Supporting Information

for

Stainless steel-initiated thiosulfonylations of unactivated alkenes under solvent-free conditions in a mixer mill

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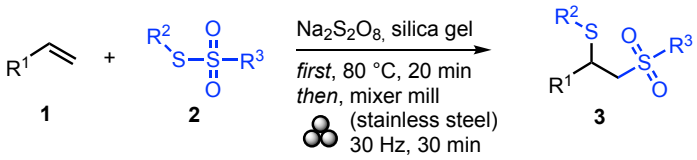
1. General information

Unless otherwise indicated, all materials were purchased from commercial suppliers and used without further purification. Alkenes and thiosulfonates are known compounds. Mechanochemical reactions were performed in a RETSCH Mixer Mill MM400. Both jars and balls (10 mm in diameter) were made of stainless steel and yttria-stabilised zircona (ZrO_2-Y). The reactions were monitored by thin layer chromatography (TLC) with aluminium sheets silica gel 60 F_{254} from Merck, and flash column chromatography purifications were performed using silica gel 60 (40-63 μm) from Merck. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded with an Agilent VNMRS 400 or Agilent VNMRS 600 in deuterated solvents. Chemical shifts (δ) are reported in parts per million (ppm) and spin-spin coupling constants (*J*) are given in Hz, Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. The IR spectra were recorded with a PerkinElmer Spectrum 100 spectrometer with an attached UATR device Diamond KRS-5. All IR data were collected by attenuated total reflectance (ATR) and wavenumbers are given in cm^{-1}. Mass spectra were recorded with a Finnigan SSQ Finnigan 7000 spectrometer (EI, 70 eV). High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer.

2. Stainless steel-initiated thiosulfonylations of unactivated alkenes

2.1. General procedure

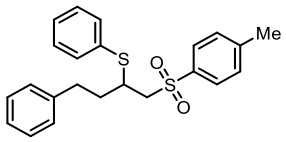


In the glove box, a combination of **1** (0.3 mmol), **2** (0.45 mmol), $Na_2S_2O_8$ (71.4 mg, 0.3 mmol), and silica gel (126.0 mg, corresponding to 2.1 mmol by weight calculated for SiO_2) were placed in a stainless steel milling jar (10 mL) with one ball (10 mm in diameter) of the same material. After sealing, the jar was kept in an oven at 80 °C for 20 min. Then, the mixture was milled at 30 Hz for 30 min. Subsequently, the content of the jar was washed out with DCM (3 × 3 mL). Note: other polar solvents such as ethyl acetate can also be used for the washing of the jar. The solvent was concentrated in vacuo, and the product was purified by flash column chromatography on silica gel (*n*-pentane/EtOAc) to afford the desired product.

To avoid the use of a solvent for the removal of the crude product from the jar, sea sand (2.0 g) can be added after the reaction is terminated. Then, the mixture is milled two times for 5 min, and the resulting compound composite is directly subjected to flash column chromatography (on silica gel) for product purification.

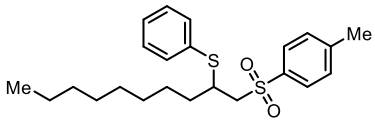
2.2. Characterizing data

Phenyl(4-phenyl-1-tosylbutan-2-yl)sulfane (3aa)



Following the general procedure using **1a** (39.6 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (111.7 mg, 94% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 7.22 – 7.12 (m, 5H), 7.08 – 7.03 (m, 2H), 3.35 – 3.20 (m, 3H), 3.01 – 2.89 (m, 1H), 2.88 – 2.77 (m, 1H), 2.60 – 2.48 (m, 1H), 2.43 (s, 3H), 1.94 – 1.82 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.7, 140.9, 135.6, 132.9, 132.1, 129.9, 129.2, 128.9, 128.6, 128.1, 127.6, 126.3, 60.7, 41.8, 34.5, 32.6, 21.7. **IR** (ATR): ν = 3390, 3058, 2922, 2858, 2325, 1594, 1445, 1302, 1142, 1024, 815 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 396 (63). 240 (43), 131 (100), 91 (53), 65 (11). **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{24}O_2S_2Na^+$ 419.1109, found 419.1105.

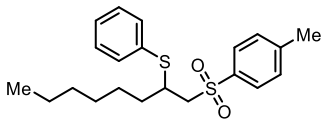
Phenyl(1-tosyldecan-2-yl)sulfane (3ab)



Following the general procedure using **1b** (42.1 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (106.0 mg, 87% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.16 – 7.10 (m, 5H), 3.39 (tt, *J* = 9.3, 3.3 Hz, 1H), 3.25 (dd, *J* = 14.5, 3.1 Hz, 1H), 3.18 (dd, *J* = 14.5, 9.6 Hz, 1H), 2.37 (s, 3H), 2.03 – 1.93 (m, 1H), 1.57 – 1.45 (m, 2H), 1.42 – 1.32 (m, 1H), 1.26 – 1.13 (m, 10H), 0.82 (t, *J* = 7.0 Hz, 3H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 144.8, 136.6, 133.4, 132.1, 130.0, 129.3, 128.1, 127.5, 60.7, 42.8, 33.4, 32.0, 29.5, 29.3, 29.3, 26.6, 22.8, 21.8, 14.2. **IR** (ATR): ν = 3058, 2924, 2855, 1594, 1462, 1315, 1141, 1086, 1021, 811 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 404 (42), 249 (100), 200 (10), 157 (22), 150 (63), 138 (30), 123 (39), 109 (18), 69 (14). **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{32}O_2S_2Na^+$ 427.1736, found 427.1728.

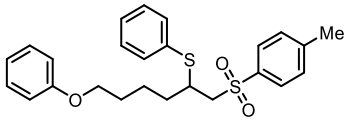
Phenyl(1-tosyloctan-2-yl)sulfane (3ac)



Following the general procedure using **1c** (33.6 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (96.0 mg, 85% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.18 (m, 5H), 3.47 (tt, *J* = 9.3, 3.3 Hz, 1H), 3.33 (dd, *J* = 14.5, 3.1 Hz, 1H), 3.26 (dd, *J* = 14.5, 9.7 Hz, 1H), 2.44 (s, 3H), 2.10 – 2.02 (m, 1H), 1.66 – 1.53 (m, 2H), 1.49 – 1.39 (m, 1H), 1.35 – 1.22 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 144.8, 136.5, 133.4, 132.1, 130.0, 129.2, 128.1, 127.5, 42.8, 33.4, 31.7, 28.9, 26.5, 22.7, 21.7, 14.2. **IR** (ATR): ν = 3060, 2925, 2857, 1593, 1465, 1313, 1141, 1086, 814 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 376 (59), 221 (100), 150 (59), 123 (36), 110 (33), 91 (27), 69 (34).**HRMS** (ESI) *m/z*: [M+Na]$^+$ calcd for $C_{21}H_{28}O_2S_2Na^+$ 399.1423, found 399.1422.

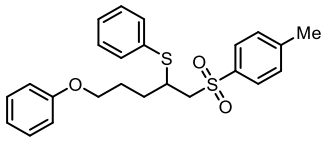
(6-Phenoxy-1-tosylhexan-2-yl)(phenyl)sulfane (3ad)



Following the general procedure using **1d** (52.8 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (112.2 mg, 85% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 – 7.63 (m, 2H), 7.32 – 7.27 (m, 4H), 7.25 – 7.19 (m, 5H), 6.95 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 2H), 3.97 (t, *J* = 5.7 Hz, 2H), 3.52 – 3.46 (m, 1H), 3.36 (dd, *J* = 14.5, 3.0 Hz, 1H), 3.27 (dd, *J* = 14.5, 9.8 Hz, 1H), 2.44 (s, 3H), 2.21 – 2.11 (m, 1H), 1.87 – 1.75 (m, 3H), 1.73 – 1.63 (m, 2H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 159.1, 144.9, 136.5, 133.0, 132.4, 130.1, 129.5, 129.3, 128.0, 127.7, 120.7, 114.6, 67.4, 60.7, 42.8, 33.0, 28.9, 23.2, 21.7. **IR** (ATR): ν = 3059, 2934, 2867, 1594, 1492, 1298, 1242, 1140, 1028, 814 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 440 (39), 347 (23), 284 (35), 191 (100), 175 (59), 123 (20), 81 (61). **HRMS** (ESI) *m/z*: [M+Na]$^+$ calcd for $C_{25}H_{28}O_3S_2Na^+$ 463.1372, found 463.1362.

(5-Phenoxy-1-tosylpentan-2-yl)(phenyl)sulfane (3ae)

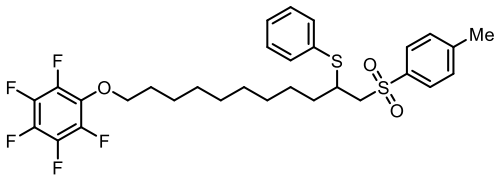


Following the general procedure using **1e** (48.6 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (113.8 mg, 89% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 – 7.53 (m, 2H), 7.23 – 7.18 (m, 2H), 7.17 – 7.10 (m, 7H), 6.89 – 6.85 (m, 1H), 6.82 – 6.78 (m, 2H), 3.94 – 3.84 (m, 2H), 3.43 (tt, *J* = 9.7, 3.3 Hz, 1H), 3.29 (dd, *J*

= 14.5, 2.9 Hz, 1H), 3.19 (dd, *J* = 14.5, 9.8 Hz, 1H), 2.32 (s, 3H), 2.28 – 2.18 (m, 1H), 2.08 – 1.98 (m, 1H), 1.95 – 1.86 (m, 1H), 1.69 (dtd, *J* = 14.3, 9.6, 4.8 Hz, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 158.9, 144.9, 136.2, 132.8, 132.5, 130.0, 129.5, 129.3, 128.1, 127.8, 120.8, 114.6, 67.2, 60.8, 42.6, 30.1, 26.4, 21.7. **IR** (ATR): ν = 3059, 2925, 2870, 1594, 1492, 1299, 1240, 1140, 1039, 816 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 426 (41), 333 (100), 270 (23), 177 (24), 161 (38), 150 (66), 123 (22), 91 (30), 67 (12). **HRMS** (ESI) *m/z*: [M+Na]$^{+}$ calcd for $C_{24}H_{26}O_3S_2Na^{+}$ 449.1216, found 449.1212.

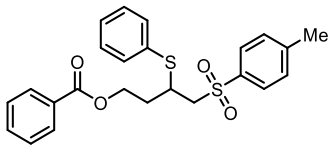
[11-(Perfluorophenoxy)-1-tosylundecan-2-yl](phenyl)sulfane (3af)



Following the general procedure using **1f** (100.9 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (131.4 mg, 73% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 – 7.64 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.17 (m, 5H), 4.15 (t, *J* = 6.6 Hz, 2H), 3.48 (tt, *J* = 9.3, 3.3 Hz, 1H), 3.32 (dd, *J* = 14.5, 3.0 Hz, 1H), 3.25 (dd, *J* = 14.5, 9.7 Hz, 1H), 2.45 (s, 3H), 2.12 – 2.04 (m, 1H), 1.77 (dt, *J* = 15.1, 6.7 Hz, 2H), 1.66 – 1.55 (m, 2H), 1.46 (p, *J* = 7.5, 7.0 Hz, 3H), 1.38 – 1.24 (m, 8H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 144.9, 136.6, 133.4, 132.1, 130.1, 129.3, 128.1, 127.6, 76.0, 60.7, 42.8, 33.4, 29.9, 29.5, 29.4, 29.3, 29.2, 26.6, 25.6, 21.8. **IR** (ATR): ν = 3058, 2927, 2856, 1513, 1486, 1314, 1143, 1025, 816 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 600 (48), 445 (100), 334 (23), 200 (8), 150 (56), 123 (30), 91 (18), 55 (17). **HRMS** (ESI) *m/z*: [M+Na]$^{+}$ calcd for $C_{30}H_{33}O_3F_5S_2Na^{+}$ 623.1684, found 623.1678.

3-(Phenylthio)-4-tosylbutyl benzoate (3ag)

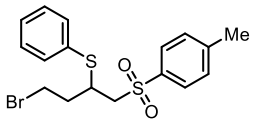


Following the general procedure using **1g** (52.8 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (80.5 mg, 61% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.17 (m, 7H), 4.63 – 4.51 (m, 2H), 3.57 (tt, *J* = 10.0, 3.1 Hz, 1H), 3.43 (dd, *J* = 14.6, 2.9 Hz, 1H), 3.34 (dd, *J* = 14.6, 10.0 Hz, 1H), 2.74 – 2.66 (m, 1H), 2.40 (s, 3H), 1.99 (ddt, *J* = 14.9, 9.8, 4.8 Hz, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 166.4, 145.0,

136.0, 133.2, 132.8, 132.5, 130.3, 130.1, 129.8, 129.4, 128.5, 128.1, 128.1, 62.0, 60.8, 40.3, 32.5, 21.7. **IR** (ATR): ν = 3060, 2960, 1716, 1595, 1448, 1270, 1139, 1024, 710 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 440 (12), 284 (92), 163 (100), 135 (25), 105 (70), 91 (37), 77 (26), 65 (12). **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{24}O_4S_2Na^+$ 463.1008, found 463.1008.

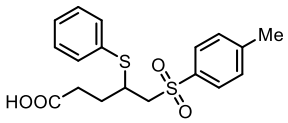
(4-Bromo-1-tosylbutan-2-yl)(phenyl)sulfane (3ah)



Following the general procedure using **1h** (40.2 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (109.8 mg, 92% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.6 (d, *J* = 7.9 Hz, 2H), 7.2 (d, *J* = 7.8 Hz, 2H), 7.2 – 7.2 (m, 1H), 7.1 – 7.1 (m, 4H), 3.6 (td, *J* = 10.1, 5.3 Hz, 1H), 3.6 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.5 (tt, *J* = 10.5, 2.9 Hz, 1H), 3.3 (dd, *J* = 14.6, 2.6 Hz, 1H), 3.2 (dd, *J* = 14.6, 10.3 Hz, 1H), 2.7 – 2.6 (m, 1H), 2.4 (d, *J* = 2.1 Hz, 3H), 2.0 – 1.9 (m, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 145.0, 135.5, 132.9, 131.8, 130.0, 129.3, 128.2, 128.1, 60.6, 41.9, 35.5, 30.4, 21.7. **IR** (ATR): ν = 3057, 2967, 1594, 1477, 1437, 1298, 1144, 1085, 812, 747 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 399 (77), 245 (100), 200 (15), 163 (23), 135 (84), 123 (58), 91 (79), 65 (39). **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{17}H_{19}O_2S_2Na^+$ 420.9902, found 420.9903.

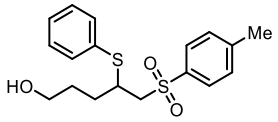
4-(Phenylthio)-5-tosylpentanoic acid (3ai)



Following the general procedure using **1i** (30.0 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (99.4 mg, 91% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.16 (m, 5H), 3.48 (tt, *J* = 10.0, 3.2 Hz, 1H), 3.39 (dd, *J* = 14.1, 2.8 Hz, 1H), 3.23 (dd, *J* = 14.0, 9.8 Hz, 1H), 2.74 – 2.62 (m, 2H), 2.59 – 2.50 (m, 1H), 2.43 (s, 3H), 1.89 – 1.78 (m, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 178.9, 145.1, 136.0, 132.7, 132.2, 130.1, 129.4, 128.2, 128.1, 60.9, 42.3, 31.2, 28.1, 21.8. **IR** (ATR): ν = 3057, 2923, 2164, 1707, 1595, 1439, 1292, 1138, 814 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 364 (28), 347 (19), 208 (100), 191 (16), 149 (44), 135 (21), 91 (37), 65 (17). **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{20}O_4S_2Na^+$ 387.0695, found 387.0697.

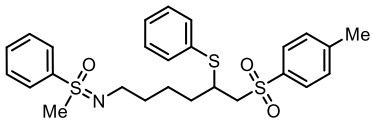
4-(Phenylthio)-5-tosylpentan-1-ol (3aj)



Following the general procedure using **1j** (25.8 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (82.0 mg, 78% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.17 (m, 5H), 3.68 (t, *J* = 6.1 Hz, 2H), 3.51 (ddt, *J* = 9.6, 6.1, 3.1 Hz, 1H), 3.34 (dd, *J* = 14.5, 2.9 Hz, 1H), 3.27 (dd, *J* = 14.5, 9.9 Hz, 1H), 2.44 (s, 3H), 2.26 – 2.16 (m, 1H), 1.92 – 1.83 (m, 1H), 1.81 – 1.66 (m, 3H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 145.0, 136.3, 133.1, 132.2, 130.1, 129.3, 128.0, 127.7, 62.2, 60.7, 42.4, 29.8, 29.6, 21.8. **IR** (ATR): ν = 3525, 3057, 2926, 1594, 1477, 1441, 1294, 1139, 1083, 746 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 350 (20), 333 (10), 194 (53), 150 (100), 135 (17), 123 (18), 91 (35), 85 (32). **HRMS** (ESI) *m/z*: [M+Na]$^+$ calcd for $C_{18}H_{22}O_3S_2Na^+$ 373.0903, found 373.0912.

Methyl(phenyl){[5-(phenylthio)-6-tosylhexyl]imino}-λ^6-sulfanone (3ak)



Following the general procedure using **1k** (71.1 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a colorless oil (104.0 mg, 69% yield).

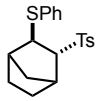
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.65 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.16 (m, 5H), 3.47 – 3.40 (m, 1H), 3.31 (dd, *J* = 14.5, 3.2 Hz, 1H), 3.27 – 3.20 (m, 1H), 3.09 (s, 3H), 3.00 – 2.92 (m, 1H), 2.79 (dq, *J* = 13.5, 6.9 Hz, 1H), 2.44 (s, 3H), 2.09 – 2.01 (m, 1H), 1.70 – 1.62 (m, 1H), 1.62 – 1.47 (m, 4H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 144.8, 139.8, 136.5, 133.3, 133.0, 132.2, 132.2, 130.0, 129.6, 129.2, 128.8, 128.1, 127.6, 60.7, 45.3, 43.7, 43.6, 42.9, 33.3, 32.4, 32.3, 24.4, 24.4, 21.8. **IR** (ATR): ν = 3058, 2927, 2855, 1593, 1444, 1297, 1232, 1135, 976, 741 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 502 (5), 392 (47), 346 (100), 168 (31), 141 (43), 91 (13). **HRMS** (ESI) *m/z*: [M+H]$^+$ calcd for $C_{26}H_{32}NO_3S_3^+$ 502.1539, found 502.1541.

Phenyl(2-tosylcyclopentyl)sulfane (3an)

Following the general procedure using **1n** (20.4 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) the product as a white solid (95.6 mg, 96% yield).

Mp: 99 – 101 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.16 (m, 5H), 3.94 (dt, *J* = 6.7, 3.0 Hz, 1H), 3.45 – 3.39 (m, 1H), 2.43 (s, 3H), 2.30 – 2.19 (m, 2H), 2.16 – 2.06 (m, 1H), 1.95 – 1.84 (m, 2H), 1.80 – 1.74 (m, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 144.7, 135.3, 134.2, 132.0, 130.0, 129.1, 128.6, 127.4, 69.8, 48.0, 33.6, 26.1, 24.6, 21.7. **IR** (ATR): ν = 3053, 2959, 2873, 1593, 1442, 1296, 1142, 1022, 900, 814 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 332 (31), 177 (80), 176 (100), 123 (7), 91 (19), 67 (41), 65 (12). **HRMS** (ESI) *m/z*: [M+Na]$^+$ calcd for $C_{18}H_{20}O_2S_2Na^+$ 355.0797, found 355.0807.

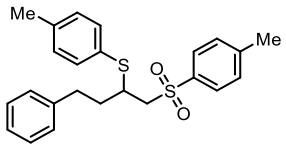
Phenyl(3-tosylbicyclo[2.2.1]heptan-2-yl)sulfane (3ao)



Following the general procedure using **1o** (28.2 mg, 0.3 mmol) and **2a** (118.8 mg, 0.45 mmol) afforded the product as a white solid (78.0 mg, 73% yield).

Mp: 105 – 106 °C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.77 – 7.75 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.20 (m, 5H), 3.77 (ddd, *J* = 6.1, 3.9, 2.1 Hz, 1H), 2.84 (dd, *J* = 4.5, 1.5 Hz, 1H), 2.69 (dd, *J* = 6.4, 1.7 Hz, 1H), 2.43 (s, 3H), 2.38 (tt, *J* = 4.2, 1.5 Hz, 1H), 2.11 – 2.05 (m, 1H), 2.02 (dp, *J* = 10.5, 2.0 Hz, 1H), 1.67 (tt, *J* = 12.5, 4.8 Hz, 1H), 1.47 – 1.38 (m, 2H), 1.27 – 1.18 (m, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 144.8, 135.8, 135.1, 131.9, 129.9, 129.0, 128.8, 127.3, 72.6, 51.7, 41.6, 39.5, 36.9, 29.6, 22.5, 21.8. **IR** (ATR): ν = 3053, 2955, 2878, 1593, 1477, 1295, 1140, 1086, 810, 743 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 358 (23), 202 (95), 174 (100), 123 (14), 91 (26), 65 (10). **HRMS** (ESI) *m/z*: [M+Na]$^+$ calcd for $C_{20}H_{22}O_2S_2Na^+$ 381.0953, found 381.0963.

(4-Phenyl-1-tosylbutan-2-yl)(*p*-tolyl)sulfane (3ba)

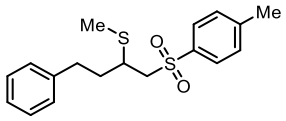


Following the general procedure using **1a** (39.6 mg, 0.3 mmol) and **2b** (125.1 mg, 0.45 mmol) afforded the product as a colorless oil (111.0 mg, 90% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.33 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.29 – 7.22 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.02 – 6.93 (m, 4H), 3.31 (dd, *J* = 14.5, 2.6 Hz, 1H), 3.23 (dd, *J* = 14.5, 9.9 Hz, 1H), 3.15 (tt, *J* = 10.0, 2.9 Hz, 1H), 2.98 – 2.90 (m, 1H), 2.83 (dt, *J* = 13.6, 8.3 Hz, 1H),

2.54 – 2.45 (m, 1H), 2.42 (s, 3H), 2.31 (s, 3H), 1.89 – 1.81 (m, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 144.4, 140.8, 137.9, 135.6, 132.9, 129.8, 129.7, 128.8, 128.4, 128.0, 126.1, 60.5, 42.1, 34.3, 32.5, 21.6, 21.1. **IR** (ATR): ν = 3027, 2922, 2860, 1597, 1492, 1302, 1143, 1019, 810 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 410 (93), 254 (47), 131 (100), 91 (55), 65 (9). **HRMS** (ESI) *m/z*: [M+Na]$^{+}$ calcd for $C_{24}H_{26}O_2S_2Na^{+}$ 433.1266, found 433.1265.

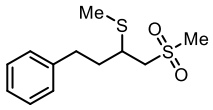
Methyl(4-phenyl-1-tosylbutan-2-yl)sulfane (3ca)



Following the general procedure using **1a** (39.6 mg, 0.3 mmol) and **2c** (90.9 mg, 0.45 mmol) afforded the product as a colorless oil (88.0 mg, 88% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 – 7.59 (m, 2H), 7.32 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 7.20 – 7.15 (m, 2H), 3.40 (dd, *J* = 14.5, 3.5 Hz, 1H), 3.32 (dd, *J* = 14.5, 9.1 Hz, 1H), 2.92 – 2.81 (m, 2H), 2.72 (ddd, *J* = 13.6, 8.9, 7.7 Hz, 1H), 2.44 (s, 3H), 2.31 – 2.23 (m, 1H), 1.95 (s, 3H), 1.84 (dtd, *J* = 14.3, 9.3, 4.8 Hz, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 144.9, 141.1, 136.4, 130.0, 128.7, 128.5, 128.1, 126.1, 61.5, 40.2, 34.9, 32.6, 21.7, 13.2. **IR** (ATR): ν = 3058, 3027, 2920, 1916, 1597, 1448, 1298, 1142, 1085, 816 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 334 (34), 178 (59), 138 (16), 131 (100), 91 (58), 65 (11). **HRMS** (ESI) *m/z*: [M+Na]$^{+}$ calcd for $C_{18}H_{22}O_2S_2Na^{+}$ 357.0953, found 357.0951.

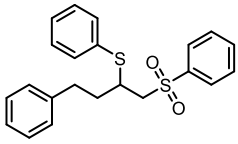
Methyl[1-(methylsulfonyl)-4-phenylbutan-2-yl]sulfane (3ea)



Following the general procedure using **1a** (39.6 mg, 0.3 mmol) and **2e** (56.7 mg, 0.45 mmol) afforded the product as a colorless oil (61.0 mg, 79% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.18 (m, 3H), 3.34 (dd, *J* = 14.6, 6.3 Hz, 1H), 3.22 (dd, *J* = 14.6, 6.7 Hz, 1H), 3.16 – 3.08 (m, 1H), 2.98 (s, 3H), 2.91 – 2.85 (m, 1H), 2.81 – 2.75 (m, 1H), 2.23 – 2.15 (m, 1H), 2.13 (s, 3H), 1.95 (dtd, *J* = 14.3, 9.3, 5.2 Hz, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 140.9, 128.7, 128.6, 126.3, 59.8, 42.6, 40.3, 35.7, 32.6, 13.3. **IR** (ATR): ν = 3024, 2923, 2859, 1601, 1494, 1295, 1126, 962, 750 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 258 (30), 178 (45), 131 (100), 91 (64), 65 (9). **HRMS** (ESI) *m/z*: [M+Na]$^{+}$ calcd for $C_{12}H_{18}O_2S_2Na^{+}$ 281.0640, found 281.0644.

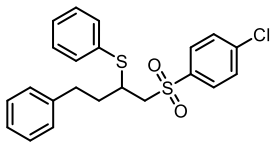
Phenyl[4-phenyl-1-(phenylsulfonyl)butan-2-yl]sulfane (3fa)



Following the general procedure using **1a** (39.6 mg, 0.3 mmol) and **2f** (112.5 mg, 0.45 mmol) afforded the product as a colorless oil (100.9 mg, 88% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.30 (dd, *J* = 8.4, 7.4 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.15 (m, 3H), 7.14 – 7.09 (m, 1H), 7.05 (dd, *J* = 8.4, 6.9 Hz, 2H), 6.98 – 6.91 (m, 2H), 3.25 – 3.18 (m, 2H), 3.18 – 3.12 (m, 1H), 2.90 – 2.84 (m, 1H), 2.76 (dt, *J* = 13.6, 8.3 Hz, 1H), 2.49 (dtd, *J* = 14.4, 8.5, 2.8 Hz, 1H), 1.85 – 1.76 (m, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 140.8, 138.5, 133.6, 132.9, 132.1, 129.3, 128.9, 128.6, 128.1, 127.6, 60.5, 41.7, 34.5, 32.6. **IR** (ATR): ν = 3060, 2922, 2858, 1811, 1582, 1478, 1445, 1306, 1145, 1108, 812 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 382 (100), 240 (60), 131 (96), 91 (31), 77 (9). **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{22}O_2S_2Na^+$ 405.0953, found 405.0956.

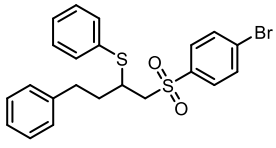
{1-[(4-Chlorophenyl)sulfonyl]-4-phenylbutan-2-yl}(phenyl)sulfane (3ga)



Following the general procedure using **1a** (39.6 mg, 0.3 mmol) and **2g** (127.8 mg, 0.45 mmol) afforded the product as a colorless oil (102.3 mg, 82% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.27 (m, 7H), 7.25 – 7.21 (m, 1H), 7.15 (t, *J* = 7.7 Hz, 2H), 7.04 (dt, *J* = 8.4, 1.3 Hz, 2H), 3.32 – 3.23 (m, 2H), 3.15 – 3.07 (m, 1H), 3.00 – 2.93 (m, 1H), 2.90 – 2.83 (m, 1H), 2.63 – 2.53 (m, 1H), 1.94 – 1.84 (m, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 140.7, 140.3, 136.6, 132.6, 132.5, 129.5, 129.5, 129.3, 129.0, 128.6, 127.8, 126.3, 60.5, 41.9, 34.4, 32.5. **IR** (ATR): ν = 3058, 2924, 1580, 1473, 1398, 1312, 1150, 1085, 818 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 416 (100), 240 (61), 131 (83), 91 (23), 65 (4). **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{21}ClO_2S_2Na^+$ 439.0564, found 439.0562.

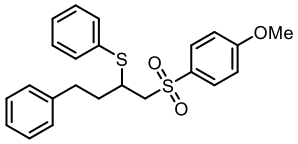
{1-[(4-Bromophenyl)sulfonyl]-4-phenylbutan-2-yl}(phenyl)sulfane (3ha)



Following the general procedure using **1a** (39.6 mg, 0.3 mmol) and **2h** (147.6 mg, 0.45 mmol) afforded the product as a colorless oil (117.0 mg, 85% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 2H), 7.28 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.24 – 7.21 (m, 1H), 7.20 – 7.17 (m, 2H), 7.16 – 7.12 (m, 3H), 7.07 (dd, *J* = 8.4, 6.9 Hz, 2H), 6.96 – 6.93 (m, 2H), 3.19 – 3.16 (m, 2H), 3.03 – 2.98 (m, 1H), 2.91 – 2.84 (m, 1H), 2.82 – 2.74 (m, 1H), 2.52 – 2.44 (m, 1H), 1.84 – 1.76 (m, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 140.7, 137.2, 132.7, 132.6, 132.6, 129.6, 129.4, 129.0, 129.0, 60.6, 42.0, 34.5, 32.5. **IR** (ATR): ν = 3084, 2923, 1803, 1547, 1470, 1312, 11501065, 868, 817 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 460 (57), 240 (55), 131 (100), 91 (33), 65 (5). **HRMS** (ESI) *m/z*: [M+Na]$^+$ calcd for $C_{22}H_{21}O_2S_2BrNa^+$ 483.0059, found 483.0058.

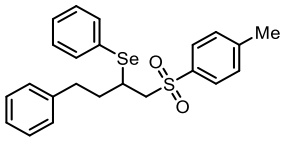
{1-[(4-Methoxyphenyl)sulfonyl]-4-phenylbutan-2-yl}(phenyl)sulfane (3ia)



Following the general procedure using **1a** (39.6 mg, 0.3 mmol) and **2i** (126.0 mg, 0.45 mmol) afforded the product as a colorless oil (80.0 mg, 65% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 – 7.41 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.25 – 7.21 (m, 1H), 7.19 – 7.16 (m, 2H), 7.09 – 7.07 (m, 2H), 6.86 – 6.83 (m, 2H), 3.90 (s, 3H), 3.33 – 3.22 (m, 3H), 3.00 – 2.93 (m, 1H), 2.86 (dt, *J* = 13.8, 8.3 Hz, 1H), 2.58 (dtd, *J* = 14.3, 8.4, 2.6 Hz, 1H), 1.95 – 1.87 (m, 1H). **^{13}C {^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 163.7, 140.9, 133.0, 132.2, 130.3, 130.1, 129.3, 129.0, 128.6, 127.6, 114.5, 60.9, 55.8, 41.8, 34.5, 32.6. **IR** (ATR): ν = 3062, 2923, 2066, 1592, 1494, 1300, 1138, 1023, 835 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 412 (76), 240 (71), 131 (100), 91 (32), 77 (8). **HRMS** (ESI) *m/z*: [M+Na]$^+$ calcd for $C_{23}H_{24}O_3S_2Na^+$ 435.1059, found 435.1055.

Phenyl(4-phenyl-1-tosylbutan-2-yl)selane (3ja)



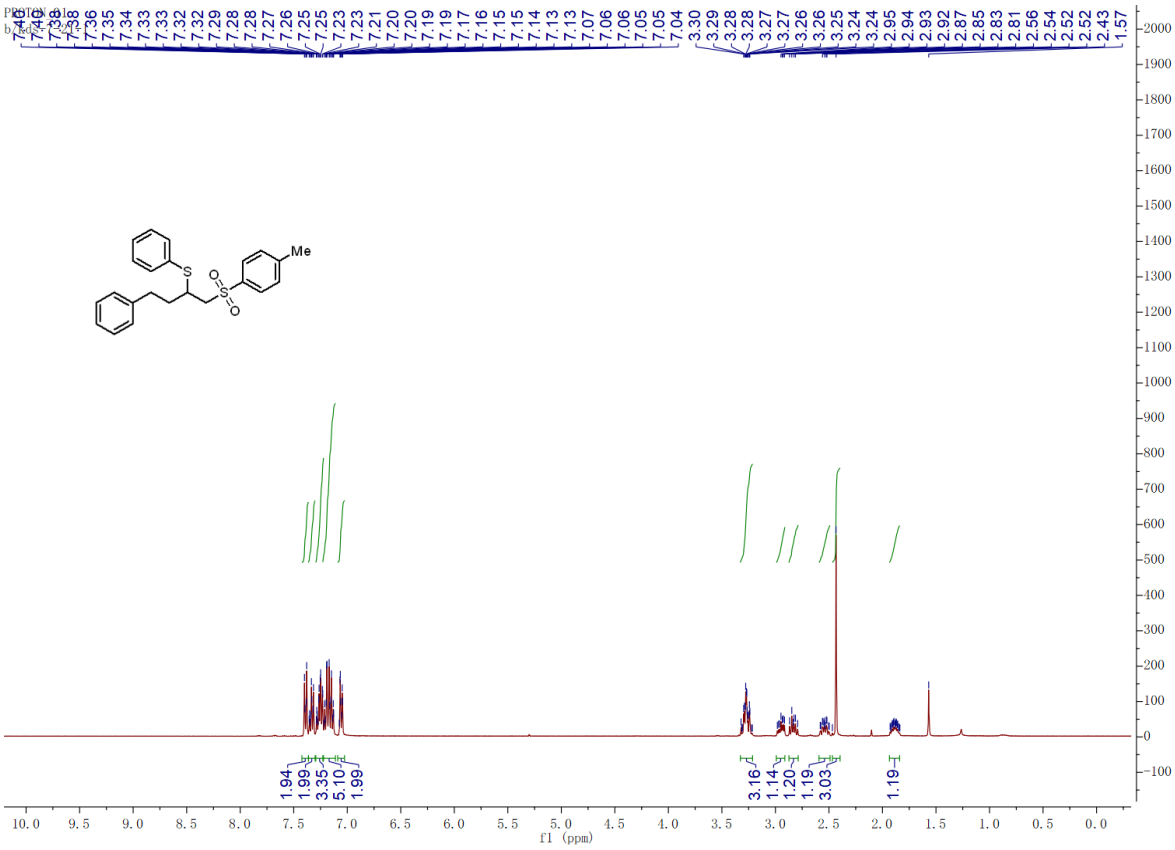
Following the general procedure using **1a** (39.6 mg, 0.3 mmol) and **2j** (140.4 mg, 0.45 mmol) afforded the product as a yellow oil (117.0 mg, 88% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.28 (m, 2H), 7.24 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.19 – 7.16 (m, 4H), 7.15 – 7.13 (m, 2H), 7.10 – 7.05 (m, 4H), 3.39 – 3.26 (m, 2H), 3.17 (tt, *J* = 10.2, 3.1 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.74 – 2.65 (m, 1H), 2.51 – 2.41 (m, 1H), 2.34 (s, 3H), 1.88 – 1.79 (m, 1H). **^{13}C**

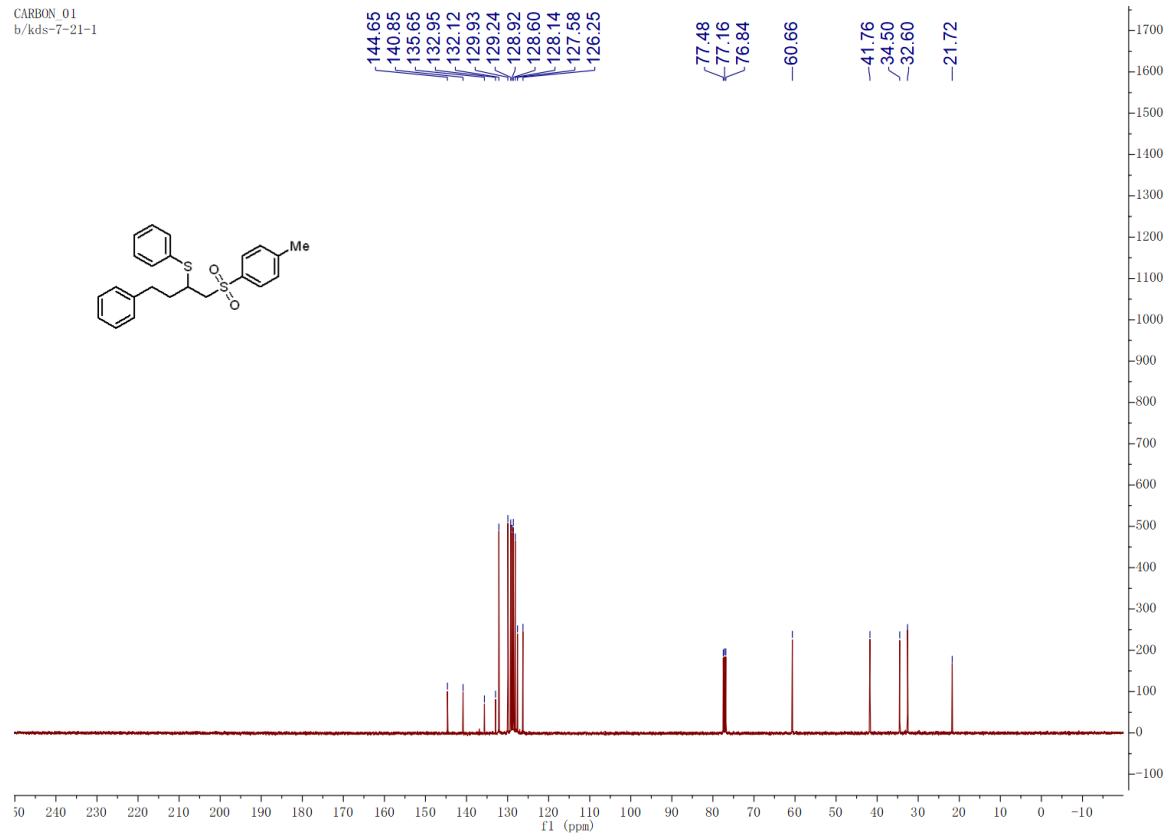
{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 144.5, 140.8, 135.6, 134.9, 129.9, 129.3, 128.8, 128.5, 128.1, 128.0, 127.4, 126.2, 61.8, 36.6, 34.8, 33.4, 21.6. **IR** (ATR): ν = 3059, 3028, 2921, 2856, 1596, 1444, 1301, 1139, 1021, 814 cm^{-1}. **MS** (EI, 70 eV): *m/z* (%) = 444 (43), 289 (9), 157 (11), 131 (100), 91 (36). **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{24}O_2SSeNa^+$ 467.0554, found 467.0547.

3. NMR Spectra

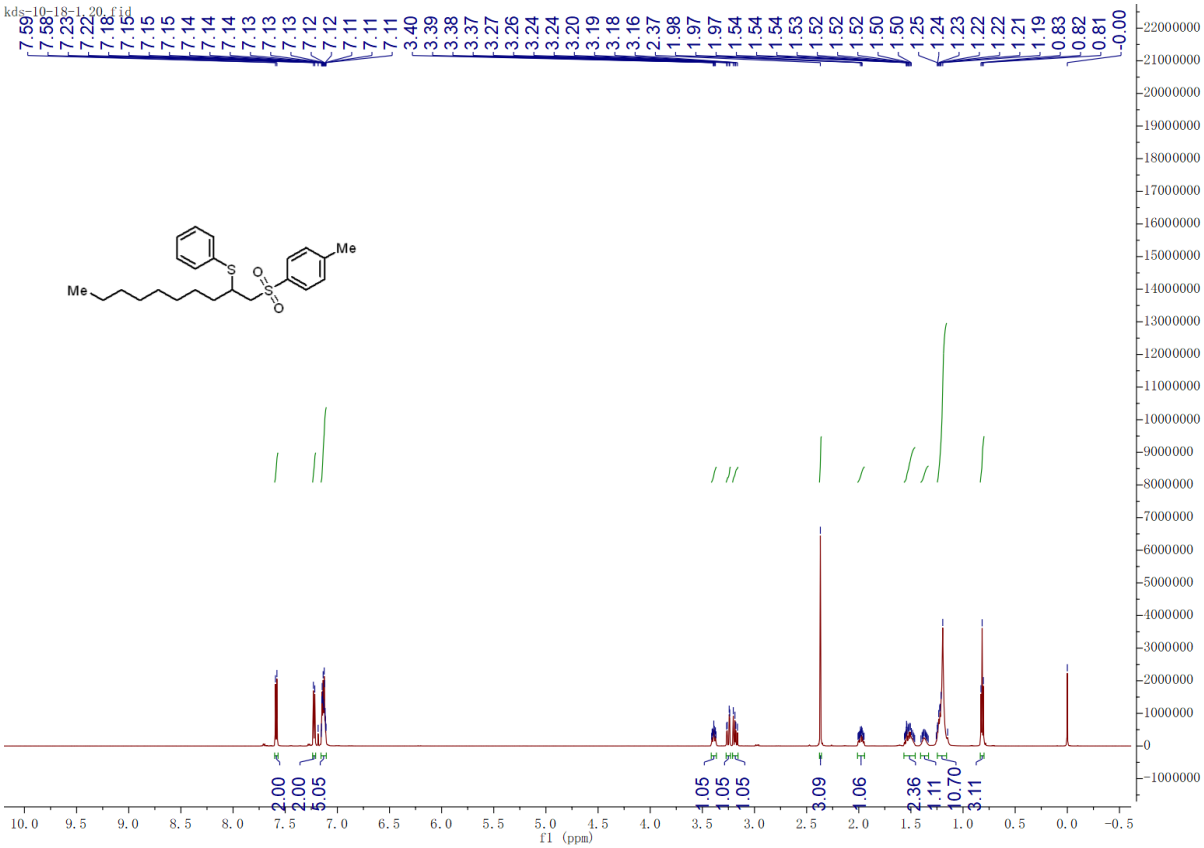
^{1}H NMR spectrum of compound **(3aa)** (400 MHz, $CDCl_3$)



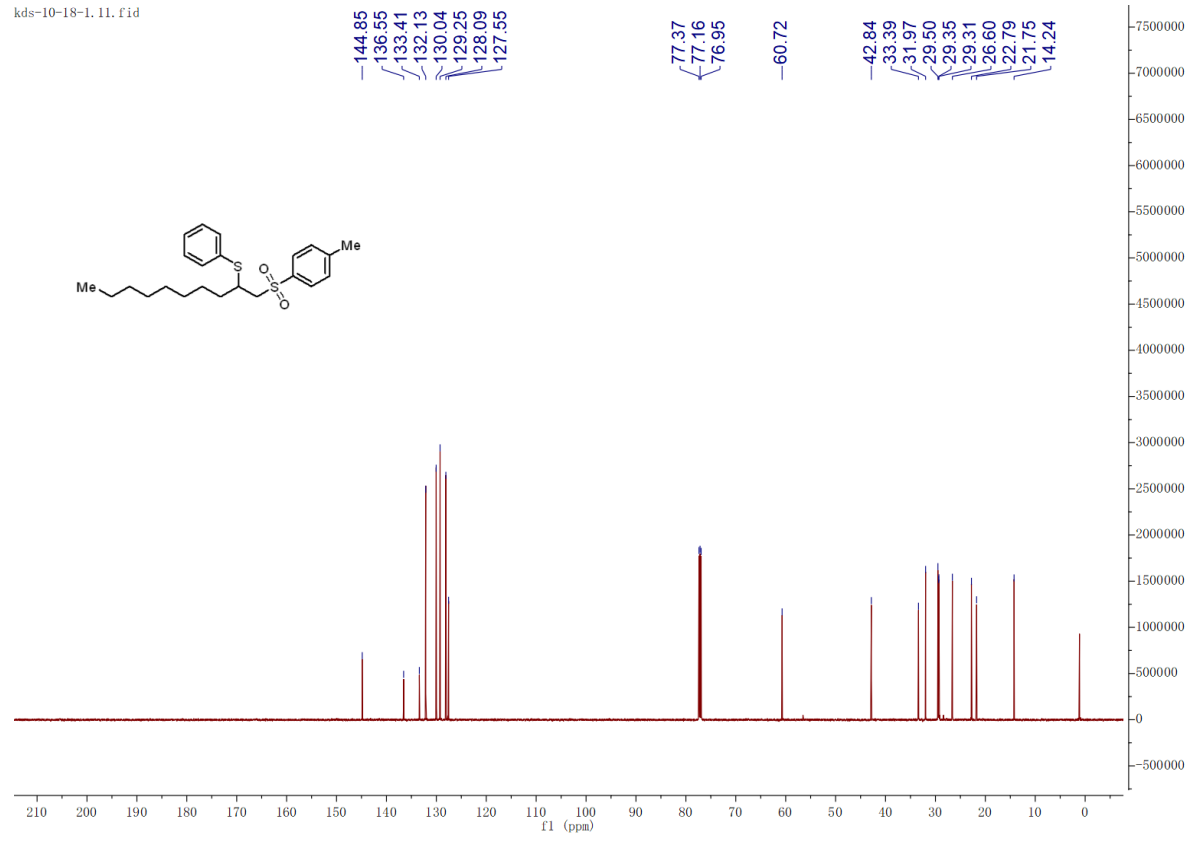
^{13}C{^{1}H} NMR spectrum of compound **(3aa)** (101 MHz, $CDCl_3$)



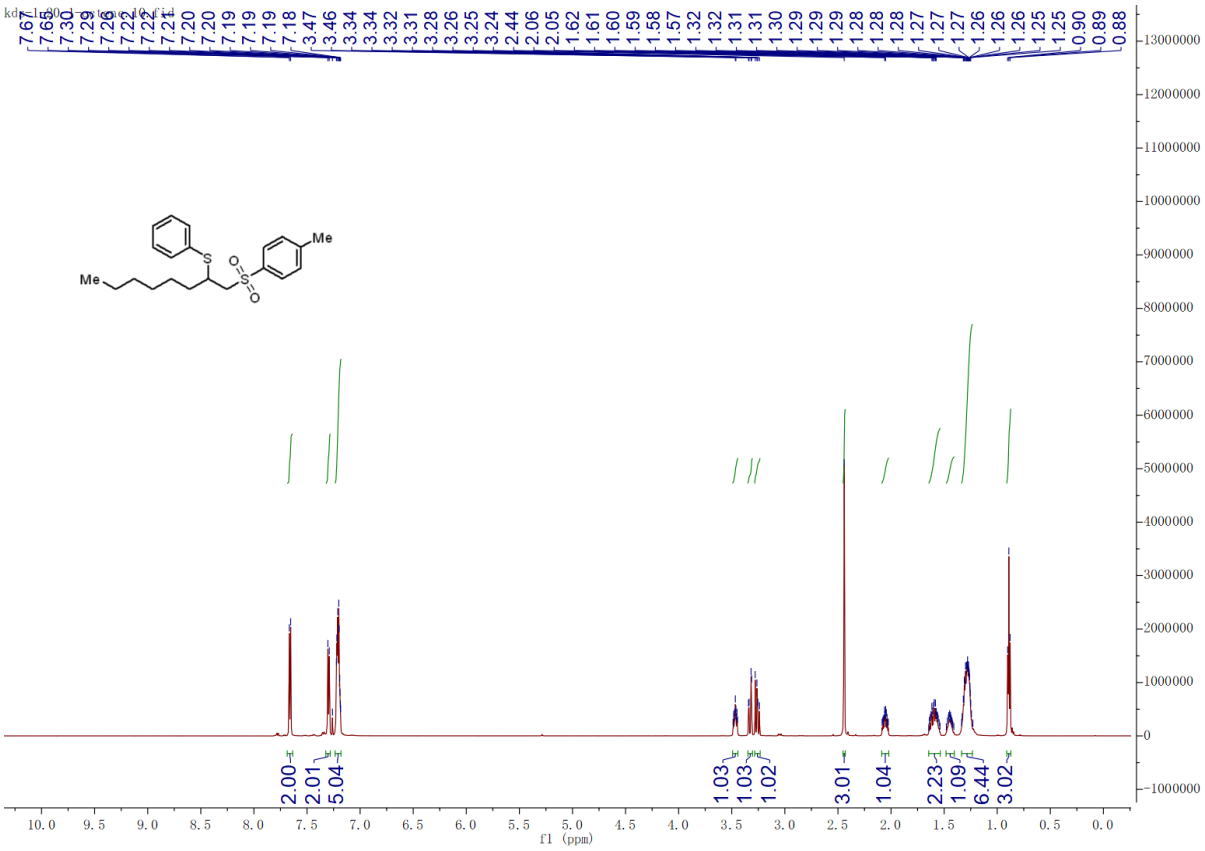
^{1}H NMR spectrum of compound **(3ab)** (600 MHz, $CDCl_3$)



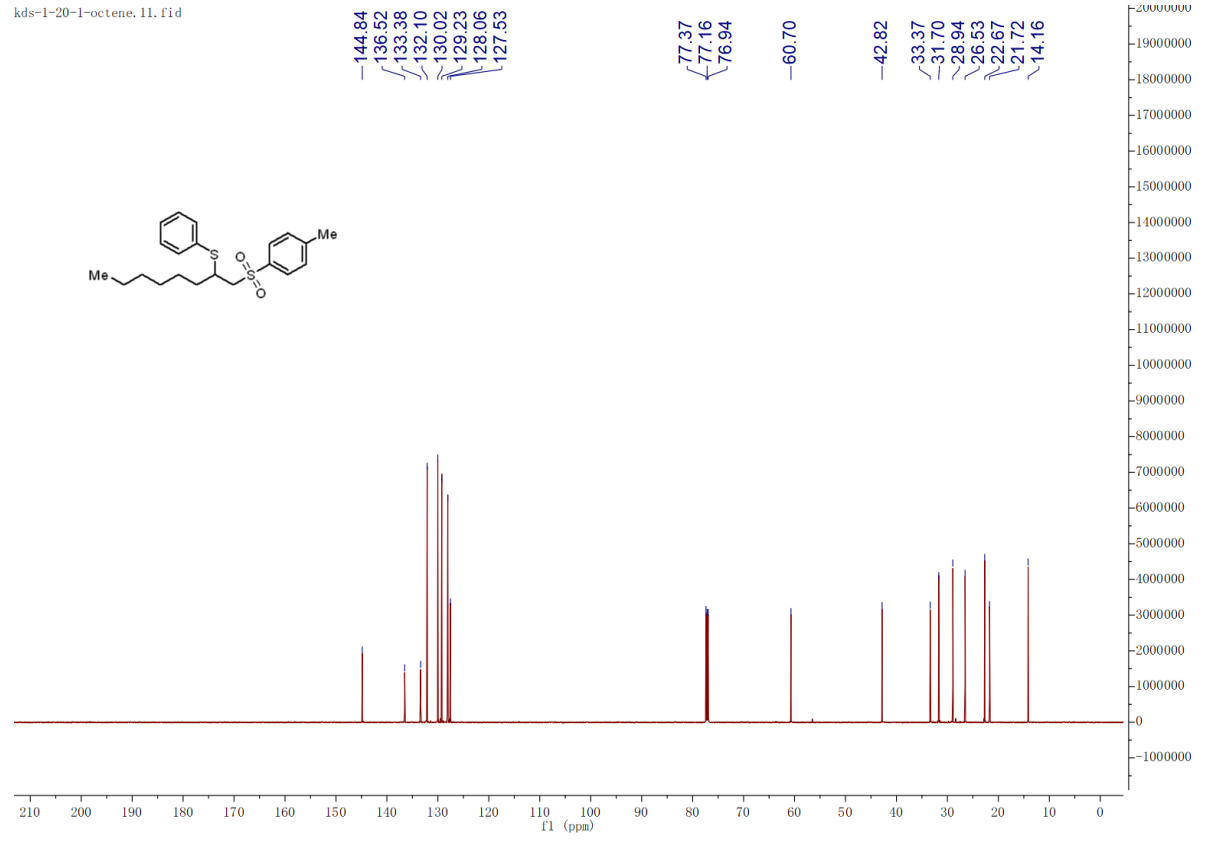
^{13}C{^{1}H} NMR spectrum of compound **(3ab)** (151 MHz, $CDCl_3$)



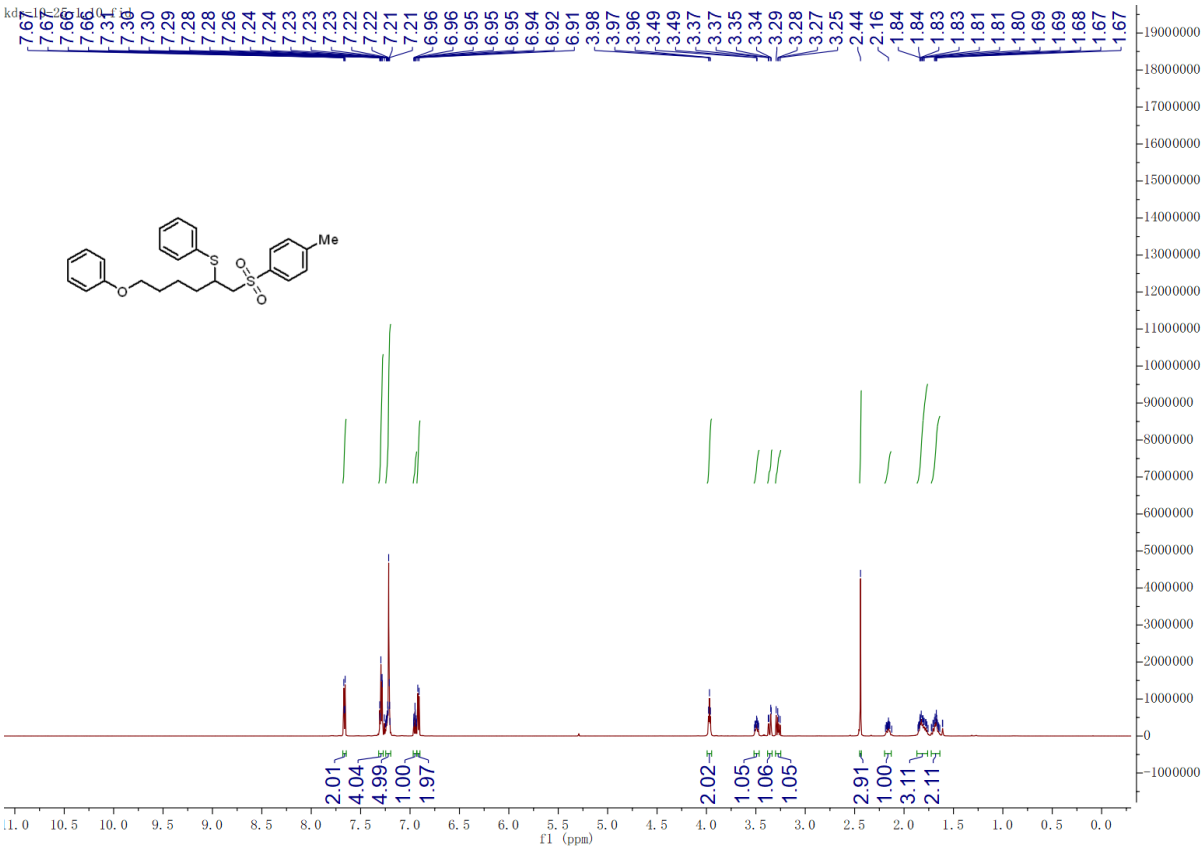
^{1}H NMR spectrum of compound **(3ac)** (600 MHz, $CDCl_3$)



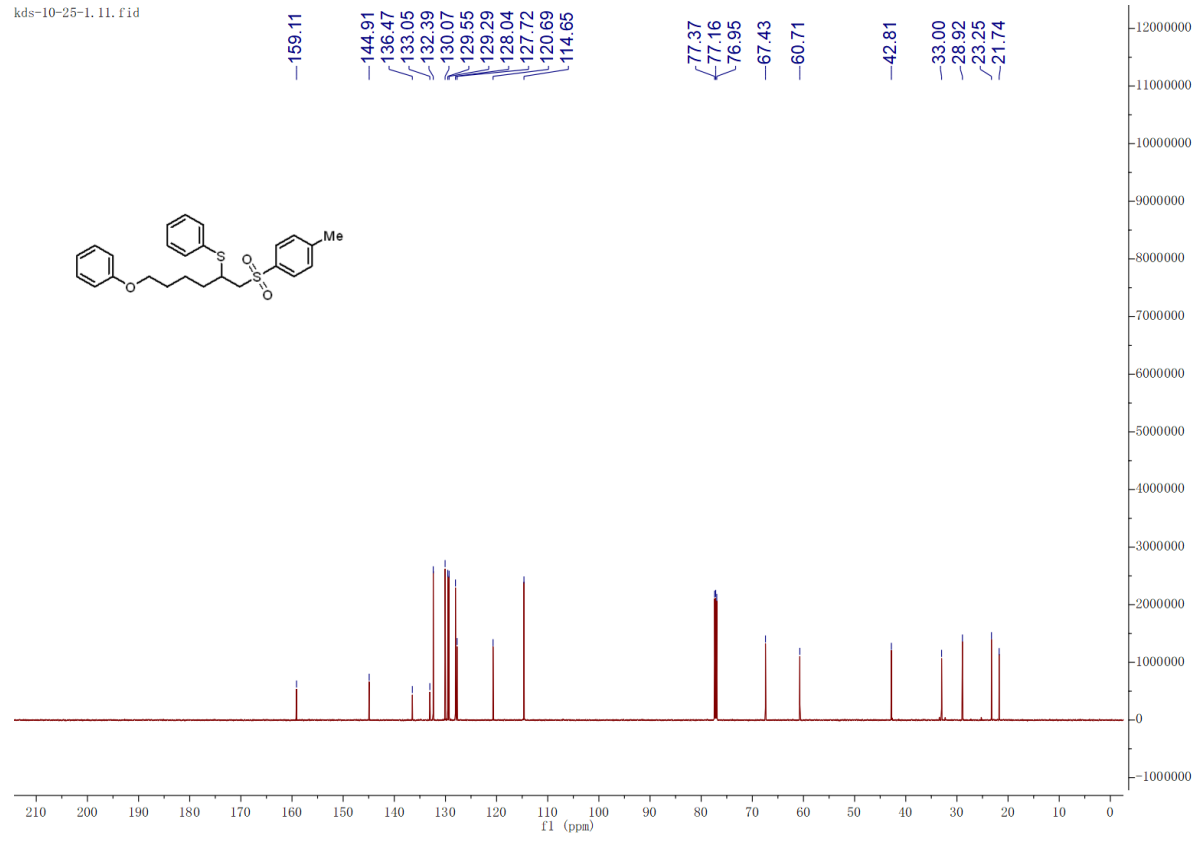
^{13}C{^{1}H} NMR spectrum of compound **(3ac)** (151 MHz, $CDCl_3$)



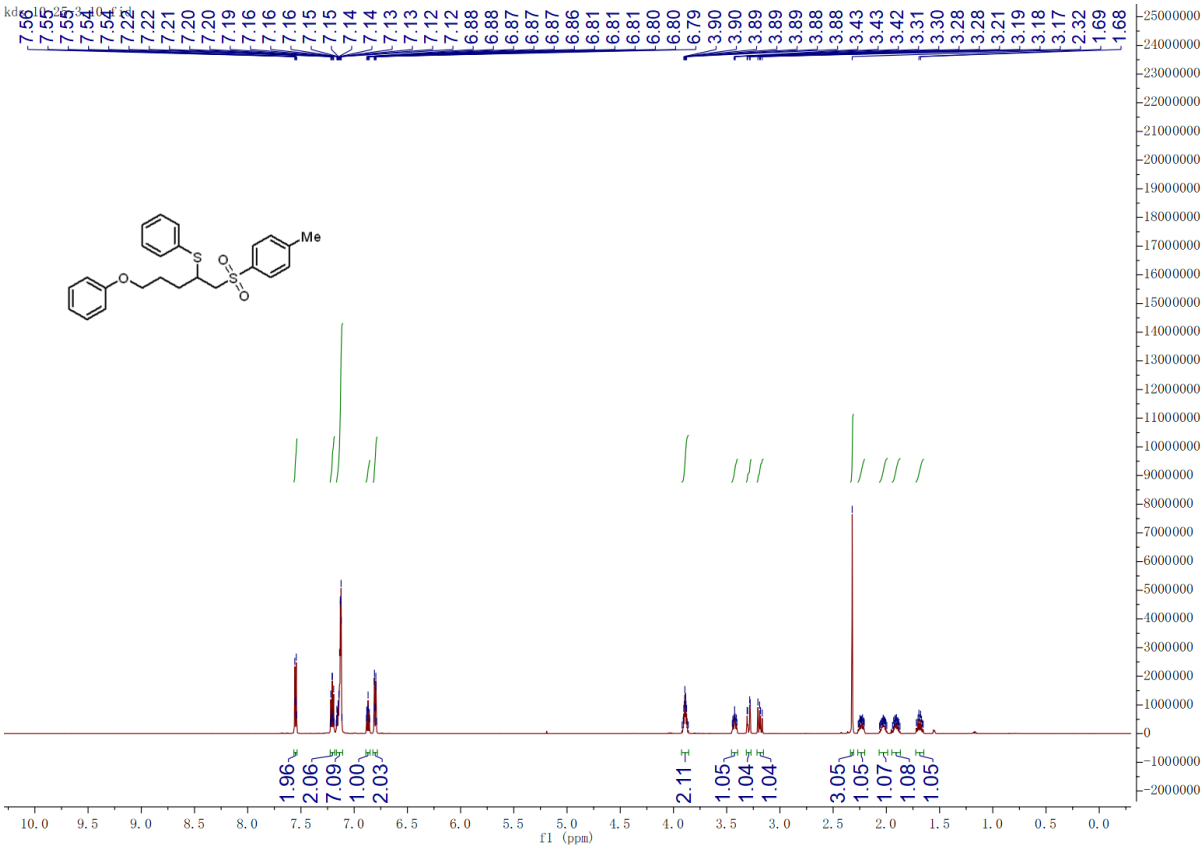
^{1}H NMR spectrum of compound **(3ad)** (600 MHz, $CDCl_3$)



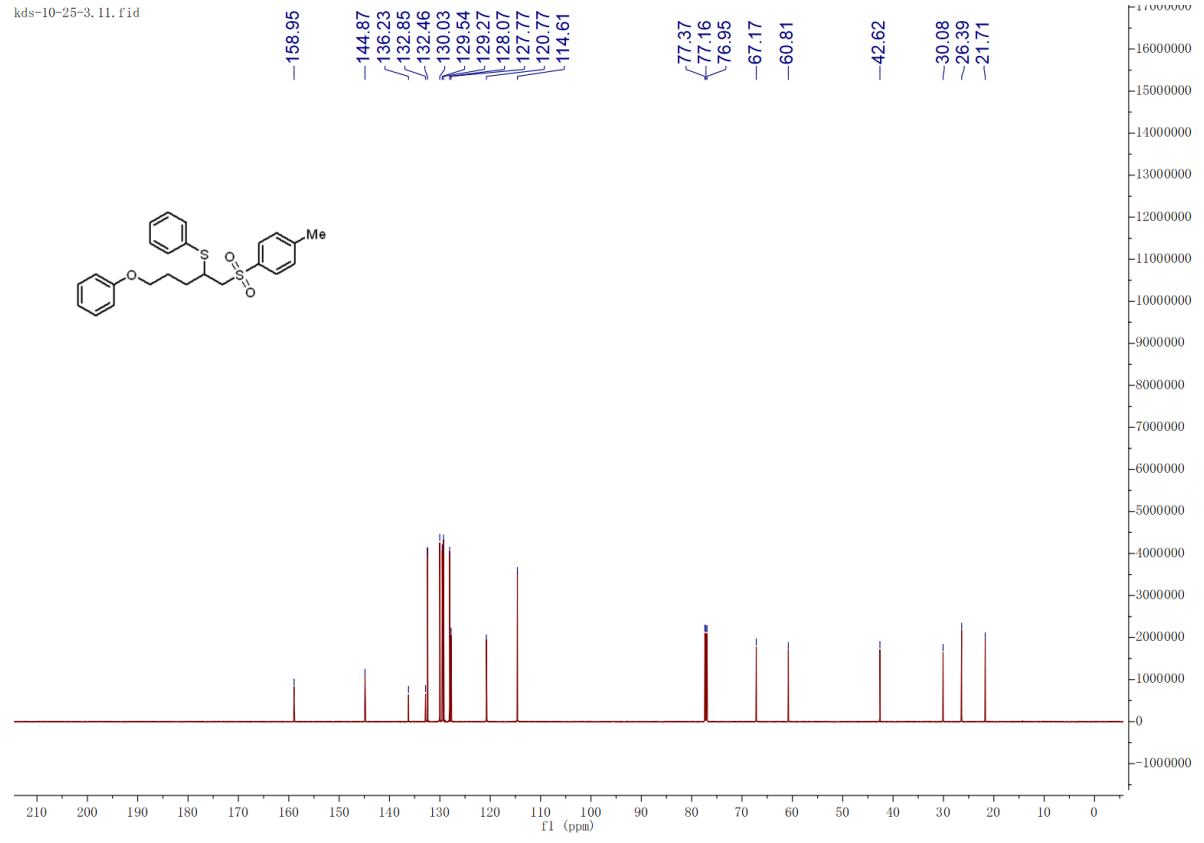
^{13}C{^{1}H} NMR spectrum of compound **(3ad)** (151 MHz, $CDCl_3$)



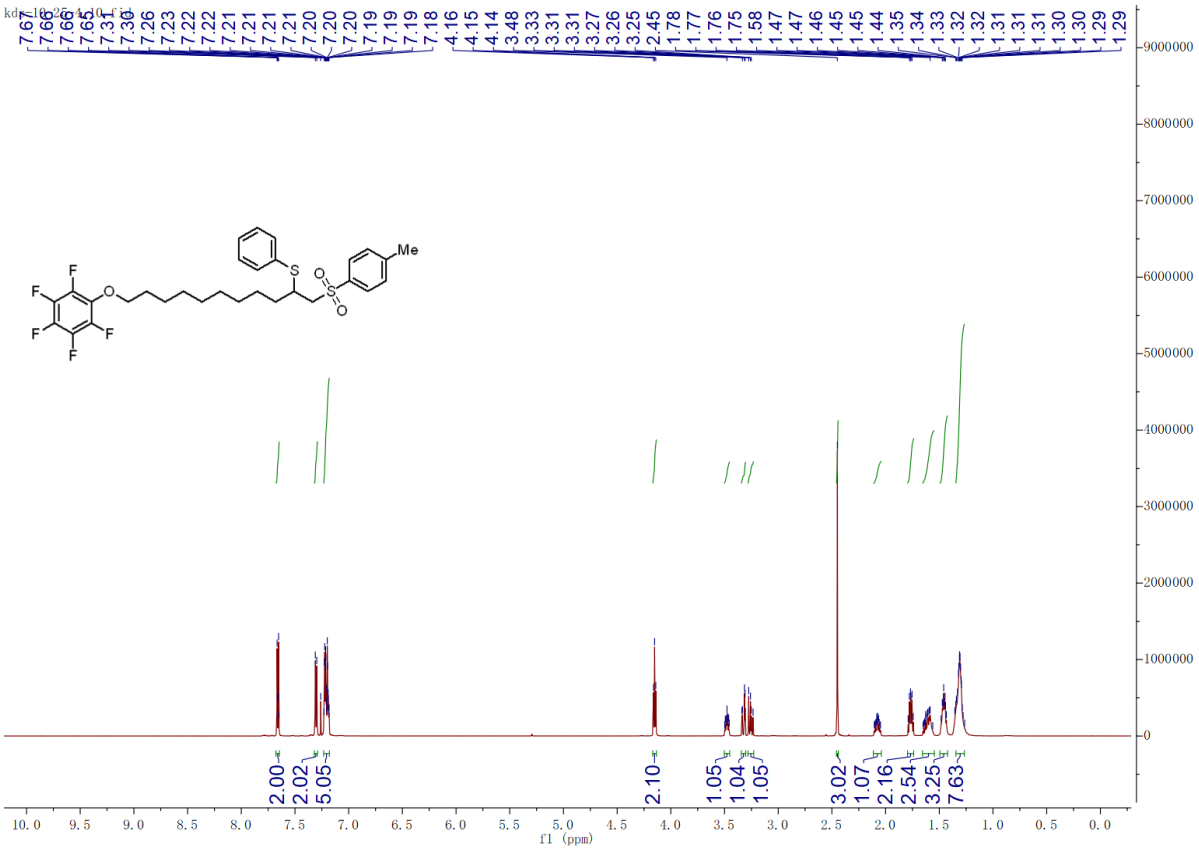
^{1}H NMR spectrum of compound **(3ae)** (600 MHz, $CDCl_3$)



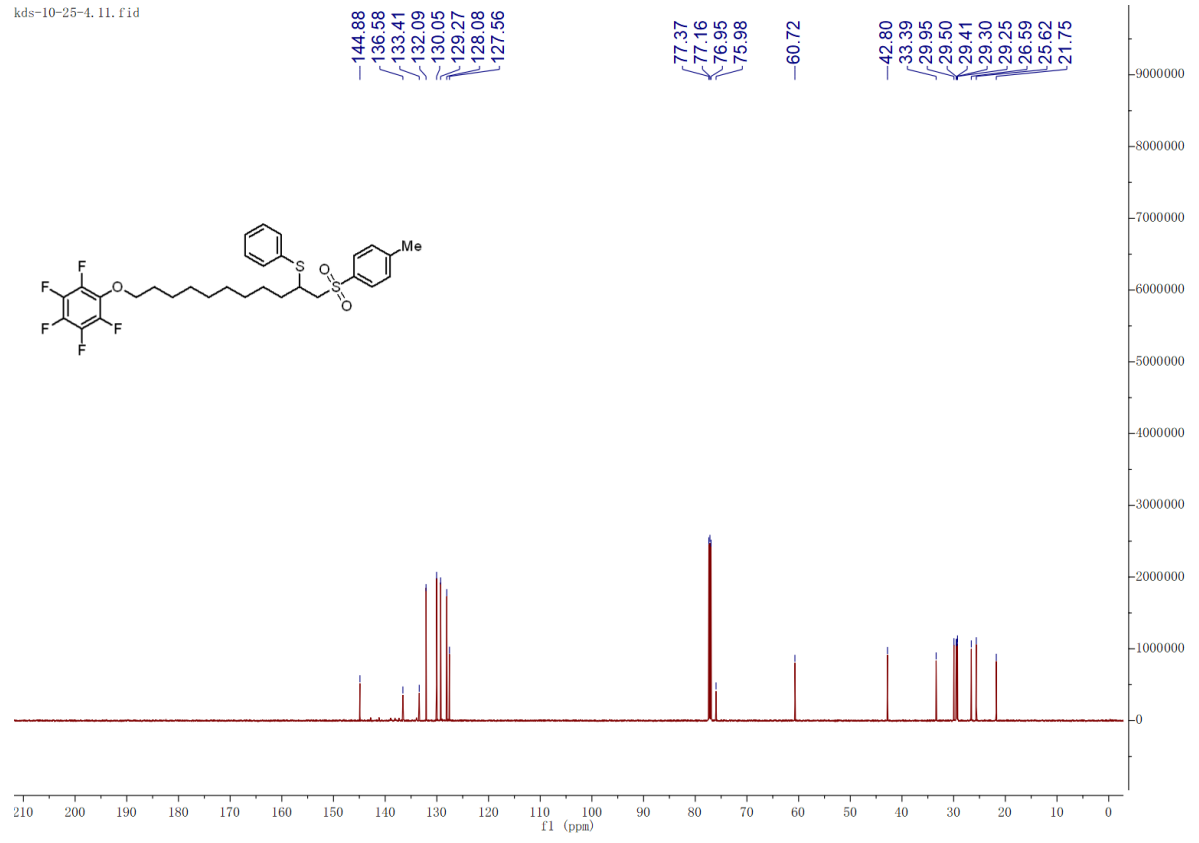
^{13}C{^{1}H} NMR spectrum of compound **(3ae)** (151 MHz, $CDCl_3$)



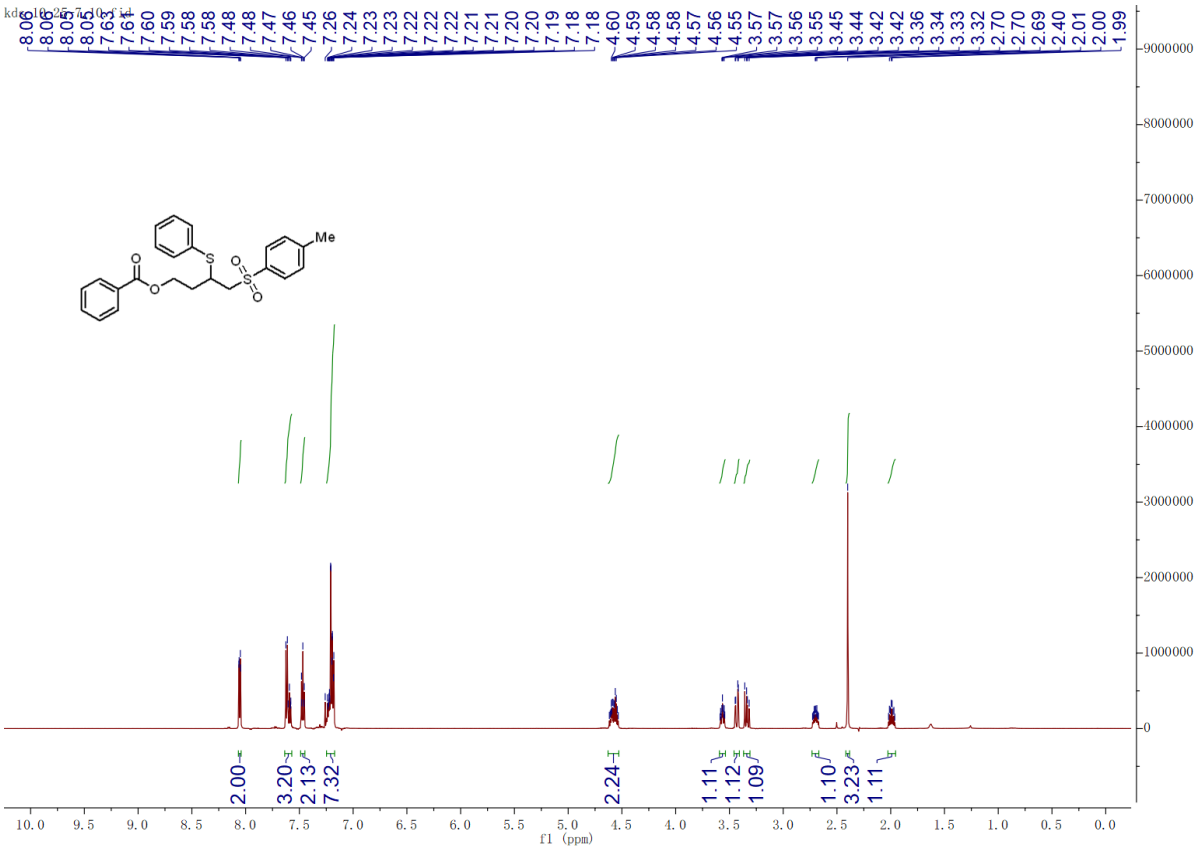
^{1}H NMR spectrum of compound **(3af)** (600 MHz, $CDCl_3$)



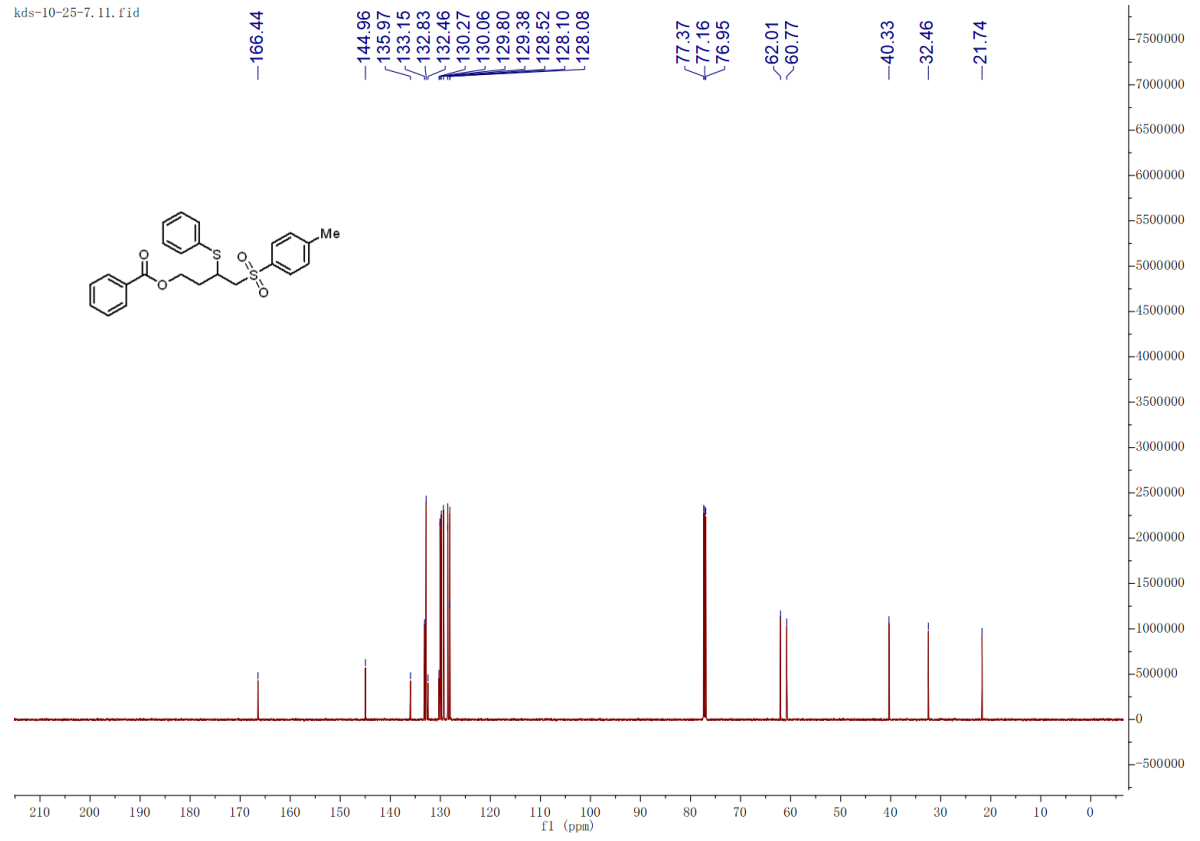
^{13}C{^{1}H} NMR spectrum of compound **(3af)** (151 MHz, $CDCl_3$)



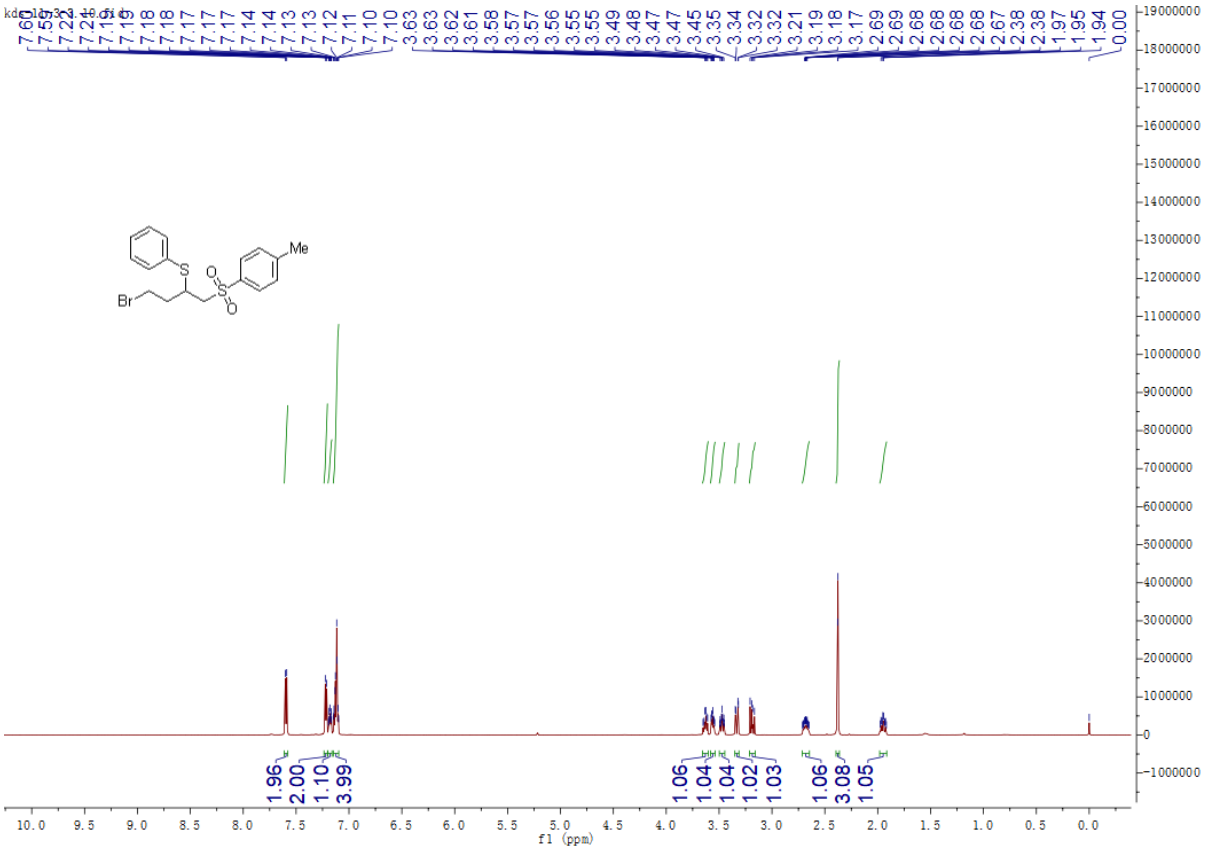
^{1}H NMR spectrum of compound **(3ag)** (600 MHz, $CDCl_3$)



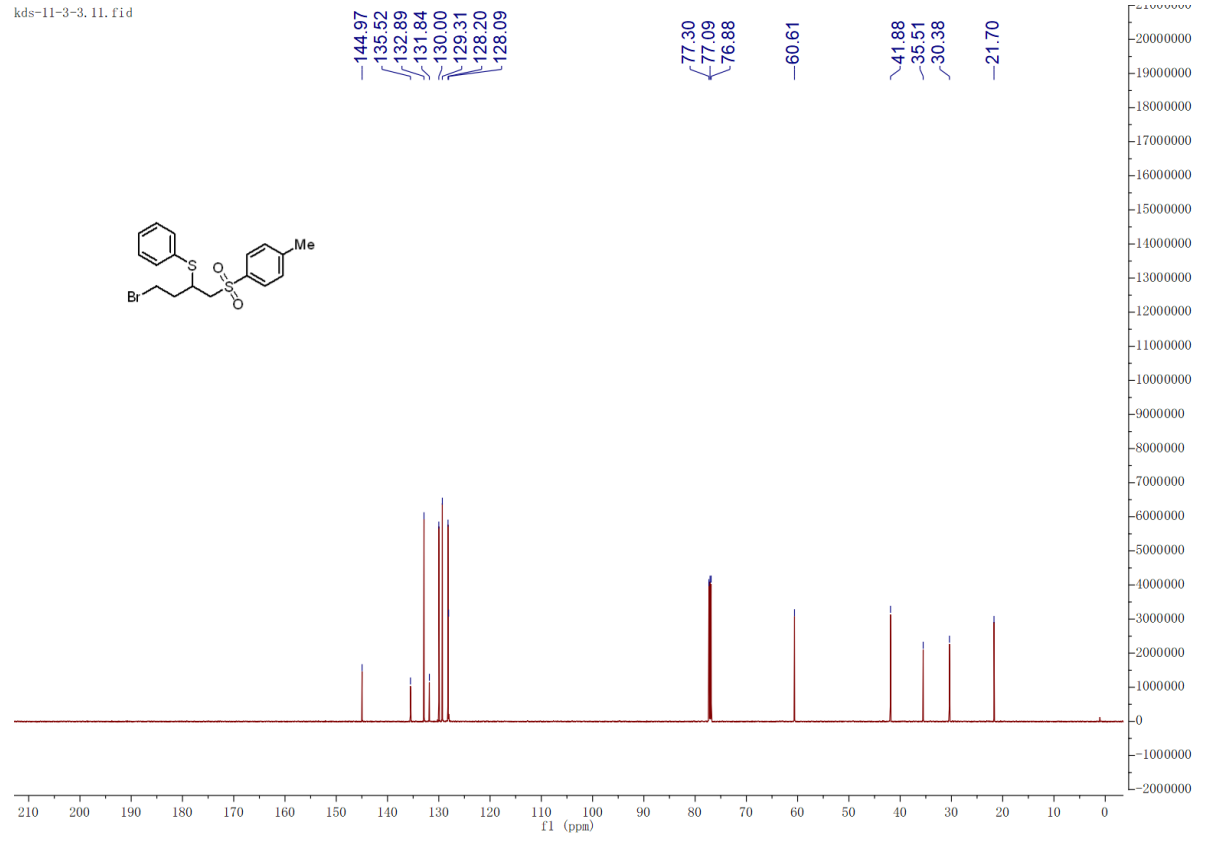
^{13}C{^{1}H} NMR spectrum of compound **(3ag)** (151 MHz, $CDCl_3$)



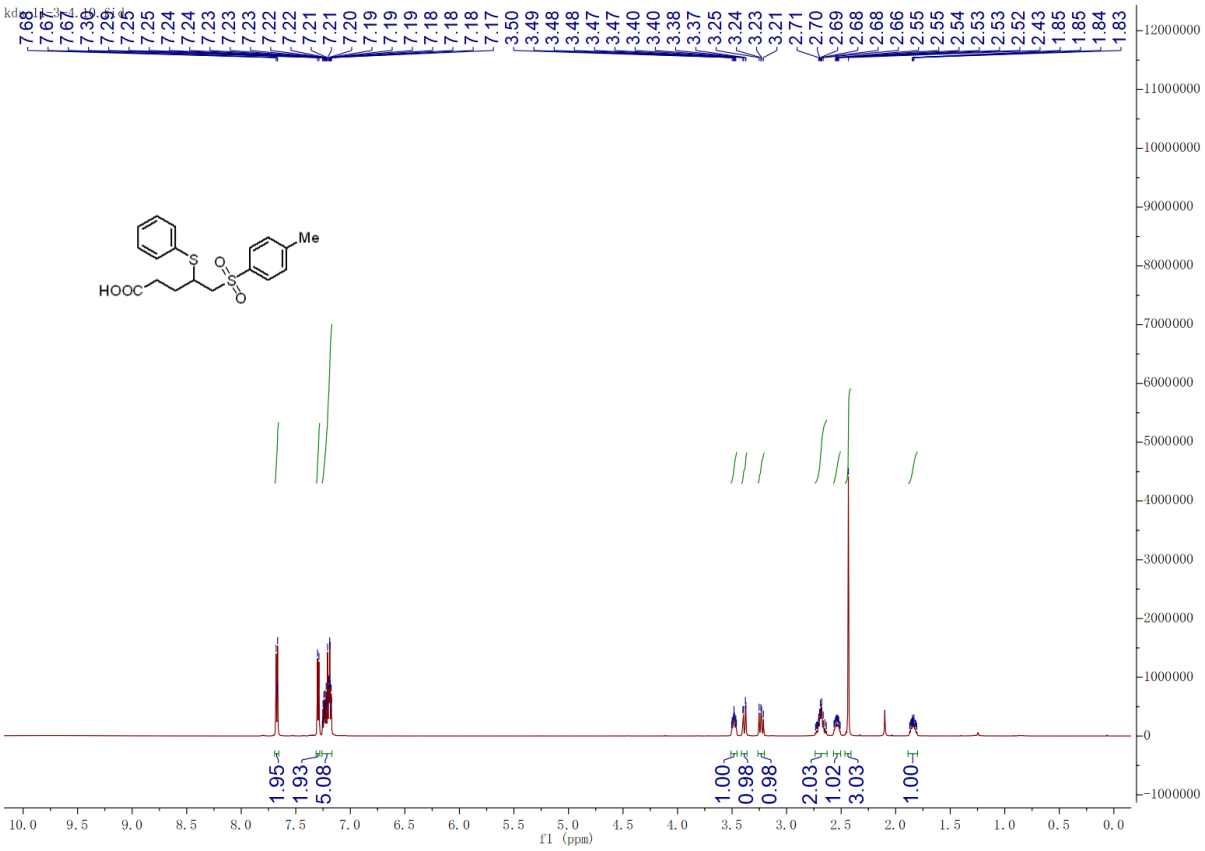
^{1}H NMR spectrum of compound **(3ah)** (600 MHz, $CDCl_3$)



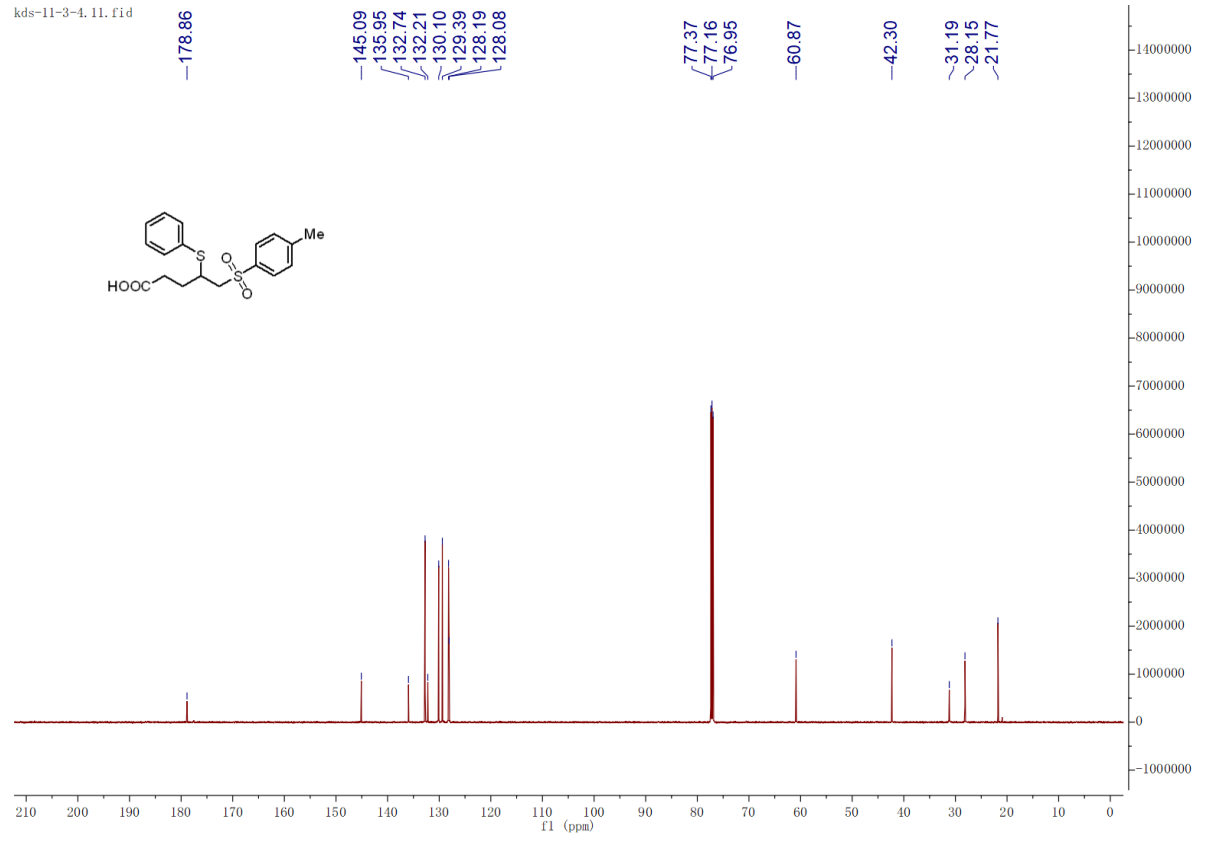
^{13}C{^{1}H} NMR spectrum of compound **(3ah)** (151 MHz, $CDCl_3$)



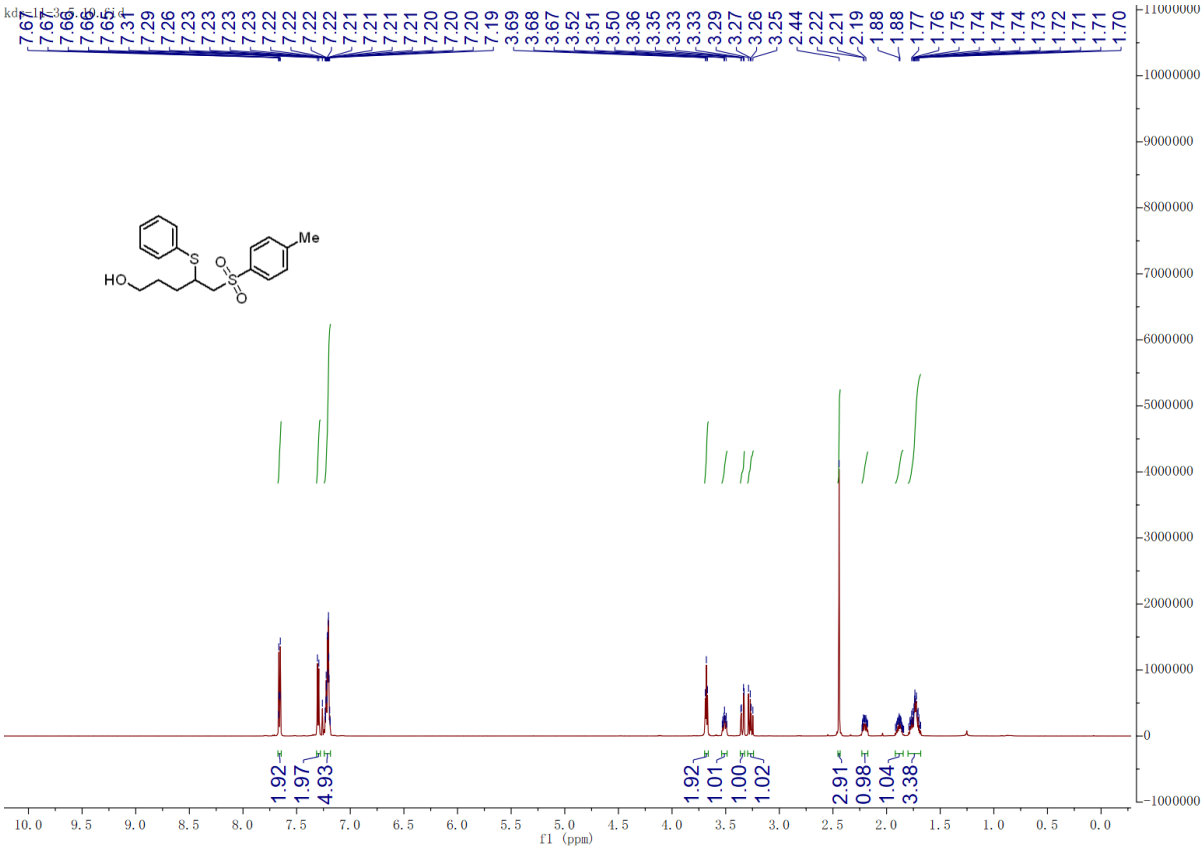
^{1}H NMR spectrum of compound **(3ai)** (600 MHz, $CDCl_3$)



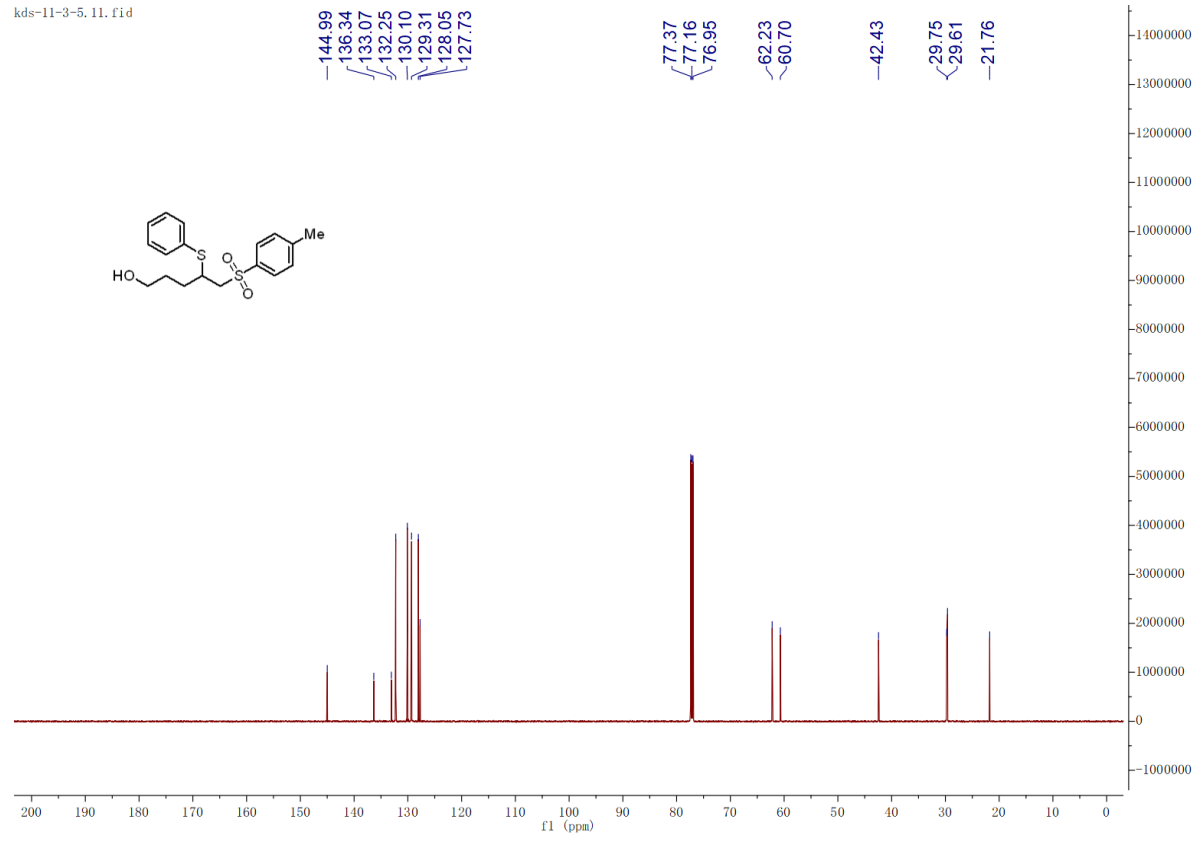
^{13}C{^{1}H} NMR spectrum of compound **(3ai)** (151 MHz, $CDCl_3$)



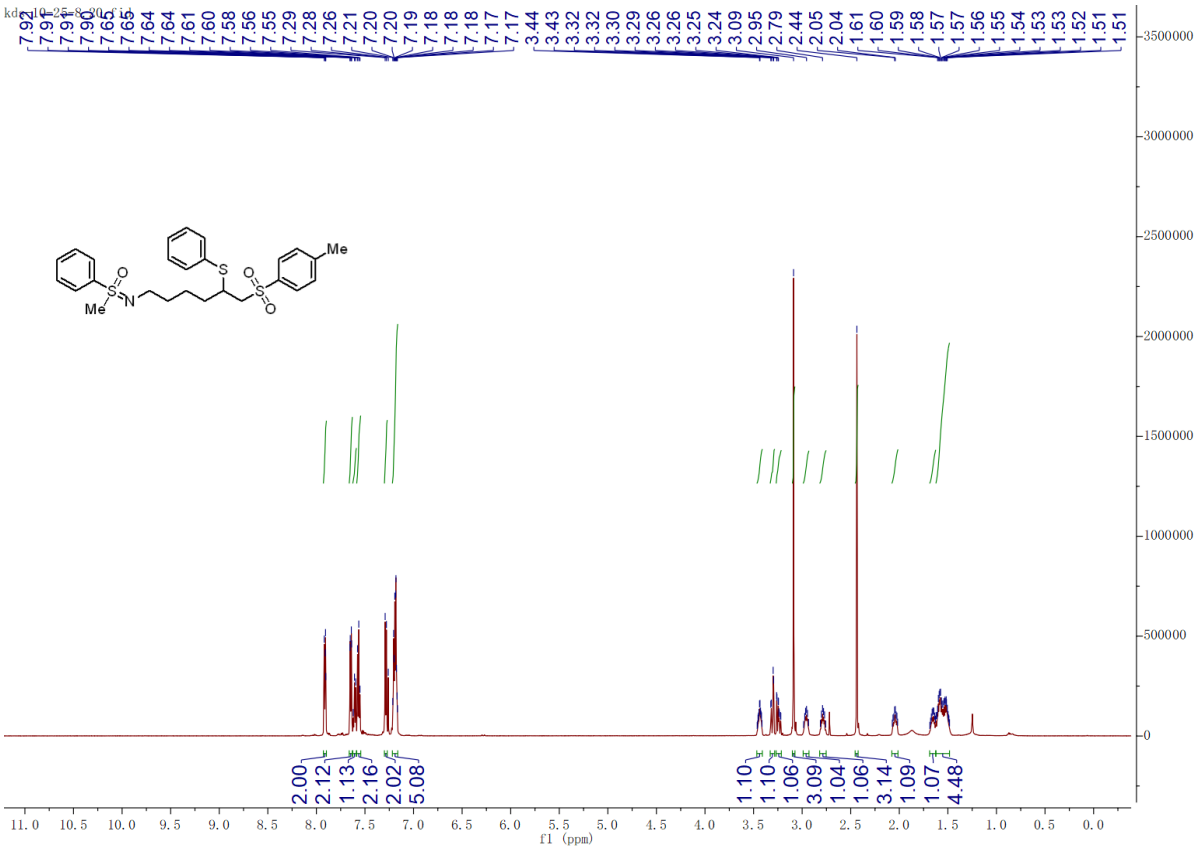
^{1}H NMR spectrum of compound **(3aj)** (600 MHz, $CDCl_3$)



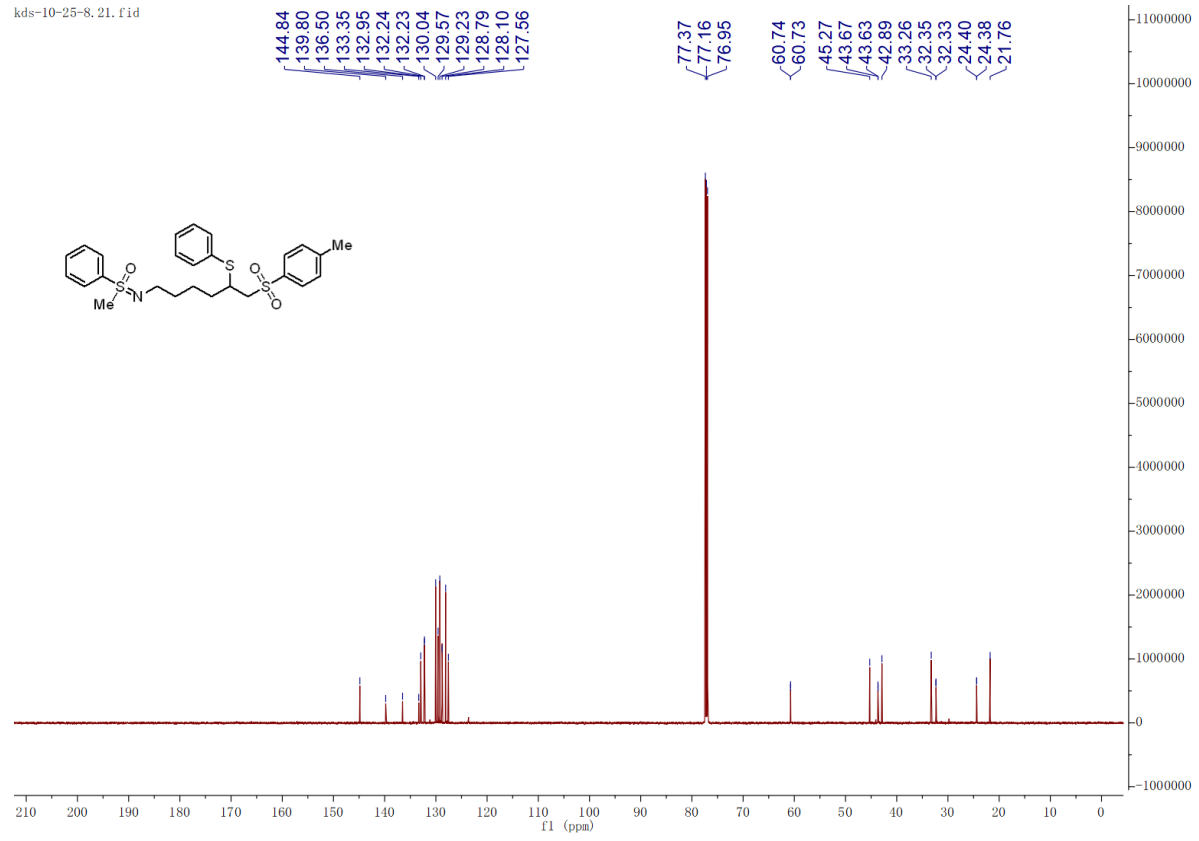
^{13}C{^{1}H} NMR spectrum of compound **(3aj)** (151 MHz, $CDCl_3$)



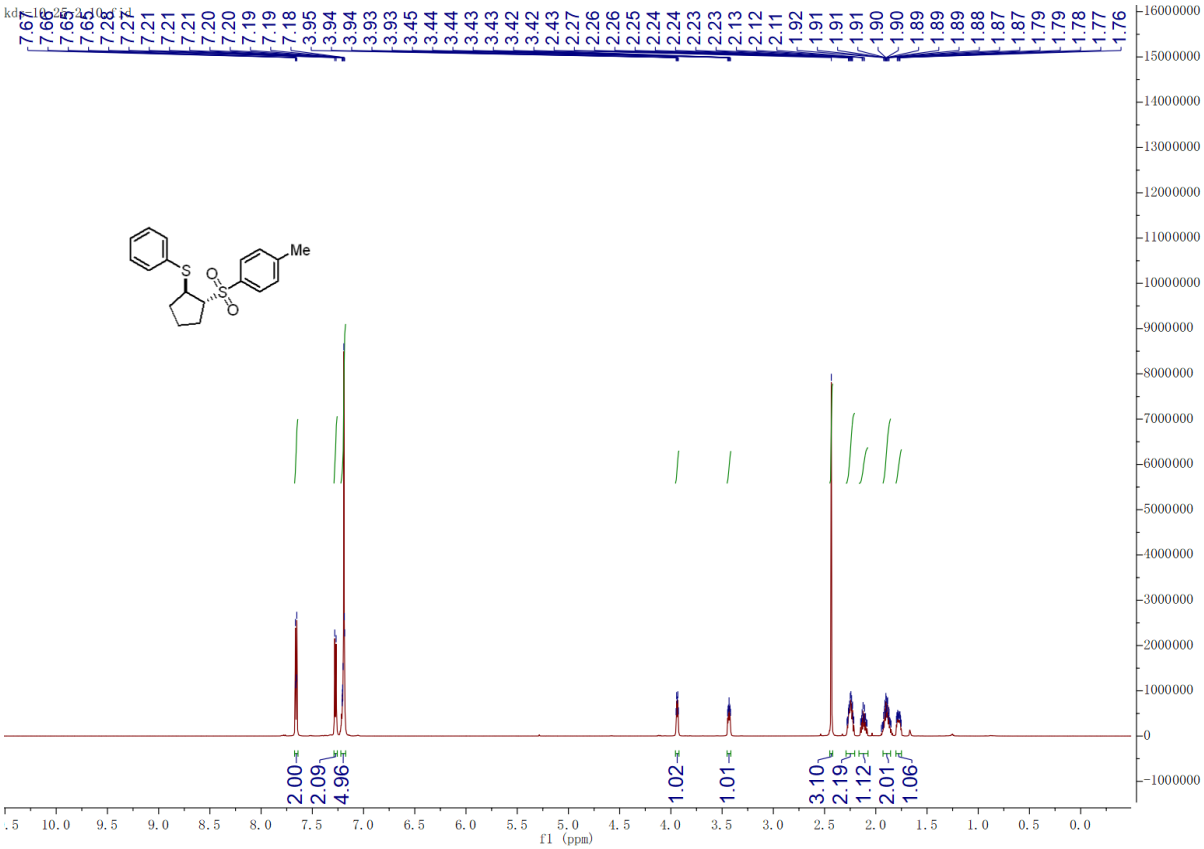
^{1}H NMR spectrum of compound **(3ak)** (600 MHz, $CDCl_3$)



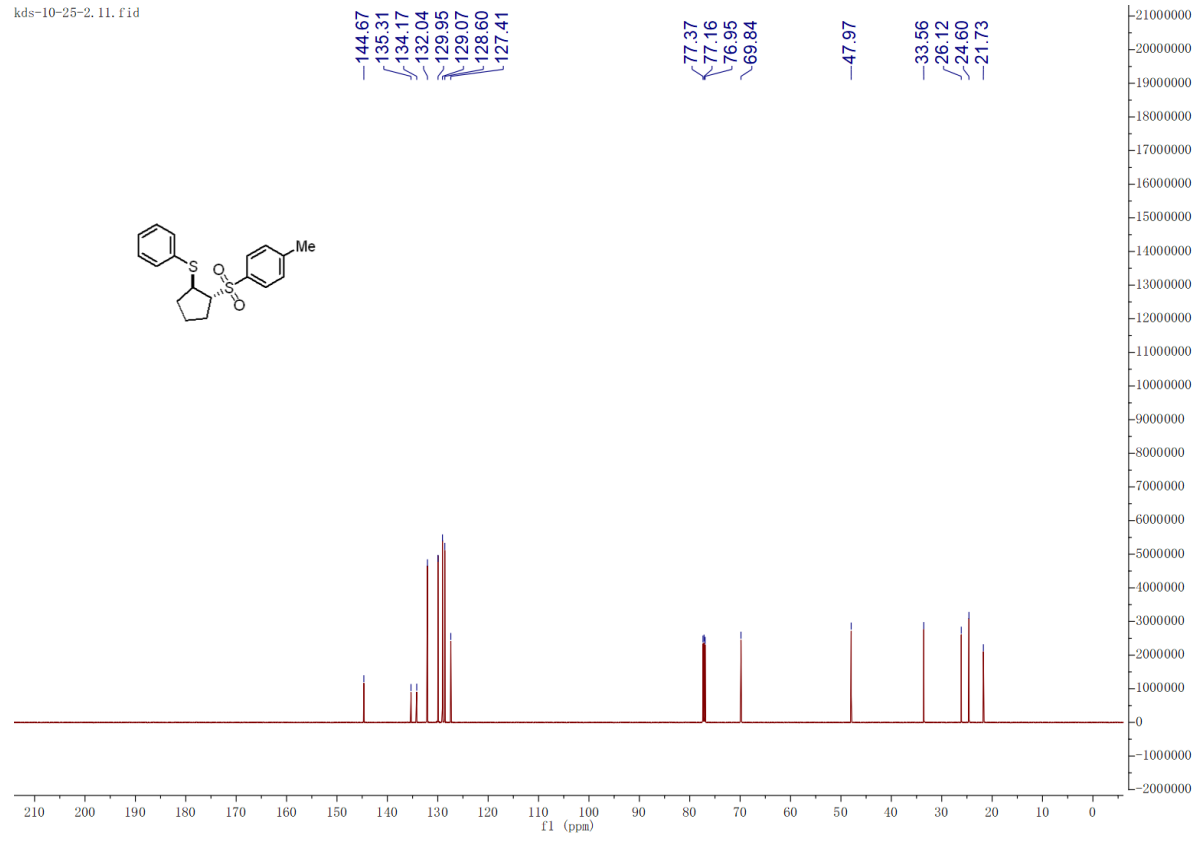
^{13}C{^{1}H} NMR spectrum of compound **(3ak)** (151 MHz, $CDCl_3$)



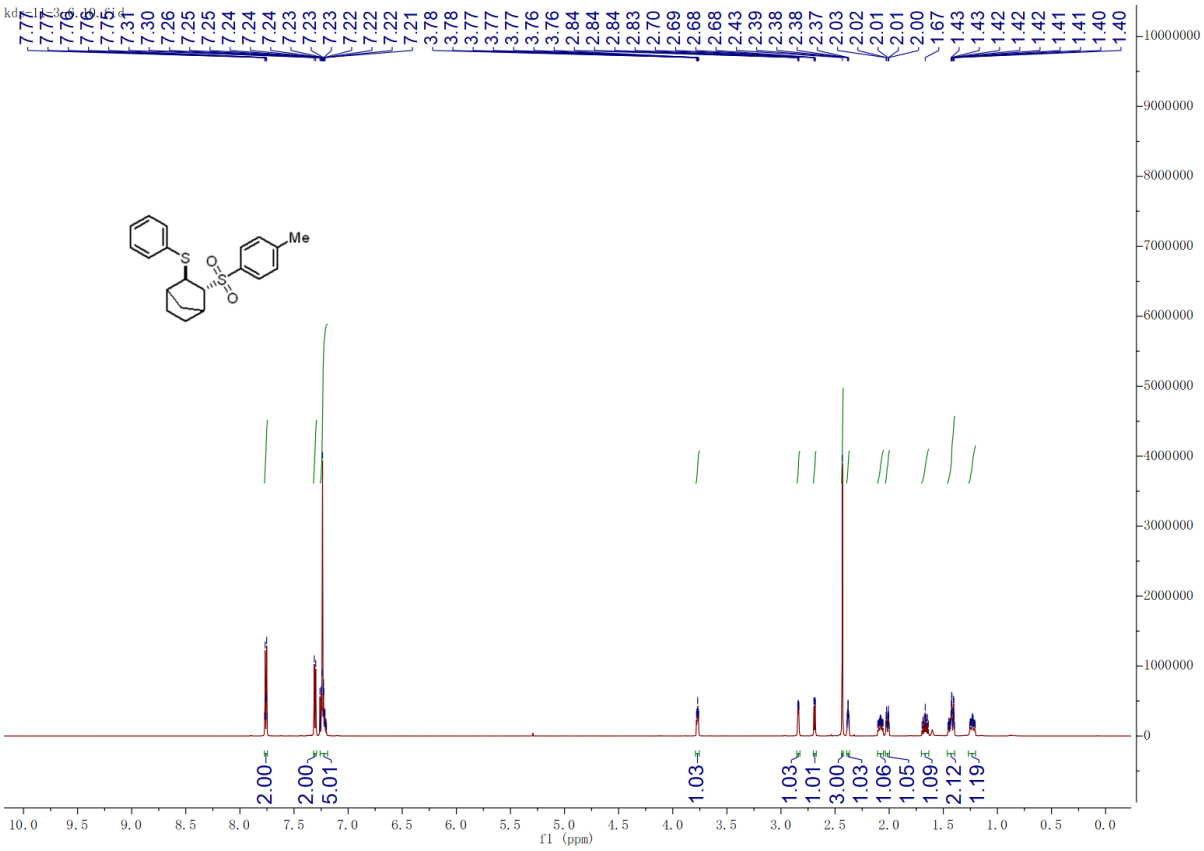
^{1}H NMR spectrum of compound **(3an)** (600 MHz, $CDCl_3$)



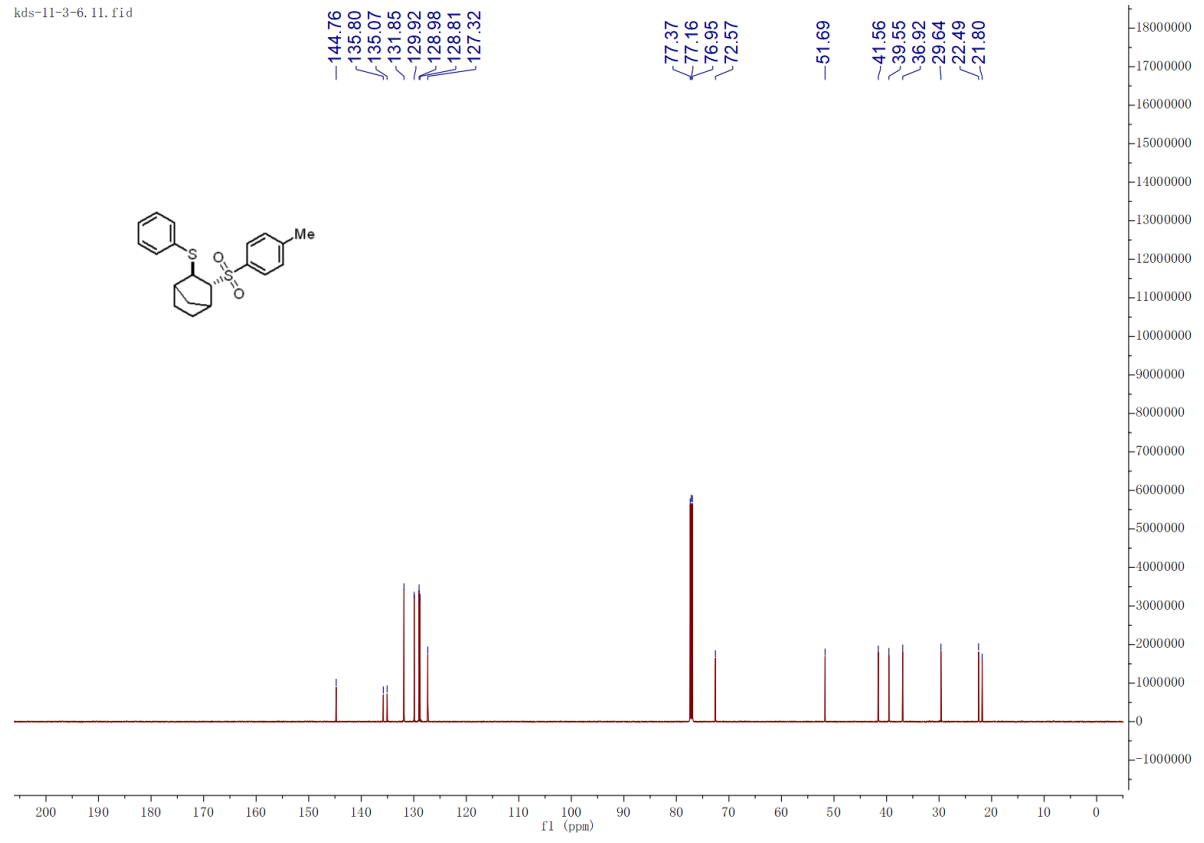
^{13}C{^{1}H} NMR spectrum of compound **(3an)** (151 MHz, $CDCl_3$)



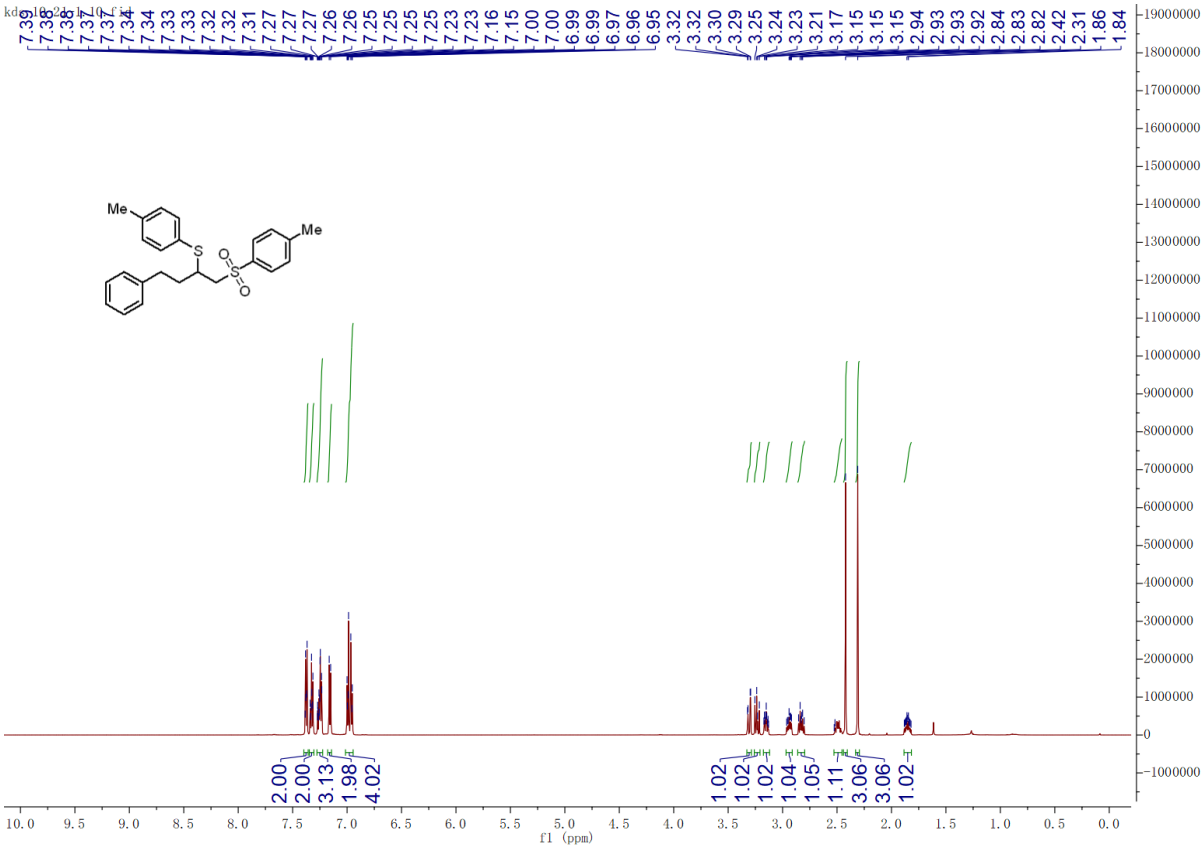
^{1}H NMR spectrum of compound **(3ao)** (600 MHz, $CDCl_3$)



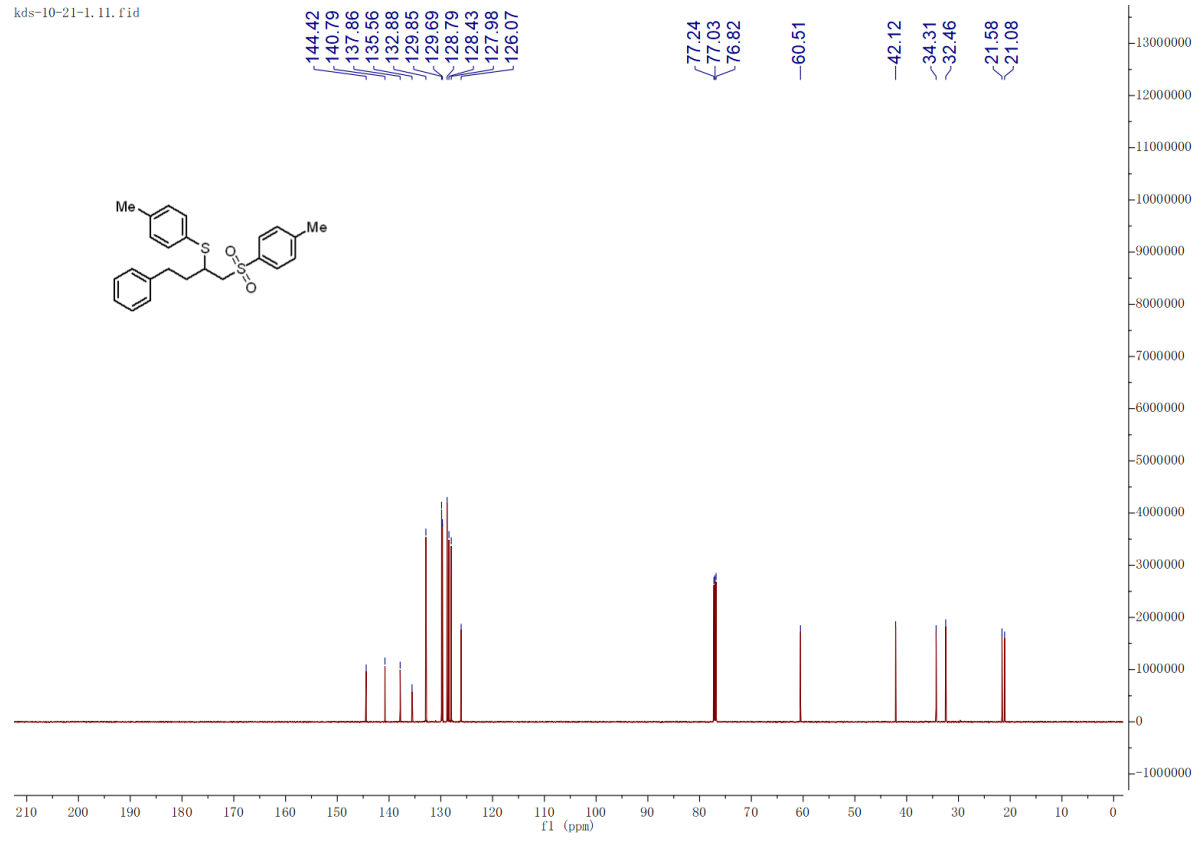
^{13}C{^{1}H} NMR spectrum of compound **(3ao)** (151 MHz, $CDCl_3$)



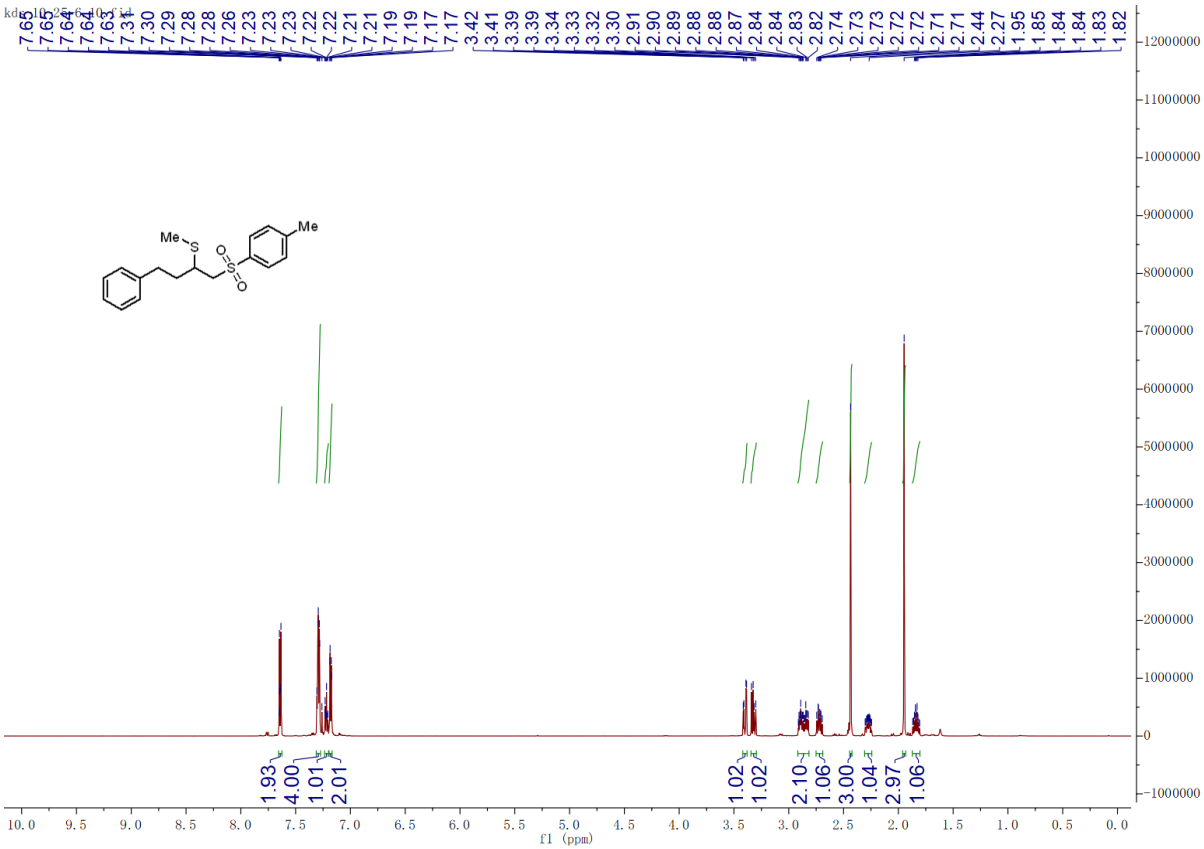
^{1}H NMR spectrum of compound **(3ba)** (600 MHz, $CDCl_3$)



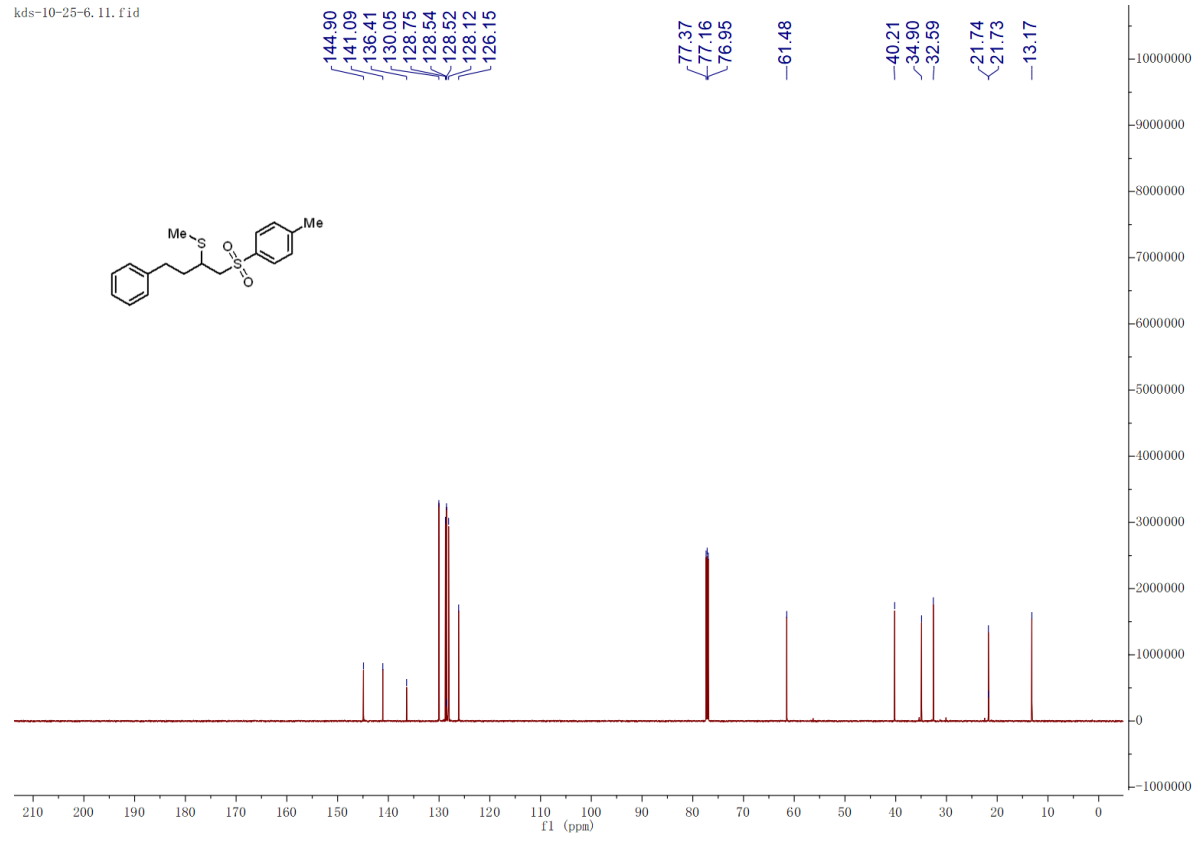
^{13}C{^{1}H} NMR spectrum of compound **(3ba)** (151 MHz, $CDCl_3$)



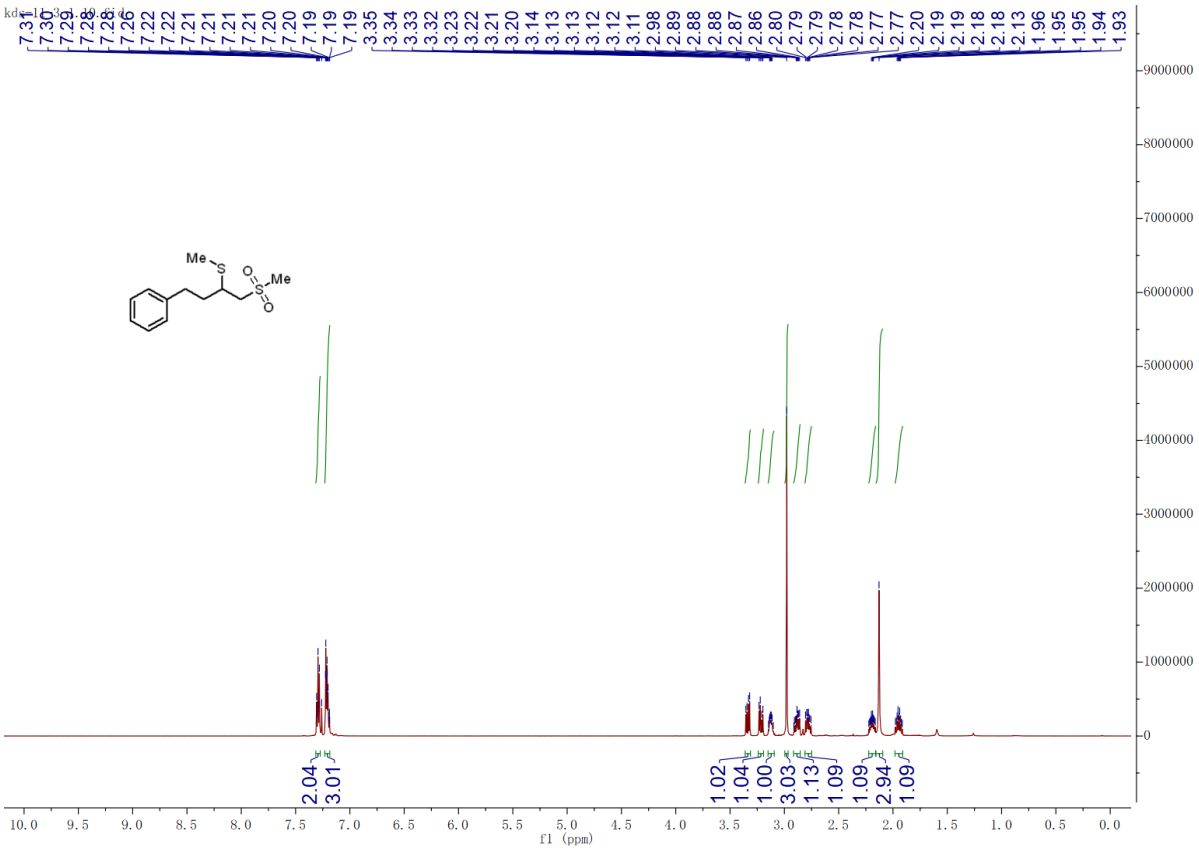
^{1}H NMR spectrum of compound **(3ca)** (600 MHz, $CDCl_3$)



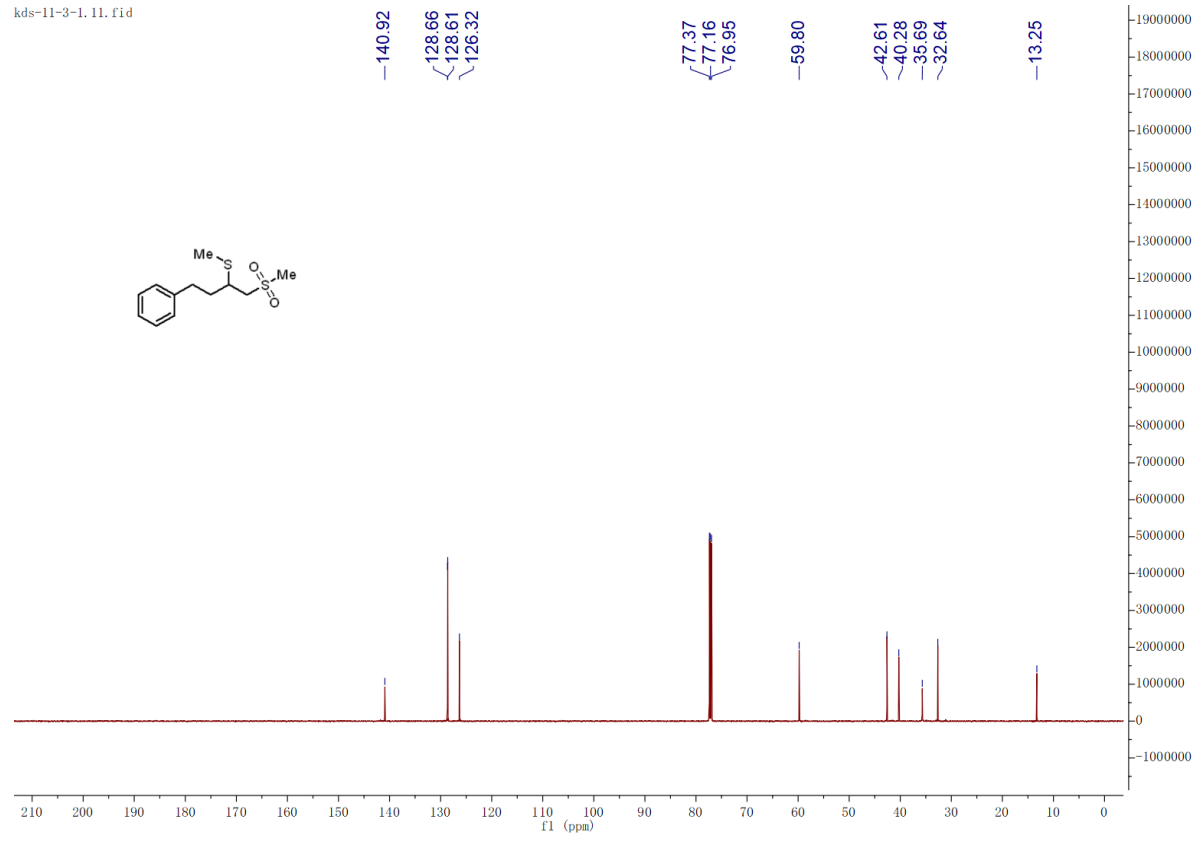
^{13}C{^{1}H} NMR spectrum of compound **(3ca)** (151 MHz, $CDCl_3$)



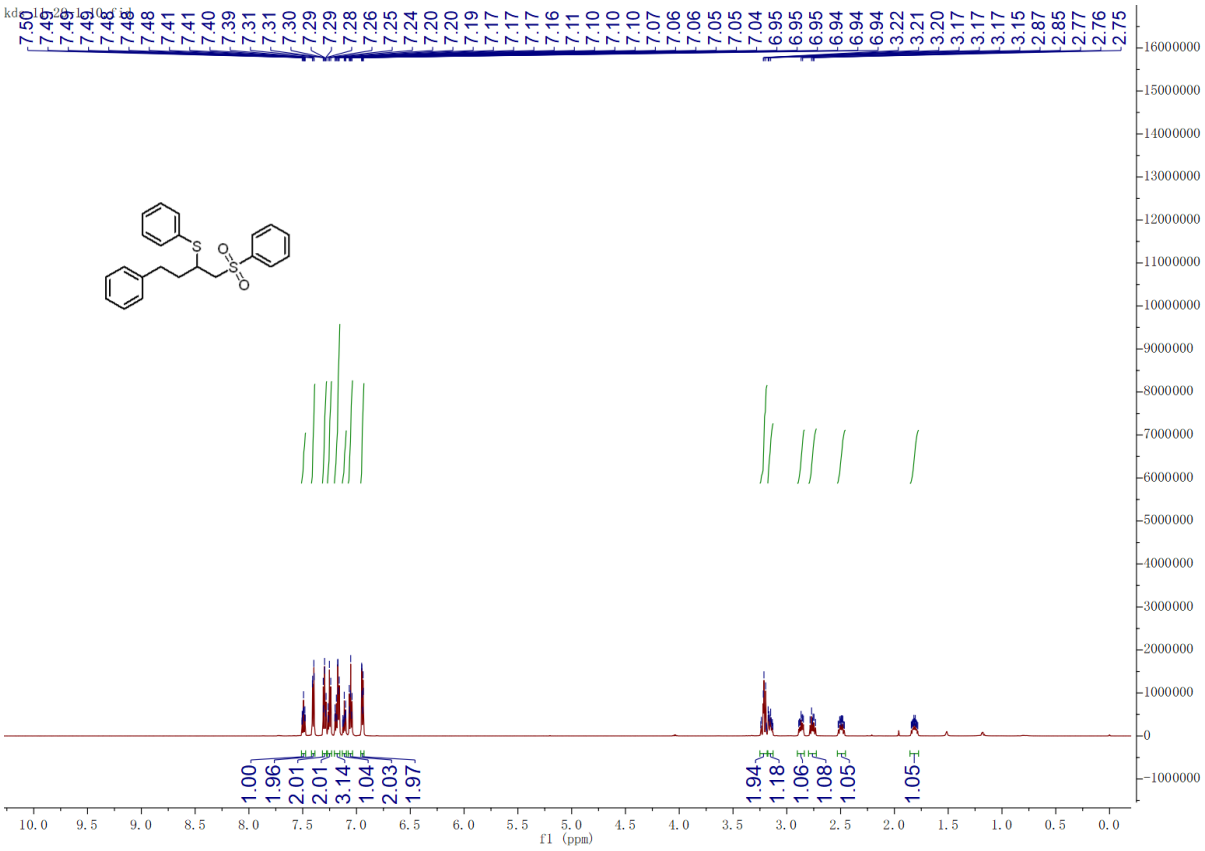
^{1}H NMR spectrum of compound **(3ea)** (600 MHz, $CDCl_3$)



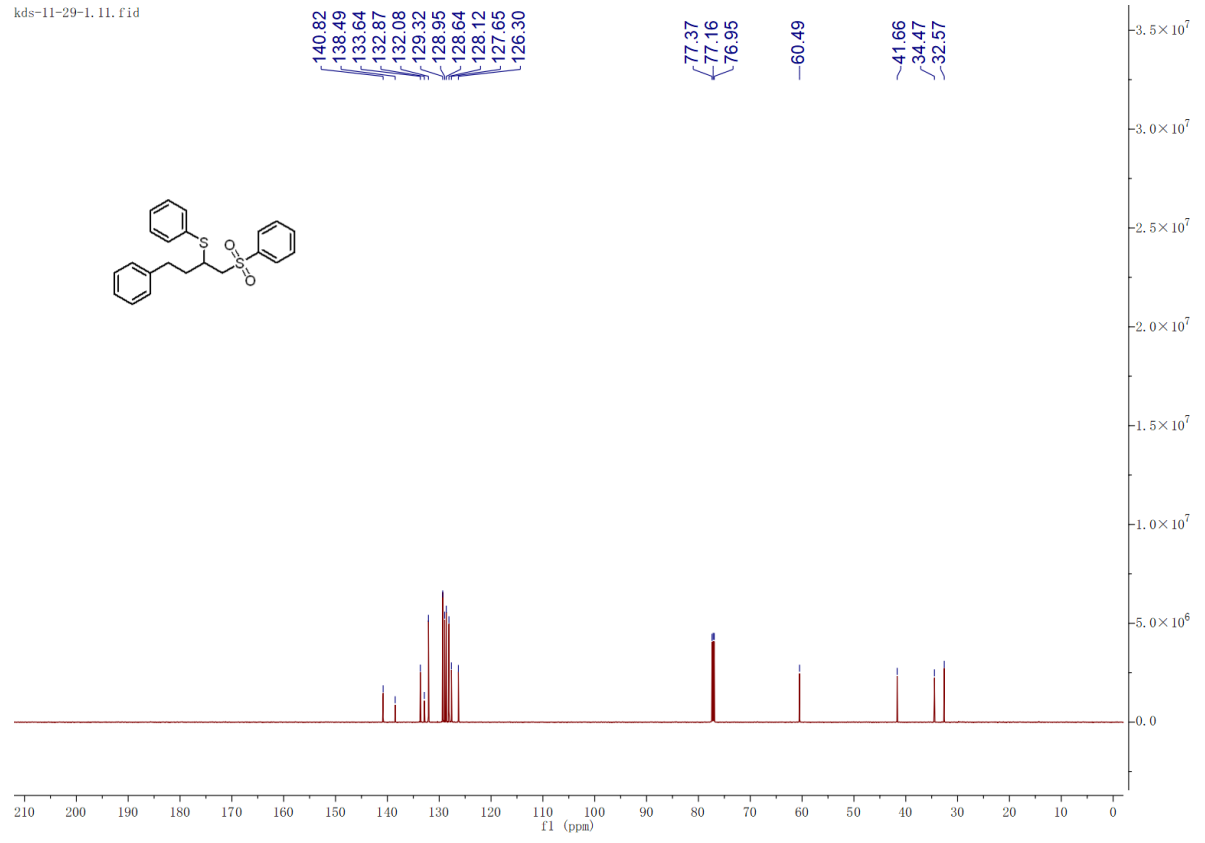
^{13}C{^{1}H} NMR spectrum of compound **(3ea)** (151 MHz, $CDCl_3$)



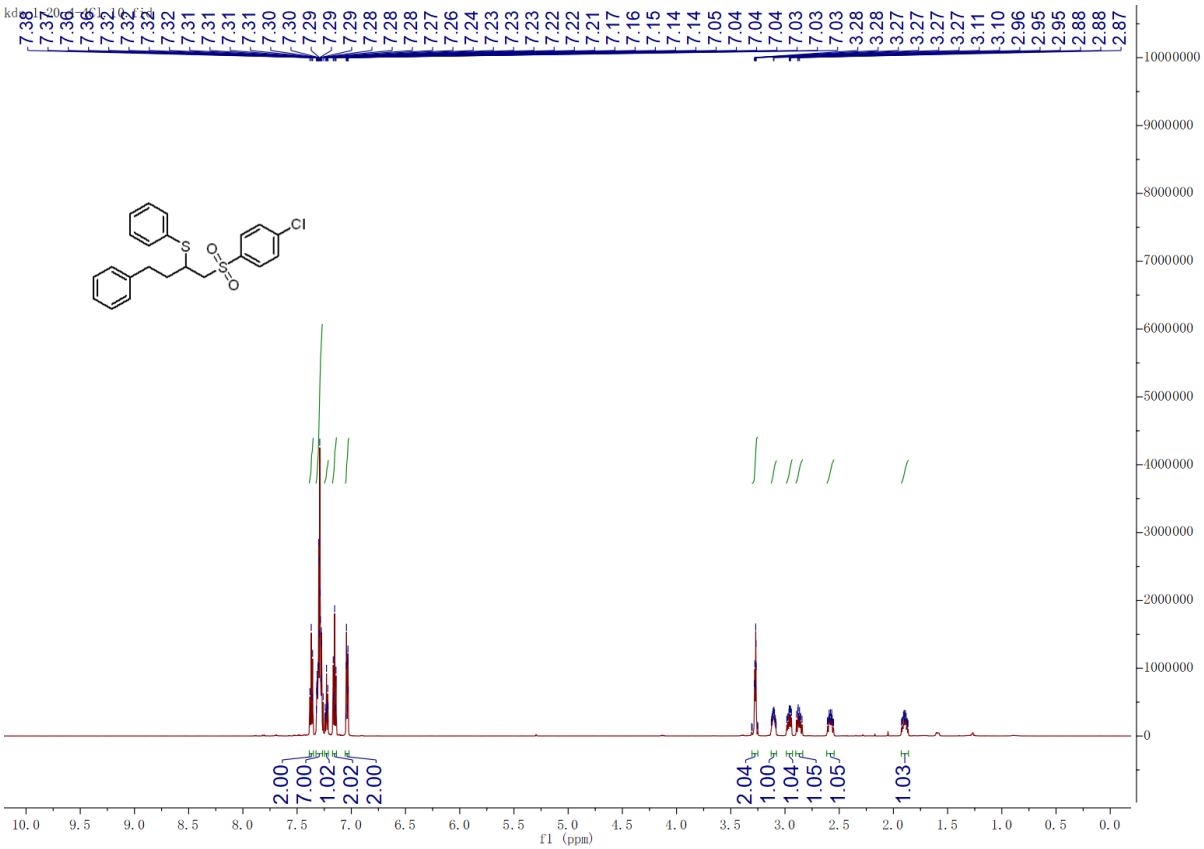
^{1}H NMR spectrum of compound **(3fa)** (600 MHz, $CDCl_3$)



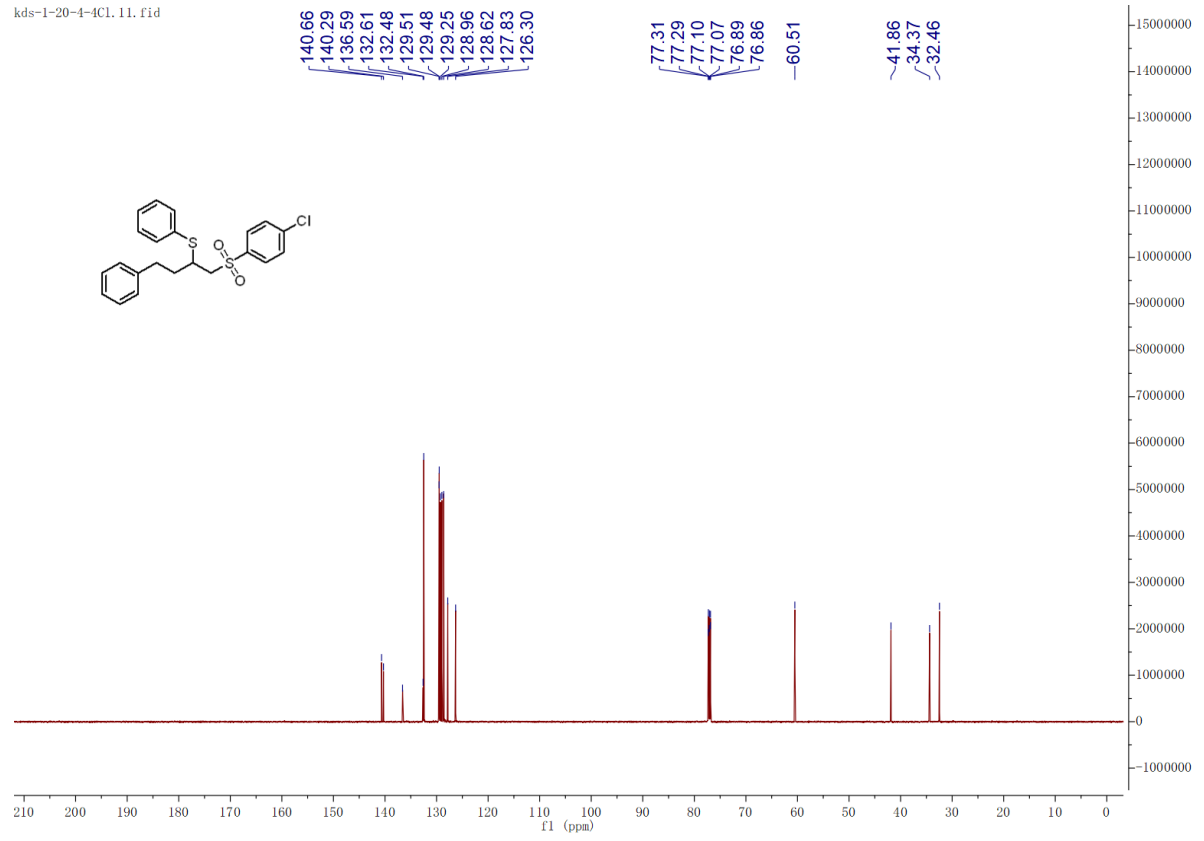
^{13}C{^{1}H} NMR spectrum of compound **(3fa)** (151 MHz, $CDCl_3$)



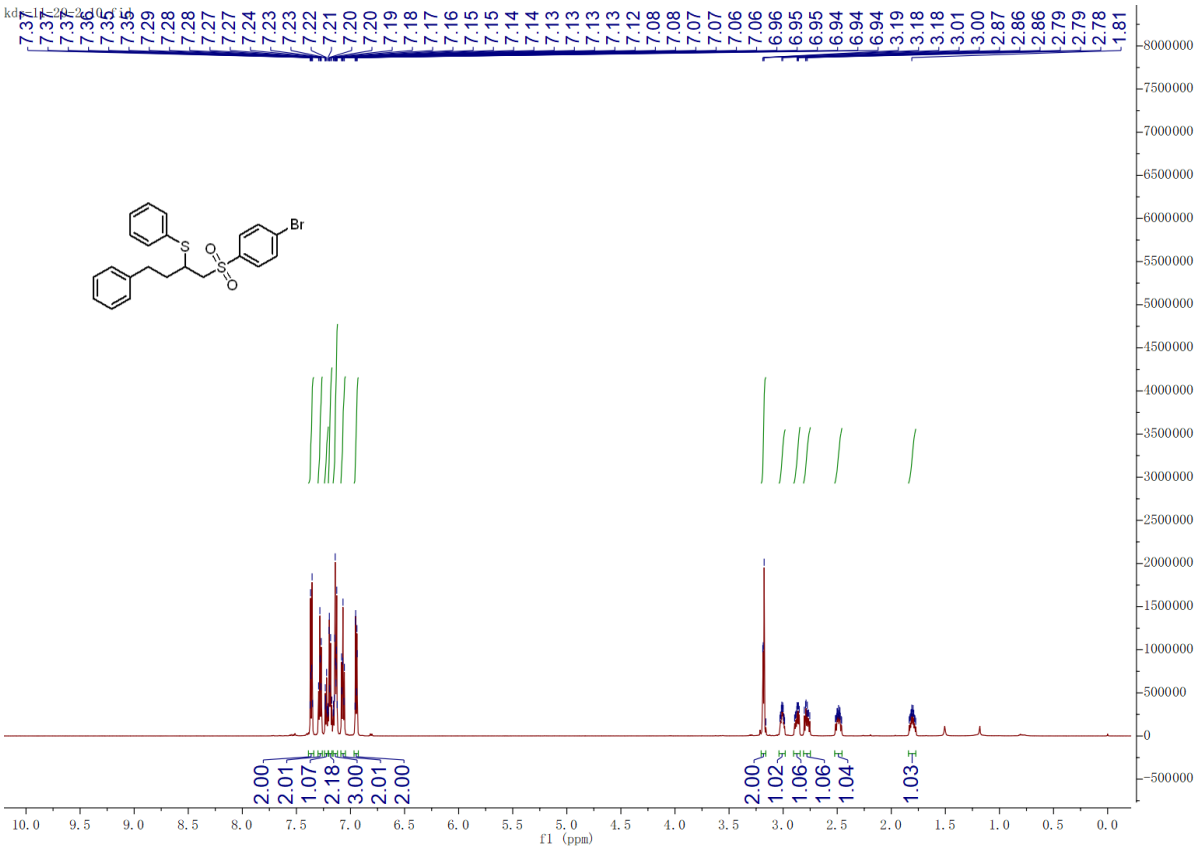
^{1}H NMR spectrum of compound **(3ga)** (600 MHz, $CDCl_3$)



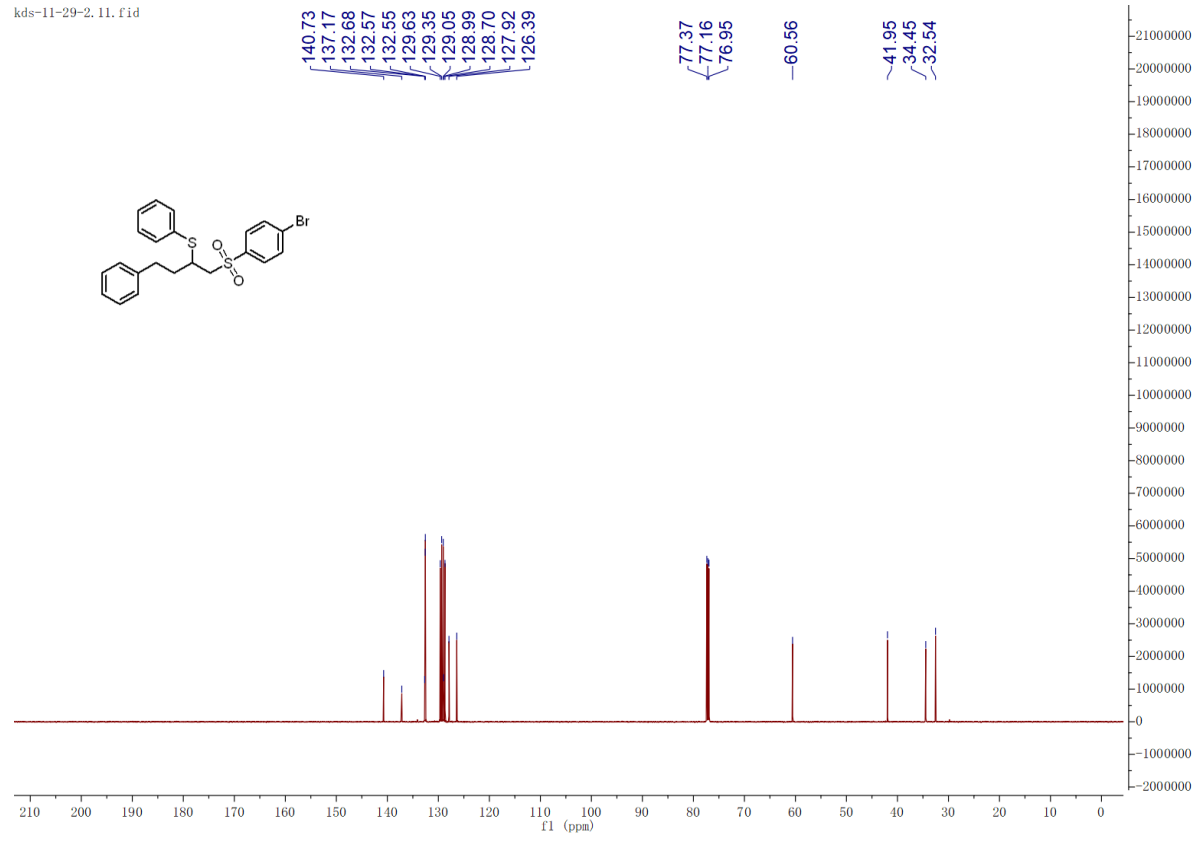
^{13}C{^{1}H} NMR spectrum of compound **(3ga)** (151 MHz, $CDCl_3$)



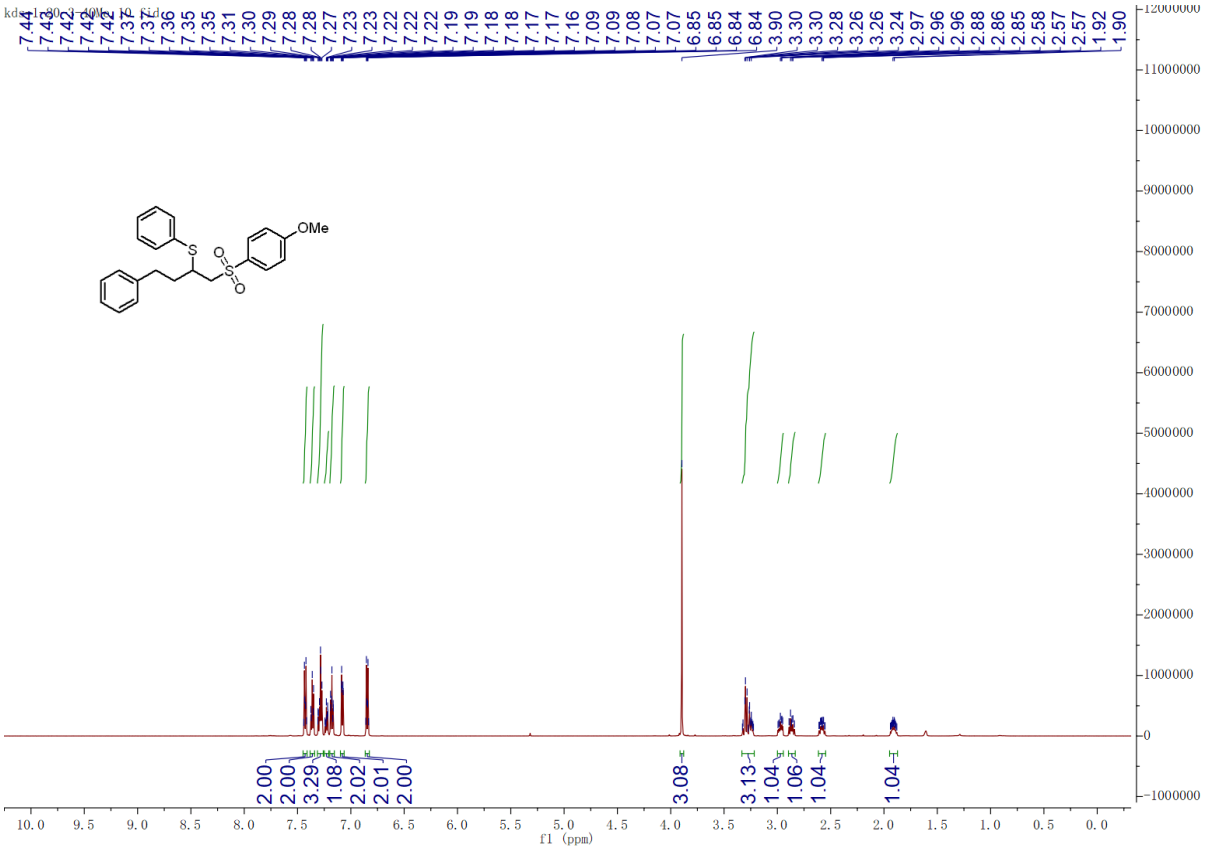
^{1}H NMR spectrum of compound **(3ha)** (600 MHz, $CDCl_3$)



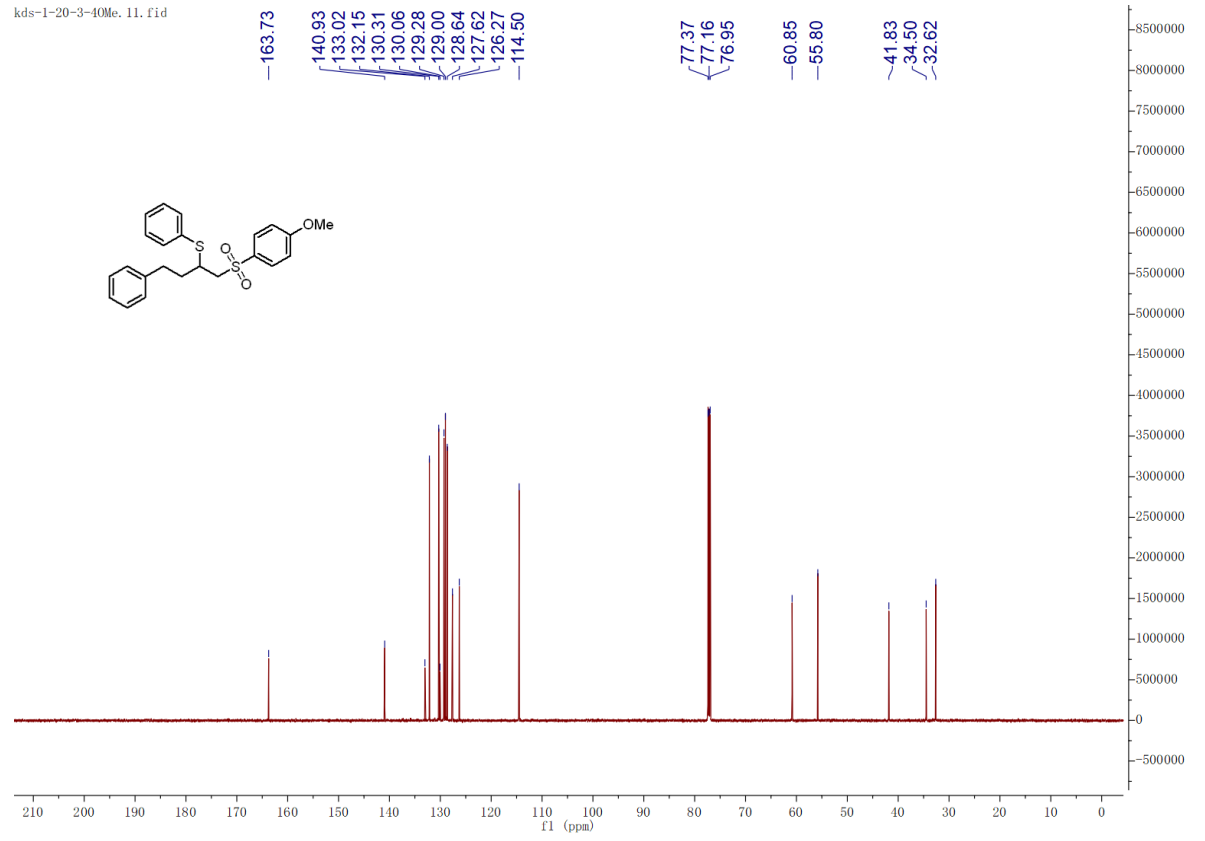
^{13}C{^{1}H} NMR spectrum of compound **(3ha)** (151 MHz, $CDCl_3$)



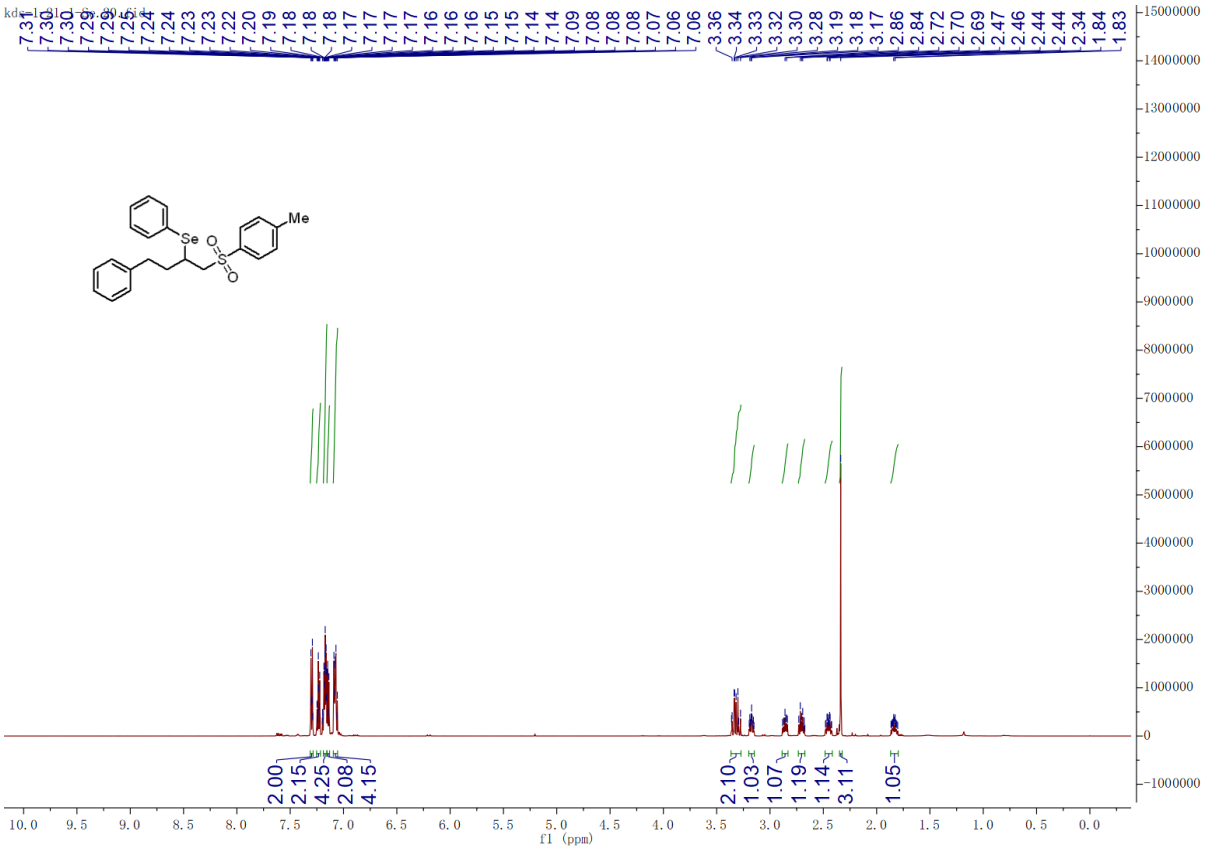
^{1}H NMR spectrum of compound **(3ia)** (600 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR spectrum of compound **(3ia)** (151 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **(3ja)** (600 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR spectrum of compound **(3ja)** (151 MHz, $CDCl_3$)