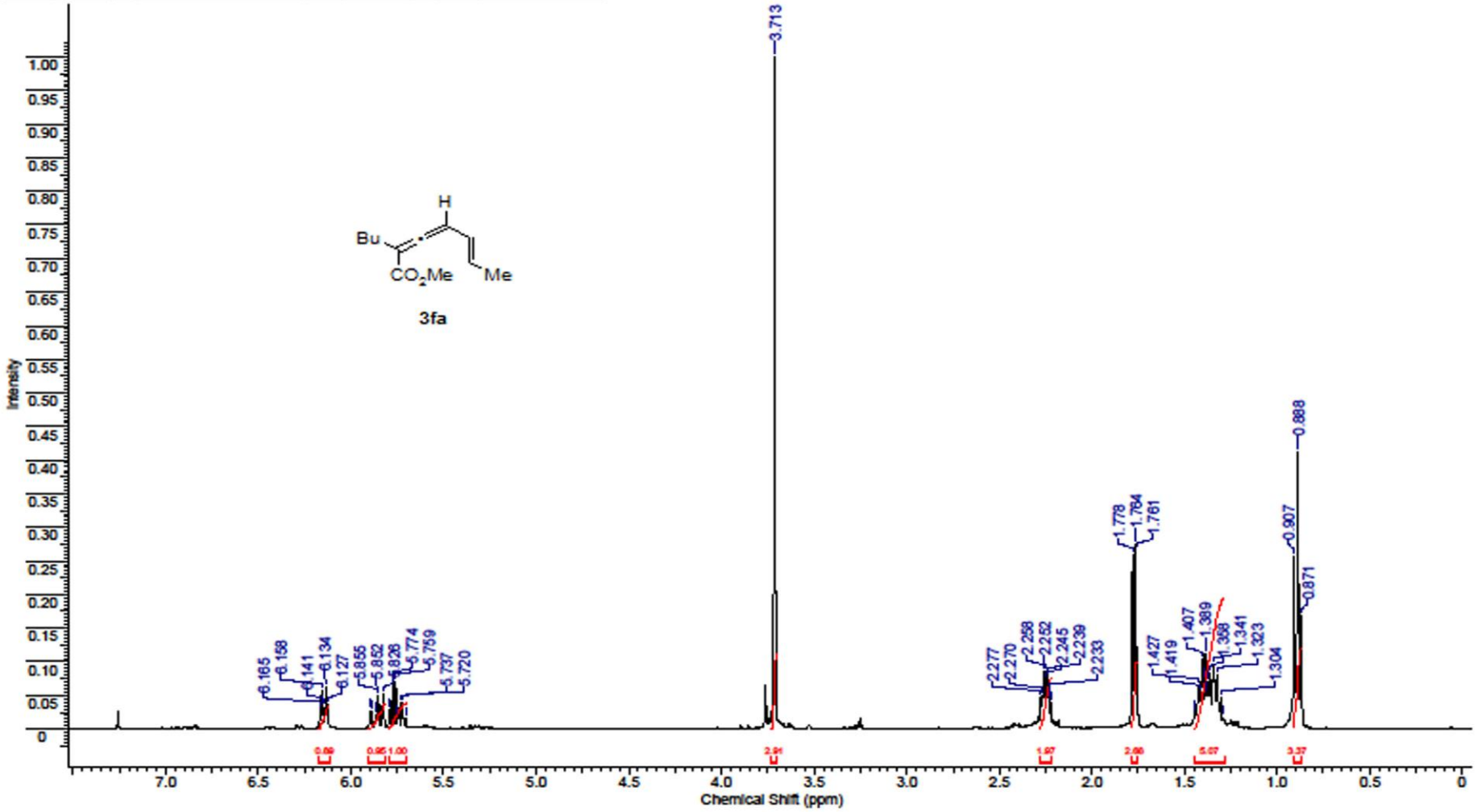
| *Points Count* | 16384 | *Pulse Sequence* | s2pul | *Solvent* | CHLOROFORM-D |
| *Sweep Width (Hz)* | 6410.26 | *Temperature (degree C)* | 25.000 | | |



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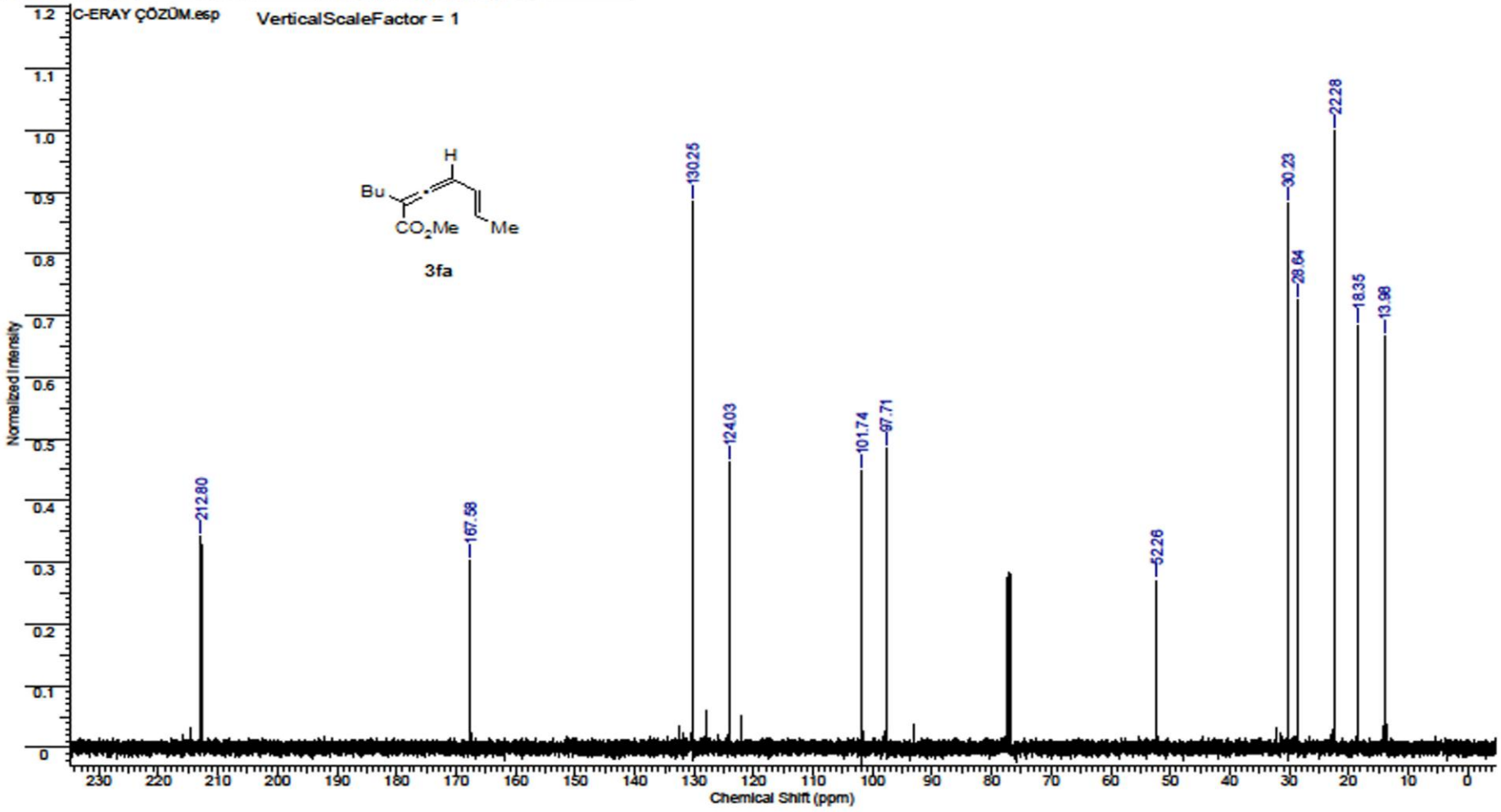
| ***Nucleus*** | 13C | ***Number of Transients*** | 256 | ***Original Points Count*** | 32768 | ***Points Count*** | 32768 |
| ***Pulse Sequence*** | s2pul | ***Solvent*** | CHLOROFORM-d | | | ***Spectrum Offset (Hz)*** | 11066.1650 |
| ***Sweep Width (Hz)*** | 25510.20 | ***Temperature (degree C)*** | 25.000 | | | | |



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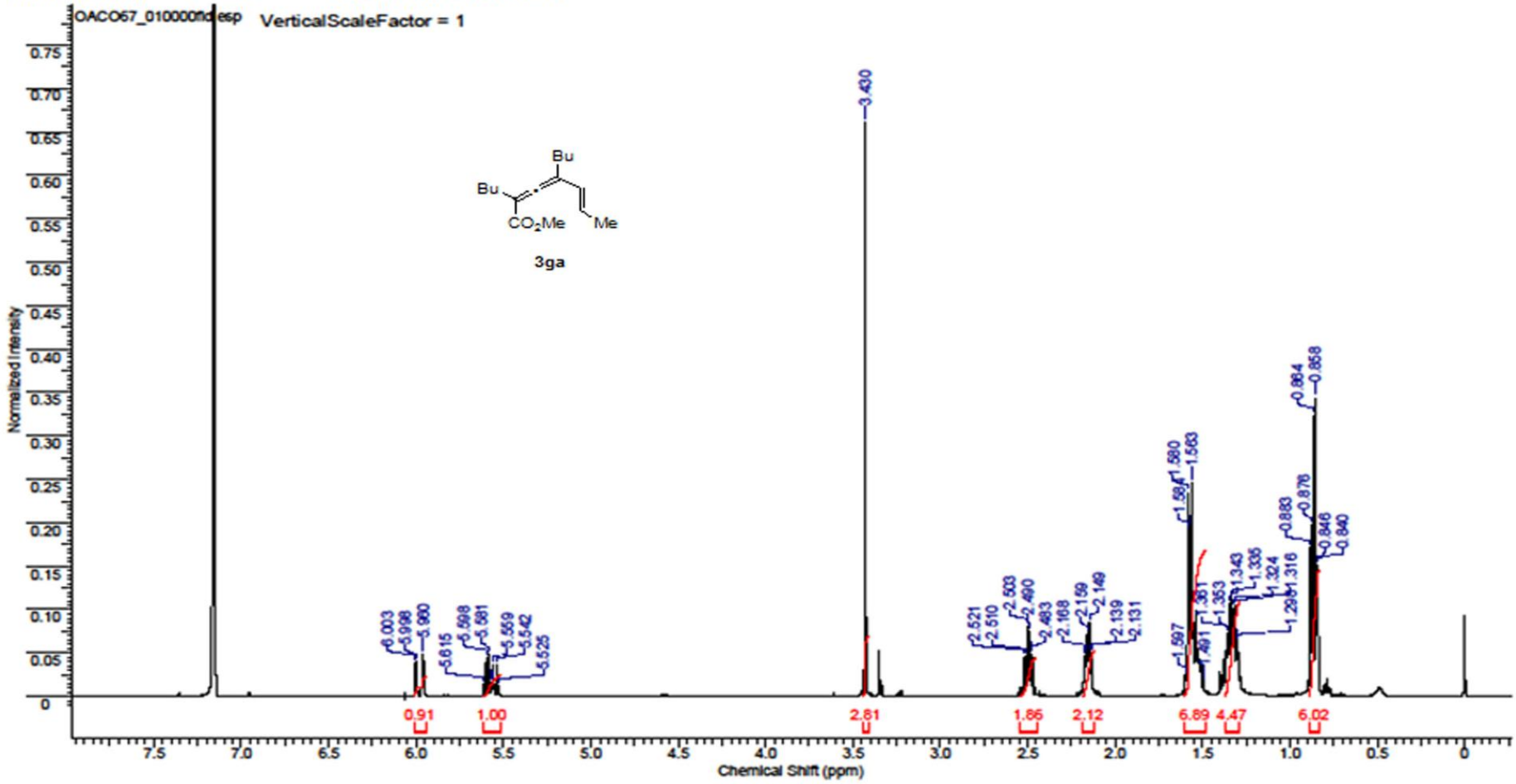
| Frequency (MHz) | 400.13 | Nucleus | 1H | Number of Transients | 16 | Origin | spect |
| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zg30 |
| Receiver Gain | 203.20 | SW(cyclical) (Hz) | 8223.68 | Solvent | BENZENE-d6 | Spectrum Offset (Hz) | 2425.8818 |
| Sweep Width (Hz) | 8223.43 | Temperature (degree C) | 27.000 | | | | |



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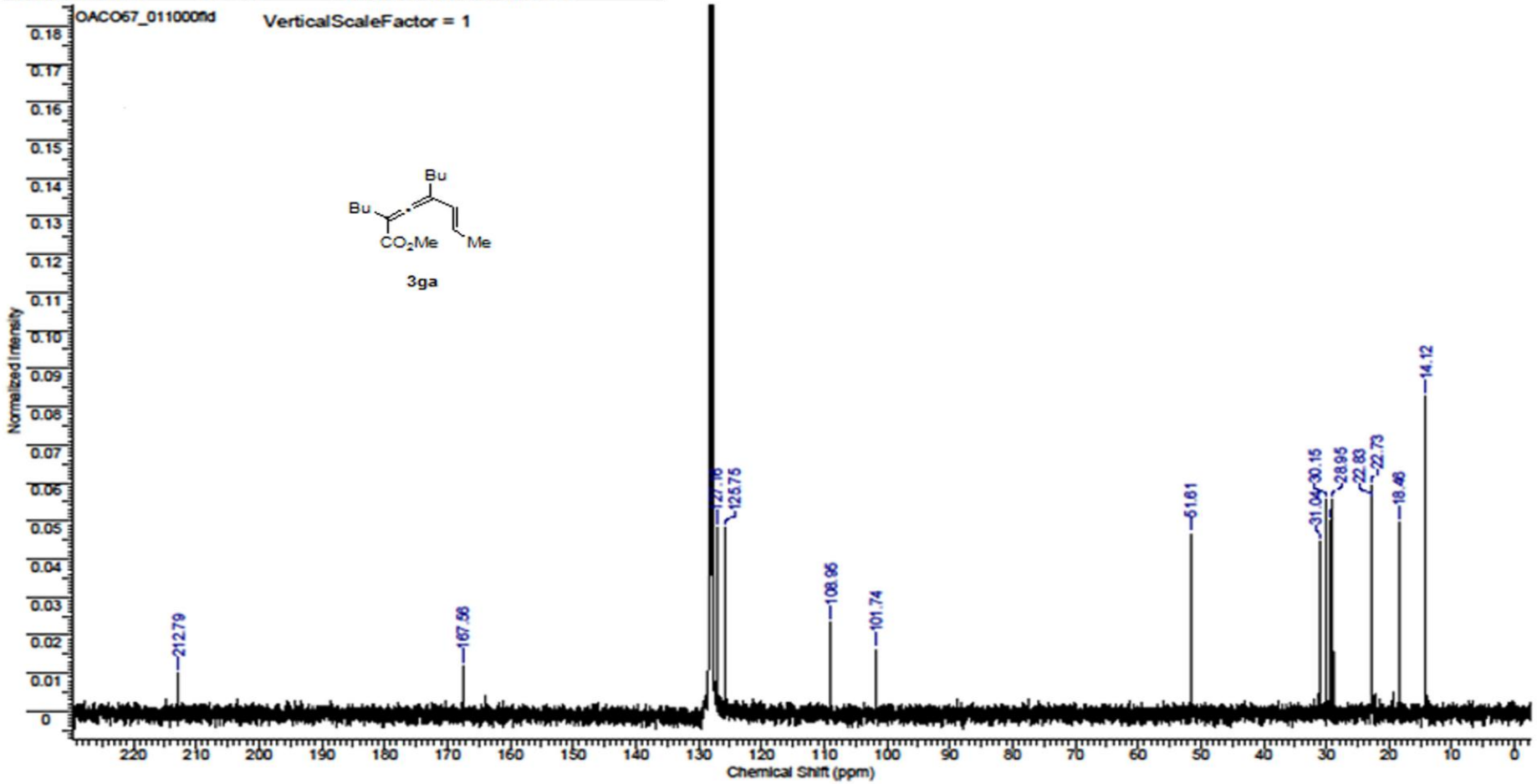
| Frequency (MHz) | 100.63 | Nucleus | 13C | Number of Transients | 320 | Origin | spect |
| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zgpg30 |
| Receiver Gain | 4096.00 | SW(cyclical) (Hz) | 31847.13 | Solvent | BENZENE-d6 | Spectrum Offset (Hz) | 12693.1709 |
| Sweep Width (Hz) | 31846.16 | Temperature (degree C) | 27.000 | | | | |



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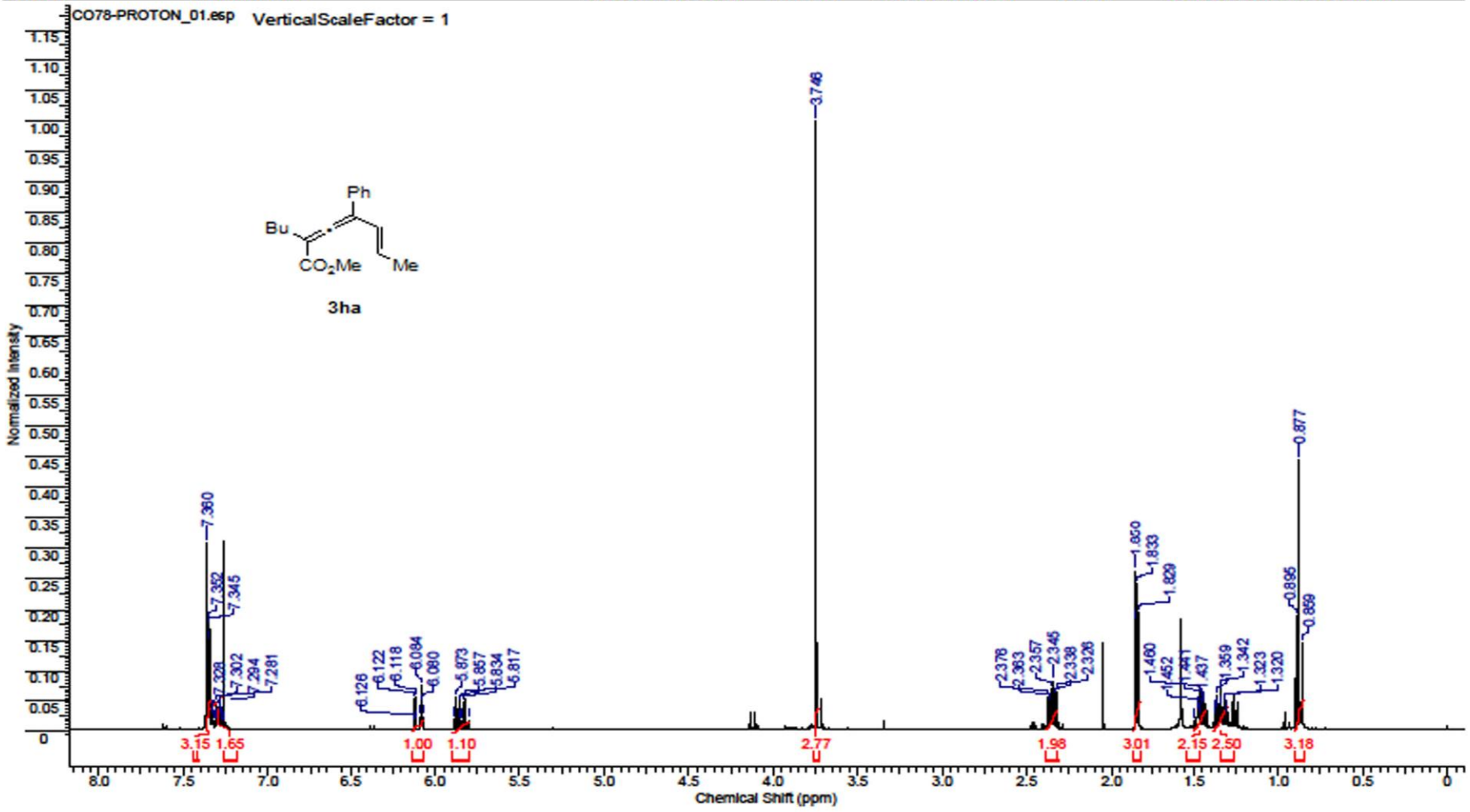
| Solvent | CHLOROFORM-d | | | Spectrum Offset (Hz) | 2397.9546 | Sweep Width (Hz) | 6410.26 | Temperature (degree C) | 28.000 |



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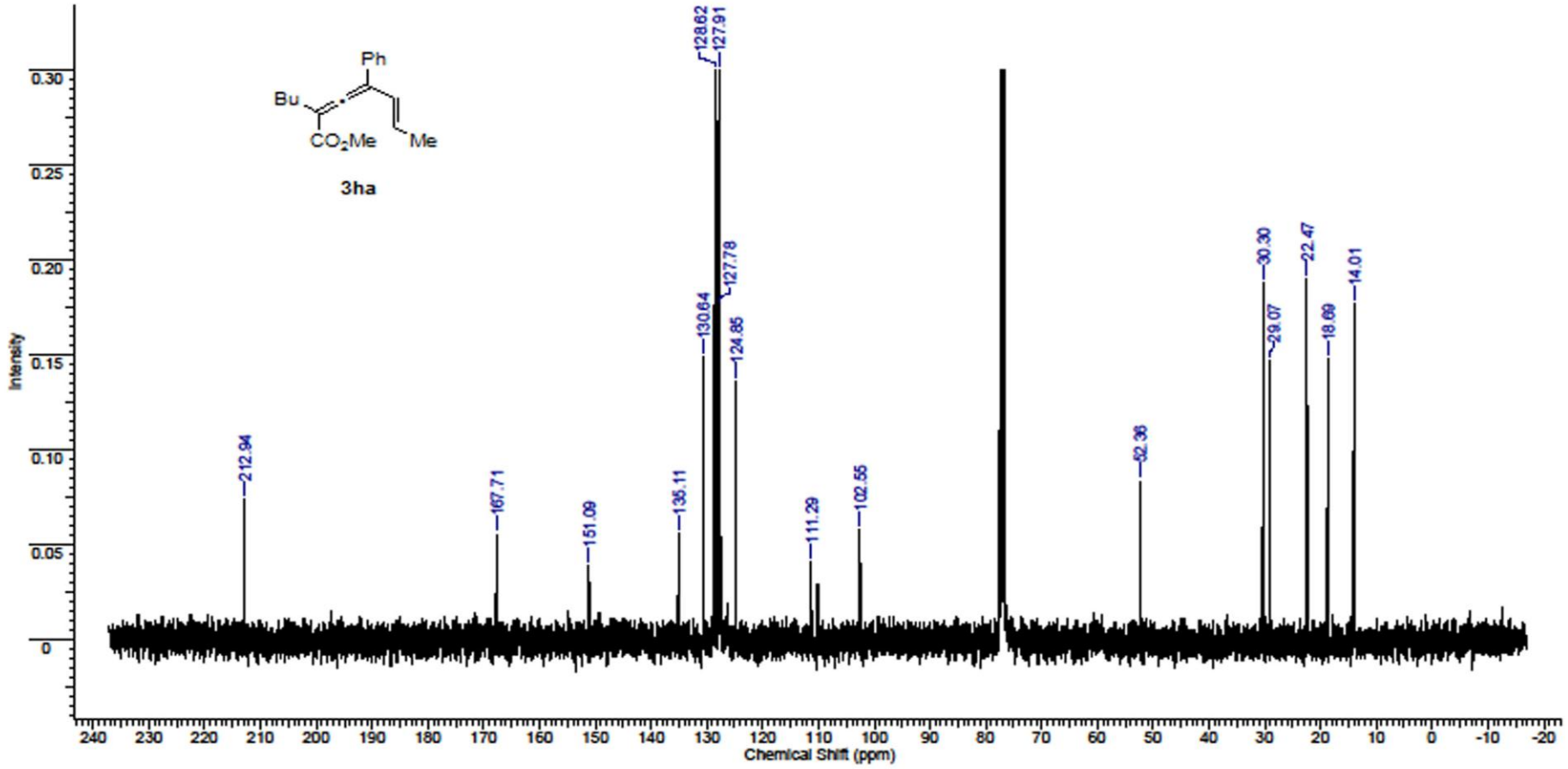
| *Pulse Sequence* | s2pul | *Solvent* | CHLOROFORM-D | | | *Sweep Width (Hz)* | 25510.20 |
| *Temperature (degree C)* | 28.000 | | | | | | |



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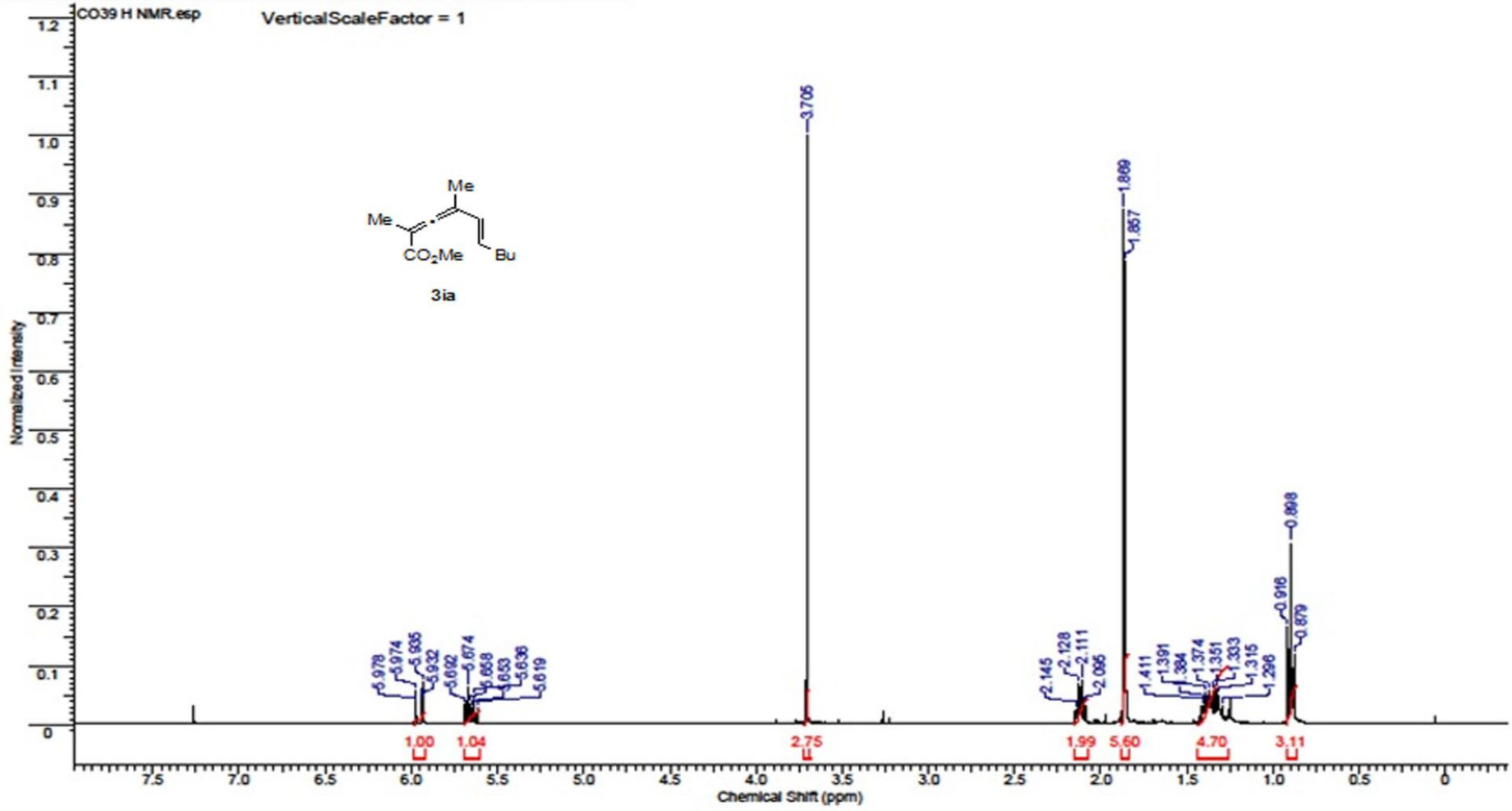
| ***Pulse Sequence*** | s2pul | ***Solvent*** | CHLOROFORM-d | | | ***Spectrum Offset (Hz)*** | 2397.1353 |
| ***Sweep Width (Hz)*** | 6410.26 | ***Temperature (degree C)*** | 25.000 | | | | |



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| Date Stamp | Apr 19 2010 | File Name | C:\Users\özge\Desktop\ERAY-ACD ÇIKACAKLAR\CO39\MU-CO39-TEKRAR_19Apr2010\CARBON_01 | | | | |
| Frequency (MHz) | 100.47 | Nucleus | 13C | Number of Transients | 256 | Original Points Count | 32768 |
| Points Count | 32768 | Pulse Sequence | s2pul | Receiver Gain | 60.00 | Solvent | CHLOROFORM-d |
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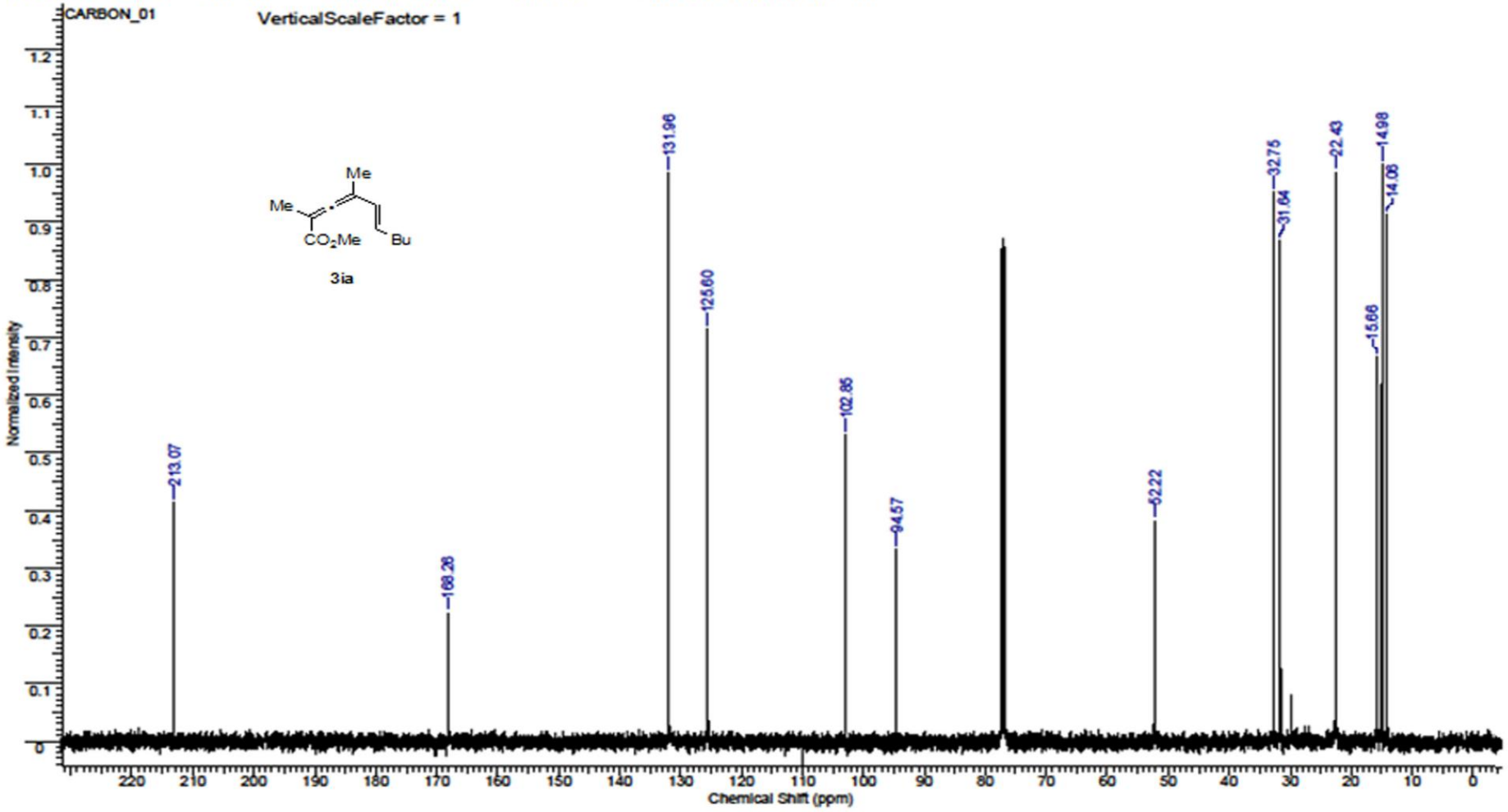

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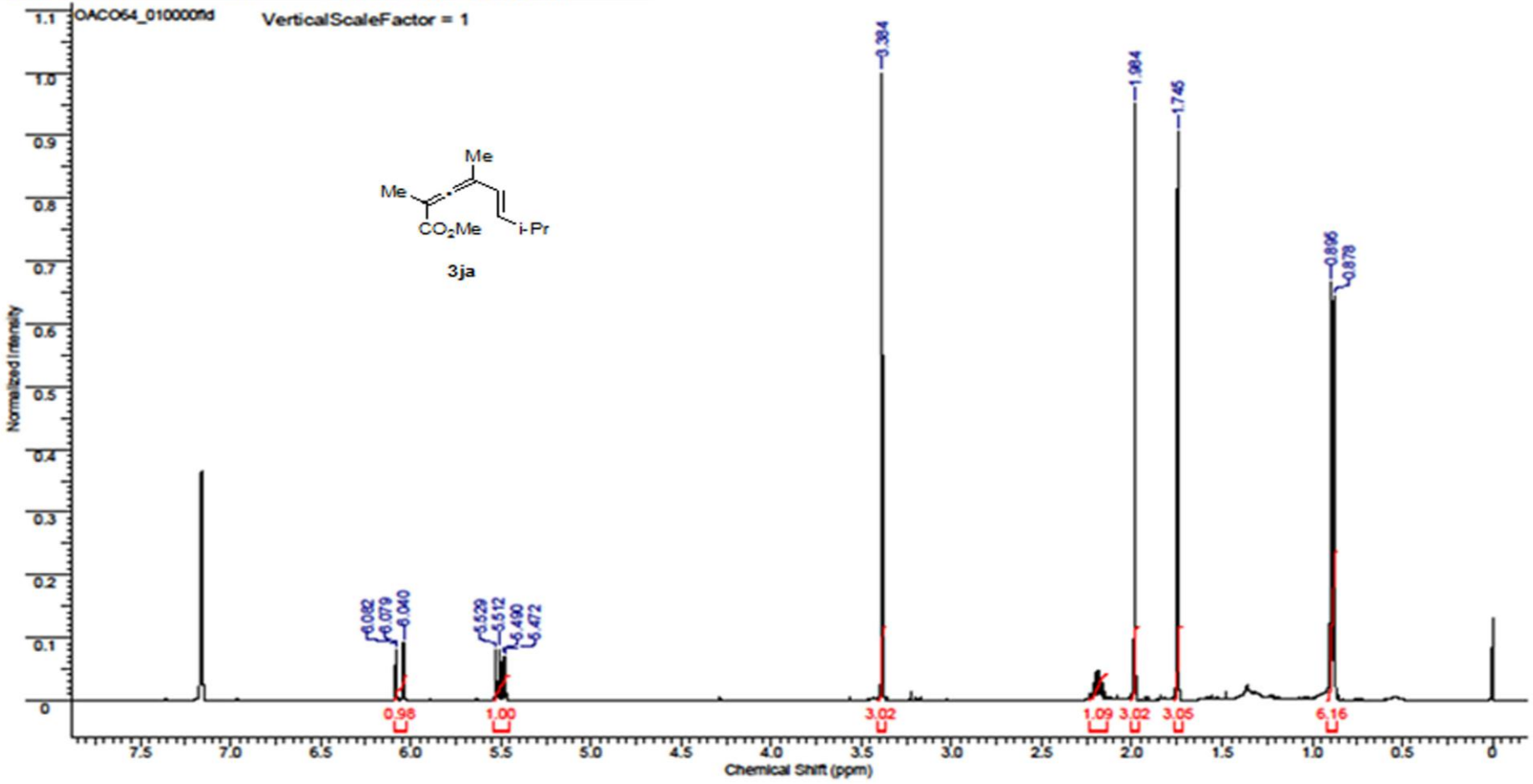
| Frequency (MHz) | 400.13 | Nucleus | 1H | Number of Transients | 16 | Origin | spect |
| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zg30 |
| Receiver Gain | 228.10 | SW(cyclical) (Hz) | 8223.68 | Solvent | BENZENE-d6 | Spectrum Offset (Hz) | 2425.8818 |
| Sweep Width (Hz) | 8223.43 | Temperature (degree C) | 27.000 | | | | |



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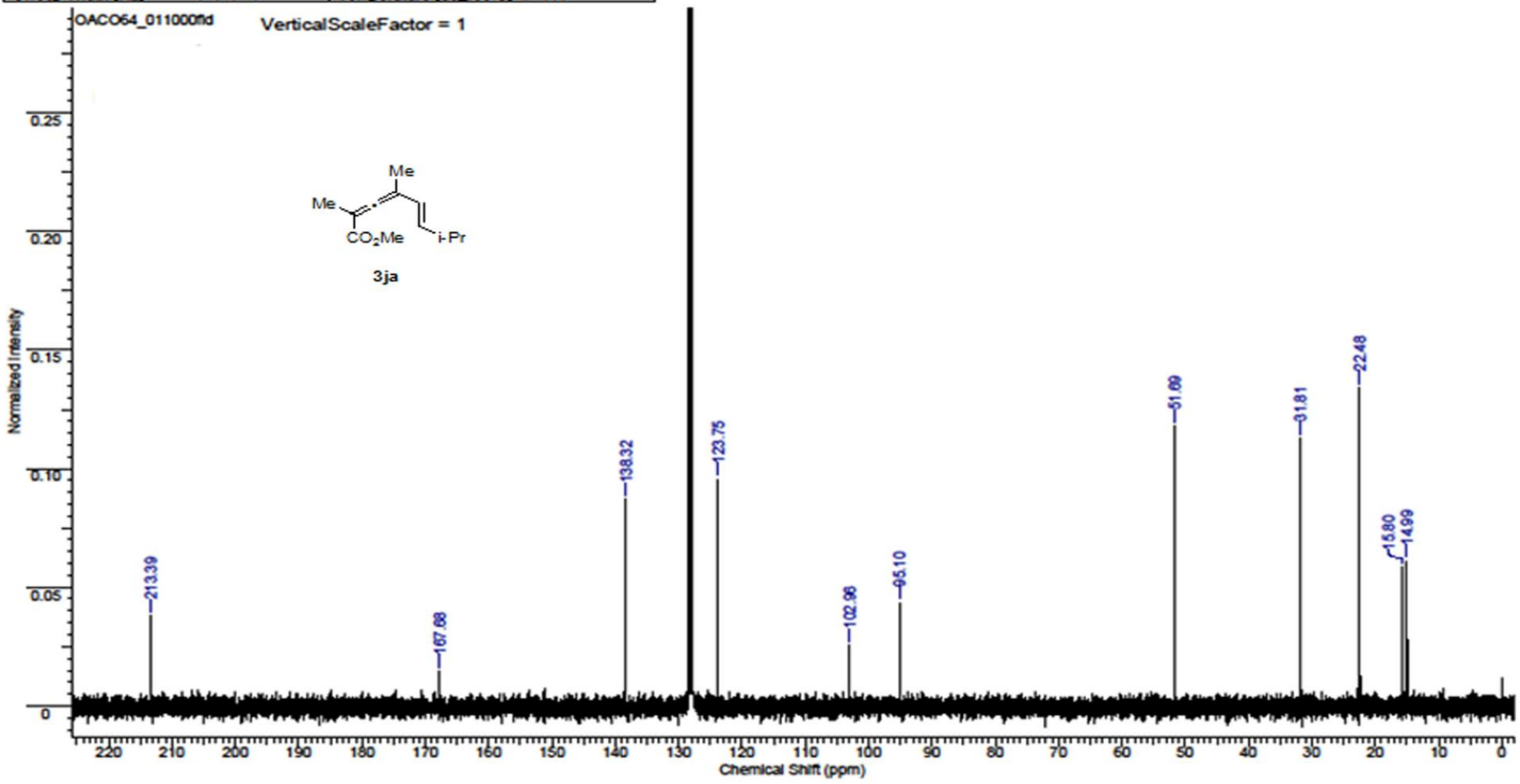
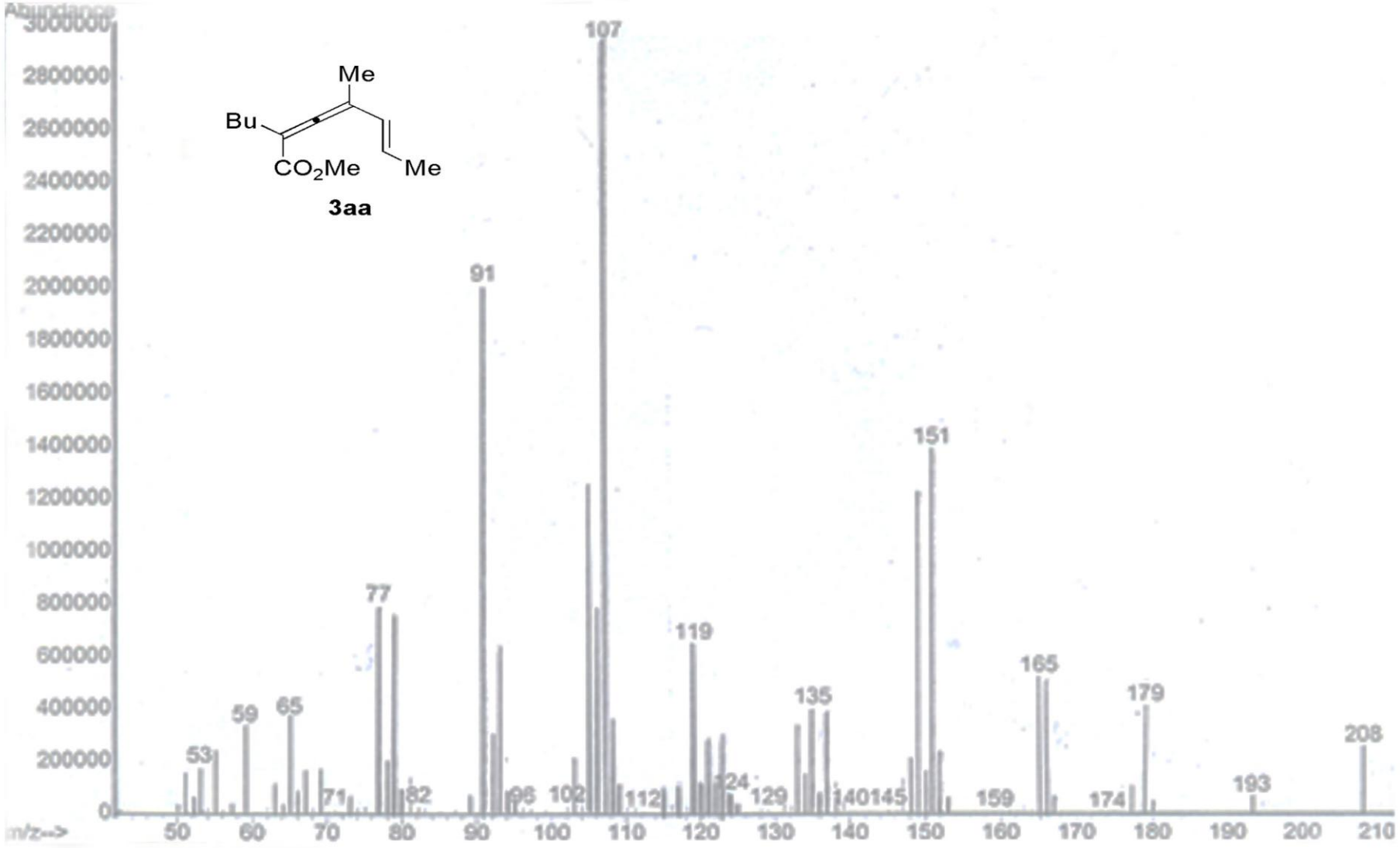
| Frequency (MHz) | 100.63 | Nucleus | 13C | Number of Transients | 320 | Origin | spect |
| Original Points Count | 32768 | Owner | guest | Points Count | 32768 | Pulse Sequence | zgpg30 |
| Receiver Gain | 4096.00 | SW(cyclical) (Hz) | 31847.13 | Solvent | BENZENE-d6 | Spectrum Offset (Hz) | 12693.1709 |
| Sweep Width (Hz) | 31846.16 | Temperature (degree C) | 27.000 | | | | |



# APPENDIX E

# MASS SPECTRUMS OF PRODUCTS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Me
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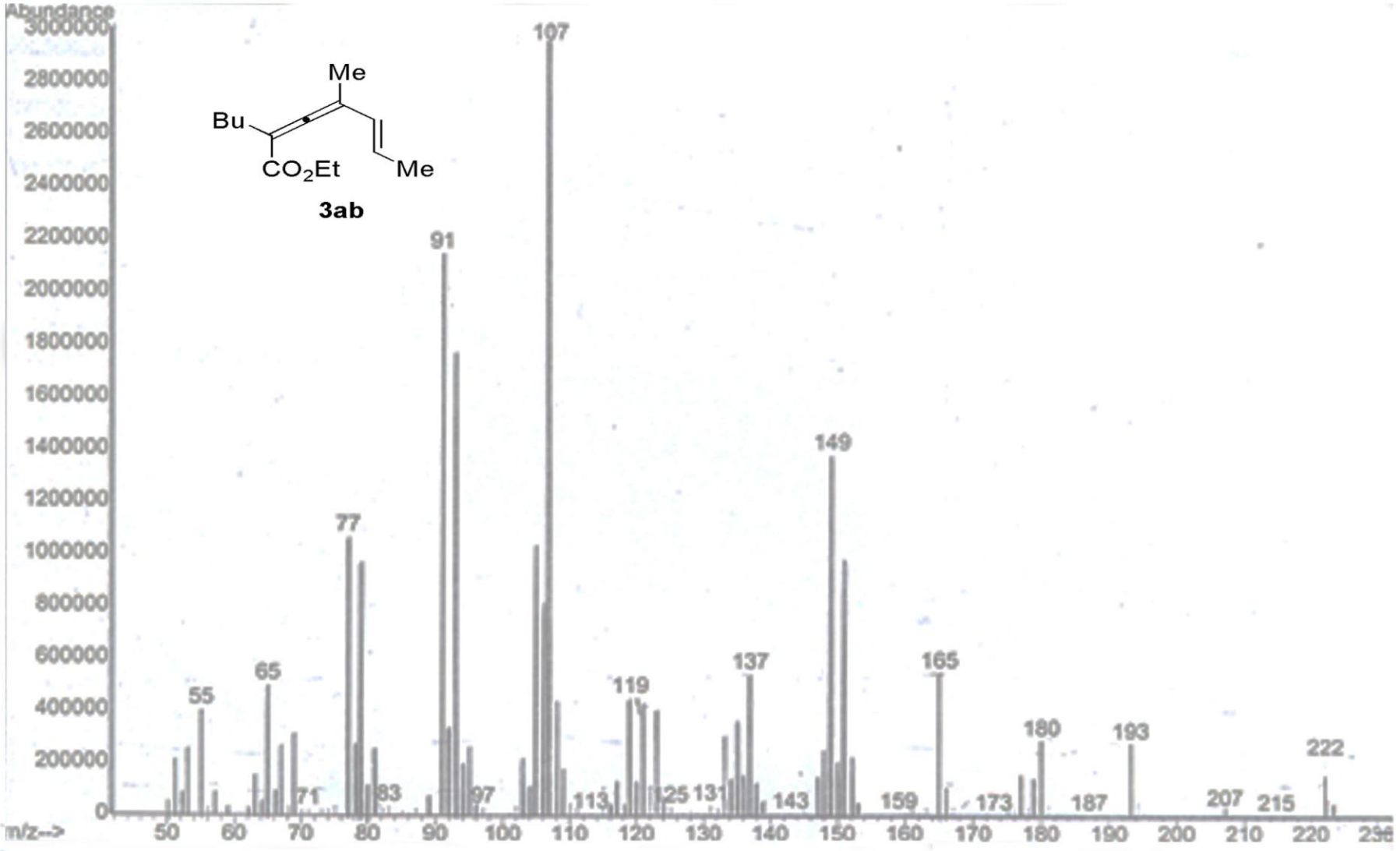
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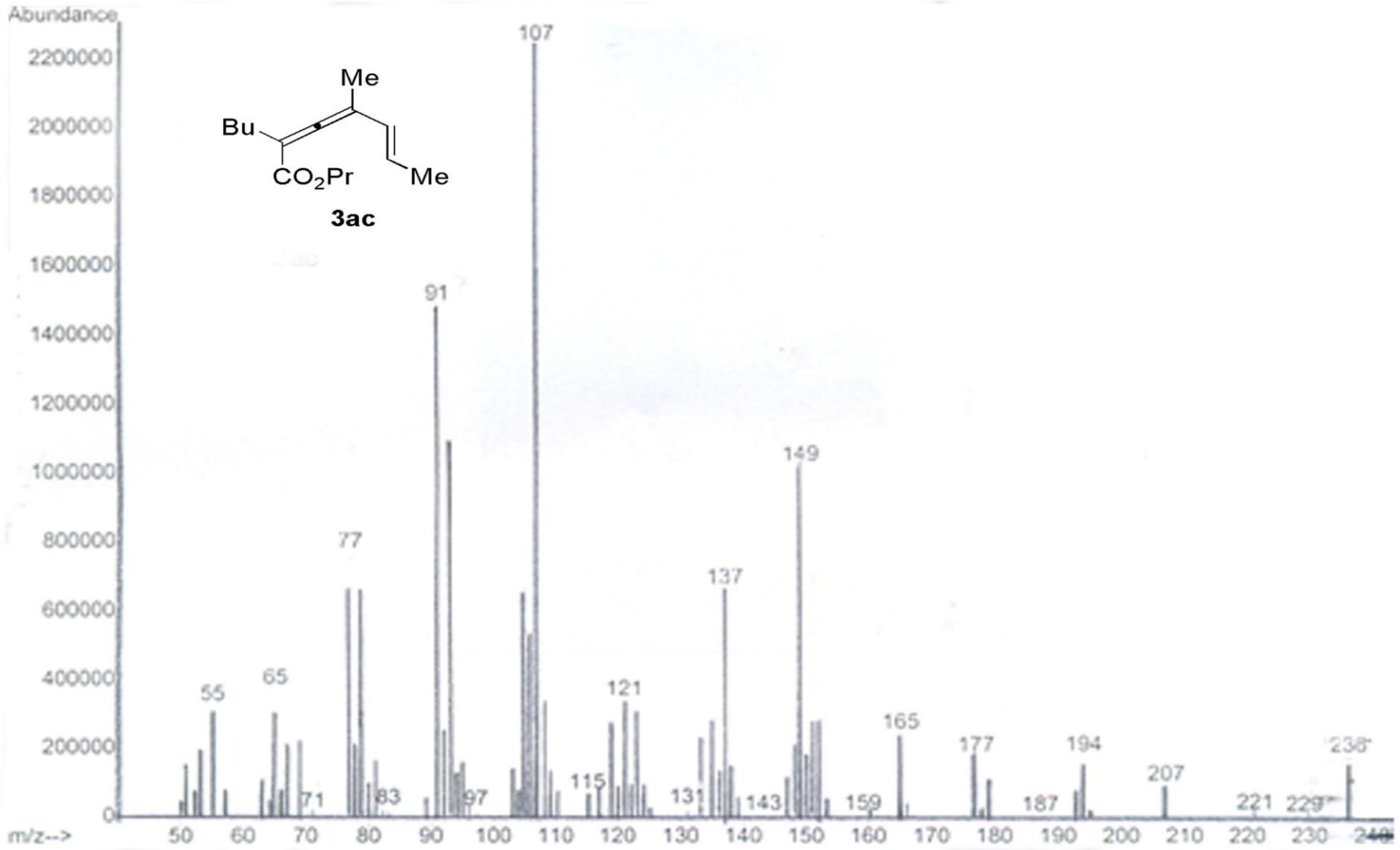
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CO2Pr
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3ac
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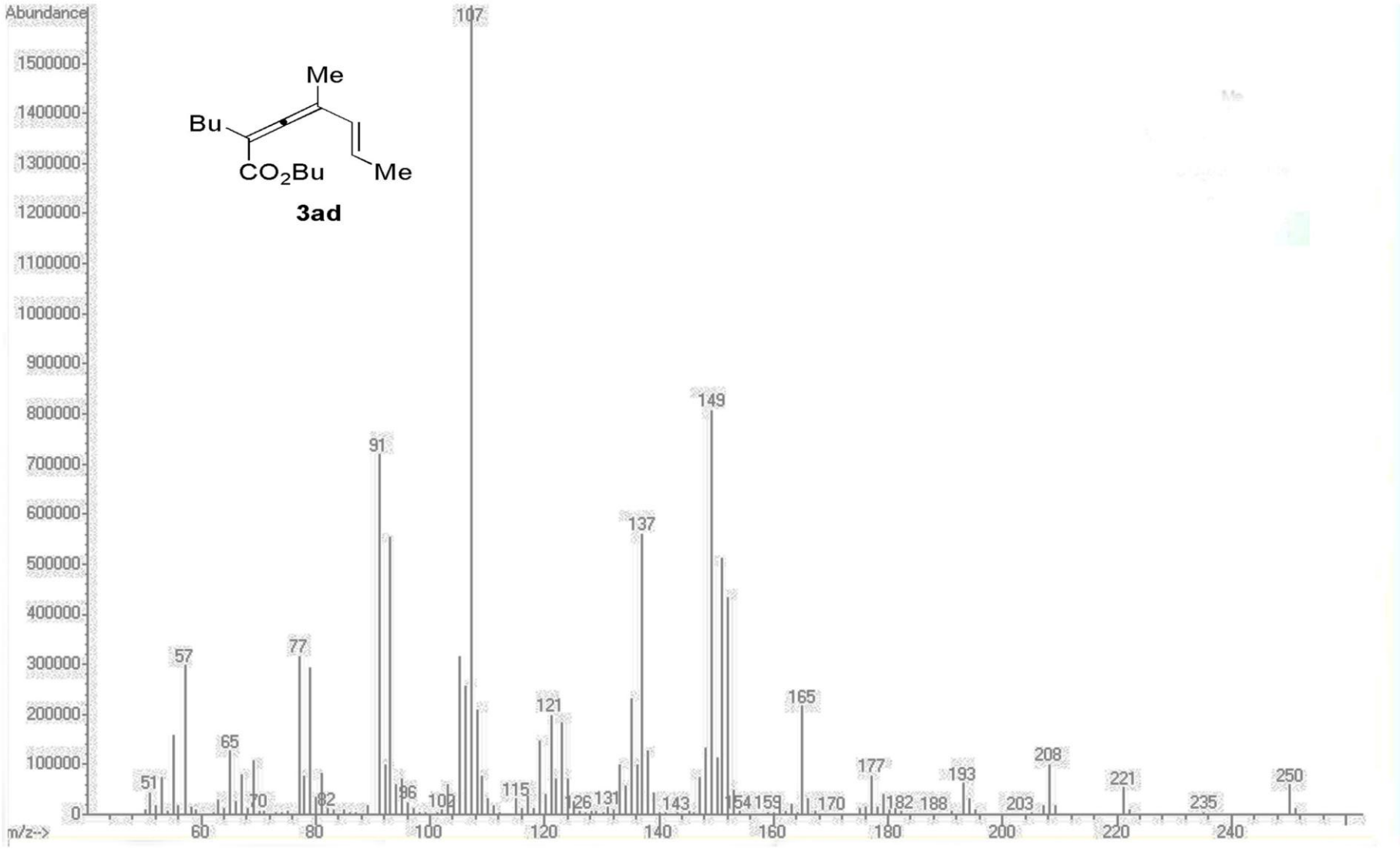
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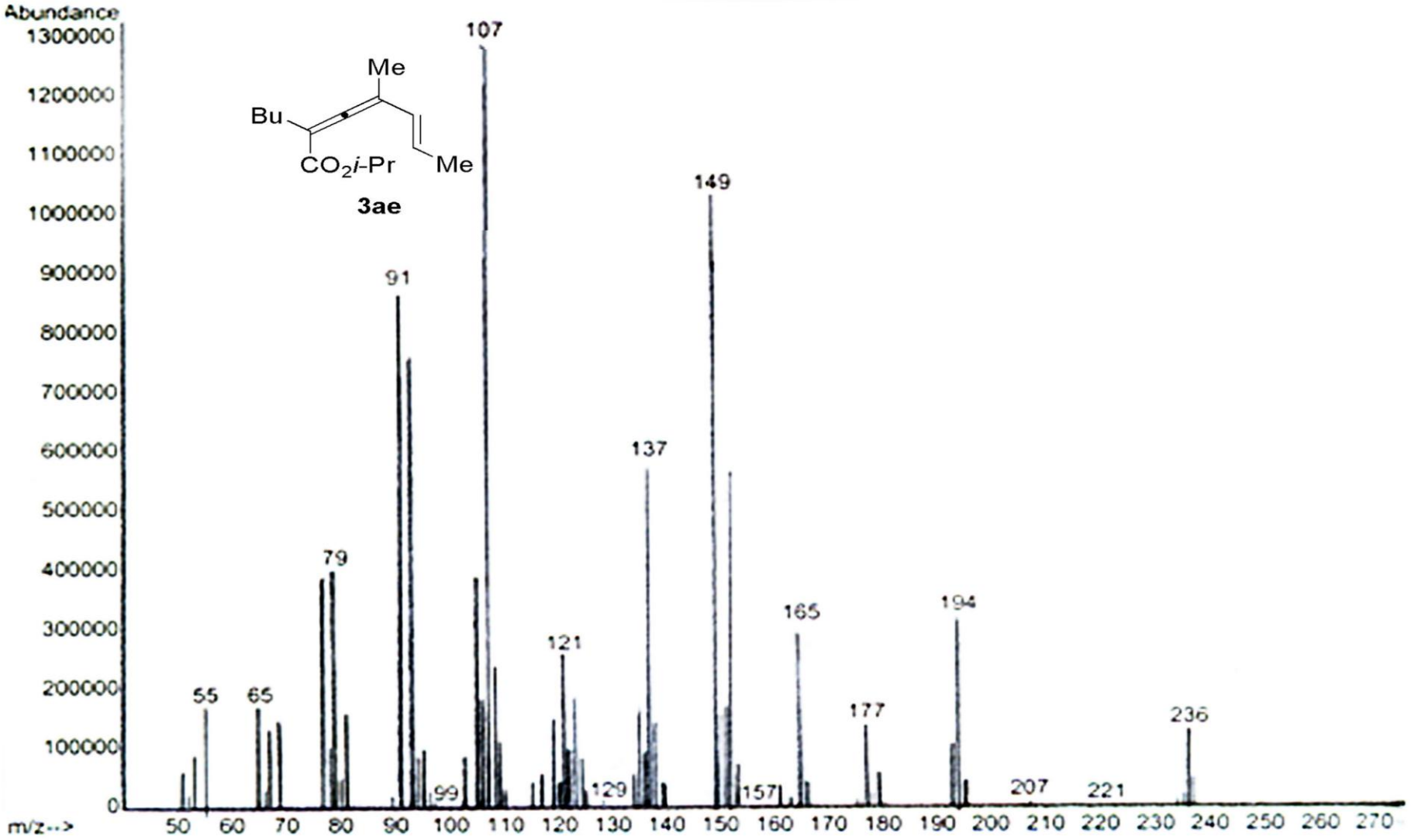
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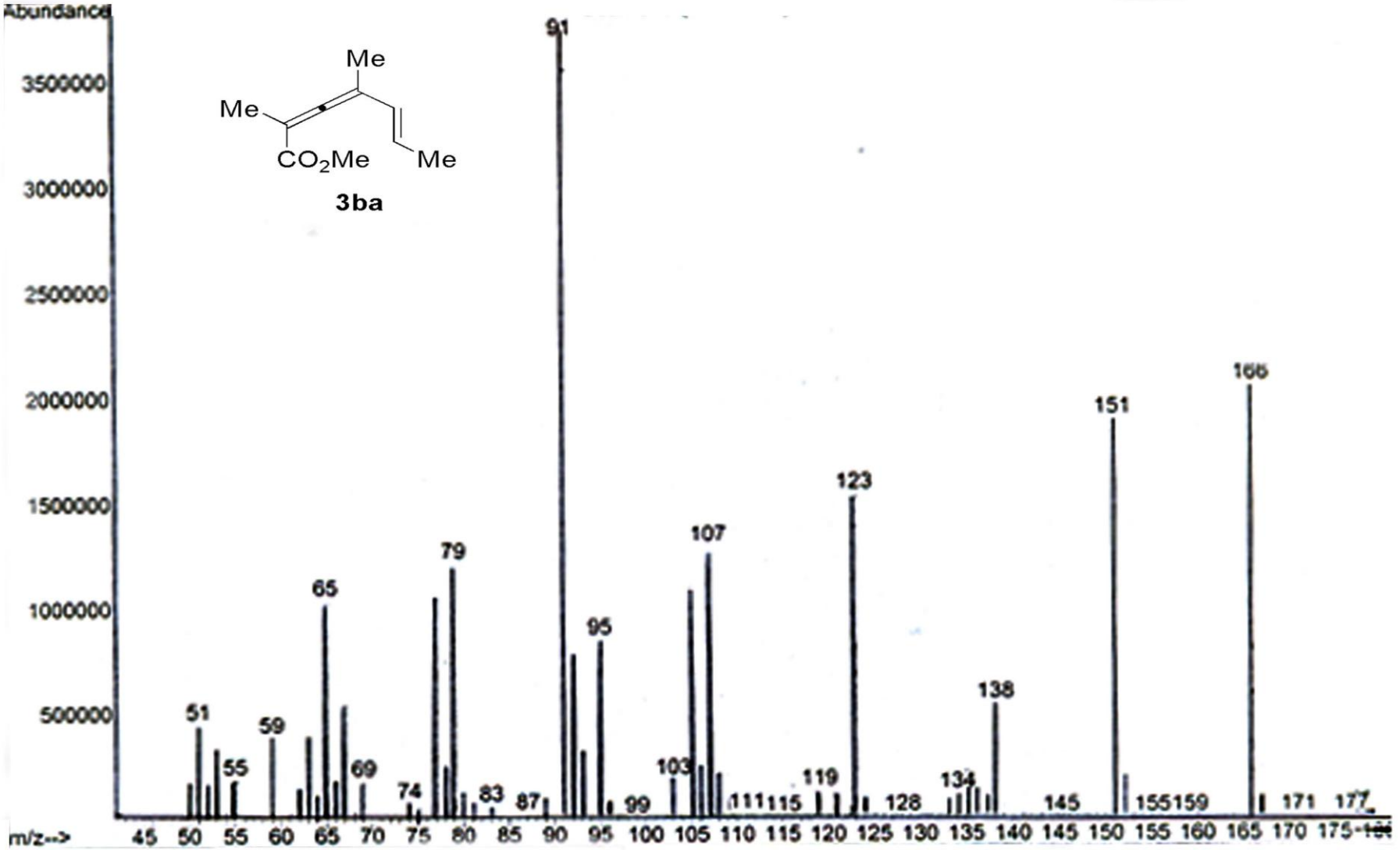
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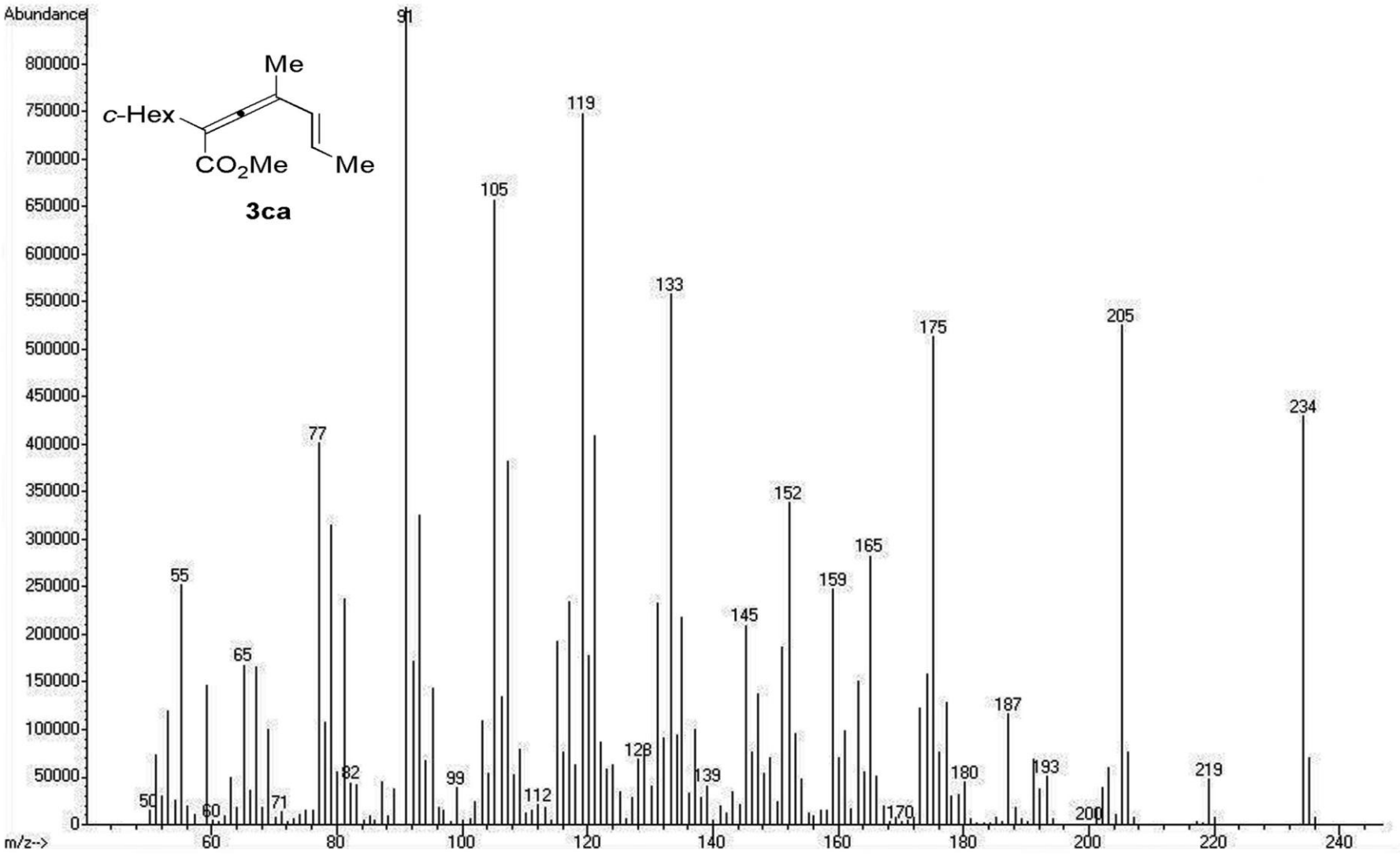
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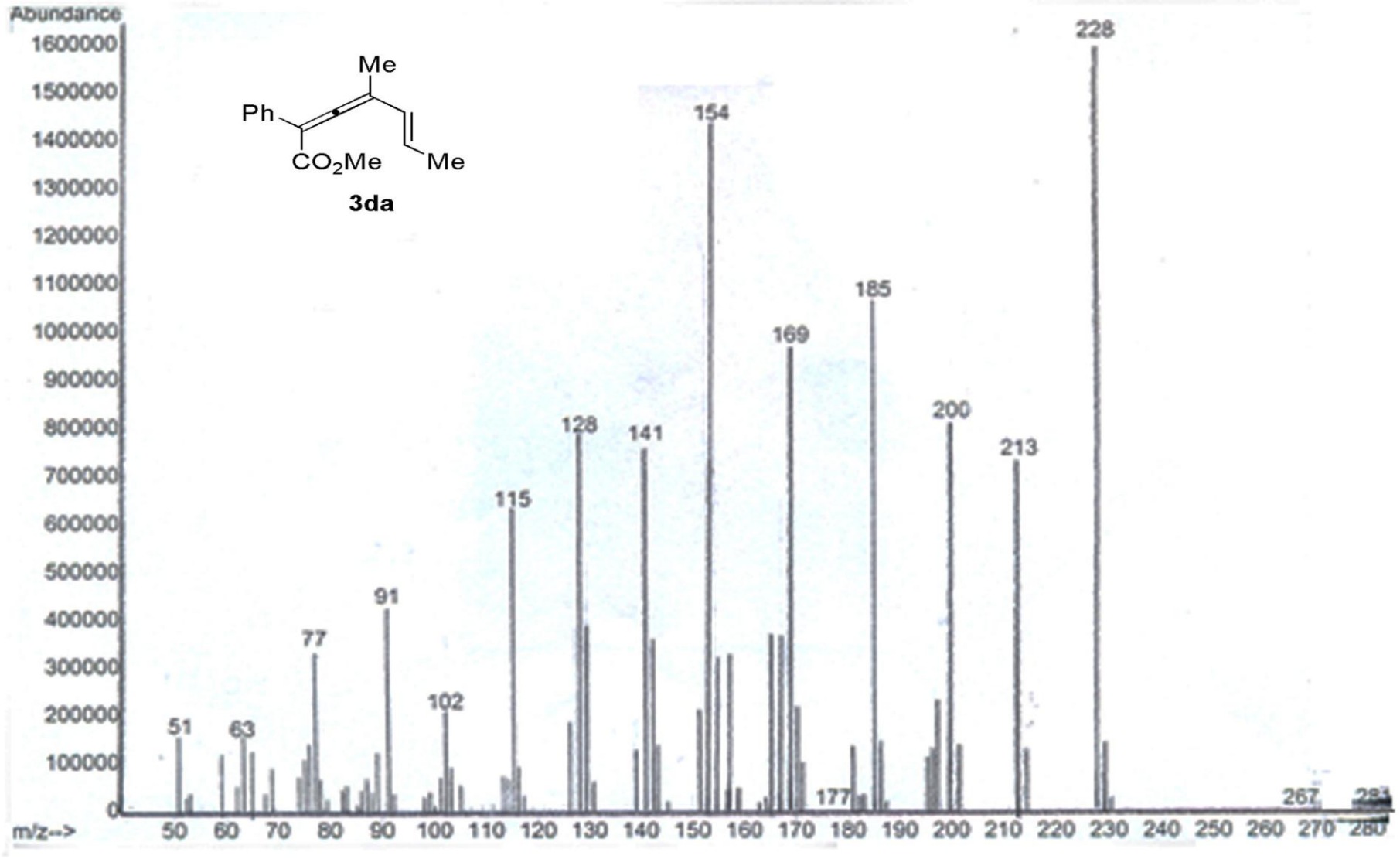
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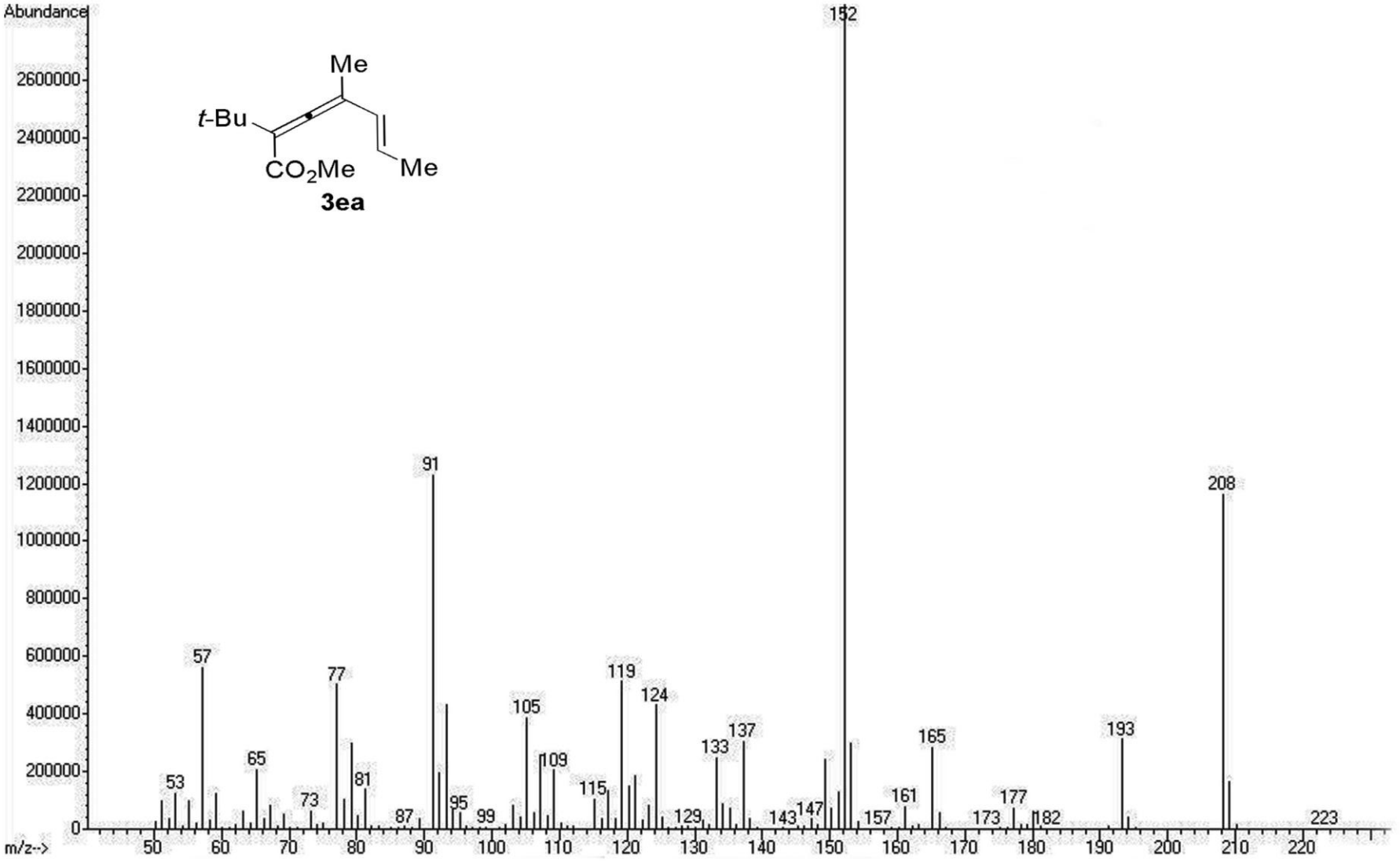
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3ea
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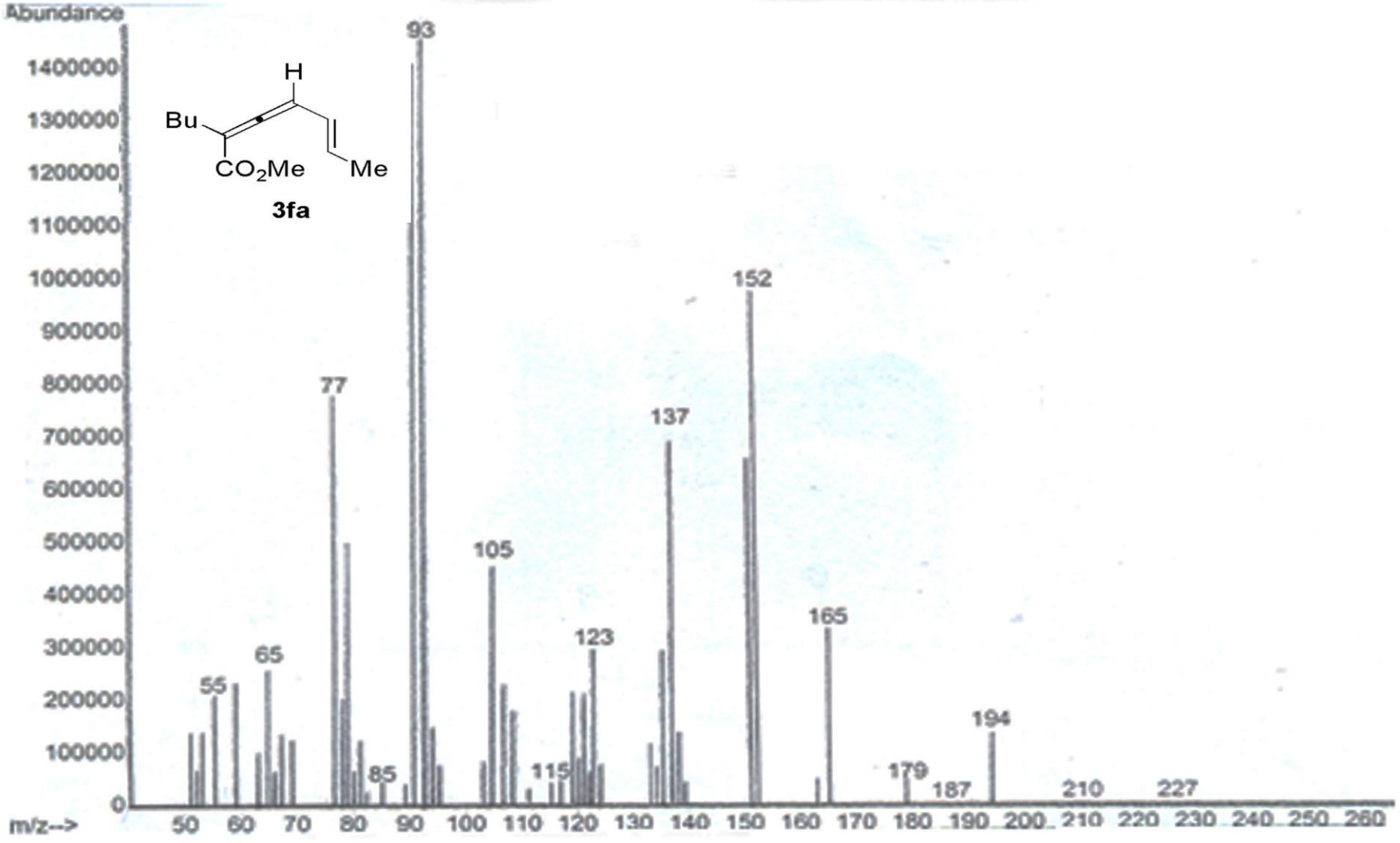
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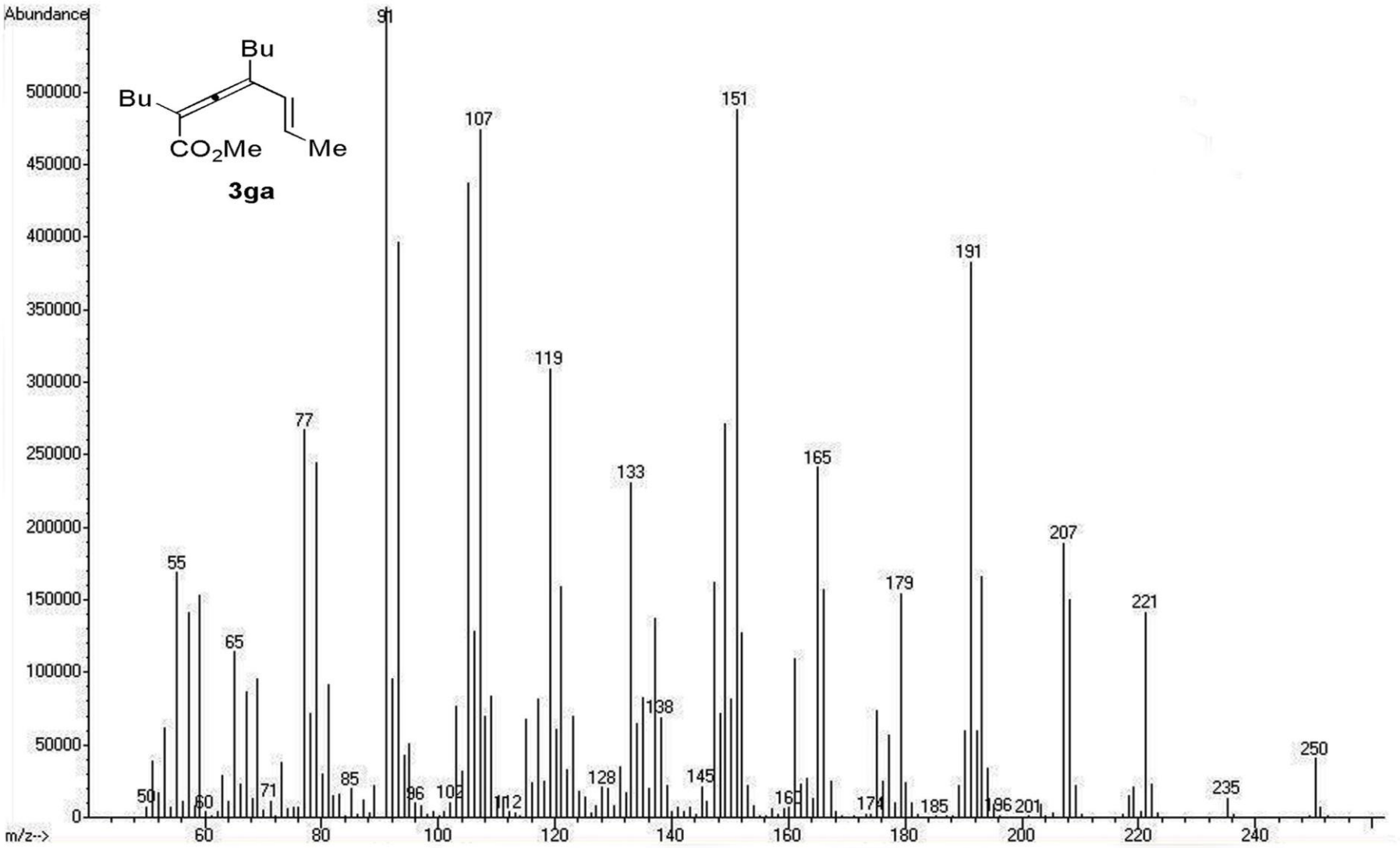
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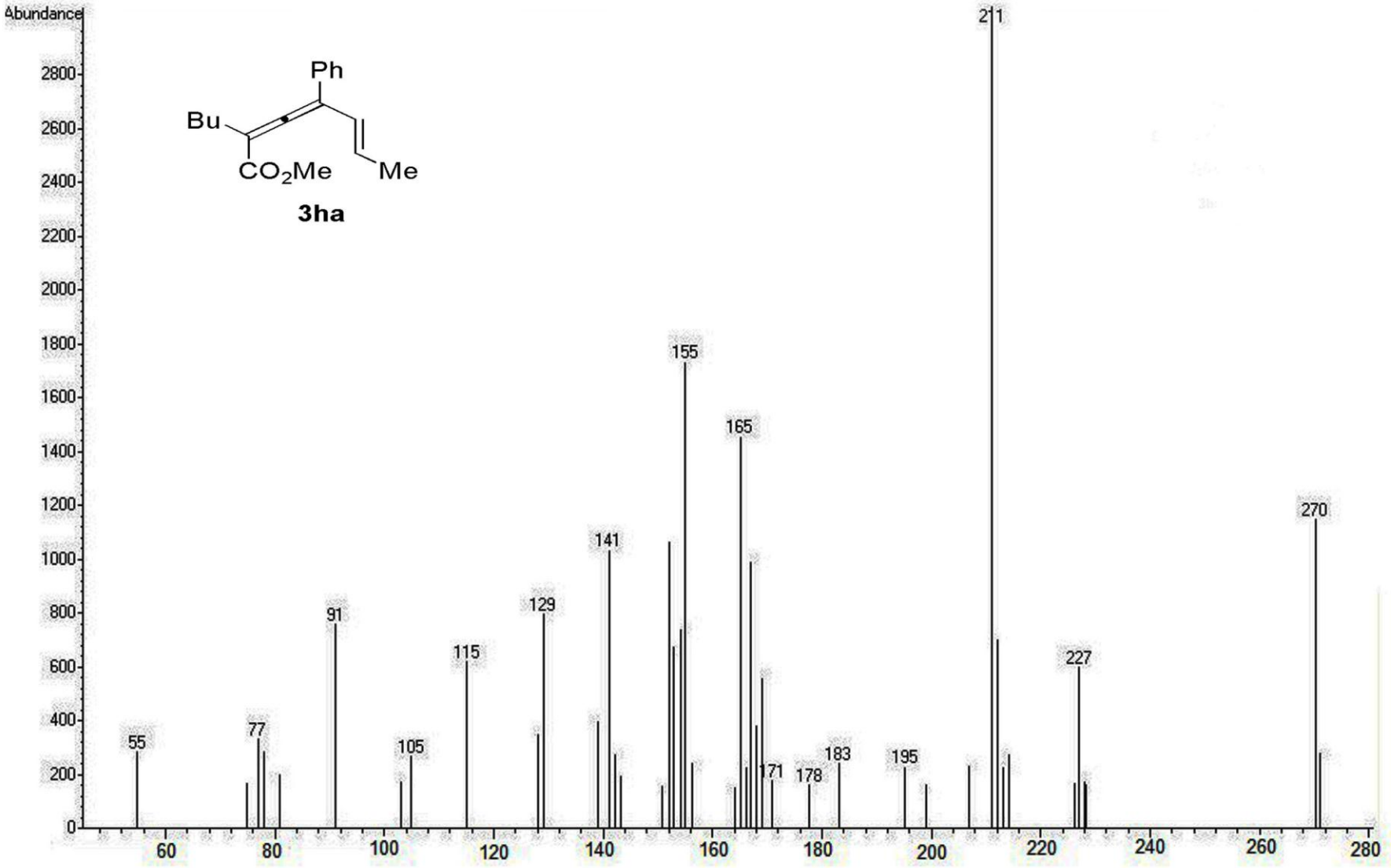
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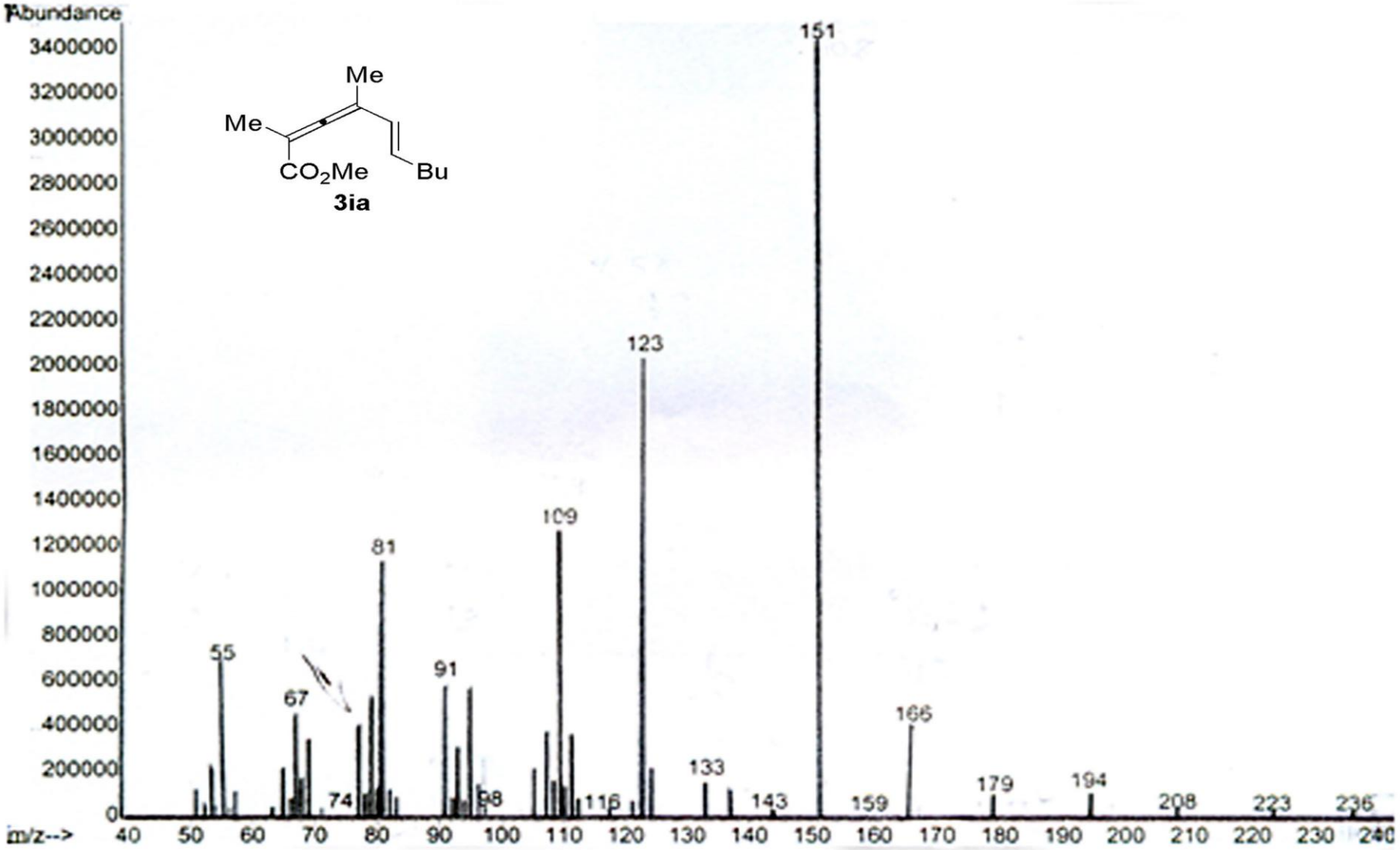
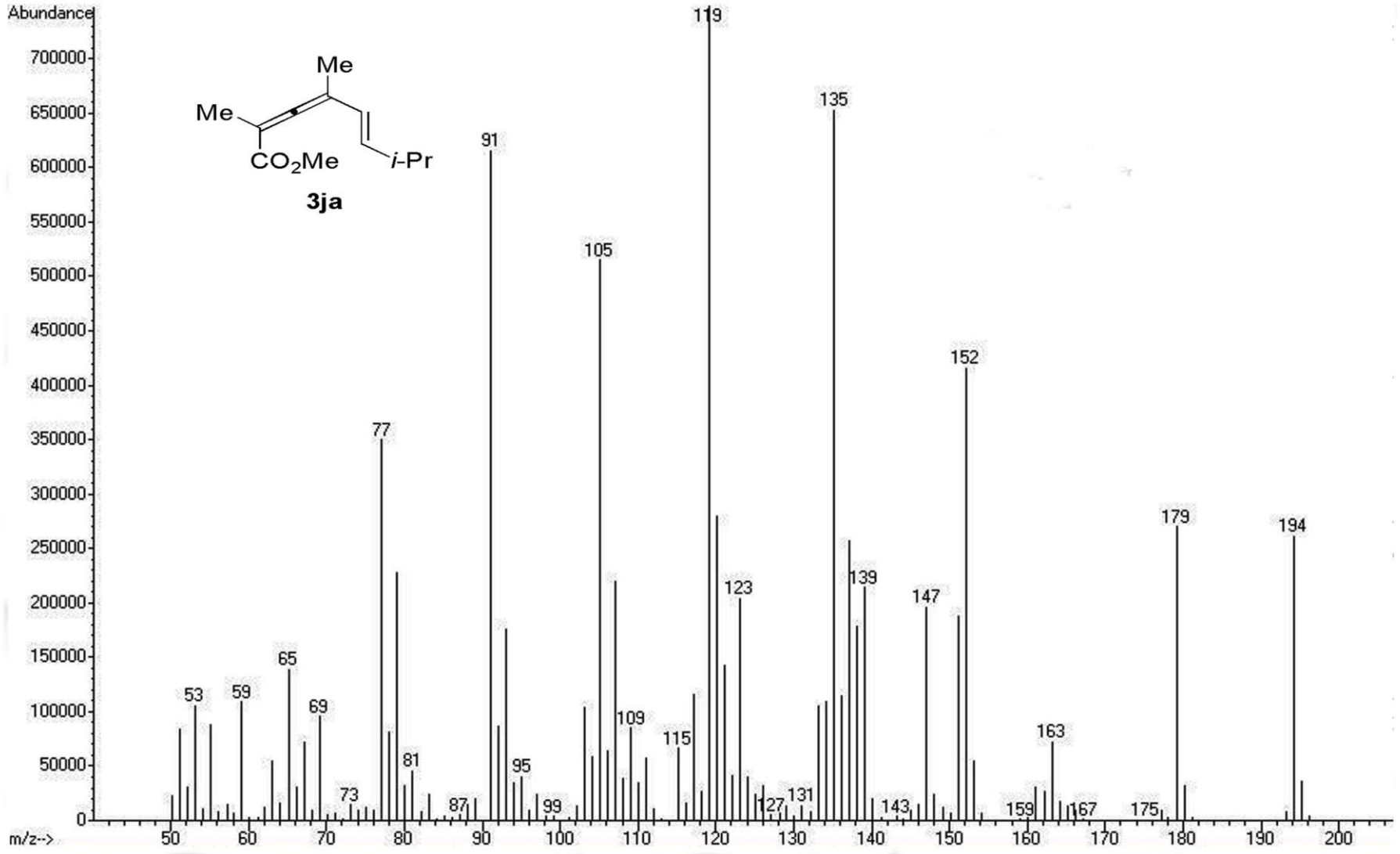
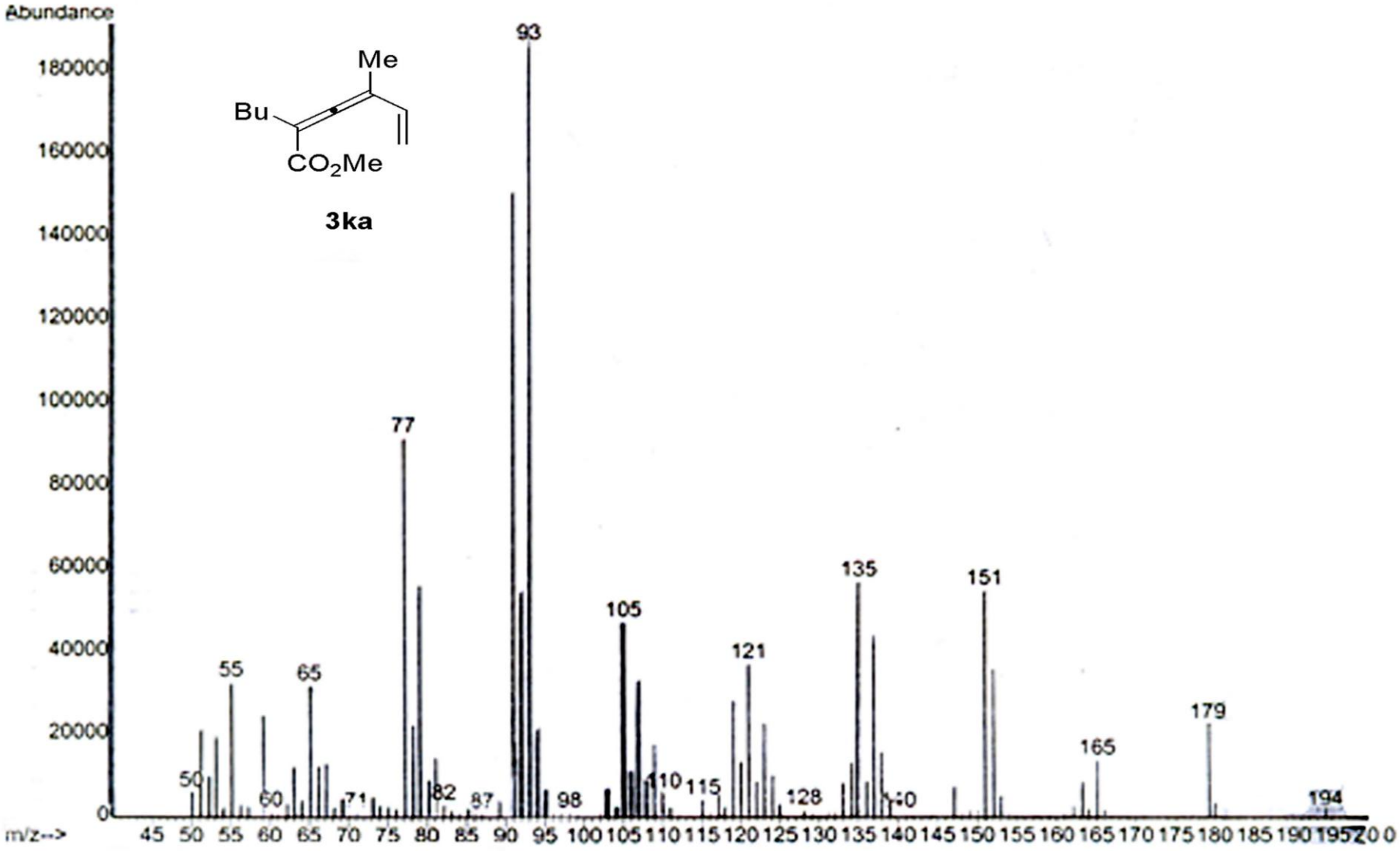
195
171
178
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
60
80
100
120
140
160
180
200
220
240
260
280

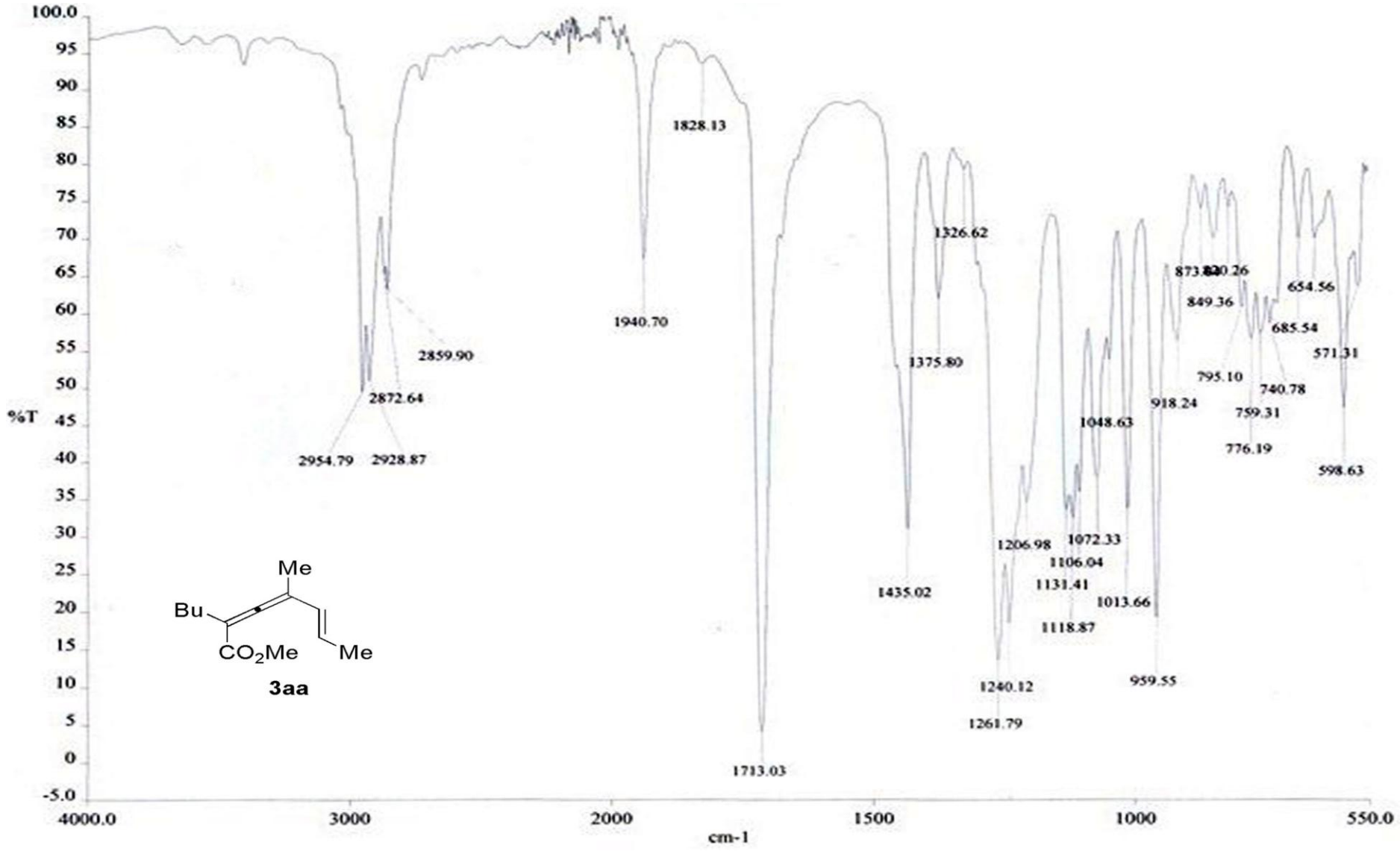

Abundance
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240
151
123
109
81
55
91
67
166
133
179
194
74
98
116
143
159
208
223
236
Me
Me
CO2Me
Bu
3ia

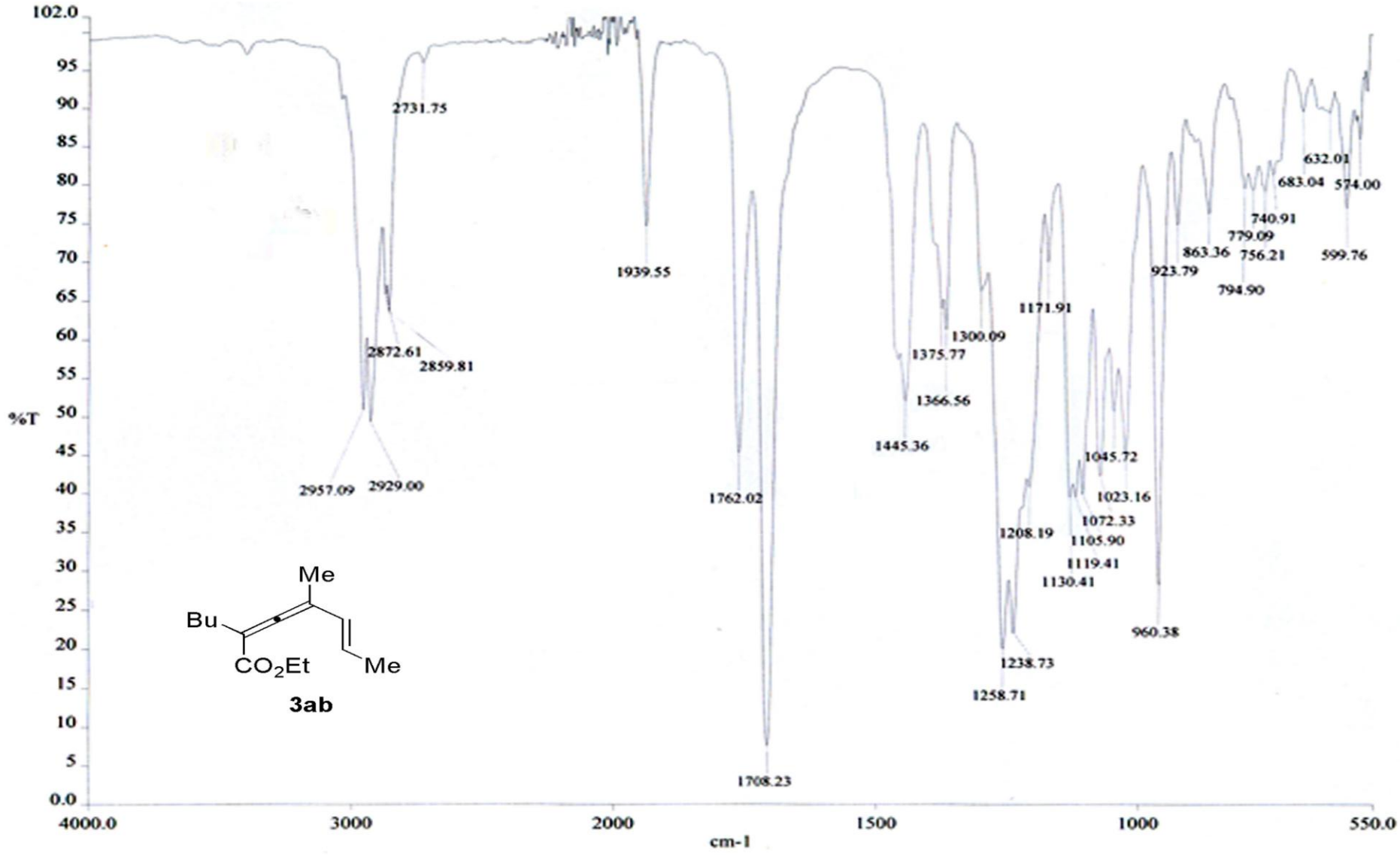

Abundance
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
Me
Me
CO2Me
i-Pr
3ja
119
135
91
105
152
77
179
194
139
123
147
65
53
59
69
109
115
163
81
95
73
87
99
127
131
143
159
167
175

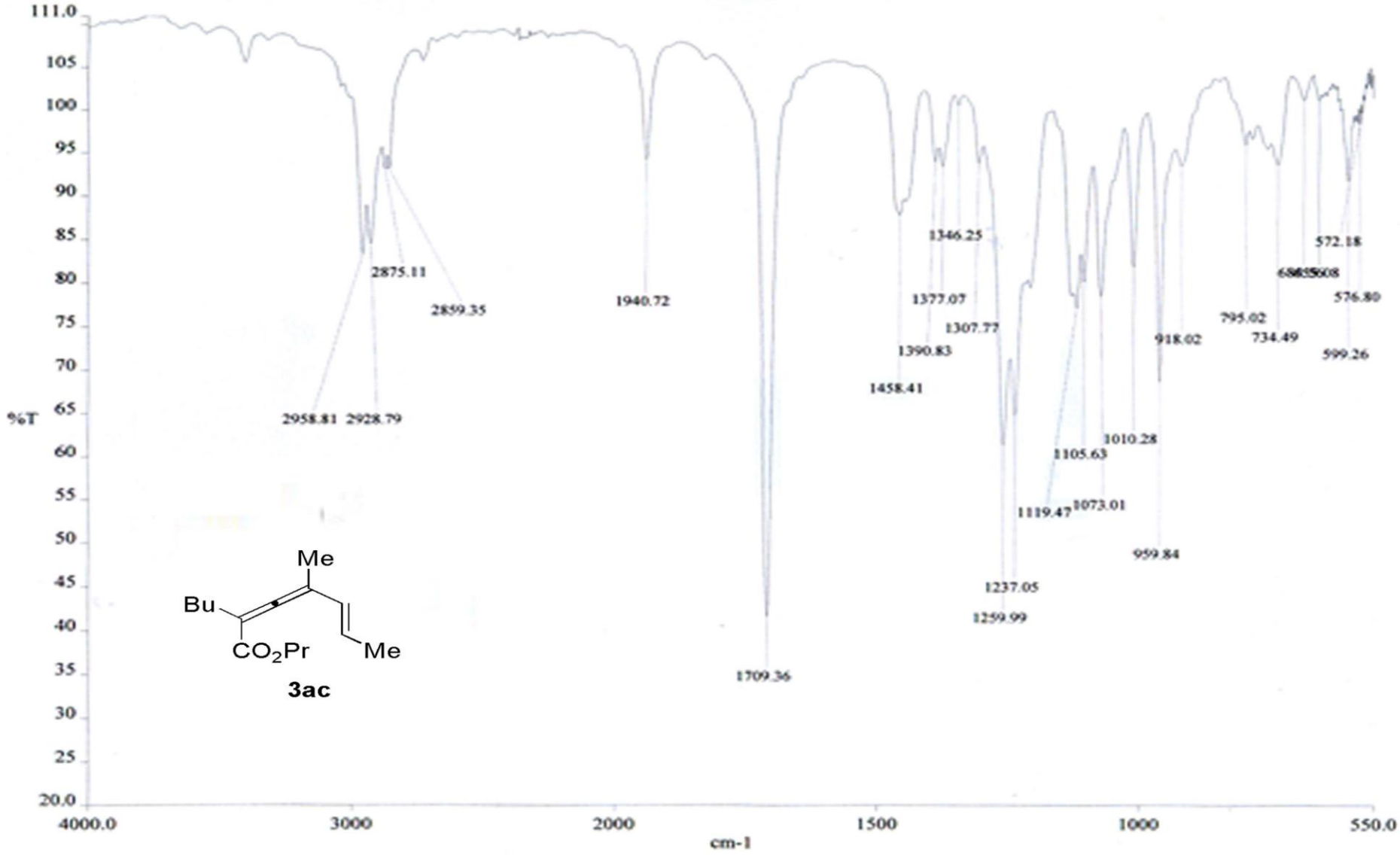

Abundance
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
m/z-->
45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200
Me
Bu
CO2Me
3ka
93
77
105
135
151
121
55
65
179
165
194
50
60
71
82
87
98
110
115
128

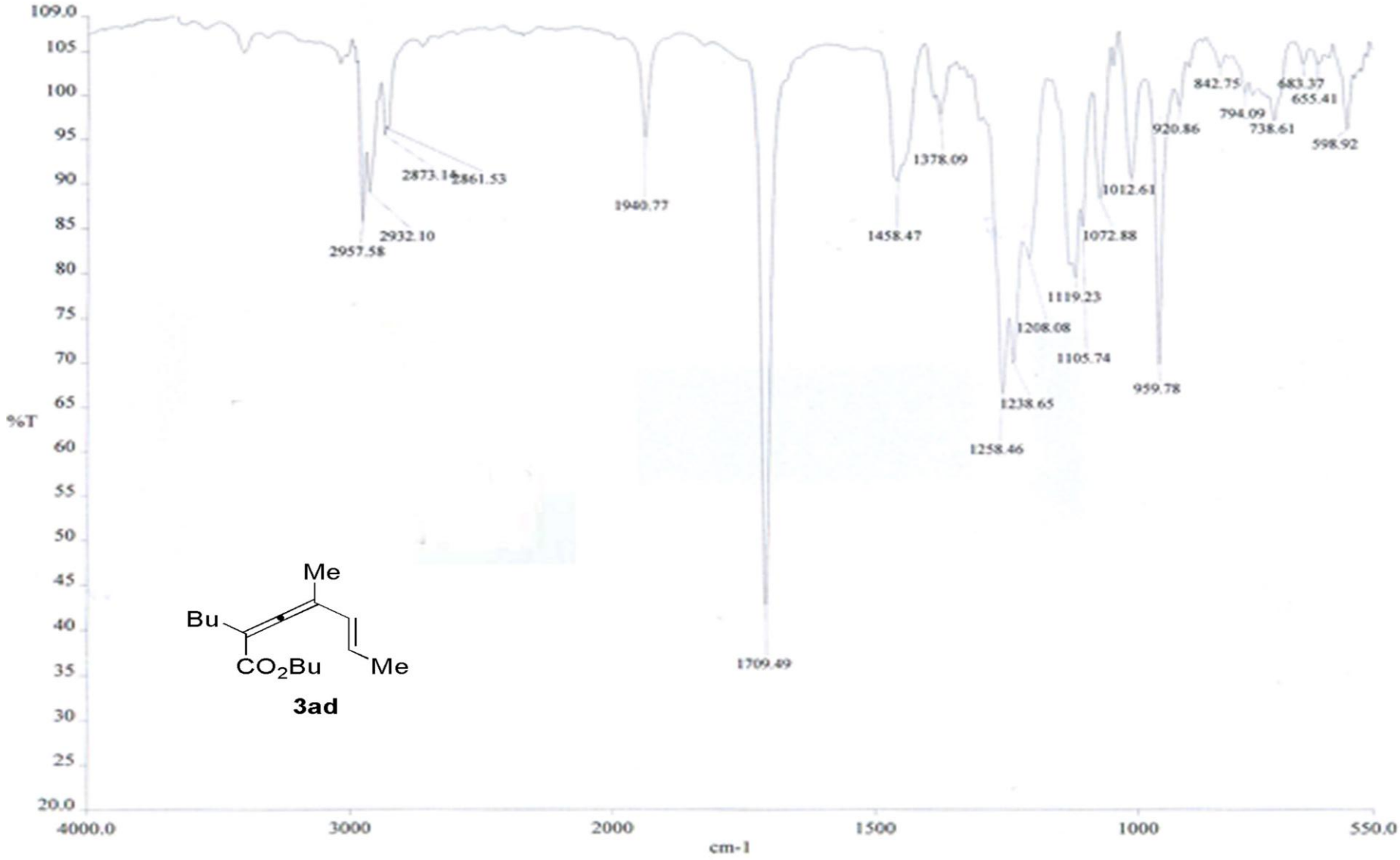
# APPENDIX F

# FT-IR SPECTRUMS OF PRODUCTS

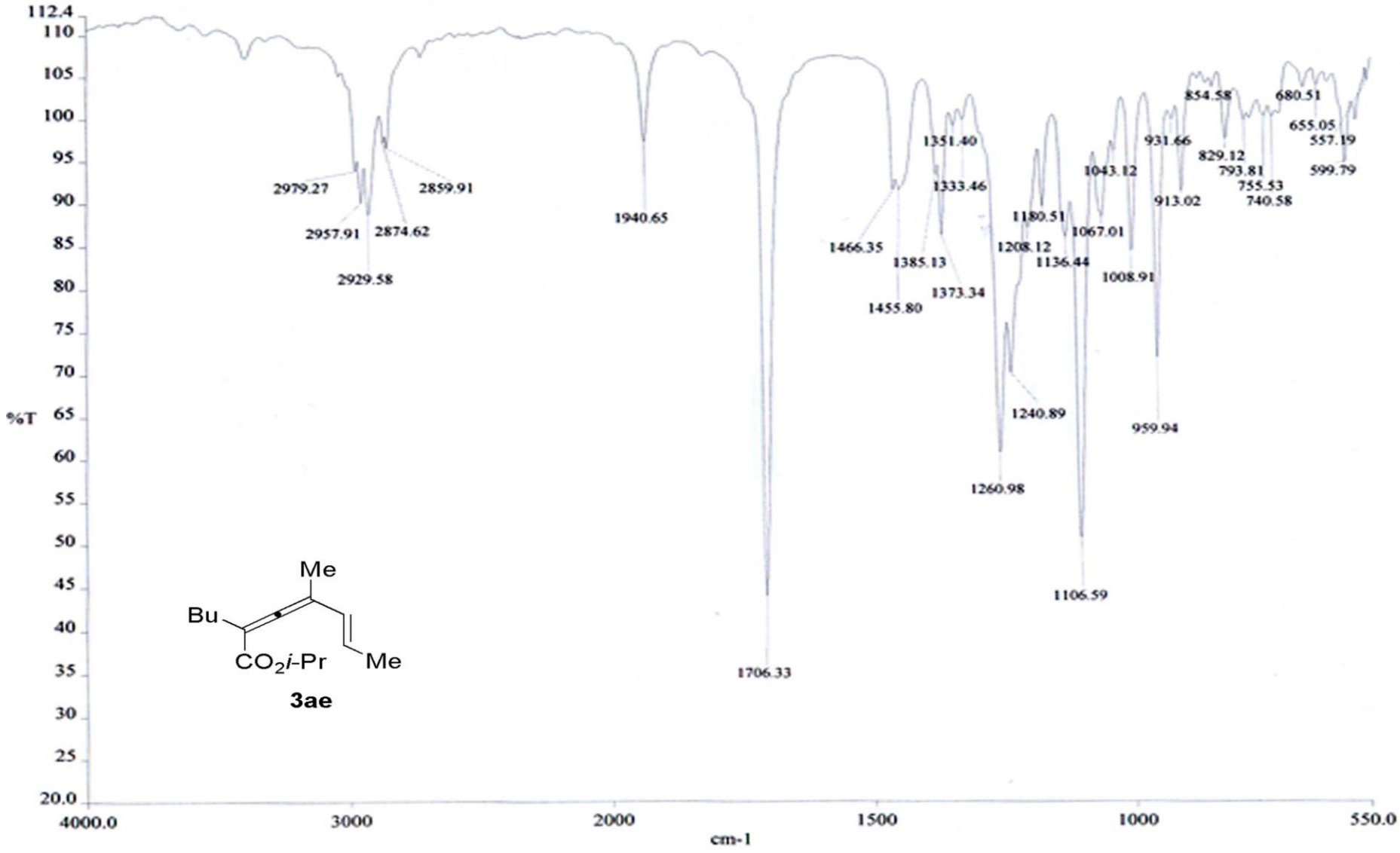

100.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2954.79
2928.87
2872.64
2859.90
1940.70
1828.13
1713.03
1435.02
1375.80
1326.62
1261.79
1240.12
1206.98
1131.41
1118.87
1106.04
1072.33
1048.63
1013.66
959.55
918.24
873.82
849.36
820.26
795.10
776.19
759.31
740.78
685.54
654.56
598.63
571.31
Me
Bu
CO2Me
Me
3aa

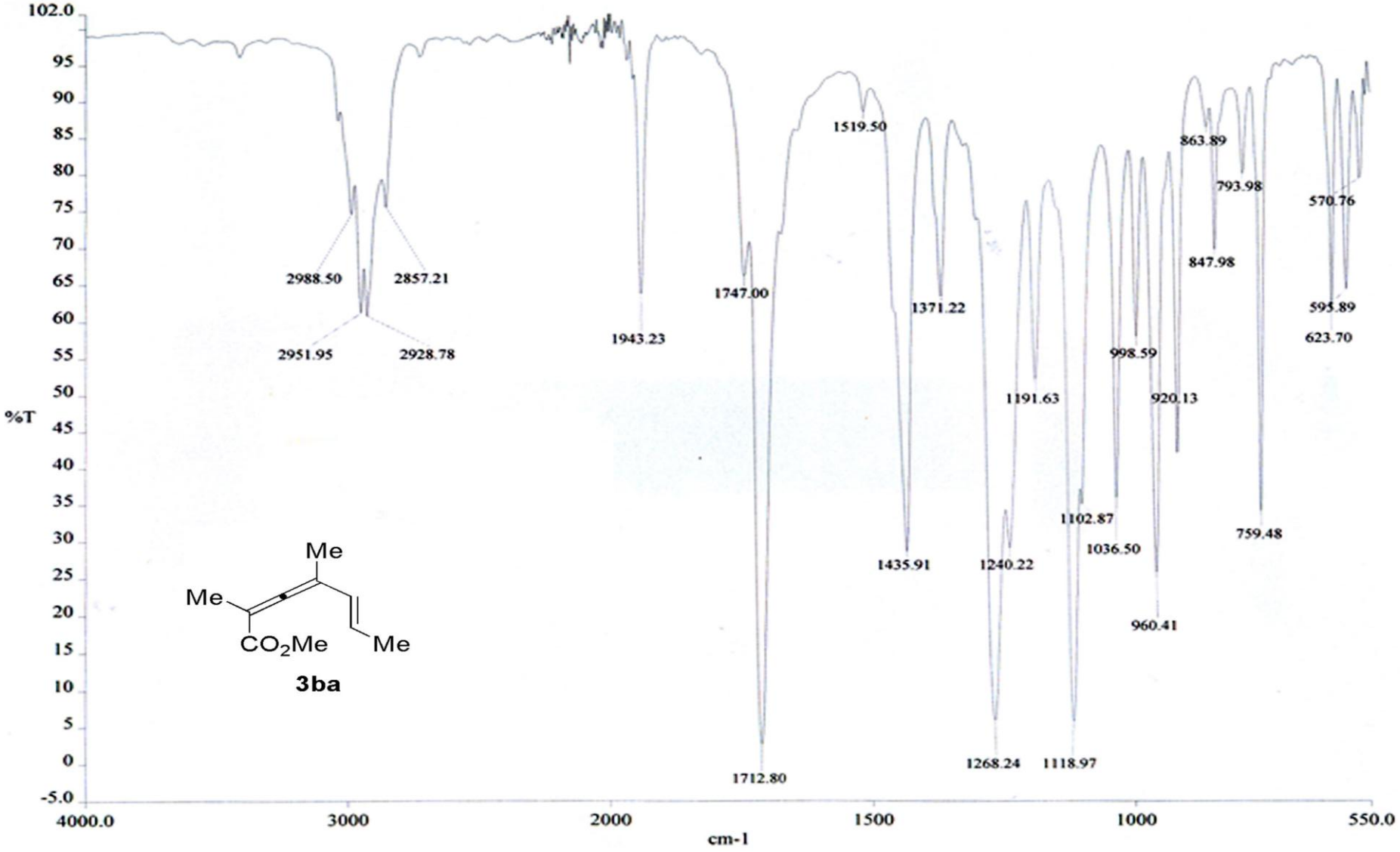

102.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2957.09
2929.00
2872.61
2859.81
2731.75
1939.55
1762.02
1708.23
1445.36
1375.77
1366.56
1300.09
1258.71
1238.73
1208.19
1171.91
1130.41
1119.41
1105.90
1072.33
1045.72
1023.16
960.38
923.79
863.36
794.90
779.09
756.21
740.91
683.04
632.01
599.76
574.00
Me
Bu
CO2Et
Me
3ab

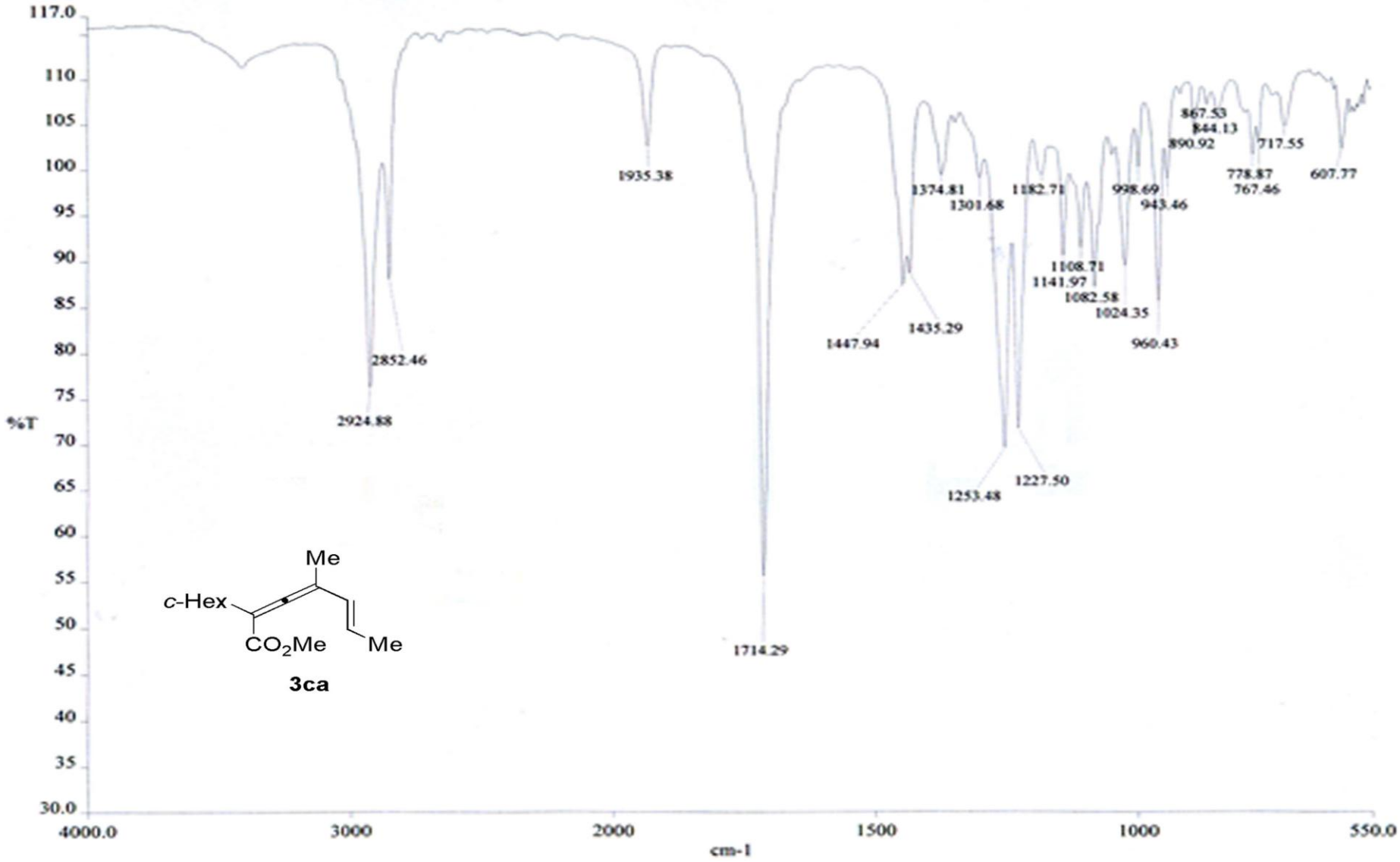

111.0
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2958.81
2928.79
2875.11
2859.35
1940.72
1709.36
1458.41
1390.83
1377.07
1346.25
1307.77
1259.99
1237.05
1119.47
1105.63
1073.01
1010.28
959.84
918.02
795.02
734.49
599.26
576.80
572.18
Me
Bu
CO2Pr
Me
3ac

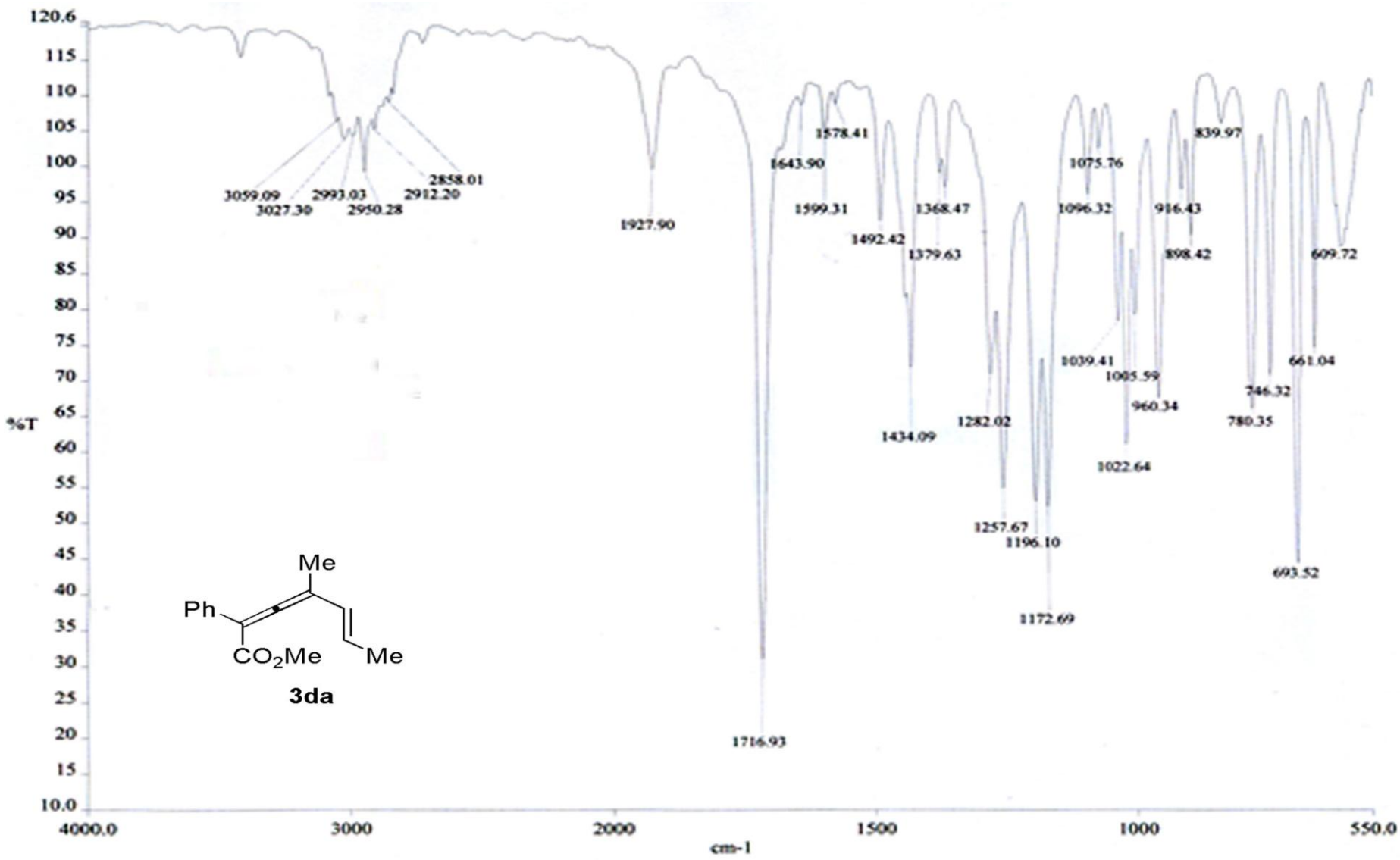

109.0
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2957.58
2932.10
2873.14
2861.53
1940.77
1709.49
1458.47
1378.09
1258.46
1238.65
1208.08
1119.23
1105.74
1072.88
1012.61
959.78
920.86
842.75
794.09
738.61
683.37
655.41
598.92
Me
Bu
CO2Bu
Me

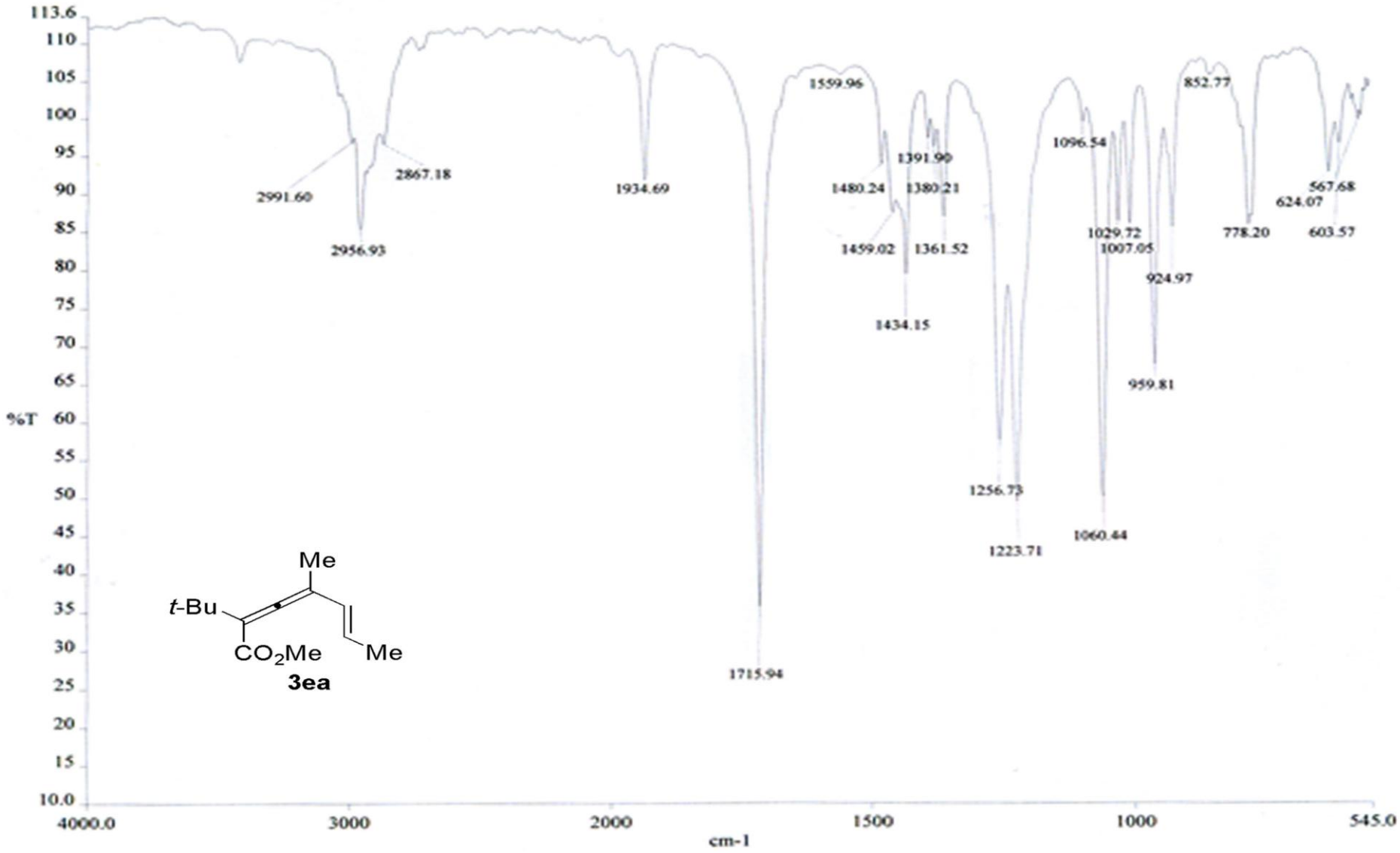
**3ad**

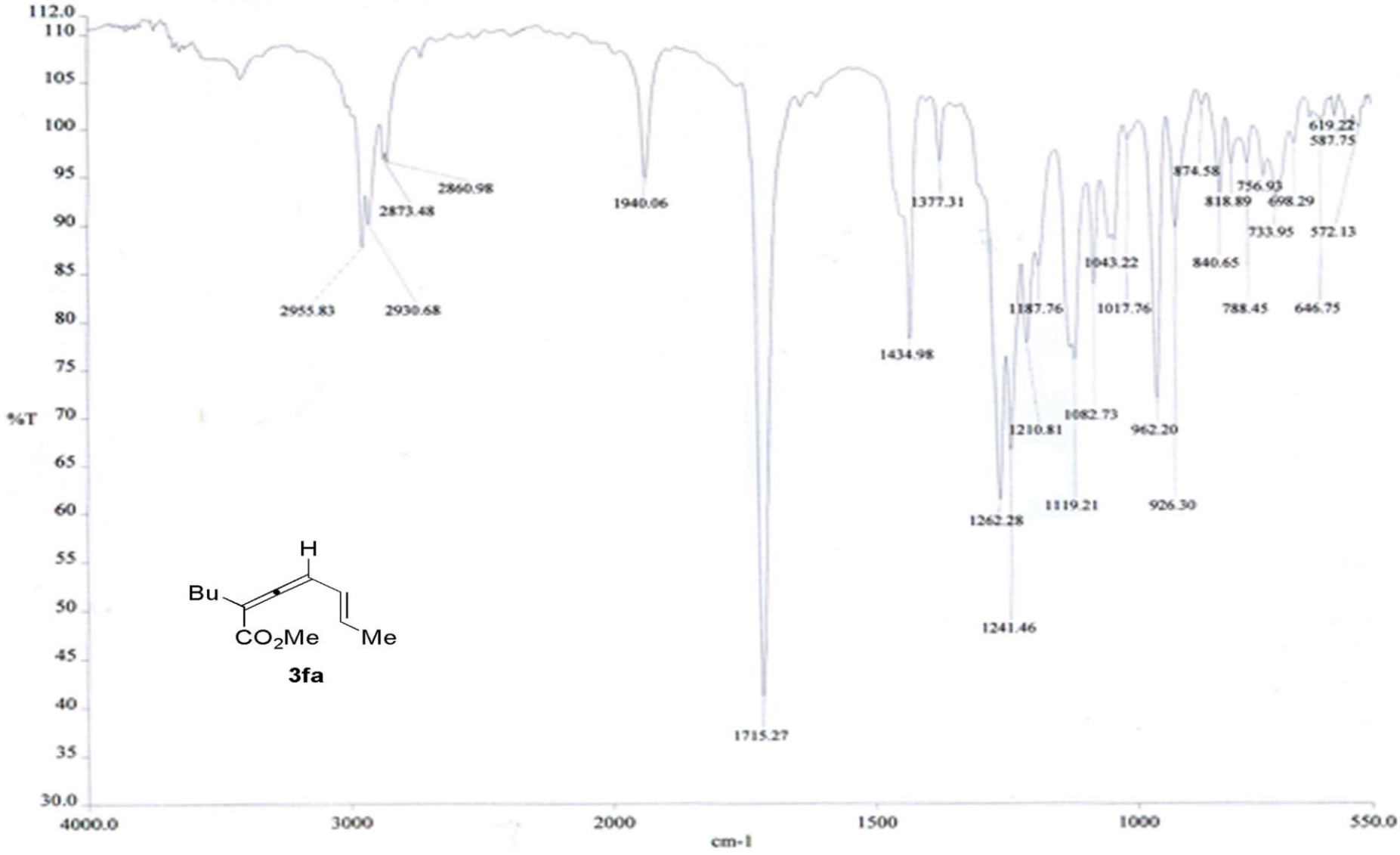

112.4
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2979.27
2957.91
2929.58
2874.62
2859.91
1940.65
1706.33
1466.35
1455.80
1385.13
1373.34
1351.40
1333.46
1260.98
1240.89
1208.12
1180.51
1136.44
1106.59
1067.01
1043.12
1008.91
959.94
931.66
913.02
854.58
829.12
793.81
755.53
740.58
680.51
655.05
599.79
557.19
Me
Bu
CO2i-Pr
Me
3ae

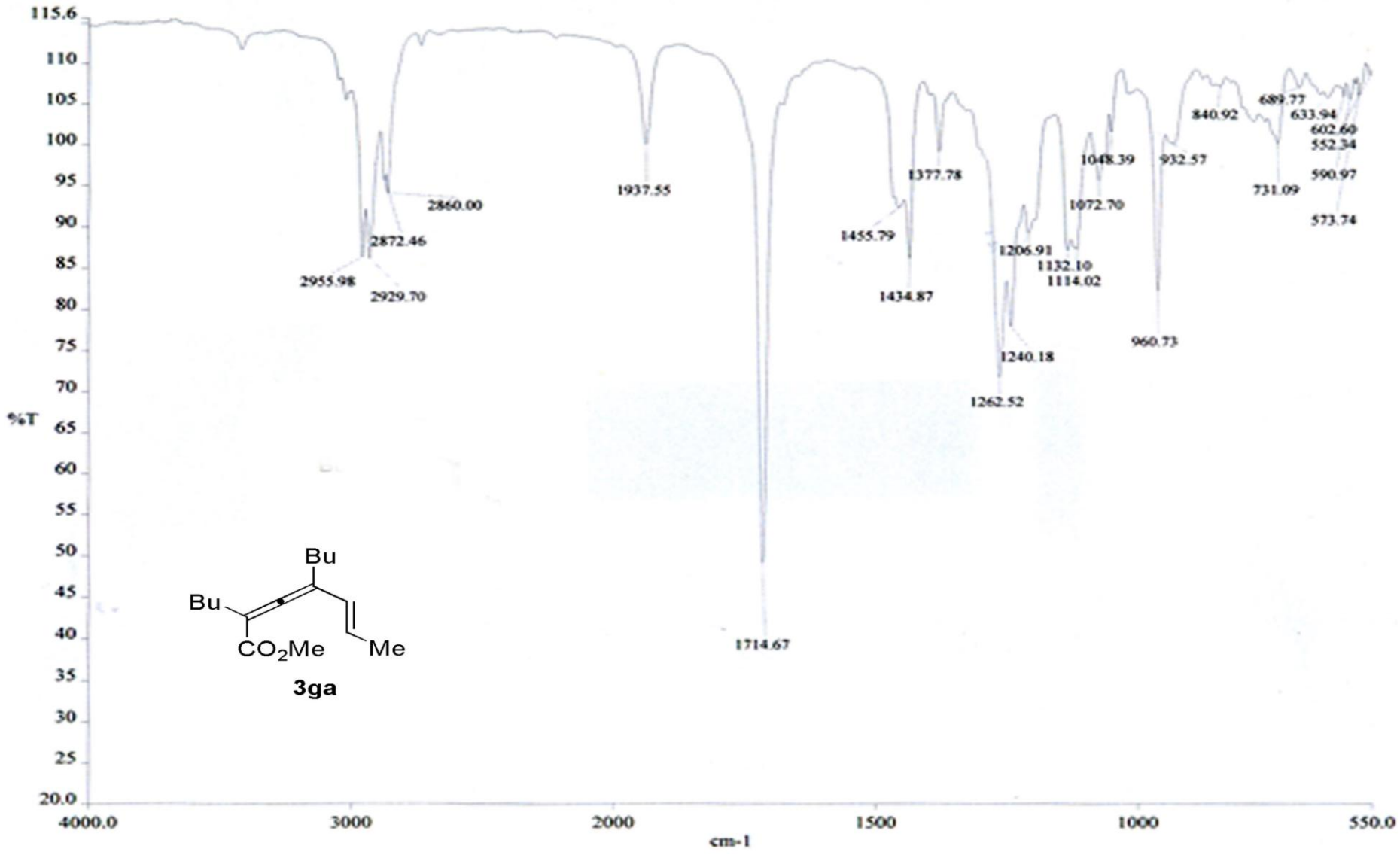

102.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2988.50
2857.21
2951.95
2928.78
1943.23
1747.00
1519.50
1371.22
1435.91
1712.80
1191.63
1240.22
1268.24
1102.87
1118.97
998.59
1036.50
920.13
960.41
863.89
847.98
793.98
759.48
595.89
623.70
570.76
Me
Me
CO2Me
Me
3ba


117.0
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2924.88
2852.46
1935.38
1714.29
1447.94
1435.29
1374.81
1301.68
1253.48
1227.50
1182.71
1141.97
1108.71
1082.58
1024.35
998.69
960.43
943.46
890.92
867.53
844.13
778.87
767.46
717.55
607.77
Me
c-Hex
CO2Me
Me
3ca

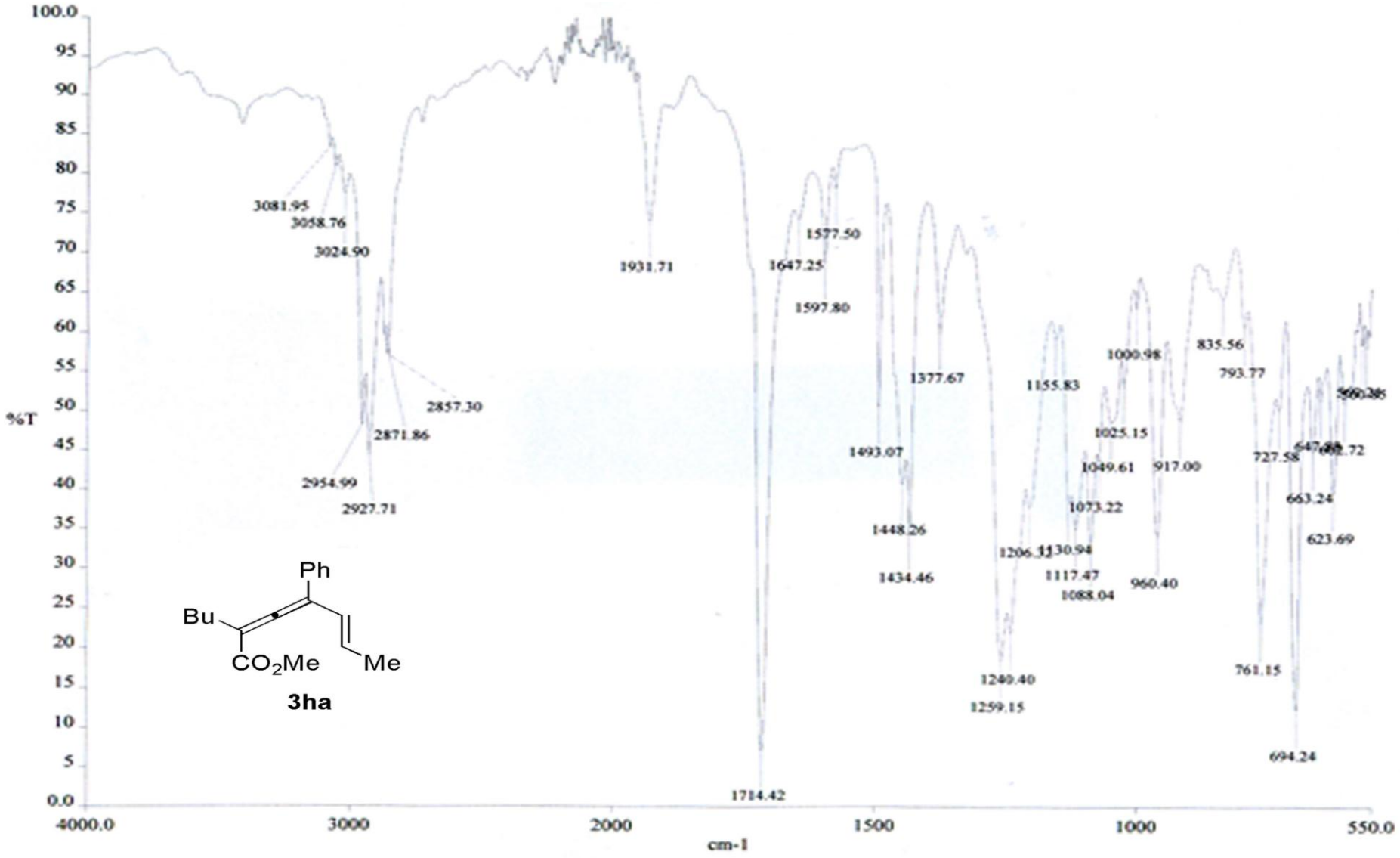

120.6
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
3059.09
3027.30
2993.03
2950.28
2912.20
2858.01
1927.90
1716.93
1643.90
1599.31
1578.41
1492.42
1434.09
1379.63
1368.47
1282.02
1257.67
1196.10
1172.69
1096.32
1075.76
1039.41
1005.59
1022.64
960.34
916.43
898.42
839.97
780.35
746.32
693.52
661.04
609.72
Me
Ph
CO2Me
Me
3da


113.6
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10.0
%T
4000.0
3000
2000
1500
1000
545.0
cm-1
2991.60
2956.93
2867.18
1934.69
1715.94
1559.96
1480.24
1459.02
1434.15
1391.90
1380.21
1361.52
1256.73
1223.71
1096.54
1060.44
1029.72
1007.05
959.81
924.97
852.77
778.20
624.07
603.57
567.68
Me
t-Bu
CO2Me
Me
3ea

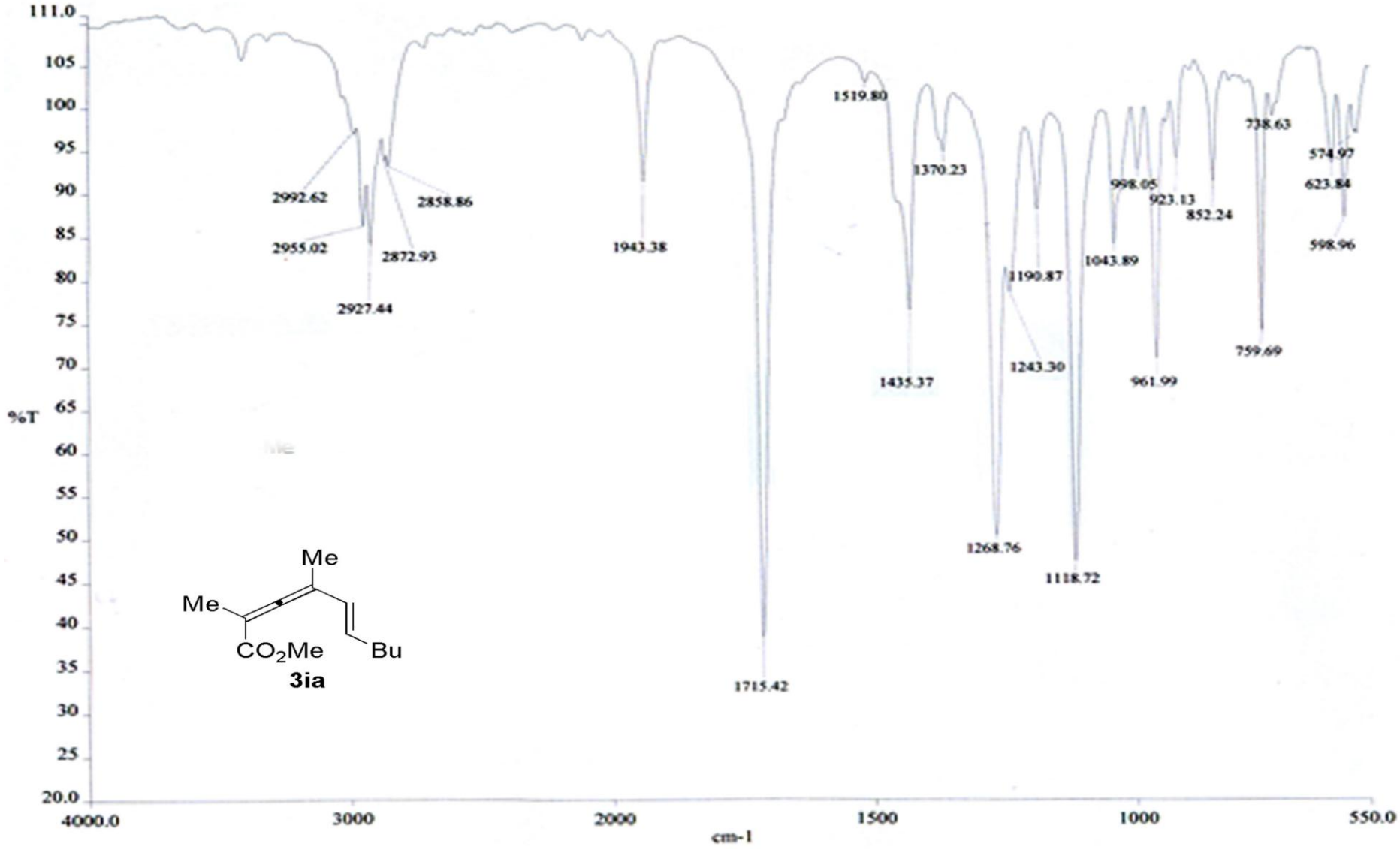

112.0
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2955.83
2930.68
2873.48
2860.98
1940.06
1715.27
1434.98
1377.31
1262.28
1241.46
1210.81
1187.76
1119.21
1082.73
1043.22
1017.76
962.20
926.30
874.58
840.65
818.89
788.45
756.93
733.95
698.29
646.75
619.22
587.75
572.13
H
Bu
CO2Me
Me
3fa

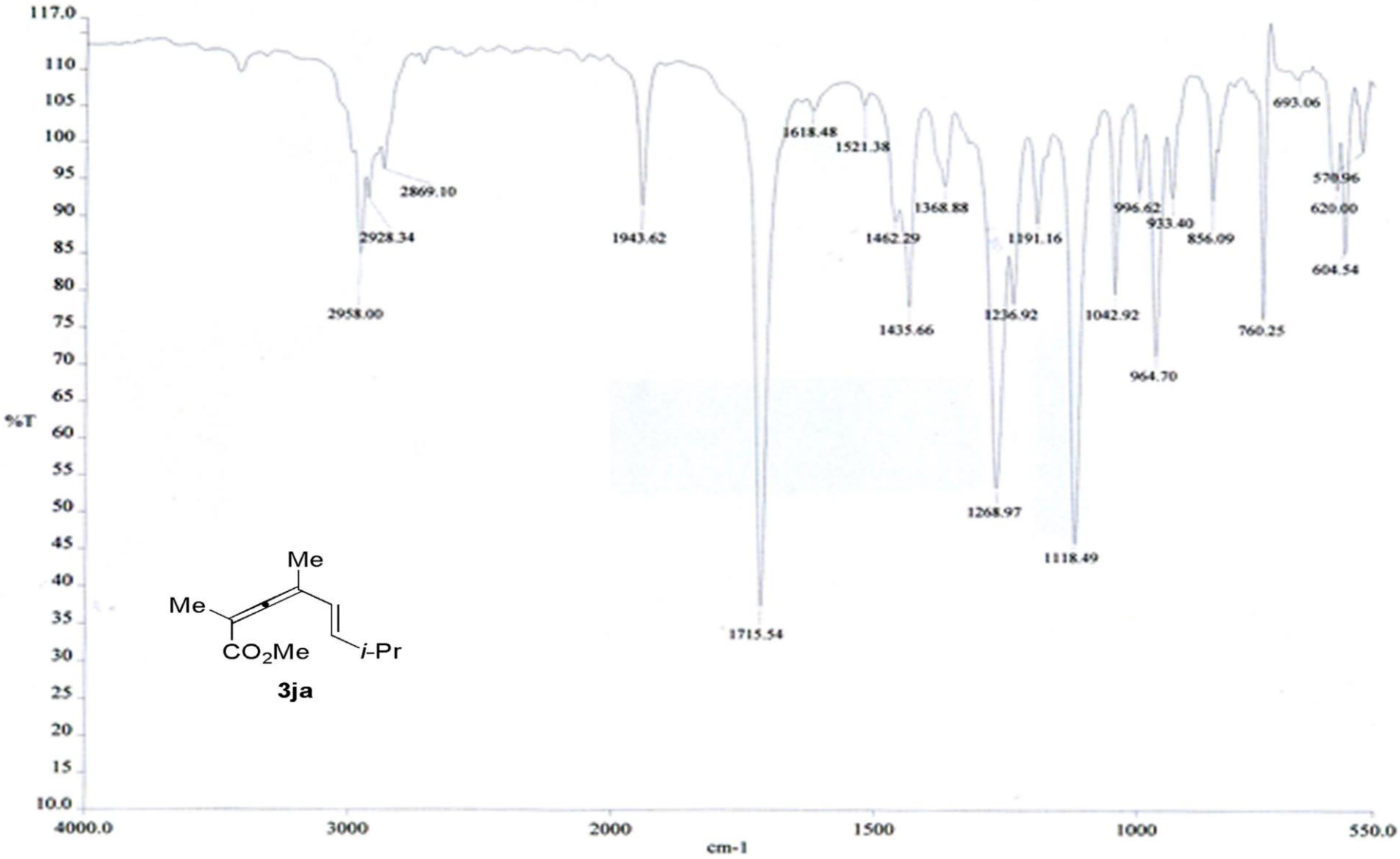

115.6
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2955.98
2872.46
2929.70
2860.00
1937.55
1714.67
1455.79
1377.78
1434.87
1262.52
1206.91
1240.18
1132.10
1114.02
1072.70
1048.39
960.73
932.57
840.92
731.09
689.77
633.94
602.60
590.97
573.74
552.34
Bu
Bu
CO2Me
Me

**3ga**


100.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
3081.95
3058.76
3024.90
2954.99
2927.71
2871.86
2857.30
1931.71
1714.42
1647.25
1597.80
1577.50
1493.07
1448.26
1434.46
1377.67
1259.15
1240.40
1206.33
1155.83
1130.94
1117.47
1088.04
1073.22
1049.61
1025.15
1000.98
960.40
917.00
835.56
793.77
761.15
727.58
694.24
663.24
623.69
Ph
Bu
CO2Me
Me

**3ha**


111.0
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2992.62
2955.02
2927.44
2872.93
2858.86
1943.38
1715.42
1519.80
1435.37
1370.23
1268.76
1243.30
1190.87
1118.72
1043.89
998.05
961.99
923.13
852.24
759.69
738.63
623.84
598.96
574.97
Me
Me
CO2Me
Bu
3ia

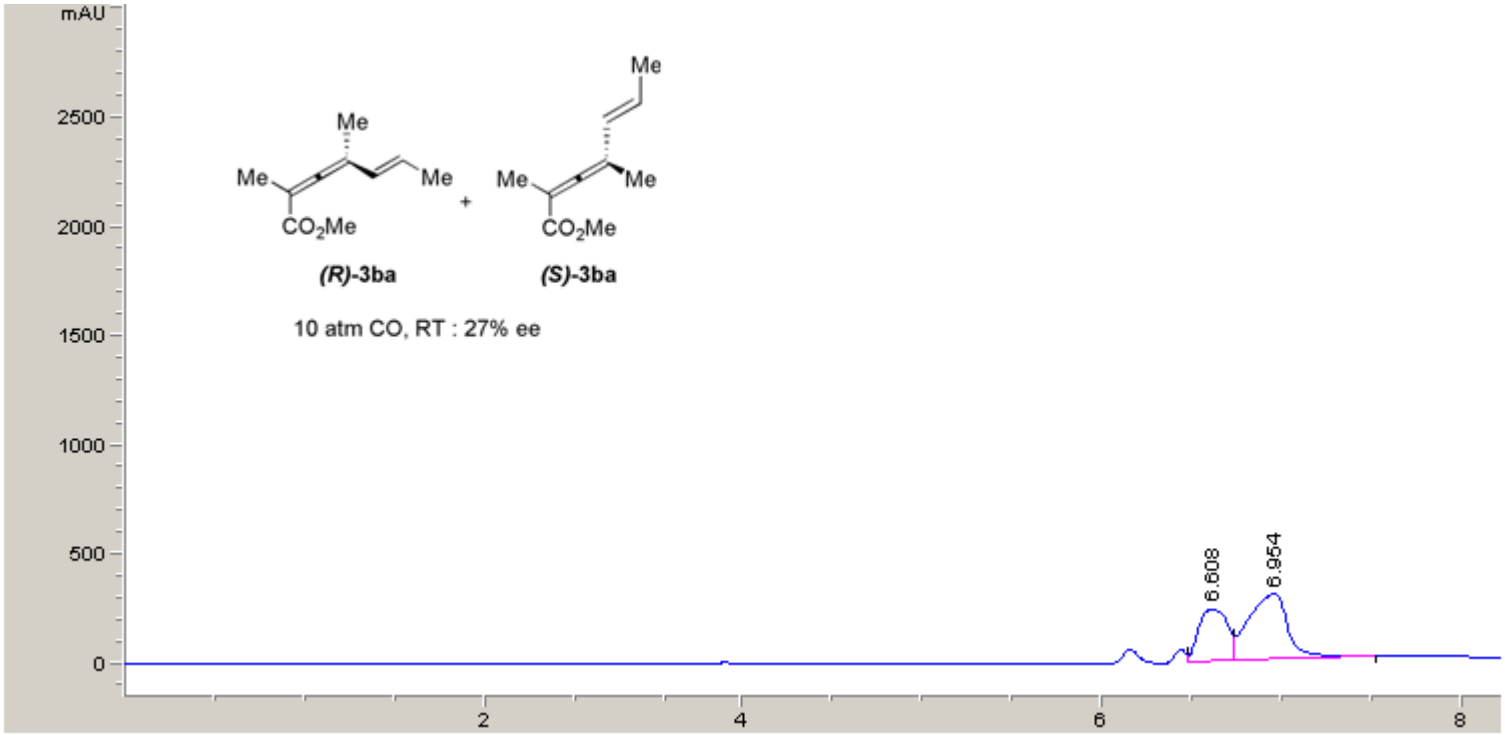

117.0
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10.0
%T
4000.0
3000
2000
1500
1000
550.0
cm-1
2958.00
2928.34
2869.10
1943.62
1715.54
1618.48
1521.38
1462.29
1435.66
1368.88
1268.97
1236.92
1191.16
1118.49
1042.92
996.62
964.70
933.40
856.09
760.25
693.06
620.00
604.54
Me
Me
CO2Me
i-Pr

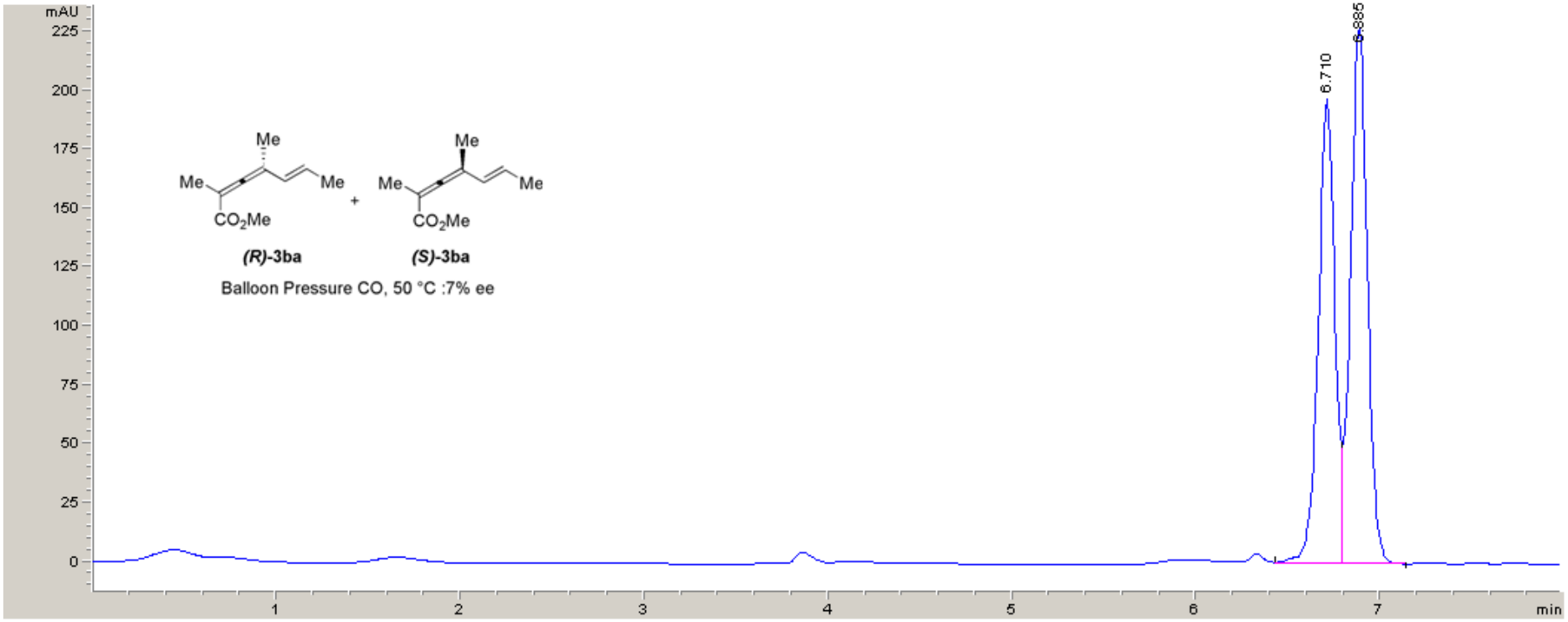
**3ja**

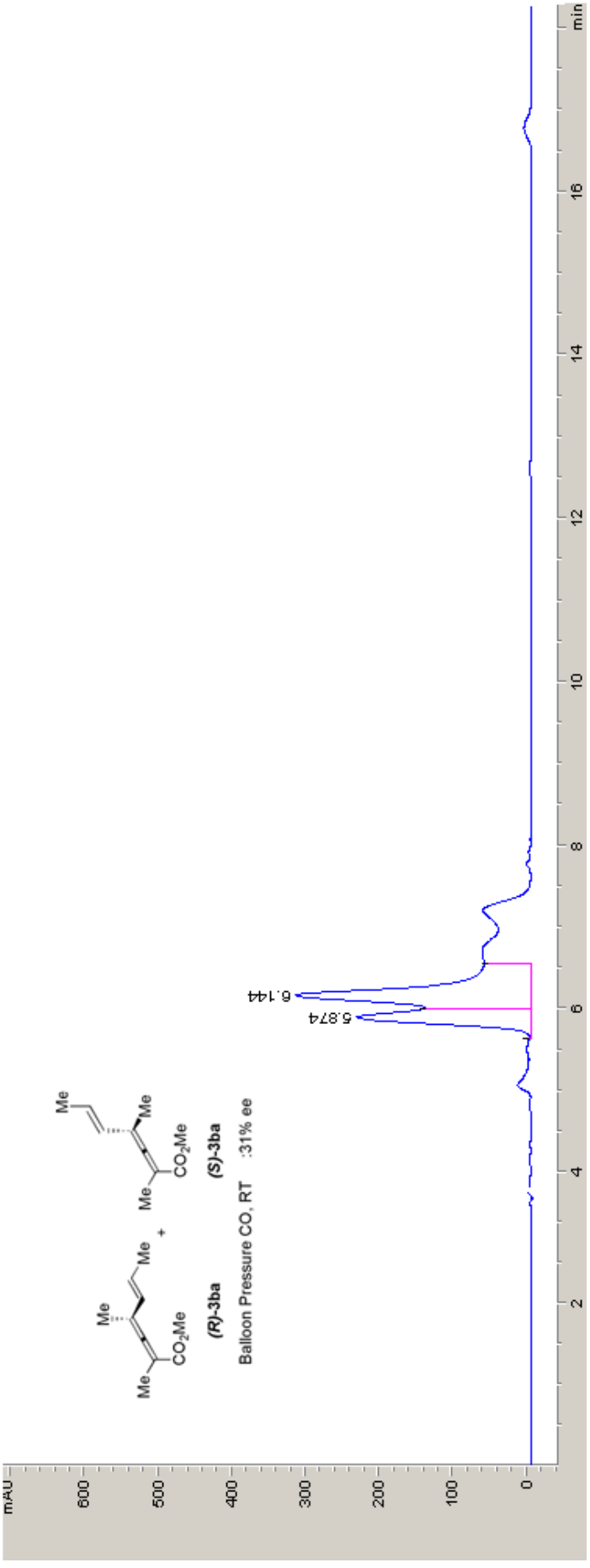
# APPENDIX G

# HPLC CHROMATOGRAMS OF REACTANTS AND PRODUCTS

mAU
1750
1500
1250
1000
750
500
250
0
2
4
6
8
min
7.900
8.249
Me
Me
Me
MeO2CO
(R,Z)-1b
(94.5% ee)


mAU
2500
2000
1500
1000
500
0
2
4
6
8
6.608
6.954
Me
Me
Me
CO2Me
Me
Me
Me
CO2Me
(R)-3ba
(S)-3ba
10 atm CO, RT : 27% ee


mAU
225
200
175
150
125
100
75
50
25
0
1
2
3
4
5
6
7
min
6.710
6.885
Me
Me
CO2Me
(R)-3ba
Me
Me
CO2Me
(S)-3ba
Balloon Pressure CO, 50 °C ;7% ee


mAU
600
500
400
300
200
100
0
2
4
6
8
10
12
14
16
min
6.144
5.874
Me
Me
Me
Me
Me
CO2Me
(S)-3ba
+
Me
Me
Me
Me
CO2Me
(R)-3ba
Balloon Pressure CO, RT :31% ee