Electronic Supplementary Material (ESI) for Chemical Science.

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Supplementary Information for:

Metal- and Oxidant-Free Electrochemical Synthesis of Sulfinic Ester from Thiols and Alcohols

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Table of Contents

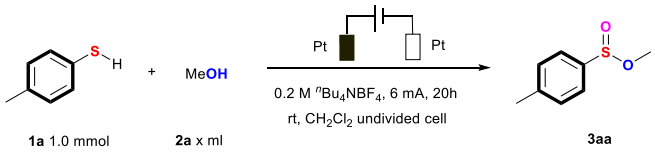
1. General information

All commercial materials were used as received unless otherwise noted. Commercially available chemicals were obtained from Energy Chemical, TCI, Alfa Aesar, J&K. ^{1}H NMR spectra were recorded at 400 MHz using TMS as the internal standard, and ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz using TMS as the internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t), and broad resonances (br). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument. Electrolysis reactions were conducted using a DJS-292B DC power supply purchased from Shanghai Xinrui Instruments Co., Ltd., China. Cyclic voltammetry experiments were carried out in an equipment of CHI761E. CV curves were recorded using a three-electrode scheme. The working electrode was a glassy carbon electrode, A platinum electrode served as counter electrode. Ag/AgCl was used as the reference electrode. The working electrode was polished before recording each CV curve.

2. General procedure of the synthesis of the products

2.1 Screening the amount of alcohols

A set of experiments were carried out to see the relationship between the amount of MeOH and reaction yield (Figure S1). The results strongly suggested that increasing the amount of MeOH benefits the product yield, and >80% yields were obtained when using 0.8-1.2 mL of MeOH.



entry	x	yield
1	0.2	56.4
2	0.4	67.6
3	0.6	79.3
4	0.8	85.2
5	1.0	87.0
6	1.2	87.8

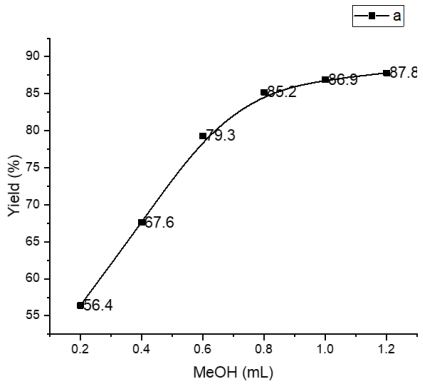
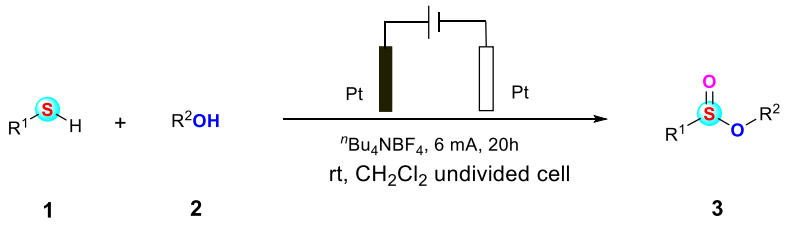
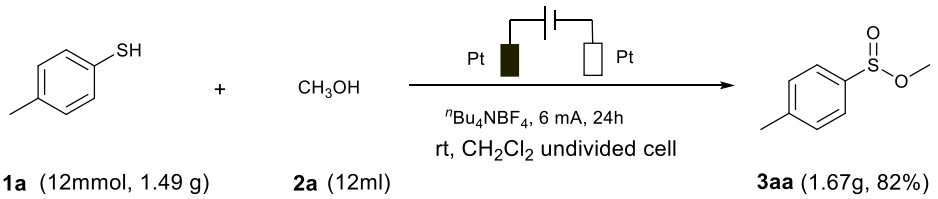


Figure S1. the influence of the amount of MeOH on yield



1 **2** **3**

General procedure A for the preparation of products 3: An undivided cell was equipped with a platinum plate (1.0 × 1.0 cm^2) as the anode and a platinum plate (1.0× 1.0 cm^2) as the cathode and connected to a DC regulated power supply (Figure S2). A mixture of thiophenol **1** (1.0 mmol), alcohol **2** (1.0 mL) and *n*-Bu_4NBF_4 (1.0 mmol) in CH_2Cl_2 (4.0 mL) were added to the undivided cell. The electrolysis was carried out at room temperature using a constant current of 6 mA until complete consumption of the substrate (monitored by TLC, about 20 h). Then, the reaction mixture was concentrated under vacuum. Subsequently, water was added and the mixture was extracted with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (EtOAc:Hex, 1:50 to 1:30) to afford sulfinic ester derivatives **3**.



1a (12mmol, 1.49 g) **2a** (12ml) **3aa** (1.67g, 82%)

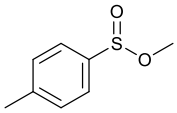
General procedure B for gram scale synthesis of 3aa: An undivided cell was equipped with a platinum plate (1.0 × 1.0 cm^2) as the anode and a platinum plate (1.0× 1.0 cm^2) as the cathode and connected to a DC power supply (Figure S1). A mixture of 4-methylthiophenol **1a** (12.0 mmol), methanol **2a** (12.0 mL) and *n*-Bu_4NBF_4 (12.0 mmol) in CH_2Cl_2 (40.0 mL) were added to an undivided cell. The electrolysis was carried out at room temperature using a constant current of 6 mA until complete consumption of the substrate (monitored by TLC). Then, the reaction mixture was concentrated under vacuum. Subsequently, water was added and the mixture was extracted with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (EtOAc:Hex, 1:50 to 1:30) to afford methyl 4-methylbenzenesulfinate (**3aa**, 1.67 g, 82%).

Notes:

1. MeOH and CH_2Cl_2 can be recovered by rotary evaporation for repeated use.
2. When solvent was recovered by rotary evaporation, the given residue could be washed with water to remove or recycle *n*-Bu_4NBF_4.

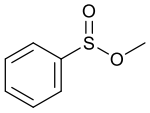
Figure S2. Electrolysis setup

Characterization data of the products



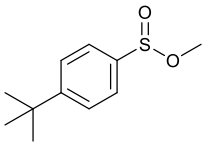
Methyl 4-methylbenzenesulfinate (3aa)

R_f 0.26 (hexane/EtOAc = 30/1); Colorless oily liquid (148 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 3.47 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.9, 129.7, 125.4, 49.3, 21.5. HRMS-ESI: calcd for $C_{10}H_{14}NaO_2S$ $[M + Na]^+$, 221.0607, found: 221.0606.



Methyl benzenesulfinate (3ba)

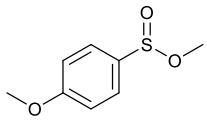
R_f 0.26 (hexane/EtOAc = 30/1); Colorless oily liquid (133 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.59 – 7.58 (m, 3H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 132.2, 129.1, 125.4, 49.6. HRMS-ESI: calcd for $C_7H_8NaO_2S$ $[M + Na]^+$, 179.0137, found: 179.0134.



Methyl 4-(tert-butyl)benzenesulfinate (3ca)

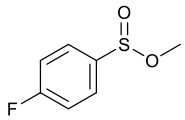
R_f 0.30 (hexane/EtOAc = 30/1); Colorless oily liquid (174 mg, 82% yield); ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 3.53 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 140.9, 126.1, 125.2, 49.7, 35.1, 31.2. HRMS-ESI: calcd for $C_{11}H_{16}NaO_2S$ $[M + Na]^+$, 235.0763, found: 235.0764.



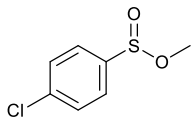
Methyl 4-methoxybenzenesulfinate (3da)

R_f 0.27 (hexane/EtOAc = 30/1); Colorless oily liquid (167 mg, 90% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 135.5, 127.2, 114.4, 55.6, 49.2. HRMS-ESI: calcd for $C_8H_{10}NaO_3S$ $[M + Na]^+$, 209.0243, found: 209.0244.



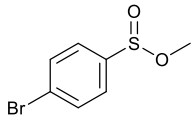
Methyl 4-fluorobenzenesulfinate (3ea)

R_f 0.28 (hexane/EtOAc = 30/1); Colorless oily liquid (136 mg, 78% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.25 – 7.21 (m, 2H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3 (d, J_{C-F} = 251.6 Hz), 139.7 (d, J_{C-F} = 3.0 Hz), 127.9 (d, J_{C-F} = 9.1 Hz), 116.5 (J_{C-F} = 24.2 Hz), 49.7. HRMS-ESI: calcd for $C_7H_7FNaO_2S$ $[M + Na]^+$, 197.0043, found: 197.0042.



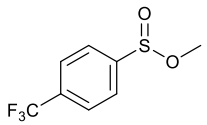
Methyl 4-chlorobenzenesulfinate (3fa)

R_f 0.24 (hexane/EtOAc = 30/1); Colorless oily liquid (137 mg, 72% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 3.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.7, 129.4, 126.9, 49.8. HRMS-ESI: calcd for $C_7H_7ClNaO_2S$ $[M + Na]^+$, 212.9747, found: 212.9746.



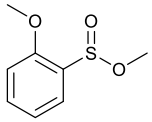
Methyl 4-bromobenzenesulfinate (3ga)

R_f 0.28 (hexane/EtOAc = 30/1); Colorless oily liquid (174 mg, 74% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.2 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 3.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 132.3, 127.1, 49.8. HRMS-ESI: calcd for $C_7H_7BrNaO_2S$ $[M + Na]^+$, 256.9242, found: 256.9240.



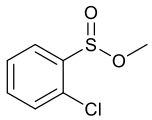
Methyl 4-(trifluoromethyl)benzenesulfinate (3ha)

R_f 0.26 (hexane/EtOAc = 30/1); Colorless oily liquid (159 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 4H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 134.6 (q, J_{C-F} = 32.7 Hz), 129.9 (q, J_{C-F} = 245.6 Hz), 126.2 (d, J_{C-F} = 3.7 Hz), 126.1, 50.1. HRMS-ESI: calcd for $C_8H_7F_3NaO_2S$ $[M + Na]^+$, 247.0011, found: 247.0010.



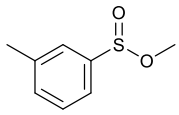
Methyl 2-methoxybenzenesulfinate (3ia)

R_f 0.23 (hexane/EtOAc = 30/1); Colorless oily liquid (113 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 7.6, 1.6 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.12 (td, J = 7.6, 0.8 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 133.9, 131.1, 126.1, 120.7, 111.3, 55.9, 50.4. HRMS-ESI: calcd for $C_8H_{10}NaO_3S$ $[M + Na]^+$, 209.0243, found: 209.0244.



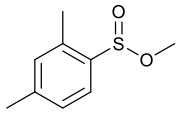
Methyl 2-chlorobenzenesulfinate (3ja)

R_f 0.26 (hexane/EtOAc = 30/1); Colorless oily liquid (110 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 1H), 7.51 – 7.44 (m, 3H), 3.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 133.4, 132.7, 130.3, 127.1, 126.6, 51.2. HRMS-ESI: calcd for $C_7H_7ClNaO_2S$ $[M + Na]^+$, 212.9747, found: 212.9748.



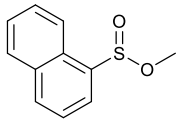
Methyl 3-methylbenzenesulfinate (3ka)

R_f 0.27 (hexane/EtOAc = 30/1); Colorless oily liquid (119 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47(s, 1H), 7.44(d, J = 8.0 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 3.42 (s, J = 1.0 Hz, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 139.2, 133.0, 128.9, 125.6, 122.5, 49.6, 21.4. HRMS-ESI: calcd for $C_8H_{10}NaO_2S$ $[M + Na]^+$, 193.0294, found: 193.0293.



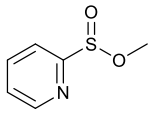
Methyl 2,4-dimethylbenzenesulfinate (3la)

R_f 0.28 (hexane/EtOAc = 30/1); Colorless oily liquid (125 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.06 (s, 1H), 3.48 – 3.43 (m, 3H), 2.44 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 138.2, 136.5, 131.9, 126.9, 124.9, 49.6, 21.4, 17.9. HRMS-ESI: calcd for $C_9H_{12}NaO_2S$ $[M + Na]^+$, 207.0450, found: 207.0451.



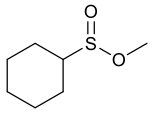
Methyl naphthalene-1-sulfinate (3ma)

R_f 0.24 (hexane/EtOAc = 30/1); Colorless oily liquid (134 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) 8.34 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 7.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), δ 7.69 – 7.60 (m, 3H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 133.7, 133.0, 129.4, 128.8, 127.6, 126.8, 124.8, 122.3, 49.5. HRMS-ESI: calcd for $C_{11}H_{10}NaO_2S$ $[M + Na]^+$, 229.0294, found: 229.0293.



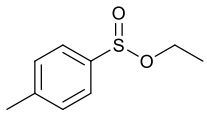
Methyl pyridine-2-sulfinate (3na)

R_f 0.28 (hexane/EtOAc = 30/1); Colorless oily liquid (111 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.0 Hz, 1H), 7.98 – 7.95(m, 2H), 7.49 – 7.46 (m, 1H), 3.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 150.2, 137.8, 126.3, 120.2, 51.2. HRMS-ESI: calcd for $C_6H_7NNaO_2S$ $[M + Na]^+$, 180.0090; found, 180.0089.



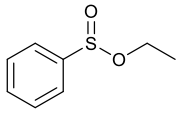
Methyl cyclohexanesulfinate (3ma)

R_f 0.25 (hexane/EtOAc = 30/1); Colorless oily liquid (122 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 3H), 2.45 – 2.37(m, 1H), 1.88 – 1.81 (m, 2H), 1.76 – 1.71 (m, 2H), 1.57 – 1.54 (m, 1H), 1.29 – 1.10 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.3, 54.7, 25.5, 24.9, 25.0, 24.33, 23.9. HRMS-ESI: calcd for $C_7H_{14}NaO_2S$ $[M + Na]^+$, 185.0607, found: 185.0606.



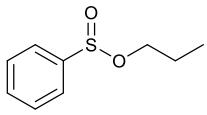
Ethyl 4-methylbenzenesulfinate (3ab)

R_f 0.24 (hexane/EtOAc = 30/1); Colorless oily liquid (164 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.12 – 4.04 (m, 1H), 3.74 – 3.67 (m, 1H), 2.41 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.9, 129.7, 125.2, 60.7, 21.5, 15.5. HRMS-ESI: calcd for $C_9H_{12}NaO_2S$ $[M + Na]^+$, 207.0450, found: 207.0447.



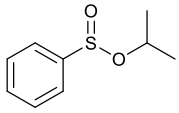
Ethyl benzenesulfinate (3bb)

R_f 0.26 (hexane/EtOAc = 30/1); Colorless oily liquid (148 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 2H), 7.62 – 7.50 (m, 3H), 4.17 – 4.09 (m, 1H), 3.79 – 3.71 (m, 1H), 1.30 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 132.0, 128.9, 125.2, 61.0, 15.5. HRMS-ESI: calcd for $C_8H_{10}NaO_2S$ [M + Na]$^+$, 193.0294, found: 193.0293.



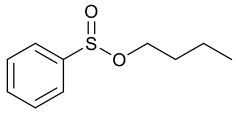
Propyl benzenesulfinate (3bc)

R_f 0.27 (hexane/EtOAc = 30/1); Colorless oily liquid (155 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.34 (m, 2H), 7.57 (d, *J* = 5.2 Hz, 3H), 4.06 – 4.01 (m, 1H), 3.65 – 3.59 (m, 1H), 1.73 – 1.64 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 132.0, 128.9, 125.2, 66.4, 23.1, 10.3. HRMS-ESI: calcd for $C_9H_{12}NaO_2S$ [M + Na]$^+$, 207.0450, found: 207.0449.



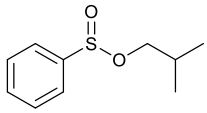
***i*-Propyl benzenesulfinate (3bd)**

R_f 0.26 (hexane/EtOAc = 30/1); Colorless oily liquid (144 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.57 – 7.55 (m, 3H), 4.65 (dt, *J* = 12.4, 6.2 Hz, 1H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.28 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 131.9, 128.9, 125.0, 72.9, 23.9, 23.7. HRMS-ESI: calcd for $C_9H_{12}NaO_2S$ [M + Na]$^+$, 207.0450, found: 207.0450.



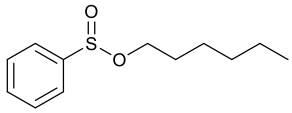
Butyl benzenesulfinate (3be)

R_f 0.28 (hexane/EtOAc = 30/1); Colorless oily liquid (179 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.52 – 7.51 (m, 3H), 4.06 – 4.00 (m, 1H), 3.64 – 3.58 (m, 1H), 1.63 – 1.56 (m, 2H), 1.38–1.29 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 131.9, 128.9, 125.2, 64.6, 31.7, 18.9, 13.5. HRMS-ESI: calcd for $C_{10}H_{14}NaO_2S$ [M + Na]$^+$, 221.0607, found: 221.0606.



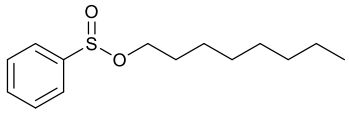
***i*-Butyl benzenesulfinate (3bf)**

R_f 0.30 (hexane/EtOAc = 30/1). Colorless oily liquid (145 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 2H), 7.57 – 7.55 (m, 3H), 3.86–3.82 (m, 1H), 3.39 – 3.35 (m, 1H), 1.96 – 1.89 (m, 1H), 0.93 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 131.9, 128.9, 125.2, 70.6, 28.6, 18.9. HRMS-ESI: calcd for $C_{10}H_{14}NaO_2S$ [M + Na]$^+$, 221.0607, found: 221.0604.



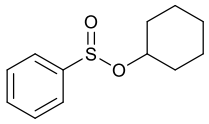
Hexyl benzenesulfinate (3bg)

R_f 0.26 (hexane/EtOAc = 30/1); Colorless oily liquid (179 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.52 (d, *J* = 3.6 Hz, 3H), 4.05 – 3.99 (m, 1H), 3.63 – 3.57(m, 1H), 1.60 (dd, *J* = 14.0, 7.0 Hz, 2H), 1.30 – 1.23 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 131.9, 128.9, 125.22, 64.8, 31.3, 29.6, 25.4, 22.4, 13.9. HRMS-ESI: calcd for $C_{12}H_{18}NaO_2S$ $[M + Na]^+$, 249.0920,found: 249.0921.



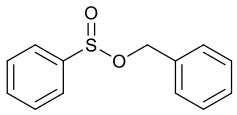
Octyl benzenesulfinate (3bh)

R_f 0.28 (hexane/EtOAc = 30/1); Colorless oily liquid (190 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 2H), 7.62 (d, *J* = 4.6 Hz, 3H), 4.15 – 4.09 (m, 1H), 3.73 – 3.67 (m, 1H), 1.74 – 1.67 (m, 2H), 1.39 – 1.33 (m, 10H), 0.95 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 131.9, 128.9, 125.2, 64.9, 31.7, 29.7, 29.2, 29.1, 25.7, 22.6, 14.0. HRMS-ESI: calcd for $C_{14}H_{22}NaO_2S$ $[M + Na]^+$, 277.1233, found: 277.1232.



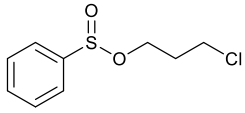
Cyclohexyl benzenesulfinate (3bi).

R_f 0.26 (hexane/EtOAc = 30/1); Colorless oily liquid (150 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.65 (m, 2H), 7.56 – 7.52 (m, 3H), 4.36 – 4.32 (m, 1H), 2.02 – 2.00 (m, 1H), 1.77 – 1.69 (m, 3H), 1.63 – 1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ145.9, 131.8, 128.9, 125.1, 33.7, 33.6, 25.1, 23.8. HRMS-ESI: calcd for $C_{12}H_{16}NaO_2S$ $[M + Na]^+$, 247.0763, found: 247.0762.



Benzyl benzenesulfinate (3bj)

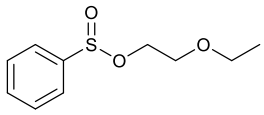
R_f 0.30 (hexane/EtOAc = 30/1); Colorless oily liquid (141 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.56 – 7.54 (m, 3H), 7.34 – 7.28 (m, 5H), 5.05 (d, *J* = 8.0 Hz, 1H), 4.58 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 141.6, 135.4, 132.2, 129.1, 128.6, 128.5, 125.4, 65.9, 29.7. HRMS-ESI: calcd for $C_{13}H_{12}NaO_2S$ $[M + Na]^+$, 255.0450, found: 255.0451.



3-Chloropropyl benzenesulfinate (3bk)

R_f 0.26 (hexane/EtOAc = 30/1); Colorless oily liquid (176 mg, 81% yield); ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.59 (dd, *J* = 5.2, 1.2 Hz, 3H), 4.24 – 4.19 (m, 1H), 3.83 – 3.77 (m, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.17 – 2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 132.3, 129.1, 125.2, 61.1, 40.9, 32.6. HRMS-ESI: calcd for $C_9H_{11}ClNaO_2S$ $[M + Na]^+$, 241.0060, found: 241.0061.

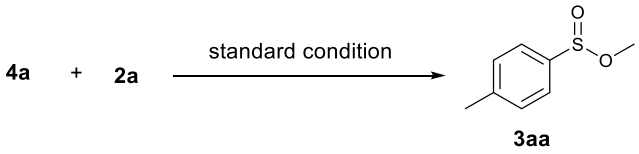


2-Ethoxyethyl benzenesulfinate (3bl)

R_f 0.28 (hexane/EtOAc = 30/1); Colorless oily liquid (145 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.75 (m, 2H), 7.57 – 7.55 (m, 3H), 4.23 – 4.18 (m, 1H), 3.79 – 3.74 (m, 1H), 3.64 (d, *J* = 4.0 Hz, 2H), 3.58 – 3.45 (m, 2H), 1.21 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 132.1, 129.0, 125.4, 69.0, 66.6, 63.5, 15.0. HRMS-ESI: calcd for $C_{10}H_{14}NaO_3S$ $[M + Na]^+$, 237.0556, found: 237.0554.

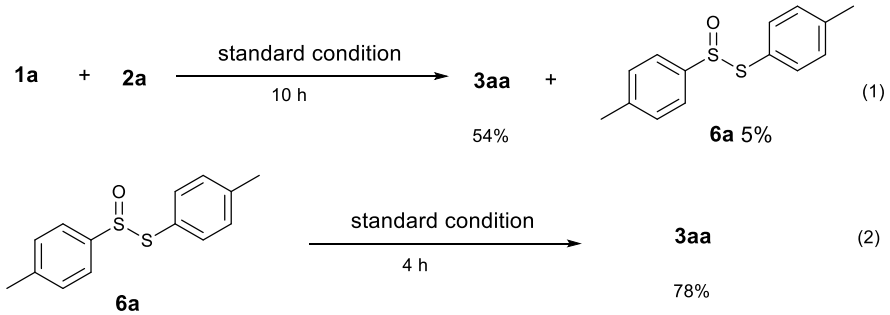
3. Control experiments

3.1 The reaction between 4a and 2a

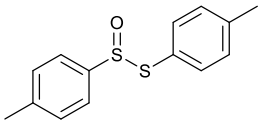


Subjecting 1,2-di-*p*-tolyldisulfane (**4a)** to methanol resulted in formation of **3aa** in 89% yield. These two control experiments implied that aryl sulfur radical was generated, and the aryl disulfide **4** was an intermediate in this reaction.

3.2 The preparation of intermediate 6

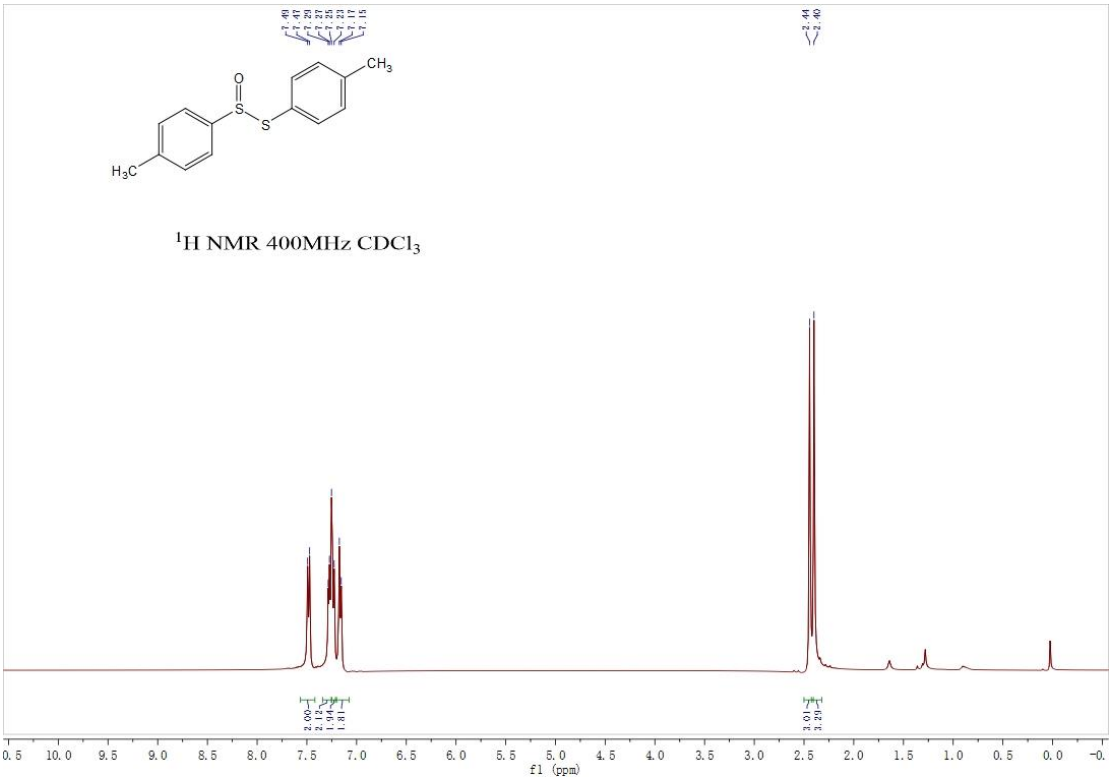


Following the general procedure A (**1a** as the starting material), the reaction time was reduced to 10 h. The thiosulfinates **6a** was obtained in 5% yield, accompanying with 54% yield of **3aa** (eq. 1). In addition, subjecting **6a** to the standard conditions for 4 h led to the formation of **3aa** in 78% yield.



4-Methylbenzenethiosulfinic acid S-(4-methylphenyl) ester (6a)

R_f 0.30 (hexane/EtOAc = 30/1); Colorless solid; m.p. = 83-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.6, 142.1, 140.5, 136.5, 130.2, 129.4, 127.6, 124.6, 21.7, 21.5. HRMS-ESI: calcd for $C_{14}H_{14}NaOS_2$ $[M + Na]^+$, 285.0378; found, 285.0381.



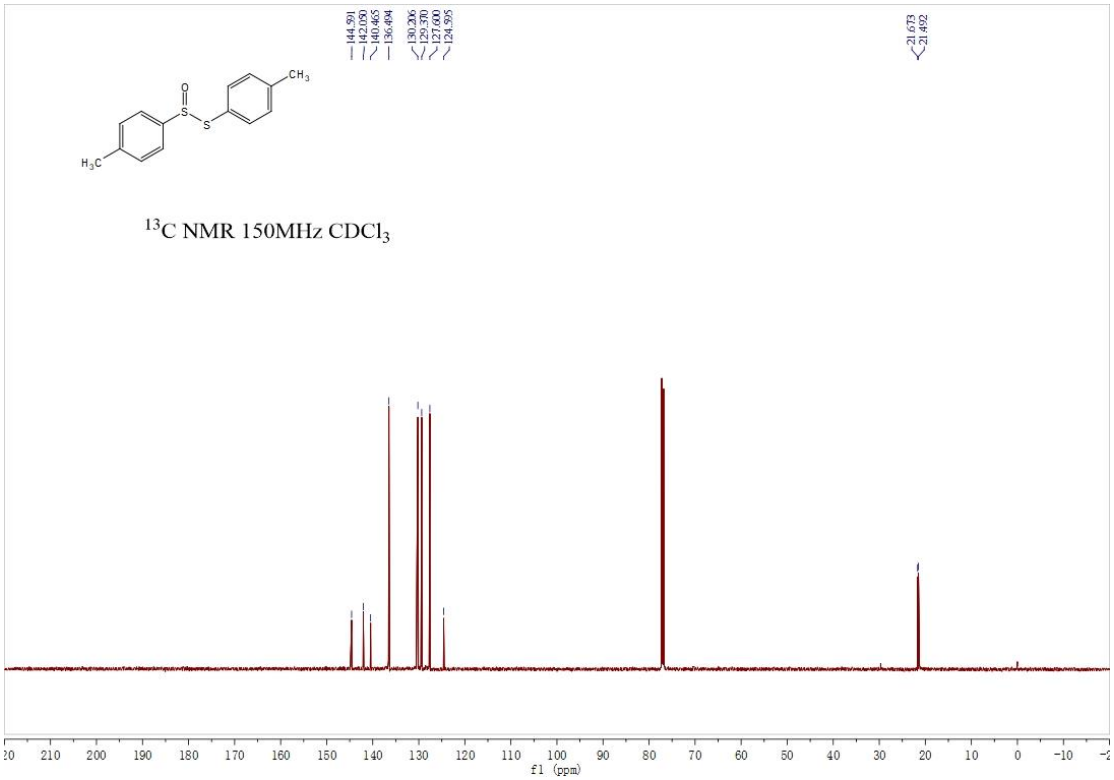
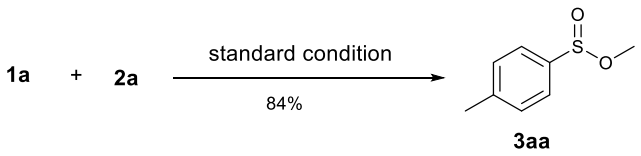


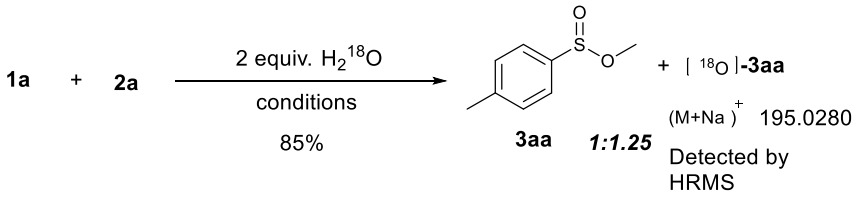
Figure S3. The NMR spectra of **6a**

3.3 The reaction of 1a and dry methanol under N_2



Subjecting thiophenol **1** to dry methanol resulted in formation of **3aa** in 84% yield. This experiment implied the alcohols may not only act as reactant but also act as oxidant to oxidize the S(II) to S(IV) spices.

3.4 The isotope labeling experiment



An isotopic labeling reaction was carried out by treatment of **1a** and **2a** in the presence of $H_2{}^{18}O$ under standard conditions, leading to a mixture of **3aa** and [^{18}O]-**3aa** (1:1.25) in 85% yield. The spectra of the mixture of **3aa** and [^{18}O]-**3aa** was listed as bellow (**Figure S4**).

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\20190322\acr0322-18o_GB7_01_421.d	Acquisition Date	3/22/2019 2:52:06 PM
Method	HPLC - MS-no column - positive.m	Operator	Demo User
Sample Name	acr0322-18o	Instrument	compact 8255754.20167
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.8 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	9.0 l/min
Scan End	1300 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

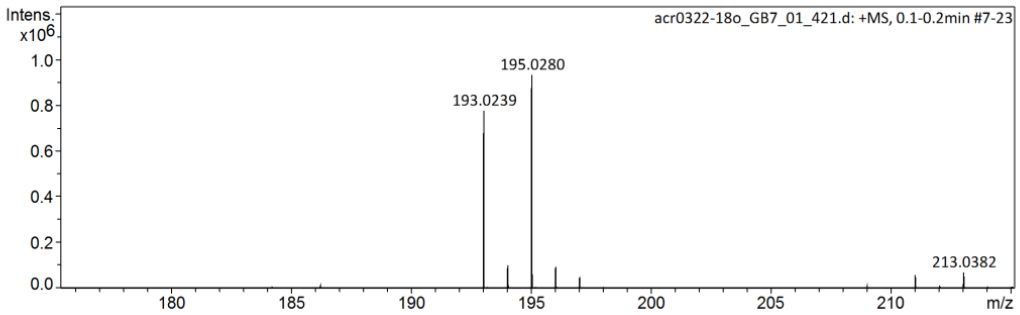


Figure S4. The HMRS spectra of the mixture of **3aa** and [^{18}O]-**3aa**.

4. Cyclic voltammetry studies

The cyclic voltammograms were recorded in an electrolyte of n-Bu_4NBF_4 (0.1 M) in MeCN (10.0 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate is 100 mV/s. According to results (Figure S5), the oxidation potential of thiol ($E_{P/2}$ = 1.908 V) could be clearly observed to obtain **4a**. However, the process to produce **3aa** couldn't be observed may due to its low reaction rate.

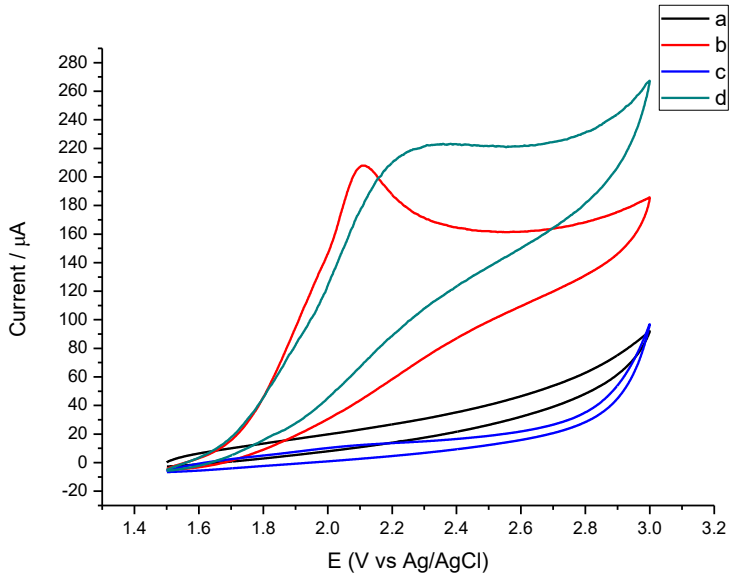


Figure S5. Cyclic voltammograms. a: Blank; b: **1a** (10 mM); c: **2a** (20 mM); d: **1a** (10 mM) + **2a** (20 mM)

Moreover, we have tested the oxidation potentials of **3aa** and **4a** with or without MeOH (Figure S6). In the CV, we can't find the oxidation potentials of **3aa**, which indicated that the further oxidation to form sulfonate did not happen in this reaction.

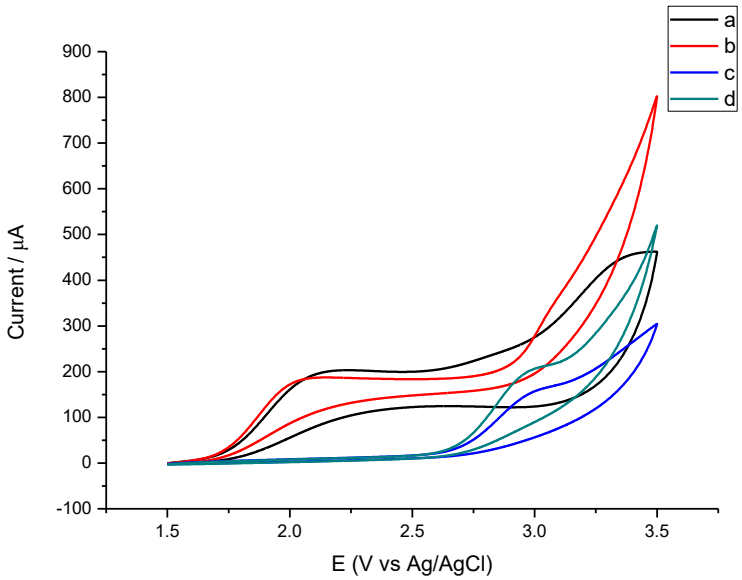
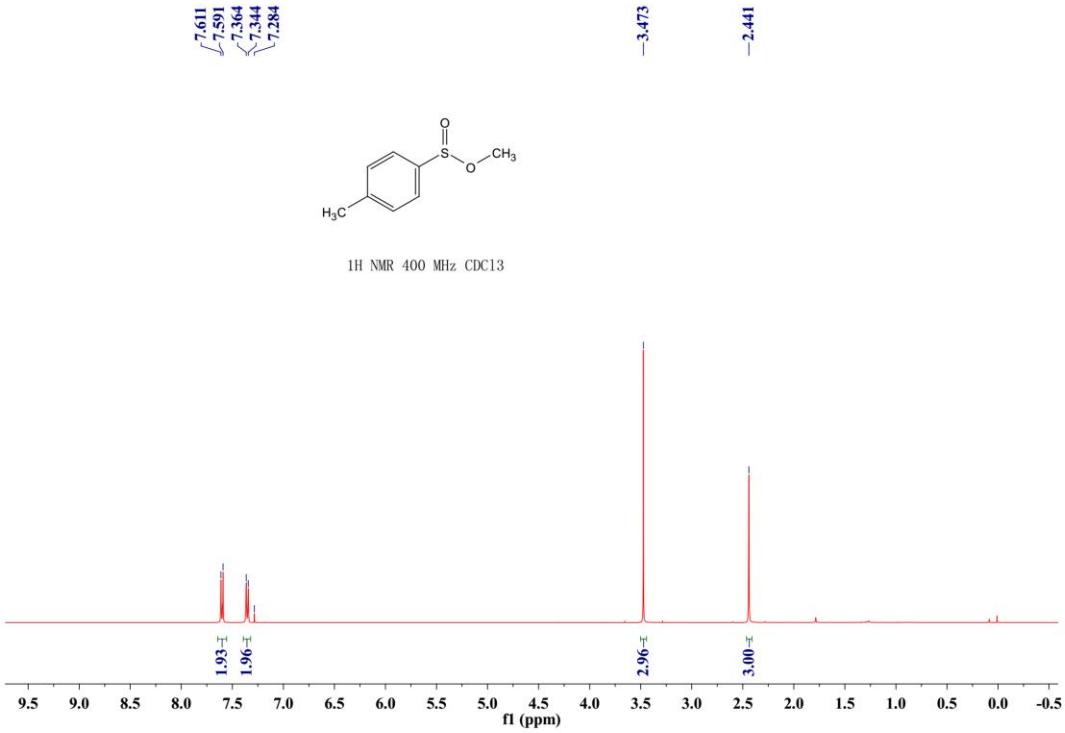
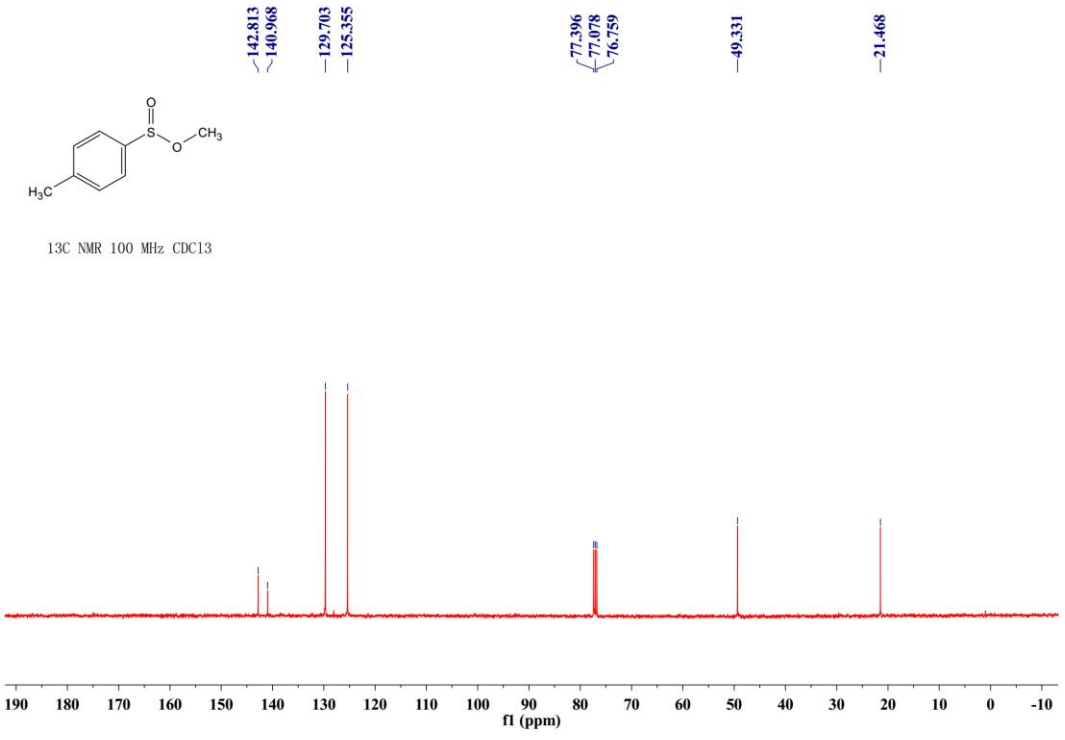


Figure S6. Cyclic voltammograms. a: **4a** (10 mM); b: **4a** (10 mM) + **2a** (20 mM); c: **3aa** (10 mM); d: **3aa** (10 mM) + **2a** (20 mM)

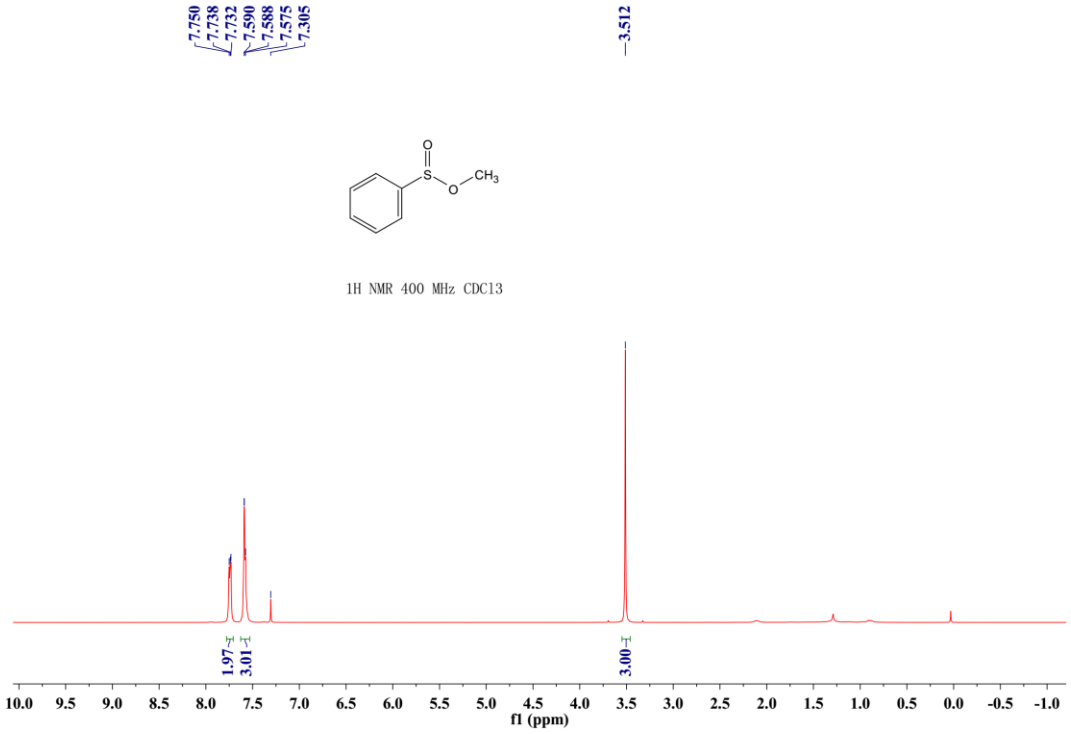
5. NMR spectra

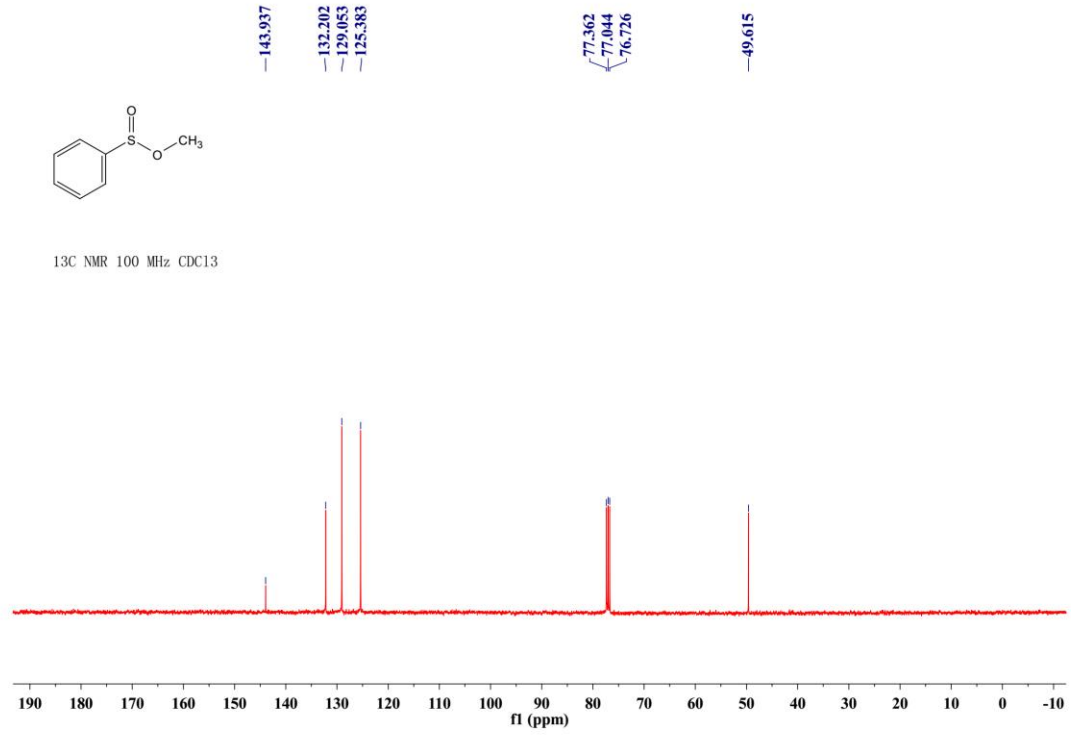
Methyl 4-methylbenzenesulfinate (3aa)



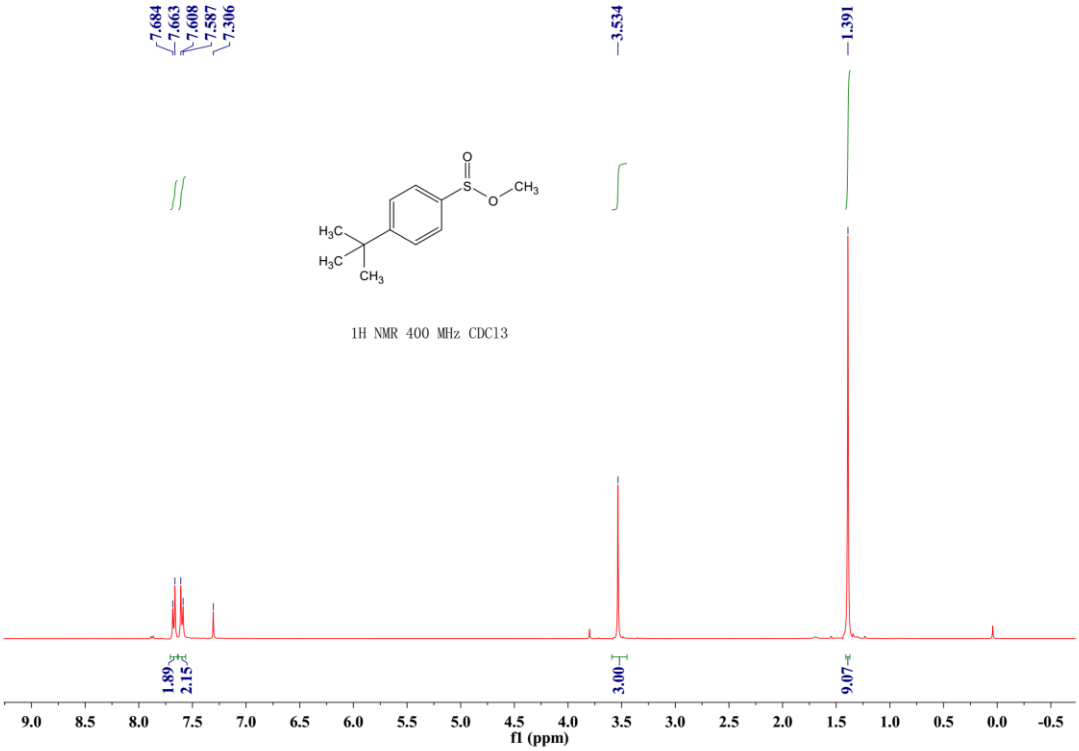


Methyl benzenesulfinate (3ba)

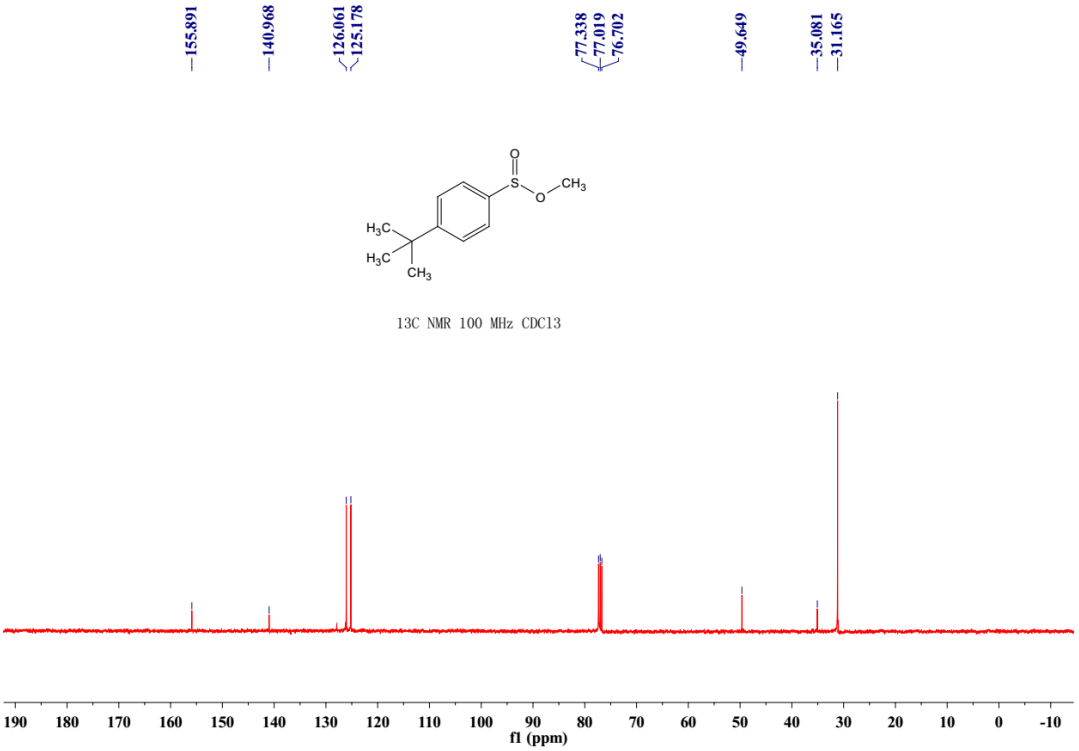




Methyl 4-(tert-butyl)benzenesulfinate (3ca)

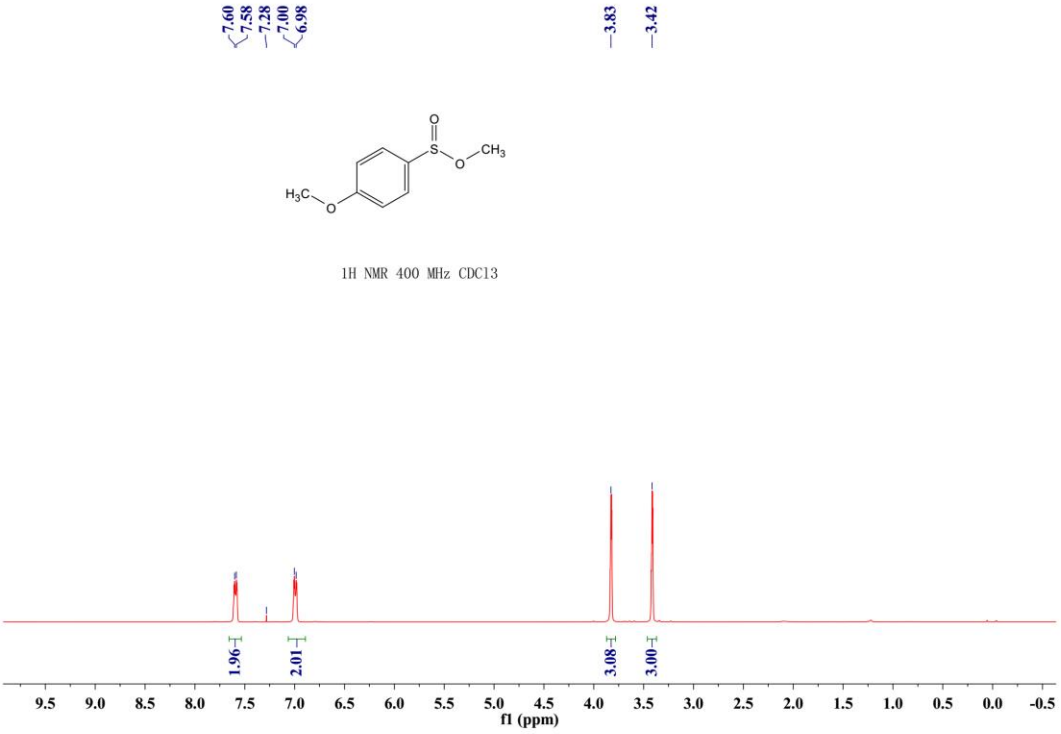


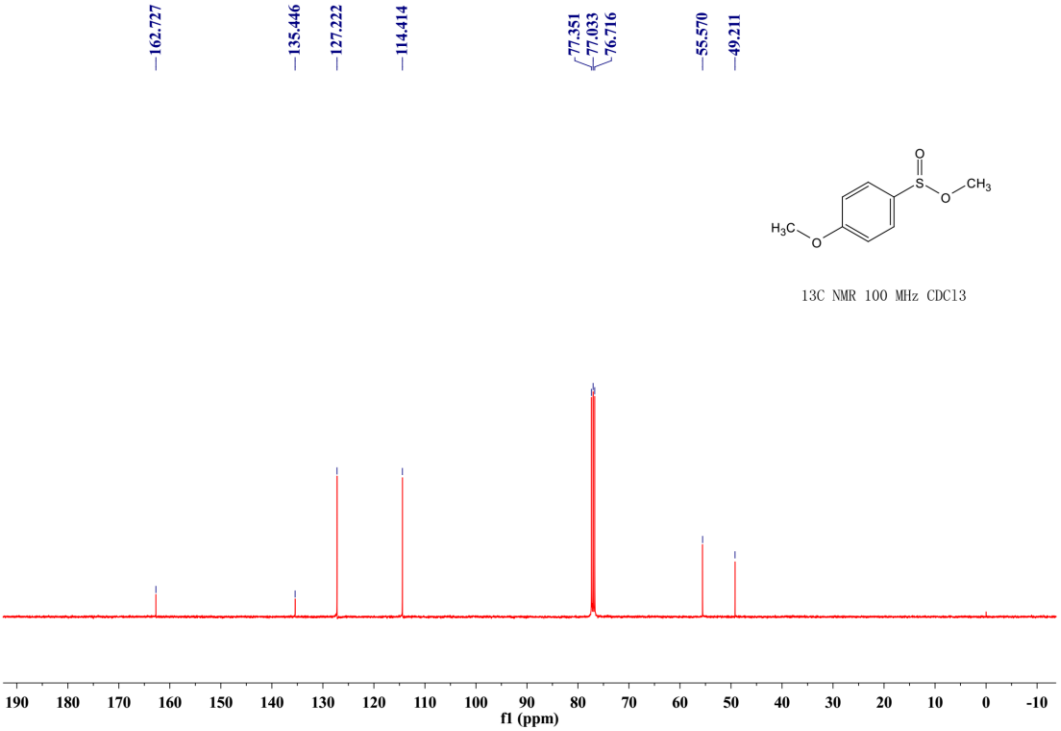
1H NMR 400 MHz CDCl3



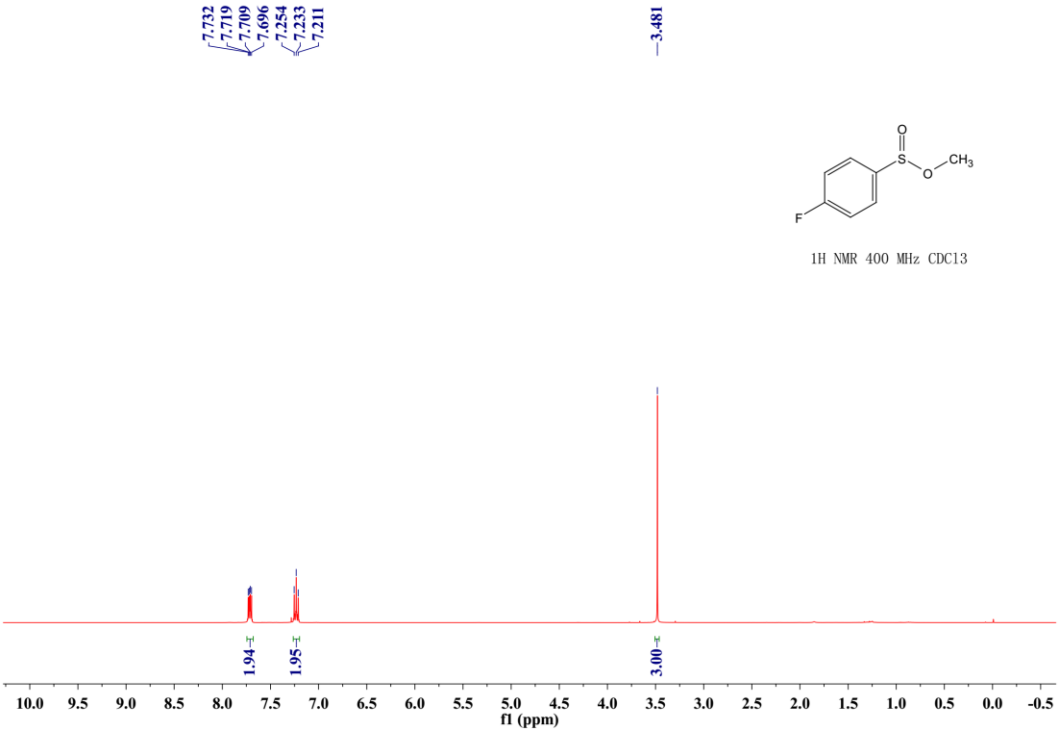
13C NMR 100 MHz CDCl3

Methyl 4-methoxybenzenesulfinate (3da)

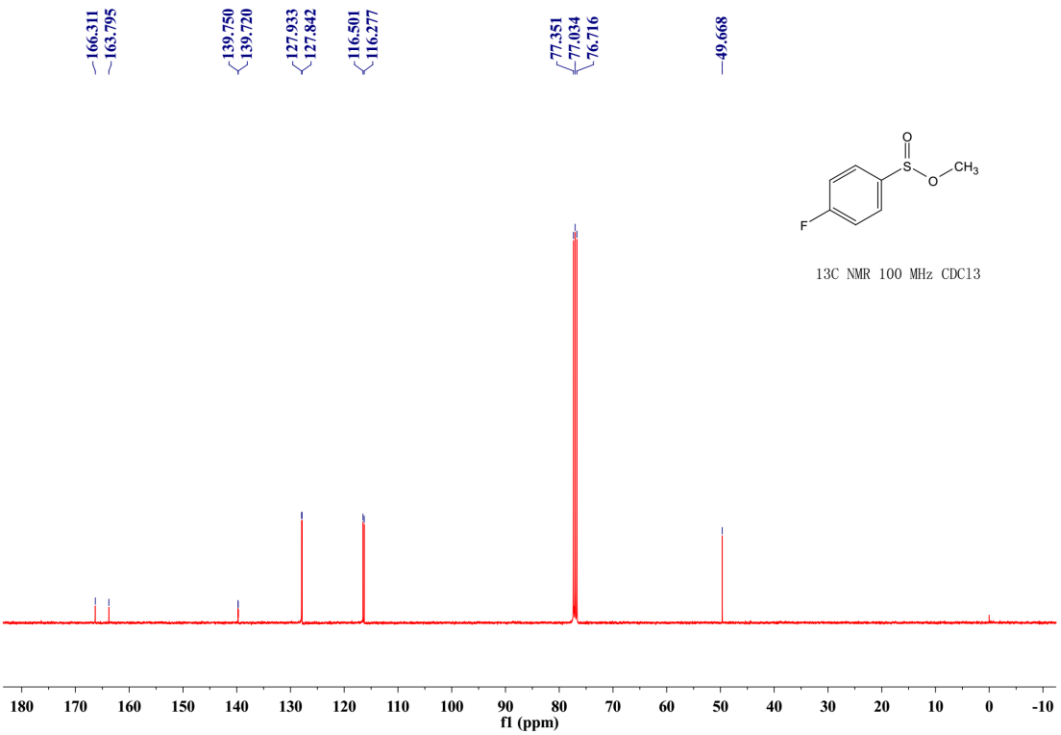




Methyl 4-fluorobenzenesulfinate (3ea)

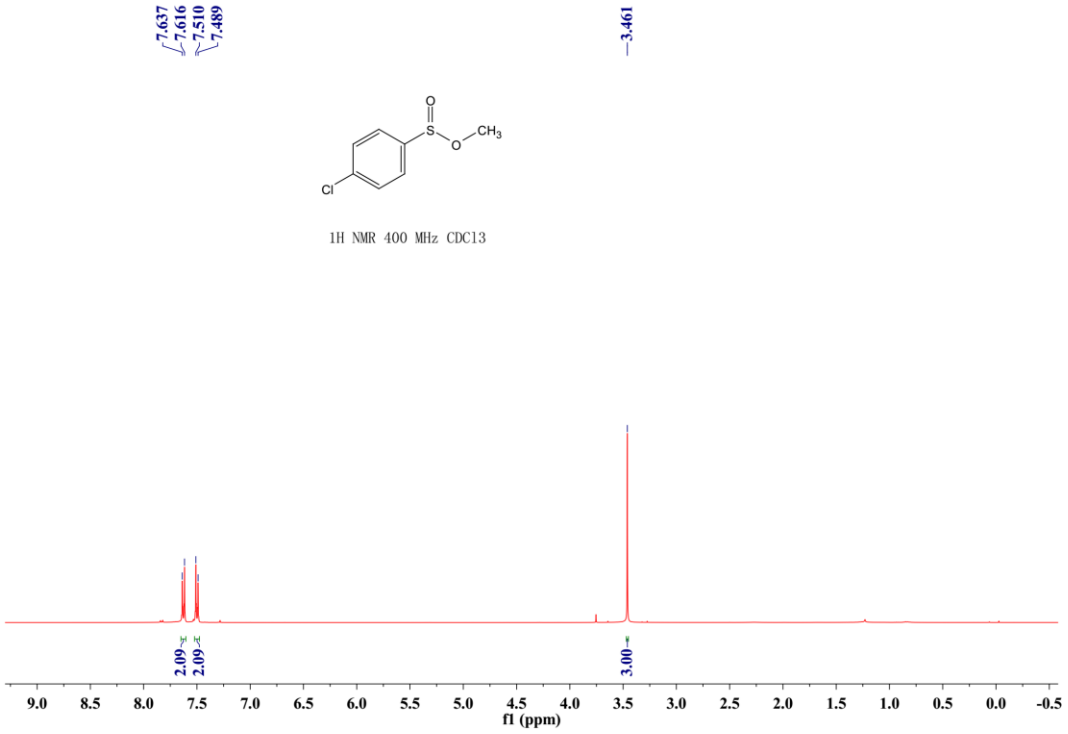


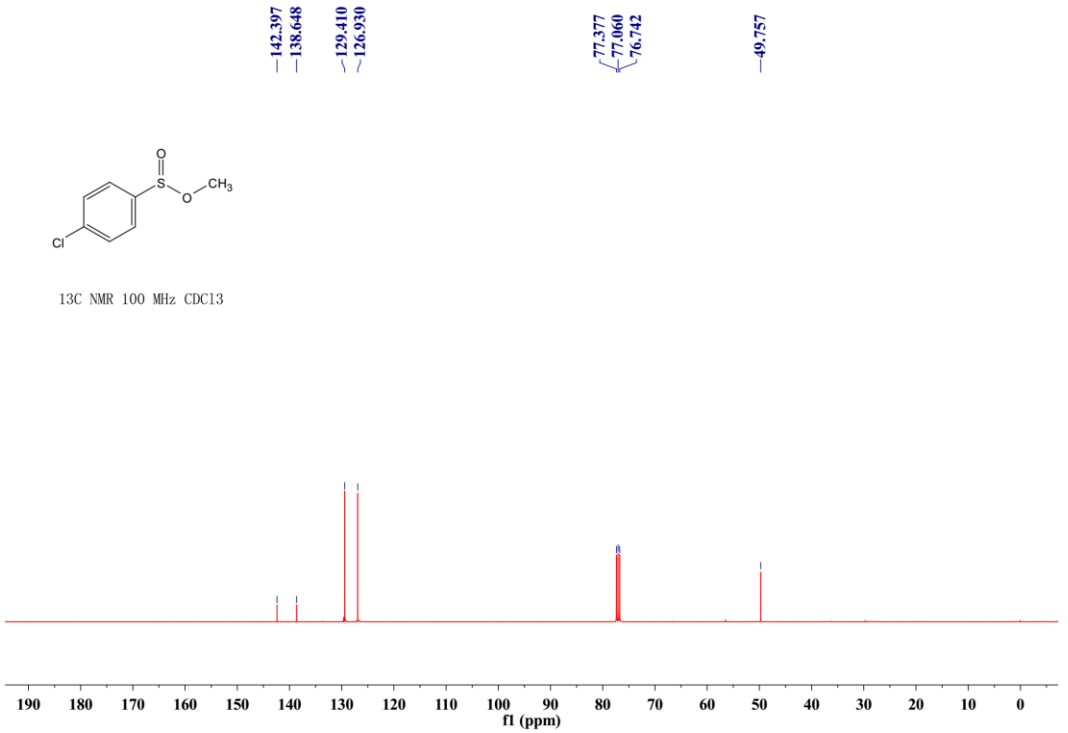
1H NMR 400 MHz CDCl3



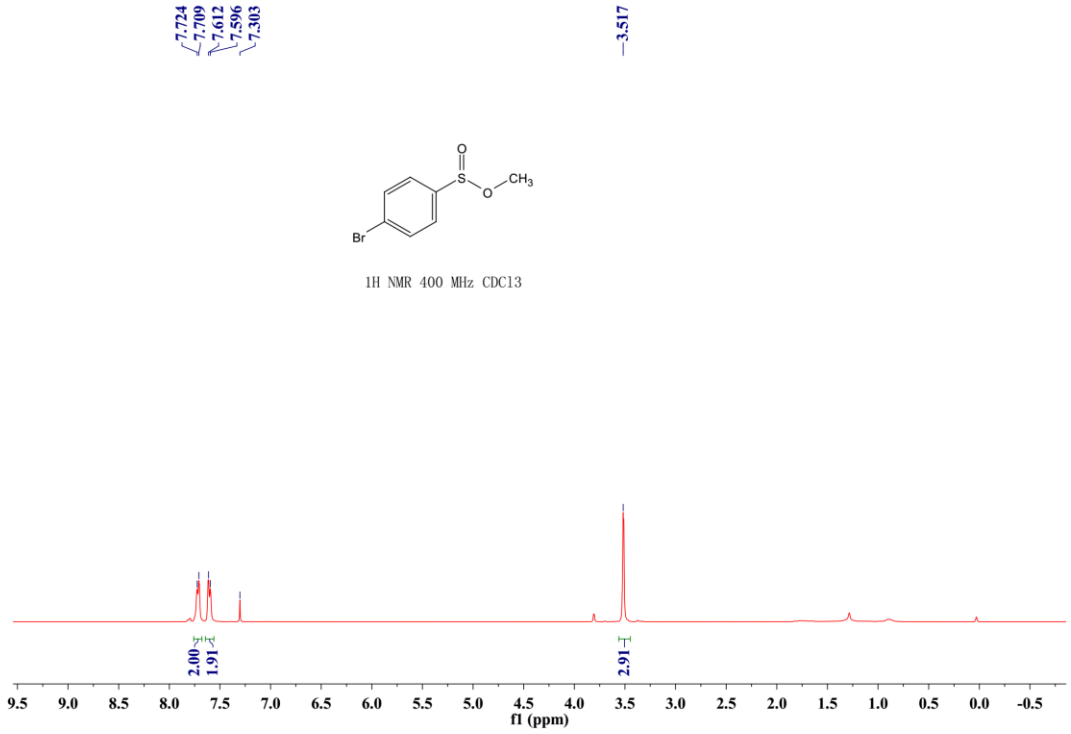
13C NMR 100 MHz CDCl3

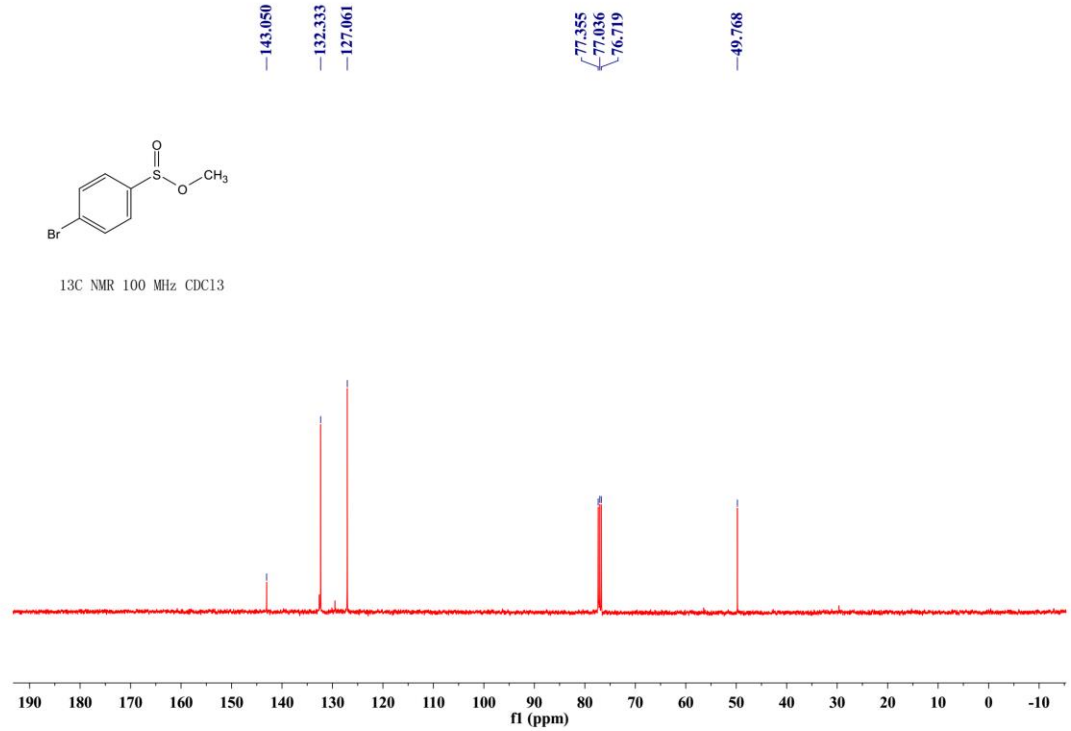
Methyl 4-chlorobenzenesulfinate (3fa)



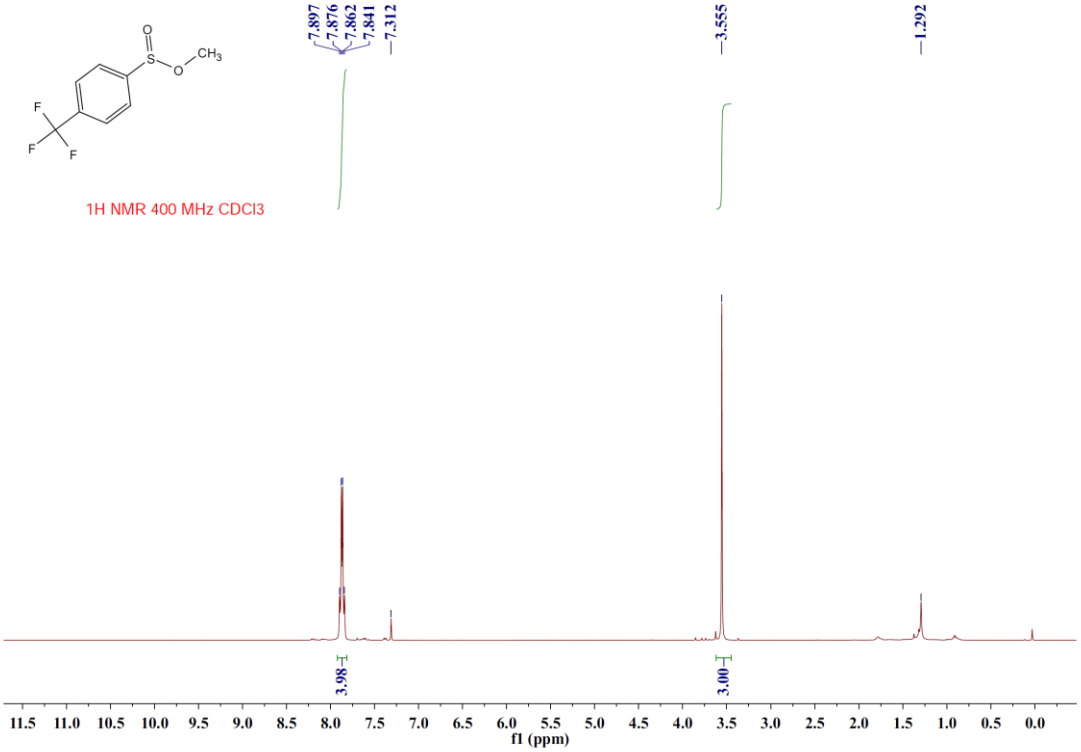


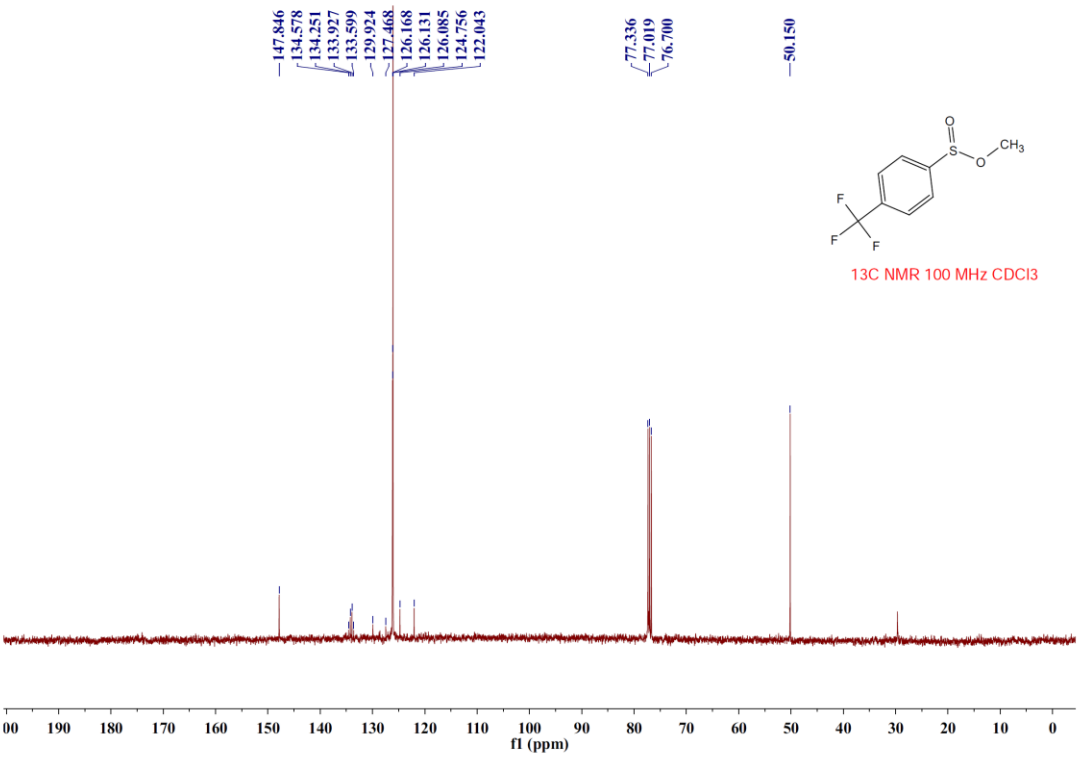
Methyl 4-bromobenzenesulfinate (3ga)



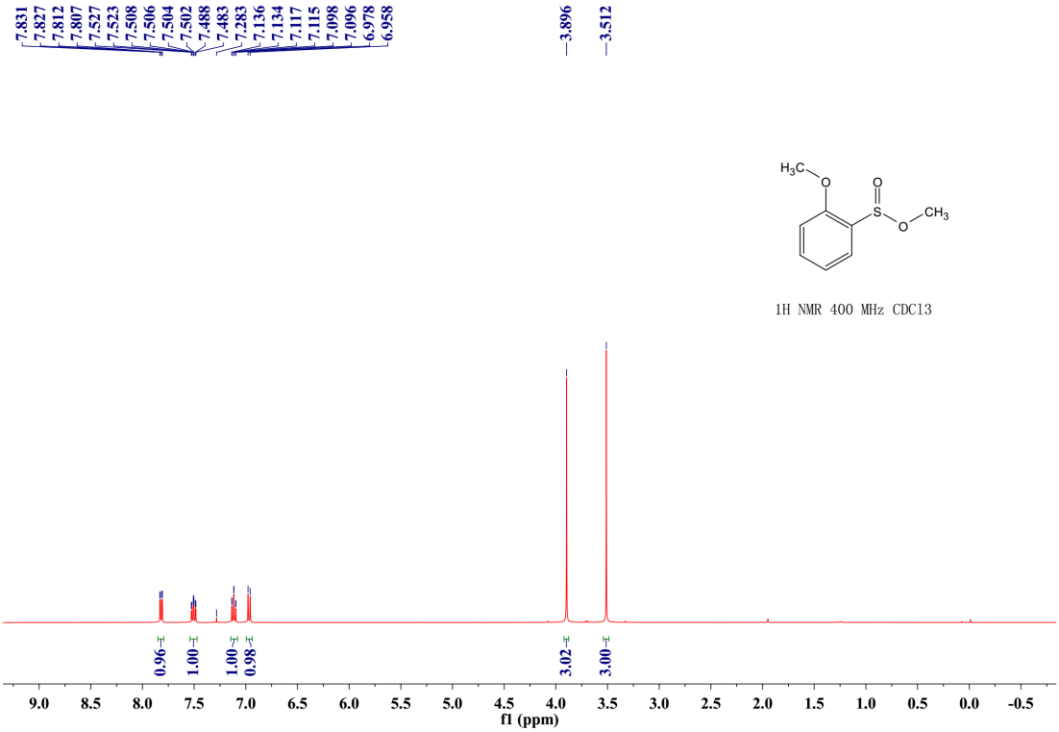


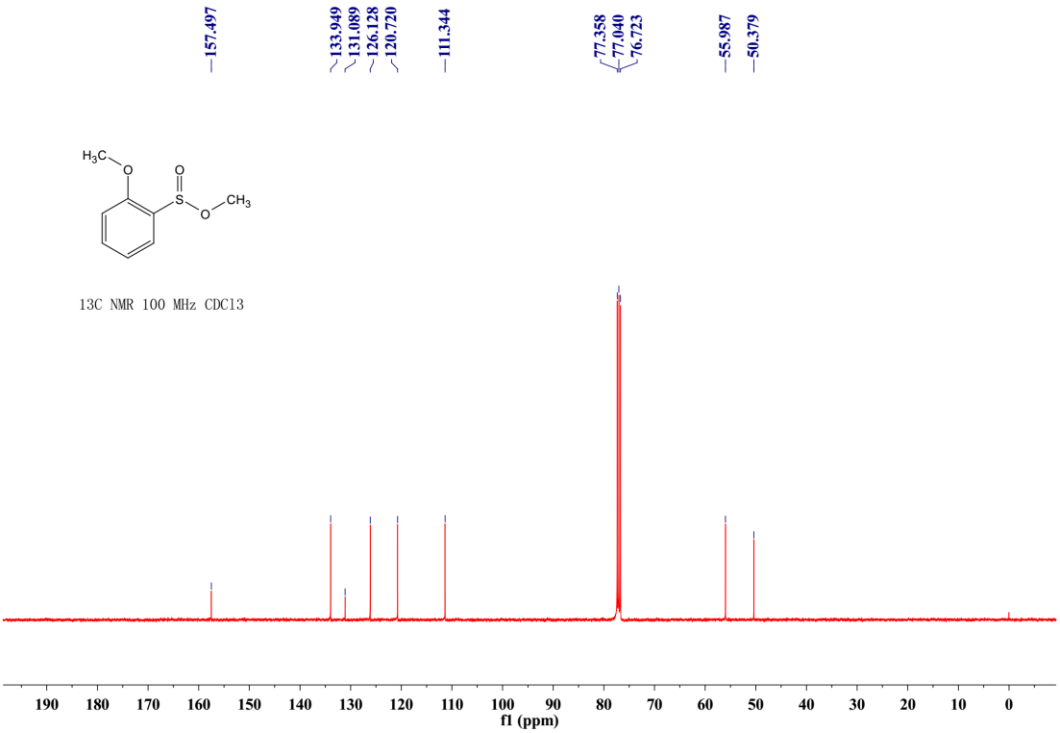
Methyl 4-(trifluoromethyl)benzenesulfinate (3ha)



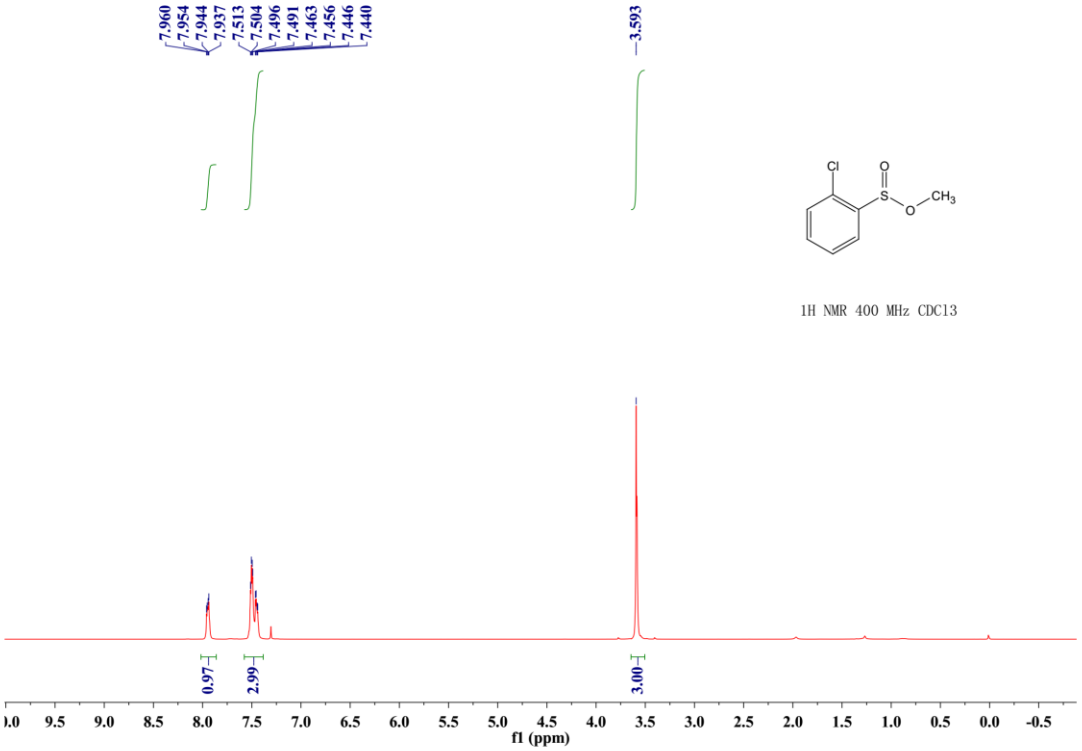


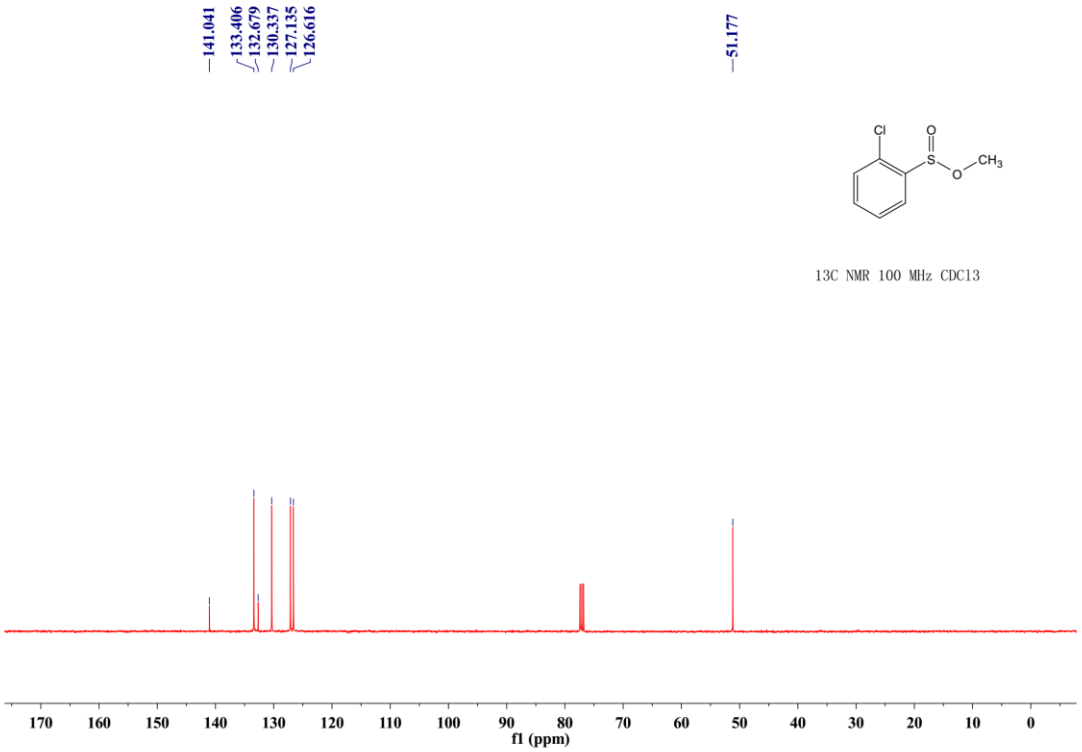
Methyl 2-methoxybenzenesulfinate (3ia)



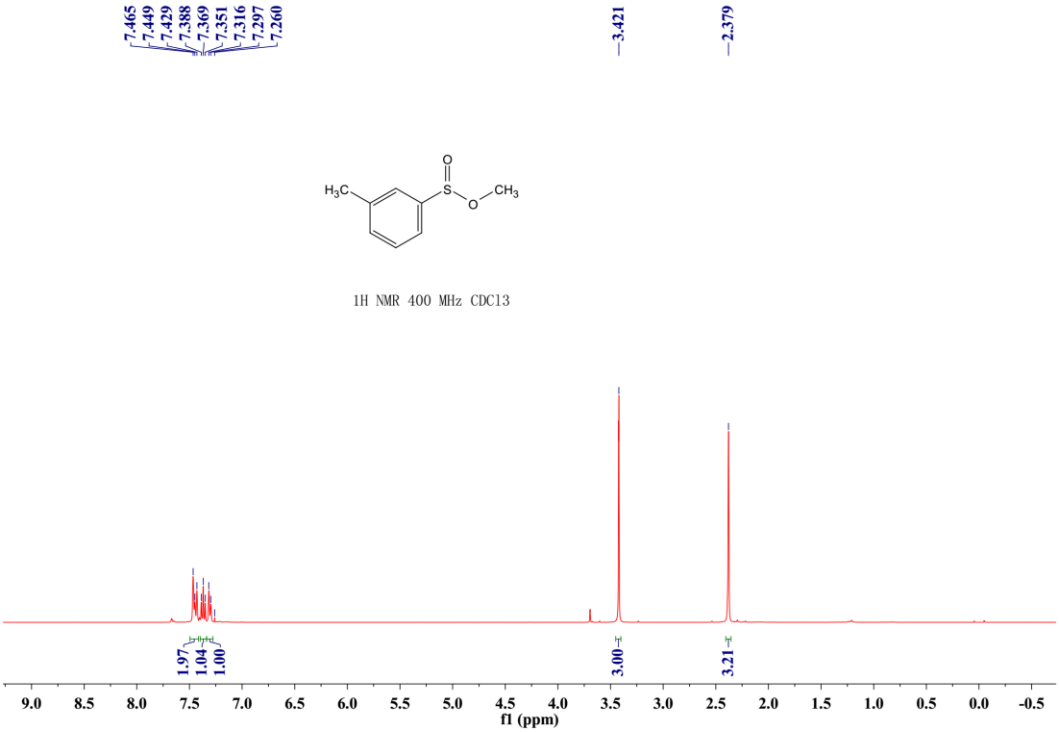


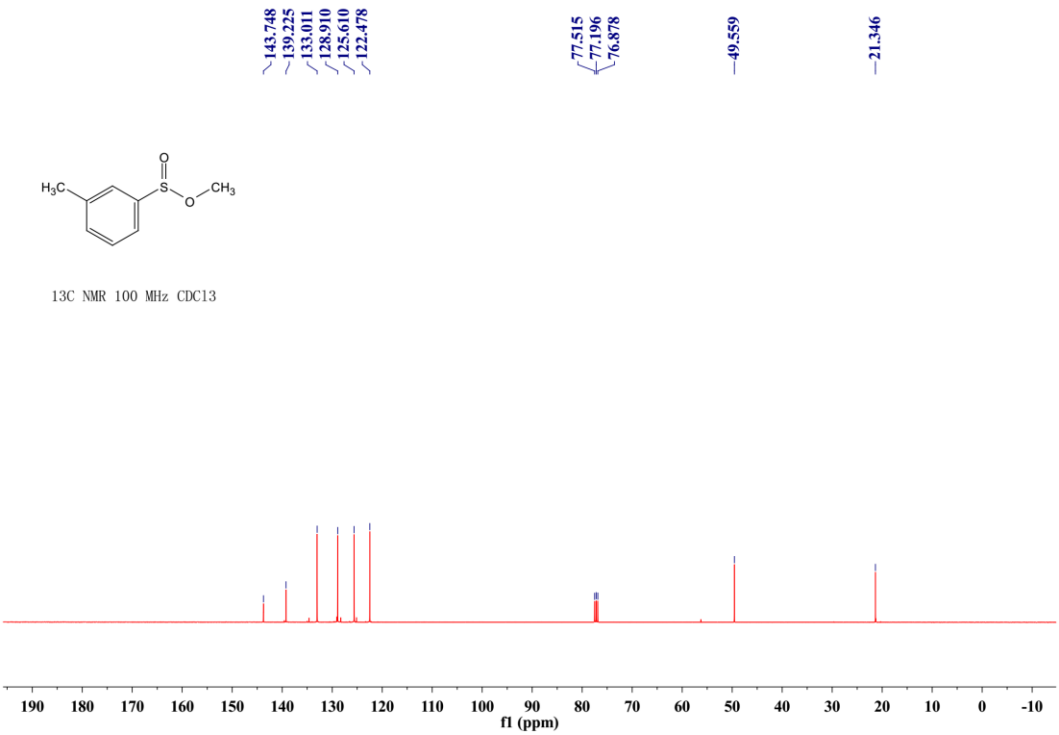
Methyl 2-chlorobenzenesulfinate (3ja)



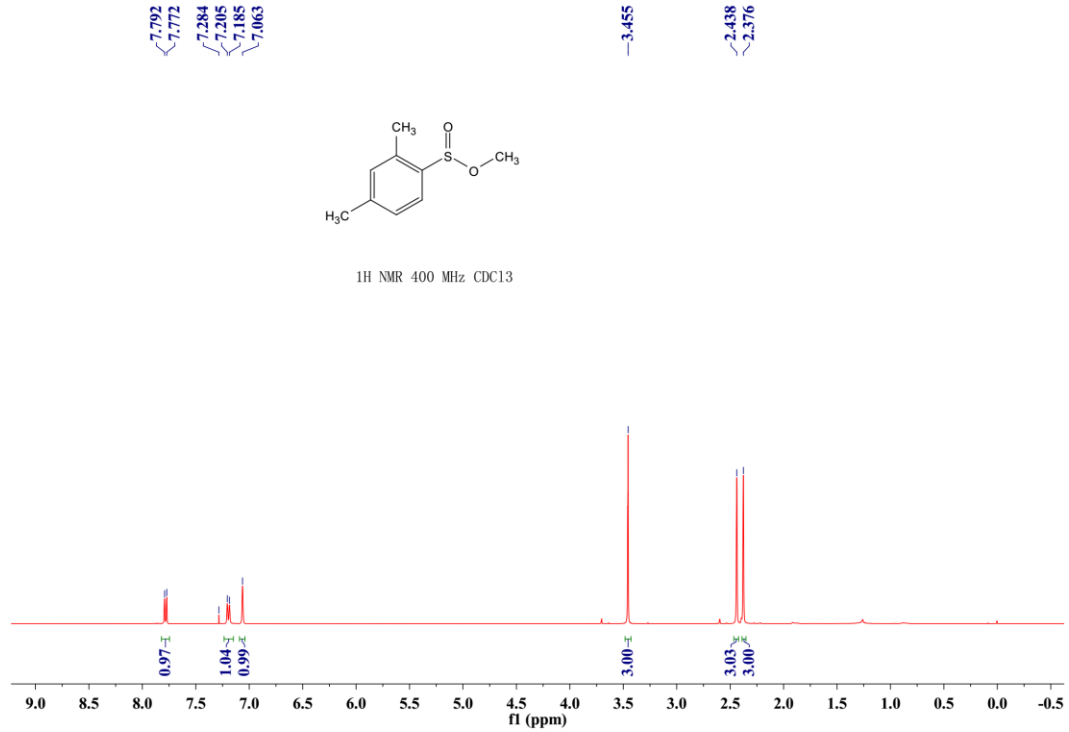


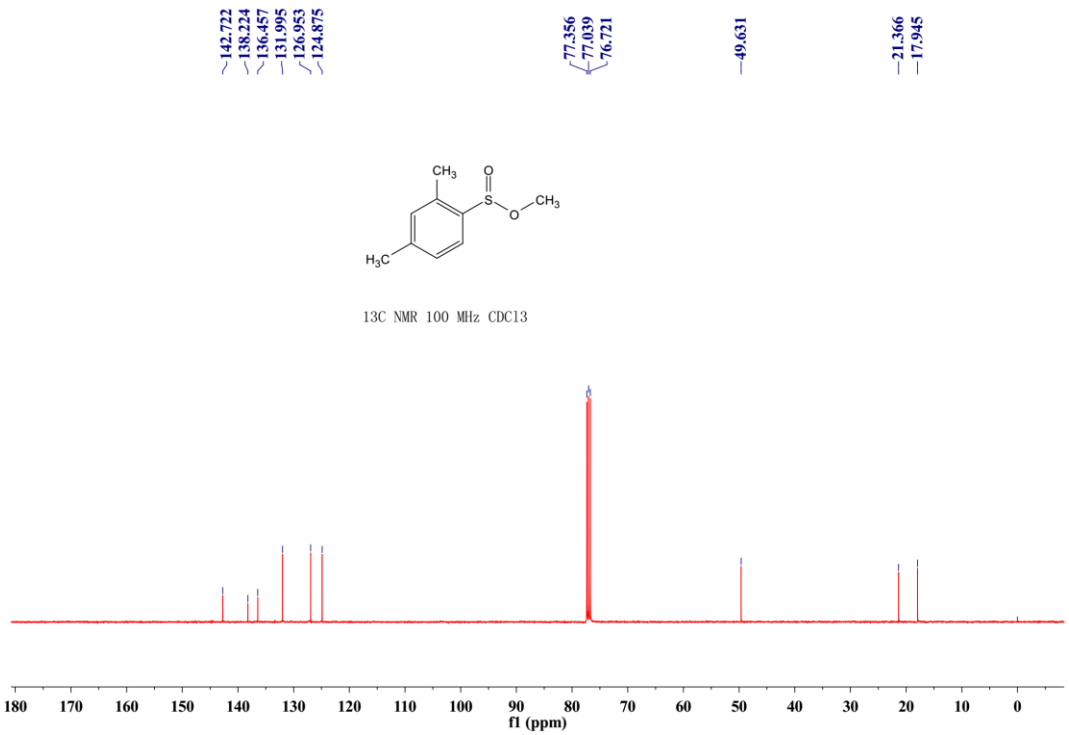
Methyl 3-methylbenzenesulfinate (3ka)



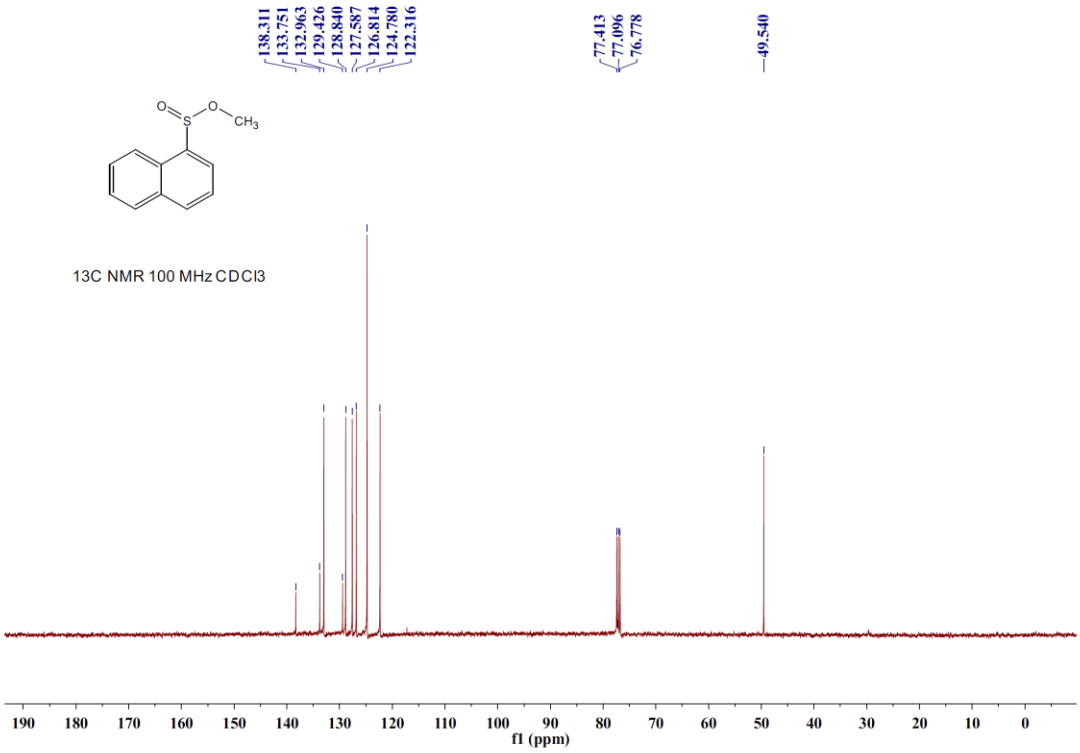


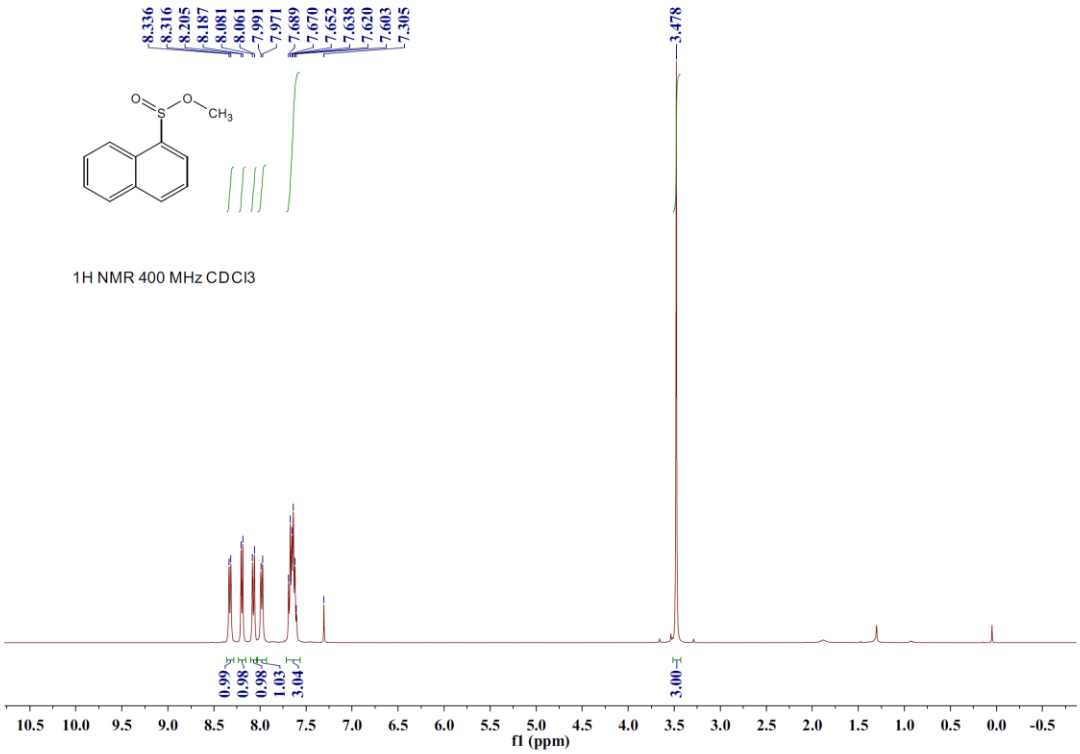
Methyl 2,4-dimethylbenzenesulfinate (3la)



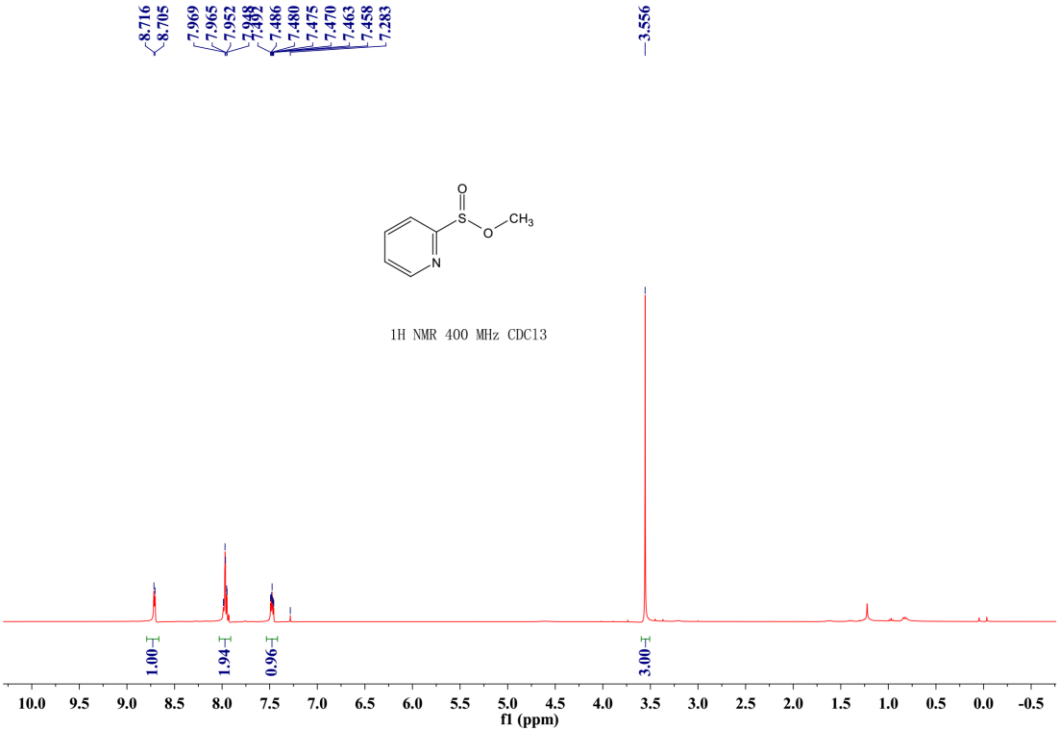


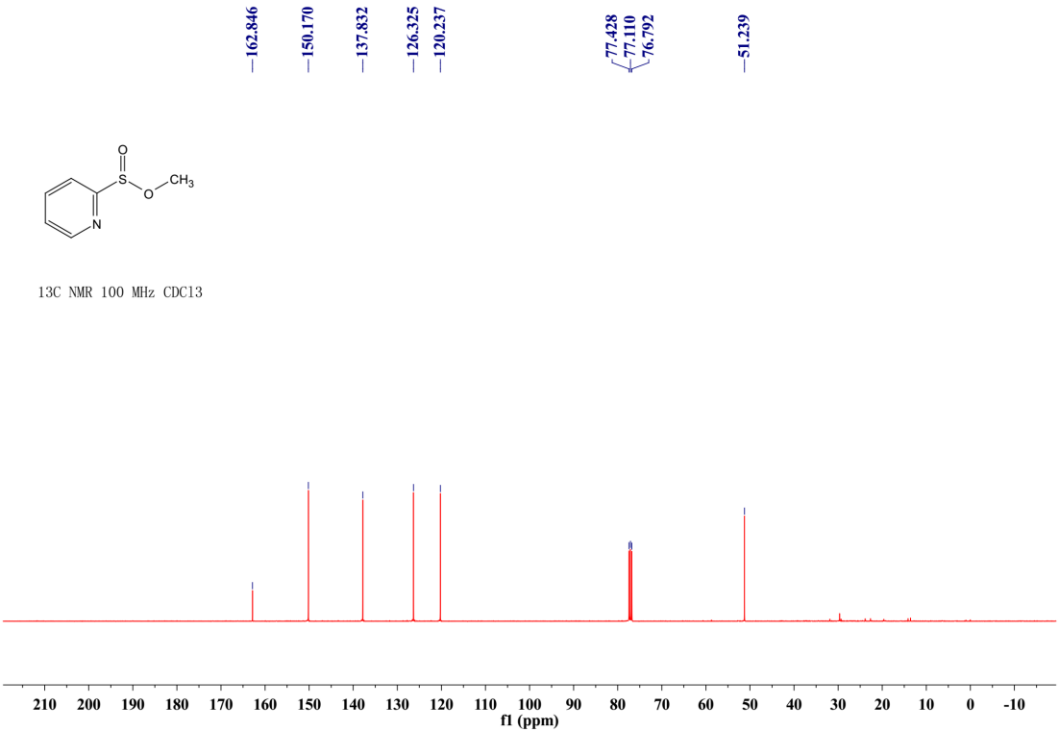
Methyl naphthalene-1-sulfinate (3ma)



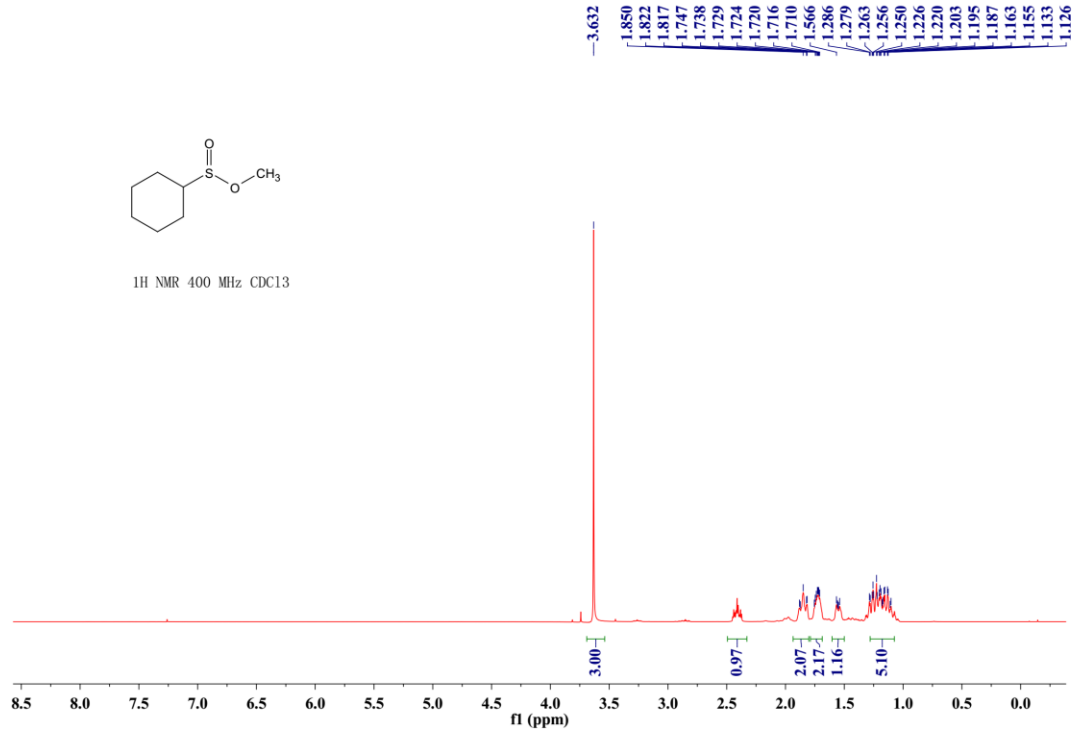


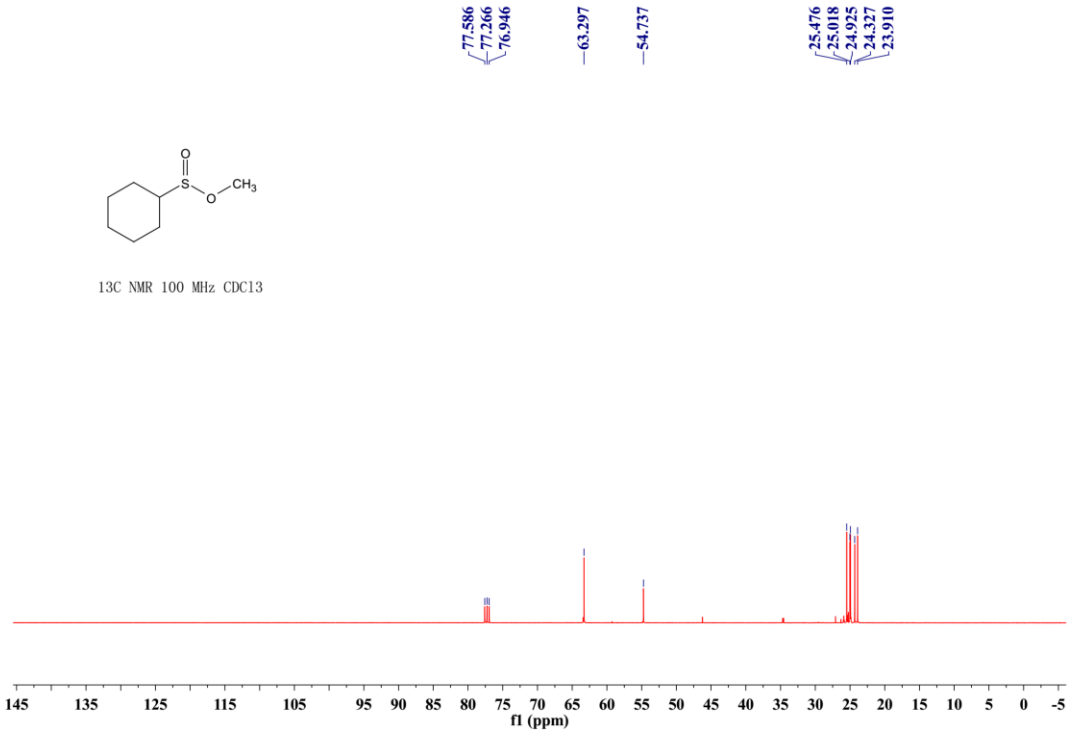
Methyl pyridine-2-sulfinate (3na)



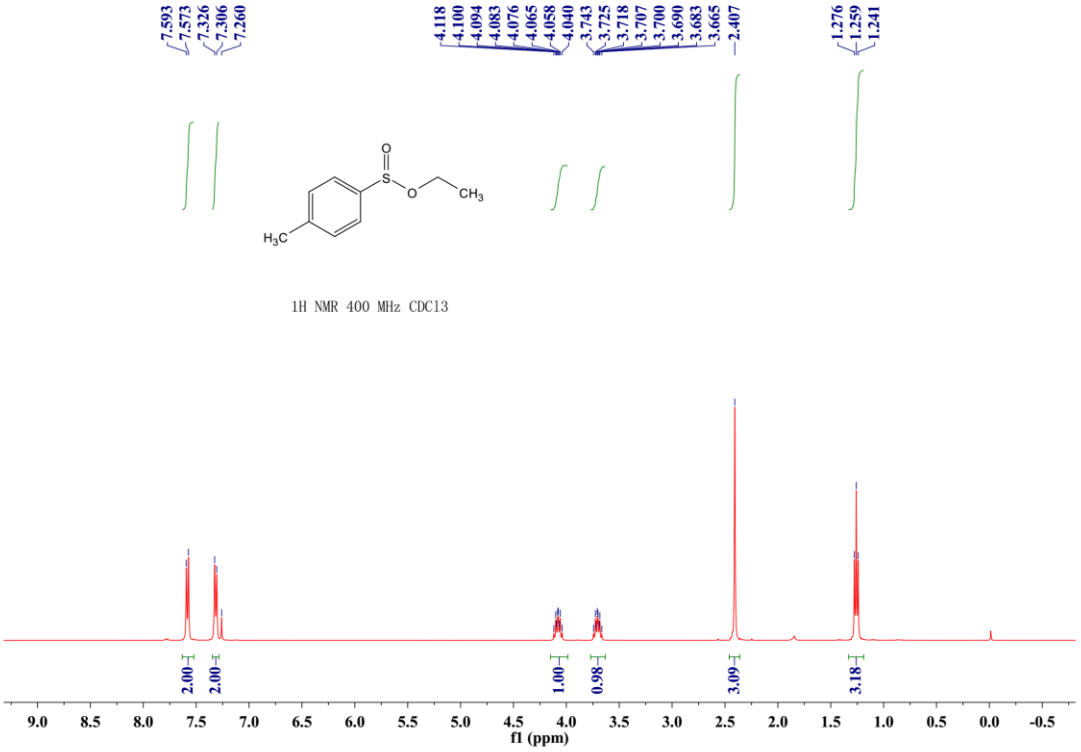


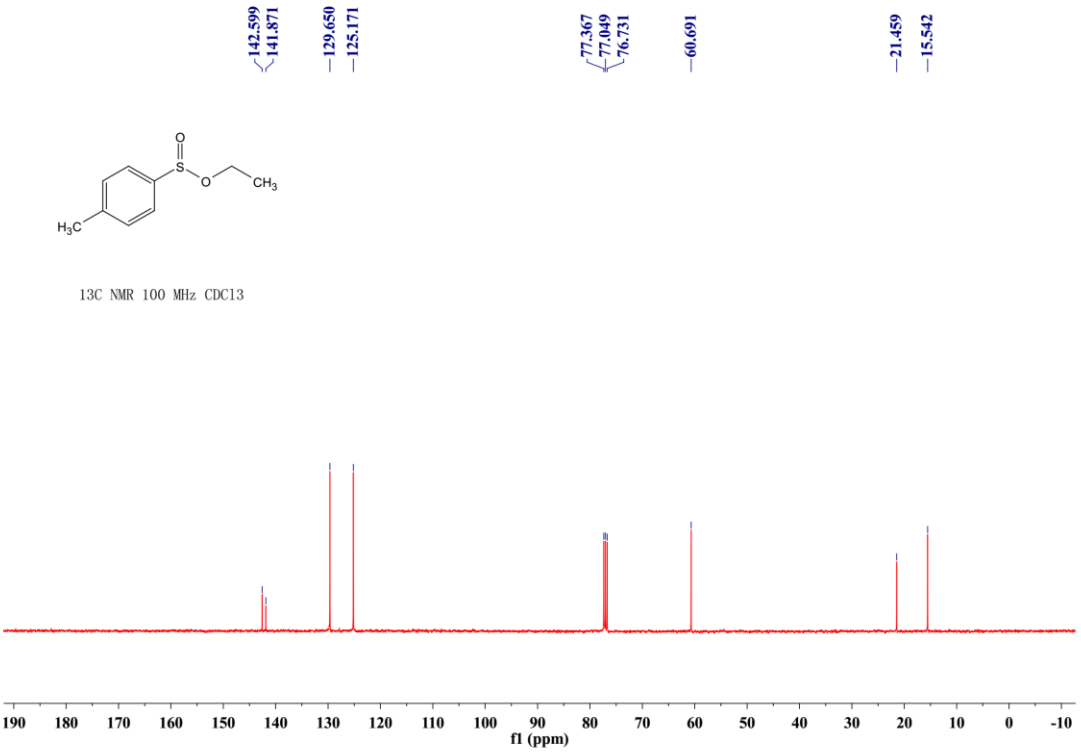
Methyl cyclohexanesulfinate (3oa)



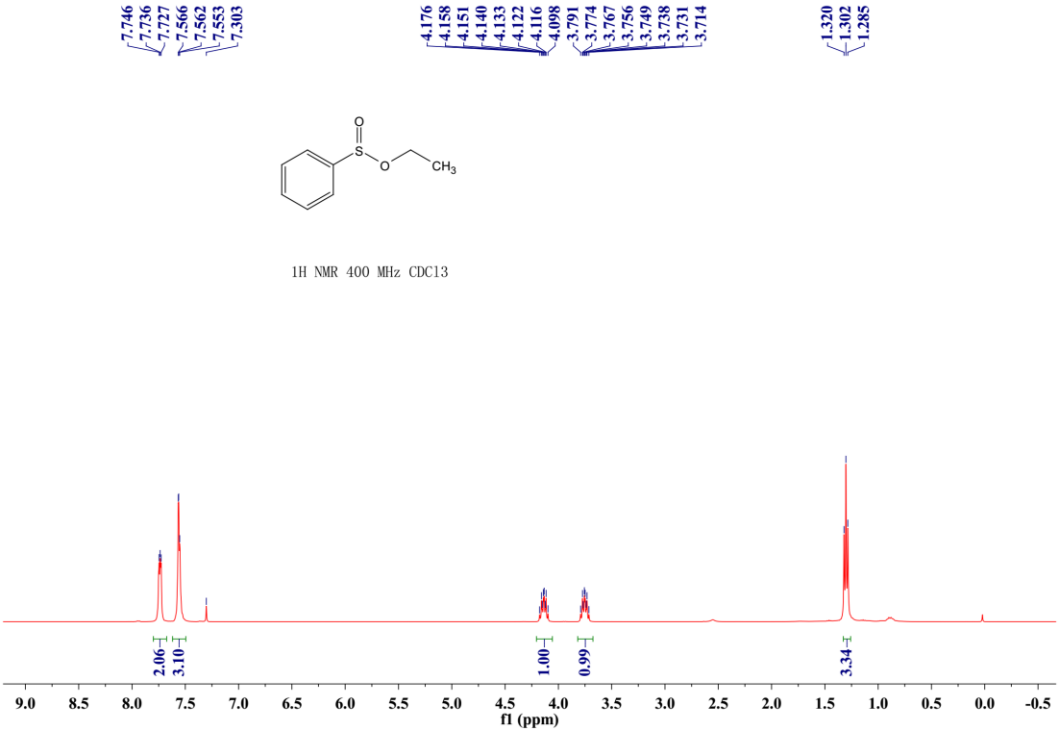


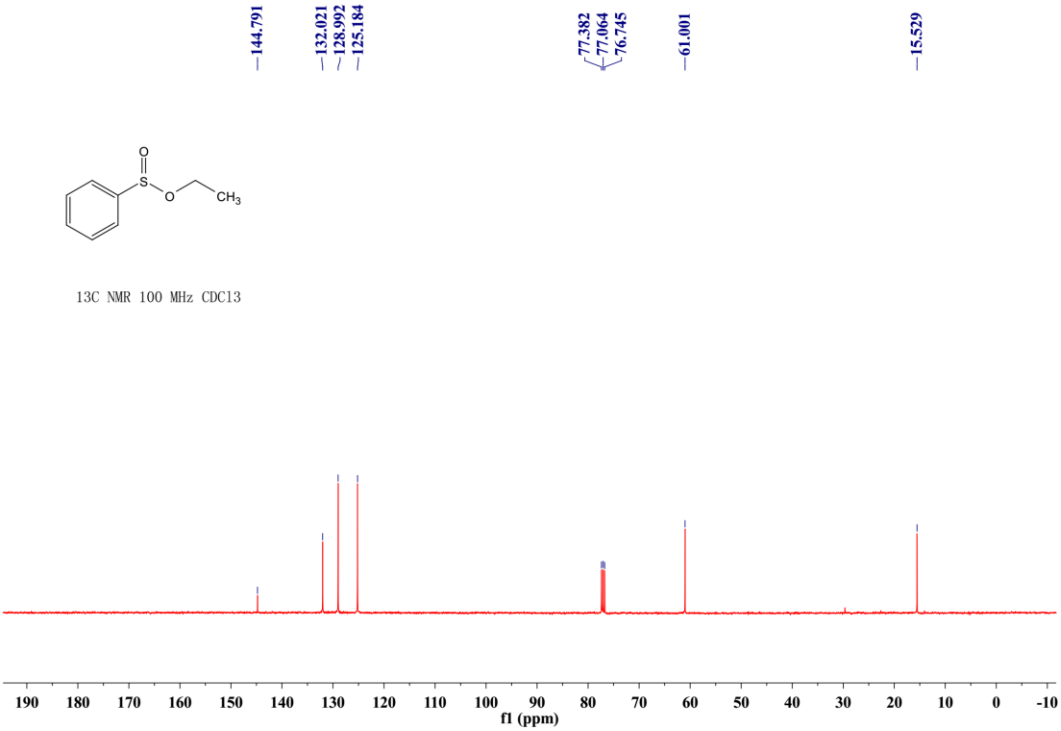
Ethyl 4-methylbenzenesulfinate (3ab)



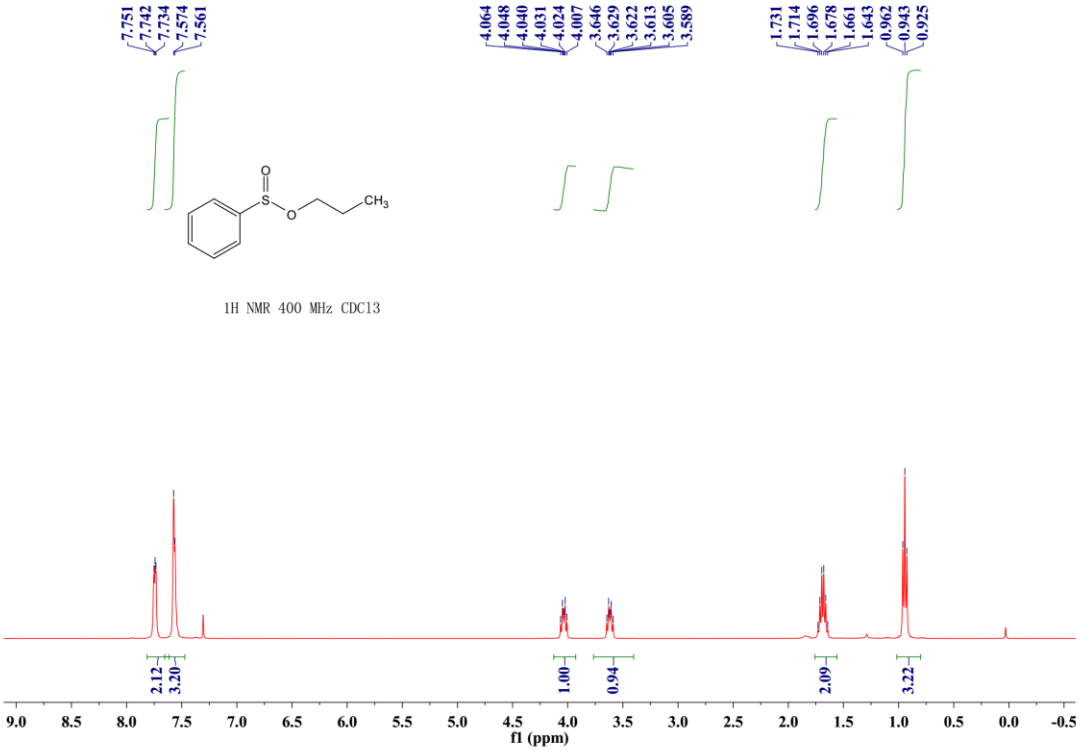


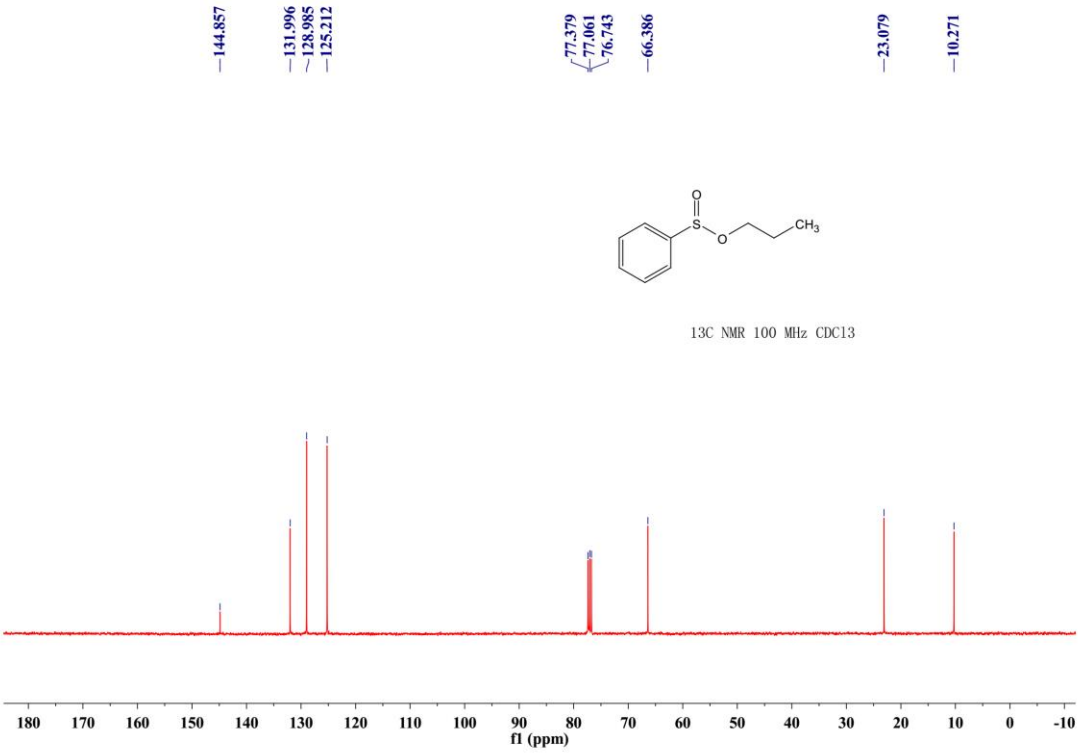
Ethyl benzenesulfinate (3bb)



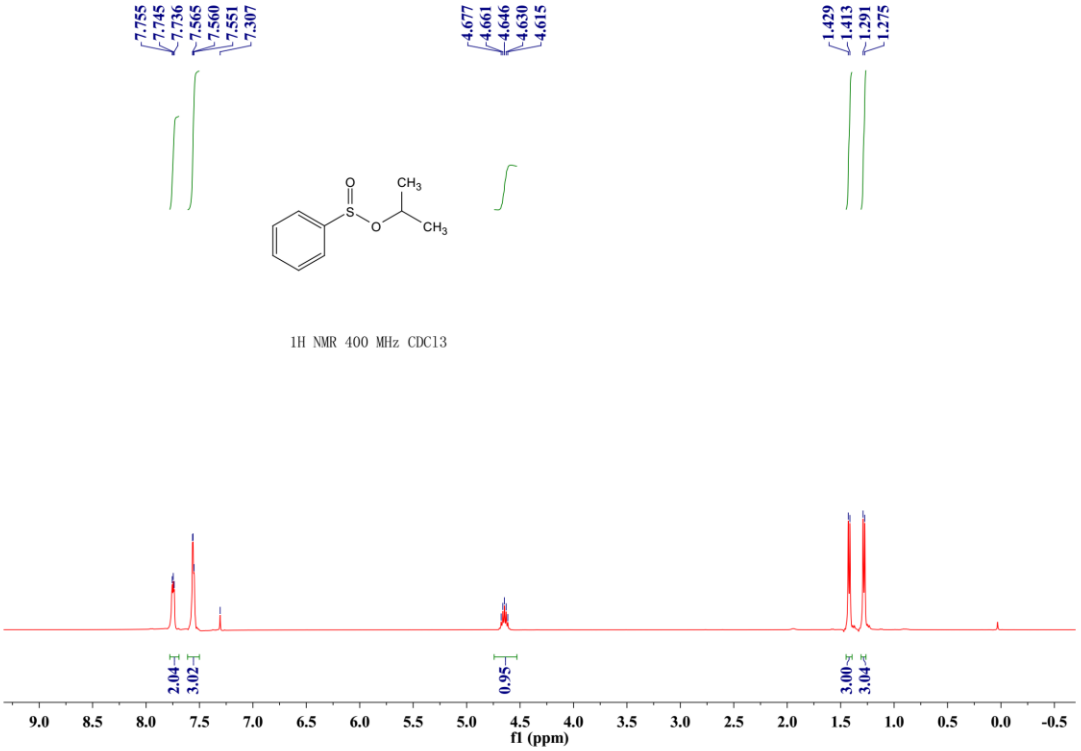


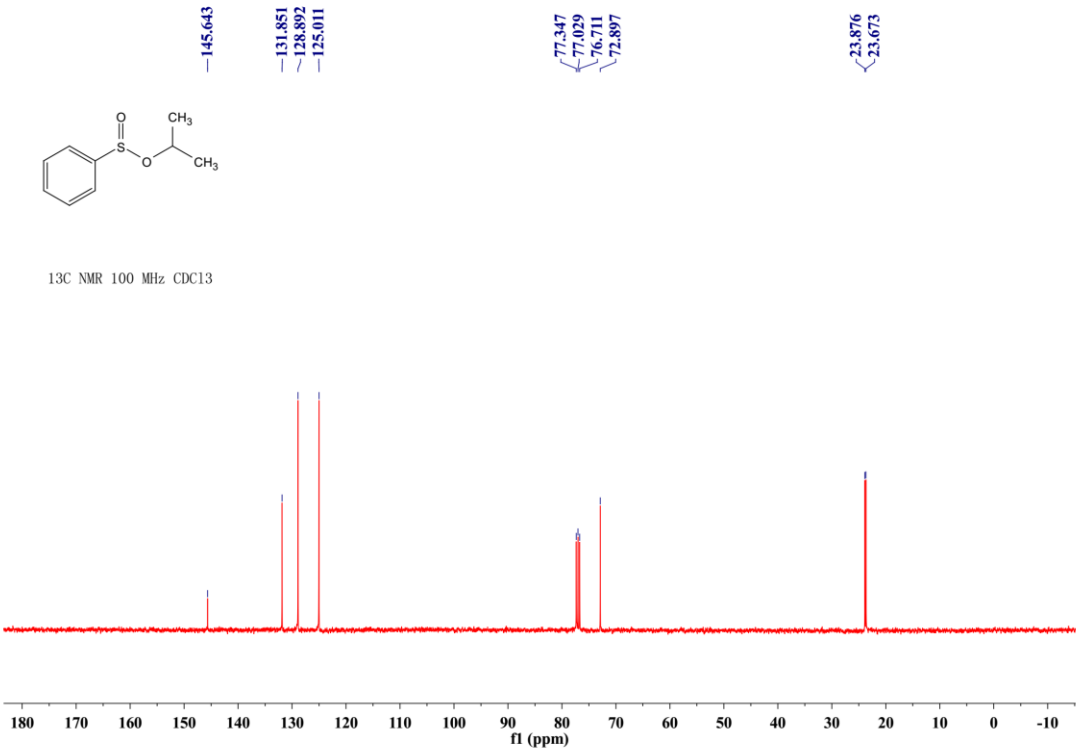
Propyl benzenesulfinate (3bc)



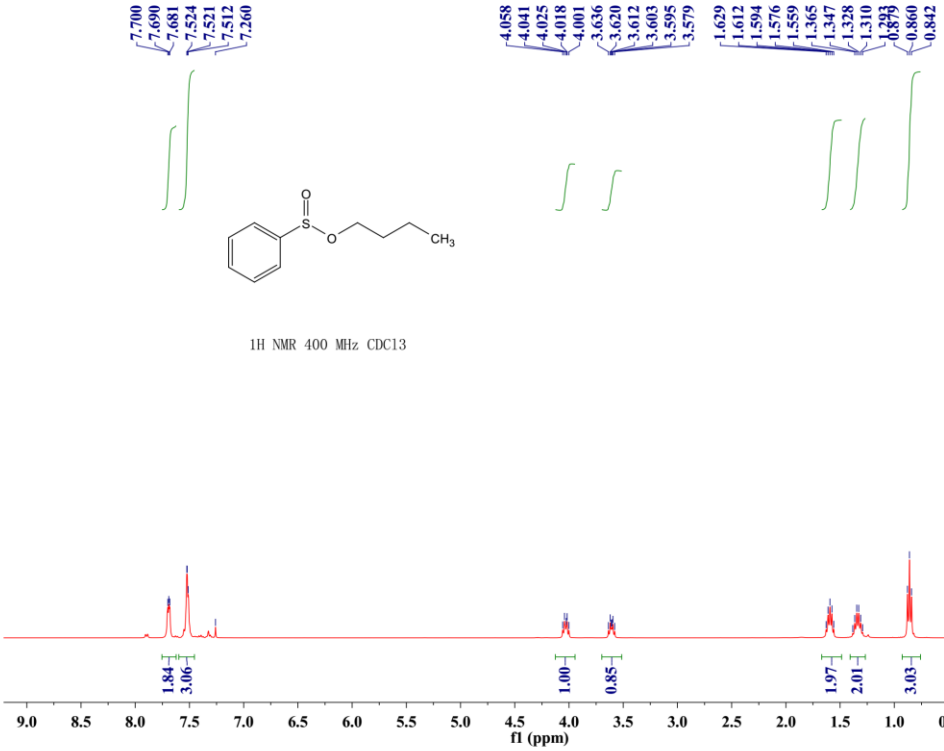


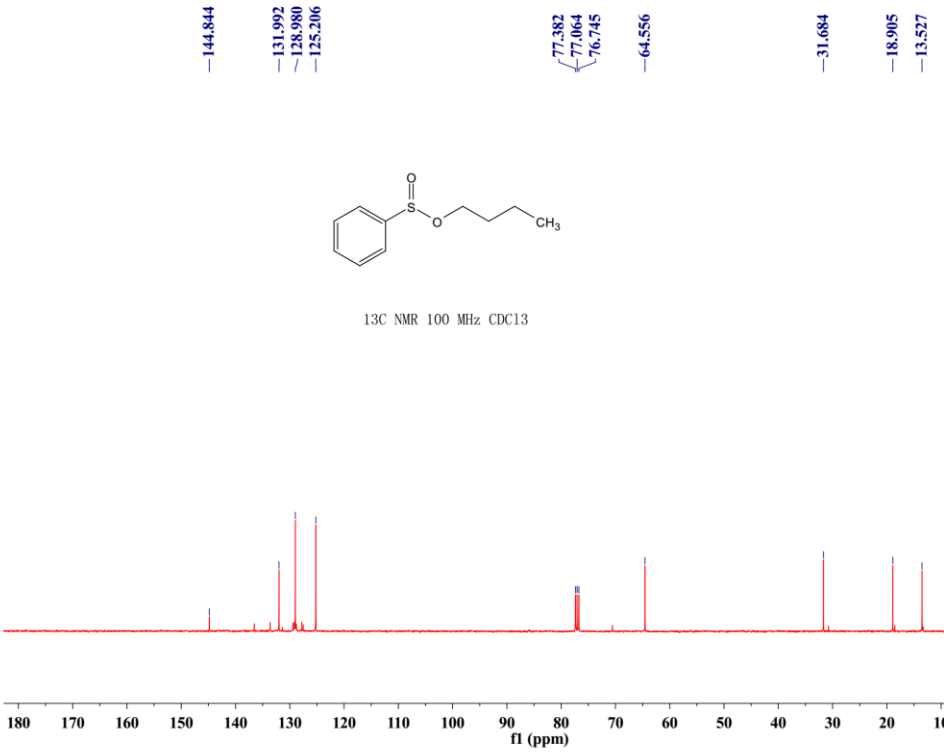
i-Propyl benzenesulfinate (3bd)



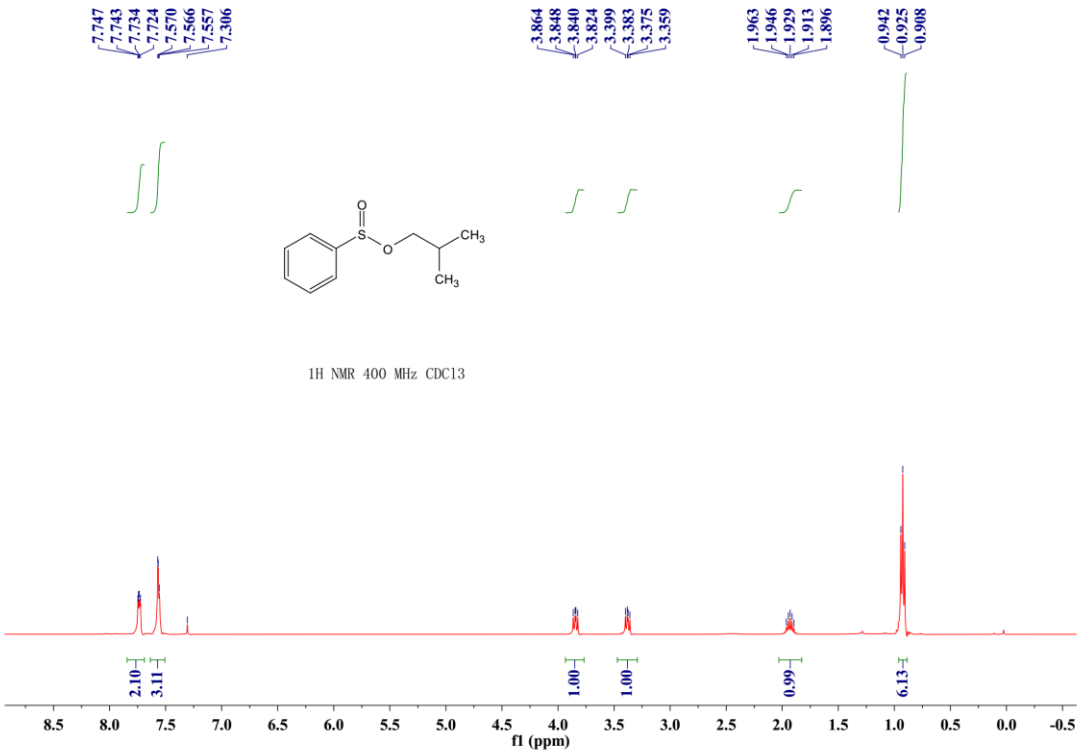


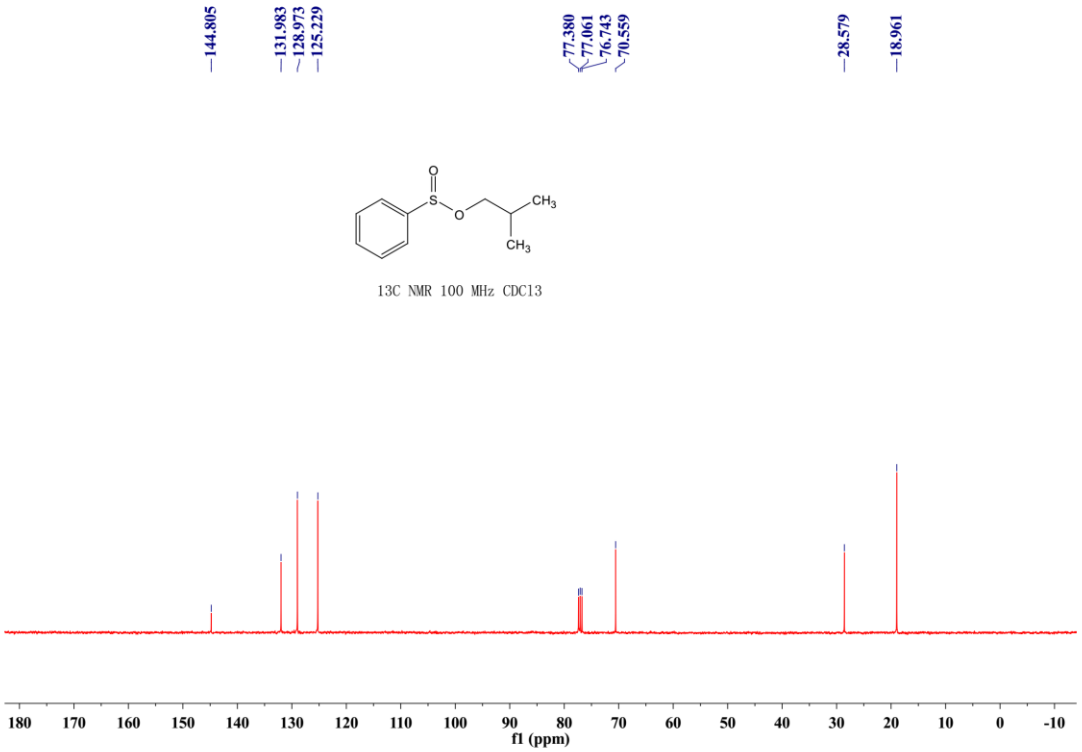
Butyl benzenesulfinate (3be)



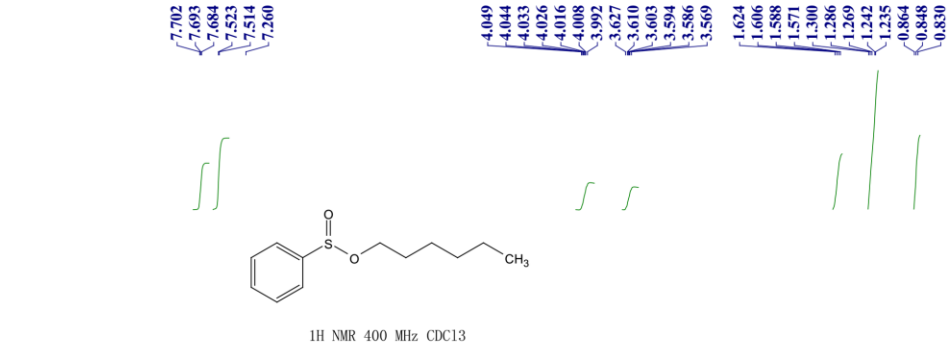


i-Butyl benzenesulfinate (3bf)

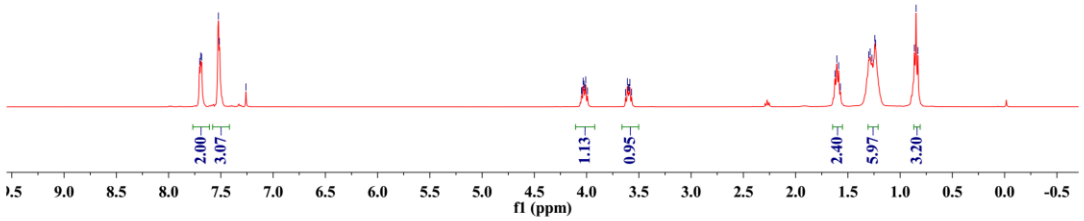




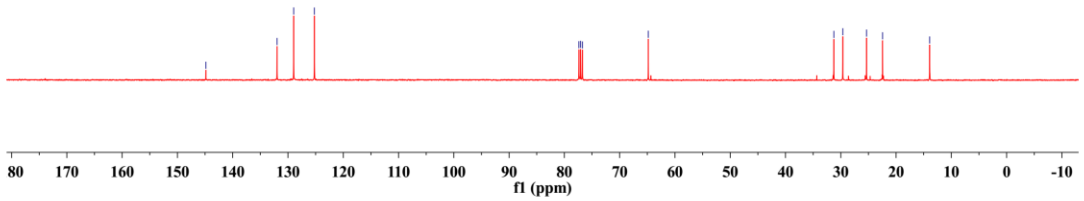
Hexyl benzenesulfinate (3bg)



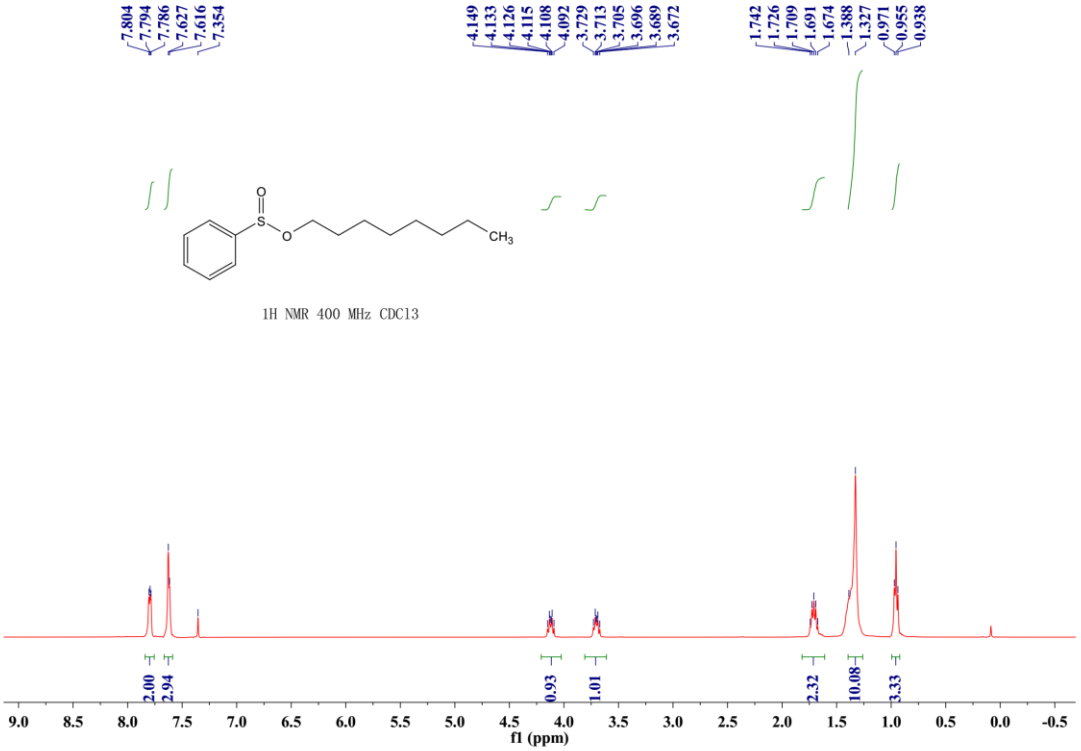
1H NMR 400 MHz CDCl3



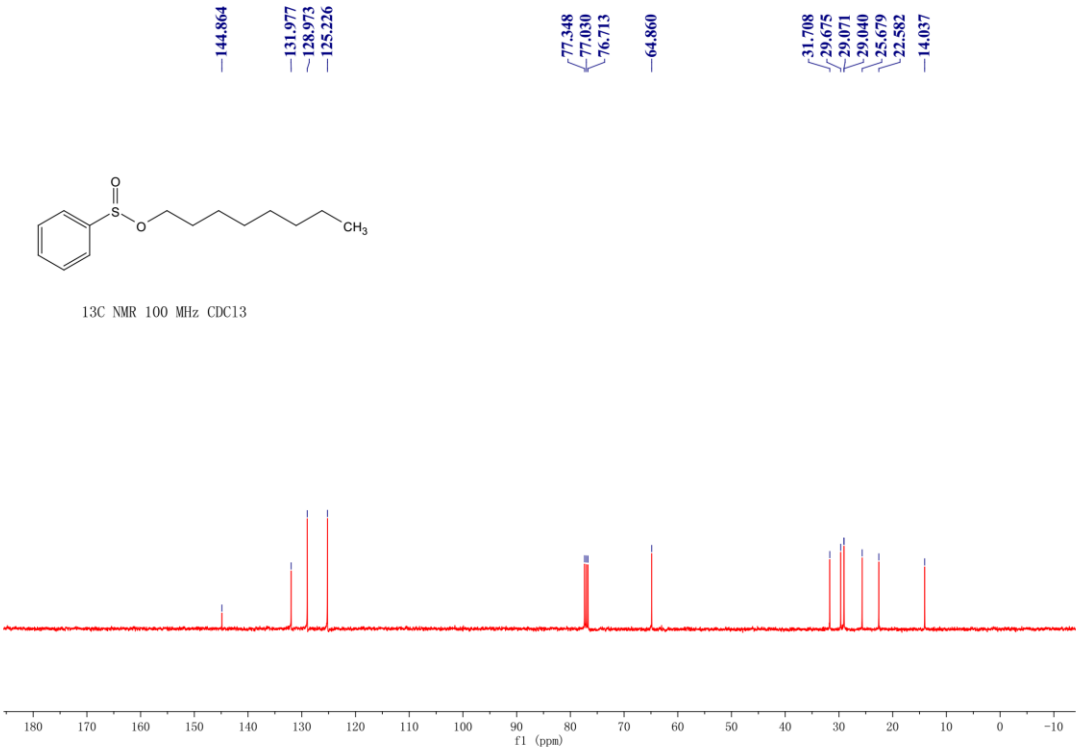
13C NMR 100 MHz CDCl3



Octyl benzenesulfinate (3bh)

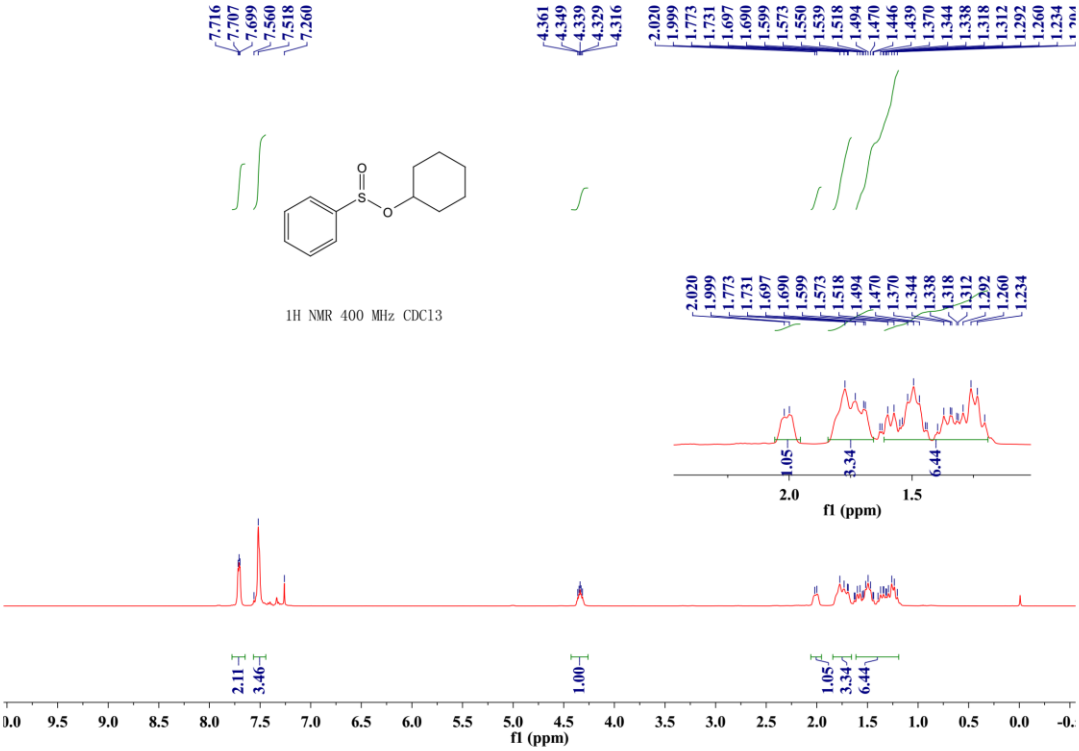


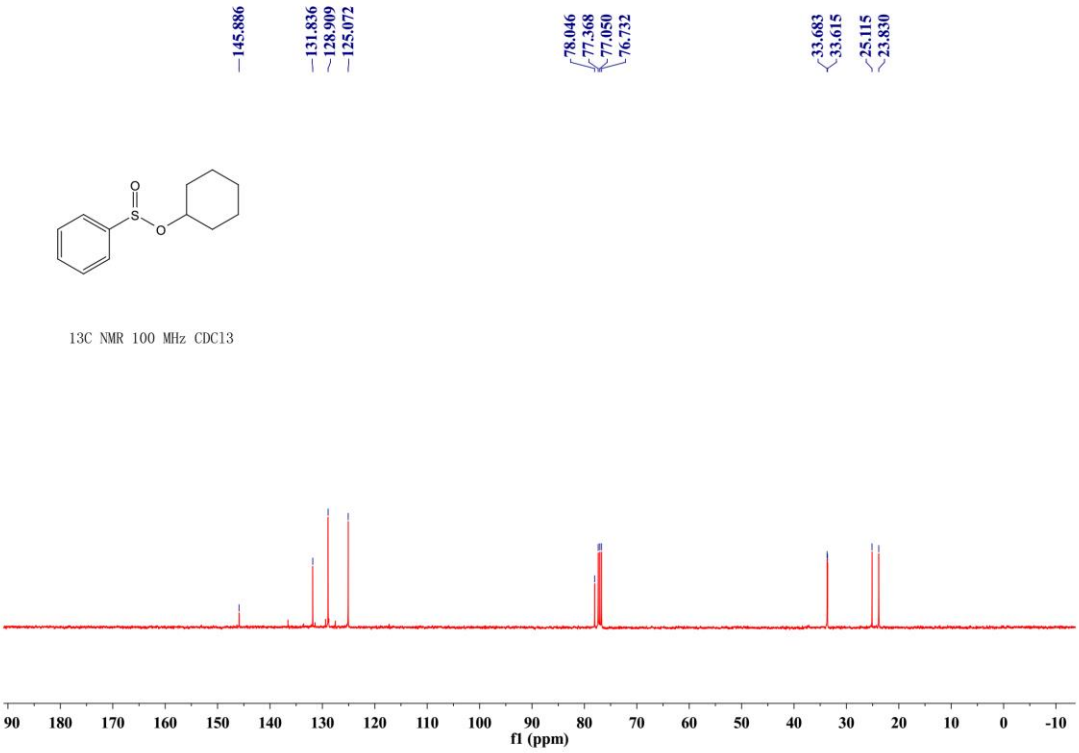
1H NMR 400 MHz CDCl3



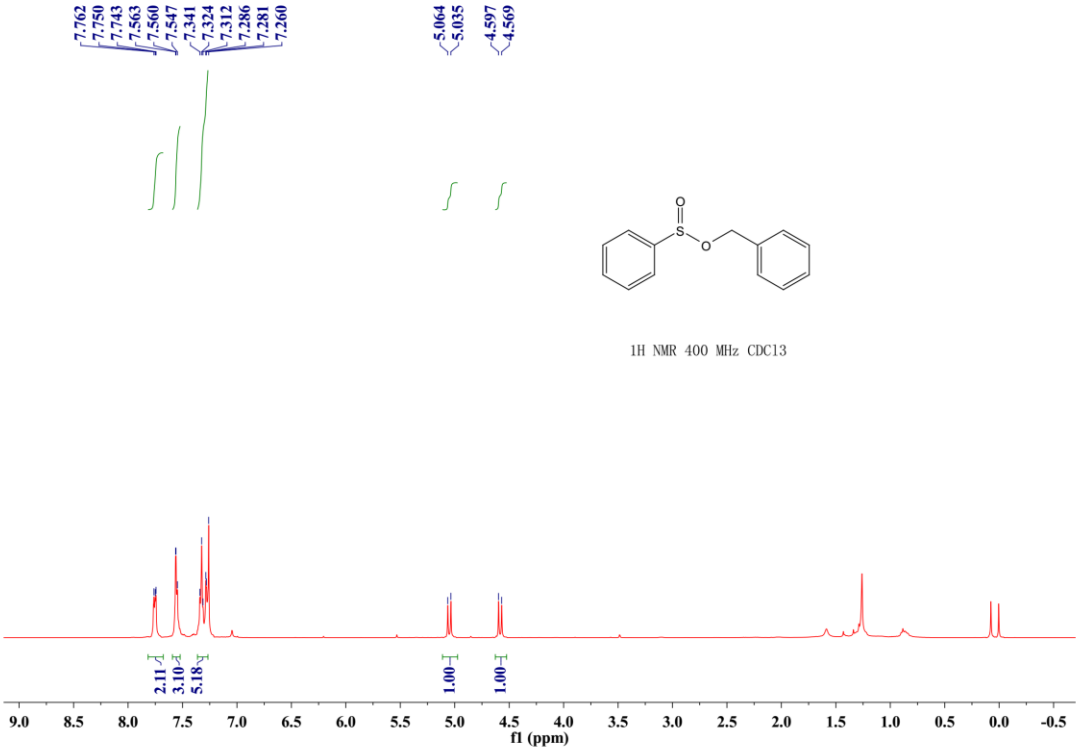
13C NMR 100 MHz CDCl3

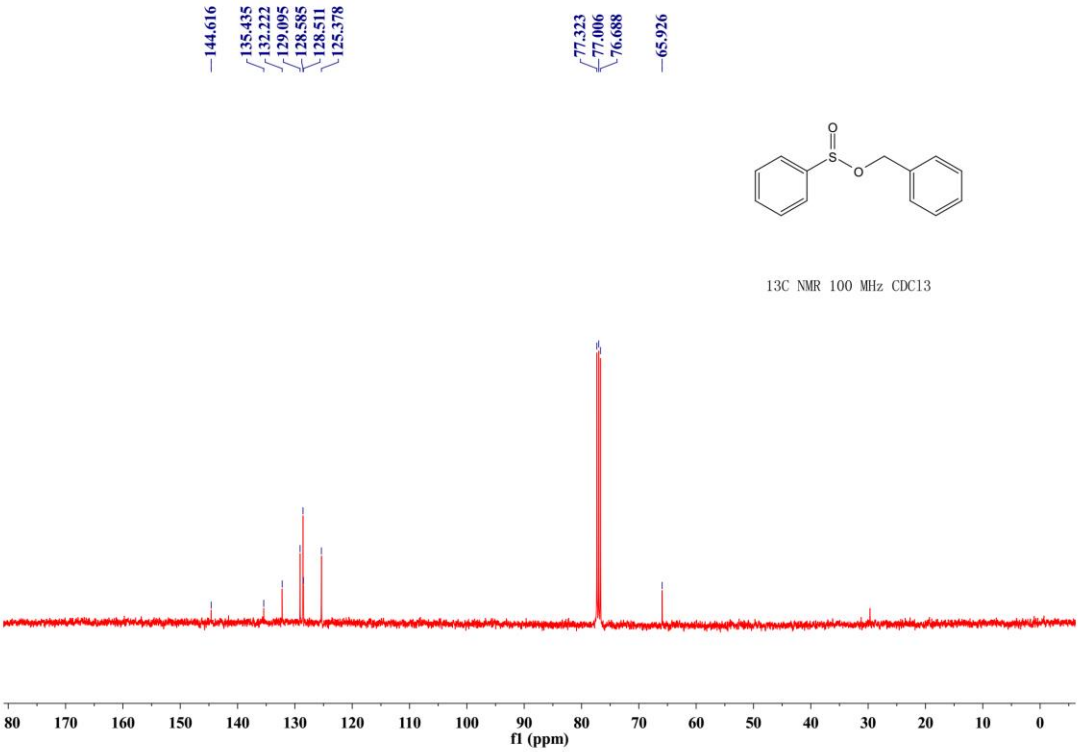
Cyclohexyl benzenesulfinate (3bi)



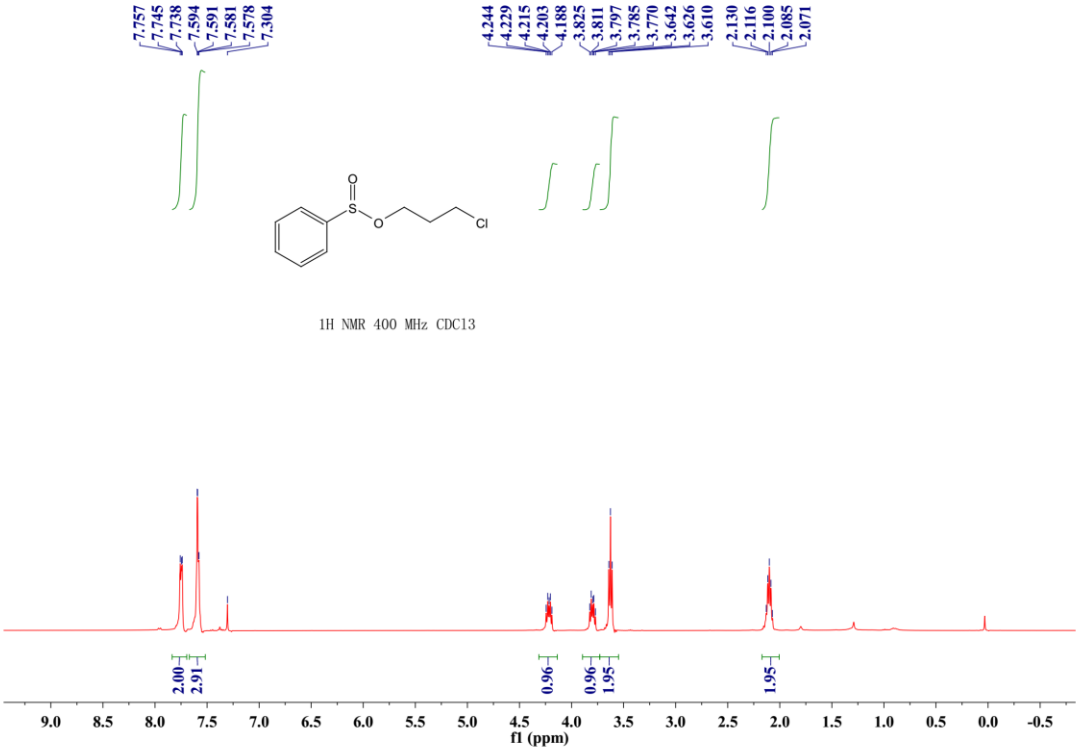


Benzyl benzenesulfinate (3bj)

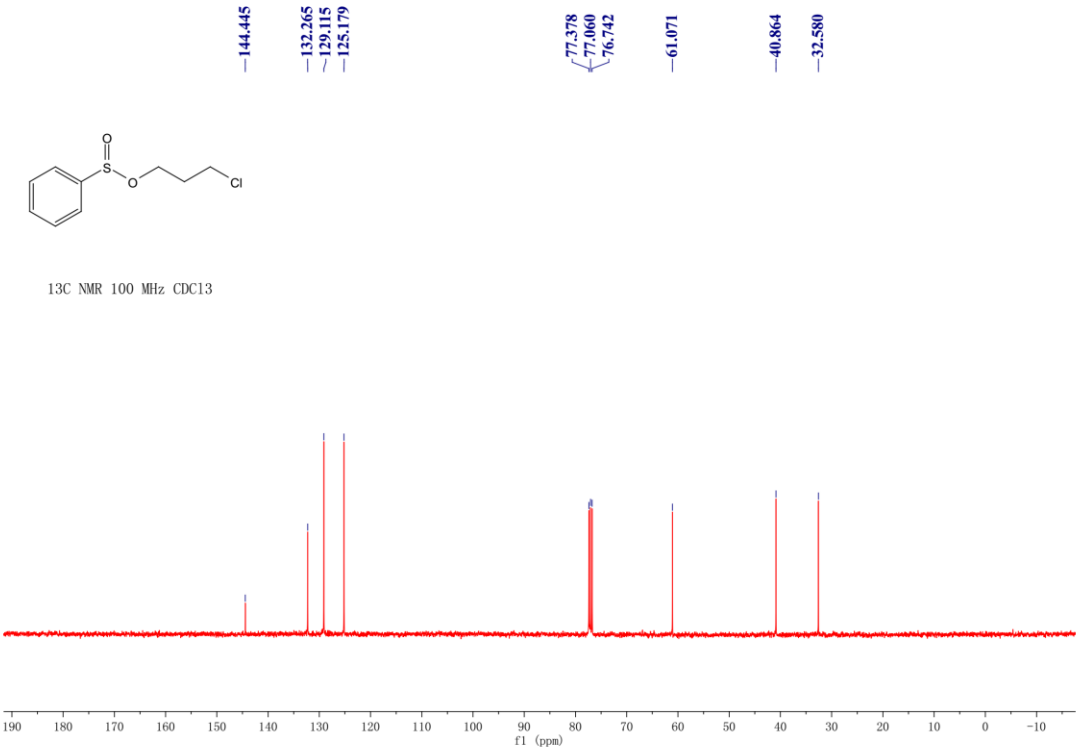




3-Chloropropyl benzenesulfinate (3bk)

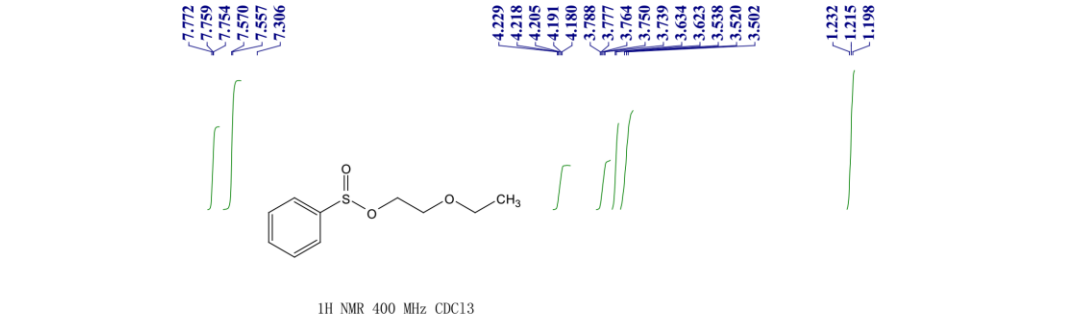


1H NMR 400 MHz CDCl3

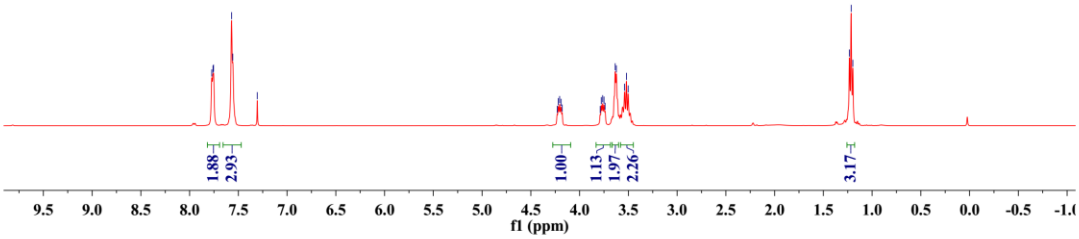


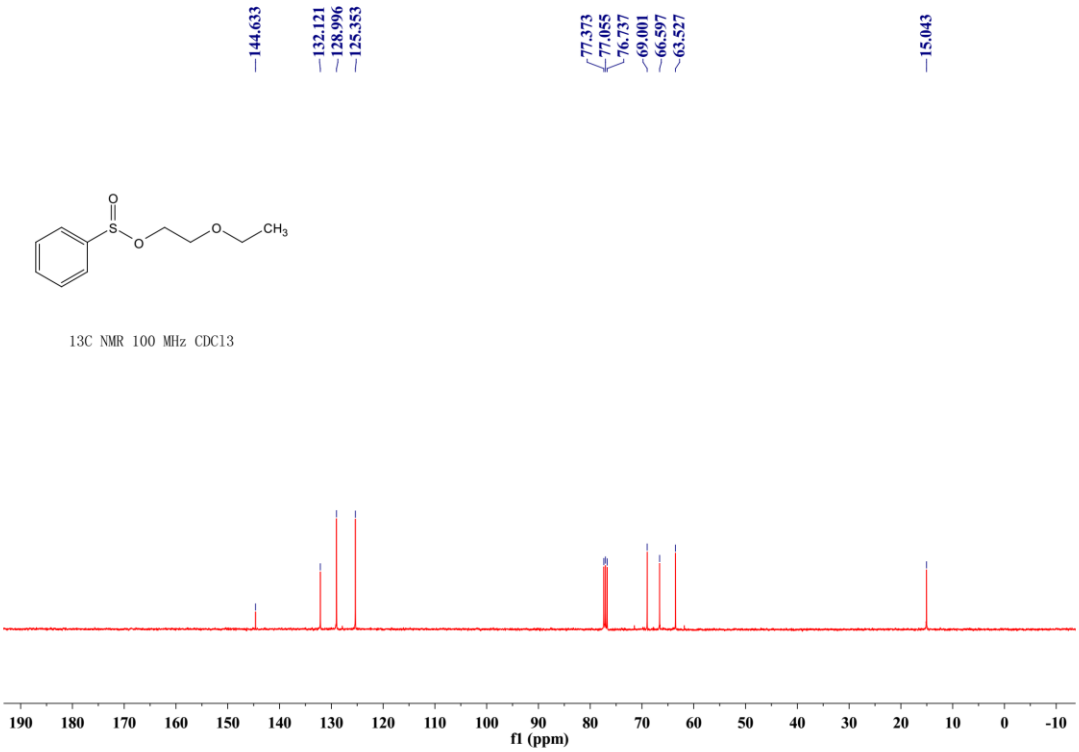
13C NMR 100 MHz CDCl3

2-Ethoxyethyl benzenesulfinate (3bl)



1H NMR 400 MHz CDCl3





13C NMR 100 MHz CDCl3