Supporting Information

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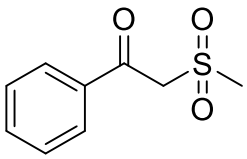
General Information

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is between 60-90 ^{o}C).

Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios. NMR spectra were recorded on a Varian Mercury spectrometer at 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR) or on a Bruker spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR). Tetramethylsilane was used as an internal standard. All 1H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument, accurate masses are reported for the molecular ion ($[M+H]^{+}$). Selective ratios were recorded with a Varian GC 2000 gas chromatography instrument with a FID detector. GC-Ms spectra were recorded on a Varian GC-Ms 3900-2100T and Shimadzu GCMS-QP2010SE.

General Procedures



2-(Methylsulfonyl)-1-phenylethan-1-one (3a)

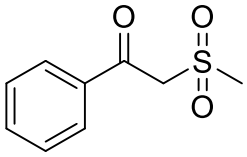
$PdCl_2$ (0.02 mmol, 3.5 mg), $Cu(PivO)_2$ (0.04 mmol, 10.64 mg) and D-Fructose (0.08 mmol, 21.6 mg) were added into an oven-dried autoclave tube equipped with a magnetic stirred bar. And DMSO (1 mL), 1, 1-stilbene (0.2 mmol, 36 mg) were injected in the tube through a syringe in turn, which was then put into the autoclave**.** After flushing the autoclave three times with O_2 (20 bar)**,** other 20 bar CO filled with the autoclave, and the pressure was adjusted to 0 bar. The autoclave was then heated up to 80 ℃ and kept stirring for 16 hours. After completion of the reaction, as indicated by TLC and GC-MS, the mixture was quenched by saturated brine and extracted with ethyl ether (3 * 10 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The pure product (yield 90%, 34.4 mg) was obtained by flash column chromatography on silica gel (petroleumether : ethyl acetate = 4 : 1).

Detailed descriptions for products:

Products from various α-substituted olefins

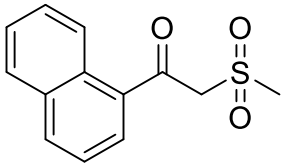
C-C cleavage (from 1,1–stilbene 1-methyl-1-phenyl–Ethylene and 2-phenylacrylic acid)

C-O bond cleavage (from diethyl(1-phenylvinyl)phosphonate)



2-(Methylsulfonyl)-1-phenylethan-1-one (3a) [1]:

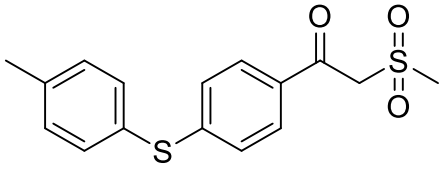
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.93 (m, 2H), 7.73 – 7.61 (m, 1H), 7.57 – 7.49 (m, 2H), 4.62 (s, 2H), 3.16 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 189.25, 135.57, 134.76, 129.25, 129.07, 61.21, 41.83. HRMS (ESI) calcd for $C_9H_{10}O_3S$ $[M+H]^+$: 199.0429; found: 199.0422.



2-(Methylsulfonyl)-1-(naphthalen-1-yl)ethan-1-one (3b):

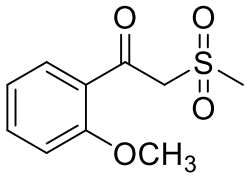
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.8 Hz, 1H), 8.09 – 8.06 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.68-7.64 (m, 1H), 7.60-7.53 (m, 2H), 4.72 (s, 2H), 3.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.61, 135.11, 133.97, 133.28, 130.95, 130.33, 129.06, 128.77, 127.03, 125.47, 124.40, 64.03, 42.11. HRMS (ESI) calcd for $C_{13}H_{12}O_3S$ $[M+H]^+$: 249.0585; found: 249.0579.

C-Br bond cleavage(from α-Br-olefins)



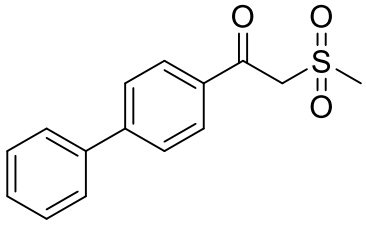
2-(Methylsulfonyl)-1-(4-(p-tolylthio)phenyl)ethan-1-one (3c):

Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.24 (m, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 4.55 (s, 2H), 3.15 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.95, 149.28, 140.01, 135.08, 132.27, 130.77, 129.76, 126.74, 126.25, 61.27, 41.77, 21.37. HRMS (ESI) calcd for $C_{16}H_{16}O_3S_2$ $[M+H]^+$: 321.0619; found: 321.0607.



1-(2-Methoxyphenyl)-2-(methylsulfonyl)ethan-1-one (3d):

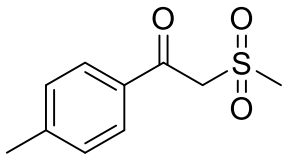
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.10 – 6.90 (m, 2H), 4.77 (s, 2H), 3.96 (s, 3H), 3.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.09, 159.26, 135.82, 131.27, 125.91, 121.18, 111.90, 65.36, 55.83, 42.47. HRMS (ESI) calcd for $C_{10}H_{12}O_3S$ $[M+H]^+$: 229.0535; found: 229.0525.



1-([1,1'-Biphenyl]-4-yl)-2-(methylsulfonyl)ethan-1-one (3e):

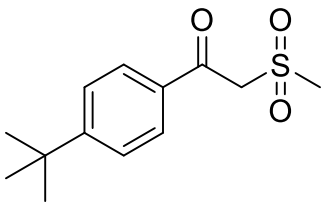
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.60 (m, 2H), 7.53 – 7.37 (m, 3H), 4.65 (s, 2H), 3.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.74, 147.42, 139.30, 134.27, 129.94, 129.09, 128.71, 127.63, 127.36, 61.34, 41.82. HRMS (ESI) calcd for $C_{15}H_{14}O_3S$ $[M+H]^+$: 275.0742; found: 275.0734.

Products from simple olefins



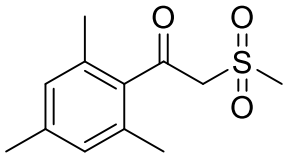
2-(Methylsulfonyl)-1-(p-tolyl)ethan-1-one (3f) [1]:

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.59 (s, 2H), 3.15 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.72 , 146.14, 133.17, 129.80, 129.45, 61.24, 41.80, 21.89. HRMS (ESI) calcd for $C_{10}H_{12}O_3S$ $[M+H]^+$: 213.0585; found: 213.0579.



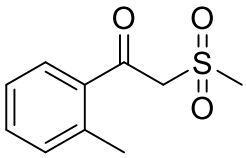
1-(4-(Tert-butyl)phenyl)-2-(methylsulfonyl)ethan-1-one (3g):

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 4.59 (s, 2H), 3.15 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.72, 158.92, 133.08, 129.34, 126.10, 61.27, 41.79, 35.39, 31.01. HRMS (ESI) calcd for $C_{13}H_{18}O_3S$ $[M+H]^+$: 255.1055; found: 255.1046.



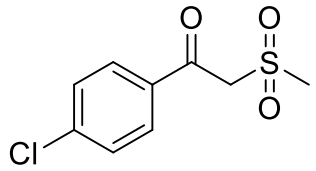
1-Mesityl-2-(methylsulfonyl)ethan-1-one (3h):

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 4.35 (s, 2H), 3.21 (s, 3H), 2.28 (s, 3H), 2.26 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.04, 140.35, 136.98, 133.83, 129.09, 65.34, 42.46, 21.07, 19.49. HRMS (ESI) calcd for $C_{12}H_{16}O_3S$ $[M+H]^+$: 241.0898; found: 241.0892.



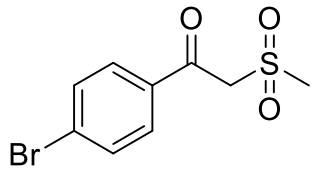
2-(Methylsulfonyl)-1-(o-tolyl)ethan-1-one (3i):

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.47 (td, *J* = 7.6, 1.1 Hz, 1H), 7.37 – 7.28 (m, 2H), 4.57 (s, 2H), 3.17 (s, 3H), 2.56 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 191.63, 140.17, 135.61, 133.21, 132.52, 130.29, 126.19, 63.33, 42.03, 21.72. HRMS (ESI) calcd for $C_{10}H_{12}O_3S$ $[M+H]^+$: 213.0585; found: 213.0580.



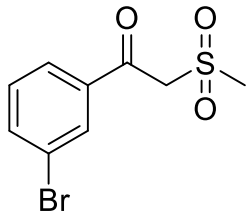
1-(4-Chlorophenyl)-2-(methylsulfonyl)ethan-1-one (3j):

White solid. ^{1}H NMR (400 MHz, d^{6}-DMSO) δ 8.28 – 7.85 (m, 2H), 7.79 – 7.31 (m, 2H), 5.14 (s, 2H), 3.17 (s, 3H). ^{13}C NMR (101 MHz, d^{6}-DMSO) δ 189.59, 139.84, 134.95, 131.37, 129.40, 61.21, 42.42. HRMS (ESI) calcd for $C_9H_9ClO_3S$ $[M+H]^+$: 233.0039; found: 233.0033.



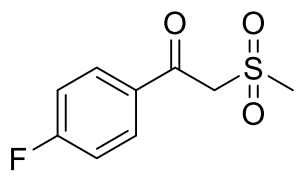
1-(4-Bromophenyl)-2-(methylsulfonyl)ethan-1-one (3k):

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J*= 8.4 Hz, 2H), 7.67 (d, *J*= 8.4 Hz, 2H), 4.59 (s, 2H), 3.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.36, 134.29, 132.44, 130.73, 130.45, 61.27, 41.77. HRMS(ESI) calcd for $C_9H_9BrO_3S$ $[M+H]^+$: 276.9534; found: 276.9528.



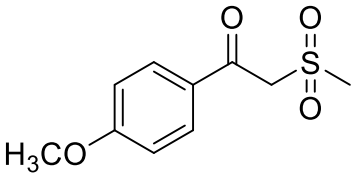
1-(3-Bromophenyl)-2-(methylsulfonyl)ethan-1-one (3l):

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 4.64 (s, 2H), 3.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.14, 137.37, 137.15, 131.87, 130.51, 127.84, 123.21, 61.03, 41.80. HRMS (ESI) calcd for $C_9H_9BrO_3S$ $[M+H]^+$: 276.9534; found: 276.9539.



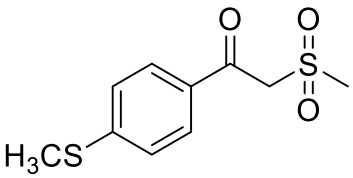
1-(4-Fluorophenyl)-2-(methylsulfonyl)ethan-1-one (3m):

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.03 (m, 2H), 7.25 – 7.16 (m, 2H), 4.59 (s, 2H), 3.15 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 187.67, 166.70 (d, *J*= 258.3 Hz), 132.23 (d, *J*= 9.8 Hz), 132.07 (d, *J*= 2.9 Hz), 116.37 (d, *J*= 22.2 Hz), 61.31, 41.75. HRMS (ESI) calcd for $C_9H_9FO_3S$ $[M+H]^+$: 217.0335; found: 217.0333.



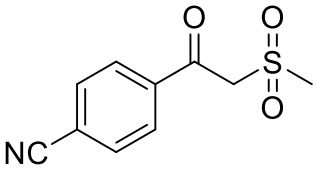
1-(4-Methoxyphenyl)-2-(methylsulfonyl)ethan-1-one (3n):

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.01 – 6.96 (m, 2H), 4.56 (s, 2H), 3.90 (s, 3H), 3.14 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 187.38, 164.86, 131.88, 128.64, 114.28, 61.15, 55.71, 41.72. HRMS (ESI) calcd for $C_{10}H_{12}O_4S$ $[M+H]^+$: 229.0535; found: 229.0529.



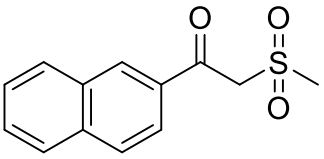
2-(Methylsulfonyl)-1-(4-(methylthio)phenyl)ethan-1-one (3o):

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.32 – 7.28 (m, 2H), 4.56 (s, 2H), 3.14 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.94, 148.85, 131.69, 129.66, 125.01, 61.20, 41.75, 14.61. HRMS (ESI) calcd for $C_{10}H_{12}O_3S_2$ $[M+H]^+$: 245.0306; found: 245.0300.



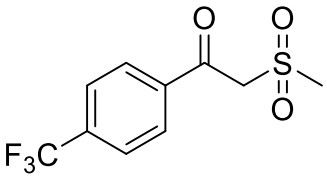
4-(2-(Methylsulfonyl)acetyl)benzonitrile (3p):

White solid. ^{1}H NMR (400 MHz, d^6-DMSO) δ 8.19 (d, *J*= 8.4 Hz, 2H), 8.07 (d, *J*= 8.4 Hz, 2H), 5.20 (s, 2H), 3.16 (s, 3H). ^{13}C NMR (101 MHz, d^6-DMSO) δ 190.07, 139.29, 133.28, 129.99, 118.45, 116.46, 61.41, 42.40. HRMS (ESI) calcd for $C_{10}H_9NO_3S$ $[M+NH_4]^+$: 241.0641; found: 241.0642$[M+NH_4]^+$.



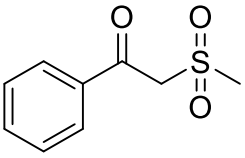
2-(Methylsulfonyl)-1-(naphthalen-2-yl)ethan-1-one (3q):

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 1.2 Hz, 1H), 8.05 – 7.97 (m, 2H), 7.90 (dd, *J* = 14.7, 8.4 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.61 – 7.55 (m, 1H), 4.75 (s, 2H), 3.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.11, 136.15, 132.94, 132.28, 132.21, 130.03, 129.60, 129.06, 127.84, 127.30, 123.71, 61.28, 41.86. HRMS (ESI) calcd for $C_{13}H_{12}O_3S$ $[M+H]^+$: 249.0585; found: 249.0575.

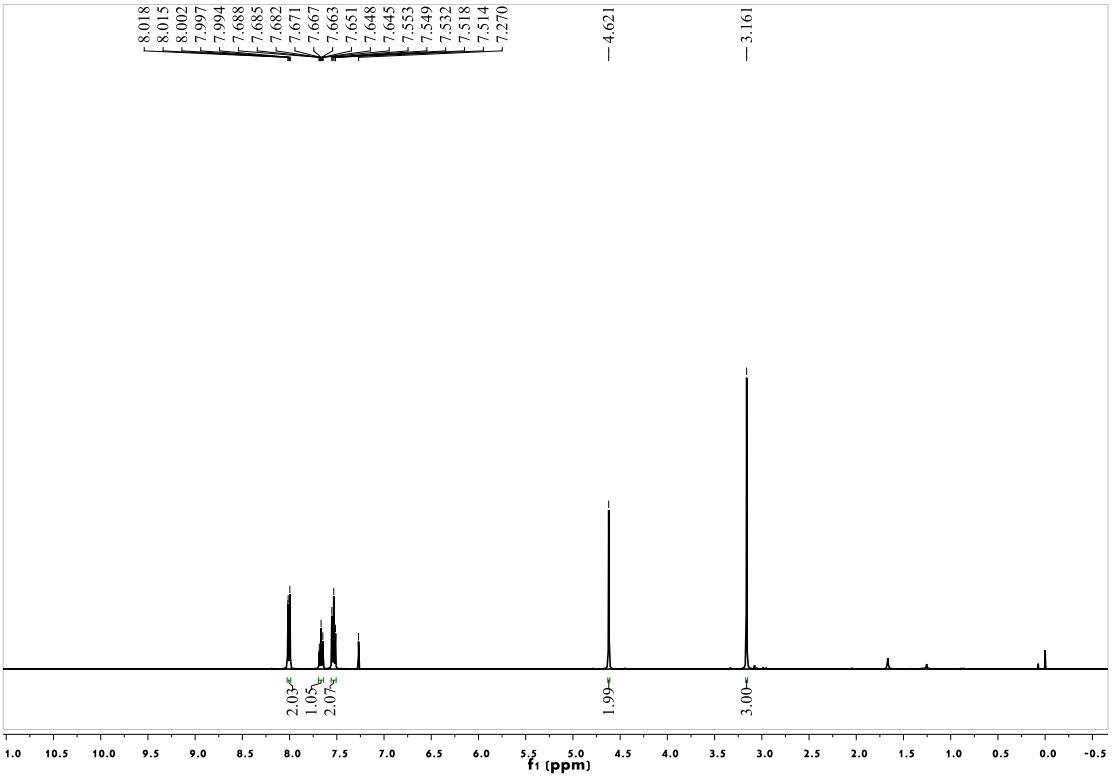


2-(Methylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3r):

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 4.65 (s, 2H), 3.17 (s, 3H).13CNMR (101MHz, $CDCl_3$) δ 188.58, 138.14, 135.80 (q, *J*= 33.3 Hz), 129.71, 126.14 (q, *J*= 4.0 Hz), 123.29 (q, *J*= 273.7 Hz), 61.48, 41.79. HRMS (ESI) calcd for $C_{10}H_9F_3O_3S$ $[M+H]^+$: 267.0303; found: 267.0299.



3a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7.645
7.553
7.549
7.532
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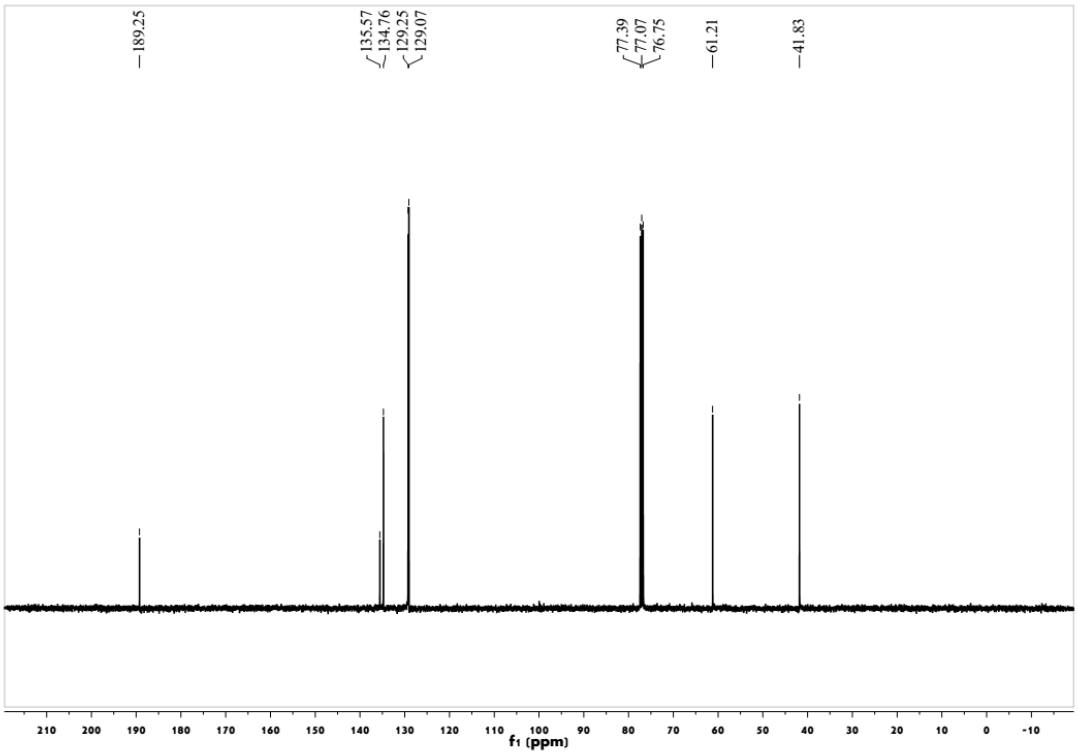
2.07
1.99
3.00
f1 (ppm)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129.07
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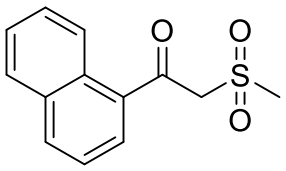
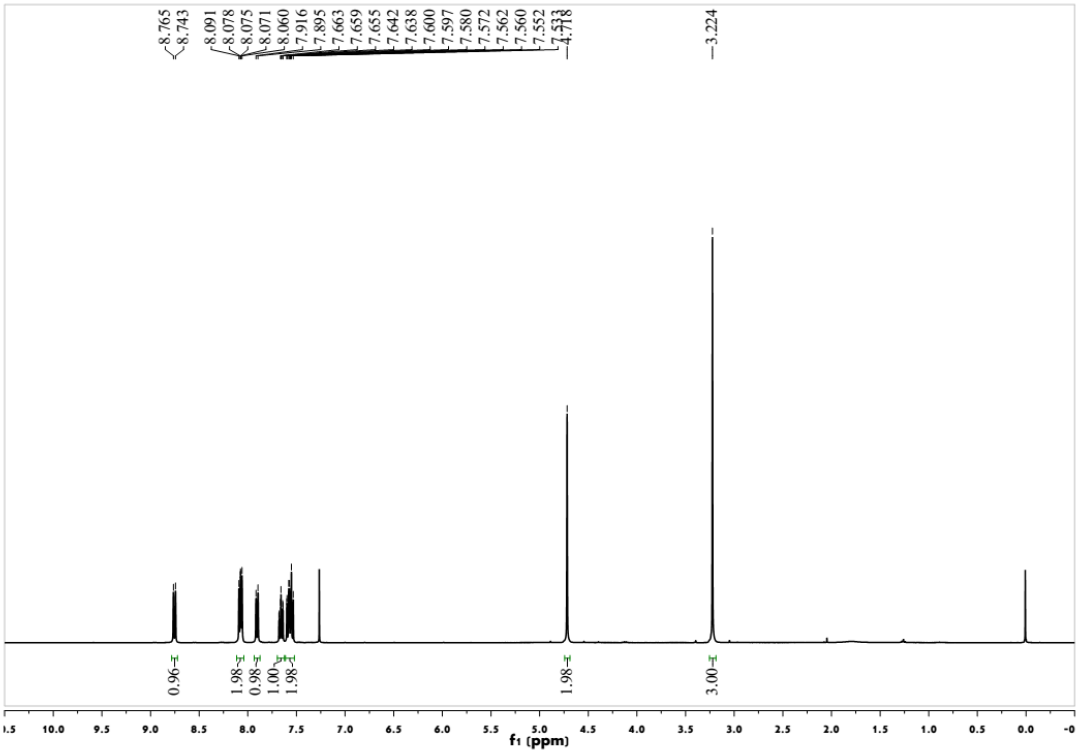
61.21
41.83
f1 (ppm)



3b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8.075
8.071
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7.659
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7.642
7.638
7.600
7.597
7.580
7.572
7.562
7.560
7.552
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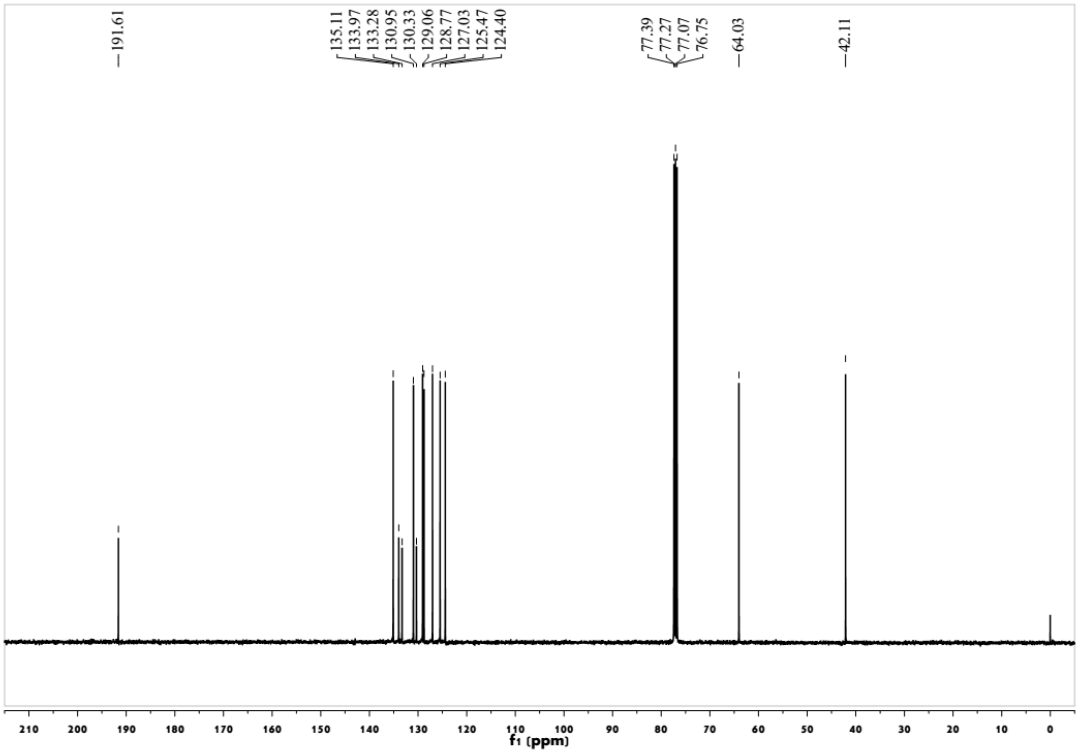
1.98
0.98
1.00
1.98
1.98
3.00
f1 (ppm)


191.61
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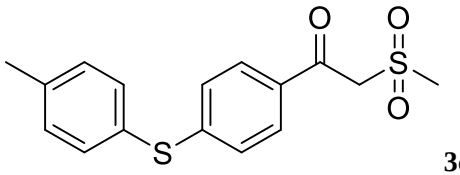
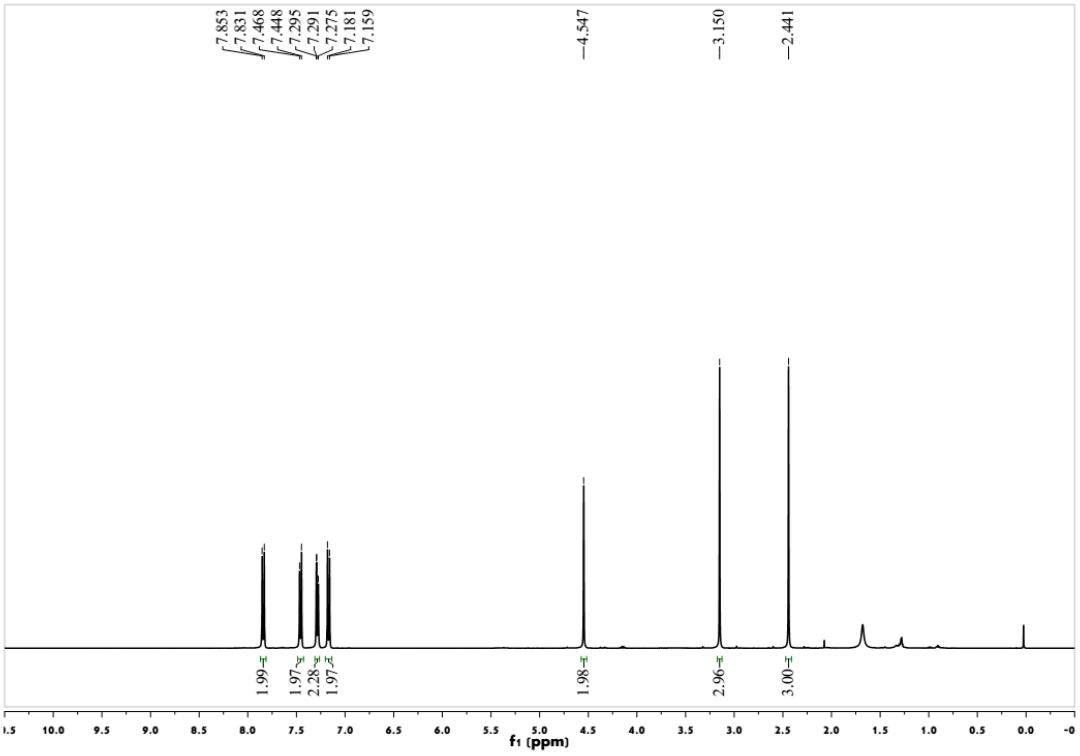
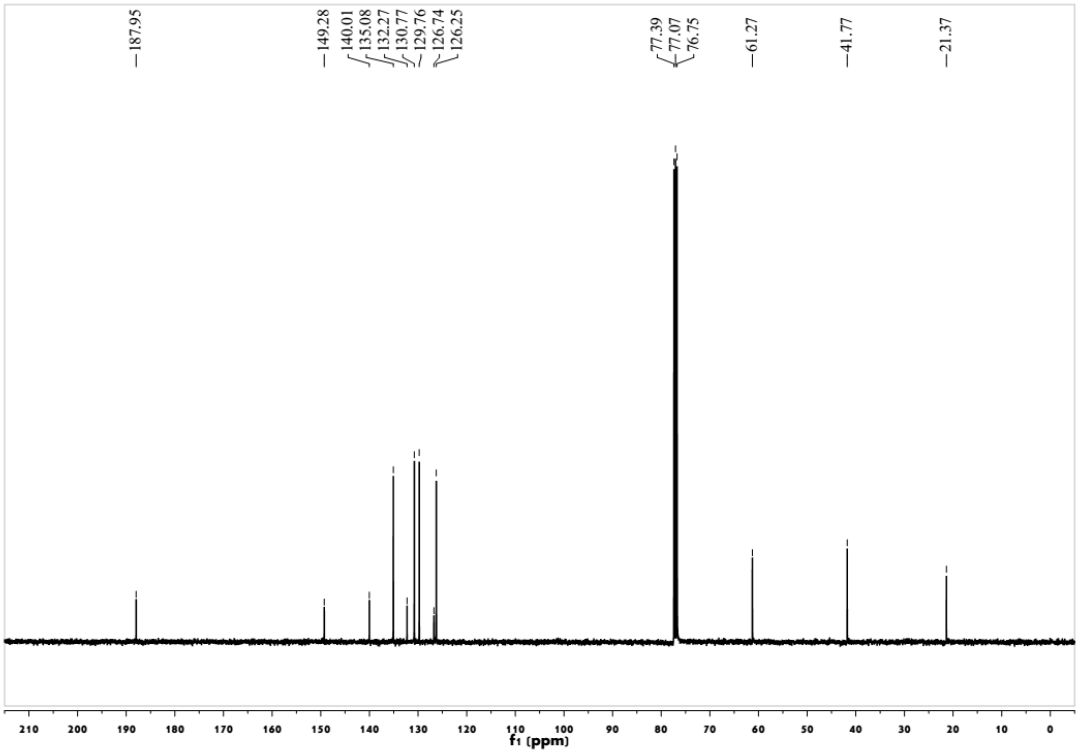
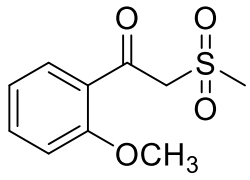
133.97
133.28
130.95
130.33
129.06
128.77
127.03
125.47
124.40
77.39
77.27
77.07
76.75
64.03
42.11
f1 (ppm)



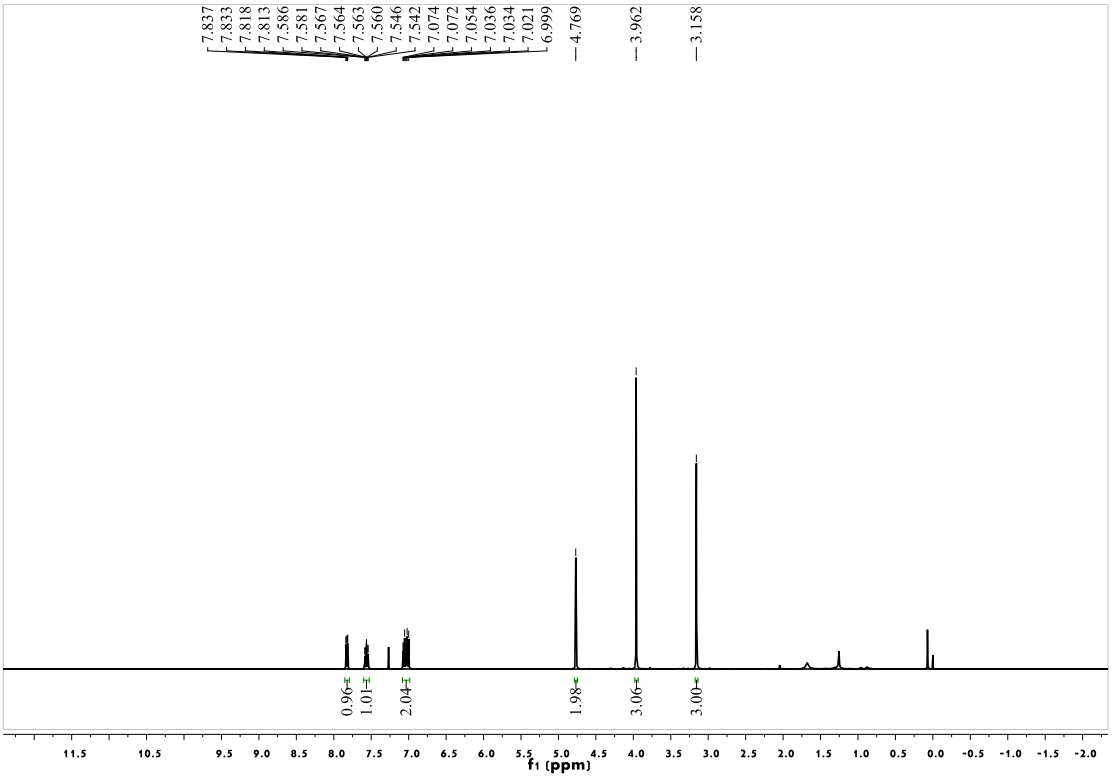
3c

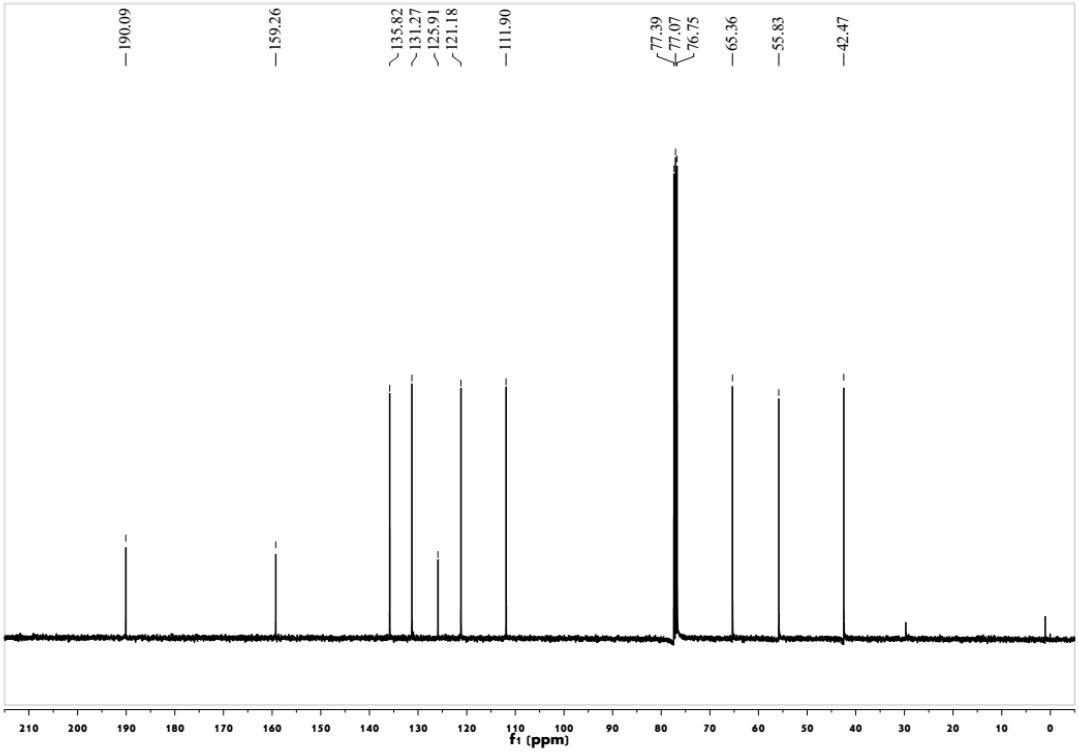

7.853
7.831
7.468
7.448
7.295
7.291
7.275
7.181
7.159
4.547
3.150
2.441
1.99
1.97
2.28
1.97
1.98
2.96
3.00
f1 (ppm)

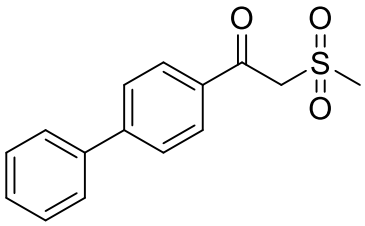

187.95
149.28
140.01
135.08
132.27
130.77
129.76
126.74
126.25
77.39
77.07
76.75
61.27
41.77
21.37
f1 (ppm)


O
O
S
O
OCH3

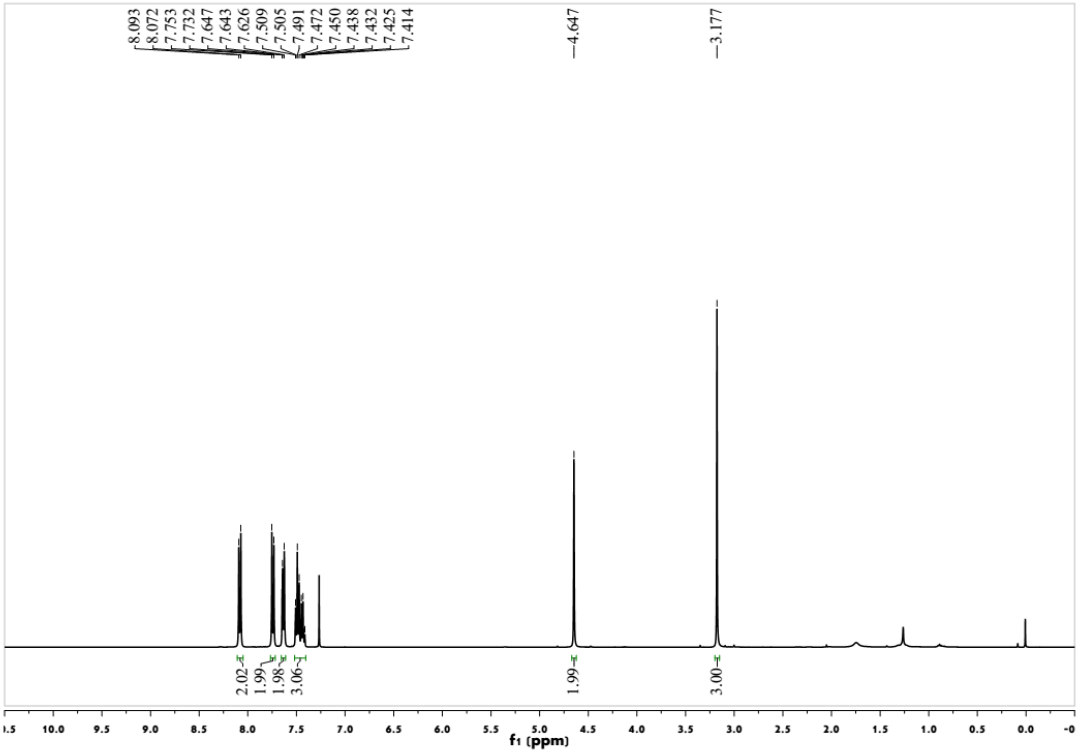
3d


7.837
7.833
7.818
7.813
7.586
7.581
7.567
7.564
7.563
7.560
7.546
7.542
7.074
7.072
7.054
7.036
7.034
7.021
6.999
4.769
3.962
3.158
0.96
1.01
2.04
1.98
3.06
3.00
f1 (ppm)


190.09
159.26
135.82
131.27
125.91
121.18
111.90
77.39
77.07
76.75
65.36
55.83
42.47
f1 (ppm)



3e


8.093
8.072
7.753
7.732
7.647
7.643
7.626
7.509
7.505
7.491
7.472
7.450
7.438
7.432
7.425
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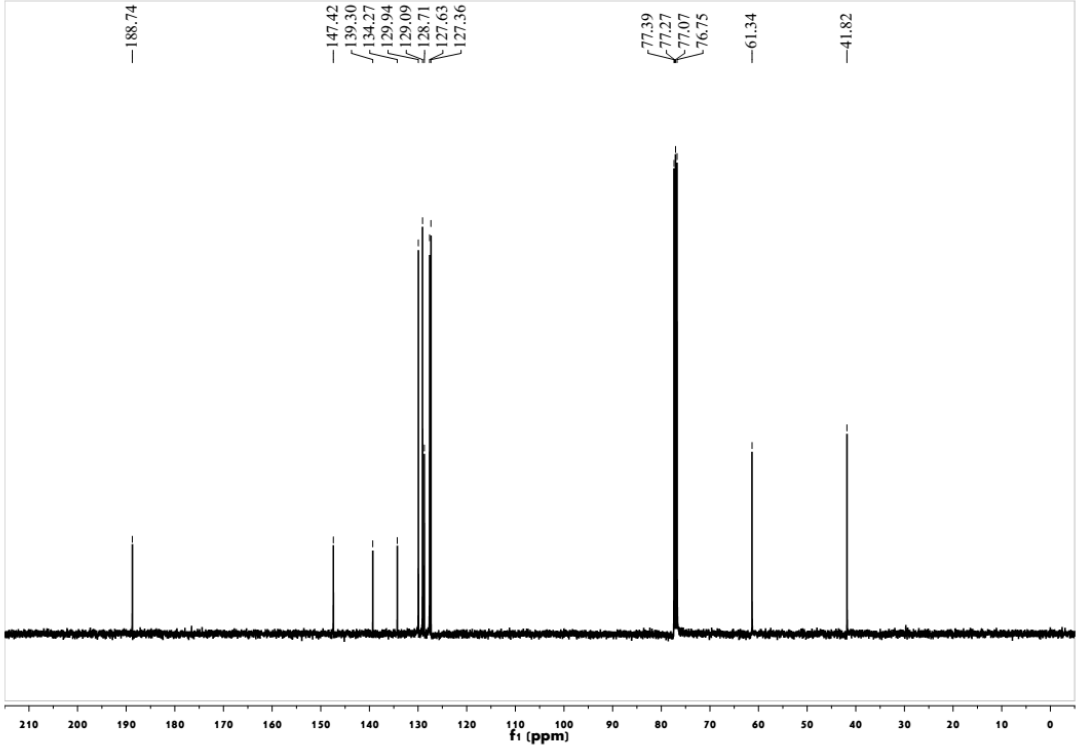
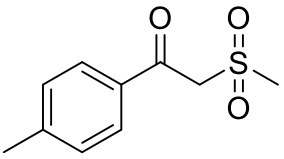
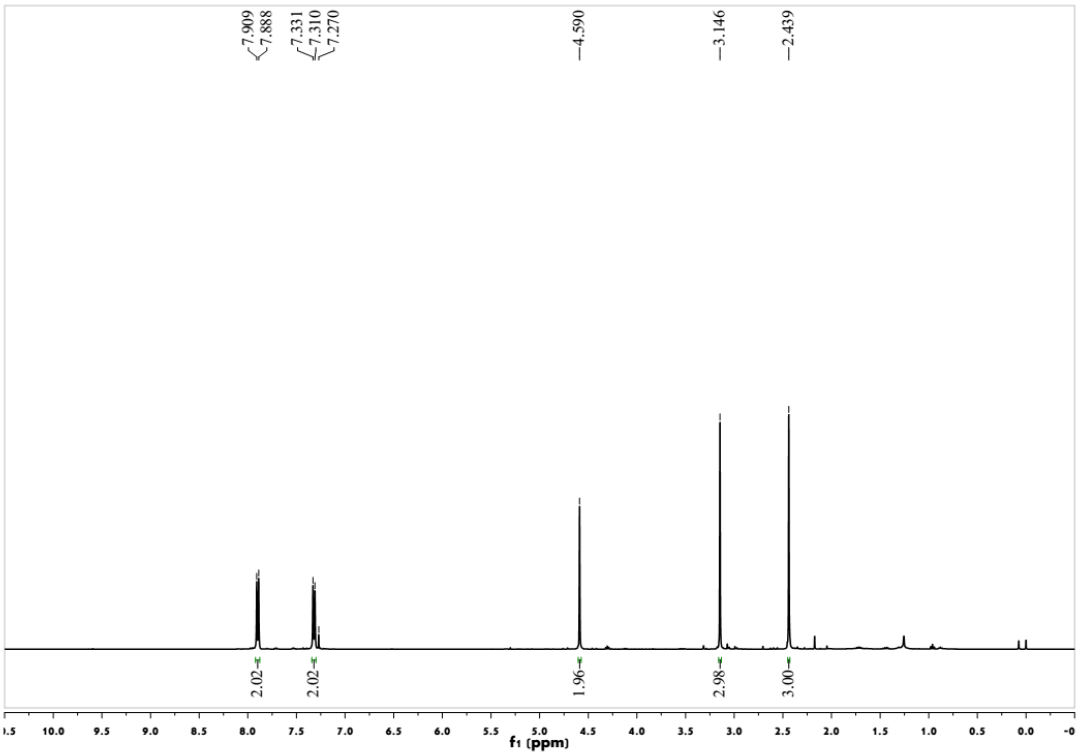
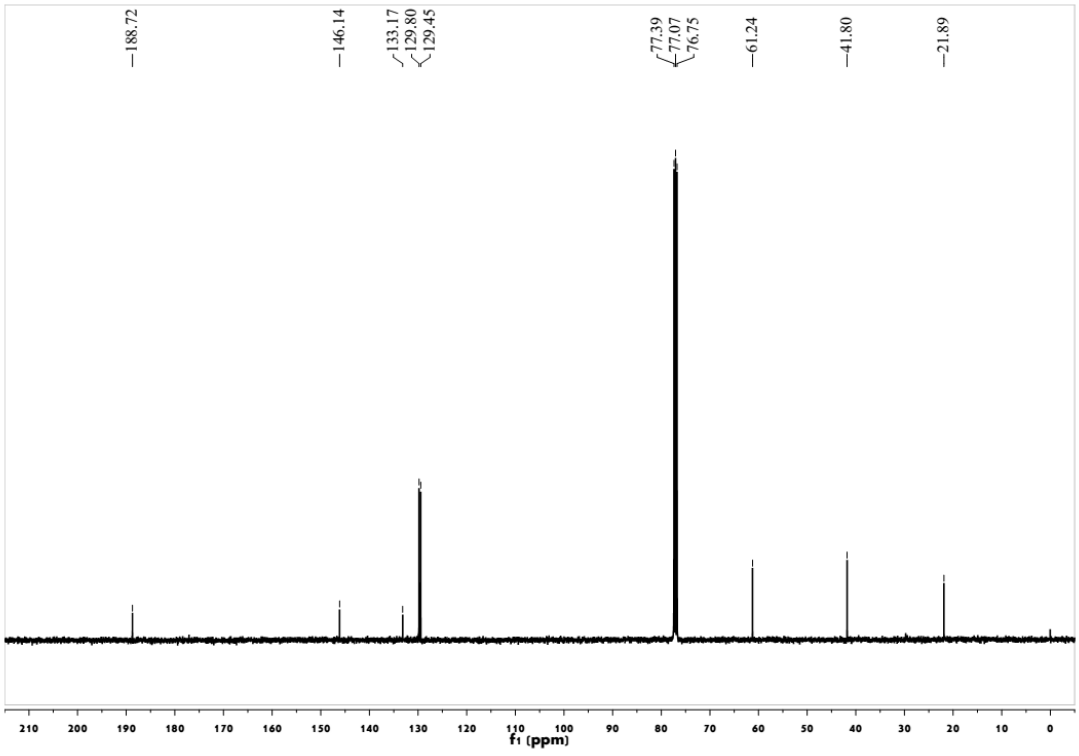
4.647
3.177
2.02
1.99
1.98
3.06
1.99
3.00
f1 (ppm)

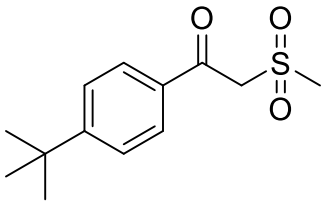

188.74
147.42
139.30
134.27
129.94
129.09
128.71
127.63
127.36
77.39
77.27
77.07
76.75
61.34
41.82
f1 (ppm)



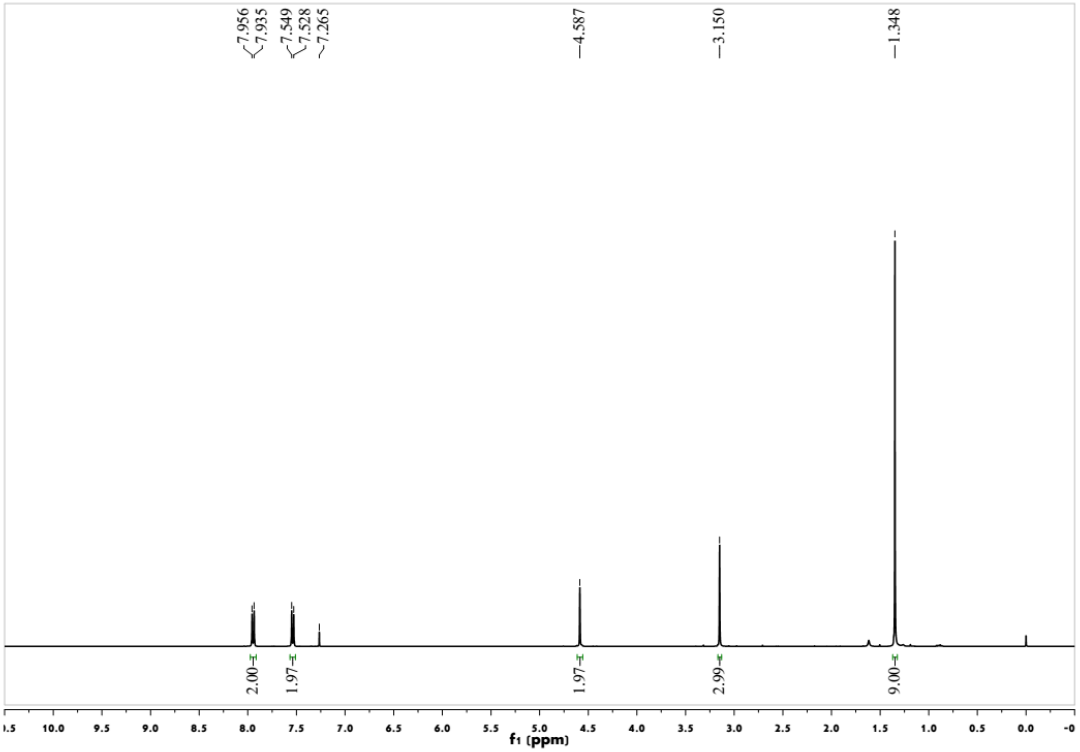
3f

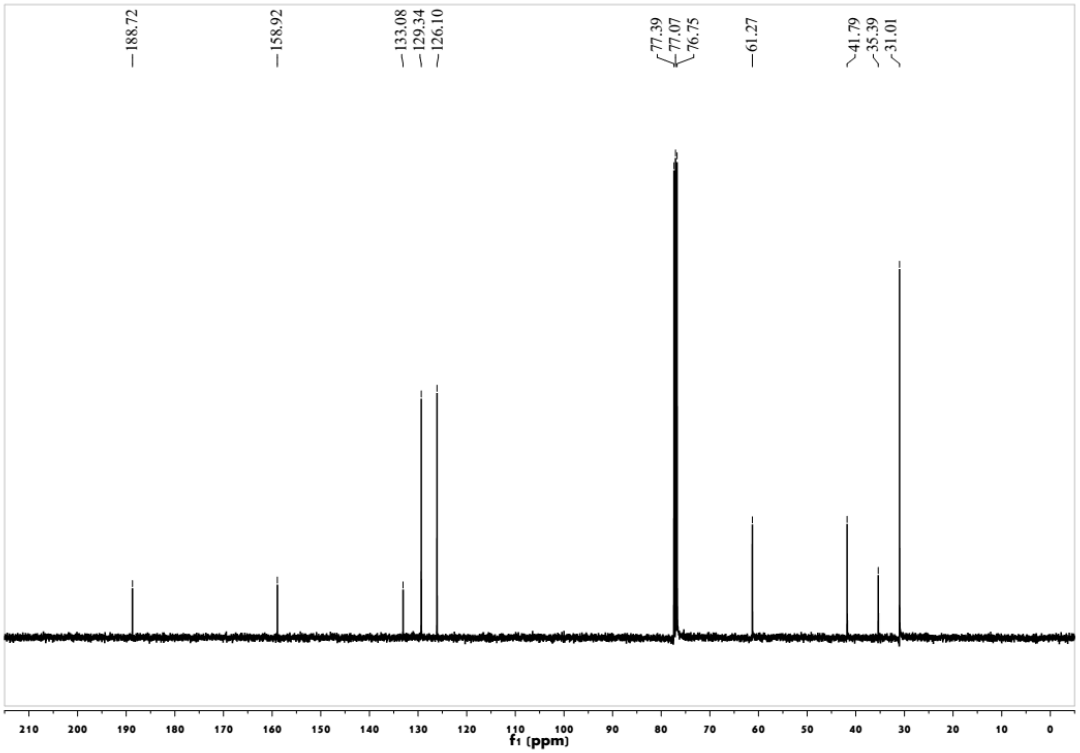

7.909
7.888
7.331
7.310
7.270
4.590
3.146
2.439
2.02
2.02
1.96
2.98
3.00
f1 (ppm)

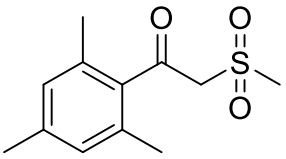

188.72
146.14
133.17
129.80
129.45
77.39
77.07
76.75
61.24
41.80
21.89
f1 (ppm)



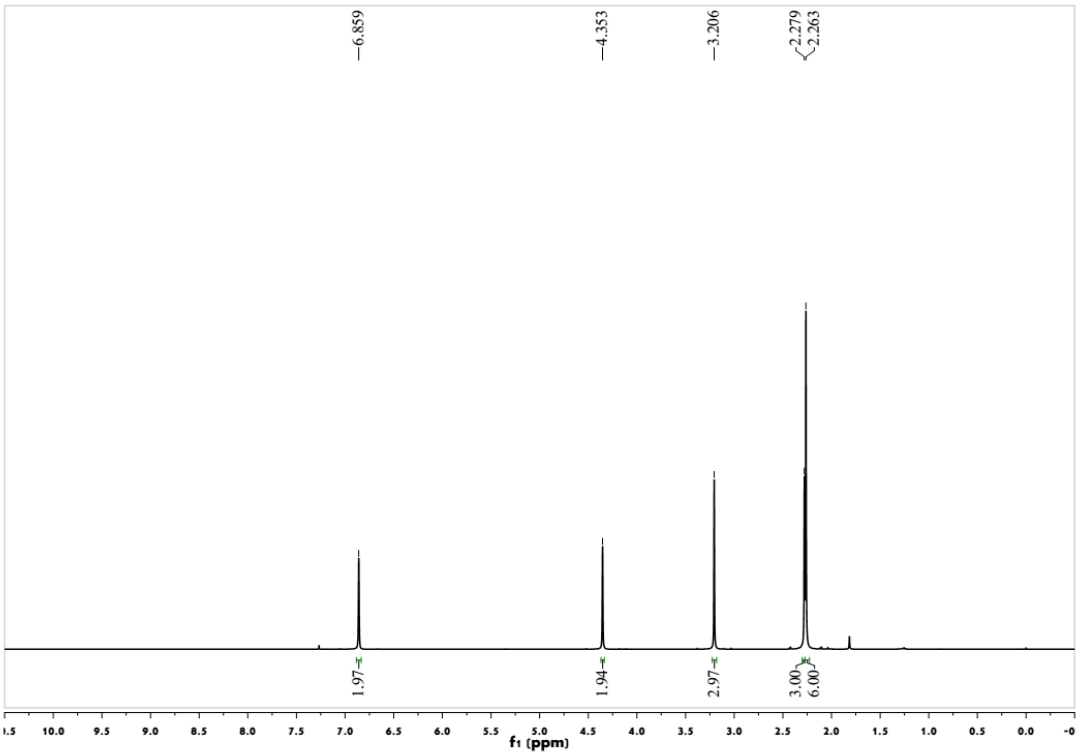
3g

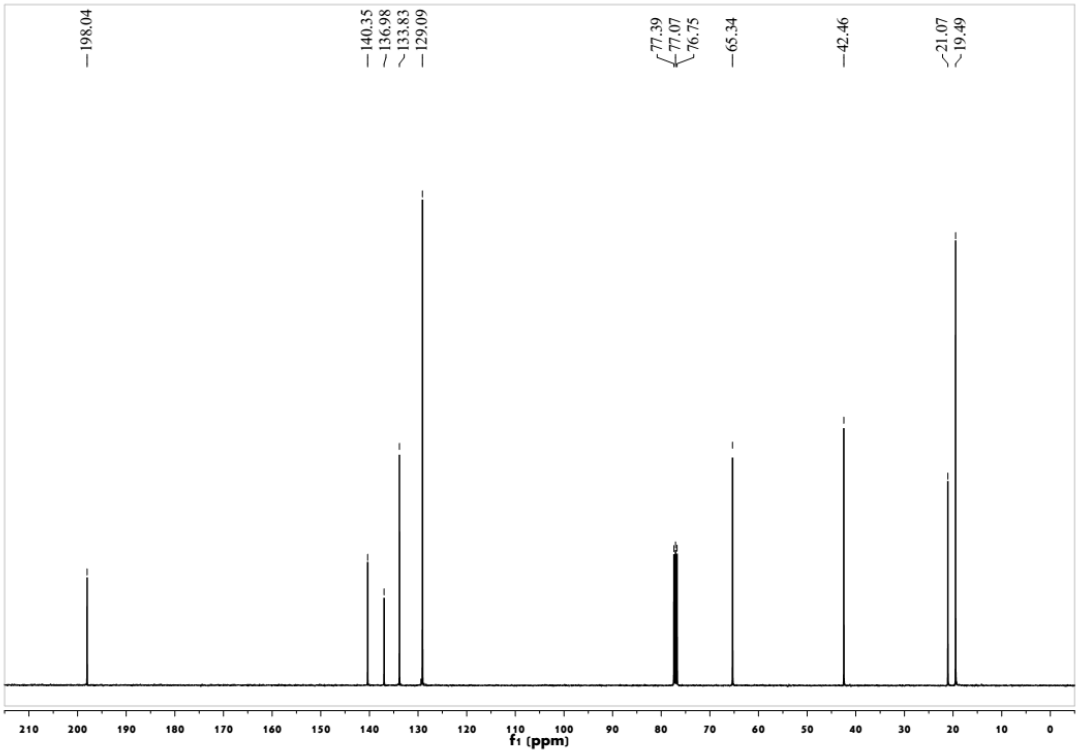

7.956
7.935
7.549
7.528
7.265
4.587
3.150
1.348
2.00
1.97
1.97
2.99
9.00
f1 (ppm)

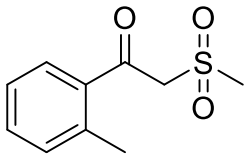

188.72
158.92
133.08
129.34
126.10
77.39
77.07
76.75
61.27
41.79
35.39
31.01
f1 (ppm)



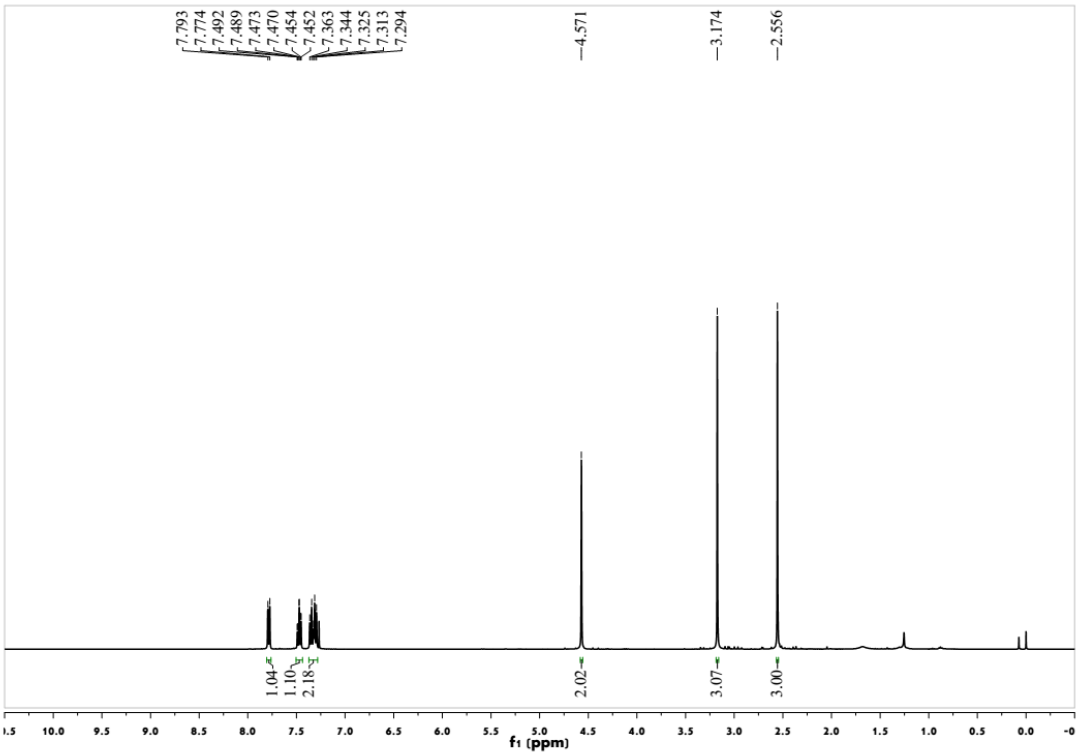
3h

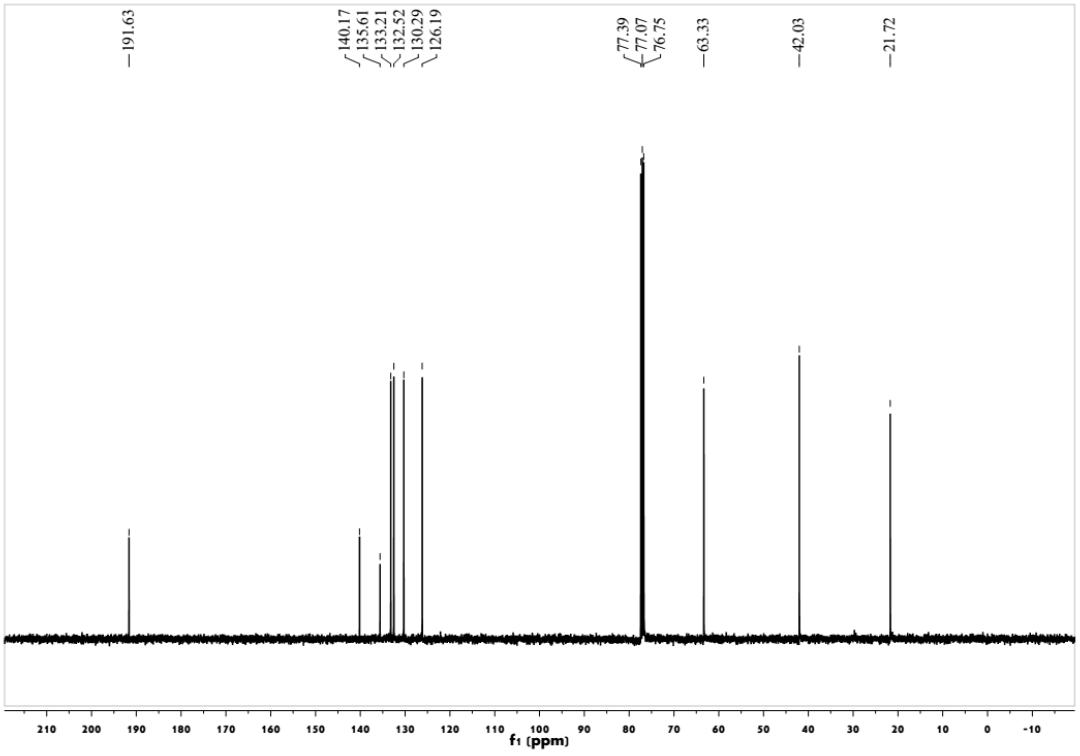

6.859
4.353
3.206
2.279
2.263
1.97
1.94
2.97
3.00
6.00
f1 (ppm)

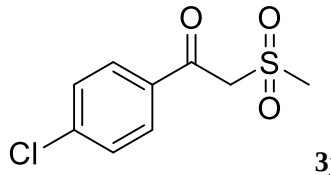

198.04
140.35
136.98
133.83
129.09
77.39
77.07
76.75
65.34
42.46
21.07
19.49
f1 (ppm)



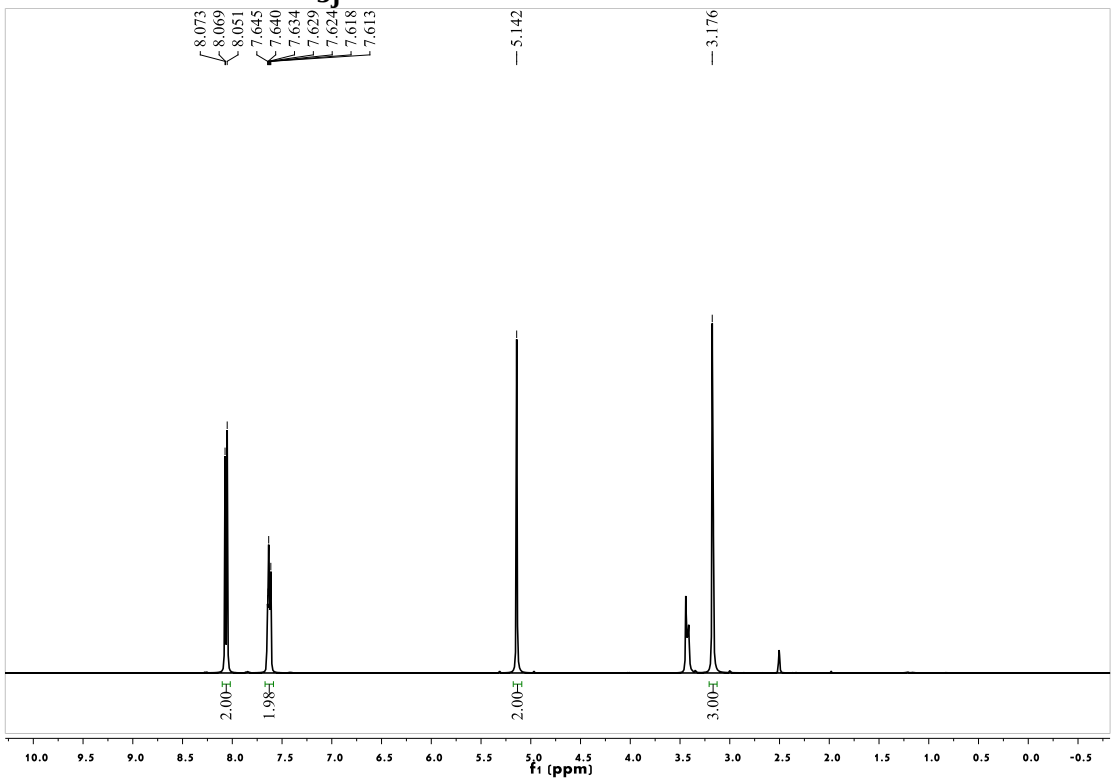
3i

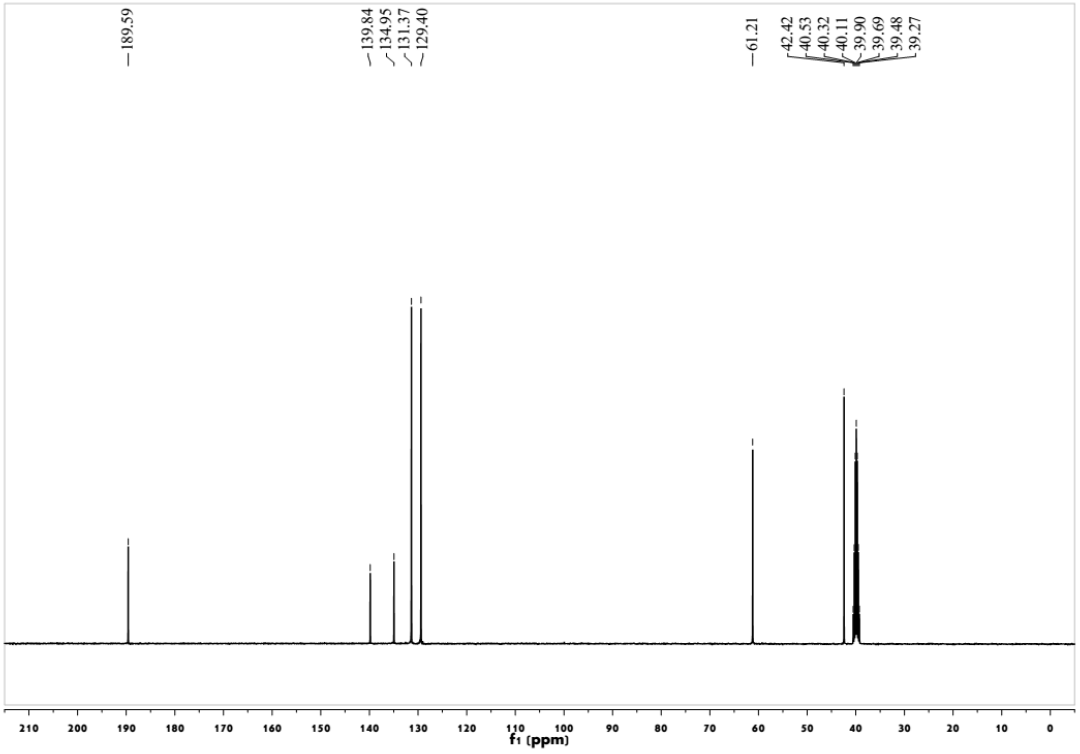

7.793
7.774
7.492
7.489
7.473
7.470
7.454
7.452
7.363
7.344
7.325
7.313
7.294
4.571
3.174
2.556
1.04
1.10
2.18
2.02
3.07
3.00
f1 (ppm)

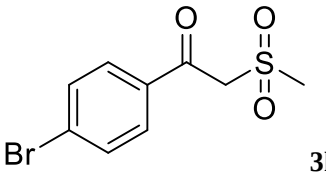

191.63
140.17
135.61
133.21
132.52
130.29
126.19
77.39
77.07
76.75
63.33
42.03
21.72
f1 (ppm)


O
O
S
O
O
Cl

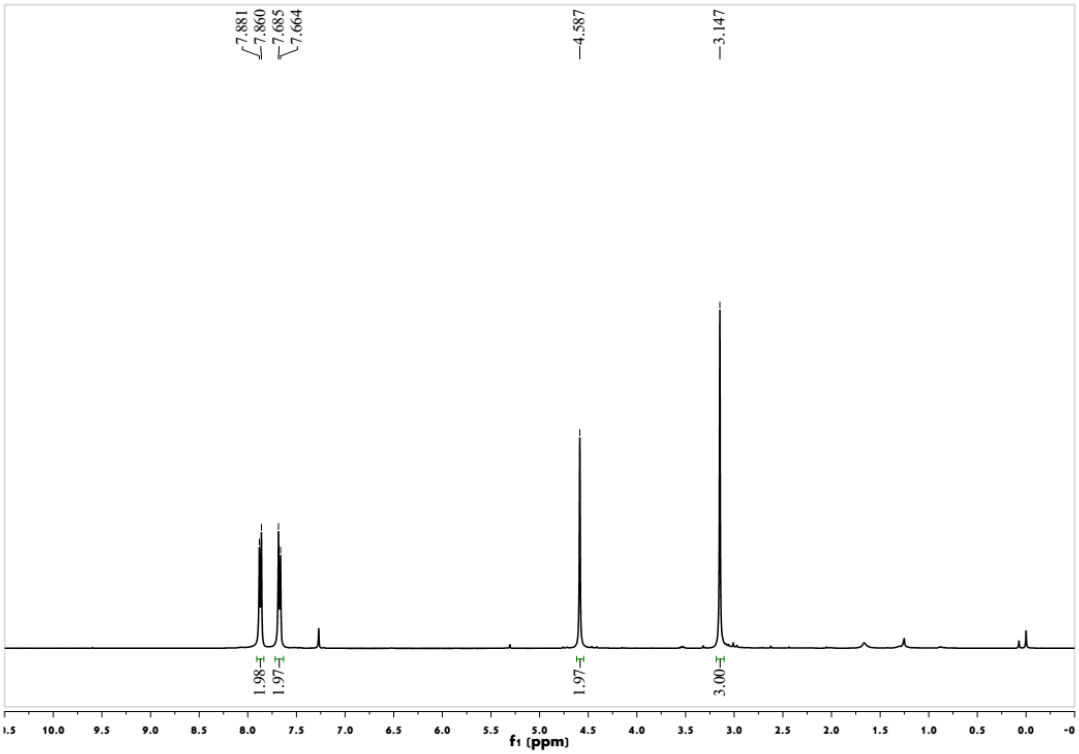
3j


8.073
8.069
8.051
7.645
7.640
7.634
7.629
7.624
7.618
7.613
5.142
3.176
2.00
1.98
2.00
3.00
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 -0.5
f1 (ppm)


189.59
139.84
134.95
131.37
129.40
61.21
42.42
40.53
40.32
40.11
39.90
39.69
39.48
39.27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
S
O
Br

3k


7.881
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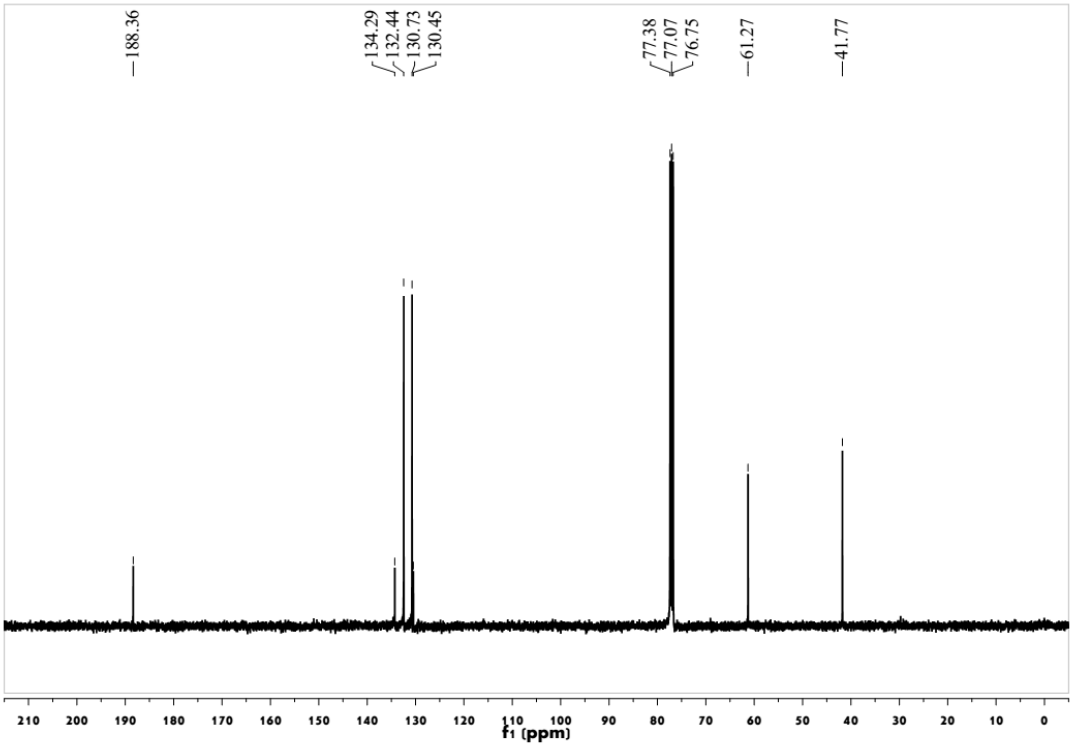
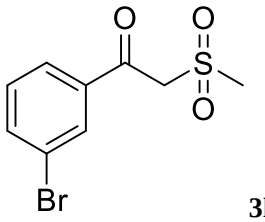
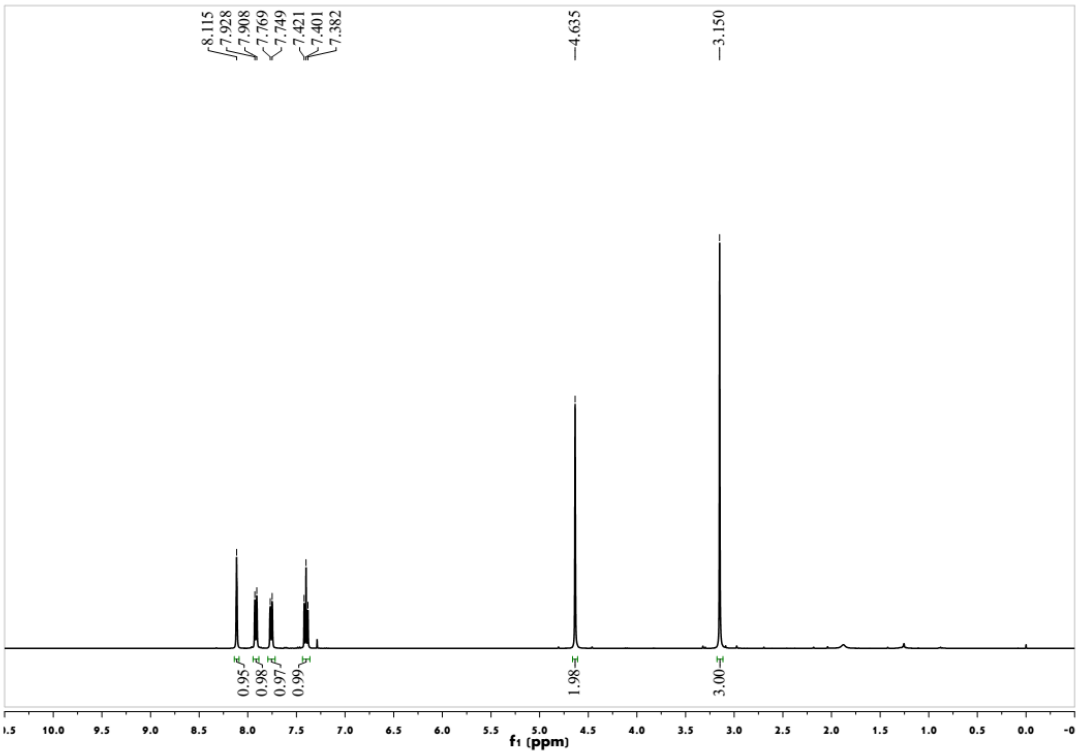
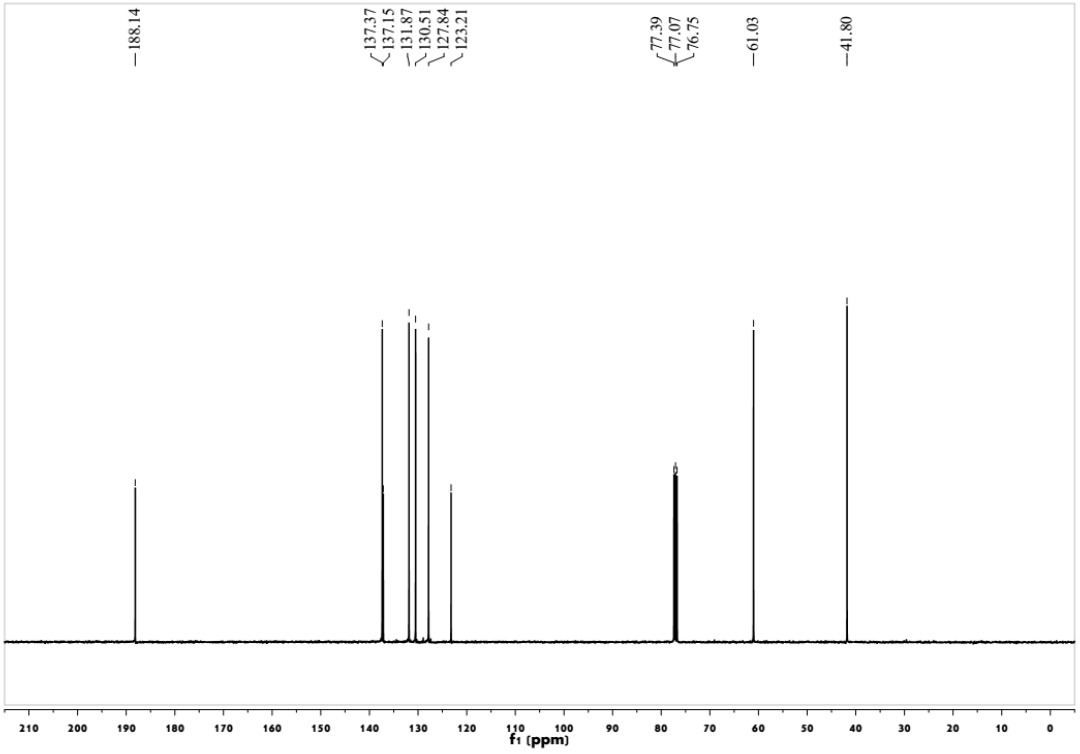
7.685
7.664
4.587
3.147
1.98
1.97
1.97
3.00
f1 (ppm)

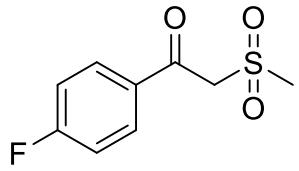

188.36
134.29
132.44
130.73
130.45
77.38
77.07
76.75
61.27
41.77
f1 (ppm)


O
O
S
O
Br

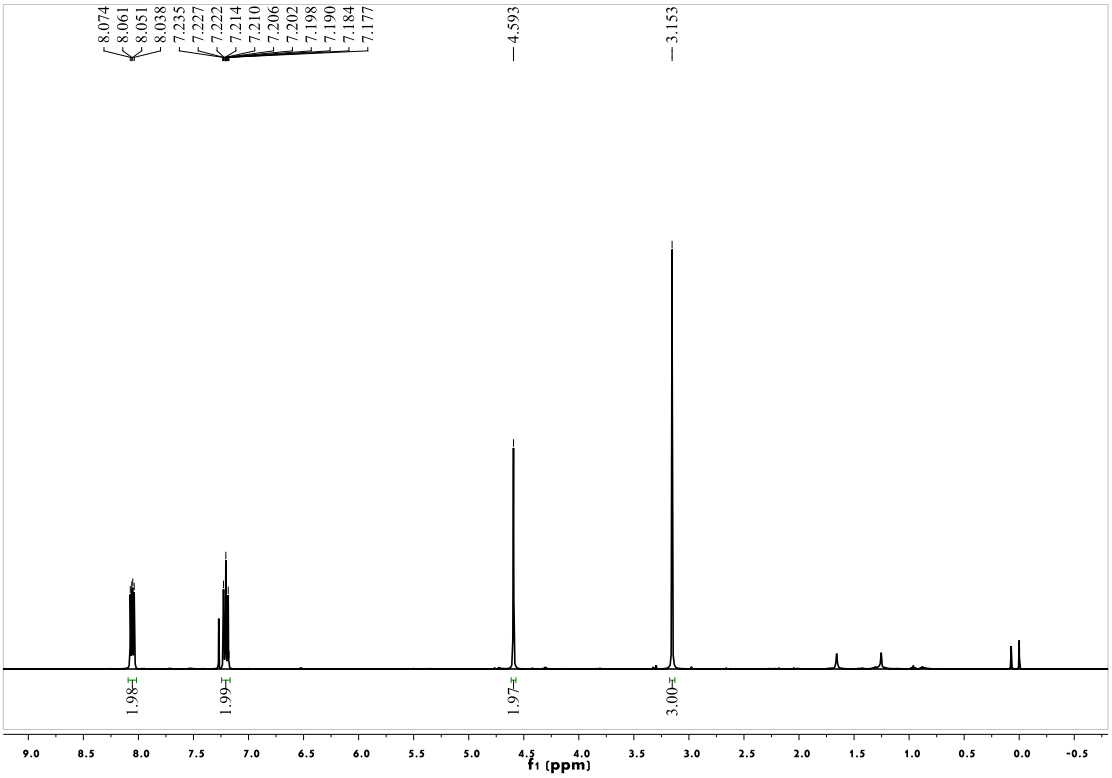
3l


8.115
7.928
7.908
7.769
7.749
7.421
7.401
7.382
4.635
3.150
0.95
0.98
0.97
0.99
1.98
3.00
f1 (ppm)


188.14
137.37
137.15
131.87
130.51
127.84
123.21
77.39
77.07
76.75
61.03
41.80
f1 (ppm)



3m


8.074
8.061
8.051
8.038
7.235
7.227
7.222
7.214
7.210
7.206
7.202
7.198
7.190
7.184
7.177
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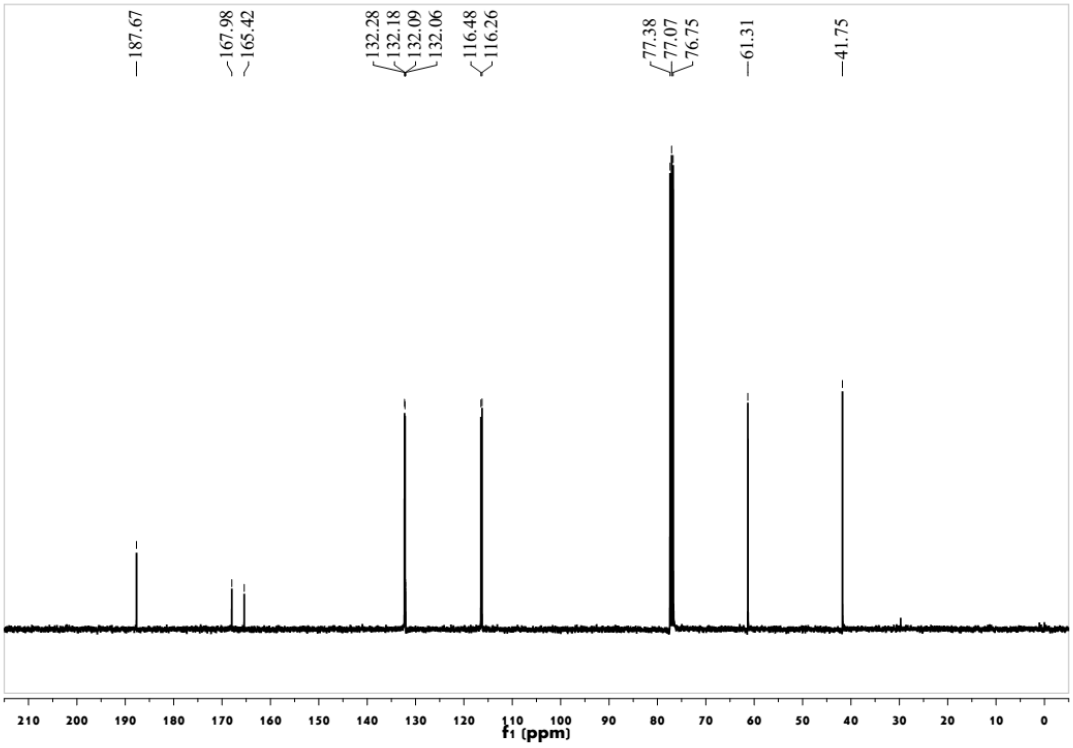
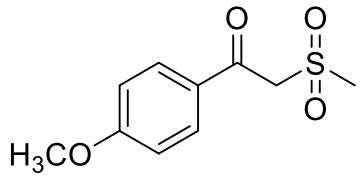
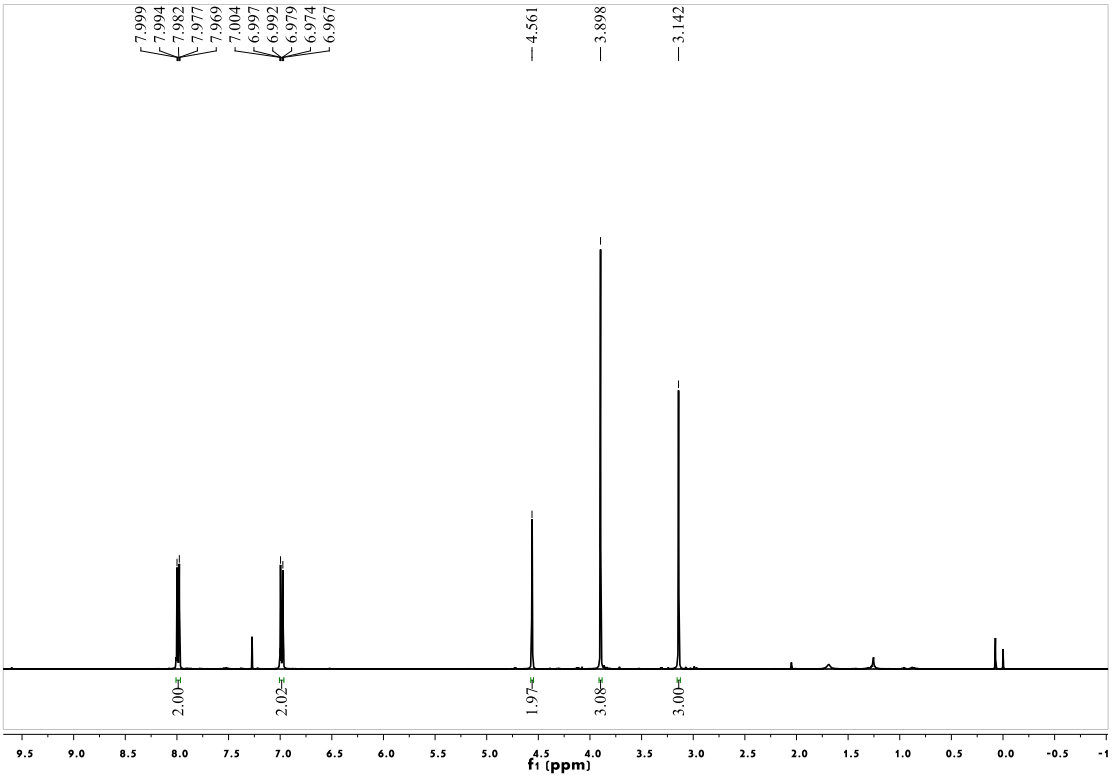
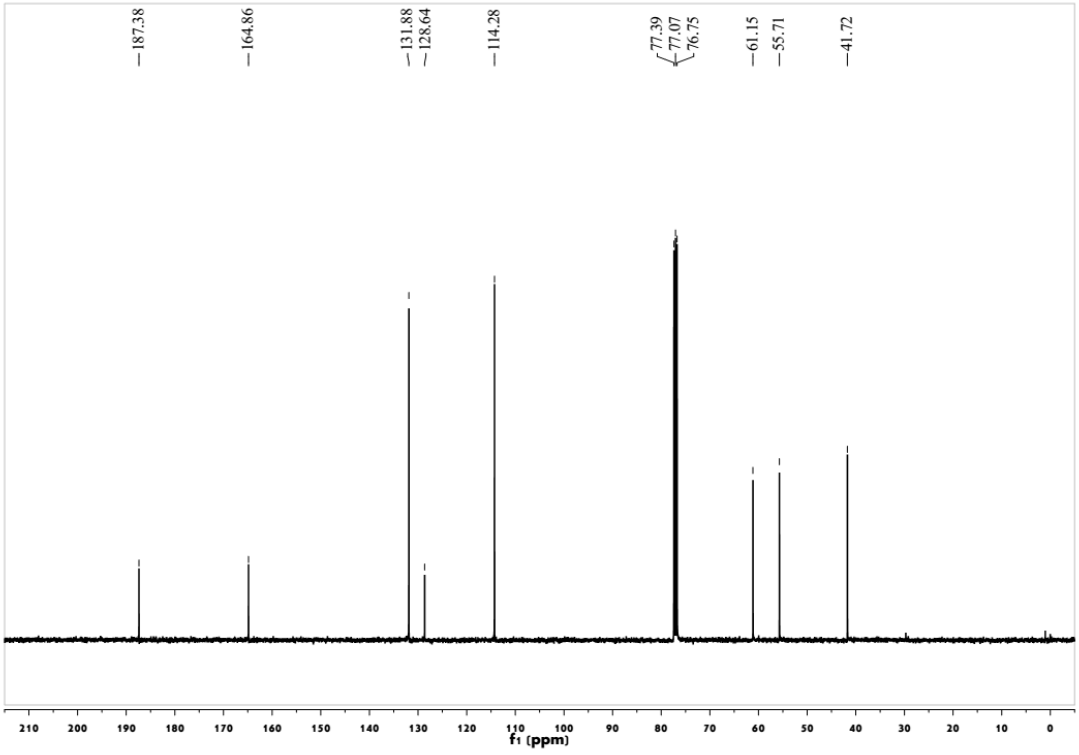
3.153
1.98
1.99
1.97
3.00
f1 (ppm)


187.67
167.98
165.42
132.28
132.18
132.09
132.06
116.48
116.26
77.38
77.07
76.75
61.31
41.75
f1 (ppm)


O
O
S
O
O
H3CO

3n


7.999
7.994
7.982
7.977
7.969
7.004
6.997
6.992
6.979
6.974
6.967
4.561
3.898
3.142
2.00
2.02
1.97
3.08
3.00
f1 (ppm)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164.86
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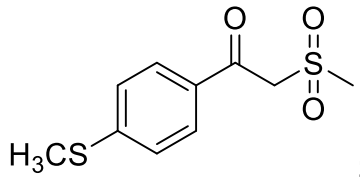
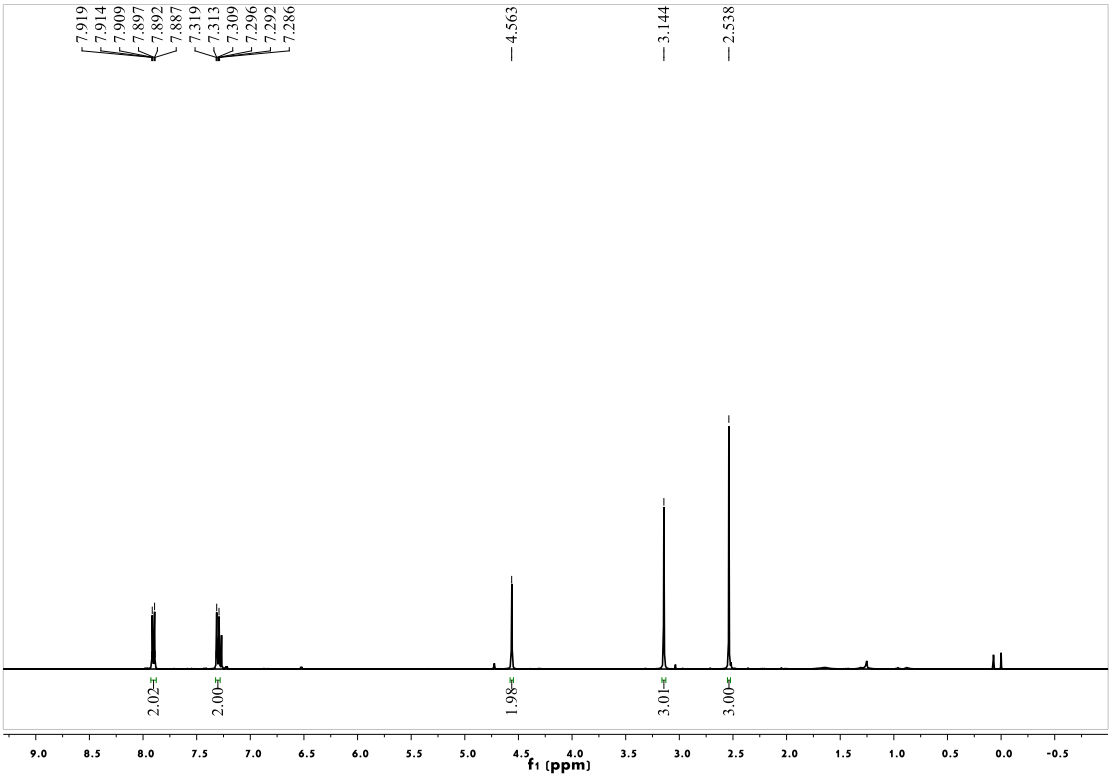
128.64
114.28
77.39
77.07
76.75
61.15
55.71
41.72
f1 (ppm)


O
O
S
O
H3CS

3o


7.919
7.914
7.909
7.897
7.892
7.887
7.319
7.313
7.309
7.296
7.292
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4.563
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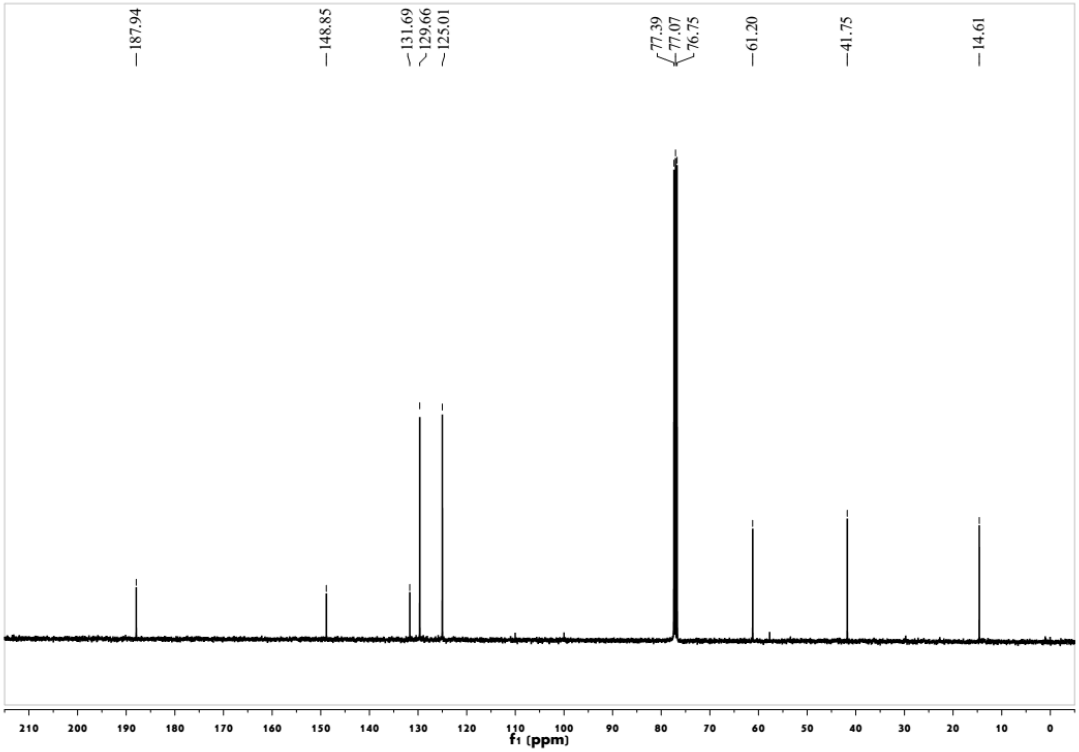
2.02
2.00
1.98
3.01
3.00
f1 (ppm)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148.85
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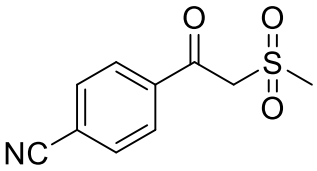
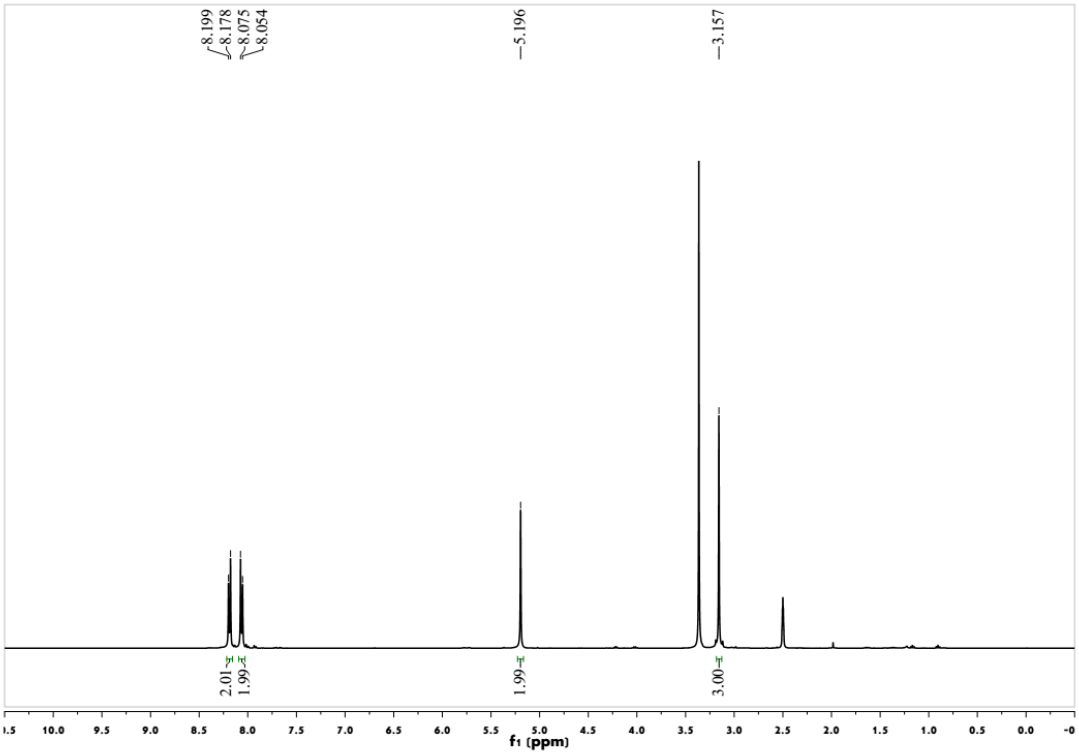
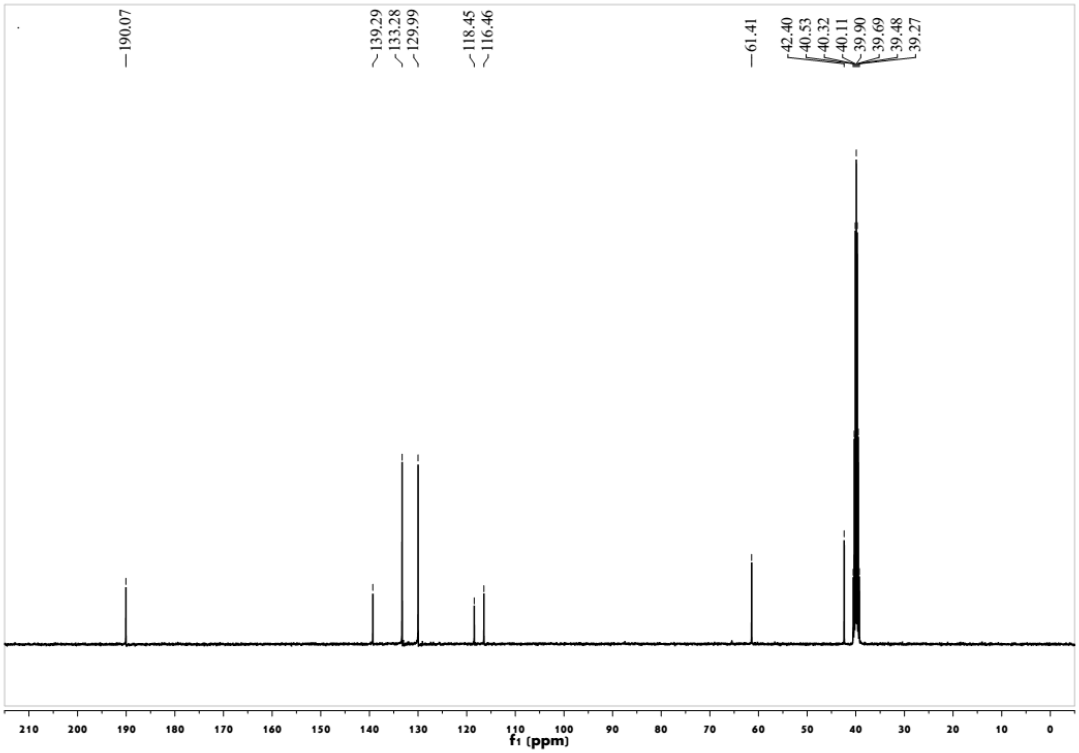
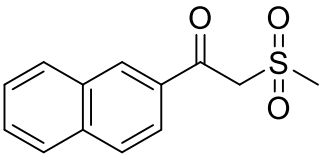
129.66
125.01
77.39
77.07
76.75
61.20
41.75
14.61
f1 (ppm)


O
O
S
O
O
NC

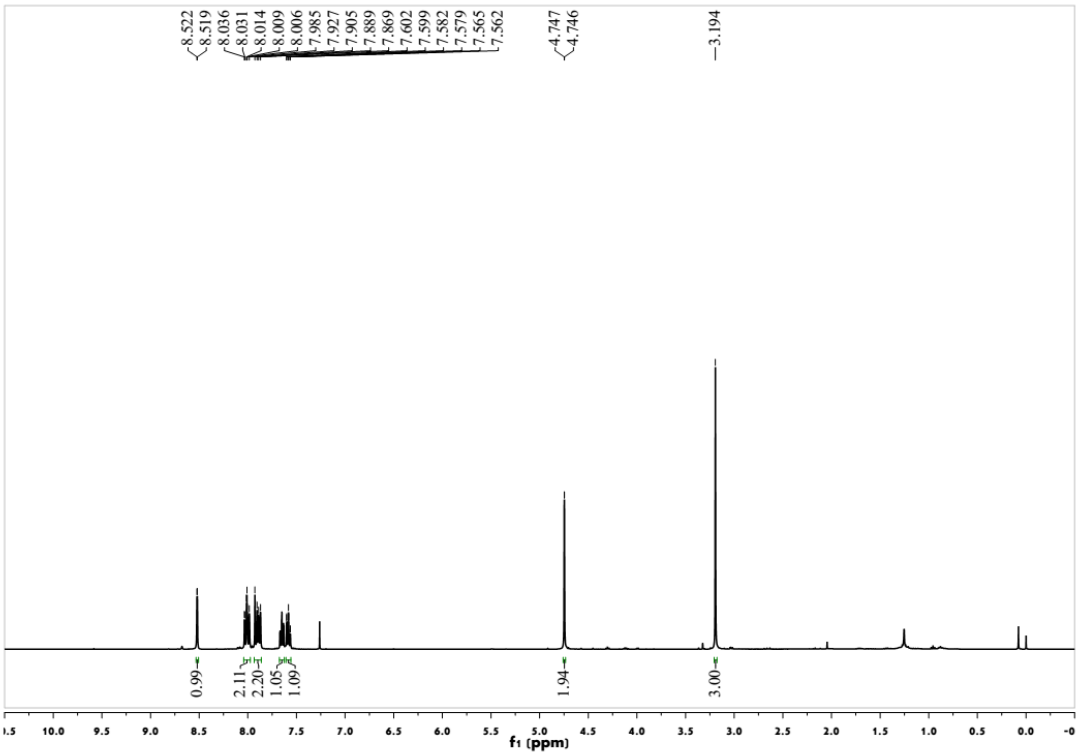
3p


8.199
8.178
8.075
8.054
5.196
3.157
2.01
1.99
1.99
3.00
f1 (ppm)


190.07
139.29
133.28
129.99
118.45
116.46
61.41
42.40
40.53
40.32
40.11
39.90
39.69
39.48
39.27
f1 (ppm)



3q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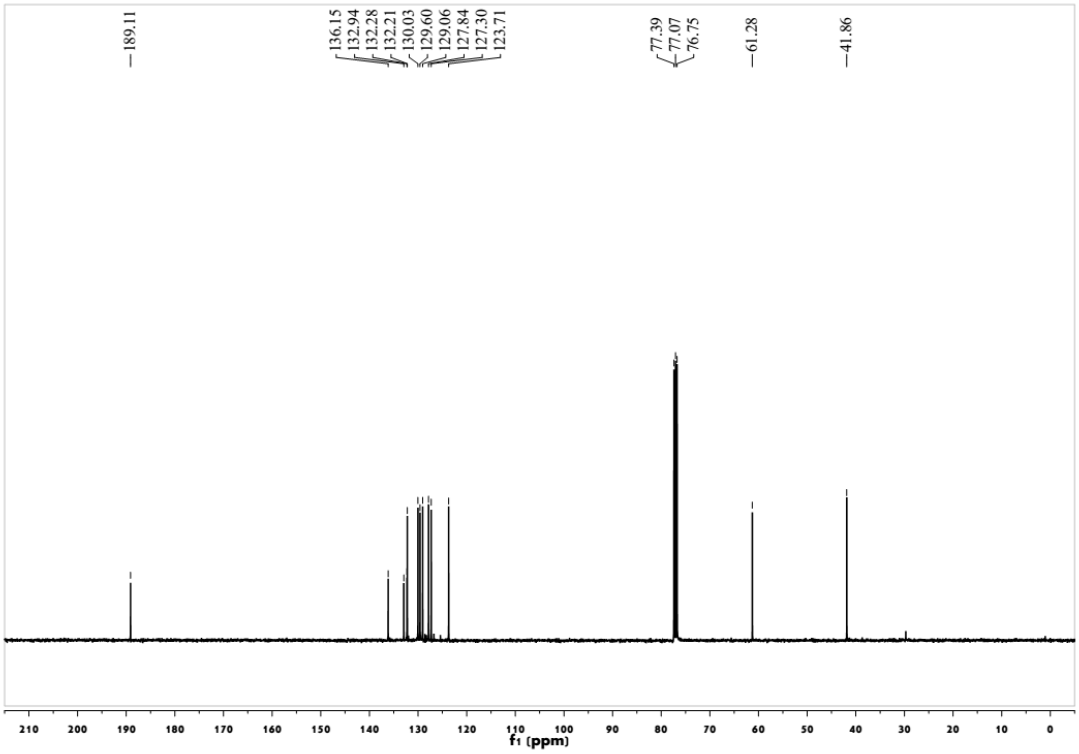
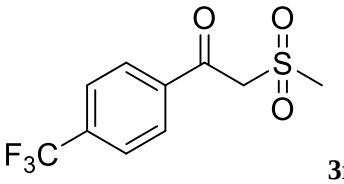
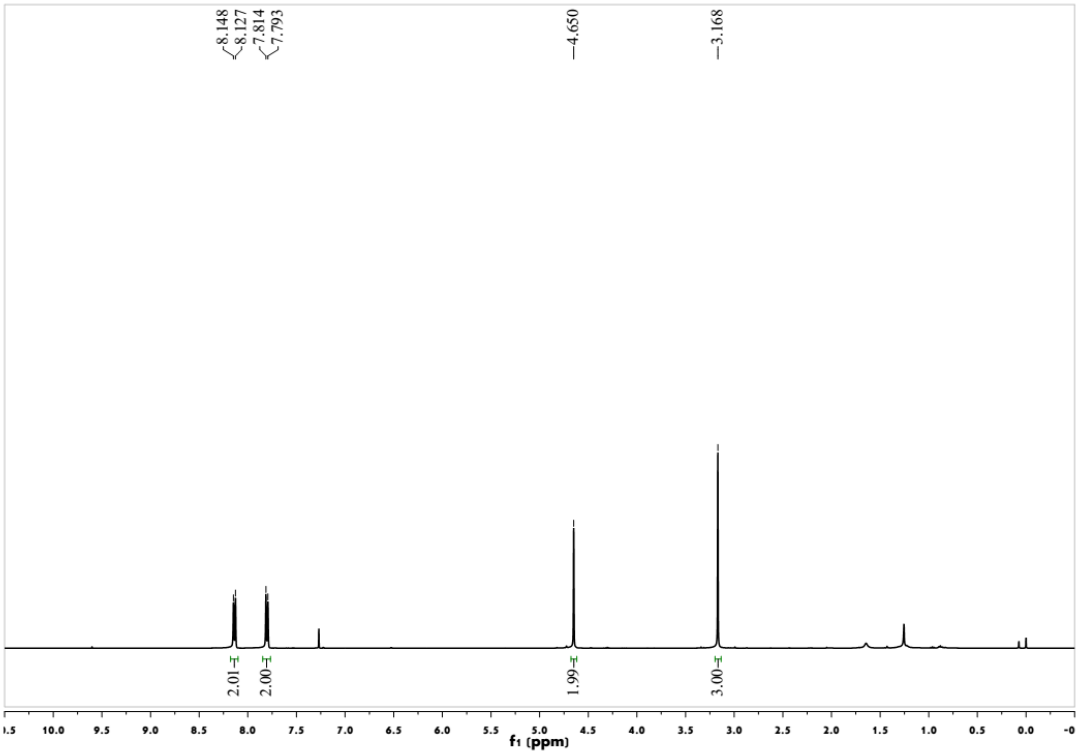
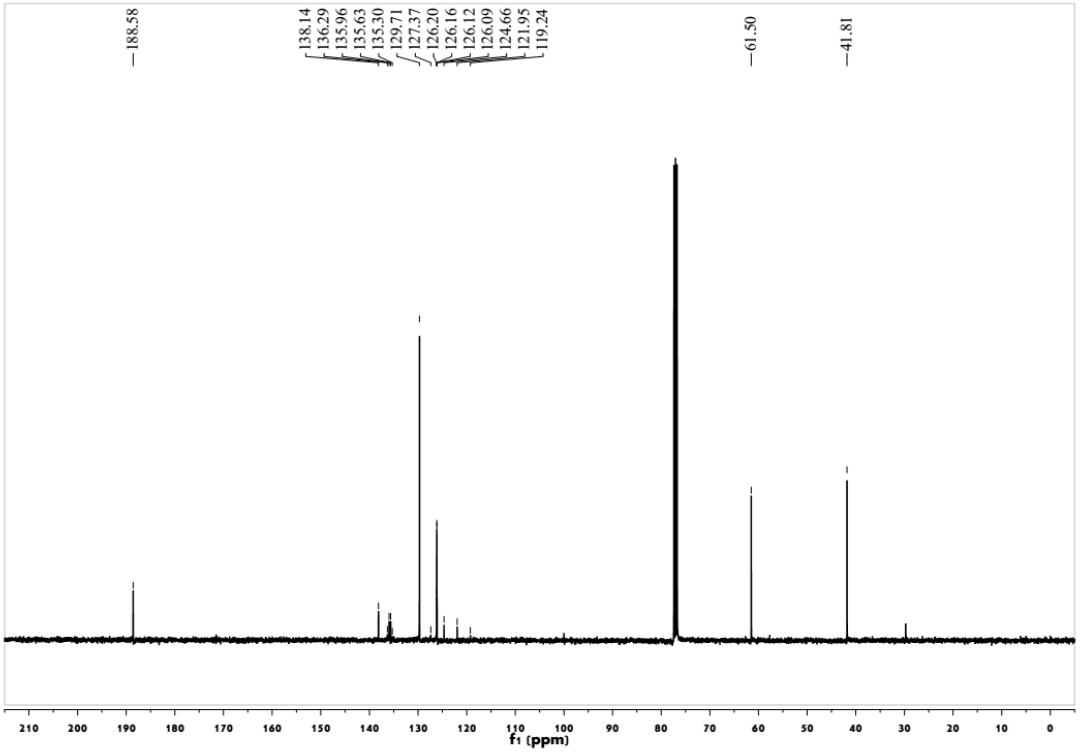
8.519
8.036
8.031
8.014
8.009
8.006
7.985
7.927
7.905
7.889
7.869
7.602
7.599
7.582
7.579
7.565
7.562
4.747
4.746
3.194
0.99
2.11
2.20
1.05
1.09
1.94
3.00
f1 (ppm)


189.11
136.15
132.94
132.28
132.21
130.03
129.60
129.06
127.84
127.30
123.71
77.39
77.07
76.75
61.28
41.86
f1 (ppm)

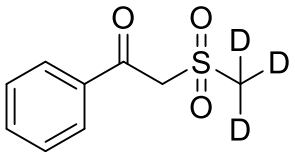


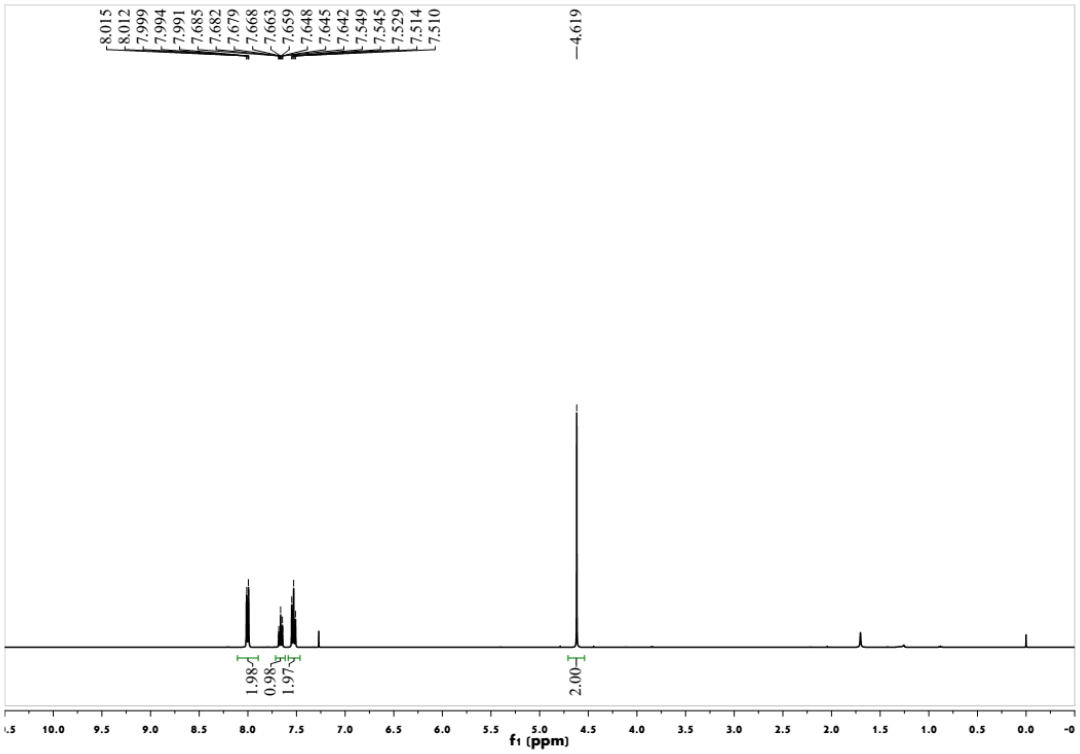
3r





3a Product from d^6-DMSO


O
O
S
O
D
D
D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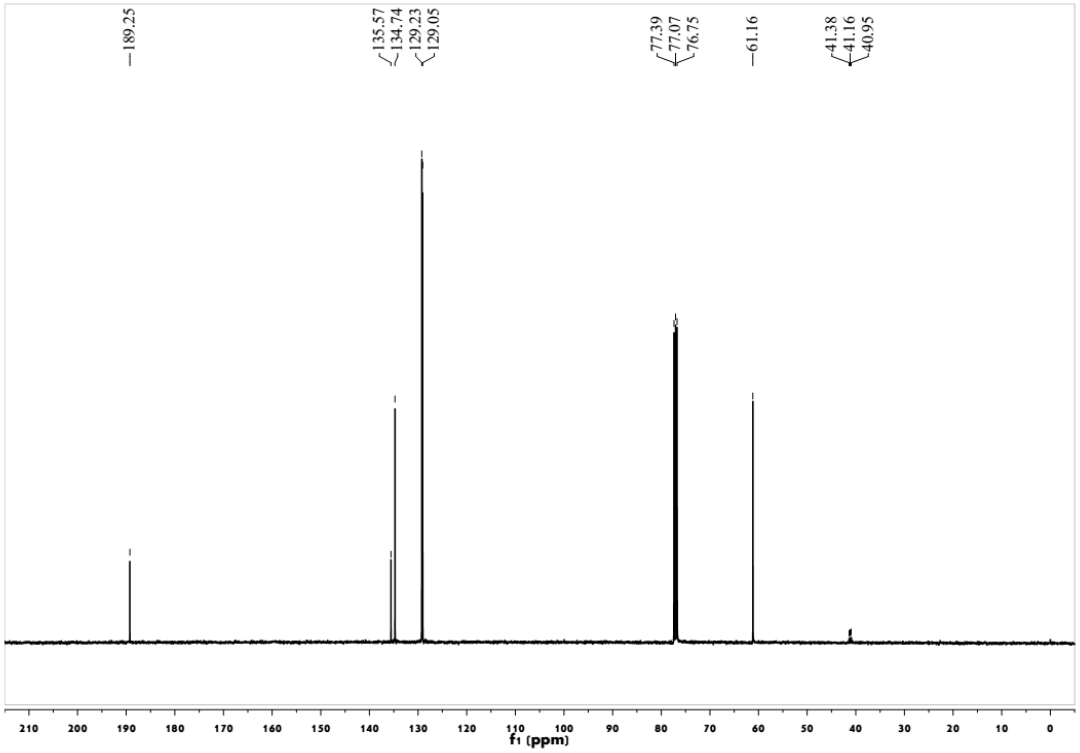
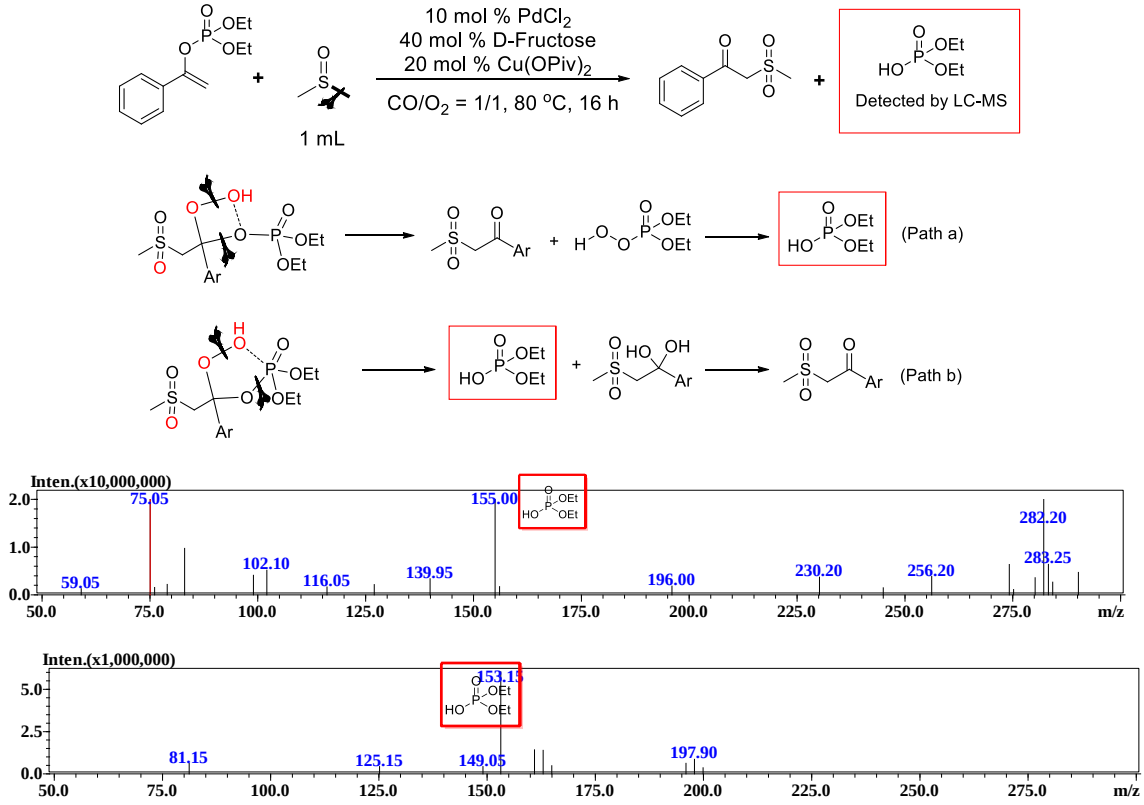
8.012
7.999
7.994
7.991
7.685
7.682
7.679
7.668
7.663
7.659
7.648
7.645
7.642
7.549
7.545
7.529
7.514
7.510
4.619
1.98
0.98
1.97
2.00
f1 (ppm)


189.25
135.57
134.74
129.23
129.05
77.39
77.07
76.75
61.16
41.38
41.16
40.95
f1 (ppm)

Identification of by-product of diethyl (1-phenylvinyl) phosphate 1e

For the substrate 1e, the diethyl hydrogen phosphate was observed (detected by LC-MS) after the completion of the reaction under the standard condition. Based on our proposed mechanism, there were two possible pathways to form the diethyl hydrogen phosphate (Scheme 1). Path a : the diethyl hydrogen phosphoroperoxoate was firstly formed via a four membered ring intermediate, then the diethyl hydrogen phosphoroperoxoate was decomposed to diethyl hydrogen phosphate. Path b: the diethyl hydrogen phosphate was formed directly via a five membered ring intermediate, and then the 2-(methylsulfonyl)-1-(naphthalen-2-yl)ethane-1,1-diol transformed to the corresponding product by intramolecular dehydration.



Scheme 1

Density functional theory (DFT) calculation to investigate the deprotonation of DMSO

Density functional theory (DFT) calculation was performed to investigate the deprotonation of DMSO. As shown in Figure 1, the coordination of DMSO to $Pd(OPiv)_2$ could form intermediate **2** with a free energy decrease of 0.1 kcal/mol. The C–H bond cleavage would occur through a concerted metalation-deprotonation (CMD) transition state 3-ts, generating a hydrogen bonding intermediate **4**.

The activation free energy for this process is found to be 28.3 kcal/mol. Considering that the reaction temperature is 80 ℃, this energy barrier is acceptable. Thus, intermediate **5** could be formed.

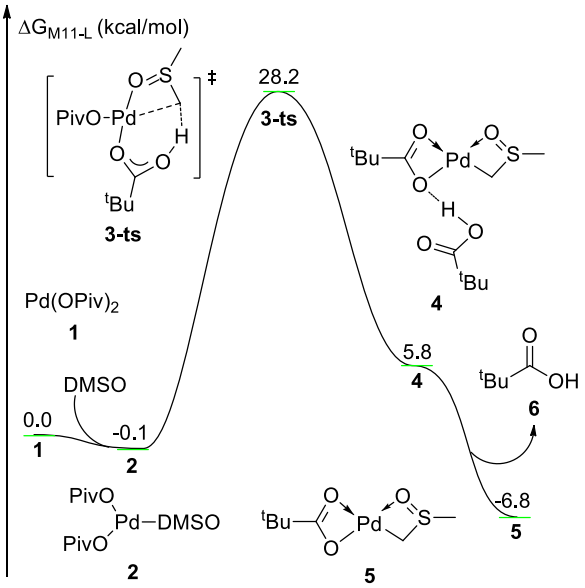


Figure 1. Free energy profile for the deprotonation of DMSO.

1. Complete reference for Gaussian 09

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, **2013**.

2. B3-LYP and M11-L absolute calculation energies, enthalpies, and free energies.

All the calculations were carried out by the GAUSSIAN 09 suit of computational programs.[1] Geometry optimizations were performed at the DFT level using the B3-LYP[2] hybrid functional with a mixed basis set of LANL08 for Pd and 6-31G(d) for other atoms. Harmonic vibrational frequency calculations were carried out at the same level to verify the characteristics of all of the optimized structure as minimals or transition states and to derive the thermochemical corrections for the enthalpies

and free energies. The solvent effects were considered by single-point energy calculations on the gas-phase stationary points. To obtain solvation-corrected relation free energies, we employed a self-consistent reaction field (SCRF) method using the SMD continuum solvation model[3] to do single-point energy calculations for all the studied species. DiMethylSulfoxide (ε = 46.826) was employed as the solvent, corresponding to the experimental conditions. To give more accurate energy information, the solvation single-point energy calculations were done at the M06-L level of theory by using a larger basis set, that LANL08 for Pd and 6-311++G(d,p) for the rest atoms.

Geometry	$E_{(elec\text{-}B3\text{-}LYP)}$[1]	$H_{(corr\text{-}B3\text{-}LYP)}$[2]	$G_{(corr\text{-}B3\text{-}LYP)}$[3]	$E_{(solv\text{-}M11\text{-}L)}$[4]	IF[5]
1	-820.805285	0.226903	0.292783	-820.9707827	
2	-1374.007957	0.297969	0.382445	-1374.220616	
3-ts	1373.949976	0.293284	0.376256	-1374.17084	-1233.4
4	-1373.995093	0.29651	0.382505	-1374.209695	
5	-1026.961039	0.164822	0.222593	-1027.107156	
6	-347.017538	0.115022	0.156654	-347.106015	
DMSO	-553.181334	0.051556	0.086483	-553.2301328	

[\1]The electronic energy calculated by B3-LYP in gas phase. [2]The thermal correction to enthalpy calculated by B3-LYP in gas phase. [3]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [4]The electronic energy calculated by M06-L in DiMethylSulfoxide solvent. [5]The B3-LYP calculated imaginary frequencies for the transition states.

3. B3-LYP geometries for all the optimized compounds and transition states.

1

C	2.44168500	0.01929800	0.00338400
O	1.76217100	1.10510500	0.00276700
O	1.75958500	-1.06740300	0.00250000
C	3.95838400	-0.00090000	0.00145200
C	4.42502500	-0.78930900	1.24744300
C	4.41824200	-0.73399400	-1.28097700
C	4.51108500	1.43360400	0.03062000
H	4.11249000	-0.29113800	2.17229100
H	4.01712200	-1.80413800	1.24801600
H	5.51888300	-0.85388200	1.25085000
H	4.09967300	-0.19608000	-2.18116300
H	5.51212700	-0.79708300	-1.29364000
H	4.01142000	-1.74844100	-1.32317200
H	5.60646700	1.40193500	0.02718500
H	4.18099400	2.00785200	-0.84043000
H	4.18568000	1.96971200	0.92749000
C	-2.44168500	0.01919700	-0.00609200
O	-1.76223200	1.10503000	-0.00573400
O	-1.75952100	-1.06747200	-0.00537500
C	-3.95836500	-0.00100000	-0.00032400
C	-4.42991300	-0.81736400	-1.22595400
C	-4.41323900	-0.70461800	1.30062300
C	-4.51117900	1.43252700	-0.05921900
H	-4.12160900	-0.34009000	-2.16317500
H	-4.02145700	-1.83173000	-1.20562500
H	-5.52375000	-0.88239200	-1.22323700
H	-4.09030700	-0.14663400	2.18693700
H	-5.50712900	-0.76631300	1.31935100
H	-4.00723000	-1.71833400	1.36401200
H	-5.60653800	1.40105400	-0.05106200
H	-4.17772900	2.02600900	0.79745900
H	-4.18916100	1.94826000	-0.96921400
Pd	-0.00000500	0.01901600	-0.00134500

2

C	-2.17902900	-0.89801100	0.28028700
C	-3.27514800	-1.97929600	0.11165100
C	-3.93615700	-1.83139000	-1.27451400
C	-2.59488900	-3.36296700	0.21573700
C	-4.32898000	-1.82891500	1.21955800
H	-4.42096600	-0.85281000	-1.38097400
H	-3.19918400	-1.93387600	-2.07528500

H	-4.70679700	-2.60070200	-1.40745300
H	-2.10726900	-3.49083600	1.18950400
H	-3.34266500	-4.15826000	0.10671000
H	-1.83791400	-3.48703500	-0.56388300
H	-5.09318200	-2.60890500	1.11535600
H	-3.87683000	-1.91489400	2.21159200
H	-4.82720900	-0.85485800	1.16730100
C	2.67697500	-0.37667000	0.01627100
O	1.74022500	-1.25037700	-0.00061000
O	2.33933800	0.83757900	-0.21825200
C	4.12797000	-0.75708100	0.26153300
C	4.86129600	-0.64633400	-1.09833500
C	4.74136600	0.24160100	1.26552300
C	4.22046700	-2.19461800	0.79985600
H	4.43918300	-1.34146200	-1.83276300
H	4.79086500	0.36827400	-1.50241200
H	5.92075900	-0.89399900	-0.96551500
H	4.24223700	0.18119700	2.23965600
H	5.80202300	0.00952200	1.41476500
H	4.65870000	1.26927300	0.90112000
H	5.27257000	-2.46148000	0.95246900
H	3.69903100	-2.29622600	1.75732000
H	3.77944900	-2.91178100	0.10185900
Pd	0.35194000	0.21510300	-0.48201600
O	-1.31337100	-0.88569000	-0.69096900
O	-2.15657100	-0.14044100	1.26210400
S	-1.18079700	3.08135400	-0.12930700
O	-0.54715500	2.00180100	-1.05968900
C	-0.63455400	2.72023100	1.56819900
H	0.44988200	2.84852500	1.59245700
H	-1.11397000	3.43972300	2.24008800
H	-0.92293300	1.68972700	1.80187100
C	-2.94362200	2.66370700	0.06276100
H	-3.40221400	3.44050300	0.68354500
H	-3.38147600	2.68472500	-0.93793300
H	-3.03244500	1.67475400	0.52039600

3-ts

S	0.39374800	3.41346400	0.06268000
O	1.31951400	2.36522400	-0.66001700
C	0.54582800	3.04662300	1.84542300
H	1.50679300	3.45367700	2.16900200
H	-0.26944900	3.54199600	2.38154300
H	0.53413900	1.96149400	1.98702700

Pd	0.04288800	0.71959500	-0.58681100
C	2.10246500	-0.88603900	0.29351600
O	1.78221400	-0.40261700	1.38032800
O	1.50366500	-0.61659800	-0.84541000
C	3.27631900	-1.88340900	0.13641700
C	2.73941300	-3.19838000	-0.46810400
C	4.32678900	-1.26538500	-0.81150700
C	3.90188100	-2.15135500	1.51399200
H	1.97749100	-3.64842700	0.17962400
H	2.29217900	-3.02657000	-1.45105700
H	3.55707700	-3.92163500	-0.57766500
H	4.71074600	-0.31884800	-0.41244200
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H	4.28044800	-1.22831600	1.96326600
H	3.16951200	-2.57822100	2.20588100
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O	-1.27577700	-0.82964300	-0.50986000
O	-2.74025000	0.59195300	0.40977800
C	-3.41603000	-1.71494600	0.18008600
C	-3.65590300	-1.89396400	1.69744600
C	-4.73382100	-1.30044400	-0.51071300
C	-2.88108300	-3.02021400	-0.42905800
H	-2.73083800	-2.17701800	2.21291000
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H	-4.39124600	-2.69004000	1.86154700
H	-4.59057600	-1.16365200	-1.58920600
H	-5.48591300	-2.08509200	-0.36938200
H	-5.12184000	-0.36686700	-0.09402400
H	-3.61965800	-3.81818500	-0.28925400
H	-2.69049900	-2.91269600	-1.50131900
H	-1.94530300	-3.32815800	0.04581700
C	-1.24721200	2.66737300	-0.28186500
H	-1.78608800	1.47565100	0.06419000
H	-1.95255500	3.15241000	0.40574300
H	-1.50956100	2.96522300	-1.30066400

4

S	-3.16345600	-2.21251100	-0.39019400
O	-3.44744600	-0.73483200	-0.91916200
C	-4.49504000	-2.50231300	0.81172400
H	-5.43981400	-2.52990400	0.26315200
H	-4.31818000	-3.46536300	1.30112100

H	-4.50342700	-1.68416300	1.53680300
C	-1.77680800	-1.75448800	0.66092000
H	-0.88331300	-2.33599700	0.42953500
H	-2.03501100	-1.76569200	1.72241900
Pd	-1.74377200	0.13558100	-0.09034200
C	-0.28214300	2.16504900	0.04674100
O	-0.05953800	1.05157700	0.68330200
O	-1.32555900	2.22179500	-0.66069600
C	0.69023300	3.33269300	0.14137100
C	1.46612500	3.38105900	-1.19936000
C	-0.12503600	4.63016400	0.32408300
C	1.67495500	3.14189200	1.30767800
H	2.05391300	2.46876900	-1.34076100
H	0.78015300	3.50153900	-2.04407500
H	2.15454700	4.23430600	-1.18832000
H	-0.67588600	4.62432400	1.27217400
H	0.55341100	5.49087800	0.33246000
H	-0.84534200	4.76101100	-0.48773200
H	2.33469800	4.01508600	1.37006300
H	1.15113400	3.04291200	2.26489200
H	2.29889600	2.25723200	1.15708100
C	2.93698400	-0.76124300	-0.01046800
O	3.20504200	0.31798100	-0.50596200
O	1.80612800	-0.98284600	0.68550800
H	1.26947500	-0.15049400	0.68981400
C	3.83268200	-2.00327000	-0.09170200
C	4.24538200	-2.40904700	1.34160900
C	3.04049400	-3.15495300	-0.74974300
C	5.07770400	-1.67124900	-0.92788700
H	4.80606200	-1.60594200	1.83396200
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H	4.89005800	-3.29517600	1.30501800
H	2.71515800	-2.88498000	-1.76143600
H	3.67565200	-4.04529800	-0.82800400
H	2.15492200	-3.41472600	-0.16240000
H	5.73211200	-2.54871200	-0.98704700
H	4.80421500	-1.37375100	-1.94488100
H	5.64230900	-0.84566100	-0.48464200

5

S	3.35809000	-0.01649100	-0.42928000
O	2.35157400	-1.22293700	-0.17078300
C	4.30200300	0.10057500	1.11984300
H	4.90047900	-0.80862000	1.21648800

H	4.95694500	0.97579800	1.06361700
H	3.60160900	0.18154600	1.95539500
C	2.13286200	1.28758600	-0.23040200
H	2.09504500	1.93150800	-1.11068500
H	2.26358400	1.84488600	0.70020500
Pd	0.61007500	-0.06175400	-0.10900300
C	-1.86845500	-0.04225100	0.03573000
O	-1.14359500	1.02091800	-0.04059800
O	-1.27788600	-1.16512200	0.04094400
C	-3.38936200	0.05092300	0.10277200
C	-3.95101000	-0.61756700	-1.17375200
C	-3.86257000	-0.73227400	1.34725400
C	-3.84646000	1.51625000	0.18305700
H	-3.63101300	-0.08090600	-2.07459600
H	-3.61259100	-1.65473200	-1.25300600
H	-5.04698000	-0.60845000	-1.14571300
H	-3.48304400	-0.27703400	2.26963300
H	-4.95787600	-0.72853100	1.39446500
H	-3.51807500	-1.76946400	1.31080700
H	-4.94129000	1.55943200	0.22524600
H	-3.44954500	2.00963200	1.07607100
H	-3.51292000	2.08714500	-0.68879400

6

C	0.94423500	0.18583300	0.00002100
O	1.52846000	1.24782100	0.00002400
O	1.61716900	-0.99610300	0.00001000
H	2.56412200	-0.76010900	0.00000000
C	-0.57276100	-0.01018800	0.00000900
C	-0.97344300	-0.80476800	-1.26381300
C	-0.97350400	-0.80489600	1.26371300
C	-1.25087600	1.36832800	0.00005100
H	-0.68863100	-0.26847800	-2.17647300
H	-0.49894400	-1.79004700	-1.28241500
H	-2.06055000	-0.94392500	-1.28152000
H	-0.68891400	-0.26861500	2.17644800
H	-2.06059300	-0.94423700	1.28126800
H	-0.49886000	-1.79010100	1.28234300
H	-2.34006700	1.24658900	0.00012600
H	-0.96719200	1.94966600	0.88265400
H	-0.96731800	1.94966700	-0.88259100

DMSO

S	0.00000000	0.24319300	-0.43966000
O	0.00000200	1.50743400	0.38731700
C	-1.36262900	-0.82193400	0.18003500
H	-2.29978100	-0.31350000	-0.05973100
H	-1.33200900	-1.79641600	-0.31745500
H	-1.27482800	-0.93374600	1.26499300
C	1.36262700	-0.82193600	0.18003500
H	1.33198700	-1.79642600	-0.31743600
H	2.29978000	-0.31351700	-0.05975900
H	1.27484900	-0.93372900	1.26499700

Reference:

1. H. Jiang, Y. Cheng, Y. Zhang and S. Yu, *Eur. J. Org. Chem.* **2013**, 5485-5492.