Supporting Information

Aqueous protocol for allylic arylation of cinnamyl acetates with sodium tetraphenylborate using Bedford-type palladacycle catalyst

Seema Arun Ghorpade[a,b], Dinesh Nanaji Sawant*[a], Dominik Renn[a], Anna Zernickel[a], Weiyuan Du[a], Nagaiyan Sekar*[b] and Jörg Eppinger*[a]

[a]*King Abdullah University of Science and Technology, Division of Physical Sciences & Engineering, KAUST Catalysis Center (KCC), Thuwal 23955-6900, Saudi Arabia. E-mail: jorg.eppinger@kaust.edu.sa, dinesh1.sawant@gmail.com*

[b]*Department of Dyestuff Technology, Institute of Chemical Technology (Deemed University), N. Parekh Marg, Matunga, Mumbai-400019, Maharashtra, India. E-mail: n.sekar@ictmumbai.edu.in*

INDEX

1. General information:

All reactions were carried out under air atmosphere. Cinnamyl acetate used as purchased from suppliers while all other cinnamyl acetates were prepared by reported literature method.[7] If not stated otherwise, reactions were run under air atmosphere in Carousel 12 Plus™ Reaction Stations from *Radleys*, which allow simultaneously stirring and heating of up to 12 reactions. HPLC-grade water was used as the solvent. Thin-layer chromatography (TLC) was performed on silica coated glass plates (Merck 60, F-254) with detection by irradiation of 254 nm UV light. Product was purified by simple purification using silica gel (60-120) mesh. All yields reported in Table 5 referred to NMR yields and products are purified by simple purification and confirmed by NMR and GCMS. While yields reported in Table 1-4 are GC yields. For the combination of gas chromatography with mass spectroscopic detection (GC-MS), a GC from Agilent 7890 A with an Agilent 5975C instrument for MS detection (inert XL EI/CI MSD with Triple-Axis Detector, EI, 70 eV) was used. GC/MS Method (80-280 °C DB-5MS): Initial 80 °C, 3 min; Ramp 25 °C/min, 280 °C, 6 min; total 17 min. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer at 295K in $CDCl_3$. Chemical shifts are reported in parts per million (δ) relative to tetamethylsilane as internal standard or to the used solvent. J (coupling constant) were reported in Hz, splitting patterns of proton are described as s (singlet), d (doublet), t (triplet), m (multiplet). All products obtained and discussed in this work have been previously reported (except product **3h** and **3i)** and characterized by suitable technique such as ^{1}H NMR, ^{13}C NMR, MS and were compared with previously reported data.

2. Experimental Procedures:

2.1 Synthesis of the palladacycle catalyst A

Step 1. ([1,1'-Biphenyl]-2-yloxy)diisopropylphosphine (Ligand A)[1]

In a Schlenk tube 2-phenylphenol (1.70 g, 10.0 mmol, 1.0 eq.) was dissolved in 50 mL of dry toluene and triethylamine (1.51 g, 14.9 mmol, 1.5 eq.) was added. After stirring the solution for 15 min at r.t. chlorodiisopropylphosphine (1.51 g, 9.9 mmol, 0.95 eq.) was added. The reaction mixture was refluxed for 16 h. After cooling to r.t. pentane (50 mL) was added. A white solid precipitated, which was removed by filtration through a pad of Celite® and washed with pentane (3 × 10 mL). The combined organic fractions were evaporated to dryness *in vacuo*yielding the phosphiniteligand (2.63 g, 92%), which was used without further purification.

Step II. Synthesis of [{Pd(μ-Cl){κ²-P,C-P(iPr)₂(OC₆H₃-2-Ph)}}₂] (Catalyst A)[1]

In a Schlenk tube ([1,1'-Biphenyl]-2-yloxy)diisopropylphosphine (2.63 g, 9.9 mmol, 1.0 eq.)and $PdCl_2$ (1.75 g, 9.9 mmol, 1.0 eq.) were dissolved in dry toluene (50 mL). The reaction mixture was refluxed for 19 h. After cooling to r.t. the solvent was removed *in vacuo.* The residue was extracted with DCM (20 mL) and filtered through a pad of Celite®. The product was precipitated from the organic solution by addition of ethanol, collected by filtration and recrystallized from DCM/EtOH.

2.2 General procedure for allylic arylation: In a 10 mL glass tube (provided with Carousel 12 Plus™ from *Radleys*) **Cat. A** (0.002 mol %, 0.1 mL stock solution in Dichloromethane) were added and Dichloromethane is evaporated under vacuum. Then corresponding (*E*)-cinnamyl acetate (**1a**, 0.20 mmol), and water (2 mL) was added followed by addition of $NaBPh_4$ (**2a**, 0.40 mmol). After addition of reactants the reaction tube containing reaction mixture was closed under air atmosphere (can be kept open as well) and magnetically stirred at 50 °C for 8 hours under air atmosphere. After completion, the reaction mixture was cooled to room temperature. Then the product was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated on rotatory evaporator to afford the crude

product. Next, product yield was checked by NMR using internal standard in $CDCl_3$ solvent. To avoid use of excess of solvents instead of column chromatography a simple purification was performed to confirm the products. The crude product was loaded on silica and transferred to sintered funnel, then simply washed with solvent heptane (5 mL X 5) followed by subsequently increasing polarity using ethyl acetate if necessary. All fractions were analyzed on GC-MS and pure fractions were mixed together and spectroscopic analysis such as GC-MS, ^1H and ^{13}C NMR were performed to confirm the products.

3. Effect of Concentration

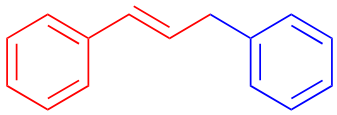
Table 1. Effect of solvent volume (Concentration)[a]

Entry	Water (mL)	**3a** yield[b] [%]
1	5	98
2	4	98
3	3	98
4	2	98

[a]Reaction Conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), Cat. A (5 mol %), water, 30 °C, 16 h, under air atmosphere. [b]GC yield.

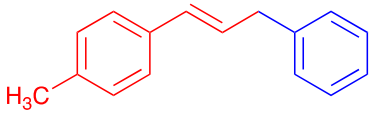
4. <u>Spectroscopic data of products:</u>

(E)-Prop-1-ene-1,3-diyldibenzene ***(3a):***[2]



GC–MS m/z (% relative intensity) 194 (M^+, 100), 193 (60),179 (48), 178 (38), 165 (15), 117 (16), 116 (38), 115 (65), 91 (25); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.21 (m, 10H), 6.57 (d, *J* = 15.5 Hz, 1H), 6.47 (dd, *J* = 15.5, 7.8 Hz, 1H), 3.65 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ140.33, 137.64, 131.25, 129.39, 128.85, 128.68, 127.28, 126.36, 126.31, 39.54.

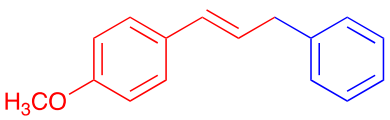
(E)-1-Methyl-4-(3-phenylprop-1-en-1-yl)benzene ***(3b):***[2]



GC–MS m/z (% relative intensity) 208 (M^+, 100), 207 (19), 194 (16), 193 (99), 178 (36), 129 (16), 116 (25), 115 (88), 91 (29); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 8H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.34 (dt, *J* = 15.7, 6.8 Hz, 1H), 3.58 (d, *J* = 6.7

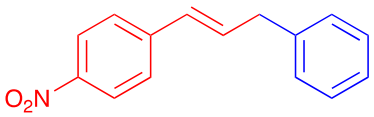
Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.34, 136.83, 134.69, 130.92, 129.19, 128.66, 128.45, 128.16, 126.12, 126.01, 39.36, 21.15.

(E)-1-Methoxy-4-(3-phenylprop-1-en-1-yl)benzene ***(3c):***[2]



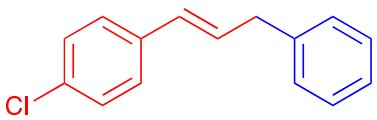
GC–MS m/z (% relative intensity) 224 (M^+, 100), 223 (27), 209 (20), 193 (27), 178 (16), 165 (16), 121 (18), 115 (44), 91 (20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 7H), 6.90 – 6.83 (m, 2H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.24 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.82 (s, 3H), 3.56 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.03, 140.65, 130.57, 130.51, 128.84, 128.65, 127.42, 127.25, 126.30, 114.12, 55.48, 39.54.

(E)-1-Nitro-4-(3-phenylprop-1-en-1-yl)benzene ***(3d):***[2]



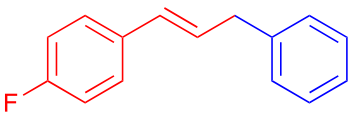
GC–MS m/z (% relative intensity) 239 (M^+, 100), 222 (34), 193 (27), 192 (78), 191 (46), 189 (18), 178 (45), 165 (28), 115 (76), 91 (40); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.20 (m, 4H), 6.64 – 6.55 (m, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 3.63 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.61, 143.94, 139.01, 134.61, 128.71, 128.68, 126.58, 126.54, 123.97, 123.63, 39.46.

(E)-1-Chloro-4-(3-phenylprop-1-en-1-yl)benzene ***(3e):***[3]



GC–MS m/z (% relative intensity) 228(M^+,64), 193 (87), 192 (16), 191 (16), 178 (39), 165 (16), 116 (21), 115 (100), 91 (23); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.21 (m, 9 H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.39 – 6.31 (m, 1H), 3.56 (d, *J* = 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.05, 136.1,132.83, 130.2, 130.02, 128.85, 128.81, 128.73, 127.51, 126.47, 39.50.

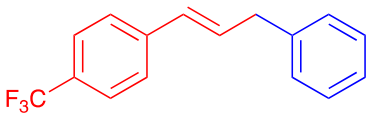
(E)-1-Fluoro-4-(3-phenylprop-1-en-1-yl)benzene ***(3f):***[3]



GC–MS m/z (% relative intensity) 161.01, 140.02, 133.84, 130.05, 129.21, 128.85, 128.72, 127.90, 126.43, 115.66, 115.45, 39.50; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.30 –

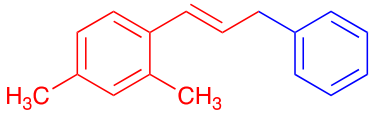
7.18 (m, 3H), 7.09 – 6.96 (m, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.7, 6.8 Hz, 1H), 3.57 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212 (M^+, 100), 211 (54), 197 (35), 196 (28), 134 (21), 133 (100), 116 (17), 115 (38), 109 (17), 91 (19).

(E)-1-(3-Phenylprop-1-en-1-yl)-4-(trifluoromethyl)benzene ***(3g):***[2]



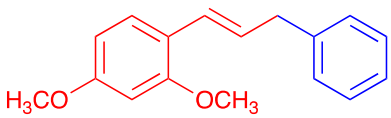
GC–MS m/z (% relative intensity) 262 (M^+, 100), 261 (26), 247 (13), 193 (62), 183 (17), 178 (27), 116 (17), 115 (64), 91 (28); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.35-7.27 (m, 5H), 6.52 – 6.48 (m, 2H), 3.60 (d, J = 3.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.90, 139.50, 132.10, 129.78, 128.67, 128.58, 126.37, 126.22, 125.45, 125.41, 39.34.

(E)-2,4-dimethyl-1-(3-phenylprop-1-en-1-yl)benzene ***(3h):***



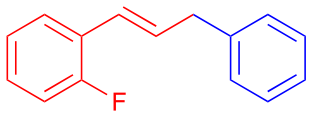
GC–MS m/z (% relative intensity) 222(M^+, 98), 208 (18), 207 (100), 192 (29), 129 (37), 128 (16), 116 (20), 115 (64), 91 (25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.27 (dd, *J* = 15.2, 6.7 Hz, 3H), 7.04 (s, 2H), 6.90 (s, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.41 – 6.33 (m, 1H), 3.58 (d, *J* = 6.2 Hz, 2H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.52, 138.13, 137.59, 131.38, 129.04, 128.88, 128.66, 127.37, 126.33, 124.24, 39.59, 21.46.

(E)-2,4-Dimethoxy-1-(3-phenylprop-1-en-1-yl)benzene ***(3i):***



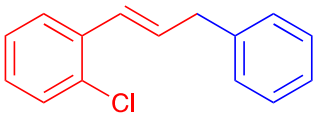
GC–MS m/z (% relative intensity) 254 (M^+, 100), 253 (25), 239 (23), 223 (42), 179 (10), 178 (16), 151 (15), 115 (30), 91 (23); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.23 (m, 6H), 6.79 (d, *J* = 15.9 Hz, 1H), 6.50 (dd, *J* = 6.9, 2.2 Hz, 2H), 6.29 (dd, *J* = 8.7, 7.1 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.61 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.06, 157.54, 140.87, 128.43, 127.72, 127.31, 126.02, 125.45, 119.65, 104.72, 98.48, 55.47, 55.39, 39.92.

(E)-1-Fluoro-2-(3-phenylprop-1-en-1-yl)benzene ***(3j):***[4]



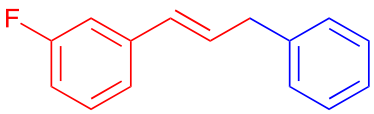
GC–MS m/z (% relative intensity) 212 (M^+, 100), 211 (56), 197 (40), 196 (28), 134 (16), 133 (32), 116 (16), 115 (34), 91 (20).

(E)-1-Chloro-2-(3-phenylprop-1-en-1-yl)benzene ***(3k):***[5]



GC–MS m/z (% relative intensity) 228(M^+, 100), 194 (15), 193 (100), 192 (18), 191 (20), 178 (44), 165 (17), 115 (57).

(E)-1-fluoro-3-(3-phenylprop-1-en-1-yl)benzene ***(3l)***[6]



GC–MS m/z (% relative intensity) 212 (M^+, 100), 211 (54), 197 (41), 196 (30), 134 (22), 133 (37), 116 (18), 115 (38), 91 (21).

5. <u>References:</u>

1 (a) A. N. Marziale, Stefan H. Faul, T. Reiner, S. Schneider and J. Eppinger, *Green Chem.,* 2010, **12**, 35; (b) A. N. Marziale, D. Jantke, S. H. Faul, T. Reiner, E. Herdtweck and J. Eppinger, *Green Chem.*, 2011, **13**, 169.

2 G. Hamasaka, F. Sakurai and Y. Uozumi, *Chem. Comm.,* 2015, **51**, 3886.

3 Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, Y. *J. Am. Chem. Soc.,* 2012, **134**, 3190.

4 X. Zhang, W. Zeng, Y. Yang, H. Huang and Y. Liang, *Synlett*, 2013, **24**, 1687.

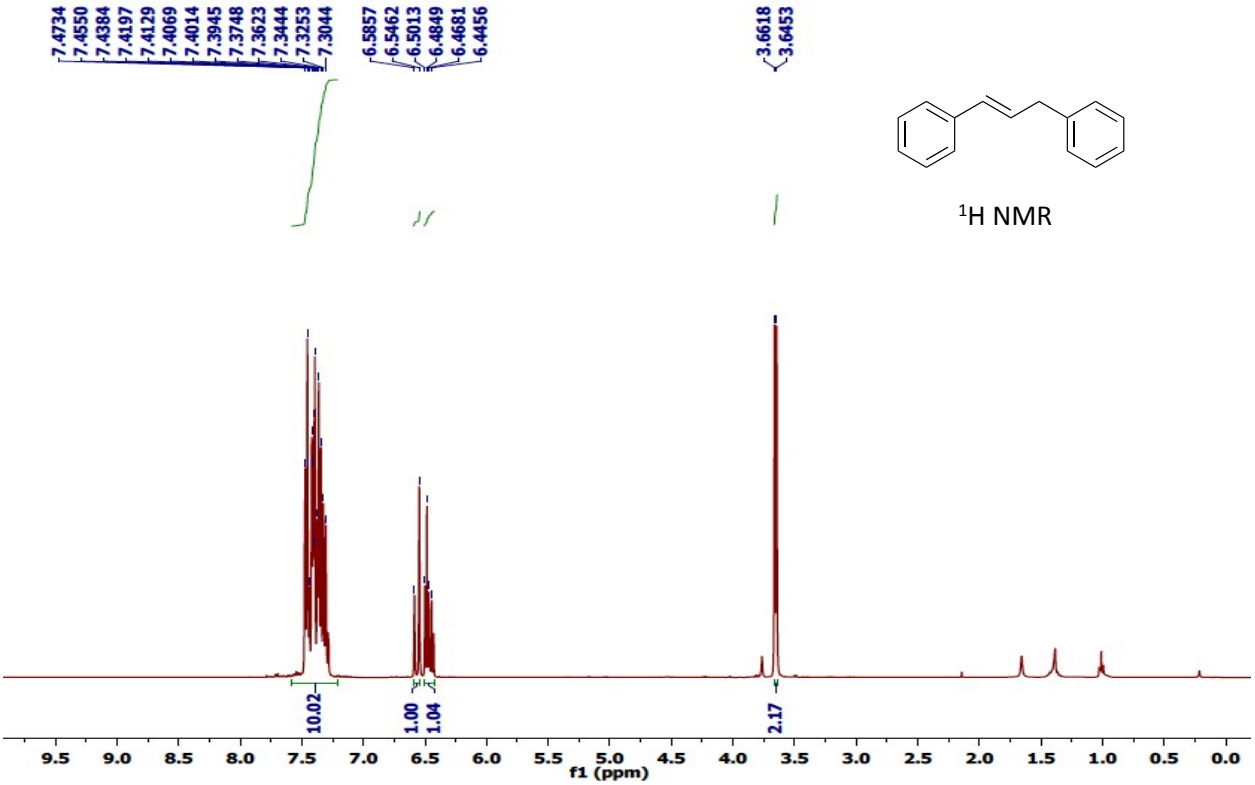
5 N. M. L. Rao, D. Banerjee and S. Giri, *J. Organomet. Chem,* 2010, **695**,1518.

6 J. Liu, X. Wen, C. Qin, X. Li, X. Luo, A. Sun, B. Zhu, S. Song and N. Jiao, *Angew. Chem. Int. Ed.,* 2017, **56**, 11940.

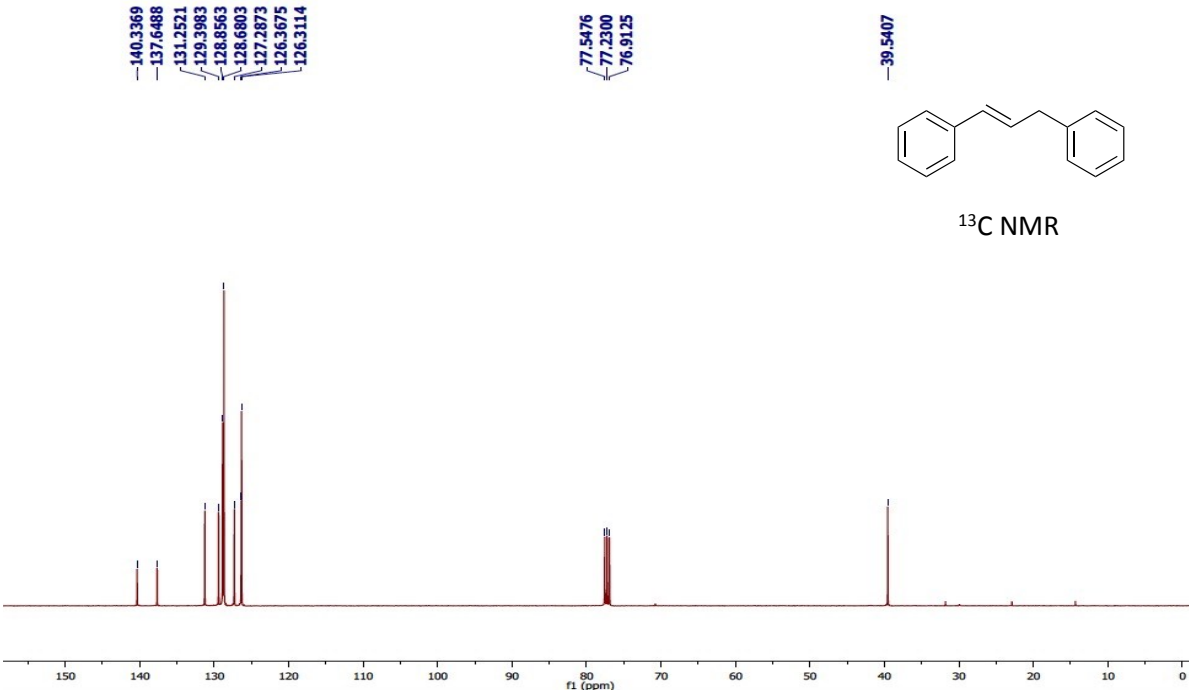
7 D. Pan, A. Chen, Y. Su, W. Zhou, S. Li, W. Jia, J. Xiao, Q. Liu, L. Zhang and N. Jiao, *Angew. Chem. Int. Ed.,* 2008, **47**, 4729.

6. Analytical Spectra's

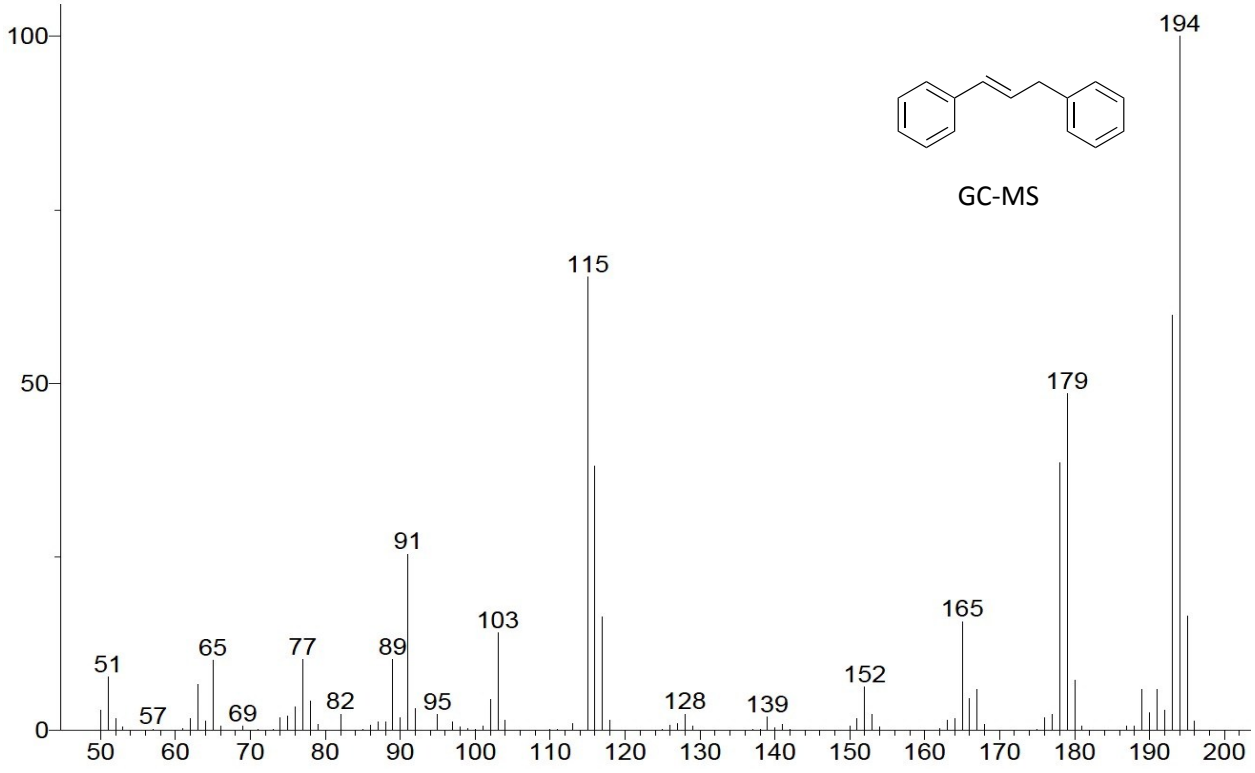
(3a) (*E*)-prop-1-ene-1,3-diyldibenzene



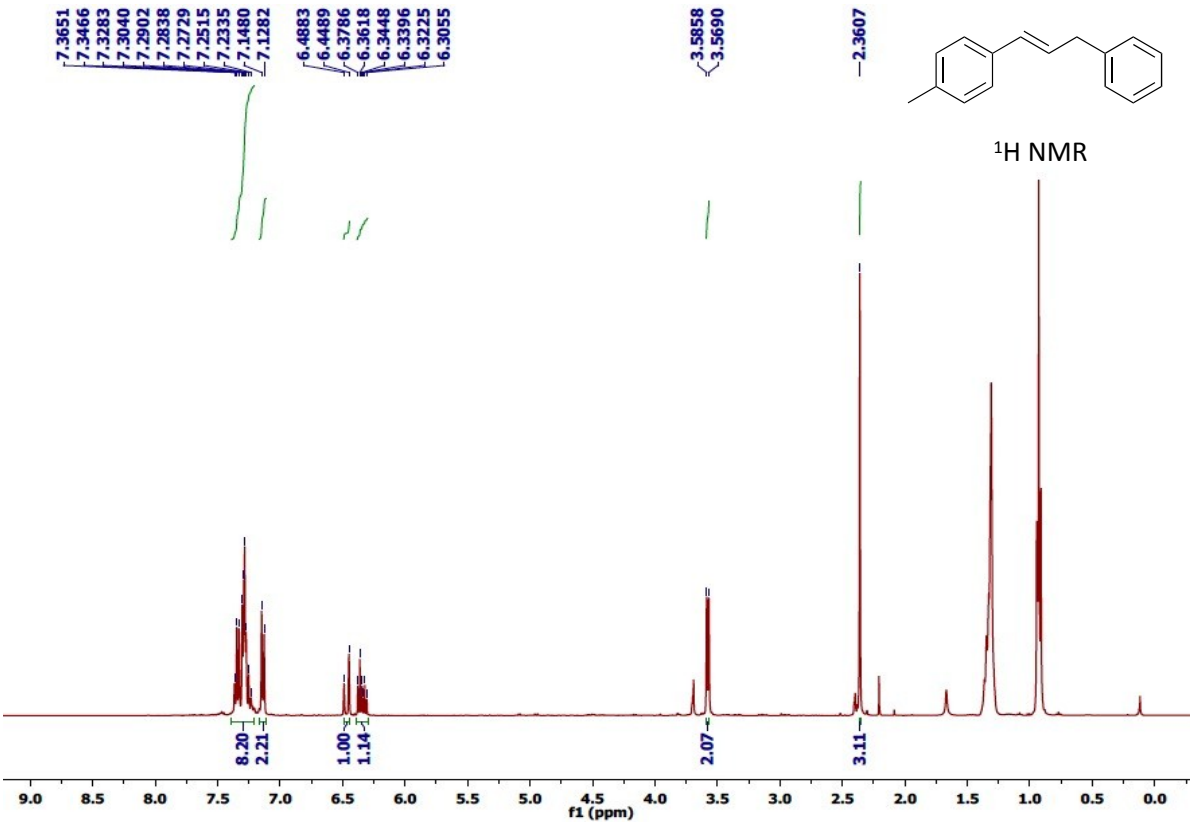
^{1}H NMR

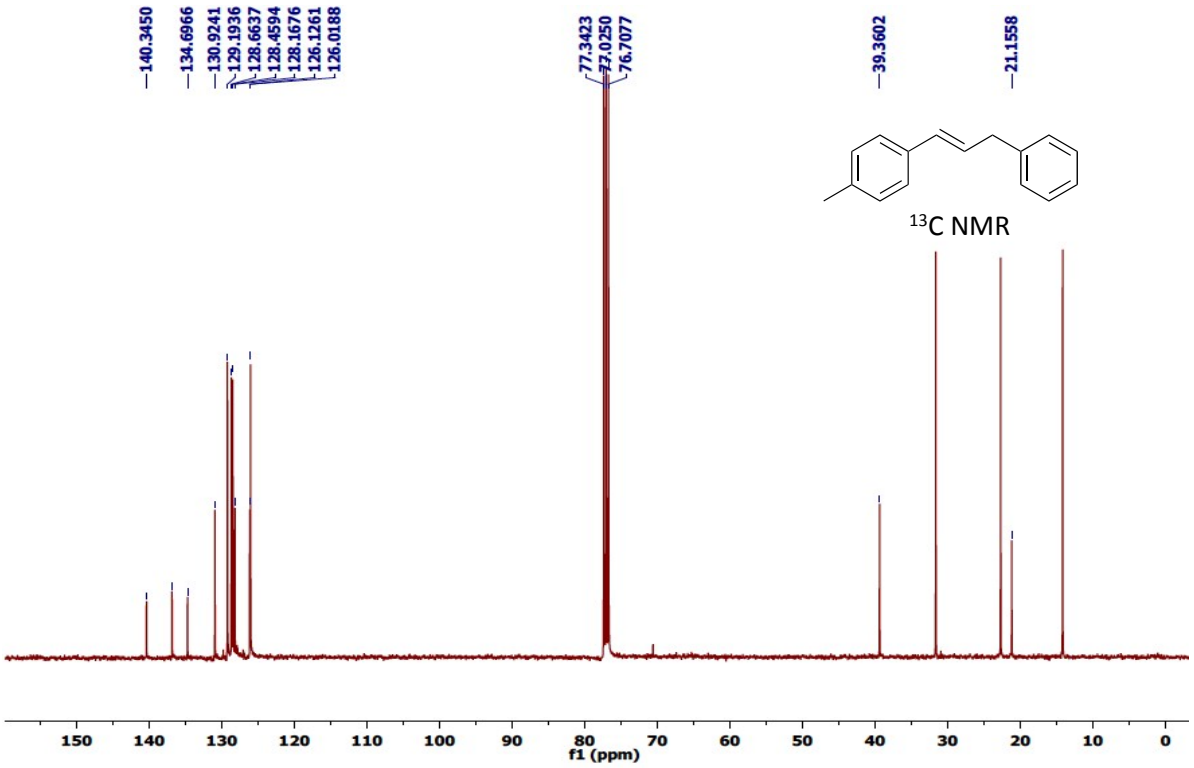


^{13}C NMR

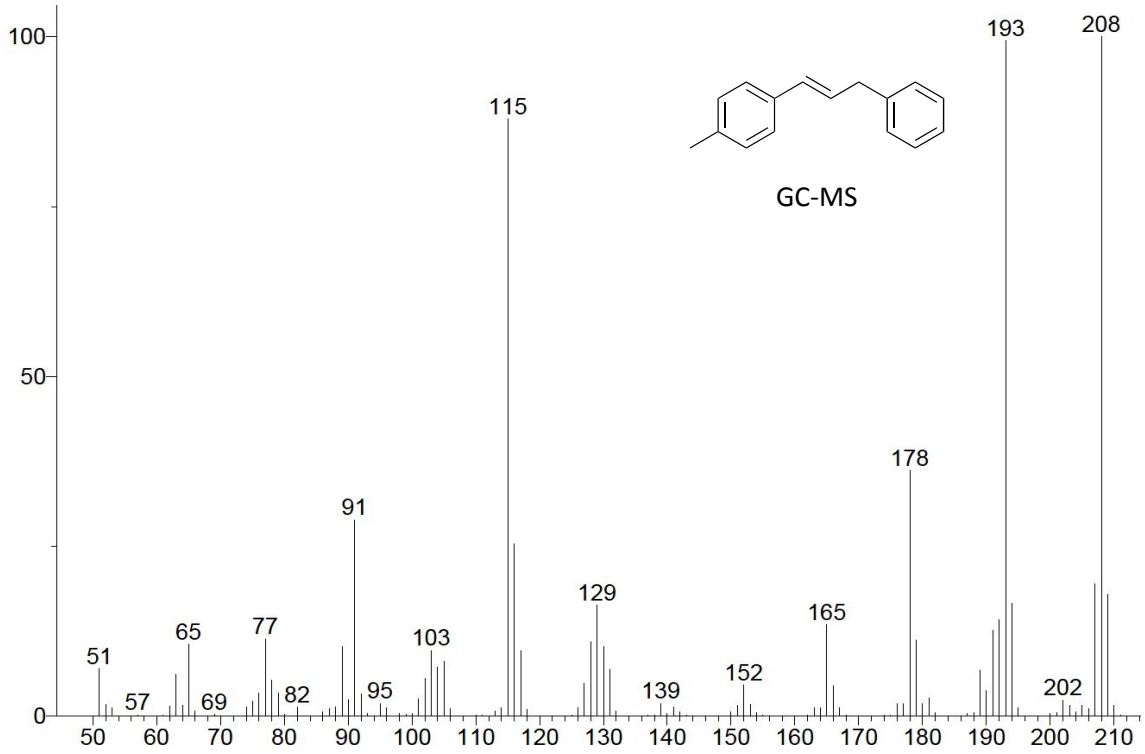


(3b) (*E*)-1-methyl-4-(3-phenylprop-1-en-1-yl)benzene



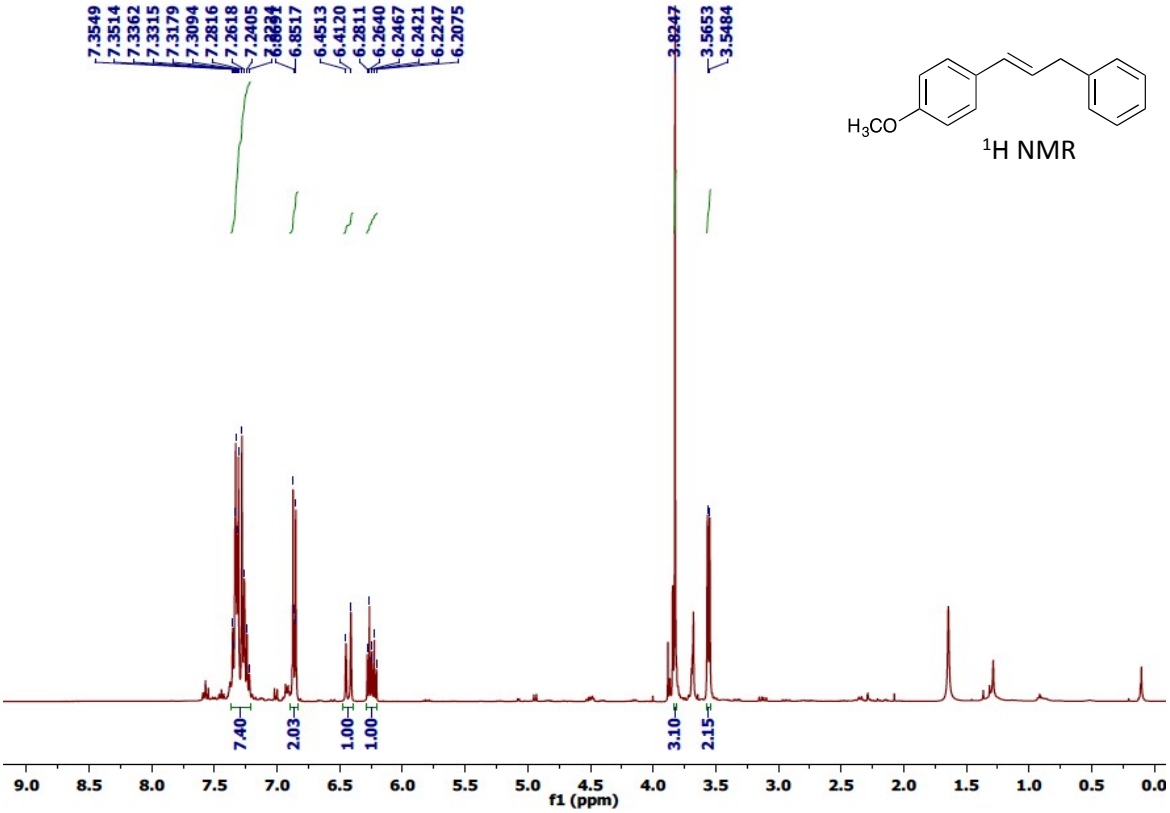

140.3450
134.6966
130.9241
129.1936
128.6637
128.4594
128.1676
126.1261
126.0188
77.3423
77.0250
76.7077
39.3602
21.1558
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

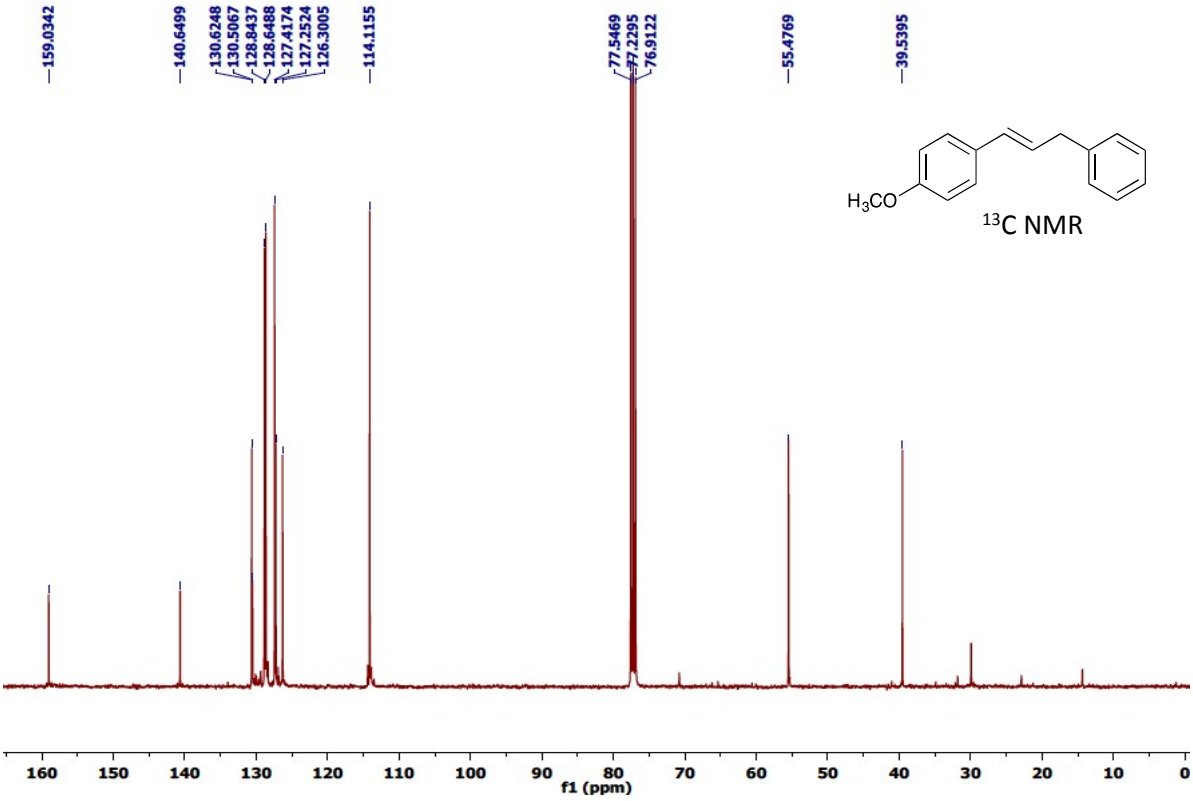
^{13}C NMR

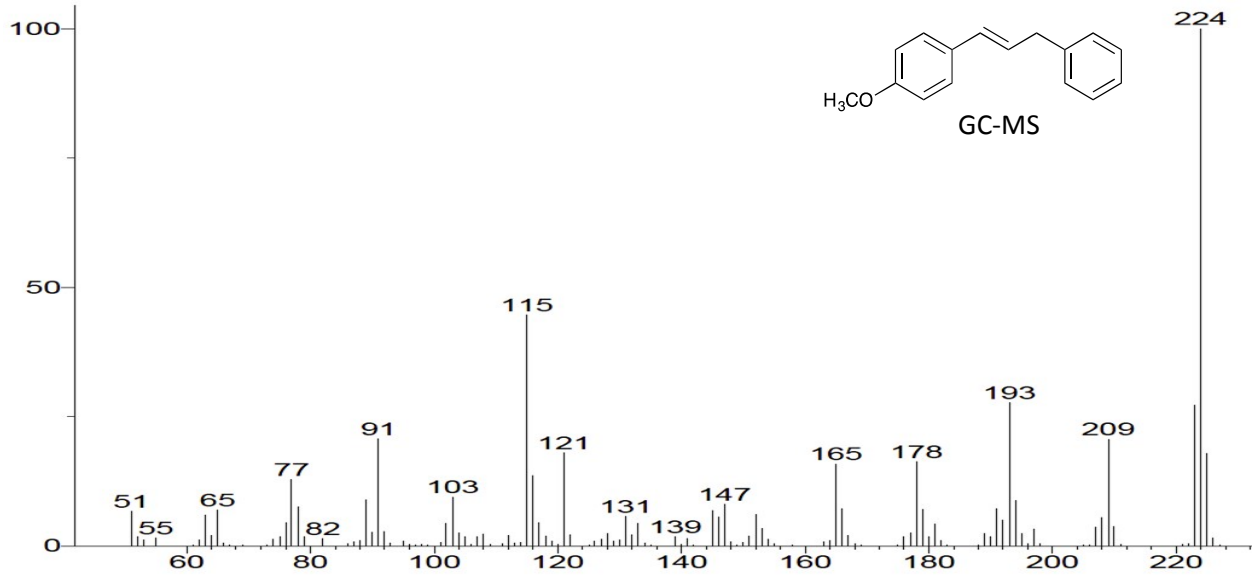

100
50
0
115
193
208
91
129
178
165
103
77
65
51
152
139
202
95
82
69
57
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

GC-MS

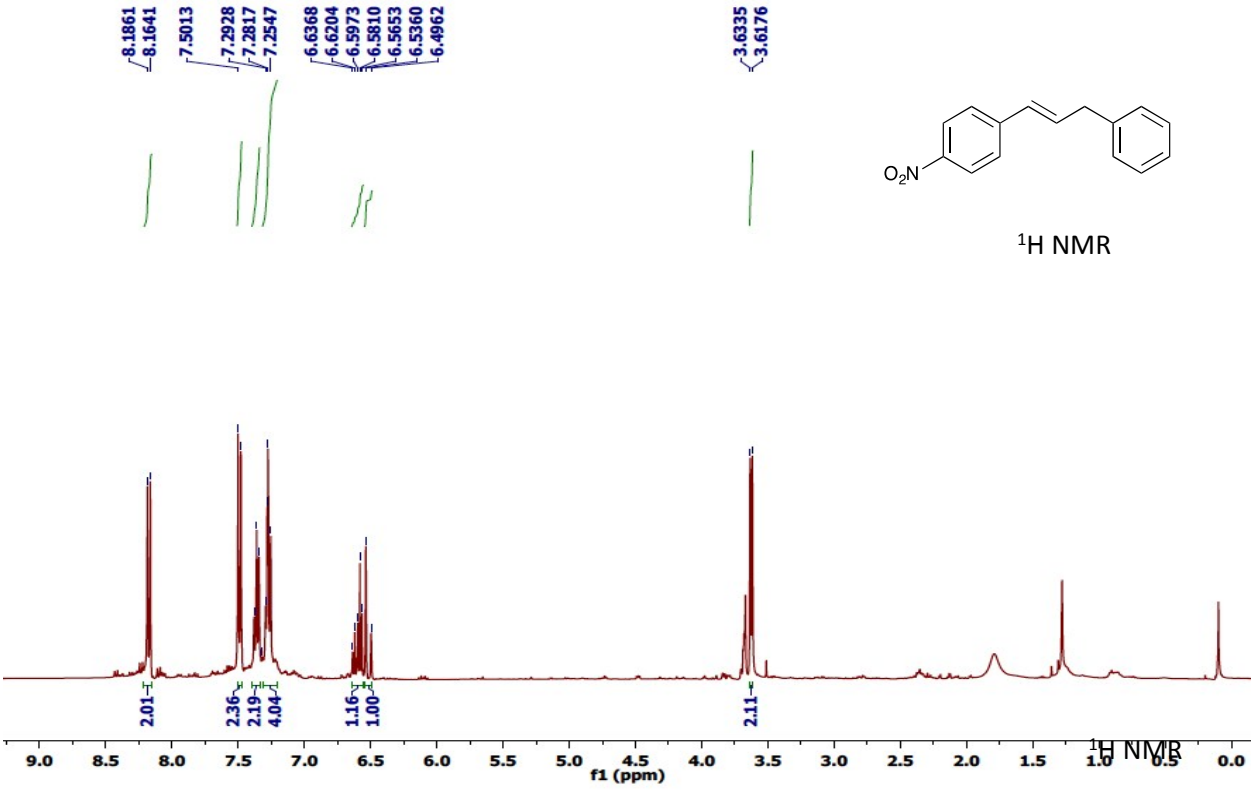
(3c) (*E*)-1-methoxy-4-(3-phenylprop-1-en-1-yl)benzene

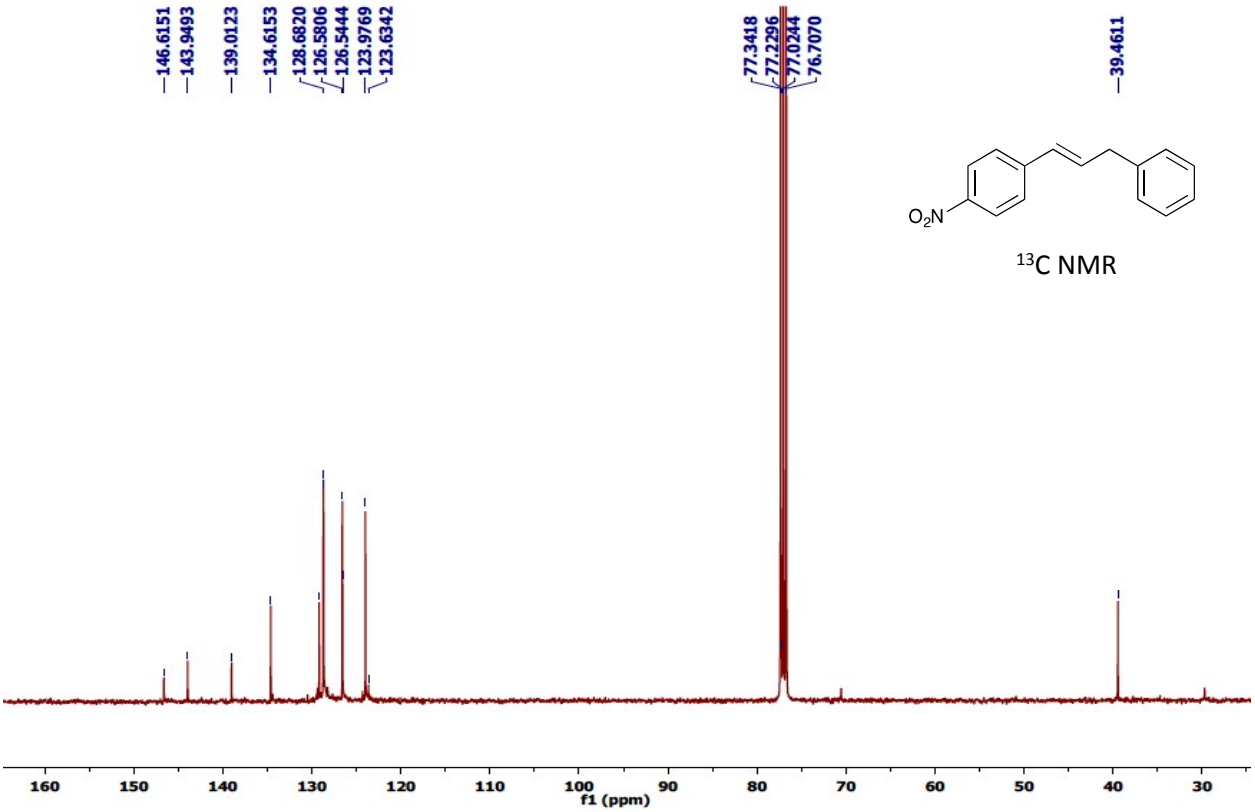


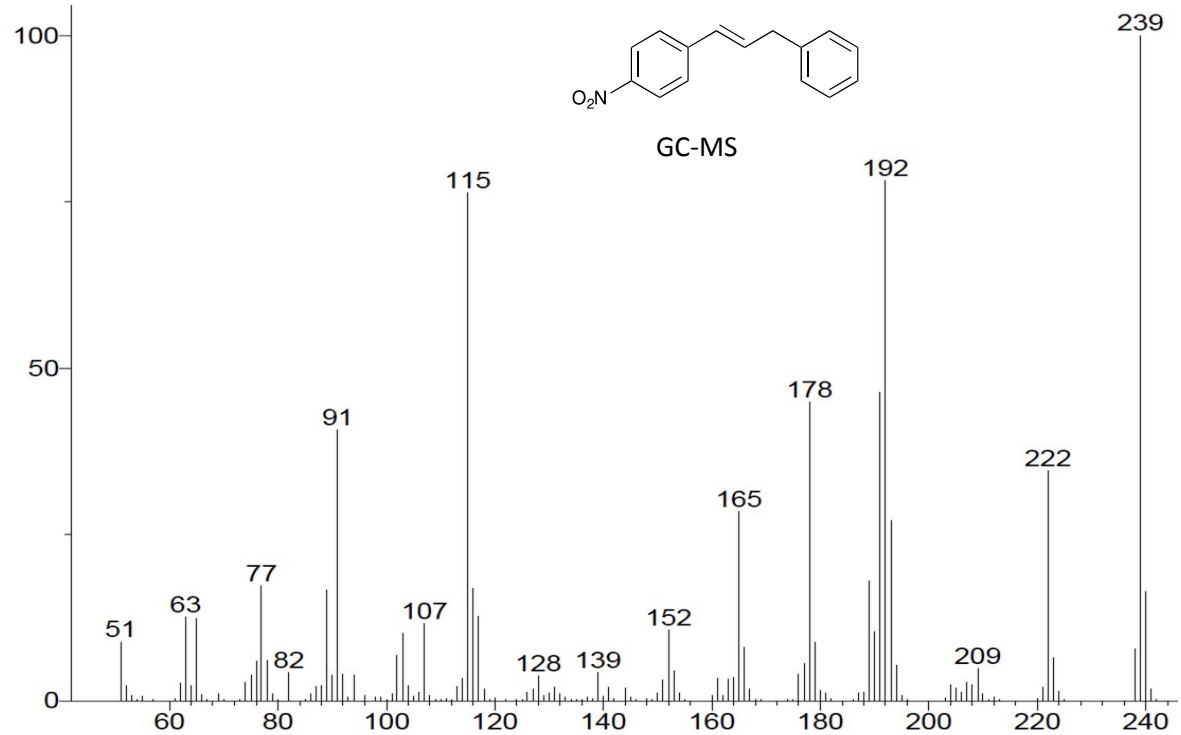




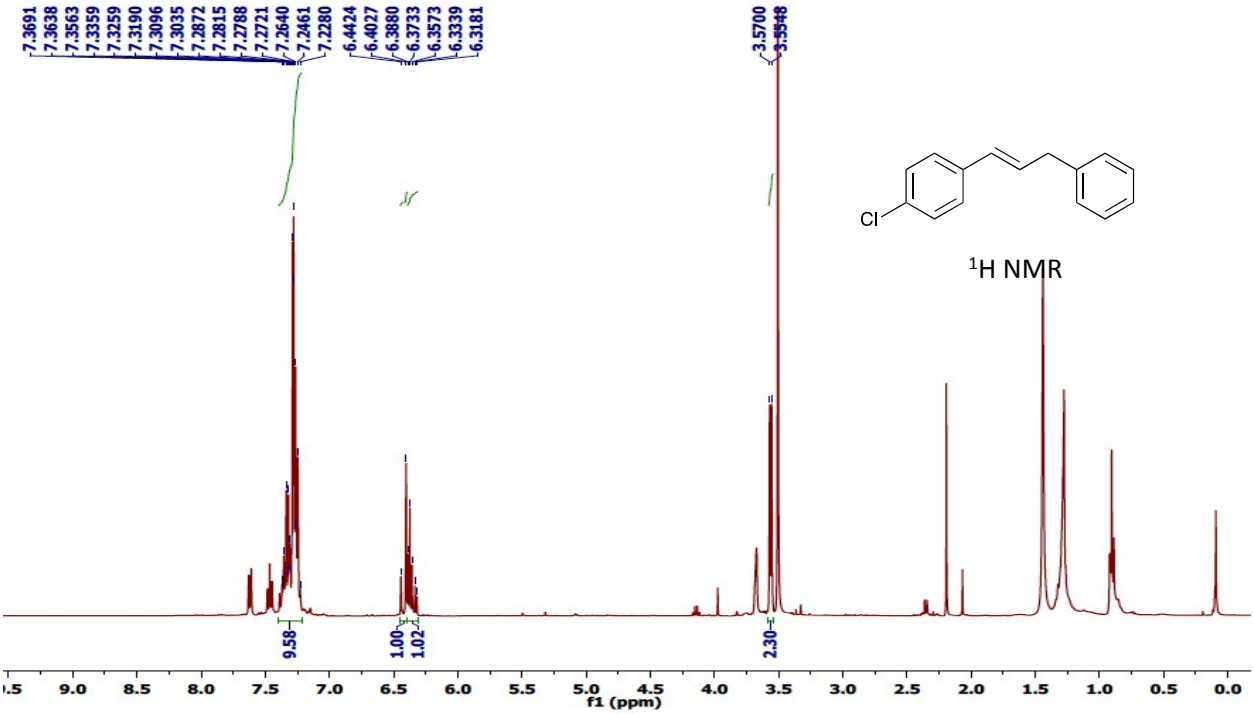
(3d) (*E*)-1-nitro-4-(3-phenylprop-1-en-1-yl)benzene



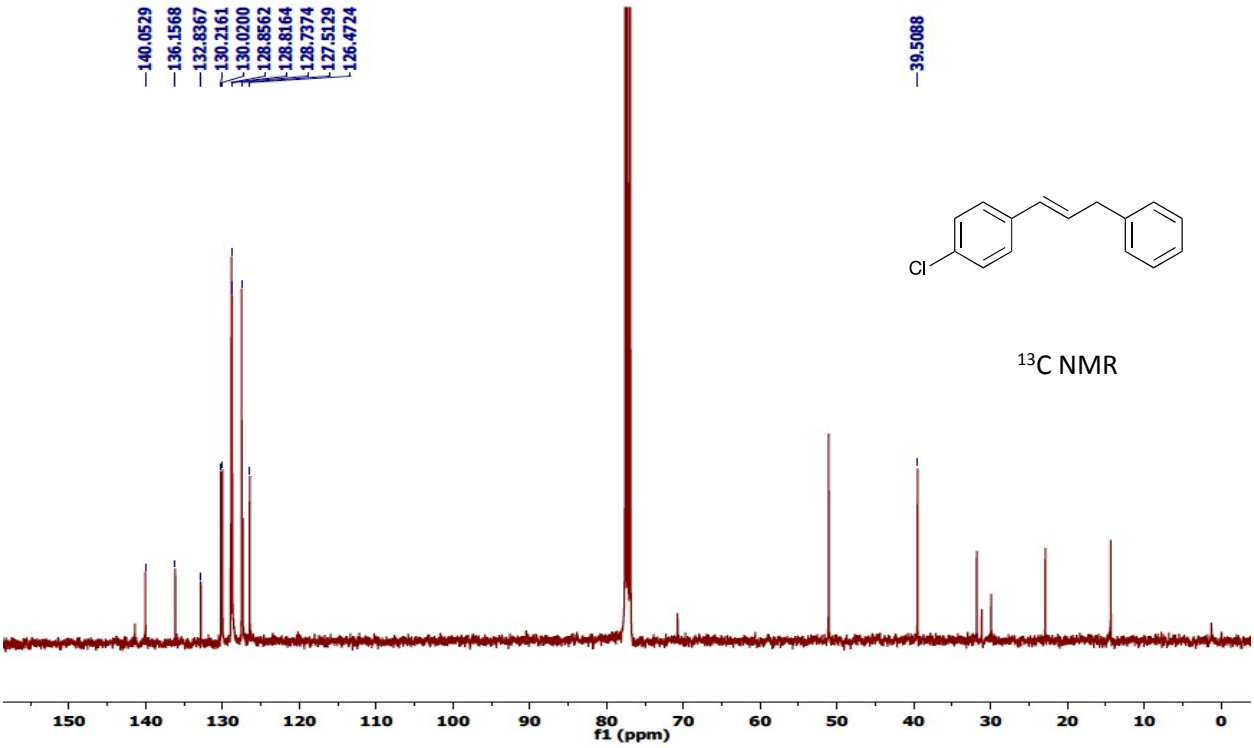

146.6151
143.9493
139.0123
134.6153
128.6820
126.5806
126.5444
123.9769
123.6342
77.3418
77.2296
77.0244
76.7070
39.4611
O2N
13C NMR
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


O2N
GC-MS
100
50
0
239
192
115
178
222
91
165
77
63
107
152
51
82
128
139
209
60
80
100
120
140
160
180
200
220
240

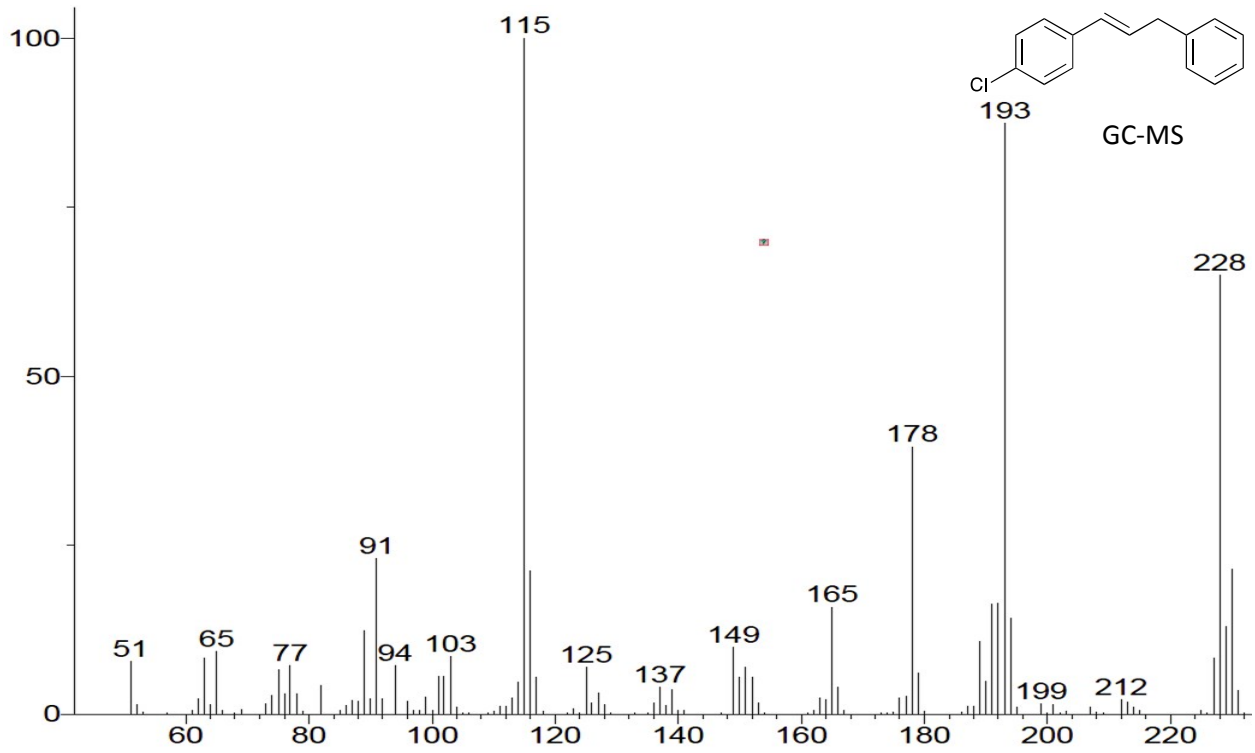
(3e) (*E*)-1-chloro-4-(3-phenylprop-1-en-1-yl)benzene



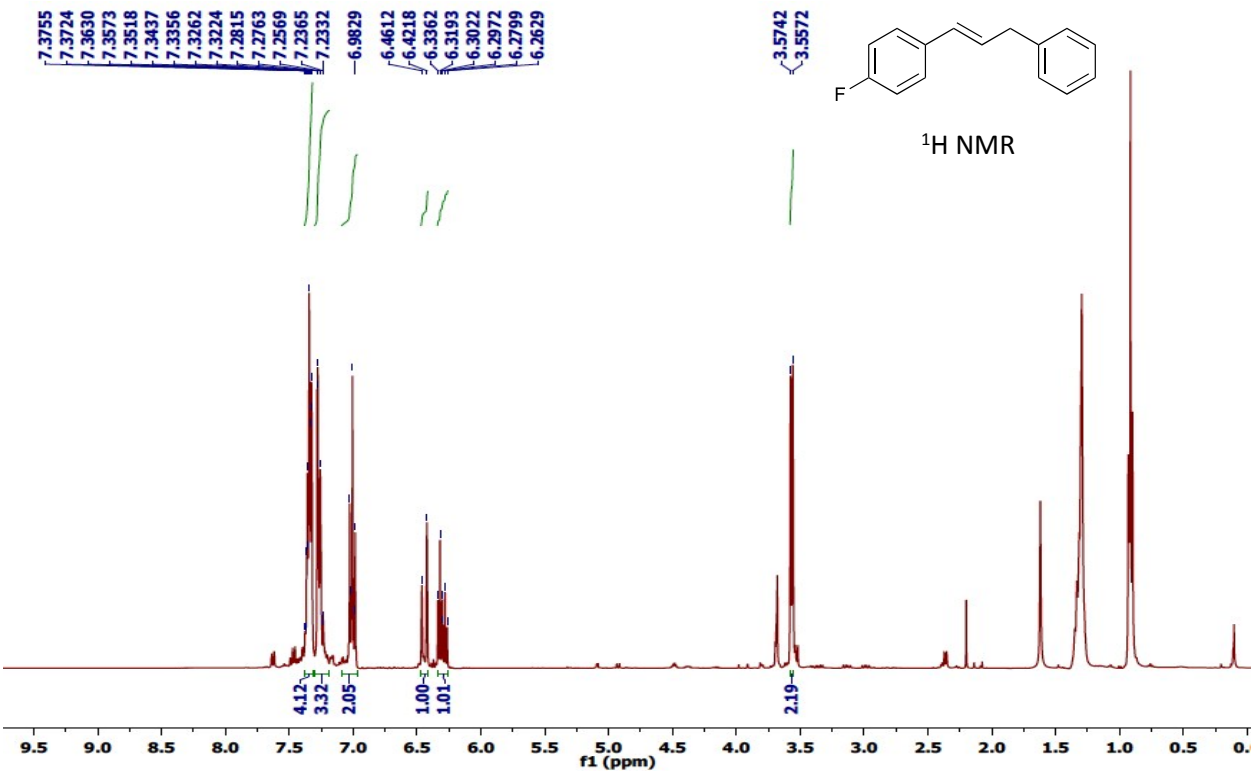
^{1}H NMR

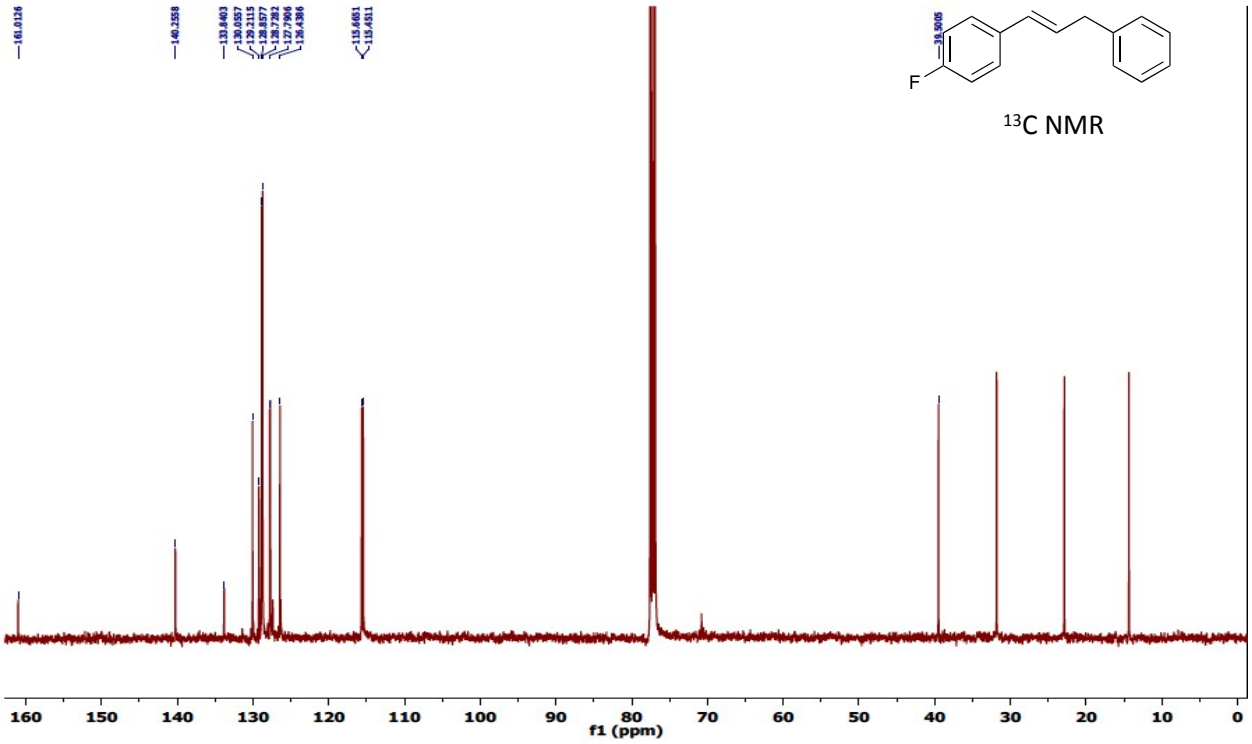


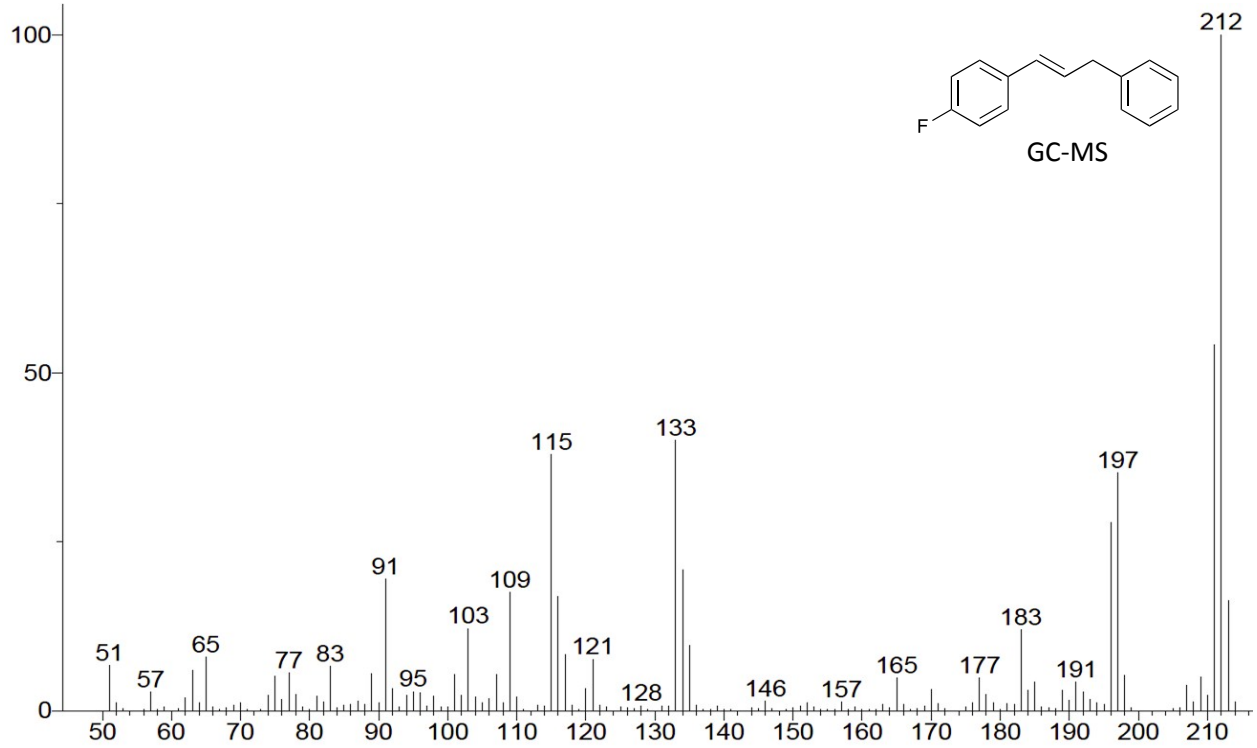
^{13}C NMR



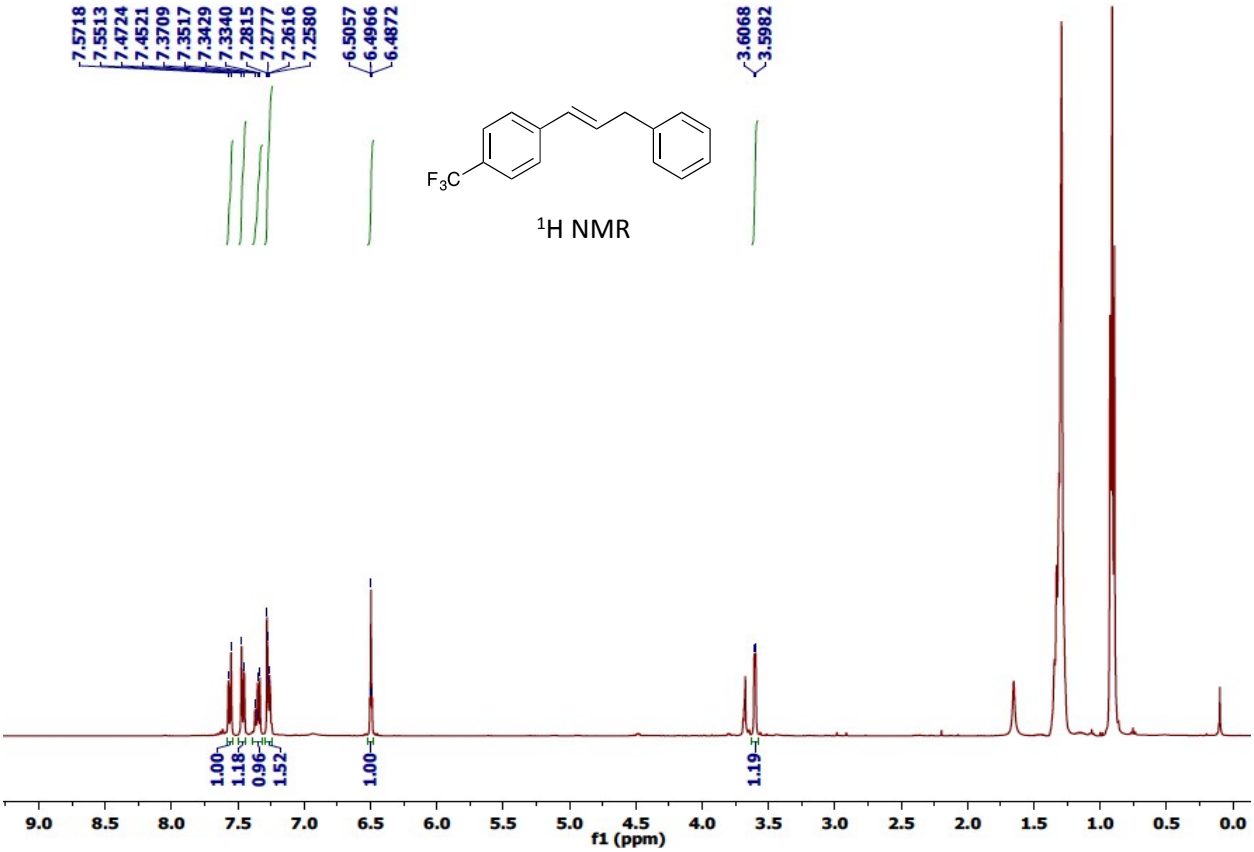
(3f) (*E*)-1-fluoro-4-(3-phenylprop-1-en-1-yl)benzene

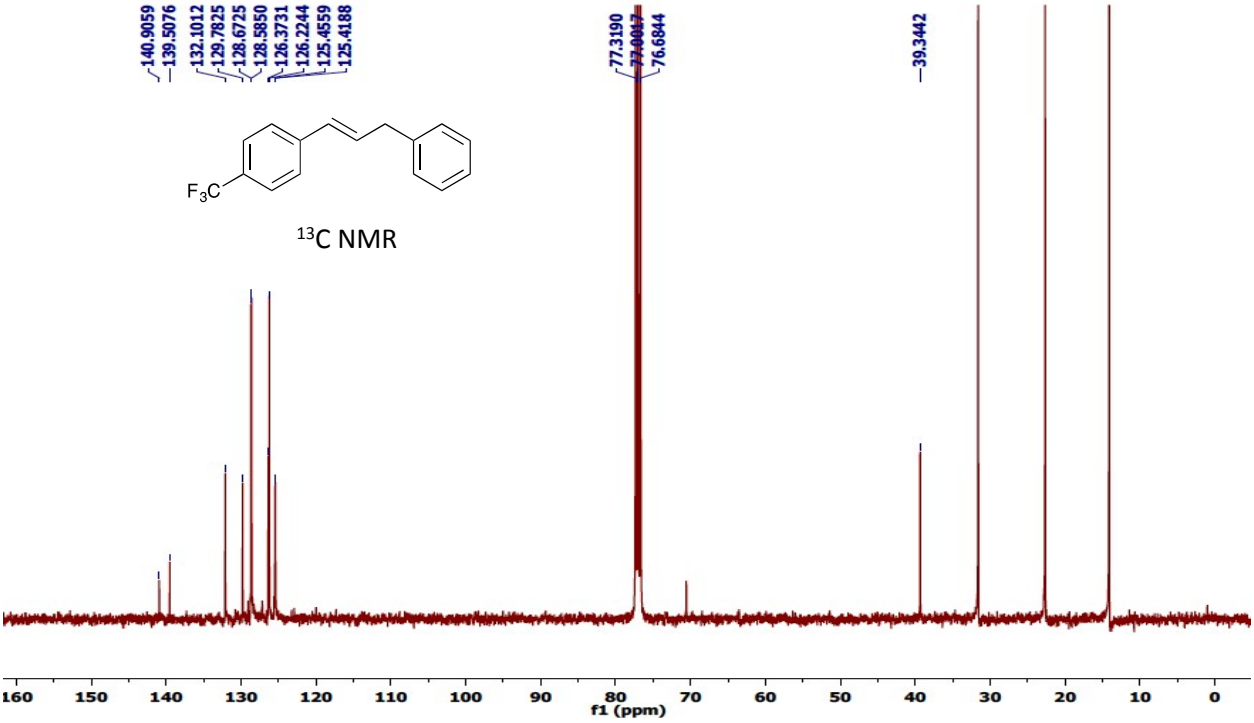


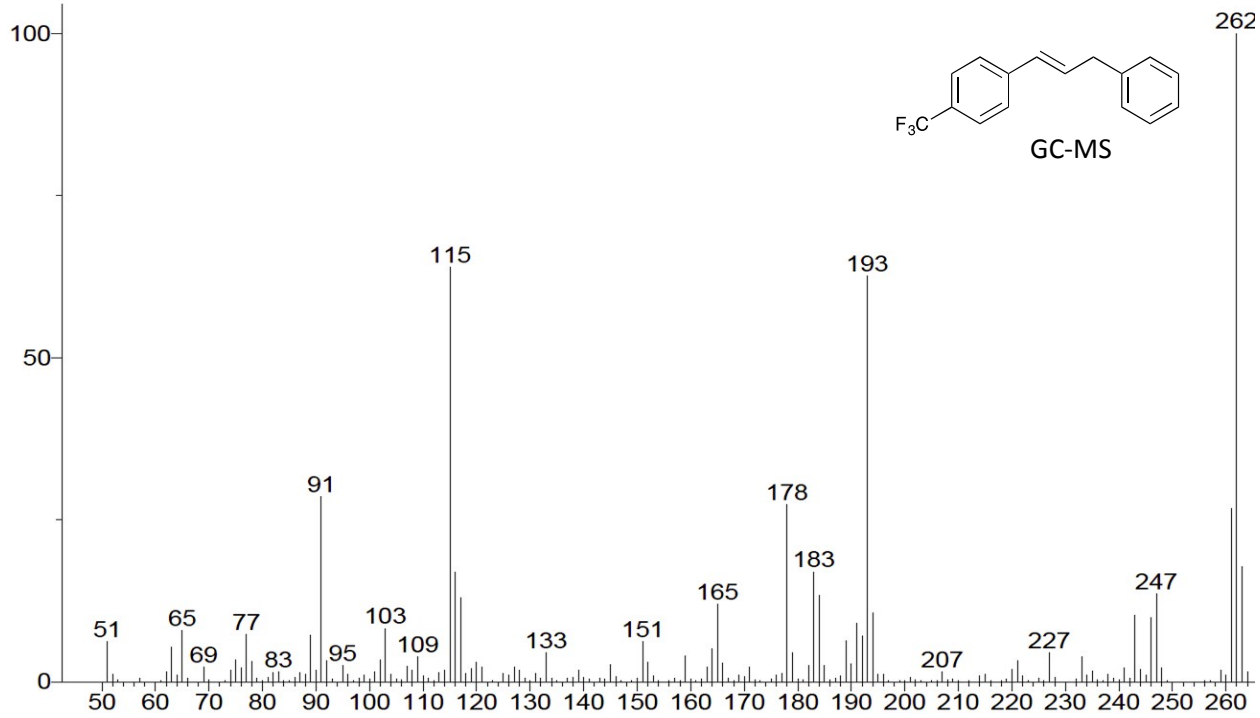

F
^{13}C NMR
f1 (ppm)


F
GC-MS

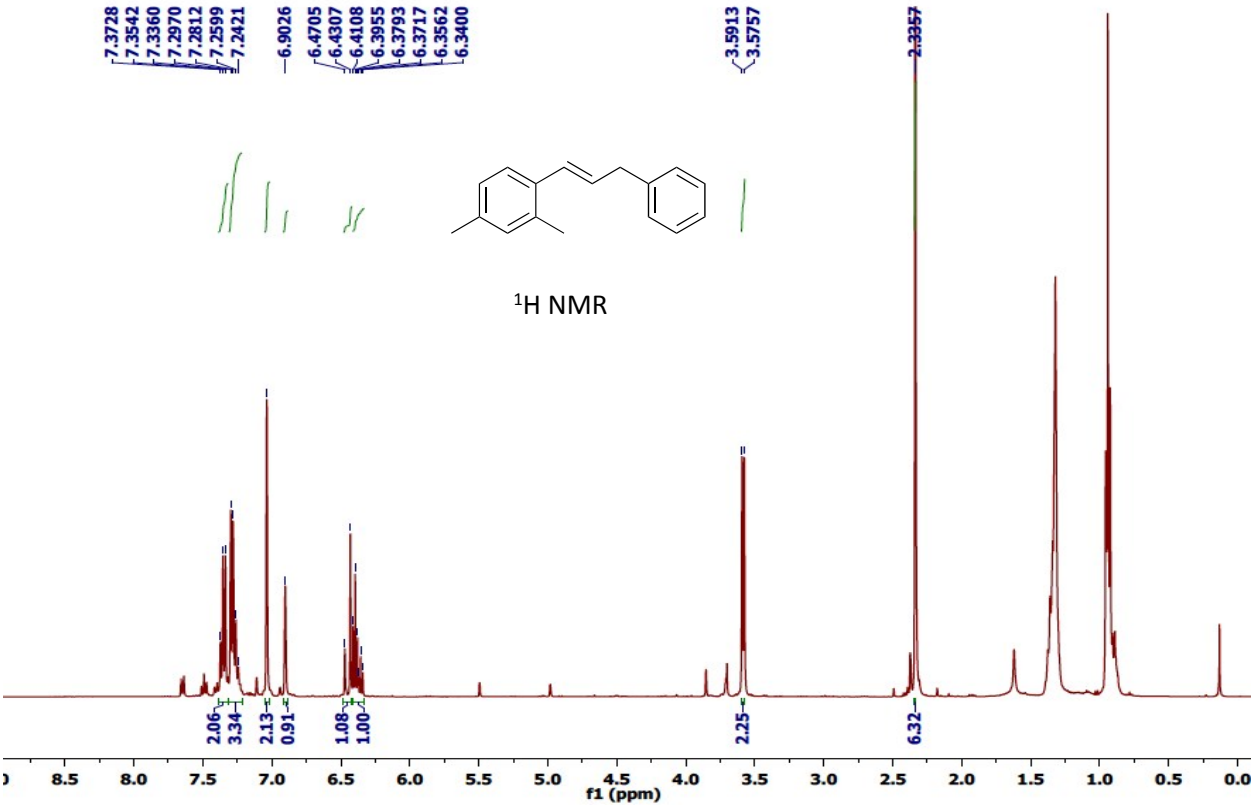
(3g) (*E*)-1-(3-phenylprop-1-en-1-yl)-4-(trifluoromethyl)benzene

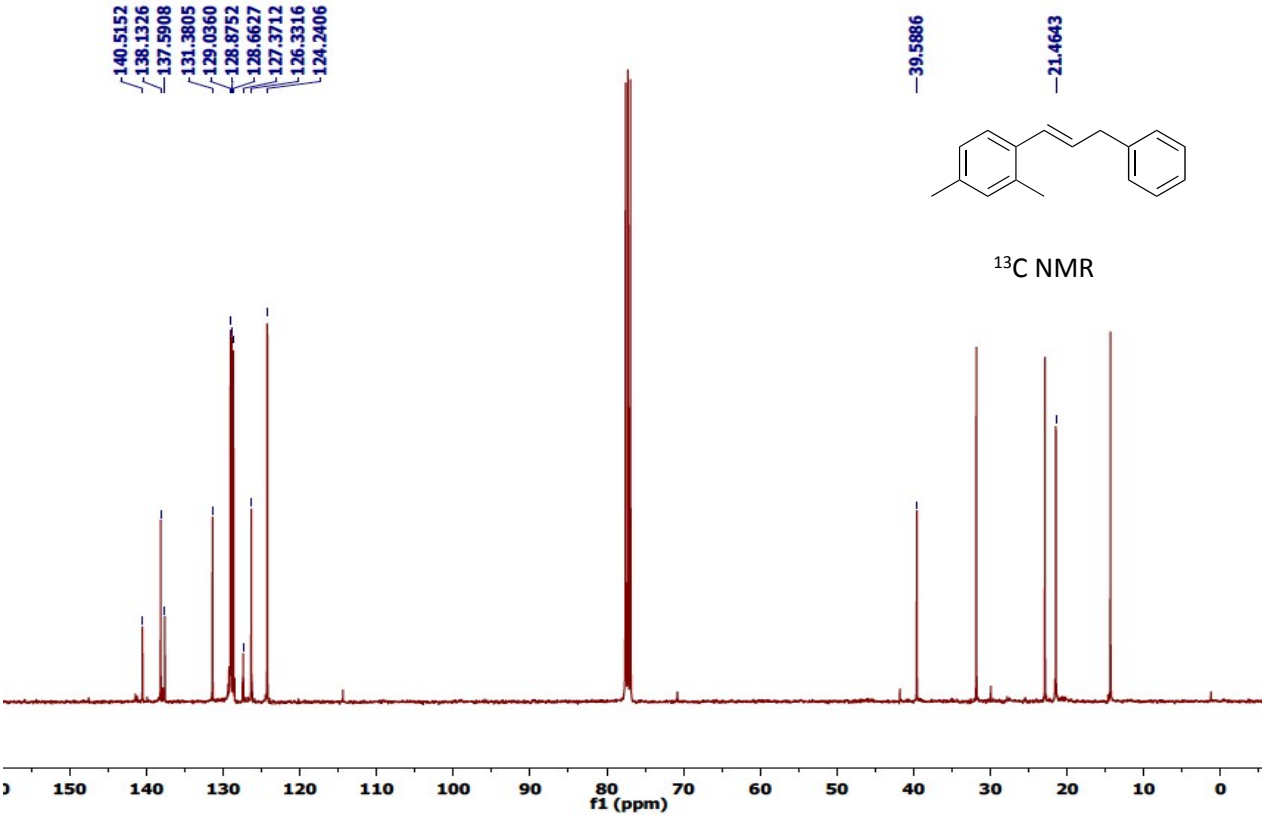




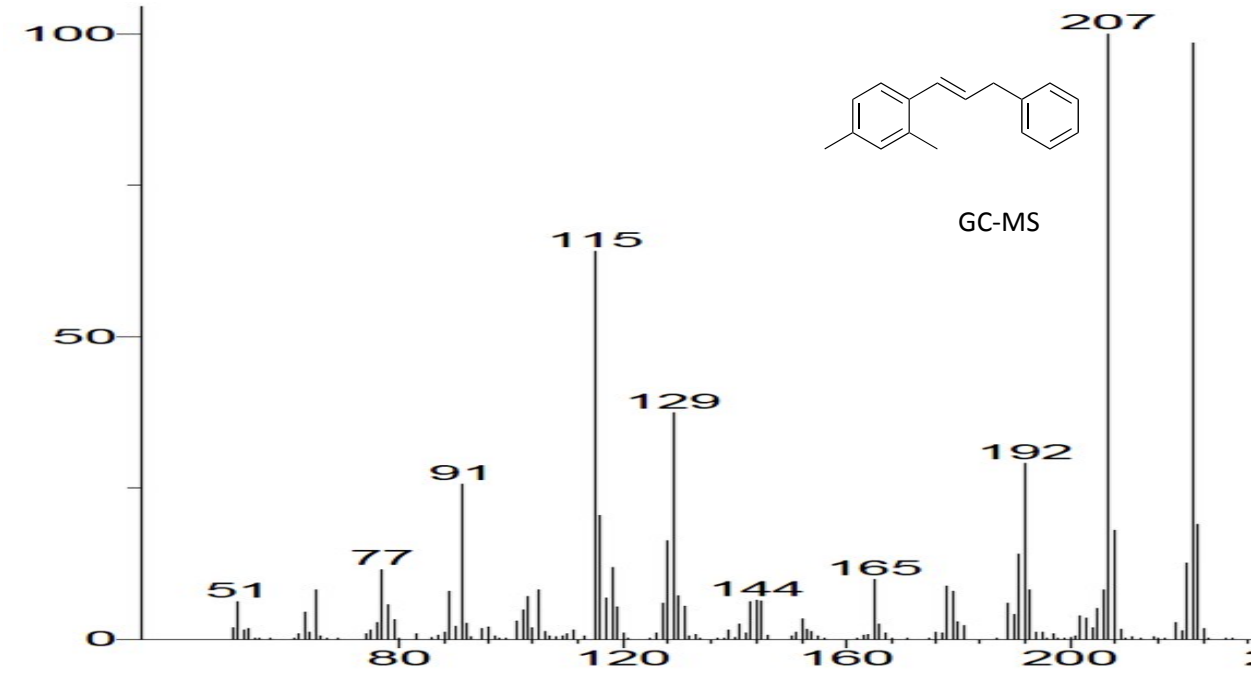


(3h) (*E*)-2,4-dimethyl-1-(3-phenylprop-1-en-1-yl)benzene



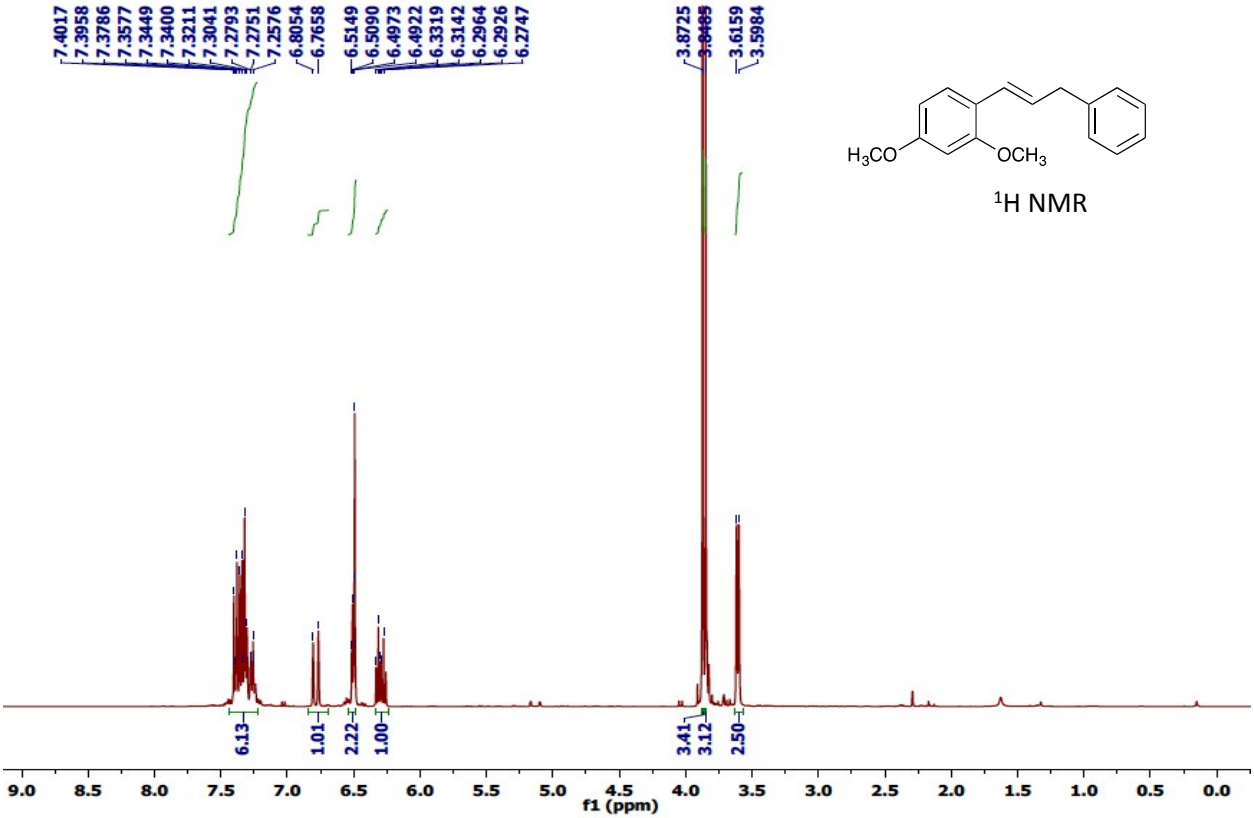

140.5152
138.1326
137.5908
131.3805
129.0360
128.8752
128.6627
127.3712
126.3316
124.2406
39.5886
21.4643
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

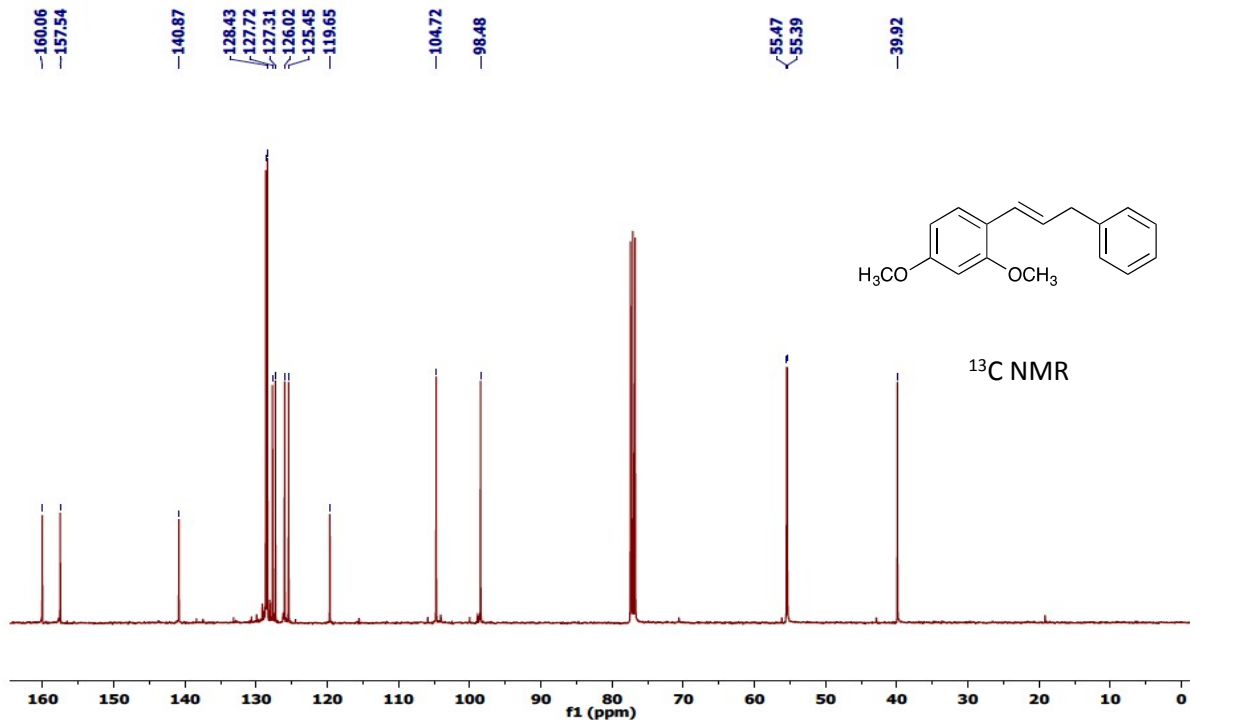
^{13}C NMR

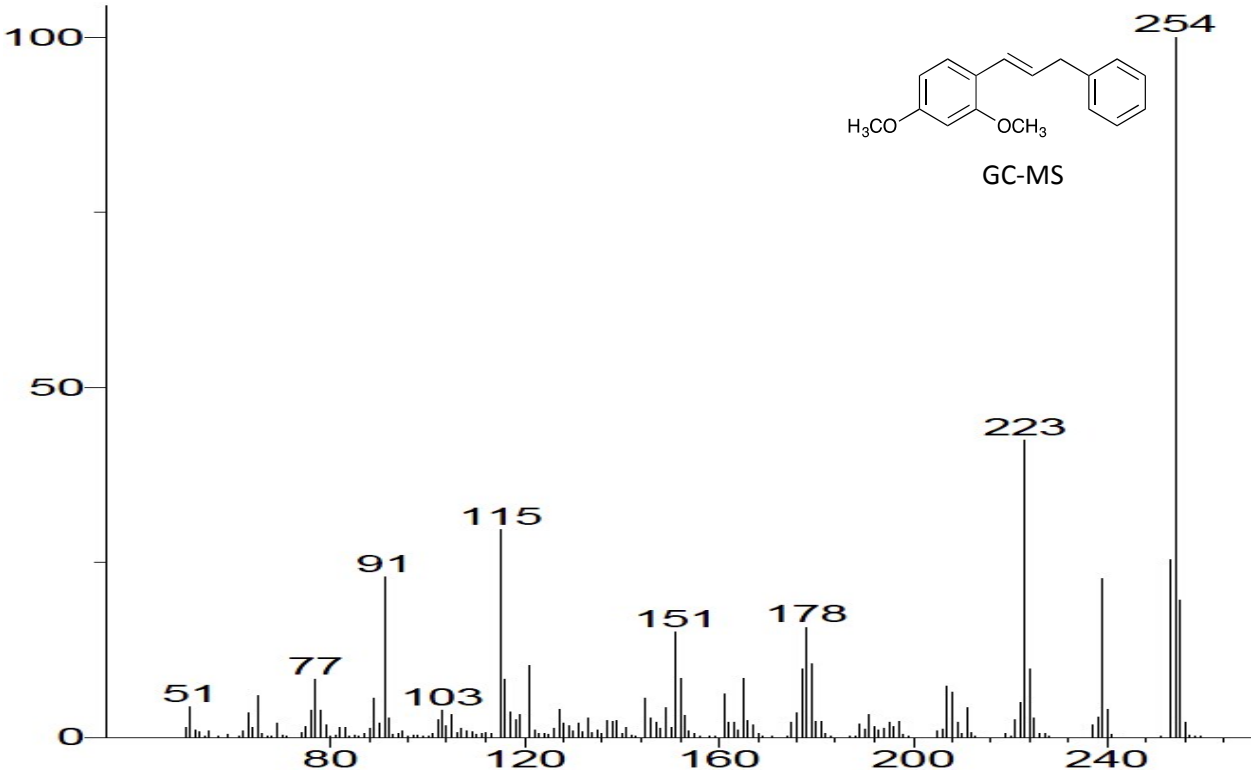

100
50
0
207
115
129
192
91
77
51
144
165
80
120
160
200

GC-MS

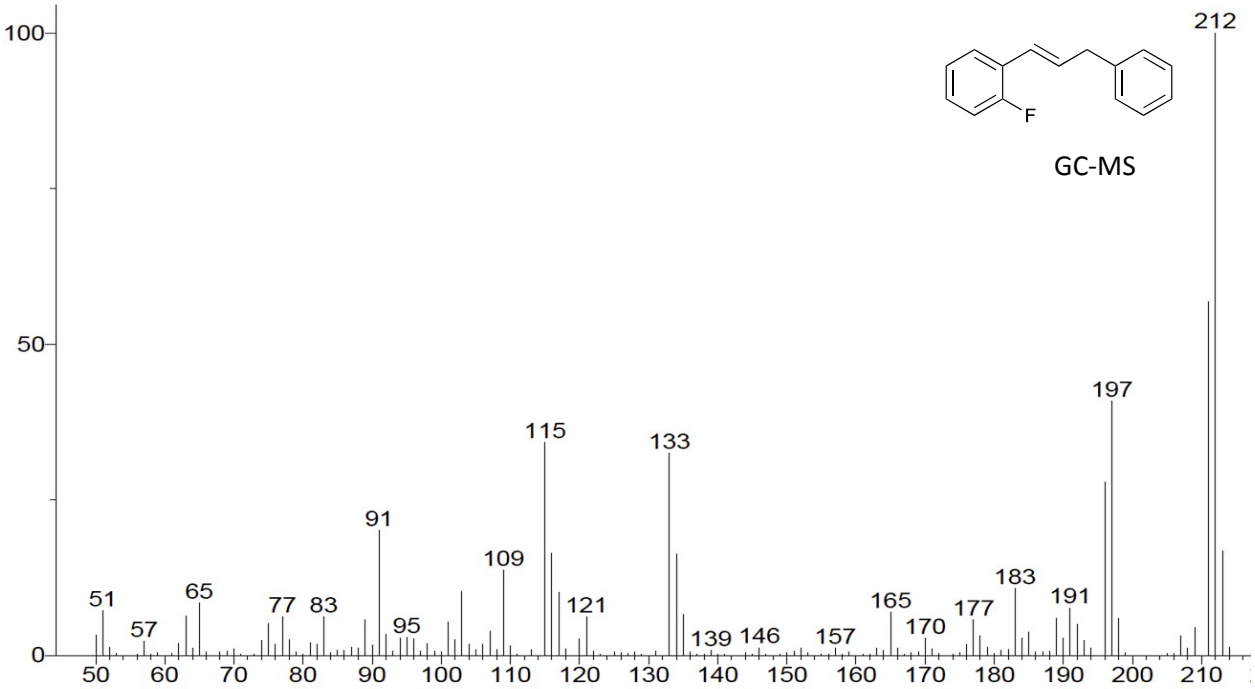
(3i) (*E*)-2,4-dimethoxy-1-(3-phenylprop-1-en-1-yl)benzene



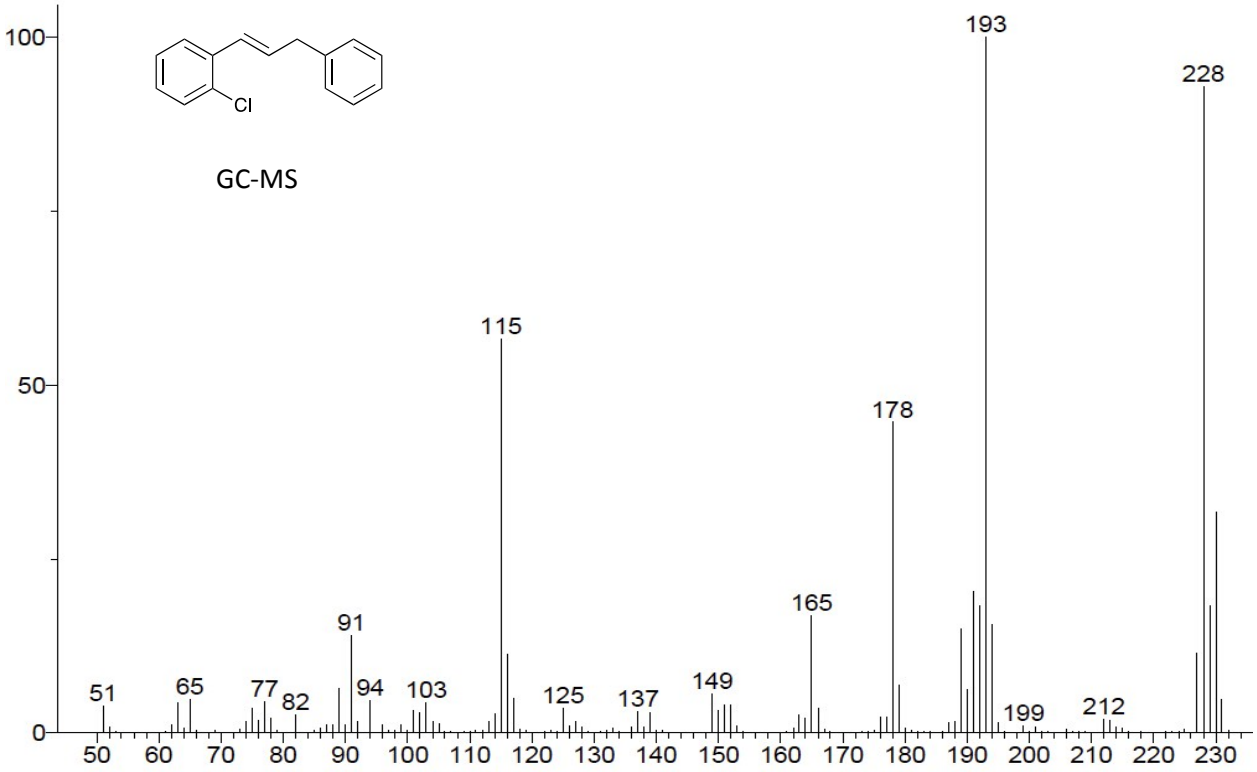




(3j) (*E*)-1-fluoro-2-(3-phenylprop-1-en-1-yl)benzene



(3k) (*E*)-1-chloro-2-(3-phenylprop-1-en-1-yl)benzene



(3l) (*E*)-1-fluoro-3-(3-phenylprop-1-en-1-yl)benzene