ESI for

PhSe(O)OH/$Al(NO_3)_3$-catalyzed selectivity controllable oxidation of sulphide owing to the synergistic effect of Se, Al and nitrate

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1. XPS analysis of the system

Details for XPS analysis sample preparation. To a 25 mL reaction tube, a piece of magnetic bar, 1 mmol of **1a**, 1 mmol of $Al(NO_3)_3 \cdot 9H_2O$ and 2 mL of water were added. The mixture was stirred at room temperature (25 °C) for 40 min. TLC analysis indicated **2a** was generated. Silica was then added into the system to absorb the samples, which was then dried by heating on rotary evaporator and sent to XPS analysis to get the information for nitrogen species. The results were given in Fig. S1.

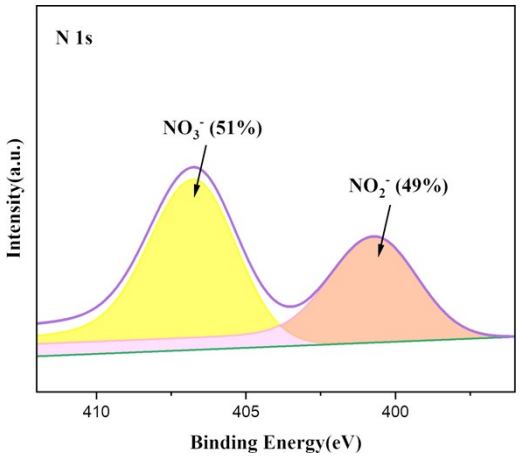


Fig. S1 XPS spectrum attesting the oxidation of sulphide by nitrate.

2. ^{77}Se NMR of the system

Sample preparation: The reaction was performed under the condition of Table 3, entry 1 in text. After 2 h of reaction, the solvent was evaporated under reduced pressure and D_2O was added to dissolve the species. The sample was sent to ^{77}Se NMR analysis. The signal at 1023.678 ppm attested the existence of PhSe(O)OOH species (*Prog. Nucl. Mag. Res. Sp.,* 1995, **27**, 1 – 323).

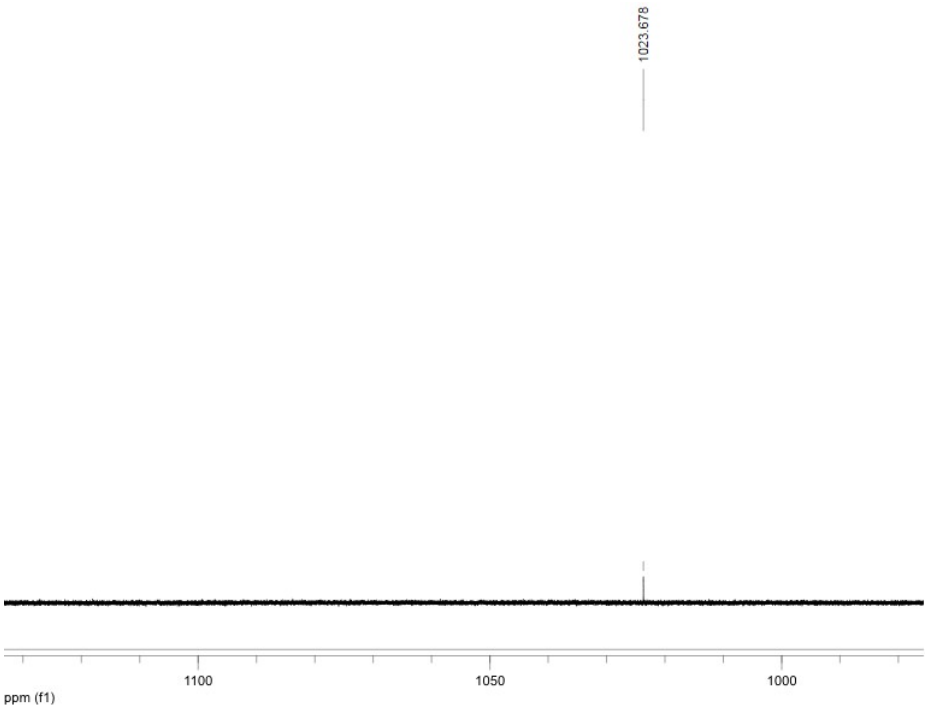


Fig. S2 ^{77}Se NMR spectrum of the reaction liquid

3. Study of the reaction process via UV-Vis spectra

Sample preparation: Three reactions were performed under the conditions described in Table 3, entry 1 in text. The systems were sent to UV-Vis analysis at different times. The results given in Fig. S3 below showed that the reaction occurred via the sulfide (0 min, starting material)-sulfoxide (40 min, partial oxidation product)-sulfone (120 min, sufficient oxidation product).

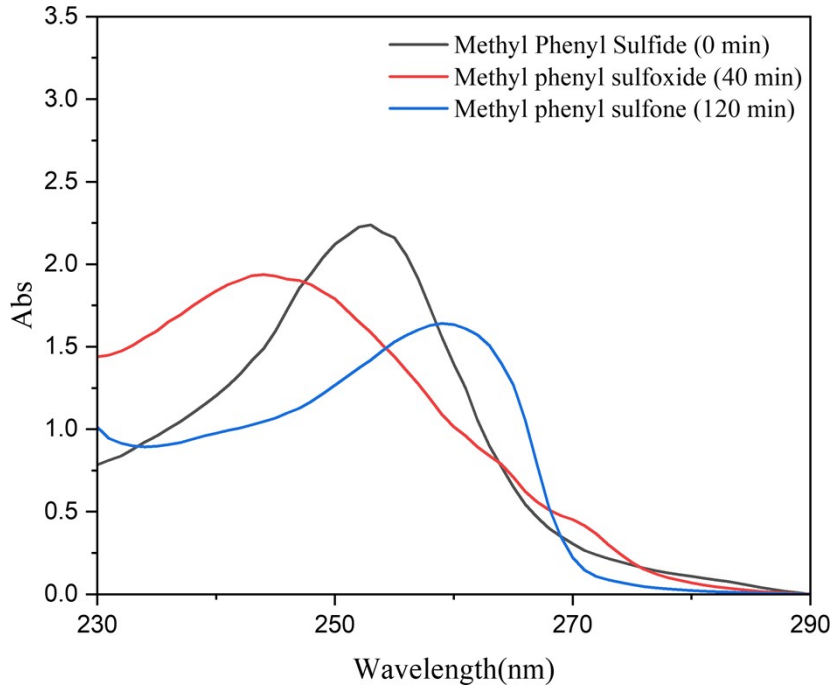
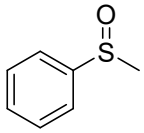
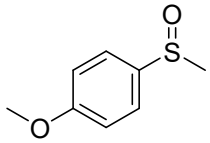


Fig. S3 UV-Vis spectra of the system

4. Characterization data of the products

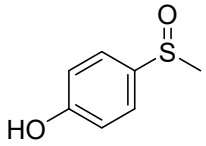


(Methylsulfinyl)benzene (2a): 115.0 mg, 82%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.57–7.65 (m, 2H), 7.41–7.53 (m, 3H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 131.0, 129.3, 123.5, 43.9; *Known compound*.[1]

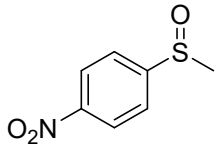


1-Methoxy-4-(methylsulfinyl)benzene (2b): 163.4 mg, 96%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.56 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 136.6, 125.4, 114.8,

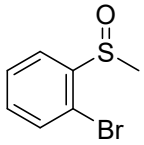
55.5, 44.0; *Known compound*.[2]



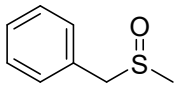
4-(Methylsulfinyl)phenol (2c): 110.9 mg, 71%; White solid, m. p. 90.8–92.2 °C (lit. 90–91°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.48 (d, J = 7.8 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 133.1, 126.1, 116.8, 43.0; *Known compound*.[3]



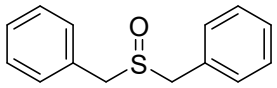
1-(Methylsulfinyl)-4-nitrobenzene (2d): 177.8 mg, 96%; White solid, m. p. 150.3–151.6 °C (lit. 150–152°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.36 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.7 Hz, 2H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 149.5, 124.7, 124.5, 43.8; *Known compound*.[2]



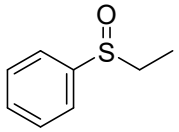
1-Bromo-2-(methylsulfinyl)benzene (2e): 179.7 mg, 82%; Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.85–7.94 (m, 1H), 7.48–7.59 (m, 2H), 7.27–7.38 (m, 1H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 132.9, 132.3, 128.7, 125.7, 118.4, 41.9; *Known compound*.[4]



((Methylsulfinyl)methyl)benzene (2f): 112.6 mg, 73%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.20–7.39 (m, 5H), 4.04 (d, J = 12.1 Hz, 1H), 3.91 (d, J = 12.9 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.0, 129.6, 129.0, 128.5, 60.3, 37.2; *Known compound*.[1]

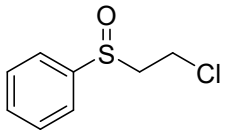


(Sulfinylbis(methylene))dibenzene (2g): 163.5 mg, 71%; White solid, m. p. 133.5–135.1 °C (lit. 134–135°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.22–7.45 (m, 10H), 3.83–3.98 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.1, 129.7, 129.0, 128.4, 57.3; *Known compound*.[1]

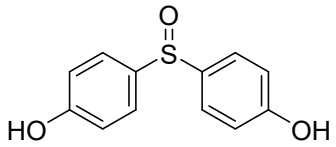


(Ethylsulfinyl)benzene (2h): 129.6 mg, 84%; Colorless oil; ^{1}H NMR (400 MHz,

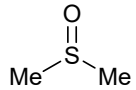
$CDCl_3$, TMS, ppm): δ 7.52–7.58 (m, 2H), 7.42–7.49 (m, 3H), 2.65–2.91 (m, 2H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 130.9, 129.1, 124.1, 50.2, 5.9; *Known compound*.[2]



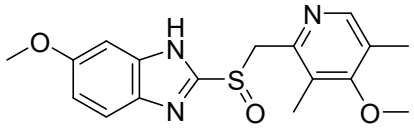
((2-Chloroethyl)sulfinyl)benzene (2i): 179.2 mg, 95%; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.47–7.55 (m, 2H), 7.36–7.43 (m, 3H), 3.47–3.57 (m, 1H), 3.76–3.87 (m, 1H), 2.97–3.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 131.4, 129.4, 123.8, 59.1, 36.7; *Known compound*.[5]



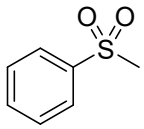
4,4'-Sulfinyldiphenol (2j): 149.9 mg, 64%; White solid, m. p. 195.3–197.6 °C (lit. 195–196°C); ^1H NMR (400 MHz, DMSO, TMS, ppm): δ 10.08 (s, 2H), 7.41 (d, J = 8.7 Hz, 4H), 6.87 (d, J = 8.7 Hz, 4H); ^{13}C NMR (100 MHz, DMSO): δ 160.3, 135.9, 126.9, 116.5; *Known compound*.[4]



Dimethyl sulfoxide (2k): 26.5 g, 68%; Liquid, b. p. 85–86 °C/21 mmHg (lit. 85 °C/20 mmHg); IR (film): 2999, 2914, 1438, 1407, 1314, 1030, 954, 702; *Known compound*.[6]

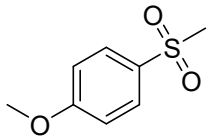


Omeprazole (2l): 117.4 g, 68%; White solid, m. p. 155.6-156.8 °C (lit. 155–157°C); ^1H NMR (400 MHz, DMSO, TMS, ppm): δ 13.41 (s, 1H), 8.15 (s, 1H), 7.54–7.48 (m, 1H), 7.10–7.04 (m, 1H), 6.92–6.85 (m, 1H), 4.77–4.63 (m, 2H), 3.77 (s, 3H), 3.65 (s, 3H), 2.16 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 163.9, 157.0, 153.5, 150.1, 149.6, 139.3, 135.1, 126.9, 126.0, 118.1, 113.8, 97.5, 60.5, 60.1, 55.9, 13.3, 11.5; *Known compound*.[2]

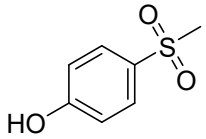


(Methylsulfonyl)benzene (3a): 123.4 mg, 79%; White solid, m. p. 87.3–88.6 °C (lit.

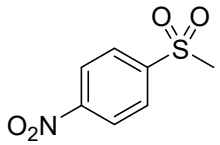
87–88°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.90–7.97 (m, 2H), 7.60–7.68 (m, 1H), 7.52–7.59 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 133.7, 129.4, 127.3, 44.5; *Known compound*.[1]



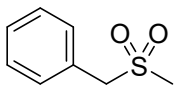
1-Methoxy-4-(methylsulfonyl)benzene (3b): 165.7 mg, 89%; White solid, m. p. 117.7–119.6 °C (lit. 118–120°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.86 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 132.3, 129.5, 114.5, 55.7, 44.8; *Known compound*.[2]



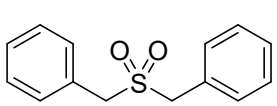
4-(Methylsulfonyl)phenol (3c): 134.3 mg, 78%; White solid, m. p. 93.5–94.9 °C (lit. 93–94°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.71–7.88 (m, 2H), 6.92–7.12 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 130.8, 129.6, 116.3, 44.9; *Known compound*.[7]



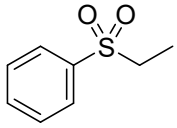
1-(Methylsulfonyl)-4-nitrobenzene (3d): 136.8 mg, 68%; Light yellow solid, m. p. 139.5–141.2 °C (lit. 139–141°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.40 (d, J = 7.4 Hz, 2H), 8.14 (d, J = 8.8 Hz, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 145.9, 129.0, 124.6, 44.2; *Known compound*.[2]



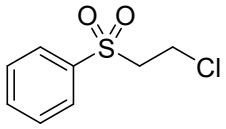
((Methylsulfonyl)methyl)benzene (3f): 127.7 mg, 75%; White solid, m. p. 124.3–125.4 °C (lit. 125–126°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.38–7.41 (m, 5H), 4.24 (s, 2H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.5, 129.9, 129.1, 128.3, 61.3, 39.0; *Known compound*.[1]



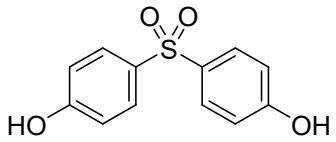
(Sulfonylbis(methylene))dibenzene (3g): 177.4 mg, 72%; White solid, m. p. 148.6–150.1 °C (lit. 148–150°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.38–7.43 (m, 10H), 4.13 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.9, 129.1, 129.0, 127.5, 58.0; *Known compound*.[1]



(Ethylsulfonyl)benzene (3h): 136.2 mg, 80%; White solid, m. p. 40.6–41.5 °C (lit. 41–42°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.85–7.91 (m, 2H), 7.61–7.66 (m, 1H), 7.52–7.58 (m, 2H), 3.09 (q, J = 7.8, 5.7 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 133.7, 129.3, 128.2, 50.6, 7.4; *Known compound*.[2]



((2-Chloroethyl)sulfonyl)benzene (3i): 155.6 mg, 76%; White solid, m. p. 54.8–56.9 °C (lit. 54–56°C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.85–7.93 (m, 2H), 7.64–7.71 (m, 1H), 7.54–7.62 (m, 2H), 3.73 (t, J = 7.7 Hz, 2H), 3.51 (t, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 134.3, 129.6, 128.1, 58.0, 35.6; *Known compound*.[8]



4,4'-Sulfonyldiphenol (3j): 222.7 mg, 89%; White solid, m. p. 246.8–247.9 °C (lit. 246–248°C); ^{1}H NMR (400 MHz, DMSO, TMS, ppm): δ 10.53 (s, 2H), 7.69 (d, J = 8.1 Hz, 4H), 6.88 (d, J = 8.7 Hz, 4H); ^{13}C NMR (100 MHz, DMSO): δ 162.1, 132.5, 129.8, 116.4; *Known compound*.[4]

Reference

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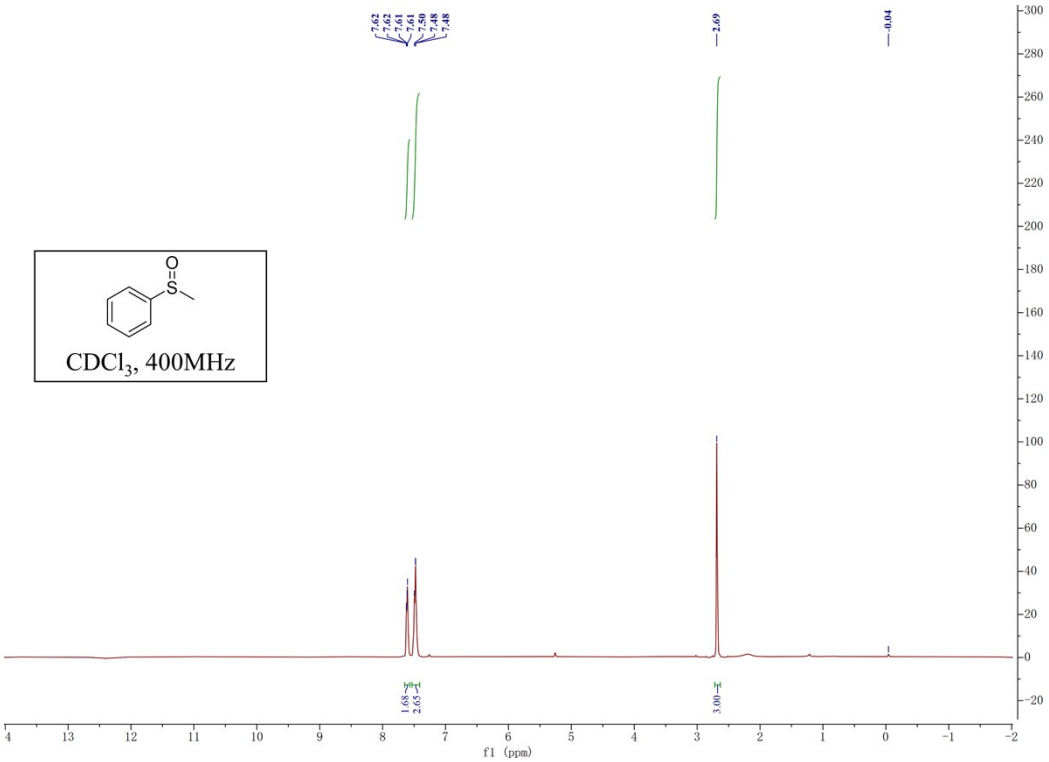
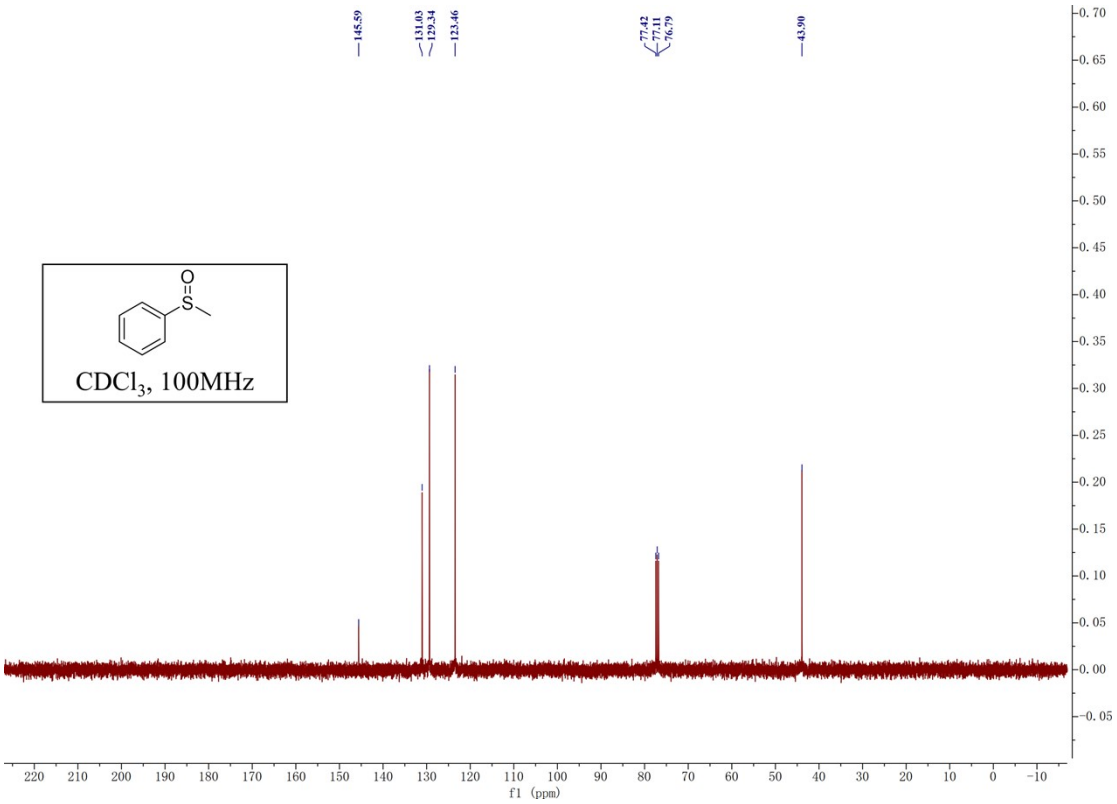
5. NMR spectra of the products

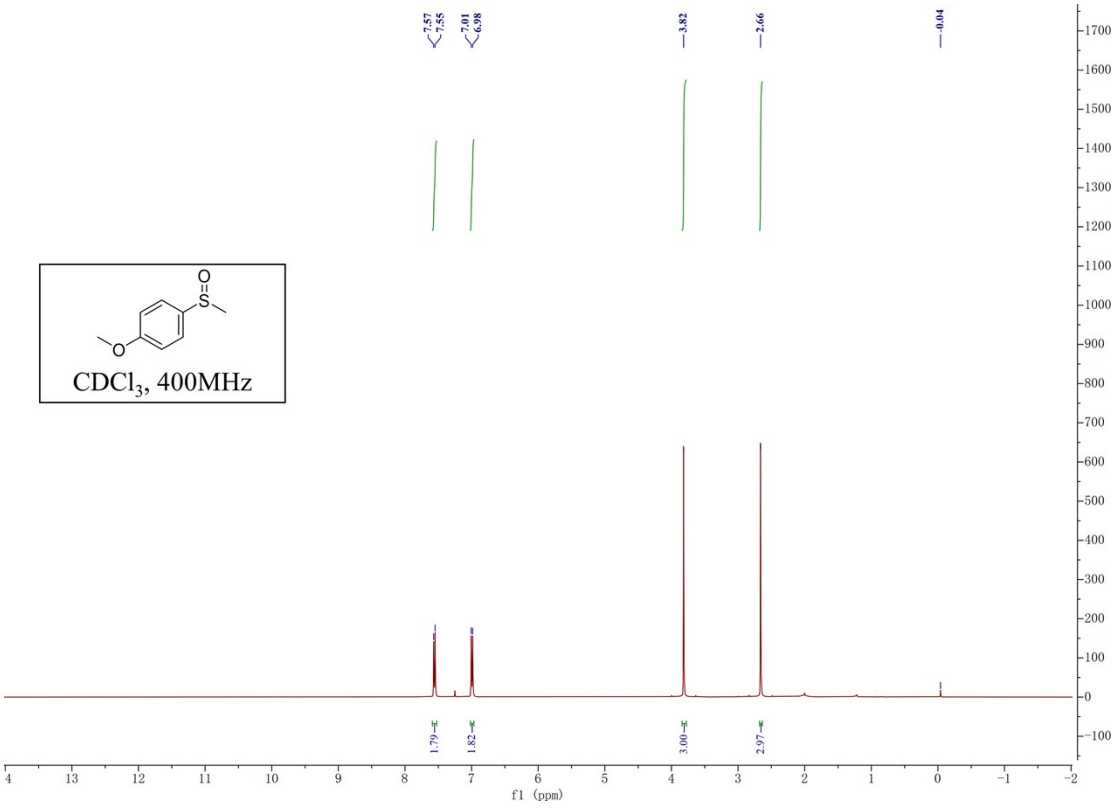
2a, ^{1}H NMR, $CDCl_3$, 400 MHz



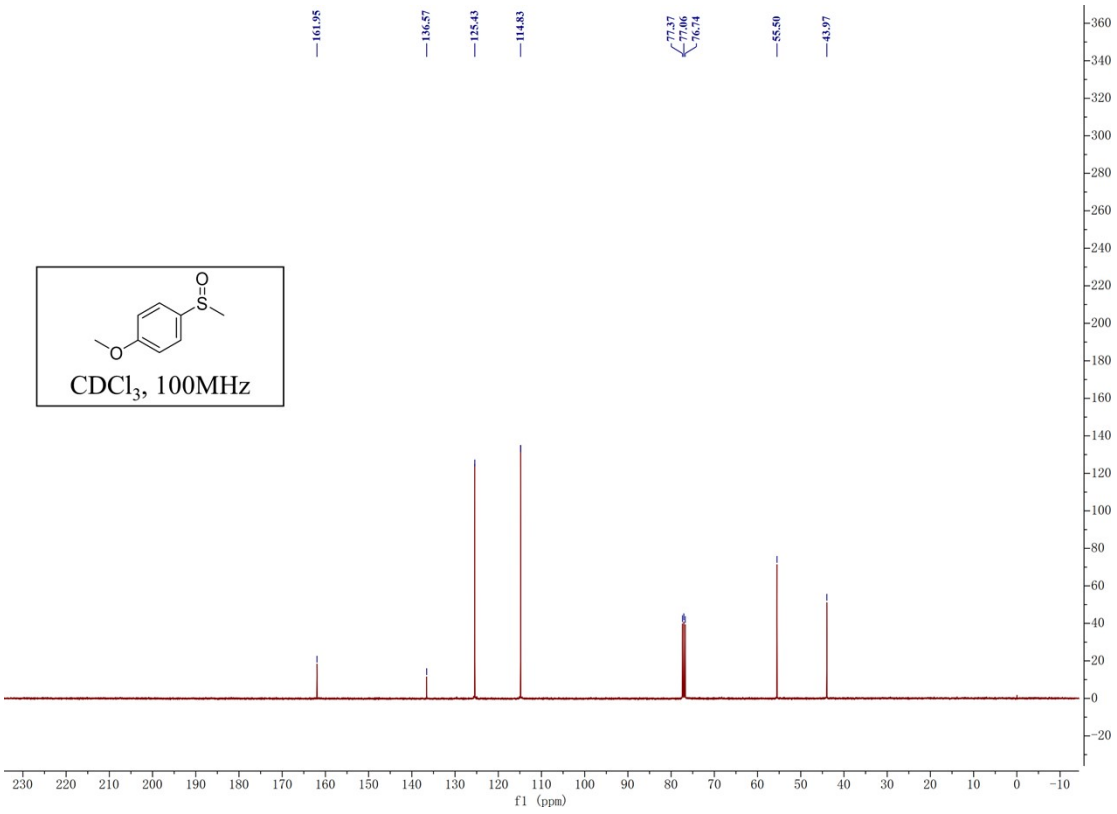
2a, ^{13}C NMR, $CDCl_3$, 100 MHz



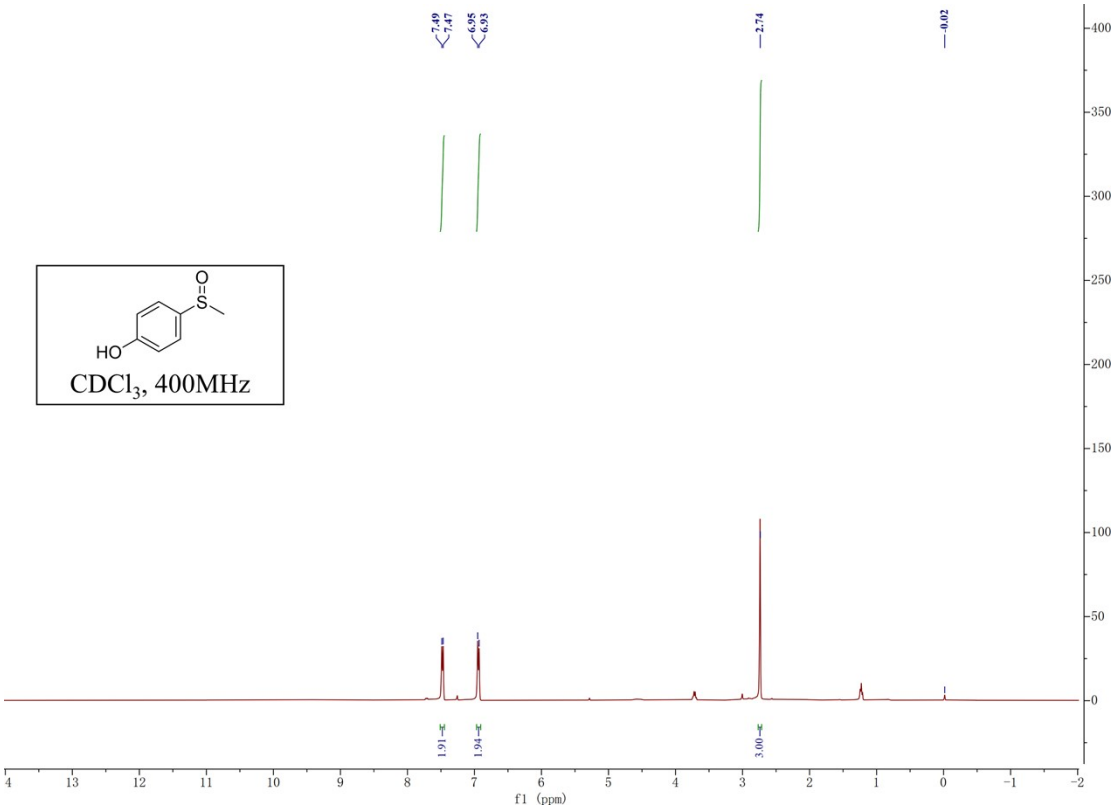
2b, ^{1}H NMR, $CDCl_3$, 400 MHz



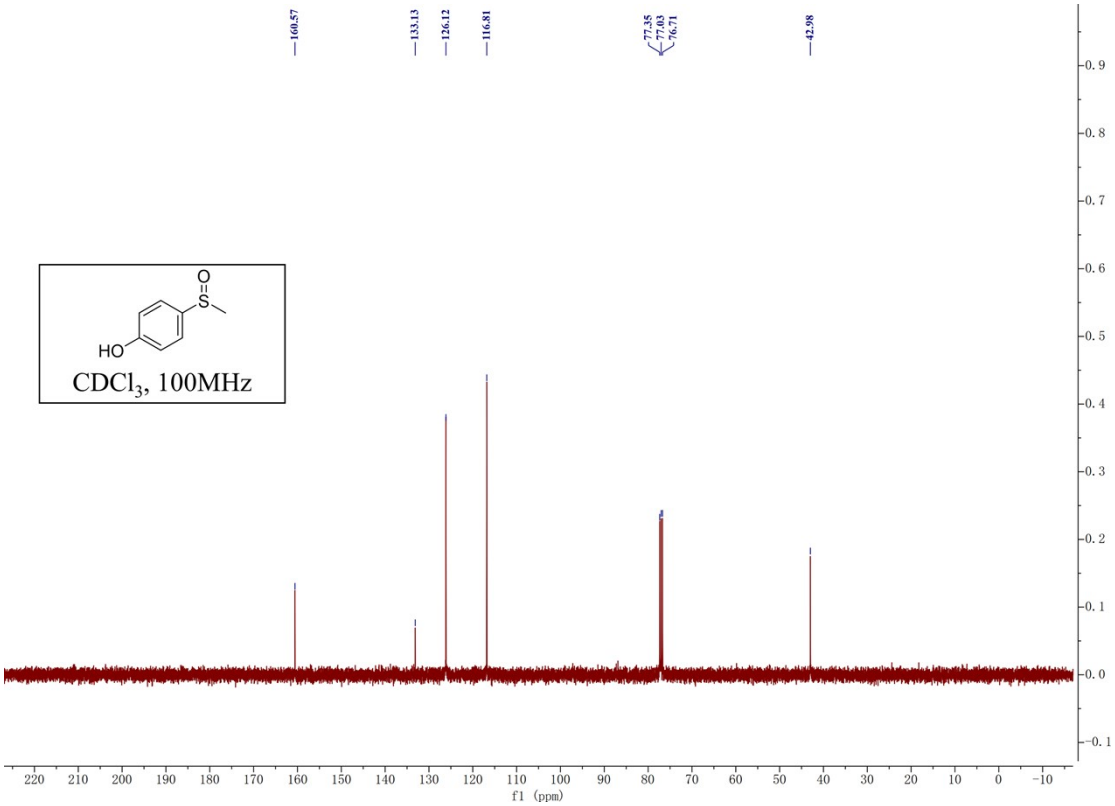
2b, ^{13}C NMR, $CDCl_3$, 100 MHz



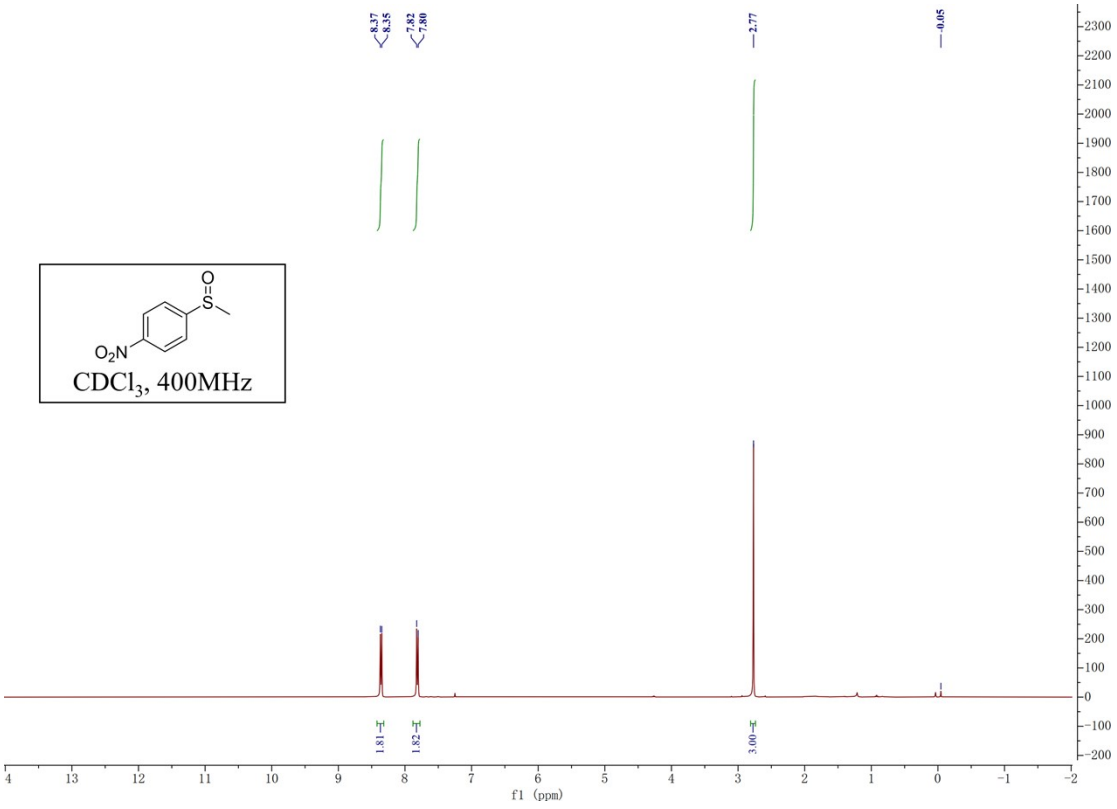
2c, ^{1}H NMR, $CDCl_3$, 400 MHz



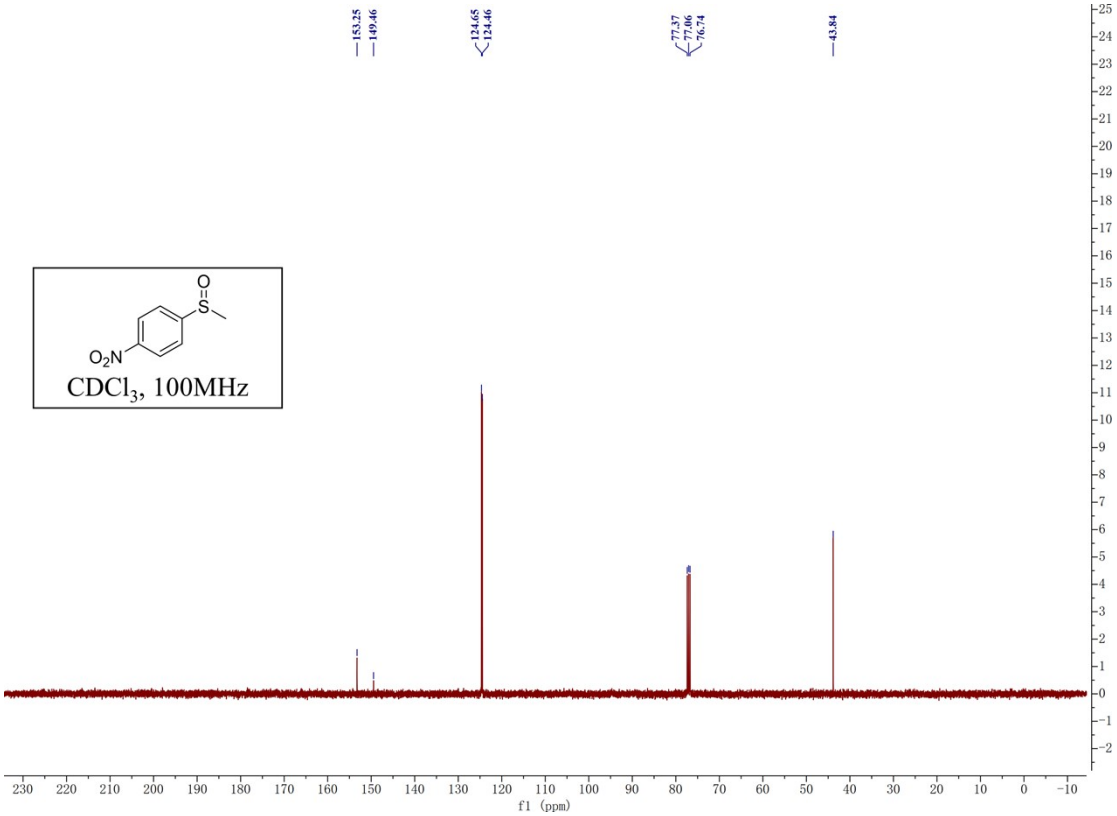
2c, ^{13}C NMR, $CDCl_3$, 100 MHz



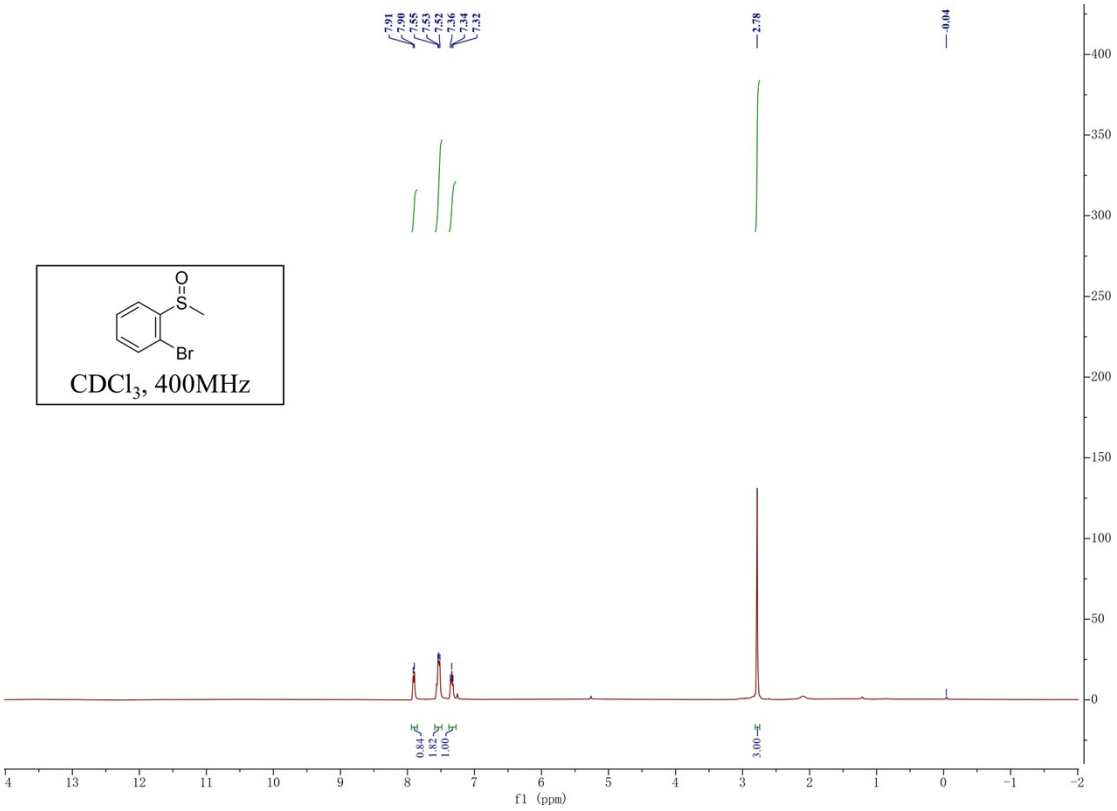
2d, ^{1}H NMR, $CDCl_3$, 400 MHz



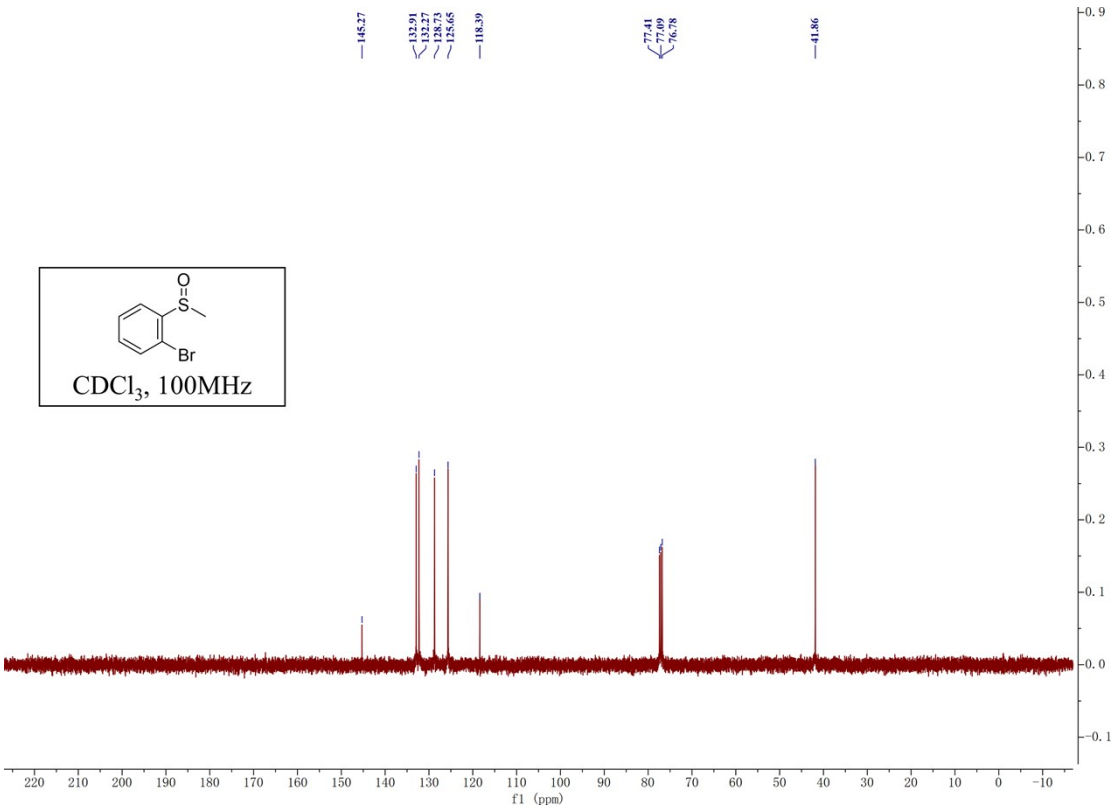
2d, ^{13}C NMR, $CDCl_3$, 100 MHz



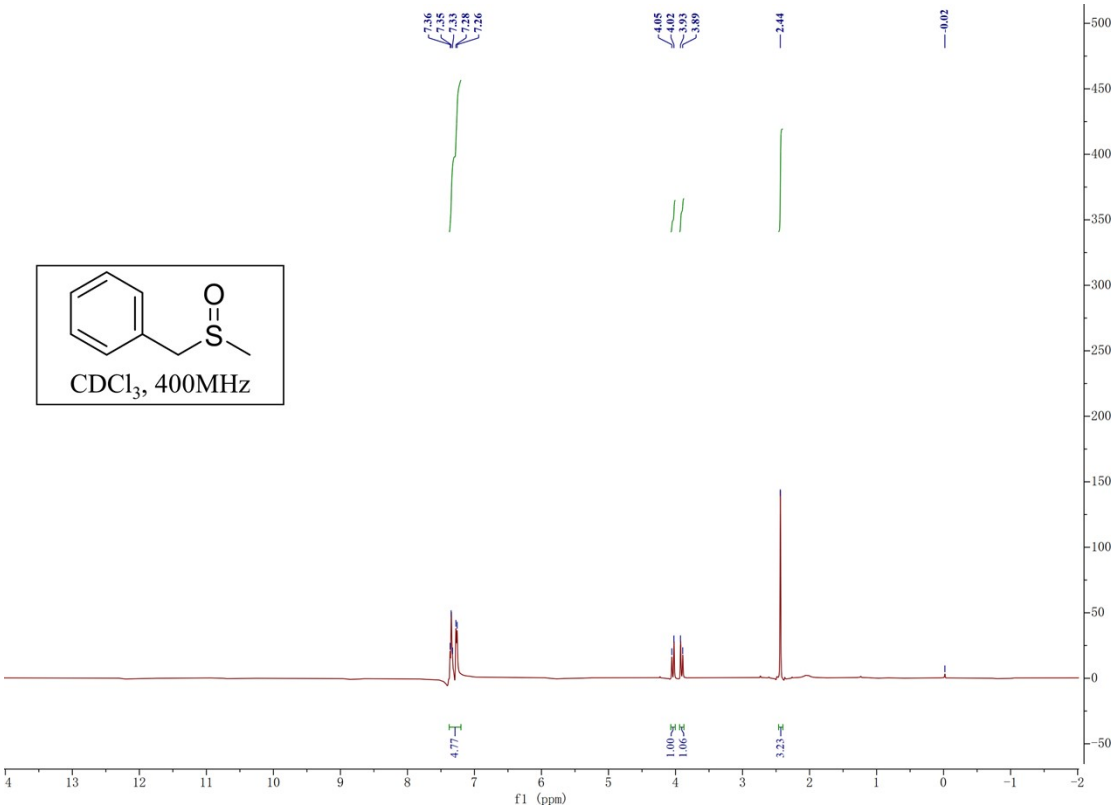
2e, ^{1}H NMR, $CDCl_3$, 400 MHz



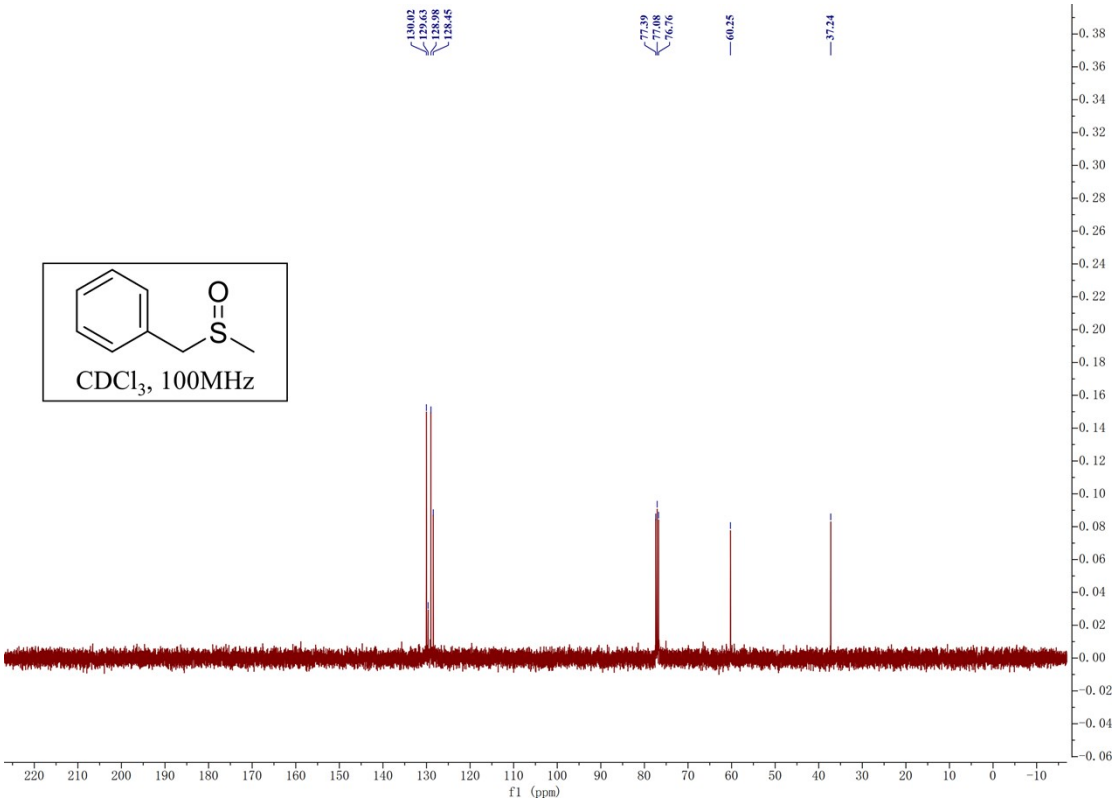
2e, ^{13}C NMR, $CDCl_3$, 100 MHz



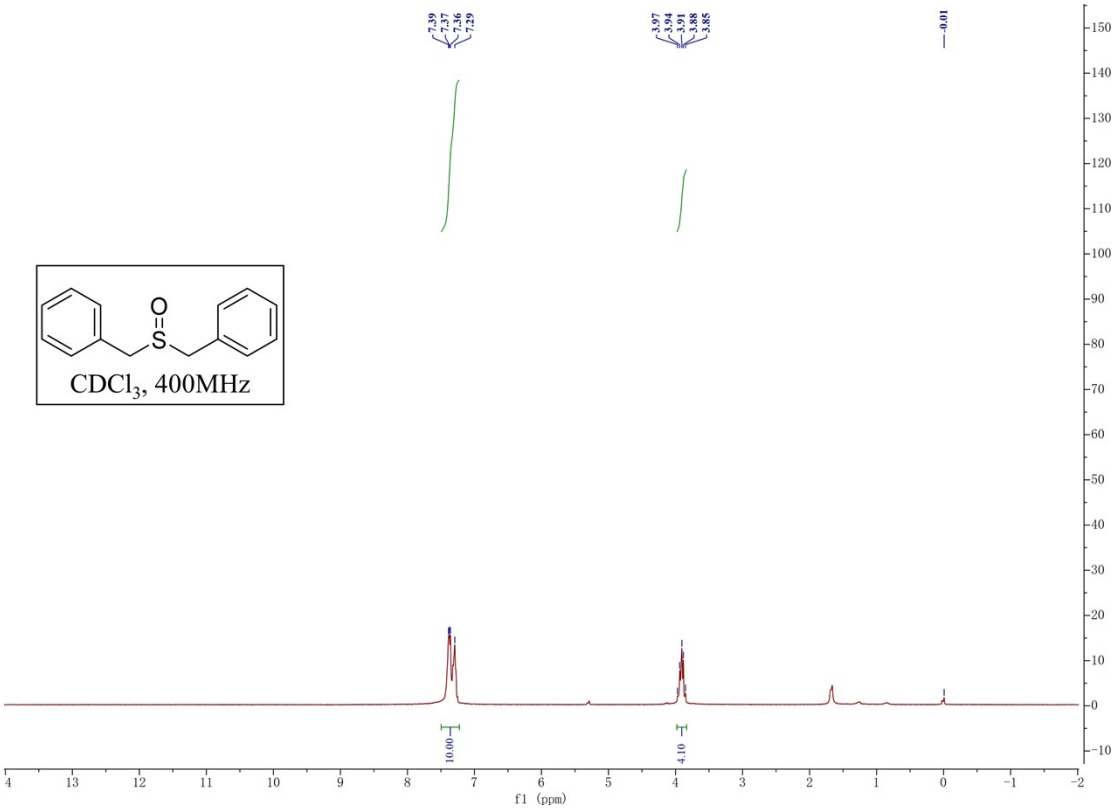
2f, ^{1}H NMR, $CDCl_3$, 400 MHz



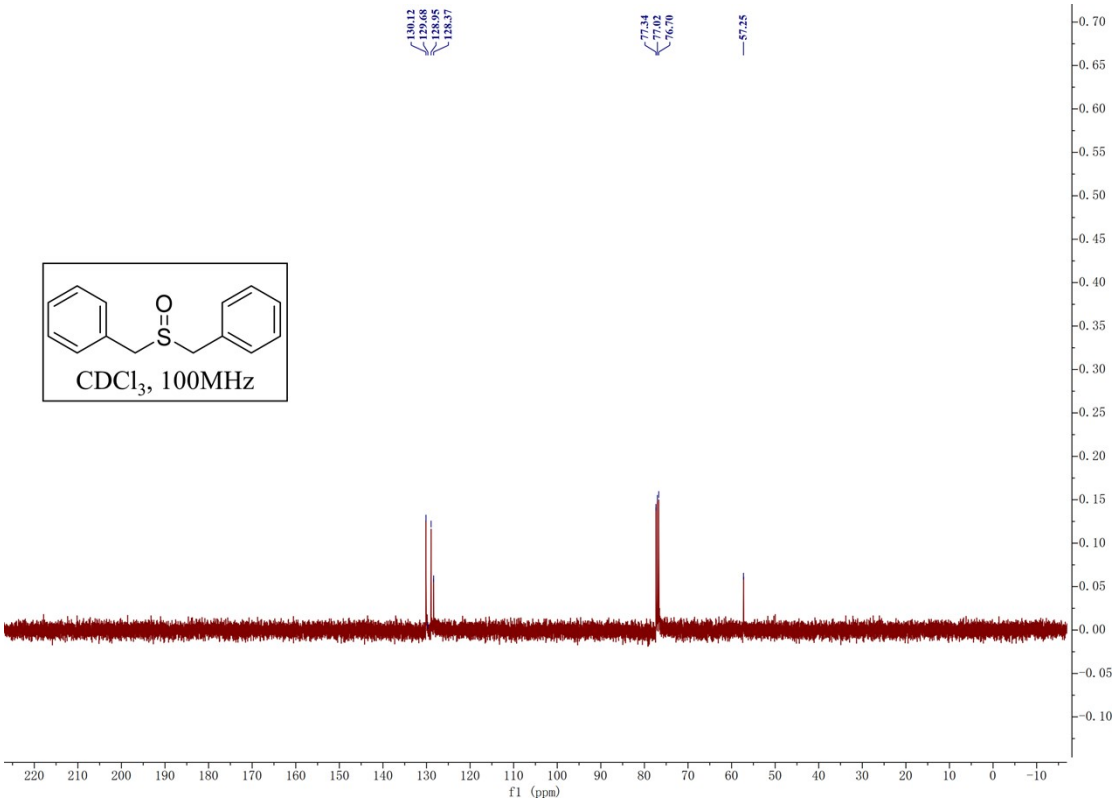
2f, ^{13}C NMR, $CDCl_3$, 100 MHz



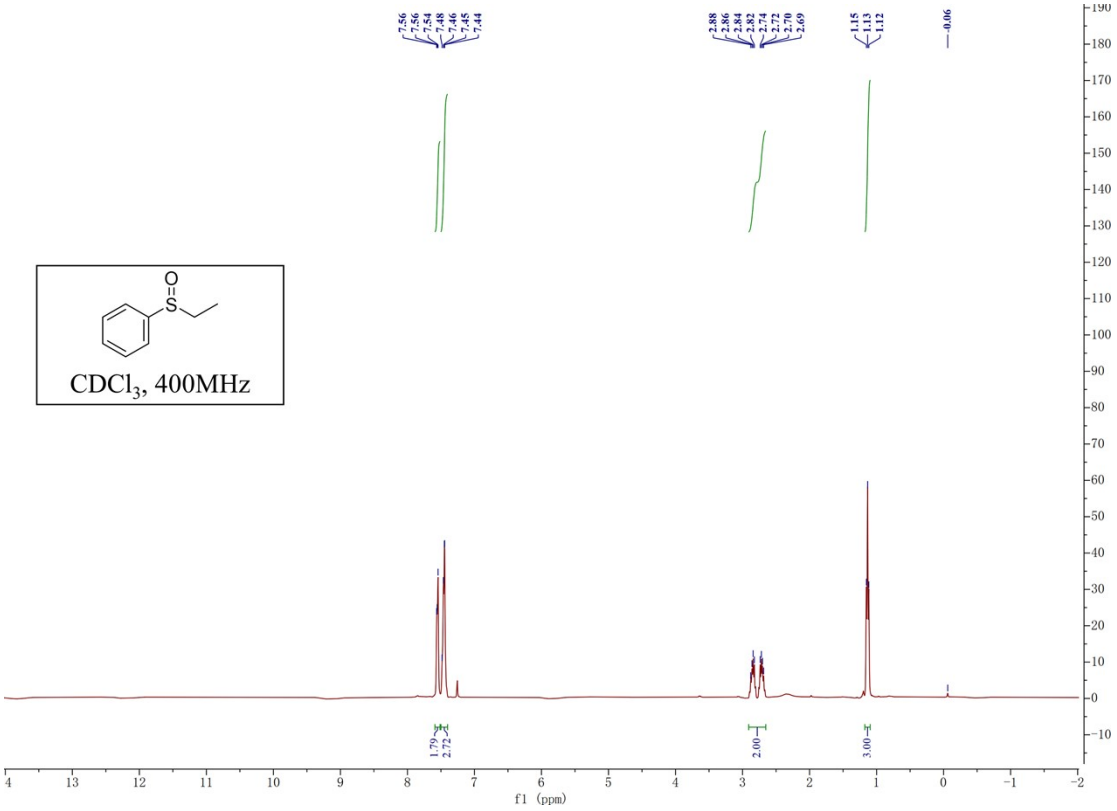
2g, ^{1}H NMR, $CDCl_3$, 400 MHz



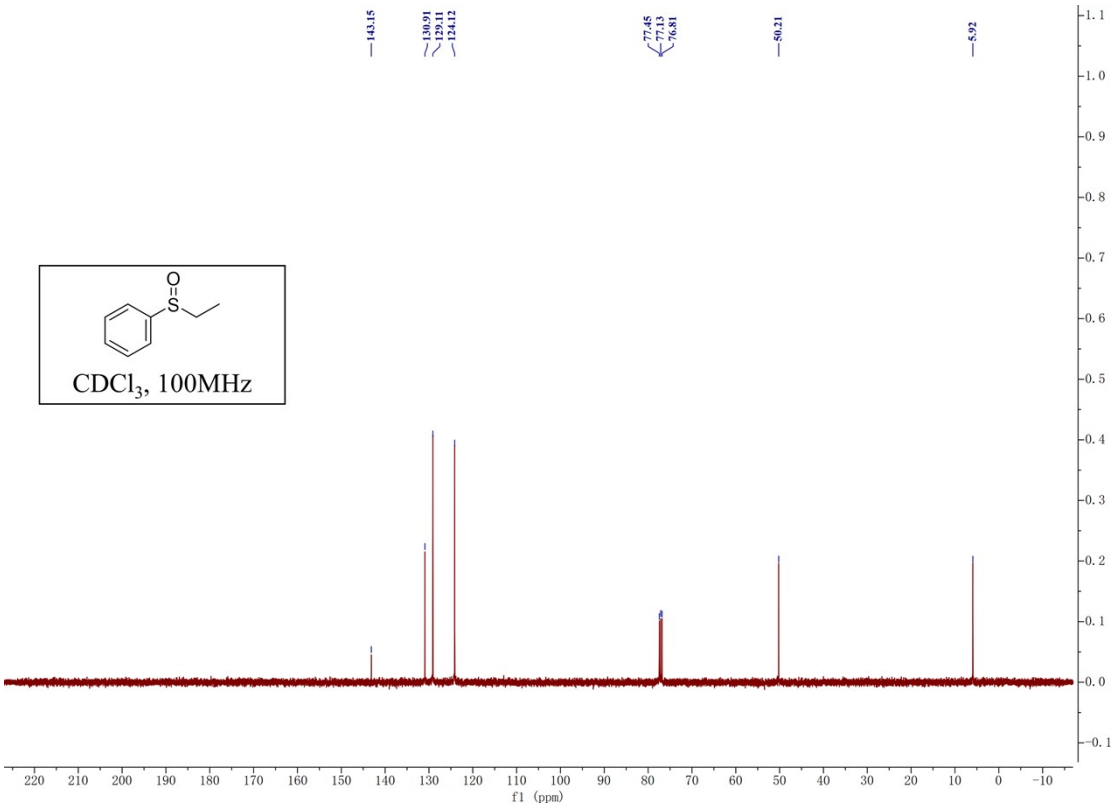
2g, ^{13}C NMR, $CDCl_3$, 100 MHz



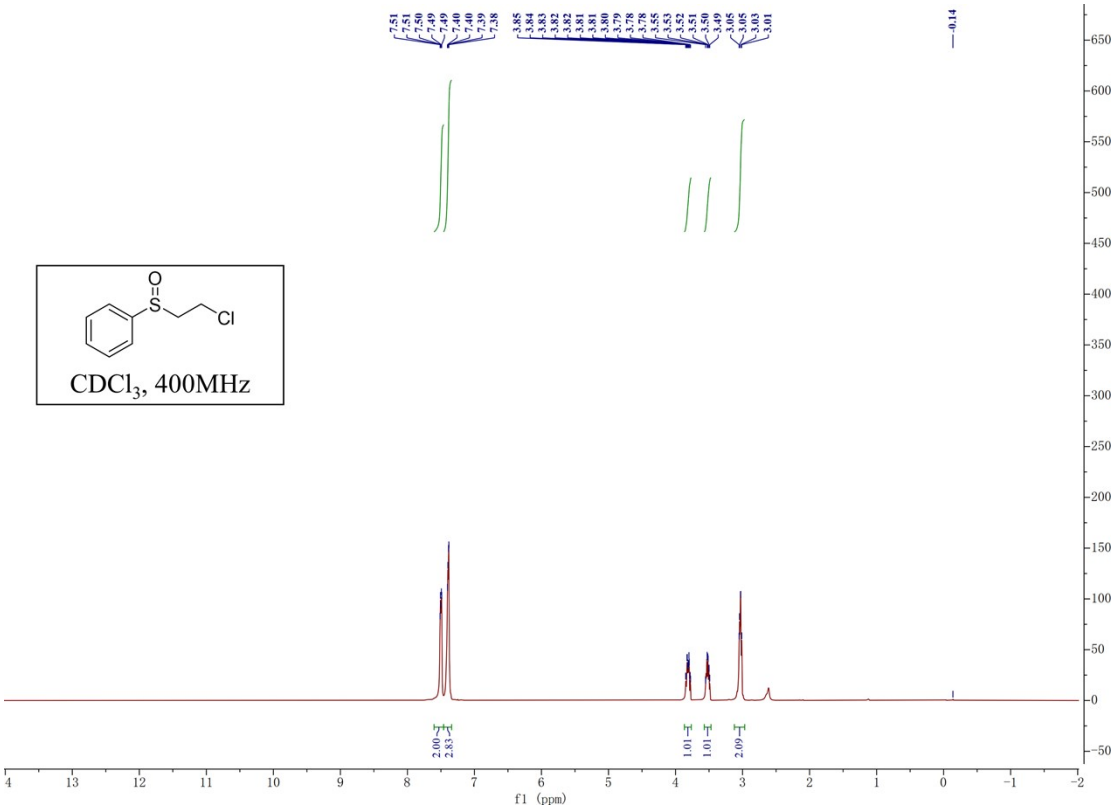
2h, ^{1}H NMR, $CDCl_3$, 400 MHz



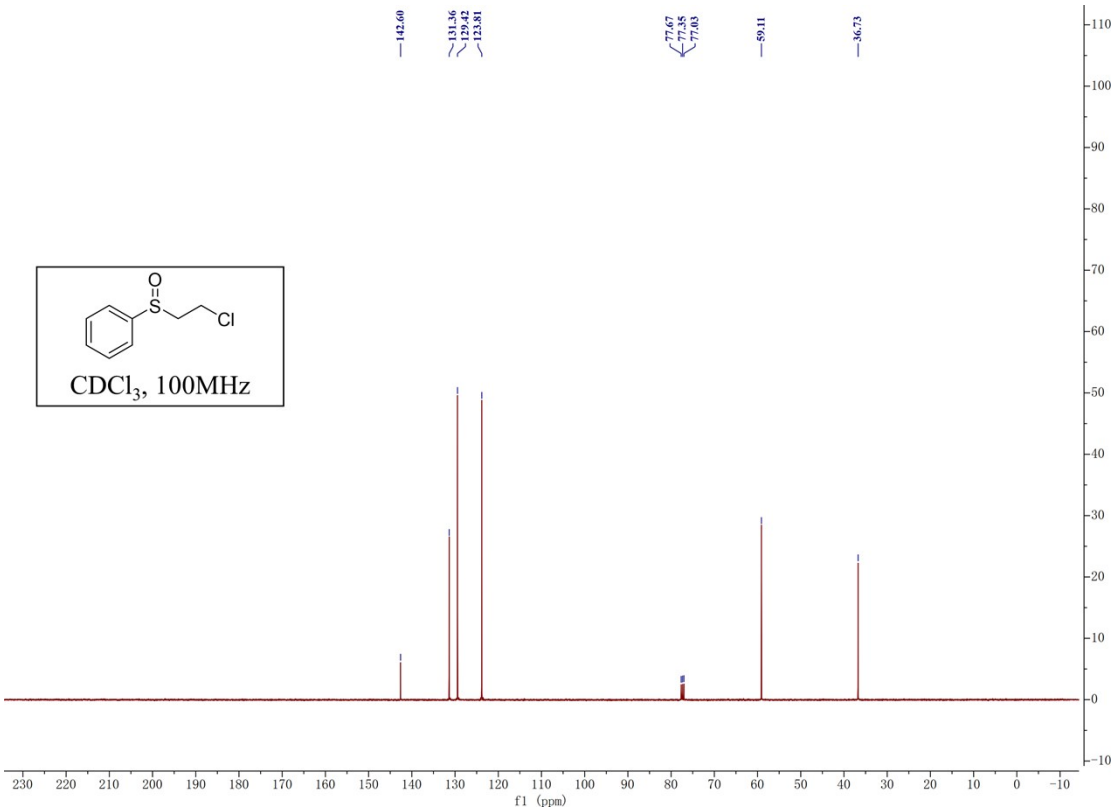
2h, ^{13}C NMR, $CDCl_3$, 100 MHz



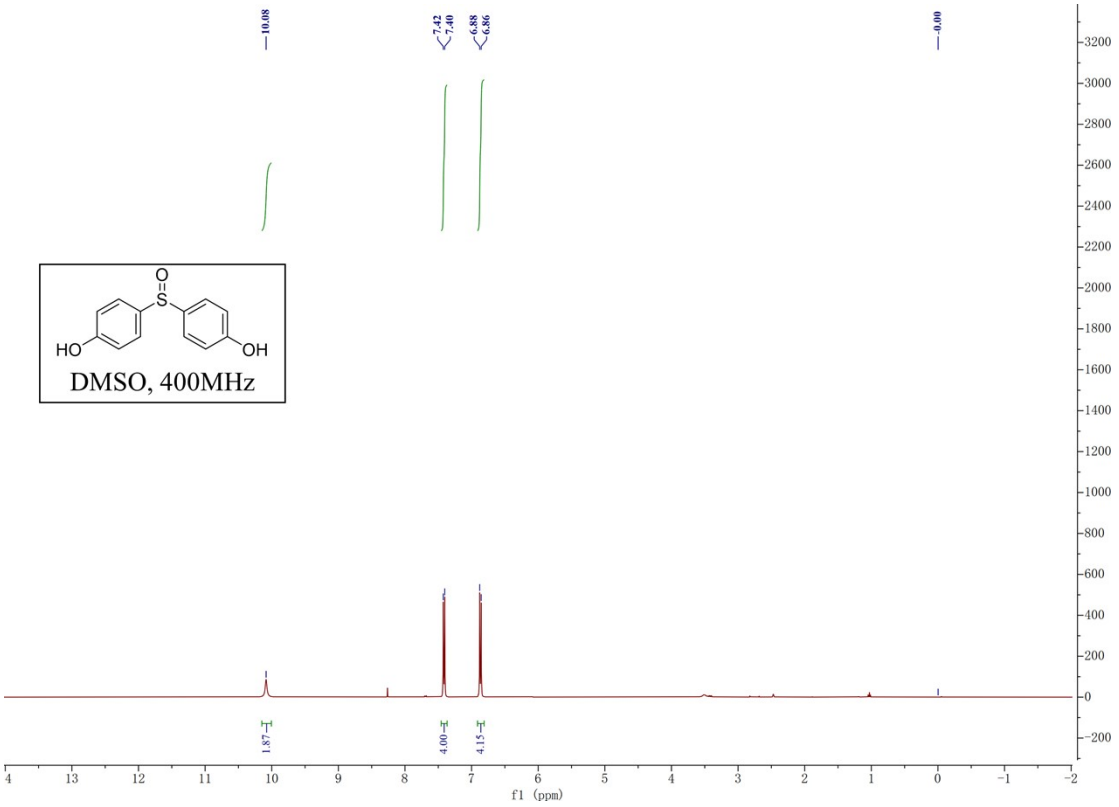
2i, ^{1}H NMR, $CDCl_3$, 400 MHz



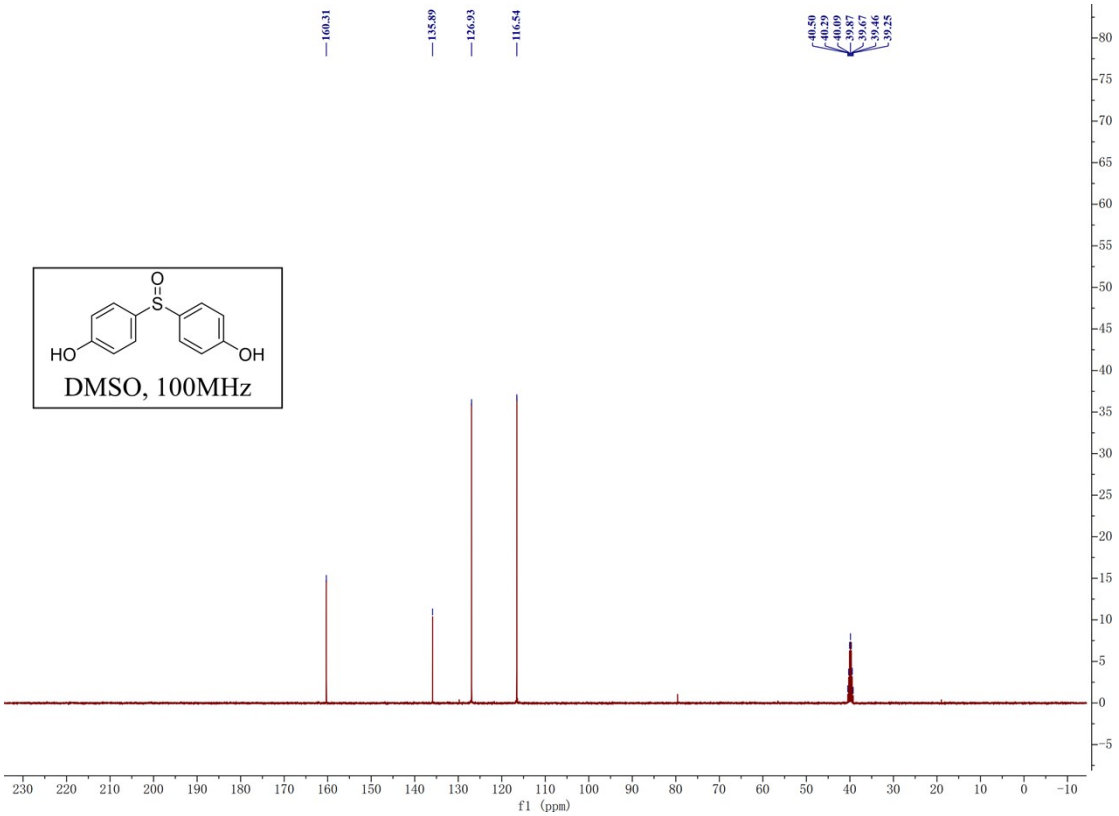
2i, ^{13}C NMR, $CDCl_3$, 100 MHz



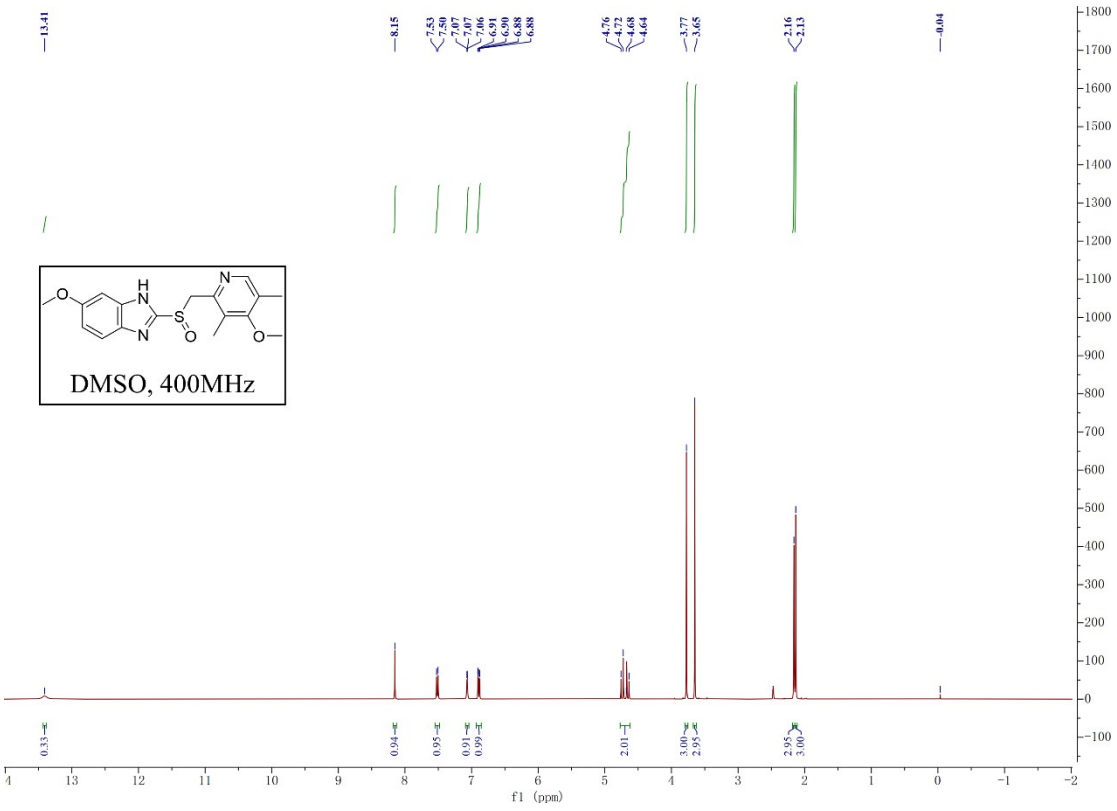
2j, ^{1}H NMR, DMSO, 400 MHz



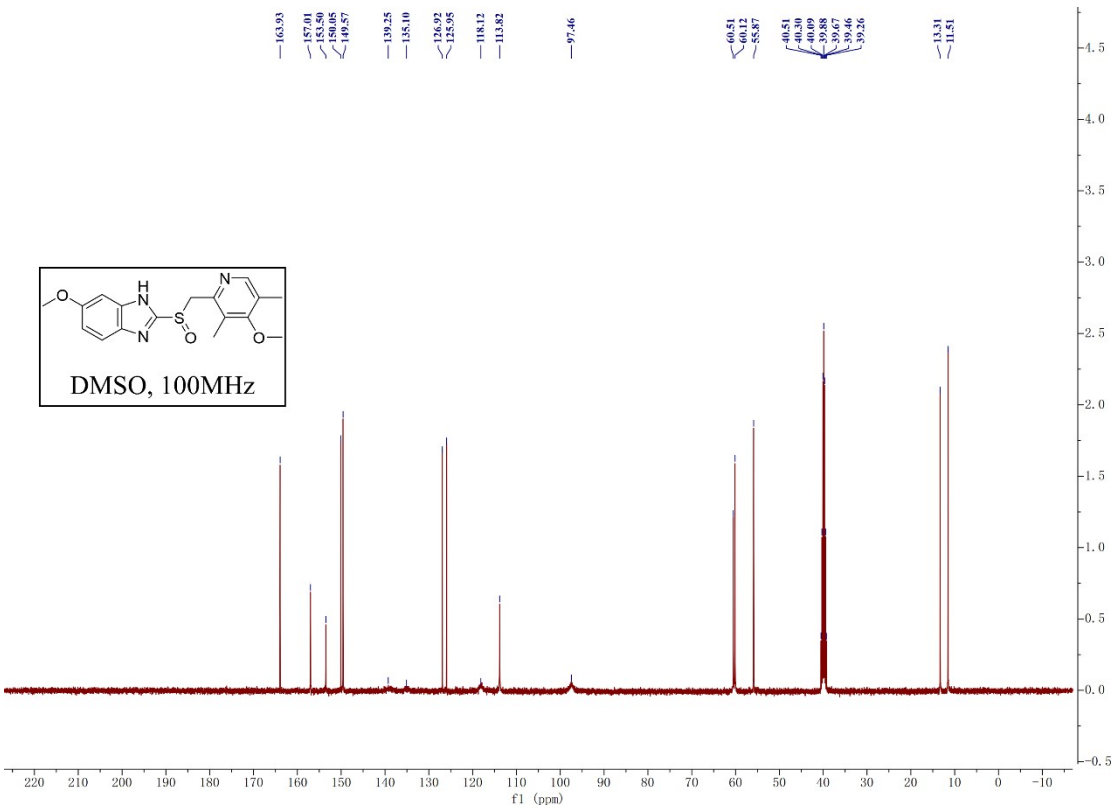
2j, ^{13}C NMR, DMSO, 100 MHz



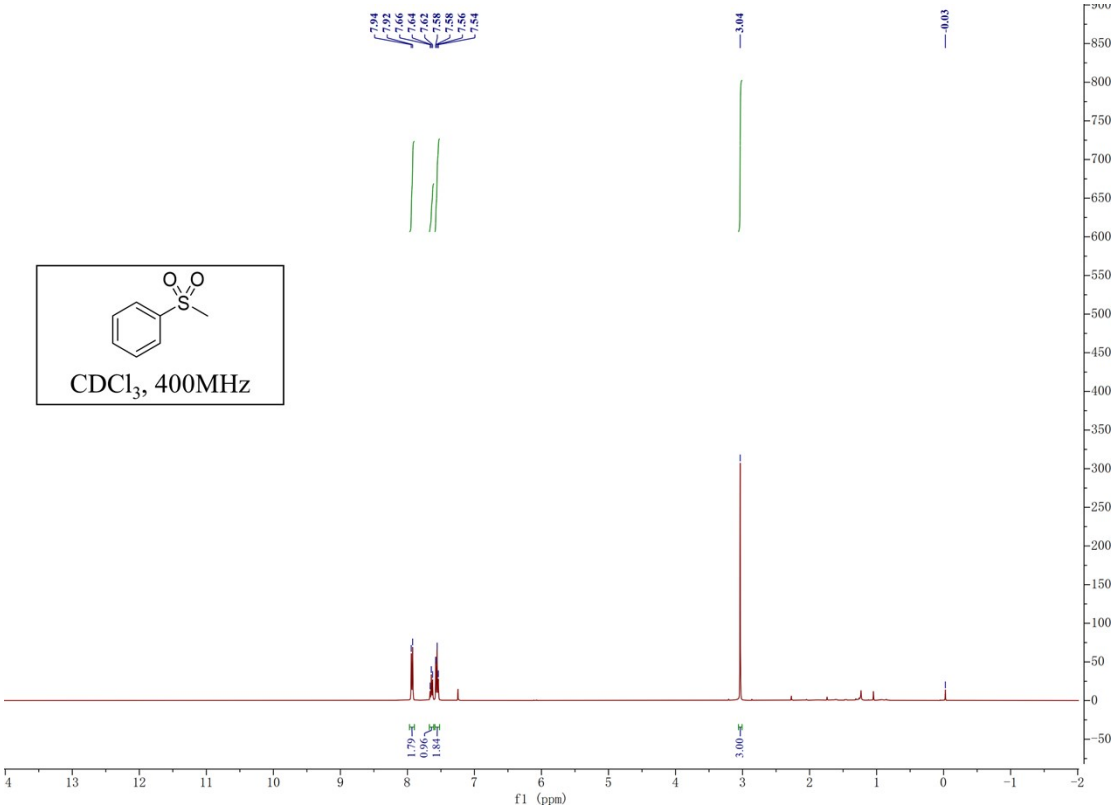
2l, ^{1}H NMR, DMSO, 400 MHz



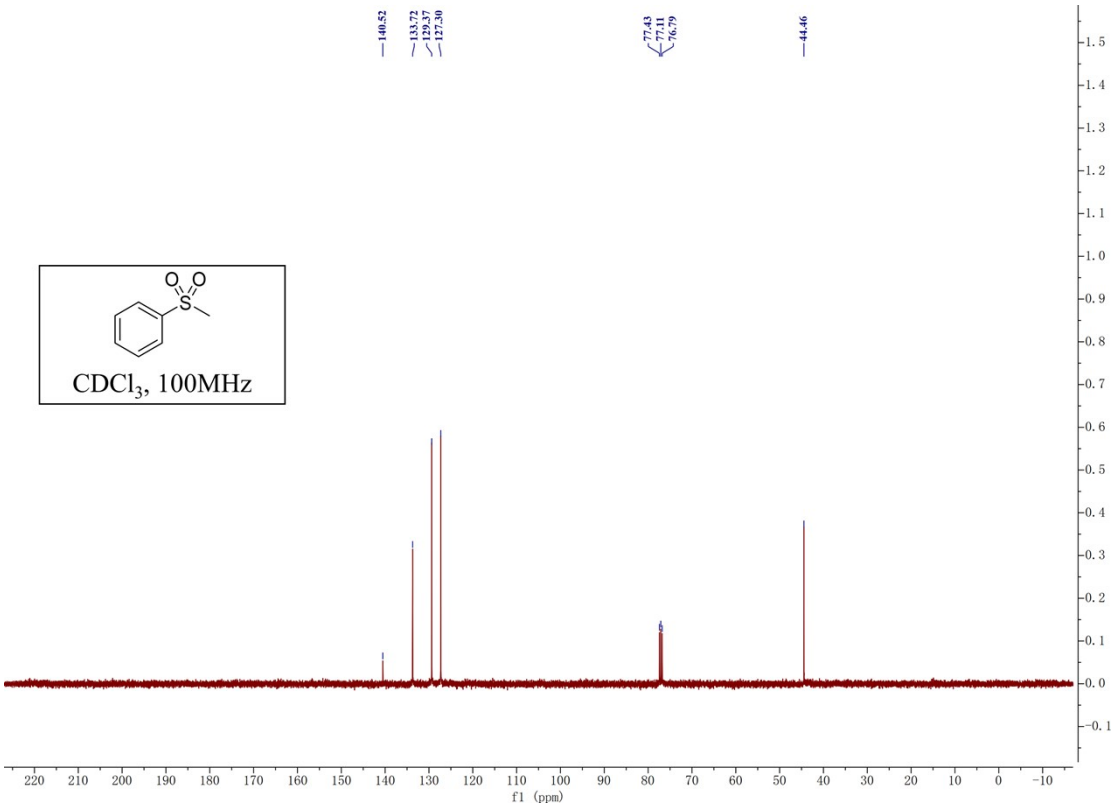
2l, ^{13}C NMR, DMSO, 100 MHz



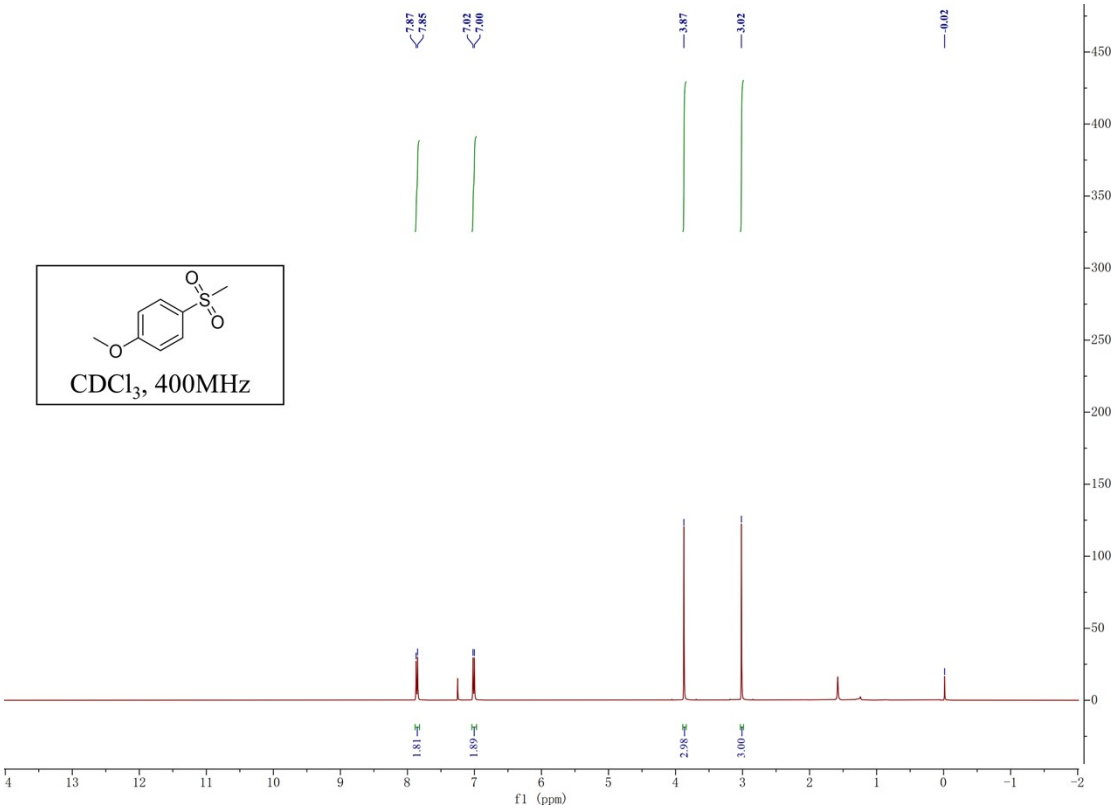
3a, ^{1}H NMR, $CDCl_3$, 400 MHz



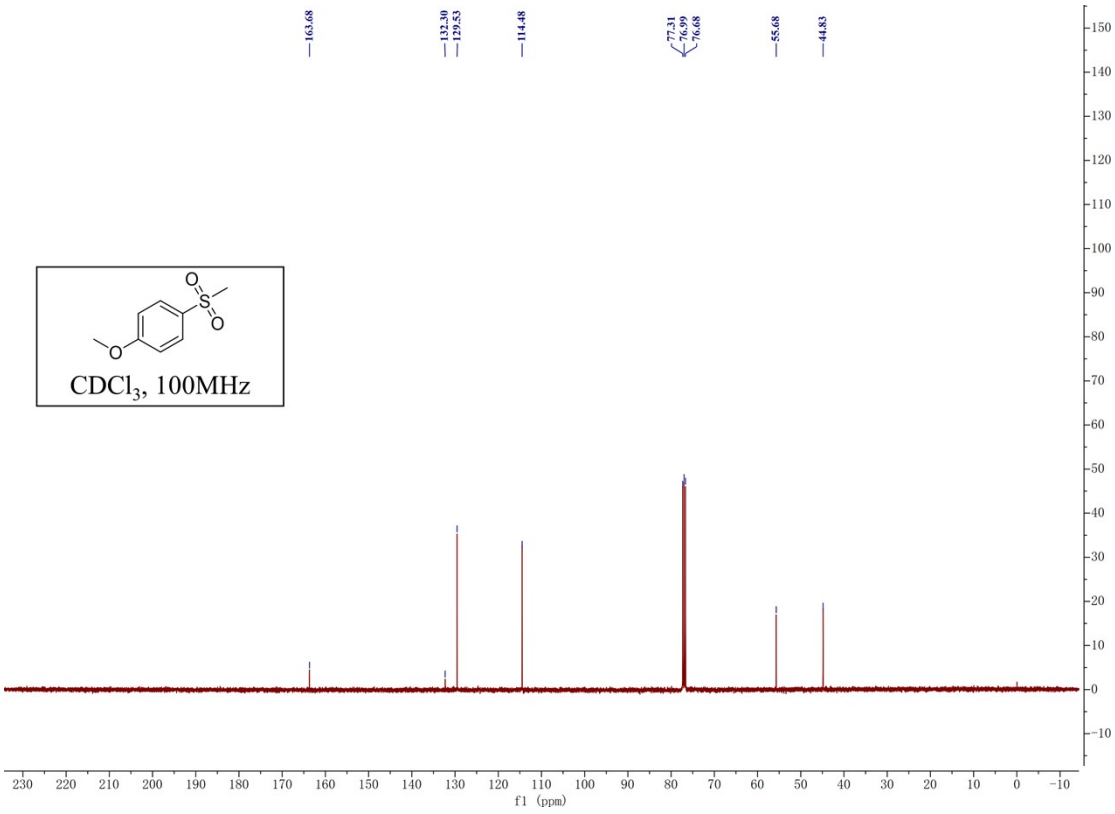
3a, ^{13}C NMR, $CDCl_3$, 100 MHz



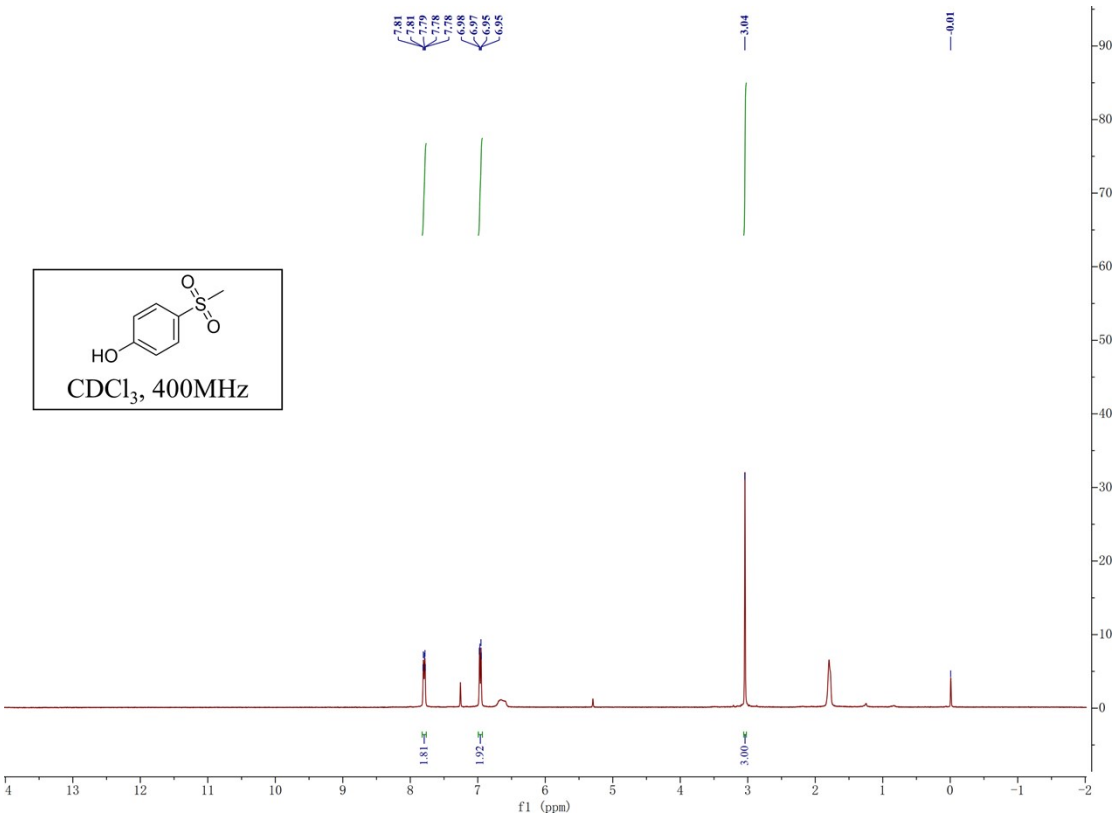
3b, ^{1}H NMR, $CDCl_3$, 400 MHz



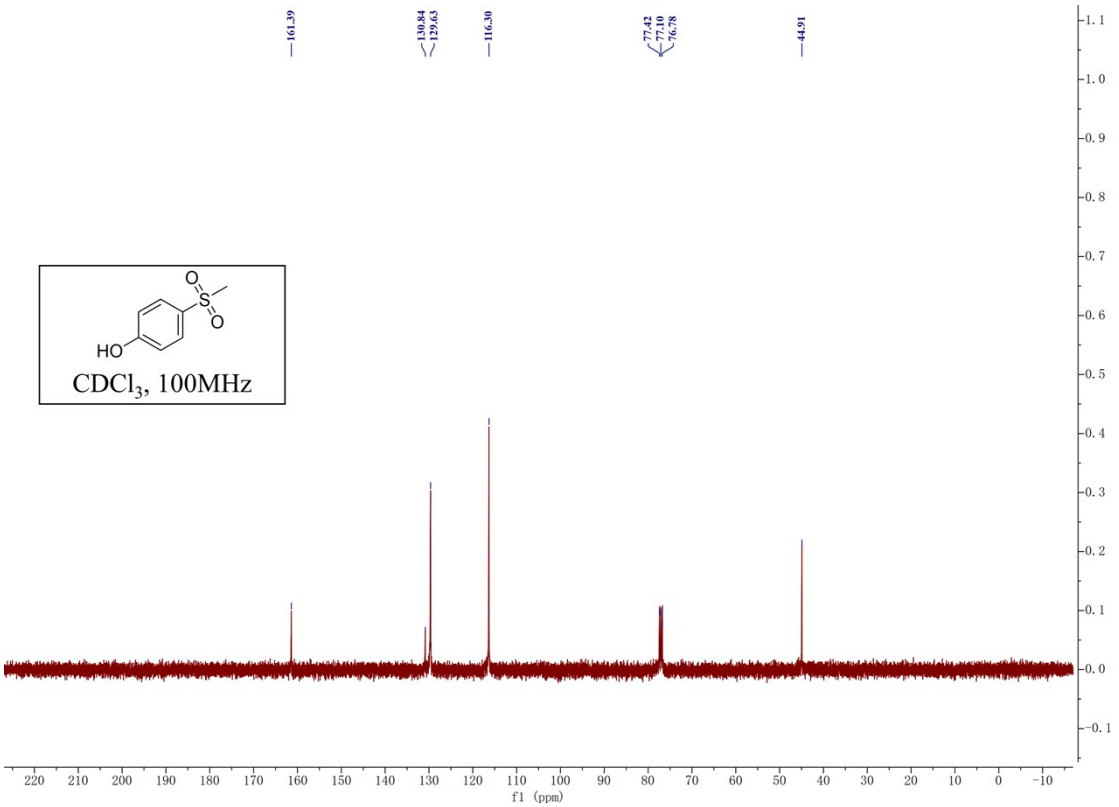
3b, ^{13}C NMR, $CDCl_3$, 100 MHz



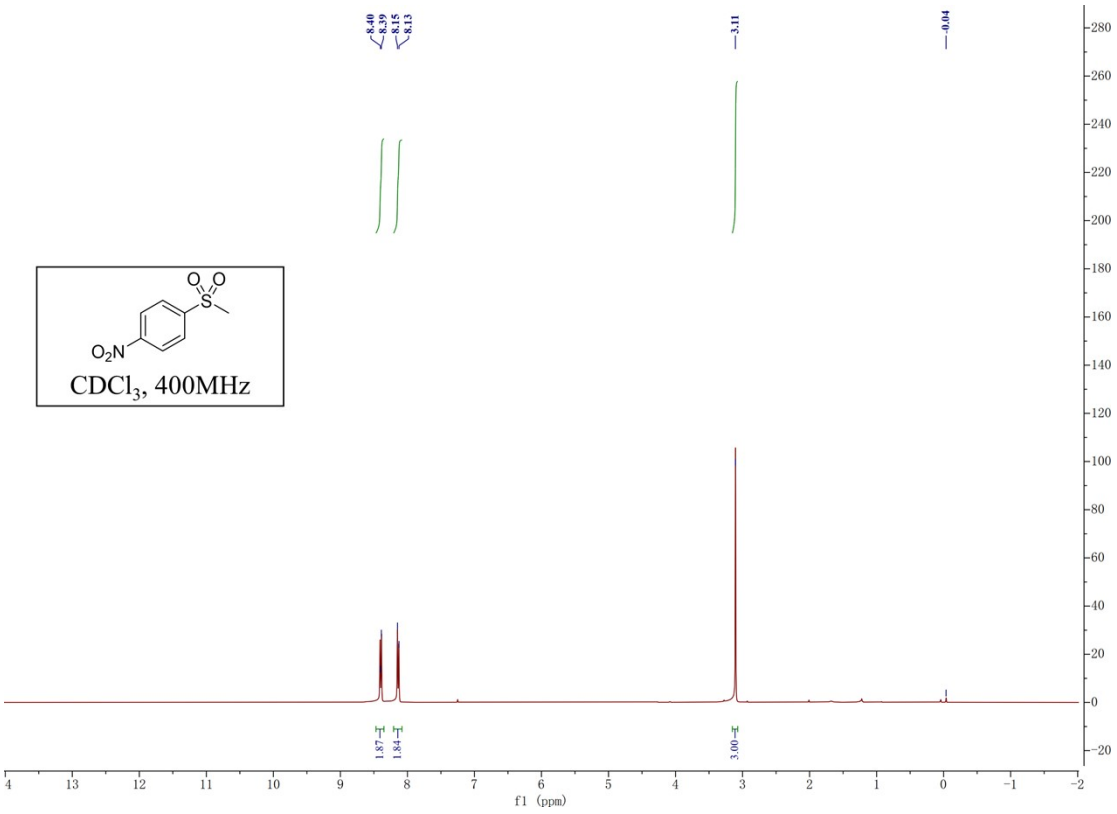
3c, ^{1}H NMR, $CDCl_3$, 400 MHz



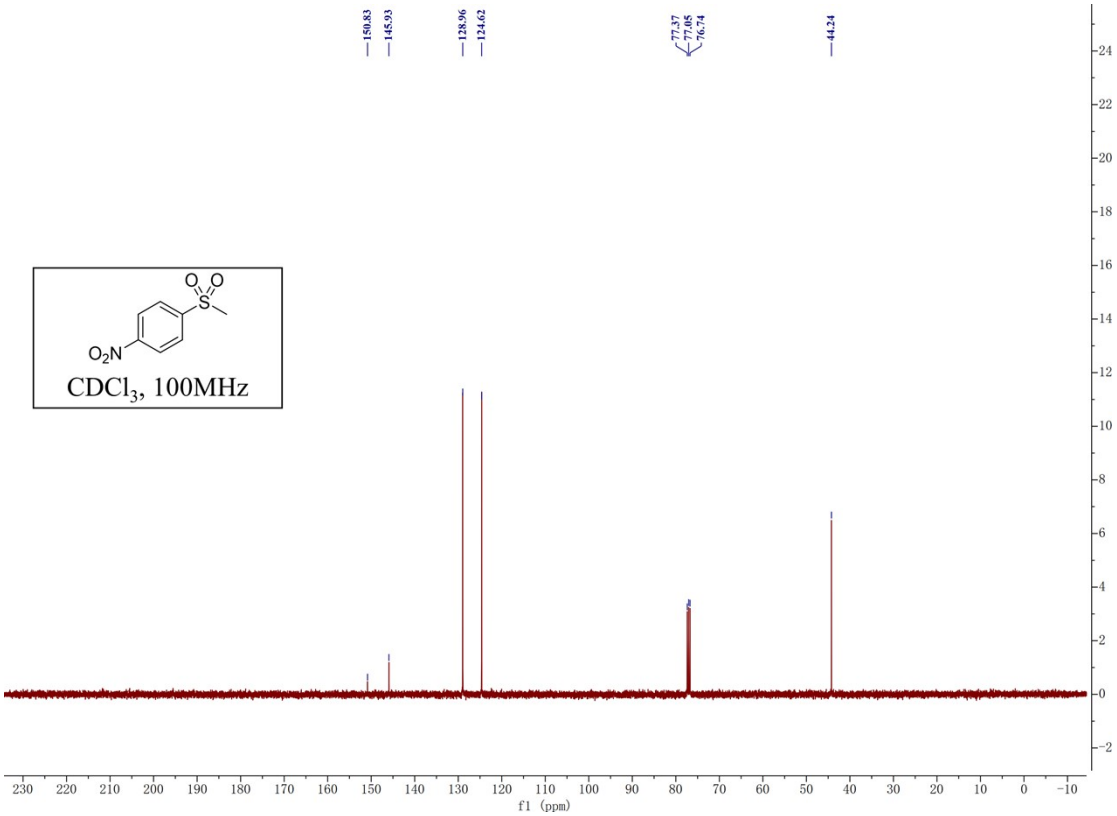
3c, ^{13}C NMR, $CDCl_3$, 100 MHz



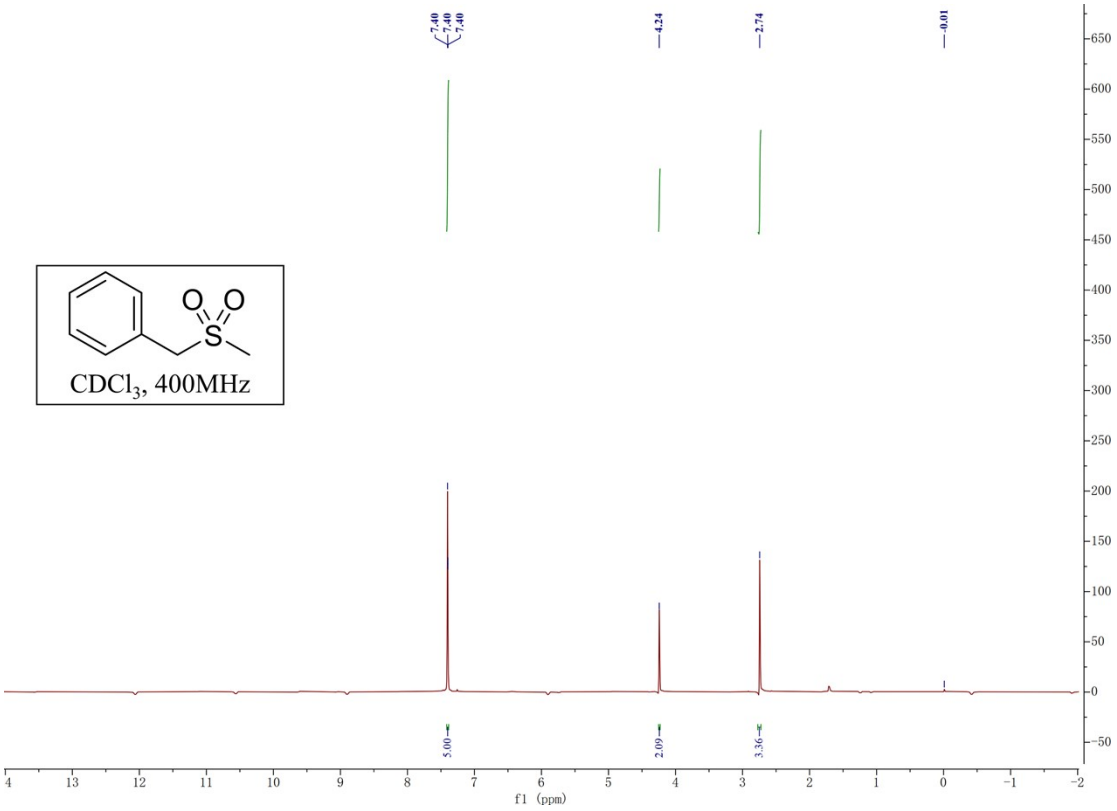
3d, ^{1}H NMR, $CDCl_3$, 400 MHz



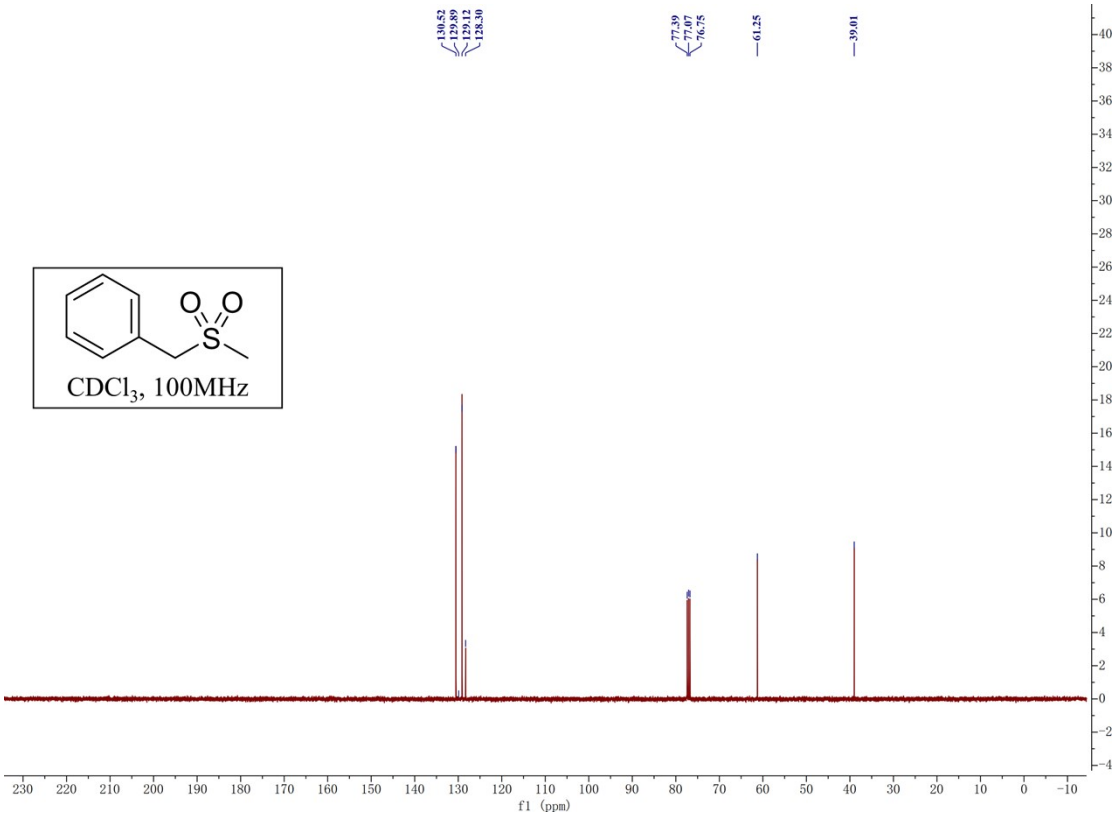
3d, ^{13}C NMR, $CDCl_3$, 100 MHz



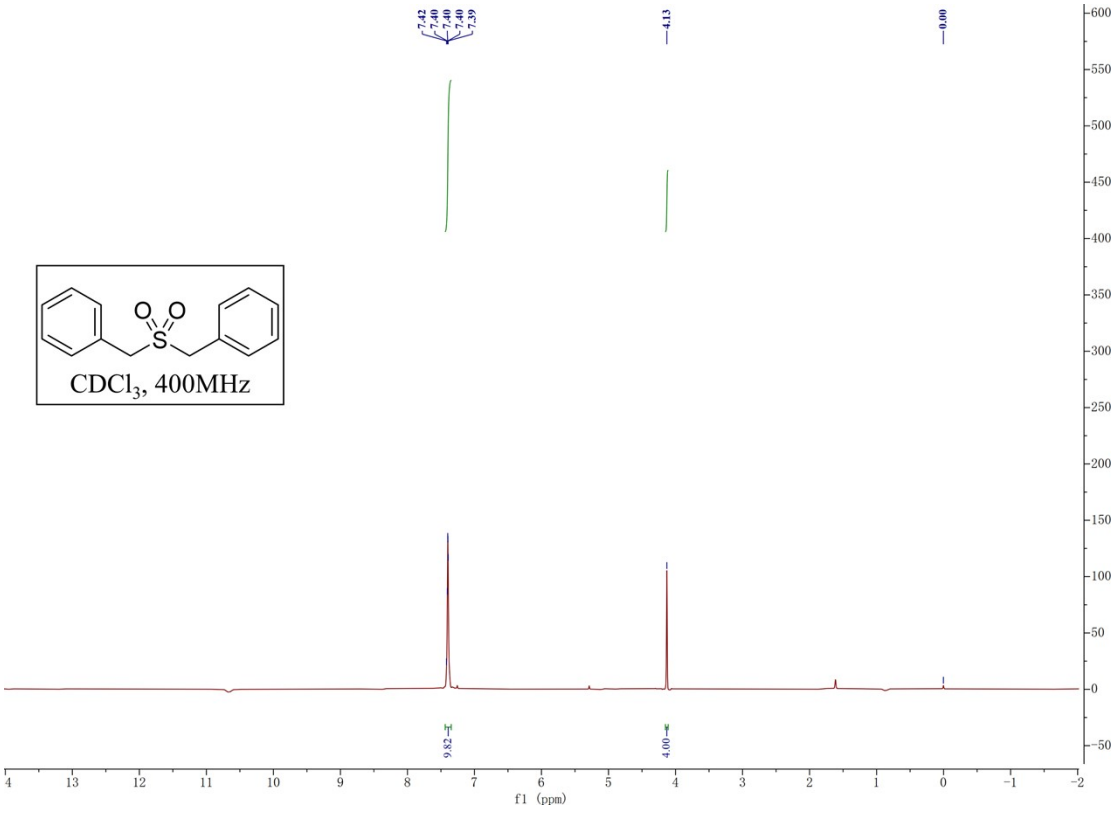
3f, ^{1}H NMR, $CDCl_3$, 400 MHz



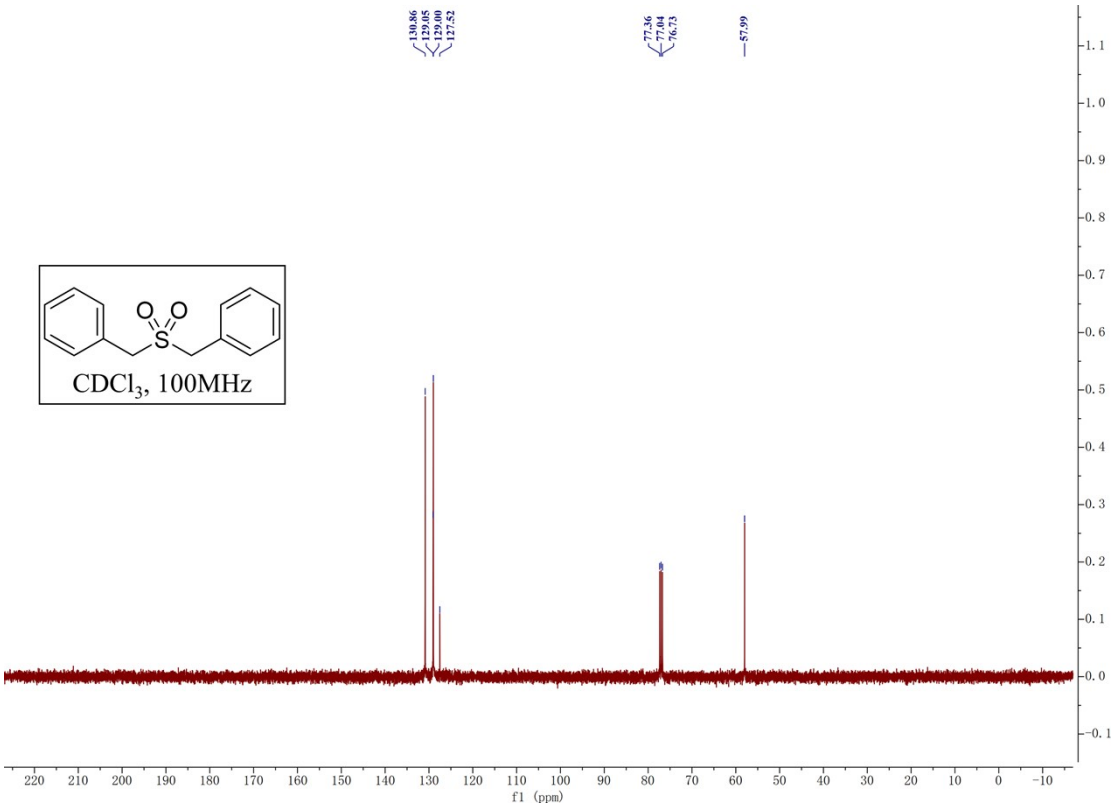
3f, ^{13}C NMR, $CDCl_3$, 100 MHz



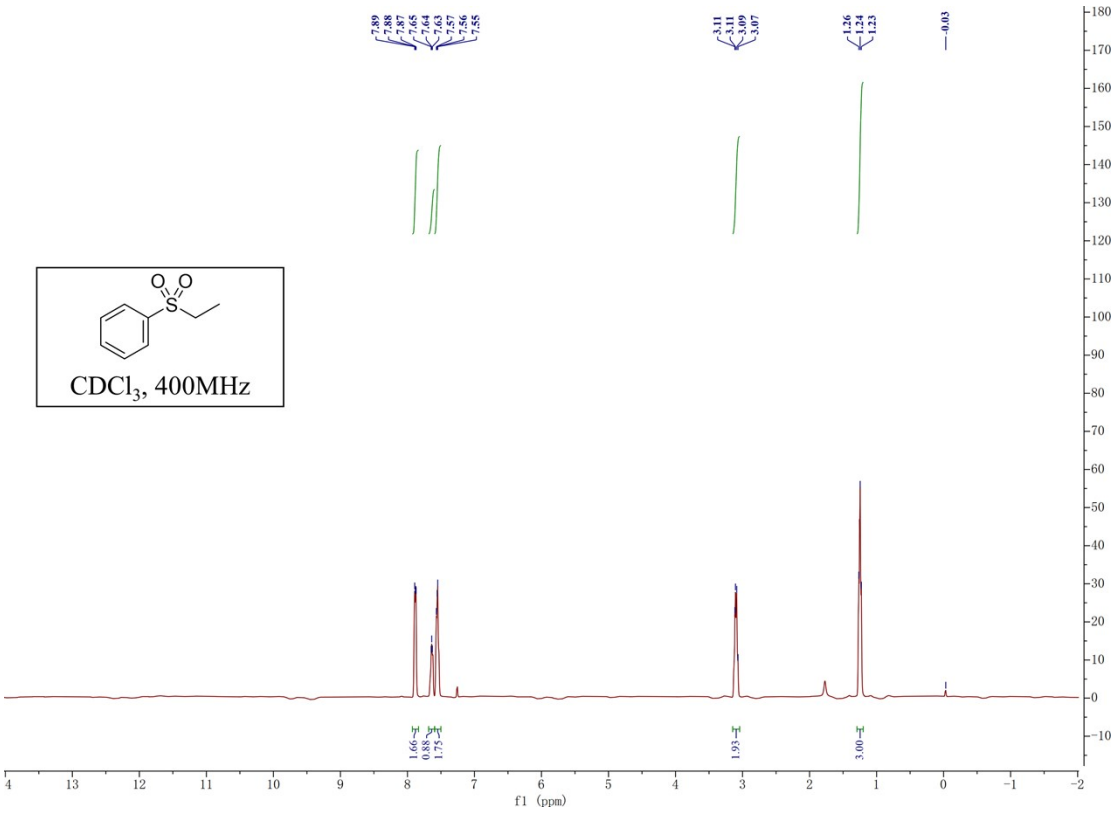
3g, ^{1}H NMR, $CDCl_3$, 400 MHz



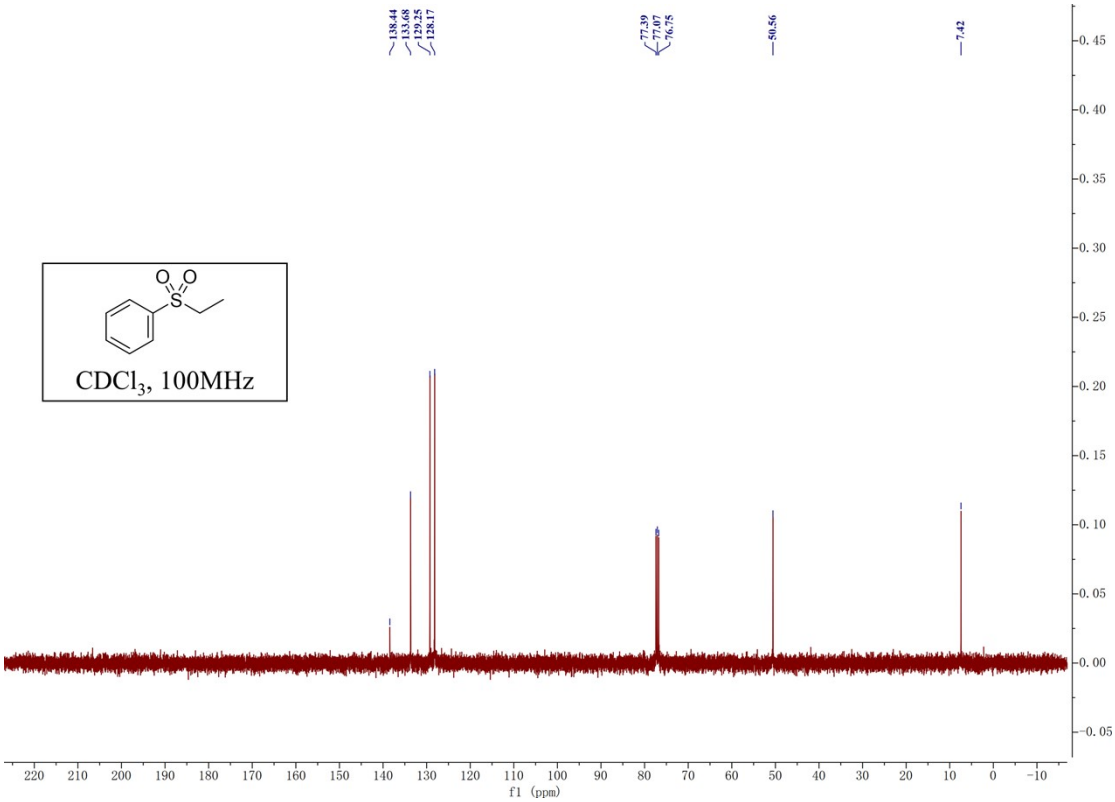
3g, ^{13}C NMR, $CDCl_3$, 100 MHz



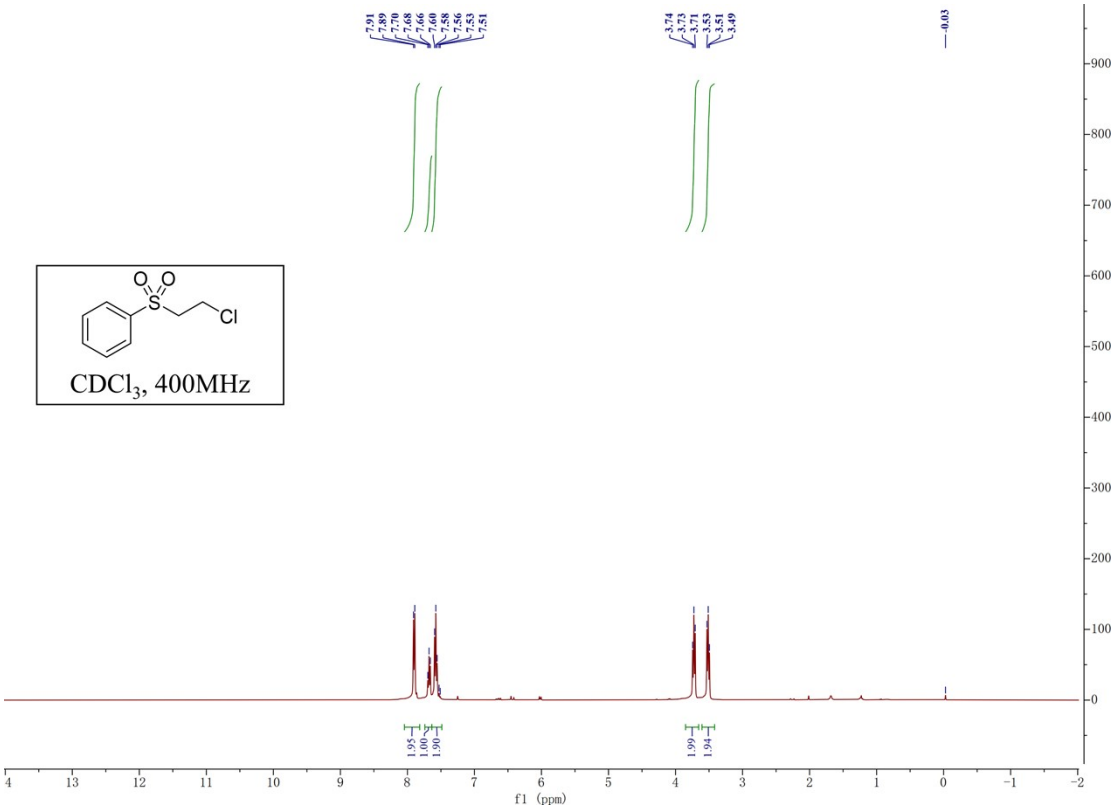
3h, ^{1}H NMR, $CDCl_3$, 400 MHz



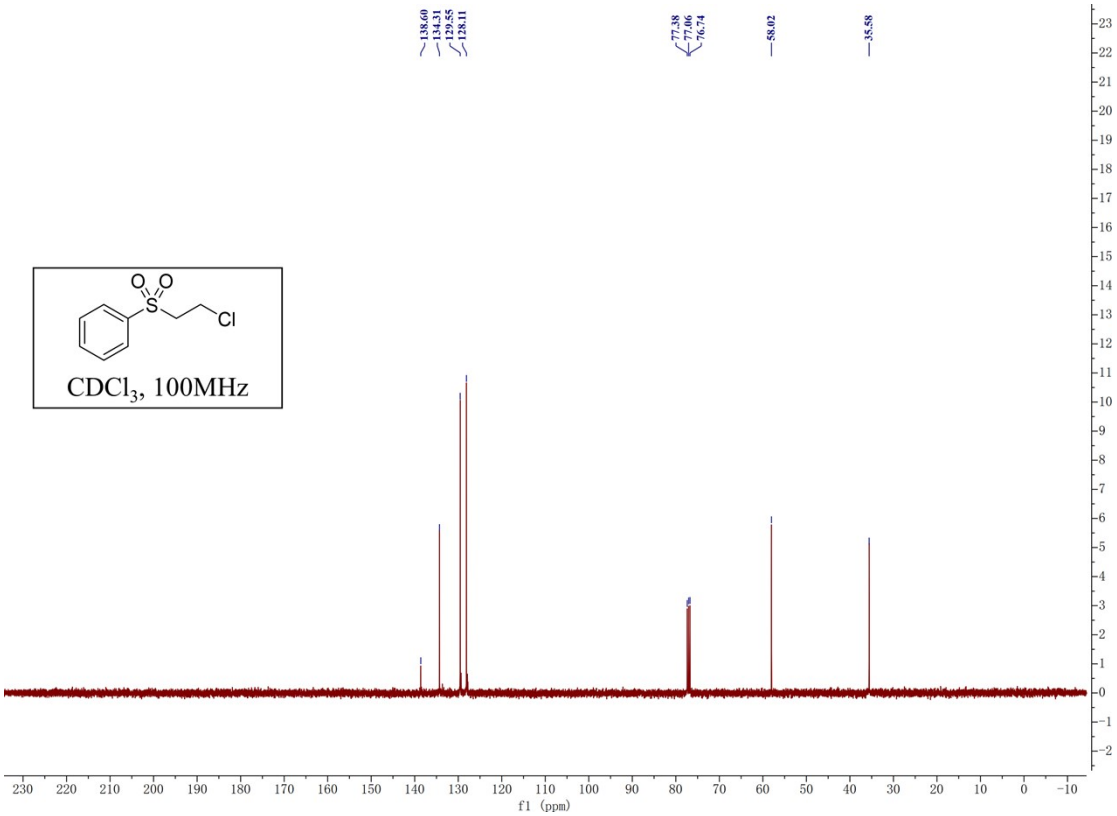
3h, ^{13}C NMR, $CDCl_3$, 100 MHz



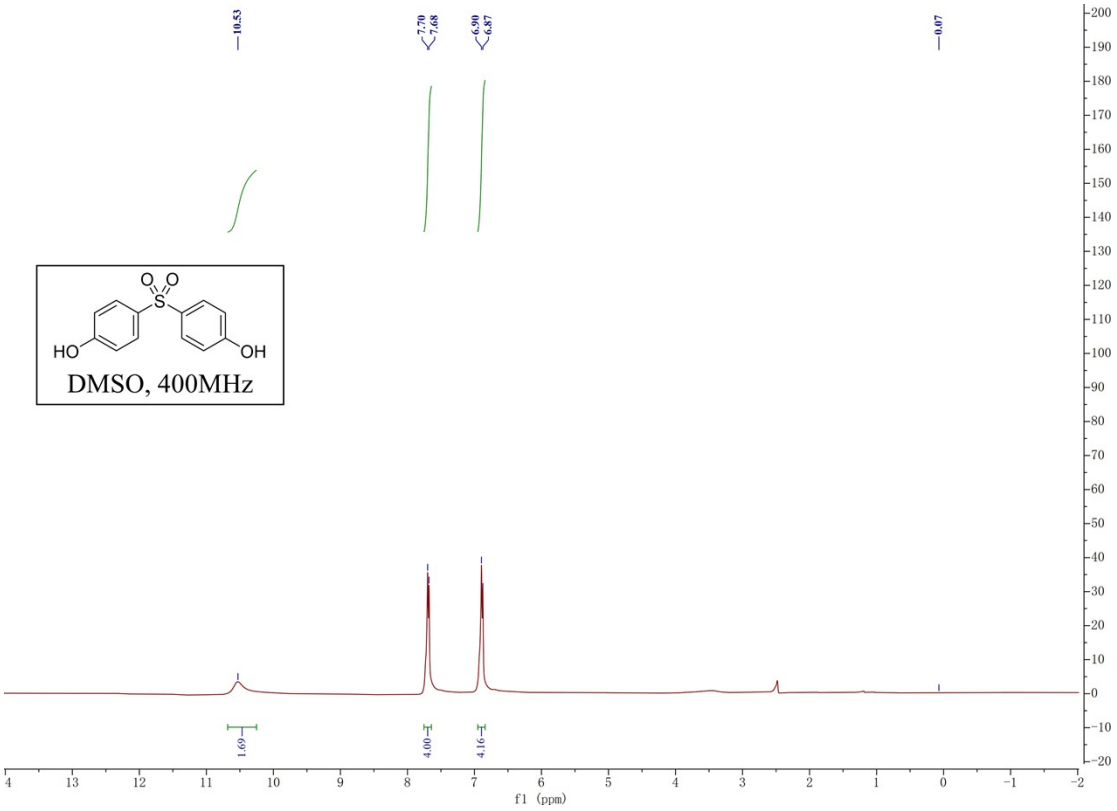
3i, ^{1}H NMR, $CDCl_3$, 400 MHz



3i, ^{13}C NMR, $CDCl_3$, 100 MHz



3j, ^{1}H NMR, DMSO, 400 MHz



3j, ^{13}C NMR, DMSO, 100 MHz