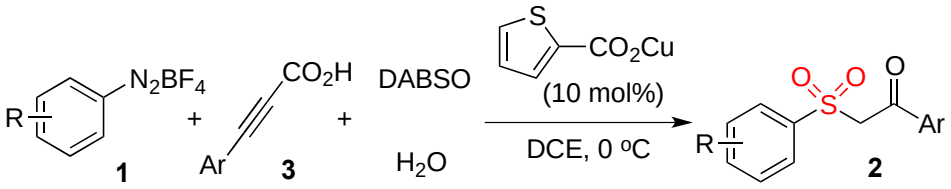
Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

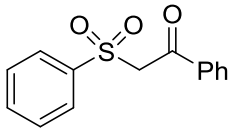
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. 1H and 13C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General experimental procedure for the copper-catalyzed reaction of aryldiazonium tetrafluoroborates **1**, 3-arylpropiolic acids **3**, sulfur dioxide, and water*

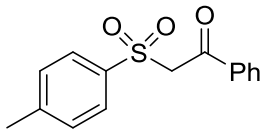


Water (0.2 mmol) was added to a solution of ((thiophene-2-carbonyl)oxy)copper (0.02 mmol), 3-arylpropiolic acid **3** (0.2 mmol), aryldiazonium tetrafluoroborate **1** (0.24 mmol) and DABCO•$(SO_2)_2$ (0.4 mmol) in DCE (1.5 mL). The mixture was stirred at 0 °C for about 2 hours. After the reaction was completed (indicated by TLC), the solvent was evaporated and the residue was purified directly by flash column chromatography (EtOAc/*n*-hexane, 1:4) to give the desired product **2**.



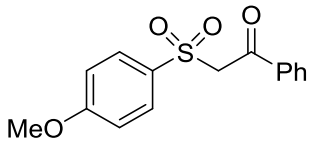
1-Phenyl-2-(phenylsulfonyl)ethan-1-one **(2a)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (m, 4H), 7.70 – 7.58 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 4.74 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 138.7, 135.7, 134.4, 134.2, 129.3, 129.2, 128.9, 128.6, 63.4.



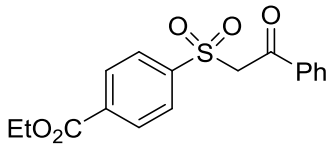
1-Phenyl-2-tosylethan-1-one **(2b)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.73 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 145.4, 135.7, 134.3, 129.8, 129.3, 128.8, 128.6, 63.6, 21.7.



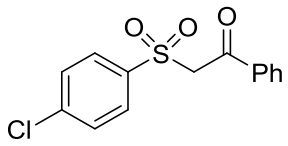
2-((4-Methoxyphenyl)sulfonyl)-1-phenylethan-1-one **(2c)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.72 (s, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3, 164.1, 135.8, 134.3, 130.9, 130.2, 129.3, 128.8, 114.3, 63.7, 55.7.



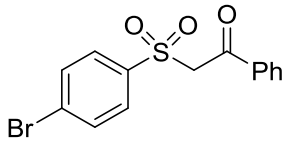
Ehyl 4-((2-oxo-2-phenylethyl)sulfonyl)benzoate **(2d)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.3 Hz, 2H), 7.96 (m, 4H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 4.79 (s, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 164.9, 142.2, 136.1, 135.5, 134.5, 130.2, 129.2, 128.9, 128.7, 63.2, 61.8, 14.2.



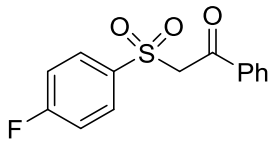
2-((4-Chlorophenyl)sulfonyl)-1-phenylethan-1-one **(2e)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.47 (m, 4H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 141.1, 137.0, 135.5, 134.6, 130.2, 129.5, 129.2, 128.9, 63.3.



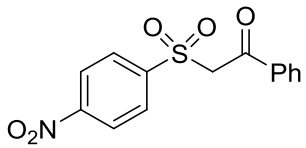
2-((4-Bromophenyl)sulfonyl)-1-phenylethan-1-one **(2f)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.81 – 7.59 (m, 5H), 7.51 (t, *J* = 7.8 Hz, 2H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 137.6, 135.5, 134.5, 132.5, 130.2, 129.8, 129.2, 128.9, 63.3.



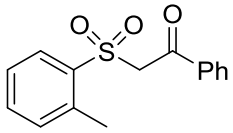
2-((4-Fluorophenyl)sulfonyl)-1-phenylethan-1-one **(2g)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 4H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 8.5 Hz, 2H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 166.1 (d, *J* = 257.4 Hz), 135.6, 134.5, 131.7, 129.2, 128.9, 116.5, 63.4.



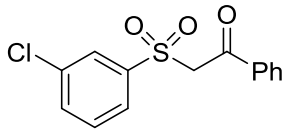
2-((4-Nitrophenyl)sulfonyl)-1-phenylethan-1-one **(2h)** [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 4.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6, 151.0, 144.0, 135.3, 134.8, 130.3, 129.2, 129.0, 124.3, 62.9.



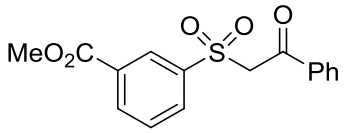
1-Phenyl-2-(*o*-tolylsulfonyl)ethan-1-one **(2i)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.1 Hz, 2H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 6.8 Hz, 1H), 7.50 (m, 3H), 7.41 – 7.32 (m, 2H), 4.77 (s, 2H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 138.3, 137.0, 135.8, 134.3, 134.2, 132.8, 130.6, 129.4, 128.8, 126.6, 62.7, 20.5.



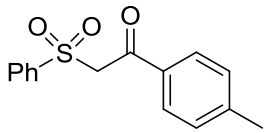
2-((3-Chlorophenyl)sulfonyl)-1-phenylethan-1-one **(2j)** [3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 3H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 3H), 4.76 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 140.3, 135.6, 135.5, 134.5, 134.4, 130.4, 129.2, 128.9, 128.7, 126.8, 63.2.



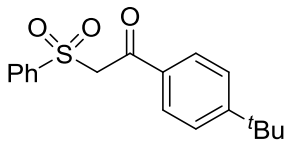
Methyl 3-((2-oxo-2-phenylethyl)sulfonyl)benzoate (2k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.65 (dd, *J* = 15.5, 7.7 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 4.79 (s, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8, 165.1, 139.3, 135.6, 135.0, 134.5, 132.7, 131.5, 129.7, 129.4, 129.2, 128.9, 63.1, 52.6.



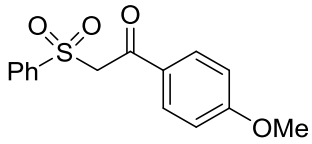
2-(Phenylsulfonyl)-1-(p-tolyl)ethan-1-one **(2l)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 5.9 Hz, 2H), 4.72 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 145.6, 138.8, 134.2, 133.3, 129.6, 129.4, 129.2, 128.6, 63.4, 21.8.



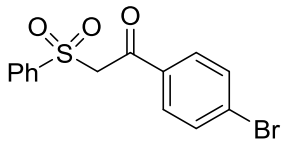
1-(4-(*tert*-Butyl)phenyl)-2-(phenylsulfonyl)ethan-1-one **(2m)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, 4H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 4.73 (s, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 158.4, 134.1, 133.2, 129.3, 129.1, 129.0, 128.6, 125.8, 63.4, 35.2, 30.9.



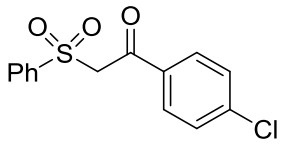
1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethan-1-one **(2n)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (m, 4H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.70 (s, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.2, 164.6, 138.8, 134.2, 131.9, 129.2, 128.9, 128.6, 114.1, 63.5, 55.7.



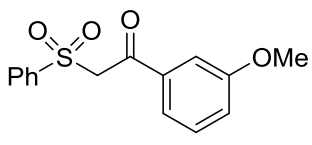
1-(4-Bromophenyl)-2-(phenylsulfonyl)ethan-1-one **(2o)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.4 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.1, 138.5, 134.4, 132.2, 130.8, 130.0, 129.3, 128.5, 63.6.



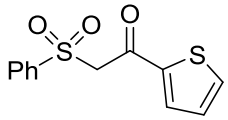
1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethan-1-one **(2p)** [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, *J* = 8.0 Hz, 4H), 7.69 (t, *J* = 7.1 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.8, 141.2, 138.6, 134.4, 134.1, 130.8, 129.3, 129.3, 128.6, 63.7.



1-(3-Methoxyphenyl)-2-(phenylsulfonyl)ethan-1-one **(2q)** [4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.32 (m, 5H), 7.15 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.74 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8, 159.9, 138.7, 137.0, 134.2, 129.8, 129.2, 128.56, 122.1, 121.2, 112.9, 63.5, 55.5.



2-(Phenylsulfonyl)-1-(thiophen-2-yl)ethan-1-one **(2r)** [5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.4 Hz, 2H), 7.81 (d, *J* = 3.8 Hz, 1H), 7.76 (d, *J* = 4.4 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.21 – 7.13 (m, 1H), 4.64 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.1, 143.1, 138.4, 136.4, 135.2, 134.3, 129.2, 128.7, 128.6, 64.6.

References

1. Lu, Q.; Zhang, J.; Peng, P.; Zhang, G.; Huang, Z.; Yi, H.; Millercd, T. J.; Lei, A. *Chem. Sci.* **2015**, 6, 4851.

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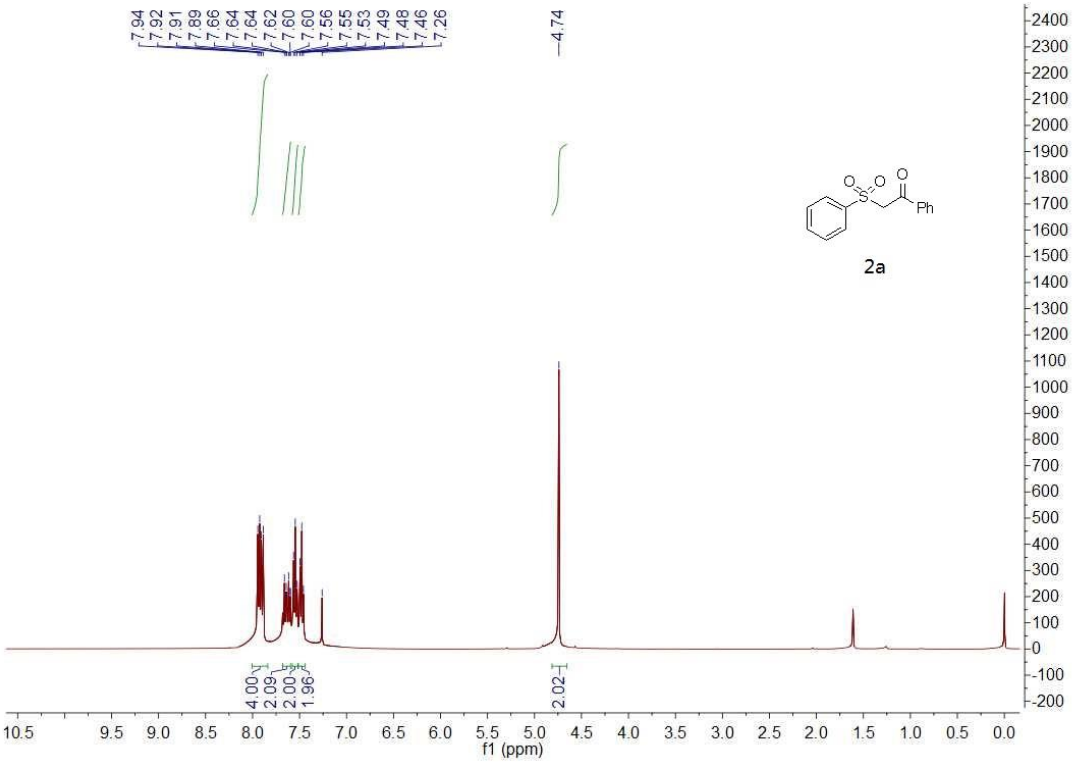
4. Tsui, G.; Glenadel, Q.; Lau, C.; Lautens, M.*Org. Lett.*, **2011**, 13, 208.

5. Xuan, J.; Feng, Z.; Chen, J.; Lu, L.; Xiao, W. *Chem. Eur. J.* **2014**, 20, 3045.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7.64
7.62
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7.60
7.56
7.55
7.53
7.49
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7.26
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4.00
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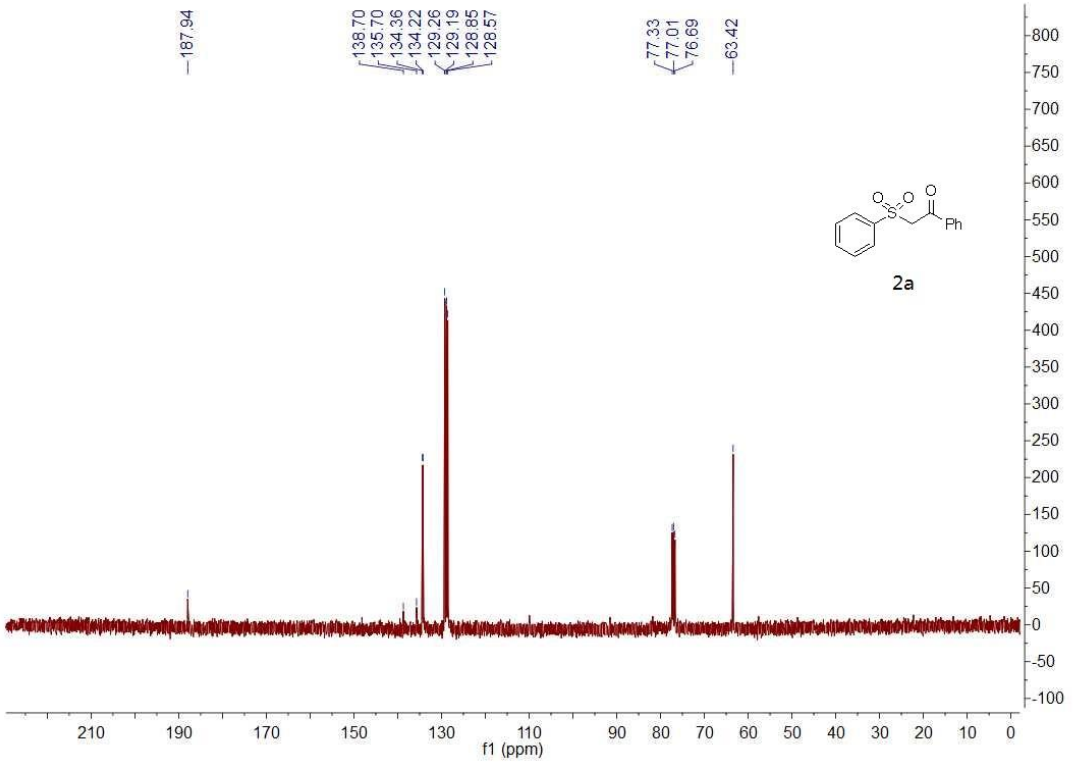
2.00
1.96
2.02
f1 (ppm)
2a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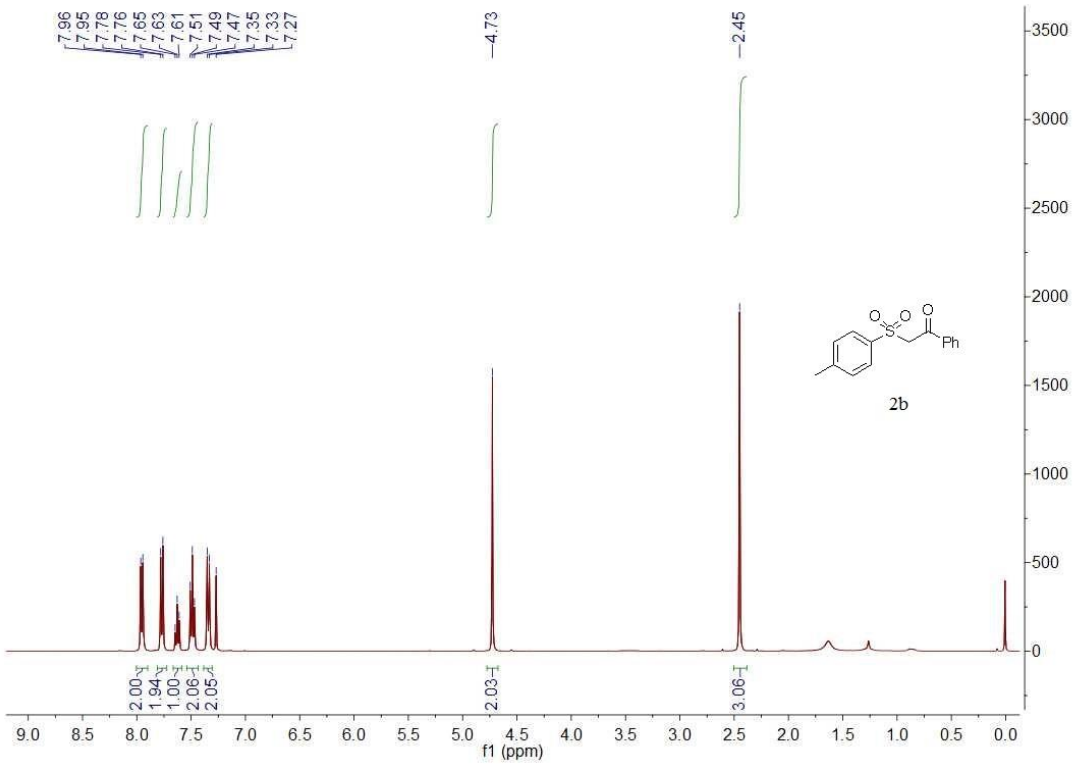
f1 (ppm)
2a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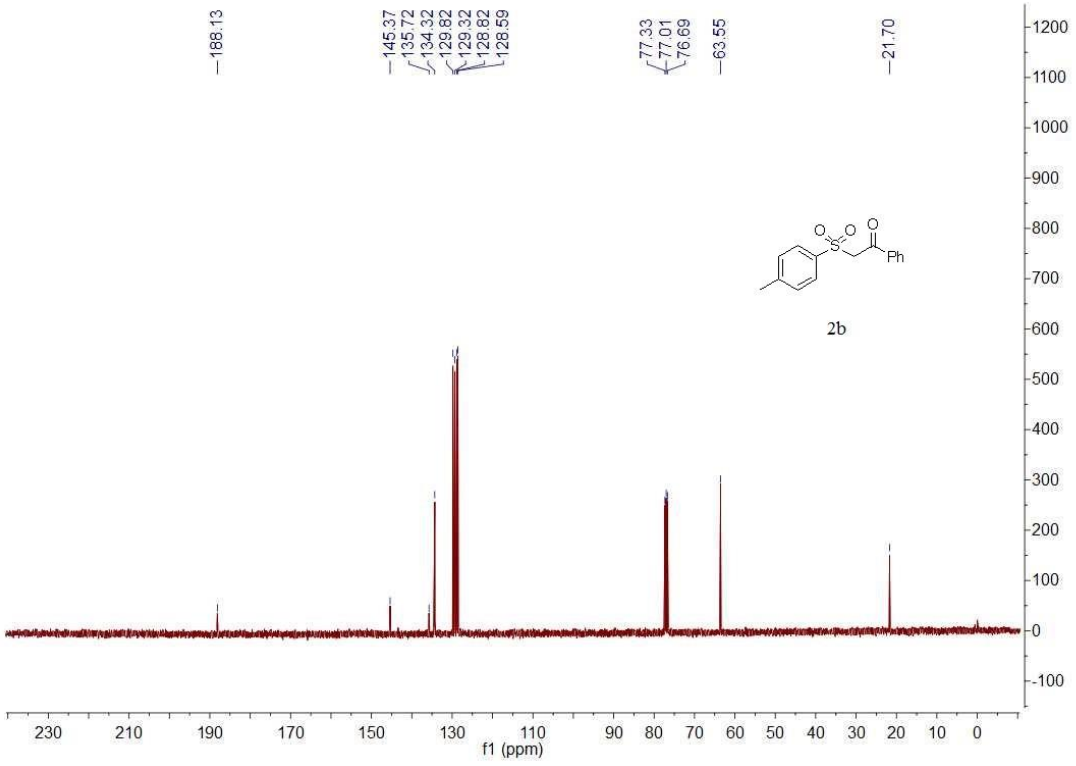
3.06
f1 (ppm)
2b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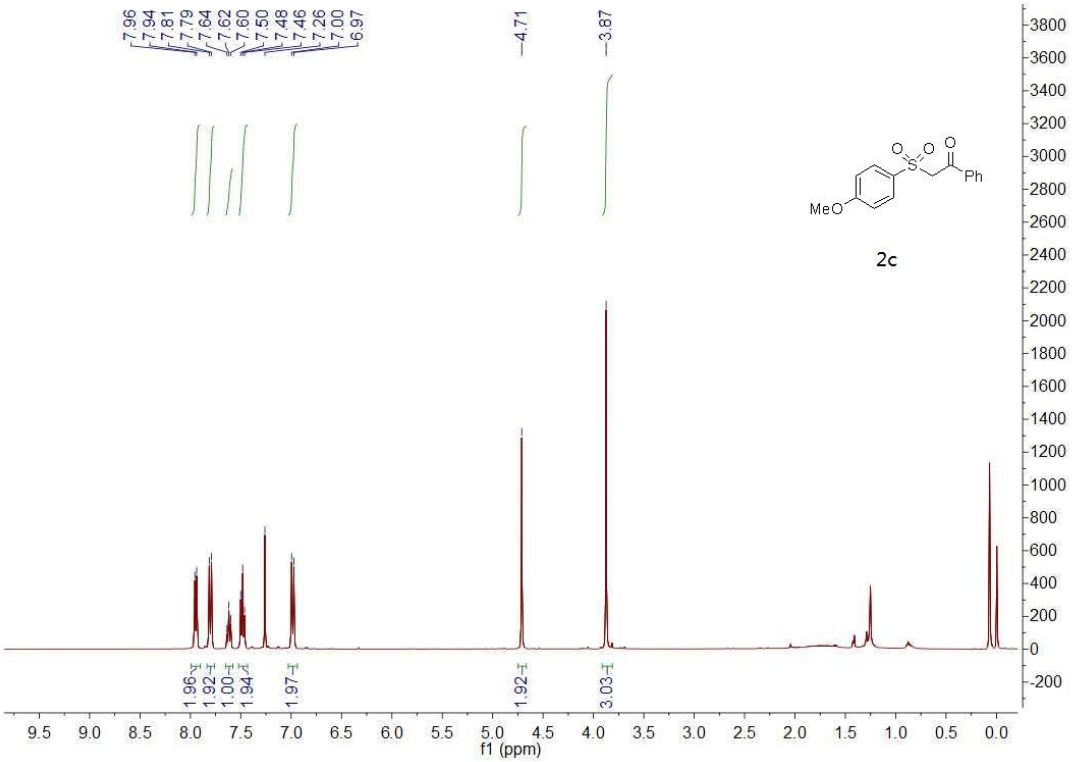
f1 (ppm)
2b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4.71
3.87
MeO
O
S
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O
Ph
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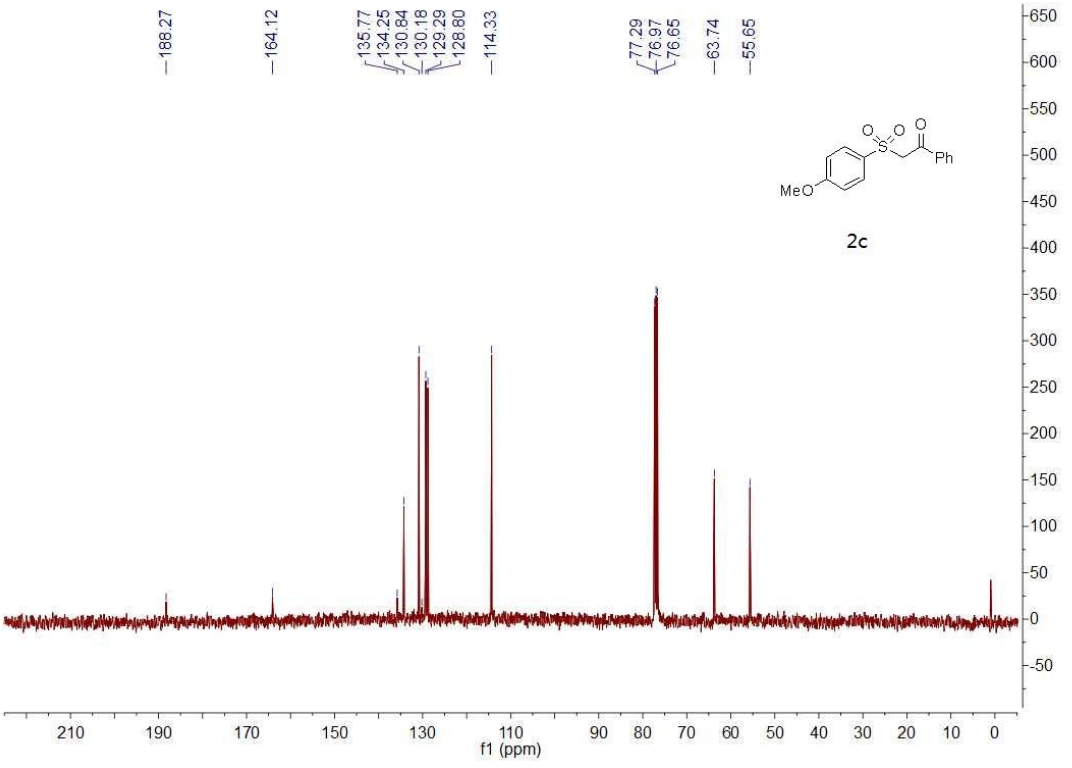
1.92
1.00
1.94
1.97
1.92
3.03
f1 (ppm)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128.80
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77.29
76.97
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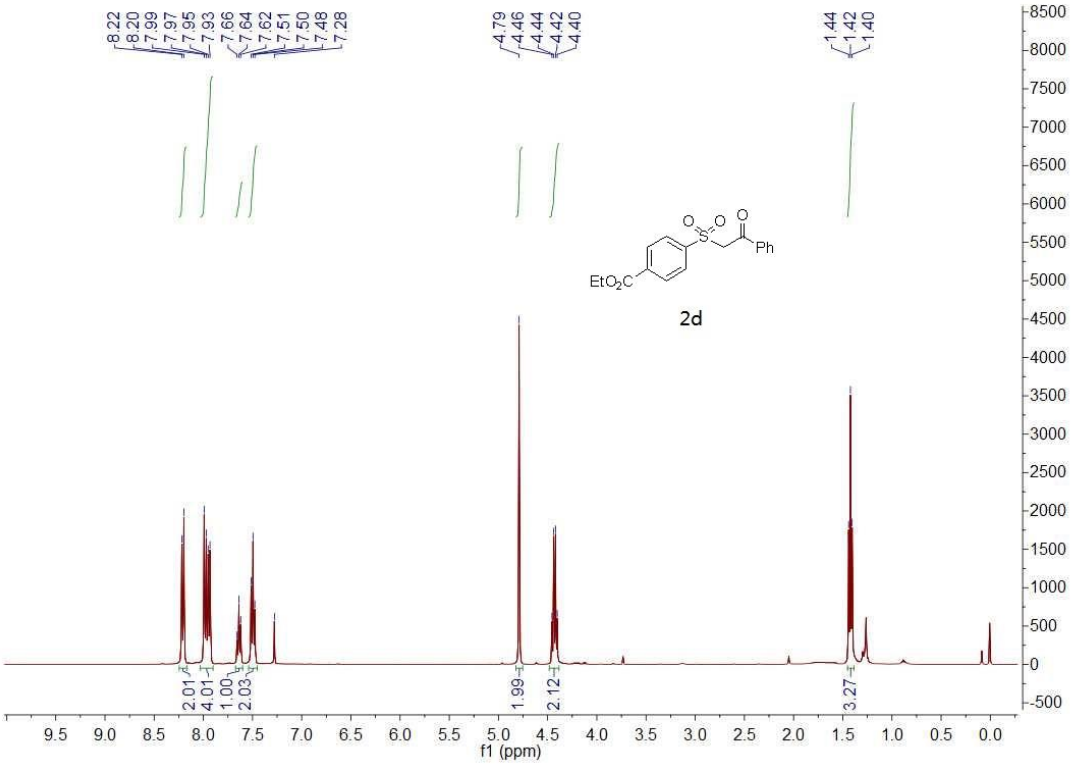
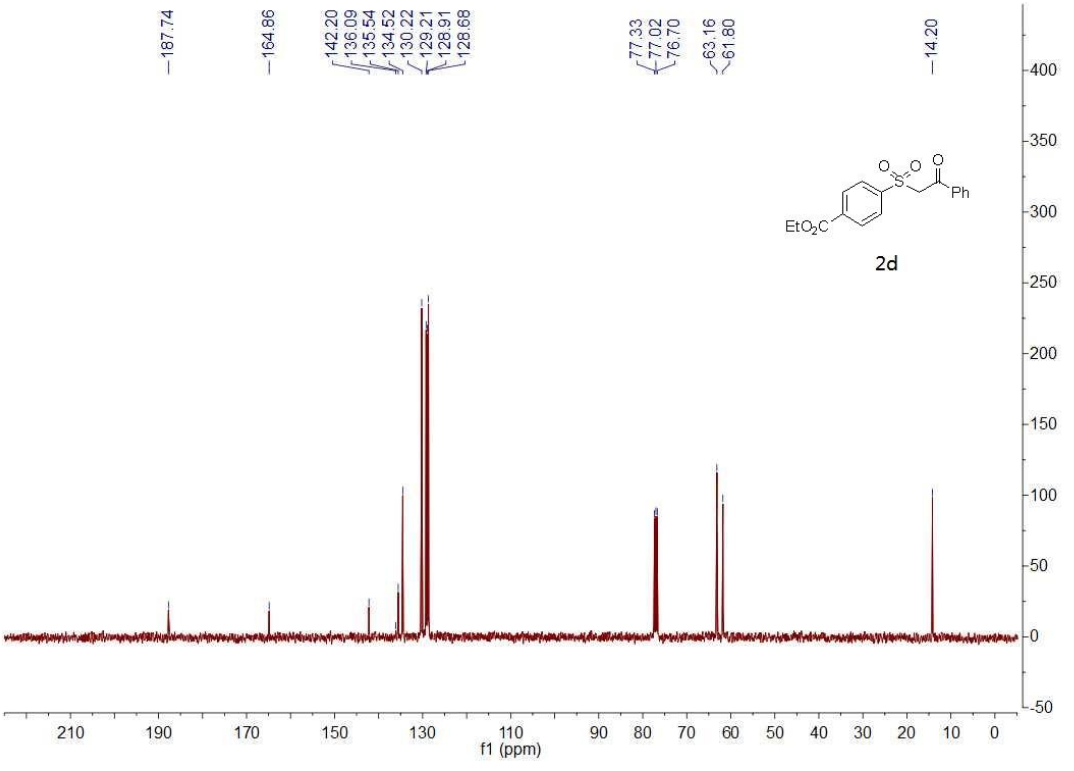
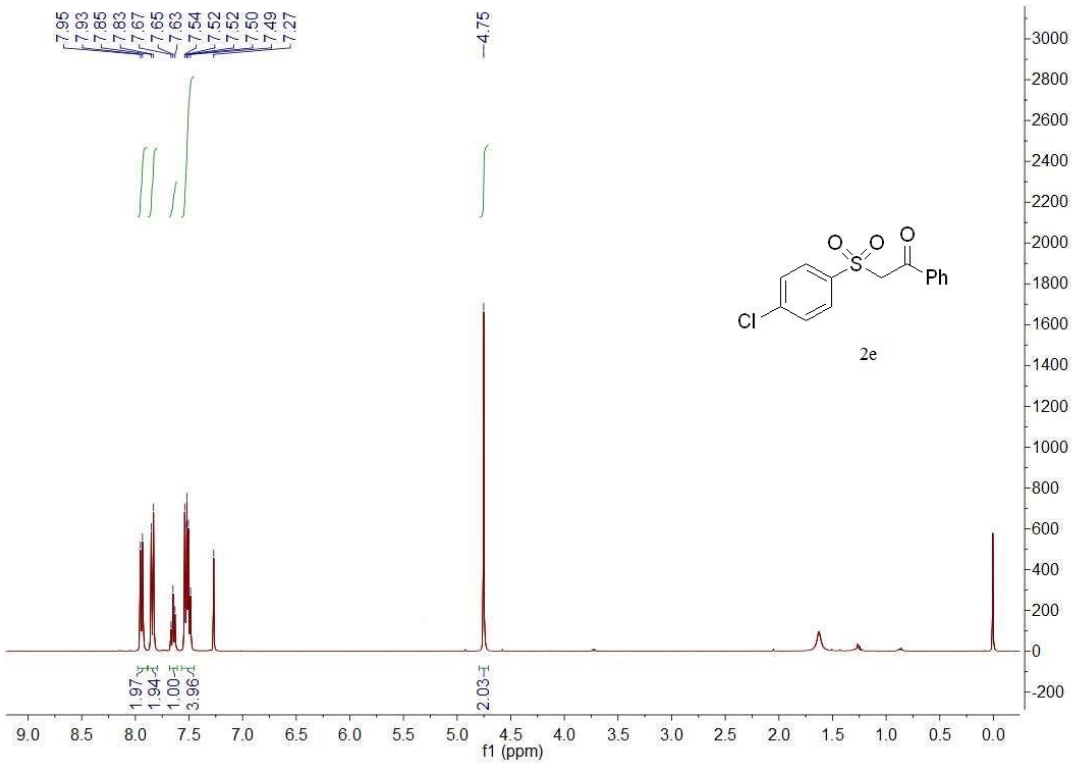
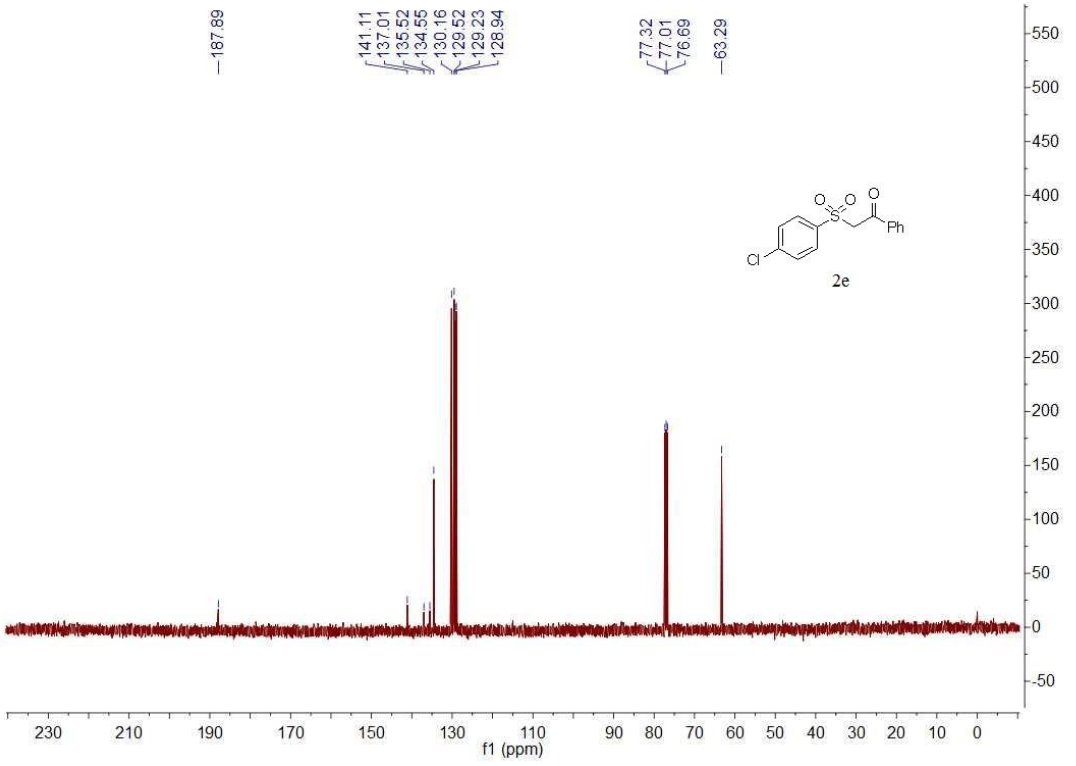
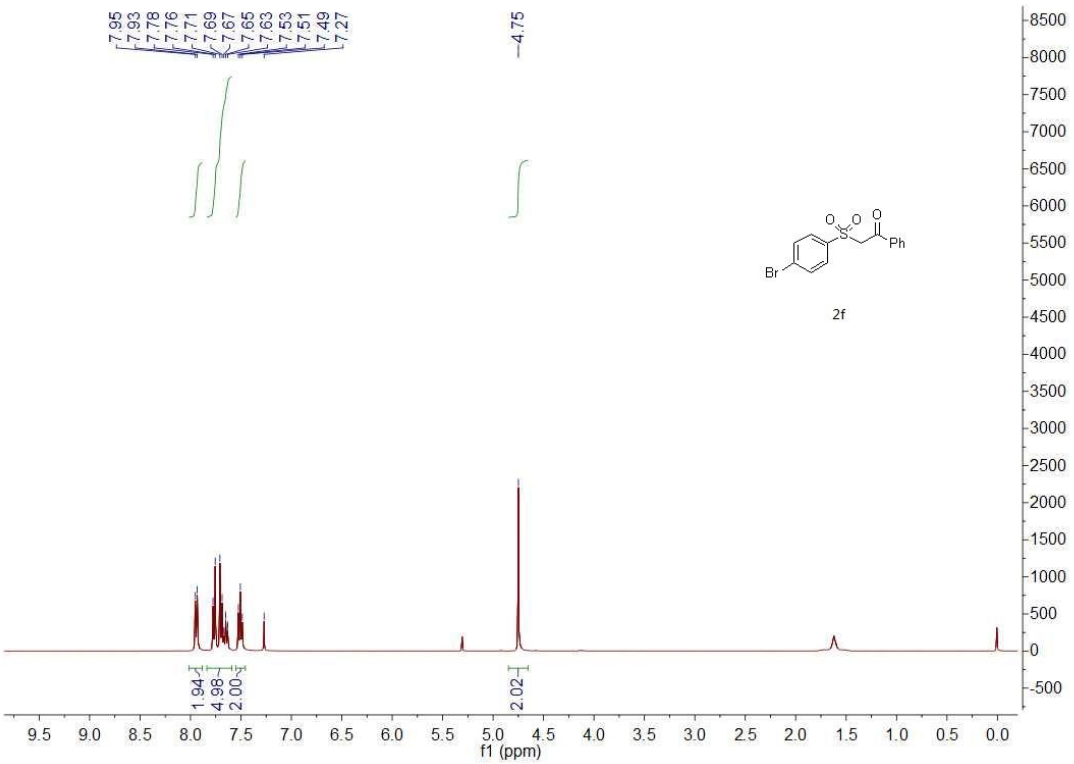
63.74
55.65
MeO
O
S
O
O
Ph
2c
f1 (ppm)

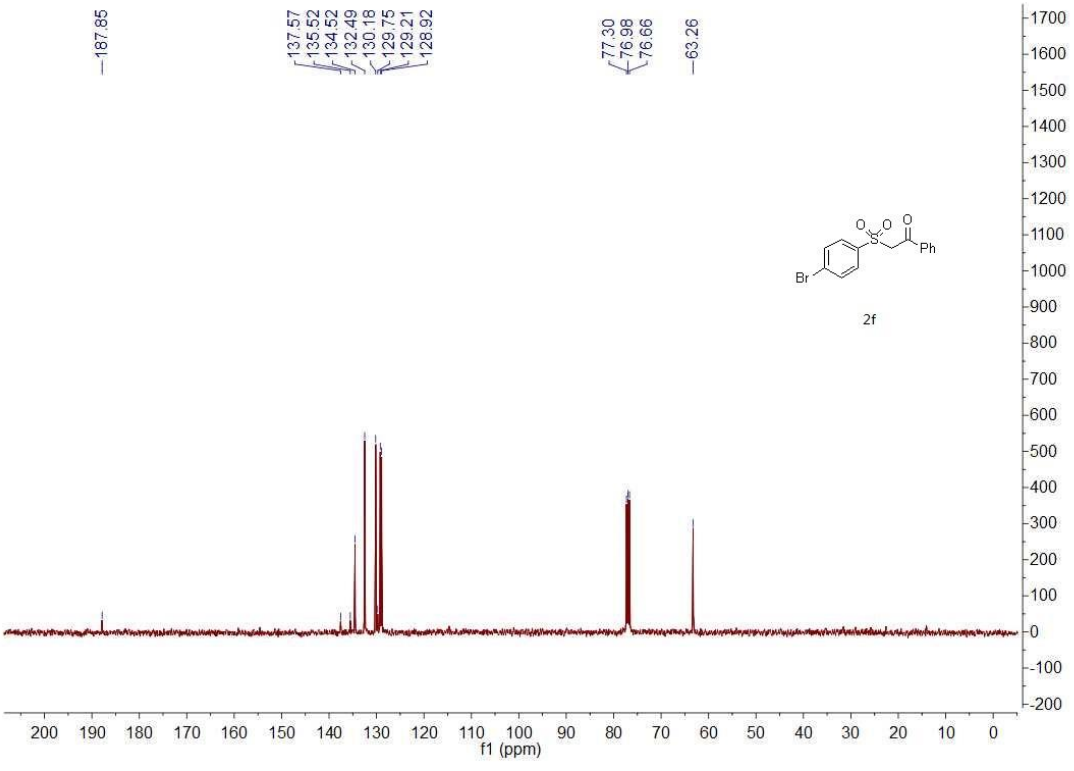

8.22
8.20
7.99
7.97
7.95
7.93
7.66
7.64
7.62
7.51
7.50
7.48
7.28
4.79
4.46
4.44
4.42
4.40
1.44
1.42
1.40
2d
2.01
4.01
1.00
2.03
1.99
2.12
3.27
f1 (ppm)

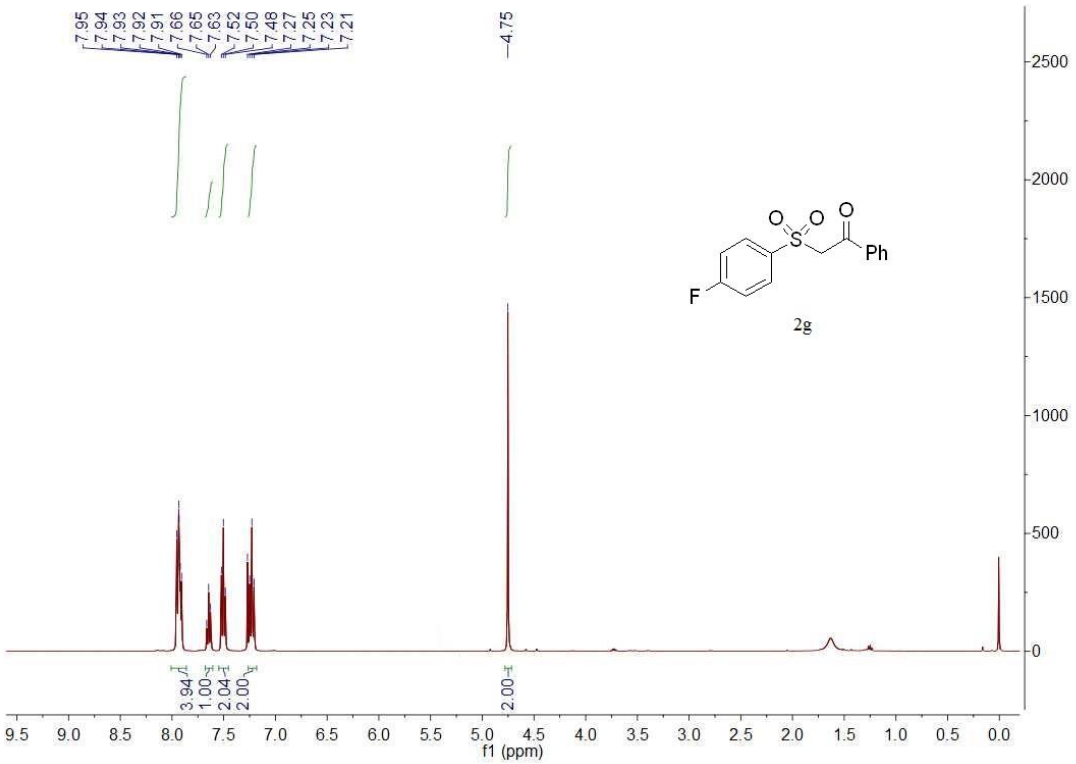

187.74
164.86
142.20
136.09
135.54
134.52
130.22
129.21
128.91
128.68
77.33
77.02
76.70
63.16
61.80
14.20
2d
f1 (ppm)

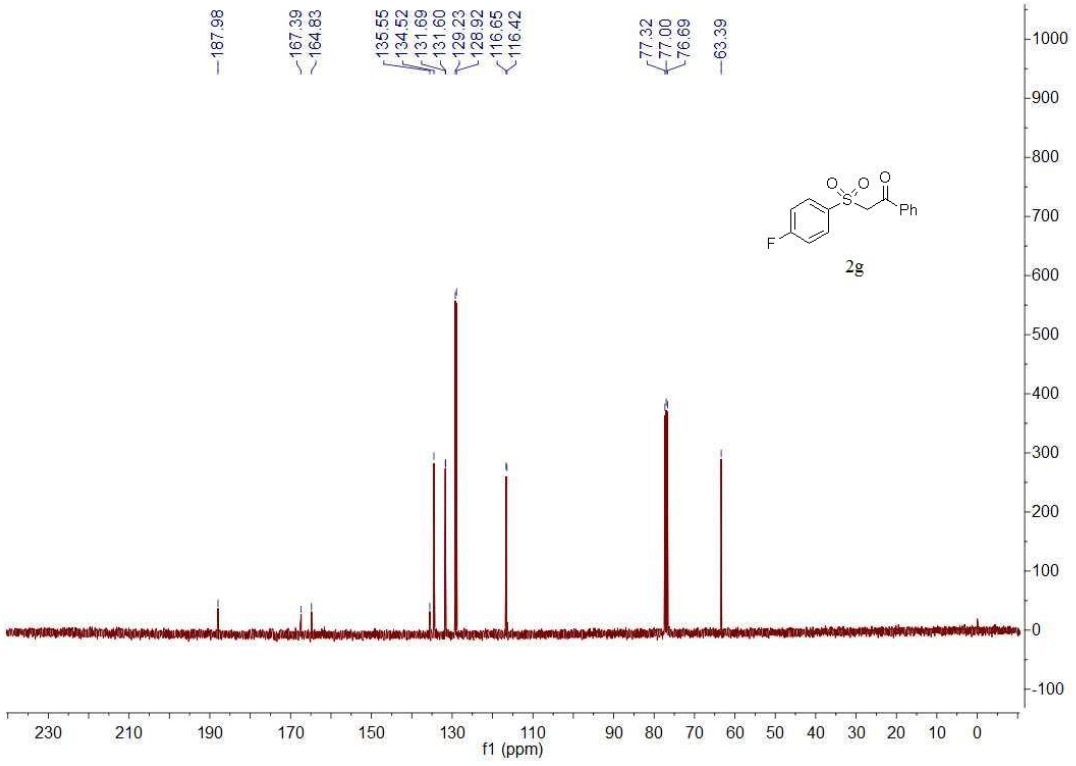

7.95
7.93
7.85
7.83
7.67
7.65
7.63
7.54
7.52
7.50
7.49
7.27
4.75
1.97
1.94
1.00
3.96
2.03
f1 (ppm)
Cl
Ph
2e

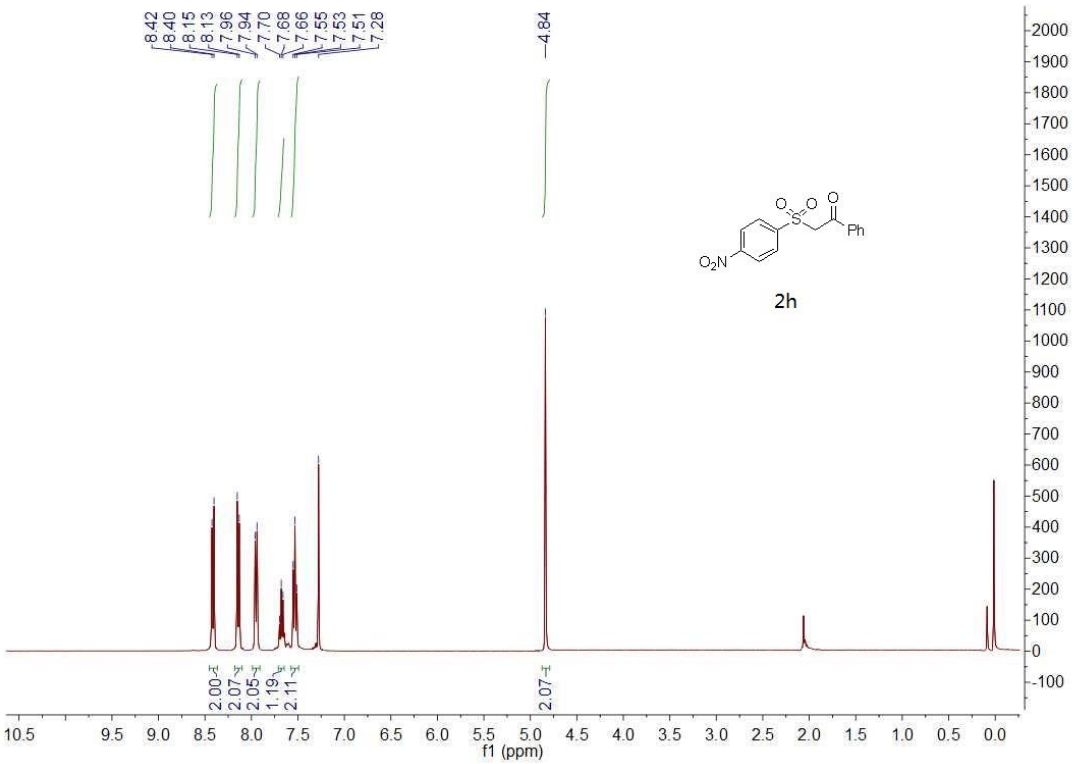

187.89
141.11
137.01
135.52
134.55
130.16
129.52
129.23
128.94
77.32
77.01
76.69
63.29
f1 (ppm)
Cl
Ph
2e


7.95
7.93
7.78
7.76
7.71
7.69
7.67
7.65
7.63
7.53
7.51
7.49
7.27
4.75
Br
Ph
2f
1.94
4.98
2.00
2.02
f1 (ppm)

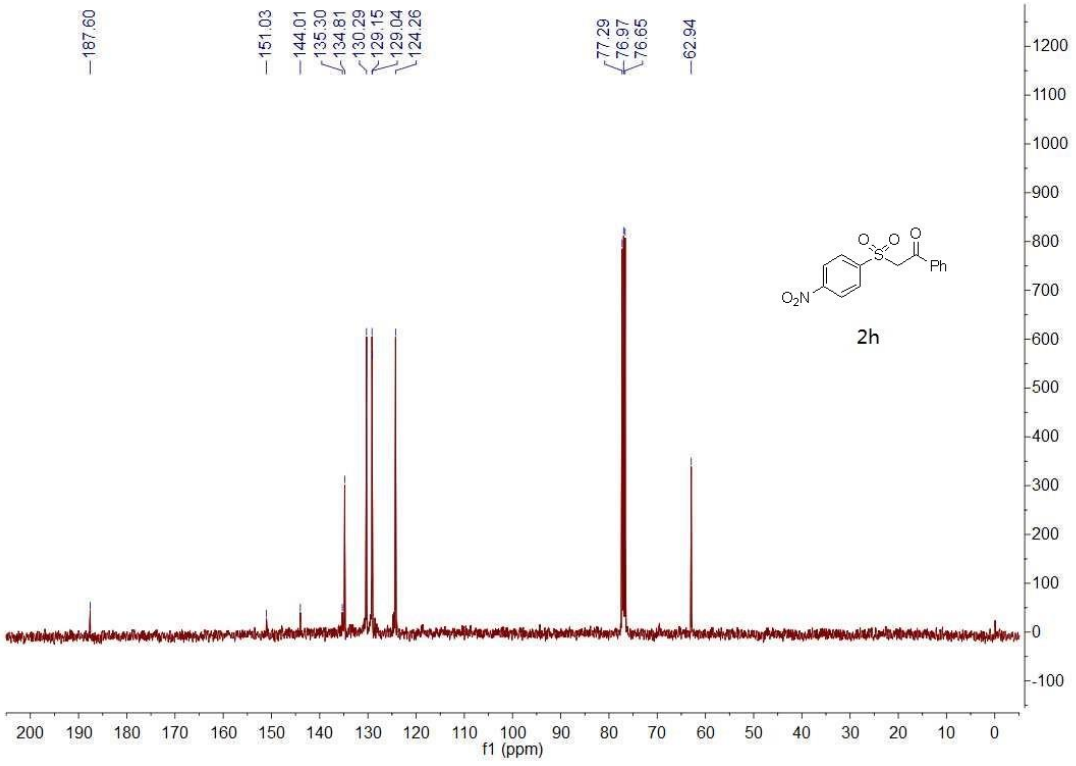

187.85
137.57
135.52
134.52
132.49
130.18
129.75
129.21
128.92
77.30
76.98
76.66
63.26
Br
Ph
2f
f1 (ppm)


7.95
7.94
7.93
7.92
7.91
7.66
7.65
7.63
7.52
7.50
7.48
7.27
7.25
7.23
7.21
4.75
3.94
1.00
2.04
2.00
2.00
f1 (ppm)
O
O
S
O
Ph
F
2g

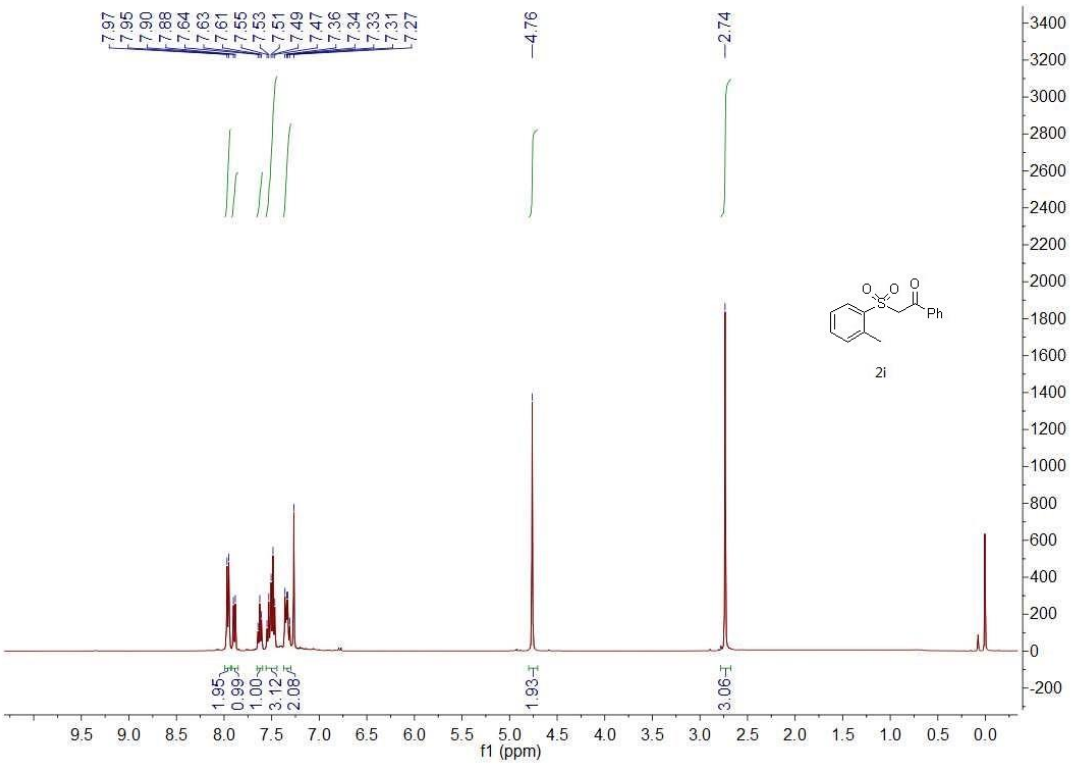

187.98
167.39
164.83
135.55
134.52
131.69
131.60
129.23
128.92
116.65
116.42
77.32
77.00
76.69
63.39
f1 (ppm)
O
O
S
O
Ph
F
2g

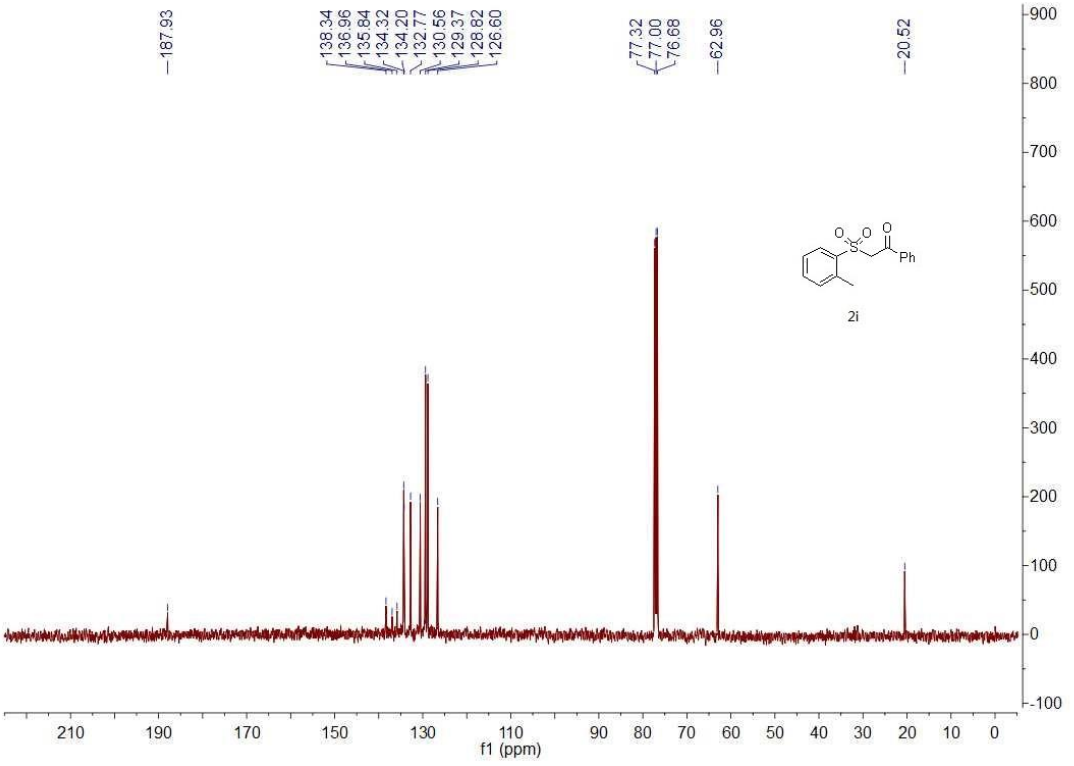

8.42
8.40
8.15
8.13
7.96
7.94
7.70
7.68
7.66
7.55
7.53
7.51
7.28
4.84
2.00
2.07
2.05
1.19
2.11
2.07
f1 (ppm)

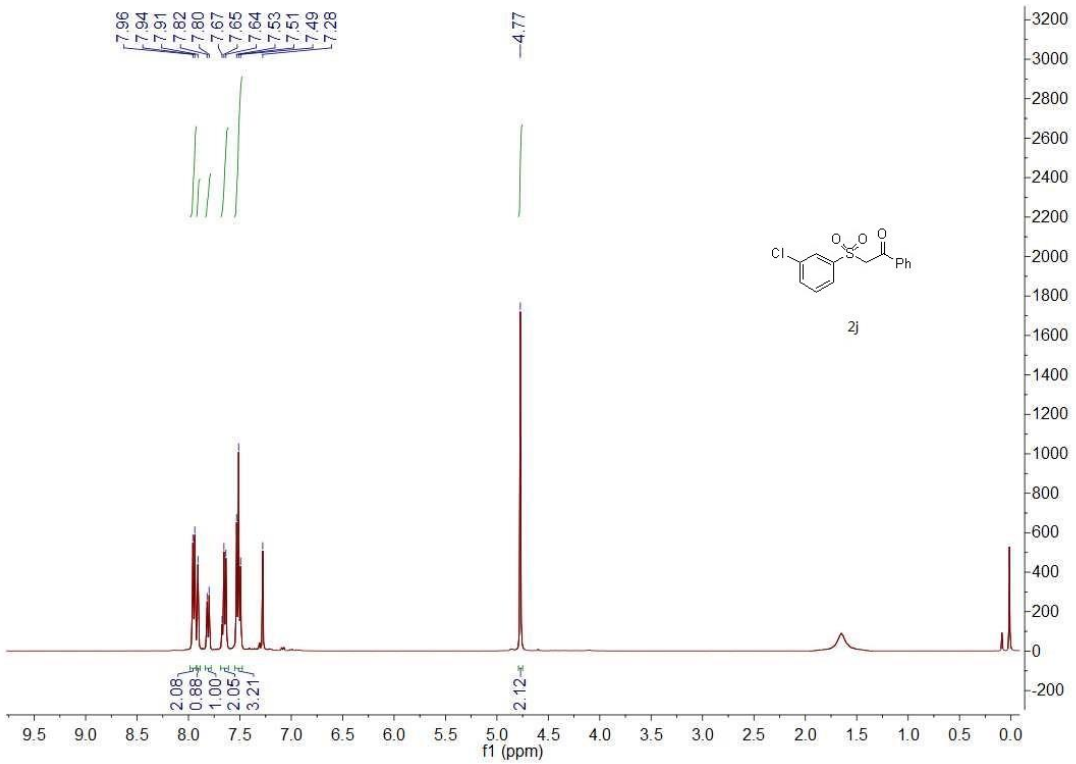
2h

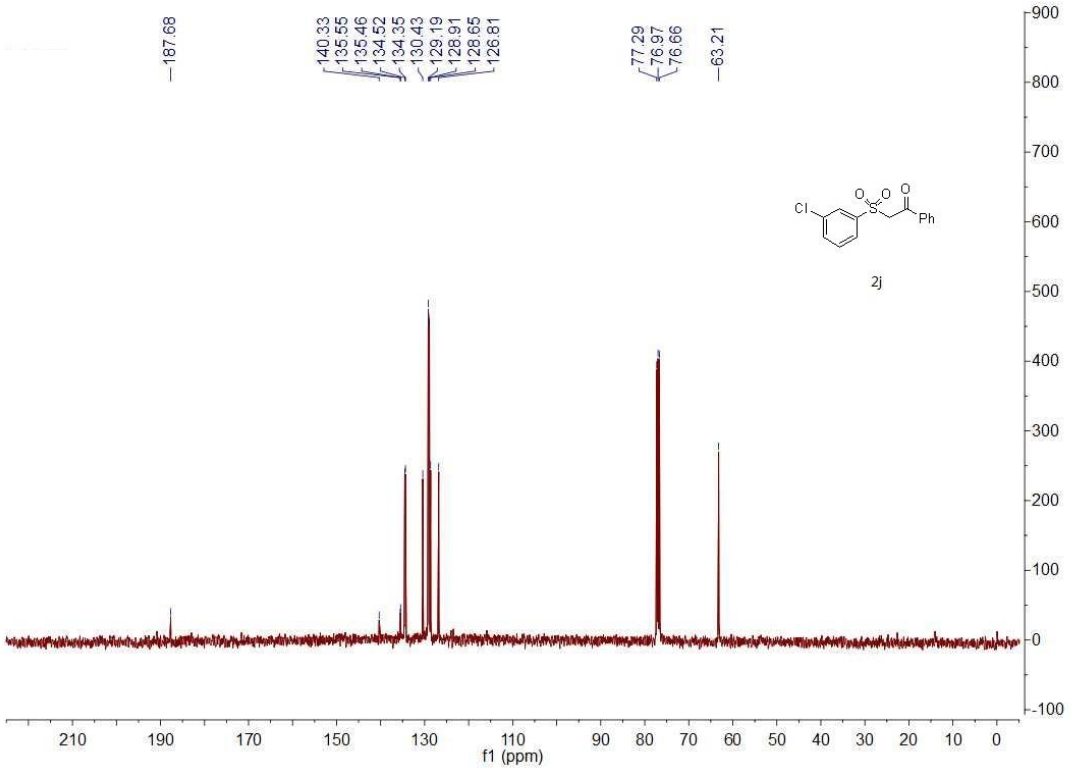

187.60
151.03
144.01
135.30
134.81
130.29
129.15
129.04
124.26
77.29
76.97
76.65
62.94
f1 (ppm)

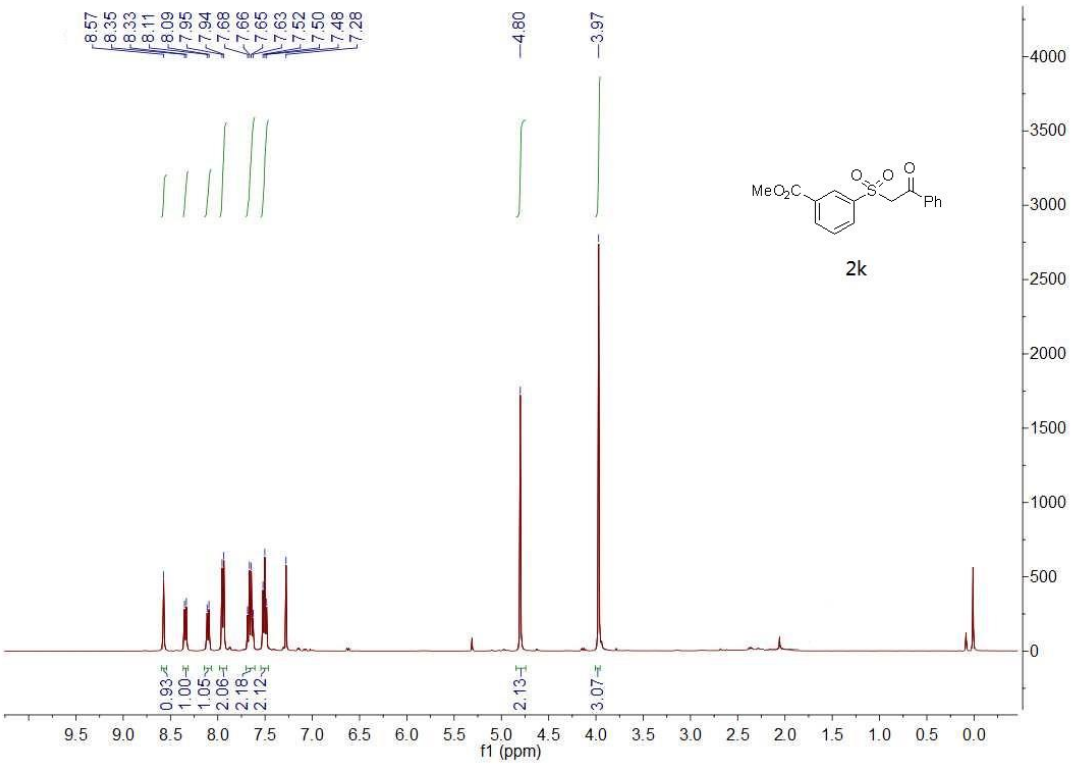
2h

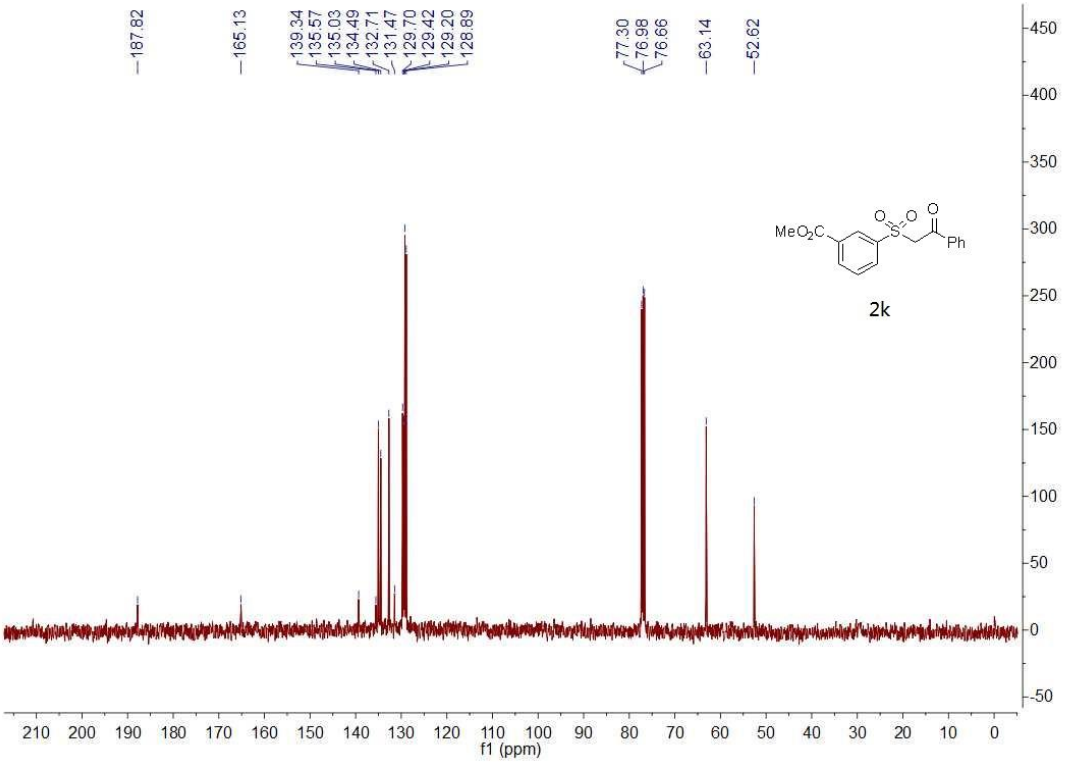

7.97
7.95
7.90
7.88
7.64
7.63
7.61
7.55
7.53
7.51
7.49
7.47
7.36
7.34
7.33
7.31
7.27
4.76
2.74
1.95
0.99
1.00
3.12
2.08
1.93
3.06
f1 (ppm)
2i

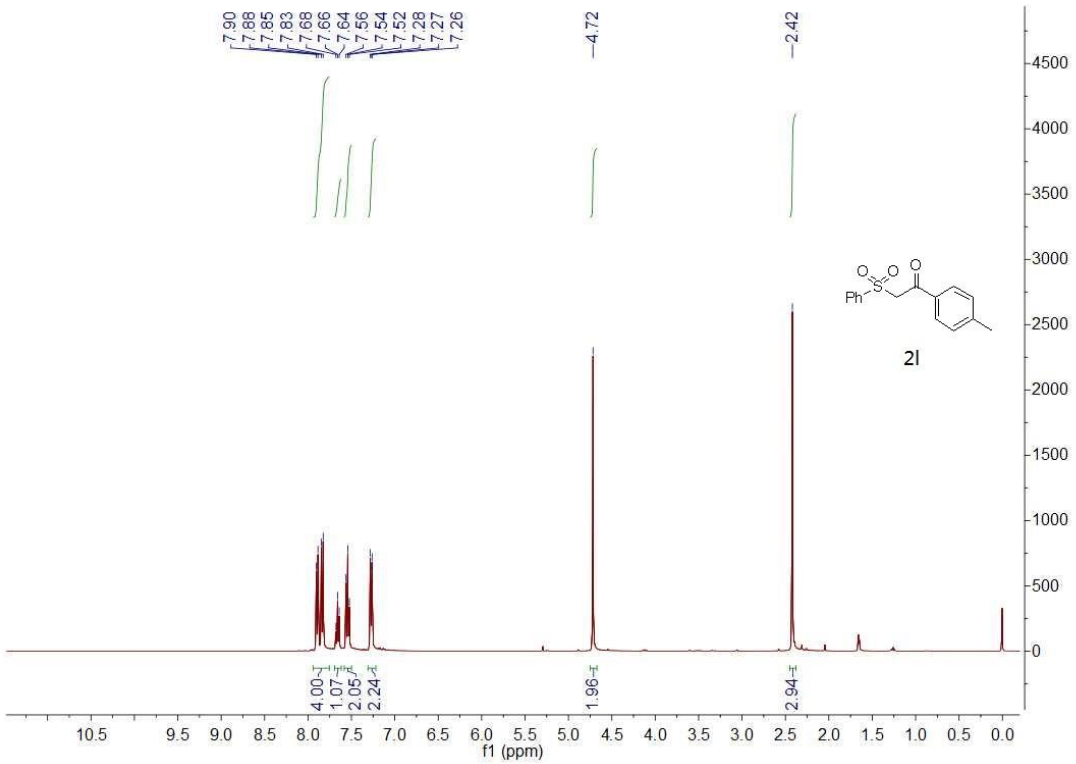

187.93
138.34
136.96
135.84
134.32
134.20
132.77
130.56
129.37
128.82
126.60
77.32
77.00
76.68
62.96
20.52
f1 (ppm)
2i


7.96
7.94
7.91
7.82
7.80
7.67
7.65
7.64
7.53
7.51
7.49
7.28
4.77
2.08
0.88
1.00
2.05
3.21
2.12
Cl
O
O
S
O
Ph
2j
f1 (ppm)

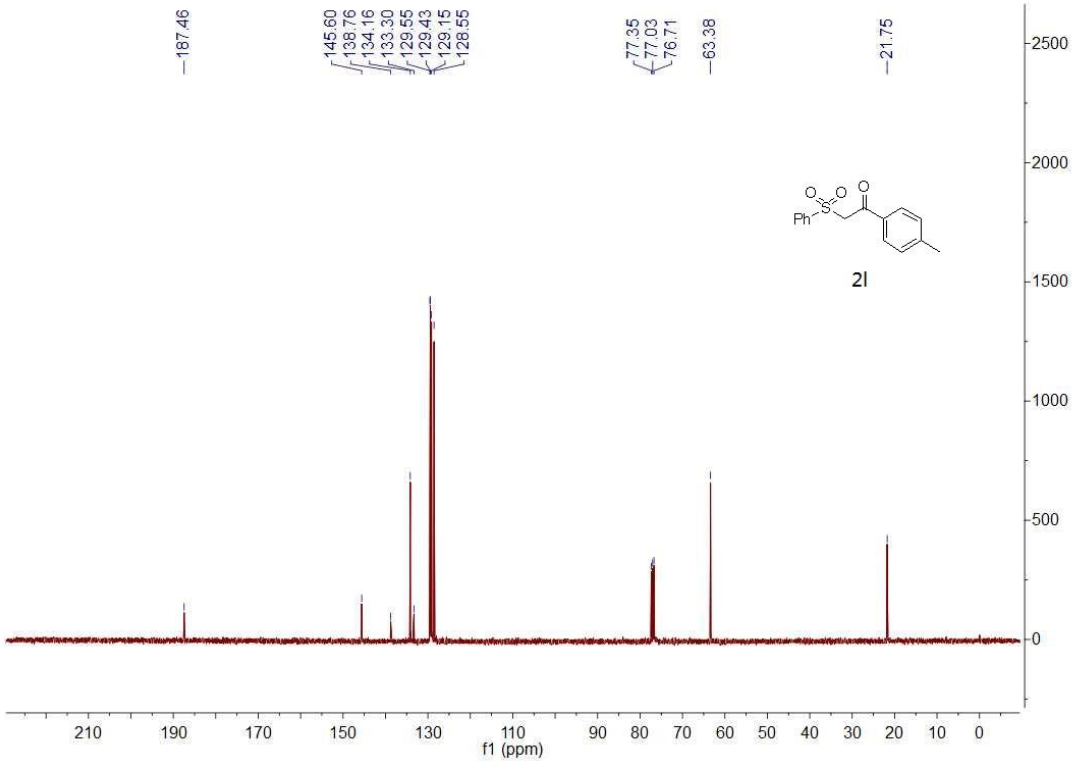

187.68
140.33
135.55
135.46
134.52
134.35
130.43
129.19
128.91
128.65
126.81
77.29
76.97
76.66
63.21
Cl
O
O
S
O
Ph
2j
f1 (ppm)


8.57
8.35
8.33
8.11
8.09
7.95
7.94
7.68
7.66
7.65
7.63
7.52
7.50
7.48
7.28
4.80
3.97
MeO2C
O
S
O
O
Ph
2k
0.93
1.00
1.05
2.06
2.18
2.12
2.13
3.07
f1 (ppm)

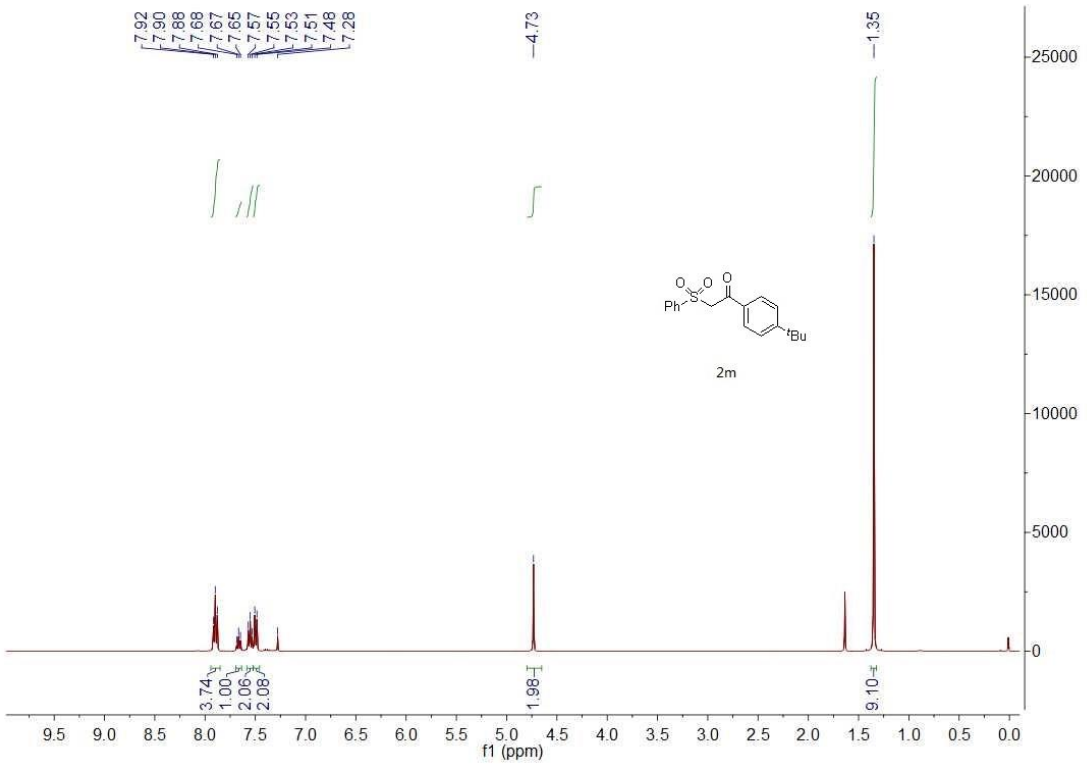

187.82
165.13
139.34
135.57
135.03
134.49
132.71
131.47
129.70
129.42
129.20
128.89
77.30
76.98
76.66
63.14
52.62
MeO2C
O
S
O
O
Ph
2k
f1 (ppm)


7.90
7.88
7.85
7.83
7.68
7.66
7.64
7.56
7.54
7.52
7.28
7.27
7.26
4.72
2.42
4.00
1.07
2.05
2.24
1.96
2.94
f1 (ppm)

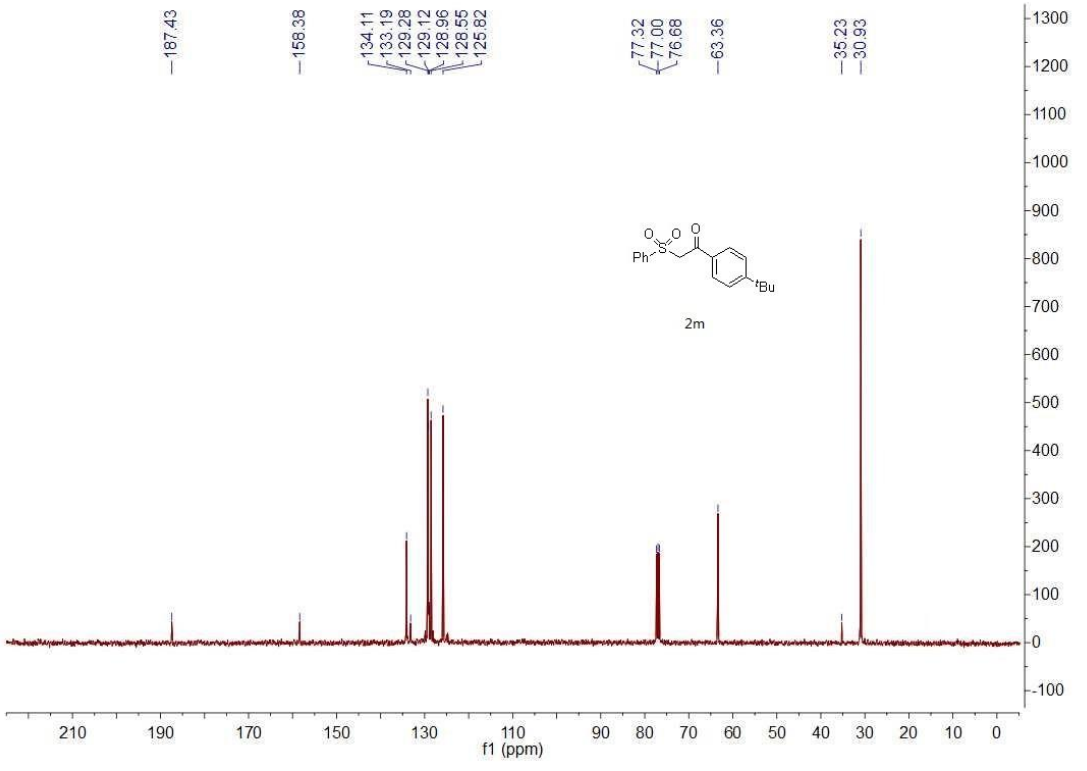
2l


187.46
145.60
138.76
134.16
133.30
129.55
129.43
129.15
128.55
77.35
77.03
76.71
63.38
21.75
f1 (ppm)

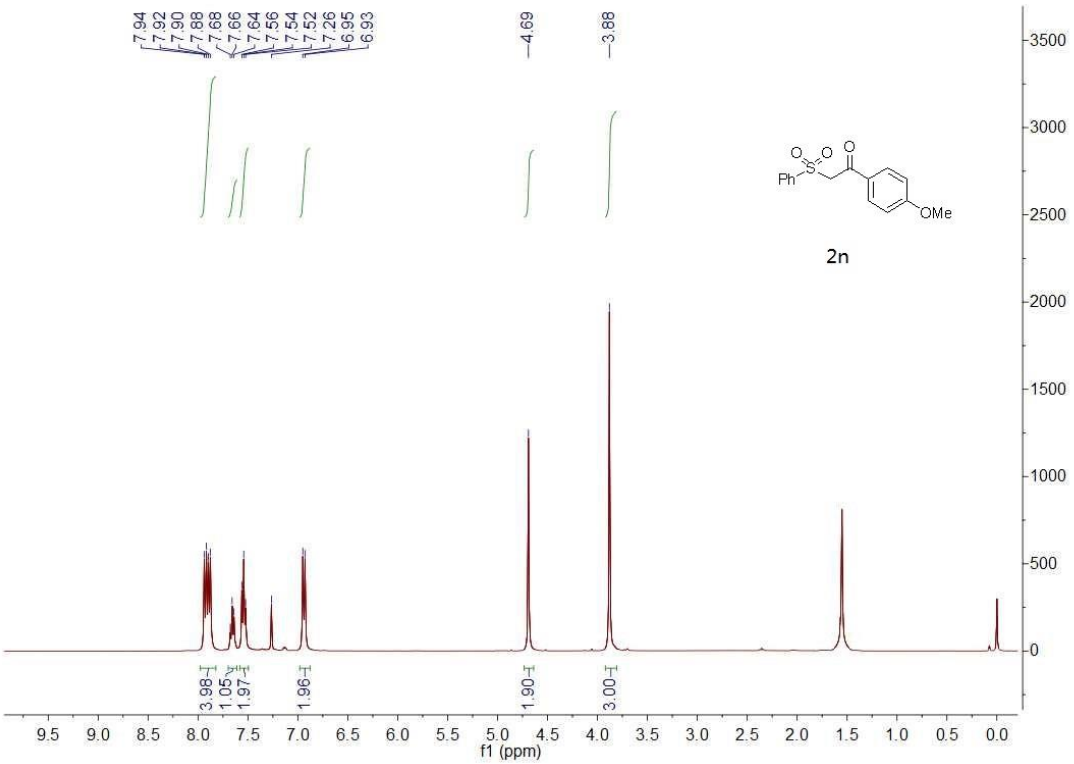
2l

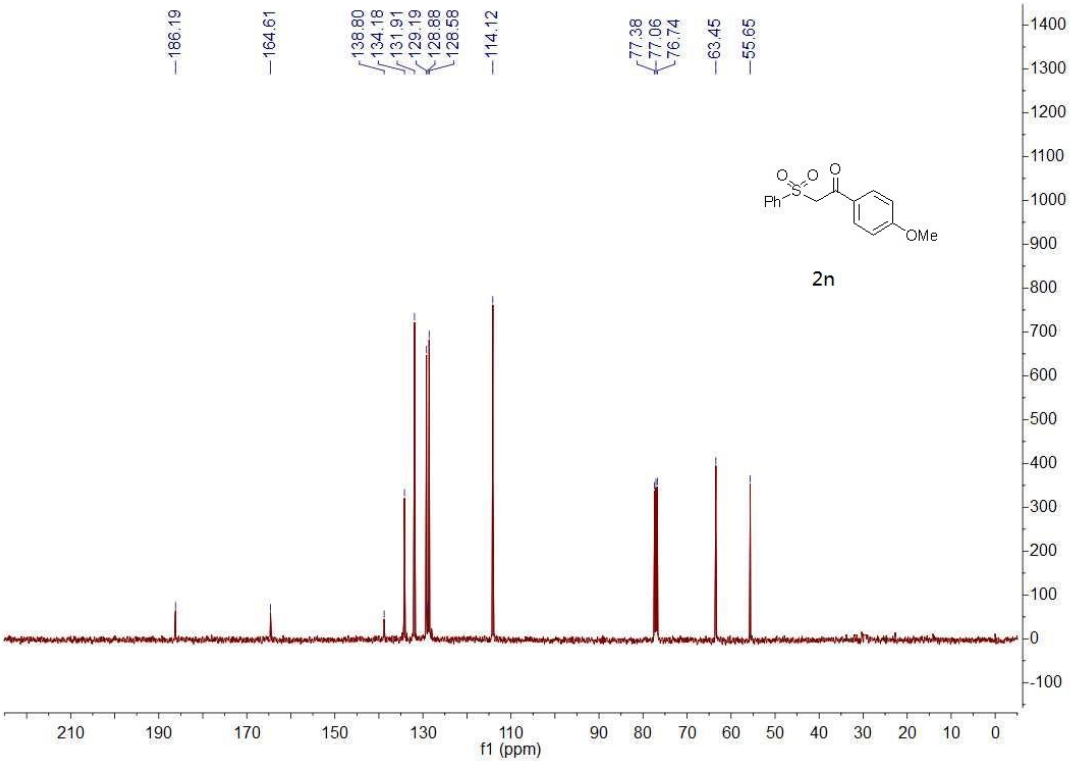

7.92
7.90
7.88
7.68
7.67
7.65
7.57
7.55
7.53
7.51
7.48
7.28
4.73
1.35
3.74
1.00
2.06
2.08
1.98
9.10
f1 (ppm)

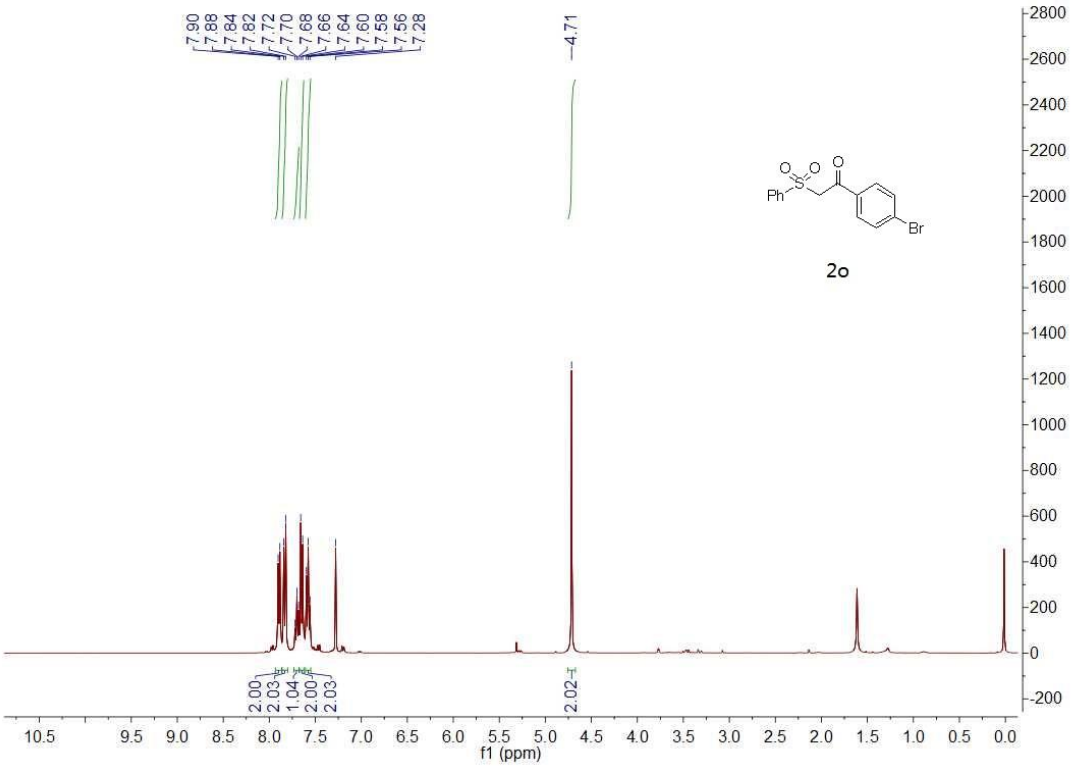
2m

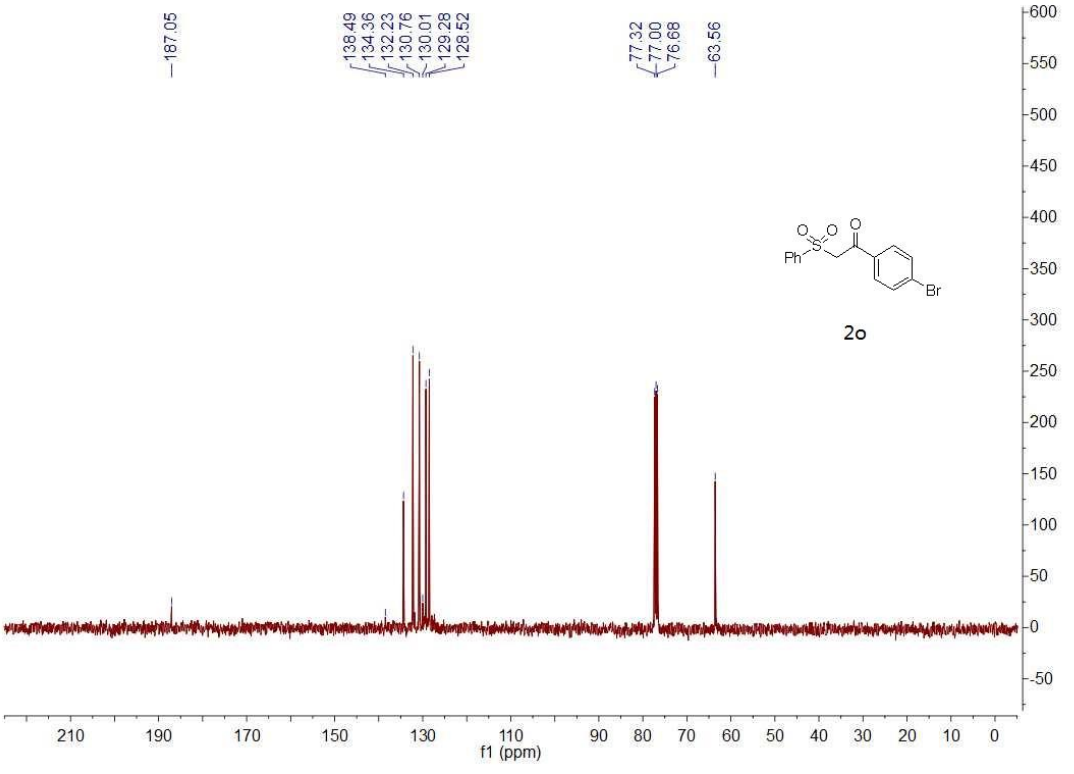

187.43
158.38
134.11
133.19
129.28
129.12
128.96
128.55
125.82
77.32
77.00
76.68
63.36
35.23
30.93
f1 (ppm)

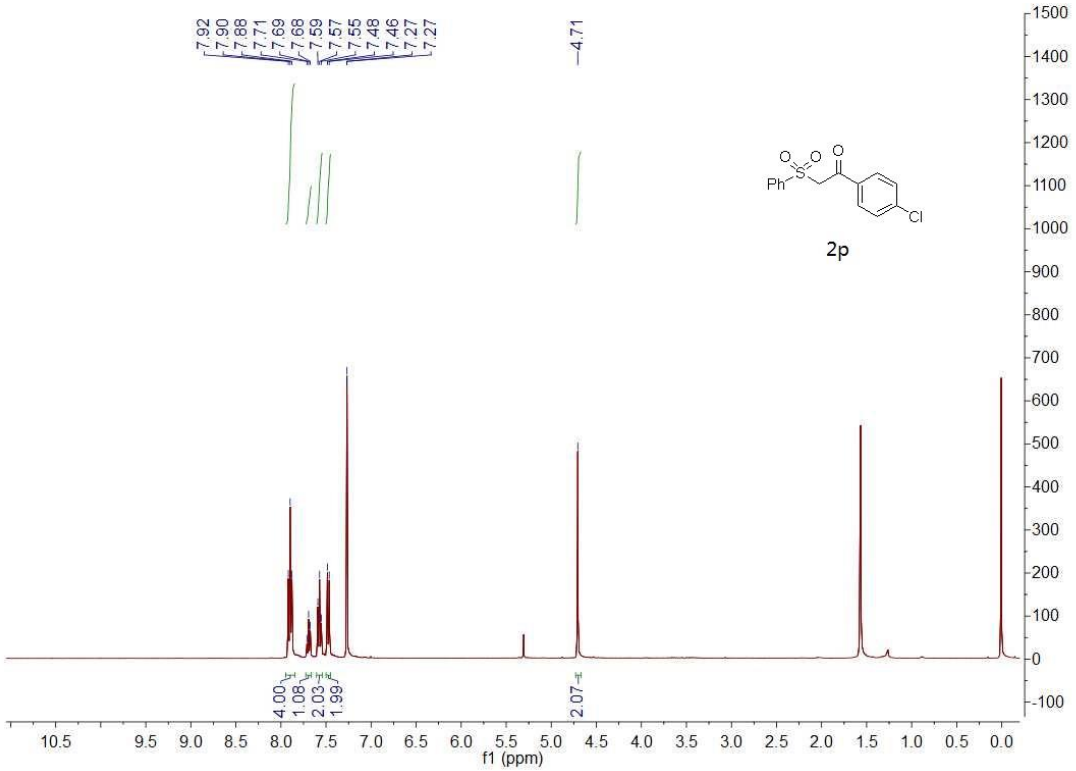
2m


7.94
7.92
7.90
7.88
7.68
7.66
7.64
7.56
7.54
7.52
7.26
6.95
6.93
4.69
3.88
Ph
OMe
2n
3.98
1.05
1.97
1.96
1.90
3.00
f1 (ppm)


186.19
164.61
138.80
134.18
131.91
129.19
128.88
128.58
114.12
77.38
77.06
76.74
63.45
55.65
Ph
OMe
2n
f1 (ppm)


7.90
7.88
7.84
7.82
7.72
7.70
7.68
7.66
7.64
7.60
7.58
7.56
7.28
4.71
Ph
S
O
O
Br
2o
2.00
2.03
1.04
2.00
2.03
2.02
f1 (ppm)


187.05
138.49
134.36
132.23
130.76
130.01
129.28
128.52
77.32
77.00
76.68
63.56
Ph
S
O
O
Br
2o
f1 (ppm)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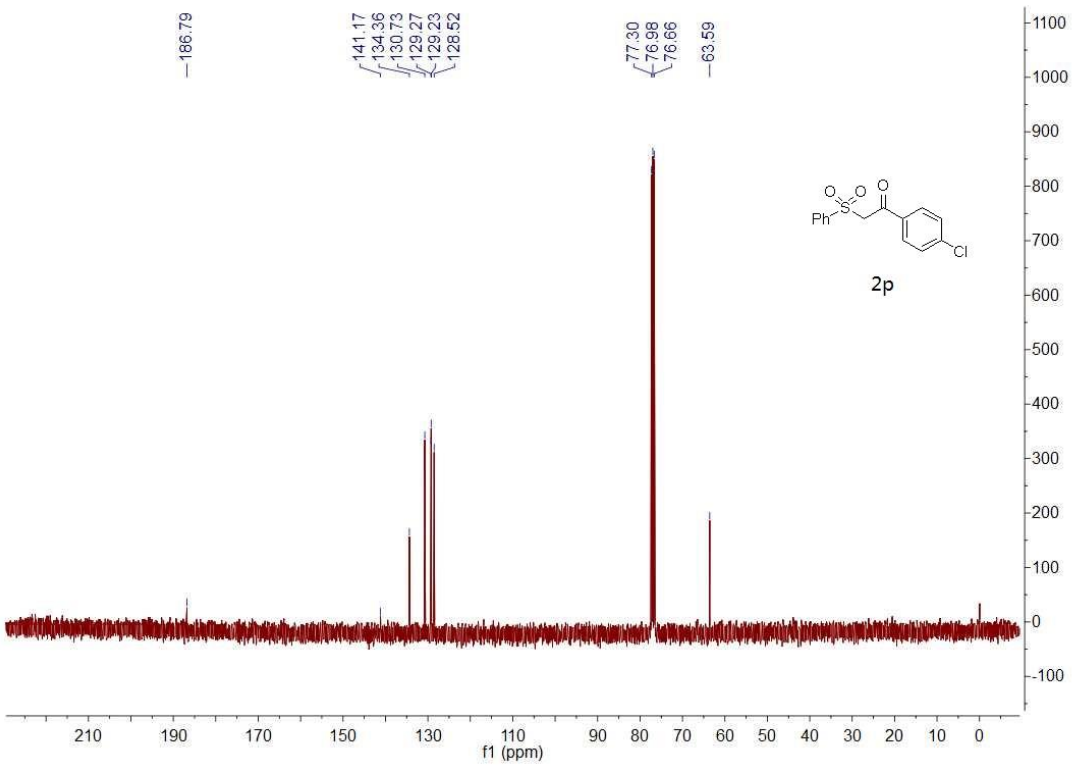
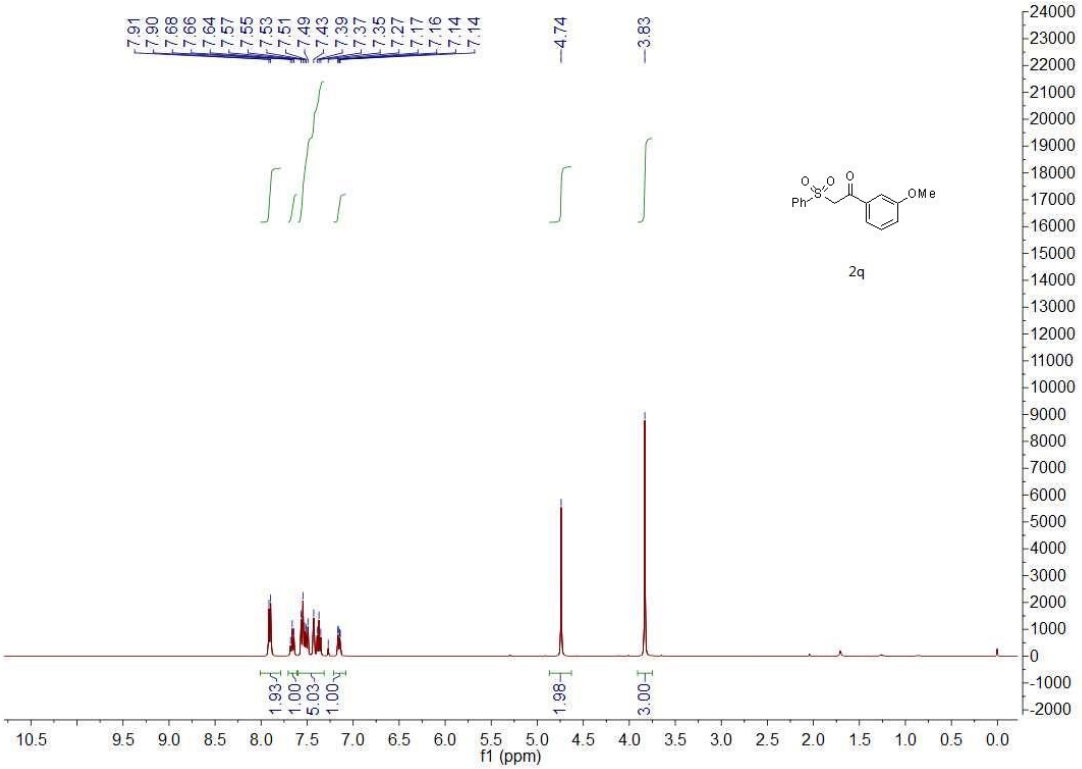
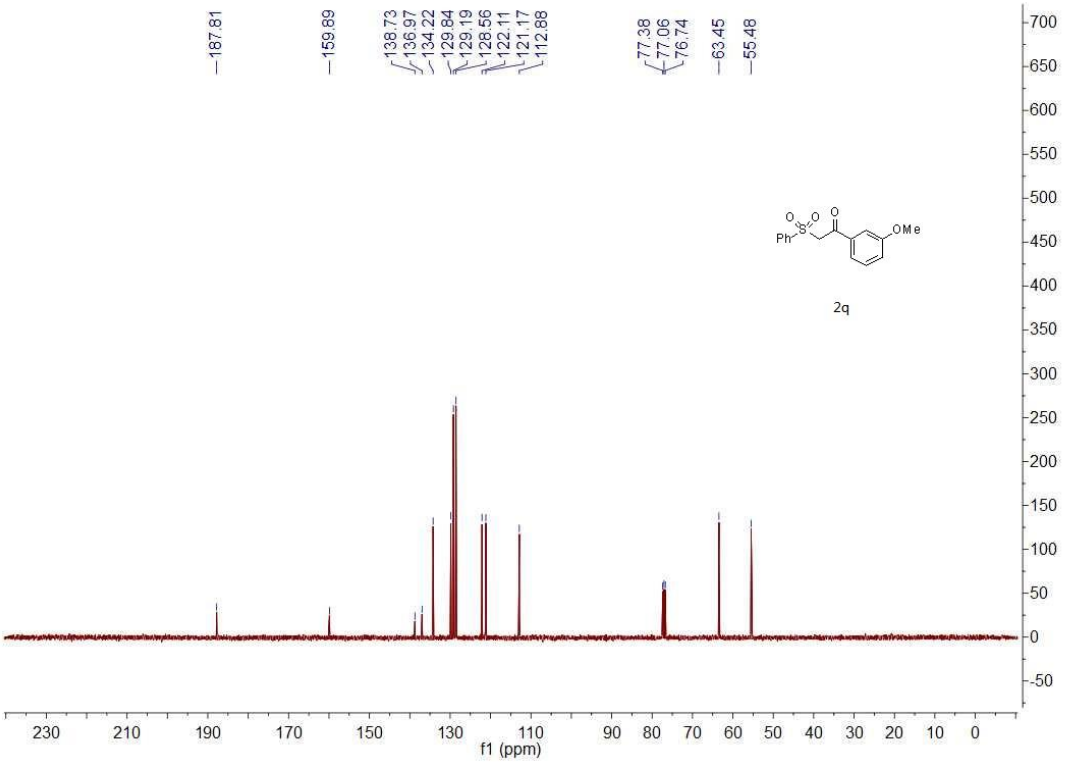
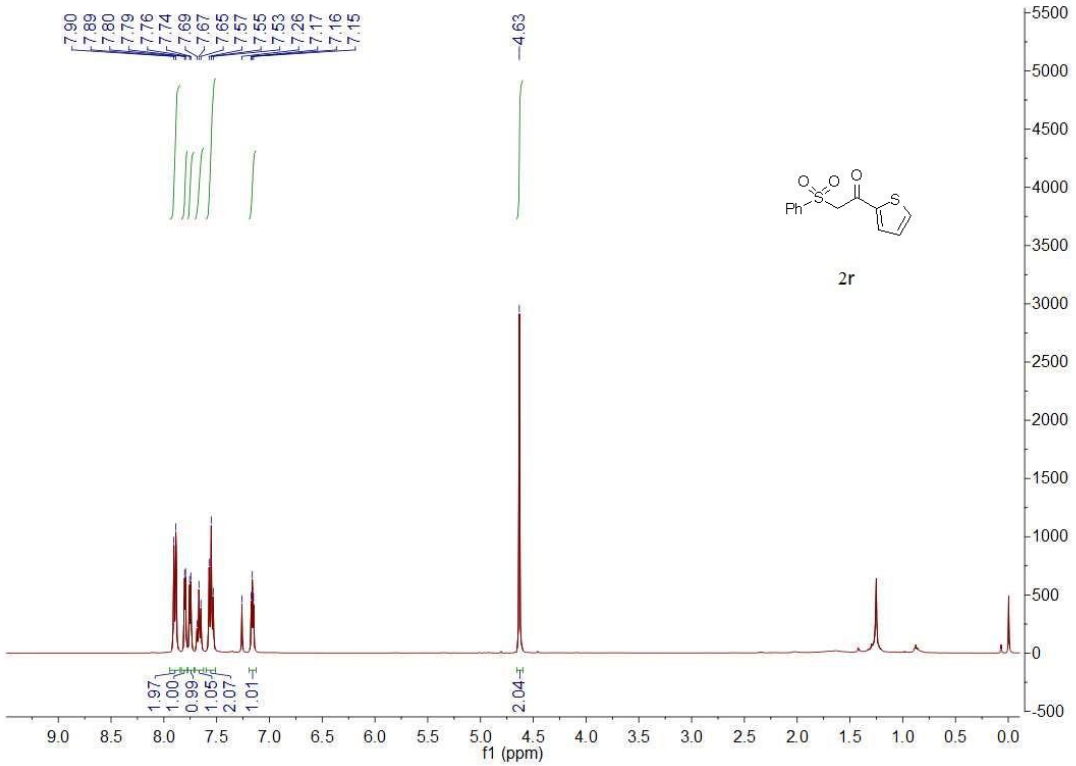
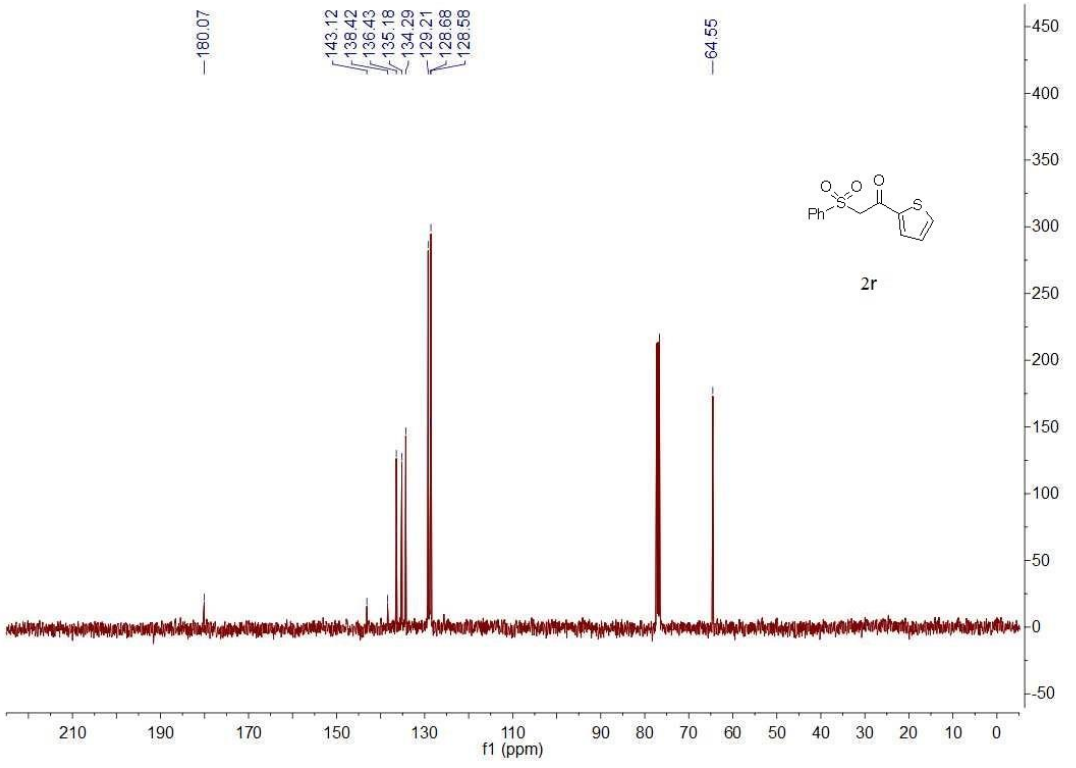
7.90
7.88
7.71
7.69
7.68
7.59
7.57
7.55
7.48
7.46
7.27
7.27
4.71
Ph
S
O
O
O
Cl
2p
4.00
1.08
2.03
1.99
2.07
f1 (ppm)


186.79
141.17
134.36
130.73
129.27
129.23
128.52
77.30
76.98
76.66
63.59
Ph
S
O
O
O
Cl
2p
f1 (ppm)


7.91
7.90
7.68
7.66
7.64
7.57
7.55
7.53
7.51
7.49
7.43
7.39
7.37
7.35
7.27
7.17
7.16
7.14
7.14
4.74
3.83
1.93
1.00
5.03
1.00
1.98
3.00
f1 (ppm)
2q


187.81
159.89
138.73
136.97
134.22
129.84
129.19
128.56
122.11
121.17
112.88
77.38
77.06
76.74
63.45
55.48
f1 (ppm)
2q


7.90
7.89
7.80
7.79
7.76
7.74
7.69
7.67
7.65
7.57
7.55
7.53
7.26
7.17
7.16
7.15
4.63
1.97
1.00
0.99
1.05
2.07
1.01
2.04
f1 (ppm)
2r


180.07
143.12
138.42
136.43
135.18
134.29
129.21
128.68
128.58
64.55
f1 (ppm)
2r