Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Nickel-Catalyzed α-Benzylation of Sulfones with Esters via C-O Activation

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1. General information

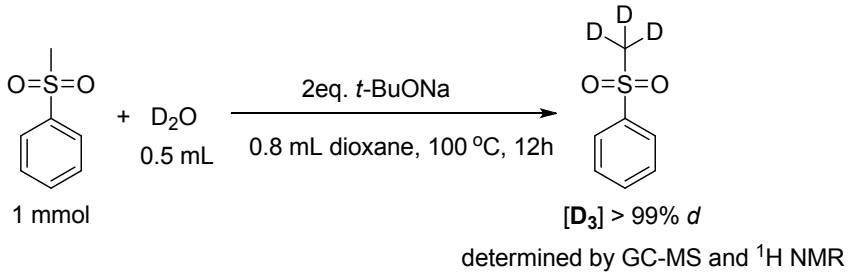
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All solvents were dried by standard methods. $Ni(COD)_2$ and phosphine ligands are stored under nitrogen in the glove box. Unless otherwise noted, all coupling reactions were performed in 10-mL glass vessel tubes. Unless otherwise noted, all reactions were carried out under N_2 atmosphere.

Flash column chromatography was performed using 200-300 mesh silica gel. Visualization on TLC was achieved by the use of UV light (254 nm). All reactions were monitored by GC, GC-MS. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Avance III-400 spectrometer. (^1H 400 MHz, ^{13}C 101 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^1H and 77.0 ppm for ^{13}C). The coupling constants J are given in Hz. Mass spectra were recorded by GCMS-QP2010 ultra spectrometer. The high-resolution mass spectrum (HRMS) was recorded on MAT 95 XP instrument. The GC yields were accorded to the authentic samples/tridecane calibration standard from Shimadzu GC-2010 plus equipped with FID system.

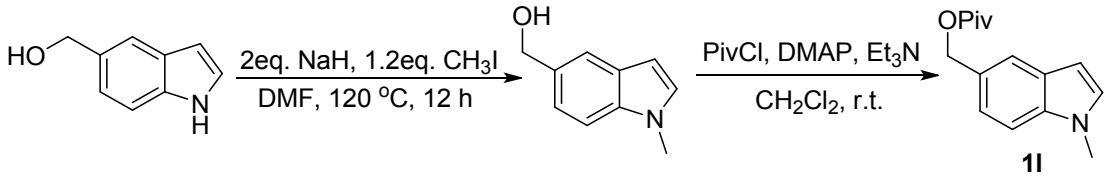
2. Preparation of substrates

Substrates **1a**, **1n**, **1o**, **1p**, **1q, 1r, 1s, 2t**, **2u**, and **2v** were prepared according to the literature procedure.[1] Substrates **2h**, **2i, 2j, 2k** were prepared according to the reported literatures.[2] Substrates **2f** was prepared via methylation of the corresponding sulfones.[3]

Preparation of deuterated pentafluorobenzene[6]

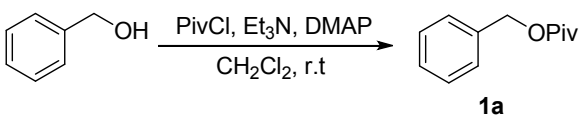


Preparation of 1l



To a solution of indole-5-methanol (2.94 g, 20 mmol) and NaH (40 mmol) in DMF (40 mL) was added CH_3I (1.2 equiv) at room temperature. After stirring for 12h at 120 °C, the reaction mixture was quenched with saturated $NaHCO_3$ (10 mL), then the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (25 mL × 3) and the combined organic layer was dried over Na_2SO_4 and then filtrated. After evaporation of the solvent under reduced pressure, the crude residue was purified by flash column chromatography to afford the methylated product (1-methyl-1H-indol-5-yl)methanol. To a solution of (1-methyl-1H-indol-5-yl)methanol and 4,4-dimethylaminopyridine (DMAP, 10 mol%) in CH_2Cl_2 (30 mL) was added triethylamine (1.2 equiv) at room temperature. Then pivaloyl chloride (1.2 equiv) was added dropwise over 3 min at 0 °C. After stirring for 15 min, the reaction mixture was quenched with saturated $NaHCO_3$ (10 mL), then the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (25 mL × 3) and the combined organic layer was dried over Na_2SO_4 and then filtrated. After evaporation of the solvent under reduced pressure, the crude residue was purified by flash column chromatography (Petroleum ether/EtOAc = 10:1) to afford the product **1l**.

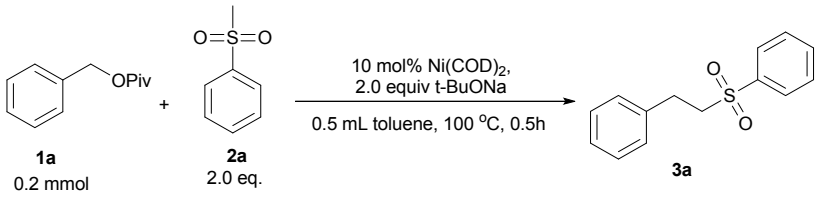
Representative procedure



To a solution of phenylmethanol (2.16 g, 20 mmol) and 4,4-dimethylaminopyridine (DMAP, 10 mol%) in CH_2Cl_2 (30 mL) was added triethylamine (3.35 mL, 24 mmol, 1.2 equiv) at room temperature. Then pivaloyl chloride (2.95 mL, 24 mmol, 1.2 equiv) was added dropwise over 3 min at 0 °C. After stirring for 15 min, the reaction mixture was quenched with saturated $NaHCO_3$ (10 mL), then the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (25 mL × 3) and the combined organic layer was dried over Na_2SO_4 and then filtrated. After evaporation of the solvent under reduced pressure, the crude residue was purified by flash column chromatography (Petroleum ether/EtOAc = 10:1) to afford the product **1a** in 90% yield.

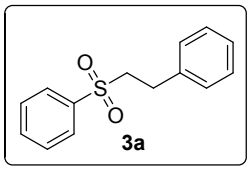
3. General procedure and spectral data for the products

A. Typical procedure of Ni-catalyzed cross coupling of benzylic pivalate with methyl phenyl sulfone

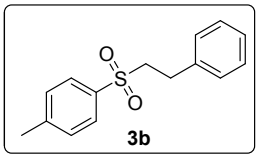


In a nitrogen-filled glove box, a 10 mL sealed schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol), $Ni(COD)_2$ (0.02 mmol), *t*-BuONa (0.4 mmol) and (methylsulfonyl)benzene (0.4 mmol) and toluene (0.5 mL). The reaction mixture was stirred at 100 °C for 0.5 hours. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel column with EtOAc. The filtrate was concentrated and the residue was further purified by column chromatography on silica gel to give the product **3a** in 71% yield.

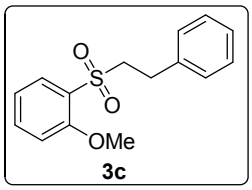
B. Spectral data for products (0.2 mmol scale)



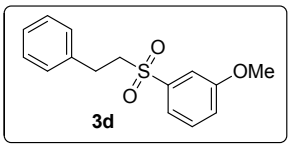
(Phenethylsulfonyl)benzene, yield for pivalate 71%, 34.9 mg; yield for carbonate 63%, 31.0 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.27–7.17 (m, 3H), 7.10 (d, *J* = 7.2 Hz, 2H), 3.38–3.34 (m, 2H), 3.06–3.02 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 139.03, 137.47, 133.85, 129.40, 128.84, 128.31, 128.10, 126.95, 57.53, 28.75. This compound is known.[4]



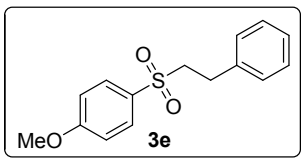
1-Methyl-4-(phenethylsulfonyl)benzene, yield 74%, 38.5 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.81 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.28–7.20 (m, 3H), 7.11 (d, J = 7.6 Hz, 2H), 3.36–3.32 (m, 2H), 3.05–3.01 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 144.82, 137.58, 136.06, 129.99, 128.81, 128.30, 128.13, 126.89, 57.64, 28.84, 21.66. This compound is known.[5]



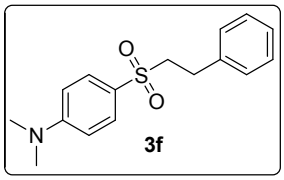
1-Methoxy-2-(phenethylsulfonyl)benzene, light yellow oil, yield 61%, 33.7 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.99–7.96 (m, 1H), 7.60–7.55 (m, 1H), 7.26–7.22 (m, 3H), 7.12–7.08 (m, 3H), 6.99 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H), 3.66–3.62 (m, 2H), 3.04–3.00 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 157.32, 137.89, 135.67, 130.60, 128.69, 128.35, 126.76, 120.82, 112.29, 56.28, 55.58, 28.65. HRMS Calcd. for $C_{15}H_{16}O_3S$ (M+) 276.0820, found 276.0802.



1-Methoxy-3-(phenethylsulfonyl)benzene, light yellow oil, yield 77%, 42.5 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.52–7.42 (m, 3H), 7.28–7.16 (m, 4H), 7.11 (d, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.38–3.34 (m, 2H), 3.07–3.02 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 160.12, 140.19, 137.48, 130.49, 128.82, 128.31, 126.94, 120.26, 120.20, 112.58, 57.47, 55.75, 28.75. HRMS Calcd. for $C_{15}H_{16}O_3S$ (M+) 276.0820, found 276.0805.

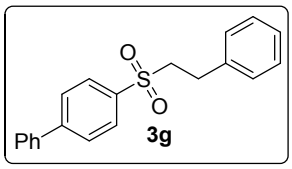


1-Methoxy-4-(phenethylsulfonyl)benzene, yield 75%, 41.4 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.86 (d, J = 8.8 Hz, 2H), 7.28–7.18 (m, 3H), 7.11 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 3.35–3.32 (m, 2H), 3.05–3.01 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 163.82, 137.62, 130.52, 130.29, 128.80, 128.30, 126.88, 114.56, 57.83, 55.73, 28.96. This compound is known.[6]



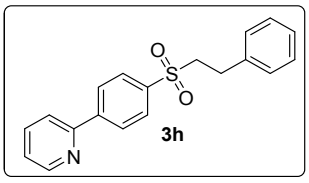
3f

N,N-dimethyl-4-(phenethylsulfonyl)aniline, yellow solid, m.p. 110 °C-112 °C, yield 41%, 23.7 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.73 (d, J = 8.8 Hz, 2H), 7.28–7.11 (m, 5H), 6.71 (d, J = 9.2 Hz, 2H), 3.32–3.28 (m, 2H), 3.07 (s, 6H), 3.05–3.00 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 153.49, 138.03, 129.79, 128.73, 128.31, 126.73, 123.91, 111.04, 58.07, 40.09, 29.17. HRMS Calcd. for $C_{16}H_{19}NO_2S$ (M+) 289.1136, found 289.1126.



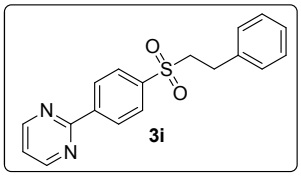
3g

4-(Phenethylsulfonyl)-1,1'-biphenyl, white solid， m.p. 108 °C-109 °C, yield 69%, 44.4 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.98 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.51–7.41 (m, 3H), 7.28–7.18 (m, 3H), 7.12 (d, J = 7.6 Hz, 2H), 3.42–3.38 (m, 2H), 3.11–3.06 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 146.79, 139.12, 137.53, 137.49, 129.15, 128.84, 128.75, 128.66, 128.35, 127.99, 127.43, 126.95, 57.65, 28.84. HRMS Calcd. for $C_{20}H_{18}O_2S$ (M+) 322.1028, found 322.1014.



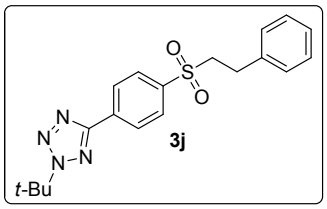
3h

2-(4-(Phenethylsulfonyl)phenyl)pyridine, white solid, m.p. 101 °C-103 °C, yield 81%, 52.3 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.74 (d, J = 4.4 Hz, 1H), 8.20 (d, J = 8.0 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.84–7.78 (m, 2H), 7.34–7.18 (m, 4H), 7.11 (d, J = 7.6 Hz, 2H), 3.42–3.38 (m, 2H), 3.08–3.04 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 155.21, 150.10, 144.61, 138.90, 137.41, 137.17, 128.85, 128.61, 128.32, 127.79, 126.96, 123.46, 121.21, 57.62, 28.87. HRMS Calcd. for $C_{19}H_{17}NO_2S$ (M+) 323.0980, found 323.0970.

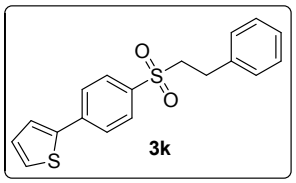


3i

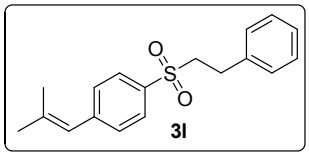
2-(4-(phenethylsulfonyl)phenyl)pyrimidine, white solid， m.p. 125 °C-127 °C, yield 83%, 53.8 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.92 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.46–7.41 (m, 2H), 7.28–7.11 (m, 6H), 3.40–3.36 (m, 2H), 3.09–3.04 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 162.91, 157.51, 142.67, 140.50, 137.38, 129.03, 128.85, 128.39, 128.32, 126.98, 120.21, 57.59, 28.81.



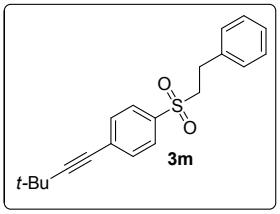
2-(Tert-butyl)-5-(4-(phenethylsulfonyl)phenyl)-2H-tetrazole, light yellow oil, yield 53%, 39.3 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.39–8.37 (m, 2H), 8.06–8.04 (m, 2H), 7.28–7.11 (m, 5H), 3.43–3.39 (m, 2H), 3.09–3.05 (m, 2H), 1.82 (s, 9H). ^{13}C NMR (100 MHz $CDCl_3$): δ 162.90, 140.04, 137.30, 133.12, 128.86, 128.72, 128.31, 127.61, 127.00, 64.51, 57.57, 29.43, 28.79.



2-(4-(Phenethylsulfonyl)phenyl)thiophene, light yellow solid， m.p. 130 °C-131 °C, yield 32%, 21.0 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.92 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.46–7.41 (m, 2H), 7.28–7.11 (m, 6H), 3.40–3.36 (m, 2H), 3.09–3.04 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 141.92, 139.73, 137.43, 137.15, 128.89, 128.84, 128.57, 128.32, 127.21, 126.95, 126.29, 125.34, 57.65, 28.85. HRMS Calcd. for $C_{18}H_{16}O_2S_2$ (M+) 328.0592, found 328.0581.



1-(2-Methylprop-1-en-1-yl)-4-(phenethylsulfonyl)benzene, colorless oil, yield 67%, 40.2 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.85 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.27–7.17 (m, 3H), 7.11 (d, J = 7.6 Hz, 2H), 6.30 (s, 1H), 3.38–3.34 (m, 2H), 3.08–3.03 (m, 2H), 1.94 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 144.50, 139.57, 137.60, 135.80, 129.40, 128.81, 128.32, 127.93, 126.90, 123.79, 57.62, 28.81, 27.14, 19.64. HRMS Calcd. for $C_{18}H_{20}O_2S$ (M+) 300.1184, found 300.1175.



1-(3,3-Dimethylbut-1-yn-1-yl)-4-(phenethylsulfonyl)benzene, white solid， m.p. 102 °C-104 °C, yield 71%, 46.3 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.83 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.29–7.19 (m, 3H), 7.10 (d, J = 7.6 Hz, 2H), 3.36–3.32 (m, 2H), 3.04–2.99 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.39, 137.18, 132.30, 130.25, 128.86, 128.30, 127.93, 126.98, 103.35, 77.86, 57.60, 30.77, 28.83, 28.14. HRMS Calcd. for $C_{20}H_{22}O_2S$ (M+) 326.1341, found 326.1332.

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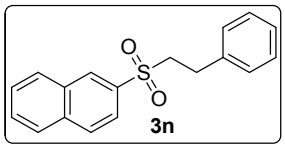
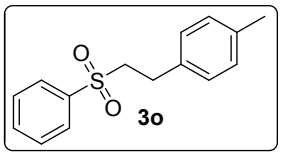
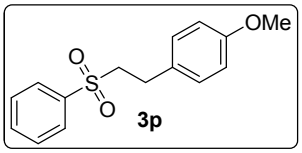


2-(Phenethylsulfonyl)naphthalene, white solid, m.p. 92 °C-94 °C, yield 66%, 39.1 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.51 (s, 1H), 8.02–7.88 (m, 4H), 7.70–7.62 (m, 2H), 7.25–7.09 (m, 5H), 3.46–3.42 (m, 2H), 3.10–3.06 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.45, 135.87, 135.37, 132.21, 130.03, 129.72, 129.46, 129.37, 128.80, 128.30, 128.03, 127.80, 126.92, 122.67, 57.58, 28.89. HRMS Calcd. for $C_{18}H_{16}O_2S$ (M+) 296.0871, found 296.0867.

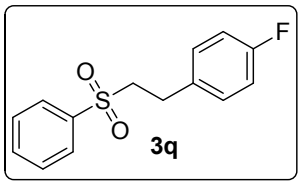


1-Methyl-4-(2-(phenylsulfonyl)ethyl)benzene, colorless oil, yield 73%, 38.0 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.94 (d, J = 8.0 Hz, 2H), 7.68–7.55 (m, 3H), 7.08–6.99 (m, 4H), 3.36–3.32 (m, 2H), 3.02–2.98 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 139.09, 136.56, 134.37, 133.77, 129.48, 129.35, 128.16, 128.10, 57.67, 28.34, 20.99.

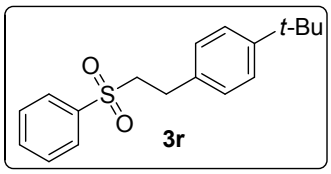


1-Methoxy-4-(2-(phenylsulfonyl)ethyl)benzene, light yellow oil, yield 76%, 42.0 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.93 (d, J = 7.2 Hz, 2H), 7.68–7.55 (m, 3H), 7.02 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 3.75 (s, 3H), 3.35–3.31 (m, 2H), 3.00–2.96 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$):

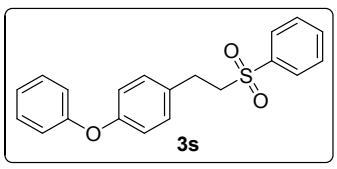
δ 158.54, 139.09, 133.78, 129.40, 129.36, 129.31, 128.08, 114.23, 57.76, 55.29, 27.92. HRMS Calcd. for $C_{15}H_{16}O_3S$ (M+) 276.0820, found 276.0812.



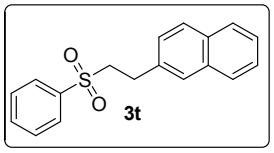
1-Fluoro-4-(2-(phenylsulfonyl)ethyl)benzene, light yellow oil, yield 62%, 32.7 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.93 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.10–7.06 (m, 2H), 6.94 (t, J = 8.4 Hz, 2H), 3.36–3.32 (m, 2H), 3.05–3.01 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 161.78 (d, $J_{C\text{-}F}$ = 244.0 Hz), 138.99, 133.88, 133.13 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.84 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.40, 128.07, 115.66 (d, $J_{C\text{-}F}$ = 21.3 Hz), 57.54, 27.98. HRMS Calcd. for $C_{14}H_{13}FO_2S$ (M+) 264.0620, found 264.0605.



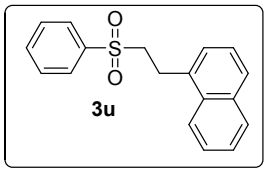
1-(Tert-butyl)-4-(2-(phenylsulfonyl)ethyl)benzene, white solid， m.p. 61 ^{o}C-62^{o}C, yield 84%, 50.7 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.93 (d, J = 8.0 Hz, 2H), 7.67–7.55 (m, 3H), 7.27 (d, J = 7.6 Hz, 2H), 7.04 (d, J = 7.6 Hz, 2H), 3.38–3.34 (m, 2H), 3.04–3.00 (m, 2H), 1.28 (s, 9H). ^{13}C NMR (100 MHz $CDCl_3$): δ 149.90, 139.12, 134.35, 133.74, 129.32, 128.08, 127.96, 125.71, 57.56, 34.43, 31.30, 28.18. HRMS Calcd. for $C_{18}H_{22}O_2S$ (M+) 302.1341, found 302.1338.



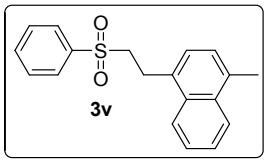
1-Phenoxy-4-(2-(phenylsulfonyl)ethyl)benzene, colorless oil, yield 65%, 43.9 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.92 (d, J = 7.6 Hz, 2H), 7.67–7.54 (m, 3H), 7.32 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 8.0 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.0 Hz, 2H), 6.86–6.75 (m, 3H), 3.37–3.32 (m, 2H), 3.03–2.99 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 157.71, 156.84, 139.46, 138.97, 133.88, 130.13, 129.84, 129.40, 128.11, 123.54, 123.06, 119.03, 118.56, 117.19, 57.30, 28.63. HRMS Calcd. for $C_{20}H_{18}O_3S$ (M+) 338.0977, found 338.0972.



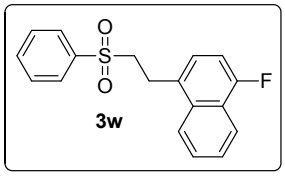
2-(2-(Phenylsulfonyl)ethyl)naphthalene, light yellow solid， m.p. 91 °C-92 °C yield 31%, 18.4 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.96 (d, J = 7.6 Hz, 2H), 7.79–7.72 (m, 3H), 7.65 (t, J = 7.6 Hz, 1H), 7.58–7.55 (m, 3H), 7.47–7.42 (m, 2H), 7.23–7.21 (m, 1H), 3.47–3.43 (m, 2H), 3.24–3.19 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 139.06, 134.85, 133.82, 133.49, 132.32, 129.37, 128.60, 128.13, 127.66, 127.46, 126.84, 126.42, 126.36, 125.85, 57.46, 28.96. HRMS Calcd. for $C_{18}H_{16}O_2S$ (M+) 296.0871, found 296.0864.



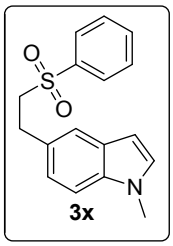
1-(2-(Phenylsulfonyl)ethyl)naphthalene, yellow solid, m.p. 98 °C-100 °C yield 46%, 27.3 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.98 (d, J = 7.2 Hz, 2H), 7.84–7.78 (m, 2H), 7.73–7.65 (m, 2H), 7.59 (t, J = 7.6 Hz, 2H), 7.51–7.45 (m, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 6.8 Hz, 1H), 3.52–3.42 (m, 4H). ^{13}C NMR (100 MHz $CDCl_3$): δ 139.05, 133.95, 133.88, 133.45, 131.23, 129.43, 129.08, 128.14, 127.93, 126.62, 126.51, 125.91, 125.55, 122.75, 56.70, 26.06. HRMS Calcd. for $C_{18}H_{16}O_2S$ (M+) 296.0871, found 296.0852.



1-Methyl-4-(2-(phenylsulfonyl)ethyl)naphthalene, white solid， m.p. 116 °C-118 °C, yield 67%, 41.6 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.01–7.98 (m, 3H), 7.80–7.78 (m, 1H), 7.69–7.66 (m, 1H), 7.61–7.49 (m, 4H), 7.20–7.14 (m, 2H), 3.49–3.42 (m, 4H), 2.63 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 139.06, 134.11, 133.83, 133.08, 131.54, 131.24, 129.40, 128.13, 126.27, 126.26, 126.23, 125.73, 125.19, 123.28, 56.81, 26.07, 19.47. HRMS Calcd. for $C_{19}H_{18}O_2S$ (M+) 310.1028, found 310.1025.

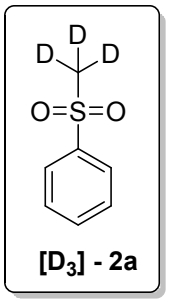


1-Fluoro-4-(2-(phenylsulfonyl)ethyl)naphthalene, light yellow solid， m.p. 91 °C-93 °C, yield 56%, 35.2 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.12–8.10 (m, 1H), 7.98 (d, J = 7.6 Hz, 2H), 7.79–7.77 (m, 1H), 7.68–7.54 (m, 5H), 7.20–7.17 (m, 1H), 7.03–6.99 (m, 1H), 3.49–3.41 (m, 4H). ^{13}C NMR (100 MHz $CDCl_3$): δ 158.27 (d, $J_{C\text{-}F}$ = 250.3 Hz), 139.01, 133.90, 132.37 (d, $J_{C\text{-}F}$ = 4.6 Hz), 129.42, 129.26 (d, $J_{C\text{-}F}$ = 4.5 Hz), 128.10, 127.55, 126.24 (d, $J_{C\text{-}F}$ = 4.7 Hz), 126.19 (d, $J_{C\text{-}F}$ = 1.8 Hz), 124.16 (d, $J_{C\text{-}F}$ = 16.2 Hz), 122.86 (d, $J_{C\text{-}F}$ = 2.8 Hz), 121.57 (d, $J_{C\text{-}F}$ = 5.7 Hz), 108.95 (d, $J_{C\text{-}F}$ = 19.9 Hz), 56.68, 25.67. HRMS Calcd. for $C_{18}H_{15}FO_2S$ (M+) 314.0777, found 314.0769.



3x

1-methyl-5-(2-(phenylsulfonyl)ethyl)-1H-indole, yield 73%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.96 (d, J = 8.0 Hz, 2H), 7.68–7.55 (m, 3H), 7.34 (s, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 3.2 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.38 (d, J = 2.4 Hz, 1H), 3.75 (s, 3H), 3.42–3.38(m, 2H), 3.15–3.13 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$):δ 139.16, 135.73, 133.72, 129.48, 129.33, 128.79, 128.16, 128.13, 121.93, 120.23, 109.58, 100.59, 58.42, 32.91, 28.94.



[D_3] - 2a

Trideutero- (methylsulfonyl)benzene, white solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.95 (d, J = 7.6 Hz, 2H), 7.69–7.5 (m, 1H), 7.60–7.57 (m, 2H).

C. References

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(2) (a) B. P. Amit, C. Sukbok, *Org. Lett.* 2015, **17**, 660; (b) S. Wang, M. Wang, L. Wang, P. Li, J. Yang, *Tetrahedron* 2011, **67**, 4800; (c) F. Peter, T. David, N. Per-Ola, *Chirality* 2003, **15**, 360.

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(6) S. Andrei, B. C. Steven, C. S. Aaron, M. Vincent *Org. Lett.*, 2013, **15**, 6226.

(7) D. W. Jimmie, J. K. Being, K. M. David, T. Ward, A. T. Jon, *J. Am. Chem. Soc.* 2010, **132**, 12179.

5. Copies of ^{1}H NMR and ^{13}C NMR spectra

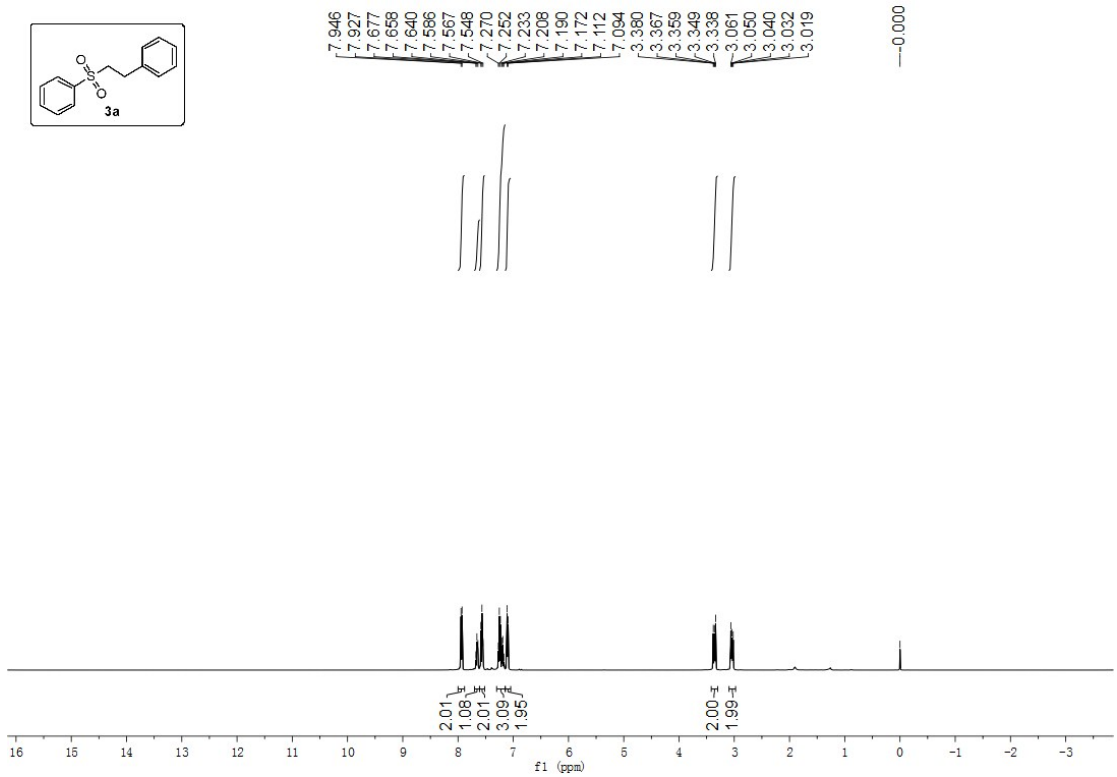

Figure 1. ^{1}H NMR spectra of **3a**

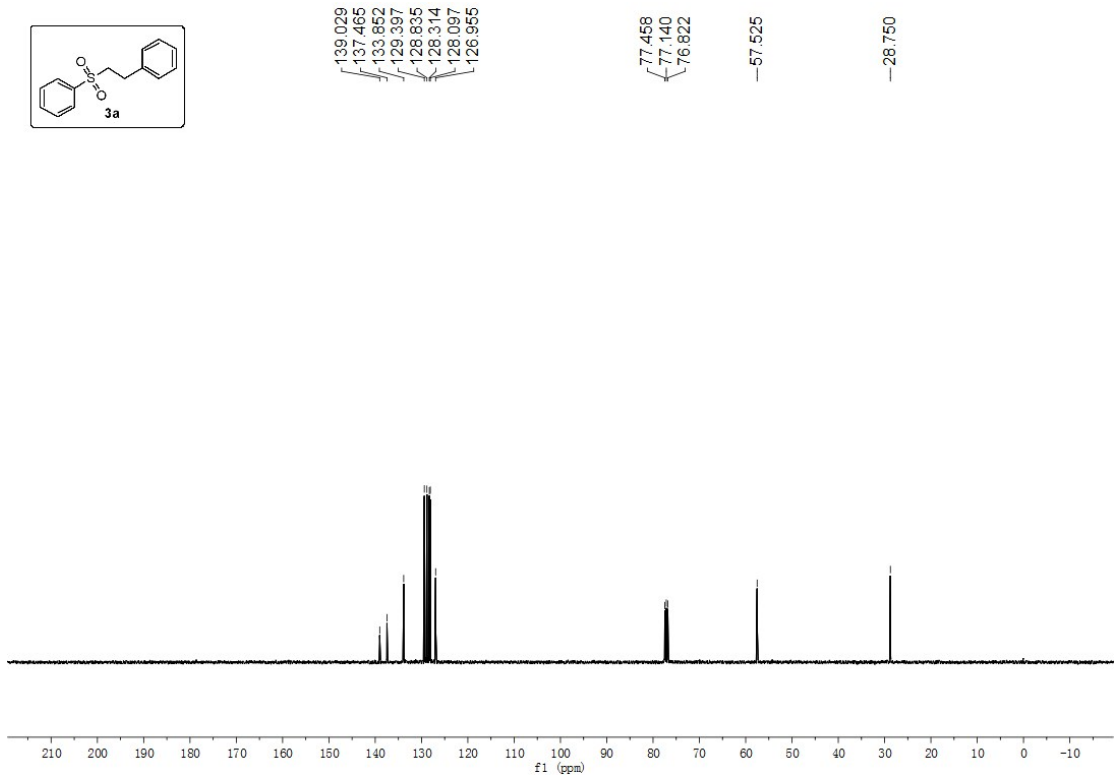

Figure 2. ^{13}C NMR spectra of **3a**

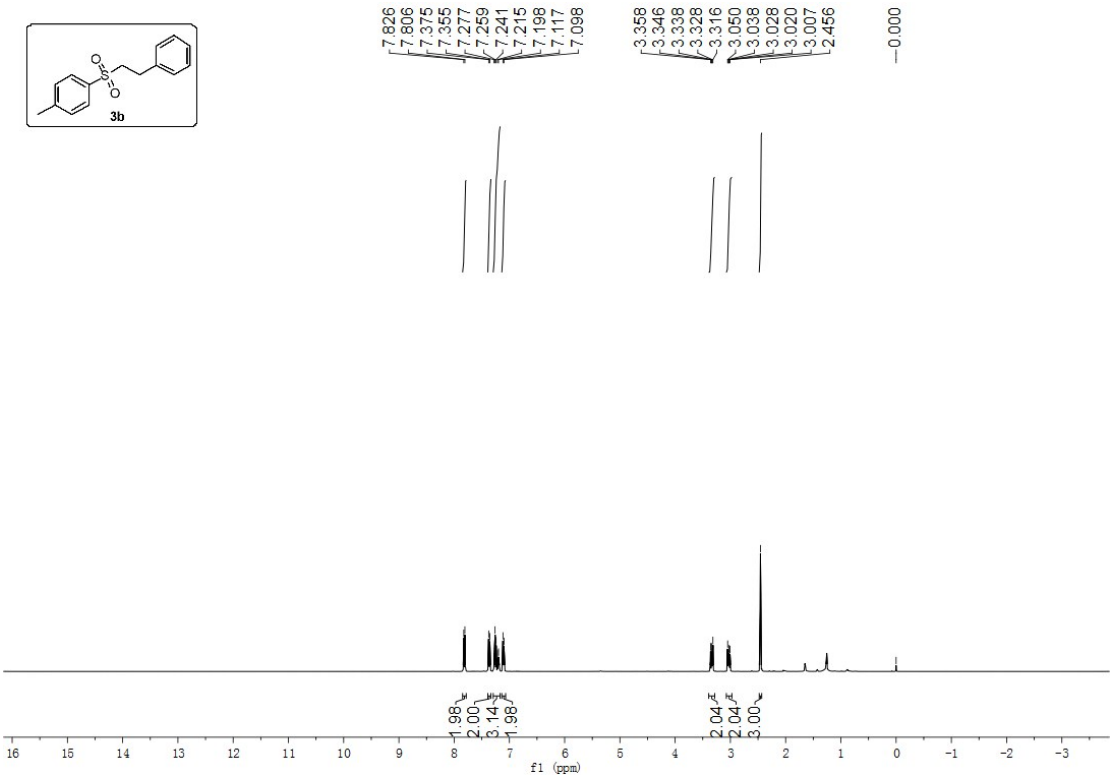

Figure 3. ^{1}H NMR spectra of **3b**

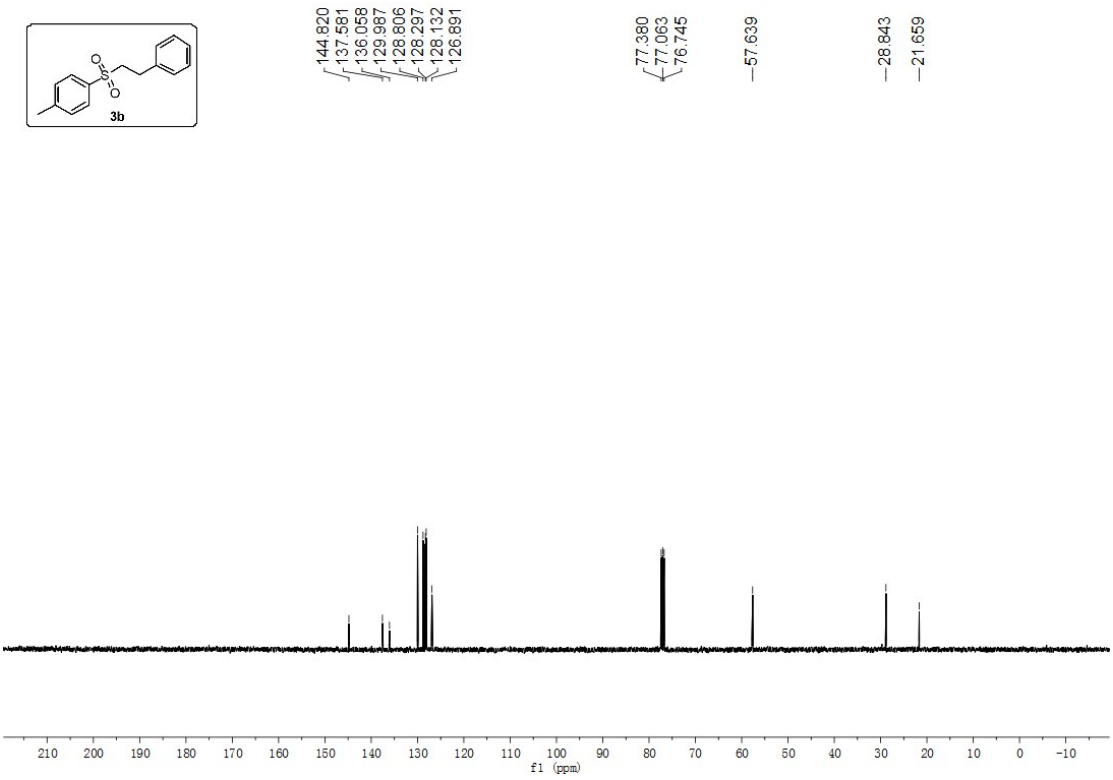

Figure 4. ^{13}C NMR spectra of **3b**

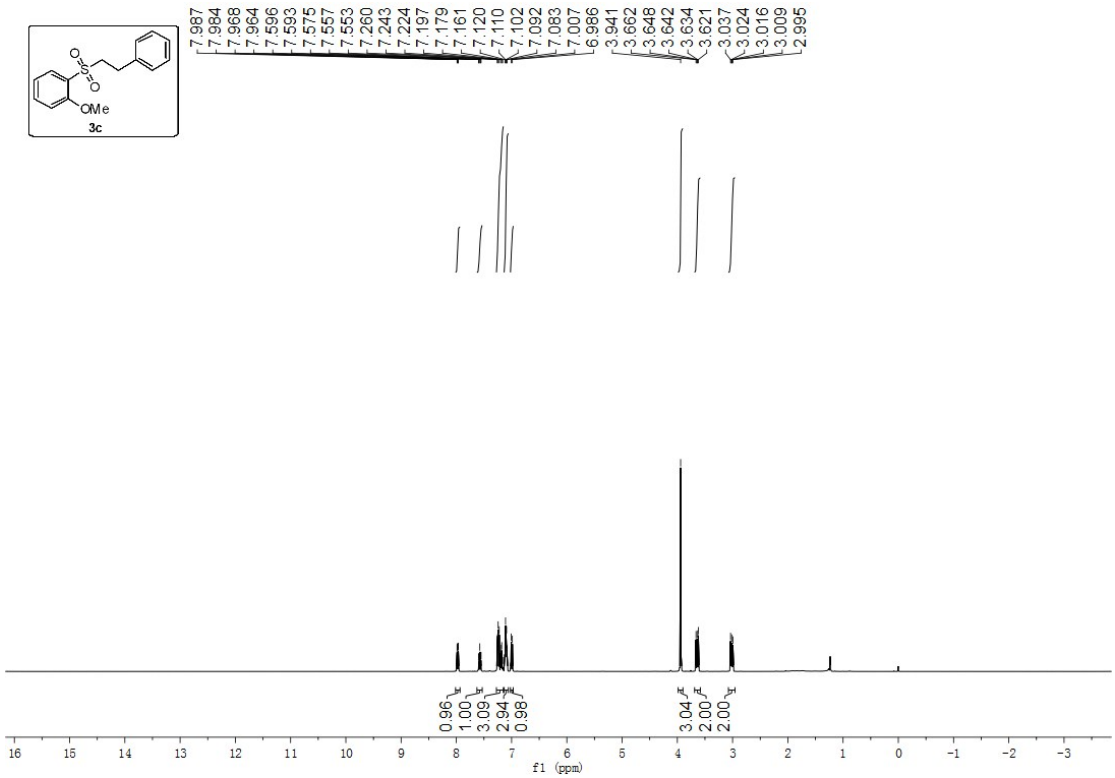

Figure 5. ^{1}H NMR spectra of **3c**

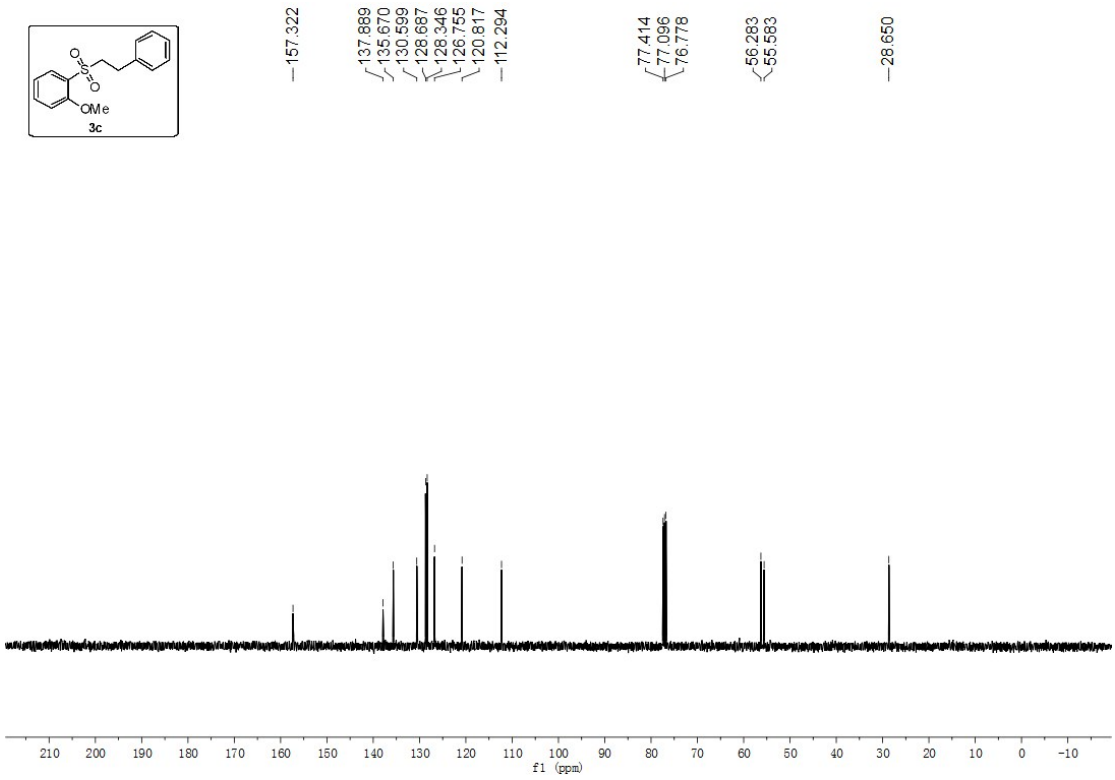

Figure 6. ^{13}C NMR spectra of **3c**

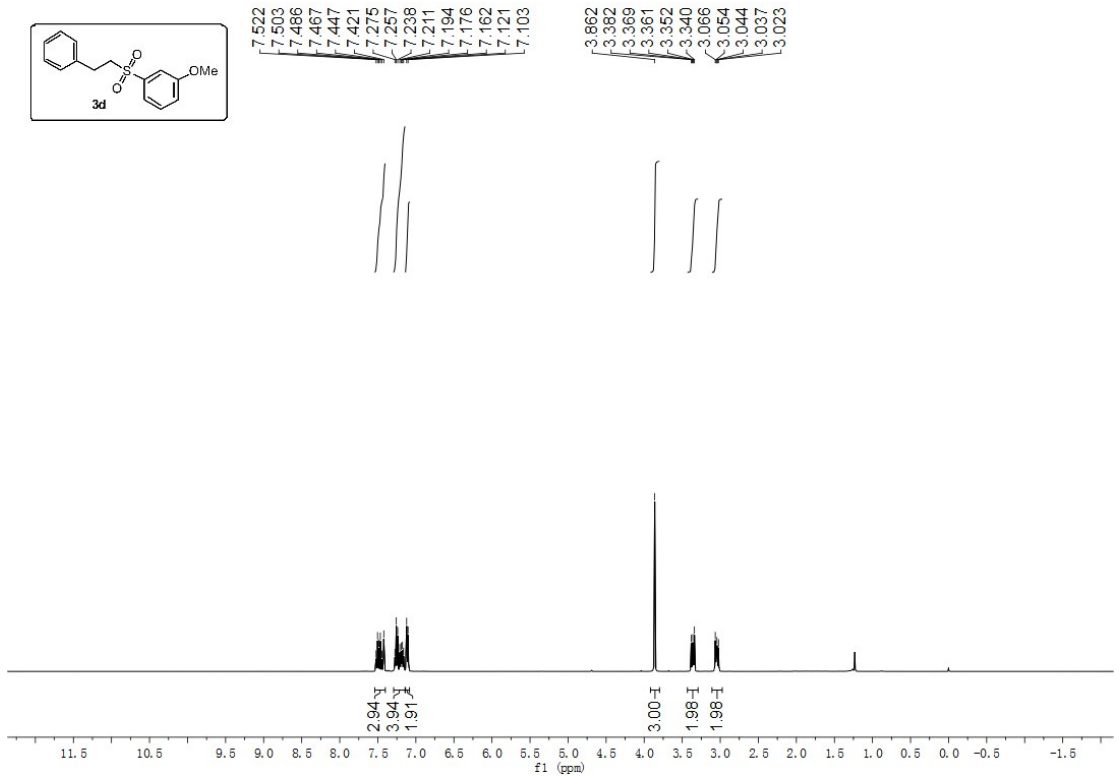

Figure 7. ^{1}H NMR spectra of **3d**

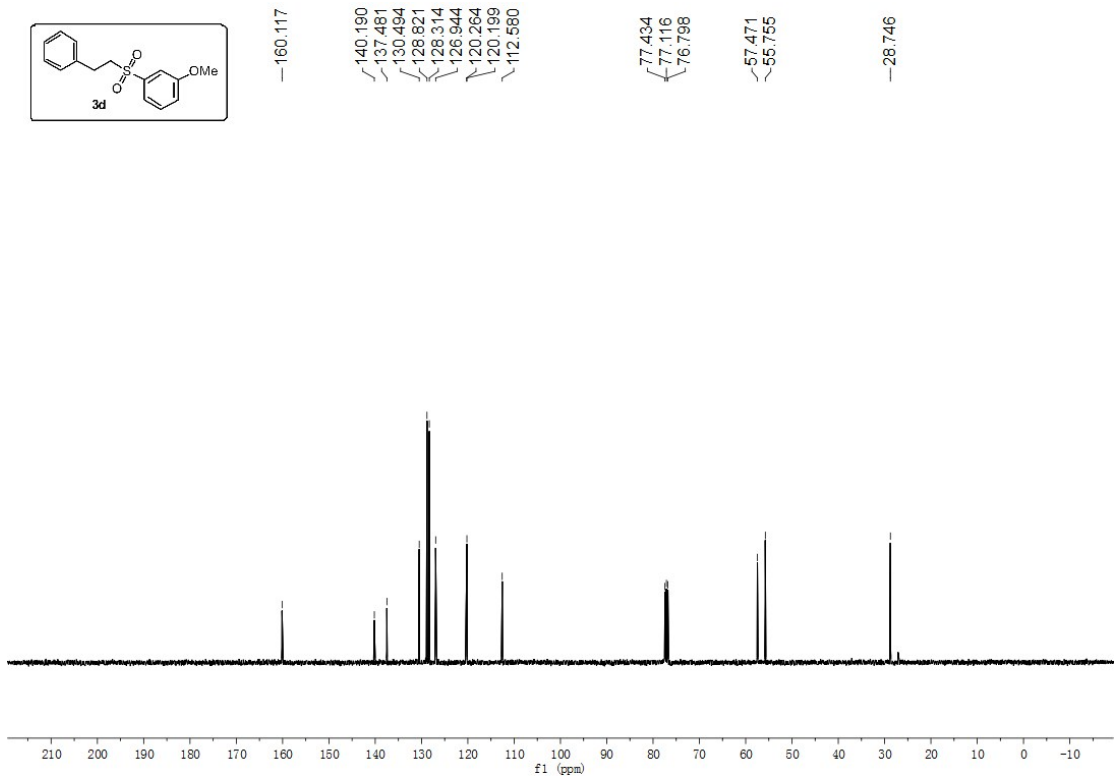

Figure 8. ^{13}C NMR spectra of **3d**

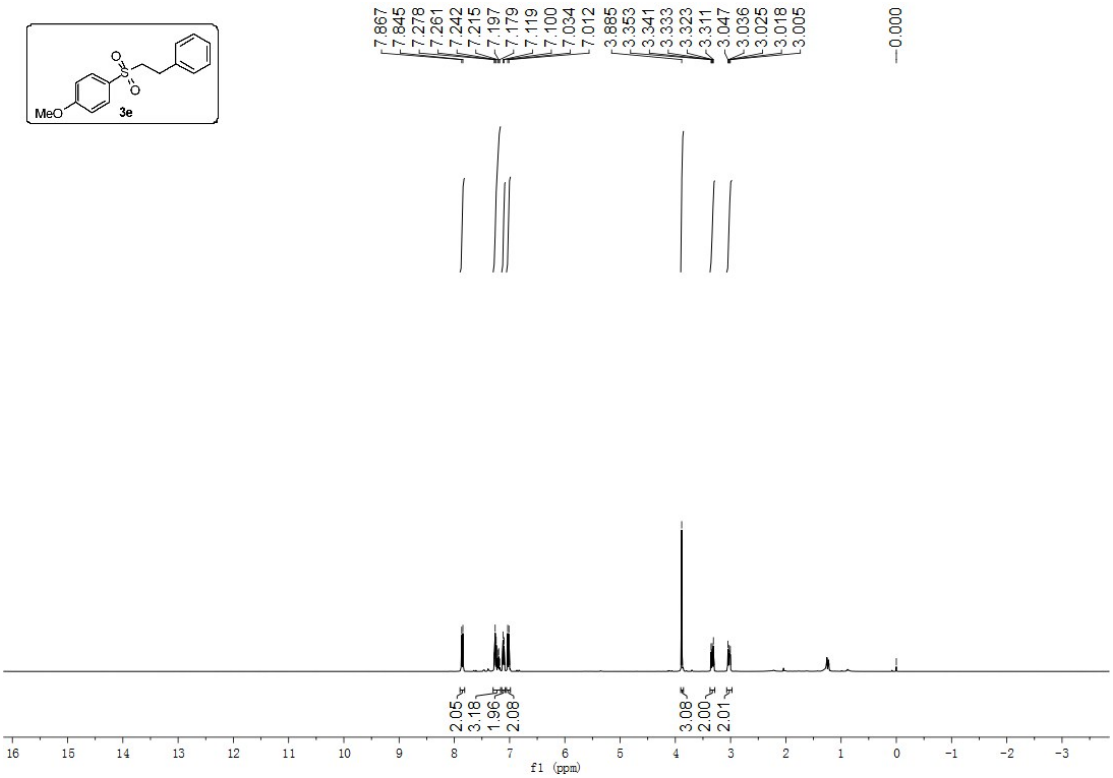

Figure 9. ^{1}H NMR spectra of **3e**

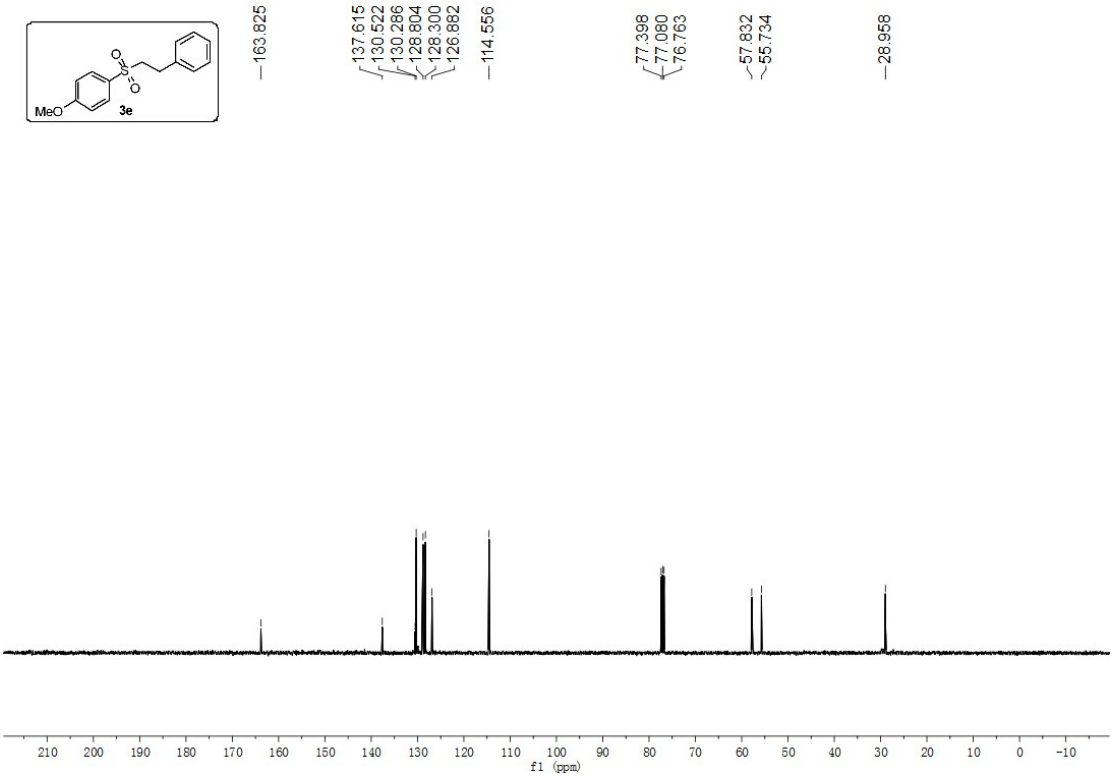

Figure 10. ^{13}C NMR spectra of **3e**

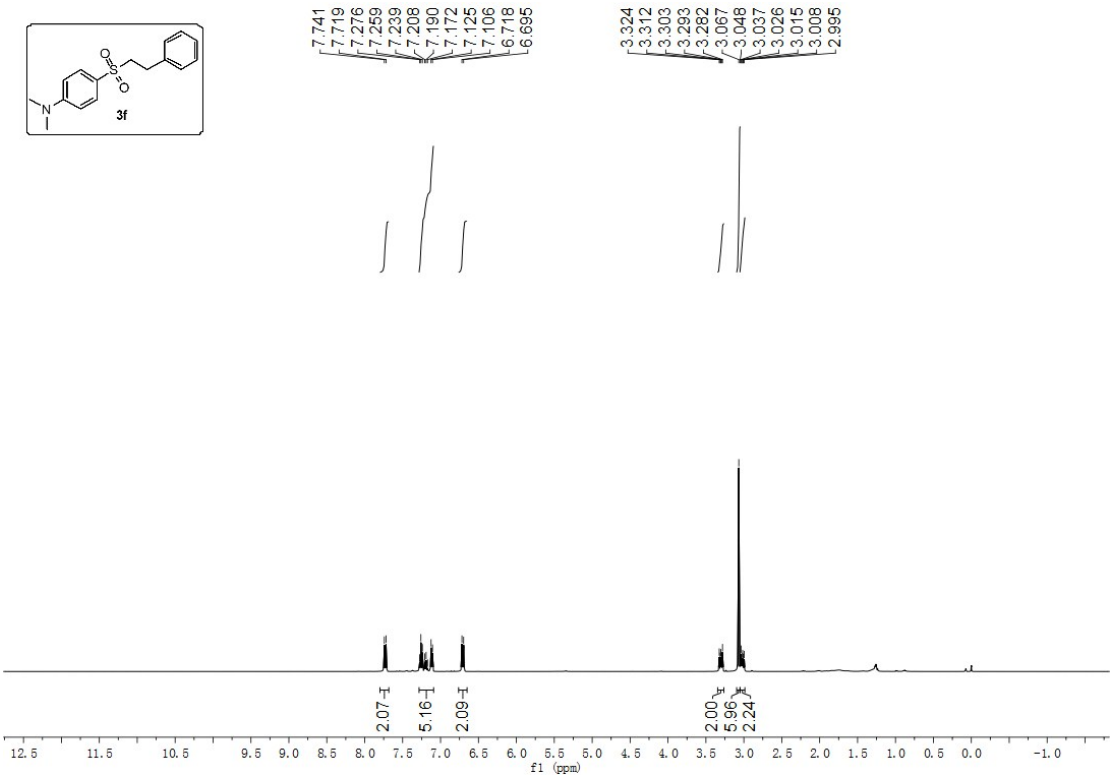

Figure 11. ^{1}H NMR spectra of **3f**

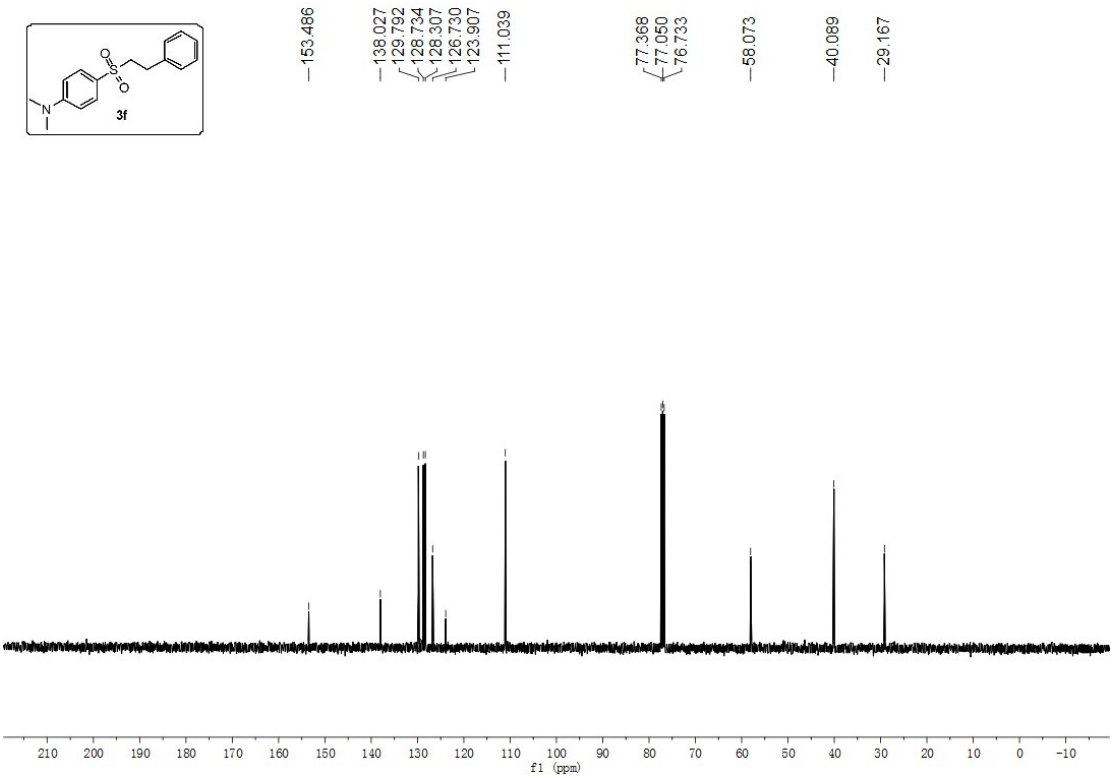

Figure 12. ^{13}C NMR spectra of **3f**

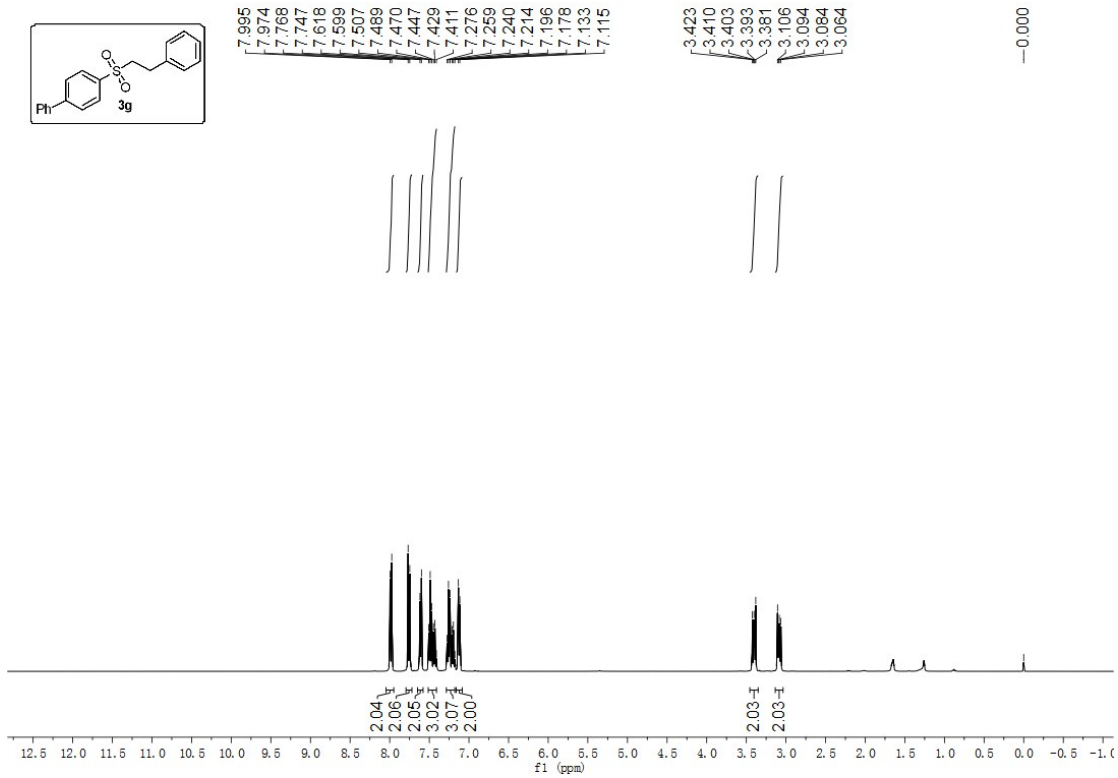

Figure 13. ^{1}H NMR spectra of **3g**

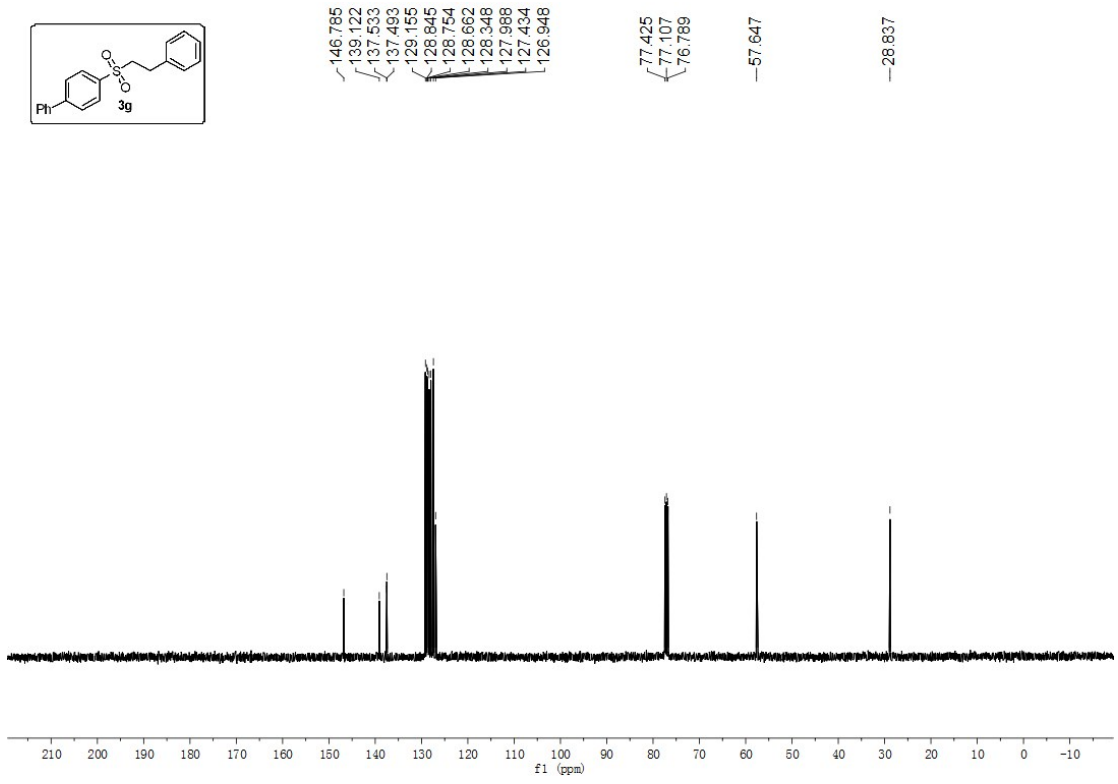

Figure 14. ^{13}C NMR spectra of **3g**

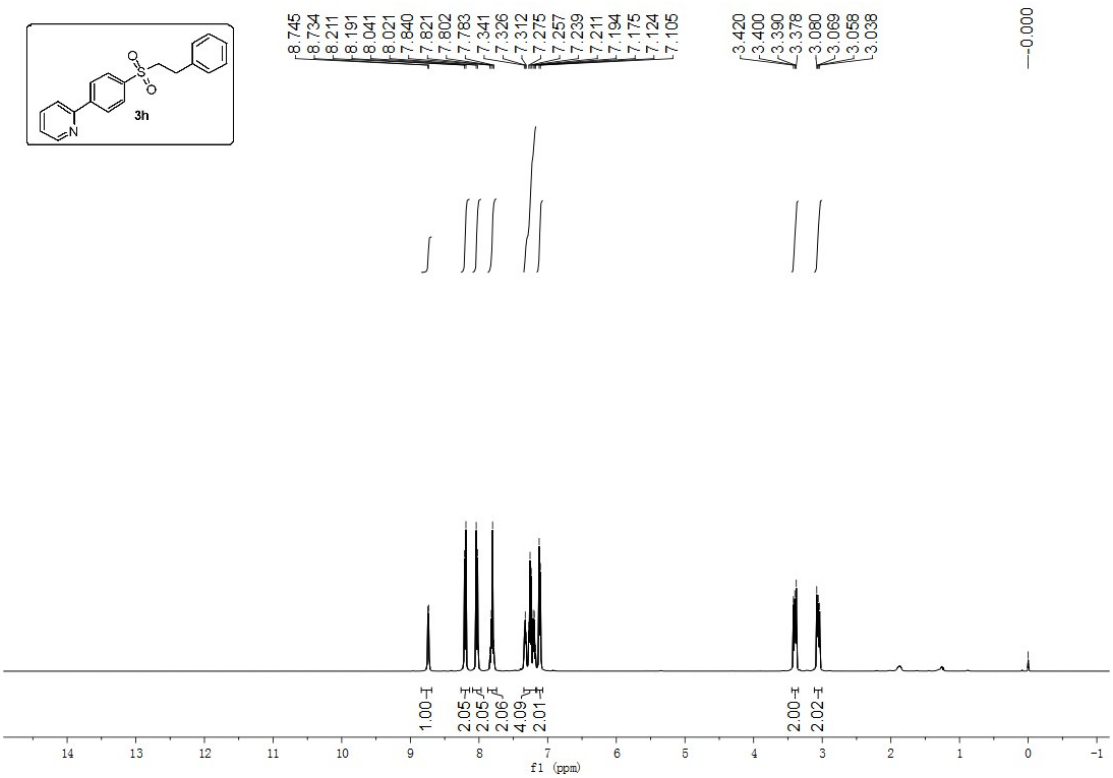

Figure 15. ^{1}H NMR spectra of **3h**

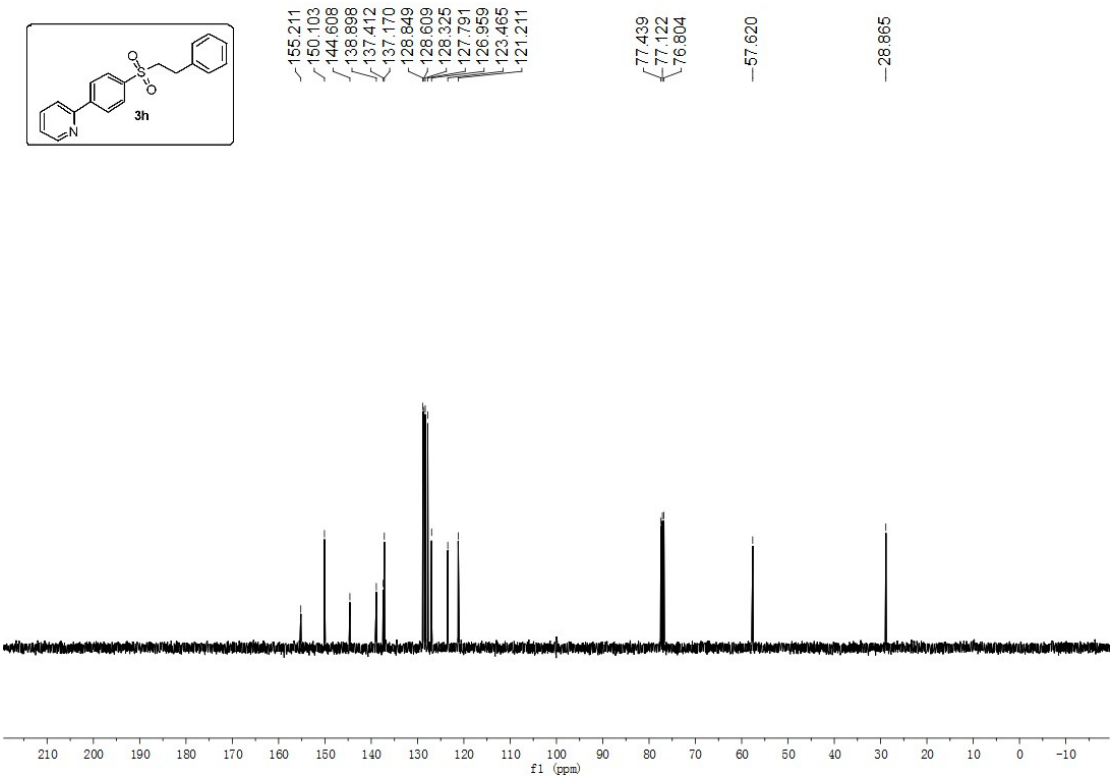

Figure 16. ^{13}C NMR spectra of **3h**

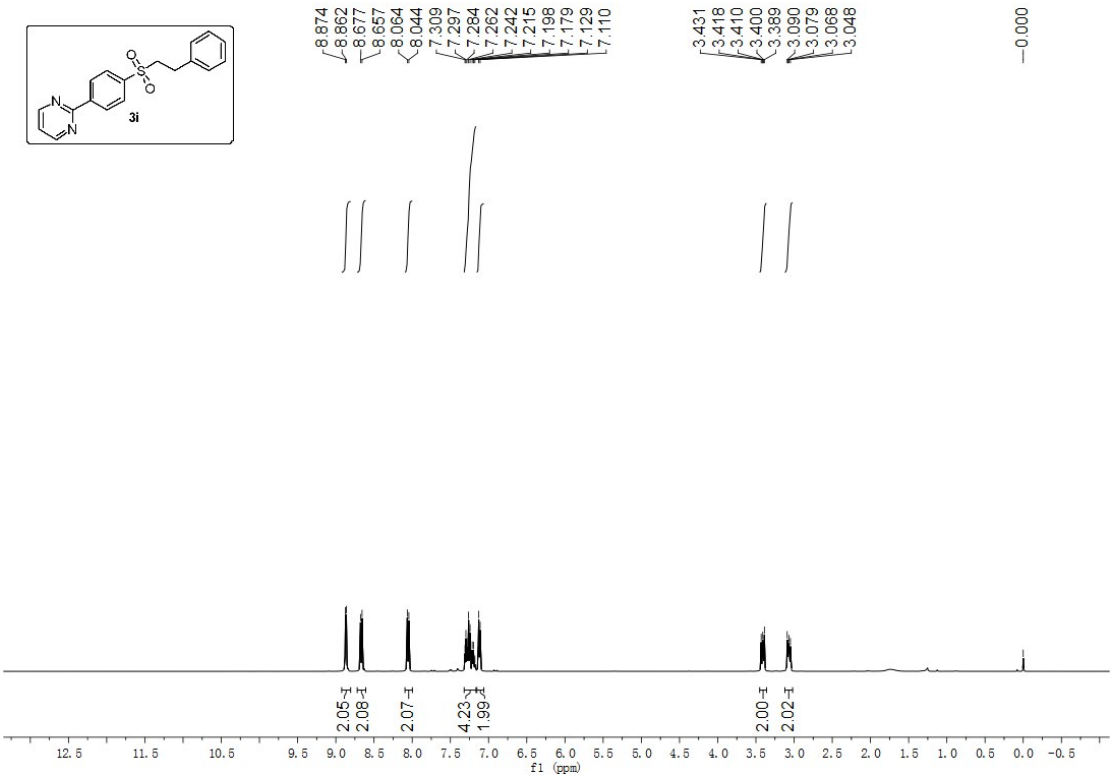

Figure 17. ^{1}H NMR spectra of **3i**

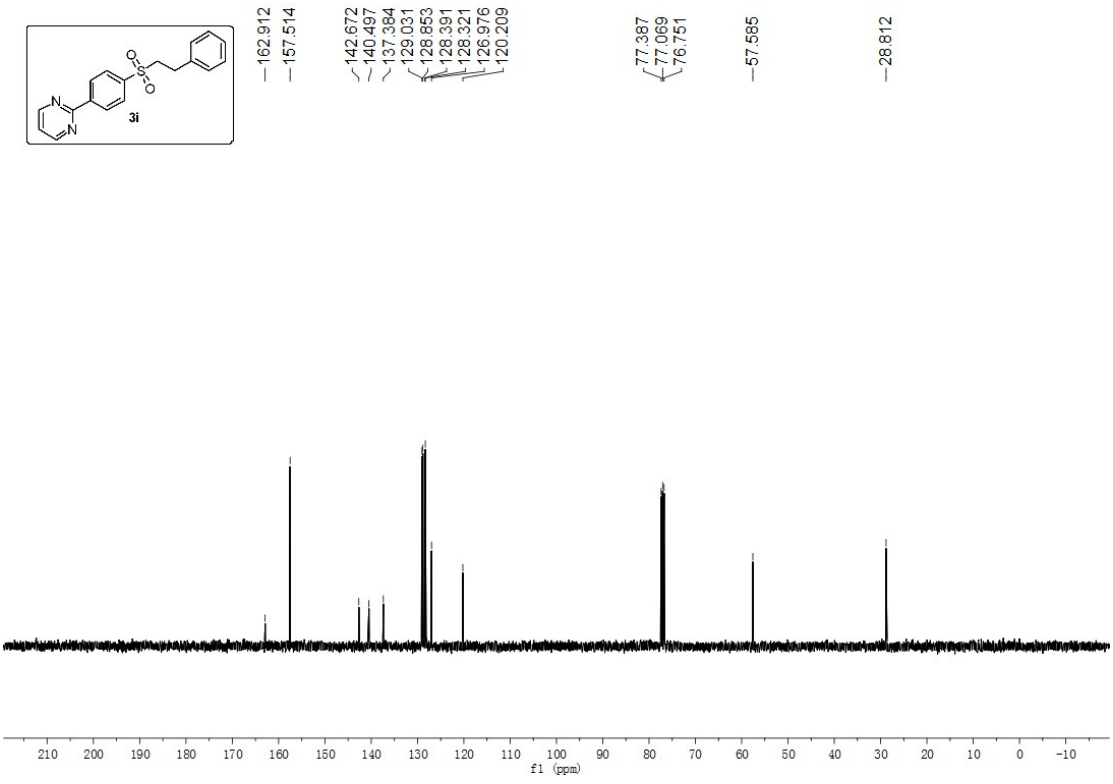

Figure 18. ^{13}C NMR spectra of **3i**

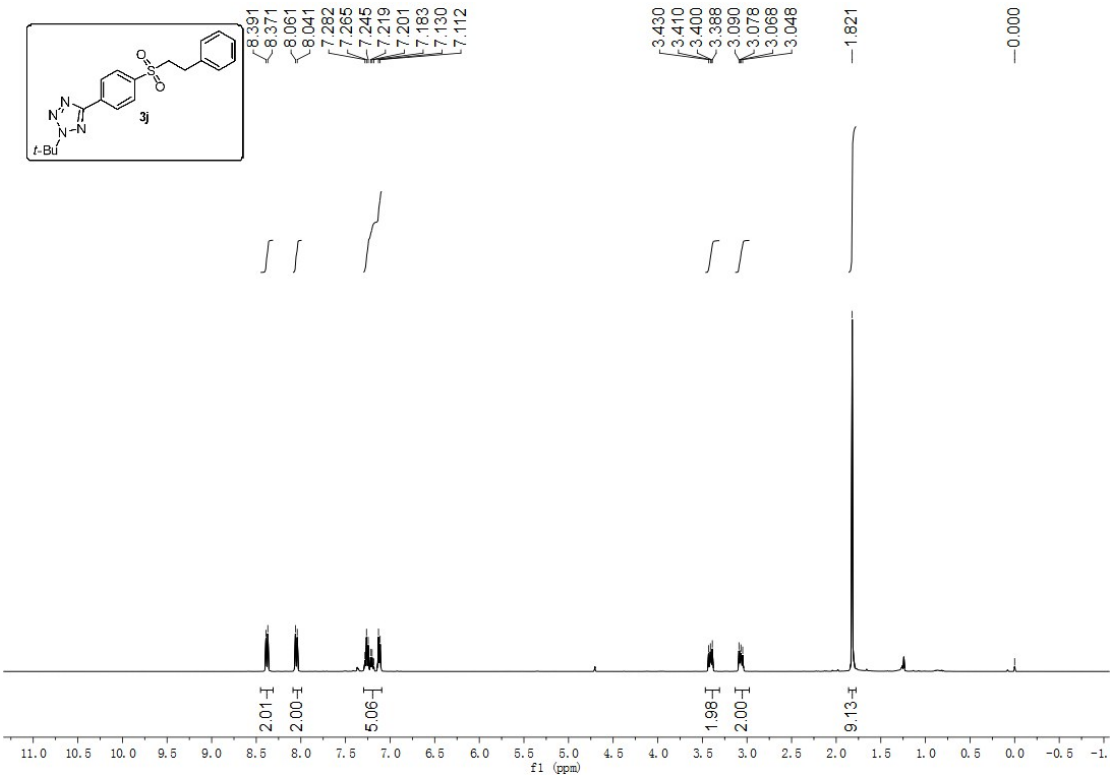

Figure 19. ^{1}H NMR spectra of **3j**

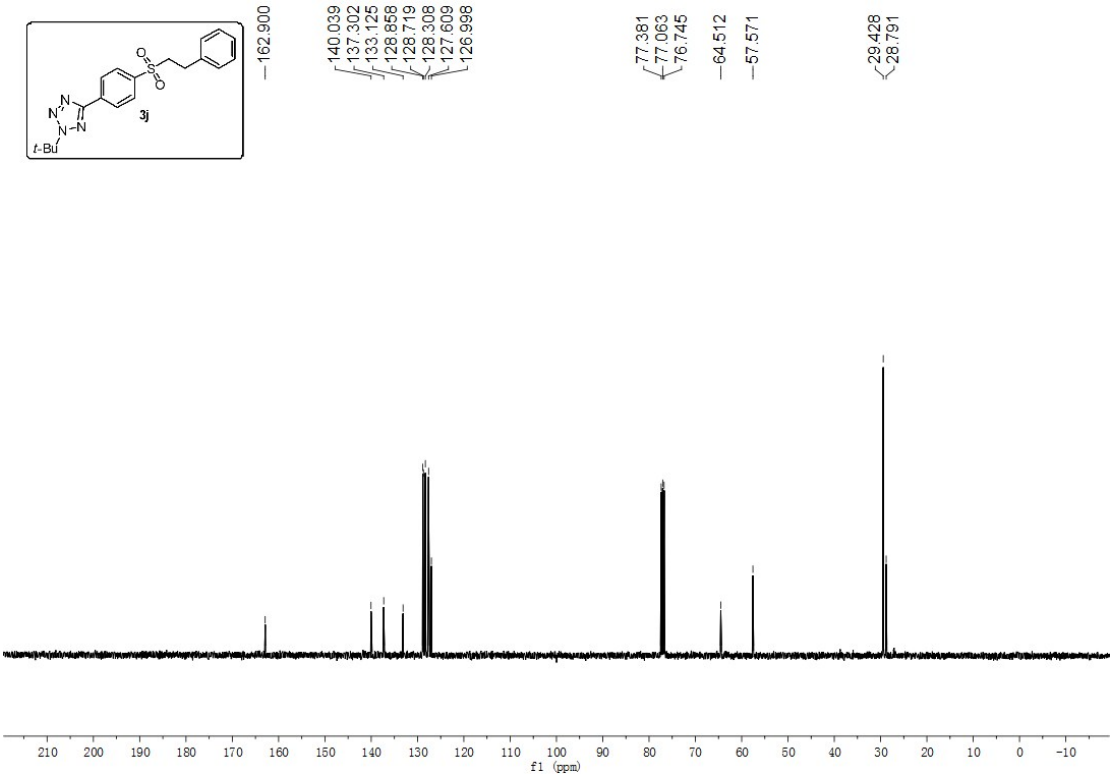

Figure 20. ^{13}C NMR spectra of **3j**

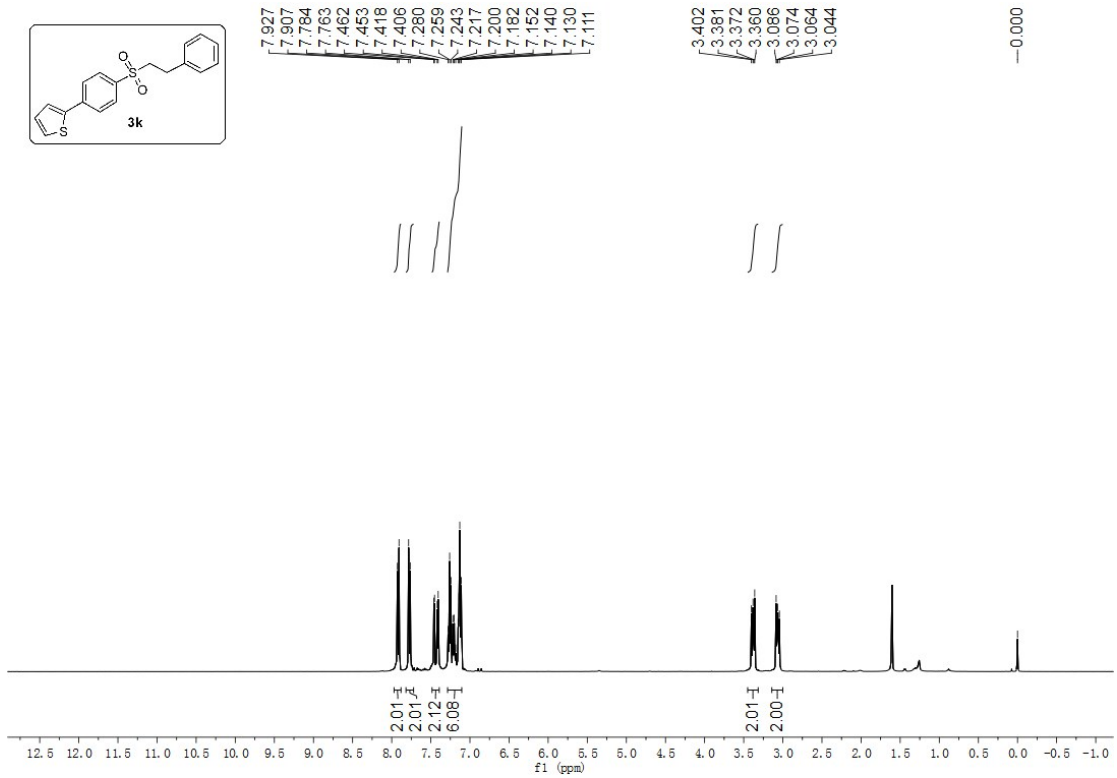

Figure 21. ^{1}H NMR spectra of **3k**

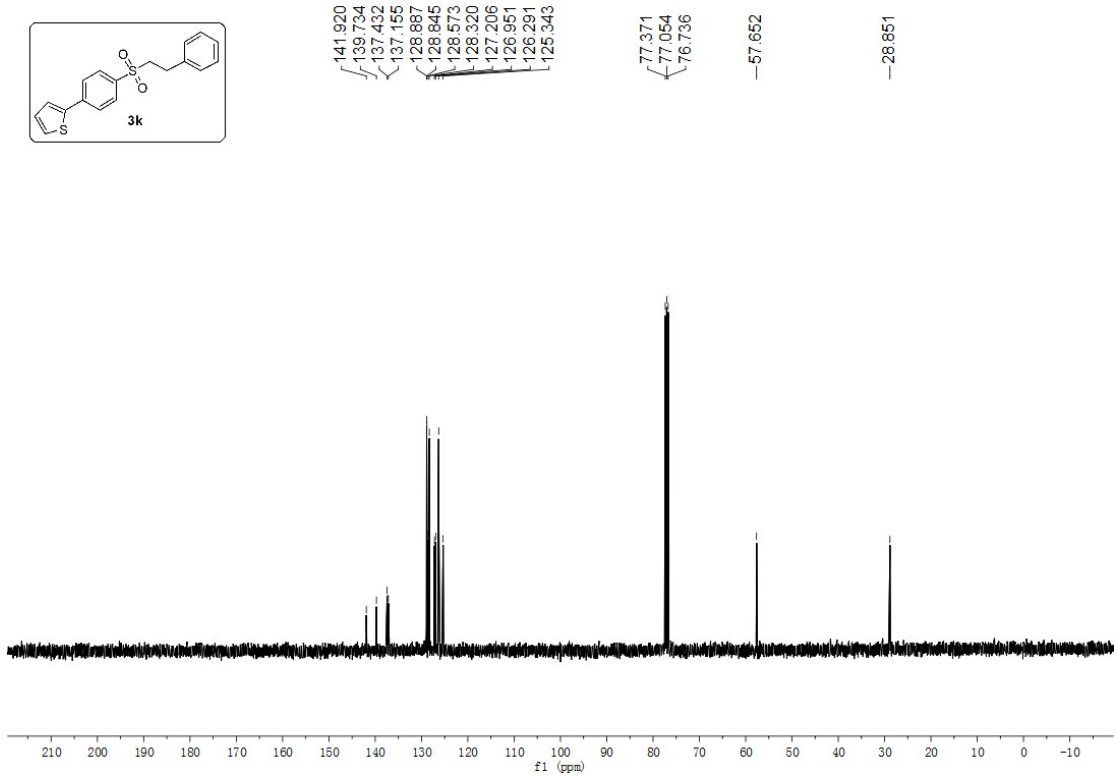

Figure 22. ^{13}C NMR spectra of **3k**

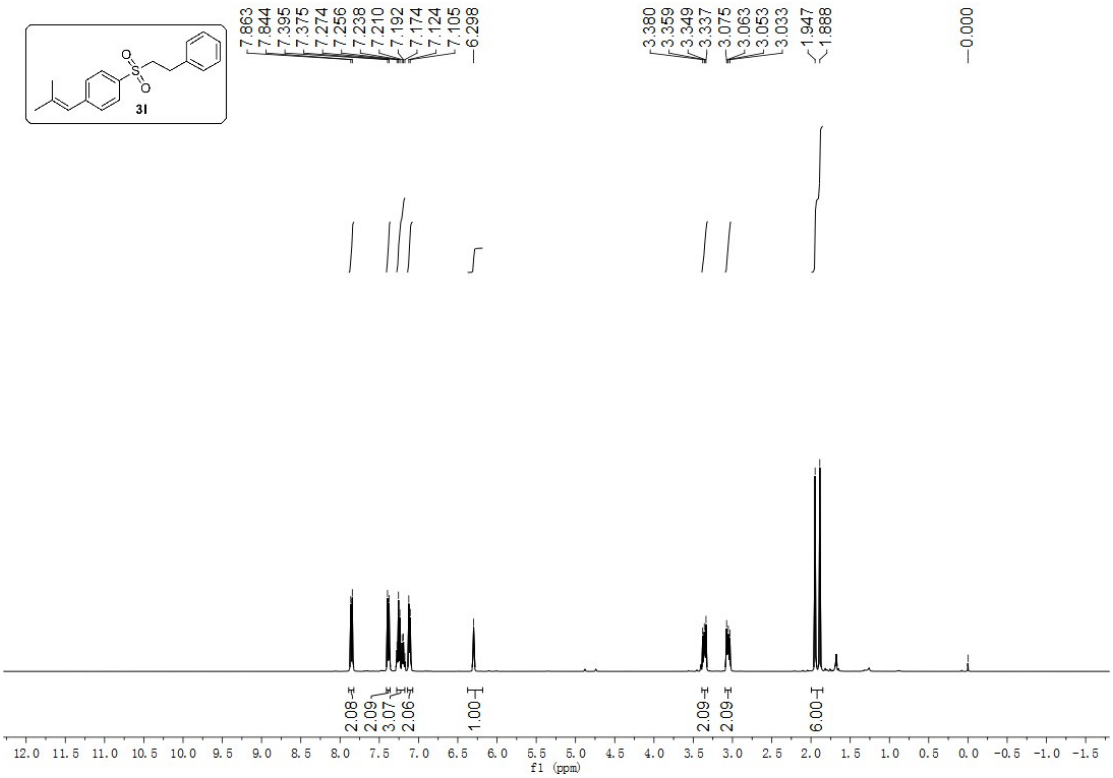

Figure 23. ^{1}H NMR spectra of **3l**

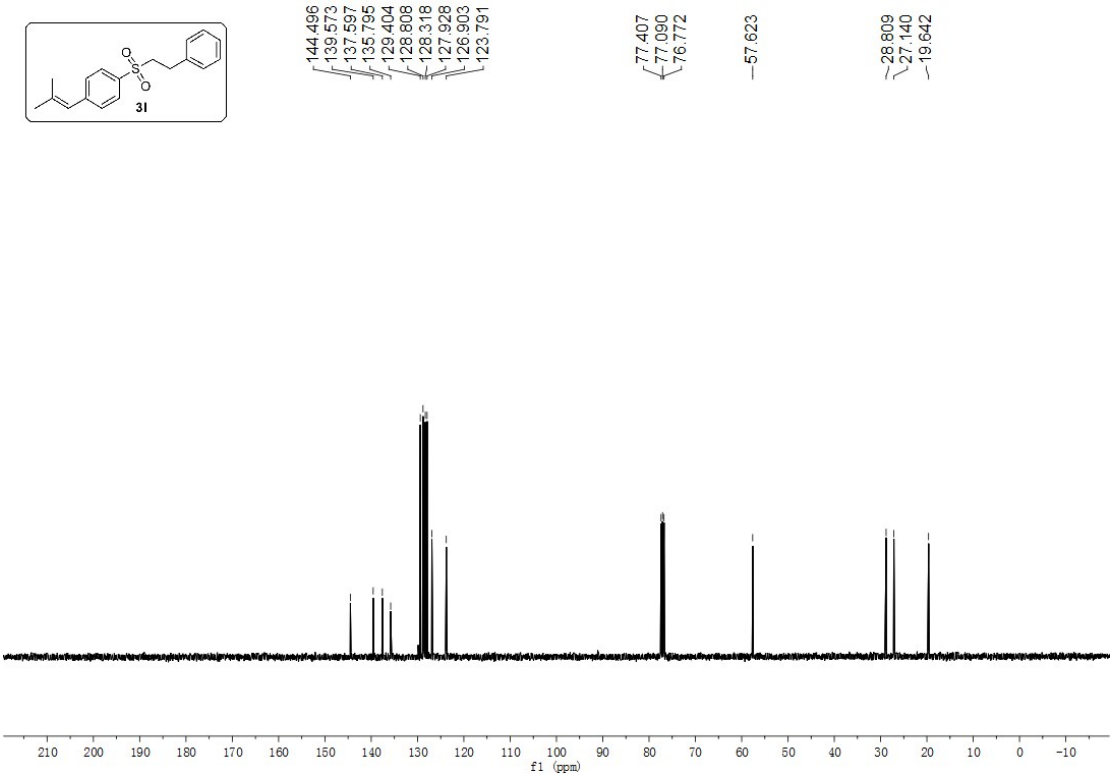

Figure 24. ^{13}C NMR spectra of **3l**

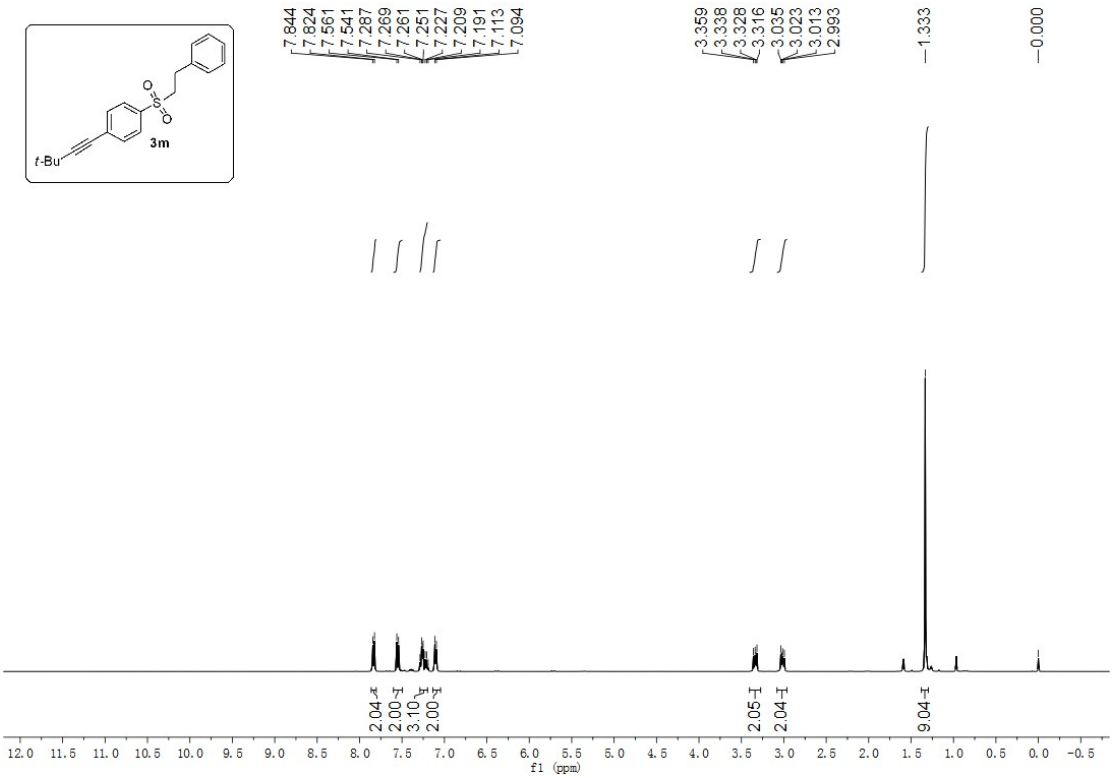

Figure 25. ^{1}H NMR spectra of **3m**

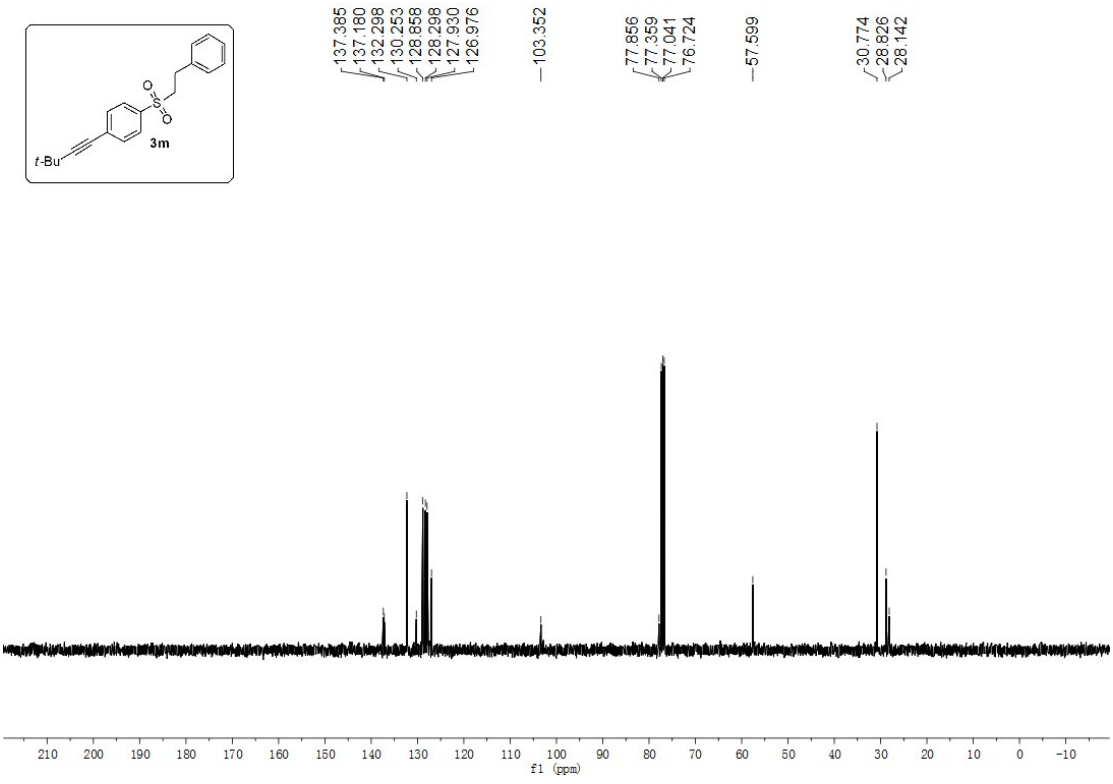

Figure 26. ^{13}C NMR spectra of **3m**

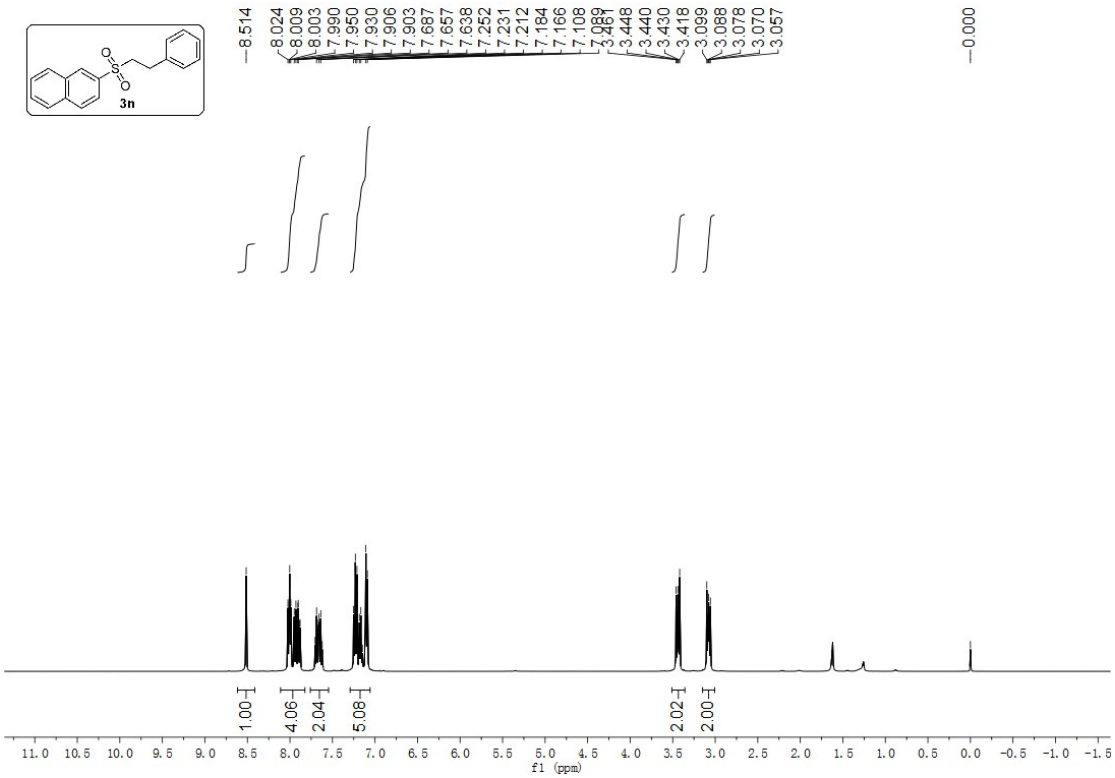

Figure 27. ^{1}H NMR spectra of **3n**

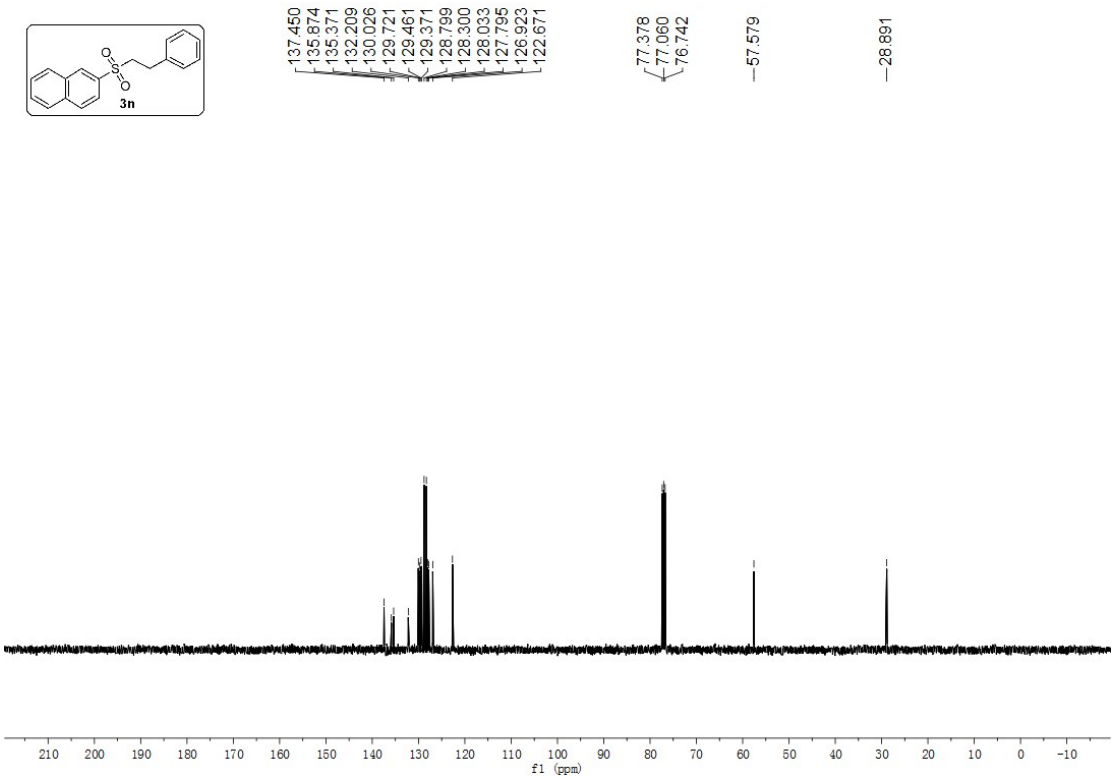

Figure 28. ^{13}C NMR spectra of **3n**

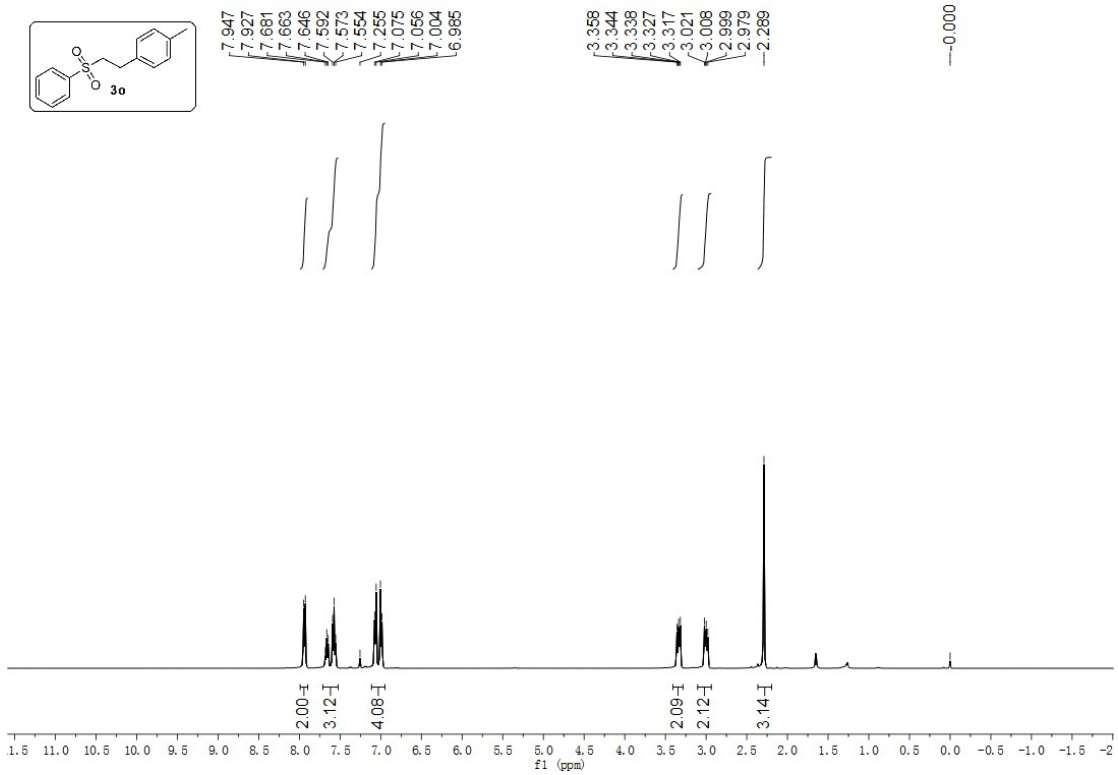

Figure 29. ^{1}H NMR spectra of **3o**

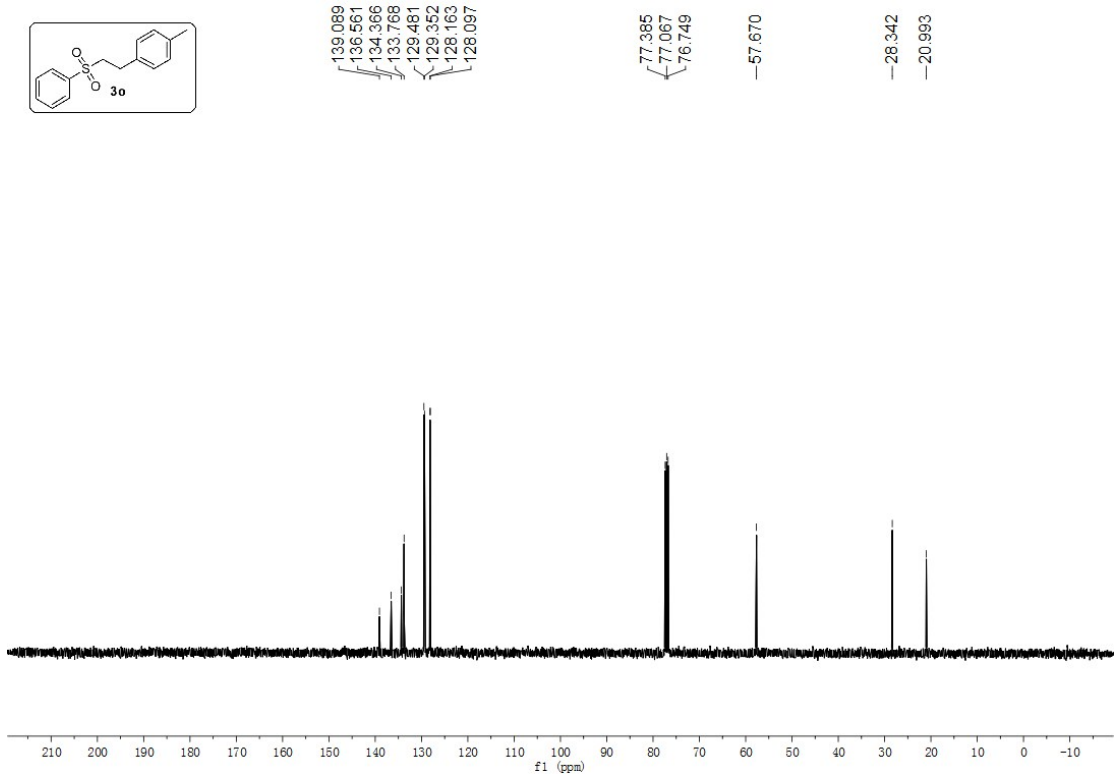

Figure 30. ^{13}C NMR spectra of **3o**

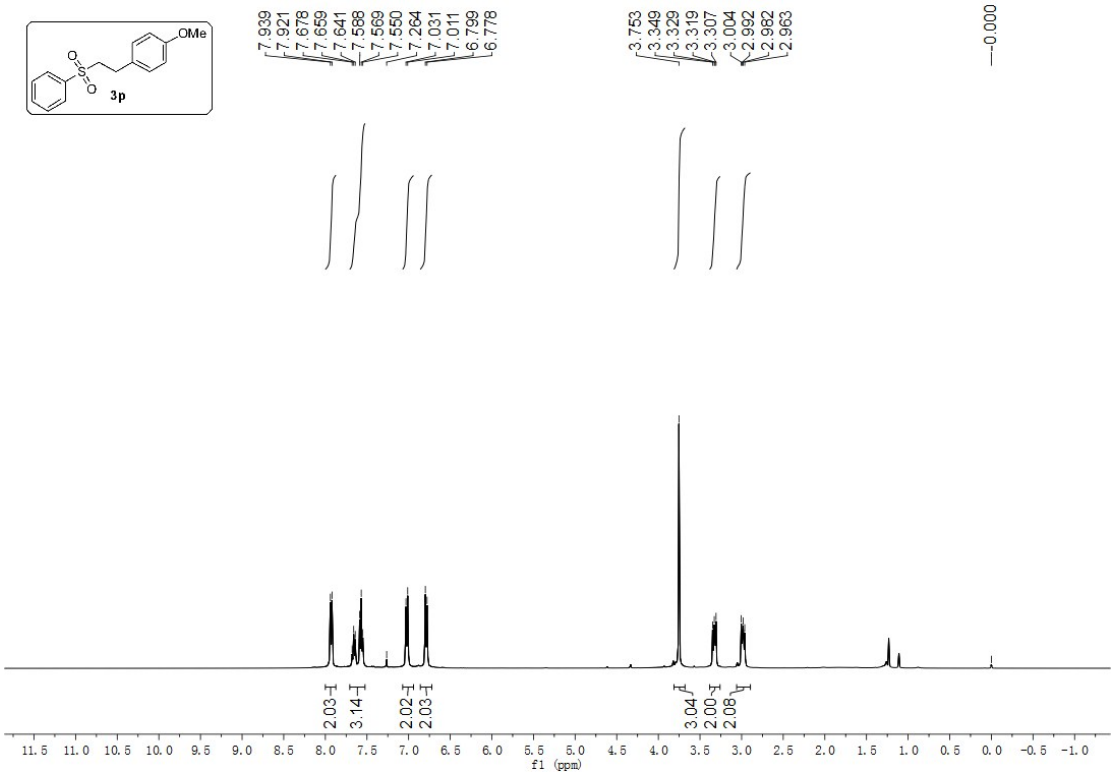

Figure 31. ^{1}H NMR spectra of **3p**

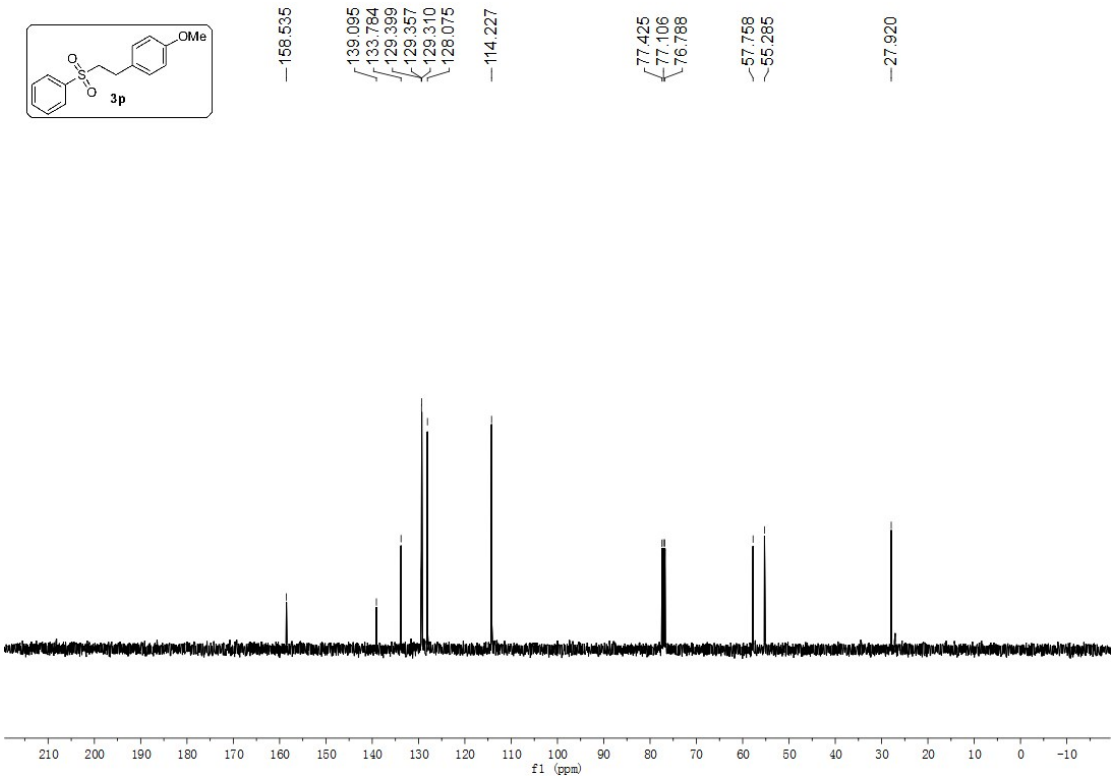

Figure 32. ^{13}C NMR spectra of **3p**

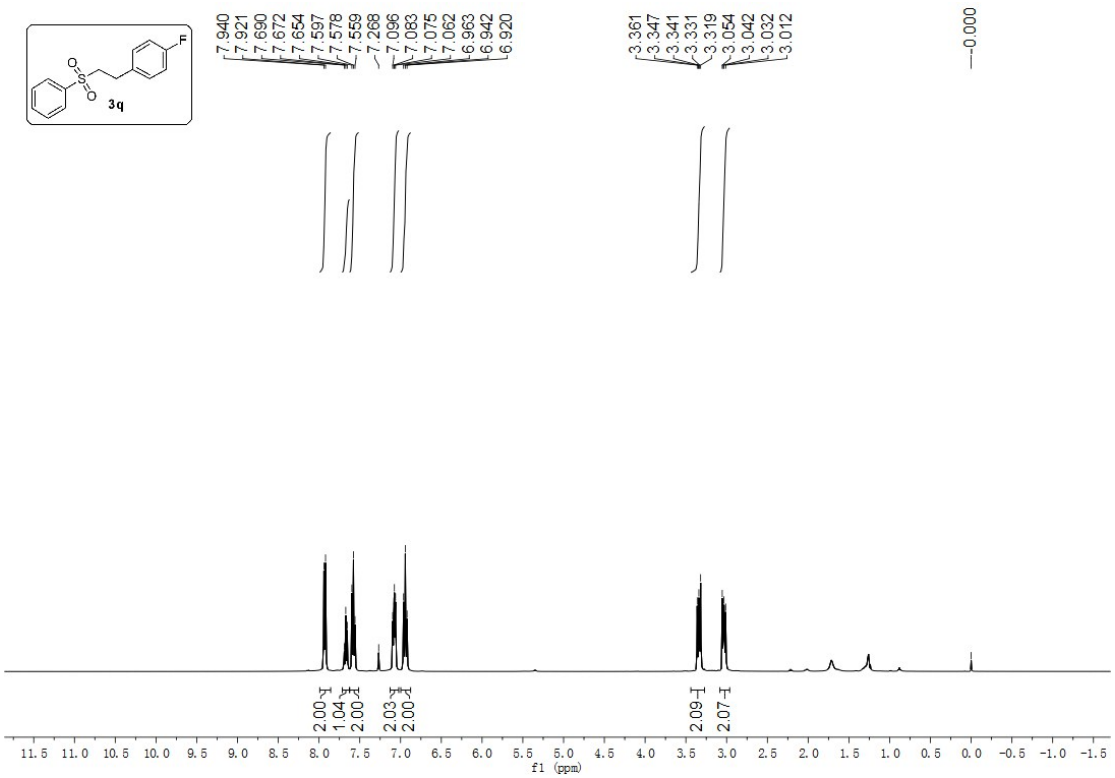

Figure 33. ^{1}H NMR spectra of **3q**

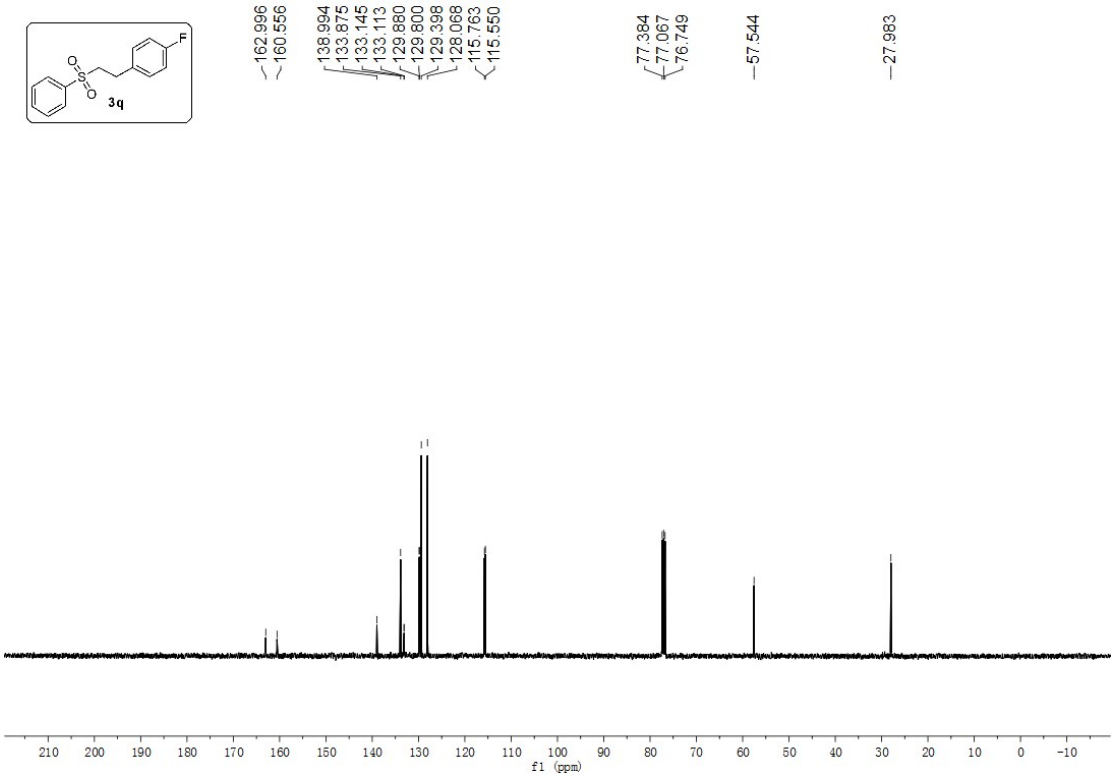

Figure 34. ^{13}C NMR spectra of **3q**

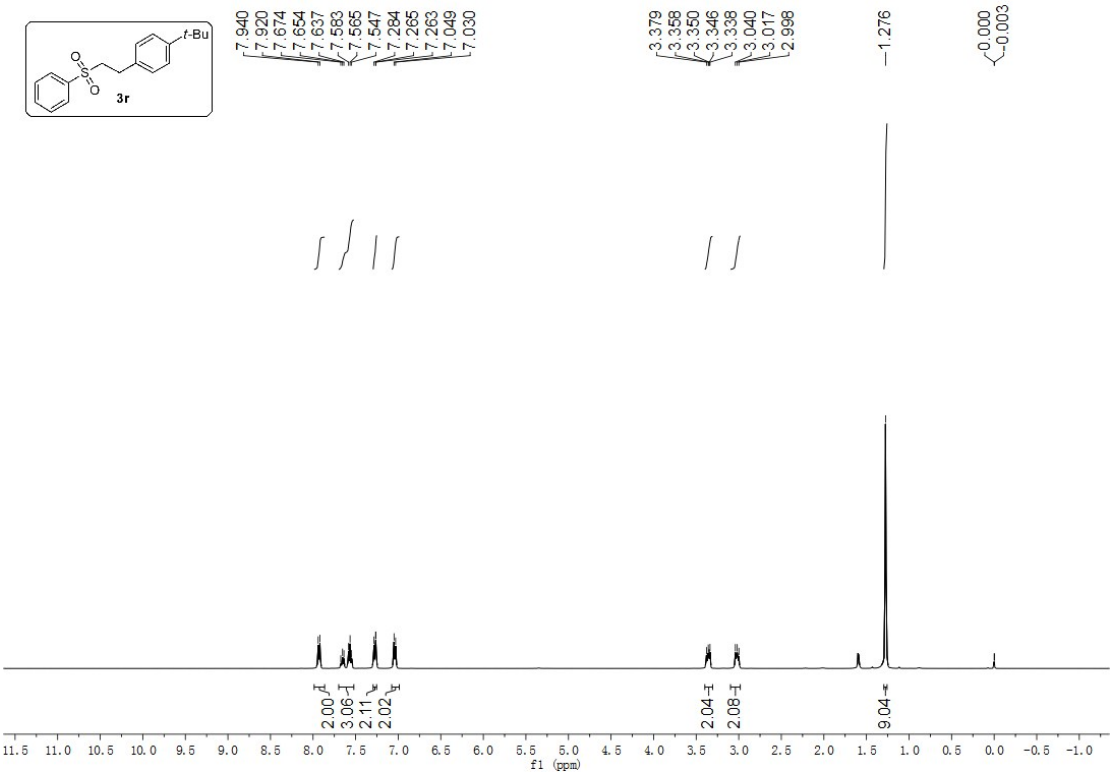

Figure 35. ^{1}H NMR spectra of **3r**

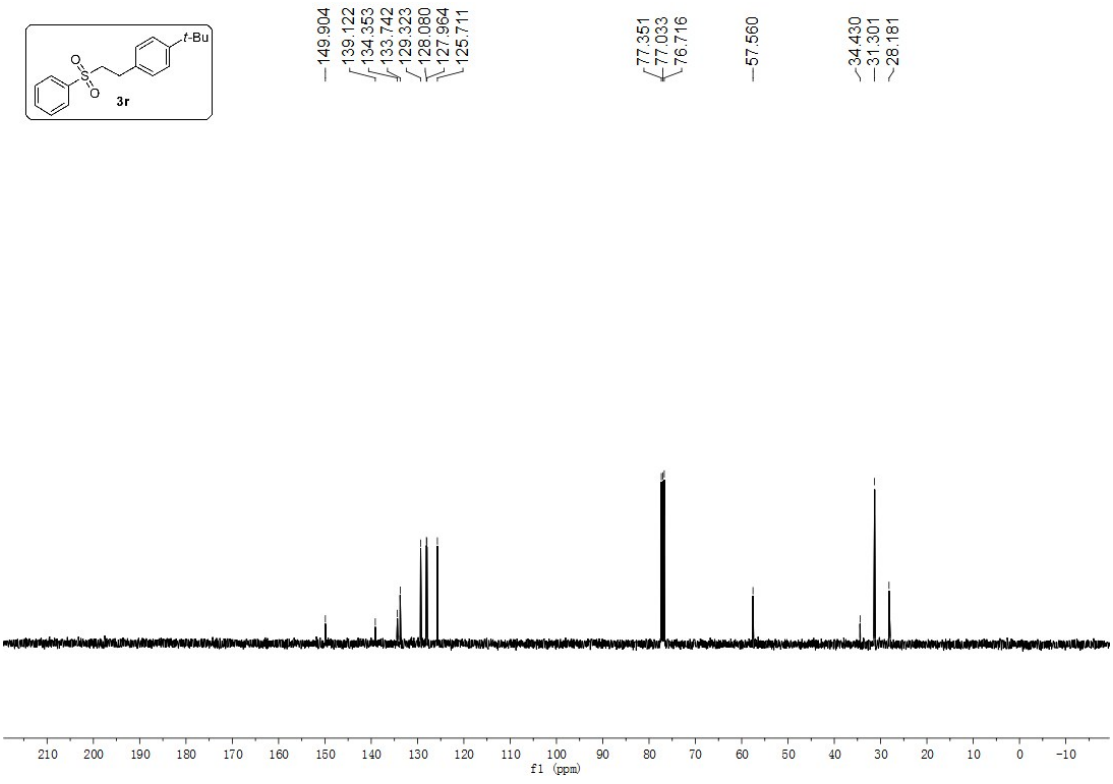

Figure 36. ^{13}C NMR spectra of **3r**

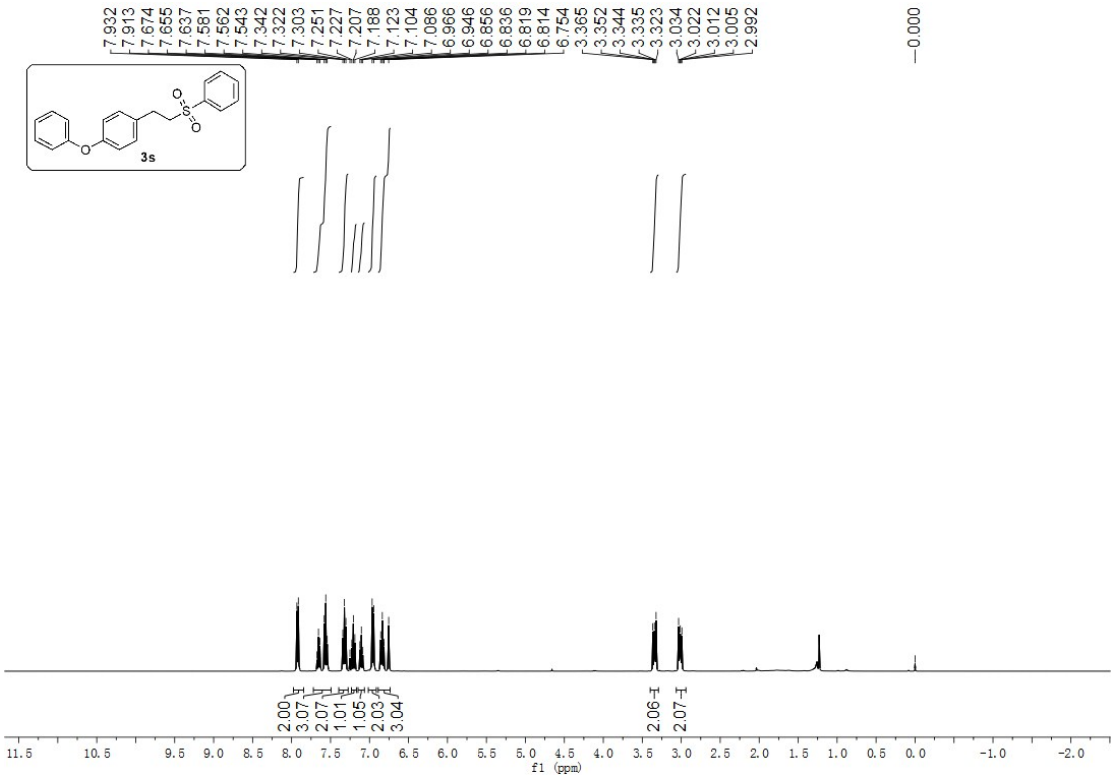

Figure 37. ^{1}H NMR spectra of **3s**

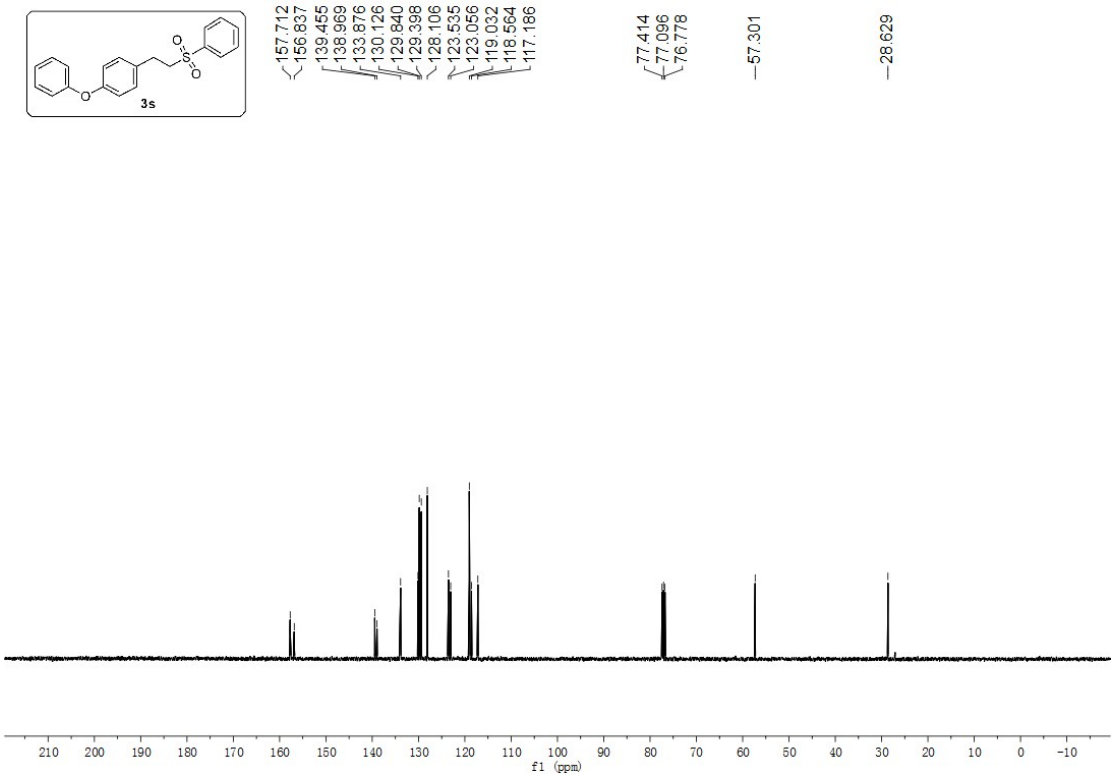

Figure 38. ^{13}C NMR spectra of **3s**

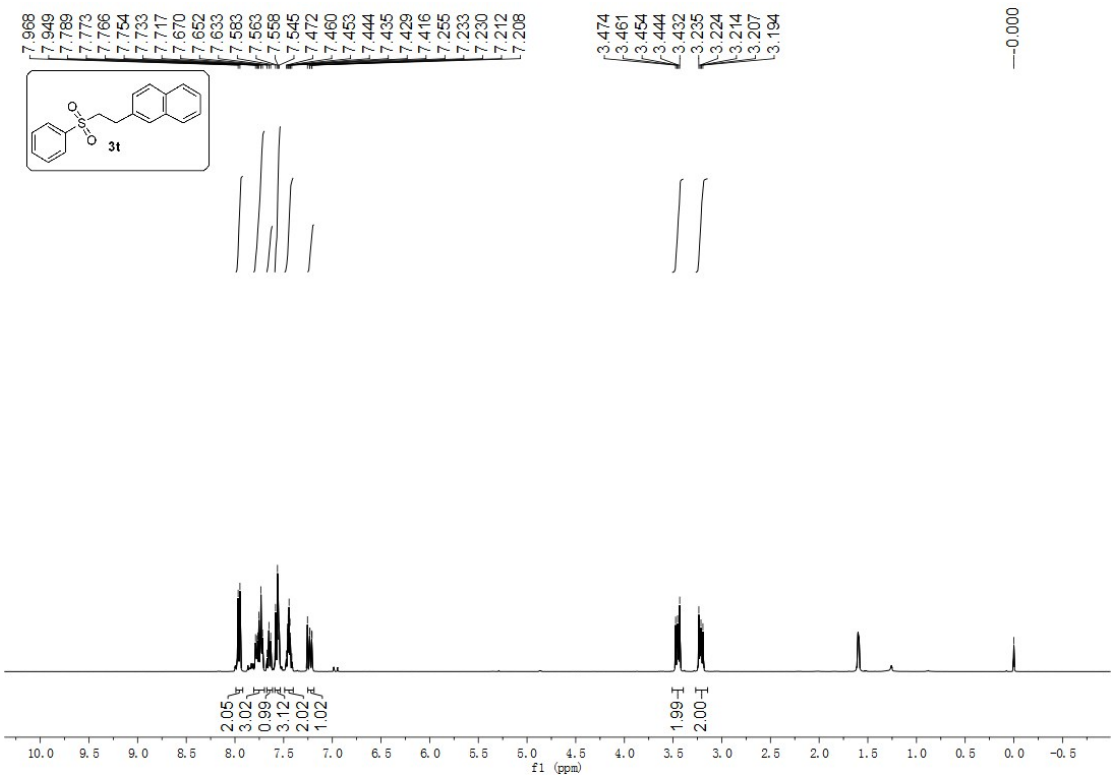

Figure 39. ^{1}H NMR spectra of **3t**

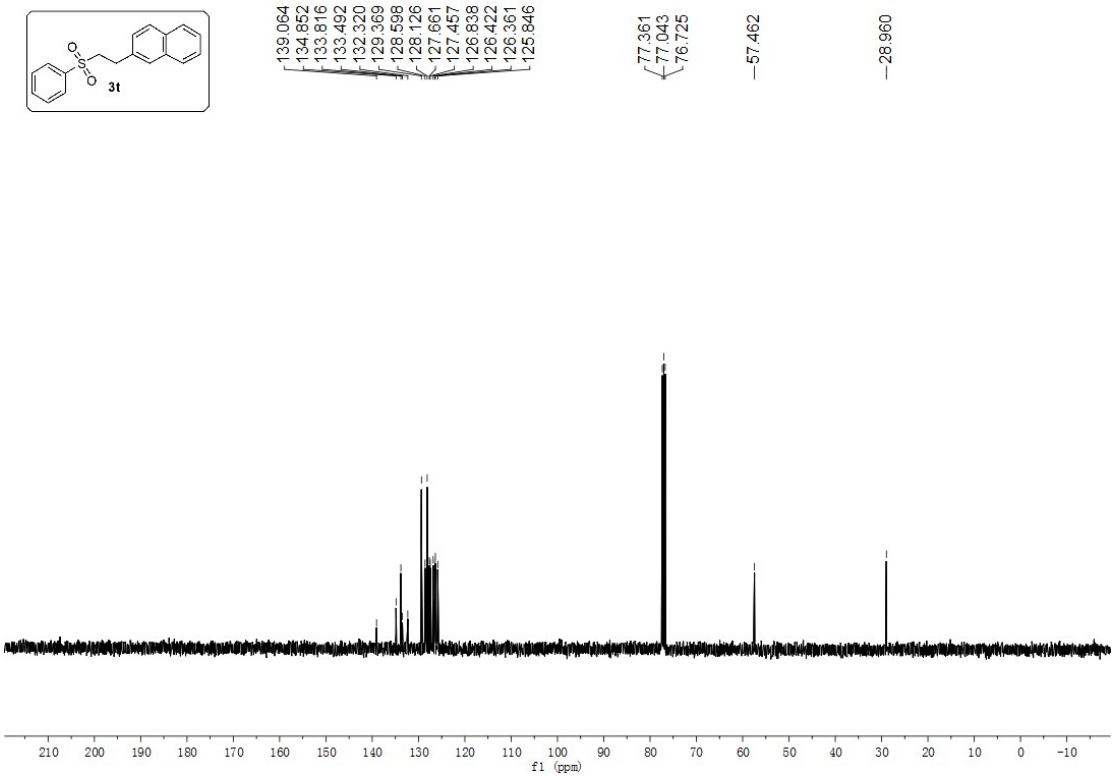

Figure 40. ^{13}C NMR spectra of **3t**

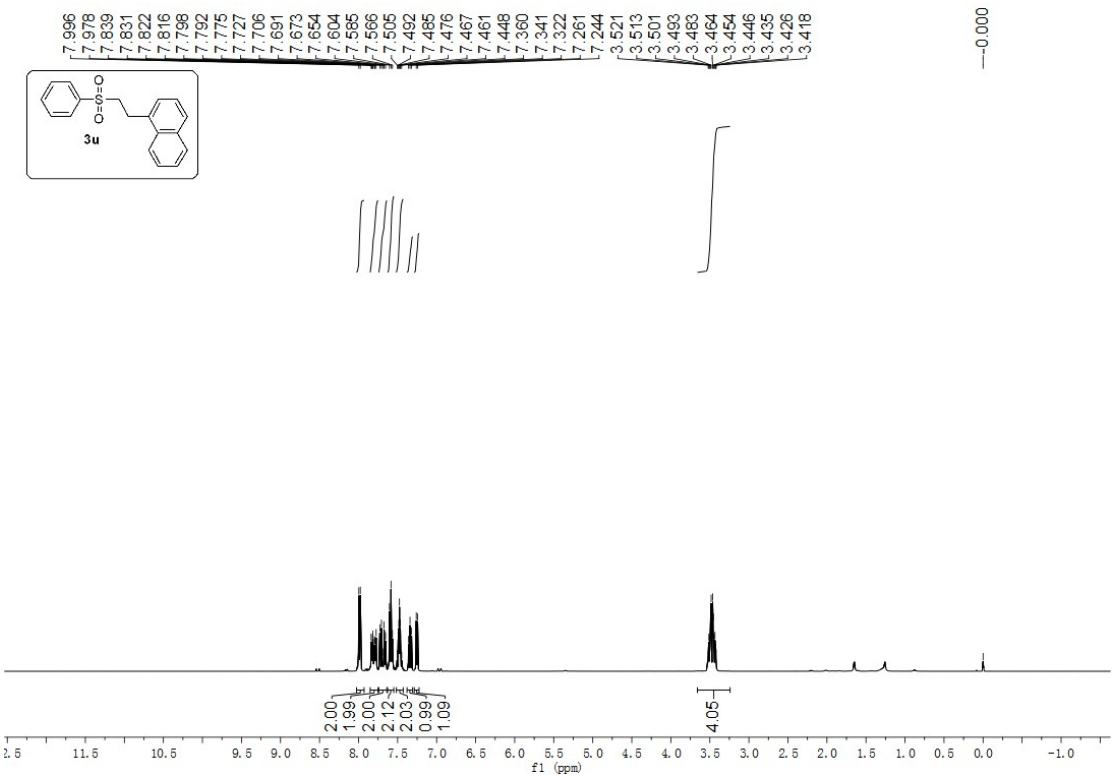

Figure 41. ^{1}H NMR spectra of **3u**

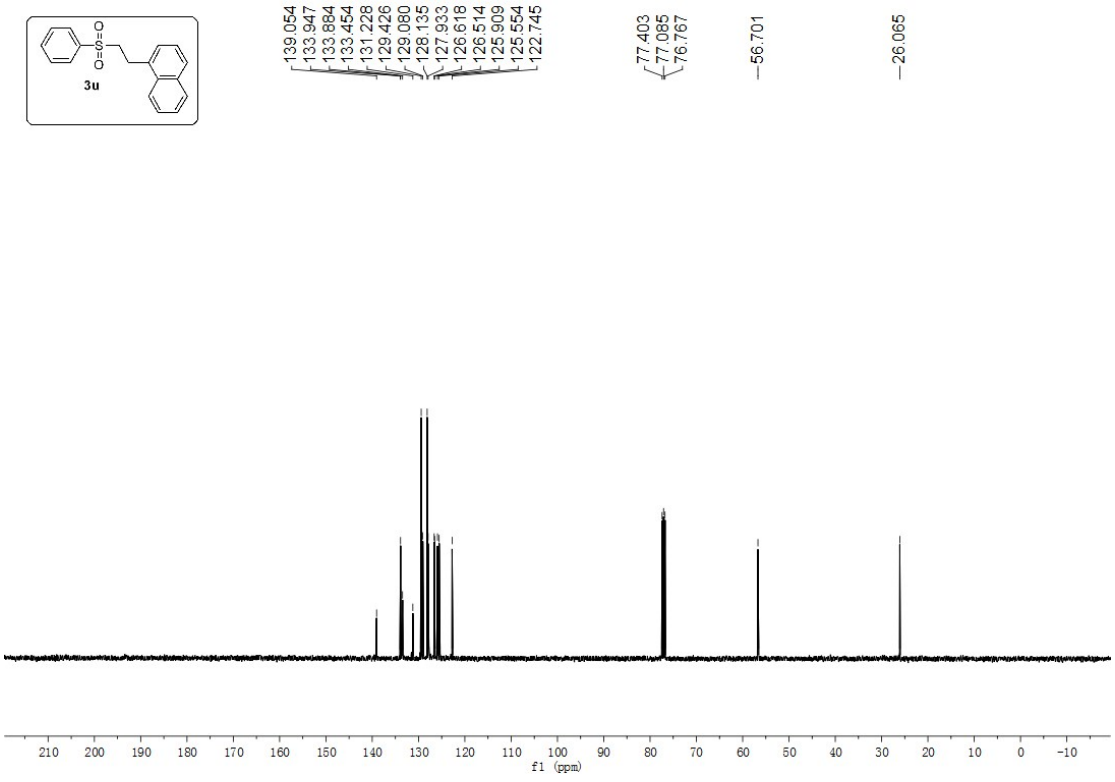

Figure 42. ^{13}C NMR spectra of **3u**

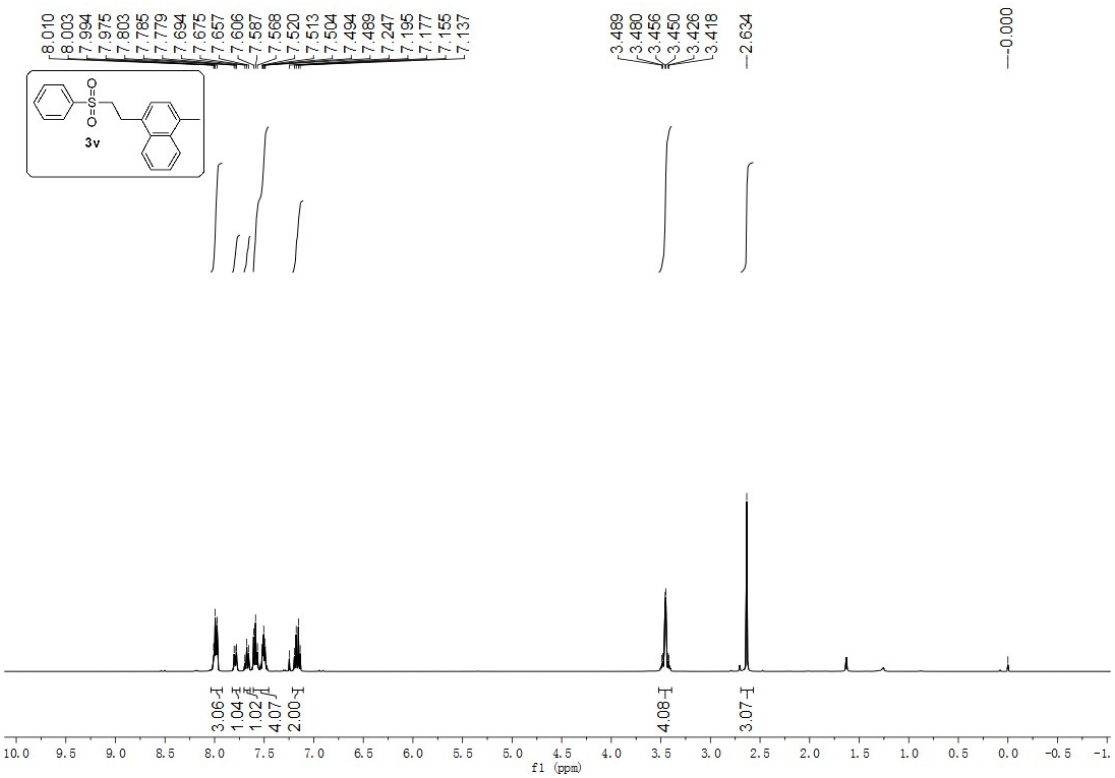

Figure 43. ^{1}H NMR spectra of **3v**

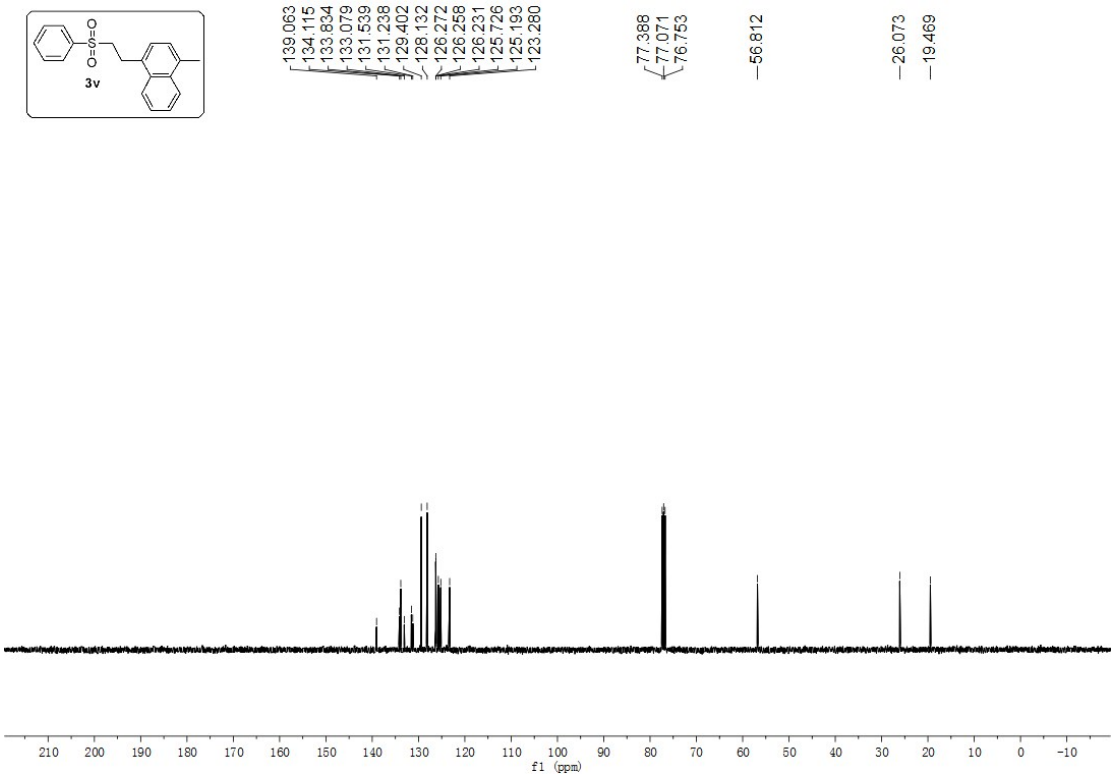

Figure 44. ^{13}C NMR spectra of **3v**

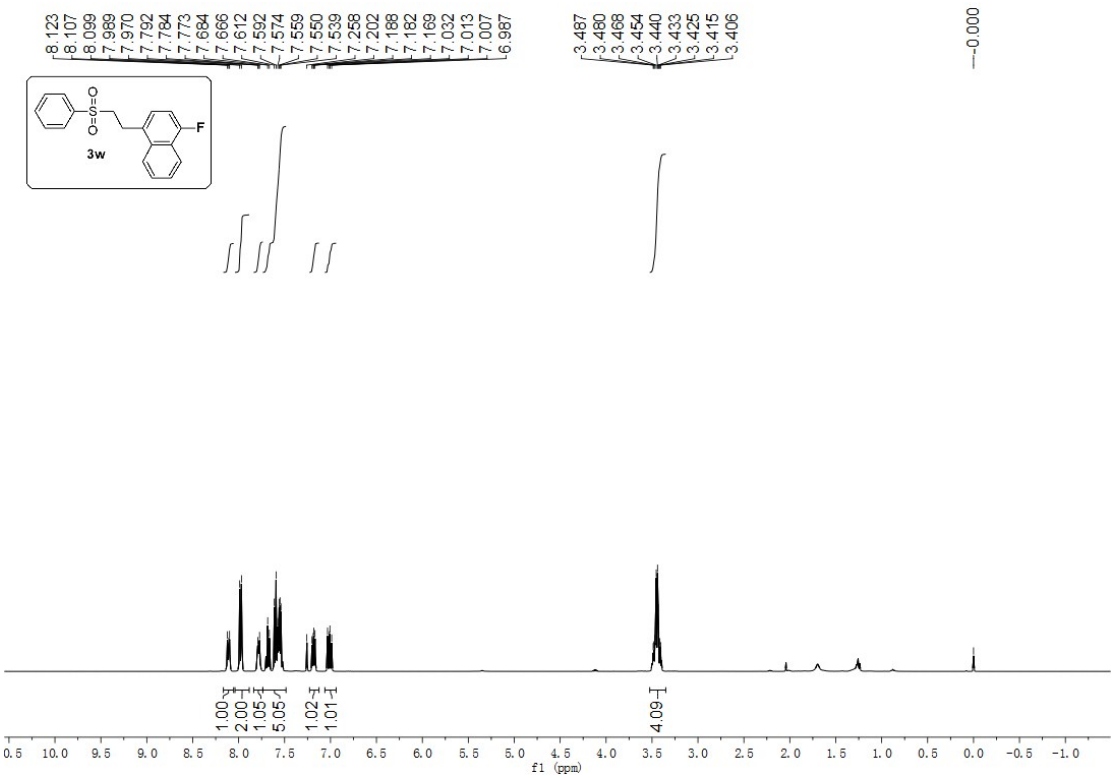

Figure 45. ^{1}H NMR spectra of **3w**

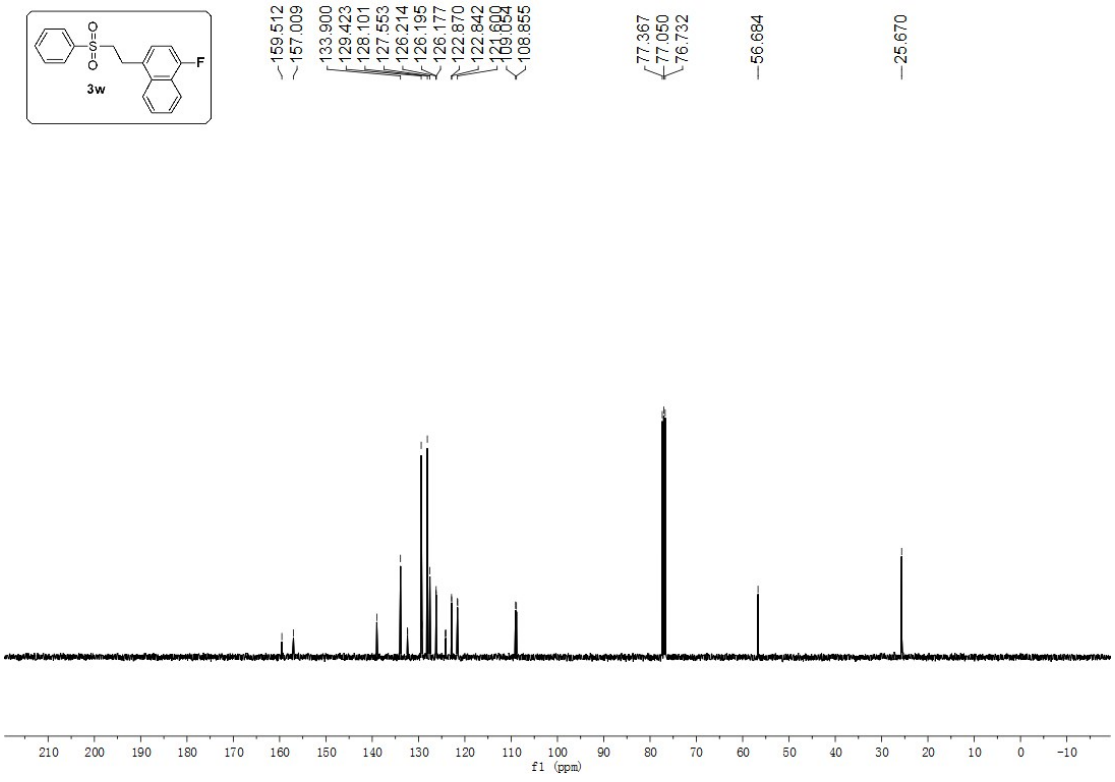

Figure 46. ^{13}C NMR spectra of **3w**

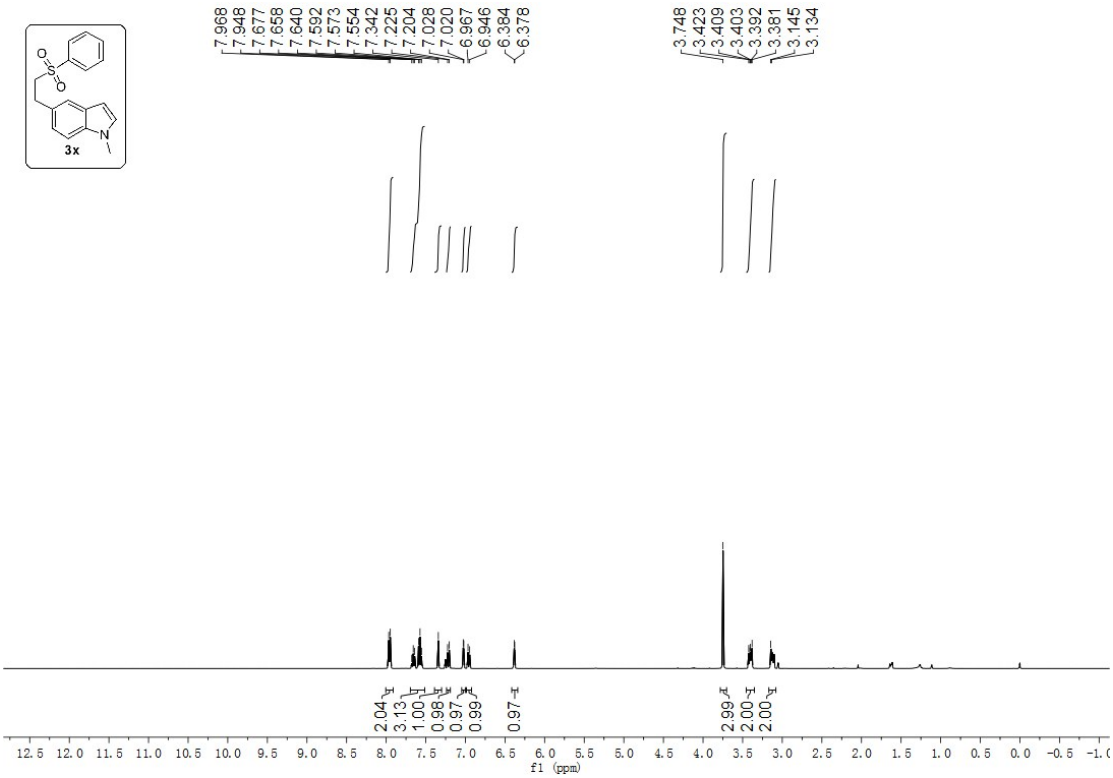

Figure 47. ^{1}H NMR spectra of **3x**

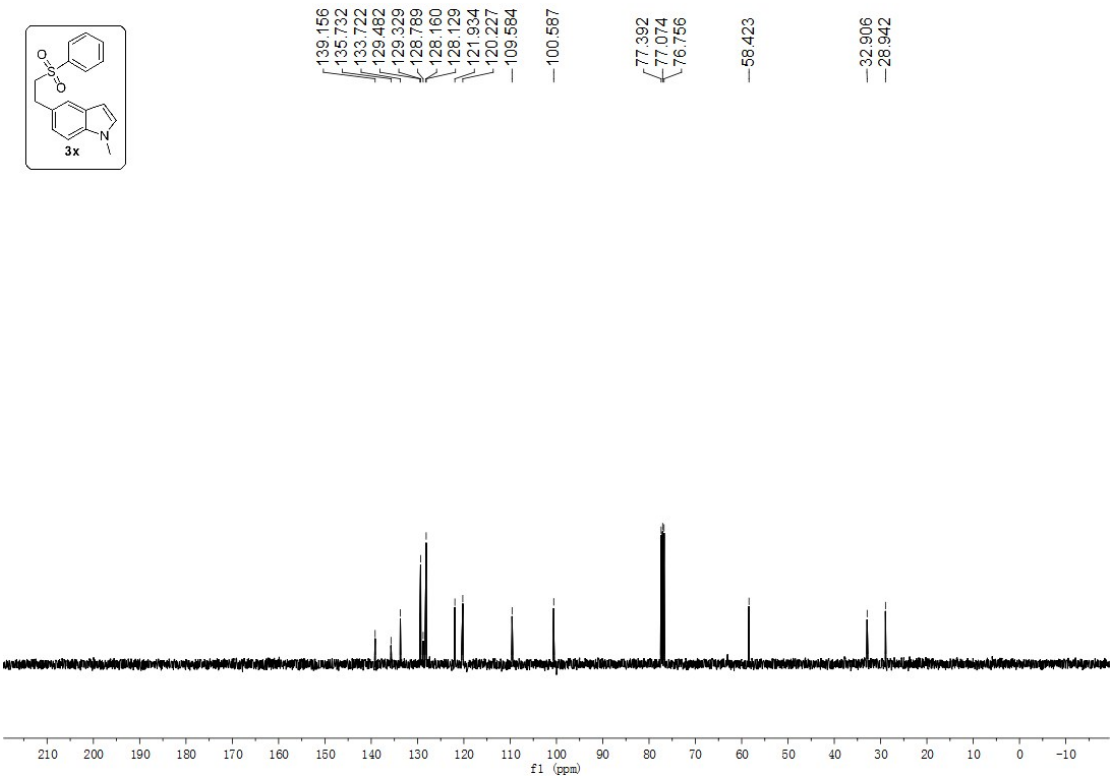

Figure 48. ^{13}C NMR spectra of **3x**

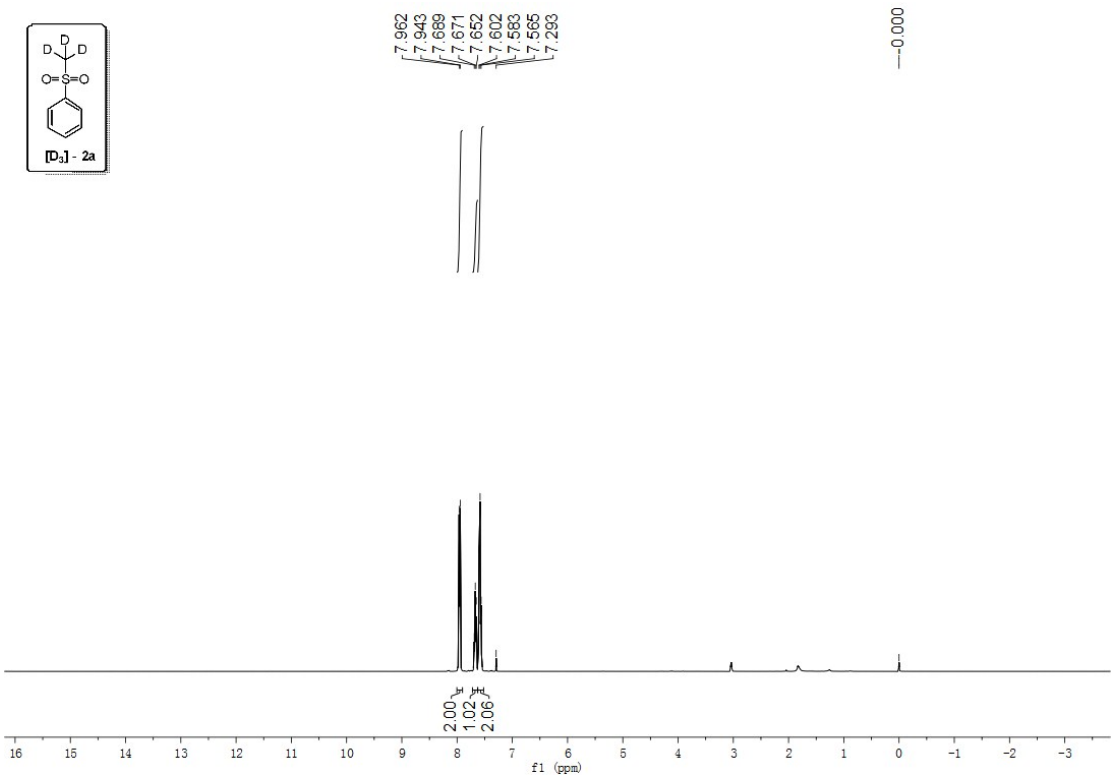

Figure 49. ^{1}H NMR spectra of **[D_3]-2a**