Dissertation

Photo-/Electrocatalytic Chemistry: Electron Transfer in Synthetic Organic Reaction

光/電気エネルギーを用いた有機電子移動反応

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Publications and Presentations

Publications:

1) **Nakayama K.**; Maeta N.; Horiguchi G.; Kamiya H.; Okada Y.*, Radical Cation Diels-Alder Reactions by TiO_2 Photocatalysis, *Organic Letters*, American Chemical Society, **2019**, *21*, 2246−2250. https://doi.org/10.1021/acs.orglett.9b00526 (Chapter 2)

2) **Nakayama K.**; Kamiya H.; Okada Y.*, EC-Backward-E Electrochemistry in Radical Cation Diels-Alder Reactions, *Journal of The Electrochemical Society*, IOP Science, **2020**, *167*, 155518. https://doi.org/10.1149/1945-7111/abb97f (Chapter 3)

3) **Nakayama K.**; Kamiya H.; Okada Y.*, Radical Cation Diels–Alder Reactions of Arylidene Cycloalkanes, *Beilstein Journal of Organic Chemistry*, Beilstein-Institut, **2022**, *18*, 1100-1106. https://doi.org/10.3762/bjoc.18.112 (Chapter 4)

Related Publications:

1) Okada Y.*; Maeta N.; **Nakayama K.**; Kamiya H., TiO_2 Photocatalysis in Aromatic "Redox Tag"-Guided Intermolecular Formal [2 + 2] Cycloadditions, *The Journal of Organic Chemistry*, American Chemical Society, **2018**, *83*, 4948−4962. **(Featured Article)** https://doi.org/10.1021/acs.joc.8b00738

Oral Presentations:

1) ○Okada Y.;* Maeta N.; Nakayama K.; Kamiya H., TiO_2 Photocatalysis in the Aromatic "Redox Tag"-Guided Intermolecular Formal [2 + 2] Cycloadditions, 233rd ECS Meeting, 2083, Seattle, WA, May, **2018. (Peer-reviewed presentation)**

2) ○Okada Y.;* Maeta N.; Nakayama K.; Kamiya H., Olefin Cross-Couplings Enabled by TiO_2 Photocatalysis, The 13th International Symposium on Organic Reactions, SIL-13A, National Chiao Tung University, Hsinchu, Taiwan, November, **2018. (Short Invited Lectures)**

3) ○Okada Y.;* Nakayama K.; Maeta, N.; Horiguchi, G.; Kamiya H., Electron-catalyzed Diels-Alder reactions by TiO_2 photocatalysis, ACS Fall 2019 National Meeting & Exposition, 258, San Diego, CA, August, **2019. (Peer-reviewed presentation)**

4) ○Nakayama K.; Kamiya H.; Okada Y.,* Photo- and Electrocatalytic Radical Cation Diels-Alder Reactions of Arylidene Cycloalkanes, GJSE 2022, Mainz, Germany, October, **2022.**

5) ○岡田 洋平,* 前田 尚也, 中山 海衣, 神谷 秀博, 界面電子移動による分子間オレフィンクロスカップリング, 第42回有機電子移動化学討論会, 2O09, プレスタワー, 6月, **2018.**

6) ○中山 海衣, 前田 尚也, 神谷 秀博, 岡田 洋平,* ホール酸化を活かしたラジカルカチオンディールスアルダー反応の開発, 日本化学会第99春季年会（2019), 1I6-34, 甲南大学 岡本キャンパス, 3月, **2019.**

7) ○Okada Y.;* Maeta N.; Nakayama K.; Kamiya H., Probing Intramolecular Electron Transfer in Redox Tag Processes, 日本化学会第99春季年会（2019), 1I6-36, 甲南大学 岡本キャンパス, 3月, **2019.**

8) ○中山海衣, 前田 尚也, 堀口元規, 神谷 秀博, 岡田 洋平,* 界面電子移動反応による極性変換ディールスアルダー反応, 電気化学会第87回大会, 2E04, 3月, **2020.**

9) ○中山 海衣, 神谷 秀博, 岡田 洋平,* 電極表面におけるラジカルカチオンディールスアルダー反応のEC-backward-E直接観測, 日本化学会第101春季年会（2021), A21-3vn, オンライン, 3月, **2021.**

10) ○中山 海衣, 神谷 秀博, 岡田 洋平,* DDQ光触媒を用いたアレーン C-H アミノ化反応, 第45回有機電子移動化学討論会, オンライン, 3月, **2022.**

11) ○中山 海衣, 神谷 秀博, 岡田 洋平,* スピロ環形成を狙った電子移動による付加環化反応, 日本化学会第102春季年会（2022), K6-3am, オンライン, 3月, **2022.**

12) ○中山 海衣, 光や電気を用いた六員環形成反応, 第40回夏の学校 電気化学会関東支部, A04, オンライン, 8月, **2022.**

Poster Presentations:

1）○Okada Y.;* Maeta N.; **Nakayama K.**; Kamiya H., TiO_2 Photocatalysis in the Aromatic "Redox Tag"-Guided Intermolecular Formal [2 + 2] Cycloadditions, No. 35, Avendi Hotel am Griebnitzsee, Potsdam, Germany, April, **2018.** **(Peer-reviewed presentation)**

2）○**Nakayama K.**; Maeta N.; Kamiya H.; Okada Y.,* Titanium Dioxide Photocatalysis-Assisted Radical Cation Diels-Alder Reactions, The 13th International Symposium on Organic Reactions, PS-20, National Chiao Tung University, Hsinchu, Taiwan, November, **2018.**

3）○Maeta N.; **Nakayama K.**; Kamiya H.; Okada Y.,* TiO_2 Photocatalytic Intermolecular [2 + 2] Cycloaddition Reactions, The 13th International Symposium on Organic Reactions, PS-22, National Chiao Tung University, Hsinchu, Taiwan, November, **2018.**

4）○**Nakayama K.**; Maeta N.; Kamiya H.; Okada Y.*, Single Electron Transfer Redox [4+2] cycloadditions, The 2021 International Chemical Congress of Pacific Basin Societies, #383, Virtual, December, **2021.**

5）○前田 尚也，**中山 海衣**，神谷 秀博，岡田 洋平,* 酸化チタン光触媒による[2+2]付加環化反応の開発，第 42 回有機電子移動化学討論会, P23，プレスタワー, 6 月, **2018.**

6）○**中山 海衣**，前田 尚也，神谷 秀博，岡田 洋平,* 酸化チタン光触媒による Radical Cation Diels-Alder 反応の開発，第 42 回有機電子移動化学討論会, P24，プレスタワー, 6 月, **2018.**

7）○**中山 海衣**，前田 尚也，堀口 元規，神谷 秀博，岡田 洋平,* 酸化チタン光触媒を活かしたラジカルカチオン付加環反応，第 43 回有機電子移動化学討論会, P37，横浜国立大学, 6 月, **2019.**

8）○**中山 海衣**，神谷 秀博，岡田 洋平,* ベンジリデン類を用いたラジカルカチオンディールスアルダー反応，第 46 回有機電子移動化学討論会, P047，オンライン, 6 月, **2022.** **（優秀ポスター賞）**

Chapter 1. General Introduction

1.1. Photo-/Electrocatalytic Chemistry

Photo-induced chemical synthesis is the fundamental process for photosynthesis that is performed by plants on Earth. Photosynthesis is a system in which chlorophyll absorbs the photo-energy to drive the process that synthesizes nutrients in biological activities. In organic chemistry, it is the best chemical synthesis since photo-energy, which is semi-permanently obtained from sunlight, is used efficiently to produce complex compounds such as sugars (Figure 1-1 (a)). Researchers have made efforts to develop photocatalytic chemistry imitating photosynthesis which is an energy-efficient chemical synthesis in these days of concern about various energy issues. A wide variety of photocatalytic syntheses has been studied ever since Giacomo Ciamician's vision in 1912 at the beginning of the 20th century.[1] Since the early works by MacMillan *et al.*, the use of transition metal complexes such as bipyridyl complexes of Ru and Ir has triggered the dramatic growth of photo-induced reactions in organic chemistry.[2, 3] By stripping down the complexity of interlinked photosystems into defined single-molecule photocatalysts, they found that Ru and Ir complexes can absorb photons, become powerful excited states, and cause redox reactions using photo-energy with high performance. Initial reports came as early as the 1980s,[4–6] the term "photoredox catalysis" became popular, and photocatalytic reactions have been brought to the fore in organic chemistry at the turn of the 21st century (Figure 1-2 (a)).[2, 7–9]

In minds of sustainability and cost, other photocatalysts studies instead of Ru and Ir were spread among the photochemistry field. Organo-photocatalysts meaning transition-metal-free such as eosin Y, methylene blue, and acridinium salts were the first object for researchers (Figure 1-2 (b)), and a wide variety of organic syntheses using them have been reported.[10–15] Sustainable transition-metal-based complexes received attention after organo-photocatalysts. As noted in seminal papers and reviews, Cr, Fe, Cu, etc. were fixed as earth-abundant elements in photoredox catalysts (Figure 1-2 (c)).[16–19] Recently, the use of semiconductor photocatalysts is starting to be focused on in organic synthesis. Titanium dioxide (TiO_2), pioneered by Honda and Fujishima,[20] is the best-known semiconductor photocatalyst, and others such as cadmium sulfide (CdS) and zinc oxide (ZnO), *etc.* exhibit activity as photocatalysts (Figure 1-2 (d)).[21–24] However, the widespread use of these catalysts was in the field of artificial photosynthesis, where valuable H_2 and O_2 were produced from H_2O,[25] and applications of semiconductors in organic synthesis are still developing.

Typically, electro-energy is categorized as sub-natural energy since it is obtained indirectly from sunlight. Electrochemical reactions which are organic synthesis using electro-energy have been undergoing a renaissance in recent years (Figure 1-1 (b)).[26–34] The beginnings of electrochemical approaches in organic synthesis date back as far as Faraday and Kolbe's reports from 1830-1840,[35,36] long before Giacomo Ciamician's mimicking concept of photosynthesis. For electrocatalytic chemistry, Baran's work which demonstrated application in large and complex molecule synthesis contributed raise value in the field of organic chemistry.[37] Synthetic organic chemistry has several advantages, in particular, there is no theoretical limit to the potential that can be applied,[38,39] and the limitation as redox potential depends only on the reaction solvent.

For photo- and electrochemistry, photosensitizers/electrodes work as "catalysts" in each and connect energy sources to chemical reactions, thus the terms "photo-/electrocatalytic chemistry" are used in organic chemistry. These reaction mechanisms are close, as caused by electron transfer between photocatalysts or electrodes and compounds.

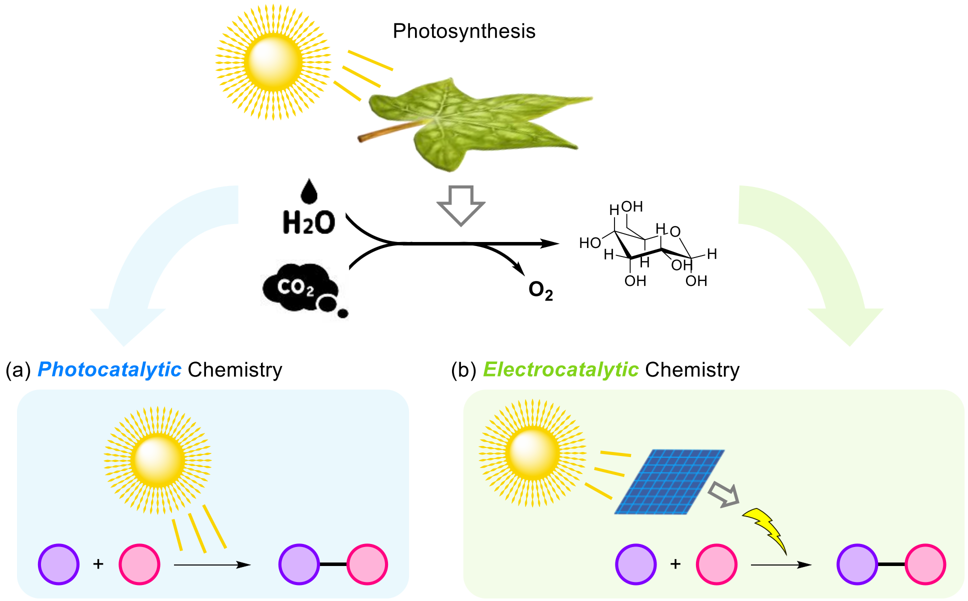
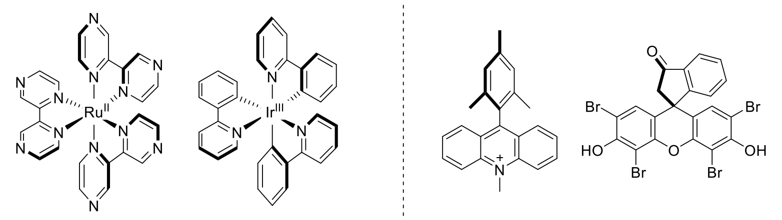
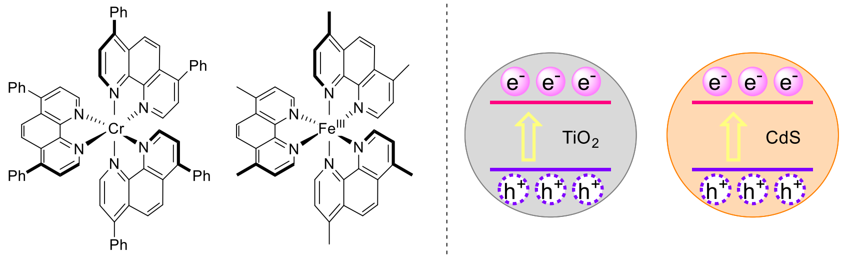


Figure 1-1. Relation between Photosynthesis and Photo-/Electrocatalytic Chemistry.



(a) Rare Metal Complexes

(b) Organic Compounds



(c) Sustainable Metal Complexes

(d) Semiconductors

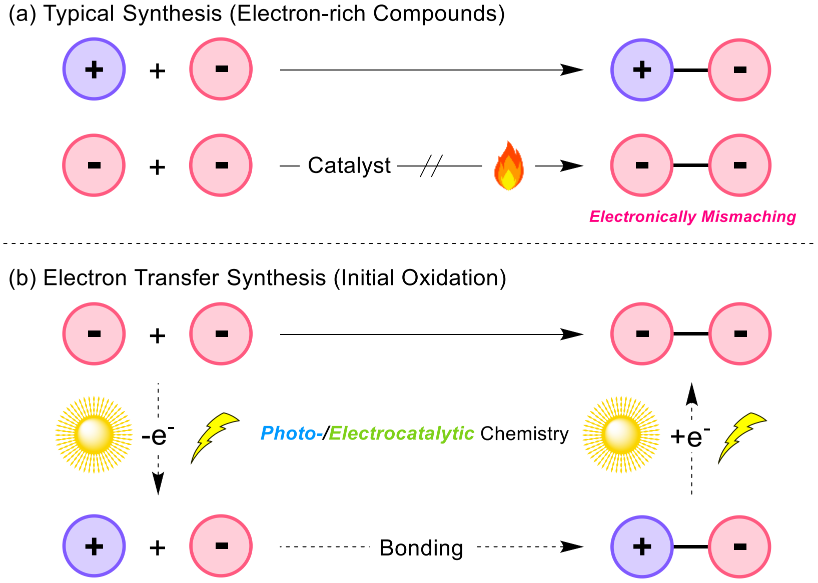
Figure 1-2. Category of Photocatalysts.

1.2. Electron Transfer Chemistry

In the case of chemical reactions by two compounds, these are electron-rich and electron-deficient compounds. Reaction hindrances have been overcome by additional catalysts, thermal energy, etc., in catalytic reactions, the activation energy of the reaction is decreased by coordination with the compounds, and in heating reactions, the reactivity of the compounds is increased by thermal energy. Since these methods are not umpolung, the reaction does not proceed when electronically mismatching compounds are used (Scheme 1-1 (a)). The electron transfer chemistry enables the bond formation using electronically mismatching materials because if the starting materials are electron-rich/deficient, electrons are taken from/given to either compound to make it a temporarily deficient/rich state, which has high reactivity. (Scheme 1-1 (b)).

Electron transfer chemistry is redox, and particularly, it is carried out using oxidative/reductive reagents so far. In contrast to reactions using redox reagents, photo-/electrochemical approaches were invented in the 1910s/1803s. [1,35] The contributions of MacMillan and Baran, [2,3,10,37,39] and the rise of energy issues have brought electron transfer chemistry using light and electrical energy back into the spotlight in recent years. Photo-/electrocatalytic organic reactions can be used for redox reactions without the use of redox reagents, which are conventionally required in stoichiometric quantities and have atom-economy problems, and the energy source is environmentally friendly. Electron transfer chemistry using photo-/electrocatalysis is expected to advance in the future. There are various types of photocatalysts and electrodes, which are generally classified according to the energy source.

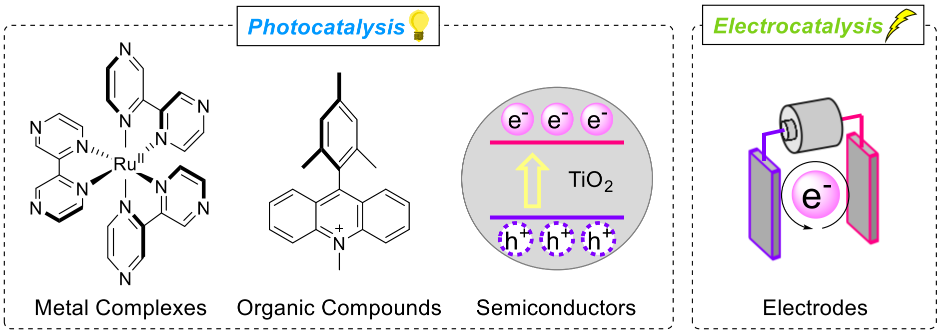
Scheme 1-1. Concepts of Electron Transfer Synthesis.



1.3. Photo-/Electrocatalytic Electron Transfer Vehicles

For photo-/electrocatalytic electron transfer chemistry, the photocatalysts and electrodes work as electron transfer vehicles, respectively. Generally, these are categorized by the corresponding energy sources, which are photo-energy and electro-energy (Figure 1-3 (a)). Photocatalysts are classified into metal complex, organo-, and semiconductor photocatalysts. On the other hand, electrocatalysts are summarized as electrodes, although there are different types of materials such as platinum and carbon. Recently, Okada *et al.* proposed a different categorization.[40,41,50,51,42–49] Metal complexes and organic compounds are molecules that can be drawn by molecular formulas, and electron transfer occurs "intermolecularly" with the target compound. In contrast, semiconductors and electrodes are not molecules but materials, and electron transfer occurs with compounds at the material "interface”. Therefore, they suggest the category of "intermolecular" and "interfacial" electron transfer vehicles by sorting them based on the electron transfer pathways, rather than energy sources. Okada *et al.* have been developing organic chemical reactions using "interfacial" electron transfer catalysts (Figure 1-3 (b)).

(a) Categorization of Energy Sources



(b) Categorization of Electron Transfer Mechanisms

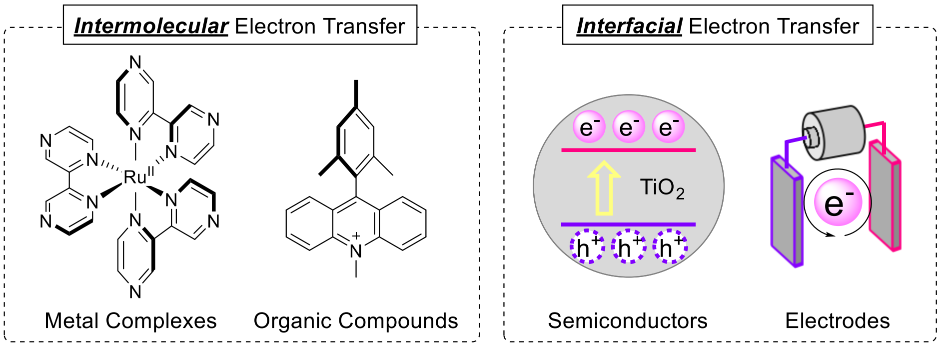


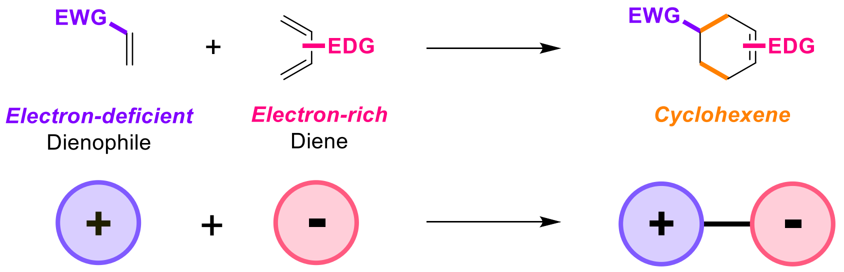
Figure 1-3. Category of Photo/Electrocatalytic Electron Transfer Vehicles.

1.4. Diels-Alder Reaction

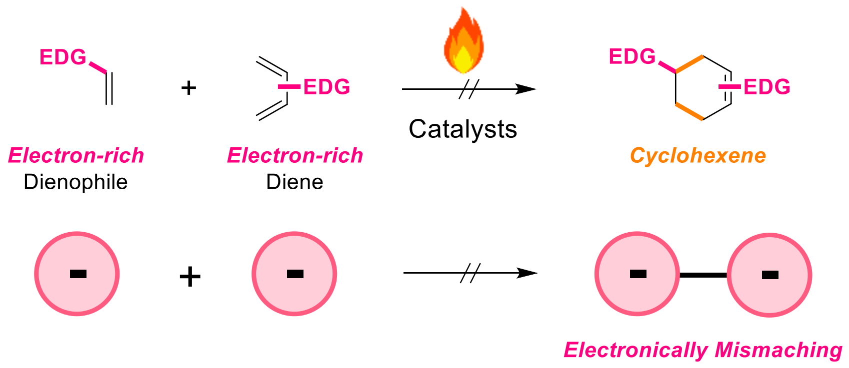
The Diels-Alder reaction, invented by Diels and Alder in 1928,[52] is known as a first choice for six-membered ring formation in synthetic organic chemistry. Researchers have focused on this reaction, and it has been extensively studied and is well-understood, including the rate of ring formation, stereoselectivity and catalytic controls.[53–56] In the 2000s, the reaction was recognized as a key reaction in biomimetic total synthesis.[57–60] The Diels-Alder reaction is classified as a pericyclic reaction in which diene and dienophile undergo cycloaddition through transition states without reaction intermediates. In general, the electron density of the compounds is differentiated to facilitate cycloadditions by the addition of electron-donating/withdrawing groups (EDG/EWG) to the diene/dienophile to make it electron-rich/deficient (Scheme 1-2 (a)). Even if both the diene and dienophile are electron-rich (deficient), the reaction would be accelerated using heating or catalysts. However, if the starting materials are unstable or the six-membered ring formation is at the late stage of natural product synthesis, harsh conditions are not very effective. In addition, there are some combinations of substrates for which the reaction is impossible even with heating or catalysts (Scheme 1-2 (b)). The radical ion Diels-Alder reaction *via* radical ion intermediates using electron transfer catalysts solves this issue.

Scheme 1-2. Effects of Electron Density on Diels-Alder Reaction.

(a) Normal Diels-Alder Reaction



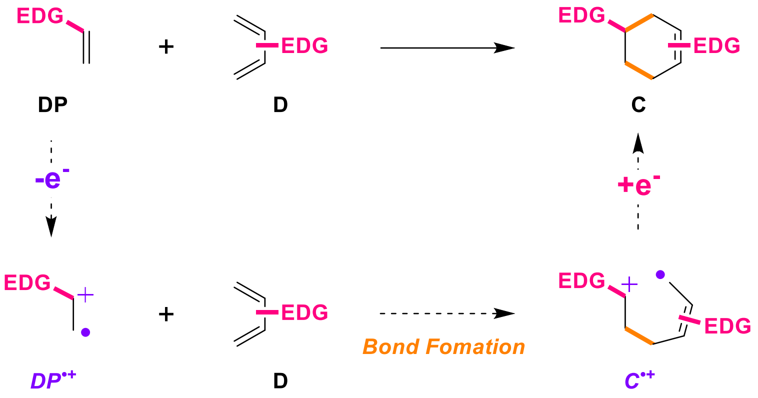
(b) Electronically Mismached Diels-Alder Reaction



1.5. Radical Ion Diels-Alder Reaction

Although the Diels-Alder reaction goes through a transition state without an intermediate, the radical ion Diels-Alder reaction has a different mechanism which is *via* a radical ion intermediate in the process. In the case of the electron-rich dienophile (**DP**) and diene (**D**) model (Scheme 1-3), the reaction is initiated by oxidation between the electron transfer catalyst and the compound. If the oxidation potential of **DP** is relatively low and easily oxidized, the initial oxidation produces **DP**$^{\bullet +}$, and the intermediate **C**$^{\bullet +}$ of cyclohexene (**C**) is generated with **D**. The highly reactive and unstable intermediate **C**$^{\bullet +}$ undergoes reduction by the electron transfer catalysts to the desired cyclohexene **C**. This reaction is a redox, in which oxidation and reduction by single electron transfer (SET) occur as a combination, and enables the formation of six-membered rings that previously required strict conditions for synthesis or were considered impossible to synthesize.

Scheme 1-3. Mechanism of Radical Cation Diels-Alder Reaction.



The radical ion Diels-Alder reaction was initially reported in the 1980s by Bauld *et al.* in the radical cation Diels-Alder reaction between electron-rich compounds with aminium salts as electron transfer catalysts.[61–63] Diels-Alder dimer, in which 1,3-cyclohexadiene was responsible for both diene and dienophile, was obtained only 30% yield under 200 °C and for 20 hours stirring conditions. Therefore, they used tris(*p*-bromophenyl)aminium hexachlorostibnate as an electron transfer device and Diels-Alder cycloadduct was formed in 70% yield after just 15 min stirring at 0 °C (Figure 1-4). In this paper, it was suggested that a chain mechanism in which the aminium salts are initial SET-oxidation and the neutral dienophile undergoes SET-reduction to form dimers.

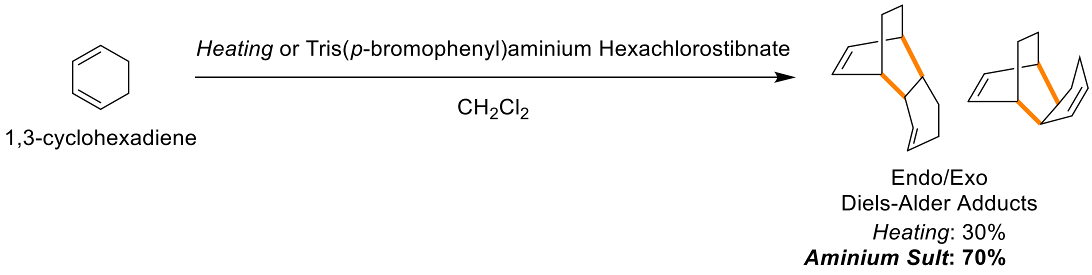
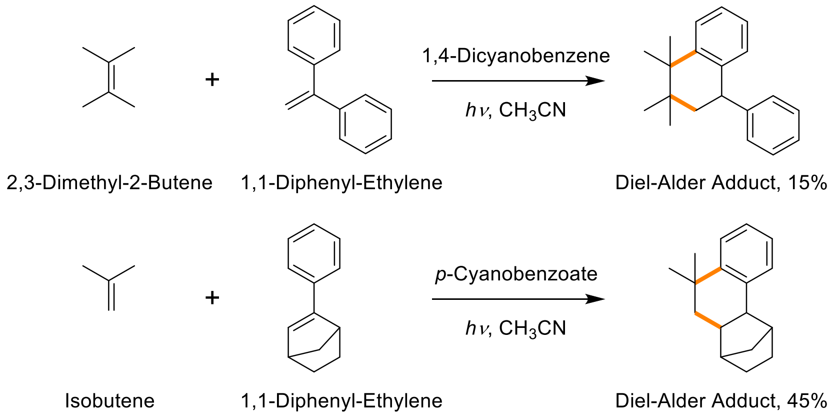


Figure 1-4. Diels-Alder Dimerizations of 1,3-cyclohexadiene.

In 1979, at the same time as Bauld's report, Maroulis and Arnold tried the radical cation Diels-Alder reaction between electron-rich compounds using organophotocatalys.[38] *p*-Cyanobenzoate and 1,4-dicyanobenzene photosensitizers promoted the cycloadditions using 1,1-diphenyl-ethylene or 2-phenylnorbornene as a diene, and isobutene or 2,3-dimethyl-2-butene as dienophile (Figure 1-5 (a)). In the same Diels-Alder dimerization of 1,3-cyclohexadiene which is reported by Bauld, Carol *et al.* succeeded to obtain the dimer in 60% yields using 9,10-dicyanoanthracene photocatalyst after irradiation in CH_2Cl_2 at room temperature (Figure 1-5 (b)).[64] However, the ring formation between 1,3-cyclohexadiene and 2,5-dimethylhexadiene, which was possible with the aminium salts, did not react with 9,10-dicyanoanthracene. They suggested that radical cation Diels-Alder reaction using 9,10-dicyanoanthracene photocatalyst has a steric hindrance to form rings due to the strong interaction in electron transfer between the photocatalyst and the compound.

(a) Maroulis and Arnold's Work in 1979



(b) Carol's Work in 1983

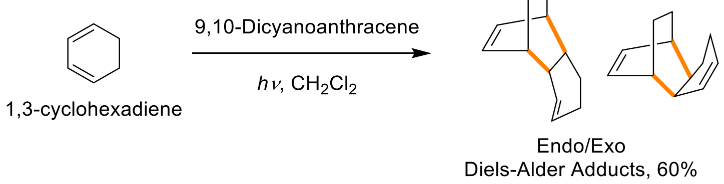
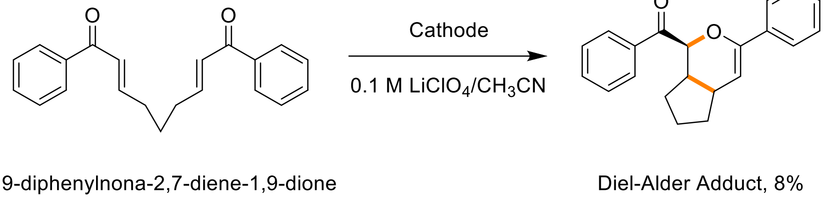


Figure 1-5. Radical Cation Diels-Alder Reactions by Organophotocatalysts.

Radical anion Diels-Alder reactions are rare, with only the electrocatalytic approach reported by Bauld and Krische *et al.* in 2002 (Figure 1-6 (a))[65] and Ru photocatalytic approach by Yoon *et al.* in 2011 (Figure 1-6 (b)).[66] Furthermore, both of these are intramolecular hetero-Diels-Alder reactions, which have different trends from the radical cation Diels-Alder reaction using aminium salts or organophotocatalysts. From the above predecessors, researchers have developed various photo-/electrocatalytic radical ion Diels-Alder reactions.[2,3,71–76,9,16,48,66–70]

(a) Bauld's Work in 2002



(b) Yoon's Work in 2011

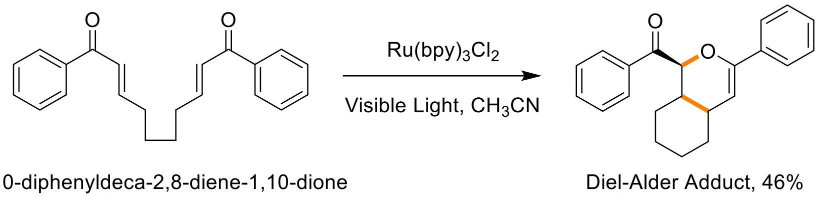


Figure 1-6. Radical Anion Diels-Alder Reactions by Photo- or Electrocatalyst.

For the radical cation Diels-Alder reaction, researchers have recently studied using *trans*-anethole as a benchmark. Starting with Ru complexes[68] reported by Yoon in 2011, metal complex photocatalysts such as Cr complexes by Ferreira[74] and Fe complexes by Kang,[67] or thioxanthylium organophotocatalyst by Tanaka and Hoshino,[70] many radical cation Diels-Alder reactions using intermolecular electron transfer photocatalysts have been reported. On the other hand, there are only a few reports on the use of interfacial electron transfer catalysts: electrocatalyst by Chiba[34,77–79]and graphitic carbon nitride (g-C_3N_4) by Zhao.[75] Okada has developed the organic synthesis using TiO_2 photocatalyst, which is an interfacial electron transfer catalyst, including [2+2] cycloaddition *via* radical cation intermediates (Figure 1-7).[80] TiO_2 has excellent chemical stability and photocatalytic properties among semiconductors, and thus, there is potential to promote radical cation Diels-Alder reaction by interfacial electron transfer.

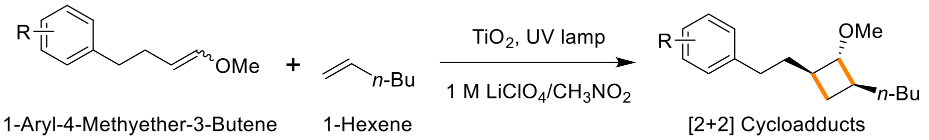


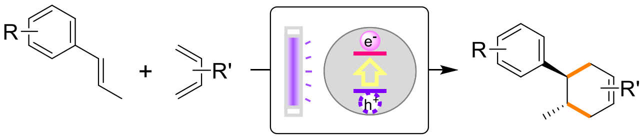
Figure 1-7. [2+2] Cycloaddition by TiO_2 Photocatalyst.

1.6. Purpose and Strategy

The purpose of this study is to apply TiO_2 photocatalysts to organic synthesis chemistry modeled on the radical cation Diels-Alder reaction of arylidenes, and to verify the difference in reactivity between TiO_2 and electrodes, which are also classified as interfacial electron transfer catalysts. First, TiO_2 photocatalytic six-membered ring formation of various β-methylstyrenes including *trans*-anethole will be attempted. Second, to clarify the difference from the previously reported radical cation Diels-Alder reaction by electrocatalysis, detailed verification of the reaction mechanism by cyclic voltammetry (CV) measurements and density functional theory (DFT) calculations will be tried. Finally, radical cation Diels-Alder reaction using model substrates, which has been considered impossible for intermolecular electron transfer catalysis, will be performed to verify the limitation of electrocatalysis and TiO_2 photocatalysis. This research will advance the field of photo-/electrocatalytic chemistry and contribute to the development of innovative synthetic organic chemistry that solves energy issues.

Chapter 2. Radical Cation Diels-Alder Reactions by TiO_2 Photocatalyst

Abstract



Radical cation Diels-Alder reaction by TiO_2 photocatalysis in $LiClO_4/CH_3NO_2$ is described. TiO_2 photocatalysis promoted the bond formation of electronically mismatching electron-rich dienes and dienophiles. The reaction is initiated by oxidative-single-electron-transfer (SET) of the dienophile and completed by reductive-SET to the radical cation intermediate.

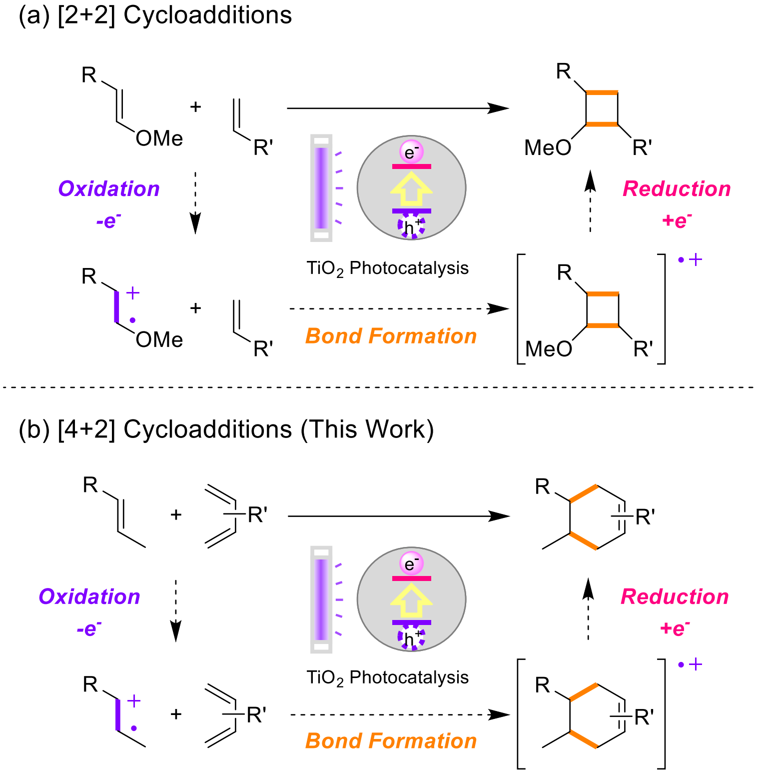
2.1. Introduction

In recent years, photocatalytic chemistry has been revived by MacMillan *et al.*[2,3,10] Photocatalytic SET is the key step, and the reactions are proceeded by photoredox. The radical cation Diels-Alder reaction, in which *trans*-anethole is a benchmark, has been extensively studied as an oxidative-SET initiated reaction by Yoon, Ferreira, Kang *et al.*[67,68,70,74,75] Chiba *et al.* demonstrated that the radical cation Diels-Alder reaction is proceeded by electrocatalysis using carbon felt electrodes with a catalytic amount of electricity.[77] They suggested the two ways of reaction mechanisms which are chain and EC-backward-E (electron transfer, chemical reaction and backward electron transfer) processes.

Okada *et al.* found that the combination of TiO_2 photocatalyst and UV light irradiation in $LiClO_4/CH_3NO_2$ promoted [2+2] cycloadditions (Scheme 2-1 (a)).[80] They proposed a mechanism whereby the reaction is initiated by SET-oxidation of TiO_2 photocatalysis, cyclization with olefins, and completed by SET-reduction of TiO_2 photocatalysis. This study found that TiO_2 photocatalysts can go through the cycloaddition *via* radical cation intermediate, expanding the potential of TiO_2 photocatalysis in synthetic organic chemistry.

Described herein is the radical cation Diels-Alder reaction of β-methystyrenes using TiO_2 photocatalysis (Scheme 2-1 (b)).

Scheme 2-1. TiO_2 Photocatalytic Cycloadditions.

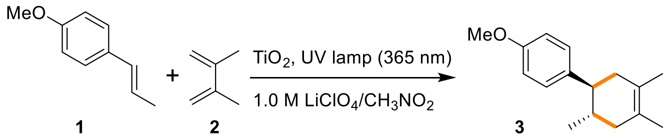


2.2. Results and Discussion

2.2.1. Optimization of the Conditions for Radical Cation Diels-Alder Reaction

The optimization of the conditions for radical cation Diels-Alder reaction using TiO_2 photocatalysis modeled on *trans*-anethole (**1**) and 2,3-dimethyl-1,3-butadiene (**2**) was investigated (Table 2-1). The corresponding six-membered ring (**3**) was obtained in good yield by the combination of TiO_2 photocatalyst and $LiClO_4/CH_3NO_2$ solvent (entry 1), and the yield decreased in the absence of TiO_2 photocatalyst (entry 2). Photocatalytic Diels-Alder reaction of **1** and **2** enabled by $LiClO_4/CH_3NO_2$ solvent was previously reported,[81] suggested that the mechanism was by energy/electron transfer catalysis of O_2 and photoexcited CH_3NO_2 (Figure S3). Then, the corresponding cycloadduct was obtained in acceptable yield. In addition, the reactivity was significantly reduced under dark conditions (entry 3, 4) and without $LiClO_4$ (entry 5), indicating that these conditions are essential for the reaction.

Table 2-1. Optimization of the Conditions for Radical Cation Diels-Alder Reaction.



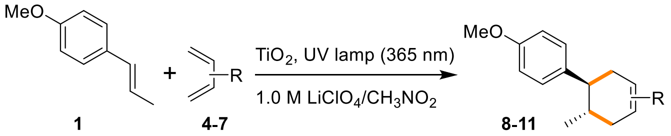
Entry	Conditions[a]	Yield (%)[b]
1		97
2	no TiO_2	71 (0)
3	no light	6 (78)
4	no TiO_2, no light	trace (79)
5	no $LiClO_4$	trace (61)

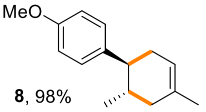
[a] Unless otherwise stated, reactions were carried out on a 0.20 mmol scale of *trans*-anethole (**1**) with 2 equiv of 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h under air. [b] Determined by ^1H NMR analysis using benzaldehyde as an internal standard. Recovered starting material is reported in parentheses.

2.2.2. Scope of Dienes for the Radical Cation Diels-Alder Reaction

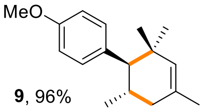
trans-Anethole (**1**) was used as a dienophile and reacted with several dienes (**4**-**7**) (Table 2-2). Isoprene (**4**) and 2,4-Dimethyl-1,3-pentadiene (**5**) gave the corresponding cycloadditions (**8**, **9**) in excellent yields. Although the cycloadduct **10** was obtained in good yield from (*E*)-1,3-pentadiene (**6**), (*Z*)-1,3-pentadiene (**7**) was not found to be productive, probably because the conformation of **7** tends to be transoid by the steric hindrance.

Table 2-2. Scope of Dienes for Radical Cation Diels-Alder Reaction.

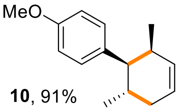




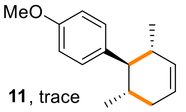
8, 98%



9, 96%



10, 91%



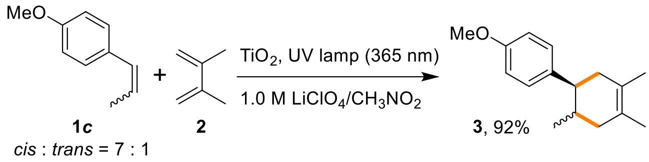
11, trace

Reactions were carried out on a 0.20 mmol scale of *trans*-anethole (**1**) with 2 equiv of the diene (**4-7**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h under air. Yields were determined by ^1H NMR analysis using benzaldehyde as an internal standard.

2.2.3. Radical Cation Diels-Alder Reaction of *cis*-Anethole (**1*c***) and Butadiene (**2**)

The effect of dienophile isomers on the reaction process was demonstrated using *cis*-anethole (**1*c***) as a starting material (Table 2-3). Whereas *trans*-cycloadduct (**3*t***) was formed from *trans*-anethole (**1*t***), **1*c*** was found to give a mixture of *cis*-/*trans*-cycloadducts (**3*c***/**3*t***) and **3*t*** was preferentially formed, investigating that this cyclohexene formation passes not transition-state but radical cation intermediate. From entry 1, the bond was rotated before diene trapping because *trans* ratio of **3** was increased (entry 1). However, **3*t*** was also produced despite the rich condition of diene (entry 3), suggesting that there were two pathways which the bond was rotated during $\mathbf{1}c^{\bullet+}$ and $\mathbf{3}c^{\bullet+}$ (Scheme 2-2).

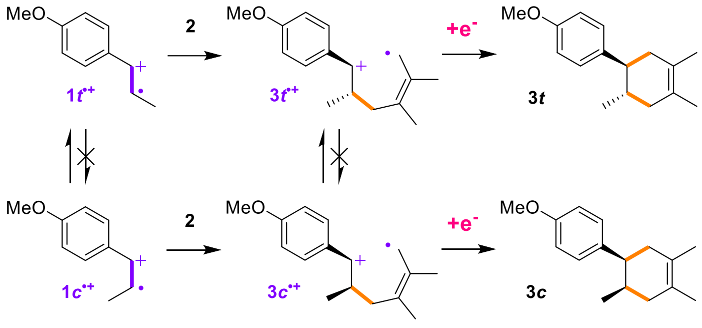
Table 2-3. Radical Cation Diels-Alder Reaction of *cis*-Anethole (1*c*) and Butadiene (2).



Entry[a]	Concentration of 2	*cis*/*trans*[b]
1	10 mM (0.20 eq.)	1:11
2	100 mM (2 eq.)	1:6
3	1000 mM (20 eq.)	1:7

[a] Reactions were carried out on a 0.20 mmol scale of *cis*-anethole (**1*c***) with 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg of TiO$_2$ in 4 mL of CH$_3$NO$_2$ using a 15 W UV lamp at rt for 2 h under air. [b] Determined by ^{1}H NMR analysis.

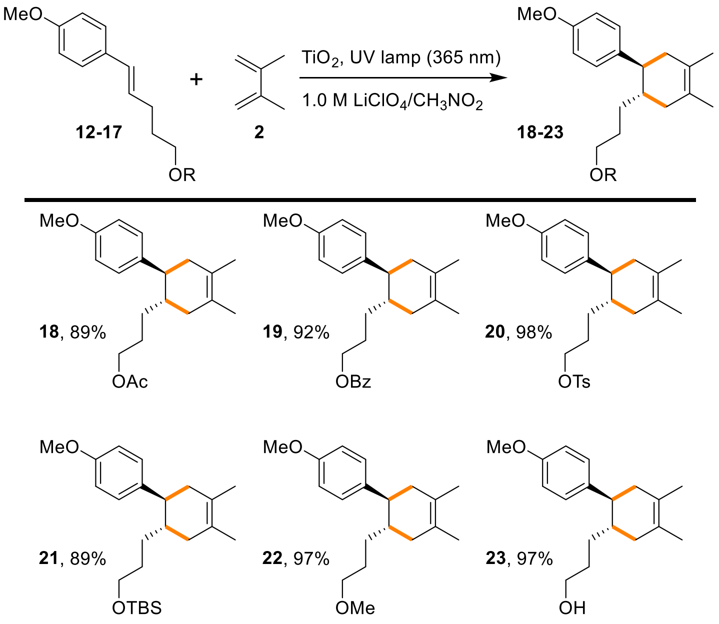
Scheme 2-2. Plausible Reaction Mechanism for the Isomerization of Cyclohexene (3).



2.2.4. Scope of 4-Methoxy β-Propylalcohol-Substituted Styrenes for the Radical Cation Diels-Alder Reaction

The ring formation of 4-methoxy β-propylalcohol-substituted styrenes (**12-17**) with 2,3-dimethyl-1,3-butadiene (**2**) was tested (Table 2-4). Generally, electron-withdrawing groups (EWG) such as acetyl (Ac), benzoyl (Bz) and tosyl (Ts) group are protection for inhibiting radical cation trapped by free alcohol; however, surprisingly, (silyl) ethers (**21**, **22**) and nonsubstituted alcohol (**23**) was found to give Diels-Alder adducts in good yields as well as protecting with EWG (**18-20**). The $LiClO_4/CH_3NO_2$ solvent system may facilitates this reaction.

Table 2-4. Scope of 4-Methoxy β-Propylalcohol-Substituted Styrenes for the Radical Cation Diels-Alder Reaction.

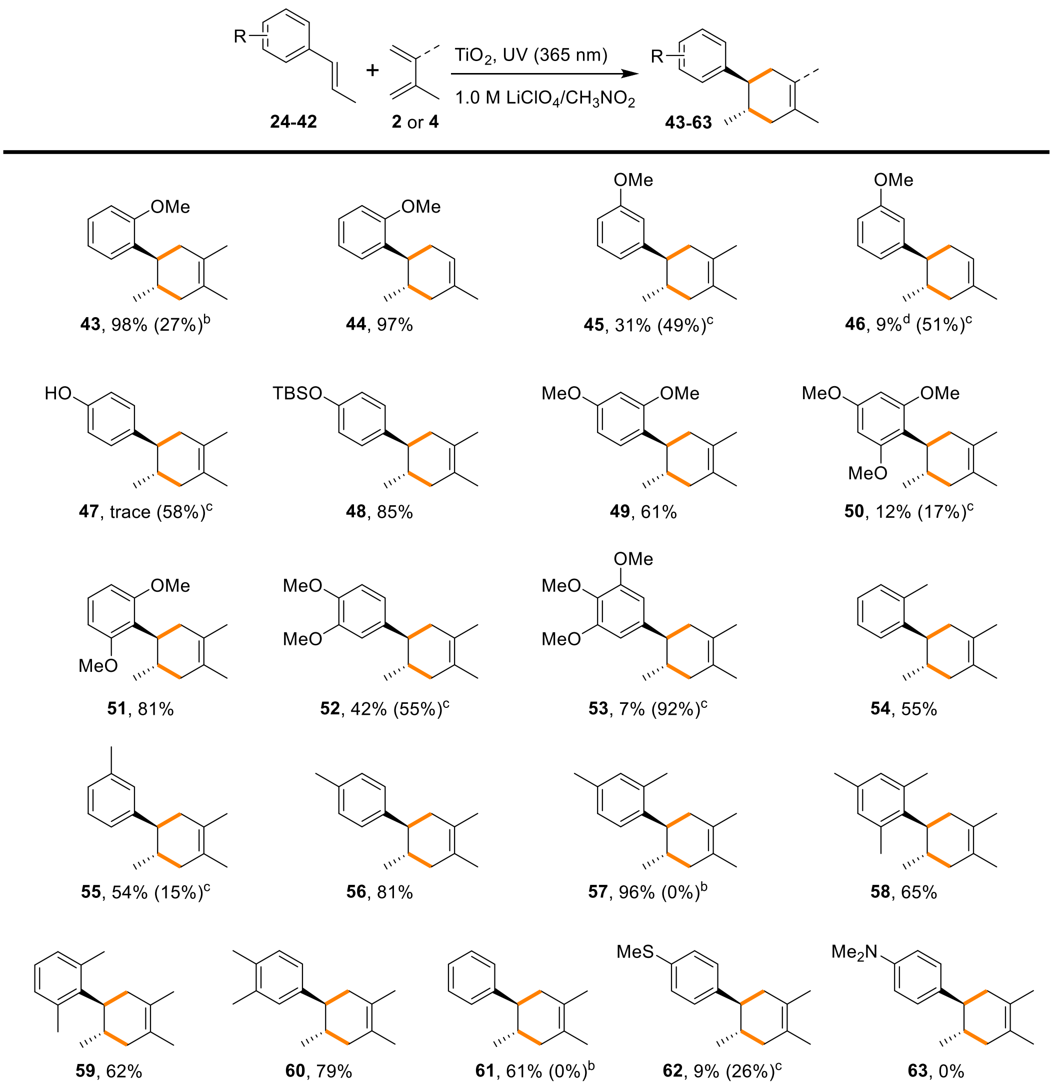


Reactions were carried out on a 0.20 mmol scale of *trans*-anethole derivatives (**12-17**) with 2 equiv of 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h. Yields were determined by ^1H NMR analysis using benzaldehyde as an internal standard.

2.2.5. Scope of β-Methylstyrenes for the Radical Cation Diels-Alder Reaction

The scope of radical cation Diels-Alder reaction was investigated using β-methylstyrene derivatives (**24**-**42**) (Table 2-5). For the substrates with methoxy groups (MeO) on the aromatic ring, ortho-substituted styrenes were found to give cyclohexenes in good yields (**43**, **44**), while meta-substituted styrene was found to be less effective for the reaction (**45**, **46**). The MeO work as an electron-donating group (EDG) or EWG depending on substitution position. When it is substituted at para- or ortho- position, it works as the EDG due to its positive resonance effect. However, meta-substituted MeO serves as an EWG due to its negative induced effect, and thus, it is negative for cyclohexene formation. The para-hydroxy (OH)-substituted styrene was not suitable (**47**), whereas the silyl protection has good effect on the reaction (**48**). It was suggested that deprotonation of free OH was the competition when radical cation intermediate was produced; thus, the corresponding cycloadduct was little detected. Although the additional MeO decreased yields in most cases (**49**-**53**), for the methyl groups (Me), yields were almost increased with the number of Me (**54**-**57**, **60**). This suggests that the additional MeO cause an inclination of electron density to aromatic ring; thus, radical cation plot tends to exist on arene, and diene could not trap styrene double bond. The meta-substituted Me had less negative impact for the reaction than MeO probably because Me serves as electron-donating group due to its positive inductive effect. About **58** and **59**, di-ortho-substituted Me interrupted the cycloaddition sterically and caused to decrease yields. Furthermore, non-substituted β-methylstyrene, which could not be synthesized by Ru photocatalysis or electrocatalysis, gave the corresponding cyclohexene (**61**) in acceptable yield. The reason was suggested that TiO_2 photocatalyst have higher oxidation potential than Ru photocatalyst, and faster reductive-SET than electrocatalysis because cathode cannot do reduction to unstable radical cation intermediate immediately after diene trapping. This result is the most significant achievement of this study, and a further detailed discussions will be investigated in next chapter.

Table 2-5. Scope of β-Methylstyrenes for the Radical Cation Diels-Alder Reaction.[a]



43, 98% (27%)^b

44, 97%

45, 31% (49%)^c

46, 9%^{d} (51%)^c

47, trace (58%)^c

48, 85%

49, 61%

50, 12% (17%)^c

51, 81%

52, 42% (55%)^c

53, 7% (92%)^c

54, 55%

55, 54% (15%)^c

56, 81%

57, 96% (0%)^b

58, 65%

59, 62%

60, 79%

61, 61% (0%)^b

62, 9% (26%)^c

63, 0%

[a] Reactions were carried out on a 0.20 mmol scale of substituted β-methylstyrenes (**24-42**) with 2 equiv of 2,3-dimethyl-1,3-butadiene (**2**) or isoprene (**4**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h under air. Yields were determined by ^1H NMR analysis using benzaldehyde as an internal standard. [b] Yields in absence of TiO_2. [c] Recovered starting material is reported in parentheses. [d] Inseparable mixture.

2.2.6. Plausible Reaction Mechanism for the Radical Cation Diels-Alder Reaction

Based on the results of various β-methylstyrenes, the reaction mechanism of the TiO_2 photocatalytic radical cation Diels-Alder reaction was estimated (Figure 2-1). The reaction is considered to proceed in a TiO_2 photoredox, starting with oxidative-SET of dienophiles by TiO_2 photocatalysis, followed by diene trapping, and finally reductive-SET to radical cation intermediates by TiO_2 photocatalysis to complete the formation of six-membered rings. Additionally, the reactive oxygen species (ROS) have potential to be involved in the reaction mechanism from additional control study (Table S1).

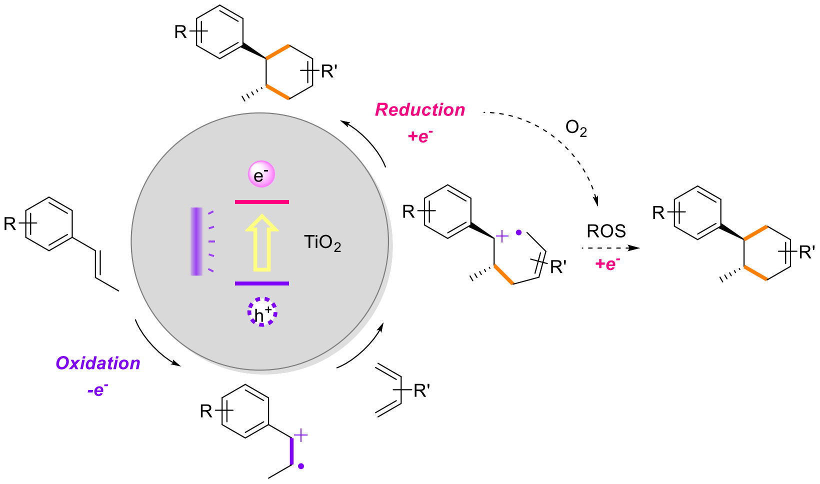


Figure 2-1. Plausible Reaction Mechanism for the Radical Cation Diels-Alder Reaction.

2.3. Conclusion

Radical cation Diels-Alder reaction of β-methylstyrenes using combination of TiO_2 photocatalyst and UV light in $LiClO_4/CH_3NO_2$ solvent was described. The yields previously reported were improved, and the six-membered ring which had been considered impossible to synthesize by Ru photocatalysis or electrocatalysis was obtained in acceptable yield. This study will lead to the extension that TiO_2 photocatalysis applies to synthetic organic chemistry.

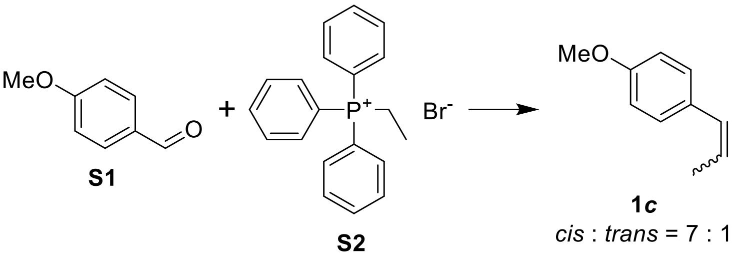
2.4 Experimental Section

2.4.1 General Remarks

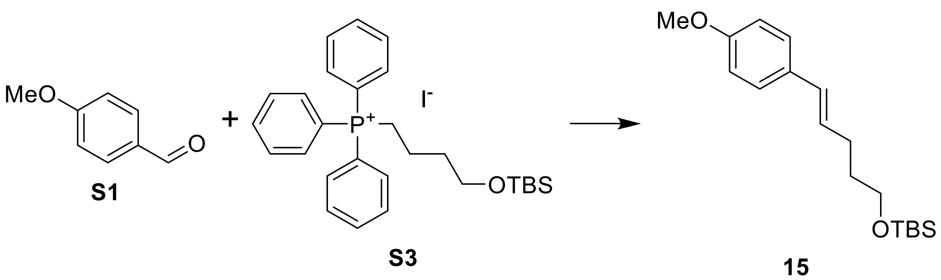
All reagents and solvents were purchased from commercial sources and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates, with detection by UV absorption (254 nm) and by heating the plates after dipping them in a solution of 12 M molybdo(VI) phosphoric acid n-hydrate in 95% ethanol. Silica gel (particle size 40－50 μm) was used for column chromatography.

^{1}H NMR spectra were collected on a 500 MHz NMR spectrometer using the deuterated solvent as an internal deuterium reference. Chemical shift data are given in δ units calibrated with residual protic solvent. The multiplicity of a signal is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. ^{13}C NMR spectra were collected at 125 MHz with proton decoupling using the deuterated solvent as an internal carbon reference. Chemical shift data are given in δ units calibrated with residual solvent. High-resolution mass spectra (HRMS) were collected on electrospray ionization (ESI)- or direct analysis in real time (DART)-time-of-flight (TOF) spectrometers.

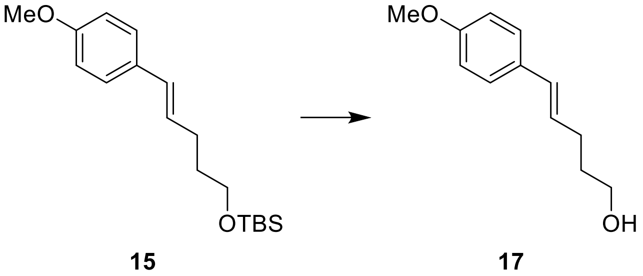
2.4.2. Synthesis and Characterization Data



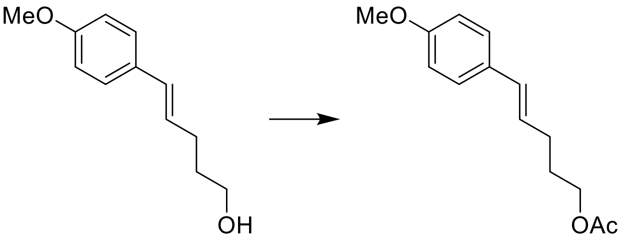
Synthesis of *cis*-Anethole (**1*c***).[82] To a solution of ethyltriphenylphosphonium bromide (**S2**, 2.78 g, 7.50 mmol) and HMPA (1.74 mL, 10.0 mmol) in THF (20 mL) stirred at r.t. was added KHMDS (1.50 g, 7.50 mmol, in 10 mL THF). The resulting reaction mixture was stirred at r.t. for 10 min, and was cooled to -78 °C. *p*-Anisaldehyde (**S1**, 608 μL, 5.00 mmol) was added and the reaction mixture was stirred at r.t. for 1 h, diluted with water, and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave the titled compound in 64% yield (473 mg, 3.19 mmol, *cis*/*trans* = 7/1).



Synthesis of *trans*-Anethole Derivative (**15**).[83] To a solution of the Wittig reagent[74] (**S3**, 17.3 g, 30.0 mmol) in THF (120 mL) stirred at -78 °C was added phenyllithium (1.6 M in butylether, 13.8 mL, 22.0 mmol). The resulting reaction mixture was stirred at r.t. for 15 min, and was cooled to -78 °C. *p*-Anisaldehyde (**S1**, 2.41 mL, 20.0 mmol) and phenyllithium (1.6 M in butylether, 13.8 mL, 22.0 mmol) were added and the reaction mixture was stirred at -78 °C, r.t., and then -78 °C for 15 min each. Hydrochloric acid (12 M, 1.83 mL, 22.0 mmol) and $\mathrm{KO}^t\mathrm{Bu}$ (2.69 g, 24.0 mmol) were added and the reaction mixture was stirred at r.t. for 15 min, diluted with hydrogen peroxide (10 mL) and water, and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 40/1) gave the titled compound 58% (3.56 g, 11.6 mmol).

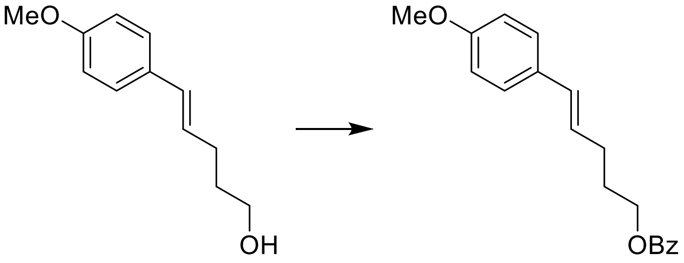


Synthesis of *trans*-Anethole Derivative (**17**). To a solution of the anethole derivative (**15**) (3.07 g, 10.0 mmol) in THF (80 mL) stirred at r.t. was added TBAF (15.0 mL, 1.0 M in THF). The resulting reaction mixture was stirred at r.t. for overnight, diluted with water, and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 1/1) gave the titled compound 77% (1.48 g, 7.71 mmol).



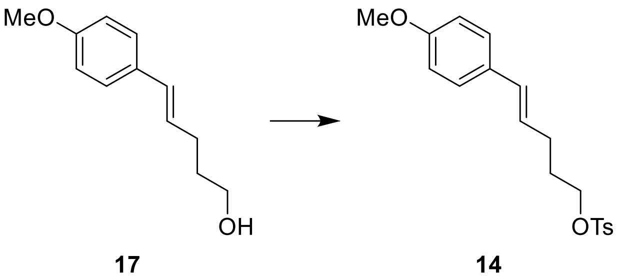
17 **12**

Synthesis of *trans*-Anethole Derivative (**12**). To a solution of the anethole derivative (**17**) (385 mg, 2.00 mmol), TEA (832 µL, 6.00 mmol), DMAP (12.2 mg, 0.10 mmol) in CH_2Cl_2 (30 mL) stirred at r.t. was added Ac_2O (567 µL, 6.00 mmol). The resulting reaction mixture was stirred at r.t. for overnight, diluted with water, and extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 4/1) gave the titled compound 88% (410 mg, 1.75 mmol).

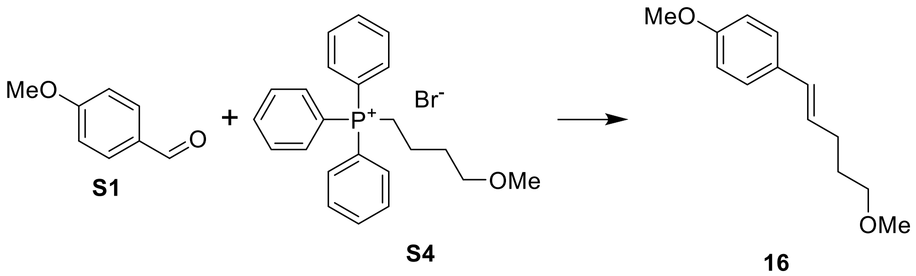


17 **13**

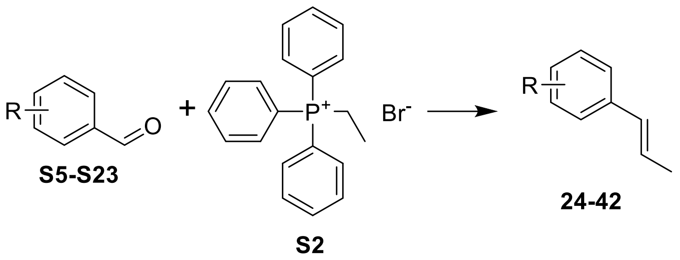
Synthesis of *trans*-Anethole Derivative (**13**). To a solution of the anethole derivative (**17**) (385 mg, 2.00 mmol), TEA (554 µL, 4.00 mmol), DMAP (12.2 mg, 0.10 mmol) in CH_2Cl_2 (30 mL) stirred at r.t. was added BzCl (346 µL, 3.00 mmol). The resulting reaction mixture was stirred at r.t. for overnight, diluted with water, and extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 4/1) gave the titled compound 99% (587 mg, 1.98 mmol).



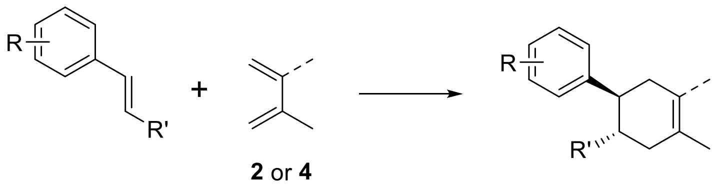
Synthesis of *trans*-Anethole Derivative (**14**). To a solution of the anethole derivative (**17**) (385 mg, 2.00 mmol), TEA (554 μL, 4.00 mmol), DMAP (12.2 mg, 0.10 mmol) in CH_2Cl_2 (30 mL) stirred at r.t. was added TsCl (572 mg, 3.00 mmol). The resulting reaction mixture was stirred at r.t. for overnight, diluted with water, and extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 4/1) gave the titled compound 64% (444 mg, 1.28 mmol).



Synthesis of *trans*-Anethole Derivative (**16**). To a solution of the Wittig reagent (**S4**, 6.44 g, 15.0 mmol) in THF (80 mL) stirred at -78 °C was added phenyllithium (1.6 M in butylether, 6.88 mL, 11.0 mmol). The resulting reaction mixture was stirred at r.t. for 15 min, and was cooled to -78 °C. *p*-Anisaldehyde (**S1**, 1.21 mL, 10.0 mmol) and phenyllithium (1.6 M in butylether, 6.88 mL, 11.0 mmol) were added and the reaction mixture was stirred at -78 °C, r.t., and then -78 °C for 15 min each. Hydrochloric acid (12 M, 917 μL, 11.0 mmol) and KO^{t}Bu (1.35 g, 12.0 mmol) were added and the reaction mixture was stirred at r.t. for 15 min, diluted with hydrogen peroxide (5 mL) and water, and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 40/1) gave the titled compound 51% (1.05 g, 5.09 mmol).

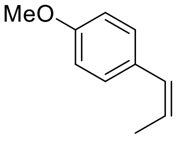


General Procedure for the Synthesis of β-Methyl Styrenes (**24**-**42**). To a solution of the Wittig reagent (**S2**, 5.57 g, 15.0 mmol) in THF (80 mL) stirred at -78 °C was added phenyllithium (1.6 M in butylether, 6.88 mL, 11.0 mmol). The resulting reaction mixture was stirred at r.t. for 15 min, and was cooled to -78 °C. The respective benzaldehyde (**S5**-**S23**, 10.0 mmol) and phenyllithium (1.6 M in butylether, 6.88 mL, 11.0 mmol) were added and the reaction mixture was stirred at -78 °C, r.t., and then -78 °C for 15 min each. Hydrochloric acid (12 M, 917 μL, 11.0 mmol) and KO^{t}Bu (1.35 g, 12.0 mmol) were added and the reaction mixture was stirred at r.t. for 15 min, diluted with hydrogen peroxide (5 mL) and water, and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 30/1) gave the titled compound.



General Procedure for Radical Cation Diels-Alder Reactions. To a solution of $LiClO_4$ (1.0 M) in dry CH_3NO_2 (4 mL) stirred at room temperature were added the respective β-methyl styrenes (0.20 mmol), dienes (0.40 mmol), and TiO_2 (100 mg). The resulting reaction mixture was stirred at room temperature in front of a 15 W UV lamp (365 nm) for 2 h (also checked by thin-layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Yields were determined by ^{1}H NMR analysis using benzaldehyde as an internal standard. Silica gel column chromatography (unless otherwise noted, hexane/ethyl acetate = 20/1) gave the desired cycloadducts.

*(Z)-1-methoxy-4-(prop-1-en-1-yl)benzene (**1c**, cis : trans = 7 : 1). Colorless oil.*



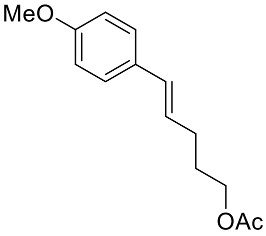
1c, *cis* : *trans* = 7 : 1

Product yield; 64% (473 mg, 3.19 mmol).

cis: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.24 (2H, d, *J* = 8.6 Hz), 6.88 (2H, d, *J* = 8.6 Hz), 6.37 (1H, dd, *J* = 11.5, 1.2 Hz), 5.70 (1H, dq, *J* = 11.5, 6.9 Hz), 3.81 (3H, s), 1.89 (3H, dd, *J* = 7.5, 2.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.1, 130.4, 130.1, 129.3, 125.2, 113.6, 55.3, 14.7.

trans: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.24 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.34 (1H, dd, *J* = 16.0, 1.2 Hz), 6.09 (1H, dq, *J* = 16.0, 6.9 Hz), 3.80 (3H, s), 1.86 (3H, dd, *J* = 6.3, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 159.0, 133.9, 130.9, 126.9, 123.5, 113.9, 30.4, 18.6; HRMS [M + H]$^+$ calculated for $C_{10}H_{13}O$ 149.0966, found 149.0996.

*(E)-5-(4-methoxyphenyl)pent-4-en-1-yl acetate (**12**, trans). Colorless oil.*

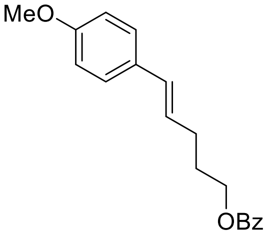


12, *trans*

Product yield; 88% (410 mg, 1.75 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.27 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.35 (1H, d, *J* = 16.0 Hz), 6.05 (1H, dt, *J* = 16.0, 6.9 Hz), 4.12 (2H, t, *J* = 6.9 Hz), 3.80 (3H, s), 2.26 (2H, dq, *J* = 6.9, 1.2 Hz), 2.05 (3H, s), 1.80 (2H, quint, *J* = 6.9 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 171.2, 158.9, 130.4, 130.1, 127.2, 127.1, 114.0, 64.0, 55.3, 29.4, 28.5, 21.1; HRMS [M + H]$^+$ calculated for $C_{14}H_{19}O_3$ 235.1334, found 235.1362.

*(E)-5-(4-methoxyphenyl)pent-4-en-1-yl benzoate (**13**, trans). Colorless oil.*

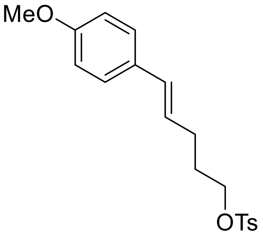


13, *trans*

Product yield; 99% (587 mg, 1.98 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.06 (2H, d, *J* = 7.5 Hz), 7.56 (1H, t, *J* = 7.5 Hz), 7.44 (2H, t, *J* = 7.5 Hz), 7.28 (2H, d, *J* = 8.6 Hz), 6.84 (2H, d, *J* = 8.6 Hz), 6.39 (1H, d, *J* = 16.0 Hz), 6.11 (1H, dt, *J* = 16.0, 6.9 Hz), 4.38 (2H, t, *J* = 6.9 Hz), 3.80 (3H, s), 2.37 (2H, q, *J* = 6.9 Hz), 1.95 (2H, quint, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 166.7, 158.9, 132.9, 130.5, 130.5, 130.2, 129.6, 128.4, 127.2, 127.1, 114.0, 64.6, 55.3, 29.6, 28.6; HRMS [M + H]$^+$ calculated for $C_{19}H_{21}O_3$ 297.1490, found 297.1497.

*(E)-5-(4-methoxyphenyl)pent-4-en-1-yl 4-methylbenzenesulfonate (**14**, trans). Colorless oil.*

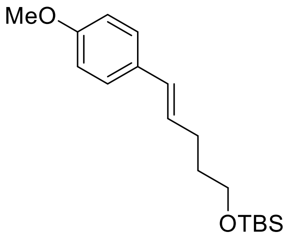


14, *trans*

Product yield; 99% (685 mg, 1.98 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.79 (2H, d, *J* = 8.6 Hz), 7.32 (2H, d, *J* = 8.6 Hz), 7.20 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.24 (1H, d, *J* = 15.5 Hz), 5.90 (1H, dt, *J* = 15.5, 6.9 Hz), 4.07 (2H, t, *J* = 6.3 Hz), 3.80 (3H, s), 2.43 (3H, s), 2.22 (2H, dq, *J* = 6.9, 1.7 Hz), 1.81 (2H, quint, *J* = 6.9 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 159.0, 144.8, 133.2, 130.7, 130.2, 129.9, 128.0, 127.2, 126.2, 114.0, 70.0, 55.0, 28.7, 22.0; HRMS [M + H]$^+$ calculated for $C_{19}H_{23}O_4S$ 347.1317, found 347.1348.

(E)-tert-butyl((5-(4-methoxyphenyl)pent-4-en-1-yl)oxy)dimethylsilane (***15***, *trans*). *Yellow oil.*

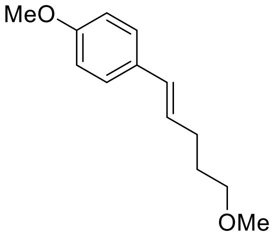


15, *trans*

Product yield; 71% (4.35 g, 14.2 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.33 (1H, d, *J* = 16.0 Hz), 6.08 (1H, dt, *J* = 16.0, 6.9 Hz), 3.79 (3H, s), 3.65 (2H, dt, *J* = 6.3, 1.2 Hz), 2.24 (2H, q, *J* = 7.5 Hz), 1.68 (2H, quint, *J* = 6.9 Hz), 0.91 (9H, d, *J* = 1.2 Hz), 0.06 (6H, d, *J* = 1.2 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.7, 130.8, 129.5, 128.4, 127.0, 114.0, 62.6, 55.3, 32.7, 29.4, 26.1, 18.4, -5.2; HRMS $[M + H]^+$ calculated for $C_{18}H_{31}O_2Si$ 307.2093, found 307.2110.

(E)-1-methoxy-4-(5-methoxypent-1-en-1-yl)benzene (***16***, *trans*). *Yellow oil.*

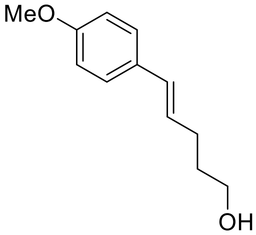


16, *trans*

Product yield; 51% (1.05 g, 5.09 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.34 (1H, d, *J* = 16.0 Hz), 6.07 (1H, dt, *J* = 16.0, 6.9 Hz), 3.80 (3H, s), 3.42 (2H, t, *J* = 6.9 Hz), 3.34 (3H, s), 2.25 (2H, dq, *J* = 6.9, 1.2 Hz), 1.74 (2H, quint, *J* = 6.3 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.7, 130.6, 129.6, 127.9, 127.0, 113.9, 72.1, 58.5, 55.2, 29.5, 29.4; HRMS $[M + H]^+$ calculated for $C_{13}H_{19}O_2$ 207.1385, found 207.1370.

(E)-5-(4-methoxyphenyl)pent-4-en-1-ol (***17***, *trans*). *White solid.*

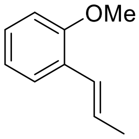


17, *trans*

Product yield; 77% (1.48 g, 7.71 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.27 (2H, d, *J* = 9.2 Hz), 6.84 (2H, d, *J* = 9.2 Hz), 6.36 (1H, d, *J* = 16.0 Hz), 6.08 (1H, dt, *J* = 16.0, 7.5 Hz), 3.80 (3H, s), 3.71 (2H, dt, *J* = 6.3, 5.4 Hz), 2.29 (2H, dq, *J* = 6.9, 1.2 Hz), 1.75 (2H, quint, *J* = 6.9 Hz), 1.29 (1H ,t, *J* = 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.8, 130.5, 129.8, 127.9, 127.1, 114.0, 62.5, 55.4, 32.5, 29.4; HRMS [M + H]$^+$ calculated for $C_{12}H_{17}O_2$ 193.1228, found 193.1250.

(E)-1-methoxy-2-(prop-1-en-1-yl)benzene (***24***, *trans*). *Yellow oil.*

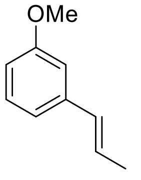


24, *trans*

Product yield; 21% (312 mg, 2.11 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.39 (1H, dd, *J* = 8.0, 1.7 Hz), 7.18 (1H, dt, *J* = 8.0, 1.7 Hz), 6.90 (1H, t, *J* = 8.0 Hz), 6.85 (1H, d, *J* = 8.0 Hz), 6.71 (1H, *J* = 15.5, 1.2 Hz), 6.24 (1H, dq, *J* = 15.5, 6.3 Hz), 3.84 (3H, s), 1.90 (3H, dd, *J* = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 156.2, 127.8, 127.1, 126.6, 126.5, 125.7, 120.7, 110.7, 55.5, 19.0; HRMS [M + H]$^+$ calculated for $C_{10}H_{13}O$ 149.0966, found 149.0948.

(E)-1-methoxy-3-(prop-1-en-1-yl)benzene (***25***, *trans*). *Yellow oil.*

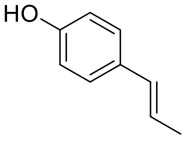


25, *trans*

Product yield; 38% (564 mg, 3.81 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.21 (1H, t, *J* = 8.0 Hz), 6.93 (1H, d, *J* = 8.0 Hz), 6.87 (1H, t, *J* = 2.3 Hz), 6.75 (1H, dd, *J* = 8.0, 2.3 Hz), 6.37 (1H, dd, *J* = 15.5, 1.7 Hz), 6.24 (1H, dq, *J* = 15.5, 6.3 Hz), 3.81 (3H, s), 1.88 (3H, dd, *J* = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 159.8, 139.5, 131.0, 129.5, 126.2, 118.6, 112.4, 111.2, 55.2, 18.6; HRMS [M + H]$^+$ calculated for $C_{10}H_{13}O$ 149.0966, found 149.0981.

(E)-4-(prop-1-en-1-yl)phenol (**26**, *trans*). *Yellow solid.*

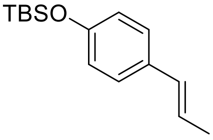


26, *trans*

Product yield; 11% (147 mg, 1.10 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.20 (2H, d, *J* = 8.6 Hz), 6.74 (2H, d, *J* = 8.6 Hz), 6.32 (1H, dd, *J* = 16.0, 1.2 Hz), 6.07 (1H, dq, *J* = 16.0, 6.9 Hz), 4.81 (1H, s), 1.84 (3H, dd, *J* = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 154.4, 131.1, 130.3, 127.2, 123.7, 115.4, 18.5; HRMS [M + H]$^+$ calculated for $C_9H_{11}O$ 135.0810, found 135.0821.

(E)-tert-butyldimethyl(4-(prop-1-en-1-yl)phenoxy)silane (***27***, *trans*). *Colorless oil.*

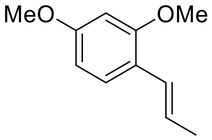


27, *trans*

Product yield; 41% (1.02 g, 4.11 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.19 (2H, d, *J* = 8.6 Hz), 6.76 (2H, d, *J* = 8.6 Hz), 6.33 (1H, dd, *J* = 15.5, 1.7 Hz), 6.09 (1H, dq, *J* = 15.5, 6.3 Hz), 1.85 (3H, dd, *J* = 6.9, 1.7 Hz), 0.97 (9H, s), 0.18 (6H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 154.7, 131.4, 130.5, 126.9, 123.6, 120.2, 25.8, 18.5, 18.3, -4.3; HRMS [M + H]$^+$ calculated for $C_{15}H_{25}OSi$ 249.1674, found 249.1648.

(E)-2,4-dimethoxy-1-(prop-1-en-1-yl)benzene (***28***, *trans*). *Yellow oil.*

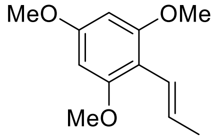


28, *trans*

Product yield; 46% (821 mg, 4.61 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.30 (1H, d, *J* = 8.6 Hz), 6.61 (1H, dd, *J* = 15.5, 1.7 Hz), 6.45 (1H, dd, *J* = 8.6, 2.3 Hz), 6.43 (1H, d, *J* = 2.3 Hz), 6.10 (1H, dq, *J* = 15.5, 6.3 Hz), 3.82 (3H, s), 3.81 (3H, s), 1.87 (3H, dd, *J* = 6.3, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 159.8, 157.2, 127.1, 125.3, 124.5, 120.2, 104.7, 98.4, 55.5, 55.4, 19.0; HRMS [M + H]$^+$ calculated for $C_{11}H_{15}O_2$ 179.1072, found 179.1095.

(E)-1,3,5-trimethoxy-2-(prop-1-en-1-yl)benzene (***29***, *trans*). *White solid.*

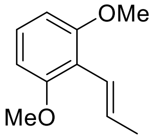


29, *trans*

Product yield; 43% (894 mg, 4.29 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.56 (1H, dd, J = 16.0, 1.2 Hz), 6.46 (1H, dq, J = 16.0, 6.3 Hz), 6.13 (2H, s), 3.82 (6H, s), 3.81 (3H, s), 1.89 (3H, dd, J = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 159.4, 158.8, 128.1, 121.0, 108.5, 90.8, 55.8, 55.4, 20.0; HRMS [M + H]$^+$ calculated for $C_{12}H_{17}O_3$ 209.1177, found 209.1182.

(E)-1,3-dimethoxy-2-(prop-1-en-1-yl)benzene (***30***, *trans*). *Yellow oil.*

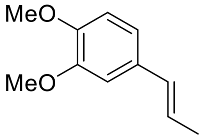


30, *trans*

Product yield; 25% (443 mg, 2.49 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.10 (1H, t, J = 8.6 Hz), 6.60 (2H, m), 6.55 (2H, d, J = 8.6 Hz), 3.84 (6H, s), 1.92 (3H, d, J = 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.0, 130.4, 127.2, 121.2, 115.2, 104.0, 55.7, 20.2; HRMS [M + H]$^+$ calculated for $C_{11}H_{15}O_2$ 179.1072, found 179.1102.

(E)-1,2-dimethoxy-4-(prop-1-en-1-yl)benzene (***31***, *trans*). *Yellow oil.*

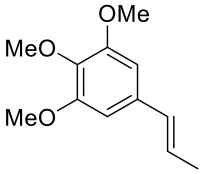


31, *trans*

Product yield; 43% (761 mg, 4.27 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.89 (1H, d, J = 1.7 Hz), 6.85 (1H, dd, J = 8.6, 1.7 Hz), 6.79 (1H, d, J = 8.6 Hz), 6.34 (1H, dd, J = 16.0, 1.7 Hz), 6.11 (1H, dq, J = 16.0, 6.9 Hz), 3.90 (3H, s), 3.87 (3H, s), 1.87 (3H, dd, J = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 149.0, 148.2, 131.2, 130.6, 123.8, 118.7, 111.2, 108.5, 55.9, 55.8, 18.4; HRMS [M + H]$^+$ calculated for $C_{11}H_{15}O_2$ 179.1072, found 179.1043.

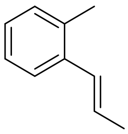
(E)-1,2,3-trimethoxy-5-(prop-1-en-1-yl)benzene (***32***, *trans*). *Yellow oil.*



32, *trans*

Product yield; 24% (491 mg, 2.36 mmol).
^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.55 (2H, s), 6.33, (1H, dd, *J* = 16.0, 1.7 Hz), 6.15 (1H, dq, *J* = 16.0, 6.3 Hz), 3.87 (6H, s), 3.83 (3H, s), 1.88 (3H, dd, *J* = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 153.3, 137.2, 133.8, 131.0, 125.4, 102.9, 61.0, 56.1, 18.4; HRMS [M + H]$^+$ calculated for $C_{12}H_{17}O_3$ 209.1177, found 209.1149.

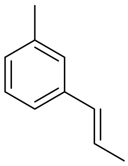
(E)-1-methyl-2-(prop-1-en-1-yl)benzene (***33***, *trans*). *Colorless oil.*



33, *trans*

Product yield; 11% (143 mg, 1.08 mmol).
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.11 (1H, s), 7.07 (1H, d, *J* = 8.0 Hz), 7.04 (1H, d, *J* = 8.0 Hz), 6.34 (1H, dd, *J* = 16.0, 1.7 Hz), 6.17 (1H, dq, *J* = 16.0, 6.3 Hz), 2.24 (3H, s), 2.23 (3H, s), 1.86 (3H, dd, *J* = 6.3, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 137.1, 134.8, 130.2, 128.9, 127.0, 126.8, 126.1, 125.5, 19.9, 18.9; HRMS [M + H]$^+$ calculated for $C_{10}H_{13}$ 133,1017, found 133.0991.

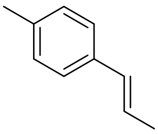
(E)-1-methyl-3-(prop-1-en-1-yl)benzene (***34***, *trans*). *Colorless oil.*



34, *trans*

Product yield; 22% (294 mg, 2.22 mmol).
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.11 (1H, s), 7.07 (1H, d, *J* = 8.0 Hz), 7.04 (1H, d, *J* = 8.0 Hz), 6.34 (1H, dd, *J* = 16.0, 1.7 Hz), 6.17 (1H, dq, *J* = 16.0, 6.3 Hz), 2.24 (3H, s), 2.23 (3H, s), 1.86 (3H, dd, *J* = 6.3, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 138.0, 137.9, 131.1, 128.4, 127.6, 126.7, 125.5, 123.0, 21.5, 18.6; HRMS [M + H]$^+$ calculated for $C_{10}H_{13}$ 133,1017, found 133.1026.

(E)-1-methyl-4-(prop-1-en-1-yl)benzene (***35***, *trans*). *Colorless oil.*

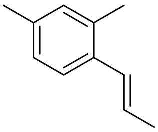


35, *trans*

Product yield; 29% (378 mg, 2.86 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.22 (2H, d, *J* = 8.0 Hz), 7.09 (2H, d, *J* = 8.0 Hz), 6.36 (1H, d, *J* = 16.0 Hz), 6.18 (1H, dq, *J* = 16.0, 6.3 Hz), 2.32 (3H, s), 1.86 (3H, d, *J* = 6.9 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.4, 135.2, 130.9, 129.2, 125.8, 124.7, 21.2, 18.5; HRMS [M + H]$^+$ calculated for $C_{10}H_{13}$ 133.1017, found 133.1023.

(E)-2,4-dimethyl-1-(prop-1-en-1-yl)benzene (***36***, *trans*). *Colorless oil.*

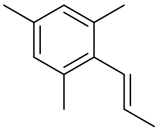


36, *trans*

Product yield; 29% (429 mg, 2.93 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29 (1H, d, *J* = 8.0 Hz), 6.95 (2H, d, *J* = 8.0 Hz) 6.55 (1H, d, *J* = 15.5 Hz), 6.06 (1H, dq, *J* = 15.5, 6.3 Hz), 2.29 (3H, s), 2.28 (3H, s), 1.89 (3H, dd, *J* = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.4, 134.7, 134.4, 131.0, 128.8, 126.8, 126.1, 125.4, 21.1, 19.8, 18.9; HRMS [M + H]$^+$ calculated for $C_{11}H_{15}$ 147.1174, found 147.1191.

(E)-1,3,5-trimethyl-2-(prop-1-en-1-yl)benzene (***37***, *cis : trans* = *1 : 7*). *Colorless oil.*



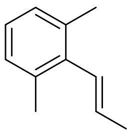
37, *cis : trans* = 1 : 7

Product yield; 21% (335mg, 2.09 mmol).

cis: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.86 (2H, s), 6.27 (1H, d, *J* = 11.5 Hz), 5.81 (1H, dq, *J* = 11.5, 6.9 Hz), 2.25 (3H, s), 2.16 (6H, s), 1.45 (3H, d, *J* = 6.9 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.0, 133.6, 131.6, 127.9, 126.7, 125.8, 20.2, 14.3.

trans: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.85 (2H, s), 6.30 (1H, d, *J* = 16.0 Hz), 5.65 (1H, dq, *J* = 16.0, 6.3 Hz), 2.26 (3H, s), 2.25 (6H, s), 1.89 (3H, dd, *J* = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 135.9, 135.6, 134.8, 130.1, 128.5, 127.3, 20.9, 18.9; HRMS [M + H]$^+$ calculated for $C_{12}H_{17}$ 161.1330, found 161.1305.

(E)-1,3-dimethyl-2-(prop-1-en-1-yl)benzene (***38***, *cis : trans* = *1 : 7*). *Colorless oil.*



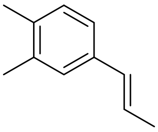
38, *cis : trans* = 1 : 7

Product yield; 11% (161 mg, 1.10 mmol).

cis: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.02 (3H, s), 6.30 (1H, d, *J* = 11.5 Hz), 5.83 (1H, dq, *J* = 11.5, 6.9 Hz), 2.20 (3H, s), 1.45 (3H, dd, *J* = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 136.6, 136.2, 128.5, 127.4, 127.0, 126.5, 20.3, 14.3.

trans: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.01 (3H, s), 6.32 (1H, d, *J* = 16.0 Hz), 5.67 (1H, dq, *J* = 16.0, 6.3 Hz), 2.27 (3H, s), 1.90 (3H, dd, *J* = 6.3, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 137.8, 136.0, 130.4, 128.5, 127.7, 126.2, 21.0, 18.9; HRMS [M + H]$^+$ calculated for $C_{11}H_{15}$ 147.1174, found 147.1151.

(E)-1,2-dimethyl-4-(prop-1-en-1-yl)benzene (***39***, *trans*). *Colorless oil.*

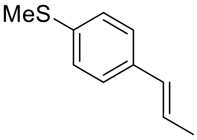


39, *trans*

Product yield; 18% (266 mg, 1.82 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.11 (1H, s), 7.06 (1H, d, *J* = 13.2 Hz), 7.04 (1H, d, *J* = 13.2 Hz), 6.34 (1H, dd, *J* = 16.0, 1.7 Hz), 6.17 (1H, dq, *J* = 16.0, 6.3 Hz), 2.34 (3H, s), 2.23 (3H, s), 1.86 (3H, dd, *J* = 6.3, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 136.6, 135.7, 135.2, 131.0, 129.9, 127.3, 124.6, 123.4, 19.9, 19.6, 18.6; HRMS [M + H]$^+$ calculated for $C_{11}H_{15}$ 147.1174, found 147.1187.

(E)-methyl(4-(prop-1-en-1-yl)phenyl)sulfane (***41***, *trans*). *Yellow solid.*

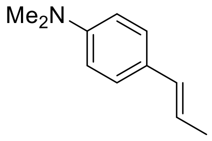


41, *trans*

Product yield; 21% (348 mg, 2.12 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.24 (2H, d, *J* = 8.6 Hz), 7.18 (2H, d, *J* = 8.6 Hz), 6.35 (1H, dd, *J* = 15.5, 1.2 Hz), 6.19 (1H, dq, *J* = 15.5, 6.3 Hz), 2.47 (3H, s), 1.87 (3H, dd, *J* = 6.3, 1.2 Hz),; ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 136.5, 134.9, 130.4, 126.8, 126.2, 125.0, 18.4, 15.9; HRMS [M + H]$^+$ calculated for $C_{12}H_{11}S$ 165.0738, found 165.0762.

(E)-N,N-dimethyl-4-(prop-1-en-1-yl)aniline (***42****, trans*). *Yellow solid.*

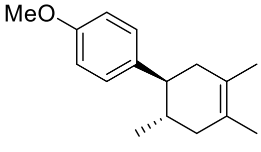


42, *trans*

Product yield; 51% (825 mg, 5.12 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.22 (2H, d, J = 8.6 Hz), 6.67 (2H, d, J = 8.6 Hz), 6.31 (1H, dd, J = 15.5, 1.7 Hz), 6.02 (1H, dq, J = 15.5, 6.9 Hz), 2.93 (6H, s), 1.84 (3H, dd, J = 6.9, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.5, 130.8, 126.7, 126.6, 121.0, 112.5, 40.4, 18.4; HRMS [M + H]$^+$ calculated for $C_{11}H_{16}N$ 162.1282, found 162.1279.

(1S,2S)-4'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***3****, trans*). *Colorless oil.*

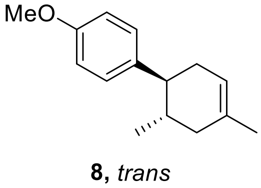


3, *trans*

Product yield; 97% (determined by NMR), isolated in 76 % (35.0 mg, 0.152 mmol). The reaction was also carried out in 1.0 mmol scale and gave the titled compound in 67% yield (155 mg, 0.673 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.08 (2H, d, J = 8.6 Hz), 6.84 (2H, d, J = 8.6 Hz), 3.79 (3H, s), 2.33 (1H, dt, J = 10.3, 5.7 Hz), 2.12 (3H, m), 1.85 (2H, m), 1.64 (3H, s), 1.61 (3H, s), 0.69 (3H, d, J = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.8, 138.3, 128.5, 125.6, 125.4, 113.7, 55.3, 47.9, 41.9, 41.7, 34.3, 20.1, 18.8, 18.7; HRMS [M + H]$^+$ calculated for $C_6H_{23}O$ 231.1749, found 231.1775.

(1S,2S)-4'-methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***8****, trans*). *Colorless oil.*

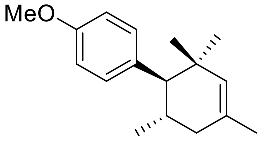


8, *trans*

Product yield; 98% (determined by NMR), isolated in 81% (35.1 mg, 0.162 mmol). The reaction was also carried out in 1.0 mmol scale and gave the titled compound in 69% yield (149 mg, 0.688 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.08 (2H, d, J = 8.6 Hz), 6.84, (2H, d, J = 8.6 Hz), 5.44 (1H, s), 3.79 (3H, s), 3.75 (1H, t, J = 6.3 Hz), 2.29 (1H, dt, J = 10.3, 5.2 Hz), 2.17 (2H, m), 2.08 (1H, dd, J = 18.3, 4.6 Hz), 1.88 (2H, m), 1.80 (1H, m), 1.69 (3H, s), 0.70 (3H, d, J = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.8, 138.3, 133.9, 128.6, 121.0, 113.7, 55.3, 47.0, 39.9, 35.4, 34.0, 23.5, 20.3

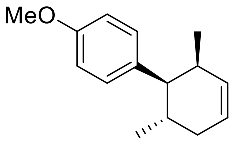
(1R,2S)-4'-methoxy-2,4,6,6-tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***9***, *trans*). Colorless oil.



9, *trans*

Product yield; 96% (determined by NMR), isolated in 91% (44.8 mg, 0.183 mmol).
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.02 (2H, dd, *J* = 32.7, 6.3 Hz), 6.82 (2H, dd, *J* = 32.7, 6.3 Hz), 5.19 (1H, s), 3.80 (3H, s), 2.18 (2H, m), 2.09 (1H, dd, *J* = 17.8, 4.0 Hz), 1.75 (1H, m), 1.66 (3H, s), 0.82 (3H, s), 0.77 (3H, s), 0.70 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.7, 133.3, 130.4, 129.4, 113.2, 112.2, 57.5, 55.2, 40.6, 36.3, 30.1, 28.8, 24.8, 23.4, 20.9; HRMS $[M + H]^+$ calculated for $C_{17}H_{25}O$ 245.1905, found 245.1926.

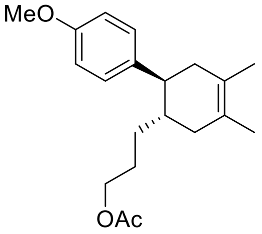
(1R,2S,6S)-4'-methoxy-2,6-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***10***, *trans*). Colorless oil.



10, *trans*

Product yield; 91% (determined by NMR), isolated in 89% (38.5 mg, 0.178 mmol).
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.06 (2H, d, *J* = 8.6 Hz), 6.84 (2H, d, *J* = 8.6 Hz), 5.74 (1H, dt, *J* = 9.7, 2.3 Hz), 5.64 (1H, dt, *J* = 9.7, 2.3 Hz), 3.80 (3H, s), 2.66 (1H, dd, *J* = 10.9, 5.7 Hz), 2.26 (2H, m), 2.13 (1H, m), 1.80 (1H, dq, *J* = 9.2, 2.3 Hz), 0.83 (3H, d, *J* = 6.3 Hz), 0.74 (3H, d, *J* = 7.45 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.7, 135.5, 133.5, 130.2, 125.2, 113.3, 55.2, 50.5, 35.6, 34.8, 26.5, 20.6, 16.9; HRMS $[M + H]^+$ calculated for $C_{15}H_{20}O$ 217.1592, found 217.1563.

3-((1S,2S)-4'-methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)propyl acetate (***18**, trans*). *Colorless oil.*

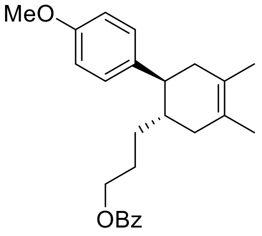


18, *trans*

Product yield; 89% (determined by NMR), isolated in 66% (41.7 mg, 0.132 mmol). Eluent; hexane/ethyl acetate = 4/1.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.06 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 3.94 (1H, m), 3.87 (1H, m), 3.79 (3H, s), 2.43 (1H, dt, *J* = 10.3, 5.7 Hz), 2.13 (3H, m), 1.96 (3H, s), 1.78 (2H, m), 1.66 (1H, m), 1.65 (3H, s), 1.61 (3H, s), 1.44 (1H, m), 1.23 (1H ,m), 0.94 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 171.2, 157.9, 137.9, 128.5, 125.5, 124.9, 113.9, 64.7, 55.3, 46.3, 41.8, 38.5, 38.2, 30.0, 25.7, 21.0, 18.9, 18.7; HRMS [M + H]$^+$ calculated for $C_{20}H_{29}O_3$ 317.2116, found 317.2101.

3-((1S,2S)-4'-methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)propyl benzoate (***19**, trans*). *Colorless oil.*

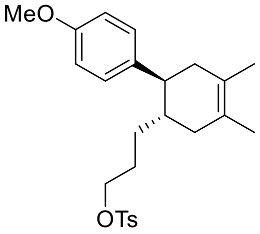


19, *trans*

Product yield; 92% (determined by NMR), isolated in 81% (61.1 mg, 0.161 mmol). Eluent; hexane/ethyl acetate = 4/1.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (2H, dd, *J* = 8.0, 1.2 Hz), 7.53 (1H, tt, *J* = 8.0, 1.2 Hz), 7.40 (2H, t, *J* = 8.0 Hz), 7.07 (2H, d, *J* = 8.6 Hz), 6.80 (2H, d, *J* = 8.6 Hz), 4.17 (2H, t, *J* = 6.3 Hz), 3.75 (3H, s), 2.46 (1H, dt, *J* = 10.3 5.7 Hz), 2.14 (2H, m), 1.80 (3H, m), 1.66 (3H, s), 1.62 (3H, s), 1.57 (1H, m), 1.39 (1H, m), 1.04 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.6, 157.8, 137.8, 132.8, 130.49, 129.5, 128.5, 128.3, 125.5, 124.9, 113.8, 65.0, 55.2, 46.3, 41.8, 38.4, 38.2, 30.1, 25.7, 18.9, 18.7; HRMS [M + H]$^+$ calculated for $C_{25}H_{31}O_3$ 379.2273, found 379.2302.

3-((1S,2S)-4'-methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)propyl 4-methylbenzenesulfonate (***20***, *trans*). *Colorless oil.*

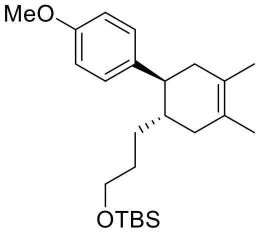


20, *trans*

Product yield; 98% (determined by NMR), isolated in 47% (40.3 mg, 0.0940 mmol). Eluent; hexane/ethyl acetate = 4/1.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.70 (2H, d, *J* = 8.0 Hz), 7.30 (2H, d, *J* = 8.0 Hz), 7.01 (2H, d, *J* = 8.6 Hz), 6.82 (2H, d, *J* = 8.6 Hz), 3.86 (2H, m), 3.80 (3H, s), 2.44 (3H, s), 2.38 (1H, dt, *J* = 10.3, 5.7 Hz), 2.09 (3H, m), 1.69 (3H, m), 1.43 (1H, m), 1.15 (1H, m), 0.88 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.9, 144.6, 137.6, 133.3, 129.8, 128.5, 127.9, 125.5, 124.7, 113.9, 70.9, 55.3, 46.2, 41.6, 38.8, 38.1, 29.7, 26.1, 21.7, 18.9, 18.7; HRMS [M + H]$^+$ calculated for $C_{25}H_{33}O_4S$ 429.2099, found 429.2090.

tert-butyl(3-((1S,2S)-4'-methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)propoxy)dimethylsilane (***21***, *trans*). *Colorless oil.*

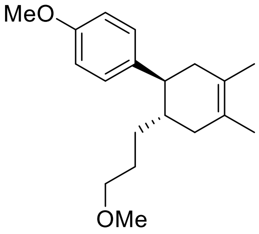


21, *trans*

Product yield; 89% (determined by NMR), isolated in 55% (42.9 mg, 0.110 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.06 (2H, d, *J* = 8.6 Hz), 6.82 (2H, d, *J* = 8.6 Hz), 3.79 (3H, s), 3.44 (2H, t, *J* = 6.9 Hz), 2.42 (1H, dt, *J* = 10.3, 5.7 Hz), 2.12 (3H, m), 1.76 (2H, m), 1.65(3H, s), 1.61 (3H, s), 1.53 (1H, m), 1.32 (1H, m), 1.23 (1H, m), 0.86 (1H, m), 0.82 (9H, s), -0.03 (3H, s), -0.04 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.8, 138.1, 128.6, 125.4, 125.1, 113.8, 63.6, 55.3, 46.5, 41.8, 38.9, 38.4, 30.1, 30.0, 26.0, 19.0, 18.7, 18.4, -5.2; HRMS [M + H]$^+$ calculated for $C_{24}H_{41}O_2Si$ 389.2876, found 389.2895.

(1S,2S)-4'-methoxy-2-(3-methoxypropyl)-4,5-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***22**, trans*). *Colorless oil.*

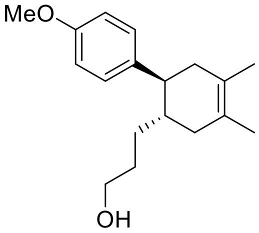


22, *trans*

Product yield; 97% (determined by NMR), isolated in 61% (35.3 mg, 0.122 mmol). Eluent; hexane/ethyl acetate = 4/1.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.06 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 3.79 (3H, s), 3.25 (3H, s), 3.21 (2H, m), 2.44 (1H, dt, *J* = 10.3, 6.3 Hz), 2.12 (3H, m), 1.77 (2H, m), 1.65 (3H, s), 1.61 (3H, s), 1.59 (1H, m), 1.37 (1H, m), 1.22 (1H, m), 0.93 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.8, 138.1, 128.5, 125.4, 125.1, 113.8, 73.3, 58.5, 55.3, 46.3, 41.8, 38.8, 38.2, 30.4, 26.7, 18.9, 18.7; HRMS [M + H]$^+$ calculated for $C_{19}H_{29}O_2$ 289.2167, found 289.2185.

3-((1S,2S)-4'-methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)propan-1-ol (***23**, trans*). *Colorless oil.*

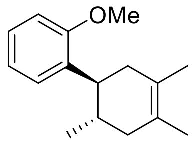


23, *trans*

Product yield; 97% (determined by NMR), isolated in 92% (50.3 mg, 0.183 mmol). Eluent; hexane/ethyl acetate = 1/1.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.07 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 3.79 (3H, s), 3.48 (2H, m), 2.44 (1H, dt, *J* = 10.3, 5.7 Hz), 2.14 (3H, m), 1.78 (2H, m), 1.65 (3H, s), 1.62 (3H, s), 1.58 (1H, m), 1.37 (1H, m), 1.25 (1H, m), 1.08 (1H, s), 0.94 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.8, 138.0, 128.5, 125.4, 125.0, 113.9, 63.3, 55.3, 46.6, 41.8, 38.7, 38.3, 30.0, 29.9, 18.9, 18.7; HRMS [M + H]$^+$ calculated for $C_{18}H_{27}O_2$ 275.2011, found 275.2034.

(1S,2S)-2'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***43***, *trans*). *Colorless oil.*

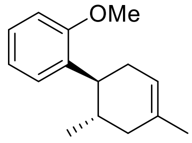


43, *trans*

Product yield; 98% (determined by NMR), isolated in 83% (38.2 mg, 0.166 mmol). The reaction was also carried out in 1.0 mmol scale and gave the titled compound in 63% yield (146 mg, 0.634 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.15 (1H, dd, J = 7.5, 1.7 Hz), 7.14 (1H, d, J = 7.5 Hz), 6.92 (1H, dt, J = 7.5, 1.7 Hz), 6.85 (1H, d, J = 8.0 Hz), 3.79 (3H, s), 2.95 (1H, dt, J = 10.9, 5.2 Hz), 2.16 (1H, m), 2.06 (2H, d, J = 16.0 Hz), 1.99 (1H, m), 1.85 (1H, m), 1.64 (3H, s), 1.61 (3H, s), 0.72 (3H, d, J = 6.9 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.6, 134.2, 127.9, 126.6, 125.7, 125.3, 120.8, 110.7, 55.5, 41.7, 40.2, 33.1, 19.7, 18.9, 18.8; HRMS [M + H]$^+$ calculated for $C_{16}H_{23}O$ 231.1749, found 231.1755.

(1S,2S)-2'-methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***44***, *trans*). *Colorless oil.*

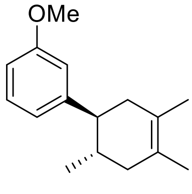


44, *trans*

Product yield; 97% (determined by NMR), isolated in 82% (35.5 mg, 0.164 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.15 (2H, m), 6.92 (1H, dt, J = 8.0, 1.2 Hz), 6.86 (1H, d, J = 8.0 Hz), 5.45 (1H, s), 3.79 (3H, s), 2.91 (1H, q, J = 8.6), 2.17 (2H, m), 2.05 (2H, m), 1.83 (1H, m), 1.70 (3H, s), 0.74 (3H, d, J = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.6, 134.2, 133.8, 127.9, 126.6, 121.2, 120.7, 110.7, 55.5, 39.9, 33.6, 32.8, 23.6, 19.9; HRMS [M + H]$^+$ calculated for $C_{15}H_{21}O$ 217.1592, found 217.1599.

(1S,2S)-3'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***45***, *trans*). *Colorless oil.*

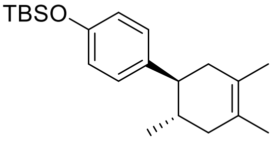


45, *trans*

Product yield; 31% (determined by NMR), isolated in 25% (11.4 mg, 0.0499 mmol). Eluent; hexane.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21 (1H, m), 6.77 (1H, d, J = 8.0 Hz), 6.73 (2H, m), 3.80 (3H, s), 2.36 (1H, dt, J = 10.9, 5.7 Hz), 2.16 (2H, m), 2.08 (1H, d, J = 16.0 Hz), 1.86 (2H, m), 1.64 (3H, s), 1.62 (3H, s), 0.72 (3H, d, J = 6.3 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.7, 148.0, 129.3, 125.5, 125.4, 120.3, 113.7, 110.9, 55.2, 48.9, 41.6, 41.7, 34.1, 20.1, 18.8, 18.7; HRMS [M + H]$^+$ calculated for $C_{16}H_{23}O$ 231.1749, found 231.1730.

tert-butyldimethyl(((1'S,2'S)-2',4',5'-trimethyl-1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane (***47***, *trans*). *Colorless oil.*

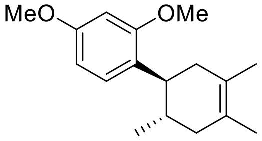


48, *trans*

Product yield; 85% (determined by NMR), isolated in 67% (43.8 mg, 0.133 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.00 (2H, d, J = 8.6 Hz), 6.75 (2H, d, J = 8.6 Hz), 2.30 (1H, dt, J = 10.9, 5.7 Hz), 2.10 (3H, m,), 1.81 (2H, m), 1.63 (3H, s), 1.61 (3H, s), 0.98 (9H, s), 0.67 (3H, d, J = 6.3 Hz), 0.18 (6H, s); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 153.7, 138.8, 128.5, 125.6, 125.3, 119.8, 48.0, 41.8, 41.8, 34.5, 25.8, 20.1, 18.8, 18.8, 18.3, -4.3; HRMS [M + H]$^+$ calculated for $C_{21}H_{35}OSi$ 331.2457, found 331.2427.

(1S,2S)-2',4'-dimethoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***49***, *trans*). *Colorless oil.*

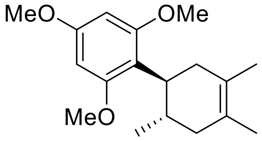


49, *trans*

Product yield; 61% (determined by NMR), isolated in 30% (15.7 mg, 0.0603 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.03 (1H, d, *J* = 8.0 Hz), 6.46 (2H, m), 3.79 (3H, s), 3.77 (3H, s), 2.84 (1H, dt, *J* = 10.9, 5.2 Hz), 2.14 (1H, m), 2.05 (2H, m), 1.94 (1H, m), 1.83 (1H, m), 1.64 (3H, s), 1.61 (3H, s), 0.72 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.6, 158.5, 128.2, 126.6, 125.8, 125.3, 104.3, 98.5, 55.5, 55.3, 41.8, 40.3, 33.2, 19.7, 18.9, 18.8; HRMS [M + H]$^+$ calculated for $C_{17}H_{25}O_2$ 261.1854, found 261.1884.

(1S,2S)-2',4',6'-trimethoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***50***, *trans*). *Colorless oil.*

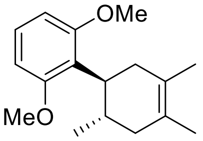


50, *trans*

Product yield; 12% (determined by NMR), isolated in 10% (5.65 mg, 0.0195 mmol). Eluent; hexane/ethyl acetate = 40/1.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.13 (2H, s), 3.81 (1H, m), 3.80 (3H, s), 3.76 (6H, s), 3.08 (1H, dt, *J* = 11.5, 5.2 Hz), 2.55 (1H, t, *J* = 13.8 Hz), 2.39 (1H, m), 2.01 (1H, m), 1.80 (2H, m), 1.64 (3H, s), 1.60 (3H, s), 0.66 (3H, d, *J* = 6.30 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 159.1, 126.4, 125.4, 113.7, 91.4, 91.0, 55.3, 42.5, 38.1, 37.3, 31.1, 29.8, 19.8, 19.0, 18.9; HRMS [M + H]$^+$ calculated for $C_{18}H_{27}O_3$ 291.1960, found 291.1958.

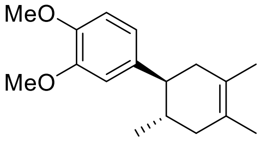
(1S,2S)-2',6'-dimethoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***51***, *trans*). *Colorless oil.*



51, *trans*

Product yield; 81% (determined by NMR), isolated in 79% (41.2 mg, 0.158 mmol).
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.10 (1H, t, *J* = 8.6 Hz), 6.53 (2H, d, *J* = 8.6 Hz), 3.76 (6H, s), 3.21 (1H, dt, *J* = 11.5, 5.2 Hz), 2.60 (1H, t, *J* = 13.8 Hz), 2.46 (1H, m), 2.01 (1H, dd, *J* = 17.2, 4.0 Hz), 1.84 (1H, m), 1.78 (1H, m), 1.65 (3H, s), 1.61 (3H, s), 0.67 (3H, d, *J* = 6.9 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.6, 158.8, 126.8, 126.3, 125.4, 121.2, 104.5, 104.3, 56.2, 55.3, 42.4, 38.5, 36.9, 31.0, 19.8, 19.0, 18.8; HRMS $[M + H]^+$ calculated for $C_{17}H_{25}O_2$ 261.1854, found 261.1855.

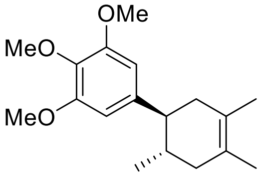
(1S,2S)-3',4'-dimethoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***52***, *trans*). *Colorless oil.*



52, *trans*

Product yield; 42% (determined by NMR), isolated in 26% (13.4 mg, 0.0515 mmol). Eluent; hexane/ethyl acetate = 40/1.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.80 (1H, d, *J* = 8.0 Hz), 6.71 (2H, m), 3.87 (3H, s), 3.86 (3H, s), 2.33 (1H, dt, *J* = 10.3, 5.7 Hz) 2.18 (1H, m), 2.13 (1H, d, *J* = 5.7 Hz), 2.08 (1H, d, *J* = 12.6 Hz), 1.85 (2H, m), 1.65 (3H, s), 1.62 (3H, s), 0.71 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.9, 147.1, 138.9, 125.4,125.4, 119.6, 111.1, 110.6, 55.9, 55.8, 48.4, 41.8, 41.7, 34.3, 20.1, 18.8, 18.7; HRMS $[M + H]^+$ calculated for $C_{17}H_{25}O_2$ 261.1854, found 261.1863.

(1S,2S)-3',4',5'-trimethoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***53***, *trans*). *Colorless oil.*

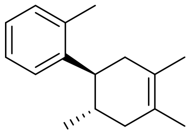


53, *trans*

Product yield; 7% (determined by NMR), isolated in 2% (1.34 mg, 0.00461 mmol). Eluent; hexane/ethyl acetate = 40/1.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.39 (2H, s), 3.85 (6H, s), 3.83 (3H, s), 2.32 (1H, dt, *J* = 10.3, 5.7 Hz), 2.18 (2H, m), 2.09 (1H, d, *J* = 13.2 Hz), 1.85 (2H, m), 1.65 (3H, s), 1.63 (3H, s), 0.74 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 153.2, 142.1, 136.1, 125.4, 125.3, 104.5, 60.9, 56.1, 49.2, 41.7, 41.6, 34.3, 29.8, 26.1, 18.8, 18.7; HRMS [M + H]$^+$ calculated for $C_{18}H_{27}O_3$ 291.1960, found 291.1969.

(1S,2S)-2,2',4,5-tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***54***, *trans*). *Colorless oil.*

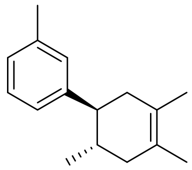


54, *trans*

Product yield; 55% (determined by NMR), isolated in 48% (20.7 mg, 0.0966 mmol). Eluent; acetonitrile using ODS silica.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.17 (2H, m) 7.13 (1H, d, *J* = 7.5 Hz), 7.07 (1H, dt, *J* = 7.5, 2.3 Hz), 2.73 (1H, m), 2.32 (3H, s), 2.11 (3H, m), 1.97 (1H, m), 1.86 (1H, m), 1.66 (3H, s), 1.62 (3H, s), 0.72 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 144.2, 136.0, 130.1, 126.3, 126.2, 125.7, 125.5, 125.4, 42.9, 41.7, 41.1, 33.9, 20.0, 19.7, 18.9, 18.7, ; HRMS [M + H]$^+$ calculated for $C_{16}H_{23}$ 215.1800, found 215.1788.

(1S,2S)-2,3',4,5-tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***55***, *trans*). *Colorless oil.*

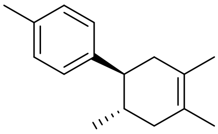


55, *trans*

Product yield; 54% (determined by NMR), isolated in 49% (21.0 mg, 0.0980 mmol). Eluent; acetonitrile using ODS silica.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.18 (1H, t, *J* = 8.0 Hz), 7.00 (1H, d, *J* = 8.0 Hz), 6.97 (2H, d, *J* = 8.6 Hz), 2.34 (1H, dt, *J* = 10.9, 5.7 Hz), 2.33 (3H, s), 2.18 (1H, m), 2.09 (2H, m), 1.90 (1H, m), 1.83 (1H, m), 1.65 (3H, s), 1.61 (3H, s), 0.70 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 146.1, 137.8, 128.6, 128.3, 126.7, 125.6, 125.4, 124.8, 48.8, 41.9, 41.7, 34.1, 21.6, 20.2, 18.9, 18.8; HRMS [M + H]$^+$ calculated for $C_{16}H_{23}$ 215.1800, found 215.1818.

(1S,2S)-2,4,4',5-tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***56***, *trans*). *Colorless oil.*

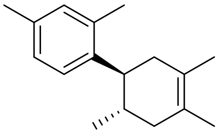


56, *trans*

Product yield; 81% (determined by NMR), isolated in 78% (33.4 mg, 0.156 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.10 (2H, d, *J* = 8.0 Hz), 7.06 (2H, d, *J* = 8.0 Hz), 2.35 (1H, dt, *J* = 10.3, 5.7 Hz), 2.32 (3H, s), 2.17 (1H, m), 2.08 (2H, m), 1.85 (2H, m), 1.64 (3H, s), 1.61 (3H, s), 0.70(3H, d, *J* = 5.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 143.1, 135.3, 129.1, 127.6, 125.6, 125.4, 48.4, 41.9, 41.7, 34.1, 21.1, 20.1, 18.8, 18.7; HRMS [M + H]$^+$ calculated for $C_{16}H_{23}$ 215.1800, found 215.1804.

(1S,2S)-2,2',4,4',5-pentamethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (***57***, *trans*). *Colorless oil.*

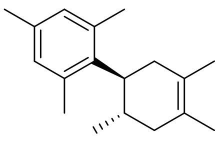


57, *trans*

Product yield; 96% (determined by NMR), isolated in 63% (28.8 mg, 0.126 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.05 (1H, d, *J* = 8.0 Hz), 6.99 (1H, d, *J* = 8.0 Hz), 6.95 (1H, s), 2.68 (1H, m), 2.28 (6H, s), 2.09 (3H, m), 1.95 (1H, m), 1.85 (1H, m), 1.65 (3H, s), 1.61 (3H, s), 0.72 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 141.2, 135.8, 134.7, 131.0, 127.1, 126.1, 125.8, 125.4, 42.6, 41.8, 41.2, 33.9, 21.0, 19.9, 19.7, 18.9, 18.7; HRMS [M + H]$^+$ calculated for $C_{17}H_{25}$ 229.1956, found 229.1980.

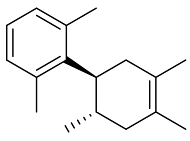
*(1S,2S)-2,2',4,4',5,6'-hexamethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (**58**, trans). Colorless oil.*



58, *trans*

Product yield; 65% (determined by NMR), isolated in 59% (28.6 mg, 0.118 mmol).
^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.82 (1H, s), 6.78 (1H, s), 2.96 (1H, dt, *J* = 12.0, 5.7 Hz), 2.36 (3H, s), 2.32 (2H, m), 2.29 (3H, s), 2.23 (3H, s), 2.04 (1H, dd, *J* = 16.6, 3.4 Hz), 1.95 (1H, dd, *J* = 17.8, 4.6 Hz), 1.81 (1H, m), 1.65 (H, s), 1.61 (3H, s), 0.72 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 137.9, 137.1, 136.2, 134.9, 131.1, 129.3, 125.9,125.8, 44.1, 42.5, 37.2, 31.5, 22.0, 21.5, 20.7, 19.6, 19.1, 18.7; HRMS [M + H]$^+$ calculated for C$_{18}$H$_{27}$ 243.2113, found 243.2102.

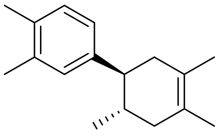
*(1S,2S)-2,2',4,5,6'-pentamethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (**59**, trans). Colorless oil.*



59, *trans*

Product yield; 62% (determined by NMR), isolated in 58% (26.6 mg, 0.116 mmol).
^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.96 (3H, m), 3.01 (1H, dt, *J* = 12.0, 5.7 Hz), 2.40 (3H, s), 2.36 (3H, m), 2.33 (3H, s), 2.05 (1H, dd, *J* = 16.6, 4.0 Hz), 1.97 (1H, dd, *J* = 17.8, 4.0 Hz), 1.82 (2H, m), 1.66 (3H, s), 1.62 (3H, s), 0.72 (3H, d, *J* = 6.9 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 141.0, 137.2, 136.3, 130.4, 128.4, 125.9, 125.7, 125.6, 44.5, 42.5, 37.0, 31.5, 22.1, 21.6, 19.5, 19.1, 18.7; HRMS [M + H]$^+$ calculated for C$_{17}$H$_{25}$ 229.1956, found 229.1979.

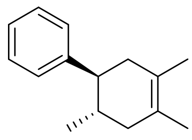
*(1S,2S)-2,3',4,4',5-pentamethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (**60**, trans). Colorless oil.*



60, *trans*

Product yield; 79% (determined by NMR), isolated in 73% (33.3 mg, 0.146 mmol).
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.05 (1H, d, *J* = 8.0 Hz), 6.93 (1H, s), 6.90 (1H, d, *J* = 8.0 Hz), 2.31 (1H, dt, *J* = 10.9, 5.7 Hz), 2.24 (3H, s), 2.23 (3H, s), 2.16 (1H, m), 2.08 (1H, dd, *J* = 16.6, 2.3 Hz), 1.88 (1H, m), 1.82 (1H, m), 1.64 (3H, s), 1.61 (3H, s), 0.71 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 143.6, 136.3, 134.0, 129.6, 129.1, 125.6, 125.3, 125.0, 48.4, 42.1, 41.7, 34.0, 20.2, 20.0, 19.5, 18.8, 18.7; HRMS [M + H]$^+$ calculated for C$_{17}$H$_{25}$ 229.1956, found 229.1929.

*(1S,2S)-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (**61**, trans). Colorless oil.*

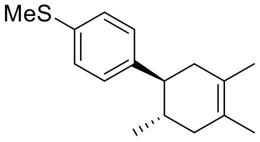


61, *trans*

Product yield; 61% (determined by NMR), isolated in 51% (20.4 mg, 0.102 mmol). Eluent; acetonitrile using ODS silica.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.30 (1H, d, J = 8.0 Hz), 7.28 (1H, d, J = 8.0 Hz), 7.18 (3H, m), 2.38 (1H, dt, J = 10.3, 5.2 Hz), 2.19 (1H, m), 2.10 (2H, m), 1.93 (1H, m), 1.83 (1H, m), 1.65 (3H, s), 1.62 (3H, s), 0.70 (3H, d, J = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 146.2, 128.4, 127.8, 126.0, 125.5, 125.4, 48.8, 41.8, 41.7, 34.1, 20.1, 18.8, 18.7; HRMS [M + H]$^+$ calculated for $C_{17}H_{25}$ 201.1643, found 201.1625.

*methyl(-2',4',5'-trimethyl-1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-yl)sulfane (**62**, trans). Colorless oil.*



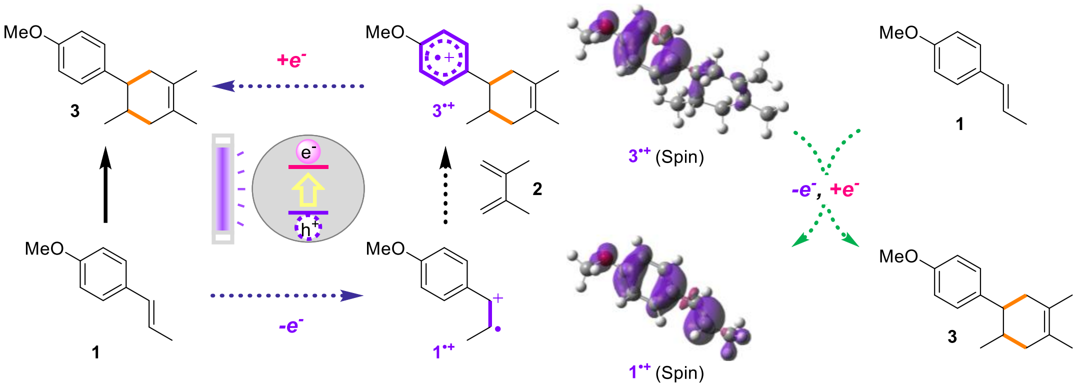
62, *trans*

Product yield; 9% (determined by NMR), isolated in 7% (3.45 mg, 0.0140 mmol). Eluent; hexane.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.21 (2H, d, J = 8.6 Hz), 7.10 (2H, d, J = 8.6 Hz), 2.48 (3H, s), 2.35 (1H, dt, J = 10.3, 5.7 Hz), 2.12 (1H, m), 1.86 (2H, m), 1.64 (3H, s), 1.61 (3H, s), 0.70 (3H, d, J = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 143.4, 135.2, 128.3, 127.1, 125.5, 125.4, 48.2, 41.7, 41.6, 34.1, 20.1, 18.8, 18.7, 16.4; HRMS [M + Na]$^+$ calculated for $C_{15}H_{20}SNa$ 269.1334, found 269.1330.

Chapter 3. Electrochemical EC-Backward-E in Radical Cation Diels-Alder Reactions

Abstract



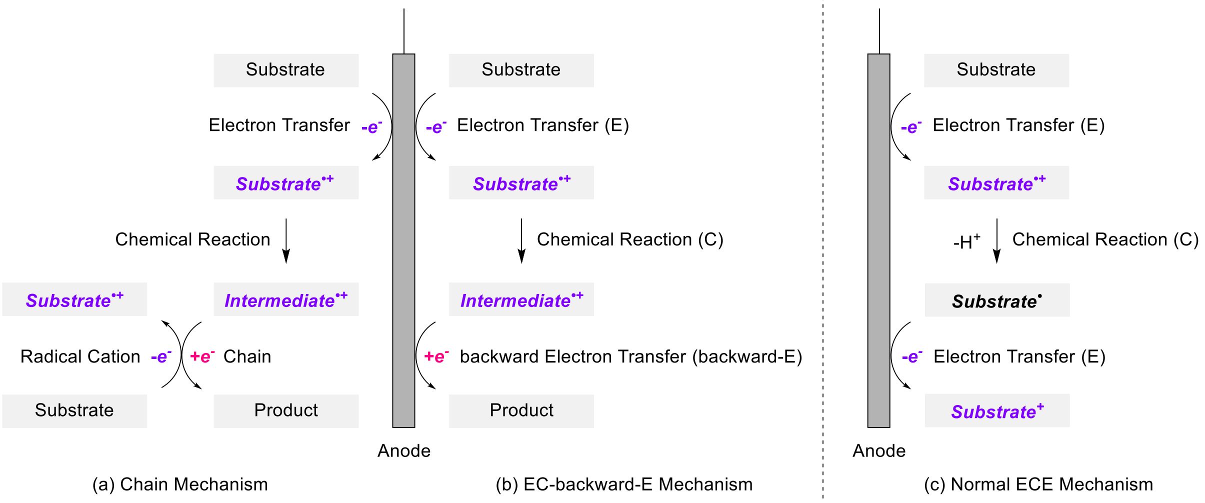
Cascade processes involving electron transfer (E), chemical reaction (C), and backward electron transfer (backward-E) are known as EC-backward-E mechanisms; however, have rarely been directly observed. Herein, the direct observation of the EC-backward-E process in the radical cation Diels-Alder reaction was demonstrated by cyclic voltammetry (CV) measurements. The highest occupied orbital (HOMO) and spin density plotted by density functional theory (DFT) calculations provide a reasonable understanding of plausible reaction mechanism.

3.1. Introduction

In the previous chapter, we demonstrated the TiO_2 photocatalytic radical cation Diels-Alder reaction with β-methylstyrenes.[84] Particularly, *trans*-β-methylstyrene, which was impossible to form cyclohexene by Ru photocatalysis and electrocatalysis, was found to give cycloadduct with 2,3-dimethyl-1,3-butadiene by TiO_2 photocatalysis. The reaction mechanism was proposed to be TiO_2 photocatalytic redox neutral, whereas the difference of TiO_2 photocatalytic/electrocatalytic redox and the structure formulas of radical cation intermediates were not clarified.

Chiba *et al.* proposed the chain and EC-backward-E processes as reaction mechanism in the radical cation Diels-Alder reaction by electrocatalysis.[34,77] The chain process is a mechanism in which, after single electron transfer (SET)-oxidation of dienophile by anode and coupling with diene, the neutral dienophile undergoes the SET-reduction of radical cation intermediate (Scheme 3-1 (a)).[79,85,86] This mechanism is suggested by the amount of electricity required for the reaction and the cyclic voltammetry (CV) analysis. In contrast, the EC-backward-E process (Scheme 3-1 (b)) differs from the general electron transfer, chemical reaction, electron transfer (ECE) process (Scheme 3-1 (c)). When the oxidation potential of $(\text{intermediate})^{\bullet+}$ is significantly higher, not only than that of substrate, but than that of the anode, backward-E may be possible. EC-backward-E process is directly observed by analysis of cyclic voltammetry measurement, and it is rare phenomena because there are many factors for appearance, such as an appropriate scan rate and the correlation of oxidation potential between starting materials, intermediates and anode.[87–93]

Scheme 3-1. Diagram of Chain, EC-backward-E and normal ECE Mechanisms.



TiO_2 photocatalysis is categorized in interfacial electron transfer, also called a wireless electrode,[20] and required for the $LiClO_4/CH_3NO_2$ solvent system in the [2+2] cycloaddition and radical cation Diels-Alder reaction,[80,84] suggesting that it has properties similar to electrocatalysis. If the TiO_2 photocatalyst is considered as an electrode, it equals single electrode combined two electrode activities: the excited electrons/holes are the cathodes/anodes. If a redox reaction is carried out by single TiO_2 particle, the TiO_2 photocatalytic electron transfer is considered to be similar to the EC-backward-E process.

In this study, the mechanistic analysis of the radical cation Diels-Alder reaction using β-methylstyrenes is demonstrated in detail to better clarify the difference of reactivity between TiO_2 photocatalysis and electrocatalysis. Direct observation of EC-backward-E processes is tried by CV measurements, and the mechanisms are supported by density functional theory (DFT) calculations of the highest occupied molecular orbitals (HOMO) and spin density.

3.2. Results and Discussion

3.2.1. Plausible Reaction Mechanism for the Radical Cation Diels-Alder Reaction Supported by CV Analyses and DFT Calculations of *trans*-Anethole (**1**) and Butadiene (**2**)

Cyclic voltammograms of *trans*-anethole (**1**) and butadiene (**2**) were measured (Figure 3-1). There is no difference between the simple measurement of **1** (2 mM) and in the presence of 2 eq. (4 mM) of **2**, possibly because the trapping $\mathbf{1}^{\bullet+}$ by **2** was slower than the sweep from 1.0 V to 1.5 V (50 mVs^{-1}), or the diffusion of $\mathbf{1}^{\bullet+}$ from the working electrode was faster than the trapping of **2**. The oxidation potential of the corresponding Diels-Alder adducts **3** is 1.32 V vs Ag/AgCl, and its peak was slightly observed in measurements with **1** (2 mM) and 2 eq. (4 mM) of **2**, suggesting that the ring formation tends to occur far away from the working electrode in the bulk. In sharp contrast, in the measurement with **1** (2 mM) and 20 eq. (40 mM) of **2**, a current of peak around 1.2 V *vs* Ag/AgCl, which is the oxidation of **1**, decreased and around 1.5 V *vs* Ag/AgCl, which is the oxidation of **3**, increased. These two phenomena have potential to provide evidence that the chain and EC-backward-E mechanism is underway. The attenuation of the oxidation current of **1** was caused by the presence of an excess amount of **2** in the bulk. **2** trapped simultaneously $\mathbf{1}^{\bullet+}$ produced, immediately $\mathbf{3}^{\bullet+}$ took backward discharge, thereby decreasing the apparent current. If this process was taking place, it was the pieces of evidence for the EC-backward-E mechanism, since a redox was carried out by the single electrode. The increase of the oxidation current of **3** was caused also due to the faster trapping of **2** than the diffusion of $\mathbf{1}^{\bullet+}$ from the working electrode and the successive formation of **3** by backward-E. It should be noted that both phenomena have potential to be observed due to the chain mechanism. However, since Okada *et al.* reported that the current efficiency indicating the turnover rate of chain decreased at low concentrations of **1**,[79] it is unlikely that chain is actively rotating in this CV measurement. Therefore, it can be concluded that the phenomenon observed in this study is due to the EC-backward-E process.

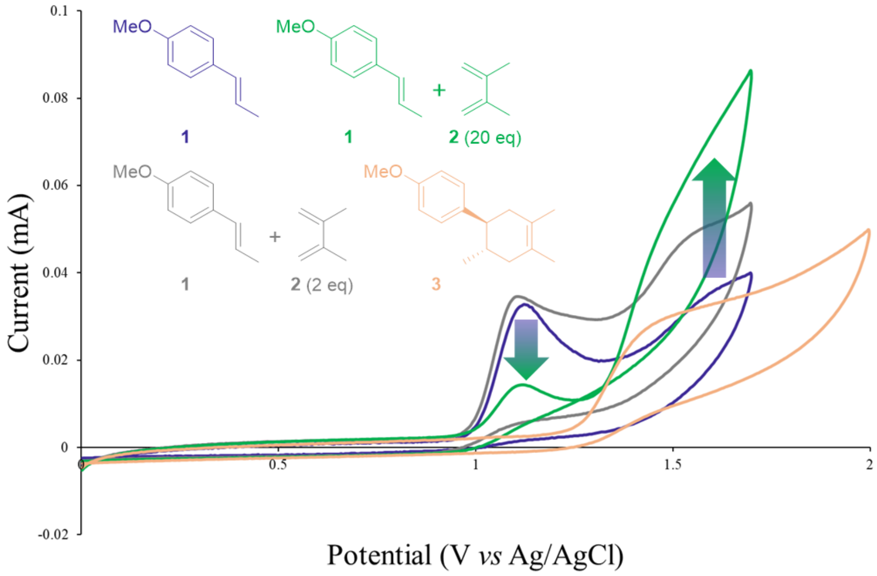


Figure 3-1. Cyclic Voltammograms of *trans*-Anethole (1) and Cyclohexene (3).

For the radical cation Diels-Alder reaction of **1** and **2**, the spin density plots of the intermediates (**1**$^{\bullet+}$, **3**$^{\bullet+}$) and the HOMO plots of **1**, **3** and **2** were calculated by DFT (Figure 3-2). Although the calculations of HOMO and spin density plots are sometimes mismatched depending on structural formulas, the plots of HOMO (**1**) and spin density (**1**$^{\bullet+}$), HOMO (**3**) and spin density (**3**$^{\bullet+}$) are similar each other. From the spin density of **3**$^{\bullet+}$ which was selectivity localized onto the aromatic ring, the structural formula of **3**$^{\bullet+}$ was imaged closer reality.

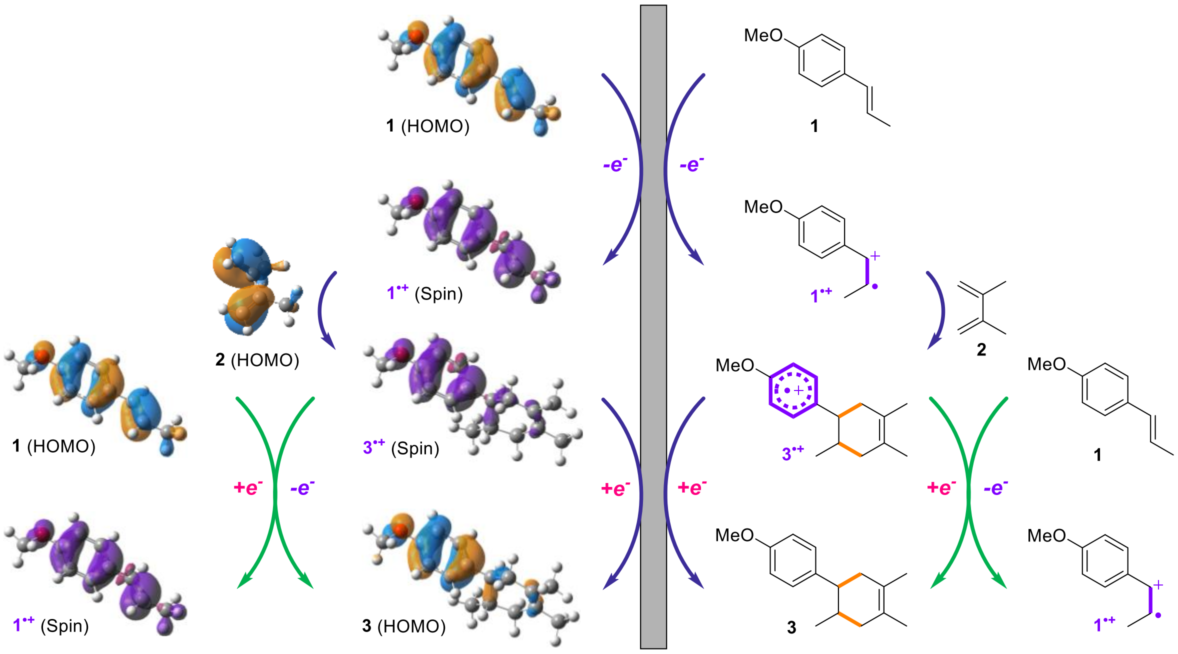
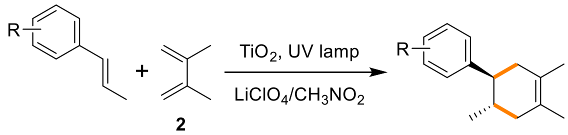


Figure 3-2. HOMO/Spin Density Plots for the Plausible Reaction Mechanism of 1 and 2.

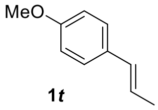
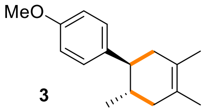
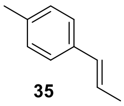
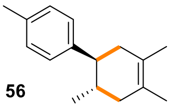
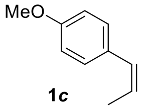
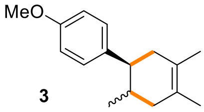
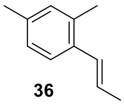
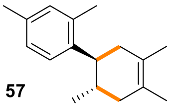
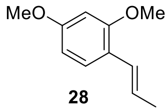
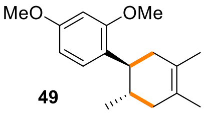
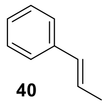
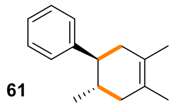
3.2.2. Correlation between Cycloaddition Yields and Cyclic Voltammograms

The oxidation potentials of cyclohexene (**3**, **49**, **56**, **57**, **61**), which were formed acceptably in the TiO_2 photocatalytic radical cation Diels-Alder reactions, were measured (Table 3-1). Direct observation of EC-backward-E for these starting materials (**1*c***, **28**, **35**, **36**, **40**), as well as for **1*t***, was found not only **1*c*** (Figure 3-3), but also 4-methyl (**35**) (Figure 3-4) and 2,4-dimethyl *trans*-*β*-methylstyrenes (**36**) (Figure 3-5). Since the oxidation potential of cyclohexene **61** was almost as high as that of **40**, this pair was not matched in this CV analysis. For **28** which was found to give cycloaddition in acceptable yield, the CV did not show the EC-backward-E process. However, an increase of current in the product oxidation potential was observed (Figure 3-6). In addition, the CV of **29**, which was less reactivity, showed neither the current attenuation of **29** nor the current increase of **50** (Figure 3-7). **28** and **29** are substrates with additional methoxy group on the aryl ring of **1*t***; hence, the radical cation reactivity of **28**$^{\bullet+}$and **29**$^{\bullet+}$ may exist in the aryl ring rather than the double bond of styrene. Therefore, the reaction with **2** was not proceeded smoothly and the chain/EC-backward-E processes could not be observed.

Table 3-1. E^{OX} **of** ***β*****-Methylstyrenes and Corresponding Diels-Alder Adducts.**



2
E^{ox} = 1.52 V

Substrate	Product	Substrate	Product
 E^{ox} = 0.96 V	 97%, E^{ox} = 1.32 V	 E^{ox} = 1.26 V	 81%, E^{ox} = 1.37 V
 E^{ox} = 1.02 V	 92%, E^{ox} = 1.32 V	 E^{ox} = 1.21 V	 96%, E^{ox} = 1.34 V
 E^{ox} = 0.82 V	 61%, E^{ox} = 1.07 V	 E^{ox} = 1.34 V	 61%, E^{ox} = 1.31 V

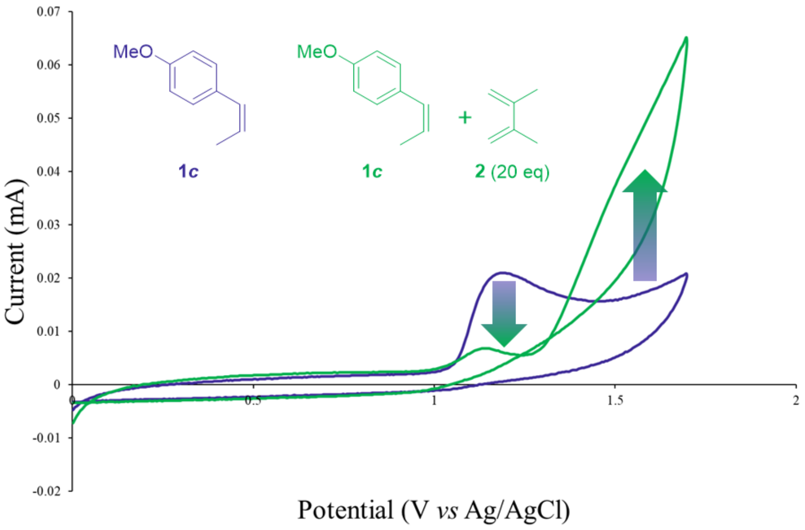


Figure 3-3. Cyclic Voltammograms of *cis*-Anethole (1*c*).

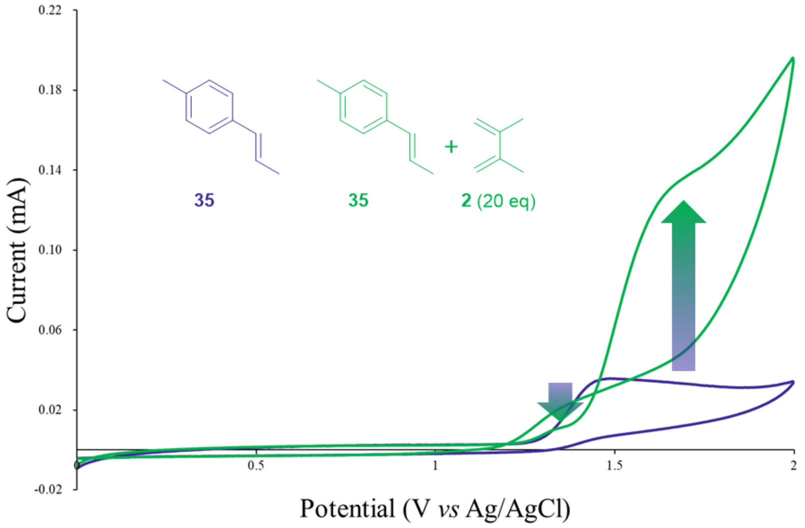


Figure 3-4. Cyclic Voltammograms of 4-Methyl *trans*- β -Methylstyene (35).

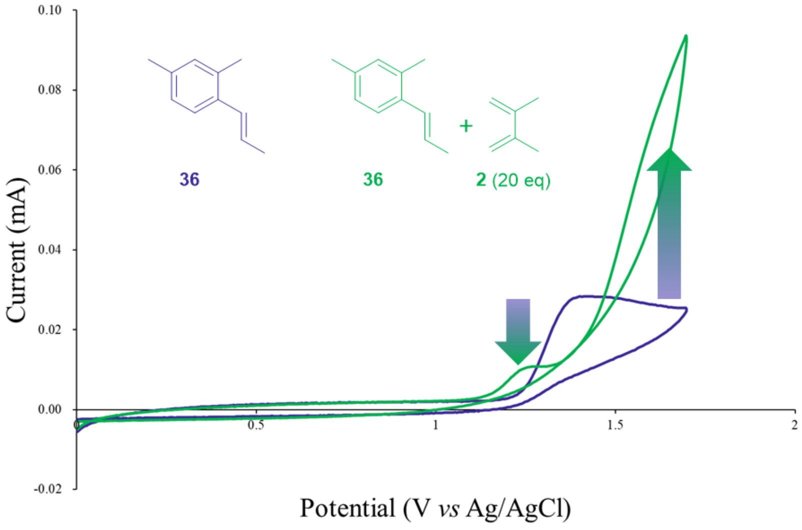


Figure 3-5. Cyclic Voltammograms of 2,4-Dimethyl *trans*- β -Methylstyene (36).

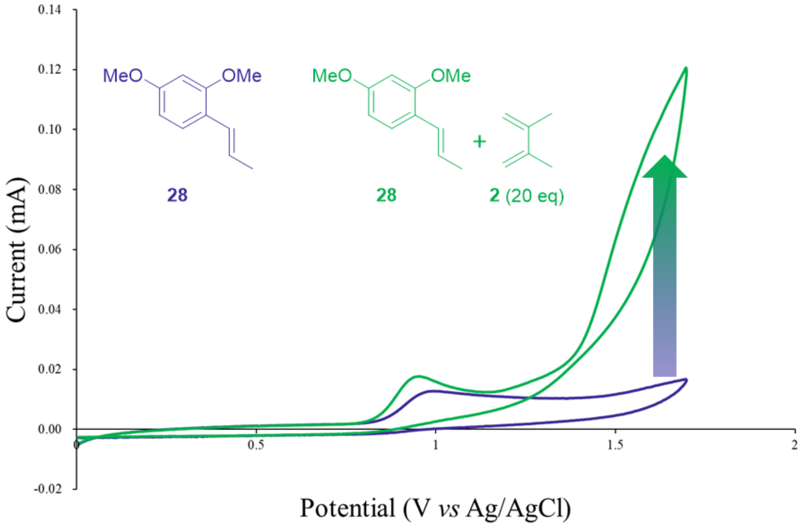


Figure 3-6. Cyclic Voltammograms of 2,4-Dimethoxy *trans*- β -Methylstyene (28).

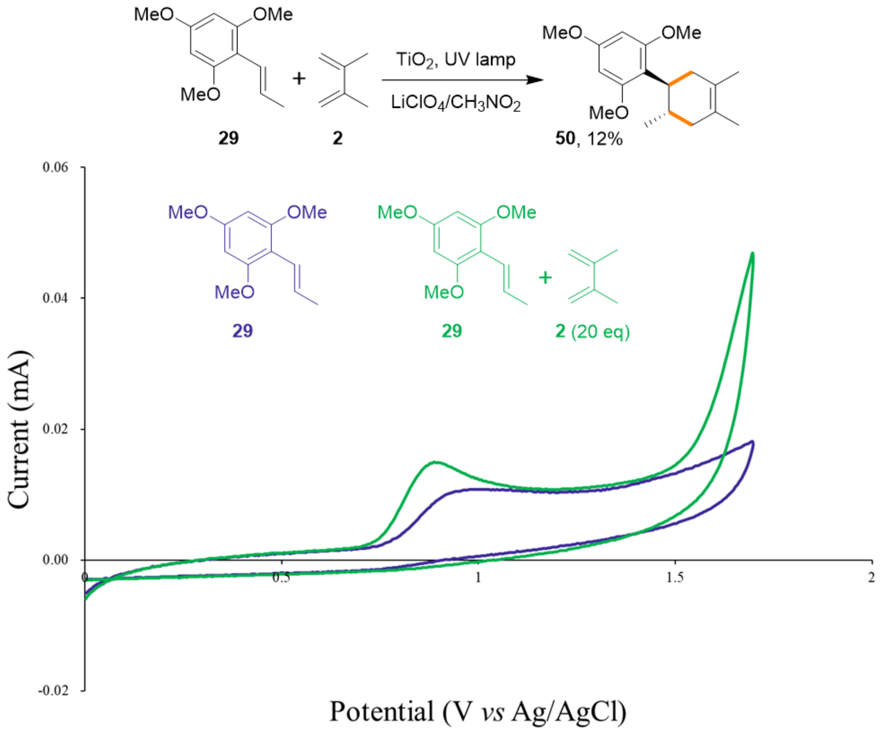


Figure 3-7. Radical Cation Diels-Alder Reaction and Cyclic Voltammograms of 2,4,6-Trimethoxy *trans*-β-Methylstyene (29).

3.2.3. Plausible Reaction Mechanism for the Radical Cation Diels-Alder Reaction Supported by CV Analyses and DFT Calculations of 2,4-Dimethyl *trans*-β-Methylstyrene

For 2,4-dimethyl *trans*-β-methylstyrene (**36**), which gave the cycloadducts **57** in good yield, and for which chain/EC-backward-E processes were clearly observed in the CV measurements, the spin density plots of the radical cation intermediates ($\mathbf{36}^{\bullet+}$ and $\mathbf{57}^{\bullet+}$) and the HOMO plots of compounds (**36** and **57**) were calculated by DFT (Figure 3-8). Surprisingly, the spin density of $\mathbf{57}^{\bullet+}$ and the HOMO of **57** were selectivity localized onto the double bond of cyclohexene. The yield of **57** by electrocatalysis was lower than by TiO_2 photocatalysis, and the amount of electricity required for the reaction was not catalytic (Scheme S1). It was suggested that $\mathbf{57}^{\bullet+}$ was less stable than $\mathbf{3}^{\bullet+}$, and chain process was little included in the reaction mechanism. The stability of (intermediate) $^{\bullet+}$ may have correlation with the cycloaddition. If so, it was possible to say that **40** was not found to be reacted with **2** because $\mathbf{60}^{\bullet+}$ was also less stable than $\mathbf{3}^{\bullet+}$.

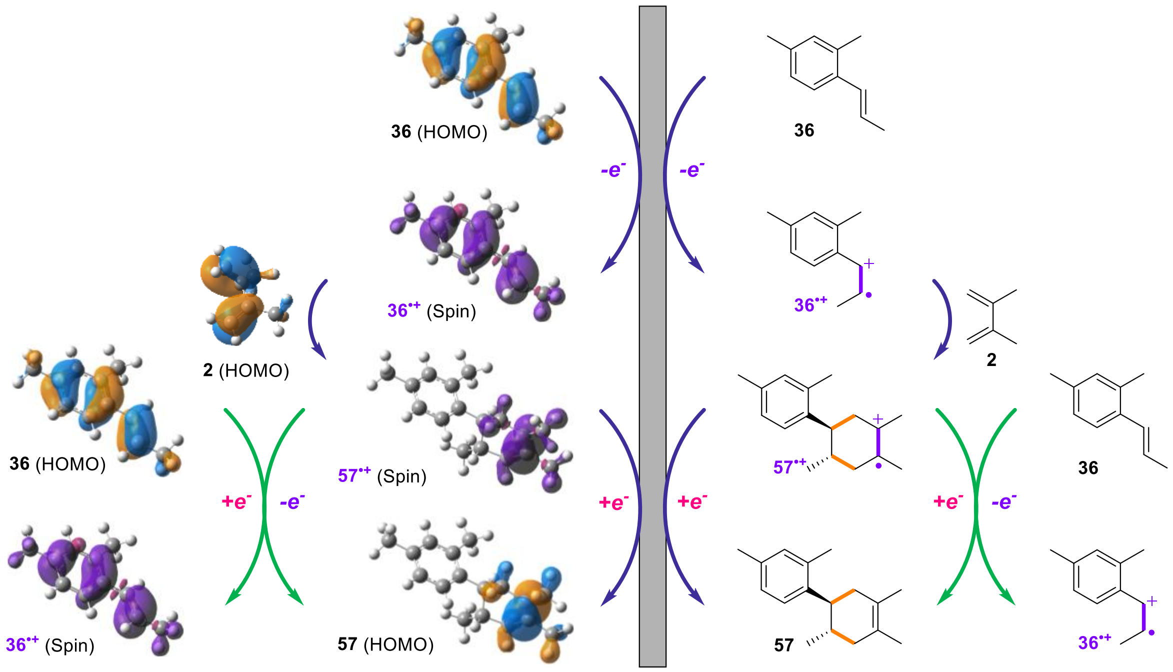


Figure 3-8. HOMO/Spin Density Plots for the Plausible Reaction Mechanism of 36 and 2.

3.3. Conclusion

Direct observation of EC-backward-E processes in the radical cation Diels-Alder reaction was demonstrated by the CV analysis. Plausible reaction mechanisms were supported by DFT calculations of substrates and radical cation intermediates. This mechanistic study will clarify the difference in reactivities between electrocatalysis and TiO_2 photocatalysis.

3.4. Experimental Section

3.4.1. General Procedure for Radical Cation Diels-Alder Reactions

trans-β-Methylstyrenes (0.20 mmol), 2,3-dimethyl-1,3-butadiene (**2**, 0.40 mmol), and TiO_2 (100 mg) were added to a solution of $LiClO_4$ (1.0 M) in CH_3NO_2 (4 ml) stirred at room temperature. The resultant reaction mixture was stirred at room temperature in front of a 15 W UV lamp (365 nm) for 2 h, diluted with water, and then extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. Yields reported here were determined by ^1H nuclear magnetic resonance spectroscopy (NMR) analysis. Silica gel column chromatography was conducted on a 0.40 mmol scale (2 batches of reactions) using hexane/ethyl acetate.

3.4.2. Cyclic Voltammetry Measurements

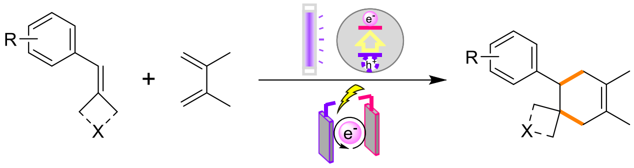
Cyclic voltammograms were recorded by three-electrode method using a glassy carbon working electrode, platinum counter electrode, and Ag/AgCl reference electrode at a scan rate of 50 mV s^{-1}. The concentration of *trans*-β-methylstyrenes was 2 mM in the presence of 2 eq. (4 mM) or 20 eq. (40 mM) of **2**.

3.4.3. Density Functional Theory (DFT) Calculations

Structural optimization of all stationary points and frequency analyses were conducted at the B3LYP level of DFT with the 6–311G++(2d,2p) basis set in nitromethane (polarizable continuum model (PCM)). No imaginary frequency was observed for any of the compounds.

Chapter 4. Radical Cation Diels-Alder Reactions of Arylidene Cycloalkane by Photo-/Electrocatalyst

Abstract



Radical cation Diels-Alder reaction of arylidene cycloalkanes by titanium dioxide photocatalysis and electrocatalysis is described, and a spiro ring system is lead to construct. Although the mechanism remains unclear, arylidene cyclobutane is found to be much more effective in the reaction than other cycloalkanes. The reaction is completed by a substoichiometric amount of electricity, which likely involves a radical cation chain pathway.

4.1. Introduction

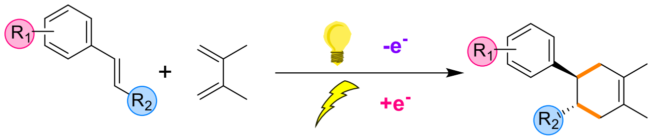
As described in chapter 2 and 3, radical cation Diels-Alder reaction of β-methylstyrenes by TiO_2 photocatalysis was demonstrated,[84] and the mechanism was proposed to undergo a chain and EC-backward-E process.[94] Based on the reaction scope and the plausible reaction mechanism, it was suggested that TiO_2 photoredox has some advantages in the radical cation Diels-Alder reaction on TiO_2 photocatalyst and electrode, which are categorized within the interfacial electron transfer catalysts, with $LiClO_4/CH_3NO_2$ system. [4+2] cycloadducts of *trans*-β-methylstyrene was only obtained in good yield by TiO_2 photocatalysis, and this is unlikely to be due to the properties of the TiO_2 material itself because other similar styrenes were found to be reacted with diene using carbon felt electrodes in electrocatalysis.

The spiro rings are one of the most important substructural formulas in organic chemistry, and syntheses of them have been developed. In radical cation Diels-Alder reaction, if cycloalkanes or heterocycles are introduced at the β-position of styrene, spiro rings are obtained by simple step synthesis. However, researchers focused on the scope of the aromatic ring or the β-mono-substituted styrene (Scheme 4-1 (a)). In only one reported, an additional methyl group at the styrene β-position of *trans*-anethole could not be reacted with diene using Ru photocatalysis. A second substituent at the β-position of styrene has a significant impact on the radical cation Diels-Alder reaction, suggesting that the arylidene cycloalkane is also difficult to form cycloadduct with diene.

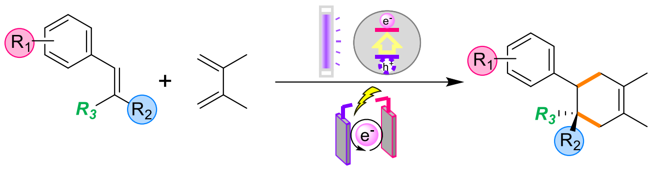
Described herein is radical cation Diels-Alder reaction of arylidene cycloalkane by photo-/electrocatalysis (Scheme 4-1 (b)). The environmentally friendly spiro ring systems were constructed.

Scheme 4-1. Concept of Radical Cation Diels-Alder Reactions of Arylidene Cycloalkane.

(a) β-Methylstyrenes D-A Reaction



(b) Arylidene Cycloalkanes D-A Reaction (This Work)

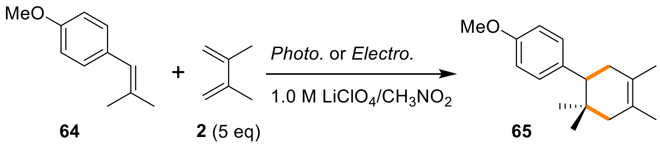


4.2. Results and Discussion

4.2.1. Radical Cation Diels-Alder Reaction of 4-Methoxy β-Dimethylstyrene

The present work began with the reaction of 4-methoxy β-dimethylstyrene (**64**) and 2,3-dimethyl-1,3-butadiene (**2**) under TiO_2 photocatalytic and electrocatalytic conditions which are previously reported as the best for radical cation Diels-Alder reaction (Table 4-1). Surprisingly, the electrocatalytic approach showed higher matching than TiO_2 photocatalytic that; however, the yields of cycloaddition were significantly lower than using *trans*-anethole under both conditions, suggesting that the additional methyl group at the β-position has significant impact on the reaction.

Table 4-1. Radical Cation Diels-Alder Reaction of 4-Methoxy β-Dimethylstyrene.[a]



64 **2** (5 eq) **65**

A: 20 h, 9% (trace)
B: 1.0 F, 43% (0%)

[a] Yields were determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. Recovered starting material is reported in parentheses. **A**: TiO_2, 15 W UV lamp (365 nm). **B**: Carbon felt electrodes, 1.3 V vs. Ag/AgCl.

Generally, tertiary radicals (or cations) are said to be more stable and less reactive than secondary ones, and furthermore, the additional methyl group at the β-position is expected to cause steric hindrance (Figure 4-1). Thus, connecting the two methyl groups to form a cycloalkane ring would reduce hindrance and lead to improve reactivity. From the above, arylidene cycloalkanes (**66**-**69**) were prepared, and the radical cation Diels-Alder reaction was examined using them (Table 4-2). Contrary to expectations, the ring formation was not successful in case of arylidene cyclopropane (**70**). The cyclopropane is the smallest ring and has large strain; therefore, **66**$^{\bullet+}$ has too much reactivity. It was suggested that starting materials were decomposed instead of reaction with diene. The arylidene cyclopentane was not found to react with diene. Since cyclohexane is generally more stable than cyclopentane, there seems to be a possibility that cyclopentane is converted into cyclohexene through **68**$^{\bullet+}$ in this condition. On the other hand, arylidene cyclobutane and cyclohexane was found to give the corresponding spiro rings (**71**, **73**) under both TiO_2 photocatalytic and electrocatalytic conditions. The spiro ring **71** was obtained in better yield than **73** likely because **67**$^{\bullet+}$ had the best balance between reactivity and stability. Although the mechanism remains unclear, a similar trend was observed in the recent report by Knowles and Romanov-Michailidis *et al.* on Ir photocatalytic [2+2] cycloaddition.[95] It cannot be directly connected because this is a [4+2] cycloaddition, and they proposed an energy transfer mechanism. However, it would be fair to say that there is some correlation between ring formation and cycloalkanes at the β-position.

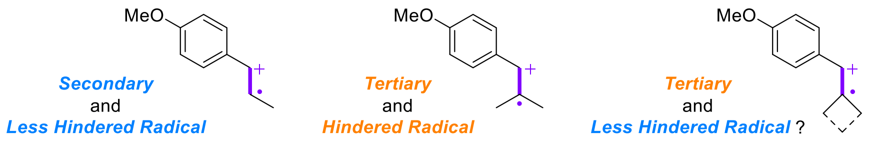
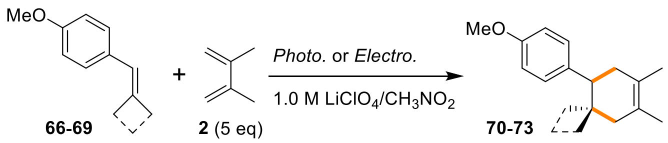
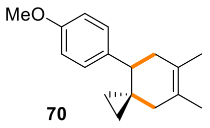
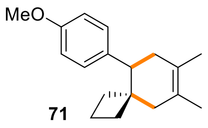
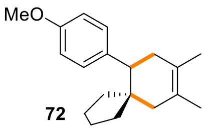
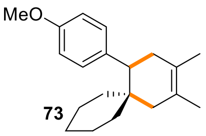


Figure 4-1. Steric Hindrance of Radical Cations.

Table 4-2. Radical Cation Diels-Alder Reactions of Arylidene Cycloalkanes.[a]



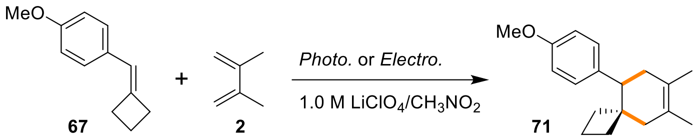
			
70	**71**	**72**	**73**
A: 6 h, 0% (0%)	**A**: 10 h, 61% (0%)	**A**: 20 h, 0% (trace)	**A**: 20 h, 31% (12%)
B: 0.5 F, 0% (0%)	**B**: 0.5 F, 66% (0%)	**B**: 0.5 F, 5% (16%)	**B**: 1.0 F, 56% (0%)

[a] Yields were determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. Recovered starting material is reported in parentheses. **A**: TiO_2, 15 W UV lamp (365 nm). **B**: Carbon felt electrodes, 1.3 V vs. Ag/AgCl.

4.2.2. Optimization of the Conditions for Radical Cation Diels-Alder Reaction

The optimization of the condition for radical cation Diels-Alder reaction using arylidene cyclobutane (**67**) (Table 4-3). For the photocatalytic approach, it was suggested that $LiClO_4$ and light were essential, and TiO_2 photocatalyst promoted the reaction (entries 1-4). The equivalent of diene (**2**) had effect on the reaction, and the yield was decreased under Ar and O_2 condition (entries 5-8). Usually, the reactive oxygen species are generated by UV irradiated TiO_2 photocatalyst using O_2, suggesting that they promote and/or inhibit the reaction. In the electrocatalytic approach, potentiostatic conditions gave better results than galvanostatic conditions (entries 9-11) likely because there was over oxidation of products under constant-current electrolysis. Furthermore, the reaction was completed at 0.5 F/mol (entry 10), suggesting that a chain process was included in the reaction mechanism.

Table 4-3. Optimization of the Conditions for Radical Cation Diels-Alder Reaction.



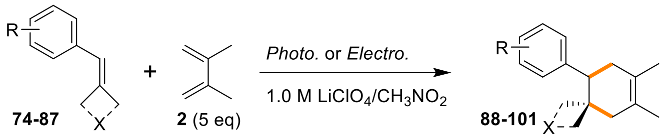
entry	condition[a]	yield (%)[b]
1		61 (0)
2	no $LiClO_4$	0 (40)
3	no light	0 (83)
4	no TiO_2	15 (32)
5	2 eq of diene	22 (0)
6	10 eq of diene	58 (0)
7	under O_2	19 (16)
8	under Ar	21 (0)
9	1.3 V vs. Ag/AgCl, 0.1 F/mol	22 (52)[c]
10	1.3 V vs. Ag/AgCl, 0.5 F/mol	66 (0)[c]
11	1.0 mA, 0.5 F/mol	46 (trace)[c]

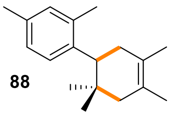
[a] Unless otherwise stated, reactions were carried out on a 0.20 mmol scale of arylidene cycloalkane (**67**) with 5 equiv of 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt under air for 10 h. [b] Determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. Recovered starting material is reported in parentheses. [c] In electrocatalysis, carbon felt electrodes were used for the reactions.

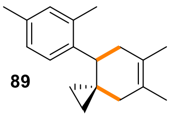
4.2.3. Scope of the Arylidene Cycloalkane for the Radical Cation Diels-Alder Reaction

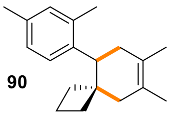
Radical cation Diels-Alder reaction was studied using arylidene cycloalkanes by photo-/electrocatalyst (Table 4-4). 2,4-Dimethyl and non-substituted arylidenes (**74-83**) were used and compared about spiro ring yields which were obtained under the best condition. As a result, TiO_2 photocatalysis gave the corresponding cycloadditions better than the electrocatalysis in most cases. Furthermore, β-cyclobutylstyrenes were found to be formed with **2** in good yields (**90**, **95**). These radical cation intermediates were not suitable and needed to accept reductive-single electron transfer (SET) quickly from electron transfer catalyst; then, TiO_2 photocatalysis have advantages for the reactions of them. In addition, 4-methoxy arylidene hetero-cycles (**84-87**) were also examined, and arylidenes, which are substituted oxetane and *boc*-azetidine at the β-position, gave good yields with diene (**98**, **100**). About 4-methoxy arylidenes, the electrocatalytic approach showed higher matching than TiO_2 photocatalytic that in most cases. It was suggested that radical cations of 4-methoxy arylidenes were reduced to starting materials by back-electron-transfer (BET) of TiO_2 photocatalysis because they were too stable and react with diene slowly. In electrocatalysis, reductive-SET was occurred after bond formation; thus, cycloadducts were obtained in good yields.

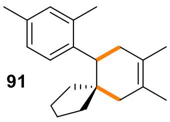
Table 4-4. Scope of the Arylidene Cycloalkanes for the Radical Cation Diels-Alder Reactions.

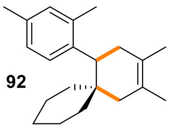


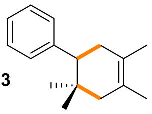
88

A: 12 h, 16% (51%)
B: 0.5 F, 10% (44%)

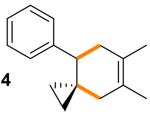
89

A: 6 h, 0% (0%)
B: 0.5 F, 0% (0%)

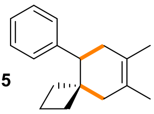
90

A: 6 h, 63% (0%)
B: 0.5 F, 37% (19%)

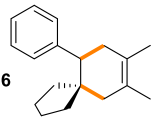
91

A: 4 h, 10% (27%)
B: 0.5 F, 17% (21%)

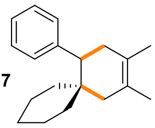
92

A: 36 h, 15% (36%)
B: 1.0 F, 13% (22%)

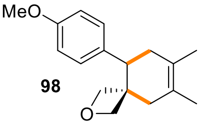
93

A: 20 h, 31% (14%)
B: 0.5 F, 8% (23%)

94

A: 6 h, 0% (0%)
B: 0.5 F, 0% (0%)

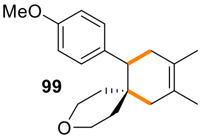
95

A: 6 h, 55% (0%)
B: 1.0 F, 7% (5%)

96

A: 4 h, 46% (7%)
B: 0.5 F, trace (22%)

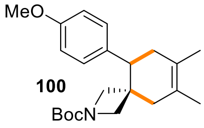
97

A: 20 h, 26% (4%)
B: 0.5 F, trace (53%)

98


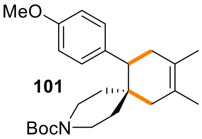
A: 6 h, 51% (0%)
B: 1.0 F, 72% (10%)^b

99


A: 6 h, trace (55%)
B: 1.5 F, 48% (0%)^b

100


A: 6 h, 54% (trace)
B: 0.5 F, 52% (10%)^b

101


A: 20 h, trace (42%)
B: 1.5 F, 18% (7%)^b

^{a}Yields were determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. Recovered starting material is reported in parentheses. **A**: TiO_2, 15 W UV lamp (365 nm). **B**: Carbon felt electrodes, 1.5 V vs. Ag/AgCl. ^{b}1.3 V vs. Ag/AgCl.

4.3. Conclusion

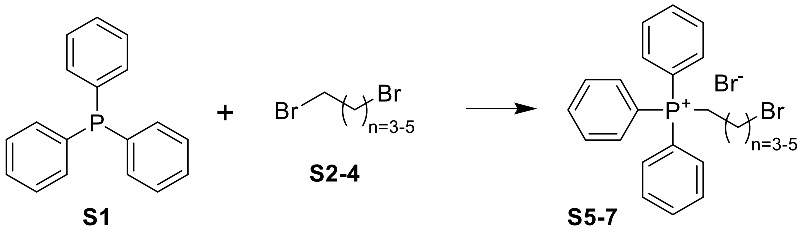
Radical cation Diels-Alder reactions of arylidene cycloalkanes have been developed using TiO_2 photocatalysis and electrocatalysis, including spiro ring systems. The addition of a methyl group at the β-position of styrenes has a significant effect on the reaction, suggesting that the reactivity depends on the ring size. Although the mechanism remains unclear, there are some correlations between cycloalkanes and cycloadditions. The results of this study will help to resolve the difference between TiO_2 photocatalysis and electrocatalysis.

4.4. Experimental Section

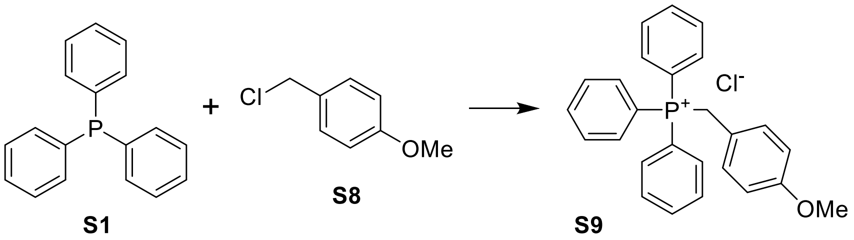
4.4.1. General Remarks

All reagents and solvents were purchased from commercial sources and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates, with detection by UV absorption (254 nm) and by heating the plates after dipping them in a solution of 12 M molybdo(VI) phosphoric acid n-hydrate in 95% ethanol. Silica gel (particle size 40–50 μm, normal or reverse-phase) was used for column chromatography. ^1H NMR spectra were collected on a 500 or 300 MHz NMR spectrometer using the deuterated solvent as an internal deuterium reference. Chemical shift data are given in δ units calibrated with residual protic solvent. The multiplicity of a signal is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. ^{13}C NMR spectra were collected at 125 MHz with proton decoupling using the deuterated solvent as an internal carbon reference. Chemical shift data are given in δ units calibrated with residual solvent. High-resolution mass spectra (HRMS) were collected on electrospray ionization (ESI)- or direct analysis in real time (DART)-time-of-flight (TOF) spectrometers.

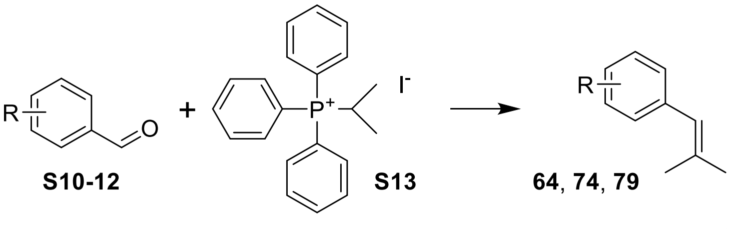
4.4.2. Synthesis and Characterization Data



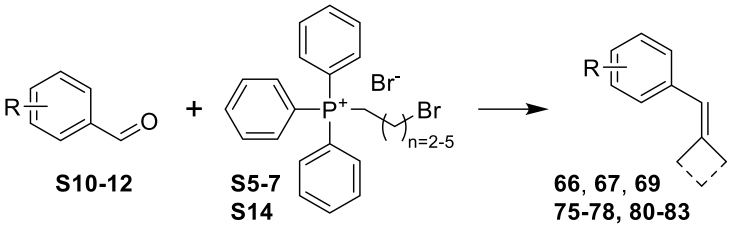
General Procedure for the Synthesis of Wittig Reagents (**S5-7**).[96] The mixture of Triphenylphosphine (**S1**, 1.3 g, 5 mmol) and respective Dibromo alkane (**S2-4**, 25 mmol) was stirred at 90 °C for 5.5 h. After that, the resulting reaction mixture was cooled at r. t., washed with Toluene, and dried *in vacuo*. The mixture was sonicated with Diethyl ether for 1 h and filtration gave the titled compound quantitatively as a white solid.



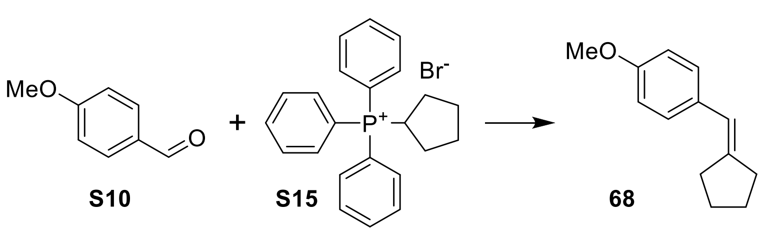
Synthesis of p-Methoxybenzyl Triphenyl Phosphonium Chloride (**S9**). To a solution of the Triphenylphosphine (**S1**, 5.2 g, 20.0 mmol) in Toluene (50 mL) stirred at r. t. was added *p*-Methoxybenzyl chloride (**S8**, 1.7 g, 20.0 mmol). The resulting reaction mixture was stirred at 110 °C for 12 h and washed with Toluene, filtration gave the titled compound in 66% yield (5.5 g, 13.2 mmol) as a white solid.



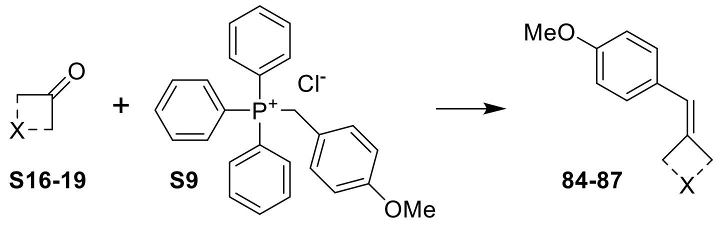
General Procedure for the Synthesis of β-Dimethyl Arylidenes (**64, 74, 79**).[97] To a solution of the Wittig reagent (**S13**, 4.3 g, 10.0 mmol) in THF (50 mL) stirred at r. t. was added $\mathrm{KO}^t\mathrm{Bu}$ (1.1 g, 10.0 mmol). The resulting reaction mixture was stirred at r. t. for 30 min, respective aldehyde (**S10-12**, 5.0 mmol) was added, and the reaction mixture was stirred at r. t. for 12 h. Hydrogen peroxide (2 mL) was added, diluted with water, and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane only) gave the titled compound.



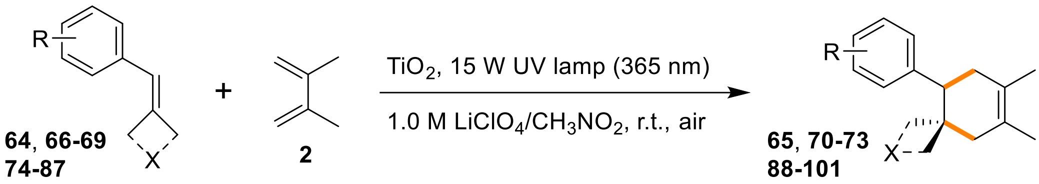
General Procedure for the Synthesis of β-Cycloalkyl Arylidenes (**66**, **67**, **69**, **74-83**).[98] To a solution of the Wittig reagent (**S5-7**, **S14**, 7.5 mmol) in THF (50 mL) stirred at r. t. was added KO^{t}Bu (1.7 g, 15.0 mmol). The resulting reaction mixture was stirred at 70 °C for 1 h, respective aldehyde (**S10-12**, 5.0 mmol) was added, and the reaction mixture was stirred at 70 °C for 3 h. After the reaction mixture was cooled to r. t. and stirred for 1 h, Hydrogen peroxide (2 mL) was added, diluted with water, and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane only or hexane/ethyl acetate = 20/1) gave the titled compound.



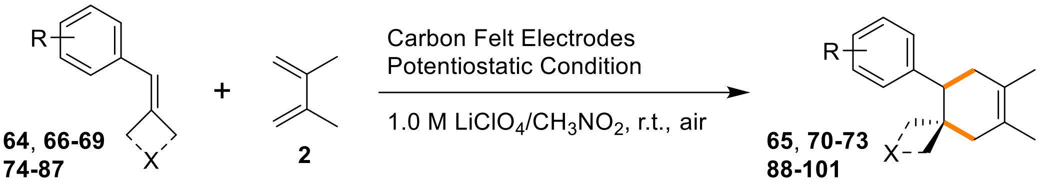
Synthesis of 4-Methoxy β-Cyclopentyl Arylidene (**68**).[99] To a solution of the Cyclopentyltriphenylphosphonium Bromide (**S15**, 5.0 mmol) in THF (25 mL) stirred at 0 °C was added *n*-butyl lithium (1.6 M in hexane, 6.3 mmol). The resulting reaction mixture was stirred at 0 °C for 1 h, *p*-Anisaldehyde (**S10**, 5.0 mmol) was added, and the reaction mixture was stirred at 0 °C for 16 h. *n*-Pentane was added to precipitate triphenylphosphine oxide, and the mixture was filtered and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave the titled compound.



General Procedure for the Synthesis of β-Heterocyclic Arylidenes (**84-87**).[95] To a solution of the Wittig reagent (**S9**, 2.1 g, 5.0 mmol) and KO^{t}Bu (561 mg, 5.0 mmol) in THF (50 mL) stirred at 0 °C was added respective cyclic ketone (**S16-19**, 6.0 mmol). The resulting reaction mixture was stirred at 0 °C for 2 h, Hydrogen peroxide (2 mL) was added, diluted with water, and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 10/1) gave the titled compound.

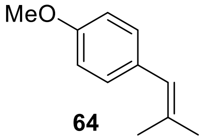


General Procedure for the TiO_2 Photocatalytic Reactions. To a solution of $LiClO_4$ (1.0 M, 426 mg) in CH_3NO_2 (4 mL) with TiO_2 (100 mg) stirred at r.t. were added the respective Arylidenes (0.20 mmol) and 2,3-Dimethyl-1,3-Butadiene (**2**, 113 µL, 1.0 mmol). The resulting reaction mixture was irradiated by a 15 W UV lamp (365 nm) at r. t. under air, diluted with water, and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. Yields reported in the manuscript were determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. Reverse phase silica gel column chromatography (acetonitrile only) and normal phase silica gel column chromatography (hexane only or hexane/ethyl acetate = 20/1) gave the target compounds.



General Procedure for the Electrolytic Reactions. To a solution of $LiClO_4$ (1.0 M, 426 mg) in CH_3NO_2 (4 mL) stirred at r. t. were added the respective Arylidenes (0.20 mmol) and 2,3-Dimethyl-1,3-Butadiene (**2**, 113 µL, 1.0 mmol). The resulting reaction mixture was electrolyzed with carbon felt electrodes (1 cm × 1 cm) at r.t. under air, diluted with water, and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. Yields reported in the manuscript were determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. Reverse phase silica gel column chromatography (acetonitrile only) and normal phase silica gel column chromatography (hexane only or hexane/ethyl acetate = 20/1) gave the target compounds.

*1-methoxy-4-(2-methylprop-1-en-1-yl)benzene (**64**).*[99] *Colorless oil.*

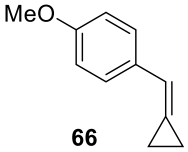


64

Product yield; 56% (458 mg, 2.8 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.16 (2H, d, J = 8.6 Hz), 6.86 (2H, d, J = 8.6 Hz), 6.21 (1H, s), 3.80 (3H, s), 1.88 (3H, s), 1.84 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.9, 134.0, 131.5, 130.0, 124.8, 113.7, 55.3, 27.0, 19.5; HRMS [M + H]$^+$ calculated for $C_{11}H_{15}O$ 163.1117, found 163.1132.

*1-(cyclopropylidenemethyl)-4-methoxybenzene (**66**). Yellow oil.*

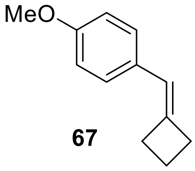


66

Product yield; 79% (633 mg, 3.9 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.47 (2H, d, J = 8.6 Hz), 6.87 (2H, d, J = 8.6 Hz), 6.69 (1H, m), 3.82 (3H, s), 1.38 (2H, dt, J = 7.5, 1.7 Hz), 1.15 (2H, dt, J = 7.5, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.8, 131.5, 127.9, 122.0, 117.8, 114.2, 55.5, 4.3, 0.8; HRMS [M + H]$^+$ calculated for $C_{11}H_{13}O$ 161.0961, found 161.0977.

*1-(cyclobutylidenemethyl)-4-methoxybenzene (**67**).*[95] *White solid.*

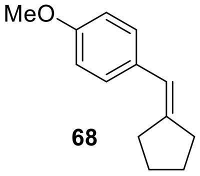


67

Product yield; 64% (560 mg, 3.2 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.14 (2H, d, J = 8.6 Hz), 6.84 (2H, d, J = 8.6 Hz), 6.02 (1H, quint, J = 2.3 Hz), 3.80 (3H, s), 3.01 (2H, t, J = 7.5 Hz), 2.86 (2H, t, J = 7.5 Hz), 2.10 (2H, quint, J = 8.0 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.9, 142.4, 131.2, 128.4, 120.4, 114.0, 55.5, 32.8, 32.7, 18.6; HRMS [M + H]$^+$ calculated for $C_{12}H_{15}O$ 175.1117, found 175.1140.

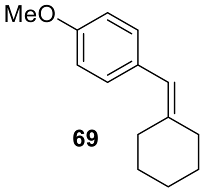
*1-(cyclopentylidenemethyl)-4-methoxybenzene (**68**).*[99] *Colorless oil.*


68

Product yield; 25% (181 mg, 1.0 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.24 (2H, d, *J* = 8.6 Hz), 6.86 (2H, d, *J* = 8.6 Hz), 6.30 (1H, s), 3.81 (3H, s), 2.52 (2H, t, *J* = 6.9 Hz), 2.46 (2H, t, *J* = 6.9 Hz), 1.77 (2H, quint, *J* = 6.9 Hz), 1.65 (2H, quint, *J* = 6.9 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.7, 144.9, 132.0, 129.2, 120.3, 113.8, 55.4, 36.1, 31.2, 27.5, 26.0; HRMS [M + H]$^+$ calculated for $C_{13}H_{17}O$ 189.1274, found 189.1298.

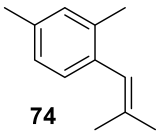
*1-(cyclohexylidenemethyl)-4-methoxybenzene (**69**).*[99] *Colorless oil.*


69

Product yield; 98% (989 mg, 4.9 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.13 (2H, d, *J* = 8.6 Hz), 6.85 (2H, d, *J* = 8.6 Hz), 6.16 (1H, s), 3.80 (3H, s), 2.36 (2H, t, *J* = 5.7 Hz), 2.24 (2H, t, *J* = 5.7 Hz), 1.61 (4H, m), 1.54 (2H, quint, *J* = 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 157.9, 142.4, 131.2, 130.2, 121.6, 113.7, 55.4, 37.8, 29.6, 28.9, 28.1, 27.0; HRMS [M + H]$^+$ calculated for $C_{14}H_{19}$ 203.1430, found 203.1444.

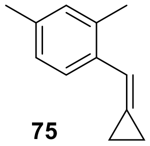
*2,4-dimethyl-1-(2-methylprop-1-en-1-yl)benzene (**74**). Colorless oil.*


74

Product yield; 55% (441 mg, 2.8 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.02 (1H, d, *J* = 7.5 Hz), 6.99 (1H, s), 6.96 (1H, d, *J* = 7.5 Hz), 6.18 (1H, s), 2.30 (3H, s), 2.20 (3H, s), 1.90 (3H, s), 1.70 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 136.4, 135.9, 135.2, 134.8, 130.7, 129.6, 126.2, 124.2, 26.4, 21.3, 20.1, 19.5; HRMS [M + H]$^+$ calculated for $C_{12}H_{17}$ 161.1325, found 161.1332.

*1-(cyclopropylidenemethyl)-2,4-dimethylbenzene (**75**). Yellow oil.*

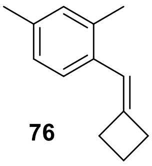


75

Product yield; 34% (266 mg, 1.7 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.64 (1H, d, J = 7.5 Hz), 6.98 (1H, d, J = 9.2 Hz), 6.97 (1H, s), 6.92 (1H, d, J = 1.7 Hz), 2.36 (3H, s), 2.30 (3H, s), 1.38 (2H, m), 1.16 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 136.5, 135.0, 134.0, 131.3, 126.9, 126.1, 124.1, 115.6, 21.3, 19.9, 4.3, 1.1; HRMS [M + H]$^+$ calculated for $C_{12}H_{15}$ 159.1168, found 159.1153.

*1-(cyclobutylidenemethyl)-2,4-dimethylbenzene (**76**). Colorless oil.*

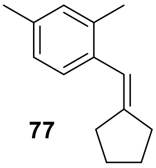


76

Product yield; 61% (609 mg, 3.5 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.11 (1H, d, J= 8.0 Hz), 6.96 (1H, s), 6.95 (1H, d, J= 8.0 Hz), 6.19 (1H, s), 2.95 (2H, t, J= 7.5 Hz), 2.87 (2H, t, J= 7.5 Hz), 2.29 (3H, s), 2.27 (3H, s), 2.07 (2H, quint, J= 7.5 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 136.5, 135.0, 134.0, 131.3, 126.9, 126.1, 124.0, 115.6, 21.3, 19.9, 4.3, 1.1; HRMS [M + H]$^+$ calculated for $C_{13}H_{17}$ 173.1325, found 173.1347.

*1-(cyclopentylidenemethyl)-2,4-dimethylbenzene (**77**). Colorless oil.*

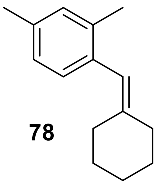


77

Product yield; 11% (107 mg, 0.57 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.19 (1H, d, J= 7.5 Hz), 6.97 (1H, s), 6.96 (1H, d, J= 7.5 Hz), 6.36 (1H, s), 2.47 (2H, t, J= 6.9 Hz), 2.40 (2H, t, J= 6.9 Hz), 2.30 (3H, s), 2.25 (3H, s), 1.69 (4H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 146.4, 135.9, 135.7, 135.2, 130.9, 128.2, 126.3, 118.8, 35.2, 31.0, 27.1, 25.9, 21.3, 20.2; HRMS [M + H]$^+$ calculated for $C_{14}H_{19}$ 187.1481, found 187.1489.

*1-(cyclohexylidenemethyl)-2,4-dimethylbenzene (**78**). Colorless oil.*

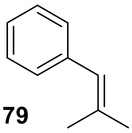


78

Product yield; 20% (200 mg, 1 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.99 (2H, d, *J* = 3.4 Hz), 6.94 (1H, d, *J* = 8.0 Hz), 6.11 (1H, s), 2.30 (3H, s), 2.26 (2H, t, *J* = 5.7 Hz), 2.20 (3H, s), 2.17 (2H, t, *J* = 5.7 Hz), 1.64 (2H, m), 1.58 (2H, m), 1.50 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 142.9, 136.6, 136.0, 134.9, 130.7, 129.7, 126.1, 121.0, 37.6, 29.9, 29.1, 28.3, 27.1, 21.3, 20.2; HRMS [M + H]$^+$ calculated for $C_{15}H_{21}$ 201.1638, found 201.1646.

*(2-methylprop-1-en-1-yl)benzene (**79**).*[100] *Colorless oil.*

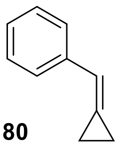


79

Product yield; 97% (638 mg, 4.8 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.31 (2H, t, *J* = 8.0 Hz), 7.22 (2H, d, *J* = 6.9 Hz), 7.18 (1H, t, *J* = 7.5 Hz), 6.27 (1H, s), 1.91 (3H, s), 1.86 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 138.9, 135.7, 129.0, 128.3, 126.0, 125.4, 27.1, 19.7; HRMS [M + H]$^+$ calculated for $C_{10}H_{13}$ 133.1012, found 133.1036.

*(cyclopropylidenemethyl)benzene (**80**). Yellow oil.*

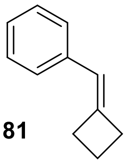


80

Product yield; 42% (273 mg, 2.1 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.54 (2H, d, *J* = 7.5 Hz), 7.33 (2H, t, *J* = 7.5 Hz), 7.21 (1H, t, *J* = 7.5 Hz), 6.76 (1H, t, *J* = 1.7 Hz), 1.43 (2H, dt, *J* = 8.0, 2.3 Hz), 1.18 (2H, dt, *J* = 8.0, 1.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 138.5, 128.7, 126.9, 126.9, 124.5, 118.5, 4.5, 0.8; HRMS [M + H]$^+$ calculated for $C_{10}H_{11}$ 131.0855, found 131.0864.

*(cyclobutylidenemethyl)benzene (**81**).*[101] *Colorless oil.*

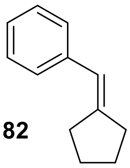


81

Product yield; 75% (539 mg, 3.7 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.29 (2H, t, *J* = 7.5 Hz), 7.20 (2H, d, *J* = 7.5 Hz), 7.14 (1H, t, *J* = 7.5 Hz),6.07 (1H, t, *J* = 2.3 Hz), 3.05 (2H, t, *J* = 8.0 Hz), 2.88 (2H, t, *J* = 8.0 Hz), 2.11 (2H, quint, *J* = 8.0 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 145.0, 138.3, 128.6, 127.3, 126.0, 121.1, 33.0, 32.9, 18.6; HRMS [M + H]$^+$ calculated for $C_{11}H_{13}$ 145.1012, found 145.1013.

*(cyclopentylidenemethyl)benzene (**82**).*[101] *Colorless oil.*

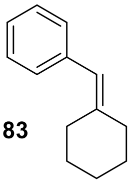


82

Product yield; 9% (74 mg, 0.47 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.31 (2H, d, *J* = 4.0 Hz), 7.30 (2H, s), 7.15 (1H, m), 6.36 (1H, t, *J* = 2.3 Hz), 2.55 (2H, t, *J* = 6.9 Hz), 2.49 (2H, t, *J* = 6.9 Hz), 1.78 (2H, quint, *J* = 6.9 Hz), 1.66 (2H, quint, *J* = 6.9 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 147.4, 139.1, 128.4, 128.2, 125.9, 121.1, 36.2, 31.4, 27.5, 25.9; HRMS [M + H]$^+$ calculated for $C_{12}H_{15}$ 159.1168, found 159.1138.

*(cyclohexylidenemethyl)benzene (**83**).*[101] *Colorless oil.*

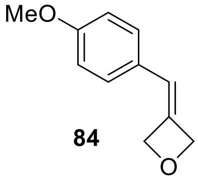


83

Product yield; 36% (312 mg, 1.8 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.30 (2H, t, *J* = 7.5 Hz), 7.20 (2H, d, *J* = 7.5 Hz), 7.18 (1H, t, *J* = 7.5 Hz), 6.23 (1H, s), 2.37 (2H, t, *J* = 5.7 Hz), 2.26 (2H, t, *J* = 5.7 Hz), 1.63 (4H, m), 1.55 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 143.7, 138.7, 129.2, 128.3, 126.0, 122.2, 37.9, 29.7, 28.9, 28.1, 27.0; HRMS [M + H]$^+$ calculated for $C_{13}H_{17}$ 173.1325, found 173.1334.

*3-(4-methoxybenzylidene)oxetane (**84**).*[95] *Yellow solid.*

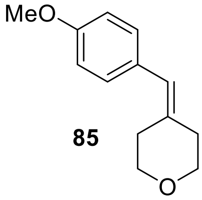


84

Product yield; 25% (225 mg, 1.3 mmol).

^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.94 (2H, d, J = 8.9 Hz), 6.87 (2H, d, J = 8.9 Hz), 6.04 (1H, t, J = 2.4 Hz), 5.55 (2H, q, J = 2.8 Hz), 5.38 (2H, q, J = 2.8 Hz), 3.81 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.7, 134.5, 129.1, 128.5, 119.2, 114.4, 80.6, 80.4, 55.5; HRMS [M + H]$^+$ calculated for $C_{11}H_{13}O_2$ 177.0910, found 177.0920.

*4-(4-methoxybenzylidene)tetrahydro-2H-pyran (**85**).*[99] *Yellow solid.*

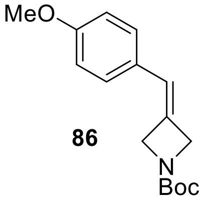


85

Product yield; 18% (184 mg, 0.90 mmol).

^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.14 (2H, d, J = 8.6 Hz), 6.86 (2H, d, J = 8.6 Hz), 6.27 (1H, s), 3.81 (3H, s), 3.78 (2H, t, J = 5.9 Hz), 3.66 (2H, t, J = 5.9 Hz), 2.53 (2H, dt, J = 5.9, 1.4 Hz), 2.38 (2H, dt, J = 5.9, 1.4 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.2, 136.5, 130.2, 130.1, 123.5, 113.8, 69.7, 68.7, 55.4, 37.4, 30.8; HRMS [M + H]$^+$ calculated for $C_{13}H_{17}O_2$ 205.1223, found 205.1230.

*tert-butyl 3-(4-methoxybenzylidene)azetidine-1-carboxylate (**86**).*[95] *Yellow solid.*

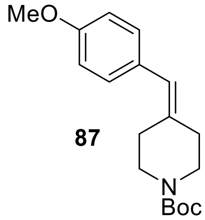


86

Product yield; 43% (597 mg, 2.2 mmol).

^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.05 (2H, d, J = 8.9 Hz), 6.88 (2H, d, J = 8.9 Hz), 6.20 (1H, t, J = 2.1 Hz), 4.81 (2H, q, J = 2.8 Hz), 4.62 (2H, q, J = 2.8 Hz), 3.81 (3H, s), 1.48 (9H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.8, 156.6, 129.2, 128.6, 128.1, 121.9, 114.4, 80.0, 55.5, 28.7; HRMS [M + H]$^+$ calculated for $C_{16}H_{22}NO_3$ 276.1594, found 276.1611.

*tert-butyl 4-(4-methoxybenzylidene)piperidine-1-carboxylate (**87**).*[102] *White solid.*

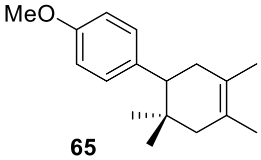


87

Product yield; 26% (402 mg, 1.3 mmol).

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.12 (2H, d, J = 8.6 Hz), 6.86 (2H, d, J = 8.6 Hz), 6.30 (1H, s), 3.80 (3H, s), 3.50 (2H, t, J = 5.2 Hz), 3.40 (2H, t, J = 5.2 Hz), 2.45 (2H, t, J = 5.2 Hz), 2.31 (2H, t, J = 5.2 Hz), 1.48 (9H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.3, 155.1, 137.3, 130.3, 124.2, 113.9, 79.8, 55.5, 36.4, 29.4, 28.7; HRMS [M + H]$^+$ calculated for $C_{18}H_{26}NO_3$ 304.1907, found 304.1887.

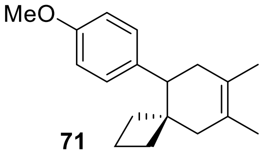
*4'-methoxy-2,2,4,5-tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (**65**). Colorless oil.*



65

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.11 (2H, d, J = 8.6 Hz), 6.81 (2H, d, J = 8.6 Hz), 3.79 (3H, s), 2.58 (1H, dd, J = 9.7, 5.7 Hz), 2.31 (1H, dd, J = 17.2, 10.3 Hz), 2.12 (1H, dd, J = 17.2, 3.4 Hz), 1.94 (1H, d, J = 17.2 Hz), 1.72 (1H, d, J = 17.8 Hz), 1.65 (3H, s), 1.64 (3H, s), 0.78 (3H, s), 0.77 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.1, 136.2, 130.1, 124.8, 124.6, 113.3, 55.5, 49.5, 47.6, 36.6, 33.4, 29.8, 22.6, 19.4, 18.9; HRMS [M + H]$^+$ calculated for $C_{17}H_{25}O$ 245.1900, found 245.1928.

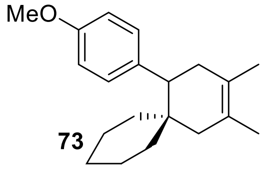
*9-(4-methoxyphenyl)-6,7-dimethylspiro[3.5]non-6-ene (**71**). Yellow oil.*



71

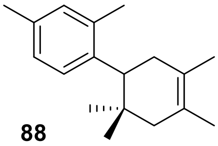
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.11 (2H, d, J = 8.6 Hz), 6.81 (2H, d, J = 8.6 Hz), 3.79 (3H, s), 2.78 (1H, t, J = 5.7 Hz), 2.33 (1H, dd, J = 18.3, 2.9 Hz), 2.12 (1H, dd, J = 17.8, 2.3 Hz), 2.01 (3H, m), 1.81 (2H, m), 1.66 (6H, m), 1.62 (2H, m), 1.41 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.1, 136.4, 129.5, 125.2, 124.7, 113.4, 55.4, 47.7, 42.8, 42.2, 35.0, 32.8, 29.8, 19.6, 19.0, 15.3; HRMS [M + H]$^+$ calculated for $C_{18}H_{25}O$ 257.1900, found 257.1899.

*5-(4-methoxyphenyl)-2,3-dimethylspiro[5.5]undec-2-ene (**73**). Colorless oil.*


73

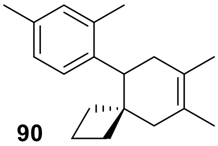
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.09 (2H, d, J = 8.0 Hz), 6.79 (2H, d, J = 8.0 Hz), 3.79 (3H, s), 2.63 (1H, t, J = 5.7 Hz), 2.27 (1H, dd, J = 17.8, 3.4 Hz), 2.15 (1H, dd, J = 17.2, 4.6 Hz), 1.98 (1H, d, J = 17.8 Hz), 1.78 (1H, d, J = 17.2 Hz), 1.68 (3H, s), 1.65 (3H, s), 1.46 (5H, m), 1.31 (1H, m), 1.13 (4H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.0, 136.7, 130.2, 130.1, 124.6, 113.2, 55.4, 39.4, 36.9, 36.0, 35.5, 32.4, 30.0, 26.8, 22.2, 22.1, 19.8, 18.9; HRMS [M + H]$^+$ calculated for $C_{20}H_{29}O$ 285.2213, found 285.2220.

*2,2,2',4,4',5-hexamethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (**88**). Colorless oil.*


88

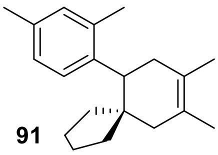
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.16 (1H, d, J = 8.6 Hz), 6.96 (1H, s), 6.95 (1H, d, J = 6.9 Hz), 3.01 (1H, dd, J = 9.7, 5.7 Hz), 2.31 (3H, s), 2.28 (3H, s), 2.26 (1H, m), 2.05 (1H, dd, J = 19.5, 4.6 Hz), 2.01 (1H, d, J = 17.2 Hz), 1.77 (1H, d, J = 16.6 Hz), 1.65 (3H, s), 1.64 (3H, s), 0.86 (3H, s), 0.80 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 139.9, 136.9, 135.2, 131.2, 127.5, 126.5, 125.1, 124.8, 48.5, 43.1, 37.5, 34.3, 28.9, 22.6, 21.2, 21.2, 19.5, 18.9; HRMS [M + H]$^+$ calculated for $C_{18}H_{27}$ 243.2107, found 243.2104.

*9-(2,4-dimethylphenyl)-6,7-dimethylspiro[3.5]non-6-ene (**90**). Colorless oil.*


90

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.17 (1H, d, J = 7.5 Hz), 7.00 (1H, d, J = 8.6 Hz), 6.99 (1H, s), 3.07 (1H, dd, J = 9.7, 5.2 Hz), 2.32 (2H, m), 2.30 (3H, s), 2.23 (3H, m), 2.21 (1H, m), 1.95 (2H, m), 1.80 (1H, m), 1.68 (3H, s), 1.64 (3H, s), 1.62 (1H, m), 1.53 (1H, m), 1.46 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 139.2, 137.3, 135.3, 131.2, 127.0, 126.8, 126.3, 124.5, 46.1, 42.9, 41.8, 35.2, 31.2, 26.9, 21.2, 20.9, 19.4, 19.1, 15.9; HRMS [M + H]$^+$ calculated for $C_{19}H_{27}$ 255.2107, found 255.2114.

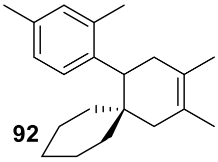
*10-(2,4-dimethylphenyl)-7,8-dimethylspiro[4.5]dec-7-ene (**91**). Colorless oil.*



91

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.17 (1H, d, J = 8.0 Hz), 6.96 (1H, s), 6.95 (1H, d, J = 8.0 Hz), 3.10 (1H, dd, J = 8.6, 4.3 Hz), 2.29 (3H, s), 2.28 (3H, s), 2.27 (1H, m), 2.12 (1H, dd, J = 17.2, 4.0 Hz), 1.97 (1H, d, J = 16.0 Hz), 1.89 (1H, d, J = 17.8 Hz), 1.65 (6H, s), 1.55 (3H, m), 1.40 (3H, m), 1.24 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 140.1, 137.1, 135.2, 131.1, 127.3, 126.7, 126.1, 125.0, 46.4, 45.0, 41.8, 37.9, 37.7, 31.9, 24.5, 23.9, 21.1, 19.6, 19.0; HRMS [M + H]$^+$ calculated for $C_{20}H_{29}$ 269.2264, found 269.2247.

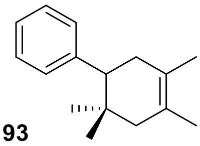
*5-(2,4-dimethylphenyl)-2,3-dimethylspiro[5.5]undec-2-ene (**92**). Colorless oil.*



92

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.15 (1H, d, J = 8.6 Hz), 6.96 (1H, s), 6.95 (1H, d, J = 6.9 Hz), 2.99 (1H, dd, J = 8.6, 6.3 Hz), 2.31 (3H, s), 2.28 (3H, s), 2.22 (1H, m), 2.20 (1H, d, J = 16.6 Hz), 2.08 (1H, dd, J = 17.8, 4.6 Hz), 1.90 (1H, d, J = 17.8 Hz), 1.69 (3H, s), 1.63 (3H, s), 1.55 (1H, m), 1.45 (2H, m), 1.40 (3H, m), 1.31 (1H, tt, J = 13.2, 3.4 Hz), 1.26 (1H, m), 0.98 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 139.8, 137.2, 135.1, 131.1, 128.0, 126.5, 125.3, 124.4, 44.6, 39.6, 36.8, 36.6, 30.0, 29.4, 26.6, 22.1, 22.1, 21.5, 21.2, 19.7, 18.9; HRMS [M + H]$^+$ calculated for $C_{21}H_{31}$ 283.2420, found 283.2420.

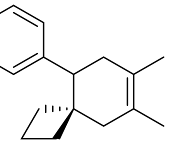
*2,2,4,5-tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (**93**). Colorless oil.*



93

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.25 (2H, d, J = 7.5 Hz), 7.19 (3H, m), 2.63 (1H, dd, J = 9.7, 5.7 Hz), 2.36 (1H, m), 2.14 (1H, dd, J = 16.6, 4.0 Hz), 1.96 (1H, d, J = 17.2 Hz), 1.74 (1H, d, J = 16.6 Hz), 1.66 (3H, s), 1.65 (3H, s), 0.80 (3H, s), 0.79 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 144.2, 129.3, 127.9, 126.3, 124.8, 124.6, 50.4, 47.6, 36.4, 33.3, 29.8, 22.6, 19.4, 18.9; HRMS [M + H]$^+$ calculated for $C_{16}H_{23}$ 215.1794, found 215.1783.

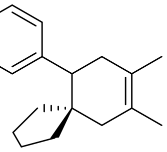
*6,7-dimethyl-9-phenylspiro[3.5]non-6-ene (**95**). Colorless oil.*



95

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.26 (2H, m), 7.19 (3H, m), 2.84 (1H, t, J = 5.7 Hz), 2.35 (1H, d, J = 16.6 Hz), 2.16 (1H, d, J = 15.5 Hz), 2.04 (3H, m), 1.83 (2H, m), 1.67 (3H, s), 1.66 (1H, m), 1.66 (3H, s), 1.62 (1H, m), 1.41 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 144.3, 128.7, 128.1, 126.2, 125.2, 124.8, 48.5, 42.7, 42.1, 34.8, 33.0, 29.9, 19.6, 19.0, 15.3; HRMS [M + H]$^+$ calculated for C$_{17}$H$_{23}$ 227.1794, found 227.1780.

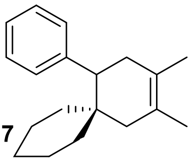
*7,8-dimethyl-10-phenylspiro[4.5]dec-7-ene (**96**). Colorless oil.*



96

^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.30 (2H, t, J = 6.3 Hz), 7.19 (1H, s), 7.18 (2H, d, J = 7.5 Hz), 2.70 (1H, t, J = 5.7 Hz), 2.35 (1H, m), 2.22 (1H, m), 1.81 (2H, q, J = 16.6 Hz), 1.68 (3H, s), 1.66 (3H, s), 1.53 (4H, m), 1.41 (3H, m), 1.07 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 145.4, 129.0, 128.0, 126.1, 125.3, 125.2, 48.8, 45.7, 42.6, 38.3, 37.0, 35.1, 24.4, 24.1, 19.7, 19.0; HRMS [M + H]$^+$ calculated for C$_{18}$H$_{25}$ 241.1951, found 241.1964.

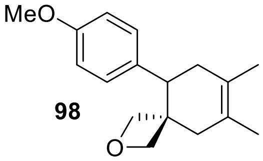
*2,3-dimethyl-5-phenylspiro[5.5]undec-2-ene (**97**). Colorless oil.*



97

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.24 (2H, m), 7.18 (3H, m), 2.68 (1H, t, J = 5.7 Hz), 2.30 (1H, dd, J = 17.8, 4.0 Hz), 2.20 (1H, dd, J = 17.8, 5.2 Hz), 2.00 (1H, d, J = 17.2 Hz), 1.80 (1H, d, J = 17.8 Hz), 1.69 (3H, s), 1.66 (3H, s), 1.46 (5H, m), 1.33 (1H, m), 1.13 (4H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 144.7, 129.4, 127.9, 126.2, 124.6, 124.6, 49.9, 39.3, 37.0, 35.8, 35.5, 32.5, 26.8, 22.2, 22.1, 19.8, 18.9; HRMS [M + H]$^+$ calculated for C$_{19}$H$_{27}$ 255.2107, found 255.2116.

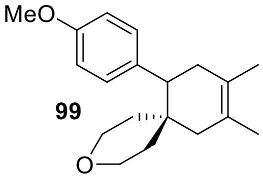
*9-(4-methoxyphenyl)-6,7-dimethyl-2-oxaspiro[3.5]non-6-ene (**98**). Colorless oil.*



98

^{1}H NMR (CDCl$_3$, 500 MHz) *δ* 7.11 (2H, d, *J* = 8.6 Hz), 6.82 (2H, d, *J* = 8.6 Hz), 4.69 (1H, d, *J* = 5.7 Hz), 4.47 (1H, d, *J* = 5.7 Hz), 4.31 (1H, d, *J* = 5.7 Hz), 4.11 (1H, d, *J* = 5.7 Hz), 3.78 (3H, s), 3.23 (1H, dt, *J* = 3.2 2.9 Hz), 2.42 (1H, m), 2.33 (1H, d, *J* = 17.2 Hz), 2.18 (1H, d, *J* = 19.5 Hz), 2.14 (1H, d, *J* = 21.2 Hz), 1.69 (3H, s), 1.67 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) *δ* 158.5, 135.1, 129.2, 125.8, 124.1, 113.9, 83.2, 80.2, 55.4, 44.6, 42.8, 39.9, 35.0, 19.5, 19.0; HRMS [M + H]$^+$ calculated for $C_{17}H_{23}O_2$ 259.1693, found 259.1670.

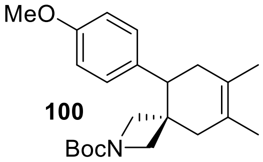
*11-(4-methoxyphenyl)-8,9-dimethyl-3-oxaspiro[5.5]undec-8-ene (**99**). Colorless oil.*



99

^{1}H NMR (CDCl$_3$, 500 MHz) *δ* 7.07 (2H, d, *J* = 8.6 Hz), 6.80 (2H, d, *J* = 8.6 Hz), 3.78 (3H, s), 3.72 (2H, m), 3.61 (1H, dt, *J* = 11.5, 2.9 Hz), 3.52 (1H, dt, *J* = 11.5, 2.9 Hz), 2.64 (1H, t, *J* = 5.7 Hz), 2.36 (1H, dd, *J* = 17.8, 5.2 Hz), 2.15 (1H, m), 1.99 (2H, m), 1.70 (3H, s), 1.67 (3H, s), 1.49 (2H, m), 1.43 (1H, ddt, *J* = 14.3, 2.9, 2.3 Hz), 1.04 (1H, ddt, *J* = 13.2, 2.9, 2.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) *δ* 158.3, 135.8, 130.1, 125.0, 124.1, 113.5, 64.1, 55.5, 48.9, 37.7, 36.5, 35.4, 33.9, 33.5, 30.0, 19.8, 18.9; HRMS [M + H]$^+$ calculated for $C_{19}H_{27}O_2$ 287.2006, found 287.2034.

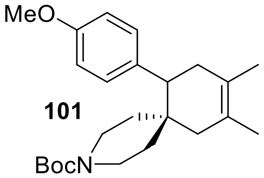
*tert-butyl 9-(4-methoxyphenyl)-6,7-dimethyl-2-azaspiro[3.5]non-6-ene-2-carboxylate (**100**). Yellow oil.*



100

^{1}H NMR (CDCl$_3$, 500 MHz) *δ* 7.11 (2H, d, *J* = 8.6 Hz), 6.82 (2H, d, *J* = 8.6 Hz), 3.88 (1H, d, *J* = 8.6 Hz), 3.78 (3H, s), 3.66 (1H, d, *J* = 8.0 Hz), 3.52 (1H, d, *J* = 8.0 Hz), 3.28 (1H, d, *J* = 8.6 Hz), 2.99 (1H, dt, *J* = 4.0, 2.3 Hz), 2.43 (1H, dd, *J* = 16.6, 3.4 Hz), 2.15 (3H, m), 1.67 (6H, s), 1.41 (9H, s); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) *δ* 158.5, 156.9, 134.9, 129.4, 125.9, 124.1, 113.9, 79.4, 55.5, 45.0, 40.7, 37.5, 35.3, 28.7, 19.5, 19.0; HRMS [M + H]$^+$ calculated for $C_{22}H_{32}NO_3$ 358.2377, found 385.2348.

*tert-butyl 11-(4-methoxyphenyl)-8,9-dimethyl-3-azaspiro[5.5]undec-8-ene-3-carboxylate (**101**). White solid.*



101

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.06 (2H, d, *J* = 8.6 Hz), 6.80 (2H, d, *J* = 8.6 Hz), 3.79 (3H, s), 3.72 (2H, m), 3.01 (1H, dt, *J* = 13.8, 2.3 Hz), 2.91 (1H, t, *J* = 9.7 Hz), 2.63 (1H, t, *J* = 5.7 Hz), 2.33 (1H, d, *J* = 16.0 Hz), 2.16 (1H, d, *J* = 16.6 Hz), 1.98 (1H, d, *J* = 16.6 Hz), 1.87 (1H, d, *J* = 17.2 Hz), 1.69 (3H, s), 1.67 (3H, s), 1.42 (9H, s), 1.32 (3H, m), 1.13 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 158.3, 155.3, 130.1, 125.0, 124.0, 113.5, 79.4, 55.5, 48.5, 37.6, 35.7, 34.2, 30.0, 28.7, 19.8, 18.9; HRMS [M + H]$^+$ calculated for $C_{24}H_{36}NO_3$ 386.2690, found 386.2668.

Chapter 5. Conclusion

The purpose of this research was development of TiO_2 photocatalytic and electrocatalytic electron transfer chemistry modeling the radical cation Diels-Alder reaction.

In chapter 2, radical cation Diels-Alder reaction of β-methylstyrenes by TiO_2 photocatalysis have been demonstrated. Optimization of controls and scope of dienes were examined using *trans*-anethole as a model, suggesting that TiO_2 photocatalysis promoted cycloadditions and steric hindrance of diene have effect for the reaction. Isomerization using *cis*-anethole showed that mechanism was stepwise and there were two ways that isomers were produced before or after trapping of diene. It was found that a non-protected alcohol introduced at the β-position of styrenes gave cycloadducts in good yields. Significantly, the corresponding cyclohexene of *trans*-β-methylstyrene was obtained in acceptable yield by TiO_2 photocatalysis, which was impossible to synthesize by Ruthenium photocatalysis and electrodes electrocatalysis. The reaction mechanism was proposed that it is mainly SET-oxidation and SET-reduction by TiO_2 photocatalysis.

In chapter 3, the reaction mechanism of the Photo-/Electrocatalytic Radical Cation Diels-Alder reaction described in Chapter 2 was analyzed by CV measurements and supported by DFT calculations. The EC-backward-E process, which SET-redox was occurred on single electrode, was successfully observed using CV analysis for β-methylstyrenes which was found to be reacted with diene. The reasonable radical cation intermediates were designed from the HOMO and spin density plots using DFT calculations. In case of 2,4-dimethyl *trans*-β-methylstyrene and diene, spin density plots were on its cyclohexene double bond, suggesting that this intermediate was unstable and had to receive reductive-SET immediately for cycloaddition. Therefore, TiO_2 photoredox had an advantage for this reaction.

In chapter 4, radical cation Diels-Alder reaction of arylidene cycloalkanes by interfacial electron transfer catalysis has been demonstrated. The cycloaddition of 4-methoxyβ-dimethylstyrene and diene was obtained less than using *trans*-anethole under TiO_2 photocatalytic and electrodes electrocatalytic conditions, suggesting that the additional methyl group at the β-position of styrene caused steric hindrance and interrupted the reaction. The 4-methoxy, 2,4-dimethyl and non-substituted β-cycloalkane styrenes were prepared to examine the effect of tying up two methyl groups; unexpectedly, the arylidene cyclobutane was found to give spiro ring in acceptable yield, and 4-methoxy β-cycloalkane styrenes were reacted with diene by more electrocatalytic condition than photocatalytic condition. It was suggested that TiO_2 photocatalytic reductive-SET seems to decrease the reactivity of intermediates in case of 4-methoxy β-disubstituted styrenes.

This research will support to use of TiO_2 photocatalyst in synthetic organic chemistry and understand the interfacial electron transfer catalysts. I hope that this study will promote the sustainable synthetic chemistry field and lead to a breakthrough in the various energy problems facing us today.

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I would like to Professor Hidehiro Kamiya for useful discussion. He accepted my chief advisor, and my dissertation review and hearing were held smoothly by his adjustment. I am grateful to Associate Professor Yohei Okada for constructive advice. He was my vice advisor, and I was interested in organic chemistry by him. All discussions with him had significant value and improved my research to publications. I wish to thank Professor Akio Saito for hospitable supports. Although the research was not included in this dissertation, he accepted me as a laboratory rotation member, and spread my view of synthetic organic chemistry. I would thank Professor Kenji Ogino, Associate Professor Nobuyuki Akai, and Associate Professor Kazuya Nakata for important suggestions to brush dissertation up. Additionally, I appreciate the feedback offered by Doctor Naoya Maeta, Doctor Genki Horiguchi and Assistant Professor Shohei Yamashita. Finally, I was fortunate laboratory member and have enjoyed research discussion; thus, I want to give a special thanks to them. I am also grateful to my family and best friends for continuous support.

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Supporting Information

S1. General TiO$_2$ Analysis Data

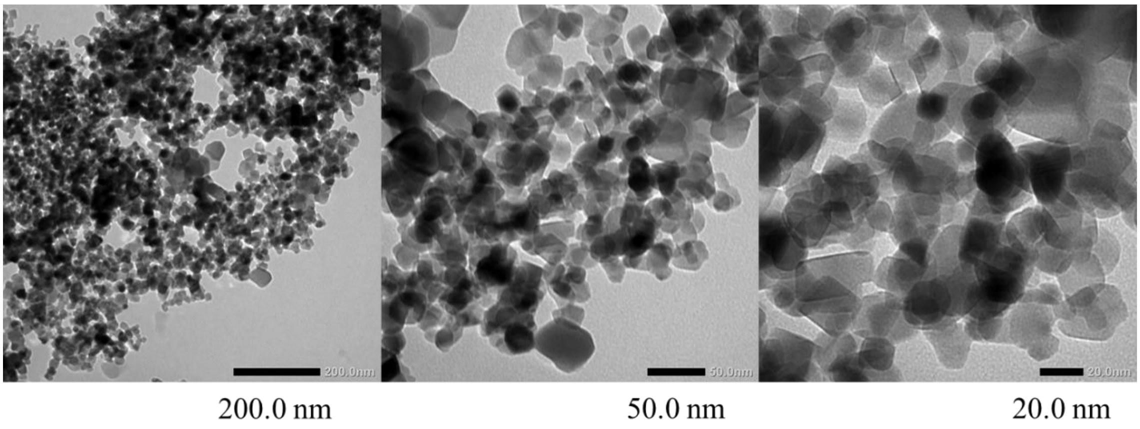


Figure S1. TEM Images of TiO$_2$ Photocatalyst used in This Work.

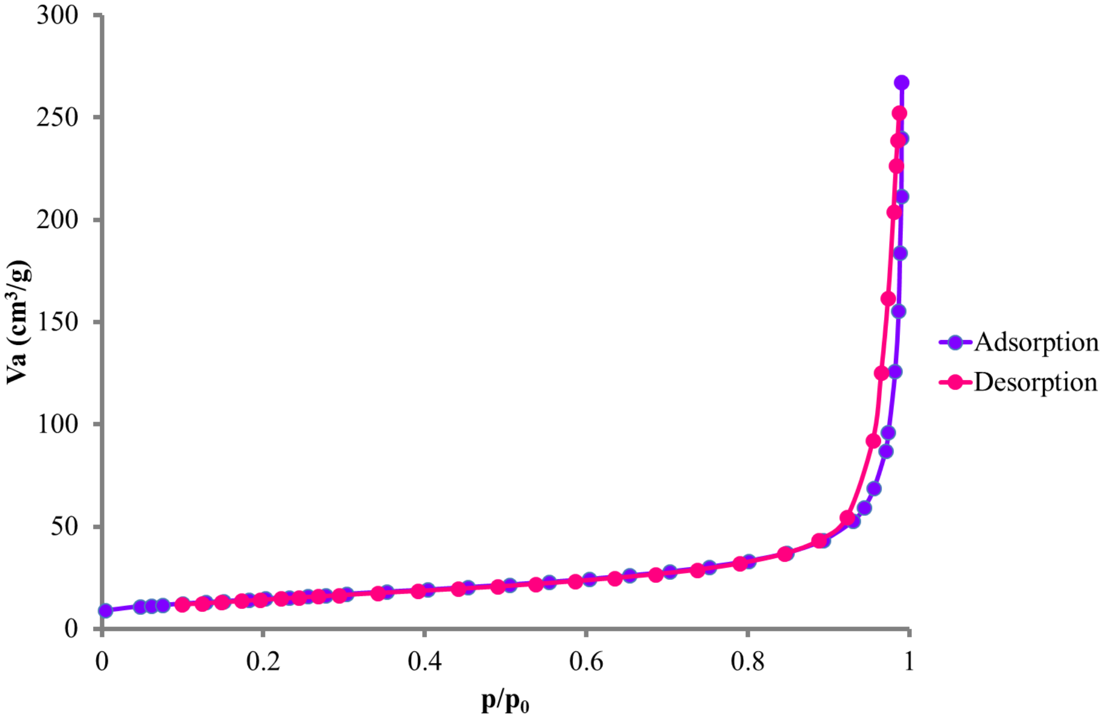


Figure S2. Adsorption Isotherm of TiO$_2$ Photocatalyst used in This Work.

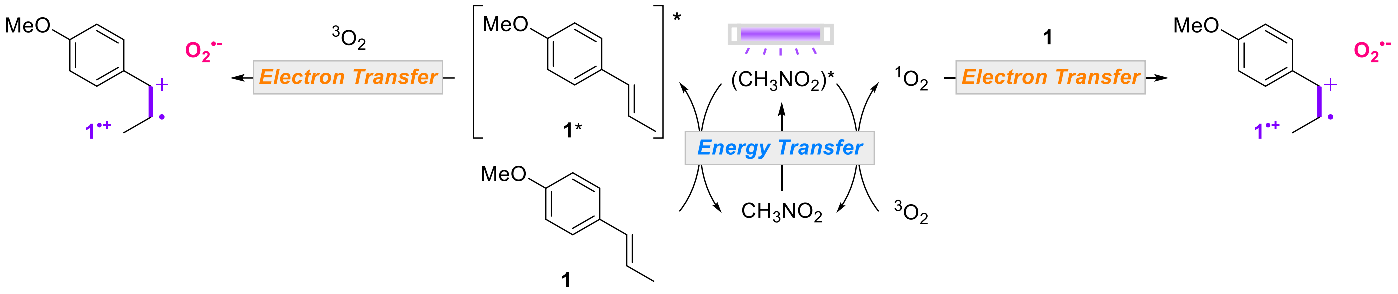
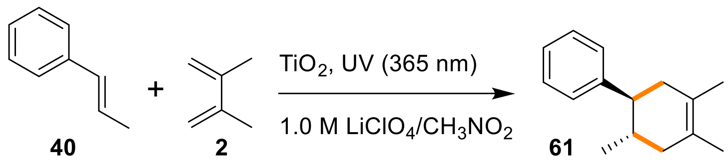


Figure S3. Plausible Reaction Mechanism by Energy/Electron Transfer Catalysis.

Additional Control Study for Radical Cation Diels-Alder Reaction of β-Methylstyrenes and Dienes. About atmosphere, the reaction condition was examined using *trans*-β-methylstyrene (**40**) and 2,3-dimethyl-1,3-budadiene (**2**), and O_2 concentration had an impact for the reaction.

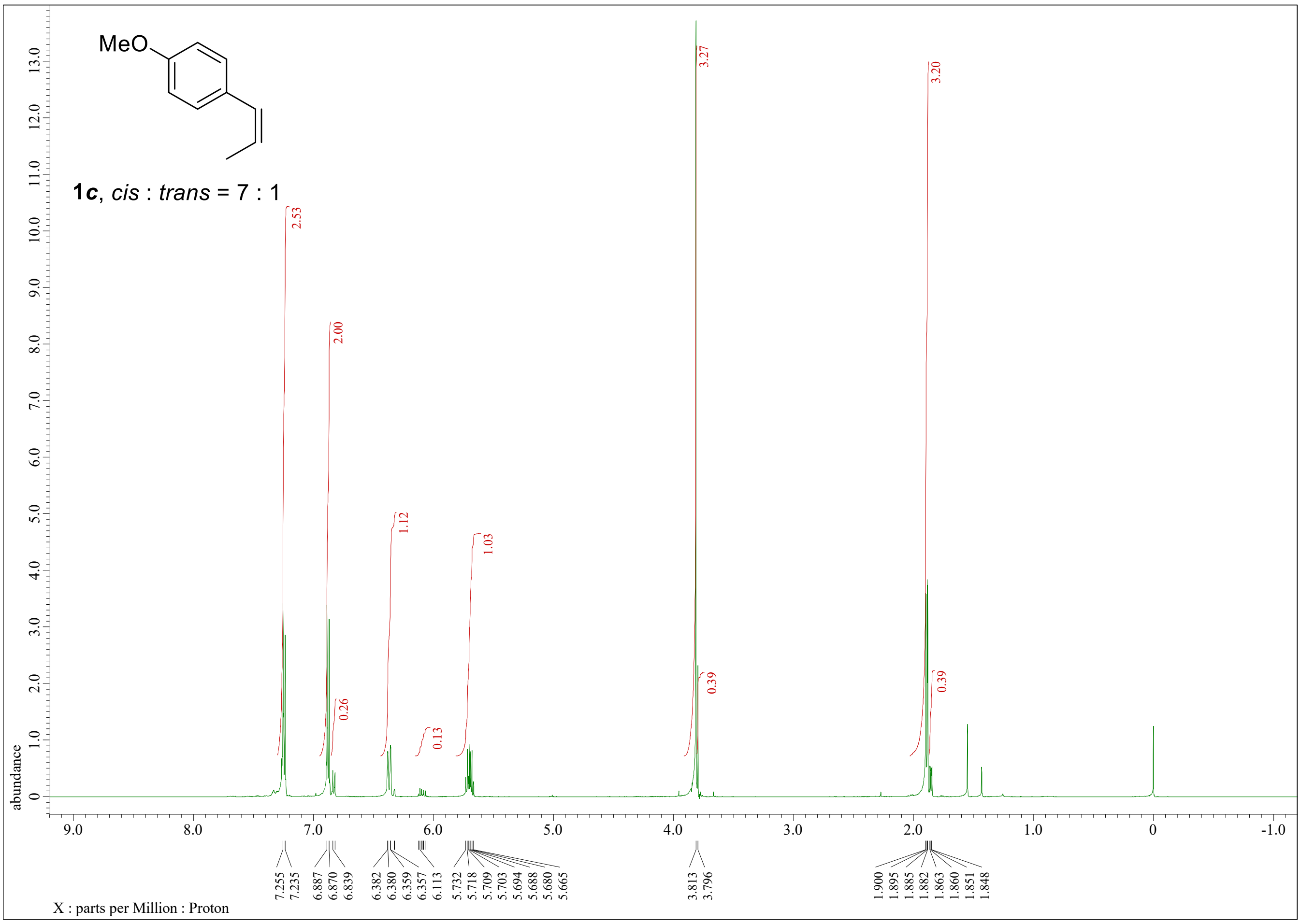
Table S1. Control Studies for Radical Cation Diels-Alder Reaction of 40 and 2.[a]



entry	Condition	yield (%)
1	under Ar	11 (42)
2	under O_2	11 (26)

[a] Reactions were carried out on a 0.20 mmol scale of *trans*-β-methylstyrene (**40**) with 2 equiv of 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h. Yields were determined by ^1H NMR analysis using benzaldehyde as an internal standard.

General Procedure for Radical Cation Diels-Alder Reactions (1.0 mmol Scale). To a solution of $LiClO_4$ (1.0 M) in CH_3NO_2 (20 mL) stirred at room temperature were added the respective β-methyl styrenes (1.00 mmol), dienes (2.00 mmol), and TiO_2 (500 mg). The resulting reaction mixture was stirred at room temperature in front of a 15 W UV lamp (365 nm) for 2 h (also checked by thin-layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Yields were determined by ^1H NMR analysis using benzaldehyde as an internal standard. Silica gel column chromatography (unless otherwise noted, hexane/ethyl acetate = 20/1) gave the desired cycloadducts.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1c, *cis* : *trans* = 7 : 1
abundance
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1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
2.53
2.00
0.26
1.12
0.13
1.03
3.27
0.39
3.20
0.39
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.255
7.235
6.887
6.870
6.839
6.382
6.380
6.359
6.357
6.113
5.732
5.718
5.709
5.703
5.694
5.688
5.680
5.665
3.813
3.796
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1.895
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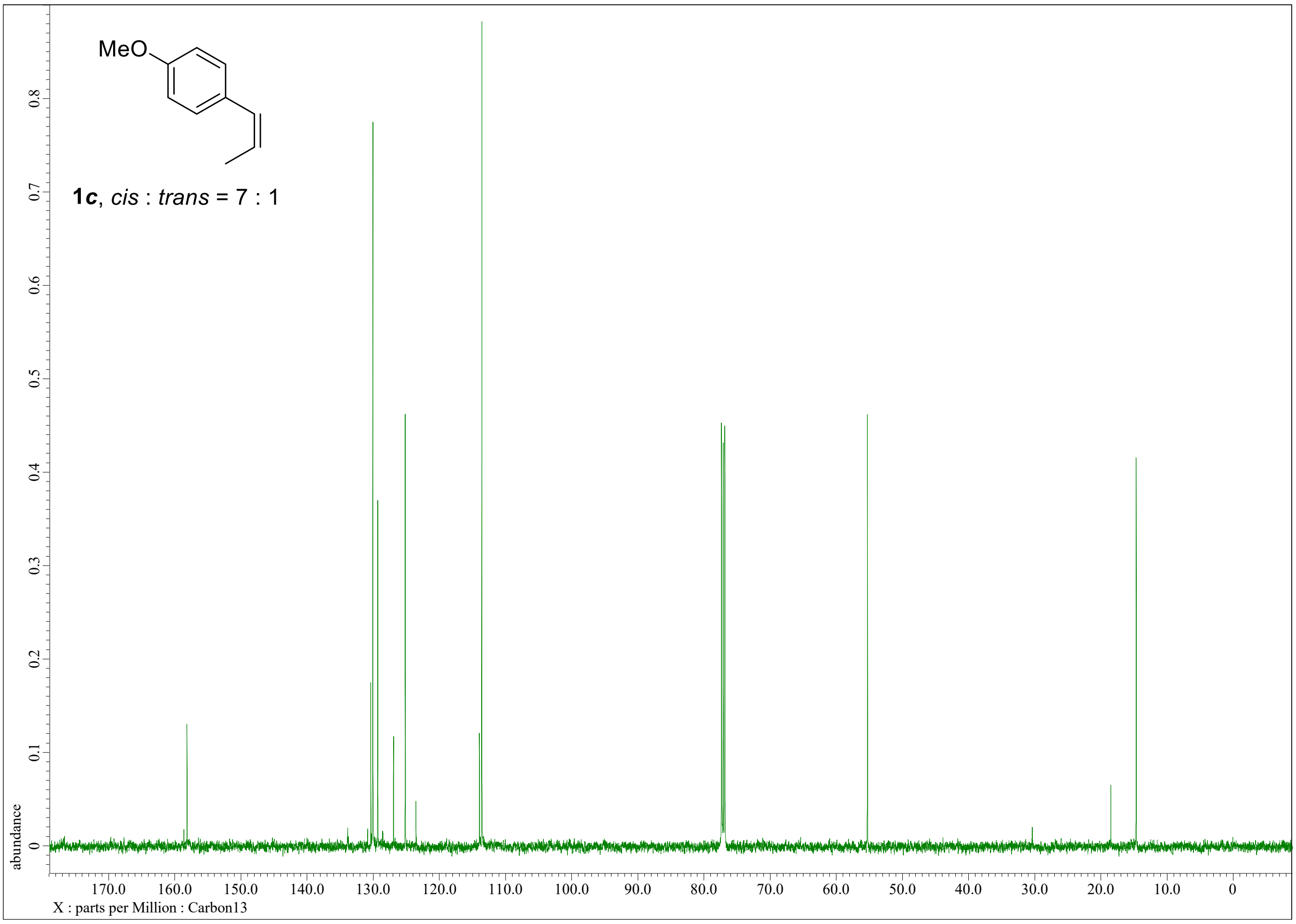
1.882
1.863
1.860
1.851
1.848
X : parts per Million : Proton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abundance
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0.3
0.4
0.5
0.6
0.7
0.8
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
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70.0
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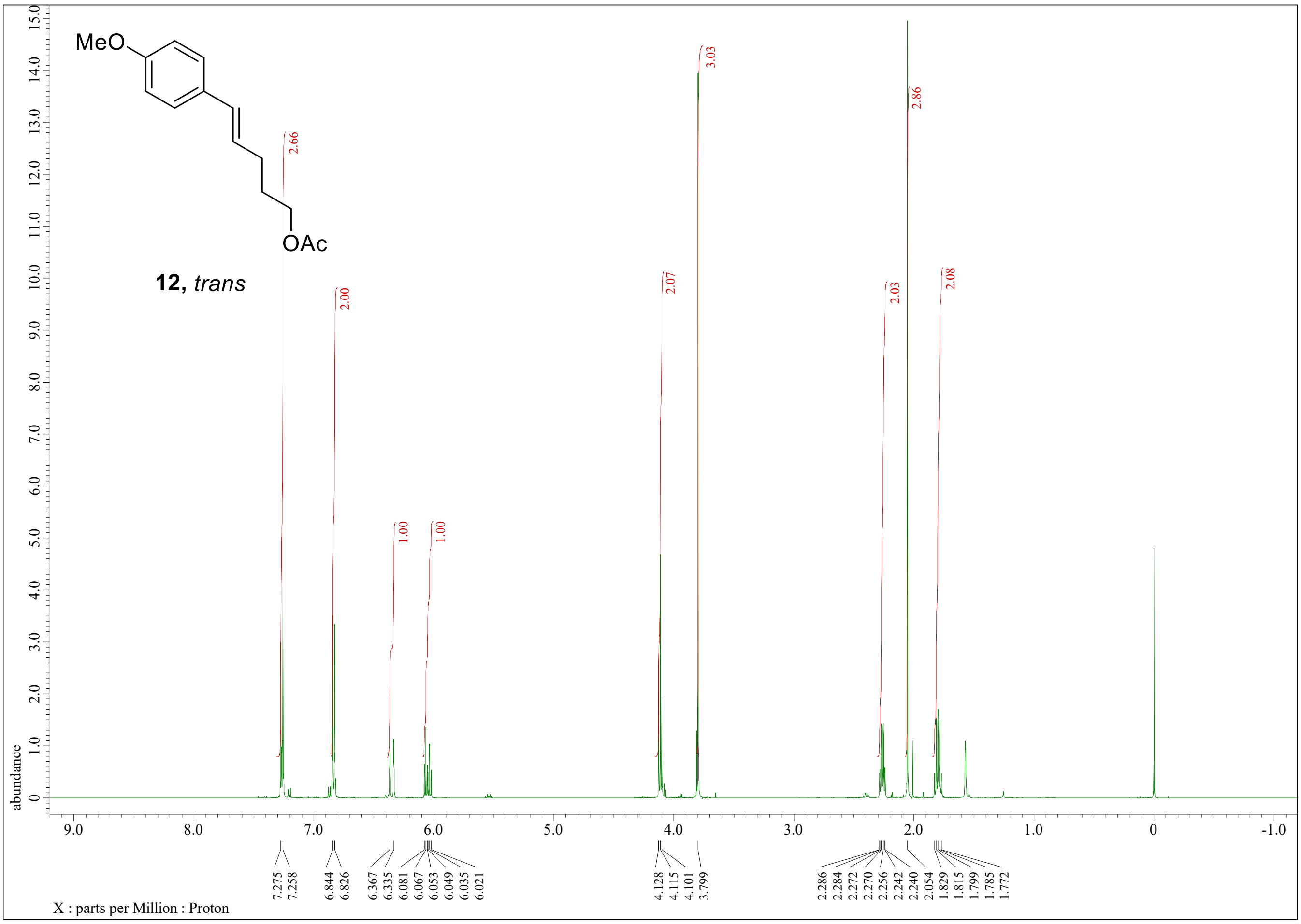
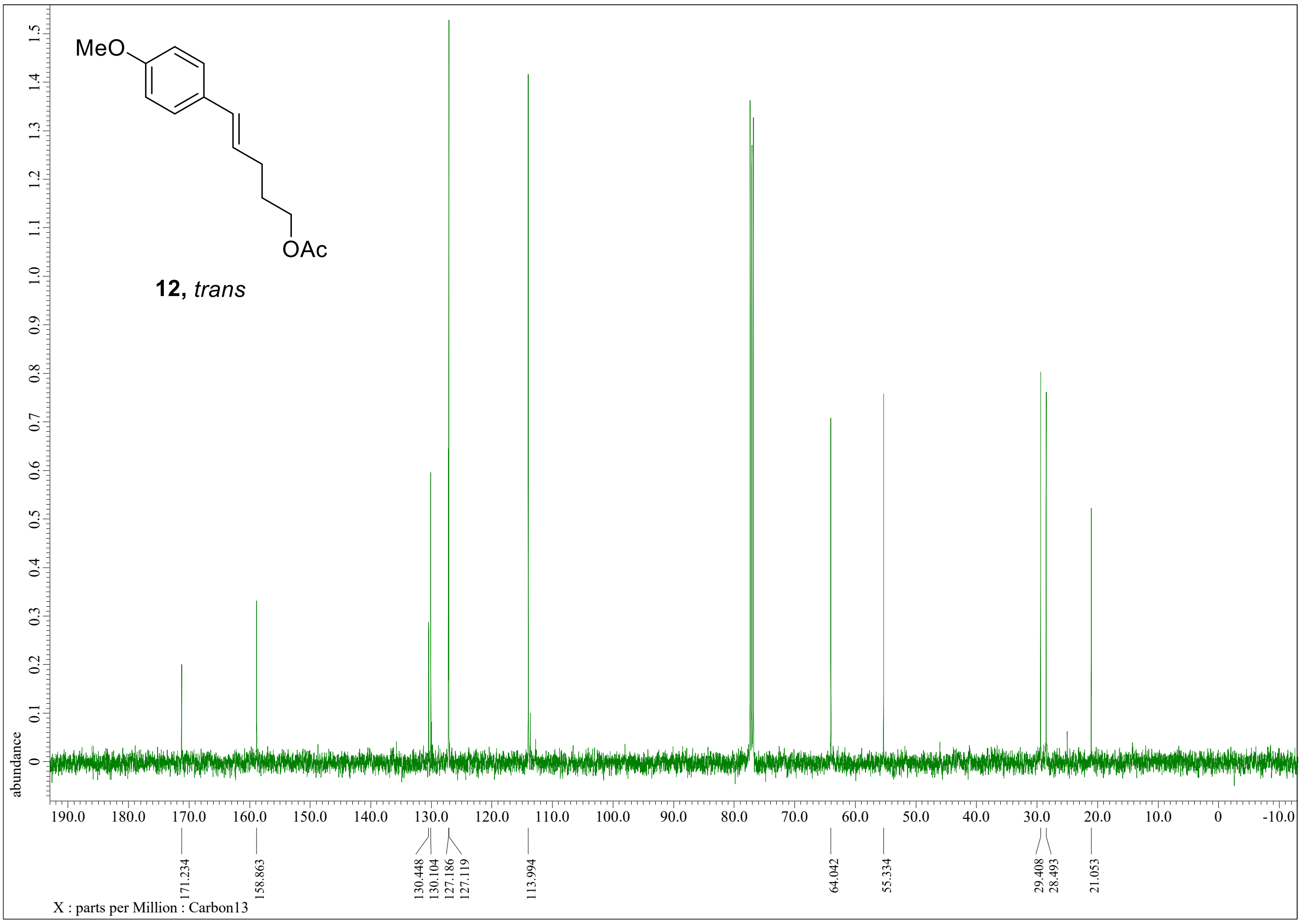
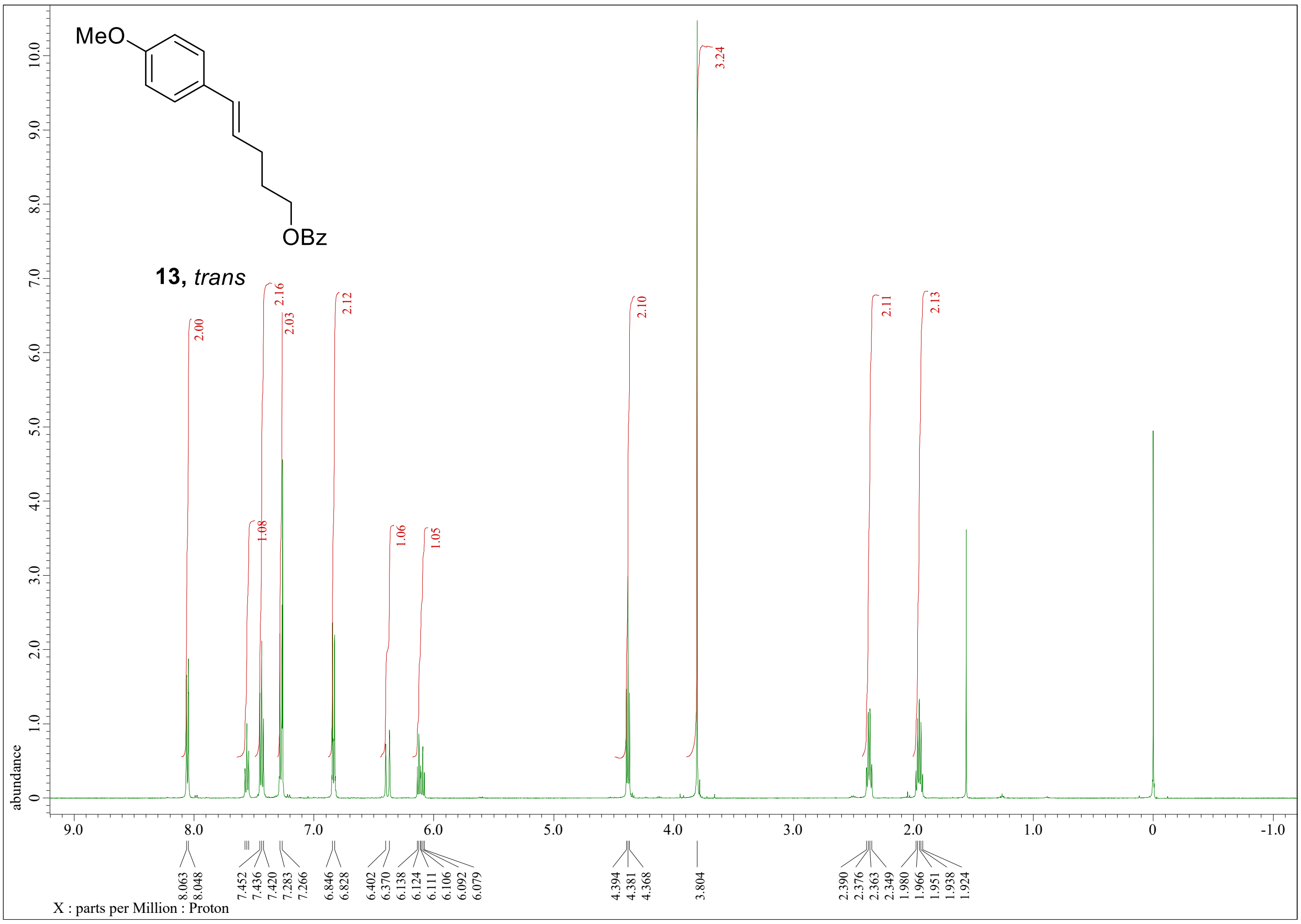
20.0
10.0
0
X : parts per Million : Carbon13



12, *trans*



12, *trans*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2.16
2.03
2.12
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1.05
2.10
3.24
2.11
2.13
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
8.063
8.048
7.452
7.436
7.420
7.283
7.266
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6.828
6.402
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6.111
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4.368
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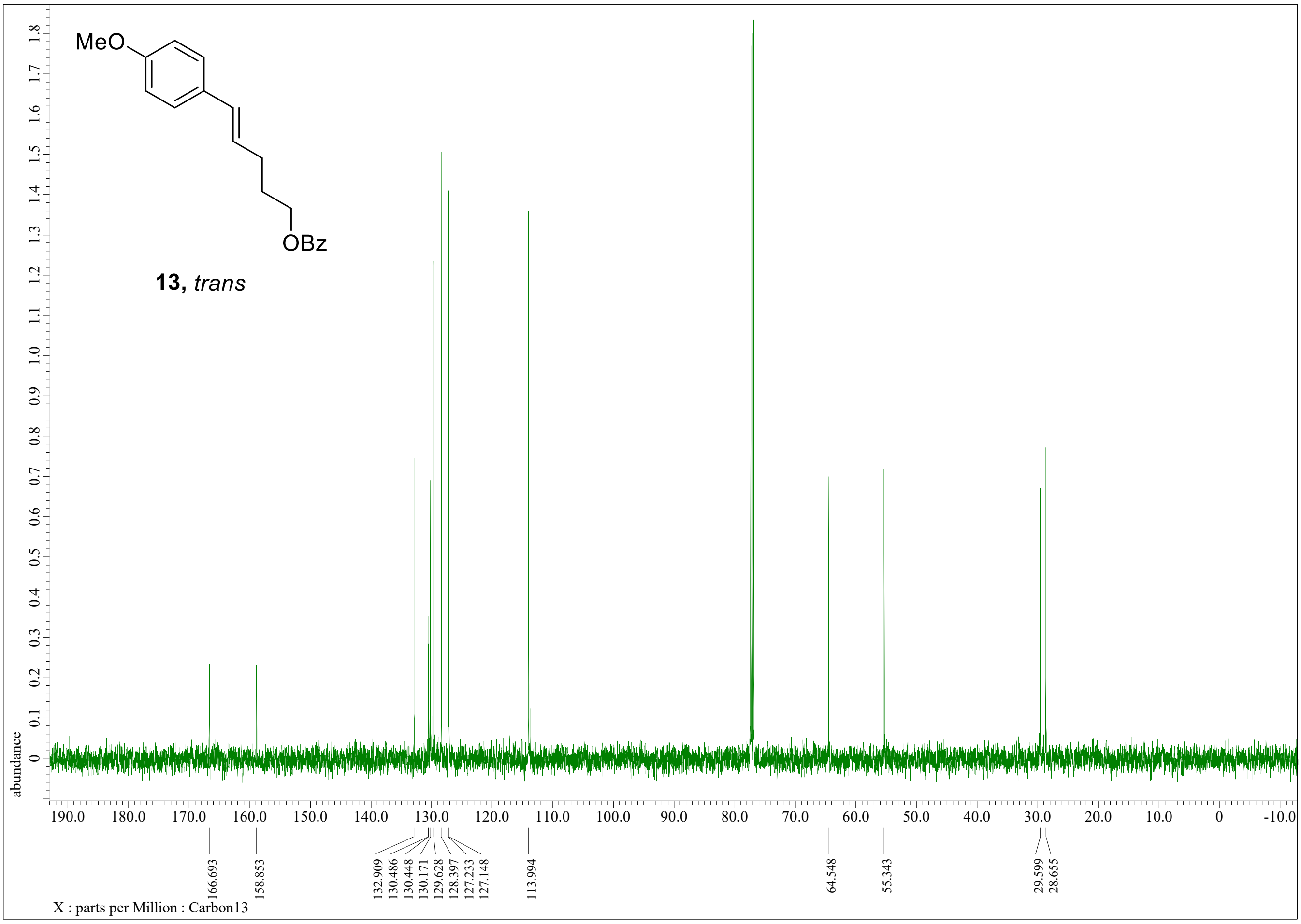
X : parts per Million : Proton


MeO
OBz
13, trans
abundance
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0.7
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0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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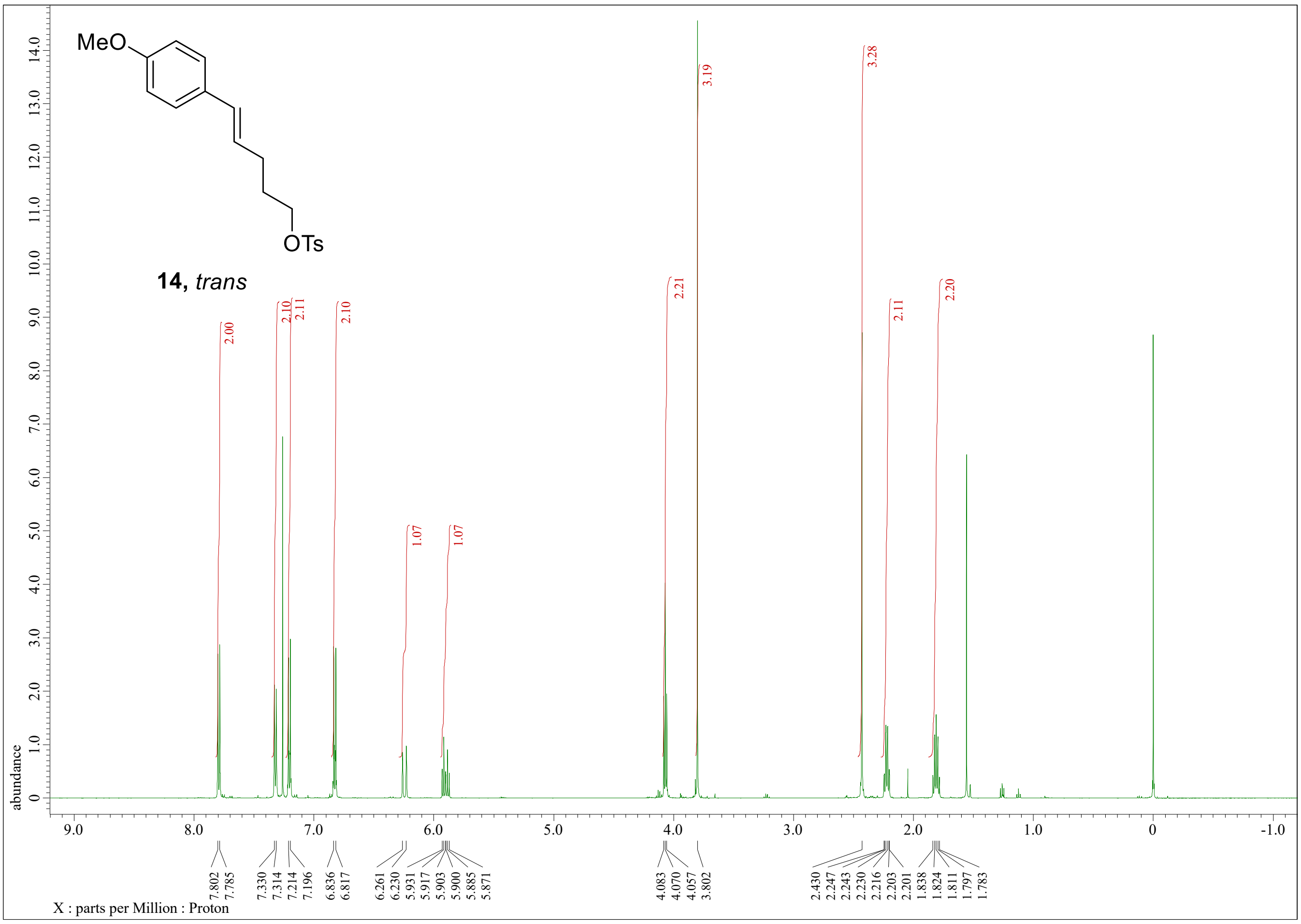
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2.20
abundance
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2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
7.802
7.785
7.330
7.314
7.214
7.196
6.836
6.817
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5.931
5.917
5.903
5.900
5.885
5.871
4.083
4.070
4.057
3.802
2.430
2.247
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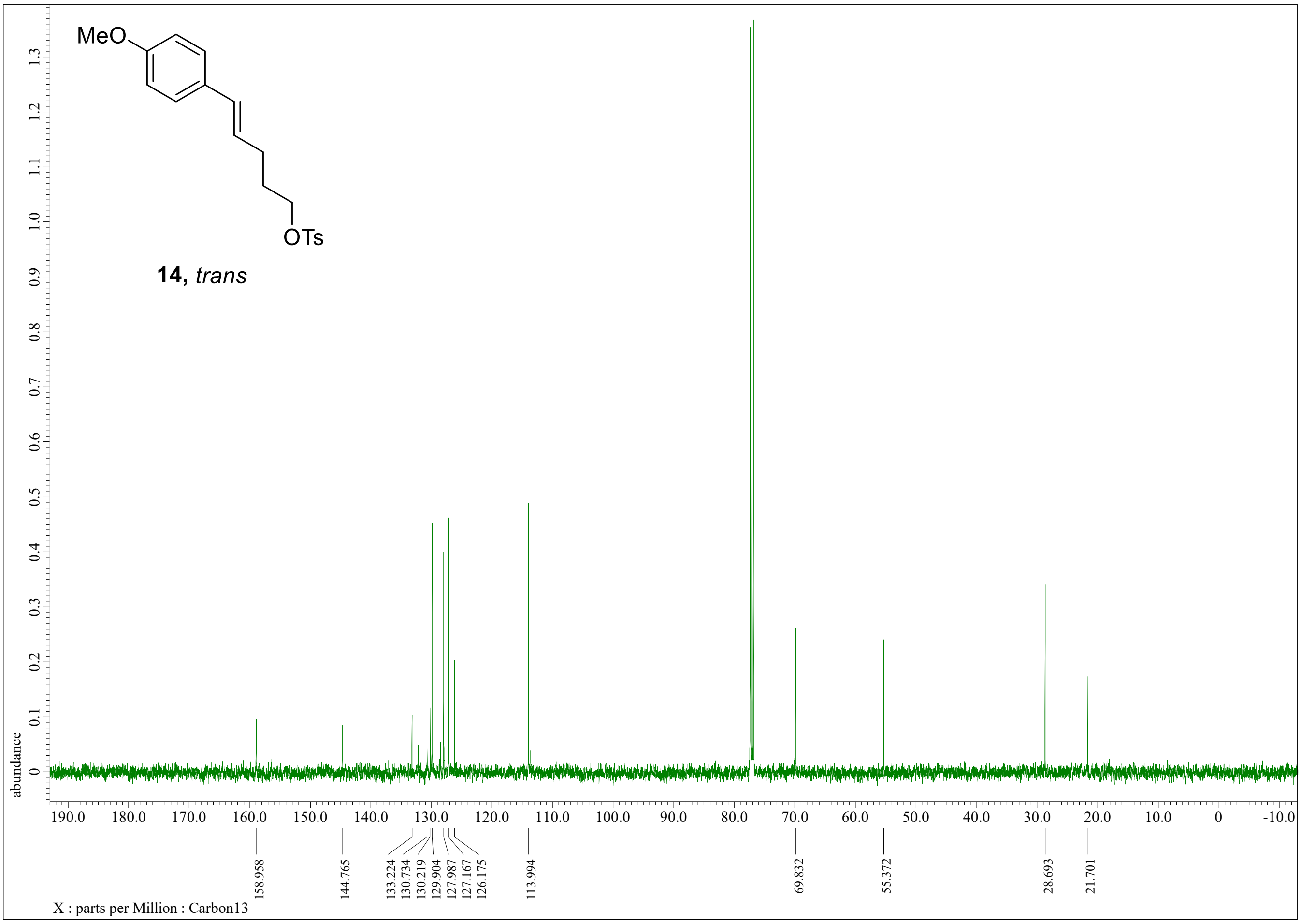
1.783
X : parts per Million : Proton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0.4
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0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
158.958
144.765
133.224
130.734
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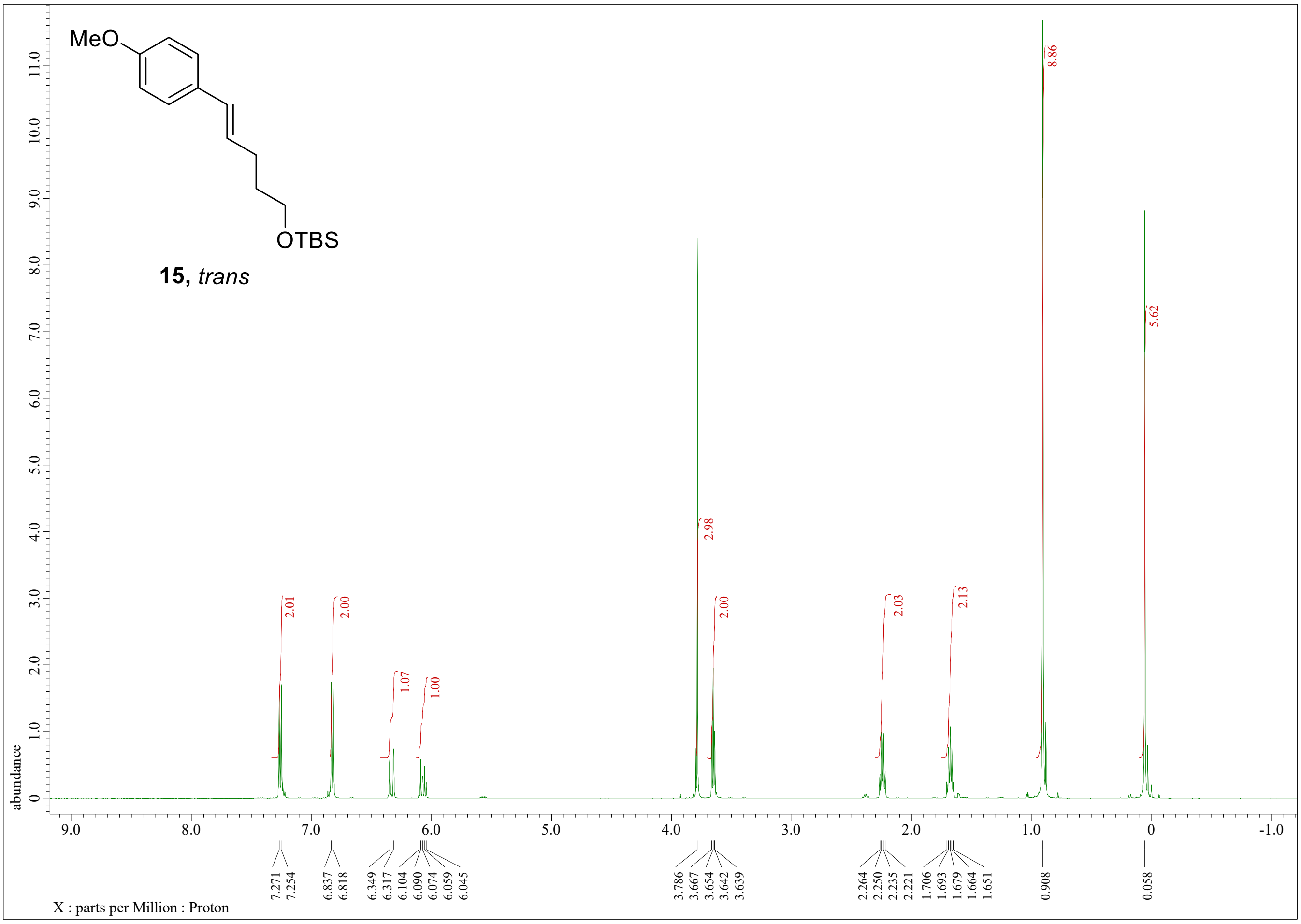
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2.00
2.03
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9.0
8.0
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5.0
4.0
3.0
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1.0
0
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7.271
7.254
6.837
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6.349
6.317
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6.059
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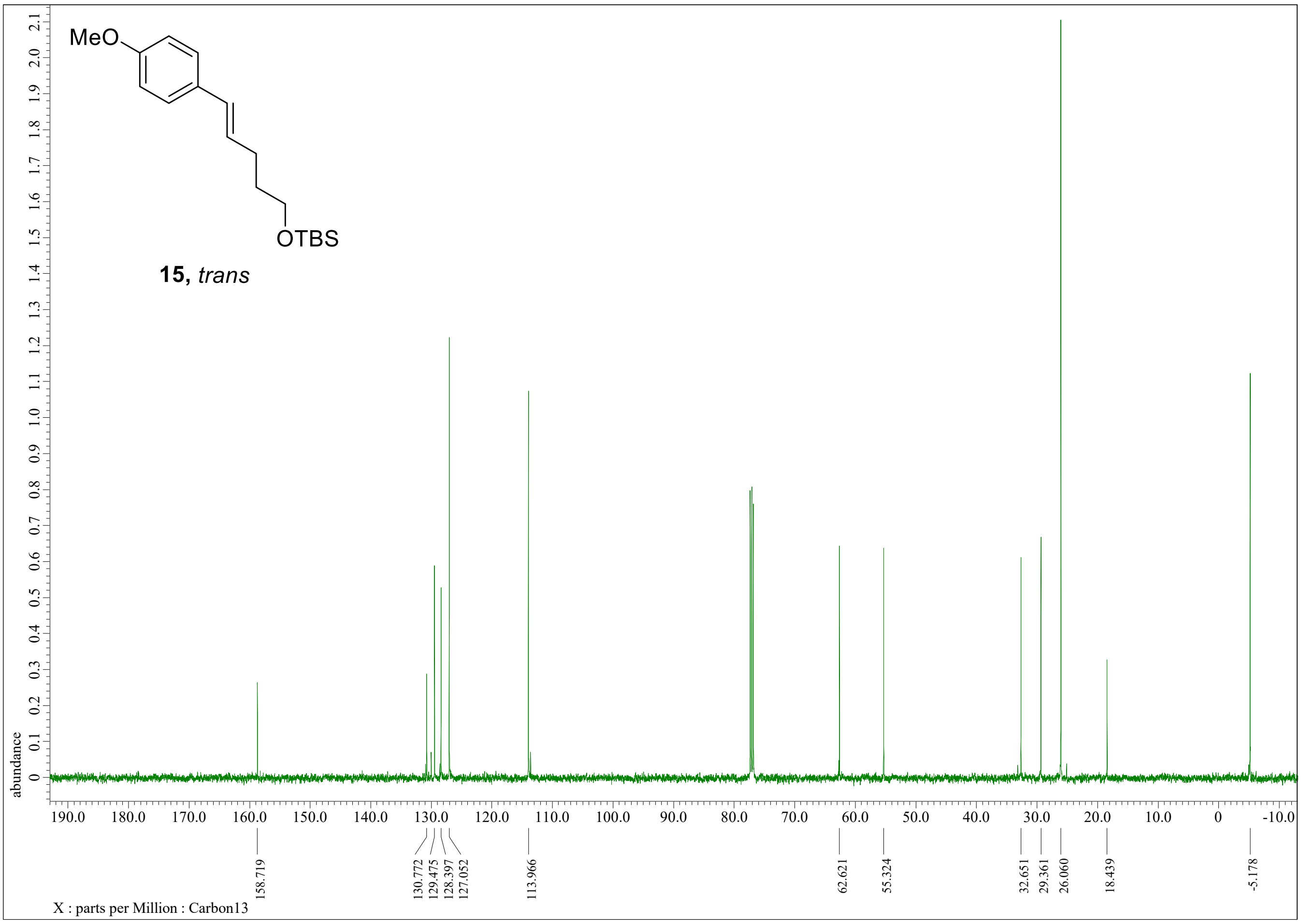
X : parts per Million : Proton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0.5
0.4
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0
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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
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20.0
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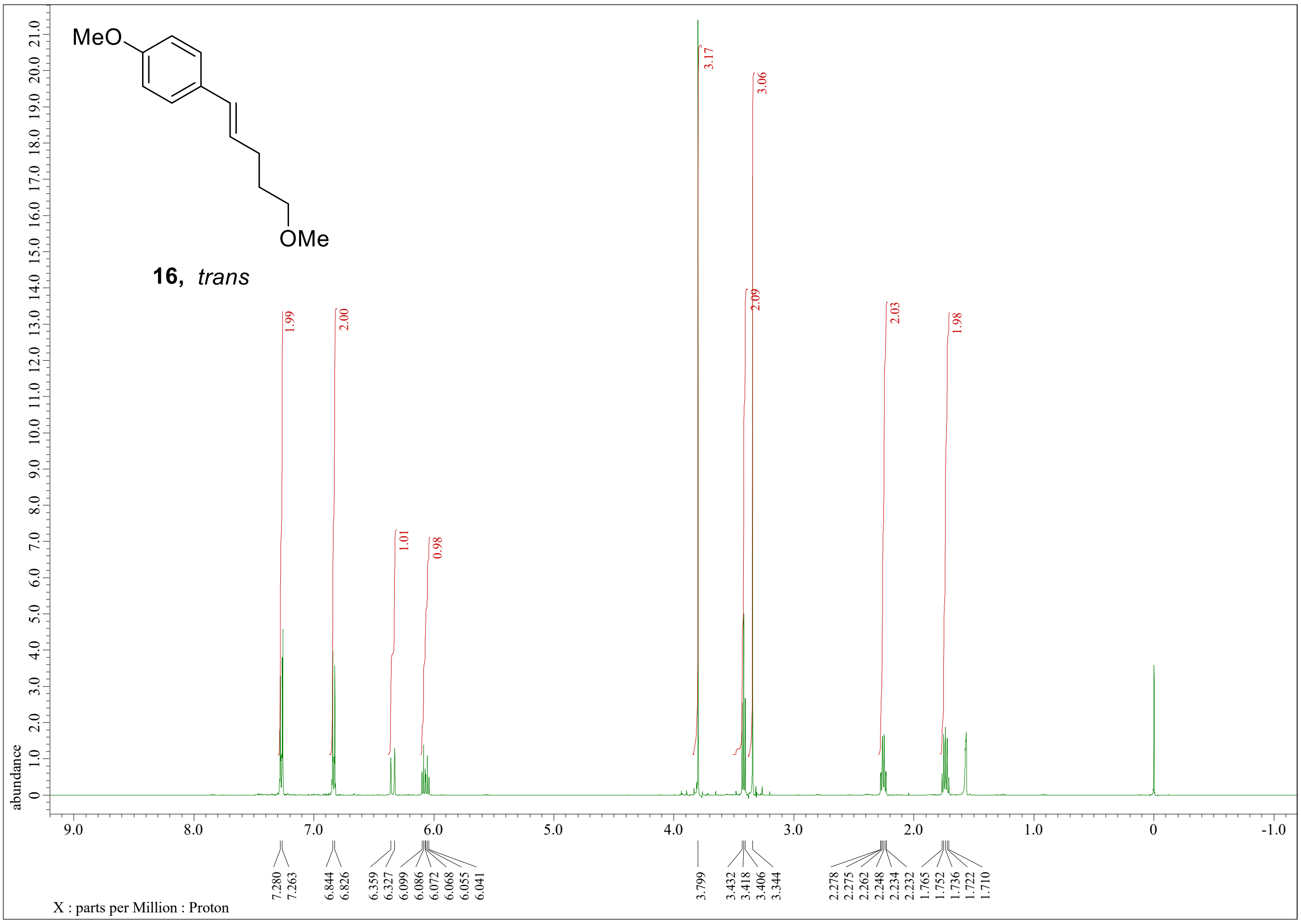
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2.09
2.03
1.98
1.99
2.00
1.01
0.98
abundance
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
7.280 7.263 6.844 6.826 6.359 6.327 6.099 6.086 6.072 6.068 6.055 6.041
3.799
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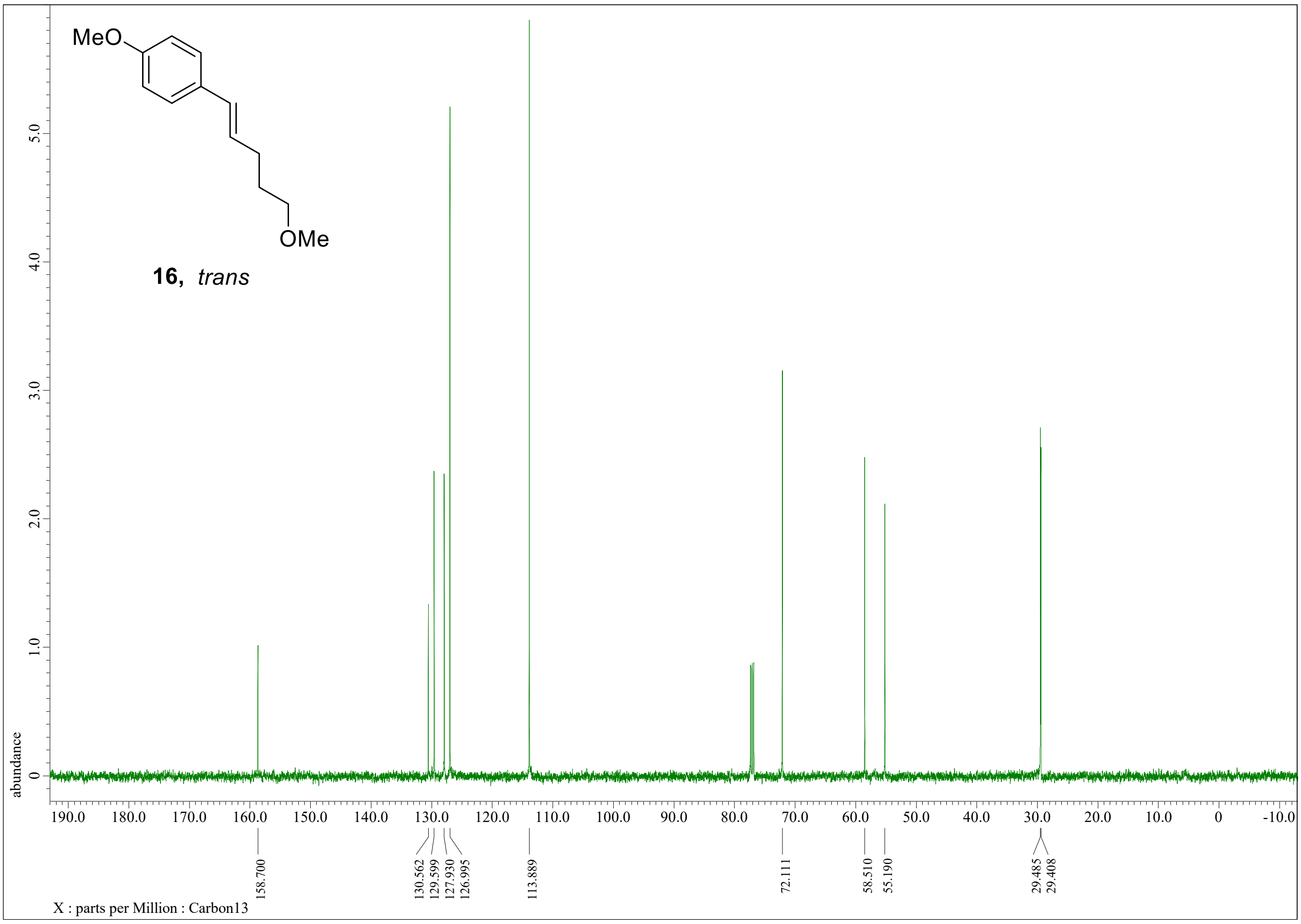
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OMe
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abundance
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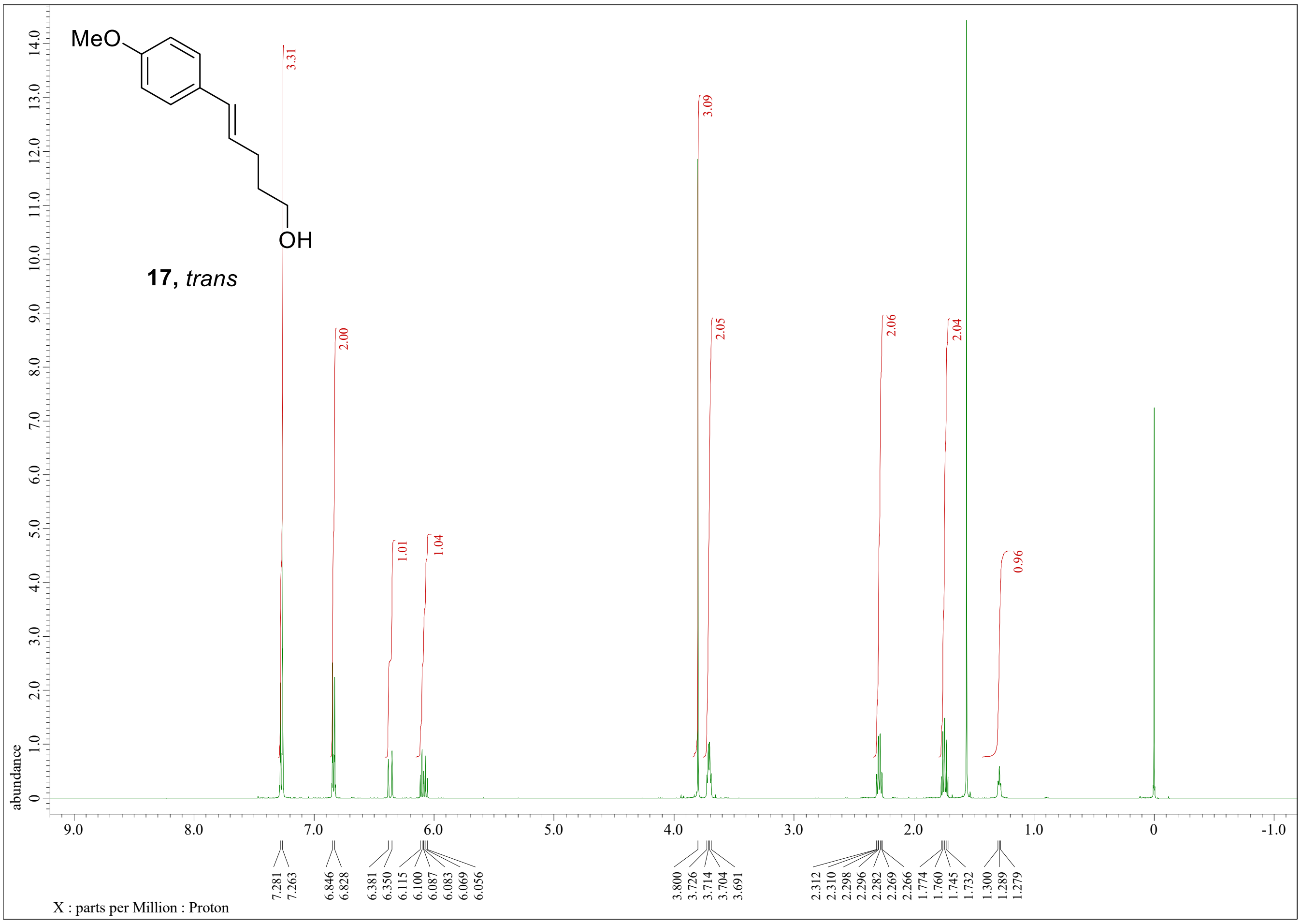
113.889
72.111
58.510
55.190
29.485 29.408
X : parts per Million : Carbon13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2.00
1.01
1.04
3.09
2.05
2.06
2.04
0.96
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
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7.263
6.846
6.828
6.381
6.350
6.115
6.100
6.087
6.083
6.069
6.056
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2.298
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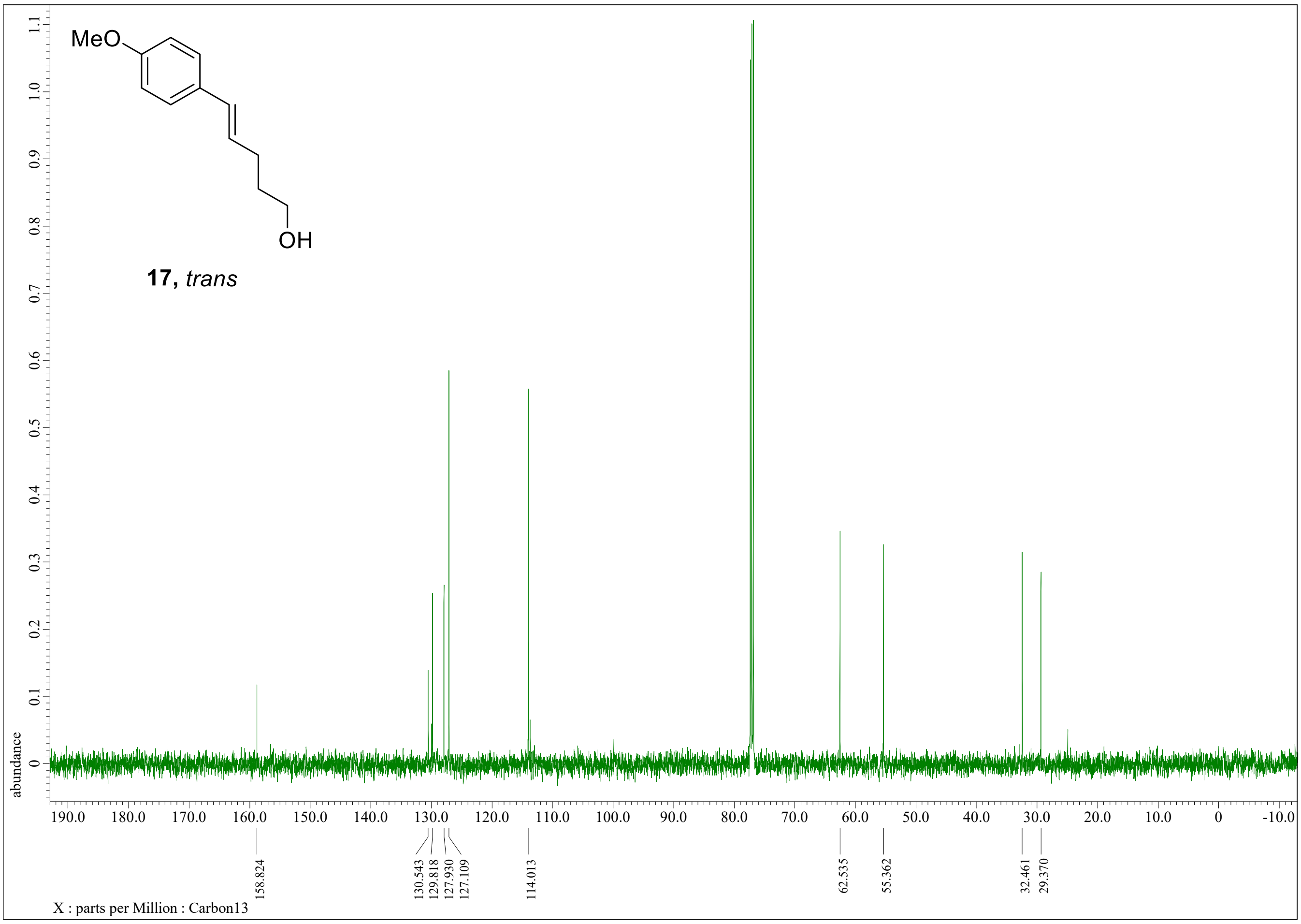
X : parts per Million : Proton


MeO
OH
17, trans
abundance
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190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
158.824
130.543
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127.930
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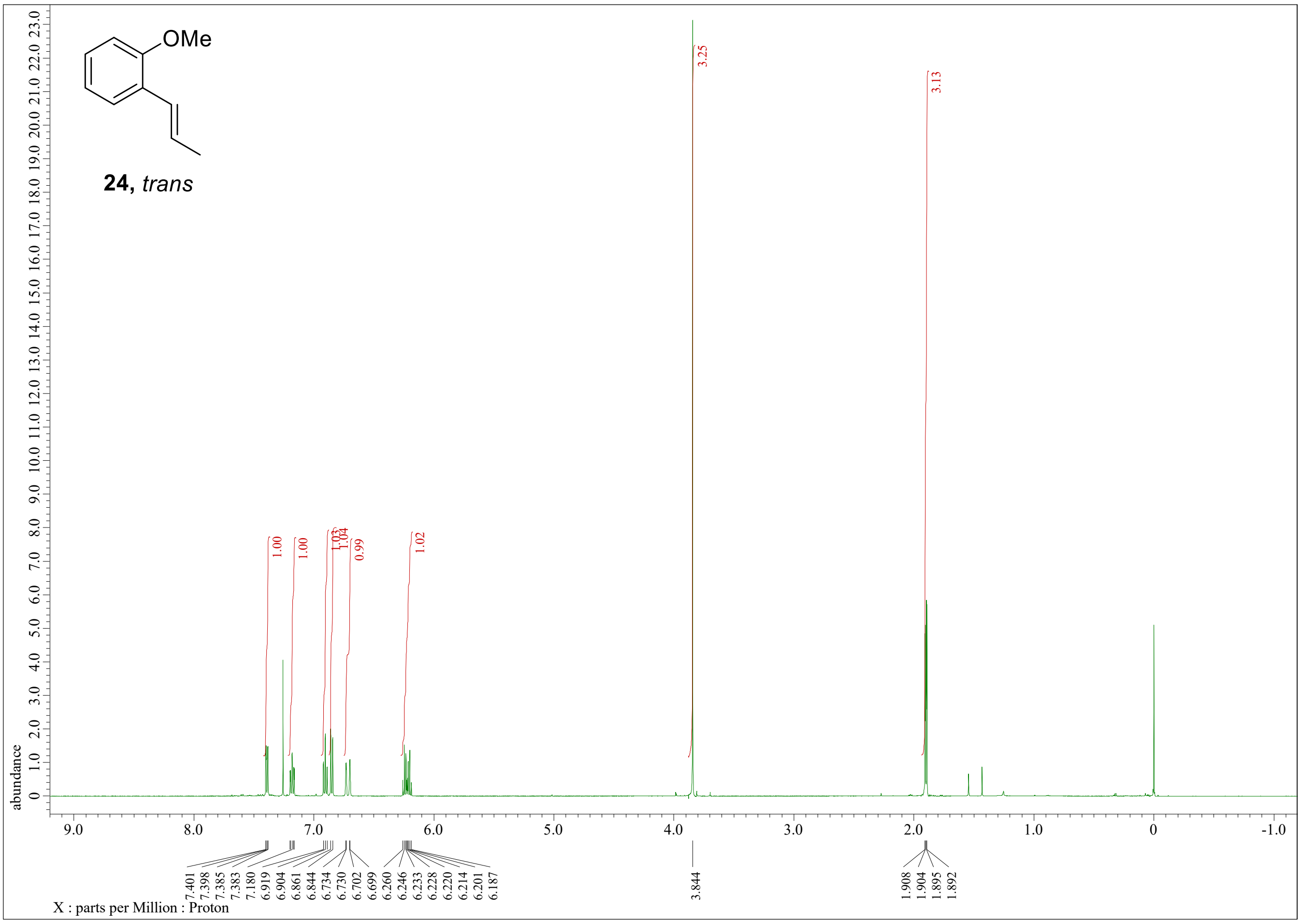
114.013
62.535
55.362
32.461
29.370
X : parts per Million : Carbon13


OMe
24, trans
abundance
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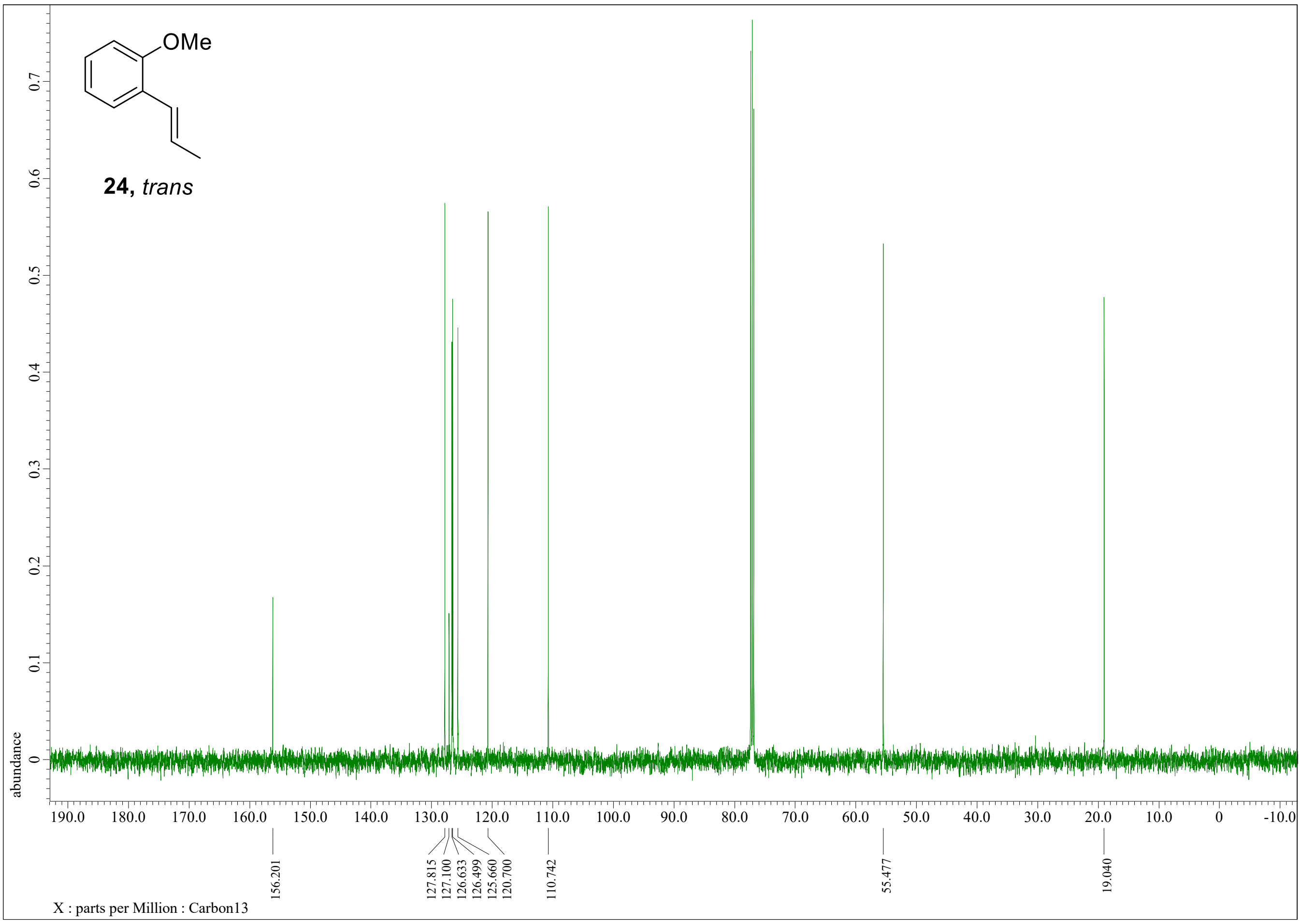
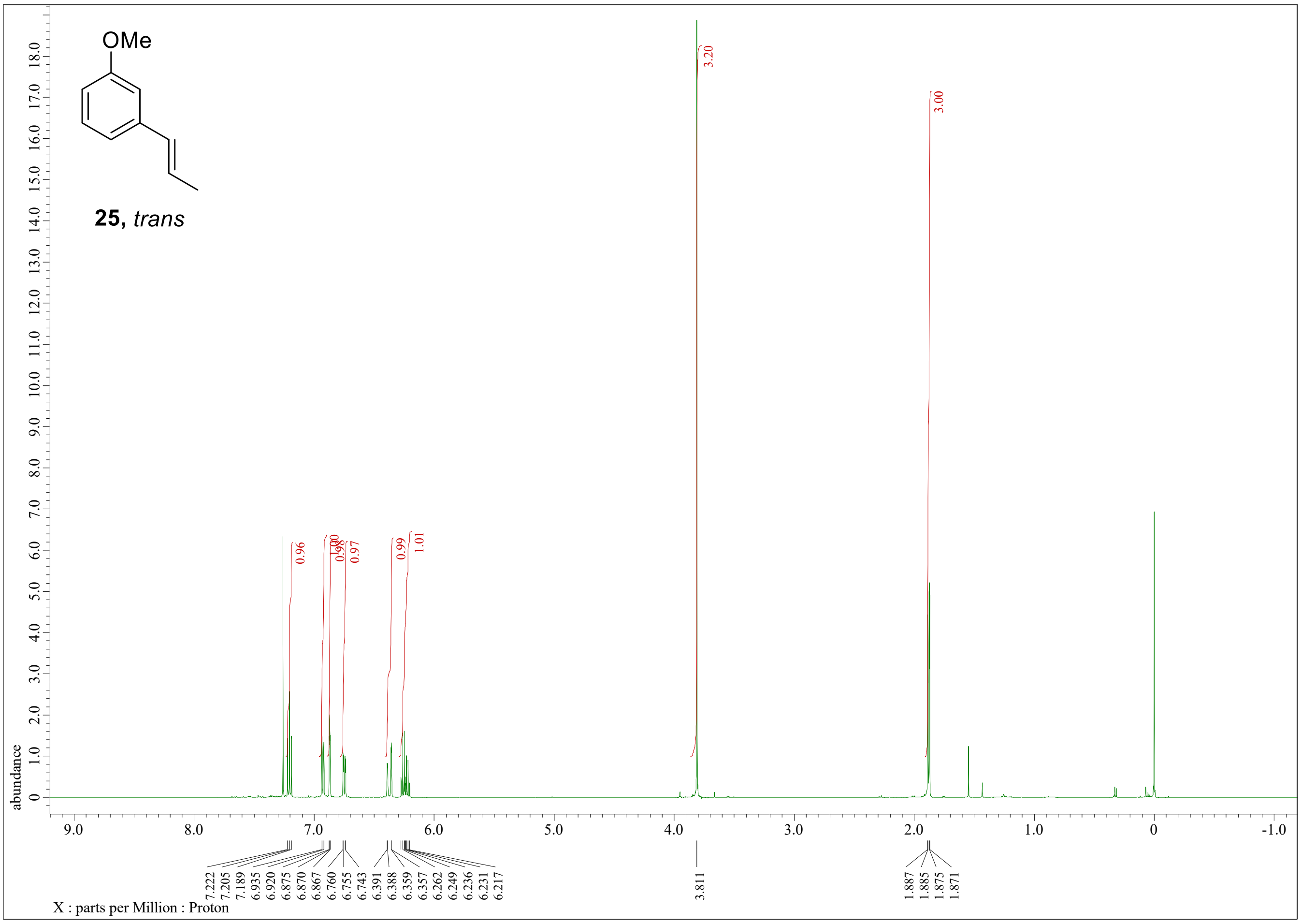
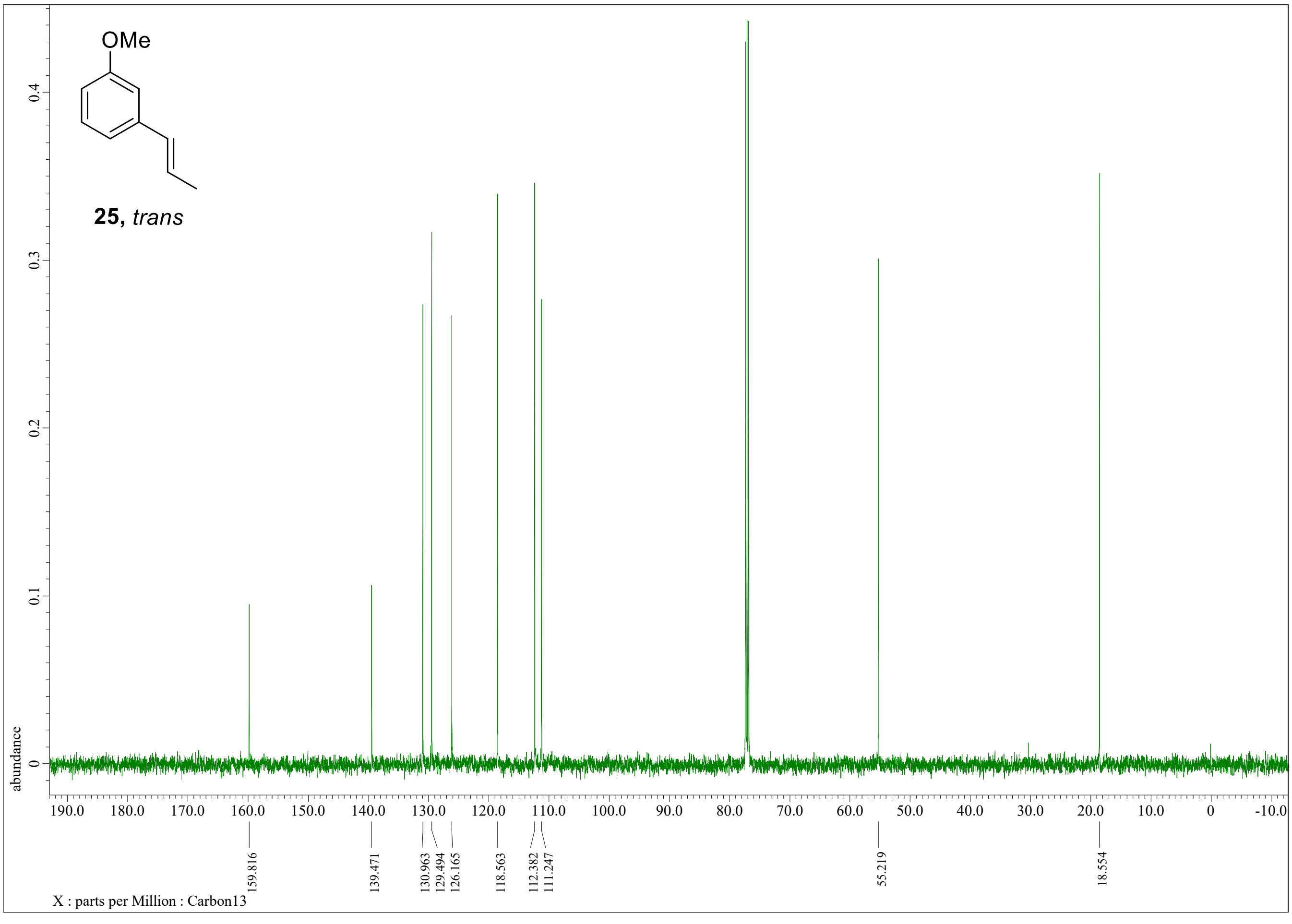
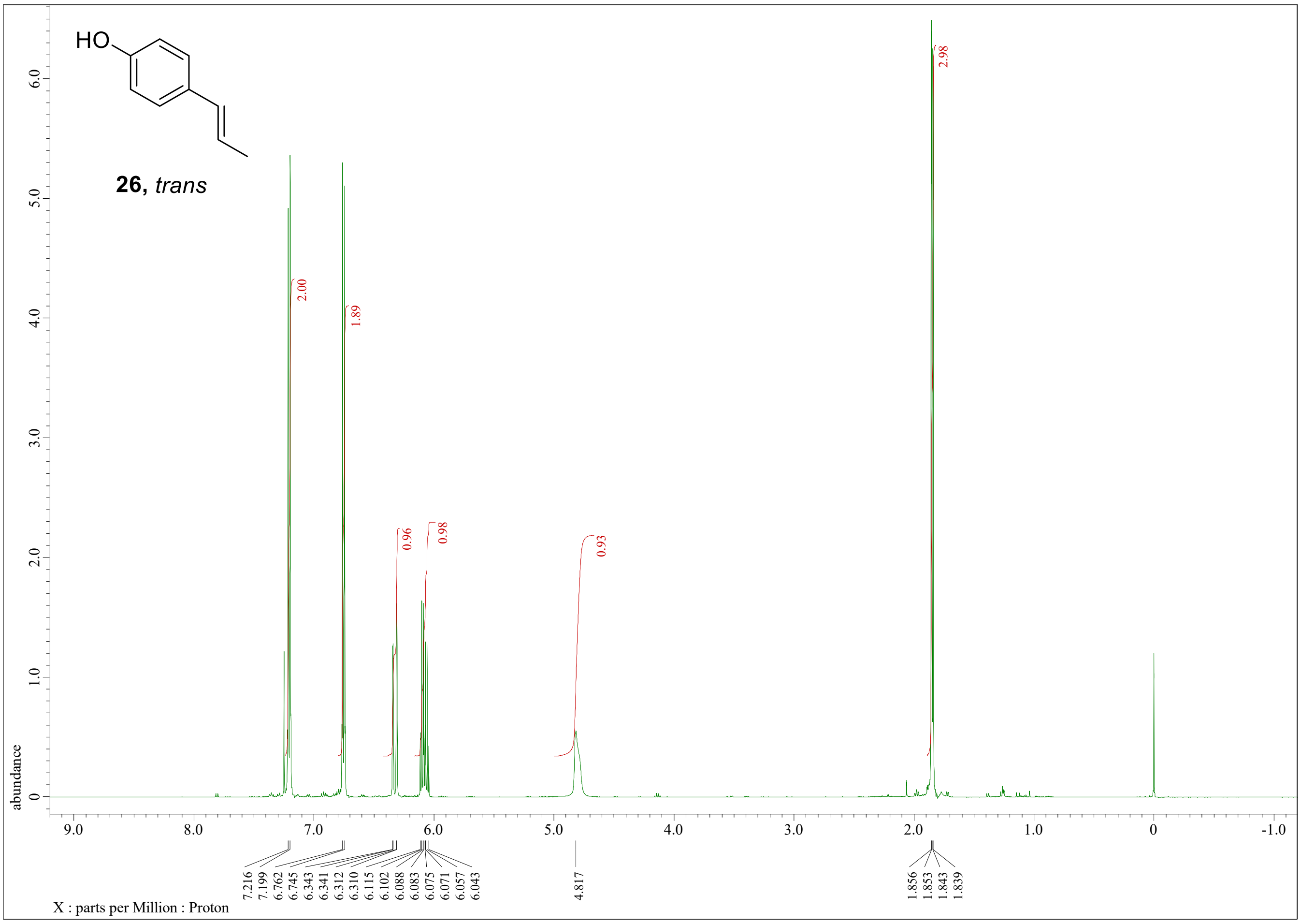
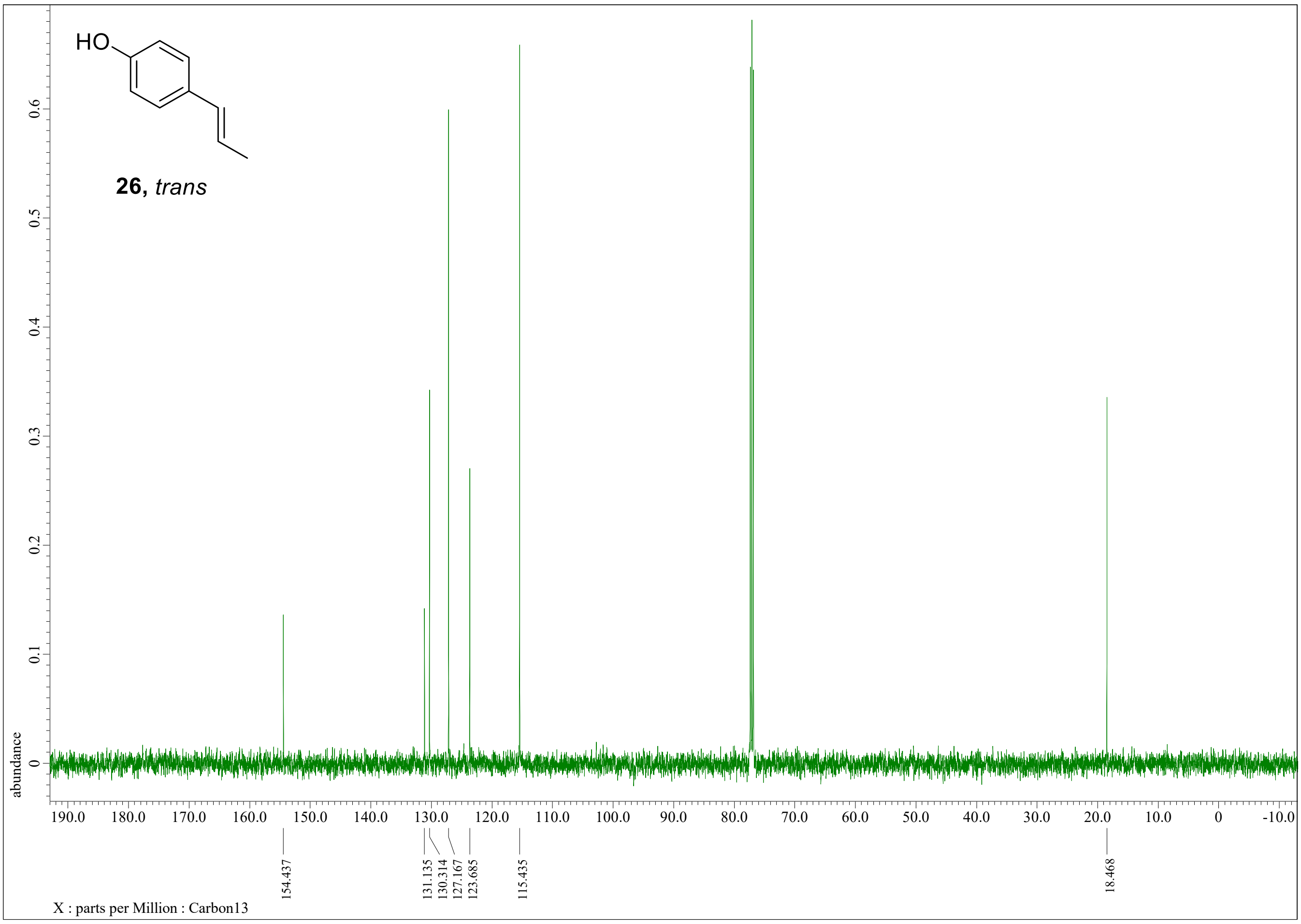
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
1.00
1.00
1.03
1.04
0.99
1.02
3.25
3.13
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.401
7.398
7.385
7.383
7.180
6.919
6.904
6.861
6.844
6.734
6.730
6.702
6.699
6.260
6.246
6.233
6.228
6.220
6.214
6.201
6.187
3.844
1.908
1.904
1.895
1.892
X : parts per Million : Proton

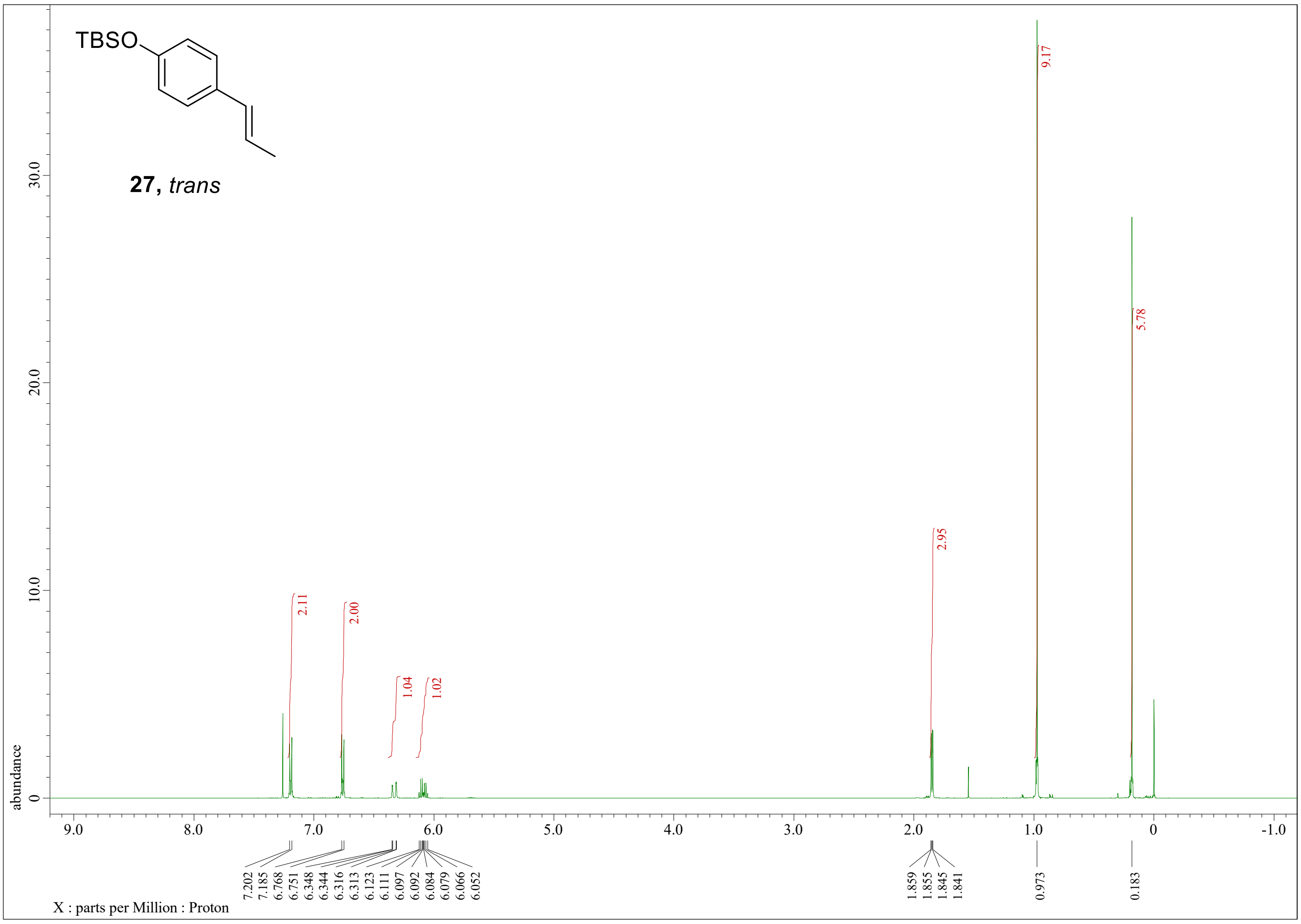

OMe
24, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
156.201
127.815
127.100
126.633
126.499
125.660
120.700
110.742
55.477
19.040
X : parts per Million : Carbon13

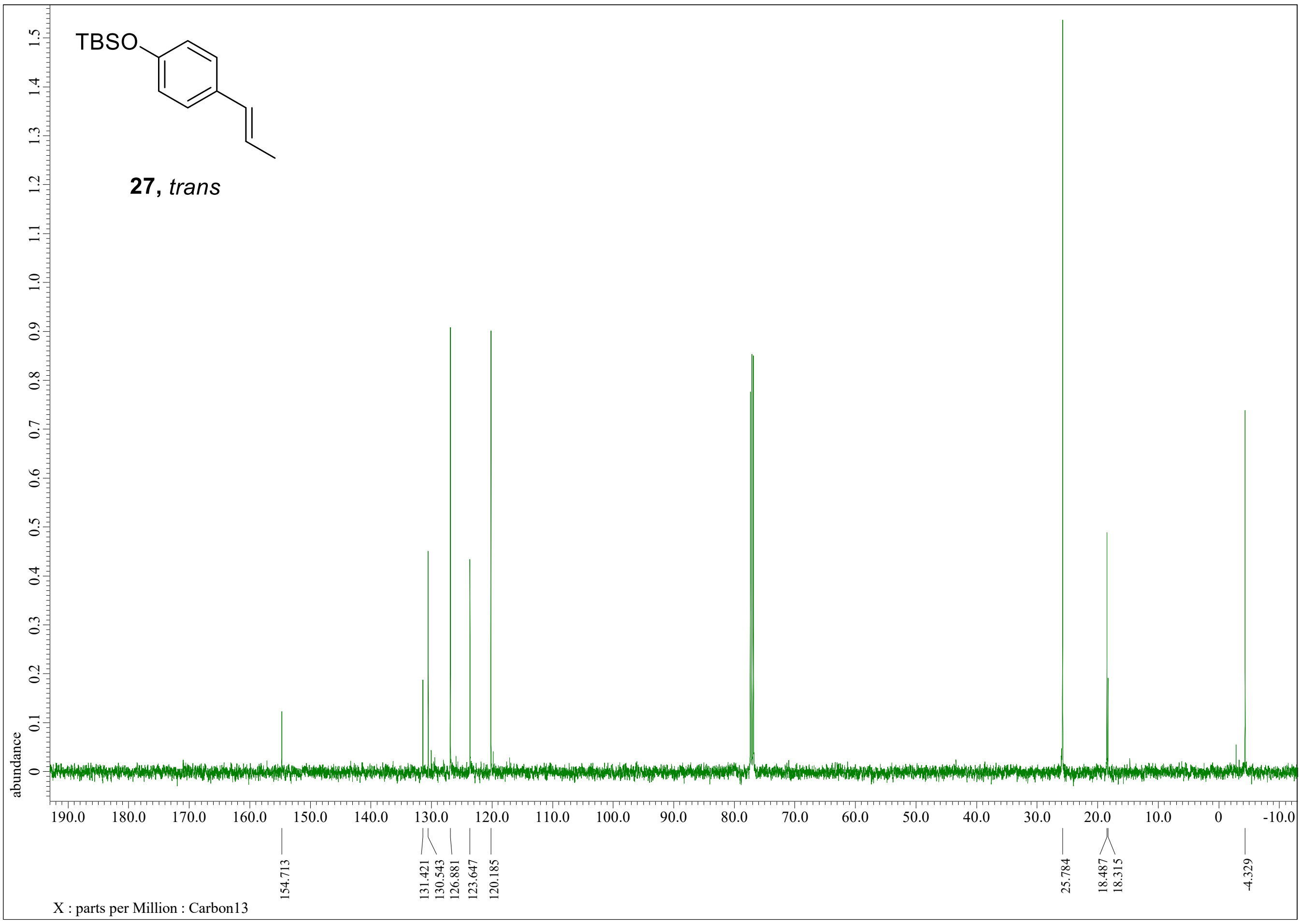

OMe
25, trans
abundance
0.96
1.00
0.98
0.97
0.99
1.01
3.20
3.00
7.222
7.205
7.189
6.935
6.920
6.875
6.870
6.867
6.760
6.755
6.743
6.391
6.388
6.359
6.357
6.262
6.249
6.236
6.231
6.217
3.811
1.887
1.885
1.875
1.871
X : parts per Million : Proton

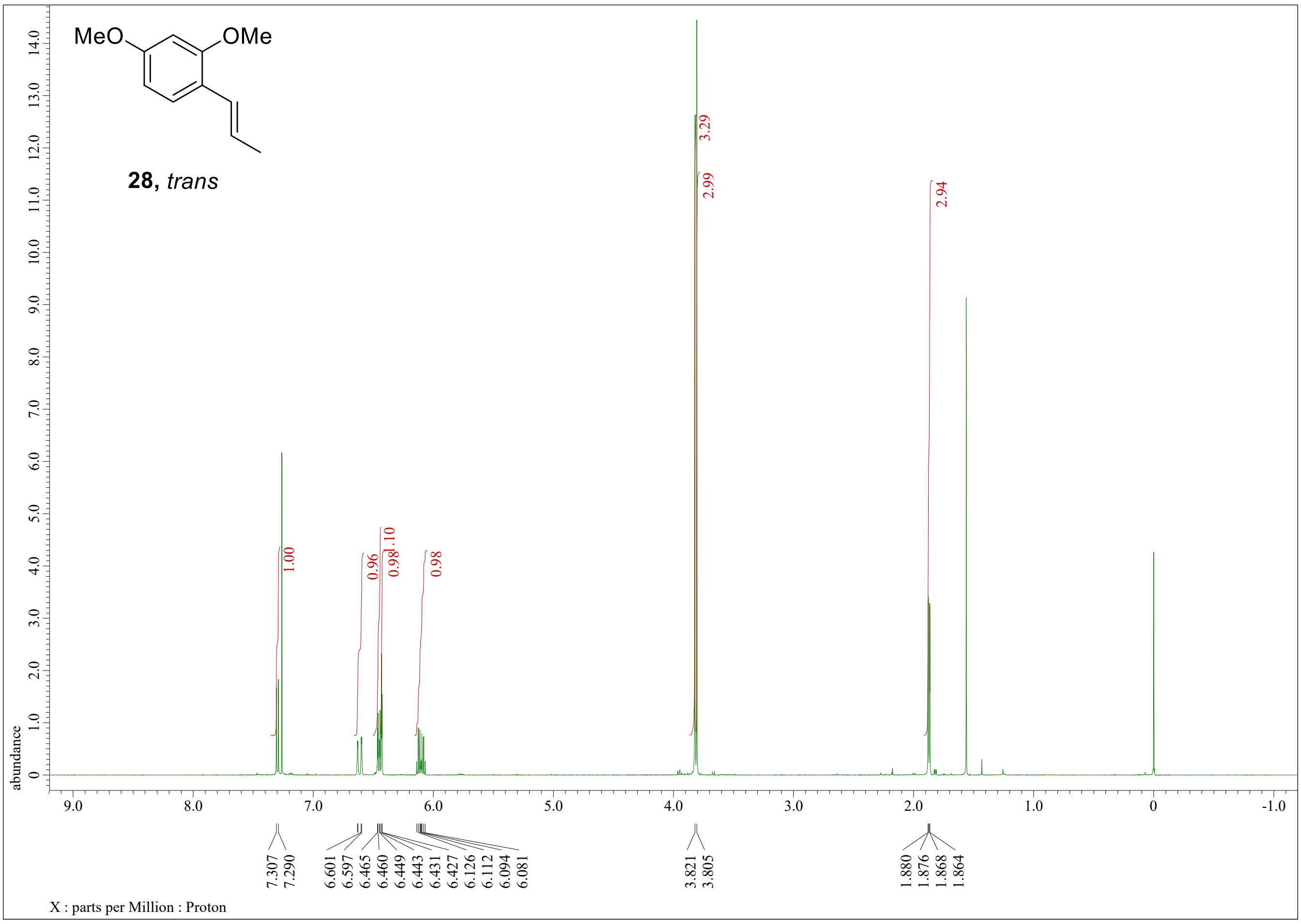

OMe
25, trans
abundance
159.816
139.471
130.963
129.494
126.165
118.563
112.382
111.247
55.219
18.554
X : parts per Million : Carbon13

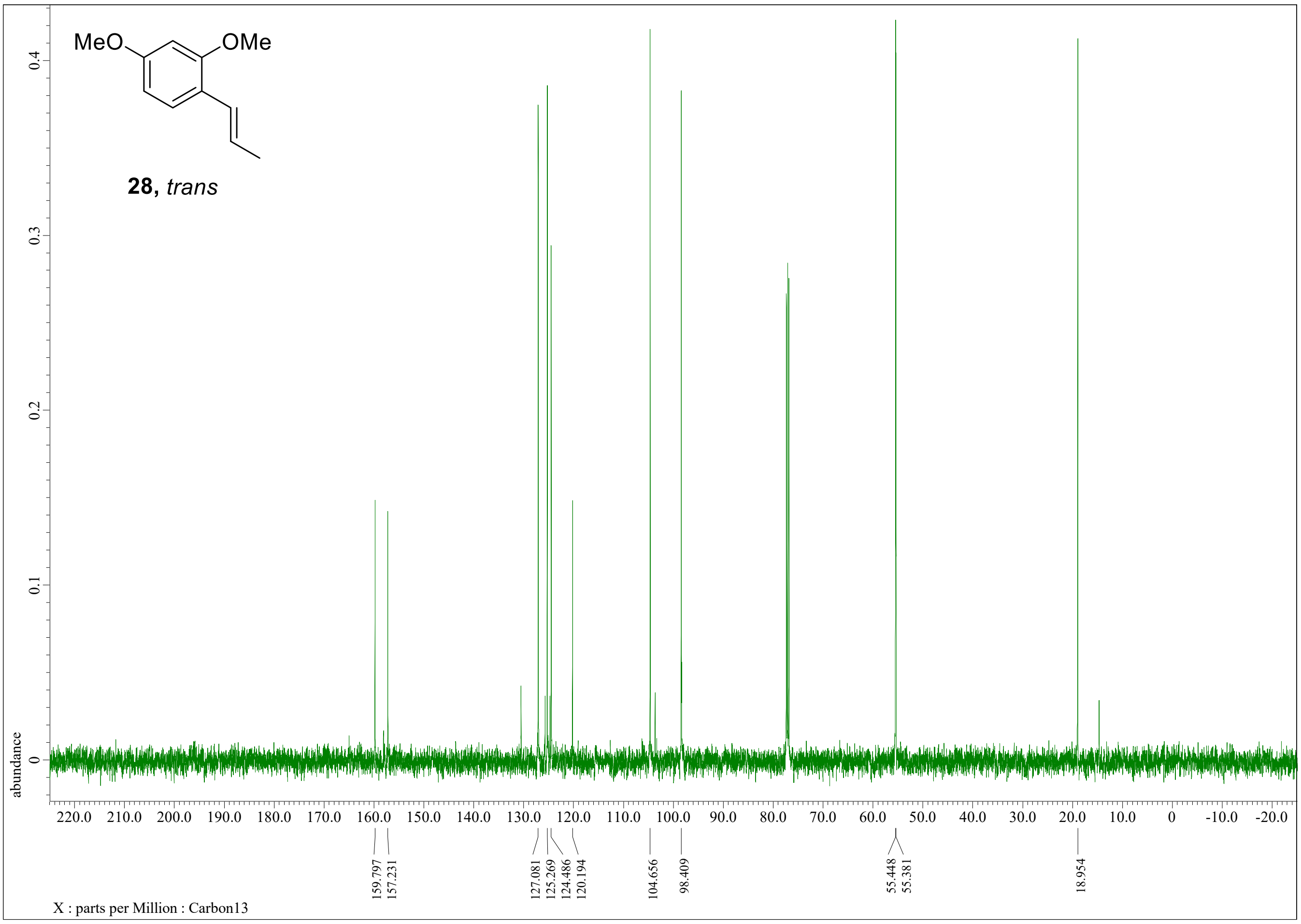

HO
26, trans
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
2.00
1.89
0.96
0.98
0.93
2.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.216
7.199
6.762
6.745
6.343
6.341
6.312
6.310
6.115
6.102
6.088
6.083
6.075
6.071
6.057
6.043
4.817
1.856
1.853
1.843
1.839
X : parts per Million : Proton

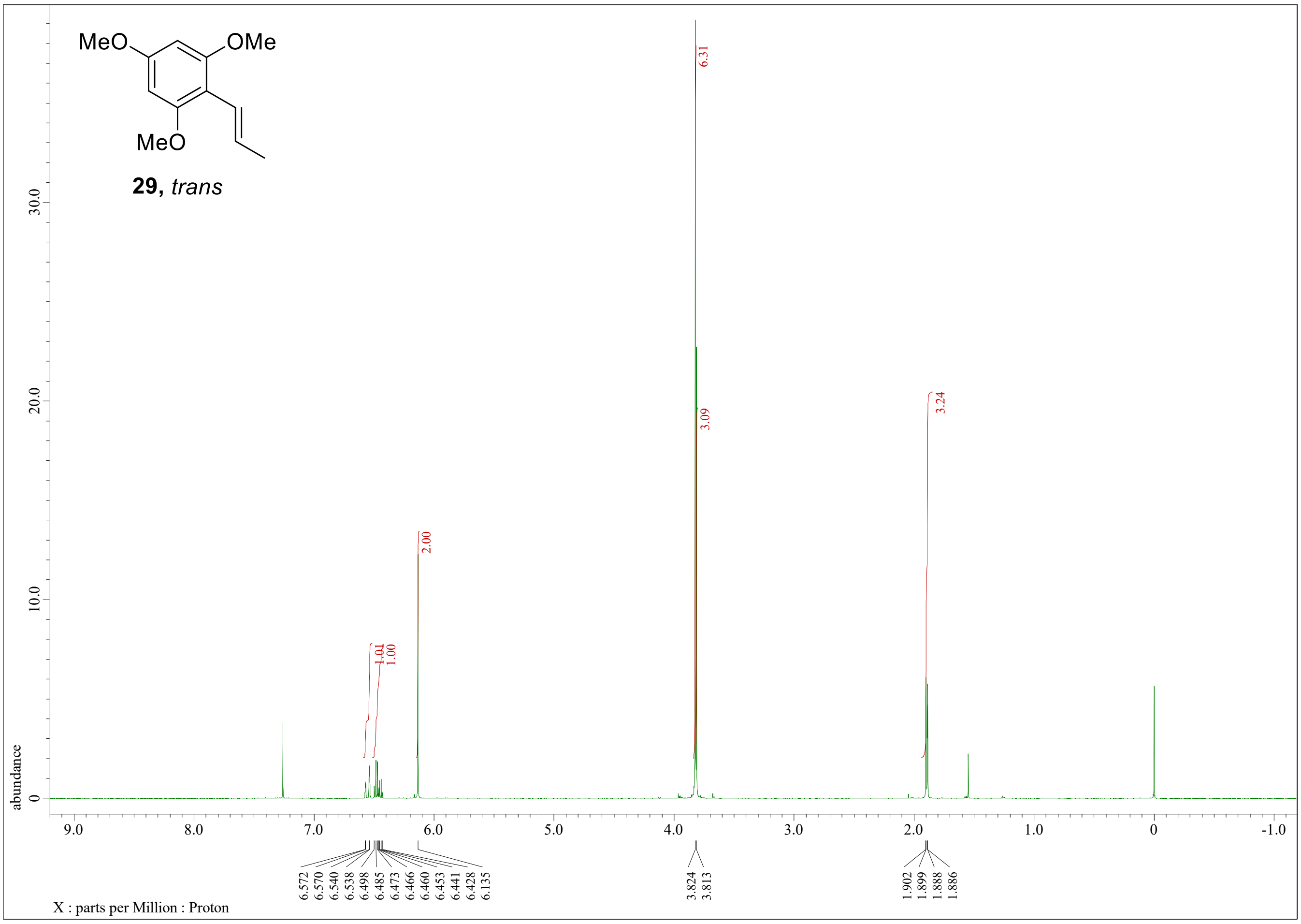

HO
26, trans
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
154.437
131.135
130.314
127.167
123.685
115.435
18.468
X : parts per Million : Carbon13

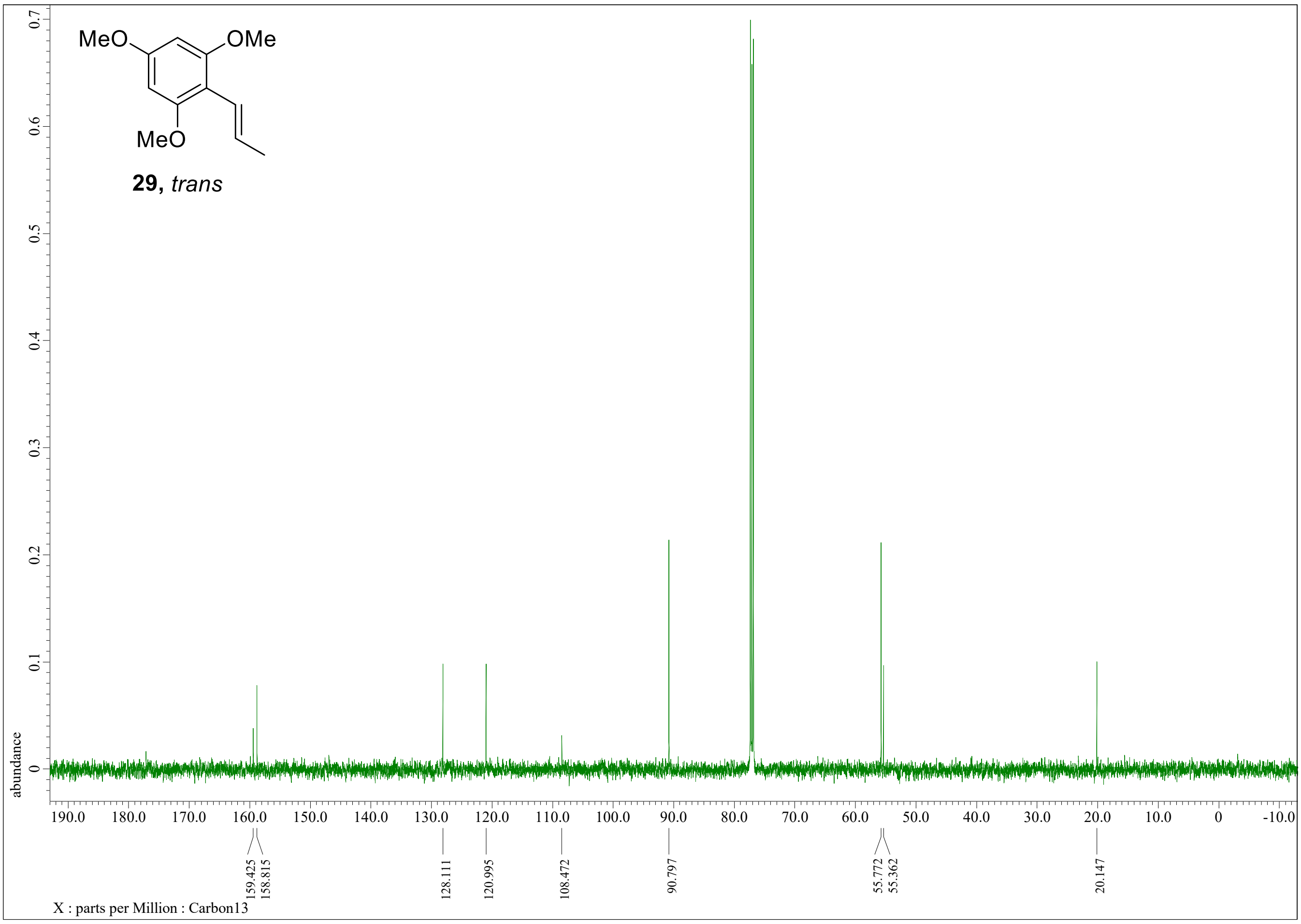

TBSO
27, trans
2.11
2.00
1.04
1.02
2.95
9.17
5.78
abundance
0
10.0
20.0
30.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.202
7.185
6.768
6.751
6.348
6.344
6.316
6.313
6.123
6.111
6.097
6.092
6.084
6.079
6.066
6.052
1.859
1.855
1.845
1.841
0.973
0.183
X : parts per Million : Proton

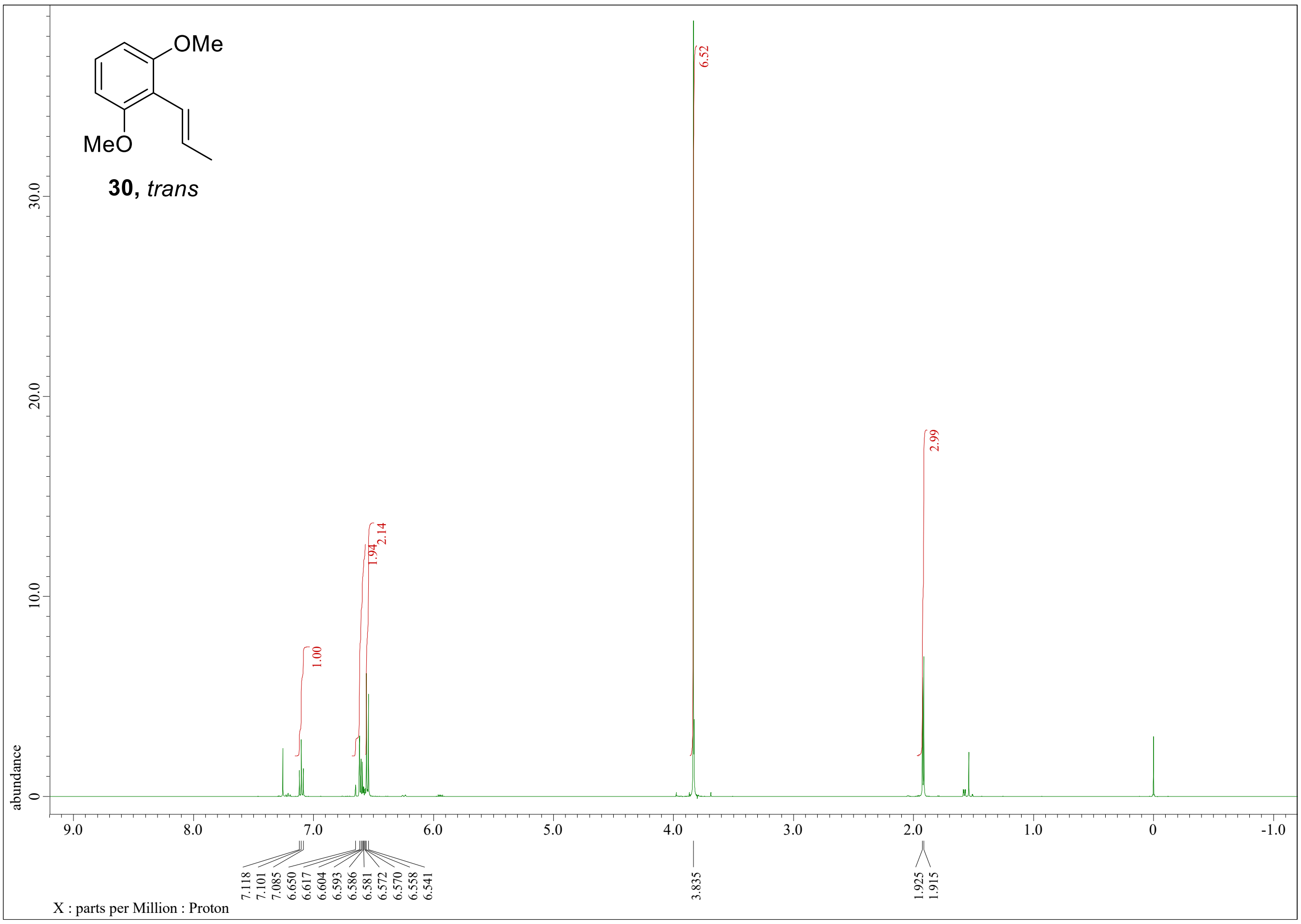

TBSO
27, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
154.713
131.421
130.543
126.881
123.647
120.185
25.784
18.487
18.315
-4.329
X : parts per Million : Carbon13

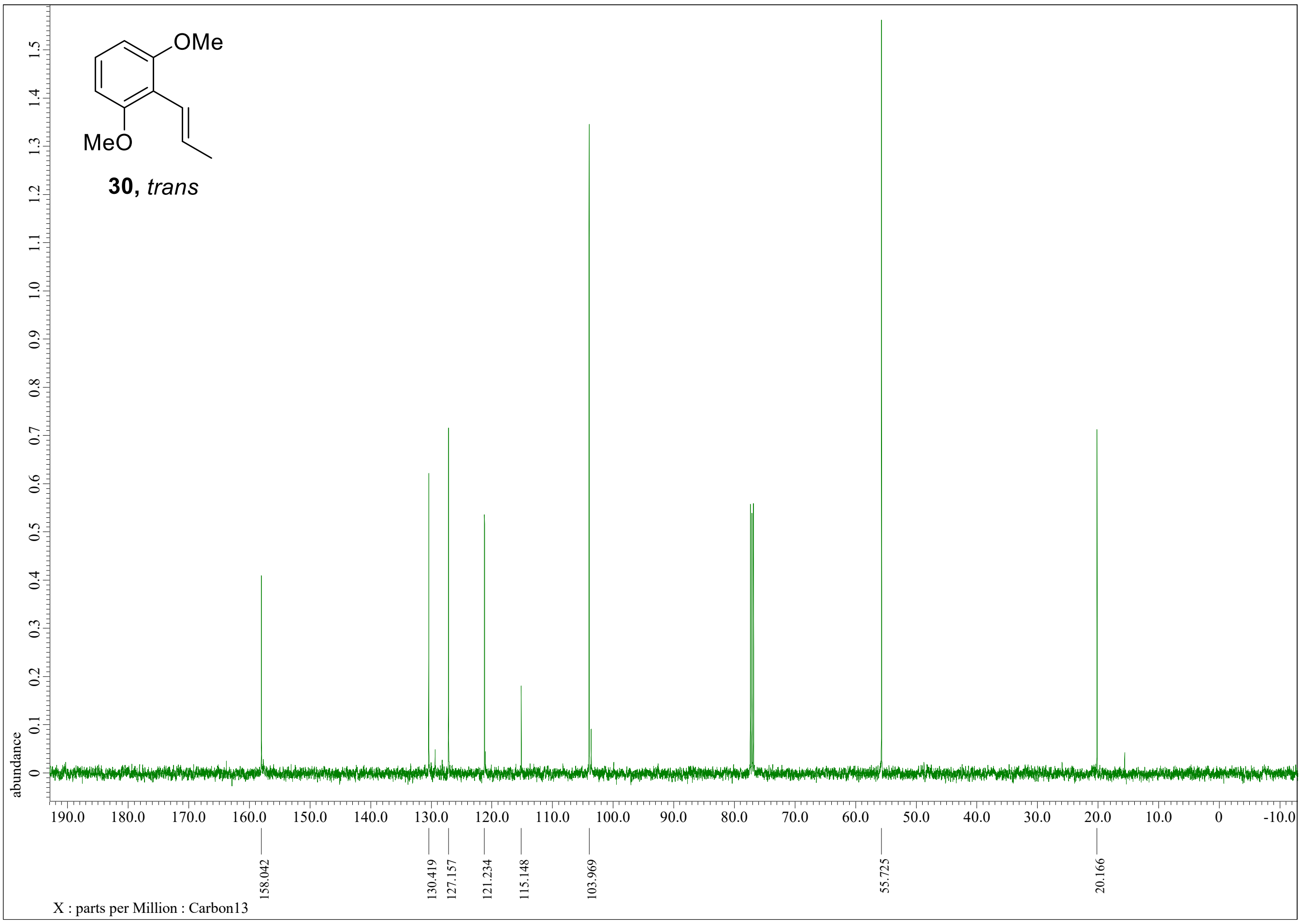

MeO
OMe
28, trans
1.00
0.96
0.98
1.10
0.98
3.29
2.99
2.94
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.307
7.290
6.601
6.597
6.465
6.460
6.449
6.443
6.431
6.427
6.126
6.112
6.094
6.081
3.821
3.805
1.880
1.876
1.868
1.864
X : parts per Million : Proton

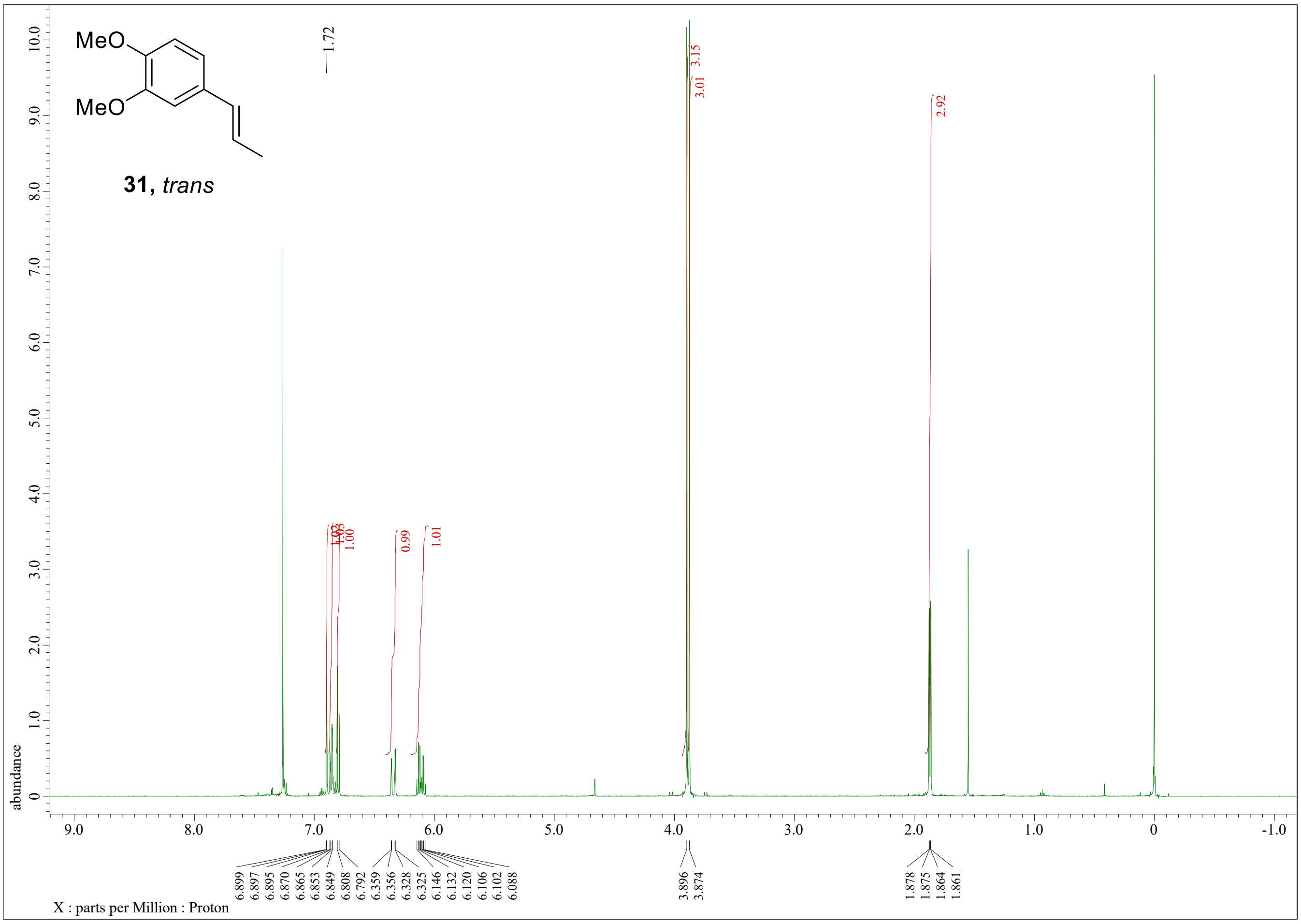

MeO
OMe
28, trans
abundance
0
0.1
0.2
0.3
0.4
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
159.797
157.231
127.081
125.269
124.486
120.194
104.656
98.409
55.448
55.381
18.954
X : parts per Million : Carbon13

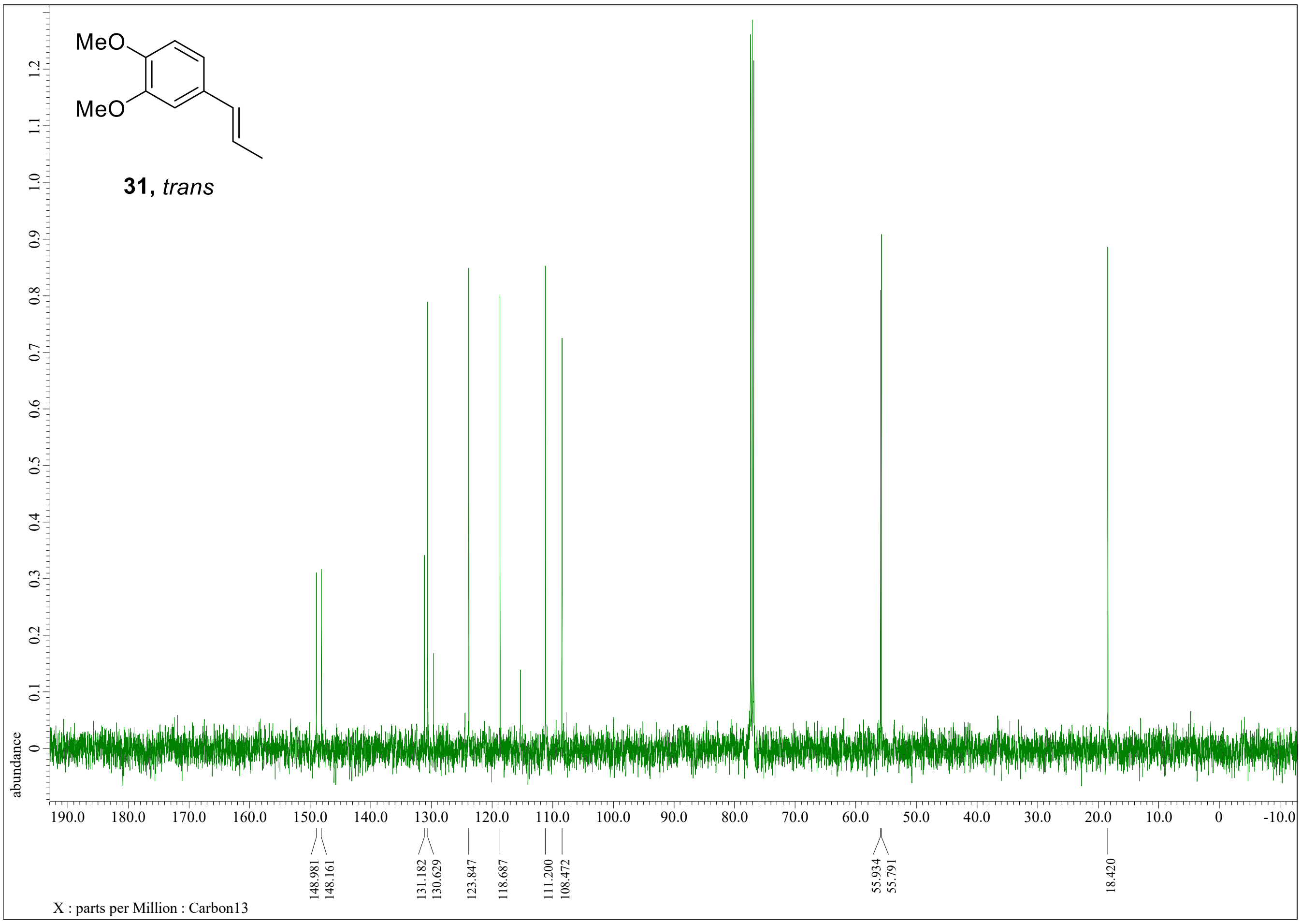

MeO
OMe
MeO
29, trans
6.31
3.09
3.24
2.00
1.01
1.00
30.0
20.0
10.0
0
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.572
6.570
6.540
6.538
6.498
6.485
6.473
6.466
6.460
6.453
6.441
6.428
6.135
3.824
3.813
1.902
1.899
1.888
1.886
X : parts per Million : Proton

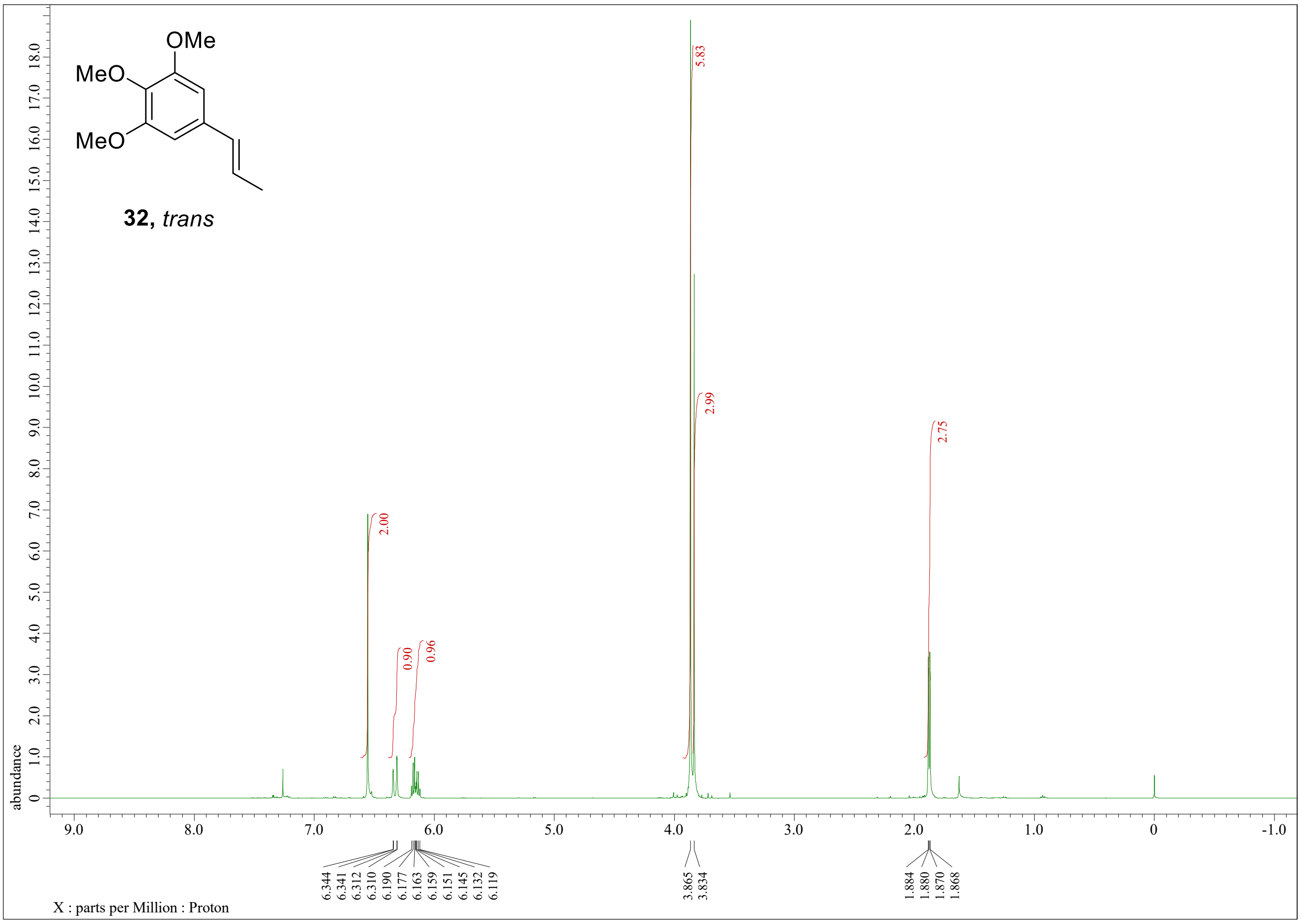

MeO
OMe
MeO
29, trans
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
159.425
158.815
128.111
120.995
108.472
90.797
55.772
55.362
20.147
X : parts per Million : Carbon13

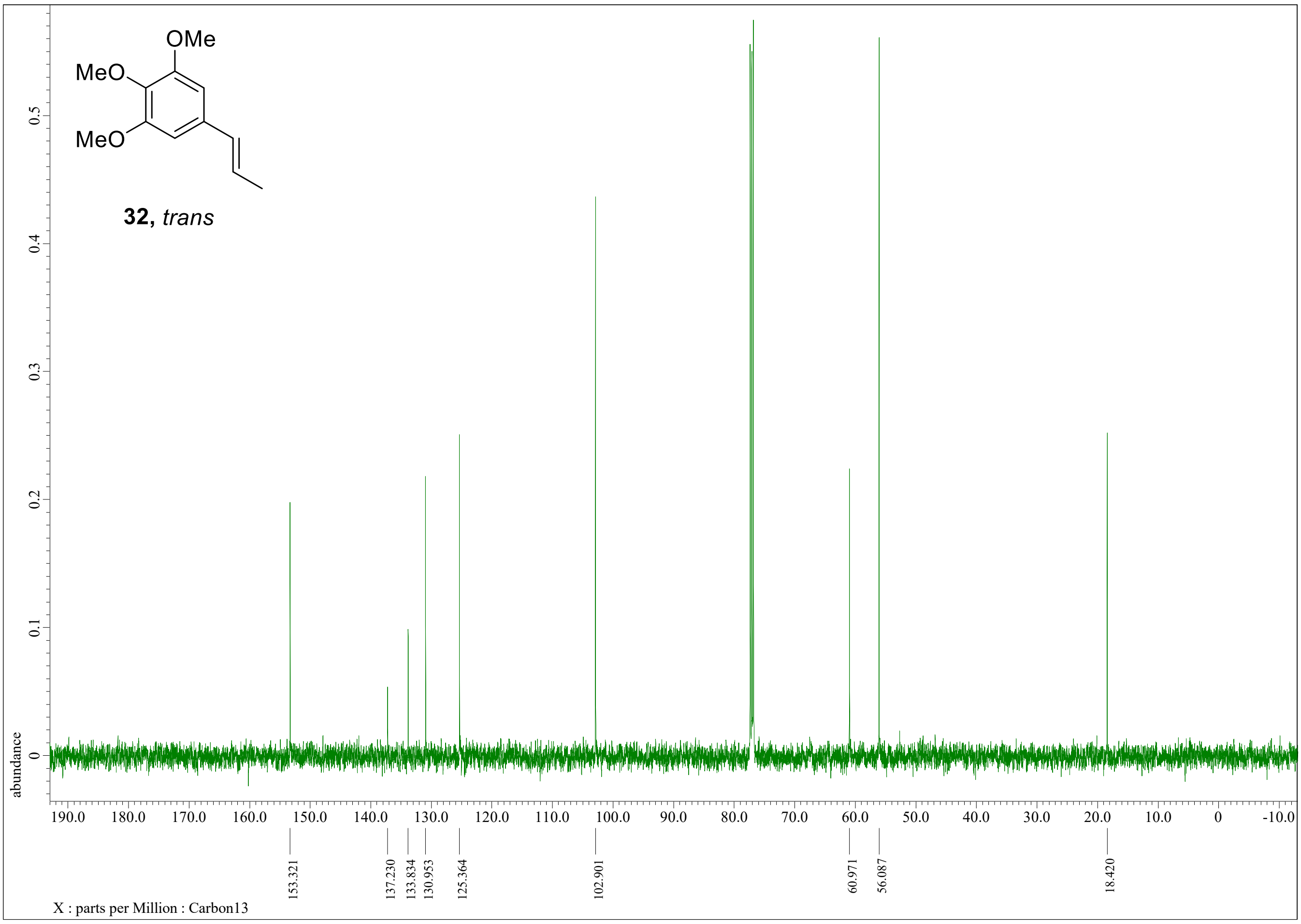

OMe
MeO
30, trans
abundance
0
10.0
20.0
30.0
1.00
1.94
2.14
6.52
2.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.118
7.101
7.085
6.650
6.617
6.604
6.593
6.586
6.581
6.572
6.570
6.558
6.541
3.835
1.925
1.915
X : parts per Million : Proton

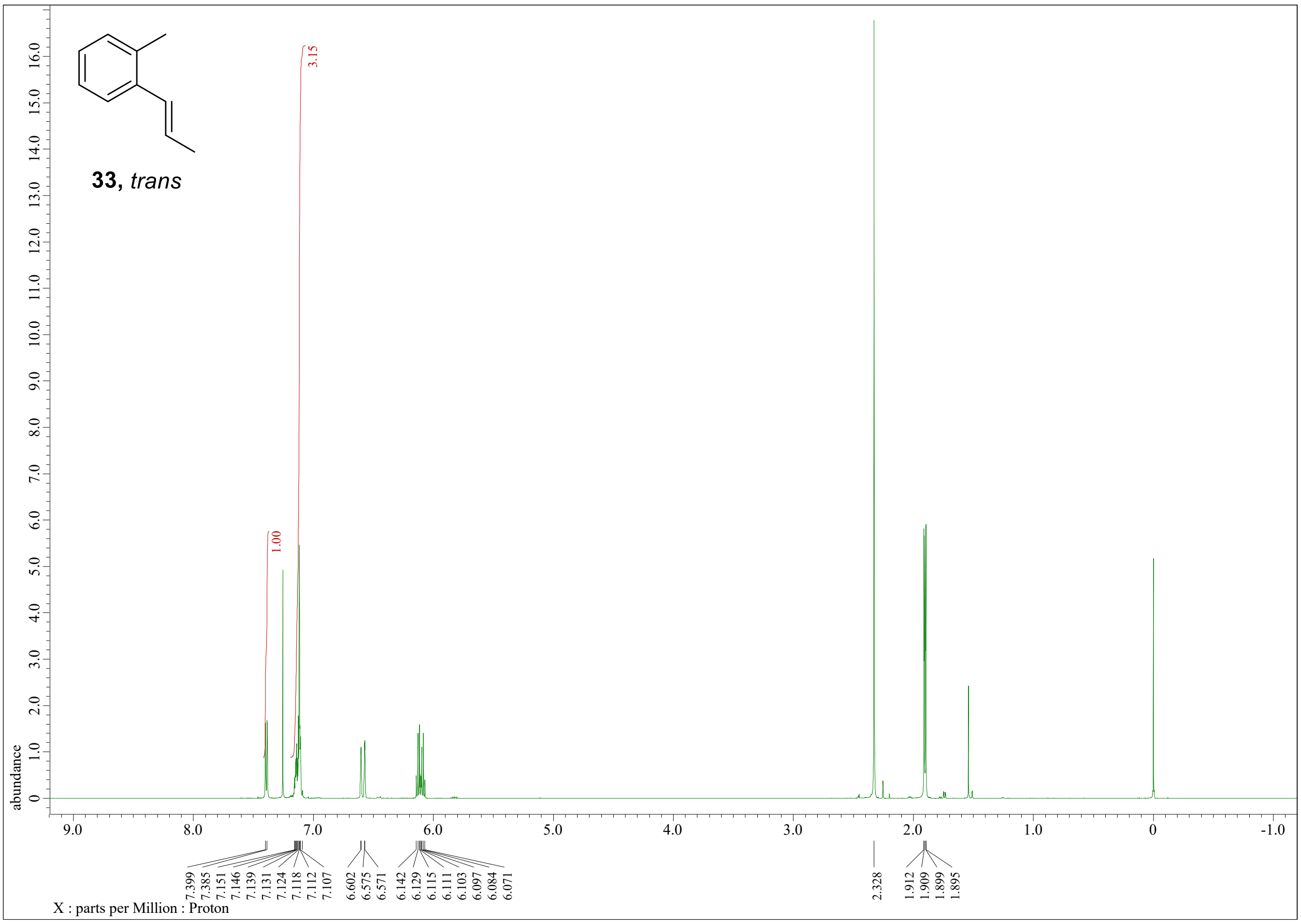

OMe
MeO
30, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
158.042
130.419
127.157
121.234
115.148
103.969
55.725
20.166
X : parts per Million : Carbon13

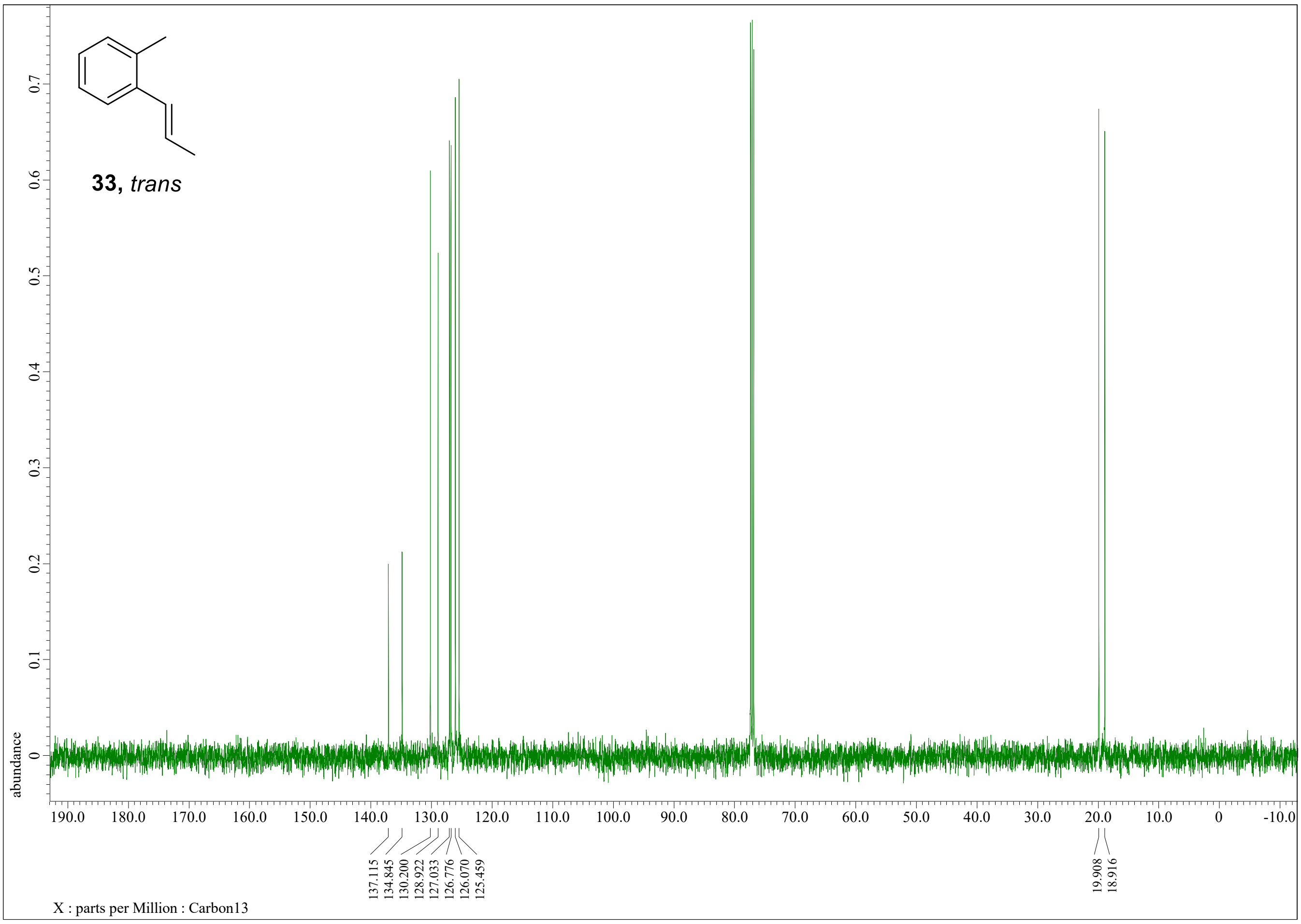

MeO
MeO
31, trans
1.72
3.15
3.01
2.92
1.00
0.99
1.01
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.899
6.897
6.895
6.870
6.865
6.853
6.849
6.808
6.792
6.359
6.356
6.328
6.325
6.146
6.132
6.120
6.106
6.102
6.088
3.896
3.874
1.878
1.875
1.864
1.861
X : parts per Million : Proton

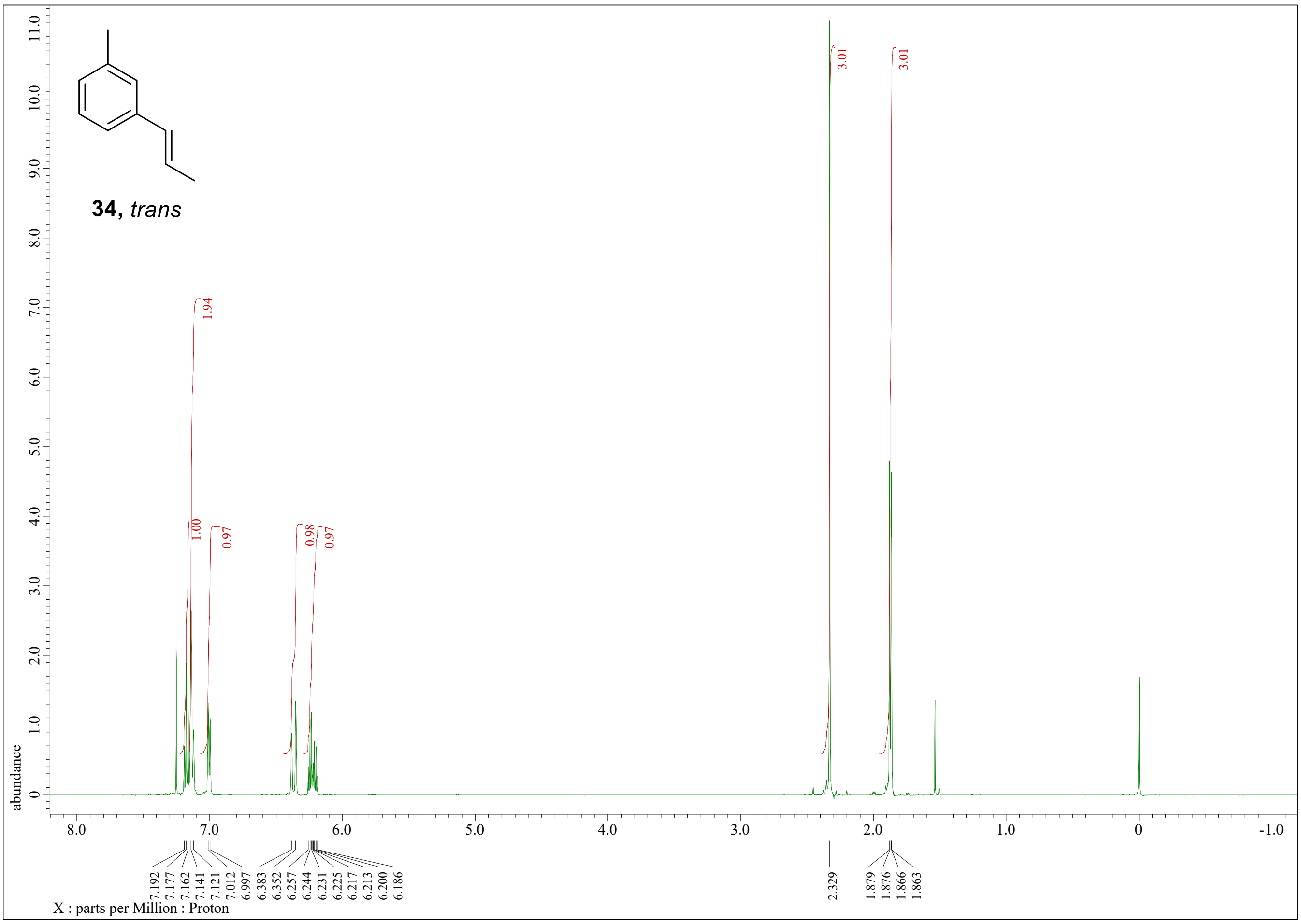

MeO
MeO
31, trans
abundance
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
148.981
148.161
131.182
130.629
123.847
118.687
111.200
108.472
55.934
55.791
18.420
X : parts per Million : Carbon13

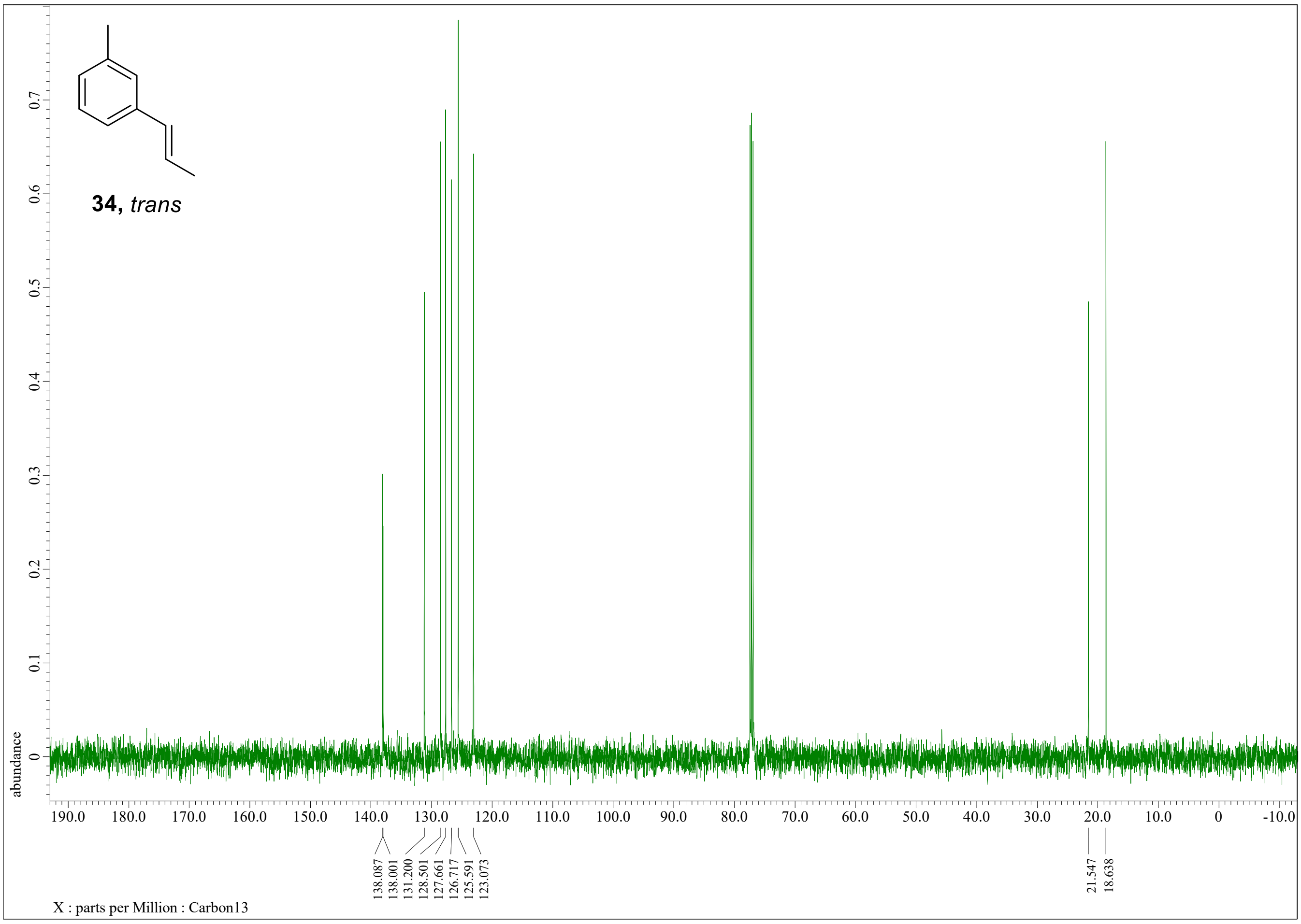

OMe
MeO
MeO
32, trans
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
5.83
2.99
2.75
2.00
0.90
0.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.344
6.341
6.312
6.310
6.190
6.177
6.163
6.159
6.151
6.145
6.132
6.119
3.865
3.834
1.884
1.880
1.870
1.868
X : parts per Million : Proton

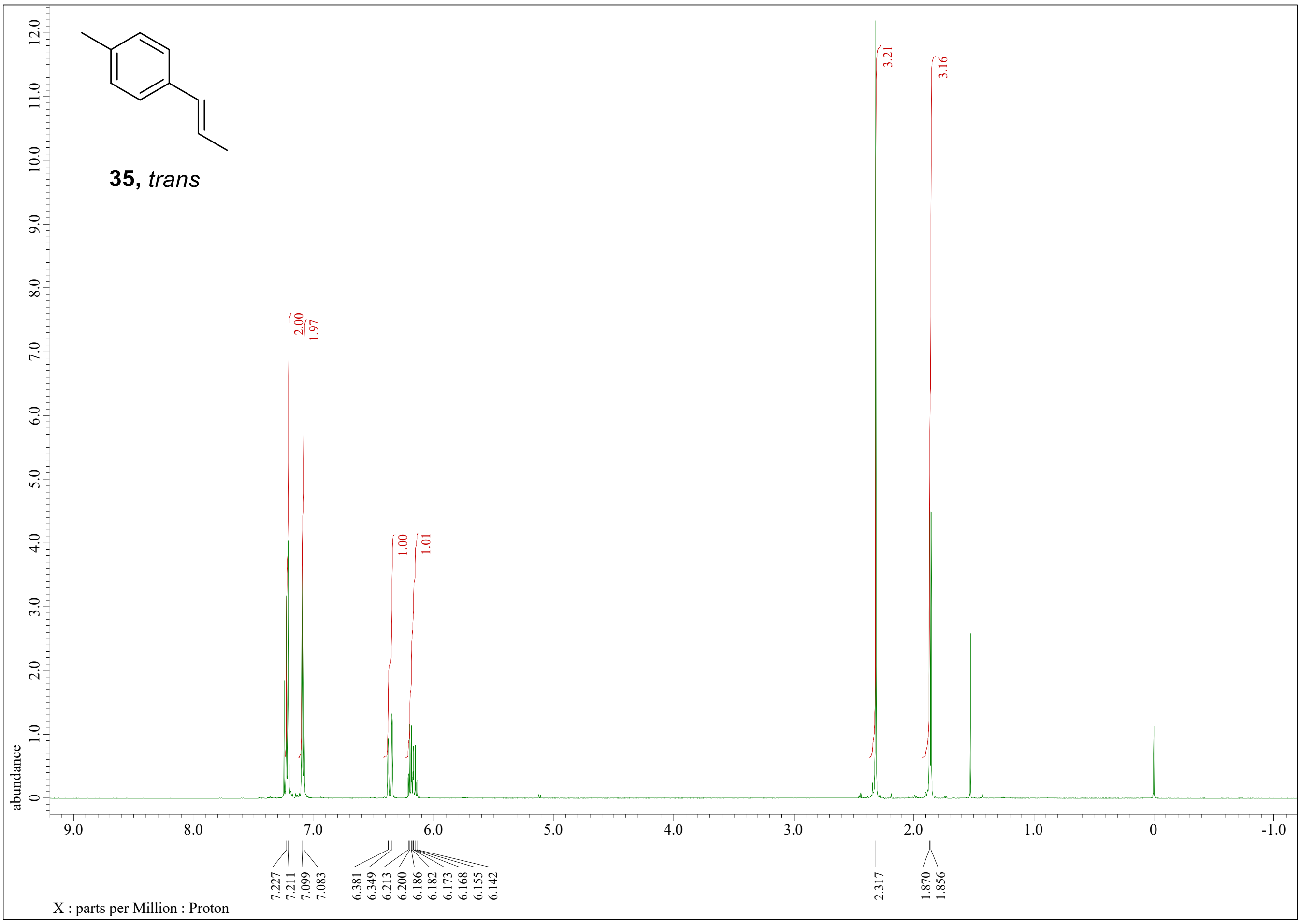

OMe
MeO
MeO
32, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
153.321
137.230
133.834
130.953
125.364
102.901
60.971
56.087
18.420
X : parts per Million : Carbon13

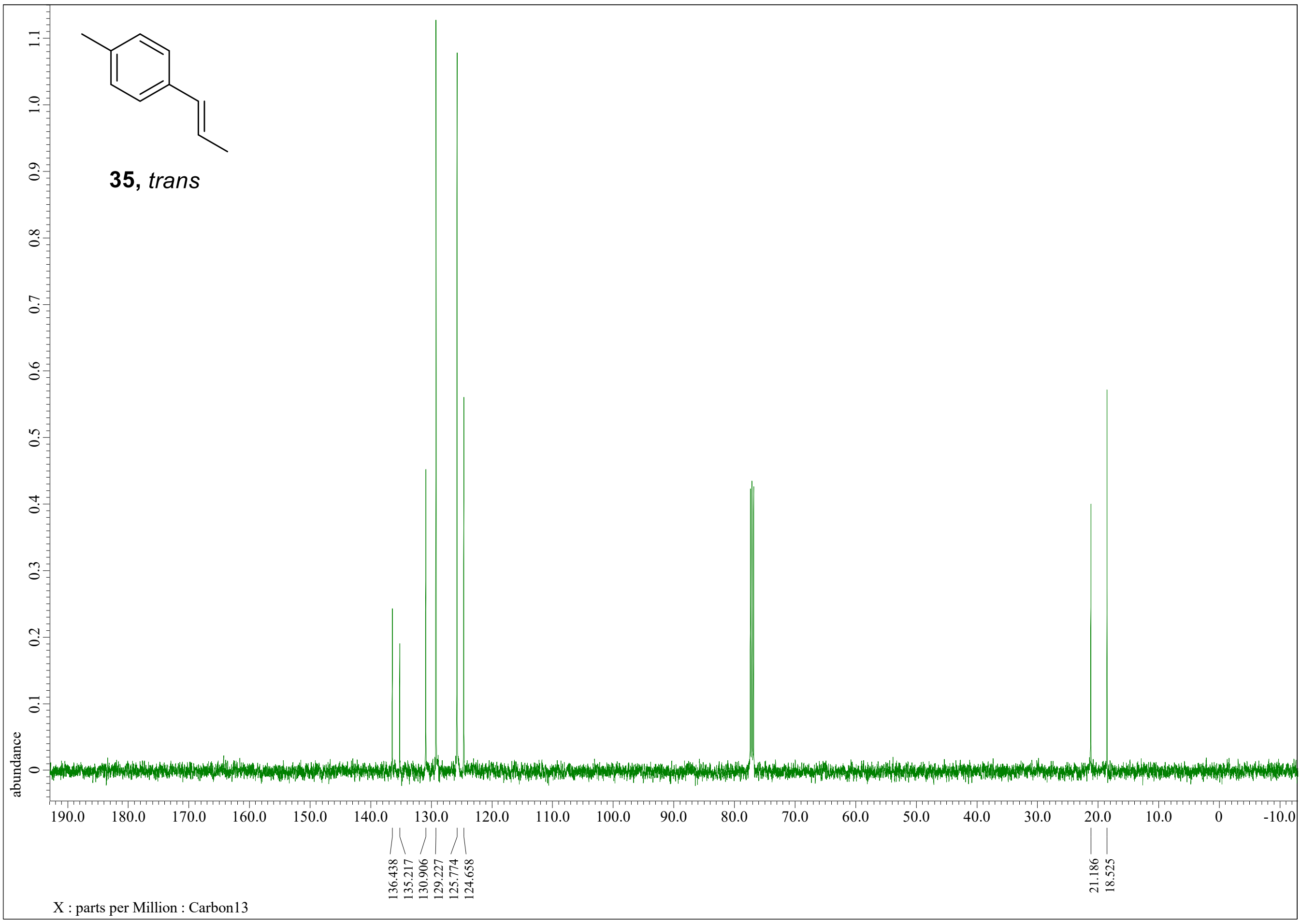

33, *trans*
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
1.00
3.15
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.399
7.385
7.151
7.146
7.139
7.131
7.124
7.118
7.112
7.107
6.602
6.575
6.571
6.142
6.129
6.115
6.111
6.103
6.097
6.084
6.071
2.328
1.912
1.909
1.899
1.895
X : parts per Million : Proton

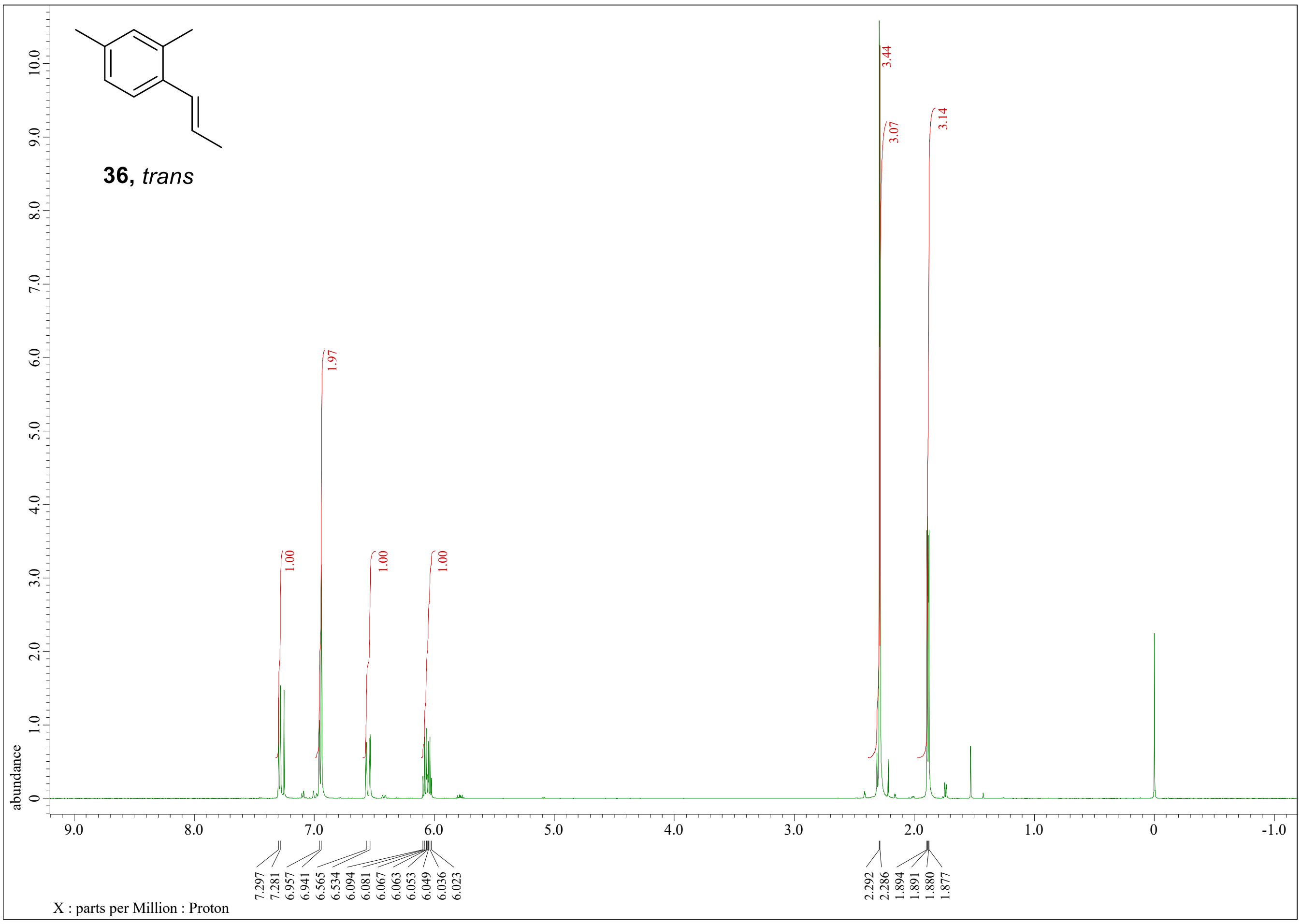

33, *trans*
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
137.115
134.845
130.200
128.922
127.033
126.776
126.070
125.459
19.908
18.916
X : parts per Million : Carbon13


34, trans
abundance
X : parts per Million : Proton
1.94
1.00
0.97
0.98
0.97
3.01
3.01
7.192
7.177
7.162
7.141
7.121
7.012
6.997
6.383
6.352
6.257
6.244
6.231
6.225
6.217
6.213
6.200
6.186
2.329
1.879
1.876
1.866
1.863

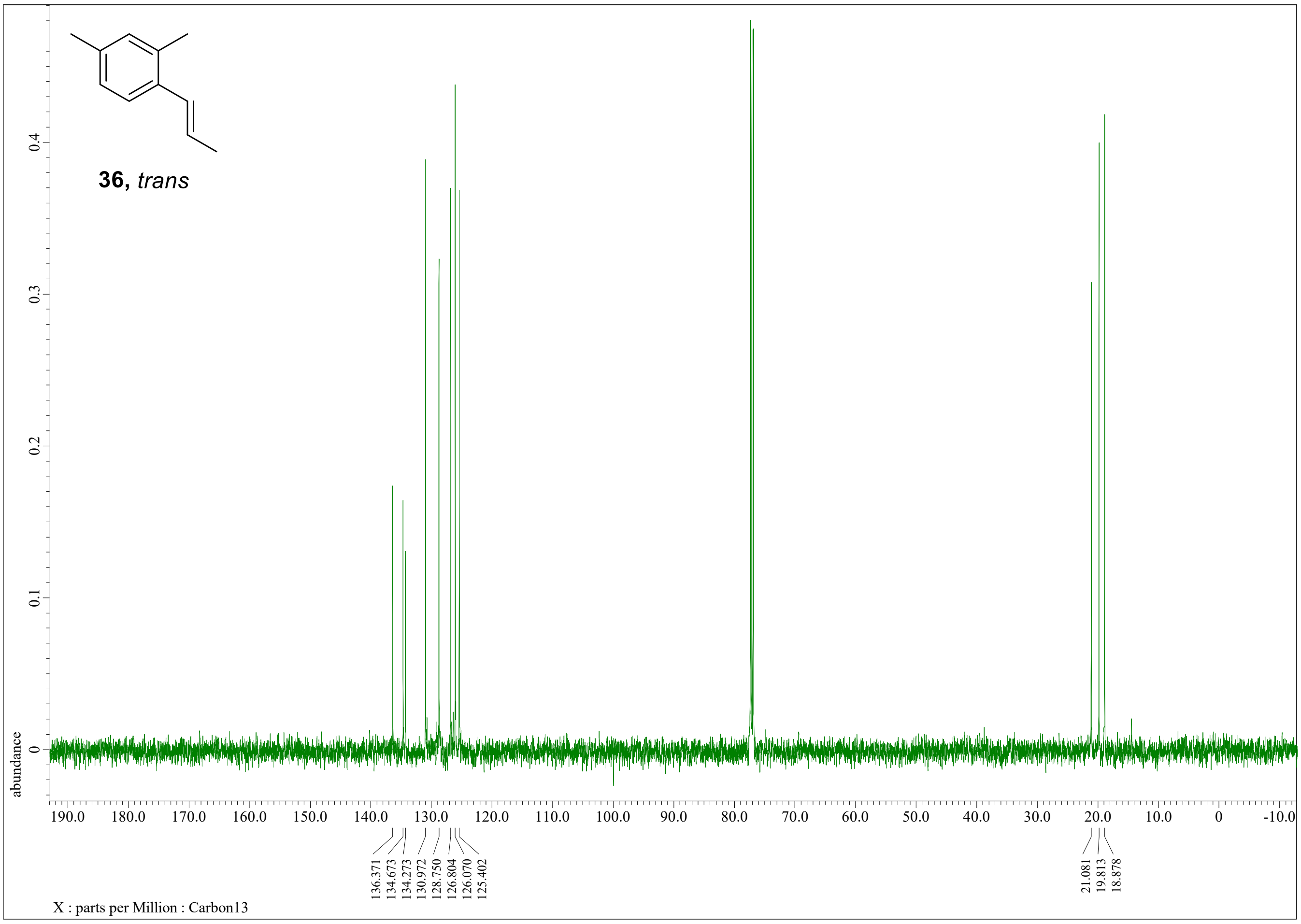

34, trans
abundance
X : parts per Million : Carbon13
138.087
138.001
131.200
128.501
127.661
126.717
125.591
123.073
21.547
18.638


35, trans
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
2.00
1.97
1.00
1.01
3.21
3.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.227
7.211
7.099
7.083
6.381
6.349
6.213
6.200
6.186
6.182
6.173
6.168
6.155
6.142
2.317
1.870
1.856
X : parts per Million : Proton

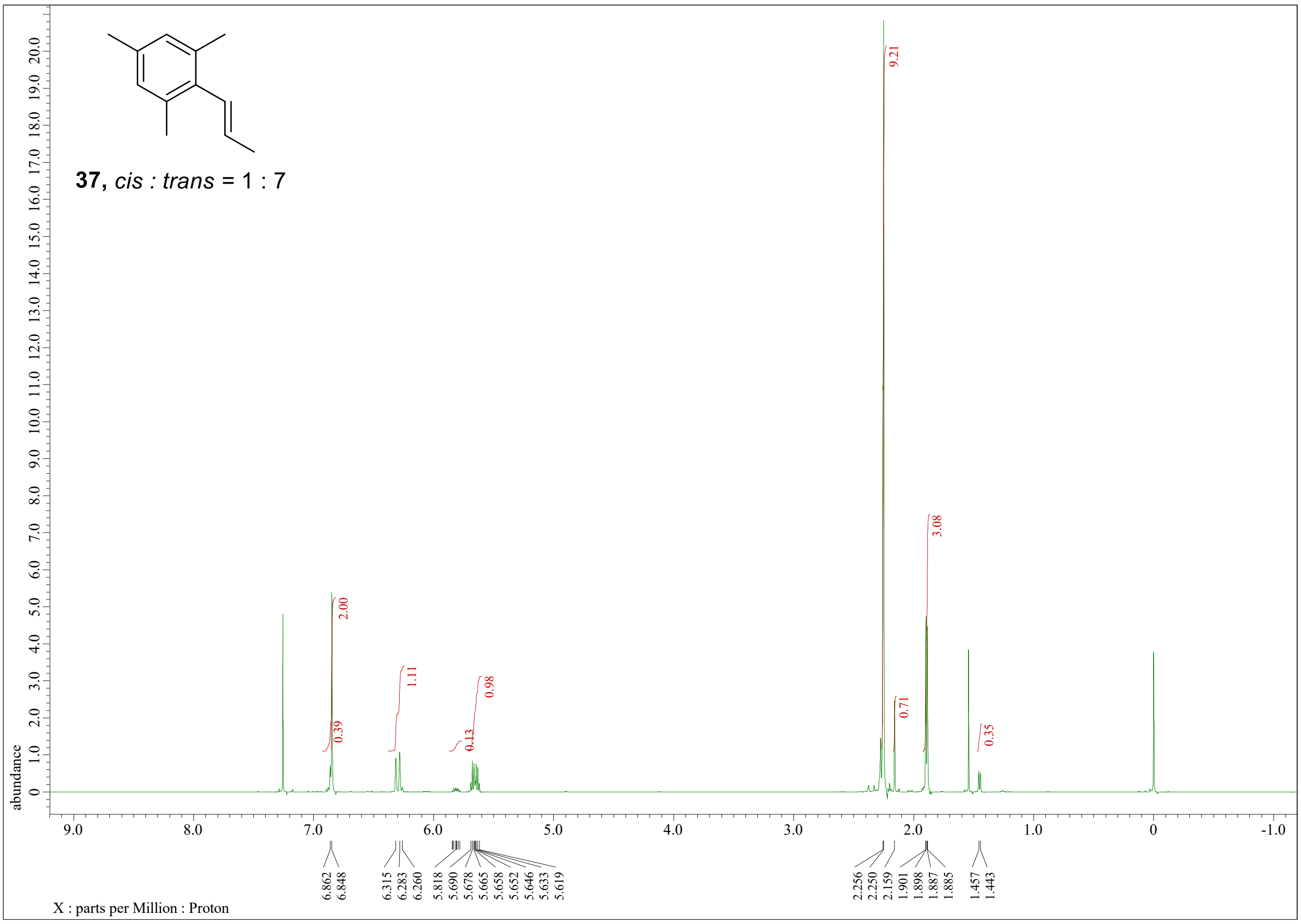

35, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
136.438
135.217
130.906
129.227
125.774
124.658
21.186
18.525
X : parts per Million : Carbon13

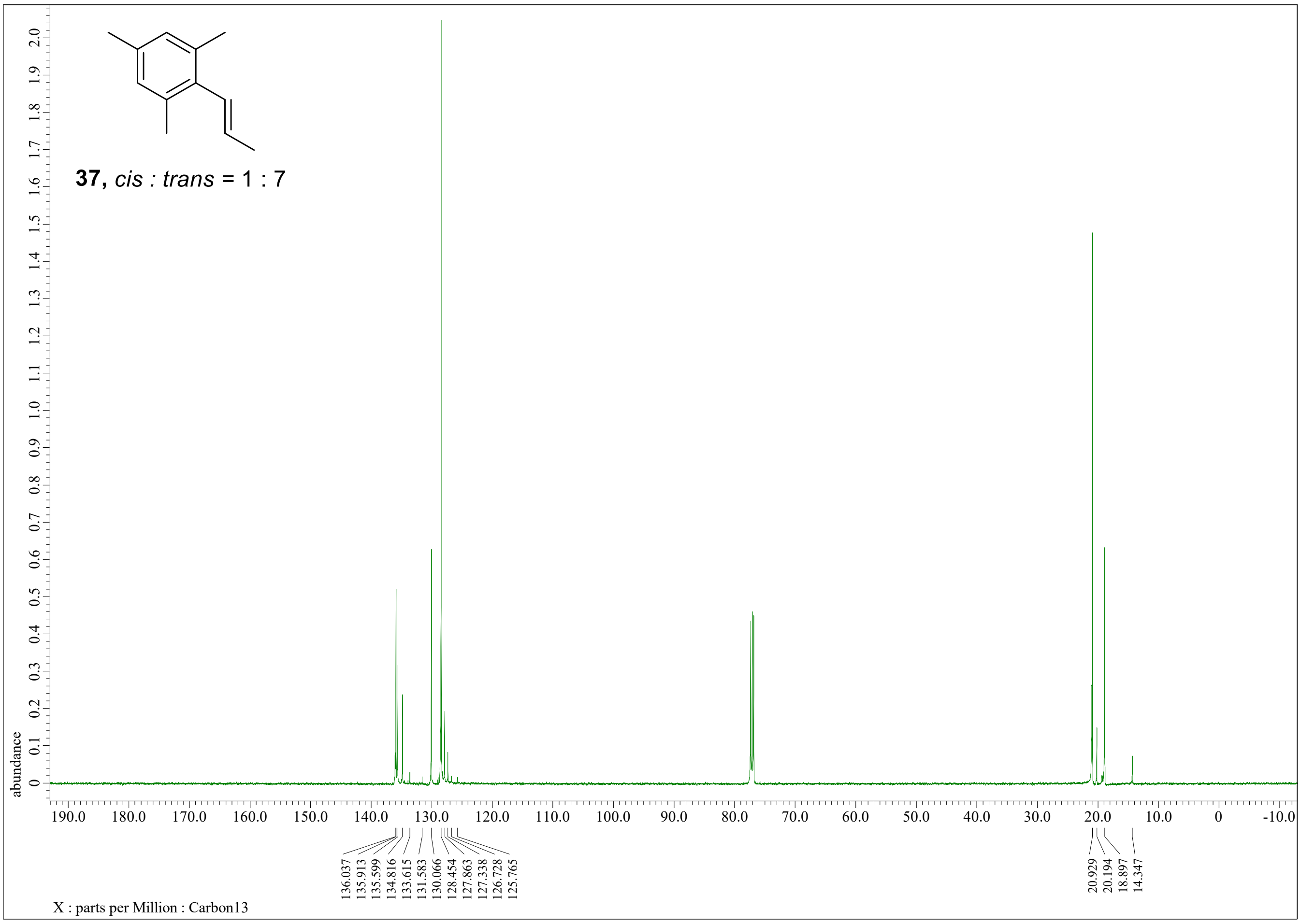


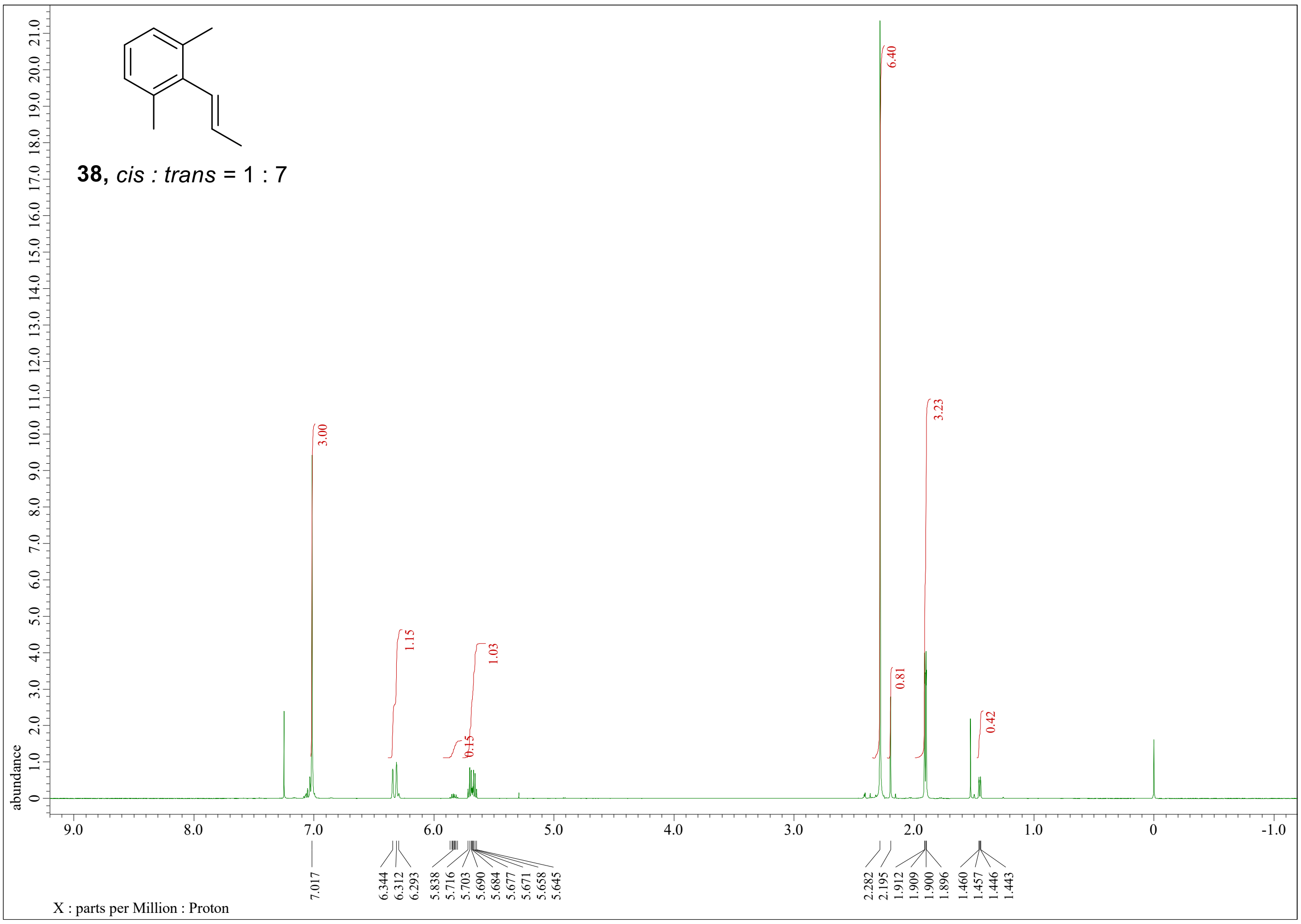
36, ***trans***



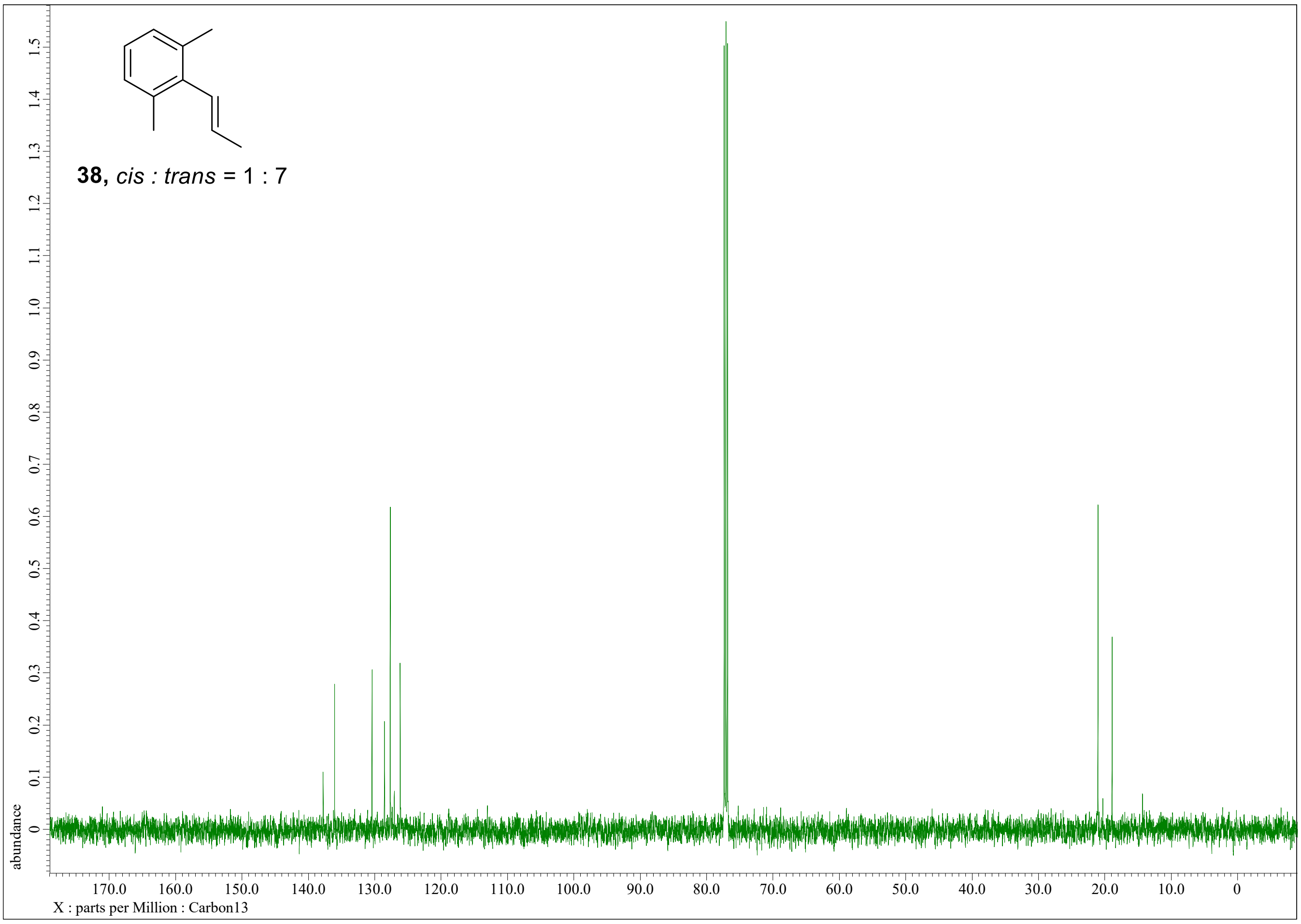
36, ***trans***


37, cis : trans = 1 : 7
abundance
9.21
3.08
2.00
1.11
0.98
0.71
0.39
0.13
0.35
6.862
6.848
6.315
6.283
6.260
5.818
5.690
5.678
5.665
5.658
5.652
5.646
5.633
5.619
2.256
2.250
2.159
1.901
1.898
1.887
1.885
1.457
1.443
X : parts per Million : Proton

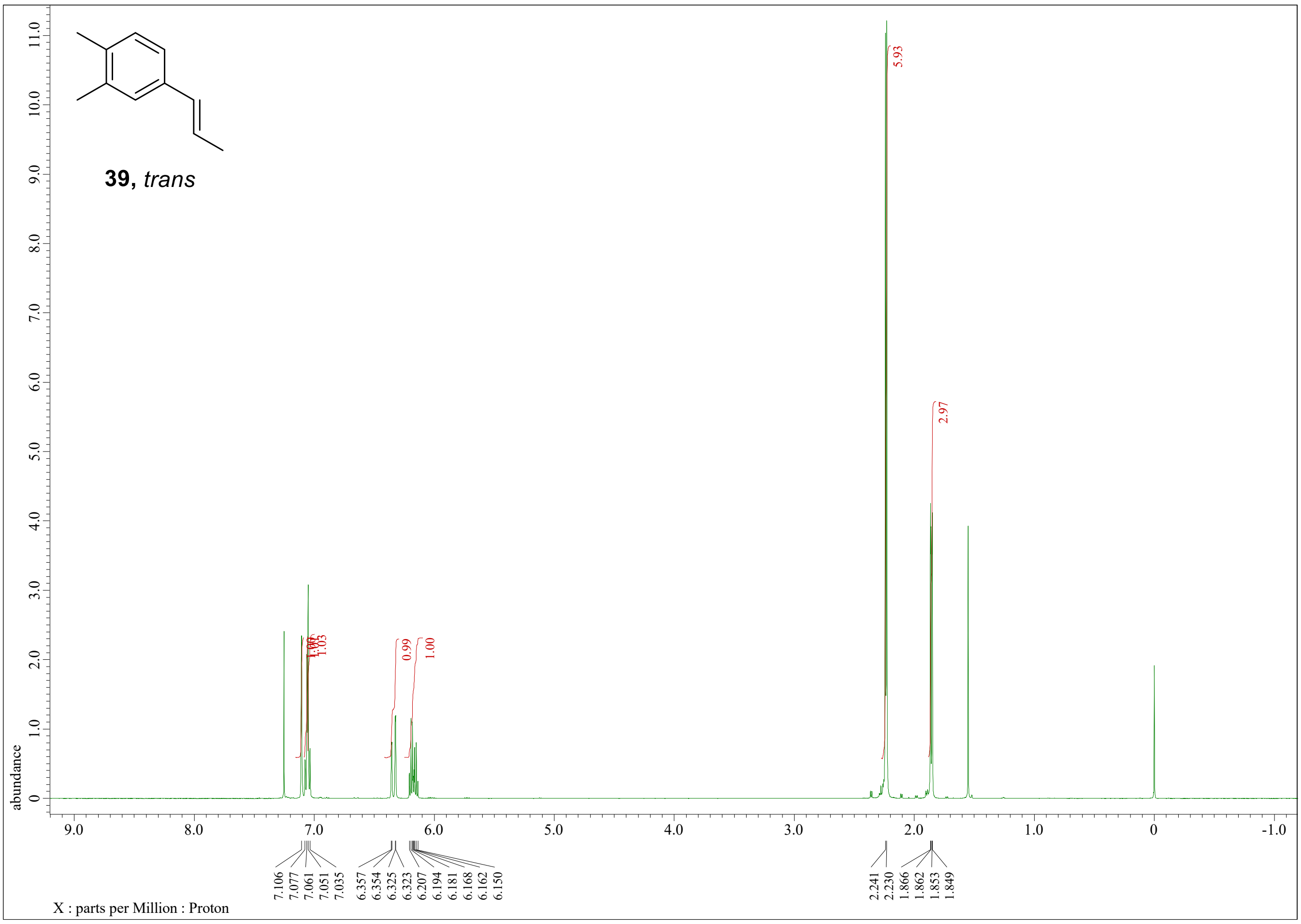

37, cis : trans = 1 : 7
abundance
136.037
135.913
135.599
134.816
133.615
131.583
130.066
128.454
127.863
127.338
126.728
125.765
20.929
20.194
18.897
14.347
X : parts per Million : Carbon13

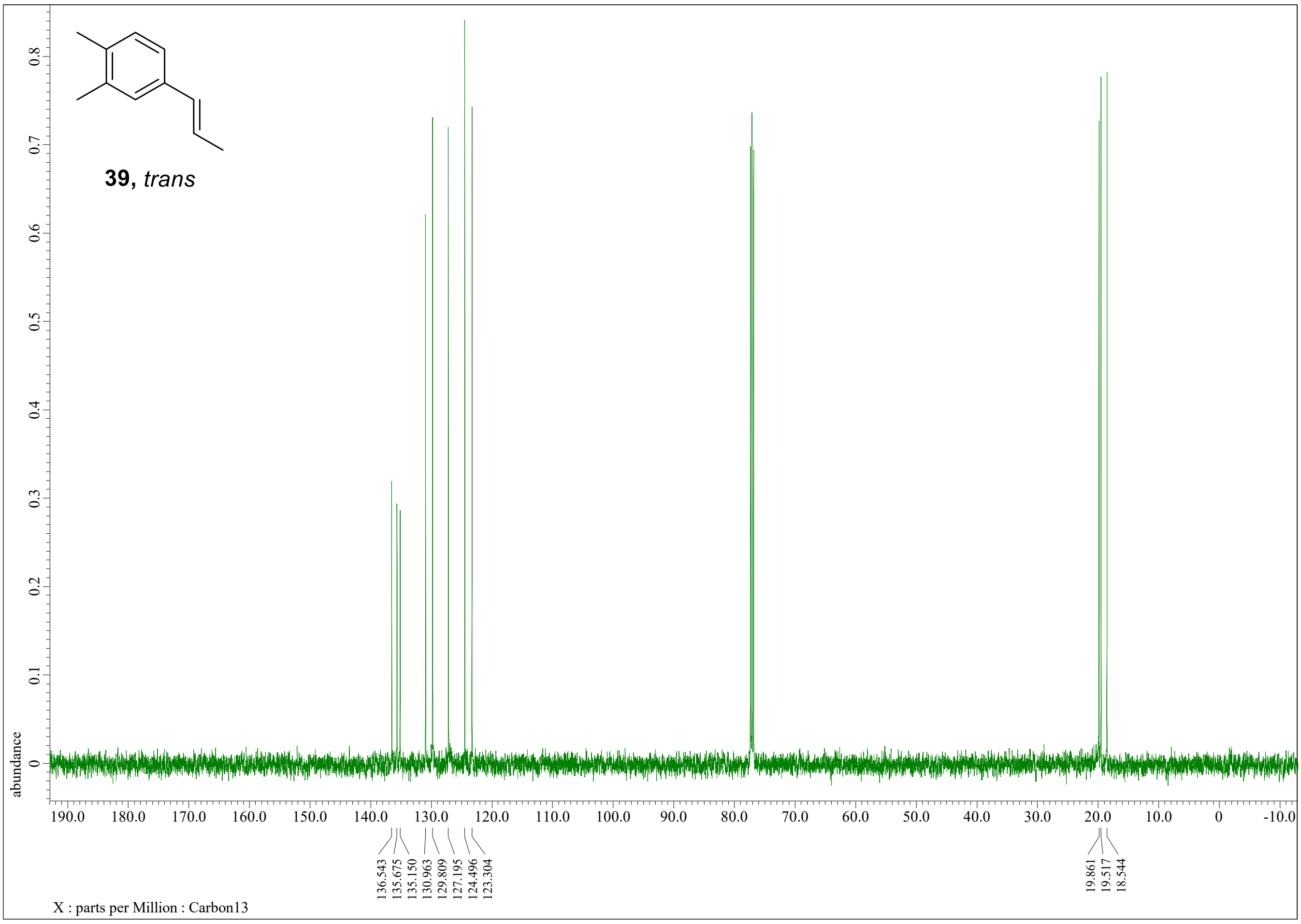


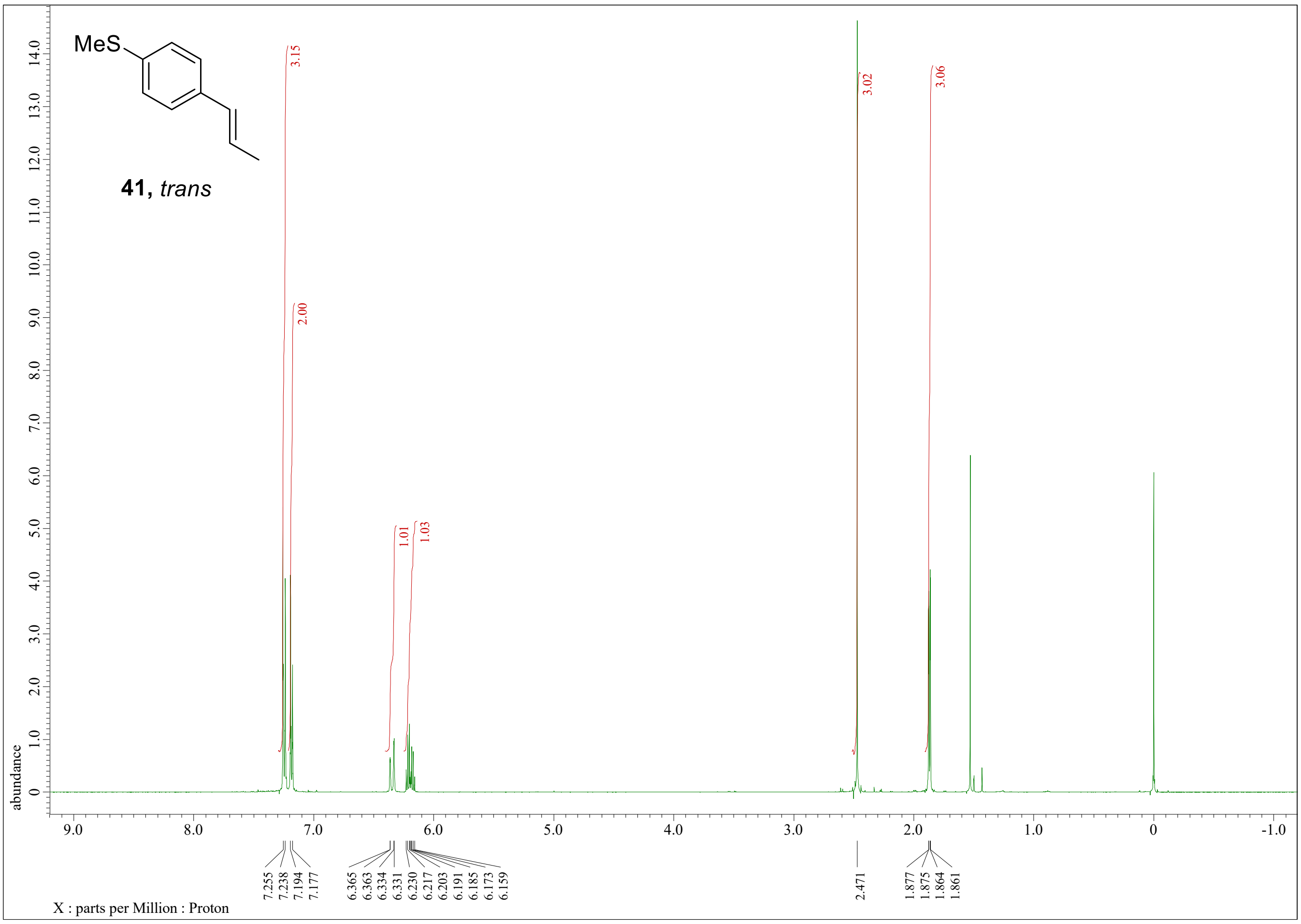
38, *cis* : *trans* = 1 : 7

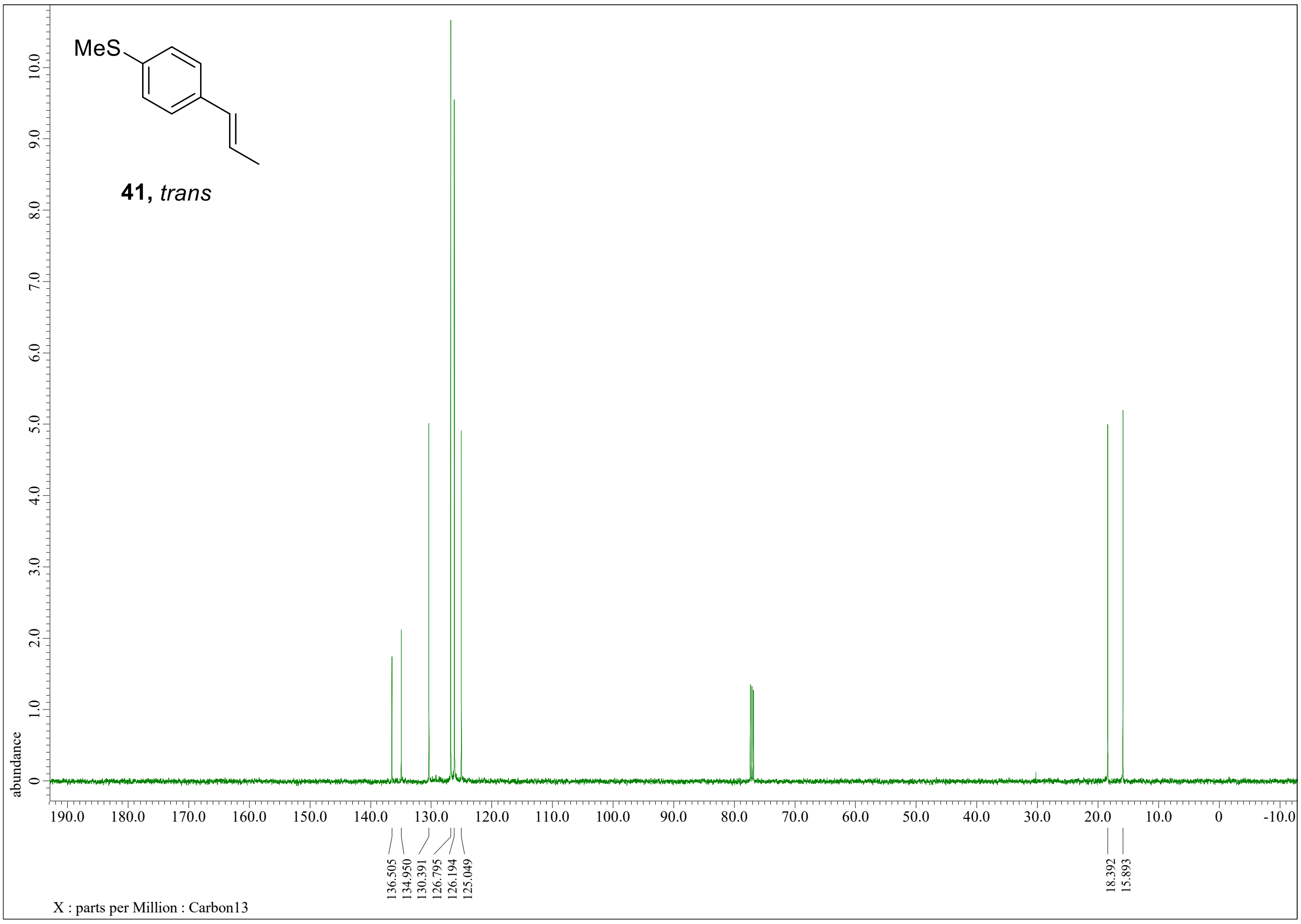


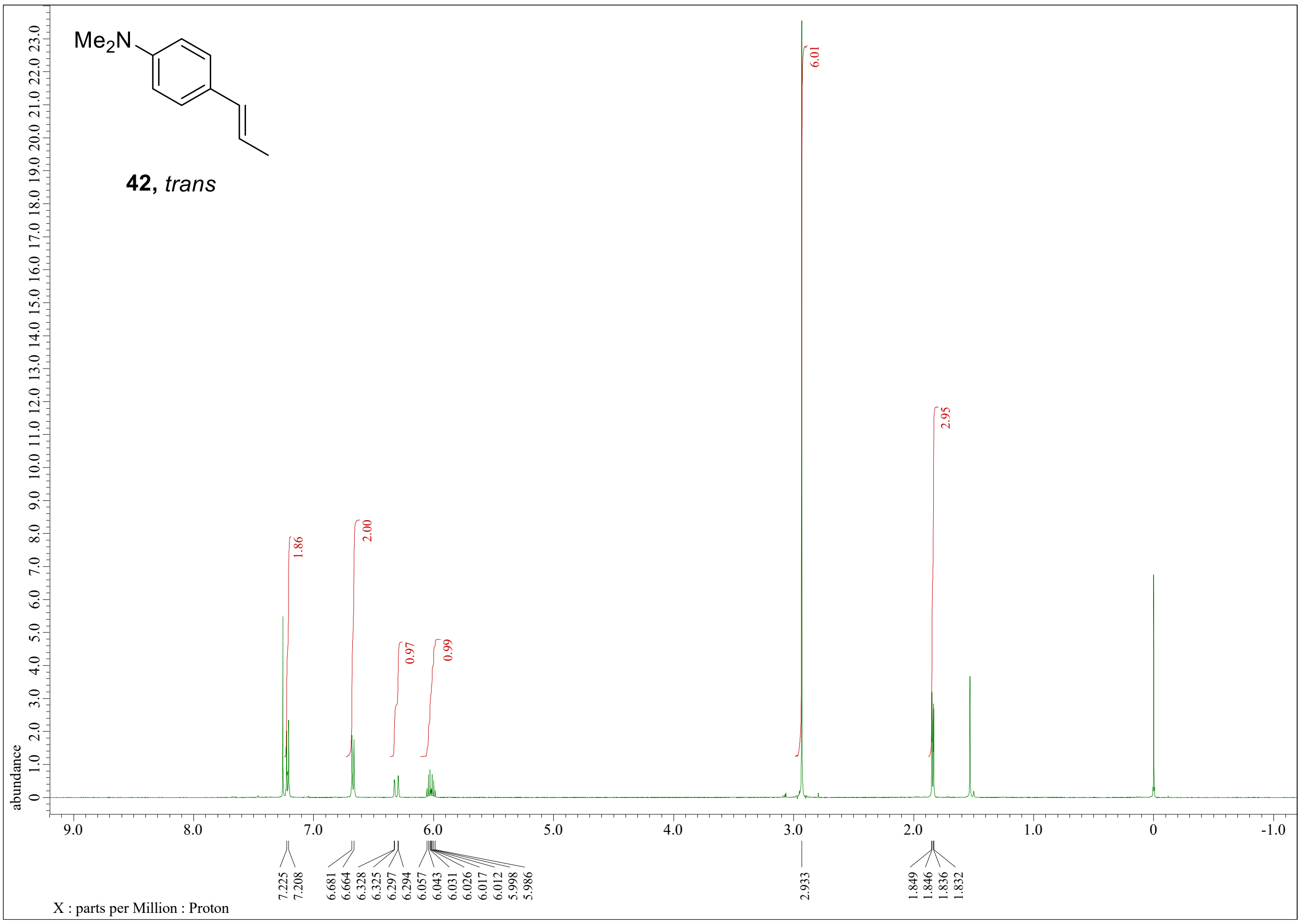
38, *cis* : *trans* = 1 : 7

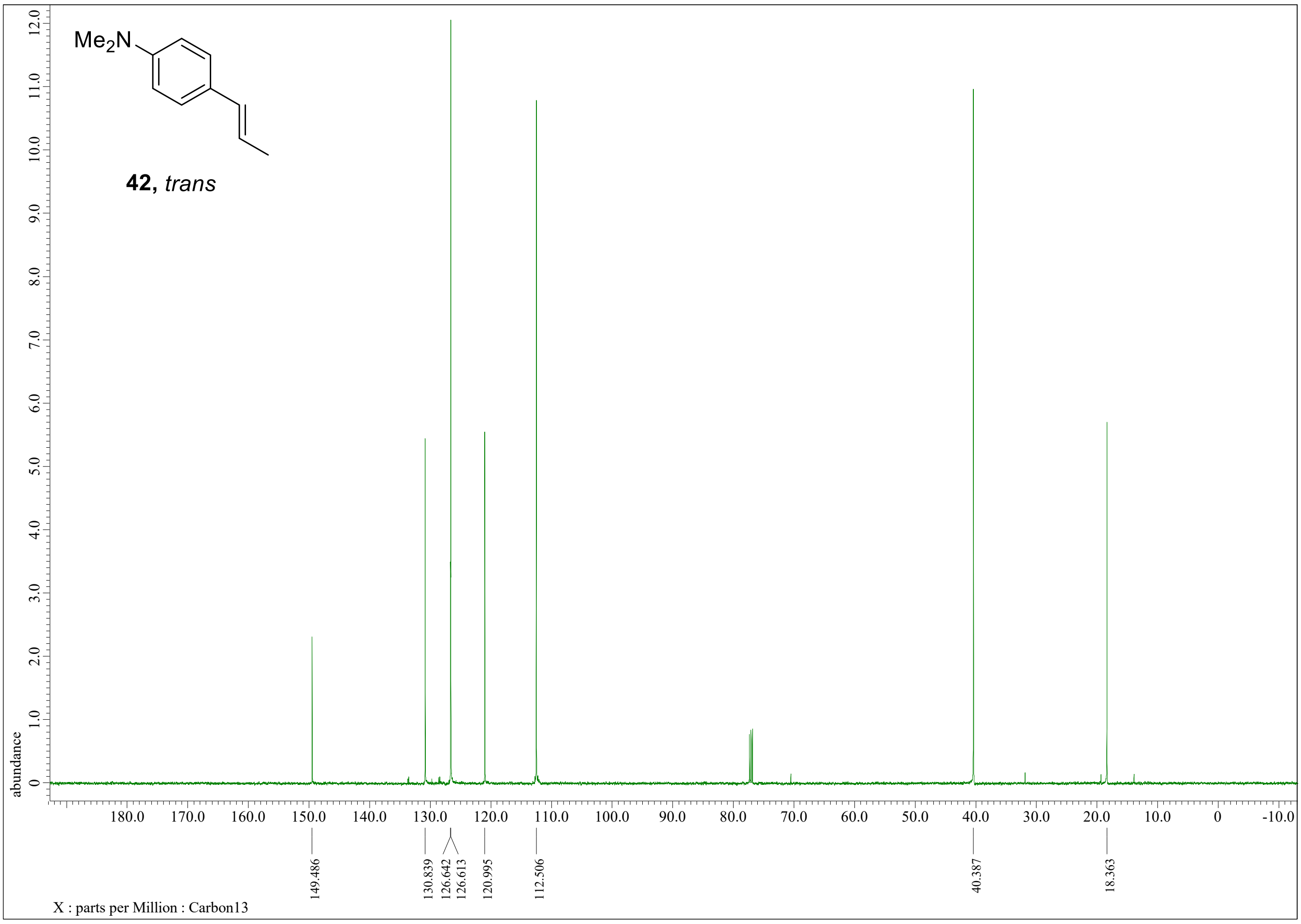

39, trans
abundance
5.93
2.97
1.00
1.03
0.99
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
11.0
10.0
7.106
7.077
7.061
7.051
7.035
6.357
6.354
6.325
6.323
6.207
6.194
6.181
6.168
6.162
6.150
2.241
2.230
1.866
1.862
1.853
1.849
X : parts per Million : Proton

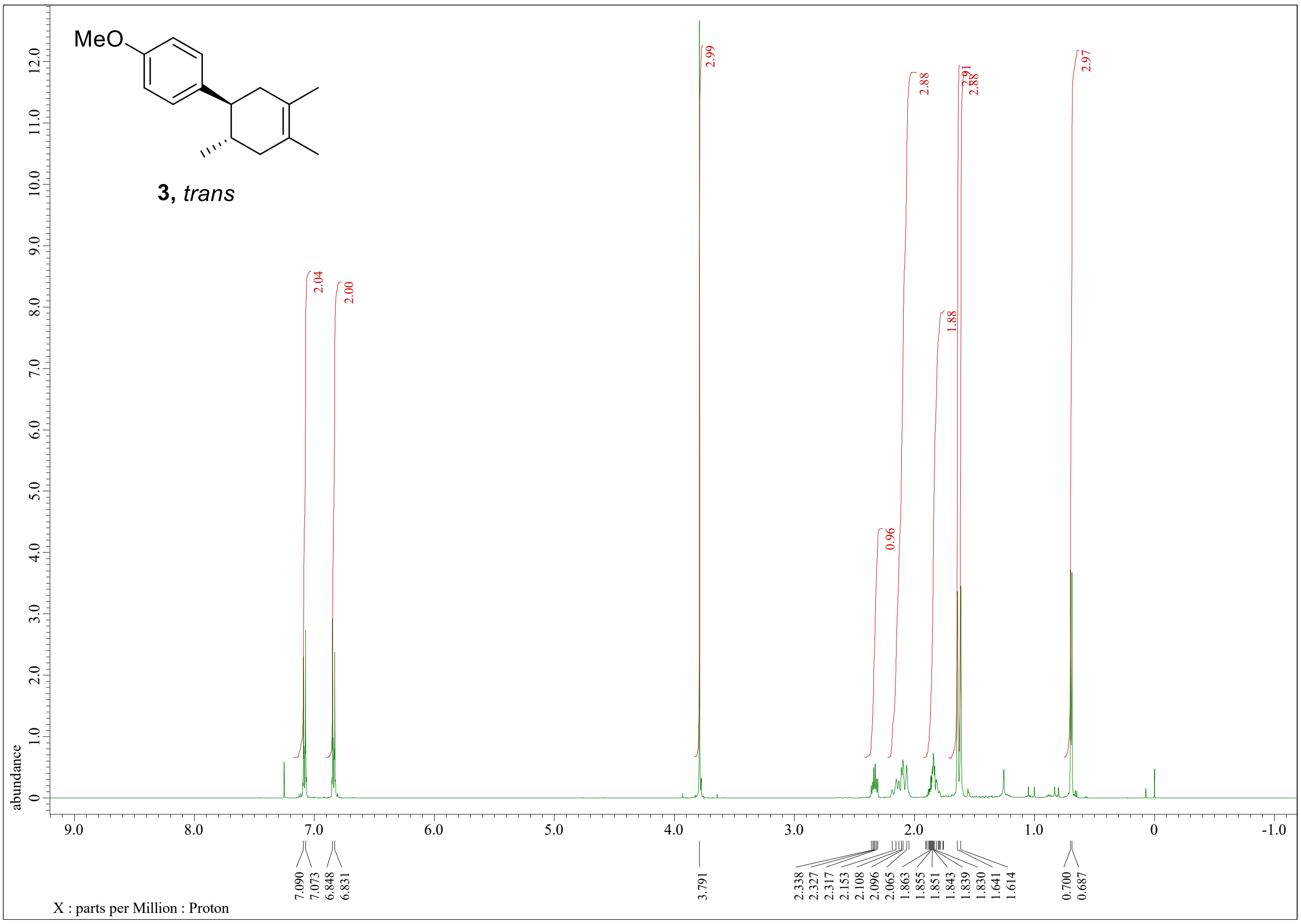

39, trans
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
136.543
135.675
135.150
130.963
129.809
127.195
124.496
123.304
19.861
19.517
18.544
X : parts per Million : Carbon13

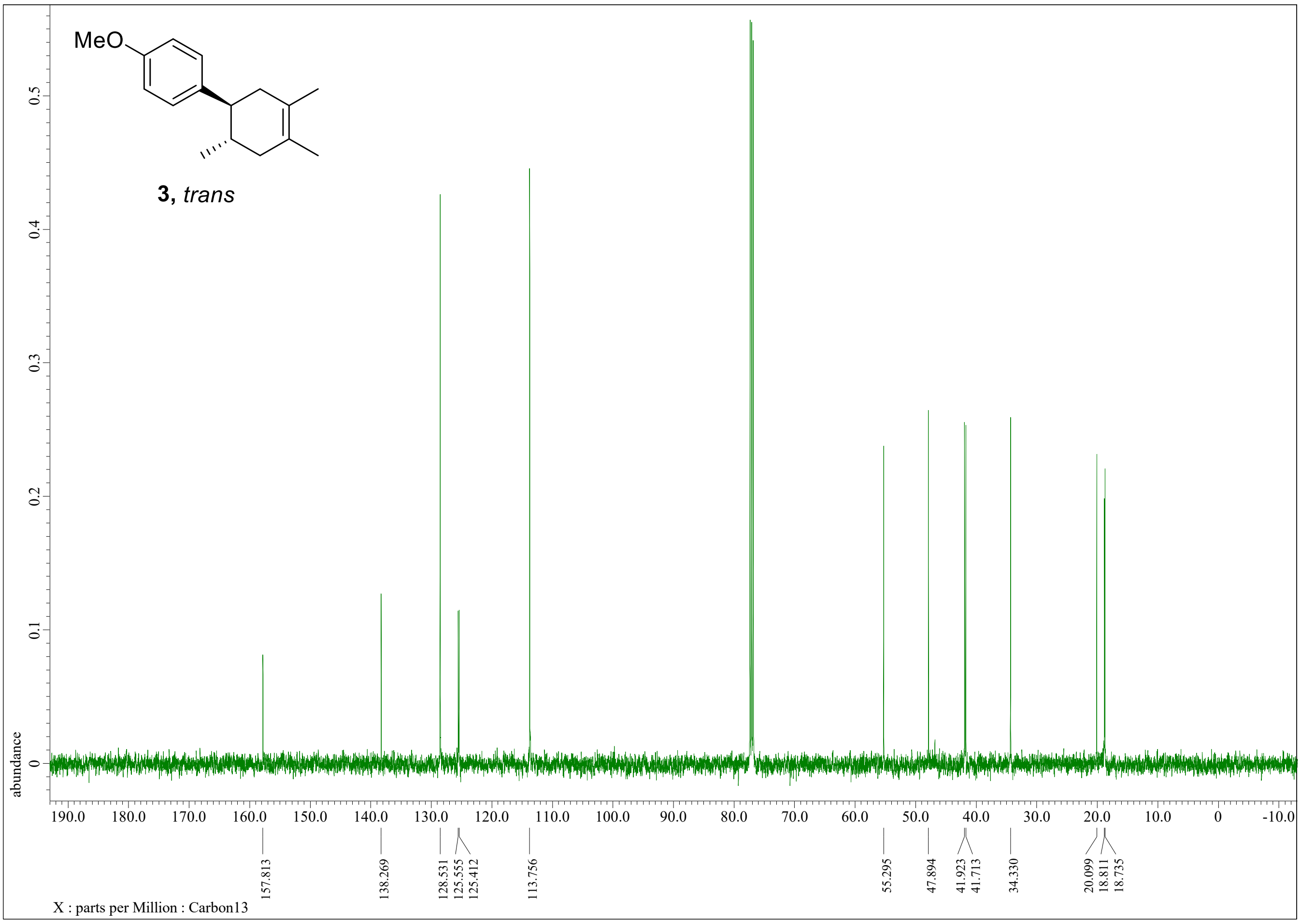

MeS
41, trans
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
3.15
2.00
1.01
1.03
3.02
3.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.255
7.238
7.194
7.177
6.365
6.363
6.334
6.331
6.230
6.217
6.203
6.191
6.185
6.173
6.159
2.471
1.877
1.875
1.864
1.861
X : parts per Million : Proton

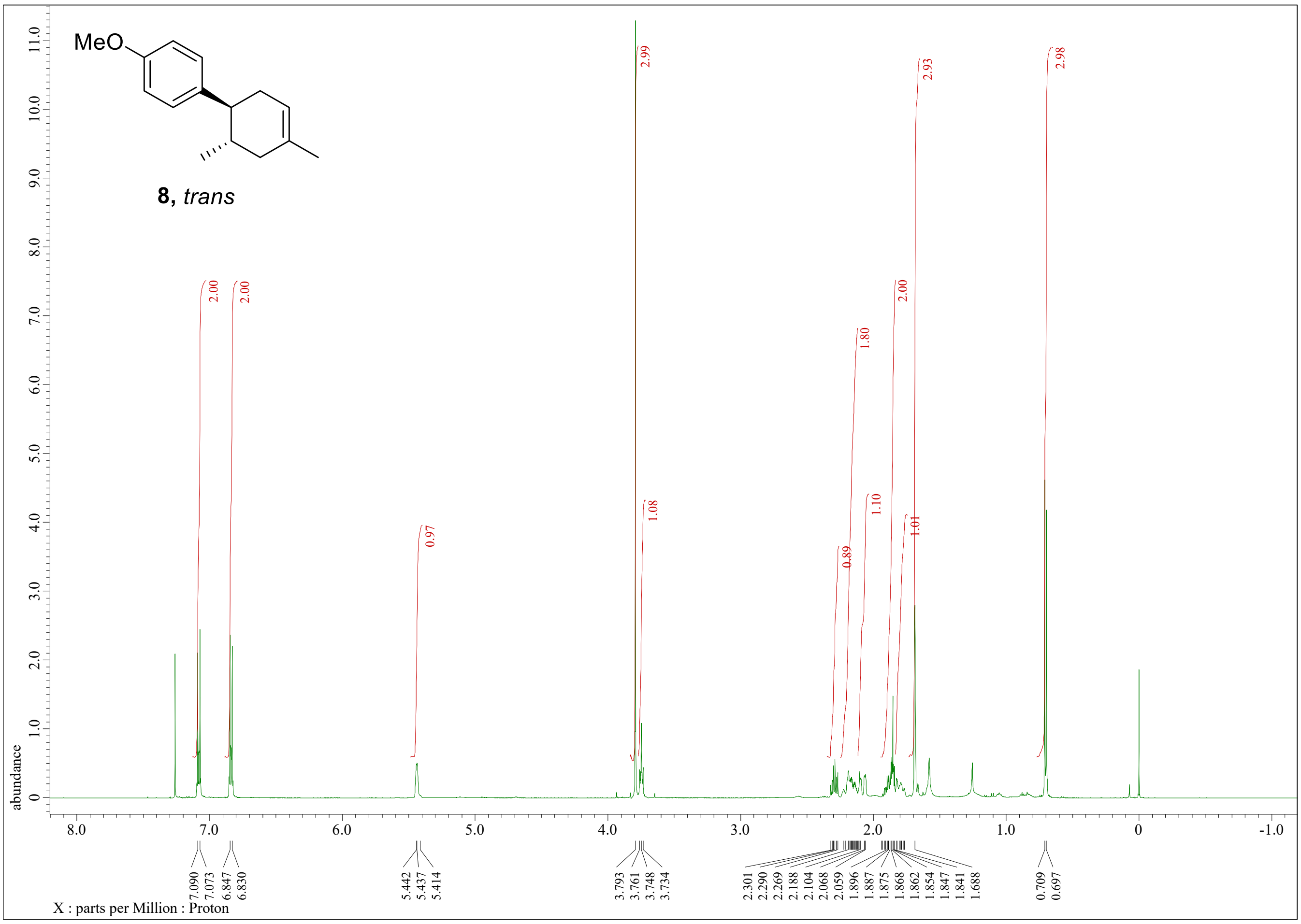

MeS
41, trans
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
136.505
134.950
130.391
126.795
126.194
125.049
18.392
15.893
X : parts per Million : Carbon13

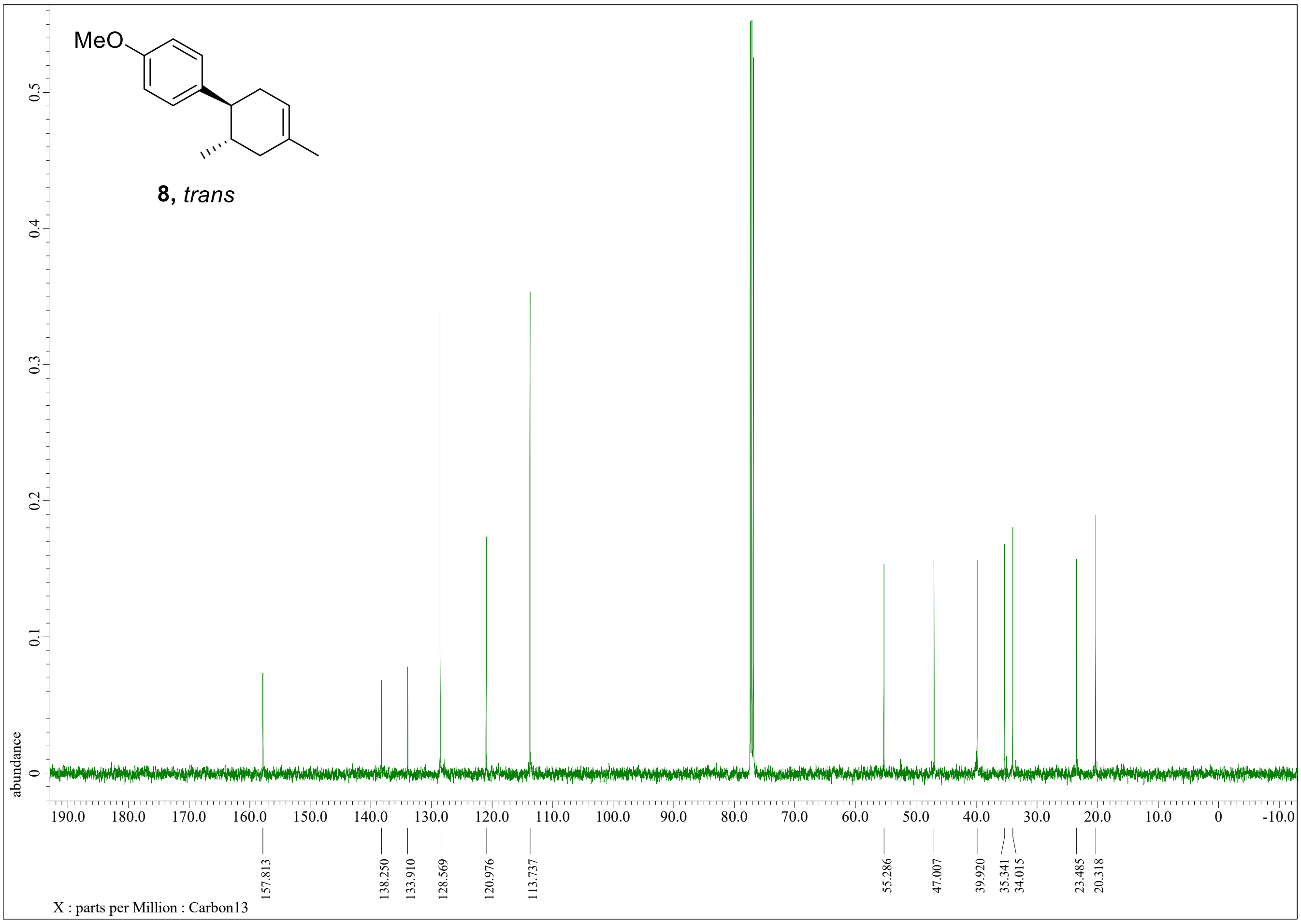

42, *trans*

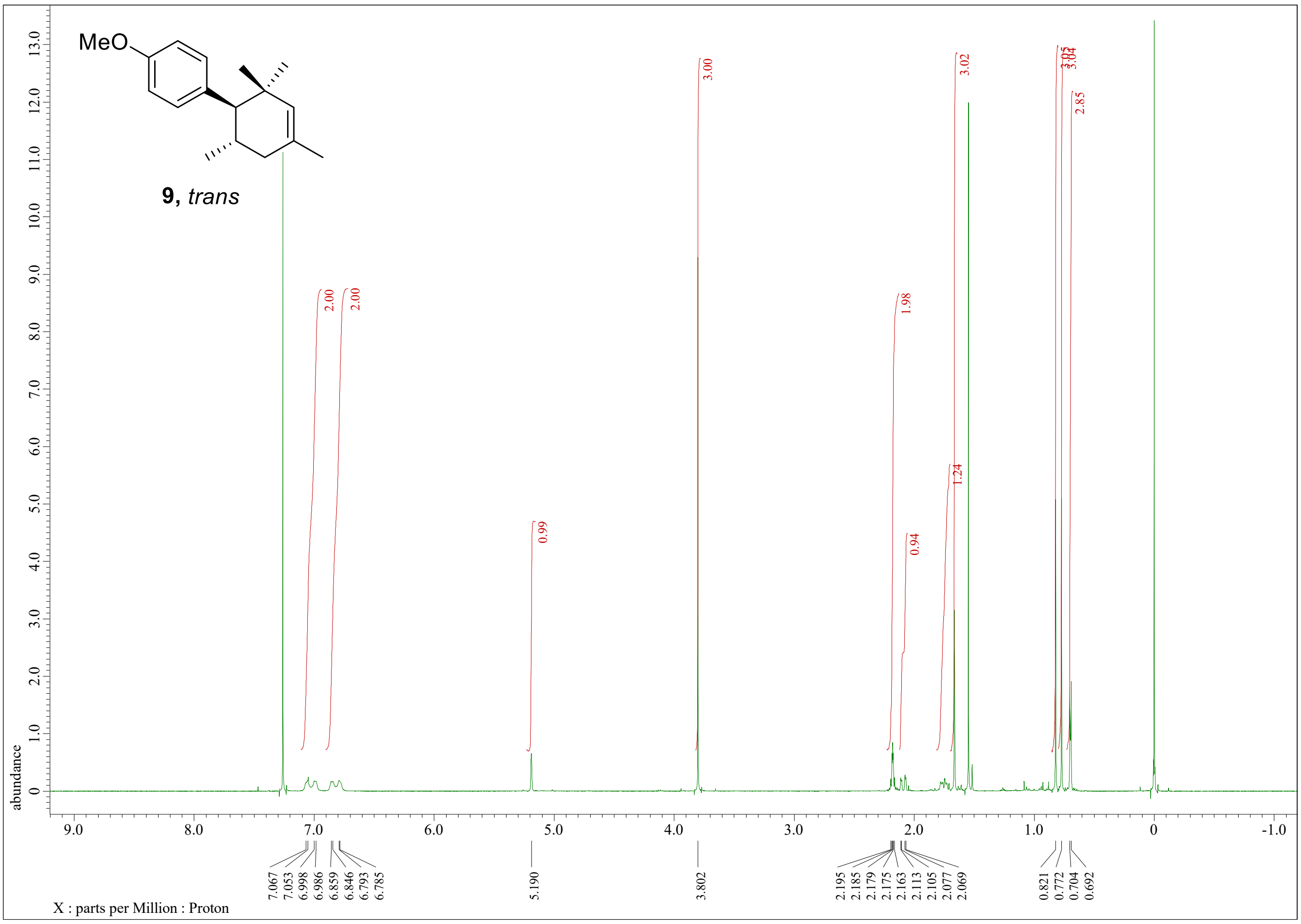

42, *trans*

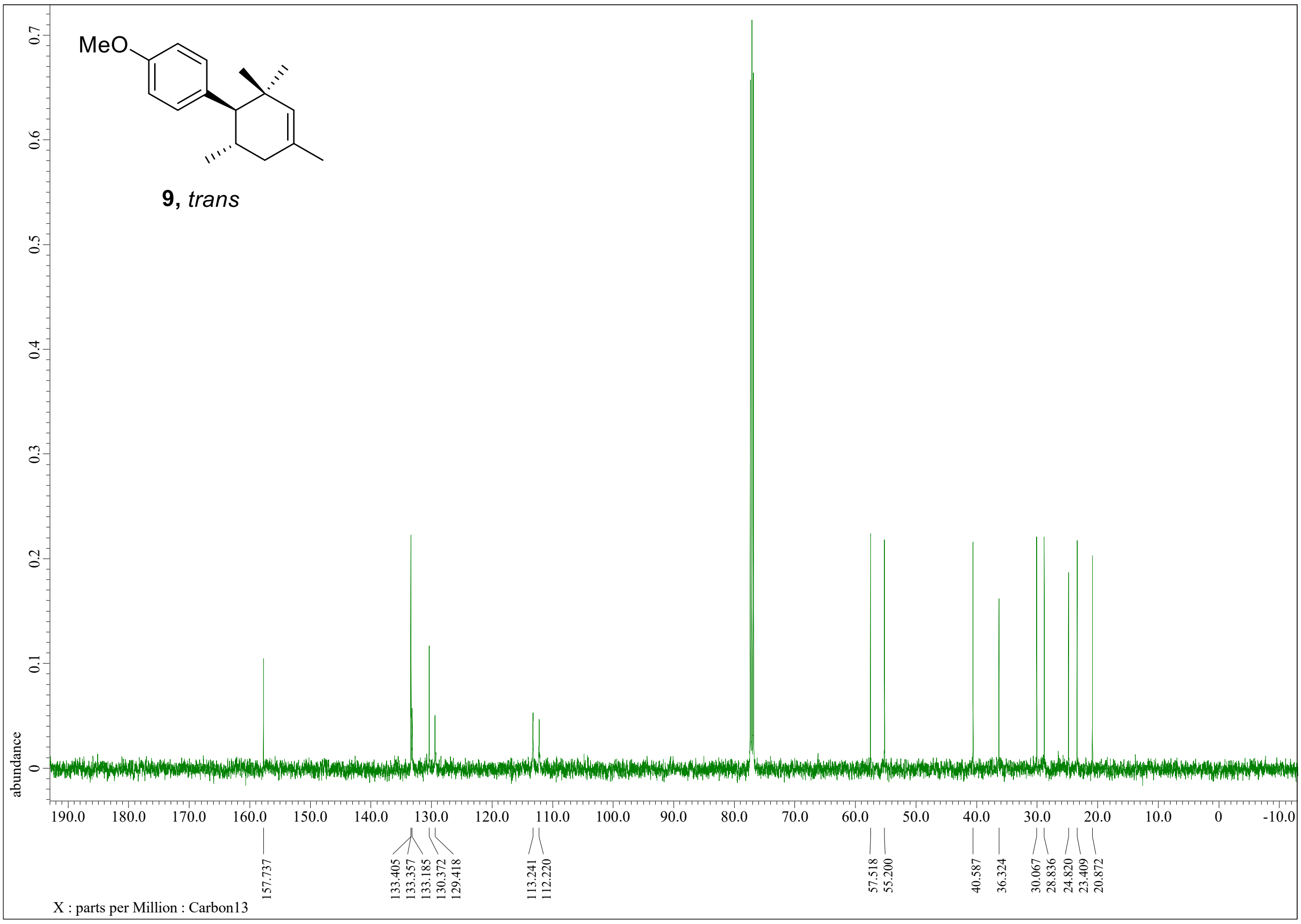

MeO
3, trans
2.04
2.00
2.99
0.96
2.88
1.88
2.91
2.88
2.97
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.090
7.073
6.848
6.831
3.791
2.338
2.327
2.317
2.153
2.108
2.096
2.065
1.863
1.855
1.851
1.843
1.839
1.830
1.641
1.614
0.700
0.687
X : parts per Million : Proton

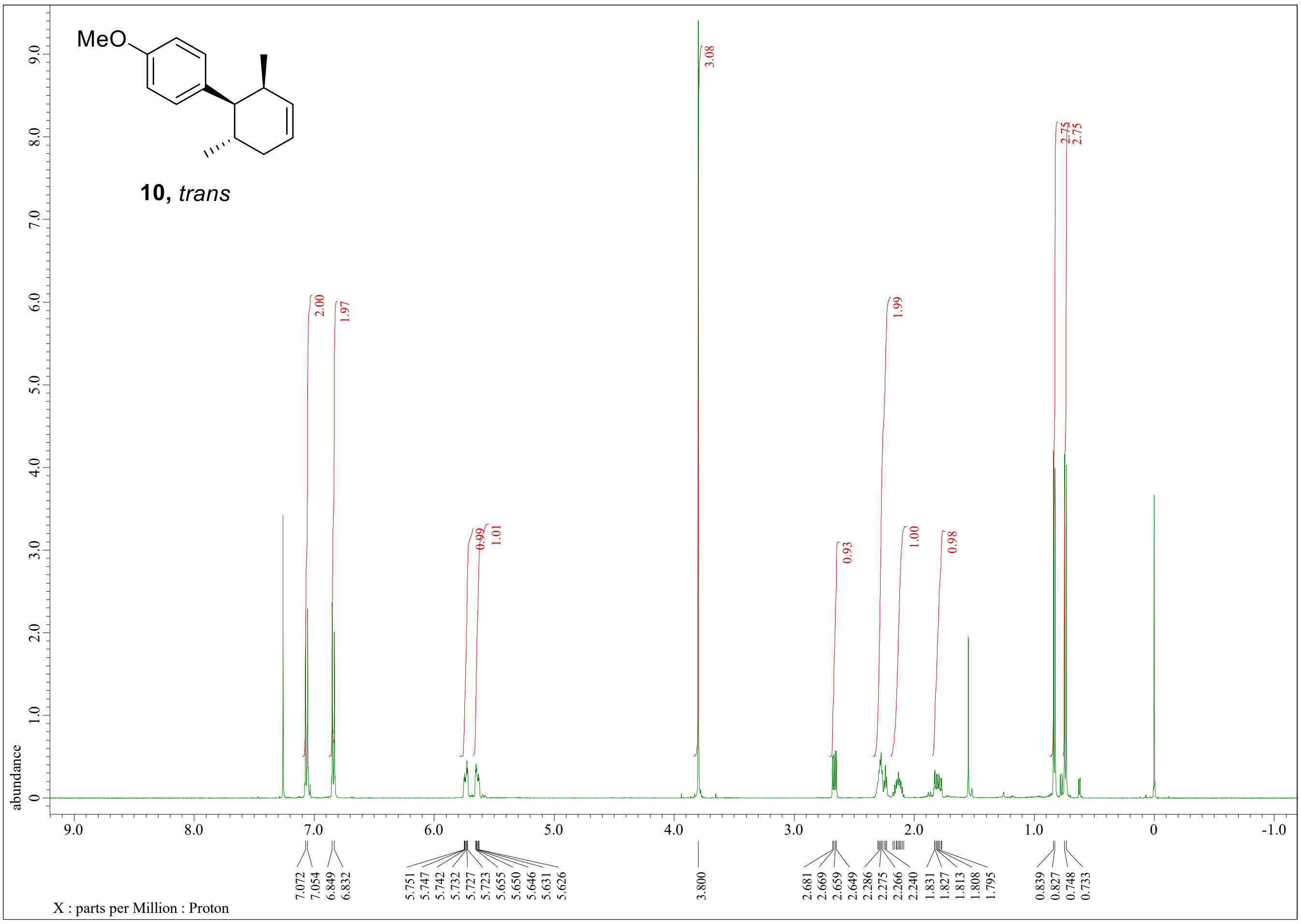

MeO
3, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
157.813
138.269
128.531
125.555
125.412
113.756
55.295
47.894
41.923
41.713
34.330
20.099
18.811
18.735
X : parts per Million : Carbon13

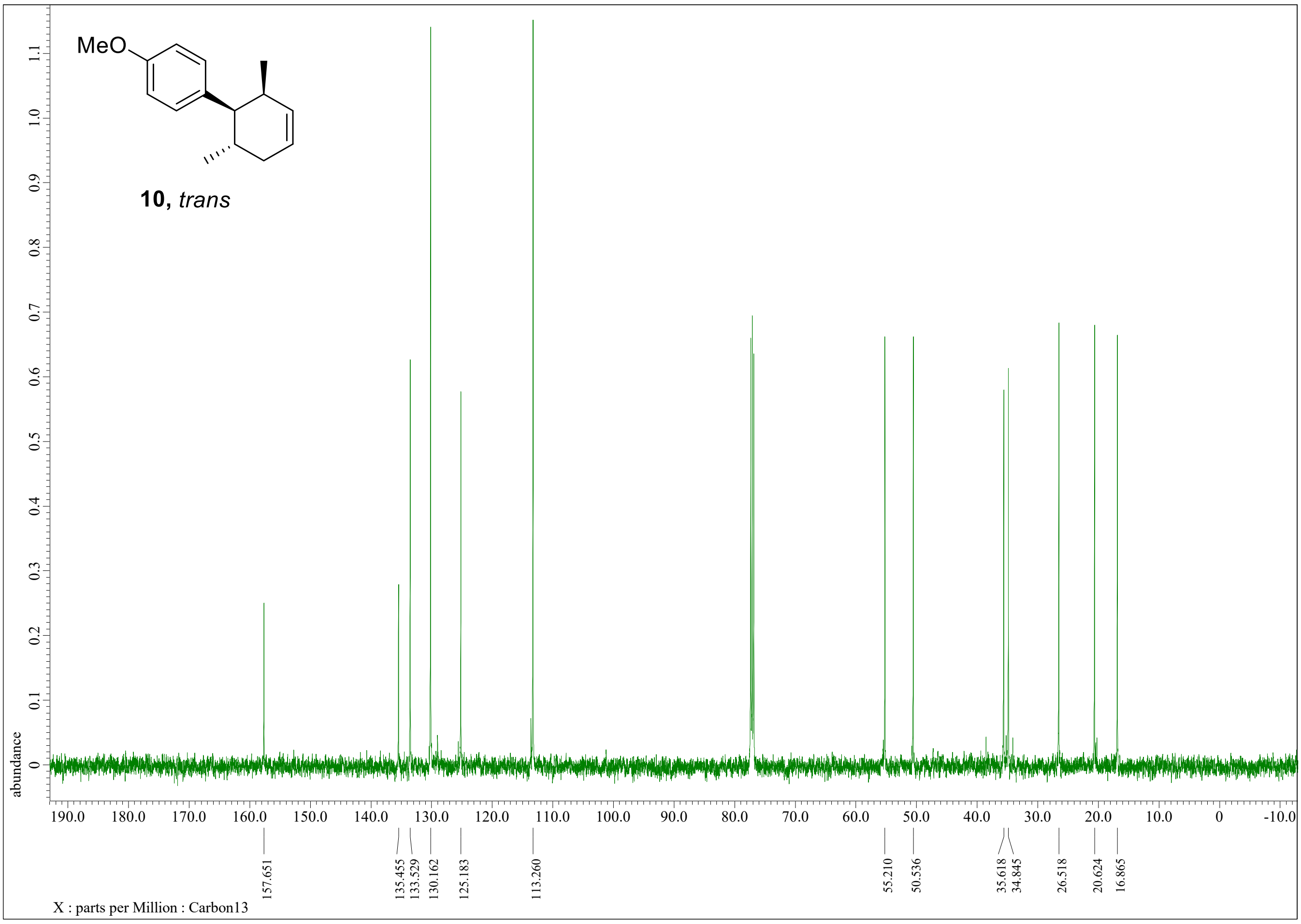

8, *trans*

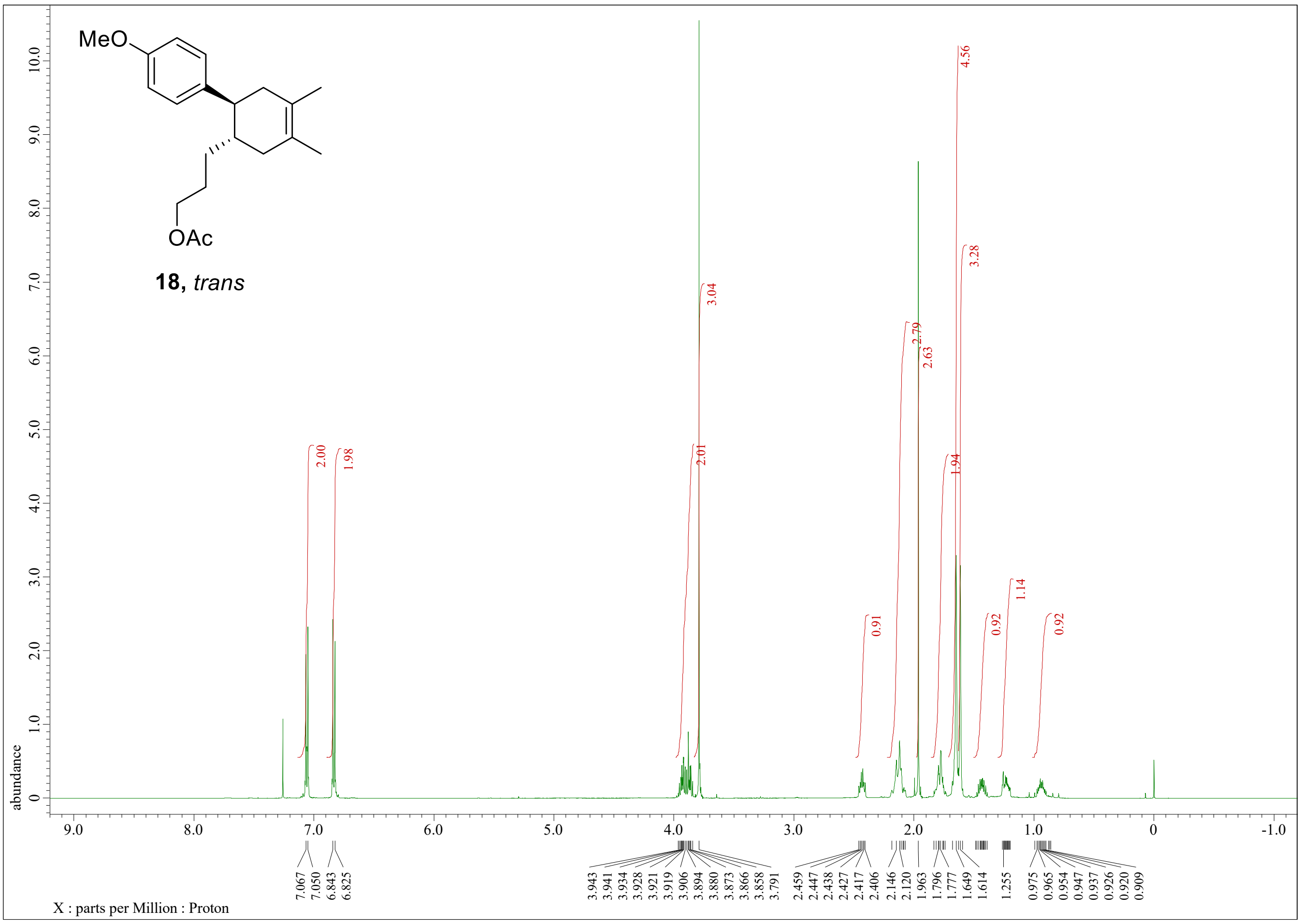

8, *trans*

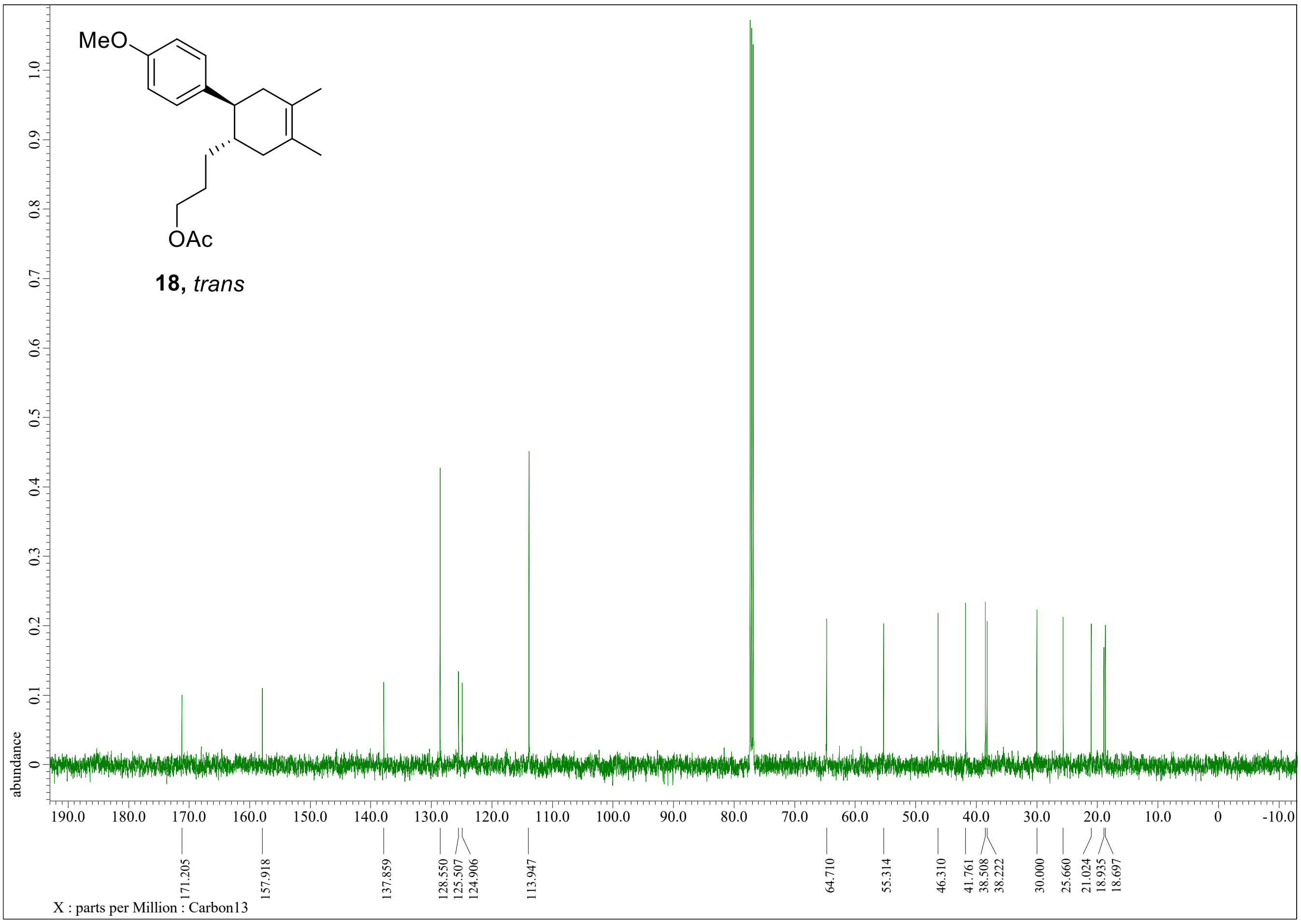

MeO
9, trans
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
2.00
2.00
0.99
3.00
1.98
0.94
1.24
3.02
3.05
3.04
2.85
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.067
7.053
6.998
6.986
6.859
6.846
6.793
6.785
5.190
3.802
2.195
2.185
2.179
2.175
2.163
2.113
2.105
2.077
2.069
0.821
0.772
0.704
0.692
X : parts per Million : Proton

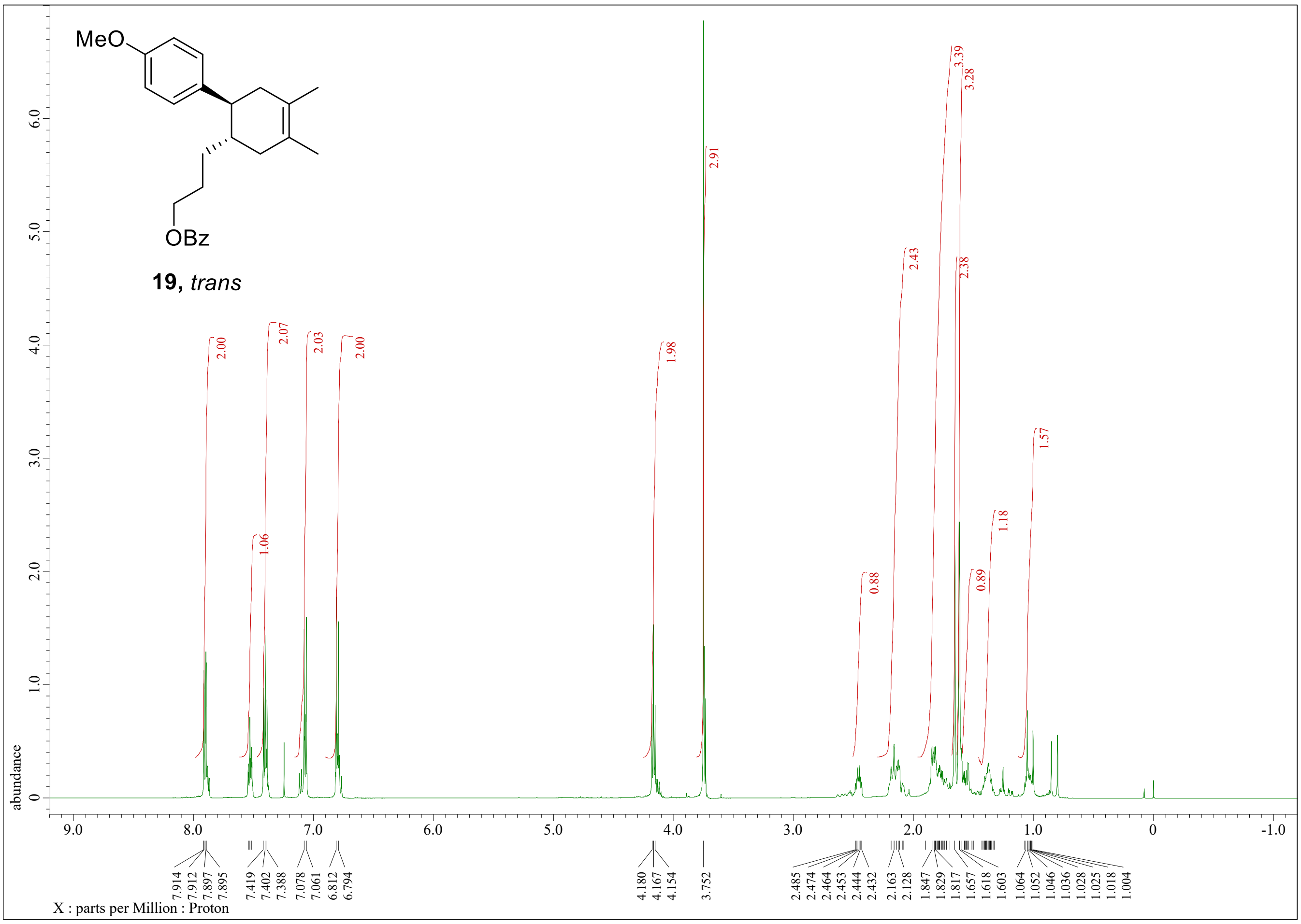

MeO
9, trans
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
157.737
133.405
133.357
133.185
130.372
129.418
113.241
112.220
57.518
55.200
40.587
36.324
30.067
28.836
24.820
23.409
20.872
X : parts per Million : Carbon13


MeO
10, trans
abundance
3.08
2.00
1.97
0.99
1.01
0.93
1.99
1.00
0.98
2.75
2.75
7.072
7.054
6.849
6.832
5.751
5.747
5.742
5.732
5.727
5.723
5.655
5.650
5.646
5.631
5.626
3.800
2.681
2.669
2.659
2.649
2.286
2.275
2.266
2.240
1.831
1.827
1.813
1.808
1.795
0.839
0.827
0.748
0.733
X : parts per Million : Proton

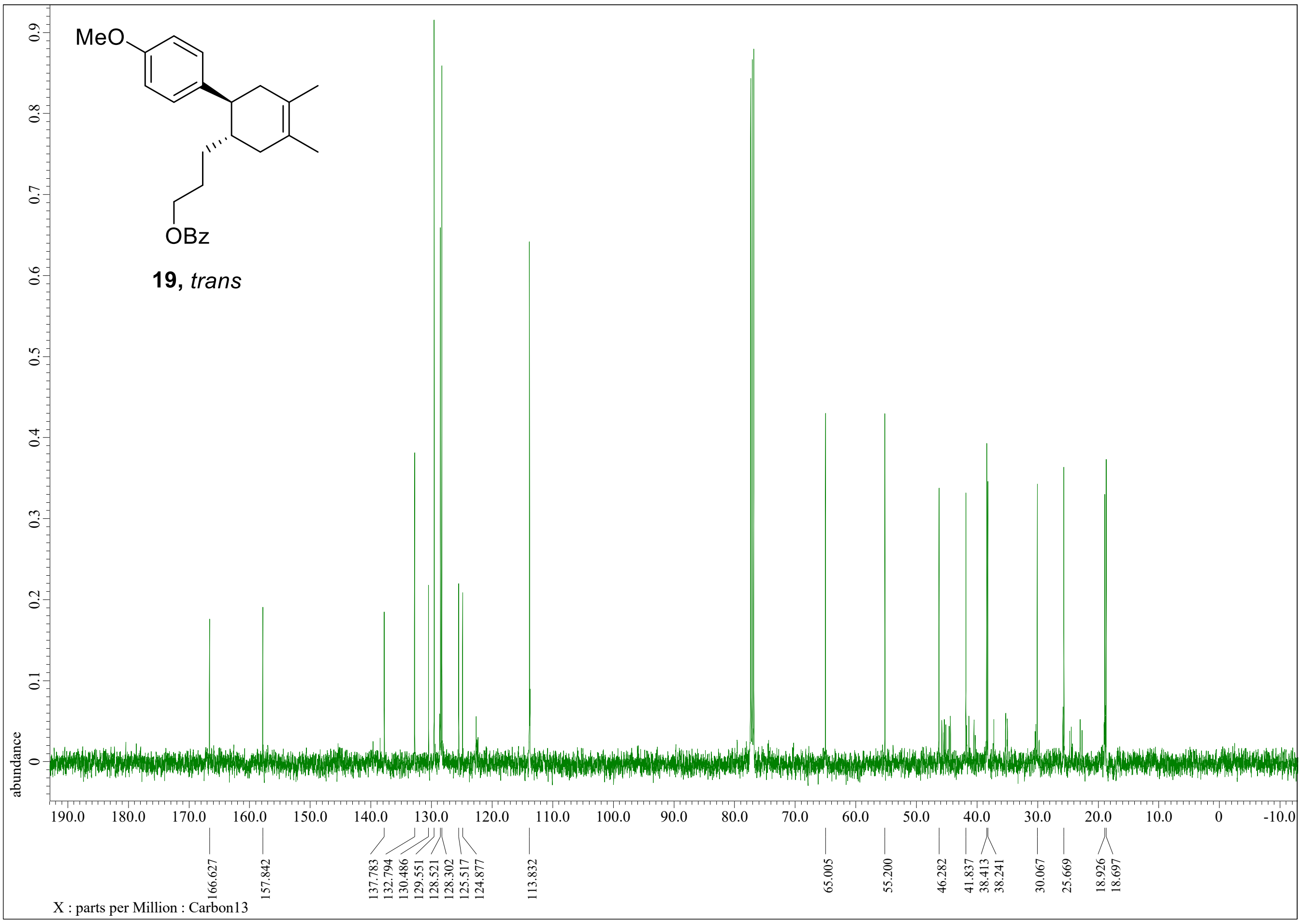

MeO
10, trans
abundance
157.651
135.455
133.529
130.162
125.183
113.260
55.210
50.536
35.618
34.845
26.518
20.624
16.865
X : parts per Million : Carbon13


MeO
OAc
18, trans
2.00
1.98
2.01
3.04
0.91
2.79
2.63
1.94
4.56
3.28
0.92
1.14
0.92
7.067
7.050
6.843
6.825
3.943
3.941
3.934
3.928
3.921
3.919
3.906
3.894
3.880
3.873
3.866
3.858
3.791
2.459
2.447
2.438
2.427
2.417
2.406
2.146
2.120
1.963
1.796
1.777
1.649
1.614
1.255
0.975
0.965
0.954
0.947
0.937
0.926
0.920
0.909
abundance
X : parts per Million : Proton

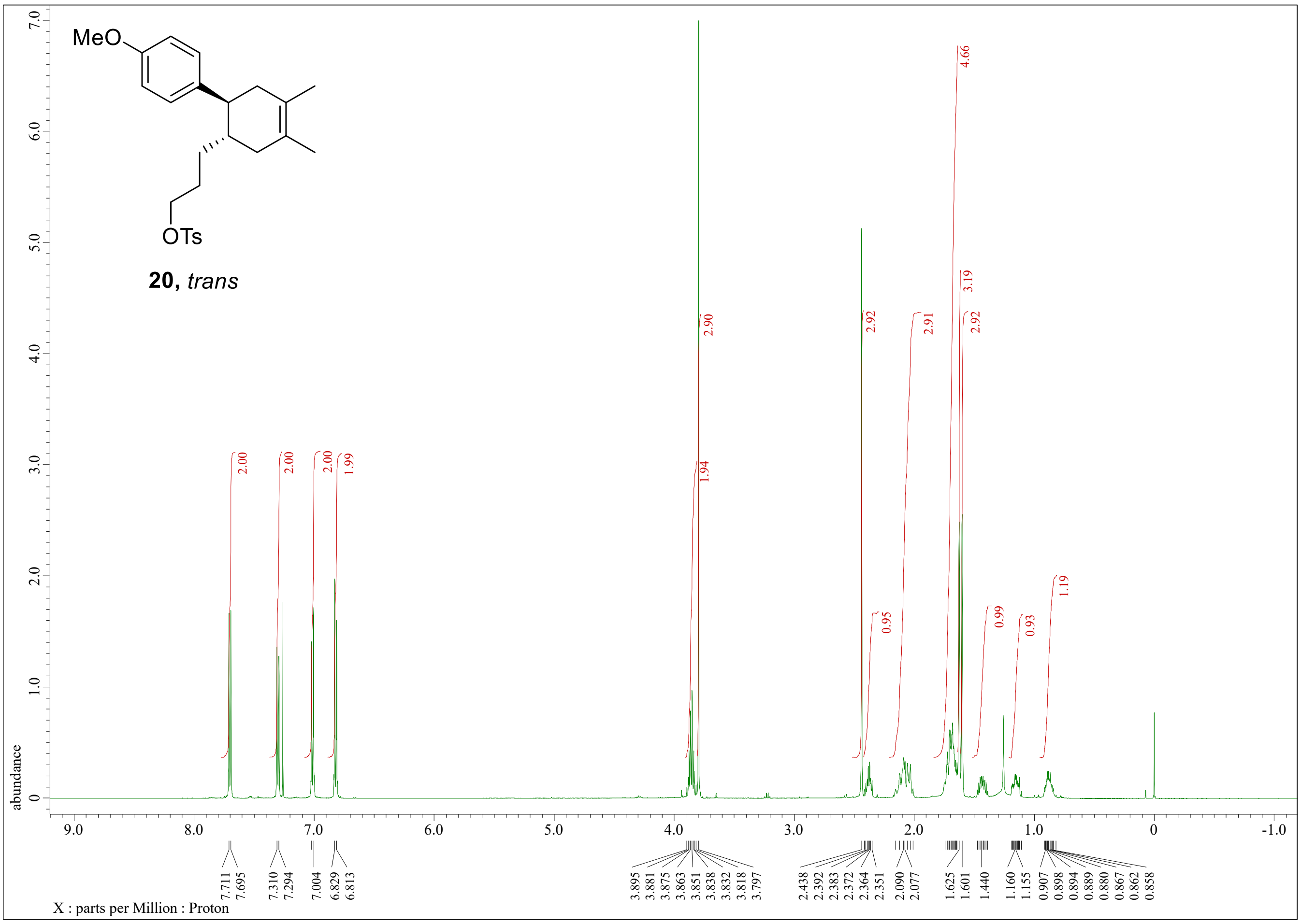

MeO
OAc
18, trans
171.205
157.918
137.859
128.550
125.507
124.906
113.947
64.710
55.314
46.310
41.761
38.508
38.222
30.000
25.660
21.024
18.935
18.697
abundance
X : parts per Million : Carbon13

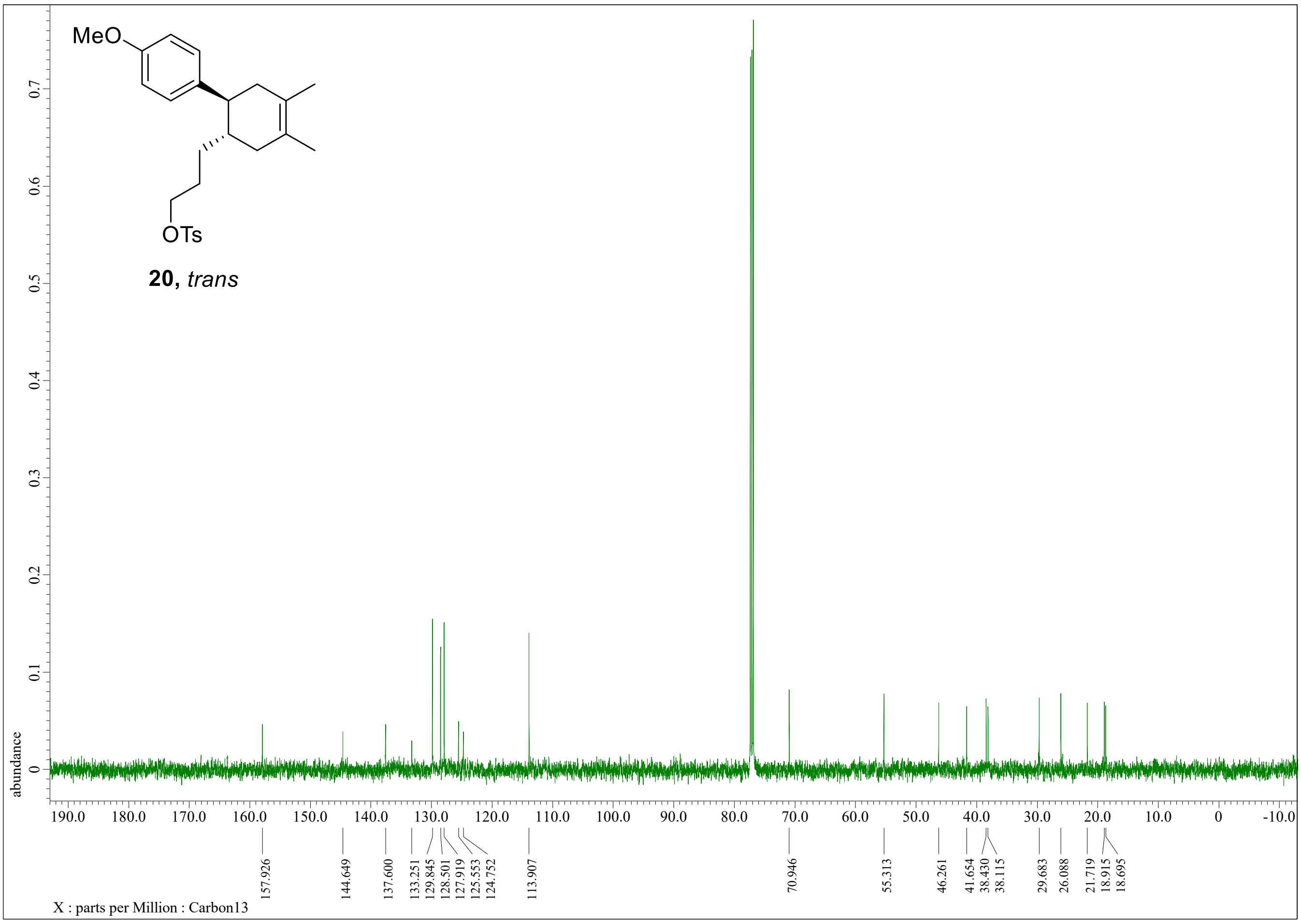


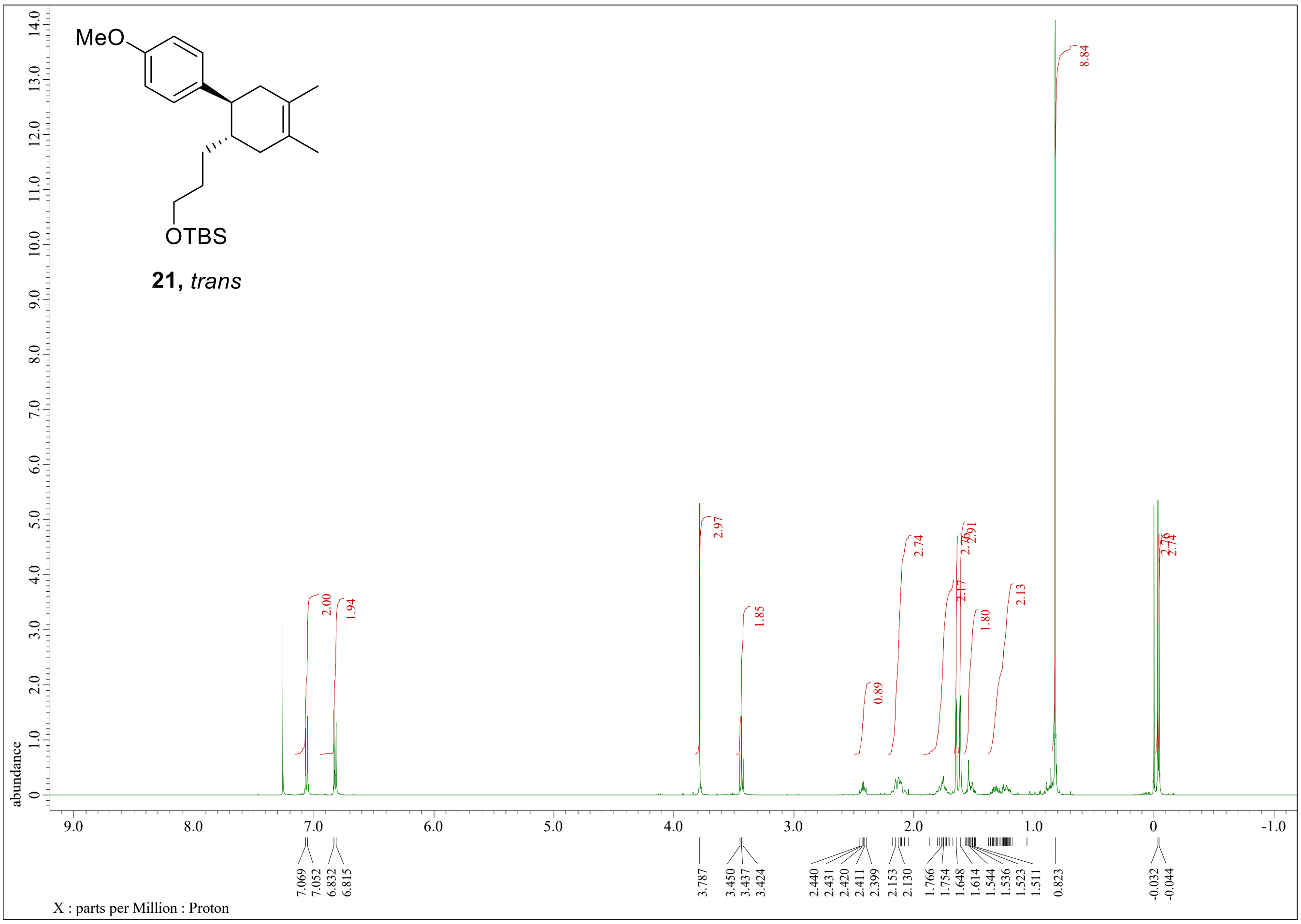
19, *trans*



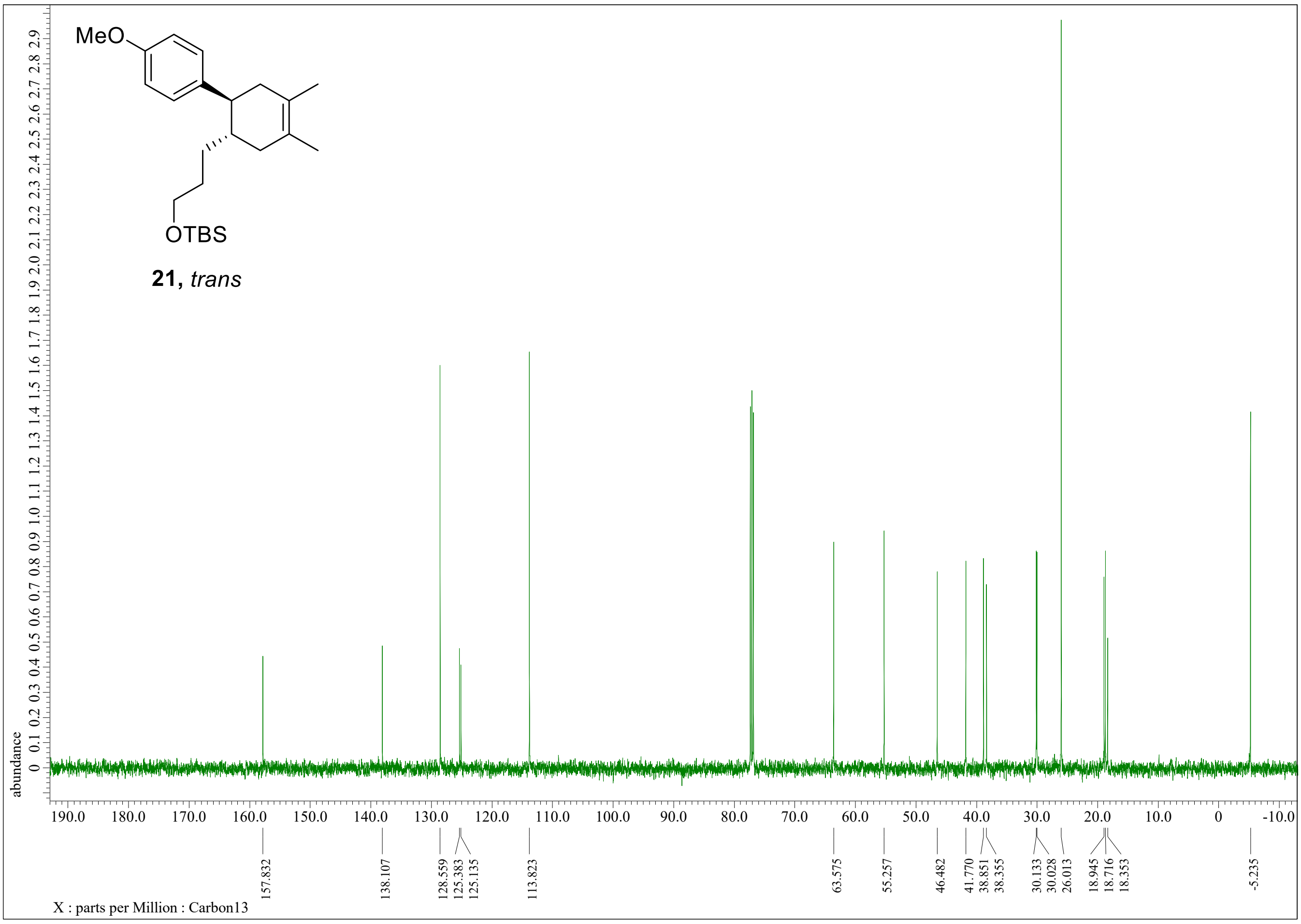
19, *trans*


20, *trans*

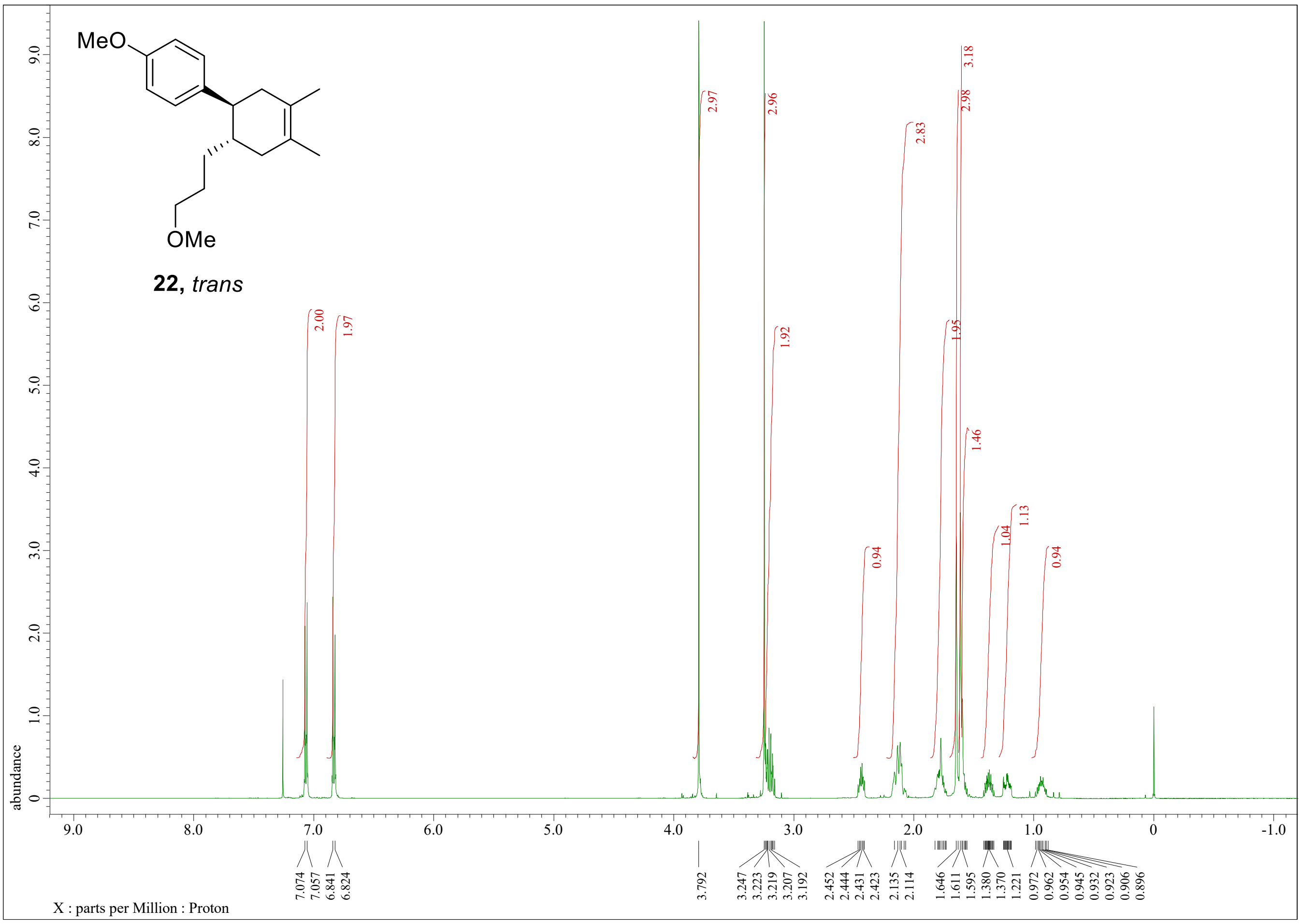

20, *trans*

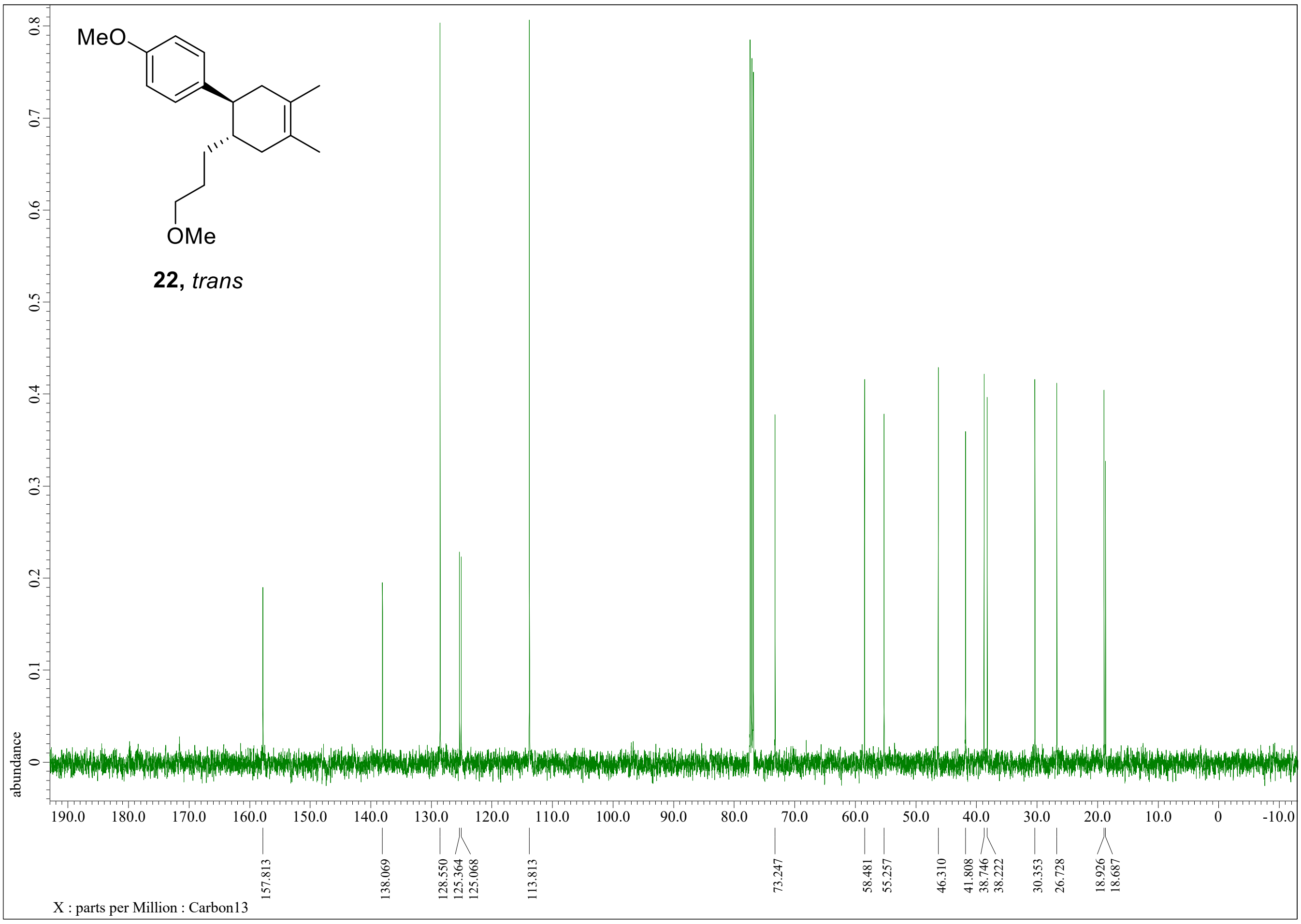


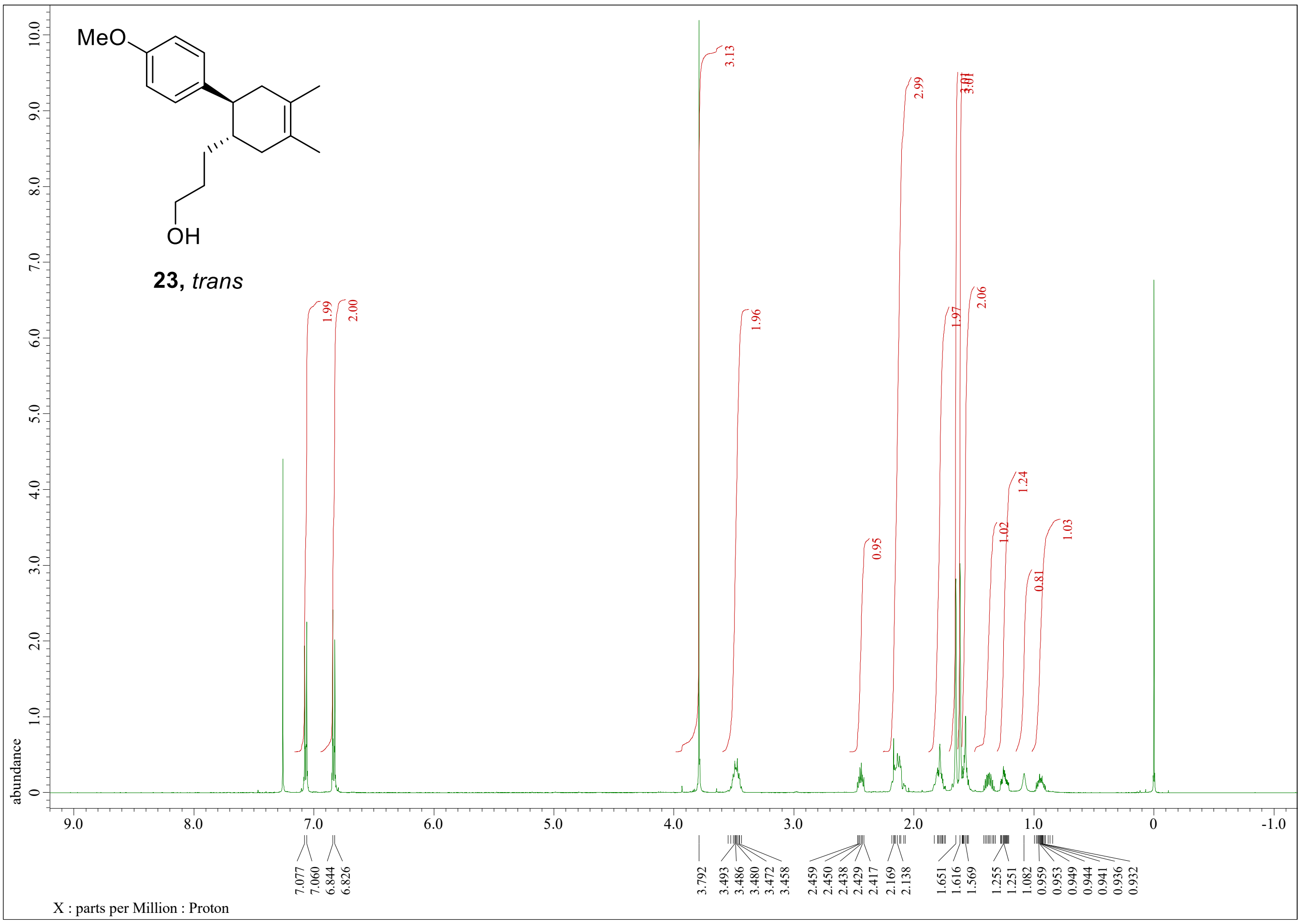
21, *trans*

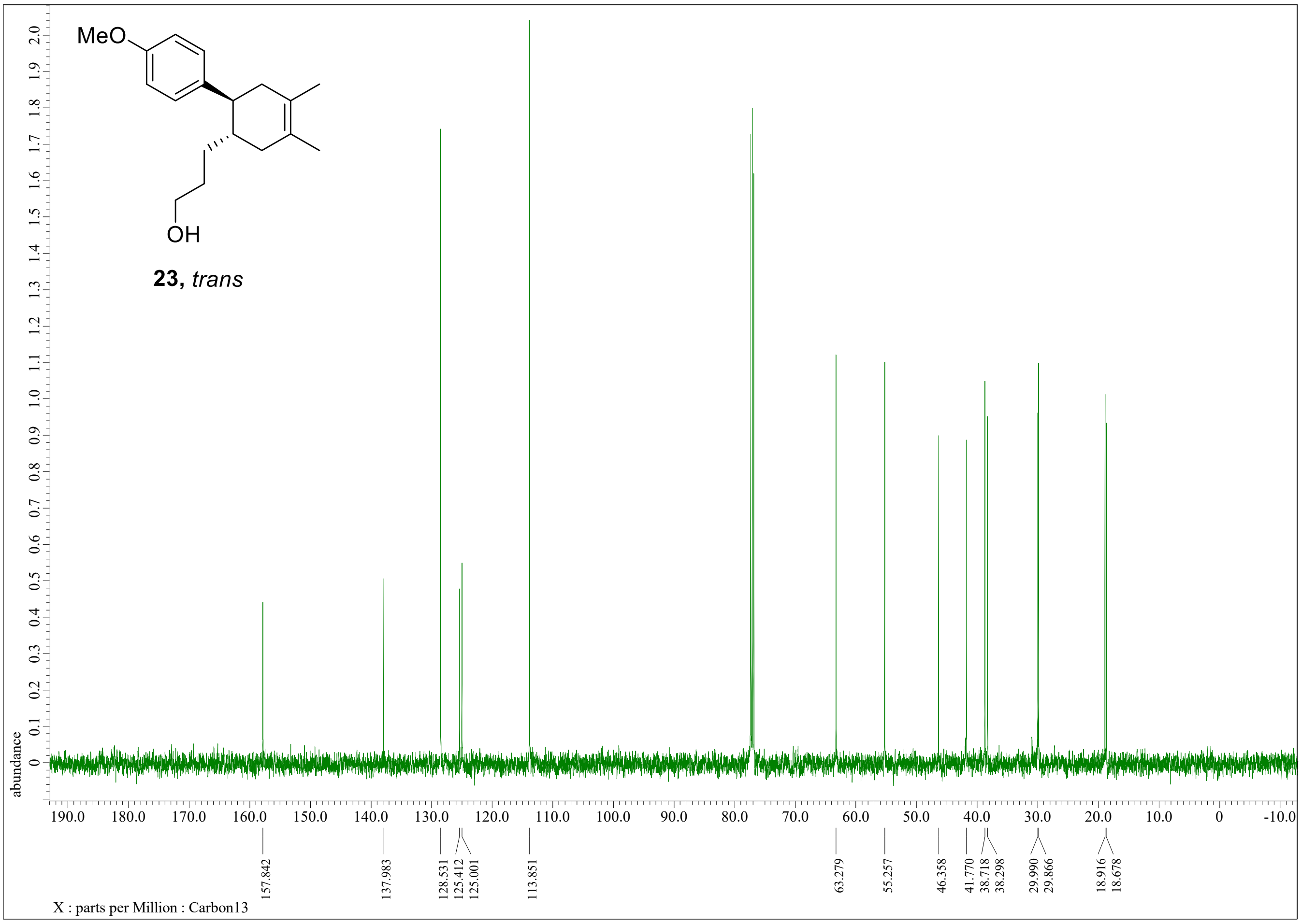


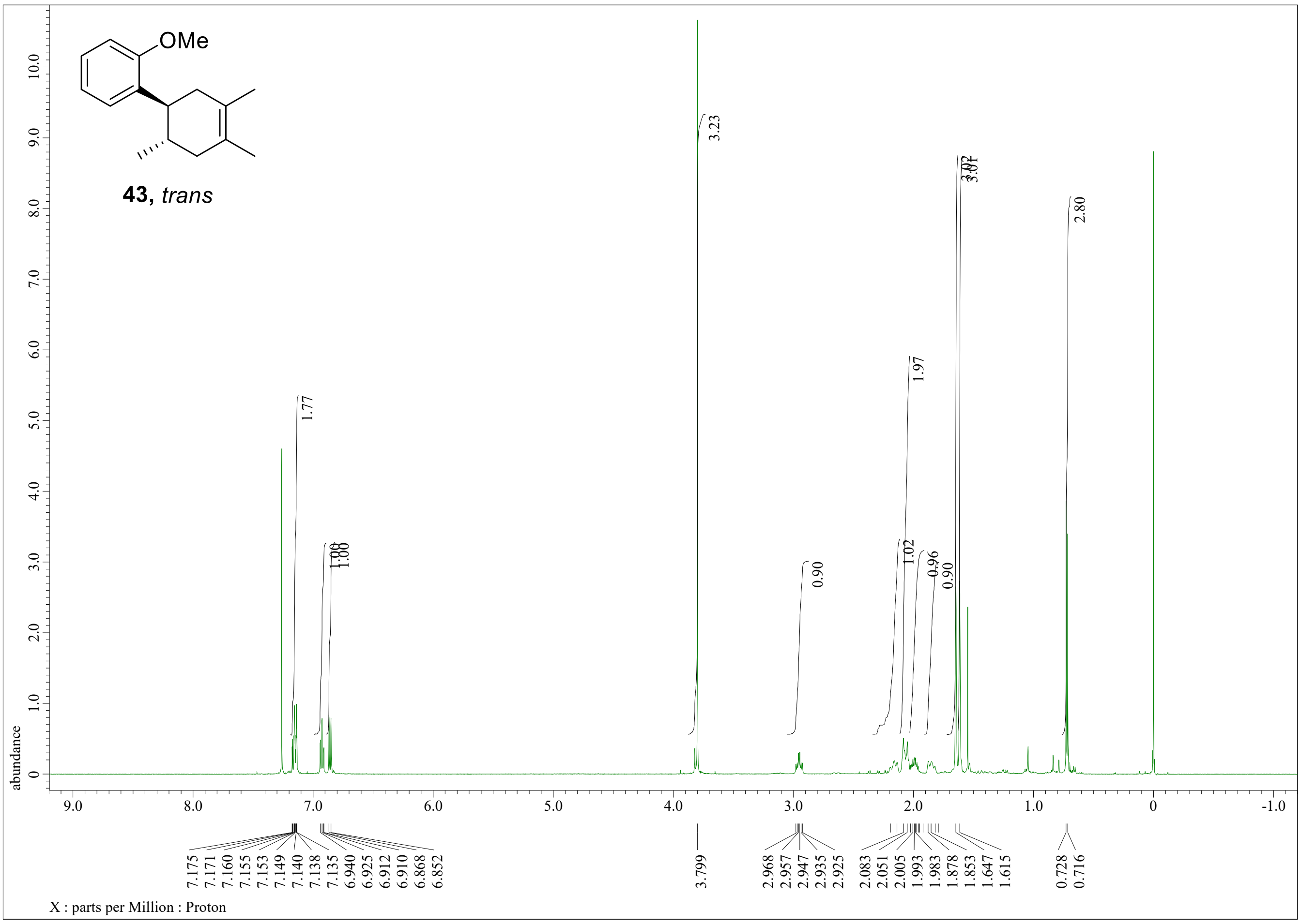
21, *trans*

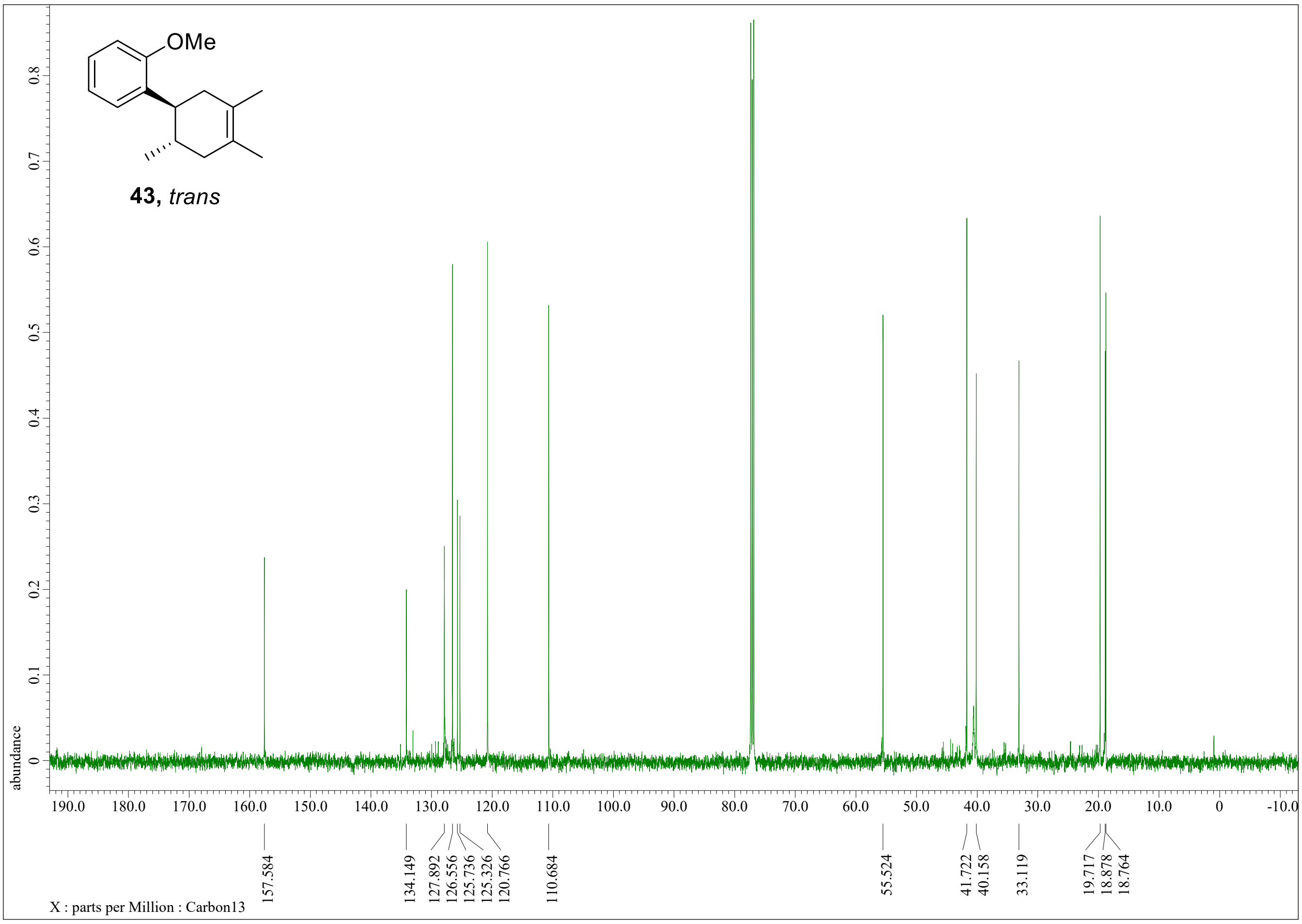

MeO
OMe
22, trans
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
2.00
1.97
2.97
2.96
1.92
0.94
2.83
1.95
2.98
3.18
1.46
1.04
1.13
0.94
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.074
7.057
6.841
6.824
3.792
3.247
3.223
3.219
3.207
3.192
2.452
2.444
2.431
2.423
2.135
2.114
1.646
1.611
1.595
1.380
1.370
1.221
0.972
0.962
0.954
0.945
0.932
0.923
0.906
0.896
X : parts per Million : Proton

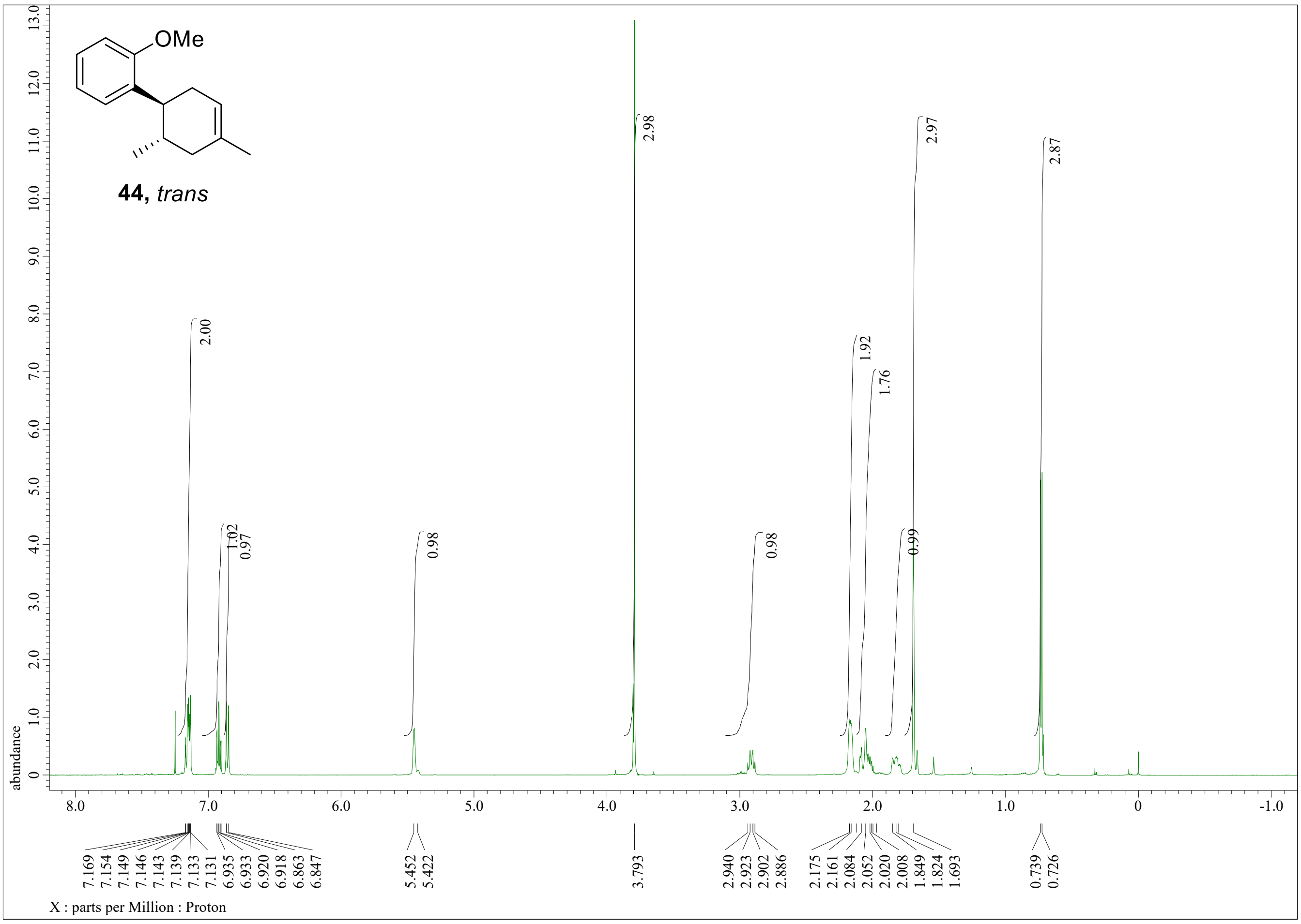

MeO
OMe
22, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
157.813
138.069
128.550
125.364
125.068
113.813
73.247
58.481
55.257
46.310
41.808
38.746
38.222
30.353
26.728
18.926
18.687
X : parts per Million : Carbon13

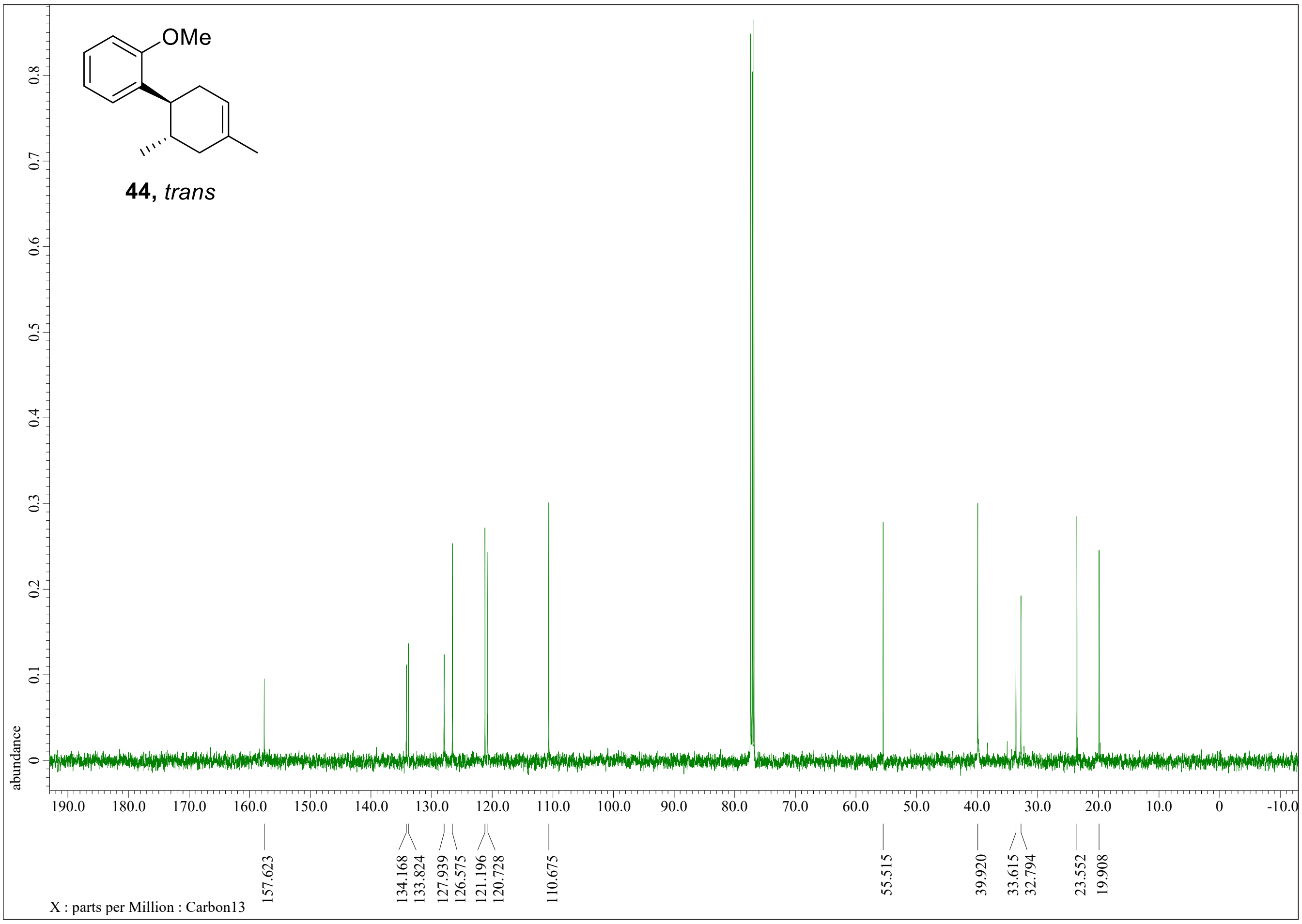

MeO
OH
23, trans
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.99
2.00
3.13
1.96
0.95
2.99
3.01
3.01
1.97
2.06
1.02
1.24
0.81
1.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.077
7.060
6.844
6.826
3.792
3.493
3.486
3.480
3.472
3.458
2.459
2.450
2.438
2.429
2.417
2.169
2.138
1.651
1.616
1.569
1.255
1.251
1.082
0.959
0.953
0.949
0.944
0.941
0.936
0.932
X : parts per Million : Proton

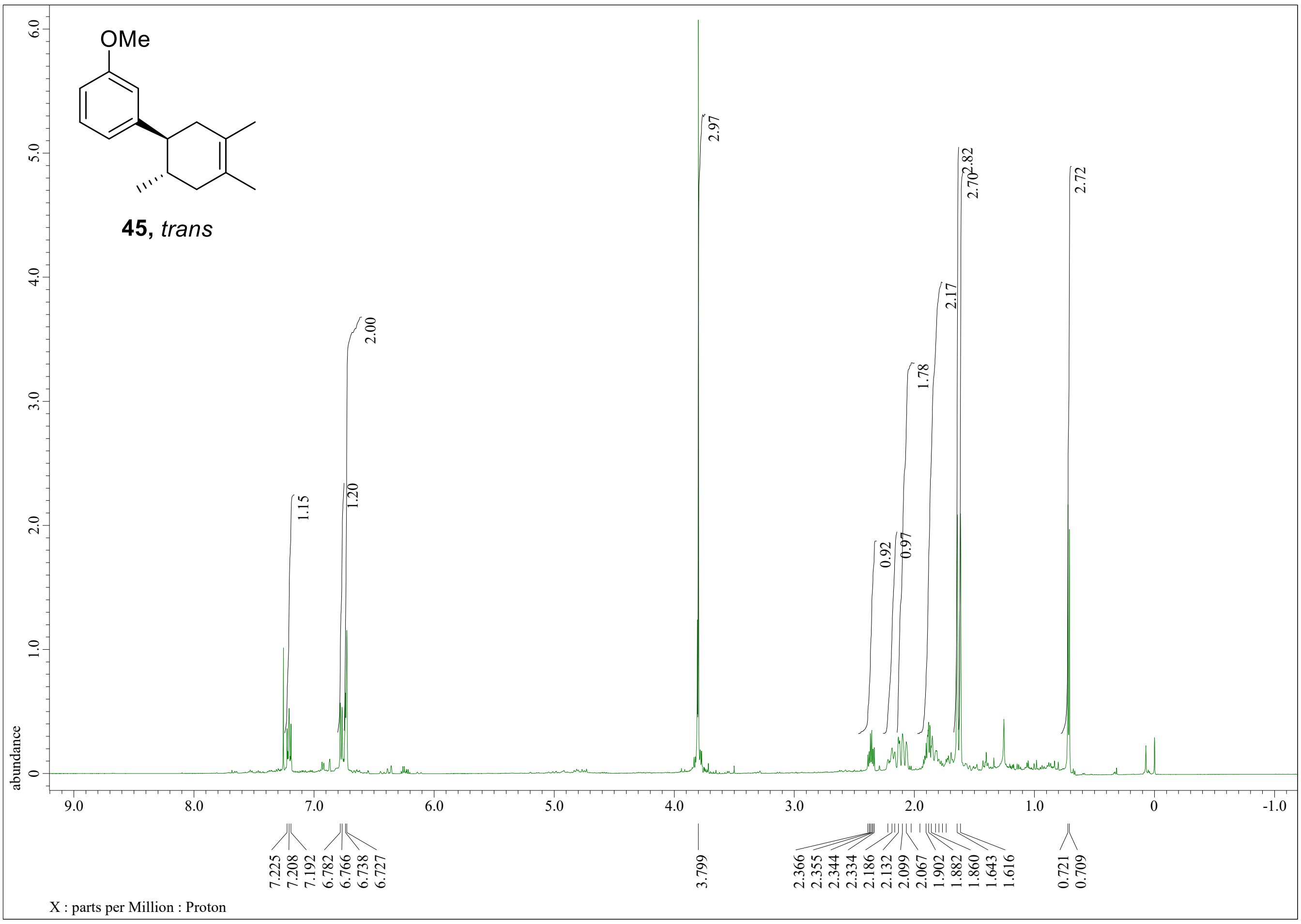

MeO
OH
23, trans
abundance
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
157.842
137.983
128.531
125.412
125.001
113.851
63.279
55.257
46.358
41.770
38.718
38.298
29.990
29.866
18.916
18.678
X : parts per Million : Carbon13

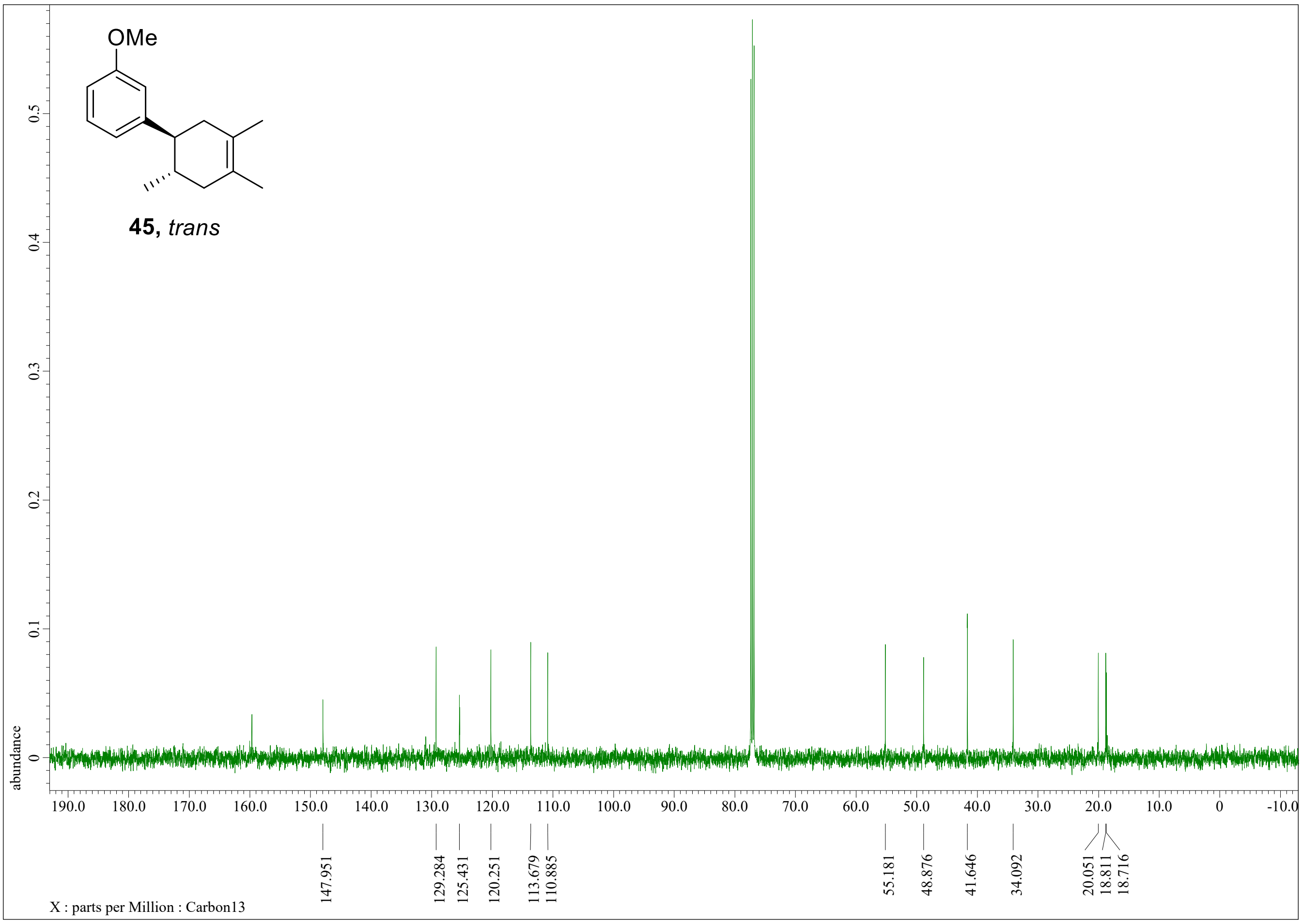

OMe
43, trans
3.23
1.77
1.00
1.00
0.90
1.02
1.97
0.96
0.90
3.02
3.01
2.80
7.175
7.171
7.160
7.155
7.153
7.149
7.140
7.138
7.135
6.940
6.925
6.912
6.910
6.868
6.852
3.799
2.968
2.957
2.947
2.935
2.925
2.083
2.051
2.005
1.993
1.983
1.878
1.853
1.647
1.615
0.728
0.716
abundance
X : parts per Million : Proton

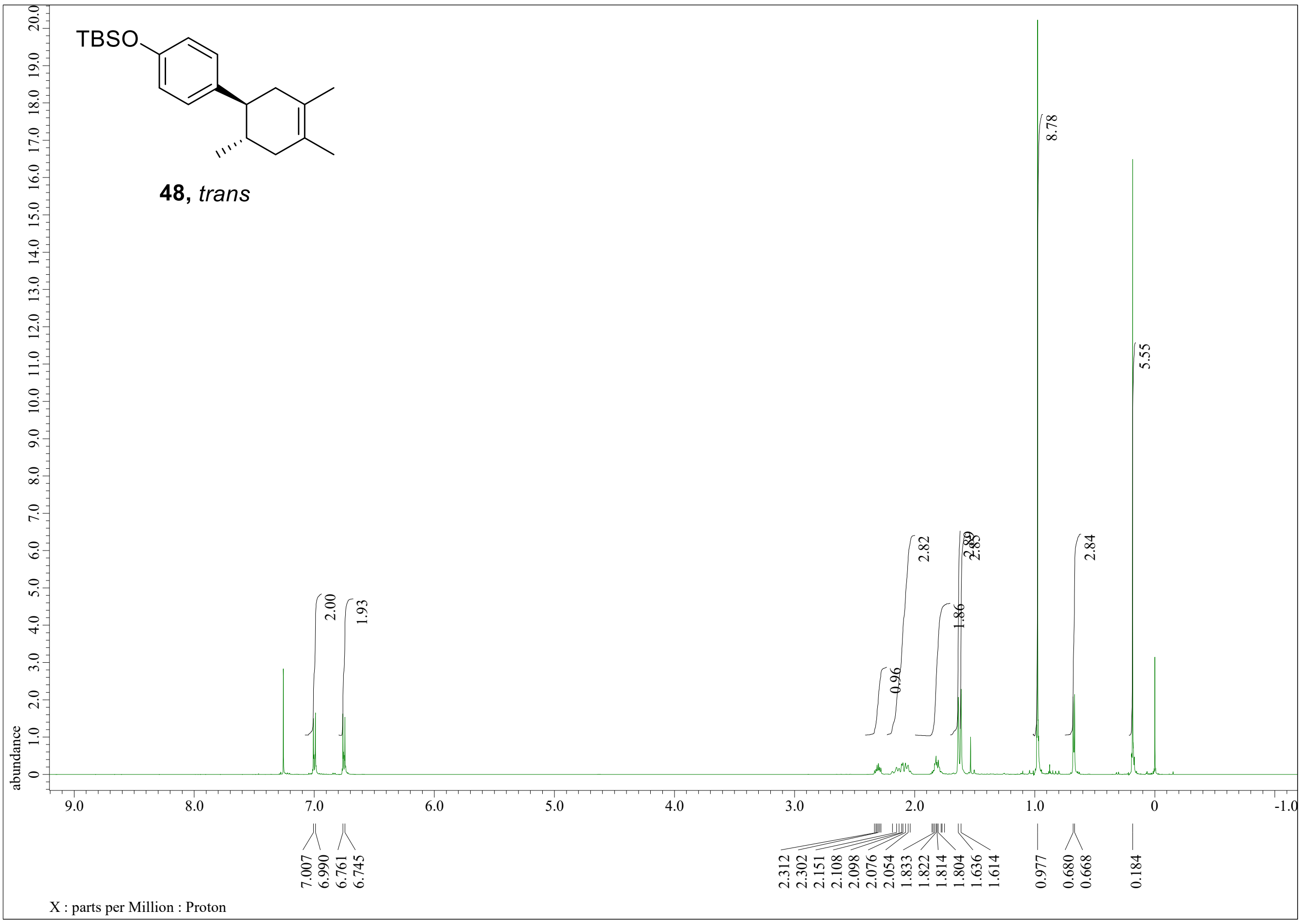

OMe
43, trans
157.584
134.149
127.892
126.556
125.736
125.326
120.766
110.684
55.524
41.722
40.158
33.119
19.717
18.878
18.764
abundance
X : parts per Million : Carbon13


OMe
44, *trans*
2.00
1.02
0.97
0.98
2.98
0.98
1.92
1.76
0.99
2.97
2.87
7.169
7.154
7.149
7.146
7.143
7.139
7.133
7.131
6.935
6.933
6.920
6.918
6.863
6.847
5.452
5.422
3.793
2.940
2.923
2.902
2.886
2.175
2.161
2.084
2.052
2.020
2.008
1.849
1.824
1.693
0.739
0.726
abundance
X : parts per Million : Proton

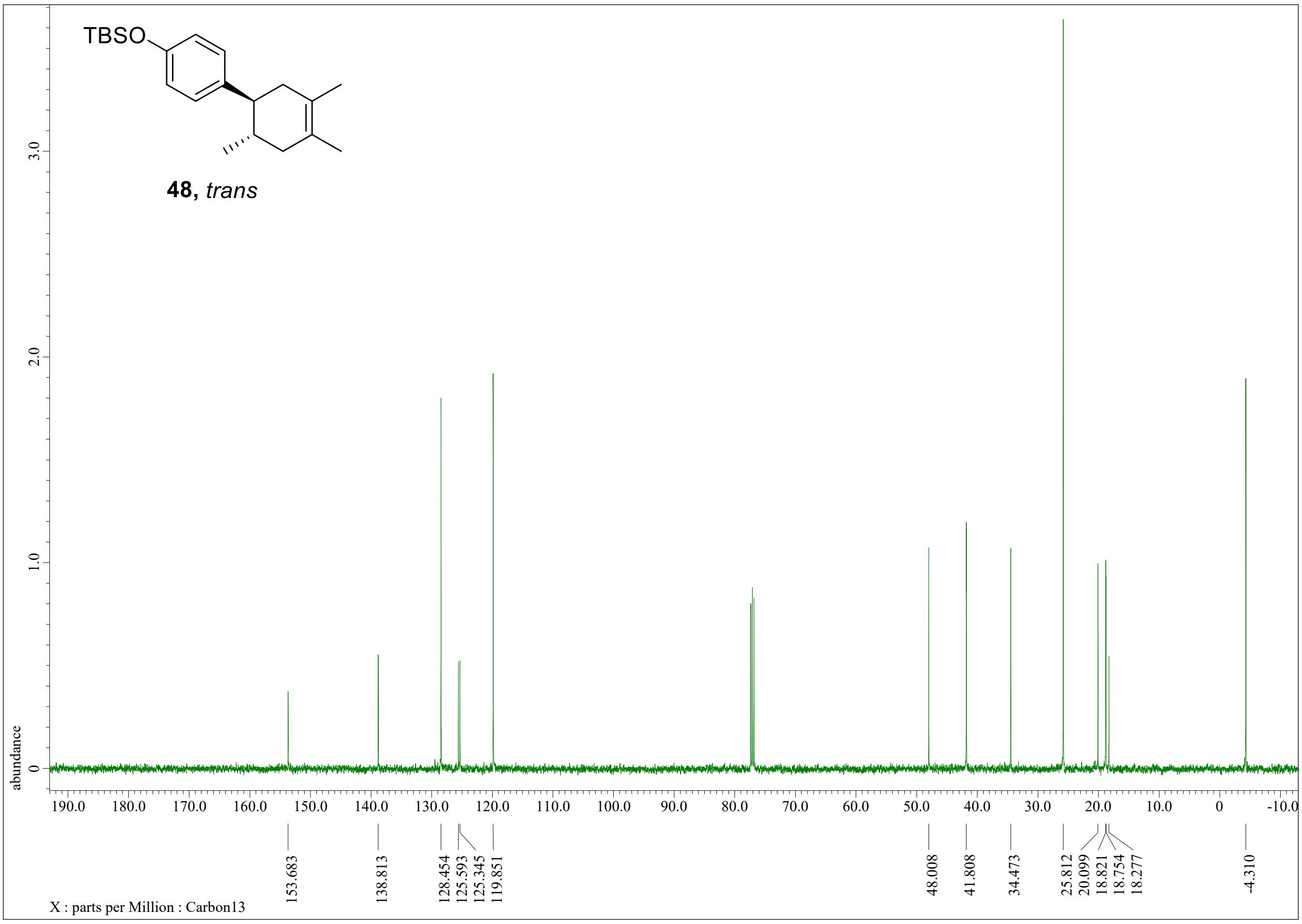

OMe
44, *trans*
157.623
134.168
133.824
127.939
126.575
121.196
120.728
110.675
55.515
39.920
33.615
32.794
23.552
19.908
abundance
X : parts per Million : Carbon13


OMe
45, trans
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
1.15
1.20
2.00
2.97
0.92
0.97
1.78
2.17
2.82
2.70
2.72
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.225
7.208
7.192
6.782
6.766
6.738
6.727
3.799
2.366
2.355
2.344
2.334
2.186
2.132
2.099
2.067
1.902
1.882
1.860
1.643
1.616
0.721
0.709
X : parts per Million : Proton

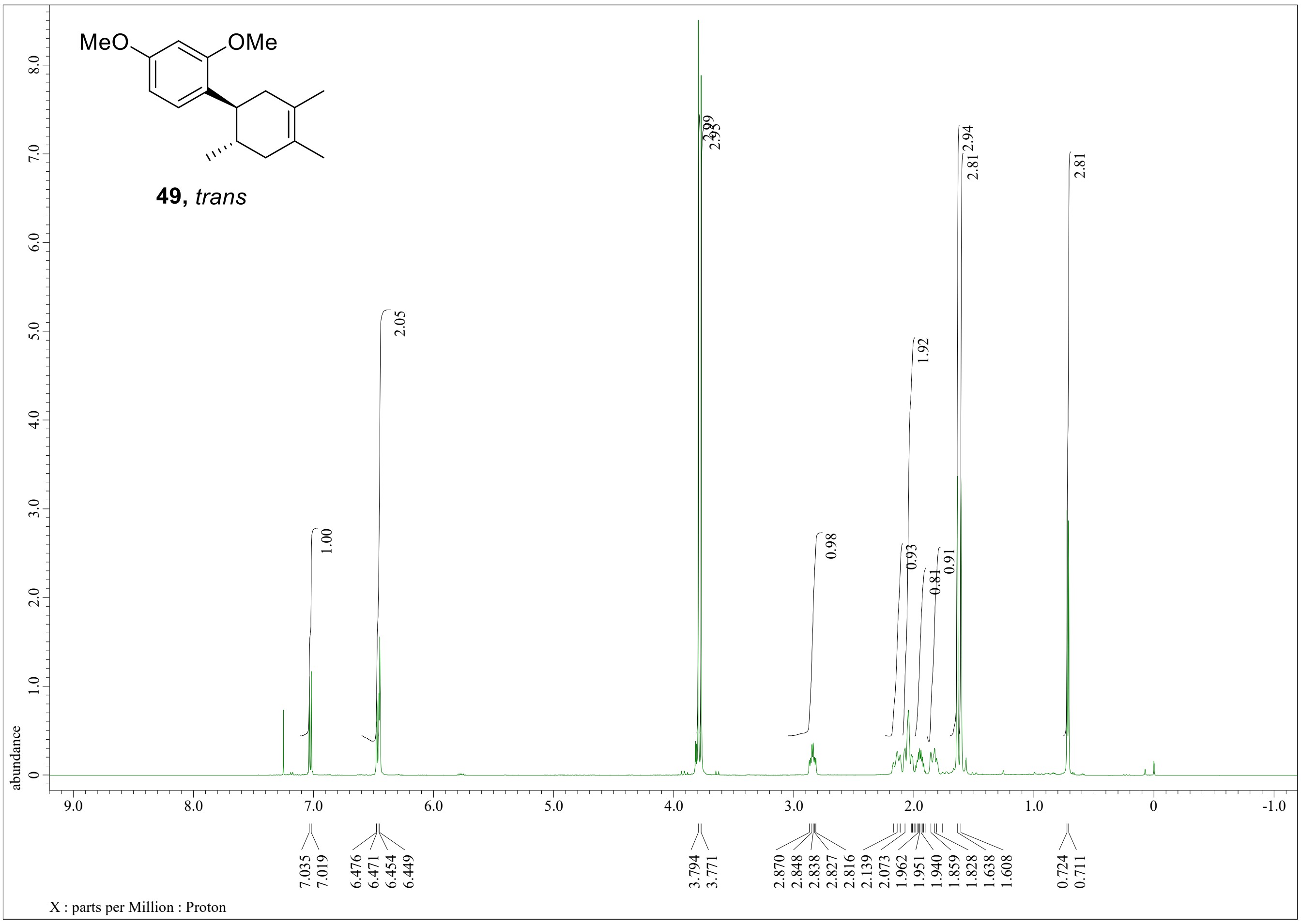

OMe
45, trans
0.5
0.4
0.3
0.2
0.1
0
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
147.951
129.284
125.431
120.251
113.679
110.885
55.181
48.876
41.646
34.092
20.051
18.811
18.716
X : parts per Million : Carbon13

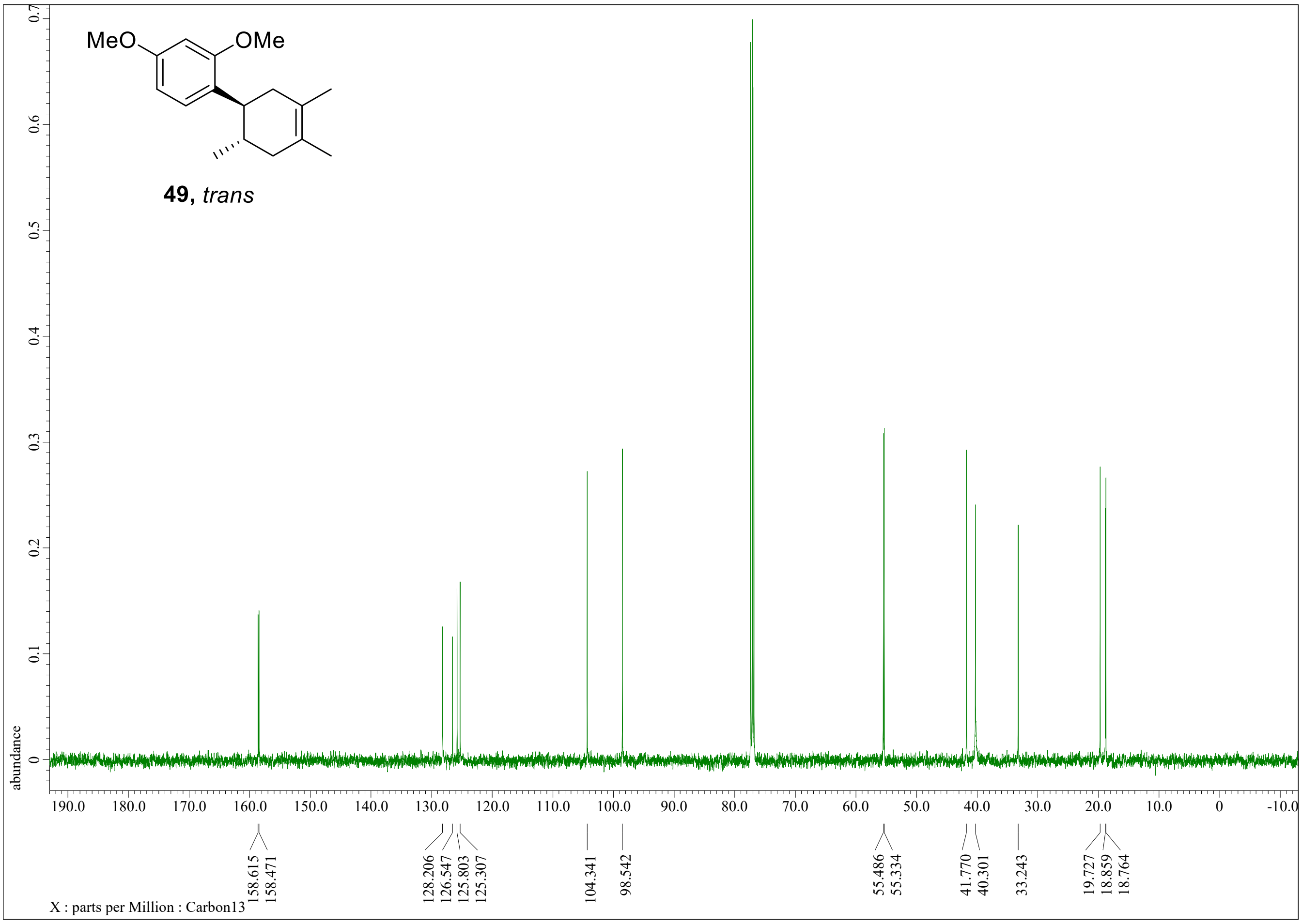


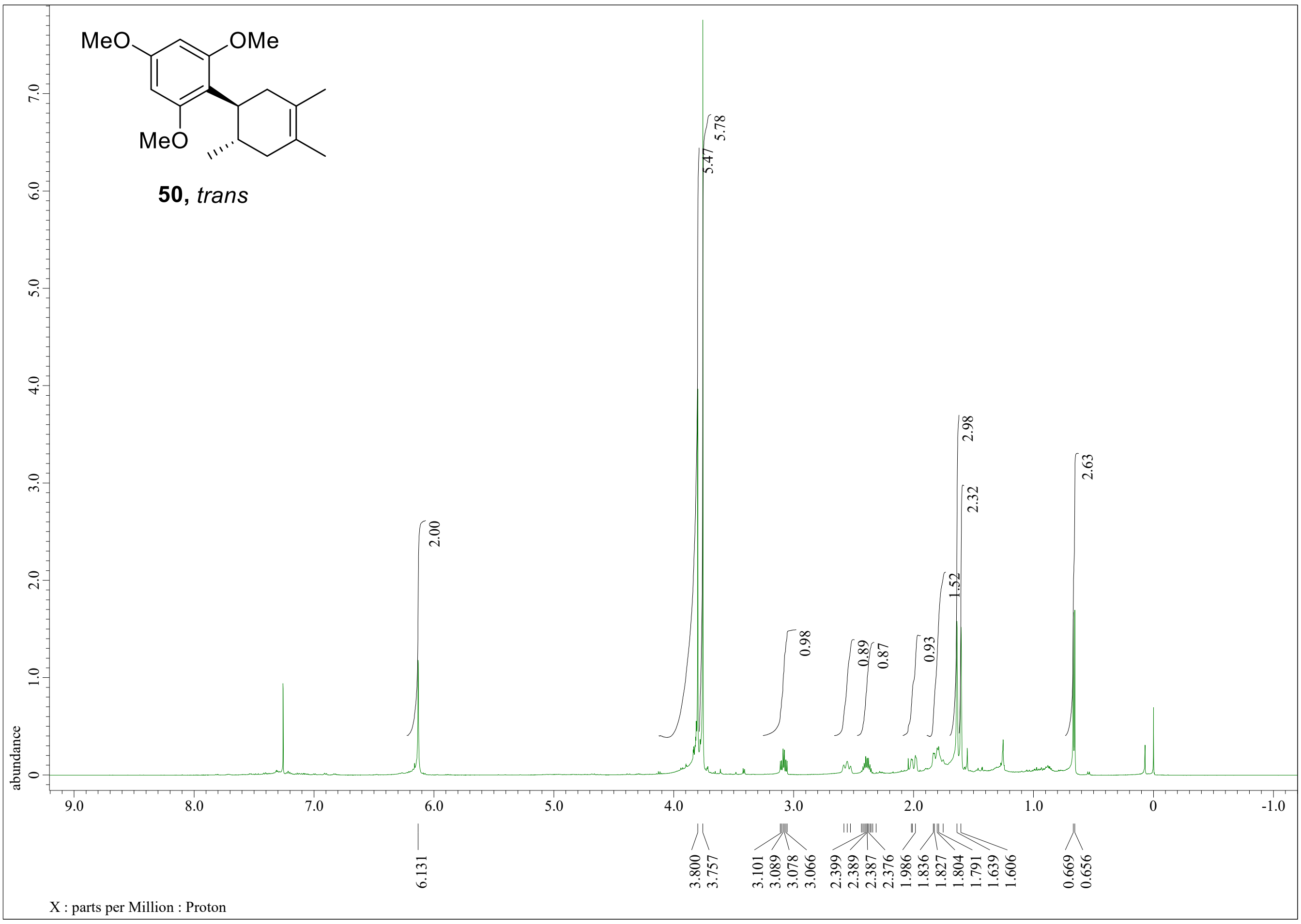
48, *trans*

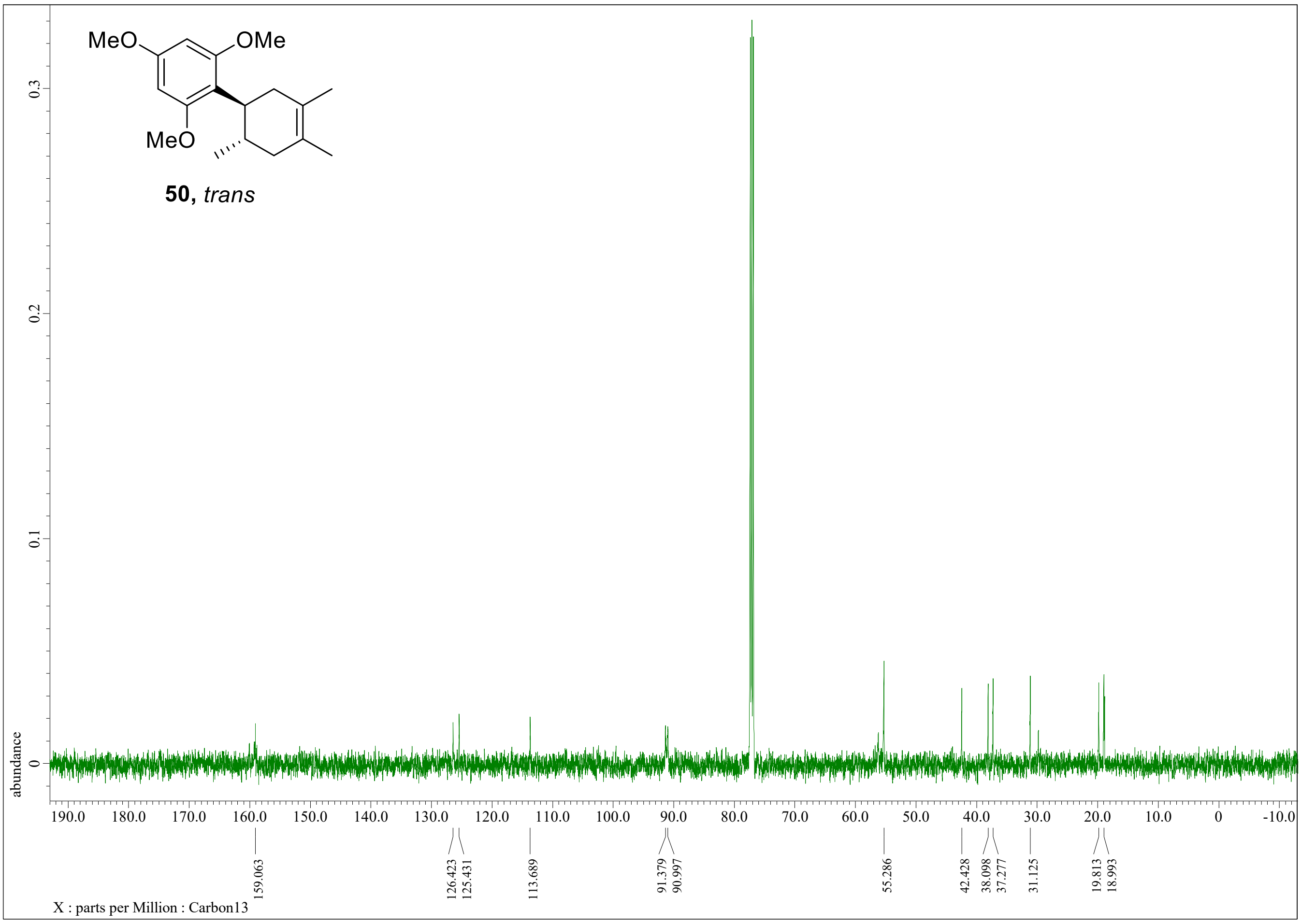


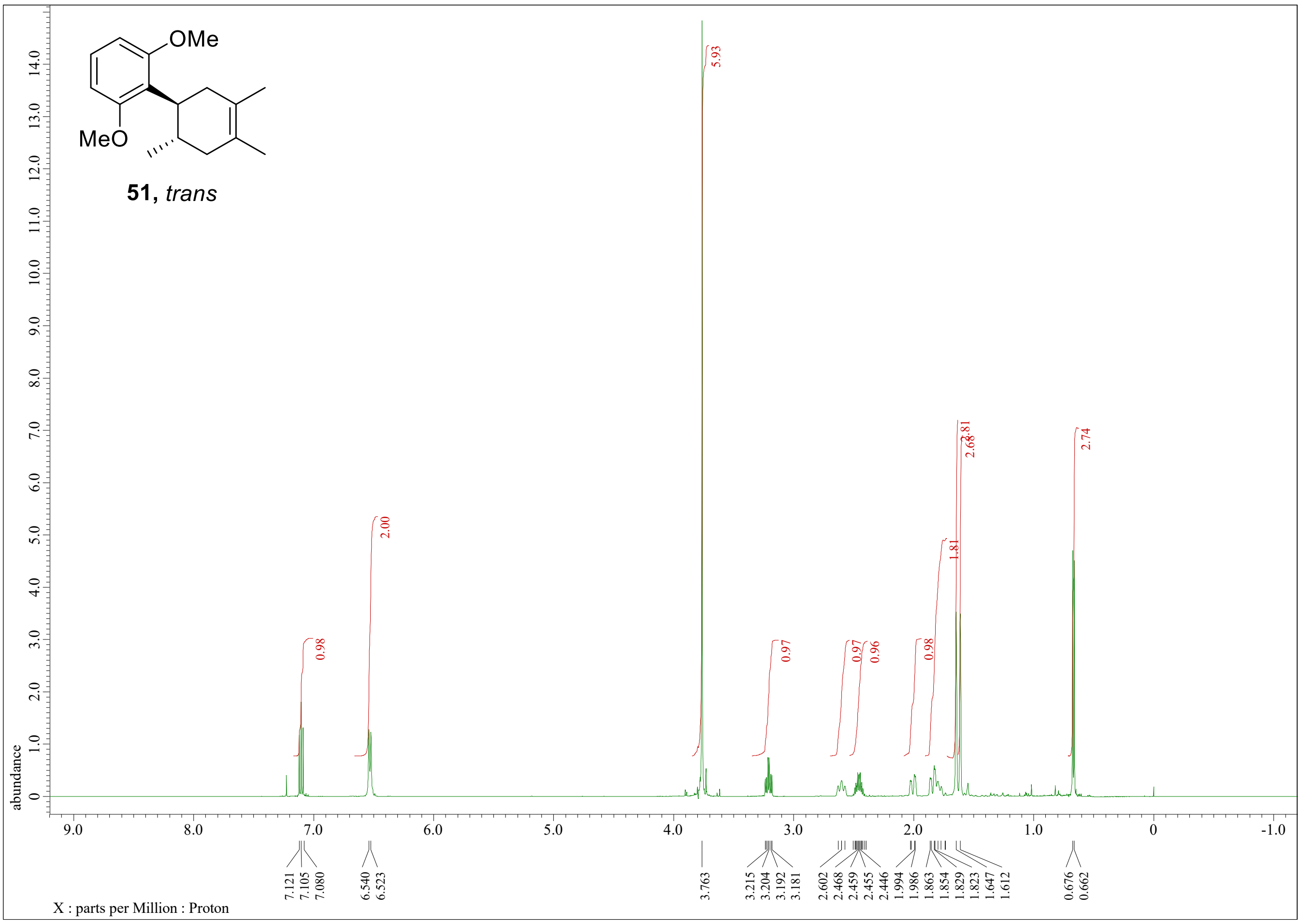
48, *trans*

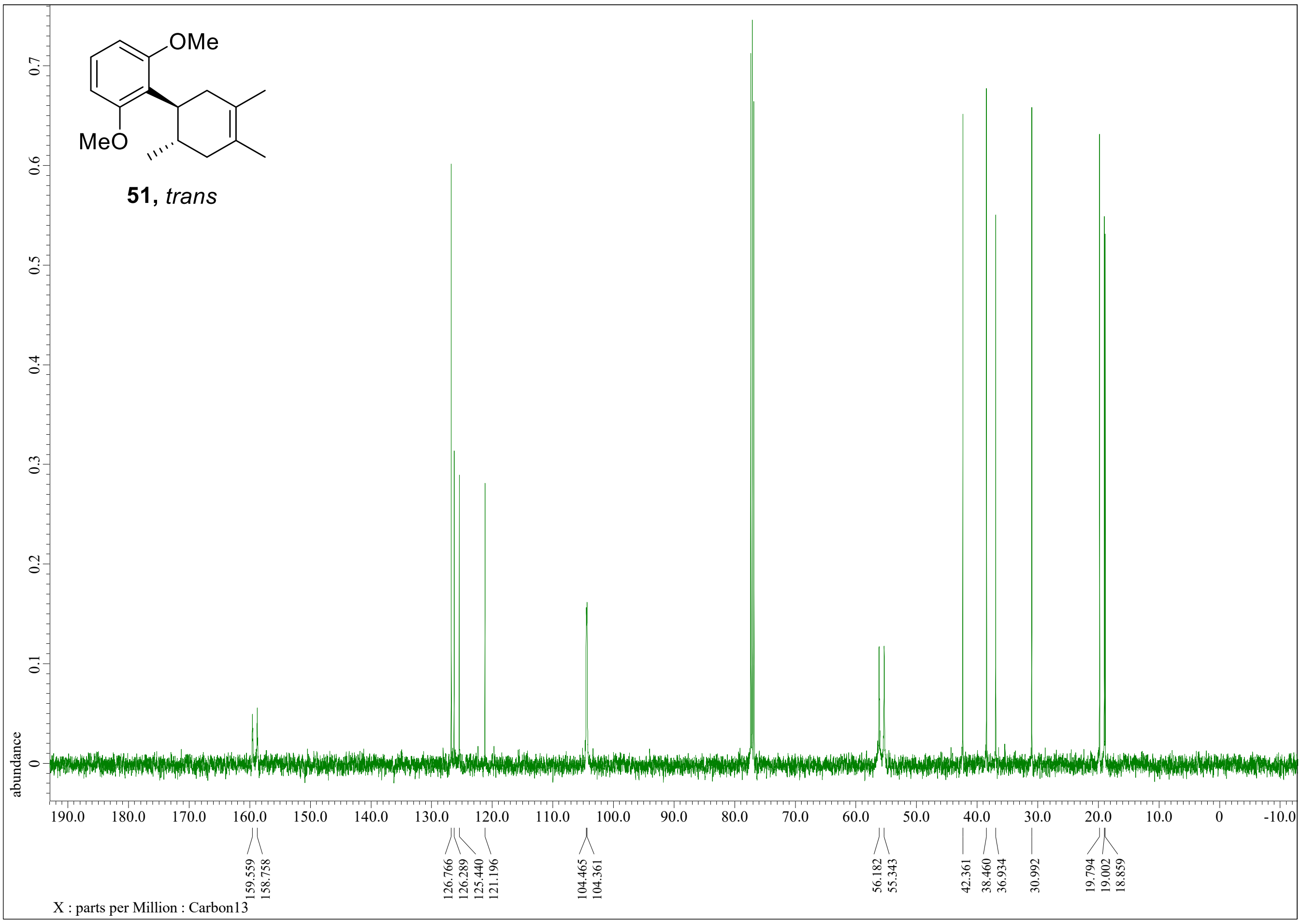

MeO
OMe
49, trans
abundance
X : parts per Million : Proton
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
1.00
2.05
2.99
2.95
0.98
1.92
0.93
0.81
0.91
2.94
2.81
2.81
7.035
7.019
6.476
6.471
6.454
6.449
3.794
3.771
2.870
2.848
2.838
2.827
2.816
2.139
2.073
1.962
1.951
1.940
1.859
1.828
1.638
1.608
0.724
0.711

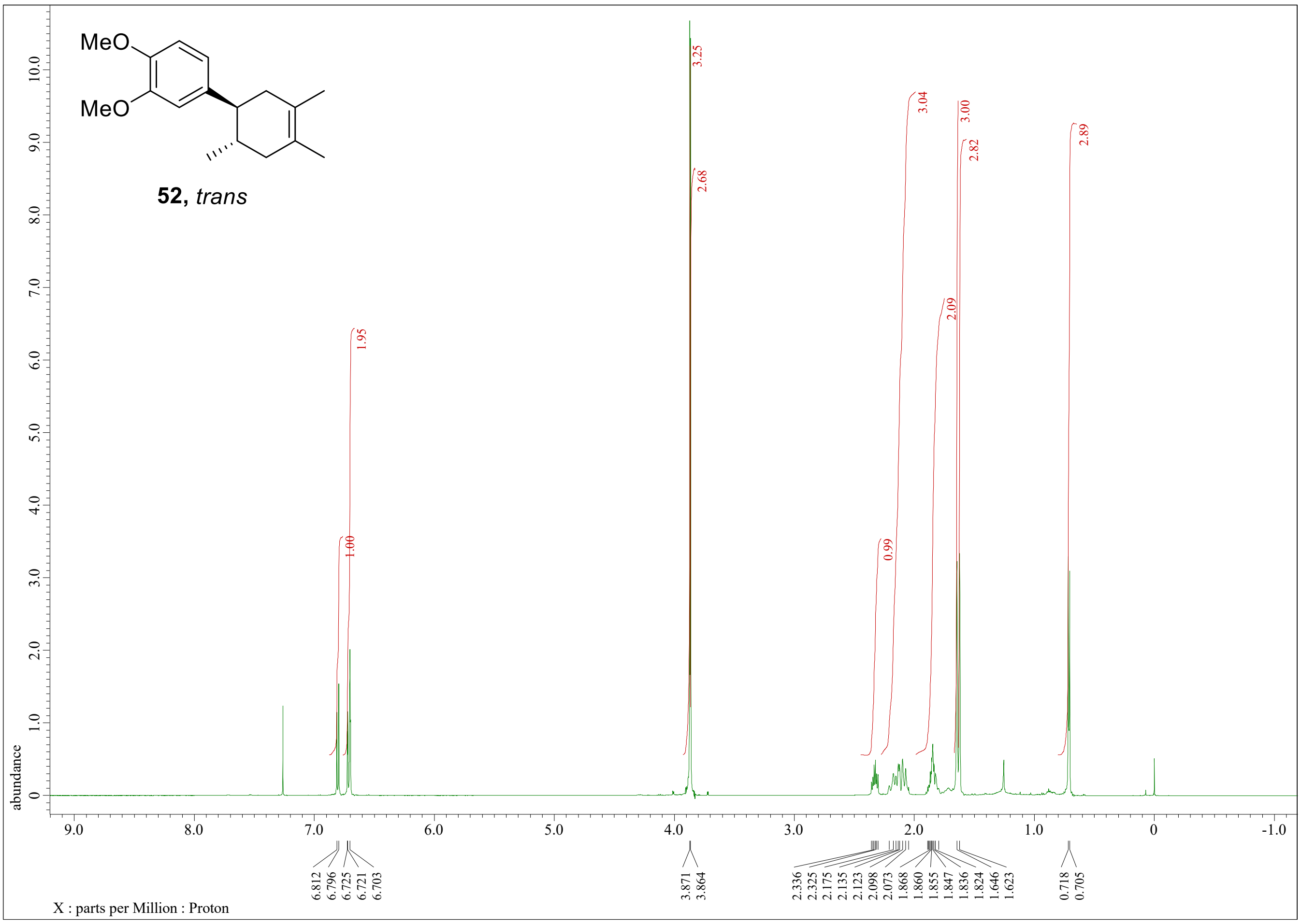

MeO
OMe
49, trans
abundance
X : parts per Million : Carbon13
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
158.615
158.471
128.206
126.547
125.803
125.307
104.341
98.542
55.486
55.334
41.770
40.301
33.243
19.727
18.859
18.764

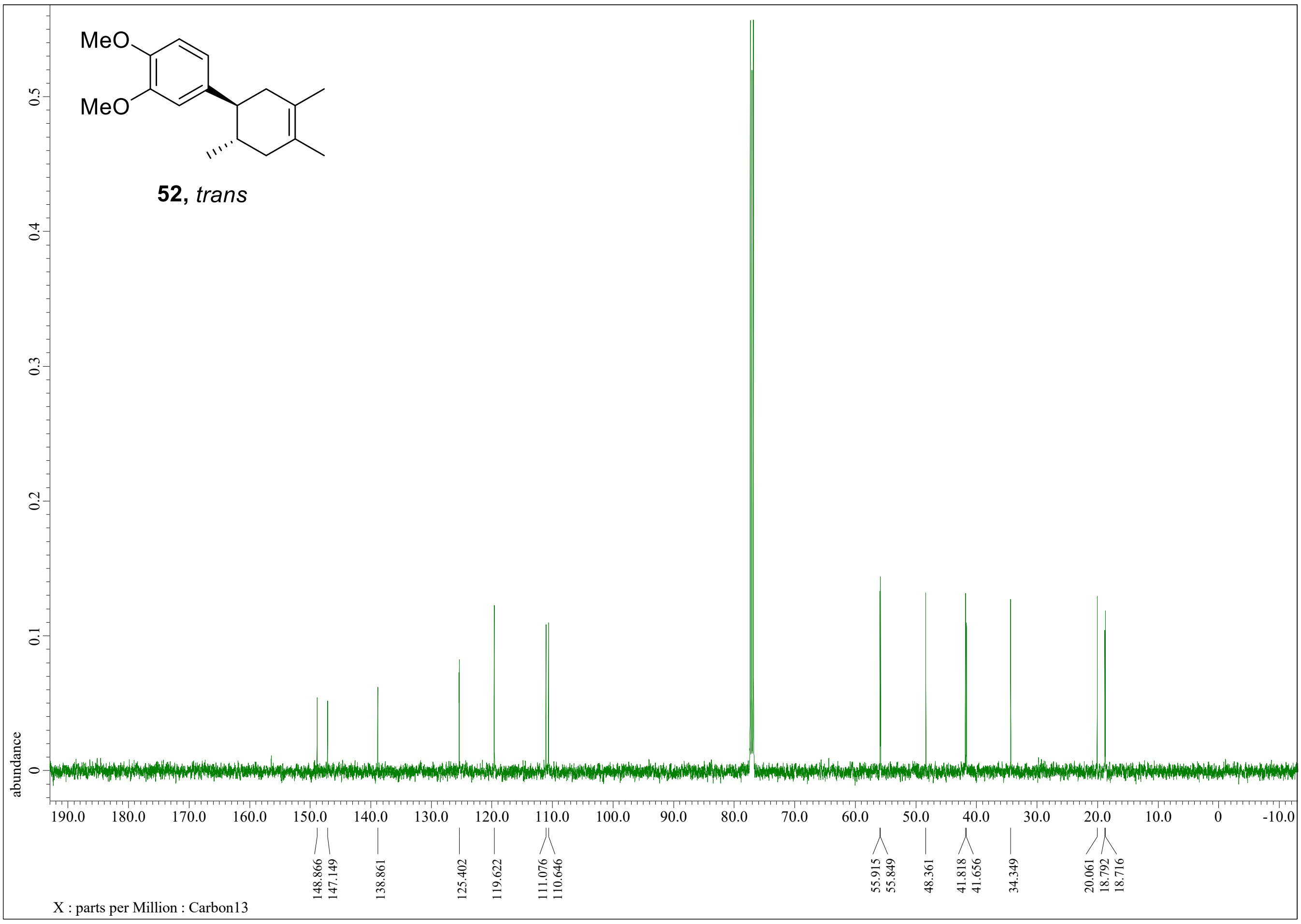

MeO
OMe
MeO
50, *trans*
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
2.00
5.47
5.78
0.98
0.89
0.87
0.93
1.52
2.98
2.32
2.63
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.131
3.800
3.757
3.101
3.089
3.078
3.066
2.399
2.389
2.387
2.376
1.986
1.836
1.827
1.804
1.791
1.639
1.606
0.669
0.656
X : parts per Million : Proton

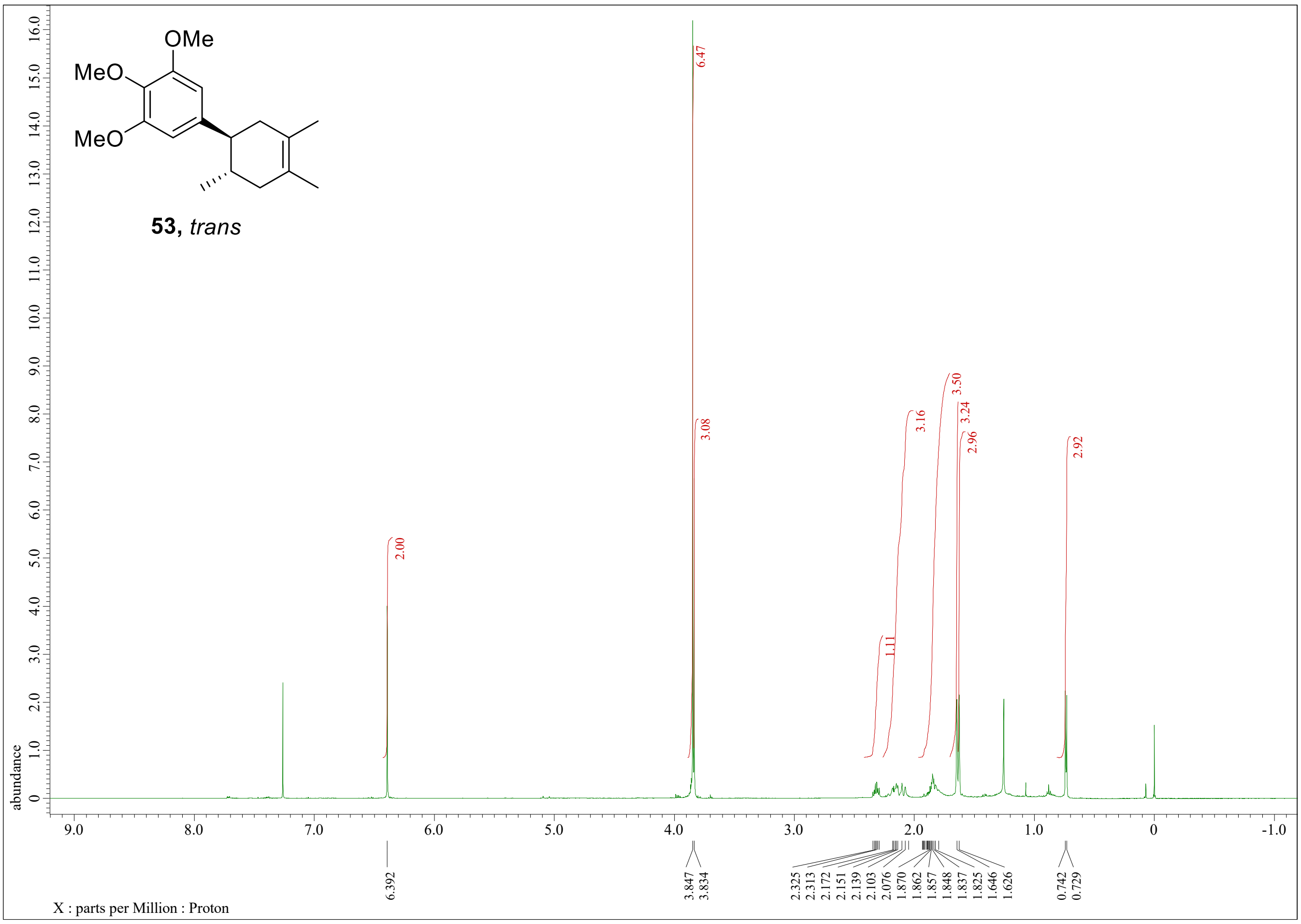

MeO
OMe
MeO
50, *trans*
abundance
0
0.1
0.2
0.3
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
159.063
126.423
125.431
113.689
91.379
90.997
55.286
42.428
38.098
37.277
31.125
19.813
18.993
X : parts per Million : Carbon13

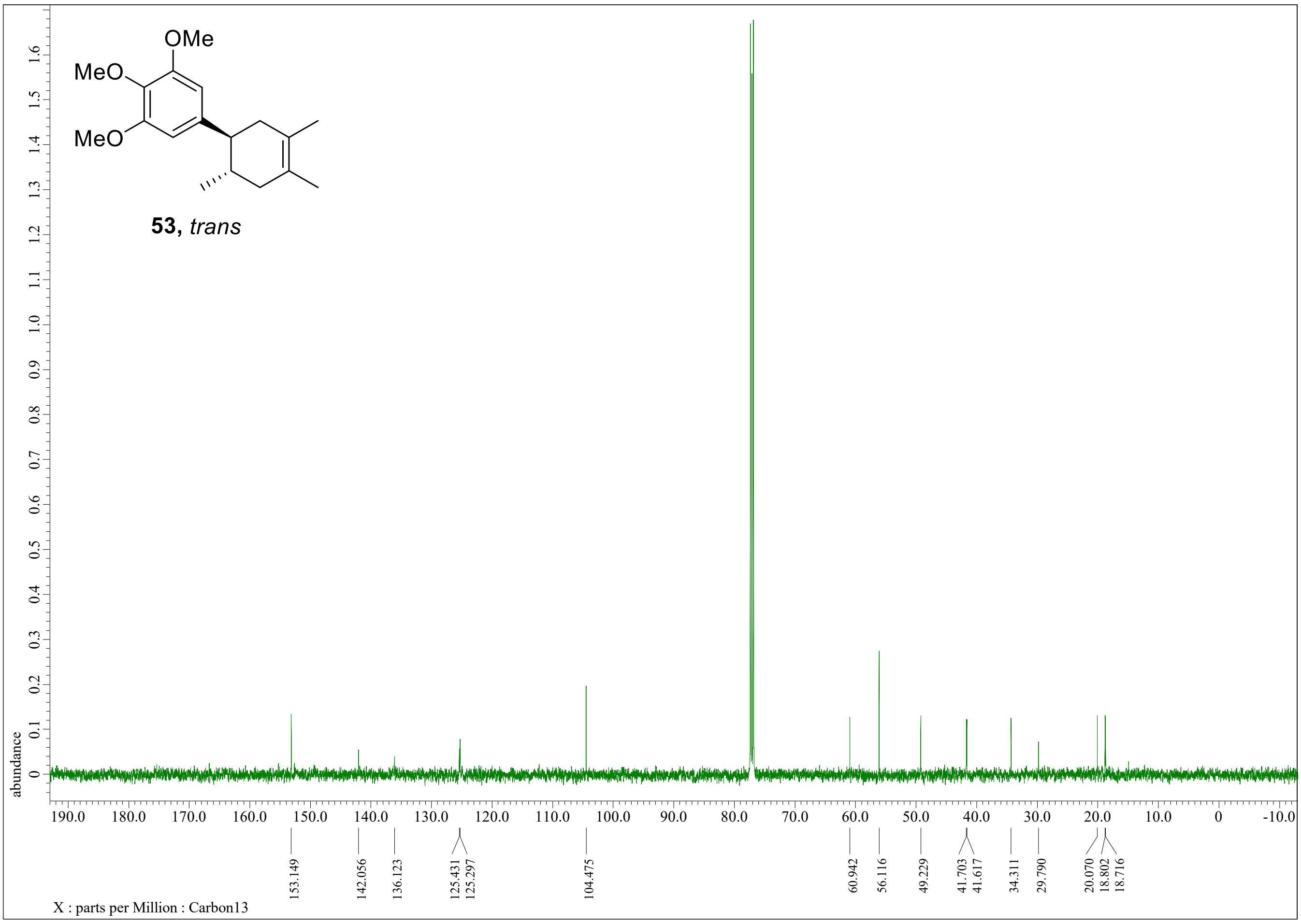

OMe
MeO
51, trans
5.93
2.00
0.98
0.97
0.97
0.96
0.98
1.81
2.81
2.68
2.74
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.121
7.105
7.080
6.540
6.523
3.763
3.215
3.204
3.192
3.181
2.602
2.468
2.459
2.455
2.446
1.994
1.986
1.863
1.854
1.829
1.823
1.647
1.612
0.676
0.662
X : parts per Million : Proton

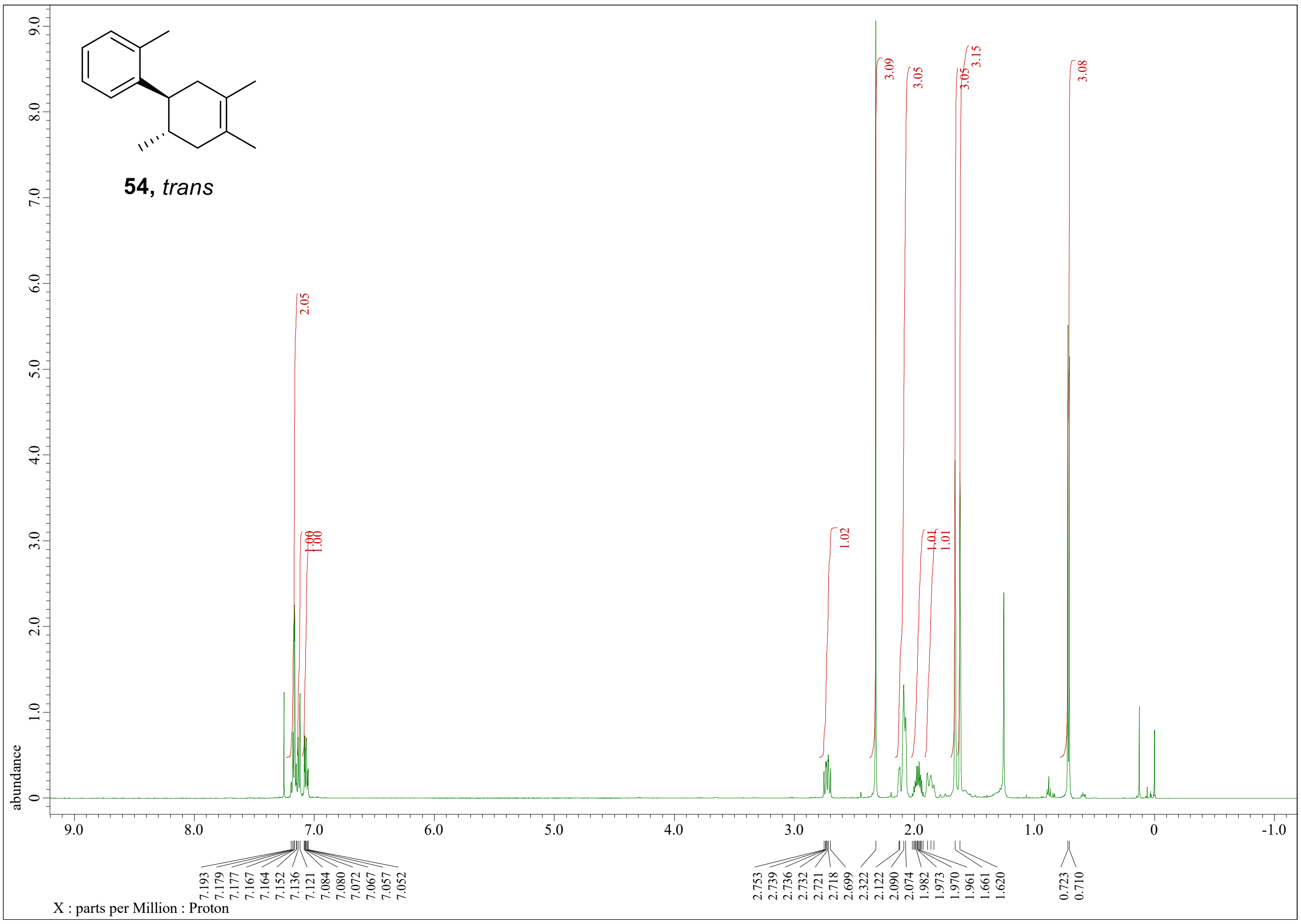

OMe
MeO
51, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
159.559
158.758
126.766
126.289
125.440
121.196
104.465
104.361
56.182
55.343
42.361
38.460
36.934
30.992
19.794
19.002
18.859
X : parts per Million : Carbon13

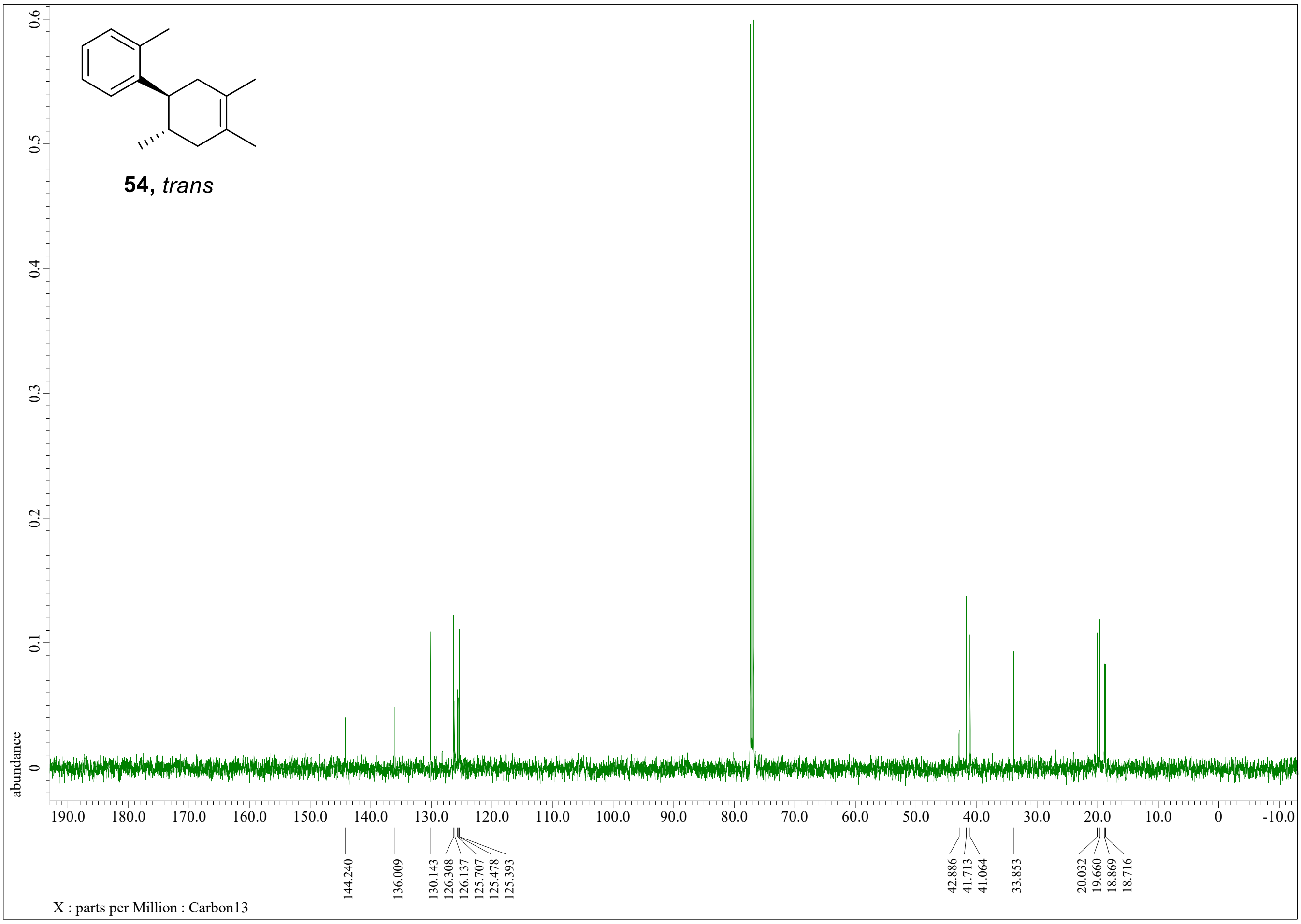

MeO
MeO
52, trans
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.25
2.68
3.04
3.00
2.82
2.89
2.09
1.95
1.00
0.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.812
6.796
6.725
6.721
6.703
3.871
3.864
2.336
2.325
2.175
2.135
2.123
2.098
2.073
1.868
1.860
1.855
1.847
1.836
1.824
1.646
1.623
0.718
0.705
X : parts per Million : Proton

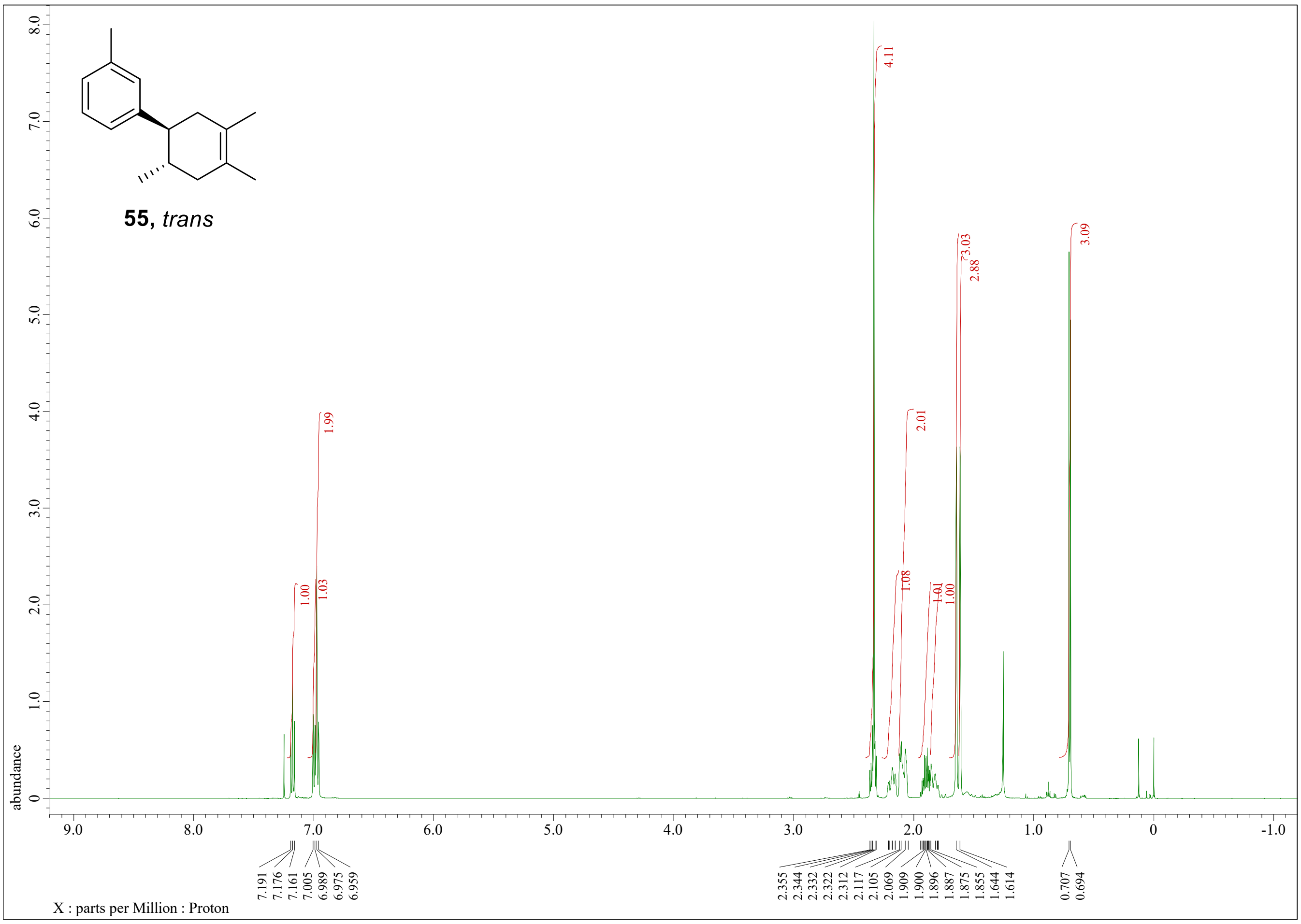

MeO
MeO
52, trans
abundance
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
148.866
147.149
138.861
125.402
119.622
111.076
110.646
55.915
55.849
48.361
41.818
41.656
34.349
20.061
18.792
18.716
X : parts per Million : Carbon13

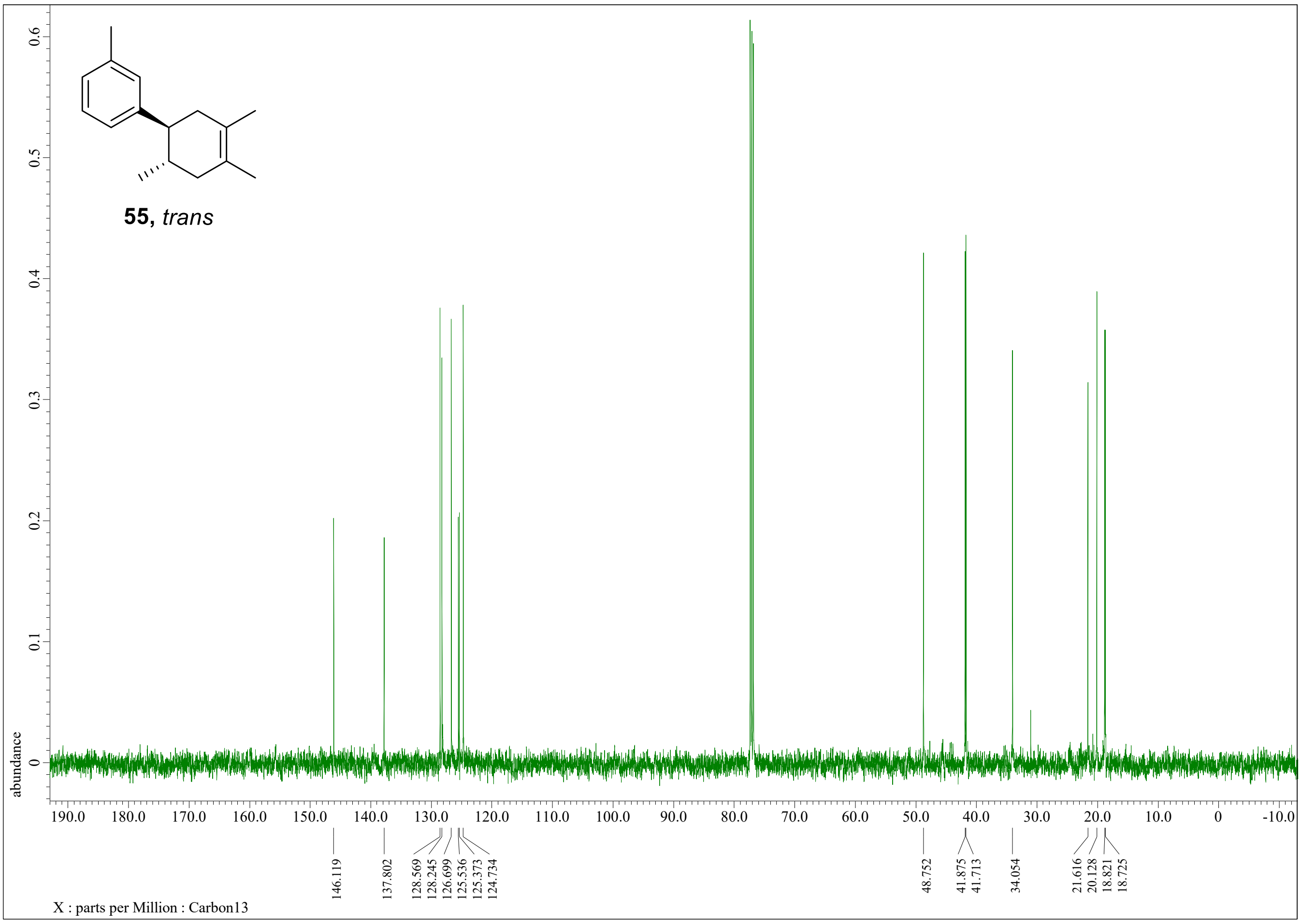

OMe
MeO
MeO
53, trans
abundance
6.47
3.08
2.00
1.11
3.16
3.50
3.24
2.96
2.92
6.392
3.847
3.834
2.325
2.313
2.172
2.151
2.139
2.103
2.076
1.870
1.862
1.857
1.848
1.837
1.825
1.646
1.626
0.742
0.729
X : parts per Million : Proton

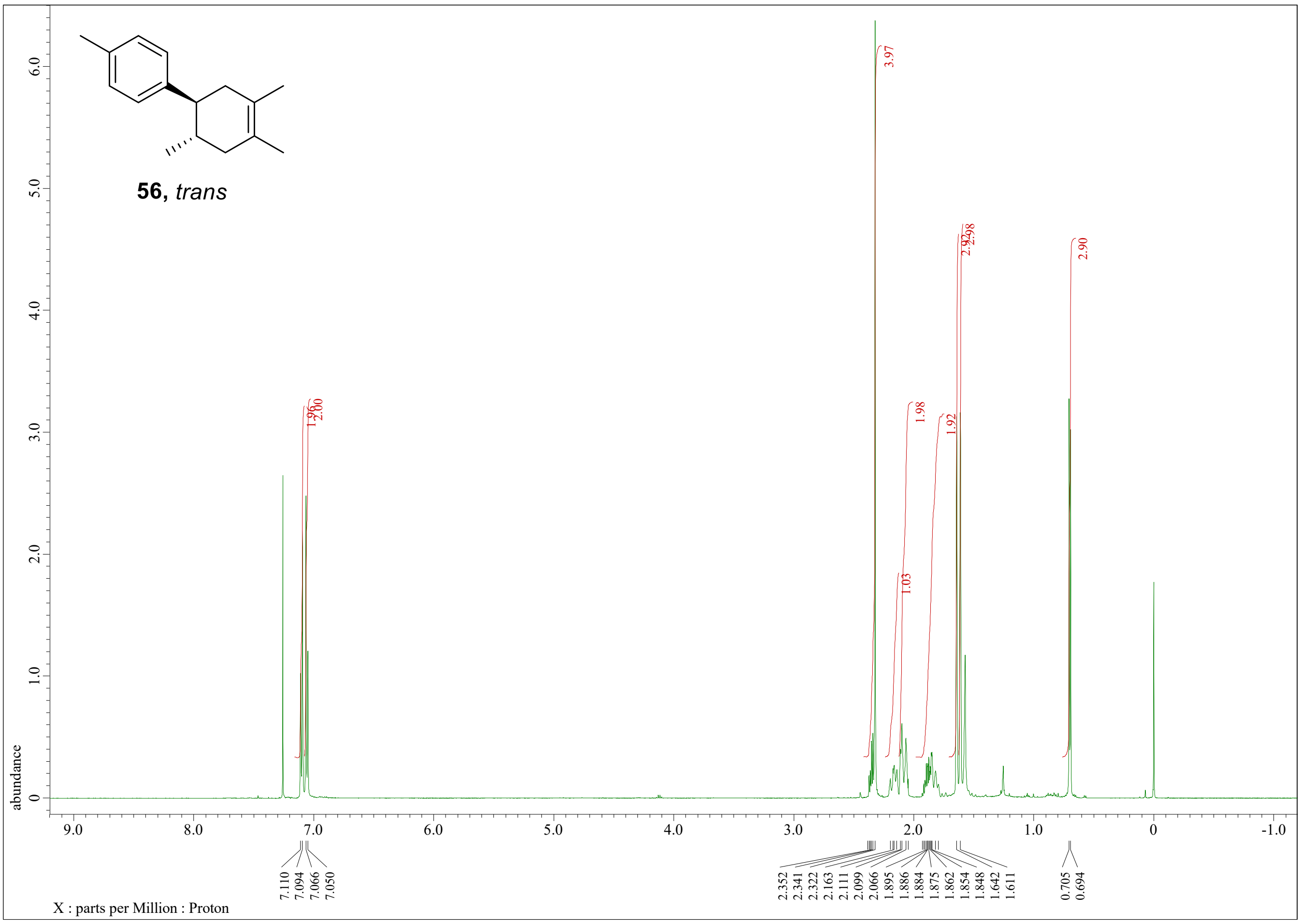

OMe
MeO
MeO
53, trans
abundance
153.149
142.056
136.123
125.431
125.297
104.475
60.942
56.116
49.229
41.703
41.617
34.311
29.790
20.070
18.802
18.716
X : parts per Million : Carbon13

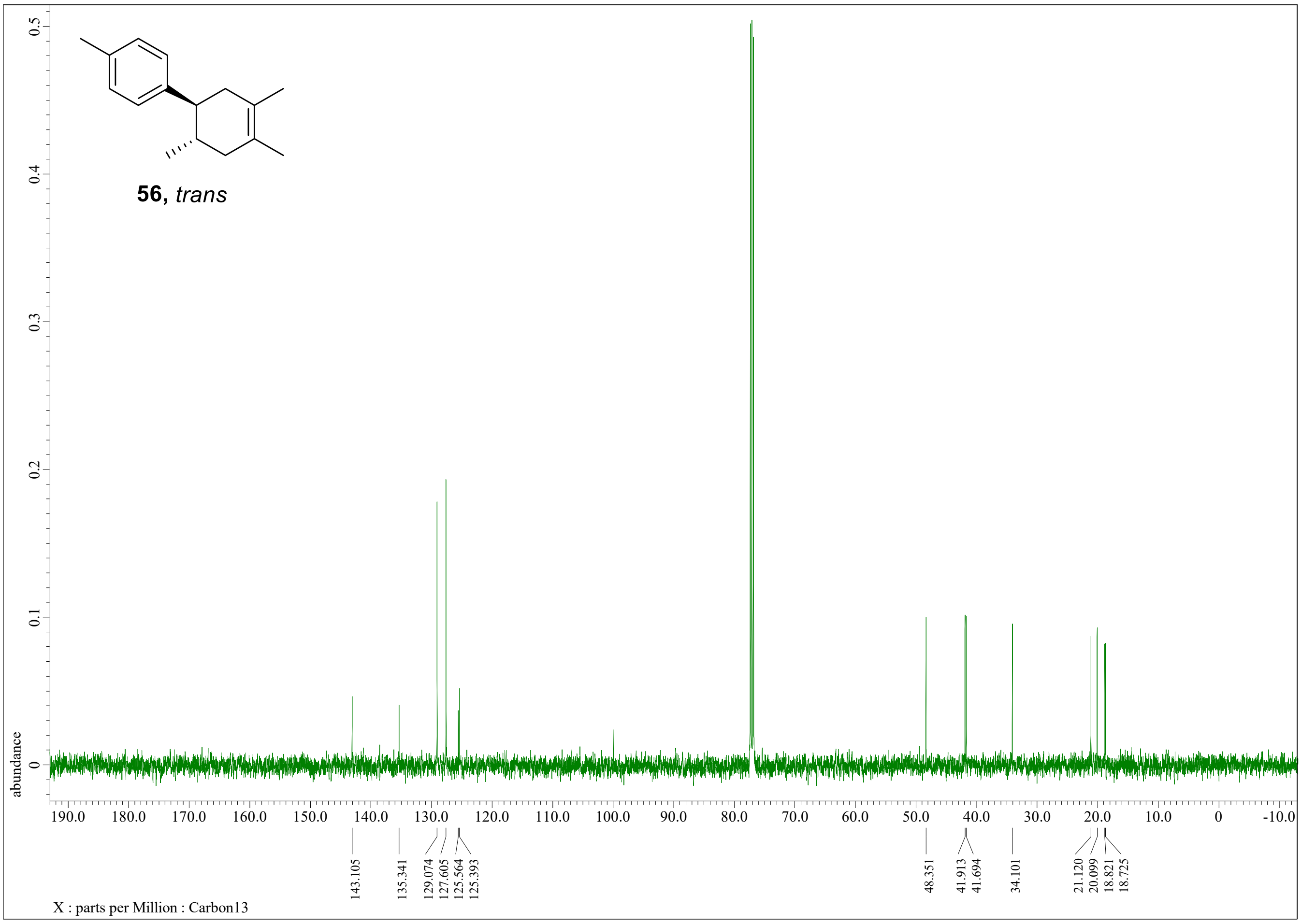

54, trans
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.05
1.00
1.00
1.02
3.09
3.05
1.01
1.01
3.05
3.15
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.193
7.179
7.177
7.167
7.164
7.152
7.136
7.121
7.084
7.080
7.072
7.067
7.057
7.052
2.753
2.739
2.736
2.732
2.721
2.718
2.699
2.322
2.122
2.090
2.074
1.982
1.973
1.970
1.961
1.661
1.620
0.723
0.710
X : parts per Million : Proton

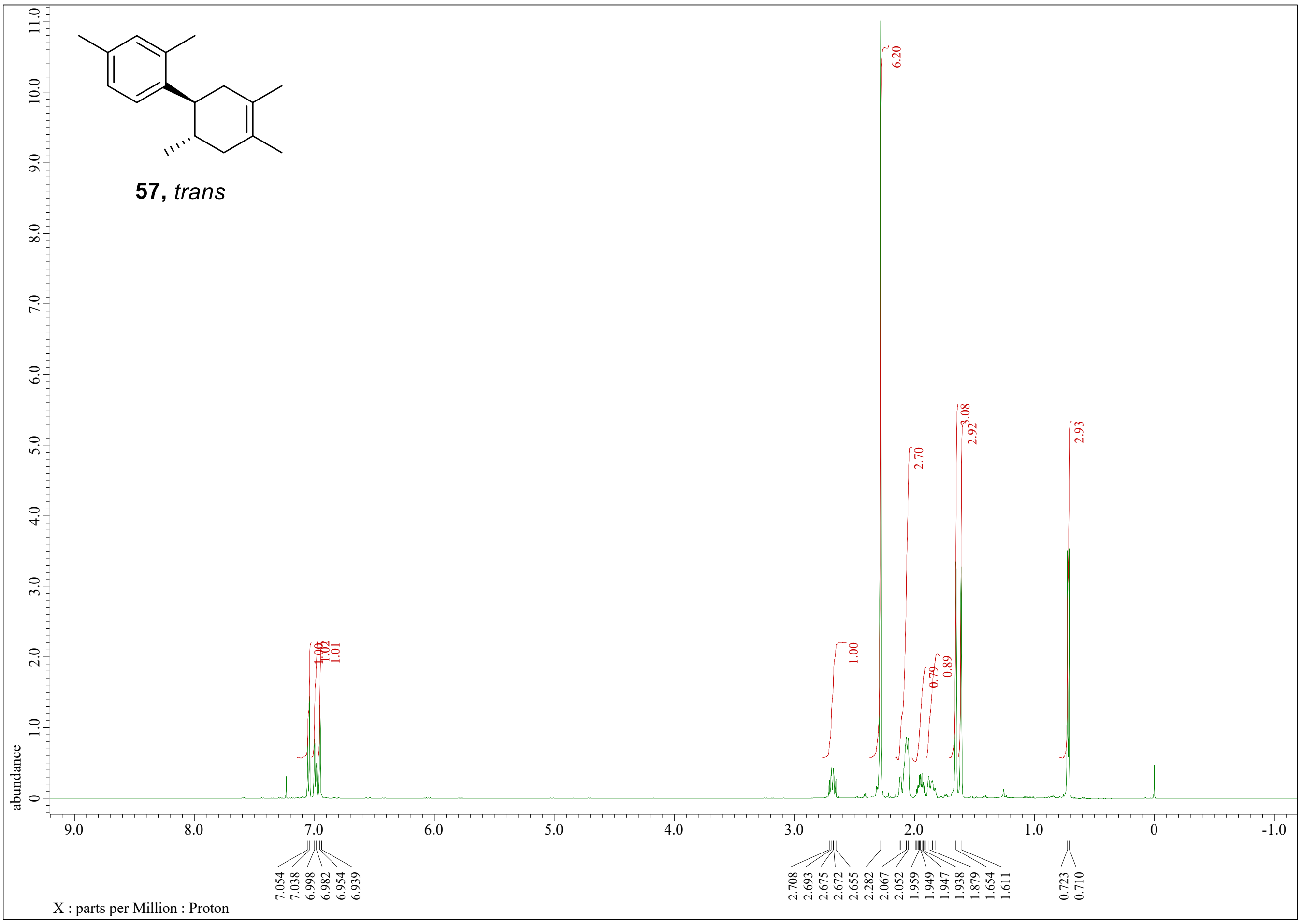

54, trans
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
144.240
136.009
130.143
126.308
126.137
125.707
125.478
125.393
42.886
41.713
41.064
33.853
20.032
19.660
18.869
18.716
X : parts per Million : Carbon13

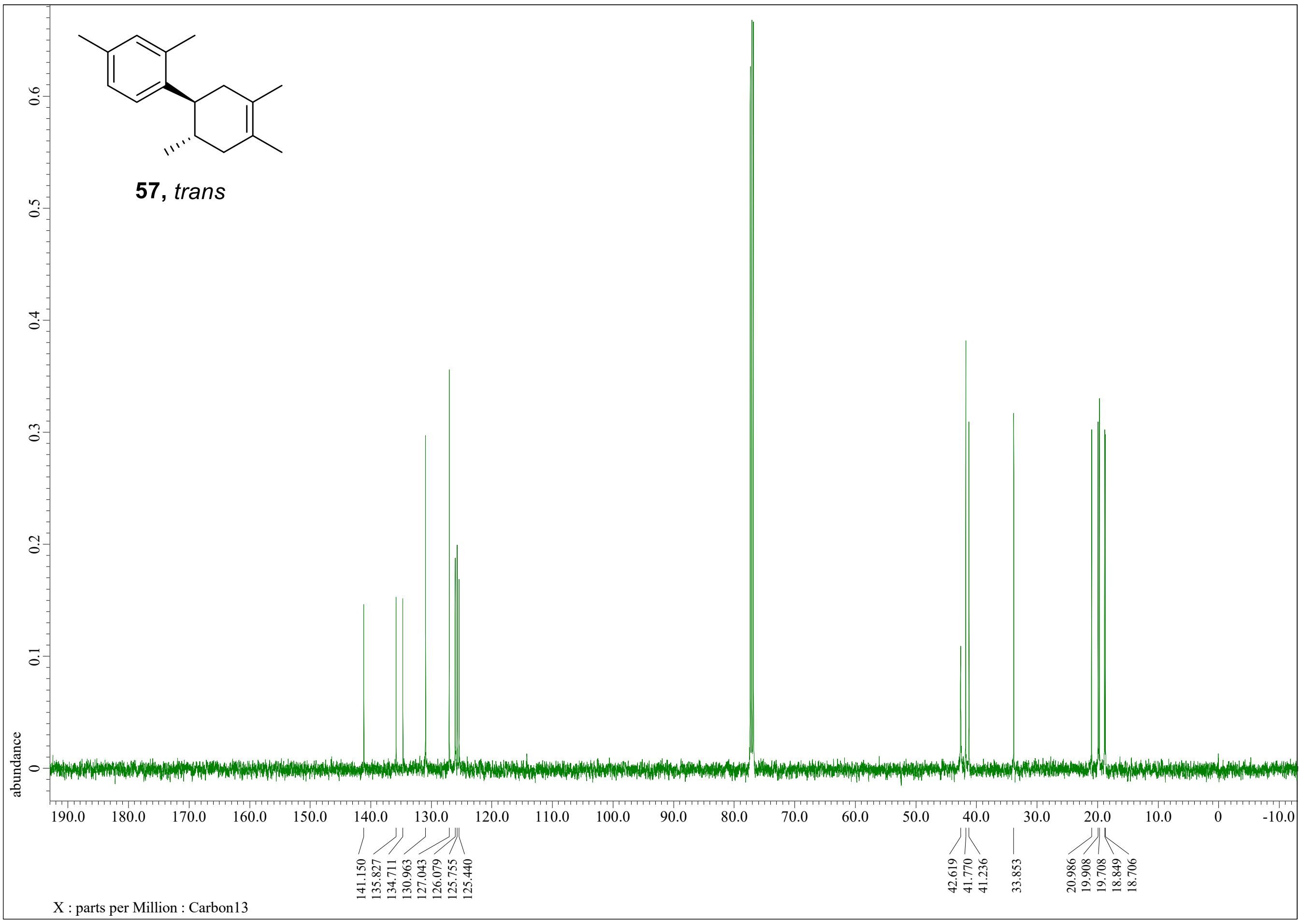

55, trans
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4.11
3.03
2.88
3.09
2.01
1.99
1.00
1.03
1.08
1.01
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.191
7.176
7.161
7.005
6.989
6.975
6.959
2.355
2.344
2.332
2.322
2.312
2.117
2.105
2.069
1.909
1.900
1.896
1.887
1.875
1.855
1.644
1.614
0.707
0.694
X : parts per Million : Proton

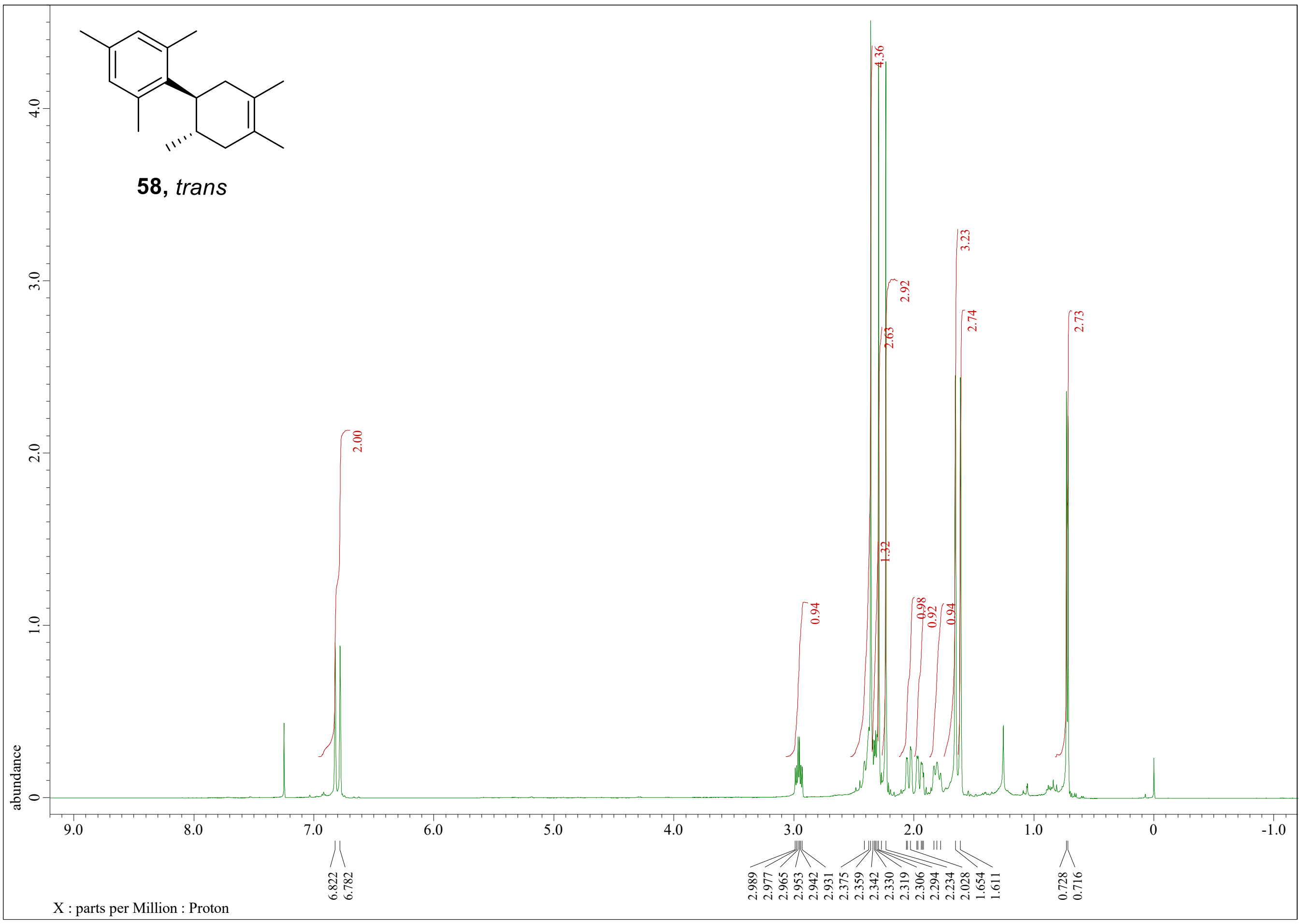

55, trans
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
146.119
137.802
128.569
128.245
126.699
125.536
125.373
124.734
48.752
41.875
41.713
34.054
21.616
20.128
18.821
18.725
X : parts per Million : Carbon13


56, trans
abundance
X : parts per Million : Proton
1.96
2.00
3.97
1.03
1.98
1.92
2.97
2.98
2.90
7.110
7.094
7.066
7.050
2.352
2.341
2.322
2.163
2.111
2.099
2.066
1.895
1.886
1.884
1.875
1.862
1.854
1.848
1.642
1.611
0.705
0.694


56, trans
abundance
X : parts per Million : Carbon13
143.105
135.341
129.074
127.605
125.564
125.393
48.351
41.913
41.694
34.101
21.120
20.099
18.821
18.725


57, trans
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
1.00
1.02
1.01
1.00
6.20
2.70
0.79
0.89
3.08
2.92
2.93
7.054
7.038
6.998
6.982
6.954
6.939
2.708
2.693
2.675
2.672
2.655
2.282
2.067
2.052
1.959
1.949
1.947
1.938
1.879
1.654
1.611
0.723
0.710
X : parts per Million : Proton


57, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
141.150
135.827
134.711
130.963
127.043
126.079
125.755
125.440
42.619
41.770
41.236
33.853
20.986
19.908
19.708
18.849
18.706
X : parts per Million : Carbon13


58, trans
abundance
0
1.0
2.0
3.0
4.0
2.00
0.94
4.36
2.63
1.32
2.92
0.98
0.92
0.94
3.23
2.74
2.73
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.822
6.782
2.989
2.977
2.965
2.953
2.942
2.931
2.375
2.359
2.342
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2.294
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2.028
1.654
1.611
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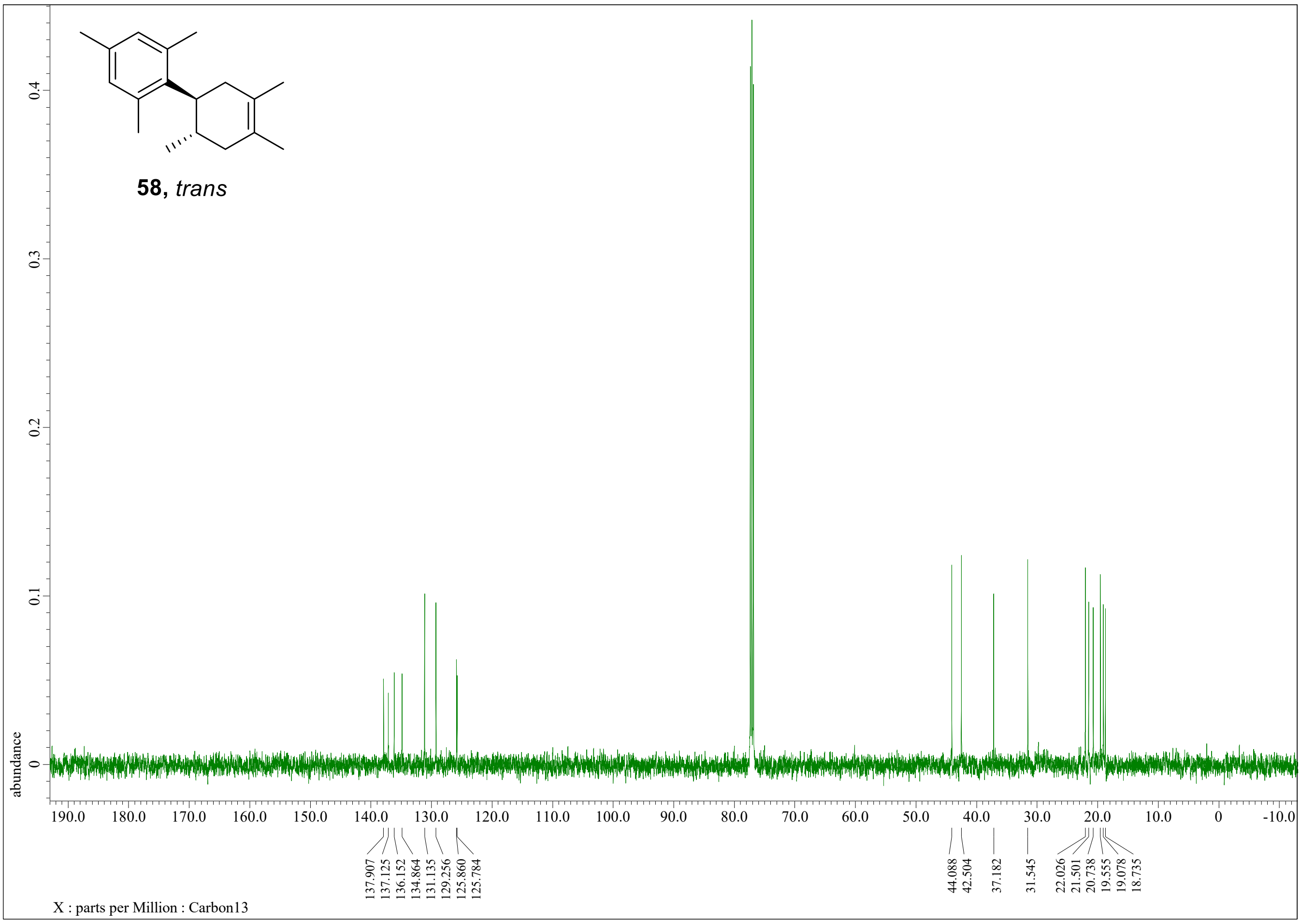
X : parts per Million : Proton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abundance
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0.2
0.3
0.4
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180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
137.907
137.125
136.152
134.864
131.135
129.256
125.860
125.784
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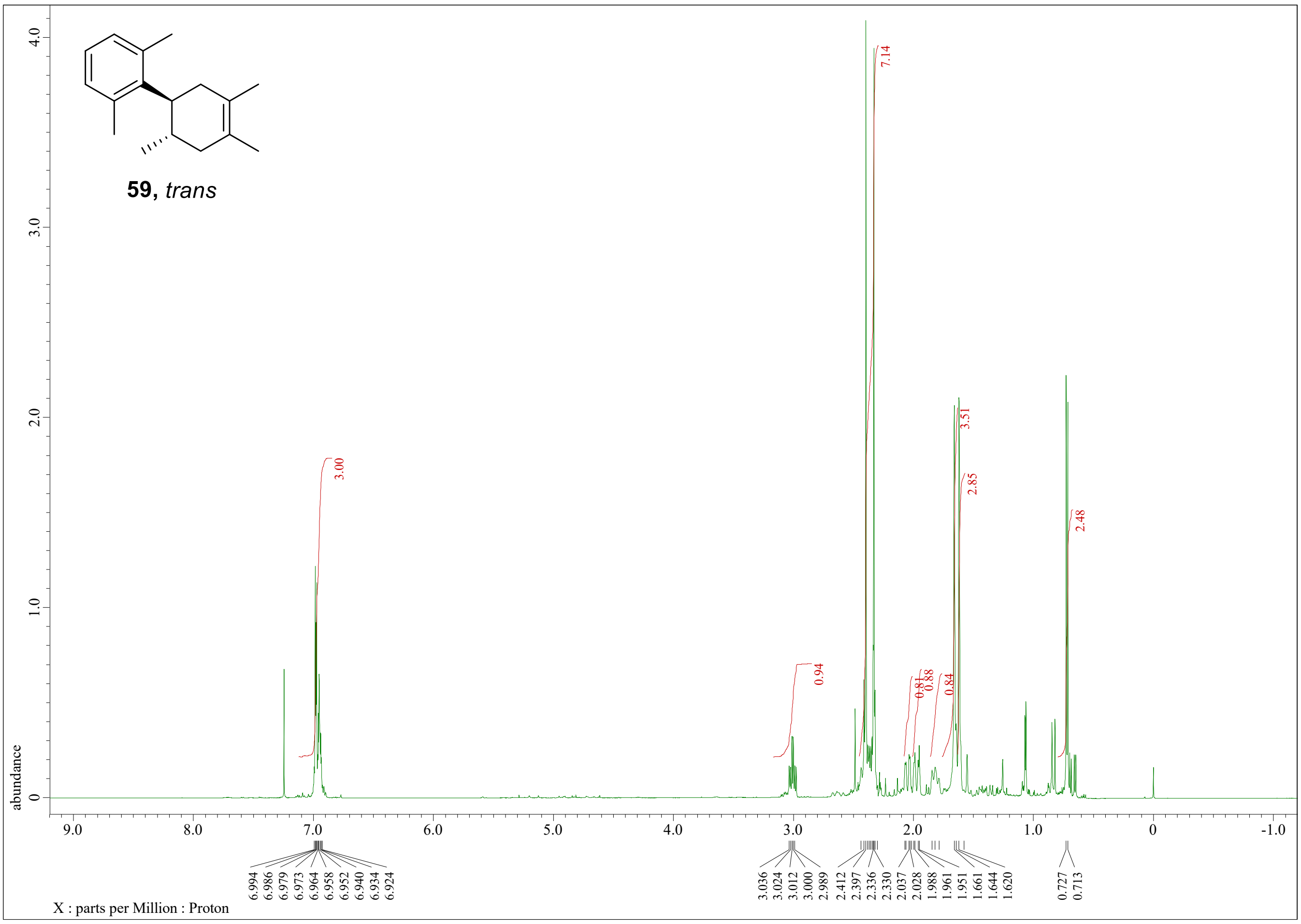
31.545
22.026
21.501
20.738
19.555
19.078
18.735
X : parts per Million : Carbon13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abundance
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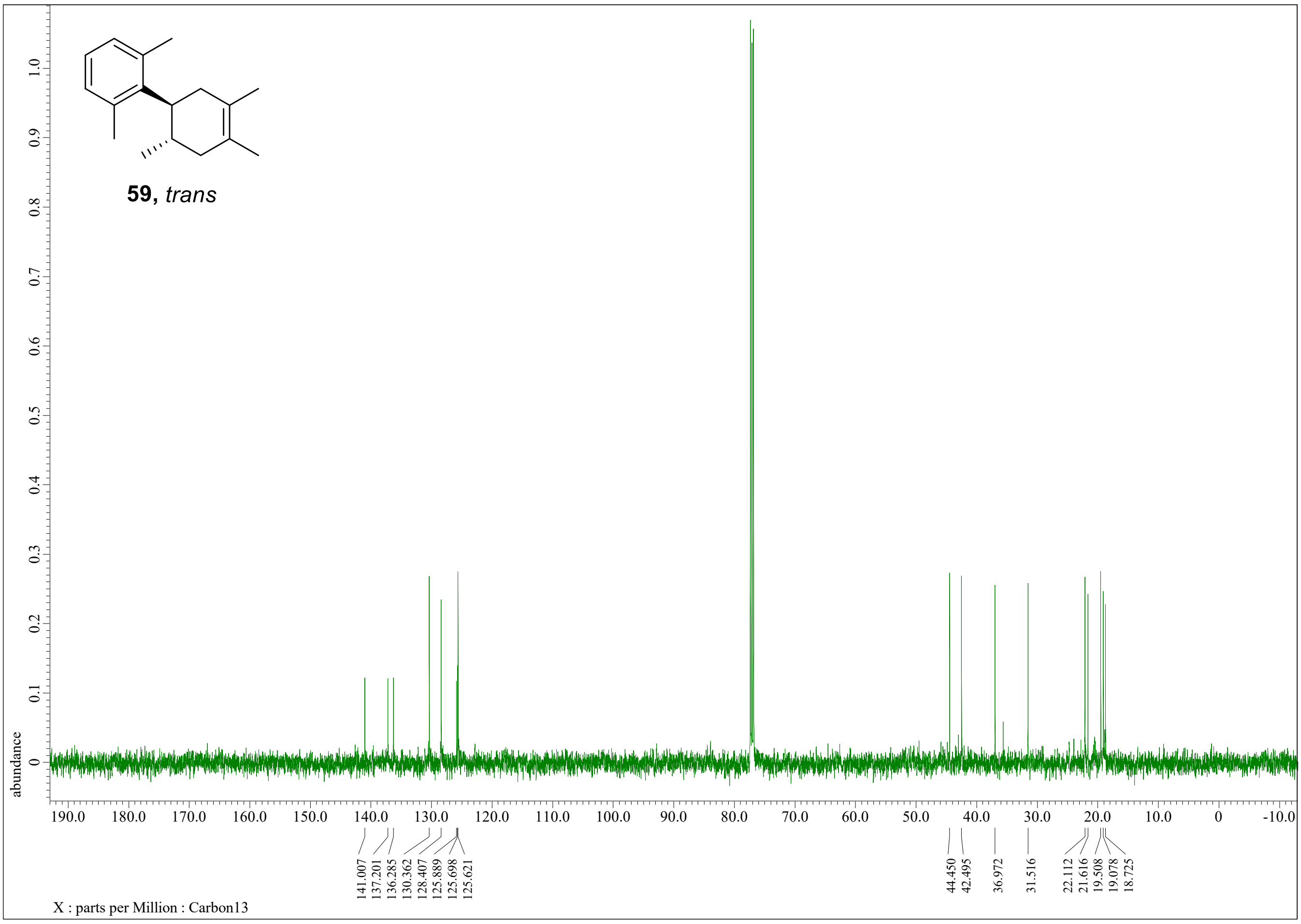
2.0
1.0
0
7.14
3.51
2.85
2.48
3.00
0.94
0.81
0.88
0.84
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.994
6.986
6.979
6.973
6.964
6.958
6.952
6.940
6.934
6.924
3.036
3.024
3.012
3.000
2.989
2.412
2.397
2.336
2.330
2.037
2.028
1.988
1.961
1.951
1.661
1.644
1.620
0.727
0.713
X : parts per Million : Proton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abundance
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0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
141.007
137.201
136.285
130.362
128.407
125.889
125.698
125.621
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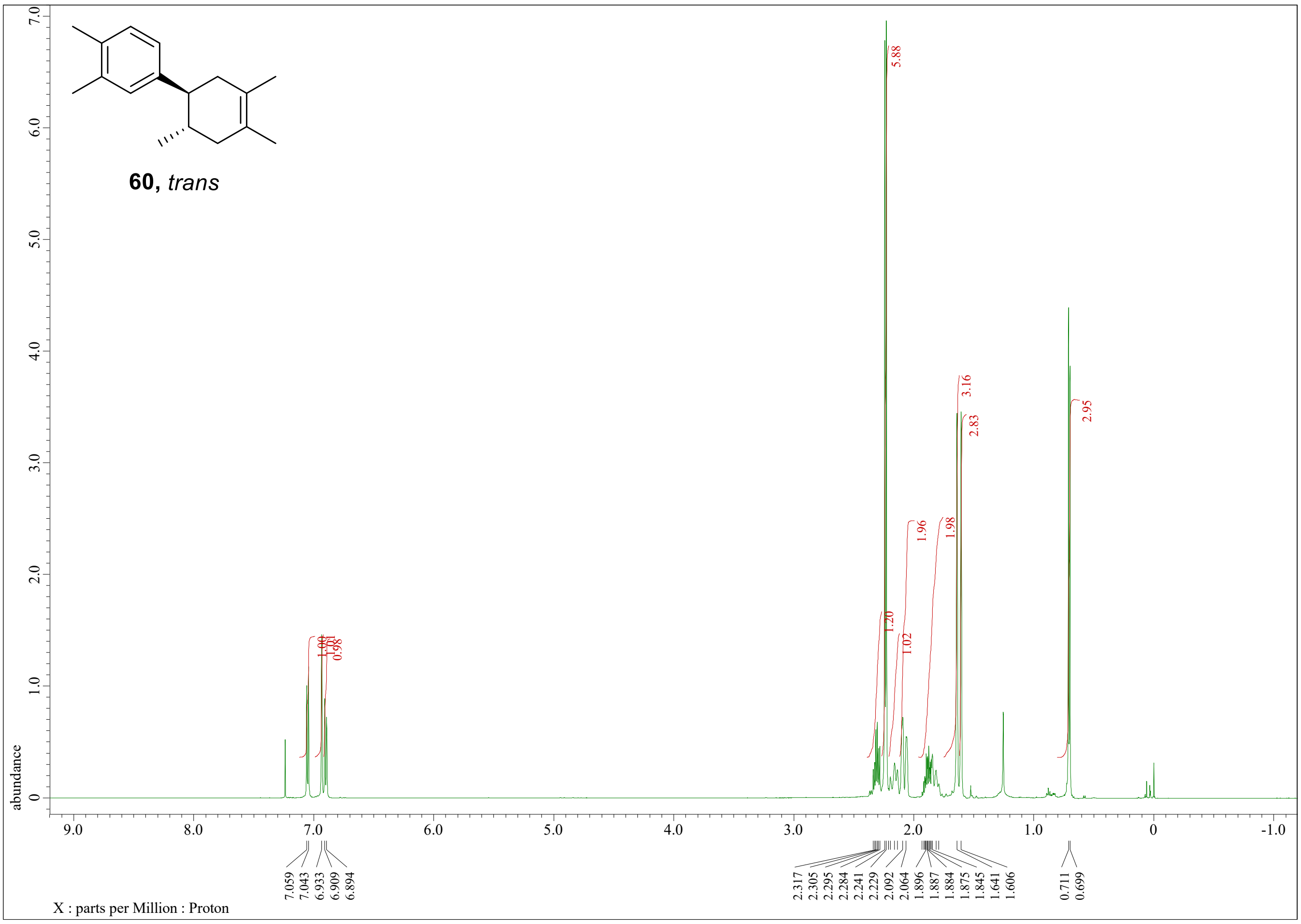
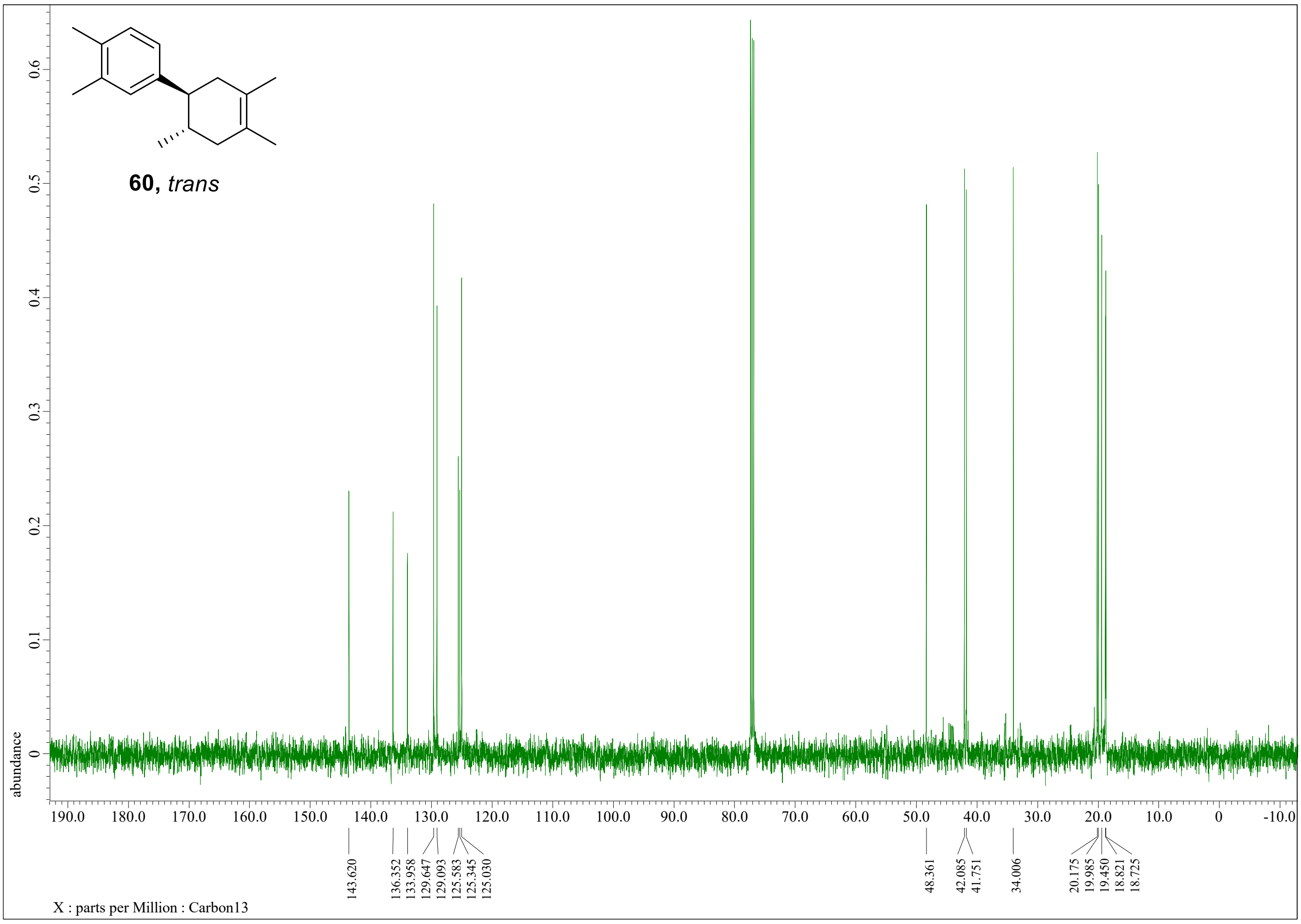
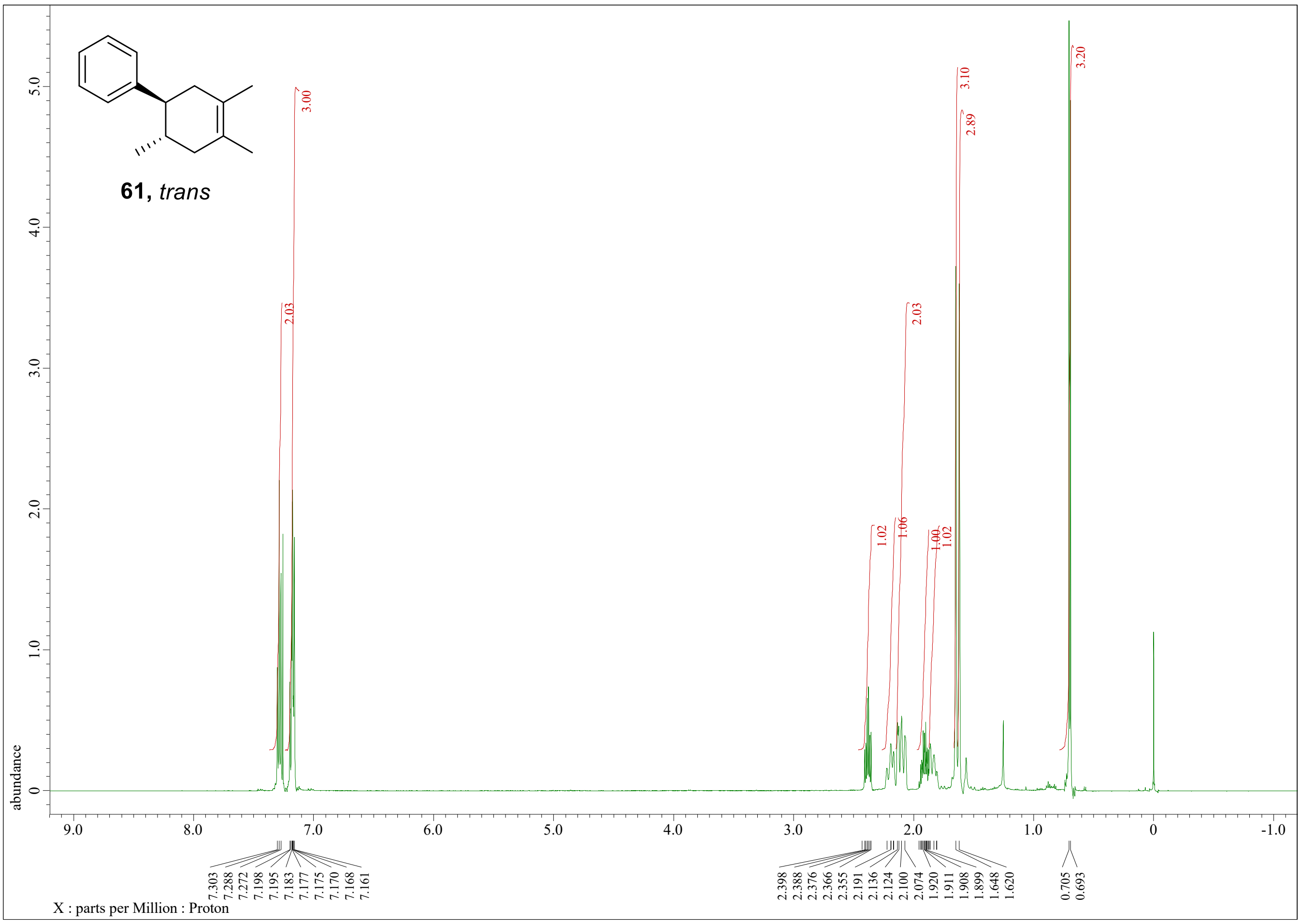
22.112
21.616
19.508
19.078
18.725
X : parts per Million : Carbon13


60, *trans*


60, *trans*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abundance
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2.0
3.0
4.0
5.0
2.03
3.00
1.02
1.06
2.03
1.00
1.02
3.10
2.89
3.20
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.303
7.288
7.272
7.198
7.195
7.183
7.177
7.175
7.170
7.168
7.161
2.398
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2.191
2.136
2.124
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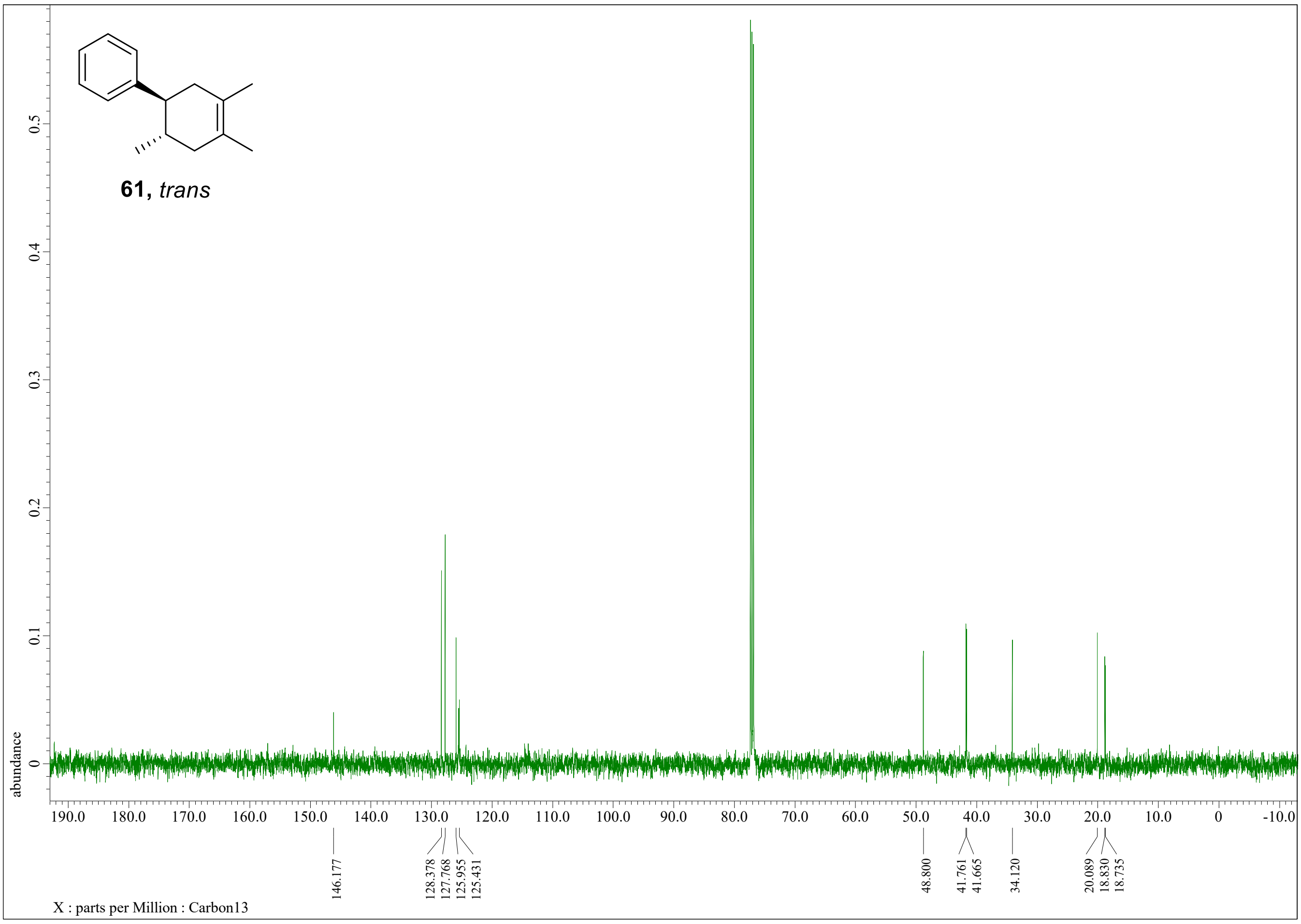
1.648
1.620
0.705
0.693
X : parts per Million : Proton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abundance
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0.2
0.3
0.4
0.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
146.177
128.378
127.768
125.955
125.431
48.800
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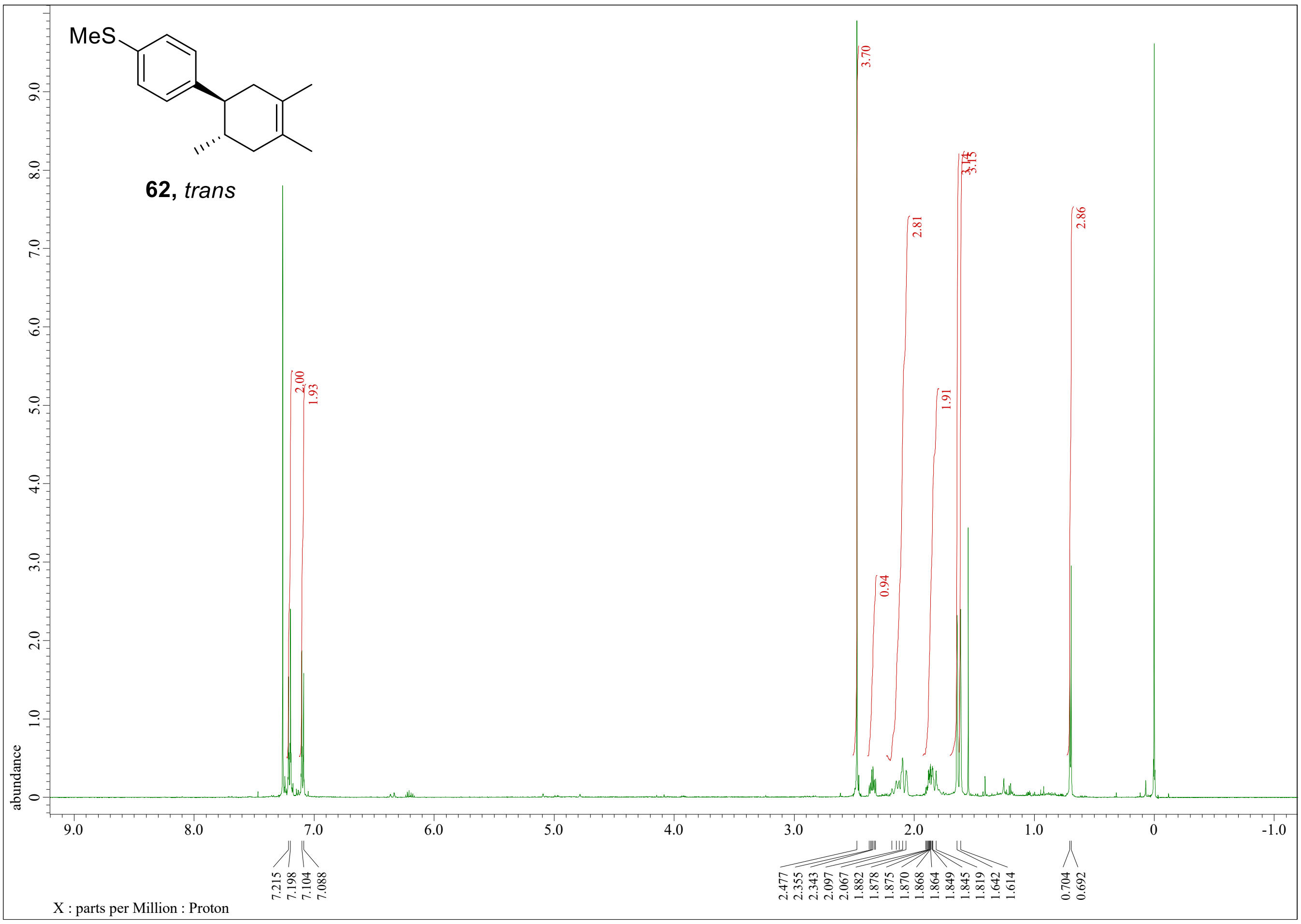
41.665
34.120
20.089
18.830
18.735
X : parts per Million : Carbon13


MeS
62, trans
abundance
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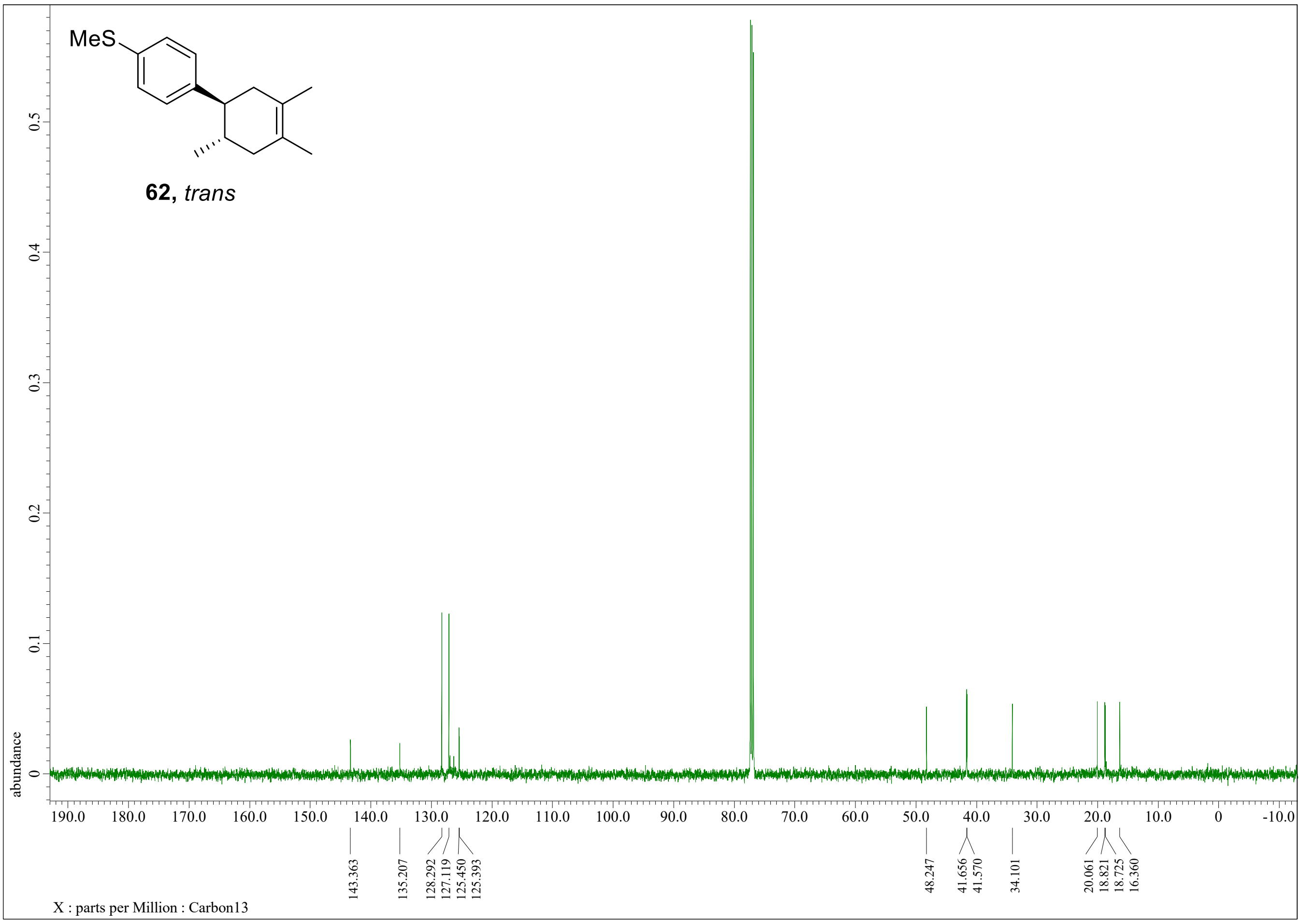
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
2.00
1.93
3.70
0.94
2.81
1.91
3.14
3.15
2.86
7.215
7.198
7.104
7.088
2.477
2.355
2.343
2.097
2.067
1.882
1.878
1.875
1.870
1.868
1.864
1.849
1.845
1.819
1.642
1.614
0.704
0.692
X : parts per Million : Proton


MeS
62, trans
abundance
0
0.1
0.2
0.3
0.4
0.5
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
143.363
135.207
128.292
127.119
125.450
125.393
48.247
41.656
41.570
34.101
20.061
18.821
18.725
16.360
X : parts per Million : Carbon13

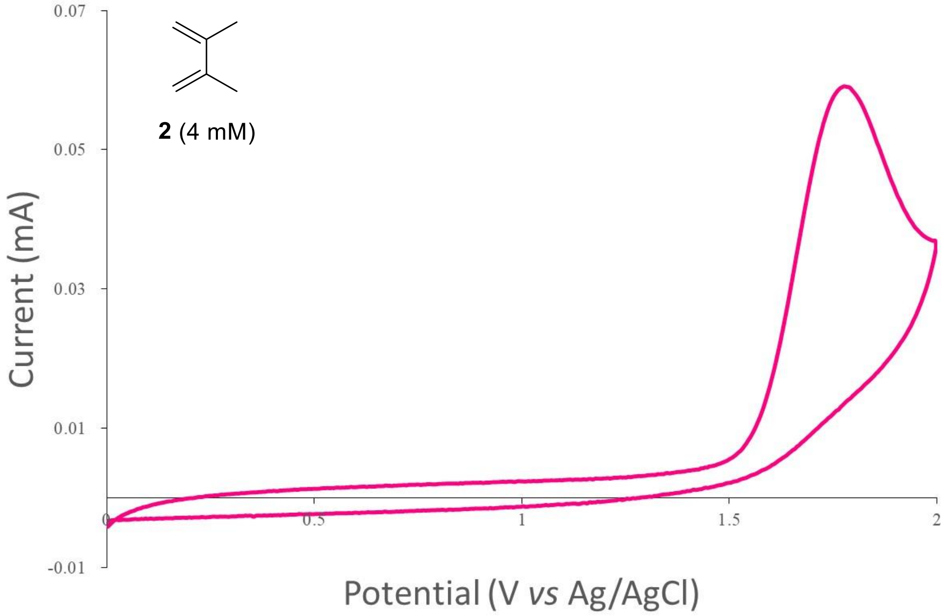


Figure S4. Cyclic Voltammogram of 2,3-Dimethyl-1,3-Butadiene (2, 4 mM).

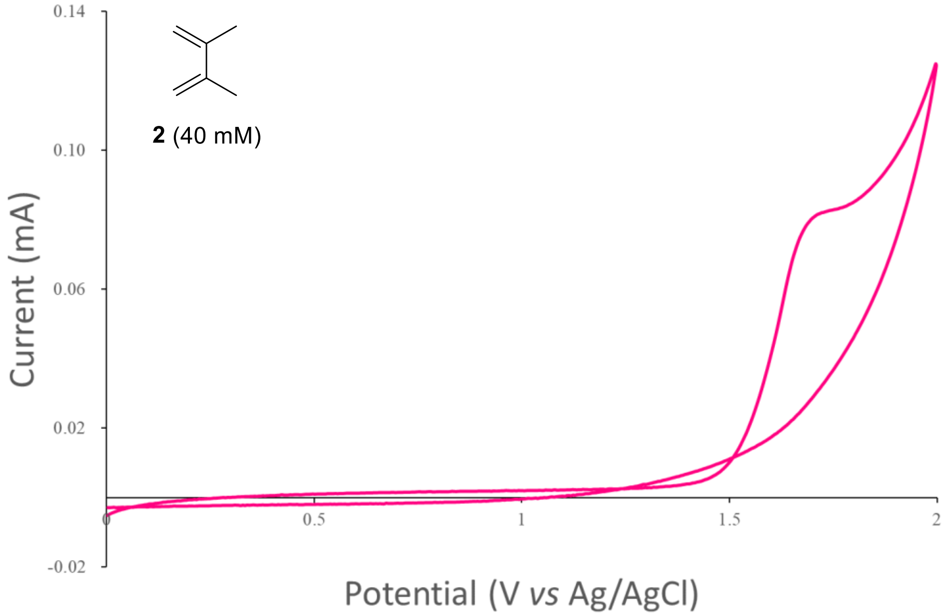


Figure S5. Cyclic Voltammogram of 2,3-Dimethyl-1,3-Butadiene (2, 40 mM).

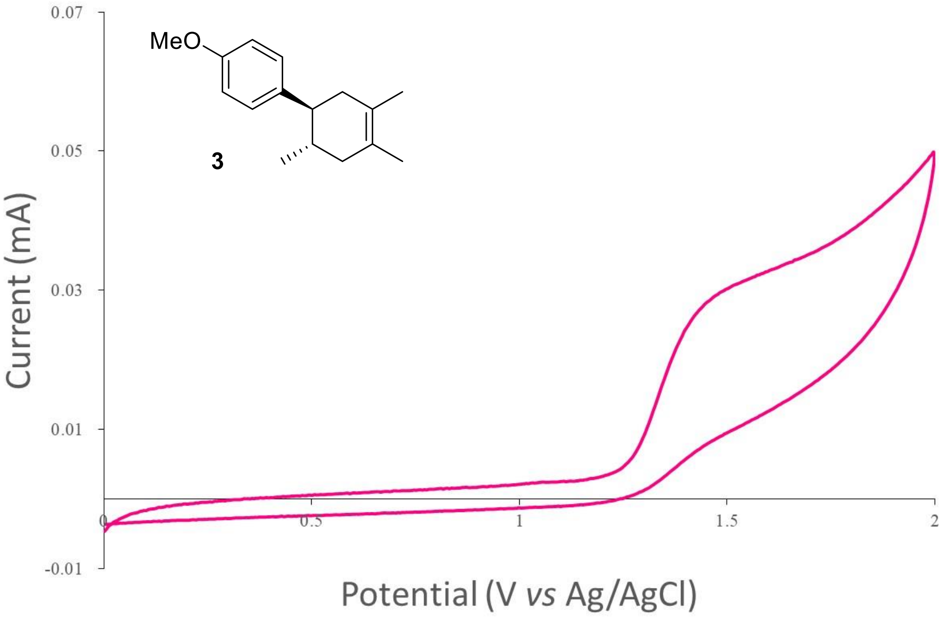


Figure S6. Cyclic Voltammogram of Diels-Alder Adduct (3).

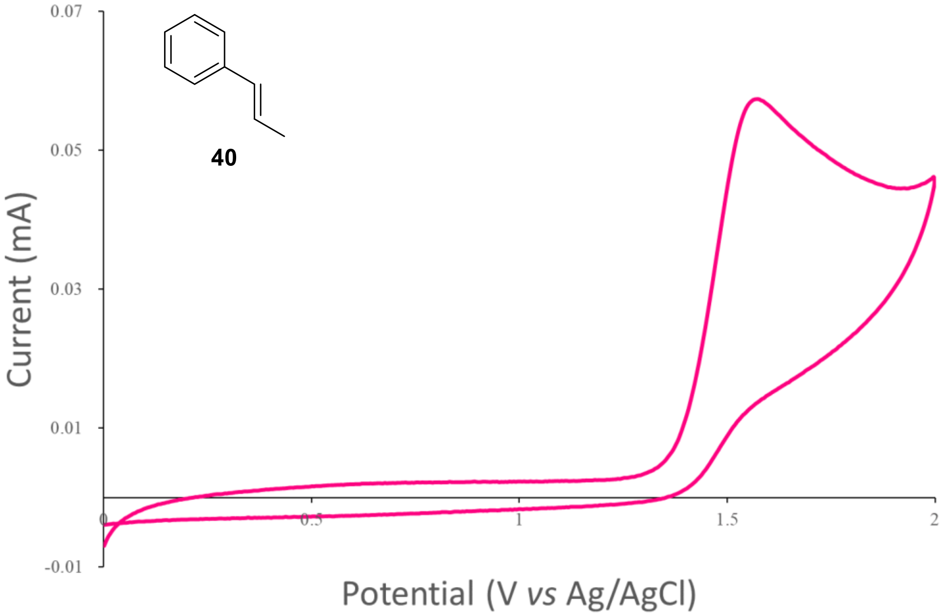


Figure S7. Cyclic Voltammogram of *trans*-β-Methylstyrene (40).

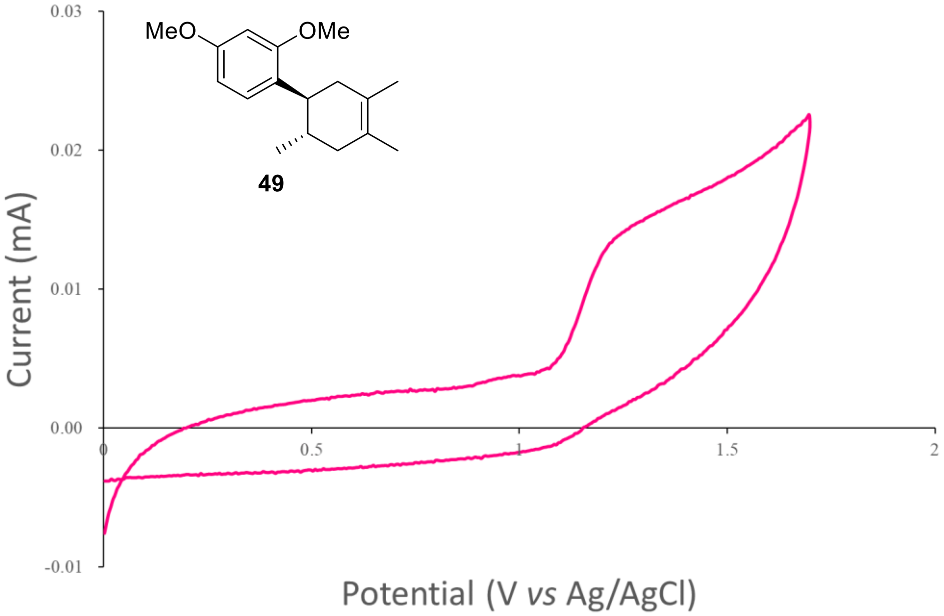


Figure S8. Cyclic Voltammogram of Diels-Alder Adduct (49).

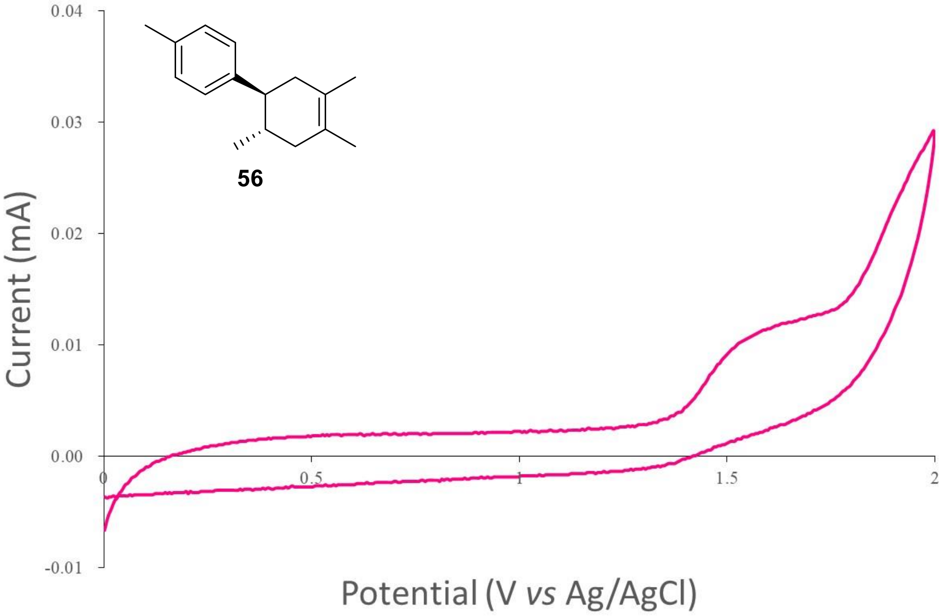


Figure S9. Cyclic Voltammogram of Diels-Alder Adduct (56).

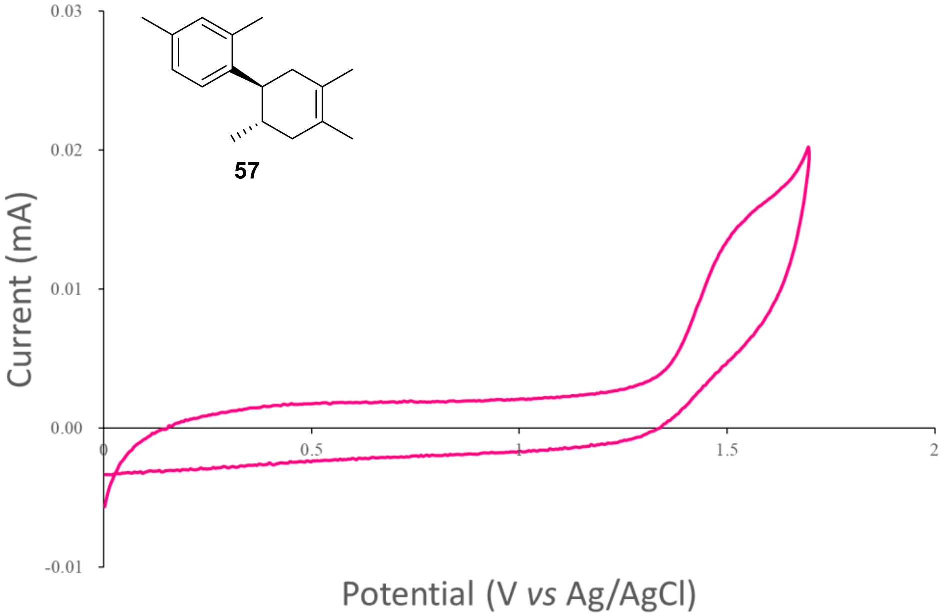


Figure S10. Cyclic Voltammogram of Diels-Alder Adduct (57).

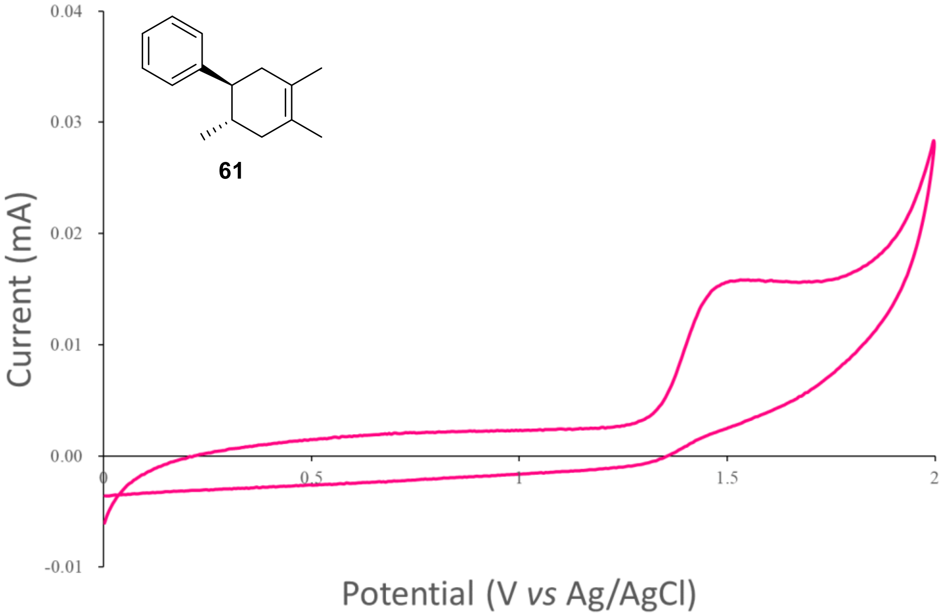
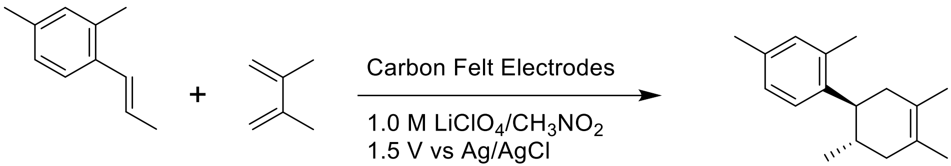


Figure S11. Cyclic Voltammogram of Diels-Alder Adduct (61).

Additional Electrocatalytic Radical Cation Diels-Alder Reaction. The reaction of 2,4-dimethyl β-methylstyrene (**36**) and 2,3-dimethyl-1,3-budadiene (**2**) was examined under potentiostatic condition using carbon felt electrodes at 1.5 V vs Ag/AgCl. As a result, the yield of **57** in electrocatalysis was lower than that in TiO_2 photocatalysis.

Scheme S1. Electrocatalytic Radical Cation Diels-Alder Reaction of 36 and 2.



36, 0.2 mmol

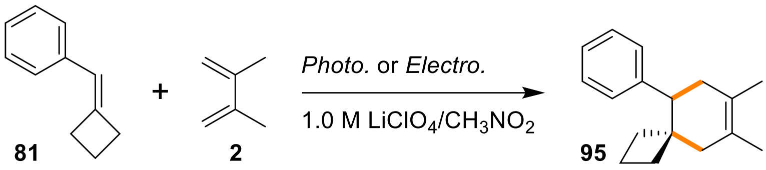
2, 2 eq

57, 46%

Yield was determined by ^1H NMR analysis using benzaldehyde as an internal standard.

Additional Control Study for Radical Cation Diels-Alder Reaction of Arylidene Cycloalkanes and Dienes. The reaction was examined using β-cyclobutylstyrene (**81**) and 2,3-dimethyl-1,3-budadiene (**2**) under TiO_2 photocatalytic and electrocatalytic conditions. In this case, the superiority of TiO_2 photocatalysis was apparent.

Table S2. Control Studies for Radical Cation Diels-Alder Reaction of 81 and 2.



entry	condition[a]	yield (%)[b]
1		55 (0)
2	no $LiClO_4$	0 (28)
3	no light	0 (trace)
4	no TiO_2	0 (26)
5	2 eq of diene	34 (0)
6	10 eq of diene	47 (trace)
7	CH_3CN solvent	13 (17)
8	under O_2	33 (trace)
9	under Ar	9 (18)
10	for 4h	50 (6)
11	1.5 V vs. Ag/AgCl, 0.5 F/mol	3 (24)[c]
12	1.5 V vs. Ag/AgCl, 1.0 F/mol	7 (5)[c]

[a]Unless otherwise stated, reactions were carried out on a 0.20 mmol scale of arylidene cycloalkane (**81**) with 5 equiv of 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt under air for 6 h. [b]Determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. Recovered starting material is reported in parentheses. [c]In electrocatalysis, carbon felt electrodes were used for the reactions.

Cyclic voltammograms were recorded on 2 mM of arylidenes in 4 mL of CH_3NO_2. 1.0 M of $LiClO_4$ was used as the supporting electrolyte, a Glassy Carbon (GC) disk was used as the working electrode, and a Pt wire was used as the counter electrode. All potentials are referenced against the Ag/AgCl redox couple. The scan late is 50 mV/s.

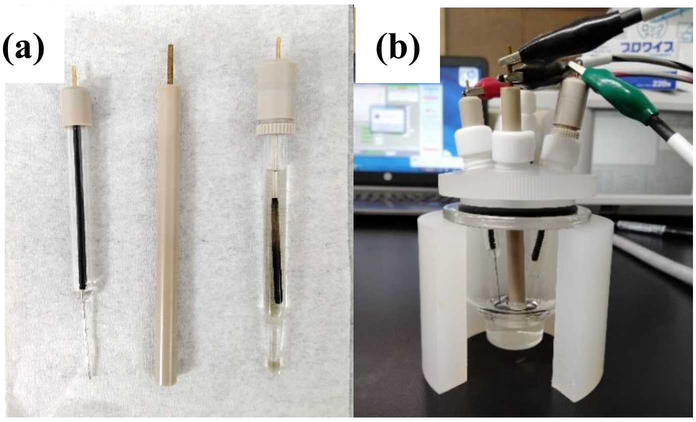


Figure S12. (a) Photograph of using Electrodes in this Electrochemical Measurements, from left Pt wire, GC disk, and Ag/AgCl electrode, (b) Setup of Cyclic Voltammetry Measurements.

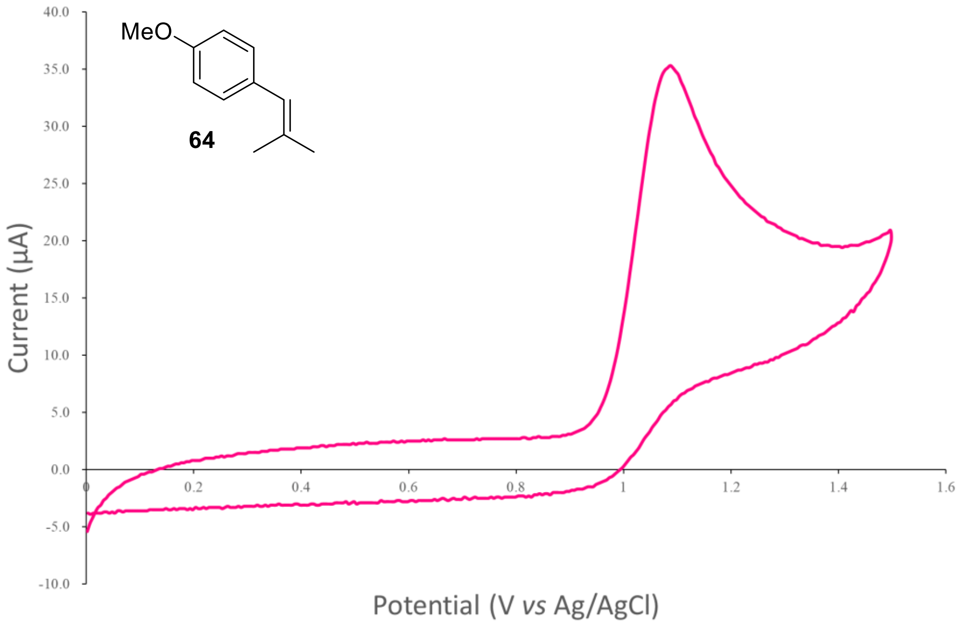


Figure S13. Cyclic Voltammogram of 4-Methoxy β -Dimethylstyrene (64).

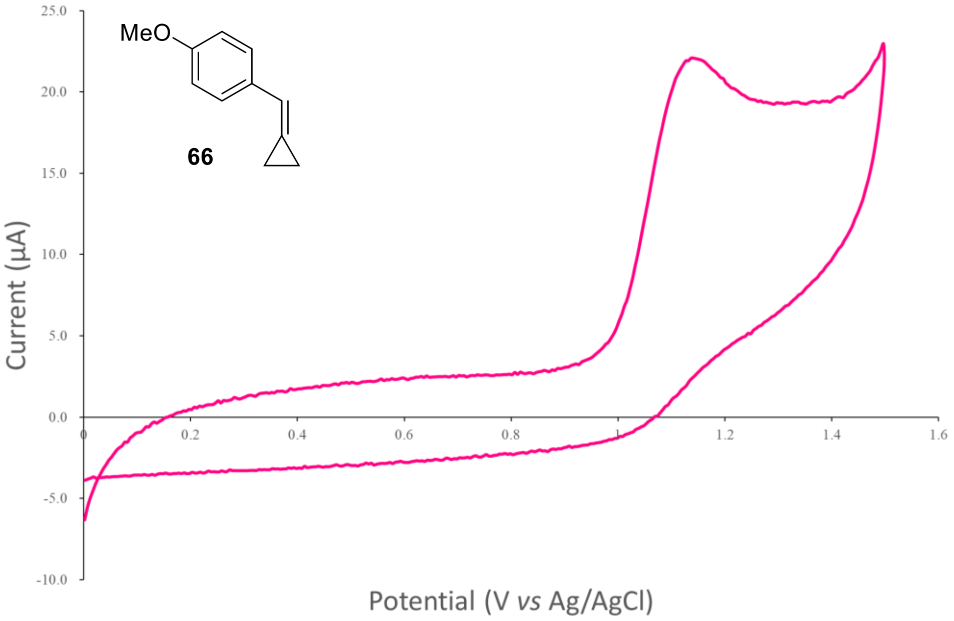


Figure S14. Cyclic Voltammogram of 4-Methoxy β-Cyclopropylstyrene (66).

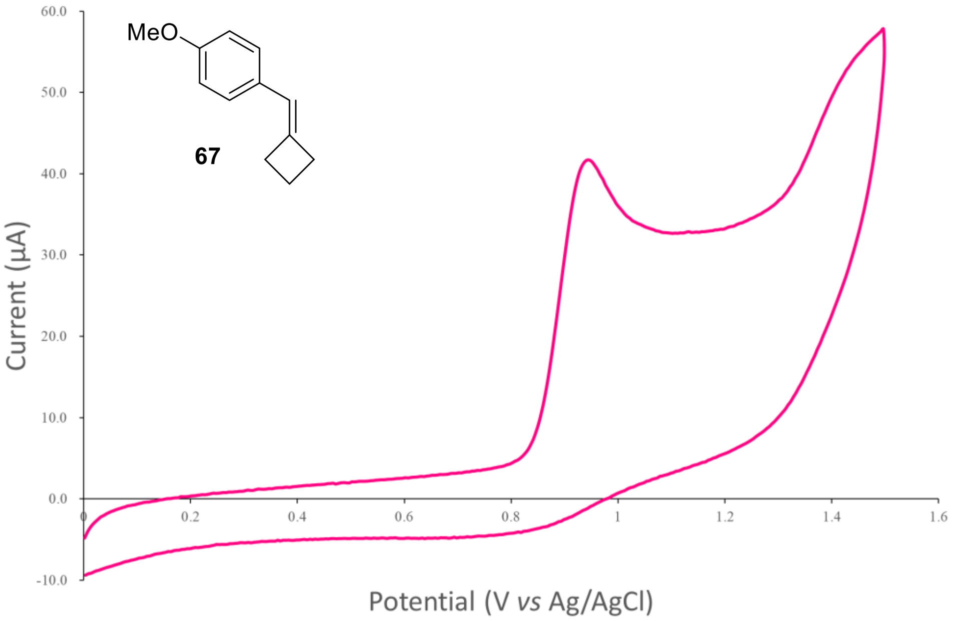


Figure S15. Cyclic Voltammogram of 4-Methoxy β-Cyclobutyllstyrene (67).

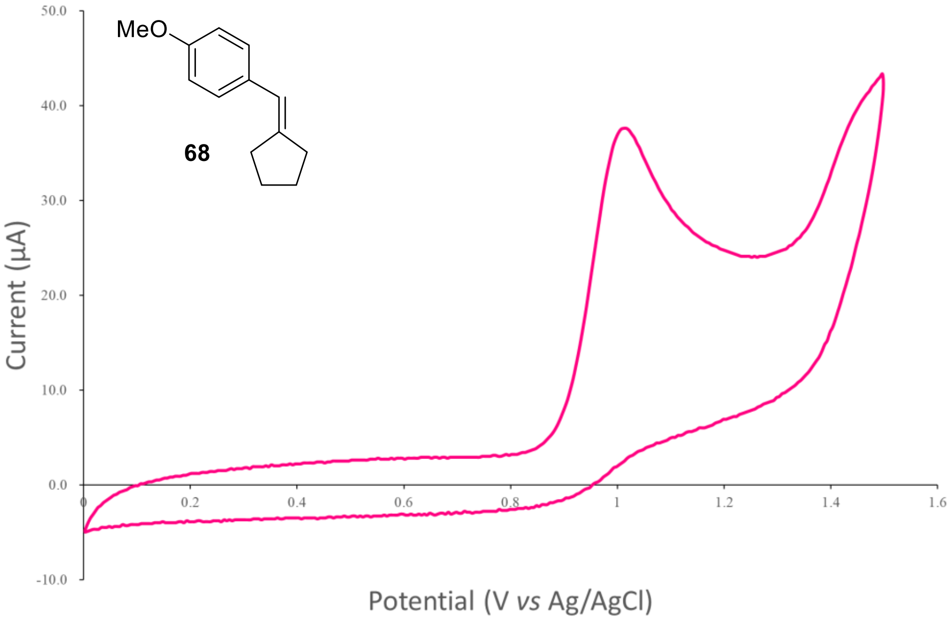


Figure S16. Cyclic Voltammogram of 4-Methoxy β-Cyclopentylstyrene (68).

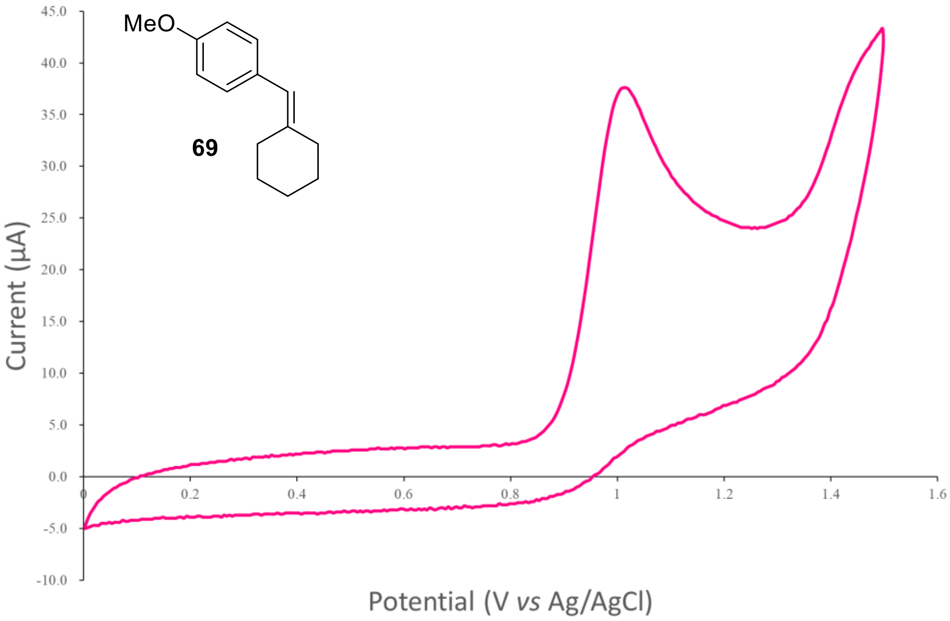


Figure S17. Cyclic Voltammogram of 4-Methoxy β-Cyclohexylstyrene (69).

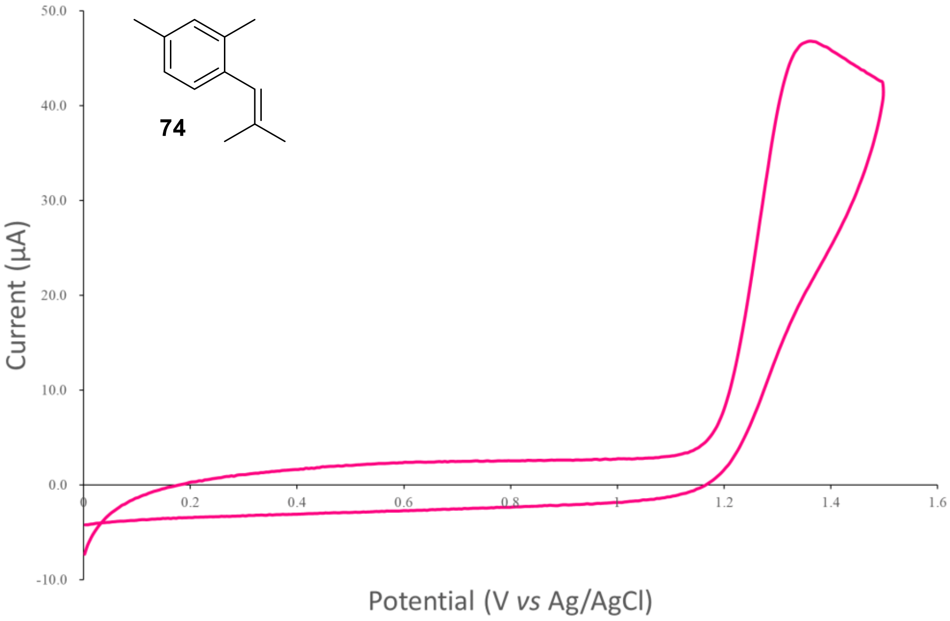


Figure S18. Cyclic Voltammogram of 2,4-Dimethyl β-Dimethylstyrene (74).

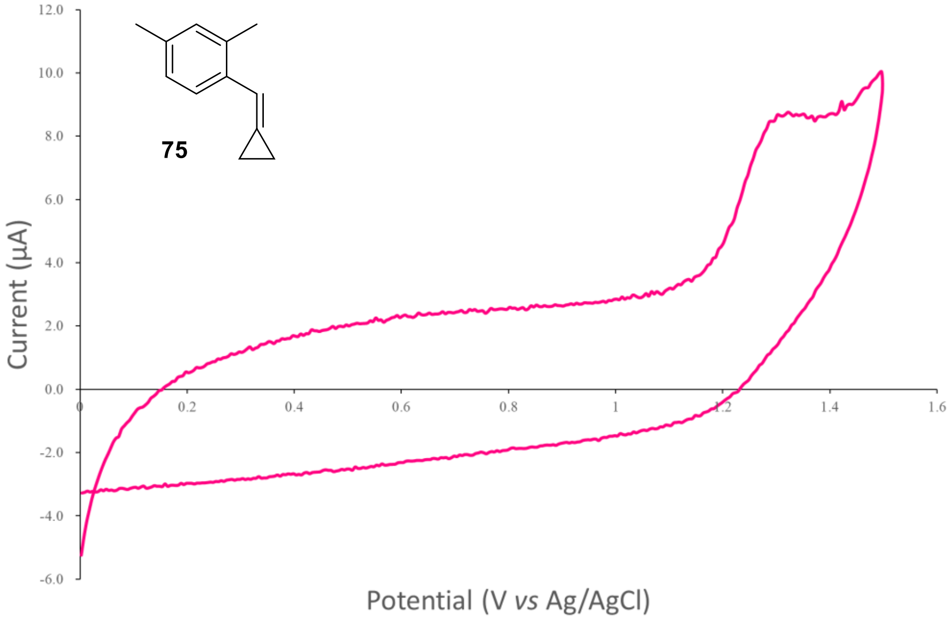


Figure S19. Cyclic Voltammogram of 2,4-Dimethyl β-Dimethylstyrene (75).

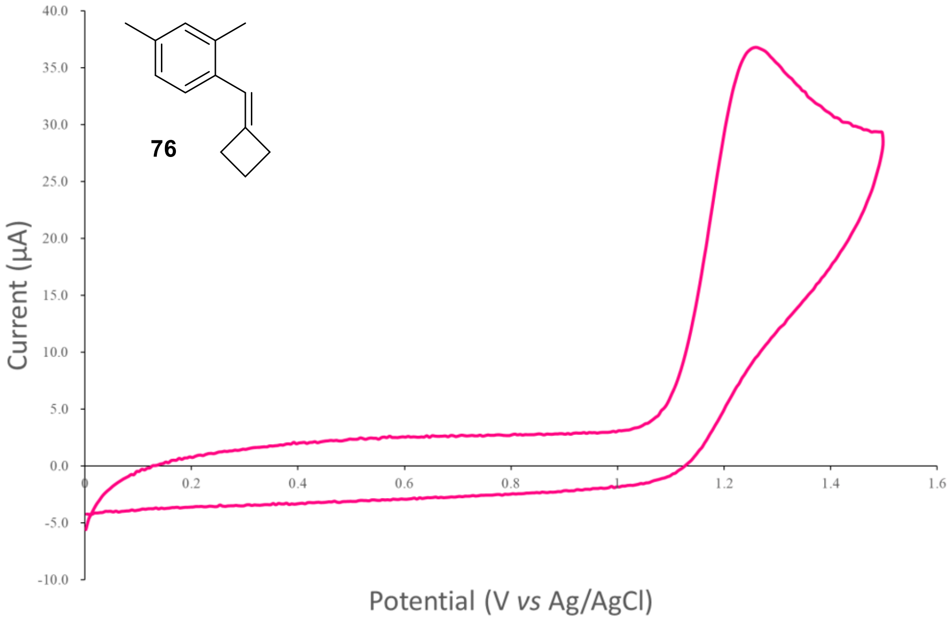


Figure S20. Cyclic Voltammogram of 2,4-Dimethyl β -Cyclopropylstyrene (76).

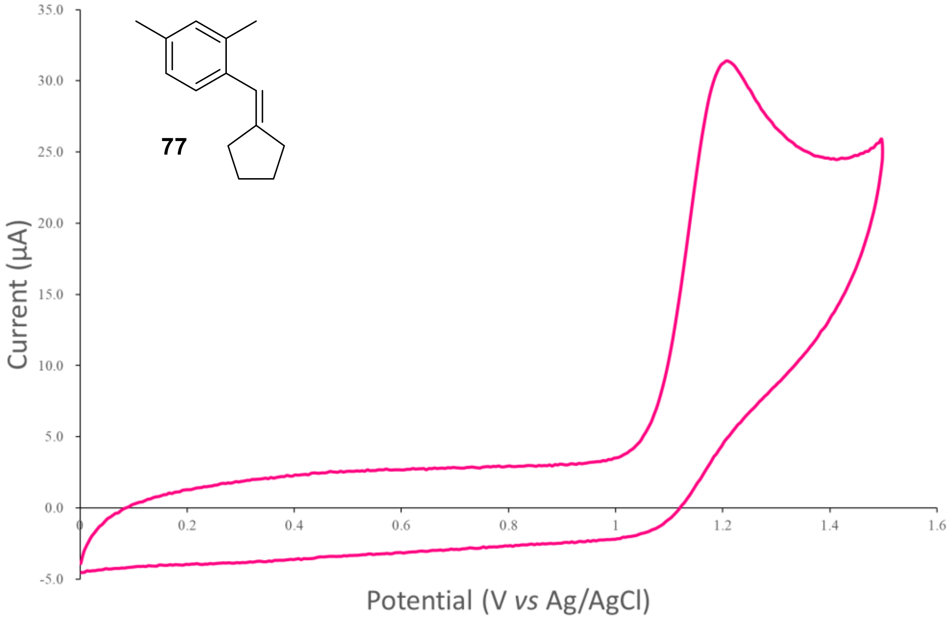


Figure S21. Cyclic Voltammogram of 2,4-Dimethyl β -Cyclopentylstyrene (77).

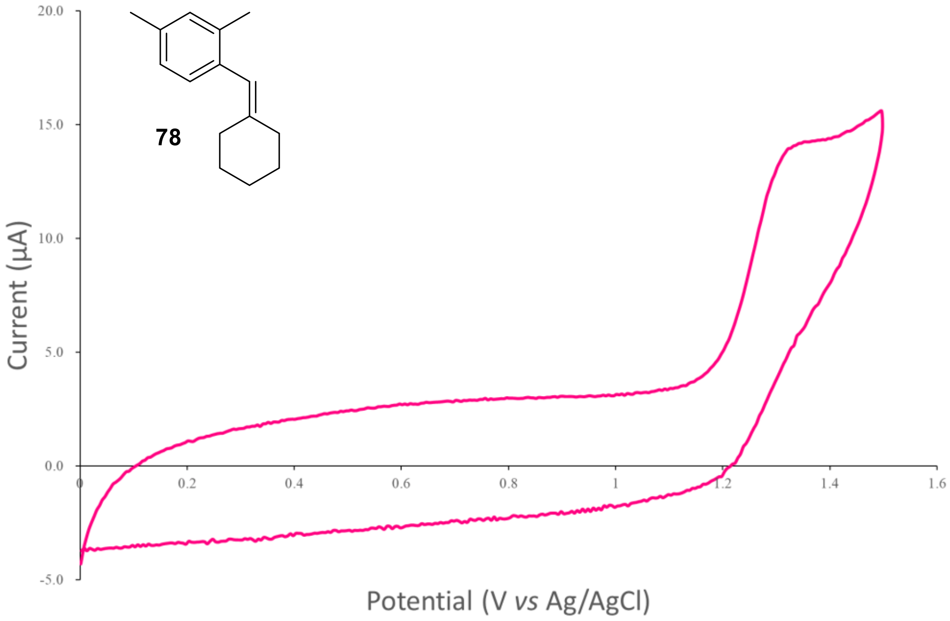


Figure S22. Cyclic Voltammogram of 2,4-Dimethyl β-Cyclohexylstyrene (78).

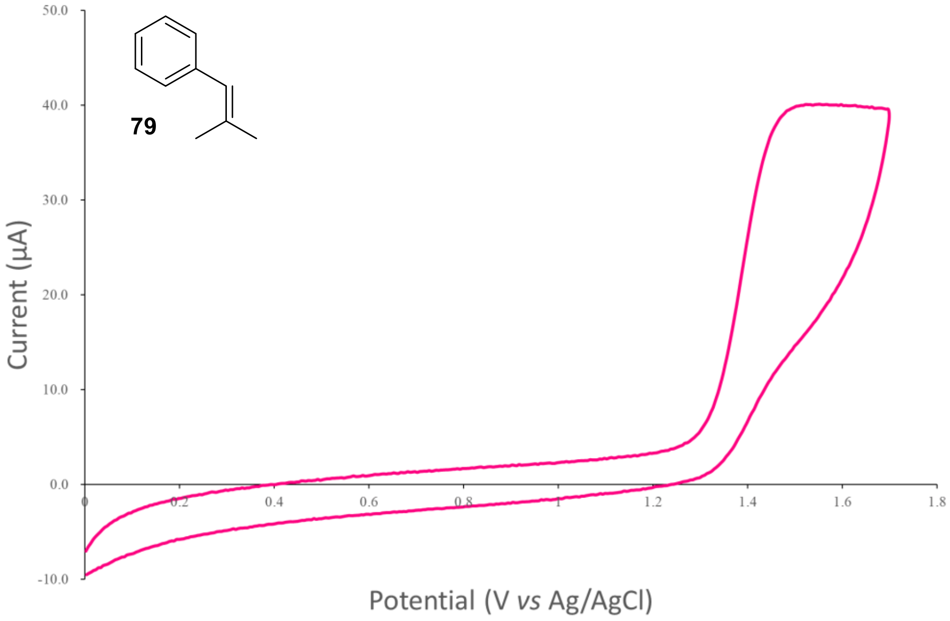


Figure S23. Cyclic Voltammogram of β-Dimethylstyrene (79).

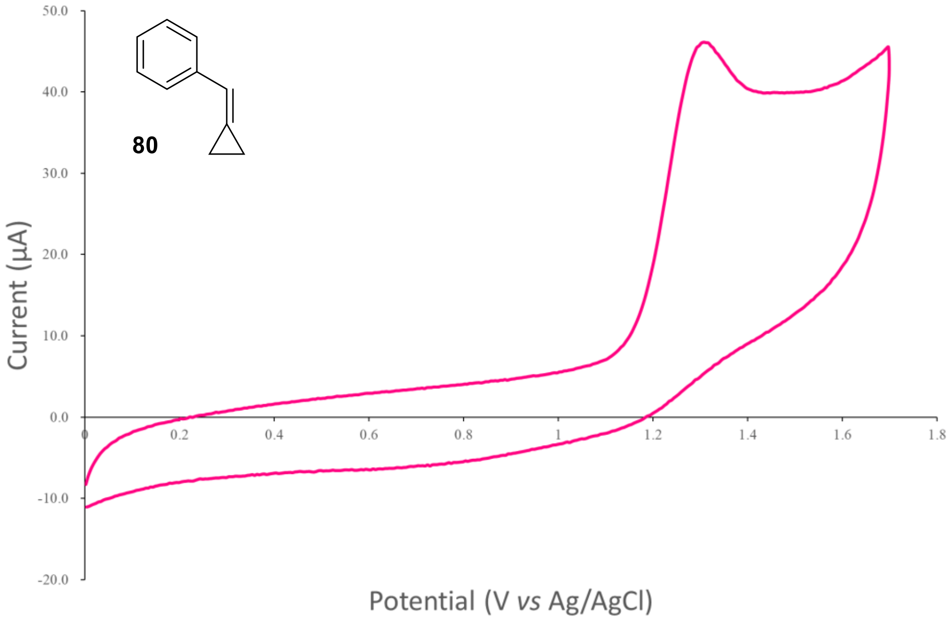


Figure S24. Cyclic Voltammogram of β -Cyclopropylstyrene (80).

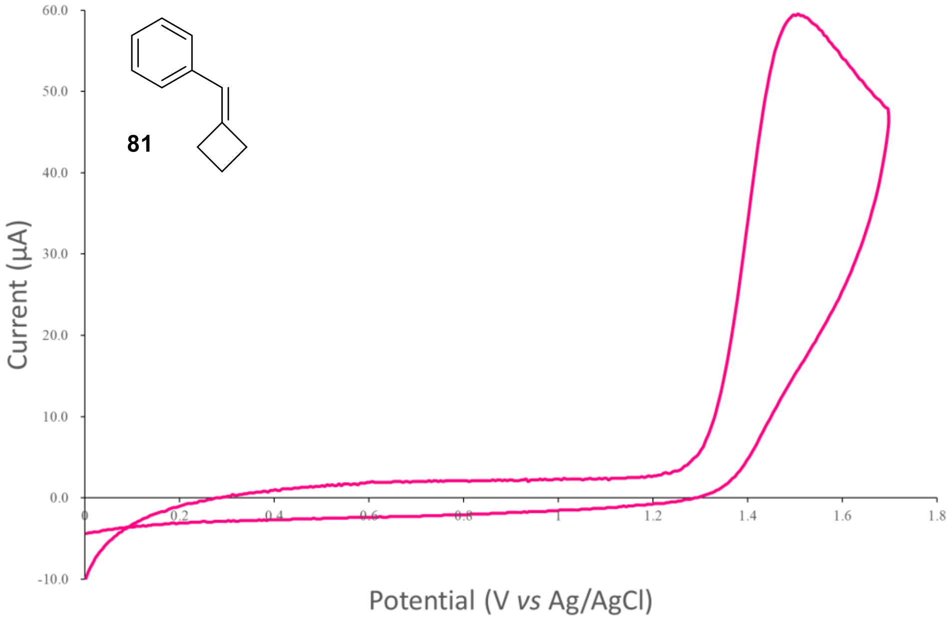


Figure S25. Cyclic Voltammogram of β -Cyclobutylstyrene (81).

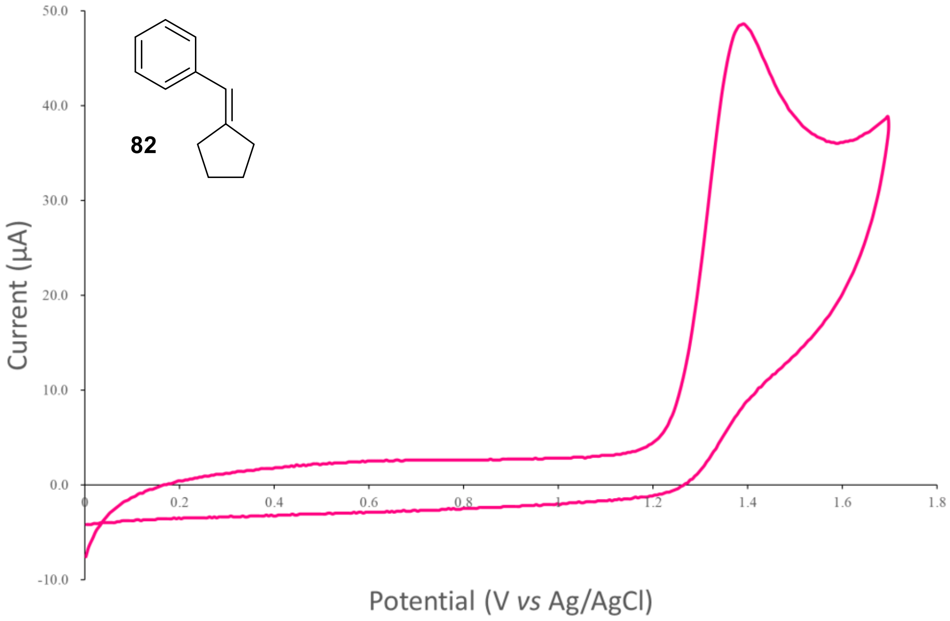


Figure S26. Cyclic Voltammogram of β-Cyclopentylstyrene (82).

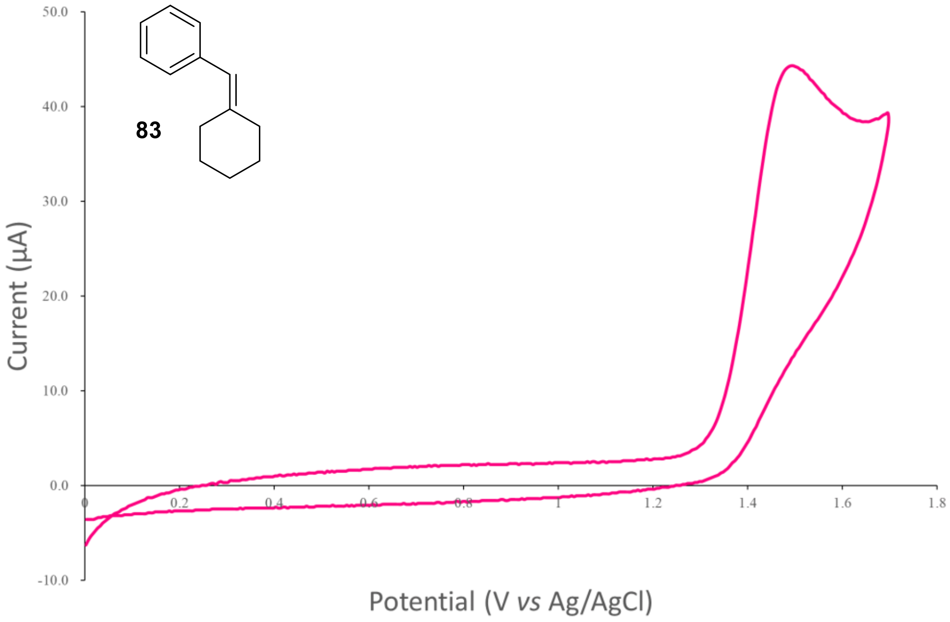


Figure S27. Cyclic Voltammogram of β-Cyclohexylstyrene (83).

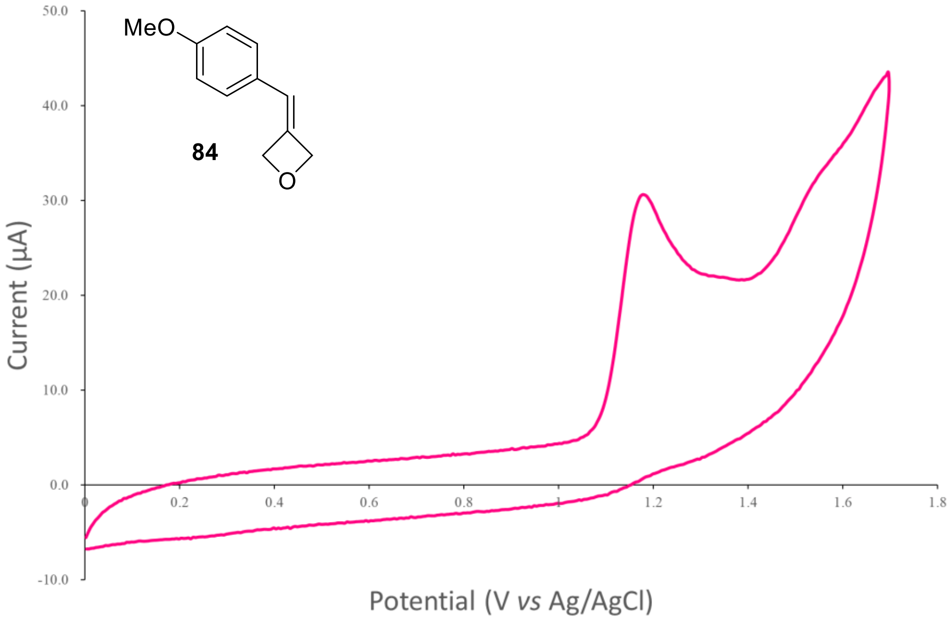


Figure S28. Cyclic Voltammogram of 4-Methoxy β-Oxetanylstyrene (84).

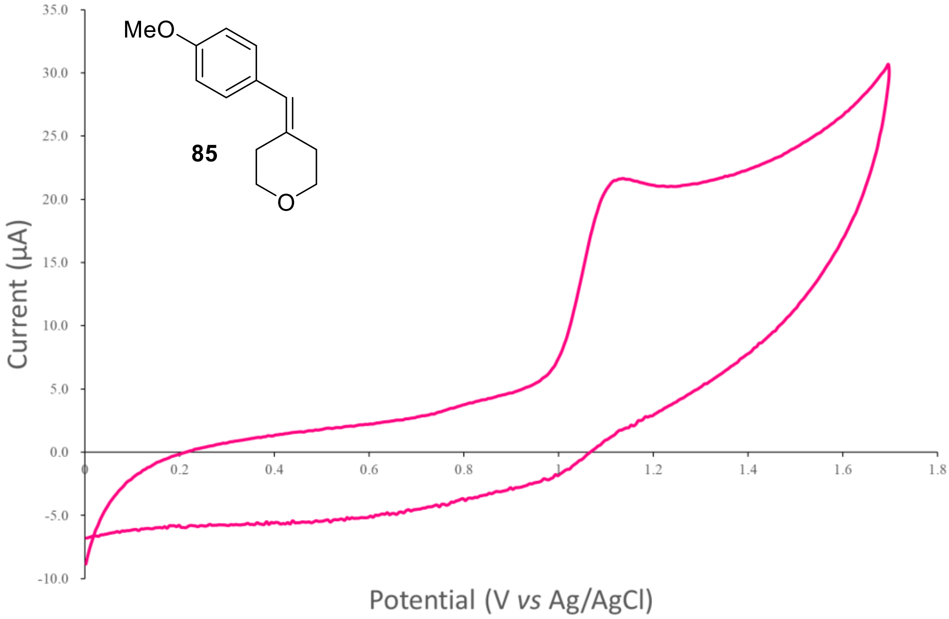


Figure S29. Cyclic Voltammogram of 4-Methoxy β-Oxanylstyrene (85).

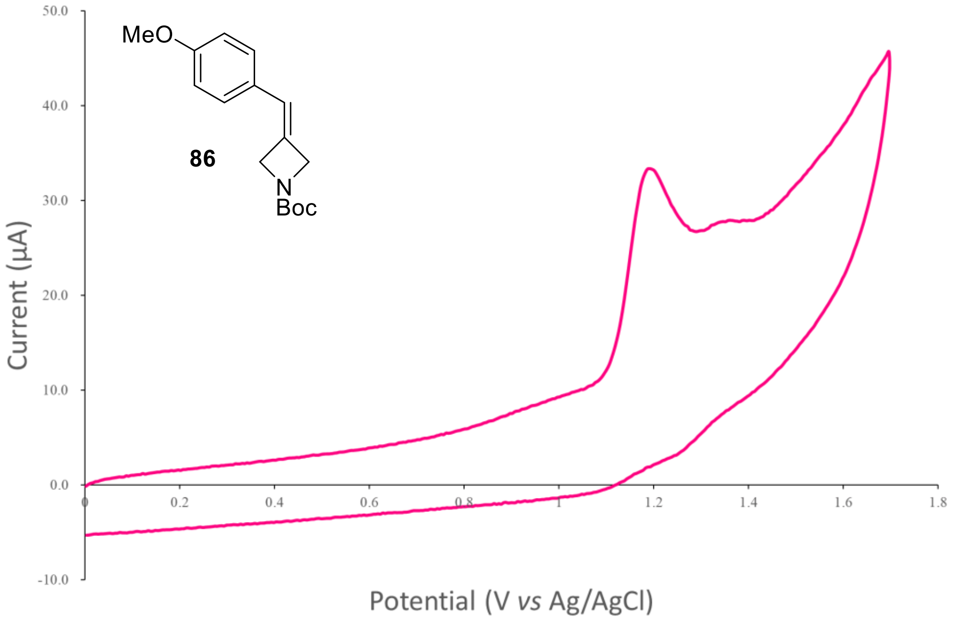


Figure S30. Cyclic Voltammogram of 4-Methoxy β -Azetylstyrene (86).

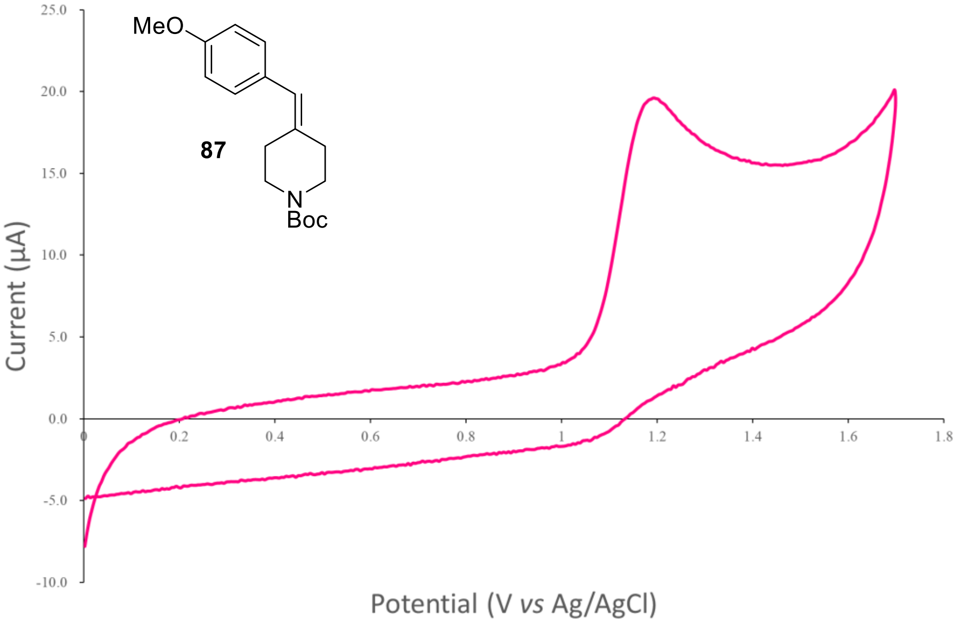
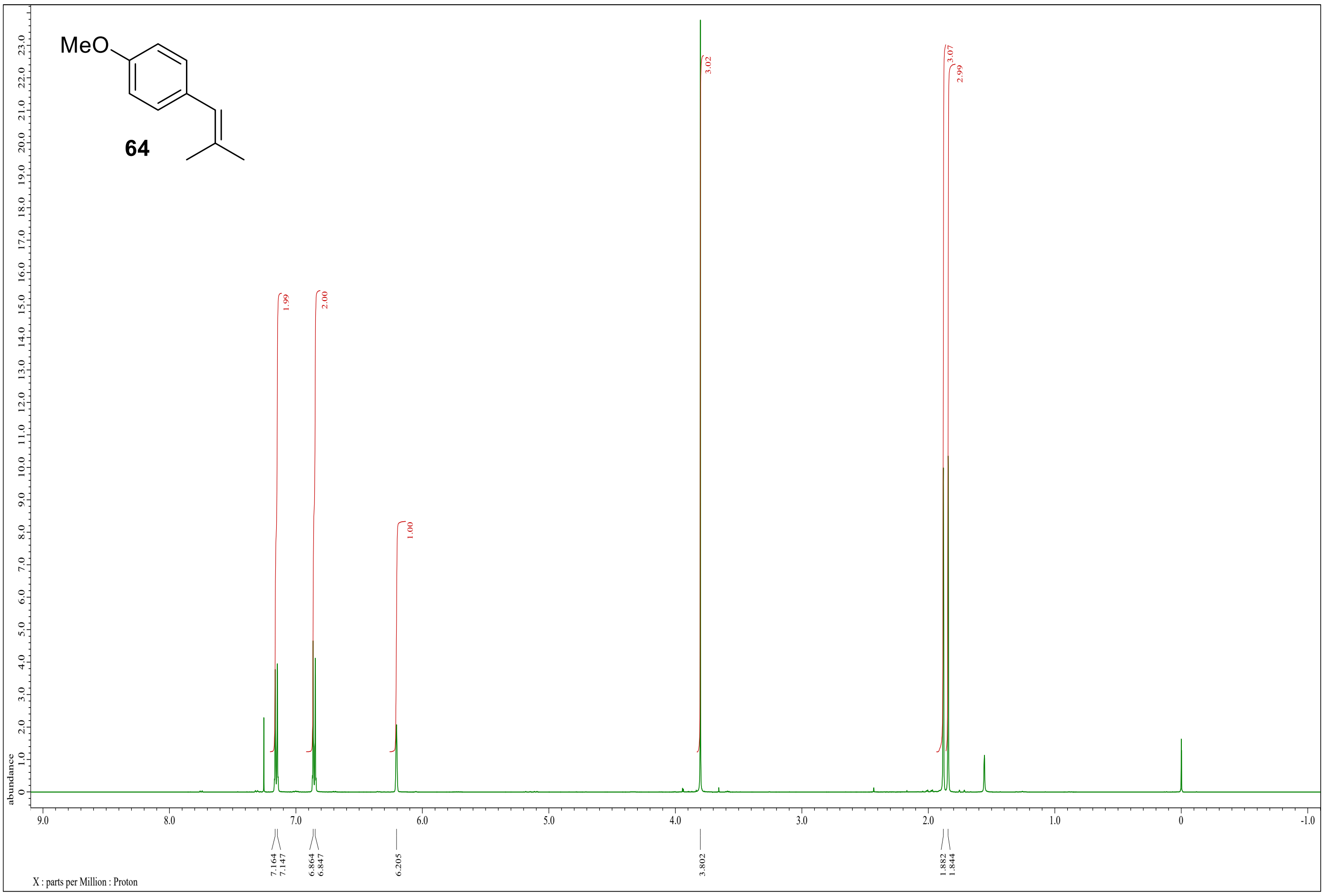


Figure S31. Cyclic Voltammogram of 4-Methoxy β -Pyperidinylstyrene (87).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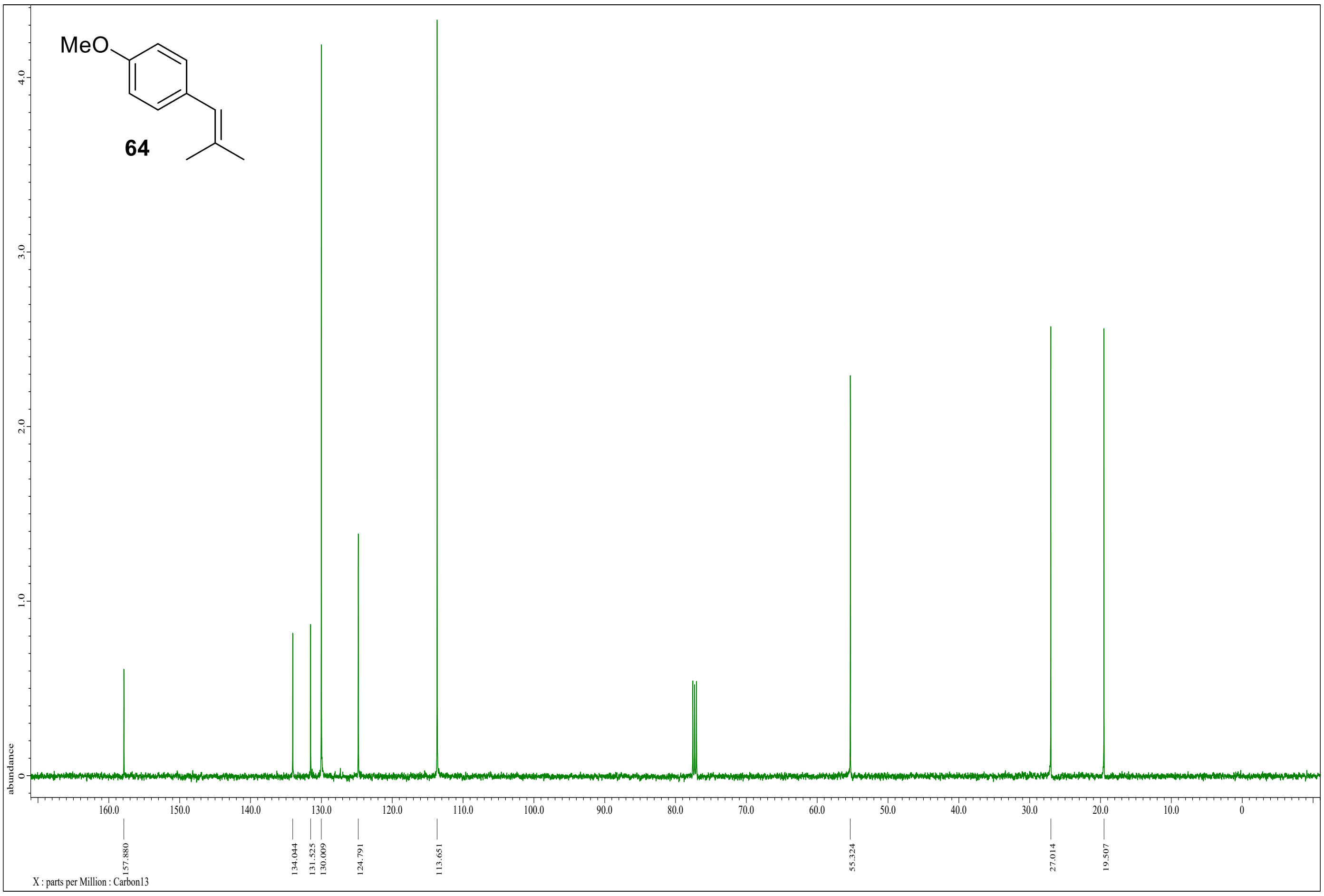
1.99
2.00
1.00
3.02
3.07
2.99
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
7.164
7.147
6.864
6.847
6.205
3.802
1.882
1.844
X : parts per Million : Proton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abundance
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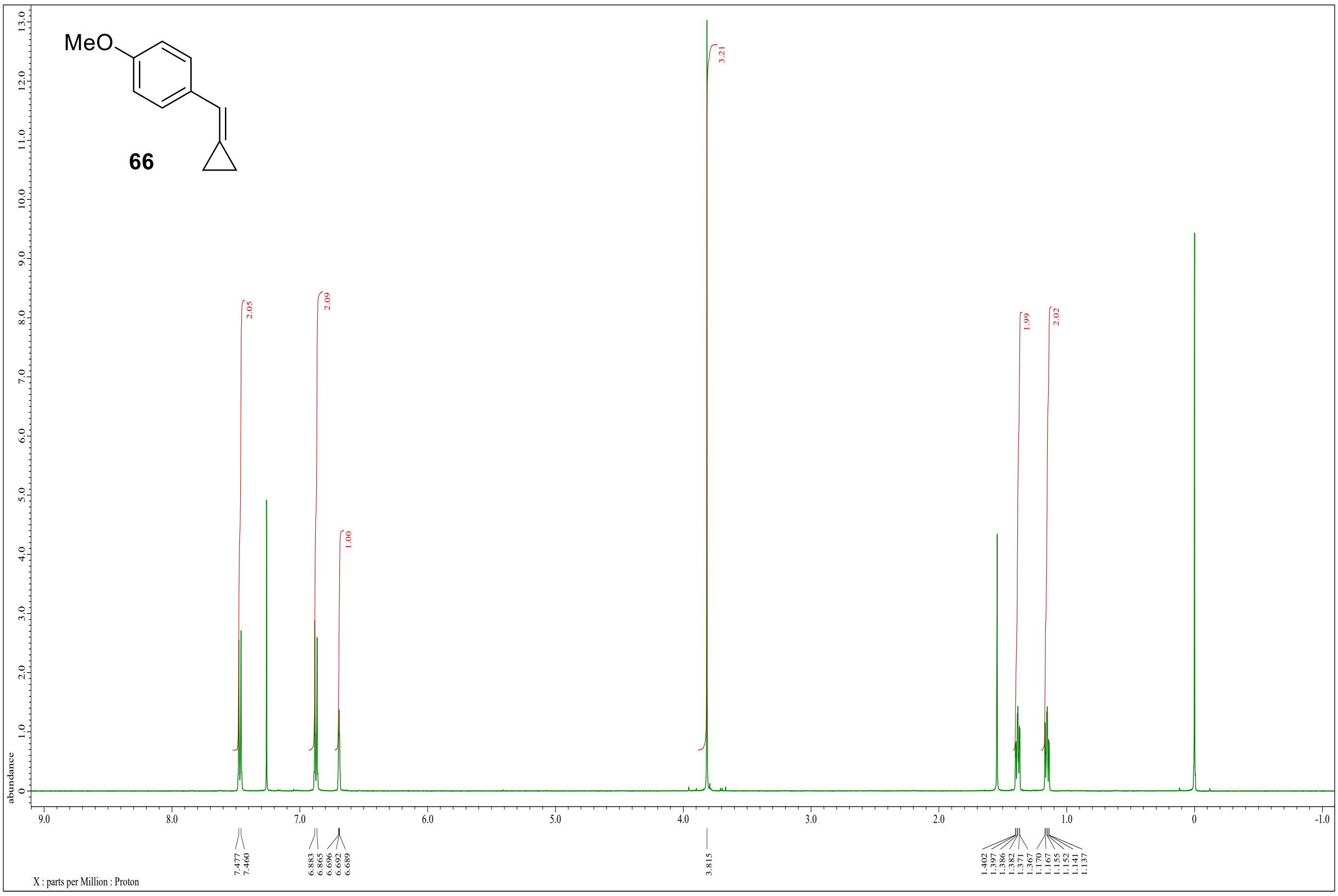
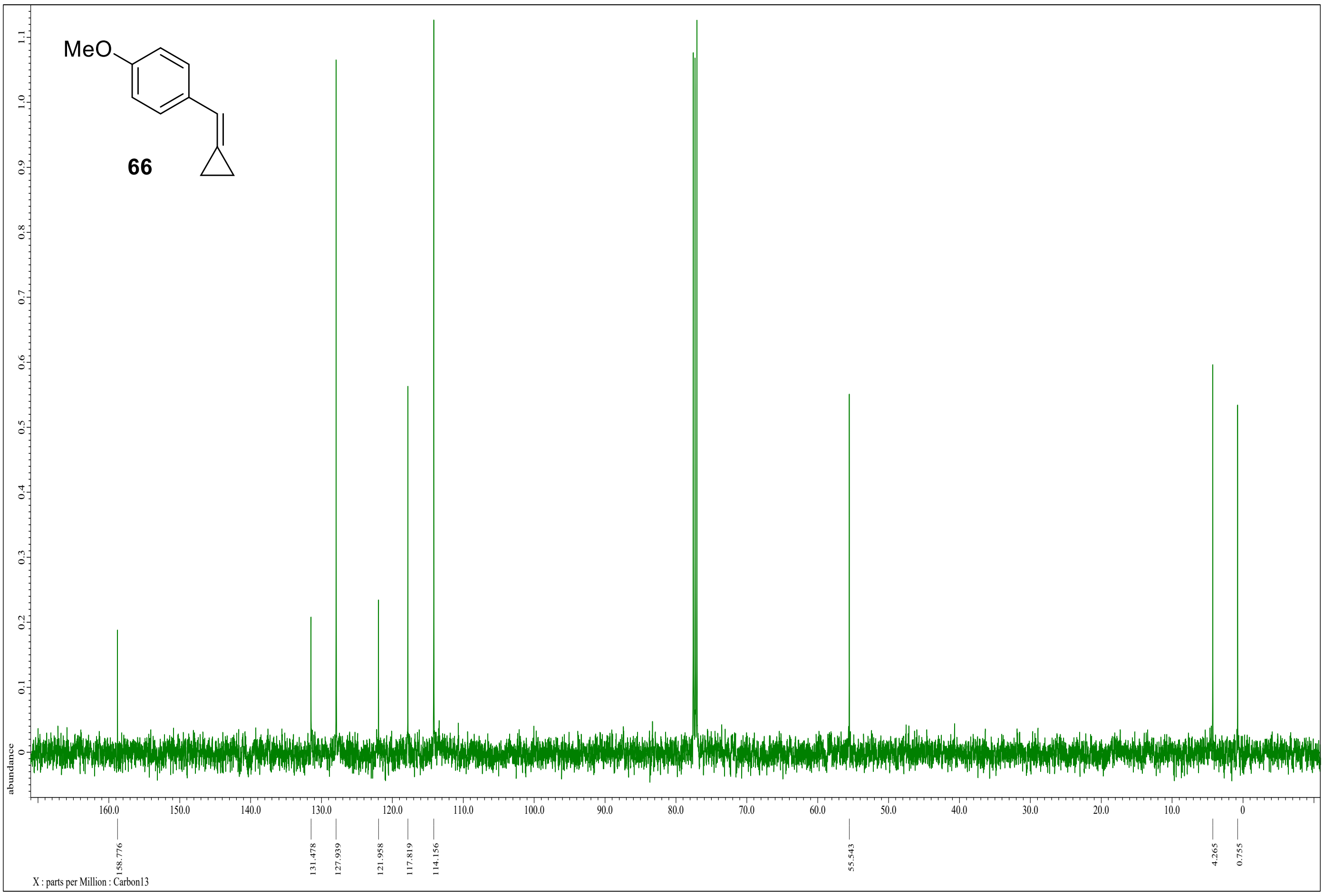
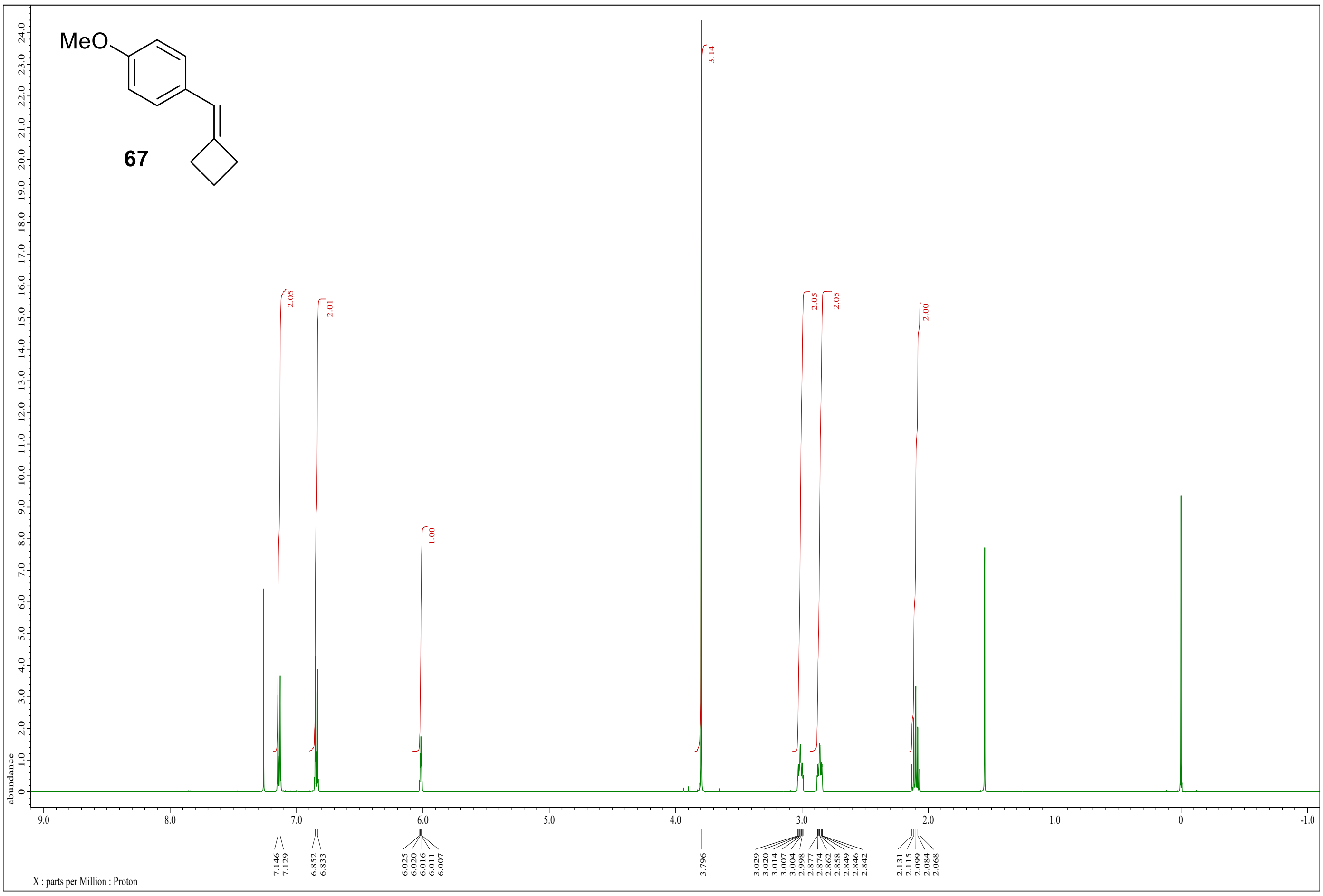
157.880
134.044
131.525
130.009
124.791
113.651
55.324
27.014
19.507
X : parts per Million : Carbon13

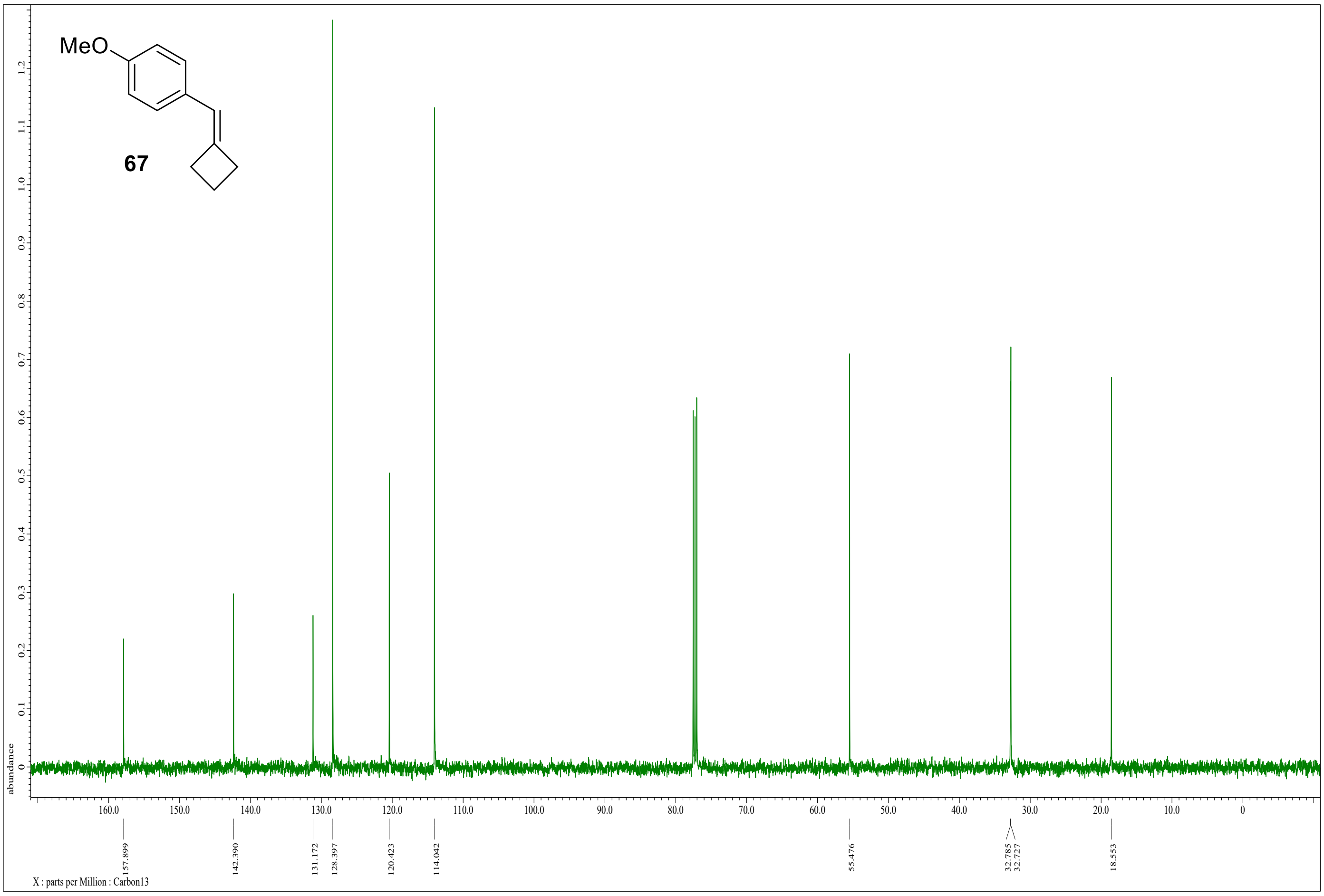


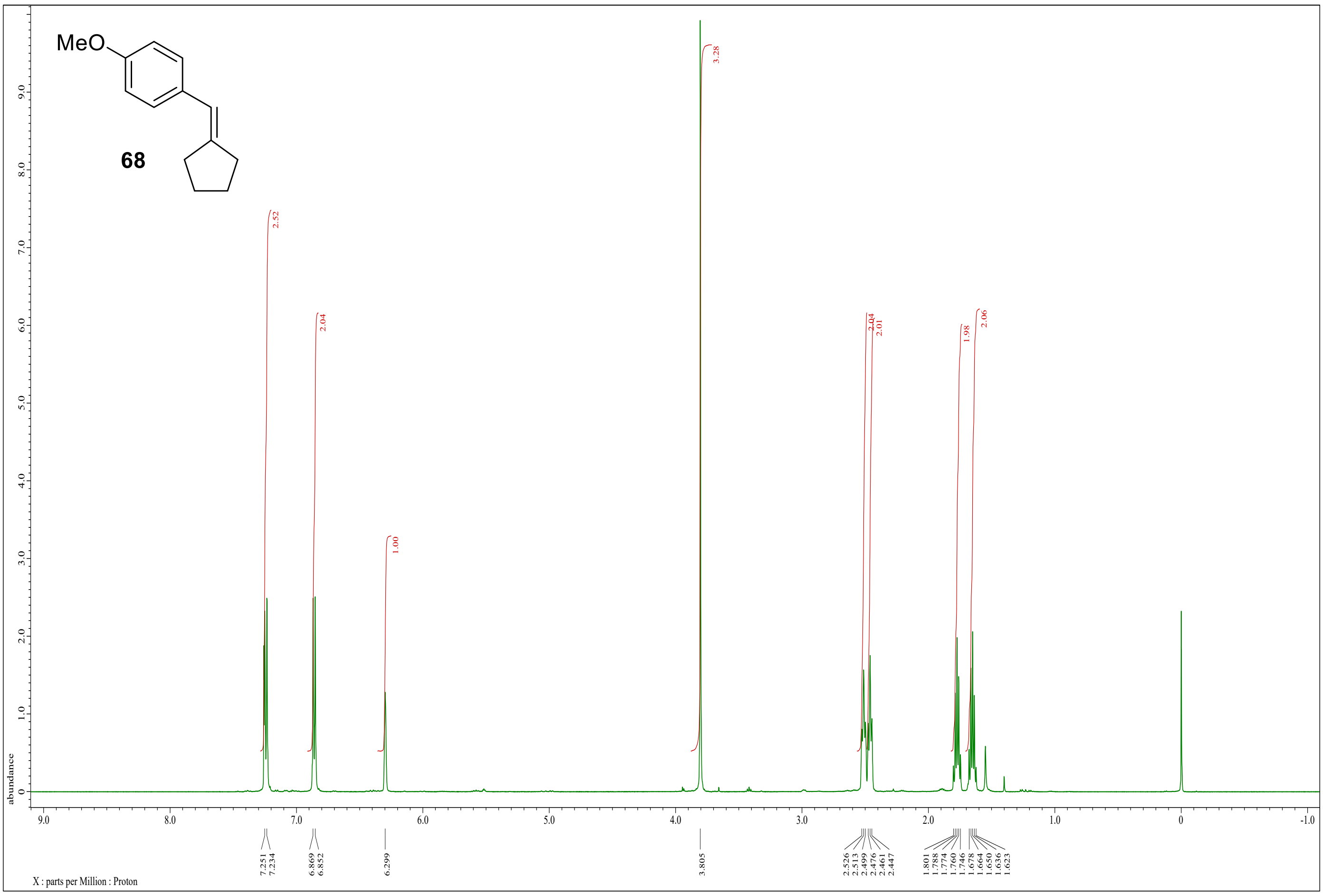
MeO
66
abundance
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.05
2.09
1.00
3.21
1.99
2.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.477
7.460
6.883
6.865
6.696
6.692
6.689
3.815
1.402
1.397
1.386
1.382
1.371
1.367
1.170
1.167
1.155
1.152
1.141
1.137
X : parts per Million : Proton

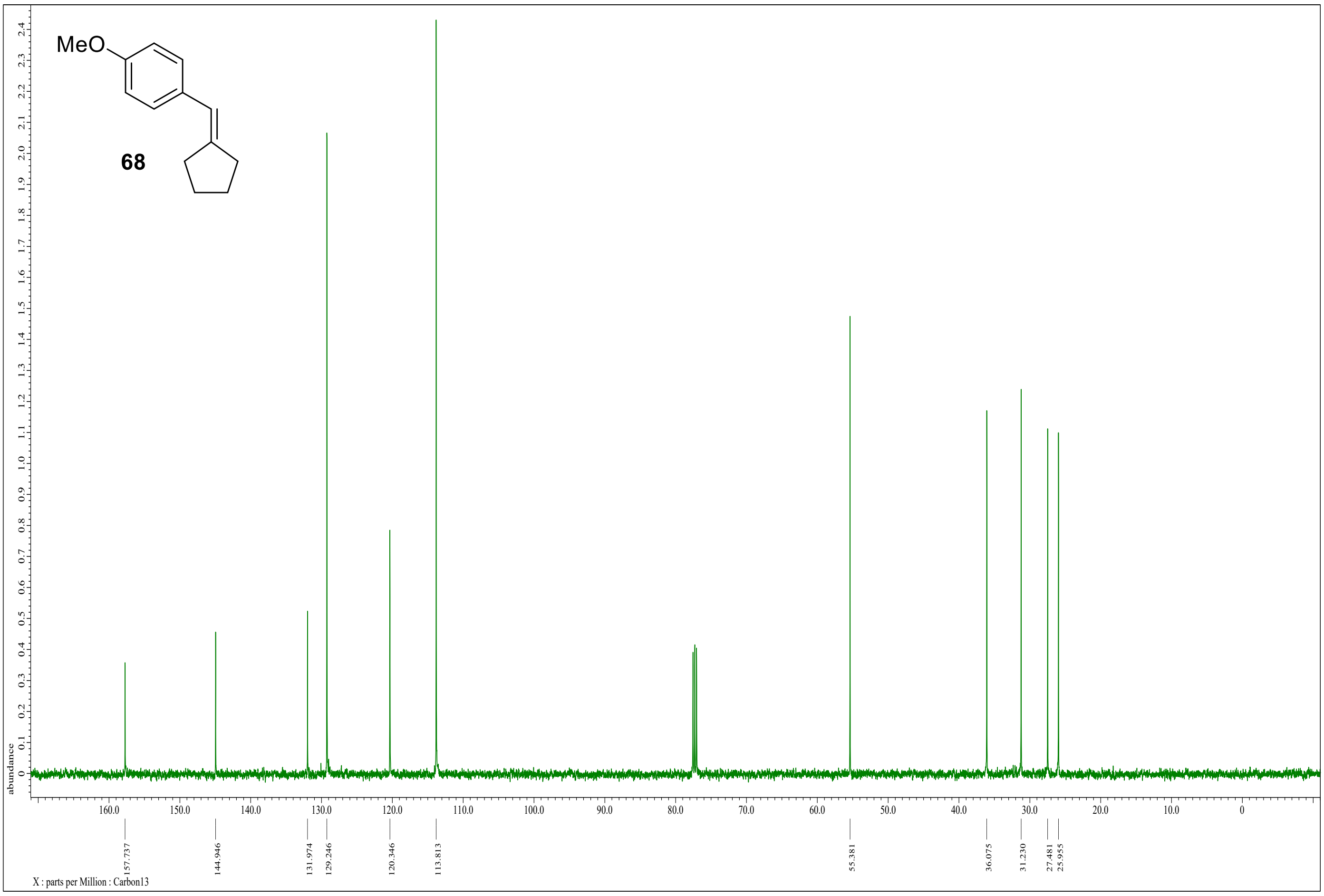


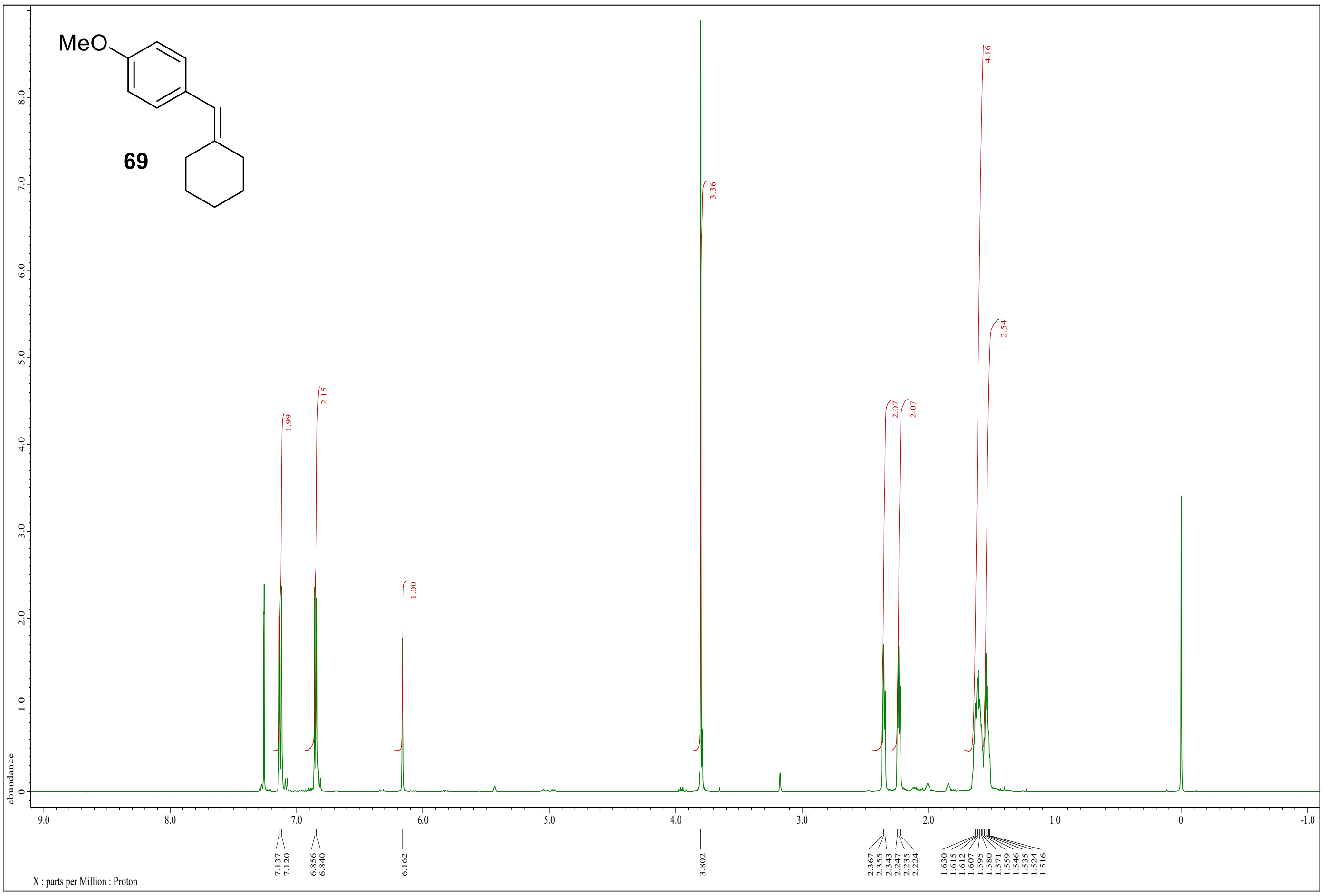
MeO
66
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.776
131.478
127.939
121.958
117.819
114.156
55.543
4.265
0.755
X : parts per Million : Carbon13

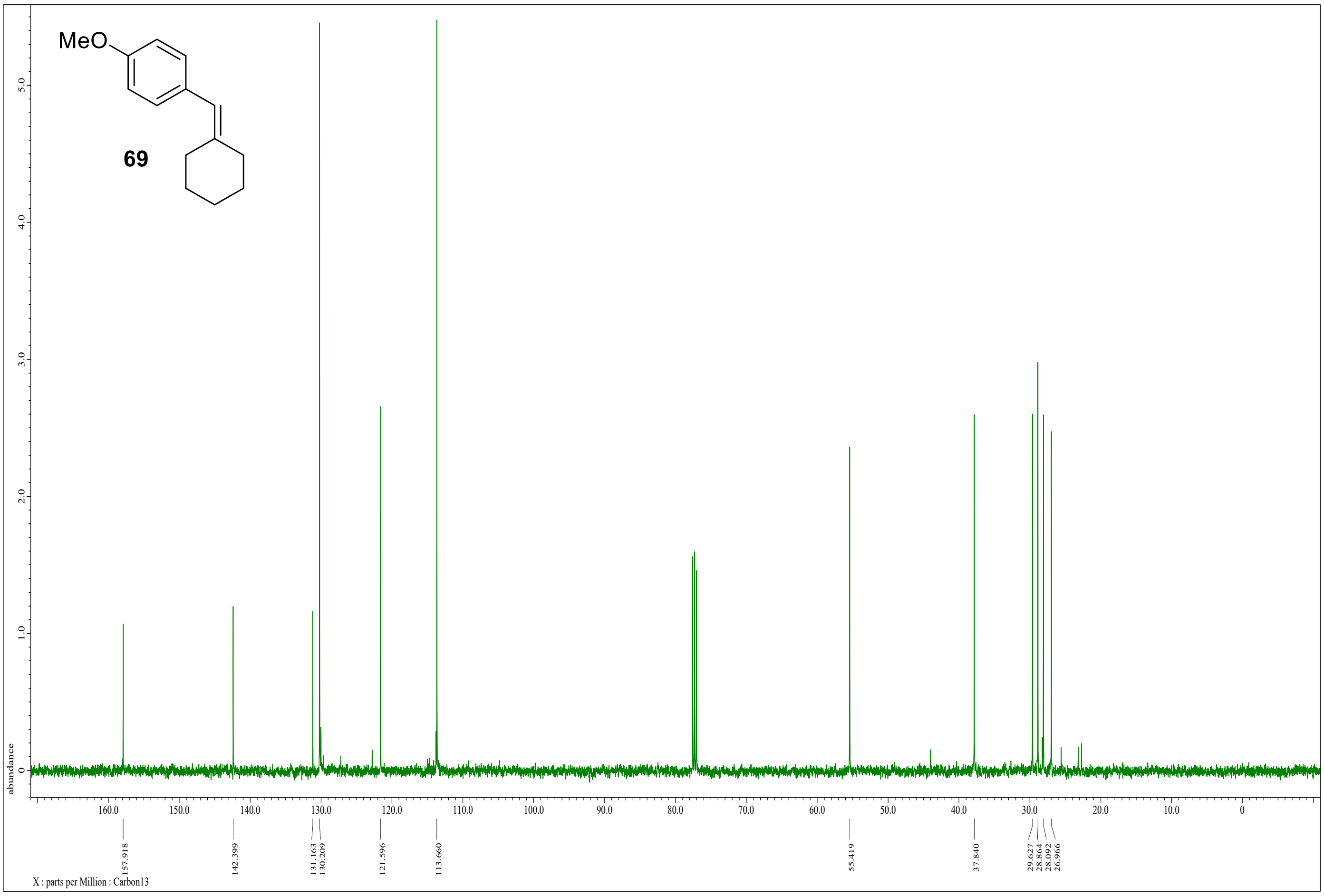

MeO
67
3.14
2.05
2.01
1.00
2.05
2.05
2.00
abundance
X : parts per Million : Proton
7.146
7.129
6.852
6.833
6.025
6.020
6.016
6.011
6.007
3.796
3.029
3.020
3.014
3.007
3.004
2.998
2.877
2.874
2.862
2.858
2.849
2.846
2.842
2.131
2.115
2.099
2.084
2.068

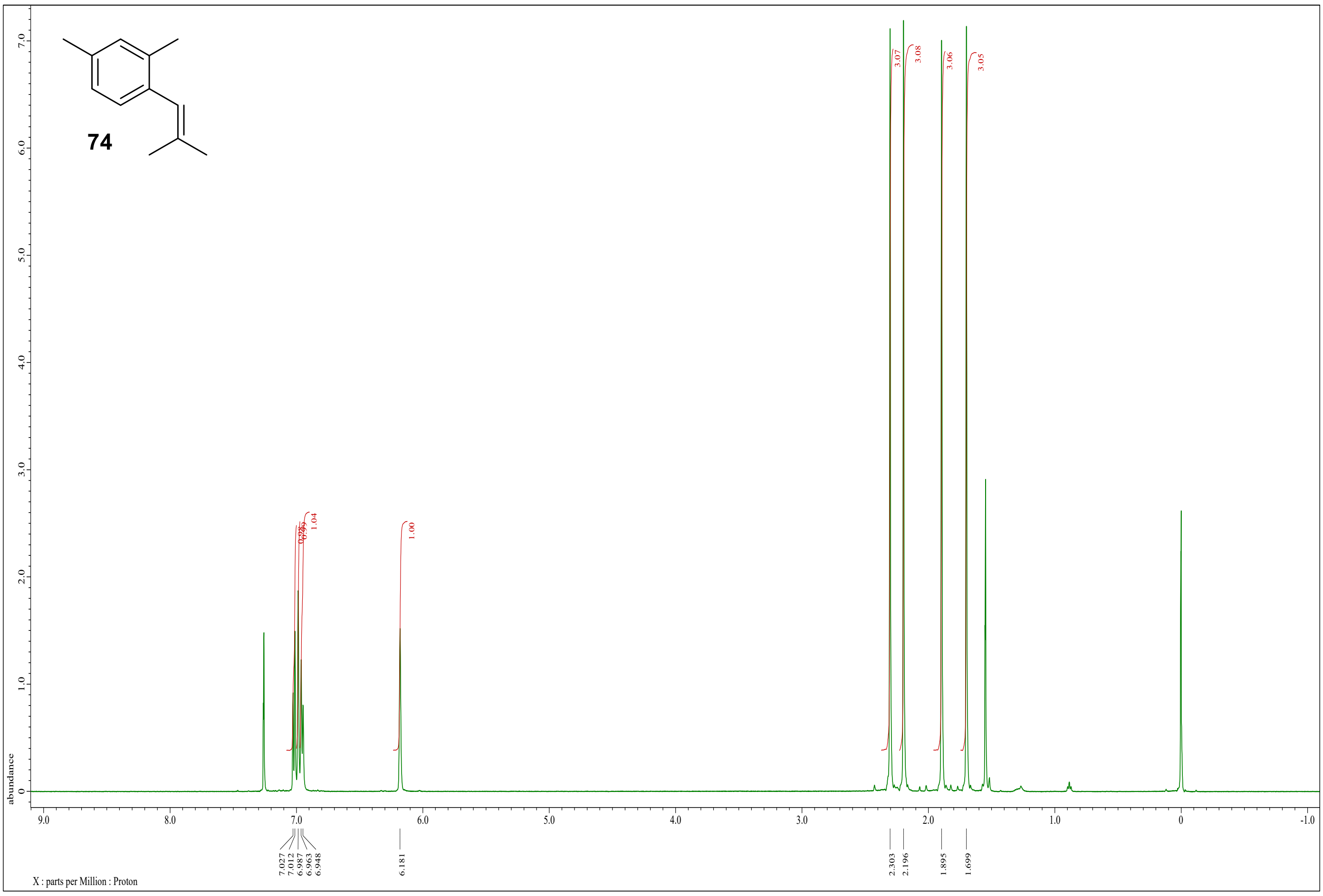

MeO
67
abundance
X : parts per Million : Carbon13
157.899
142.390
131.172
128.397
120.423
114.042
55.476
32.785
32.727
18.553

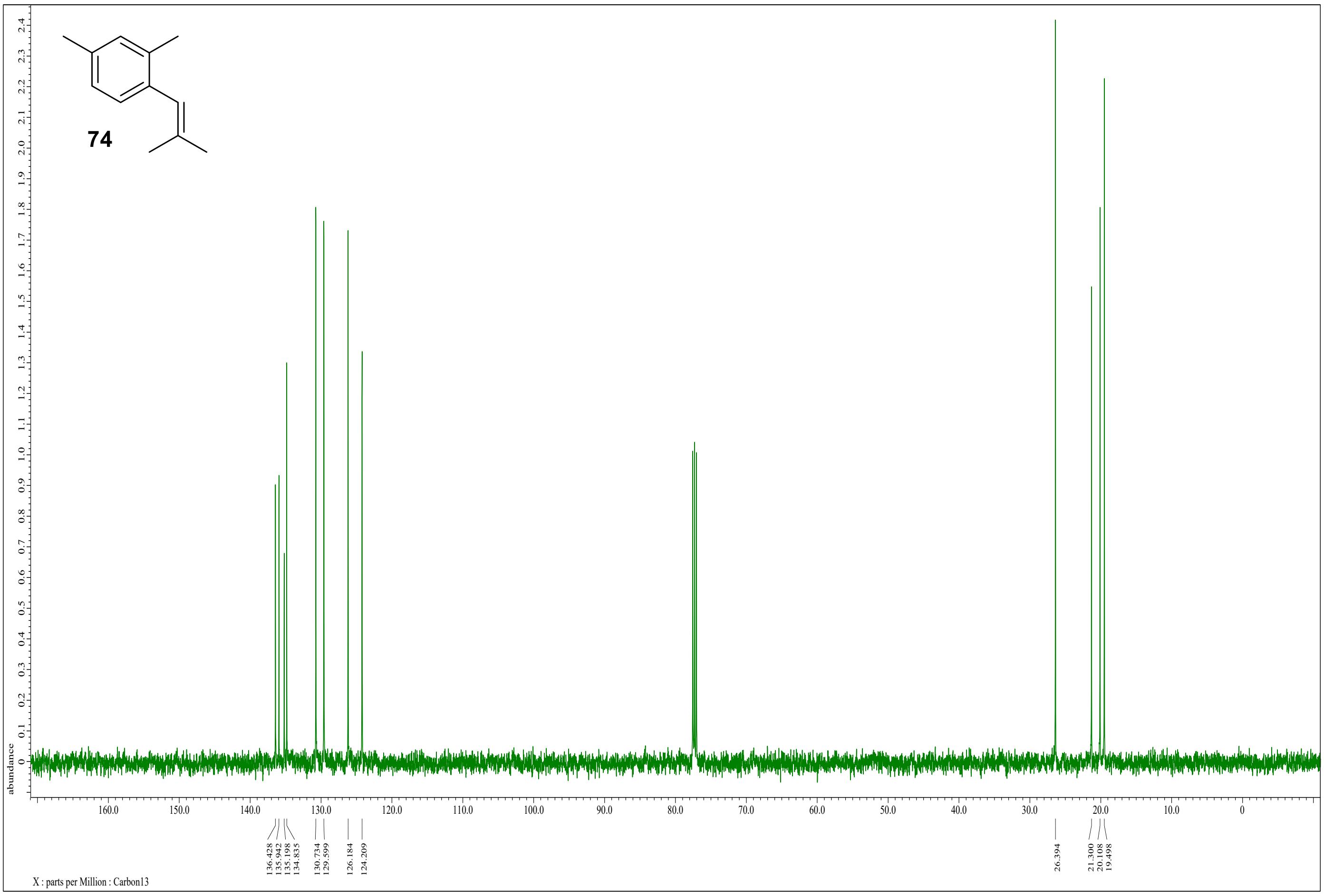

MeO
68
2.52
2.04
1.00
3.28
2.04
2.01
1.98
2.06
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.251
7.234
6.869
6.852
6.299
3.805
2.526
2.513
2.499
2.476
2.461
2.447
1.801
1.788
1.774
1.760
1.746
1.678
1.664
1.650
1.636
1.623
X : parts per Million : Proton

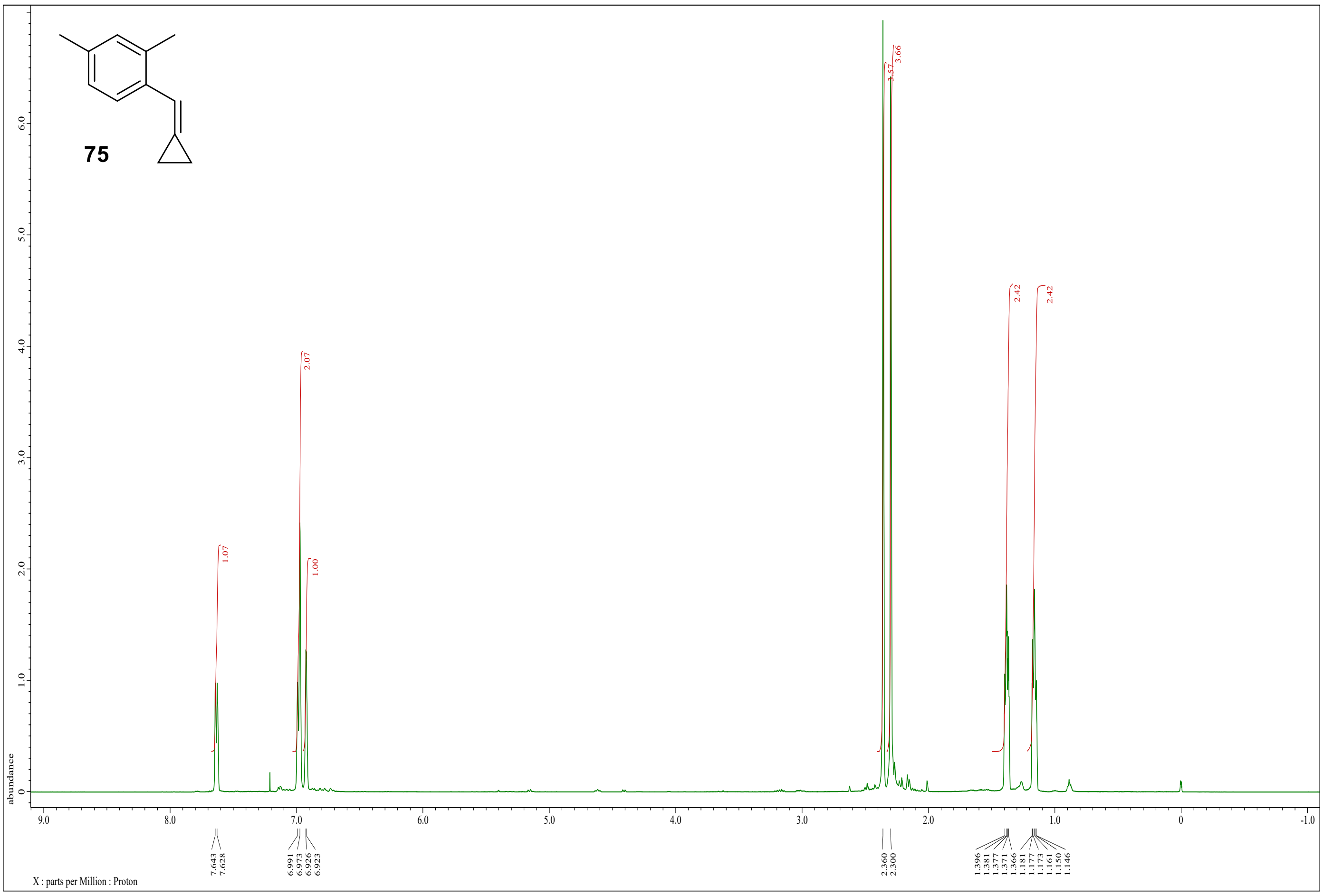

MeO
68
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
157.737
144.946
131.974
129.246
120.346
113.813
55.381
36.075
31.230
27.481
25.955
X : parts per Million : Carbon13

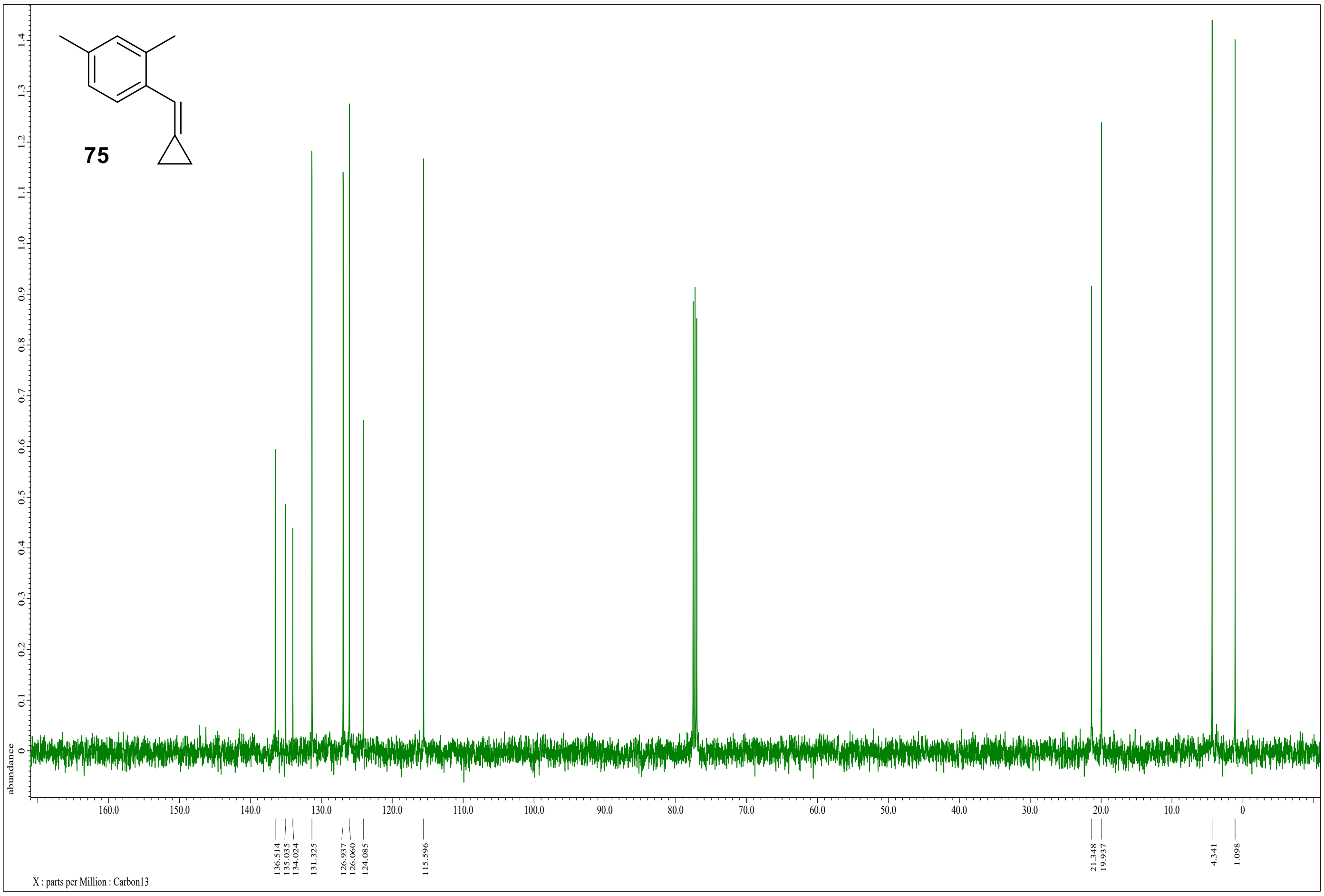

MeO
69
abundance
1.99
2.15
1.00
3.36
2.07
2.07
4.16
2.54
7.137
7.120
6.856
6.840
6.162
3.802
2.367
2.355
2.343
2.247
2.235
2.224
1.630
1.615
1.612
1.607
1.595
1.580
1.571
1.559
1.546
1.535
1.524
1.516
X : parts per Million : Proton

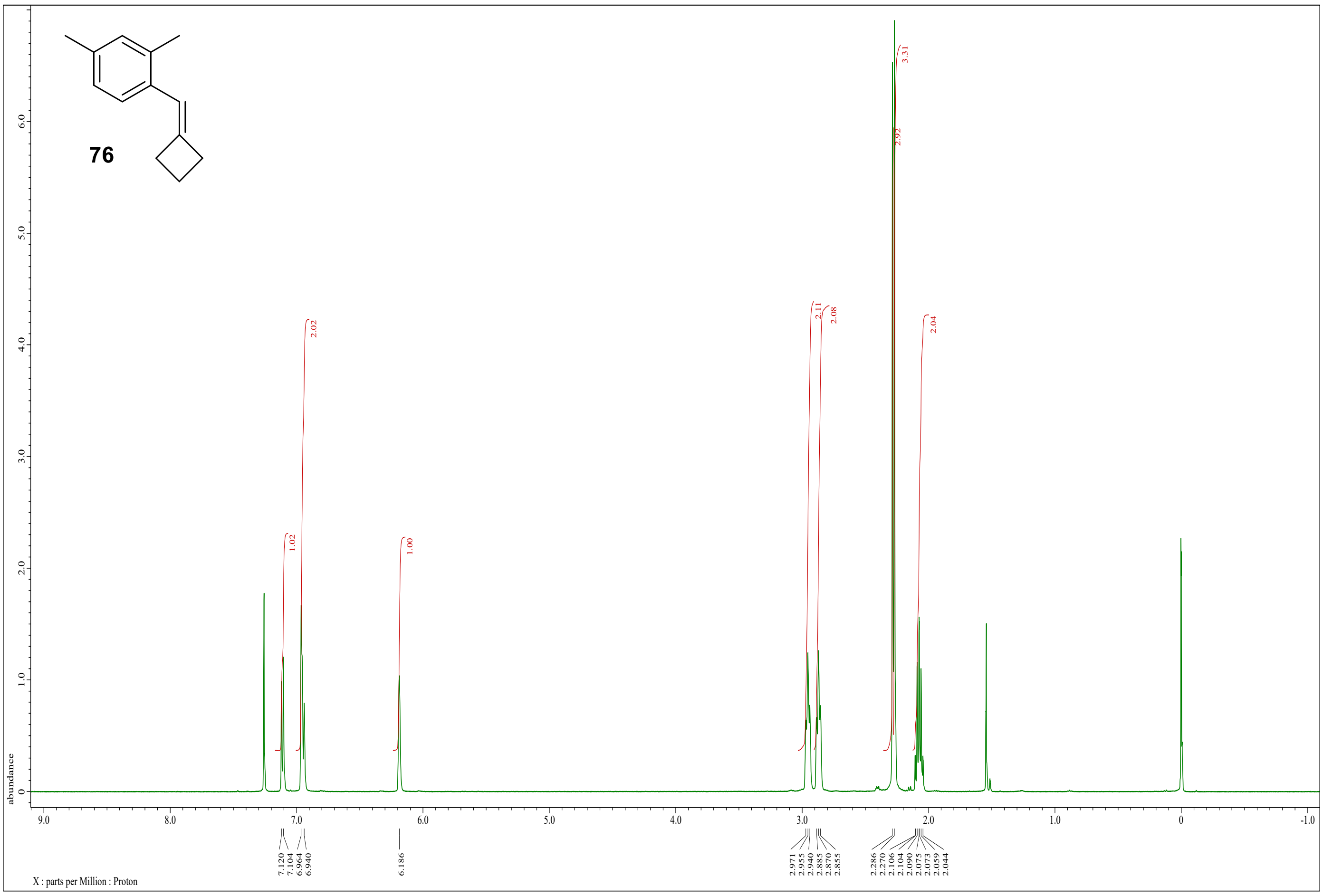

MeO
69
abundance
157.918
142.399
131.163
130.209
121.596
113.660
55.419
37.840
29.627
28.864
28.092
26.966
X : parts per Million : Carbon13

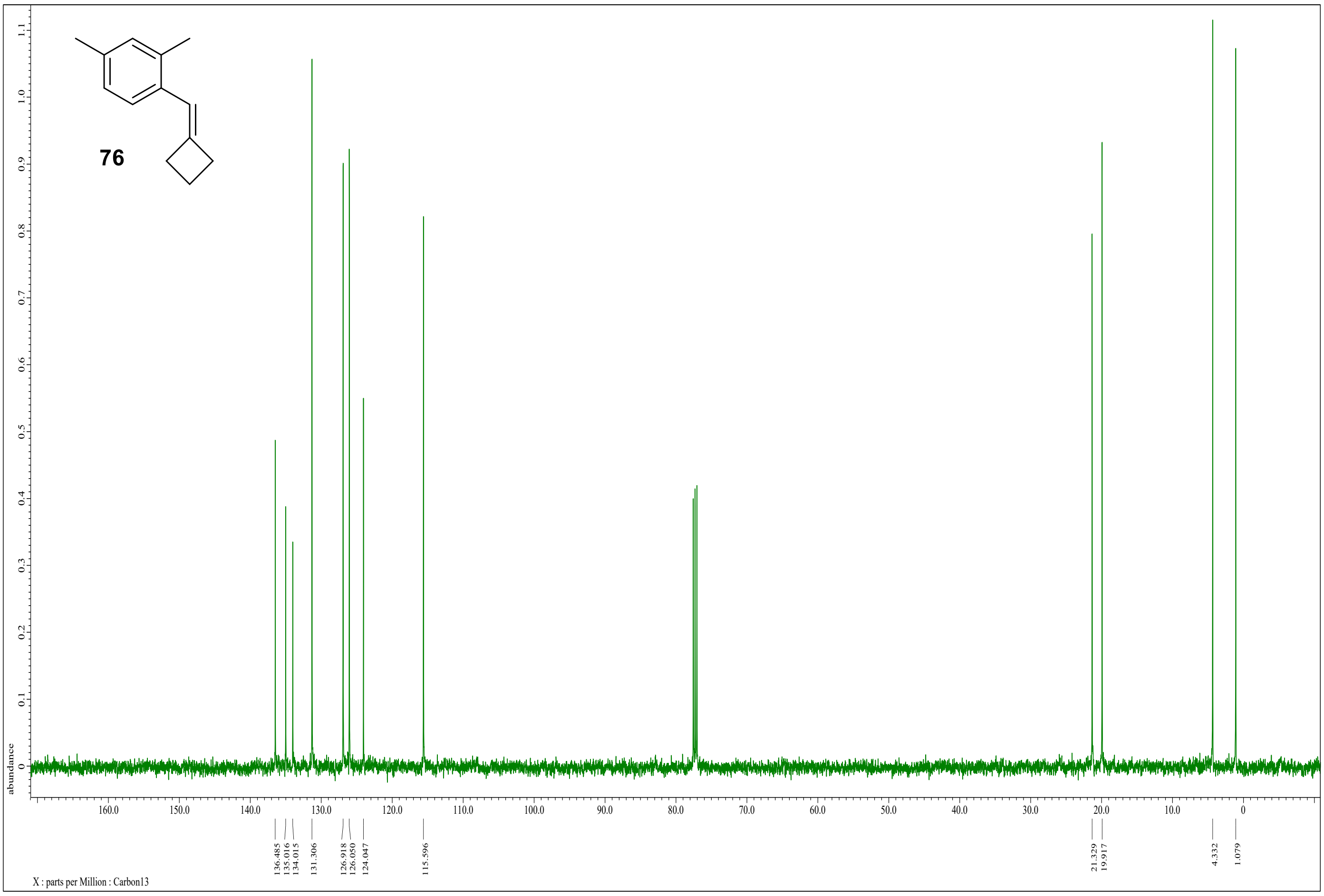

74
abundance
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.07
3.08
3.06
3.05
1.04
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.027
7.012
6.987
6.963
6.948
6.181
2.303
2.196
1.895
1.699
X : parts per Million : Proton

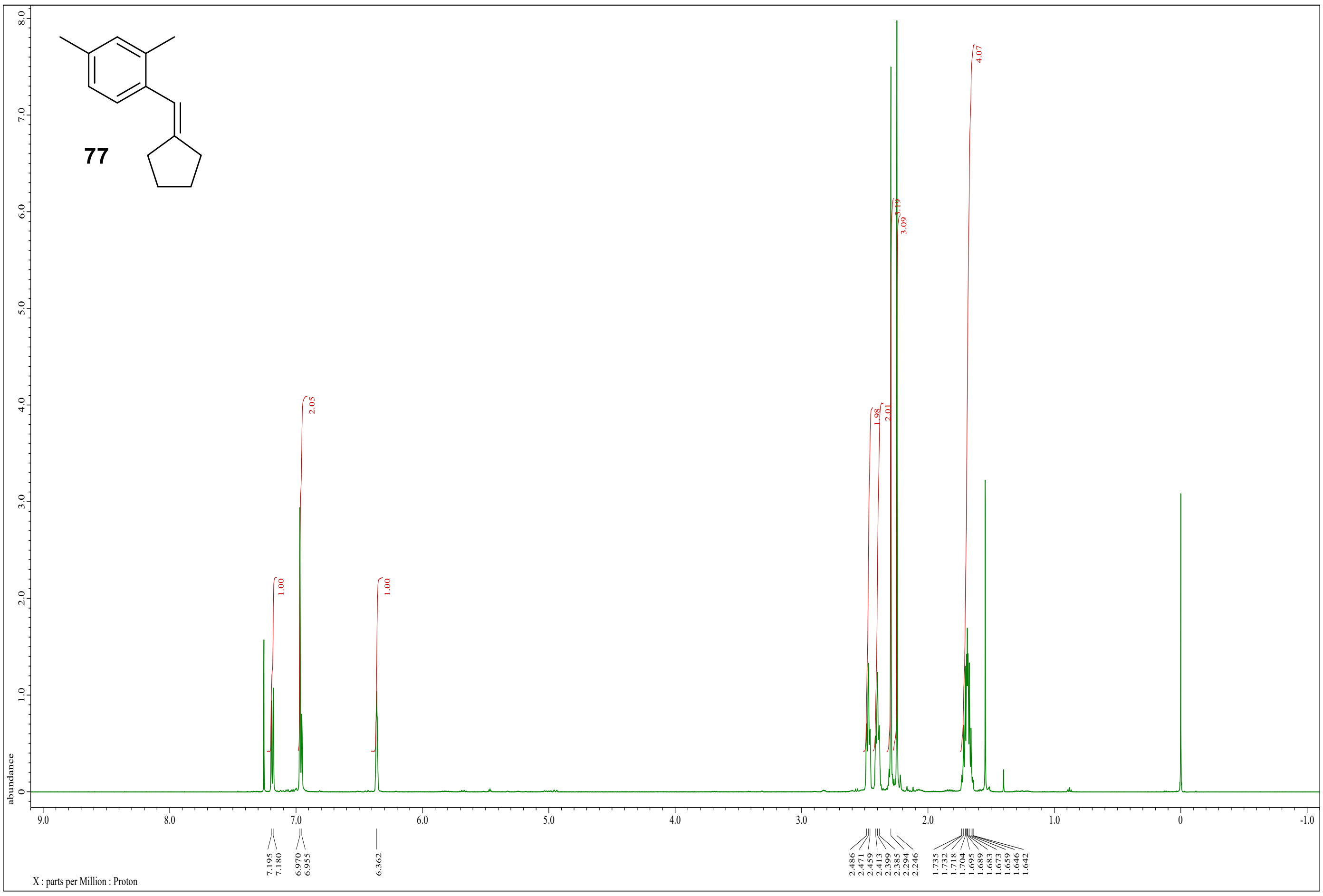

74
abundance
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
136.428
135.942
135.198
134.835
130.734
129.599
126.184
124.209
26.394
21.300
20.108
19.498
X : parts per Million : Carbon13

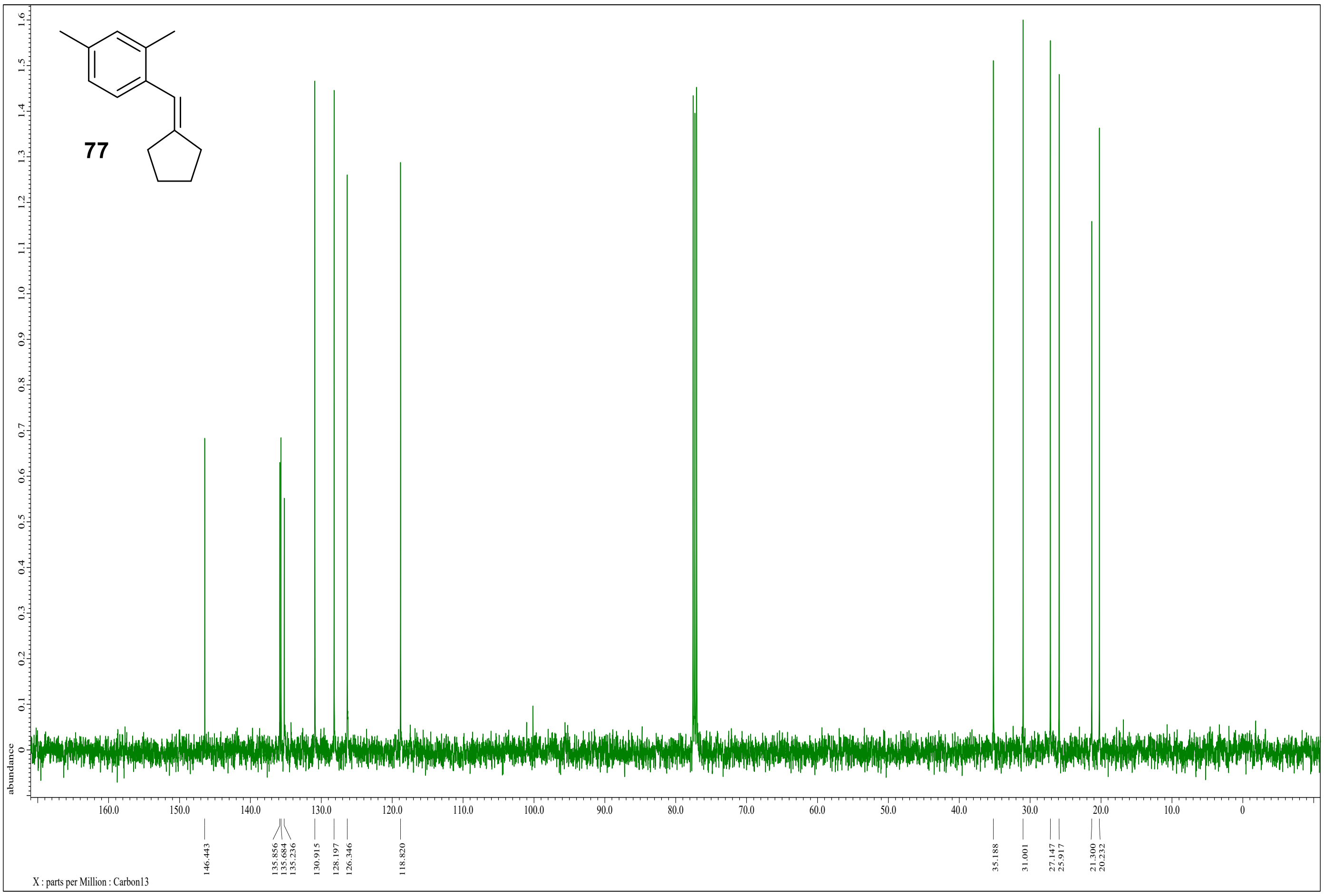

75
1.07
2.07
1.00
3.57
3.66
2.42
2.42
abundance
7.643
7.628
6.991
6.973
6.926
6.923
2.360
2.300
1.396
1.381
1.377
1.371
1.366
1.181
1.177
1.173
1.161
1.150
1.146
X : parts per Million : Proton

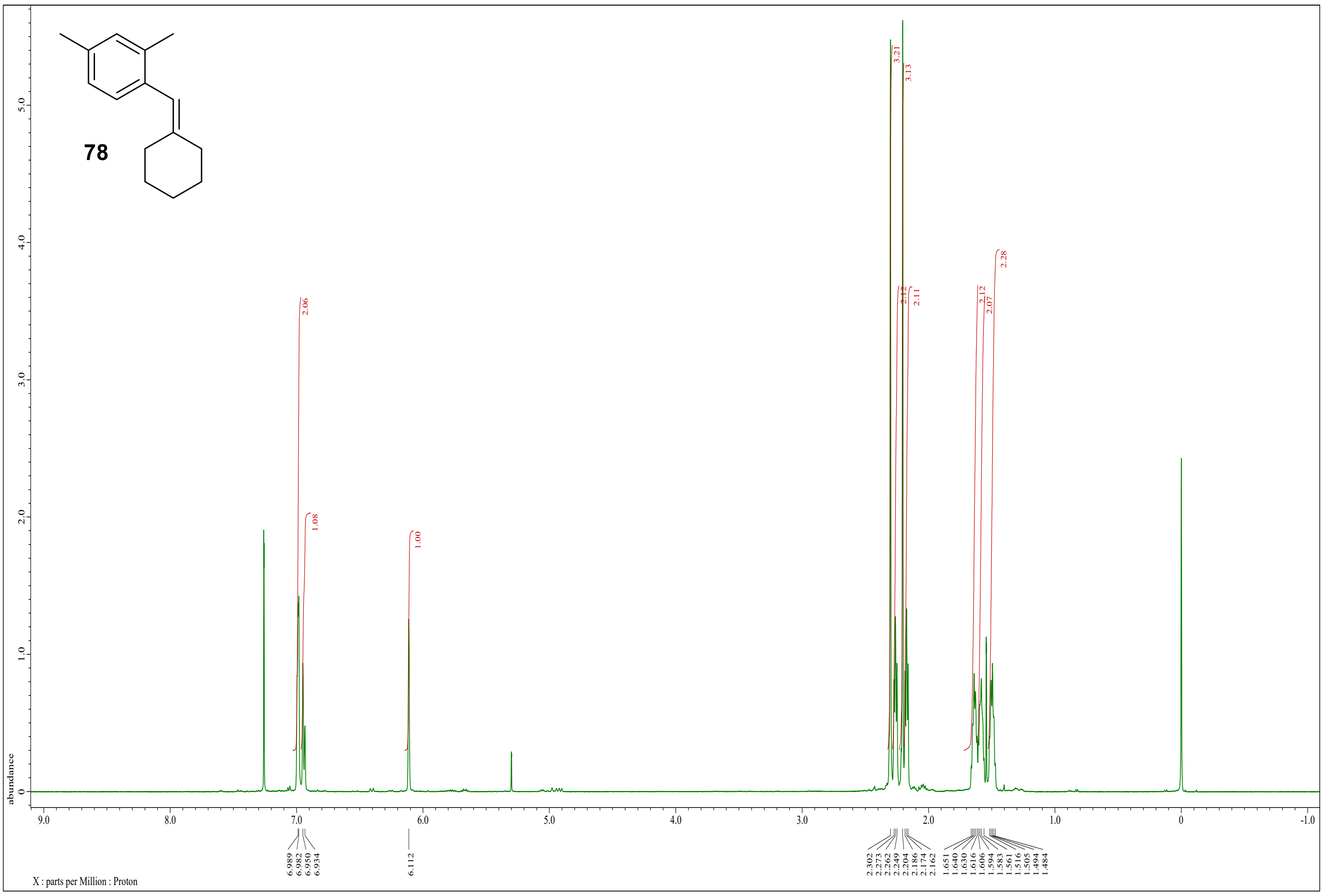

75
abundance
136.514
135.035
134.024
131.325
126.937
126.060
124.085
115.596
21.348
19.937
4.341
1.098
X : parts per Million : Carbon13

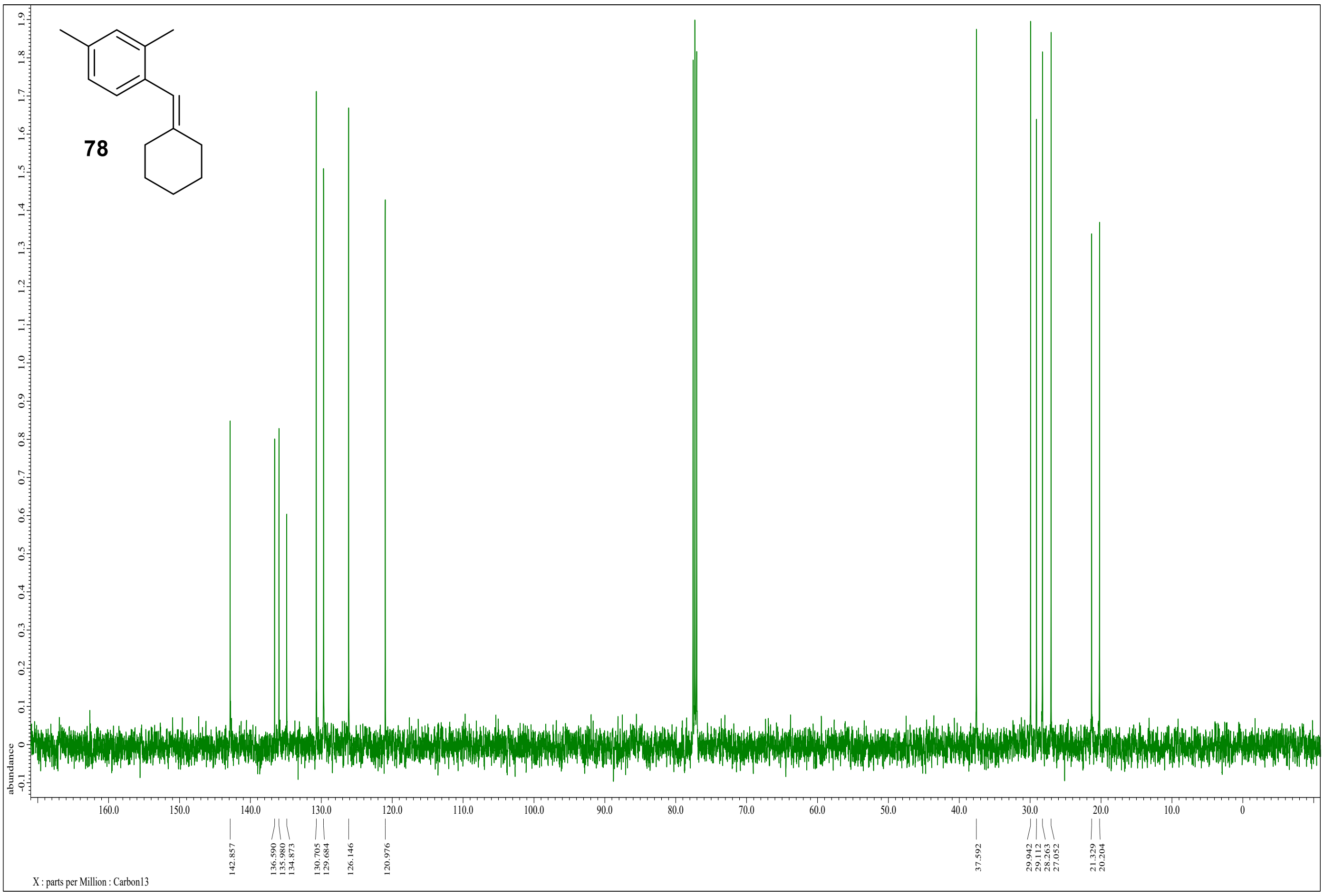

76
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
1.02
2.02
1.00
2.11
2.08
3.31
2.92
2.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.120
7.104
6.964
6.940
6.186
2.971
2.955
2.940
2.885
2.870
2.855
2.286
2.270
2.106
2.104
2.090
2.075
2.073
2.059
2.044
X : parts per Million : Proton

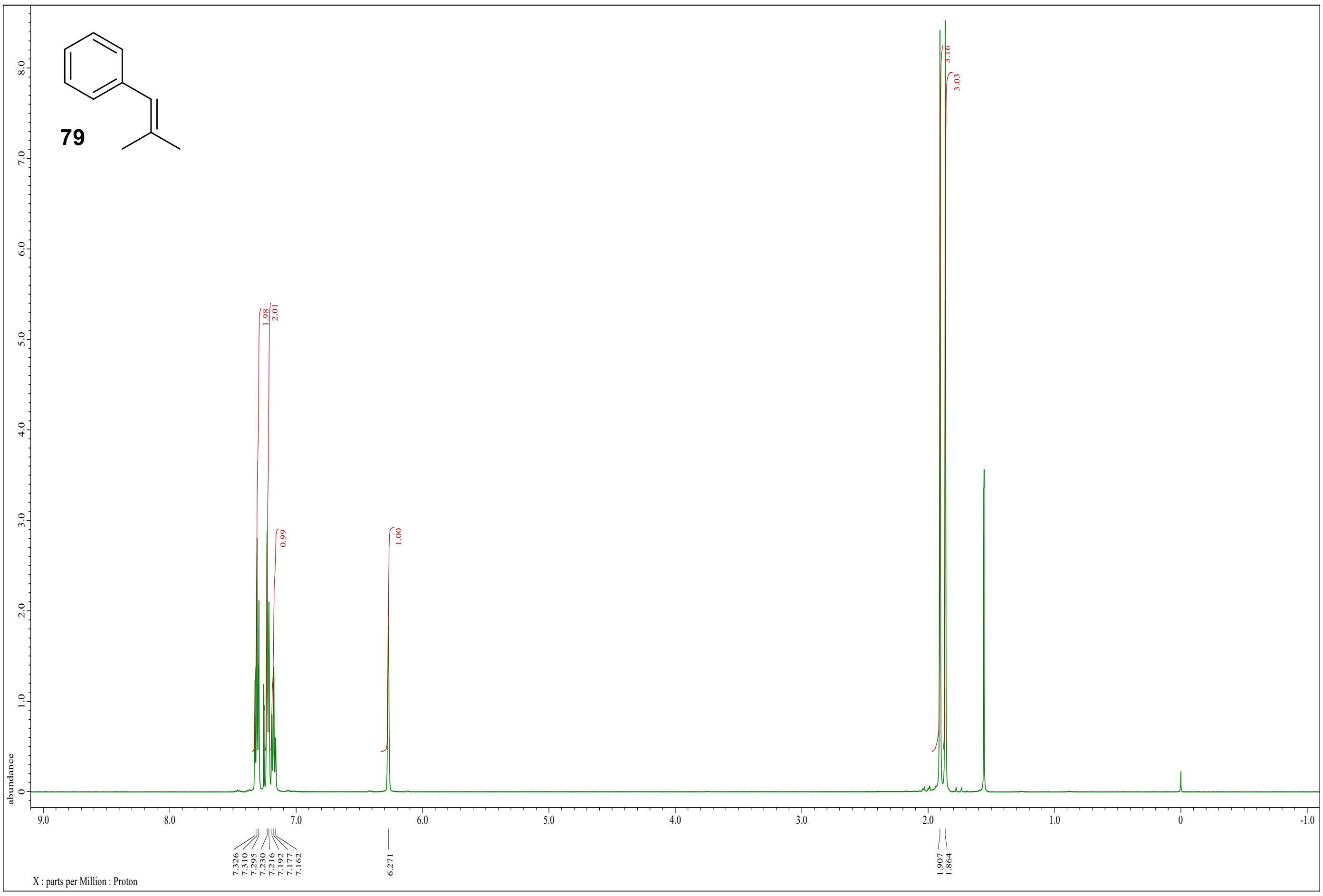

76
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
136.485
135.016
134.015
131.306
126.918
126.050
124.047
115.596
21.329
19.917
4.332
1.079
X : parts per Million : Carbon13

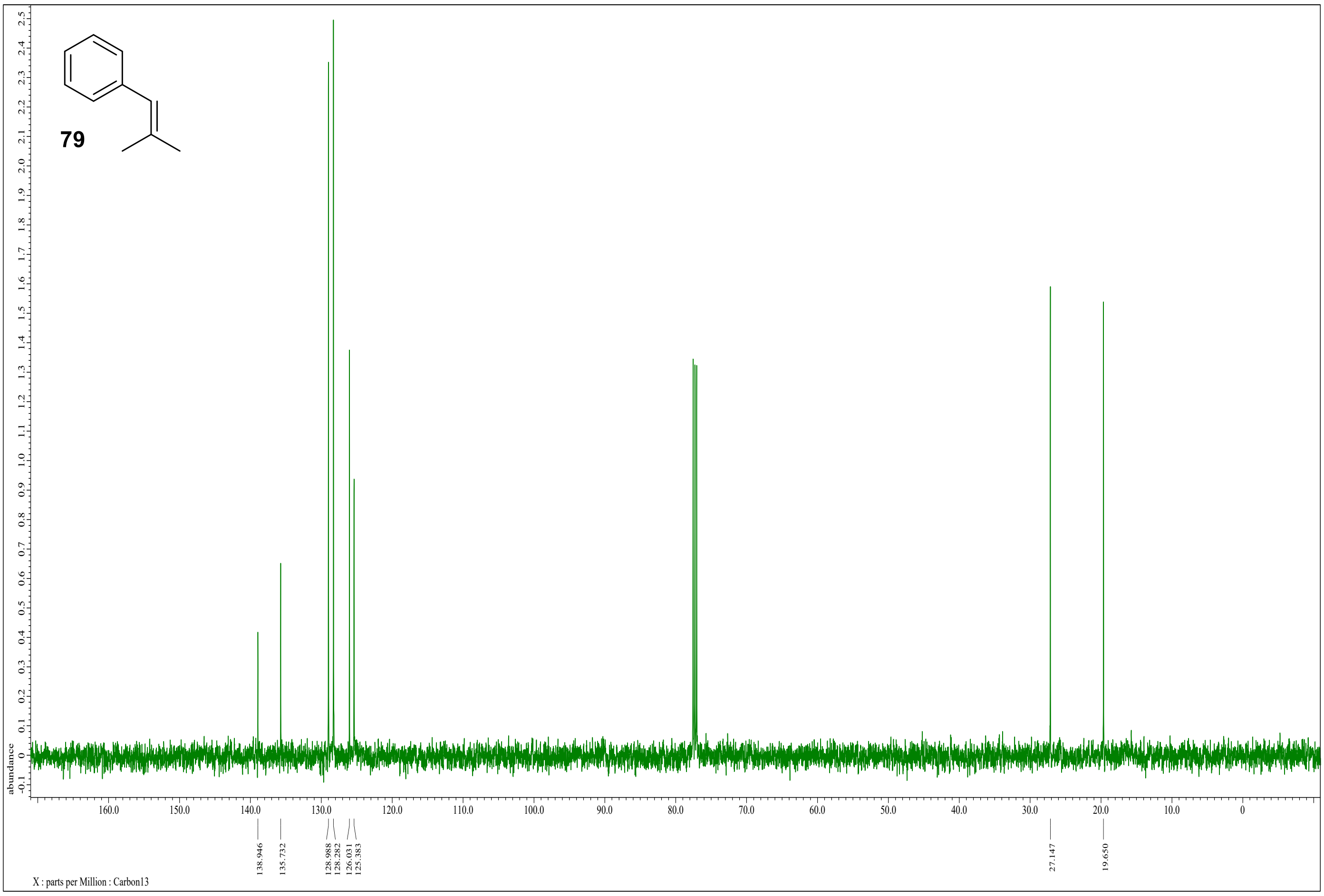

77
abundance
X : parts per Million : Proton
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
1.00
2.05
1.00
1.98
2.01
3.17
3.09
4.07
7.195
7.180
6.970
6.955
6.362
2.486
2.471
2.459
2.413
2.399
2.385
2.294
2.246
1.735
1.732
1.718
1.704
1.695
1.689
1.683
1.673
1.659
1.646
1.642

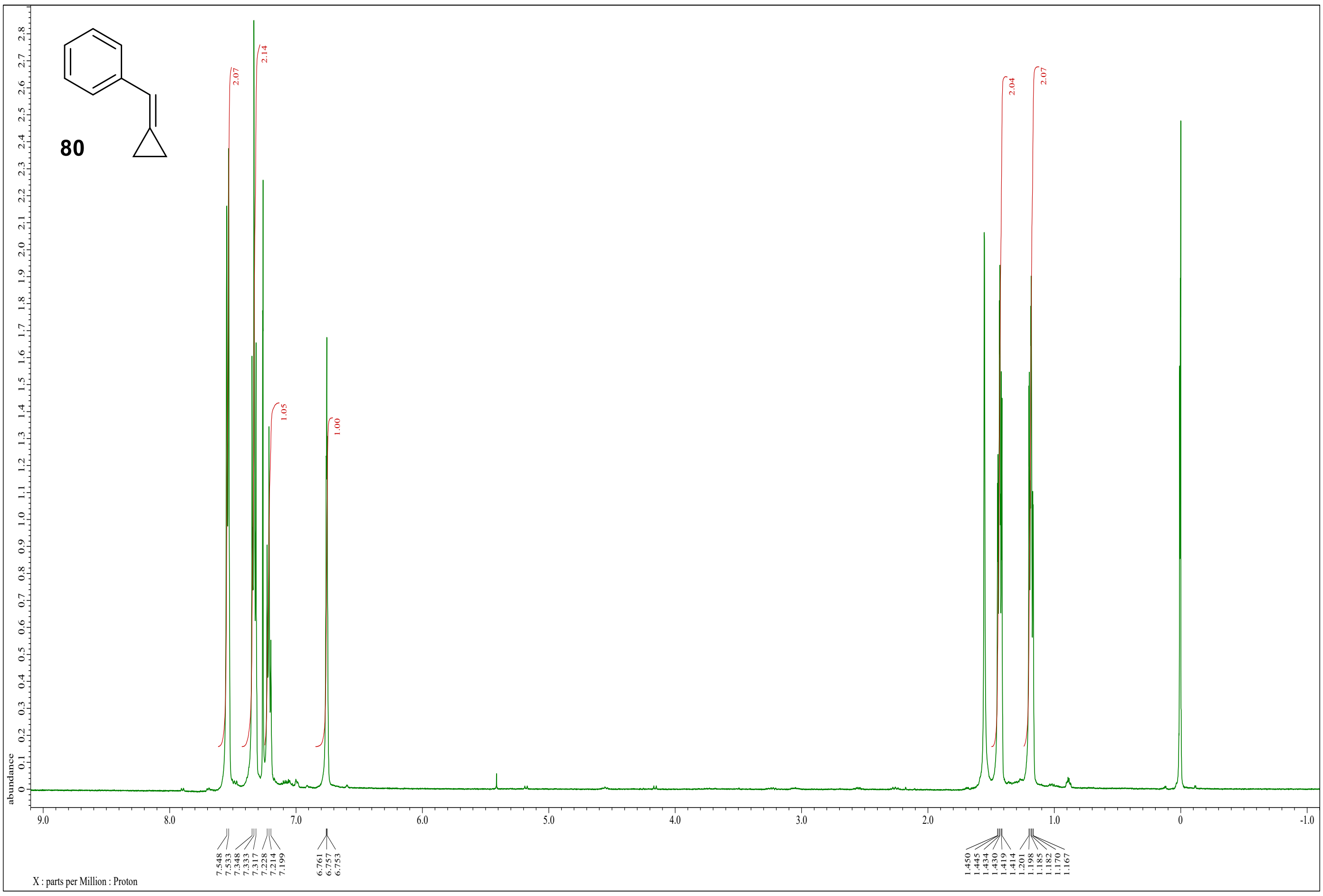

77
abundance
X : parts per Million : Carbon13
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
146.443
135.856
135.684
135.236
130.915
128.197
126.346
118.820
35.188
31.001
27.147
25.917
21.300
20.232

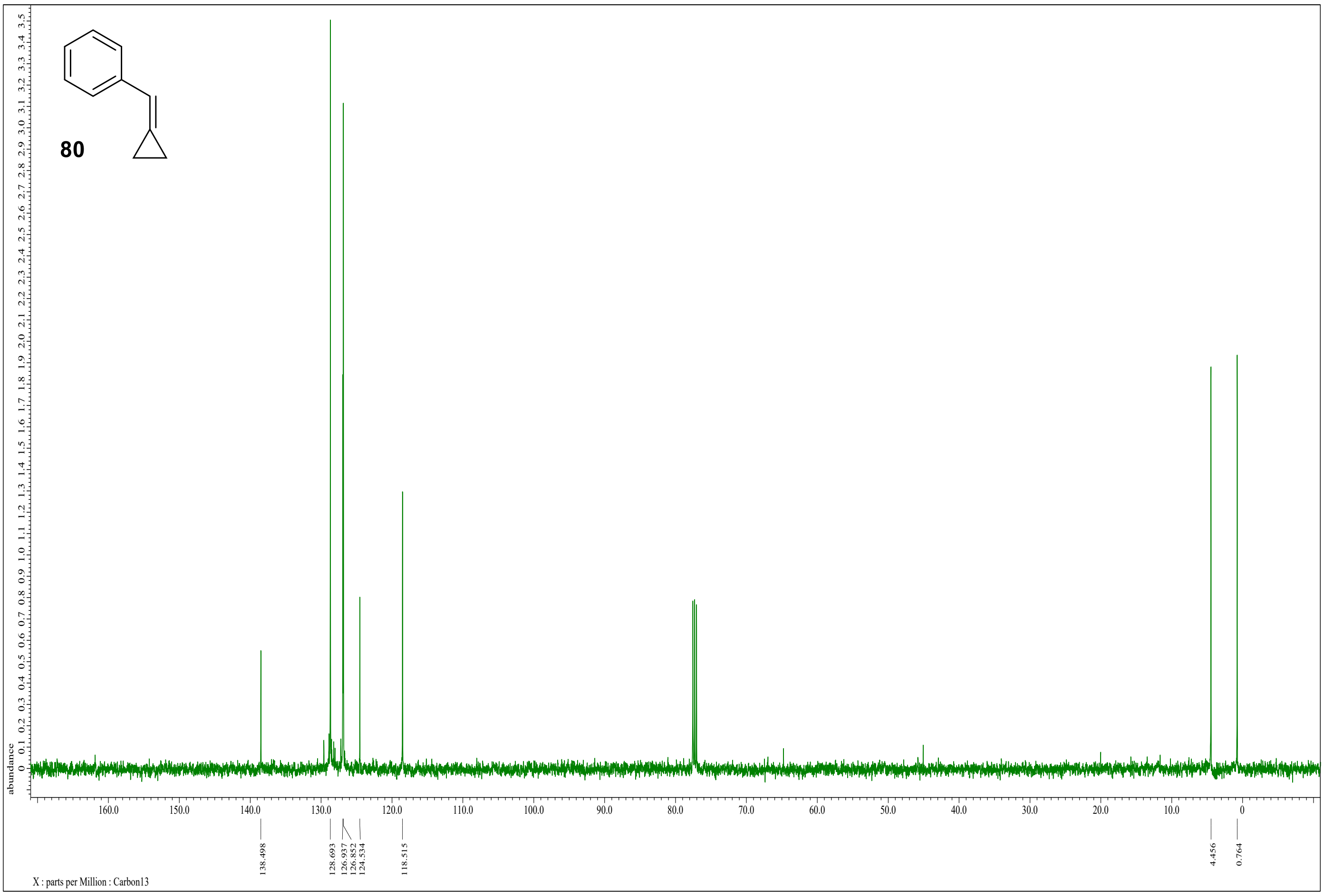

78
abundance
0
1.0
2.0
3.0
4.0
5.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
2.06
1.08
1.00
3.21
3.13
2.12
2.11
2.12
2.07
2.28
6.989
6.982
6.950
6.934
6.112
2.302
2.273
2.262
2.249
2.204
2.186
2.174
2.162
1.651
1.640
1.630
1.616
1.606
1.594
1.583
1.561
1.516
1.505
1.494
1.484
X : parts per Million : Proton

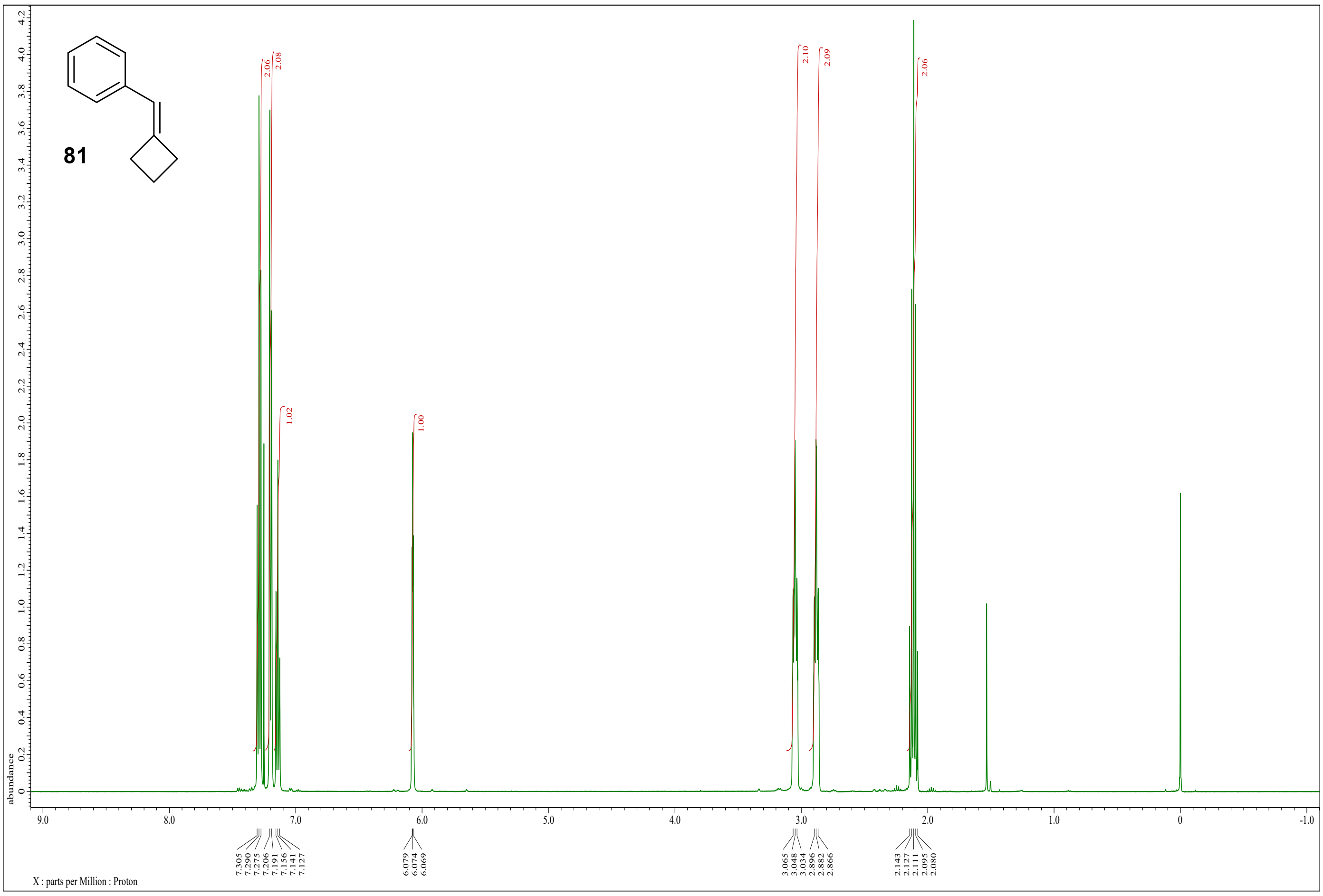

78
abundance
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.857
136.590
135.980
134.873
130.705
129.684
126.146
120.976
37.592
29.942
29.112
28.263
27.052
21.329
20.204
X : parts per Million : Carbon13

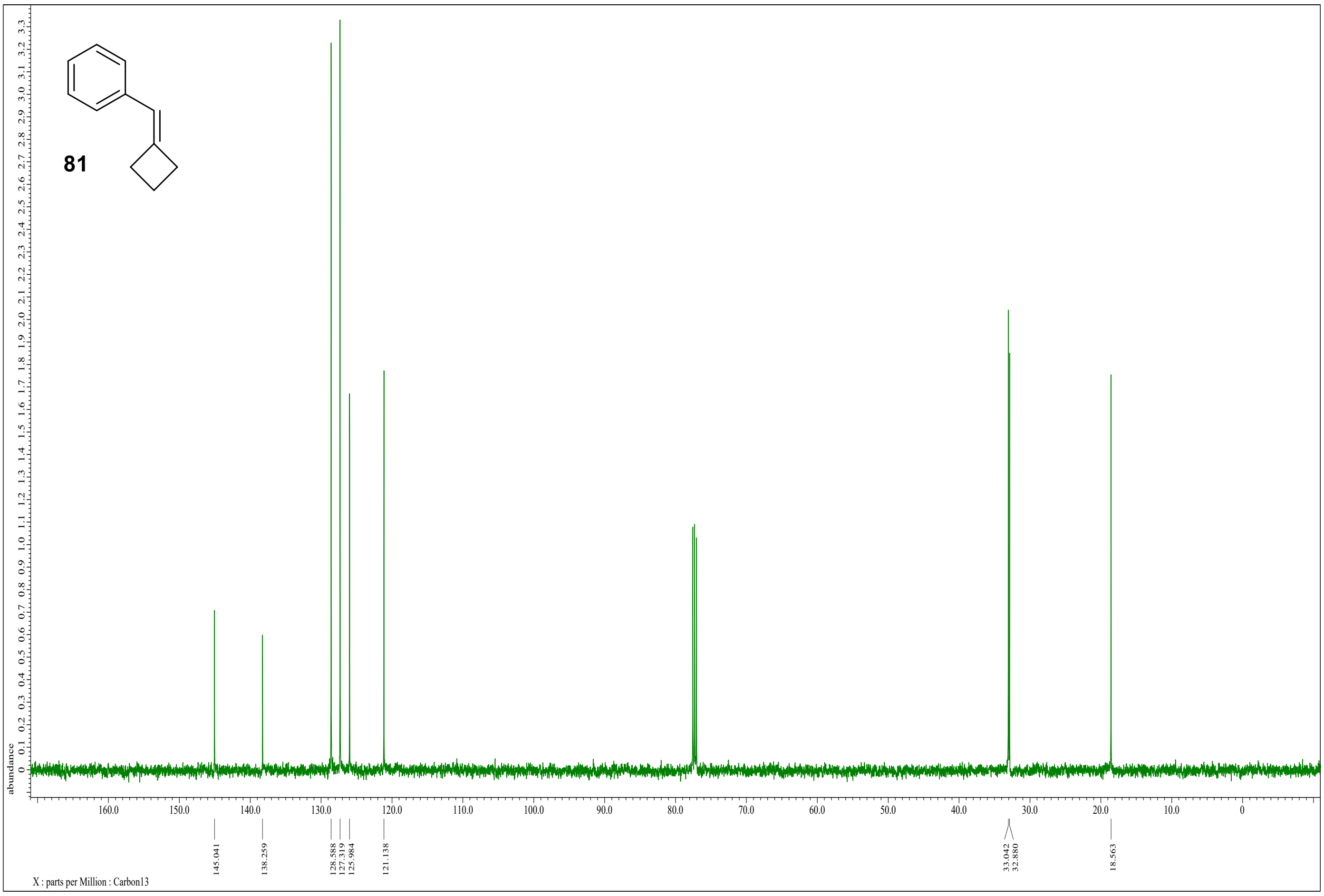

79
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
1.98
2.01
0.99
1.00
3.16
3.03
7.326
7.310
7.295
7.230
7.216
7.192
7.177
7.162
6.271
1.907
1.864
X : parts per Million : Proton

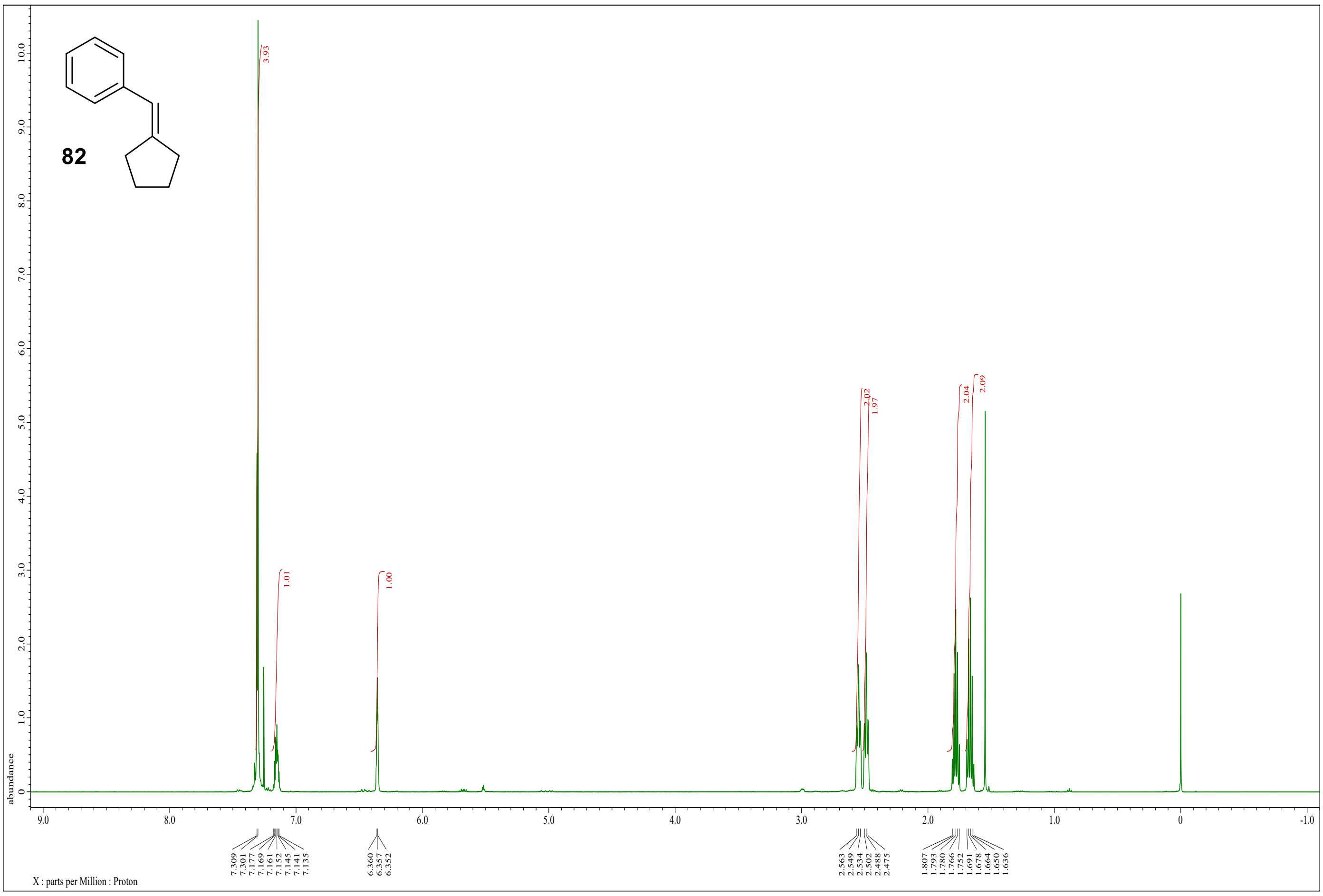

79
abundance
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.946
135.732
128.988
128.282
126.031
125.383
27.147
19.650
X : parts per Million : Carbon13

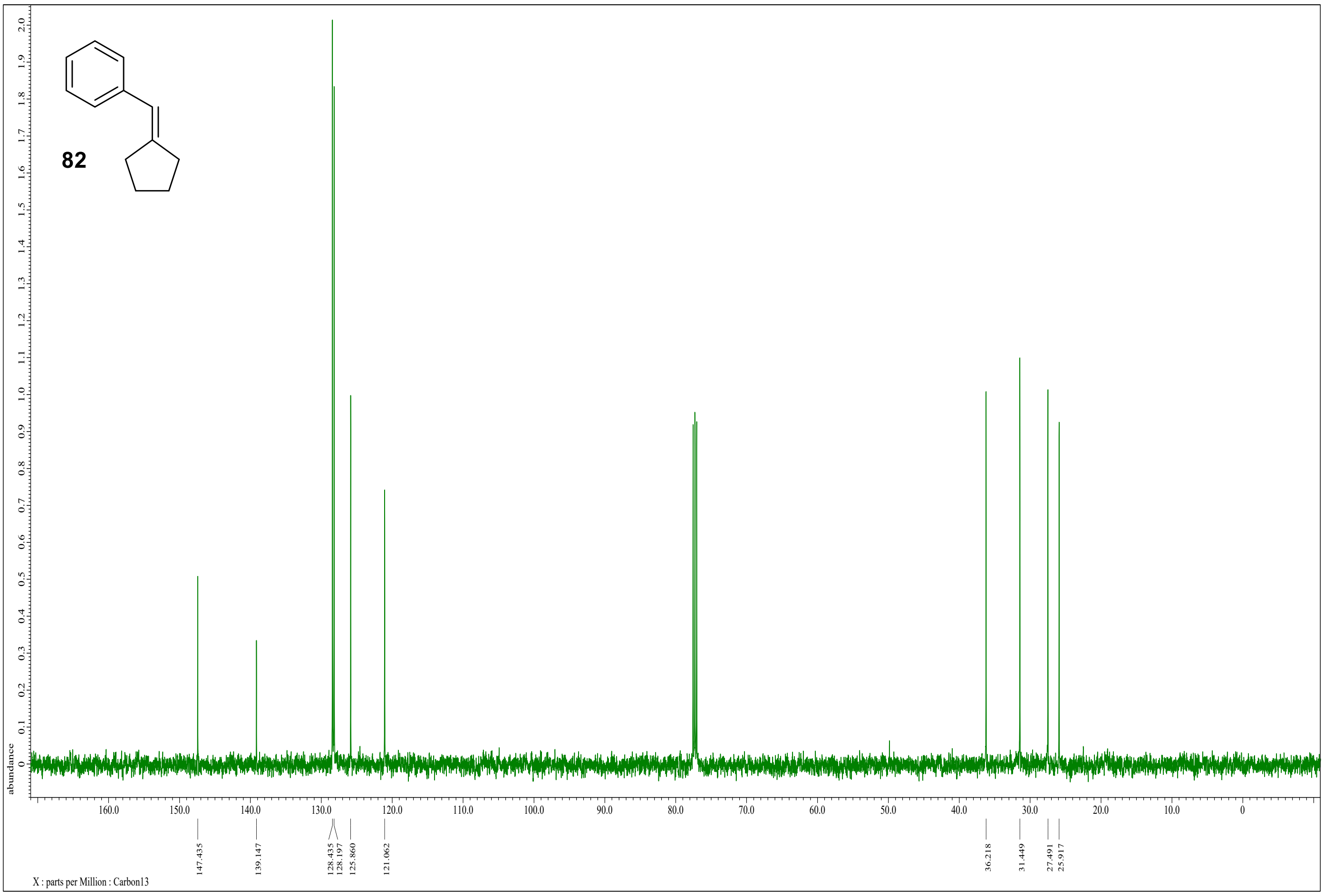

80
abundance
2.07
2.14
1.05
1.00
2.04
2.07
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
7.548
7.533
7.348
7.333
7.317
7.228
7.214
7.199
6.761
6.757
6.753
1.450
1.445
1.434
1.430
1.419
1.414
1.201
1.198
1.185
1.182
1.170
1.167
X : parts per Million : Proton

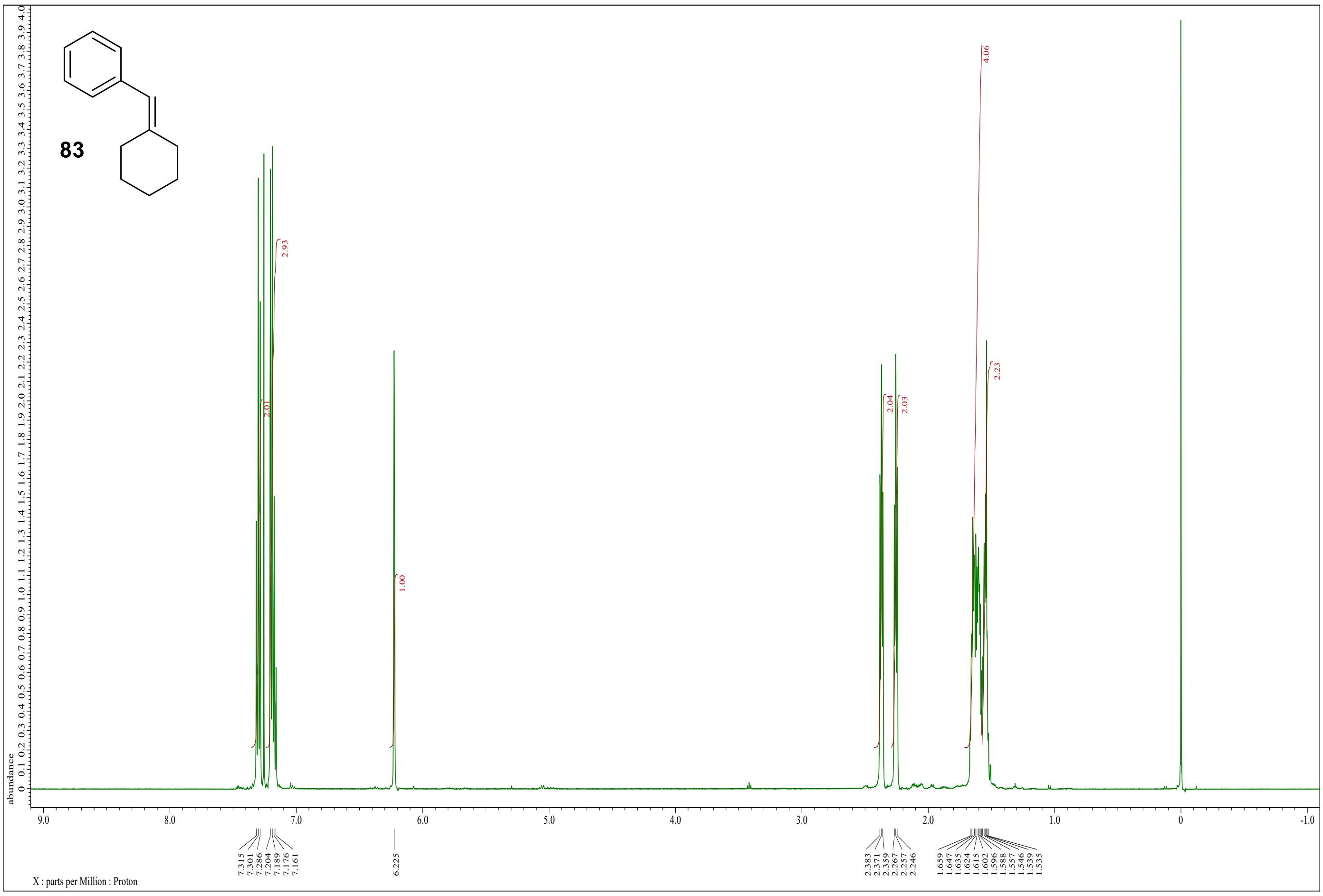

80
abundance
160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
138.498
128.693
126.937
126.852
124.534
118.515
4.456
0.764
X : parts per Million : Carbon13

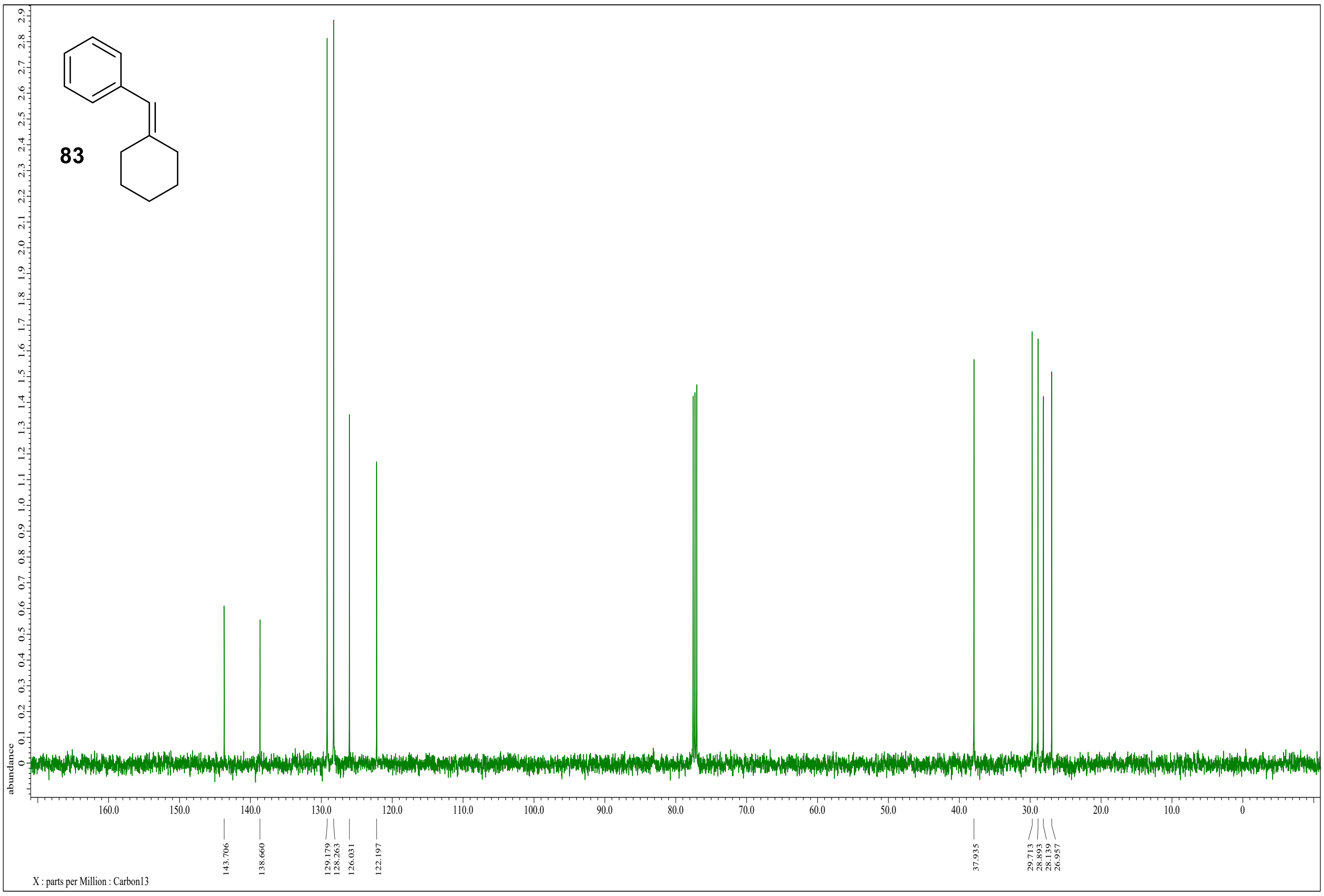

81
abundance
2.06
2.08
1.02
1.00
2.10
2.09
2.06
7.305
7.290
7.275
7.206
7.191
7.156
7.141
7.127
6.079
6.074
6.069
3.065
3.048
3.034
2.896
2.882
2.866
2.143
2.127
2.111
2.095
2.080
X : parts per Million : Proton

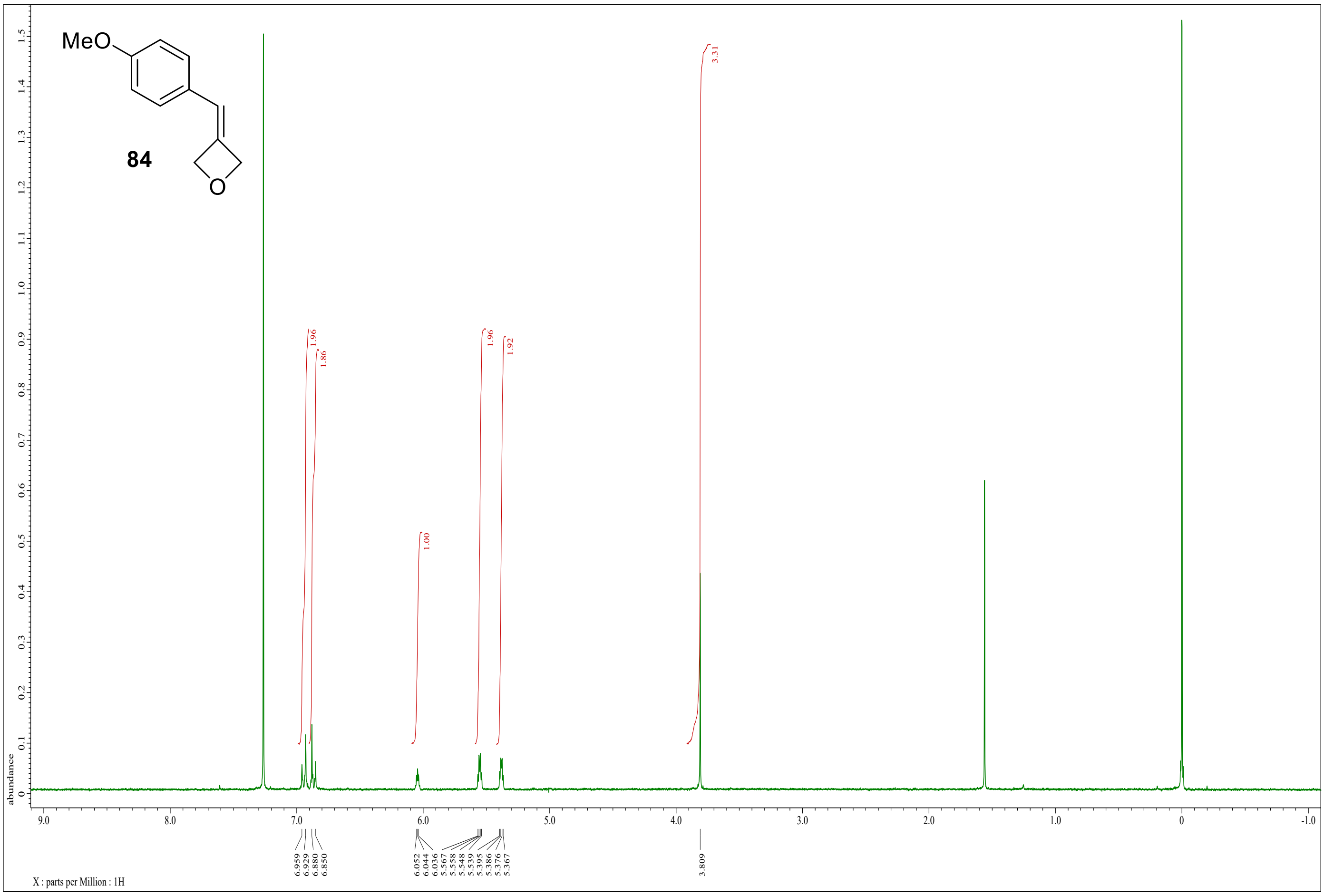

81
abundance
145.041
138.259
128.588
127.319
125.984
121.138
33.042
32.880
18.563
X : parts per Million : Carbon13

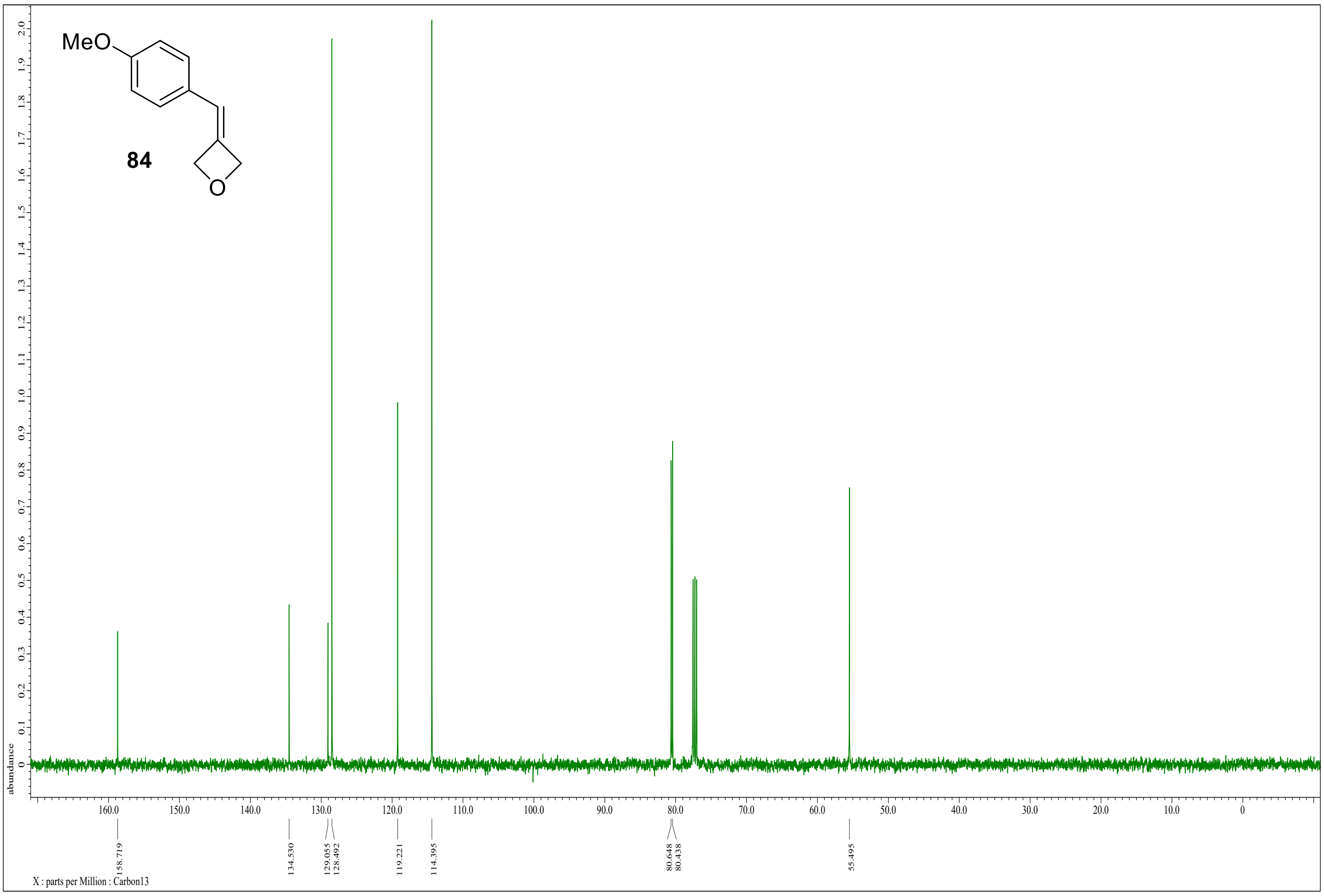

82
3.93
1.01
1.00
2.02
1.97
2.04
2.09
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.309
7.301
7.177
7.169
7.161
7.152
7.145
7.141
7.135
6.360
6.357
6.352
2.563
2.549
2.534
2.502
2.488
2.475
1.807
1.793
1.780
1.766
1.752
1.691
1.678
1.664
1.650
1.636
X : parts per Million : Proton

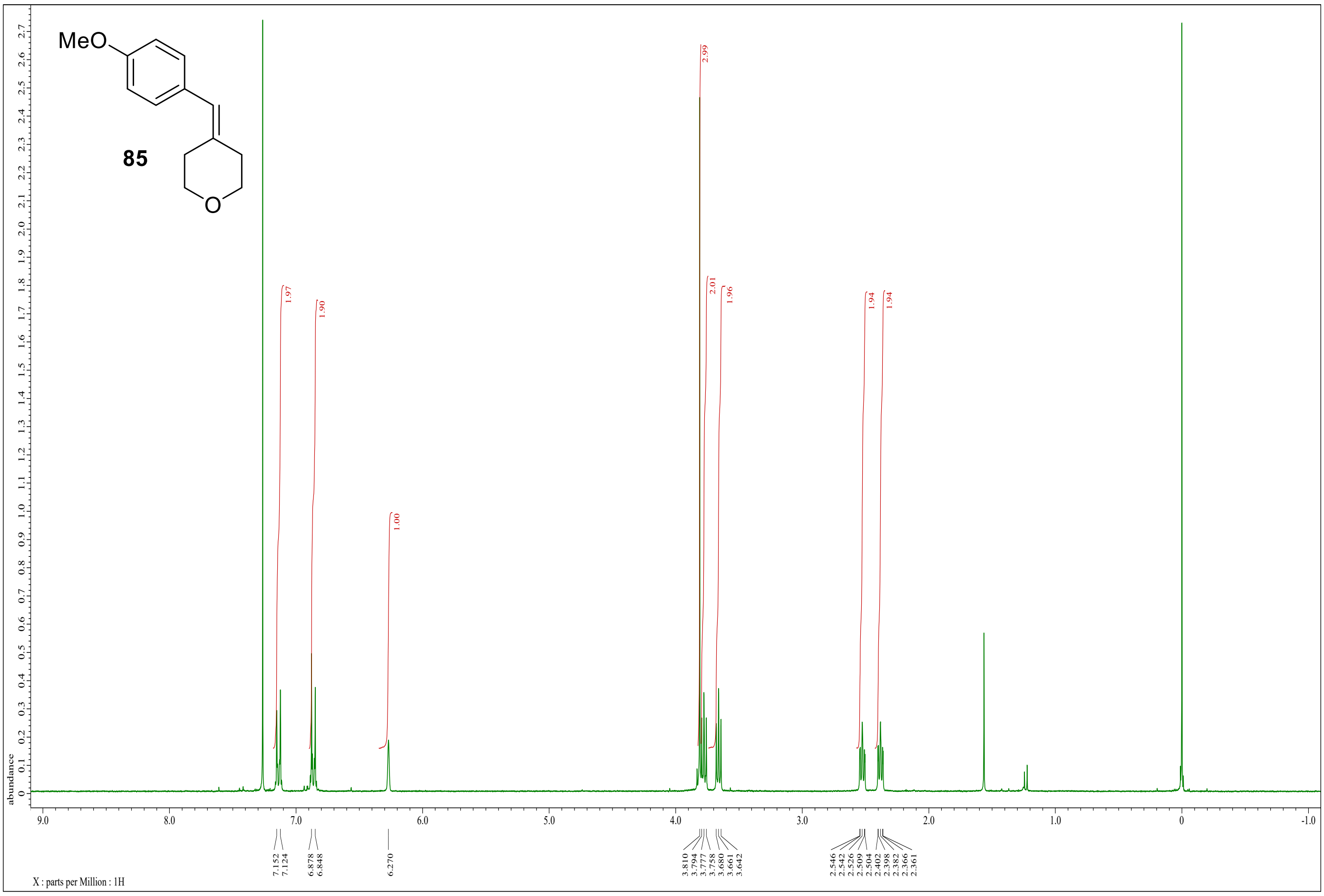

82
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
147.435
139.147
128.435
128.197
125.860
121.062
36.218
31.449
27.491
25.917
X : parts per Million : Carbon13

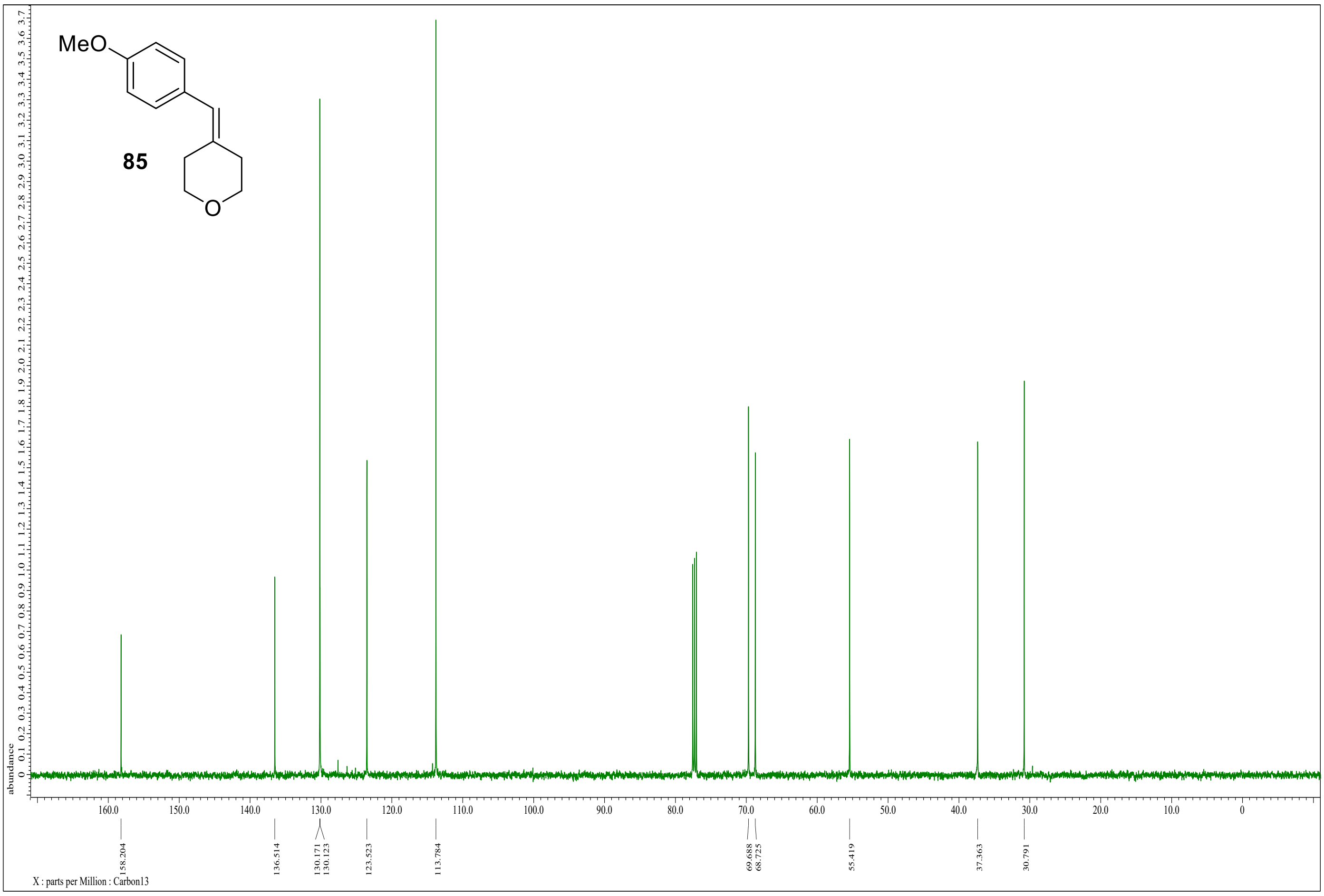

83
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
2.01
2.93
1.00
2.04
2.03
4.06
2.23
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.315
7.301
7.286
7.204
7.189
7.176
7.161
6.225
2.383
2.371
2.359
2.267
2.257
2.246
1.659
1.647
1.635
1.624
1.615
1.602
1.596
1.588
1.557
1.546
1.539
1.535
X : parts per Million : Proton

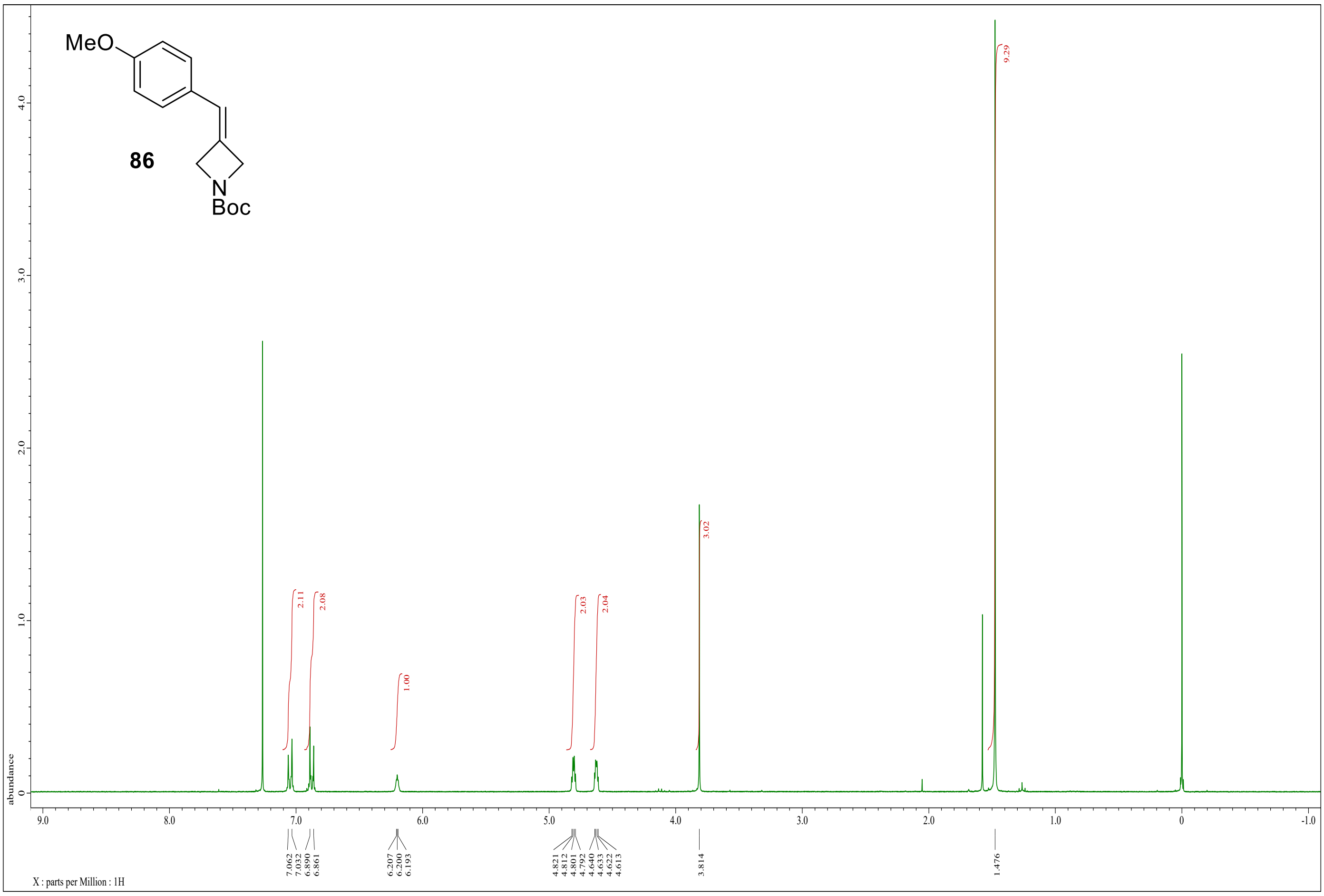

83
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
143.706
138.660
129.179
128.263
126.031
122.197
37.935
29.713
28.893
28.139
26.957
X : parts per Million : Carbon13

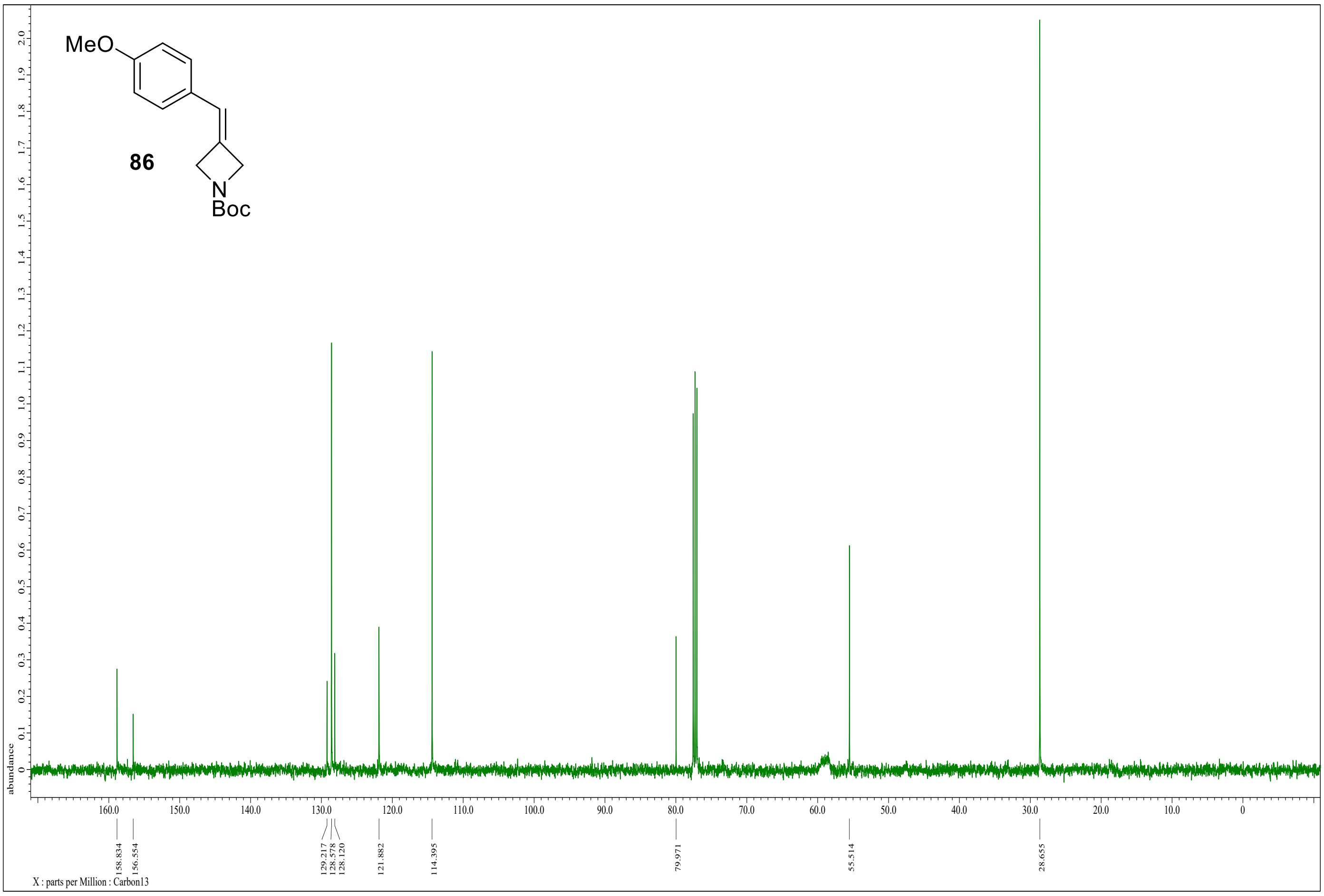

MeO
84
O
1.96
1.86
1.00
1.96
1.92
3.31
abundance
6.959
6.929
6.880
6.850
6.052
6.044
6.036
5.567
5.558
5.548
5.539
5.395
5.386
5.376
5.367
3.809
X : parts per Million : 1H

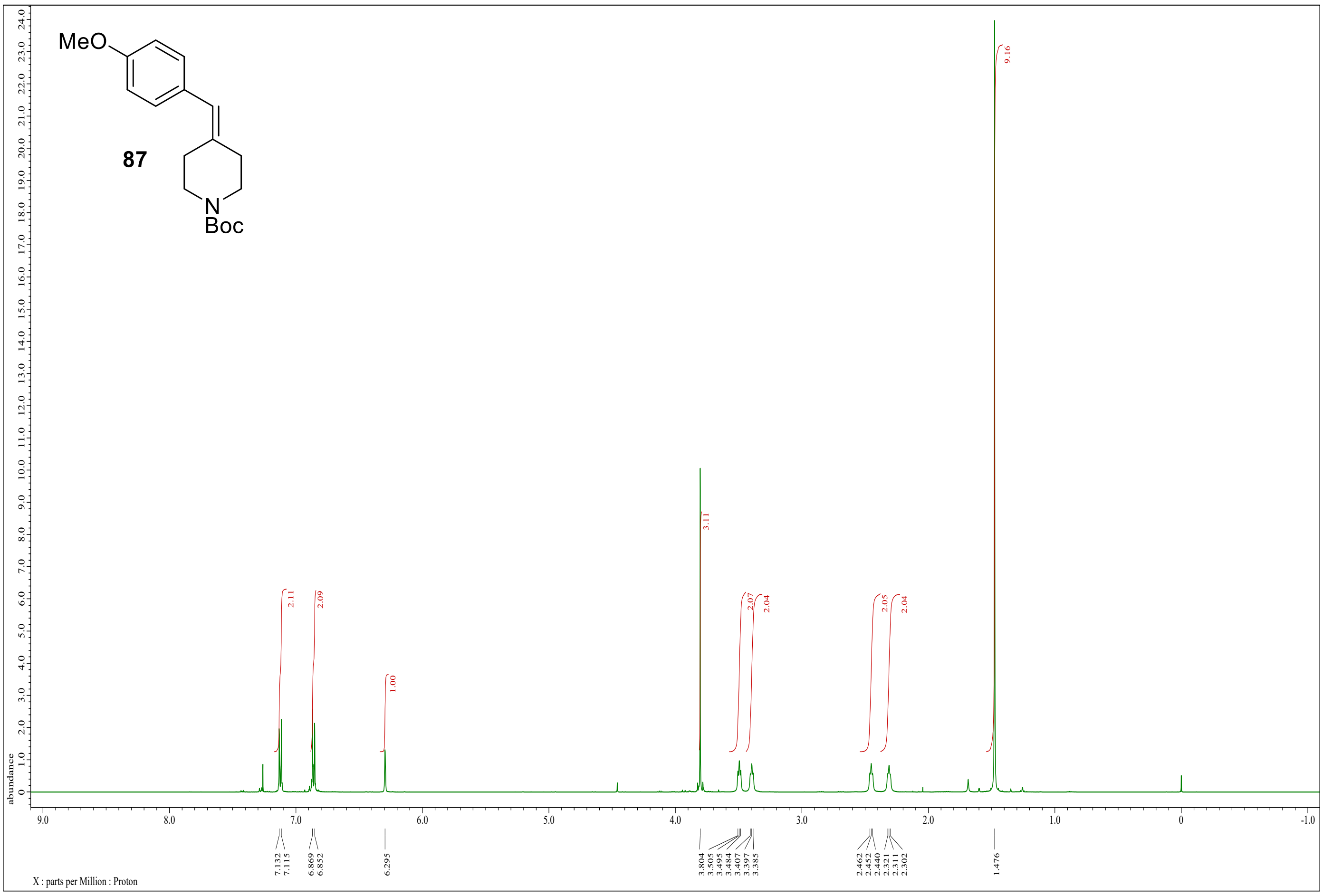

MeO
84
O
abundance
158.719
134.530
129.055
128.492
119.221
114.395
80.648
80.438
55.495
X : parts per Million : Carbon13

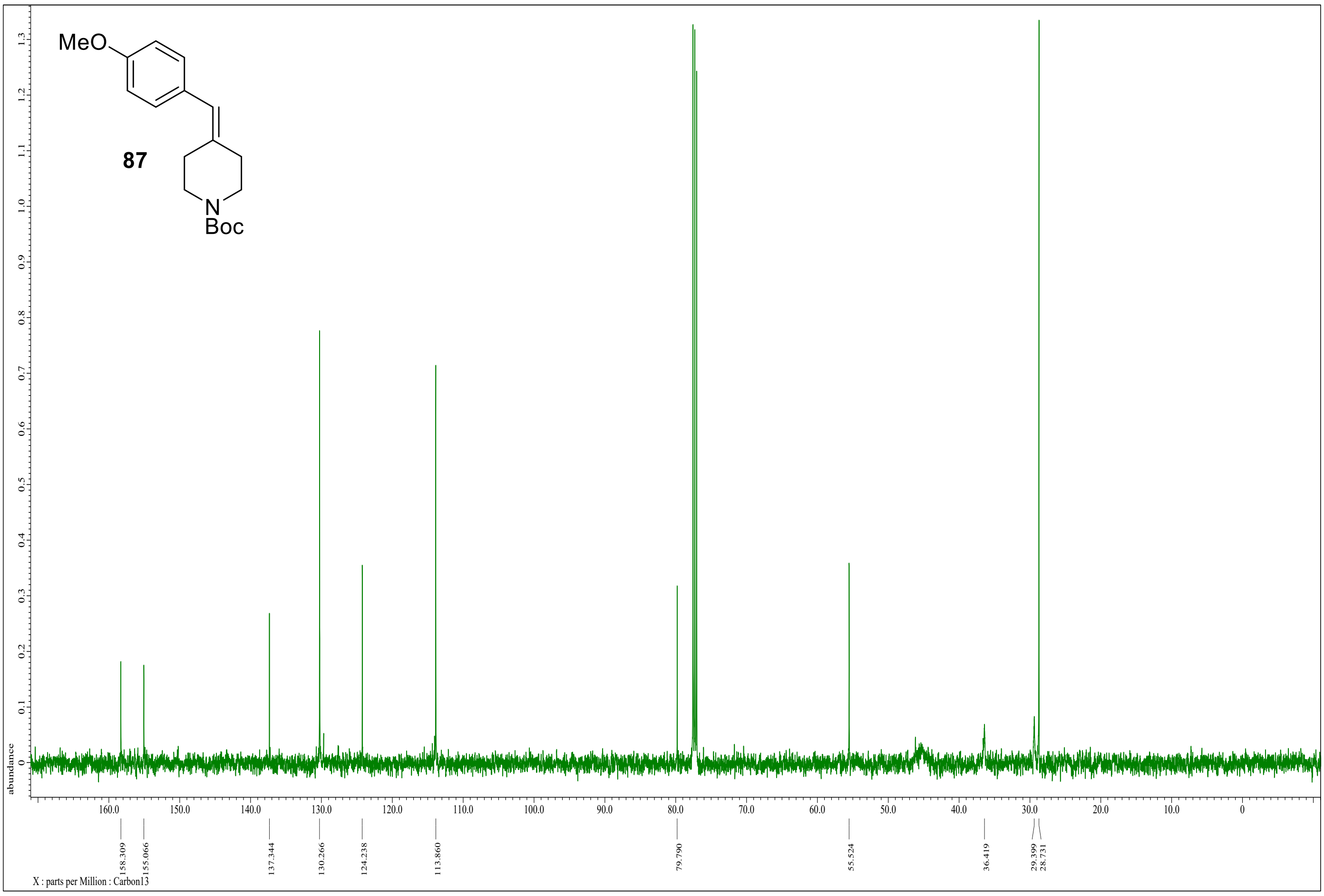

MeO
85
O
abundance
2.99
1.97
1.90
1.00
2.01
1.96
1.94
1.94
7.152
7.124
6.878
6.848
6.270
3.810
3.794
3.777
3.758
3.680
3.661
3.642
2.546
2.542
2.526
2.509
2.504
2.402
2.398
2.382
2.366
2.361
X : parts per Million : 1H

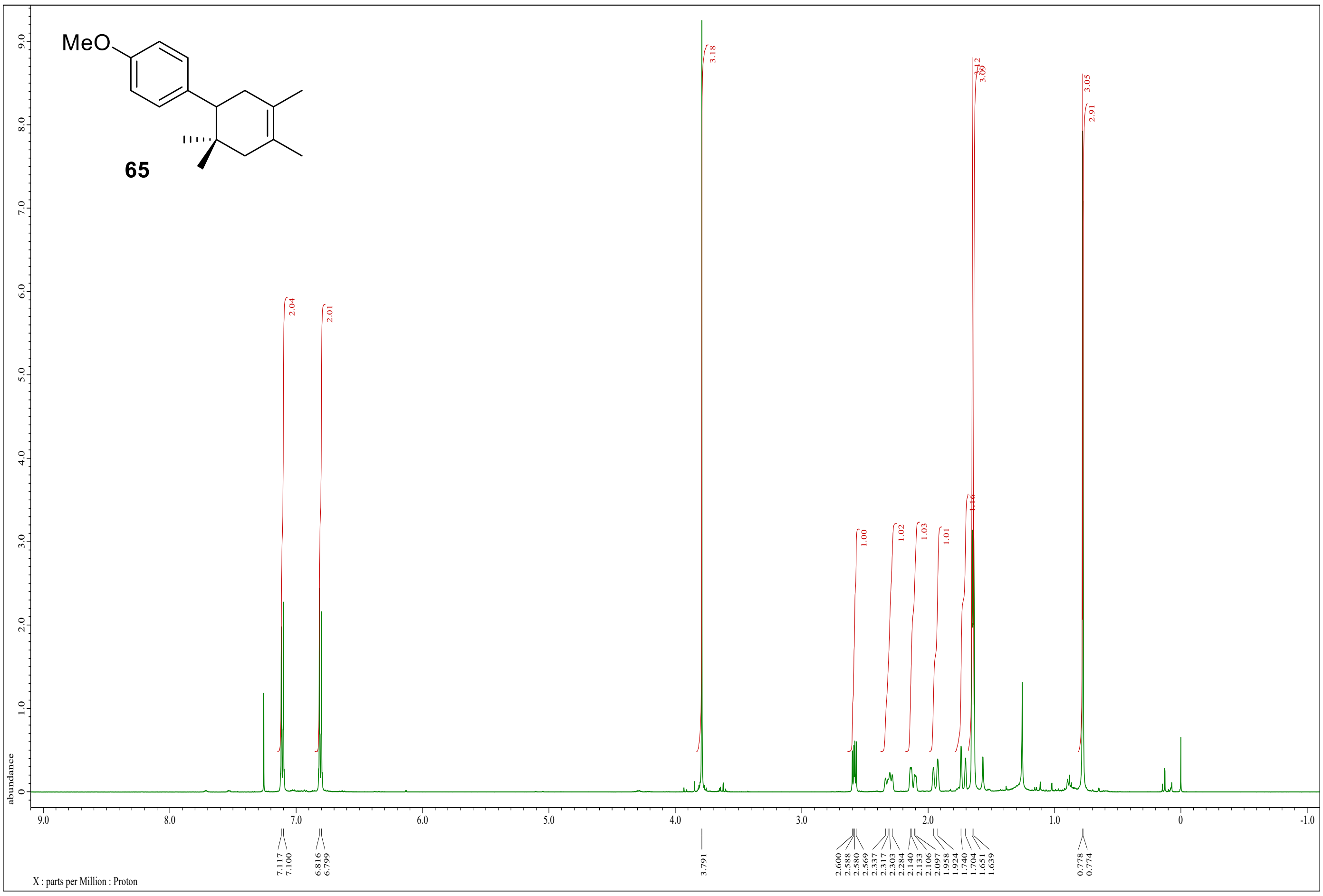

MeO
85
O
abundance
158.204
136.514
130.171
130.123
123.523
113.784
69.688
68.725
55.419
37.363
30.791
X : parts per Million : Carbon13

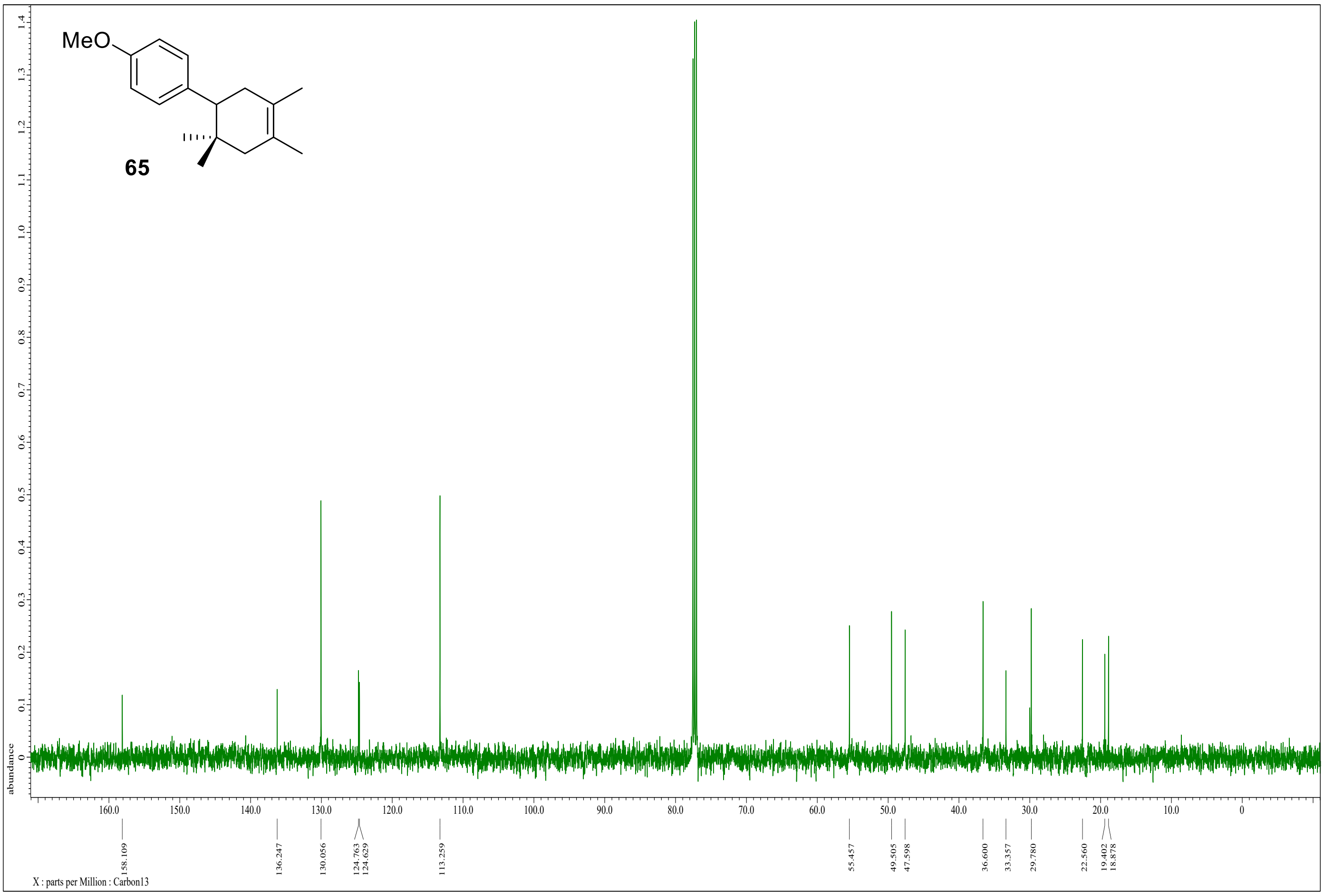

MeO
86
N
Boc
abundance
X : parts per Million : 1H
2.11
2.08
1.00
2.03
2.04
3.02
9.29
7.062
7.032
6.890
6.861
6.207
6.200
6.193
4.821
4.812
4.801
4.792
4.640
4.633
4.622
4.613
3.814
1.476

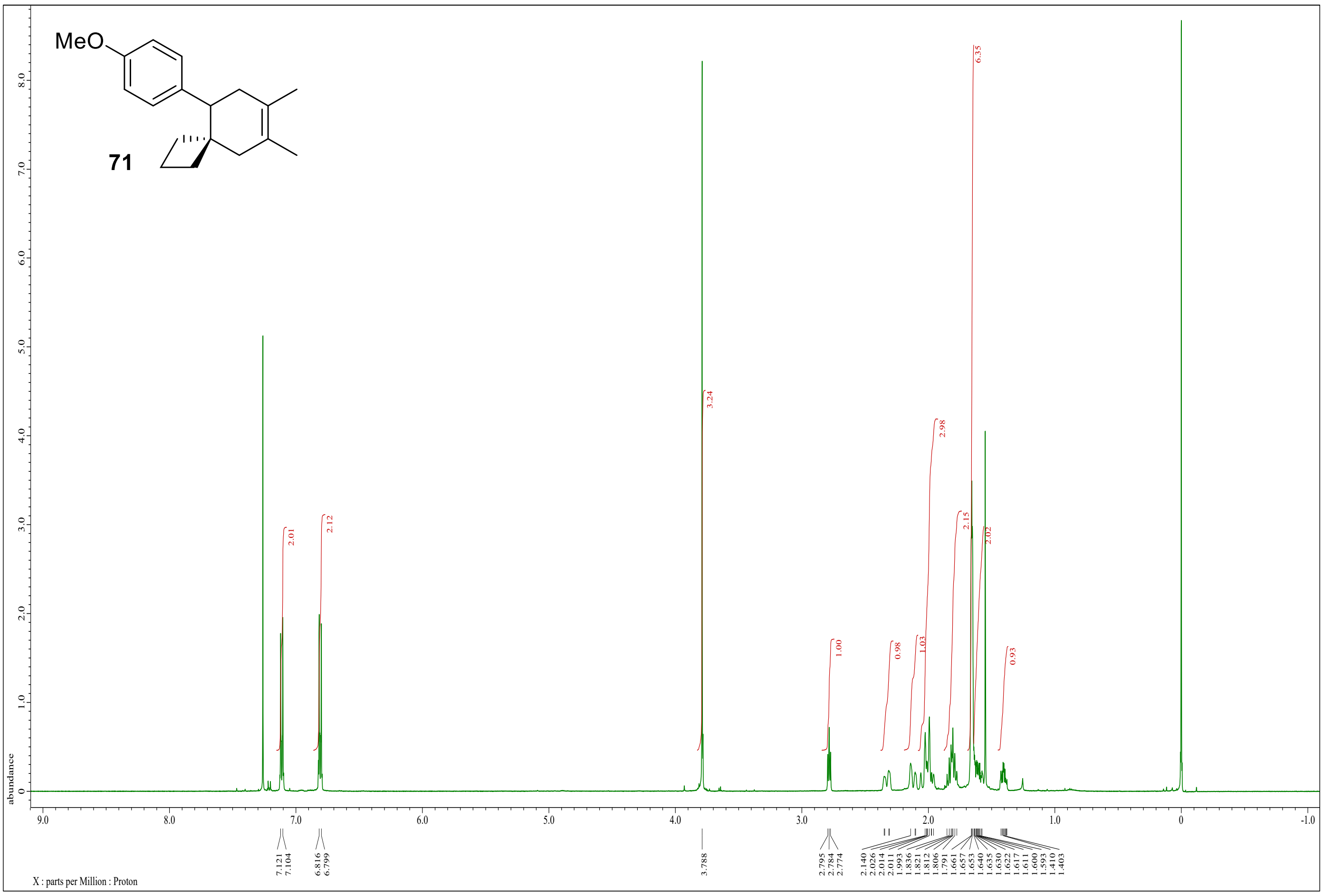

MeO
86
N
Boc
abundance
X : parts per Million : Carbon13
158.834
156.554
129.217
128.578
128.120
121.882
114.395
79.971
55.514
28.655

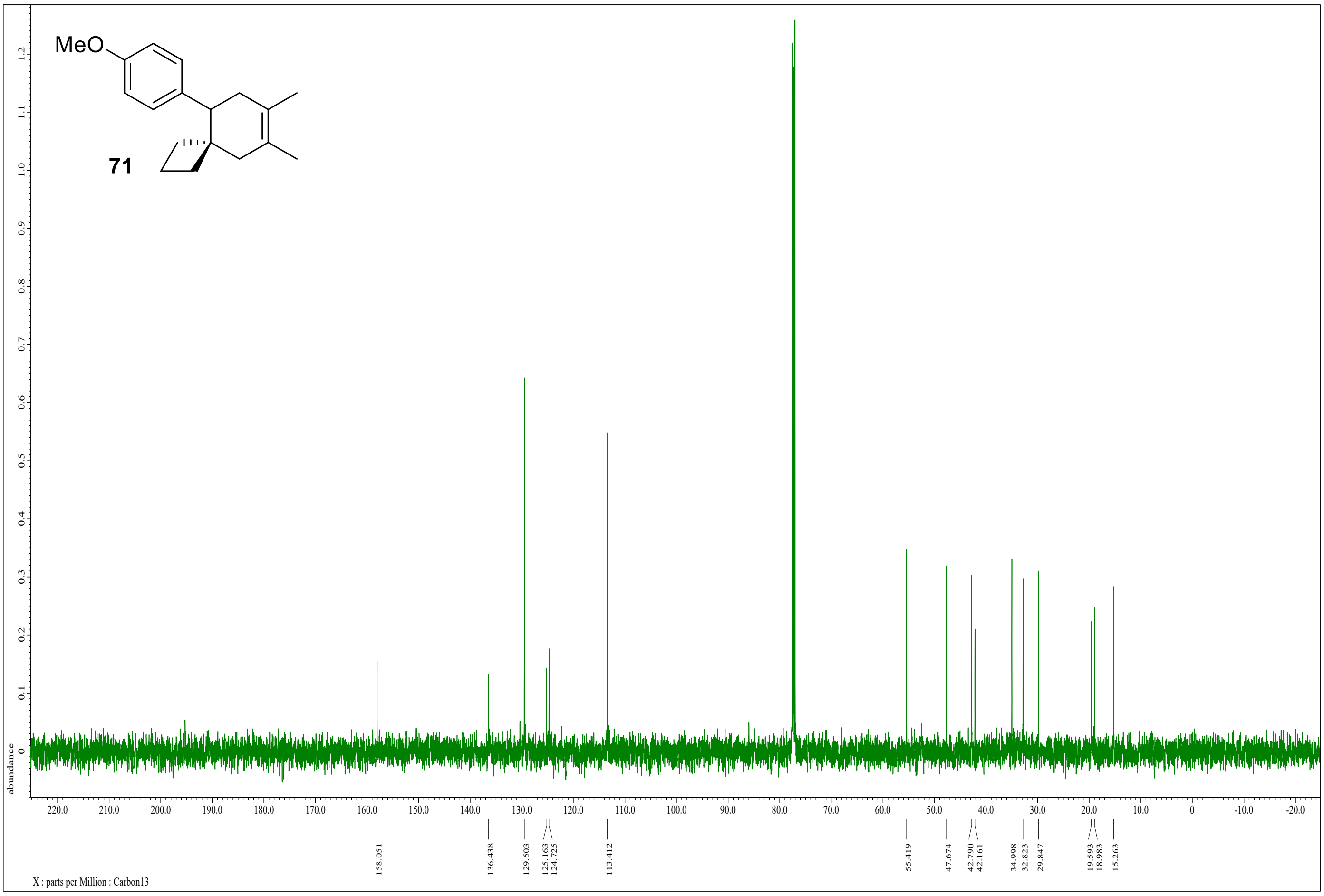

MeO
87
N
Boc
abundance
2.11
2.09
1.00
3.11
2.07
2.04
2.05
2.04
9.16
7.132
7.115
6.869
6.852
6.295
3.804
3.505
3.495
3.484
3.407
3.397
3.385
2.462
2.452
2.440
2.321
2.311
2.302
1.476
X : parts per Million : Proton

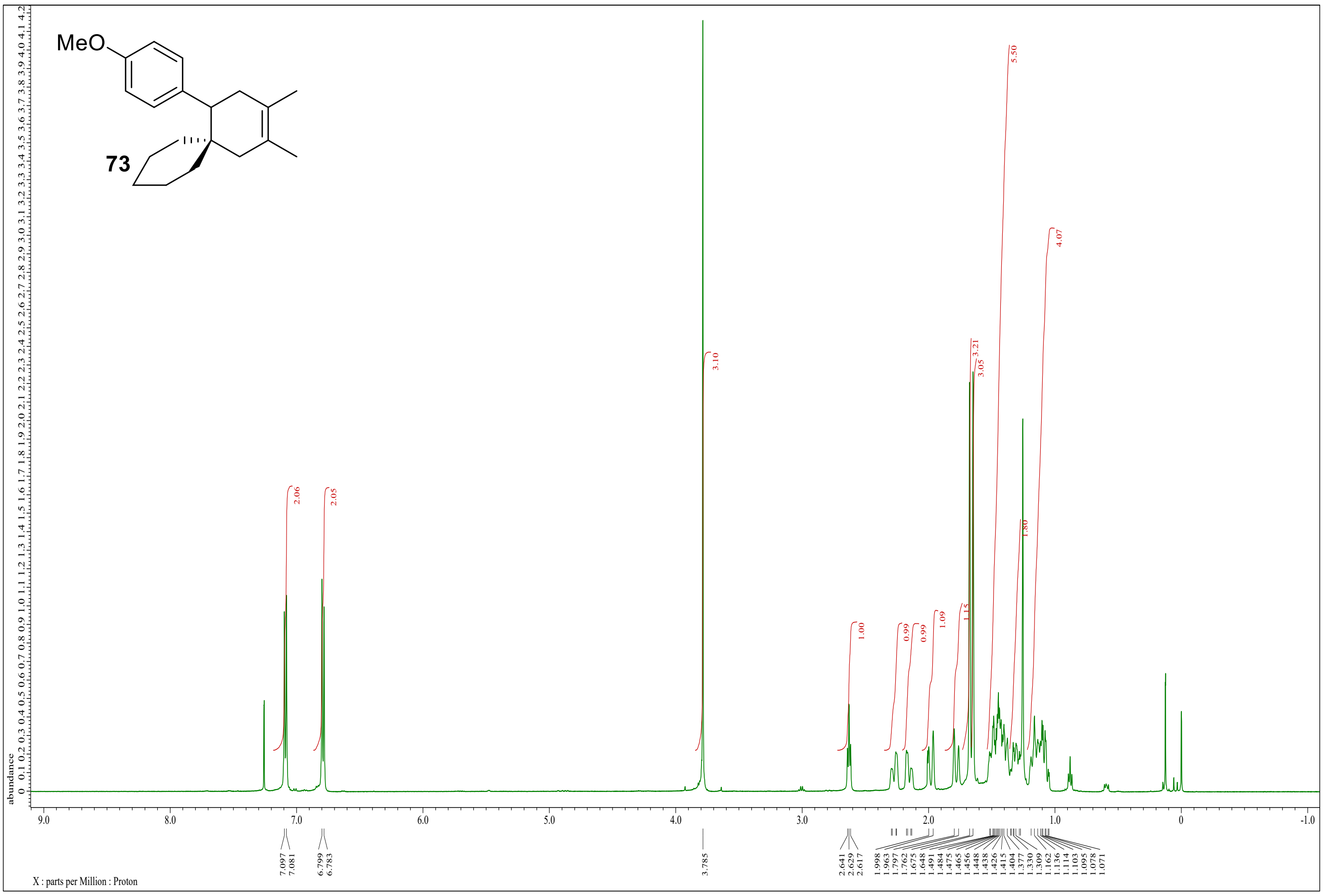

MeO
87
N
Boc
abundance
158.309
155.066
137.344
130.266
124.238
113.860
79.790
55.524
36.419
29.399
28.731
X : parts per Million : Carbon13

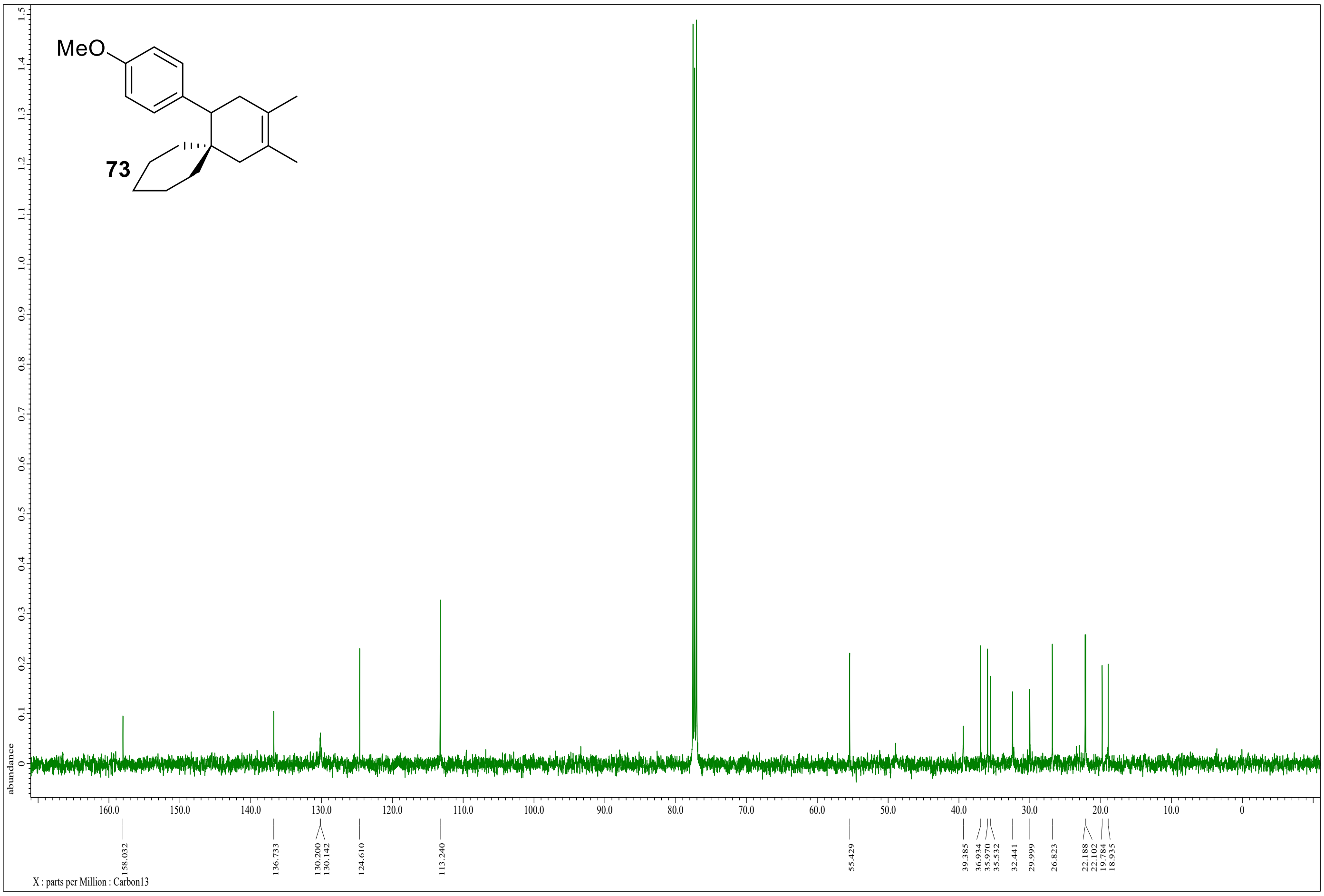

MeO
65
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
2.04
2.01
3.18
1.00
1.02
1.03
1.01
1.16
3.12
3.09
3.05
2.91
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.117
7.100
6.816
6.799
3.791
2.600
2.588
2.580
2.569
2.337
2.317
2.303
2.284
2.140
2.133
2.106
2.097
1.958
1.924
1.740
1.704
1.651
1.639
0.778
0.774
X : parts per Million : Proton

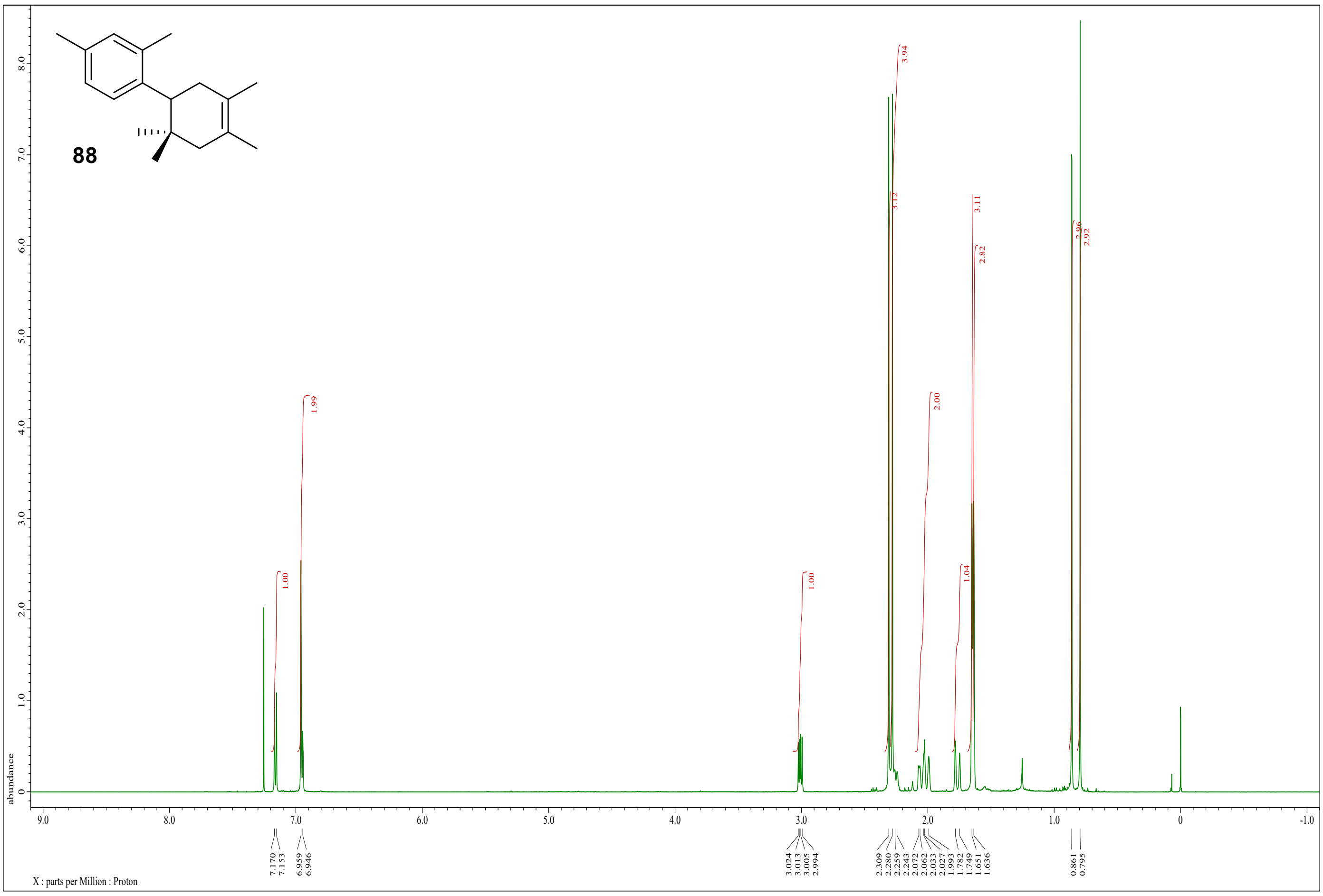

MeO
65
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.109
136.247
130.056
124.763
124.629
113.259
55.457
49.505
47.598
36.600
33.357
29.780
22.560
19.402
18.878
X : parts per Million : Carbon13

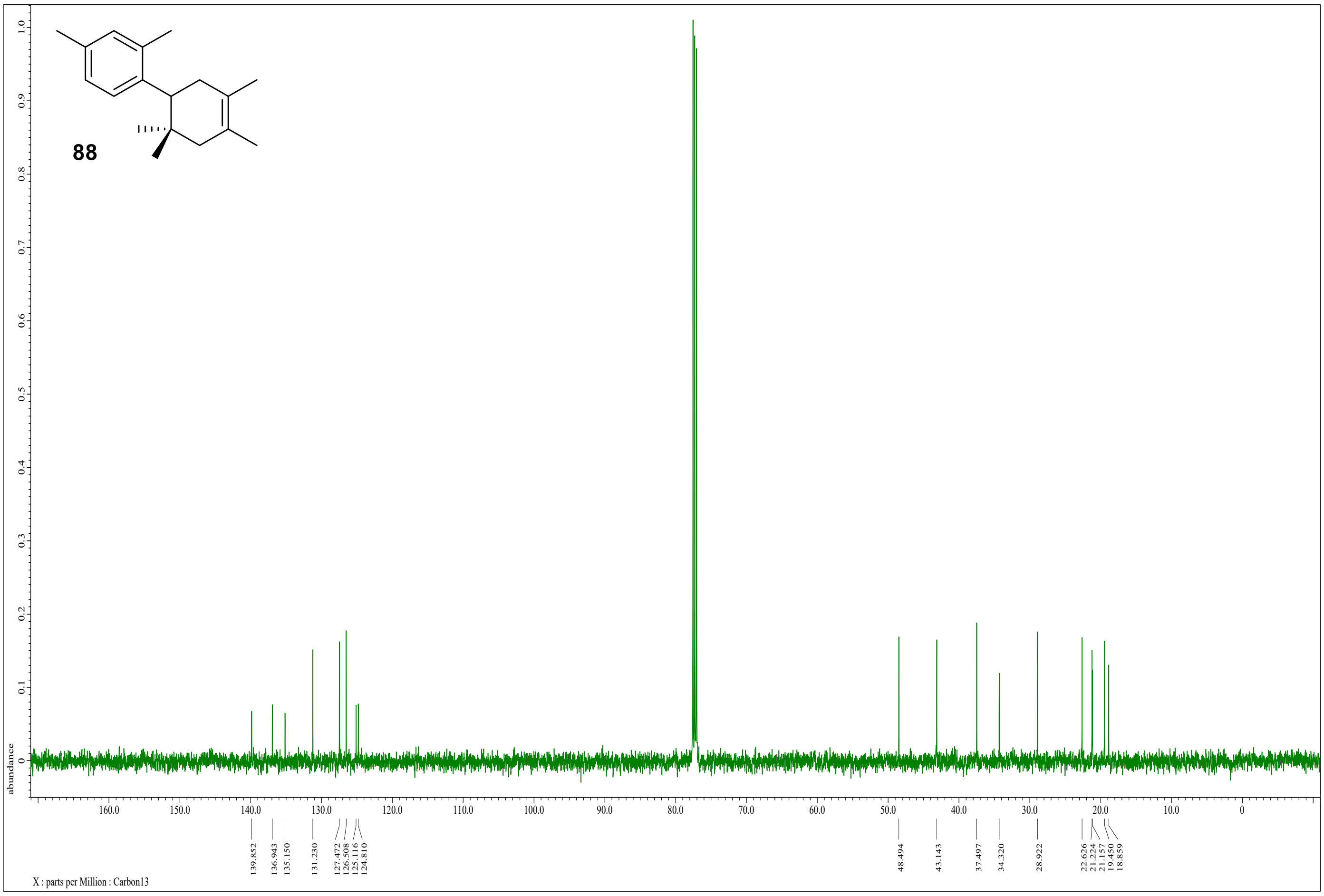

MeO
71
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
2.01
2.12
3.24
1.00
0.98
1.03
2.98
2.15
6.35
2.02
0.93
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.121
7.104
6.816
6.799
3.788
2.795
2.784
2.774
2.140
2.026
2.014
2.011
1.993
1.836
1.821
1.812
1.806
1.791
1.661
1.657
1.653
1.640
1.635
1.630
1.622
1.617
1.611
1.600
1.593
1.410
1.403
X : parts per Million : Proton

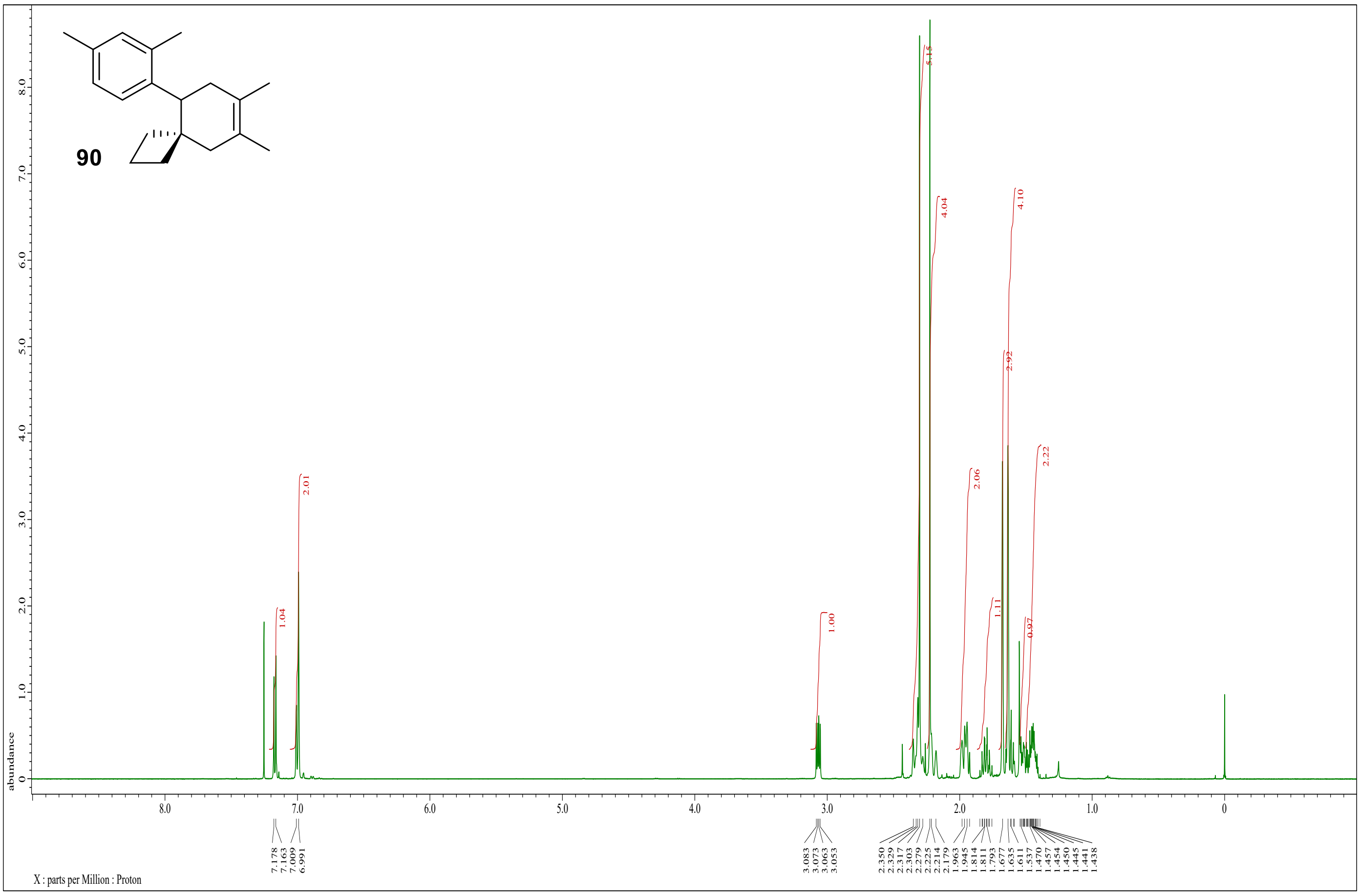

MeO
71
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
158.051
136.438
129.503
125.163
124.725
113.412
55.419
47.674
42.790
42.161
34.998
32.823
29.847
19.593
18.983
15.263
X : parts per Million : Carbon13

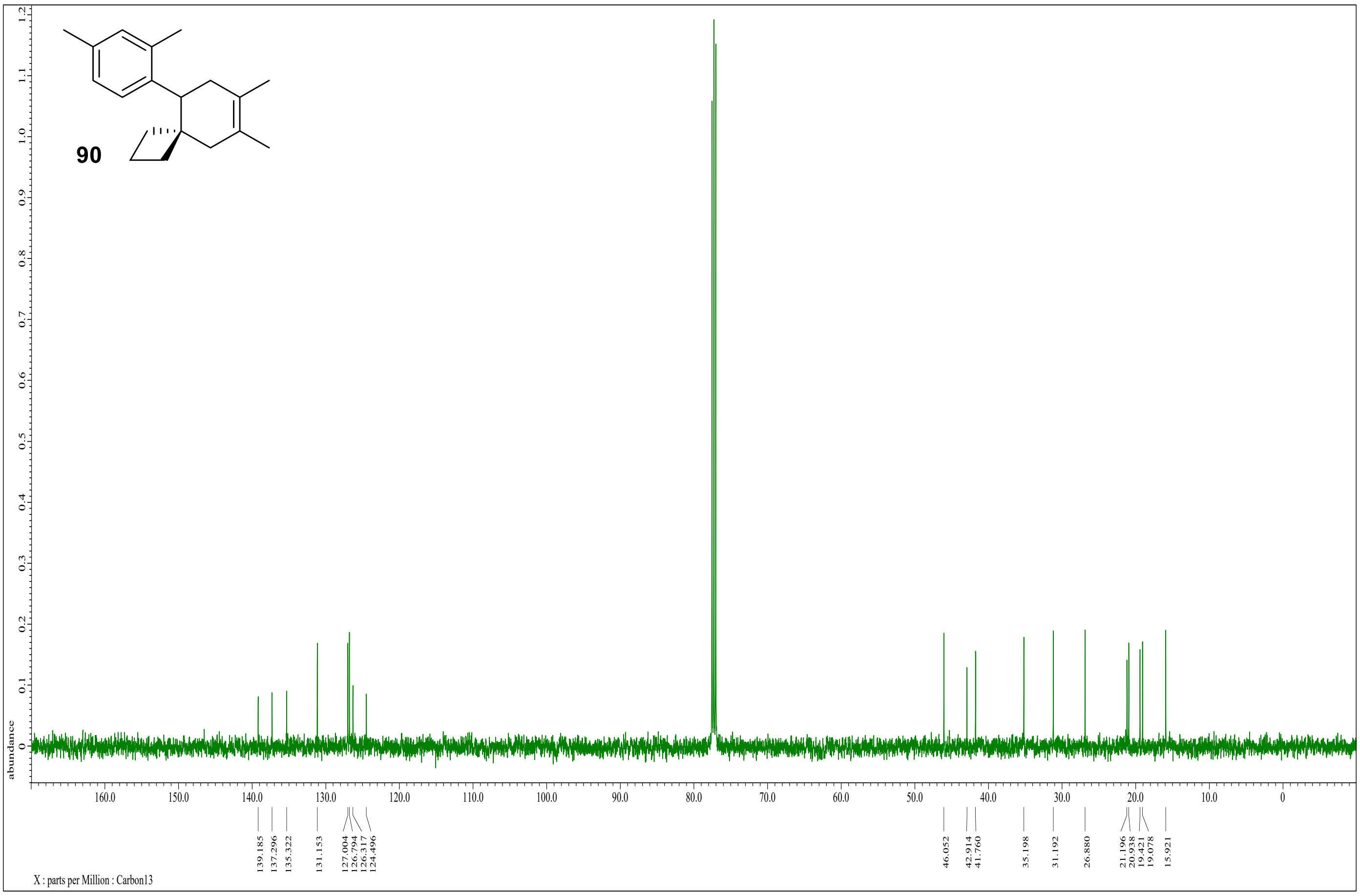

MeO
73
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 4.0 4.1 4.2
2.06
2.05
3.10
1.00
0.99
0.99
1.09
1.15
3.21
3.05
5.50
1.80
4.07
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
7.097
7.081
6.799
6.783
3.785
2.641
2.629
2.617
1.998
1.963
1.797
1.762
1.675
1.648
1.491
1.484
1.475
1.465
1.456
1.448
1.438
1.426
1.415
1.404
1.377
1.330
1.309
1.162
1.136
1.114
1.103
1.095
1.078
1.071
X : parts per Million : Proton

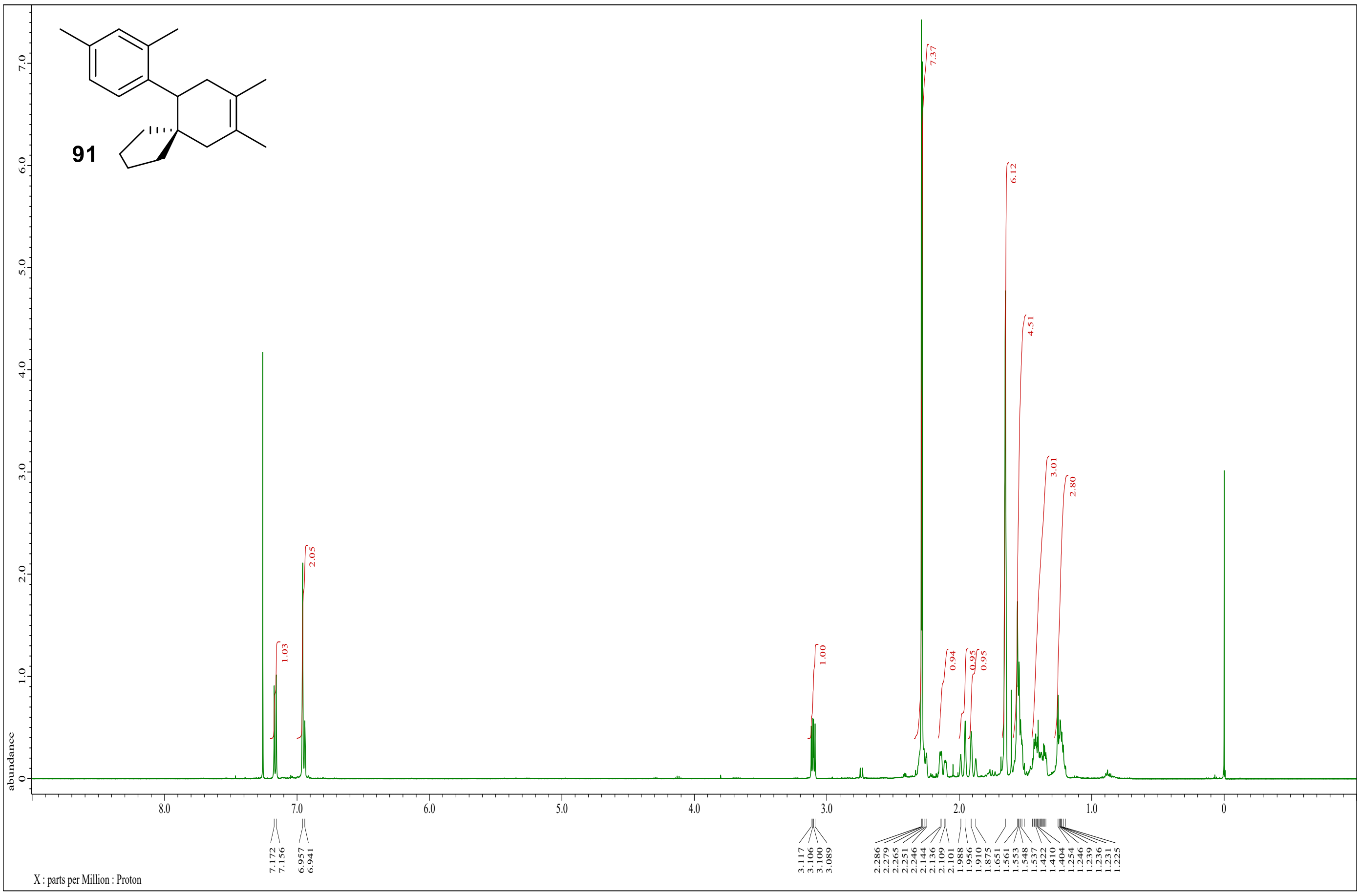

MeO
73
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
158.032
136.733
130.200
130.142
124.610
113.240
55.429
39.385
36.934
35.970
35.532
32.441
29.999
26.823
22.188
22.102
19.784
18.935
X : parts per Million : Carbon13

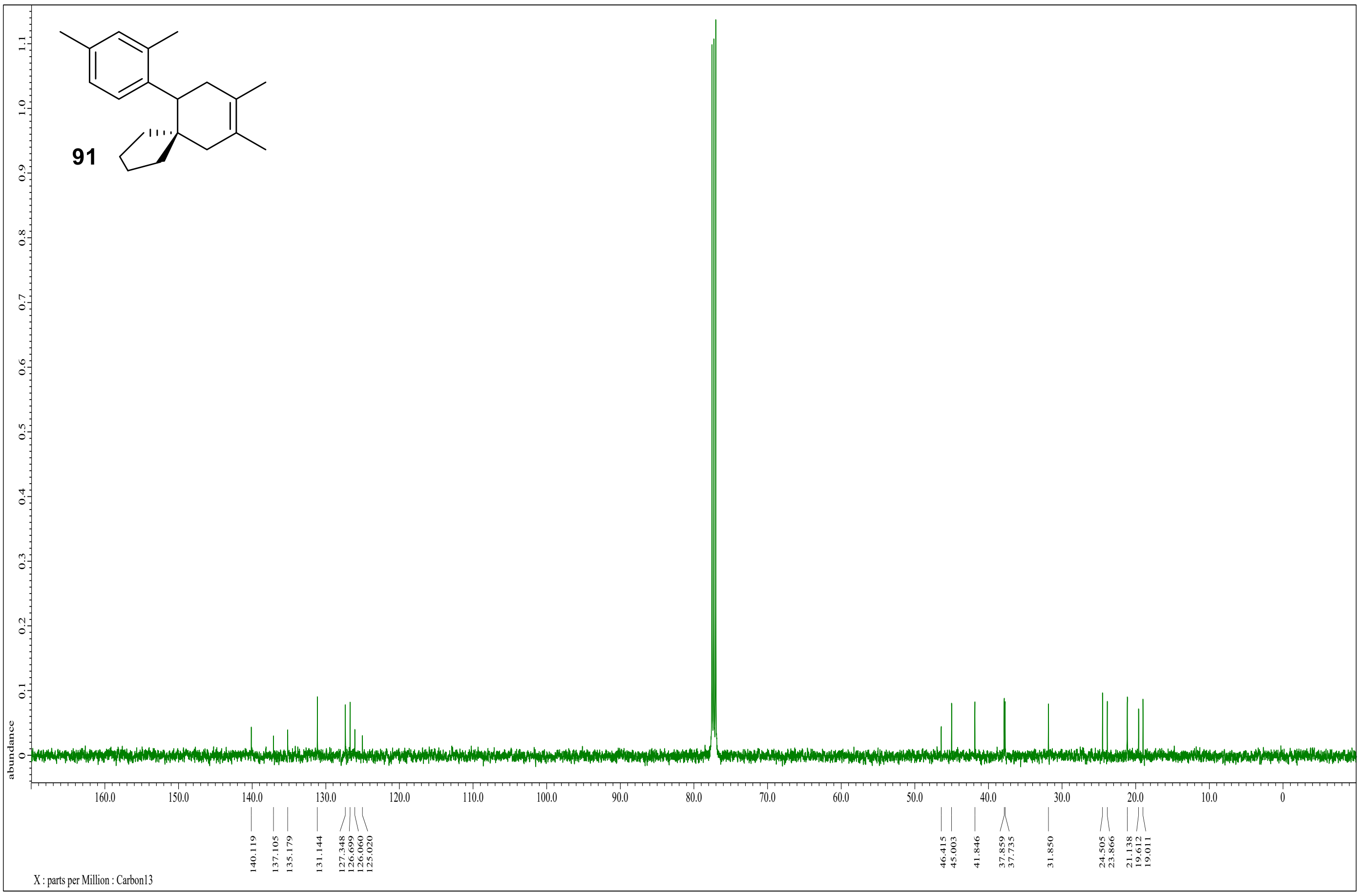

88
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.00
1.99
1.00
3.94
3.12
2.00
1.04
3.11
2.82
2.96
2.92
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.170
7.153
6.959
6.946
3.024
3.013
3.005
2.994
2.309
2.280
2.259
2.243
2.072
2.062
2.033
2.027
1.993
1.782
1.749
1.651
1.636
0.861
0.795
X : parts per Million : Proton

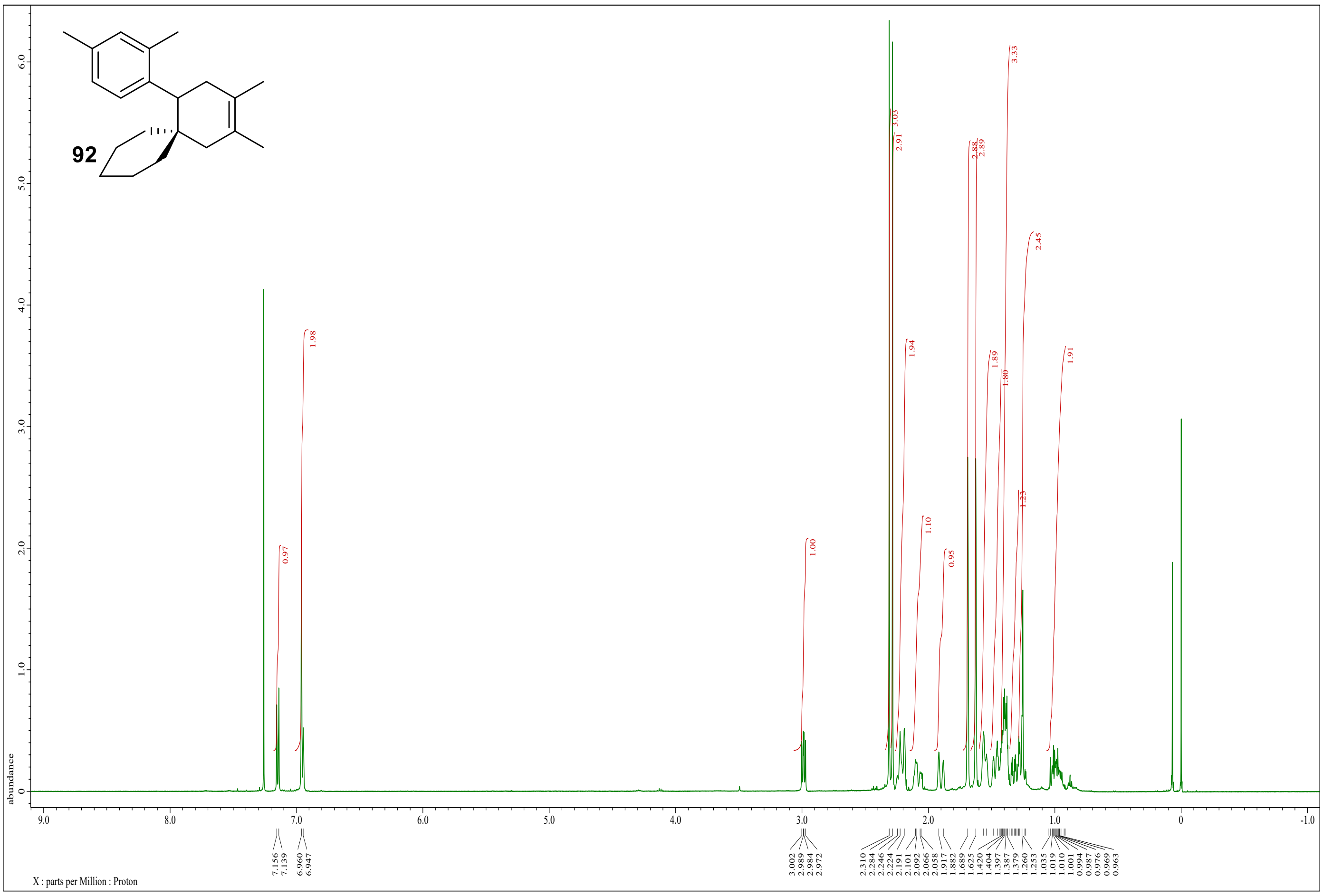

88
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
139.852
136.943
135.150
131.230
127.472
126.508
125.116
124.810
48.494
43.143
37.497
34.320
28.922
22.626
21.224
21.157
19.450
18.859
X : parts per Million : Carbon13

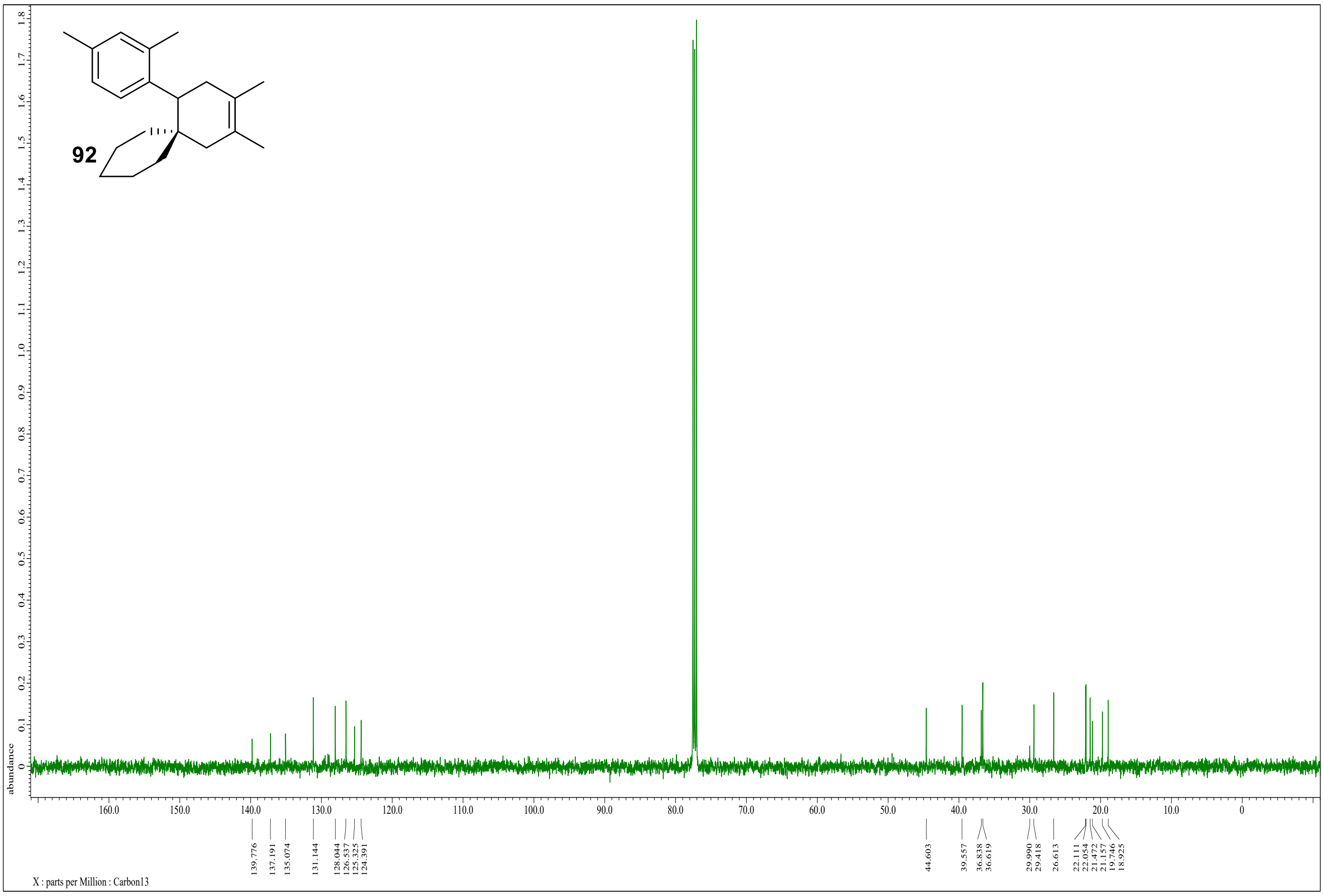

90
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
1.04
2.01
1.00
5.15
4.04
2.06
1.11
2.92
0.97
4.10
2.22
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.178
7.163
7.009
6.991
3.083
3.073
3.063
3.053
2.350
2.329
2.317
2.303
2.279
2.225
2.214
2.179
1.963
1.945
1.814
1.811
1.793
1.677
1.635
1.611
1.537
1.470
1.457
1.454
1.450
1.445
1.441
1.438
X : parts per Million : Proton

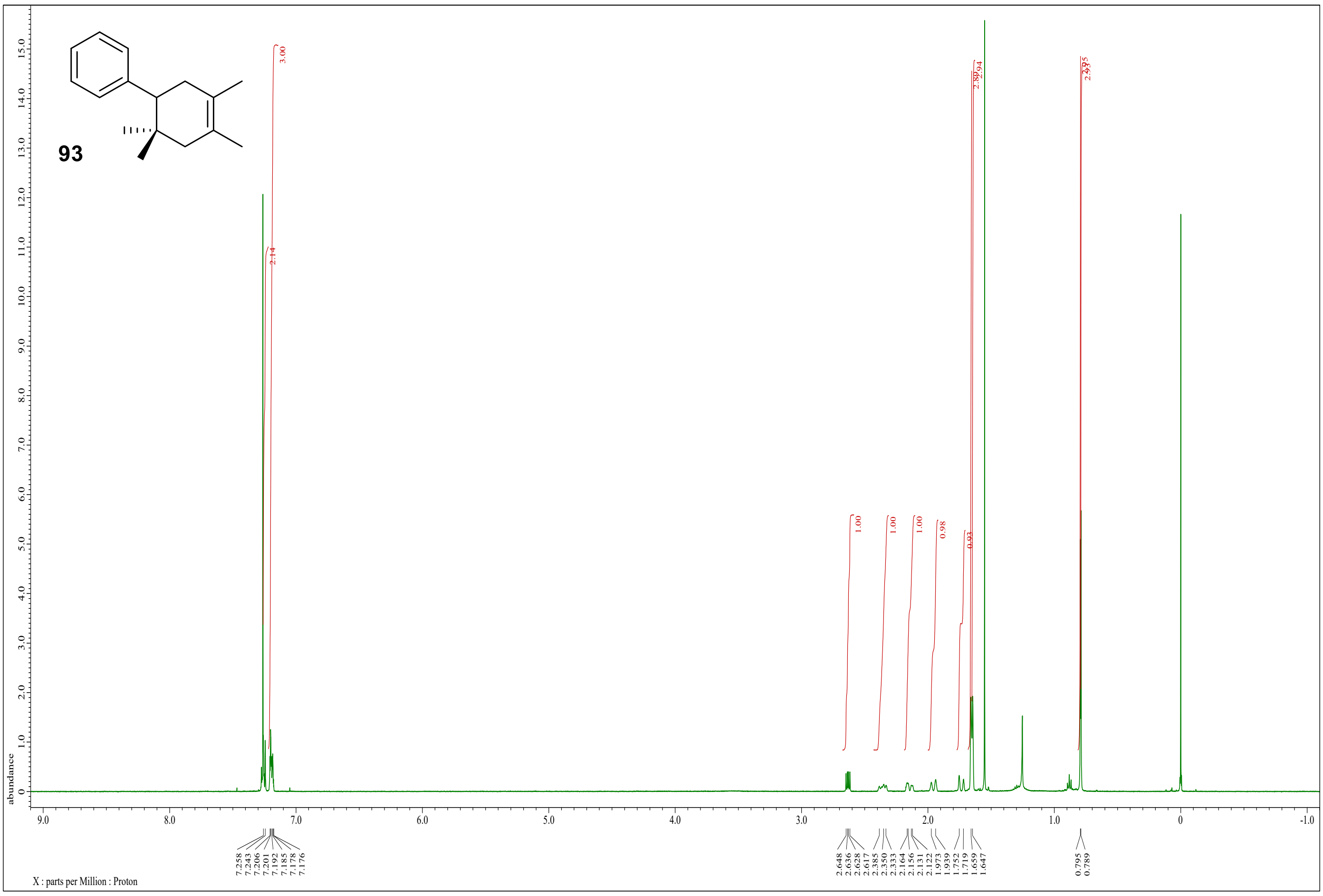

90
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
139.185
137.296
135.322
131.153
127.004
126.794
126.317
124.496
46.052
42.914
41.760
35.198
31.192
26.880
21.196
20.938
19.421
19.078
15.921
X : parts per Million : Carbon13

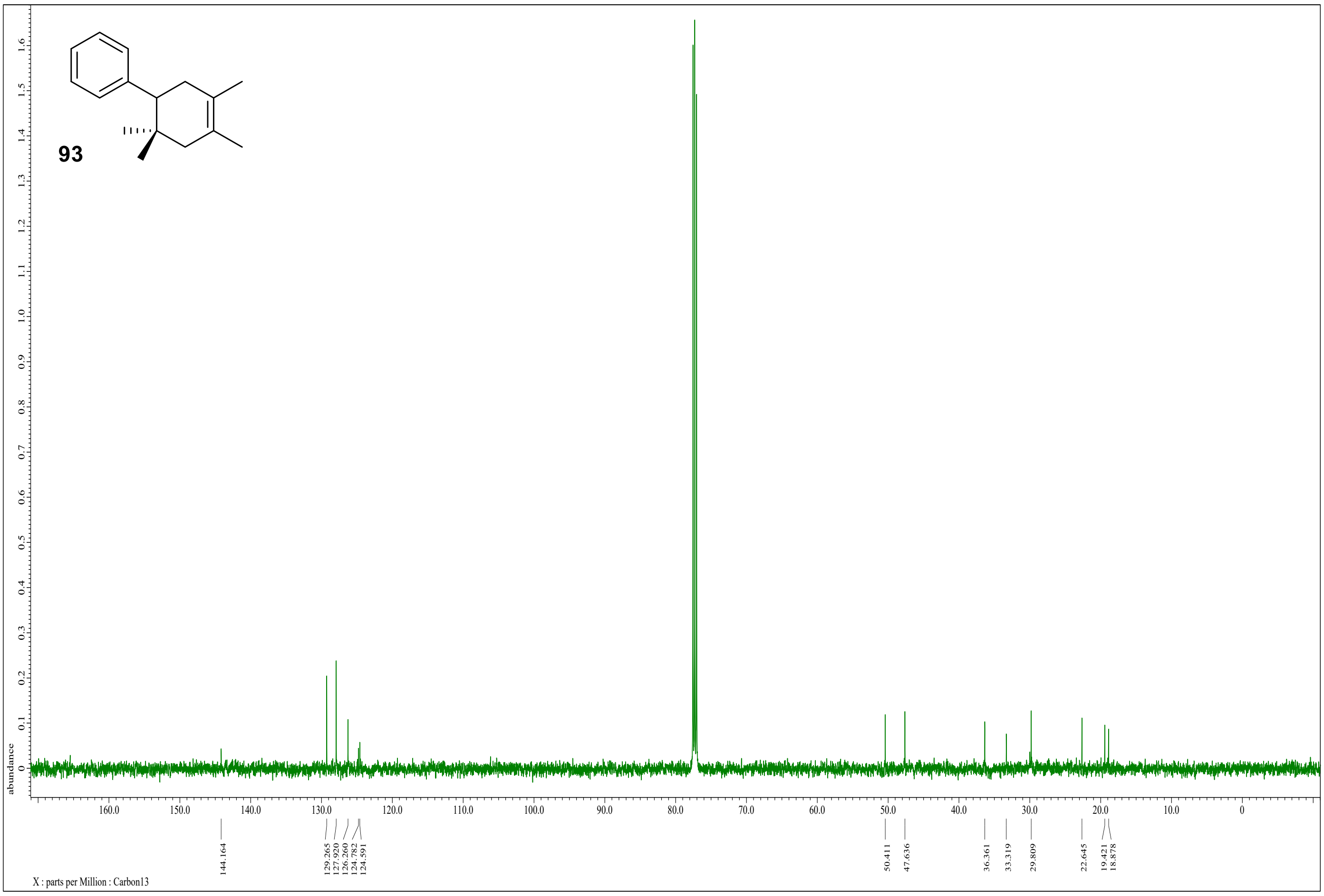

91
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
1.03
2.05
1.00
7.37
0.94
0.95
0.95
6.12
4.51
3.01
2.80
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.172
7.156
6.957
6.941
3.117
3.106
3.100
3.089
2.286
2.279
2.265
2.251
2.246
2.144
2.136
2.109
2.101
1.988
1.956
1.910
1.875
1.651
1.561
1.553
1.548
1.537
1.422
1.410
1.404
1.254
1.246
1.239
1.236
1.231
1.225
X : parts per Million : Proton

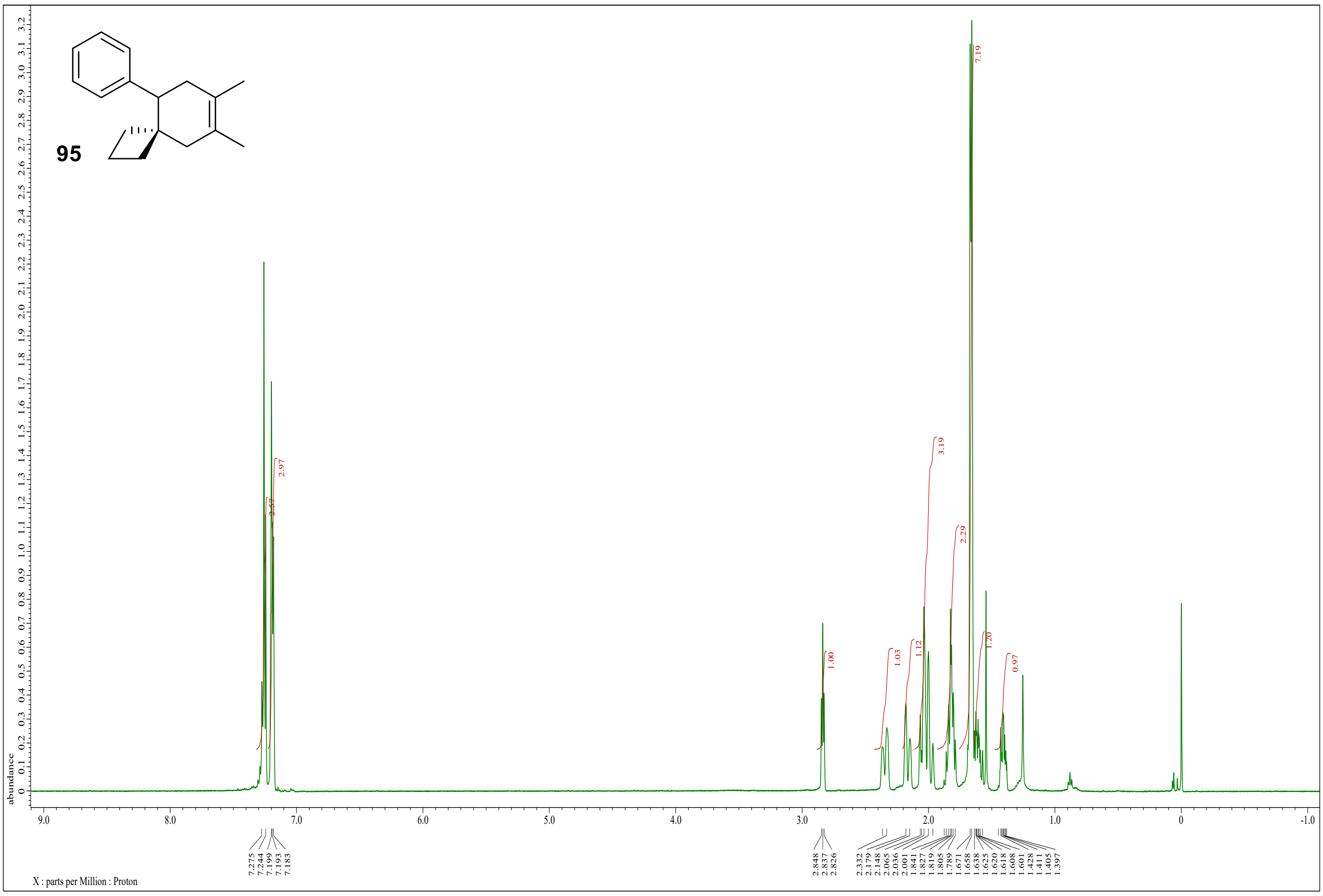

91
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
140.119
137.105
135.179
131.144
127.348
126.699
126.060
125.020
46.415
45.003
41.846
37.859
37.735
31.850
24.505
23.866
21.138
19.612
19.011
X : parts per Million : Carbon13

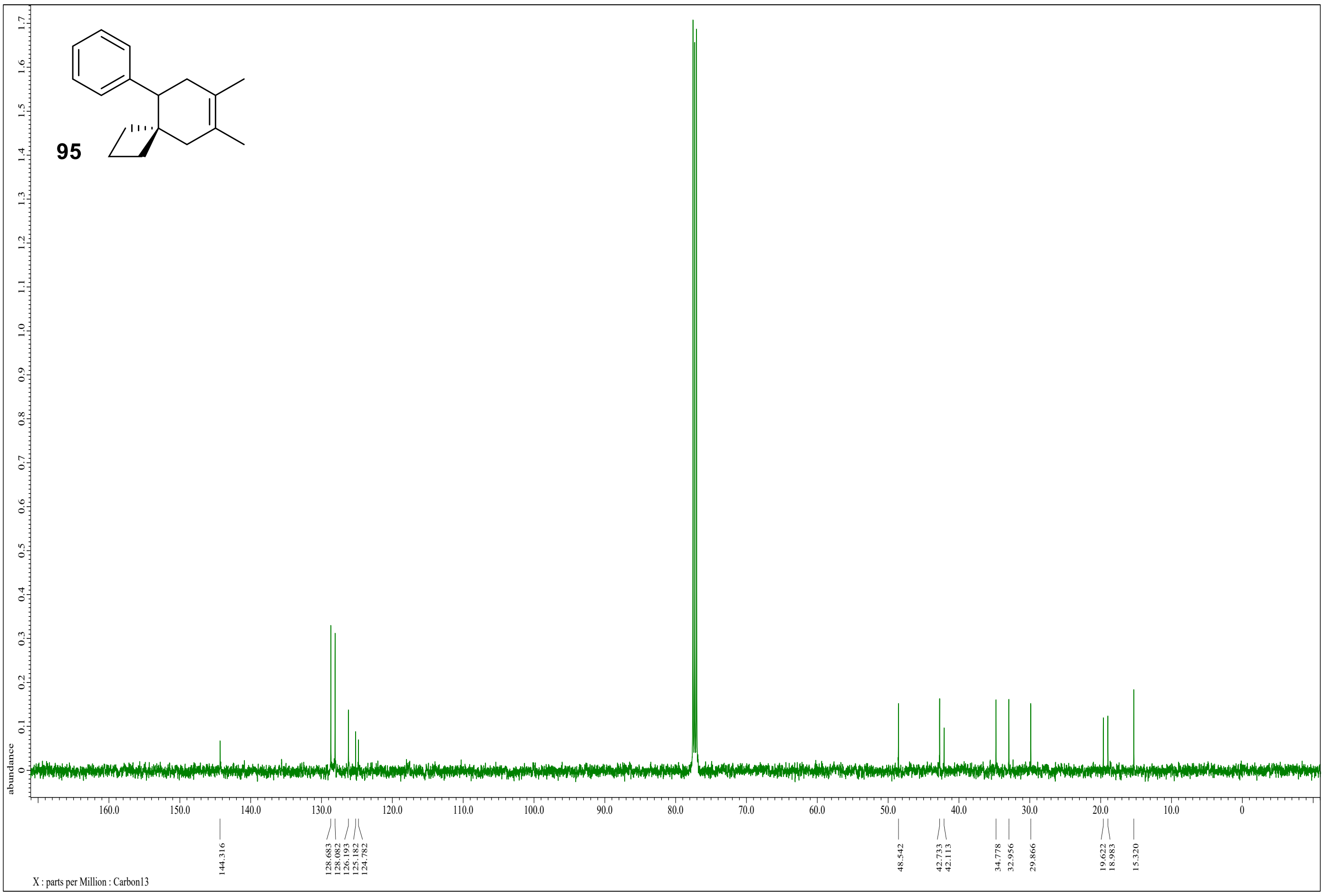

92
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
0.97
1.98
1.00
3.03
2.91
1.94
1.10
0.95
2.88
2.89
1.89
1.80
3.33
1.23
2.45
1.91
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.156
7.139
6.960
6.947
3.002
2.989
2.984
2.972
2.310
2.284
2.246
2.224
2.191
2.101
2.092
2.066
2.058
1.917
1.882
1.689
1.625
1.420
1.404
1.397
1.387
1.379
1.260
1.253
1.035
1.019
1.010
1.001
0.994
0.987
0.976
0.969
0.963
X : parts per Million : Proton

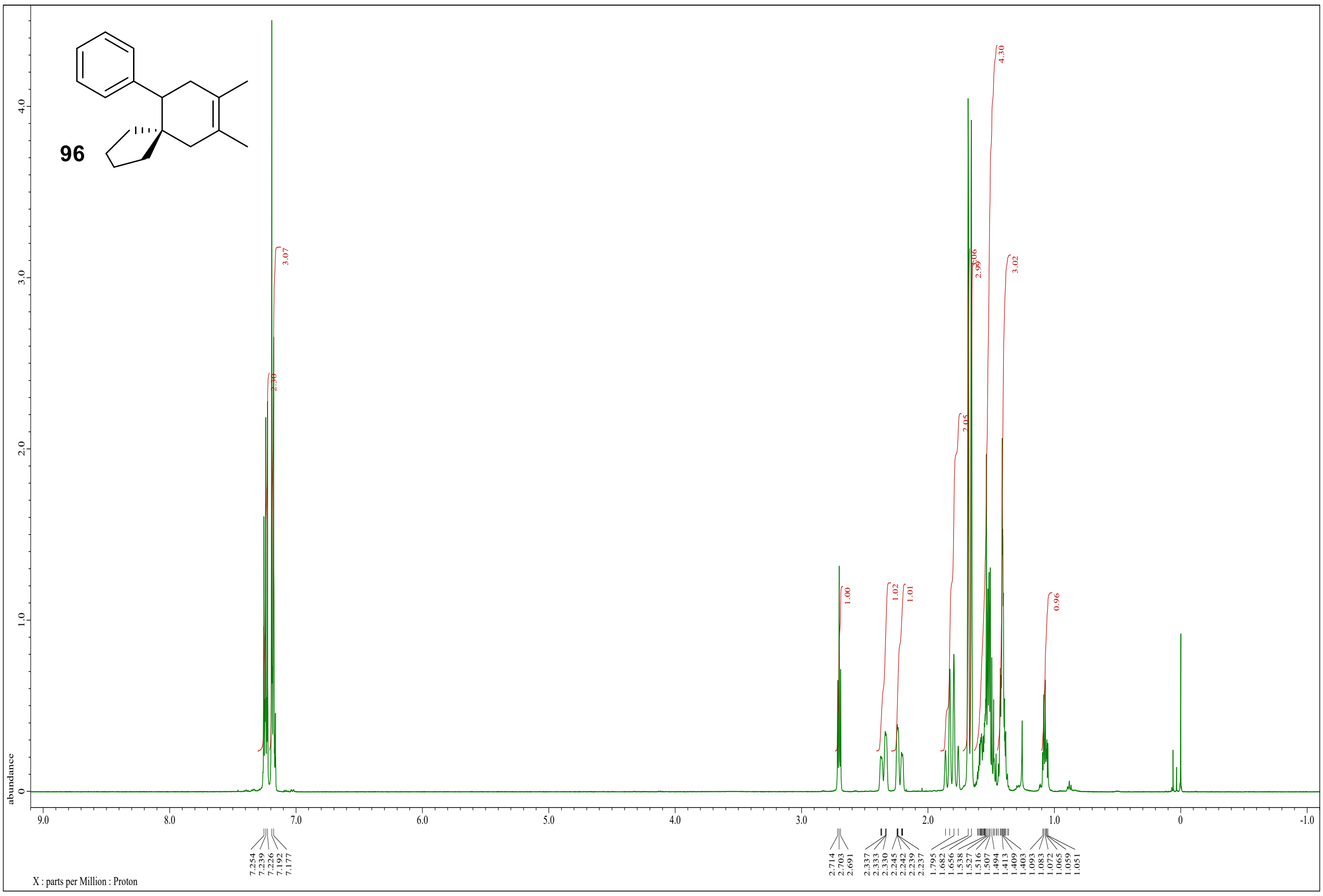

92
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
139.776
137.191
135.074
131.144
128.044
126.537
125.325
124.391
44.603
39.557
36.838
36.619
29.990
29.418
26.613
22.111
22.054
21.472
21.157
19.746
18.925
X : parts per Million : Carbon13

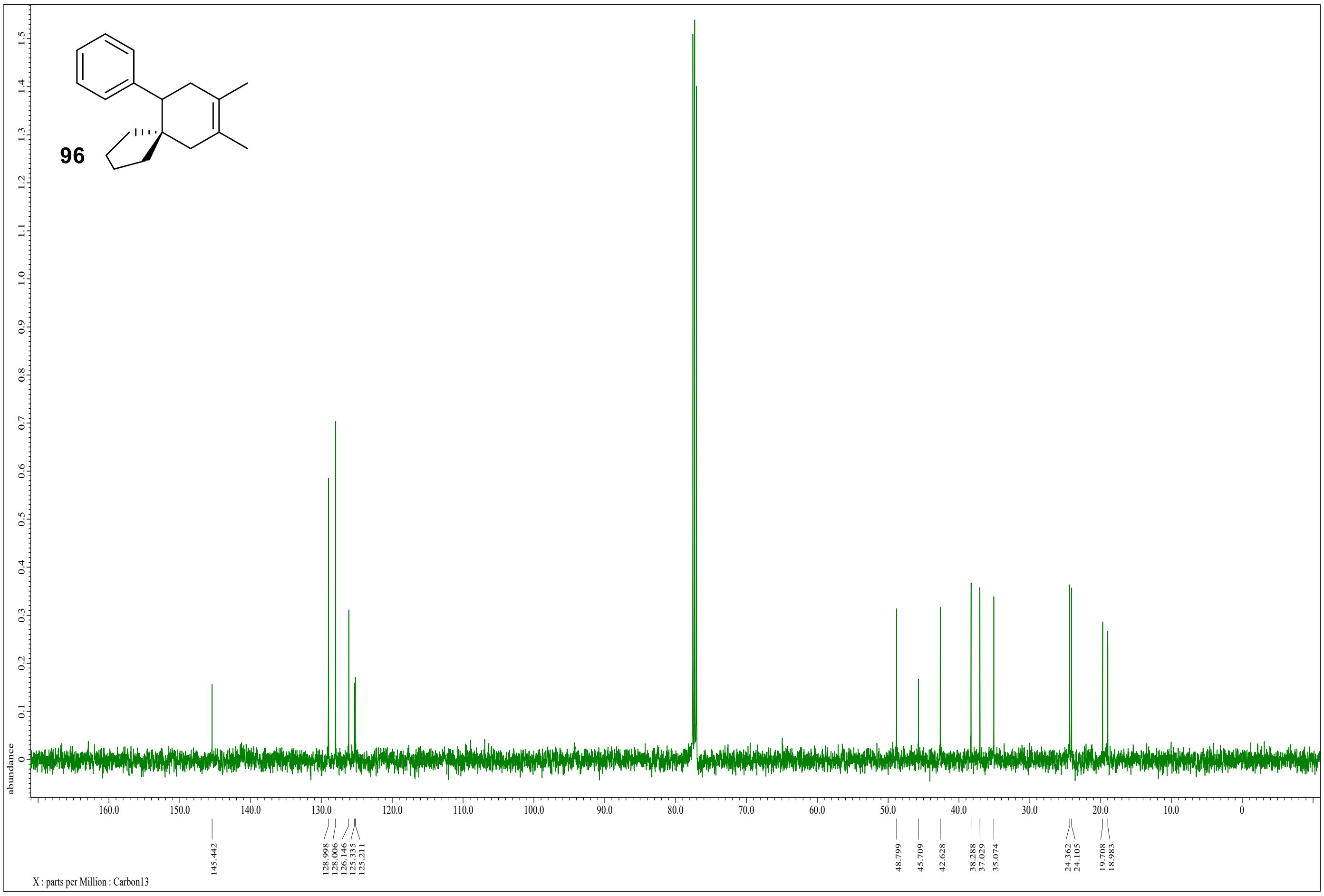

93
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
abundance
3.00
2.14
1.00
1.00
1.00
0.98
0.93
2.89
2.94
2.95
2.93
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.258
7.243
7.206
7.201
7.192
7.185
7.178
7.176
2.648
2.636
2.628
2.617
2.385
2.350
2.333
2.164
2.156
2.131
2.122
1.973
1.939
1.752
1.719
1.659
1.647
0.795
0.789
X : parts per Million : Proton

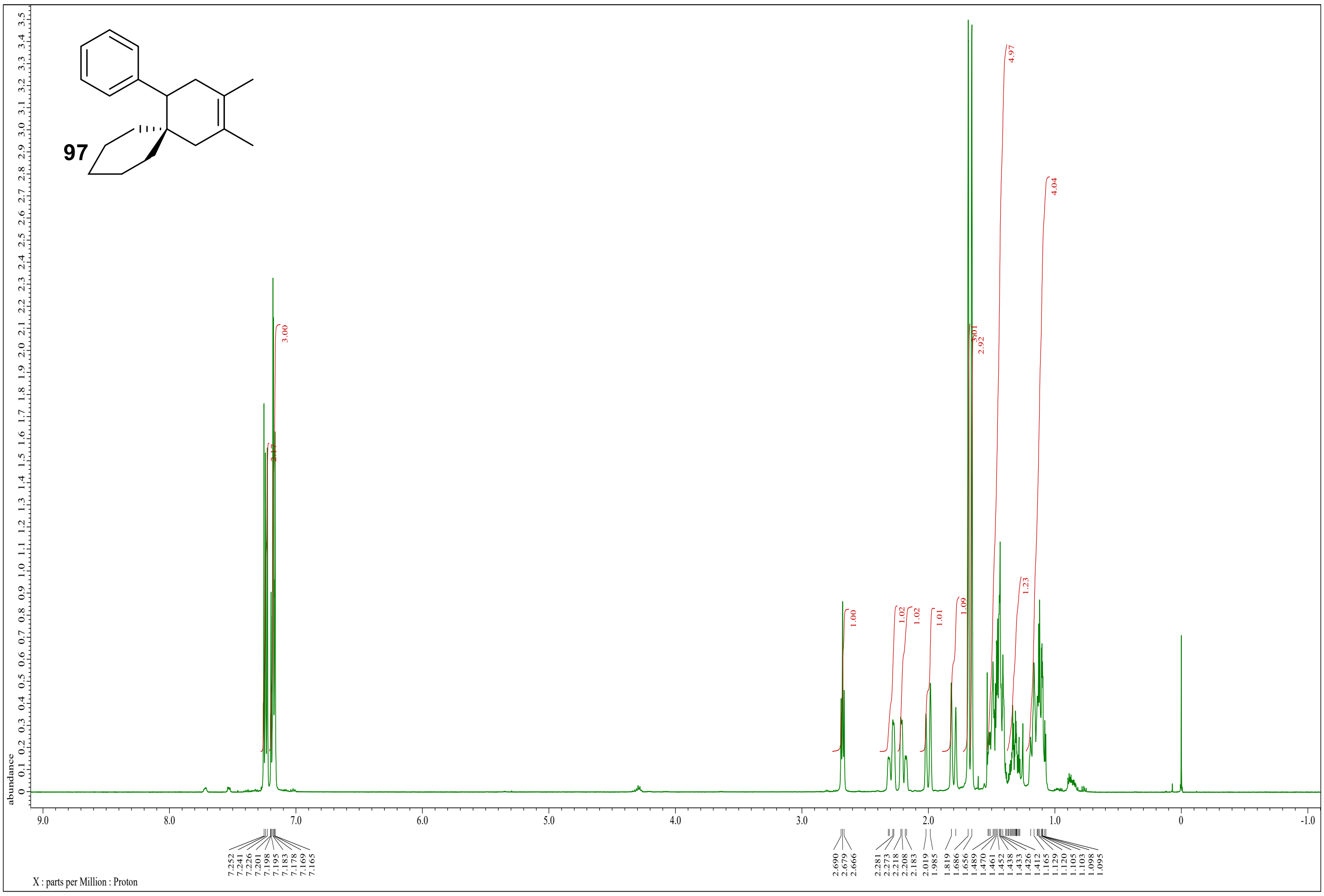

93
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
144.164
129.265
127.920
126.260
124.782
124.591
50.411
47.636
36.361
33.319
29.809
22.645
19.421
18.878
X : parts per Million : Carbon13

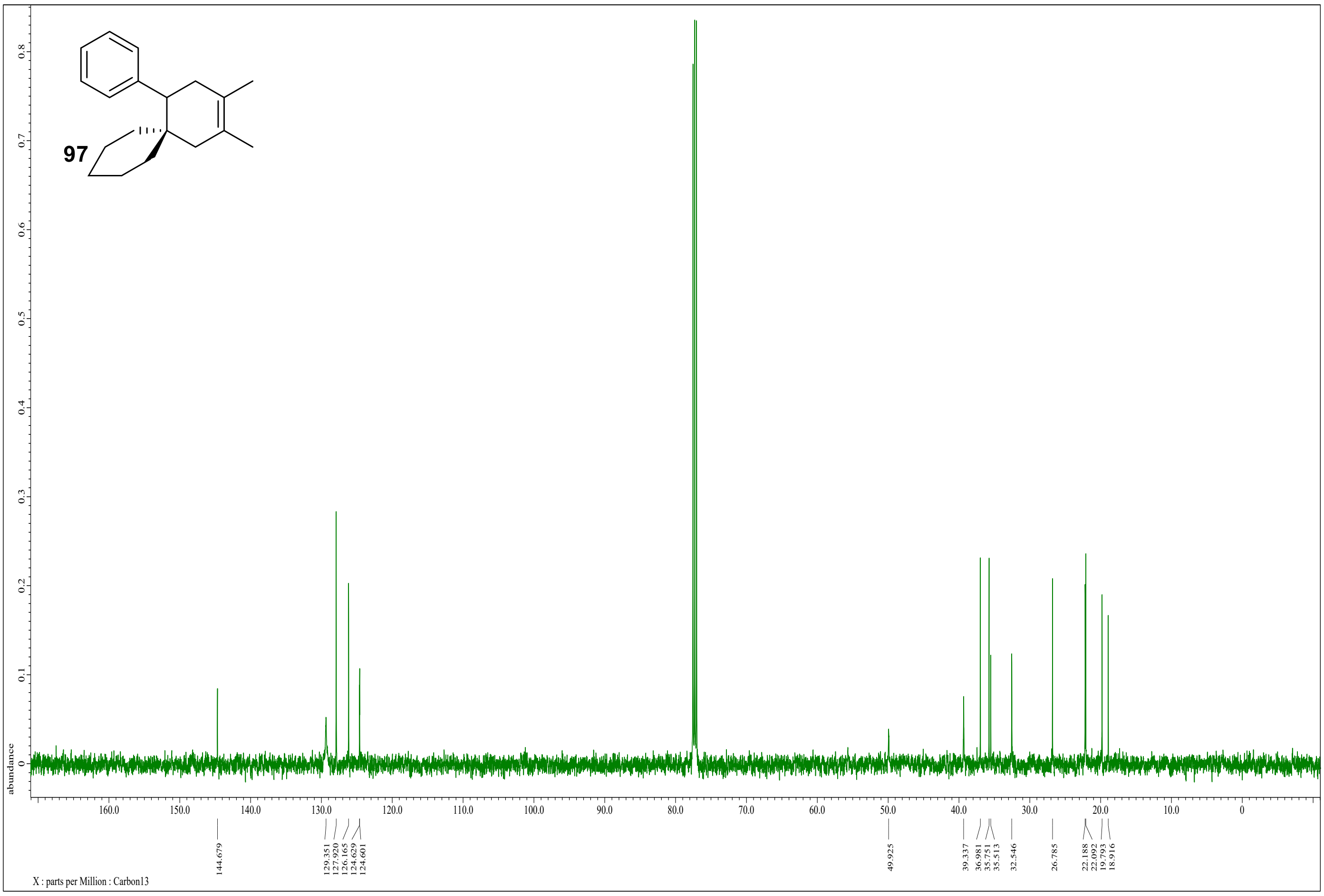

95
abundance
3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
2.57
2.97
1.00
1.03
1.12
3.19
2.29
7.19
1.20
0.97
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
7.275 7.244 7.199 7.193 7.183
2.848 2.837 2.826
2.332 2.179 2.148 2.065 2.036 2.001 1.841 1.827 1.819 1.805 1.789 1.671 1.658 1.638 1.625 1.620 1.618 1.608 1.601 1.428 1.411 1.405 1.397
X : parts per Million : Proton

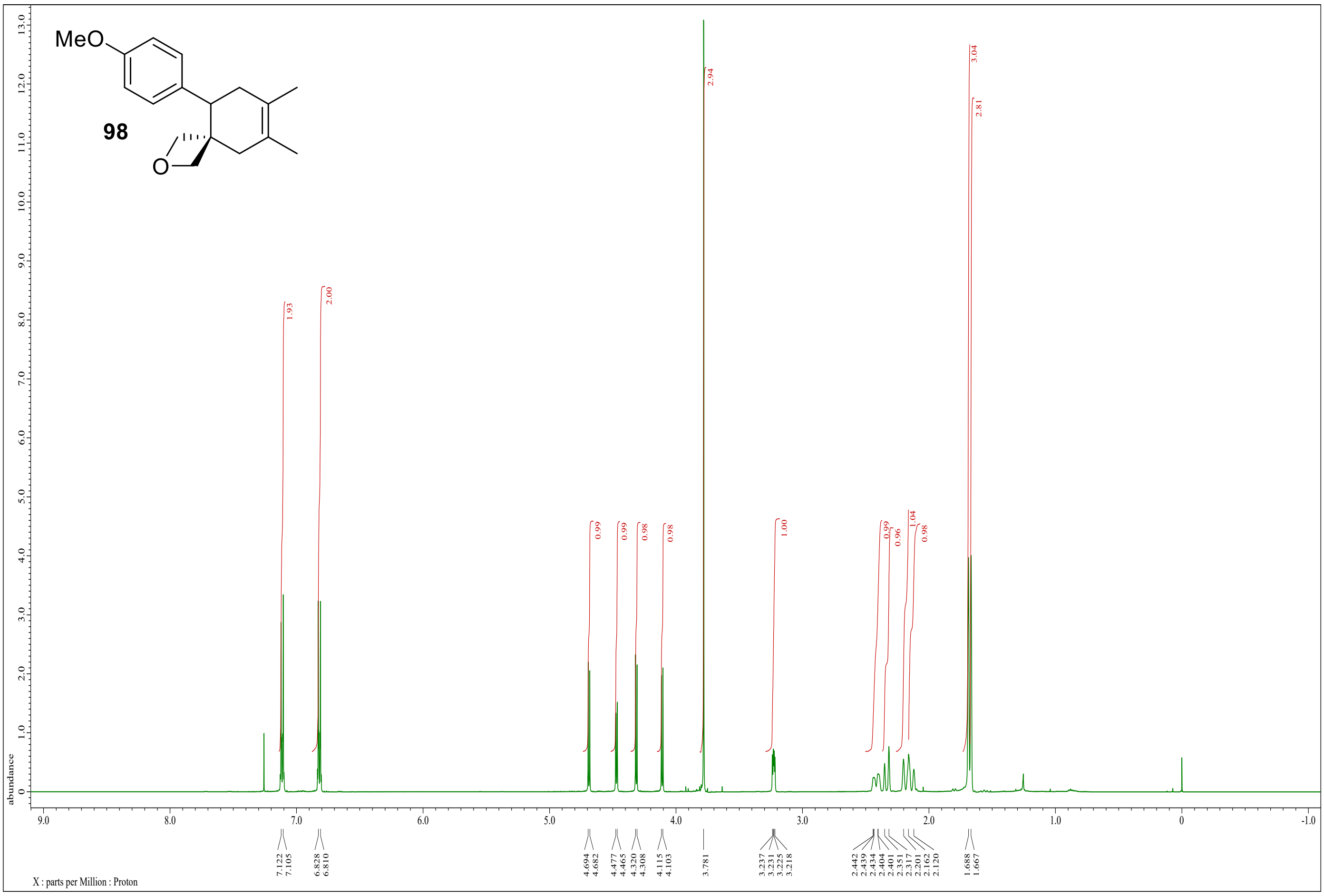

95
abundance
1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
144.316
128.683 128.082 126.193 125.182 124.782
48.542
42.733 42.113
34.778 32.956 29.866
19.622 18.983
15.320
X : parts per Million : Carbon13

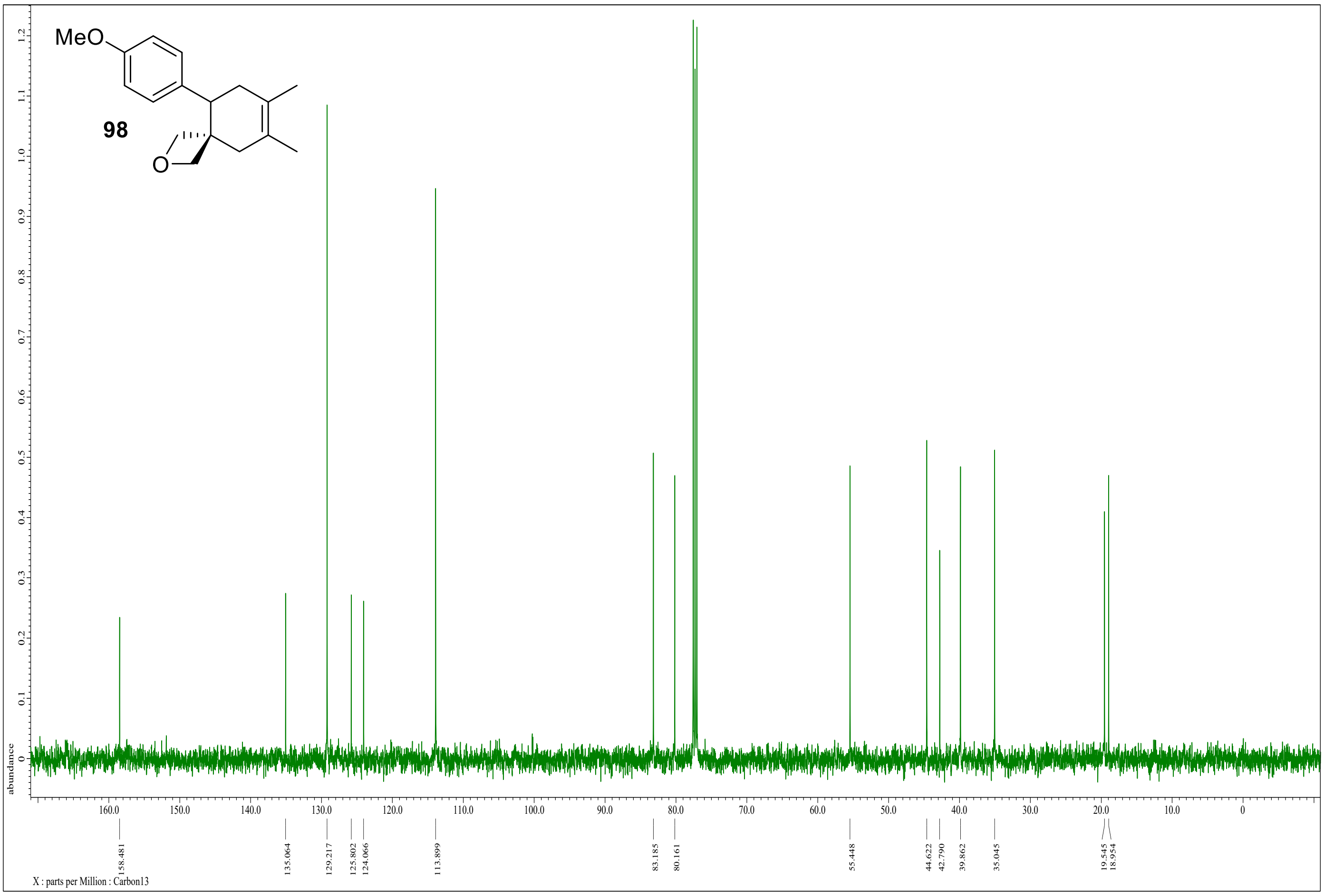

96
abundance
0
1.0
2.0
3.0
4.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
3.07
2.30
1.00
1.02
1.01
2.05
3.06
2.99
4.30
3.02
0.96
7.254
7.239
7.226
7.192
7.177
2.714
2.703
2.691
2.337
2.333
2.330
2.245
2.242
2.239
2.237
1.795
1.682
1.656
1.538
1.527
1.516
1.507
1.494
1.413
1.409
1.403
1.093
1.083
1.072
1.065
1.059
1.051
X : parts per Million : Proton

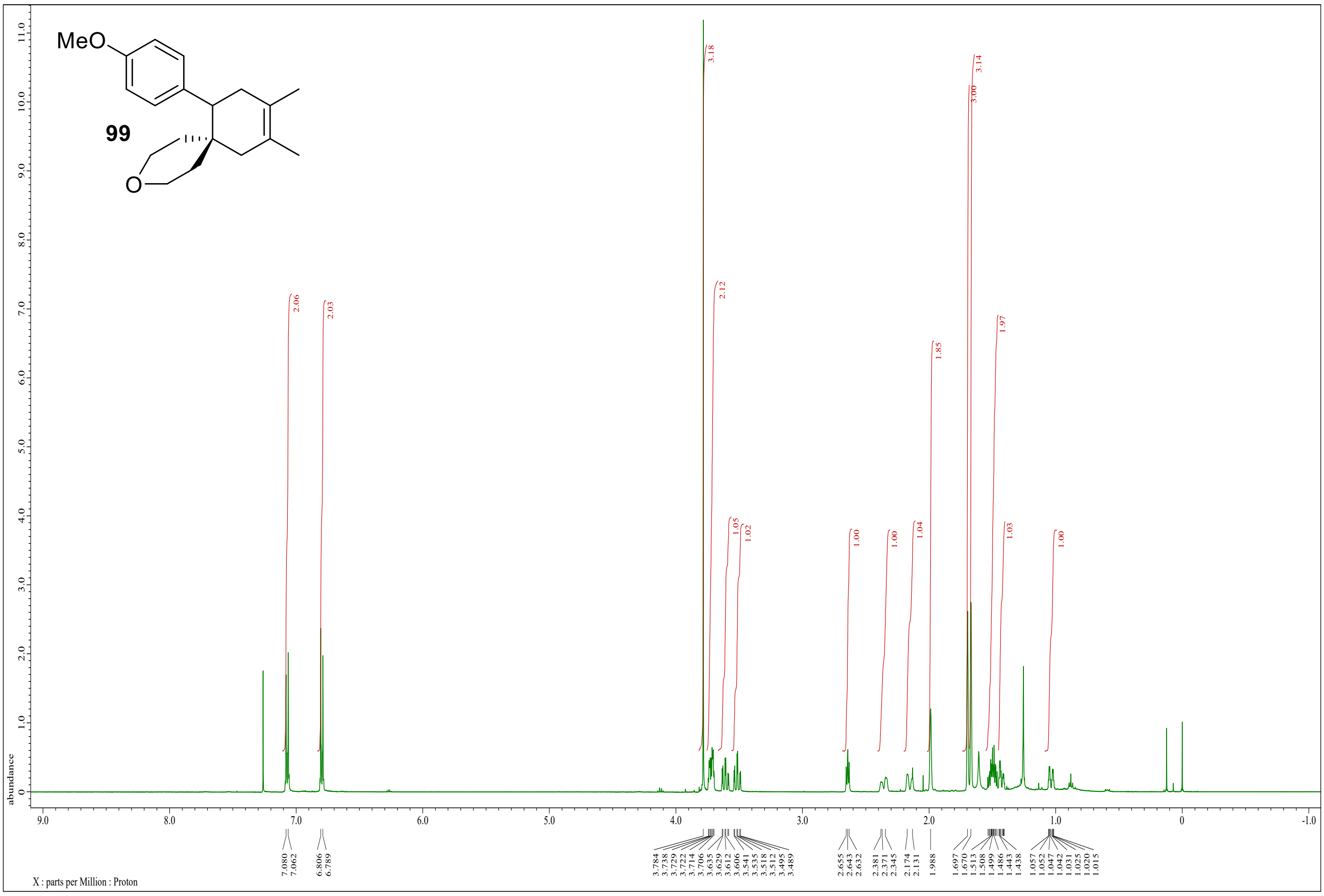

96
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.442
128.998
128.006
126.146
125.335
125.211
48.799
45.709
42.628
38.288
37.029
35.074
24.362
24.105
19.708
18.983
X : parts per Million : Carbon13

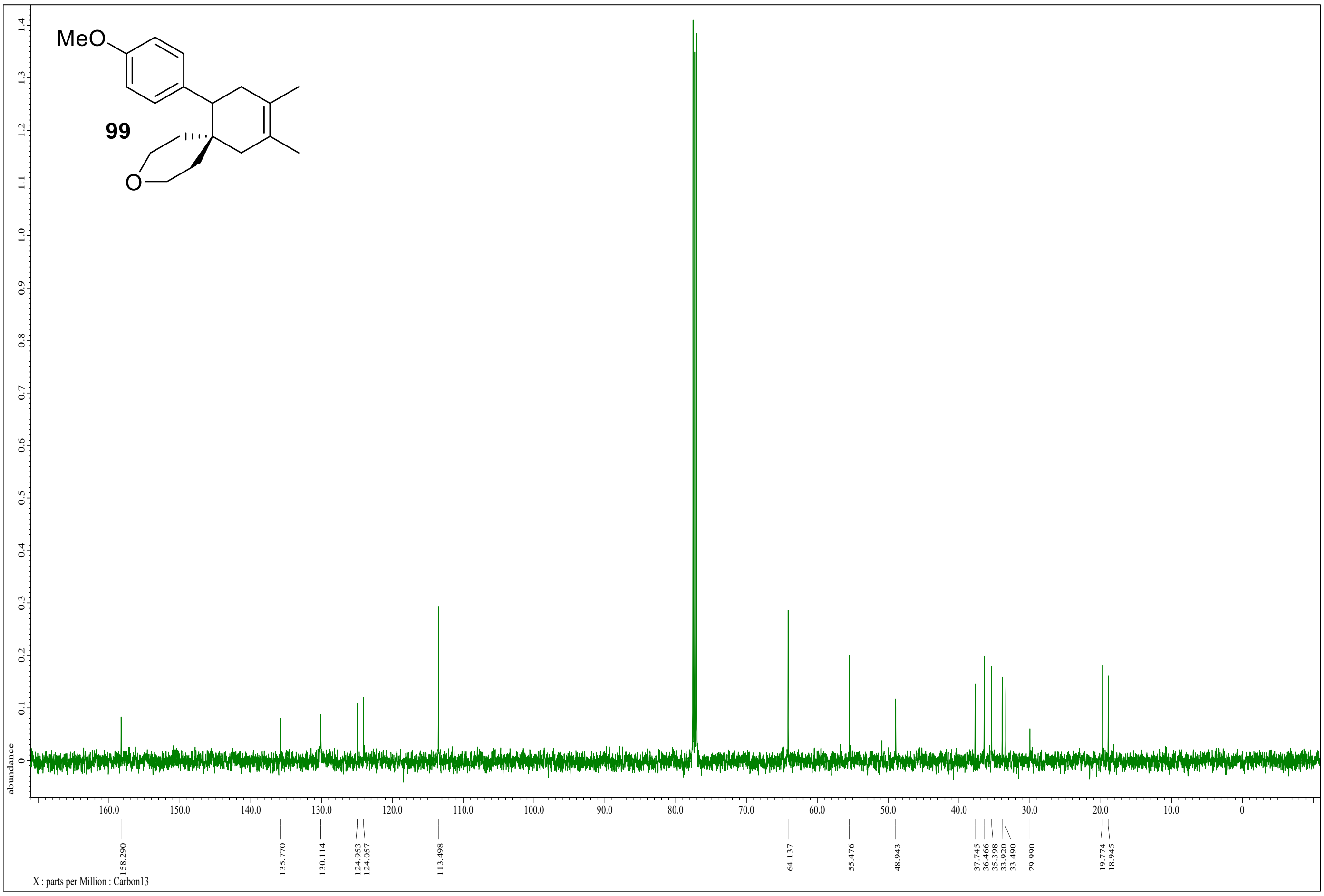

97
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0 3.1 3.2 3.3 3.4 3.5
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
2.17
3.00
1.00
1.02
1.02
1.01
1.09
3.01
2.92
4.97
1.23
4.04
7.252 7.241 7.226 7.201 7.198 7.195 7.183 7.178 7.169 7.165
2.690 2.679 2.666
2.281 2.273 2.218 2.208 2.183 2.019 1.985
1.819 1.686 1.656 1.489 1.470 1.461 1.452 1.438 1.433 1.426 1.412 1.165 1.129 1.120 1.105 1.103 1.098 1.095
X : parts per Million : Proton

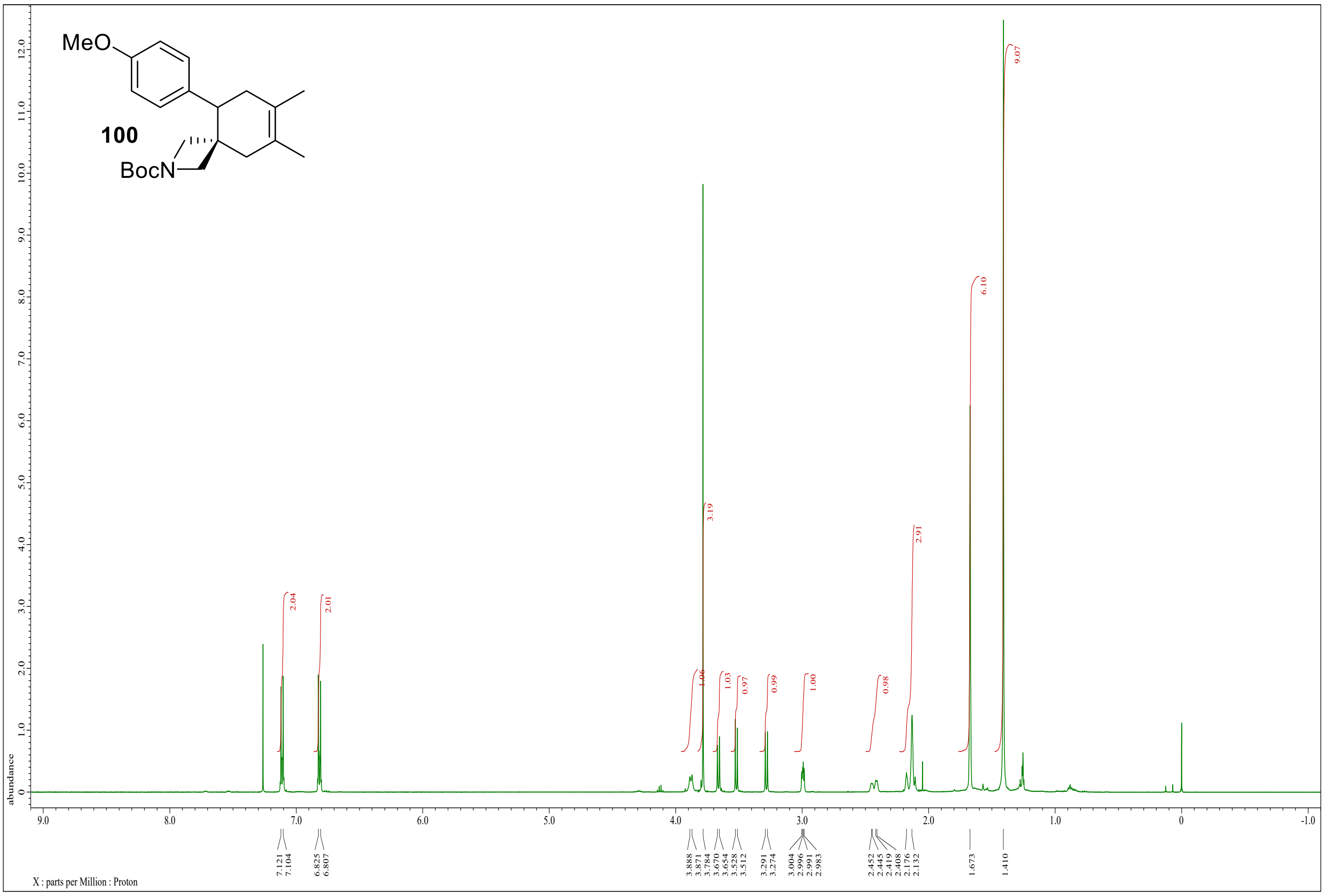

97
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8
160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
144.679
129.351 127.920 126.165 124.629 124.601
49.925
39.337 36.981 35.751 35.513 32.546
26.785
22.188 22.092 19.793 18.916
X : parts per Million : Carbon13

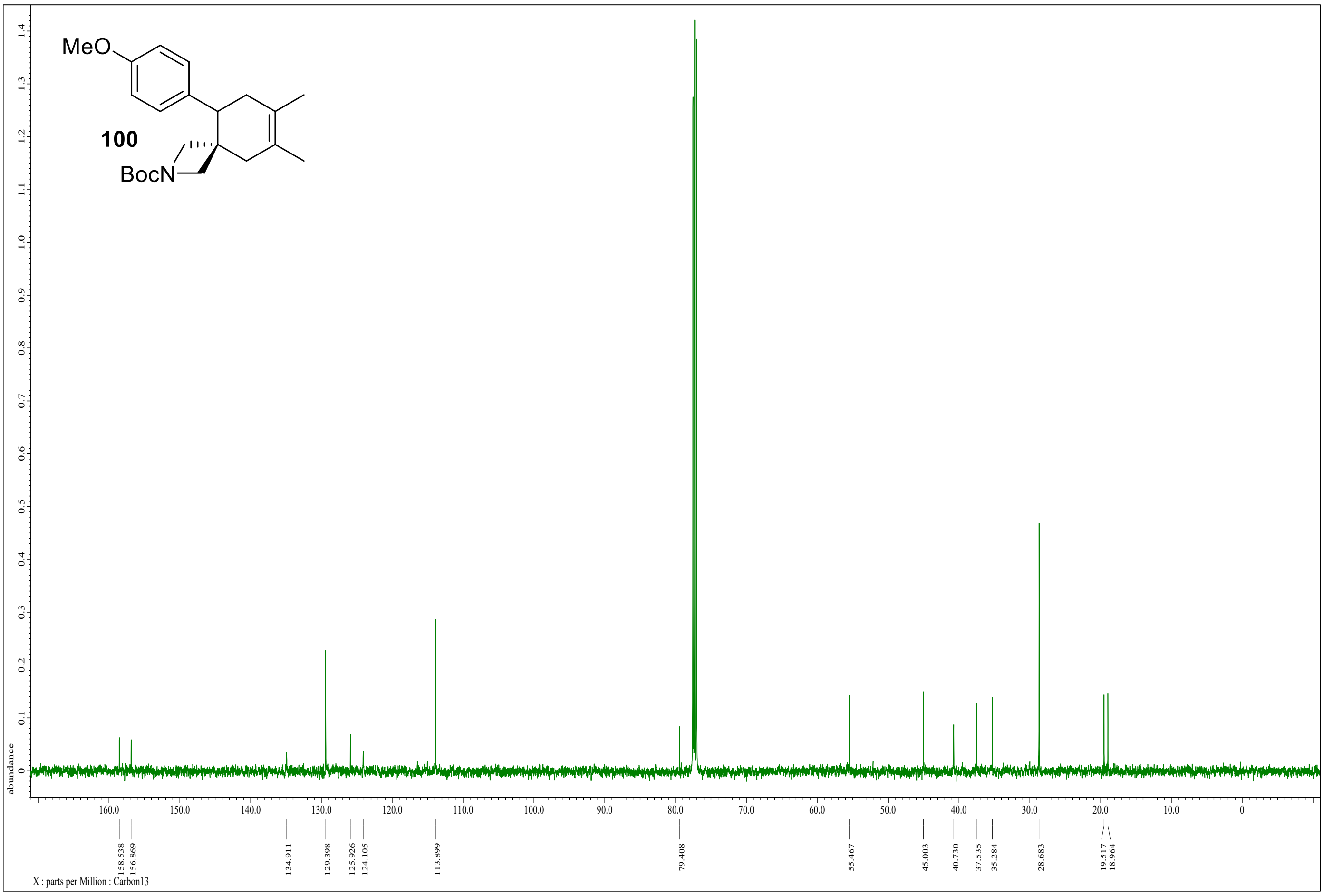

MeO
98
O
1.93
2.00
0.99
0.99
0.98
0.98
2.94
1.00
0.99
0.96
1.04
0.98
3.04
2.81
7.122
7.105
6.828
6.810
4.694
4.682
4.477
4.465
4.320
4.308
4.115
4.103
3.781
3.237
3.231
3.225
3.218
2.442
2.439
2.434
2.404
2.401
2.351
2.317
2.201
2.162
2.120
1.688
1.667
abundance
X : parts per Million : Proton

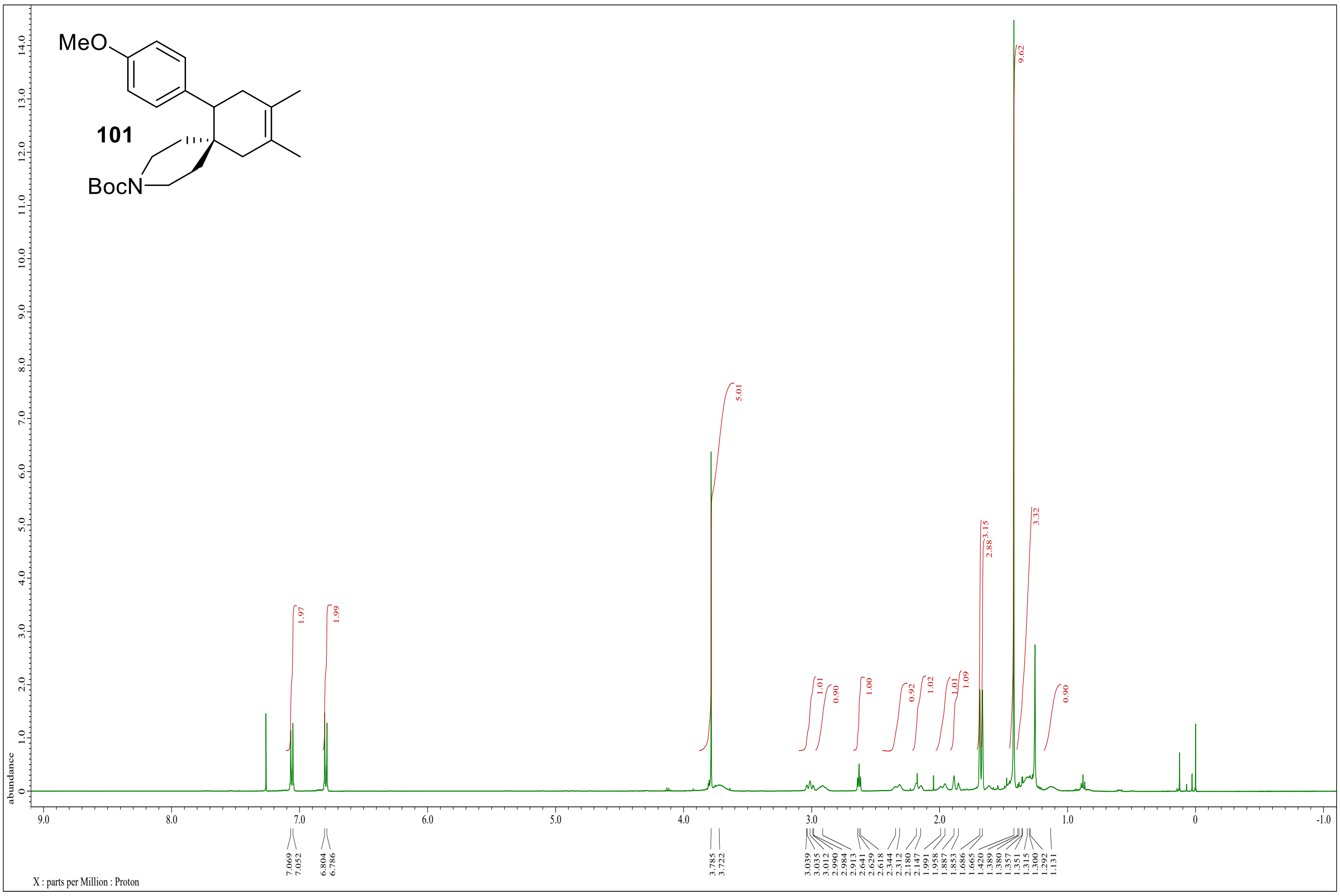

MeO
98
O
158.481
135.064
129.217
125.802
124.066
113.899
83.185
80.161
55.448
44.622
42.790
39.862
35.045
19.545
18.954
abundance
X : parts per Million : Carbon13

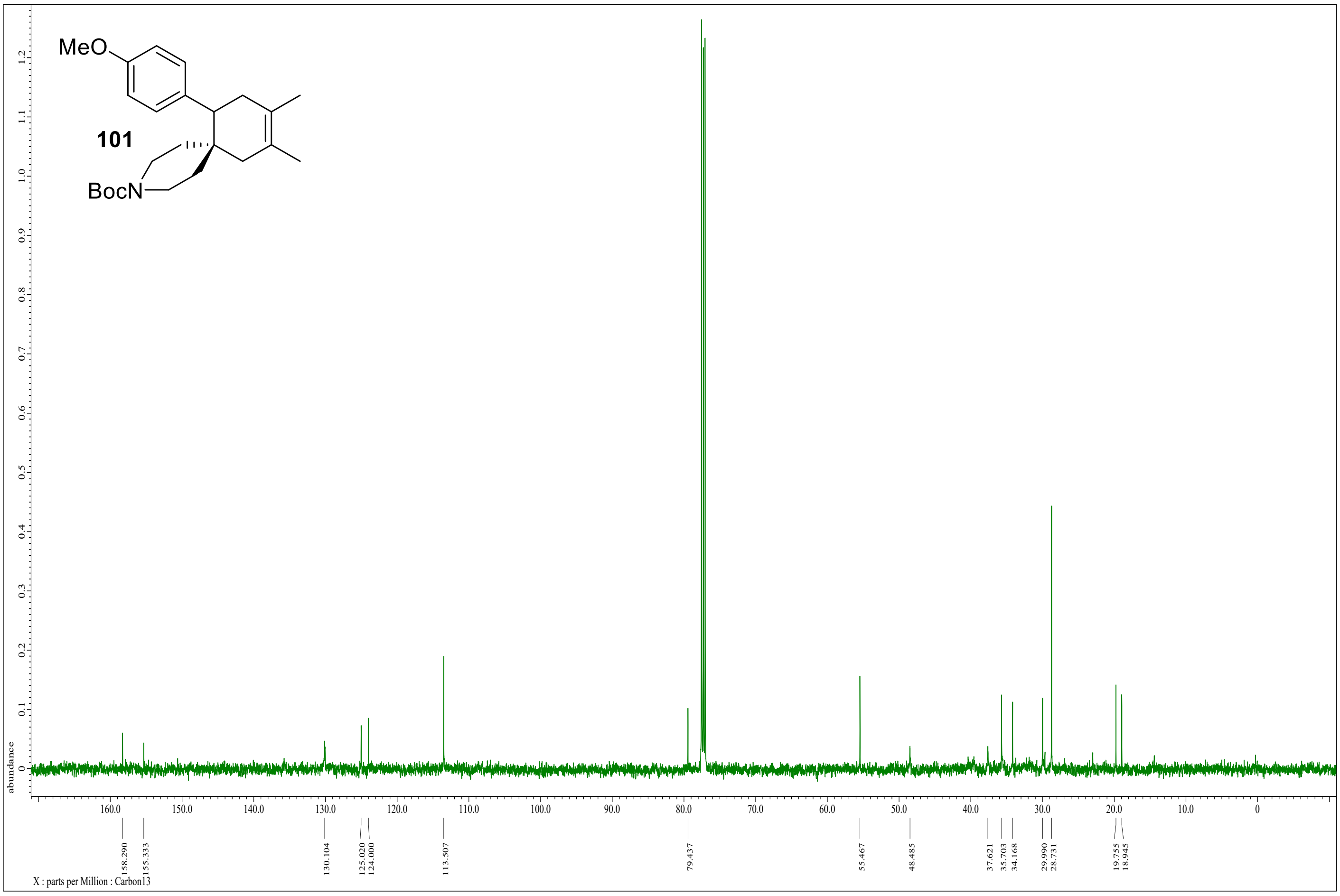

MeO
99
O
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.06
2.03
3.18
2.12
1.05
1.02
1.00
1.00
1.04
1.85
3.00
3.14
1.97
1.03
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.080
7.062
6.806
6.789
3.784
3.738
3.729
3.722
3.714
3.706
3.635
3.629
3.612
3.606
3.541
3.535
3.518
3.512
3.495
3.489
2.655
2.643
2.632
2.381
2.371
2.345
2.174
2.131
1.988
1.697
1.670
1.513
1.508
1.499
1.486
1.443
1.438
1.057
1.052
1.047
1.042
1.031
1.025
1.020
1.015
X : parts per Million : Proton


MeO
99
O
abundance
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.290
135.770
130.114
124.953
124.057
113.498
64.137
55.476
48.943
37.745
36.466
35.398
33.920
33.490
29.990
19.774
18.945
X : parts per Million : Carbon13


MeO
100
BocN
abundance
2.04
2.01
1.06
3.19
1.03
0.97
0.99
1.00
0.98
2.91
6.10
9.07
7.121
7.104
6.825
6.807
3.888
3.871
3.784
3.670
3.654
3.528
3.512
3.291
3.274
3.004
2.996
2.991
2.983
2.452
2.445
2.419
2.408
2.176
2.132
1.673
1.410
X : parts per Million : Proton


MeO
100
BocN
abundance
158.538
156.869
134.911
129.398
125.926
124.105
113.899
79.408
55.467
45.003
40.730
37.535
35.284
28.683
19.517
18.964
X : parts per Million : Carbon13


MeO
101
BocN
abundance
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.97
1.99
5.01
1.01
0.90
1.00
0.92
1.02
1.01
1.09
3.15
2.88
9.62
3.32
0.90
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.069
7.052
6.804
6.786
3.785
3.722
3.039
3.035
3.012
2.990
2.984
2.913
2.641
2.629
2.618
2.344
2.312
2.180
2.147
1.991
1.958
1.887
1.853
1.686
1.665
1.420
1.389
1.380
1.357
1.351
1.315
1.300
1.292
1.131
X : parts per Million : Proton


MeO
101
BocN
abundance
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.290
155.333
130.104
125.020
124.000
113.507
79.437
55.467
48.485
37.621
35.703
34.168
29.990
28.731
19.755
18.945
X : parts per Million : Carbon13