Nucleophilic Functionlization of Thianthrenium Salts under Base Conditions

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# **1. General Information.**

All new compounds were fully characterized. All reactions and manipulations involving air-sensitive compounds were performed using standard Schlenk techniques. Anhydrous MeCN was purchased from Annaiji Chemical and was used as received. 1H and 13C NMR spectra were recorded on an Agilent DD2 400 MHz spectrometer. The chemical shifts in 1H NMR spectra were recorded relative to CDCl3 (δ 7.26). The chemical shifts in 13C NMR spectra were recorded relative to CDCl3 (δ 77.0). The High-resolution mass spectral (HRMS) data were obtained on quadrupole-type Bruker Dalton MAXIS (APCI). Gas analyses were conducted with a Shimadzu GC-2014 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and an FID detector. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

# **2.** **General Procedure for Synthesis of Starting Materials**

**General Procedure A**

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A flame-dried 100 mL flask was placed under an atmosphere of nitrogen and charged with a stir bar and alcohol (5.0 mmol, 1.0 equiv). The alcohol was dissolved in CH2Cl2 (20.0 mL) and cooled to -30 °C before adding pyridine (483 µL, 6.0 mmol, 1.2 equiv). While stirring, triflic anhydride (1.0 mL, 29.3 mmol, 1.20 equiv) was added dropwise, and then the reaction mixture stirred for 3 h while remaining at -5 °C. While the flask was still in a -5 °C bath, 0.5 M H2SO4 (30 mL) was added. The flask was removed from the cold bath, and the mixture was transferred to a separatory funnel and extracted with 3×20 mL of CH2Cl2. The organic layers were combined and washed 1× 50mL of distilled water. The collected organic layers were then dried over MgSO4, then filtered and concentrated to a 10 mL liquid under vacuum (without heating), which was used directly in the next step.

Flame-dried 25 mL Schlenk tube was added thianthrene (1.08g, 5.0 mmol), then the above liquid was added. The mixture was stired at 55 °C for 24 h. The mixture was carefully condensed under reduced pressure at 25 ºC and purified by precipitation with Et2O/DCM. Most of the unreacted dibenzothiophene was removed by repeating the precipitation procedure 2 or 3 times. If the salt still did not precipitate, it was sub*j*ected to silica gel chromatography with acetone/DCM.1

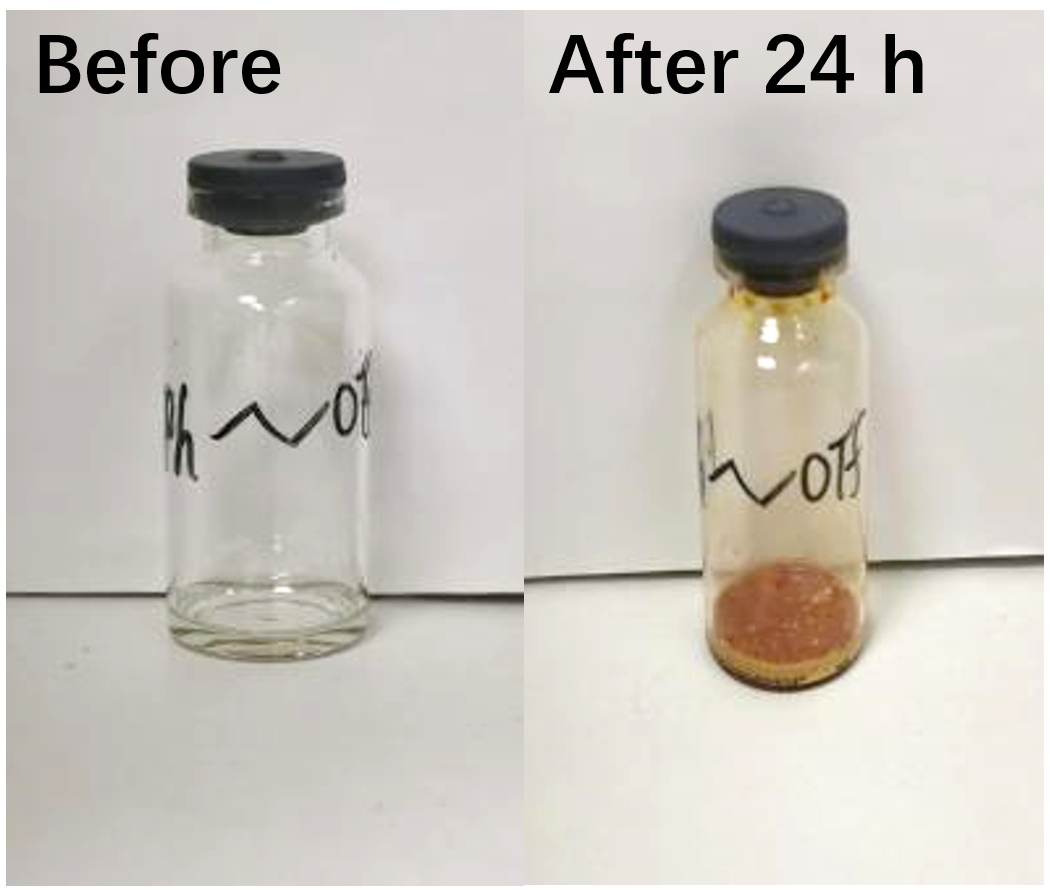
**Method B:**



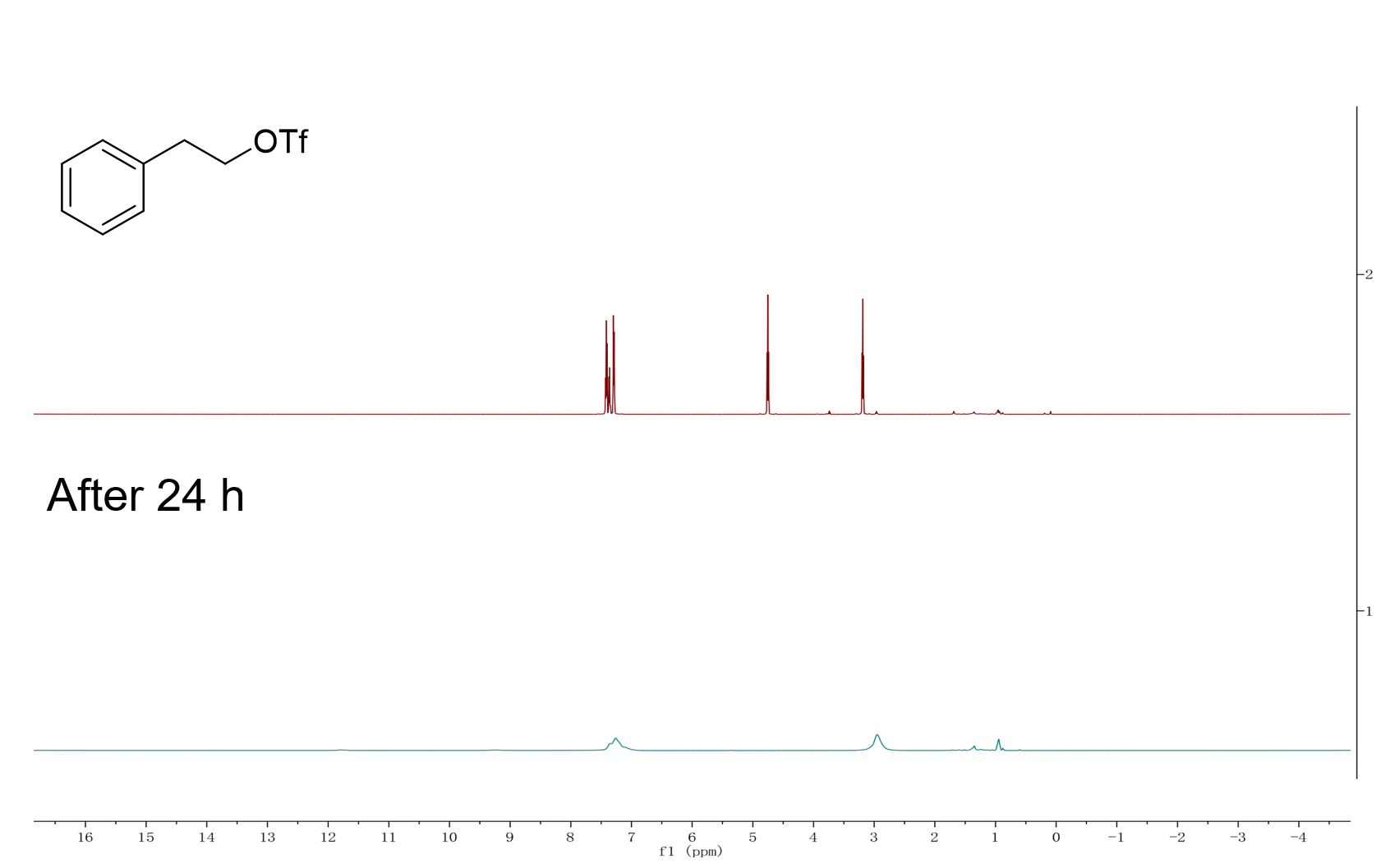
A solution of alcohol (20 mmol) in ethyl formate (60 ml) was treated with 0.4 mmol of Bi(OTf)3. The reaction mixture was stirred under reflux conditions for 5 h. Evaporation of the solvent followed by silica-gel chromatography gave the pure formate.

To a stirred mixture of Thianthrene (1.08 g, 5.0 mmol) and formate (10.0 mmol), cooled in an ice-bath, was added 2.5 ml of trifluoromethanesulfonic acid. The mixture was removed from the ice-bath and stirred for 10 h at room temperature, after which it was poured into 100 ml of water. The resulting suspension was extracted with DCM. The collected organic layers were then dried over MgSO4, then filtered and concentrated under reduced pressure at 25 ºC and purified by precipitation with Et2O/DCM. Most of the unreacted dibenzothiophene was removed by repeating the precipitation procedure 2 or 3 times.1

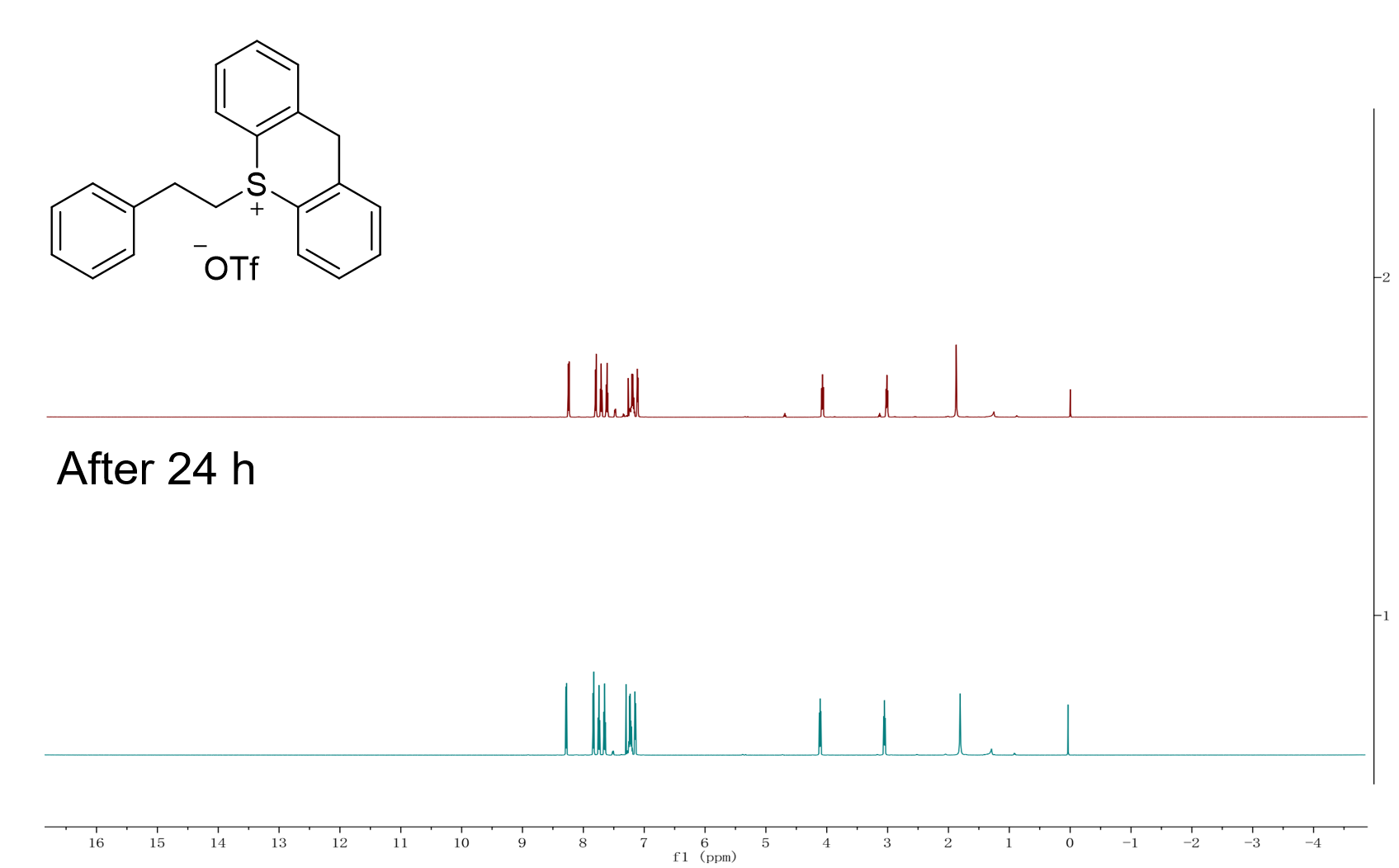
Alkyl thianthrenium salts exhibit greater stability and are more amenable to long-term preservation when compared to alkyl trifluoromethanesulfonate compounds. For instance, when phenethyl trifluoromethanesulfonate is exposed to air at room temperature for 24 hours, its initially colorless and transparent appearance transforms into a deep yellow hue (Scheme S1). Our comparison of the NMR data reveals that compound has undergone decomposition, resulting in the formation of unidentified by-products. By comparison, alkyl thianthrenium salt **1a** do not exhibit significant changes after being placed in the air for 24 hours (Scheme S3).



Scheme S1



Scheme S2



Scheme S3

# **3. Experimental Procedures**

**General procedure for the synthesis of thioetherification product:**



To a 10 mL Schlenk tube was added alkyl sulfonate **1** (0.3 mmol,1.5 equiv), thiophenol **2** (0.2 mmol, 1.0 equiv), DIPEA (0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL). The resulting mixture was stirred at room temperature for 16 h. The reaction mixture was quenched with dichloromethane. The organic layer was concentrated and purified by silica gel chromatography (petroleum ether and ethyl acetate) to afford the desired product **3**.

**Gram-scale reaction:**



To a 50 mL Schlenk tube was added alkyl sulfonate 1a (6 mmol, 2.82 g, 1.5 equiv), thiophenol 2a (5 mmol, 0.96 g, 1.0 equiv), DIPEA (10 mmol, 1.77 mL, 2.0 equiv) and anhydrous acetonitrile (10 mL). The resulting mixture was stirred at room temperature for 16 h. After the reaction was completed, it was quenched with water. The residue was then extracted with CH2Cl2 (3 × 20 mL) and the combined organic layers were dried over anhydrous Na2SO4. The organic layer was concentrated in vacuo, resulting in a Colorless oil. It was then concentrated and purified by silica gel chromatography to afford **3aa** (1.01 g, yield: 69%).

**(4-bromophenyl)(phenethyl)sulfane (3aa)**2



Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2a** (38.3 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3aa** (55.4 mg, 88%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.16 (m, 5H), 3.16 (t, *J* = 7.8 Hz, 2H), 2.98 – 2.89 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 139.9, 135.7, 132.0, 130.7, 128.6, 128.5, 126.7, 119.8, 35.5, 35.2 ppm. **HRMS m/z (ESI):** calcd for C14H13BrS (M + H)+ 292.9994, found 292.9996.

**(5-bromophenyl)(4-fluorophenethyl)sulfane (3ba)**



Following the general procedure, the reaction of **1b** (146.7 mg, 0.3 mmol, 1.5 equiv.), **2a** (38.3 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ba** (47.9 mg, 77%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.10 (m, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 3.17 – 3.09 (m, 2H), 2.94 – 2.85 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 161.6 (d, *J* = 244.6 Hz), 135.5 (d, *J* = 3.2 Hz), 135.4, 132.0, 130.8, 129.9 (d, *J* = 7.9 Hz), 119.9, 115.3 (d, *J* = 21.2 Hz), 35.3, 34.6 ppm. **19F NMR (376 MHz, Chloroform-d)** δ -116.42 ppm. **EI-MS (m/z, relative intensity)**: 311.21 (M+, 55), 309.94 (55), 202.94 (64), 200.93 (72), 123.07 (86), 122.03 (100), 109.02 (50), 103.01 (42).

**(4-bromophenyl)(4-chlorophenethyl)sulfane (3ca)**2



Following the general procedure, the reaction of **1c** (151.5 mg, 0.3 mmol, 1.5 equiv.), **2a** (38.3 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ca** (57.8 mg, 88%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d )**δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.16 – 3.08 (m, 2H), 2.92 – 2.83 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 138.2, 135.3, 132.4, 132.0, 130.9, 129.9, 128.7, 120.0, 35.1, 34.8 ppm. **HRMS m/z (ESI):** calcd for C14H12BrClS (M + Na)+ 348.9424, found 348.9428.

**(4-bromophenethyl)(4-bromophenyl)sulfane (3da)**3

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Following the general procedure, the reaction of **1d** (164.7 mg, 0.3 mmol, 1.5 equiv.), **2a** (38.3 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3da** (56.3 mg, 76%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.42 (dd, *J* = 8.5, 2.1 Hz, 4H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 3.16 – 3.08 (m, 2H), 2.90 – 2.83 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 138.8, 135.3, 132.0, 131.6, 130.9, 130.3, 120.4, 120.0, 35.0, 34.8 ppm. **HRMS m/z (APCI):** calcd for C14H12Br2S (M)+ 369.9026, found 369.9024.

**(5-bromophenyl)(4-iodophenethyl)sulfane (3ea)**



Following the general procedure, the reaction of **1e** (178.9 mg, 0.3 mmol, 1.5 equiv.), **2a** (38.3 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ea** (74.5 mg, 89%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.62 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.1 Hz, 2H), 3.16 – 3.08 (m, 2H), 2.90 – 2.81 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 139.4, 137.6, 135.3, 132.0, 130.9, 130.6, 120.0, 91.8, 35.0, 34.9 ppm. **HRMS m/z (ESI):** calcd for C14H12BrIS (M + Na)+ 440.8780, found 440.8718.

**(6-bromophenyl)(4-isocyanophenethyl)sulfane (3fa)**



Following the general procedure, the reaction of **1f** (148.8 mg, 0.3 mmol, 1.5 equiv.), **2a** (38.3 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3fa** (40.4 mg, 64%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 3.14 (t, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 145.2, 134.8, 132.3, 132.1, 131.1, 129.4, 120.3, 118.8, 110.5, 35.4, 34.7 ppm. **HRMS m/z (ESI):** calcd for C15H12BrNS (M + Na)+ 339.9766, found 339.9756.

**(7-bromopentyl)(4-bromophenyl)sulfane (3ga)**

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Following the general procedure, the reaction of **1g** (158.7 mg, 0.3 mmol, 1.5 equiv.), **2a** (38.3 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ga** (49.5 mg, 73%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 3.39 (t, *J* = 6.7 Hz, 2H), 2.90 (t, *J* = 7.1 Hz, 2H), 1.86 (p, *J* = 6.8 Hz, 2H), 1.71 – 1.51 (m, 4H) ppm. 1**3C NMR (101 MHz, Chloroform-d)** δ 135.8, 131.9, 130.6, 119.6, 33.49, 33.46, 32.2, 28.1, 27.3 ppm. **HRMS m/z (APCI):** calcd for C11H14Br2S (M + H)+ 336.9256, found 339.9245.

**1,6-bis((4-bromophenyl)thio)hexane (3ha)**



Following the general procedure, the reaction of **1h** (179.6 mg, 0.3 mmol, 1.5 equiv.), **2a** (76.6 mg, 0.4 mmol, 2.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ha** (124.9 mg, 89%) as a white solid. **1H NMR (400 MHz, Chloroform-d)** δ 7.38 (d, *J* = 8.5 Hz, 4H), 7.16 (d, *J* = 8.5 Hz, 4H), 2.87 (t, *J* = 7.3 Hz, 4H), 1.68 – 1.59 (m, 4H), 1.42 (p, *J* = 3.7 Hz, 4H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 136.0, 131.9, 130.4, 119.5, 33.5, 28.8, 28.2 ppm. **m.p.:** 73.6-78.8 ℃. **HRMS m/z (ESI):** calcd for C18H20Br2S2 (M + H)+ 458.9446, found 458.9445.

**(4-bromophenyl)(cyclododecyl)sulfane (3ia)**



Following the general procedure, the reaction of **1i** (160.4 mg, 0.3 mmol, 1.5 equiv.), **2a** (38.3 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ia** (41.3 mg, 58%) as a white solid. **1H NMR (400 MHz, Chloroform-d)** δ 7.40 (dd, *J* = 11.7, 8.5 Hz, 3H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.22 (ddd, *J* = 12.1, 7.2, 4.7 Hz, 1H), 1.69 (dq, *J* = 15.4, 8.3, 7.5 Hz, 2H), 1.54 – 1.23 (m, 18H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 132.76, 132.23, 131.82, 129.41, 45.04, 29.81, 24.18, 23.84, 23.37, 23.35, 22.09 ppm. **m.p.:** 43.1-47.3 ℃. **HRMS m/z (ESI):** calcd for C18H27BrS (M + H)+ 355.1090, found 355.1008.

**Diphenethylsulfane (3ab)**4



Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2b** (27 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ab** (46.3 mg, 95%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.38 – 7.29 (m, 4H), 7.29 – 7.18 (m, 6H), 2.96 – 2.87 (m, 4H), 2.87 – 2.77 (m, 4H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 140.6, 128.5, 126.4, 36.4, 33.8 ppm. **HRMS m/z (ESI):** calcd for C16H18S (M + Na)+ 265.1021, found 265.1003.

**phenethyl(*p*-tolyl)sulfane (3ac)**5



Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2c** (25 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ea** (28.0 mg, 61%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.35 – 7.26 (m, 4H), 7.25 – 7.17 (m, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.18 – 3.10 (m, 2H), 2.96 – 2.87 (m, 2H), 2.34 (s, 3H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 140.3, 136.2, 132.5, 130.1, 129.7, 128.5, 126.4, 35.84, 35.77, 21.0 ppm. **HRMS m/z (ESI):** calcd for C15H16 S (M + Na)+ 251.0865, found 251.0857.

**(4-(tert-butyl)phenyl)(phenethyl)sulfane (3ad)**



Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2d** (38.3 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ad** (51.4 mg, 95%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.40 – 7.31 (m, 6H), 7.26 (t, *J* = 8.7 Hz, 3H), 3.23 – 3.16 (m, 2H), 3.02 – 2.93 (m, 2H), 1.36 (s, 9H) ppm. **13C NMR (101 MHz, Chloroform-d)**δ 149.3, 140.4, 132.7, 129.5, 128.5, 126.4, 126.0, 35.9, 35.5, 34.5, 31.3 ppm. **HRMS m/z (ESI):** calcd for C18H22S (M + Na)+ 293.1334, found 293.1331.

**(4-methoxyphenyl)(phenethyl)sulfane (3ae)**6

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Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2e** (25 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether/ethyl acetate 100:1), afford **3ae** (39.2 mg, 80%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.39 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.13 – 3.05 (m, 2H), 2.93 – 2.84 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 158.9, 140.4, 133.3, 128.5, 128.4, 126.4, 114.6, 55.4, 37.3, 35.9 ppm. **HRMS m/z (ESI):** calcd for C15H16OS (M + Na)+ 267.0814, found 267.0794.

**(4-chlorophenyl)(phenethyl)sulfane(3af)**5



Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2f** (28.9 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3af** (36.6mg, 74%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.35 – 7.22 (m, 7H), 7.20 (d, *J* = 6.9 Hz, 2H), 3.20 – 3.12 (m, 2H), 2.97 – 2.87 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 139.9, 134.9, 132.0, 130.6, 129.1, 128.6, 128.5, 126.6, 35.5, 35.4 ppm. **HRMS m/z (ESI):** calcd for C14H13ClS (M + Na)+ 271.0319, found 271.0297.

**phenethyl(4-(trifluoromethyl)phenyl)sulfane(3ag)**



Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2g** (28 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ag** (36.0 mg, 64%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.53 (d, J = 8.2 Hz, 2H), 7.41 – 7.29 (m, 4H), 7.24 (dd, J = 15.8, 6.9 Hz, 3H), 3.28 – 3.19 (m, 2H), 3.02 – 2.93 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 142.1, 139.7, 128.6 (d, *J* = 13.1 Hz), 127.4, 126.7, 125.7 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 271.6 Hz), 35.2, 33.9 ppm. **19F NMR (471 MHz, Chloroform-d)** δ -62.4 ppm. **HRMS m/z (ESI)**: calcd for C15H13F3S (M + H)+ 283.0763, found 283.0755.

1. **bromophenyl)(phenethyl)sulfane (3ah)**



Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2h** (21 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ah** (47.4 mg, 81%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.47 (s, 1H), 7.33 (t, *J* = 7.3 Hz, 3H), 7.24 (dd, *J* = 16.7, 7.5 Hz, 4H), 7.15 (t, *J* = 7.9 Hz, 1H), 3.22 – 3.15 (m, 2H), 2.99 – 2.91 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 139.8, 139.0, 131.1, 130.2, 128.8, 128.6, 128.5, 127.2, 126.6, 122.9, 35.4, 34.8 ppm. **HRMS m/z (ESI):** calcd for C14H13BrS (M + Na)+ 314.9814, found 314.9803.

1. **chlorophenyl)(phenethyl)sulfane (3ai)**

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Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2i** (23 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ai** (40.8 mg, 82%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.38 (d, *J* = 7.1 Hz, 1H), 7.36 – 7.19 (m, 7H), 7.12 (t, *J* = 7.1 Hz, 1H), 3.26 – 3.14 (m, 2H), 3.03 – 2.93 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 140.0, 135.8, 133.6, 129.7, 128.6, 128.5, 128.4, 127.1, 126.6, 126.5, 35.2, 33.9 ppm. **HRMS m/z (ESI):** calcd for C14H13ClS (M + Na)+ 271.0319, found 271.0297.

1. **fluorophenyl)(phenethyl)sulfane (3aj)**

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Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2j** (22 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3aj** (40.5 mg, 87%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.44 – 7.37 (m, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.27 – 7.17 (m, 4H), 7.14 – 7.04 (m, 2H), 3.22 – 3.12 (m, 2H), 2.98 – 2.87 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 161.5 (d, *J* = 245.4 Hz), 140.0, 132.2 (d, *J* = 15.1 Hz), 128.6, 128.5, 126.5, 124.4, 123.0 (d, *J* = 17.8 Hz), 115.7 (d, *J* = 22.0 Hz), 35.8, 34.8 ppm. **19F NMR (376 MHz, Chloroform-d)** δ -109.3 ppm. **HRMS m/z (ESI):** calcd for C14H13FS (M + Na)+ 255.0614, found 255.0610.

**(2,6-dimethylphenyl)(phenethyl)sulfane (3ak)**

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Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2k** (27 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ak** (31.8 mg, 54%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.29 (d, *J* = 7.0 Hz, 2H), 7.24 – 7.06 (m, 6H), 2.98 – 2.88 (m, 2H), 2.88 – 2.79 (m, 2H), 2.54 (s, 6H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 143.1, 140.5, 133.4, 128.4, 128.4, 128.2, 128.1, 126.3, 36.5, 36.4, 22.1 ppm. **HRMS m/z (ESI):** calcd for C16H18S (M + Na)+ 265.1021, found 265.1008.

**2-(Phenethylthio)pyridine(3al)**7

****

Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2l** (23 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3al** (37.8 mg, 90%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 8.50 – 8.42 (m, 1H), 7.51 – 7.43 (m, 1H), 7.35 – 7.20 (m, 5H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.98 (dd, *J* = 7.3, 4.9 Hz, 1H), 3.48 – 3.40 (m, 2H), 3.07 – 2.99 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 158.9, 149.4, 140.5, 135.9, 128.6, 128.4, 126.4, 122.4, 119.3, 35.8, 31.5 ppm. **HRMS m/z (ESI):** calcd for C13H13NS (M + Na)+ 238.0661, found 238.0644.

**3-(phenethylthio)thiophene (3am)**

****

Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2m** (19 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3am** (31.5 mg, 71%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.37 (d, *J* = 4.6 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.12 (m, 4H), 7.00 (dd, *J* = 5.3, 3.5 Hz, 1H), 3.09 – 3.01 (m, 2H), 2.96 – 2.88 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 140.0, 134.4, 133.6, 129.2, 128.6, 128.5, 127.6, 126.4, 40.1, 36.0 ppm. **HRMS m/z (ESI):** calcd for C12H12S2 (M + Na)+ 243.0273, found 243.0258.

**2-(phenethylthio)benzo[d]oxazole (3an)**

****

Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2n** (30.2 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3an** (44.6 mg, 87%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 7.63 (d, *J* = 7.0 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.21 (m, 7H), 3.61 – 3.51 (m, 2H), 3.21 – 3.11 (m, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 164.8, 151.8, 142.0, 139.4, 128.7, 128.6, 126.8, 124.3, 123.8, 118.5, 109.9, 35.6, 33.5 ppm. **HRMS m/z (ESI):** calcd for C15H13NSO (M + Na)+ 278.0610, found 278.0640.

**2-(phenethylthio)-1H-benzo[d]imidazole (3ao)**



Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2o** (30.0 mg, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at room temperature for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ao** (36.0 mg, 71%) as a white solid. **1H NMR (400 MHz, Chloroform-d)** δ 7.52 (s, 2H), 7.30 – 7.14 (m, 7H), 3.55 (t, *J* = 7.4 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 150.11, 139.60, 128.74, 128.52, 126.61, 122.33, 35.84, 34.09 ppm. **m.p.:**145.0-151.7 ℃. **HRMS m/z (ESI):** calcd for C15H14N2S (M + Na)+ 277.0770, found 277.0750.

**General procedure for the synthesis of amination products:**



To a 10 mL Schlenk tube was added alkyl sulfonate **1a** (0.3 mmol,1.5 equiv), amines **2** (0.2 mmol, 1.0 equiv), DIPEA (0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL). The resulting mixture was stirred at 80 ℃ for 16 h. The reaction mixture was quenched with dichloromethane. The organic layer was concentrated and purified by silica gel chromatography (petroleum ether and ethyl acetate) to afford the desired product **3**.

**N-phenethylaniline (3ap)**

****

Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2p** (18 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at 80 ℃ for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ap** (20.7 mg, 53%) as a Pale yellow. **1H NMR (400 MHz, Chloroform-d)** δ 7.39 – 7.04 (m, 7H), 6.79 – 6.48 (m, 3H), 3.68 (s, 1H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.92 (t, *J* = 6.6 Hz, 2H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 148.0, 139.3, 129.3, 128.8, 128.6, 126.4, 117.5, 113.0, 45.0, 35.5 ppm. **HRMS m/z (ESI):** calcd for C14H15N (M + Na)+ 220.1097, found 220.1099.

**N-methyl-N-phenethylaniline(3aq)**8



Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2q** (22 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at 80 ℃ for 16 h. After column chromatography on silica (eluent: petroleum ether), afford 3aq (30.0 mg, 71%) as a colorless liquid. **1H NMR (400 MHz, Chloroform-d)** δ 7.38 – 7.14 (m, 7H), 6.80 – 6.67 (m, 3H), 3.65 – 3.51 (m, 2H), 2.95 – 2.83 (m, 5H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 148.8, 139.8, 129.3, 128.8, 128.5, 126.2, 116.2, 112.2, 54.8, 38.5, 32.9 ppm. **HRMS m/z (ESI):** calcd for C15H17N (M + Na)+ 234.1253, found 234.1261.

**N-methyl-N-(naphthalen-1-ylmethyl)-2-phenylethan-1-amine (3ar)**

****

Following the general procedure, the reaction of **1a** (141.3 mg, 0.3 mmol, 1.5 equiv.), **2r** (33 µL, 0.2 mmol, 1.0 equiv), DIPEA (71 µL, 0.4 mmol, 2.0 equiv) and anhydrous acetonitrile (2 mL) at 80 ℃ for 16 h. After column chromatography on silica (eluent: petroleum ether), afford **3ar** (48.6 mg, 88%) as a colorless oil. **1H NMR (400 MHz, Chloroform-d)** δ 8.22 (s, 1H), 7.82 (d, *J* = 25.4 Hz, 2H), 7.45 (dd, *J* = 22.7, 4.8 Hz, 4H), 7.35 – 7.15 (m, 5H), 3.97 (s, 2H), 2.86 (dt, *J* = 40.6, 6.9 Hz, 4H), 2.32 (s, 3H) ppm. **13C NMR (101 MHz, Chloroform-d)** δ 140.6, 134.7, 133.9, 132.5, 128.8, 128.4, 128.3, 128.0, 127.4, 125.9, 125.8, 125.6, 125.1, 124.7, 60.6, 59.8, 42.1, 33.7 ppm. **HRMS m/z (ESI):** calcd for C20H21N (M + Na)+ 298.1566, found 298.1555.

**4. Mechanistic Studies**

**Radical trapping experiment with TEMPO**



To a 10 mL Schlenk tube was added alkyl sulfonate 1a (0.3 mmol, 141 mg, 1.5 equiv), thiophenol 2a (0.2 mmol, 38.32 g, 1.0 equiv), DIPEA (0.4 mmol, 71 µL, 2.0 equiv), TEMPO(0.4 mmol, 62.5 mg, 2 equiv) and anhydrous acetonitrile (2 mL). The resulting mixture was stirred at room temperature for 16 h. After the reaction was completed, it was quenched with water. The residue was then extracted with CH2Cl2 (3 × 20 mL) and the combined organic layers were dried over anhydrous Na2SO4. The organic layer was concentrated in vacuo, resulting in a Colorless oil. It was then concentrated and purified by silica gel chromatography to afford **3aa** (yield : 46%).

**Radical trapping experiment with BHT**



To a 10 mL Schlenk tube was added alkyl sulfonate 1a (0.3 mmol, 141 mg, 1.5 equiv), thiophenol 2a (0.2 mmol, 38.32 g, 1.0 equiv), DIPEA (0.4 mmol, 71 µL, 2.0 equiv), BHT(0.4 mmol, 62.5 mg, 2 equiv) and anhydrous acetonitrile (2 mL). The resulting mixture was stirred at room temperature for 16 h. After the reaction was completed, it was quenched with water. The residue was then extracted with CH2Cl2 (3 × 20 mL) and the combined organic layers were dried over anhydrous Na2SO4. The organic layer was concentrated in vacuo, resulting in a Colorless oil. It was then concentrated and purified by silica gel chromatography to afford **3aa** (yield : 83%).

# **5. References**

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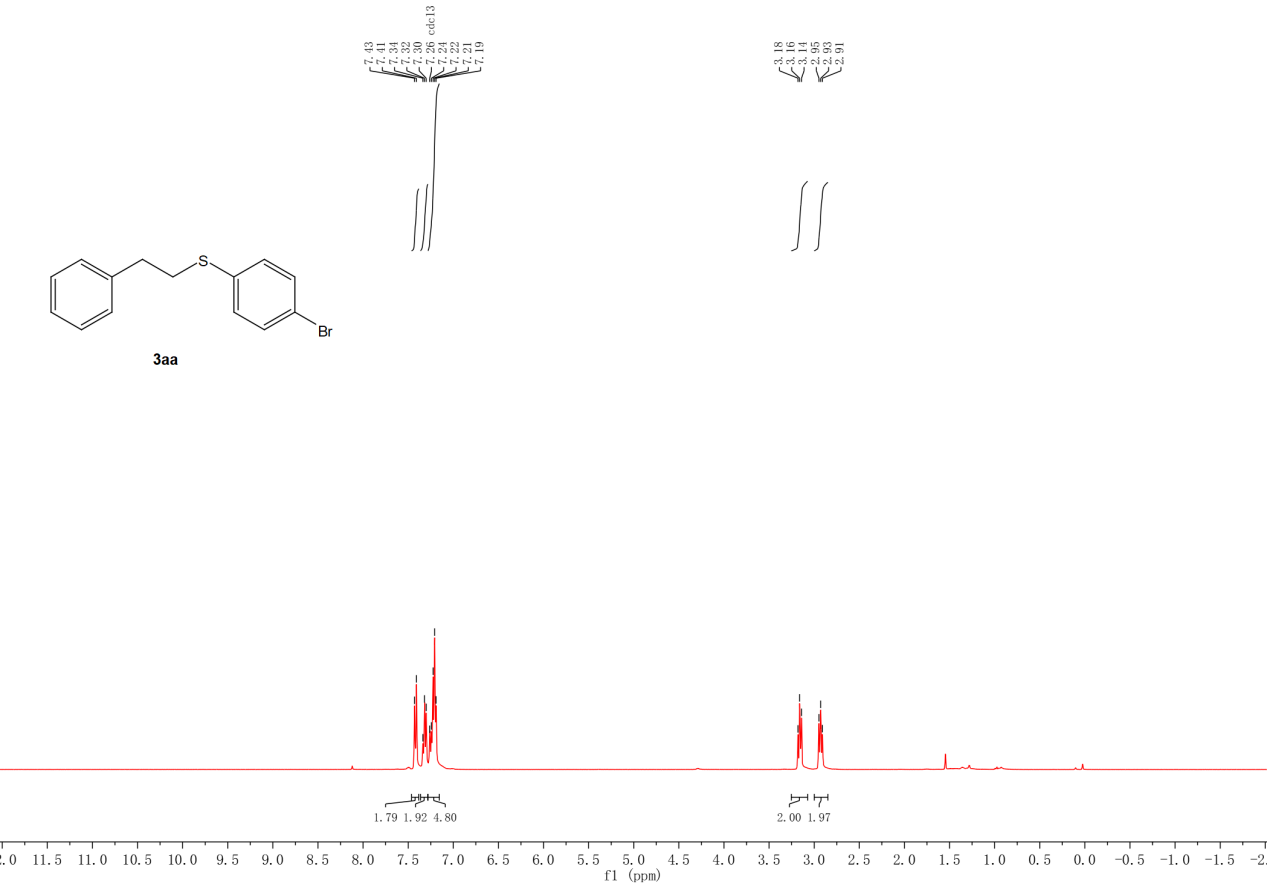
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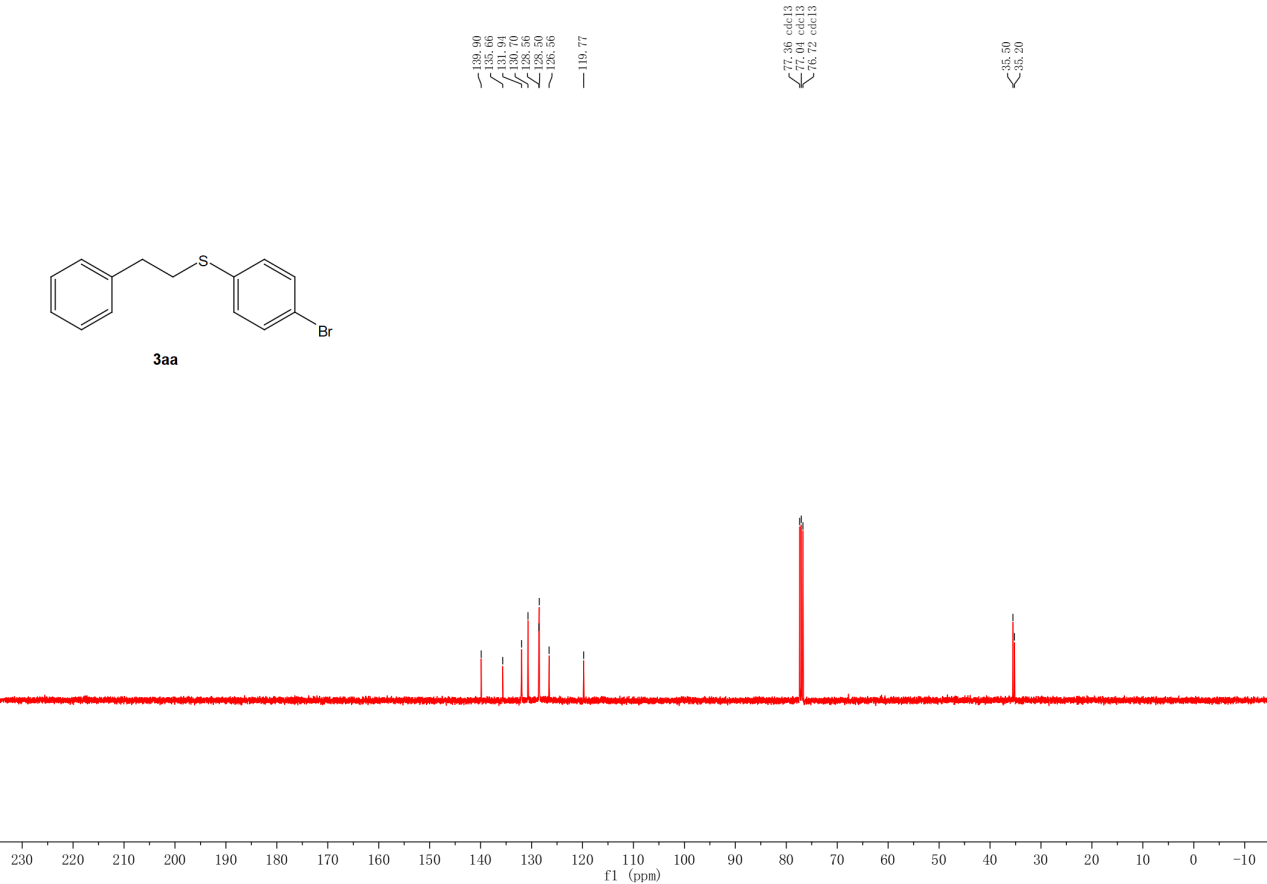
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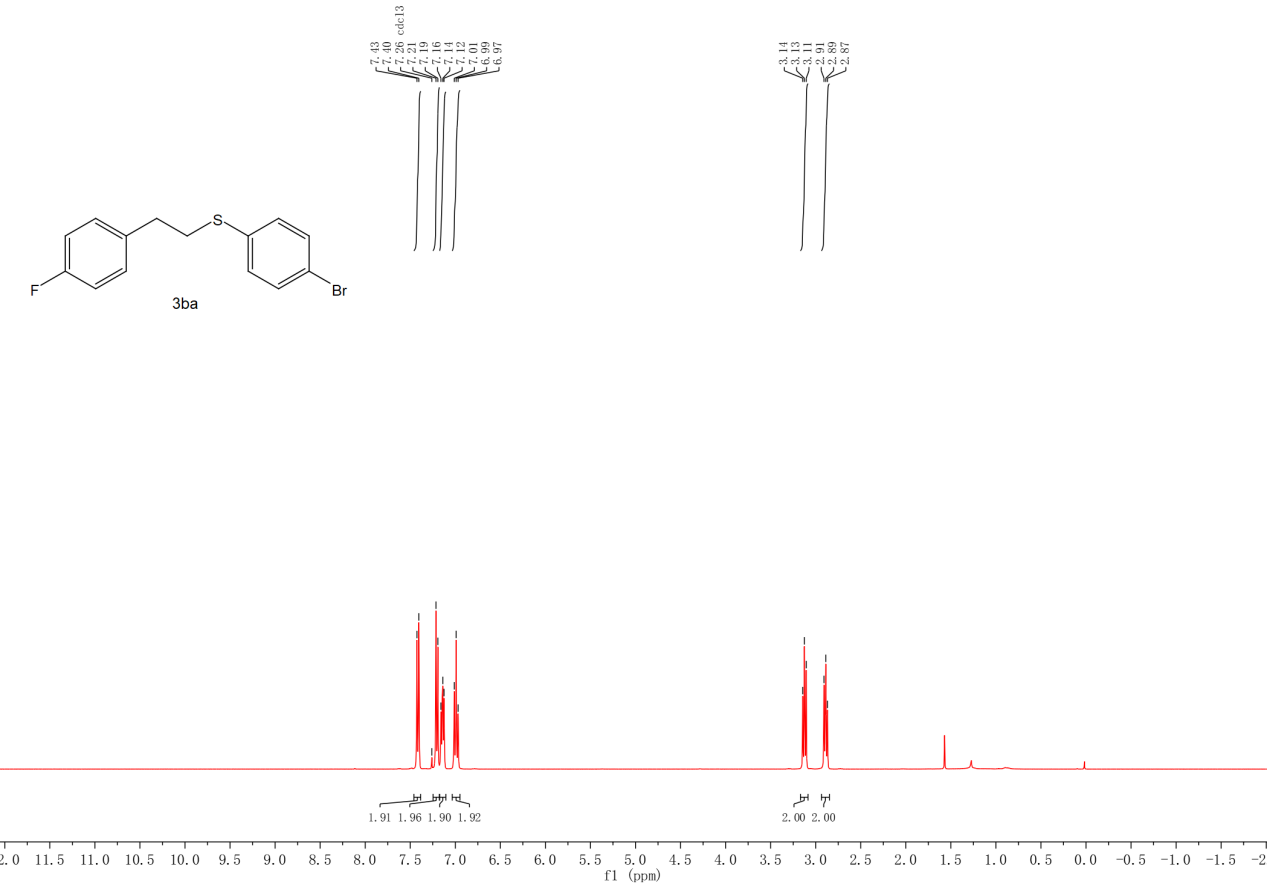
# **6. Spectra of 1H NMR, 13C NMR**



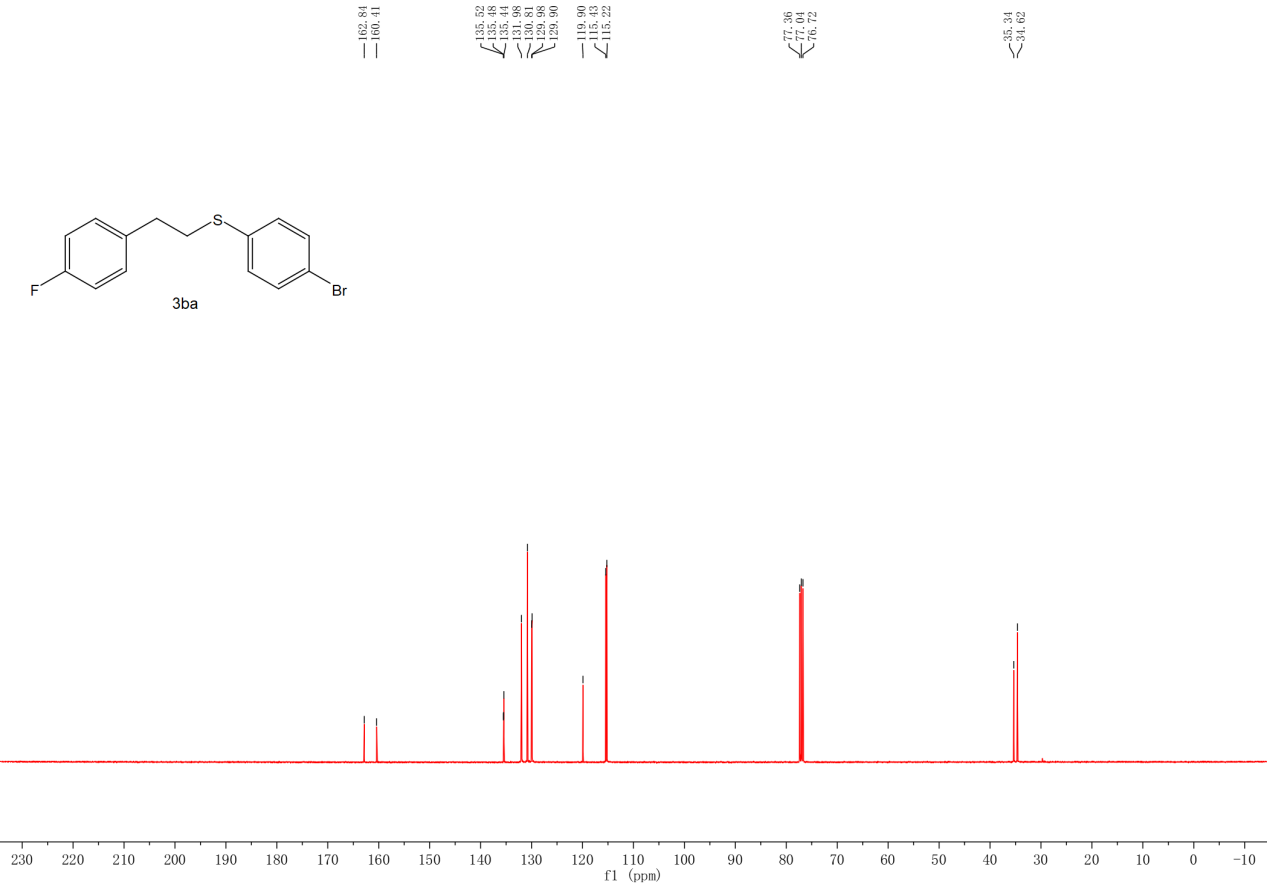
**Figure S1.** 1H NMR spectra (400 MHz) of **3aa** in CDCl3.



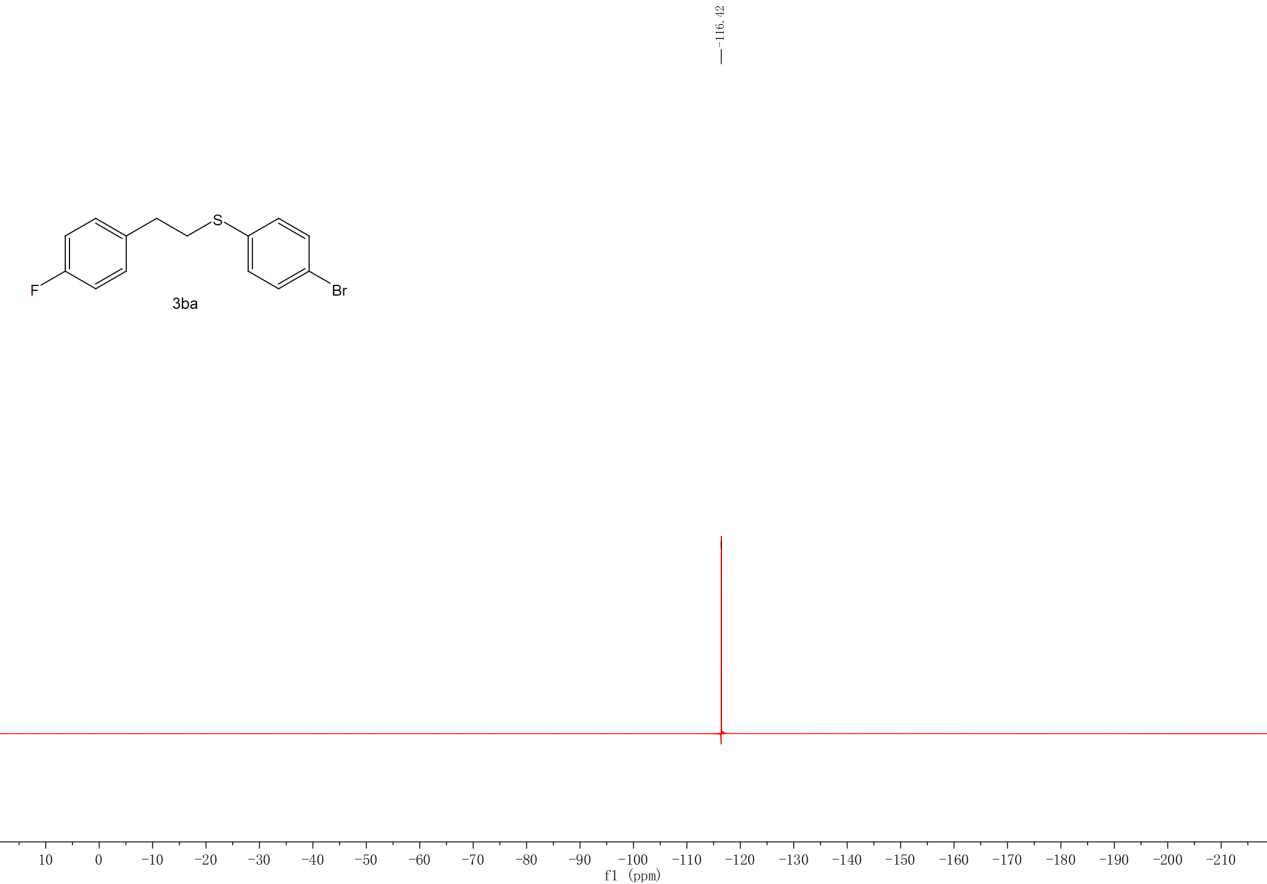
**Figure S2.** 13C NMR spectra (400 MHz) of **3aa** in CDCl3.



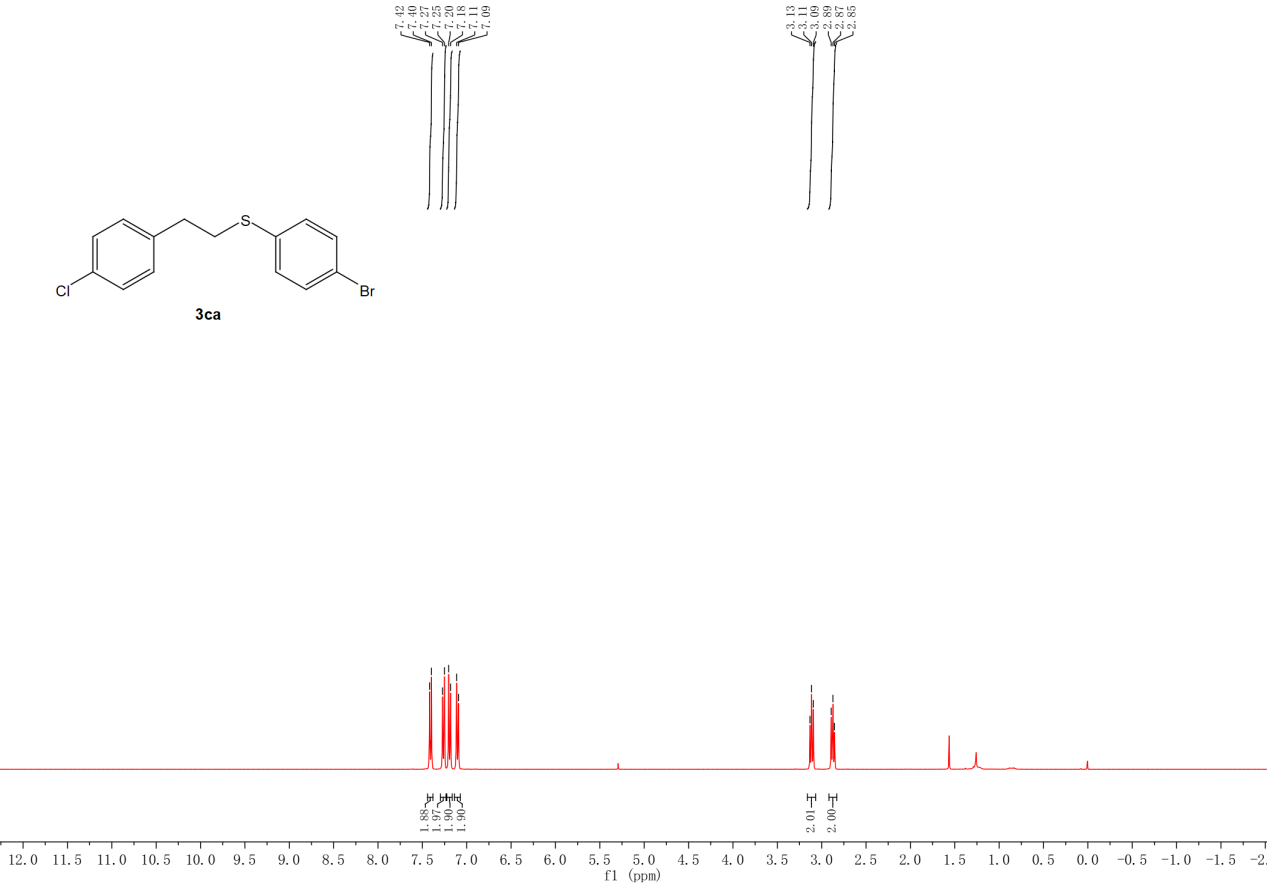
**Figure S3.** 1H NMR spectra (400 MHz) of **3ba** in CDCl3.



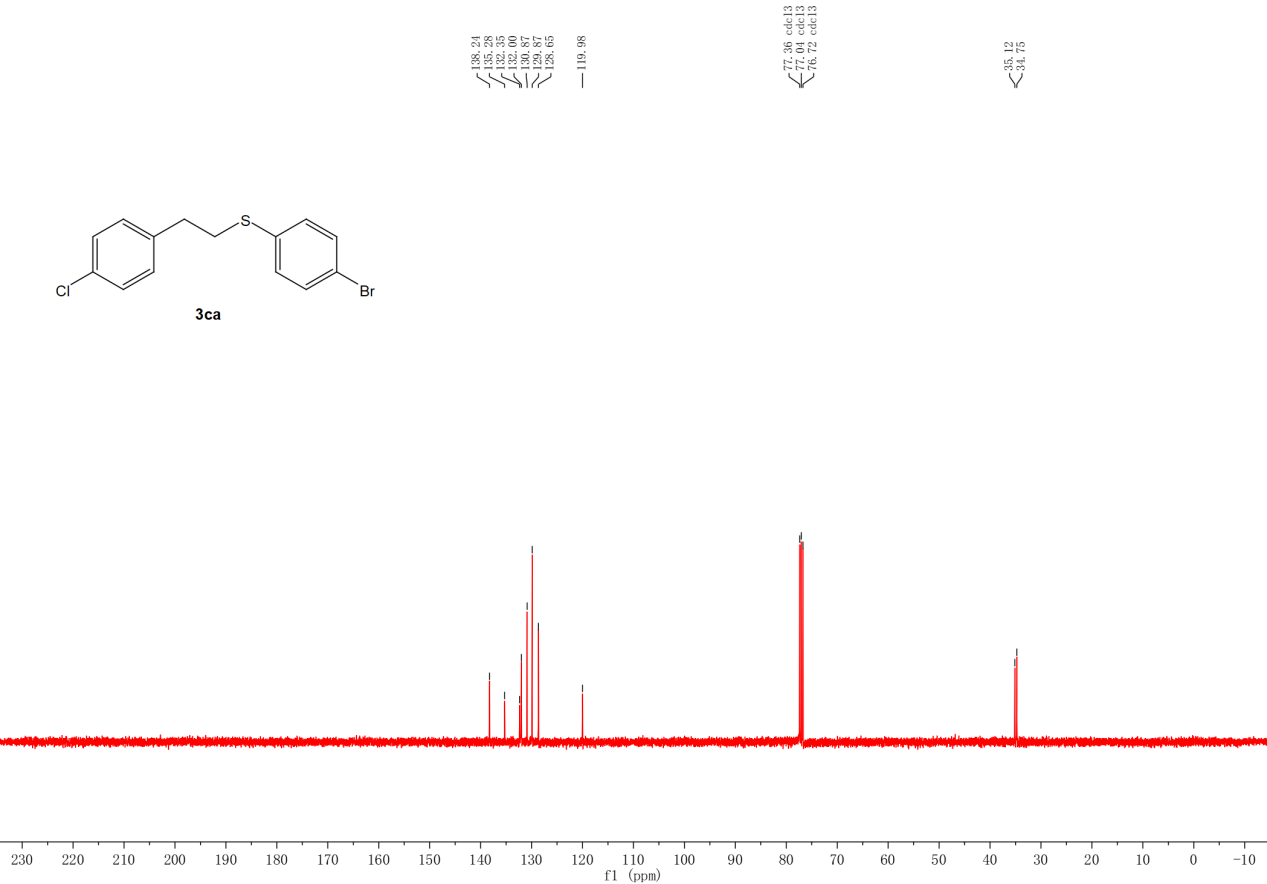
**Figure S4.** 13C NMR spectra (400 MHz) of **3ba** in CDCl3.



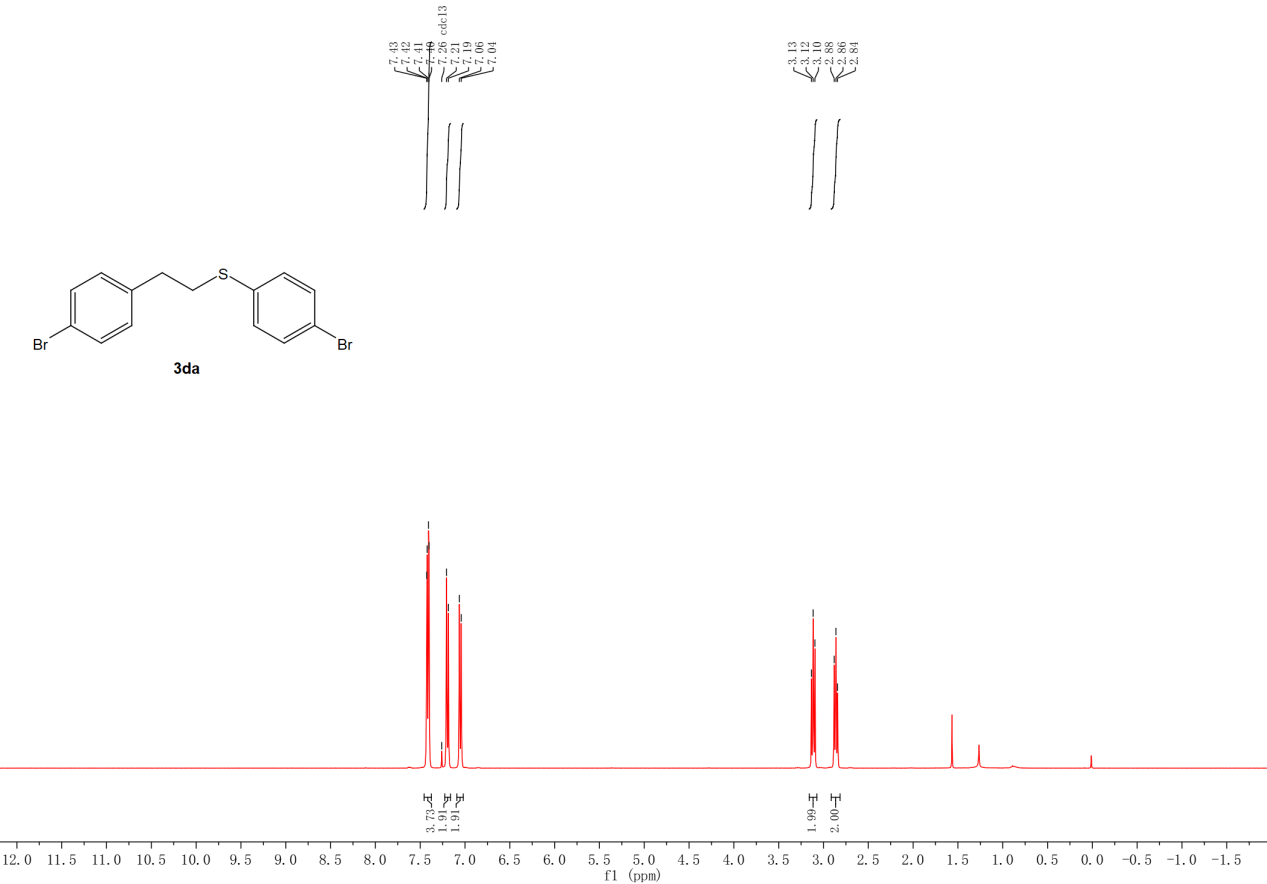
**Figure S5.** 19F NMR spectra (400 MHz) of **3ba** in CDCl3.



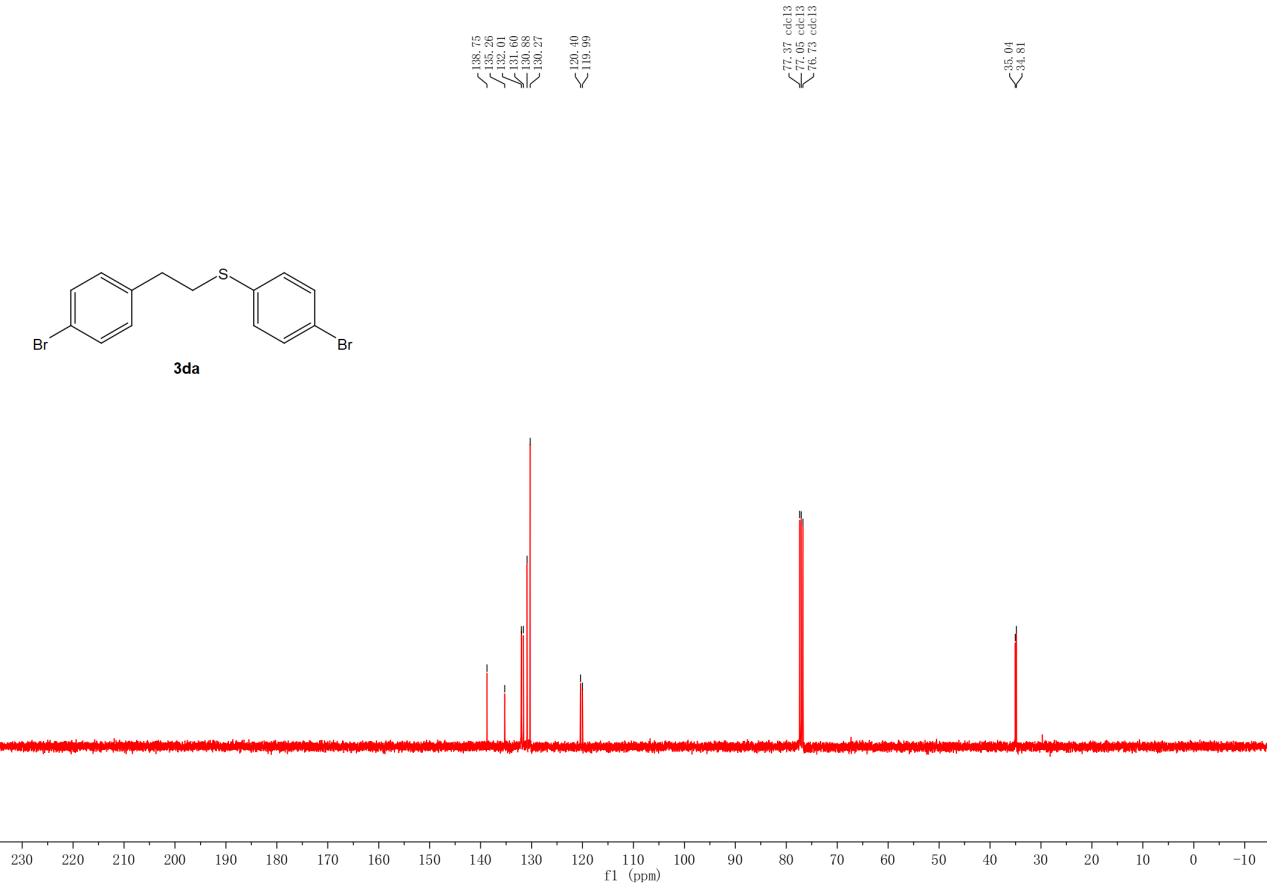
**Figure S6.** 1H NMR spectra (400 MHz) of **3ca** in CDCl3.



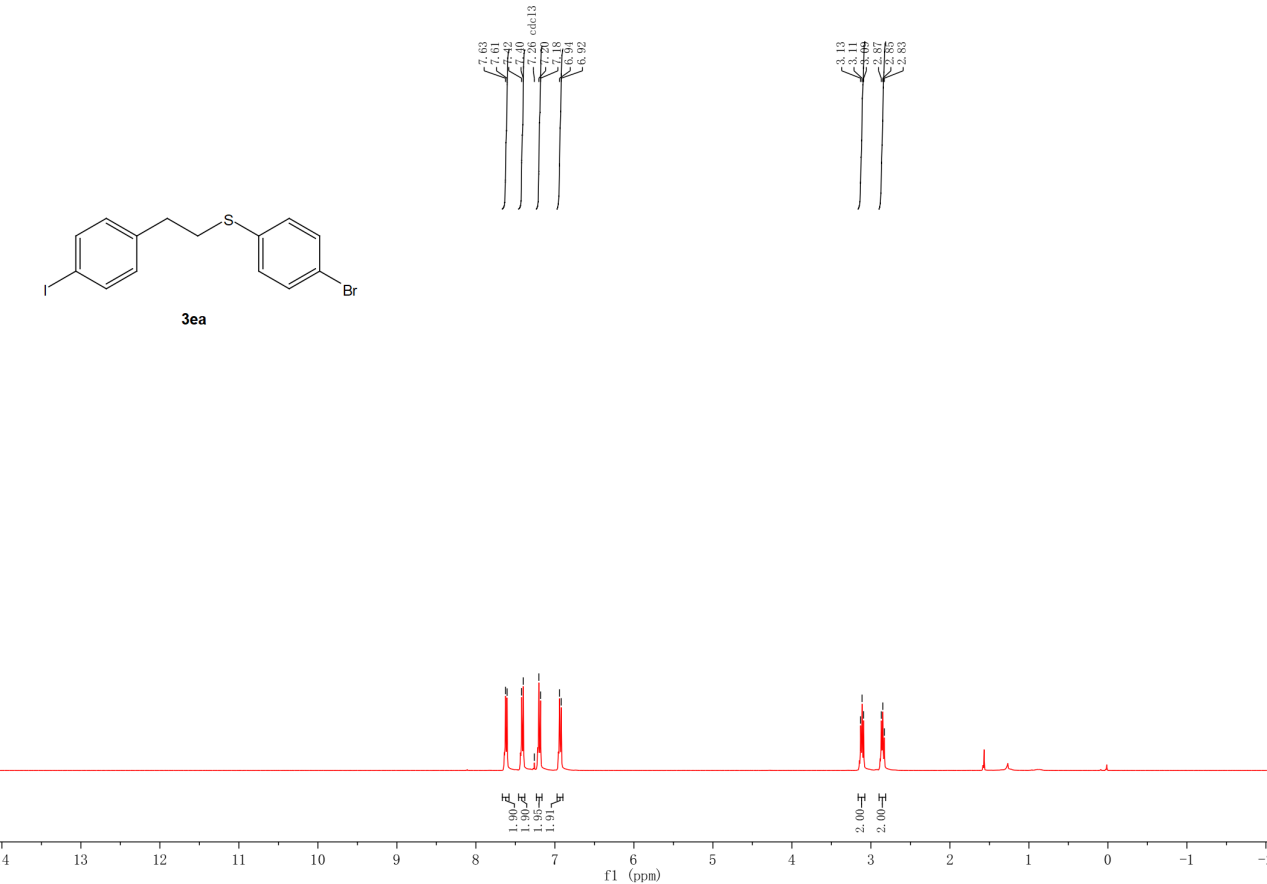
**Figure S7.** 13C NMR spectra (400 MHz) of **3ca** in CDCl3.



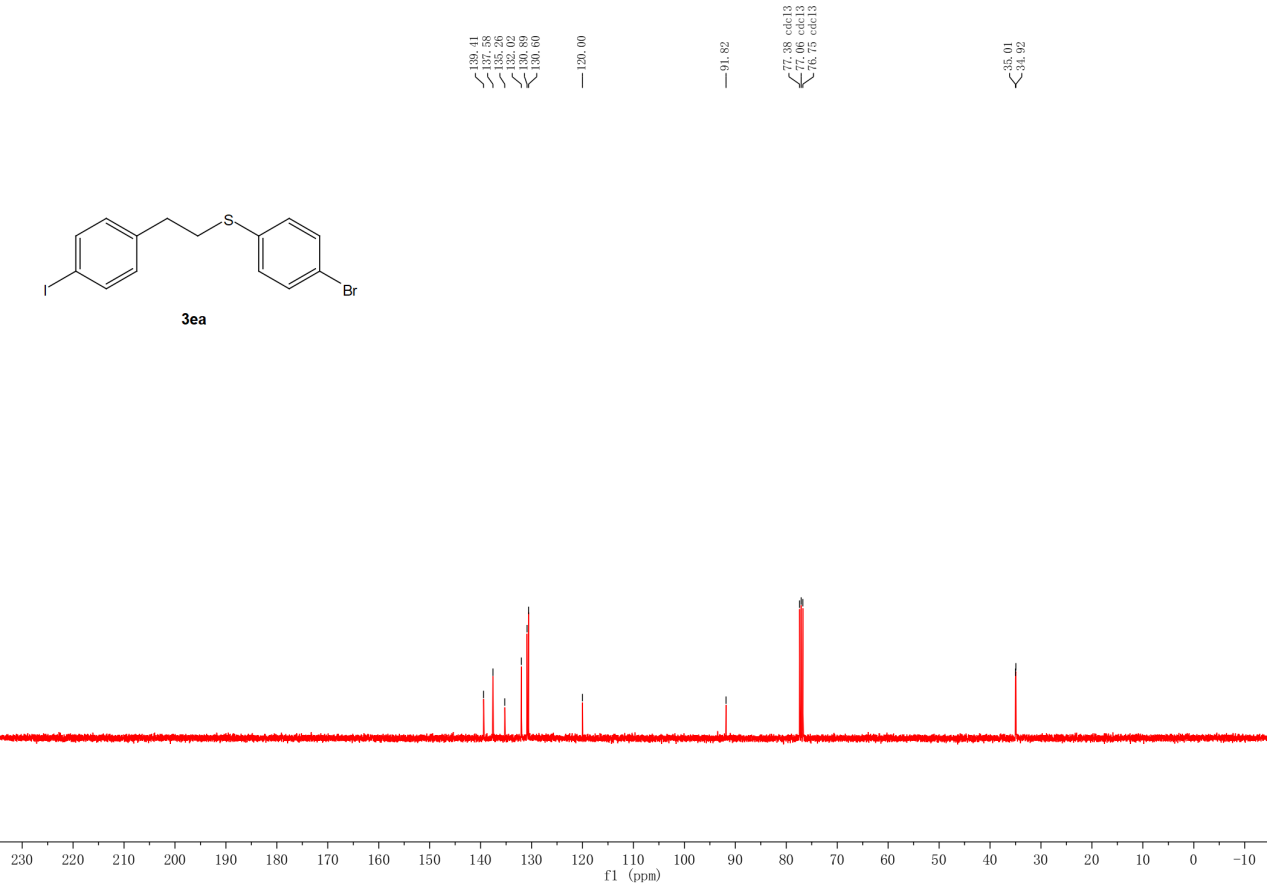
**Figure S8.** 1H NMR spectra (400 MHz) of **3da** in CDCl3.



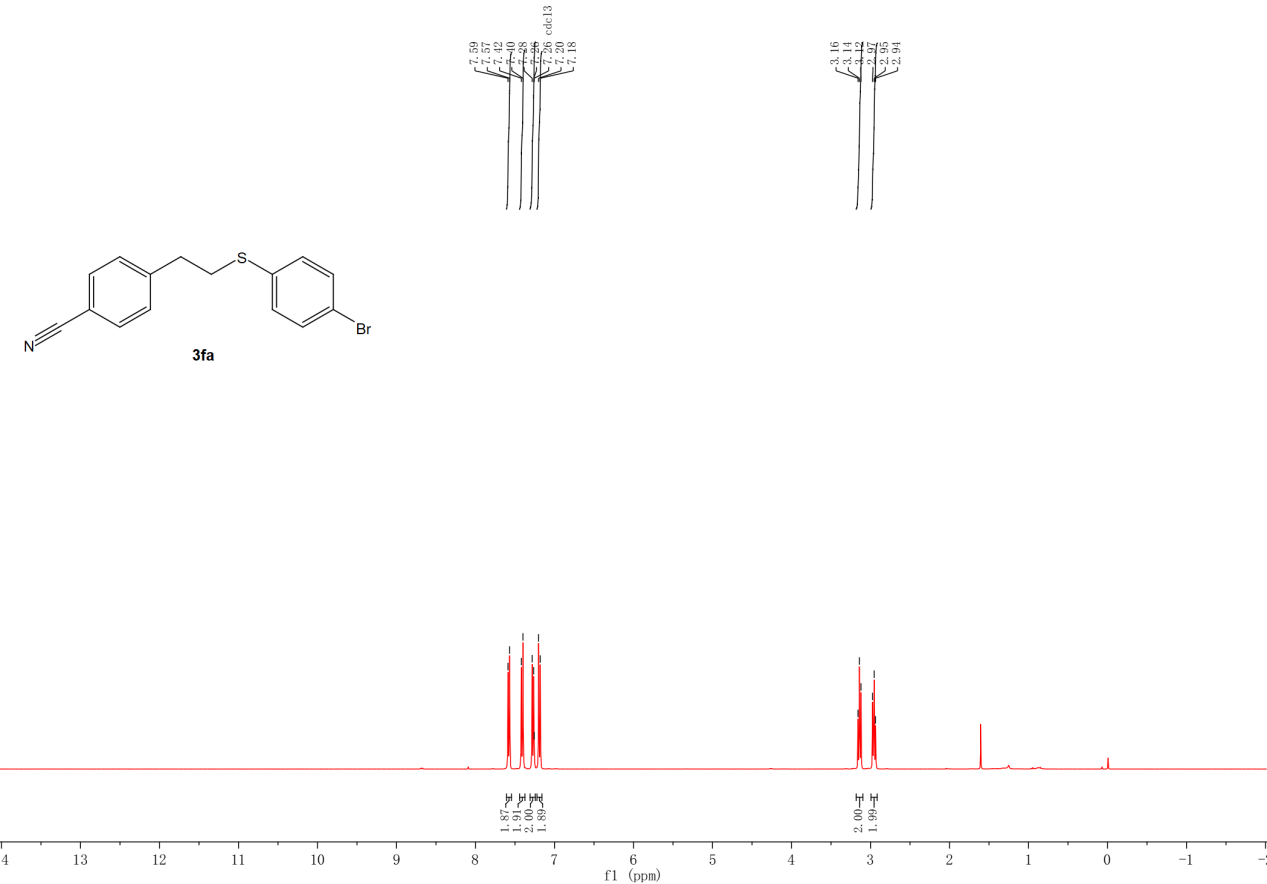
**Figure S9.** 13C NMR spectra (400 MHz) of **3da** in CDCl3.



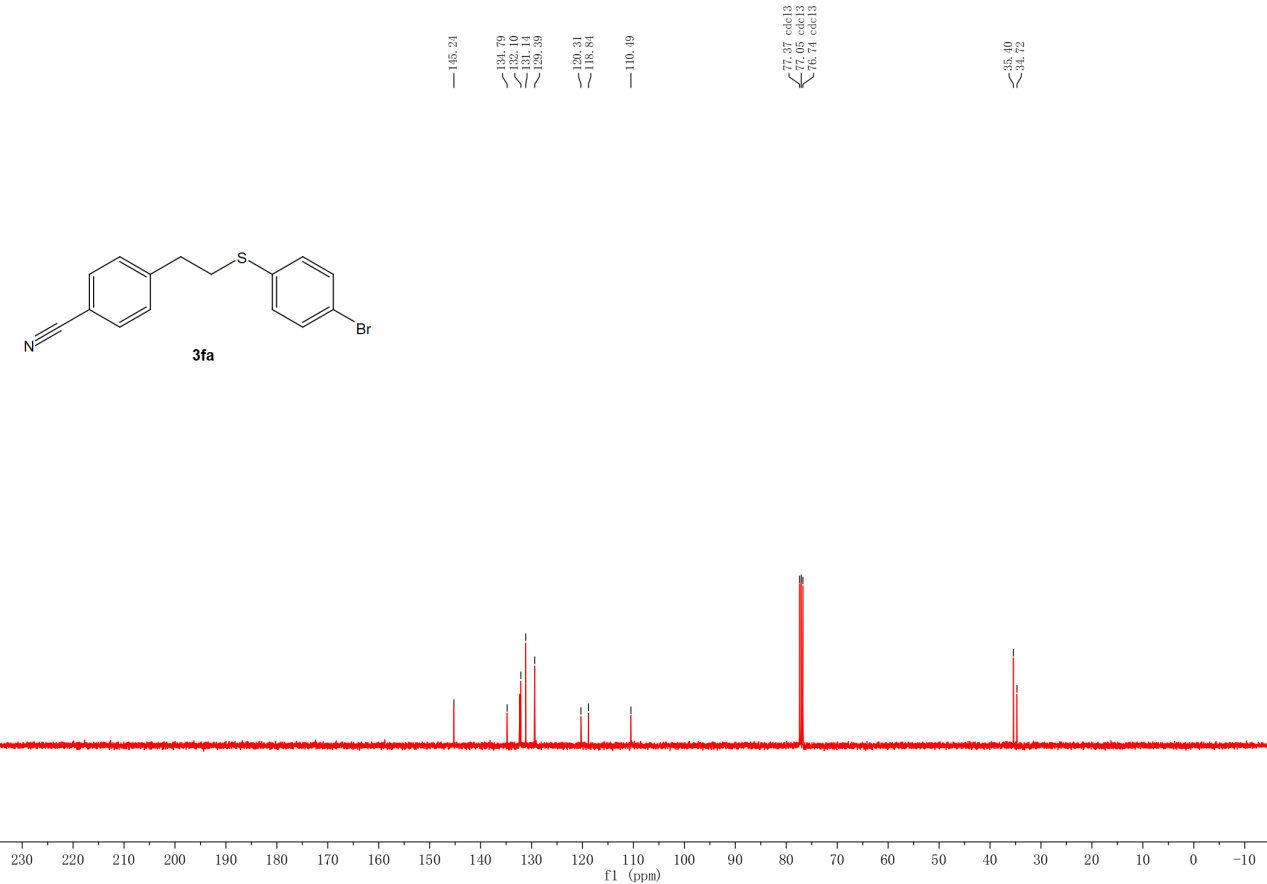
**Figure S10.** 1H NMR spectra (400 MHz) of **3ea** in CDCl3.



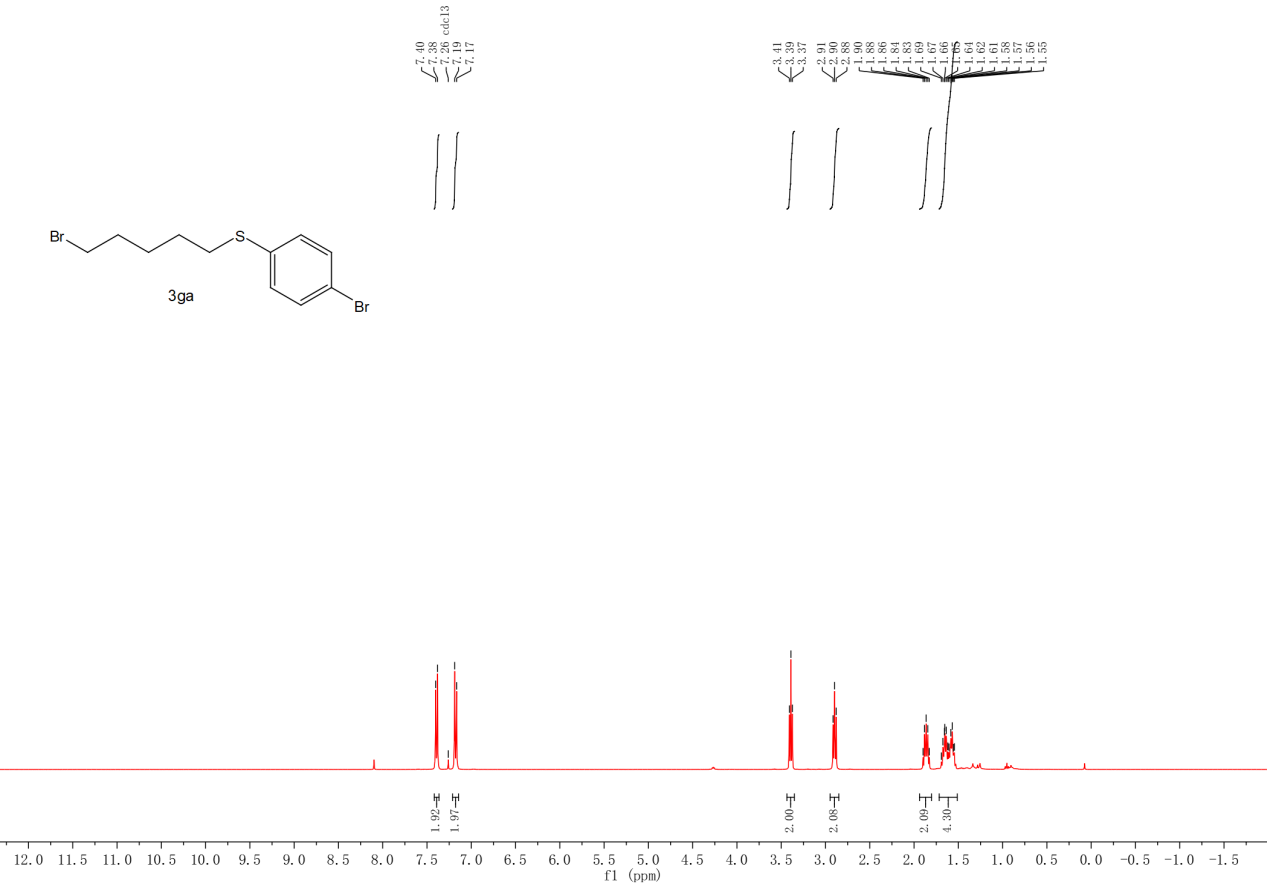
**Figure S11.** 13C NMR spectra (400 MHz) of **3ea** in CDCl3.



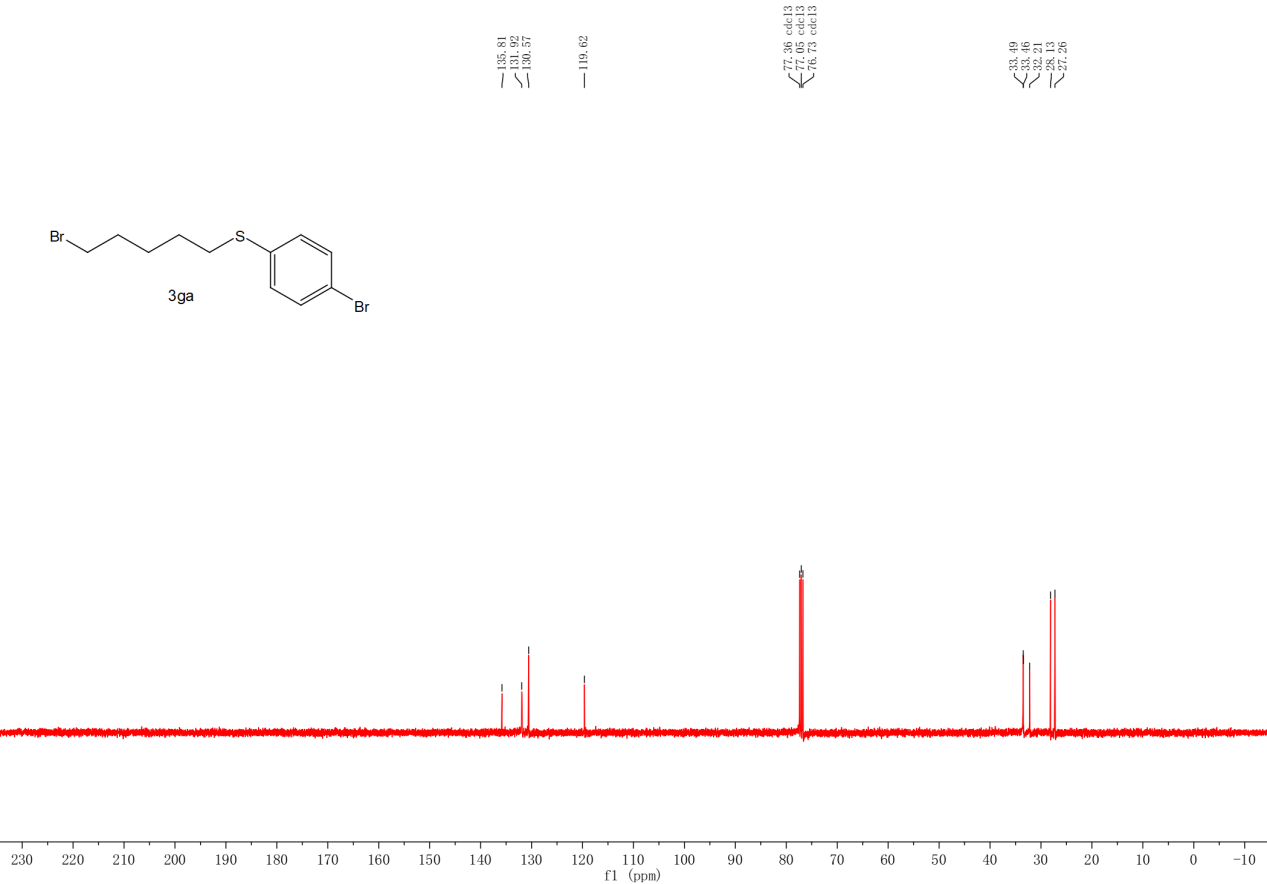
**Figure S12.** 1H NMR spectra (400 MHz) of **3fa** in CDCl3.



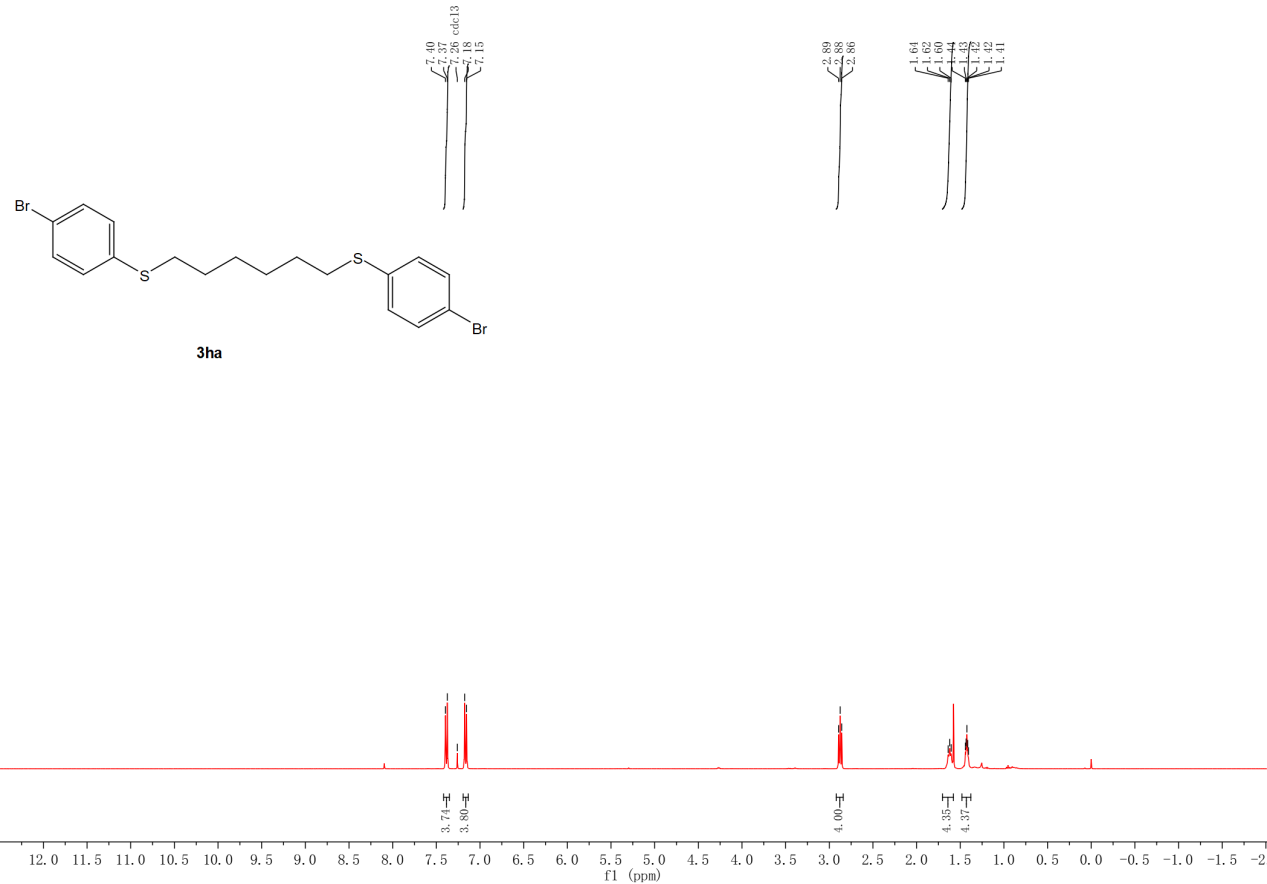
**Figure S13.** 13C NMR spectra (400 MHz) of **3fa** in CDCl3.



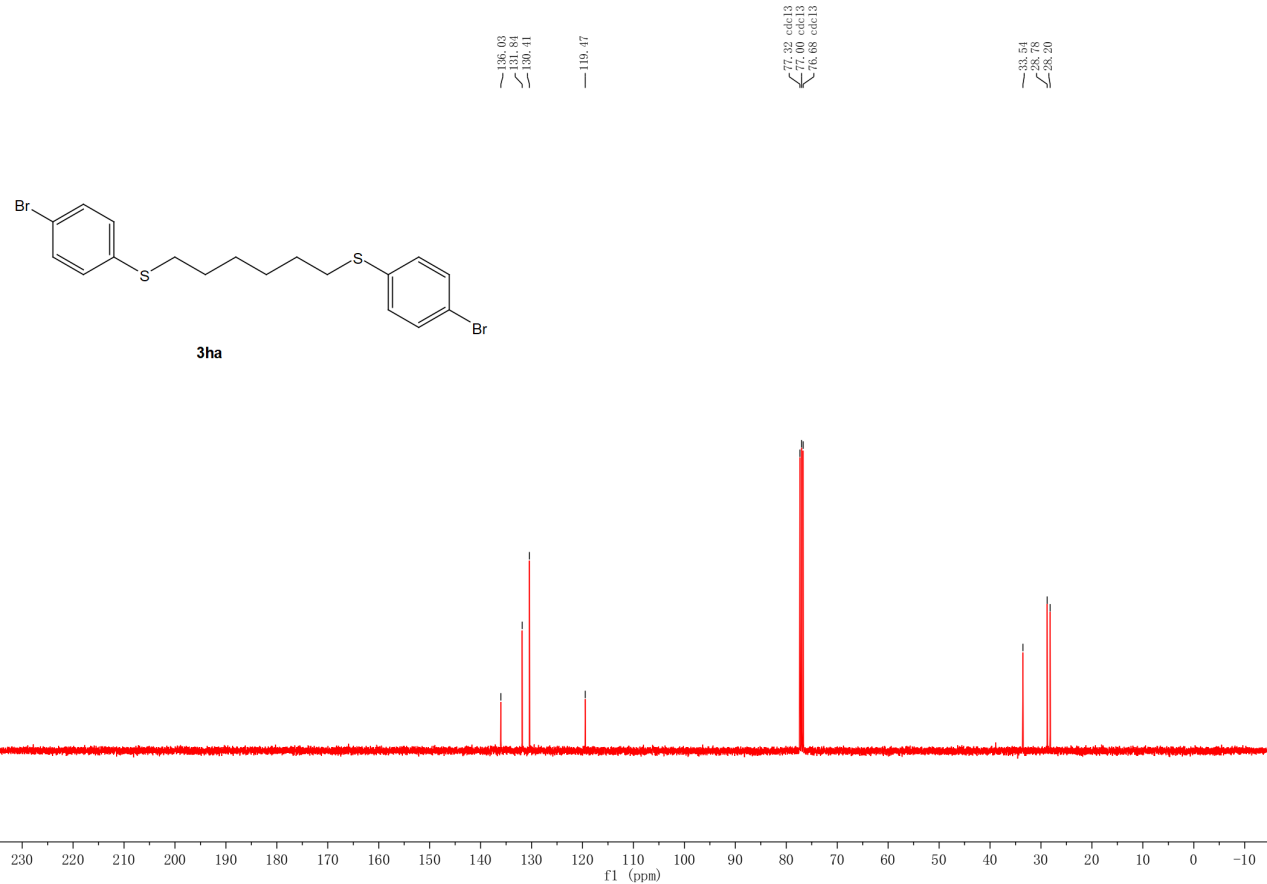
**Figure S14.** 1H NMR spectra (400 MHz) of **3ga** in CDCl3.



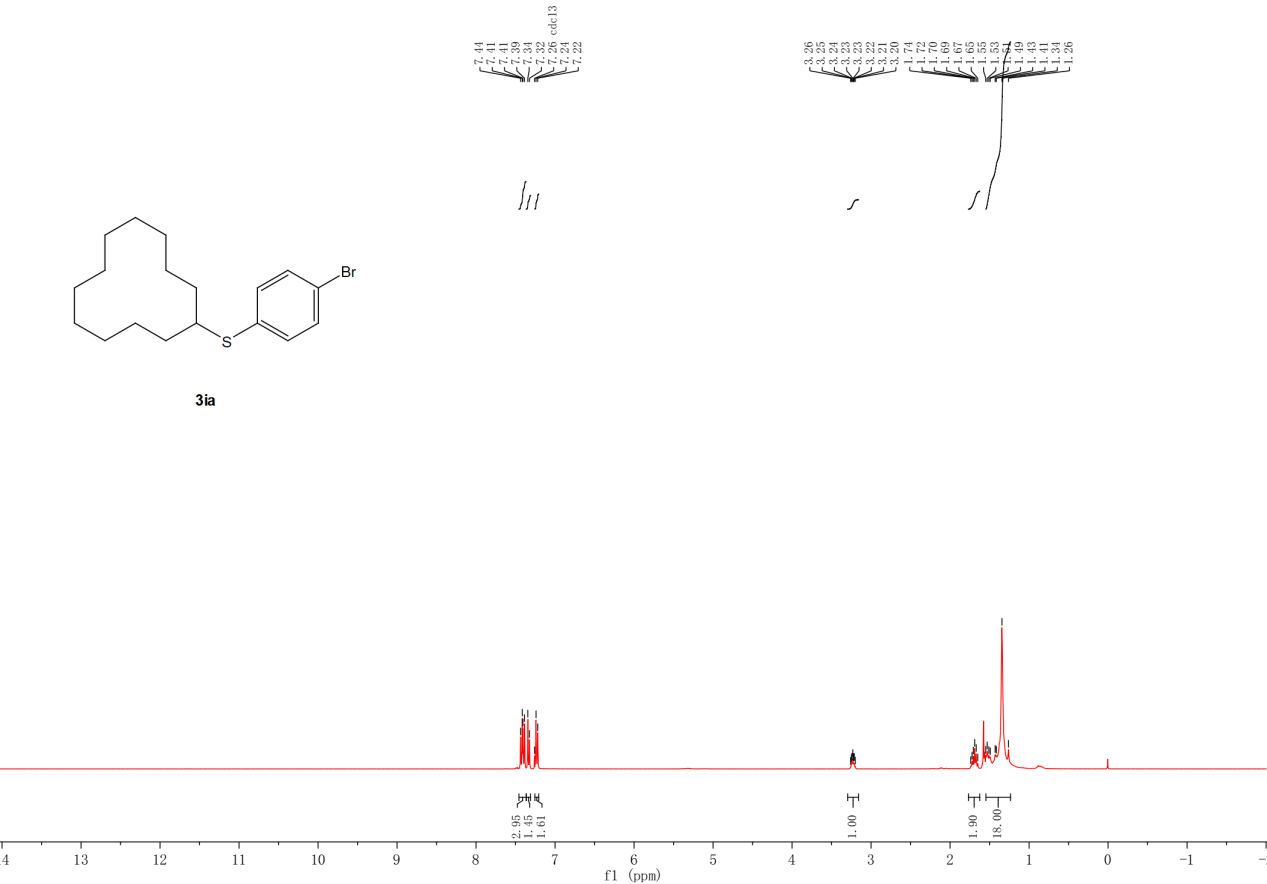
**Figure S15.** 13C NMR spectra (400 MHz) of **3ga** in CDCl3.



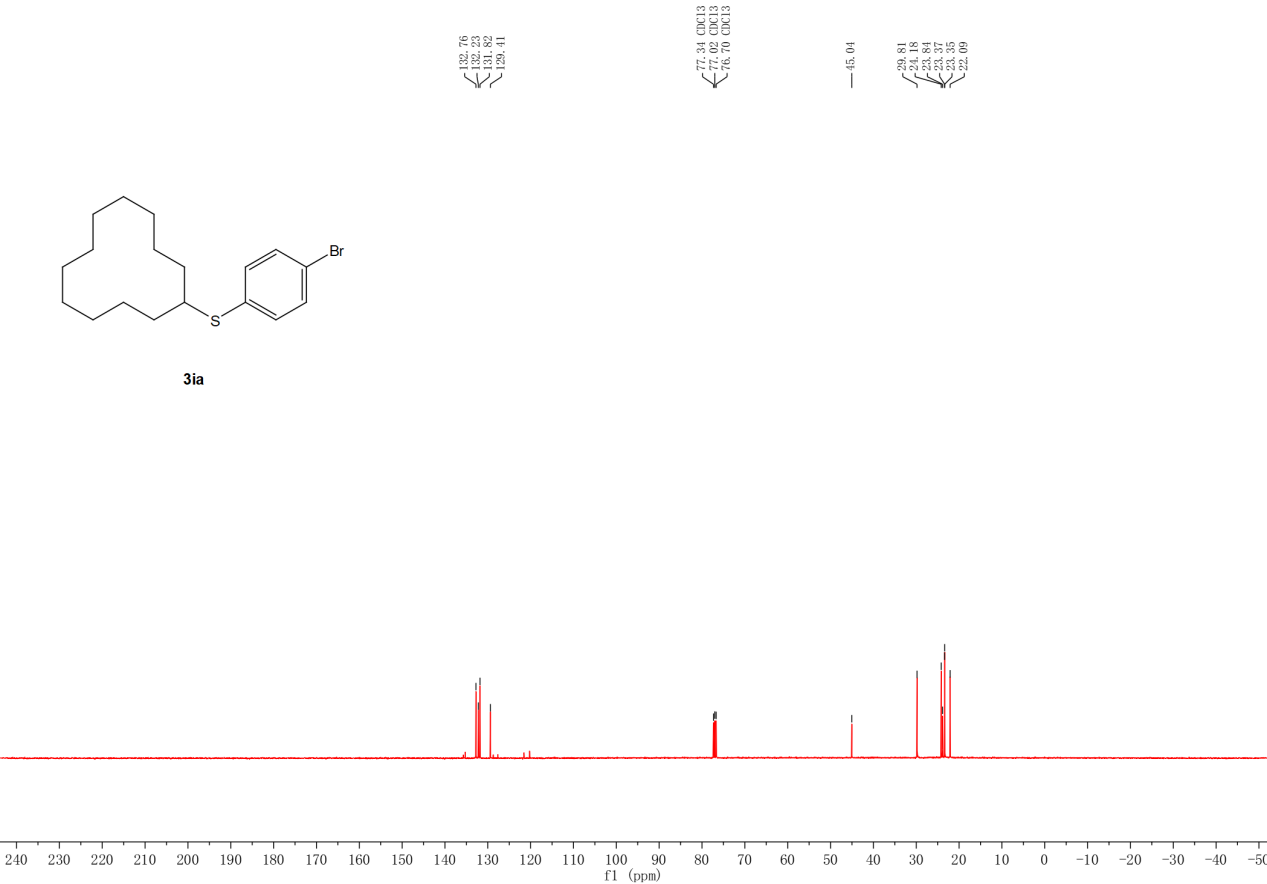
**Figure S16.** 1H NMR spectra (400 MHz) of **3ha** in CDCl3.



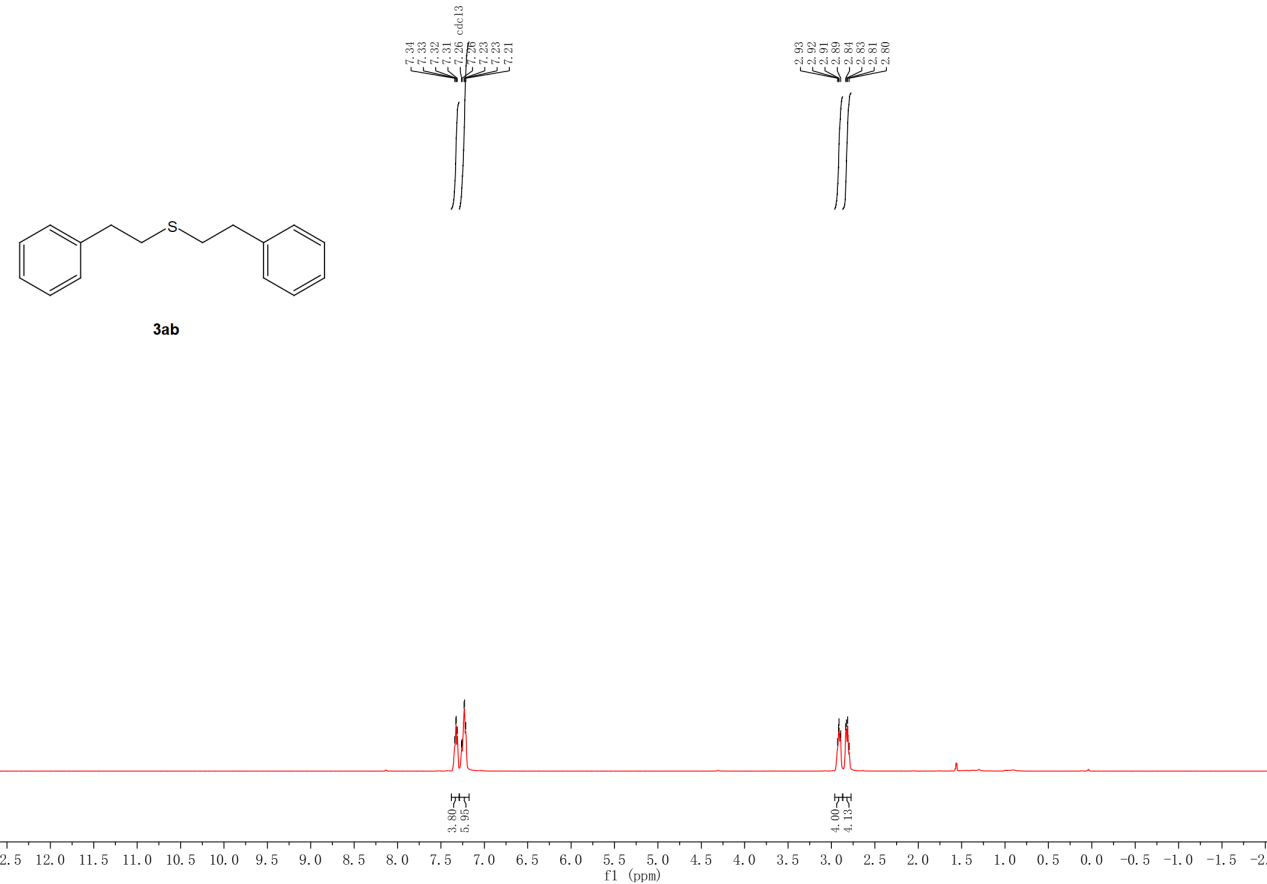
**Figure S17.** 13C NMR spectra (400 MHz) of **3ha** in CDCl3.



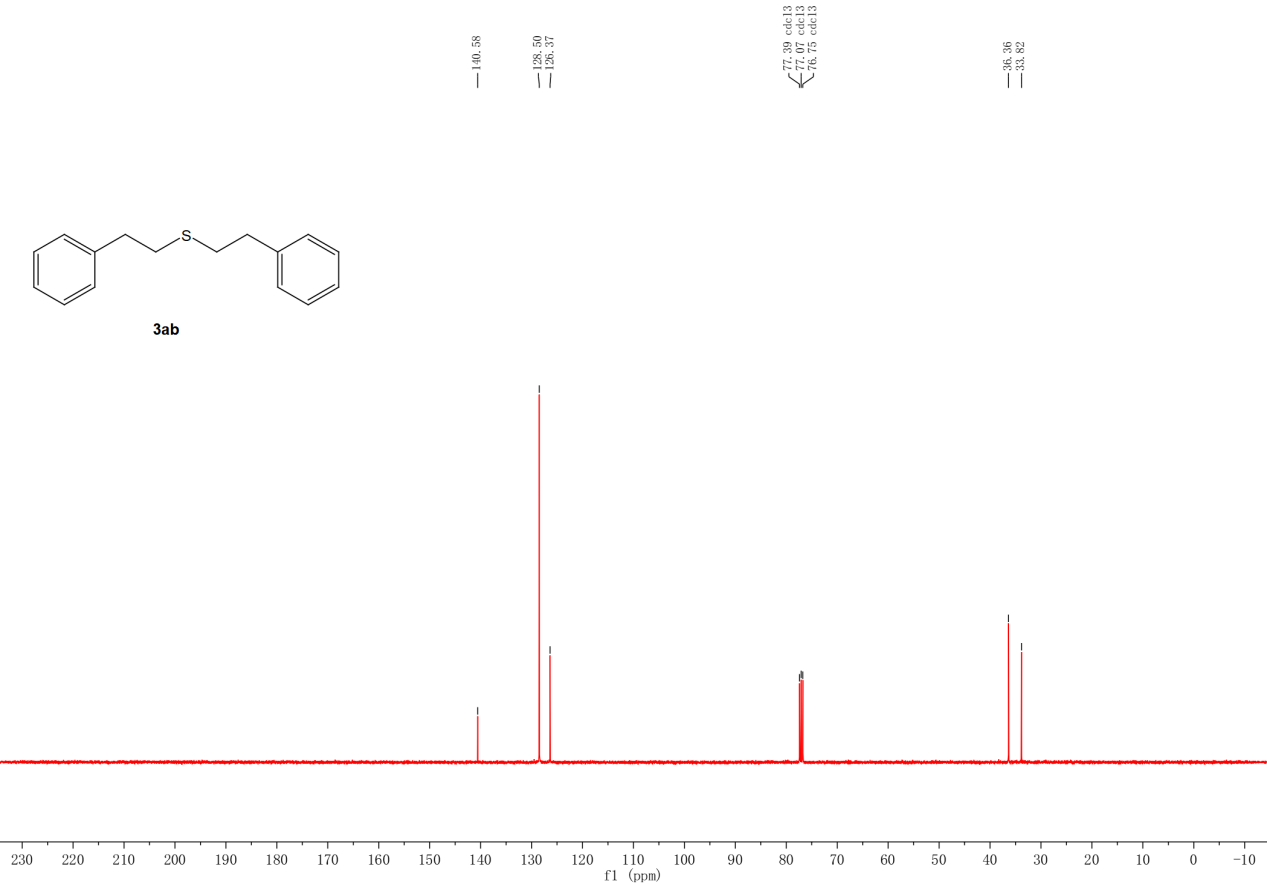
**Figure S18.** 1H NMR spectra (400 MHz) of **3ia** in CDCl3.



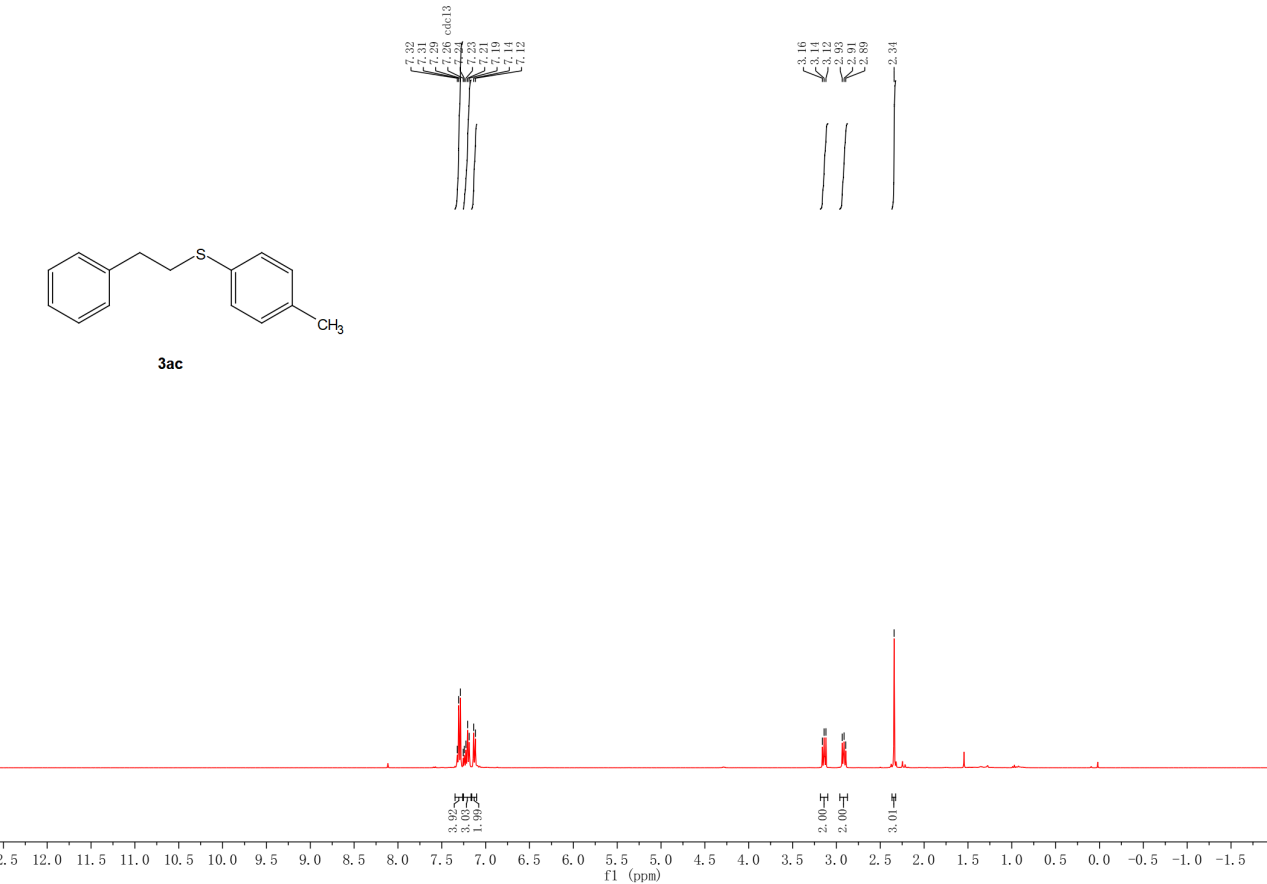
**Figure S19.** 13C NMR spectra (400 MHz) of **3ia** in CDCl3.



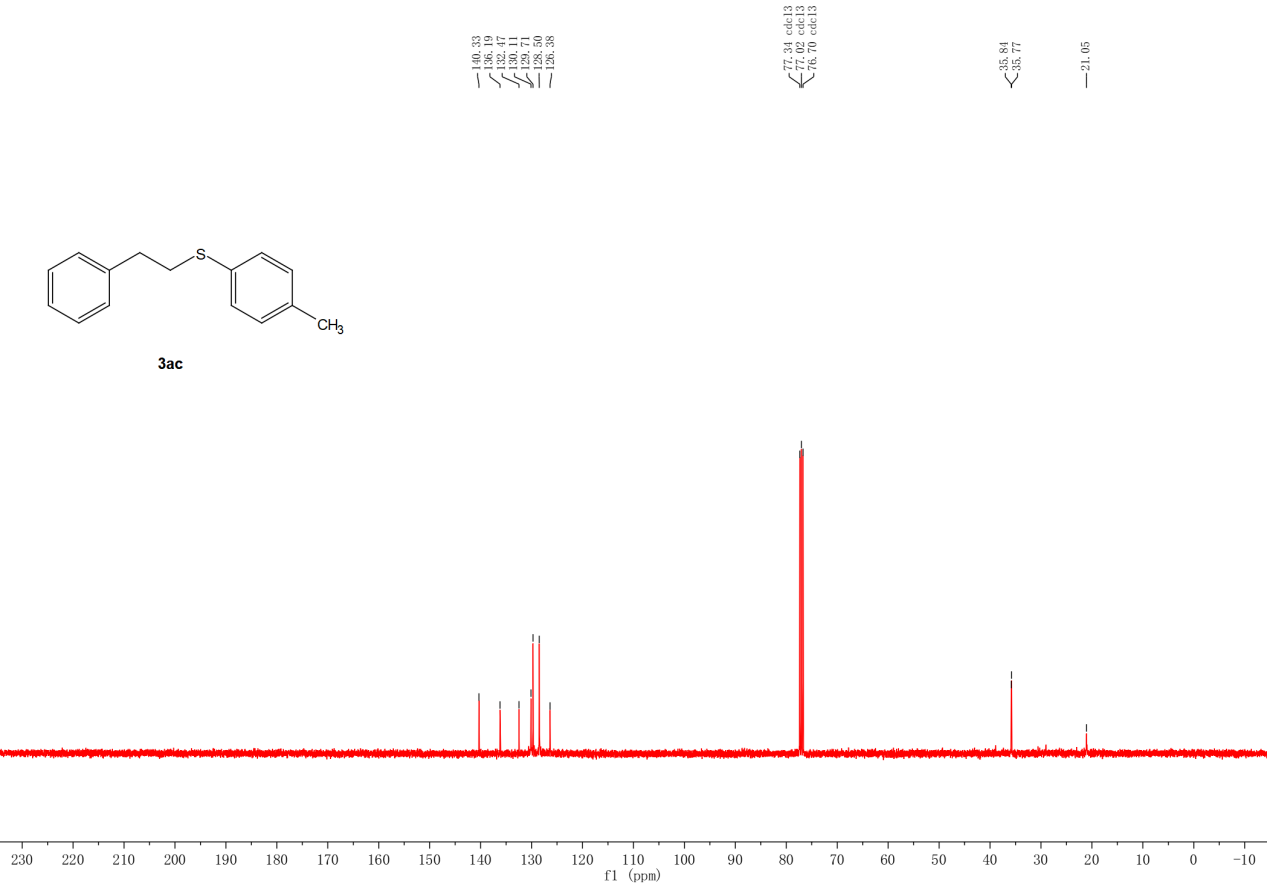
**Figure S20.** 1H NMR spectra (400 MHz) of **3ab** in CDCl3.



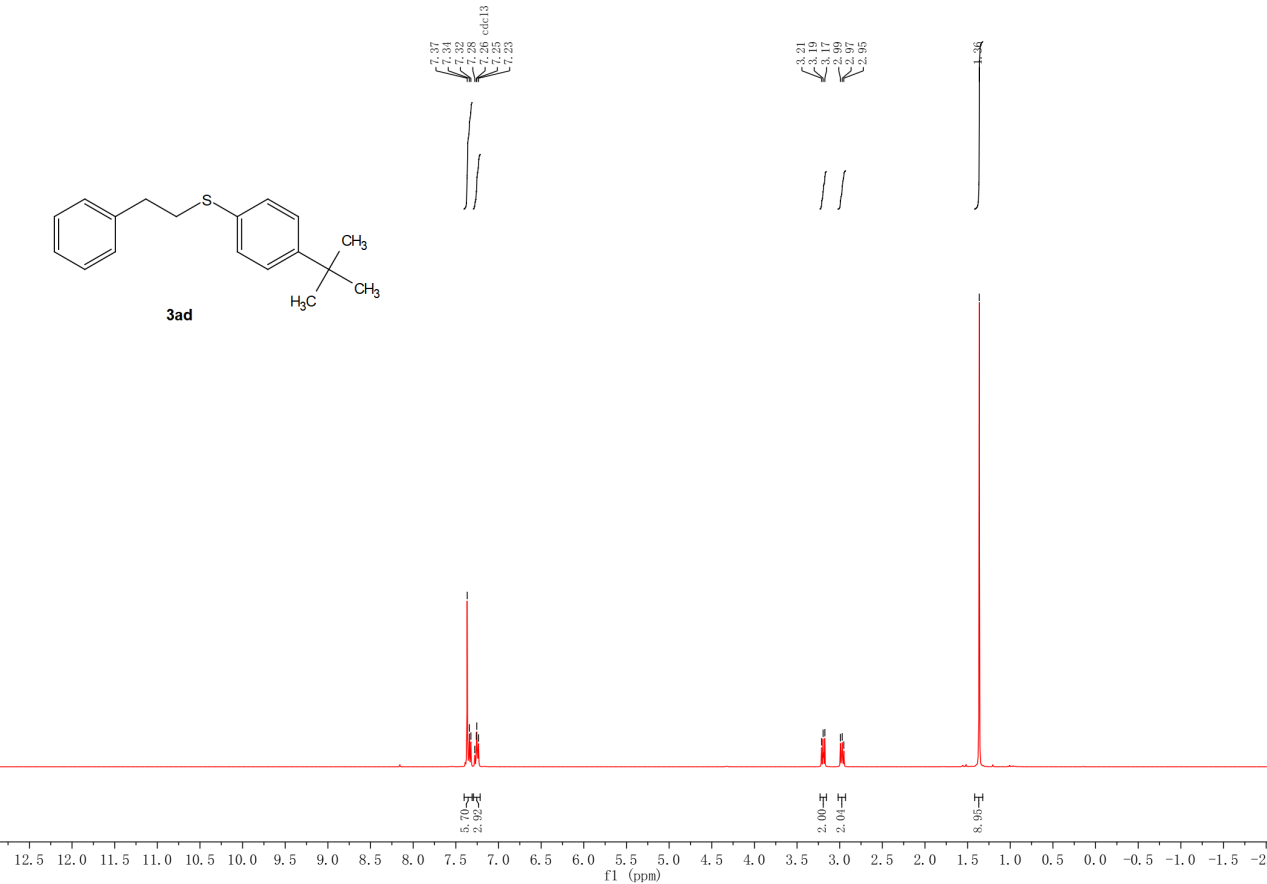
**Figure S21.** 13C NMR spectra (400 MHz) of **3ab** in CDCl3.



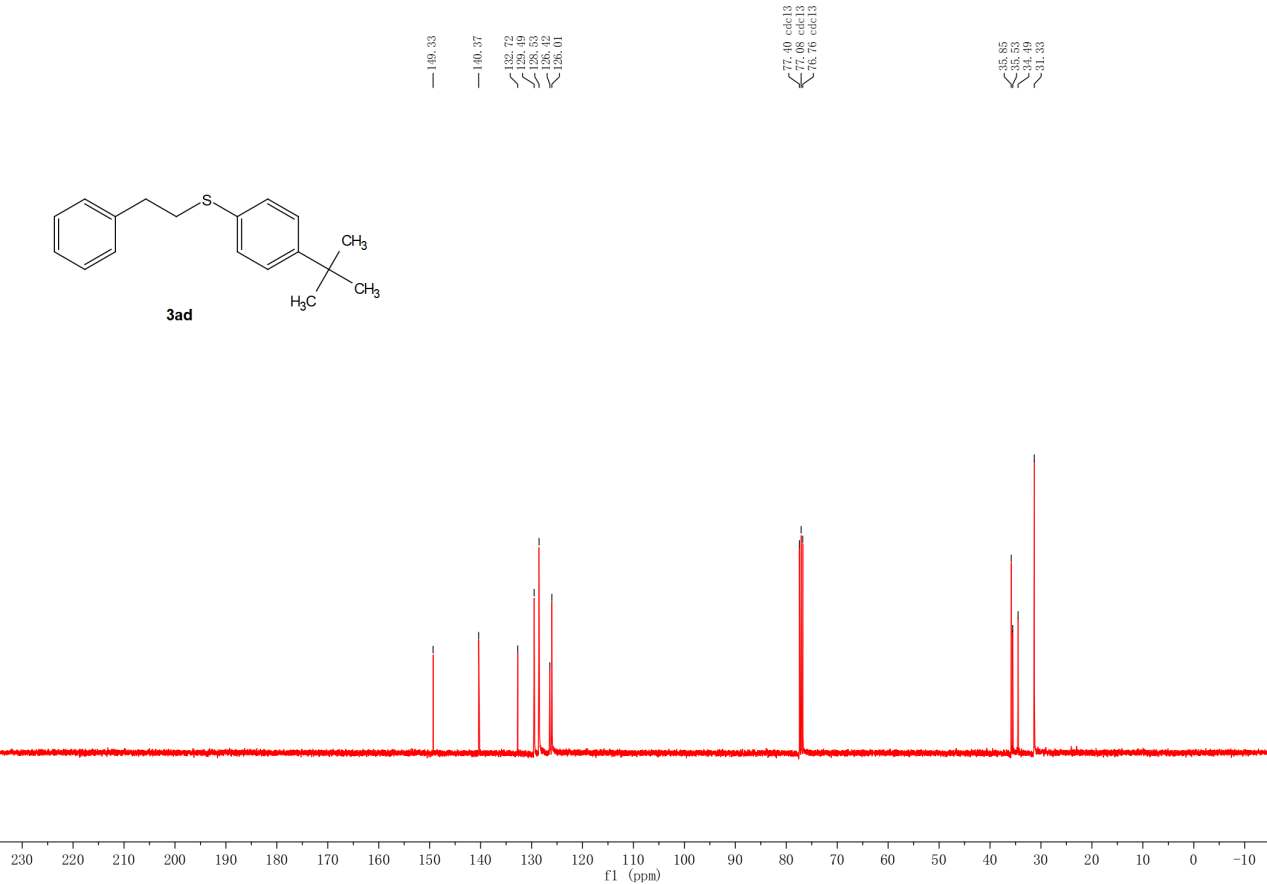
**Figure S22.** 1H NMR spectra (400 MHz) of **3ac** in CDCl3.



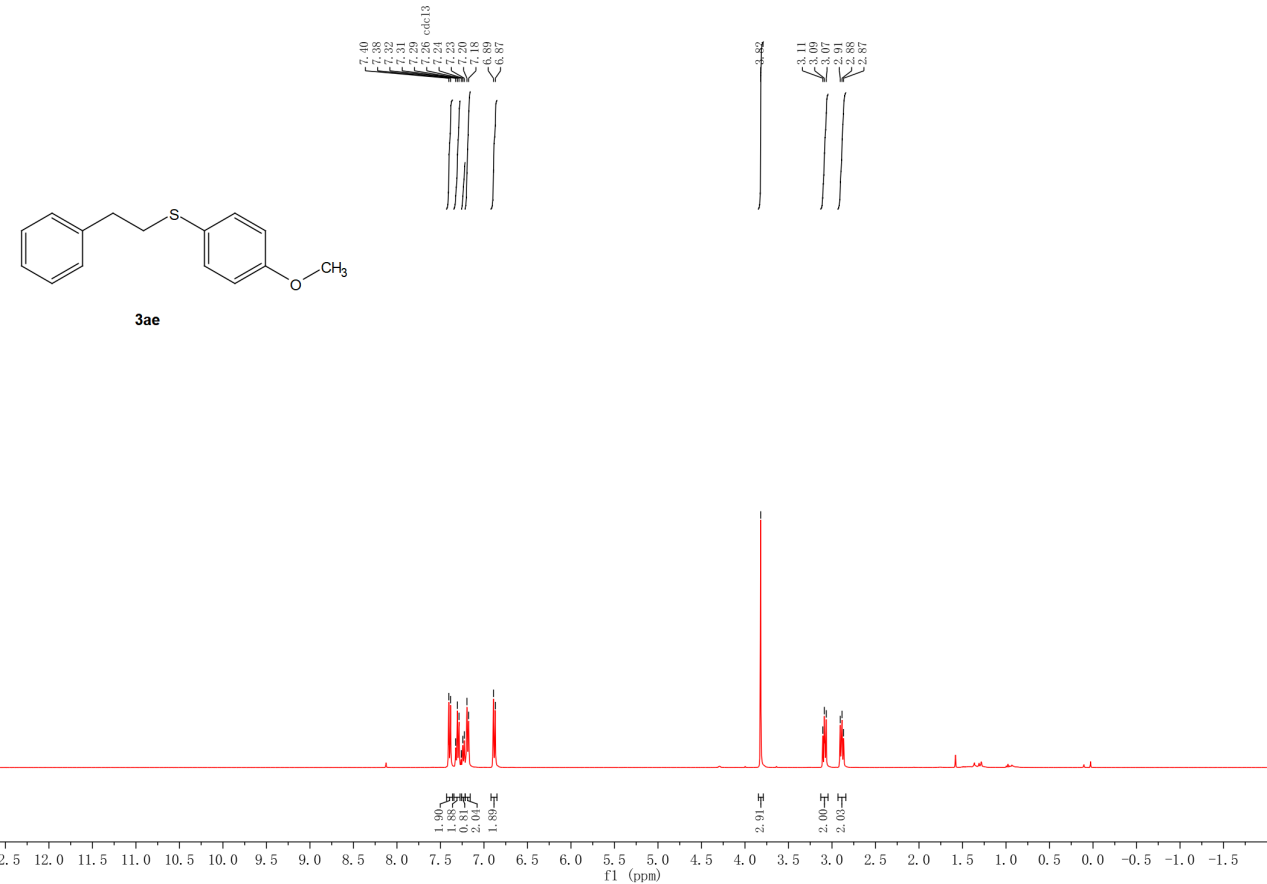
**Figure S23.** 13C NMR spectra (400 MHz) of **3ac** in CDCl3.



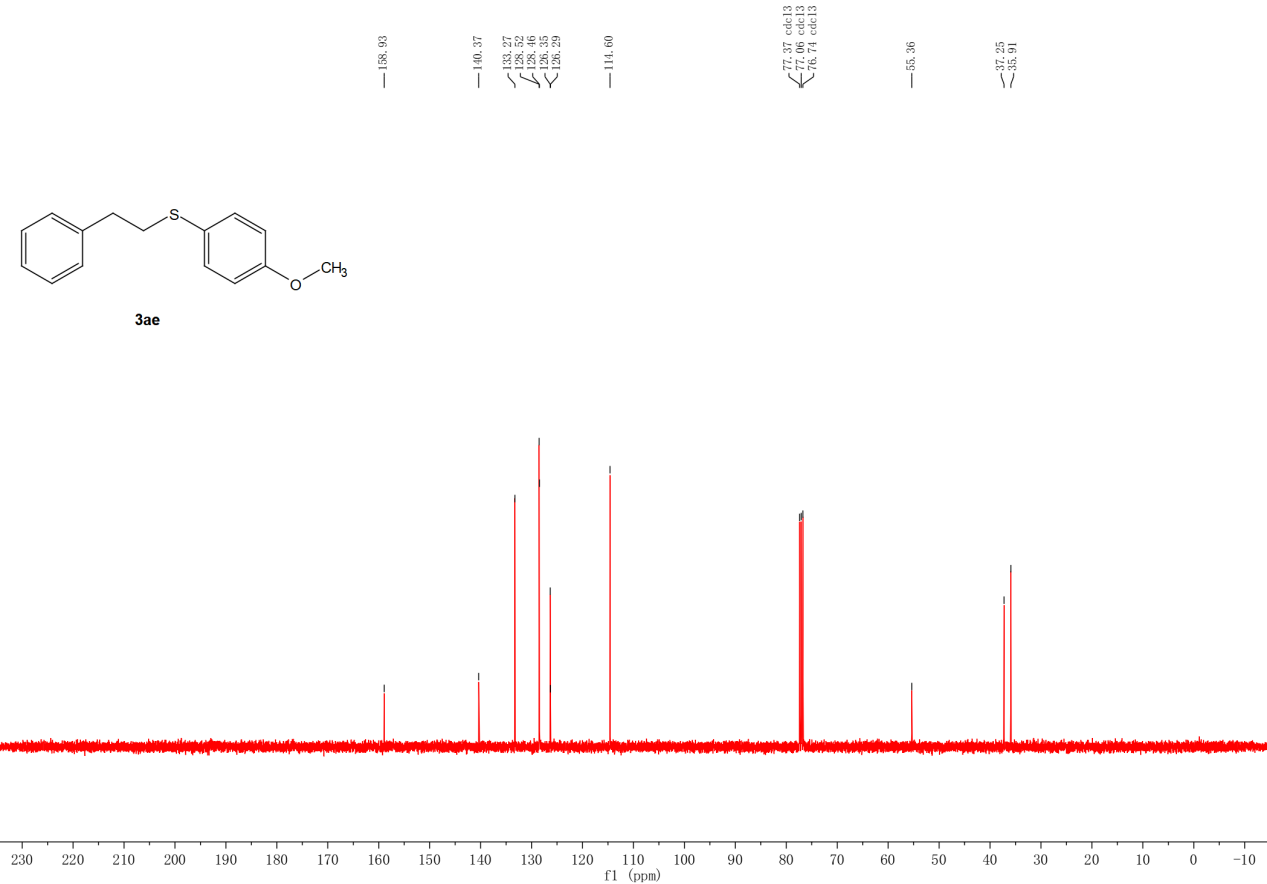
**Figure S24.** 1H NMR spectra (400 MHz) of **3ad** in CDCl3.



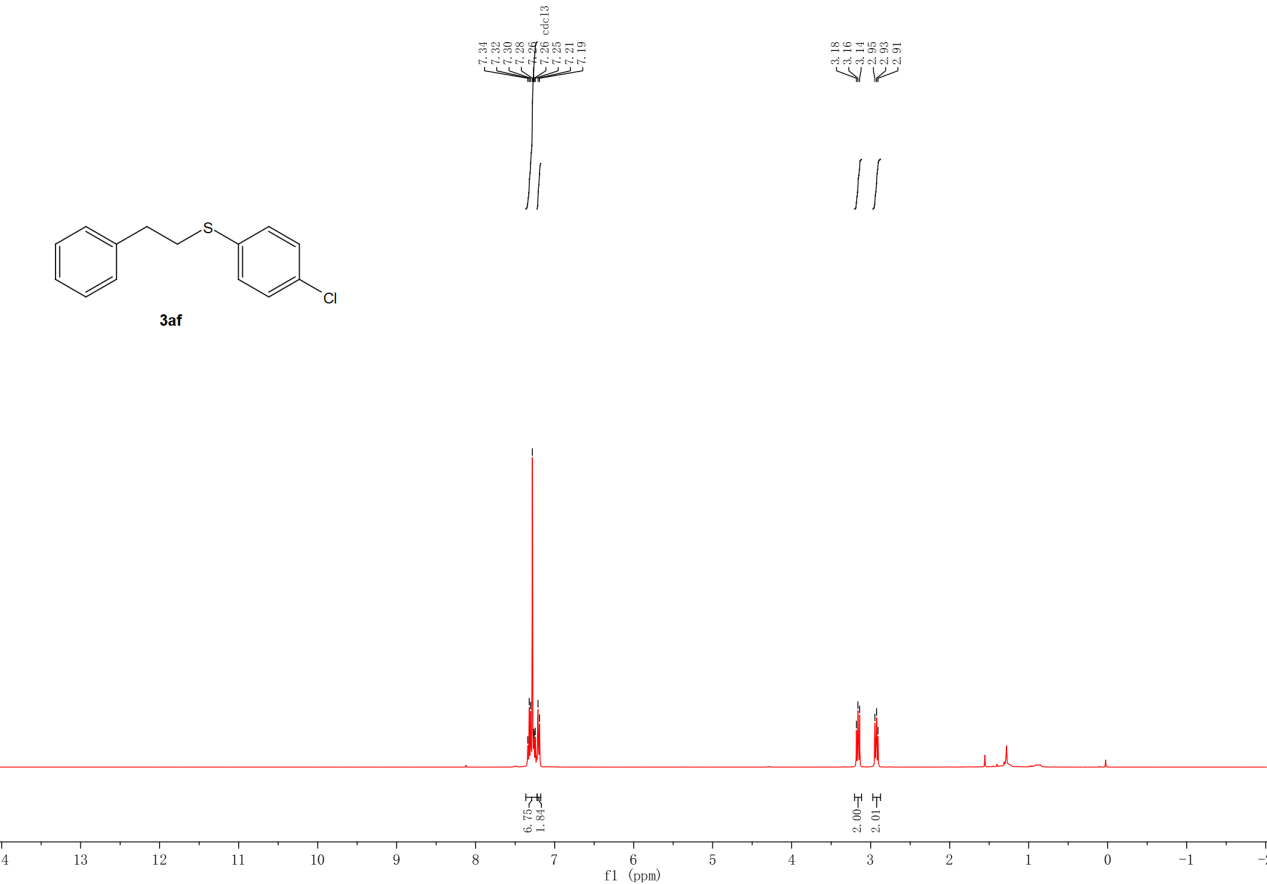
**Figure S25.** 13C NMR spectra (400 MHz) of **3ad** in CDCl3.



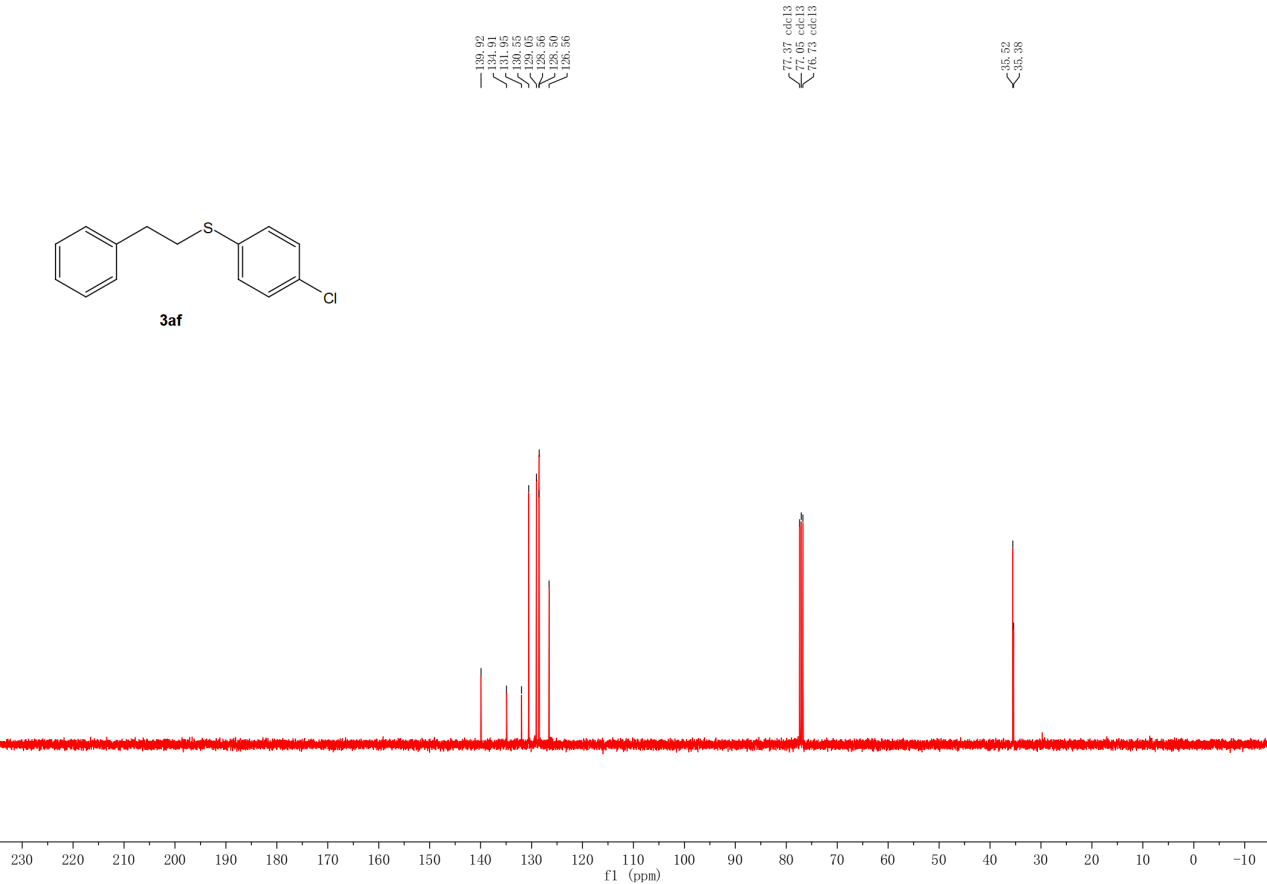
**Figure S26.** 1H NMR spectra (400 MHz) of **3ae** in CDCl3.



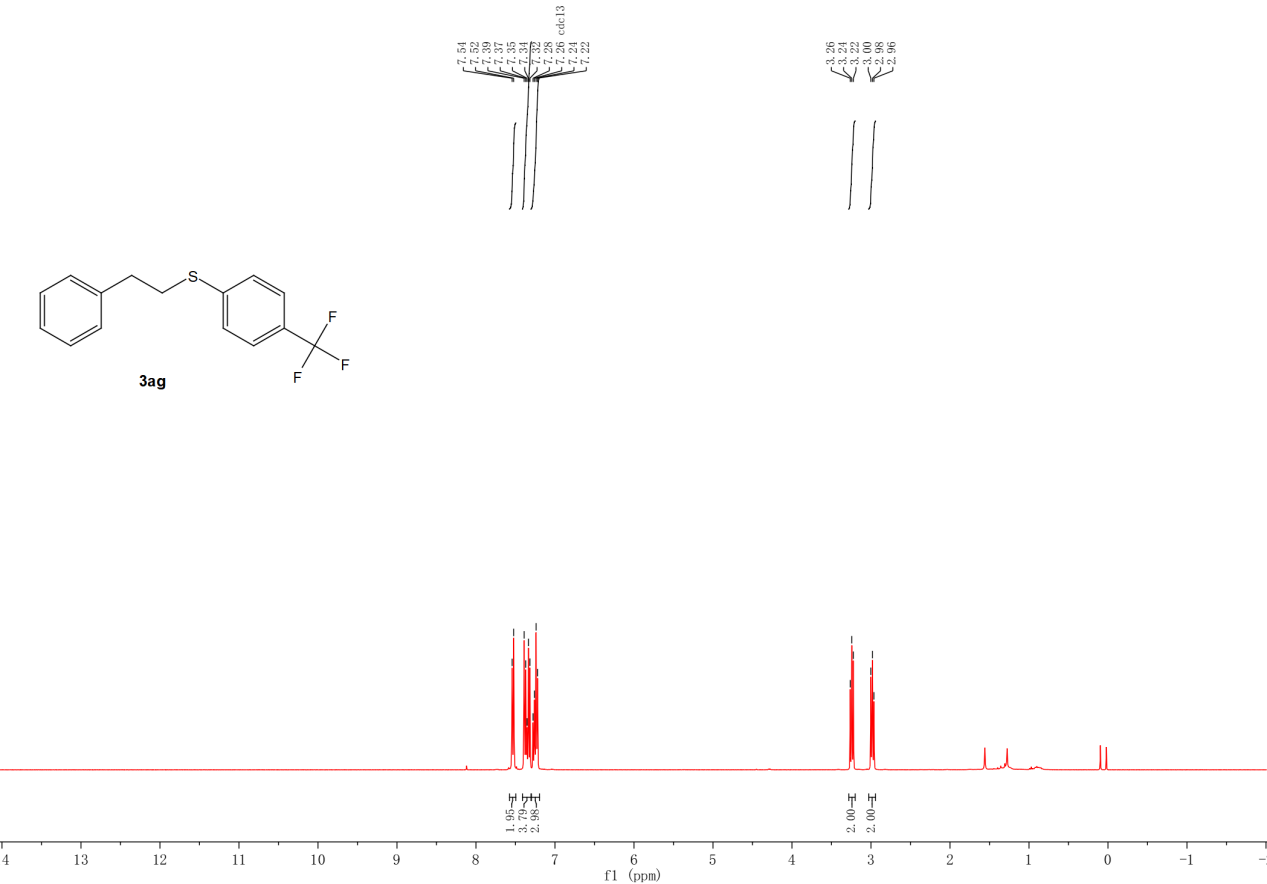
**Figure S27.** 13C NMR spectra (400 MHz) of **3ae** in CDCl3.



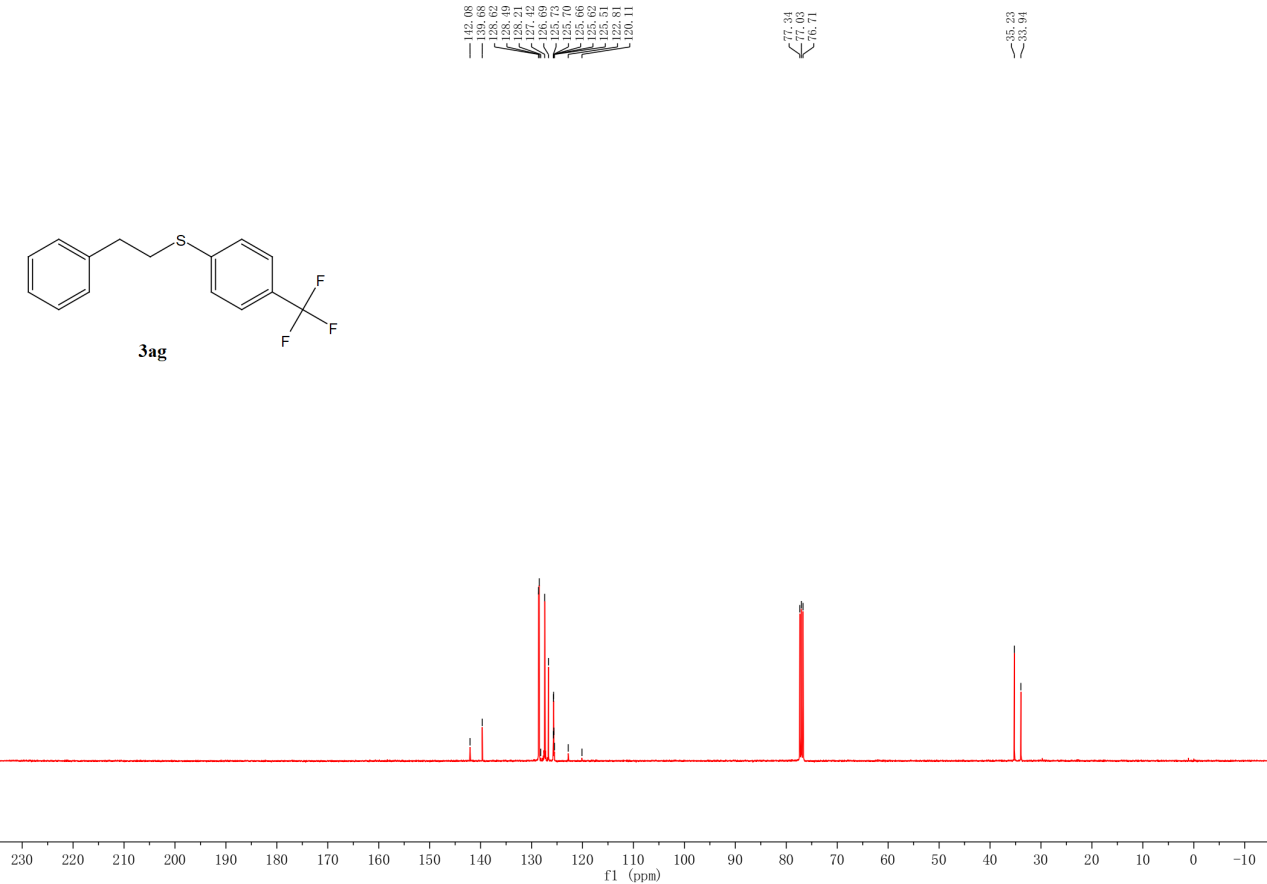
**Figure S28.** 1H NMR spectra (400 MHz) of **3af** in CDCl3.



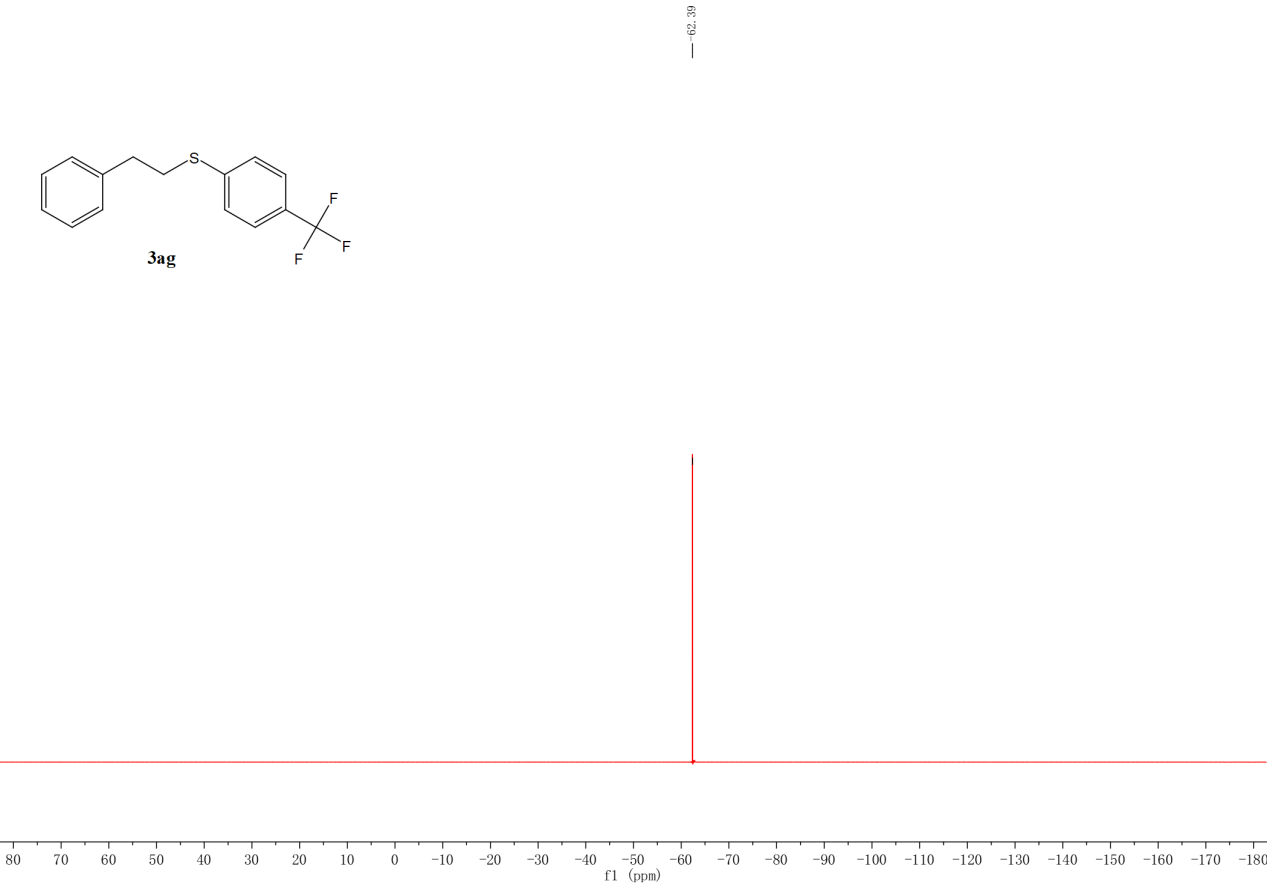
**Figure S29.** 13C NMR spectra (400 MHz) of **3af** in CDCl3.



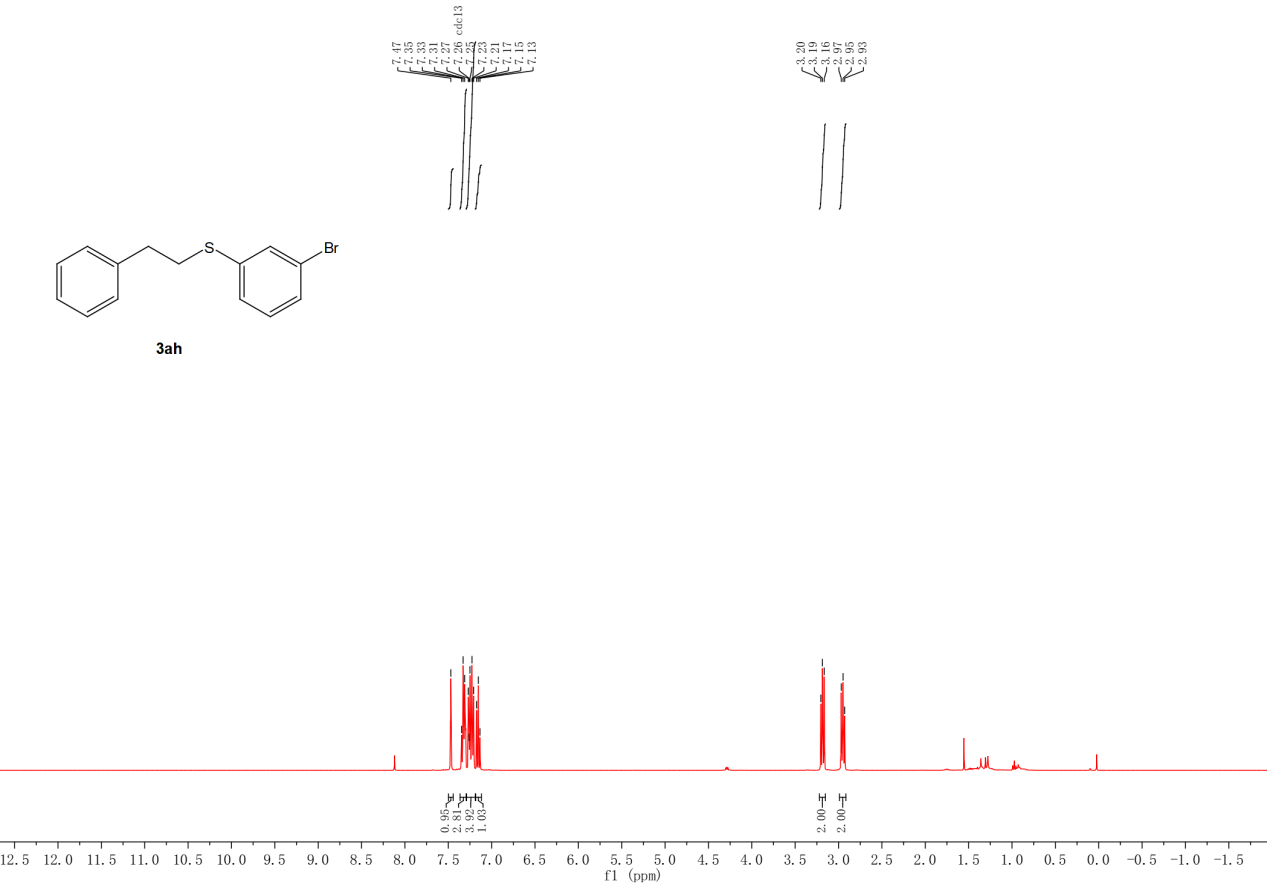
**Figure S30.** 1H NMR spectra (400 MHz) of **3ag** in CDCl3.



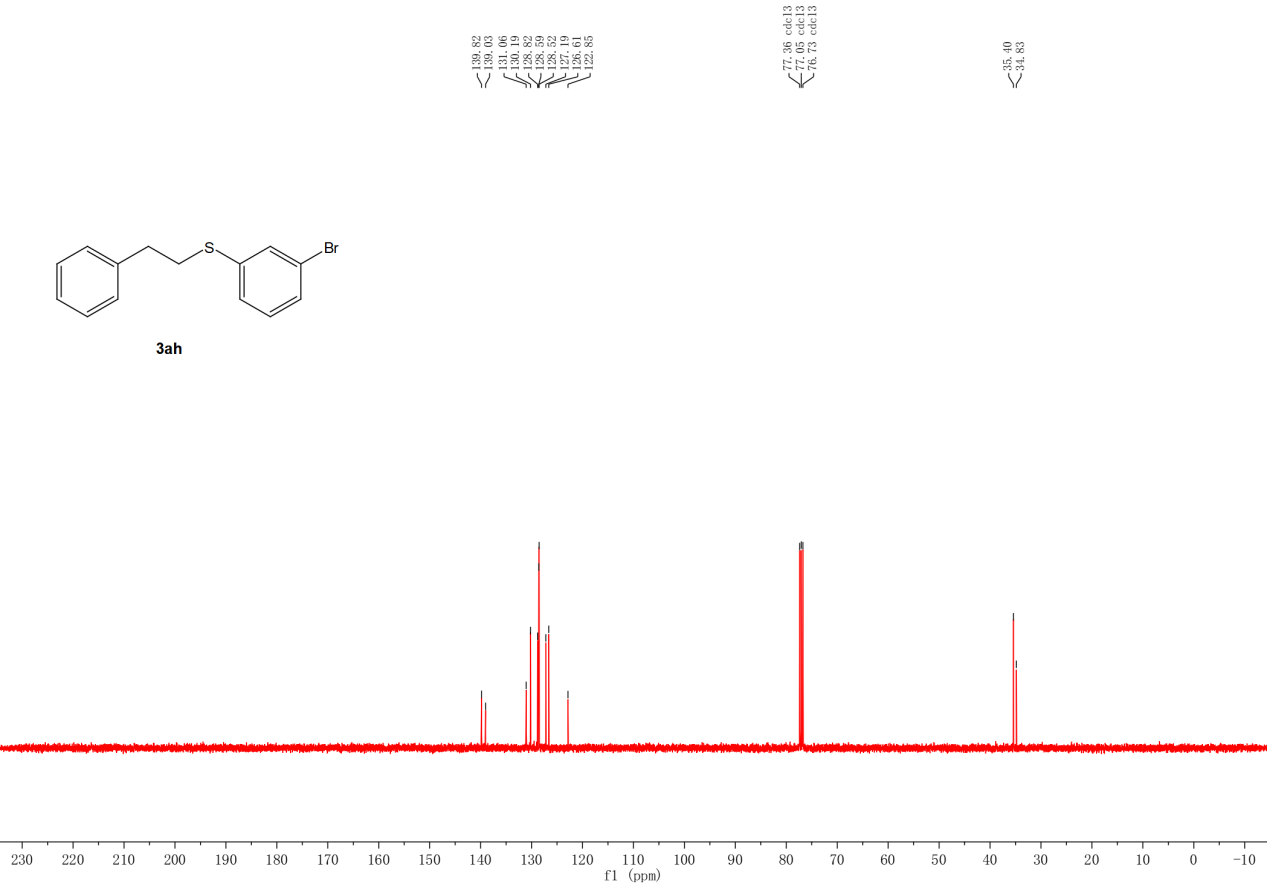
**Figure S31.** 13C NMR spectra (400 MHz) of **3ag** in CDCl3.



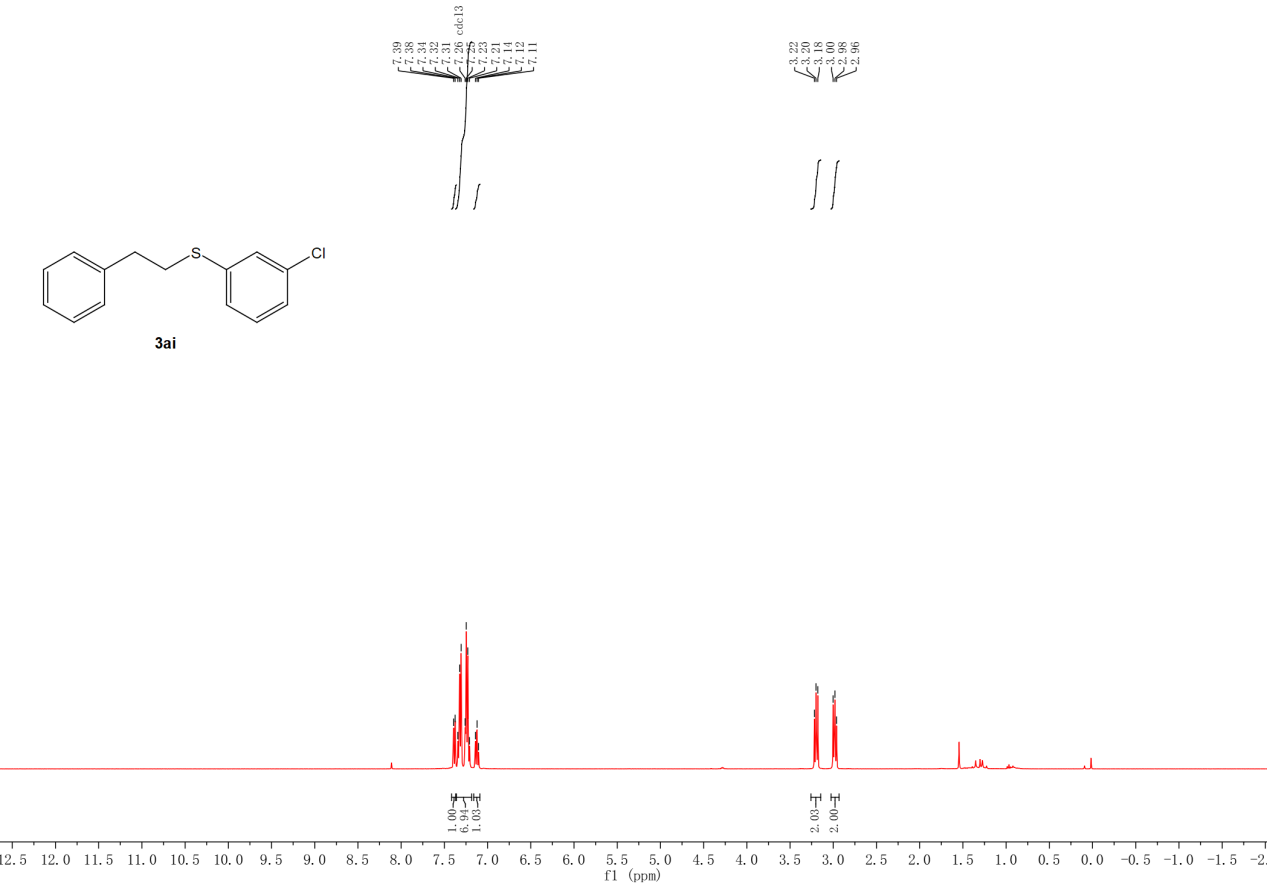
**Figure S32.** 19F NMR spectra (400 MHz) of **3ag** in CDCl3.



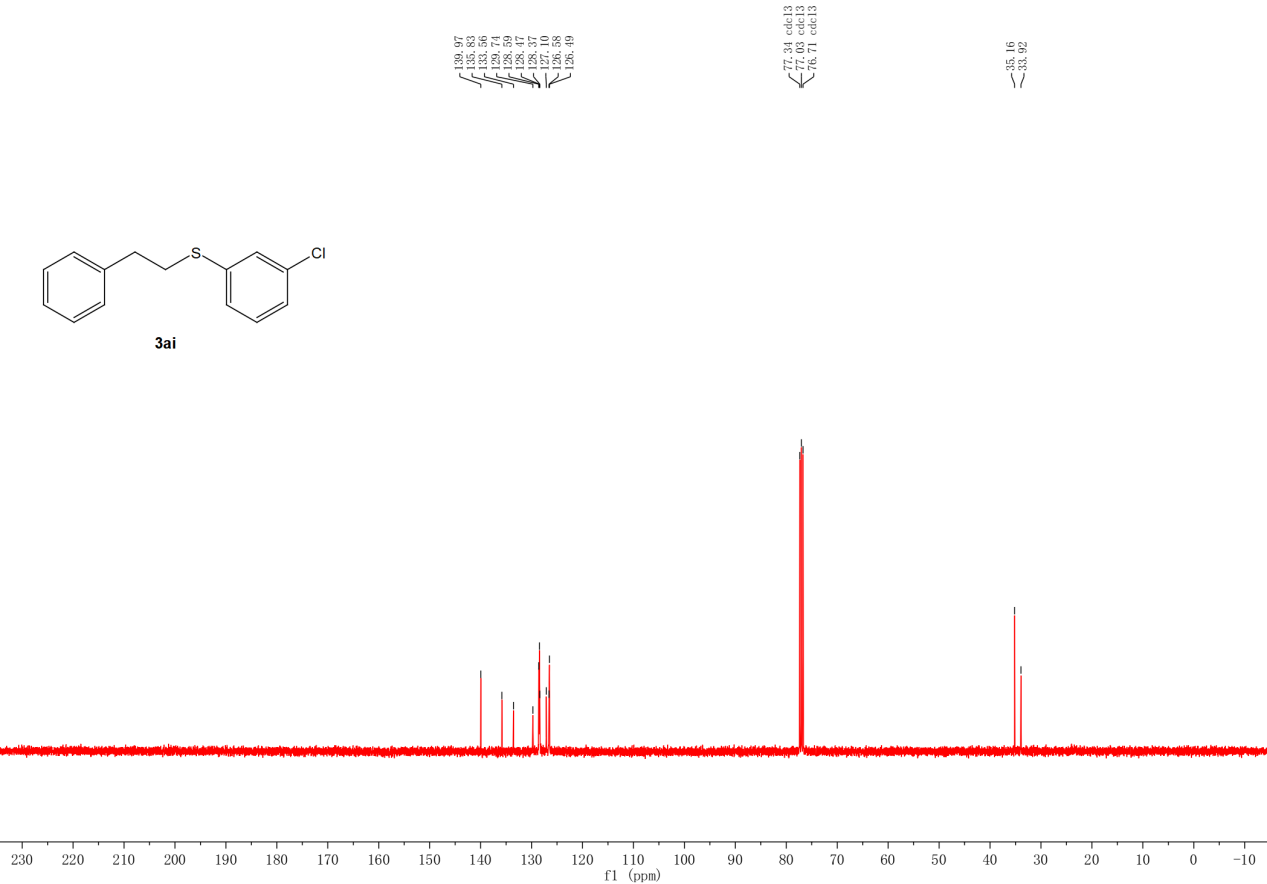
**Figure S33.** 1H NMR spectra (400 MHz) of **3ah** in CDCl3.



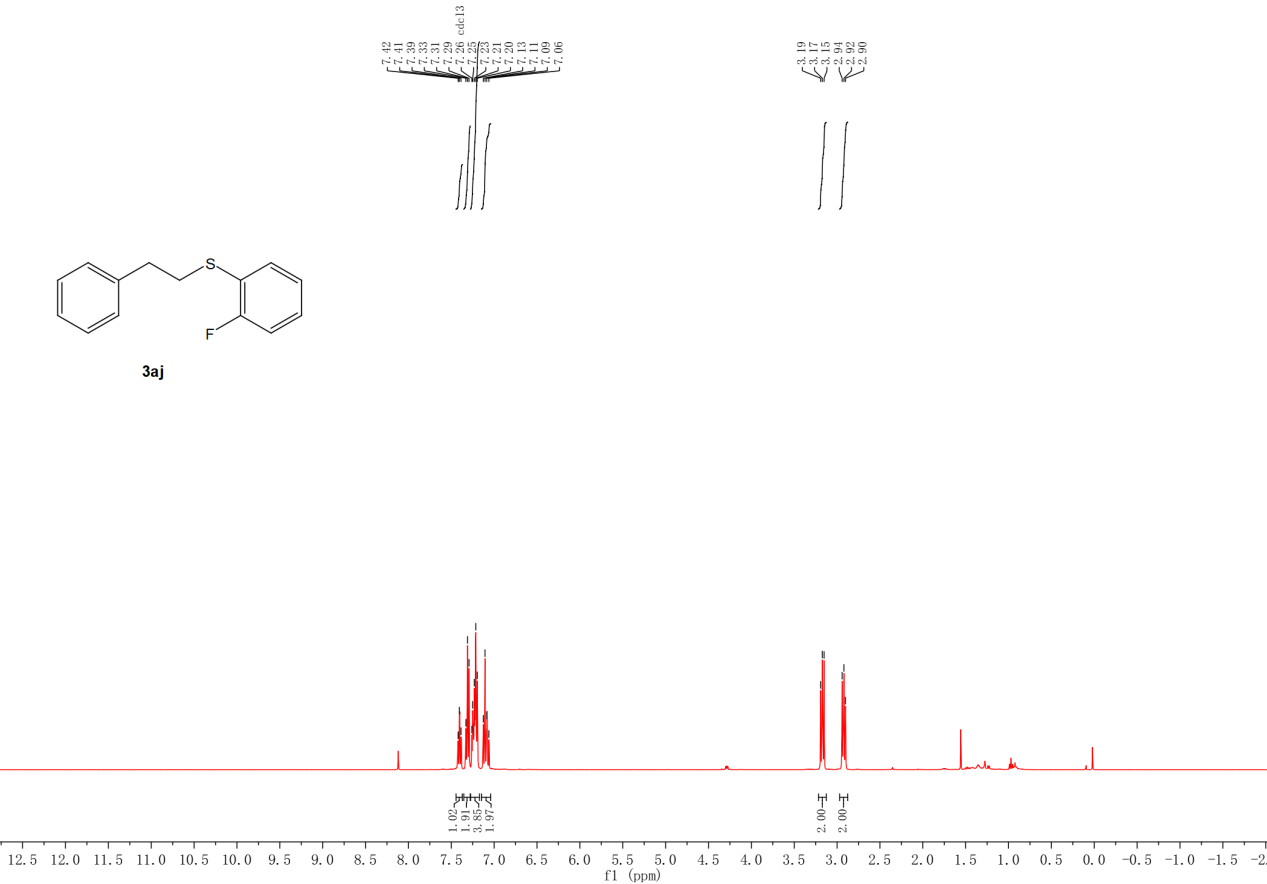
**Figure S34.** 13C NMR spectra (400 MHz) of **3ah** in CDCl3.



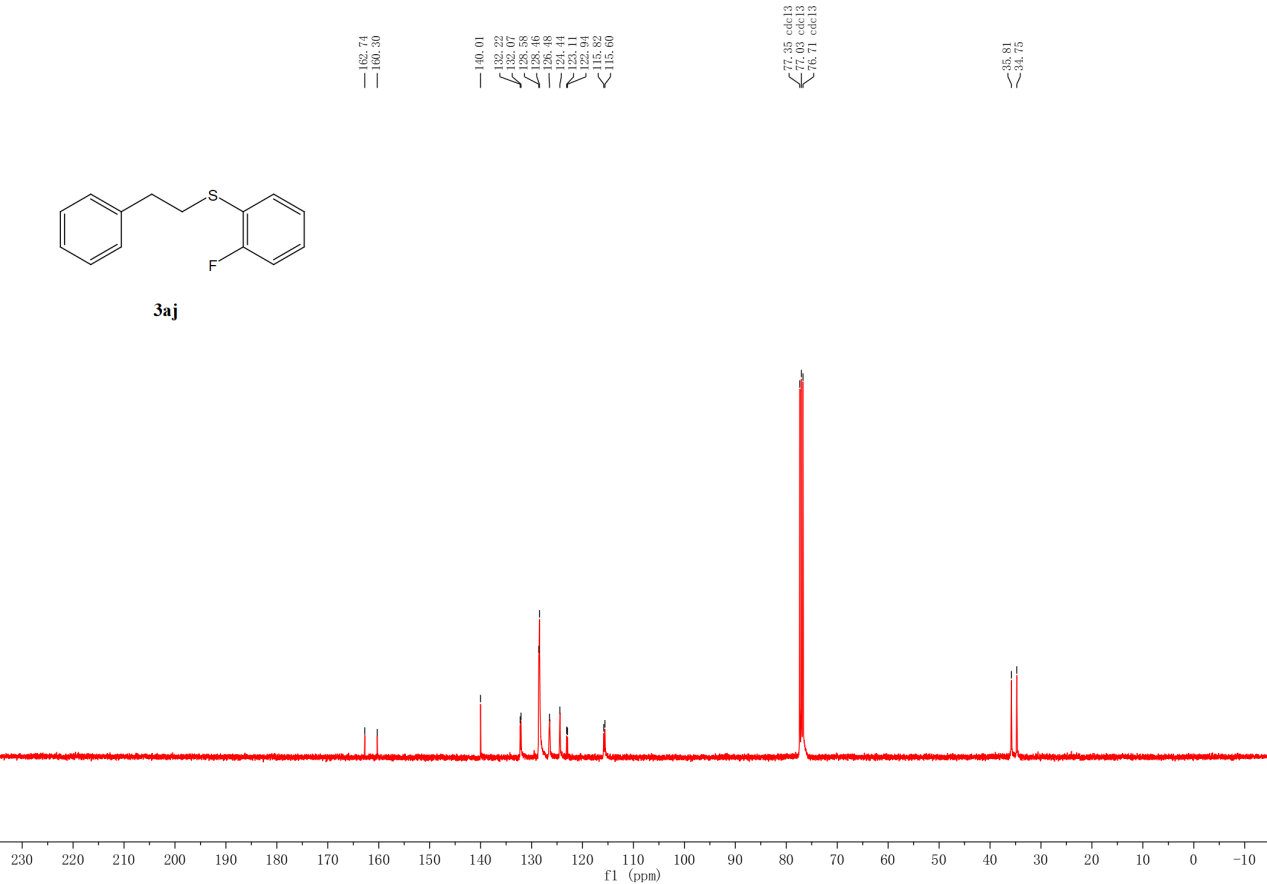
**Figure S35.** 1H NMR spectra (400 MHz) of **3ai** in CDCl3.



**Figure S36.** 13C NMR spectra (400 MHz) of **3ai** in CDCl3.



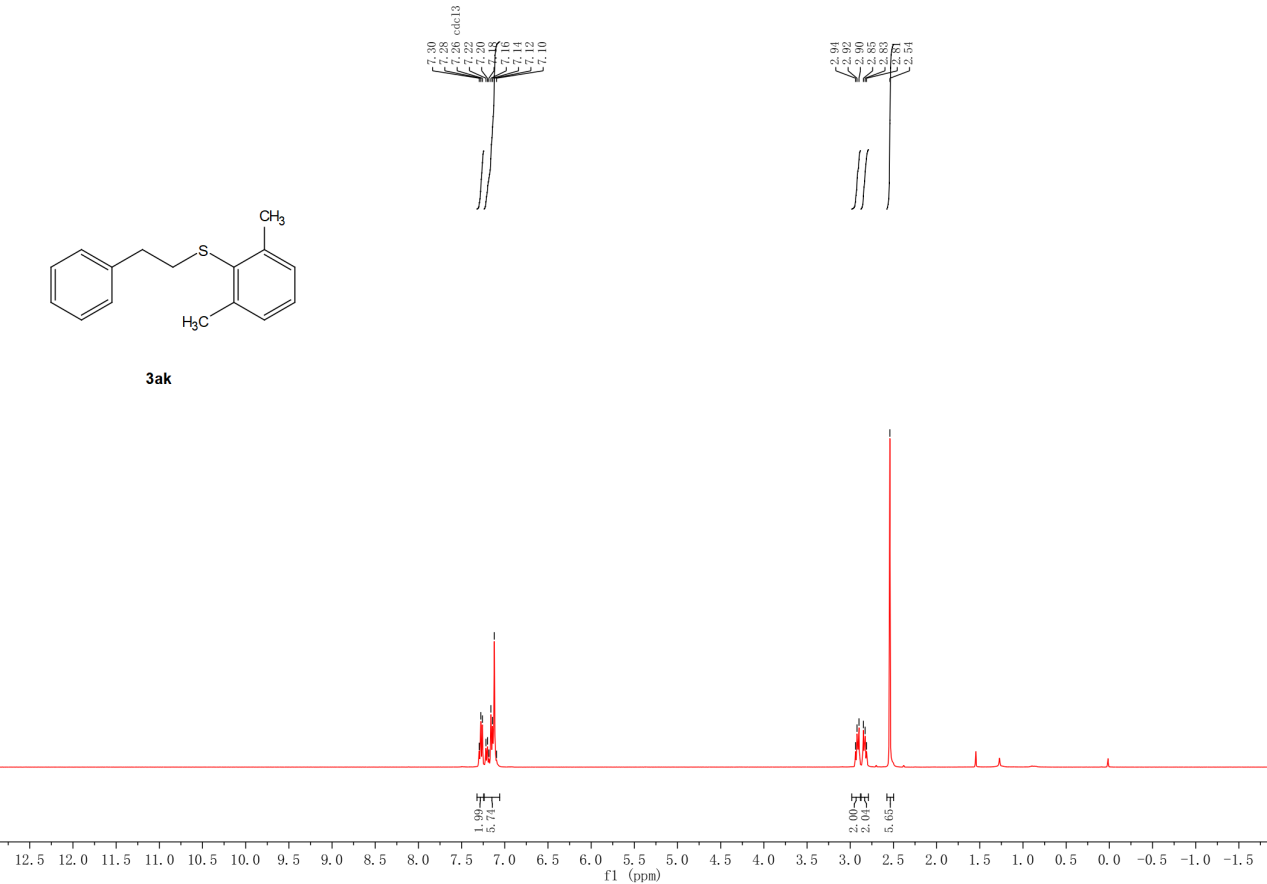
**Figure S37.** 1H NMR spectra (400 MHz) of **3aj** in CDCl3.



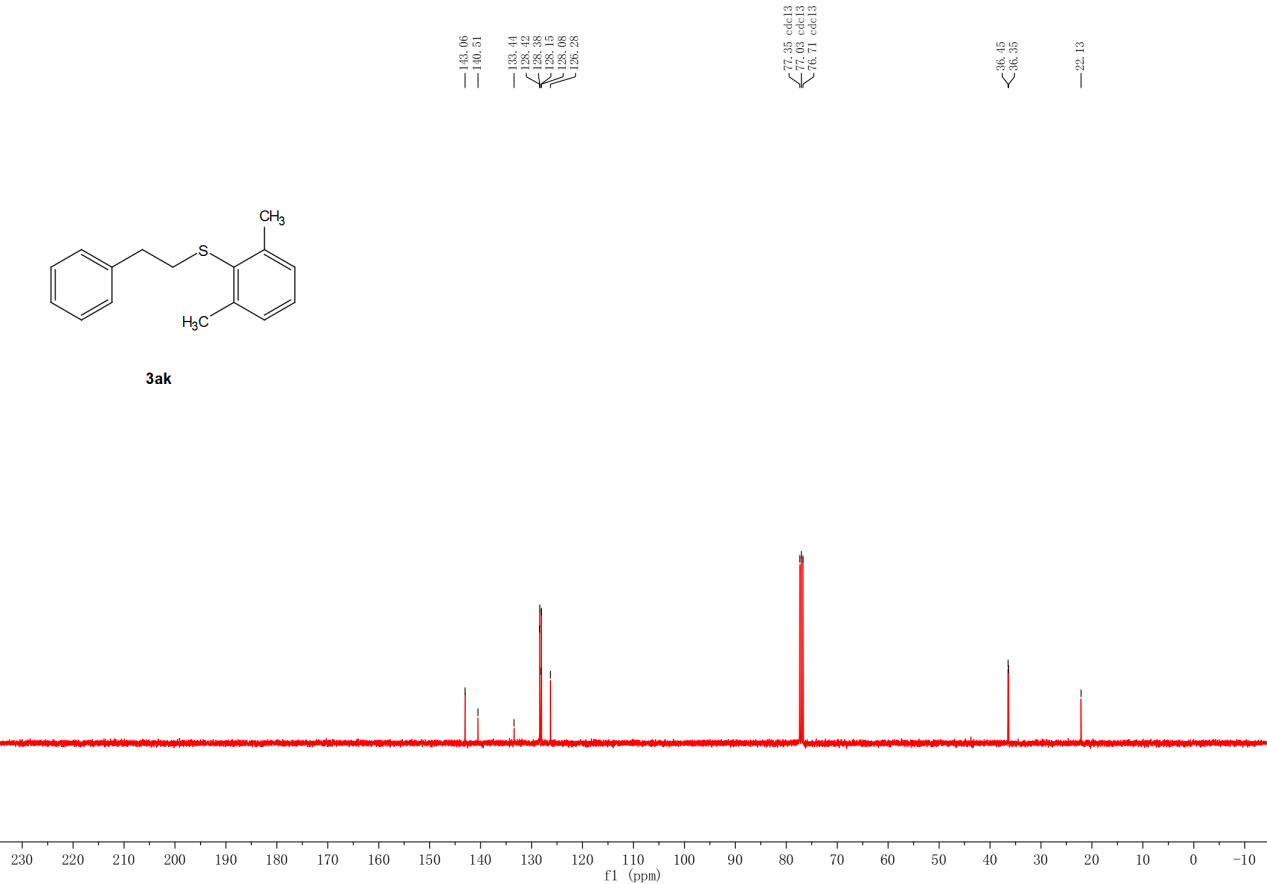
**Figure S38.** 13C NMR spectra (400 MHz) of **3aj** in CDCl3.



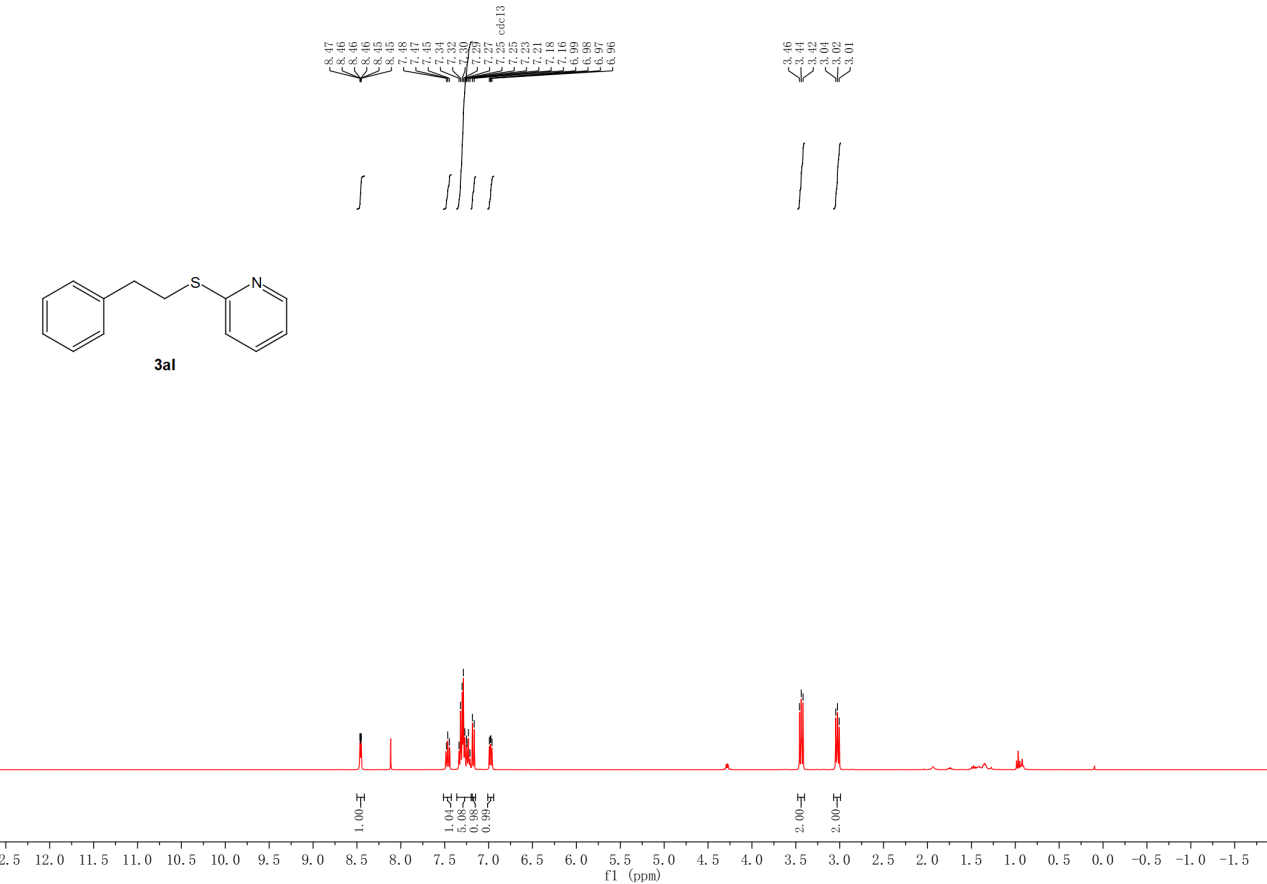
**Figure S39.** 19F NMR spectra (400 MHz) of **3aj** in CDCl3.



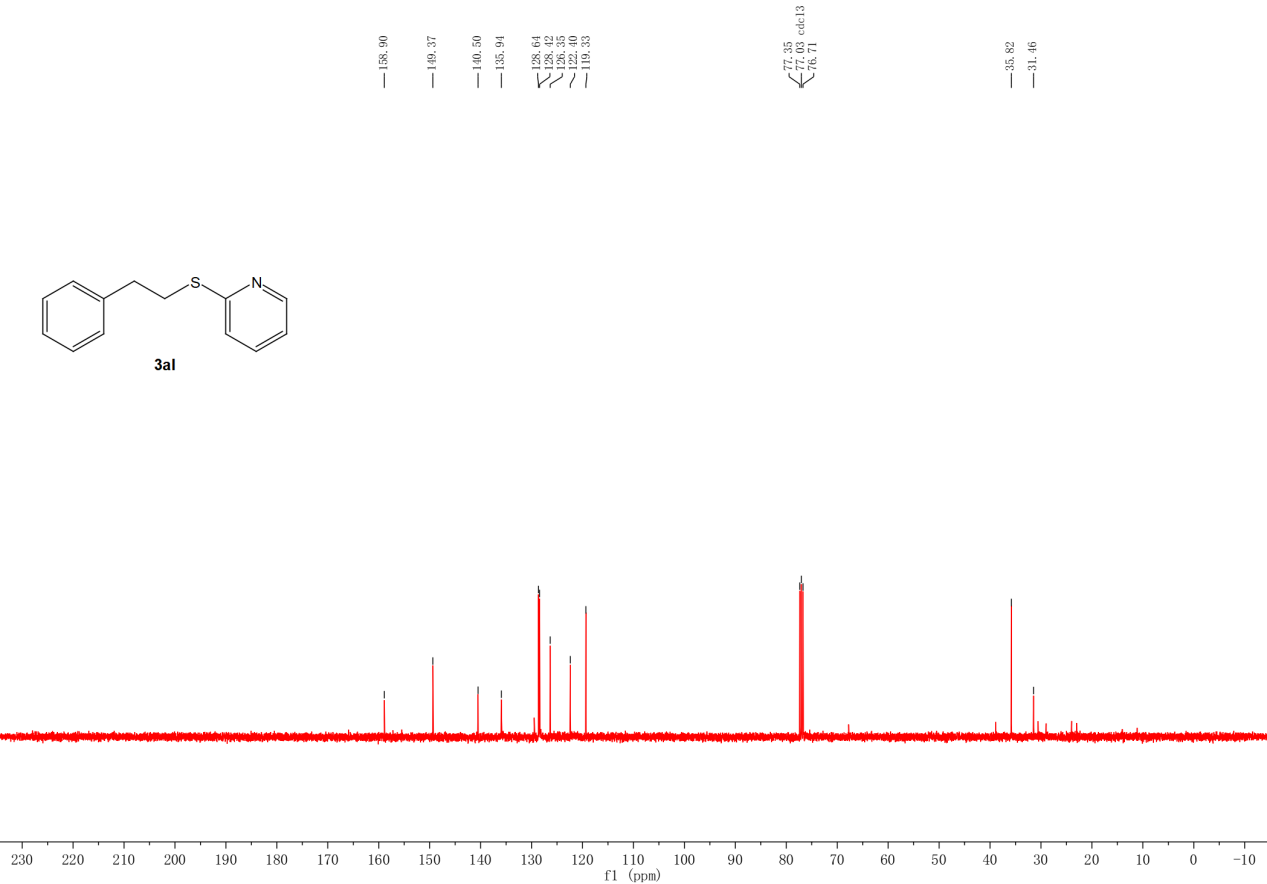
**Figure S40.** 1H NMR spectra (400 MHz) of **3ak** in CDCl3.



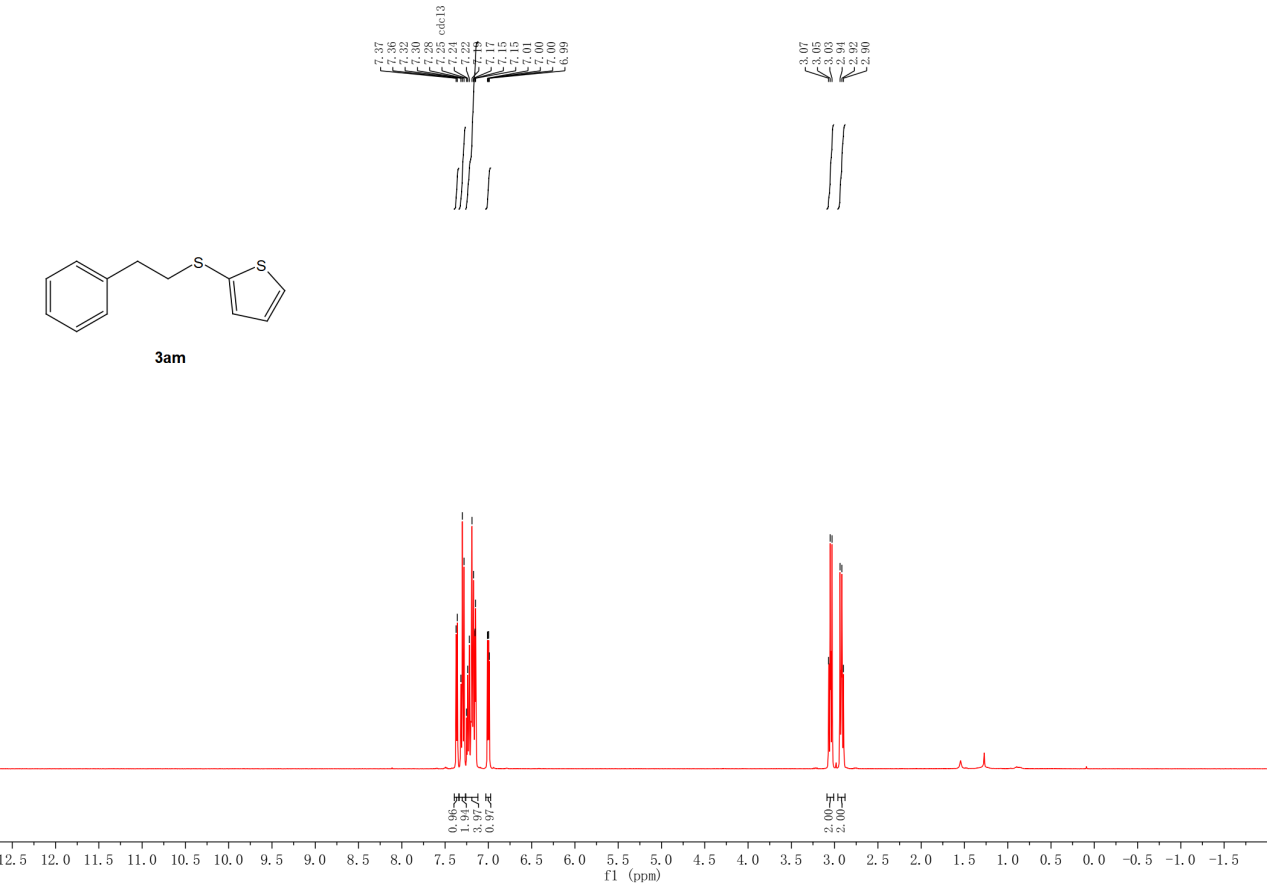
**Figure S41.** 13C NMR spectra (400 MHz) of **3ak** in CDCl3.



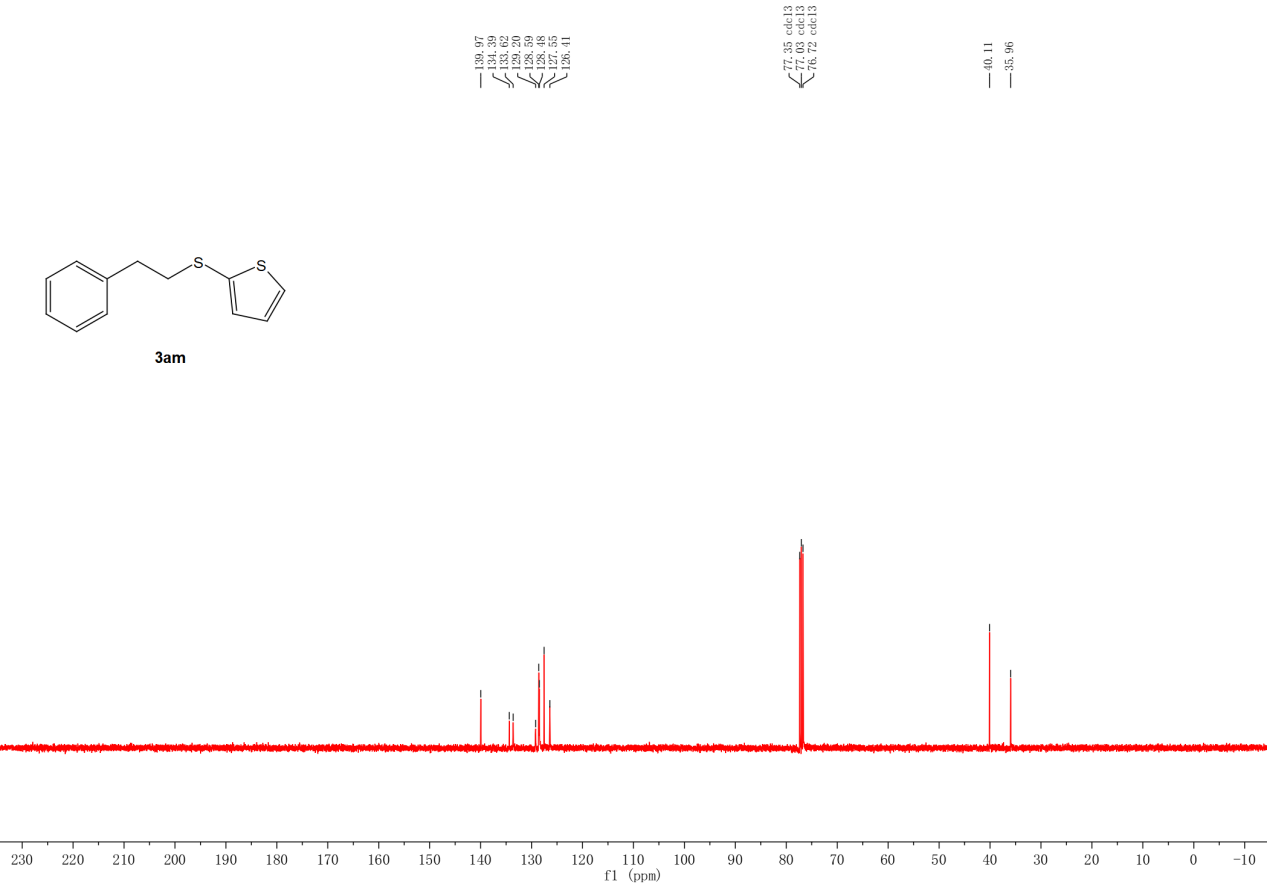
**Figure S42.** 1H NMR spectra (400 MHz) of **3al** in CDCl3.



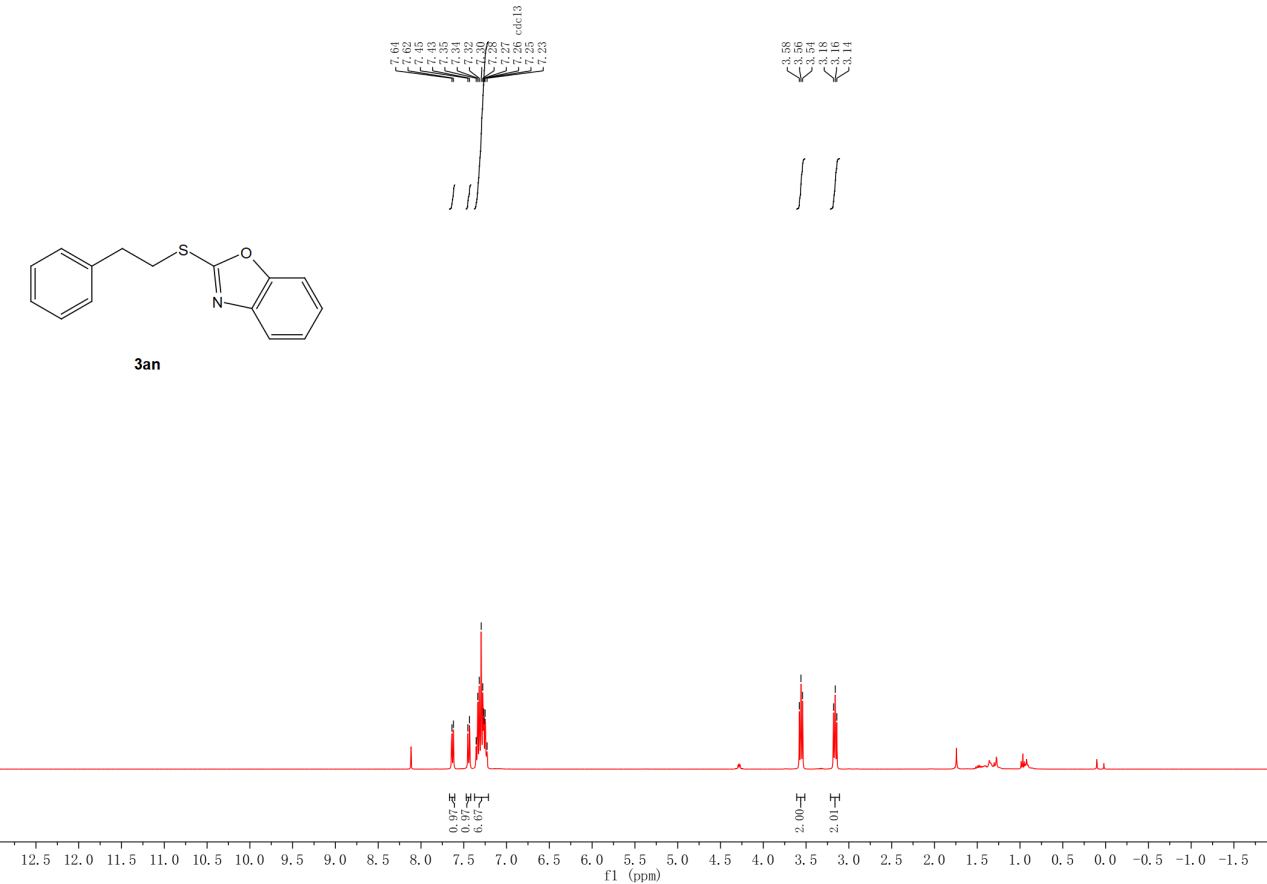
**Figure S43.** 13C NMR spectra (400 MHz) of **3al** in CDCl3.



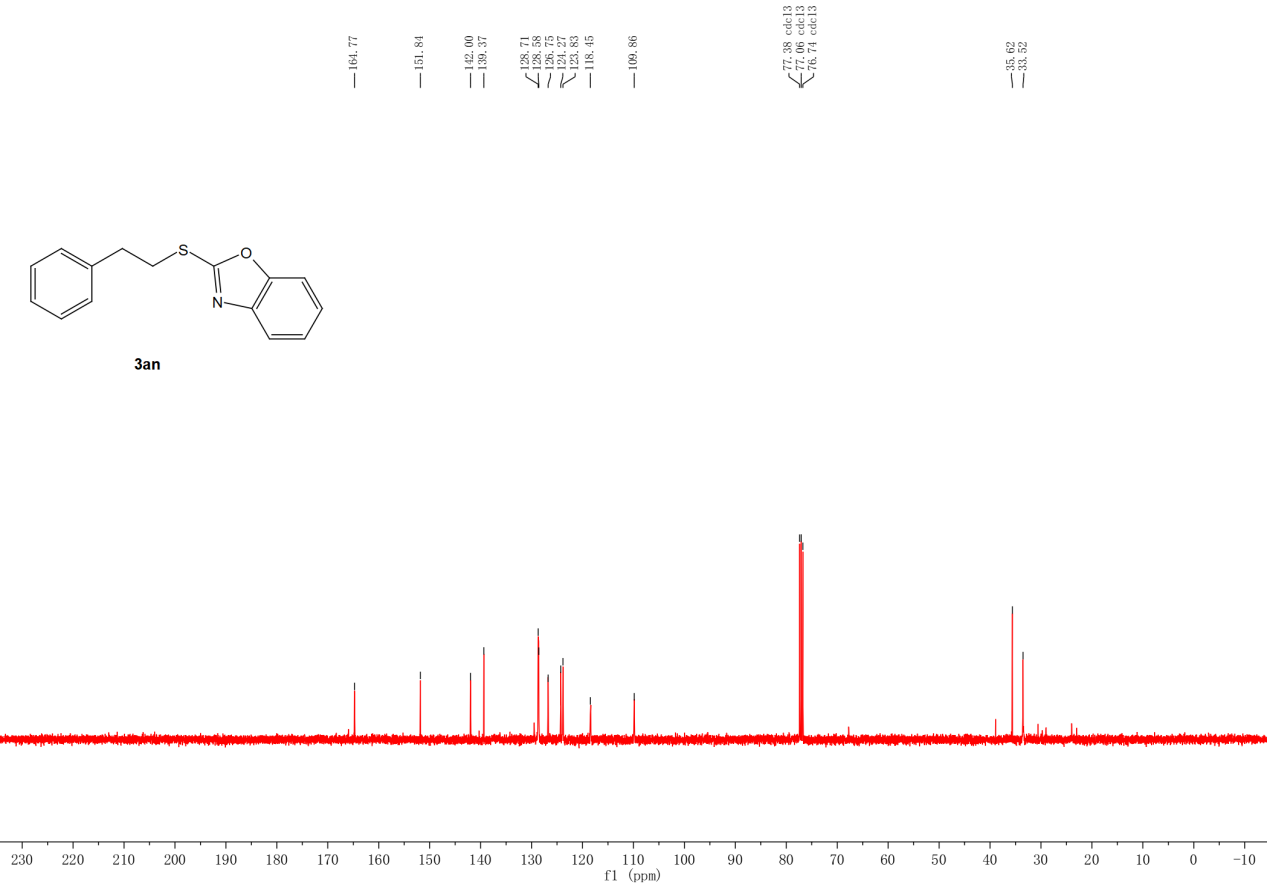
**Figure S44.** 1H NMR spectra (400 MHz) of **3am** in CDCl3.



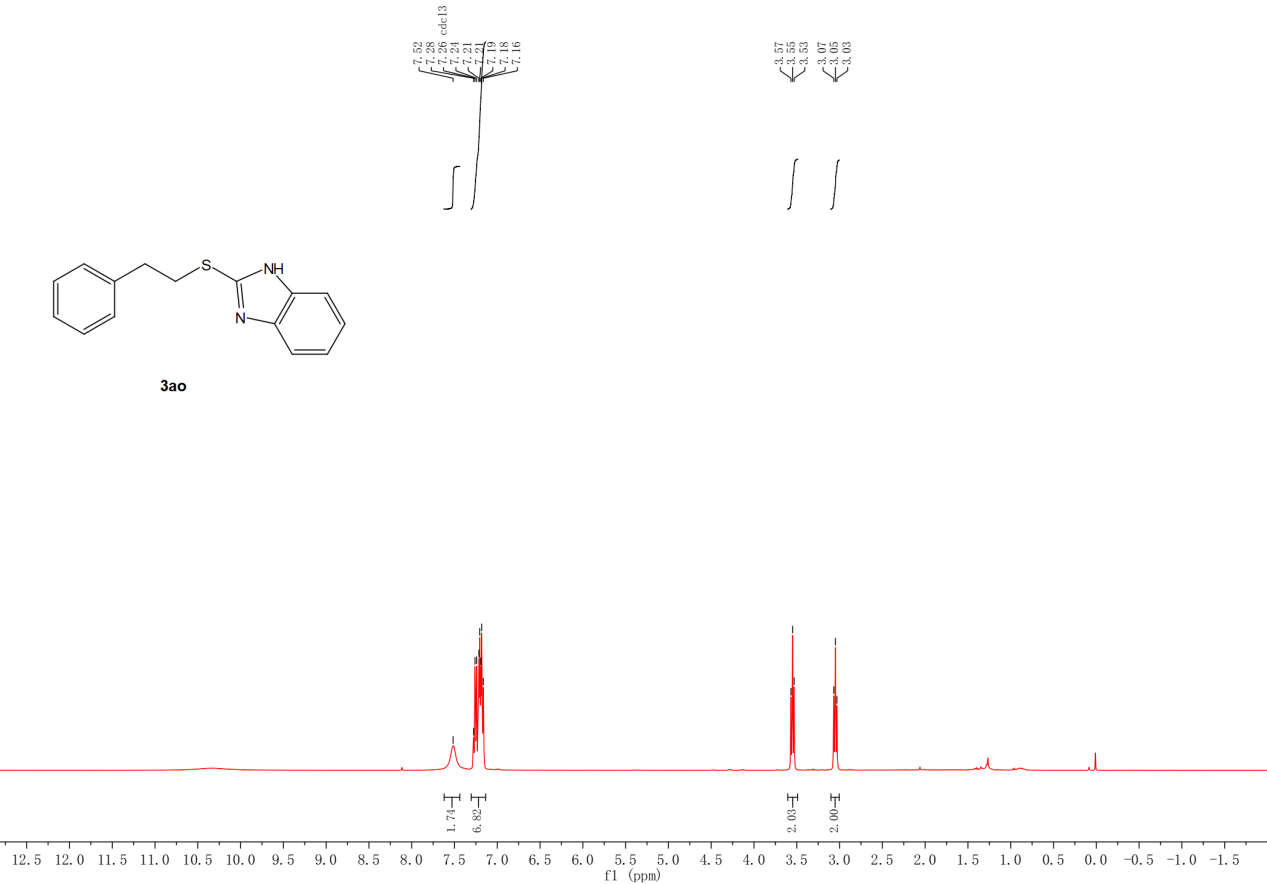
**Figure S45.** 13C NMR spectra (400 MHz) of **3am** in CDCl3.



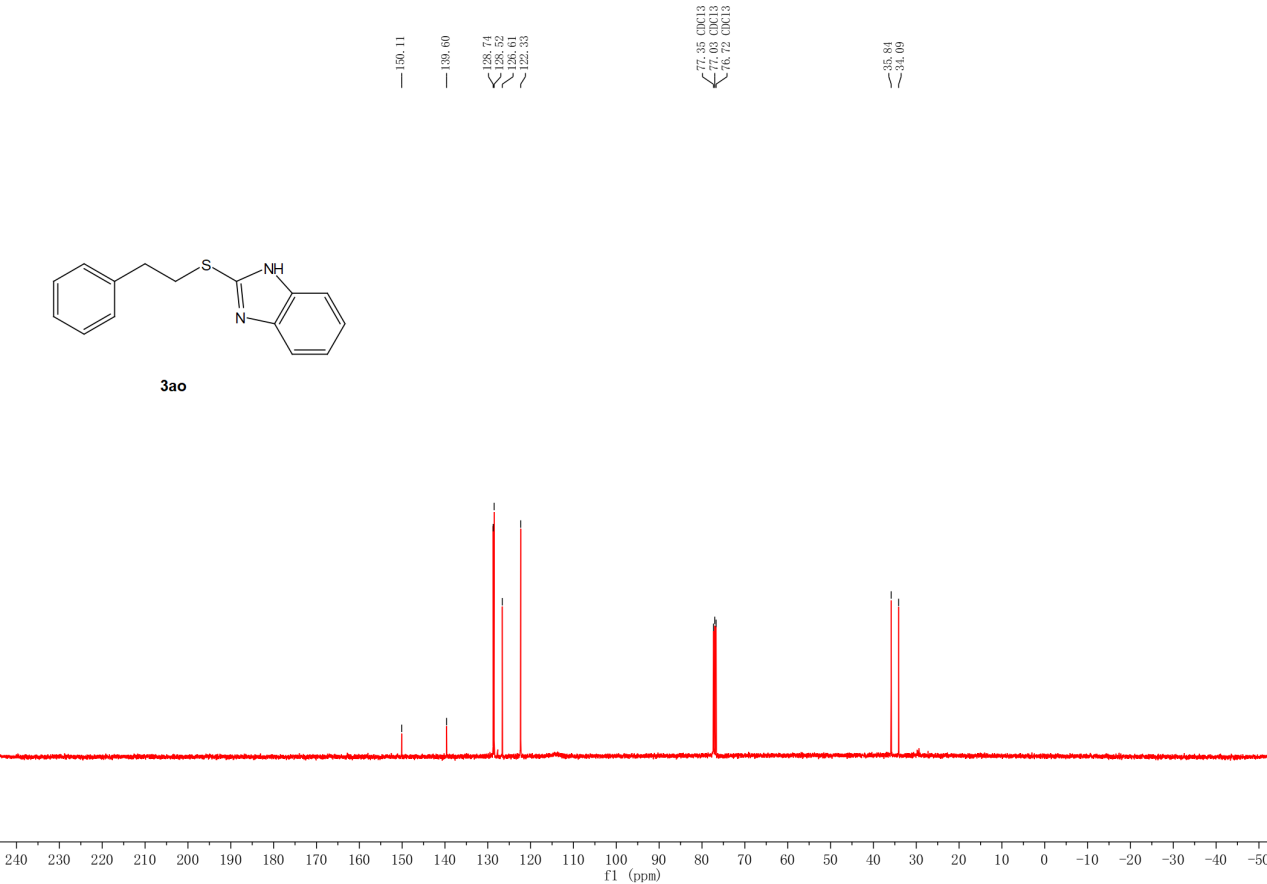
**Figure S46.** 1H NMR spectra (400 MHz) of **3an** in CDCl3.



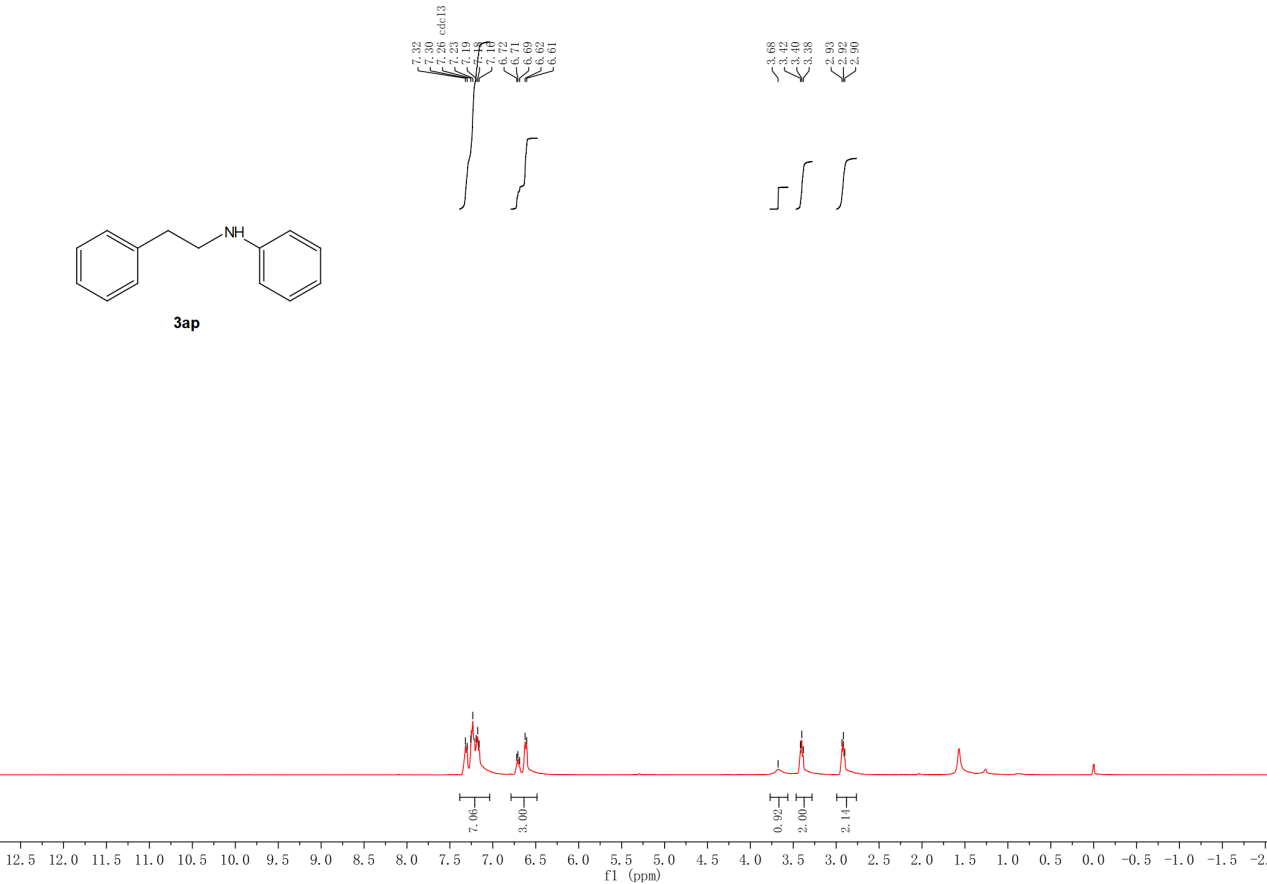
**Figure S47.** 13C NMR spectra (400 MHz) of **3an** in CDCl3.



**Figure S48.** 1H NMR spectra (400 MHz) of **3ao** in CDCl3.



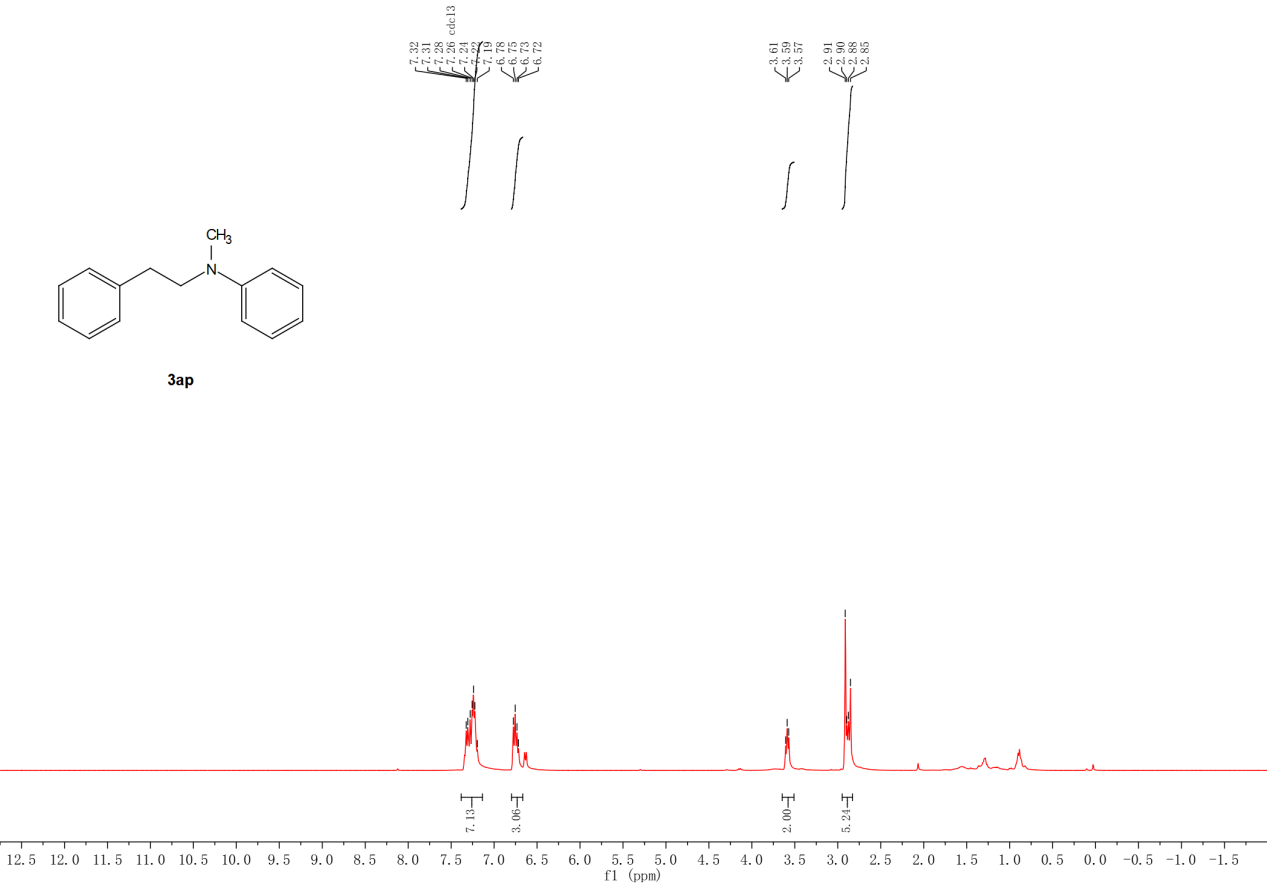
**Figure S49.** 13C NMR spectra (400 MHz) of **3ao** in CDCl3.



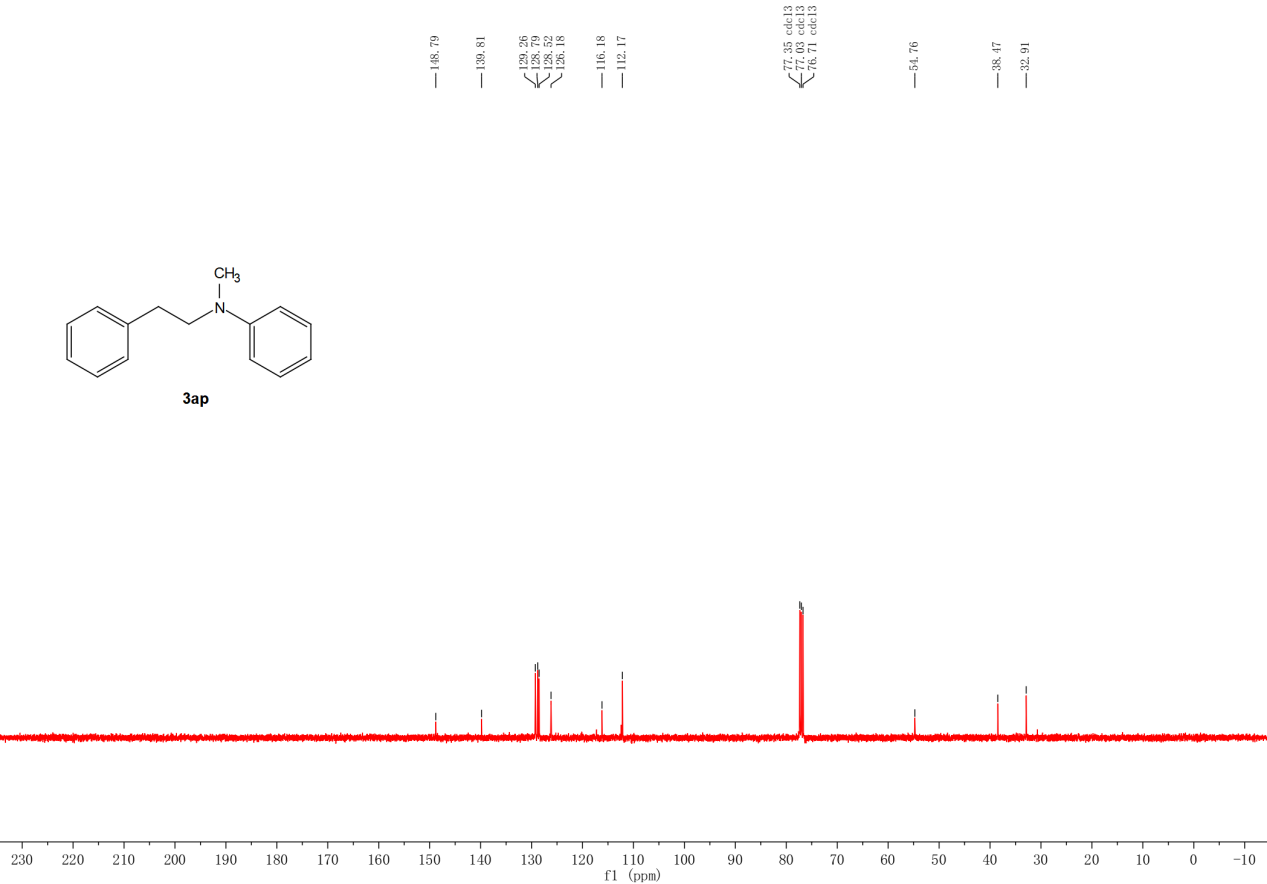
**Figure S50.** 1H NMR spectra (400 MHz) of **3ap** in CDCl3.



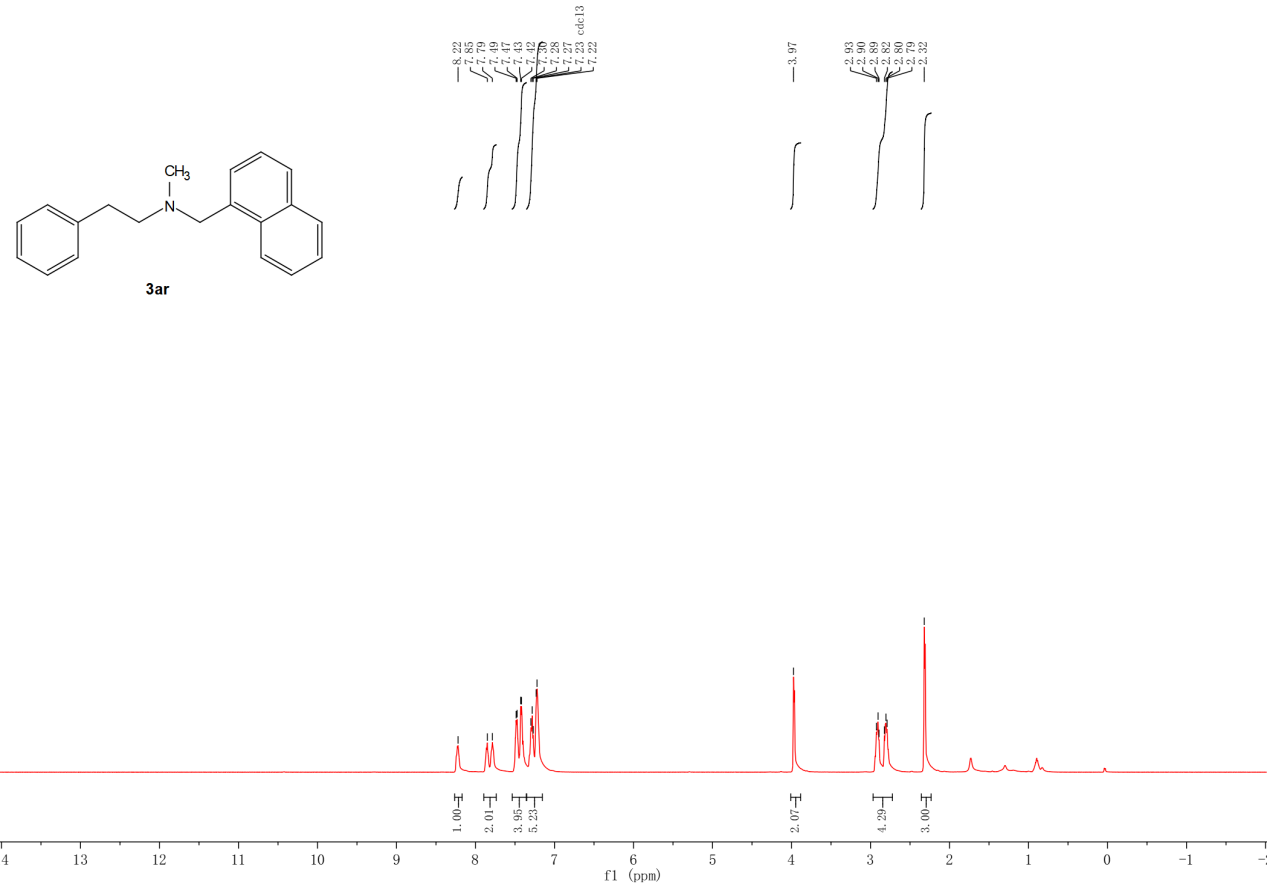
**Figure S51.** 13C NMR spectra (400 MHz) of **3ap** in CDCl3.



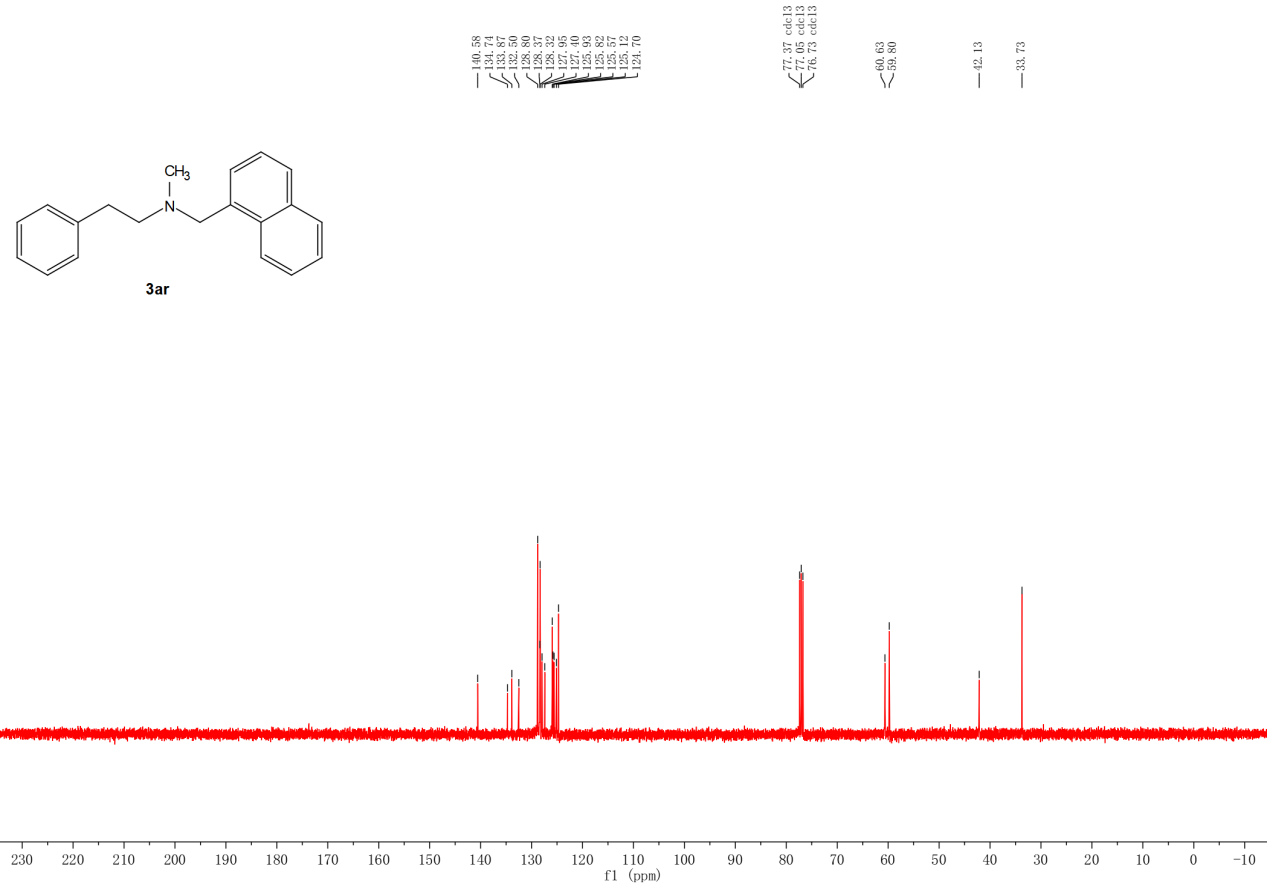
**Figure S52.** 1H NMR spectra (400 MHz) of **3aq** in CDCl3.



**Figure S53.** 13C NMR spectra (400 MHz) of **3aq** in CDCl3.



**Figure S54.** 1H NMR spectra (400 MHz) of **3ar** in CDCl3.



**Figure S55.** 13C NMR spectra (400 MHz) of **3ar** in CDCl3.