PALLADIUM-CATALYZED ALKOXYCARBONYLATION REACTIONS OF (*E*)-2-EN-4-YNE CARBONATES

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ABSTRACT

PALLADIUM-CATALYZED ALKOXYCARBONYLATION REACTIONS OF (*E*)-2-EN-4-YNE CARBONATES

Transition metal-catalyzed carbon-carbon bond formation reactions are well-rounded methods to synthetic organic chemistry. One type of these reactions is the alkoxycarbonylation reactions performed in the presence of a transition metal catalyst, an alcohol and carbon monoxide atmosphere.

Investigations on palladium-catalyzed alkoxycarbonylation reaction of allylic compounds leading to β,γ-unsaturated esters have been performed. Moreover propargyl derivatives are prominent reactants for palladium-catalyzed alkoxycarbonylation reactions to yield allene esters which proceed through a σ-allenylpalladium intermediate. Palladium-catalyzed alkoxycarbonylation reaction of some enantio-enriched propargylic derivatives that facilitate unique centre-to-axis chirality transfer is still inadequate and essential.

In this study, the palladium-catalyzed alkoxycarbonylation reaction of *E*-configured 2,4-enyne carbonates which afforded exclusively ester functionalized (*E*)-configured vinylallenes through the formation of σ-vinylallenylpalladium species was performed. Moreover the chirality transfer of the proposed method was also surveyed over an enantio-enriched *E*-enyne carbonate.

ÖZET

(*E*)-2-EN-4-İN KARBONATLARIN PALADYUM KATALİZLİ ALKOKSİKARBONİLASYON TEPKİMELERİ

Geçiş metal-katalizli karbon-karbon bağ oluşum tepkimeleri sentetik organik kimyada yaygın olarak kullanılan bir yöntemdir. Paladyum katalizörü, metanol ve karbon monoksit varlığında gerçekleştirilen alkoksikarbonilasyon tepkimeleri bu tepkimelerden bir tanesidir.

β,γ-doymamış esterlerin oluşumu ile sonuçlanan allilik bileşiklerin paladyum katalizli alkoksikarbonilasyon tepkimeleri üzerinde çalışmalar yapılmıştır. Bunun yanı sıra σ-allenilpaladyum ara yapısı üzerinden ilerleyen ve allen ester yapılarının oluşumunu sağlayan paladyum katalizli alkoksikarbonilasyon tepkileri için propargil türevleri önde gelen başlangıç maddeleridir. Enantiomerik açıdan zengin propargil türevlerinin paladyum-katalizli karbonilasyon tepkimeleri ile merkezden eksene kiralitenin aktarımına olanak sağlayabilen yöntemler hala yetersiz seviyede bulunmakta ve çok önemlidir.

Bu çalışmada, *E*-2-en-4-in karbonat yapılarının *σ*-allenpalladyum ara yapısı üzerinden ilerleyerek vinilallen ester yapılarını oluşturan paladyum katalizli alkoksikarbonilasyon tepkimeleri gerçekleştirilmiştir. Ayrıca enantiomerik açıdan zenginleştirilmiş *E*-enin karbonat yapıları kullanılarak önerilen yöntemin kiralite transfer özellikleri de araştırılmıştır.

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CHAPTER 1

INTRODUCTION

Since the first cobalt-catalyzed hydroformylation reaction was performed by Roelen in 1939 transition-metal catalyzed carbonylation reaction, in which carbon monoxide used as a reactant, became the efficacious method to synthesize the compounds comprising a carbonyl functionality. Catalytic carbonylation reaction of unsaturated hydrocarbons in the presence of CO and a nucleophile showed by Reppe in 1953 accelerated the synthesis of α-β unsaturated carbonyl compounds showing biological activity via catalytic carbonylation reactions.

For a few decades, the synthesis of allenes has become a hot research topic due to its unique reactivity toward many synthetic reactions and its importance as a reaction intermediate for organic synthesis. Although allenes attract the attention of many medicinal and organic chemists owing to the existence of allenyl moieties in many natural products and biologically active compounds catalytic stereoselective synthesis of allenes are still deficient and indispensable.

Many C-C-coupling reactions using organometallic reagents such as Grignard, organolithium, organocopper, organozinc and organoindium are well-known and widespread methods and a number of which can produce allene structures. For instance, readily available alkynes bearing a leaving group on the propargylic position is prominent reactants for C-C bond forming reactions to yield the allene derivatives.

After the first palladium-catalyzed carbonylation reaction of propargylic compounds reported in 1966 (Tsuji, *et al*. 1995), the Pd-catalyzed alkoxycarbonylation reaction of propargylic derivatives under mild conditions have become a substantial method for the synthesis of allenyl esters.

Propargylic compounds such as propargylic carbonates, phosphates, and mesylates having a vinyl functionality can undergo palladium-catalyzed transformations in the presence of a hard or soft nucleophile as a coupling partner to afford vinylallenes, which are valuable building blocks toward various synthetic applications (Molander, *et al.* 2006, Ma, *et al.* 2003, Chen, *et al.* 2011).

In 2011, Akpınar *et al.* showed that the palladium-catalyzed alkoxycarbonylation reactions of *Z*-configured conjugated enyne carbonates, the allenes with an ester functionality on one of the end allenyl carbon.

In this study, the applicability of the palladium-catalyzed alkoxycarbonylation reaction was also investigated for *E*-configured 2,4-enyne carbonates. The palladium-catalyzed alkoxycarbonylation reaction of *E*-configured 2,4-enyne carbonates afforded exclusively the (*E*)-configured ester functionalized vinylallenes via σ-vinylallenylpalladium species. Moreover the carbonylation reaction of enantioriched *E*-enyne carbonates leading to synthesis of enantioenriched vinylallenes was also surveyed.

CHAPTER 2

LITERATURE WORKS

2.1. Transition Metal-Catalyzed Carbonylation of Alkenes

To synthesize variety of saturated carbonyl compounds such as carboxylic acids, anhydrides, esters, amides, amino acids, etc., transition metal catalyzed carbonylation reaction of olefins are versatile method (Chaudhari, *et al.* 2005). The name of the carbonylation reaction changes according to type of the nucleophile such as water, hydrogen and alcohol. The palladium-catalyzed alkoxycarbonylation of alkenes with CO and alcohols, also named as hydro esterification, have become crucial by virtue the high abundance of palladium as a synthetic method to lead to branched and linear esters (Figure 2.1) (Beller, *et al.* 2009).

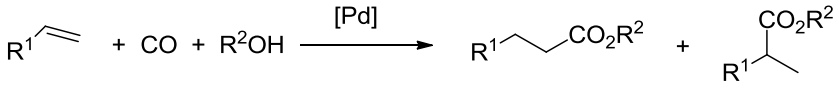


Figure 2.1. Palladium-catalyzed hydroesterification of alkenes.

Two types of catalytic cycles have been proposed for the hydroesterification reaction of olefins (Claver *et al.* 2001).

Based on the first mechanism, a cycle starts with the formation of a Pd-alkoxycarbonyl complex. The insertion of alkene to the Pd-carbon bond of a Pd-alkoxycarbonyl intermediate and consecutive alcoholysis yield an ester and regenerate the palladium complex (Figure 2.2).

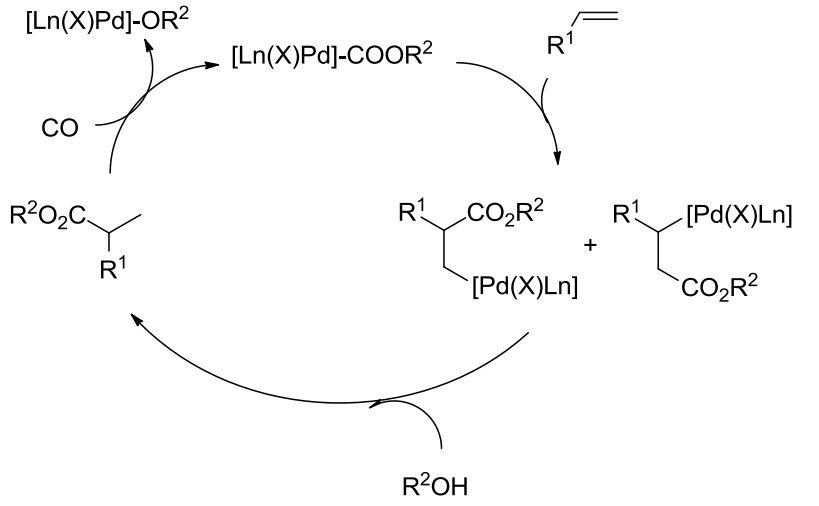


Figure 2.2. Mechanisms for the palladium-catalyzed hydroesterification of alkenes via Pd-alkoxycarbonyl intermediate

In the second reaction mechanism, the alkene is estimated to insert the Pd-H bond to produce Pd-alkyl intermediate. Then a migratory insertion of CO to the Pd-carbon bond of the alkyl metal complex gives acyl-palladium intermediates. A subsequent nucleophilic attack of alcohol produces a linear or branched ester (Figure 2.3).

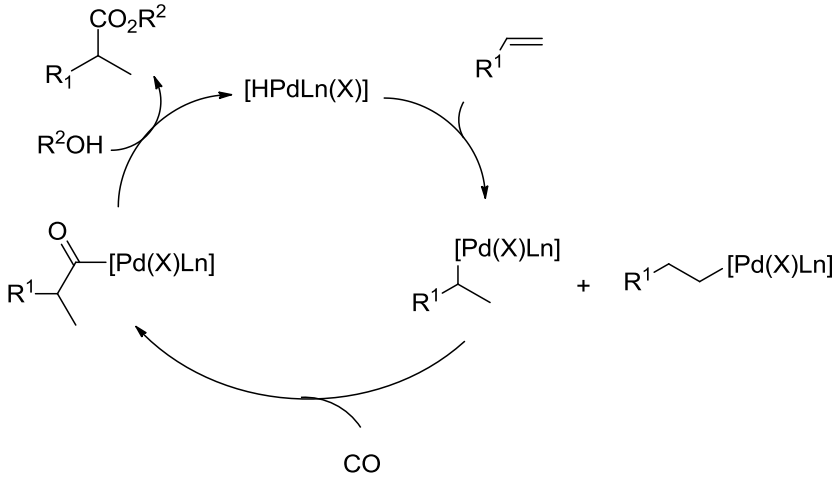


Figure 2.3. Mechanisms for the palladium-catalyzed hydroesterification of alkenes via acyl- palladium intermediate

A chemoselective- and regioselective alkoxycarbonylation reactions can be performed to yield only one of the branched or linear ester under an appropriate reaction condition and catalytic system.

2.1.1. Carbonylation Reaction of Allyl Compounds

In 1964, Tsuji et al. showed that π-allylpalladium chloride can be converted to 3-butenoate under carbon monoxide pressure in alcohol via using $PdCl_2$ as catalyst Figure 2.4).

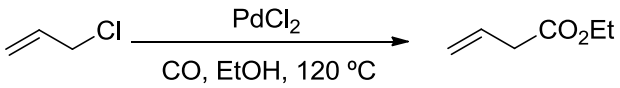


Figure 2.4. Palladium-catalyzed carbonylation reaction of 3-chloroprop-1-ene

In 1984, Tsuji and coworkers described a first catalytic system consisting $Pd(OAc)_2/PPh_3$ to carry out the palladium catalyzed alkoxycarbonylation reaction of allylic carbonates, which give β,γ-unsaturated esters, at elevated 50 ºC under atmospheric or higher pressures of carbon monoxide and neutral conditions (Figure 2.5).

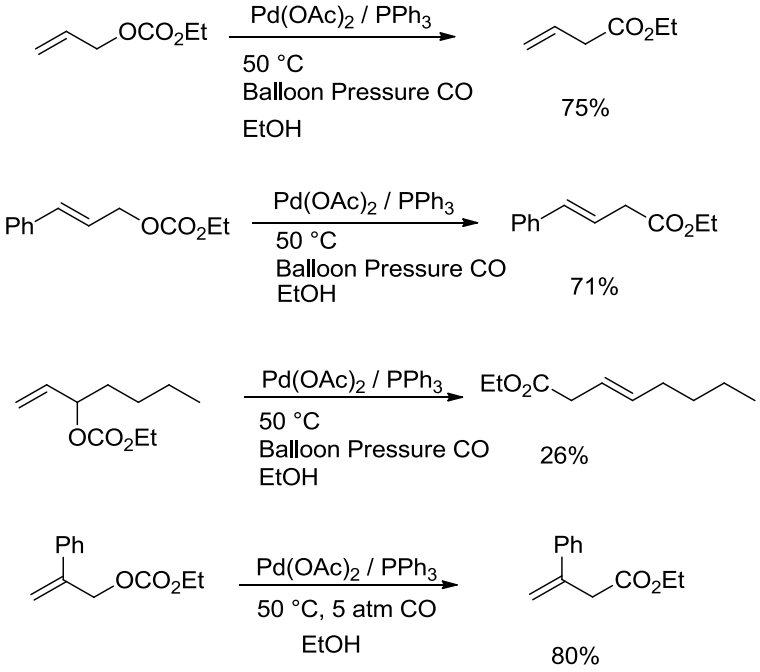


Figure 2.5 Palladium-catalyzed alkoxycarbonylation of allyl carbonates

According to the proposed mechanisms, the oxidative addition of palladium to an allyl carbonate and subsequent decarboxylation form a π-allylpalladium alkoxide intermediate. The following carbon monoxide insertion can take place via two possible paths. These are the insertion of carbon monoxide to the π-allylpalladium bond to give a 3-butenoylpalladium complex and the insertion into the palladium-alkoxide bond to give a (carboalkoxy)(π-ally1)palladium complex. Finally a reductive elimination step leads to the formation a β,γ-unsaturated ester structure and regeneration of Pd(0) species (Figure 2.6).

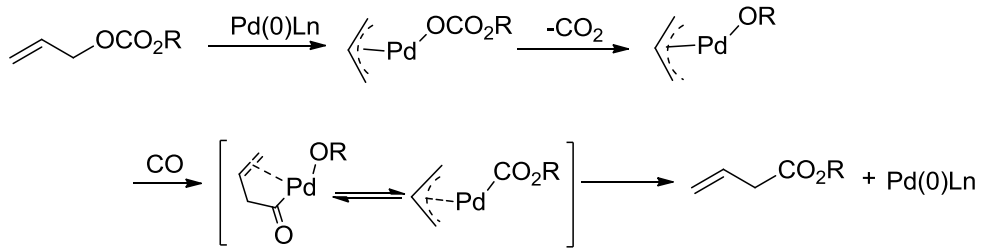


Figure 2.6. Alkoxycarbonylation mechanism of allyl carbonates

In 1993, Murahashi and his co-workers demonstrated that the allyl phosphates are excellent reactants for palladium-catalyzed alkoxycarbonylation reaction. The reaction is carried out in the presence of 2 mol% of $Pd_2(dba)_3CHCl_3$, 2 mol% of PPh_3, and 1 equiv. of *i*-Pr_2NEt in ethanol to obtain the β,γ-unsaturated esters with high yields. The branched phosphates give linear β,γ-unsaturated esters and the reaction can cause the isomerization of β,γ-unsaturated esters (Figure 2.7).

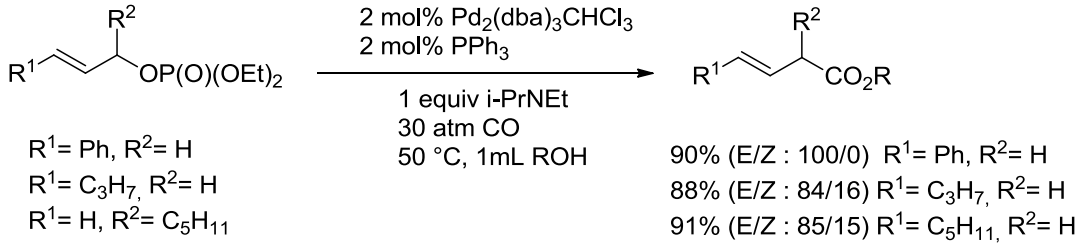


Figure 2.7. Palladium-catalyzed alkoxycarbonylation of allyl phosphates

Also allyl acetates produce β,γ-unsaturated esters via palladium-catalyzed alkoxycarbonylation reactions under the condition containing NaBr as a cocatalyst (Figure 2.8). Sodium bromide accelerates the reaction because the insertion of carbon

monoxide into π-allylpalladium bromide complex proceeded by the ligand exchange of acetate with bromide after the generation of π-allylpalladium acetate complex is facile (Murahashi *et al*. 1993).

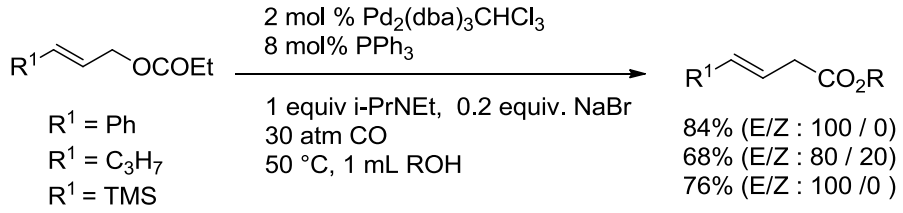


Figure 2.8. Palladium-catalyzed alkoxycarbonylation of allyl acetates

2.2. Palladium-Catalyzed Alkoxycarbonylation of Alkynes

The alkoxycarbonylation reaction of simple alkynes that produces the *α,β*-unsaturated esters an extensive process, which is performed over Pd catalysts in the presence of alcohols. The selectivity in formation of linear or branched esters may differentiate depending on the catalytic system and reaction conditions (Figure 2.9).

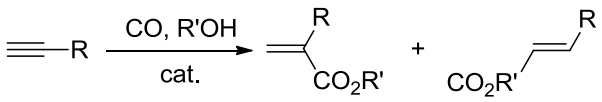


Figure 2.9. Pd-catalyzed alkoxycarbonylation of terminal alkynes

In 1998, Scrivanti et al. reported two feasible paths for the alkoxycarbonylation reaction of terminal alkynes based on the literature and deuterium labeled studies. First mechanism starts with the formation of an (alkoxycarbonyl)-palladium by the insertion of CO into a Pd-OR bond. Carboalkoxy moiety on a carbon atom of the triple bond of the 1-alkyne π-coordinated to the metal center shifts and finally protonation gives the desired branched esters. (Figure 2.10)

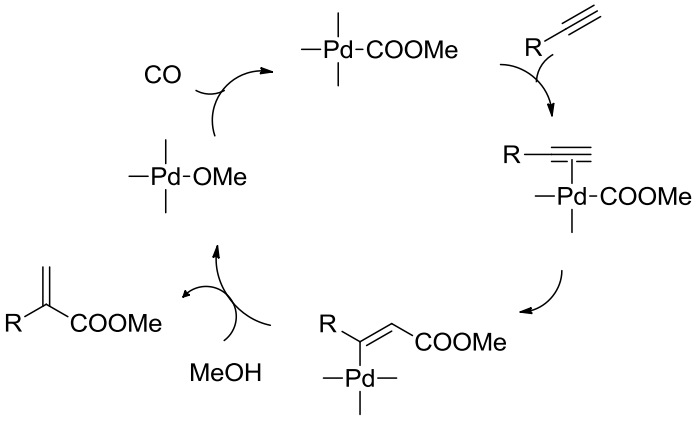


Figure 2.10. The mechanism of alkoxycarbonylation of alkynes via (alkoxycarbonyl) palladium intermediate

The second mechanism involves the insertion of terminal alkyne into the palladium-hydrogen bond resulted the vinyl palladium intermediate. Insertion of CO to Pd-C bond and alcoholysis led to branched esters. (Figure 2.11)

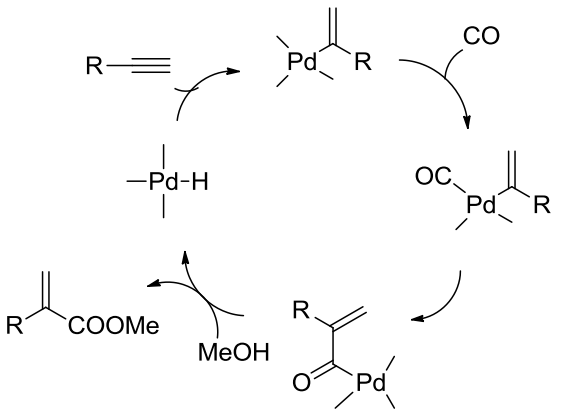


Figure 2.11. The mechanism of alkoxycarbonylation reaction of alkynes via palladium-hydride formation

In 1998, Reetz and coworkers showed that the palladium catalyzed alkoxycarbonylation reaction is applicable to symmetrical terminal alkynes in the presence of $Pd(OAc)_2/PPh_2Py$ catalytic systems (Figure 2.12).

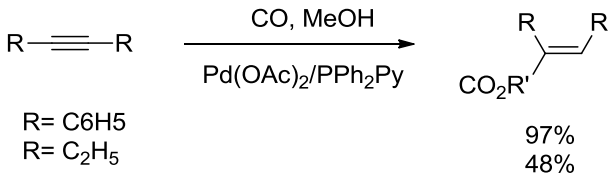


Figure 2.12. Palladium-catalyzed alkoxycarbonylation reaction of internal alkynes

2.2.1. Pd-Catalyzed Reactions of Propargyl Compounds

Pd(0)-catalyzed reactions of various propargyl compounds proceed by formation of two different intermediates which are *σ*-allenylpalladium or the propargylpalladium (or σ-prop-2-ynylpalladium) structures (Figure 2.13) (Elsevier *et al*. 1983-1986).

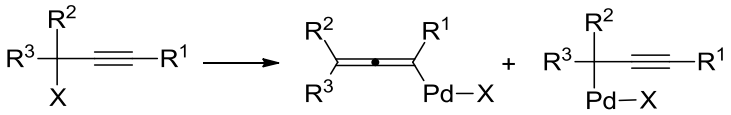


Figure 2.13. Palladium-catalyzed reaction of propargyl compounds including two intermediate

A propargylpalladium intermediate can undergo hydrogenolysis to generate alkynes or *β*-H elimination to yield conjugated enynes (Figure 2.14) (Tsuji, *et al*. 1995).

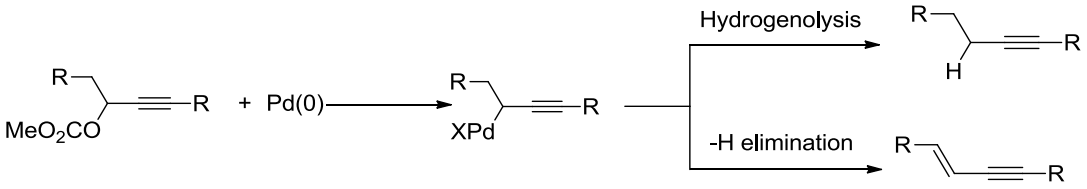


Figure 2.14. Reaction of *σ*-prop-2- ynylpalladium intermediate

Depending on the reactants an σ-allenylpalladium intermediate can undergo three types of reactions.

First type of reaction involves nucleophilic attack such as *β*-keto esters and malonates at the central sp hybridized carbon atom of the *σ*-allenylpalladium intermediate. The Pd-carbene complex is generated from the nucleophilic attack. The carbine intermediate takes a proton and forms *π*-allylpalladium complex. Further

reaction of nucleophile and π-allylpalladium results in formation of the alkene containing nucleophiles on its olefinic and allylic carbons (Figure 2.15).

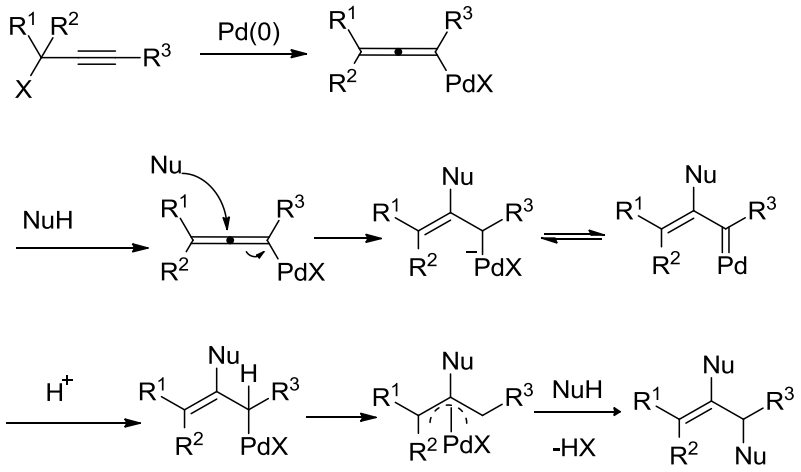


Figure 2.15. Reaction of σ-allenylpalladium which involves nucleophilic attack (Source: Meijere, *et al.* 2004)

The second type of reaction occurs by the transmetallation between the *σ*-allenylpalladium and hard nucleophiles such as metal hydrides, Grignard reagents and organozinc reagents. Allene products are formed as a result of the reductive elimination (Figure 2.16) (Tsuji, *et al.* 2004).

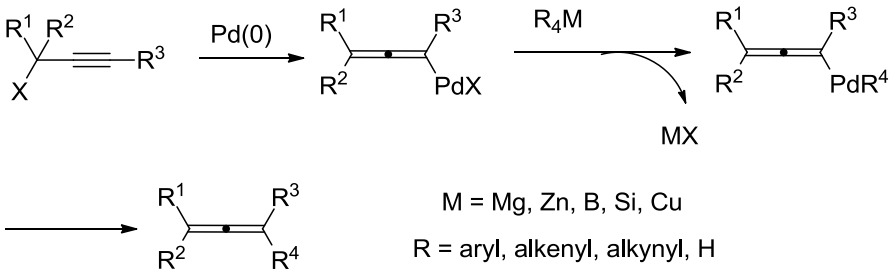


Figure 2.16. Reaction of σ-allenylpalladium which involves transmetallation

In the third type of reactions, the insertions of unsaturated bonds of alkenes, alkynes, or CO into the σ-bond between palladium and sp^2 carbon of the *σ*-allenylpalladium complex takes place (Figure 2.17).

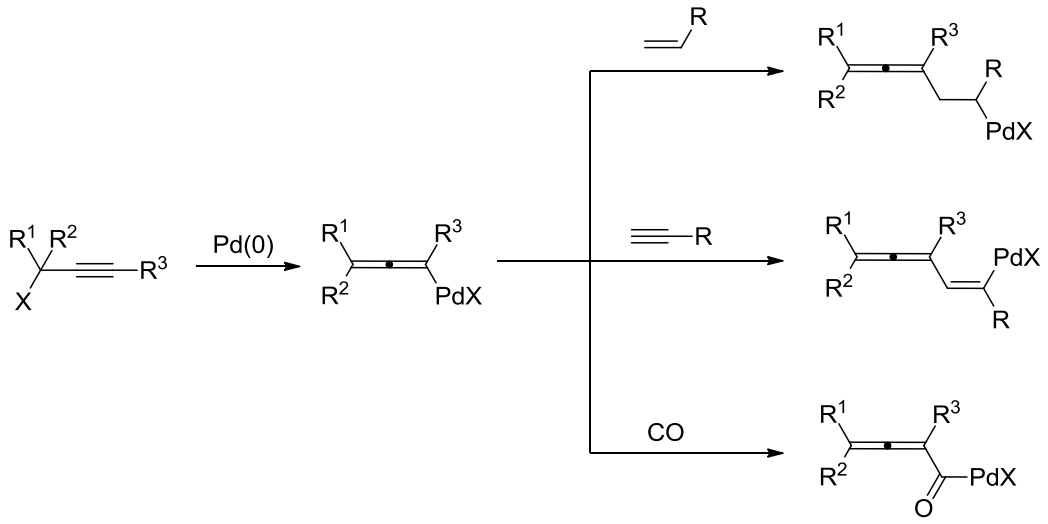


Figure 2.17. Reactions of *σ*-allenylpalladium which involves insertion
(Source: Meijere, *et al*. 2004)

2.2.2. Carbonylation Reactions of Propargylic Compounds Containing a Leaving Group

As mentioned in the previous section, alkynes bearing different leaving groups on its propargylic position can undergo different types of transformations which are transmetallation, nucleophilic attack and insertion in the presence of palladium. The common and key point of this transformation is the formation of the *σ*-allenylpalladium complex. Carbon monoxide can easily insert the bond between palladium and the carbon atom of the *σ*-allenylpalladium complex. As a result of this property, propargyl compounds can give palladium catalyzed mono- and dicarbonylation reaction related to the reaction conditions (Tsuji, *et al.*1993).

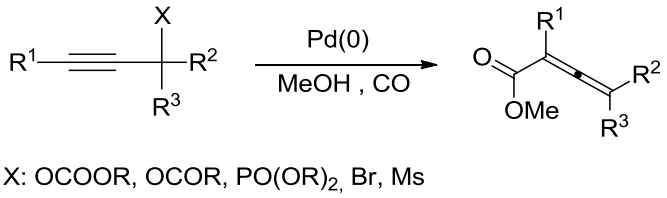


Figure 2.18. Pd(0)-catalyzed alkoxycarbonylation of propargyl compounds

In 1986, Tsuji and coworkers published the first palladium-catalyzed carbonylation reaction of propargyl carbonates to generate the 2,3-dienyl carboxylates in the presence of $Pd_2(dba)_3.CHCl_3/PPh_3$ catalytic systems (Figure 2.19).

Unlike the primary propargylic carbonates having terminal triple bond which forms the desired product with low yield a tertiary propargyl carbonates having terminal triple bond give the carbonylation reaction with excellent yield. Secondary carbonates having internal alkyne moiety is also suitable to carbonylation to high yields of allenyl ester (Figure 2.19).

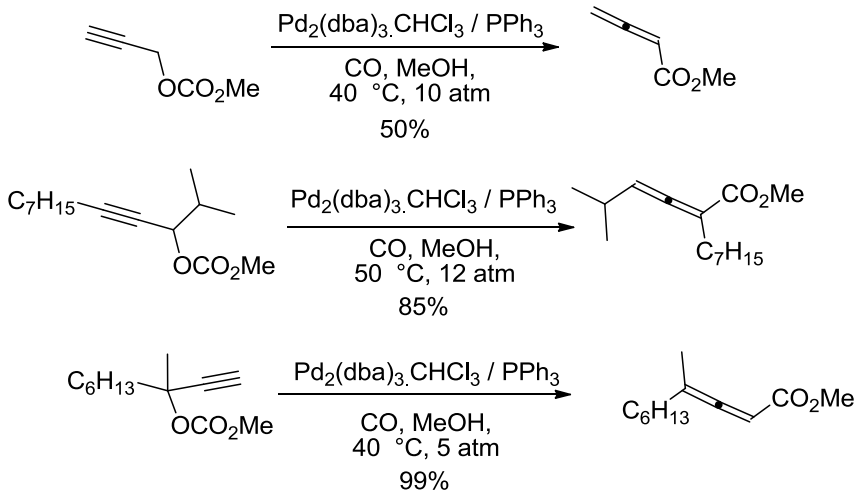


Figure 2.19. Alkoxycarbonylation of propargyl carbonates

They noted that the 2,4-dienyl carboxylate was formed instead of allenyl esters as the reaction was performed in ether, instead of methanol (Figure 2.20).

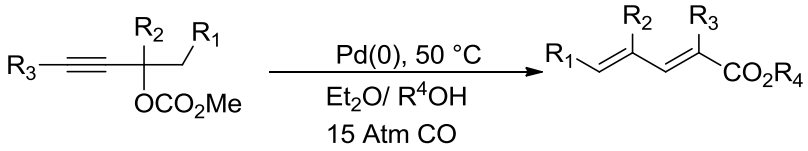


Figure 20. Alkoxycarbonylation of propargyl carbonates to form 2,4-dienyl carboxylate

Their proposed reaction mechanism starts with the oxidative addition of Pd(0) to propargyl carbonate followed by decarboxylation to generate an (allenyl)palladium alkoxide complex. After coordination of carbon monoxide to the complex and insertion

into the palladium-carbon bond, reductive elimination gives the allenyl esters and regenerates the Pd(0) (Figure 2.21).

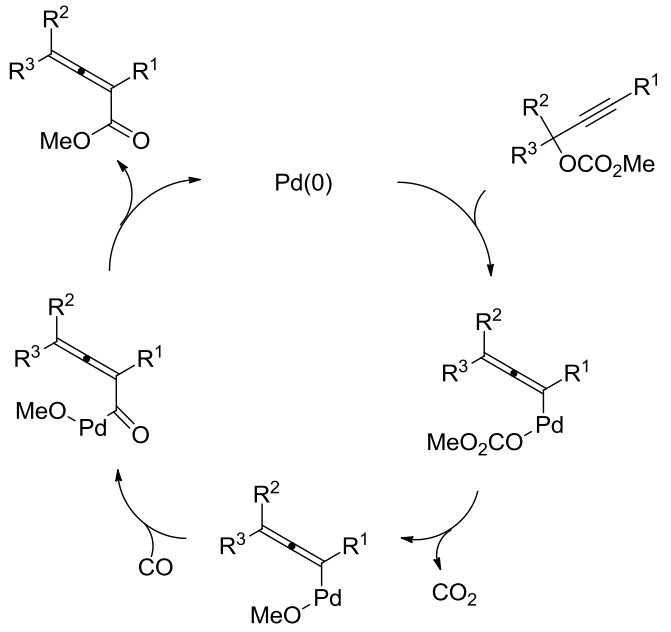


Figure 2.21. Pd-catalyzed alkoxycarbonylation mechanism of propargylic carbonates

In the presence of 20 atm pressure of carbon monoxide and methanol, an optically active 2,3-dienoate could be synthesized under the $Pd(OAc)_2$/1,6-bis(diphenylphosphino)hexane catalytic system when optically active propargyl phosphates were used (Figure 2.22) (Tsuji *et al.* 1995).

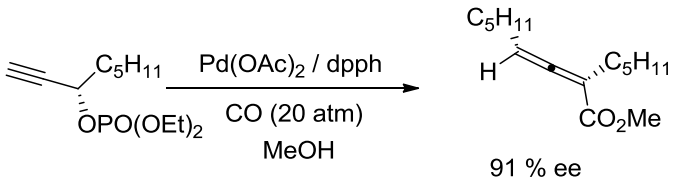


Figure 2.22. Carbonylation reaction of optically active propargylic phosphates (Source: Tsuji *et al.* 1995)

Palladium catalyzed carbonylation reaction of enantioriched propargylic mesylates can lead to formation of enantioriched allenyl esters by exposure of the mesylates to CO and $Pd(PPh_3)_4$ in the presence of an alcohol(Figure 2.23). However the centre to axial chirality transfer failed when a propargylic carbonate was carbonylated instead (Marshall *et al.* 1997).

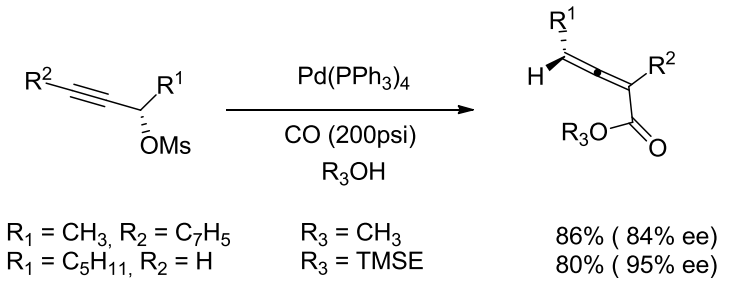


Figure 2.23. Carbonylation reaction of propargylic mesylate to give optically active allenes (Source: Marshall *et al.* 1997).

2.3. Synthesis of Vinylallenes

Developing methods to synthesize vinyl allenes bearing cumulenic and vinylic group has come prominence because of its widespread use in organic reaction such as inter- and intramolecular Diels-Alder reactions, cycloisomerization reactions and cyloaddition reactions.

2.3.1. Synthesis of Vinylallenes with Grignard Reagent

In 1972, Gore *et al*. performed the reaction of 1-chloro-2-en-4-ynes with methylmagnesium iodide and trimethylsilylmagnesium chloride to produce vinyl substituted allenes (Figure 2.24).

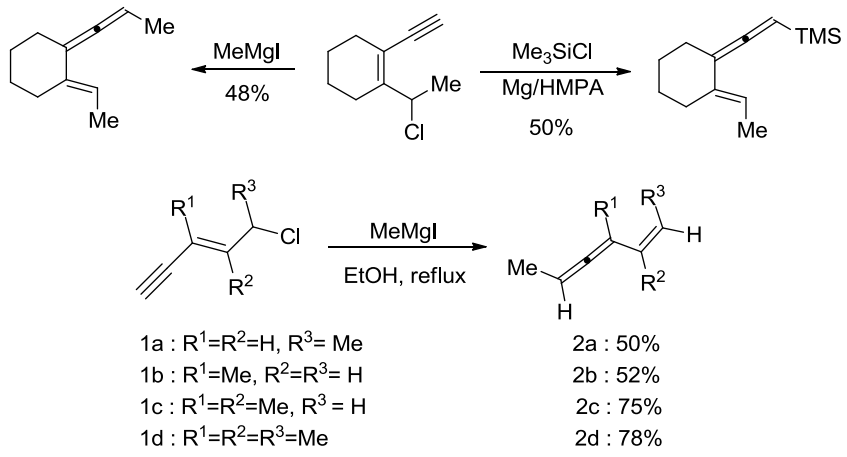


Figure 2.24. The reaction of chloro-enynes with Grignard reagents

The applicability of this process is limited owing to the fact that other Grignard reagents except methylmagnesium iodide and trimethylsilylmagnesium chloride completely failed to yield desired vinylallenes.

2.3.2. Synthesis of Vinylallenes with Organocopper Reagents

Previously 1,5-(S_N2'')-type reaction of 2-en-4-yne acetates with various lithium dialkylcuprates affording vinylallenes with excellent yields was reported. The method is apparently is not diastereoselective, yielding vinyl allene compounds as *E*- and *Z*-mixtures (Figure 2.25).

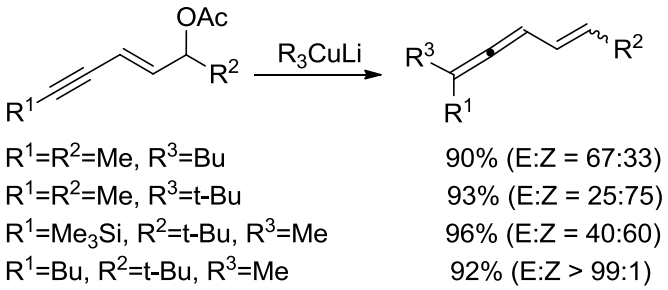


Figure 2.25. 1,5-(S_N2'')-type Substitution reaction of enyne acetates with dialkyl cuprates (Source: Krause *et al.* 1999)

E-enyne oxirane was also found to be reactive reagents toward copper catalyzed 1,5-(S_N2'')-type reactions. The substrate reacted cleanly with the *tert*-butylcuprate to afford the alkylated vinylallene bearing hydroxyl group on its vinylic position (Figure 2.26).

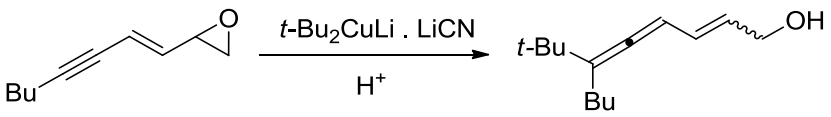


Figure 2.26. 1,5-(S_N2'')-type Substitution reaction of enyne oxiranes with dialkyl cuprates (Source: Krause *et al*. 1999)

2.3.3. Palladium-Catalyzed Synthesis of Vinylallene By Organozinc Reagent

Ma and coworkers demonstrated that the palladium catalyzed coupling reaction of propargyl mesylate with alkoxycarbonylethenyl zinc complexes can form vinyl allenes with excellent yields in the presence of a catalyst system resulting from the combination of 2- diphenylphosphino-2'-hydroxy-1,1'-binaphthalene (L) and [{PdCl(π-C_3H_5)}$_2$] (Ma, et al. 2003) (Figure 2.27).

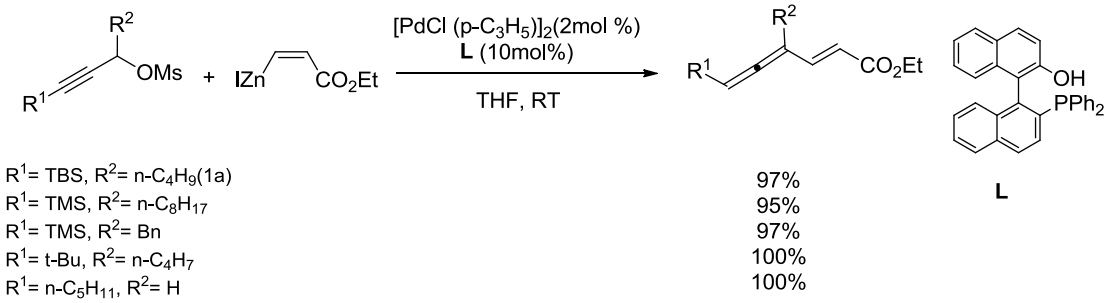


Figure 2.27. Synthesis of Vinylallenes by organozinc reagents

2.3.4. Palladium-catalyzed Synthesis of Vinylallenes By N-tosylhydrazone Salt

New synthetic method reported by Chen showed that diazo compound generated *in-situ* from *N*-tosylhydrazone salt in the presence of base can tend as a nucleophile and react with the propargylic carbonates to form *tri*- and *tetra*- substituted vinylallene structures in the presence of [$Pd_2(dba)_3$] as a catalyst (Figure 2.28) (Chen, *et al*. 2011).

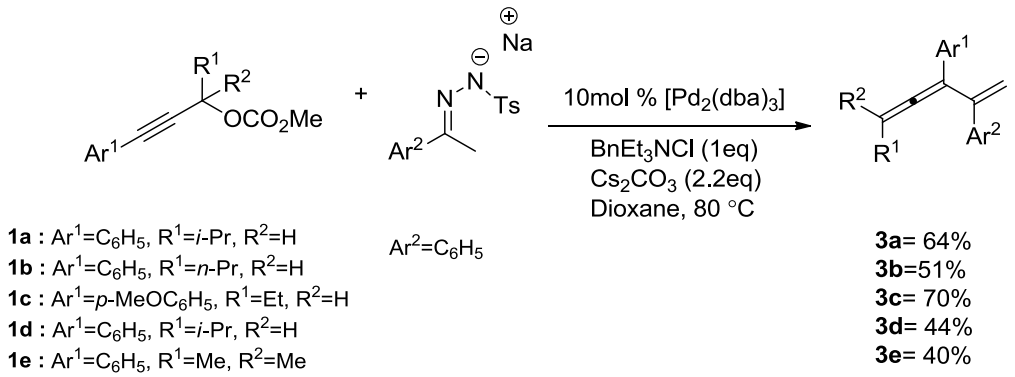


Figure 2.28. Synthesis of vinylallene synthesis by *N*-tosylhydrazone Salt (Source: Chen, *et al.* 2011)

2.3.5.Palladium-Catalyzed Synthesis of Vinylallene by Alkenyl Trifluoroborates

In addition to synthesis of several racemic allenes having different functional groups, central to axial chirality transfer was investigated utilizing Pd(0)-catalyzed cross-coupling reaction of enantioriched propargylic carbonates and phosphates with alkenyltrifluoroborates (Molander, *et al.*2006) (Figure 2.29).

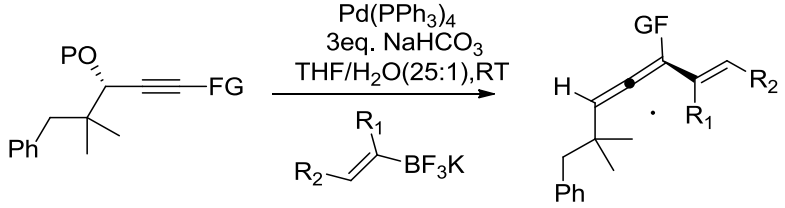


Figure 2.29. Synthesis of vinylallene by alkenyltrifluoroborates (Source: Molander, *et al.*2006)

2.3.6. Rh(I)-Catalyzed Reaction of the (*Z*)-Enyne Acetate with Organoboronic Acids

In 2011, Üçüncü, *et al.* reported that rhodium(I)-catalyzed reaction of (*Z*)-2-en-4-yne acetates with organoboronic acids afforded vinylallenes. The reaction is suitable

for arylboronic acids having both electron-withdrawing or -donating groups (Figure 2.30).

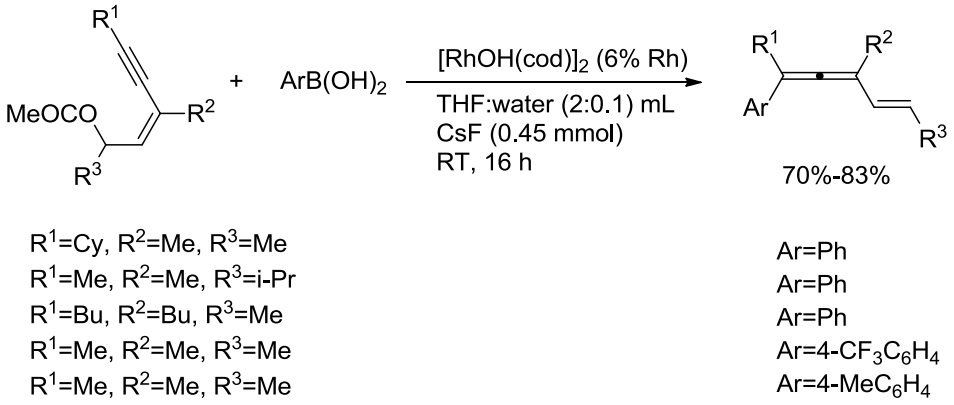


Figure 2.30. Rh(I)-Catalyzed Reaction of the (*Z*)-Enyne Acetate with Organoboronic Acids

2.3.7. Palladium-Catalyzed Reaction of 2-en-4-yne Carbonates with Organoboronic Acids

Üçüncü and coworkers also proved that arylboronic acids having different electron deficient or electron donating substituents are good coupling partner for (*E*)- and (*Z*)-configured enyne carbonates under the palladium-catalyst conditions, yielding exclusively the (*E*)-configured vinylallenes (Figure 2.31).

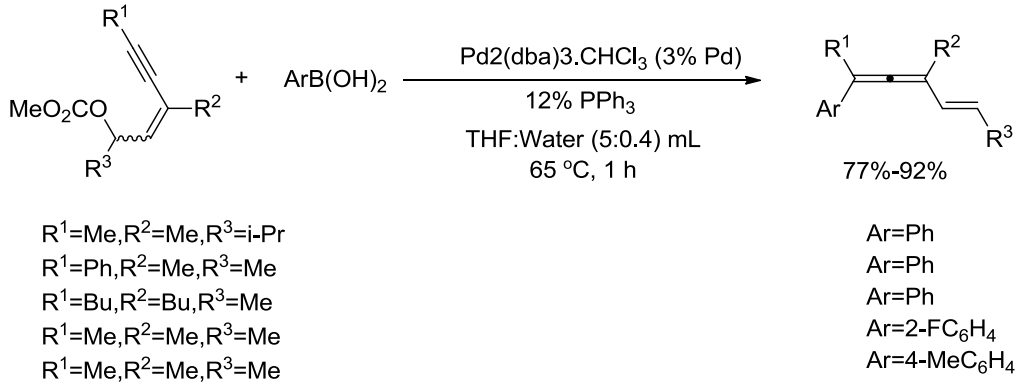
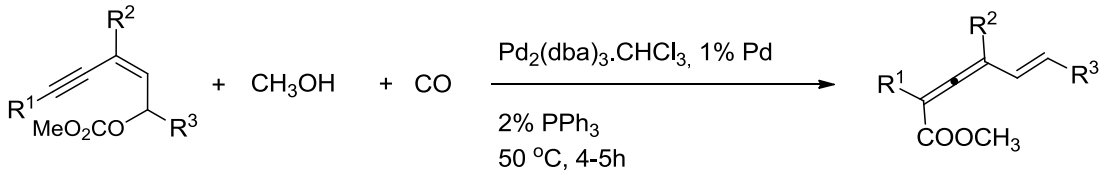


Figure 2.31. Palladium-Catalyzed Reaction of 2-en-4-yne Carbonates with Organoboronic Acids

The Pd(0)-catalyzed 1,5-substitution type reactions of 2-en-4-yne and organoboronic acids proceeded through the formation of σ-vinylallenylpalladium (II) intermediate and transmetallation type reaction of σ-vinylallenylpalladium (II) intermediate and organoboronic acids.

2.3.8. Palladium-Catalyzed Alkoxycarbonylation Reaction of (*Z*)-2-en-4-yne Carbonates

For the first time the synthesis of vinylallenyl esters was investigated by Akpınar *et al*. in 2011. Conjugated (*Z*)-enyne having a carbonate as a leaving group at allylic moiety underwent Pd(0)-catalyzed reaction to lead to 2,3,5-trienoate products with high yields (Figure 2.32).



$R^1=R^2=R^3=$ Me	87 %
$R^1=$ Ph, $R^2=R^3=$ Me	83 %
$R^1=R^2=$ Me, $R^3=$ Bu	87 %

Figure 2.32. Palladium-Catalyzed Alkoxycarbonylation Reaction of (*Z*)-2-en-4-yne Carbonates

Palladium-catalyzed alkoxycarbonylation reaction is also applied to an enantioriched (*Z*)-enyne. It was found that the reaction proceeded with complete racemization.

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 was dried over Mg turnings in the presence of iodine and stored on 3Å molecular sieves under Argon. Pyridine was dried over CaH_2 and stored on 3Å molecular sieves under Argon.

3.2. Synthesis of Substrates

3.2.1. Synthesis of *E*-Enyne Alcohols S6g, h, j, l, m-o:

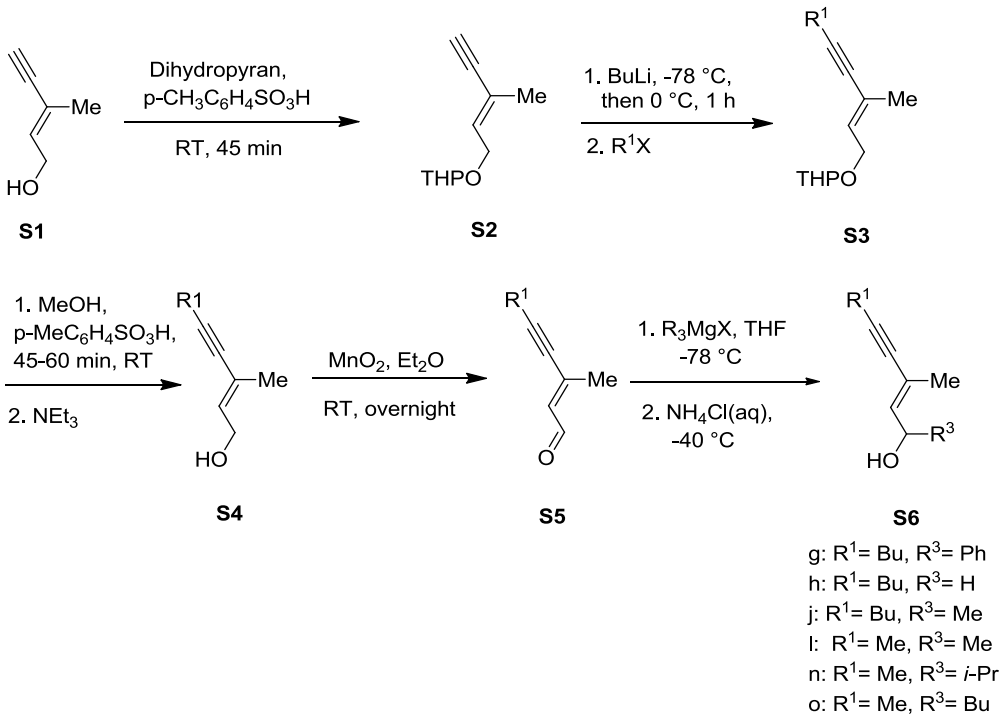


Figure 3.1. Synthesis of *E*-Enyne Alcohols **S6g, h, j, m-o**

To the mixture of commercially available, (*E*)-pent-2-en-4-yn-1-ol (**S1**) (9.6 g, 100 mmol) and 3,4-dihydropyran (11 mL) was added *p*-toluenesulfonic acid (220 mg, 0.1 mmol) and then stirred for 45 min at room temperature. Then, the mixture was diluted with 200 mL of dry THF under argon and cooled to -78 °C. At that temperature, a 120 mmol hexane solution of BuLi (1.6 M, 75 mL) was added dropwise via a syringe. After stirring the reaction mixture for 1 h at 0 °C, 19 mL of alkyl halide (≈300 mmol) was added dropwise. The mixture was stirred overnight at room temperature when the alkyl halide used was MeI, or 5 days at 65 °C when BuBr 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 $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was used in the following step without any other purification. (Betzer, *et al*. 1997)

To a solution of the preceding crude compound (**S3**) in methanol (300 mL) p-toluenesulfonic acid (6 g, 30 mmol) was added and the resulting solution stirred at RT for 45-60 min. Then, triethylamine was added (9 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 ***E*-S4** (yields: R^1= Me, 86%; Bu, 65%). (Purpura and Krause 1999)

To the solution of (**S4**) (≈65 mmol) in 250 mL of dry diethyl ether, 114 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 (Betzer, *et al*. 1997).

The crude aldehyde (**S5**) was dissolved in 140 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 115 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 vacuum, and the crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate, yields: ***E*-S6**; R^1= Me, R^3= Me, 65%; R^1= Me, R^3= *i*-Pr, 60%; R^1= Me, R^3= Bu, 70%; R^1= Bu, R^3= Me, 65%; R^1= Bu, R^3=H, 65%; R^1= Bu, R^3= Ph, 52%).

To synthesize R^1=Ph en-yne alcohol (**S6m**) Sonagashira coupling was applied in second step. A mixture of (**S2)** (≈17 mmol), $PdCl_2(PPh_3)_2$ (105.3 mg, 0.15 mmol), and CuI (16.5 mg, 0.085 mmol), in 70 mL of Et_3N was stirred for 5 min at 50°C under Ar, and then, to this mixture was added phenyl acetylene (19 mmol). The mixture was stirred at 50°C 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 vacuum and the product (**S3**) was purified by column chromatography on silica gel (hexane/ethyl acetate, yield: 85%) (Takeuchi, *et al*. 2000).

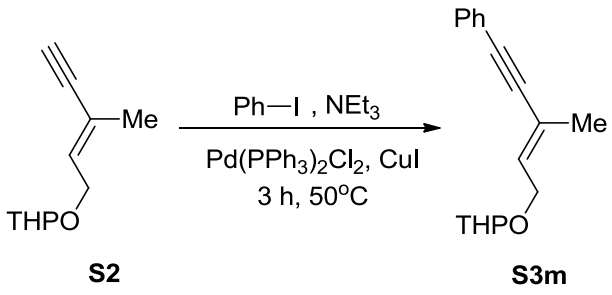


Figure 3.2. Synthesis of **S3m** (R^1= Ph) by Sonagashira Coupling of **S2** (Source: Takeuchi, *et al*. 2000).

3.2.2. Synthesis of *E*-Enyne Alcohols S6a-b, d-e:

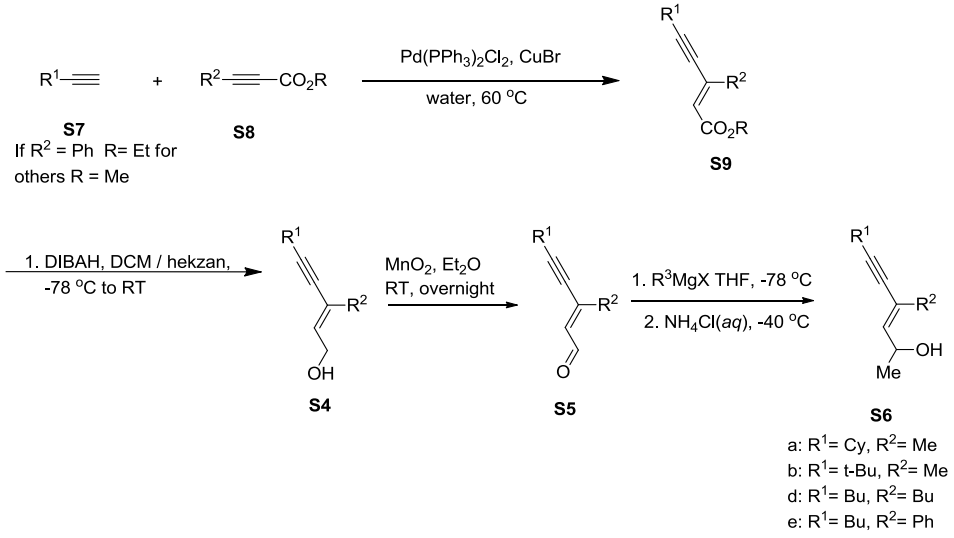


Figure 3.3. Synthesis of *E*-Enyne Alcohols **S6a-b, d-e**.

A mixture of terminal alkyne (**S7**) (50 mmol), alkynoic ester (**S8**) (25 mmol), CuBr (225 mg, 1.25 mmol) and $PdCl_2(PPh_3)_2$ (465 mg ,0.625 mmol) in 50 mL water was stirred at 60 °C temperature under Ar for 48 h. (To synthesis of compound having R^1 = Cy, R^2 = Me, the mixture was stirred for 24 h). After completion of the reaction, the reaction mixture was allowed to be cold to room temperature and extracted with Et_2O. Combined extracts 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, (**S9**) : R^1= Cy, R^2= Me, 85%; R^1= t-Bu, R^2= Me, 75%; R^1= Bu, R^2= Bu, 90%; R^1= Bu, R^2= Ph, 84%) (Chen, *et al.* 2004).

To the 250 mL of flask ≈20 mmol **S9** and 44 mL of dry dichloromethane was added. The stirred solution was cooled to -78 °C and 40 mL of a 1 M solution of diisobutylaluminum hydride in hexane was added dropwise with a syringe. After addition of complete, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature and stirred at RT for 16 hours. The mixture was hydrolyzed at -20 °C by dropwise addition of water and extracted with dichloromethane. Combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product **(S4)** was purified by column chromatography on silica gel (hexane/ethyl acetate) (Shintani, *et al.* 2005).

To the solution of (**S4**) (≈10 mmol) in 39 mL of dry diethyl ether, 17.6 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. (Betzer, *et al.* 1997)

The crude aldehyde (**S5**) was dissolved in 21 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 18 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 vacuum, and the crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate, yields: ***E*-S6**; R^1= Bu, R^2= Bu, 40%; R^1= Bu, R^2=Ph, 39%; R^1= Cy, R^2= Me, 39%; R^1= t-Bu, R^2= Me; 34%).

3.2.3. Synthesis of *E*-Enyne Alcohol S6c:

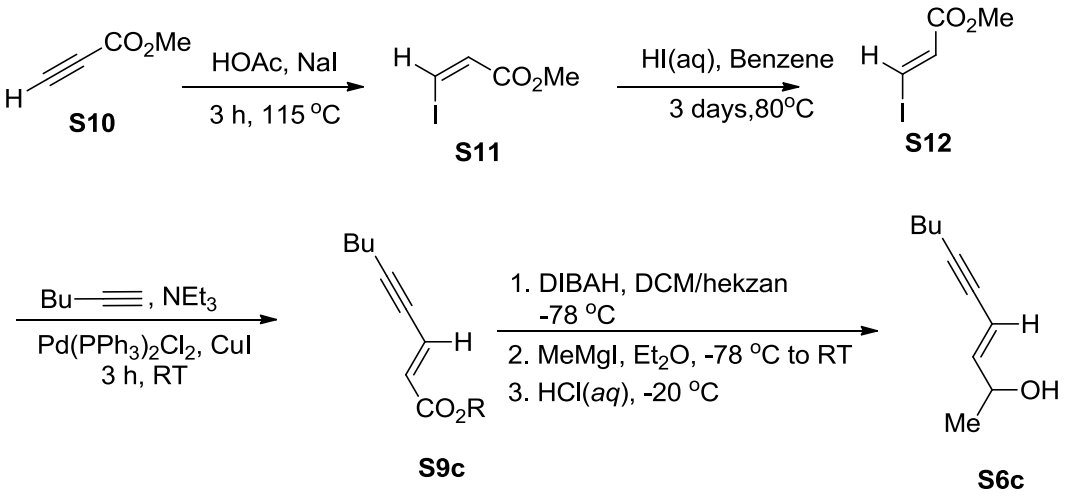


Figure 3.4. Synthesis of *E*-Enyne Alcohols **S6c**

To a solution of alkynoic ester (S10) (≈40 mmol) and acetic acid (240 mmol, 13.8 mL) (512 mmol, 20.8 mL when (S10) was added ethyl 3-phenylpropiolate and sodium iodide (9.6 g, 64 mmol) 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, (**S11**): 84%) (Piers, *et al.* 1994).

To the solution of (**S11**) (≈25 mmol) in 13 ml benzene (1.8M), 0.3 equivalent solution of hydroiodic acid (%57 v/v, 1.0 mL) was added. The reaction mixture was stirred for 3 days at 80 °C temperature. After the reaction mixture was allowed to cool down to room temperature, diluted with 12 mL diethyl ether and washed with 5 mL of saturated sodium thiosulphate solution. The aqueous phase was extracted with diethyl ether and this combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. (**S11**/**S12**=96/4) (Garrais, *et al*. 2009).

The mixture of crude (**S12**) (≈25 mmol), $PdCl_2(PPh_3)_2$ (151.2 mg, 0.23 mmol), and CuI (23.5 mg, 0.13 mmol), in 100 mL of Et_3N was stirred for 10 min at room temperature under Ar, and then, to this mixture was added a terminal alkyne (28.8 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 vacuum and the product (**S9c**) was purified by column chromatography on silica gel (hexane/ethyl acetate, yield: 88%) (Takeuchi, *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 ≈10 mmol of (**S9c**) and 20 mL of anhydrous dichloromethane. The stirred solution was cooled to -78 °C and 6 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 (11 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 20 mL of a 1 M aqueous solution of hydrochloric acid, followed by addition of 30 mL of ether. The organic layer was separated and extracted with ether. The combined extracts were dried over $MgSO_4$. The solvent was evaporated in vacuum. The product (**S6c**) was purified by column chromatography on silica gel (hexane/ethyl acetate; yield: 50%) (Marek, *et al.* 1998).

3.2.4. Synthesis of *E*-Enyne Alcohol S6f:

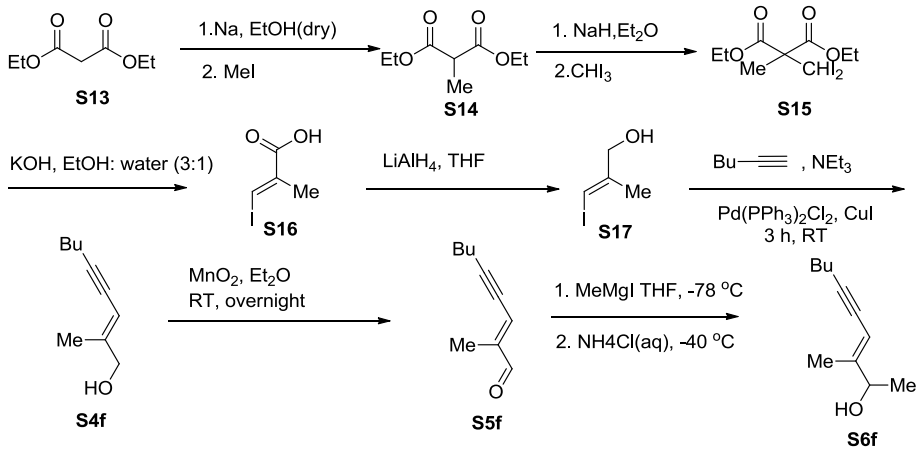


Figure 3.5. Synthesis of *E*-Enyne Alcohol **S6f**

A dry, two-necked, round-bottomed 250-mL flask equipped with a reflux condenser and an Ar gas inlet, was charged with 75 mL of anhydrous absolute ethanol. Metallic sodium (3.48 g, 150 mmol) was cut into small pieces and added into the ethanol and stirred. After all sodium was dissolved, diethylmalonate (**S13**) (23 mL, 150 mmol) was added to the solution. The reaction mixture was treated with iodomethane (9.8 mL, 157,5 mmol) by dropwise addition via a syringe. The mixture was heated until the mixture reached its boiling point. After 4 hours the reaction mixture was concentrated under a reduced pressure. The mixture was diluted with diethyl ether and water and phases were separated. The aqueous layer was extracted with ether, and the combined extracts were dried over $MgSO_4$, filtered and evaporated in vacuo. The crude product (**S14**) was used in the next step. (Weiner, *et al*.1937).

The crude (**S14**) (≈50 mmol) was slowly added to the solution of NaH (25 g, 52 mmol) in 63 mL dry Et_2O via syringe and the reaction mixture was refluxed for a further 2.5 h. $CHCl_3$ (19.8 g, 50 mmol) was added in one portion and the mixture was refluxed for 20h. After cooling to 0°C , hydrochloric acid solution (18 mL, 10%) was added and the resulting mixture was stirred about 10 min. The organic phase decanted and dried over $MgSO_4$, filtered and concentrated under a reduced pressure. The remaining residue was diluted with petroleum ether and precipitated iodoform was removed by filtration. The product (**S15**) was purified by distillation at 130 °C and 12 bar. (Yield= 65%) (Baker, *et al.*1990)

The solution of (**S15**) (≈33 mmol), KOH (5.6 g, 0,1 mol) and EtOH: H_2O (3:1, 45 mL) were refluxed for 24 h and cooled to room temperature. The reaction mixture was concentrated under reduced pressure and diluted with solution of K_2CO_3 (27mL, %10) and washed with dichloromethane (9mL x 2). The basic solution is acidified with HCl (aq) (12M). The aqueous phase extracted with dichloromethane (7mL x 7). The combined organic phases was dried over $MgSO_4$, filtered and concentrated under vacuo. The residue (**S16**) was purified by crystallization with petroleum ether (Yield= 89%) (Baker, *et al.*1990).

To the solution of (*E*)-3-iodo-2-methylprop-2-enoic acid (**S16**) (≈29 mmol) in 48 mL of dry THF, lithium aluminium hydride (1.1g ,29mmol) was slowly added at 0 °C temperature under Ar. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours. The reaction mixture was recooled to 0 °C and quenched with saturated aqueous Na_2SO_4 by dropwise addition. The mixture was diluted with ether and 40 mL of aqueous H_2SO_4 (2M) was added. The organic phase was decanted and the aqueous phase was extracted with DCM. The combined organic phases was washed with 10 mL of K_2CO_3 (10%) and the aqueous phase extracted with DCM. The combined organic phases was dried over $MgSO_4$, filtered and the solvent was removed under vacuo. The product (**S17**) was purified by column chromatography on silica gel (hexane/ethyl acetate; yield:65%) (Baker, *et al.*1990).

The mixture of (**S17**) (≈8.5 mmol), $PdCl_2(PPh_3)_2$ (51.2 mg, 0.077 mmol), and CuI (8.1 mg, 0.041 mmol), in 37 mL of Et_3N was stirred for 10 min at room temperature under Ar, and then, to this mixture was added a 1- hexyne (9.6 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 vacuum and the product (**S21**) was purified by column chromatography on silica gel (hexane/ethyl acetate, yields: 86%) (Takeuchi, *et al.* 2000).

To the solution of (**S4f**) (≈7 mmol) in 30 mL of dry diethyl ether, 12.0 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 (**S5f**) was used in the next step. (Betzer, *et al.* 1997)

The crude aldehyde (**S5f**) was dissolved in 14 mL of anhydrous THF and treated at -78 °C with 1.2 equivalent ethereal solution of R_3MgI (1.6 M) 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 12 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 vacuum, and the crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate, yield (**S6f**): 45 %)

3.2.5. Synthesis of *E*-Enyne Alcohol S6i:

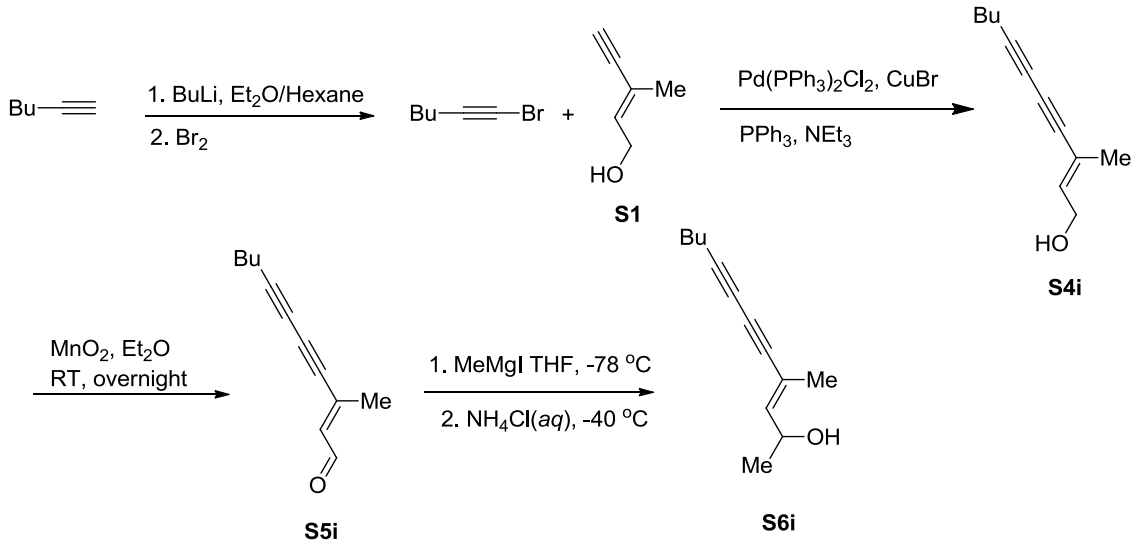


Figure 3.6. Synthesis of *E*-Enyne Alcohol **S6i**

To a solution of 1-hex-1-yne (2.3 mL, 20 mmol) in 17 mL Et_2O was added the 24 mmol hexane solution of BuLi (12 mL, 2 M) dropwise via a syringe. The resulted solution was stirred magnetically for 15 min then cooled to -20 °C. 28 Mmol Br_2 (1.43 mL) was added dropwise via syringe to the solution and reaction mixture was stirred at room temperature. The reaction mixture was quenched by slow addition of water at -20 °C temperature and organic phase was decanted. The organic phase was washed 3 times with 7 mL of saturated aqueous $Na_2S_2O_3$. The combined organic phase was dried over $MgSO_4$, filtered and concentrated under vacuum. The crude 1-bromo-hex-1-yne was used for the following step (Kloster-Jensen, *et al*. 1966).

A suspension of $[PdCl_2(PPh_3)_2]$ (273 mg, 0.4 mmol), CuI (147 mg, 0.8 mmol), PPh_3 (203 mg, 0.8 mmol) and 1-bromohex-1-yne (≈20 mmol) in degassed Et_3N (200 mL) was stirred for 30 min, treated with commercially available, (*E*)-pent-2-en-4-yn-1-

ol (1.9 g, 0.48 mmol), and stirred at 25°C for 12 h. The reaction mixture was diluted with EtOAc and washed with cold (≈ 0°C) saturated *aqueous* solution of NH_4Cl. The *aqueous* phase was extracted with EtOAc and the organic phase was dried over $MgSO_4$, filtered and evaporated. The crude **(S4i)** was purified by column chromatography on silica gel (hexane/ethyl acetate, yields: 30 %) (Xu, *et al.* 2005).

To the solution of (**S4i**) (≈7 mmol) in 30 mL of dry diethyl ether, 12.0 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 (**S5i**) was used in the next step (Betzer, *et al.* 1997).

The crude aldehyde (**S5i**) was dissolved in 14 mL of anhydrous THF and treated at -78 °C with 1.2 equivalent ethereal solution of MeMgI (1.6-2.0 M) 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 12 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 vacuum, and the crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate, yield (**S6i**): 65 %).

3.2.6. Synthesis of *E*-Enyne Carbonate E-1k:

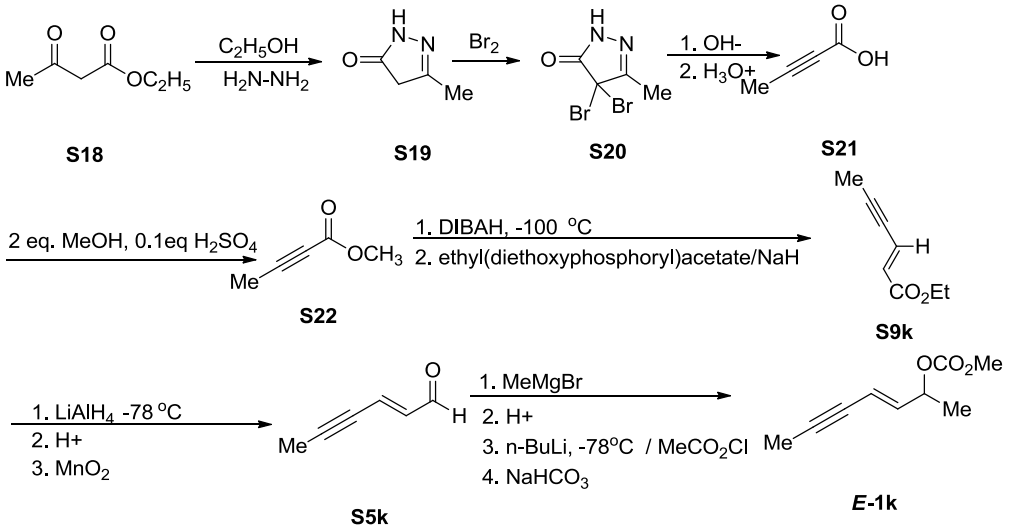


Figure 3.7. Synthesis of (*E*)-Enyne Carbonate ***E*-1k**

To a solution of hydrazine monohydrate (100 g, 2 mol) in ethanol (120 ml) ethyl acetoacetate (**S18**) (260 g, 2 mol) was added dropwise at room temperature. After addition was complete, the reaction mixture was stirred for 2h at room temperature and then cooled to 0°C, precipitate was filtered off and washed with cold ethanol (yield: 90%) (Simmross, *et al*. 1981).

The solution of 3-methyl-2-pyrazolin-5-one (**S19**) (167 g, 1.7 mol) in acetic acid (300 mL) was added dropwise to the acetic acid (200 mL) solution of bromine (544 g, 6.8 mol) at 0°C and stirred for 3 h at room temperature. The solution was poured into water (10 L). The crystals were filtered off and washed to neutralize with water and dried under high vacuum (Yield; 78%) (Simmross, *et al*. 1981).

10 % solution of NaOH (4000 mL) at -5°C was added dropwise to the solution of 4,4-dibromo-3-methyl-2-pyrazolin-5-one (**S20**) (256 g, 1 mol) in Et2O (1200 mL). The solution was stirred at 0°C for 1 h and additional 1h at room temperature. The solution was neutralized by conc. HCl in an ice bath and extracted with diethylether by extractor for 3 days. The solution was dried with MgSO4 and solvent was removed in vacuo. The crude product (S10) was purified by sublimation at 60°C under 0.02 torr pressure (Yield: 90%) (Simmross, *et al*. 1981).

To a solution of H_2SO_4 (4.4 mL) in methanol (92 mL) was carefully added a solution of 2-butynoic acid (8.0 g, 95.2 mmol, 1.0 equivalent) in methanol (180 mL). The reaction mixture was stirred for 4 days at room temperature. Water (280 mL) was added, followed by Et_2O (280 mL). The phases were separated and the aqueous phase was extracted with Et_2O (3 x 2800 mL). The organics were combined, washed with water (1 L), saturated aqueous sodium carbonate (1 L), then water (1 L), then dried over sodium sulfate, filtered, and carefully concentrated in vacuo to afford methyl but-2-ynoate (**S22**) (yield: 65%) (Trost, *et al*. 2011).

To a solution of (5.88 g , 60.0 mmol) of methyl 2-butynoate (**S22**) in of diethyl ether (300 ml), DIBAH (102 ml, 102 mmol, 1.0 M in hexane) was added dropwise at -80°C and stirred for 2 h. In a second flask ethyl(diethoxyphosphoryl) acetate (66.0 mmol) of in THF (100 ml) was added dropwise to a suspension of NaH (3.6 g, 90 mmol, 60% in paraffin oil) in THF (100 ml). After 10 min the solution of the ethyldiethoxyphosphoryl)acetate reagent was cooled to -80°C and transferred via a teflon tube to the other flask. The mixture was warmed to room temperature and stirred for 2 h. After acidification with 2 N HCl the layers were separated and the aqueous layer was extracted several times with diethyl ether and the combined organic layers

were dried with $MgSO_4$. The solvent was removed in vacuo; the crude product was purified by kugelrohr distillation (40-50°C under 0.1 Torr pressure) as a colorless liquid (**S9k**) (Koop, *et al.* 1996).

A suspension of 23.1 mmol of $LiAlH_4$ in 46 ml of diethyl ether was cooled to -60°C and 2.9 g (21 mmol) of (**S9k**) in 21 ml of diethyl ether was added dropwise. After stirring for 1 h at -60°C, 2 ml of a saturated NH_4Cl solution was added and the mixture was warmed up to room temperature and filtered through Celite; the residue was washed with diethyl ether, the combined filtrates were dried with $MgSO_4$, and the solvent was removed in vacuo. A solution of the crude alcohol thus obtained in 80 ml of diethyl ether was added to a thoroughly stirred suspension of 55 g (0.63 mol) of activated MnO_2 and the mixture was stirred for 16 h at room temp. The mixture was then filtered through celite and solvent was removed in vacuo (Betzer, *et al*. 1997).

18 mmol of the aldehyde (**S5k**) was dissolved in 40 mL of Et_2O and treated at -80°C with 7.2 mL (21.6 mmol) of MeMgBr (3 M in diethyl ether). Within 2 h the mixture was warmed with stirring to -40°C and then hydrolyzed by addition of saturated NH_4Cl solution. After extraction with diethyl ether, the combined organic layers were washed with water and dried with $MgSO_4$. The solvent was removed in vacuo, and the crude alcohol was dissolved in 16 mL THF and was added 10.8 mL (21.6 mmol) *n*-BuLi at -78°C and the mixture was stirred for 1 h. Then methylchloroformate was added dropwise at -78°C. The solution was gradually warmed up to RT and stirred for 15 h. The reaction was quenched by the addition of a saturated $NaHCO_3$ solution and extracted with ethylacatate and dried over $MgSO_4$. The solvents were evaporated under a vacuum to give an oily product ***E*-1k**, which was purified by column chromatography (silica gel, cyclohexane/ ethyl acetate/ triethylamine, 100 : 6 : 1) (Mandai, *et al.* 1994).

3.2.7. Synthesis of (*S*,*E*)-4-methyldec-3-en-5-yn-2-ol

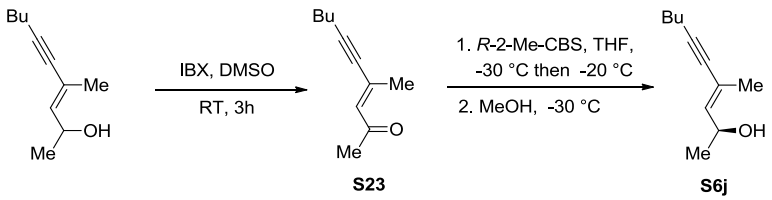


Figure 3.8. Synthesis of (*S*,*E*)-4-methyldec-3-en-5-yn-2-ol

2-Iodoxybenzoic acid (IBX) (6,6 g, 24 mmol) was added to a solution of secondary enyne alcohol (≈12 mmol) in DMSO (34 mL). After 3h, the reaction mixture was diluted with water and filtered. After extraction with diethyl ether, the combined organic layers was dried over $MgSO_4$, and filtered. The solvent was removed in vacuum, and the crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate, yield: 90 %) (Frigerio, *et al*. 2005).

To the solution *R*-2-Me-CBS-oxazaborolidine (821 mg, 1 mmol in 30 mL of THF) was added $BH_3.SMe_2$ (0.25 mL, 2 mmol) and the mixture was cooled to -30 °C temperature. $BH_3.SMe_2$ (0.5 mL, 4 mmol) reagent and the solution of enynone (**S23**) (≈5 mmol) in 5 mL THF were slowly added to the reaction mixture at the same time over a period of 2 h via a syringe. The reaction mixture was warmed to -20 °C and stirred for 6 h. After the reaction mixture was recooled to -30 °C, MeOH (≈15 mL) was added slowly. The solution was warmed to room temperature and stirred until the gas evolution complete. The reaction mixture was concentrated under a reduced pressure and the crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate, yield: 40 %) (Corey, *et al.* 1998). Enantiomeric purity was determined as 82.8% ee by GC method using a Hydodex-beta-3P column (25 m, 0.25 mm ID). $[\alpha]_D^{23}$= -0.33° (c= 0.242 g/100 mL, in CH_2Cl_2). Specific rotation was determined according to equation 3.1. Its hydroxyl group was modified to carbonate as described method.

$$[\alpha]_D^T = \frac{\text{Observed Rotation,}(\alpha)}{\text{Path length,1 (dm)} \times \text{Concentration of Sample, c (g/100mL)}} \qquad (3.1)$$

3.2.8. Synthesis of *(R,E)*-4-methyldec-3-en-5-yn-2-ol

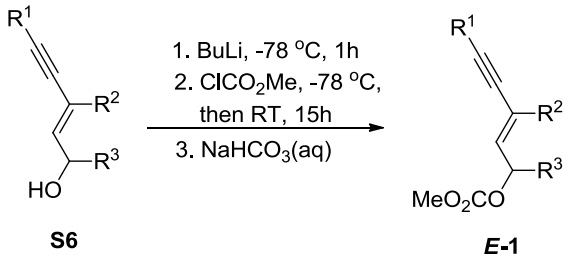
%70 TBHP in water (50 mL), and then toluene (60 mL) were added to a seperatory funnel (No shaking preferred). The aqueous layer was separated and the organic layer was transferred to a two-necked flask equipped with a Dean-Stark trap, a reflux condenser, and a thermometer. After addition of several boiling chips, the solution was refluxed at 90 °C under Ar until all water was collected. The solution of TBHP in toluene was stored over activated 4 Å molecular sieves (Hill, *et al*. 1993).

In order to determine TBHP concentration, 22 g of NaI was added into a flask containing 100 mL of isopropanol. The resulting solution was refluxed for ≈10 min, cooled to RT and filtered. 10 mL of sodium iodide-isopropanol solution was added to the solution of glacial acetic acid (2 mL) in isopropanol (25 mL). To this solution TBHP in toluene (0.2 mL) was added and refluxed for ≈1 min. Mixture was diluted with 100 mL of distilled water and immediately titrated with 0.1 N $Na_2S_2O_3$ untill disappearance of yellow iodine color. Concentration of TBHP was determined as 4.3 M using the equation 3.2 (Verhoeven, *et al*. 1979).

$$\text{M of TBHP} = \frac{\text{mL of Sodium thiosulphate used for titration} \times \text{Normality of Sodium thiosulphate}}{\text{mL of TBHP} \times 2} \quad (3.2)$$

Sharpless's kinetic resolution (Verhoeven, *et al*. 1979) method was employed for the preparation of (*R,E*)-4-methyldec-3-en-5-yn-2-ol. Accordingly, 6.4 mmol of $Ti(OiPr)_4$, and 7.7 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 6.4 mmol of racemic mixture of (*E*)-4-methyldec-3-en-5-yn-2-ol was added and then stirred for 30 min at -30 °C. Then, 12.8 mmol of dry *t*-butyl hydroperoxide (4.3 M in toluene) was added and left in a freezer (-20 °C) for 18.5 h. After completion, a pre-cooled (0 °C) 10.3 mL aqueous solution of 11.9 mmol $FeSO_4$ and 19.2 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 30 mL of Et_2O was added. The ethereal solution was cooled to 0 °C, and 30 mL of aqueous NaOH was added and stirred at this temperature for 1.5 h. Extraction with ether, drying with $MgSO_4$, and following column chromatography on silica gel using hexane/ethyl acetate eluent yielded the isolated product at 36%. Enantiomeric purity was determined as 98.9% ee by GC method using a Hydodex-beta-3P column (25 m, 0.25 mm ID). $[\alpha]_D^{23}$= 0.93° (c= 0.96 g/100 mL, $CHCl_3$). Specific rotation was determined according to equation 3.1. (Verhoeven, *et al.* 1979). Its hydroxyl group was modified to carbonate as described method.

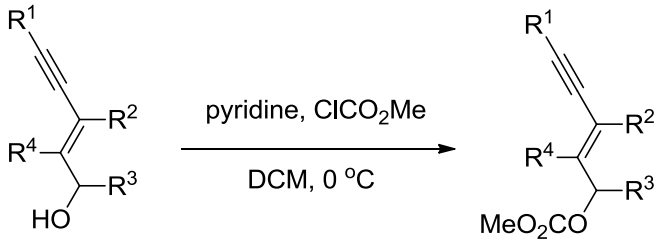
3.2.9. Typical Procedures for the Preparation of Enyne Carbonates



S6 ***E*-1**

Figure 3.9. Synthesis of *E*-Enyne Carbonates ***E*-1a-e, h, k-o**

An enyne alcohol (**S6a-e, h, k-o**) (8.945 mmol) was dissolved in 8 mL THF and was added 5 mL (10.74 mmol) *n*-BuLi at -78°C and the mixture was stirred for 1 h. Then 1.05 mL (13.4 mmol) of methyl chloroformate was added dropwise at -78°C. The solution was gradually warmed up to RT and stirred for 15 h. The reaction was quenched by the addition of a saturated $NaHCO_3$ solution and extracted with Et_2O and dried over $MgSO_4$. The solvents were evaporated under a vacuum to give an oily product, which was purified by column chromatography (silica gel, (hexane/NEt_3 (1 vol. %), yields: ***E*-1a**, 45%; ***E*-1b**, 55 %; ***E*-1c**, 50 %; ***E*-1d**, 50 %; ***E*-1e**, 52 %; ***E*-1h**, 60 %; ***E*-1k,** 60% ***E*-1l** , 55%; ***E*-1m**, 50%; ***E*-1n**, 60%***; E*-1o,** 50%) (Mandai, *et al.* 1994).



S6 ***E*-1**

Figure 3.10. Synthesis of *E*-Enyne Carbonates ***E*-1f-g, i-j**

In another method, an alcohol (**S6f-g, i-j**) (≈5.7 mmol) was dissolved in 72 mL DCM and was added 3.7 mL (45.69 mmol) of pyridine and the mixture was cooled to 0°C. 1.4 mL (17.1 mmol) of methyl chloroformate was added dropwise at -0 °C. The solution was stirred for 3 h. The reaction was quenched by the addition of water and extracted with DCM and dried over $MgSO_4$. The solvents were evaporated under a

vacuum to give an oily product, which was purified by column chromatography (silica gel, (hexane/NEt_3 (1 vol. %), yields: ***E*-1f**, 87%; ***E*-1g**, 88%; ***E*-1i**, %62; ***E*-1j**, 70%, **(*S*)-*E*-1j**, 70%) (Zhao, *et al*. 2012).

3.3. Characterization of Reactants

The synthesized reactants were analyzed by GC (Agilent/6990N) equipped with Thermo TR-5MS (30 m, 0.25mm ID) column, GC-MS (Thermo/ISQ) equipped with Thermo TR-5MS (30 m, 0.25mm ID) column 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 Bellingham Standley ADO 410 polarimeter. Enantiopure enyne alcohols were analyzed by GC (Shimadzu GC 2010).

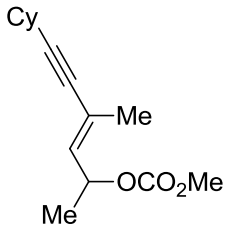


Figure 3.11. (*E*)-6-cyclohexyl-4-methylhex-3-en-5-yn-2-yl methyl carbonate

***E*-1a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.97 (dd, *J*=15.2, 1.6Hz, 1H), 5.67 (dq, *J*= 15.2, 6.8 Hz, 1H), 3.70 (s, 3H),2.39 (tt, *J* =11.6, 3.2Hz, 1H), 1.87(s, 3H), 1.83-1.63(m, 8H), 1.33(qt, *J*= 12.8,3.2Hz,2H),1.15(tt, *J*= 12.4-3.2Hz,1H), 1.00 dq, *J*=12.4,3.2Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.3, 133.7, 122.5, 93.6, 82.5, 71.7, 54.7, 32.8, 29.6, 26.0, 25.0, 20.5, 18.4; FTIR (ν_{max}/cm^{-1}): 3423, 2931, 2855, 2217, 1744, 1443, 1327, 1257, 1151, 1036, 939, 864, 791; MS (EI, *m/z*): 250 (4, M^+), 191 (45), 175 (36), 159 (29), 145 (24), 131 (54), 117 (42), 109 (100), 105 (74), 91 (93), 81 (44), 79 (47),77 (40), 55 (34) 43 (55). HRMS (EI, m/z, M^+): 250.1564 (calculated), 250.1557 (found).

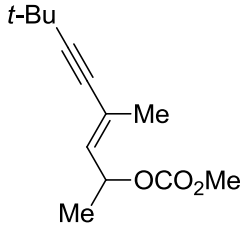


Figure 3.12. Methyl (*E*)-4,7,7-trimethyloct-3-en-5-yn-2-yl carbonate

***E*-1b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.66 (dd, *J*=9.2, 1.2Hz, 1H), 5.44 (dq, *J*= 9.2, 6.4 Hz, 1H), 3.75 (s, 3H), 1.87(s, 3H), 1.33(d, *J*= 6.4, Hz, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.3, 133.7, 122.5, 97.7, 81.0, 71.7, 54.7, 31.1, 27.9, 20.5, 18.4; FTIR (ν_{max}/cm^{-1}): 2969, 2929, 2902, 2868, 2205, 1744, 1442, 1327, 1255, 1150, 1038, 948, 938, 864, 791; MS (EI, *m/z*): 224 (6, M^+), 165 (98), 167 (23), 149 (53), 133 (74), 123 (32), 121 (41), 107 (54), 105 (100), 93(44), 91 (96), 79 (41), 77 (42), 43 (90). HRMS (EI, *m/z*, M^+): 224.14070 (calculated), 224.14027 (found).

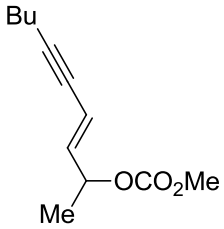


Figure 3.13. (*E*)-dec-3-en-5-yn-2-yl methyl carbonate

***E*-1c:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.98 (dd, *J*=16.0, 6.8Hz, 1H), 5.72 (d, *J*= 16Hz, 1H), 5.19 (quint, *J*= 6.8 Hz, 1H), 3.76 (s, 3H), 2.29 (t, *J*= 6.8Hz, 2H), 1.53- 1.39 (m, 4H), 1.36(d, *J*= 6.4Hz, 3H), 0.90 (t, *J*= 7.2Hz, 3H); ^{13}C NMR (101 MHz, $CDCl^3$) δ: 155.1, 139.6, 113.1, 92.6, 78.0, 74.6, 54.8, 30.8, 22.1, 20.2, 19.2, 13.7; FTIR (ν_{max}/cm^{-1}):2958, 2934, 2873, 2217, 1745, 1441, 1256, 1154, 1036, 942, 868, 791; MS (EI, *m/z*): 210 (2, M^+), 168 (8), 151 (66), 135 (34), 119 (11), 109 (27), 105 (22), 95 (61), 91 (100), 79 (52), 77 (38), 65 (33), 43 (67); HRMS (EI, *m/z*, M^+): 210.12505 (calculated), 210.12495 (found).

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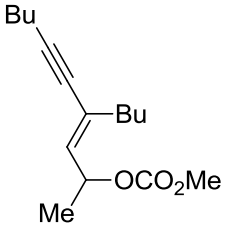


Figure 3.14. (*E*)-4-butyldec-3-en-5-yn-2-yl methyl carbonate

***E*-1d:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.66 (d, *J*= 8.8, 1H), 5.46 (dq, *J*=9.2, 6.4 Hz, 1H), 3.74 (s, 3H), 2.28(t, *J*= 6.8Hz, 2H), 1.52 – 1.31(m, 1H), 1.18 (t, *J*= 6.4Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.2, 133.5, 127.8, 90.2, 81.5, 71.4, 54.7, 31.5, 30.94, 30.75, 22.4, 22.1, 20.8, 19.1, 14.1, 13.7; FTIR (ν_{max}/cm^{-1}):2957,2932, 2862, 2219, 1744, 1441, 1259, 1151, 1036, 941, 866, 791; MS (EI, *m/z*): 266 (1, M^+), 207 (24), 191 (14), 161 (9), 148 (14), 119 (29), 105 (55), 91 (83), 77 (50), 55 (52), 43 (100); HRMS: (ESI, *m/z*, $(M+H)^+$): 267.19562 (calculated), 223.19547 (found).

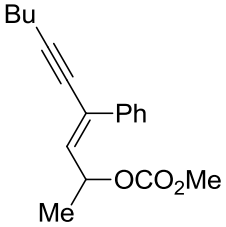


Figure 3.15.Methyl (*E*)-4-phenyldec-3-en-5-yn-2-yl carbonate

***E*-1e:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 -7.29 (m, 5H), 5.99 (d, *J*= 5.6Hz, 1H), 5.33 (dq, *J*= 9.6, 6.4Hz, 1H), 3.73 (s, 3H), 2.32(t, *J*= 7.2Hz, 2H), 1.55 -1.40 (m, 4H), 1.37(d, *J*= 6.8Hz, 3H), 0.91 (t, *J*= 7.4Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ: 154.9, 137.4, 135.1, 128.48, 128.43, 128.1, 127.3, 91.7, 81.5, 72.3, 54.7, 30.8, 22.1, 20.8, 19.2, 13.7; FTIR (ν_{max}/cm^{-1}):3019, 2957, 2933, 2873, 1744, 1442, 1258, 1154, 1029, 941, 866, 791, 772, 736, 699; MS (EI, *m/z*): 286 (2,M^+), 227 (25), 211 (20), 195 (18), 185 (14), 171 (23), 168 (51), 167 (39), 153 (35), 141 (24), 129 (22), 115 (21), 105 (8), 91 (22), 81 (21), 77 (13), 43 (100); HRMS: (ESI, *m/z*, $(M+H)^+$): 287.16473 (calculated), 287.16417 (found).

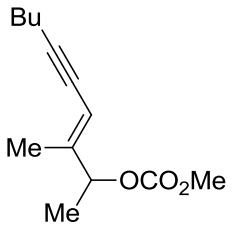


Figure 3.16. Methyl (*E*)-3-methyldec-3-en-5-yn-2-yl carbonate

***E*-1f:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.55 (s, 1H), 5.16 (q, *J*= 6.4 Hz,1H), 3.76 (s, 3H), 2.34 (td, *J*= 6.8,1.6 Hz, 2H), 1.87 (s, 3H), 1.54-1.48 (m, 2H), 1.47-1.40 (m, 2H), 1.36 (d, *J*=6.8Hz, 3H),0.92 (t, *J*= 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.1, 147.0, 107.9, 95.8, 77.9, 77.3, 54.8, 31.1, 22.1, 19.4, 19.2, 14.9, 13.7; FTIR (ν_{max}/cm^{-1}):2982, 2957, 2934, 2861, 2215, 1746, 1441, 1328, 1256,1067, 938, 871, 853, 791; MS (EI, *m/z*): 224 (4, M^+), 165 (31), 149 (15), 148 (12), 119 (13), 109 (25), 106 (37), 105 (50), 93(26), 91 (100), 79 (32), 77 (31), 43 (40); HRMS: (ESI, *m/z*, $(M+H)^+$): 225.14861 (calculated), 225.14852 (found).

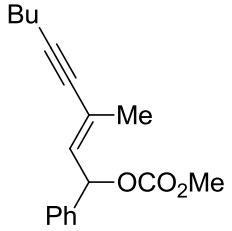


Figure 3.17. Methyl (*E*)-3-methyl-1-phenylnon-2-en-4-ynyl carbonate

***E*-1g:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, *J* =4.4Hz, 4H), 7.43-7.29(m, 1H), 6.34 (d, *J*= 9.2Hz, 1H), 5.93 (d, J= 9.2Hz, 1H), 3.77 (s, 3H), 2.28 (t, *J*= 7.2, Hz, 2H), 1.85 (s, 3H), 1.97 (d, *J*= 1.2Hz, 3H),1.53 - 1.44 (m, 2H),1.43- 1.35(m, 2H), 0.91 (t, *J*= 7.2Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ:155.2, 138.8, 132.2, 128.7, 128.3, 126.6, 123.1, 90.2, 82.4, 76.1, 54.8, 30.8, 22.0, 19.0, 18.5, 13.6; FTIR (ν_{max}/cm^{-1}):3085, 3059, 3028, 2957, 2931, 2872, 2215, 1746, 1440, 1311, 1255, 1217, 942, 907, 878, 789, 763, 696; MS (EI, *m/z*): 242 (16), 227 (31), 199 (38), 185 (34), 165 (37), 153 (36), 152 (42), 141 (36), 128 (30), 115 (36), 105 (100), 91 (86), 77 (97), 41 (51).

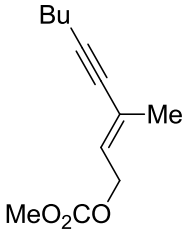


Figure 3.18. Methyl (*E*)-3-methylnon-2-en-4-ynyl carbonate

***E*-1h:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.83 (t, *J*= 7.2Hz, 1H), 4.67 (d, *J*= 7.2Hz, 2H), 3.77 (s, 3H), 2.29 (t, *J*= 6.8, Hz, 2H), 1.85 (s, 3H), 1.53 (quint, *J*= 7.2Hz, 2H), 1.41 (sext, *J*=7.2Hz, 2H), 0.91 (t, *J*= 7.2Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.8, 127.9, 124.9, 90.1, 82.5, 64.0, 55.0, 30.9, 22.1, 19.1, 18.2, 13.7; FTIR (ν_{max}/cm^{-1}):2958, 2933, 2873, 2219, 1748, 1442, 1378, 1329, 1254, 943, 791; MS (EI, *m/z*): 210 (2, M^+), 168 (16), 151 (22), 135 (30), 119 (8), 109 (16), 105 (20), 95 (71), 92 (100), 91 (71), 81(30), 79 (53), 77 (42); HRMS (EI, *m/z*, M^+): 210.12505 (calculated), 210.12565 (found).

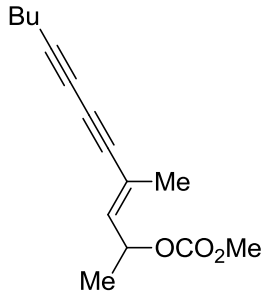


Figure 3.19. Methyl (*E*)-4-methyldodeca-3-en-5,7-diyn-2-yl carbonate

***E*-1i:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.86 (dq, *J*= 9.2, 1.6 Hz, 1H), 5.43 (dq, *J*= 9.2, 6.4 Hz, 1H), 3.76 (s, 3H), 2.32 (t, *J*= 6.4 Hz, 2H), 1.90 (d, 3H), 1.56-1.39 (m, 4H), 1.37 (d, J=6.4Hz, 3H), 0.91 (t, J= 7.2Hz, 3H); MS (EI, *m/z*): 248 (14, M^+), 206 (7), 189 (60), 173 (66),161 (13), 147 (33), 142 (22), 128 (47), 115 (49), 105 (37); 91 (66), 77 (41), 63 (19), 43 (100); HRMS: (ESI, *m/z*, $(M+H)^+$): 249.14850 (calculated), 249.14852 (found).

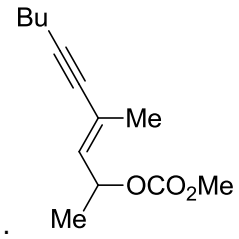


Figure 3.20. Methyl (*E*)-4-methyldec-3-en-5-yn-2-yl carbonate

***E*-1j:** ^{1}H NMR (400 MHz, C_6D_6) δ: 5.86 (dq, *J*= 9.2, 1.6 Hz 1H), 5.48 (dq, *J*= 8.8, 6.4 Hz, 1H), 3.31 (s, 3H), 2.10 (t, *J*= 6.8 Hz, 2H), 1.86 (d, *J*= 1.6 Hz, s, 3H), 1.37-1.24 (m, 4H), 1.10 (d, *J*= 6.8 Hz, 3H), 0.76 (t, *J*= 7.2 Hz, 3H); ^{13}C NMR: (101 MHz, C_6D_6): δ: 155.7, 134.6, 122.9, 89.6, 83.3, 71.3, 54.1, 31.1, 22.2, 20.3, 19.2, 18.4, 13.7; FTIR (ν_{max}/cm^{-1}): 2958, 2933, 2873, 2220, 1743, 1638, 1441, 1326, 1257, 1154, 1036, 939, 865, 792; MS (EI, *m/z*): 224 (6, M^+), 182 (9), 165 (70), 149 (50), 133 (19), 119 (41), 105 (77), 91 (100), 77 (53); HRMS: (ESI, *m/z*, $(M+H)^+$): 225.14873 (calculated), 225.14852 (found). ***(R,E)*-1j:** $[\alpha]_D^{23}$= 2.44° (c= 0.96g/100 mL, in $CHCl_3$). ***(S)-E*-1j:** $[\alpha]_D^{23}$= -2.12° (c= 0.93 g/100 mL, in CH_2Cl_2).

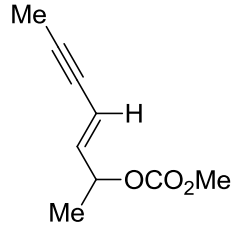


Figure 3.21. (*E*)-hept-3-en-5-yn-2-yl methyl carbonate

***E*-1k:** ^{1}H NMR (400 MHz, C_6D_6) δ: 5.99 (dd, J_{AB}= 15.6, 6.8 Hz, 1H), 5.67 (d, J_{AB}= 15.6 Hz, 1H), 5.15 (quint, *J*= 6.6 Hz, 1H), 3.73 (s, 3H), 1.90 (d, *J*= 1.6 Hz, 3H), 1.33 (d, *J*= 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ: 155.0, 139.6, 112.9, 87.9, 75.4, 54.7, 20.1, 4.3; FTIR (ν_{max}/cm^{-1}): 2984, 2958, 2920, 2854, 2223, 1743, 1638, 1441, 1255, 1036, 941, 871, 790; MS (EI, *m/z*): 168 (3, M^+), 153 (3), 109 (100), 91 (83), 77 (47).

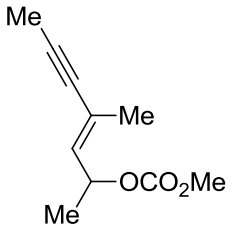


Figure 3.22. Methyl (*E*)-4-methylhept-3-en-5-yn-2-yl carbonate

***E*-1l:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.66 (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*= 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.3, 134.0, 122.4, 85.0, 81.7, 71.6, 54.7, 20.5, 18.2, 4.3; FTIR (ν_{max}/cm^{-1}): 2981, 2957, 2920, 2853, 2227, 1742, 1639, 1441, 1327, 1255, 1154, 1034, 938, 898, 864, 791; MS (EI, *m/z*):182 (13, M^+), 167 (5), 123 (100), 107 (84), 91 (99), 79 (62). HRMS (EI, m/z, M^+): 182.09375 (calculated), 182.09455 (found).

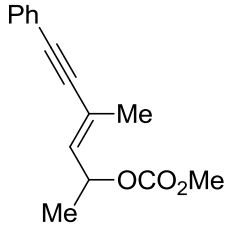


Figure 3.23. Methyl (*E*)-4-methyl-6-phenylhex-3-en-5-yn-2-yl carbonate

***E*-1m:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.45 (m, 2H), 7.28-7.33 (m, 3H), 5.87 (dq, *J*= 8.8, 1.2 Hz, 1H), 5.50 (dq, *J*= 8.8, 6.4 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, 131.7, 128.4, 123.3, 121.9, 91.3, 88.5, 71.6, 54.8, 20.4, 18.0; FTIR (ν_{max}/cm^{-1}): 3059, 2982, 2956, 2923, 1741, 1489, 1441, 1328, 1255, 1142, 1036, 942, 866, 754, 690; MS (EI, *m/z*): 244 (6, M^+), 185 (100), 167 (90), 153 (95), 152 (88), 141 (44), 128 (38), 115 (54), 102 (22), 91 (35), 77 (36). HRMS (EI, m/z, M^+): 244.10940 (calculated), 244.10998 (found).

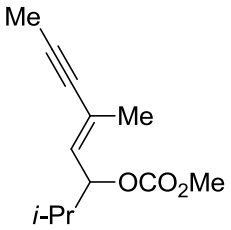


Figure 3.24. Methyl (*E*)-2,5-dimethyloct-4-en-6-yn-3-yl carbonate

***E*-1n:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.63 (d, *J*= 9.6 Hz, 1H), 5.07 (dd, *J*= 9.6, 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 (100 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; FTIR (ν_{max}/cm^{-1}): 2960, 2920, 2876, 2222, 1743, 1639, 1441, 1254, 966, 934, 791; MS (EI, *m/z*): 210 (9, M^+), 195 (3), 167 (100), 151 (85), 135 (41), 123 (42), 119 (92), 108 (71), 91 (82), 77 (59). HRMS (EI, m/z, M^+): 210.12505 (calculated), 210.10403 (found).

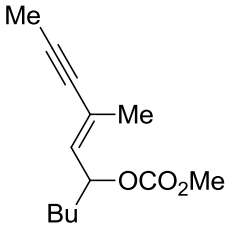


Figure 3.25. Methyl (*E*)-7-methyldec-6-en-8-yn-5-yl carbonate

***E*-1o:** ^{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; FTIR (ν_{max}/cm^{-1}): 2957, 2930, 2862, 2222, 1743, 1638, 1441, 1380, 1321, 1259, 1152, 1091, 1036, 933, 879, 866, 791;MS (EI, *m/z*): 224 (4, M^+), 167 (31), 148 (26), 133 (19), 123 (38), 119 (51), 105 (47), 91 (94), 77 (56). HRMS (EI, m/z, M^+): 224.1407 (calculated), 224.44375 (found).

3.4. General Procedure for Carbonylation Reactions

Method A:

The substrate, a palladium compound, ligand, and an alcohol (5 mL) were added, successively to a Schlenk apparatus 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 all vinylallene products appeared as colorless oil and coupling constants of olefinic protons and NOE studies confirm *E*-configured structures.

Method B:

A palladium compound, phosphine ligand and an alcohol (0.5 mL) were added, successively to a Schlenk apparatus that is attached to an Ar line and the mixture was stirred magnetically for a period of time. The substrate in an alcohol (1.2 mL) was added and a CO balloon was fixed to the reaction vessel and then, the mixture was stirred magnetically in a preheated oil bath.

For high pressure carbonylation reactions mixture of enyne, ligand, catalyst and alcohol (5 mL) 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. After cooling reactor, the reaction mixture was recovered with diethyl ether.

3.5. Characterization of Products

The synthesized reactants were analyzed by GC (Agilent/6990N) equipped with Thermo TR-5MS (30 m, 0.25mm ID) column, GC-MS (Thermo/ISQ) equipped with Thermo TR-5MS (30 m, 0.25mm ID) column 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 Bellingham Standley ADP 410 polarimeter. Enantiomeric purities were determined by HPLC (Agilent/1200).

For the calculation of amount of products, response factors were determined on GC using the equation (3.3). For this purpose dodecane was used as an internal standard.

$$\mathrm{RF} = \frac{\text{Area of internal standard} \times \text{Amount of compound}}{\text{Area of compound} \times \text{Amount of internal standard}} \qquad (3.3)$$

The equation (3.4) was used to calculate the amount of products.

$$\text{Amount of compound} = \frac{\text{Amount of internal standard}}{\text{Area of internal standard}} \times \text{R.F.} \times \text{Area of compound} \qquad (3.4)$$

^{1}H-NMR technique was also used for the quantitative analyses of products using *p*-anisaldehyde or toluene as internal standards (Equation 3.5).

$$\text{Amount of sample} = \text{amount of ISTD} \times \frac{\text{Amount of sample}}{\text{Area of ISTD}} \times \frac{\text{Number of H represented by the integral for the sample}}{\text{Number of H represented by the integral for ISTD}} \qquad (3.5)$$

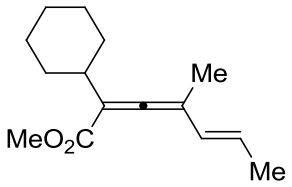


Figure 3.26. (*E*)-methyl 2-cyclohexyl-4-methylhepta-2,3,5-trienoate

2aa: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.97 (dd, *J*=15.2, 1.6Hz, 1H), 5.67 (dq, *J*= 15.2, 6.8 Hz, 1H), 3.69 (s, 3H),2.39 (tt, *J*= 11.6, 3.2Hz, 1H) 1.87(s, 3H), 1.83- 1.63(m, 8H), 1.33 (qt, *J*= 12.8, 3.2Hz, 2H) 1.15 (tt, *J*= 12.8, 3.6Hz, 1H), 1.01 (qd, *J*= 12.4, 3.2Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 211.4, 166.6, 126.2, 125.2, 104.7, 104.0,

51.0, 36.6, 32.0, 31.9, 25.5, 25.2, 17.5, 14.1; FTIR (ν_{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).

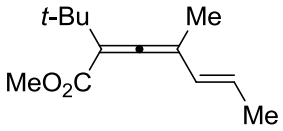


Figure 3.27. (*E*)-methyl 2-tert-butyl-4-methylhepta-2,3,5-trienoate

2ba: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.98 (dq, *J*=15.1, 1.6Hz, 1H), 5.66 (dq, *J*= 15.1, 6.8 Hz, 1H), 3.67 (s, 3H), 1.86 (s, 3H), 1.80 (dd, *J*= 6.8, 1.6 Hz, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 210.6, 166.0, 126.4, 125.0, 107.6, 102.9, 50.7, 33.3, 28.6, 17.5, 14.1; FTIR (ν_{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).

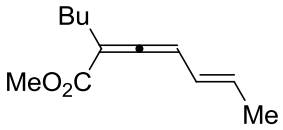


Figure 3.28. (*E*)-methyl 2-butylhepta-2,3,5-trienoate

2ca: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.15 (dt, *J*=10.0, 2.8Hz, 1H), 5.90- 5.84 (m, 1H), 5.76 (dq, *J*= 15.2, 6.4 Hz, 1H), 3.72 (s, 3H), 2.29- 2.23 (m, 2H), 1.78(d, *J*= 6.4Hz 3H), 1.45 -1.31 (m, 4H), 0.90 (t, *J*= 6.8Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 211.8, 166.6, 129.3, 123.1, 100.8, 96.8, 51.3, 29.3, 27.7, 21.3, 17.4, 13.0; FTIR (ν_{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).

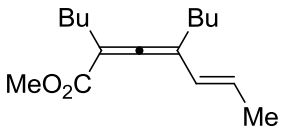


Figure 3.29. Methyl 2-butyl-4-(*E*)-prop-1-enyl)octa-2,3-dienoate

2da: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.90 (dd, *J*=15.6, 1.6Hz, 1H), 5.72 (dq, *J*= 14.8, 6.8 Hz, 1H), 3.70 (s, 3H), 1.79(dd, *J*=6.4, 1.6Hz, 3H), 2.27-2.18 (m, 4H), 1.47-1.30 (m, 8H), 0.90 (t, *J*= 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 212.6, 168.2, 126.5, 126.0, 108.9, 101.2, 52.1, 30.5, 29.8, 29.0, 28.7, 22.62, 22.47, 18.6, 14.1; FTIR (ν_{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).

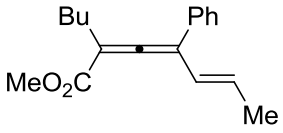


Figure 3.30. (*E*)-methyl 2-butyl-4-phenylhepta-2,3,5-trienoate

2ea: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 -7.34 (m, 4H), 7.31-7.27 (m, 1H), 6.12 (dd, *J*= 15.2, 1.6Hz, 1H), 5.86 (dq, *J*= 15.2, 6.8Hz, 1H), 3.75 (s, 3H), 2.37 (dq, *J*= 12.4, 7.6Hz, 2H), 1.85 (dd, *J*= 6.8, 1.6Hz, 3H), 1.51 -1.44 (m, 2H), 1.35(sext, *J*= 7.4Hz, 2H), 0.89 (t, *J*= 3.2Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 212.9, 167.7, 135.6, 130.6, 128.6, 127.9, 127.8,124.9, 111.3, 102.5, 52.3, 30.3, 29.1, 22.5, 18.7, 14.0; FTIR (ν_{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).

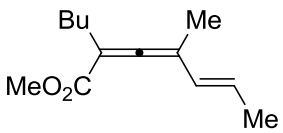


Figure 3.31. (*E*)-methyl 2-butyl-4-methylhepta-2,3,5-trienoate

2ja: ^{1}H NMR (400 MHz, C_6D_6): 6.03 (dd, *J*= 15.2, 1.6 Hz, 1H), 5.43 (dq, *J*= 15.2, 6.8 Hz, 1H), 3.42 (s, 3H), 2.46 (t, *J*= 8.0 Hz, 2H), 1.74 (s, 3H), 1.56-1.47 (m, 5H), 1.31 (sex, *J*= 7.2Hz 2H), 0.85 (t, *J*= 8.0 Hz, 3H); ^{13}C NMR: (100 MHz, C_6D_6) δ: 213.1, 167.5, 127.7, 126.0, 104.0, 100.2, 51.6, 30.8, 29.4, 22.6, 18.3, 15.0, 14.1; FT-IR(ν_{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).

(*R*)-2ja: The enantiomers of this product was separated on a Chiralpak IC column (0.46 cm/ 25 cm) with hexane:2-propanol= 99:0.5, flow= 1 mL/min. 59.4 ee% $[\alpha]_D^{27}$= -0.11° (c=1.22 g/100mL, in CH_2Cl_2)

(*S*)-2ja: The enantiomers of this product was separated on a Chiralcel OJ-H column (0.46 cm/ 25 cm) with hexane flow= 0.4 mL/min. 72.1 ee%. $[\alpha]_D^{23}$= 0.25° (c= 0.80g/100 mL), in $CHCl_3$)

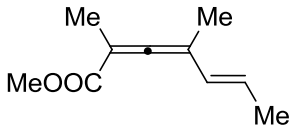


Figure 3.32. (*E*)-methyl 2,4-dimethylhepta-2,3,5-trienoate

2la: ^{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 (ν_{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).

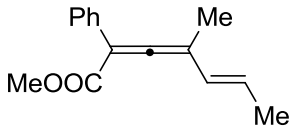


Figure 3.33. (*E*)-methyl 4-methyl-2-phenylhepta-2,3,5-trienoate

2ma: ^{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 (ν_{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).

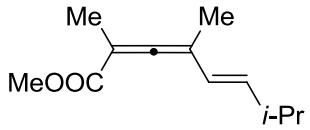


Figure 3.34. (*E*)-methyl 2,4,7-trimethylocta-2,3,5-trienoate

2na: ^{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 (ν_{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).

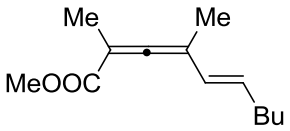


Figure 3.35. (*E*)-methyl 2,4-dimethyldeca-2,3,5-trienoate

2oa: ^{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(ν_{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).

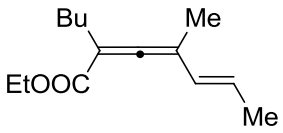


Figure 3.36. (*E*)-ethyl 2-butyl-4-methylhepta-2,3,5-trienoate

2jb: ^{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 (ν_{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).

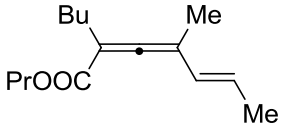


Figure 3.37. (*E*)-propyl 2-butyl-4-methylhepta-2,3,5-trienoate

2jc: ^{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 (ν_{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).

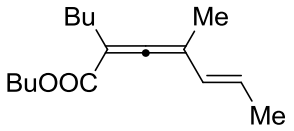


Figure 3.38. (*E*)-butyl 2-butyl-4-methylhepta-2,3,5-trienoate

2jd: ^{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 (ν_{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).

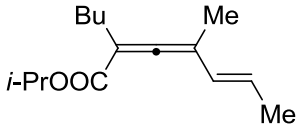


Figure 3.39. (*E*)-propyl 2-butyl-4-methylhepta-2,3,5-trienoate

2je: ^{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 (ν_{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).

CHAPTER 4

RESULTS AND DISCUSSION

It was demonstrated in this study the Pd(0)-catalyzed alkoxycarbonylation reaction of (*E*)-2-en-4-yne carbonates in an alcohol and under carbon monoxide atmosphere affords vinylallene esters. As judged from NMR studies, the reactions proceeded diastereoselectively to yield exclusively (*E*)-configured products (Figure 4.1).

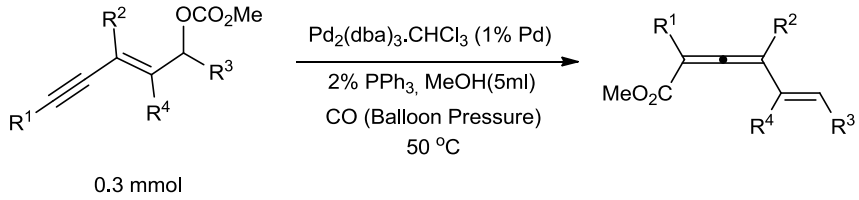
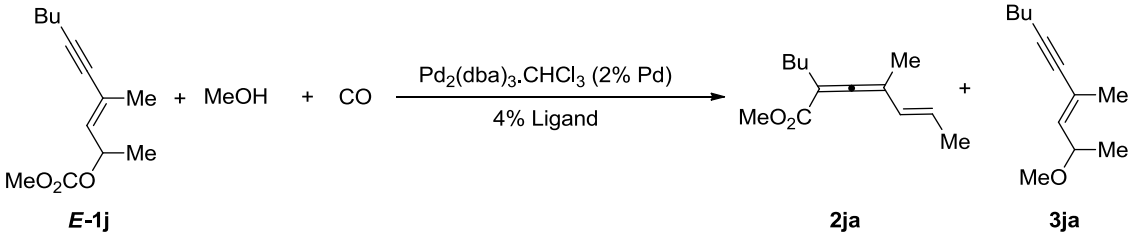


Figure 4.1. Pd(0)-catalyzed alkoxycarbonylation of *E*-enyne carbonates

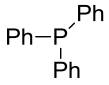
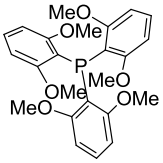
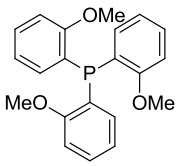
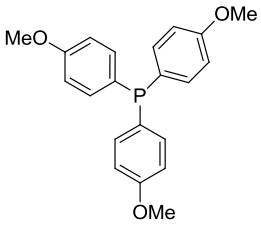
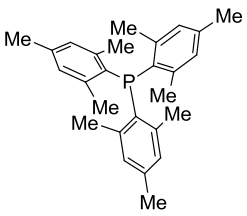
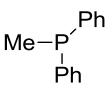
To optimize the reaction condition, various reaction conditions, such as reaction temperature, pressure of CO, type of ligand, amount of the catalyst and the ratio of catalyst to ligand were screened.

Palladium-catalyzed alkoxycarbonylation reactions of enyne carbonate (***E*-1j**) were performed by using various mono-dentate phosphine, phosphite and arsine ligands in the presence of $Pd_2(dba)_3.CHCl_3$ (2 mol% Pd)/ Ligand (4mol%) at RT under balloon atmosphere of CO (Table 4.1). Tris(2,6-dimethoxyphenyl)phosphine, tris(2-methoxyphenyl)phosphine, tris(4-methoxyphenyl)phosphine, triphenylphosphine and benzyldiphenylphosphine ligands exhibited high reactivities, ensuring the high yield of the vinylallene **2ja** formation with complete conversions (Table 4.1, entries 1,2,3,4,9). Diethylphosphite, diphenylphosphite, $Me(Ph)_2P$, $(4\text{-}CF_3C_6H_4)_3P$ and $(2\text{-}C_4H_3O)_3P$ ligands showed lower activities and their presence also led to formation of an S_N2 product **3ja** in low yields (Table 4.1, entries 6,7,8,10,12). Ligands including Ph_3As, Cy_3P, $(2,4,6\text{-}CH_3C_6H_2)_3P$ and (2-Biphenyl)di-*tert*-butylphosphine were ineffective for the alkoxycarbonylation reaction (Table 4.1, entries 5, 11,13,14,).

Table 4.1. Effect of Various Mono-dentate Ligands on Pd(0)-Catalyzed Alkoxycarbonylation Reactions of *E*-Enyne Carbonate ***E*-1j**[a]

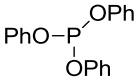
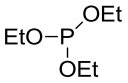
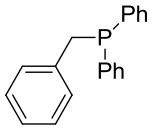
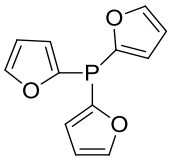
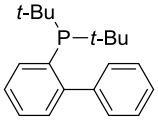
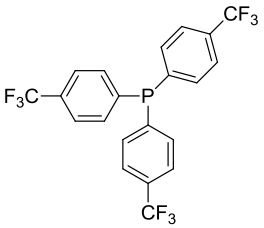
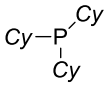
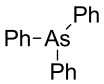


***E*-1j** **2ja** **3ja**

Entry	Ligand	Temperature(^{o}C)	Time(h)	**2ja** %	**3ja** %
1[b]		RT	7	93	-
2[b]		RT	5.5	91	-
3[d]		RT	5.5	93	-
4[d]		RT	23	93	-
5[c,d]		RT	23	Trace	-
6[c,e]		RT	23	41	4

(cont. on next page)

Table 4.1. (cont.)

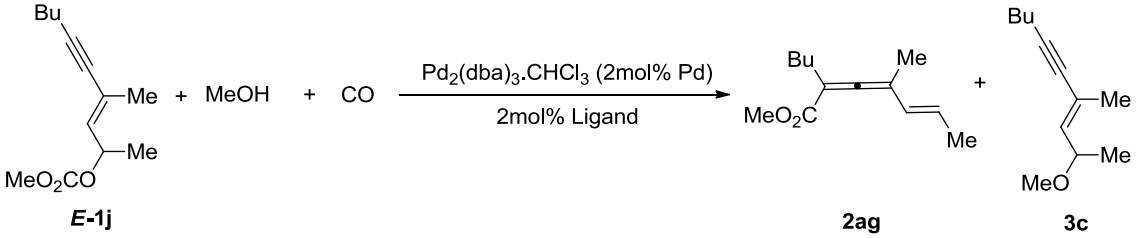
7[c,d]		RT	24	67	4
8[c,d]		RT	24	44	5
9[b]		RT	23	93	-
10[c,d]		RT	23	59	4
11[c,d]		RT	23	Trace	-
12[c,e]		RT	22	71	-
13[c,d]		RT	22	36	-
14[c,e]		RT	50	Trace	-

[a] Mehod A: ***E*-1j**: 0.3mmol, MeOH: 5mL, CO: balloon pressure [b] Isolated yield. [c] No complete conversion [d] Determined by NMR using *p*-anisaldehyde as an internal standard. [e] Determined by GC using dodecane as an internal standard.

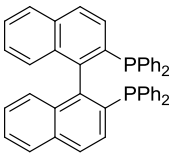
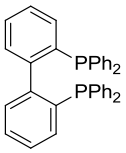
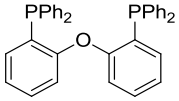
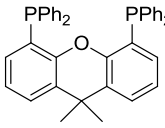
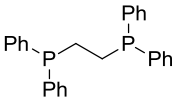
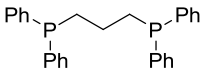
Palladium-catalyzed alkoxycarbonylation reactions were also carried out by using bi-dentate phosphine ligands. But only bis[(2-diphenylphosphino)phenyl] ether and xantphos ligands showed efficient activities to yield vinylallene with complete conversion (Table 4.2; entry 3,4). Other phosphine derivatives dppe and dppp showed lower activities to form the product **2ja** (Table 4.2; entries 5,6) and dppb, dppf, BiPhep and BINAP ligands were either non-active or showed very low activities (Table 4.2; entries 1,2,7,8). As judged from the reaction periods *ortho*-OMe substituted mono dentate phosphines (Table 4.2; entries 2,3) and Xanthphos and DPEphos (Table 4.2;

entries 3,4) ligands appear relatively more active ligands as compared to PPh_3. However PPh_3 were the choice of ligand for the further investigation of the method because of its lower cost.

Table 4.2 Effect of Various Bidentate Ligands on Pd(0)-Catalyzed Alkoxycarbonylation Reactions of *E*-Enyne Carbonate ***E*-1j**[a]

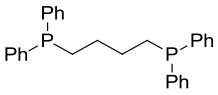
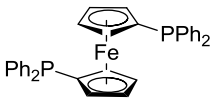


***E*-1j** **2ag** **3c**

Entry	Ligand	Temperature(°C)	Time(h)	**2ja** %	**3ja** %
1[c]		RT	31	Trace	-
2[c]		RT	28	Trace	14
3[b]		RT	5	93	-
4[b]		RT	4	93	-
5[c]		RT	25	64	-
6[c]		RT	26	42	13

(cont. on next page)

Table 4.2. (cont.)

7[c]		RT	26	16	8
8[c]		RT	24	30	9

[a] Method A: ***E*-1j**: 0.3mmol, MeOH: 5mL, CO: balloon pressure [b] Isolated yield. [c] No complete conversion [d.] Determined by NMR using *p*-anisaldehyde as an internal standart. [e] Determined by GC using dodecane as an internal standard.

The alkoxycarbonylation reaction was also applied to the enyne carbonate (***E*-1j**) in the presence of $Pd_2(dba)_3.CHCl_3$ (2mol% Pd(0)) and 4mol% 1,3-bis(2,6-di-*i*-propylphenyl)imidazol-2-ylidene catalytic system. However, the enyne alcohol **6ja** was formed instead of the desired carbonylative product without complete conversion.

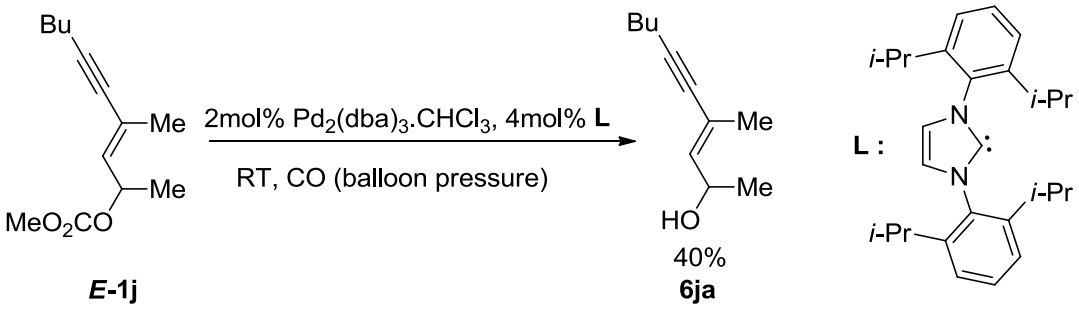
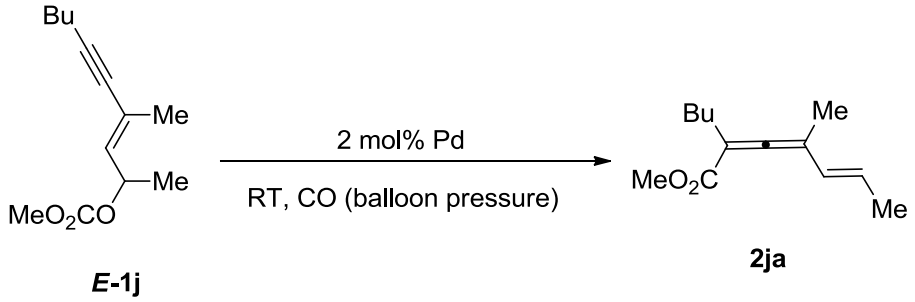


Figure 4.2. Pd(0)-catalyzed alkoxycarbonylation of *E*-enyne carbonates **(*E*-1j)** in the presence of NHC ligand

In the presence of tetrakistriphenylphosphinopalladium complex the alkoxycarbonylation reaction of *E*-enyne carbonate ***E*-1j** after 24h with methanol and carbon monoxide under balloon pressure at RT formed the vinylallene ester with an excellent yield (Table 4.3, entry 1). Using $Pd_2(dba)_3.CHCl_3$/ Ph_3P with a Pd/PPh_3 ratio of 1/2 decreased the reaction time to 7 hours for complete conversion. Decreasing the palladium to ligand ratio from 1/2 to 1/4 caused a decrease in the catalyst activity (Table 4.3, entries 2,3) Using $Pd_2(dba)_3.CHCl_3$/ Xantphos with a ratio of 1/1 also decreased the reaction time from 24 hours to 4 hours for complete conversion (Table 4.3, entries 4,5).

Table 4.3. Effect of Catalyst and Catalyst/Ligand Ratio on Pd(0)-Catalyzed Alkoxycarbonylation Reactions of *E*-Enyne Carbonates ***E*-1j**



***E*-1j** **2ja**

Entry	%2 mol Pd(0)	Ligand (mole %)	Yield (%)	Time (h)
1[d]	$Pd(PPh_3)_4$	-	94	24
2[b]	$Pd_2(dba)_3.CHCl_3$	PPh_3 (4)	93	7
3[c,d]	$Pd_2(dba)_3.CHCl_3$	PPh_3 (8)	26	7
4[b]	$Pd_2(dba)_3.CHCl_3$	Xantphos (2)	93	4
5[b]	$Pd_2(dba)_3.CHCl_3$	Xantphos (4)	93	24

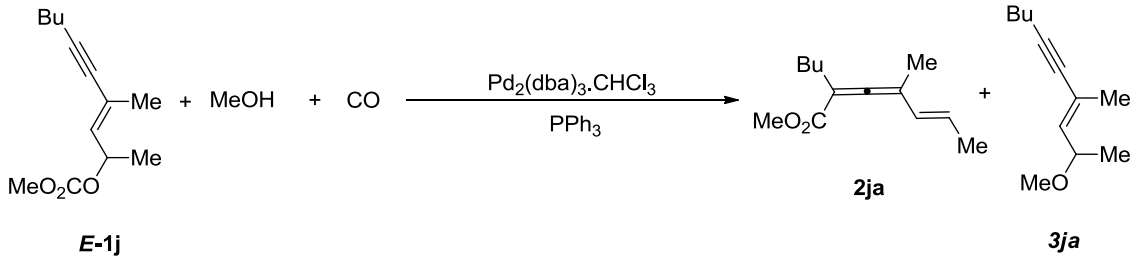
[a]Method A: ***E*-1j**: 0.3mmol, MeOH: 5mL, CO: balloon pressure [b] Isolated yield. [c] No complete conversion.[d] Determined by GC using dodecane as an internal standard.

The effect of reaction temperature was also investigated. The reaction achieved a complete conversion within 4h at elevated temperature (50 °C) in the presence of 1 mol% of Pd source and 2 mol% PPh_3 (Table 4.4, entry 2). At room temperature and in the presence of 2 mol% Pd source and 4 mol% PPh_3 the reaction resulted in to yield the vinylallene ester structure **2ja** within 7 hours (Table 4.4, entry 3). A complete conversion could be provided even at 10 °C of reaction temperature albeit at a prolonged reaction time (Table 4.4, entry 4). The conversion of enyne carbonate could not be complete at 0 °C of reaction temperature even at higher Pd loading 3% (Table 4.4, entry 6).

The alkoxycarbonylation reaction of *E*-2-en-4-yne carbonate ***E*-1j** in the presence of 0.25 mol% $Pd_2(dba)_3.CHCl_3$ and 2 equivalent of PPh_3 with respect to palladium gave vinylallene at a low yield 45% with complete conversion (Table 4.4, entry 1).

The application of higher CO pressure (10 Atm) seemed no effect on carbonylation reaction of ***E*-1j** (Table 4.4, entry 3,4).

Table 4.4.Effect of Amount of Pd/PPh_3 Catalyst system, CO Pressure and Temperature on Pd(0)-catalyzed Alkoxycarbonylation Reactions of *E*-Enyne Carbonates ***E*-1j**



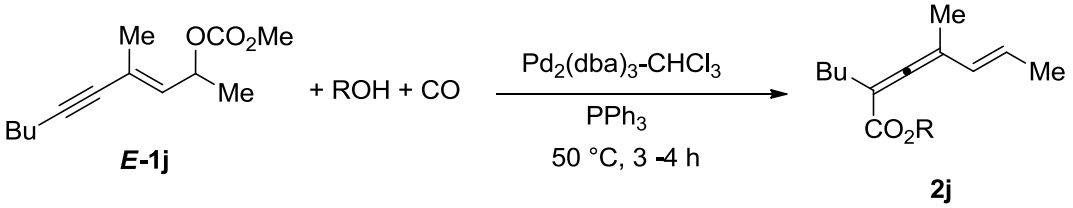
E*-1j** **2ja** ***3ja

Entry	$Pd_2(dba)_3$·CHCl (%mol Pd(0))	PPh_3	P_{CO} (Atm)	T(^oC)	**2ja** %	**3ja** %	Time (h)
1[d]	0.25 mol%	0.5 mol%	Balloon	50	45	12	24
2[b]	1 mol%	2 mol%	Balloon	50	90	-	4
3[b]	2 mol%	4 mol%	Balloon	RT	93	-	7
4[b]	2 mol%	4 mol%	Balloon	10	91	-	48
5[d]	2 mol%	4 mol%	10	RT	94	-	6
6[c]	3 mol%	6 mol%	Balloon	0	38	-	73

[a] Method A: ***E*-1j**: 0.3mmol, MeOH: 5mL [b] Isolated yield. [c] No complete conversion. Determined by GC using dodecane as an internal standard. [d]Determined by NMR with using *p*-anisaldehyde as internal standard.

The alkoxycarbonylation reaction of *E*-configured enyne carbonate ***E*-1j** in the presence of different alcohols formed ester functionalized allene derivatives **2ja-2je.** Although the alkoxycarbonylation of enyne carbonate ***E*-1j** in the presence of MeOH, EtOH, PrOH and BuOH formed desired allene esters just within 3-4 h in the range of 80-91% isolated yields (Table 4.5, Entries 1-4), a lower yield of 2,3,5-trienoate product **2je** could also be obtained with *i*-propyl alcohol after 6h (Table 4.5, Entry 5).

Table 4.5.Pd(0)-catalyzed alkoxycarbonylative reaction of ***E*-1j** with various alcohols[a,c]



Entry	ROH	Isolated yield (%)
1	MeOH	88 (**2ja**)
2	EtOH	81 (**2jb**)
3	PrOH	91 (**2jc**)
4	BuOH	80 (**2jd**)
5	*i*-PrOH	67 (**2je**)[b]

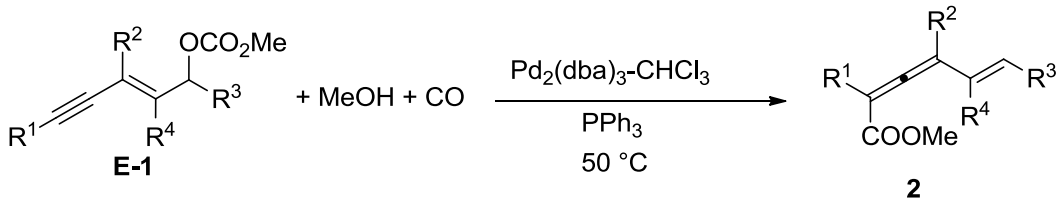
[a] Method A: ***E*-1j**: 0.3 mmol, ROH: 5 mL, CO: balloon pressure, 1 mol% Pd, 2 mol% PPh_3. [b] 6h h. [c] Akpinar G. E. master thesis iyte library P.S.N: QD505 .A315 2011

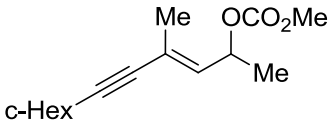
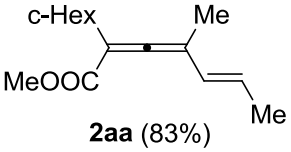
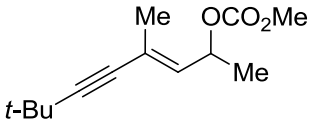
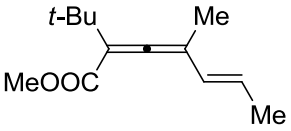
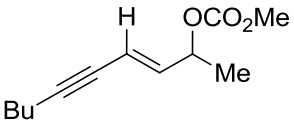
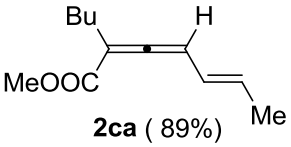
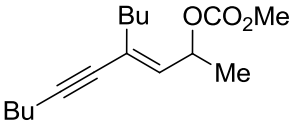
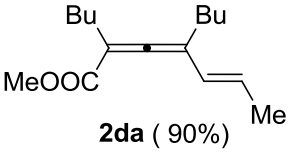
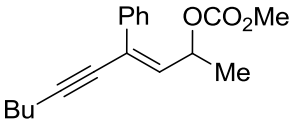
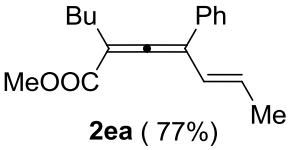
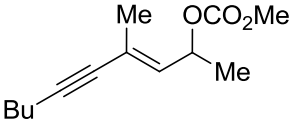
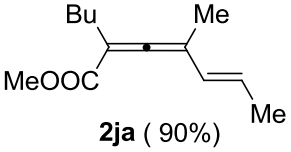
The scope of (*E*)-2-en-4-yne carbonates having different substituent groups on alkynyl, olefinic and allylic positions was surveyed. The methodology can tolerate the (*E*)-2-en-4-yne carbonates having butyl, phenyl, cyclohexyl and bulky tertiary butyl on its alkynyl terminus (R^1) in spite of the fact that the enyne carbonate bearing *tertiary* butyl and methyl group on its alkynyl position required 1h longer reaction period and gave the desired product with a moderate yield (Table 4.6, entries 1,2,6,8,9).

The enyne carbonates having hydrogen, butyl, and phenyl group on its olefinic position (R^2) were also reactive substrates toward Pd(0)-catalyzed alkoxycarbonylation reaction to lead to vinylallenyl esters (Table 4.6,entries 3,4,5,6). But the *E*-configured enyne carbonate ***E*-1l** having hydrogen on its olefinic position (R^2) and methyl group on its alkynyl terminus (R^1) led to a complex mixture (containing only small amounts of the desired vinylallenes) when subjected to the Pd(0)-catalyzed carbonylation reaction as determined by ^{1}H-NMR analysis (Table 4.6, entry 7).

The enyne carbonate ***E*-1n** bearing a isopropyl group on its allylic position (R^3) was tolerated to afford the desired product **2na** with high yield (Table 4.6, entry 10) in spite of the fact that enyne carbonate ***E*-1o** having butyl group on its allylic position required 1h longer reaction period and gave the desired product **2oa** (Table 4.6, entry 11).

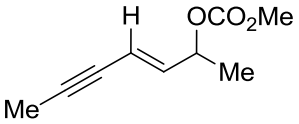
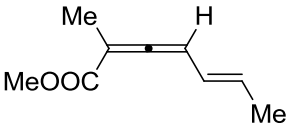
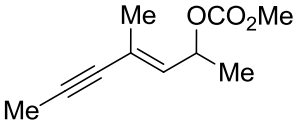
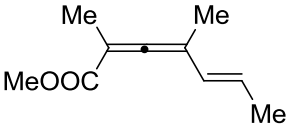
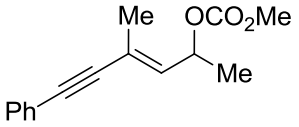
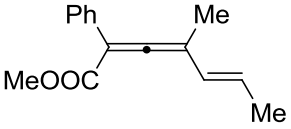
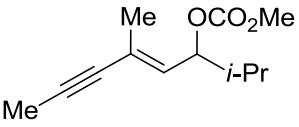
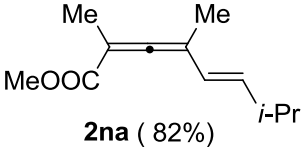
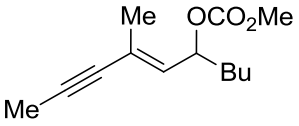
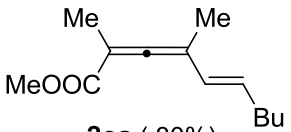
Table 4.6.Pd(0)-Catalyzed Alkoxycarbonylation Reactions of Various *E*-Enyne Carbonates [a]



Entry	Enyne carbonate	Time (h)	Product (yield)[b]
1[b]	 ***E*-1a**	4	 **2aa** (83%)
2[b]	 ***E*-1b**	5	 **2ba** (67%)
3[b]	 ***E*-1c**	4	 **2ca** (89%)
4[b]	 ***E*-1d**	5	 **2da** (90%)
5[b]	 ***E*-1e**	4	 **2ea** (77%)
6[b,c]	 ***E*-1j**	4	 **2ja** (90%)

(cont. on next page)

Table 4.6. (cont.)

7[b,c]	 ***E*-1k**	16	 **2ka** (20%)
8[b,c]	 ***E*-1l**	5	 **2la** (66%)
9[b,c]	 ***E*-1m**	4	 **2ma** (81%)
10[b,c]	 ***E*-1n**	4	 **2na** (82%)
11[b,c]	 ***E*-1o**	6	 **2oa** (80%)

[a] Method A: ***E*-1** 0.3 mmol, MeOH: 5 mL, CO: balloon pressure, 1 mol% Pd, 2 mol% PPh_3. [b] Isolated yield.[c] Akpinar G. E. master thesis iyte library P.S.N: QD505 .A315 2011

The (*E*)-2-en-4-yne carbonate (***E*-1f**) bearing hydrogen on its R^2 position and methyl on its olefinic position near the allylic carbon led, however to the mixture of allene structures under the optimum conditions (Figure 4.3).

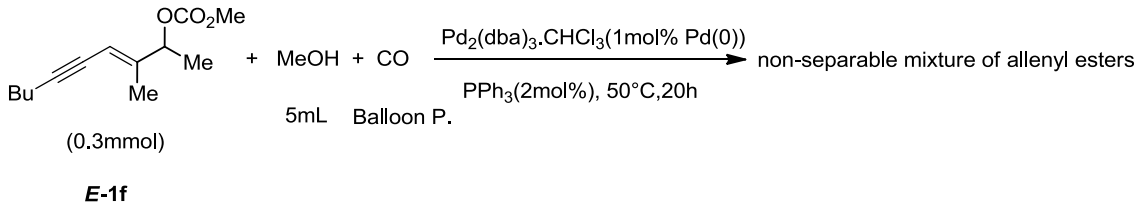


Figure 4.3. Pd(0)-catalyzed alkoxycarbonylation of *E*-enyne carbonate **(*E*-1f)**

The consequence of the allylic substitution on reactivity of enyne carbonate were also examined. It was observed that the reactivity of the enyne carbonates highly based on the nature of the allylic position. Unlike the enyne carbonates substituting a

methyl group on R^3 position, the phenyl substituted enyne carbonate (***E*-1g**) did not give the desired carbonylation product, rather produced a non-separable mixture of allylic methoxy substituted structures with 63% yield of an S_N2' and 21% yield of an S_N2 products (Figure 4.4).

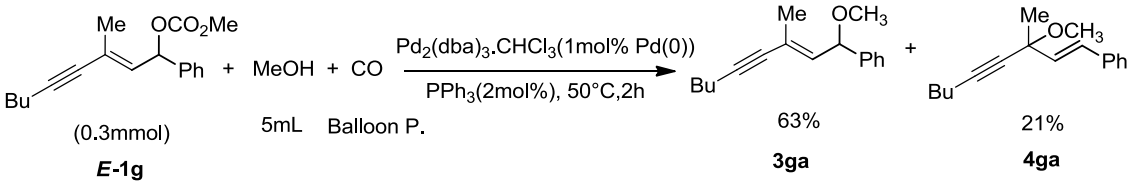


Figure 4.4. Pd(0)-catalyzed alkoxycarbonylation of *E*-enyne carbonate (***E*-1g**)

The alkoxycarbonylation reaction of a primary enyne carbonate (***E*-1h**) accompanied formation of a directly alkoxycarbonylated product **6ha** along with the expected allenyl product **2ha** without complete conversion (Figure 4.5).

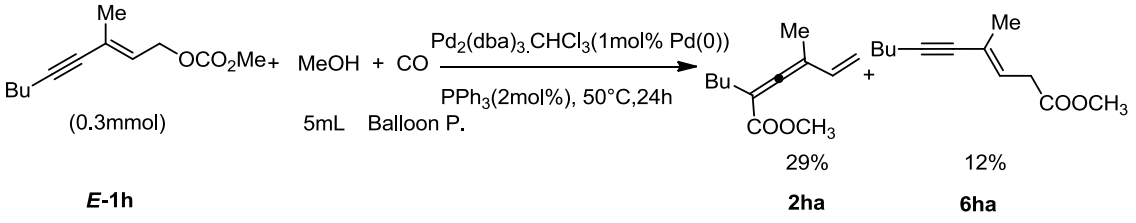


Figure 4.5. Pd(0)-catalyzed alkoxycarbonylation of *E*-enyne carbonate **(*E*-1h)**

The carbonylation reaction was also performed with the (*E*)-2-en-4,5-diyne carbonate (***E*-1i**), which led to form complex mixture without complete conversion (Figure 4.6).

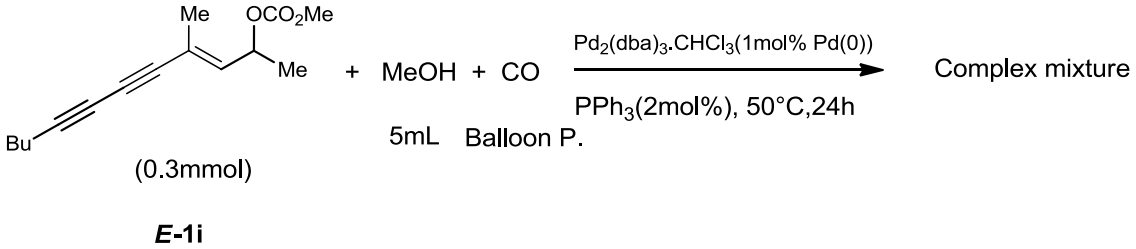


Figure 4.6. Pd(0)-catalyzed alkoxycarbonylation of *E*-endiyne carbonate (***E*-1i**)

The alkoxycarbonylation reaction pathway starts with *in-situ* formation of active Pd(0) species. The reaction pursues two possible pathways to form a σ-allenylpalladium intermediate **(B)**. First possible path includes oxidative addition of Pd(0) followed by decarboxylation to form allyl palladium intermediate **(A)**. A shift of Pd to far alkynyl carbon give the σ-allenylpalladium intermediate **(B)**. 1,5-S_N2'' type Pd(0)-substitution may also cause the formation of vinylallenylpalladium intermediate **(B)** The reaction cycle continues with insertion of CO to the Pd-carbon bond and reaction of alcohol. The cycle finalizes by a reductive elimination and regeneration of Pd(0) species.

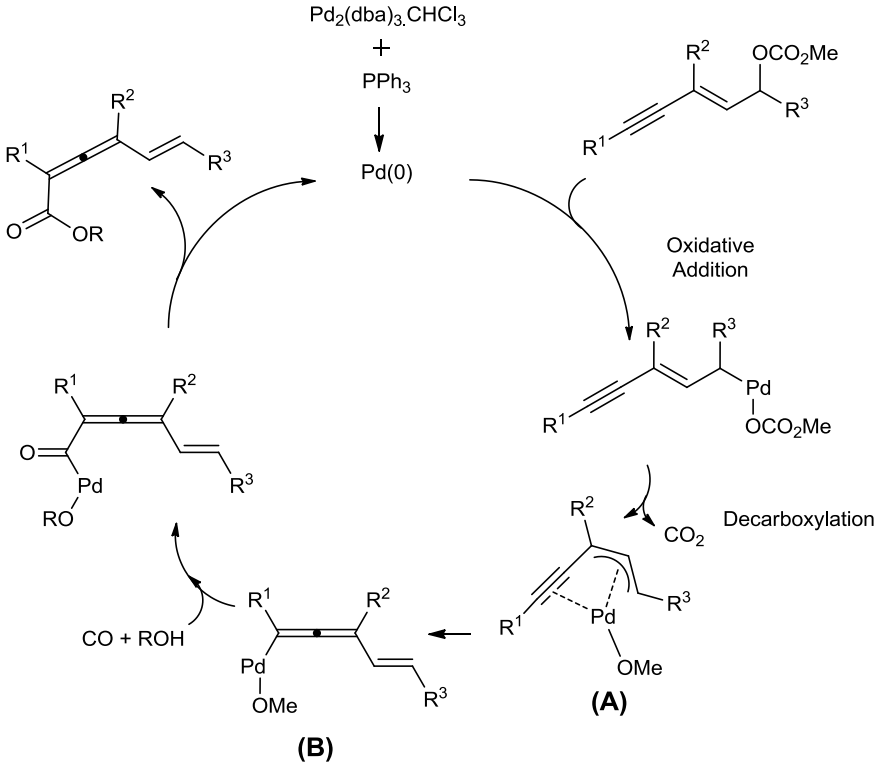
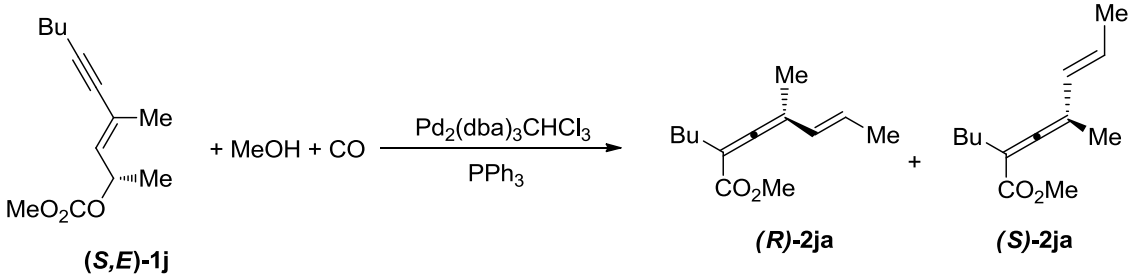


Figure 4.7. Proposed reaction mechanism of alkoxycarbonylation of (*E*)-enyne carbonates.

We also investigated possible chiral transfer characteristics of the method. The alkoxycarbonylation reaction of ***(S,E)*-1j** (82.8% ee) performed at 50 °C gave the allene ester structure with only 10.9 ee % (Table 4.7, entry 1). Decreasing the reaction temperature from 50 °C to room temperature resulted slight increase in enantiopurity of allene to 12% (Table 4.7, entry 2). Also, the alkoxycarbonylation reaction of ***(S,E)*-1j** at 10 °C showed slight effect on the order of chirality transfer (Table 4.7 entry 4). Mixing first the Pd compound and the triphenylphosphine ligand in MeOH about 10 min at RT

prior to the addition of the substrate had slight effect on the enantioselectivity of the process (Table 4.7, entry 3).

Table 4.7. Pd(0)-Catalyzed Alkoxycarbonylation Reactions of *E*-Enyne Carbonate **(*S,E*)-1j** at Different Reaction Temperatures [a]

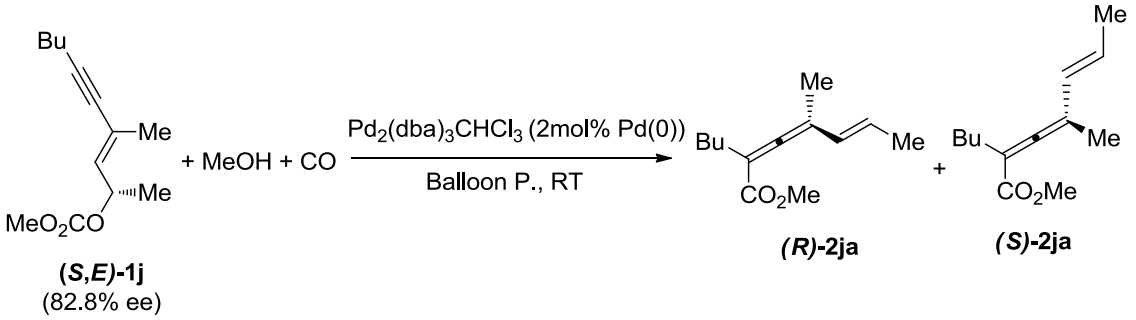


Entry	$Pd_2(dba)_3.CHCl_3$ Pd(0) %	PPh_3	T(^oC)	Time (h)	ee (%)	Yield (%)
1[b]	1mol%	2mol%	50	4	10.9	90
2[b]	2mol%	4mol%	RT	9	12	93
3[b,c]	2mol%	4mol%	RT	9	17.1	91
4[b]	2mol%	4mol%	10	46	14.4	91

[a] Method A: **(*S, E*)-1j**: 0.1mmol, MeOH: 1.7 mL, CO: balloon pressure [b] Isolated yield [c] Method B: **(*S, E*)-1j**: 0.1mmol, MeOH: 1.7 mL, CO: balloon pressure. Pd(0) formed by mixing $Pd_2(dba)_3.CHCl_3$ and PPh_3 in methanol (0.5 mL) for10 min and then reactant (0.1 mmol) in methanol (1.2 mL) was added.

The effect of phosphine ligands on the stereosectivity of the Pd(0)-catalyzed-alkoxycarbonylation of the enantiomerically enriched enyne carbonate was also demonstrated. The **(*S,E*)-1j** did not undergo the carbonylation reaction with *R*-Segphos (Table 4.8, entry 6). Although using tris(2,6-dimethoxyphenyl)phosphine in the alkoxycarbonylation reaction gave almost racemic vinylallene ester structures, using tris(2-methoxyphenyl)phosphine slightly affected the chirality transfer (Table 4.8, entry 2,3). A bidentate ligand xantphos and tetrakistriphenylphosphinopalladium were superior to tris(2,6-dimethoxyphenyl)phosphine and tris(2-methoxyphenyl)phosphine and PPh_3 ligands (Table 4.8, entry 3,5). Using 4/1 ratio of P/Pd and mixing first the Pd compound and the Xantphos ligand in MeOH about 10 min at RT prior to the addition of the substrate caused increase in the enantioselectivity of the process (Table 4.8, entry 4).

Table 4.8. Pd(0)-catalyzed Alkoxycarbonylation Reactions of (*E*)-Enyne Carbonate ***(S,E)*-1j** with Different Ligands[a]



Entry	Palladium (Pd(0)%)	Ligand(%)	Time(h)	ee (%)	**2ja**%
1[b]	$Pd_2(dba)_3.CHCl_3$(2 mol%)	Tris(2,6-dimethoxyphenyl)phosphine (4 mol %)	6	6.7	91
2[b]	$Pd_2(dba)_3.CHCl_3$(2 mol%)	Tris(2-methoxyphenyl)phosphine (4 mol%)	6	12.1	93
3[b]	$Pd_2(dba)_3.CHCl_3$(2 mol%)	Xantphos (2 mol%)	4.5	44	91
4[b,d]	$Pd_2(dba)_3.CHCl_3$(2 mol%)	Xantphos (4 mol%)	17	59.4	93
5[b]	$Pd(PPh_3)_4$ (2 mol%)	-	40	41.6	91
6[c]	$Pd_2(dba)_3.CHCl_3$(2 mol%)	(*R*)-Segphos (4 mol%)	72	-	-

[a] Method A: **(*S,E*)-1j**: 0.1mmol, MeOH: 1.7 mL, Ballon pressure CO [b] Isolated yield. [c] Not complete conversion.Determined by NMR with using *p*-anisaldehyde as internal standard. [d] Method B: **(*S,E*)-1j**: 0.1mmol, MeOH: 1.7 mL, Ballon pressure CO. Pd(0) formed by mixing Pd source and ligand in 0.5 mL MeOH for 10 min and then reactant in methanol (1.2 mL) was added.

S,S-Chiraphos ligand, however, ligand led to the formation of a nonseperable mixture of trace amount of allene 2ja and (*E*)-2-methoxy-4-methyldec-3-en-5-yne **3ja** and (*E*)-4-methoxy-4-methyldec-2-en-5-yne **3jb** (Figure 4.8).

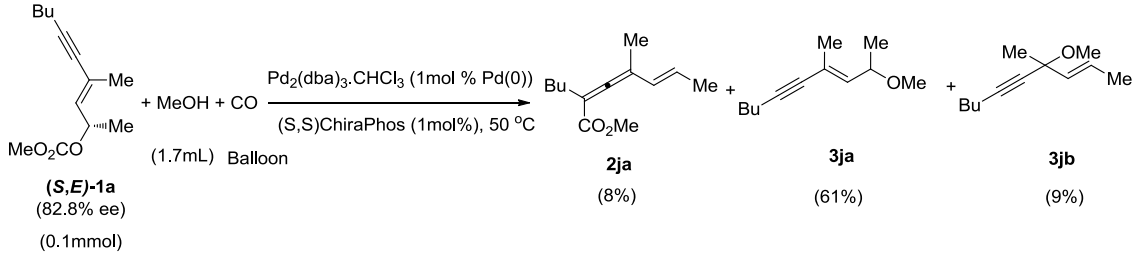
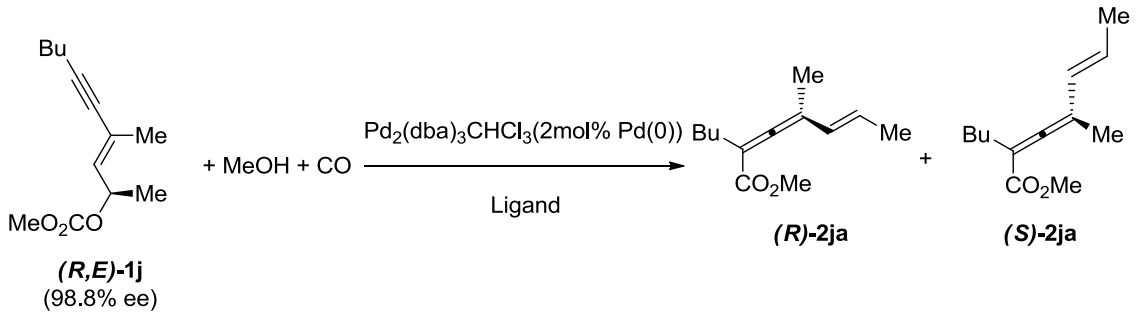


Figure 4.8. Pd(0)-catalyzed Alkoxycarbonylation Reactions of *E*-Enyne Carbonate **(*S,E*)-1j** with *S,S*-Chiraphos

Using 4/1 ratio of P/Pd and mixing first the Pd compound and the PPh_3 and tris *para*-trifluoromethylphenylphosphine ligands in MeOH about 1h at RT under Ar prior to the addition of the substrate (*E)*-enyne carbonate **(*R,E)*-1j** having 98.8% enantiopurity formed vinylallene **2ja** having almost same enantiopurity, even though the reaction of **(*R,E)*-1j** in the presence of tris*para*-trifluoromethylphenylphosphine did not give complete convertion (Table 4.9 entries 3,4). Using xantphos showed an increase in chirality transfer and resulted to form 61% ee allene (Table 4.9 entries 1).

Table 4.9. Pd(0)-Catalyzed Alkoxycarbonylation Reactions of *(E)*-Enyne Carbonate ***(R,E)*-1j** with Different Ligands[a]



Entry	Ligand	T(^{o}C)	Time (h)	ee (%)	Yield (%)
1[b]	4mol% Xantphos	RT	27	61.7	93
2[b]	4mol% DPEphos	RT	4	72.1	90
3[b,c,d]	8mol% P(4-$CF_3C_6H_4)_3$	RT	25	58.2	56
4[b]	8mol% PPh_3	RT	20	54.3	90

[a] Method B: **(*R,E)*-1j**: 0.1mmol, MeOH: 1.7 mL, CO: balloon pressure. Pd(0) formed by mixing $Pd_2(dba)_3.CHCl_3$ and ligand in metanol (0.5 mL) for 1h and then reactant in methanol (1.2 mL) was added. [b] Isolated yield.[c] No complete conversion. 31% of reactant was in reaction medium. [d]Determined by NMR with using toluene as internal standard.

The alkoxycarbonylation of (*R,E*)-1j in the presence of DPEphos showed superiority compared to the other phosphine ligands used giving 72% enantiomerically enriched vinylallene **(*S*)-2aj** that is an anti product (Figure 4.9).

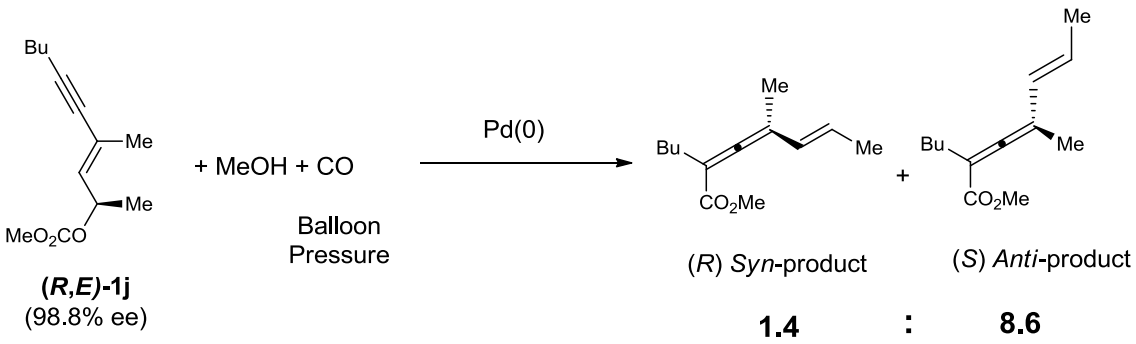


Figure 4.9. Pd(0)-catalyzed Alkoxycarbonylation Reactions of Enyne Carbonate **(*R,E*)-1j** with DPEphos

The investigations showed that the chirality transfer is severely dependent on the nature of the ligand used in the alkoxycarbonylation reactions. The reason for this dependence could be alteration in the rates of oxidative addition, CO insertion and reductive elimination steps that can be excuse for the isomerization of π-allylpalladium intermediate.

CHAPTER 5

CONCLUSION

In this study the palladium-catalyzed alkoxycarbonylation reactions of (*E*)-2-en-4-yne carbonate derivatives which led to the ester funtionalized vinylallene products was described.

The optimization studies showed that the palladium-catalyzed alkoxycarbonylation reactions could be performed in the presence of triphenylphosphine, xantphos, tris(2-methoxyphenyl)phosphine, tris(2,6-dimethoxyphenyl)phosphine and DPEphos ligands upon using 2/1 ratio of P/Pd. The coordinatively saturation of palladium with phosphines rendered the decrease of the catalyst activity.

The reaction could be performed successfully under balloon atmosphere of CO. That the application of higher CO pressures did not influence the reaction activity may imply that CO insertion is not a rate determining step of the overall reaction cycle.

Chirality transfer ability of the method was found to be partial. The highest ee% (app. 72%) of the product, so far, could be obtained when reacting an enantio-enriched enyne carbonate by using DPEphos ligand with a P/Pd ratio of 4.

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APPENDIX A

^{1}H NMR and ^{13}C NMR SPECTRUMS OF REACTANTS

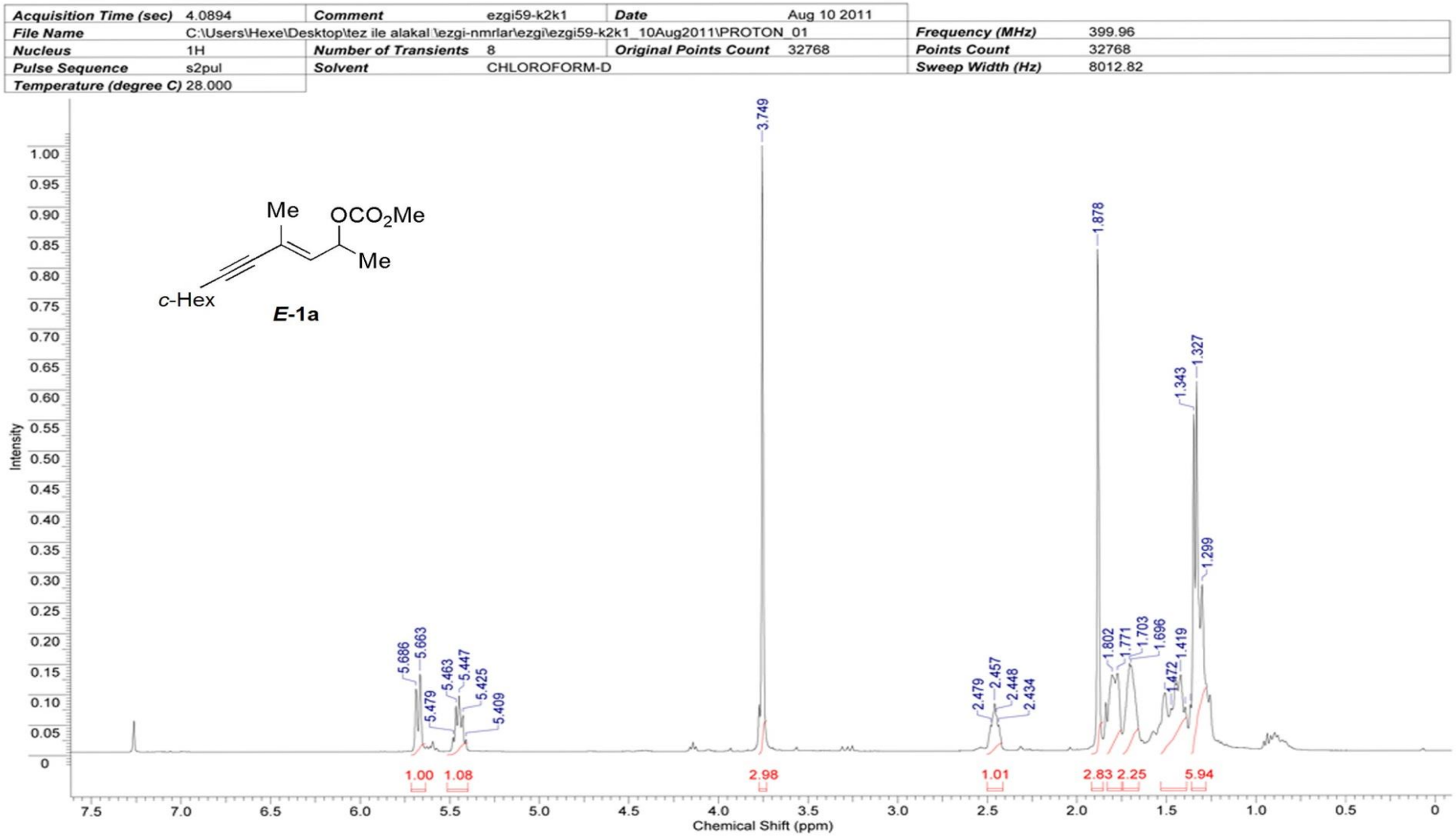

Figure A.1. [1] H NMR of (*E*)-6-cyclohexyl-4-methylhex-3-en-5-yn-2-yl methyl carbonate

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File Name	C:\Users\Hexe\Desktop\tez ile alakal\ezgi-nmrlar\ezgi\ezgi59_03Aug2011\CARBON_01					***Frequency (MHz)***	100.58
Nucleus	13C	***Number of Transients***	256	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	25510.20
Temperature (degree C)	26.000						

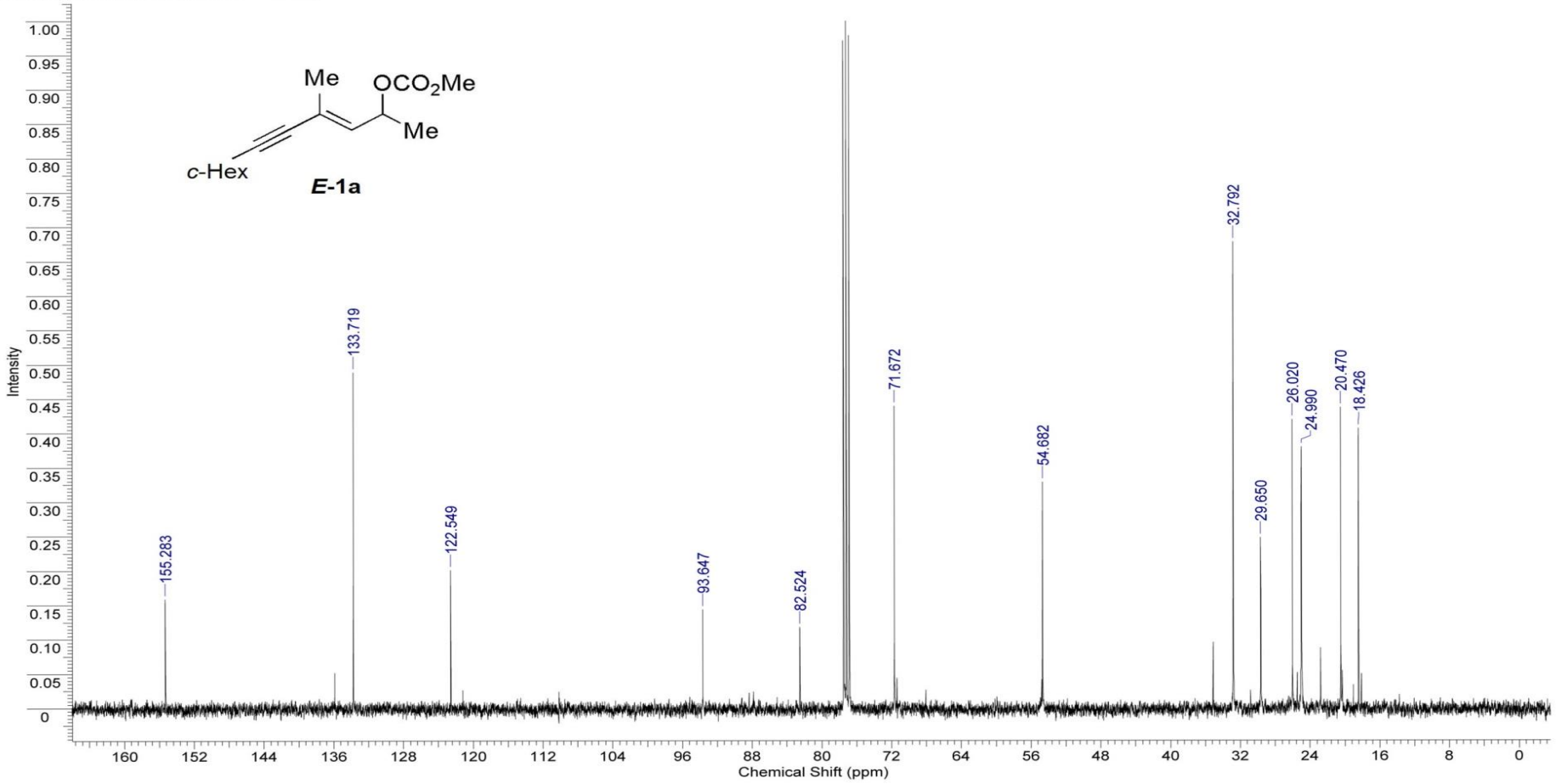

Figure A.2. ^{13}C NMR of (*E*)-6-cyclohexyl-4-methylhex-3-en-5-yn-2-yl methyl carbonate

Acquisition Time (sec)	4.0894	***Comment***	ezgi-76	***Date***	Oct 5 2011		
File Name	C:\Users\Hexe\Desktop\tez ile alakalı\ezgi-nmrlar\ezgi\ezgi-76_05Oct2011\PROTON_01					***Frequency (MHz)***	399.96
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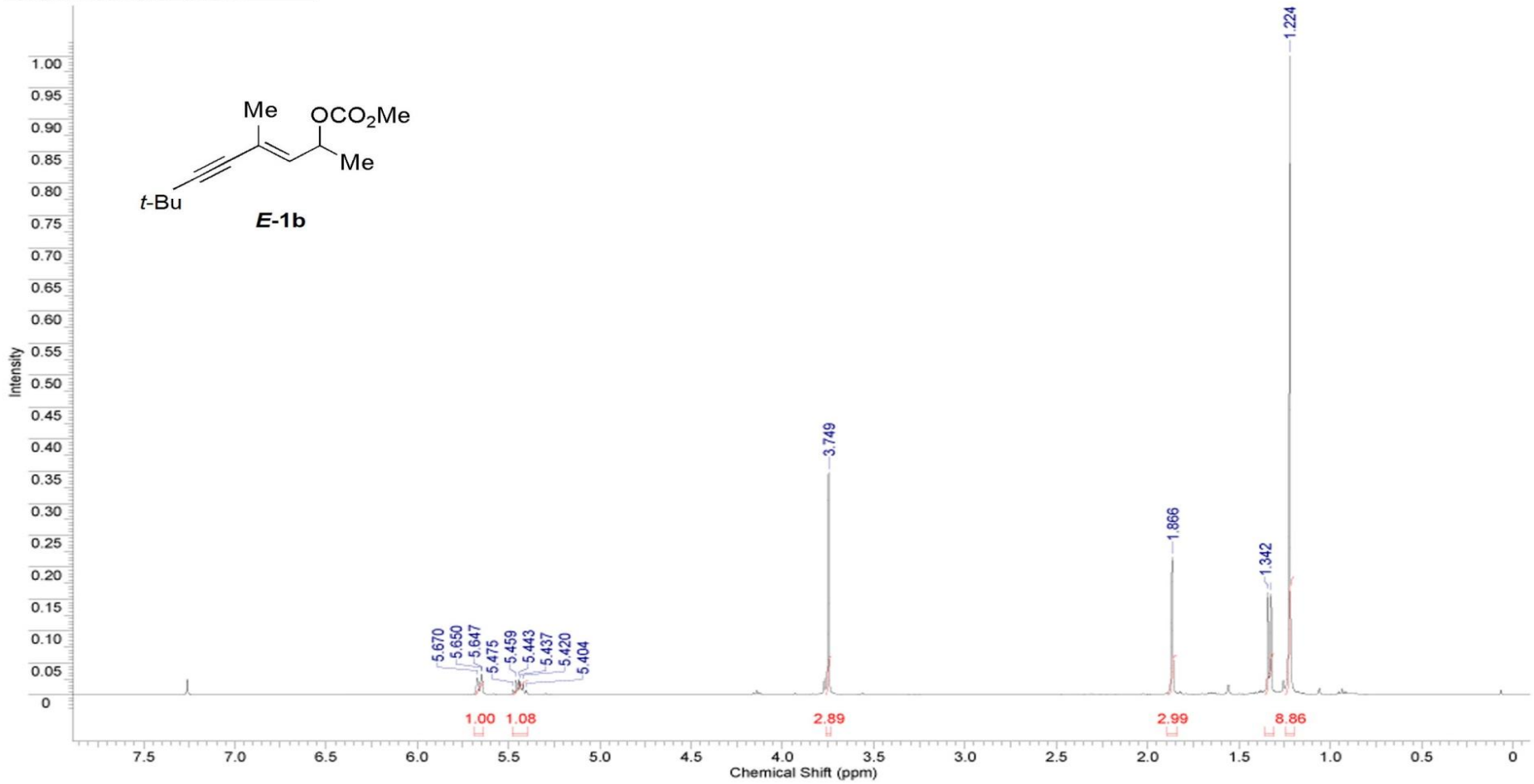

Figure A.3. ^{1}H NMR of (*E*)-methyl (4,7,7-trimethyloct-3-en-5-yn-2-yl) carbonate

Acquisition Time (sec)	1.2845	**Comment**	ezgi-76	**Date**	Oct 5 2011		
File Name	C:\Users\Hexe\Desktop\tez ile alakal\ezgi-nmrlar\ezgi\ezgi-76_05Oct2011\CARBON_01					**Frequency (MHz)**	100.58
Nucleus	13C	**Number of Transients**	256	**Original Points Count**	32768	**Points Count**	32768
Pulse Sequence	s2pul	**Solvent**	CHLOROFORM-D			**Sweep Width (Hz)**	25510.20
Temperature (degree C)	25.000						

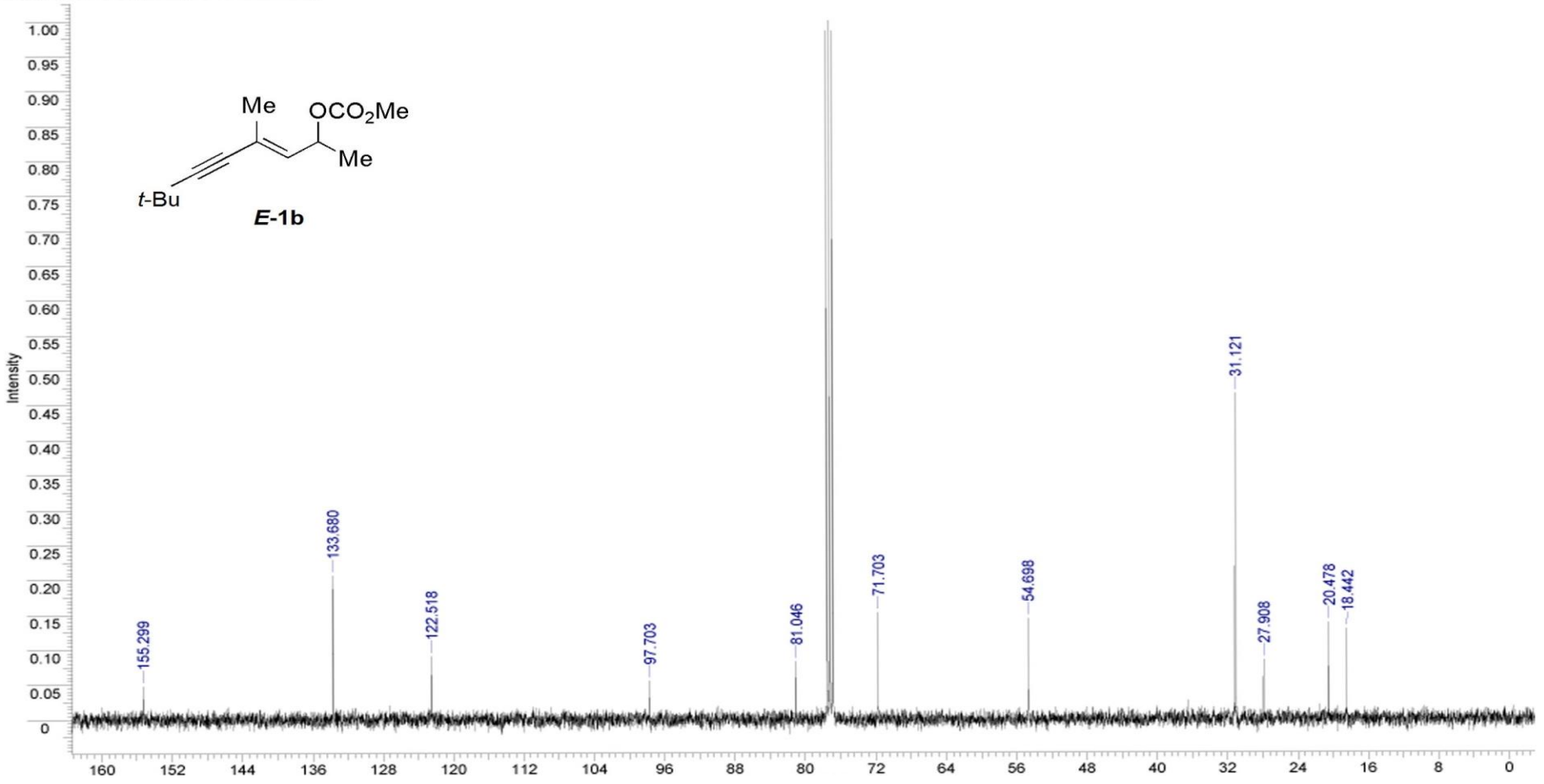

Figure A.4. ^{13}C NMR of (*E*)-methyl (4,7,7-trimethyloct-3-en-5-yn-2-yl) carbonate

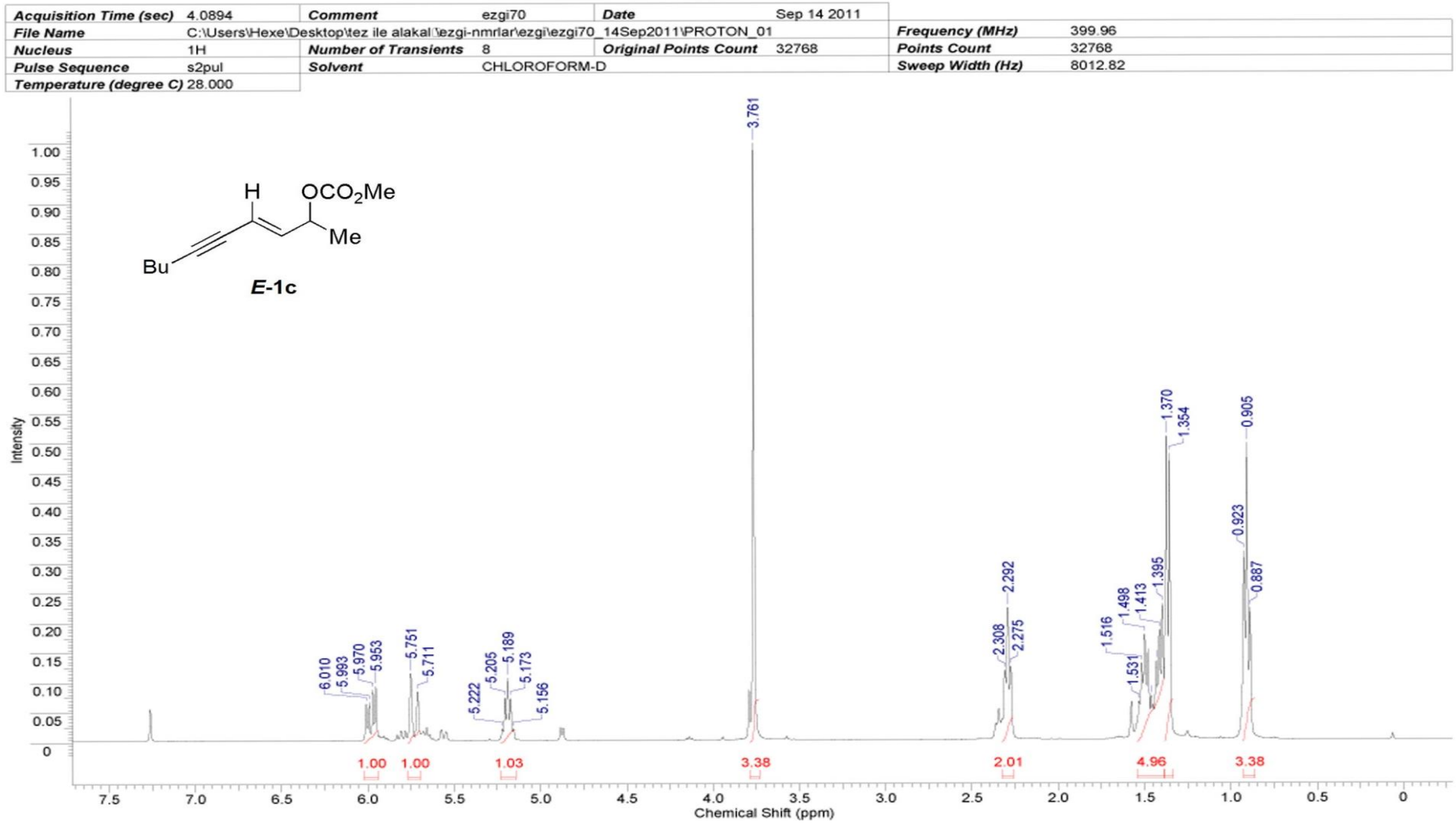

Figure A.5. ^{1}H NMR of (*E*)-dec-3-en-5-yn-2-yl methyl carbonate

Acquisition Time (sec)	1.2845	***Comment***	ezgi70	***Date***	Aug 23 2011		
File Name	C:\Users\Hexe\Desktop\tez ile alakal\ezgi-nmrlar\ezgi\ezgi70_23Aug2011\CARBON_01					***Frequency (MHz)***	100.58
Nucleus	13C	***Number of Transients***	256	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	25510.20
Temperature (degree C)	28.000						

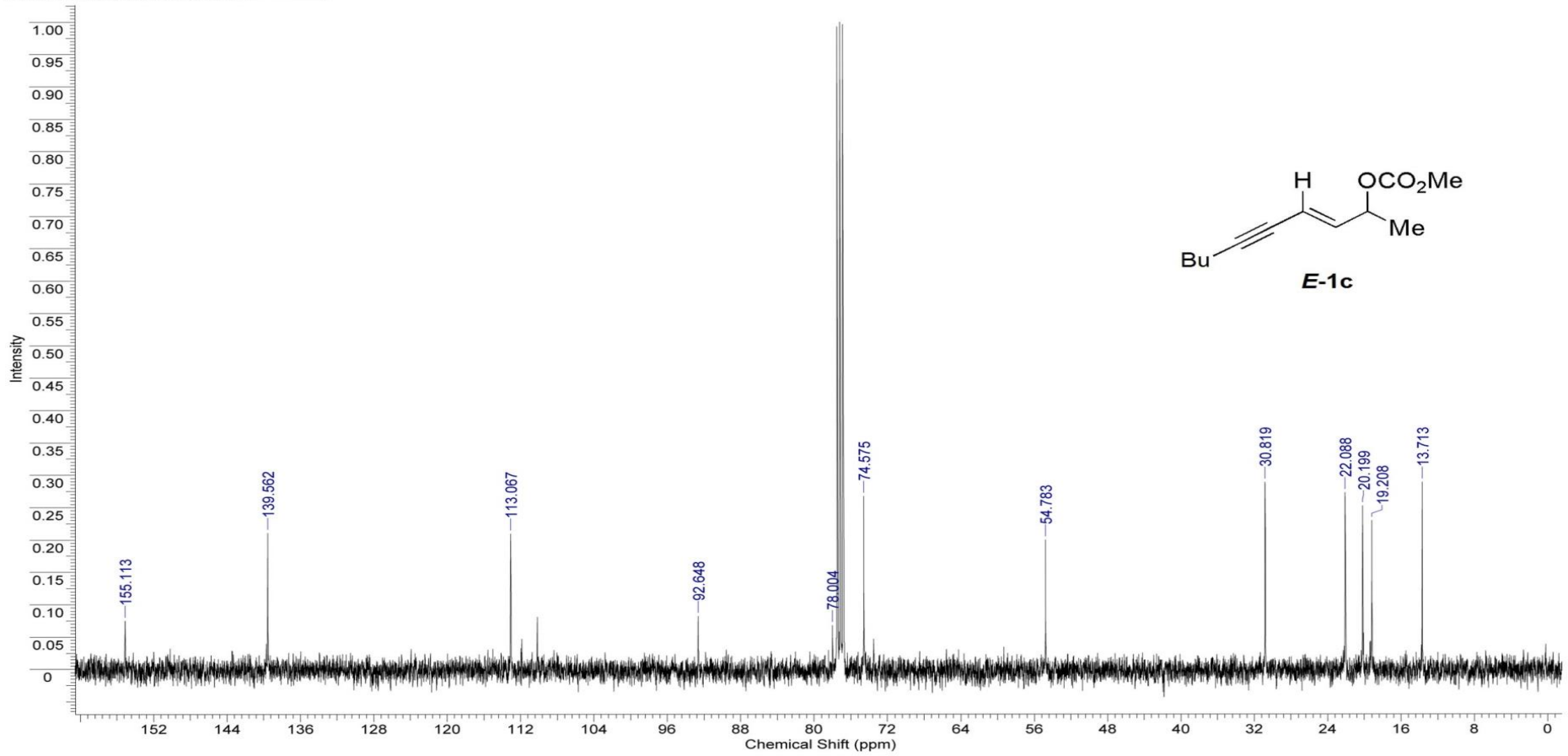

Figure A.6. ^{13}C NMR of (*E*)-dec-3-en-5-yn-2-yl methyl carbonate

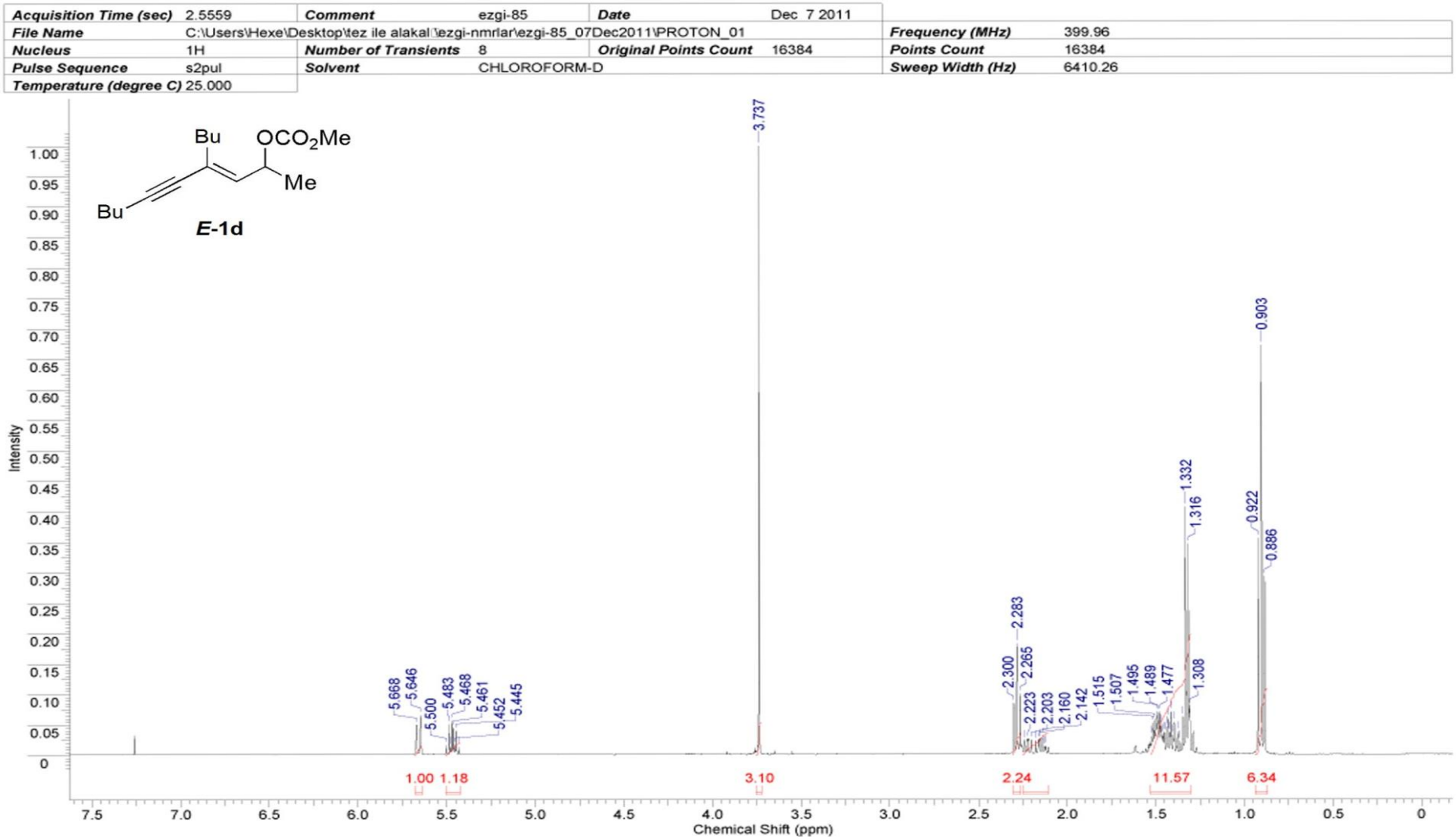

Figure A.7. ^{1}H NMR of (*E*)-4-butyldec-3-en-5-yn-2-yl methyl carbonate

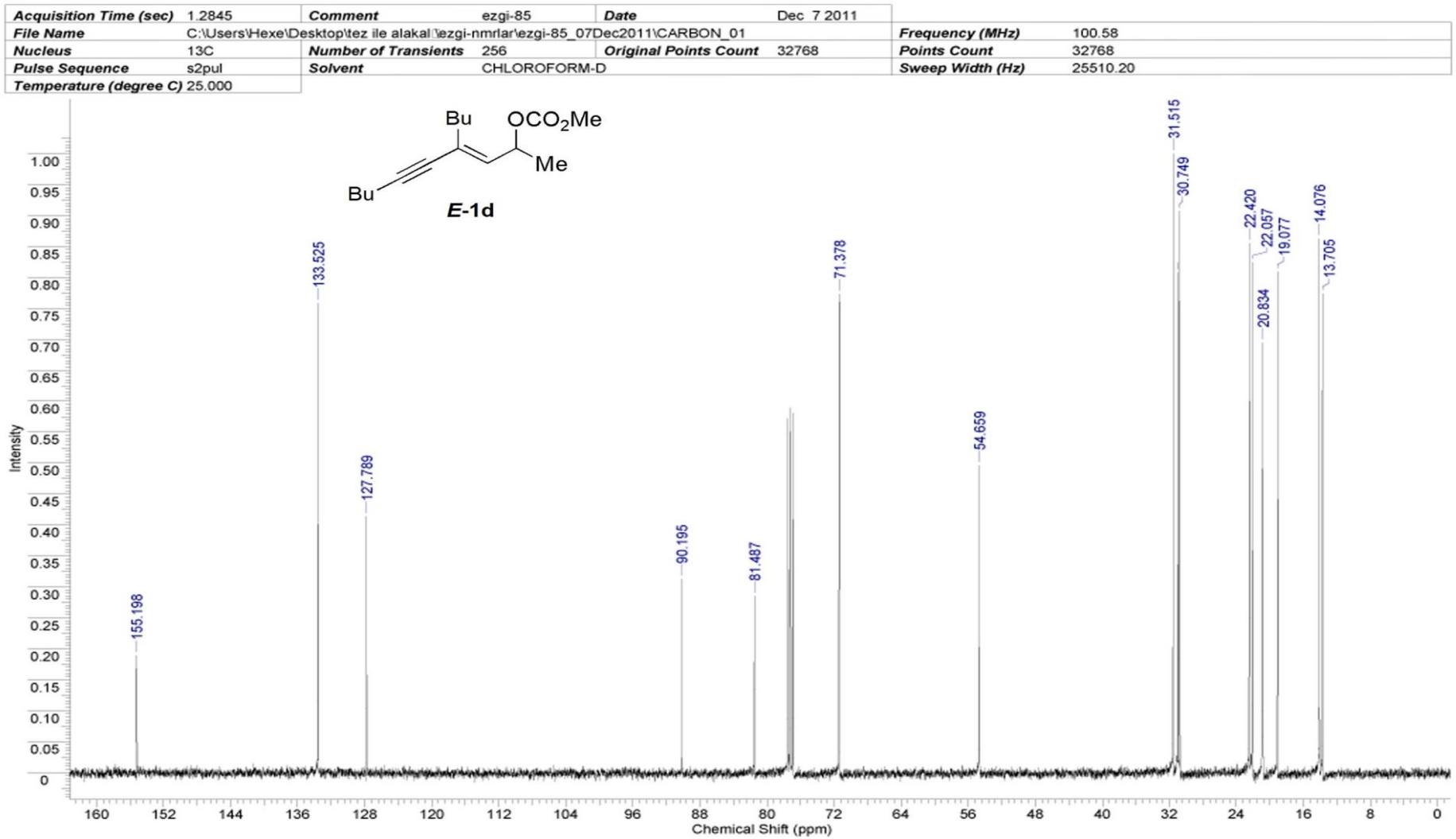

Figure A.8. ^{13}C NMR of (*E*)-4-butyldec-3-en-5-yn-2-yl methyl carbonate

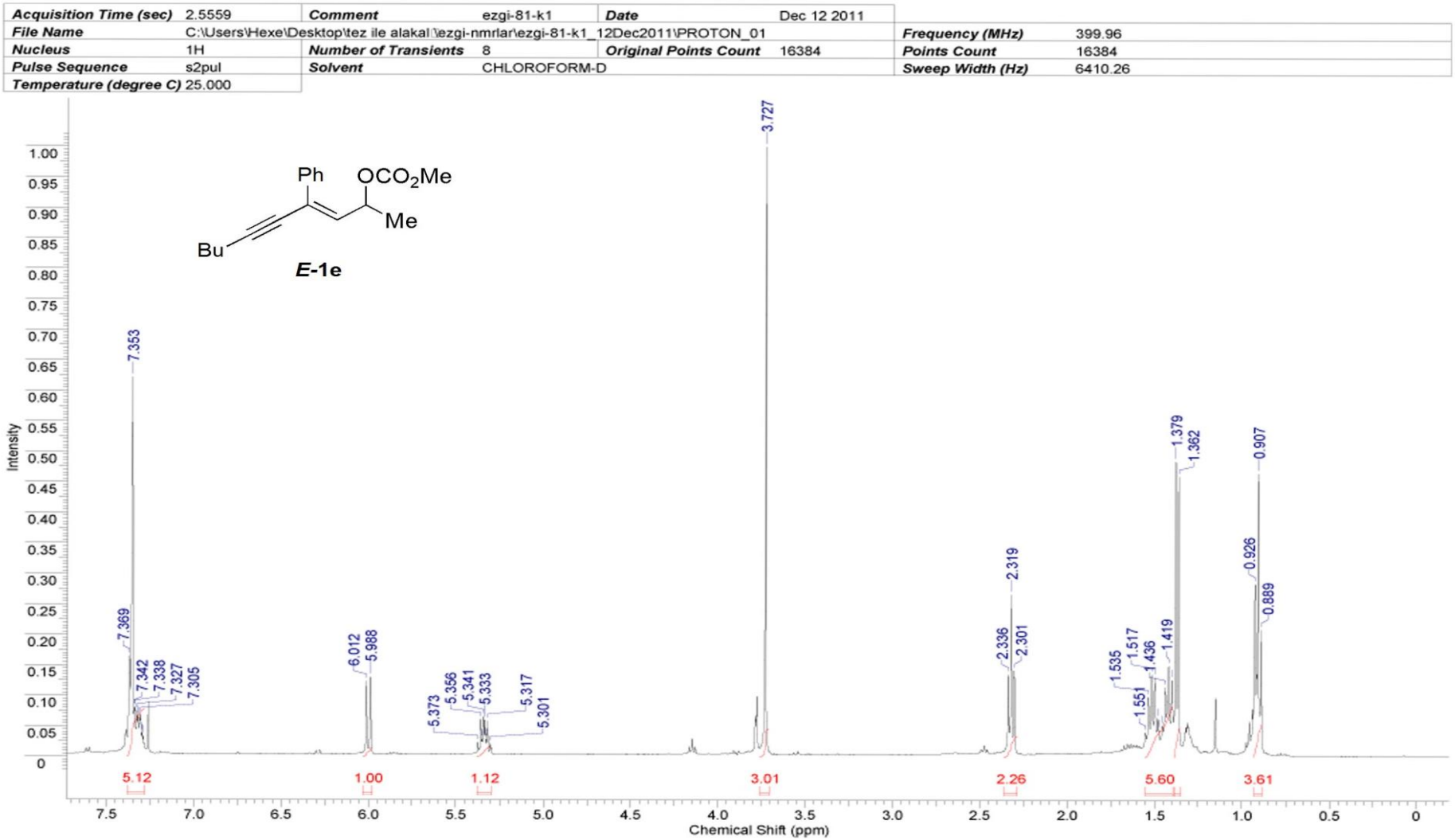

Figure A.9. ^{1}H NMR of (*E*)-methyl (4-phenyldec-3-en-5-yn-2-yl) carbonate

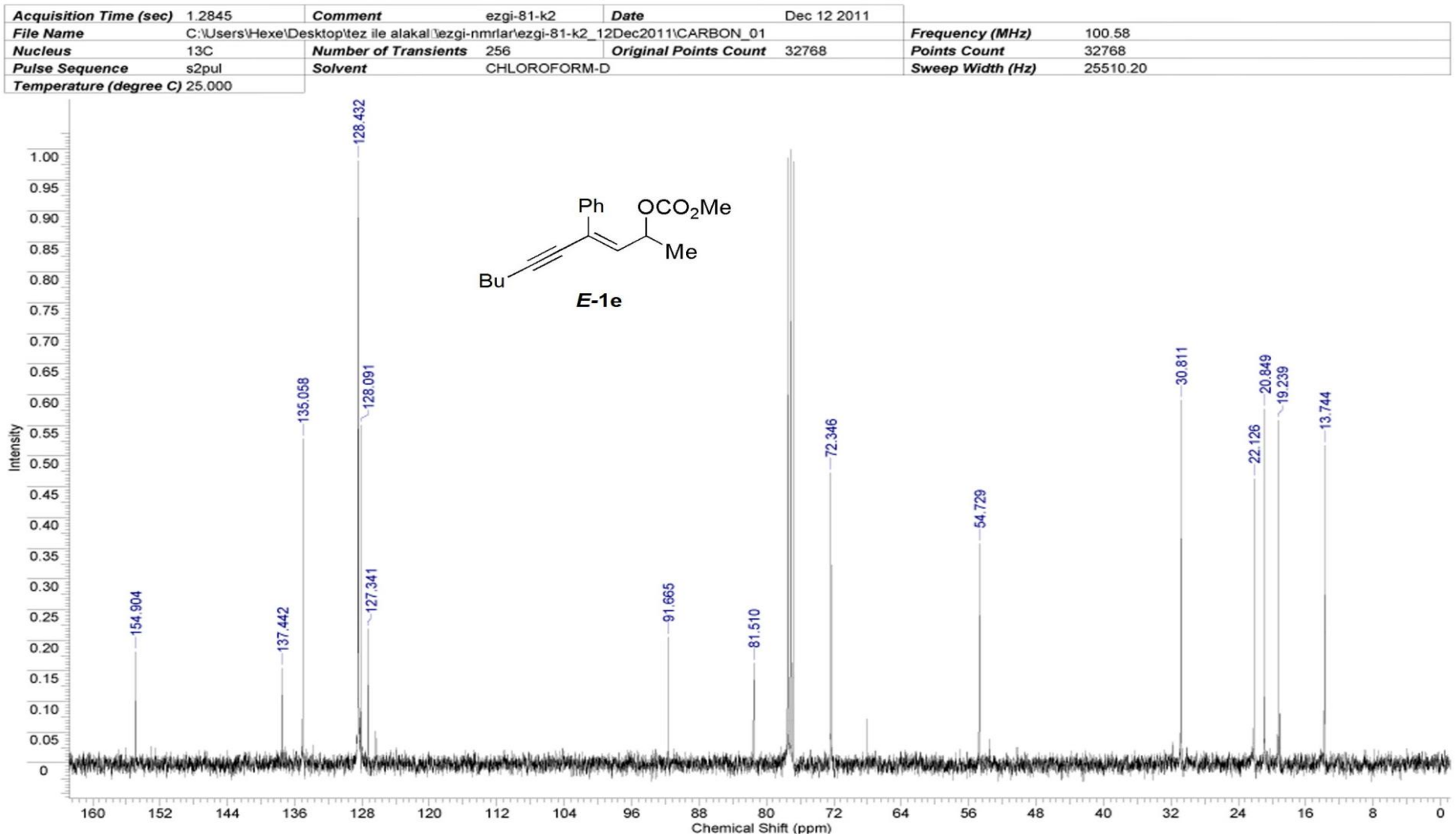

Figure A.10. ^{13}C NMR of (*E*)-methyl (4-phenyldec-3-en-5-yn-2-yl) carbonate

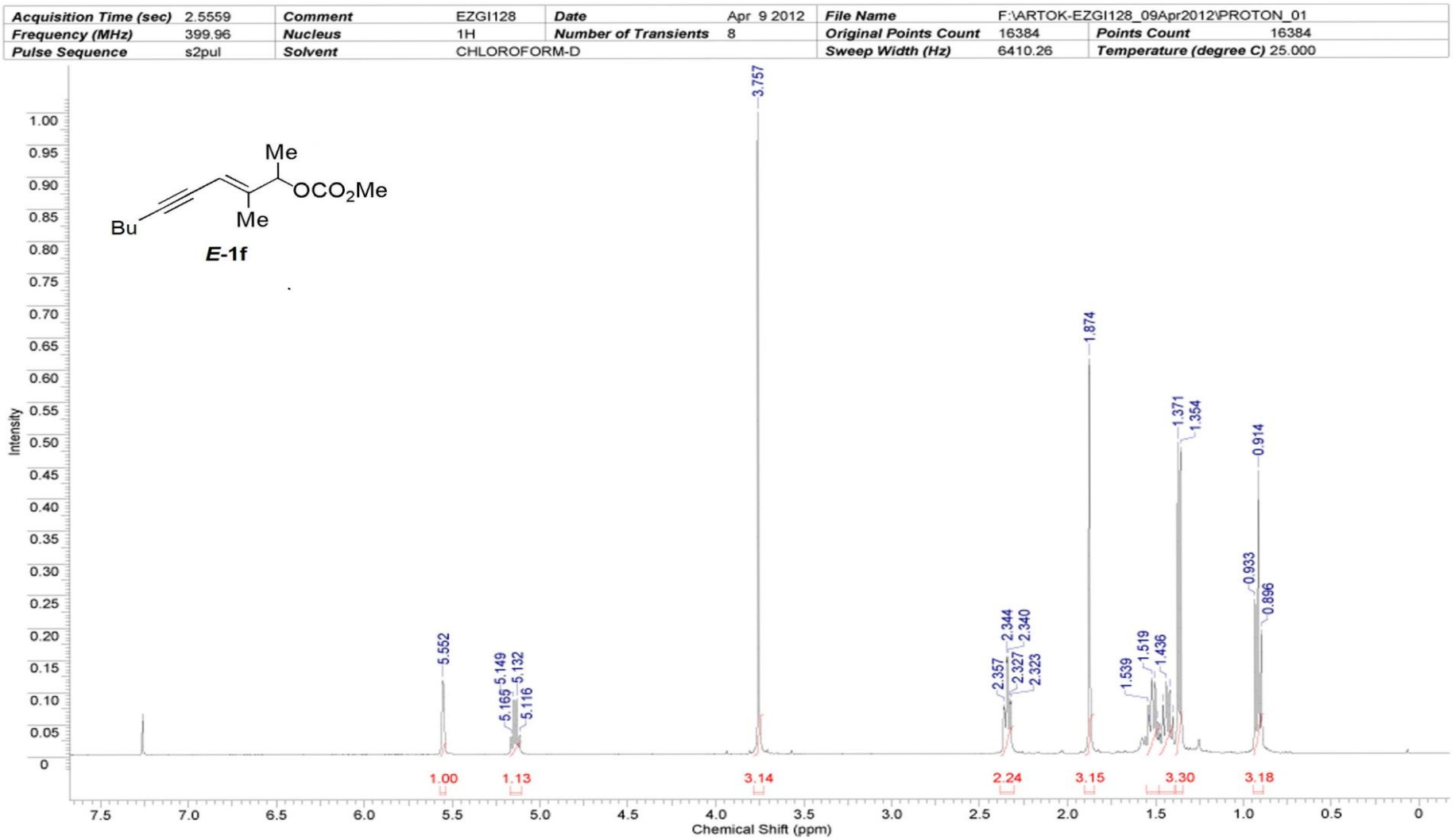

Figure A.11. ^{1}H NMR of (*E*)-methyl (3-methyldec-3-en-5-yn-2-yl) carbonate

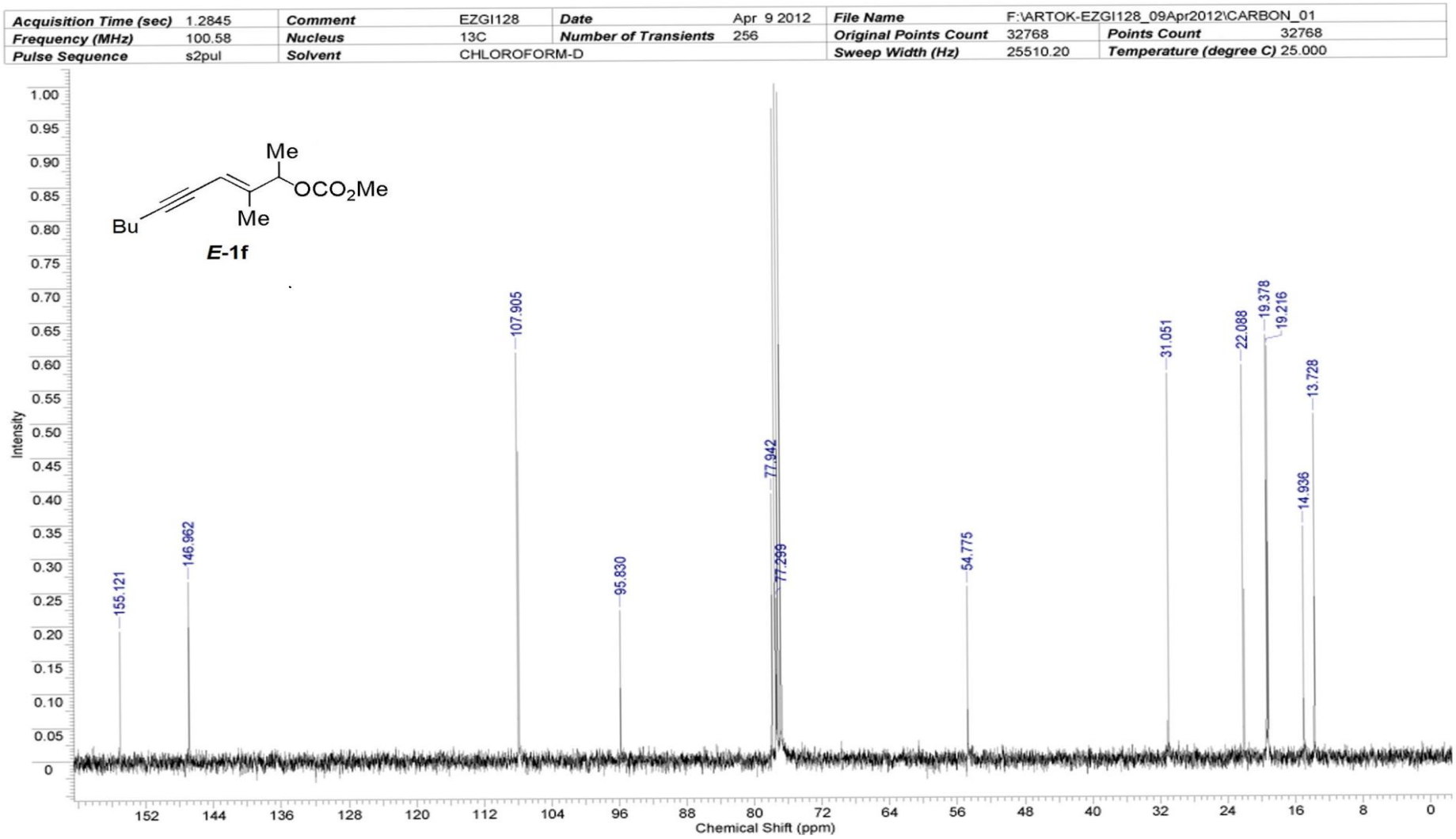

Figure A.12. ^{13}C NMR of (*E*)-methyl (3-methyldec-3-en-5-yn-2-yl) carbonate

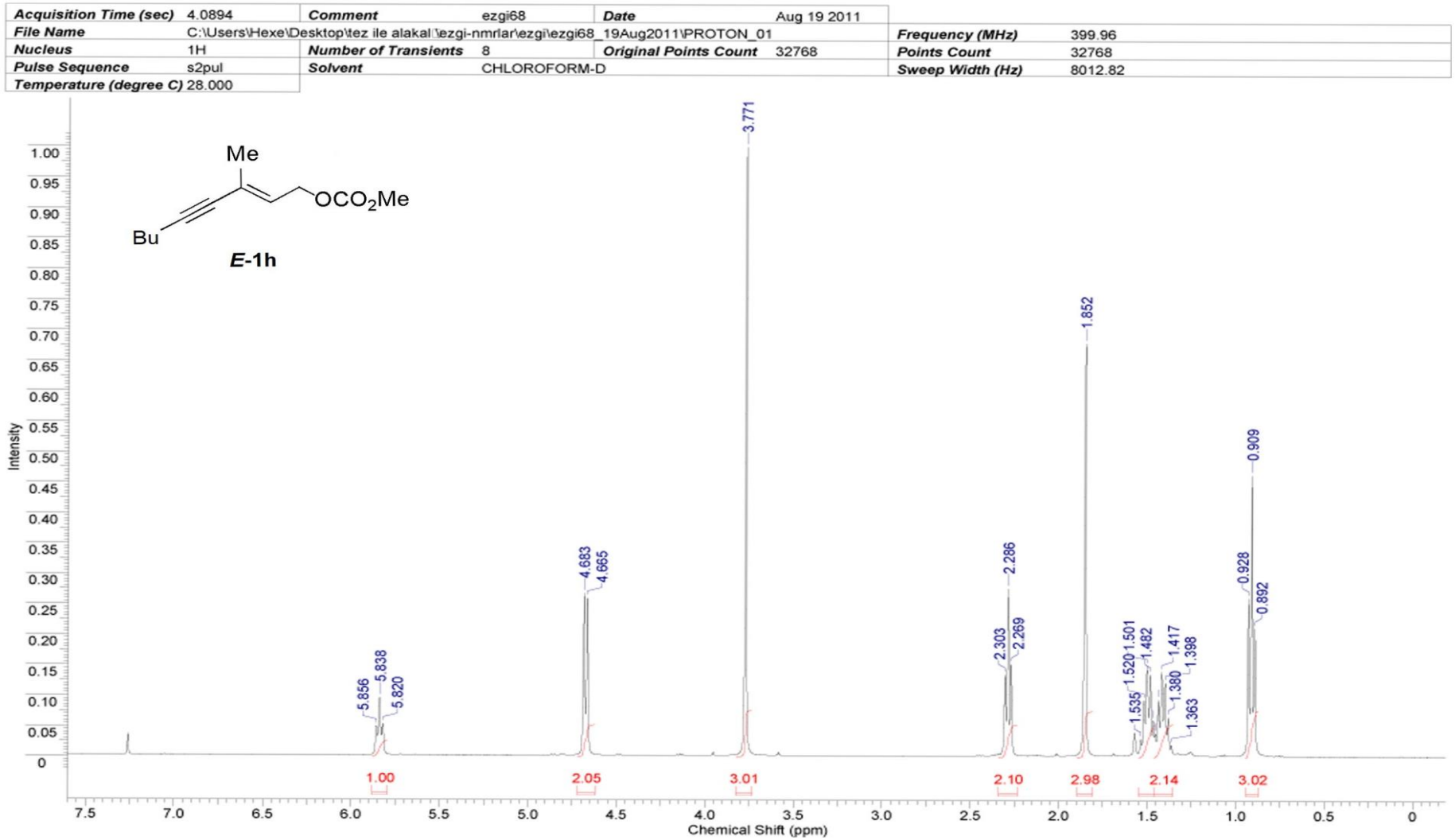

Figure A.13. ^{1}H NMR of (*E*)-methyl (3-methylnon-2-en-4-yn-1-yl) carbonate

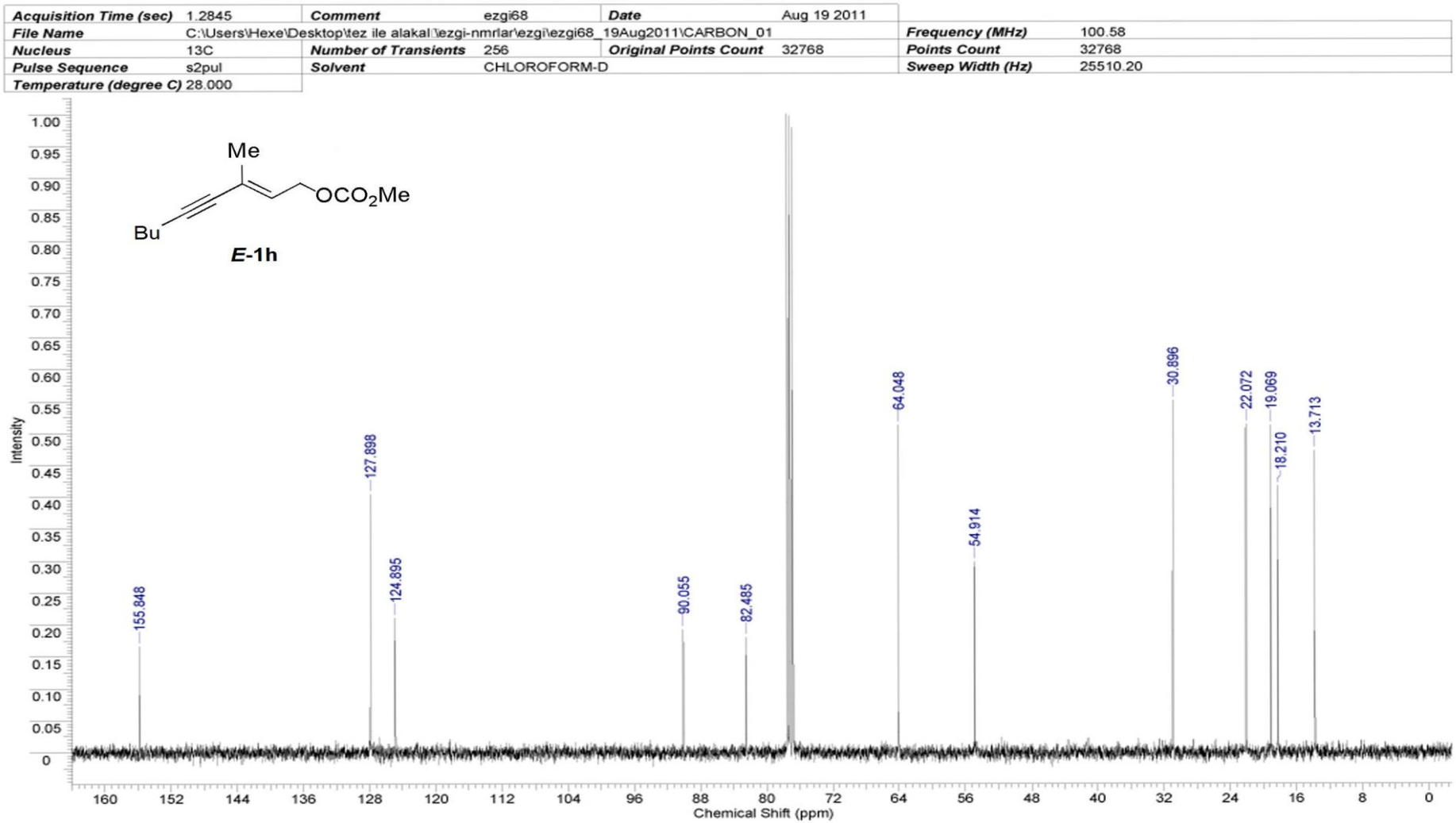

Figure A.14. ^{13}C NMR of (*E*)-methyl (3-methylnon-2-en-4-yn-1-yl) carbonate

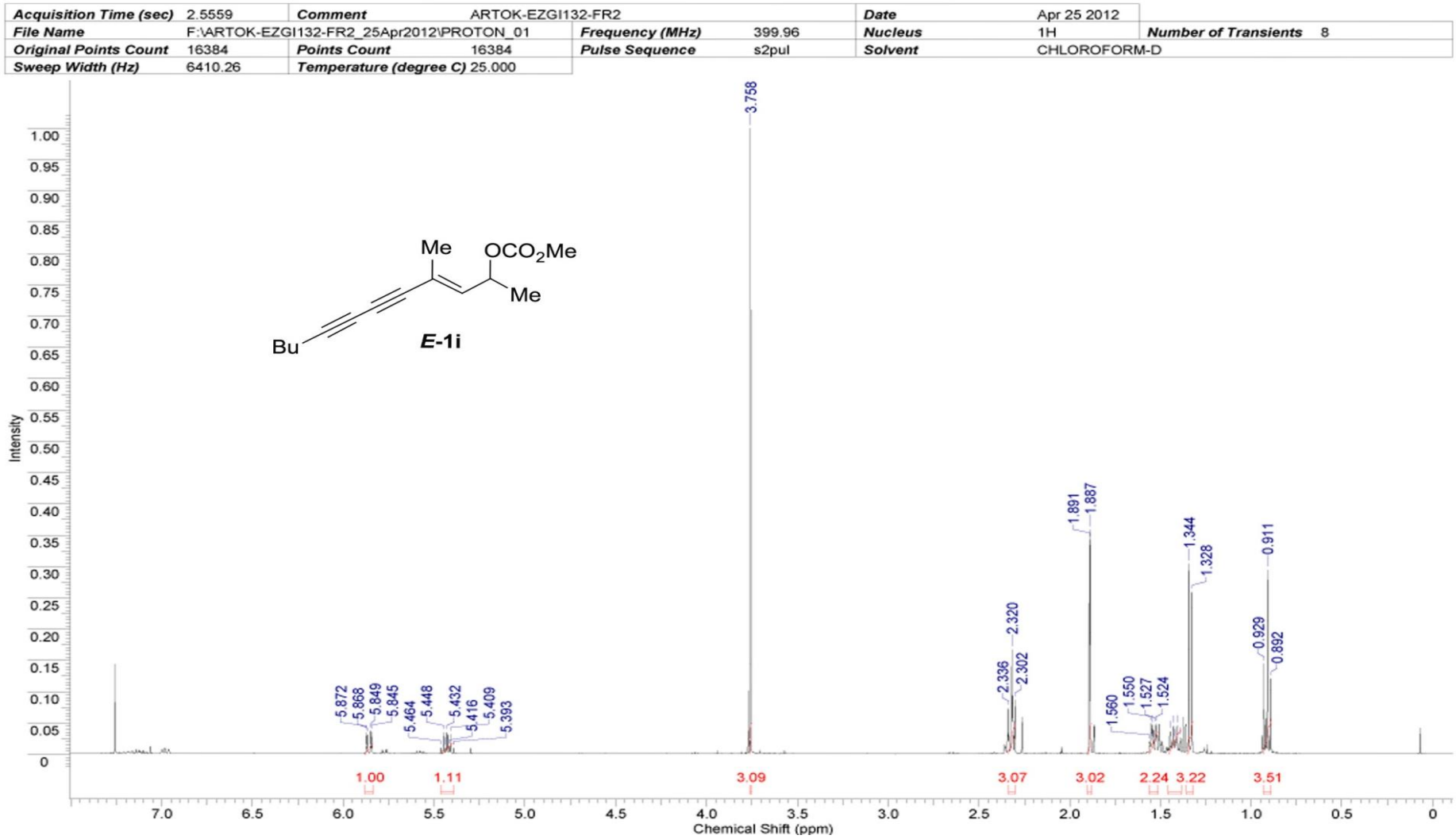

Figure A.15. ^{1}H NMR of (*E*)-methyl (4-methyldodeca-3-en-5,7-diyn-2-yl) carbonate

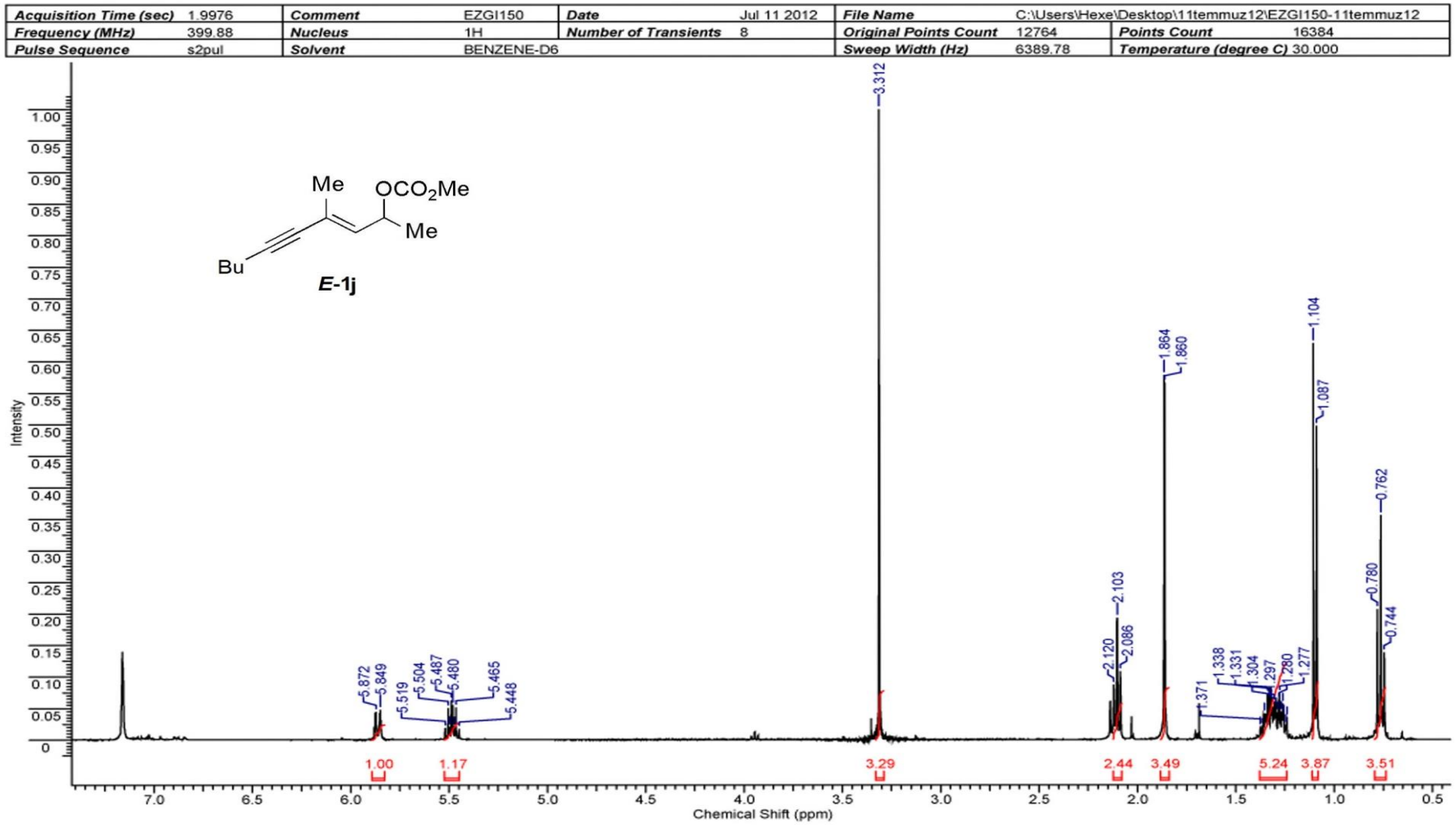

Figure A.16. ^{1}H NMR of (*E*)-methyl (4-methyldec-3-en-5-yn-2-yl) carbonate

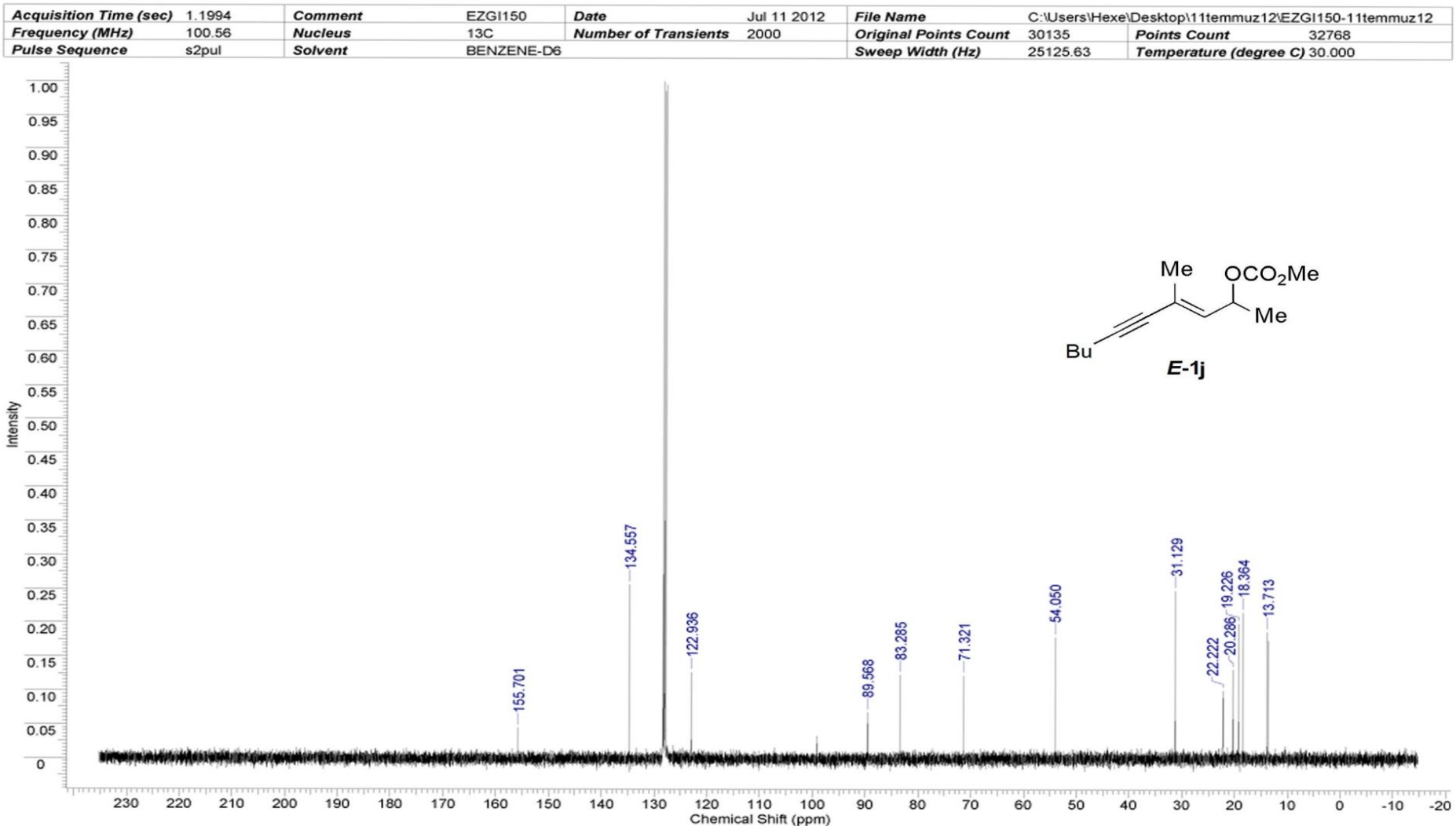

Figure A.17. ^{13}C NMR of (*E*)-methyl (4-methyldec-3-en-5-yn-2-yl) carbonate

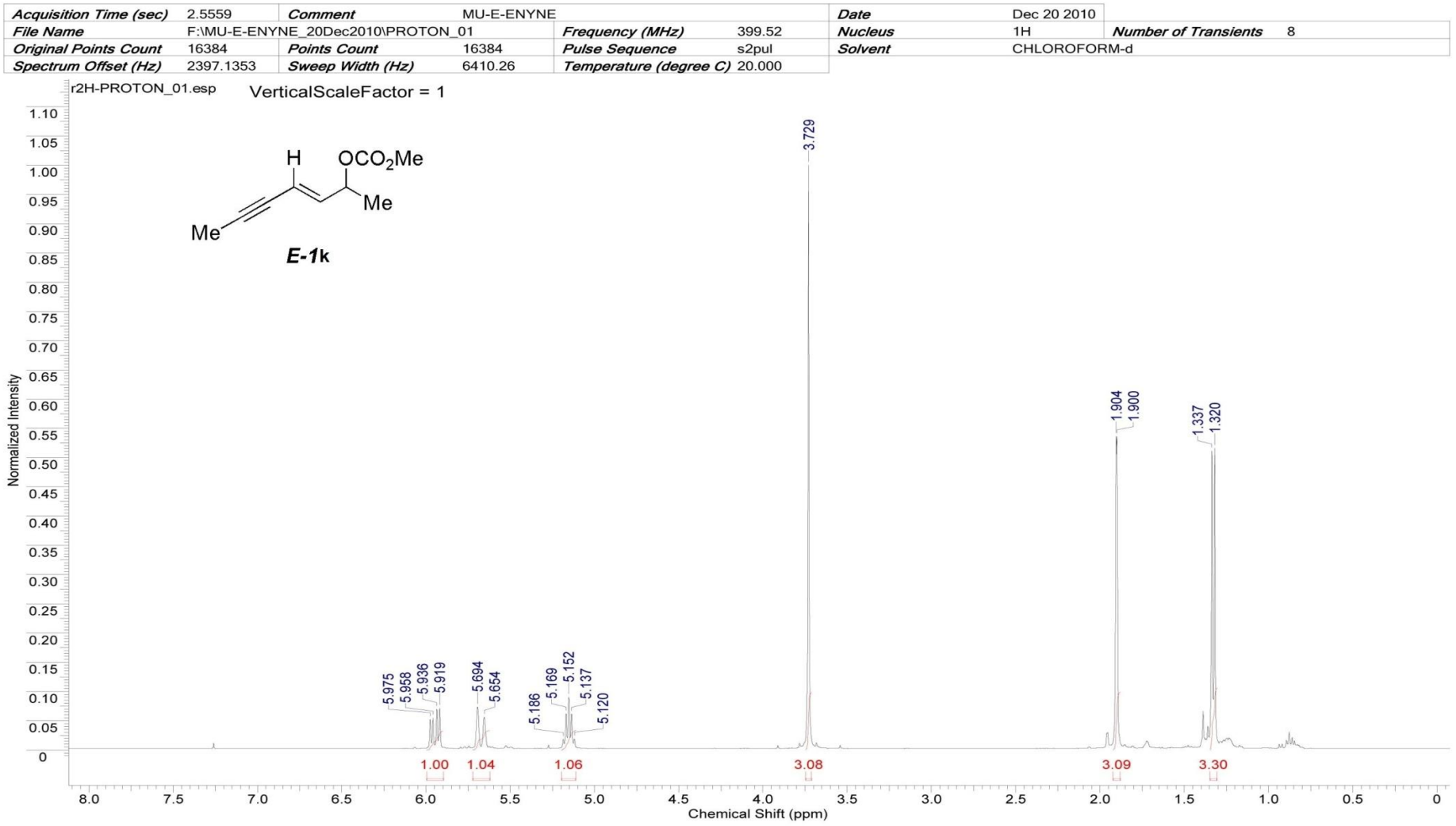

Figure A.18. ^{1}H NMR of (*E*)-hept-3-en-5-yn-2-yl methyl carbonate

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				

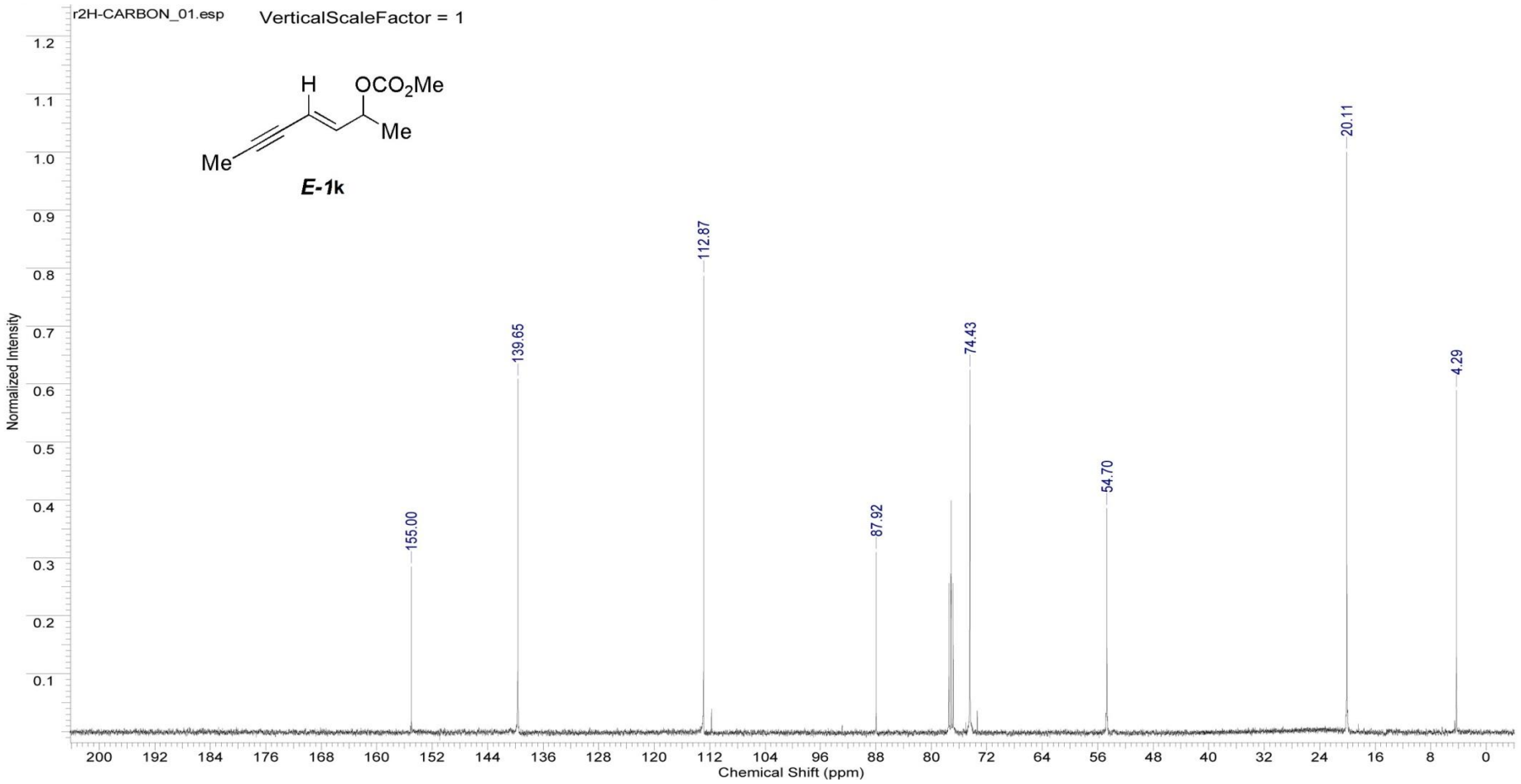

Figure A.19. ^{13}C NMR of (*E*)-hept-3-en-5-yn-2-yl methyl carbonate

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								

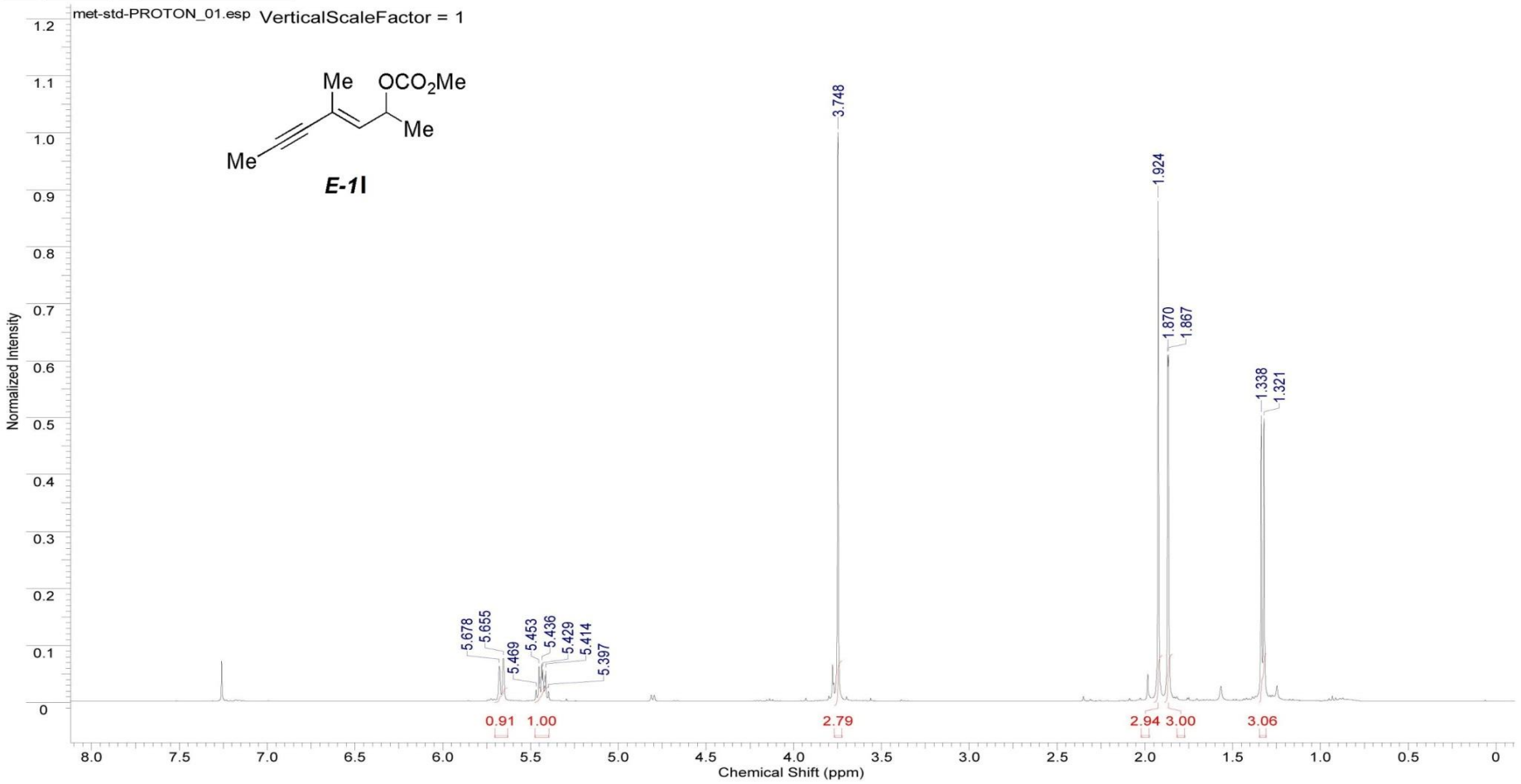

Figure A.20. ^{1}H NMR of (*E*)-methyl 4-methylhept-3-en-5-yn-2-yl carbonate

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								

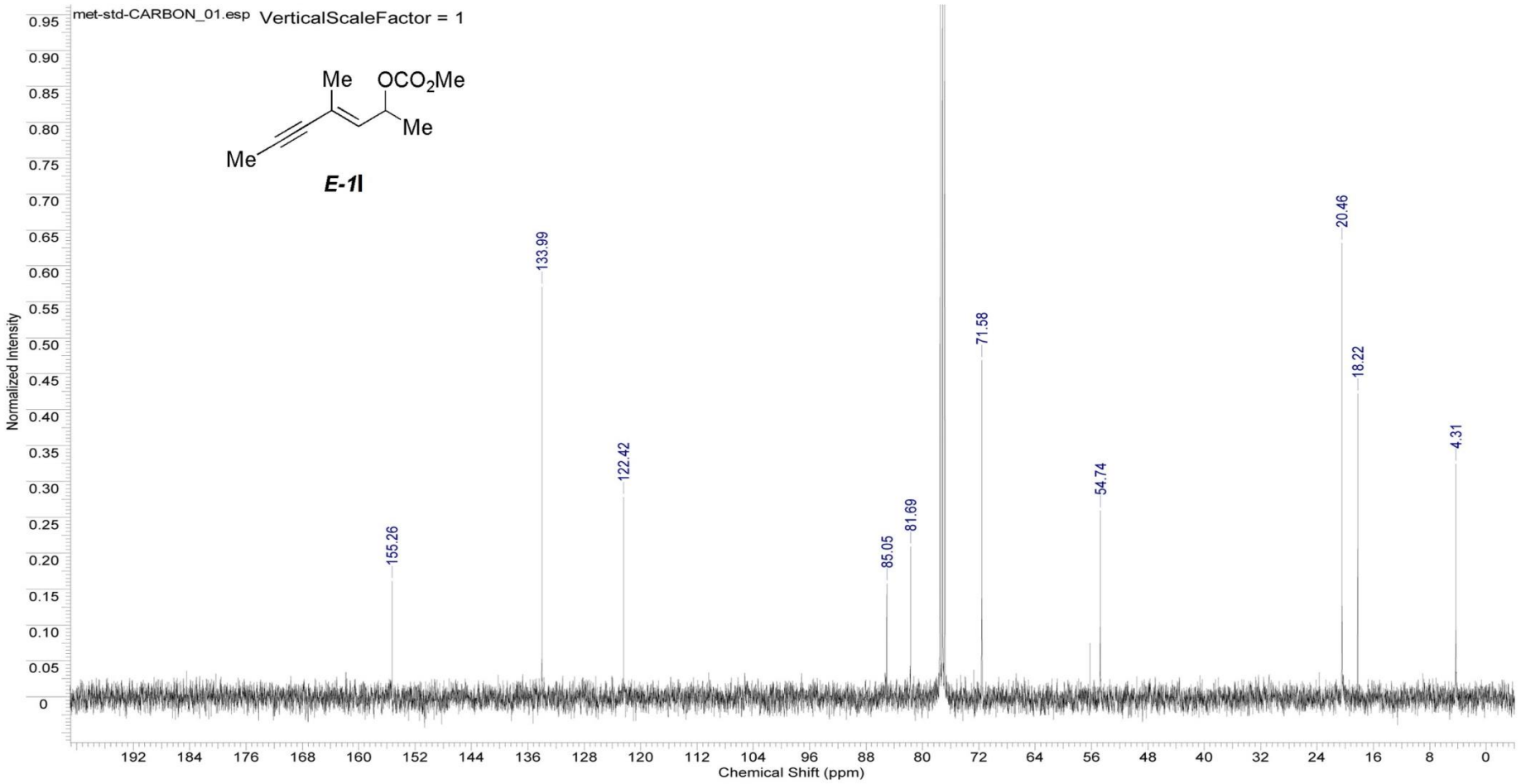

Figure A.21. ^{13}C NMR of (*E*)-methyl 4-methylhept-3-en-5-yn-2-yl carbonate

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				

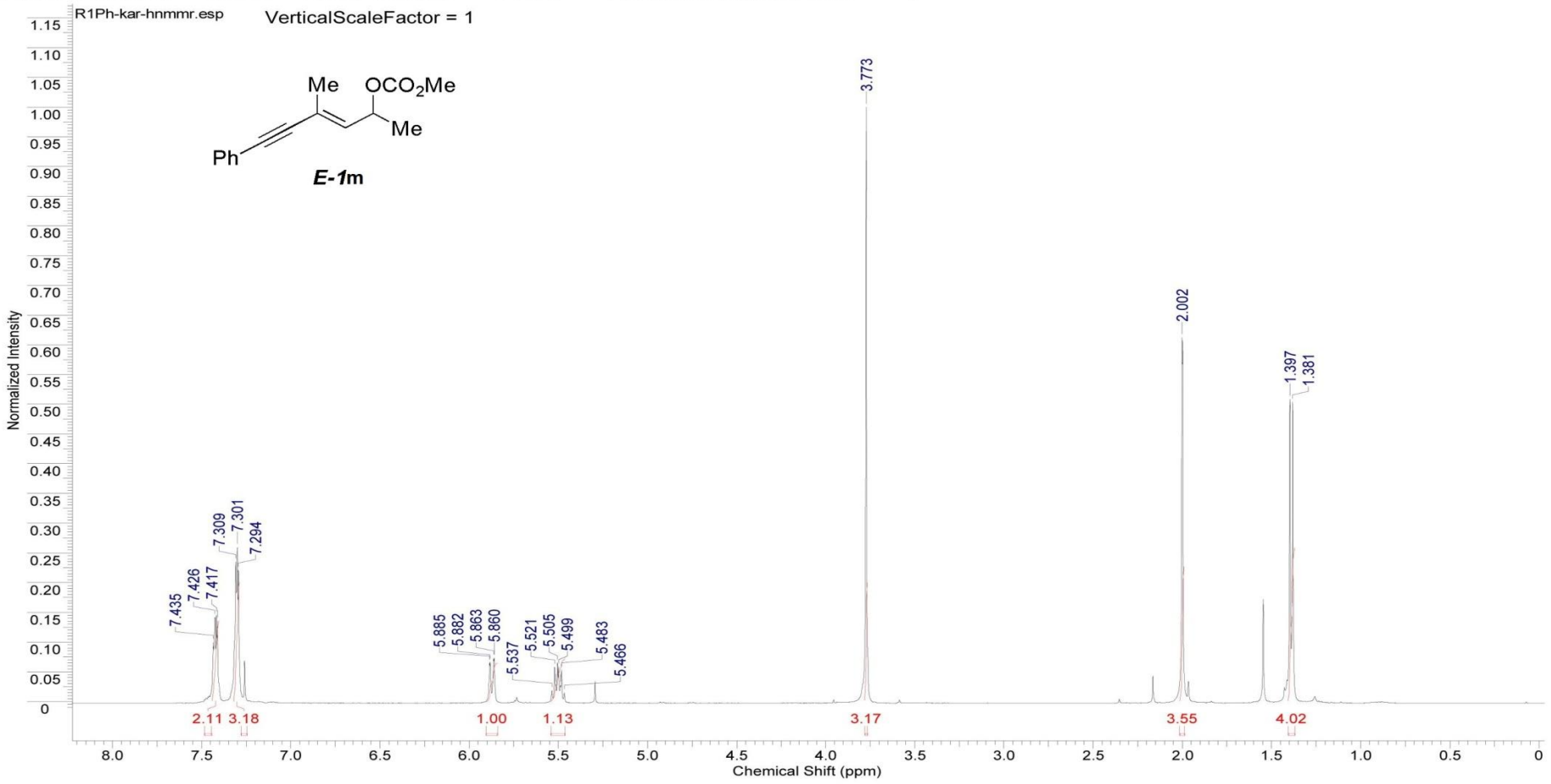

Figure A.22. ^{1} H NMR of (*E*)-methyl 4-methyl-6-phenylhex-3-en-5-yn-2-yl carbonate

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

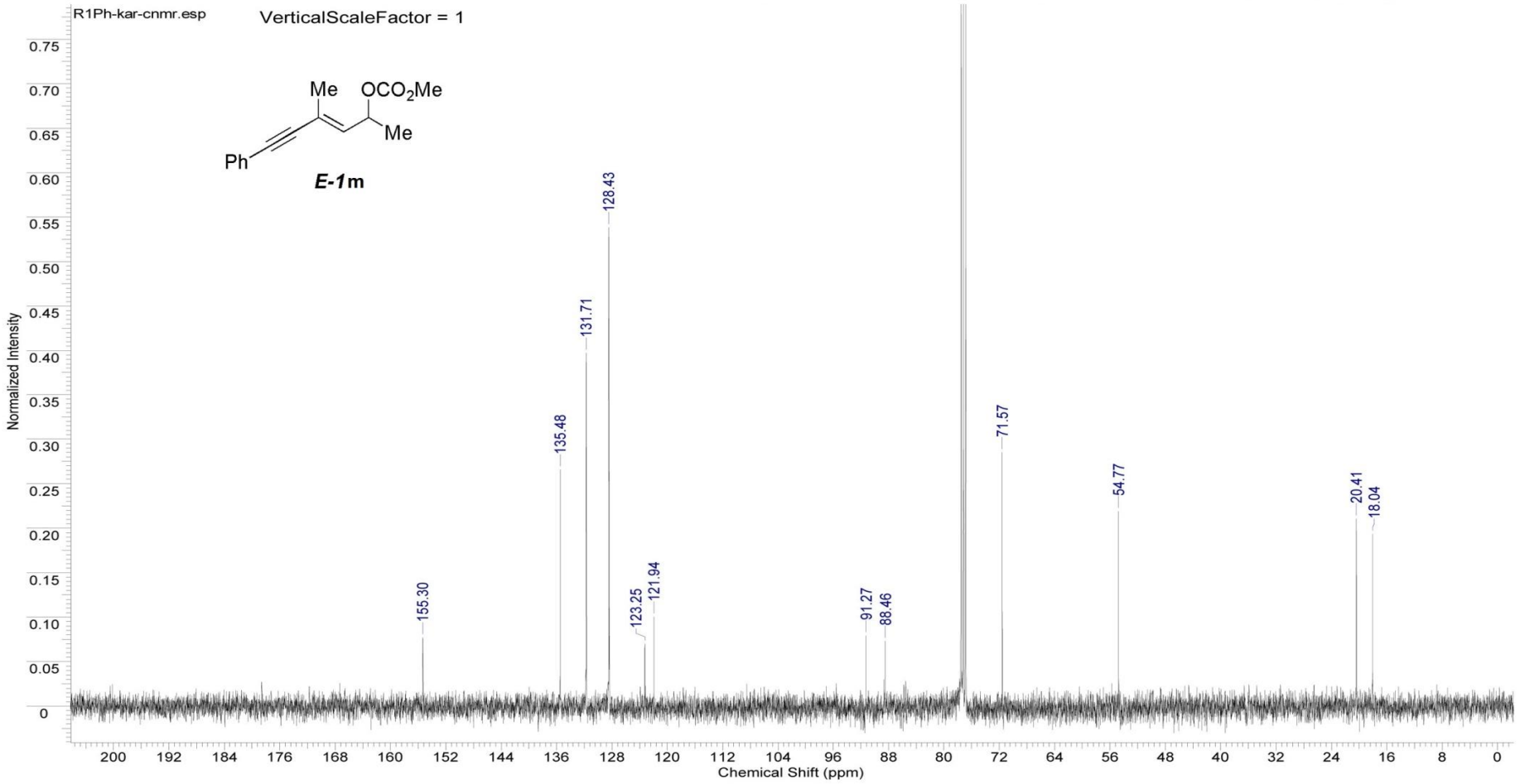

Figure A.23. ^{13}C NMR of (*E*)-methyl 4-methyl-6-phenylhex-3-en-5-yn-2-yl carbonate

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			

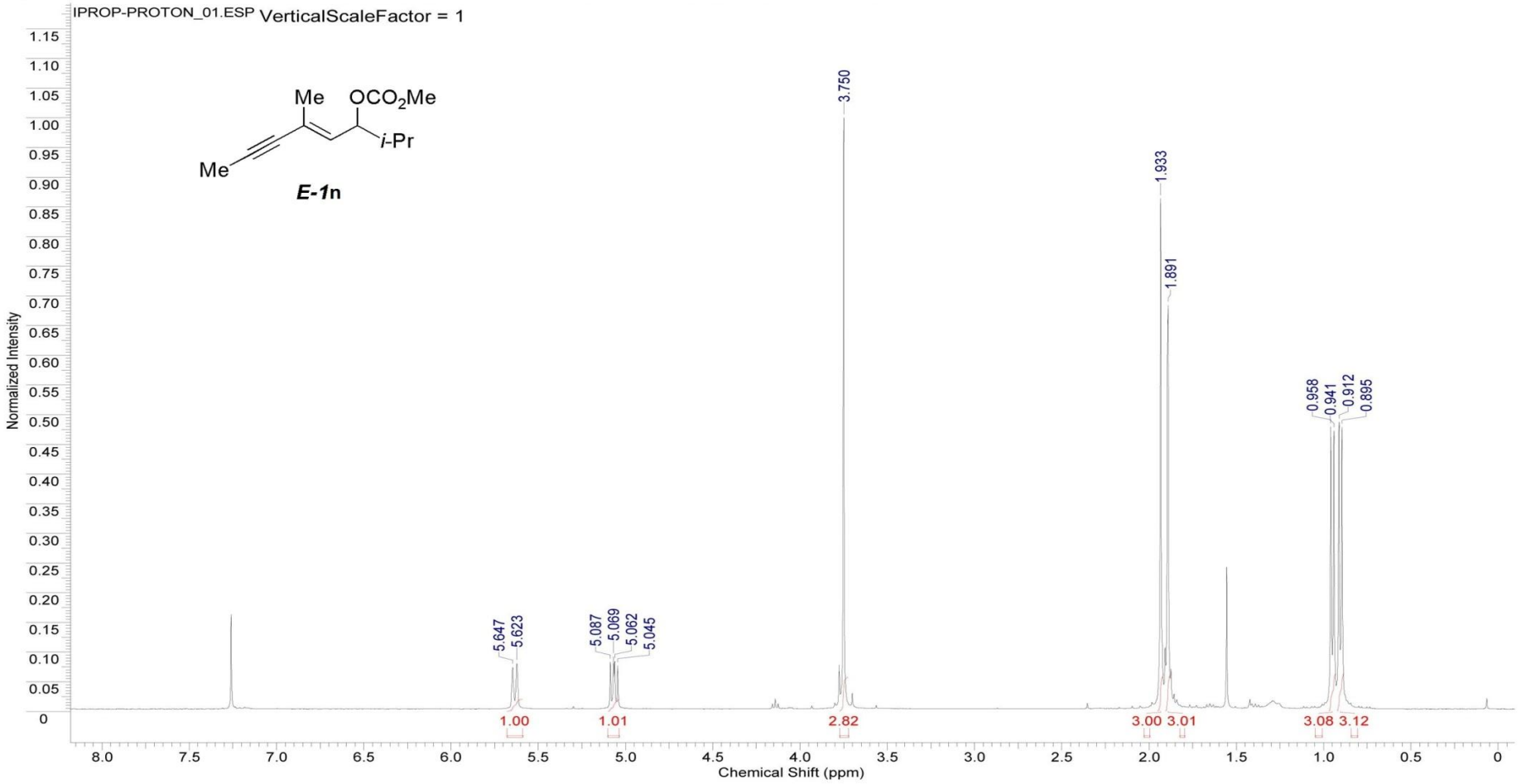

Figure A.24. ^{1} H NMR of (*E*)-2,5-dimethyloct-4-en-6-yn-3-yl methyl carbonate

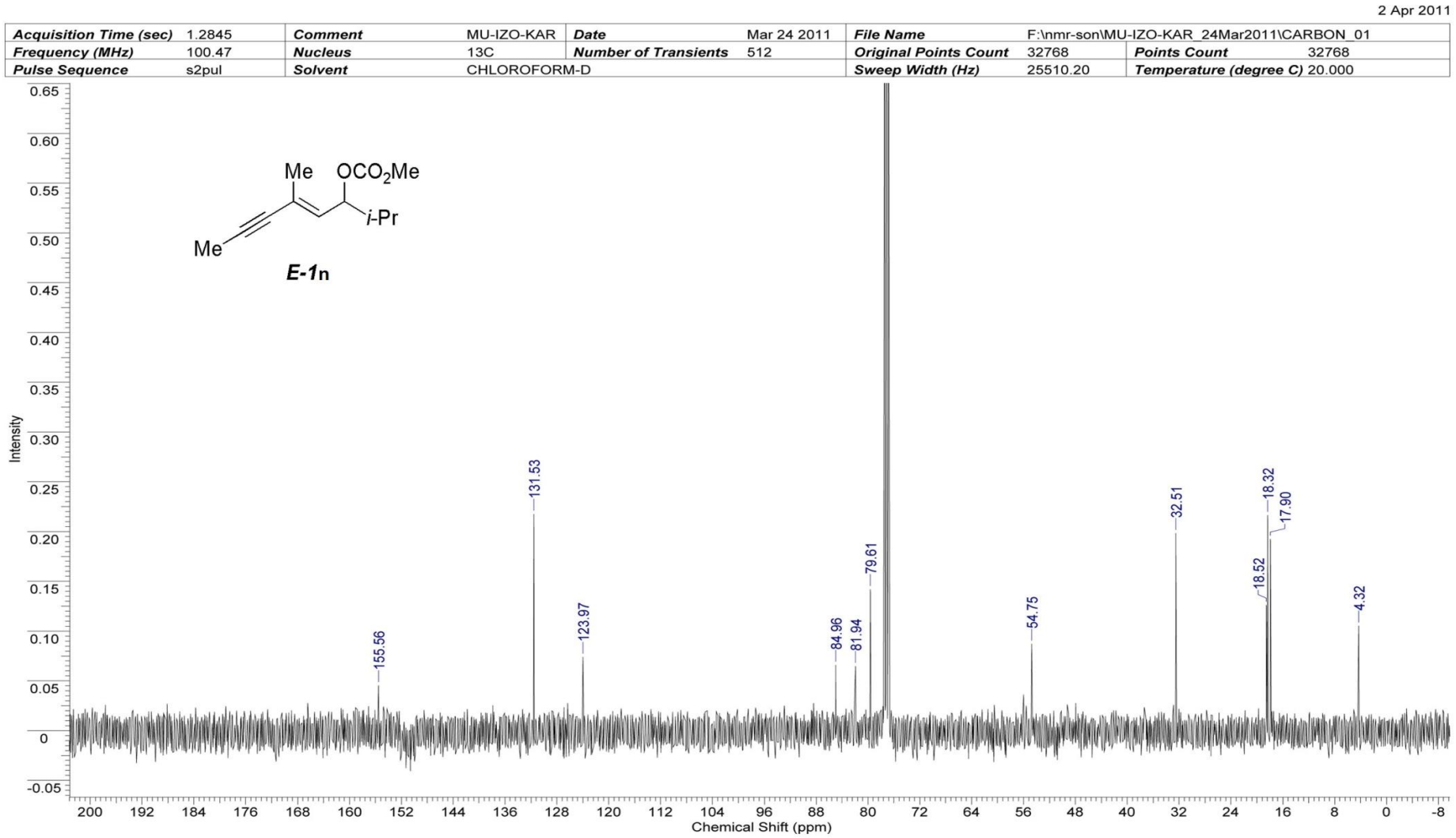

Figure A.25. ^{13}C NMR of (*E*)-2,5-dimethyloct-4-en-6-yn-3-yl methyl carbonate

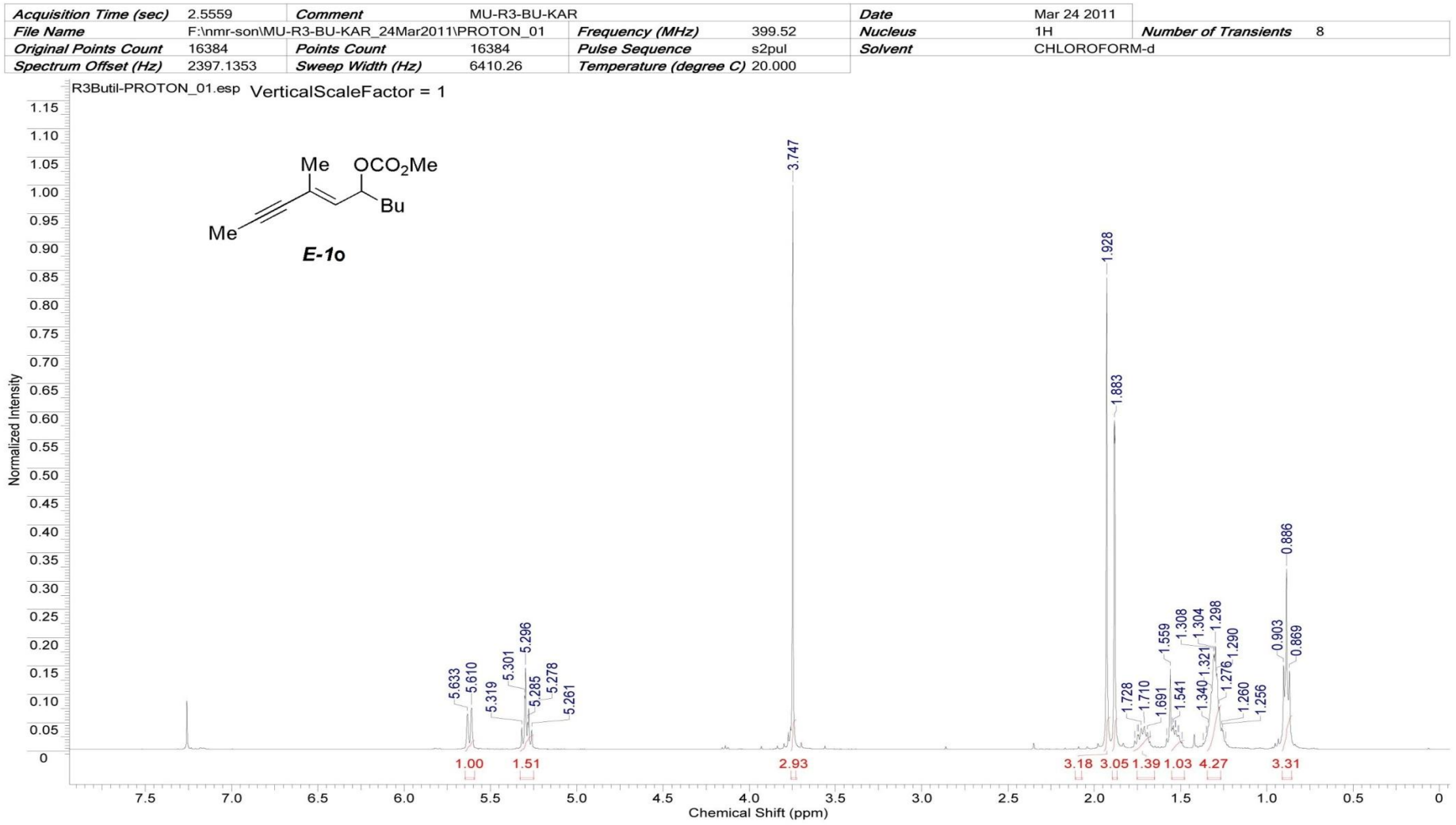

Figure A.26. [1] H NMR of (*E*)-methyl 7-methyldec-6-en-8-yn-5-yl carbonate

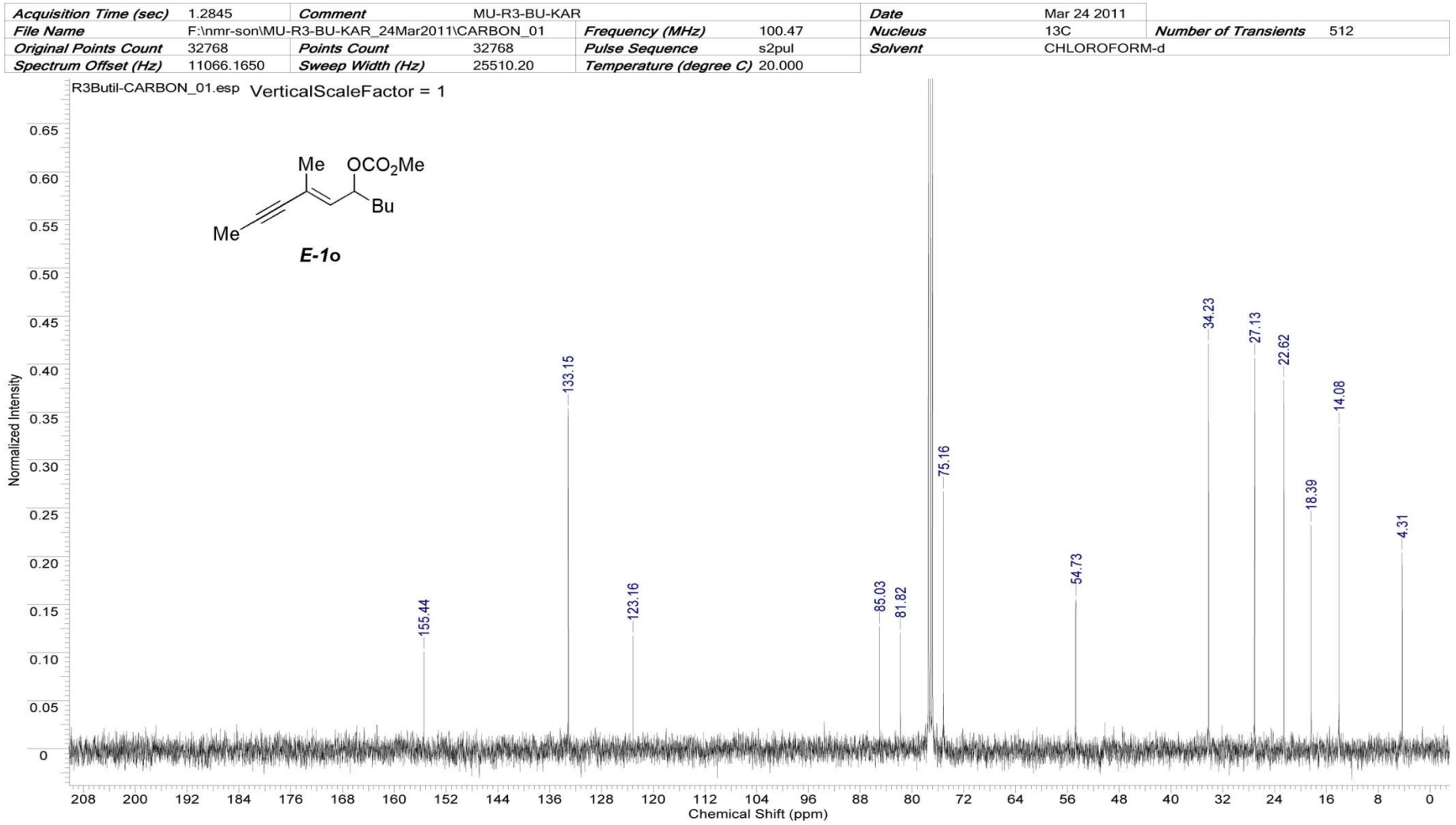

Figure A.27. ^{13}C NMR of (*E*)-methyl 7-methyldec-6-en-8-yn-5-yl carbonate

APPENDIX B

MASS SPECTRUMS OF REACTANTS

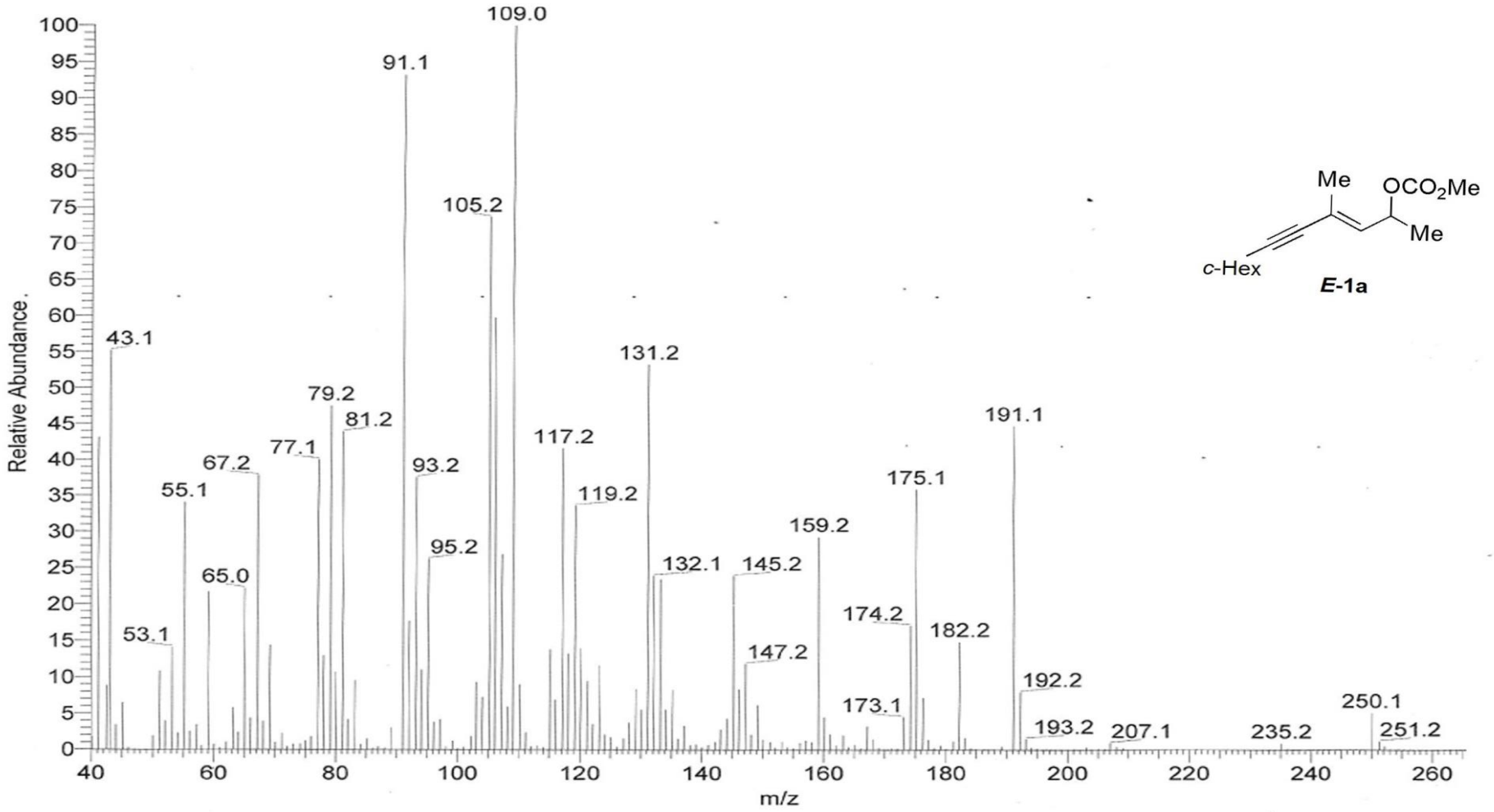

Figure B.1. Mass Spectrum of (*E*)-6-cyclohexyl-4-methylhex-3-en-5-yn-2-yl methyl carbonate

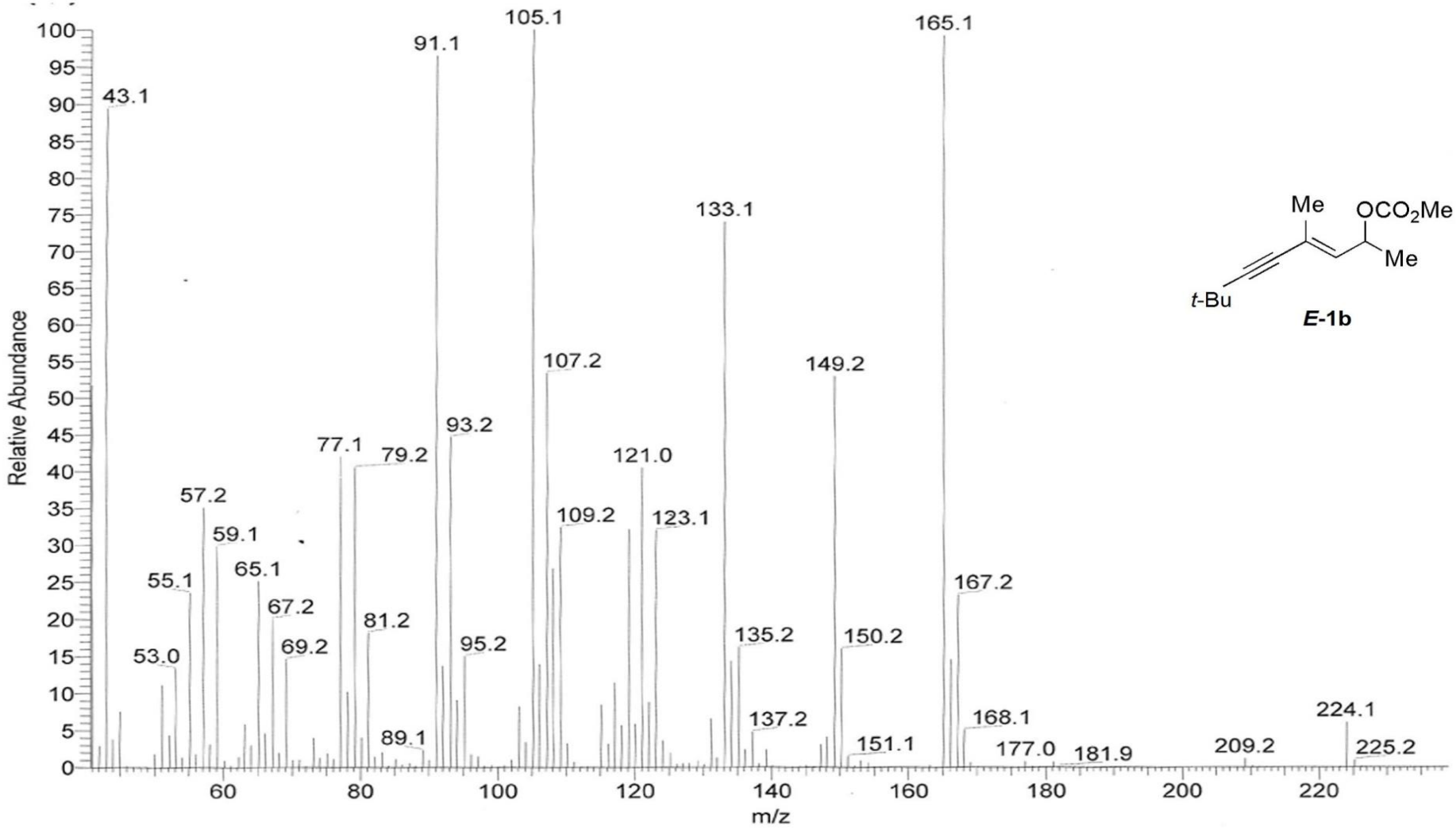

Figure B.2. Mass Spectrum of (*E*)-methyl (4,7,7-trimethyloct-3-en-5-yn-2-yl) carbonate

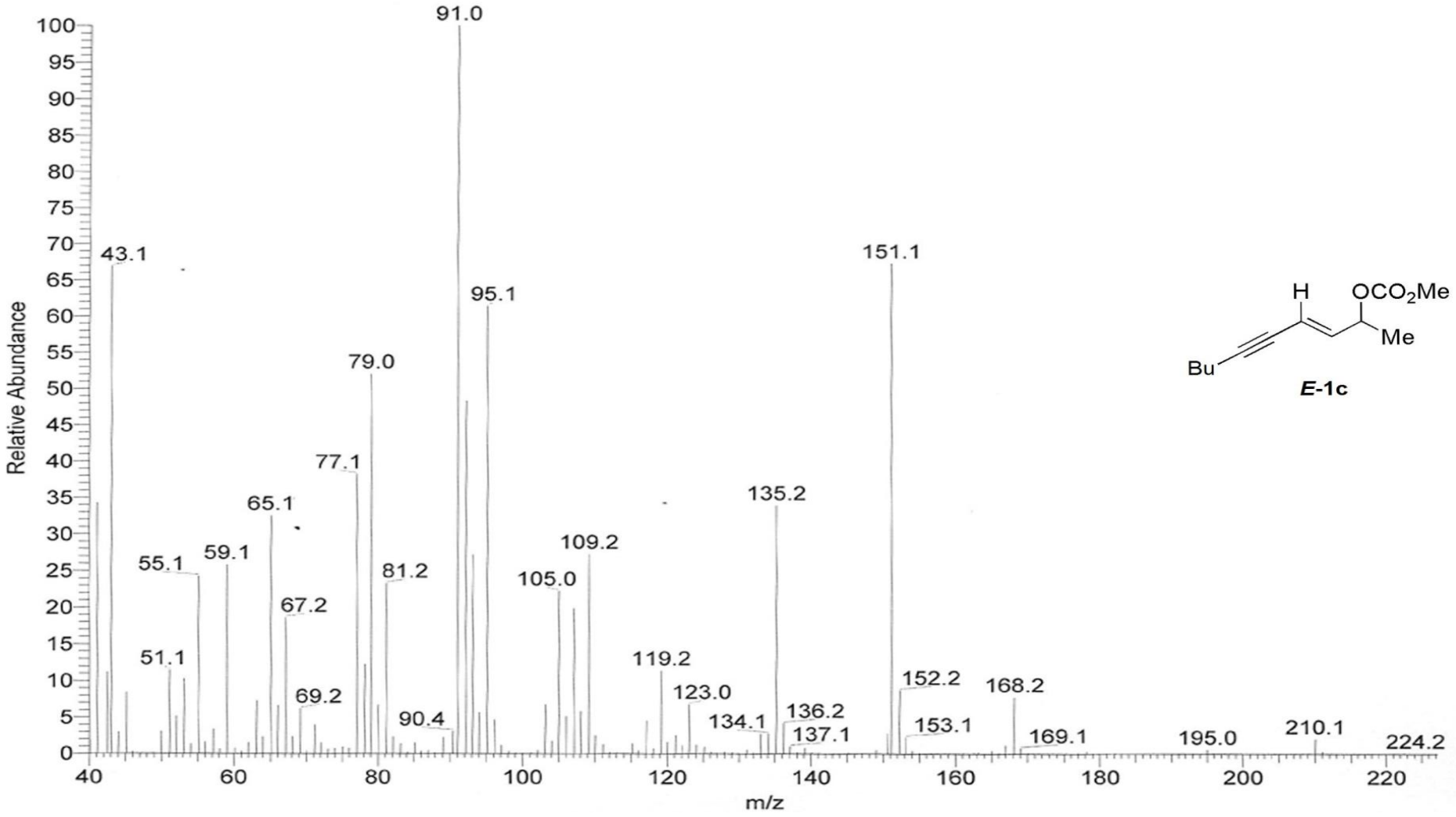

Figure B.3. Mass Spectrum of (*E*)-dec-3-en-5-yn-2-yl methyl carbonate

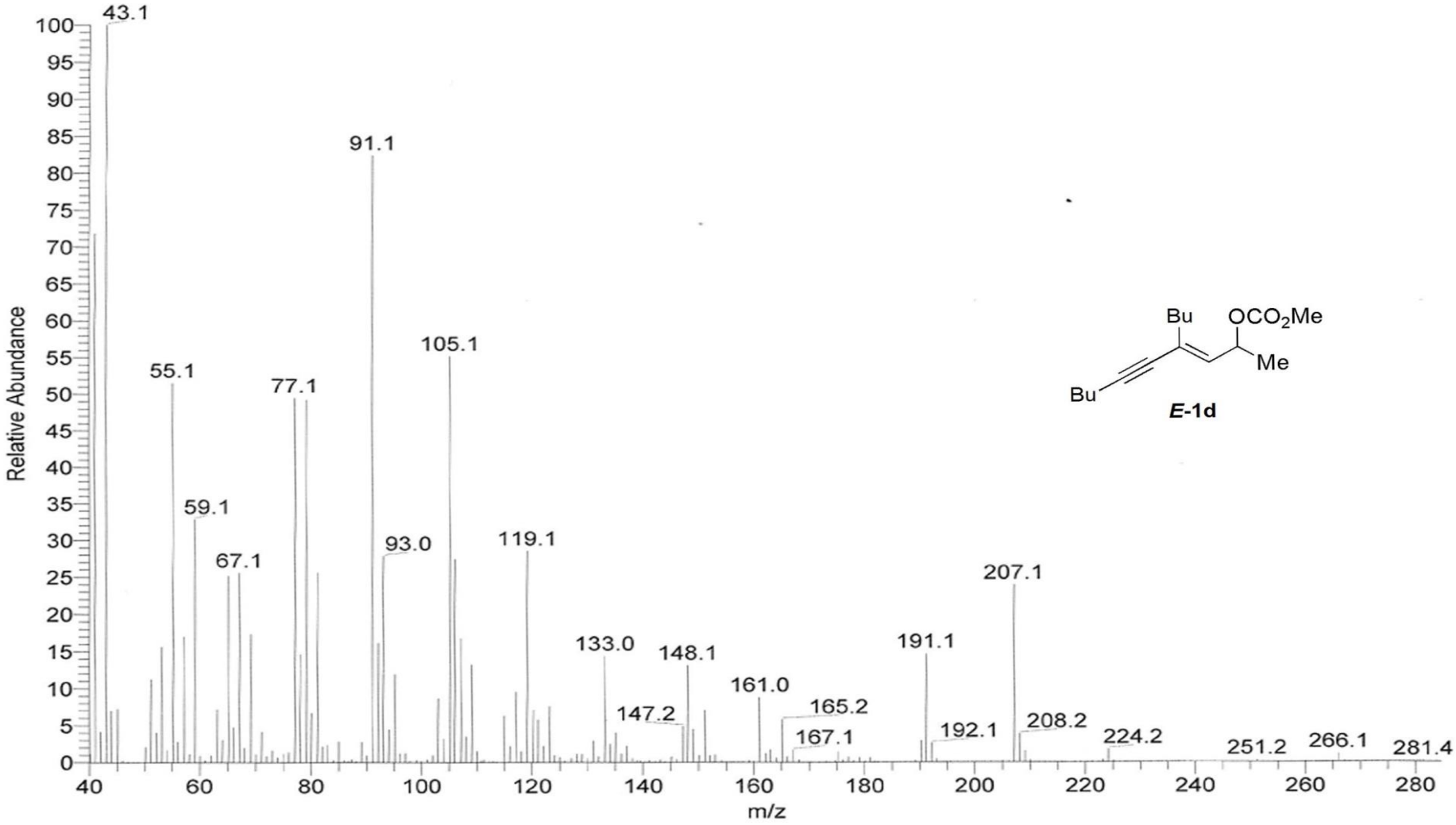

Figure B.4. Mass Spectrum of (*E*)-4-butyldec-3-en-5-yn-2-yl methyl carbonate

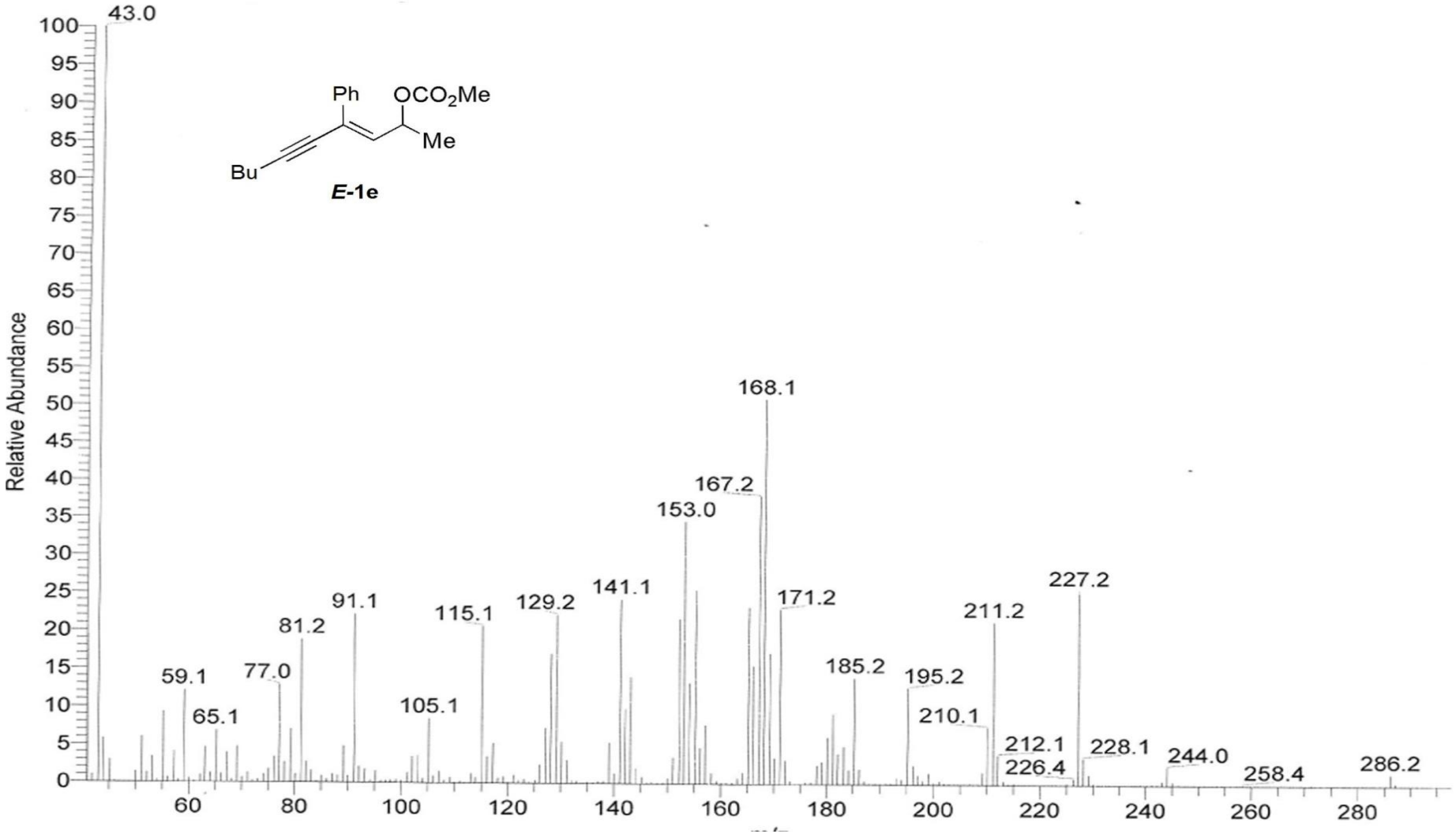

Figure B.5. Mass Spectrum of (*E*)-methyl (4-phenyldec-3-en-5-yn-2-yl) carbonate

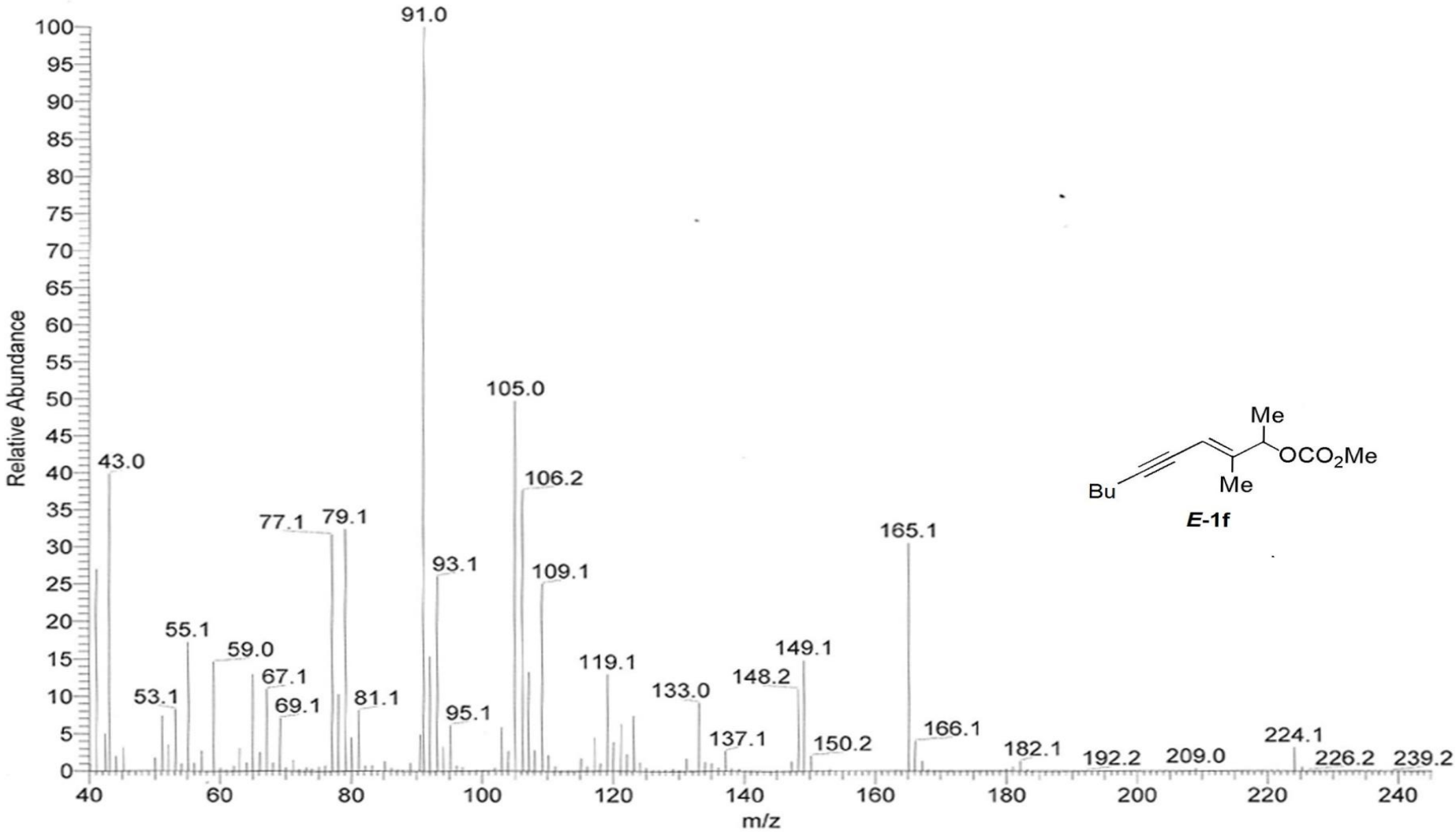

Figure B.6. Mass Spectrum of (*E*)-methyl (3-methyldec-3-en-5-yn-2-yl) carbonate

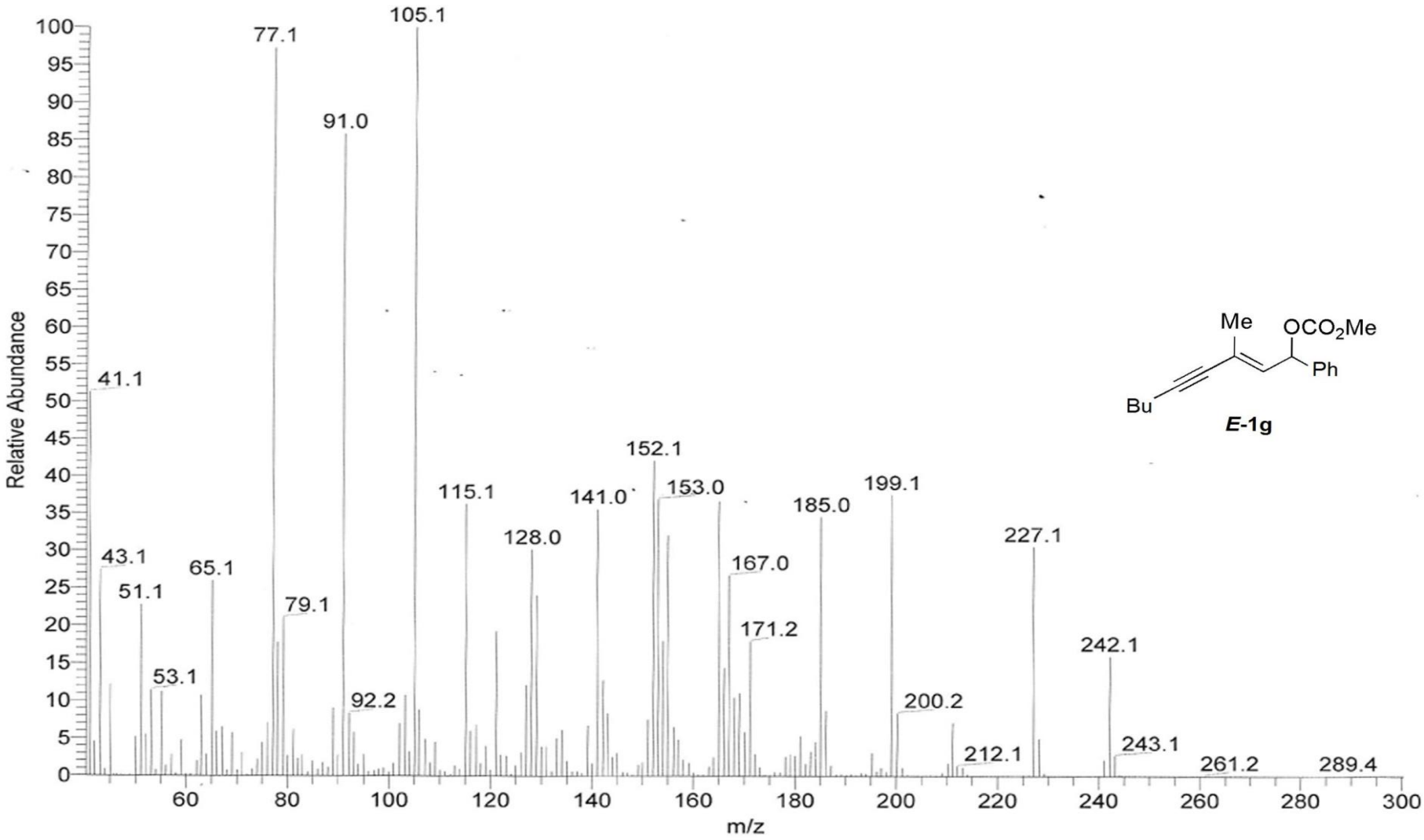

Figure B.7. Mass Spectrum of (*E*)-methyl (3-methyl-1-phenylnon-2-en-4-yn-1-yl) carbonate

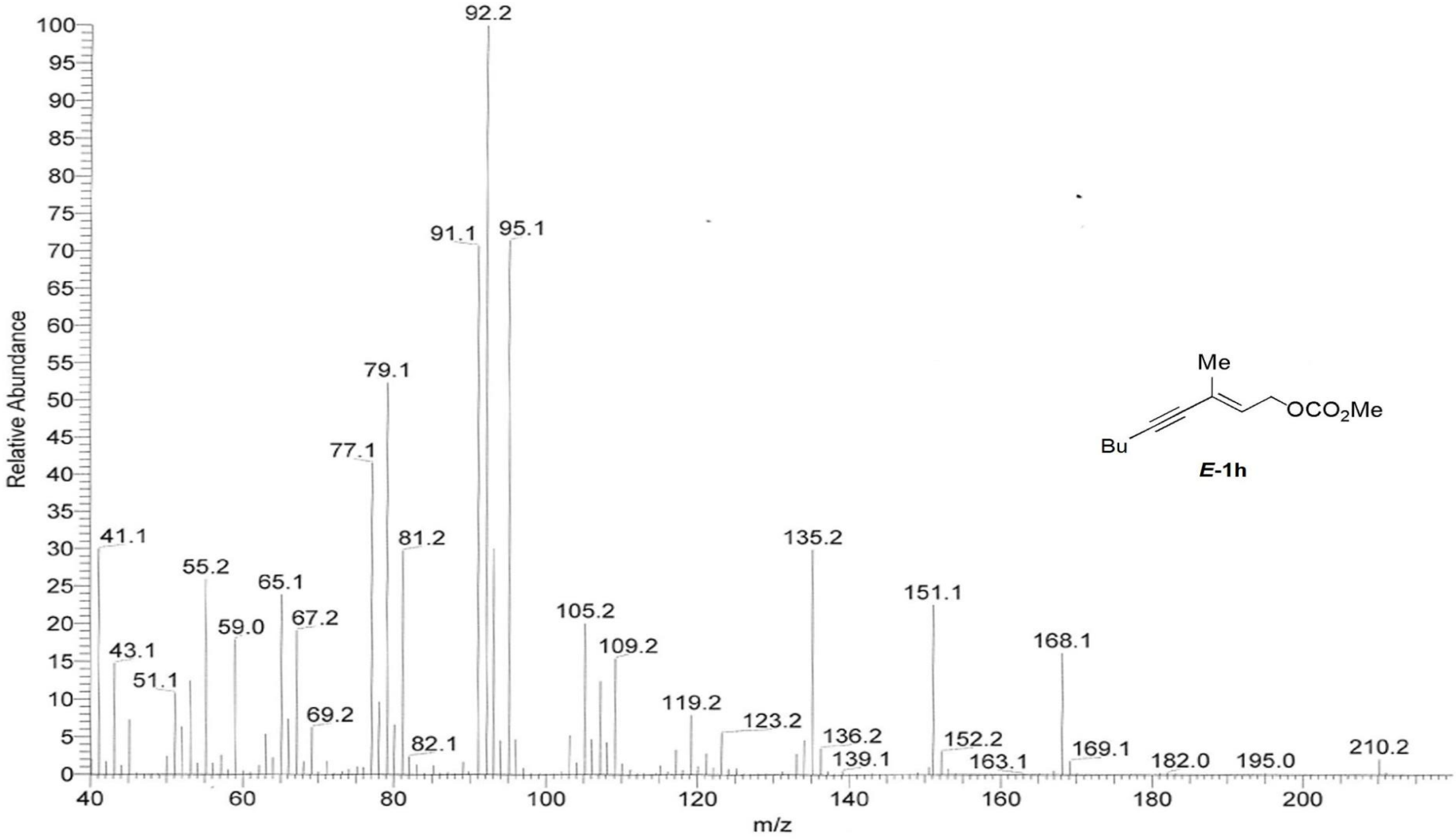

Figure B.8. Mass Spectrum of (*E*)-methyl (3-methylnon-2-en-4-yn-1-yl) carbonate

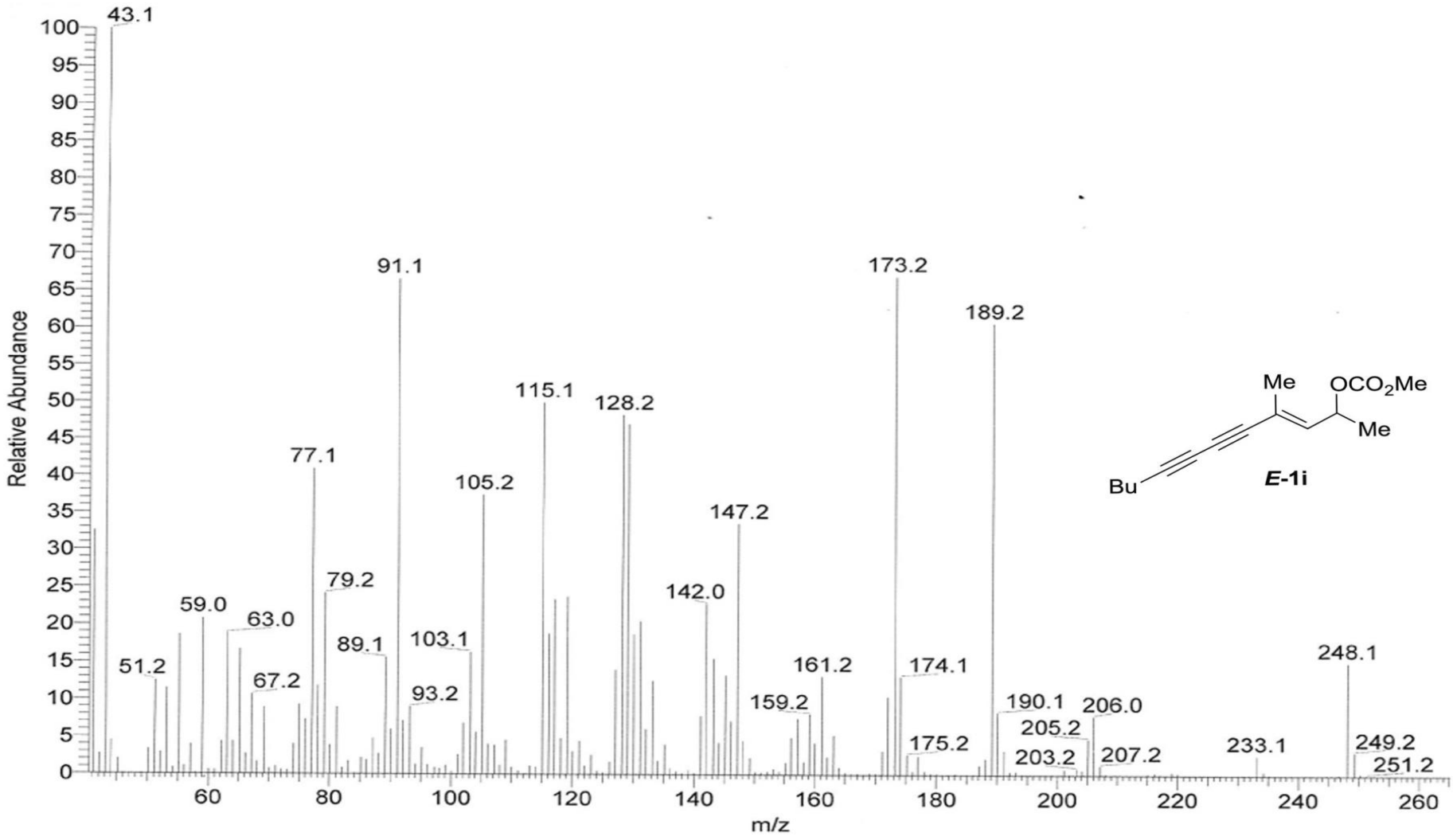

Figure B.9. Mass Spectrum of (*E*)-methyl (4-methyldodeca-3-en-5,7-diyn-2-yl) carbonate

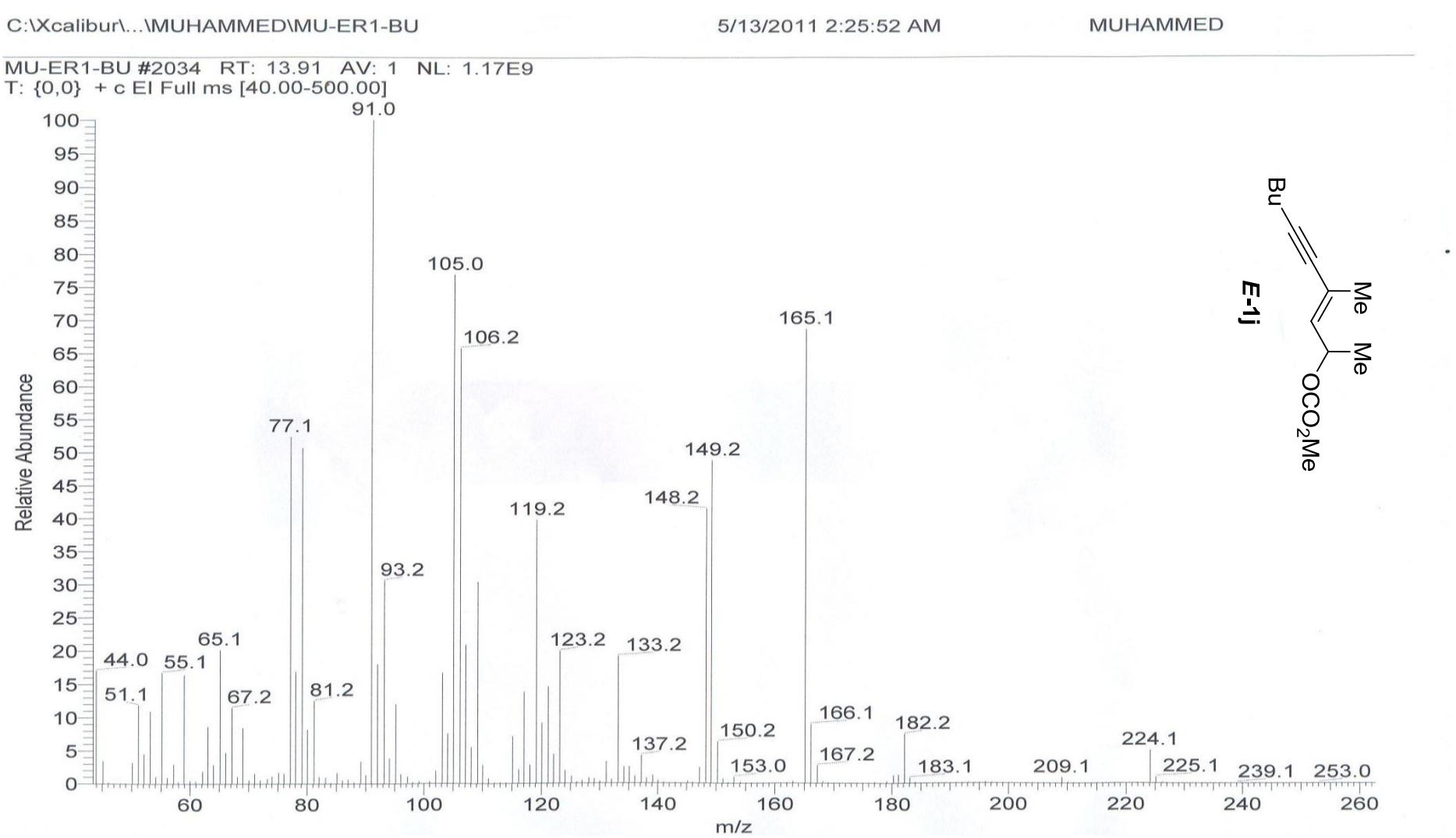

Figure B.10. Mass Spectrum of *(E)*-methyl 4-methyldec-3-en-5-yn-2-yl carbonatecarbonate

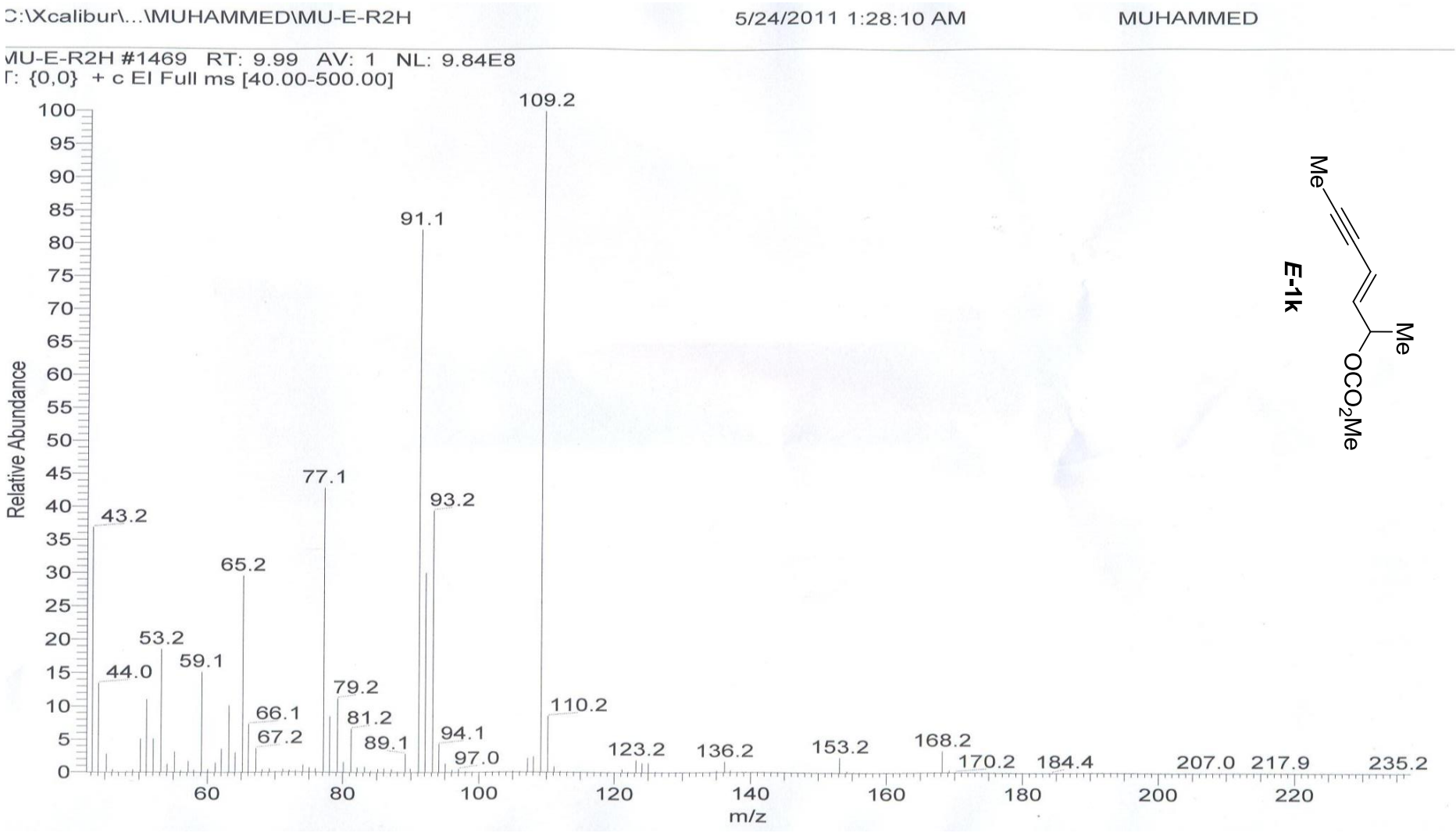

Figure B.11. Mass Spectrum of *(E)*-2,5-dimethyloct-4-en-6-yn-3-yl methyl carbonatecarbonatecarbonatecarbonatecarbonate

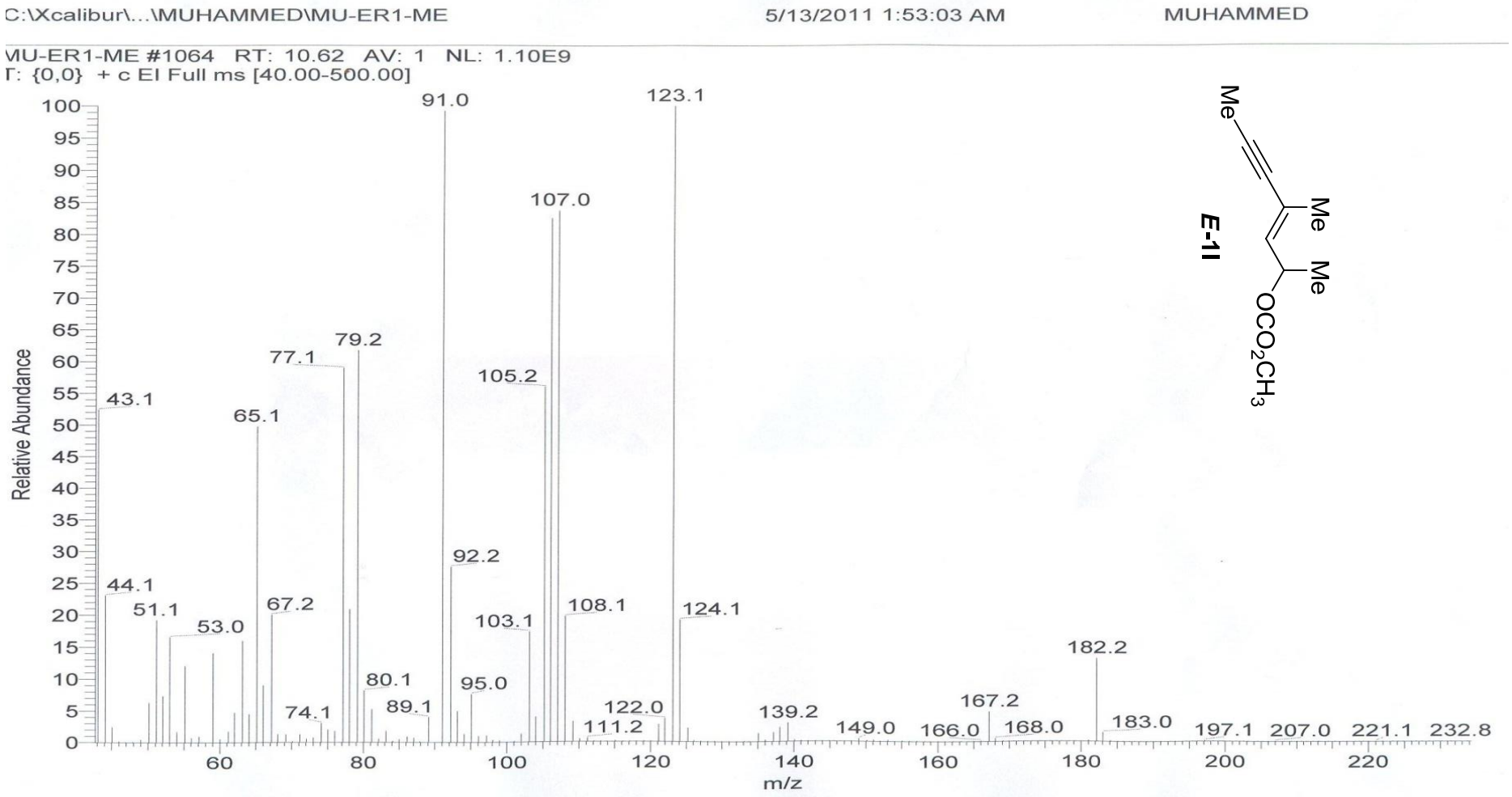

Figure B.12. Mass Spectrum of (*E*)-methyl 4-methylhept-3-en-5-yn-2-yl carbonate

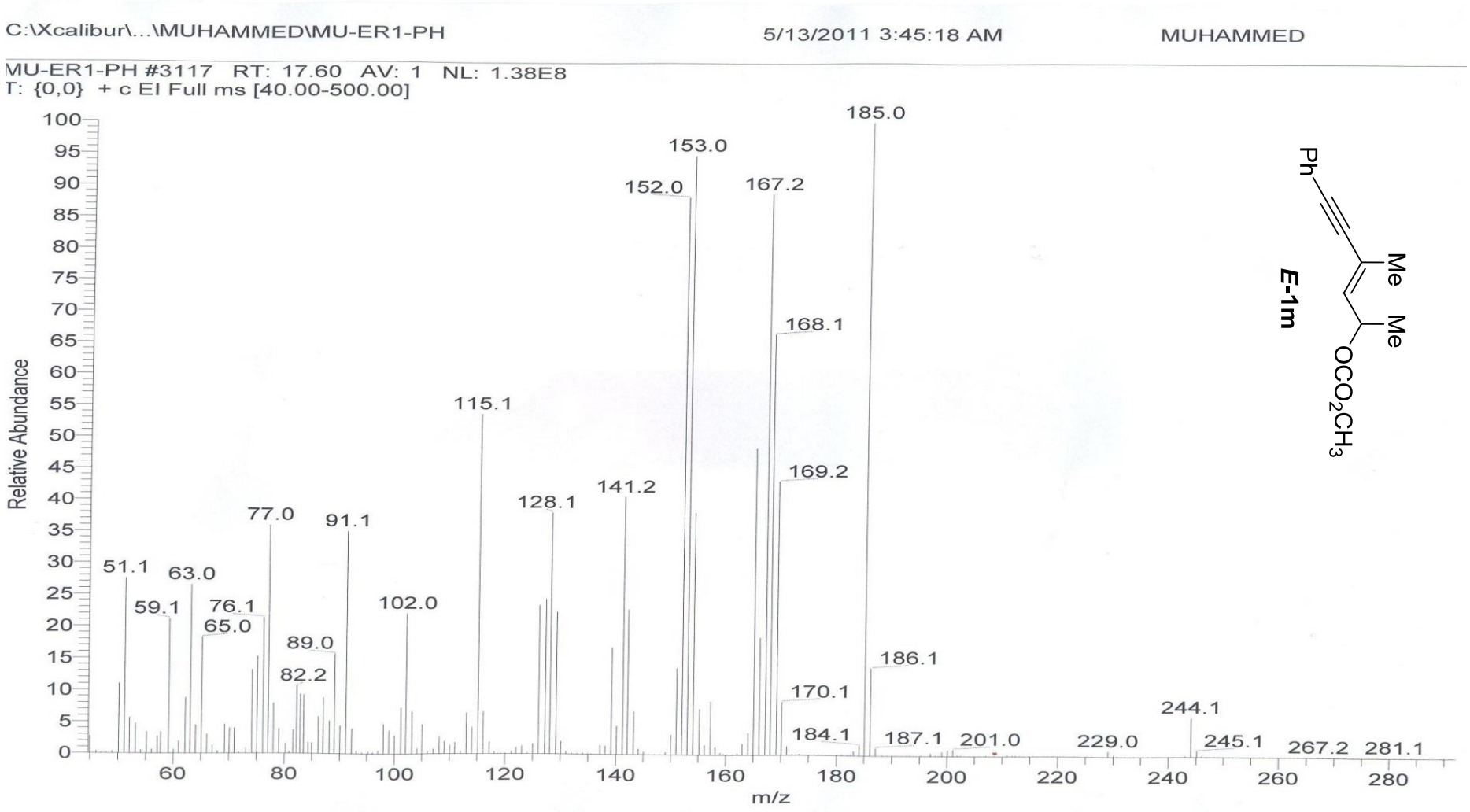

Figure B.13. Mass Spectrum of (*E*)-methyl 4-methyl-6-phenylhex-3-en-5-yn-2-yl carbonatecarbonatecarbonate

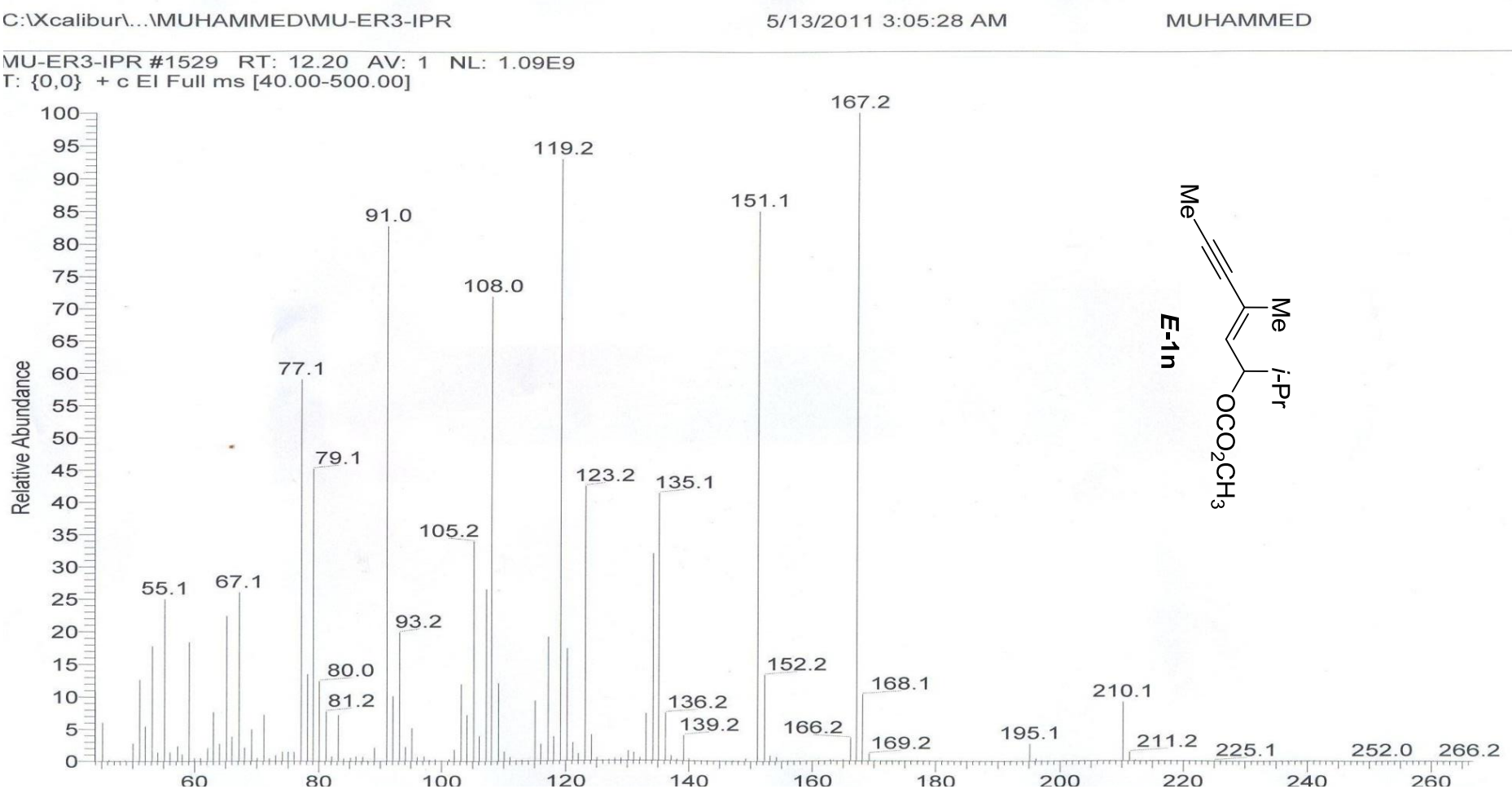

Figure B.14. Mass Spectrum of (*E*)-2,5-dimethyloct-4-en-6-yn-3-yl methyl carbonatecarbonatecarbonatecarbonatecarbonate

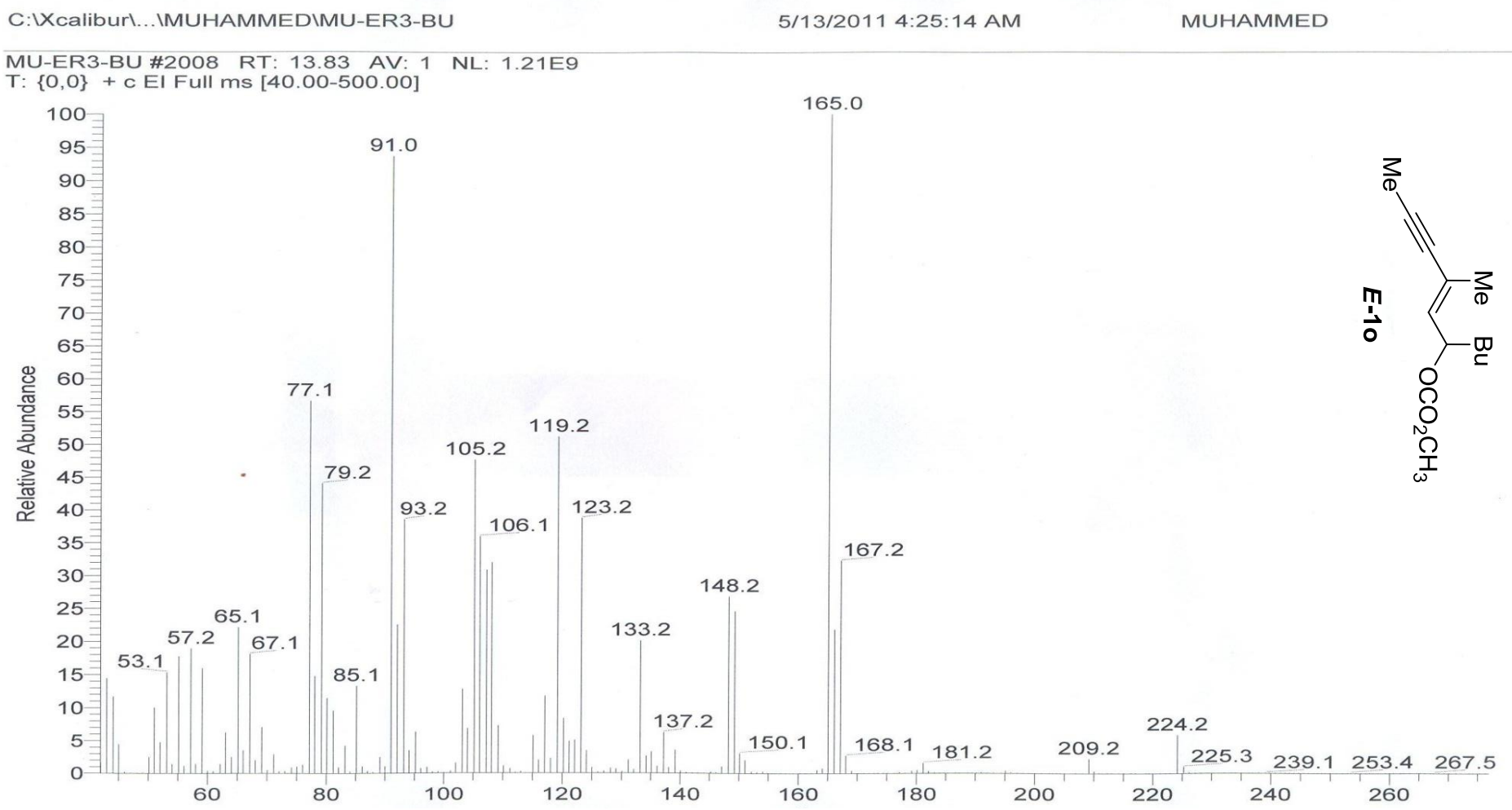

Figure B.15. Mass Spectrum of (*E*)-methyl 7-methyldec-6-en-8-yn-5-yl carbonatecarbonatecarbonatecarbonate

APPENDIX C

FTIR SPECTRUMS OF REACTANTS

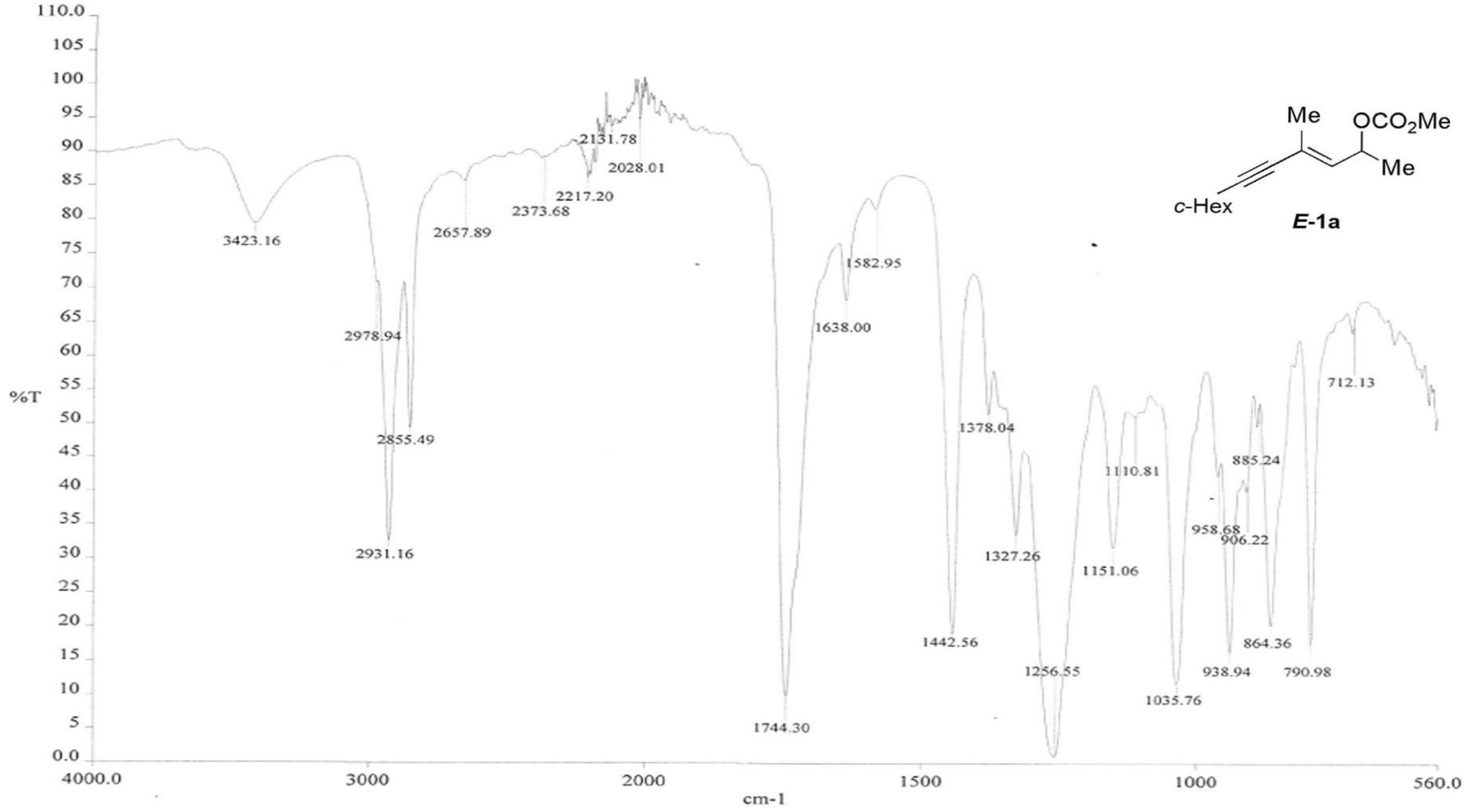

Figure C.1. FT-IR Spectrum of *(E)*-6-cyclohexyl-4-methylhex-3-en-5-yn-2-yl methyl carbonate

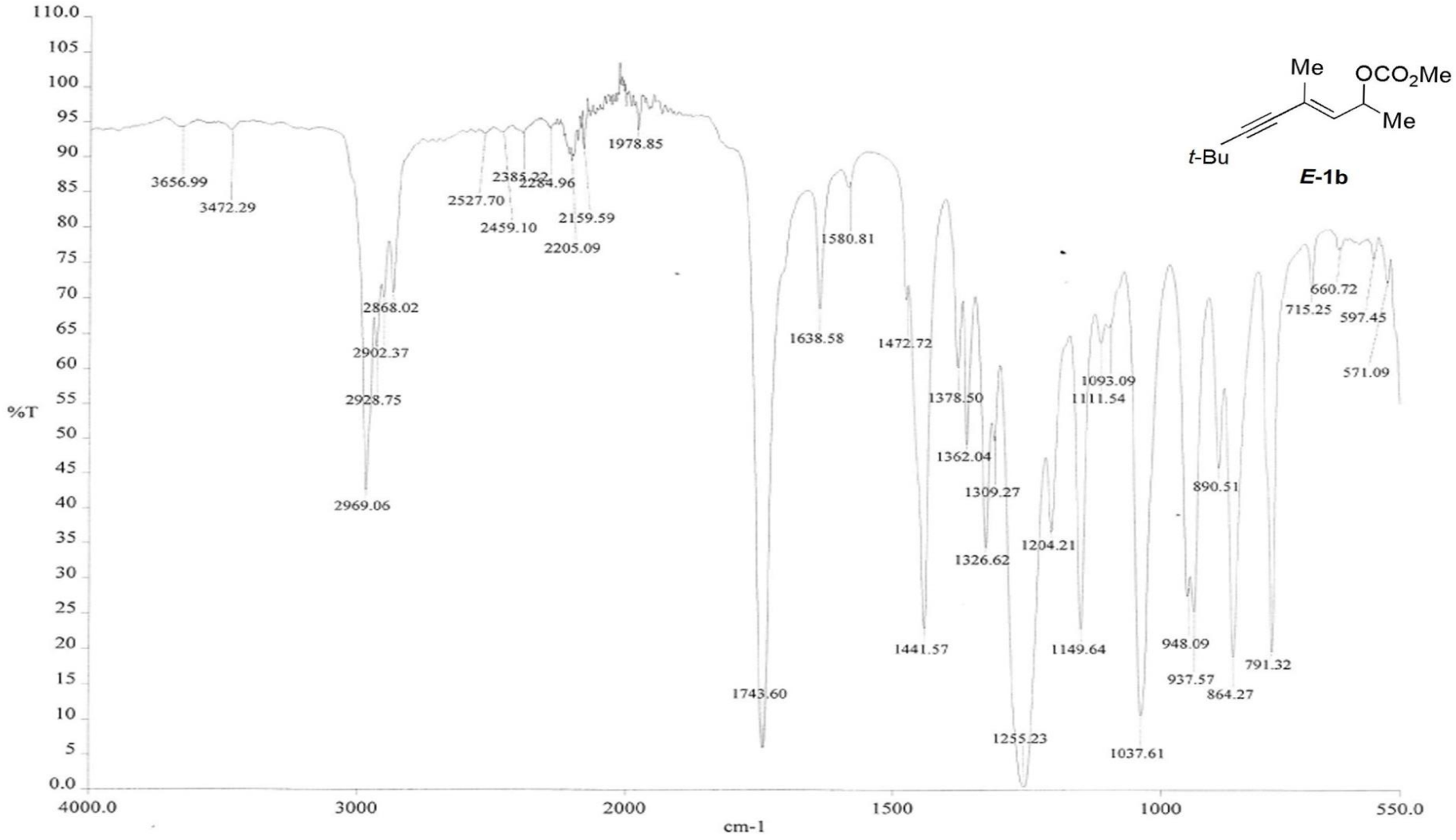

Figure C.2. FT-IR Spectrum of (*E*)-methyl (4,7,7-trimethyloct-3-en-5-yn-2-yl) carbonate

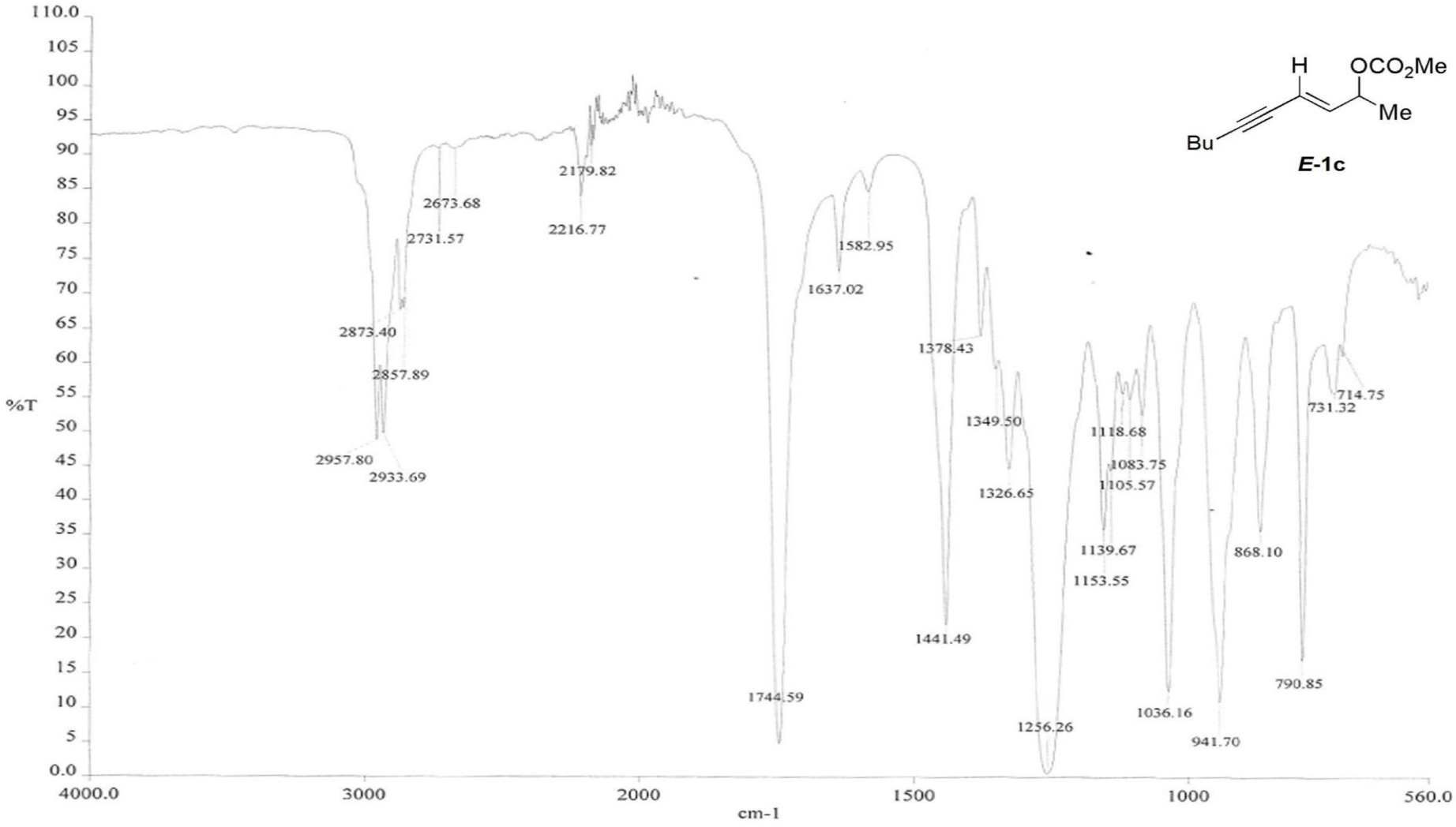

Figure C.3. FT-IR Spectrum of *(E)*-dec-3-en-5-yn-2-yl methyl carbonate

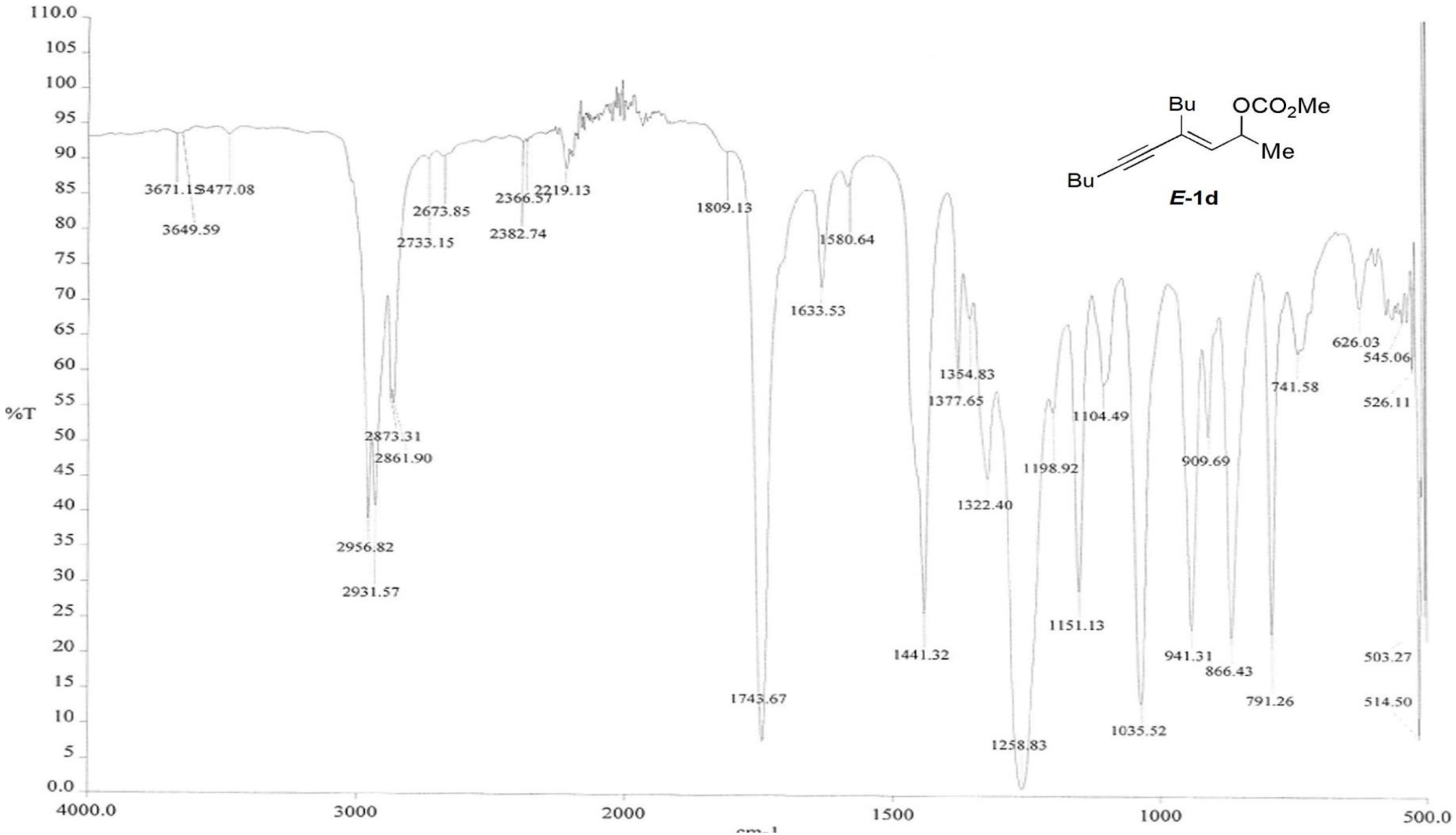

Figure C.4. FT-IR Spectrum of (*E*)-4-butyldec-3-en-5-yn-2-yl methyl carbonate

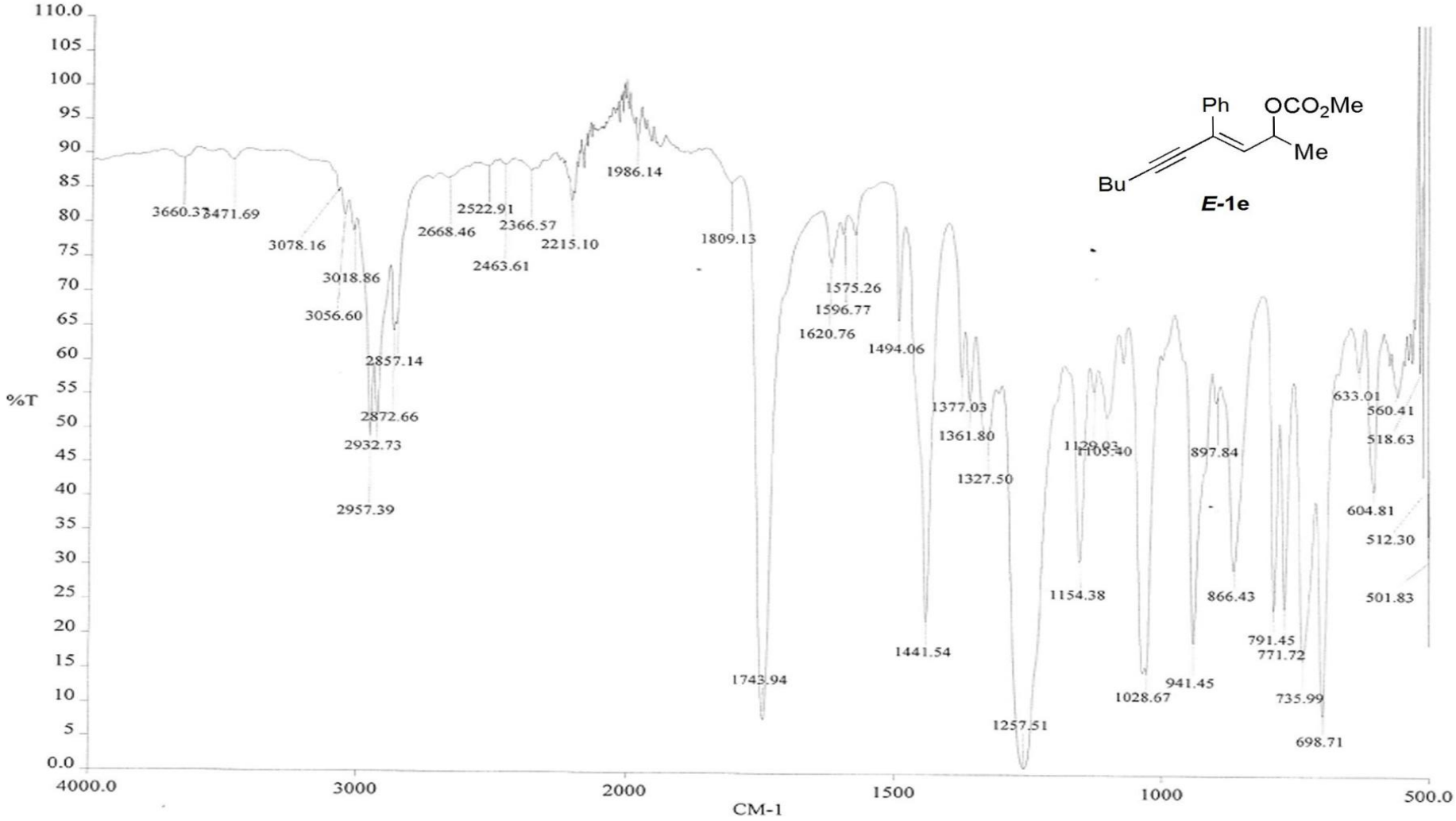

Figure C.5. FT-IR Spectrum of *(E)*-methyl (4-phenyldec-3-en-5-yn-2-yl) carbonate

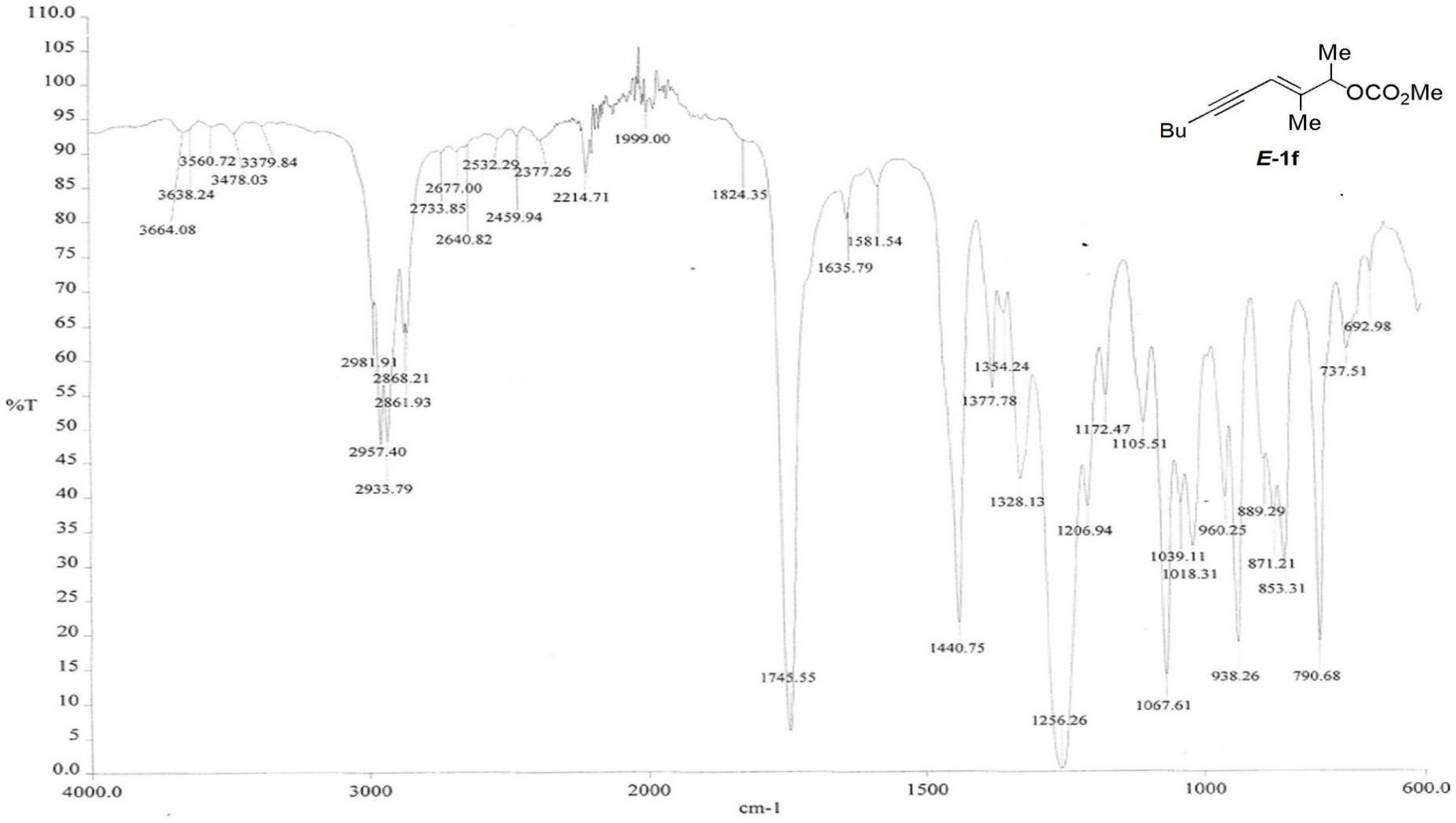

Figure C.6. FT-IR Spectrum of *(E)*-methyl (3-methyldec-3-en-5-yn-2-yl) carbonate

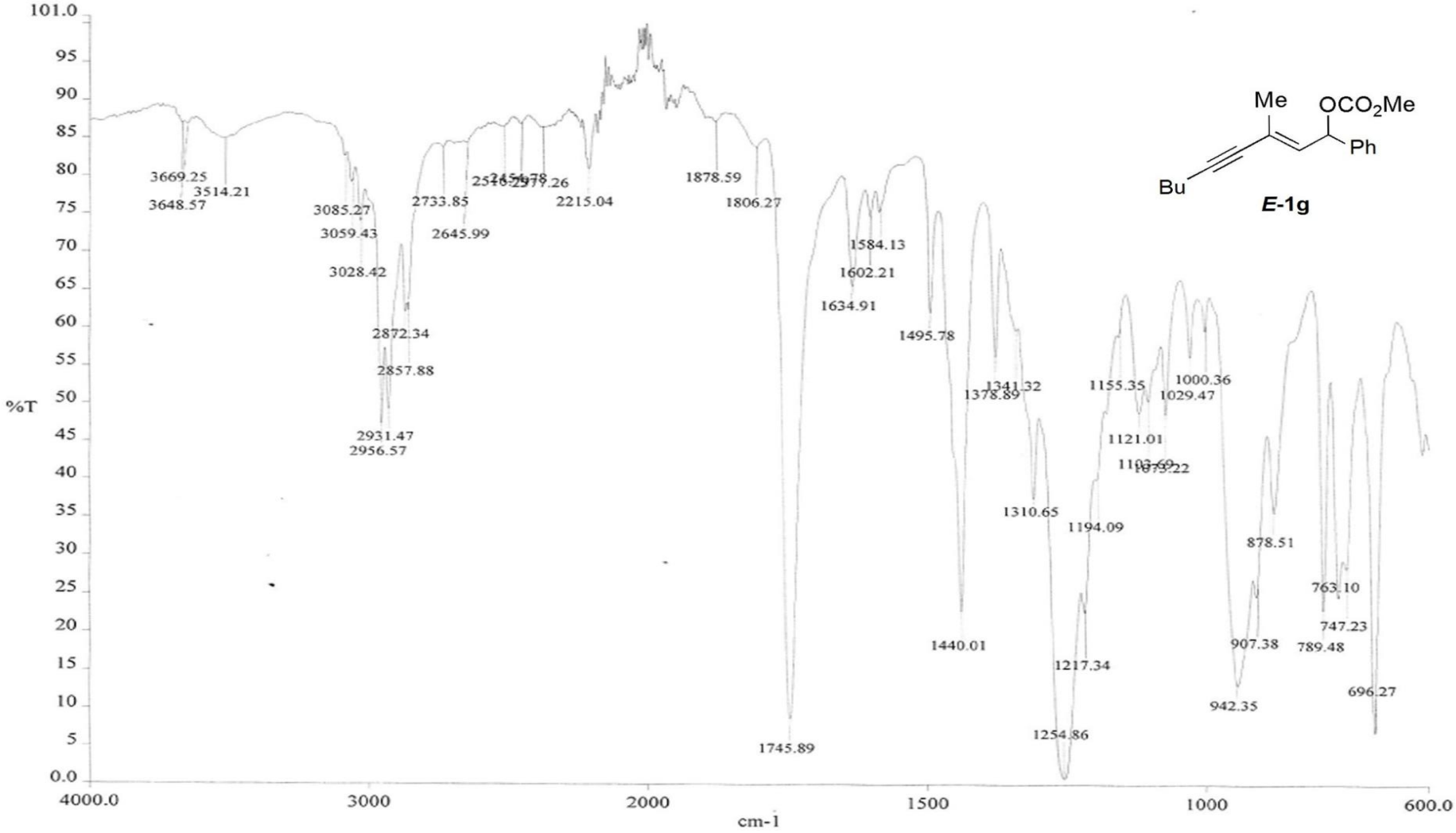

Figure C.7. FT-IR Spectrum of *(E)*-methyl (3-methyl-1-phenylnon-2-en-4-yn-1-yl) carbonate

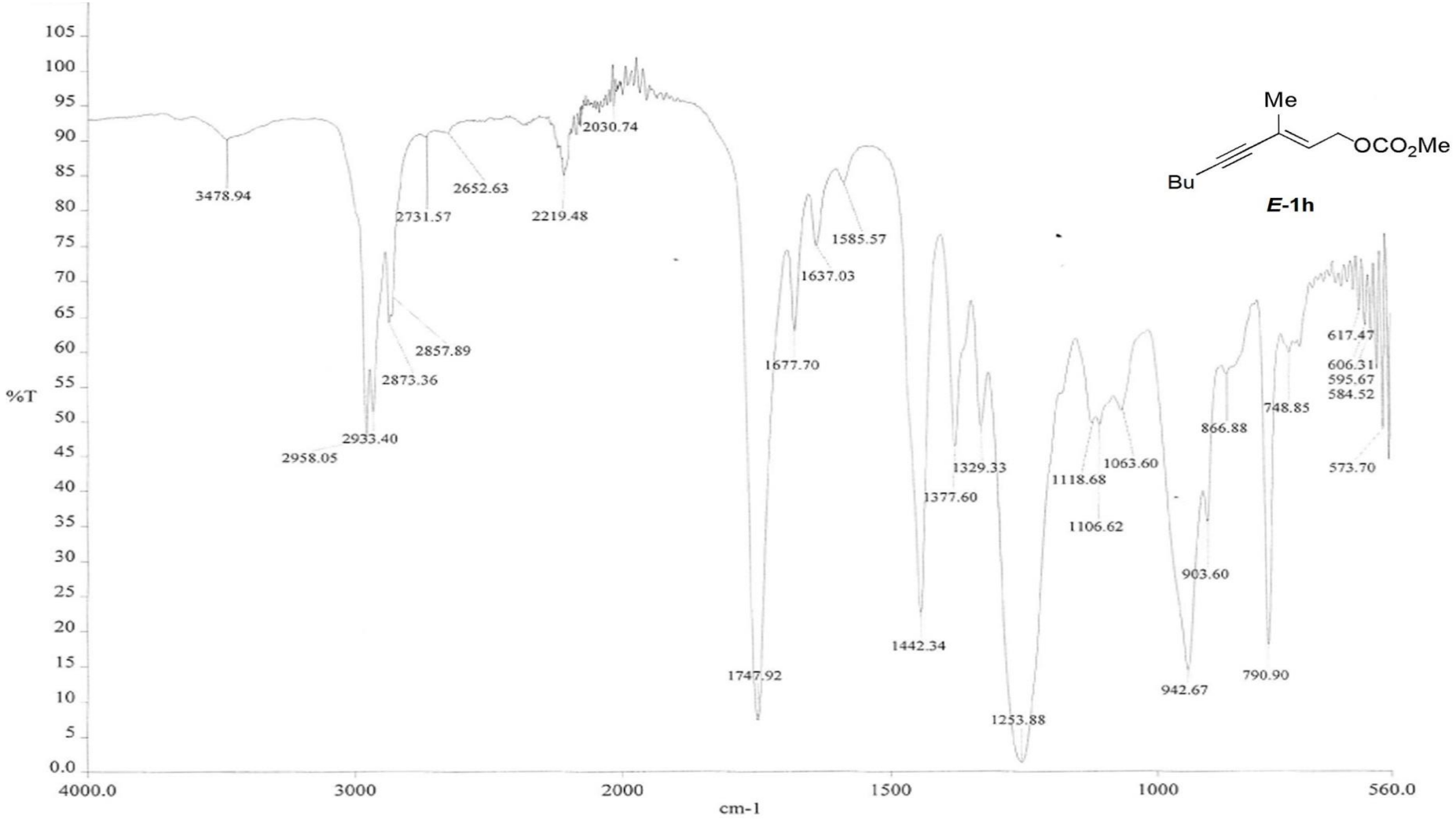

Figure C.8. FT-IR Spectrum of (*E*)-methyl (3-methylnon-2-en-4-yn-1-yl) carbonate

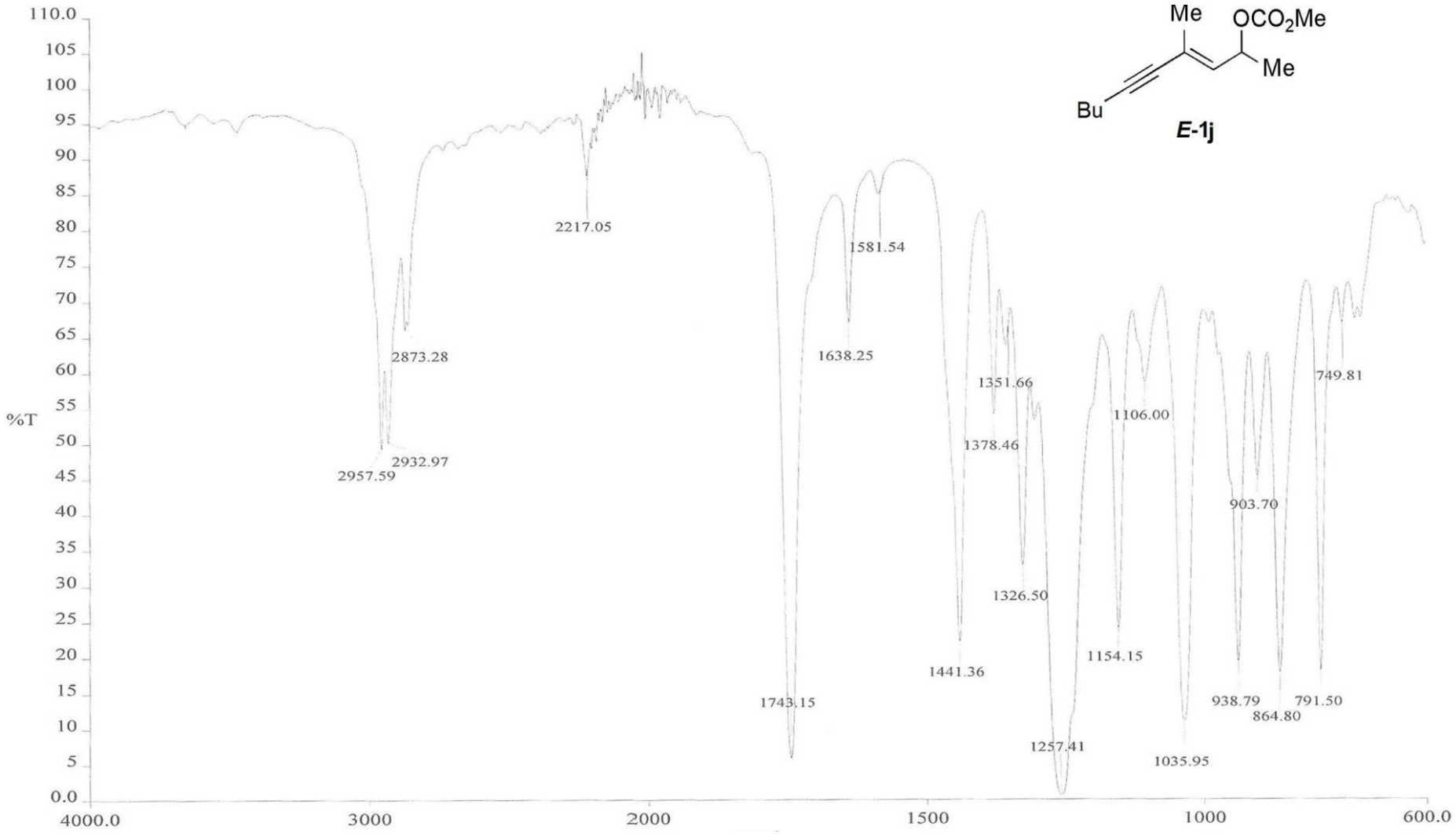

Figure C.9. FT-IR Spectrum of methyl (*E*)-4-methyldec-3-en-5-yn-2-yl carbonate

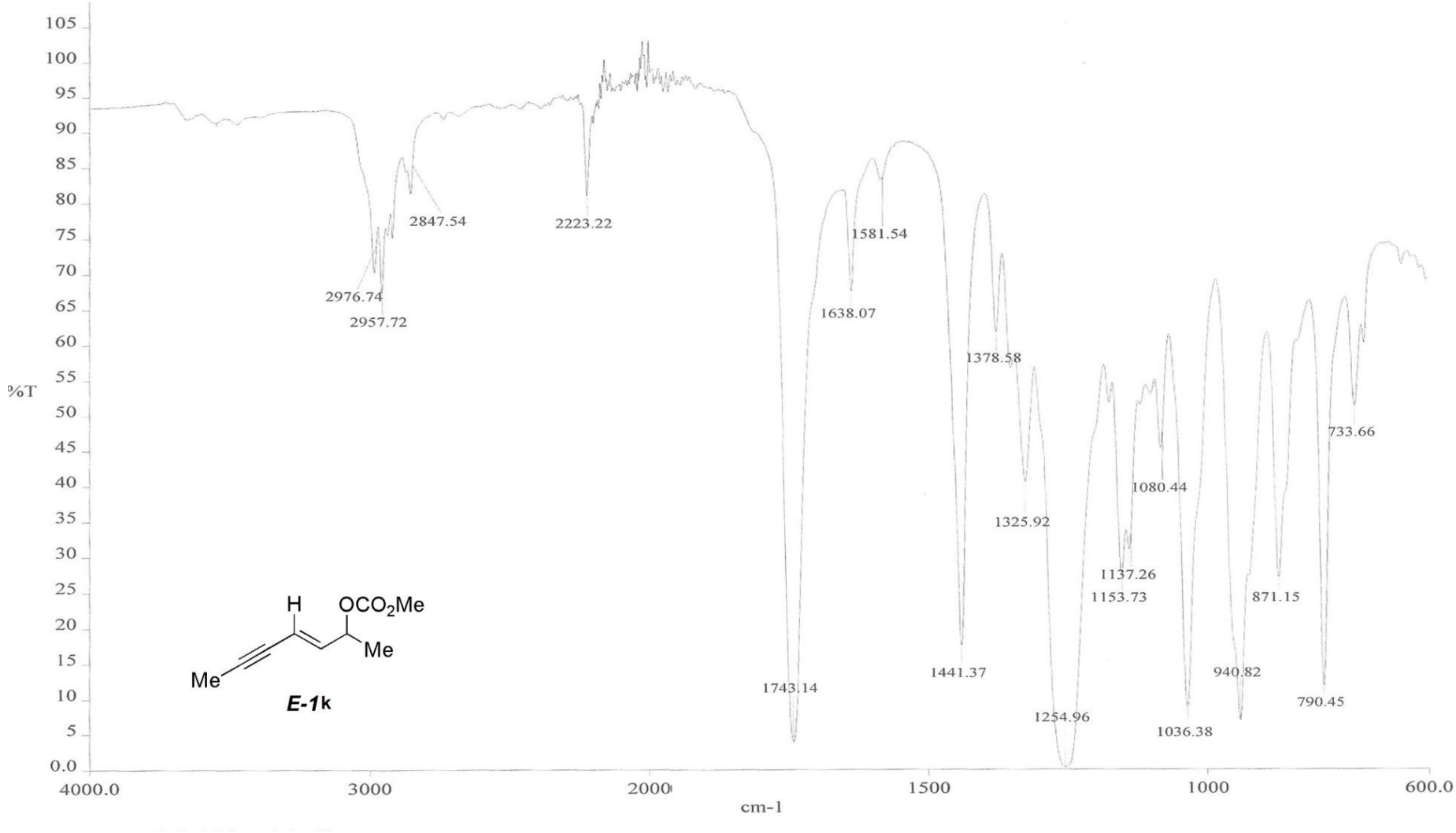

Figure C.10. FT-IR Spectrum of (*E*)-hept-3-en-5-yn-2-yl methyl

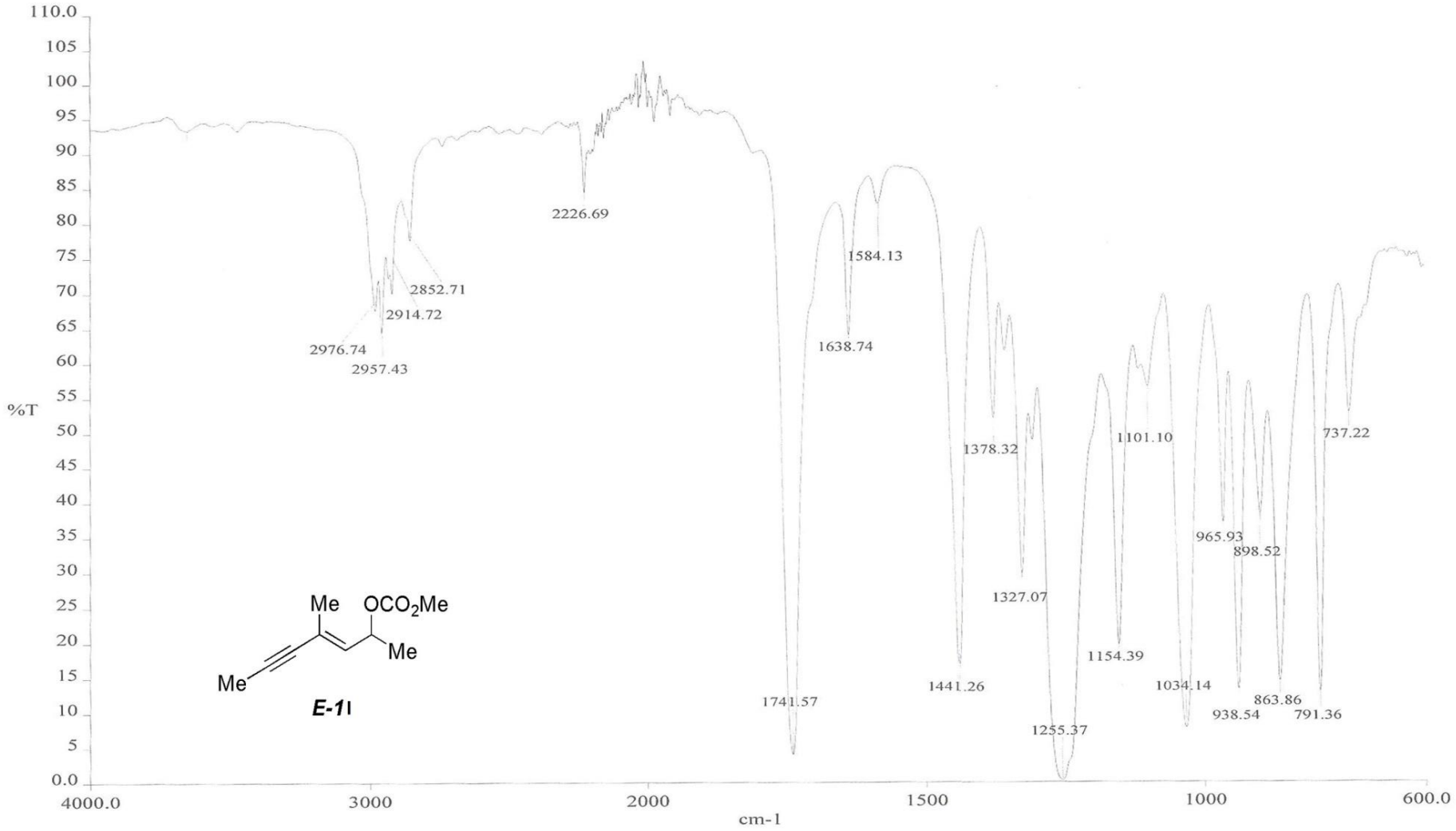

Figure C.11. FT-IR Spectrum of *(E)*-methyl 4-methylhept-3-en-5-yn-2-yl

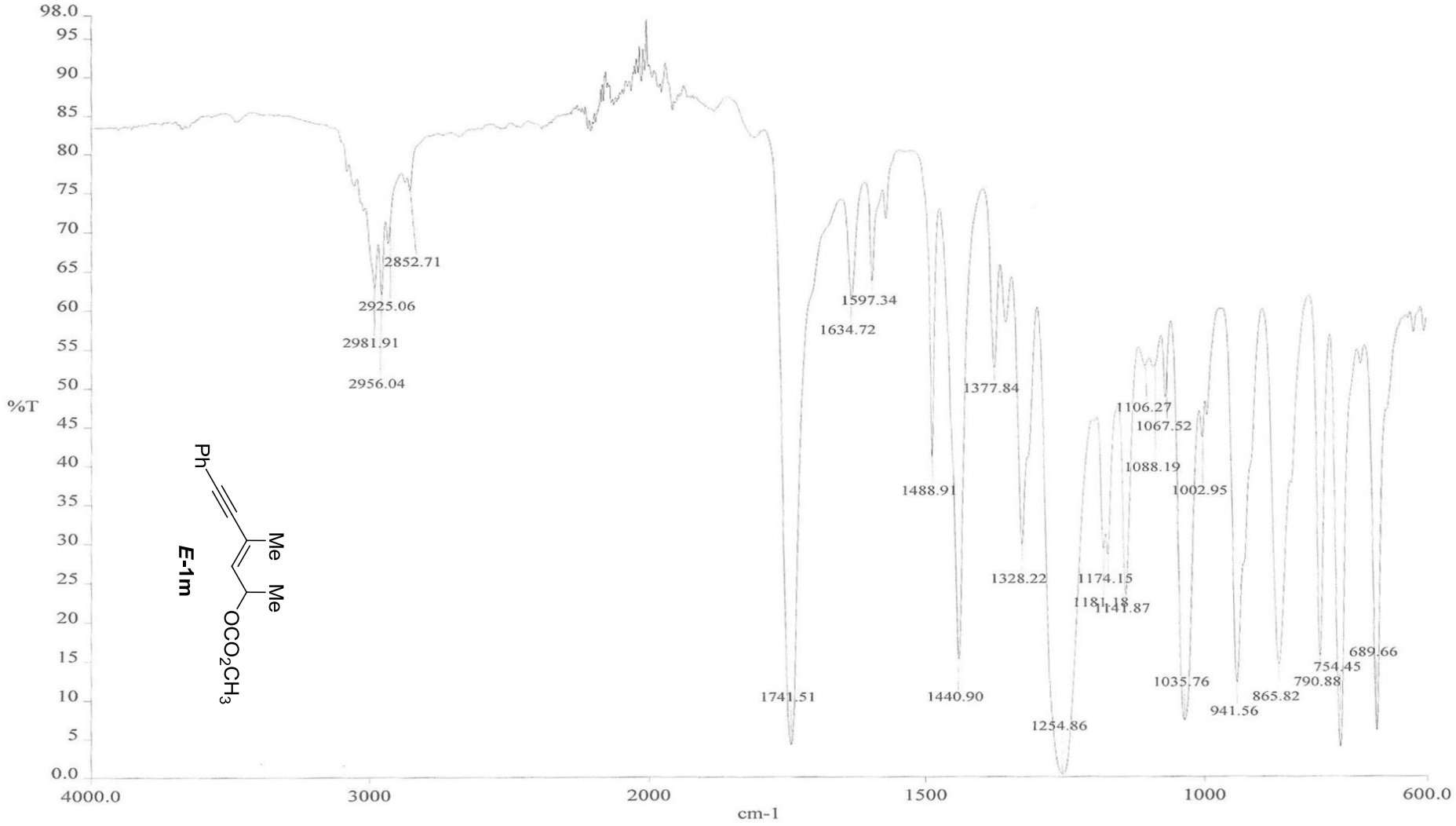

Figure C.12. FT-IR Spectrum of *(E)*-methyl 4-methyl-6-phenylhex-3-en-5-yn-2-yl

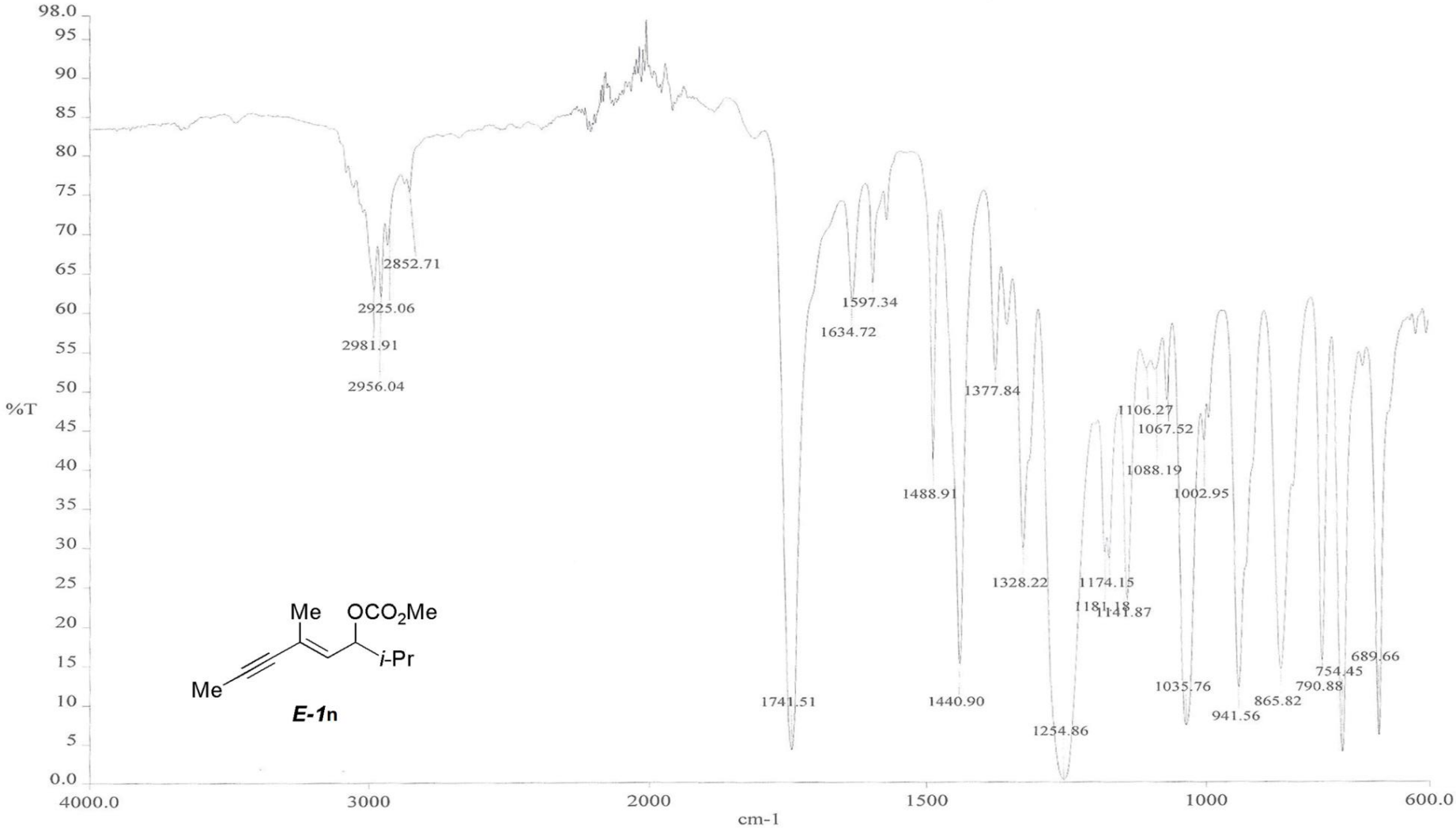

Figure C.13. FT-IR Spectrum of (*E*)-2,5-dimethyloct-4-en-6-yn-3-yl methyl

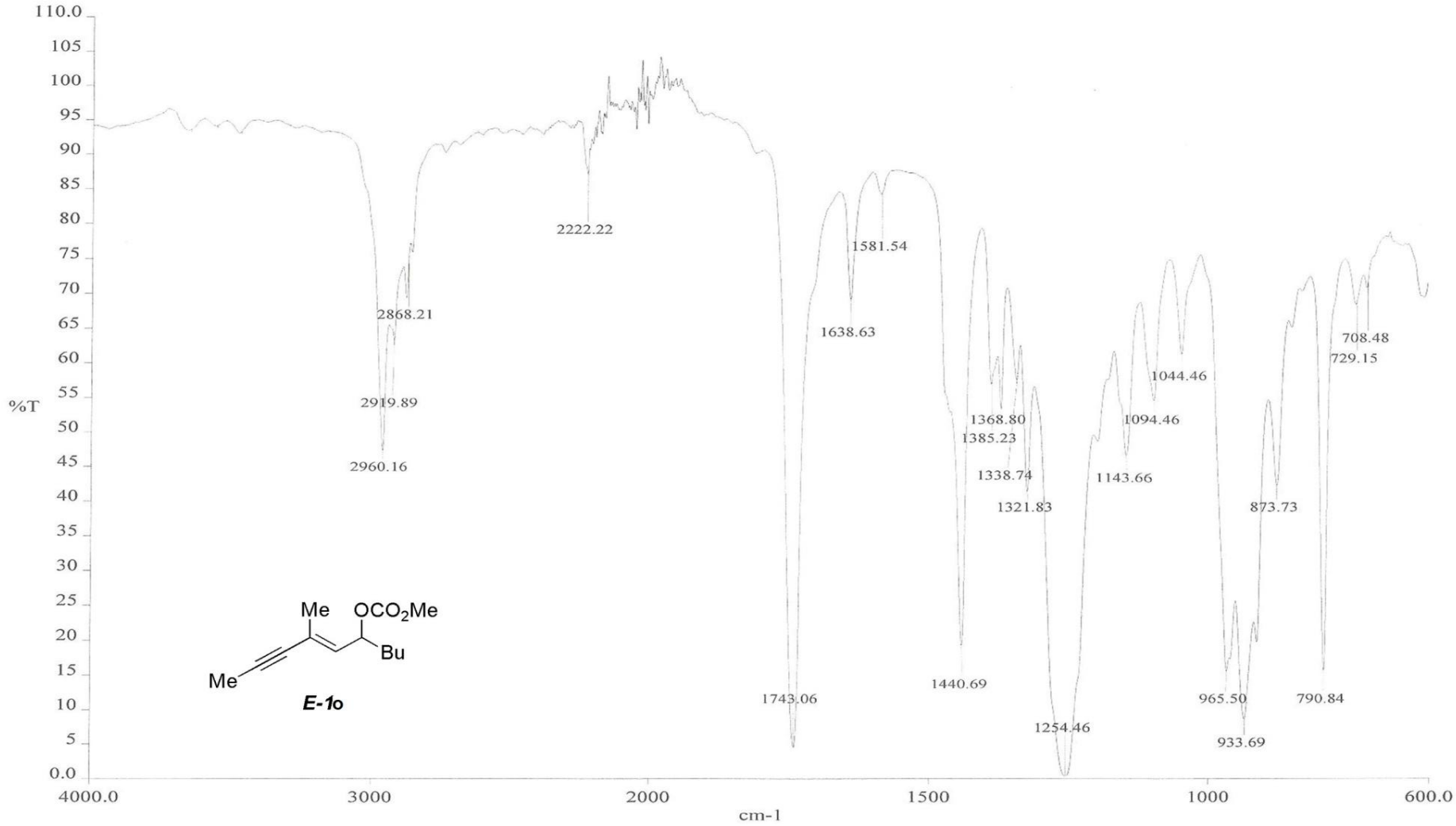

Figure C.14. FT-IR Spectrum of *(E)*-methyl 7-methyldec-6-en-8-yn-5-yl

APPENDIX D

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

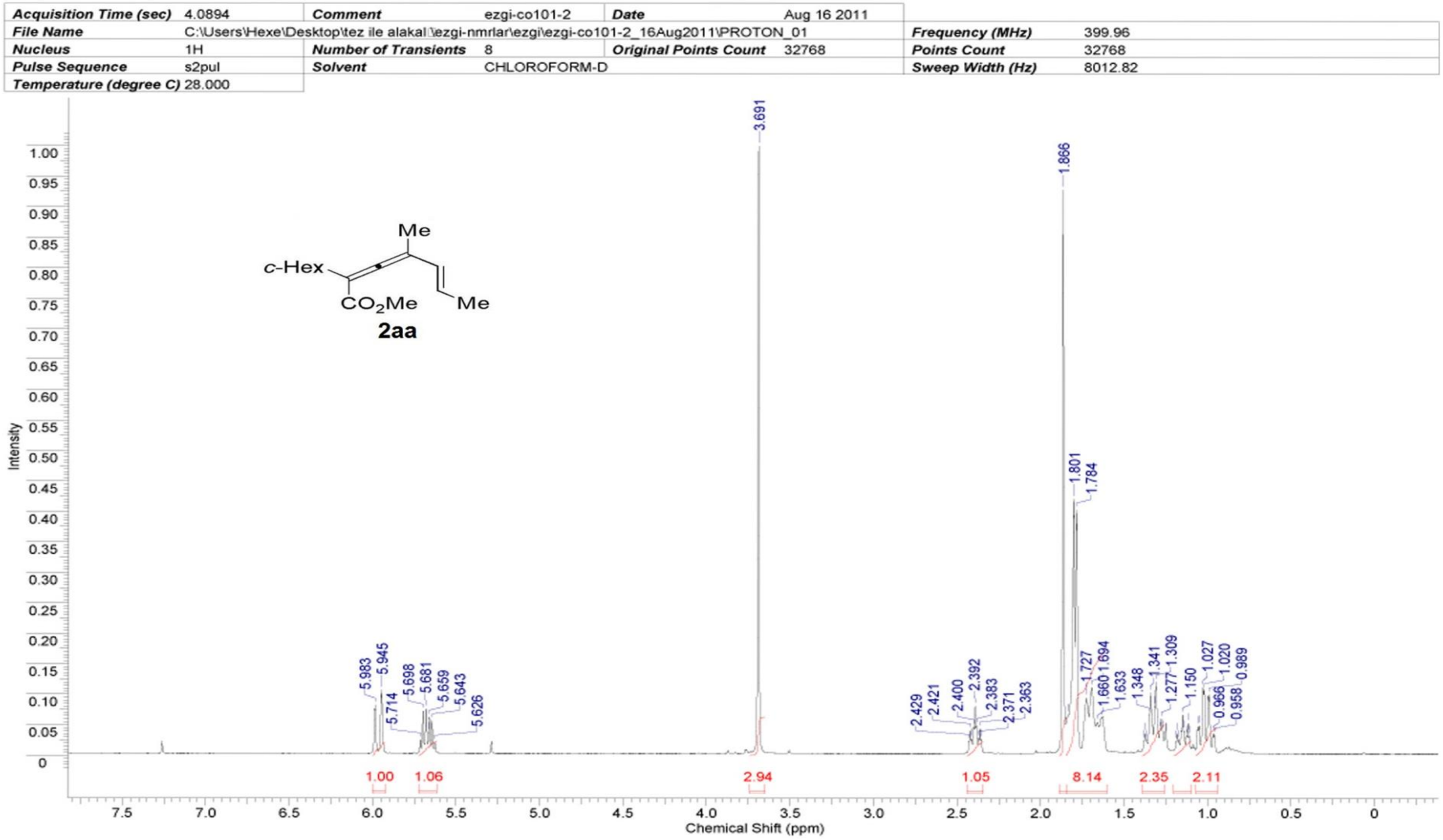

Figure D.1. [1] H NMR of (*E*)-methyl 2-cyclohexyl-4-methylhepta-2,3,5-trienoate

Acquisition Time (sec)	1.2845	***Comment***	ezgico101-2	***Date***	Aug 15 2011		
File Name	C:\Users\Hexe\Desktop\tez ile alakalı\ezgi-nmrlar\ezgi\ezgico101-2_15Aug2011\CARBON_01					***Frequency (MHz)***	100.58
Nucleus	13C	***Number of Transients***	256	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	25510.20
Temperature (degree C)	28.000						

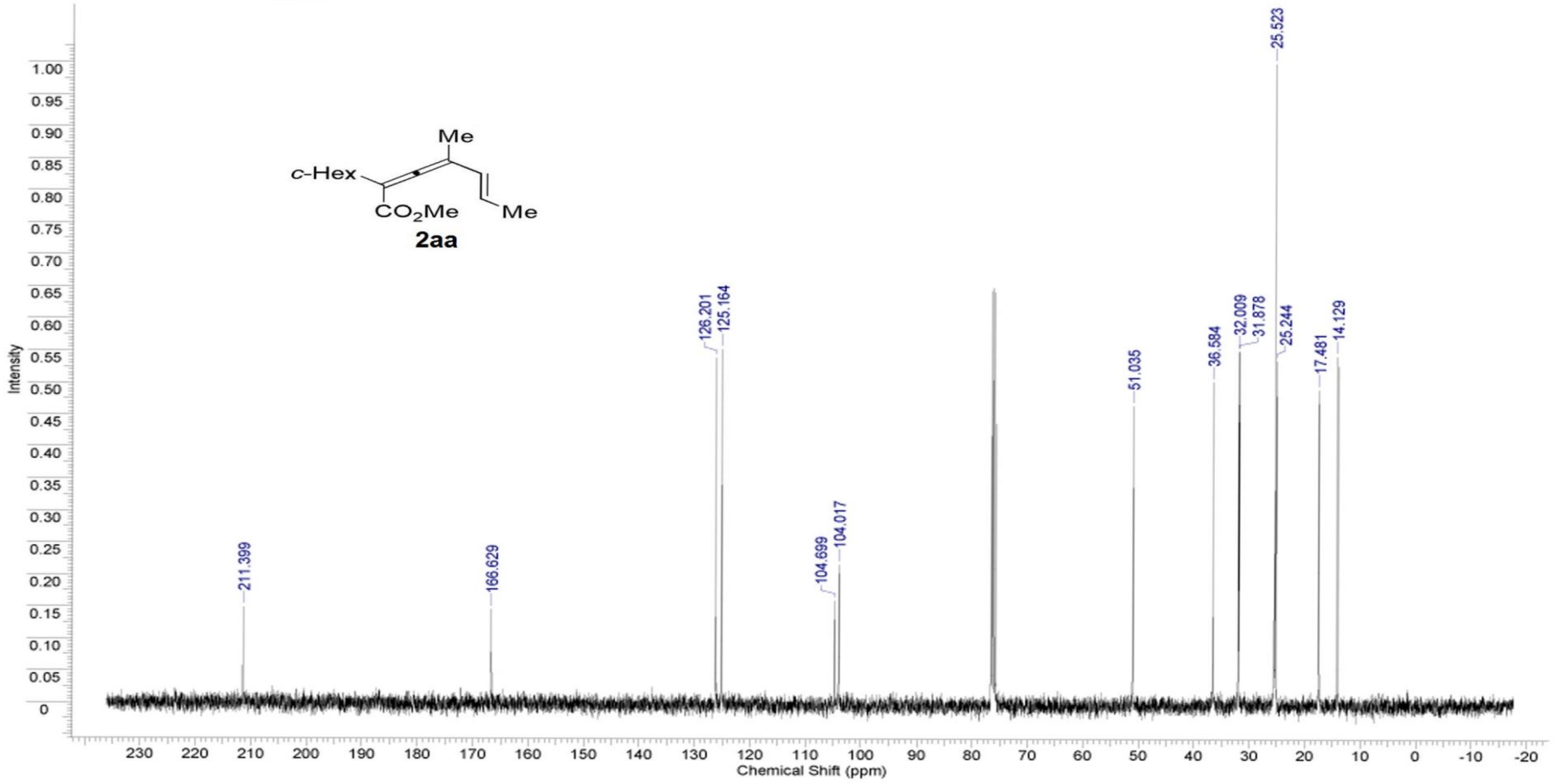

Figure D.2. ^{13} C NMR of (*E*)-methyl 2-cyclohexyl-4-methylhepta-2,3,5-trienoate

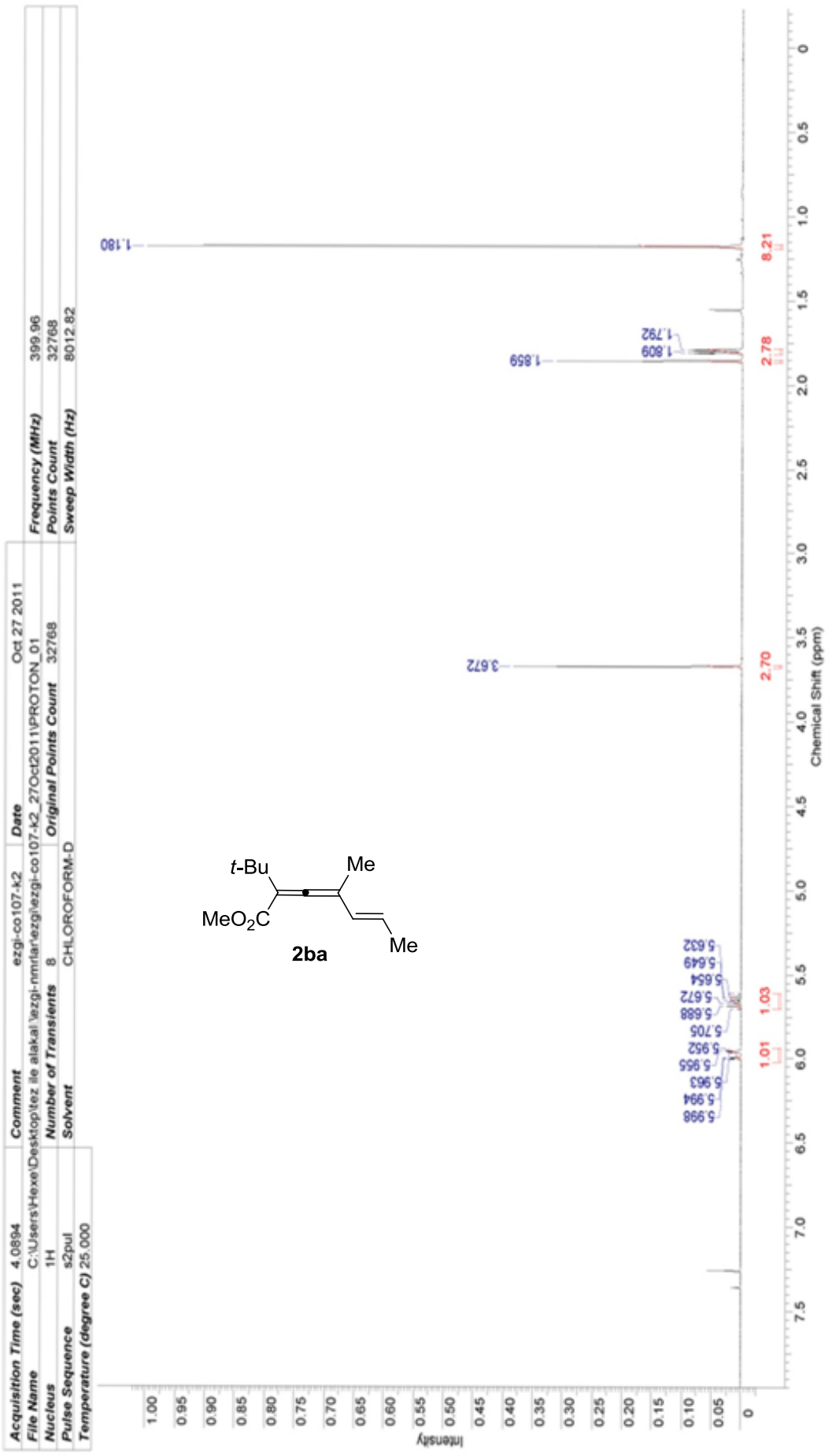

Figure D.3. ^{1}H NMR of (*E*)-methyl 2-(tert-butyl)-4-methylhepta-2,3,5-trienoate

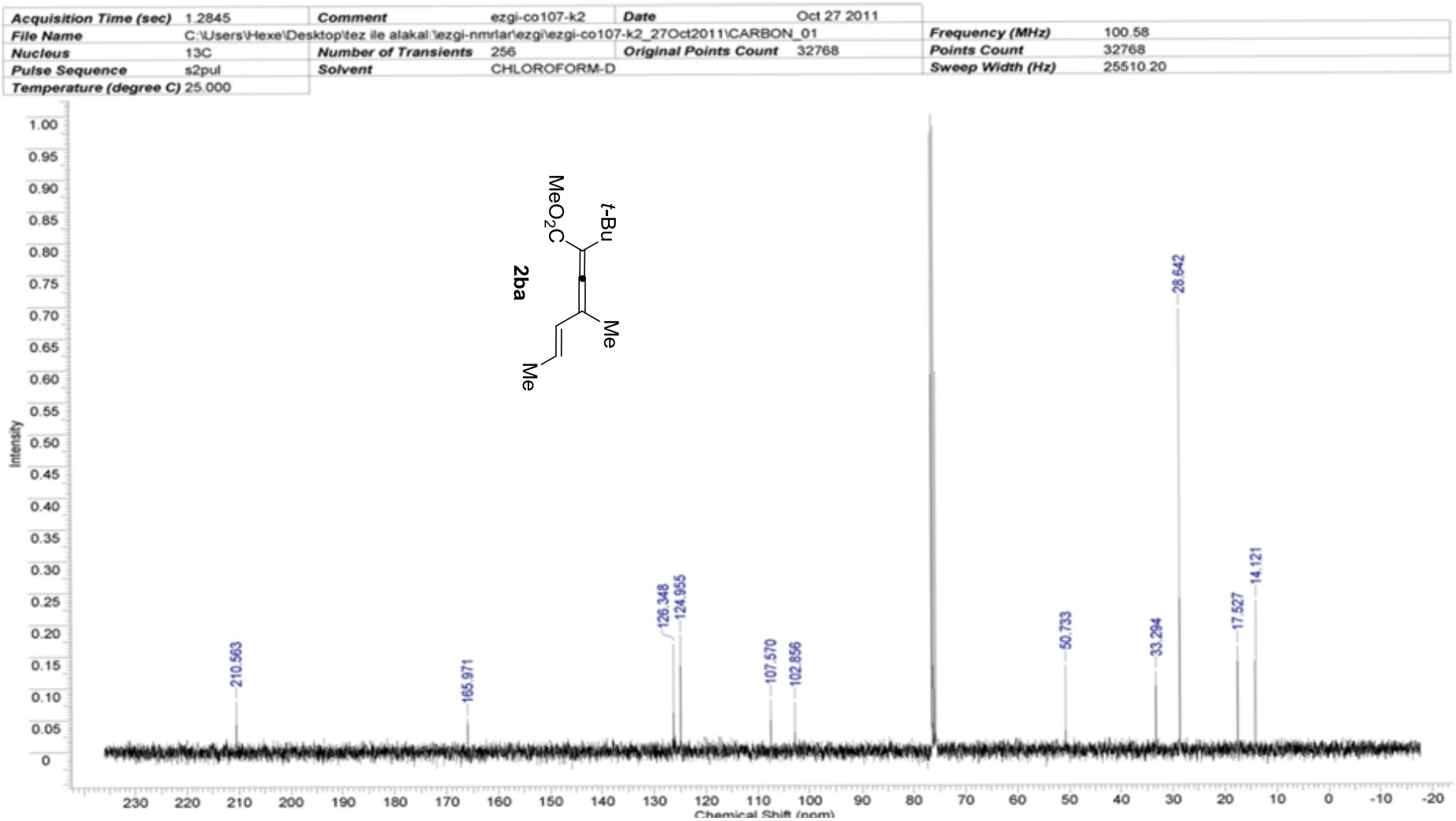

Figure D.4. ^{13} C NMR of (*E*)-methyl 2-(tert-butyl)-4-methylhepta-2,3,5-trienoate

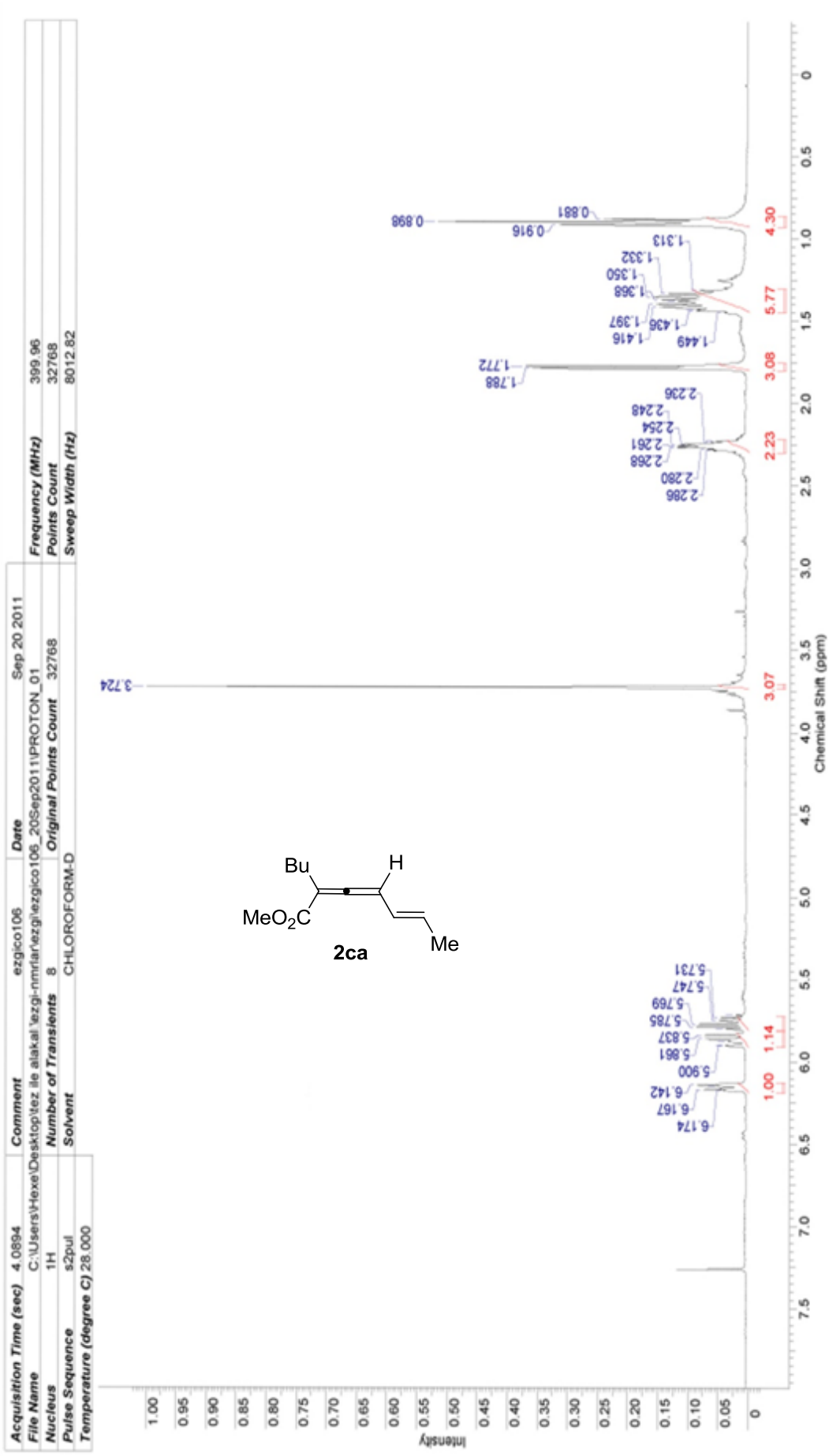

Figure D.5. ^{1}H NMR of (*E*)-methyl 2-butylhepta-2,3,5-trienoate

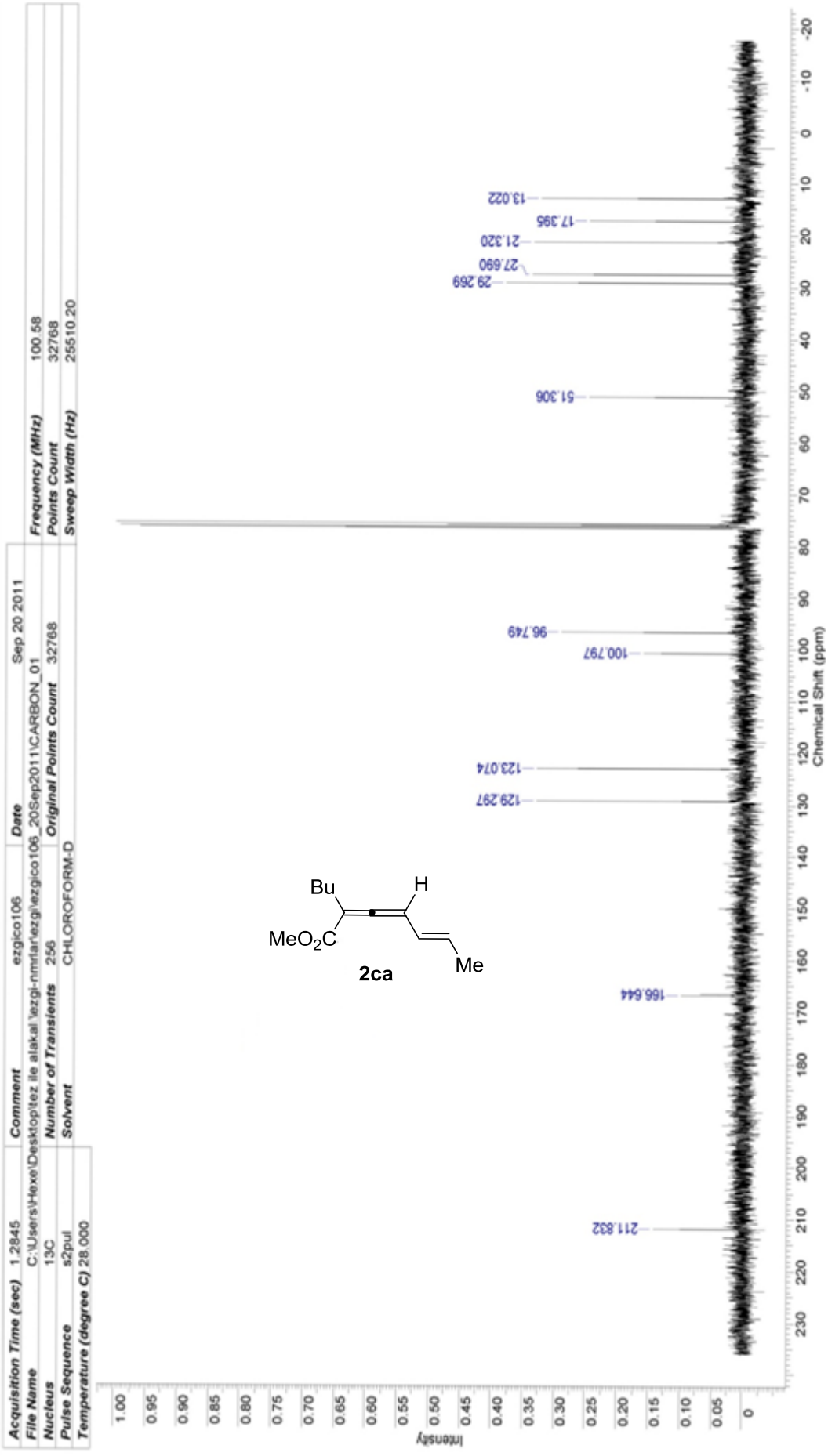

Figure D.6. ^{13}C NMR of (*E*)-methyl 2-butylhepta-2,3,5-trienoate

Acquisition Time (sec)	2.5559	*Comment*	ezgi-co108-ksm2			*Date*	Dec 9 2011
File Name	F:\ezgi-co108-ksm2_09Dec2011\PROTON_01			*Frequency (MHz)*	399.96	*Nucleus*	1H
Original Points Count	16384	*Points Count*	16384	*Pulse Sequence*	s2pul	*Solvent*	CHLOROFORM-D
Sweep Width (Hz)	6410.26	*Temperature (degree C)*	25.000				

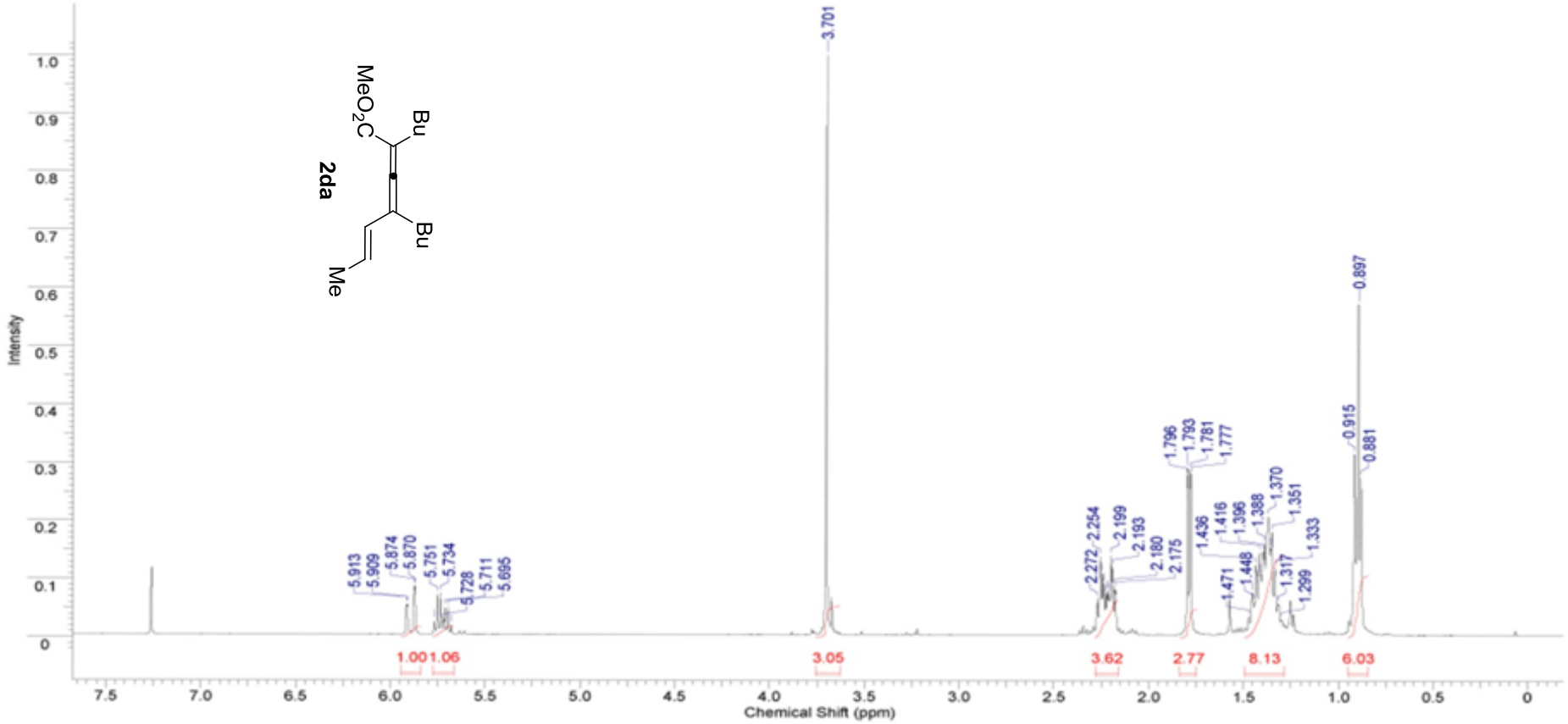

Figure D.7. [1] H NMR of (*E*)-methyl 2-butyl-4-(prop-1-en-1-yl)octa-2,3-dienoate

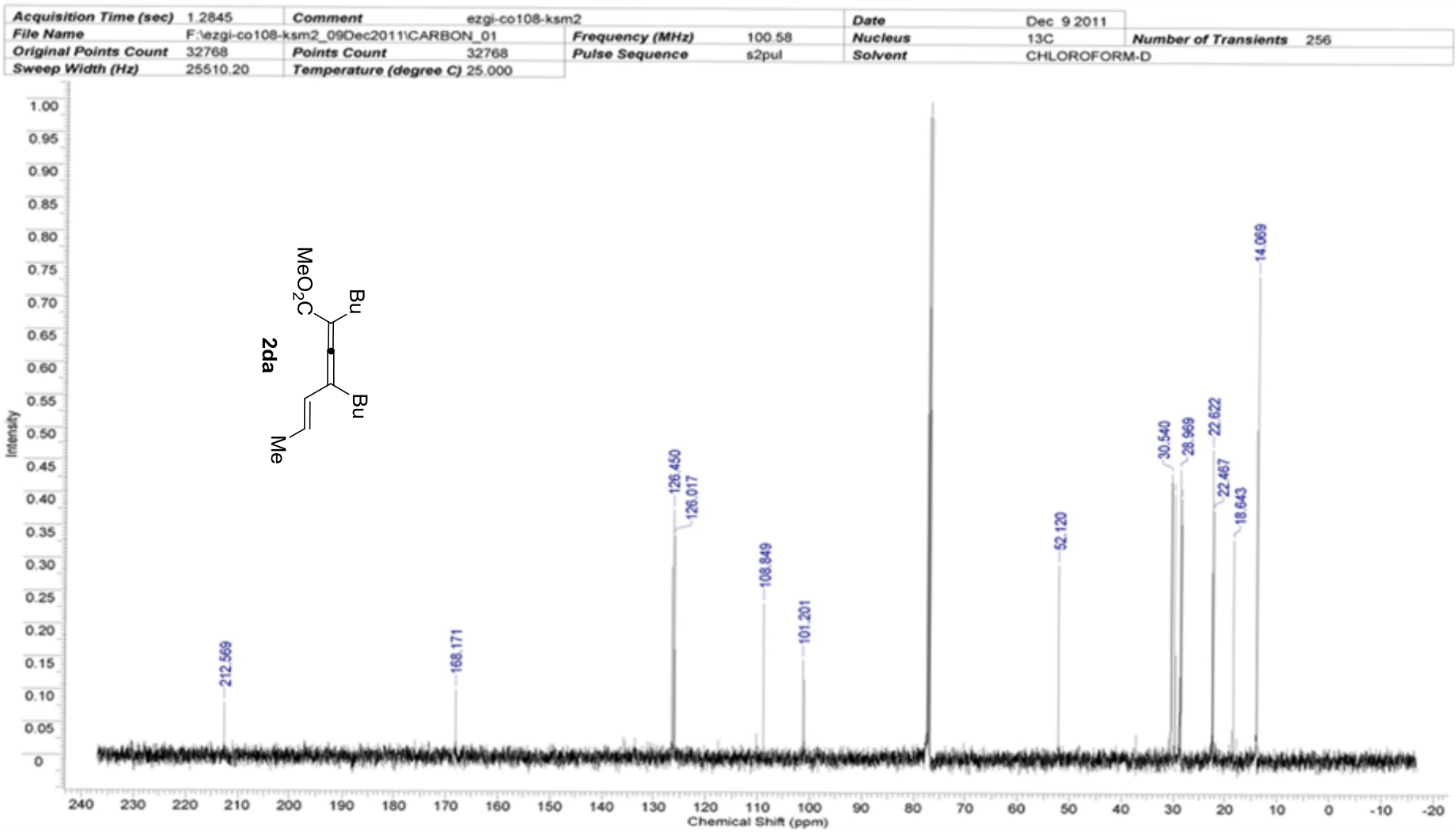

Figure D.8. ^{13} C NMR of (*E*)-methyl 2-butyl-4-(prop-1-en-1-yl)octa-2,3-dienoate

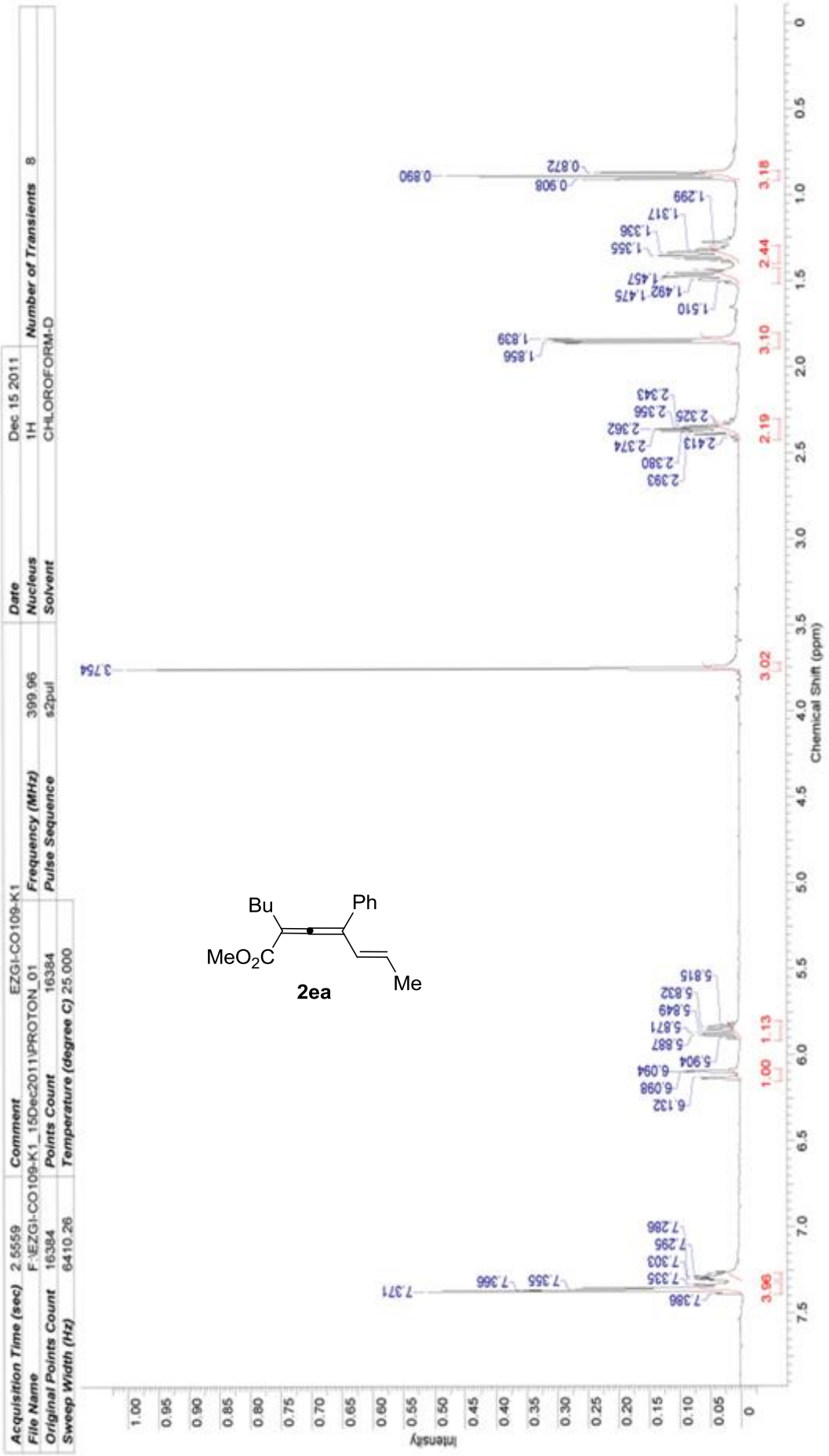

Figure D.9. ^{1}H NMR of (*E*)-methyl 2-butyl-4-phenylhepta-2,3,5-trienoate

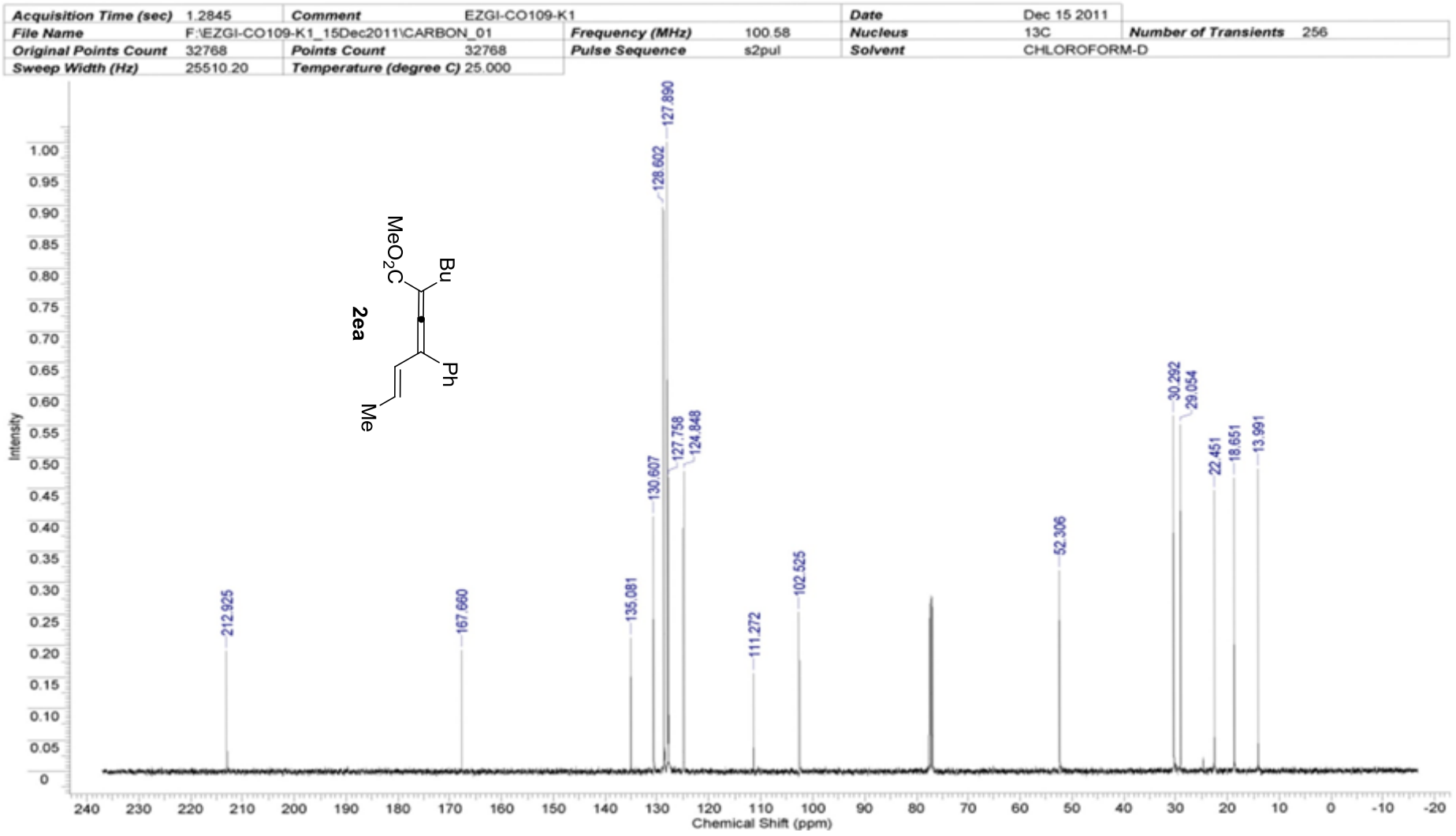

Figure D.10. ^{13} C NMR of (*E*)-methyl 2-butyl-4-phenylhepta-2,3,5-trienoate

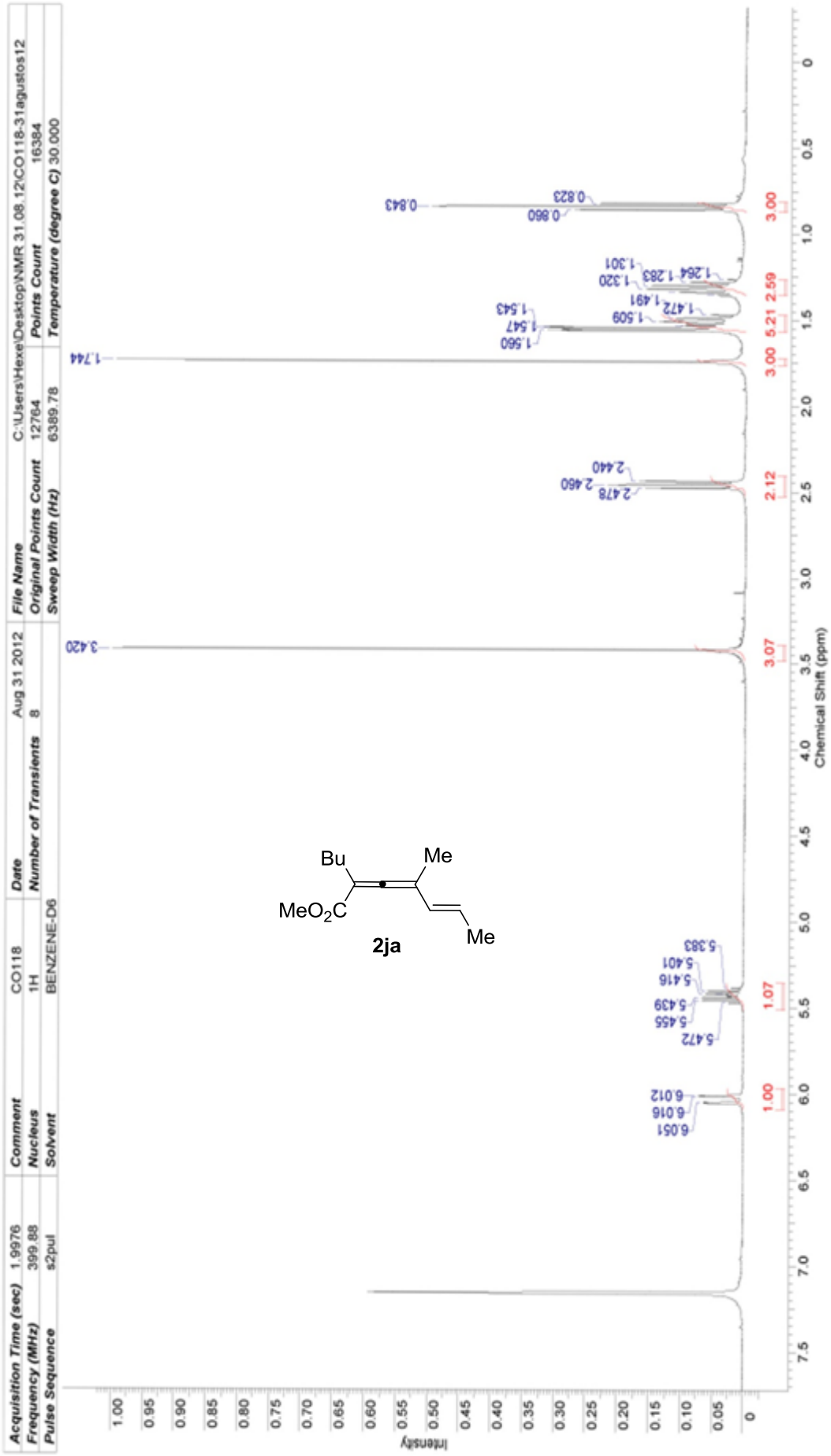

Figure D.11. ^{1}H NMR of (*E*)-methyl 2-butyl-4-methylhepta-2,3,5-trienoate

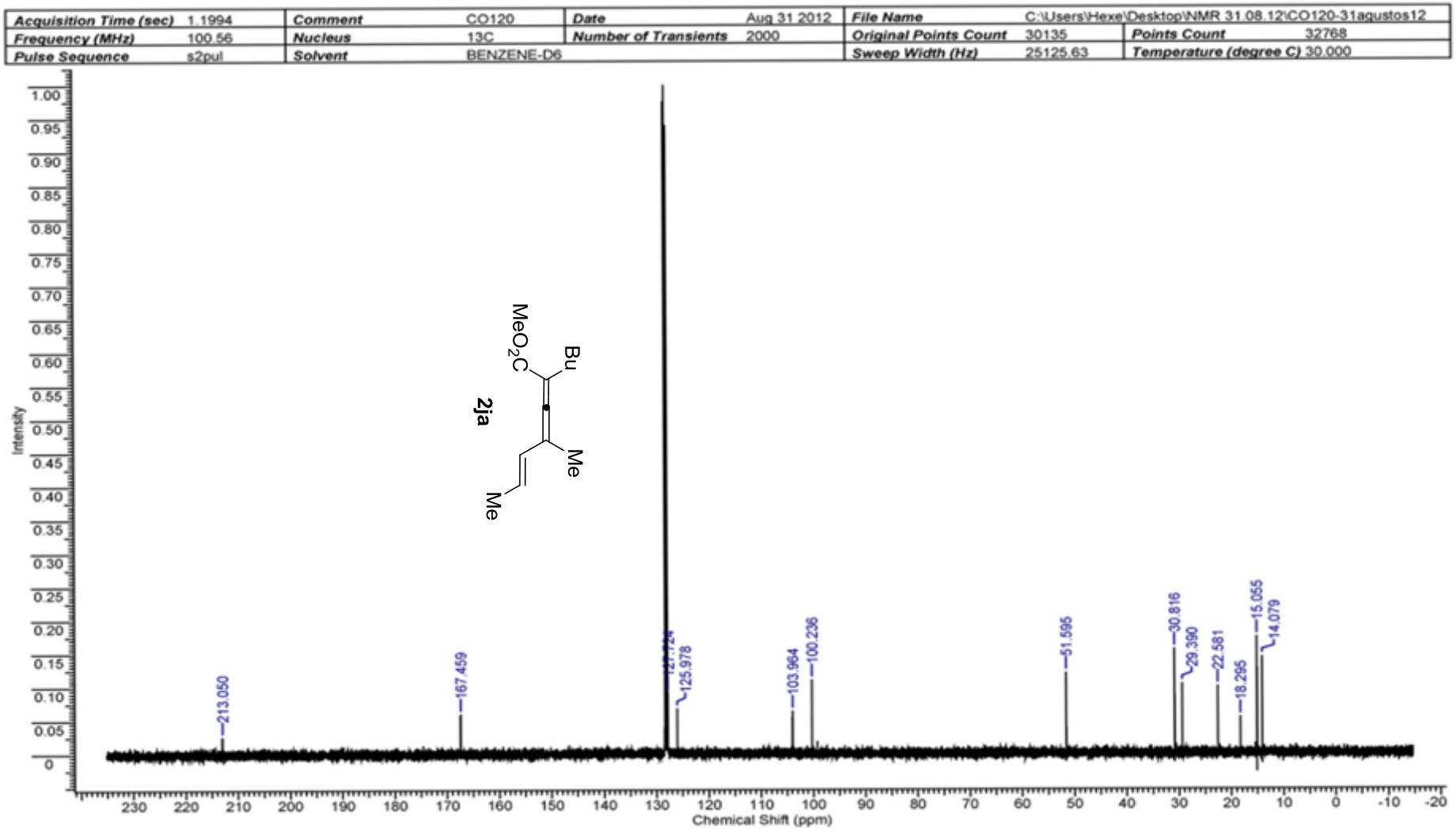

Figure D.12. ^{13} C NMR of (*E*)-methyl 2-butyl-4-methylhepta-2,3,5-trienoate

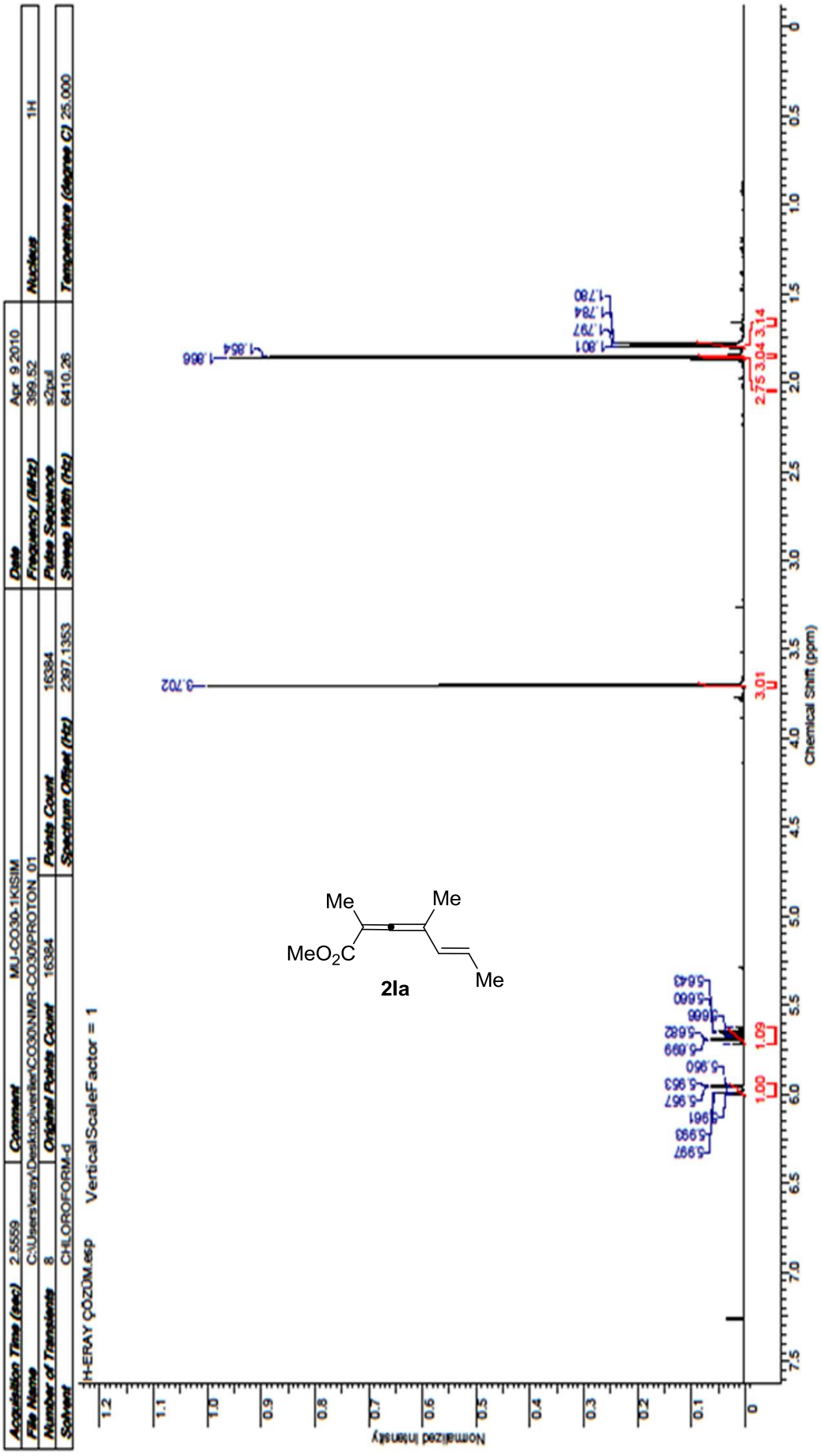

Figure D.13. ^{1}H NMR of (E)-methyl 2,4-dimethylhepta-2,3,5-trienoate

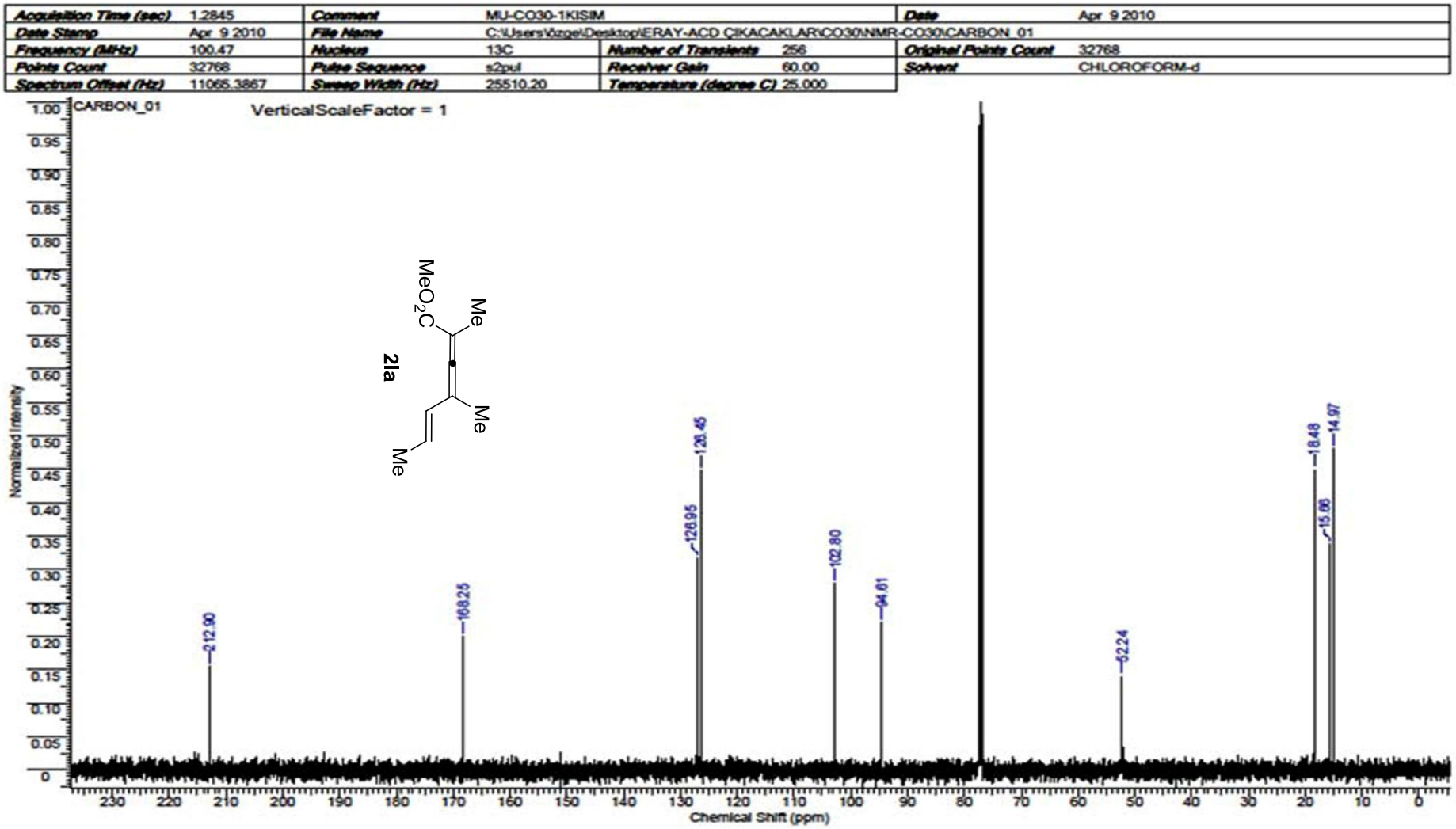

Figure D.13. ^{13} C NMR of (E)-methyl 2,4-dimethylhepta-2,3,5-trienoate

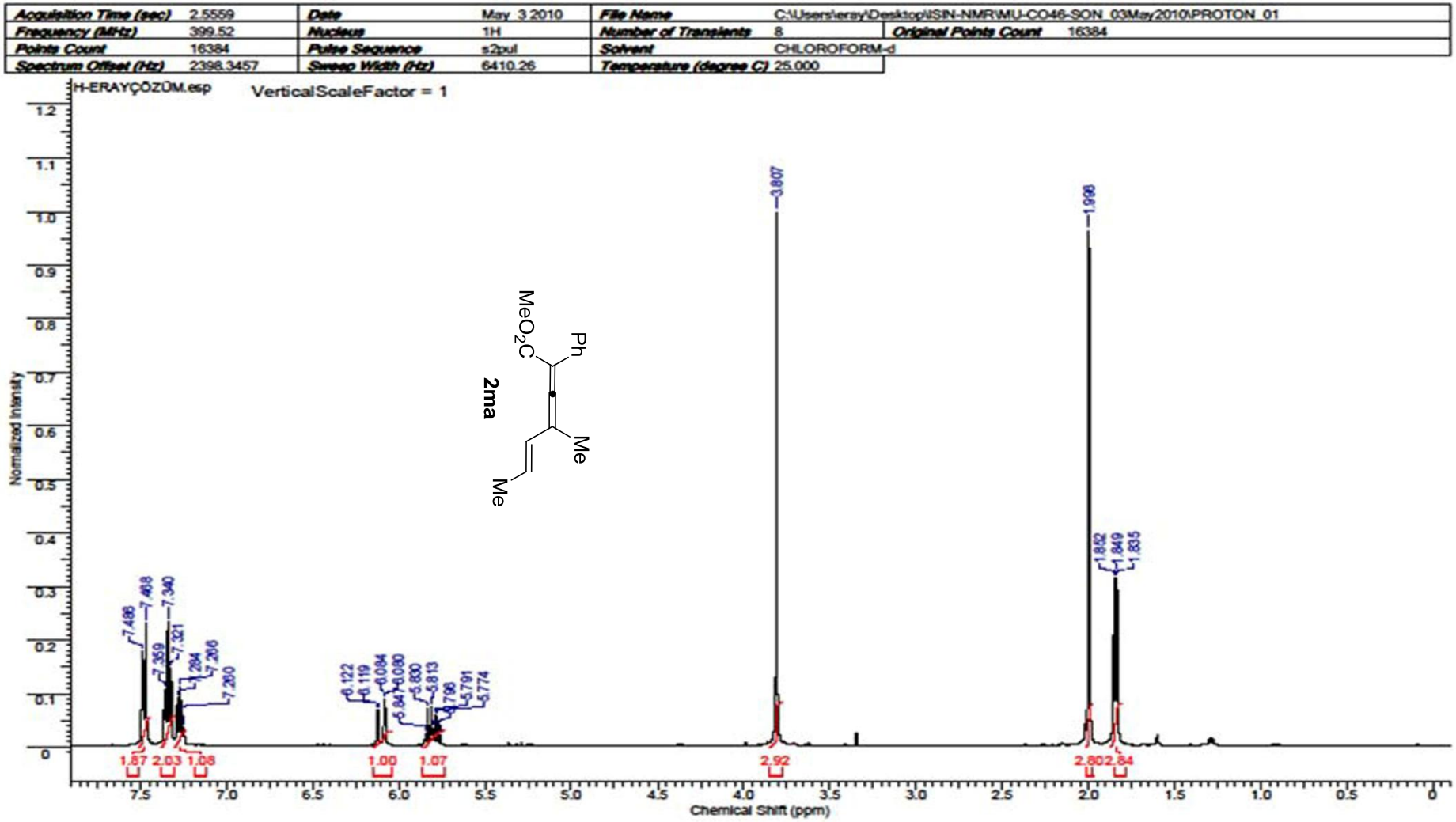

Figure D.14. [1] H NMR of (E)-methyl 4-methyl-2-phenylhepta-2,3,5-trienoate

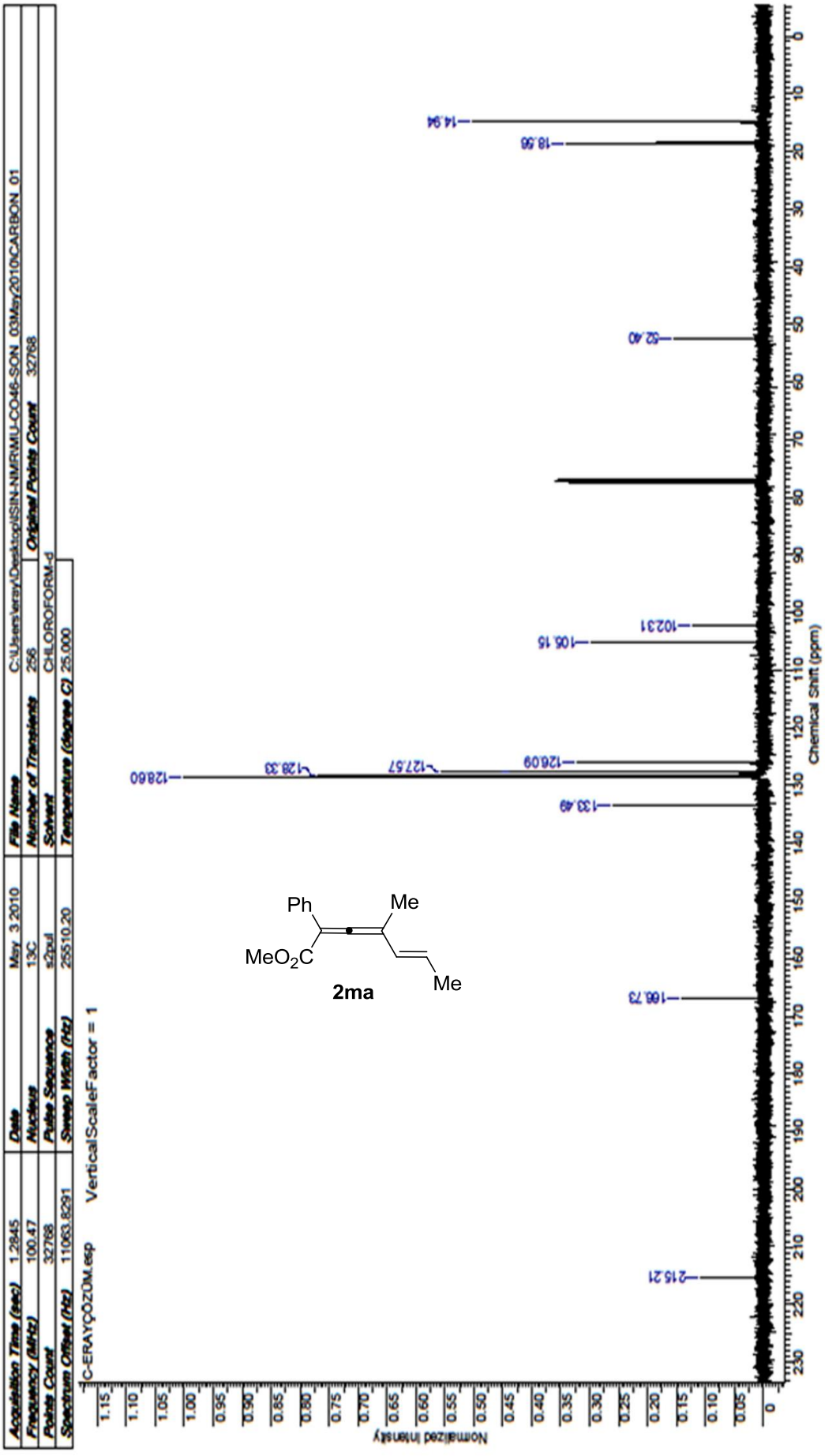

Figure D.15. ^{13}C NMR of (E)-methyl 4-methyl-2-phenylhepta-2,3,5-trienoate

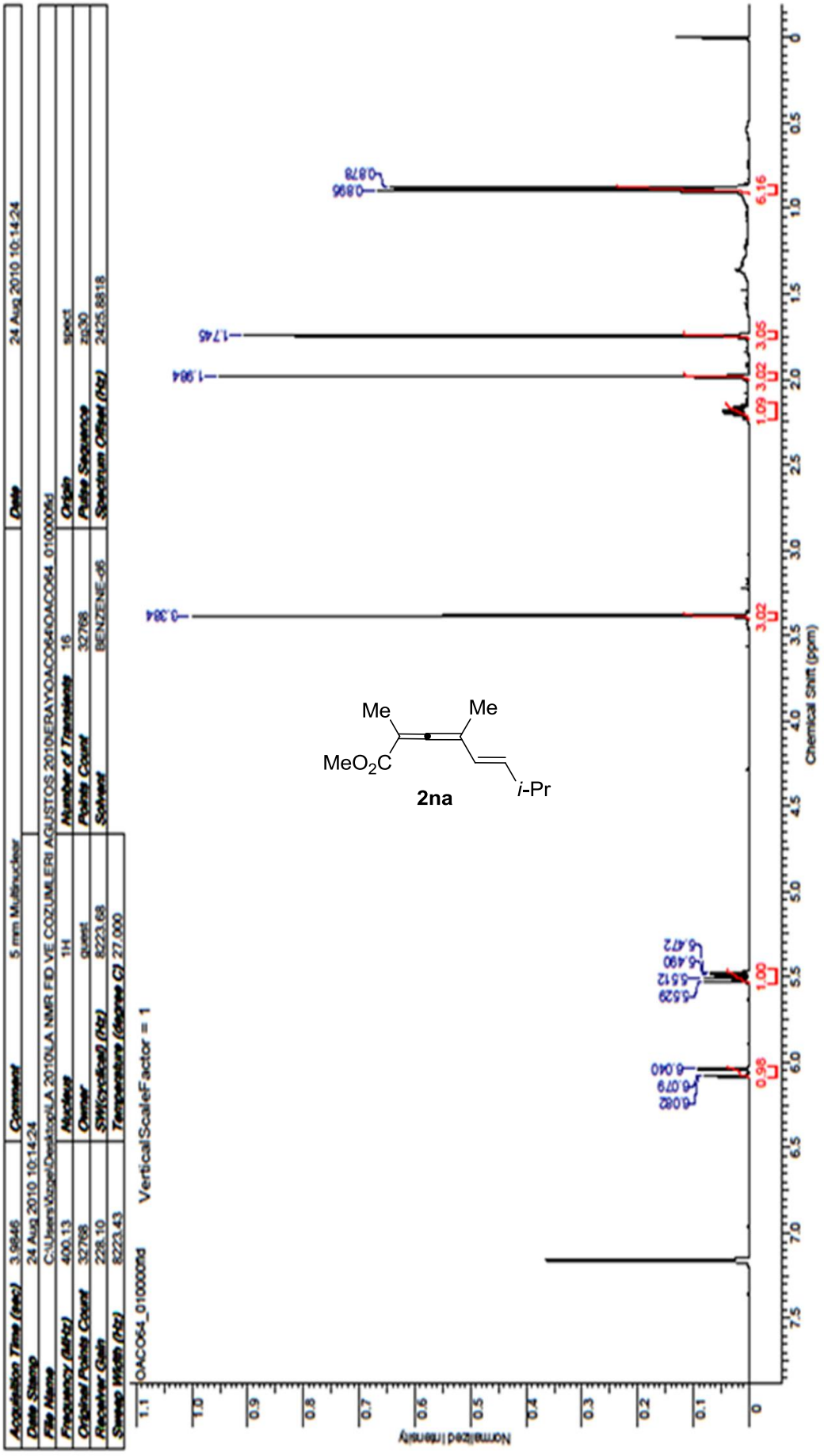

Figure D.16. ^{1}H NMR of (E)-methyl 2,4,7-trimethylocta-2,3,5-trienoate

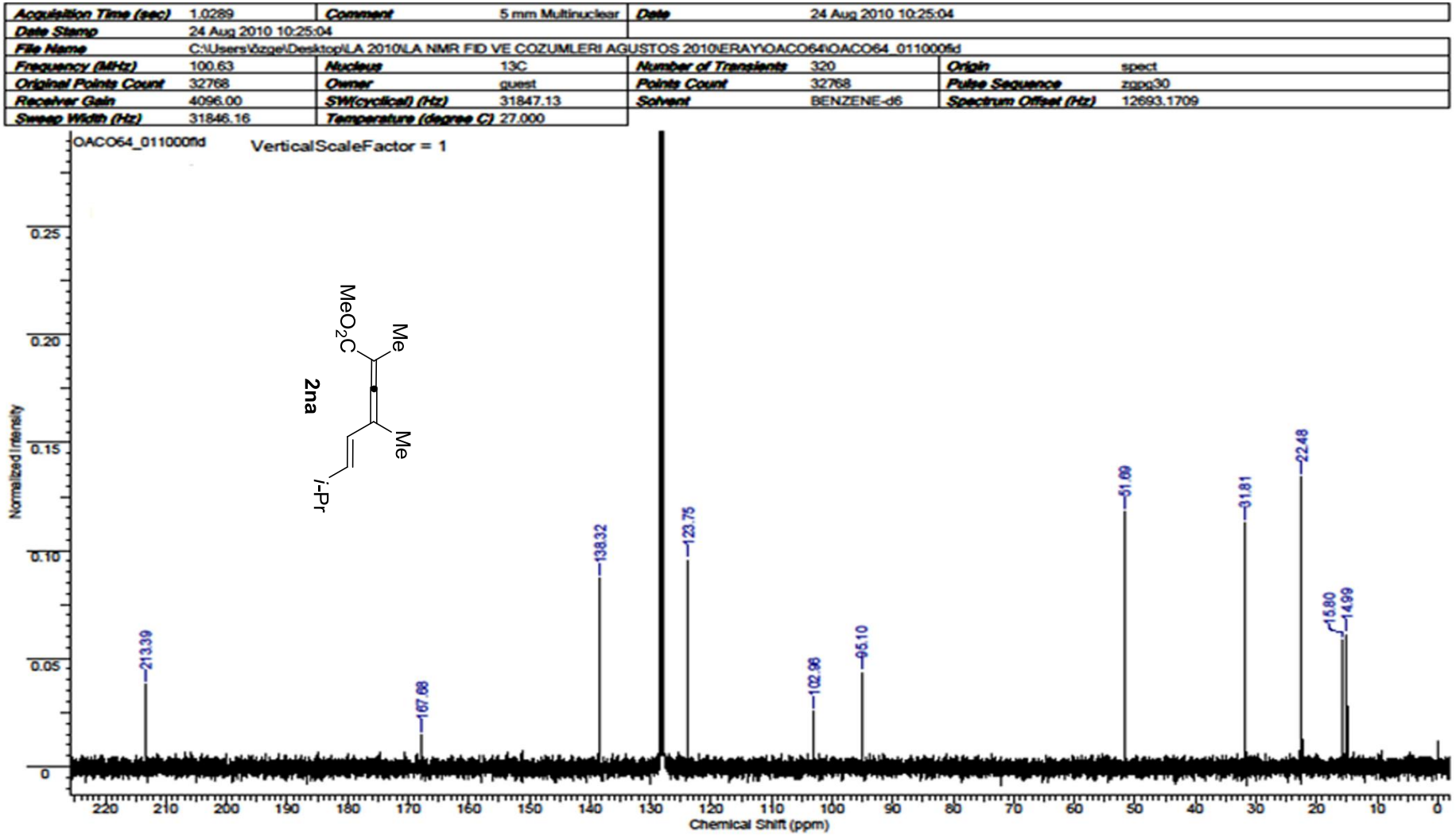

Figure D.17. ^{13} C NMR of (E)-methyl 2,4,7-trimethylocta-2,3,5-trienoate

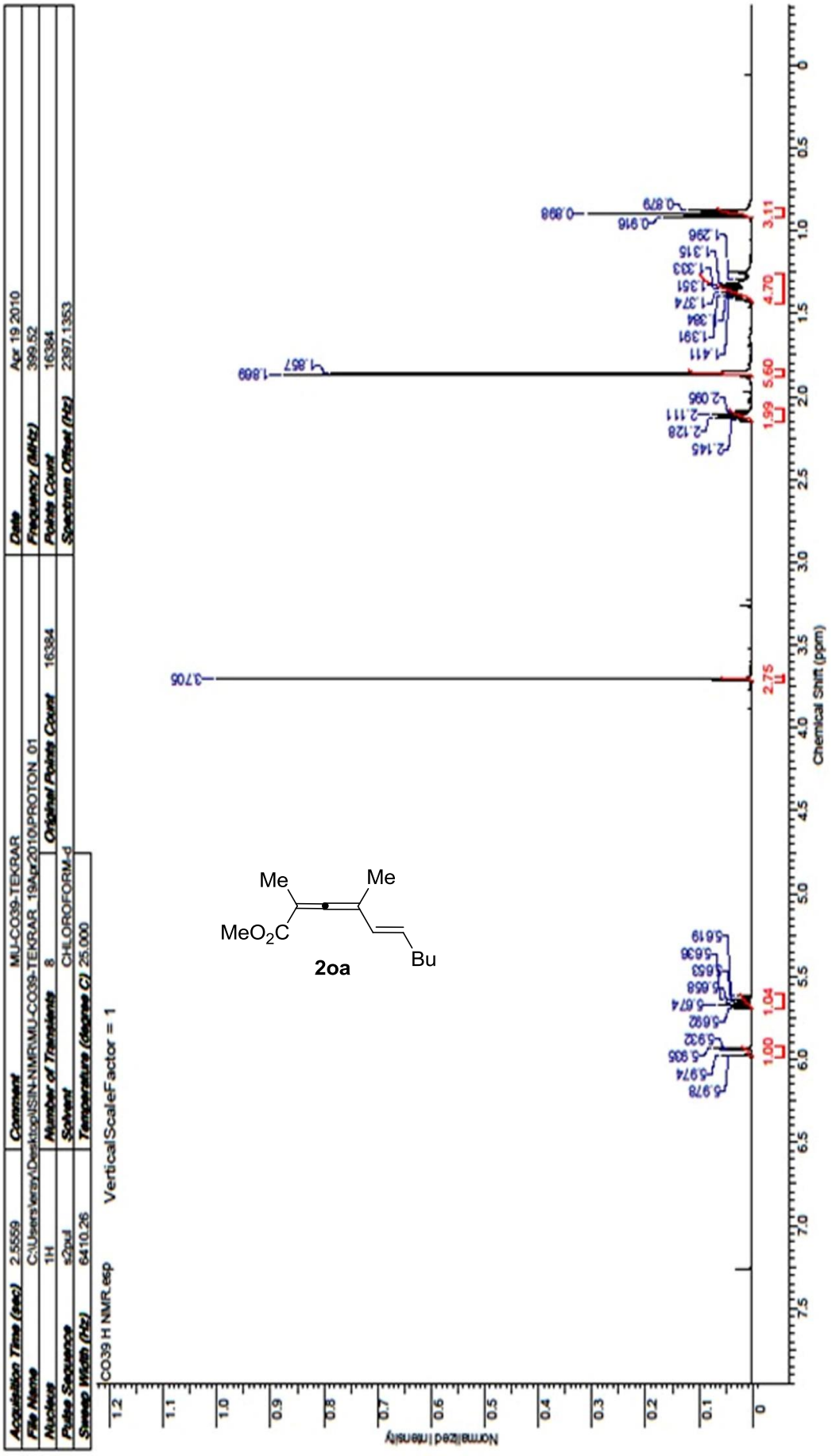

Figure D.18. ^{1}H NMR of (E)-methyl 2,4-dimethyldeca-2,3,5-trienoate

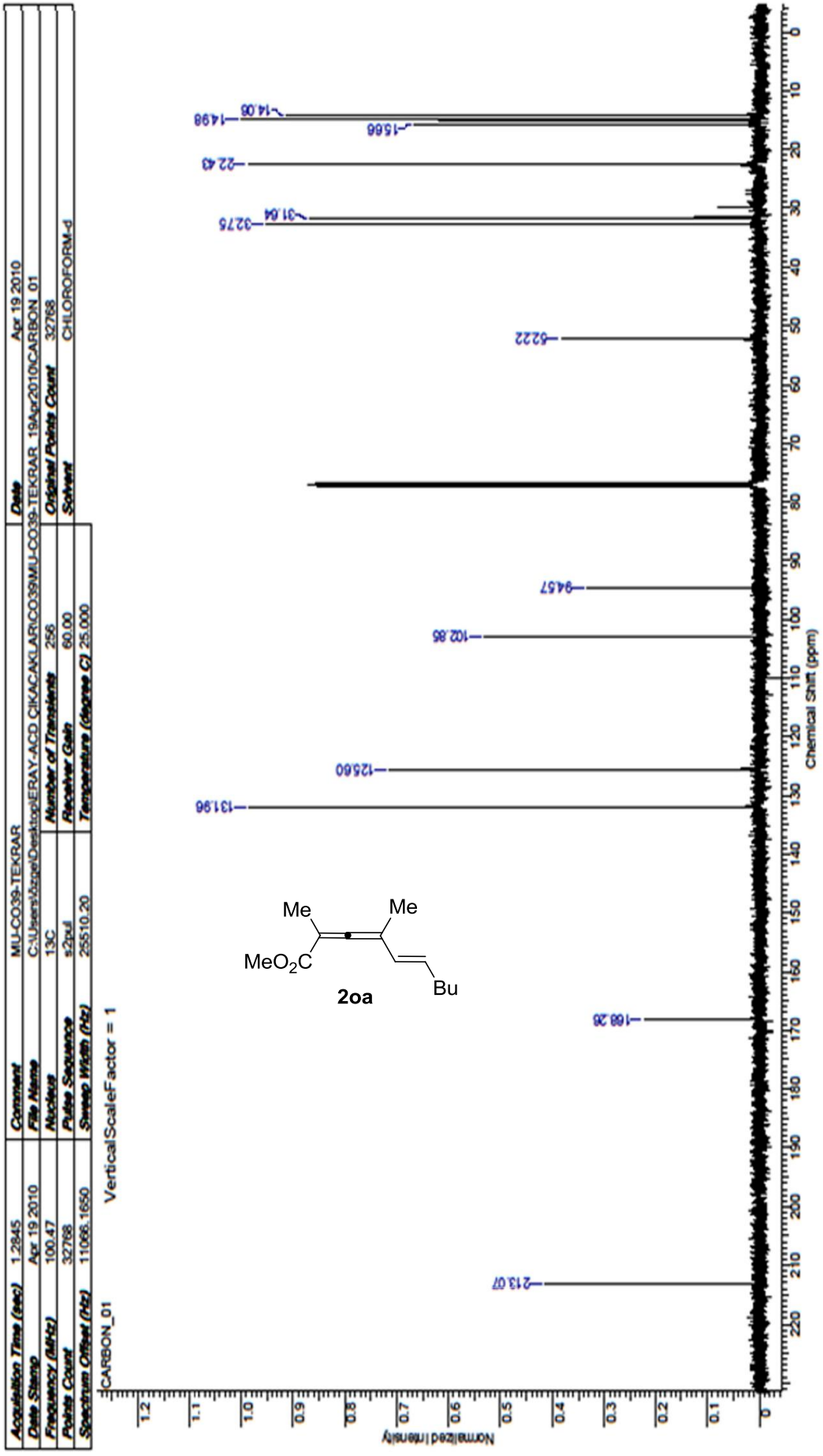

Figure D.19. ^{13}C NMR of (E)-methyl 2,4-dimethyldeca-2,3,5-trienoate

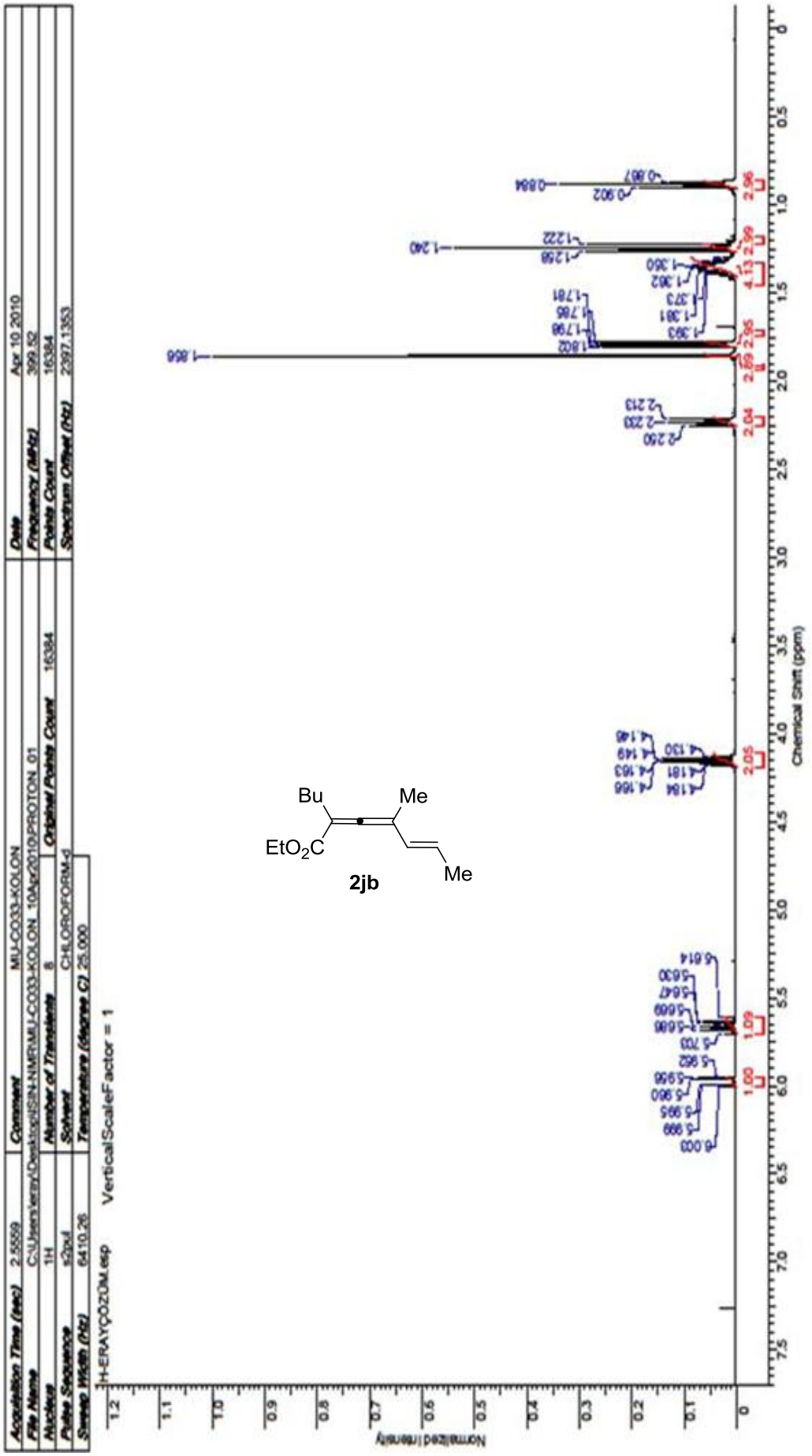

Figure D.20. ^{1}H NMR of (E)-ethyl 2-butyl-4-methylhepta-2,3,5-trienoate

Acquisition Time (sec)	1.2845	Date	Apr 10 2010	Date Stamp	Apr 10 2010		
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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		

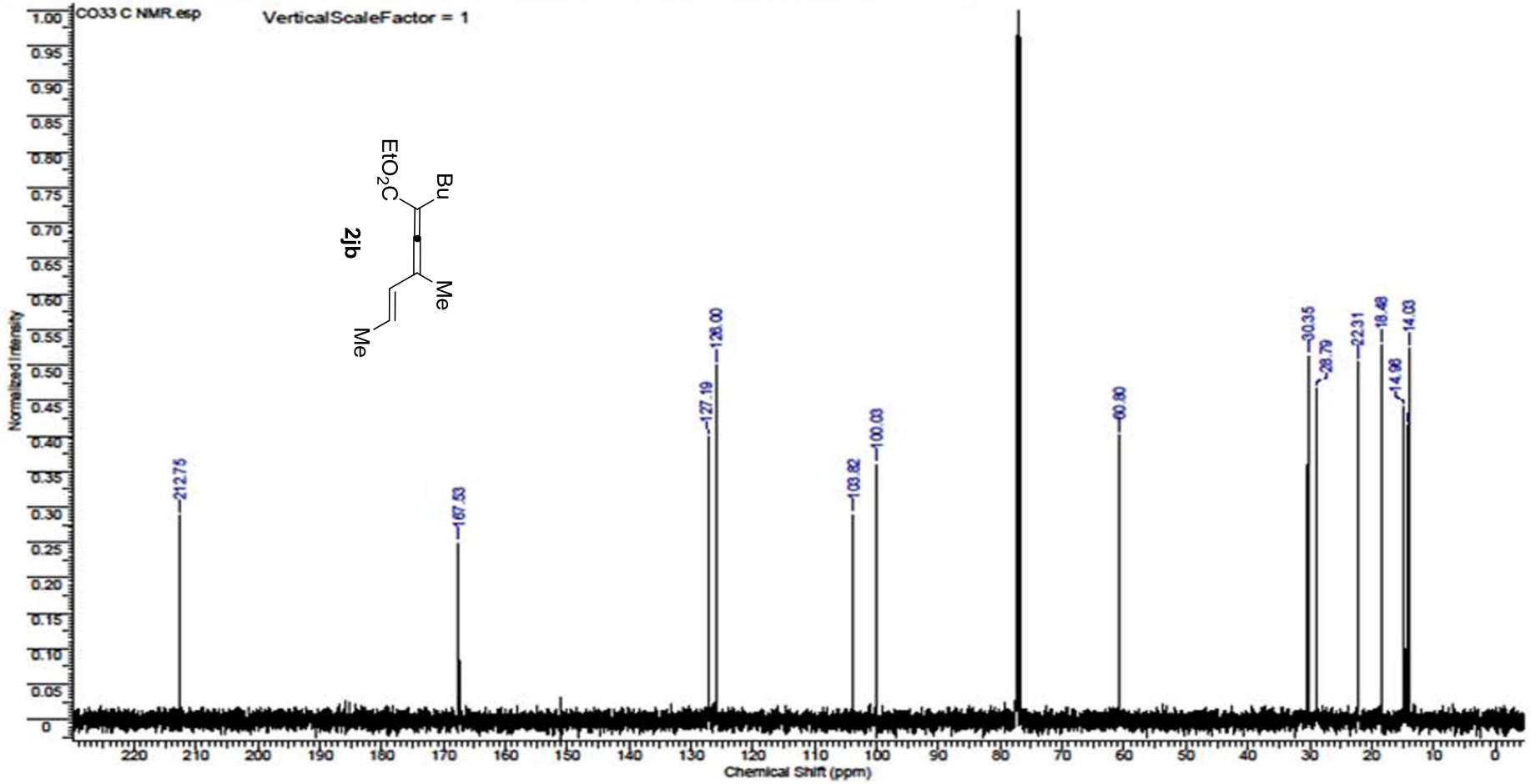

Figure D.21 ^{13} C NMR of (E)-ethyl 2-butyl-4-methylhepta-2,3,5-trienoate

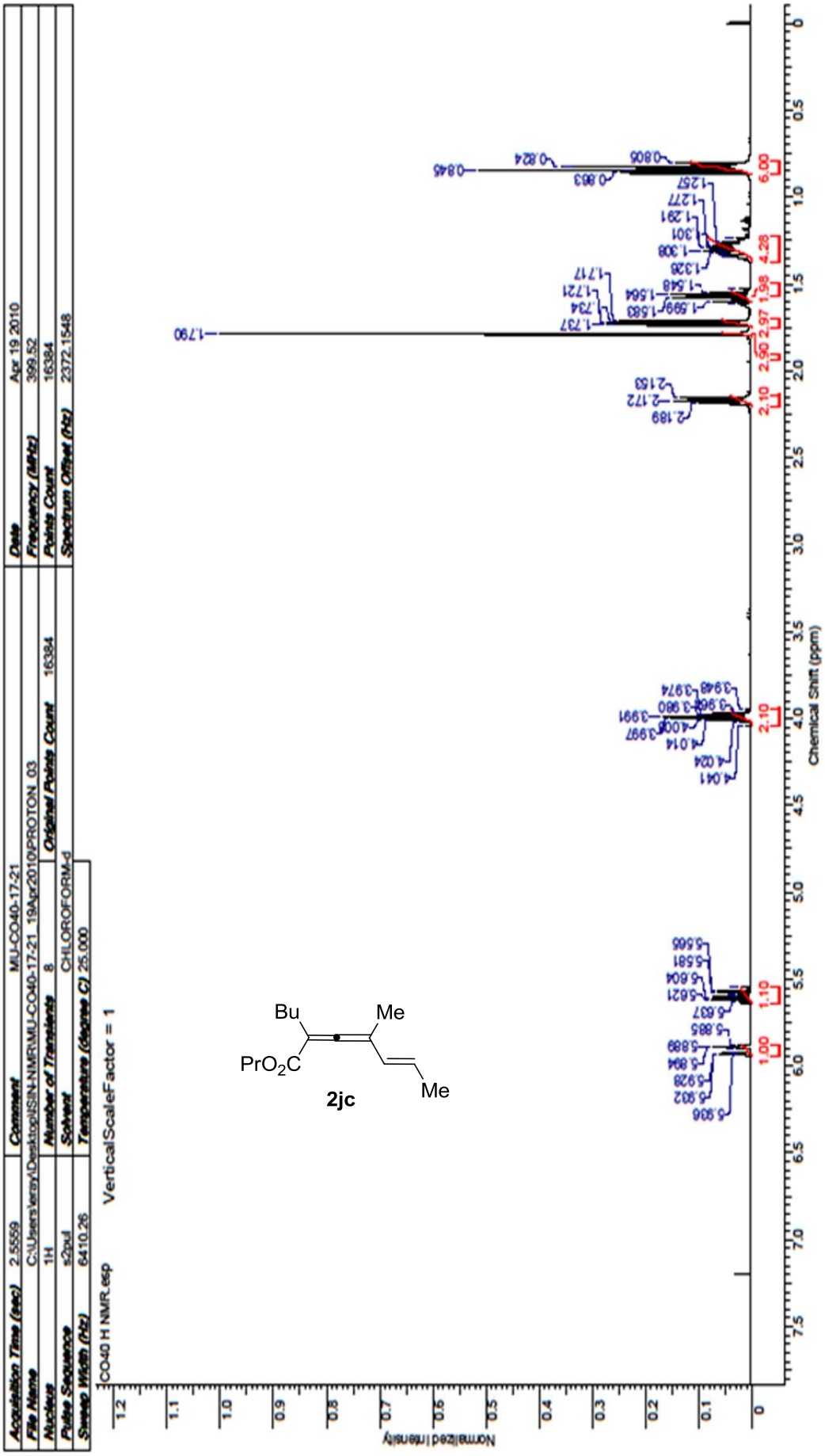

Figure D.22 ^{1}H NMR of (E)-propyl 2-butyl-4-methylhepta-2,3,5-trienoate

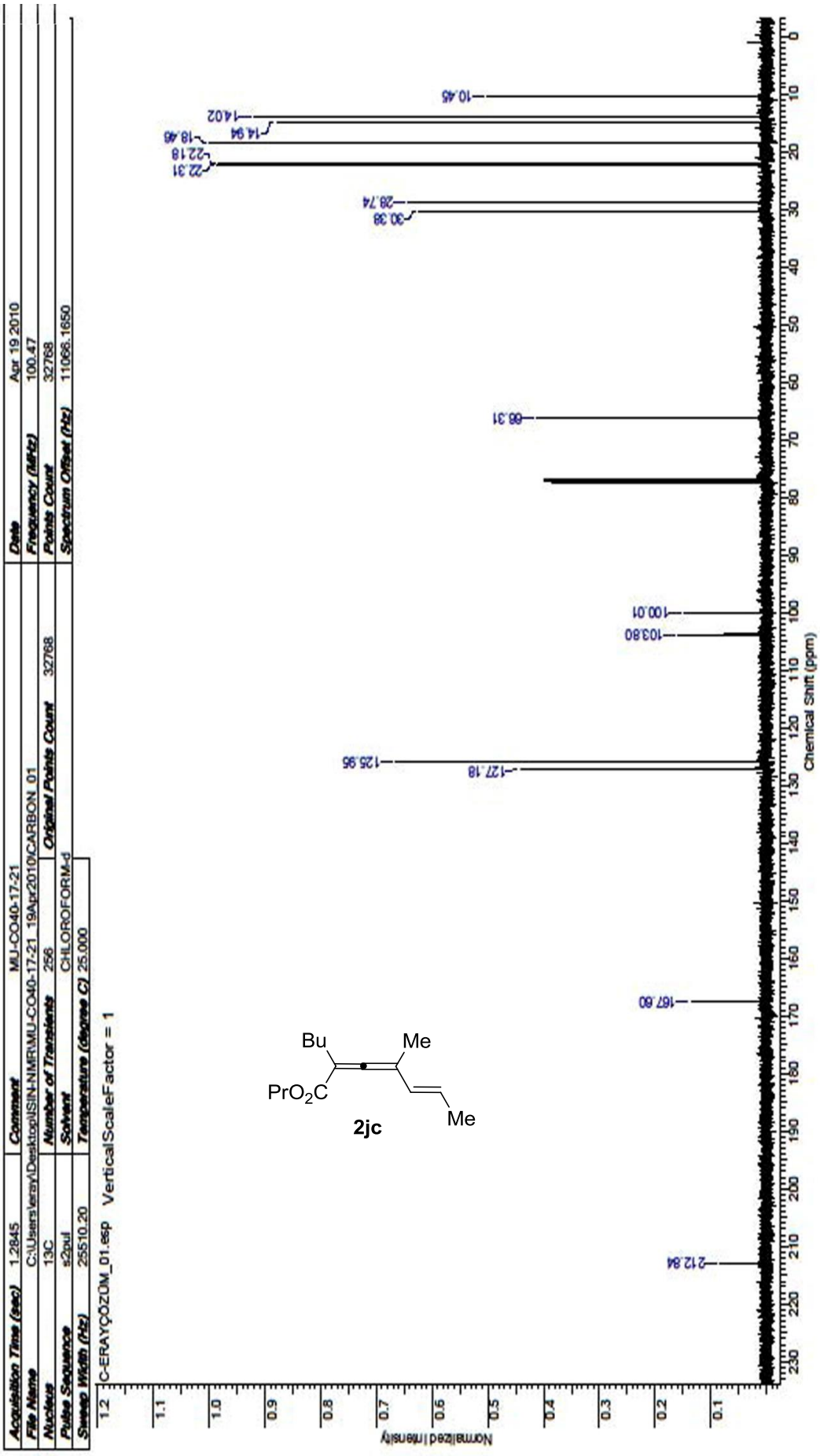

Figure D.23 ^{13}C NMR of (E)-propyl 2-butyl-4-methylhepta-2,3,5-trienoate

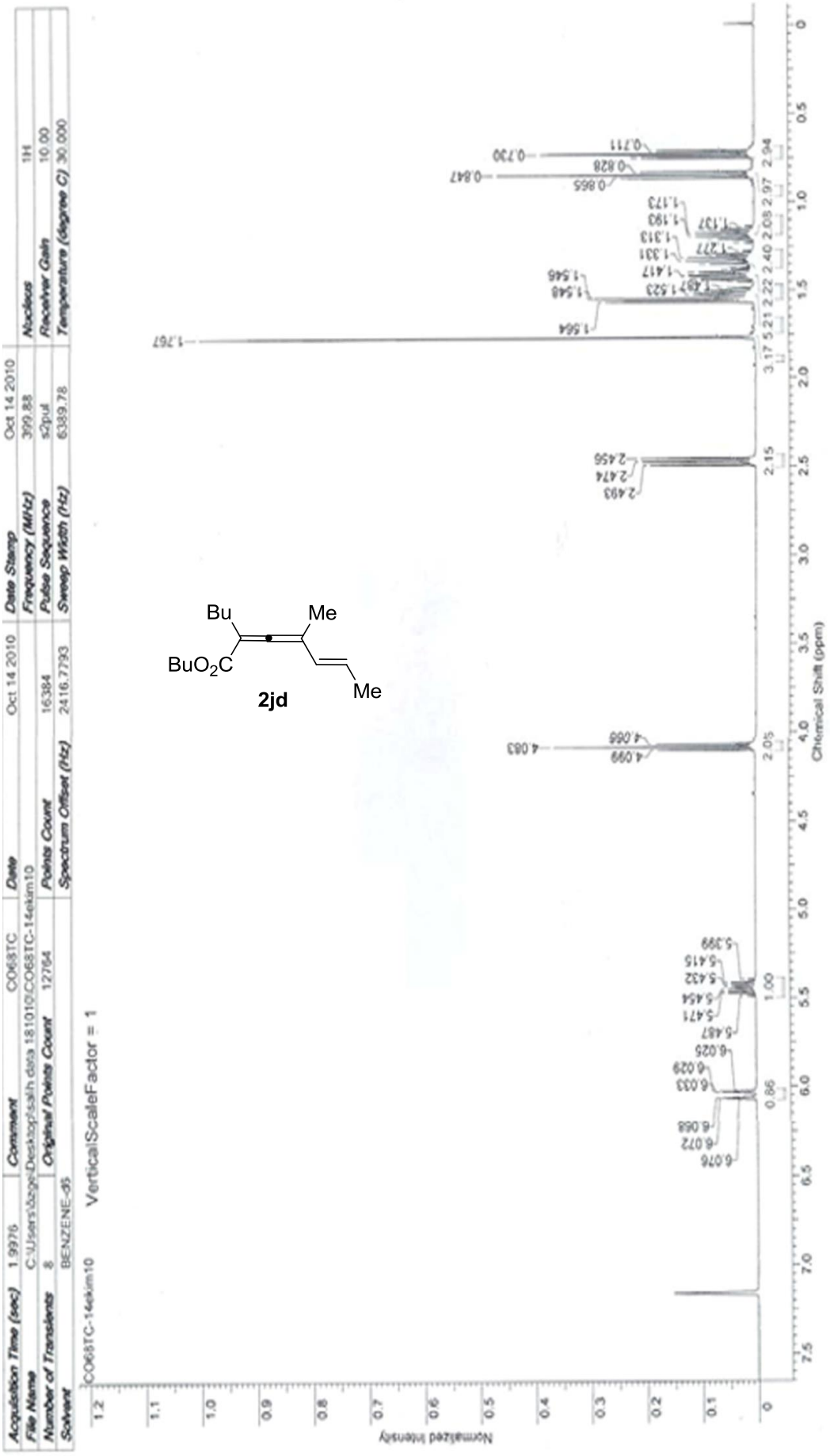

Figure D.24 ^{1}H NMR of (E)-butyl 2-butyl-4-methylhepta-2,3,5-trienoate

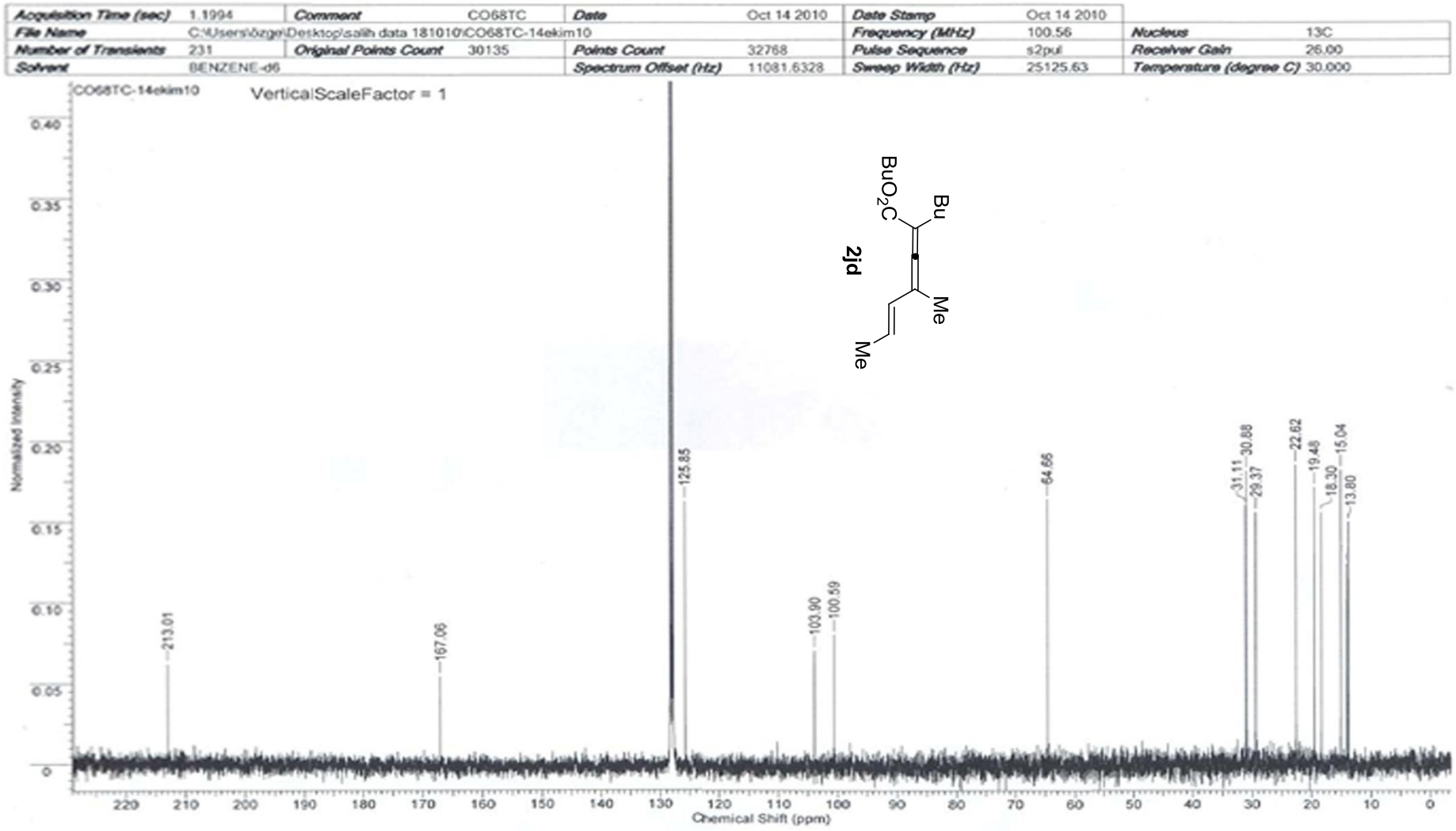

Figure D.25 ^{13}C NMR of (E)-butyl 2-butyl-4-methylhepta-2,3,5-trienoate

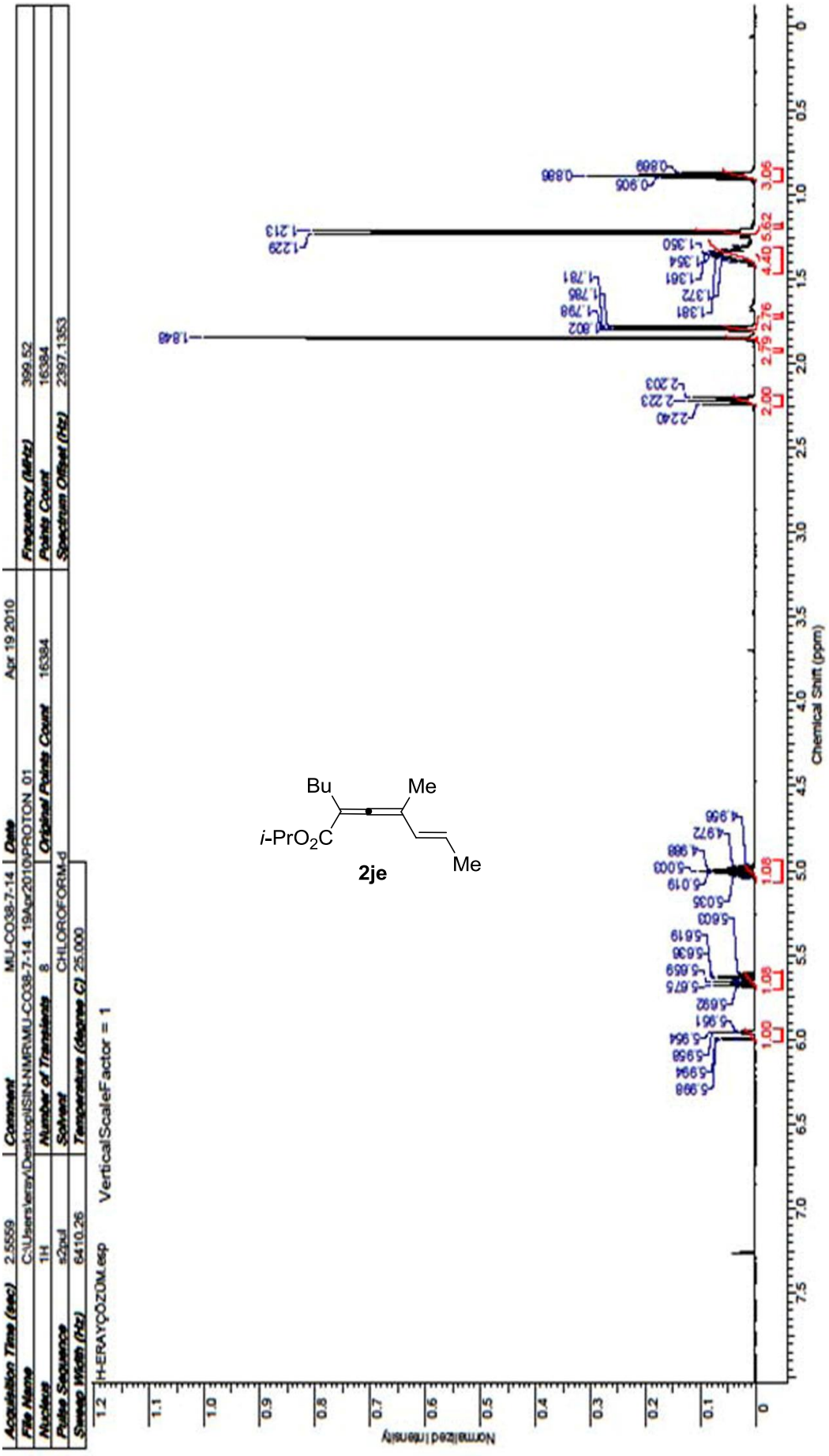

Figure D.26[1] H NMR of (E)-isopropyl 2-butyl-4-methylhepta-2,3,5-trienoate

Acquisition Time (sec)	1.2845	Comment	MU-CO38-15-23	Date	Apr 19 2010	Date Stamp	Apr 19 2010
File Name	C:\Users\özge\Desktop\ERAY-ACD ÇIKACAKLAR\CO38\MU-CO38-15-23_19Apr2010\CARBON_01					Frequency (MHz)	100.47
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		

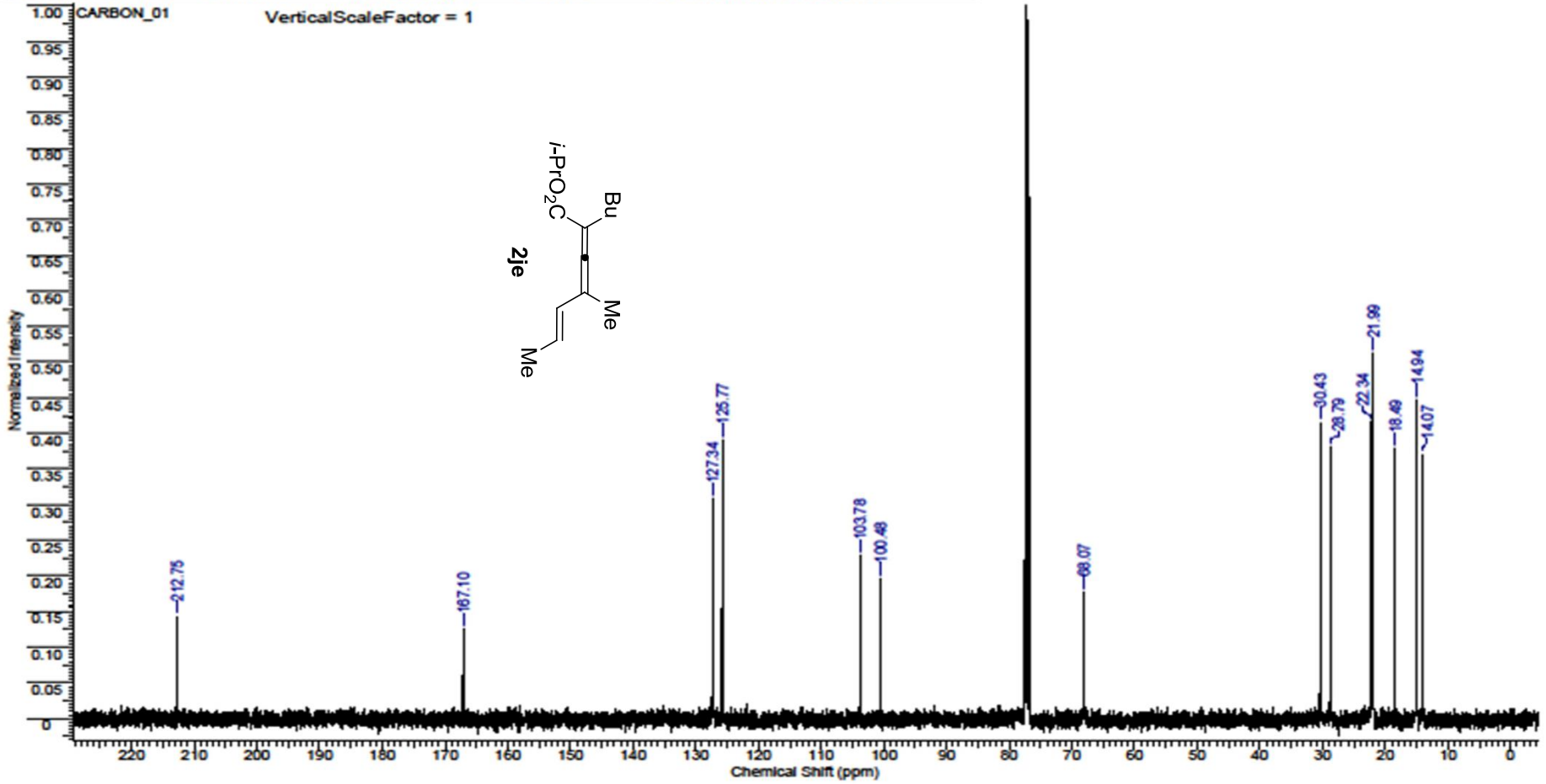

Figure D.27 ^{13}C NMR of (E)-isopropyl 2-butyl-4-methylhepta-2,3,5-trienoate

APPENDIX E.

MASS SPECTRUM OF PRODUCT

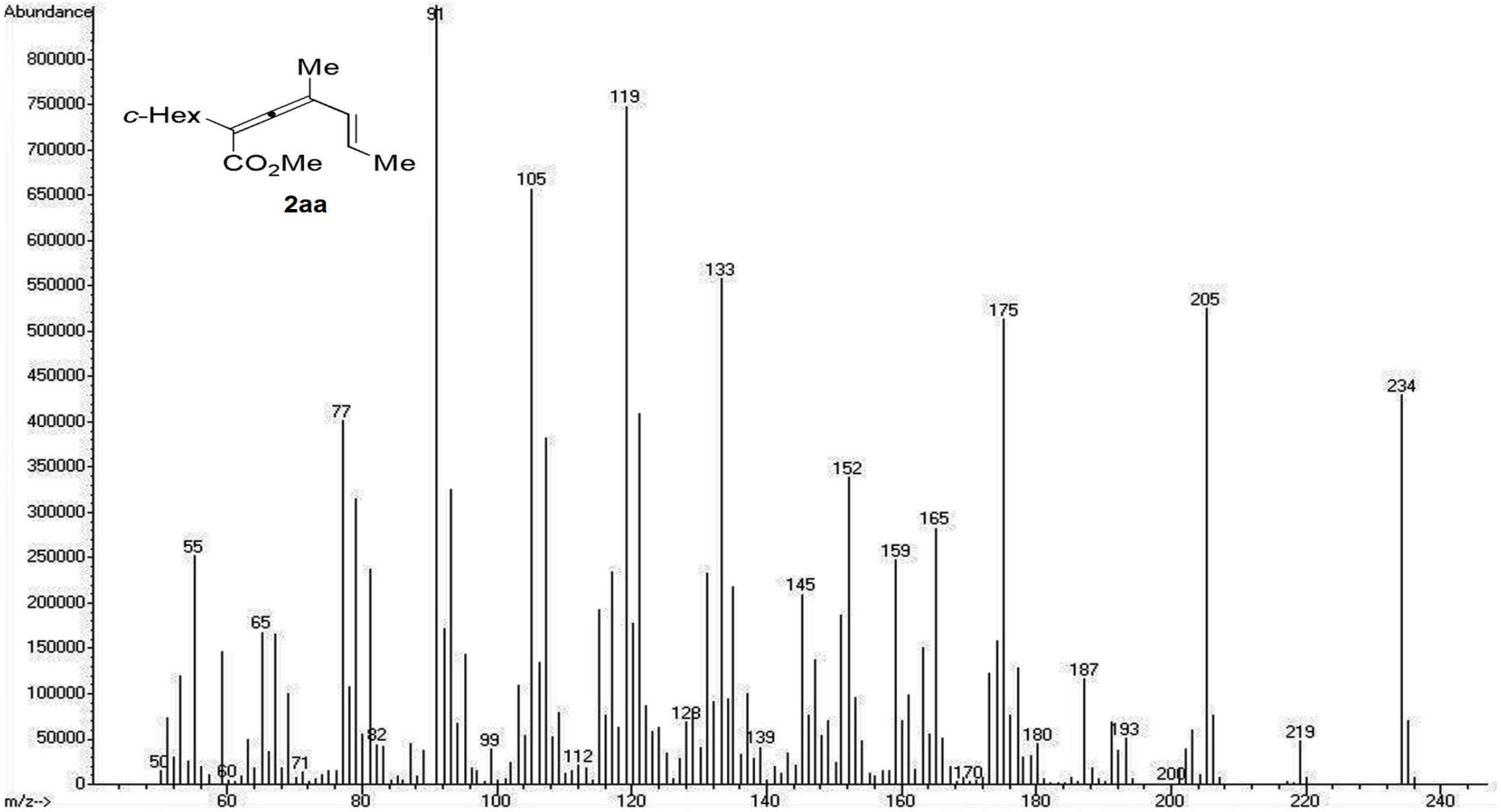

Figure E.1. Mass Spectrum of (*E*)-methyl 2-cyclohexyl-4-methylhepta-2,3,5-trienoate

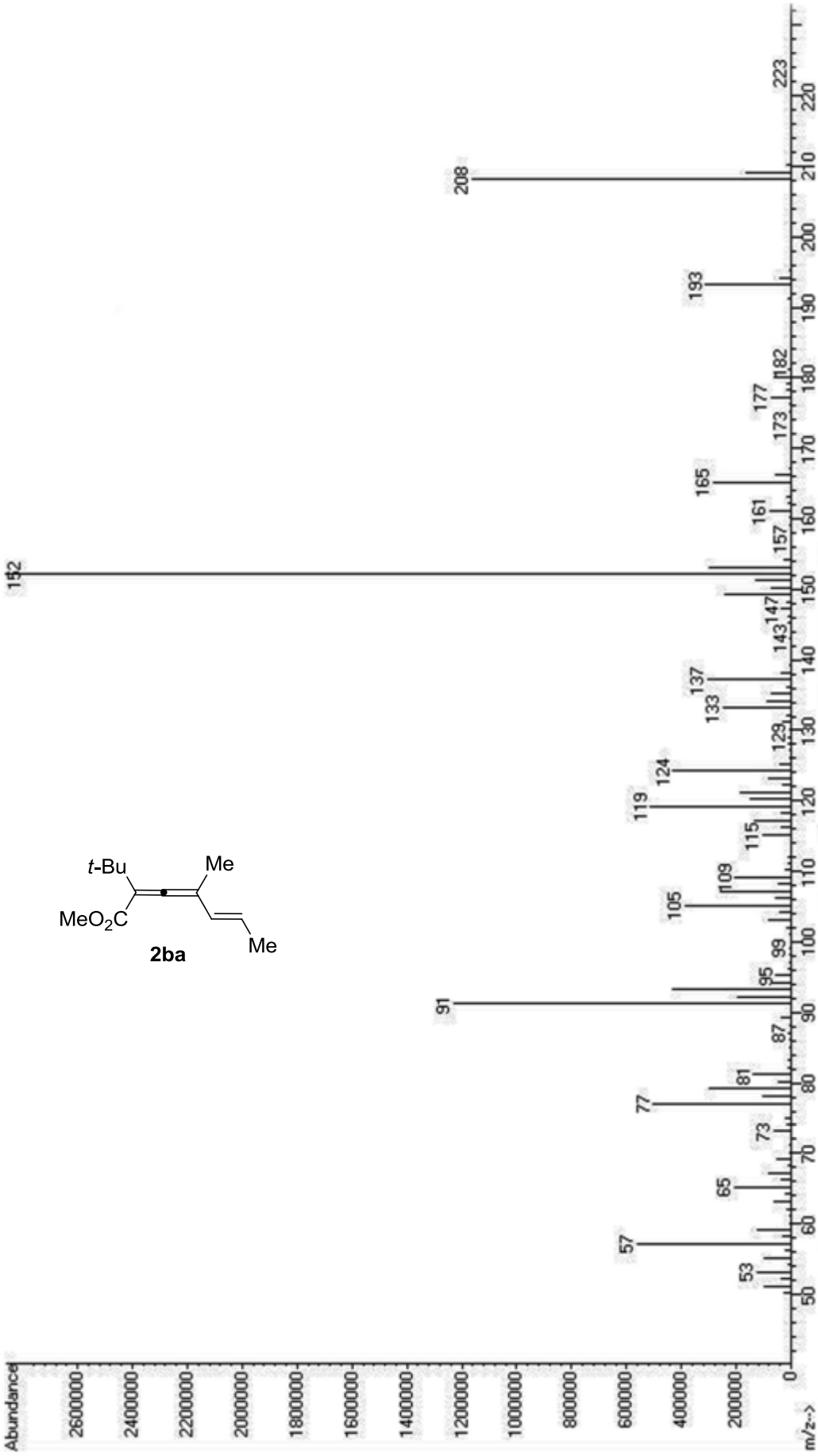

Figure E.2. Mass Spectrum of (*E*)-methyl 2-(tert-butyl)-4-methylhepta-2,3,5-trienoate

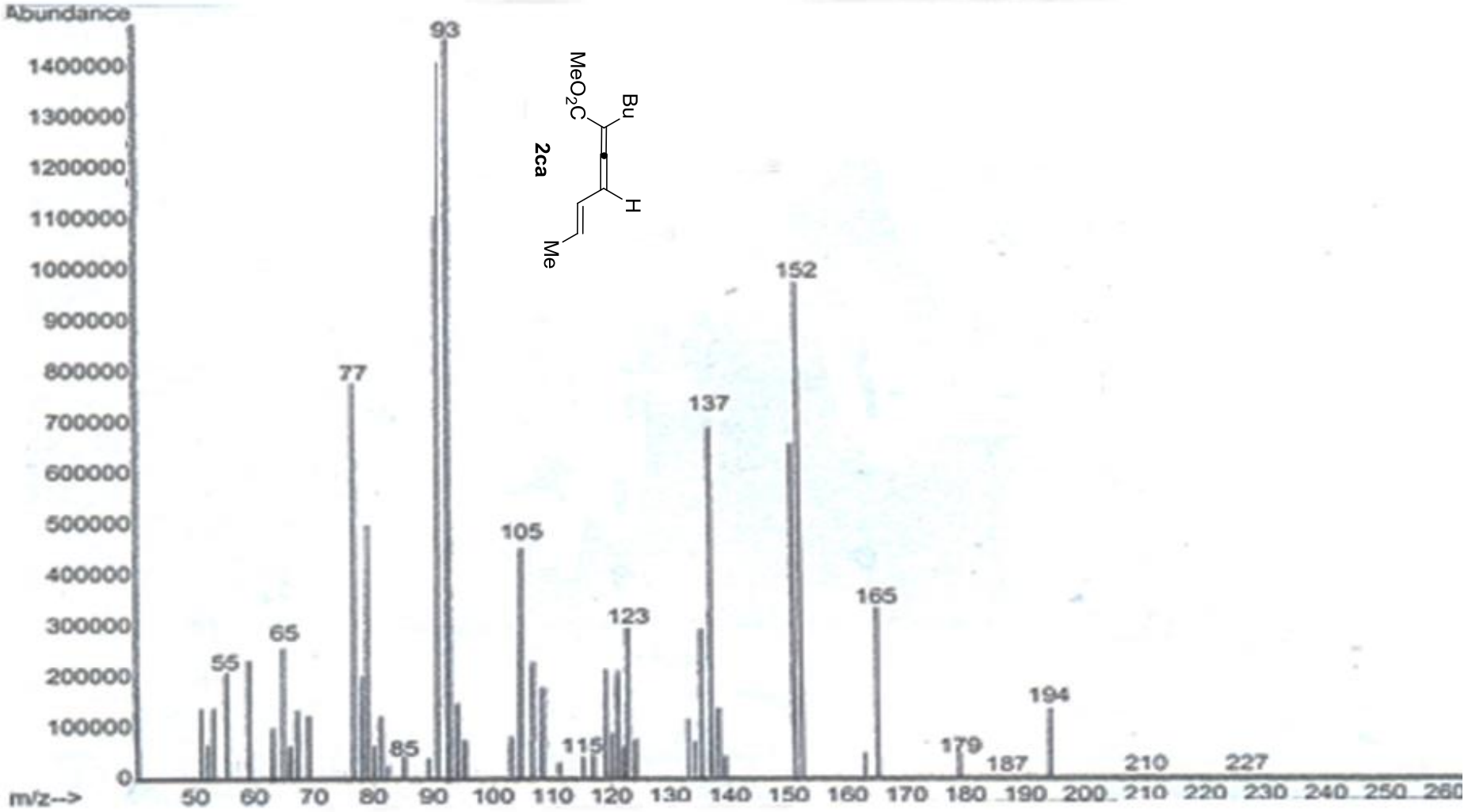

Figure E.3. Mass Spectrum of (*E*)-methyl 2-butylhepta-2,3,5-trienoate

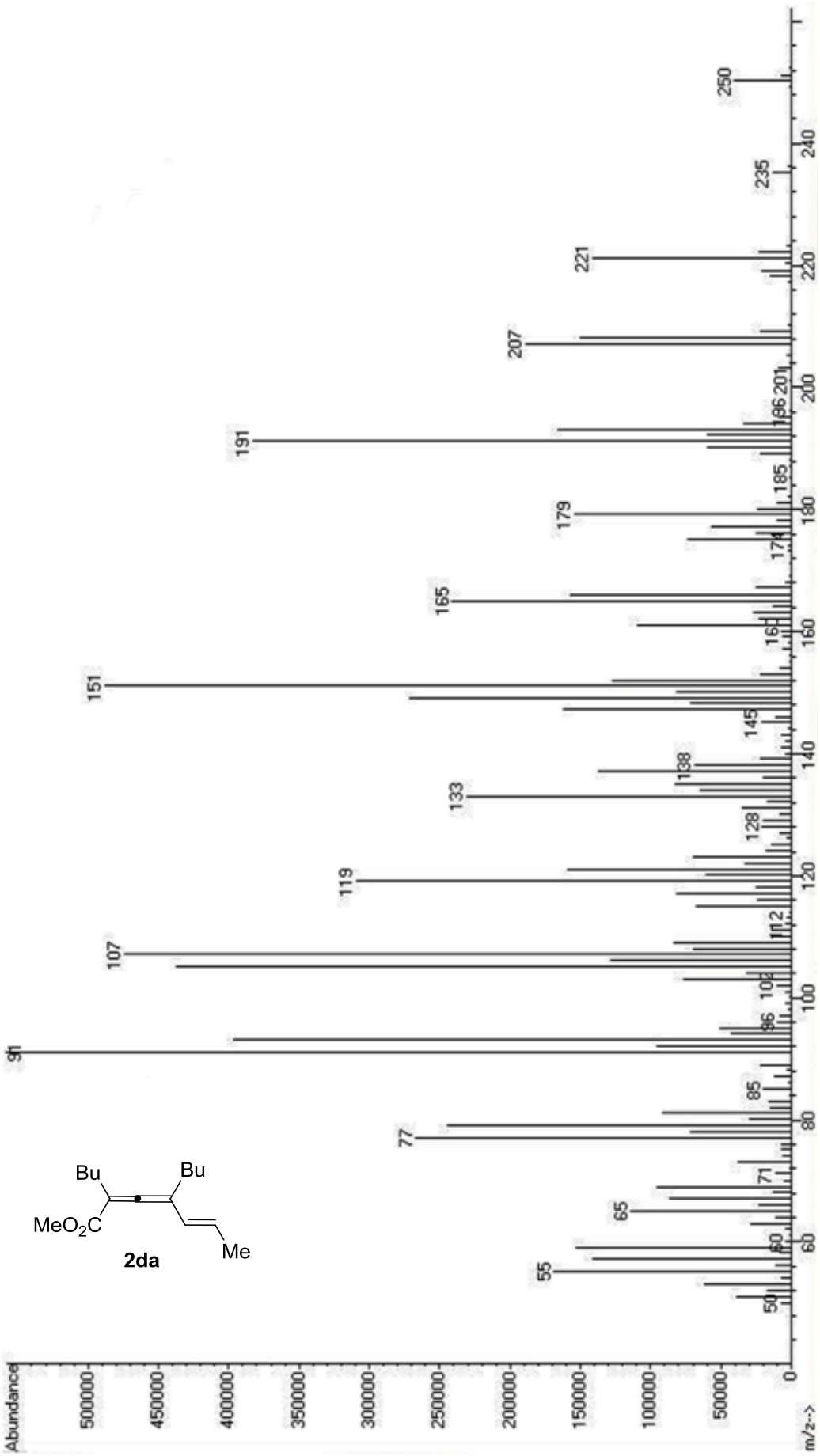

Figure E.4. Mass Spectrum of (*E*)-methyl 2-butyl-4-(prop-1-en-1-yl)octa-2,3-dienoate

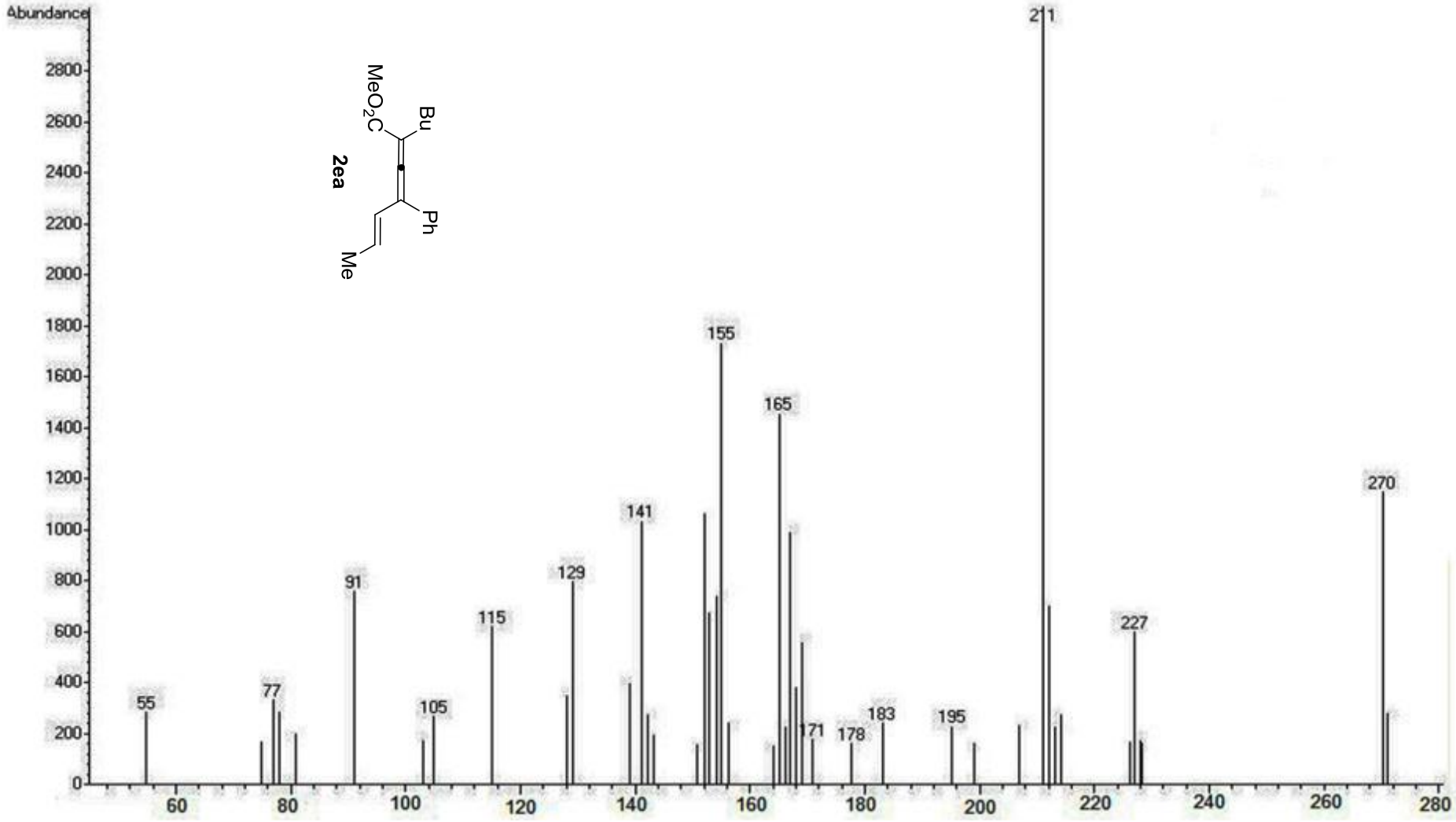

Figure E.5. Mass Spectrum of (*E*)-methyl 2-butyl-4-phenylhepta-2,3,5-trienoate

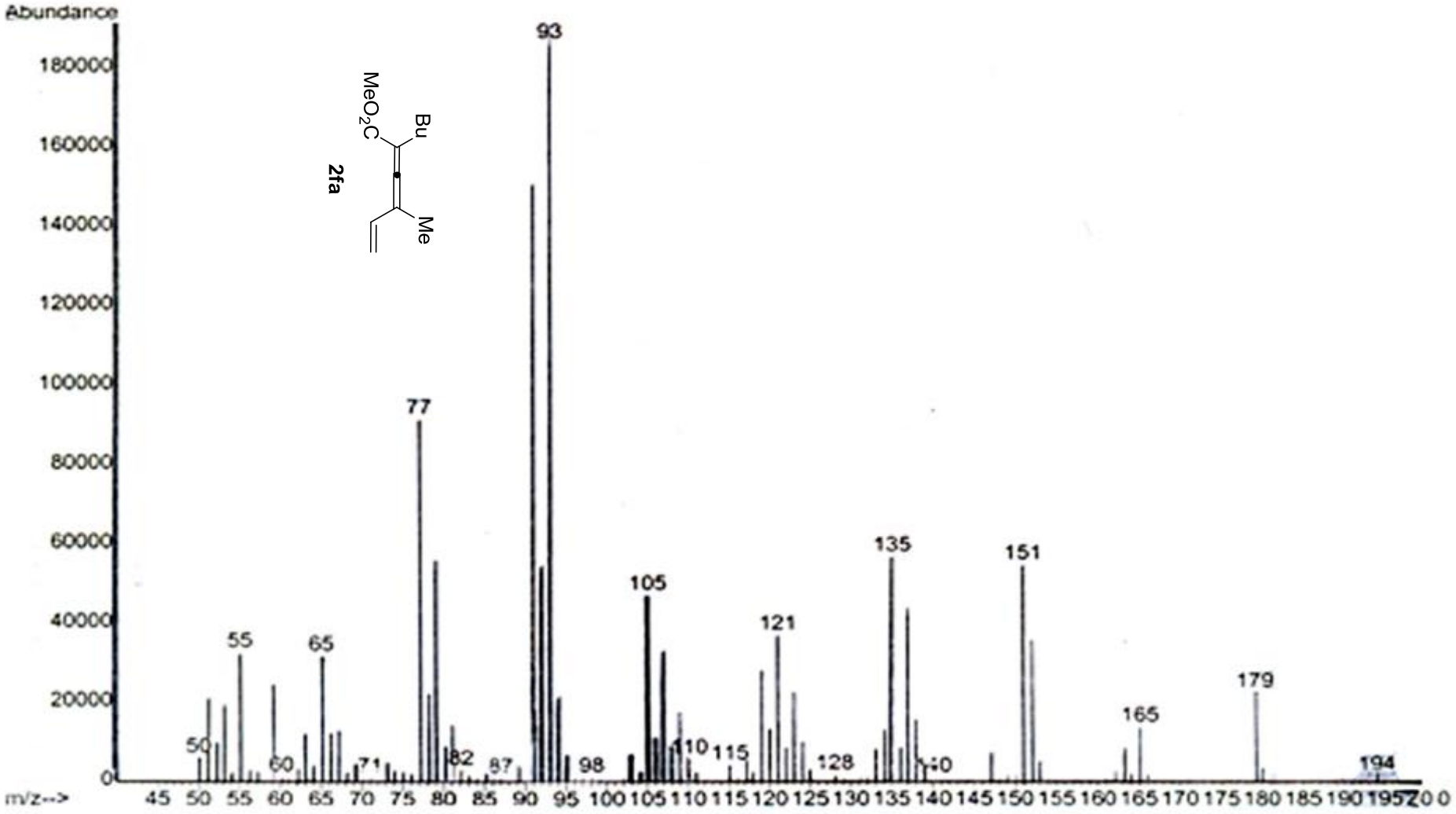

Figure E.6. Mass Spectrum of methyl 2-butyl-4-methylhexa-2,3,5-trienoate

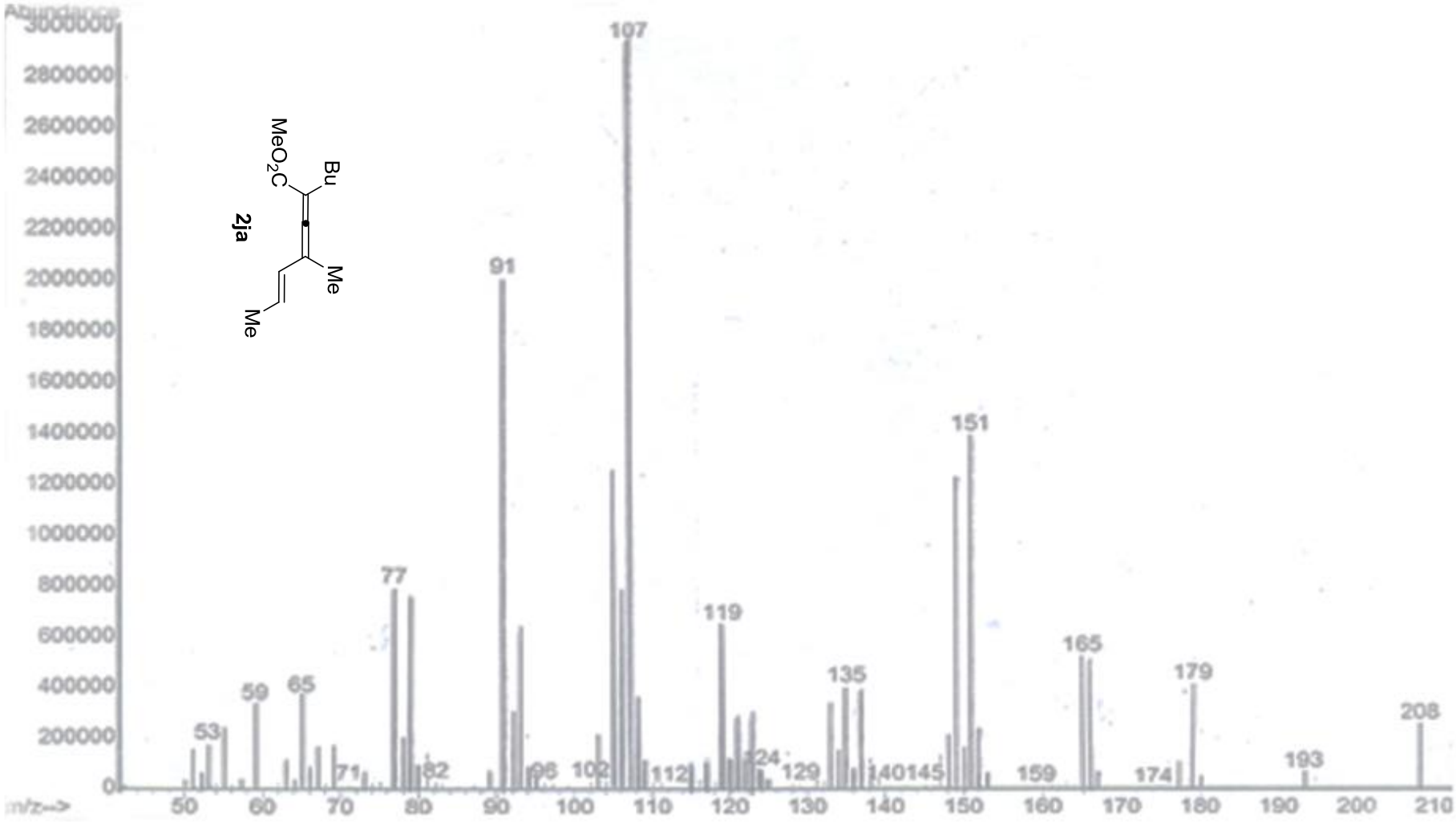

Figure E.7. Mass Spectrum of (*E*)-methyl 2-butyl-4-methylhepta-2,3,5-trienoate

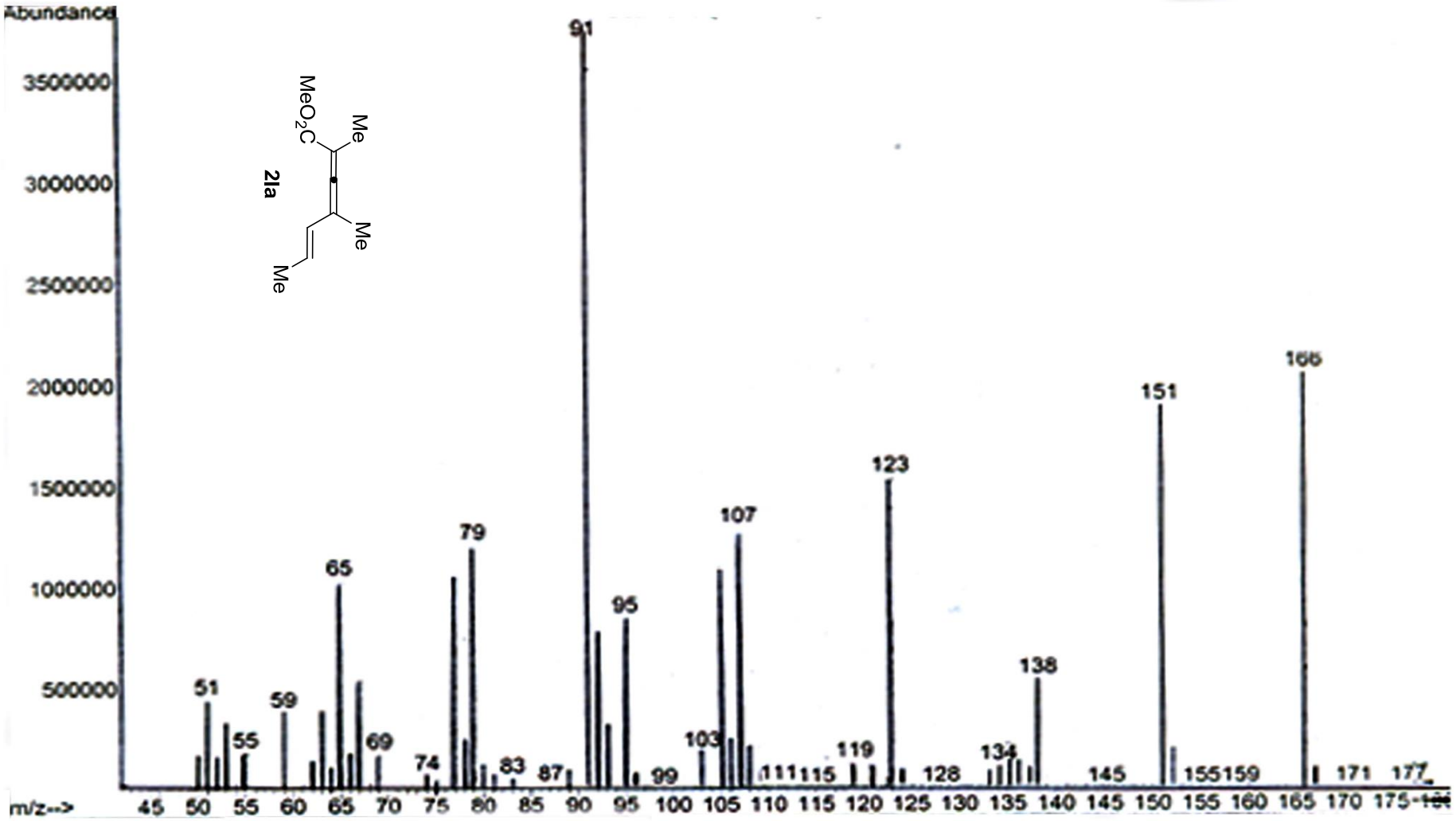

Figure E.8. Mass Spectrum of (E)-methyl 2,4-dimethylhepta-2,3,5-trienoate

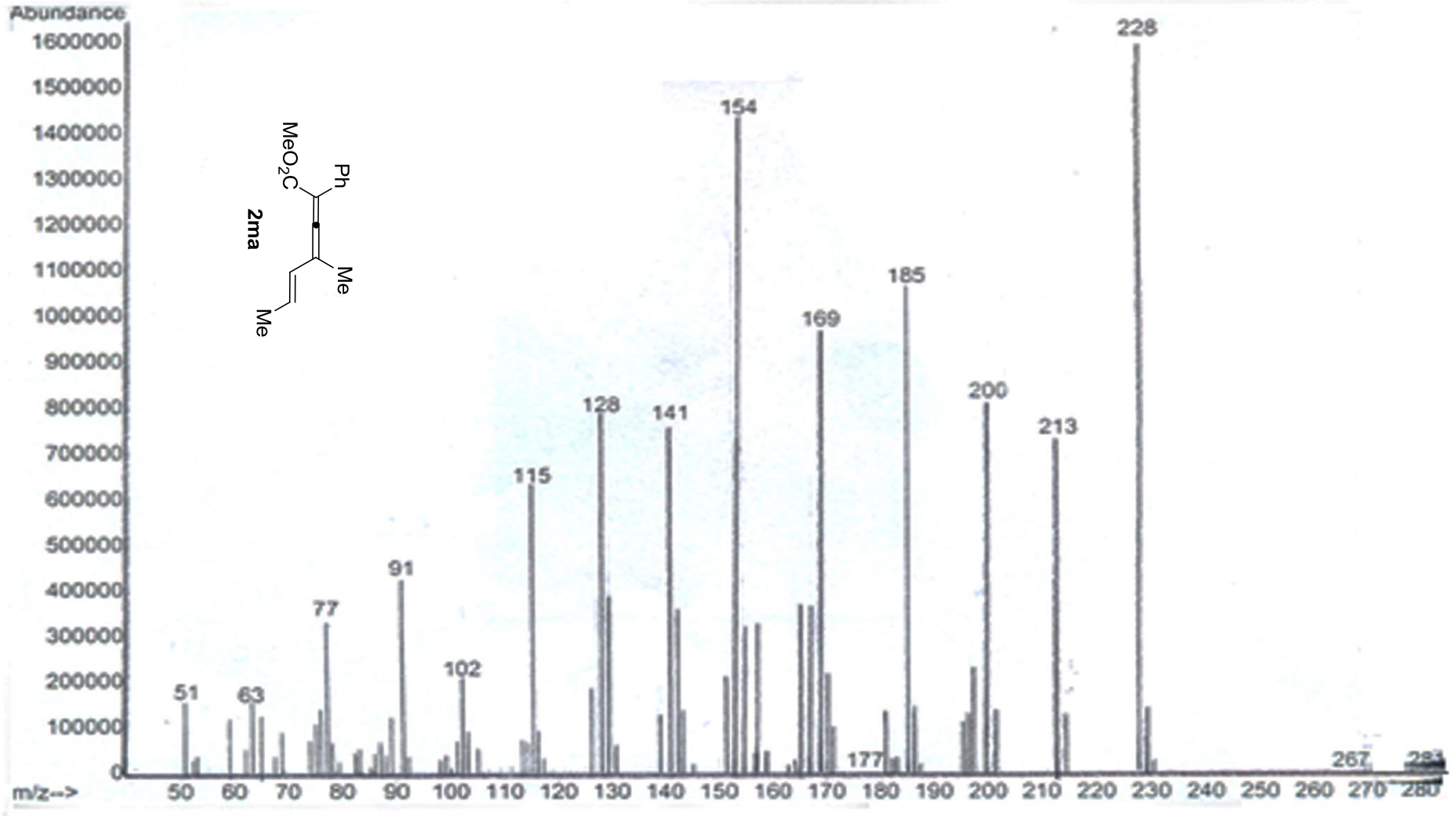

Figure E.9. Mass Spectrum of (E)-methyl 4-methyl-2-phenylhepta-2,3,5-trienoate

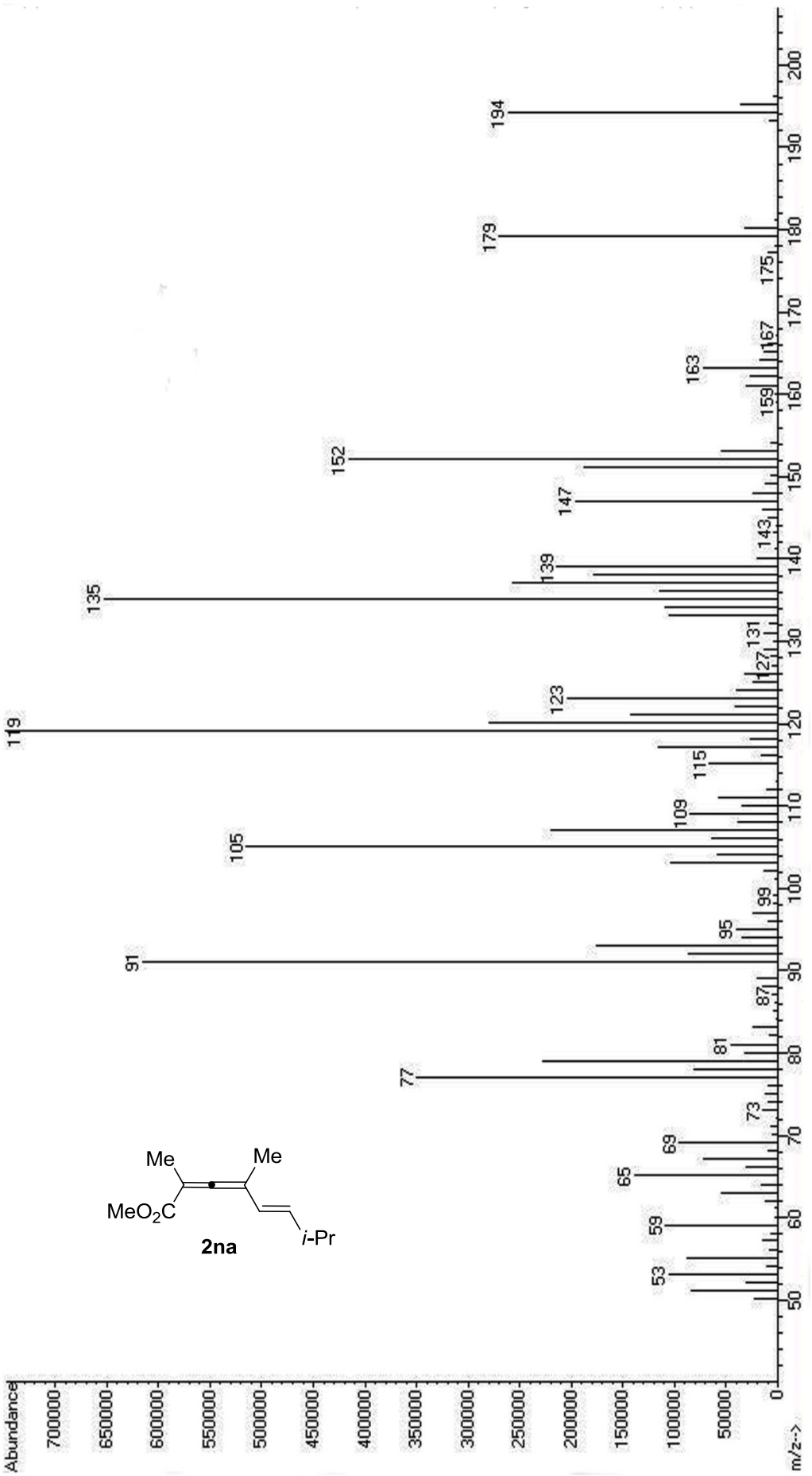

Figure E.10. Mass Spectrum of (E)-methyl 2,4,7-trimethylocta-2,3,5-trienoate

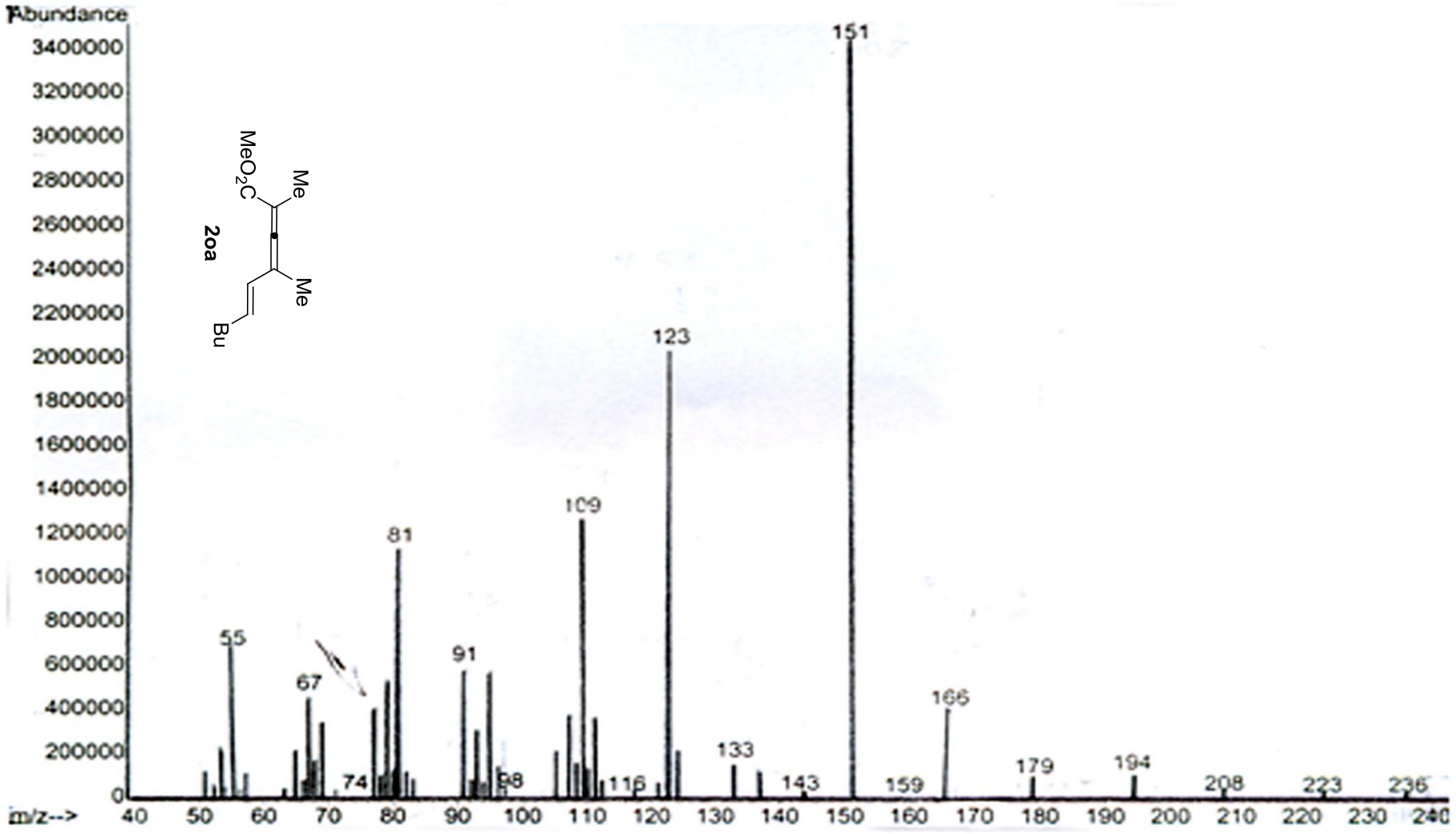

Figure E.11. Mass Spectrum of (E)-methyl 2,4-dimethyldeca-2,3,5-trienoate

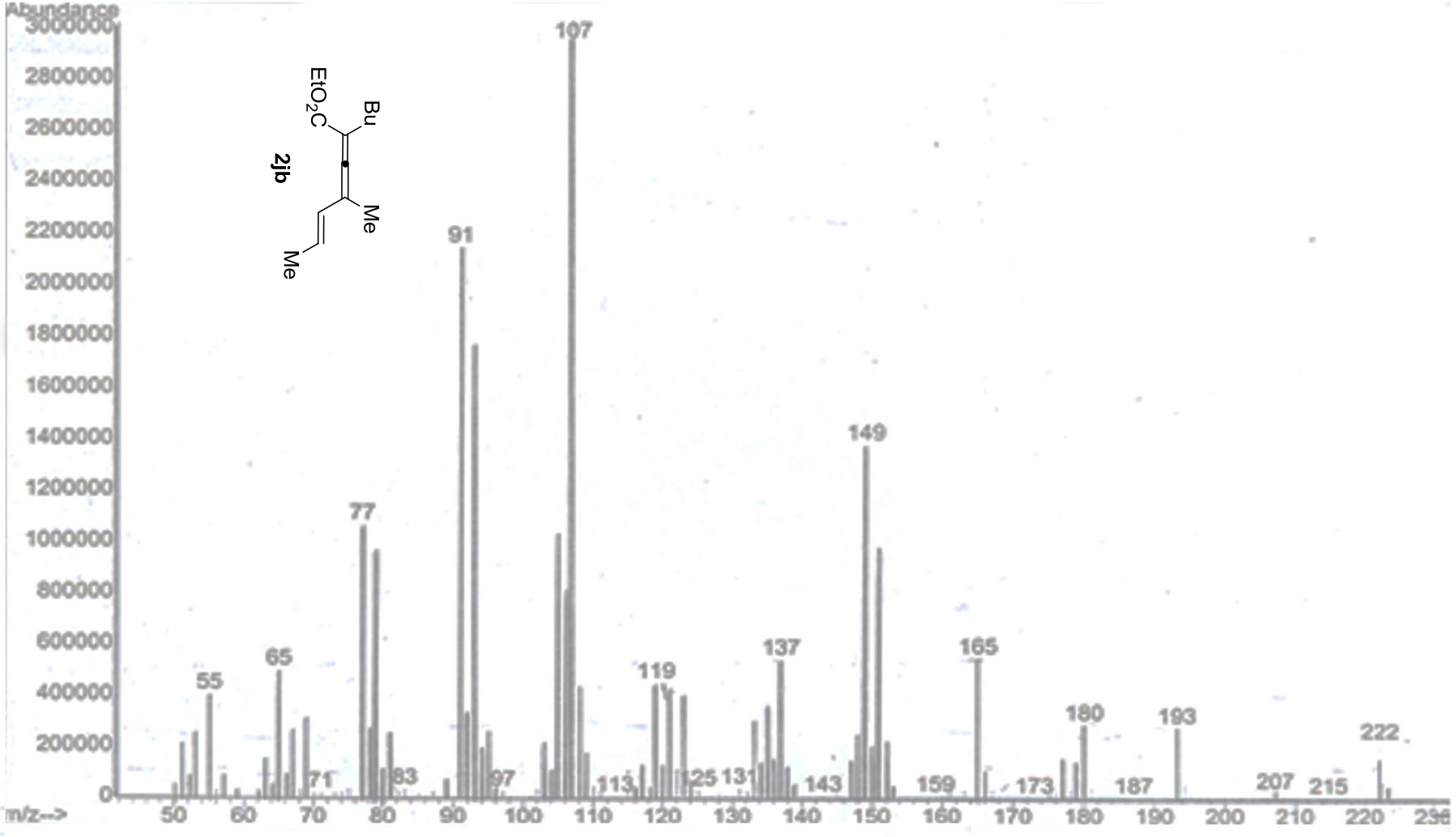

Figure E.12. Mass Spectrum of (E)-ethyl 2-butyl-4-methylhepta-2,3,5-trienoate

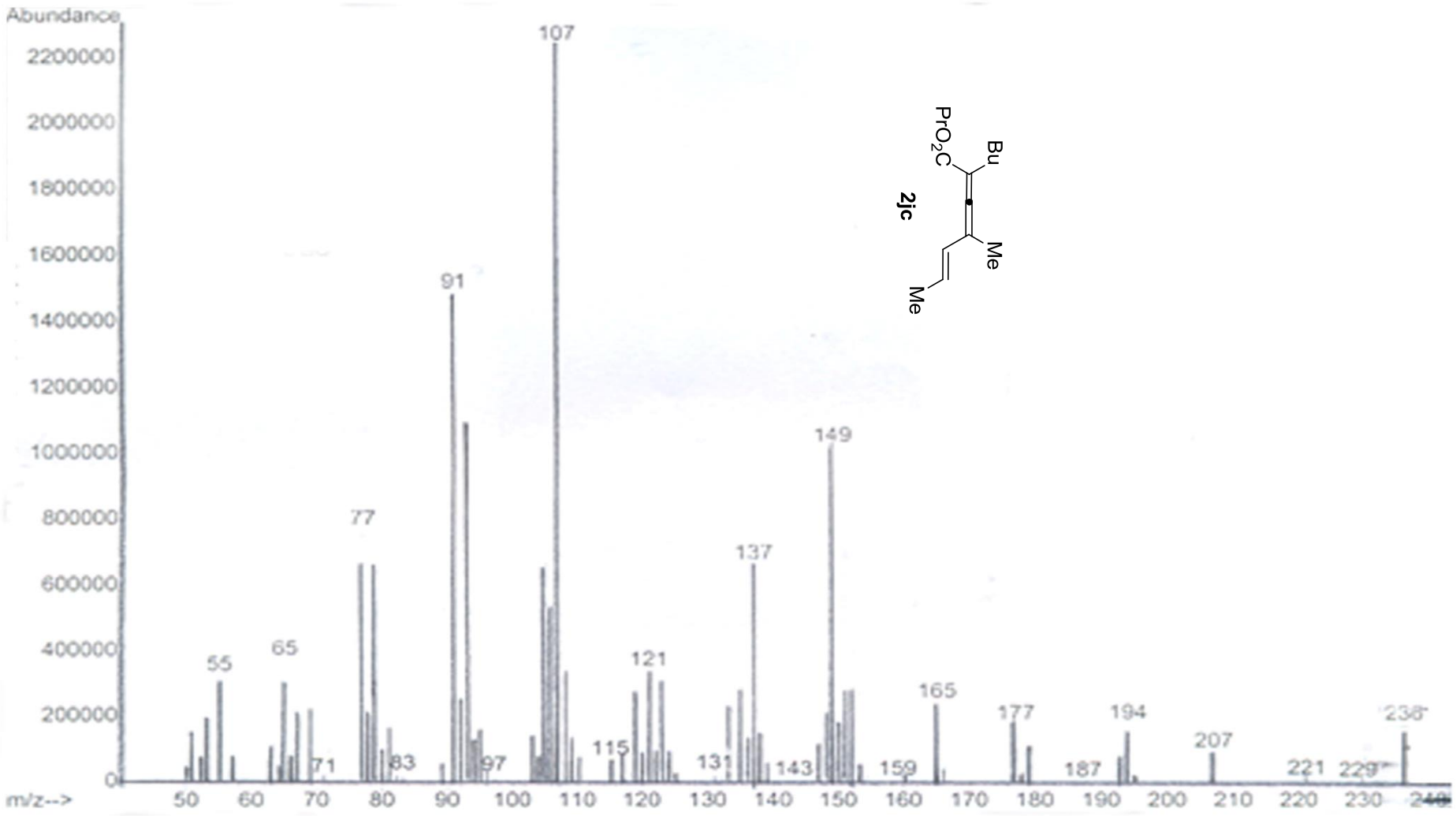

Figure E.13. Mass Spectrum of (E)-propyl 2-butyl-4-methylhepta-2,3,5-trienoate

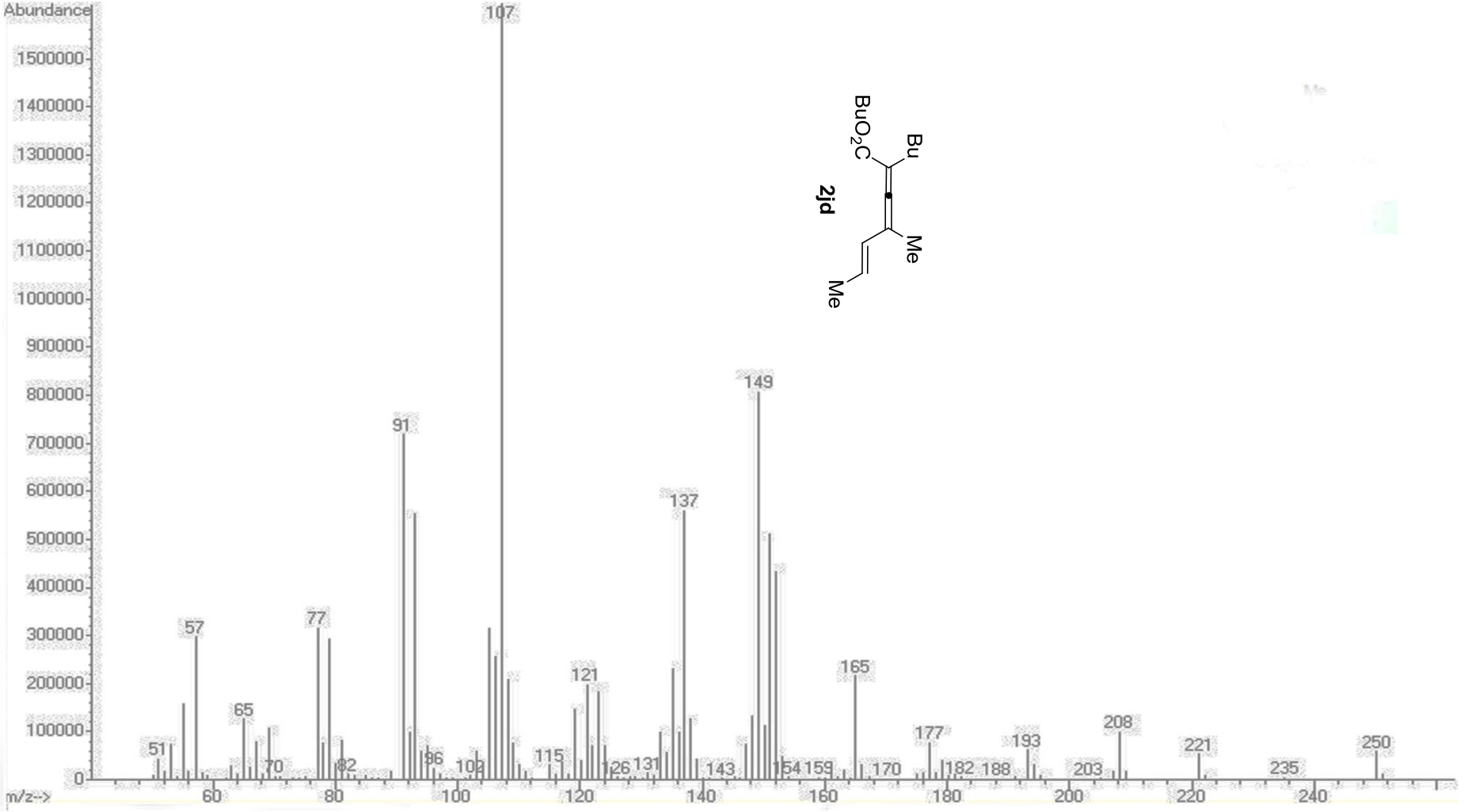

Figure E.14. Mass Spectrum of (E)-butyl 2-butyl-4-methylhepta-2,3,5-trienoate

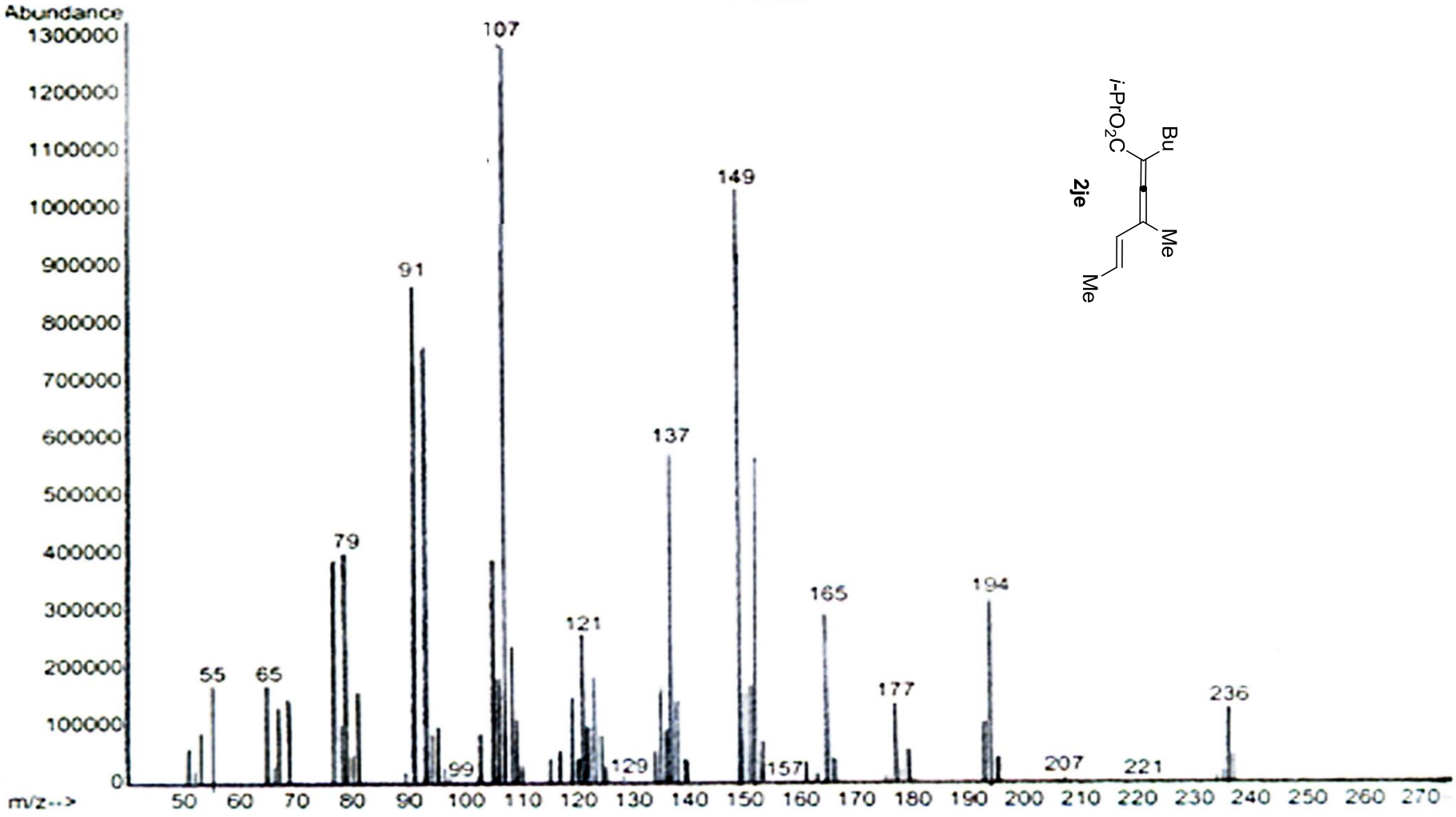

Figure E.15. Mass Spectrum of (E)-isopropyl 2-butyl-4-methylhepta-2,3,5-trienoate

APPENDIX F

FT-IR SPECTRUMS OF PRODUCTS

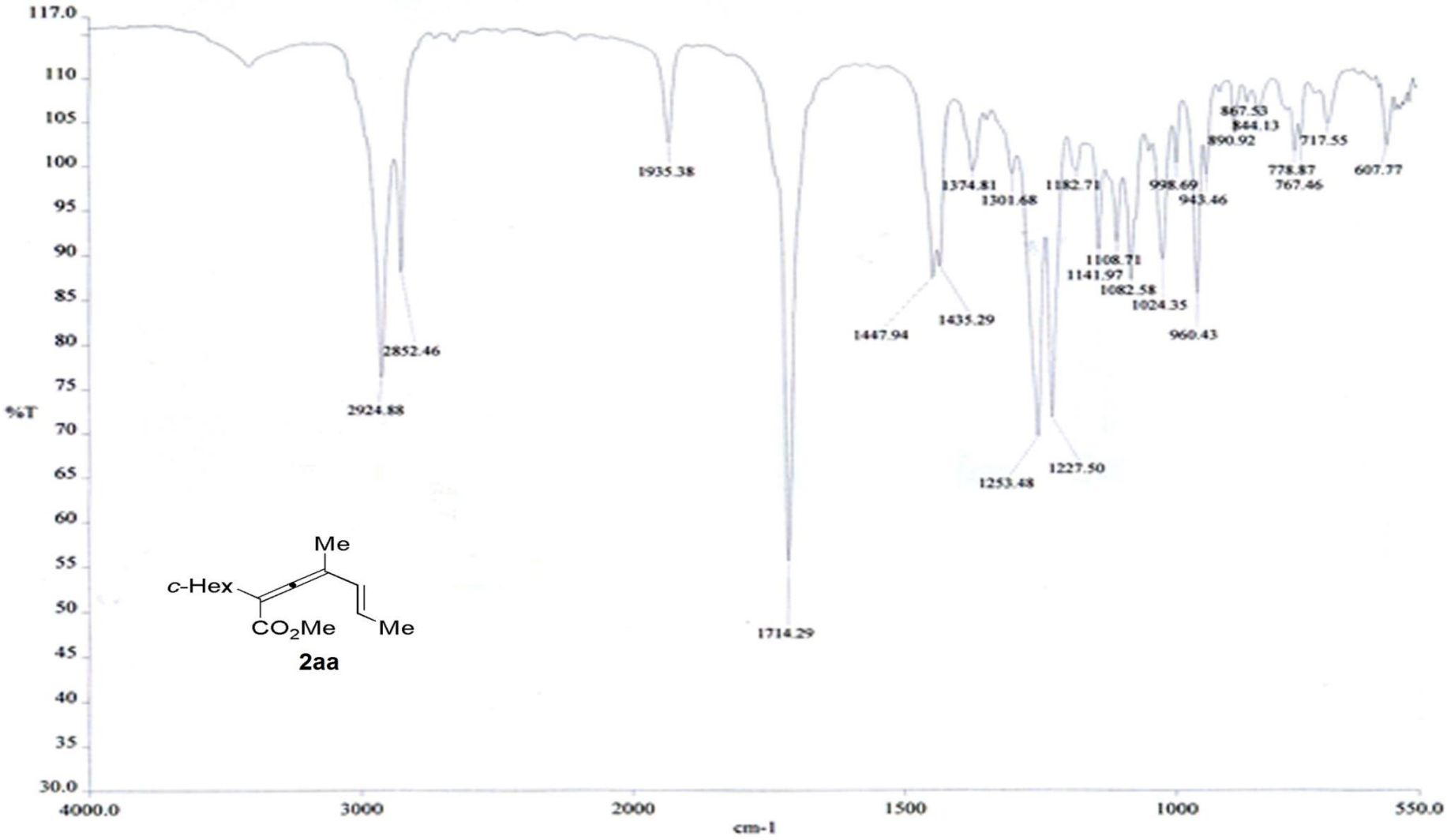

Figure F.1. FT-IR Spectrum of *(E)*-methyl 2-cyclohexyl-4-methylhepta-2,3,5-trienoate

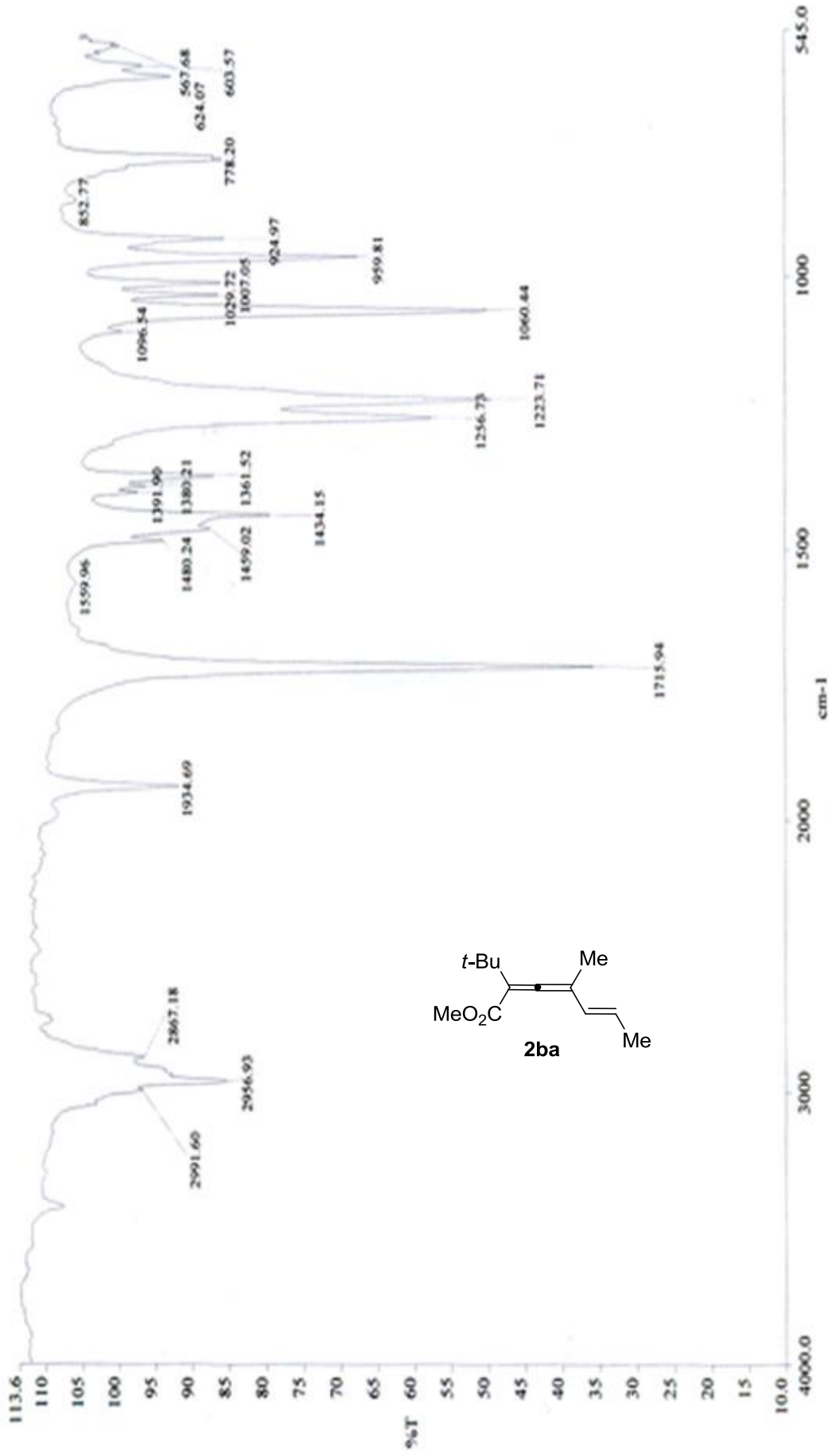

Figure F.2. FT-IR Spectrum of (*E*)-methyl 2-(tert-butyl)-4-methylhepta-2,3,5-trienoate

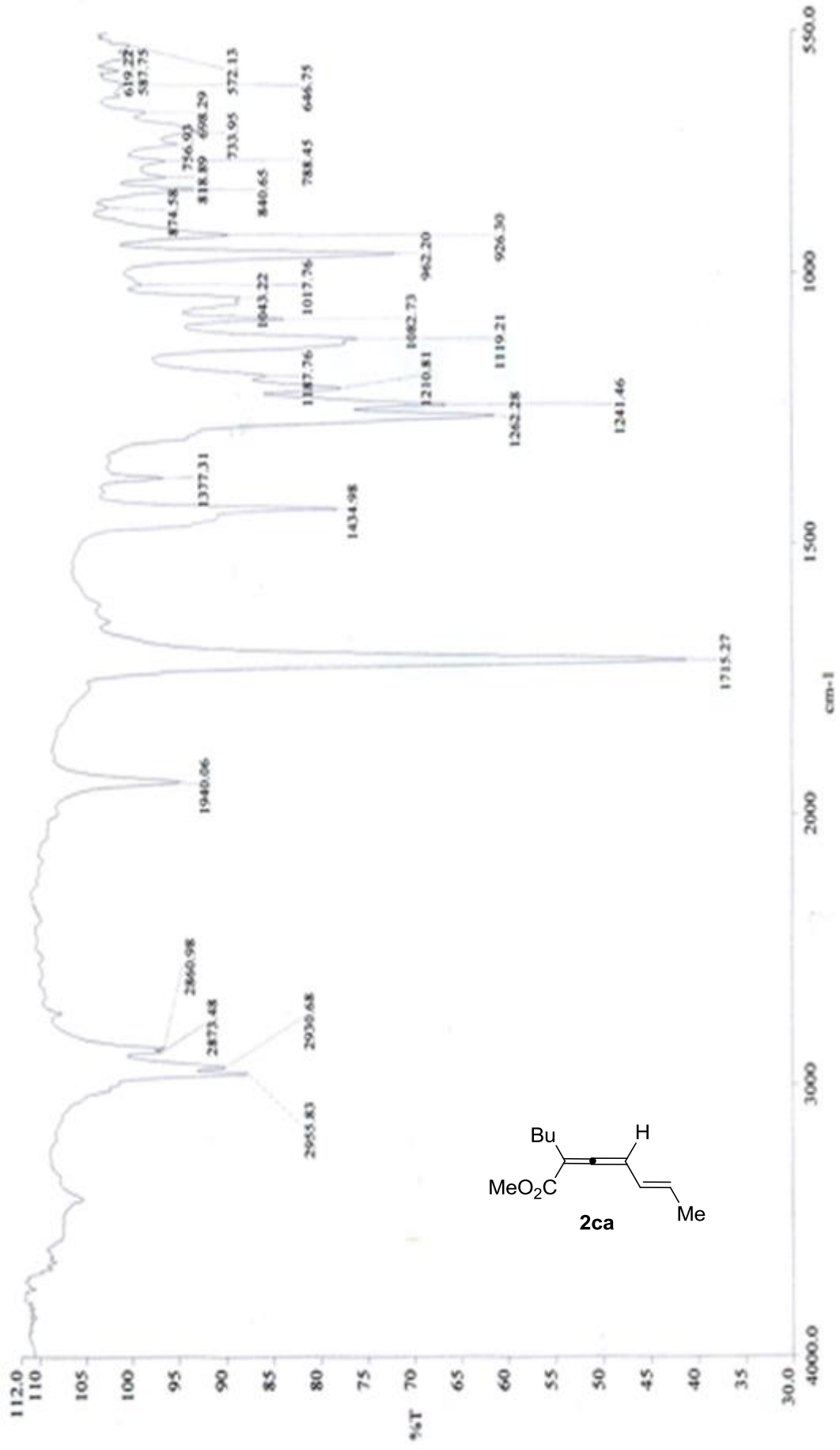

Figure F.3. FT-IR Spectrum of (*E*)-methyl 2-butylhepta-2,3,5-trienoate

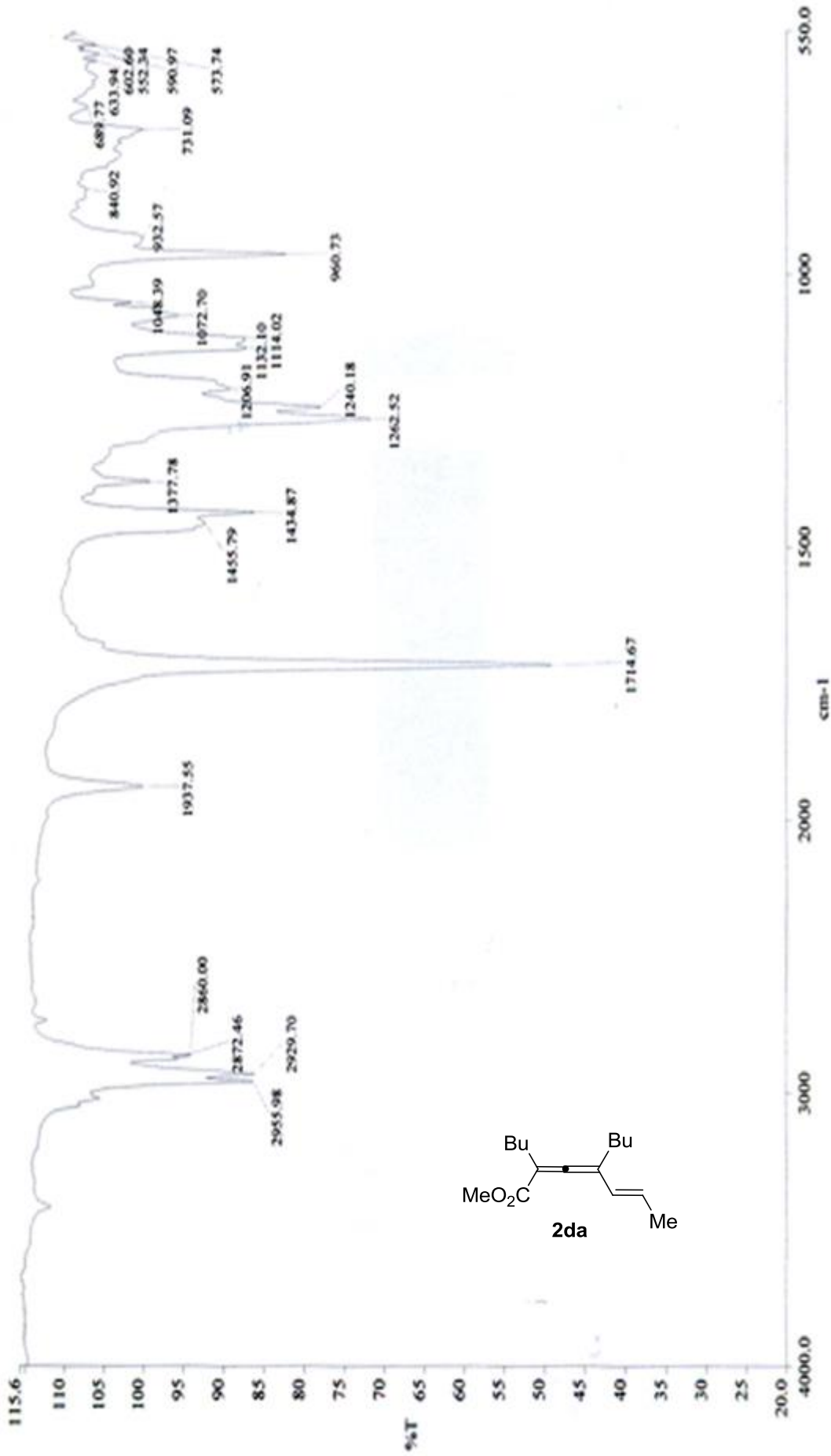

Figure F.4. FT-IR Spectrum of (*E*)-methyl 2-butyl-4-(prop-1-en-1-yl)octa-2,3-dienoate

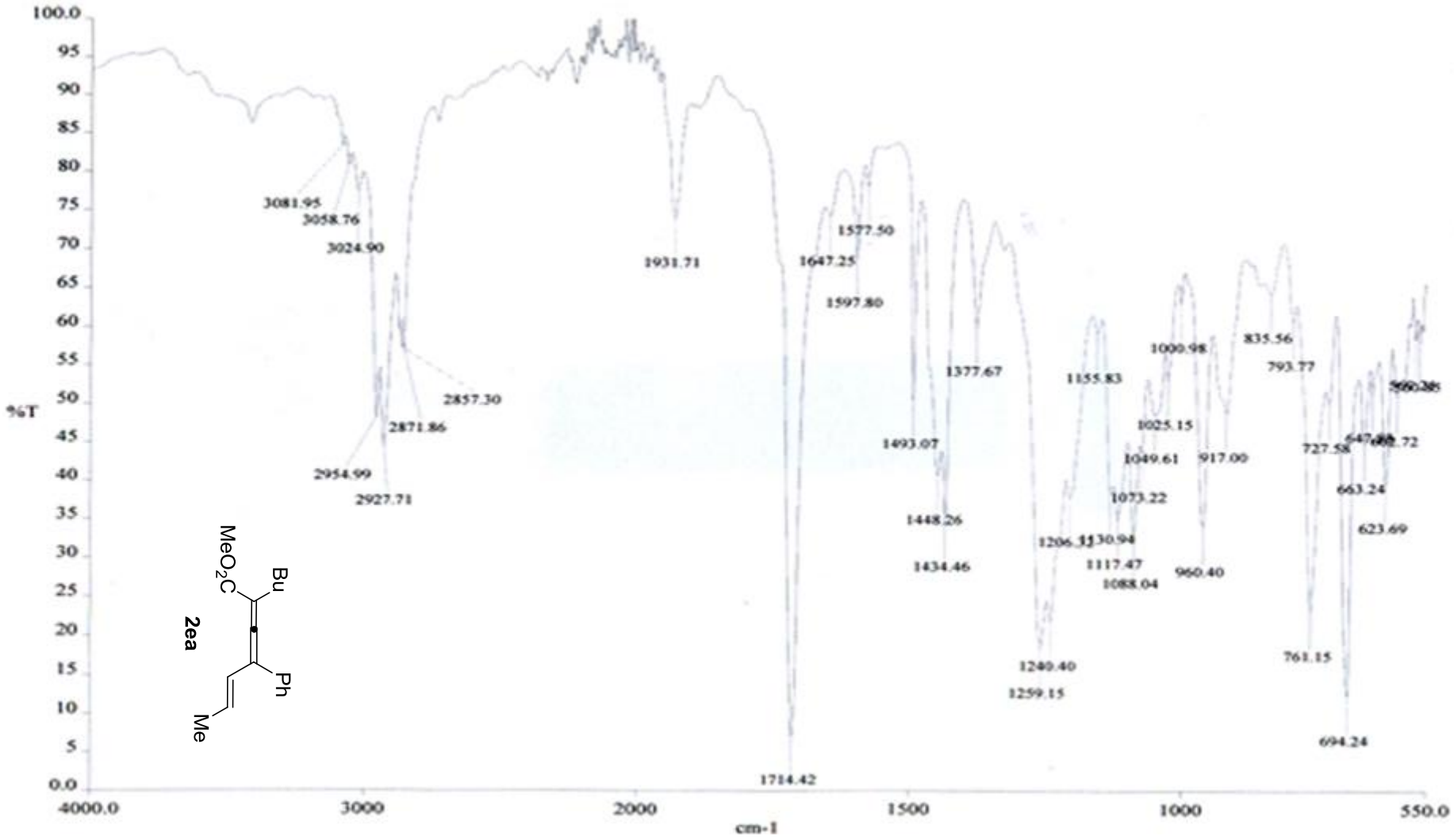

Figure F.5. FT-IR Spectrum of (*E*)-methyl 2-butyl-4-phenylhepta-2,3,5-trienoate

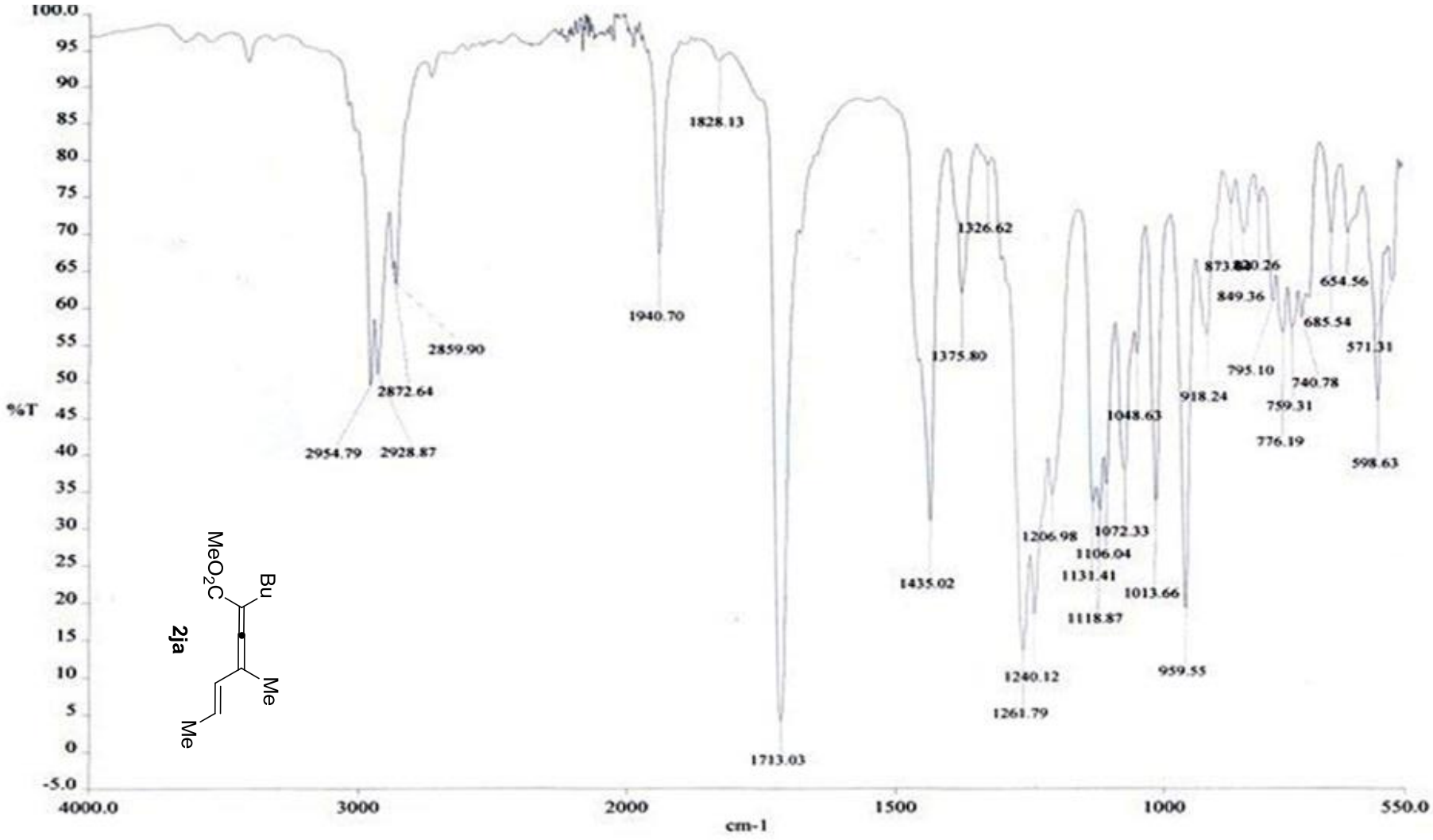

Figure F.6. FT-IR Spectrum of (*E*)-methyl 2-butyl-4-methylhepta-2,3,5-trienoate

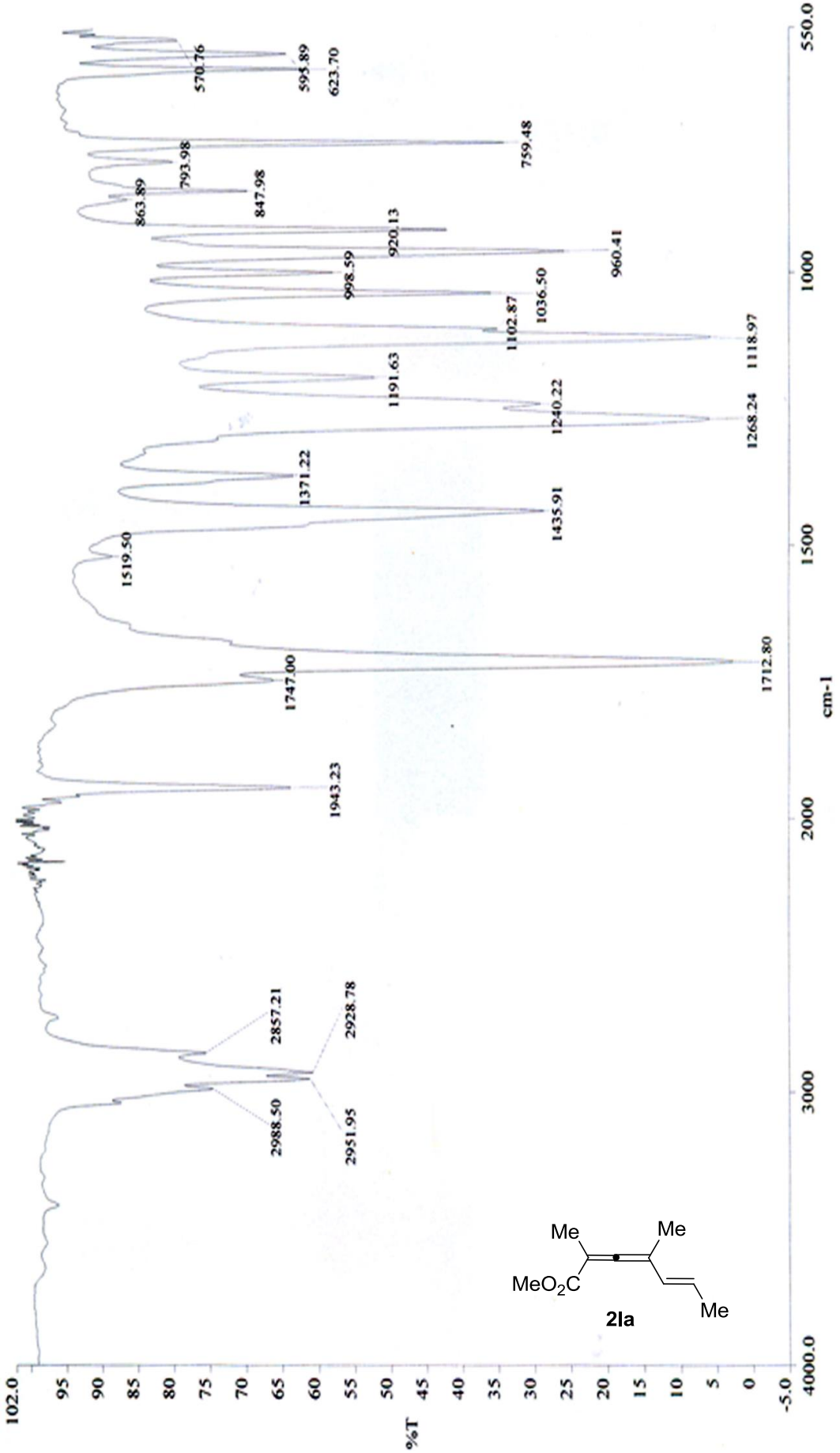

Figure F.7. FT-IR Spectrum of (E)-methyl 2,4-dimethylhepta-2,3,5-trienoate

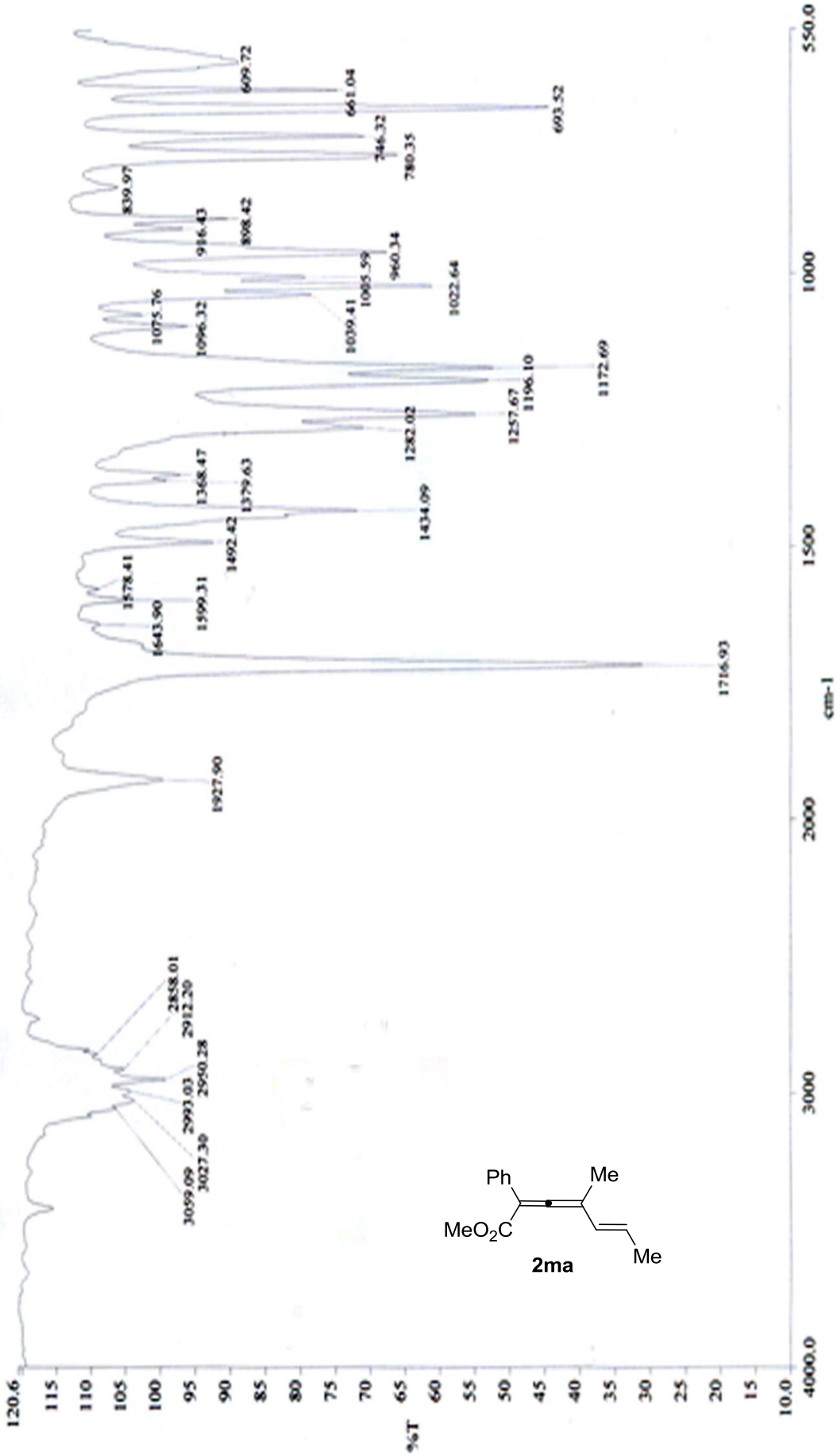

Figure F.8. FT-IR Spectrum of (*E*)-methyl 4-methyl-2-phenylhepta-2,3,5-trienoate

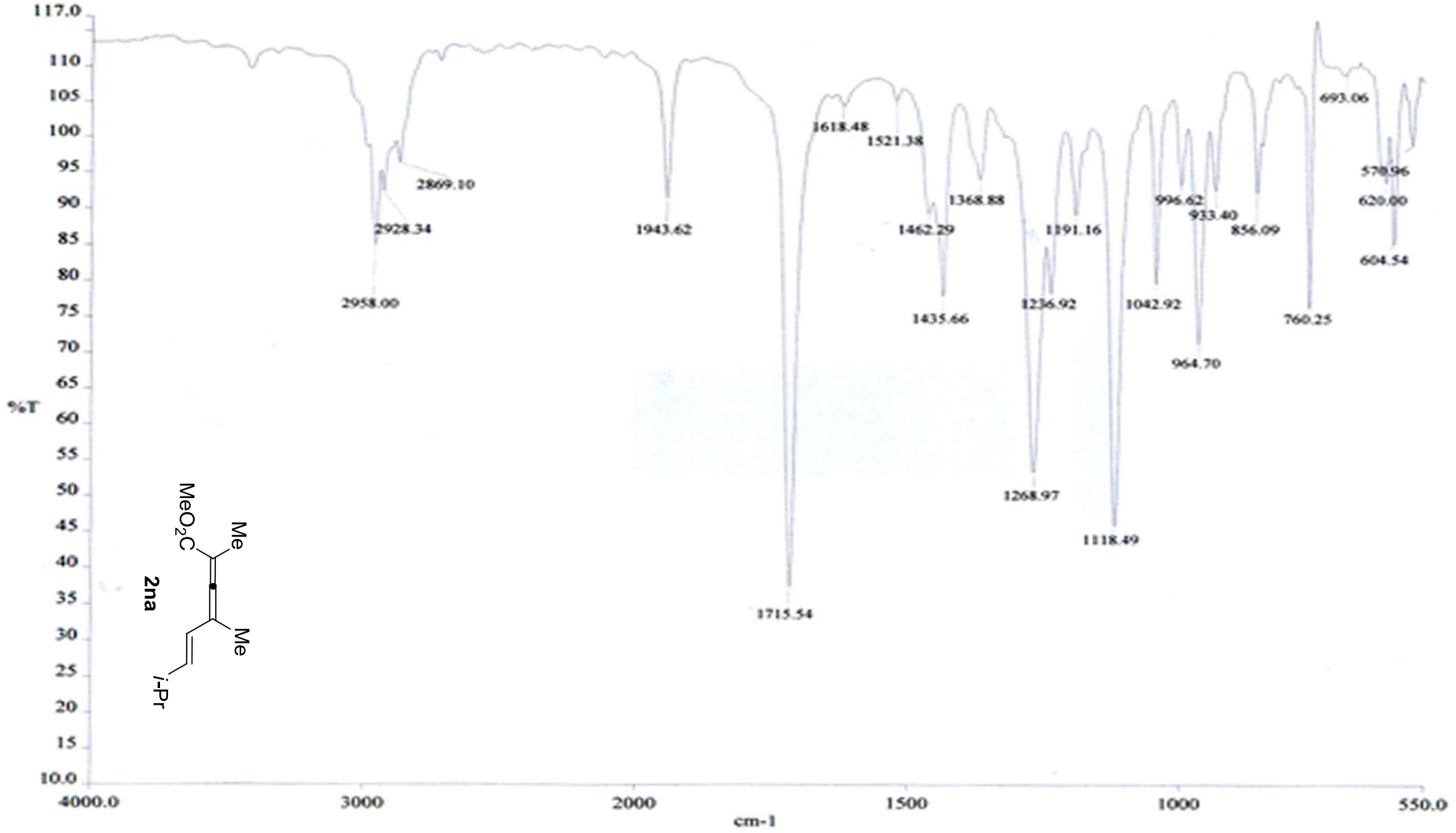

Figure F.9. FT-IR Spectrum of (E)-methyl 2,4,7-trimethylocta-2,3,5-trienoate

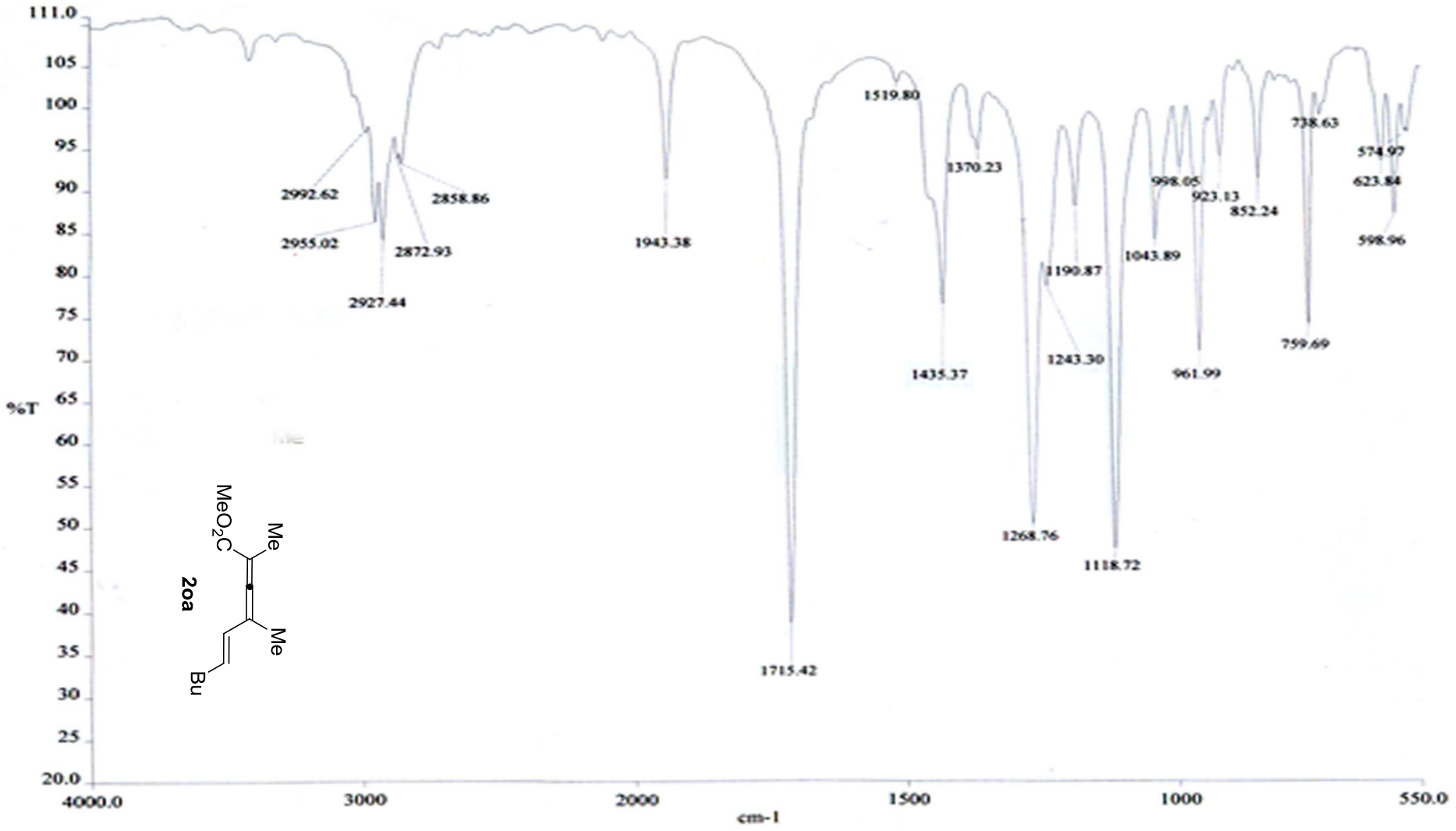

Figure F.10. FT-IR Spectrum of (E)-methyl 2,4-dimethyldeca-2,3,5-trienoate

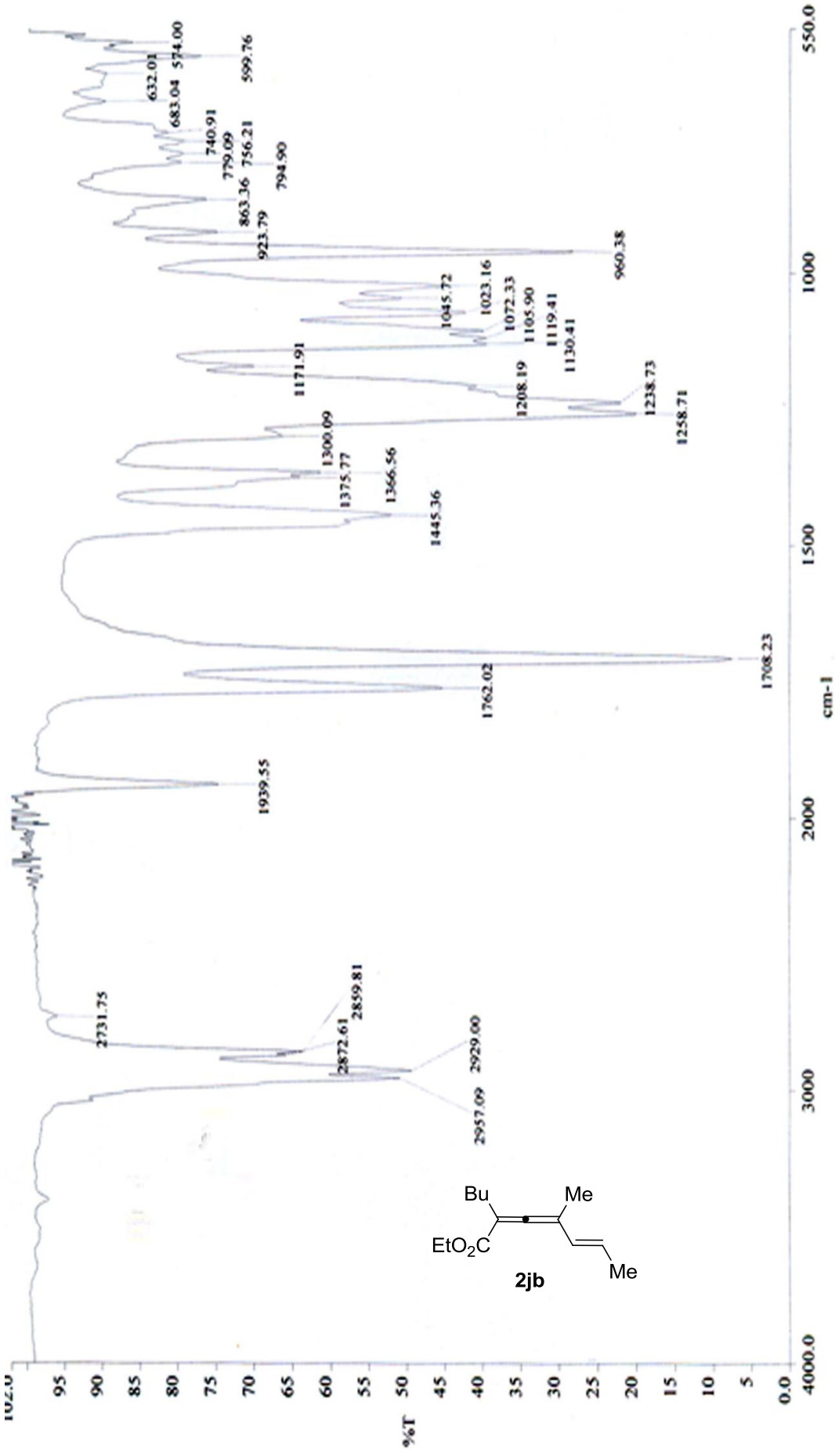

Figure F.11. FT-IR Spectrum of (E)-ethyl 2-butyl-4-methylhepta-2,3,5-trienoate

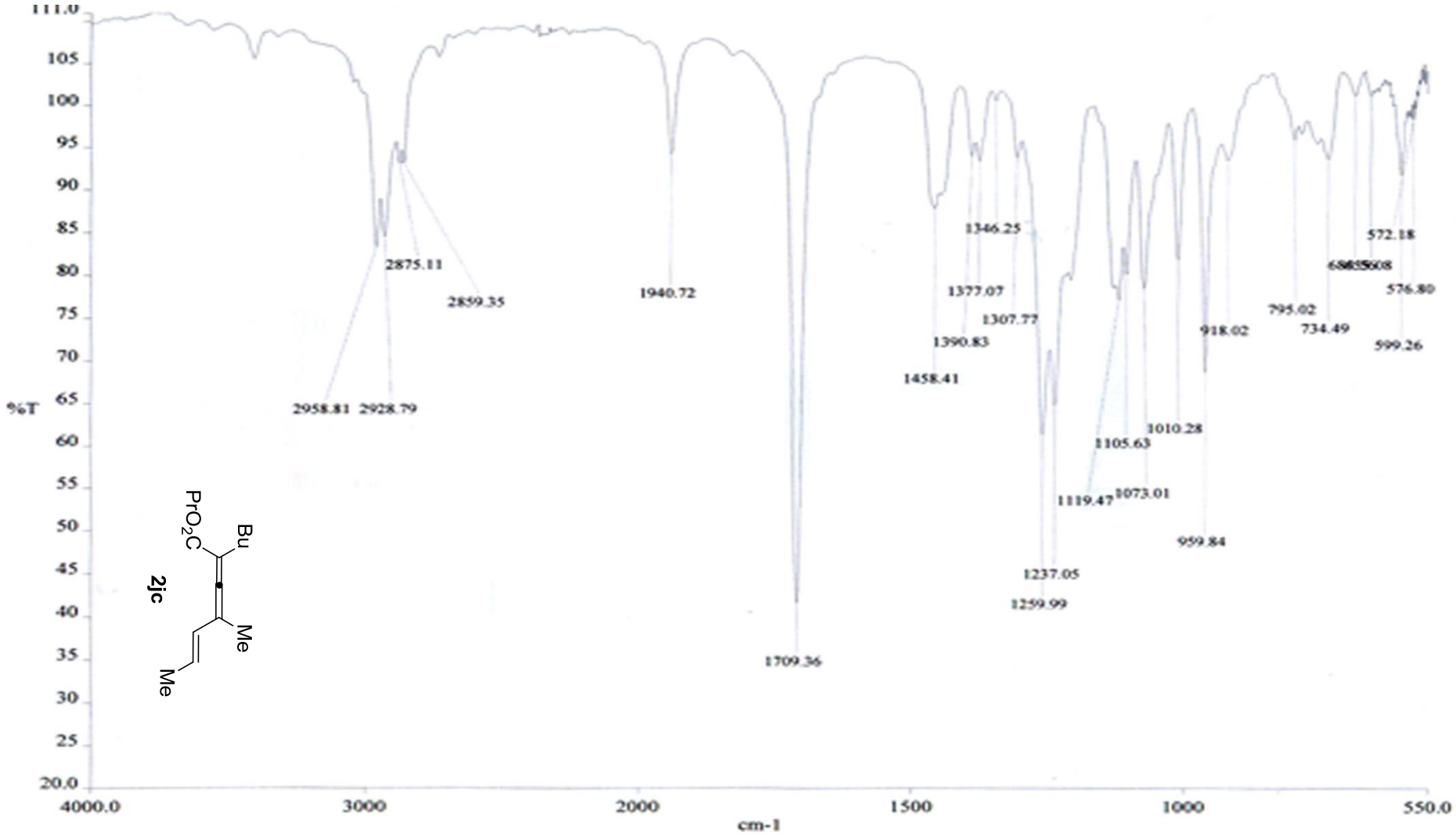

Figure F.12. FT-IR Spectrum of (E)-propyl 2-butyl-4-methylhepta-2,3,5-trienoate

Figure F.13. FT-IR Spectrum of (*E*)-butyl 2-butyl-4-methylhepta-2,3,5-trienoate

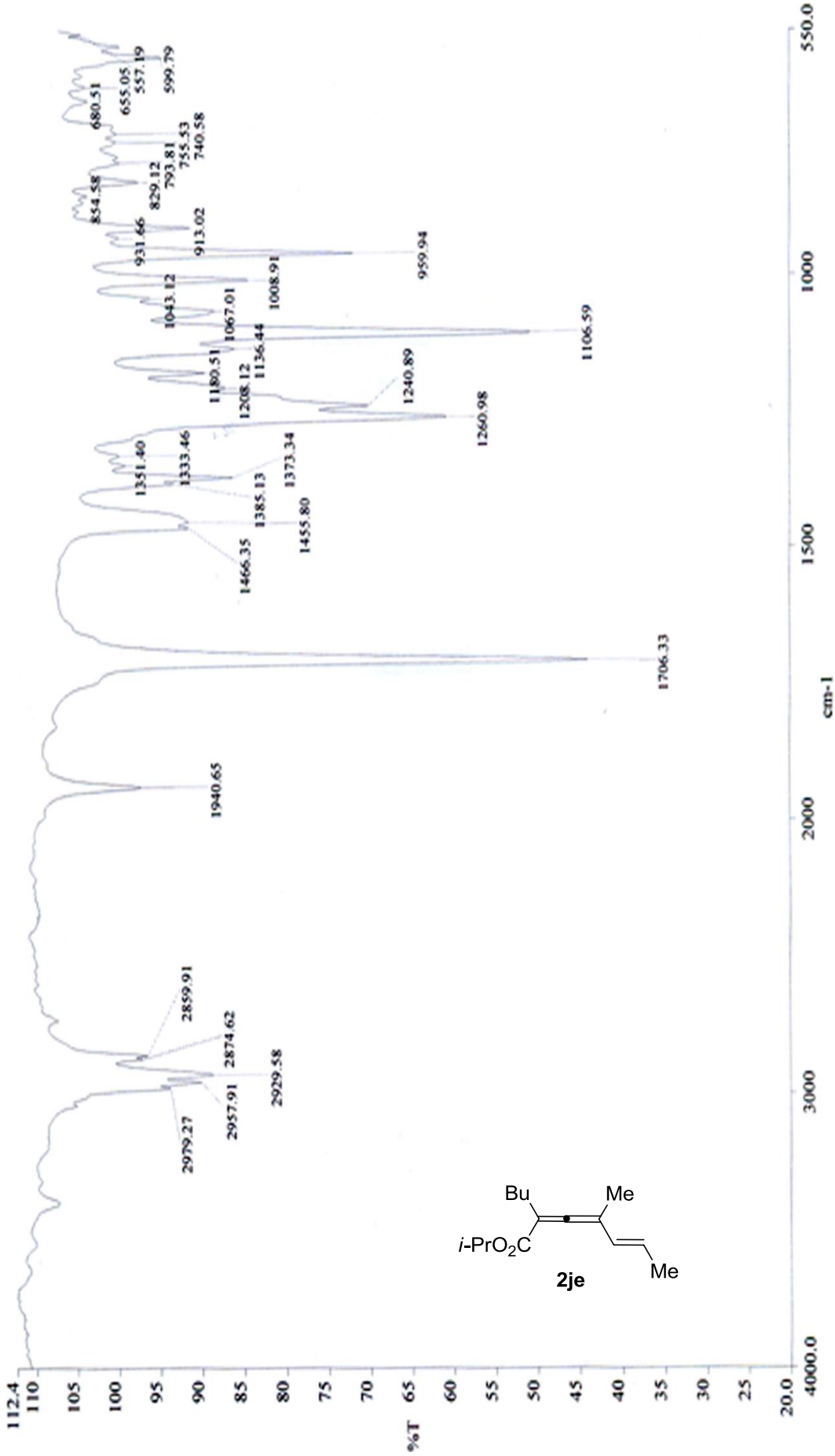

Figure F.14. FT-IR Spectrum of (*E*)-isopropyl 2-butyl-4-methylhepta-2,3,5-trienoate

APPENDIX G.

GC CHROMATOGRAMS OF REACTANTS

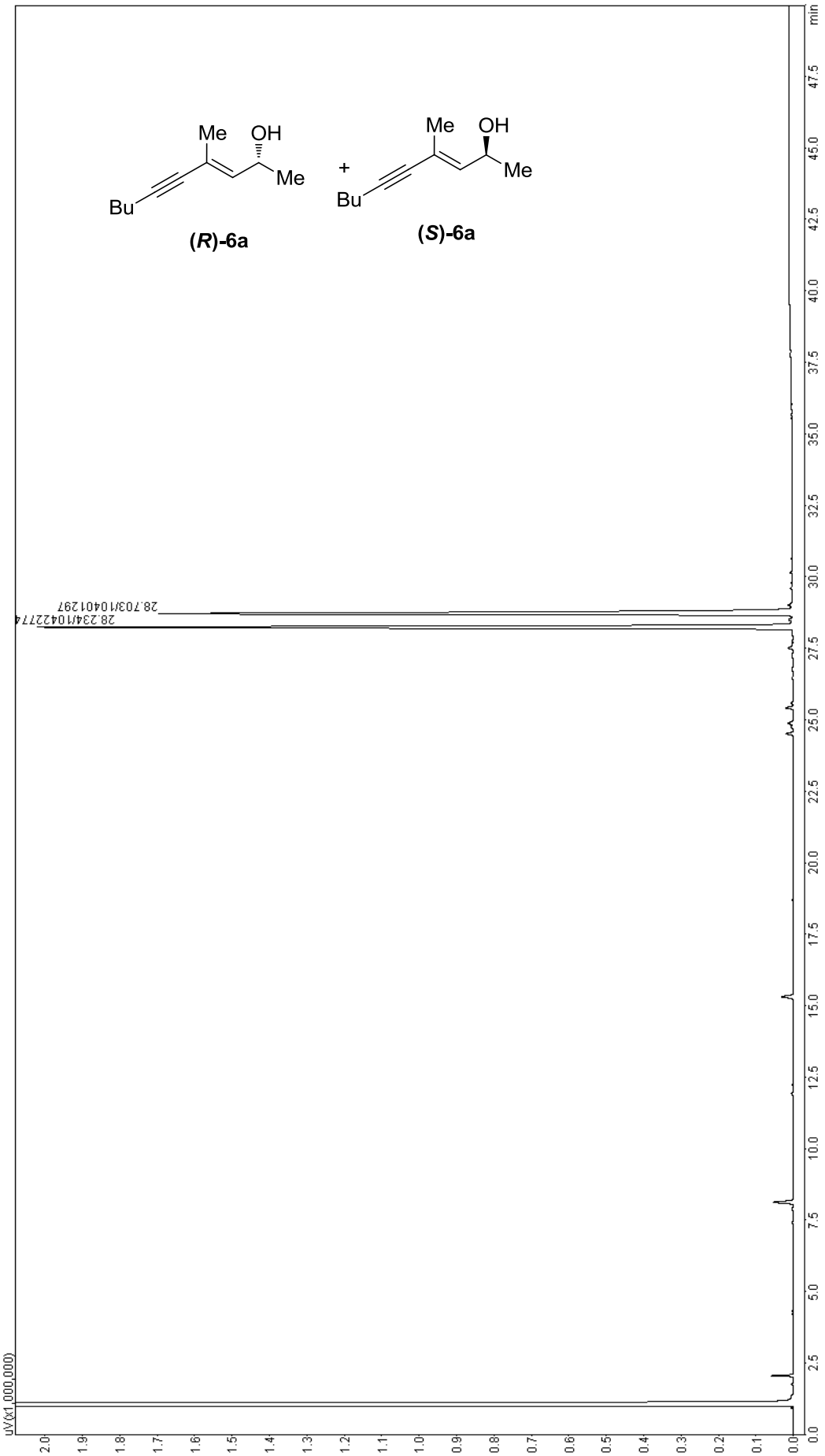

Figure G.1. GC Chromatogram of (*E*)-4-methyldec-3-en-5-yn-2-ol

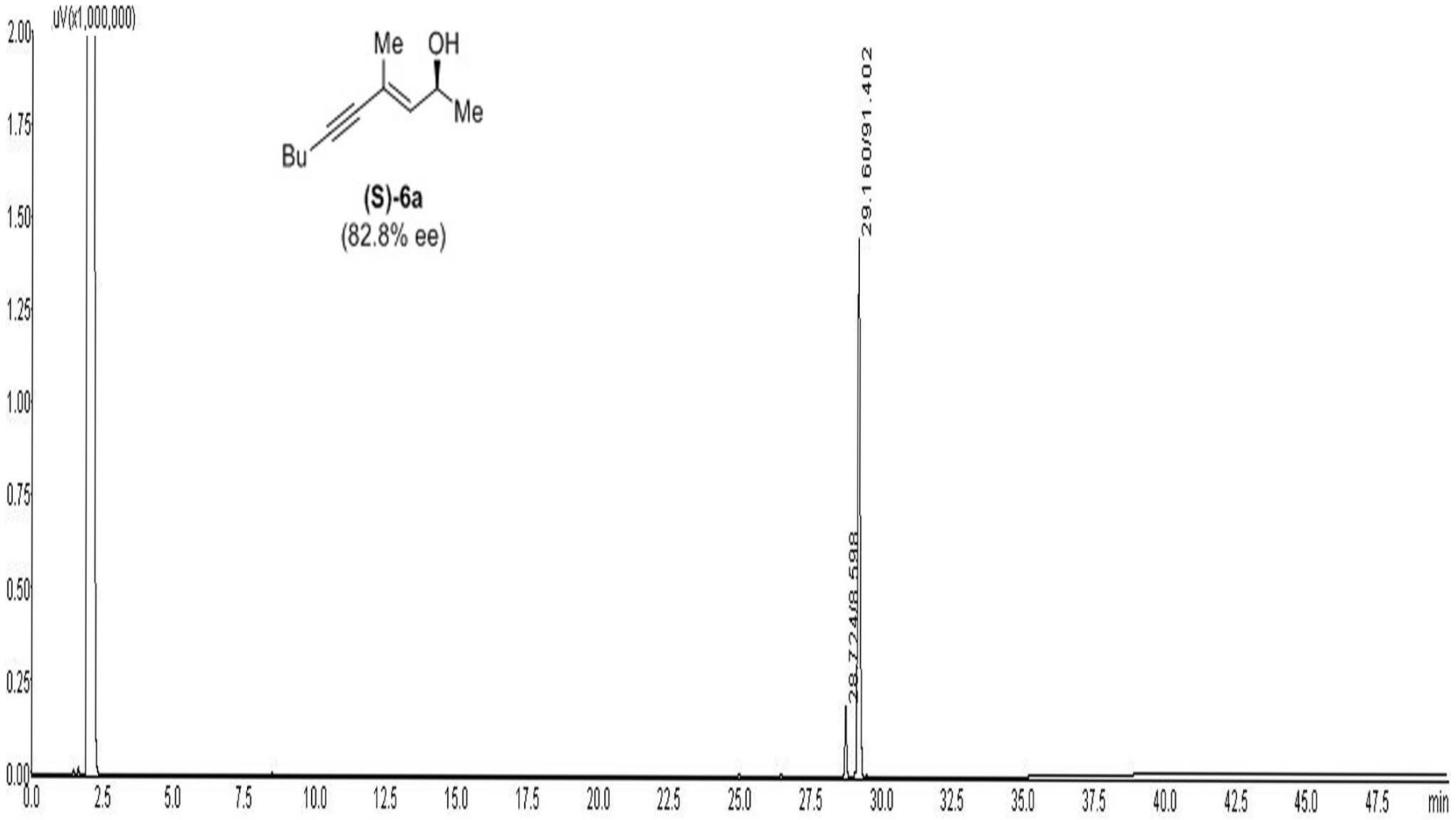

Figure G.2. GC Chromatogram of (*S*)-(*E*)-4-methyldec-3-en-5-yn-2-ol

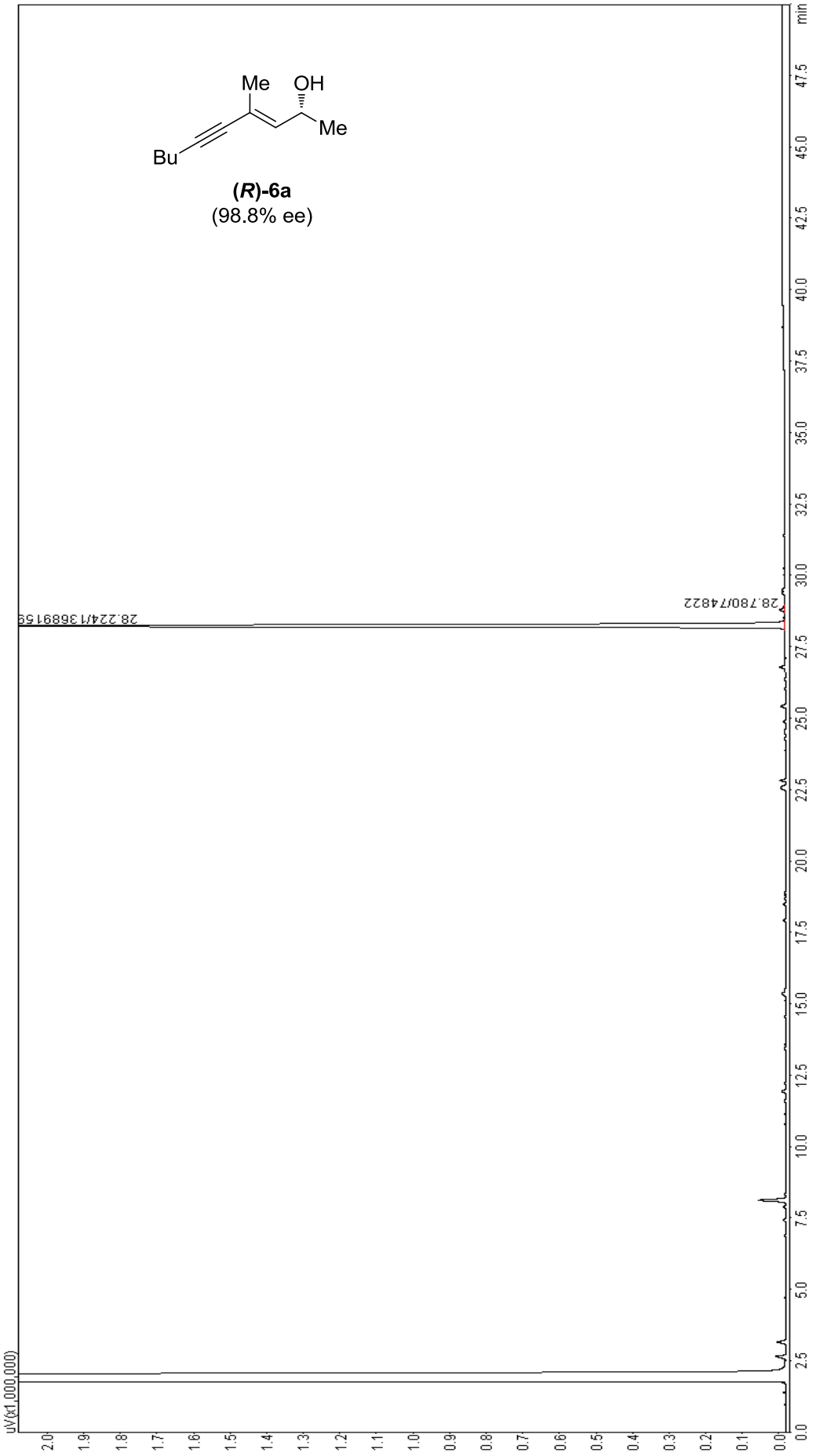

Figure G.3. GC Chromatogram of (*R*)-(*E*)-4-methyldec-3-en-5-yn-2-ol

APPENDIX H

HPLC CHROMATOGRAMS OF PRODUCTS

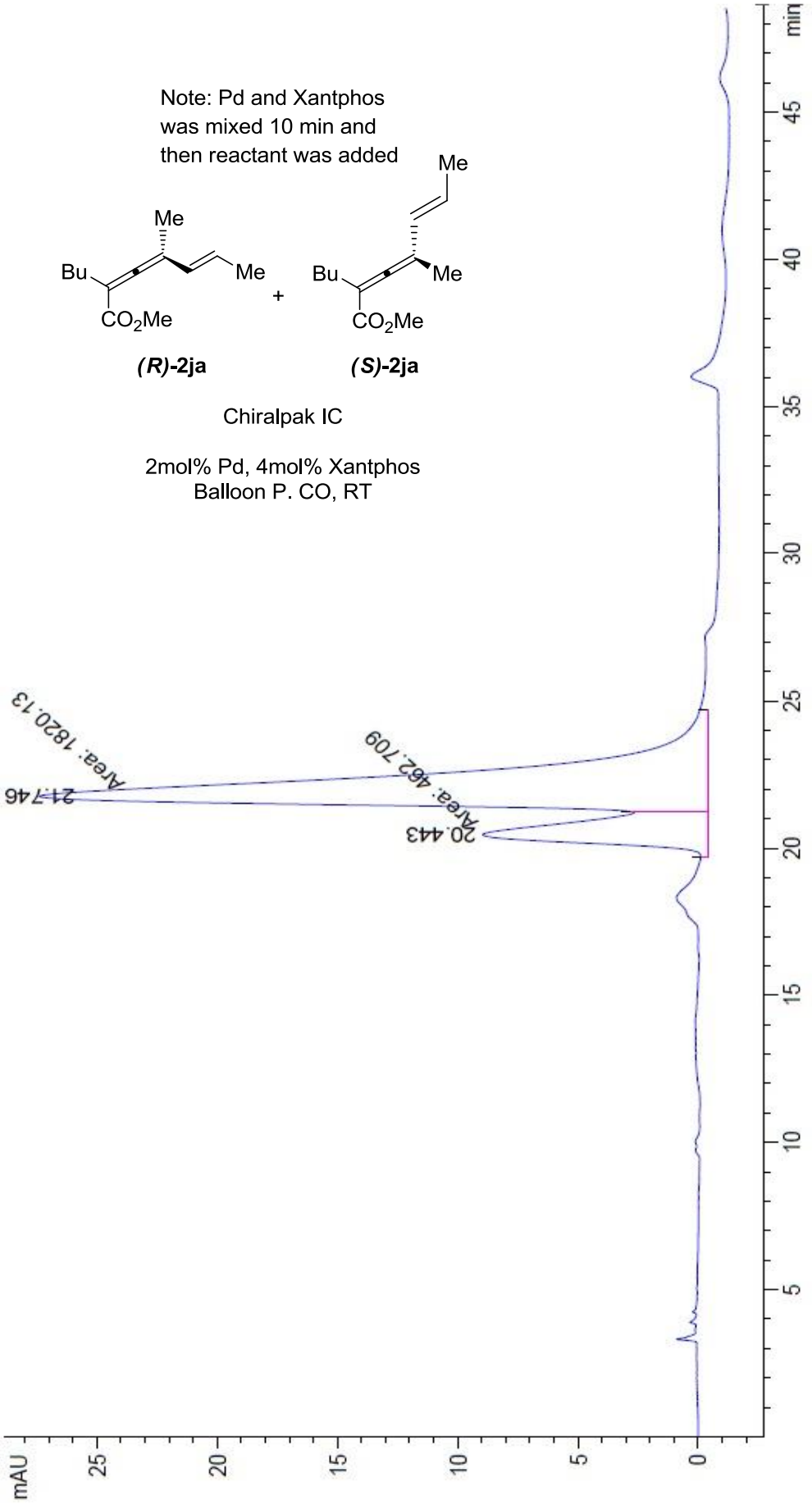

Figure H.1. HPLC Chromatogram of (*R,E*)-methyl 2-butyl-4-methylhepta-2,3,5-trienoate

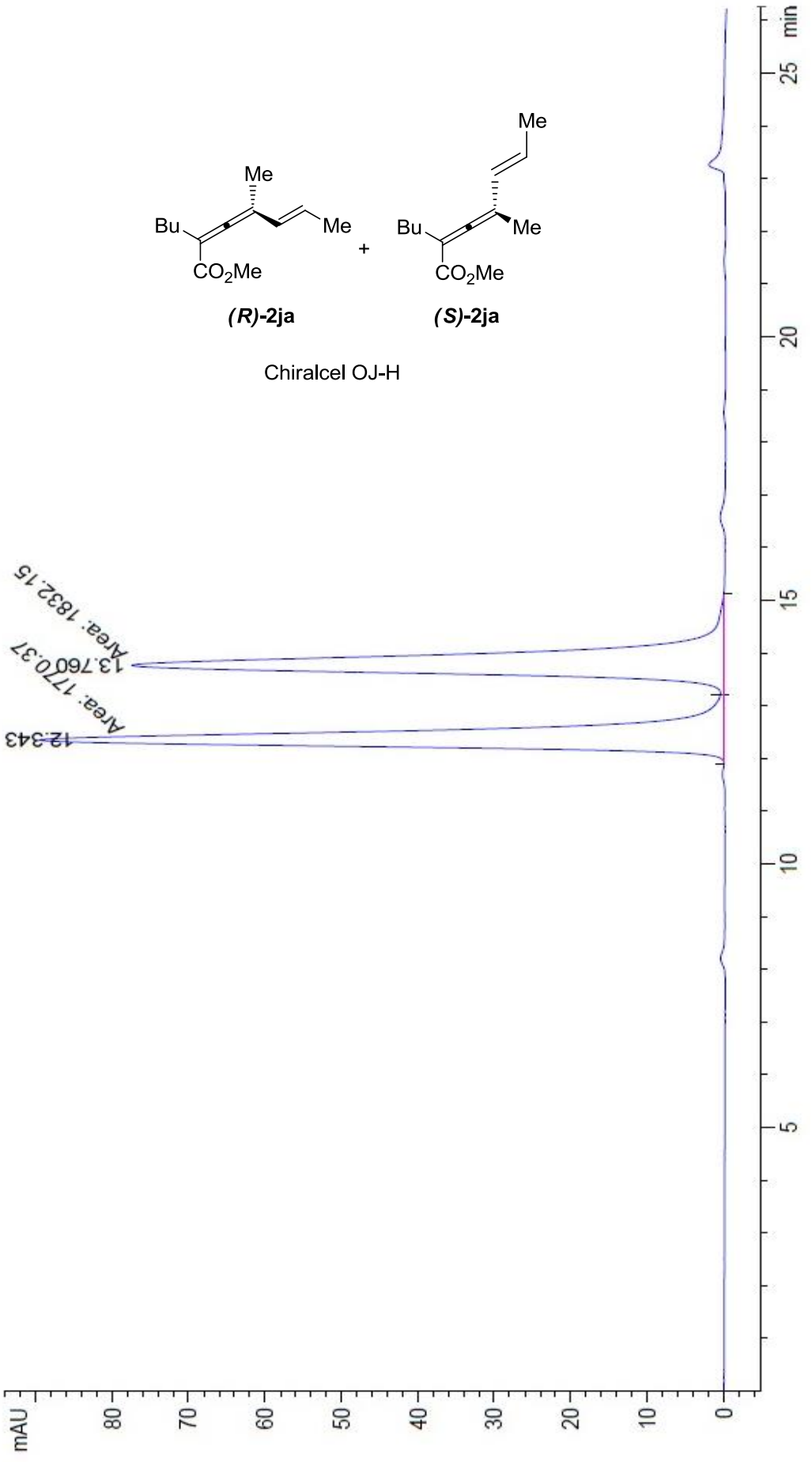

Figure H.2. HPLC Chromatogram of (*E*)-methyl 2-butyl-4-methylhepta-2,3,5-trienoate

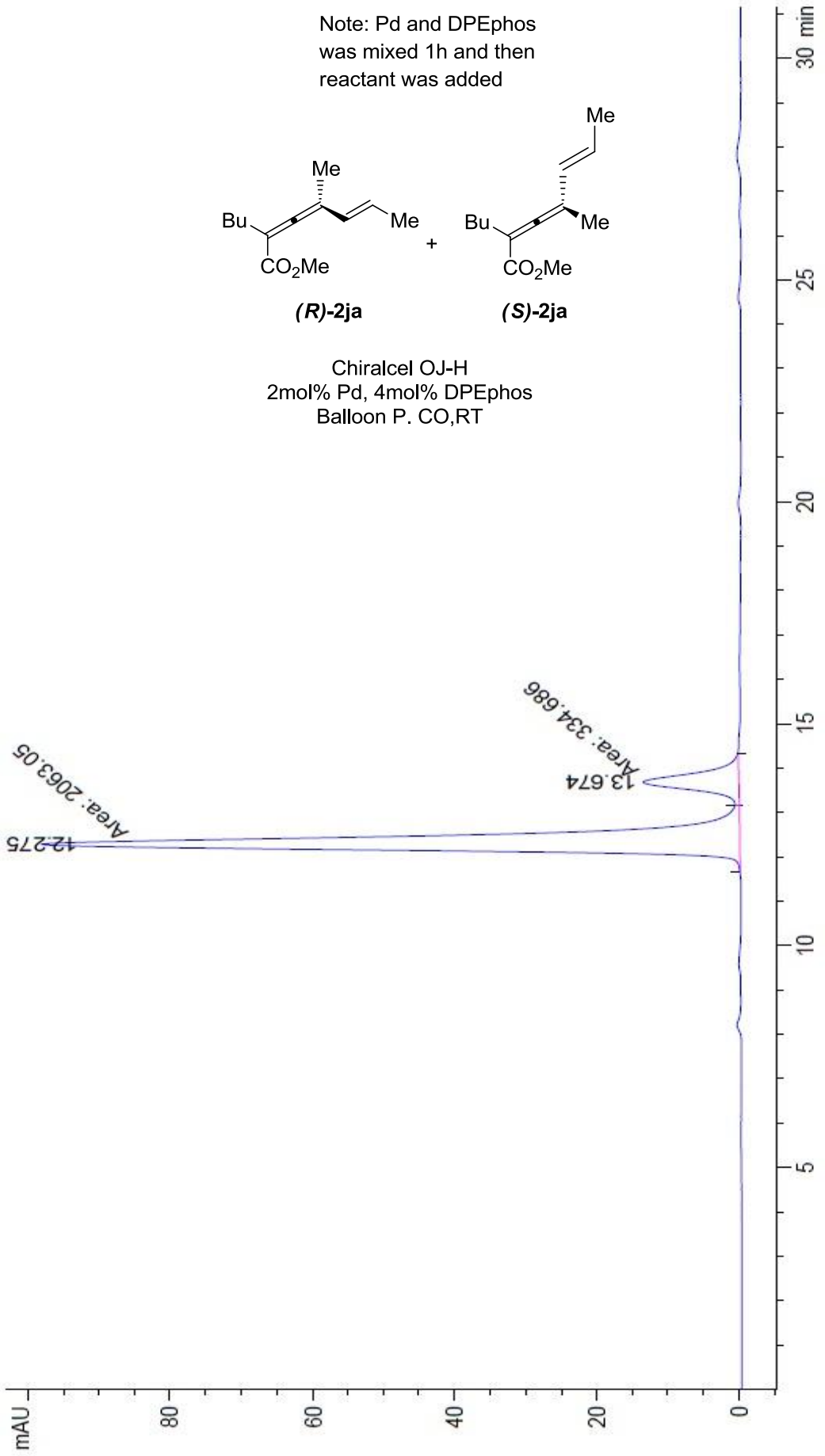

Figure H.3. HPLC Chromatogram of (*S,E*)-methyl 2-butyl-4-methylhepta-2,3,5-trienoate