Electronic Supplementary Information (ESI)

A metallosalen-based microporous organic polymer as heterogeneous carbon–carbon coupling catalyst

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Section A. Synthetic procedures of the Salen ligand and Salen-palladium monomer

Synthesis of Salen ligand

To a solution 5-bromo-2-hydrobenzaldehyde (3.0 g, 14.9 mmol) in ethanol (40 mL) was added dropwise an ethanol solution (5 mL) of ethylenediamine (0.5 mL, 7.4 mmol) at 80 ^{o}C. The reaction mixture was stirred for 4 h at this temperature, and then the mixture was cooled to room temperature. The precipitation can be obtained by filter, further purified by washing with methanol to afford target compound (3.15 g, 95%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (s, 4H, C*H*$_2$), 6.85 (d, J = 9.0 Hz, 2H), 7.34 (d, J = 3.0 Hz, 2H), 7.37 (dd, J = 9.0 Hz, J = 3.0, 2H), 8.28 (s, 2H, C*H*=N), 13.15 (s, 2H, O*H*) ppm. ^{13}C {^{1}H} (300 MHz, $CDCl_3$) δ: 60.0, 110.2, 119.1, 119.9, 133.6, 135.2, 160.0, 165.3 ppm. Anal. Calcd for $C_{16}H_{14}Br_2N_2O_2$ (426.1): C, 45.10; H, 3.31; N, 6.57. Found: C, 45.18; H, 3.36; N, 6.46. FT-IR (KBr): ν 470, 648, 698, 744, 818, 945, 1079, 1133, 1171, 1308, 1374, 1414, 1455, 1521, 1590, 1628, 2961 cm^{-1}.

Synthesis of palladium Salen monomer

A solution of $Pd(OAc)_2$ (0.158 g, 0.704 mmol) in methanol (10 mL) was added to a solution of Salen ligand (0.30 g, 0.704 mmol) in chloroform (30 mL) at room temperature. Then the mixture was refluxed and stirred for 6 h. After the mixture was cooled to room temperature, the precipitate was filtered off and washed with methanol (40 mL). After drying in vacuum, palladium-salen monomer was obtained as yellow powder (3.73 g, 84.3%). ^{1}H NMR (300 MHz, d_6-DMSO) δ: 3.83 (s, 4H, C*H*$_2$), 6.78 (d, J = 8.0 Hz, 2H), 7.36 (dd, J = 9.0 Hz, J = 3.0 Hz, 2H), 7.57 (d, J = 3.0 Hz, 2H), 8.20 (s, 2H, C*H*=N) ppm. Anal. Calcd for $C_{16}H_{12}Br_2N_2O_2Pd$ (530.51): C, 36.22; H, 2.28; N, 5.28; Found: C, 36.25; H, 2.30; N, 5.21. IR (KBr): ν 469, 549, 618, 652, 692, 743, 817, 948, 1080, 1137, 1171, 1302, 1371, 1417, 1457, 1520, 1588, 1628, 2924 cm^{-1}.

Section B. The stability of MsMOP-1

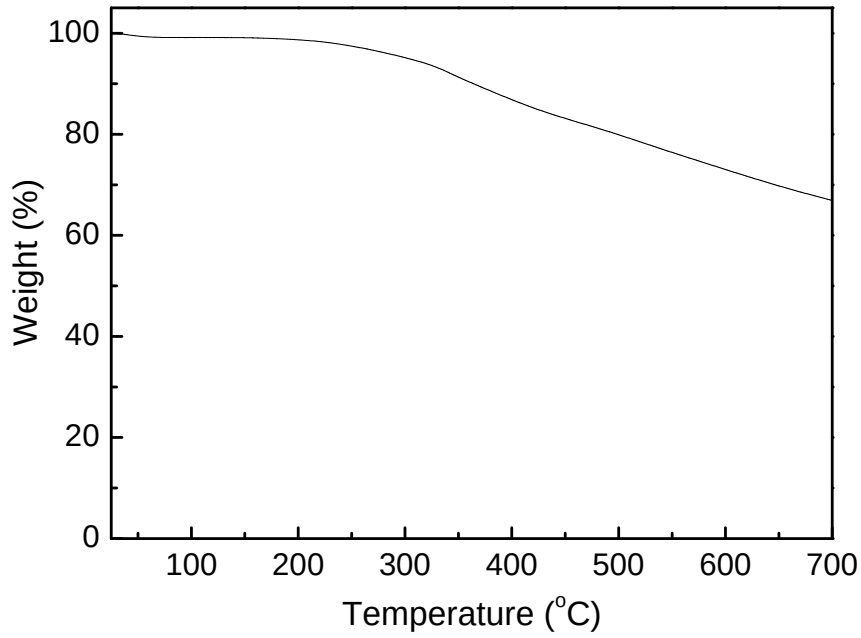


Fig. S1 TGA curve of MsMOP-1 under nitrogen.

Section C. The crystalline of MsMOP-1

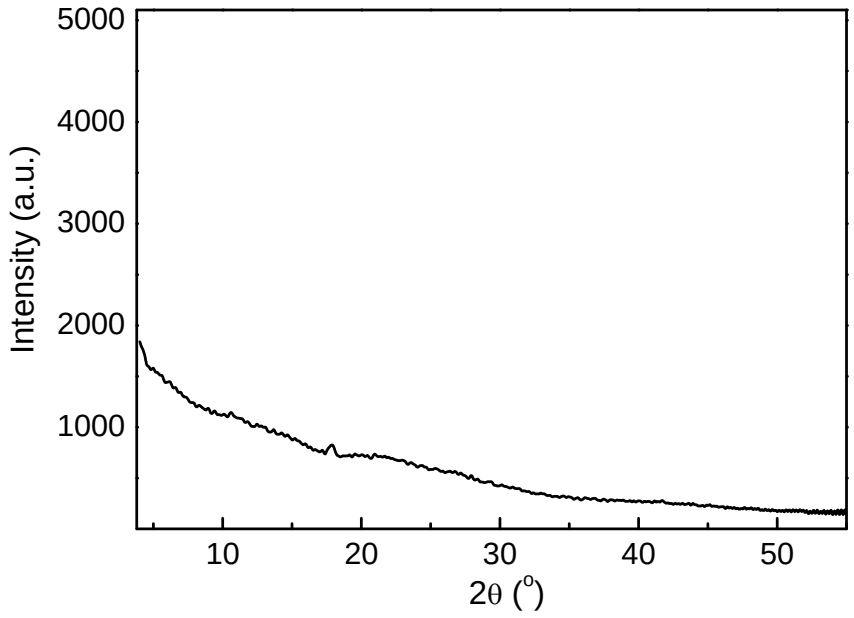


Fig. S2 PXRD curve of MsMOP-1.

Section D. The electronic adsorption spectra of MsMOP-1 and monomers

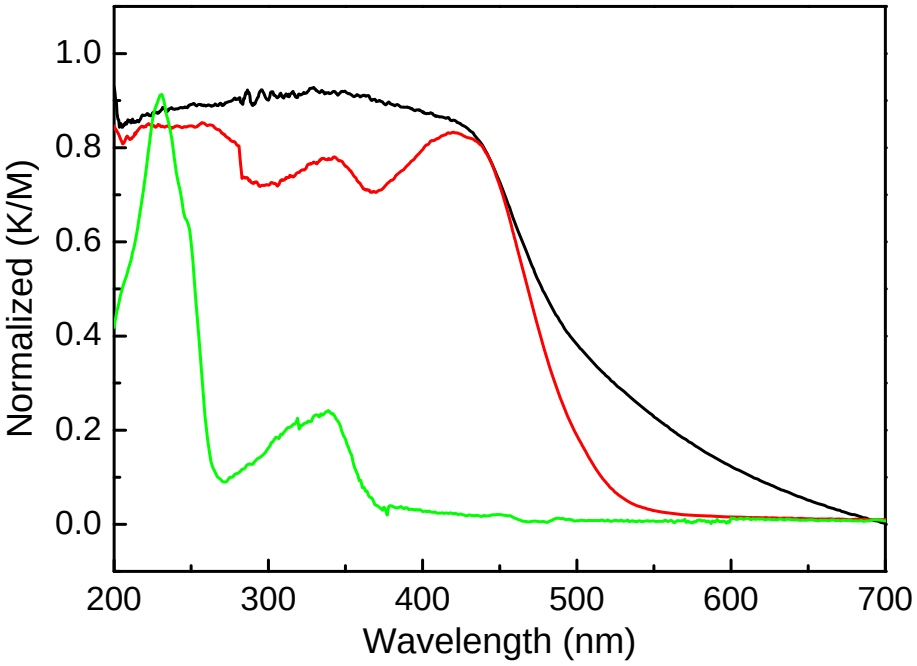


Fig. S3 The UV-vis absorption spectra of MsMOP-1 (black line), Salen-Pd monomer (red line) and 1,3,5-triethynylbenzene (green line) powder.

Section E. N_2 sorption isotherms and pore size distribution

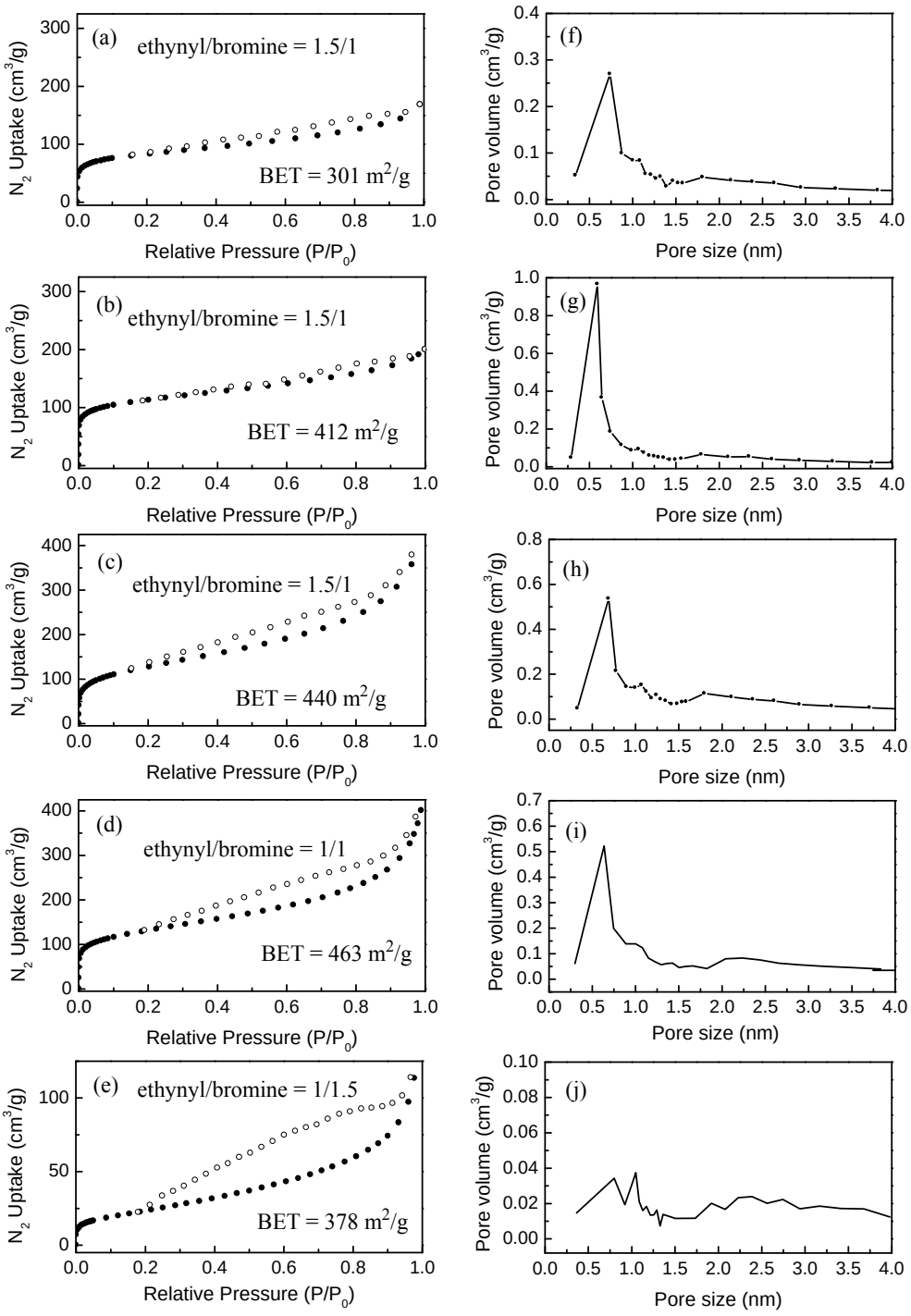


Fig. S4 (a-e) Nitrogen adsorption (●) and desorption (○) isotherm profiles of MsMOP-1 prepared in (a) THF/TEA, (b) DMF/TEA, (c) Dioxide/TEA, and (d-e) DMAc/TEA measured at 77 K. (f-j) Pore size distribution of MsMOP-1 prepared in (f) THF/TEA, (g) DMF/TEA, (h) Dioxide/TEA, (i-j) DMAc/TEA by SF modeling on the N_2 adsorption isotherms.

Section F. The SEM images

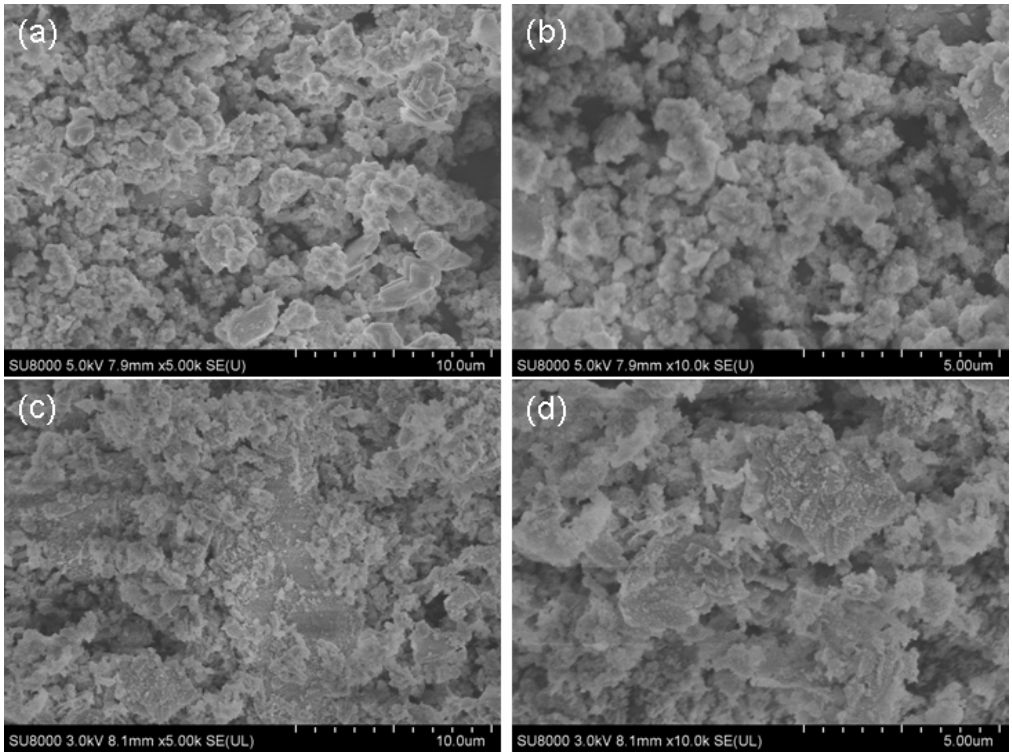


Fig. S5 SEM images of fresh (a, b) and after the fifth run (c, d) MsMOP-1 samples.

Section G. X-ray photoelectron spectroscopy of MsMOP-1

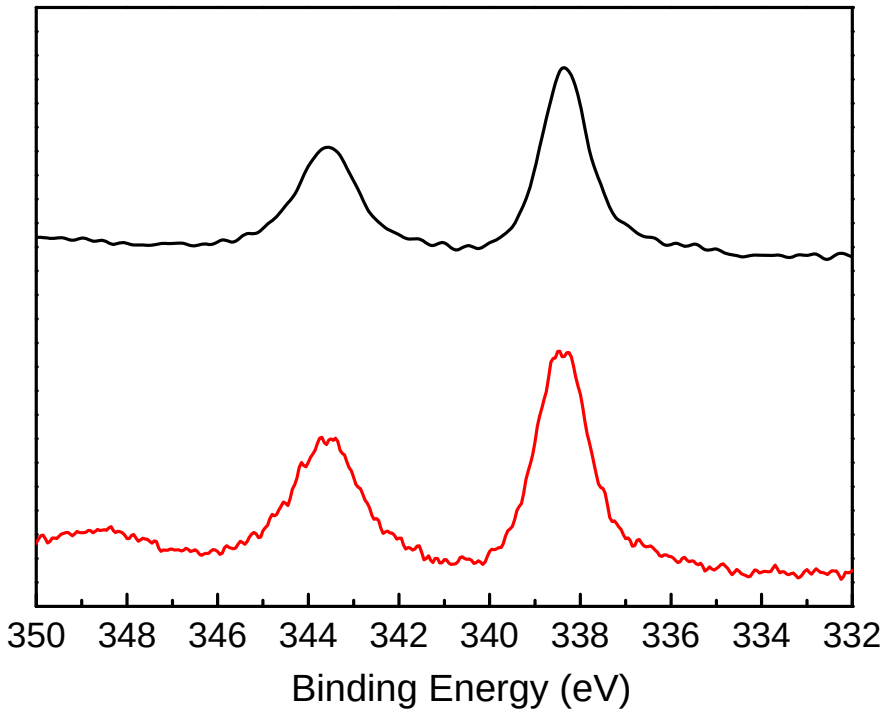
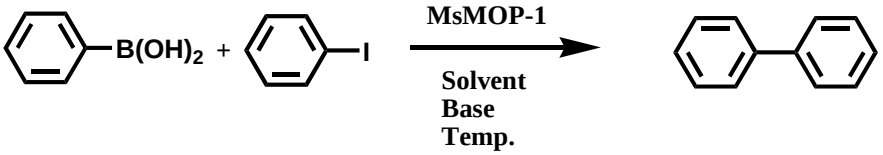


Fig. S6 XPS spectra of MsMOP-1 samples fresh (black line) and after reaction (red line).

Section H. Catalytic activity of MsMOP-1

Table S1. The Suzuki-Miyaura coupling reaction of iodobenzene with phenylboronic acid in the presence of MsMOP-1[a]



Entry	Solvent	T (°C)	Base	Time (h)	Yield (%)[b]
1	DMF	100	K_2CO_3	1	31
2	DMAc	100	K_2CO_3	1	35
3	Toulene	100	K_2CO_3	1	50
4	EtOH	80	K_2CO_3	1	98
5[c]	DMF/H_2O	100	K_2CO_3	1	71
6[d]	EtOH/H_2O	80	K_2CO_3	1	99
7[d]	EtOH/H_2O	80	K_2CO_3	0.25	94
8[d]	EtOH/H_2O	60	K_2CO_3	0.25	38
9[d]	EtOH/H_2O	60	K_2CO_3	1	80
10[d]	EtOH/H_2O	60	K_2CO_3	2	94
11	EtOH	80	Na_2CO_3	1	37
12	EtOH	80	Cs_2CO_3	1	95
13	EtOH	80	Et_3N	1	2
14[e]	EtOH	80	K_2CO_3	1	0

[a] Reaction conditions: iodobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1 mmol), MsMOP-1 (1.0 mg) and solvent (3.0 mL).

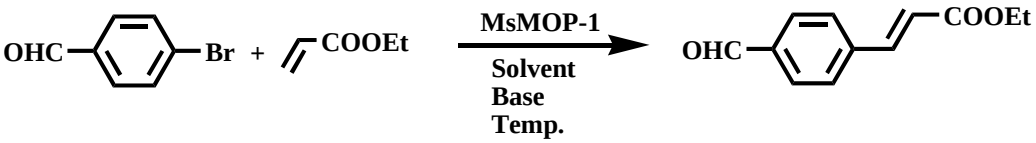
[b] Determined by GC using undecane as internal standard.

[c] DMF/H_2O (1.5 mL/1.5 mL).

[d] EtOH/H_2O (1.5 mL/1.5 mL).

[e] In the absence of MsMOP-1.

Table S2. Heck coupling reaction of 4-bromobenzaldhyde with ethyl acrylate in the presence of MsMOP-1[a]



Entry	Solvent	T (^{o}C)	Base	Time (h)	Yield (%)[b]
1	DMF	130	Et_3N	3	74
2	EtOH	130	Et_3N	3	NR
3	DMSO	130	Et_3N	3	NR
4	DMF/H_2O[c]	130	Et_3N	3	NR
5	DMAc	130	Et_3N	3	80
6	DMAc	130	K_2CO_3	3	56
7	DMAc	130	K_3PO_4	3	18

[a] Rection conditions: 4-bromobenzaldhyde (0.5 mmol), ethyl acrylate (1.5 mmol), base (1.5 mmol), MsMOP-1 (1.0 mg) and solvent (3.0 mL).

[b] Determined by GC using undecane as internal standard.

[c] DMF/H_2O (1.5 mL/1.5 mL).

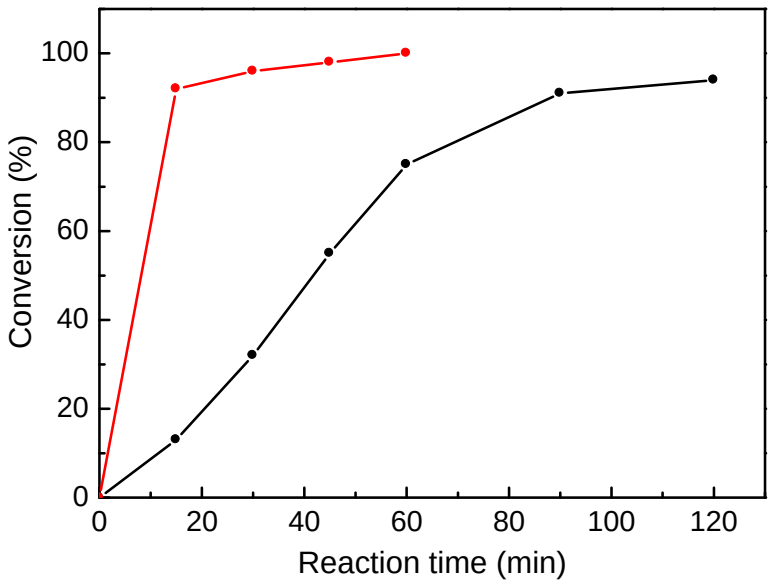
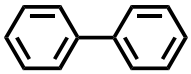
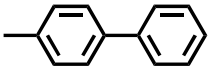


Fig. S7 Conversion for Heck coupling reaction of iodobenzene with ethyl acrylate at 100 ^{o}C (black line) and 130 ^{o}C (red line).

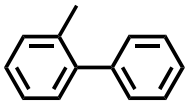
Section I. The characterization of cross-coupling products



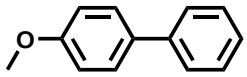
Biphenyl: White solid; m.p. 69-70°C (lit.,[1] 69 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.38 (t, *J* = 6.0 Hz, 2H), 7.48 (t, *J* = 6.0 Hz, 4H), 7.63 (d, *J* = 9.0 Hz, 4H) ppm. GC-MS retention time 4.30 min., m/z (EI) 154 (M^+, 100), 76 (74), 51 (58).



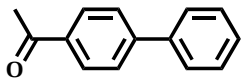
4-Methylbiphenyl: White solid; m.p. 86-87°C (lit.,[1] 87-88 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.26 (d, *J* = 9.0 Hz, 2H), 7.31-7.35 (m, 1H), 7.43 (t, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H) ppm. GC-MS retention time 4.99 min., m/z (EI) 168 (M^+, 100), 152 (28), 115 (16), 91 (13).



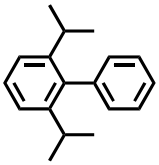
2-Methylbiphenyl: Colourless oil; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.24-7.28 (m, 4H), 7.31-7.37 (m, 3H), 7.40-7.45 (m, 2H) ppm. GC-MS retention time 4.39 min., m/z (EI) 168 (M^+, 100), 153 (46), 115 (20), 83 (32).



4-Methoxybiphenyl: White solid; m.p. 85-86°C (lit.,[1] 87-88 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.99 (d, *J* = 9.0 Hz, 2H), 7.30 (m, 1H), 7.42 (t, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 2H) ppm. GC-MS retention time 5.78 min., m/z (EI) 184 (M^+, 49), 169 (31), 141 (47), 115 (100), 89 (26), 76 (31).

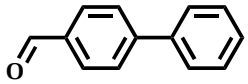


4-Acetylbiphenyl: White solid; m.p. 120-122°C (lit.,[2] 121-123 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.40 (t, *J* = 9.0 Hz, 1H), 7.48 (t, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 9.0 Hz, 2H), 8.04 (d, *J* = 9.0 Hz, 2H) ppm. GC-MS retention time 6.50 min., m/z (EI) 196 (M^+, 45), 169 (31), 181 (100), 152 (99).

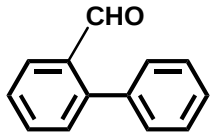


2,6-Diisopropylbiphenyl: Colourless oil; ^{1}H NMR (300MHz, $CDCl_3$) δ 1.08 (d, *J* = 9.0 Hz, 12H),

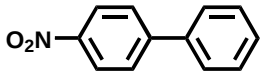
2.60 (sept, 2H, C*H*$(CH_3)_2$), 7.15-7.25 (m, 4H), 7.32-7.41 (m, 4H). GC-MS retention time 5.60 min., m/z (EI) 238 (M^+, 48), 223 (20), 181 (100), 165 (29), 89 (15).



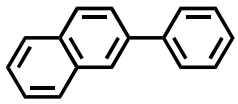
4-biphenylbenzaldehyde: White solid; m.p. 119-121°C (lit.,[1] 121 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.42 (t, *J* = 9.0 Hz, 1H), 7.49 (t, *J* = 6.0 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 9.0 Hz, 2H), 10.06 (s, 1H) ppm. GC-MS retention time 6.06 min., m/z (EI) 182 (M^+, 49), 152 (57), 76 (100).



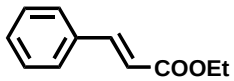
2-biphenylbenzaldehyde: Yellow oil; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.37-7.40 (m, 1H), 7.44-7.53 (m, 5H), 7.65 (td, *J* = 7.5, 1.5Hz, 1H), 8.04 (dd, *J* = 9.0, 1.5Hz, 1H), 9.99 (s, 1H) ppm. GC-MS retention time 5.64 min., m/z (EI) 182 (M^+, 100), 152 (89), 76 (99).



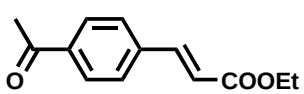
4-Nitrobiphenyl: Yellow solid; m.p. 113-114°C (lit.,[1] 114 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.45 (m, 1H), 7.51 (m, 2H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 8.31 (d, *J* = 9.0 Hz, 2H) ppm. GC-MS retention time 6.64 min., m/z (EI) 199 (M^+, 54), 152 (100), 141 (51), 115 (61), 76 (84).



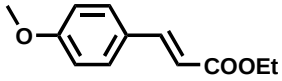
2-phenylnaphthalene: White solid; m.p. 95-96°C (lit.,[1] 96-97 °C); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.36-7.41 (m, 1H), 7.47-7.52 (m, 4H), 7.72-7.77 (m, 3H), 7.86-7.94 (m, 3H), 8.05 (s, 1H) ppm. GC-MS retention time 7.12 min., m/z (EI) 204 (M^+, 100), 101 (68), 89 (38), 76 (43).



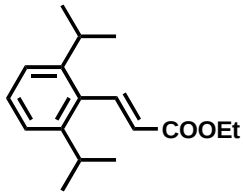
(E)-ethyl cinnamate: Colourless oil; ^{1}H NMR (300MHz, $CDCl_3$): δ 1.34 (t, 3H, CH_2CH_3), 4.27 (q, 2H, CH_2CH_3), 6.44 (d, *J* = 15 Hz, 1H), 7.38 (m, 3H), 7.53 (m, 2H), 7.69 (d, *J* = 15 Hz, 1H) ppm; GC-MS retention time 4.76 min., m/z (EI) 176 (M^+, 27), 147 (17), 131 (100), 103 (88), 77 (80).



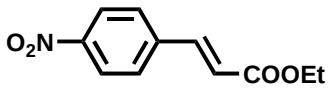
(E)-ethyl 3-(4-acetophenyl) acrylate: White solid; m.p. 43-45°C (lit.,[3] 44-46 °C); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.35 (t, 3H, CH_2CH_3), 2.62 (s, 3H, OCH_3), 4.29 (q, 2H, CH_2CH_3), 6.53 (d, J = 15 Hz, 1H), 7.62 (d, J = 9.0 Hz, 2H), 7.71 (d, J = 15 Hz, 1H), 7.98 (d, J = 9.0 Hz, 2H) ppm; GC-MS retention time 6.64 min., m/z (EI) 218 (M^+, 37), 203 (100), 175 (31), 131 (23), 102 (42), 91 (25).



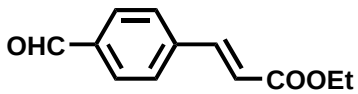
(E)-ethyl 3-(4-methoxyphenyl) acrylate: Colourless oil; ^{1}H NMR (300MHz, $CDCl_3$): δ 1.33 (t, 3H, CH_2CH_3), 3.83 (s, 3H, OCH_3), 4.25 (q, 2H, CH_2CH_3), 6.31 (d, J = 15 Hz, 1H), 6.90 (d, J = 9.0 Hz, 2H), 7.48 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 15 Hz, 1H) ppm. GC-MS retention time 6.16 min., m/z (EI) 206 (M^+, 53), 161 (100), 134 (67), 89 (42), 77 (37).



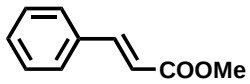
(E)-ethyl 3-(2,6-diisopropylphenyl) acrylate: Colourless oil; ^{1}H NMR (300MHz, $CDCl_3$): δ 1.19 (d, 12H, $CH(CH_3)_2$), 1.36 (t, 3H, CH_2CH_3), 3.10 (sept, 2H, $CH(CH_3)_2$), 4.29 (q, 2H, CH_2CH_3), 5.93 (d, J = 15 Hz, 1H), 7.17 (d, J = 9.0 Hz, 2H), 7.29 (t, J = 9.0 Hz, 1H), 7.94 (d, J = 15 Hz, 1H) ppm. GC-MS retention time 6.93 min., m/z (EI) 260 (M^+, 6), 143 (84), 129 (100), 115 (76), 91 (61).



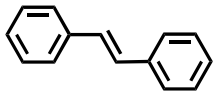
(E)-ethyl 3-(4-nitrophenyl) acrylate: Yellow solid; m.p. 133-135 °C (lit.,[4]135 °C); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.35 (t, 3H, CH_2CH_3), 4.30 (q, 2H, CH_2CH_3), 6.55 (d, J = 15 Hz, 1H), 7.68 (d, J = 9.0 Hz, 2H), 7.73 (d, J = 15 Hz, 1H), 8.26 (d, J = 9.0 Hz, 2H) ppm. GC-MS retention time 6.72 min., m/z (EI) 221 (M^+, 9), 176 (45), 130 (38), 102 (100), 90 (46).



(E)-ethyl 3-(4-formylphenyl) acrylate: Yellow solid; m.p. 39-40 °C (lit.,[5] 39.4-40.1 °C); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.36 (t, 3H, CH_2CH_3), 4.29 (q, 2H, CH_2CH_3), 6.56 (d, J = 15 Hz, 1H), 7.67-7.74 (m, 3H), 7.91 (d, J = 9.0 Hz, 2H), 10.04 (s, 1H) ppm. GC-MS retention time 6.40 min., m/z (EI) 204 (M^+, 31), 176 (26), 159 (52), 131 (56), 103 (100), 77 (72).

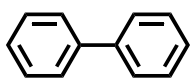


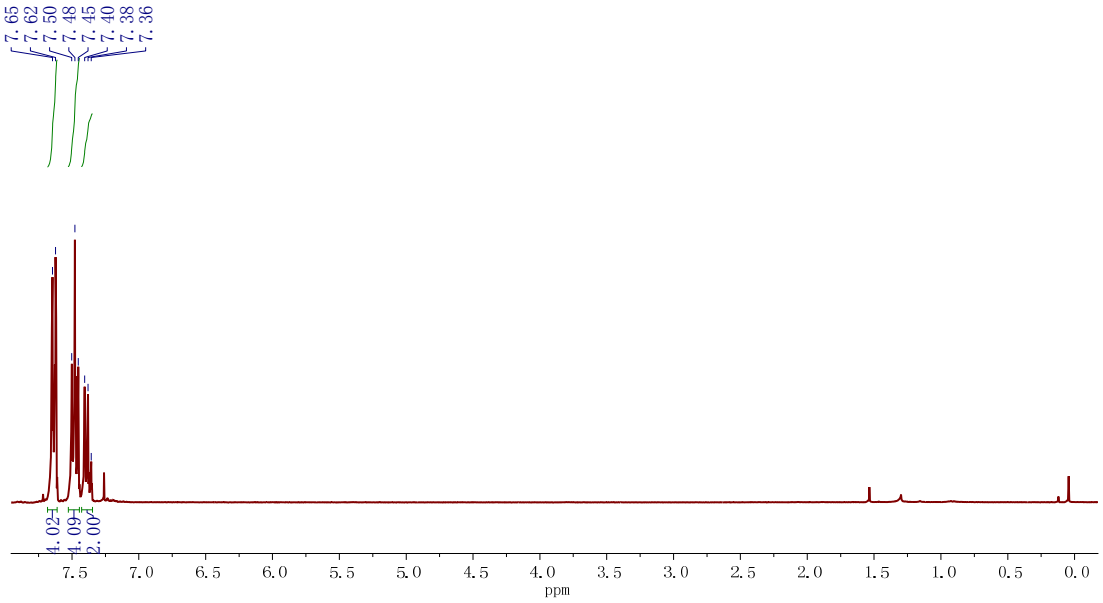
(E)-methyl cinnamate: White solid; m.p. 35-36 ^{o}C (lit.,[6] 35.8-36.5 ^{o}C); ^{1}H NMR (300MHz, $CDCl_3$): δ 3.81 (s, 3H, OCH_3), 6.45 (d, J = 15 Hz, 1H), 7.39 (m, 3H), 7.52 (m, 2H), 7.71 (d, J = 15 Hz, 1H) ppm. GC-MS retention time 4.26 min., m/z (EI) 162 (M^+, 42), 131 (91), 103 (100), 77 (83).

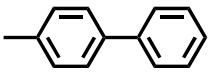


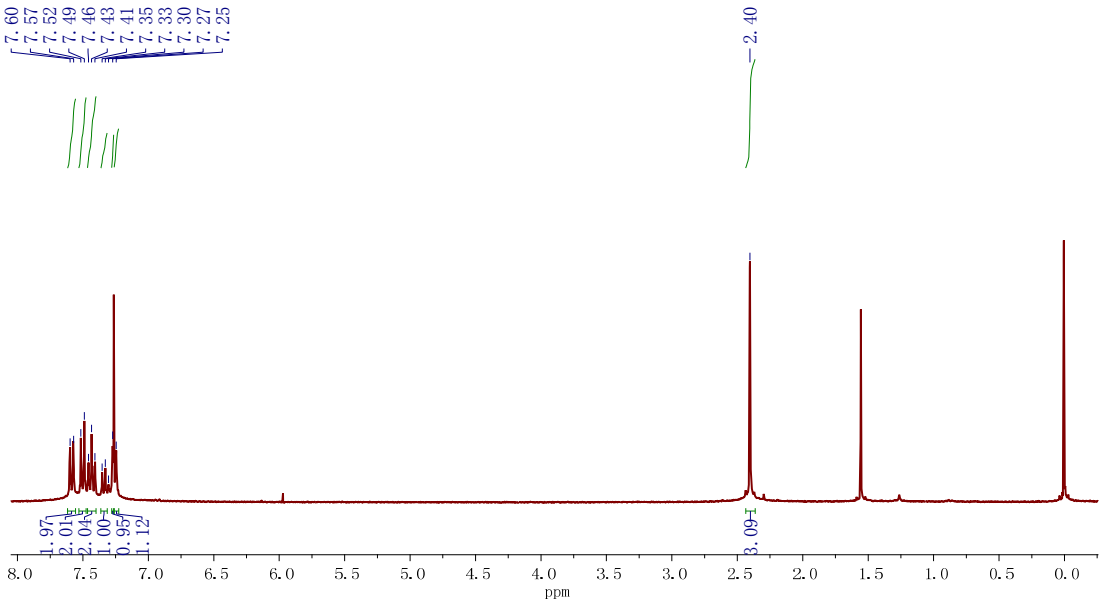
(E)-Trans-stilbene: White solid; m.p. 122-123 ^{o}C (lit.,[5] 123.9-124.6 ^{o}C);^{1}H NMR (300MHz, $CDCl_3$): δ 7.11 (s, 2H), 7.23-7.29 (m, 2H), 7.33-7.39 (m, 4H). 7.53 (d, J = 9.0 Hz, 4H) ppm. GC-MS retention time 6.04 min., m/z (EI) 180 (M^+, 100), 165 (56), 89 (67), 76 (60).

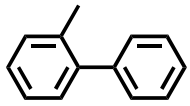
Section J. ^{1}H NMR spectra of products

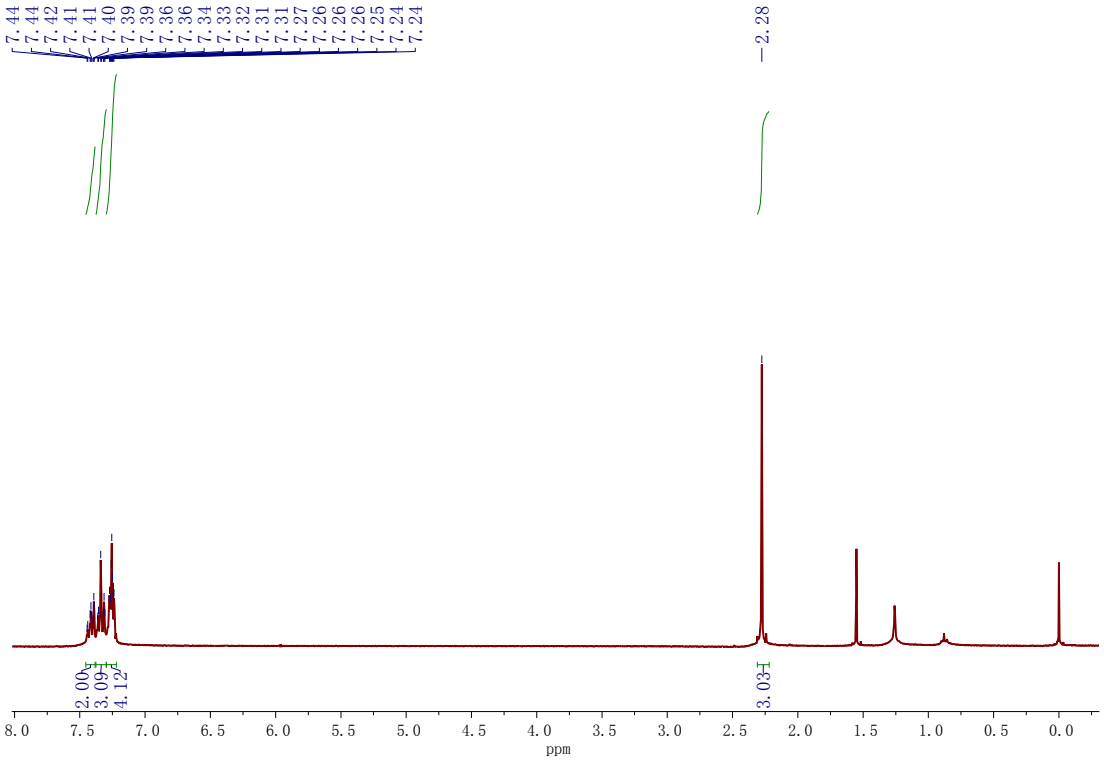








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7.44
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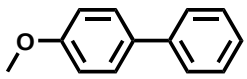
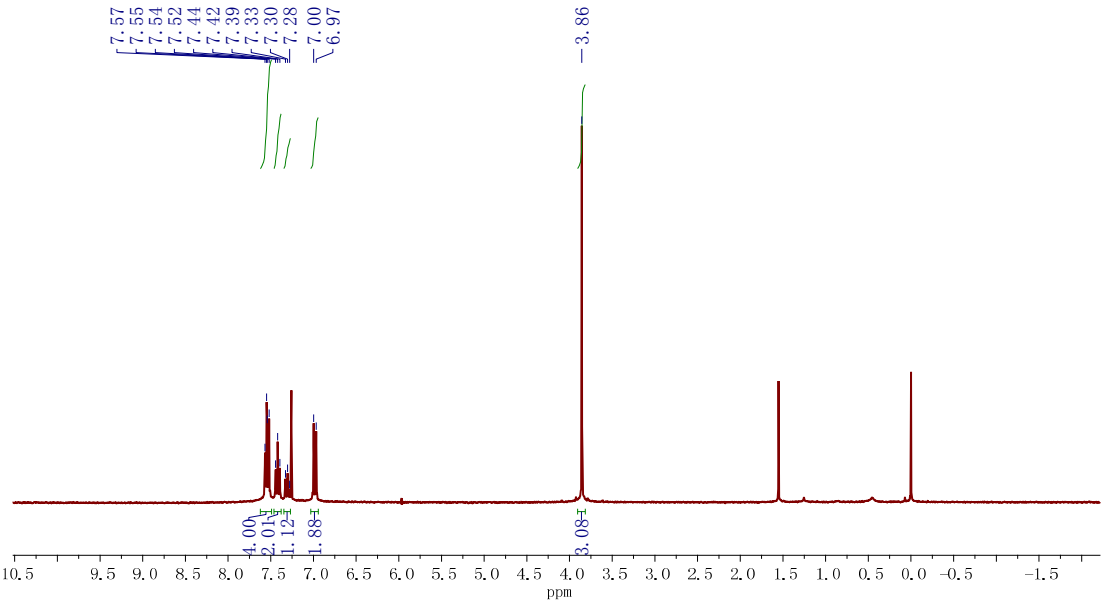
7.41
7.41
7.40
7.39
7.39
7.36
7.36
7.34
7.33
7.32
7.31
7.31
7.27
7.26
7.26
7.25
7.24
7.24
2.28
2.00
3.09
4.12
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

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7.42
7.39
7.33
7.30
7.28
7.00
6.97
3.86
4.00
2.01
1.12
1.88
3.08
10.5
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
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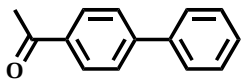
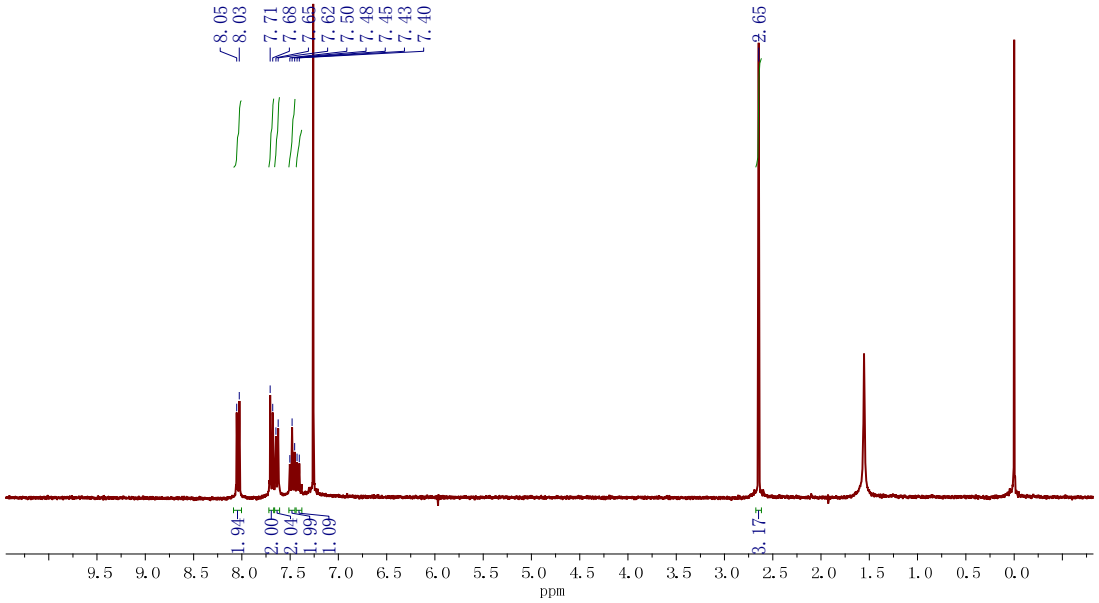
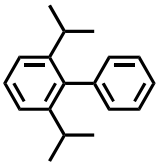
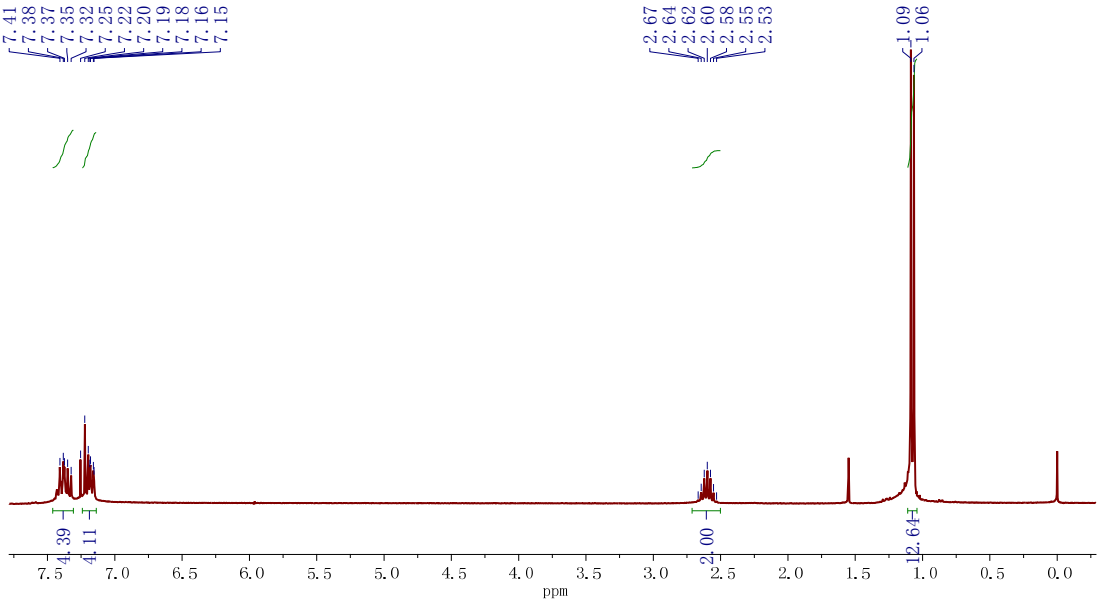
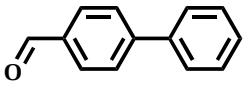
-0.5
-1.5
ppm

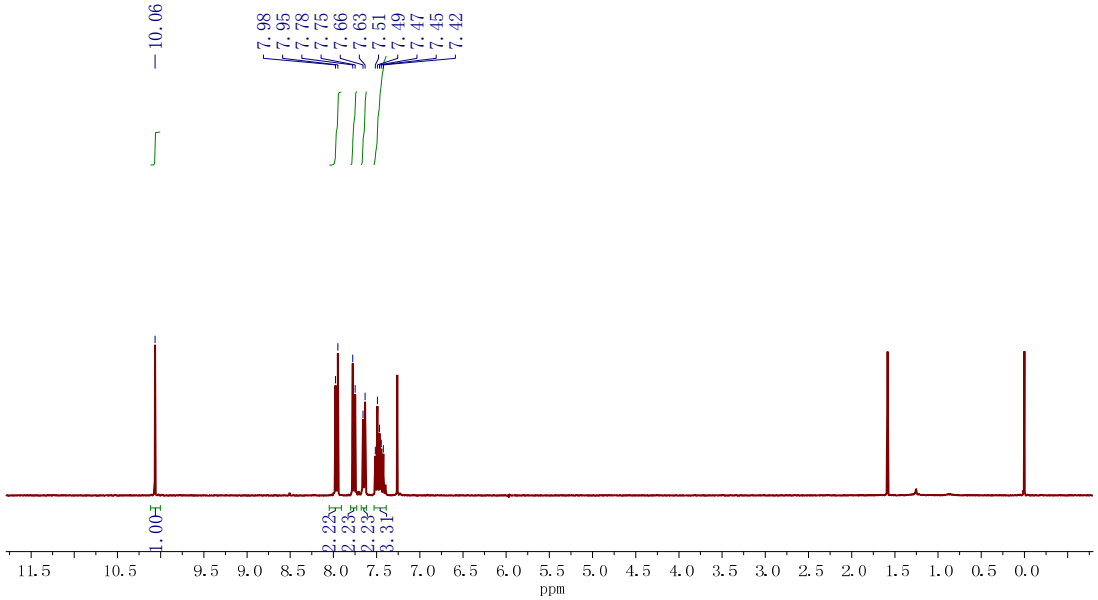









O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7.78
7.75
7.66
7.63
7.51
7.49
7.47
7.45
7.42
1.00
2.22
2.23
2.23
3.31
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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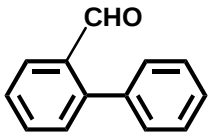
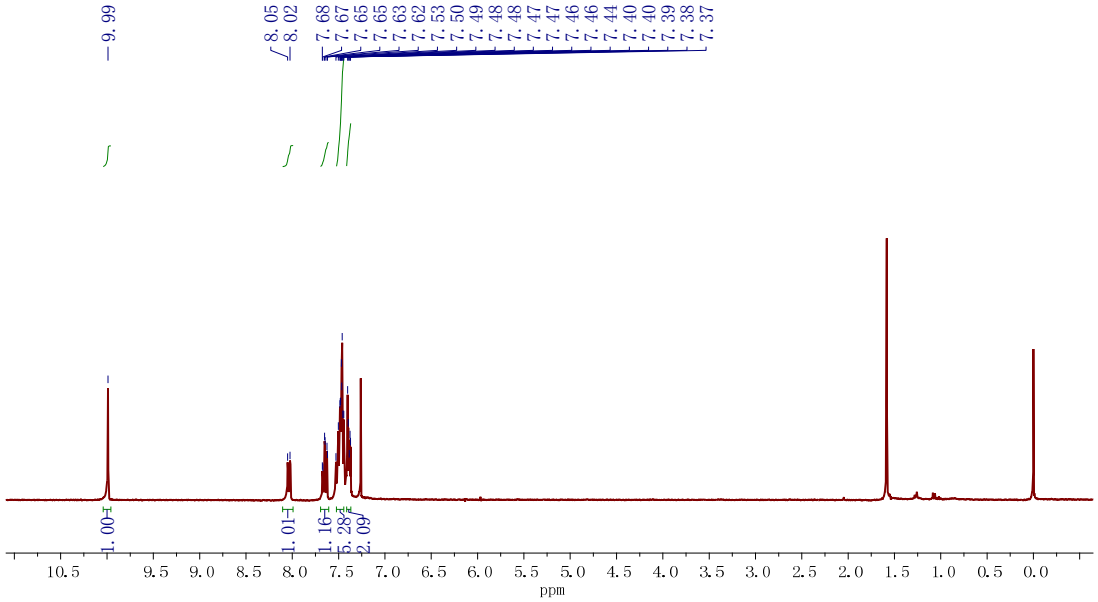
ppm


CHO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8.02
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7.65
7.63
7.62
7.53
7.50
7.49
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7.48
7.47
7.47
7.46
7.46
7.44
7.40
7.40
7.39
7.38
7.37
1.00
1.01
1.16
3.28
2.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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4.0
3.5
3.0
2.5
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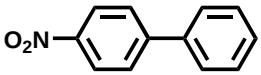
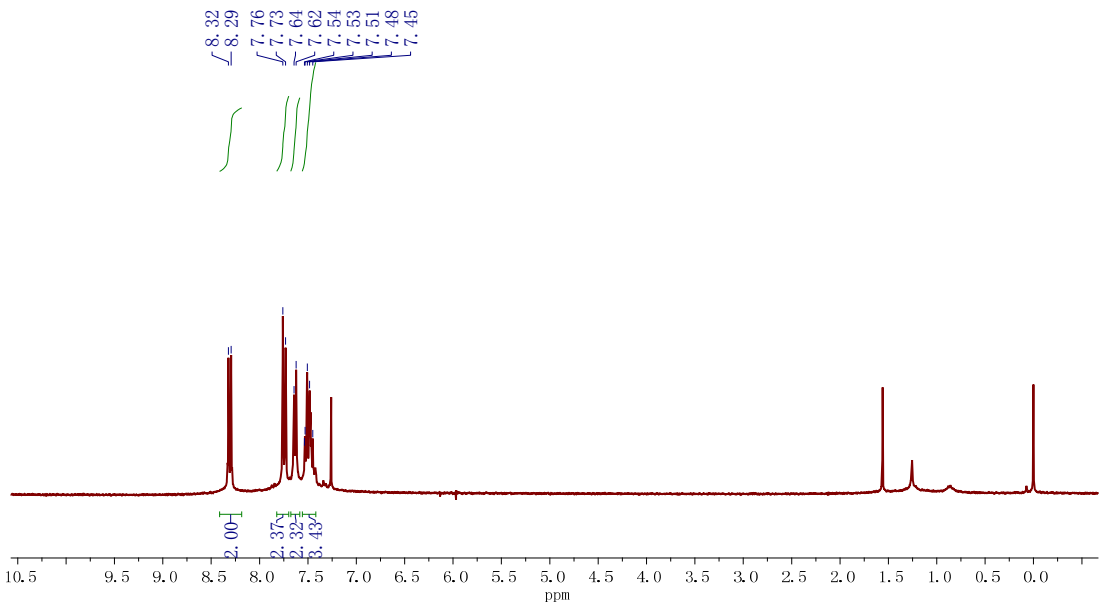
1.5
1.0
0.5
0.0
ppm


O2N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7.53
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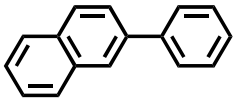
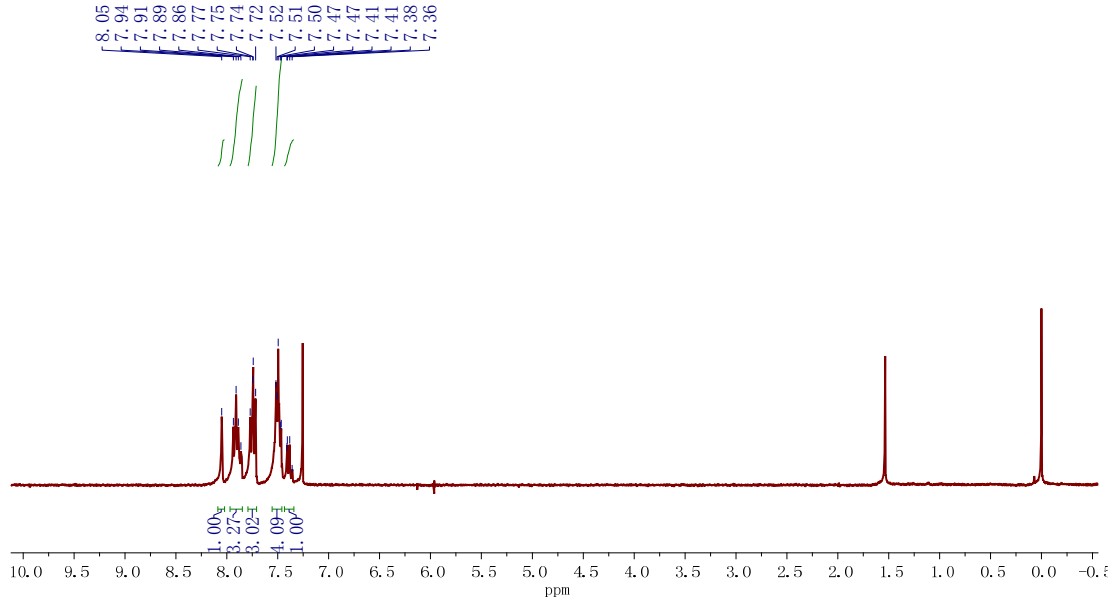
7.45
2.00
2.37
2.32
3.43
ppm

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7.74
7.72
7.52
7.51
7.50
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7.41
7.38
7.36
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3.27
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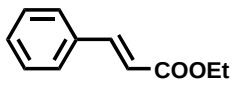
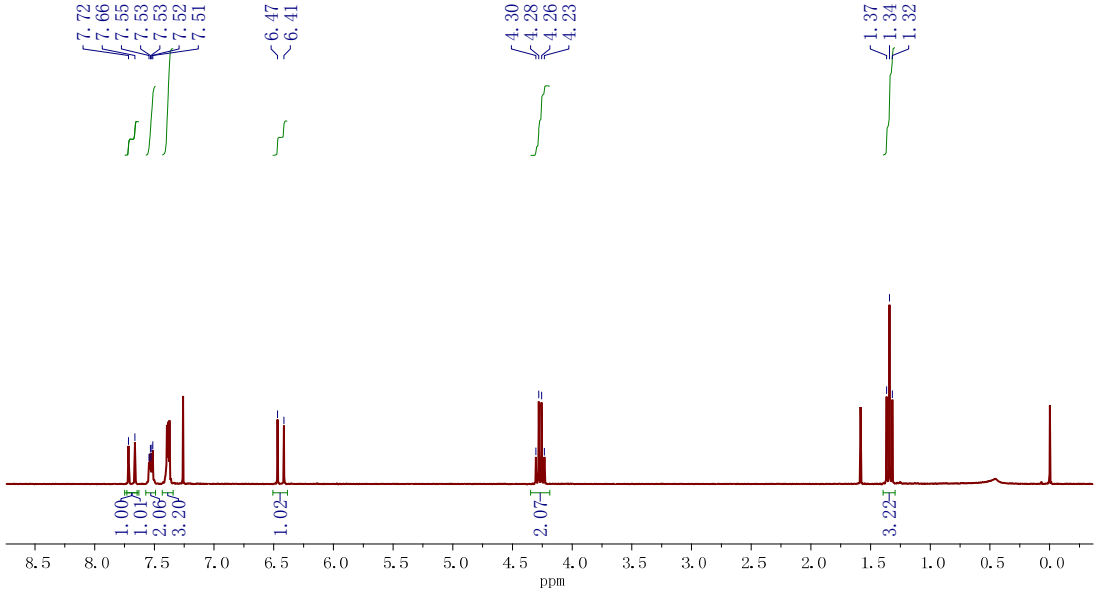
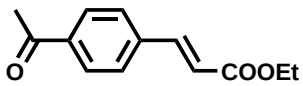
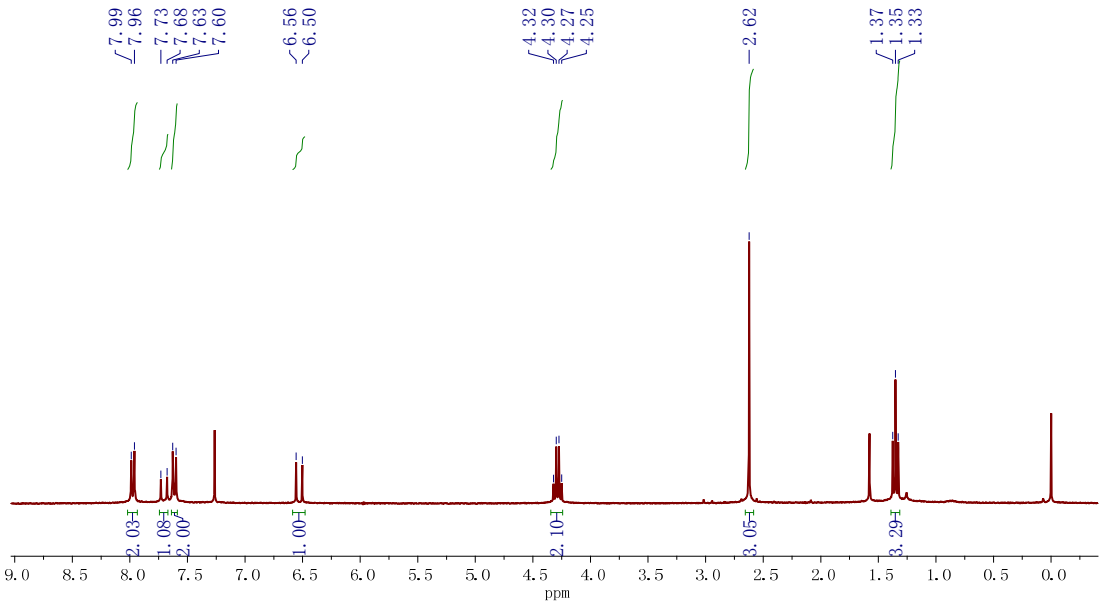
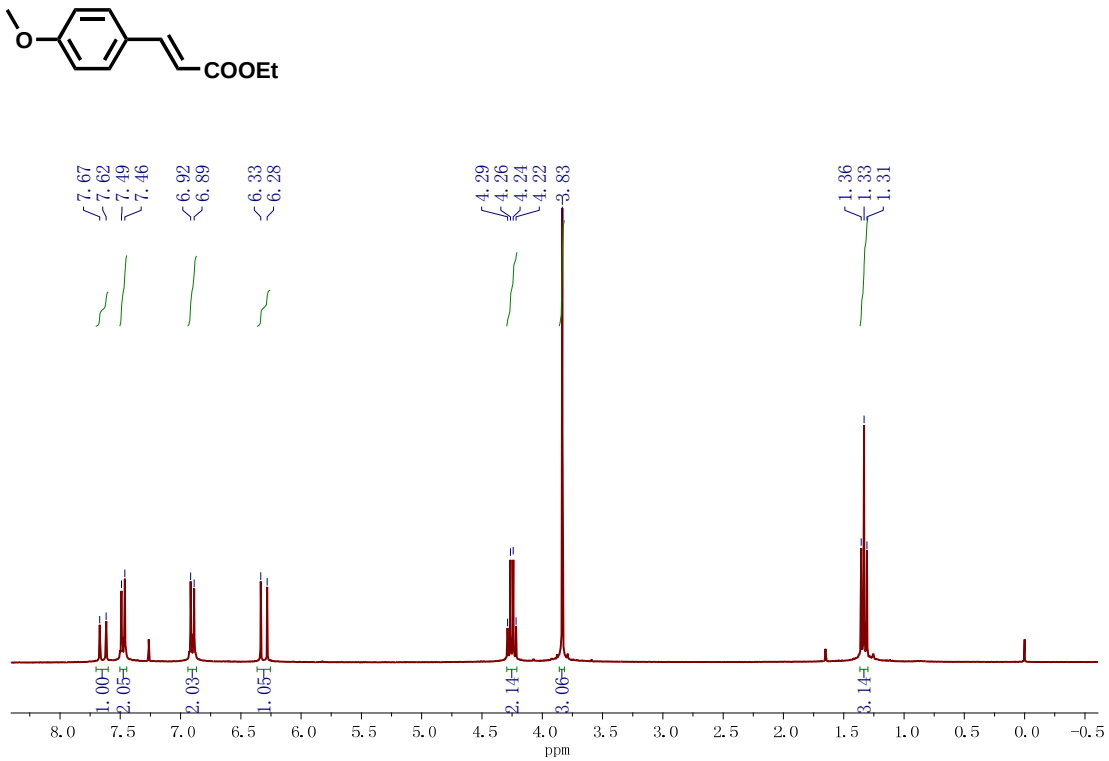
4.09
1.00
ppm

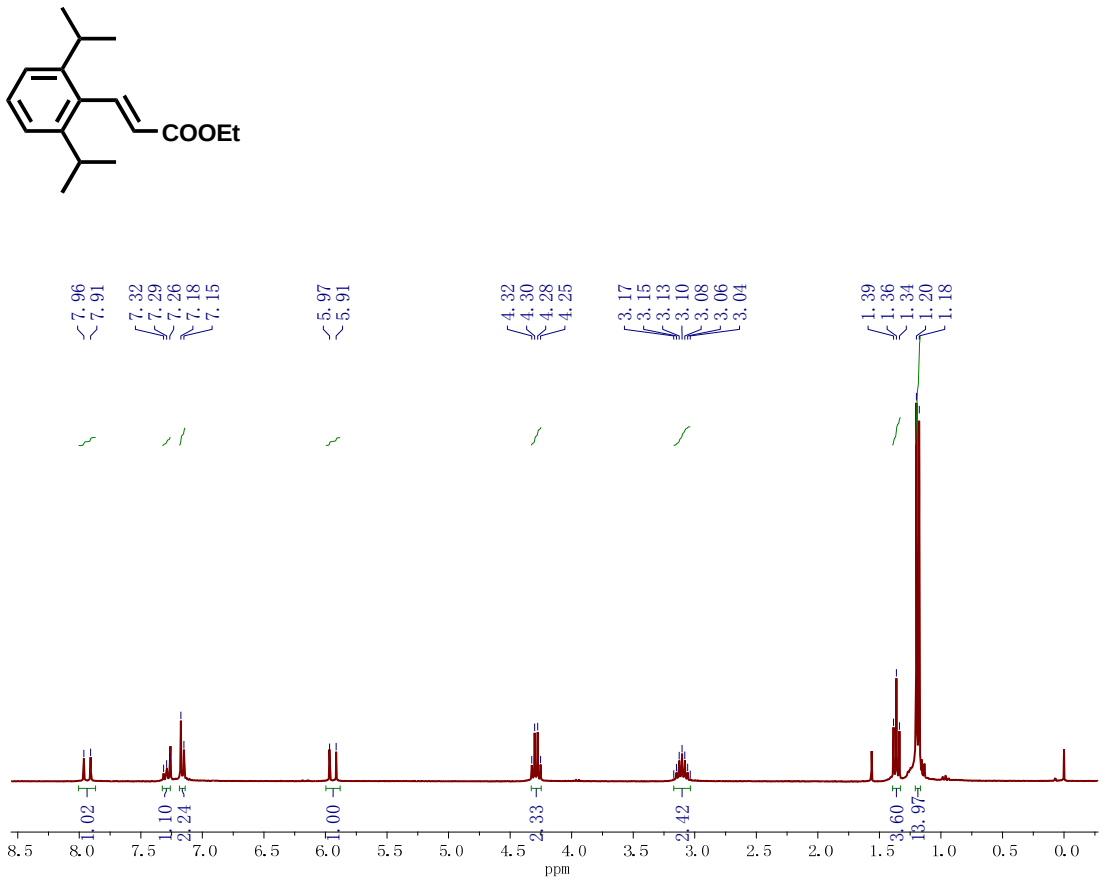


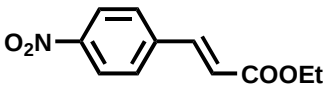


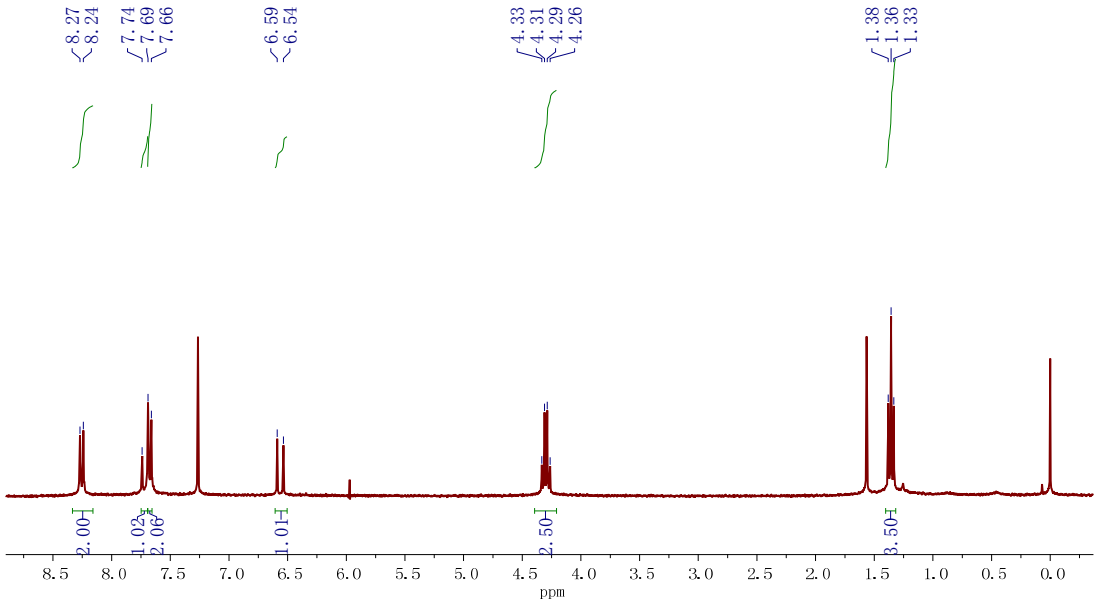









O2N
COOEt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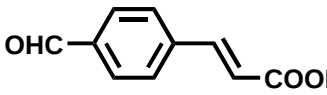
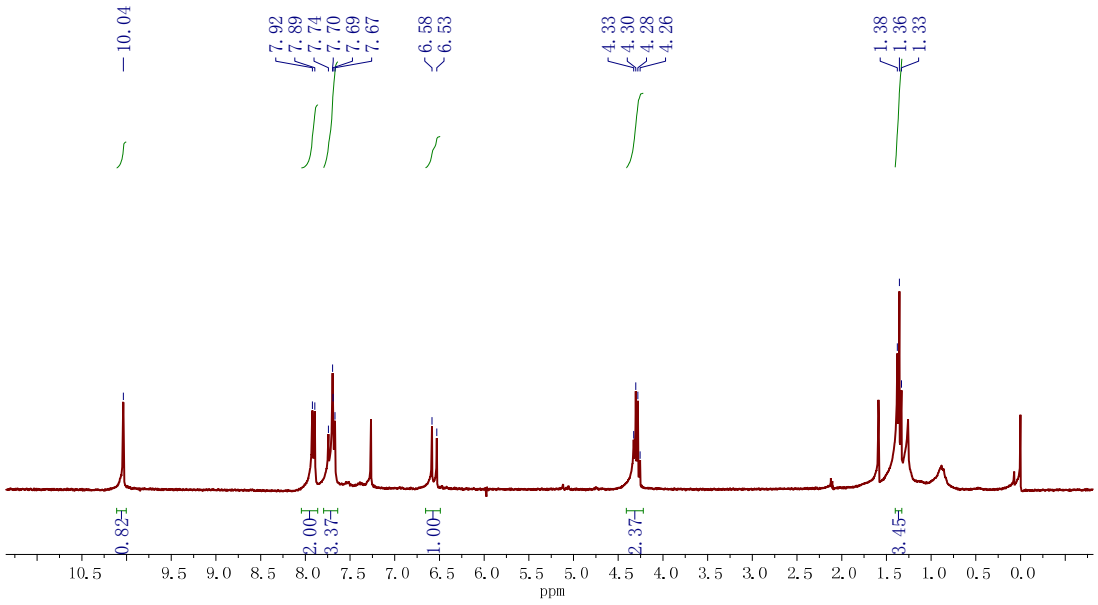
ppm


OHC
COOEt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7.67
6.58
6.53
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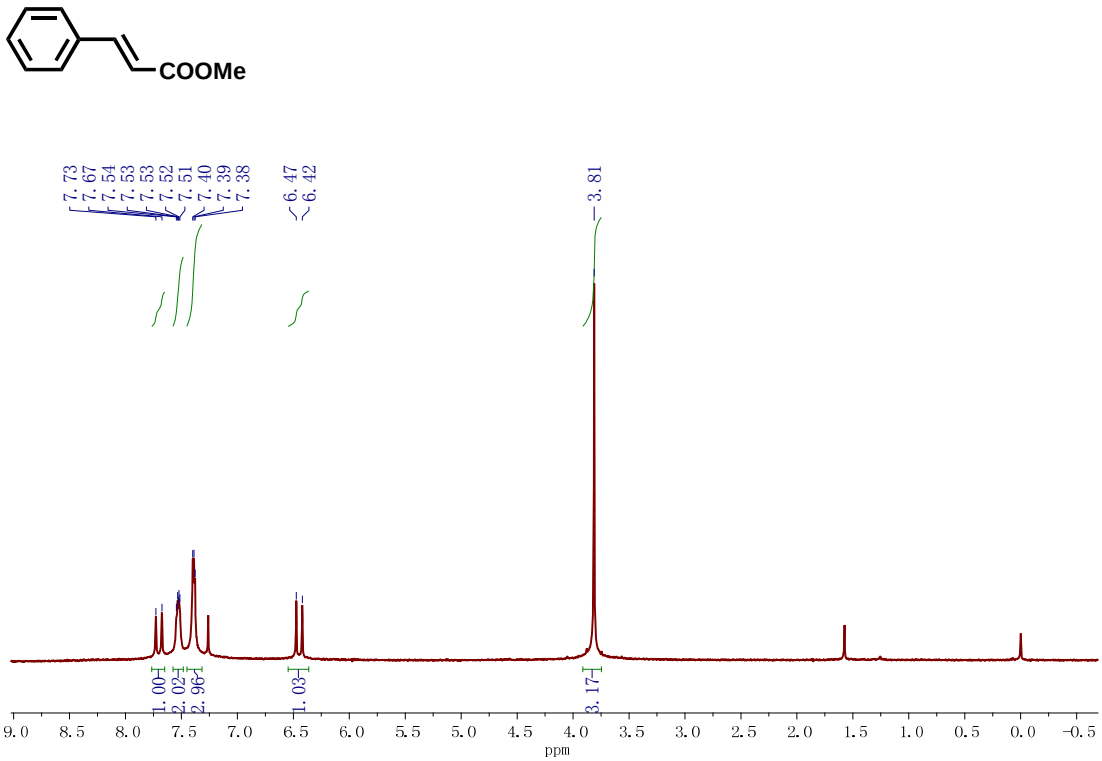
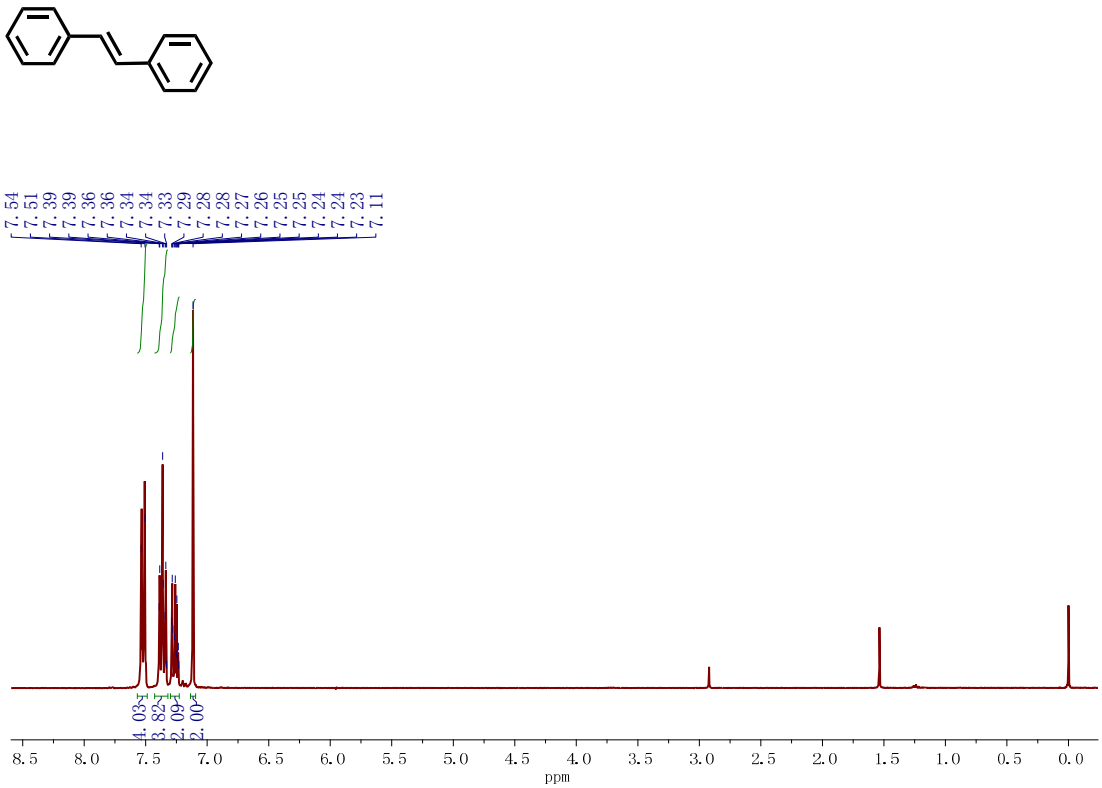
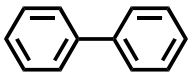
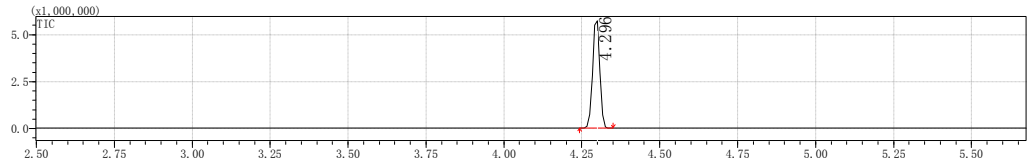
ppm

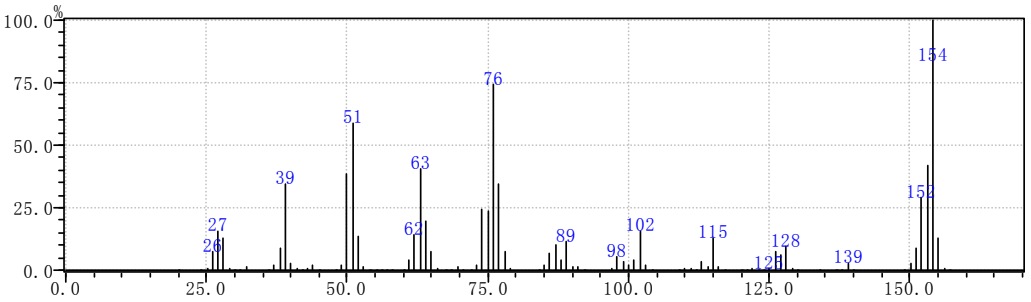


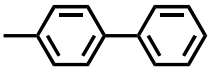


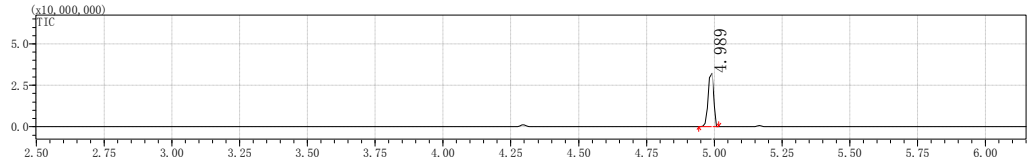
Section K. GC-MS spectra of products

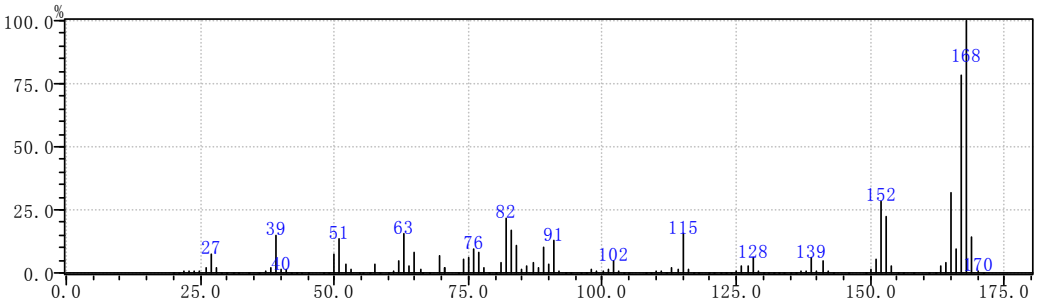


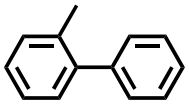


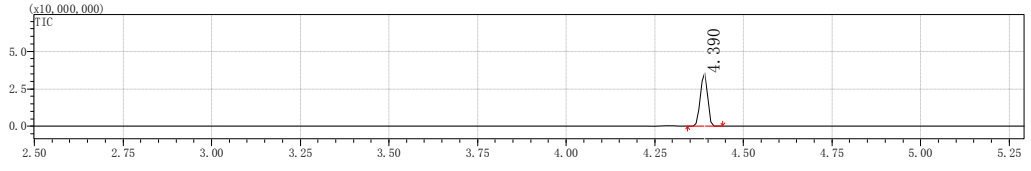








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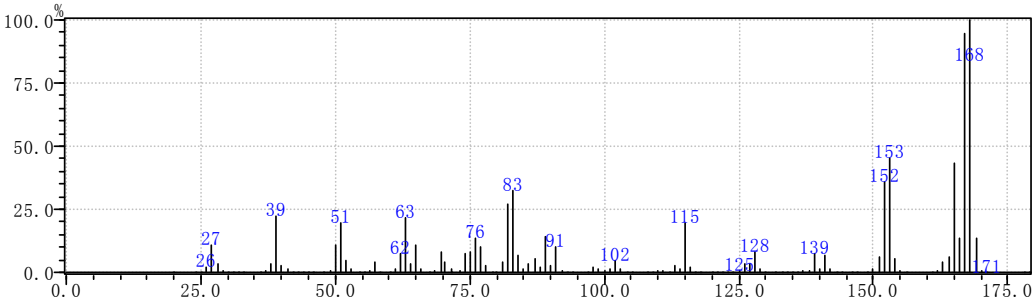
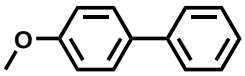
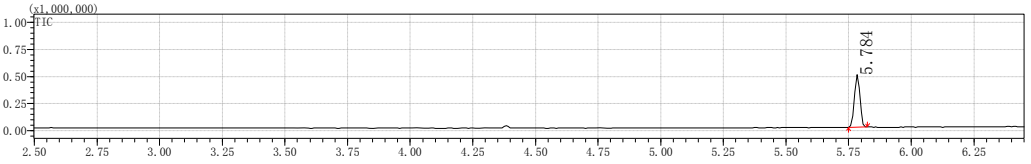
TIC
4.390


%
168
153
152
83
39
51
63
115
27
26
62
76
91
102
128
125
139
171

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TIC
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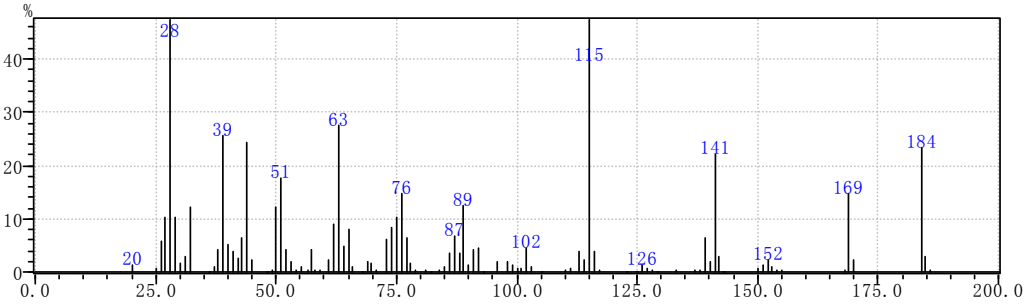
%
28
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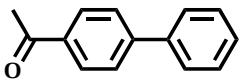

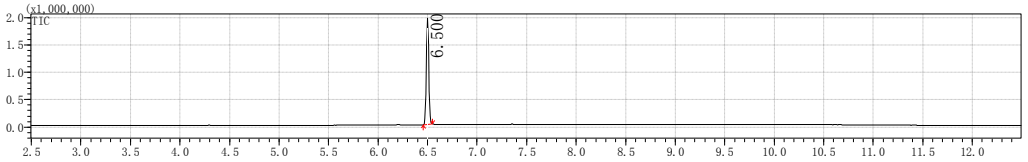
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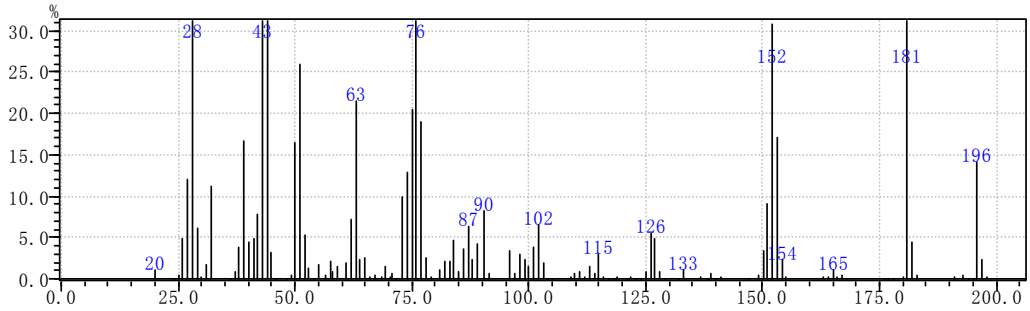
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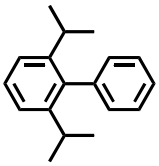

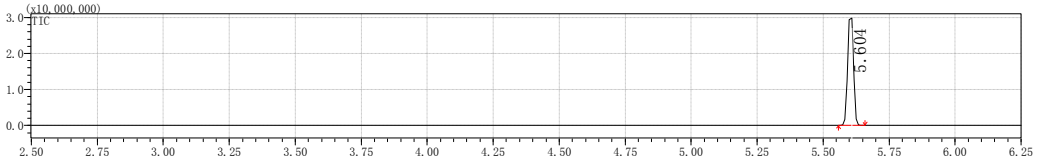
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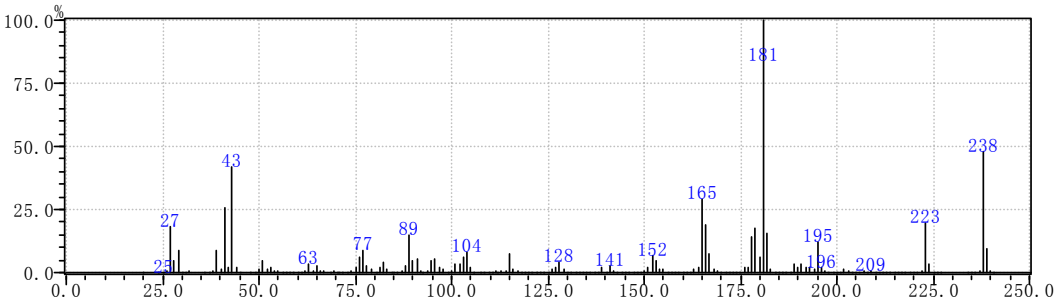
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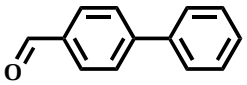
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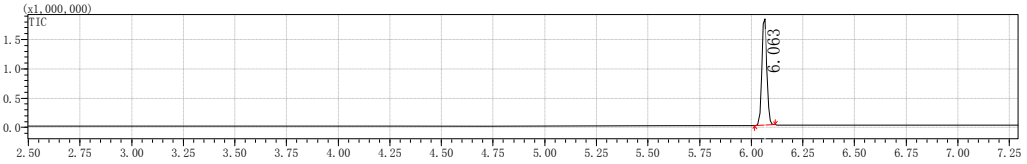
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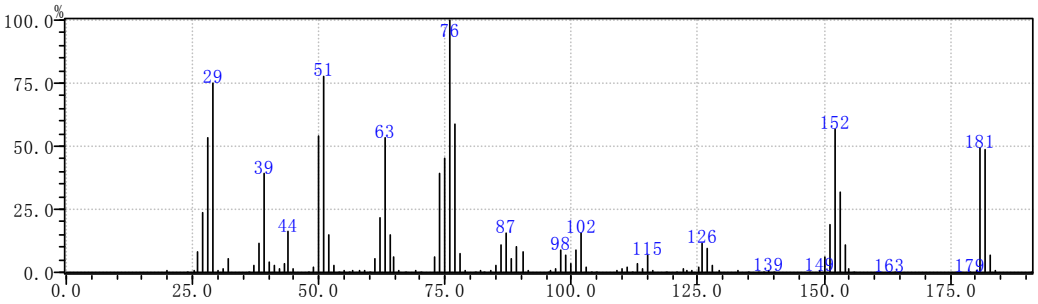
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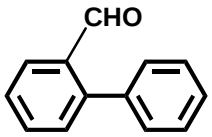
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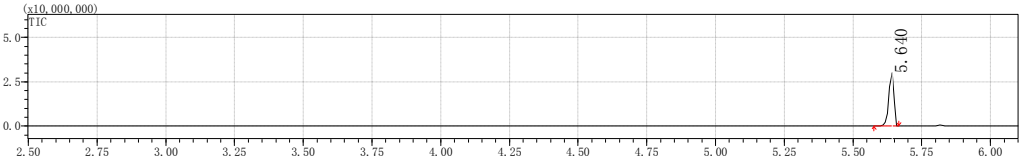
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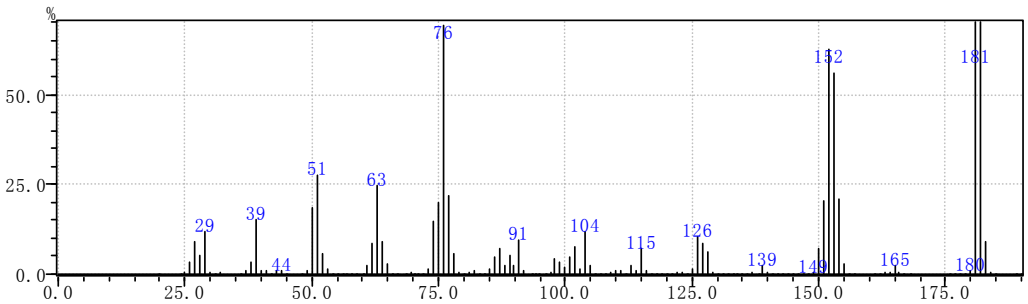
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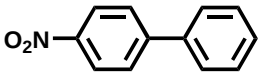
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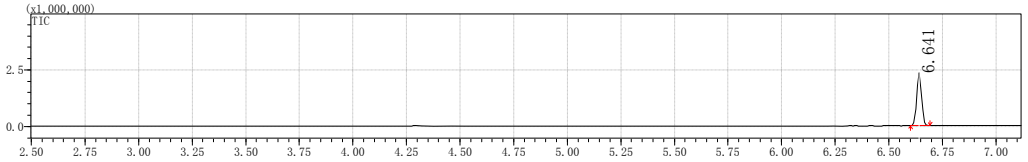
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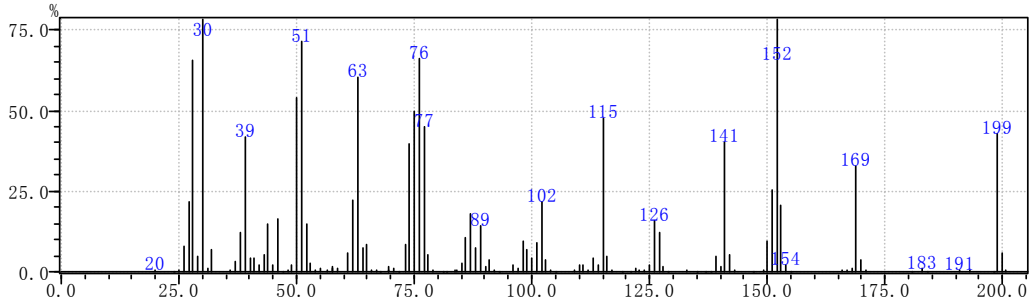
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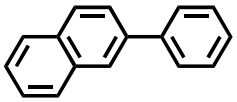

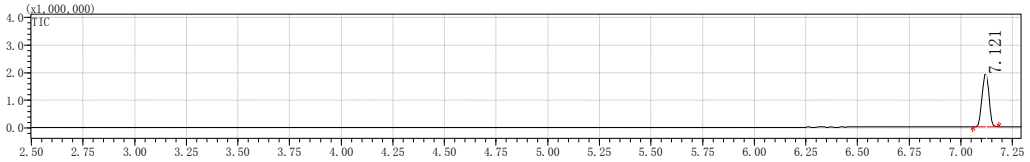
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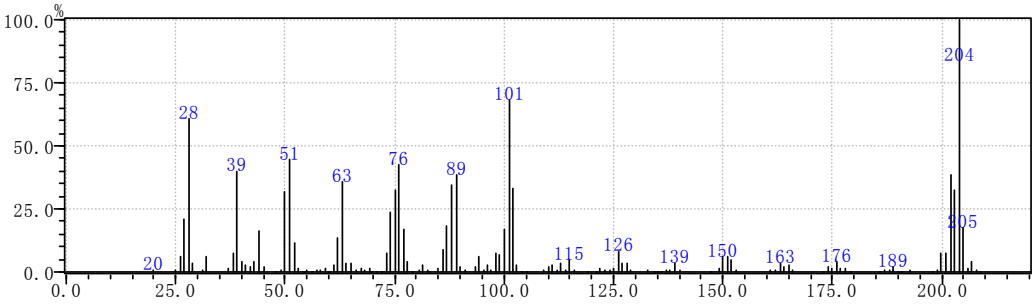
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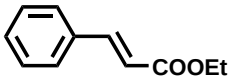
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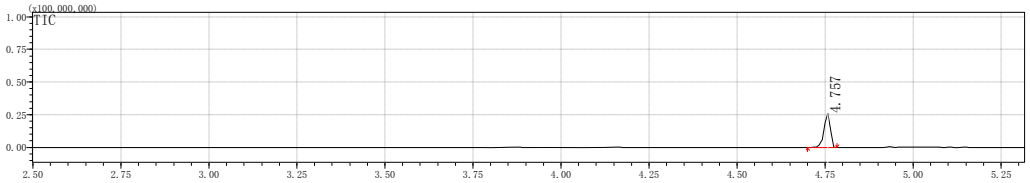
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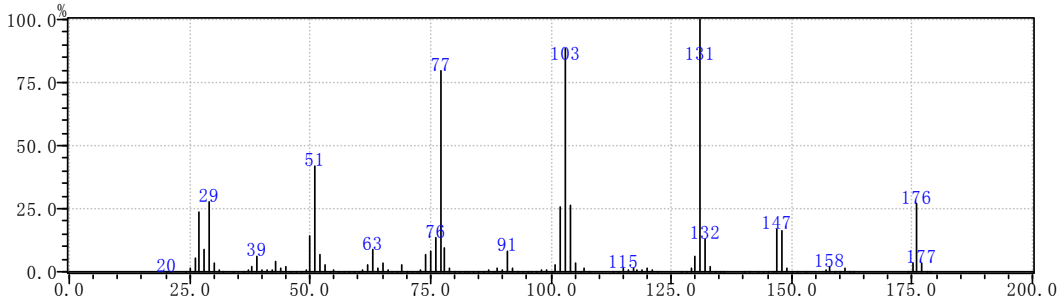
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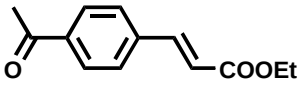
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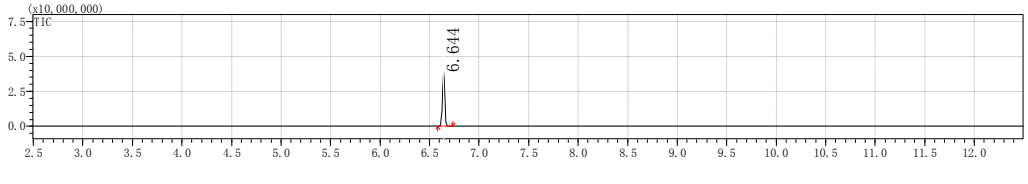
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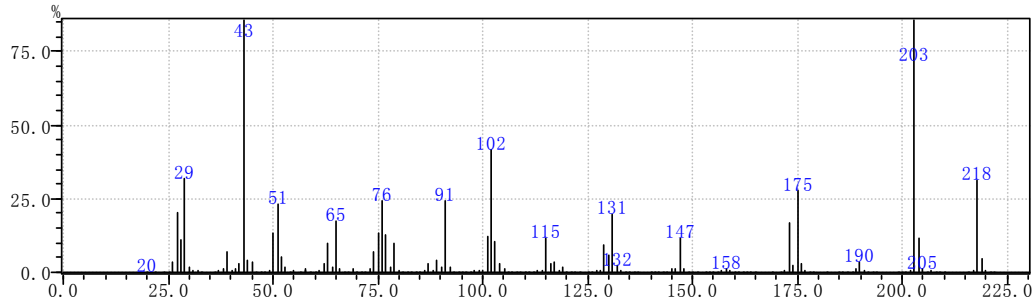
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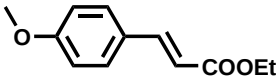
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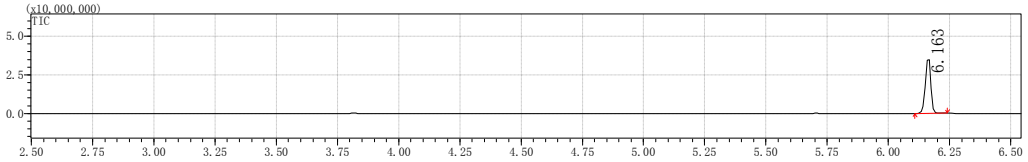
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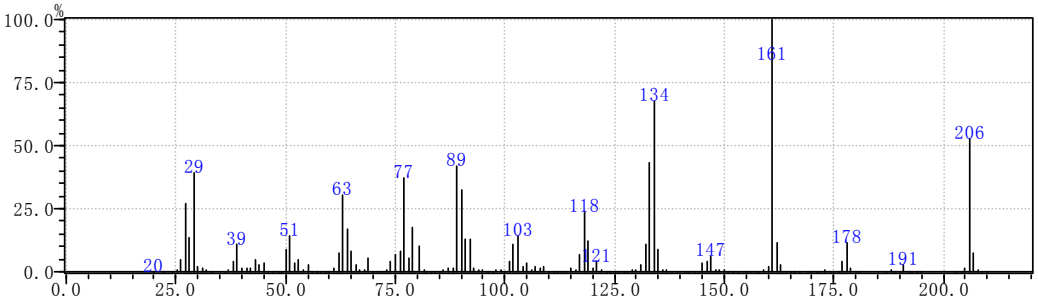
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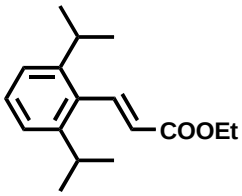
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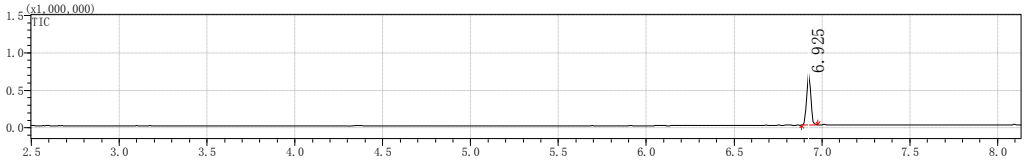
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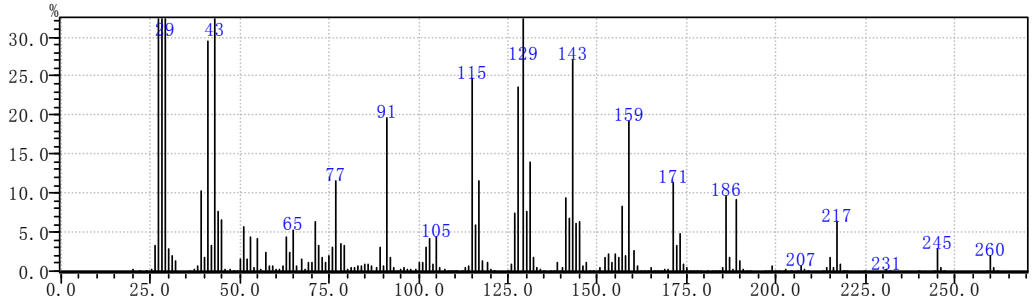
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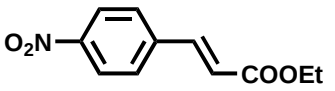
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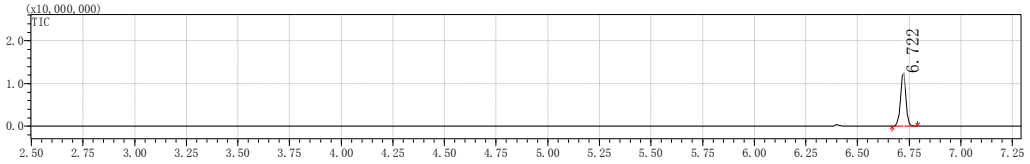
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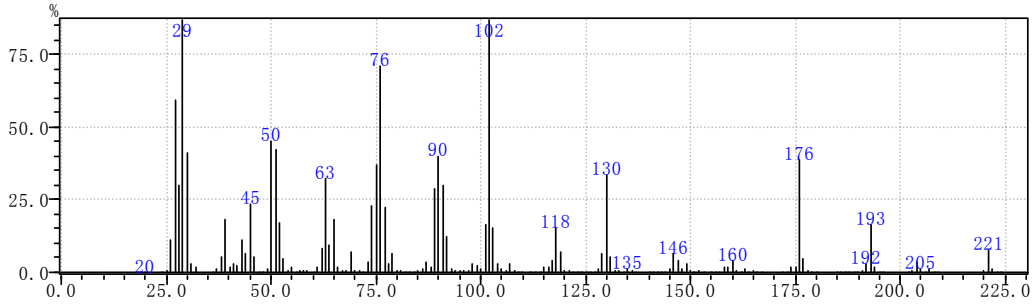
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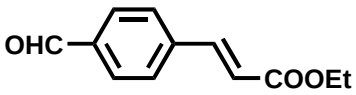
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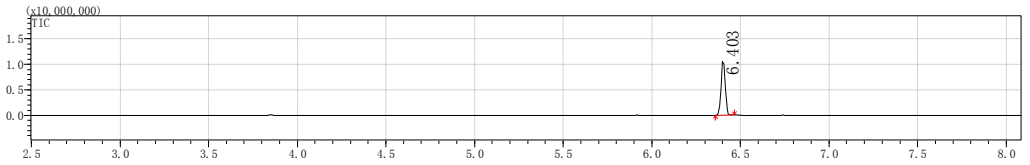
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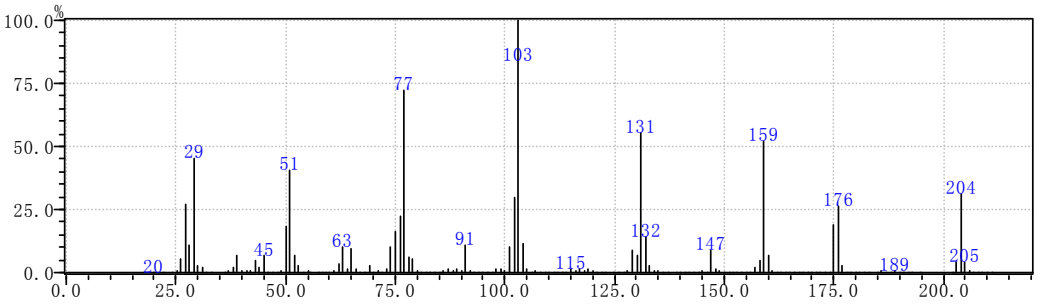
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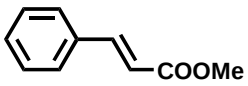
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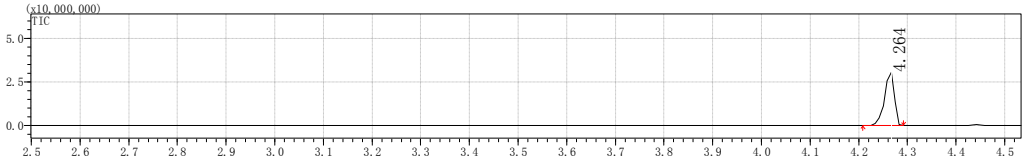
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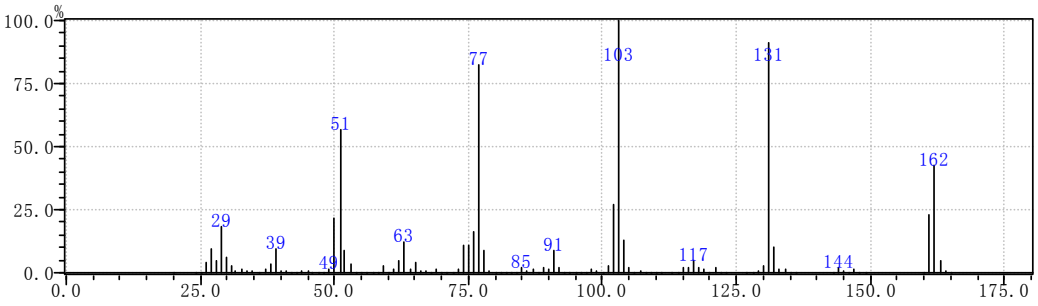
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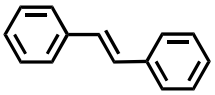

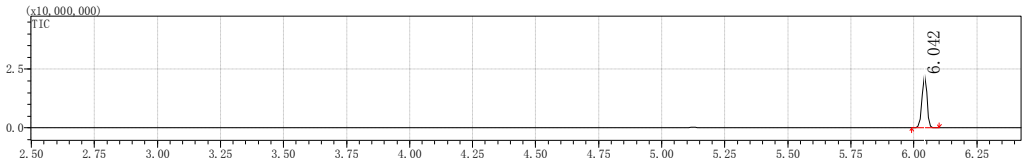
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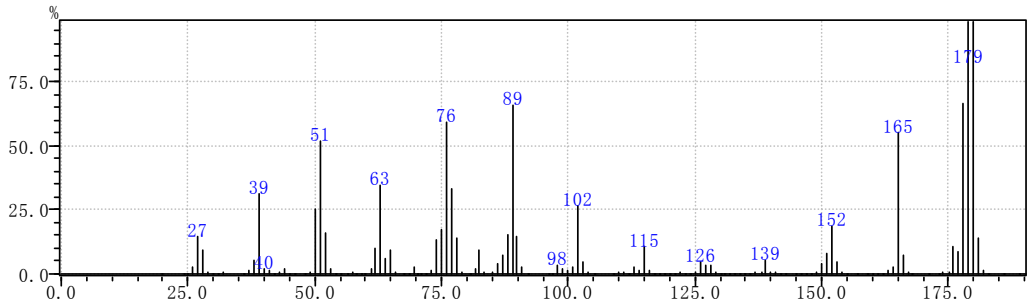
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Section L. Supporting references

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