

Supporting Information

The selective oxidation of sulfides to sulfoxides or sulfones with hydrogen peroxide catalyzed by a dendritic phosphomolybdate hybrid

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1. General information

All reactants and solvents were directly obtained from commercial sources and used without further purification. SEM patterns were obtained by FEI Q45. XRD patterns were obtained by Purkinje XD-3. IR spectra were measured by a Thermo Fisher IS5 system with a resolution of 8 cm⁻¹. ¹H and ¹³C NMR spectra were recorded with Bruker Avance-III 600 spectrometers and referenced to DMSO-*d*₆. The purity of the products was determined by HPLC with areas of peak normalization method (pump: waters 1525, detector: waters 2489. Chromatographic column: WondaSil C-18, monitoring wavelength used 210 nm).

2. Additional Figure

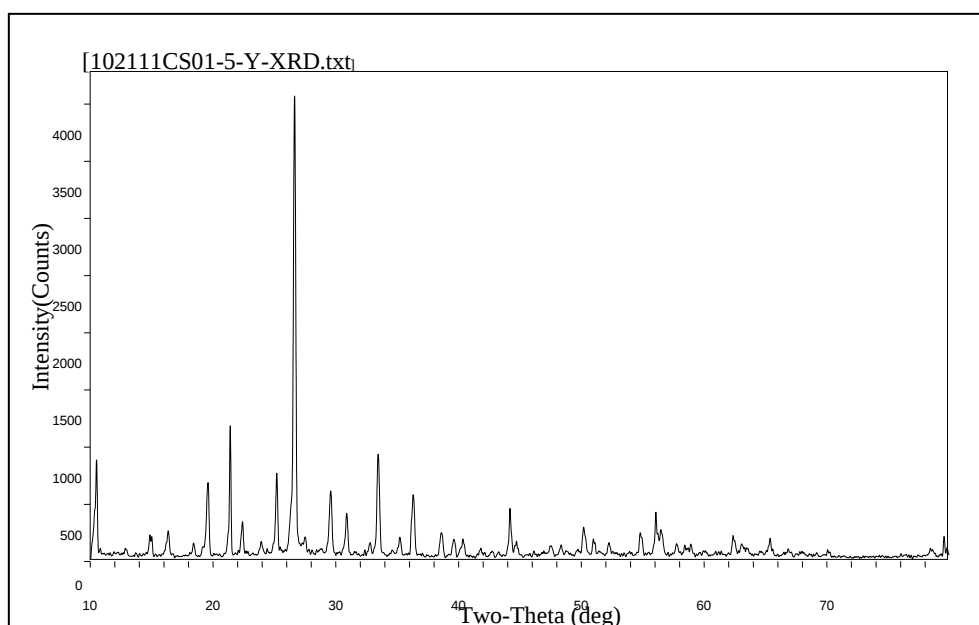
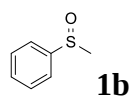


Figure S1. XRD patterns of HMo.

3. Products Characterization



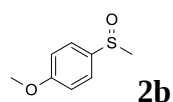
(methylsulfinyl)benzene:

methyl(phenyl)sulfane (62 mg, 0.5 mmol) afforded 63.5 mg of (methylsulfinyl)benzene as a yellow oil; yield 91%.

^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 7.71 – 7.67 (m, 2H), 7.60 – 7.53 (m, 3H), 2.74 (s, 3H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 146.85, 131.14, 129.71, 124.02, 43.70.

MS (ES^+): m/z = 141.0 $[\text{M}+\text{H}]^+$.



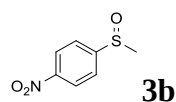
1-methoxy-4-(methylsulfinyl)benzene:

(4-methoxyphenyl)(methyl)sulfane (77 mg, 0.5 mmol) afforded 76 mg of 1-methoxy-4-(methylsulfinyl)benzene as a white solid; yield 90%.

^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 7.63 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 2.70 (s, 3H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 161.69, 137.71, 125.99, 115.20, 55.96, 43.80.

MS (ES^+): m/z = 171.1 $[\text{M}+\text{H}]^+$.



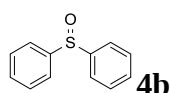
1-(methylsulfinyl)-4-nitrobenzene:

methyl(4-nitrophenyl)sulfane (85 mg, 0.5 mmol) afforded 79 mg of 1-(methylsulfinyl)-4-nitrobenzene as a light white solid; yield 85%.

^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.41 (d, $J = 8.8$ Hz, 2H), 7.98 (d, $J = 8.8$ Hz, 2H), 2.85 (s, 3H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 154.44, 149.30, 125.65, 124.72, 43.38.

MS (ES^+): $m/z = 186.0$ [$\text{M}+\text{H}$] $^+$.



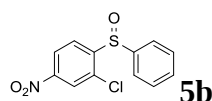
Sulfinyldibenzene:

diphenylsulfane (93 mg, 0.5 mmol) afforded 86 mg of sulfinyldibenzene as a white solid; yield 85%.

^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 7.75 – 7.70 (m, 4H), 7.55 – 7.49 (m, 6H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 146.40, 131.58, 129.99, 124.57.

MS (ES^+): $m/z = 203.0$ [$\text{M}+\text{H}$] $^+$.



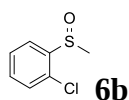
2-chloro-4-nitro-1-(phenylsulfinyl)benzene:

(2-chloro-4-nitrophenyl)(phenyl)sulfane (133 mg, 0.5 mmol) afforded only 3 mg of 2-chloro-4-nitro-1-(phenylsulfinyl)benzene as a yellow solid.

^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.41 – 8.35 (m, 2H), 8.25 (dd, $J = 8.6, 2.1$ Hz, 1H), 7.70 – 7.67 (m, 2H), 7.54 – 7.50 (m, 3H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 145.61, 145.48, 142.37, 136.88, 136.13, 132.22, 130.03, 128.09, 127.04, 125.83.

MS (ES^+): $m/z = 282.0$ [$\text{M}+\text{H}$] $^+$.

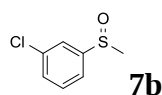


1-chloro-2-(methylsulfinyl)benzene: (2-chlorophenyl)(methyl)sulfane (80 mg, 0.5 mmol) afforded 81 mg of 1-chloro-2-(methylsulfinyl)benzene as a colorless oil; yield 93%.

^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 7.85 (dt, $J = 7.7, 1.1$ Hz, 1H), 7.68 – 7.65 (m, 1H), 7.61 – 7.58 (m, 2H), 2.80 (s, 3H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 144.28, 133.04, 130.36, 129.40, 129.08, 125.59, 41.91.

MS (ES^+): $m/z = 175.0$ [$\text{M}+\text{H}$] $^+$.

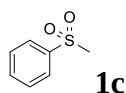


1-chloro-3-(methylsulfinyl)benzene: (3-chlorophenyl)(methyl)sulfane (80 mg, 0.5 mmol) afforded 81 mg of 1-chloro-3-(methylsulfinyl)benzene as a colorless oil; yield 93%.

^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 7.75 (d, J = 1.2 Hz, 1H), 7.66 (ddd, J = 5.4, 3.4, 1.6 Hz, 1H), 7.62 – 7.60 (m, 2H), 2.79 (s, 3H).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 149.36, 134.50, 131.62, 131.03, 123.81, 122.85, 43.57.

MS (ES^+): m/z = 175.0 $[\text{M}+\text{H}]^+$.

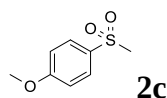


(methylsulfonyl)benzene: methyl(phenyl)sulfane (62 mg, 0.5 mmol) afforded 73 mg of (methylsulfonyl)benzene as a white solid; yield 93%.

^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 7.95 – 7.92 (m, 2H), 7.76 – 7.73 (m, 1H), 7.66 (dd, J = 8.5, 7.1 Hz, 2H), 3.22 (s, 3H).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 141.33, 134.08, 129.89, 127.36, 43.95.

MS (ES^+): m/z = 157.0 $[\text{M}+\text{H}]^+$.

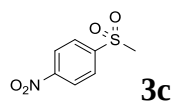


1-methoxy-4-(methylsulfonyl)benzene: (4-methoxyphenyl)(methyl)sulfane (77 mg, 0.5 mmol) afforded 88 mg of 1-methoxy-4-(methylsulfonyl)benzene as a white solid; yield 94%.

^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 7.85 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.16 (s, 3H).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 163.52, 133.05, 129.68, 115.01, 56.25, 44.44.

MS (ES^+): m/z = 187.0 $[\text{M}+\text{H}]^+$.

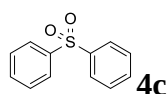


1-(methylsulfonyl)-4-nitrobenzene: methyl(4-nitrophenyl)sulfane (85 mg, 0.5 mmol) afforded 93 mg of 1-(methylsulfonyl)-4-nitrobenzene as a light white solid; yield 92%.

^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 8.46 (d, J = 8.9 Hz, 2H), 8.22 (d, J = 8.8 Hz, 2H), 3.36 (s, 3H).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 150.86, 146.46, 129.27, 125.10, 43.48.

MS (ES^+): m/z = 201.9 $[\text{M}+\text{H}]^+$.

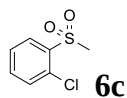


Sulfonyldibenzene: diphenylsulfane (93 mg, 0.5mmol) afforded 101 mg of sulfonyldibenzene as a white solid; yield 93%.

^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 7.99 – 7.96 (m, 4H), 7.71 – 7.68 (m, 2H), 7.63 (dd, J = 8.4, 7.0 Hz, 4H).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 141.58, 134.21, 130.25, 127.82.

MS (ES⁺): m/z = 219.1 [M+H]⁺.

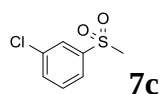


1-chloro-2-(methylsulfonyl)benzene: (2-chlorophenyl)(methyl)sulfane (80 mg, 0.5mmol) afforded only 2 mg of 1-chloro-2-(methylsulfonyl)benzene as a colorless oil.

¹H NMR (600 MHz, DMSO-*d*₆) δ 8.06 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.77 – 7.74 (m, 2H), 7.66 – 7.62 (m, 1H), 3.38 (s, 3H).

¹³C NMR (151 MHz, DMSO-*d*₆) δ 138.40, 135.88, 132.45, 131.72, 130.75, 128.65, 42.90.

MS (ES⁺): m/z = 191.0 [M+H]⁺.



1-chloro-3-(methylsulfonyl)benzene: (3-chlorophenyl)(methyl)sulfane (80 mg, 0.5mmol) afforded 87 mg of 1-chloro-3-(methylsulfonyl)benzene as a colorless oil; yield 91%.

¹H NMR (600 MHz, DMSO-*d*₆) δ 7.99 (t, *J* = 1.9 Hz, 1H), 7.90 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 3.30 (s, 3H).

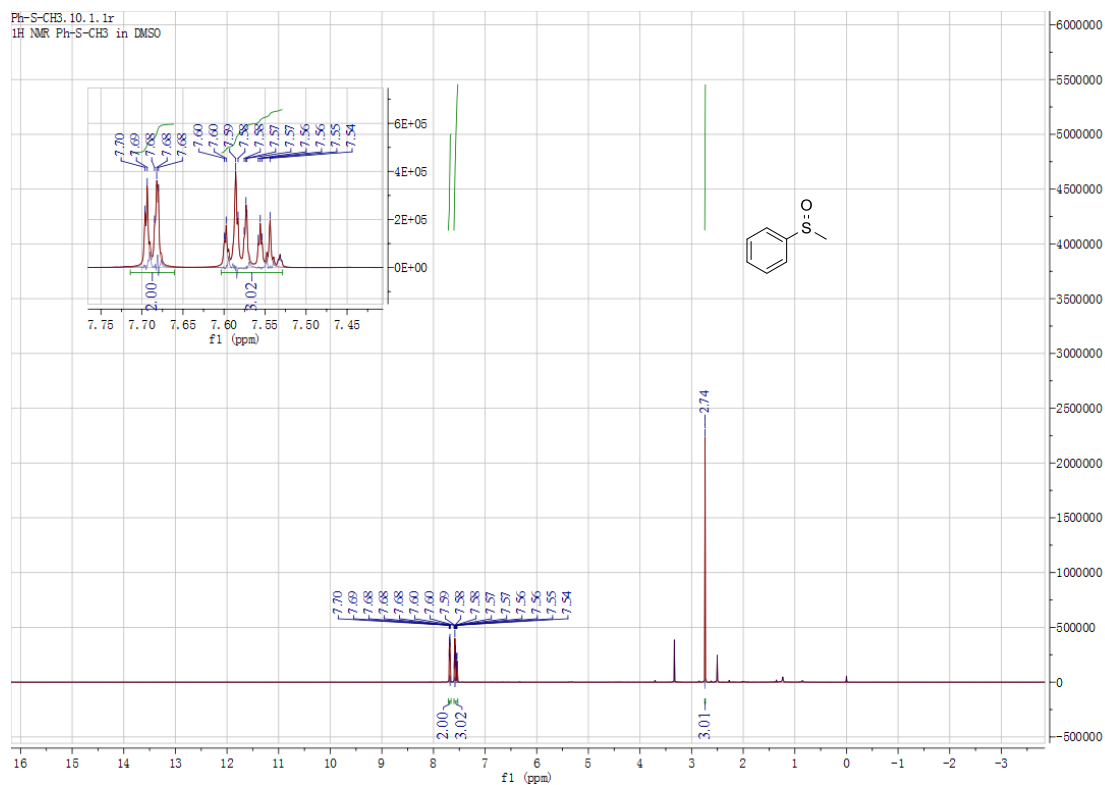
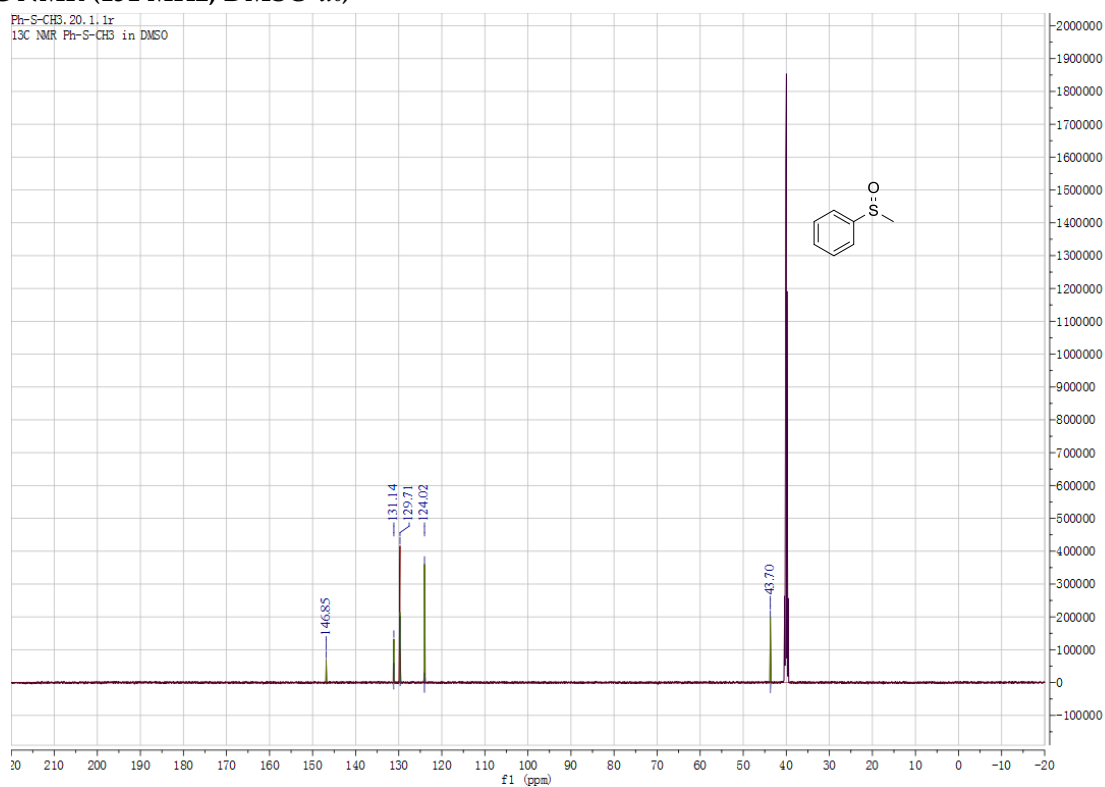
¹³C NMR (151 MHz, DMSO-*d*₆) δ 143.17, 134.46, 134.07, 131.93, 127.24, 126.12, 43.65.

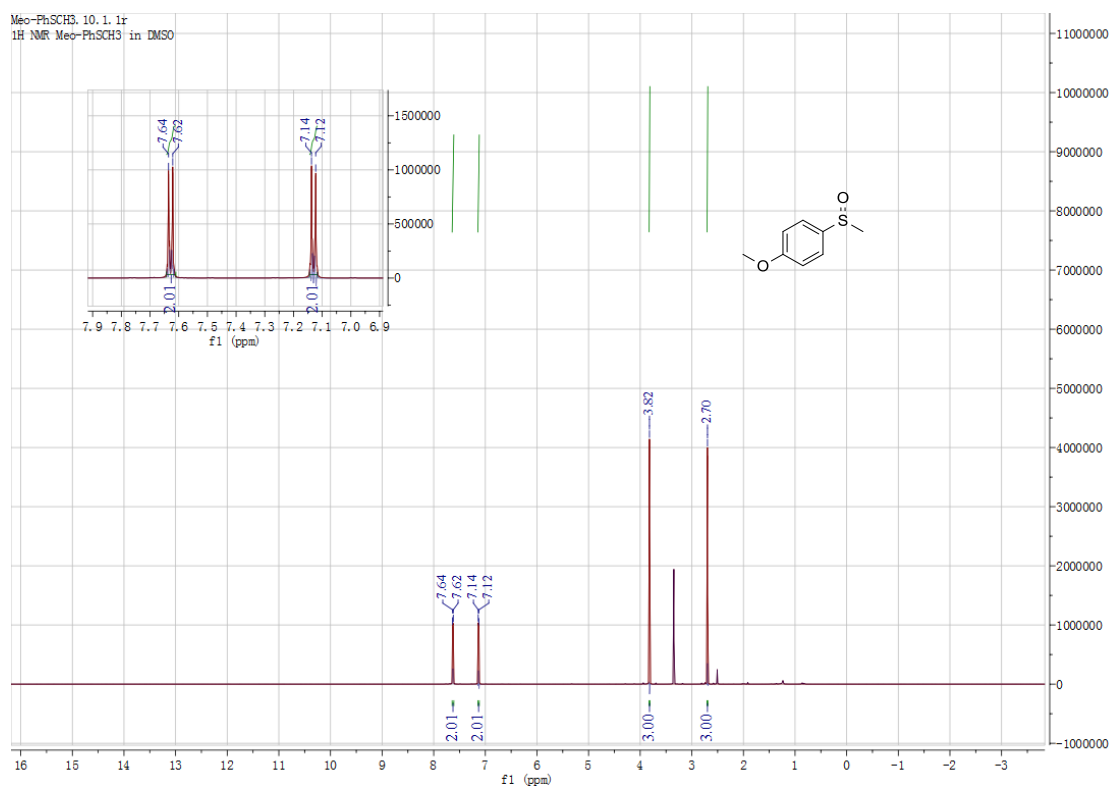
MS (ES⁺): m/z = 191.0 [M+H]⁺.

4. NMR Spectra

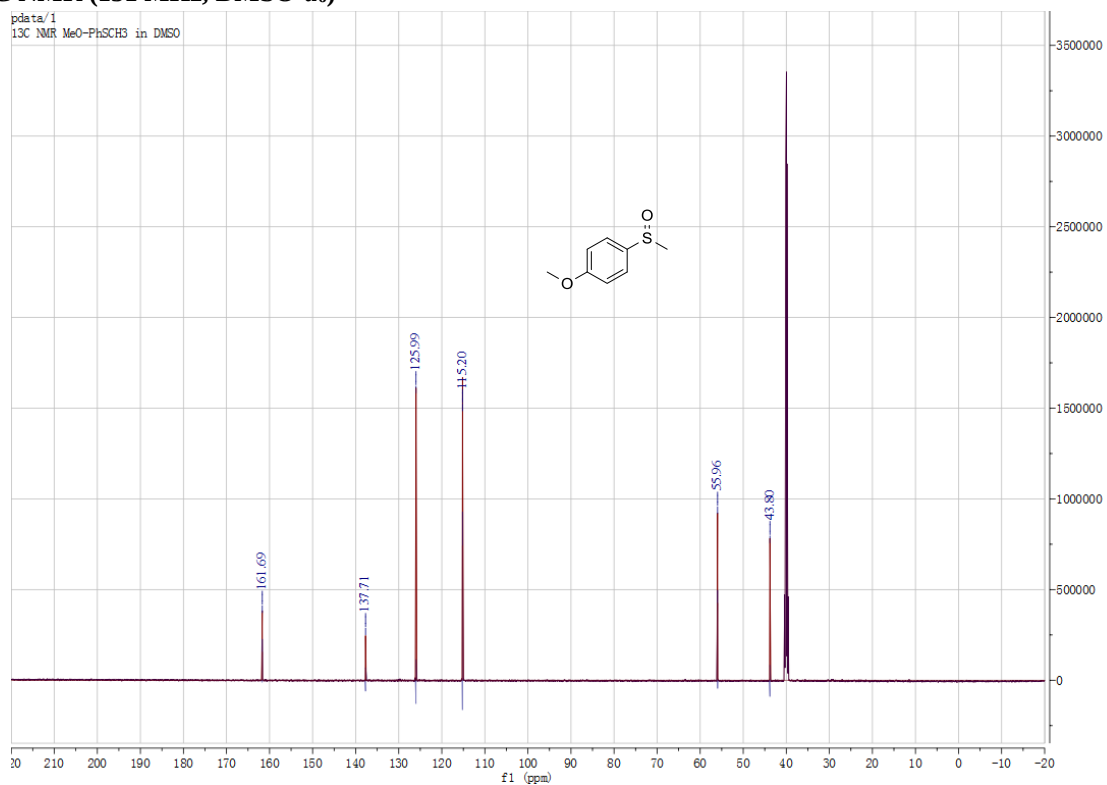
(methylsulfinyl)benzene

¹H NMR (600 MHz, DMSO-*d*₆)

**¹³C NMR (151 MHz, DMSO-*d*₆)****1-methoxy-4-(methylsulfinyl)benzene****¹H NMR (600 MHz, DMSO-*d*₆)**

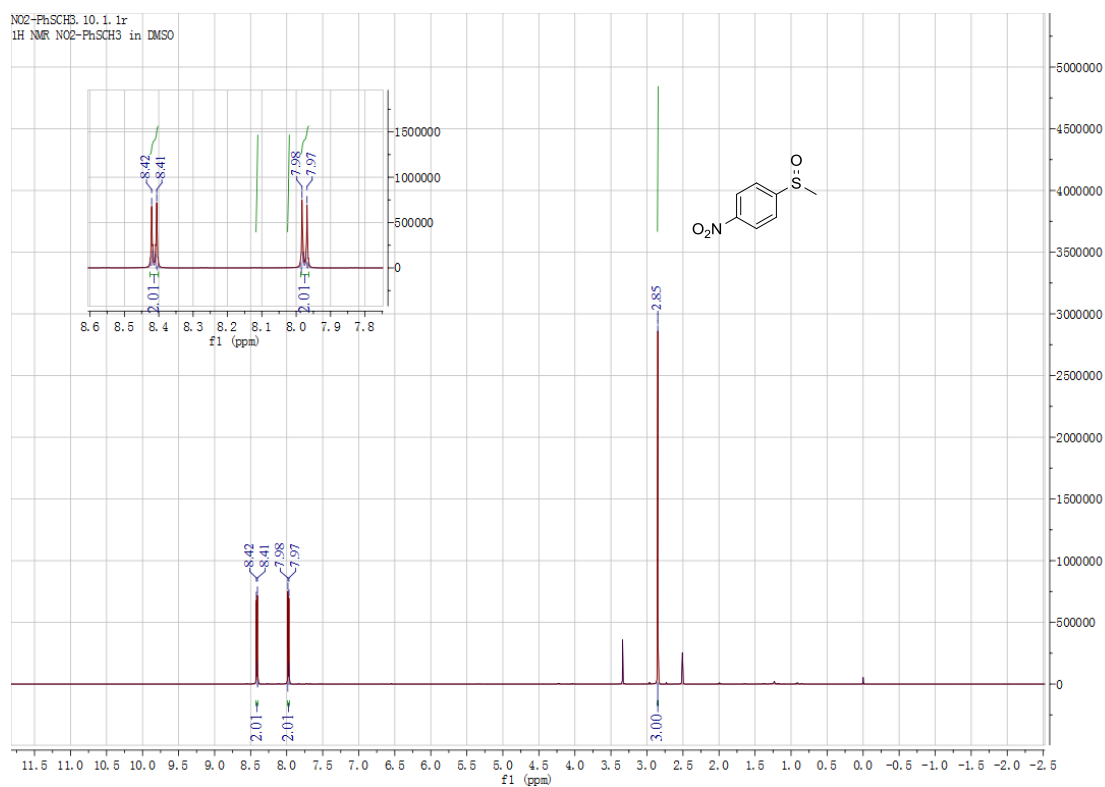
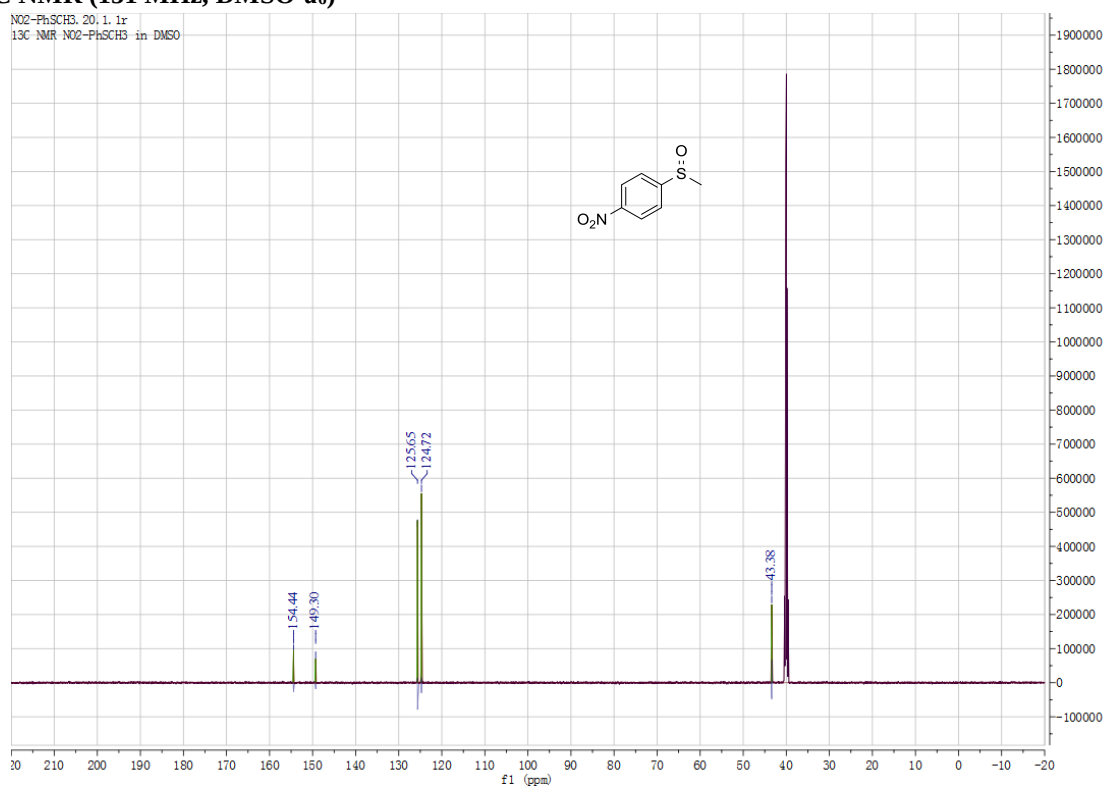


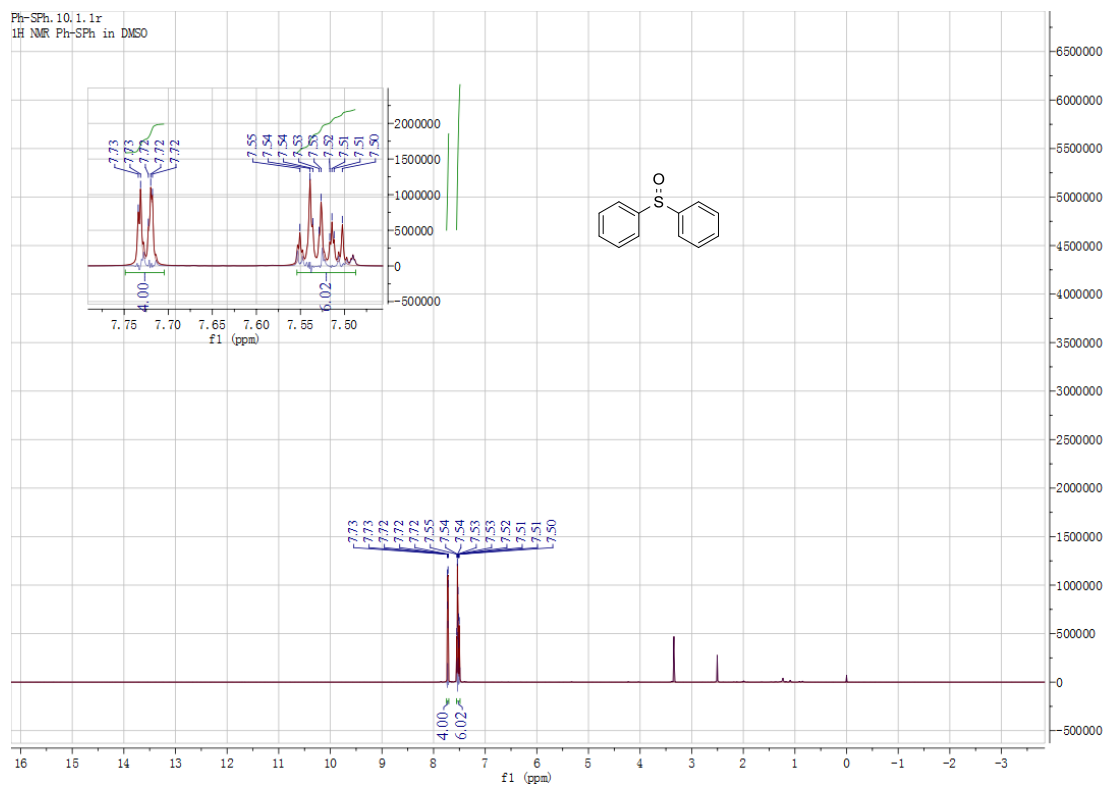
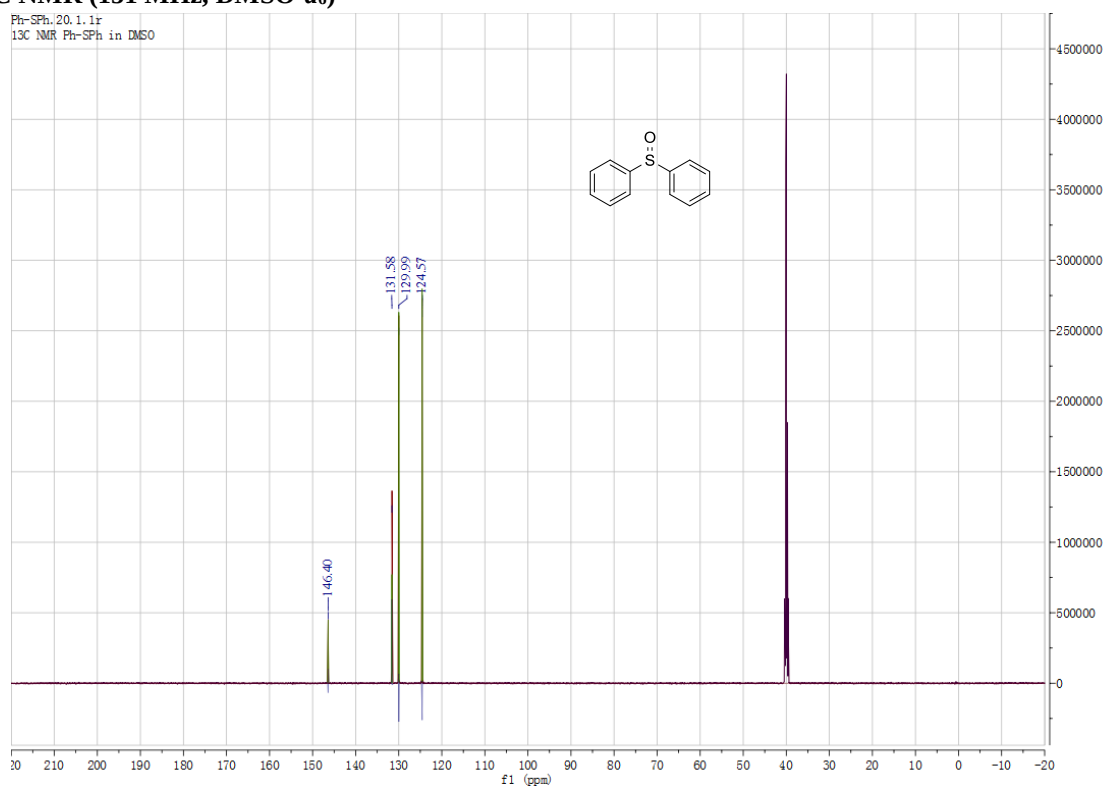
¹³C NMR (151 MHz, DMSO-*d*₆)

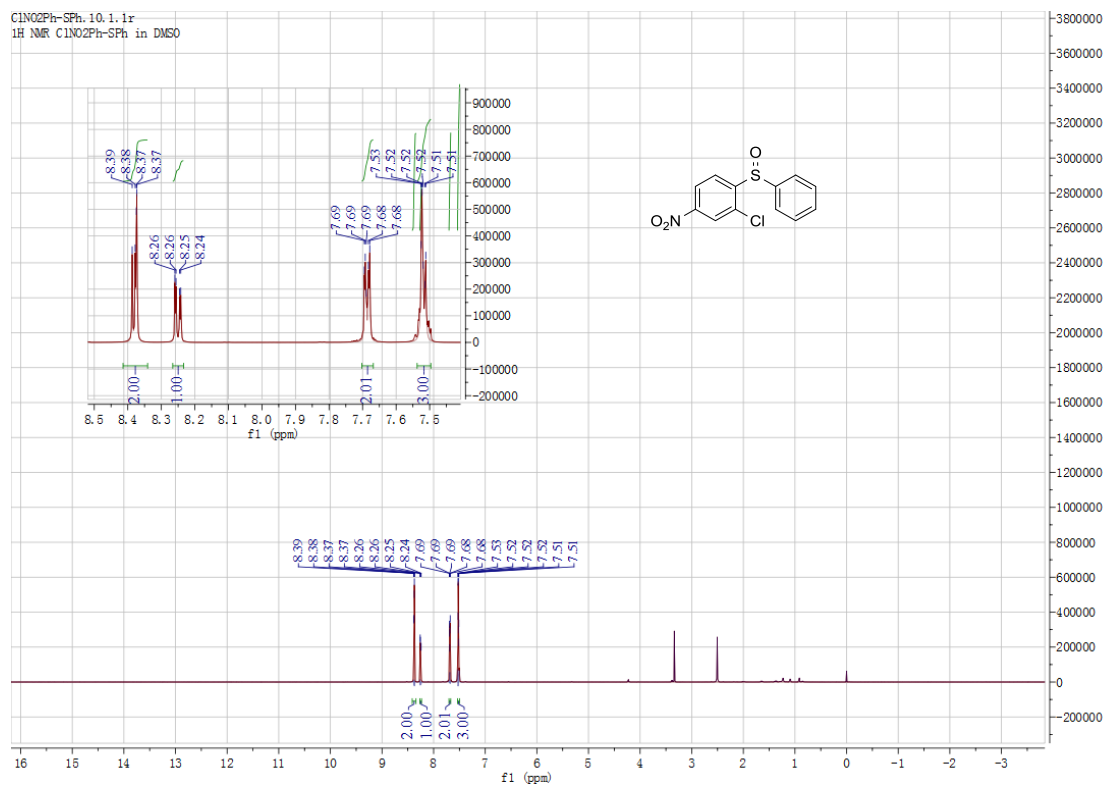
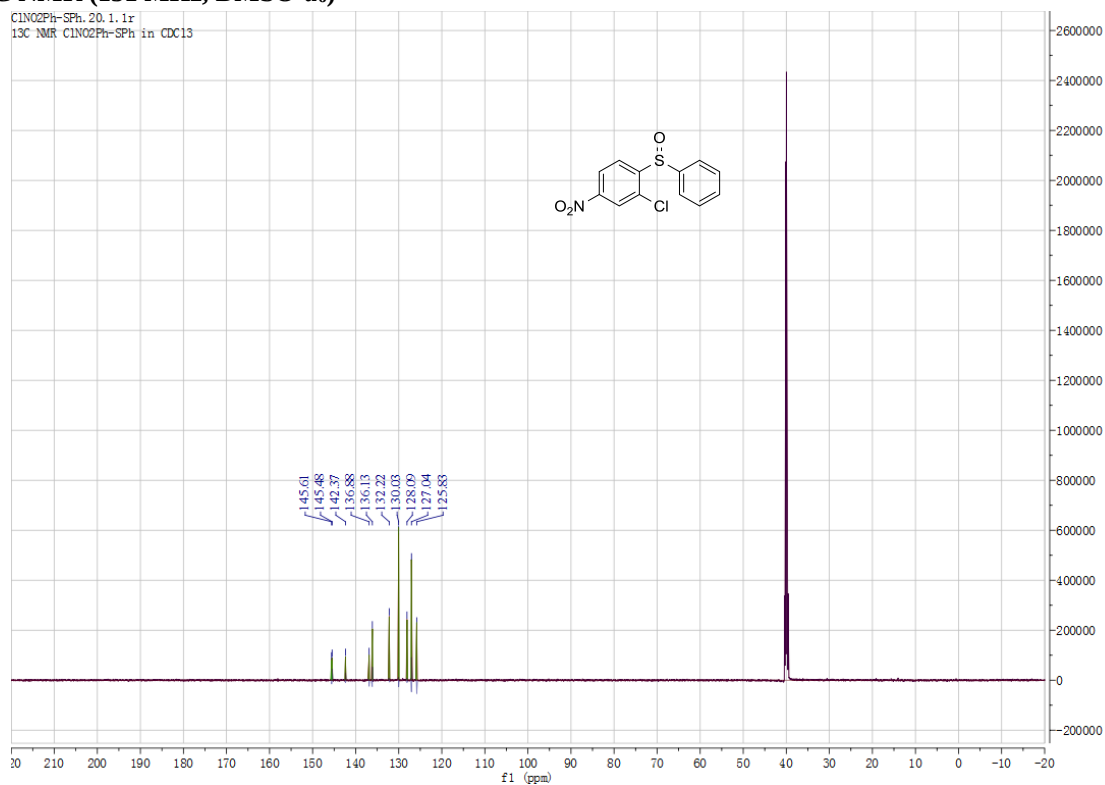


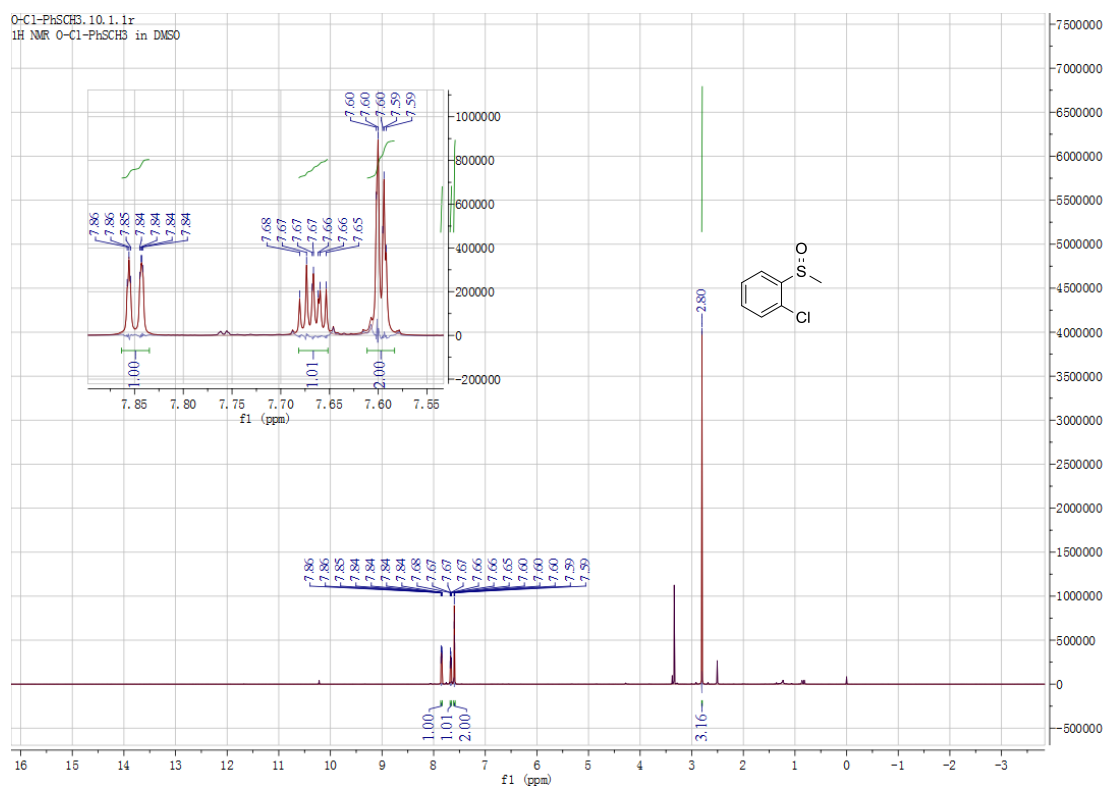
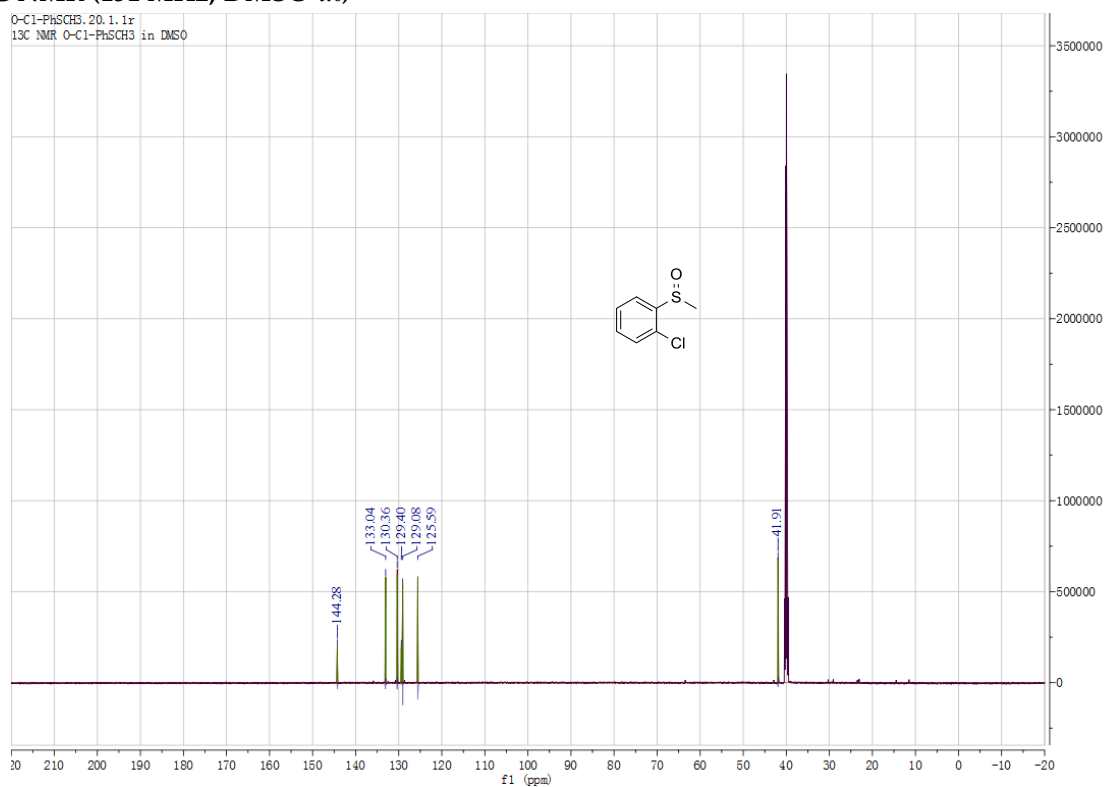
1-(methylsulfinyl)-4-nitrobenzene

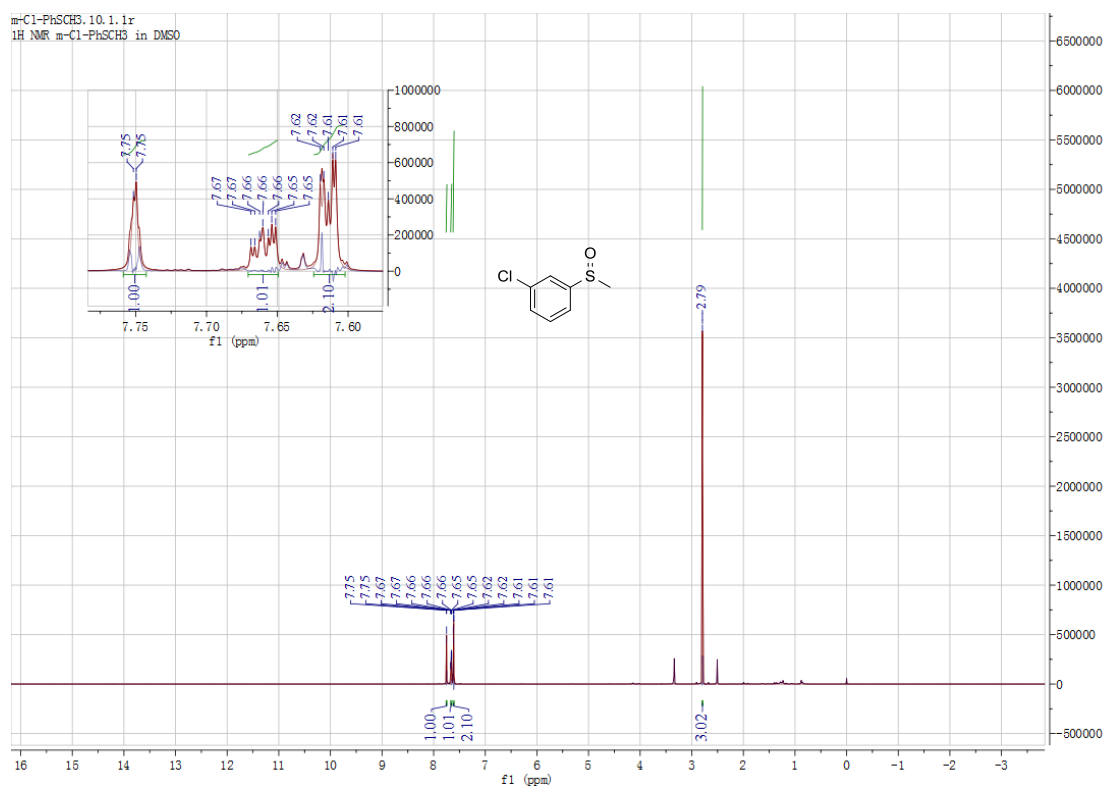
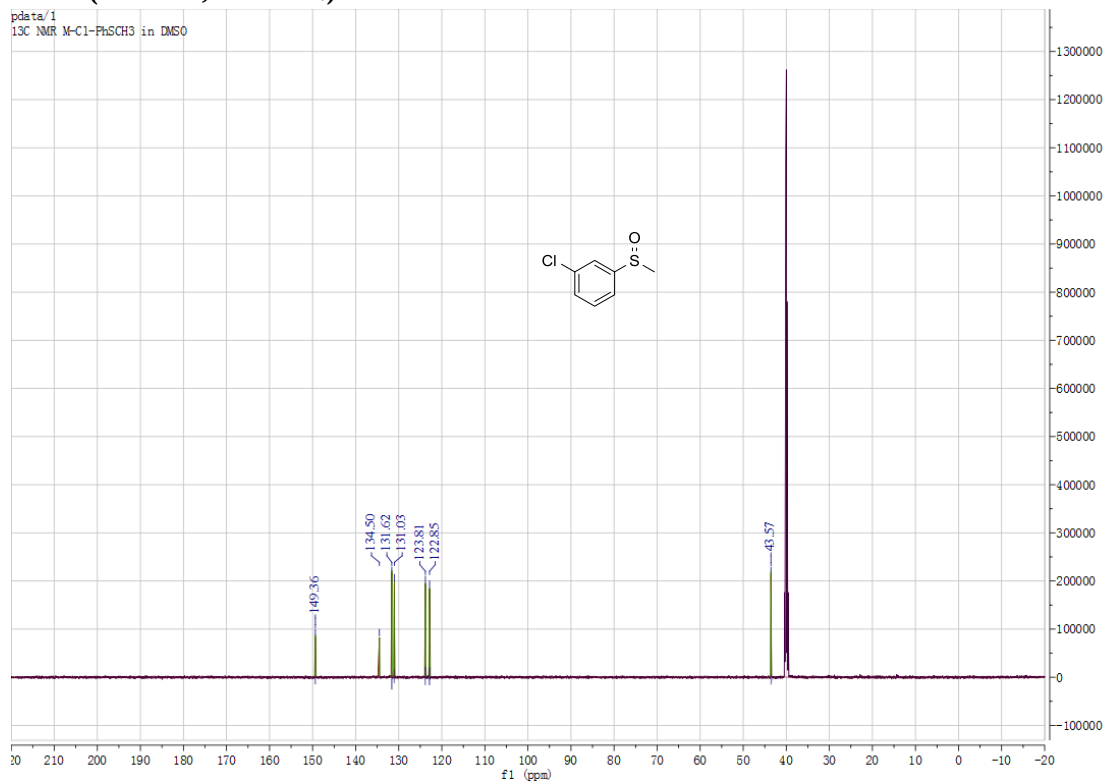
¹H NMR (600 MHz, DMSO-*d*₆)

**¹³C NMR (151 MHz, DMSO-*d*₆)****sulfinyldibenzene****¹H NMR (600 MHz, DMSO-*d*₆)**

**¹³C NMR (151 MHz, DMSO-*d*₆)****2-chloro-4-nitro-1-(phenylsulfinyl)benzene****¹H NMR (600 MHz, DMSO-*d*₆)**

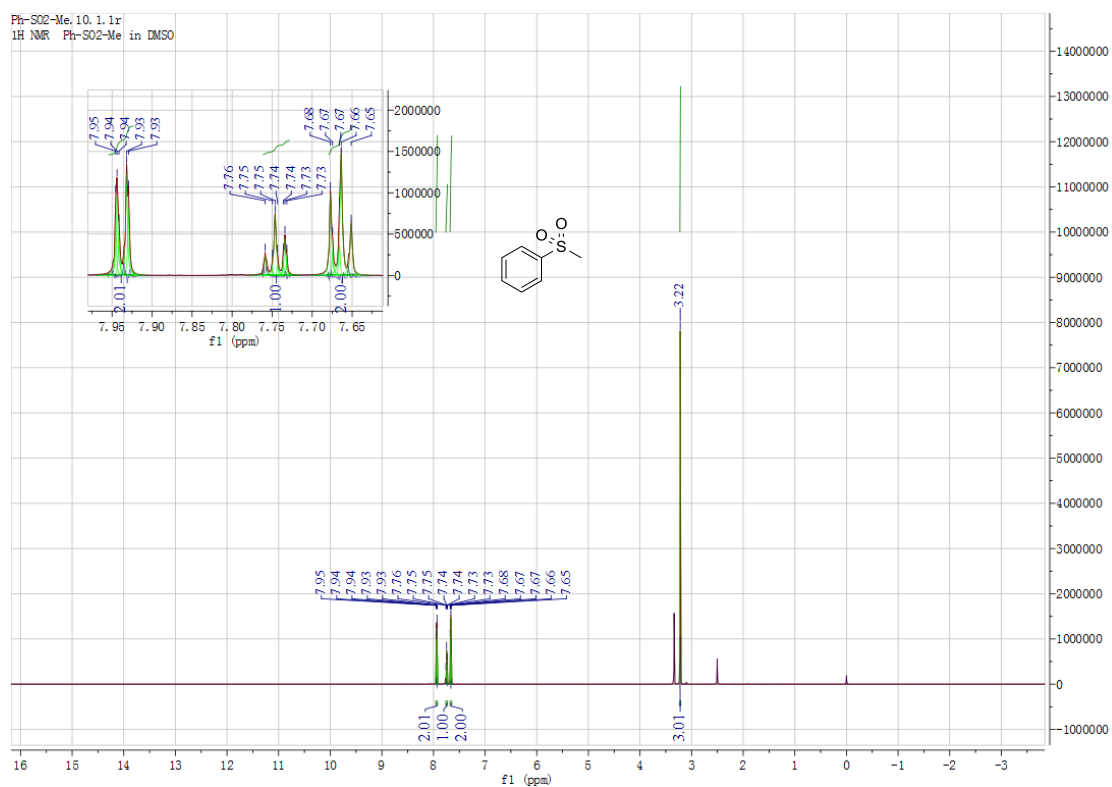
**¹³C NMR (151 MHz, DMSO-*d*₆)****1-chloro-2-(methylsulfinyl)benzene****¹H NMR (600 MHz, DMSO-*d*₆)**

**¹³C NMR (151 MHz, DMSO-*d*₆)****1-chloro-3-(methylsulfinyl)benzene****¹H NMR (600 MHz, DMSO-*d*₆)**

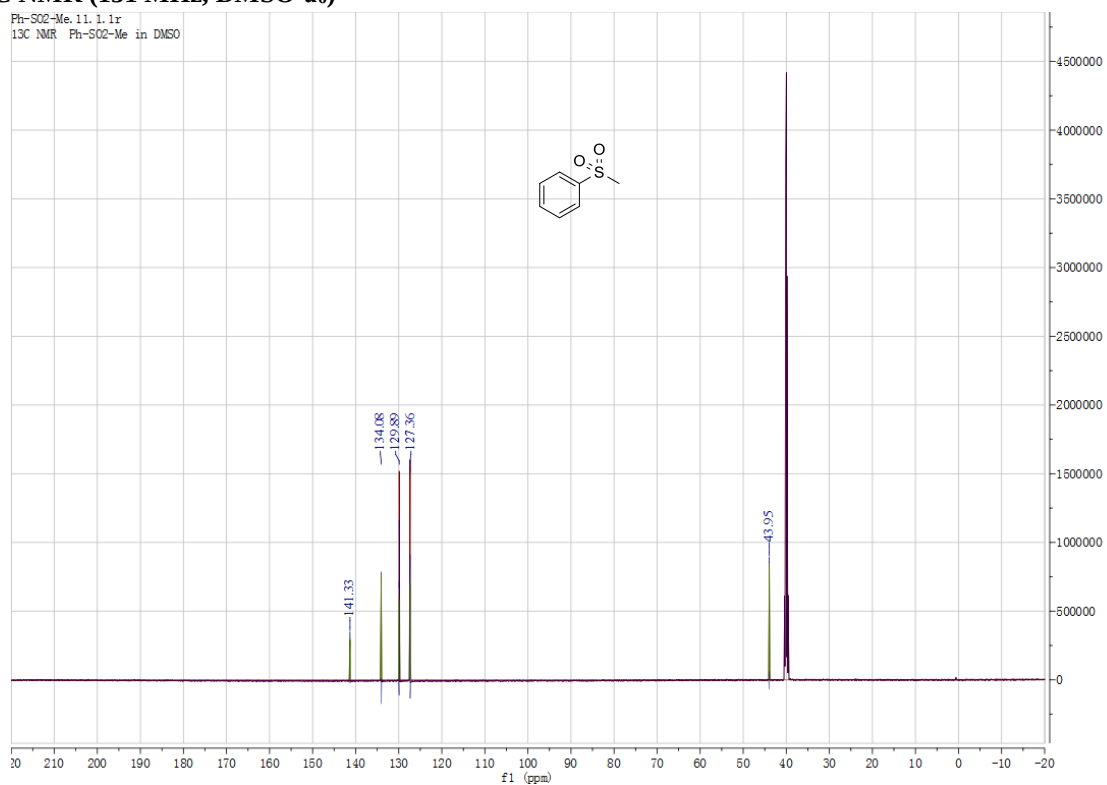
**¹³C NMR (151 MHz, DMSO-*d*₆)**

(methylsulfonyl)benzene

¹H NMR (600 MHz, DMSO-*d*₆)

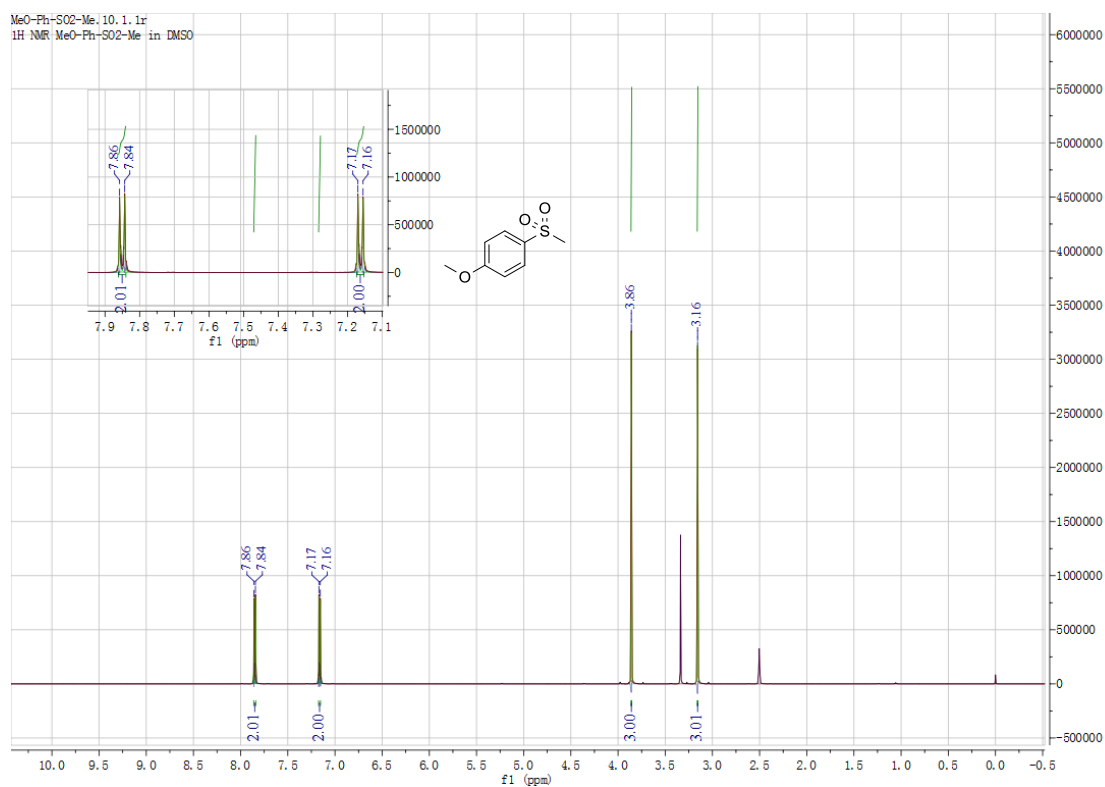
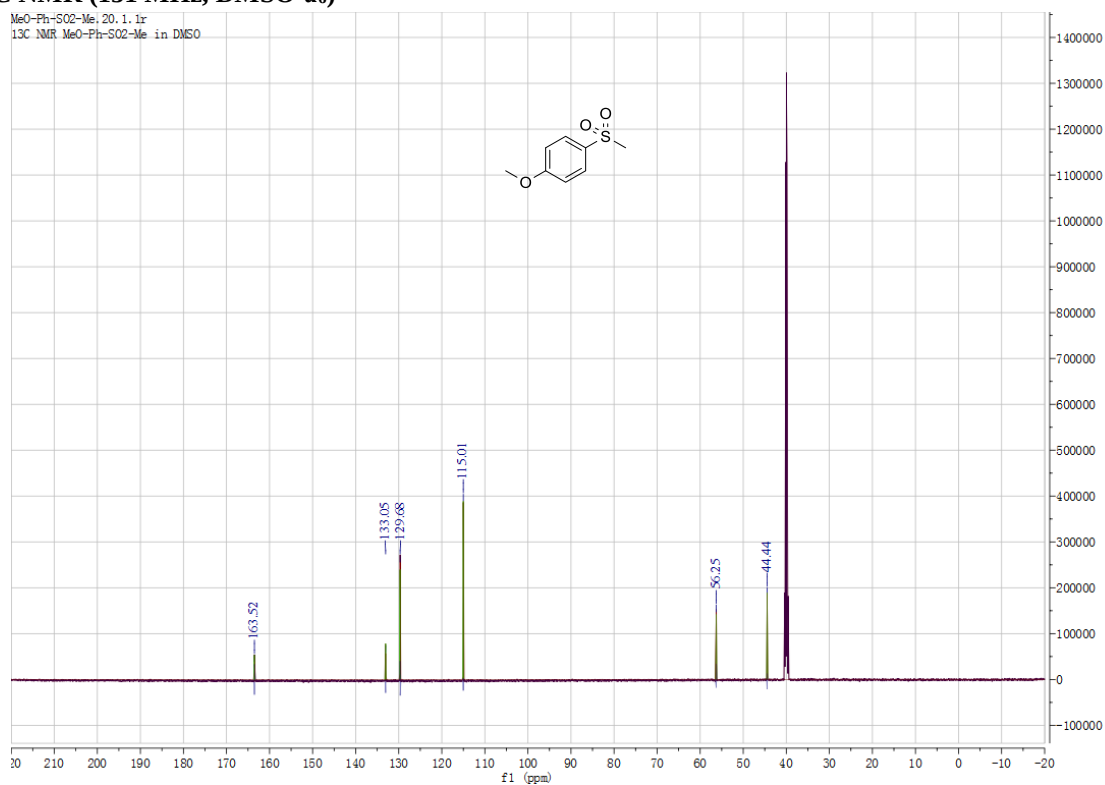


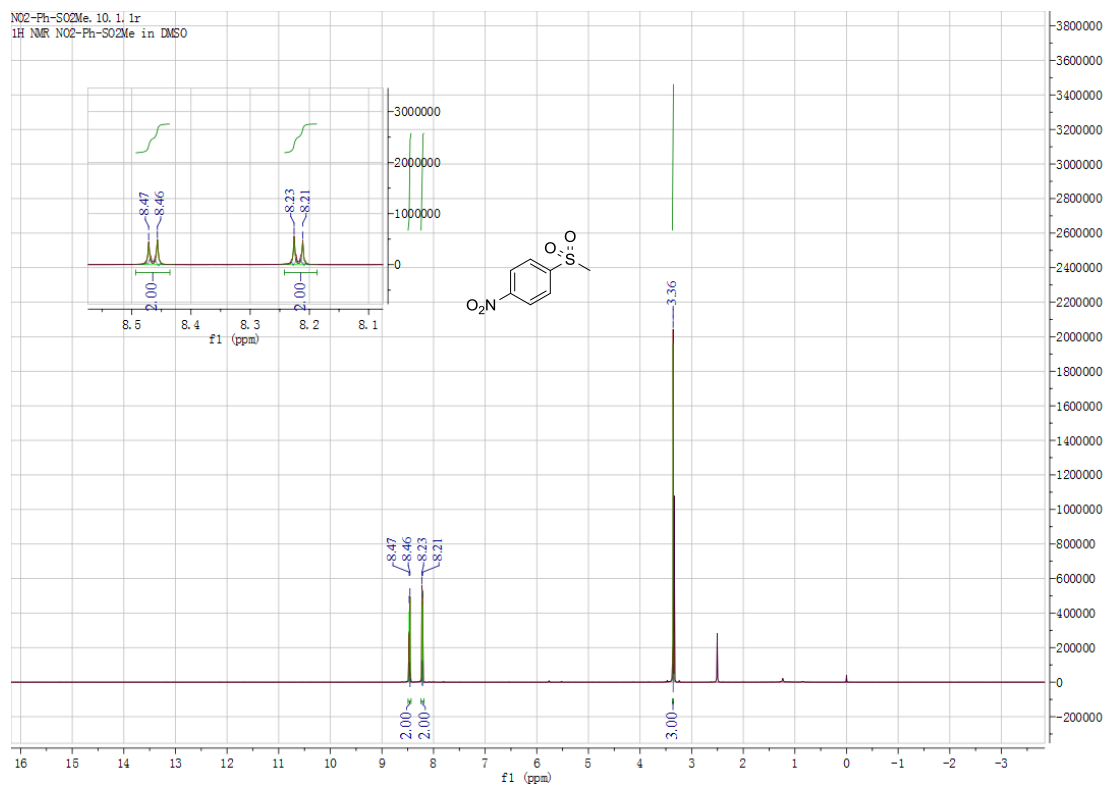
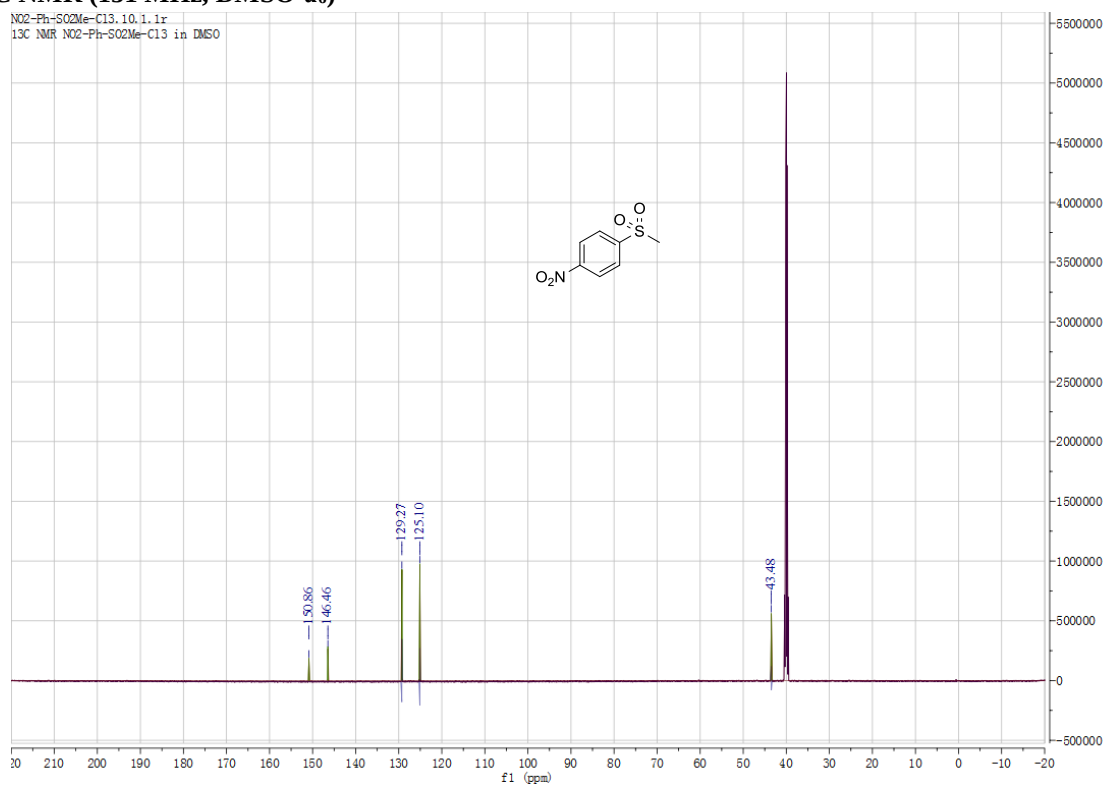
^{13}C NMR (151 MHz, DMSO- d_6)

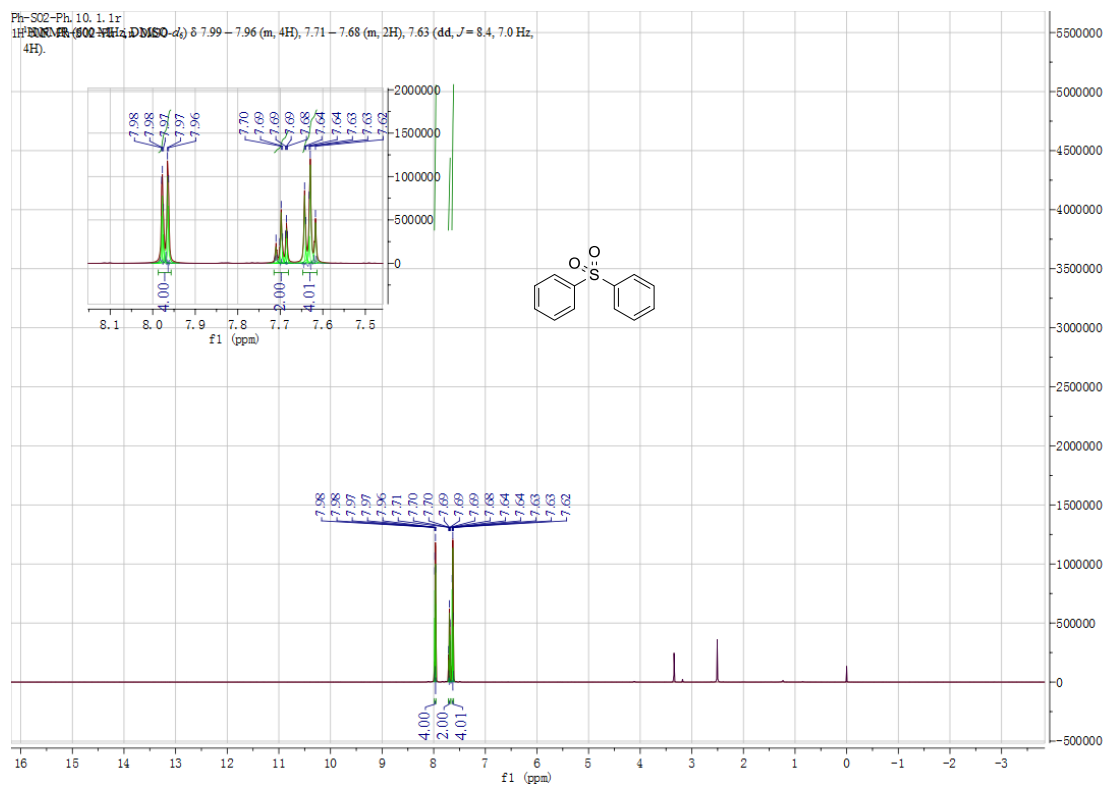
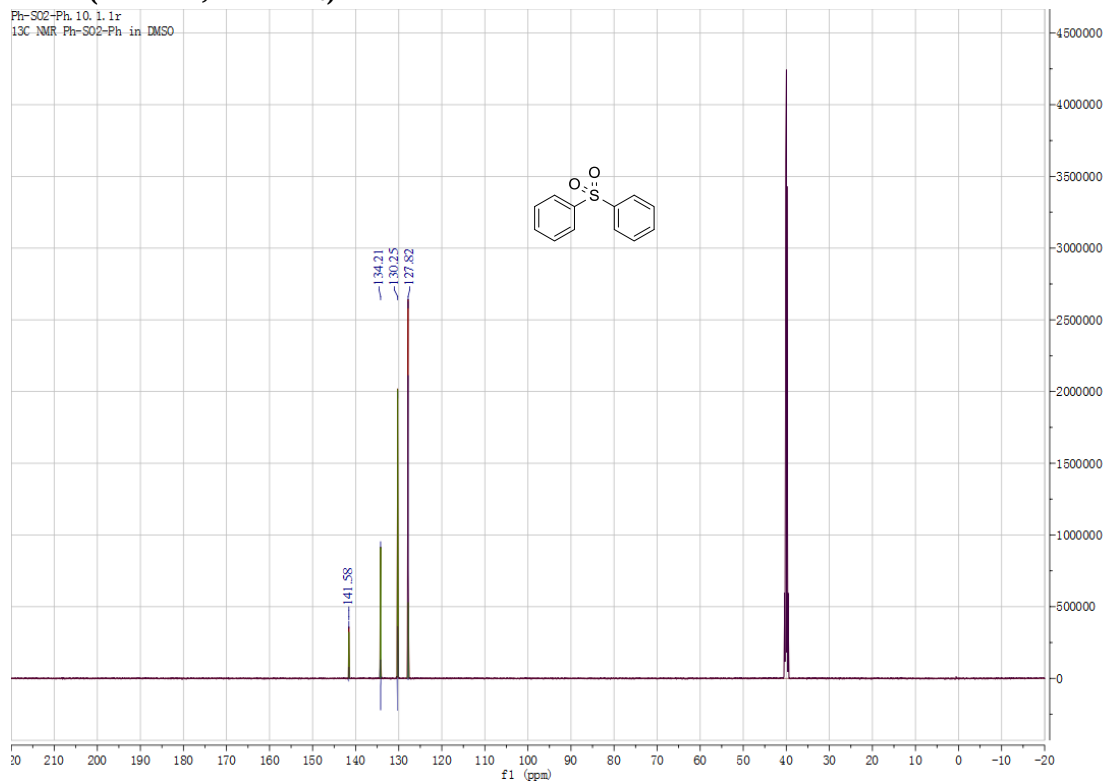


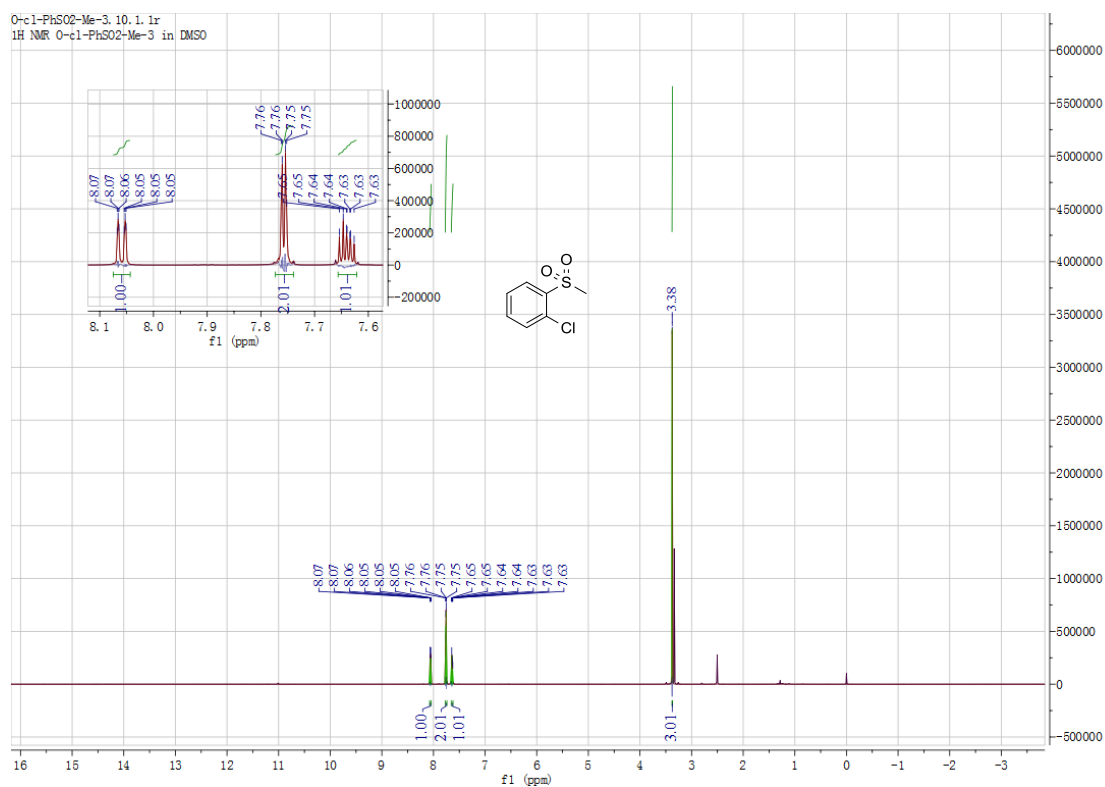
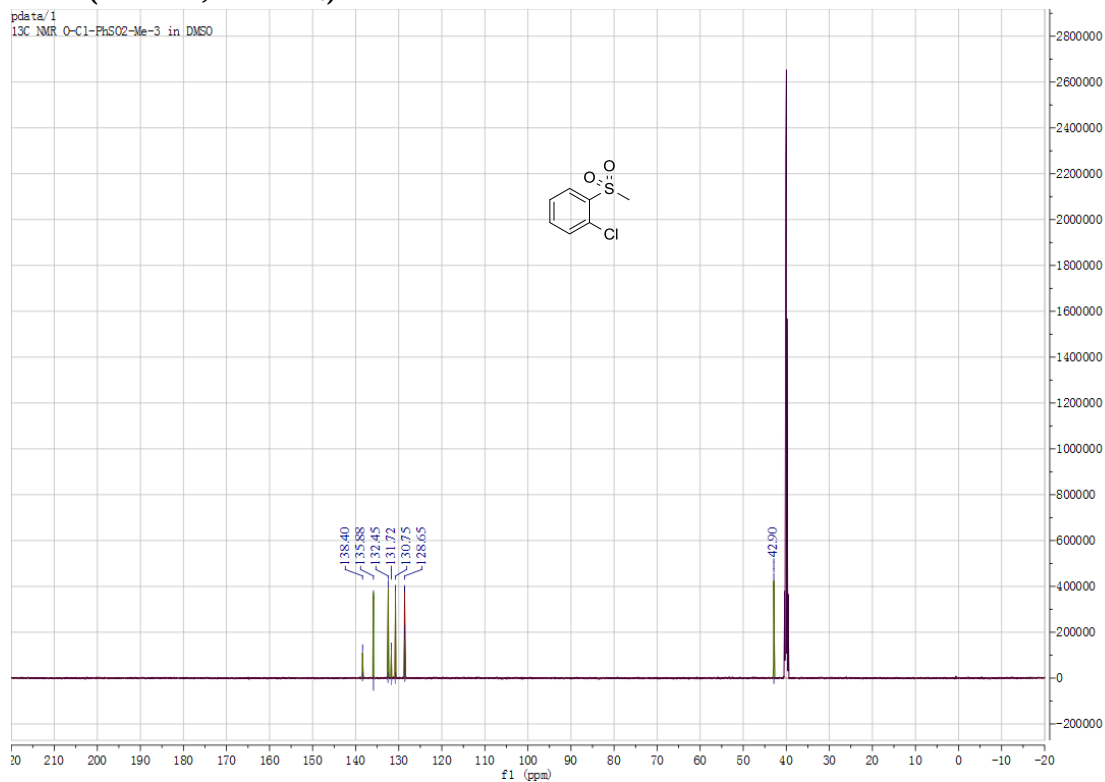
1-methoxy-4-(methylsulfonyl)benzene

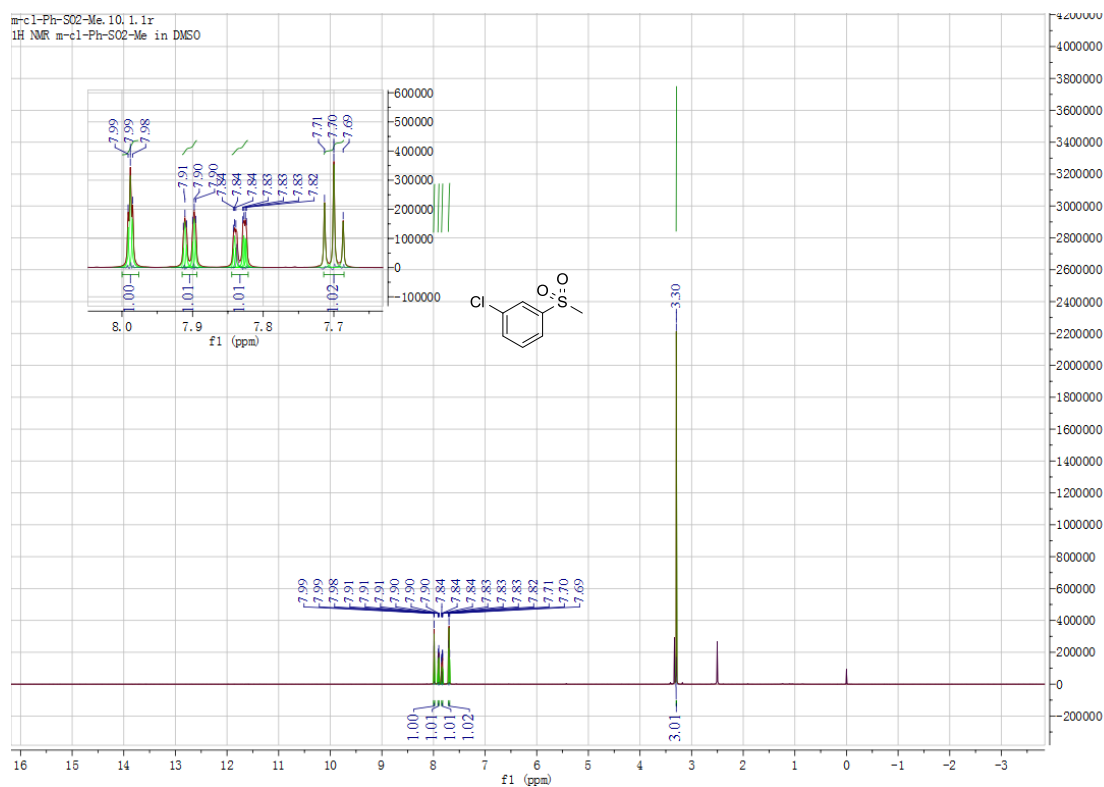
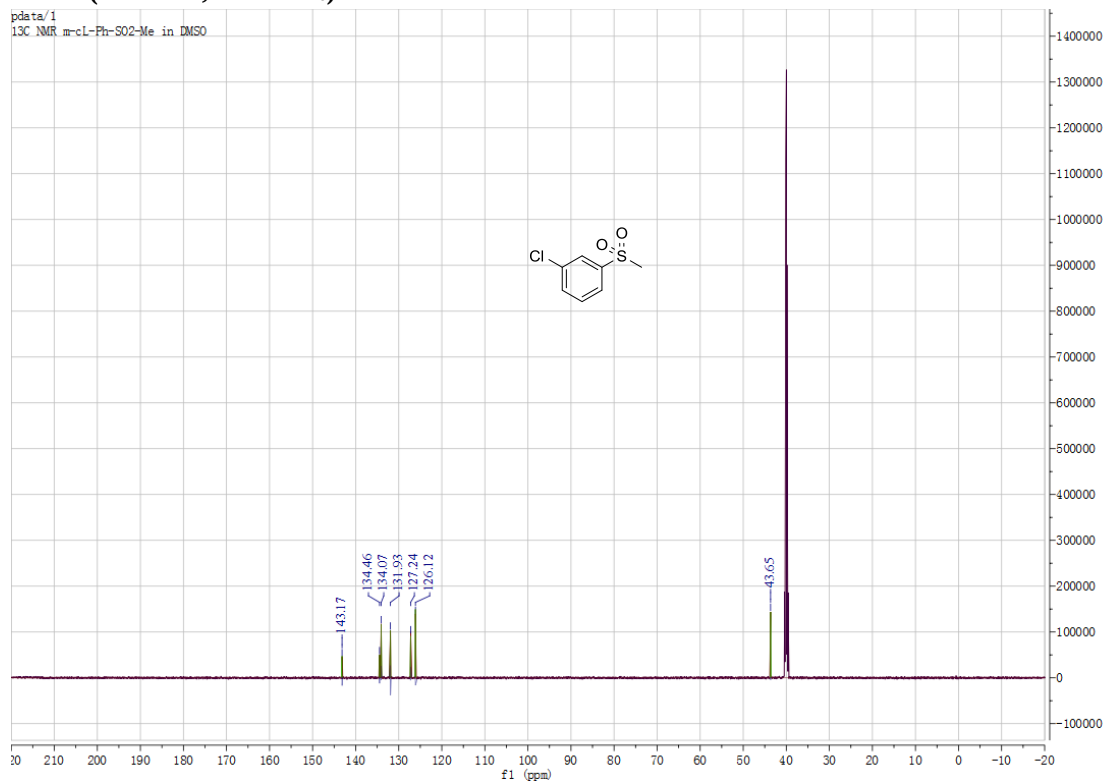
¹H NMR (600 MHz, DMSO-*d*₆)

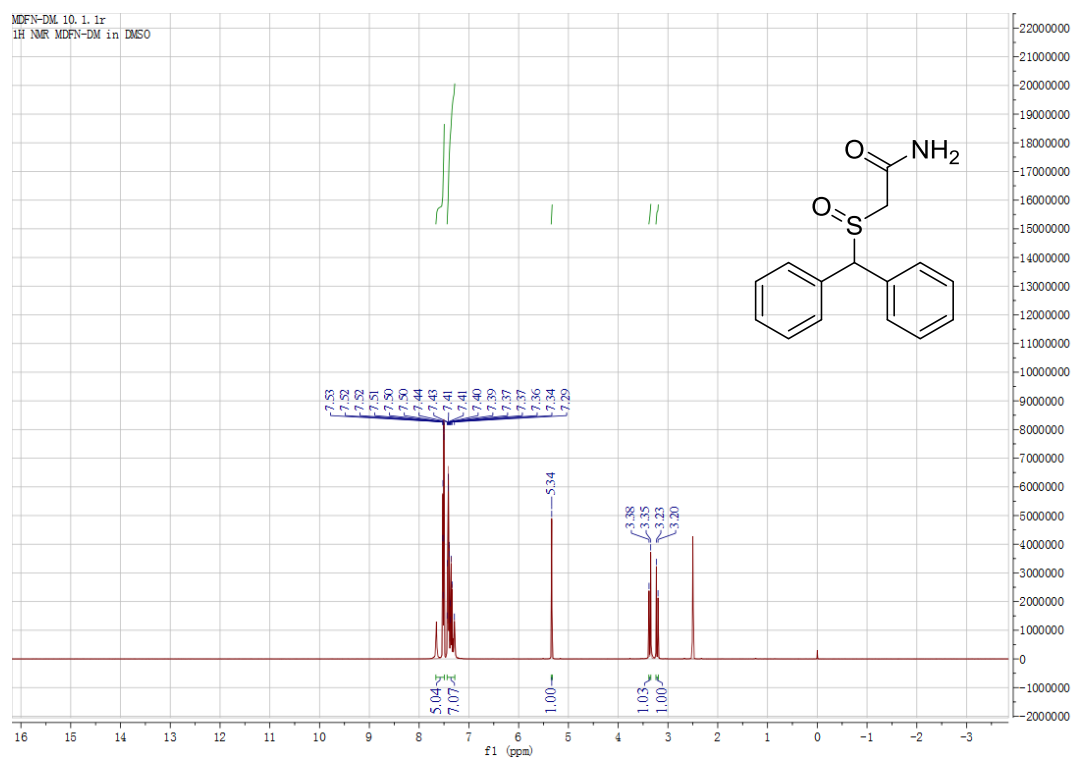
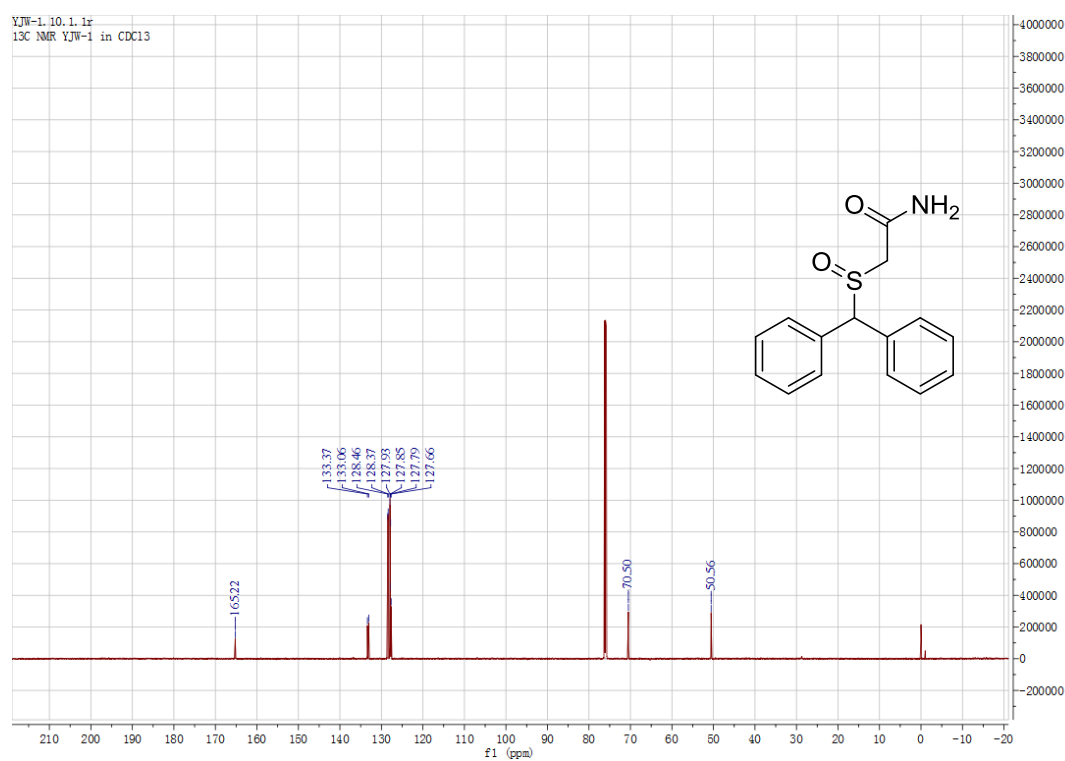
**¹³C NMR (151 MHz, DMSO-*d*₆)****1-(methanesulfonyl)-4-nitrobenzene****¹H NMR (600 MHz, DMSO-*d*₆)**

**¹³C NMR (151 MHz, DMSO-*d*₆)****Sulfonyldibenzene****¹H NMR (600 MHz, DMSO-*d*₆)**

**¹³C NMR (151 MHz, DMSO-*d*₆)****1-chloro-2-(methylsulfonyl)benzene****¹H NMR (600 MHz, DMSO-*d*₆)**

**¹³C NMR (151 MHz, DMSO-*d*₆)****1-chloro-3-(methylsulfonyl)benzene****¹H NMR (600 MHz, DMSO-*d*₆)**

**¹³C NMR (151 MHz, DMSO-*d*₆)****Modafinil****¹H NMR (600 MHz, DMSO-*d*₆)**

**¹³C NMR (151 MHz, CDCl₃)**

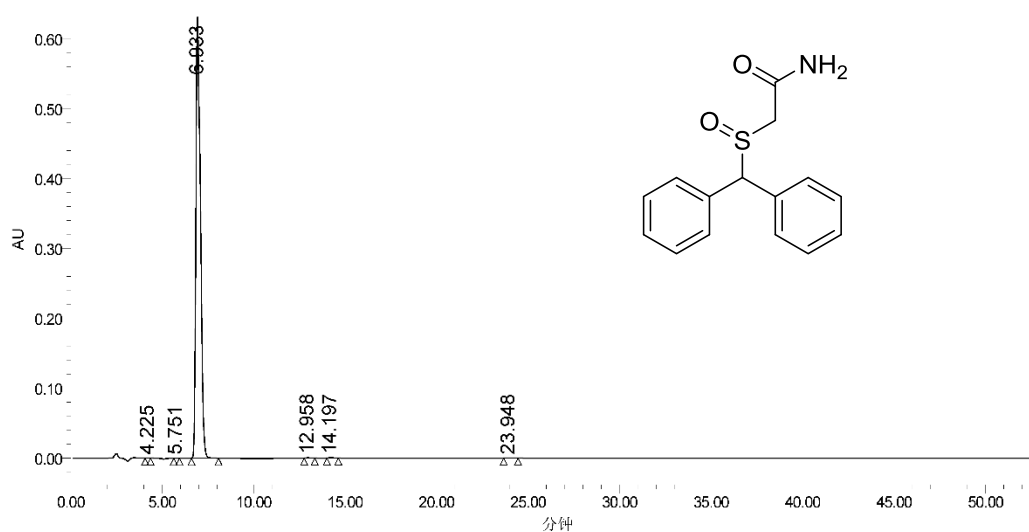
5. HPLC Spectra

Project Name wyq
Reported by User: Breeze user (Breeze)



SAMPLE INFORMATION

Sample Name:	mdfn-mo	Acquired By:	Breeze
Sample Type:	未知	Date Acquired:	2018/11/20 12:44:06 CST
Vial:	999	Acq. Method:	MDFN
Injection #:	8	Date Processed:	2018/11/20 13:41:54 CST
Injection Volume:	3000.00 ul	Channel Name:	W2489 ChA
Run Time:	200.00 Minutes	Sample Set Name:	



	RT (min)	Area (面积*sec)	% Area	Height (面积)	% Height
1	4.225	2829	0.03	271	0.04
2	5.751	1051	0.01	91	0.01
3	6.933	10845266	99.79	630715	99.79
4	12.958	7046	0.06	399	0.06
5	14.197	9013	0.08	444	0.07
6	23.948	2660	0.02	107	0.02

Mobile phase A: 10 mmol/L solution of dipotassium hydrogen phosphate adjusted to pH 3.00 ± 0.05 with phosphoric acid. Mobile phase B: acetonitrile for chromatography. A:B=75:25, UV=210 nm, Flow rate=1.0 mL/min.