Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

The Ligand and Base-Free Pd-Catalyzed Oxidative Heck Reaction of Arylboronic Acids and Olefins

Peng Sun, Yan Zhu, Hailong Yang, Hong Yan, Linhua Lu, Xiang Zhang, and

Jincheng Mao*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China.

jcmao@suda.edu.cn

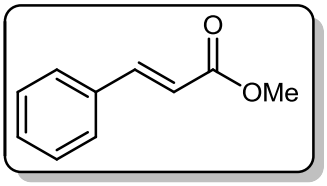
Content:

Experimental Section

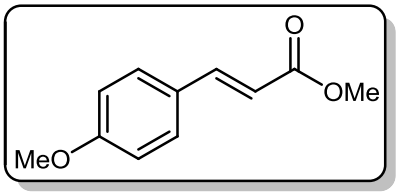
General experimental: All reactions were carried out under an air atmosphere condition unless otherwise stated. Various arylboronic acids and various olefins were purchased from Aldrich, Acros or Alfa. Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–300 mesh silica gel impregnated with a fluorescent indicator (254 nm). Column chromatography was performed on silica gel (100–200 mesh). Chemical shifts of ^{1}H NMR and ^{13}C NMR were reported in ppm (δ units) and residual non deuterated solvent was used as internal reference. The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, bs = broad signal, m = multiplet.

General procedure for base-free and ligand-free palladium-catalyzed oxidative Heck-Type coupling reactions of arylboronic acids: A mixture of arylboronic acid (0.5 mmol), olefin (3.0 mmol), $Pd(OAc)_2$ (2 mol %), DDQ (1 equiv), Ac_2O (5 equiv) and AcOH (3 mL) in a Schlenk tube was stirred under air atmosphere at 90 °C for 27 hours. After the mixture was poured into ether, it was washed with water, extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and 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.

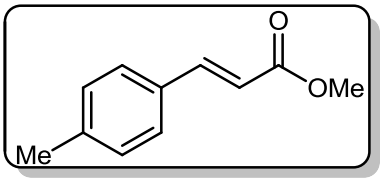
Characterization of the corresponding products:



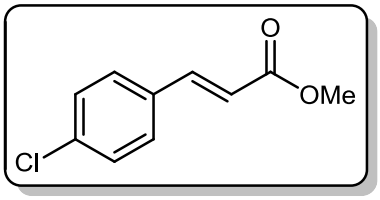
*(E)-methyl cinnamate (**3a**)*[1]. White solid; m.p. 36-38 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 3.82 (s, 3H), 6.45 (d, J = 16.0 Hz, 1H), 7.40 (t, J = 3.2 Hz, 3H), 7.52-7.55 (m, 2H), 7.71 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 52.1, 118.0, 128.4, 129.2, 130.6, 134.6, 145.2, 167.8. HRMS (ESI^+): calcd for $[C_{10}H_{10}O_2]^+$ requires m/z 162.0681, found 162.0679.



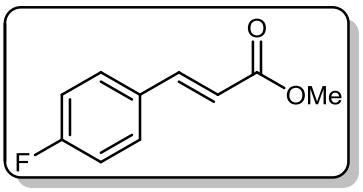
*(E)-methyl 3-(4-methoxyphenyl)acrylate (**3b**)*[1]. Yellow solid; m.p. 88-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 3.80 (s, 3H), 3.84 (s, 3H), 6.32 (d, J = 16.0 Hz, 1H), 6.91 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 51.9, 55.7, 114.6, 115.5, 127.3, 130.0, 144.8, 161.7, 168.0. HRMS (ESI^+): calcd for $[C_{11}H_{12}O_3]^+$ requires m/z 192.0786, found 192.0786



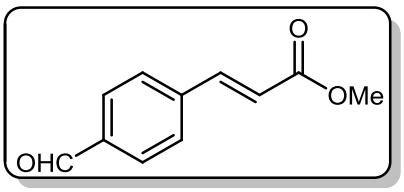
*(E)-methyl 3-(p-tolyl)acrylate (**3c**)*[1]. White solid; m.p. 57-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 2.38 (s, 3H), 3.80 (s, 3H), 6.40 (d, J = 16.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 21.8, 52.0, 116.9, 128.4, 130.0, 131.9, 141.0, 145.2, 168.0. HRMS (ESI^+): calcd for $[C_{11}H_{12}O_2]^+$ requires m/z 176.0837, found 176.0836.



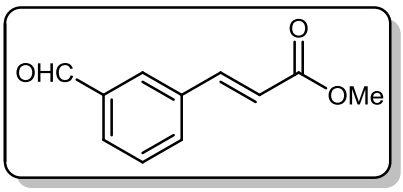
(E)-methyl 3-(4-chlorophenyl)acrylate (***3d***)[8]. White solid; m.p. 73-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 3.81 (s, 3H), 6.42 (d, J = 16.4 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 53.4, 120.0, 130.8, 130.8, 134.5, 137.8, 145.0, 168.8. HRMS (ESI^+): calcd for $[C_{10}H_9ClO_2]^+$ requires m/z 196.0291, found 196.0290.



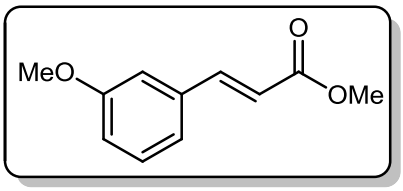
(E)-methyl 3-(4-fluorophenyl)acrylate (***3e***)[8]. Yellow solid; m.p. 46-47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 3.81 (s, 3H), 6.37 (d, J = 16.0 Hz, 1H), 7.08 (t, J = 8.6 Hz, 2H), 7.50-7.53 (m, 2H), 6.66 (d, J = 16.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 51.9, 116.3 (d, $^{2}J_{CF}$ = 21.8 Hz), 117.8, 130.1 (d, $^{3}J_{CF}$ = 8.3 Hz), 130.9, 143.8, 164.1 (d, $^{1}J_{CF}$ = 250.6 Hz), 167.5. HRMS (ESI^+): calcd for $[C_{10}H_9FO_2]^+$ requires m/z 180.0587, found 180.0588.



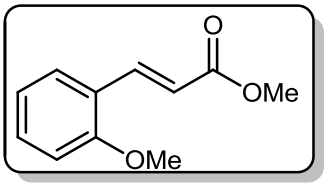
(E)-methyl 3-(4-formylphenyl)acrylate (***3f***)[2]. Yellow solid; m.p. 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 3.82 (s, 3H), 6.55 (d, J = 16.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 16.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 2H), 10.02 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 20.8, 51.8, 89.2, 119.0, 127.3, 128.2, 135.7, 137.2, 143.8, 167.1, 168.7. HRMS (ESI^+): calcd for $[C_{11}H_{10}O_3]^+$ requires m/z 190.0630, found 190.0480.



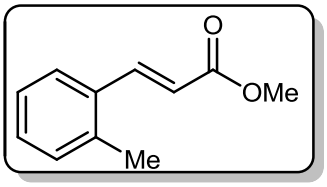
*(E)-methyl 3-(3-formylphenyl)acrylate (**3g**)*[3]. White solid; m.p. 54-56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 3.83 (s, 3H), 6.54 (d, J = 18.0 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.74 (d, J = 18.0 Hz, 2H), 7.90 (d, J = 9.0 Hz, 1H), 8.02 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 47.1, 114.9, 124.0, 124.9, 126.3, 128.8, 130.6, 132.1, 138.3, 162.1, 186.9. HRMS (ESI^+): calcd for $[C_{11}H_{10}O_3]^+$ requires m/z 190.0630, found 189.0649.



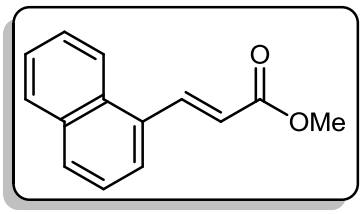
*(E)-methyl 3-(3-methoxyphenyl)acrylate (**3h**)*[10]. Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 3.79 (s, 6H), 6.42 (d, J = 15.0 Hz, 1H), 6.92 (s, 1H), 7.06 (d, J = 21.0 Hz, 2H), 7.27 (s, 1H), 7.65 (d, J = 15.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 51.9, 55.4, 113.2, 116.3, 118.3, 120.9, 130.1, 135.9, 145.0, 160.1, 167.5. HRMS (ESI^+): calcd for $[C_{11}H_{12}O_3]^+$ requires m/z 192.0786, found 193.0857.



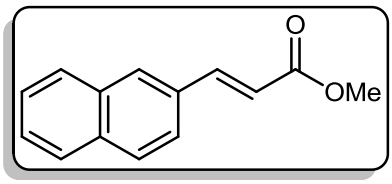
*(E)-methyl 3-(2-methoxyphenyl)acrylate (**3i**)*[10]. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 3.80 (s, 3H), 3.89 (s, 3H), 6.53 (d, J = 16.0 Hz, 1H), 6.90-6.99 (m, 2H), 7.33-7.38 (m, 1H), 7.51 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 16.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 51.6, 55.4, 111.1, 118.2, 120.7, 128.9, 131.5, 140.2, 158.3, 167.9. HRMS (ESI^+): calcd for $[C_{11}H_{12}O_3]^+$ requires m/z 192.0786, found 193.0828.



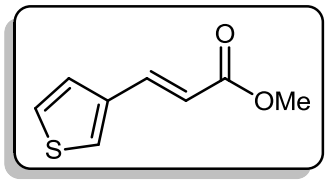
*(E)-methyl 3-(2-methylphenyl)acrylate (**3j**)*[1]. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 2.43 (s, 3H), 3.80 (s, 3H), 6.36 (d, J = 15.0 Hz, 1H), 7.20-7.25 (m, 3H), 7.54 (d, J = 6.0 Hz, 1H), 7.98 (d, J = 15.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 19.8, 51.7, 118.8, 126.3, 126.4, 130.0, 130.8, 133.3, 137.7, 142.6, 167.5. HRMS (ESI^+): calcd for $[C_{11}H_{12}O_2]^+$ requires m/z 176.0837, found 175.0700.



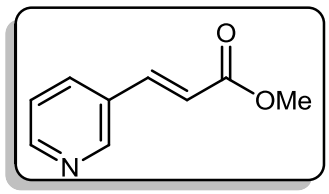
*(E)-methyl 3-(naphthalen-1-yl)acrylate (**3k**)*[9]. Light yellow oil; ^{1}H NMR (400MHz, $CDCl_3$) (δ, ppm) 3.84 (s, 3H), 6.52 (d, J = 15.6 Hz, 1H), 7.51 (m, J = 6.1 Hz, 3H), 7.72 (d, J = 7.2 Hz, 1H), 7.86(t, J = 14.8 Hz, 2H), 8.18 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$) (δ, ppm) 53.4, 120.0, 125.0, 126.6, 127.1, 127.9, 128.5, 130.4, 132.2, 133.0, 133.3, 135.3, 143.5, 169.0. HRMS (ESI^+): calcd for $[C_{14}H_{12}O_2]^+$ requires m/z 212.0837, found 212.0836.



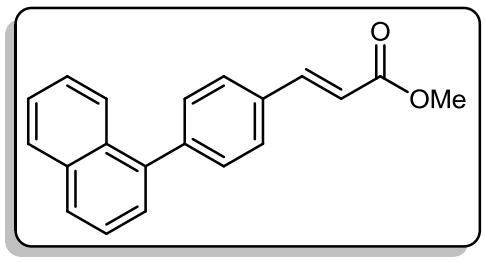
*(E)-methyl 3-(naphthalen-2-yl)acrylate (**3l**)*[9]. White solid; m.p. 82-83 °C; ^{1}H NMR (400MHz, $CDCl_3$) (δ, ppm) 3.83 (s, 3H), 6.55 (d, J = 16.0 Hz, 1H), 7.48-7.53 (m, 2H), 7.63-7.66 (d, J = 8.0 Hz, 1H), 7.80-7.87 (m, 4H), 7.91 (s, 1H). ^{13}C NMR (75MHz, $CDCl_3$) (δ, ppm) 51.7, 117.9, 123.5, 126.7, 127.2, 127.8, 128.6, 128.7, 130.0, 131.9, 133.3, 134.2, 144.9, 167.5. HRMS (ESI^+): calcd for $[C_{14}H_{12}O_2]$ requires m/z 212.0837, found 212.0837.



*(E)-methyl 3-(thiophen-3-yl)acrylate (**3m**)*[11]. White solid; m.p. 48-49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 3.80 (s, 3H, OMe), 6.27 (d, J = 16.0 Hz, 1H), 7.29-7.34 (m, 2H), 7.50 (d, J = 1.6 Hz, 1H), 7.68 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) (δ, ppm): 52.1, 117.7, 125.4, 127.4, 128.6, 137.8, 138.7, 168.1. HRMS (ESI$^+$): calcd for $[C_8H_8O_2S]^+$ requires m/z 168.0245, found 168.0243.

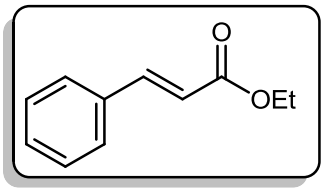


*(E)-methyl 3-(pyridin-3-yl)acrylate (**3n**)*[4]. Yellow solid; m.p. 83-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 3.83 (s, 3H), 6.53 (d, J = 16.4 Hz, 1H), 7.35 (q, J = 4.3 Hz, 1H), 7.70 (d, J = 16.4 Hz, 1H), 7.85 (d, J = 8 Hz, 1H), 8.62 (d, J = 4.8 Hz, 1H), 8.75 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) (δ, ppm) 53.6, 121.6, 125.4, 131.7, 135.8, 142.8, 151.4, 152.7, 168.4. HRMS (ESI$^+$): calcd for $[C_9H_9NO_2]^+$ requires m/z 163.0633, found 163.0632.

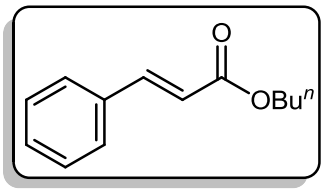


*(E)-methyl 3-(4-(naphthalen-1-yl)phenyl)acrylate (**3o**)*[12]. White solid; m.p. 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 3.84 (s, 3H), 6.53 (d, J = 16 Hz, 2H), 7.42-7.55 (m, 6H), 7.66 (d, J = 8.4 Hz, 2H), 7.80 (s, J = 16 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 52.0, 118.1, 125.6, 126.0, 126.2, 126.5, 126.5, 127.2, 128.3, 128.7, 130.9, 131.6, 133.6,

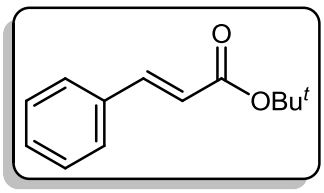
134.1, 139.5, 143.2, 144.8, 167.7. HRMS (ESI^+): calcd for $[C_{20}H_{16}O_2]^+$ requires m/z 288.1150, found 287.0958.



*(E)-ethyl cinnamate (**3p**)*[5]. Light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 1.35 (t, *J* = 7.2 Hz, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 7.39 (t, *J* = 3.2 Hz, 3H), 7.52-7.54 (m, 2H), 7.69 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 14.6, 60.8, 118.5, 128.4, 129.2, 130.54, 134.7, 144.9, 167.3. HRMS (ESI^+): calcd for $[C_{11}H_{12}O_2]^+$ requires m/z 176.0837, found 176.0837.

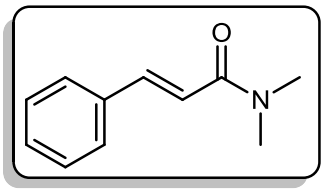


*(E)-butyl cinnamate (**3q**)* [5]. Colourless liquid; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 0.97 (t, *J* = 7.4 Hz, 3H), 1.39-1.48 (m, 2H), 1.65-1.73 (m, 2H), 4.21 (t, *J* = 6.8 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 7.37 (t, *J* = 3.2 Hz, 3H), 7.51-7.53 (m, 2H), 7.68 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 14.1, 19.5, 31.1, 64.7, 118.6, 128. 3, 129.2, 130.5, 134.7, 144.9, 167.4. HRMS (ESI^+): calcd for $[C_{13}H_{16}O_2]^+$ requires m/z 204.115, found 204.115.

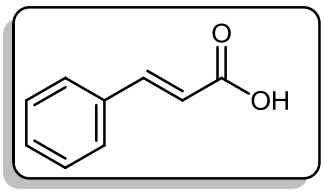


*(E)-tert-butyl cinnamate (**3r**)* [5]. Colourless liquid; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 1.54 (s, 9H), 6.37 (d, *J* = 16.0 Hz, 1H), 7.36-7.37 (m, 3H), 7.49-7.51 (m, 2H), 7.59 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 28.4, 80.7, 120.4, 128.2, 129.0, 130.2, 134.9, 143.8, 166.7. HRMS (ESI^+): calcd for $[C_{13}H_{16}O_2]^+$

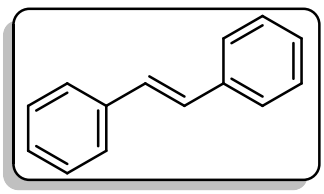
requires m/z 204.115, found 204.115.



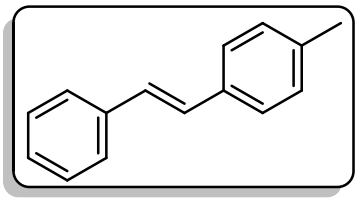
N,N-dimethylcinnamamide (***3s***)[8]. White solid; m.p. 96-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) NMR 3.13 (s, 6H), 6.89 (d, J = 16.0 Hz, 1H), 7.36-7.38 (m, 3H), 7.52-7.54 (m, 2H), 7.69 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 37.0, 117.4, 128.0, 129.0, 129.9, 135.5, 142.9, 167.0. HRMS (ESI$^+$): calcd for $[C_{11}H_{13}NO]^+$ requires m/z 175.0997, found 175.0996.



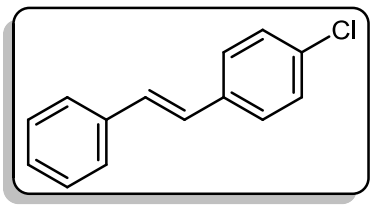
Cinnamic acid (***3t***)[7]. White solid; m.p. 132-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 6.47 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 2.0 Hz, 3H), 7.56 (t, J = 3.6 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 10.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 117.5, 128.6, 129.2, 131.0, 134.2, 147.4, 172.6. HRMS (ESI$^+$): calcd for $[C_9H_8O_2]^+$ requires m/z 148.0524, found 148.0526.



(E)-1,2-diphenylethene (***3u***)[6]. White solid; m.p. 123-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.11 (s, 2H), 7.26 (t, J = 6.0 Hz, 2H), 7.36 (t, J = 7.2 Hz, 4H), 7.52 (d, J = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 126.8, 127.9, 128.9, 137.5. HRMS (ESI$^+$): calcd for $[C_{14}H_{12}]^+$ requires m/z 180.0936, found 180.0939.



*(E)-1-methyl-4-styrylbenzene (**3v**)*[6]. White solid; m.p. 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.07 (s, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 21.5, 126.7, 127.7, 127.9, 128.8, 128.9, 129.6, 134.8, 137.8. HRMS (ESI^+): calcd for $[C_{15}H_{14}]^+$ requires m/z 194.1096, found 194.1097.



*(E)-1-chloro-4-styrylbenzene (**3w**)*[6]. White solid; m.p. 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.07 (s, 2H), 7.28 (d, J = 7.2 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 126.8, 127.6, 127.9, 128.1, 129.0, 129.1, 129.5, 133.4, 136.1, 137.2. HRMS (ESI^+): calcd for $[C_{14}H_{11}Cl]^+$ requires m/z 214.0549, found 214.0551.

References:

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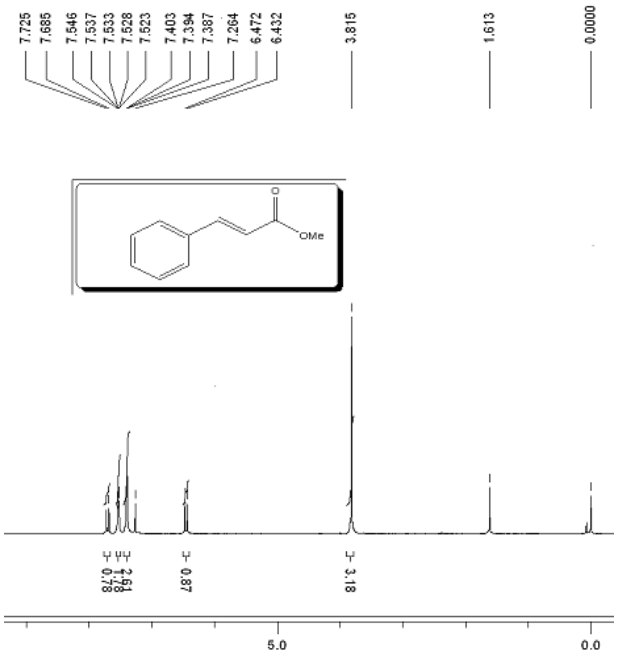
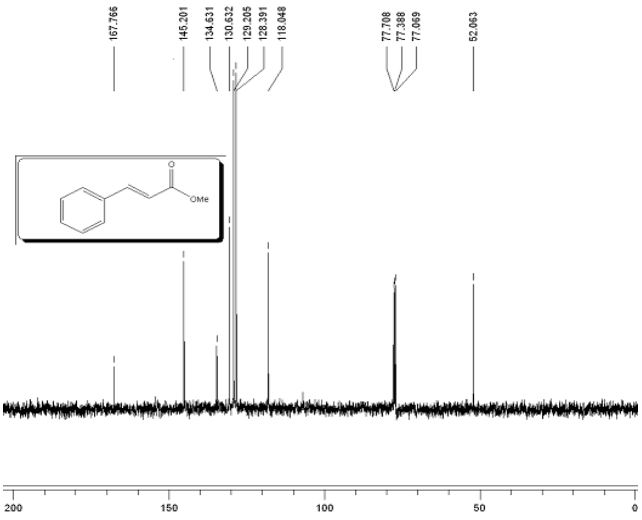
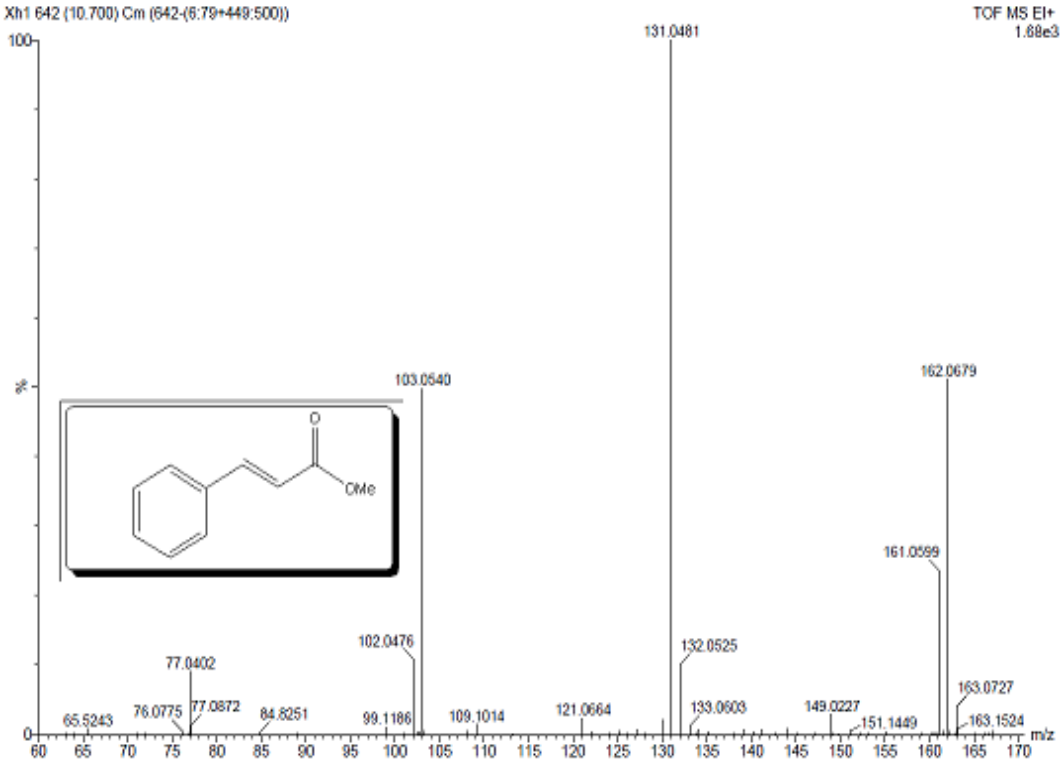
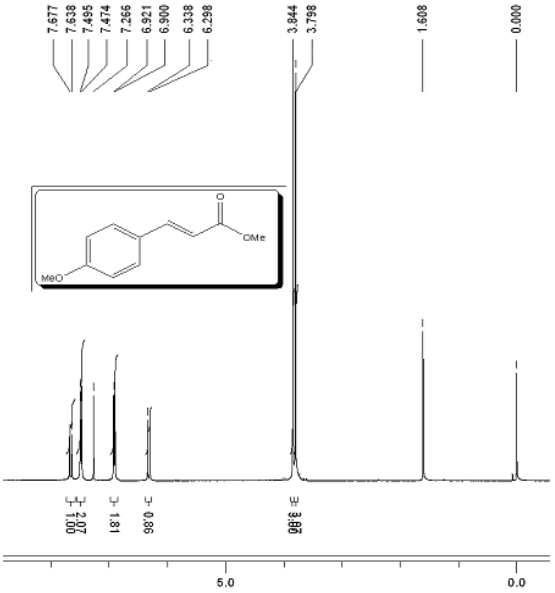
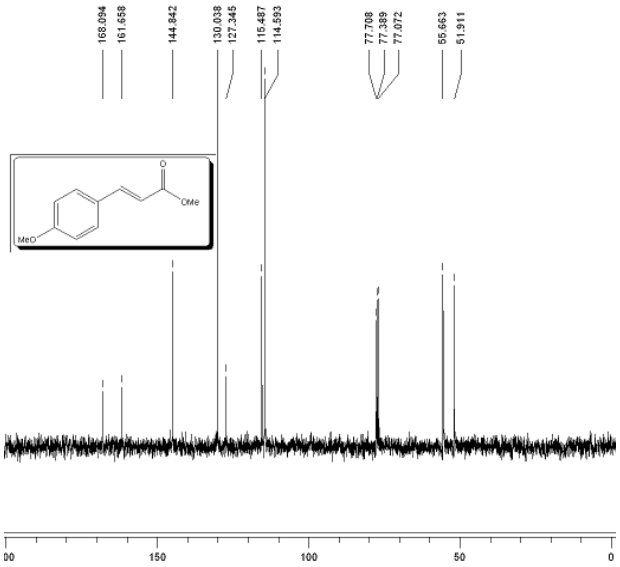
Copy of HRMS and NMR Spectra for desired products:

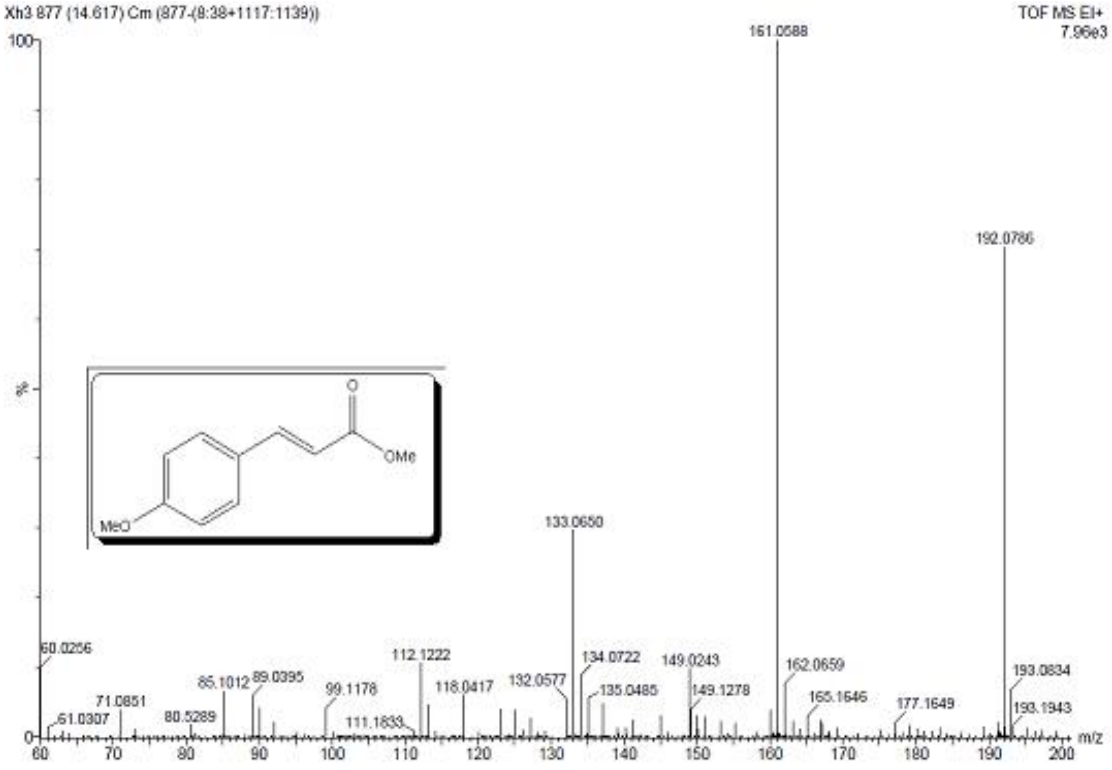


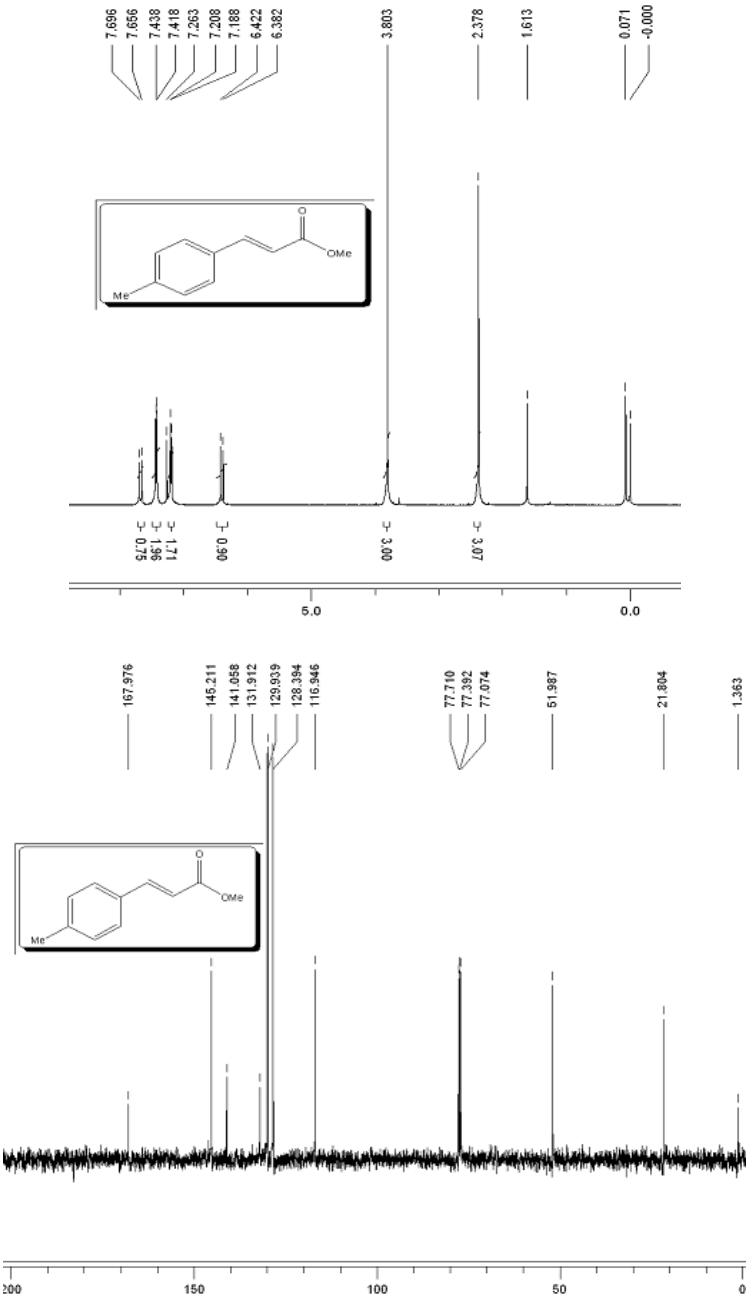


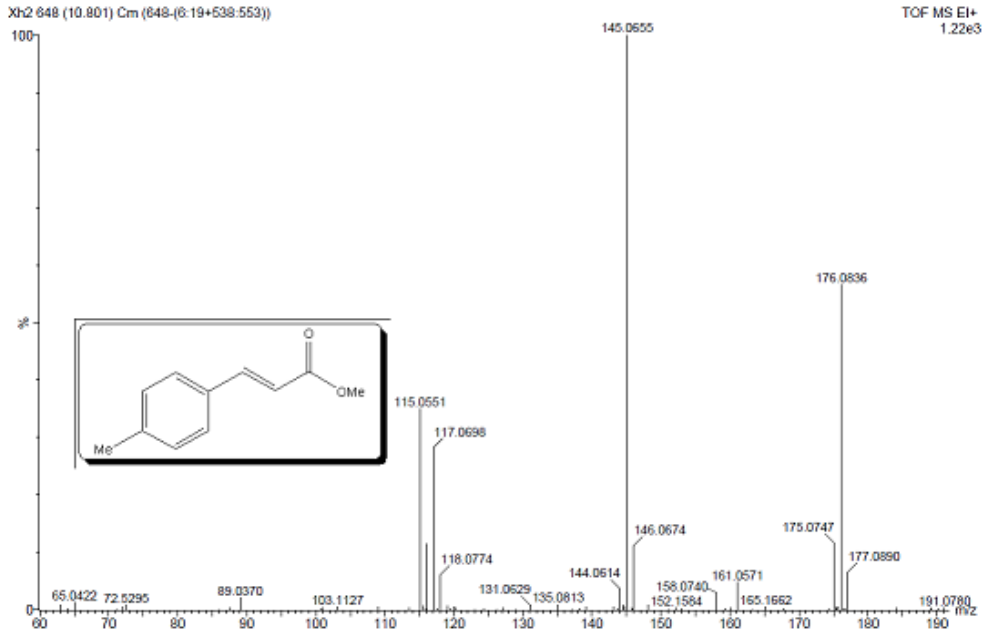


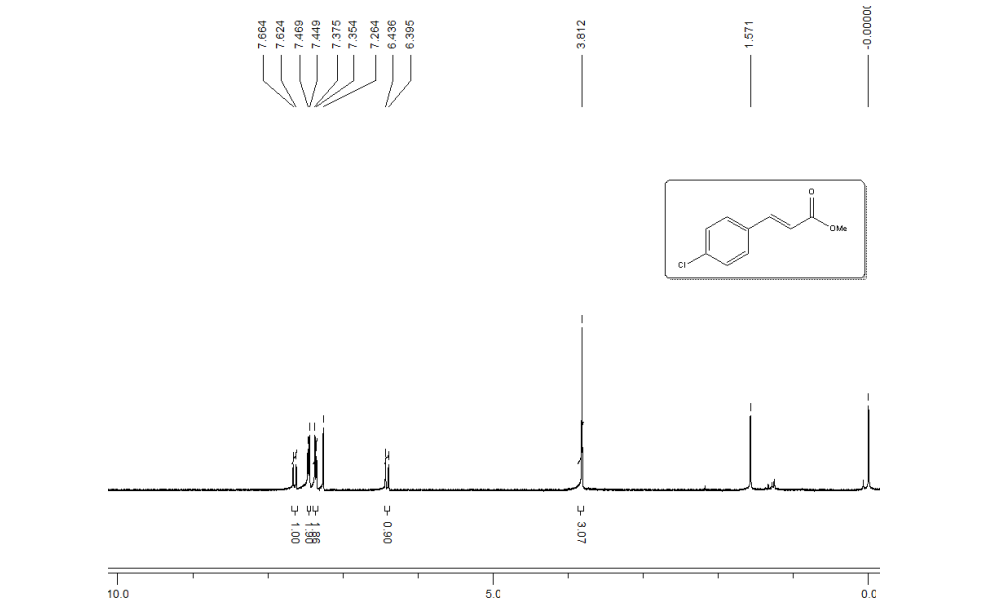


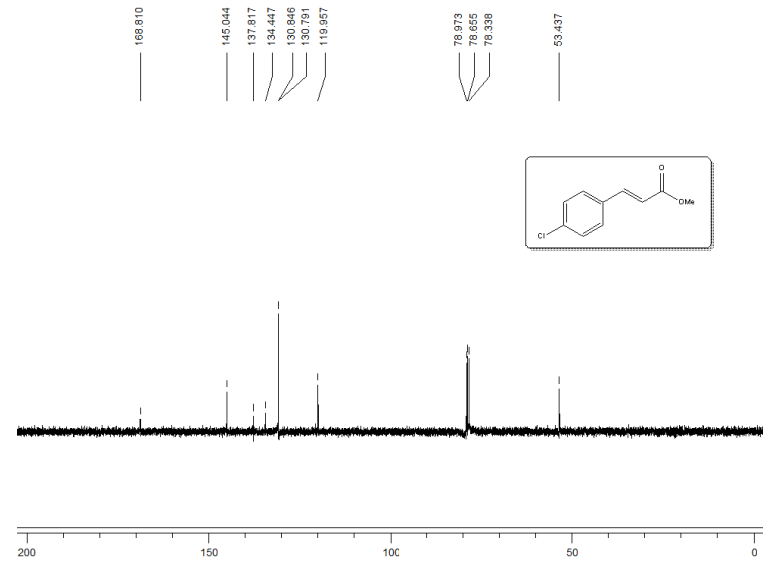


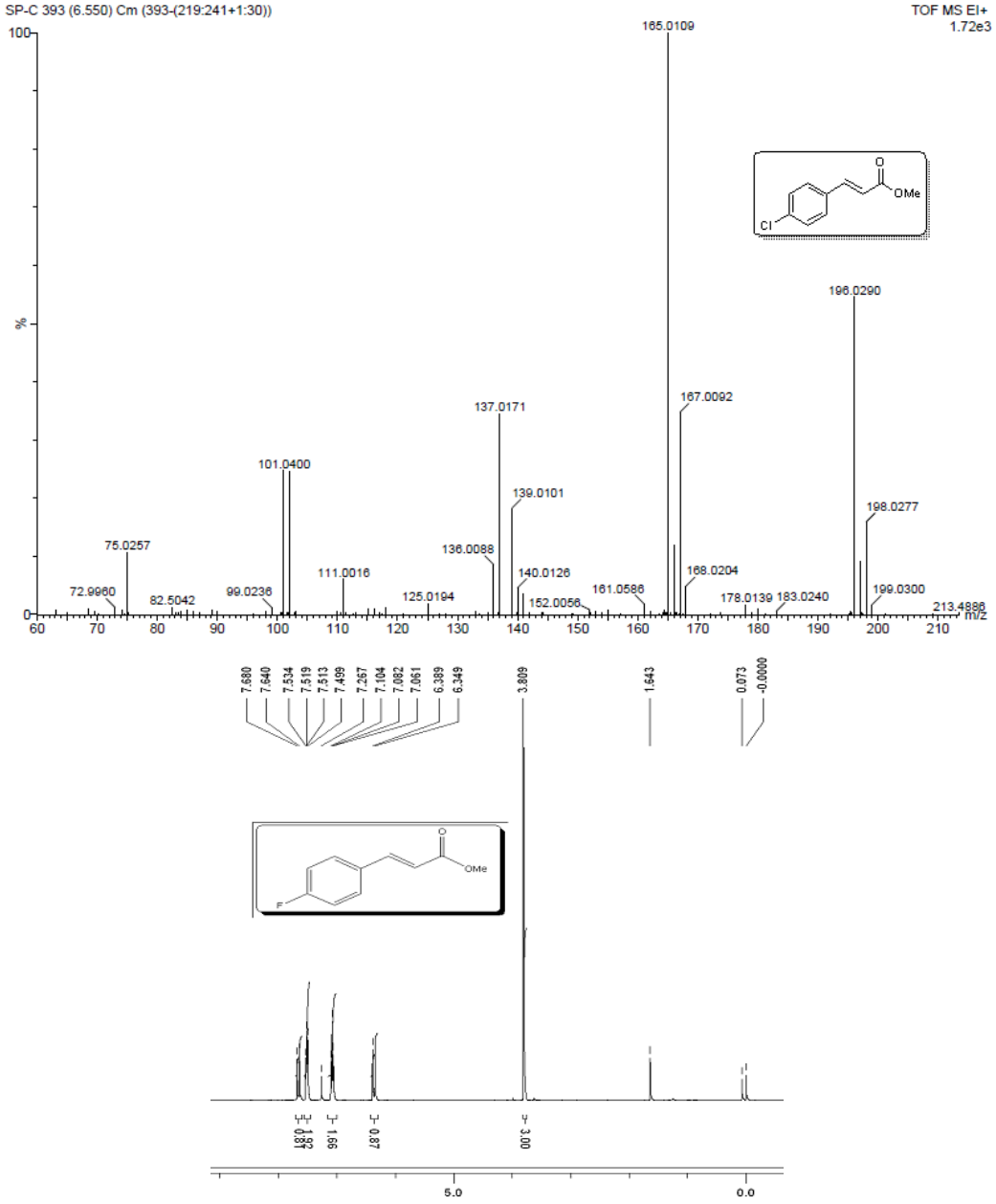


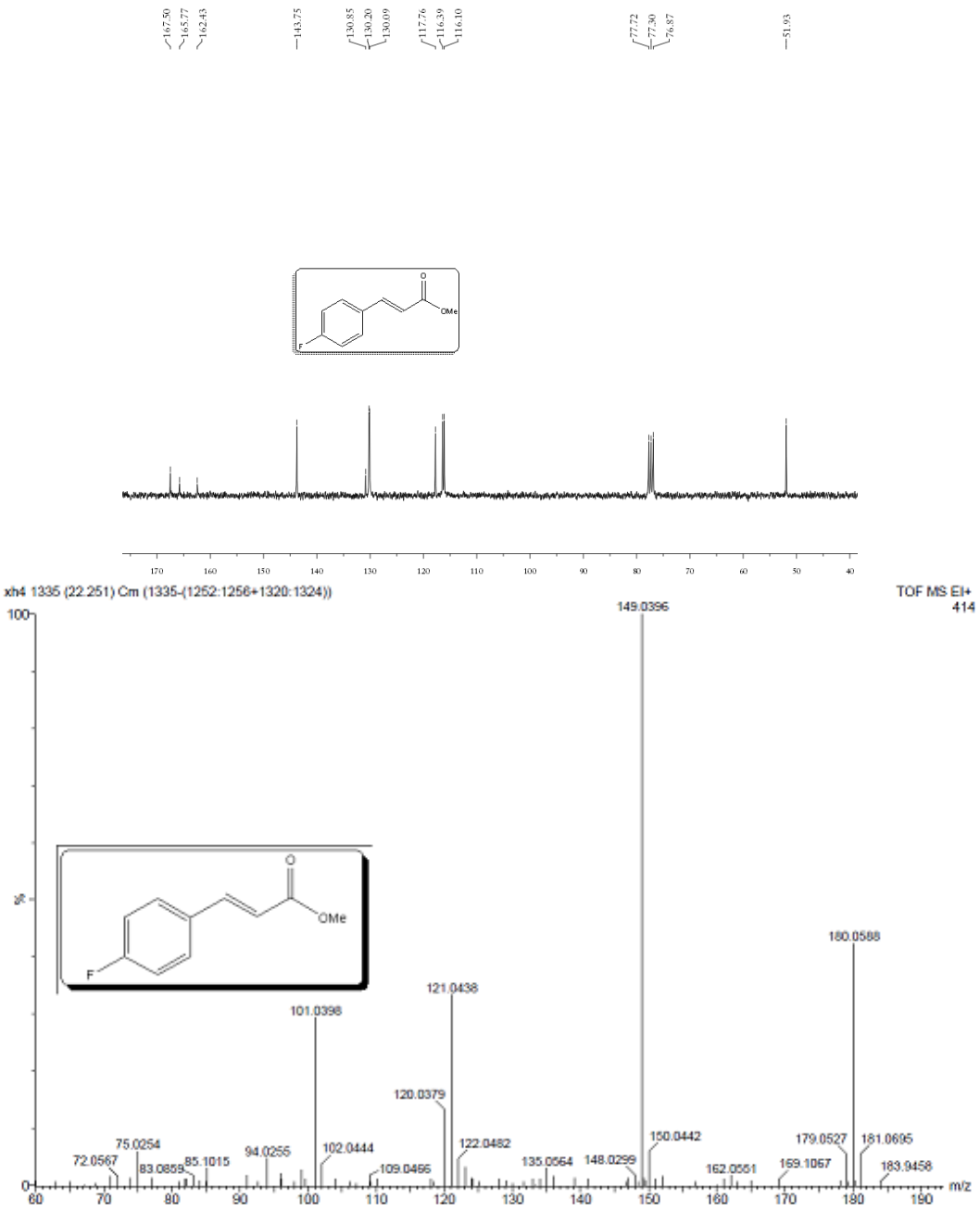


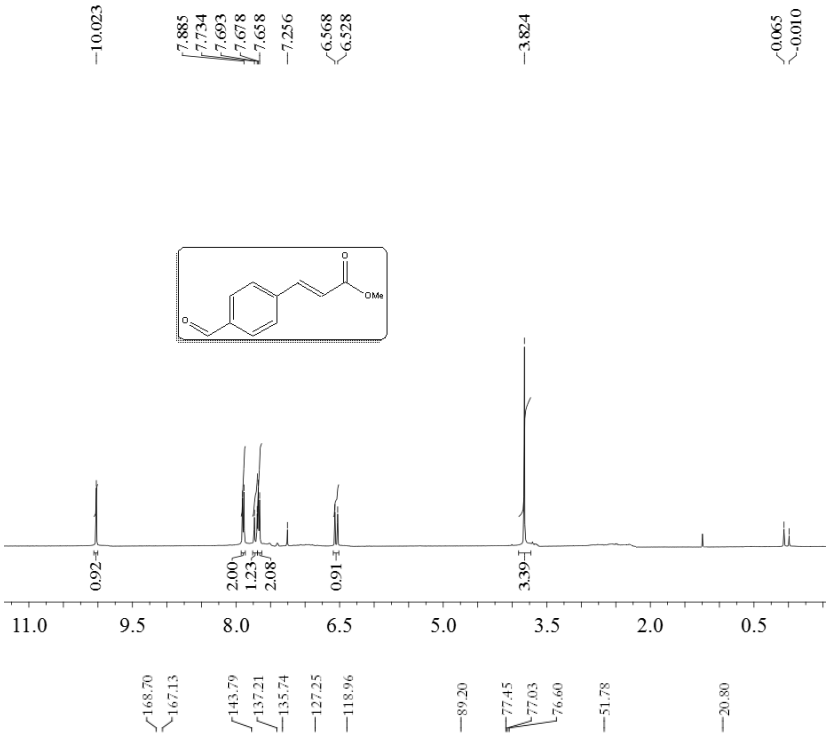

Xh2 648 (10.801) Cm (648-(6:19+538:553))
TOF MS EI+
1.22e3
145.0655
176.0836
115.0551
117.0698
146.0674
175.0747
118.0774
177.0890
144.0614
161.0571
158.0740
152.1584
165.1662
131.0629
135.0813
65.0422
72.5295
89.0370
103.1127
191.0780
OMe
Me


7.664
7.624
7.469
7.449
7.375
7.354
7.264
6.436
6.395
3.812
1.571
-0.0000
OMe
Cl
1.00
1.88
0.90
3.07
10.0
5.0
0.0


168.810
145.044
137.817
134.447
130.846
130.791
119.957
78.973
78.655
78.338
53.437
OMe
Cl
200
150
100
50
0


SP-C 393 (6.550) Cm (393-(219:241+1:30))
TOF MS EI+
1.72e3
100
%
0
165.0109
196.0290
167.0092
137.0171
101.0400
139.0101
198.0277
75.0257
136.0088
140.0126
168.0204
111.0016
161.0586
199.0300
72.9960
82.5042
99.0236
125.0194
152.0056
178.0139
183.0240
213.4886
m/z
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
Cl
O
OMe
7.680
7.640
7.534
7.519
7.513
7.499
7.267
7.104
7.082
7.061
6.389
6.349
3.809
1.643
0.073
-0.0000
F
OMe
0.87
1.66
0.87
3.00
5.0
0.0


167.50
165.77
162.43
143.75
130.85
130.20
130.09
117.76
116.39
116.10
77.72
77.30
76.87
51.93
O
OMe
F
xh4 1335 (22.251) Cm (1335-(1252:1256+1320:1324))
TOF MS EI+
414
100
%
0
149.0396
180.0588
121.0438
101.0398
120.0379
75.0254
72.0567
83.0859
85.1015
94.0255
102.0444
109.0466
122.0482
135.0564
148.0299
150.0442
162.0551
169.1067
179.0527
181.0695
183.9458
m/z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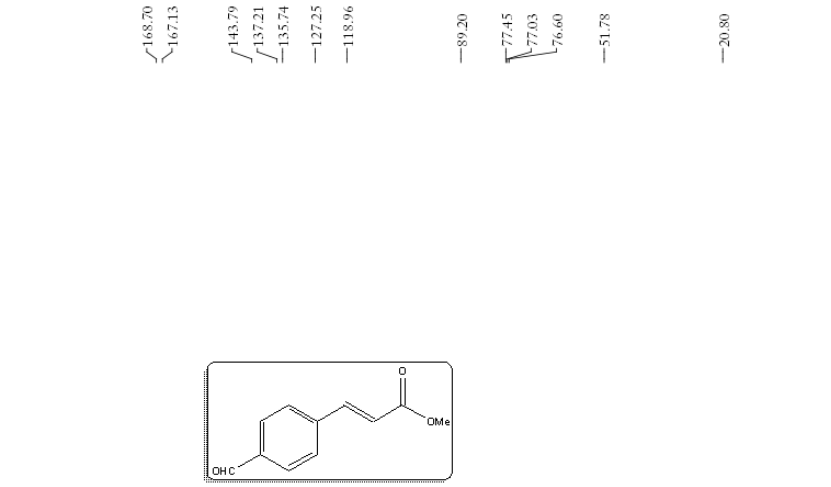
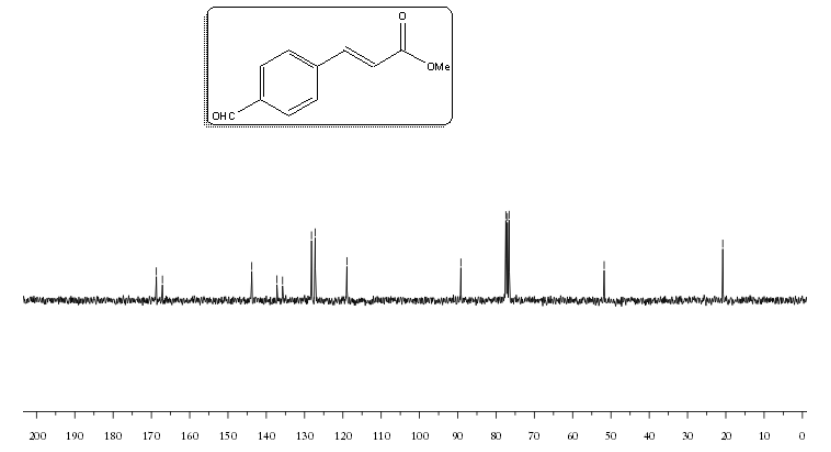
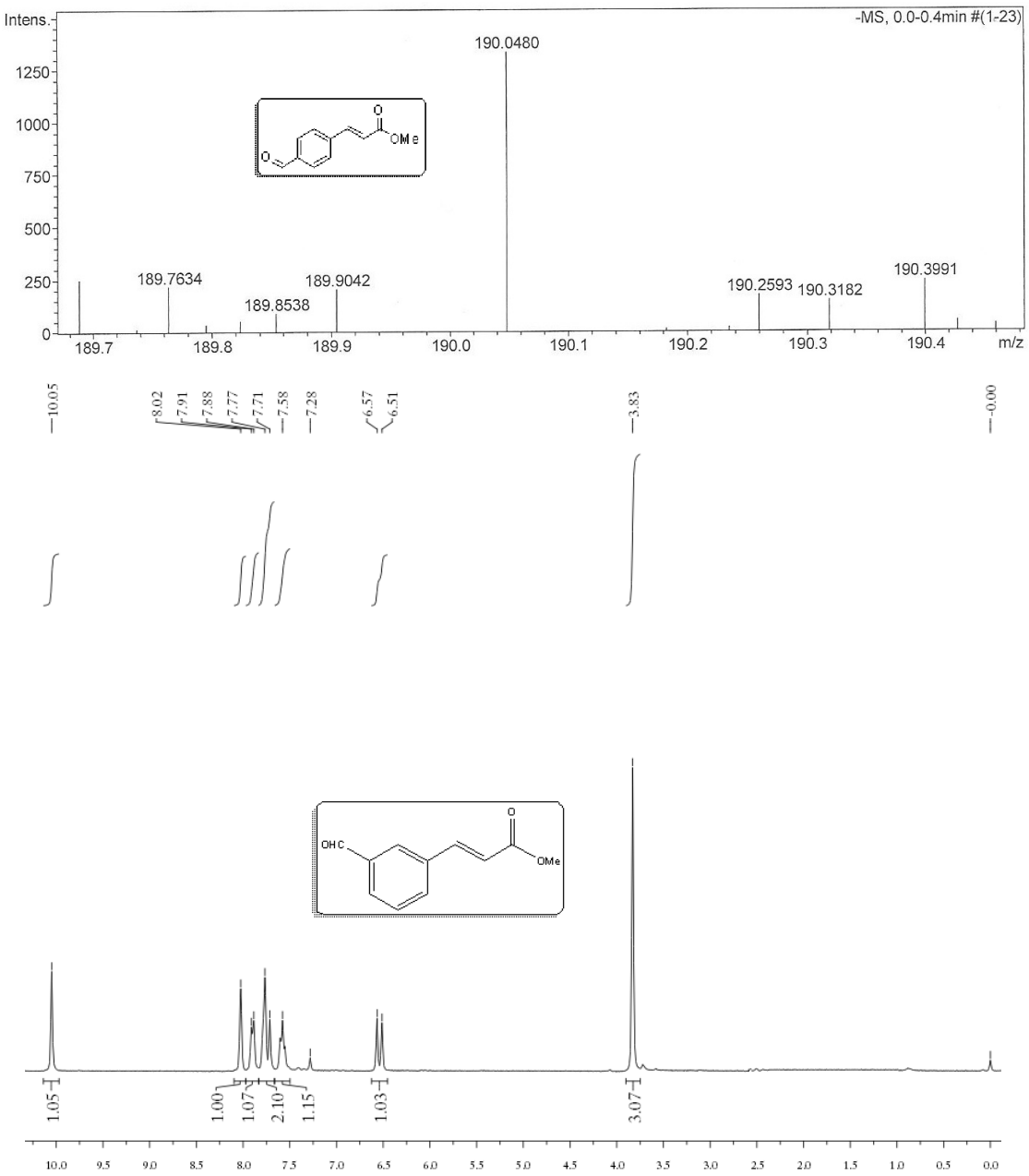
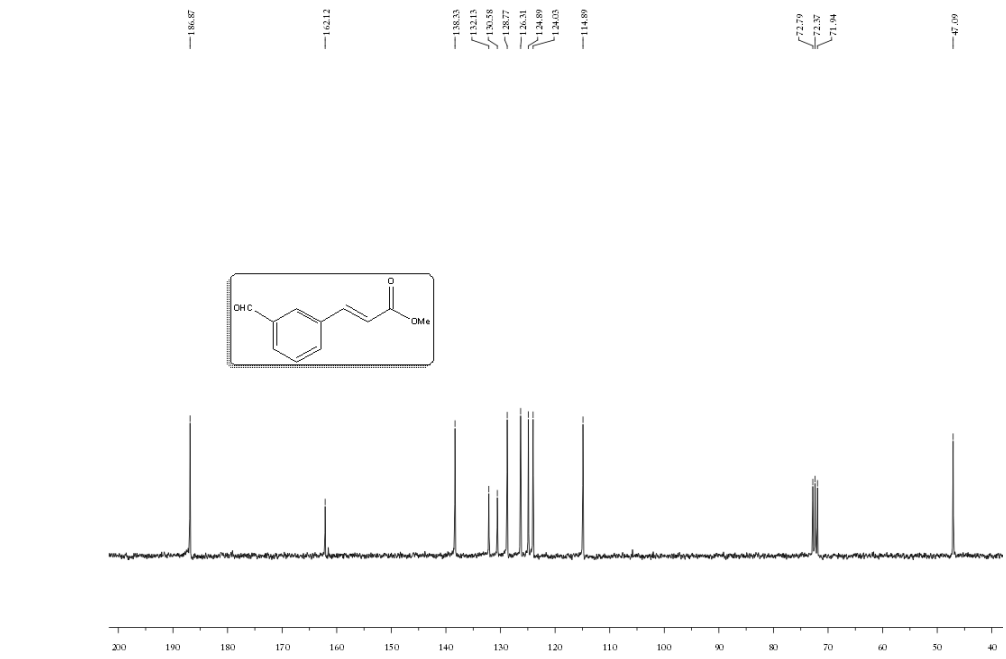
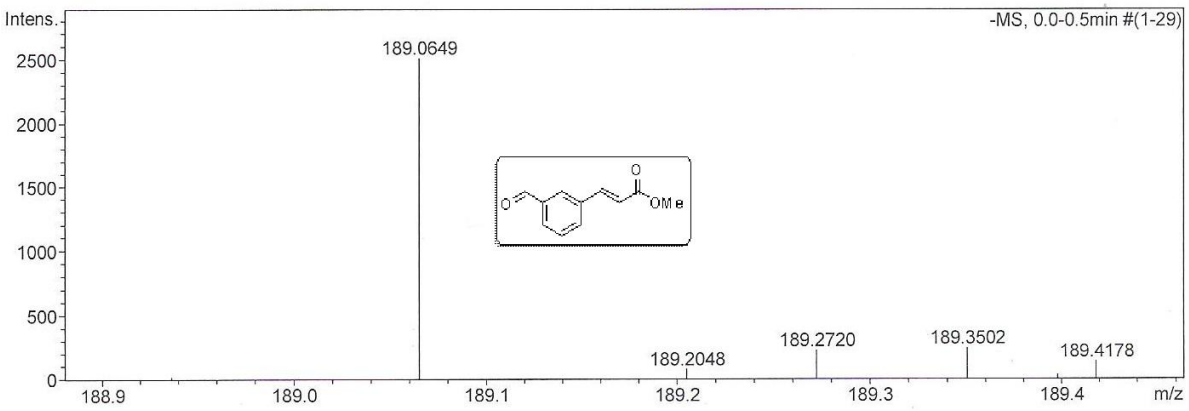
7.885
7.734
7.693
7.678
7.658
7.256
6.568
6.528
3.824
0.065
-0.010
OMe
O
0.92
2.00
1.23
2.08
0.91
3.39
11.0
9.5
8.0
6.5
5.0
3.5
2.0
0.5

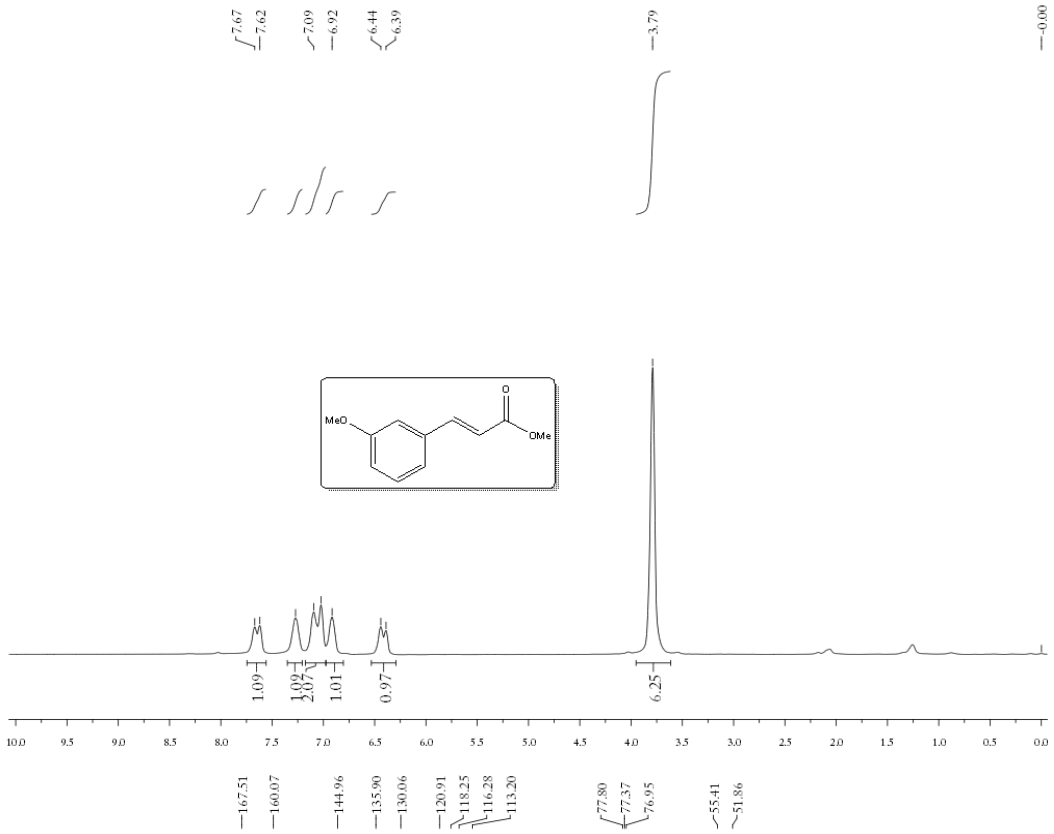

168.70
167.13
143.79
137.21
135.74
127.25
118.96
89.20
77.45
77.03
76.60
51.78
20.80

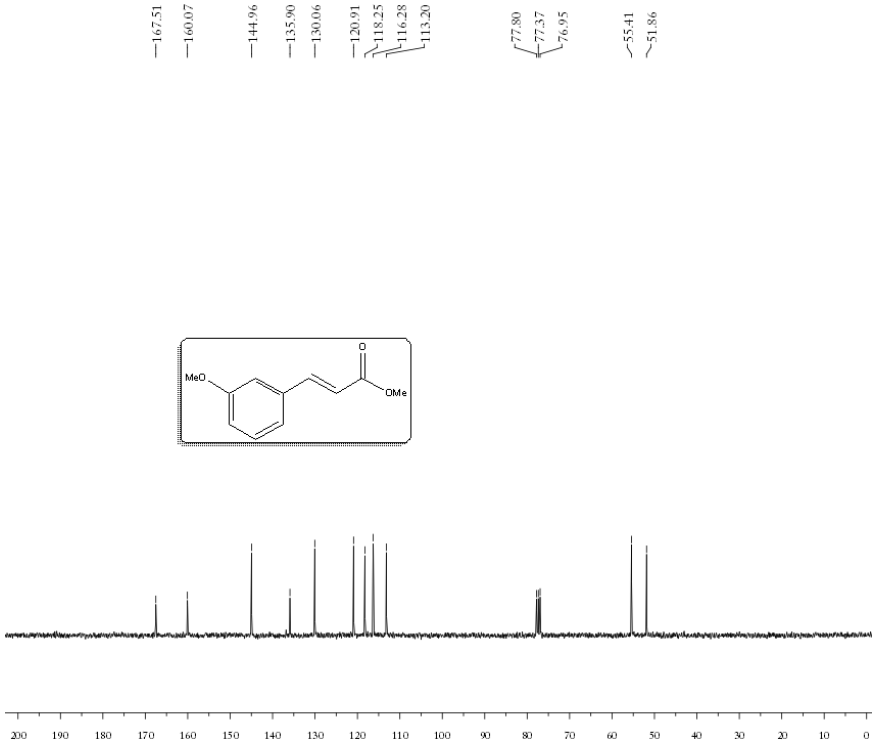

OMe
O
OHC
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0








7.67
7.62
7.09
6.92
6.44
6.39
3.79
0.00
MeO
OMe
1.09
1.09
2.07
1.01
0.97
6.25
10.0
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


167.51
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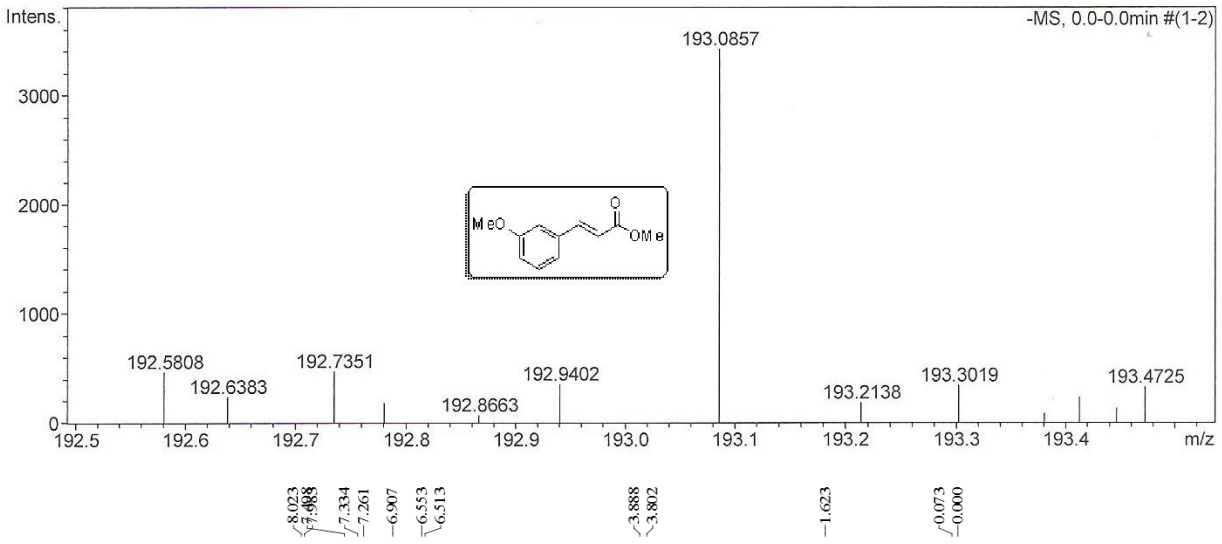
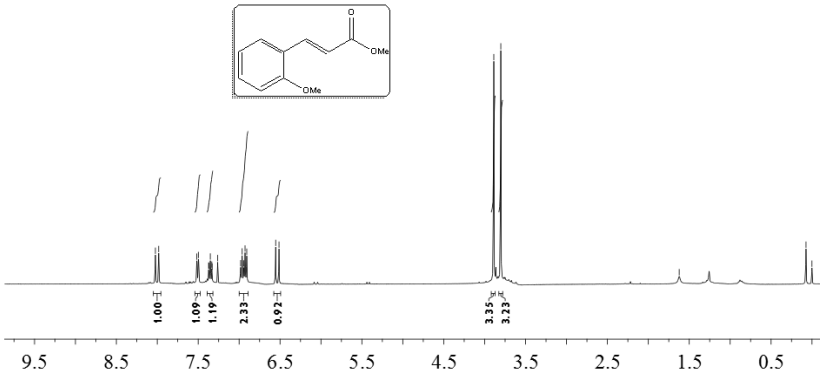
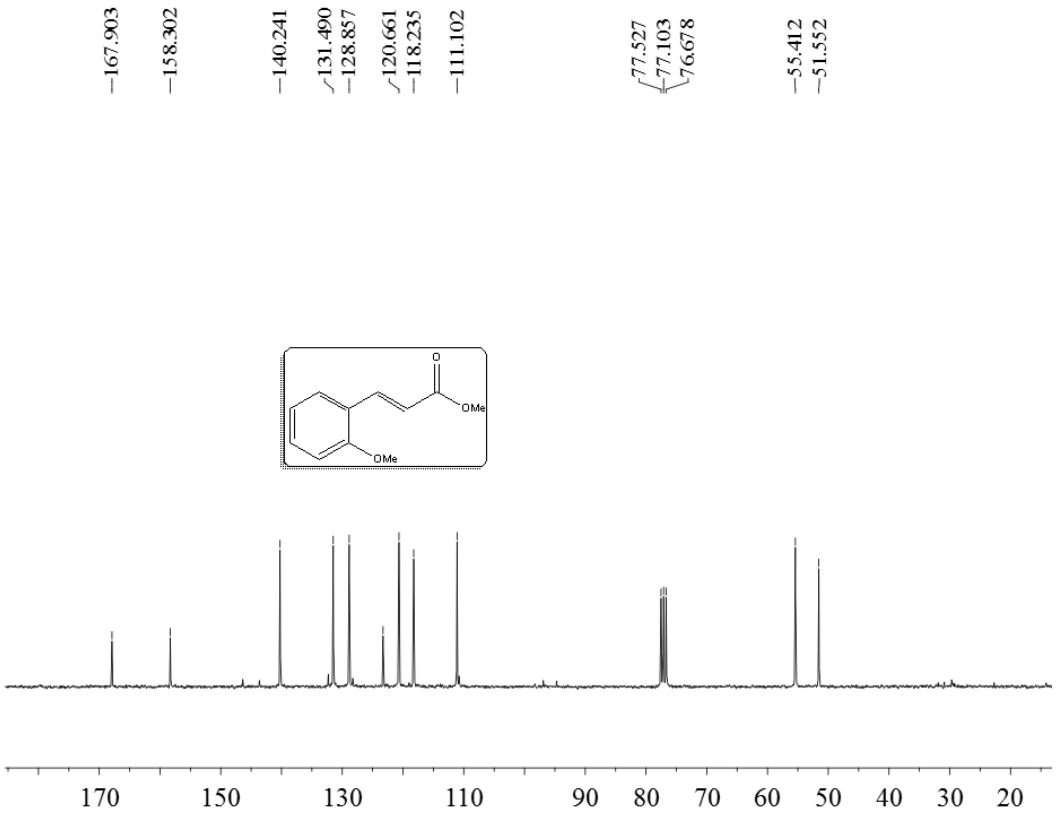
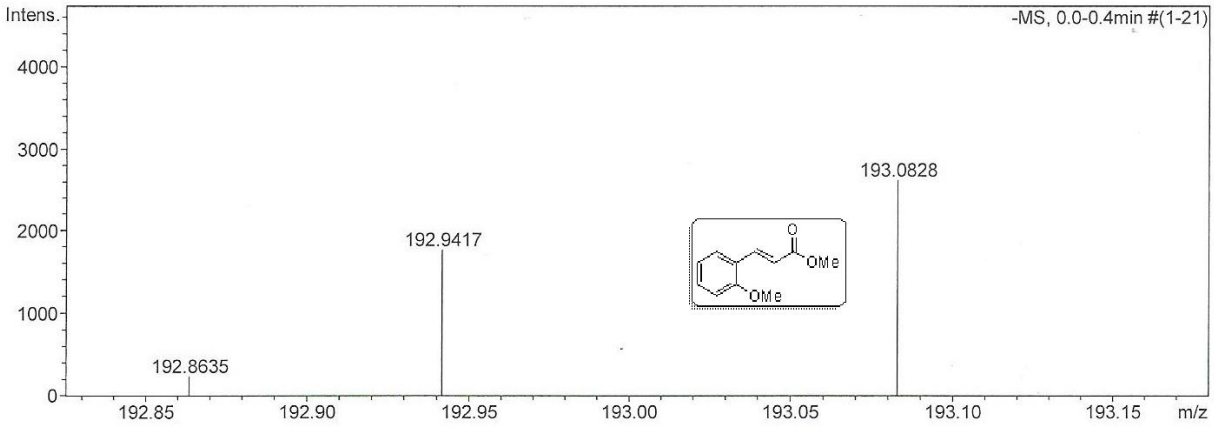
135.90
130.06
120.91
118.25
116.28
113.20
77.80
77.37
76.95
55.41
51.86
MeO
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0






167.903
158.302
140.241
131.490
128.857
120.661
118.235
111.102
77.527
77.103
76.678
55.412
51.552
O
OMe
OMe
170
150
130
110
90
80
70
60
50
40
30
20


Intens.
-MS, 0.0-0.4min #(1-21)
4000
3000
2000
1000
0
193.0828
192.9417
192.8635
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OMe
OMe
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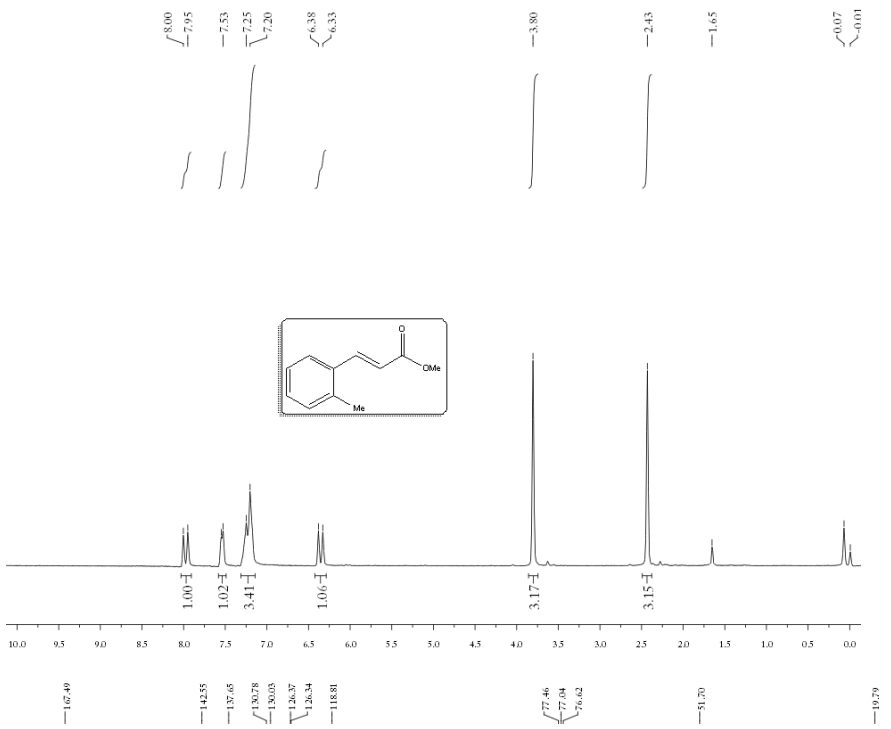
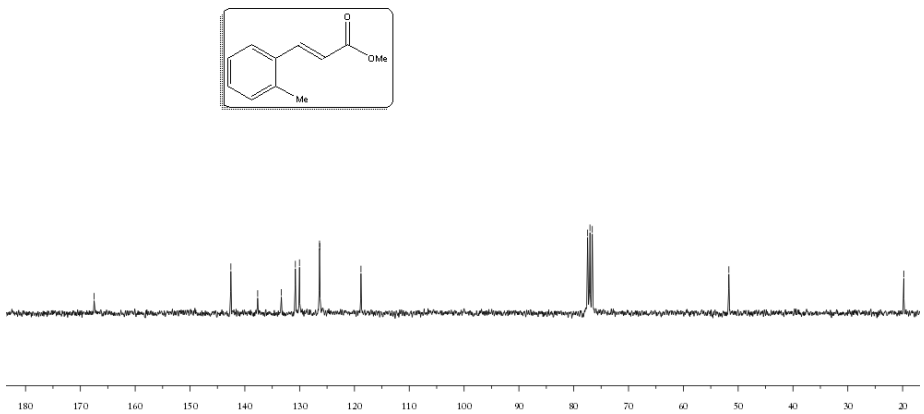
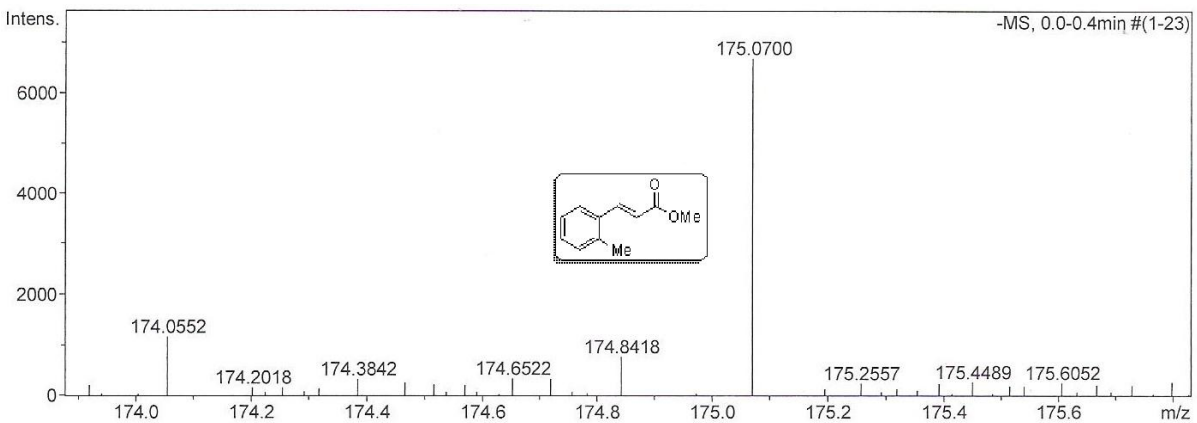
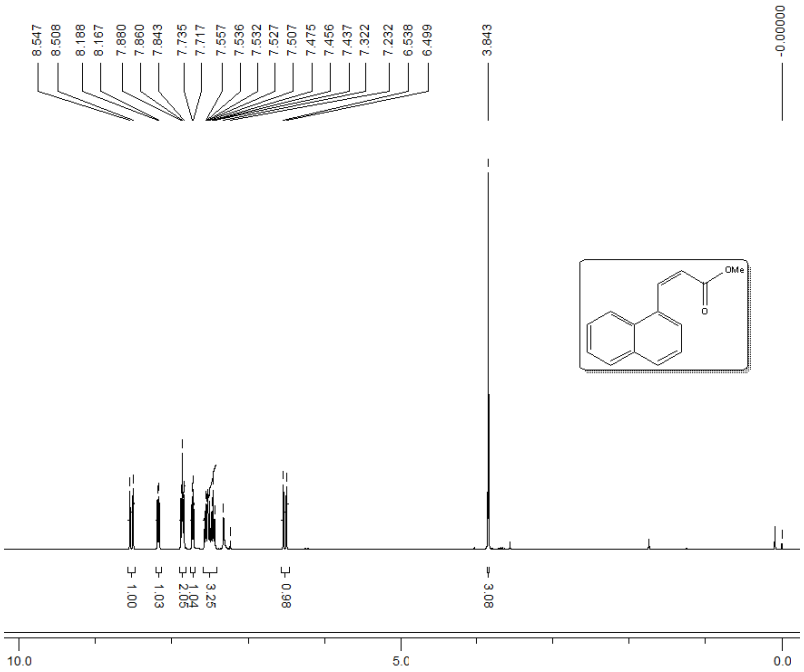
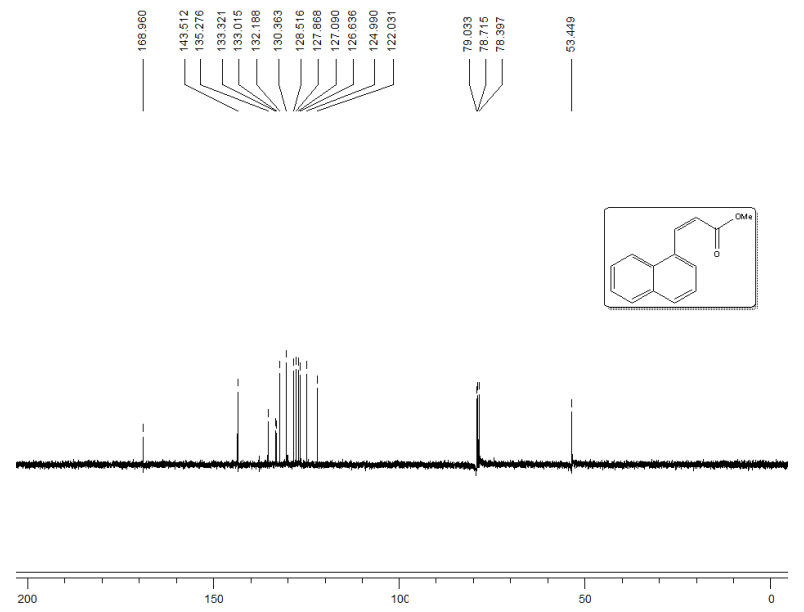
193.00
193.05
193.10
193.15
m/z

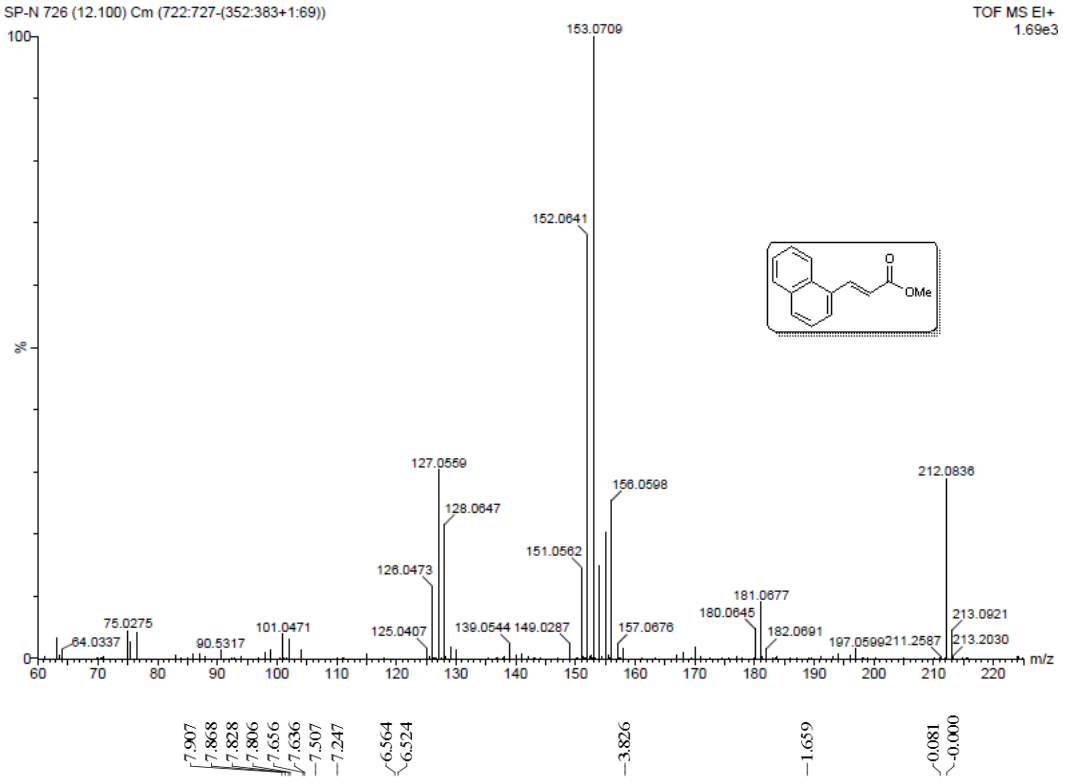


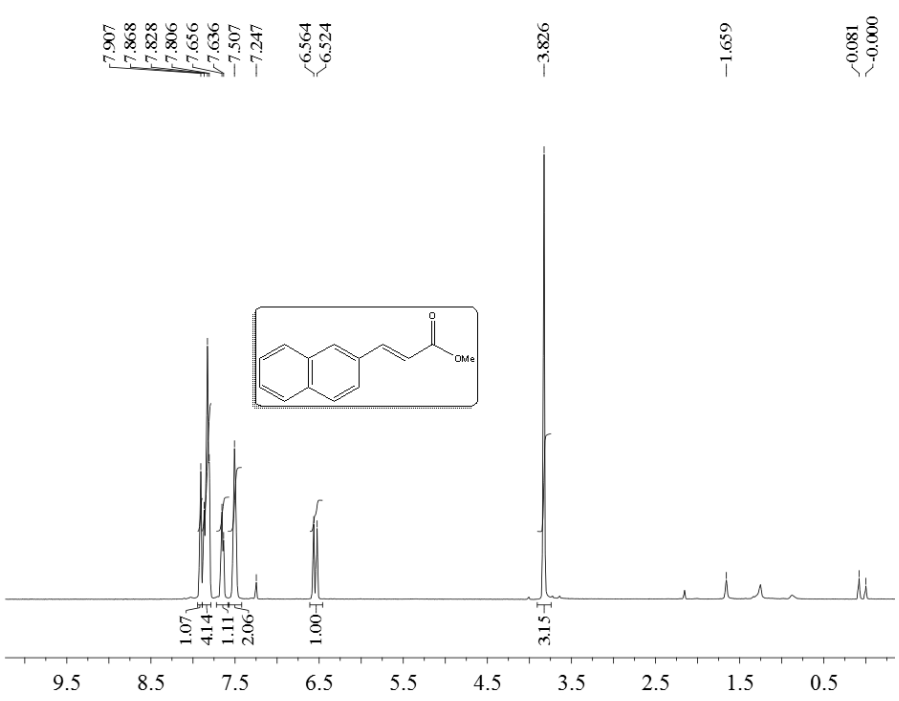


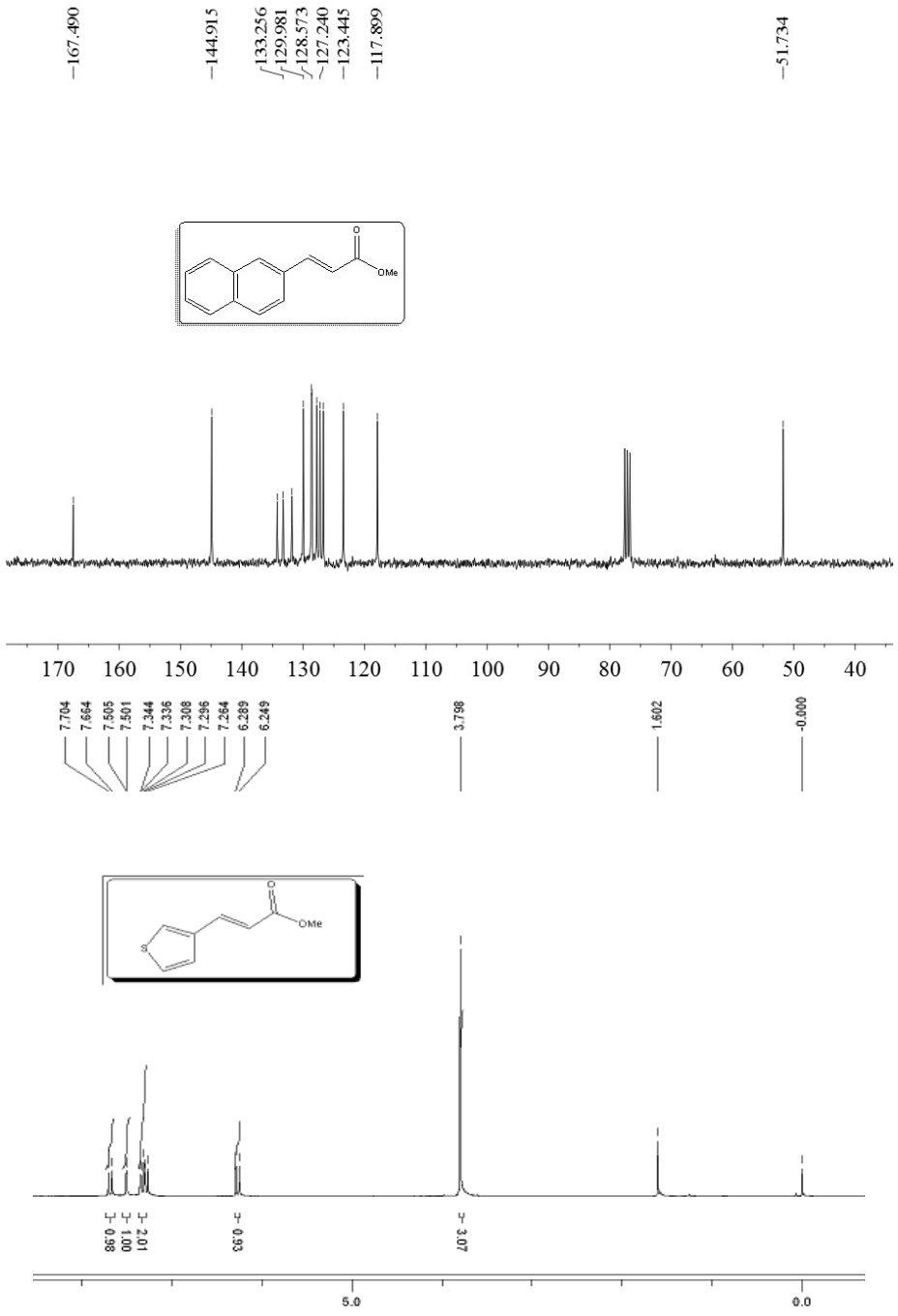


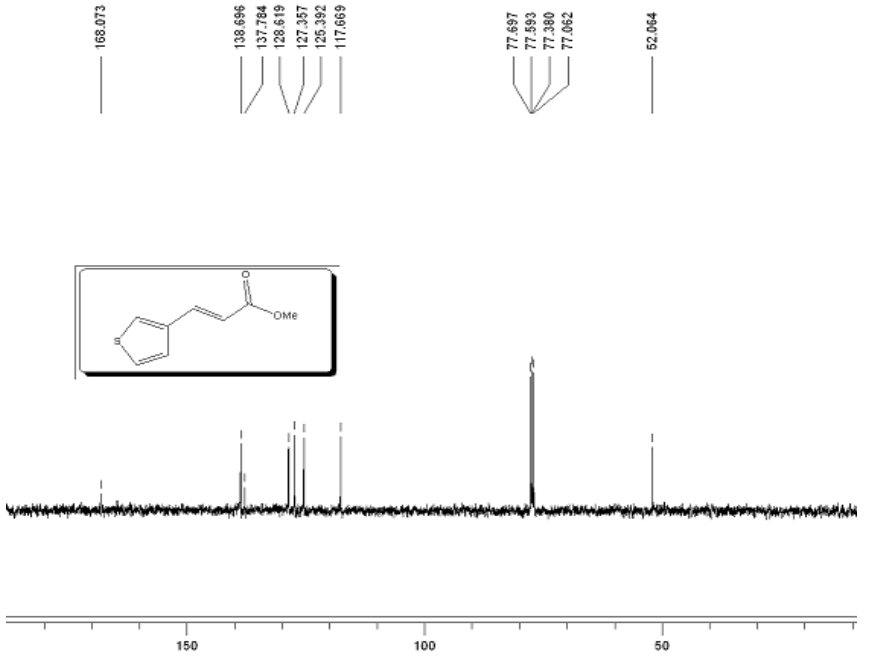


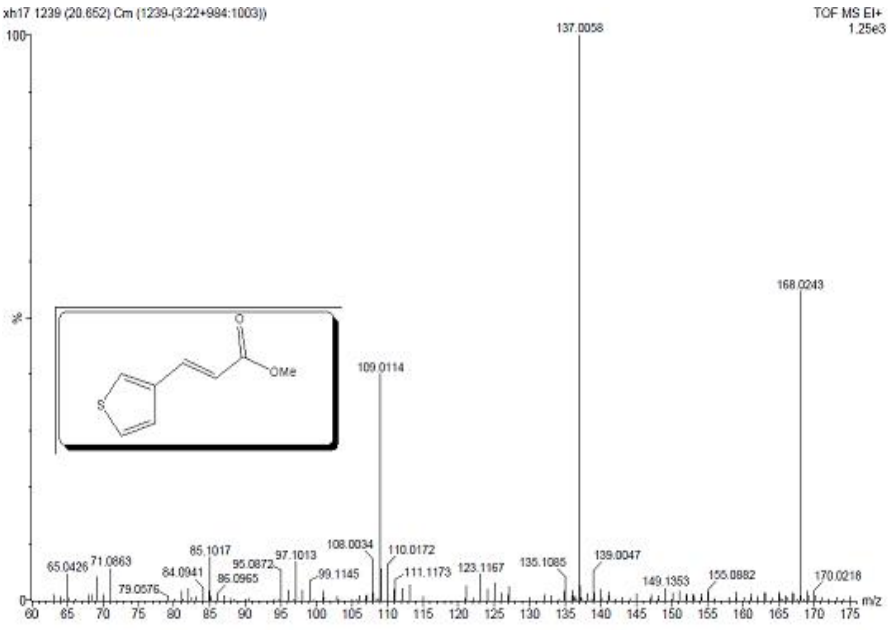


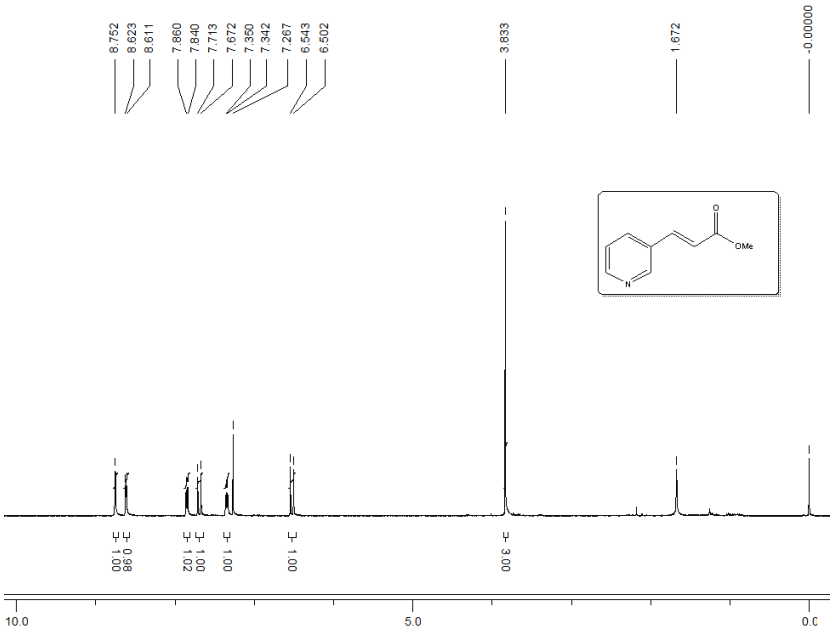

SP-N 726 (12.100) Cm (722:727-(352:383+1:69))
TOF MS EI+
1.69e3
153.0709
152.0641
127.0559
156.0598
128.0647
212.0836
151.0562
126.0473
181.0677
180.0645
213.0921
75.0275
64.0337
101.0471
90.5317
125.0407
139.0544
149.0287
157.0676
182.0691
197.0599
211.2587
213.2030
%
m/z
OMe

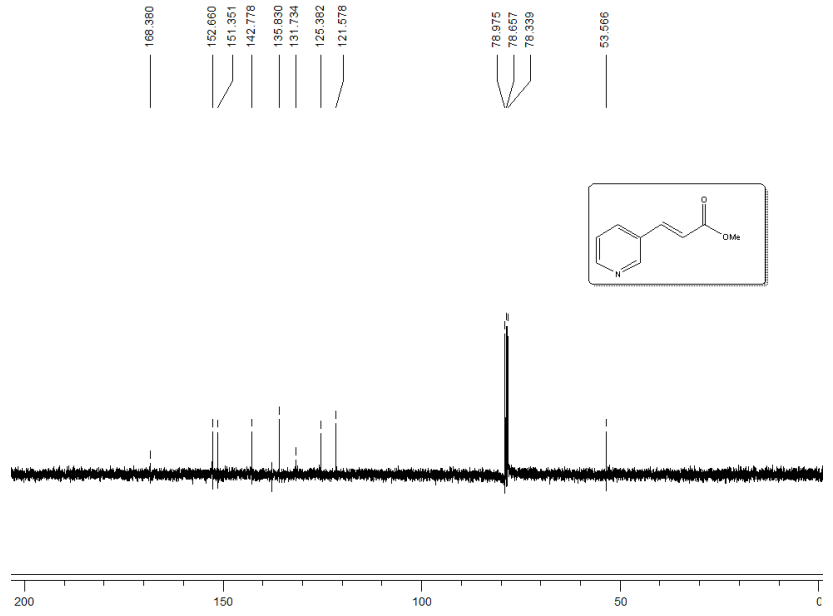

7.907
7.868
7.828
7.806
7.656
7.636
7.507
7.247
6.564
6.524
3.826
1.659
0.081
0.000
1.07
4.14
1.11
2.06
1.00
3.15
OMe

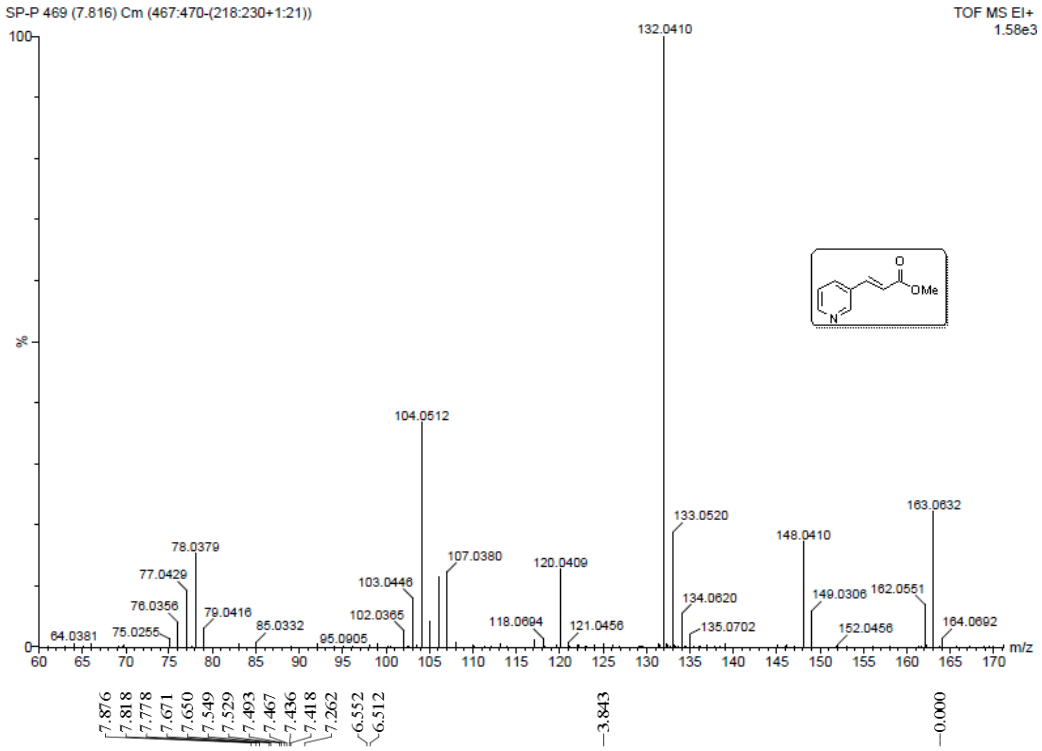

167.490
144.915
133.256
129.981
128.573
127.240
123.445
117.899
51.734
O
OMe
170 160 150 140 130 120 110 100 90 80 70 60 50 40
7.704
7.664
7.505
7.501
7.344
7.336
7.308
7.296
7.264
6.289
6.249
3.798
1.602
-0.000
O
OMe
S
0.88
1.00
2.01
0.93
3.07
5.0
0.0

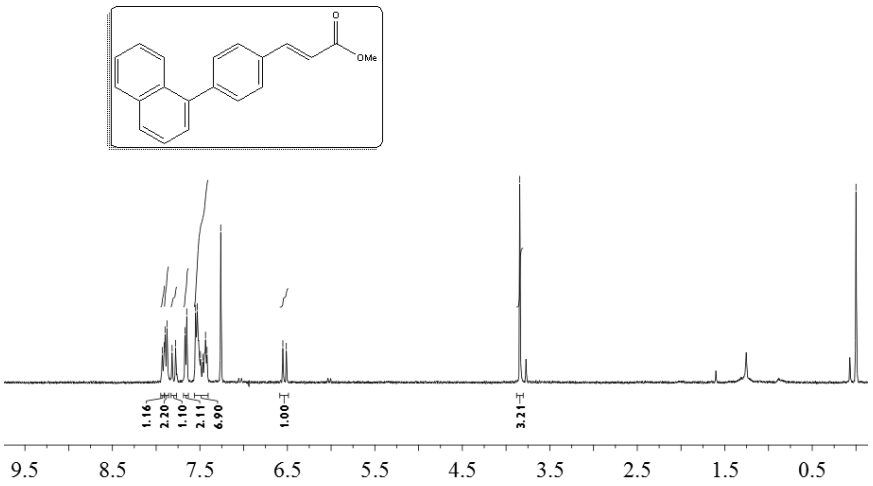


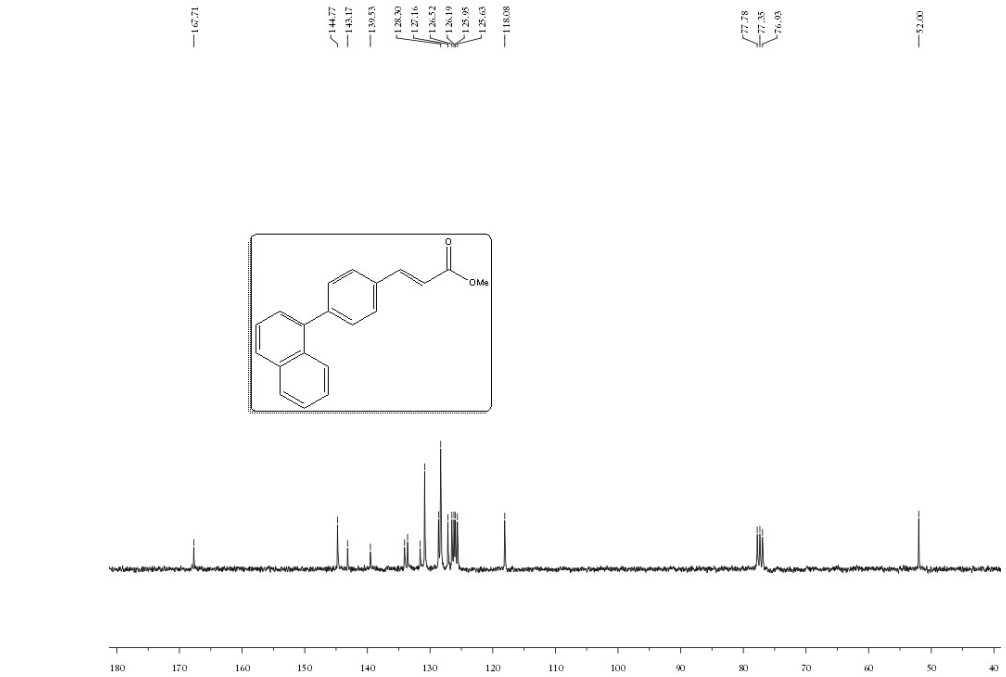


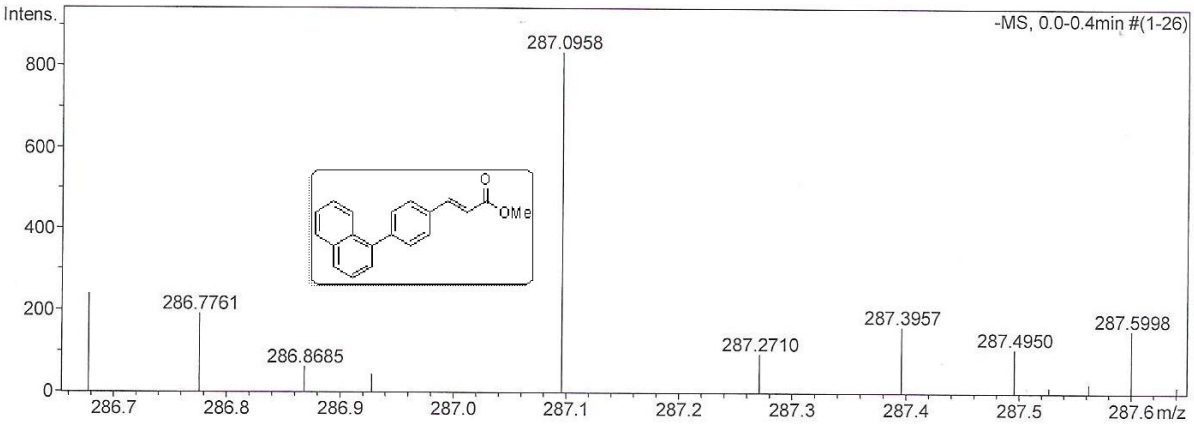


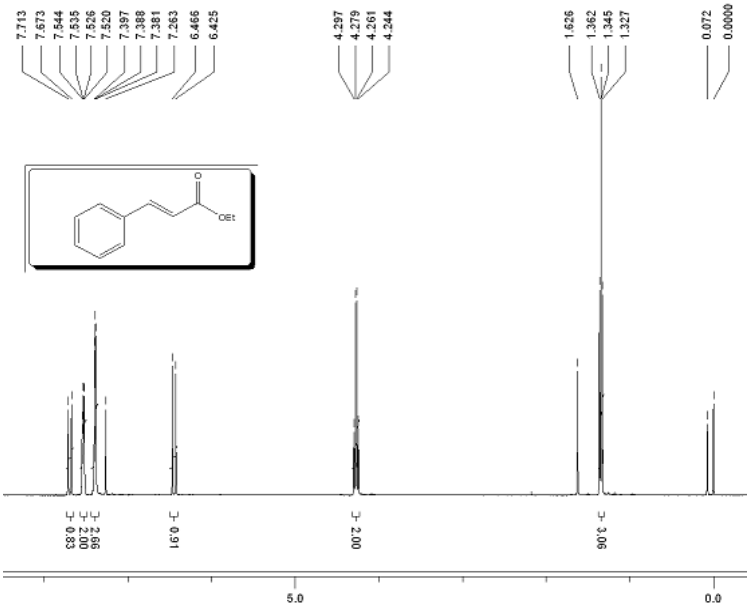


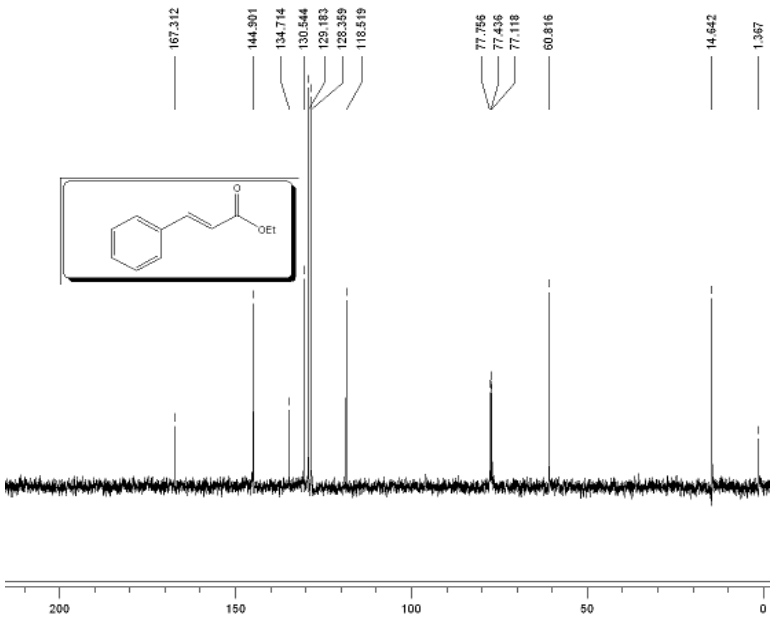

SP-P 469 (7.816) Cm (467:470-(218:230+1:21))
TOF MS EI+
1.58e3
100
%
0
132.0410
104.0512
133.0520
163.0632
148.0410
107.0380
120.0409
78.0379
77.0429
103.0446
134.0620
149.0306
162.0551
76.0356
79.0416
102.0365
118.0694
121.0456
135.0702
164.0692
75.0255
85.0332
152.0456
64.0381
95.0905
O
OMe
N
60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170
m/z
7.876
7.818
7.778
7.671
7.650
7.549
7.529
7.493
7.467
7.436
7.418
7.262
6.552
6.512
3.843
0.000

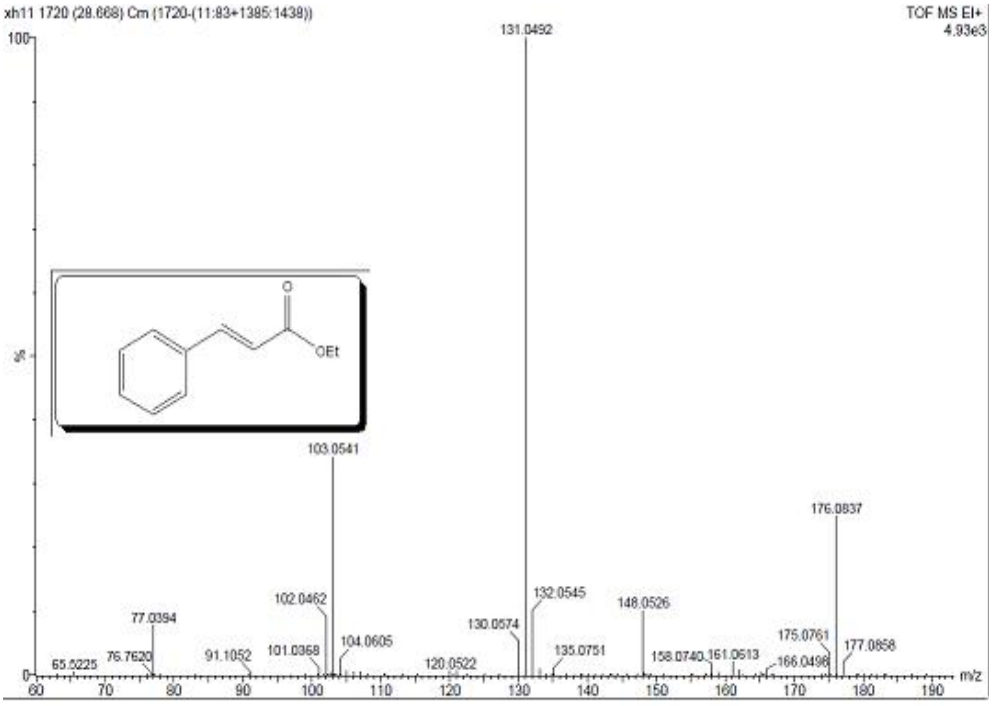

O
OMe
1.16
2.20
1.10
2.11
6.90
1.00
3.21
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5

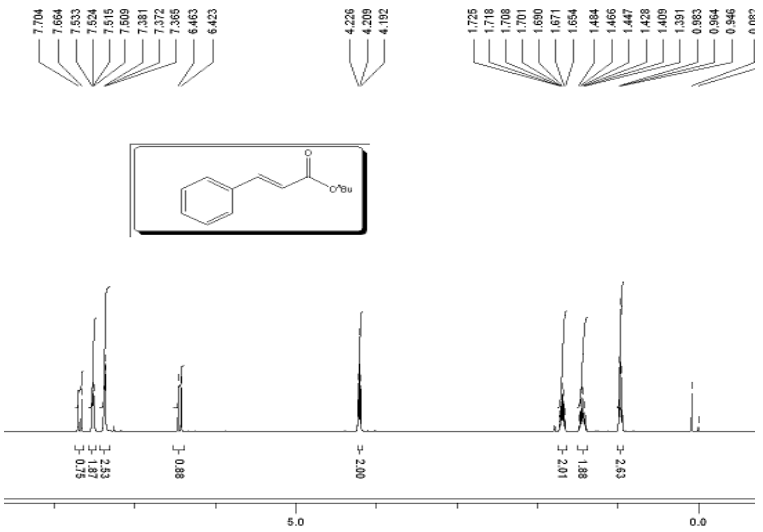


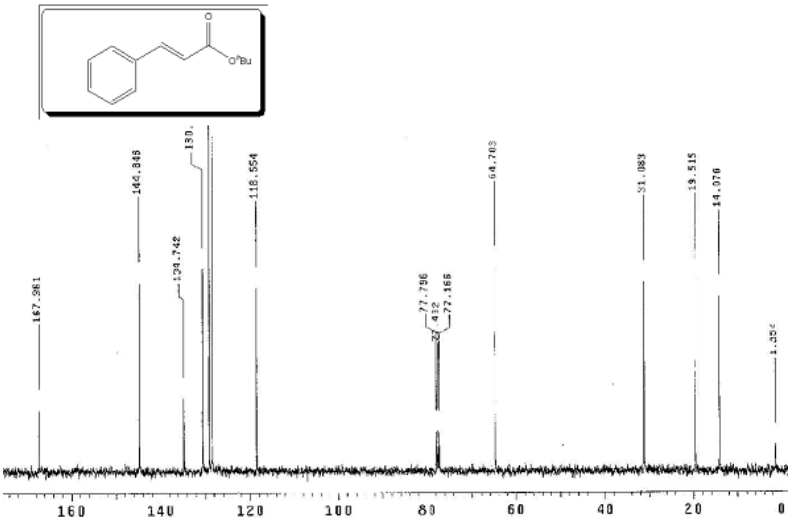


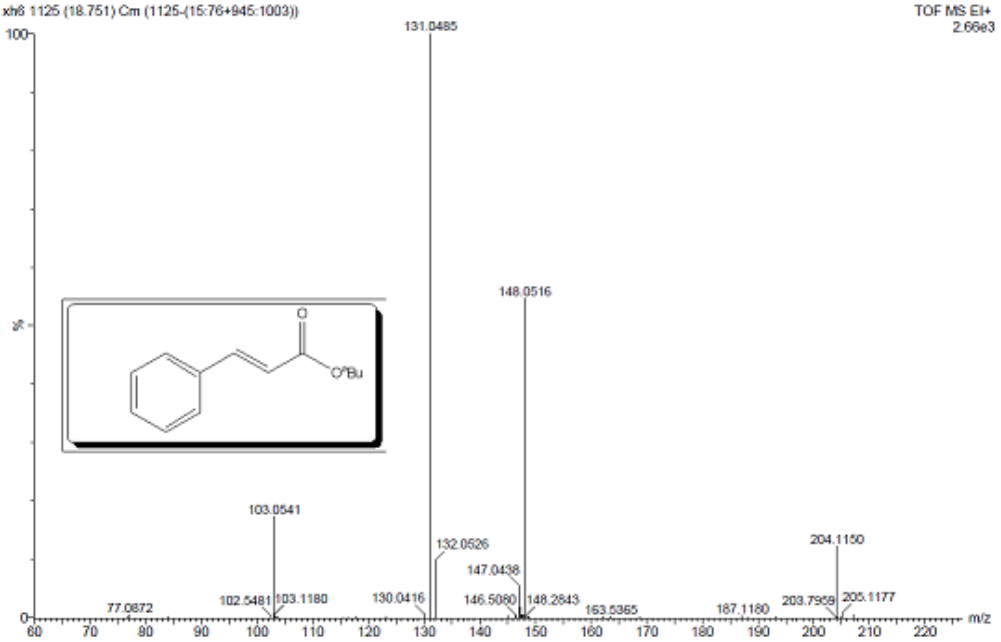


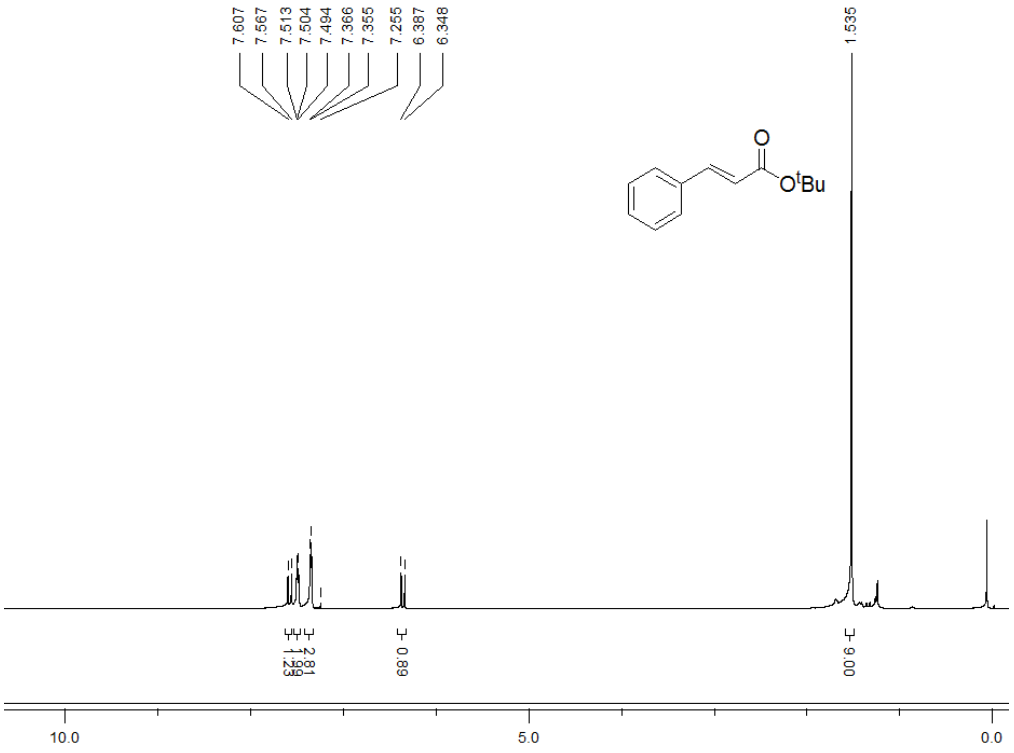


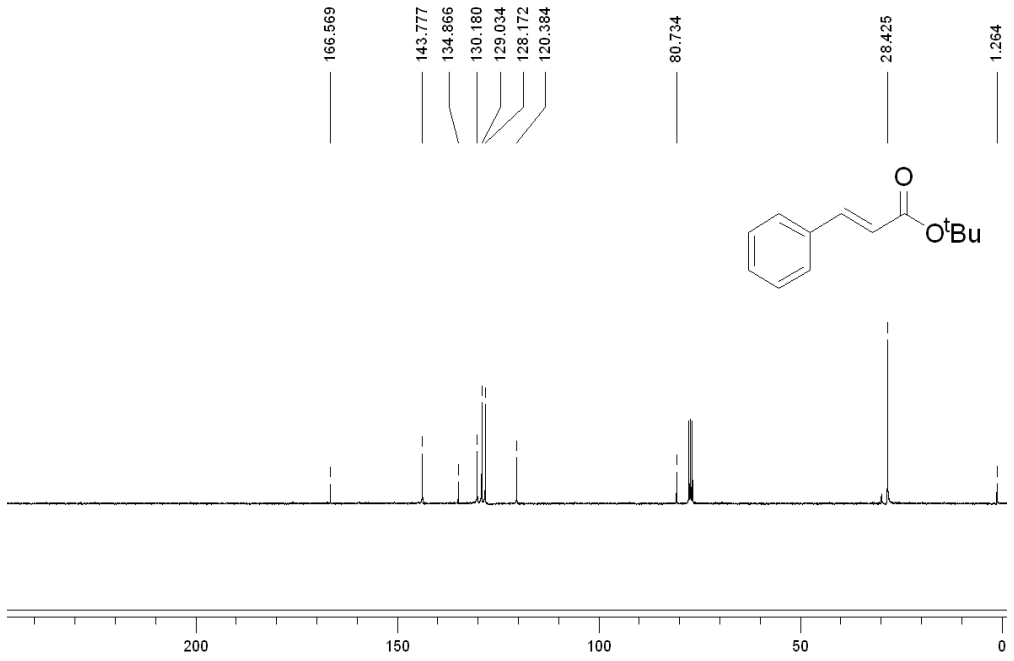


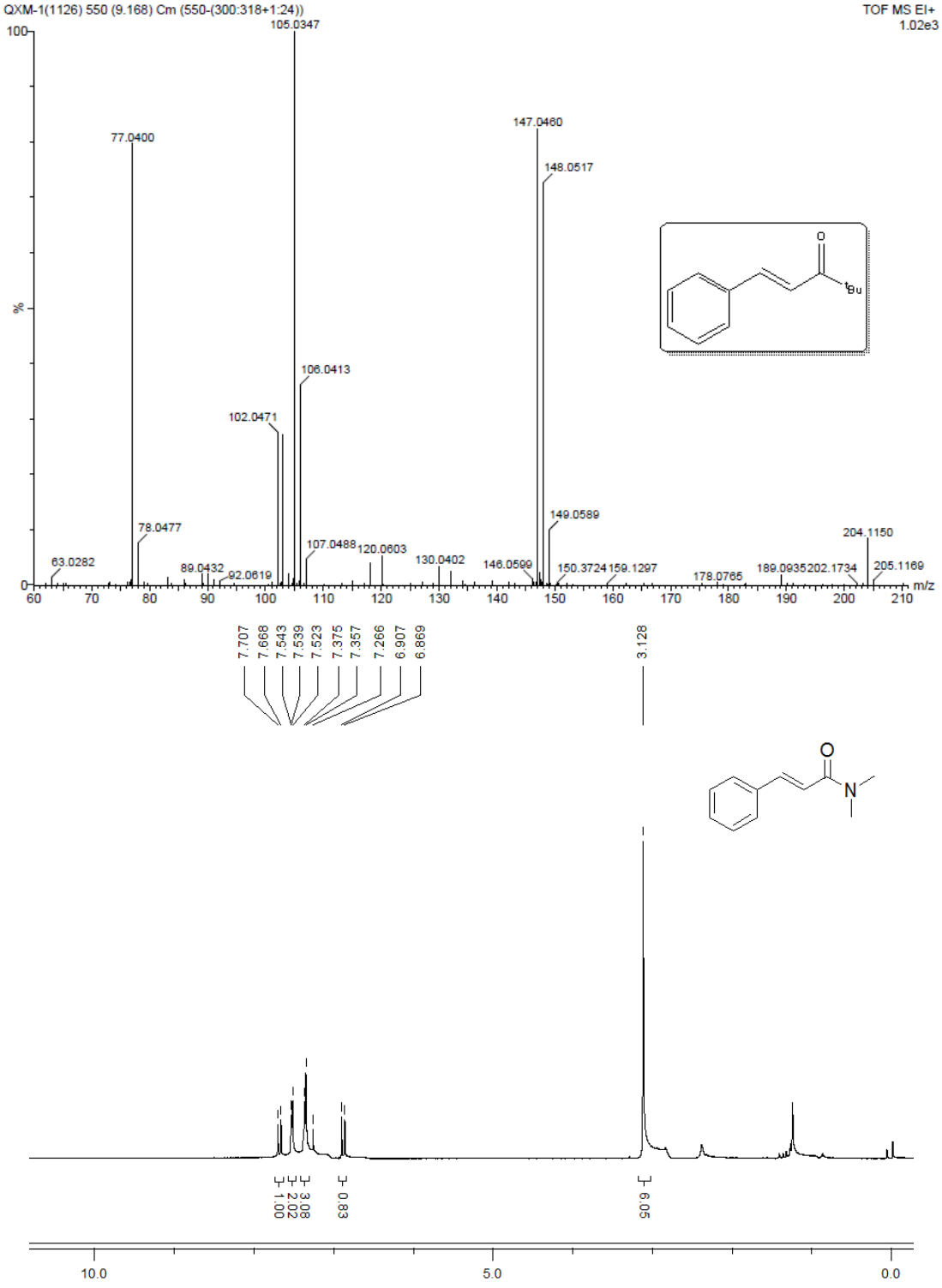


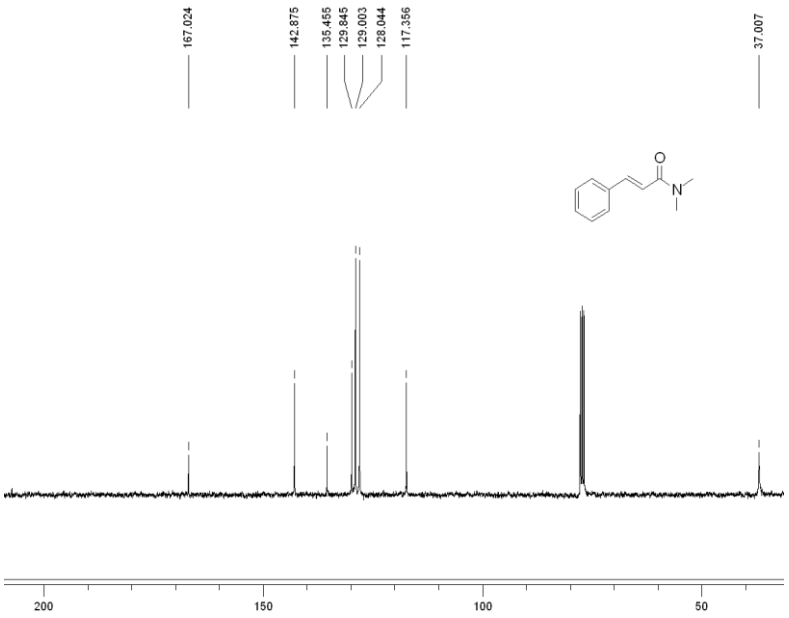


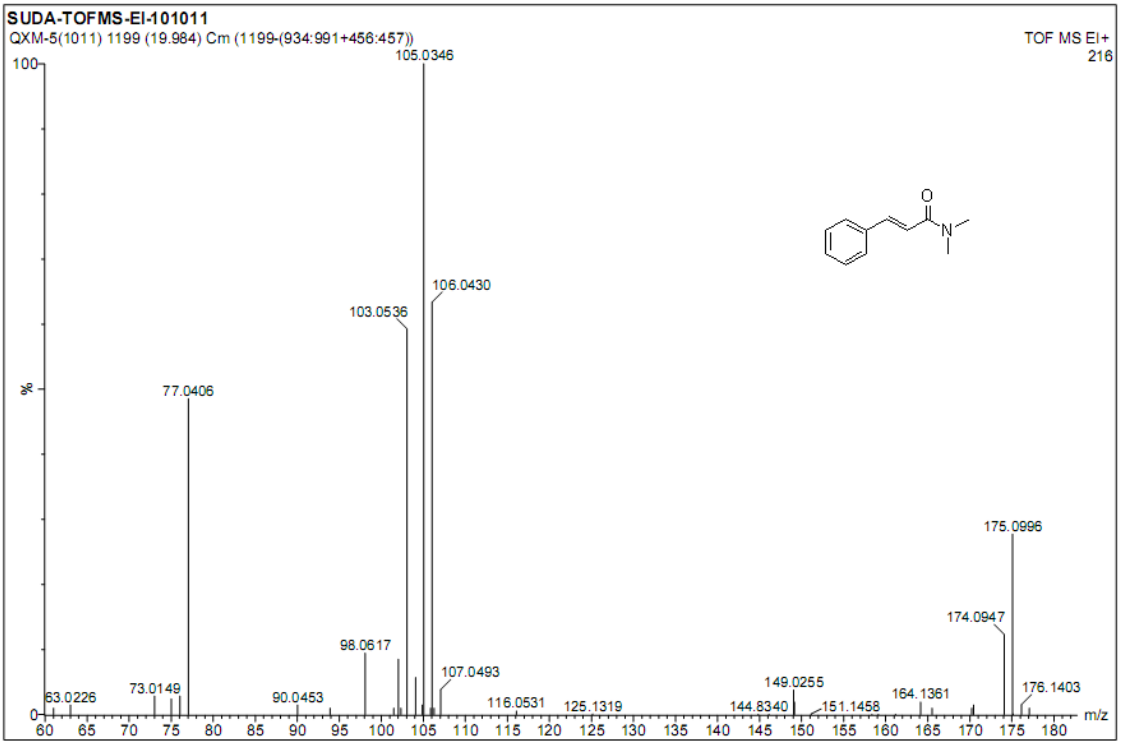


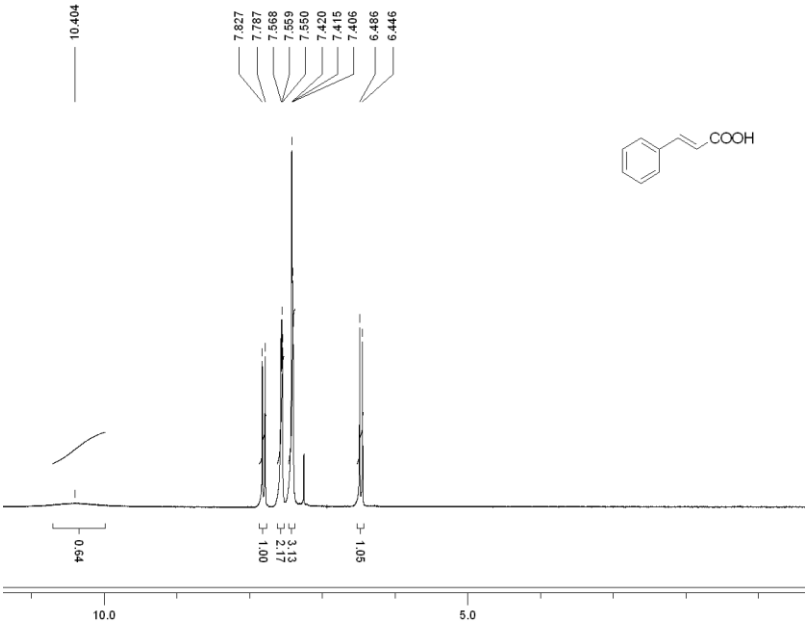


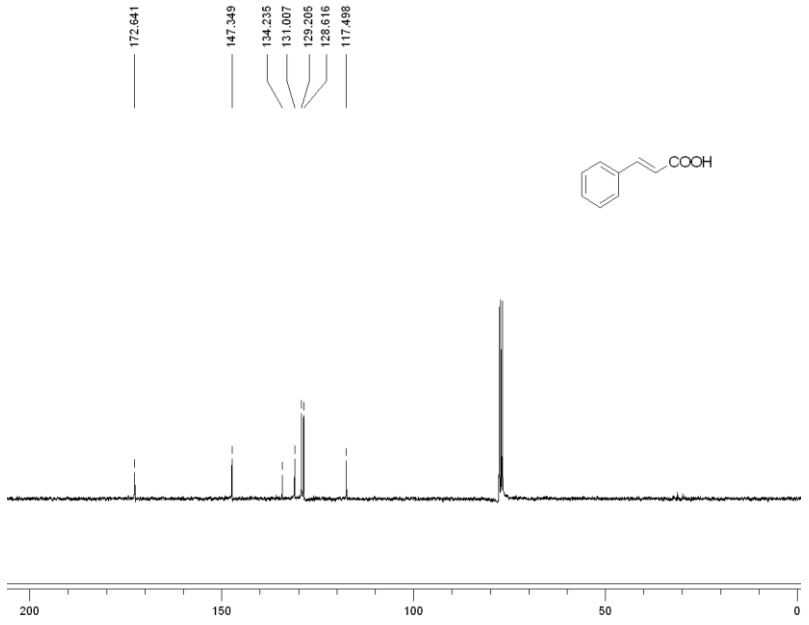


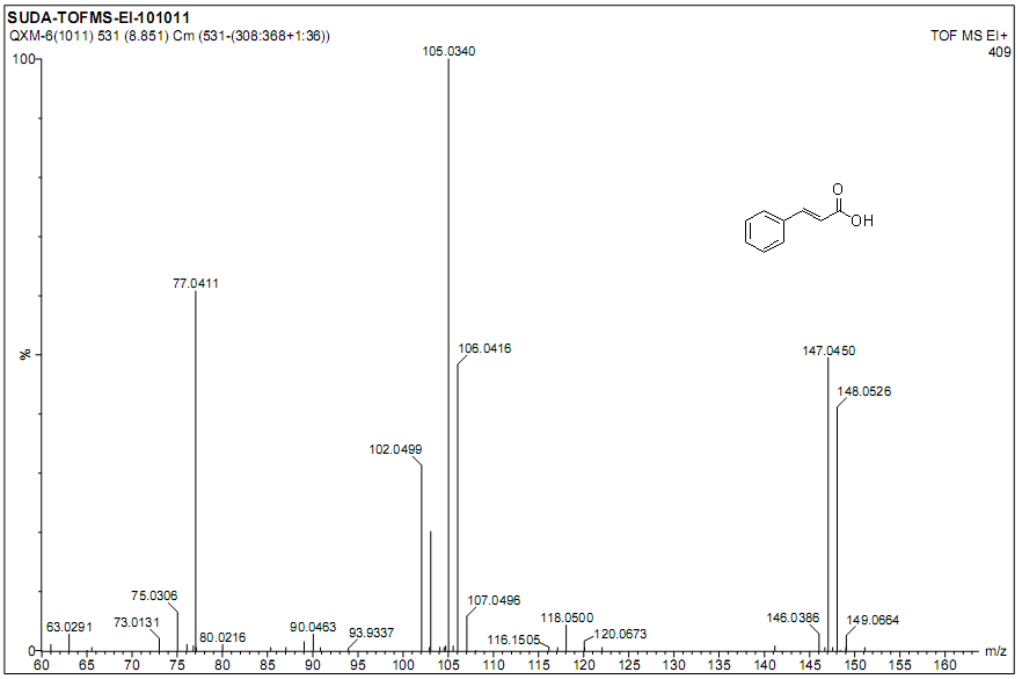

QXM-1(1126) 550 (9.168) Cm (550-(300:318+1:24))
TOF MS EI+
1.02e3
105.0347
77.0400
147.0460
148.0517
106.0413
102.0471
78.0477
149.0589
204.1150
107.0488
120.0603
63.0282
89.0432
92.0619
130.0402
146.0599
150.3724
159.1297
178.0765
189.0935
202.1734
205.1169
%
m/z
O
tBu
7.707
7.668
7.543
7.539
7.523
7.375
7.357
7.266
6.907
6.869
3.128
O
N
1.00
2.02
3.08
0.83
6.05
10.0
5.0
0.0

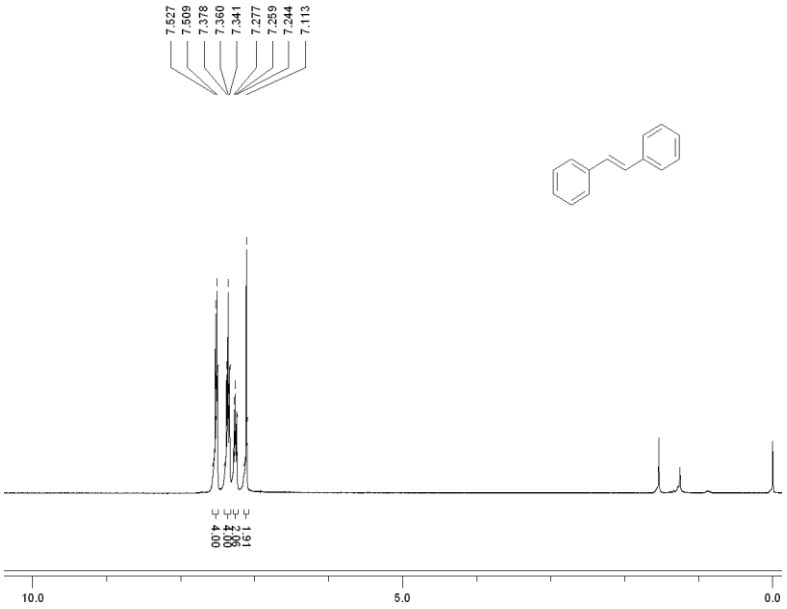

167.024
142.875
135.455
129.845
129.003
128.044
117.356
37.007
O
N
200
150
100
50

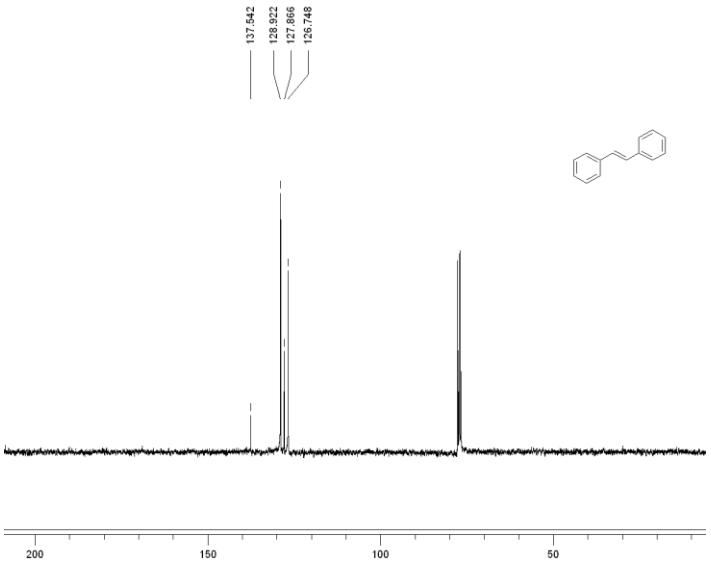

SUDA-TOFMS-EI-101011
QXM-5(1011) 1199 (19.984) Cm (1199-(934:991+456:457))
TOF MS EI+
216
100
%
0
105.0346
106.0430
103.0536
77.0406
175.0996
174.0947
98.0617
107.0493
149.0255
176.1403
164.1361
63.0226
73.0149
90.0453
116.0531
125.1319
144.8340
151.1458
O
N
60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180
m/z

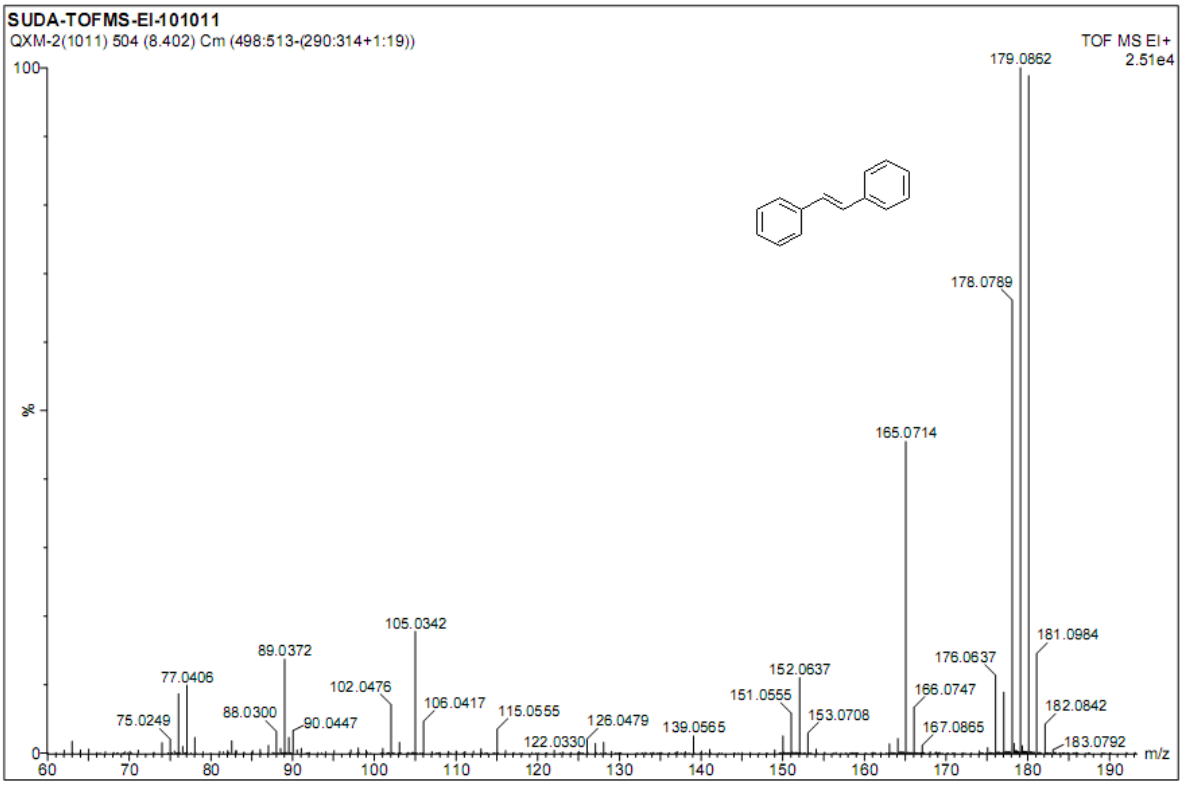


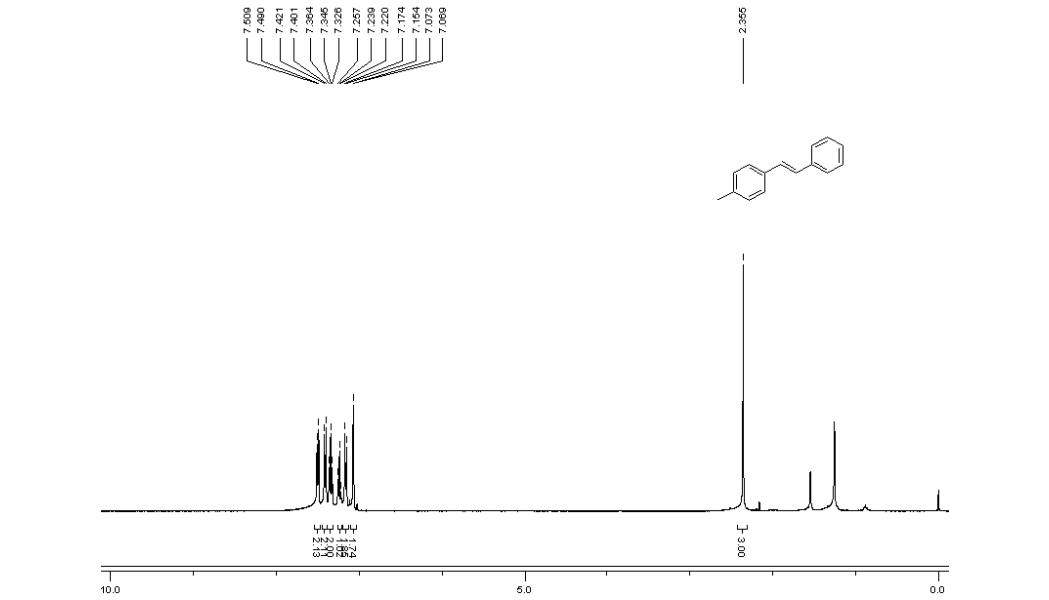


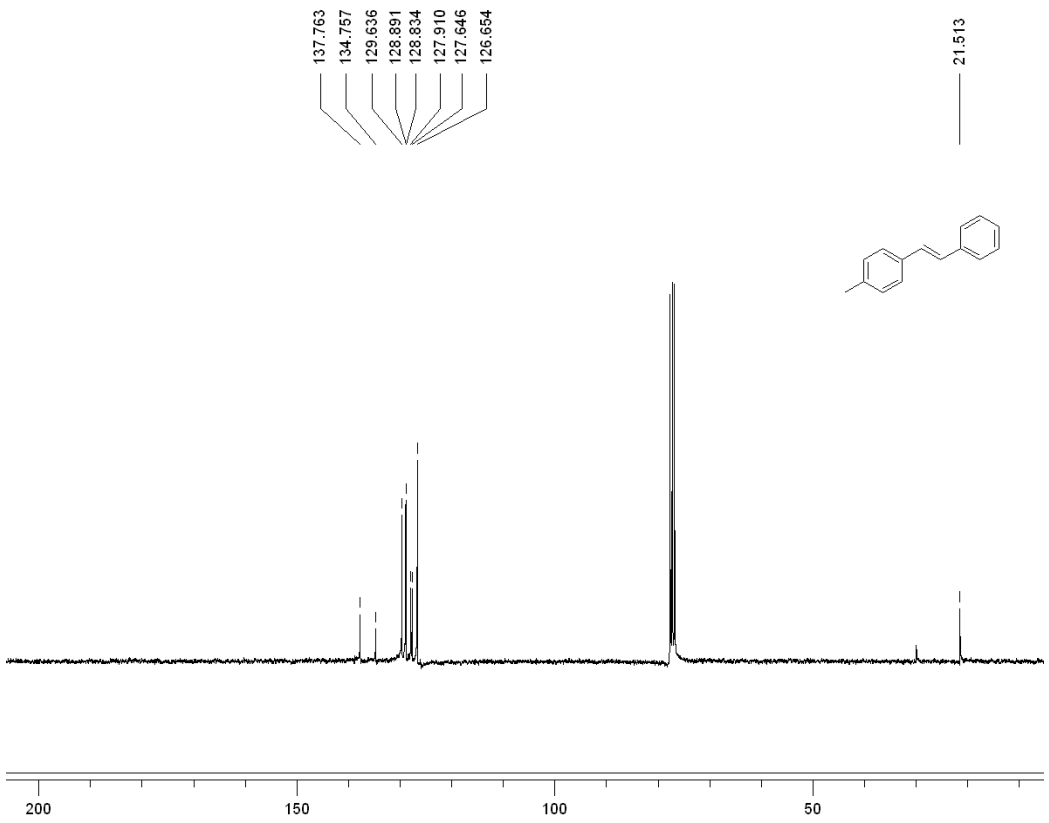


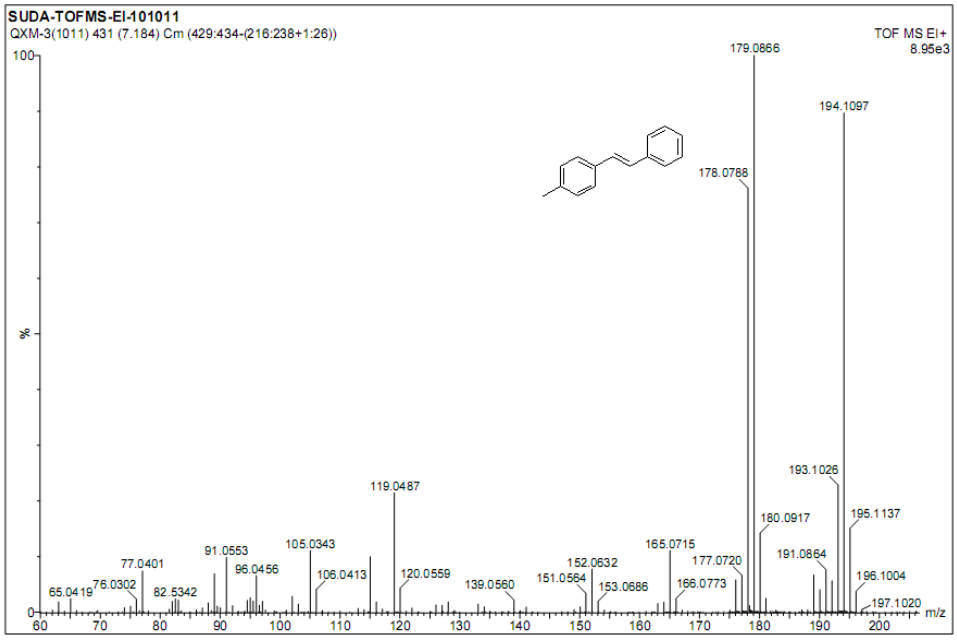


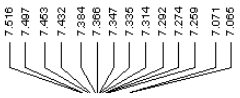


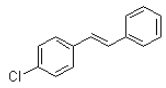


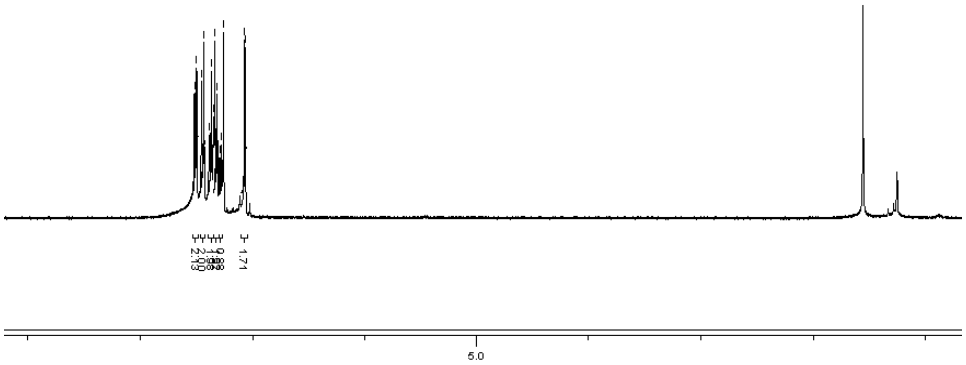


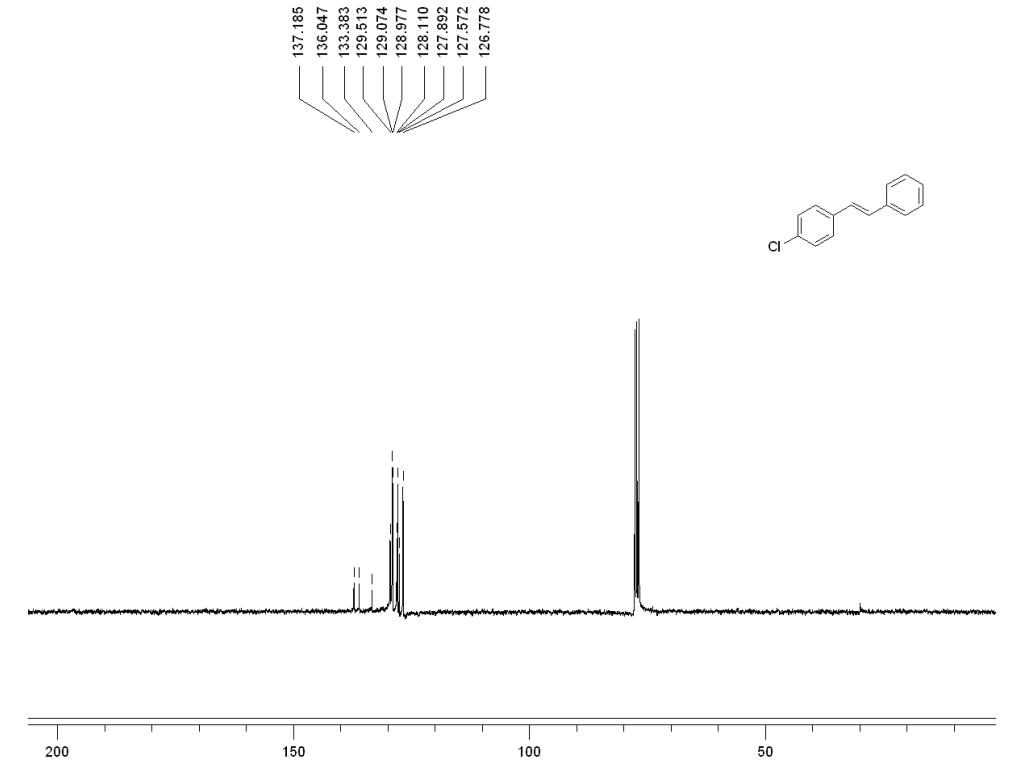


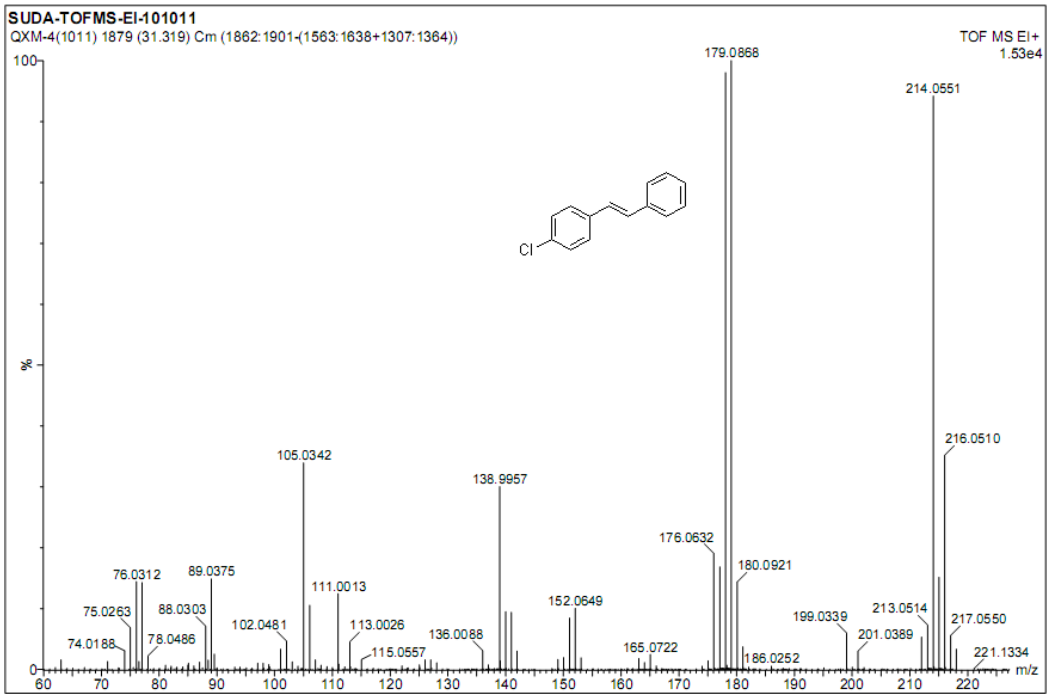

SUDA-TOFMS-EI-101011
QXM-3(1011) 431 (7.184) Cm (429:434-(216:238+1:26))
TOF MS EI+
8.95e3
100
%
0
179.0866
194.1097
178.0788
193.1026
119.0487
180.0917
195.1137
105.0343
91.0553
165.0715
191.0864
77.0401
96.0456
152.0632
177.0720
106.0413
120.0559
196.1004
65.0419
76.0302
82.5342
139.0560
151.0564
153.0686
166.0773
197.1020
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
m/z


7.516
7.497
7.463
7.432
7.394
7.366
7.347
7.335
7.314
7.292
7.274
7.259
7.071
7.065


Cl


5.0


137.185
136.047
133.383
129.513
129.074
128.977
128.110
127.892
127.572
126.778
Cl
200
150
100
50


SUDA-TOFMS-EI-101011
QXM-4(1011) 1879 (31.319) Cm (1862:1901-(1563:1638+1307:1364))
TOF MS EI+
1.53e4
100
%
0
Cl
179.0868
214.0551
216.0510
105.0342
138.9957
176.0632
180.0921
76.0312
89.0375
111.0013
152.0649
75.0263
88.0303
102.0481
113.0026
199.0339
213.0514
217.0550
74.0188
78.0486
136.0088
115.0557
165.0722
201.0389
186.0252
221.1334
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
m/z