Electronic Supplementary Material (ESI) for Green Chemistry.

Catalyst-free visible-light mediated selective oxidation of sulfides into sulfoxides under clean conditions

Qiangwen Fan[a], Longwei Zhu[a], Xuhuai Li[a], Huijun Ren[a], Guorong Wu[a,*],
Haibo Zhu[a,*] and Wuji Sun[b,*]

[a]State Key Laboratory of Nuclear Resources and Environment, School of Chemistry, Biology and Material Science, East China University of Technology, Nanchang, 330013, China

[b]School of Pharmacy, North China University of Science and Technology, Tangshan, 063210, China

**Corresponding author: ecutwugr@163.com; hbzhu@ecut.edu.cn; sunwuji@yeah.net*

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General information

Experimental section

All chemicals were purchased from commercial sources and used without further purification. Thin-layer chromatography (TLC) was conducted on silica-gel 60 F254 plates (Merck KGaA). ^1H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz using a Bruker Avance 400 spectrometer at ambient temperature (25 ^oC) with TMS as an internal standard. GC-MS were obtained by EI on a Shimadzu GC-MS 2010, Conditions: Flow ripples:1 mL/min; column oven initial temperature 50 ^oC; injection port temperature: 300 ^oC; temperature range: 50~300 ^oC. XRD experiments were conducted by using an XRD-6000 with a copper-Kα radiation source (λ = 1.54056 Å). TGA was performed on a TGA Q500 thermal analyses system with a heating rate of 10 ^oC/min from 25 to 800 ^oC under N_2 atmosphere. The UV-Vis DRS spectra were recorded on a UH4150 Spectrophotometer and fluorescence spectra was recorded on a F-7000 FL Spectrophotometer. The UV–Vis absorption spectrum of thioanisole was recorded in a mix solution of MeOH and H_2O (*v/v*=2/1) using a Shimadzu 1800 PC spectrophotometer in the spectral region of 250–800 nm.

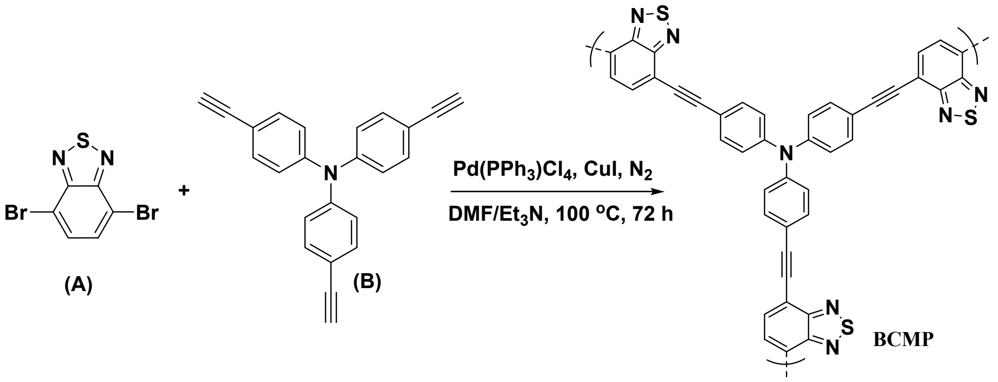
Computational details

Geometrical optimization of all stationary points along the reaction paths was performed at the B3LYP-D3/6-311+G (d) theoretical level which dispersion corrections are comprised using the Grimme's D3 model[1-5]. Frequency analysis were carried out at the same level to classify the located stationary points as minima (no imaginary frequency) and transition states (only one imaginary frequency) and also to obtain zero point energies (ZPES) and the thermodynamic correctional data. Moreover, the intrinsic reaction coordinate (IRC)[6] pathways computations were also carried out for all transition states to determine whether these transition states can connect the reactants, intermediates or products. The polarized continuum model (PCM)[7] was used was used in self-consistent reaction field (SCRF)[8] for simulating the solvent environment consisted of MeOH and H_2O (*v/v*=2/1), where the solvent parameters eps and epsinf were set as 47.860 and 1.7697, respectively. The relax scanning was performed using the PM6-D3 method[9] with the distance decreasing from 3.0 Å to 1.5

Å (stepsize=-0.1 Å). It should be noted that the thermal corrected data of **1a*** was carried out in gas state due to huge time consuming for frequency analysis of excited state in simulated solvent environment. Besides, the geometrical optimization and frequency analysis of triplet **1a**^{3,*} were performed using the unrestricted DFT method. The enthalpy of singlet oxygen was obtained by adding the experimental singlet-triplet energy difference (22.5 kcal/mol)[10] to the calculated enthalpy of triplet oxygen, as previously suggested by McKee[11], since calculation of $^1O_2$ required an extremely complex wavefunction. All the energies listed in this paper were corrected by thermal corrections, wherein the scale factors 0.9882, 1.0124 and 1.0174 were used for the corrections of zero-point energy, enthalpy and entropy, respectively[12]. All of the quantum chemical calculations were performed using the Gaussian 16 program package[13]. The S_1/T_1 minimal energy crossing point (MECP) of **1a*** was located by the sobMECP program at the B3LYP-D3/6-311+G (d) theoretical level with the default settings[14,15].

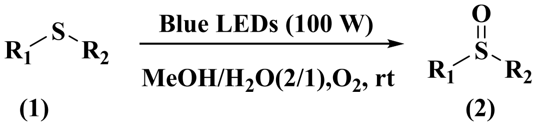
General procedures for preparing BCMP and sulfoxides

Procedures for the Synthesis of BCMP: To a 50 mL Pyrex tube added a solution of **A** (147 mg, 0.5 mmol), **B** (159 mg, 0.5 mmol), tetrakis(triphenylphosphine)-palladium(0) (40 mg) and copper(I) iodide (20 mg) in anhydrous DMF (5 mL) and Et_3N (5 mL) under nitrogen atmosphere. The reaction mixture was heated to 100 °C and stirred for 72 h. Afterwards, the reaction system was cooled to room temperature, and the precipitates (crude products) was filtered and removed the unreacted monomers or catalyst by washing the residues with $CHCl_3$, H_2O, MeOH, and acetone successively. The resulted solids were further purified by Soxhlet extraction with MeOH and $CHCl_3$ for 24 h respectively. The obtained product was dried under vacuum for 24 h at 60 °C and afforded the desired products as dark brown powder.



Scheme S1 Synthetic route of preparing **BCMP**

General procedures for the synthesis of sulfoxides: To a 25 mL shrek tube charged with O_2 balloon added a solution of sulfides (**1**, 0.2 mmol) in MeOH (6 mL) and H_2O (3 mL), the resulting mixture was subjected to visible-light irradiation (100 W blue LEDs) until totally conversion of **1** (monitored by TLC). Subsequently, organic solvent was removed under vacuum and the resulting mixture was extracted with CH_2Cl_2 (3*10 mL). The organic layers were combined and dried with anhydrous Na_2SO_4. The desired sulfoxide was afforded after removing Na_2SO_4 and CH_2Cl_2 by evaporation under vacuum or by flash chromatography (200-300 mesh silica gel) with ethyl acetate/hexane(*v/v*=1:3) as eluent.



Phenyl methyl sulfoxide(2a): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.72-2.73 (3H, d, -C*H*$_3$), 7.51-7.66(5H, m, Ph-*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 43.93, 123.47, 129.36, 131.05, 145.60.

4-NH$_2$-Phenyl methyl sulfoxide (2b): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.69 (3H, d, -C*H*$_3$), 3.63-4.11 (2H, br, -N*H*$_2$), 6.73-6.75 (2H, d, Ph-*H*), 7.42-7.44(2H, d, Ph-*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 43.59, 115.02, 125.77, 132.50, 149.99.

4-OMe-Phenyl methyl sulfoxide (2c): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.60 (3H, s, -C*H*$_3$), 3.74 (3H, s, -OC*H*$_3$), 6.92-6.94 (2H, d, Ph-*H*), 7.49-7.51(2H, d, Ph-*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 43.80, 55.46, 114.78, 125.41, 136.30, 161.87.

3-OMe-Phenyl methyl sulfoxide (2d): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.72-2.73

(3H, t, -C$\underline{H}_3$), 3.84-3.85 (3H, t, -OC$\underline{H}_3$), 7.00-7.43 (4H, m, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 43.81, 55.44, 107.90, 115.40, 117.17, 130.26, 146.95, 160.32.

4-F-Phenyl methyl sulfoxide (2e): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 2.65 (3H, s, -C$\underline{H}_3$), 7.14-7.17 (2H, m, Ph-$\underline{H}$), 7.58-7.60 (2H, m, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 44.09, 116.59(J=90.0 Hz), 125.82(J=35.0 Hz), 141.03(J=10.0 Hz), 163.28, 165.27.

4-Cl-Phenyl methyl sulfoxide (2f): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 2.73 (3H, d, -C$\underline{H}_3$), 7.50-7.53 (2H, m, Ph-$\underline{H}$), 7.59-7.61 (2H, m, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 44.06, 124.99, 129.66, 137.23, 144.20.

4-Br-Phenyl methyl sulfoxide (2g): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 2.73 (3H,s, -C$\underline{H}_3$), 7.52-7.54 (2H, m, Ph-$\underline{H}$), 7.67-7.69 (2H, m, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 44.01, 125.17, 125.46, 132.58, 144.85.

4-NO$_2$-Phenyl methyl sulfoxide (2h): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 2.82 (3H,s, -C$\underline{H}_3$), 7.85-7.87(2H, d, Ph-$\underline{H}$), 8.40-8.42 (2H, m, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 43.85, 124.51, 124.71, 149.49, 153.18.

2-Cl-Phenyl methyl sulfoxide (2i): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 2.83 (3H,s, -C$\underline{H}_3$), 7.39-7.46 (2H, m, Ph-$\underline{H}$), 7.47-7.56 (1H, t, Ph-$\underline{H}$), 7.95-7.97 (1H, t, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 41.69, 125.30, 128.18, 129.77, 129.79, 132.02, 143.58.

2-Br-Phenyl methyl sulfoxide (2j): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 2.71 (3H,s, -C$\underline{H}_3$), 7.27-7.28 (1H, m, Ph-$\underline{H}$), 7.44-7.49 (2H, m, Ph-$\underline{H}$), 7.82-7.85 (1H, t, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 41.79, 118.31, 125.53, 128.67, 132.27, 132.84, 145.13.

Phenyl ethyl sulfoxide (2k): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 1.09-1.12 (3H,t, -C$\underline{H}_3$), 2.66-2.84 (2H, m, -C$\underline{H}_2$CH$_3$), 7.40-7.45 (3H, m, Ph-$\underline{H}$), 7.52-7.53 (2H, d, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 5.91, 50.19, 124.11, 129.12, 130.92, 143.12.

Phenyl cyclopropyl sulfoxide (2l): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 0.88-1.01 (3H, m, -*cyclopropyl*-$\underline{H}$), 1.18-1.19 (1H, m, -*cyclopropyl*-$\underline{H}$), 2.23-2.26 (1H, m, -*cyclopropyl*-$\underline{H}$), 7.48-7.50 (3H, m, Ph-$\underline{H}$), 7.65 (2H, s, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 2.25, 3.33, 33.59, 123.86, 129.07, 130.84, 144.69.

Phenyl benzyl sulfoxide (2m): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 3.97-4.08 (2H, m, -*PhC*$\underline{H}_2$-), 6.96-6.97 (2H, d, Ph-$\underline{H}$), 7.21-7.26 (3H, m, Ph-$\underline{H}$), 7.35-7.44 (5H, m, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 63.48, 124.43, 128.86, 128.45, 128.88, 129.11, 130.39, 131,21, 142.67.

(4-(phenylsulfinyl)phenyl)methanol (2n): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 4.67 (2H, s, -*PhC*$\underline{H}_2$-), 7.40-7.45 (5H, m, Ph-$\underline{H}$), 7.53-7.55 (2H, d, Ph-$\underline{H}$), 7.58-7.60 (2H, m, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 64.20, 124.76, 125.04, 127.58, 129.39, 131.18, 143.84, 144.94, 145.10.

Dibenzyl sulfoxide (2o): ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 3.86-3.94 (4H, q, -*PhC*$\underline{H}_2$-), 7.28-7.30 (4H, m, Ph-$\underline{H}$), 7.35-7.40 (6H, m, Ph-$\underline{H}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 57.31, 128.41, 129.00, 130.12, 130.18.

Sulindac (3a): ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 2.16 (3H, s, -*C*$\underline{H}_3$), 2.83 (3H, s, -SO*C*$\underline{H}_3$), 3.59 (2H, s, -*C*$\underline{H}_2$-),6.71-7.04 (3H, Ph-$\underline{H}$), 7.17 (1H, s, C=C$\underline{H}$), 7.19-7.80 (4H, Ph-$\underline{H}$), 12.46 (1H, s, -*COO*$\underline{H}$),^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 10.73, 31.55, 43.58, 106.45(J=95.0 Hz), 110.82(J=90.0 Hz), 124.4, 130.41, 133.01, 138.97, 140.78, 146.74, 162.02, 163.96, 172.05.

Oxfendazole (3b): ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 3.80 (3H, s, -O*C*$\underline{H}_3$), 7.41-7.56 (5H, m, Ph-$\underline{H}$), 7.68-7.80 (3H, m, Ph-$\underline{H}$), 11.98 (2H, br, -*N*$\underline{H}$),^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 53.13, 118.19,124.49, 129.80, 131.15, 138.29, 147.14, 149.38, 154.74.

Oxfendazole (3c): ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.96 (3H, t, -*C*$\underline{H}_3$), 1.47-1.63 (2H, m, -C$\underline{H}_2$-), 2.77-2.84 (2H, m, -C$\underline{H}_2$-), 2.80 (3H, s, -O*C*$\underline{H}_3$), 7.34-7.73 (3H, m, -Ar-$\underline{H}$), 11.95 (2H, br, -N$\underline{H}$); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 13.42, 15.89, 53.11, 58.65, 117.25, 136.59, 149.08, 154.85.

Structure characterization spectra of BCPM and sulfoxides

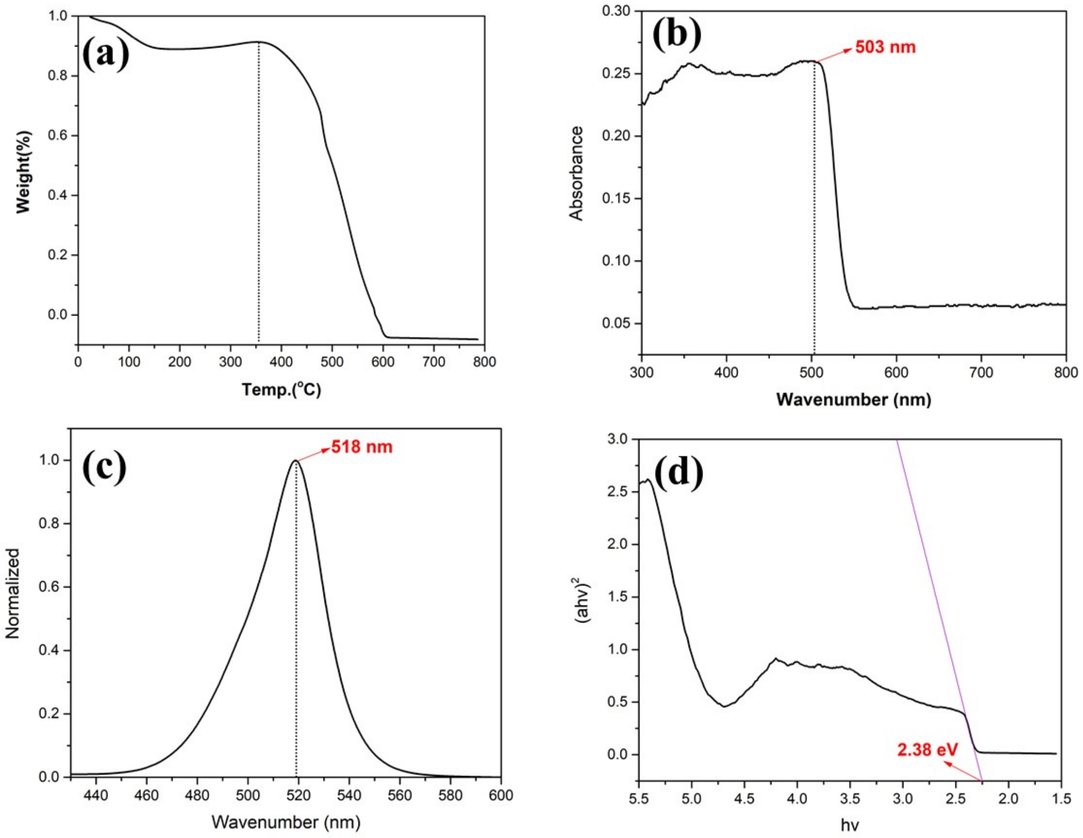


Fig. S1 Structure characterization spectra of **BCPM**. (a) TGA curve; (b)UV-Vis DRS spectra; (c) PL emission spectra; (d) Tauc fitting curve.

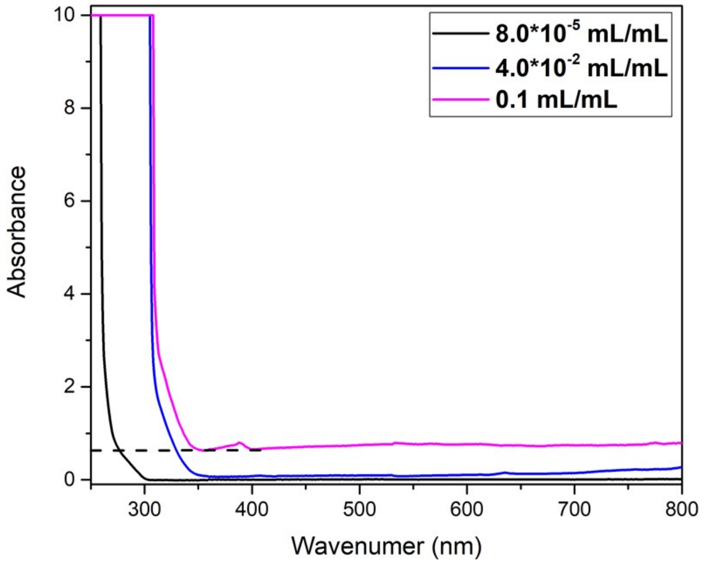
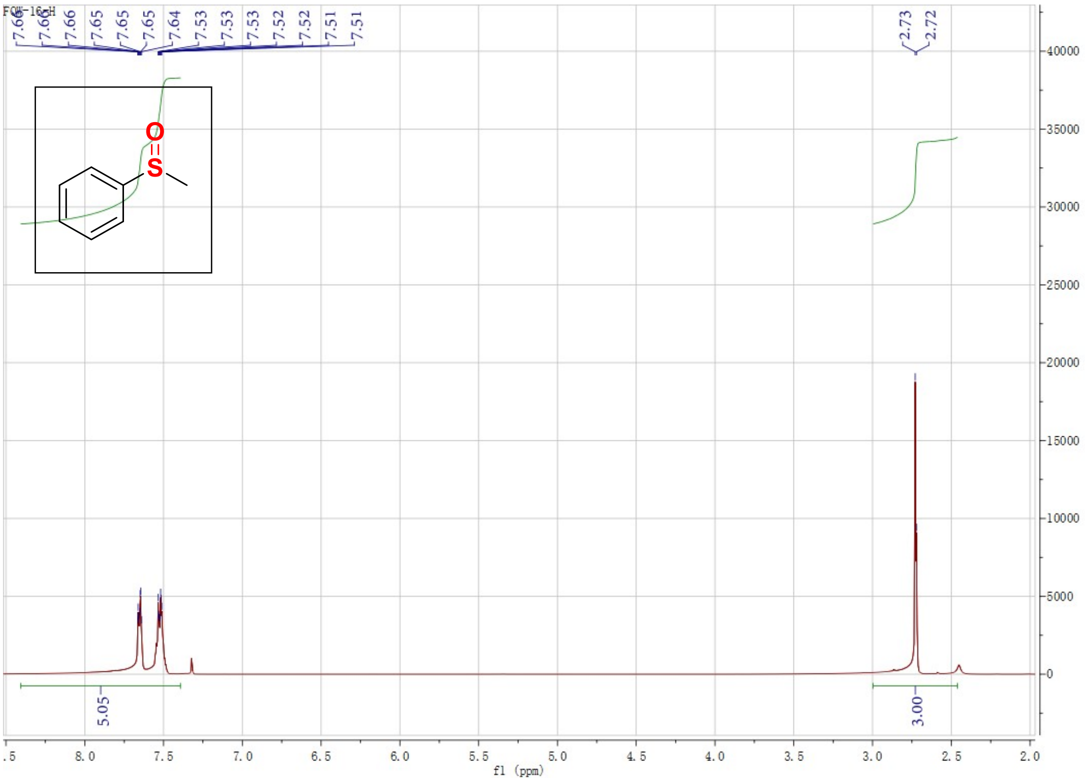
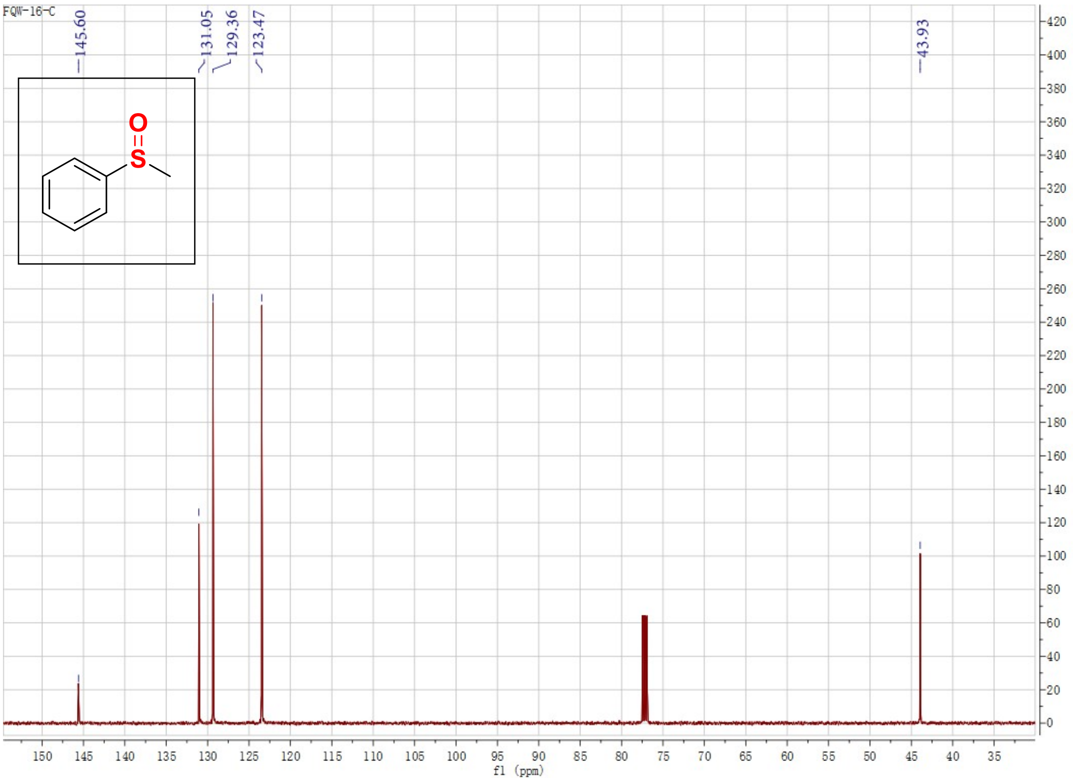


Fig.S2 UV-Vis spectra of thioanisole with different concentrations


FQW-16-H
7.66
7.66
7.66
7.65
7.65
7.65
7.64
7.53
7.53
7.53
7.52
7.52
7.51
7.51
2.73
2.72
O
S
5.05
3.00
40000
35000
30000
25000
20000
15000
10000
5000
0
.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
f1 (ppm)


FQW-16-C
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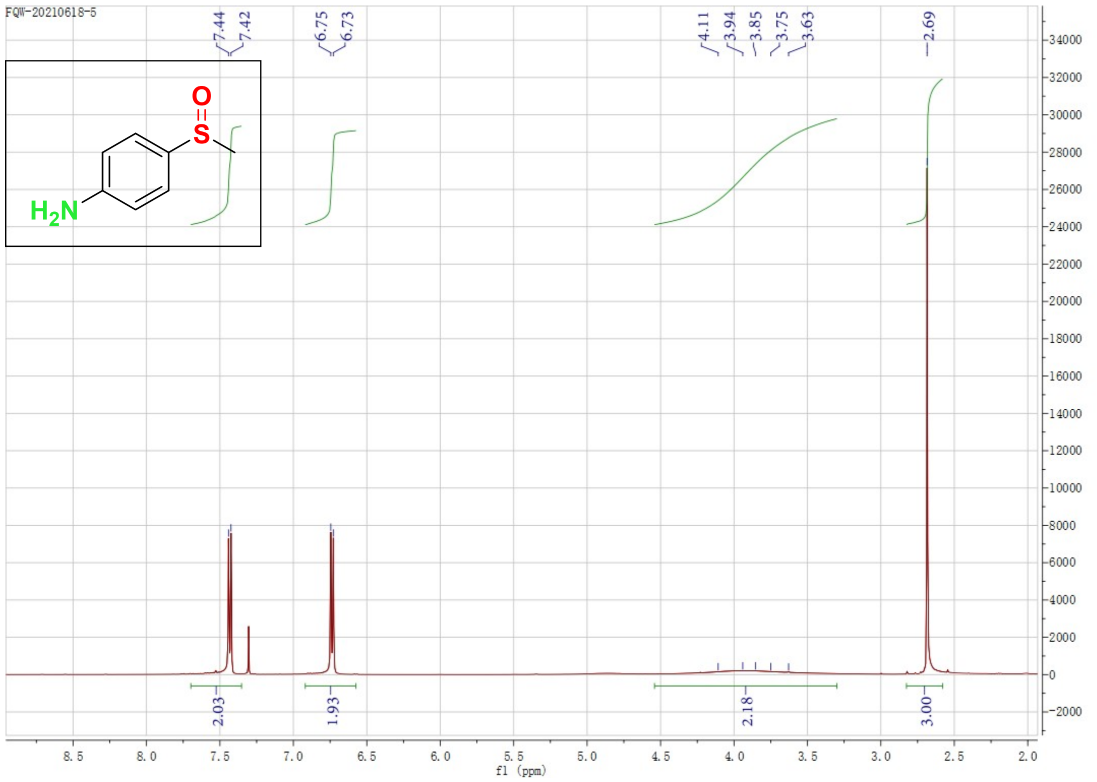
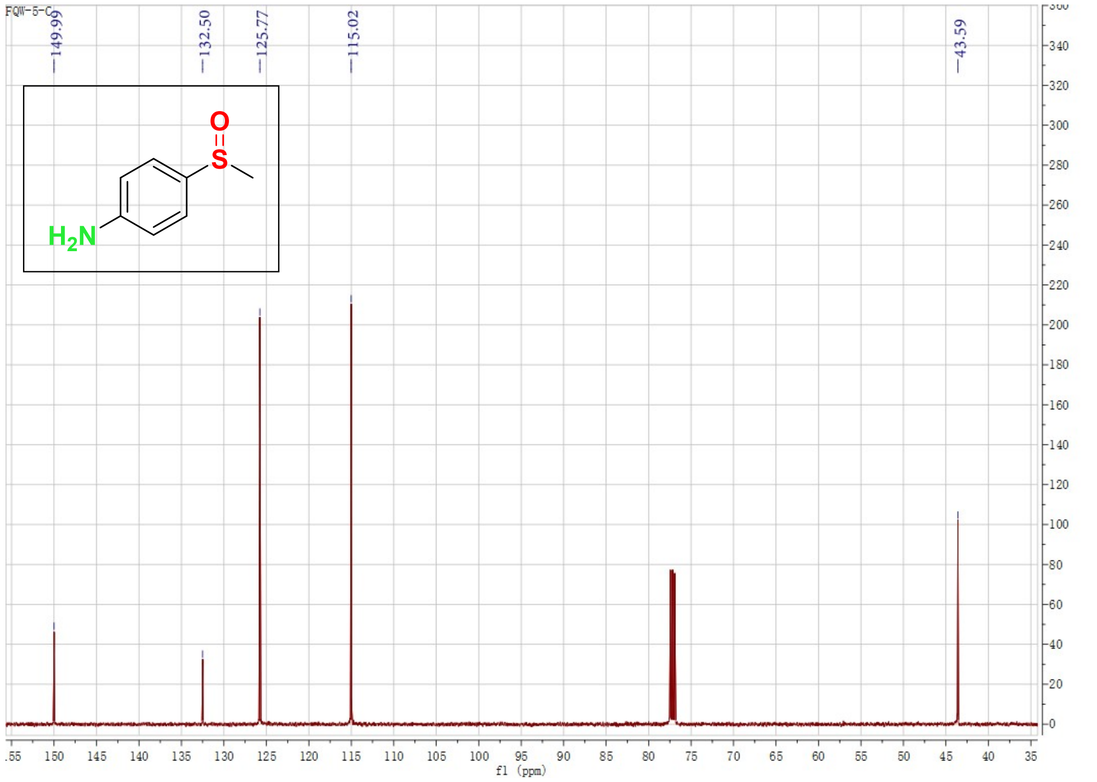
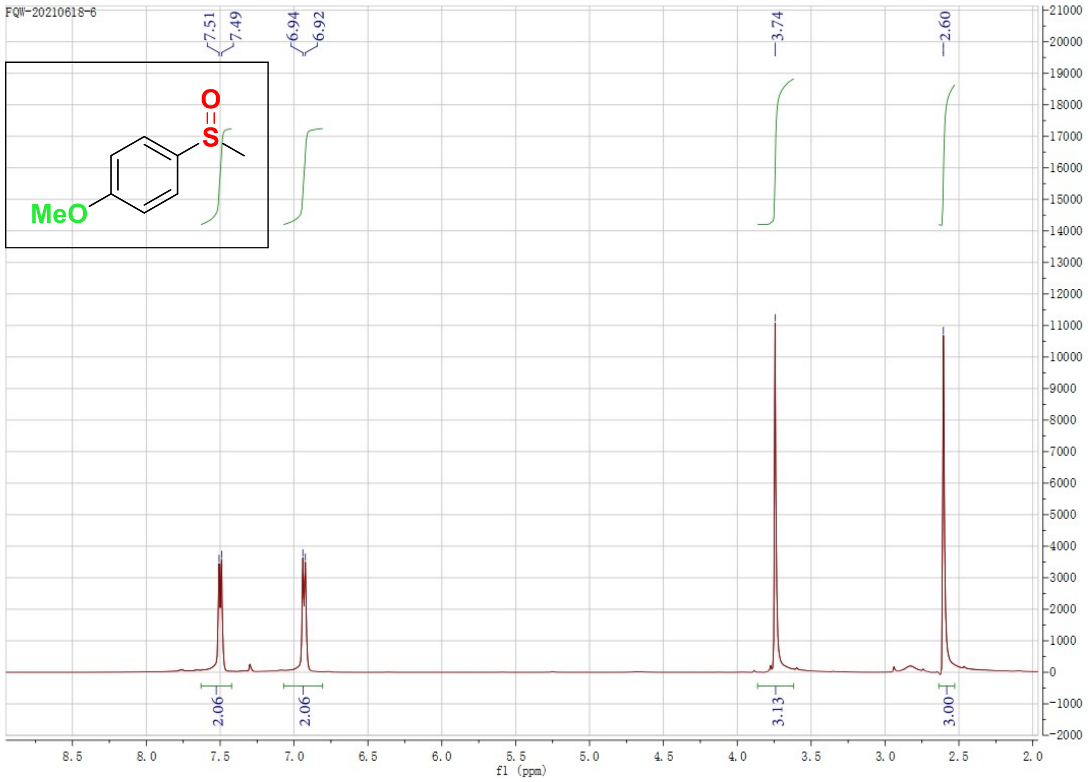
131.05
129.36
123.47
43.93
O
S
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)


FQW-20210618-5
7.44
7.42
6.75
6.73
4.11
3.94
3.85
3.75
3.63
2.69
O
S
H2N
2.03
1.93
2.18
3.00
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
f1 (ppm)
34000 32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000


FQW-5-C
149.99
132.50
125.77
115.02
43.59
O
S
H2N
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)
360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0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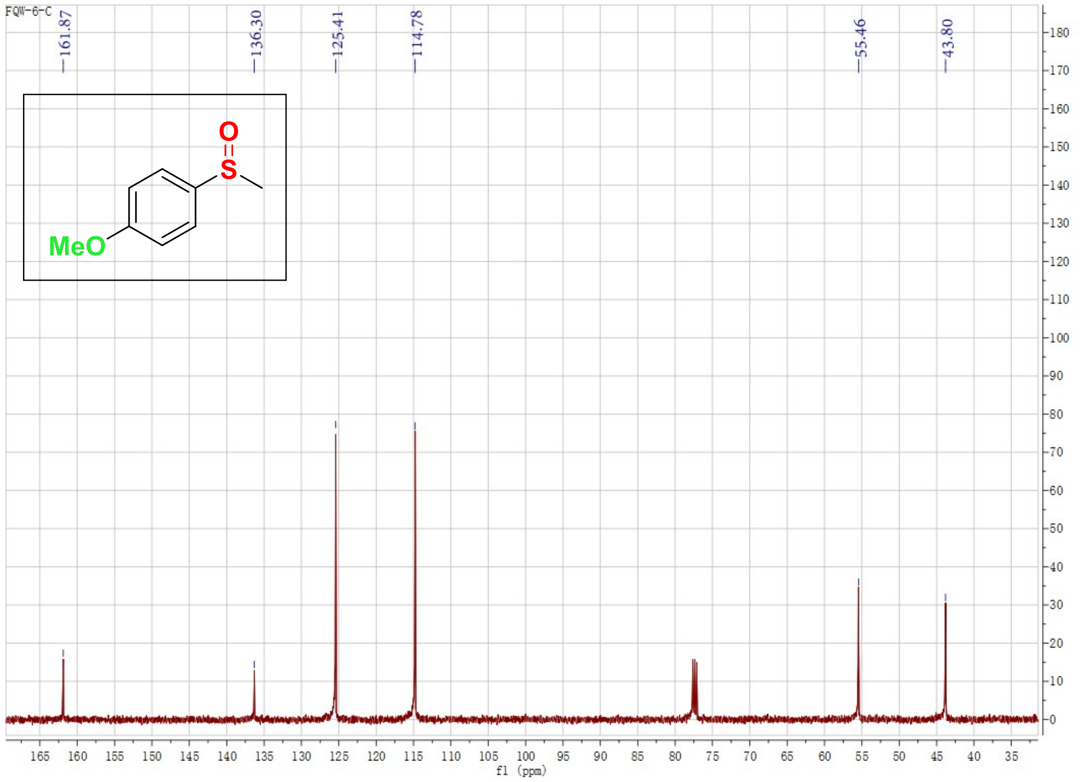
7.49
6.94
6.92
3.74
2.60
MeO
O
S
2.06
2.06
3.13
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
−2000


FQW-6-C
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136.30
125.41
114.78
55.46
43.80
MeO
O
S
165
160
155
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145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)
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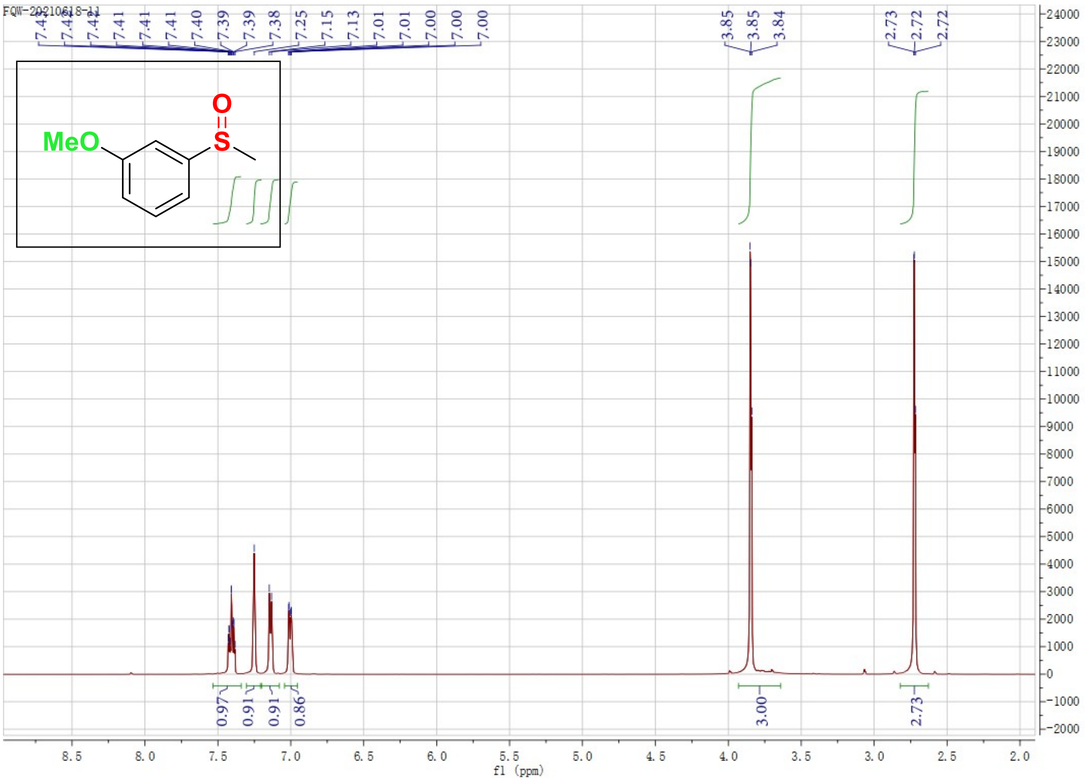
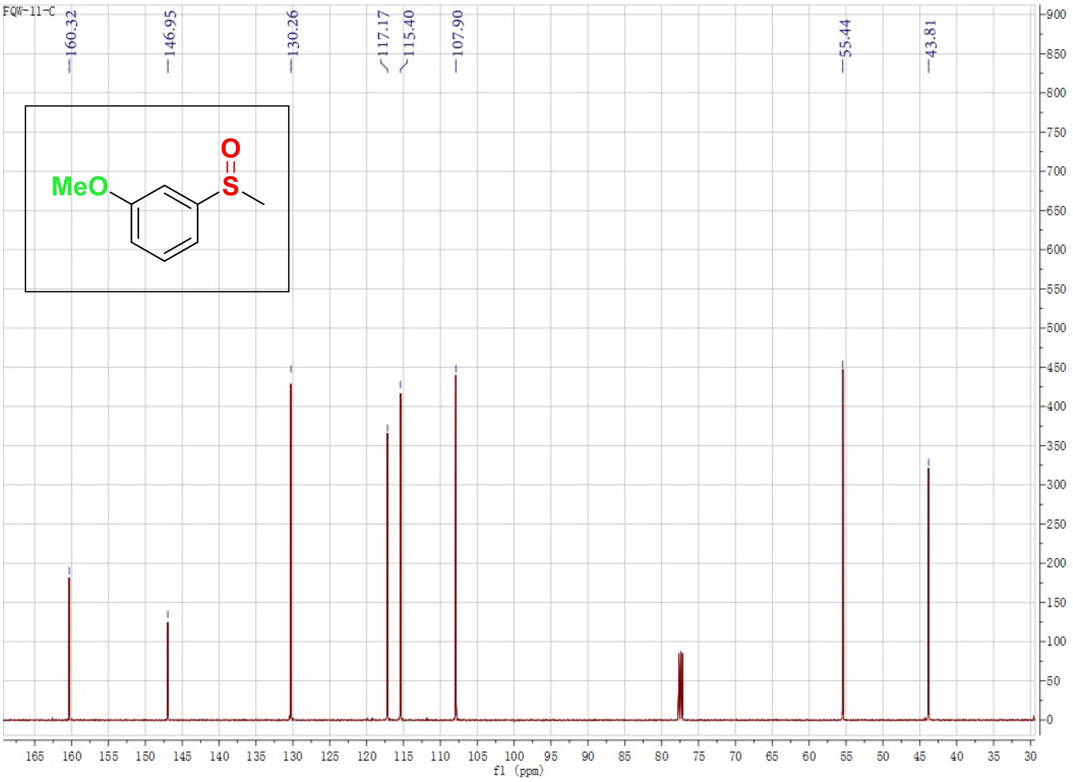
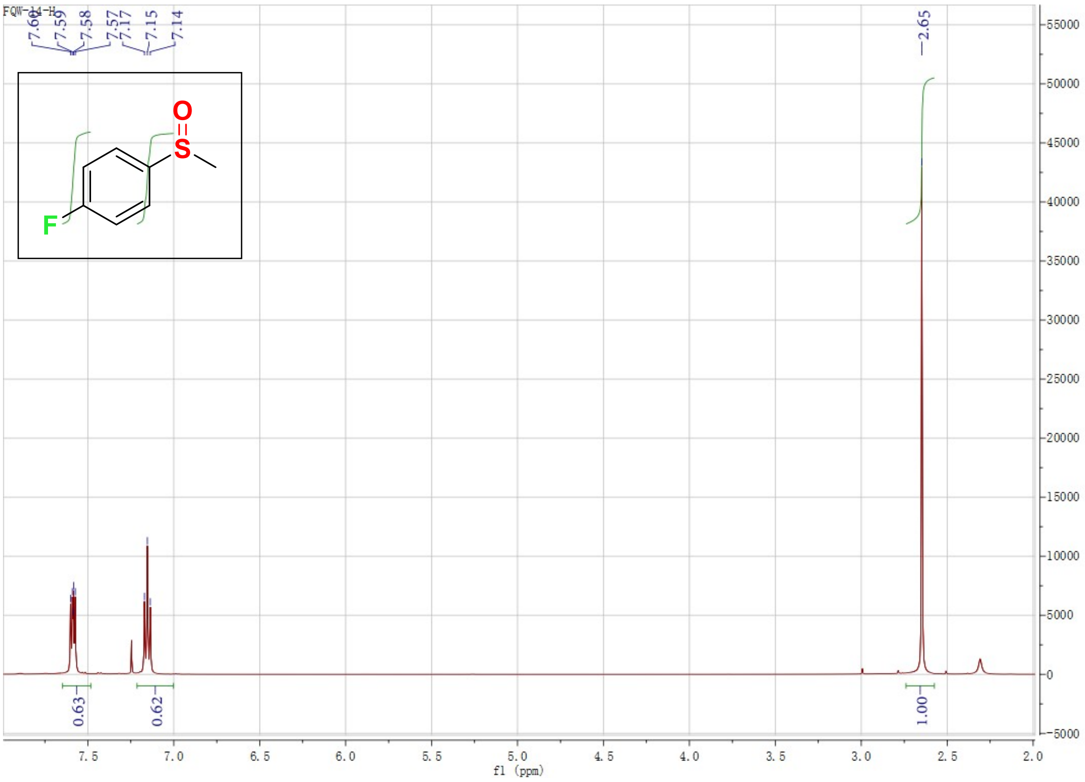
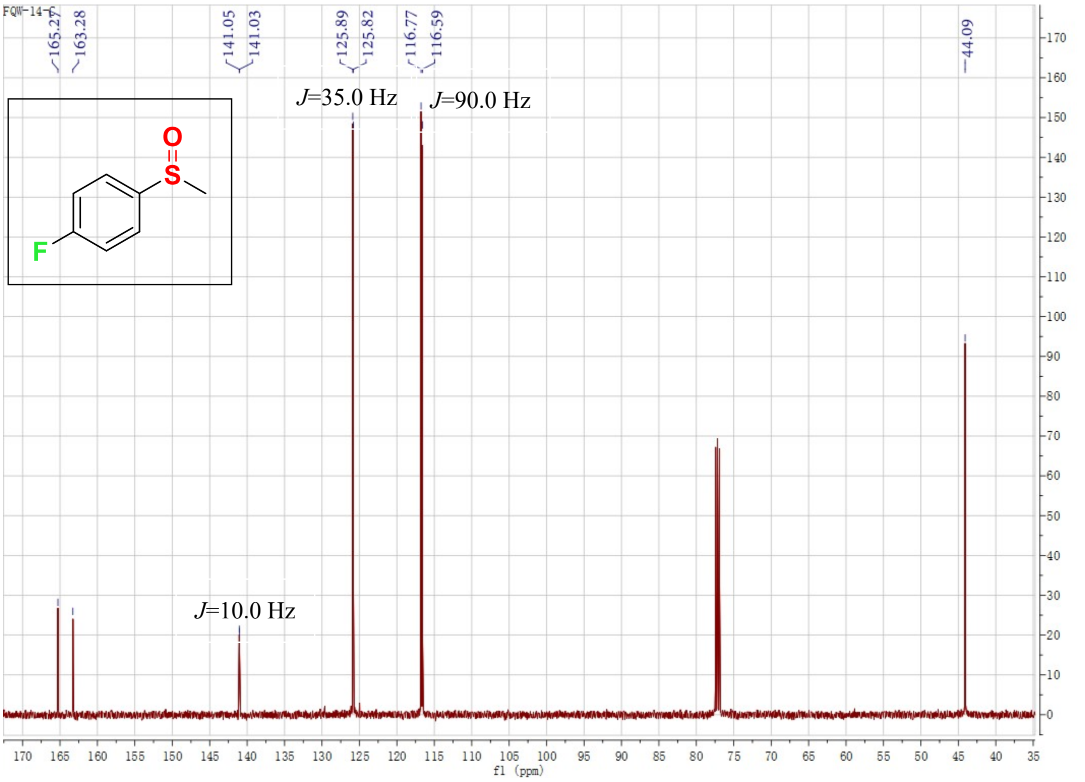
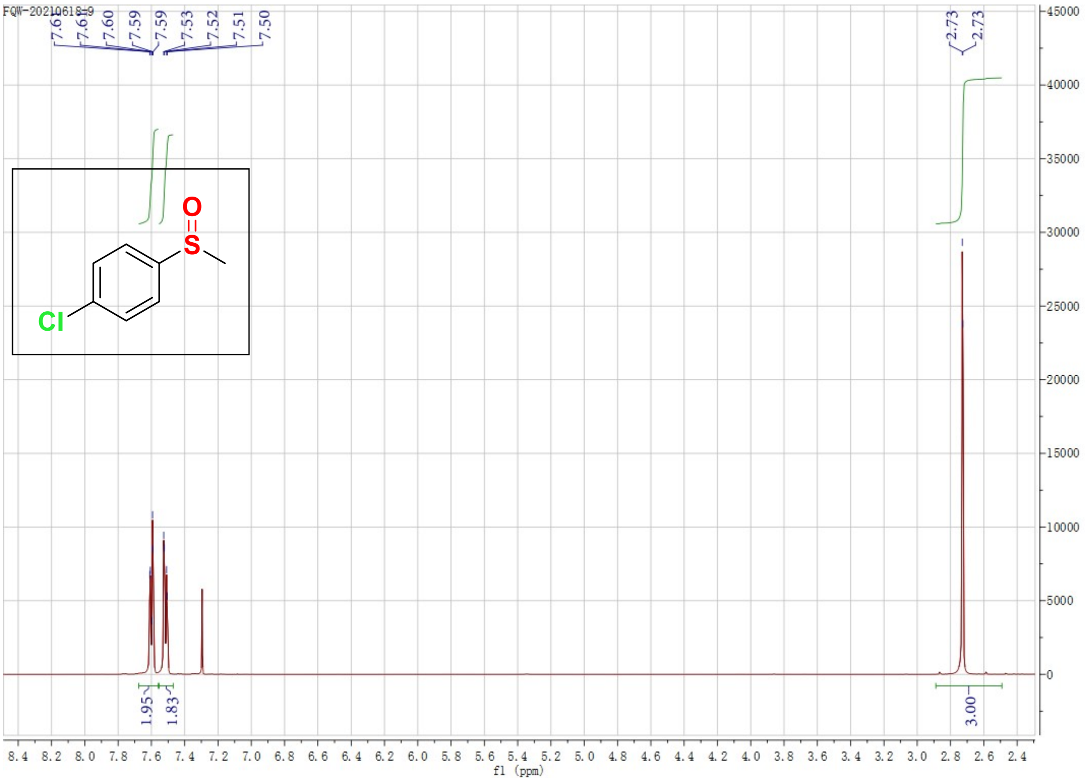
50
40
30
20
10
0

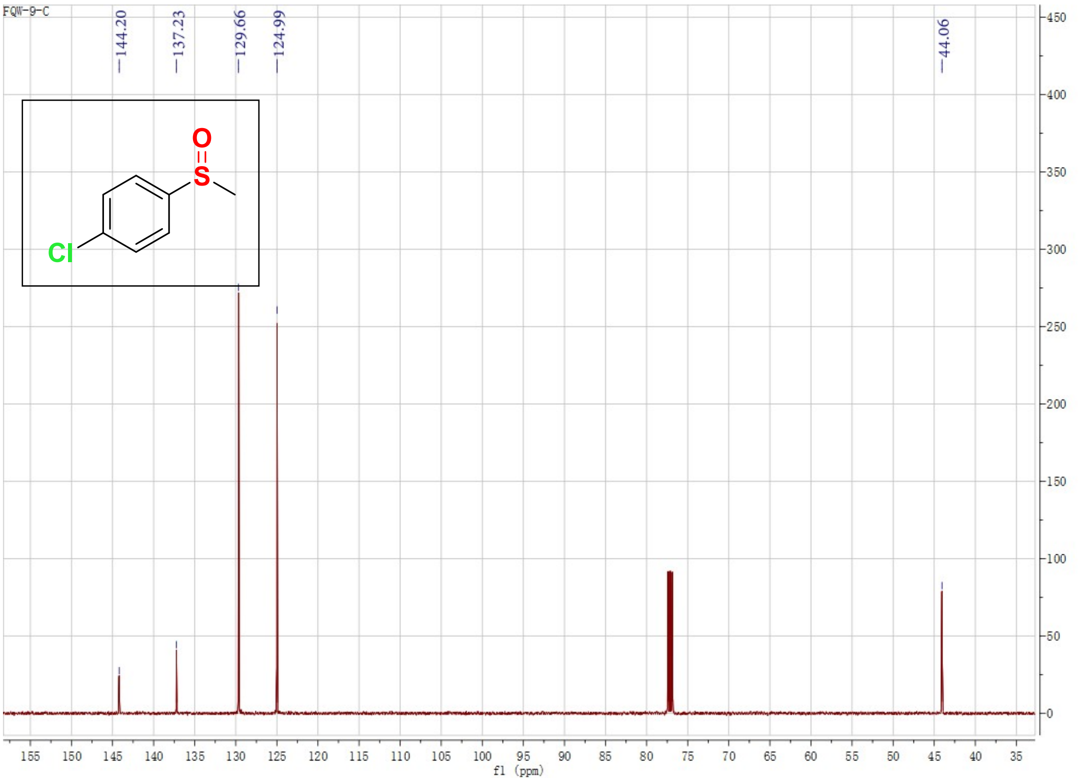

FQW-20210618-11
7.4
7.4
7.4
7.41
7.41
7.41
7.40
7.39
7.39
7.38
7.25
7.15
7.13
7.01
7.01
7.00
7.00
7.00
3.85
3.85
3.84
2.73
2.72
2.72
MeO
O
S
0.97
0.91
0.91
0.86
3.00
2.73
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
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
f1 (ppm)

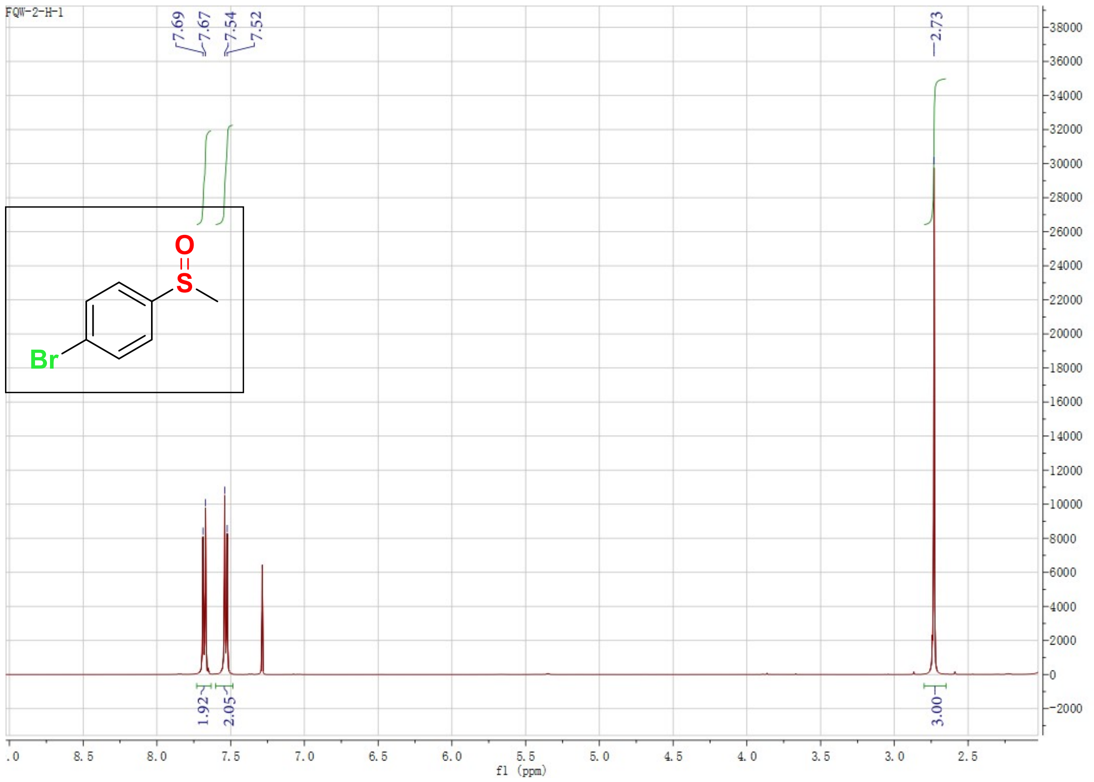

FQW-11-C
160.32
146.95
130.26
117.17
115.40
107.90
55.44
43.81
MeO
O
S
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)

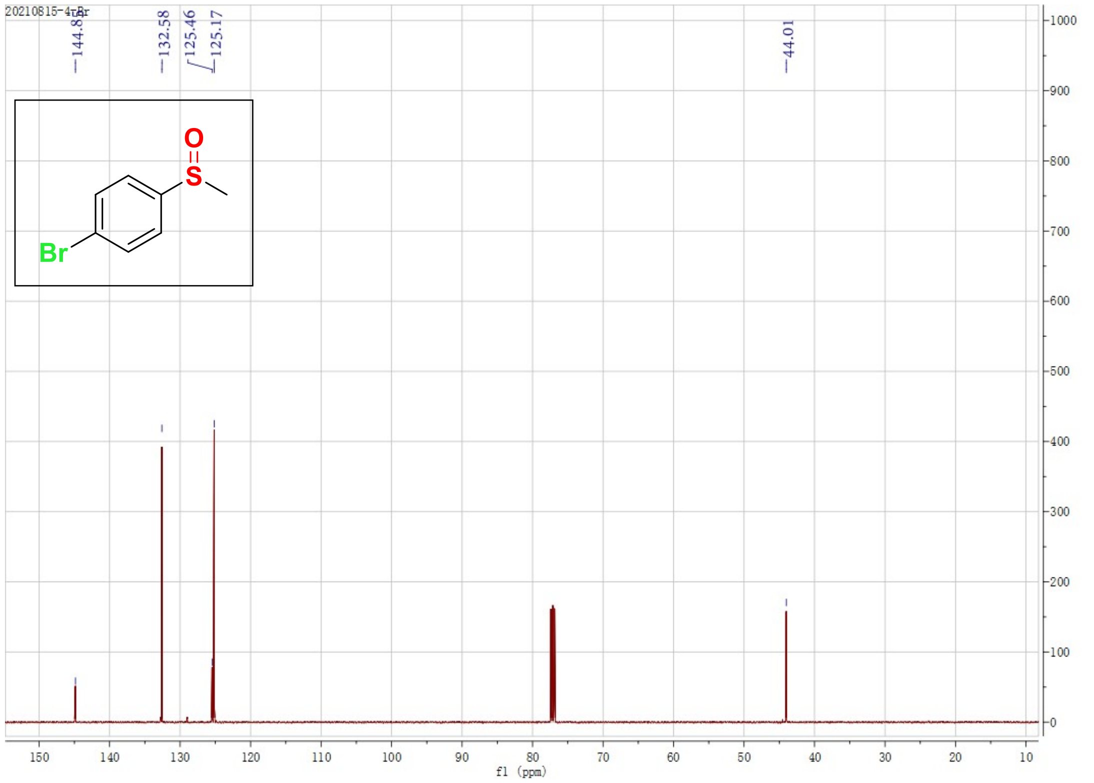

FQW-14-H
7.60
7.59
7.58
7.57
7.17
7.15
7.14
2.65
O
S
F
0.63
0.62
1.00
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

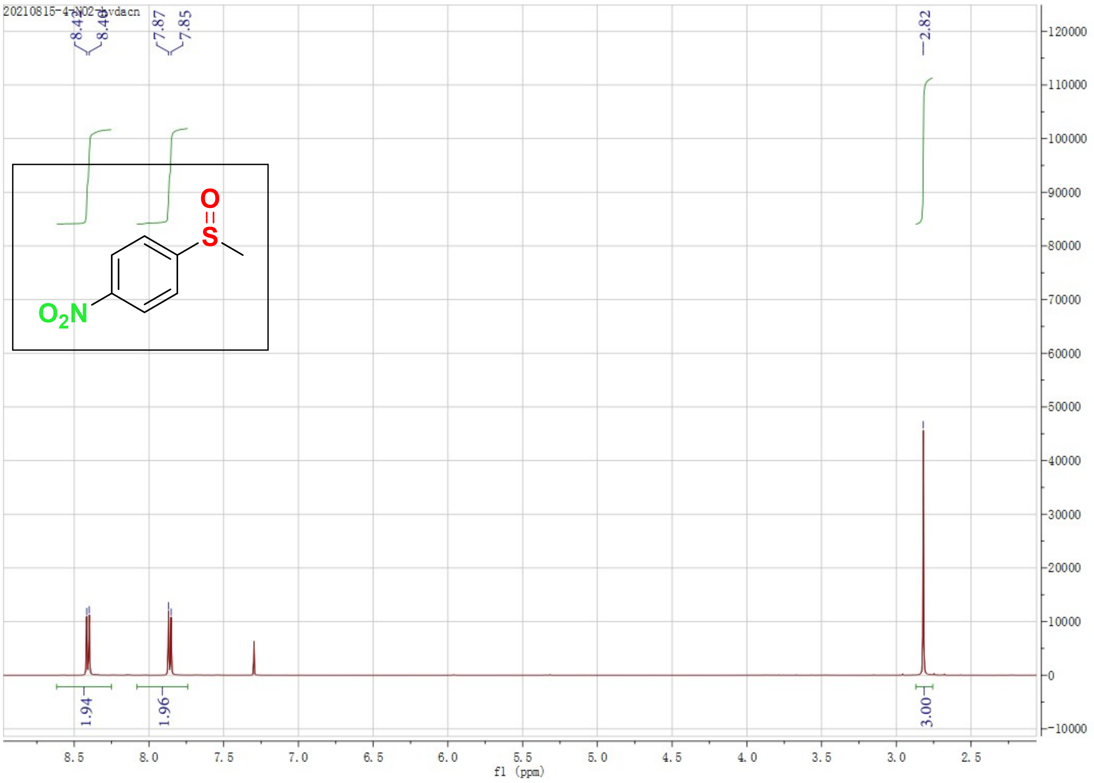

FQW-14-C
165.27
163.28
141.05
141.03
125.89
125.82
116.77
116.59
44.09
J=35.0 Hz
J=90.0 Hz
J=10.0 Hz
O
S
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)

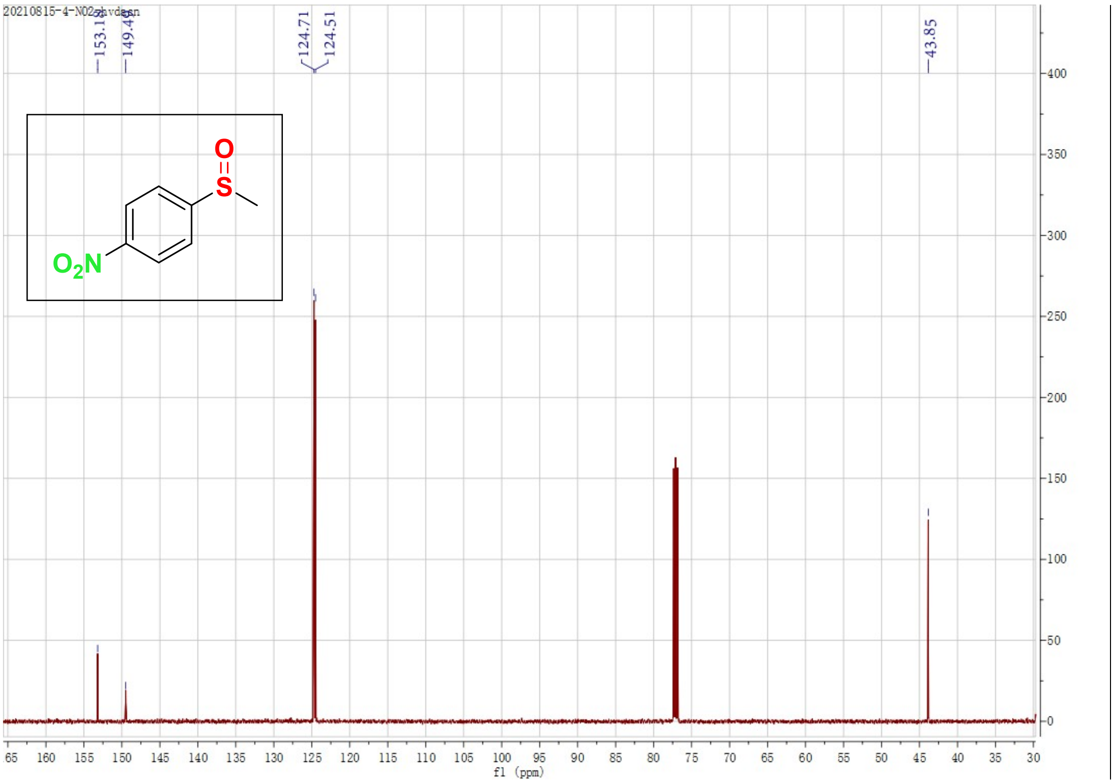

FQW-20210618-9
7.61
7.61
7.60
7.59
7.59
7.53
7.52
7.51
7.50
2.73
2.73
O
S
Cl
1.95
1.83
3.00
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
f1 (ppm)

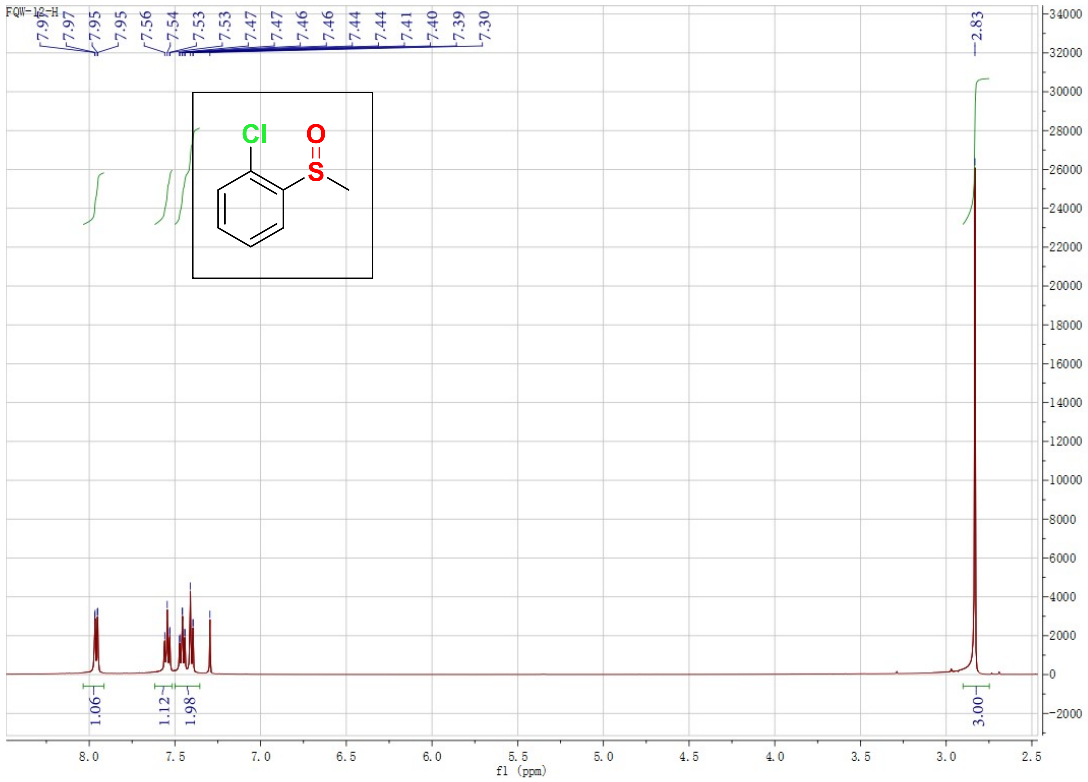

FQW-9-C
144.20
137.23
129.66
124.99
44.06
O
S
Cl
450
400
350
300
250
200
150
100
50
0
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

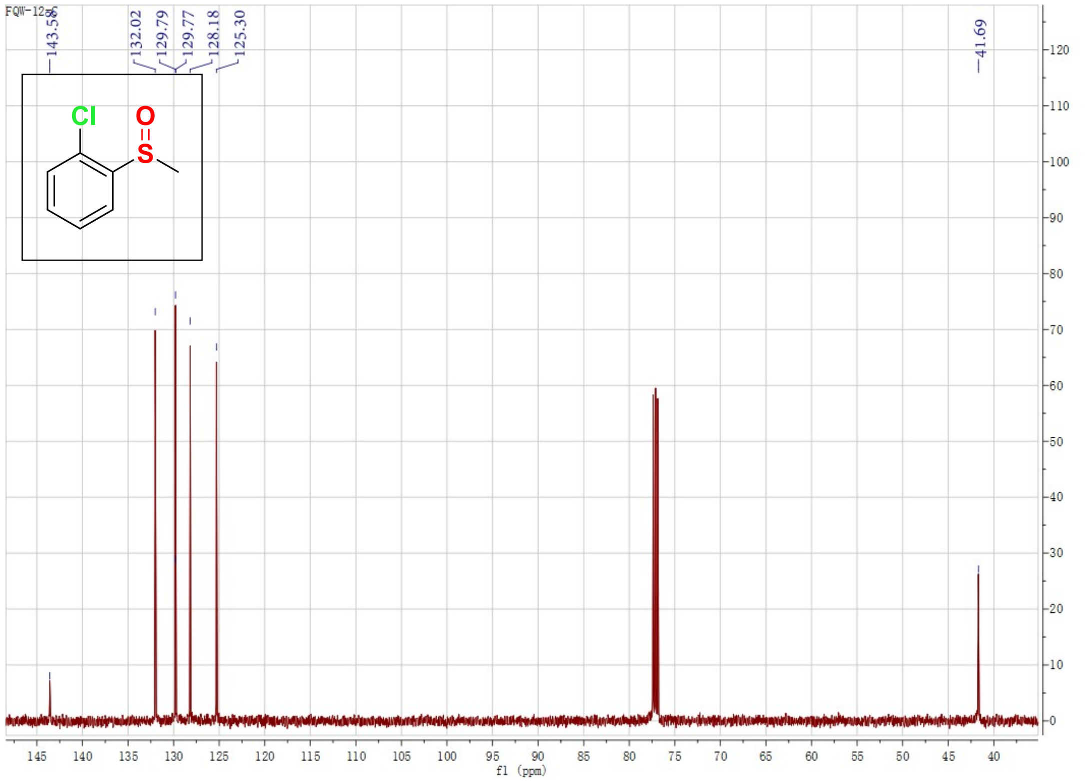

FQW-2-H-1
7.69
7.67
7.54
7.52
2.73
O
S
Br
1.92
2.05
3.00
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

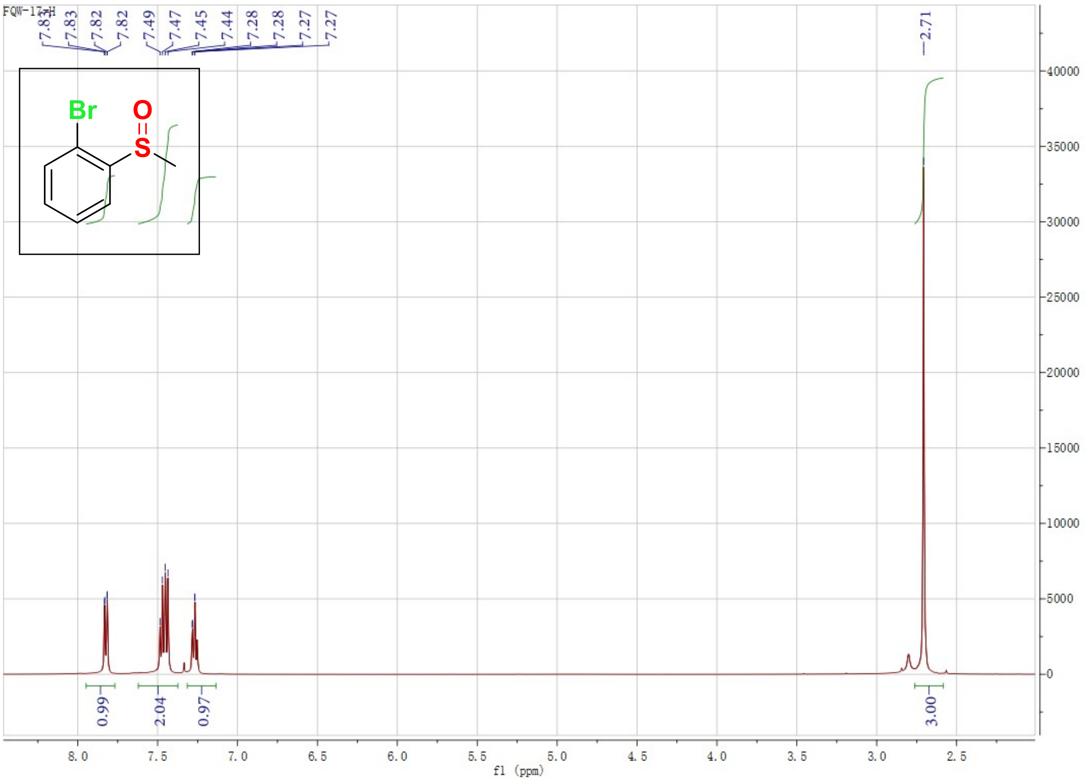

20210815-4-Br
144.85
132.58
125.46
125.17
44.01
O
S
Br
1000
900
800
700
600
500
400
300
200
100
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

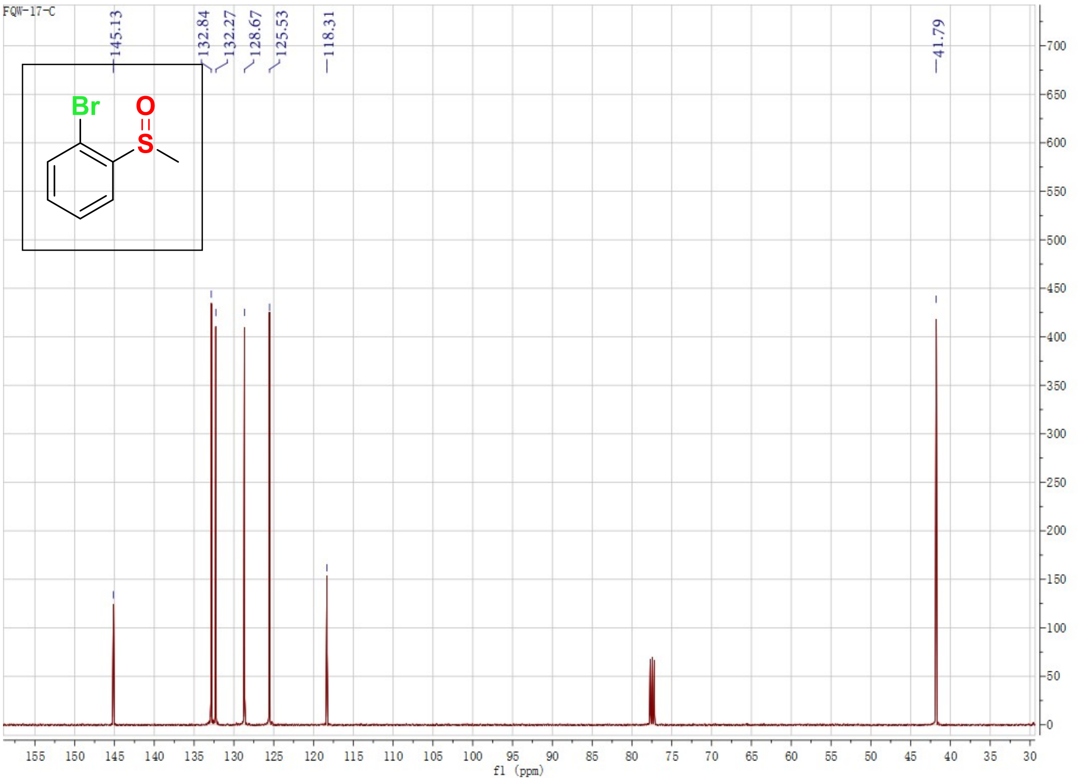

20210815-4-NO2-hvdacn
8.42
8.40
7.87
7.85
2.82
1.94
1.96
3.00
O
S
O2N
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

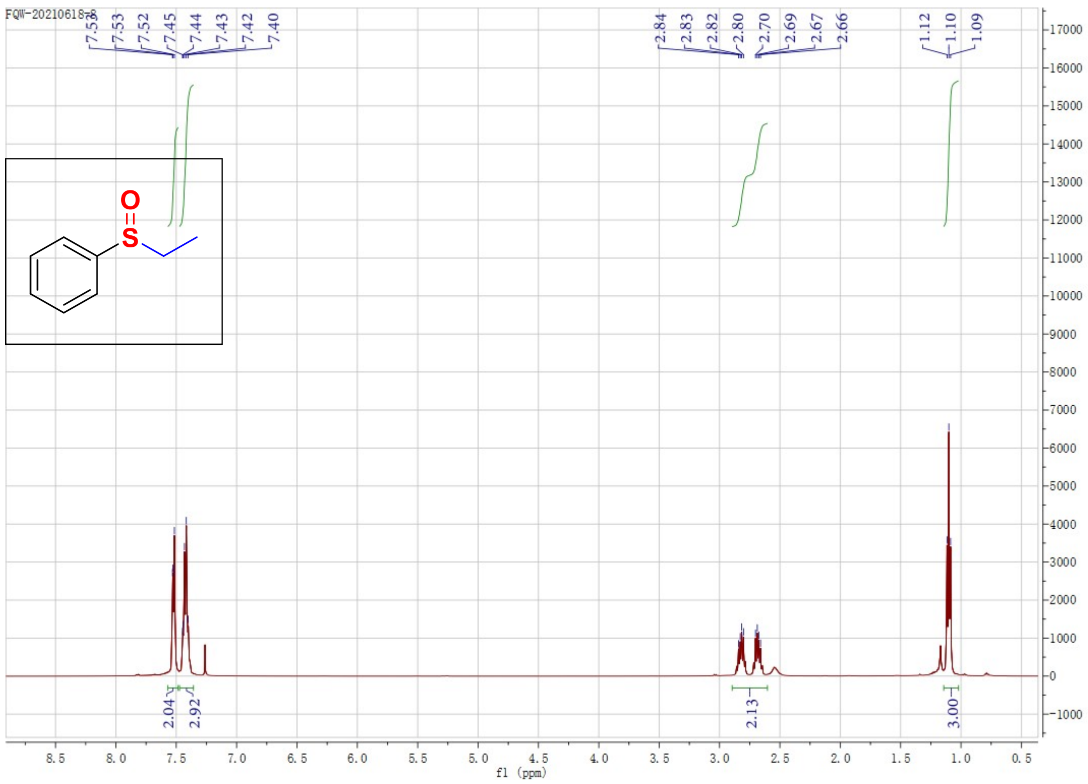

20210815-4-NO2-hvdacn
153.1
149.49
124.71
124.51
43.85
O
S
O2N
400
350
300
250
200
150
100
50
0
65
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)

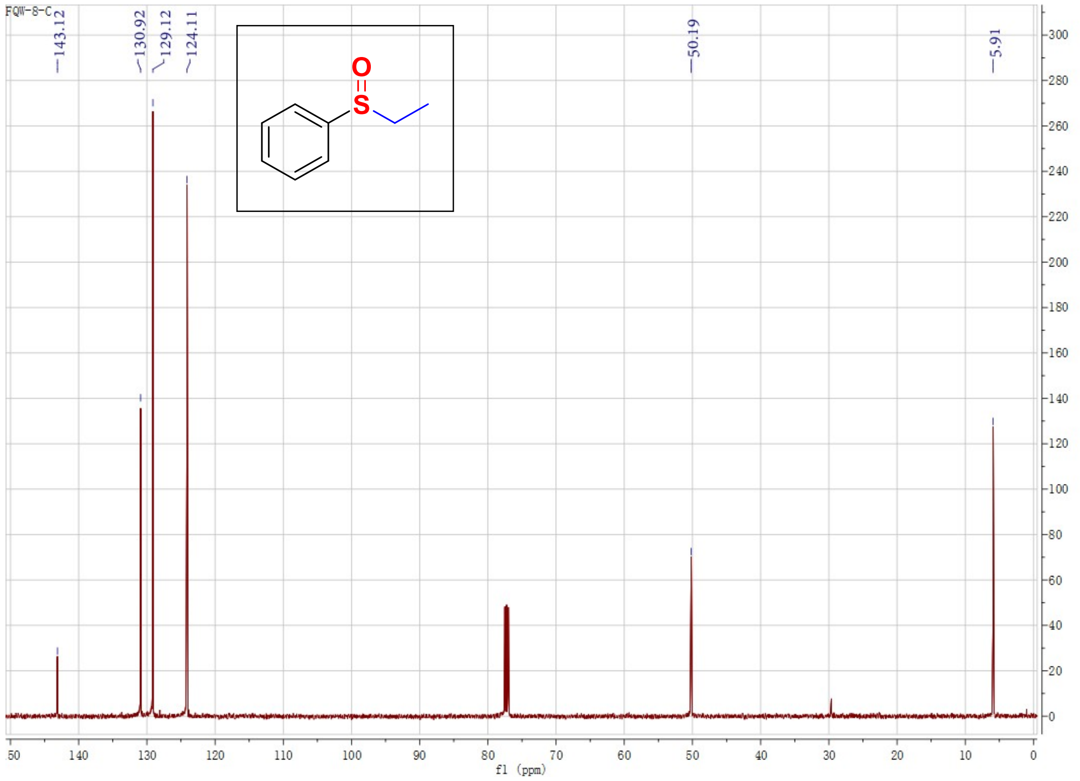

FQW-12-H
7.97
7.97
7.95
7.95
7.56
7.54
7.53
7.53
7.47
7.47
7.46
7.46
7.44
7.44
7.41
7.40
7.39
7.30
2.83
Cl
O
S
1.06
1.12
1.98
3.00
f1 (ppm)

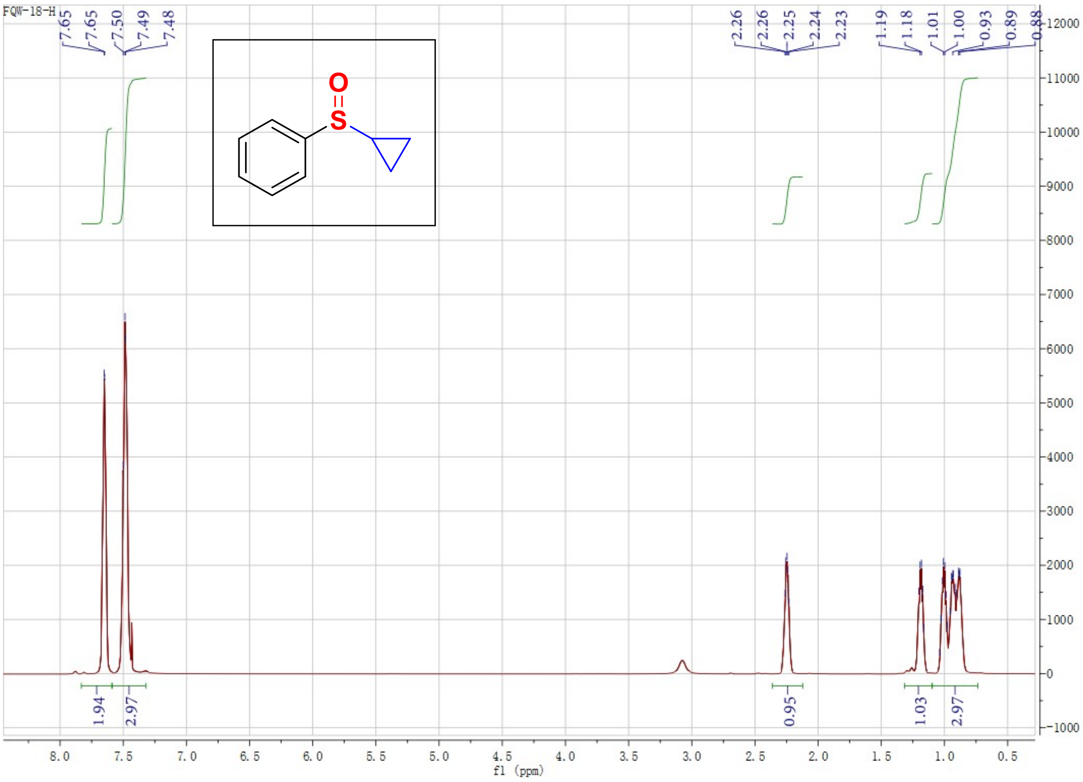

FQW-12-C
143.58
132.02
129.79
129.77
128.18
125.30
41.69
Cl
O
S
f1 (ppm)

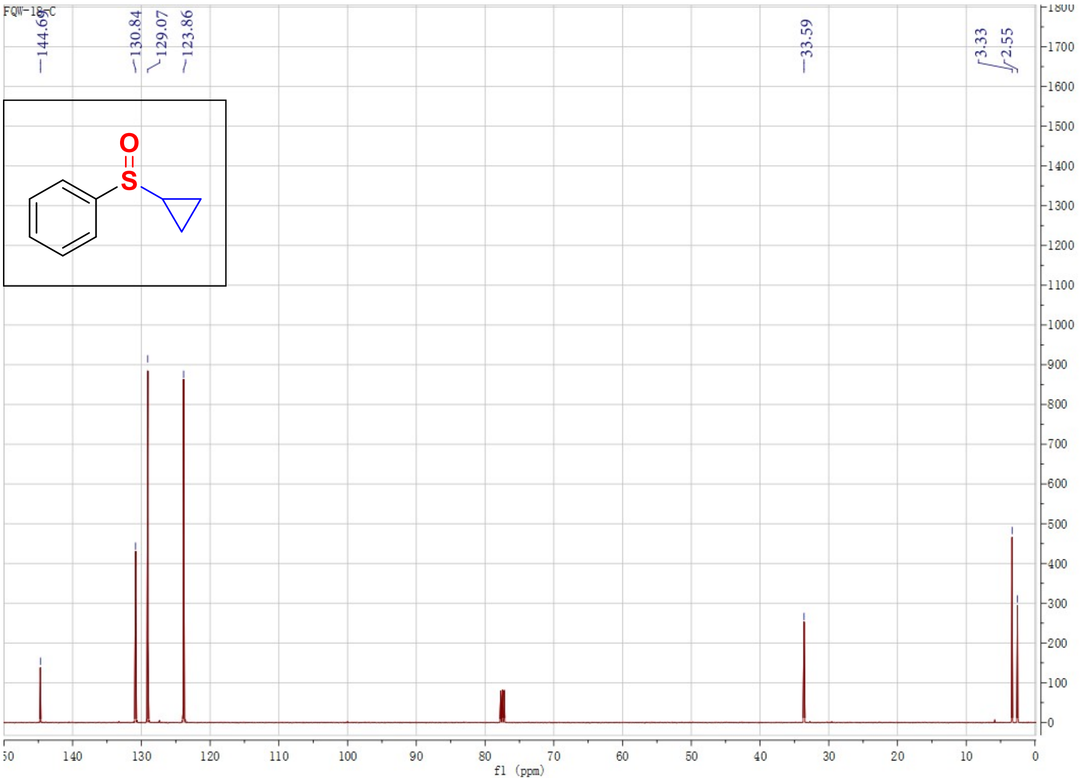

FQW-17-H
7.84
7.83
7.82
7.82
7.49
7.47
7.45
7.44
7.28
7.28
7.27
7.27
2.71
Br
O
S
0.99
2.04
0.97
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)
40000
35000
30000
25000
20000
15000
10000
5000
0

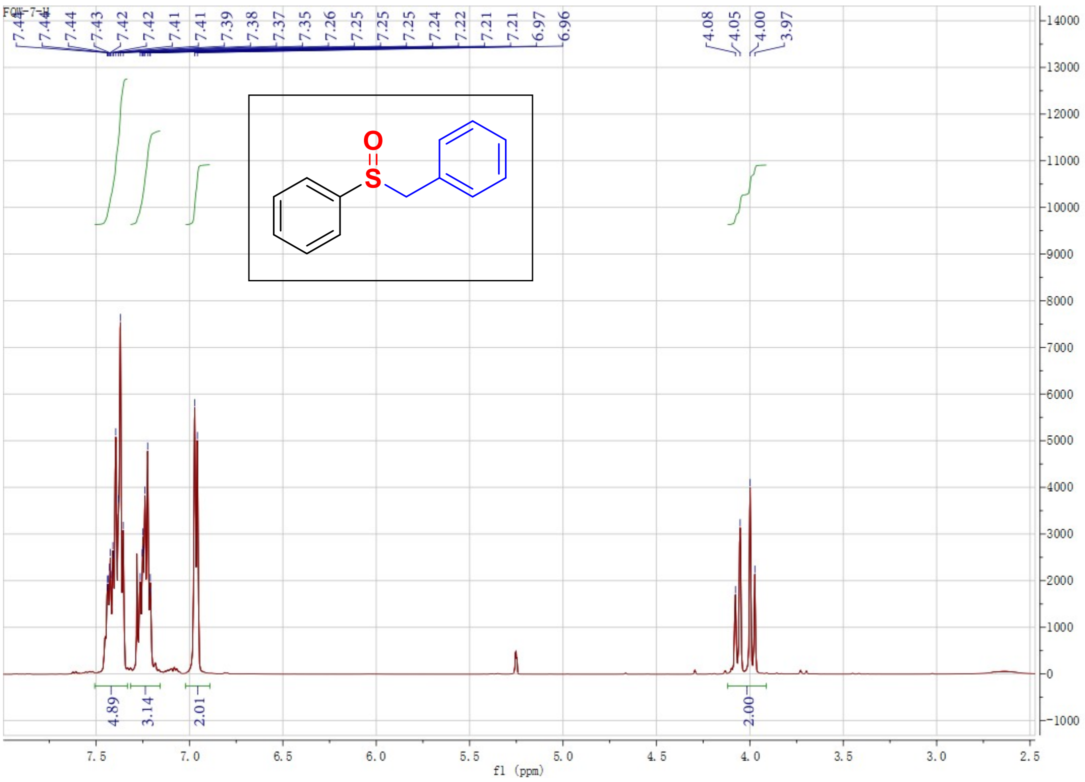

FQW-17-C
145.13
132.84
132.27
128.67
125.53
118.31
41.79
Br
O
S
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0

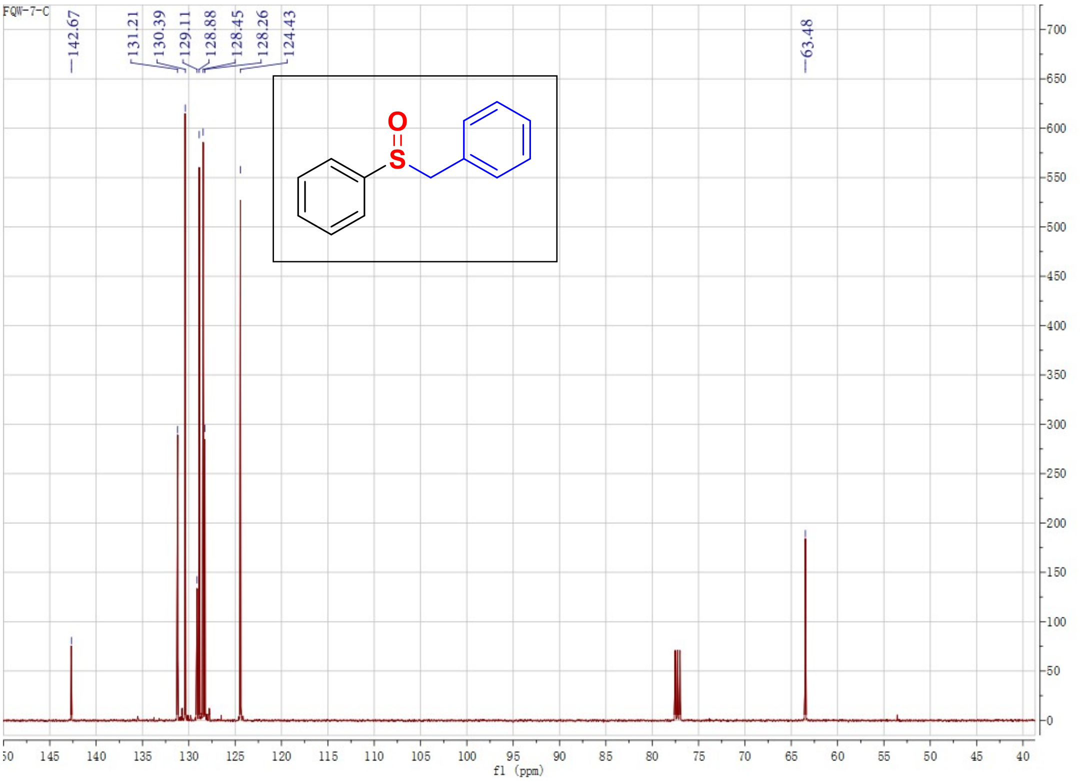

FQW-20210618-8
7.53
7.53
7.52
7.45
7.44
7.43
7.42
7.40
2.84
2.83
2.82
2.80
2.70
2.69
2.67
2.66
1.12
1.10
1.09
O
S
2.04
2.92
2.13
3.00
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

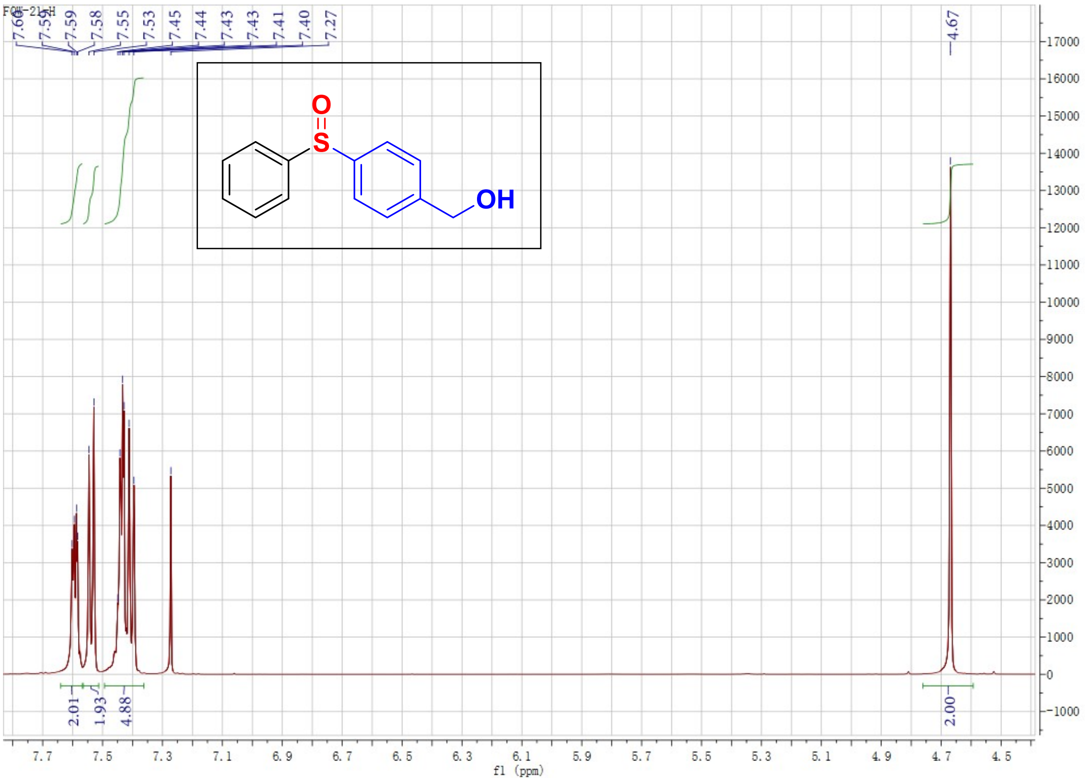

FQW-8-C
143.12
130.92
129.12
124.11
50.19
5.91
O
S
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

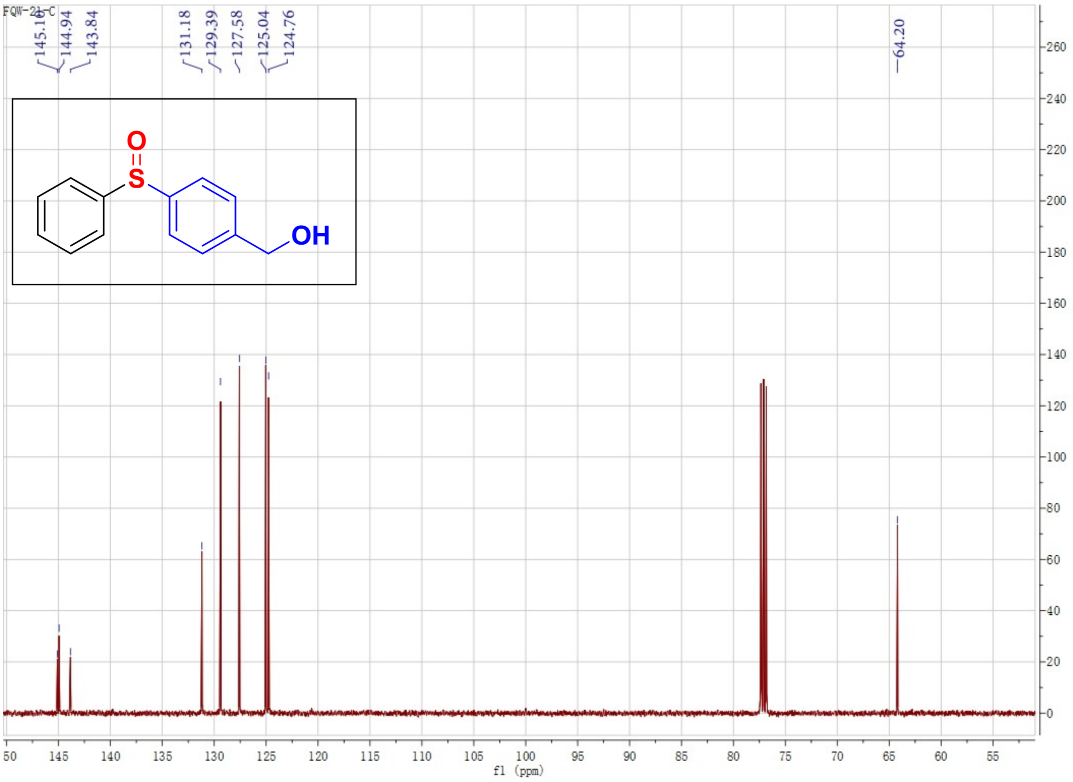

FQW-18-H
7.65
7.65
7.50
7.49
7.48
2.26
2.26
2.25
2.24
2.23
1.19
1.18
1.01
1.00
0.93
0.89
0.88
O
S
1.94
2.97
0.95
1.03
2.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

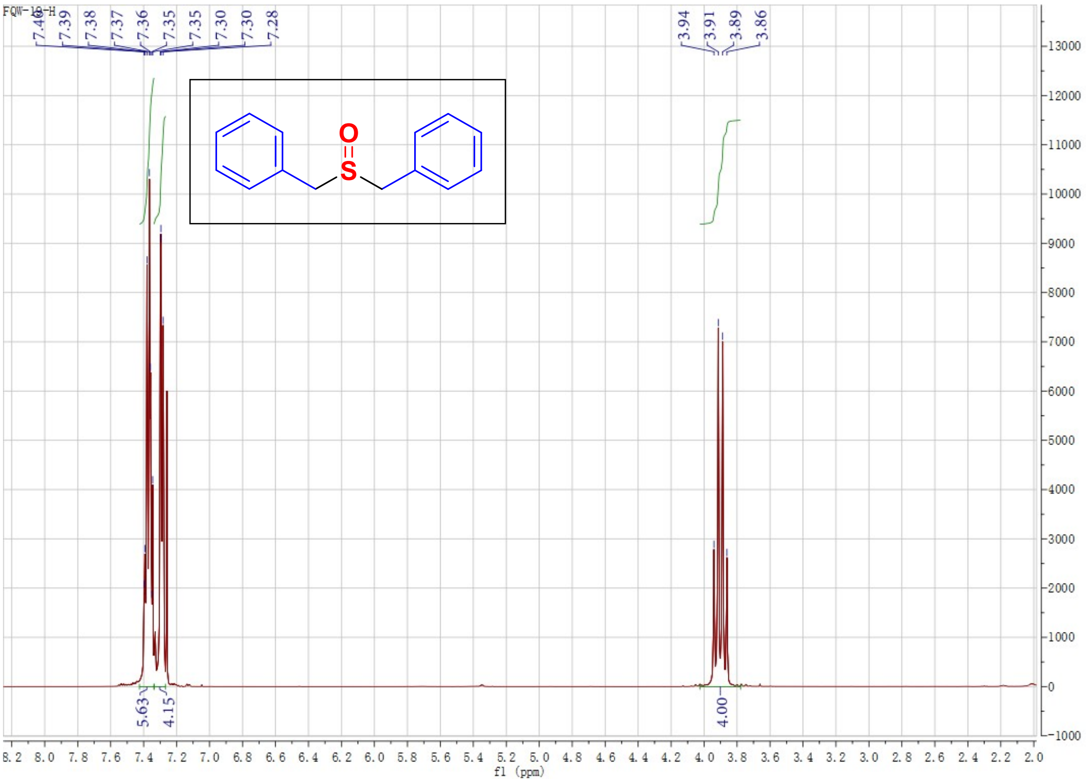

FQW-18-C
144.69
130.84
129.07
123.86
33.59
3.33
2.55
O
S
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0

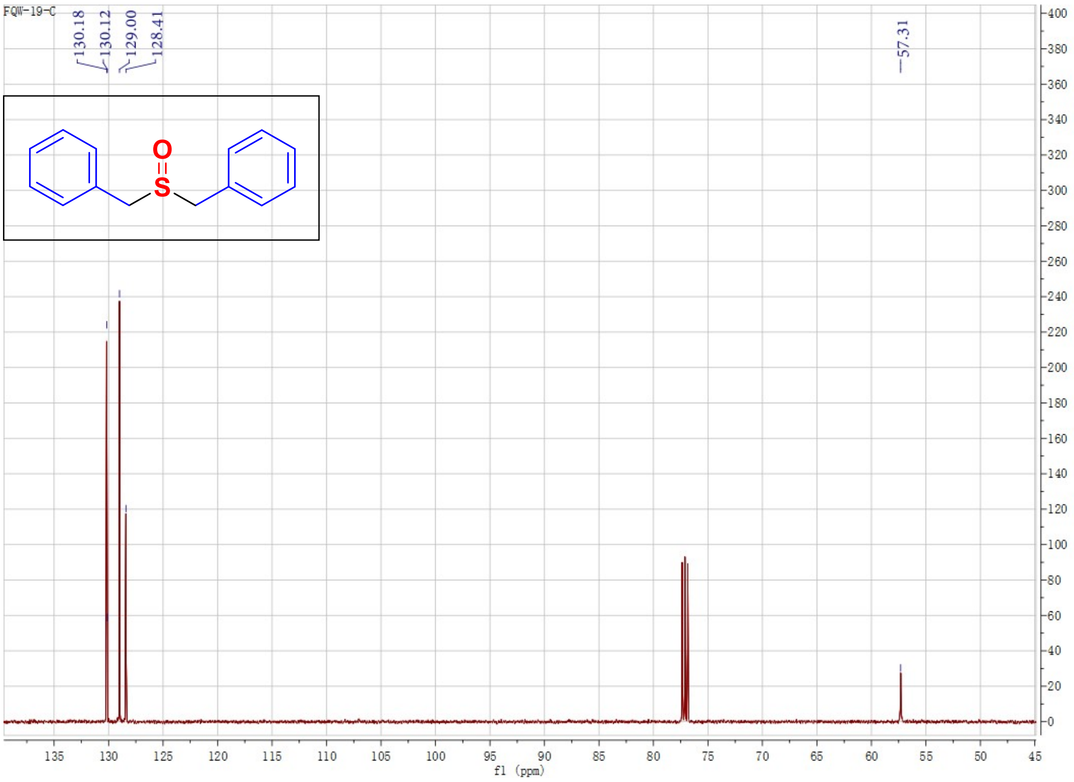

FQW-7-H
7.44
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.39
7.38
7.37
7.35
7.26
7.25
7.25
7.25
7.24
7.22
7.21
7.21
6.97
6.96
4.08
4.05
4.00
3.97
O
S
4.89
3.14
2.01
2.00
f1 (ppm)

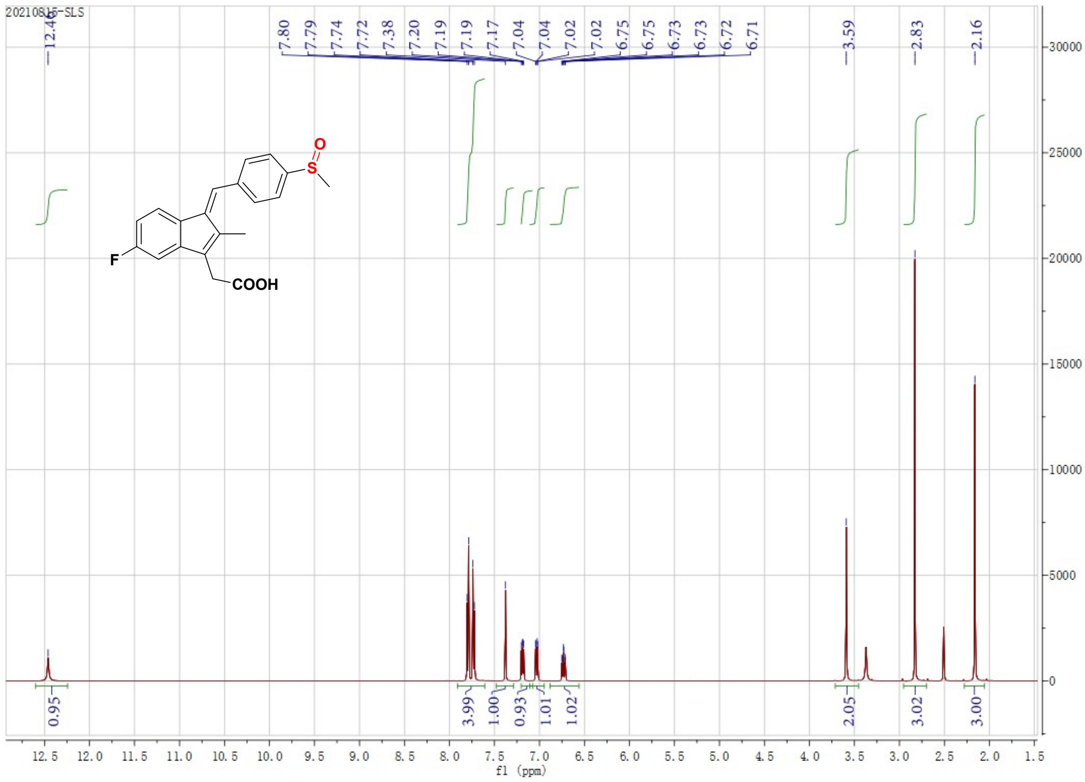

FQW-7-C
142.67
131.21
130.39
129.11
128.88
128.45
128.26
124.43
63.48
O
S
f1 (ppm)

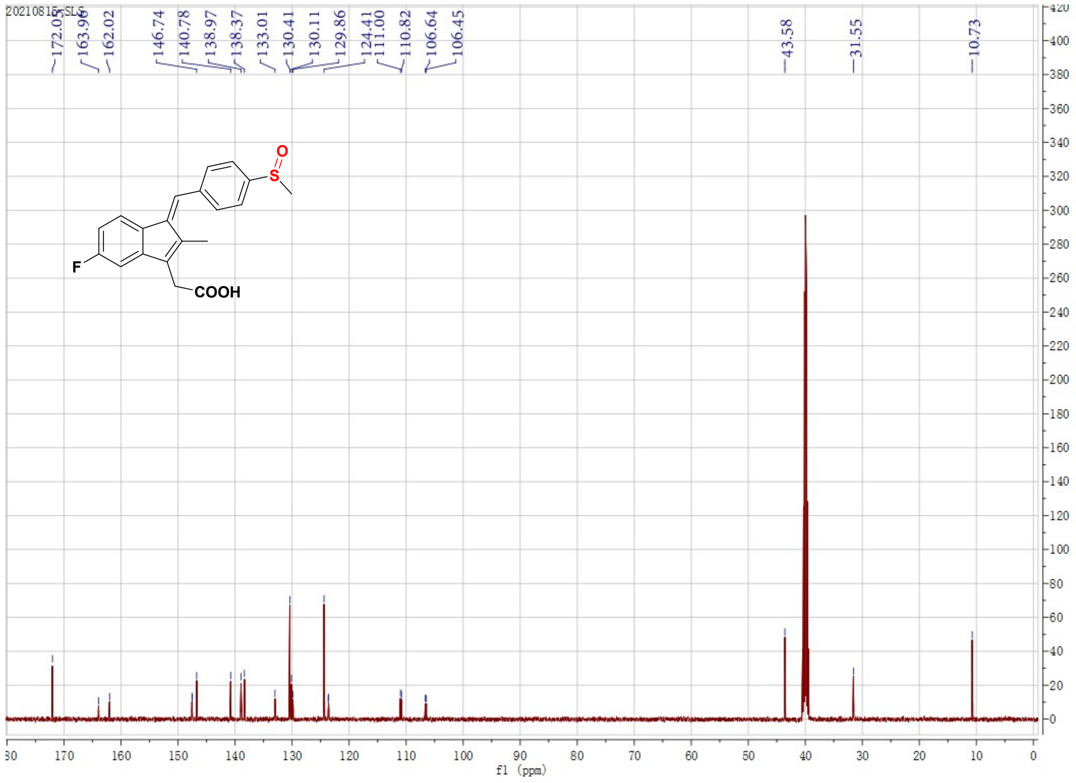

FQW-21-H
7.60
7.59
7.59
7.58
7.55
7.53
7.45
7.44
7.43
7.43
7.41
7.40
7.27
4.67
O
S
OH
2.01
1.93
4.88
2.00
f1 (ppm)

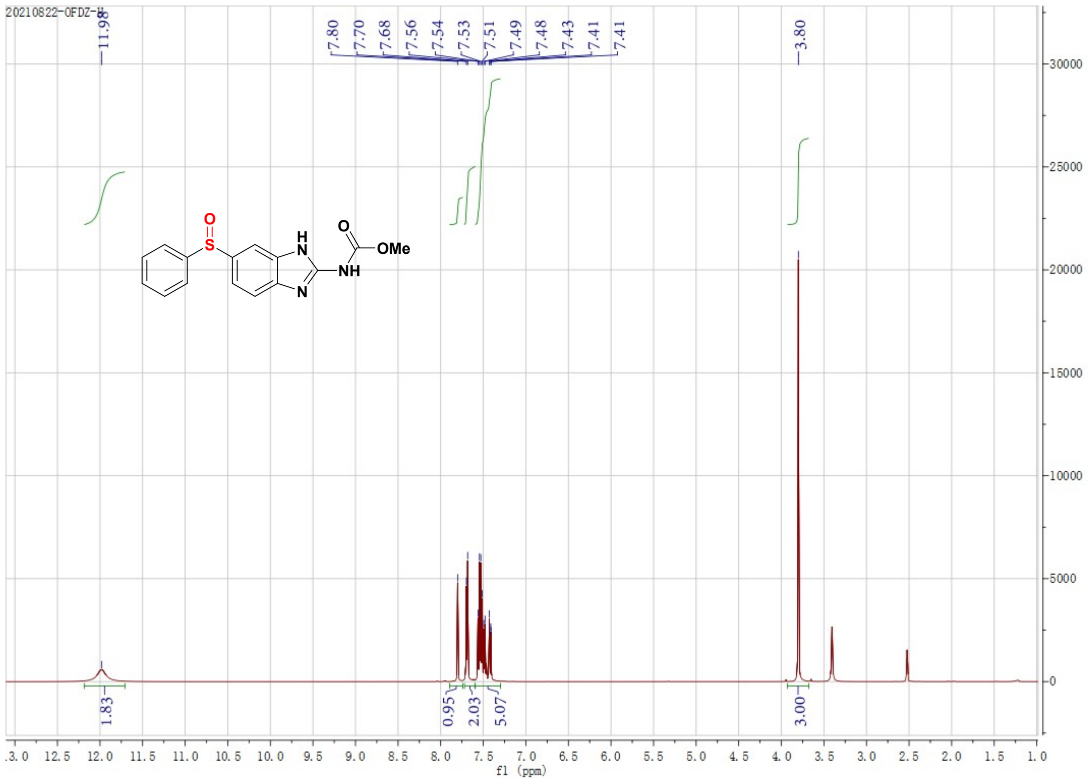

FQW-21-C
145.16
144.94
143.84
131.18
129.39
127.58
125.04
124.76
64.20
O
S
OH
f1 (ppm)


FQW-19-H
7.40
7.39
7.38
7.37
7.36
7.35
7.35
7.30
7.30
7.28
3.94
3.91
3.89
3.86
O
S
5.63
4.15
4.00
f1 (ppm)


FQW-19-C
130.18
130.12
129.00
128.41
57.31
O
S
f1 (ppm)


20210815-SLS
12.46
7.80
7.79
7.74
7.72
7.38
7.20
7.19
7.19
7.17
7.04
7.04
7.02
7.02
6.75
6.75
6.73
6.73
6.72
6.71
3.59
2.83
2.16
0.95
3.99
1.00
0.93
1.01
1.02
2.05
3.02
3.00
F
COOH
S
O
fl (ppm)


20210815-SLS
172.05
163.96
162.02
146.74
140.78
138.97
138.37
133.01
130.41
130.11
129.86
124.41
111.00
110.82
106.64
106.45
43.58
31.55
10.73
F
COOH
S
O
fl (ppm)


20210822-OFDZ-H
11.98
7.80
7.70
7.68
7.56
7.54
7.53
7.51
7.49
7.48
7.43
7.41
7.41
3.80
1.83
0.95
2.03
5.07
3.00
O
S
H
N
N
O
OMe
NH
f1 (ppm)
.3.0
12.5
12.0
11.5
11.0
10.5
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
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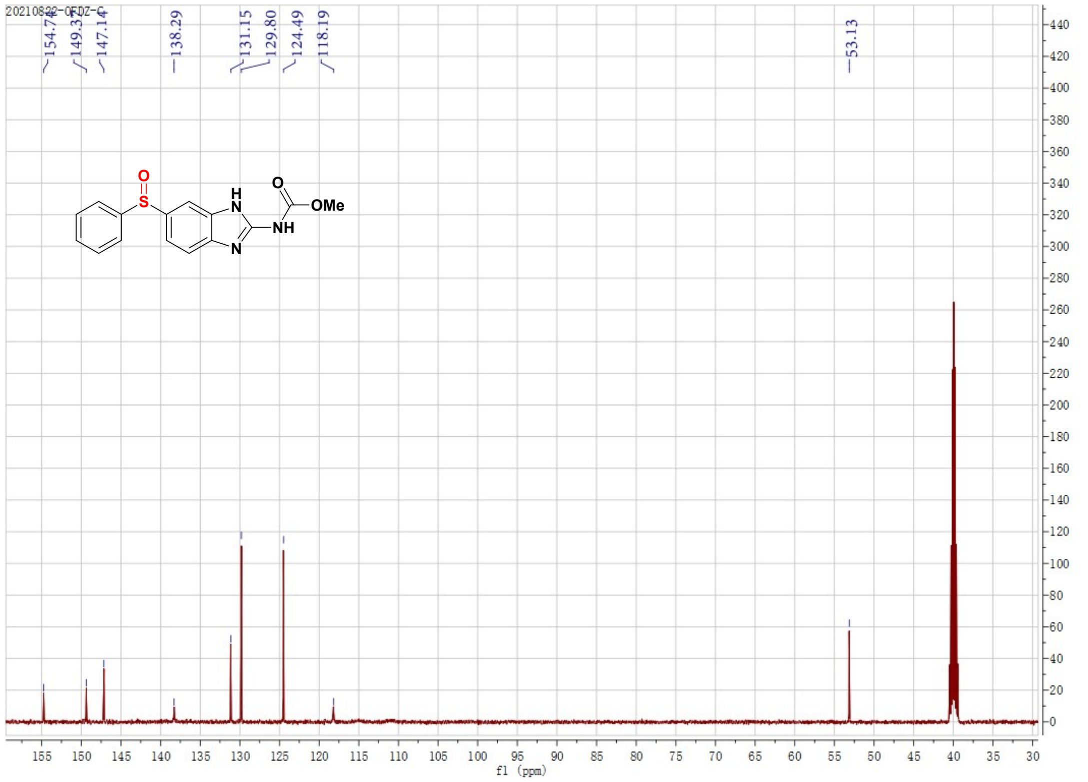
25000
20000
15000
10000
5000
0


20210822-OFDZ-C
154.74
149.32
147.14
138.29
131.15
129.80
124.49
118.19
53.13
O
S
H
N
N
O
OMe
NH
f1 (ppm)
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0

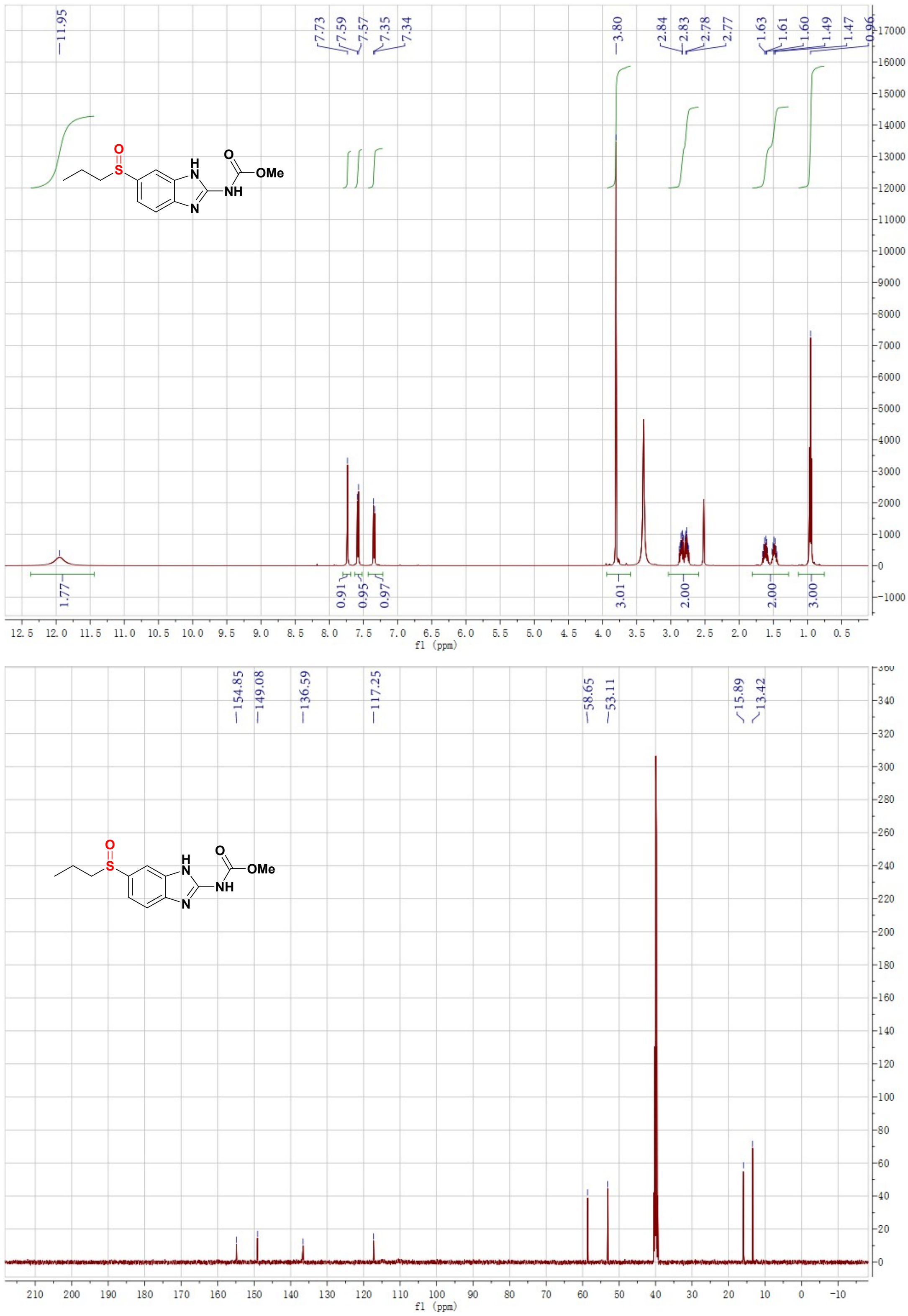


Fig.S3 ^{1}H and ^{13}C NMR spectra of sulfoxides

Cartesian coordination of stationary points

Cartesian coordination of 1a

C	-1.69988803	1.37808849	0.00006517
C	-0.33198345	1.09561001	0.00003500
C	0.10853065	-0.23319660	-0.00000516
C	-0.84006786	-1.26906326	-0.00001531
C	-2.20019740	-0.97623152	0.00001540
C	-2.63993717	0.35006426	0.00005609
H	-2.02496951	2.41364566	0.00009597
H	0.37260497	1.91739176	0.00004259
H	-0.51371495	-2.30479584	-0.00004827
H	-2.91934632	-1.78903314	0.00000677
H	-3.70079236	0.57603400	0.00008011
S	1.82641197	-0.72144940	-0.00004257
C	2.72923261	0.86198129	-0.00004446
H	2.51172980	1.44533775	0.89476634
H	3.78607220	0.59573645	-0.00007080
H	2.51168842	1.44535777	-0.89483199

****

Cartesian coordination of 1a*

C	1.71165000	1.41901100	-0.00005100
C	0.30214800	1.13430200	-0.00008300
C	-0.09179300	-0.20418000	-0.00002600
C	0.80173200	-1.30508200	0.00005700
C	2.20839700	-0.99662600	0.00007700
C	2.61656400	0.33532500	0.00002200
H	2.06516200	2.44161200	-0.00009800
H	-0.41478700	1.94400400	-0.00015700
H	0.44453700	-2.32721700	0.00011500
H	2.93927400	-1.79601100	0.00013900

H	3.68197000	0.55200000	0.00003600
S	-1.77911900	-0.70472300	-0.00009100
C	-2.76957700	0.81083300	0.00014500
H	-2.55555300	1.39891000	-0.89219200
H	-3.81394400	0.50208000	0.00014700
H	-2.55547400	1.39868000	0.89261400

****

Cartesian coordination of 1a^{3,*}

C	1.65684700	1.44361900	-0.00007700
C	0.32114300	1.16093300	-0.00005100
C	-0.14212700	-0.18556400	0.00000000
C	0.86698300	-1.31105400	0.00002100
C	2.20805800	-0.99860800	-0.00000600
C	2.65270900	0.33160100	-0.00005300
H	2.00563500	2.46944700	-0.00011700
H	-0.39452800	1.97587200	-0.00007000
H	0.52220500	-2.33845700	0.00005700
H	2.93891000	-1.80273000	0.00001000
H	3.71130600	0.56113000	-0.00007400
S	-1.78279200	-0.72345000	0.00004000
C	-2.77756800	0.80045200	0.00006100
H	-2.57809600	1.38978700	-0.89454700
H	-3.81888900	0.48214900	0.00002600
H	-2.57814100	1.38973200	0.89471500

****

Cartesian coordination of $^3O_2$

O	0.00000000	0.00000000	0.60267408
O	0.00000000	0.00000000	-0.60267408

****

Cartesian coordination of TS1

C	2.26097993	1.24915010	-0.44524782
C	0.88175049	1.08932339	-0.33690231
C	0.37030559	-0.13911101	0.08171011
C	1.21293195	-1.20908016	0.37683175
C	2.59539297	-1.03569796	0.27532935
C	3.11747221	0.18927389	-0.13544482
H	2.66741136	2.20034018	-0.77169756
H	0.21882278	1.91084470	-0.58476896
H	0.80433850	-2.16454645	0.68905494
H	3.25803162	-1.86093811	0.51263916
H	4.19103665	0.31985676	-0.21852019
S	-1.43190201	-0.44967614	0.26054833
C	-1.67738327	0.84948108	1.54193761
H	-1.47104543	1.83830705	1.13565708
H	-2.71123060	0.78558799	1.87798565
H	-0.98502804	0.62643405	2.35504741
O	-2.80213643	0.12355023	-0.65145571
O	-1.65168904	-0.42618821	-1.51272606

****

Cartesian coordination of IM1

C	2.15396592	-0.61955044	-1.20255844
C	0.78838601	-0.41568061	-1.03446880
C	0.34435936	0.17766970	0.14741134
C	1.22025267	0.55391512	1.16382984
C	2.58780635	0.35469982	0.97435234
C	3.05077012	-0.22941669	-0.20371934
H	2.51890482	-1.08460301	-2.11135641
H	0.08222438	-0.72987849	-1.79412877
H	0.84996461	0.99372202	2.08331799
H	3.28498508	0.64692893	1.75123769

H	4.11410349	-0.38963711	-0.34375097
S	-1.40662230	0.47714556	0.41424695
C	-1.76625948	1.69377649	-0.88269425
H	-1.46812025	1.28598410	-1.84662545
H	-2.83462867	1.89846605	-0.84837792
H	-1.19676743	2.59177796	-0.64691856
O	-2.14695906	-0.81243831	-0.27061280
O	-1.99309031	-1.93000790	0.69007969

****

Cartesian coordination of 2a

C	2.28289200	1.10711100	0.22823300
C	0.90431700	1.18618300	0.41882400
C	0.12593400	0.04984200	0.19942600
C	0.69452400	-1.16036000	-0.18208000
C	2.07633500	-1.22964600	-0.36632900
C	2.86808500	-0.09870100	-0.16503600
H	2.89907200	1.98454200	0.39232100
H	0.44961900	2.11980300	0.73551000
H	0.06116000	-2.02867100	-0.32562700
H	2.53212500	-2.16753300	-0.66544000
H	3.94188600	-0.15695000	-0.30716300
S	-1.67676100	0.13607300	0.46674700
C	-2.08871300	0.97783500	-1.10592100
H	-1.75235400	0.35288200	-1.93325700
H	-3.17086500	1.10392200	-1.12854200
H	-1.59554700	1.94999800	-1.12477200
O	-2.21464500	-1.29109400	0.34078900

****

Cartesian coordination of MECP

C	1.72529000	1.41942400	-0.00008100
C	0.28960300	1.12683800	0.00004300
C	-0.07520300	-0.20204000	0.00025600
C	0.78706600	-1.30821100	0.00065400
C	2.22302900	-0.99224800	0.00008200
C	2.61458100	0.33178000	-0.00040100
H	2.07804500	2.44277600	-0.00065300
H	-0.43297600	1.93262200	-0.00023600
H	0.42365900	-2.32820100	0.00003800
H	2.95408500	-1.79267500	-0.00007100
H	3.68300500	0.55010400	-0.00112300
S	-1.78507600	-0.70311700	-0.00013000
C	-2.77146300	0.81271600	0.00007800
H	-2.54000000	1.39914100	-0.89240200
H	-3.82202800	0.51772800	-0.00001100
H	-2.53999500	1.39882600	0.89275200

****

Relax scanning curve of the S and O atoms distance

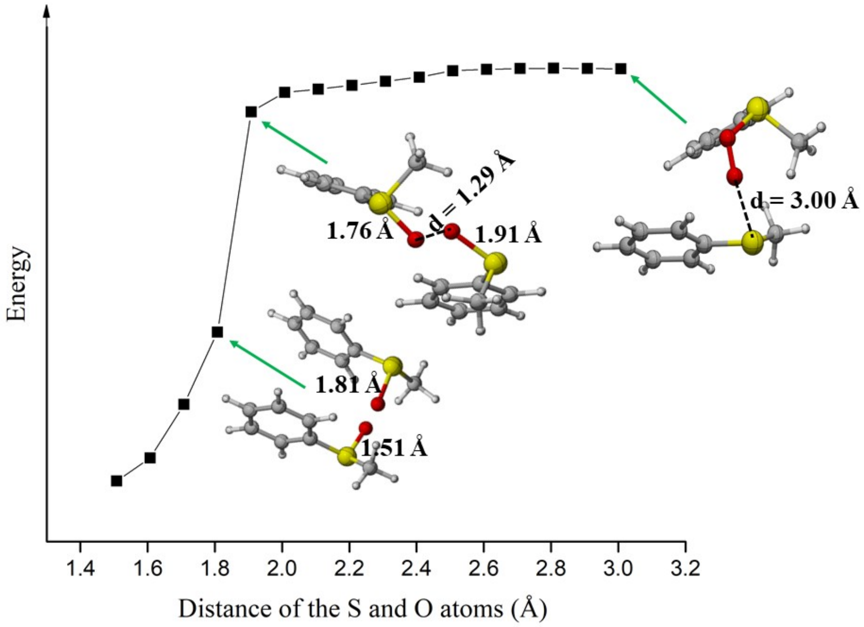


Fig S4 Relax scanning curve of the formation of S=O bond

References

1. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
2. A. D. Becke, *J.Chem. Phys.*, 1993, **98**, 1372-1377.
3. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J.Chem. Phys.*, 2010, **132**, 154104.
4. L. Goerigk and S. Grimme, *Phys. Chem. Chem. Phys.*, 2011, **13**, 6670-6688.
5. S. Grimme, *J.Comput.Chem*, 2006, **27**, 1787-1799.
6. C. Gonzalez and H. B. Schlegel, *J.Chem. Phys.*, 1989, **90**, 2154-2161.
7. V. Barone and M. Cossi, *J.Chem. Phys A*, 1998, **102**, 1995-2001.
8. B. Mennucci and J. Tomasi, *J.Chem. Phys* 1997, **106**, 5151-5158.
9. J. J. Stewart, *J. Mol. Model.*, 2007, **13**, 1173-1213.
10. P. H. Krupenie, *J. Phys. Chem. Ref. Data*, 1972, **1**, 423-534.
11. M. L. McKee, *J. Am. Chem. Soc.*, 1998, **120**, 3963-3969.
12. D. Kashinski, G. Chase, R. Nelson, O. Di Nallo, A. Scales, D. VanderLey and E. Byrd, *J.Chem. Phys A.*, 2017, **121**, 2265-2273.
13. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, G. Petersson and H. Nakatsuji, *Journal*, 2016.
14. J. Harvey, M. Aschi, H Schwarz and W. Koch, *Theor. Chem. Acc.*, 1998, **99**, 95-99.
15. Tian Lu, sobMECP program, http://sobereva.com/286 (accessed May 2, 2018).