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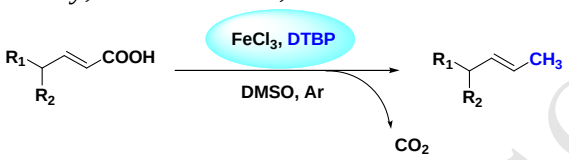

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ABSTRACT

It is the first time to find that iron-catalyzed decarboxylative methylation of α,β-unsaturated acids could be performed in the absence of any ligands. During the reaction, the configuration of the double bond could be retained. It is noteworthy that di-*tert*-butyl peroxide (DTBP) was employed not only as the oxidant, but also as the methyl source.

1. Introduction

In the past several years, the development of decarboxylative coupling of carboxylic acids has gained great attention since such transformations employed the readily available carboxylic acids as starting materials.[1] As a consequence, many efficient catalytic systems have been developed for a series of decarboxylative C-C bond formation reactions in recent years.[2] Among these carboxylic acids, cinnamic acids could be considered as the useful and direct alkenylation reagent during the decarboxylation.[3] Considering that alkenylarene molecules usually display important pharmacological and physical properties,[4] we have the special interest on such decarboxylative reaction of cinnamic acids.

Pioneering work from Fletcher, Heinz and Schiavelli established the viability of acid-catalyzed decarboxylation of cinnamic acids in various solvents.[5] In recent years, Wu has reported Palladium-catalyzed decaroxylative coupling between cinnamic acids and aryl iodides and Miura independently found that α, ω-diarylbutadienes and -hexatrienes could be prepared by decarboxylative coupling of cinnamic acids with vinyl bromides in the presence of palladium catalyst (Scheme 1-1).[6] The work from our own laboratory has demonstrated highly effective copper- or iron-catalyzed decarboxylative C(sp^2)–C(sp^3) coupling reactions *via* radical mechanism (Scheme 1-2).[7] At the same time, Liu also reported copper-catalyzed decarboxylative coupling of cinnamic acids with simple alcohols, esters etc. with good yields (Scheme 1-3).[8] Maiti and co-workers found an effective synthesis of (*E*)-nitroolefins *via* decarboxylative nitration of cinnamic aicd using ^{t}BuONO (*t*-butylnitrite) and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy).[9] Recently, Liu disclosed an example of copper- and iron-catalyzed decarboxylative tri- and difluoromethylation of cinnamic acids with CF_3SO_2Na and $(CF_2HSO_2)_2Zn$ (Scheme1-5).[10] Thus, decarboxylation of cinnamic acids gains great attention in the past several years.[11] Quite differently, in this paper, we just reported the first example of decarboxylative methylation of α,β-unsaturated acids including cinnamic acids in the presence of readily available $FeCl_3$. It is noteworthy that during the reaction, DTBP was used not only as the oxidant but also as the methyl source.

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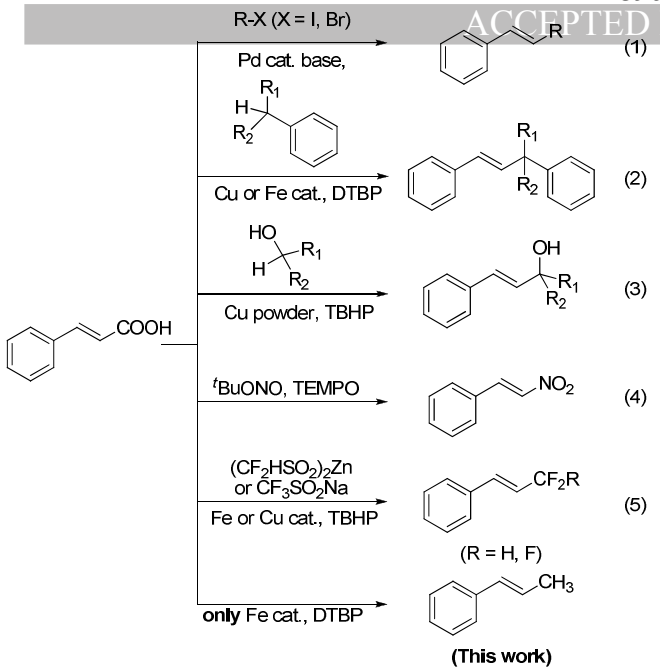


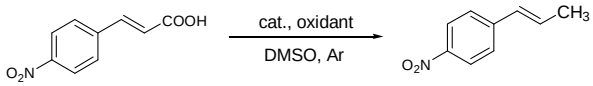
Scheme 1. Decarboxylative couplings of cinnamic acids using various catalysts.

Generally, oxidant is indispensable when it comes to decarboxylative reaction of cinnamic acids. Oxidants such as $K_2S_2O_8$, Ag_2O, *tert*-butyl hydroperoxide (TBHP), di-*tert*-butyl peroxide (DTBP), dicumyl peroxide (DCP), have been widely used. Different from inogranic oxidants, these organic peroxides such as TBHP or DTBP, just act not only as the oxidants, but also as the radical initiators since many decarboxylative reactions go through radical process.[12] In 2007, Li and co-workers reported palladium-catalyzed methylation of aryl C–H bond by using peroxides. In their work, DTBP acts as methylation reagent besides as oxidant.[13] Just recently, we have reported effective synthesis of methyl esters from benzylic acohols, aldehydes or acids via copper-catalyzed C-C cleavage from TBHP.[14] Inspired by such research, we imagine whether we could develop a reaction system through decarboxylation and methylation process by using organic peroxide as the methylation reagent.

2. Results and discussion

To begin our study, we chose *p*-nitro cinnamic acid as model substrate using CuO as catalyst and DTBP as oxidant. Various solvents were tested, and the desired product was detected only when DMSO was used as solvent and gave a yield of 42% of 2a. The detailed optimization is summarized in table 1. Very clearly, other copper catalysts such as CuI are less effective than CuO (Table 1, entries 1–4). As far as we know, iron catalyst also has a good effect on some decarboxylative reactions. For example, Li's group reported a novel iron-catalyzed decarboxylative Csp^3-Csp^2 coupling of proline derivatives and naphthol.[15] Thus, we tried to employ a series of iron catalysts. To our delight, it was found that iron catalysts were more effective than copper ones (Table 1, entries 5–14). After screening various iron catalysts, we found that $FeCl_3$ worked best and gave 52% LC yield (46% isolated yield). Then, other peroxides were also tested, including TBHP and DCP. However, both of them were less effective. Other conditions, such as temperature and reaction time were also screened and we could not get better results. During the process of condition optimizing, no byproducts were detected, and conversion of cinnamic acid for entry 13 is only 60%.

Table 1. Iron-catalyzed decarboxylative methylation of various α,β-unsaturated acids in the absence of ligand.[a]



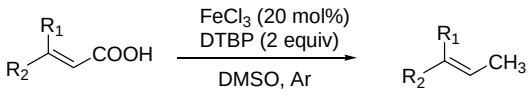
1a **2a**

Entry	Cat.	Oxidant	Yield (%)[b]
1	CuO	DTBP	42
2	CuI	DTBP	30
3	CuBr	DTBP	27
4	Copper quinolate	DTBP	38
5	$Fe(acac)_3$	DTBP	44
6	Fe powder	DTBP	38
7	$FeCl_2{\cdot}4H_2O$	DTBP	40
8	FeF_3	DTBP	48
9	$Fe_2(SO_4)_3$	DTBP	33
10	Fe_2O_3	DTBP	18
11	Fe_3O_4	DTBP	31
12	$Fe(NO_3)_3$	DTBP	30
13	$FeCl_3$	DTBP	52 (46)[c]
14	$FeSO_4{\cdot}7H_2O$	DTBP	41
15	$FeCl_3$	TBHP	41
16	$FeCl_3$	DCP	36

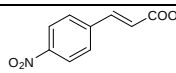
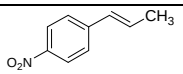
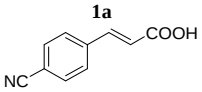
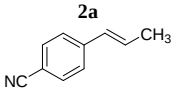
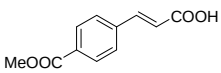
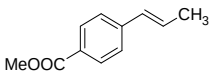
[a] Reaction conditions: *p*-nitro cinnamic acid (0.3 mmol), cat. (20 mol%), oxidant (2 equiv), DMSO (2 mL), 12 h, 130 °C, Ar. [b] LC yields, biphenyl as internal standard. [c] Isolated yield based on *p*-nitro cinnamic acid parentheses.

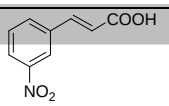
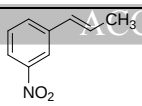
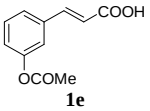
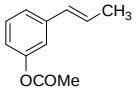
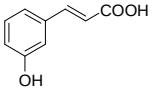
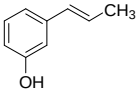
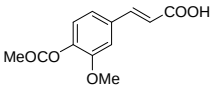
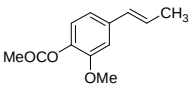
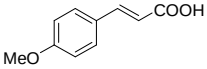
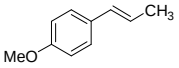
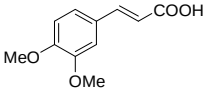
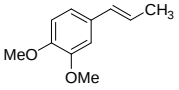
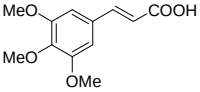
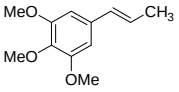
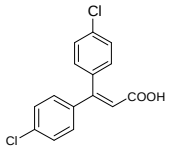
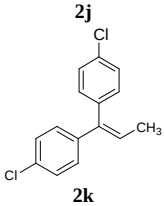
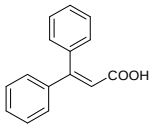
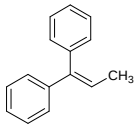
With the optimized conditions in hand, the scope of different substituted cinnamic acids was investigated. As shown in table 2, cinnamic acids with electron-withdrawing group at the *para* position of the benzene ring gave moderate yields (Table 2, entries 1–3). *Meta*-substituted cinnamic acids also can offer desired products and got certain yields (Table 2, entries 4–6). It is important to note that when methoxy-substituted cinnamic acids were used as the substrates, lower yields of the desired products were obtained (Table 2, entries 7–10). However, it was pleased to find that *β*-substituted substrates could also be tolerated by our reaction system (Table 2, entries 11–12). For example, *β*-phenyl cinnamic acid afforded the product in the yield of 42% (Table 2, entry 12).

Table 2. Iron-catalyzed decarboxylative methylation of various α,β-unsaturated acids in the absence of ligand.[a]



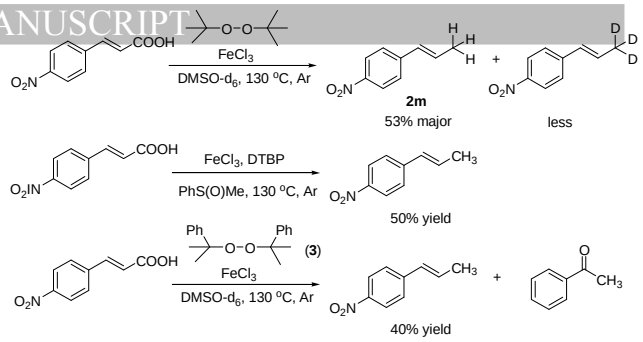
1 **2**

Entry	substrate	Product	Yield (%)[b]
1	 **1a**	 **2a**	46
2	 **1b**	 **2b**	53
3	 **1c**	 **2c**	34

4		**1d**		**2d**
5		**1e**		**2e**
6		**1f**		**2f**
7		**1g**		**2g**
8[c]		**1h**		**2h**
9[c]		**1i**		**2i**
10[c]		**1j**		**2j**
11		**1k**		**2k**
12		**1l**		**2l**

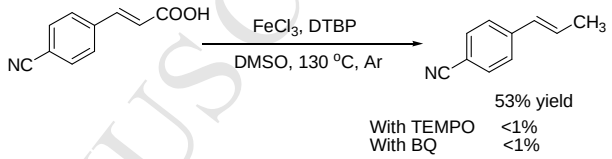
[a] Reaction conditions: α,β-Unsaturated acids (0.3 mmol), DTBP (2 equiv), $FeCl_3$ (20 mol%), DMSO (2 mL), 12 h, 130 °C, Ar. [b] Isolated yield based on *α,β*-unsaturated acids. [c] $Fe(acac)_3$ instead of $FeCl_3$.

In order to make sure that the methyl group was generated from the oxidant, the decarboxylative reaction of *p*-nitro cinnamic acid was performed in DMSO-d_6 as shown in Scheme 2. The NMR suggested that less [D]-product was acquired. When DMSO was replaced by methyl phenyl sulfoxide (MPSO), the reaction can also be carried out smoothly. When 1-(2-(2-phenylpropan-2-ylperoxy)propan-2-yl)benzene (**3**) was employed, the desired product was obtained in 40% yield as expected. In addition, a big amount of acetophenone was acquired. This suggests that the methyl group in the product was introduced from this C-C bond cleavage of the oxidant (**3**). We guess that the coordination of sulfoxide to iron ion plays an important role in the reaction process.[16]



Scheme 2. Iron-catalyzed decarboxylative methylation of p-nitro cinnamic acid in DMSO-D_6 or MPSO using DTBP or DCP as oxidants.

A series of experiments was conducted in order to explore the possible reaction mechanism. When TEMPO or BQ (benzoquinone) was added, the reaction was almost inhibited and no product was detected. These are indirect proofs that our reaction may go through a radical process.



Scheme 3. Iron-catalyzed decarboxylative methylation of p-cyano cinnamic acid.

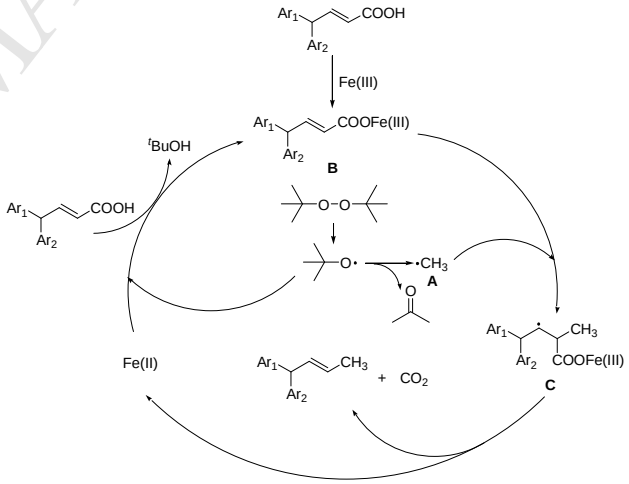


Figure 1. Proposed reaction pathways for the iron-catalyzed decarboxylative methylation.

Base on previous reports,[13, 14, 17] a proposed mechanism for the decarboxylative methylation reaction is shown in Figure 1. The catalytic cycle starts with the generation of methyl radical released from *t*-BuO·. Then, the addition of methyl radical to the *α*-position of the double bond of ferric cinnamate **B**, which is generated by the reaction of cinnamic acid with ferric chloride, would give intermediate **C**. **C** then proceeds *via* an elimination of carbon dioxide and Fe(II) to generate the product. Fe(II) will be oxidized by *t*-BuO· and regenerates **B** in the presence of cinnamic acid to complete the reaction cycle.

3. Conclusions

In conclusion, we developed a novel iron-catalyzed decarboxylative methylation reaction of cinnamic acids in the presence of DTBP as methylation resource. This reaction system could tolerate various cinnamic acids. It provides a new strategy to prepare *α*-methyl styrene. It is noteworthy that during the reaction, the configuration of the double bond could be retained. However, our protocol also shows the disadvantage of low yield. Therefore, the aim of our future work is to find out a more effective catalyst and its application in the synthesis of some biological compounds.

4. Experiment

4.1 General information

General information: All reactions were carried out under an argon atmosphere condition. Various iron catalysts, cinnamic acids and oxidants were purchased from Aldrich, Acros or Alfa. Column chromatography was generally performed on silica gel (100-200 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light (254 nm) to visualize the course of the reactions. The ^{1}H (300 MHz or 400 MHz) and ^{13}C NMR (75 MHz or 100 MHz) data were recorded on Varian 300 M or 400 M spectrometers using $CDCl_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.000 ppm) or DMSO-d_6 (δ = 39.500 ppm) as internal reference. ESI-MS and HRMS were performed by the State-authorized Analytical Center in Soochow University.

General procedure for iron-catalyzed decarboxylative methylation of cinnamic acid: A mixture of cinnamic acid (0.3 mmol), DTBP (0.6 mmol), $FeCl_3$ (20 mol%), and DMSO (2 mL) in a Schlenk tube was stirred under an argon atmosphere at 130 ^{o}C for 12 h. After that the mixture was poured into ethyl acetate, then washed with water, extracted with ethyl acetate, dried by anhydrous Na_2SO_4, then filtered and evaporated under vacuum, the residue was purified by flash column chromatography (petroleum ether or petroleum ether/ethyl acetate) to afford the corresponding coupling products.

(*E*)-1-Nitro-4-(prop-1-enyl)benzene: Yellow solid, mp: 92 – 93 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.06 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 6.43-6.35 (m, 2H), 1.86 (d, J = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 146.4, 144.4, 131.2, 129.4, 126.2, 123.9, 18.7; MS (m/z) calcd for $C_9H_9NO_2$ 163.1, found 163.1 $(M+H)^+$.

(*E*)-4-(Prop-1-enyl)benzonitrile: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.47 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.38 – 6.25 (m, 2H), 1.84 (d, J = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 142.4, 132.3, 130.2, 129.8, 126.3, 119.2, 109.9, 18.7; MS (m/z) calcd for $C_{10}H_9N$ 143.1, found 143.1 $(M+H)^+$.

(*E*)-Methyl 4-(prop-1-enyl)benzoate: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.88 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.40 – 6.23 (m, 2H), 3.82 (s, 3H), 1.83 (d, J = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.0, 142.4, 130.3, 129.8, 128.8, 128.1, 125.6, 52.0, 18.6; MS (m/z) calcd for $C_{11}H_{11}O_2$ 176.1, found 176.1 $(M+H)^+$.

(*E*)-1-Nitro-3-(prop-1-enyl)benzene: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.07 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 6.39 – 6.25 (m, 2H), 1.83 (d, J = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 148.6, 139.7, 134.8, 131.7, 129.3, 129.0, 121.3, 120.4, 18.5; MS (m/z) calcd for $C_9H_9NO_2$ 163.1, found 163.1 $(M+H)^+$.

(*E*)-3-(Prop-1-enyl)phenyl acetate: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.28 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.04 (s, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 6.29 – 6.17 (m, 1H), 2.29 (s, 3H), 1.87 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (100 MHz, $CDCl_3$) (δ, ppm) 169.5, 150.9, 139.6, 130.1, 129.3, 126.9, 123.4, 119.7, 118.6, 21.1, 18.4; MS (m/z) calcd for $C_{11}H_{12}O_2$ 176.1, found 176.1 $(M+H)^+$.

(*E*)-3-(Prop-1-enyl)phenol: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.07 (t, J = 8.0 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.73 (s, 1H), 6.59 (d, J = 8.0 Hz, 1H), 6.25 (d, J = 15.6 Hz, 1H), 6.19 – 6.07 (m, 1H), 4.94 (s, 1H), 1.78 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 155.7, 139.7, 130.6, 129.7, 126.3, 118.7, 113.8, 112.5, 18.5; MS (m/z) calcd for $C_9H_{10}O$ 134.1, found 134.1 $(M+H)^+$.

(*E*)-Methyl 2-methoxy-4-(prop-1-enyl)benzoate: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 6.94 – 6.73 (m, 3H), 6.29 (d, J = 16.0 Hz, 1H), 6.18 – 6.05 (m, 1H), 3.76 (s, 3H), 2.23 (s, 3H), 1.80 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.2, 151.0, 138.6, 137.1, 130.5, 126.1, 122.7, 118.4, 109.6, 55.8, 20.7, 18.4; MS (m/z) calcd for $C_{12}H_{14}O_3$ 206.1, found 206.1 $(M+H)^+$.

(*E*)-1-methoxy-4-(prop-1-enyl)benzene: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.25 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.33 (d, J = 15.6 Hz, 1H), 6.14 – 6.03 (m, 1H), 3.79 (s, 3H), 1.85 (dd, J = 6.4, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.5, 130.7, 130.2, 126.8, 123.5, 113.8, 55.2, 18.4; MS (m/z) calcd for $C_{10}H_{12}O$ 148.1, found 148.1 $(M+H)^+$.

(*E*)-1,2-Dimethoxy-4-(prop-1-enyl)benzene: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 6.84 – 6.69 (m, 3H), 6.26 (d, J = 15.6 Hz, 1H), 6.03 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 1.79 (dd, J = 6.8, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 148.9, 148.1, 131.1, 130.6, 123.8, 118.6, 111.1, 108.4, 55.9, 55.7, 18.3; MS (m/z) calcd for $C_{11}H_{14}O_2$ 178.1, found 178.1 $(M+H)^+$.

(*E*)-1,2,3-Trimethoxy-5-(prop-1-enyl)benzene: Colorless oil ; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 6.47 (s, 2H), 6.24 (d, J = 16.0 Hz, 1H), 6.13 – 6.01 (m, 1H), 3.78 (s, 6H), 3.75 (s, 3H), 1.79 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 153.2, 137.1, 133.7, 130.8, 125.2, 102.7, 60.8, 55.9, 18.3; MS (m/z) calcd for $C_{12}H_{16}O_3$ 208.1, found 208.1 $(M+H)^+$.

4,4'-(Prop-1-ene-1,1-diyl)bis(chlorobenzene): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.26 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 7.05 – 6.95 (m, 4H), 6.07 (q, J = 7.2 Hz, 1H), 1.66 (d, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) (δ, ppm) 140.9, 140.2, 137.9, 132.9, 132.7, 131.3, 128.5, 128.4, 128.2, 125.2, 15.7; MS (m/z) calcd for $C_{15}H_{12}Cl_2$ 263.1, found 263.1 $(M+H)^+$.

Prop-1-ene-1,1-diyldibenzene: White solid, mp: 49–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.30 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.04 (m, 8H), 6.10 (q, *J* = 7.2 Hz, 1H), 1.69 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (δ, ppm) 142.9, 142.4, 140.0, 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 124.1, 15.7, MS (m/z) calcd for $C_{15}H_{14}$ 194.1, found 194.1 $(M+H)^+$.

(*E*)-1-Nitro-4-(prop-1-enyl)benzene (2m): Yellow solid, mp: 92 – 93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.15 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 6.51 – 6.43 (m, 2H), 1.95 (d, *J* = 4.4 Hz, 3H). MS (m/z) calcd for $C_9H_9NO_2$ 163.1, found 163.1 $(M+H)^+$.

Acknowledgments

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Supporting Information

Iron-Catalyzed Decarboxylative Methylation of *α,β*-Unsaturated Acids under Ligand-Free Conditions

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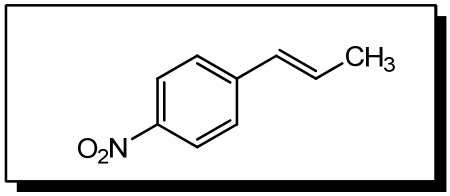
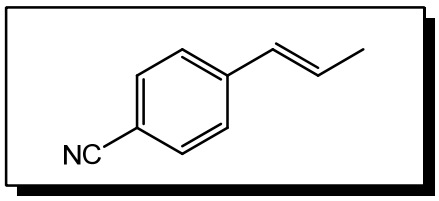
Characterization of the corresponding products:

(*E*)-1-Nitro-4-(prop-1-enyl)benzene (2a) [cas: 1879-55-6]



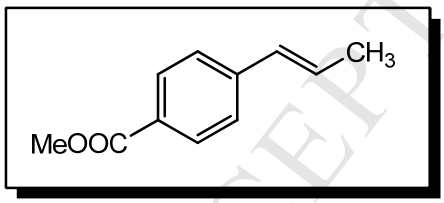
Yellow solid, mp: 92 – 93 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.06 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.43-6.35 (m, 2H), 1.86 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR (δ, ppm) 146.4, 144.4, 131.2, 129.4, 126.2, 123.9, 18.7; MS (m/z) calcd for $C_9H_9NO_2$ 164.1, found 164.1 $(M+H)^+$.

(*E*)-4-(Prop-1-enyl)benzonitrile (2b) [cas: 74254-13-0]



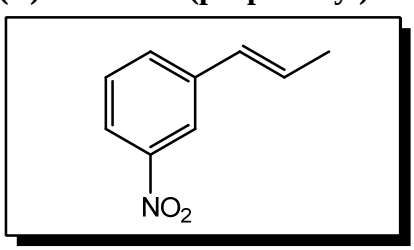
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.47 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.38 – 6.25 (m, 2H), 1.84 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR (δ, ppm) 142.4, 132.3, 130.2, 129.8, 126.3, 119.2, 109.9, 18.7; MS (m/z) calcd for $C_{10}H_9N$ 144.1, found 144.1 $(M+H)^+$.

(*E*)-Methyl 4-(prop-1-enyl)benzoate (2c) [cas: 158475-38-8]



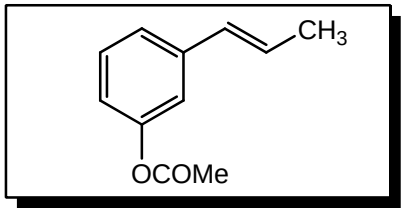
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.88 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.40 – 6.23 (m, 2H), 3.821 (s, 3H), 1.83 (d, *J* = 5.6 Hz, 3H); ^{13}C NMR (δ, ppm) 168.0, 142.4, 130.3, 129.8, 128.8, 128.1, 125.6, 52.0, 18.6; MS (m/z) calcd for $C_{11}H_{11}O_2$ 177.1, found 177.1 $(M+H)^+$.

(*E*)-1-Nitro-3-(prop-1-enyl)benzene (2d) [cas: 23204-79-7]



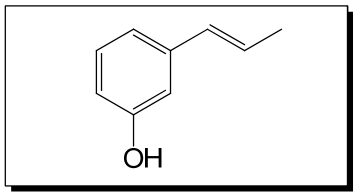
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.07 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 6.39 – 6.25 (m, 2H), 1.83 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (δ, ppm) 148.6, 139.7, 134.8, 131.7, 129.3, 129.0, 121.3, 120.4, 18.5; MS (m/z) calcd for $C_9H_9NO_2$ 164.1, found 164.1 $(M+H)^+$.

(*E*)-3-(Prop-1-enyl)phenyl acetate (2e)



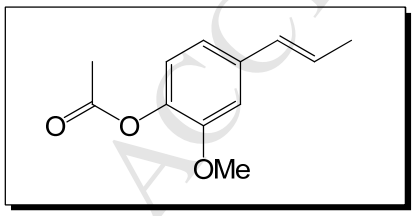
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.28 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.29 – 6.17 (m, 1H), 2.29 (s, 3H), 1.87 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (δ, ppm) 169.5, 150.9, 139.6, 130.1, 129.3, 126.9, 123.4, 119.7, 118.6, 21.1, 18.4; MS (m/z) calcd for $C_{11}H_{12}O_2$ 177.1, found 177.1 $(M+H)^+$.

(*E*)-3-(Prop-1-enyl)phenol (2f) [cas: 66921-90-2]



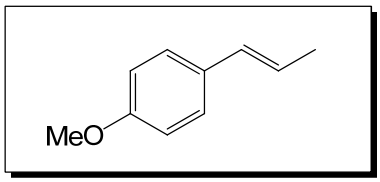
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.07 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.25 (d, *J* = 15.6 Hz, 1H), 6.19 – 6.07 (m, 1H), 4.94 (s, 1H), 1.78 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (δ, ppm) 155.7, 139.7, 130.6, 129.7, 126.3, 118.7, 113.8, 112.5, 18.5; MS (m/z) calcd for $C_9H_{10}O$ 135.1, found 135.1 $(M+H)^+$.

(*E*)-Methyl 2-methoxy-4-(prop-1-enyl)benzoate (2g) [cas: 93-29-8]



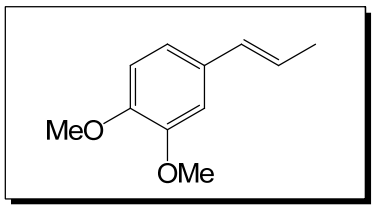
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 6.94 – 6.73 (m, 3H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.18 – 6.05 (m, 1H), 3.76 (s, 3H), 2.23 (s, 3H), 1.80 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (δ, ppm) 169.2, 151.0, 138.6, 137.1, 130.5, 126.1, 122.7, 118.4, 109.6, 55.8, 20.7, 18.4; MS (m/z) calcd for $C_{12}H_{14}O_3$ 207.1, found 207.1 $(M+H)^+$.

(*E*)-1-methoxy-4-(prop-1-enyl)benzene (2h) [cas: 4180-23-8]



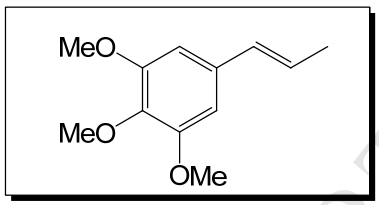
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.25 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.33 (d, J = 15.6 Hz, 1H), 6.14 – 6.03 (m, 1H), 3.79 (s, 3H), 1.85 (dd, J = 6.4, 1.6 Hz, 3H); ^{13}C NMR (δ, ppm) 158.5, 130.7, 130.2, 126.8, 123.5, 113.8, 55.2, 18.4; MS (m/z) calcd for $C_{10}H_{12}O$ 149.1, found 149.1 $(M+H)^+$.

(*E*)-1,2-Dimethoxy-4-(prop-1-enyl)benzene (2i) [cas: 6379-72-2]



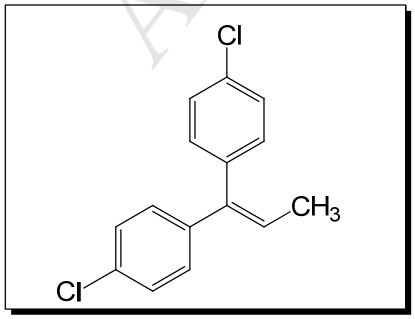
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 6.84 – 6.69 (m, 3H), 6.26 (d, J = 15.6 Hz, 1H), 6.03 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 1.79 (dd, J = 6.8, 1.6 Hz, 3H); ^{13}C NMR (δ, ppm) 148.9, 148.1, 131.1, 130.6, 123.8, 118.6, 111.1, 108.4, 55.9, 55.7, 18.3; MS (m/z) calcd for $C_{11}H_{14}O_2$ 179.1, found 179.1 $(M+H)^+$.

(*E*)-1,2,3-Trimethoxy-5-(prop-1-enyl)benzene (2j) [cas: 5273-85-8]



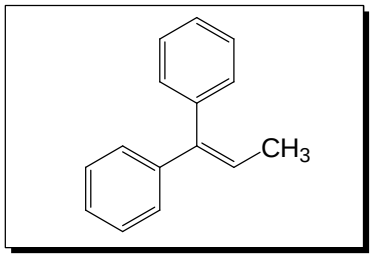
Colorless oil ; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 6.47 (s, 2H), 6.24 (d, J = 16.0 Hz, 1H), 6.13 – 6.01 (m, 1H), 3.78 (s, 6H), 3.75 (s, 3H), 1.79 (d, J = 6.8 Hz, 3H); ^{13}C NMR (δ, ppm) 153.2, 137.1, 133.7, 130.8, 125.2, 102.7, 60.8, 55.9, 18.3; MS (m/z) calcd for $C_{12}H_{16}O_3$ 209.1, found 209.1 $(M+H)^+$.

4,4'-(Prop-1-ene-1,1-diyl)bis(chlorobenzene) (2k) [cas: 3439-04-1]



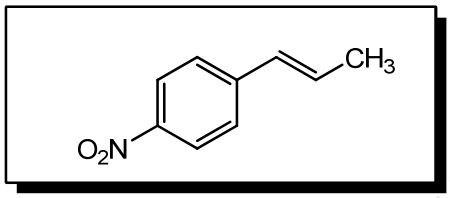
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.26 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.05 – 6.95 (m, 4H), 6.07 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (δ, ppm) 140.9, 140.2, 137.9, 132.9, 132.7, 131.3, 128.5, 128.4, 128.2, 125.2, 15.7; MS (m/z) calcd for $C_{15}H_{12}Cl_2$ 264.1, found 264.1 $(M+H)^+$.

Prop-1-ene-1,1-diyldibenzene (2l) [cas: 778-66-5]



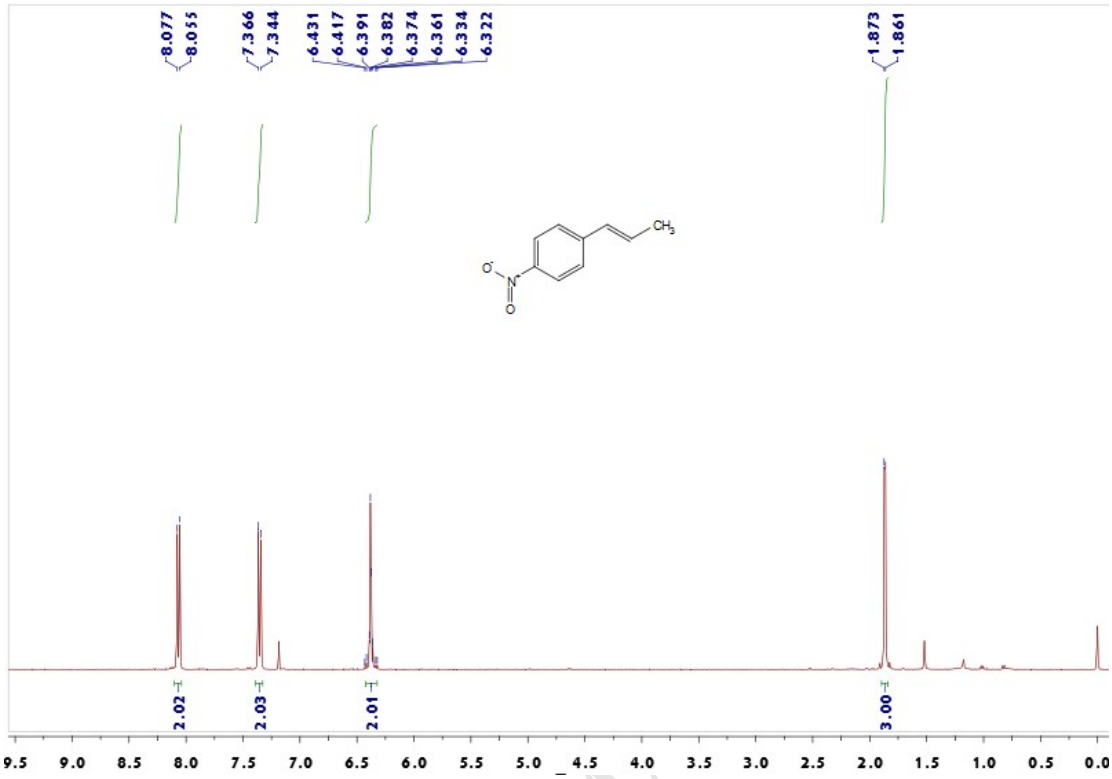
White solid, mp: 49–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.30 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.04 (m, 8H), 6.10 (q, *J* = 7.2 Hz, 1H), 1.69 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (δ, ppm) 142.9, 142.4, 140.0, 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 124.1, 15.7, MS (m/z) calcd for $C_{15}H_{14}$ 195.1, found 195.1 $(M+H)^+$.

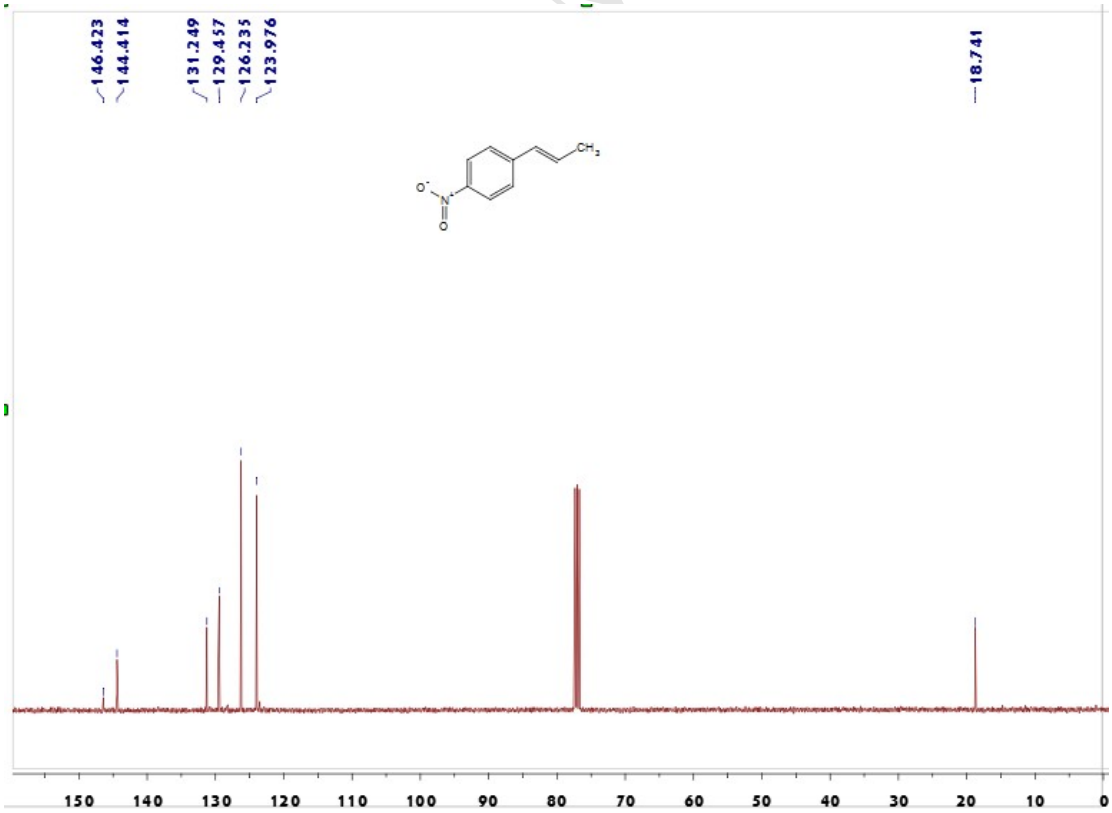
(*E*)-1-Nitro-4-(prop-1-enyl)benzene (2m) (DMSO-d_6 as reaction solvent)

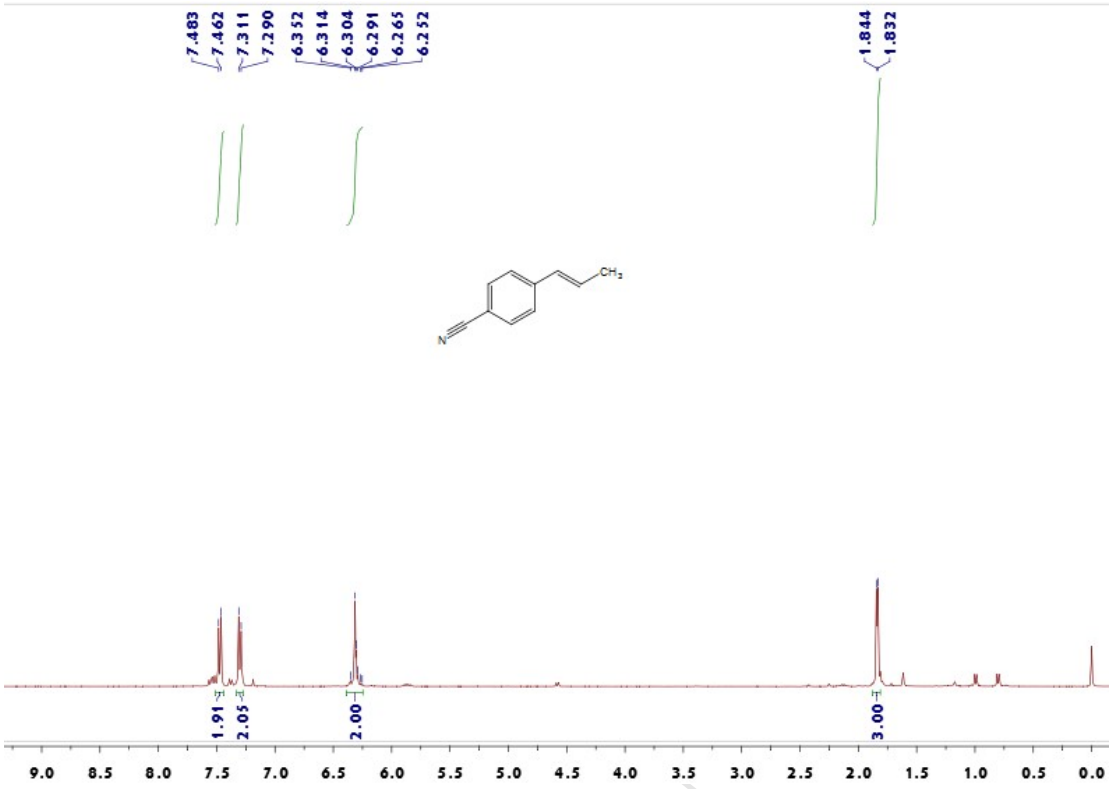


Yellow solid, mp: 92 – 93 °C; ^{1}H NMR (400MHz, $CDCl_3$) (δ, ppm) 8.15 (d, *J* = 8.8, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 6.51 – 6.43 (m, 2H), 1.95 (d, *J* = 4.4 Hz, 3H). MS (m/z) calcd for $C_9H_9NO_2$ 164.1, found 164.1 $(M+H)^+$.

Copy of HRMS and NMR Spectra for desired products:



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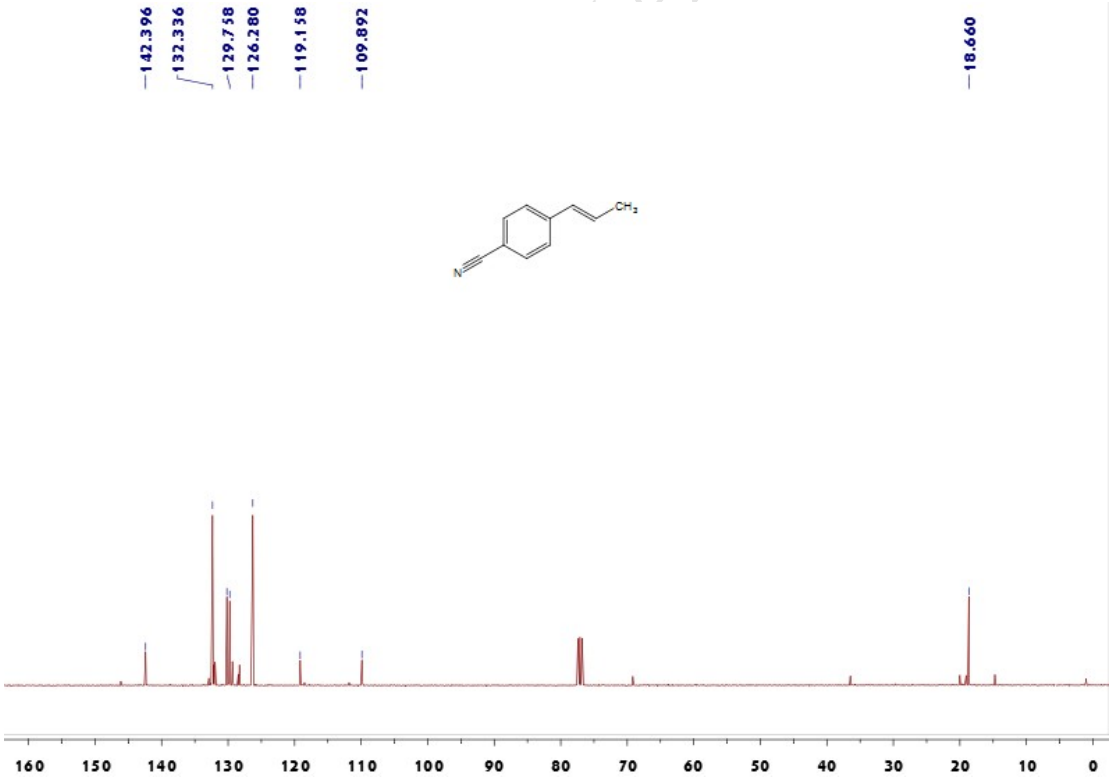
7.311
7.290
6.352
6.314
6.304
6.291
6.265
6.252
1.844
1.832
CH2
N
1.91
2.05
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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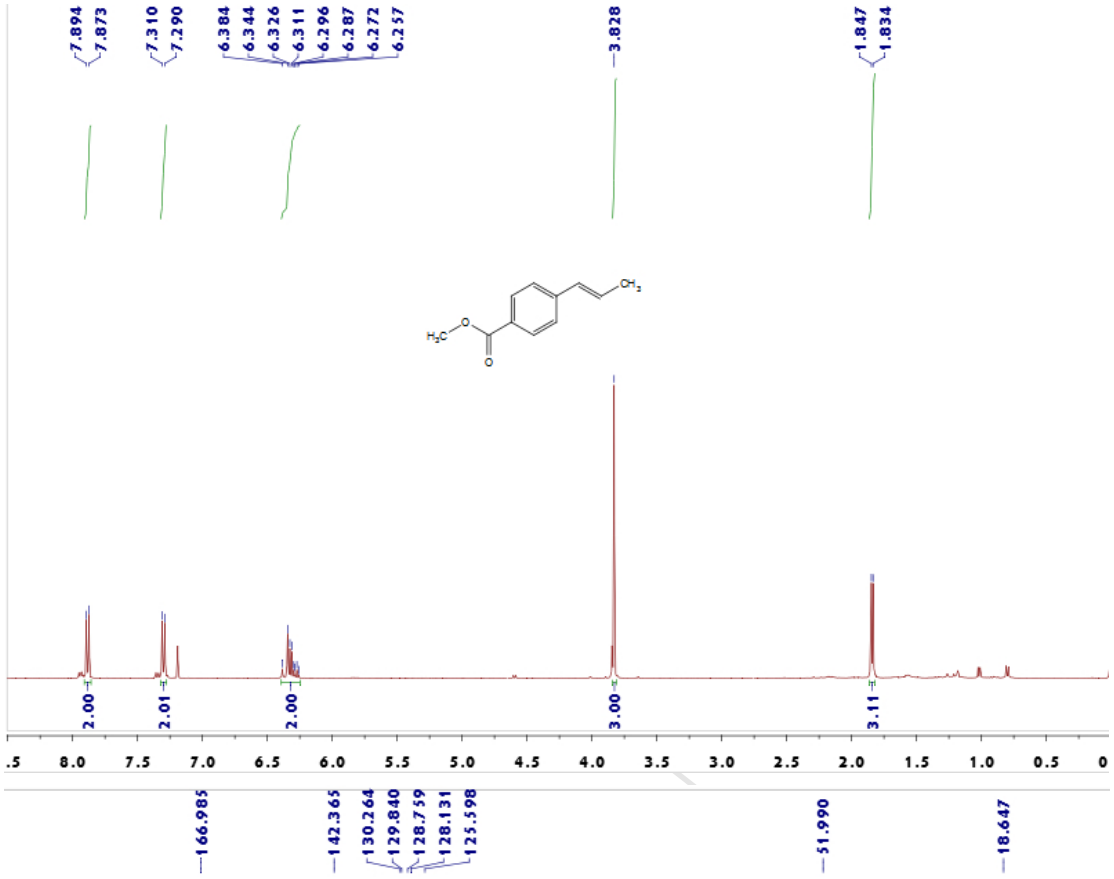
129.758
126.280
119.158
109.892
18.660
CH2
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.310
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6.344
6.326
6.311
6.296
6.287
6.272
6.257
3.828
1.847
1.834
2.00
2.01
2.00
3.00
3.11
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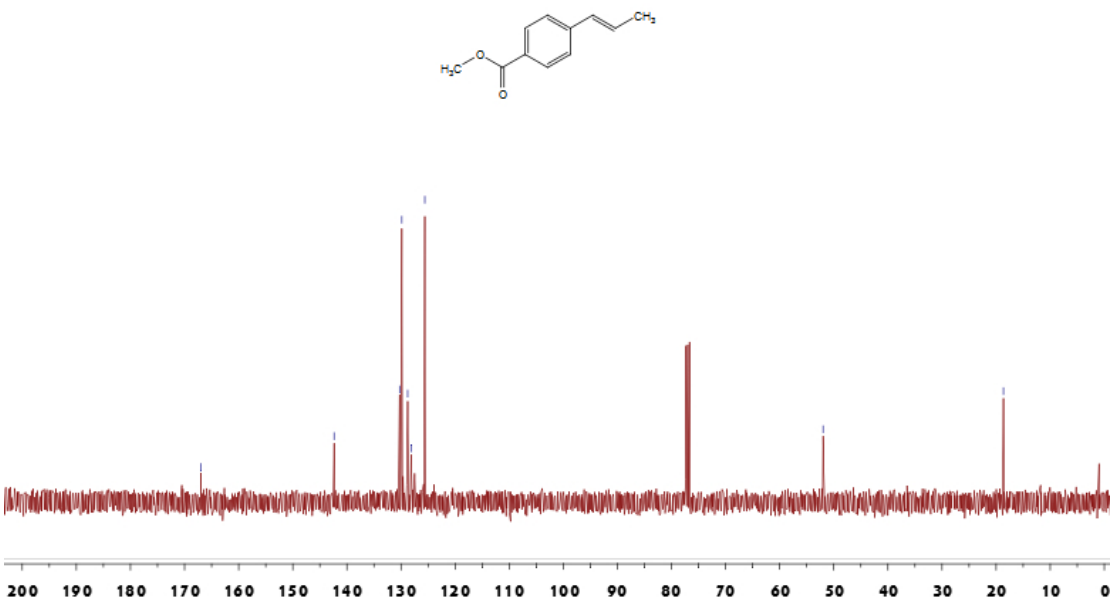
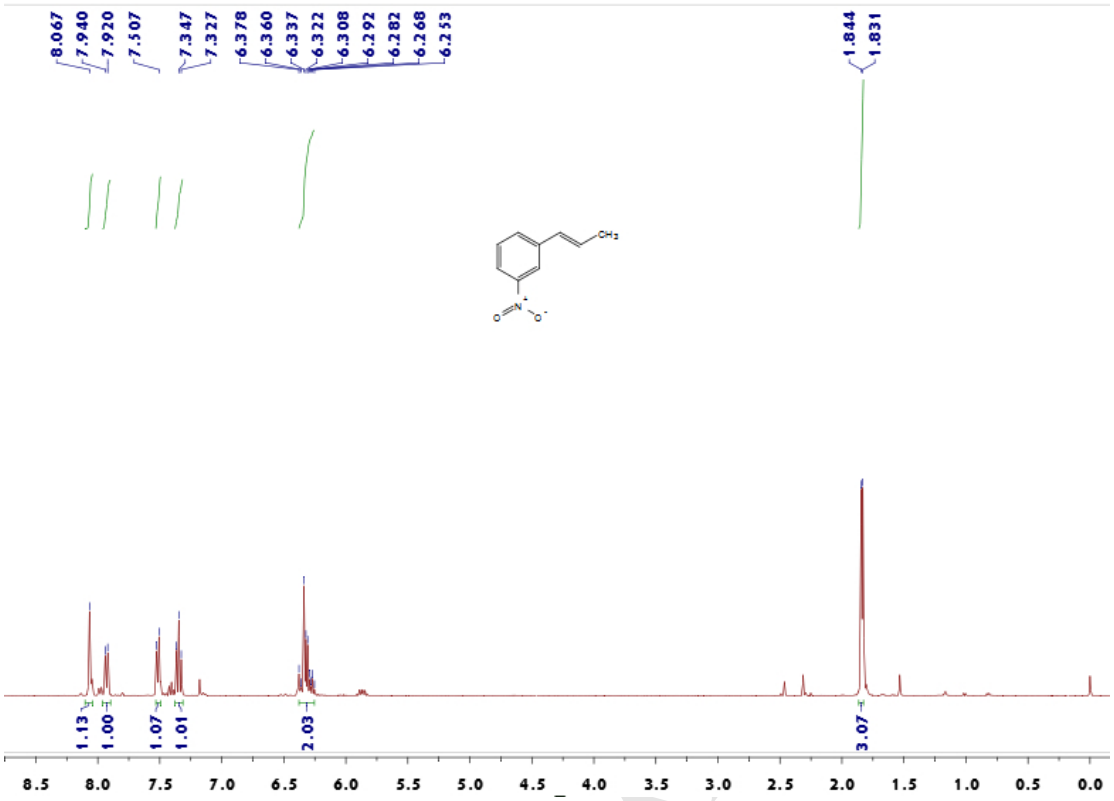
142.365
130.264
129.840
128.759
128.131
125.598
51.990
18.647

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7.920
7.507
7.347
7.327
6.378
6.360
6.337
6.322
6.308
6.292
6.282
6.268
6.253
1.844
1.831
1.13
1.00
1.07
1.01
2.03
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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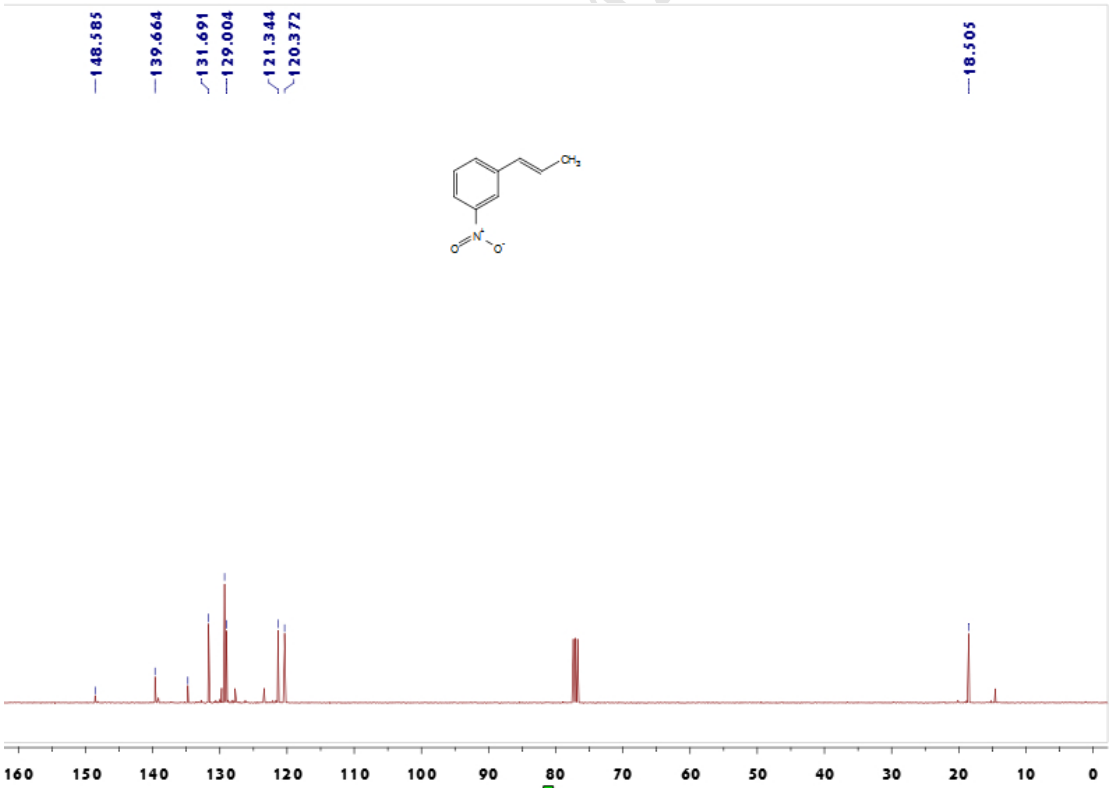
0.0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139.664
131.691
129.004
121.344
120.372
18.505
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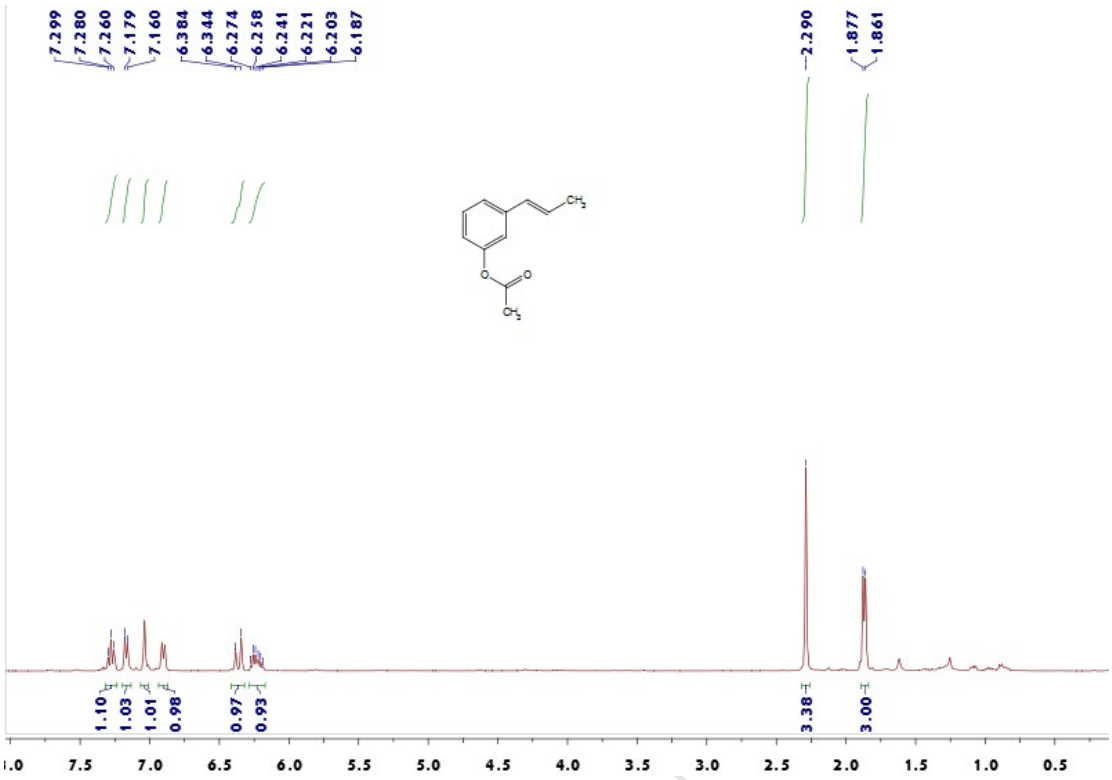
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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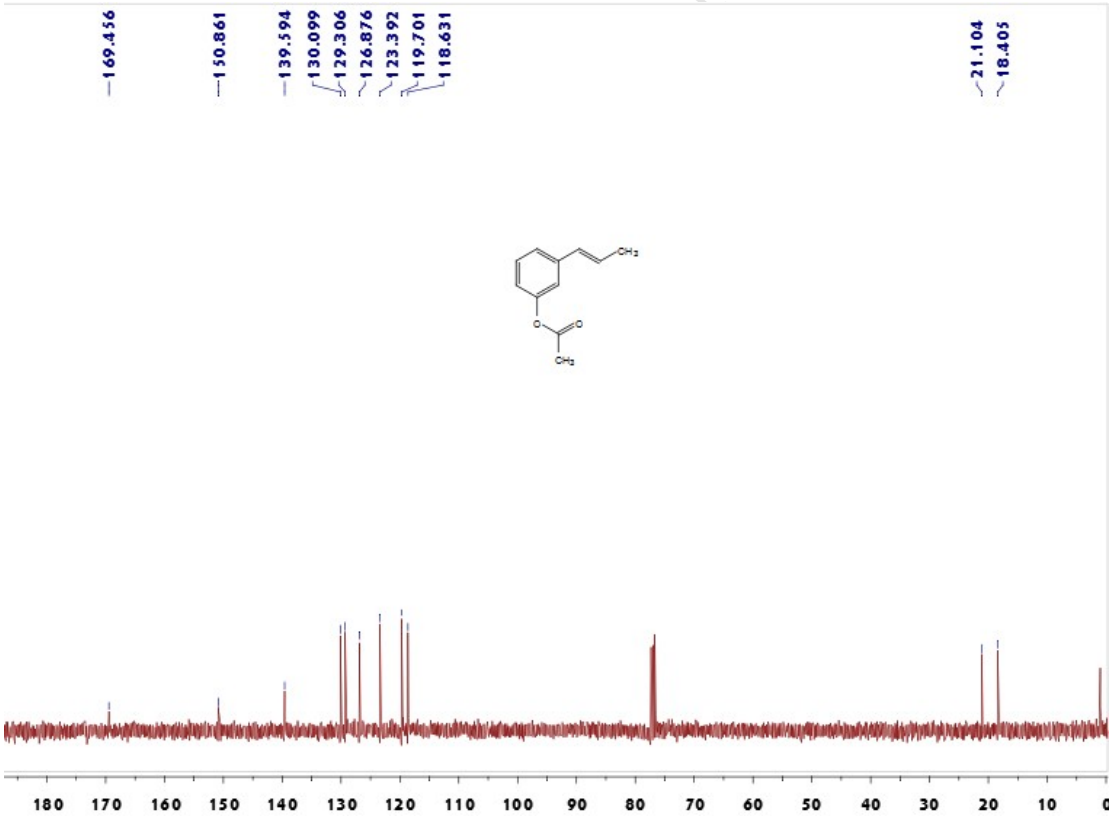
7.280
7.260
7.179
7.160
6.384
6.344
6.274
6.258
6.241
6.221
6.203
6.187
2.290
1.877
1.861
1.10
1.03
1.01
0.98
0.97
0.93
3.38
3.00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123.392
119.701
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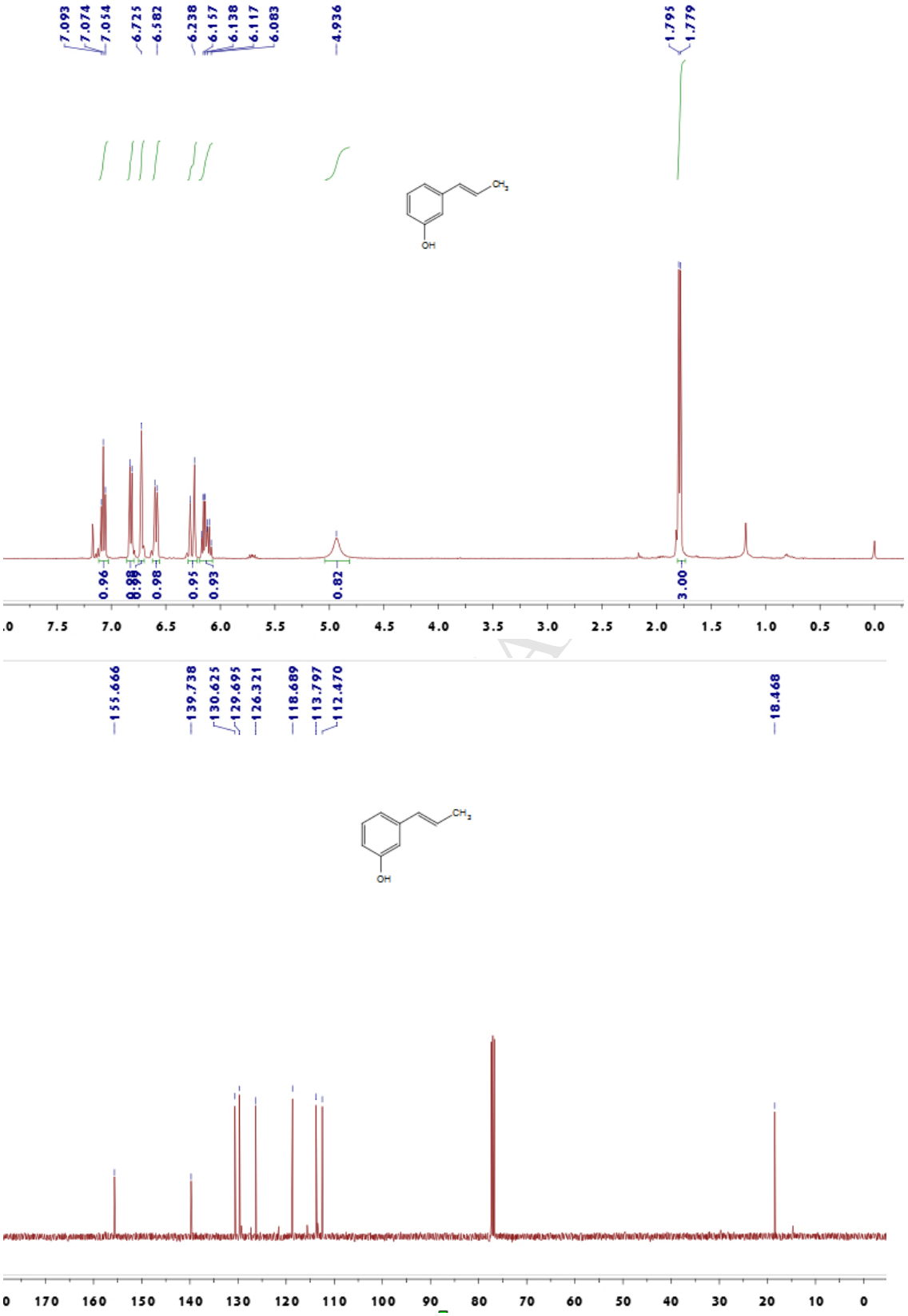
21.104
18.405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7.054
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6.582
6.238
6.157
6.138
6.117
6.083
4.936
1.795
1.779
OH
0.96
0.98
0.95
0.93
0.82
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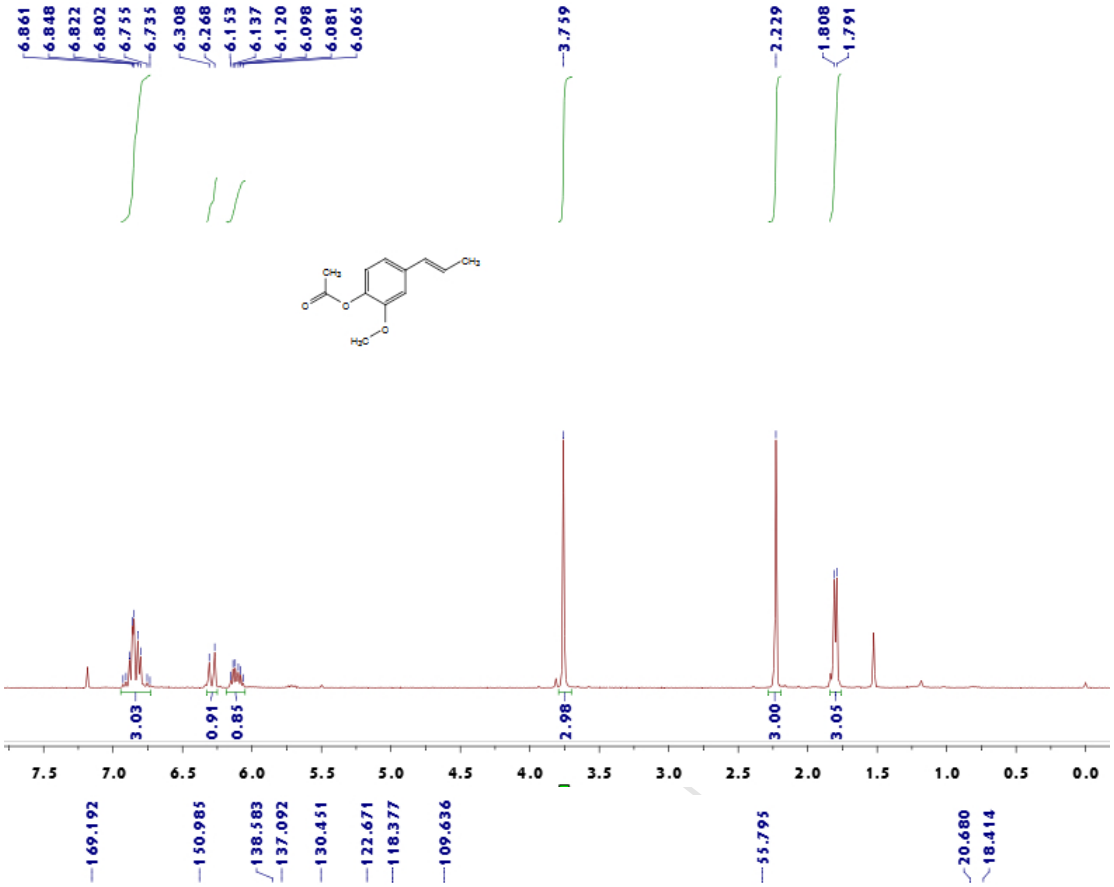
155.666
139.738
130.625
129.695
126.321
118.689
113.797
112.470
18.468
OH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6.802
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6.735
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6.268
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6.137
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6.098
6.081
6.065
3.759
2.229
1.808
1.791
3.03
0.91
0.85
2.98
3.00
3.05
7.5
7.0
6.5
6.0
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2.0
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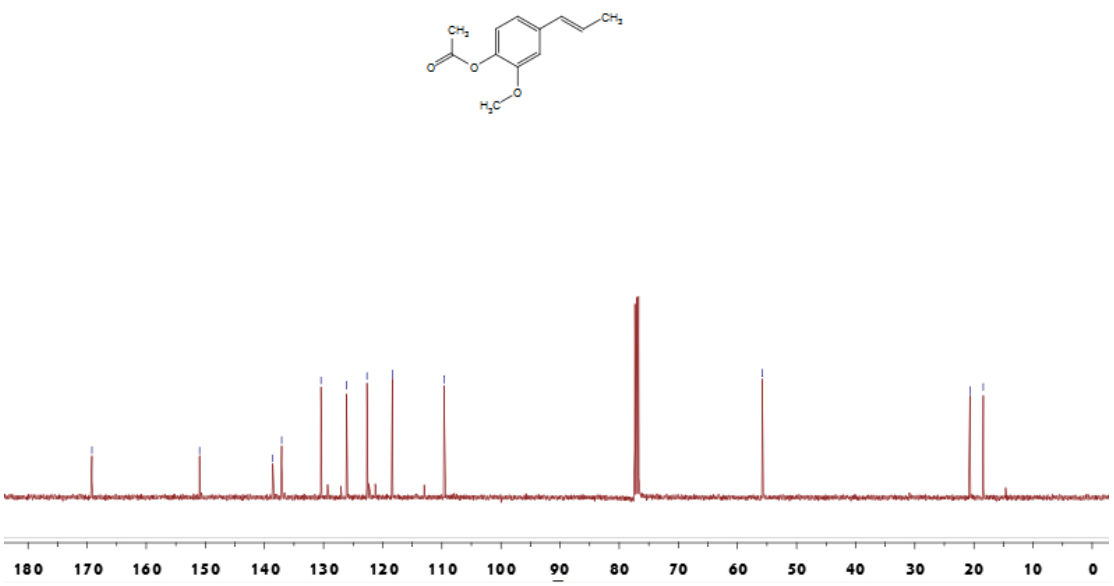
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20.680
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150
140
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120
110
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70
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30
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10
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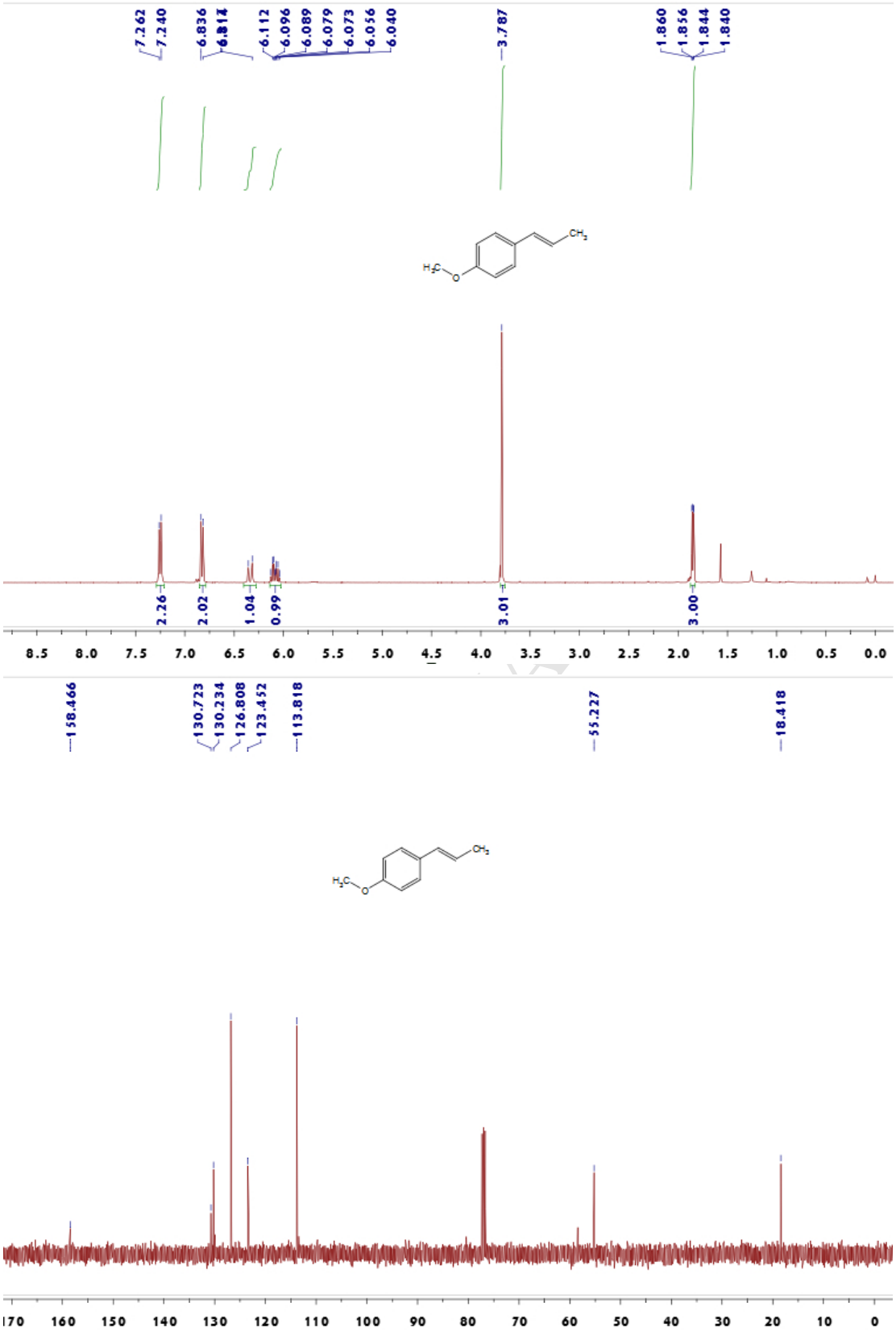
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7.240
6.836
6.814
6.112
6.096
6.089
6.079
6.073
6.056
6.040
3.787
1.860
1.856
1.844
1.840
2.26
2.02
1.04
0.99
3.01
3.00
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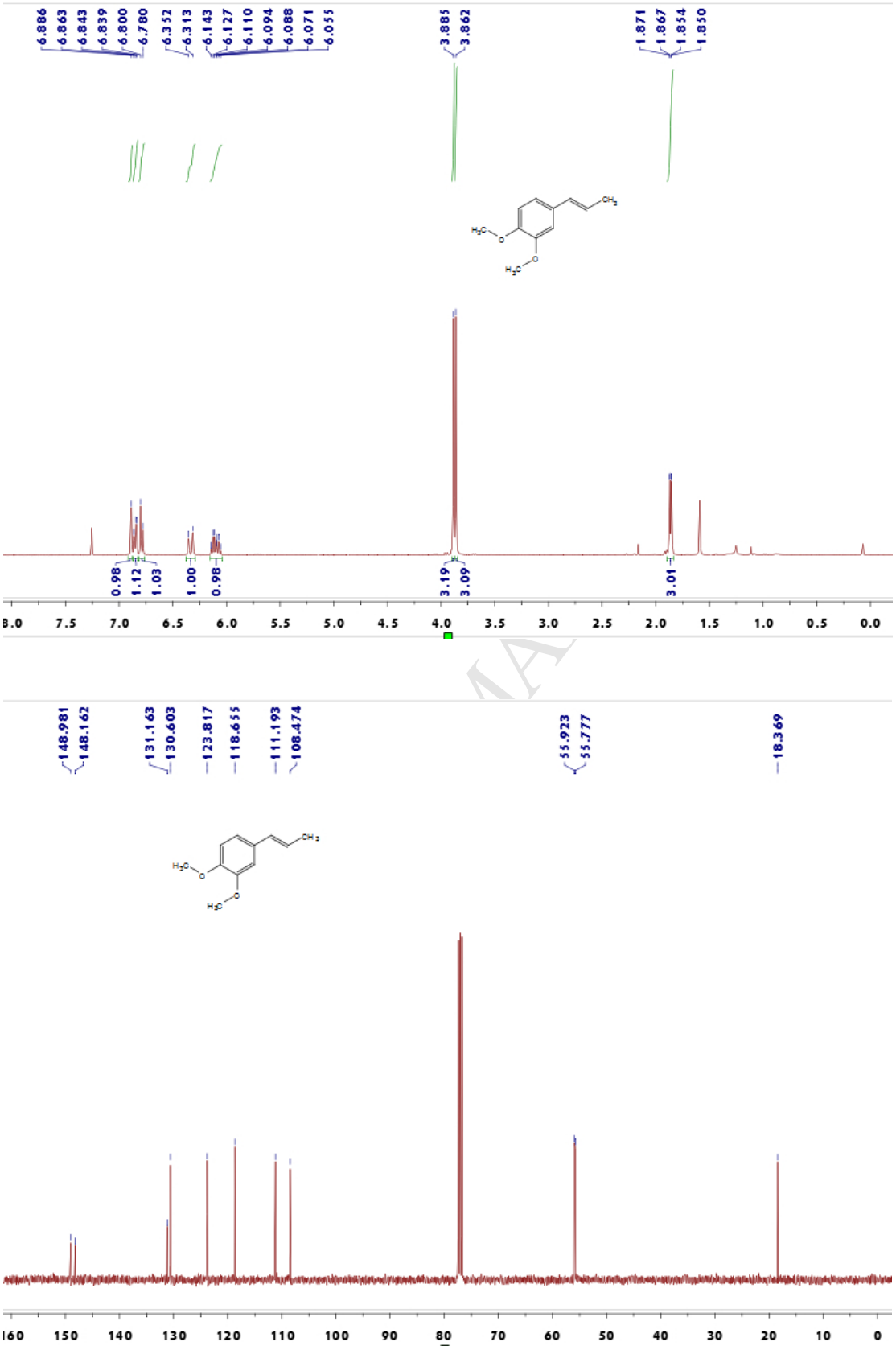
130.723
130.234
126.808
123.452
113.818
55.227
18.418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6.143
6.127
6.110
6.094
6.088
6.071
6.055
3.885
3.862
1.871
1.867
1.854
1.850
0.98
1.12
1.03
1.00
0.98
3.19
3.09
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
148.981
148.162
131.163
130.603
123.817
118.655
111.193
108.474
55.923
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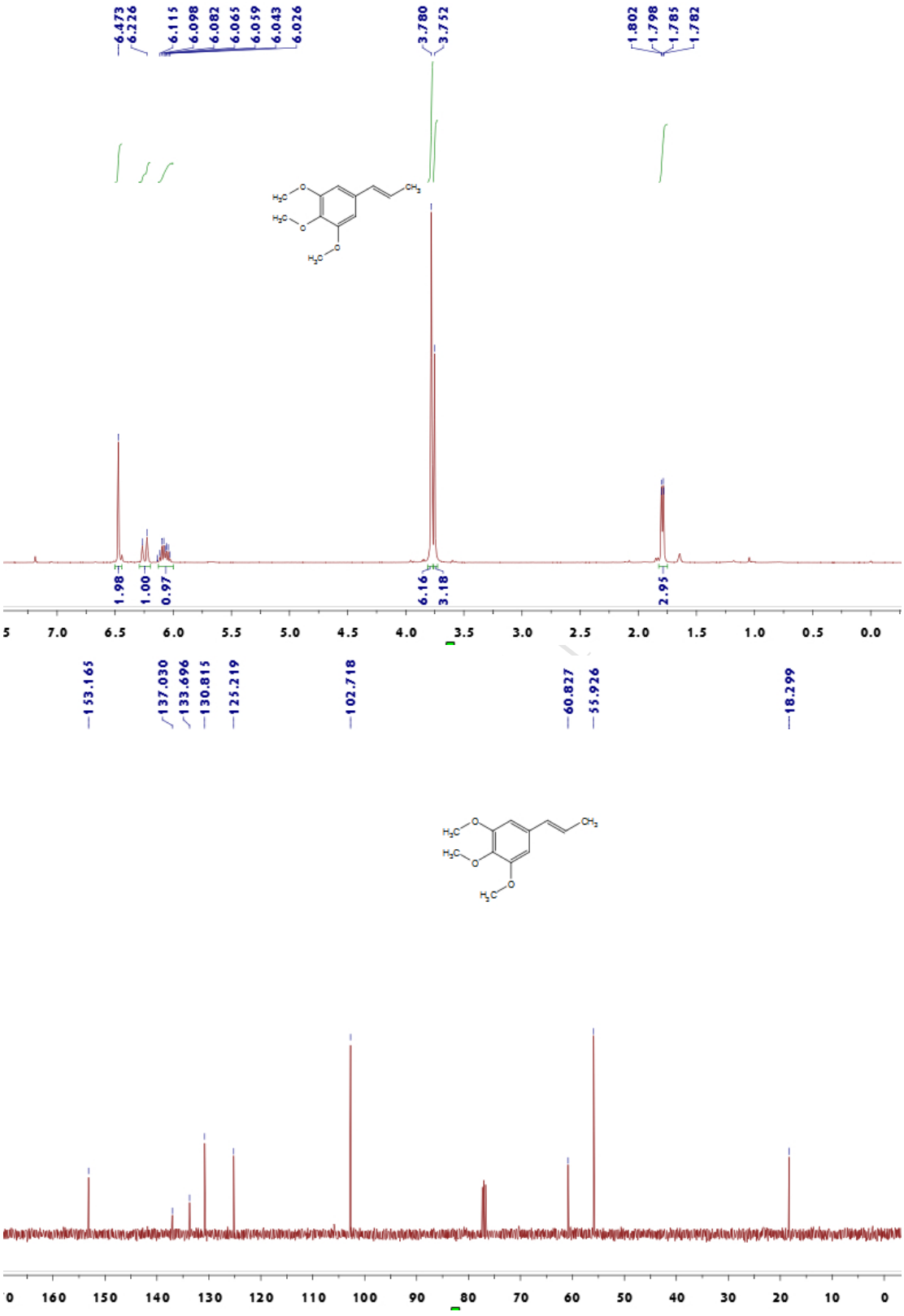
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6.082
6.065
6.059
6.043
6.026
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3.752
1.802
1.798
1.785
1.782
1.98
1.00
0.97
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3.18
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153.165
137.030
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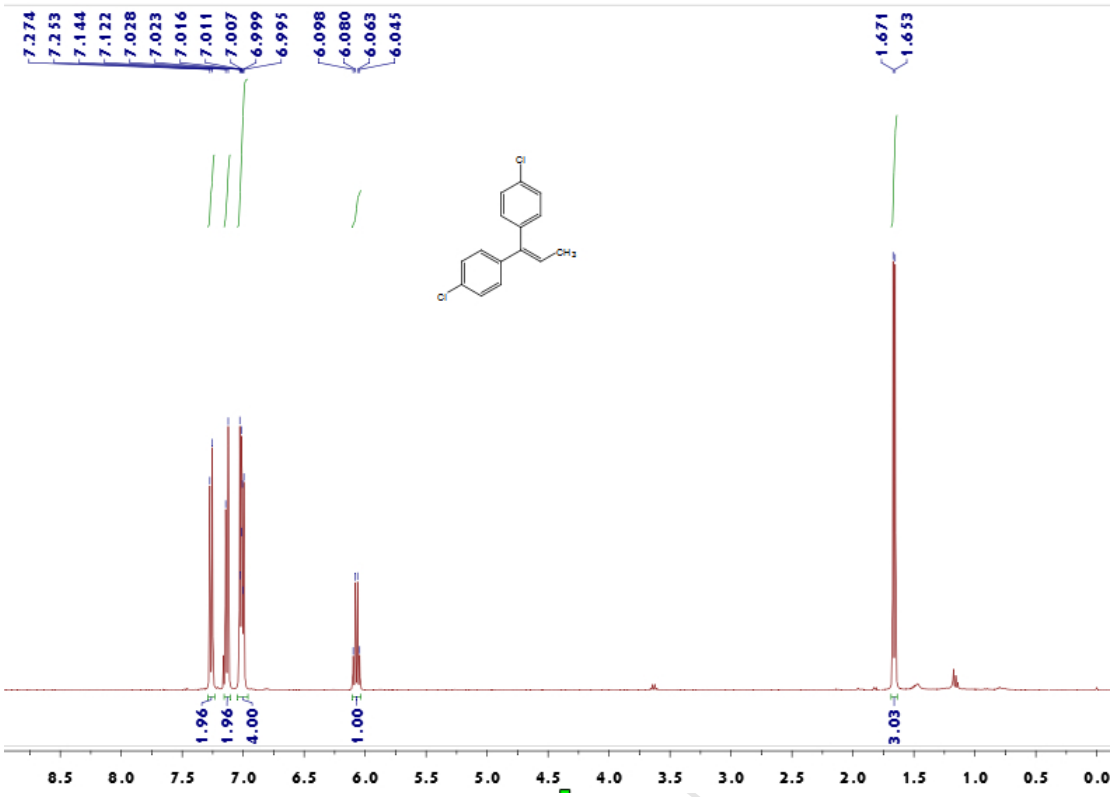
125.219
102.718
60.827
55.926
18.299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7.023
7.016
7.011
7.007
6.999
6.995
6.098
6.080
6.063
6.045
1.671
1.653
Cl
CH2
Cl
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1.96
4.00
1.00
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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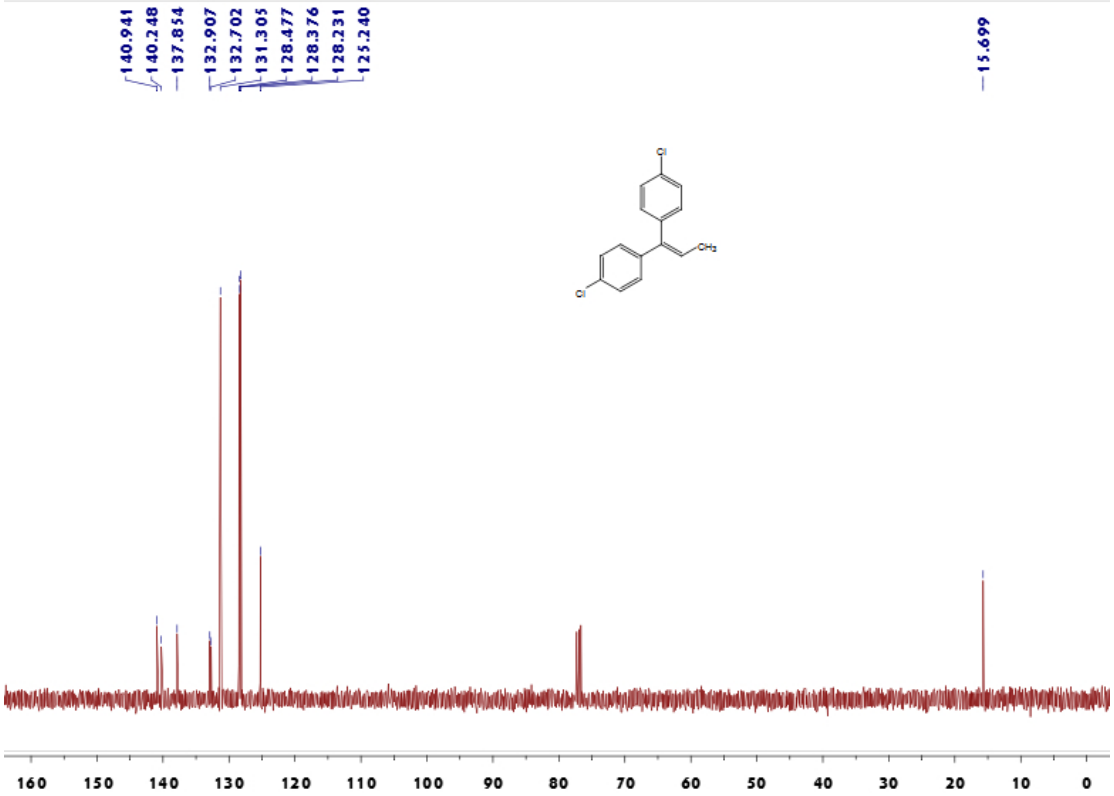
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128.376
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125.240
15.699
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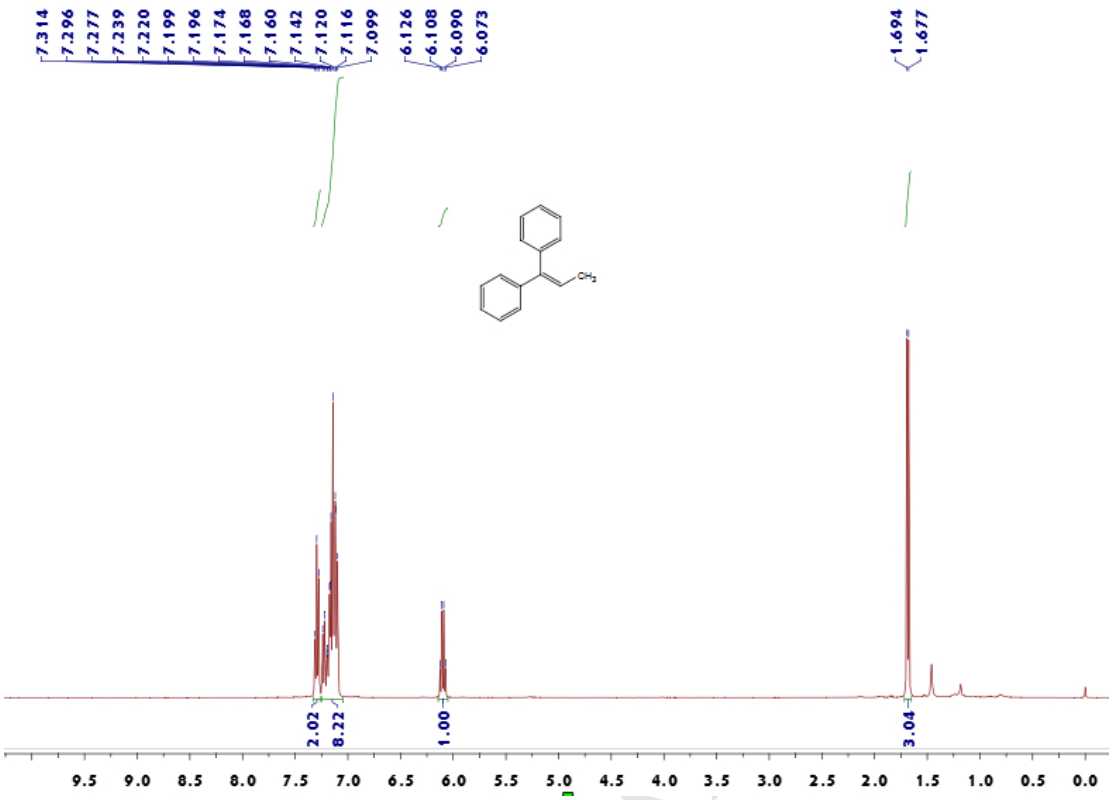
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7.196
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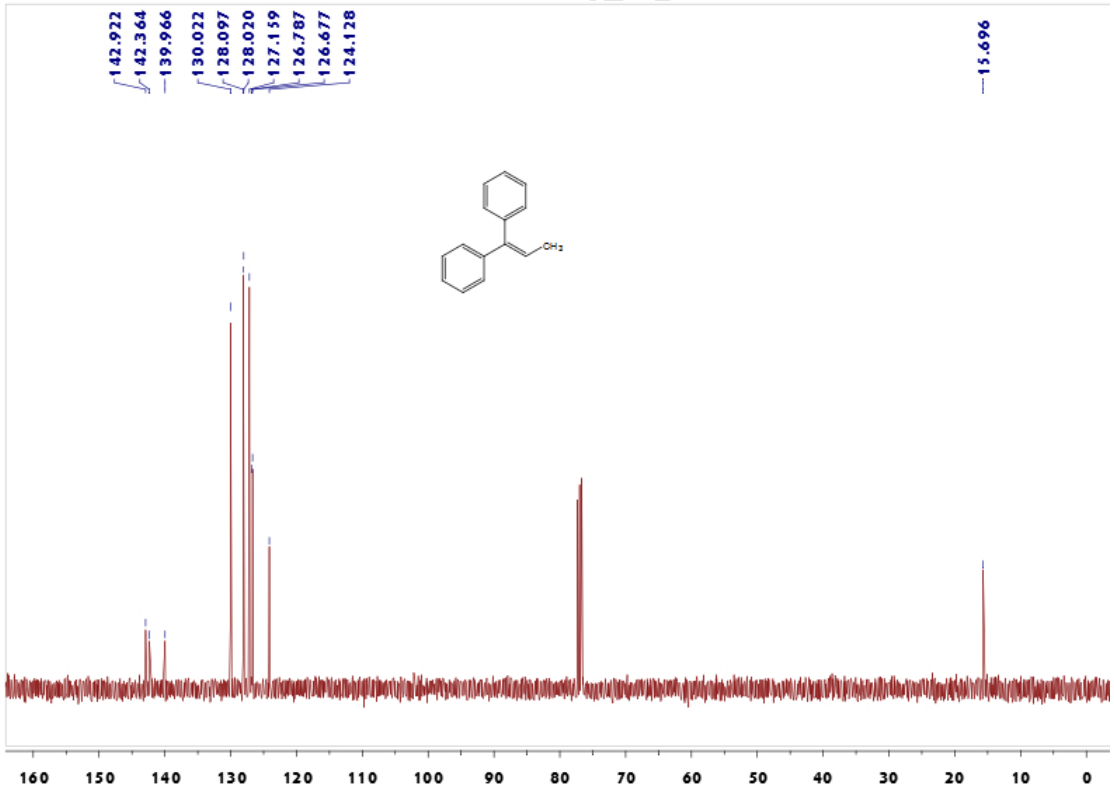
7.160
7.142
7.120
7.116
7.099
6.126
6.108
6.090
6.073
1.694
1.677
2.02
8.22
1.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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124.128
15.696
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

2m (DMSO-d_6 as reaction solvent)