Electronic supporting information (ESI)

Electrochemical and Direct C-H Methylthiolation of Electron-Rich Aromatics

Yaxing Wu,‡ Hongliang Ding,‡ Ming Zhao,* Zhong-Hai Ni, and Jing-Pei Cao

Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education), China University of Mining & Technology, Xuzhou 221116, Jiangsu, China.

E-mail: ming815zhao@163.com

1. General Information……………………………………………………………..………..…S2

2. Synthesis of starting materials…………….……………………..…………………………..…S3

3. General procedure for methylthiolation of electron-rich arenes……………………......…S3

4. General procedure for cross-coupling between aryl-thiocyanate and methanol……......S3

5. Procedure for gram scale synthesis….……………..………………….…………………..S4

6. Preliminary mechanistic studies…………………………………………………….………. S5

7. Detail descriptions for products.…………………..…………………………………...........S8

8. References……………………………………….…….……………..…….….…….…......S13

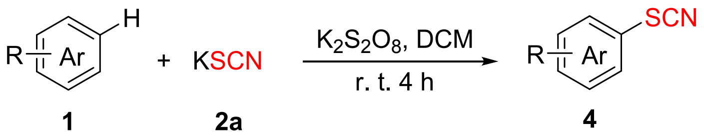
9. Copies of product NMR spectra……………..…………………..………………..……...S15

10. Copies of HRMS spectra ……………………….….………….…..…….….……...S38

1. General information

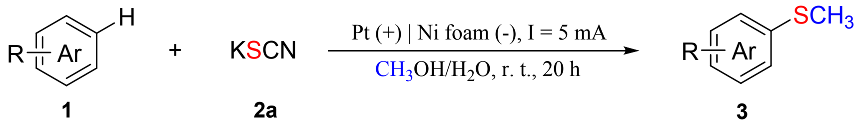
All glassware was oven dried at 80 ℃ for hours and cooled down for use. Aryl-thiocyanate prepared according to reported procedures[1]. All the reaction prepared using a high purity deionized (DI) water and the solvent of CH_3OH (99.8%) and CH_3CN (99.8%) was purchased from Sinopharm Chemical Reagent limited corporation. The deoxygenation of dideionized water, CH_3OH and CH_3CN is through Schlenk technology. Starting materials were purchased from Aladdin, Sigma-Aldrich and Sinopharm Chemical Reagent limited corporation, and their purities are between 96% and 99%. Unless otherwise stated, materials were used without further purification. The instrument for electrolysis is CHI660 electrochemical workstation (made in China). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 100-200 mesh silica gel in petroleum (bp. 60-90 ℃). ^{1}H and ^{13}C NMR data were recorded with Bruker Advance III (600 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.16 ppm, $CDCl_3$).

2. Synthesis of starting materials[1]



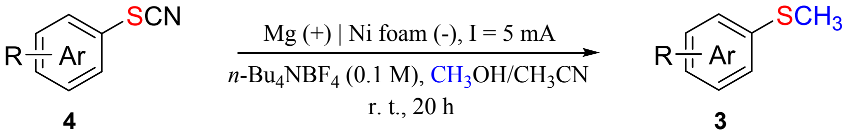
General procedure for synthesis of aryl thiocyanates. In an oven dried round bottom flask containing a mixture of electron-rich arenes (2 mmol), potassium thiocyanate (3 mmol) and potassium persulphate (4 mmol) in DCM (5 mL) were stirred for 4 h. Progress of the reaction was monitored by TLC. When the reaction was finished, the reaction mixture was filtered through sintered funnel containing silica and sodium sulphate. The Filtrate concentrated under reduced pressure to afford the crude product. This was purified by flash column chromatography on silica gel (petroleum: ethyl acetate = 1:1 - 4:1) to furnish the pure compound thiocyanate.

3. General procedure for methylthiolation of electron-rich arenes



In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, electron-rich arene **1** (1 mmol), potassium thiocyanate **2a** (5 mmol, 485.9 mg), H_2O (1 mL) and CH_3OH (9 mL) were combined and added. The bottle was equipped with platinum plate (1 × 1 cm^2) anode and nickel foam plate (2 × 3 cm^2) cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 20 h. When the reaction was finished, CH_3OH was removed with a rotary evaporator, then the reaction mixture was washed with water and extracted with ethyl acetate (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl acetate = 5:1 - 10:1).

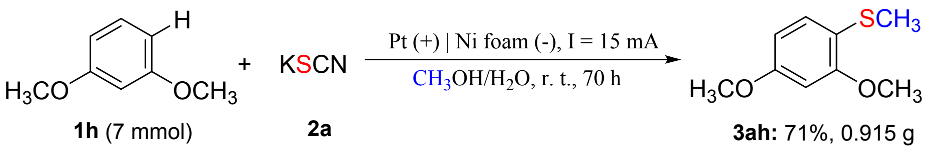
4. General procedure for cross-coupling between aryl-thiocyanate and methanol



In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, aryl-thiocyanate **4** (1 mmol), tetrabutylammonium tetrafluoroborate (1 mmol), CH_3OH (5 mL) and CH_3CN (5 mL) were combined and added. The bottle was equipped with magnesium plate (2 × 3 cm^2) anode and nickel foam plate (2 × 3 cm^2) cathode. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 20 h. When the reaction was finished, solvent was removed with a rotary evaporator, then the reaction mixture was washed with water and extracted with ethyl acetate (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl acetate = 5:1 - 10:1).

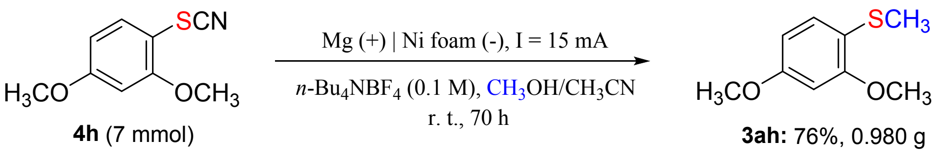
5. Procedure for gram scale synthesis.

(1) Methylthiolation of 1,3-dimethoxybenzene.



In an oven-dried undivided three-necked bottle (100 mL) equipped with a stir bar, 1,3-dimethoxybenzene **1j** (7.0 mmol, 0.967 g), potassium thiocyanate **2a** (35.0 mmol, 3.401 g), H_2O (7 mL) and CH_3OH (63 mL) were combined and added. The bottle was equipped with platinum plate (1 × 1 cm^2) anode and nickel foam plate (2 × 3 cm^2) cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 15 mA under room temperature for 70 h. When the reaction was finished, CH_3OH was removed with a rotary evaporator, then the reaction mixture was washed with water and extracted with ethyl acetate (50 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl acetate = 10:1).

(2) Cross-coupling between 1, 3-dimethoxy-4-thiocyanatobenzene and methanol.



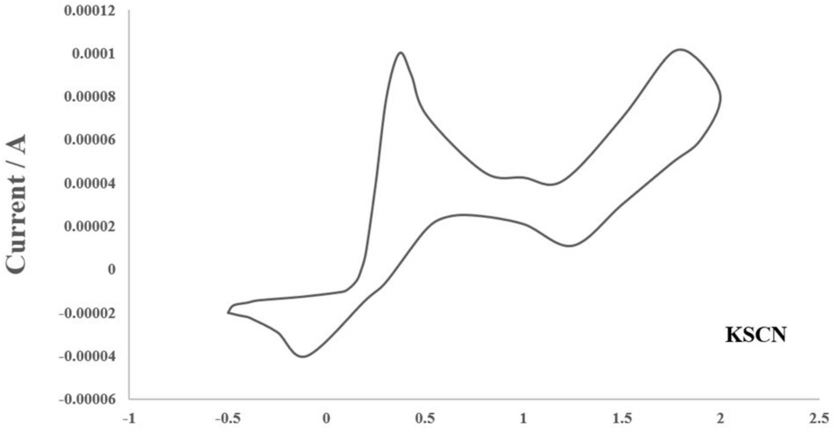
In an oven-dried undivided three-necked bottle (100 mL) equipped with a stir bar, 1, 3-dimethoxy-4-thiocyanatobenzene **4j** (7.0 mmol, 1.365 g), tetrabutylammonium tetrafluoroborate

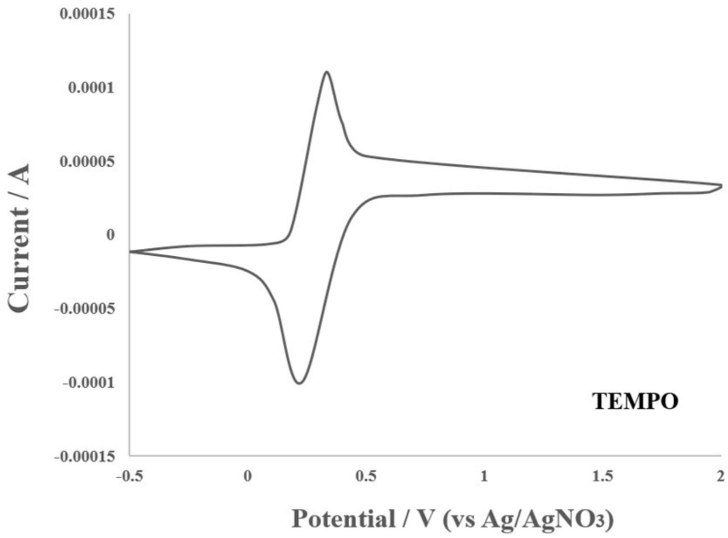
(7.0 mmol, 2.305 g), CH_3OH (35 mL) and CH_3CN (35 mL) were combined and added. The bottle was equipped with magnesium plate (2 × 3 cm^2) anode and nickel foam plate (2 × 3 cm^2) cathode. The reaction mixture was stirred and electrolyzed at a constant current of 15 mA under room temperature for 70 h. When the reaction was finished, solvent was removed with a rotary evaporator, then the reaction mixture was washed with water and extracted with ethyl acetate (50 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl acetate = 10:1).

6. Preliminary mechanistic studies.

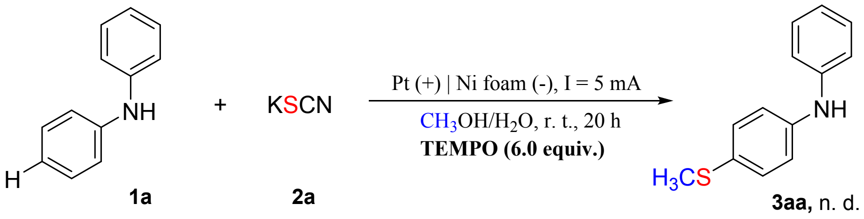
(1) Voltamometric analysis and voltammograms

The redox property of each compound was measured in solvent containing *n*-tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Cyclic voltammetry was carried out in conventional three-electrode electrochemical cell with CHI660 electrochemical workstation under nitrogen at room temperature. A glassy carbon disk electrode (diameter is 3.0 mm) was used as the working electrode. A platinum plate electrode (1×1 cm^2) was used as the counter electrode. The reference Ag/Ag^+ electrode was made by immersing a sliver wire in a solution of $AgNO_3$ (0.01 M) - *n*-Bu_4NBF_4 (0.1 M) in CH_3OH/H_2O, and separated from reaction by a salt bridge. 10 mL electrolyte solution containing 0.05 M *n*-Bu_4NBF_4 in CH_3OH/H_2O was poured into electrochemical cell in all experiments. The concentration of diphenylamine sample was 0.01 M. The scan rate was 0.1 V/s, ranging from -0.5 to 2.0 V.



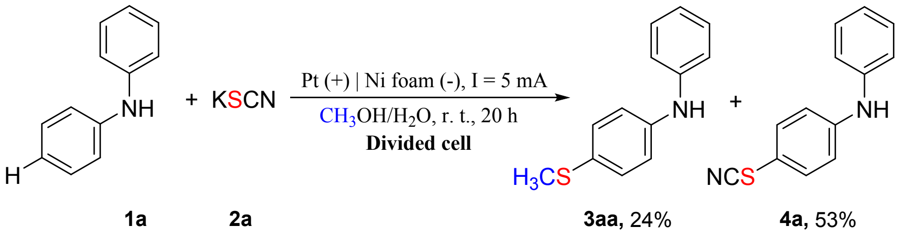


(2) The reaction of **1a** and **2a** with TEMPO under the standard conditions.



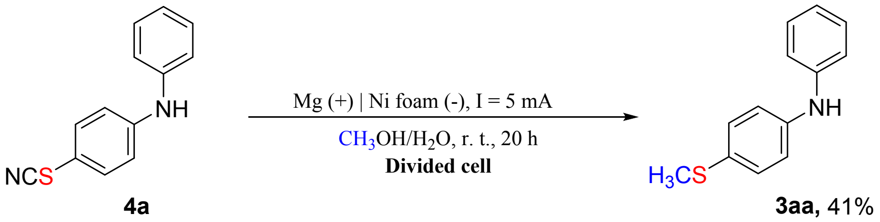
In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, diphenylamine **1a** (1 mmol), potassium thiocyanate **2a** (5 mmol), TEMPO (6 mmol), H_2O (1 mL) and CH_3OH (9 mL) were combined and added. The bottle was equipped with platinum plate (1 × 1 cm^2) anode and nickel foam plate (2 × 3 cm^2) cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 20 h. When the reaction was finished, the solution was concentrated in vacuum and the yield of **3aa** was sharply decreased.

(3) The reaction of **1a** and **2a** in divided cell.



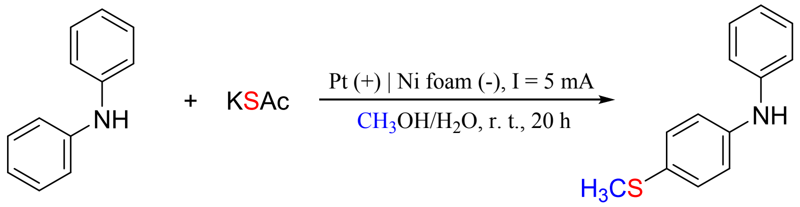
In an oven-dried divided cell (30 mL) equipped with proton exchange membrane (PEM, purchased from DuPont) and a stir bar. Diphenylamine **1a** (1 mmol), potassium thiocyanate **2a** (5 mmol), H_2O (1 mL) and CH_3OH (9 mL) were combined and added to the anode cell, tetrabutylammonium tetrafluoroborate (1 mmol), H_2O (1 mL) and CH_3OH (9 mL) were combined and added to the cathode cell. The divided cell was equipped with platinum plate (1 × 1 cm^2) anode and nickel foam plate (2 × 3 cm^2) cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 20 h. When the reaction was finished, CH_3OH was removed with a rotary evaporator, then the reaction mixture was washed with water and extracted with ethyl acetate (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel.

(4) The electrolysis of **4a** in divided cell.



In an oven-dried divided cell (30 mL) equipped with proton exchange membrane (PEM, purchased from DuPont) and a stir bar. N-phenyl-4-thiocyanatoaniline **4a** (1 mmol), tetrabutylammonium tetrafluoroborate (1 mmol), H_2O (1 mL) and CH_3OH (9 mL) were combined and added to the cathode cell, tetrabutylammonium tetrafluoroborate (1 mmol), H_2O (1 mL) and CH_3OH (9 mL) were combined and added to the anode cell. The divided cell was equipped with magnesium plate (2 × 3 cm^2) anode and nickel foam plate (2 × 3 cm^2) cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 20 h. When the reaction was finished, CH_3OH was removed with a rotary evaporator, then the reaction mixture was washed with water and extracted with ethyl acetate (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel.

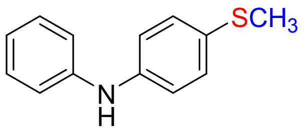
(5) The reaction of **1a** and **2b** under the standard conditions.



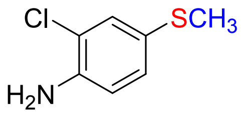
1a **2b** **3aa**, n. d.

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, diphenylamine **1a** (1 mmol), potassium thioacetate **2b** (5 mmol), H_2O (1 mL) and CH_3OH (9 mL) were combined and added. The bottle was equipped with platinum plate (1 × 1 cm^2) anode and nickel foam plate (2 × 3 cm^2) cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 20 h. When the reaction was finished, the solution was detected by TLC and GC-MS.

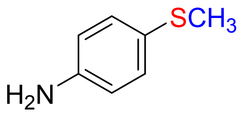
7. Detail descriptions for products.



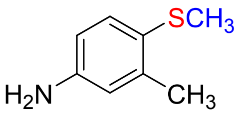
***N*-phenyl-4-methylthioaniline (3aa)[2]:** White solid was obtained with 80% isolated yield (172.2 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, J = 17.7, 8.3 Hz, 4H), 7.07 (dd, J = 15.6, 8.1 Hz, 4H), 6.97 (t, J = 7.4 Hz, 1H), 5.72 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.07, 141.42, 129.91, 129.46, 129.10, 121.15, 118.64, 117.82, 17.91.



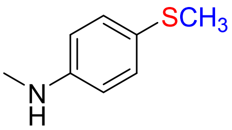
2-Chloro-4-methylthioaniline (3ab)[3]: Colorless liquid was obtained with 71% isolated yield (122.8 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, J = 2.0 Hz, 1H), 7.10 (dd, J = 8.3, 2.1 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 4.06 (s, br, 2H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.51, 130.28, 129.27, 126.76, 119.56, 116.28, 18.60.



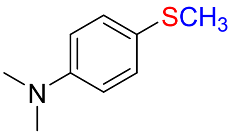
4-Methylthioaniline (3ac)[4]: Yellow oil was obtained with 64% isolated yield (89.0 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 6.68 – 6.63 (m, 2H), 3.68 (s, br, 2H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.13, 131.10, 125.83, 115.77, 18.83.



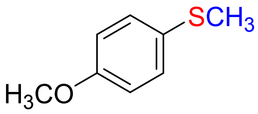
3-Methyl-4-methylthioaniline (3ad)[4]: White solid was obtained with 59% isolated yield (90.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 2.6 Hz, 1H), 6.51 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.65 (s, br, 2H), 2.39 (s, 3H), 2.36 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 145.19, 139.67, 131.00, 125.16, 117.13, 113.50, 20.47, 17.98.



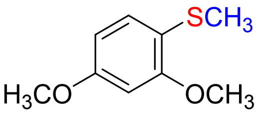
***N*-methyl-4-methylthioaniline (3ae)[5]:** Colorless liquid was obtained with 80% isolated yield (122.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 6.61– 6.57 (m, 2H), 3.76 (s, br, 1H), 2.85 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.25, 131.65, 124.05, 113.02, 30.75, 19.34.



***N, N*-dimethyl-4-methylthioaniline (3af)[6]:** Colorless liquid was obtained with 73% isolated yield (122.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 6.72 (d, J = 8.8 Hz, 2H), 2.96 (s, 6H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.42, 131.35, 118.57, 113.29, 40.67, 19.18.

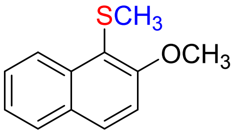


4-Methylthioanisole (3ag)[7]: yellow oil was obtained with 63% isolated yield (97.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 6.90 – 6.84 (m, 2H), 3.79 (s, 3H), 2.44 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 158.29, 130.23, 128.80, 114.48, 55.38, 18.12.

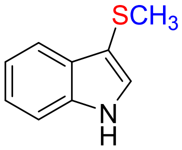


4-Methylthio-1, 3-dimethoxybenzene (3ah)[8]: Colorless liquid was obtained with 83% isolated yield (152.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.3, 3.8 Hz, 1H), 6.49 (dt, *J* = 7.5, 2.4

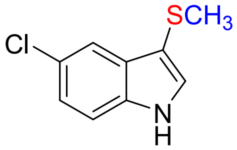
Hz, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.88, 158.56, 130.42, 117.06, 106.17, 104.88, 55.79, 55.25, 16.61.



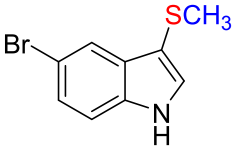
1-Methylthio-2-methoxynaphthalene (3ai)[9]: Light yellow oil was obtained with 67% isolated yield (136.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 4.08 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.22, 135.72, 130.37, 129.40, 128.26, 127.17, 125.44, 123.86, 118.03, 113.18, 56.74, 18.46.



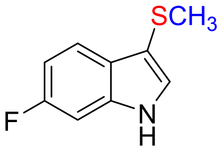
3- Methylthio-1H-indole (3aj)[10]: Colorless liquid was obtained with 31% isolated yield (50.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.88 (d, J = 7.4 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.28 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.39, 128.77, 128.00, 122.81, 120.45, 119.28, 111.75, 107.96, 20.30.



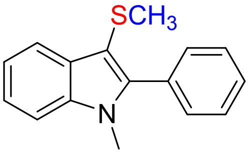
5-Chloro-3-methylthio-1H-indole (3ak)[10]: Colorless liquid was obtained with 46% isolated yield (90.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.77 (d, J = 2.0 Hz, 1H), 7.32 (d, J = 2.5 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.22 (dd, J = 8.6, 2.0 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.65, 130.00, 129.30, 126.30, 123.13, 118.79, 112.68, 108.02, 20.32.



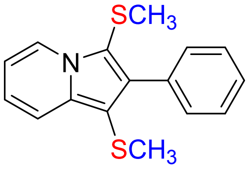
5-Bromo-3-methylthio-1H-indole (3al)[10]: Colorless liquid was obtained with 35% isolated yield (84.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.92 (d, J = 1.8 Hz, 1H), 7.34 (dd, J = 8.6, 1.9 Hz, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.93, 130.61, 129.10, 125.68, 121.90, 113.86, 113.08, 107.98, 20.35.



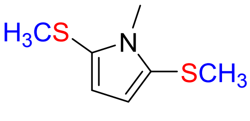
6-Fluoro-3-methylthio-1H-indole (3am)[10]: Colorless liquid was obtained with 41% isolated yield (74.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.70 (dd, *J* = 8.6, 5.3 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.07 (dd, *J* = 9.4, 2.0 Hz, 1H), 7.01 (td, *J* = 9.2, 2.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.16 (s), 159.58 (s), 136.24 (d, *J* = 12.6 Hz), 127.92 (d, *J* = 3.1 Hz), 125.25 (s), 120.11 (d, *J* = 10.2 Hz), 109.17 (d, *J* = 24.6 Hz), 97.94 (d, *J* = 26.3 Hz), 20.14 (s).



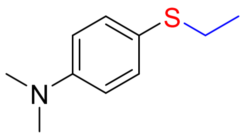
1-Methyl-2-phenyl-3-methylthio-1H-indole (3an)[10]: White solid was obtained with 32% isolated yield (81.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.63 (m, 5H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.49 (m, 1H), 7.48 – 7.45 (m, 1H), 3.78 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.21, 137.51, 131.30, 131.03, 129.75, 128.73, 128.45, 122.72, 120.66, 119.63, 110.04, 105.19, 31.59, 20.43.



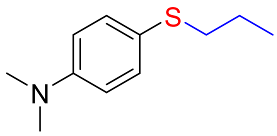
2-Phenyl-1, 3-bis(methylthio)indolizine (3ao)[11]: Yellow oil was obtained with 37% isolated yield (105.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 6.9 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.7 Hz, 1H), 6.78 (t, *J* = 6.6 Hz, 1H), 2.15 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.59, 137.11, 134.31, 130.70, 127.79, 127.27, 124.05, 120.24, 117.92, 112.41, 111.81, 102.83, 20.68, 18.57.



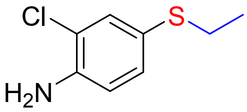
1-Methyl-2, 5-bis(methylthio)-1H-pyrrole (3ap)[12]: Colorless liquid was obtained with 31% isolated yield (53.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.35 (s), 3.77 (s), 2.31 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 126.08, 115.05, 31.09, 20.61.



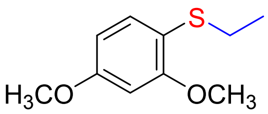
***N, N*-dimethyl-4-ethylthioaniline (3ba)[13]:** Colorless liquid was obtained with 63% isolated yield (114.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 2.97 (s, 6H), 2.81 (q, *J* = 7.3 Hz, 2H), 1.25 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.88, 134.08, 131.36, 112.88, 40.52, 30.62, 14.80.



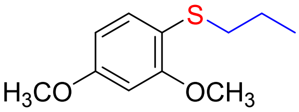
***N, N*-dimethyl-4-propylthioaniline (3bb)[14]:** White solid was obtained with 55% isolated yield (107.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 6.70 – 6.67 (m, 2H), 2.97 (s, 6H), 2.78 – 2.75 (m, 2H), 1.62 – 1.59 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.83, 133.95, 121.25, 112.87, 40.50, 38.70, 22.80, 13.33.



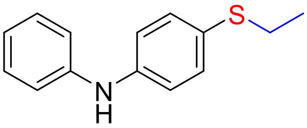
2-Chloro-4-ethylthioaniline (3bc)[13]: Colorless liquid was obtained with 70% isolated yield (131.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 2.0 Hz, 1H), 7.16 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.75 – 6.71 (m, 1H), 3.68 (s, 2H), 2.82 (q, *J* = 7.3 Hz, 2H), 1.25 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.06, 133.14, 132.06, 124.45, 119.35, 116.11, 30.25, 14.63.



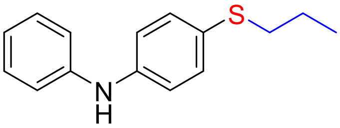
4-Ethylthio-1, 3-dimethoxybenzene (3bd)[8]: Colorless liquid was obtained with 75% isolated yield (148.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 1H), 6.45 (d, *J* = 9.4 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 2.81 (q, *J* = 7.4 Hz, 2H), 1.22 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.53, 159.66, 133.86, 114.60, 104.72, 98.96, 55.76, 55.40, 27.77, 14.41.



4-Propylthio-1, 3-dimethoxybenzene (3be)[8]: Colorless liquid was obtained with 58% isolated yield (123.1 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.30 (m, 1H), 6.47 (m, 3H), 3.88 (s, 4H), 3.81 (s, 3H), 2.78 (t, J = 7.3 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.01 (t, J = 7.3 Hz, 4H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 160.45, 159.65, 133.73, 114.90, 104.69, 98.98, 55.79, 55.43, 35.81, 22.58, 13.43.



***N*-phenyl-4-ethylthioaniline (3bf):** Yellow oil was obtained with 68% isolated yield (155.9 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.36 – 7.29 (m, 4H), 7.10 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 5.75 (s, 1H), 2.89 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 142.73, 142.28, 132.86, 129.42, 126.55, 121.38, 118.18, 118.00, 29.72, 14.70. HRMS (EI) calcd for $C_{14}H_{15}NS$ $[M-H]^-$: 228.0852; found: 228.0872.



***N*-phenyl-4-propylthioaniline (3bg):** Yellow oil was obtained with 47% isolated yield (114.3 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.36 – 7.26 (m), 7.09 (d, J = 7.8 Hz), 7.02 (d, J = 7.7 Hz), 6.97 (t, J = 7.4 Hz), 5.75 (s), 2.84 (t, J = 7.2 Hz), 1.77 – 1.67 (m), 1.04 (t, J = 7.4 Hz). ^{13}C NMR (151 MHz, CDCl$_3$) δ 142.79, 142.18, 132.70, 129.39, 126.98, 121.33, 118.14, 118.04, 77.27, 77.06, 76.85, 37.74, 22.07, 13.36. HRMS (EI) calcd for $C_{15}H_{17}NS$ $[M+H]^+$: 244.1154; found: 244.1143.

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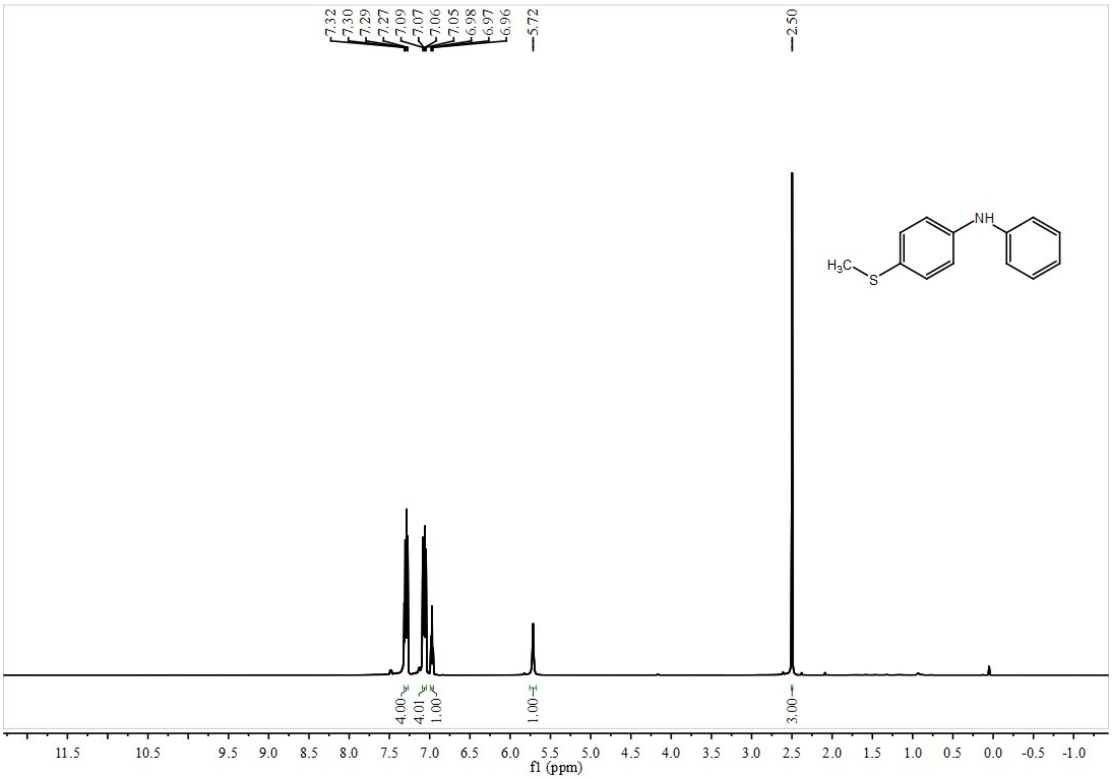
9. Copies of product NMR spectra

^{1}H NMR **3aa**



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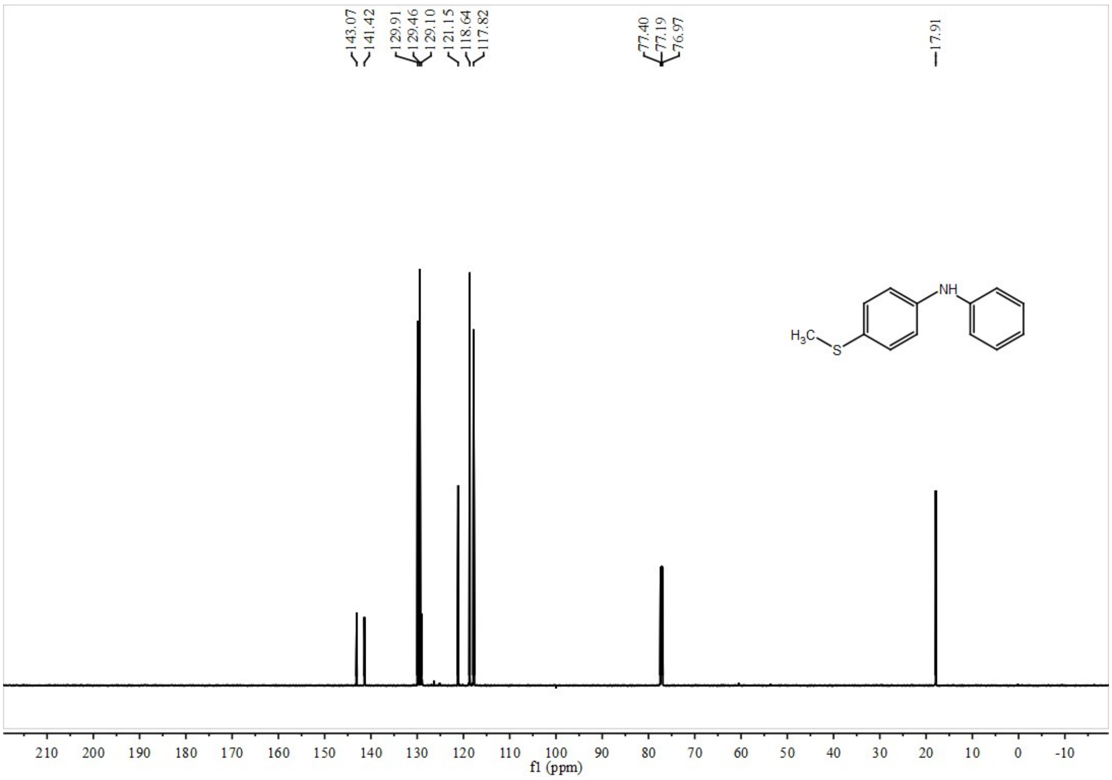

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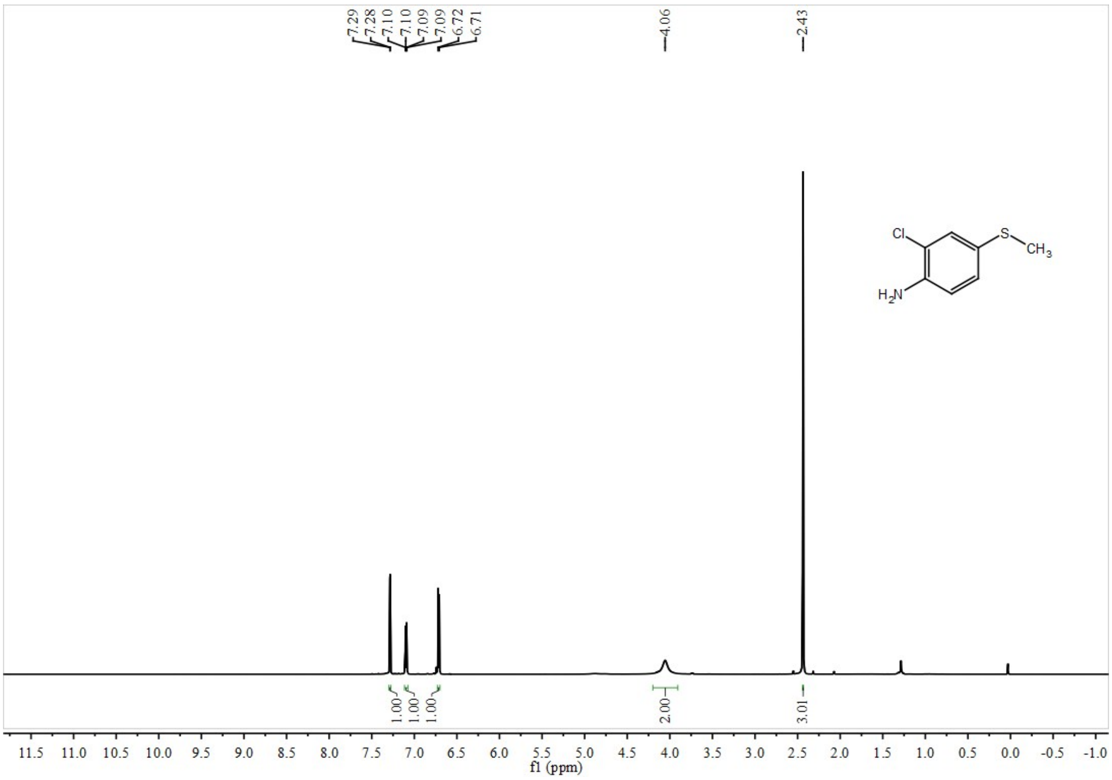

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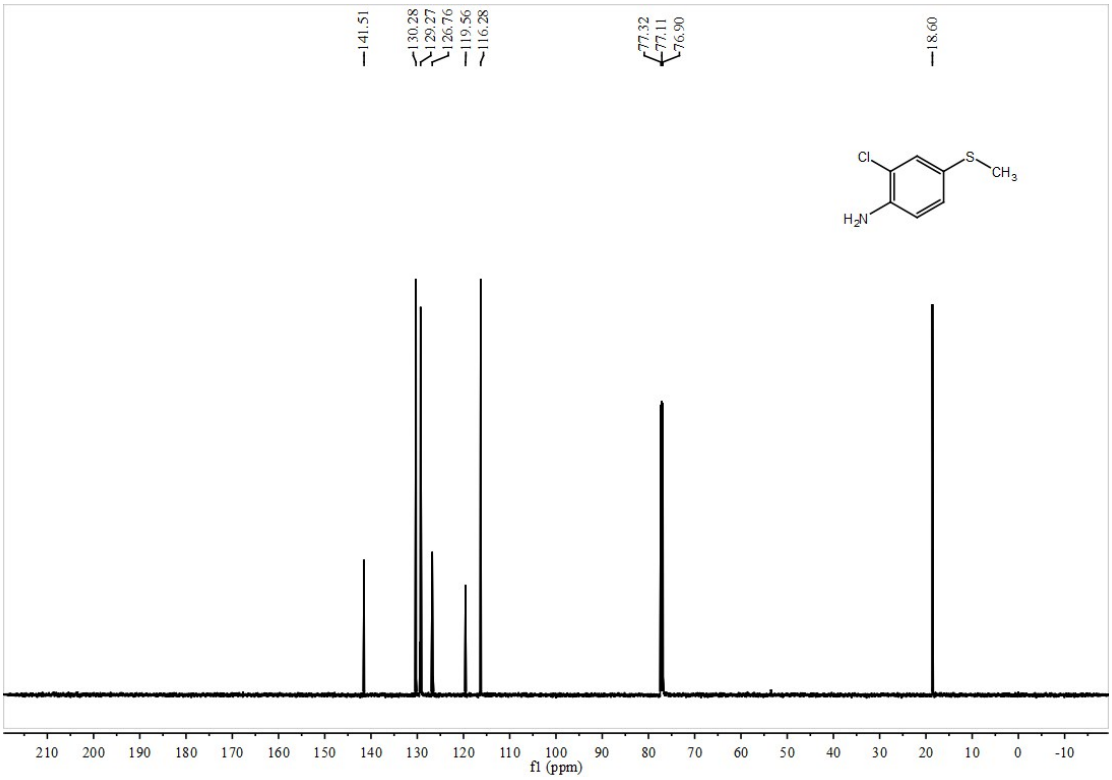

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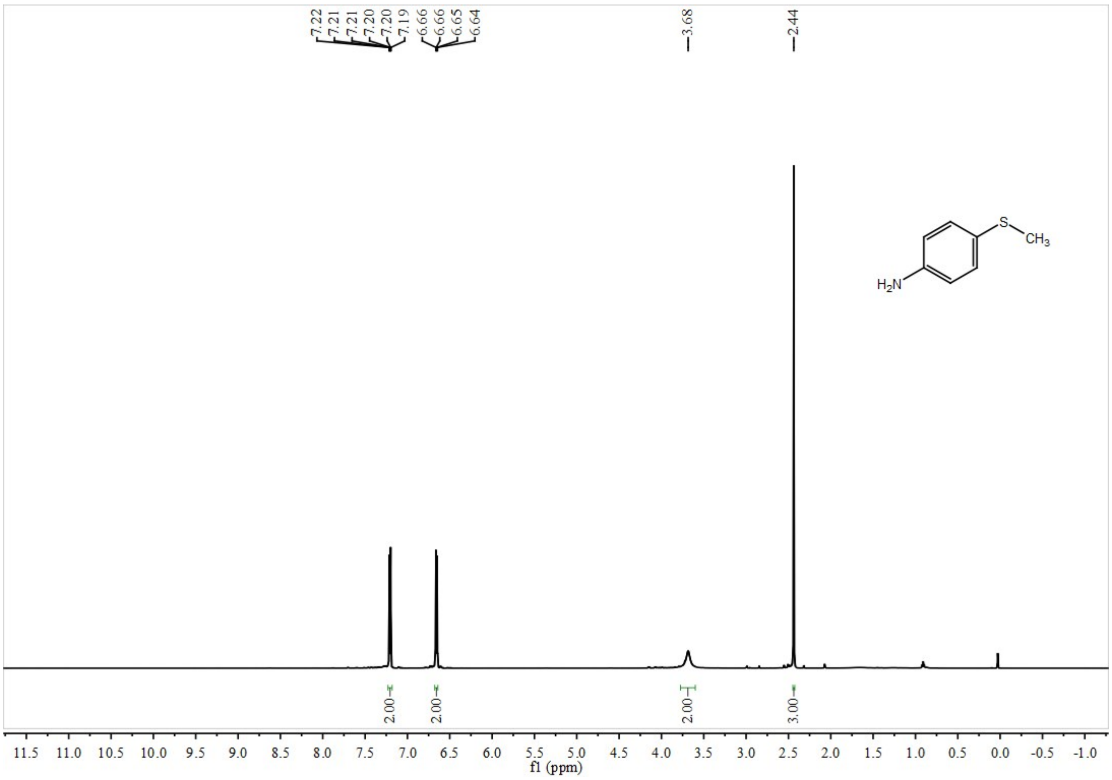

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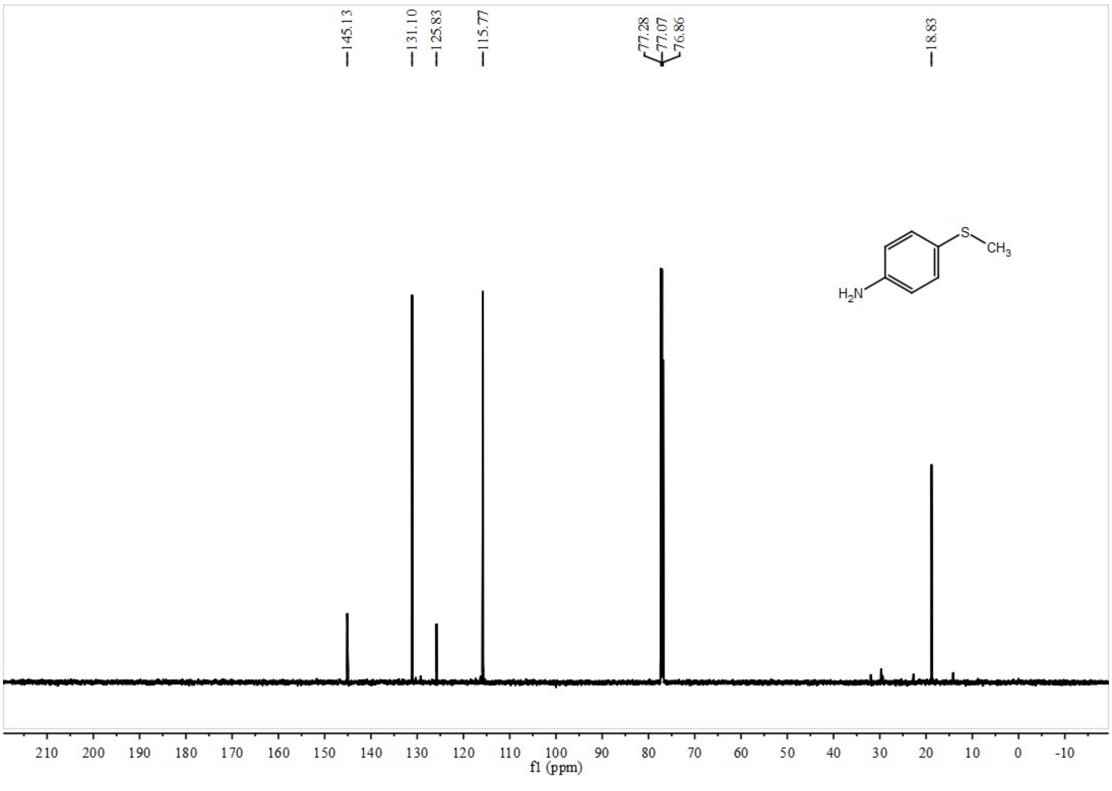

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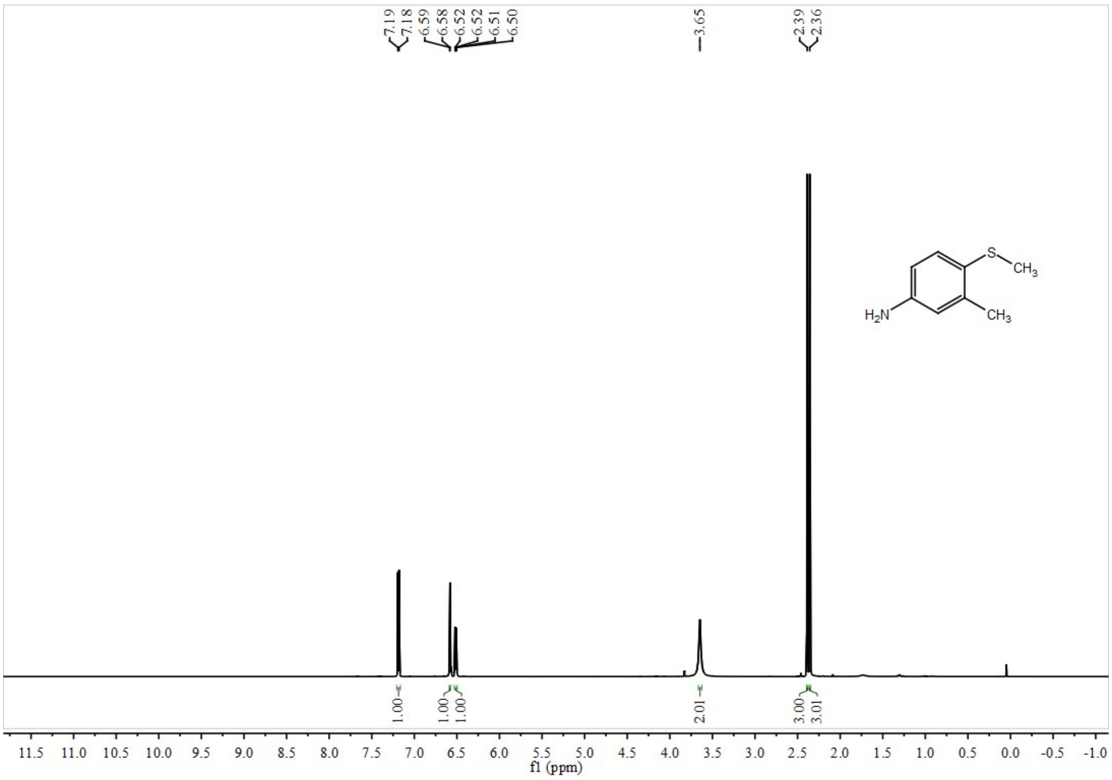

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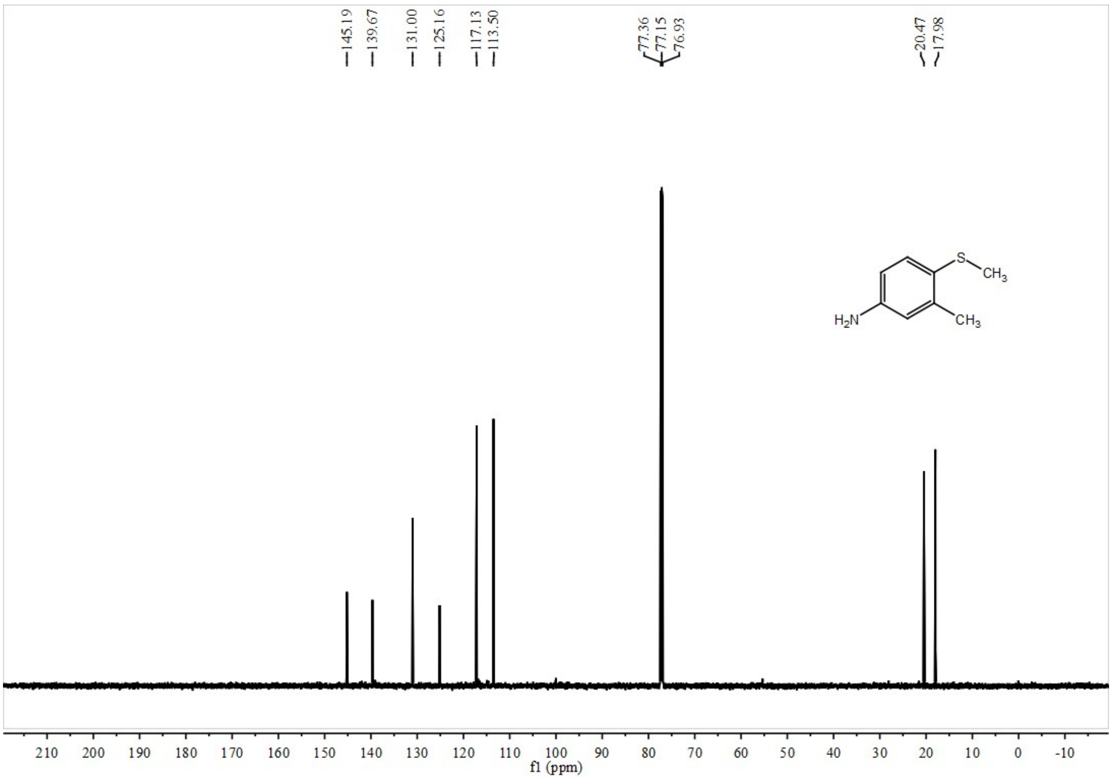

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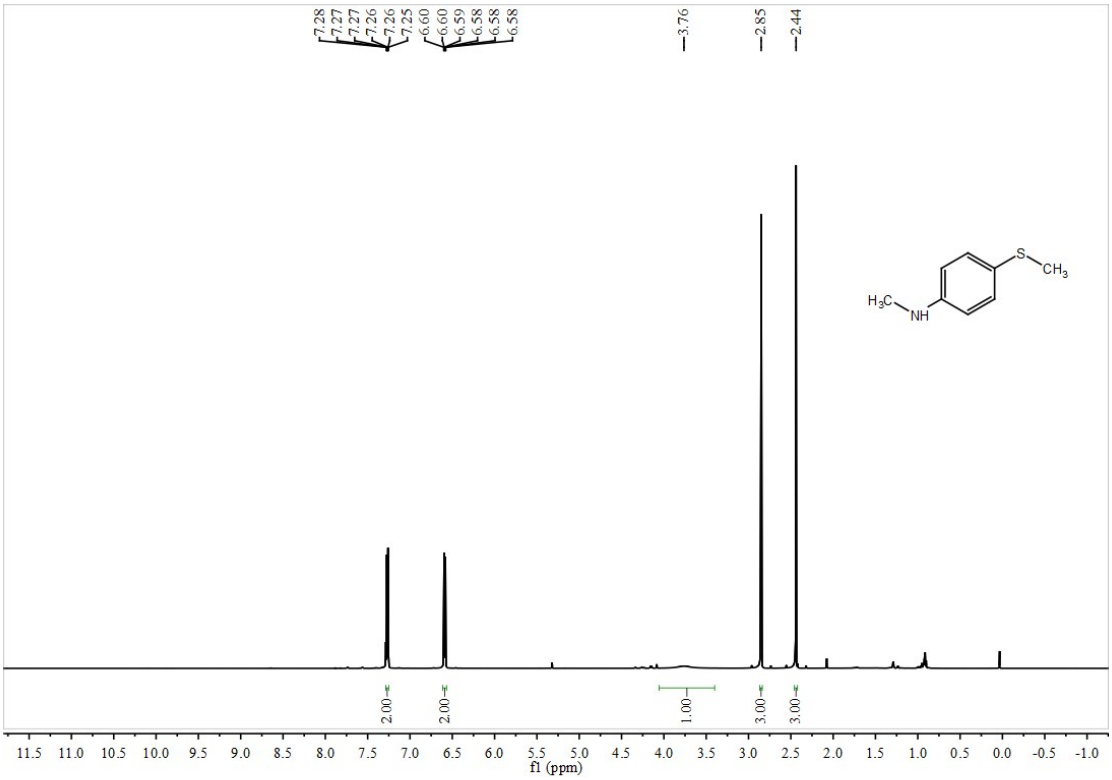

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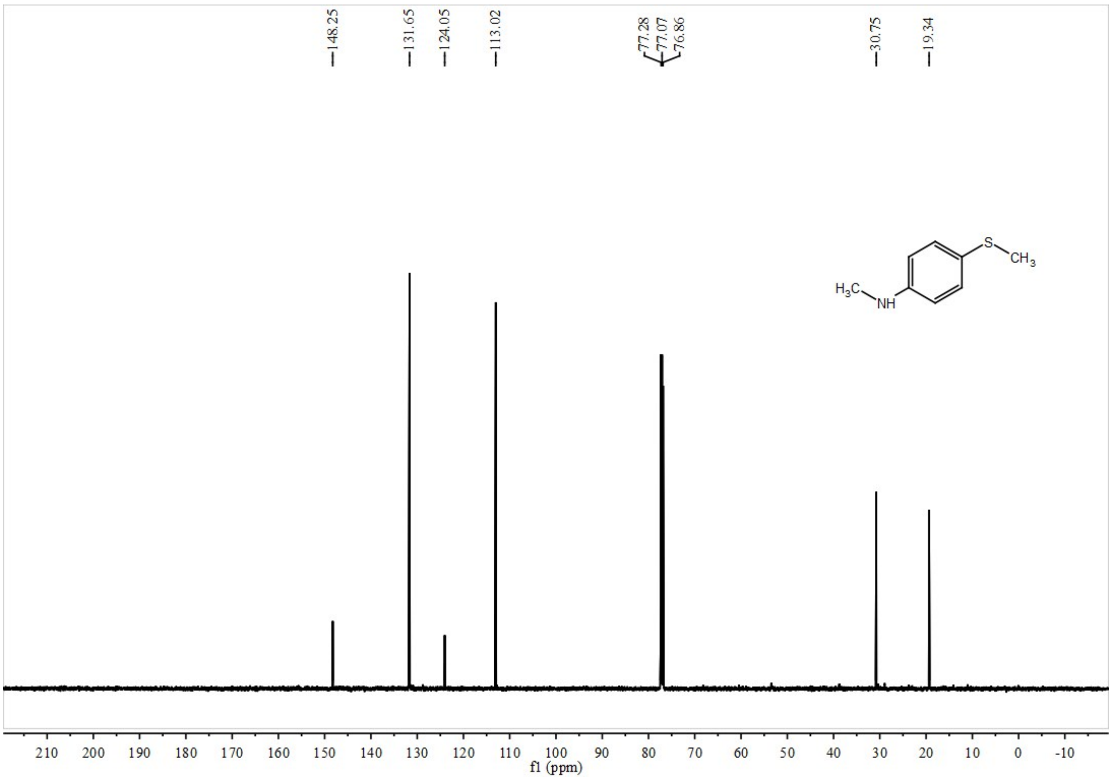

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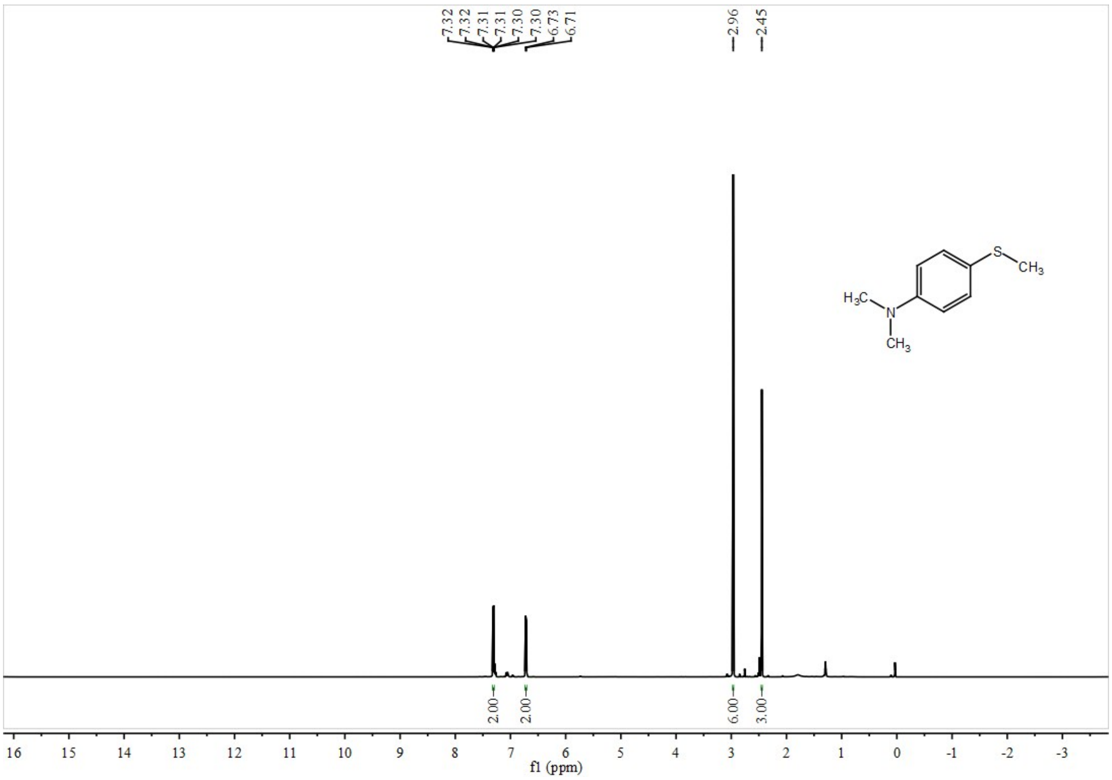

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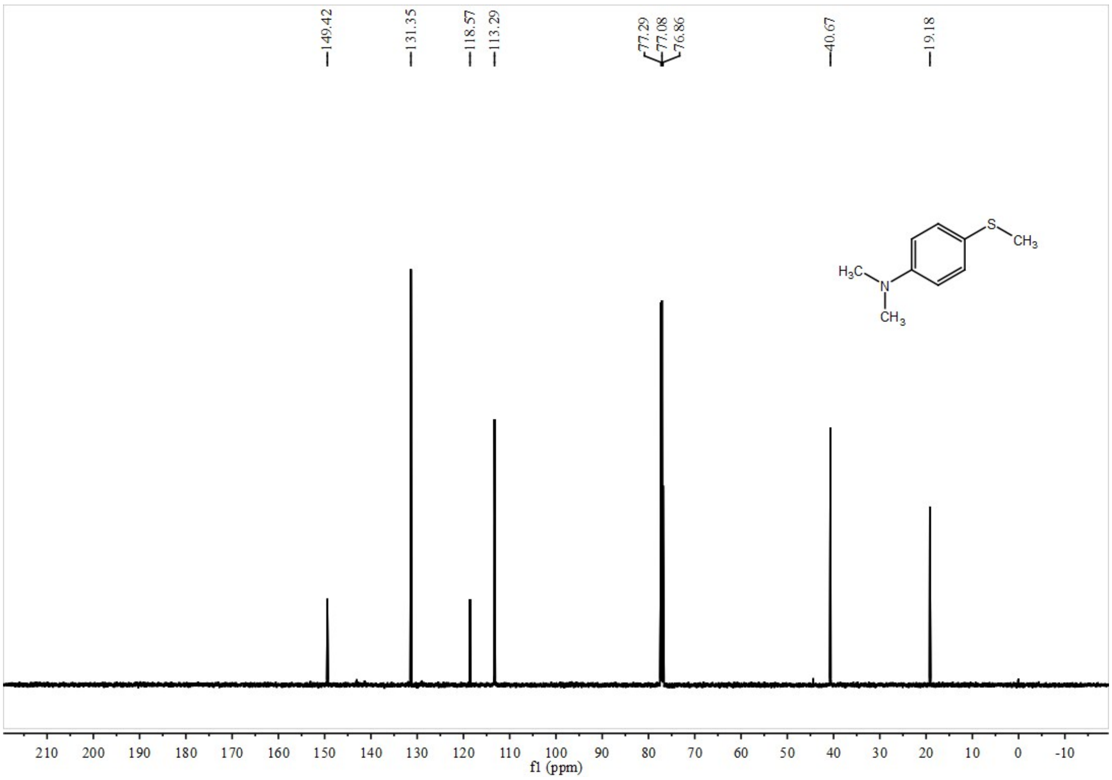

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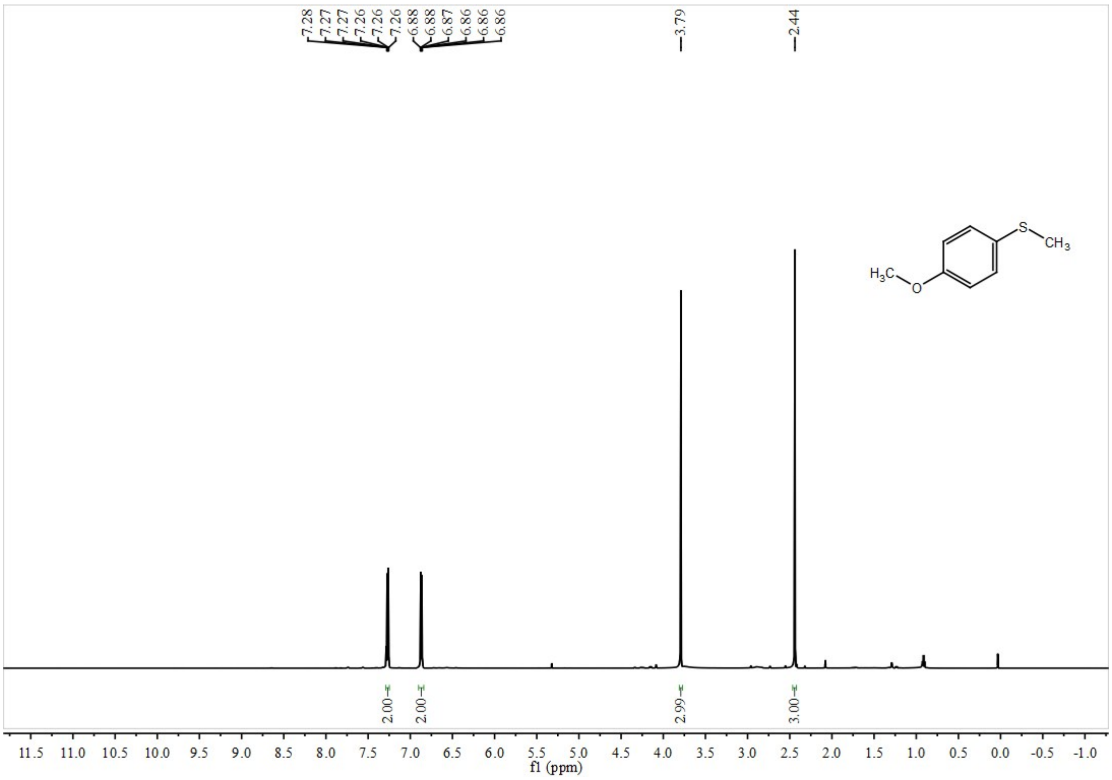

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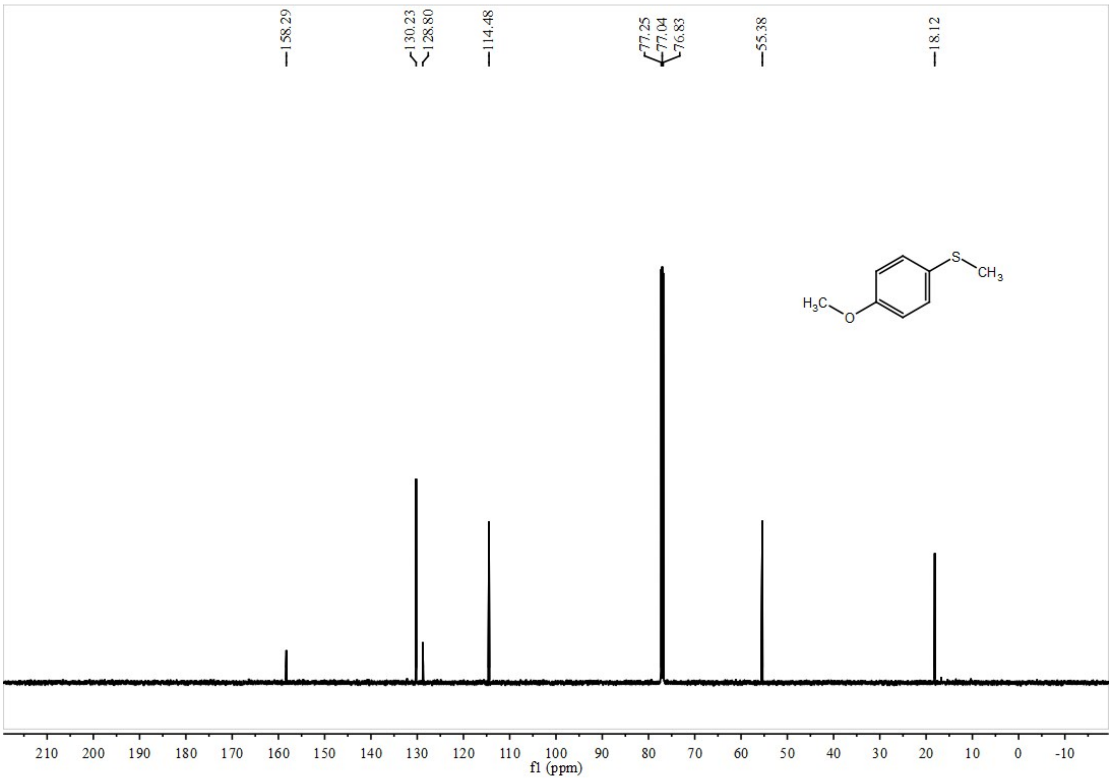

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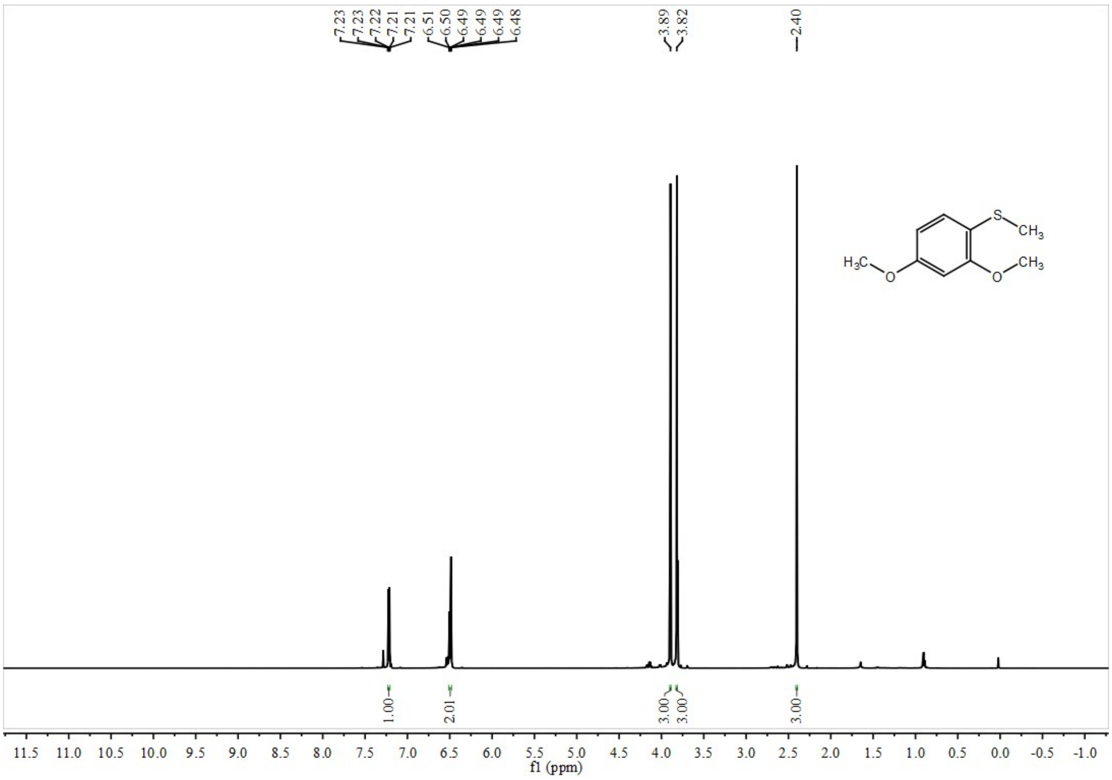

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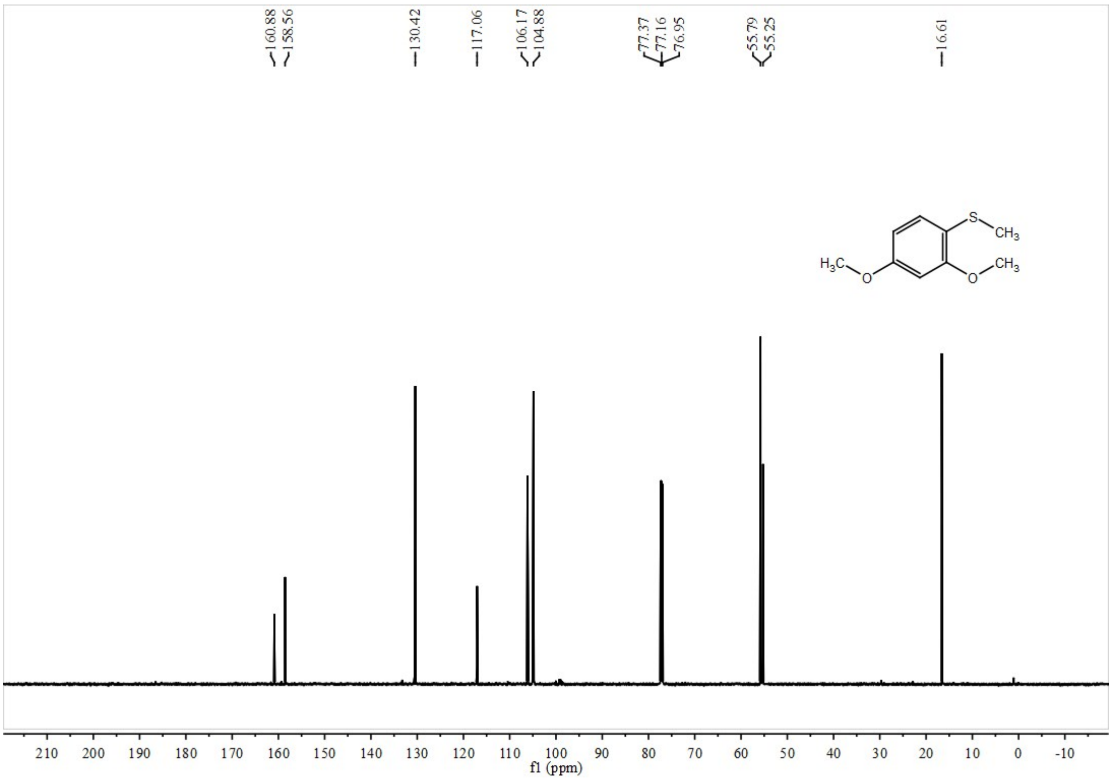

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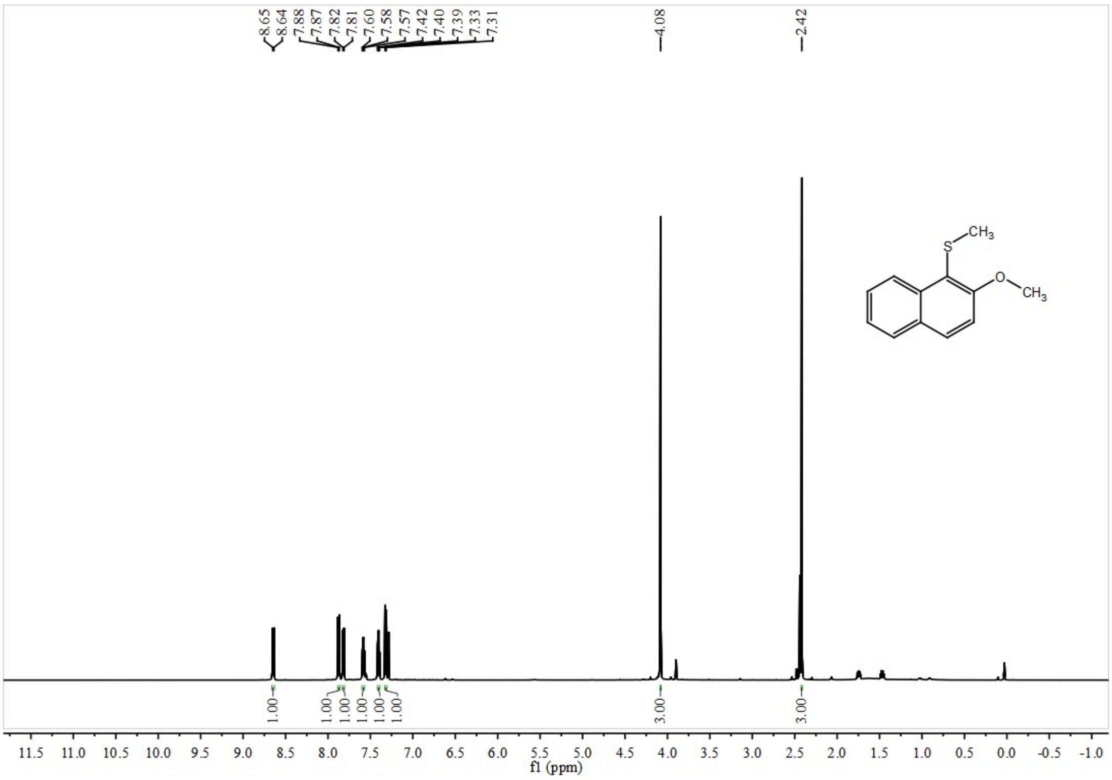

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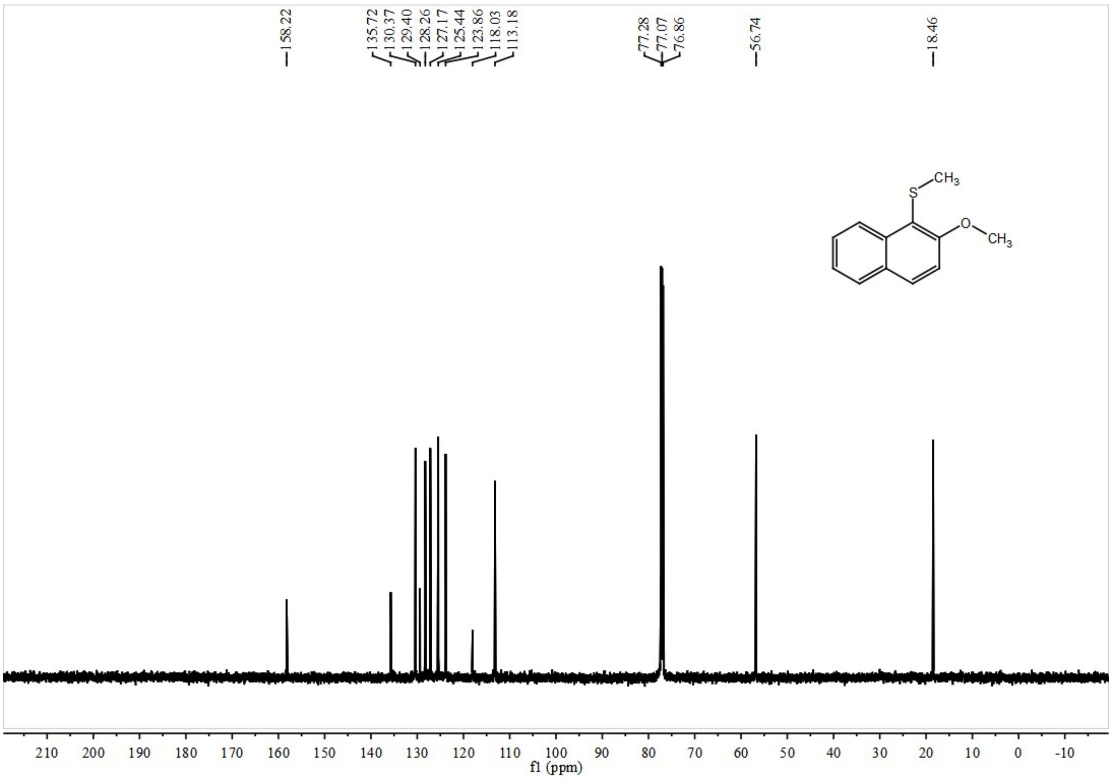

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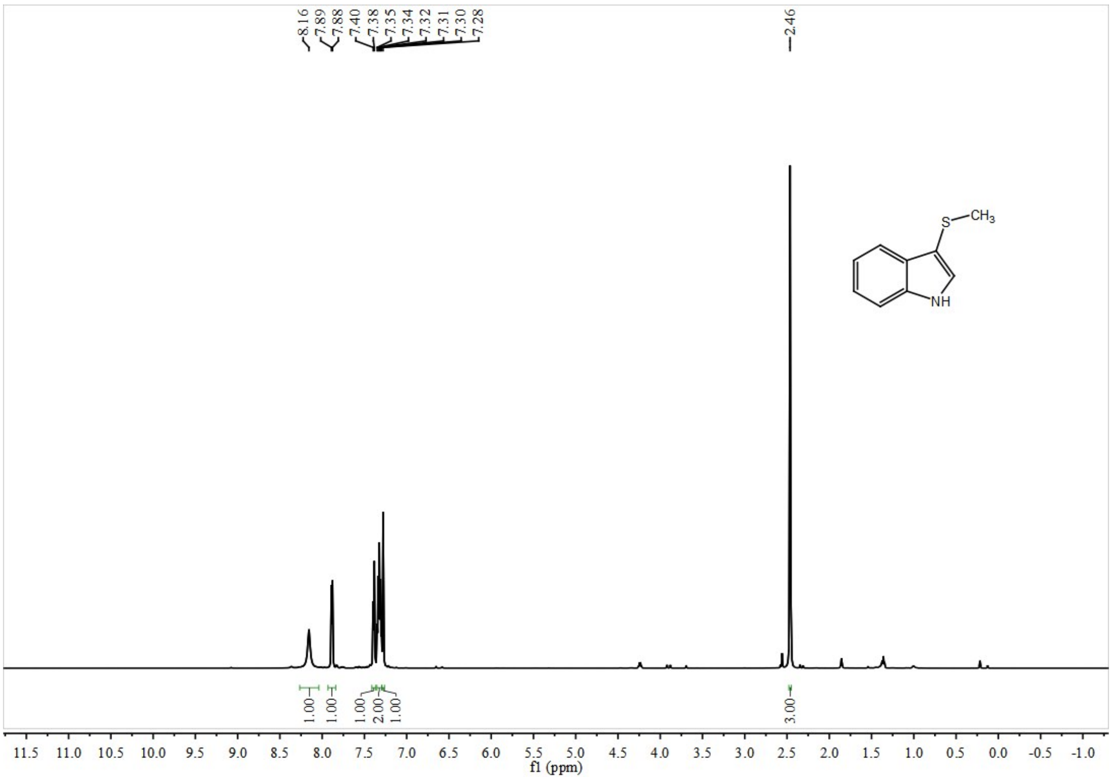

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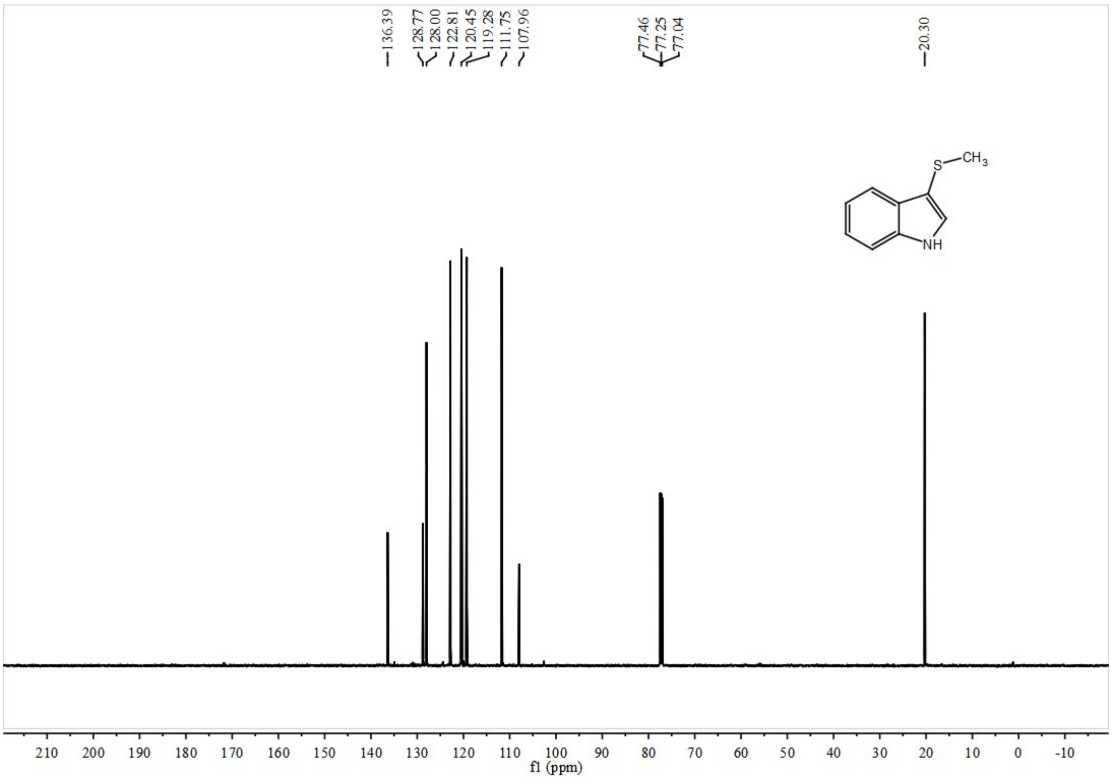

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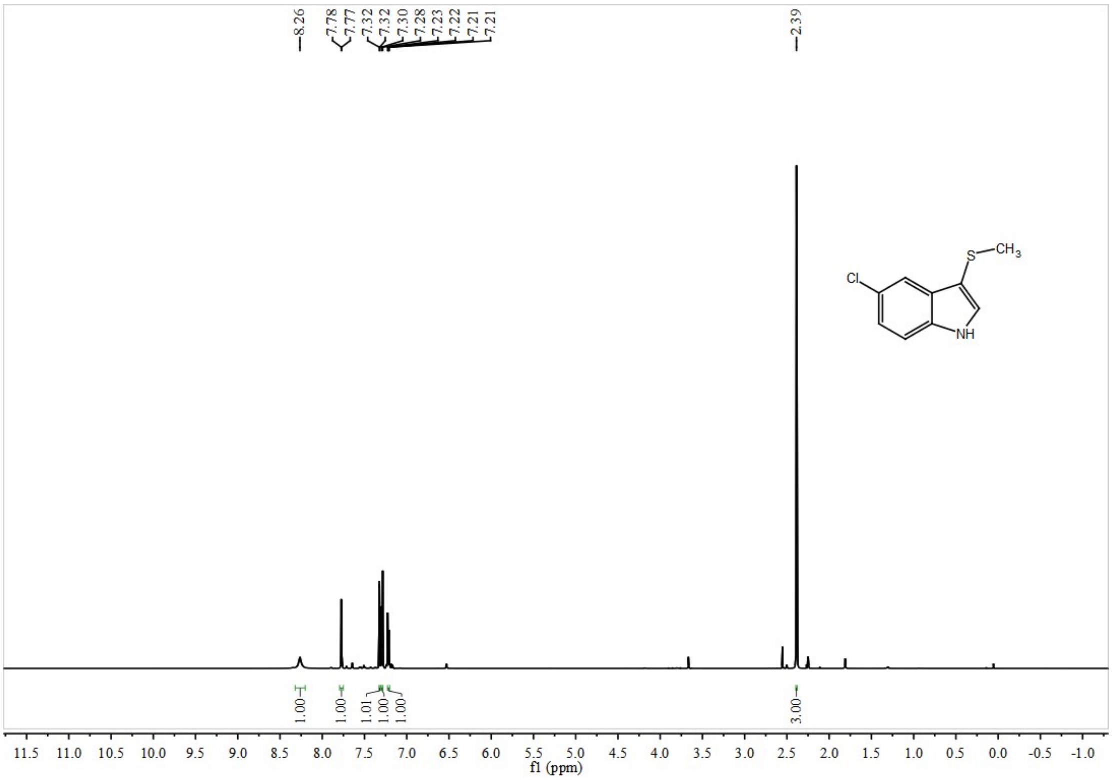

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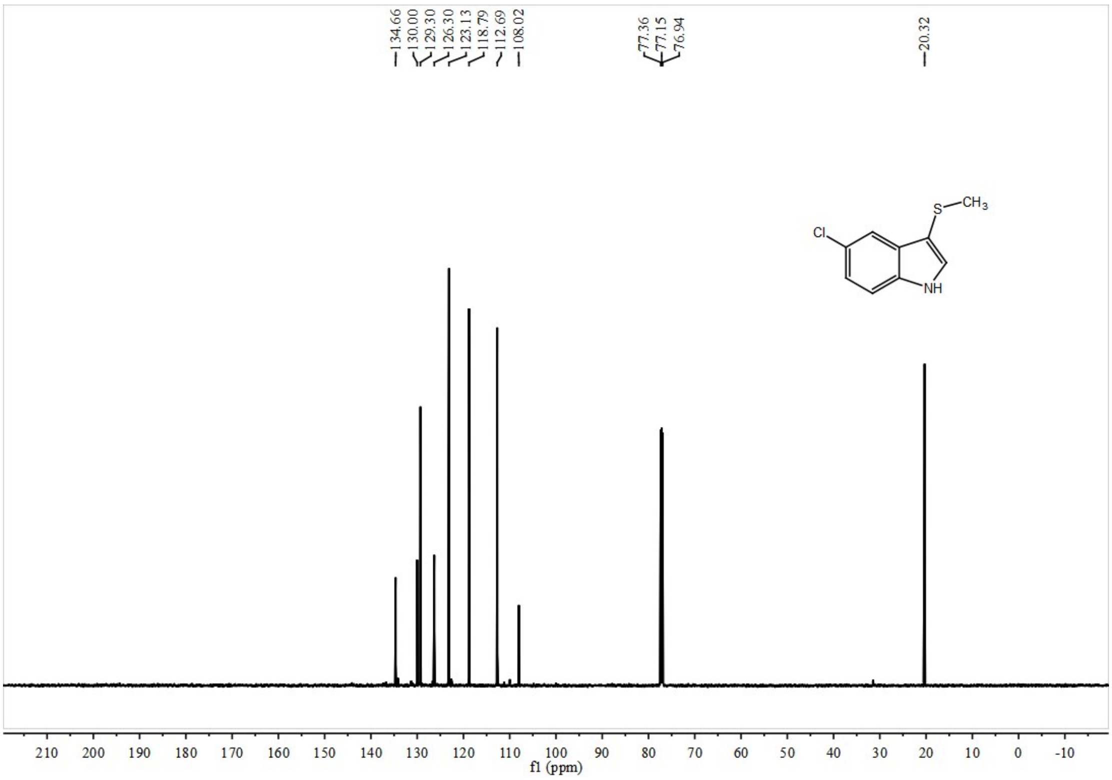

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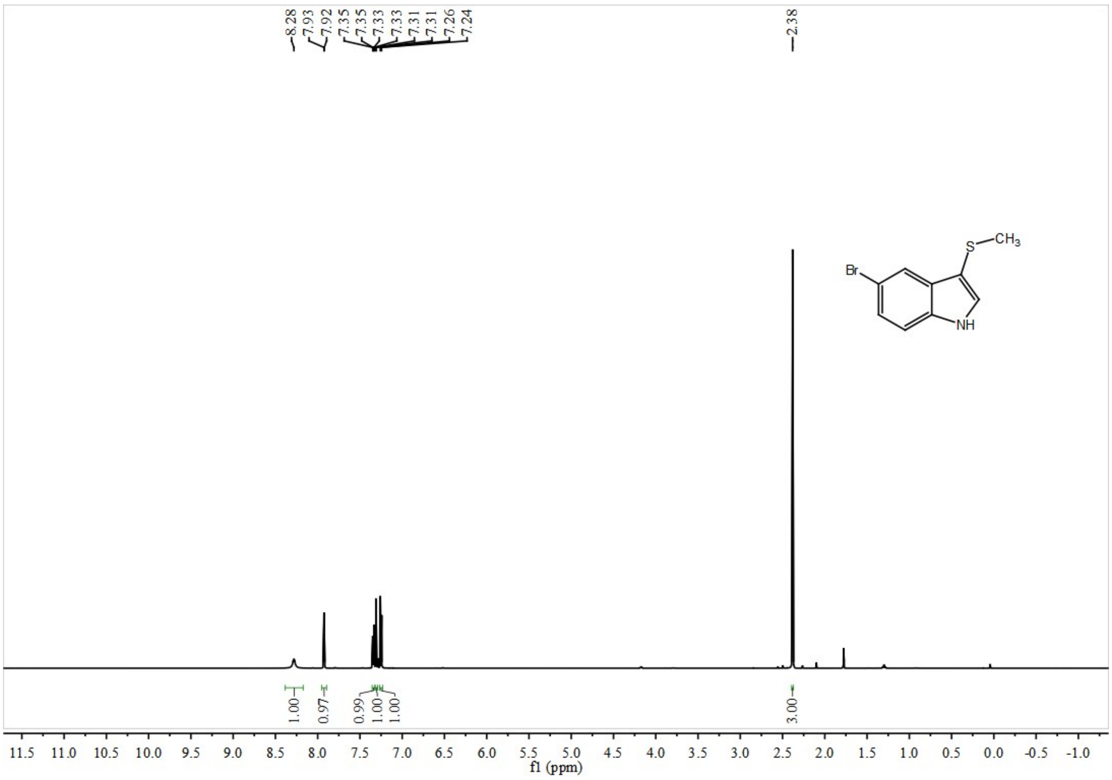

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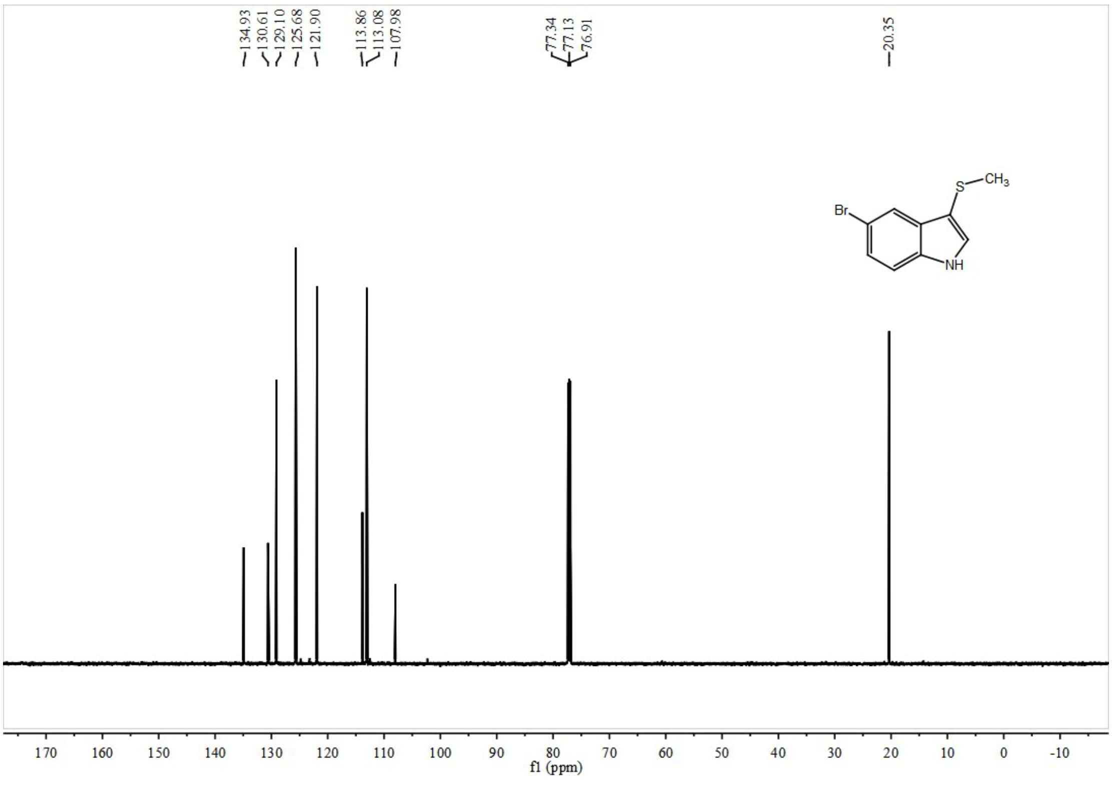

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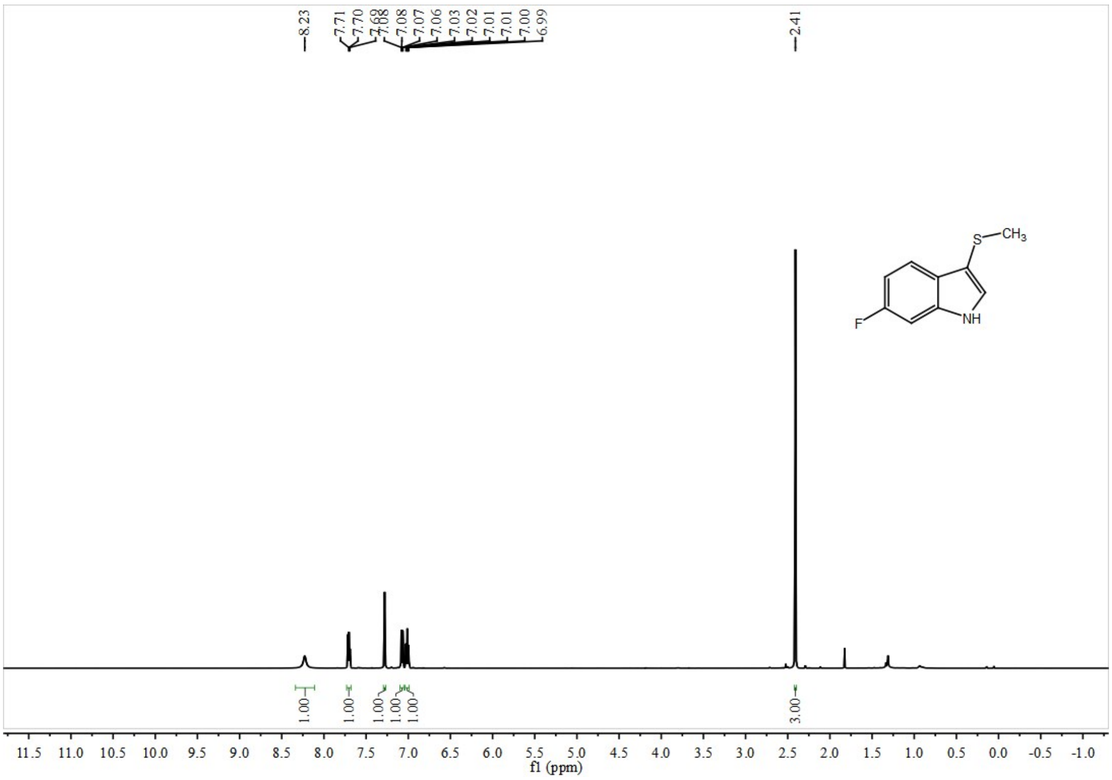

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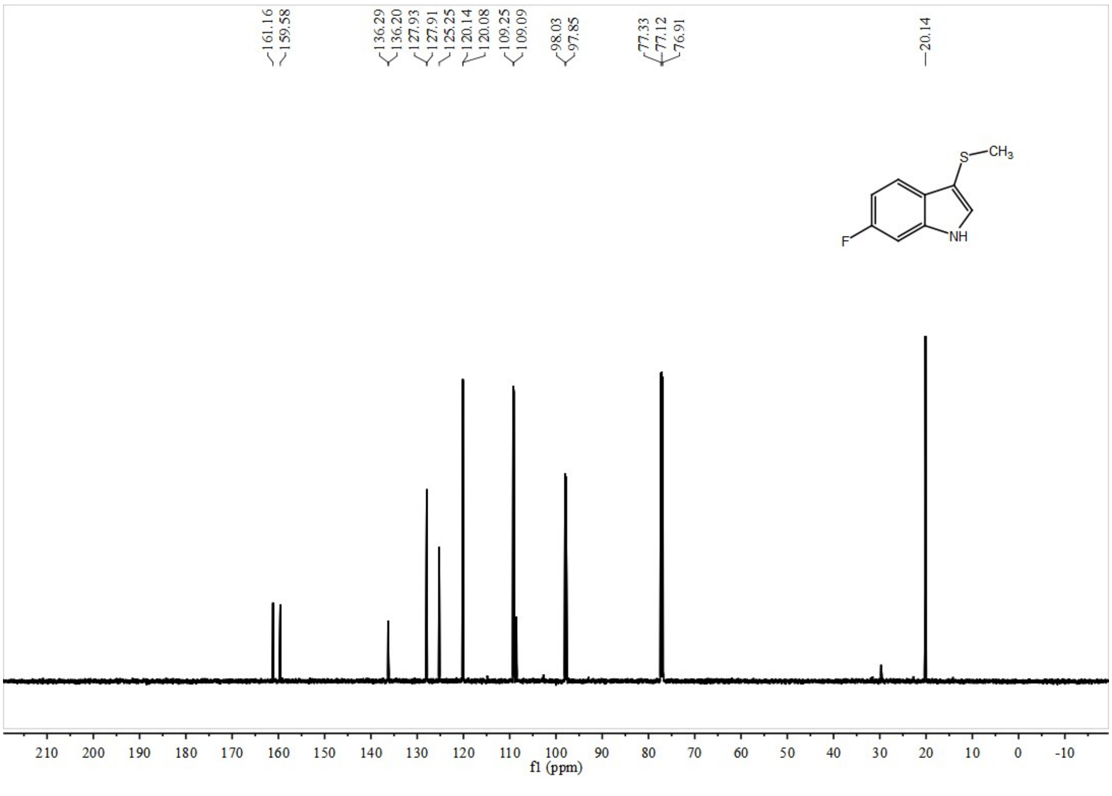

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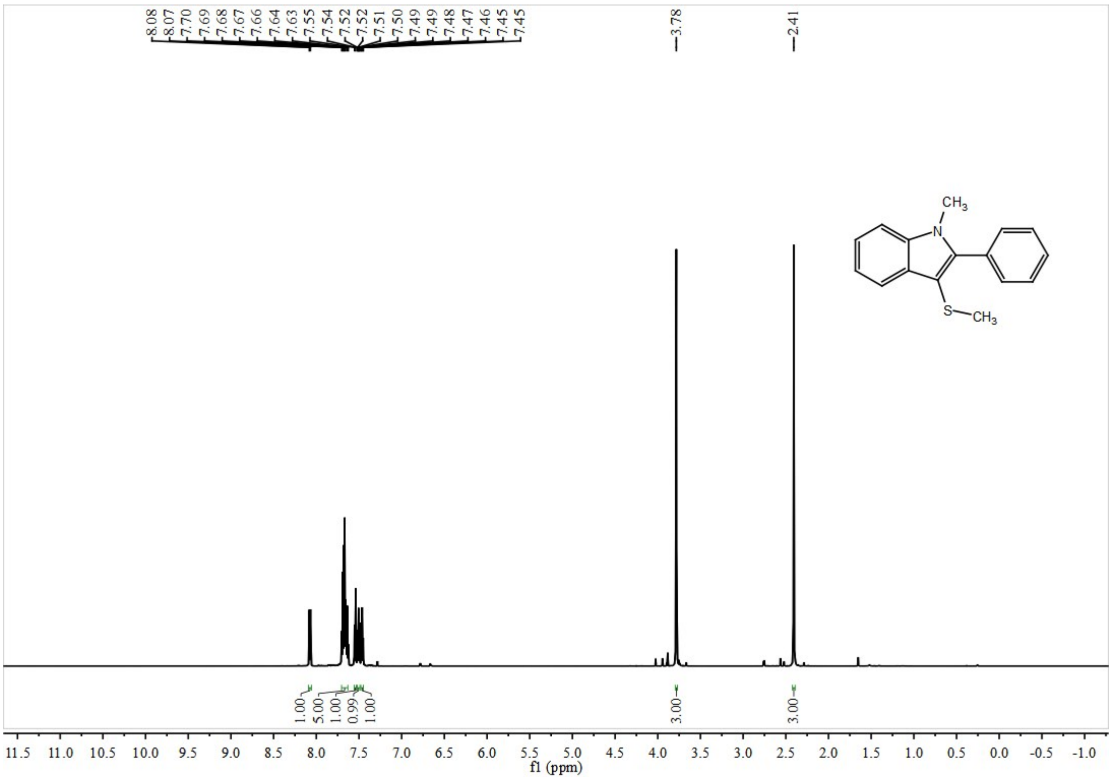

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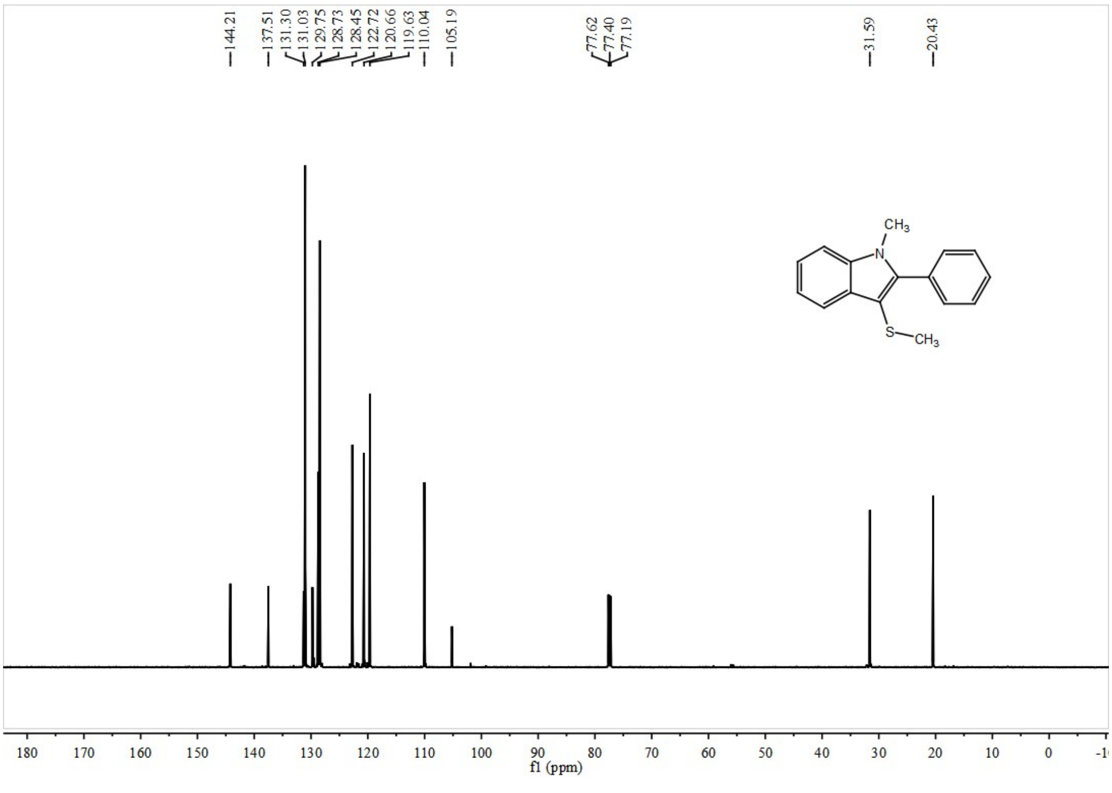

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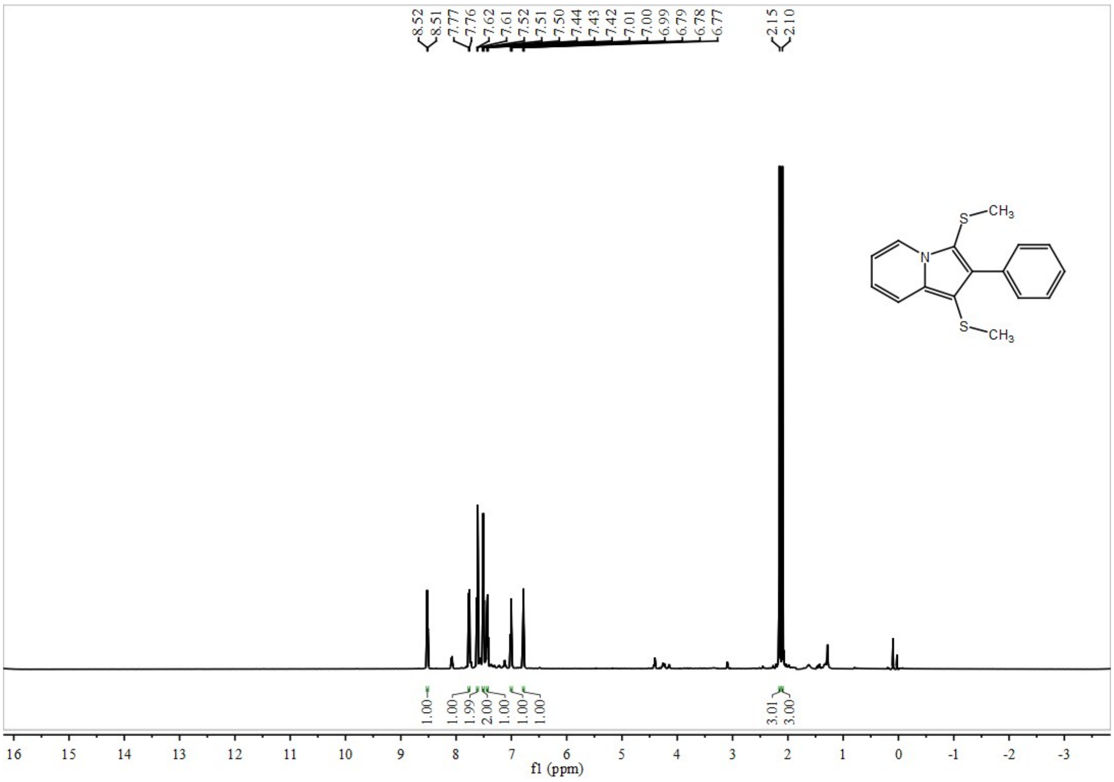

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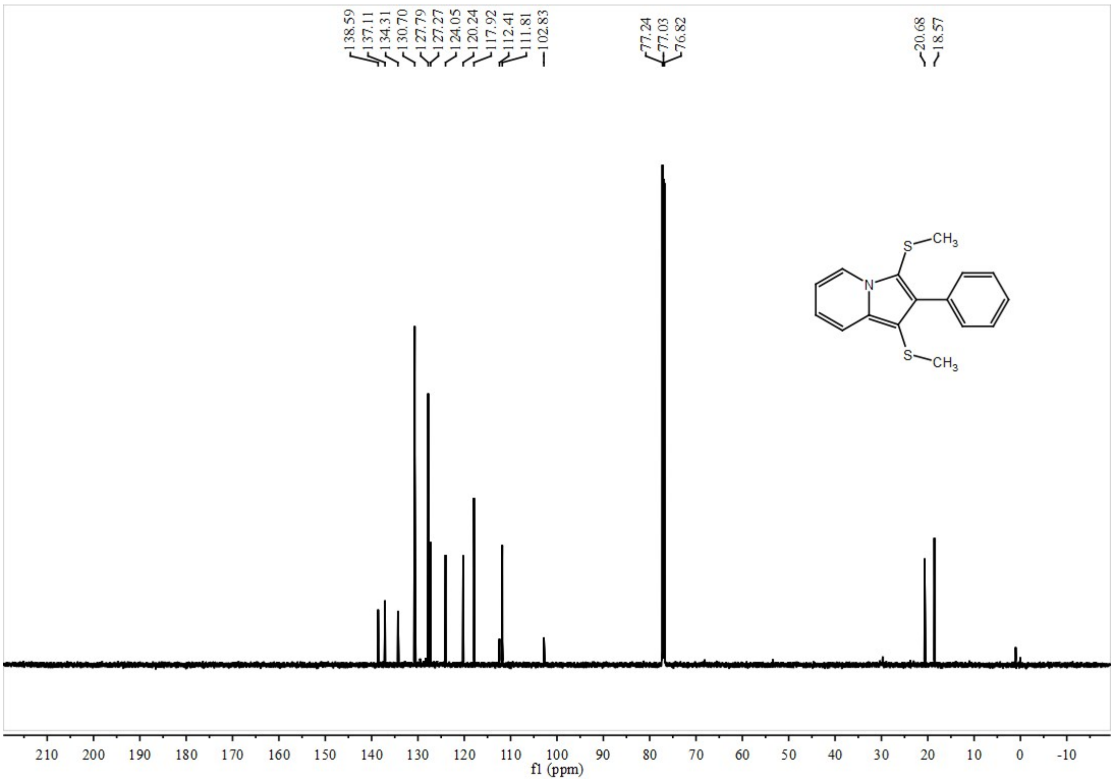

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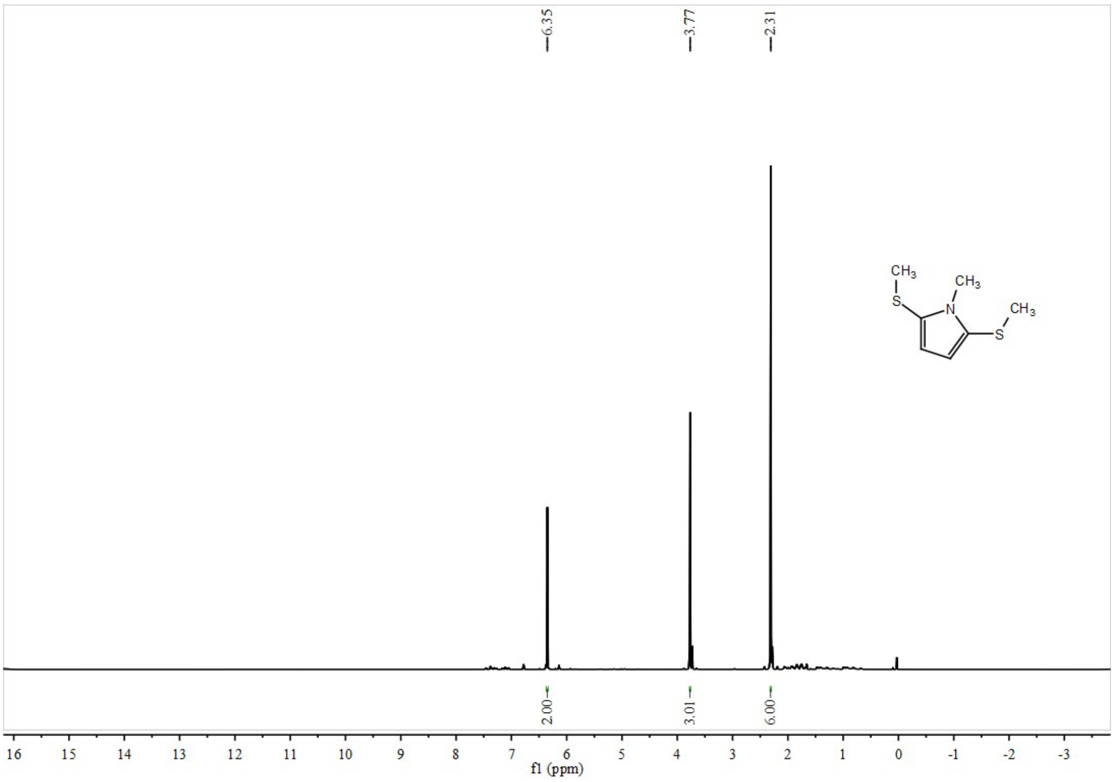

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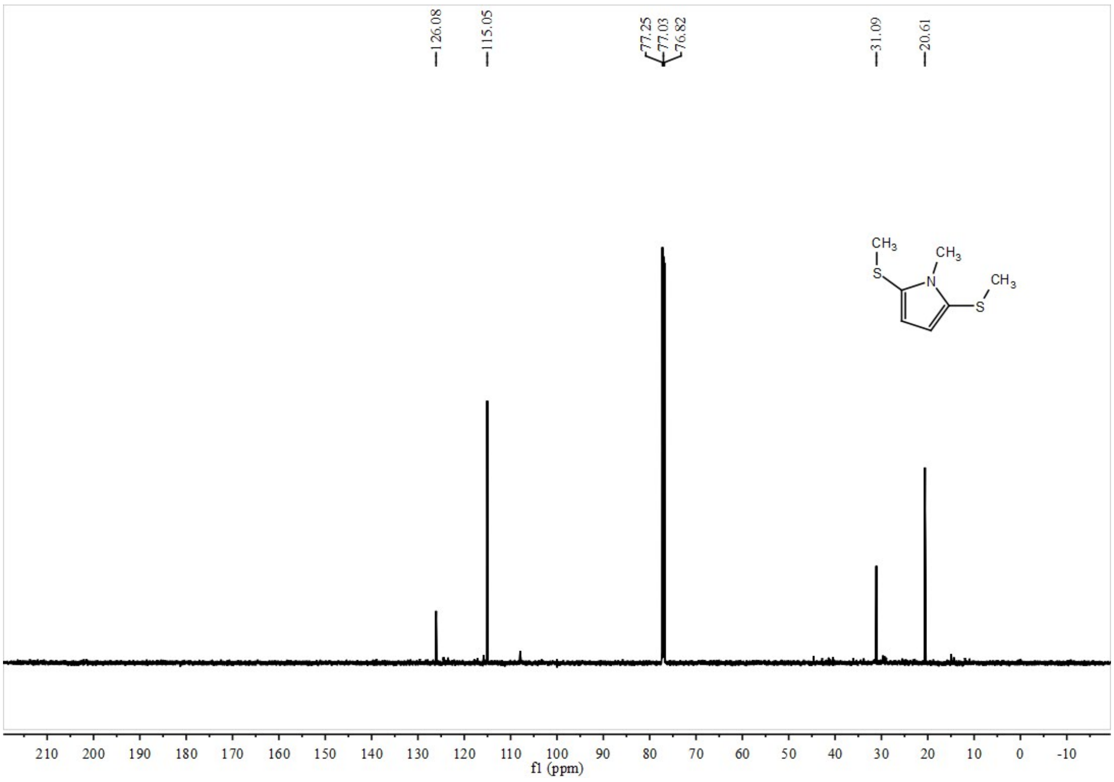

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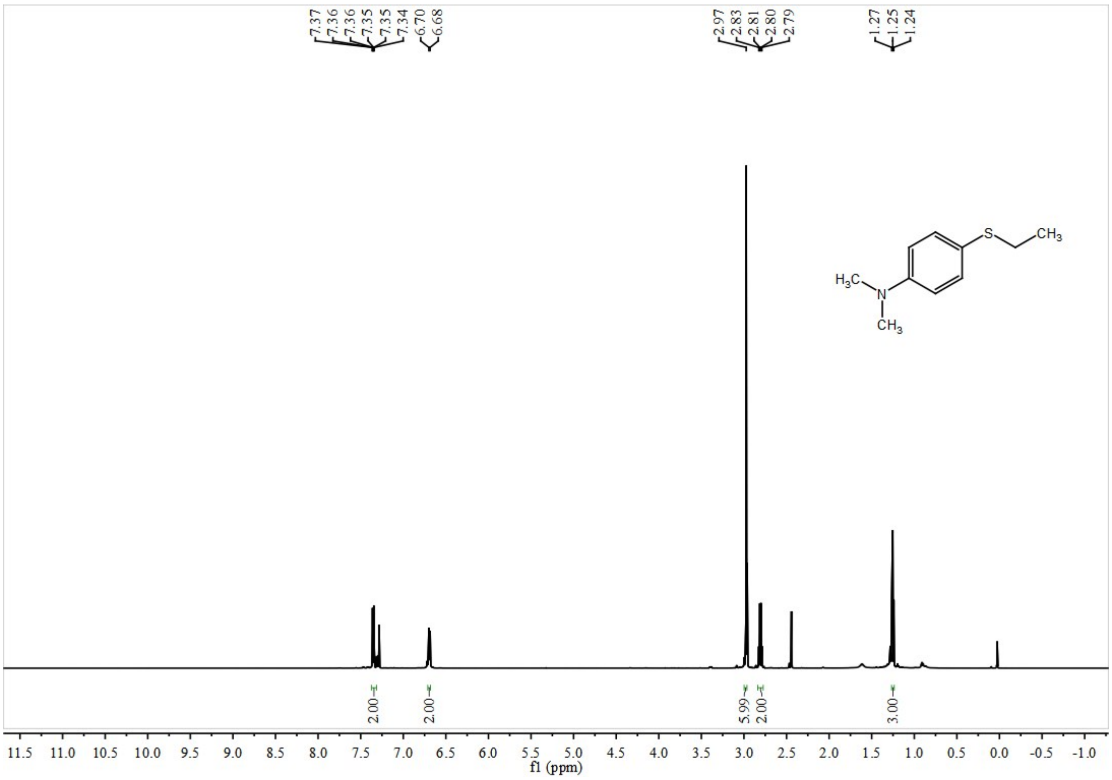

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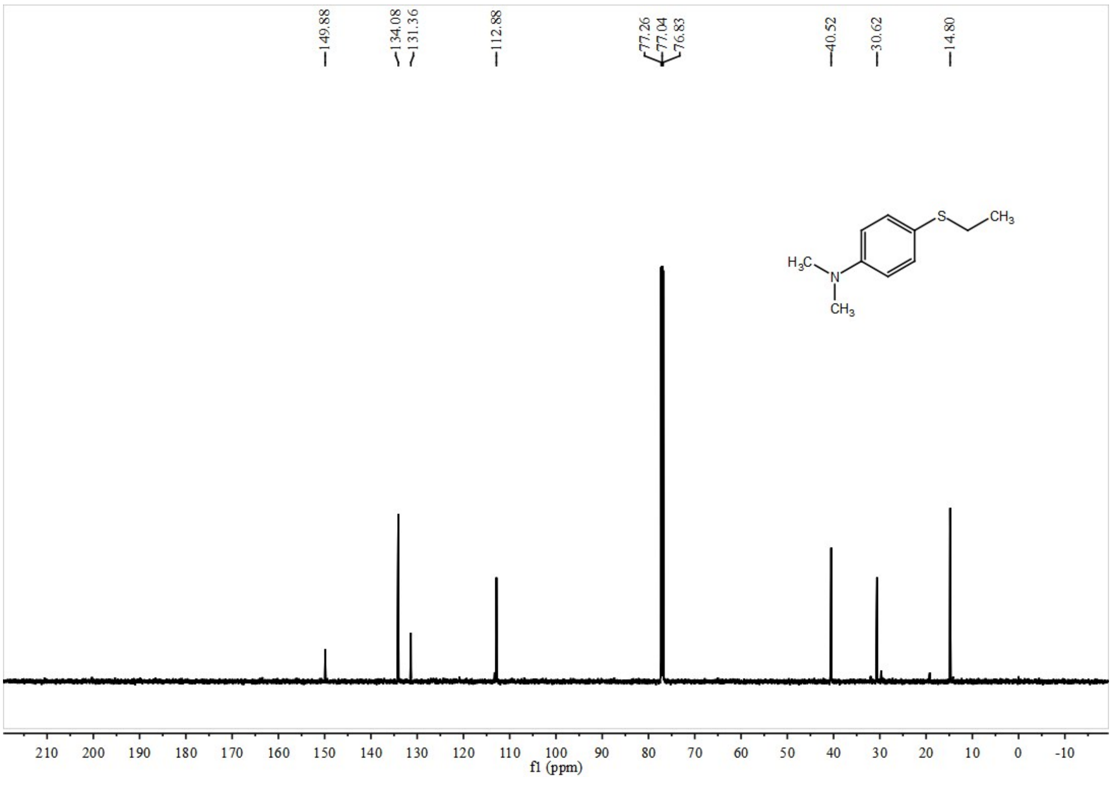

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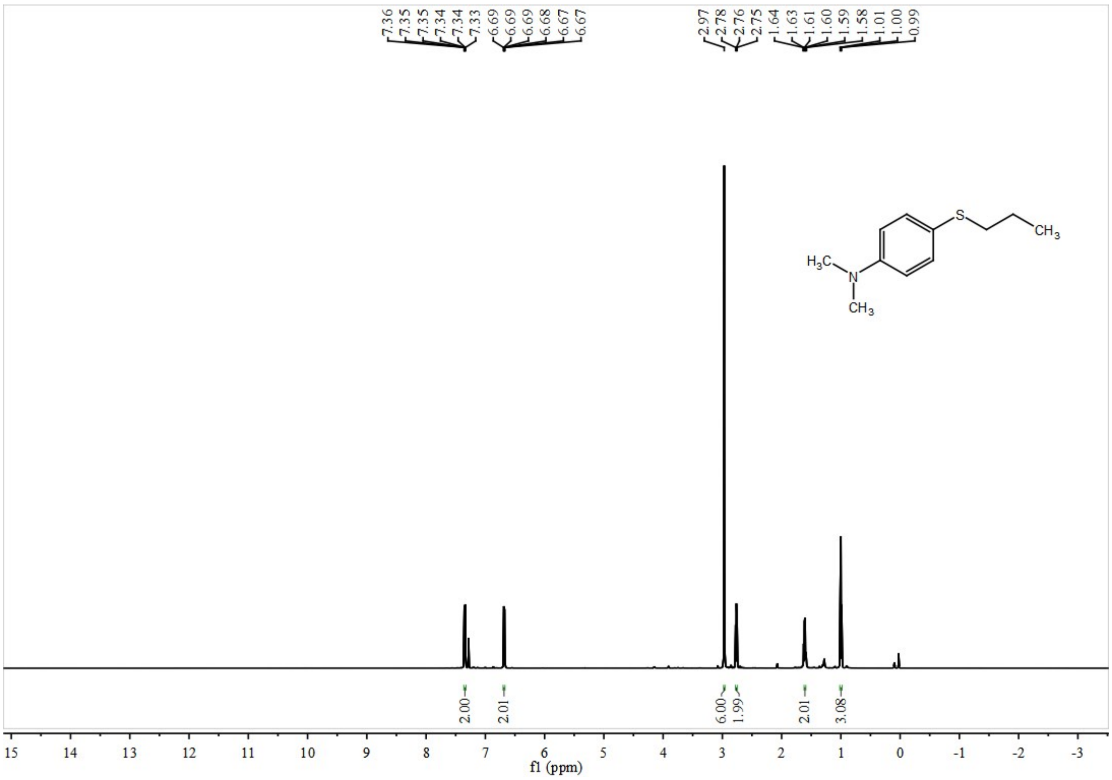

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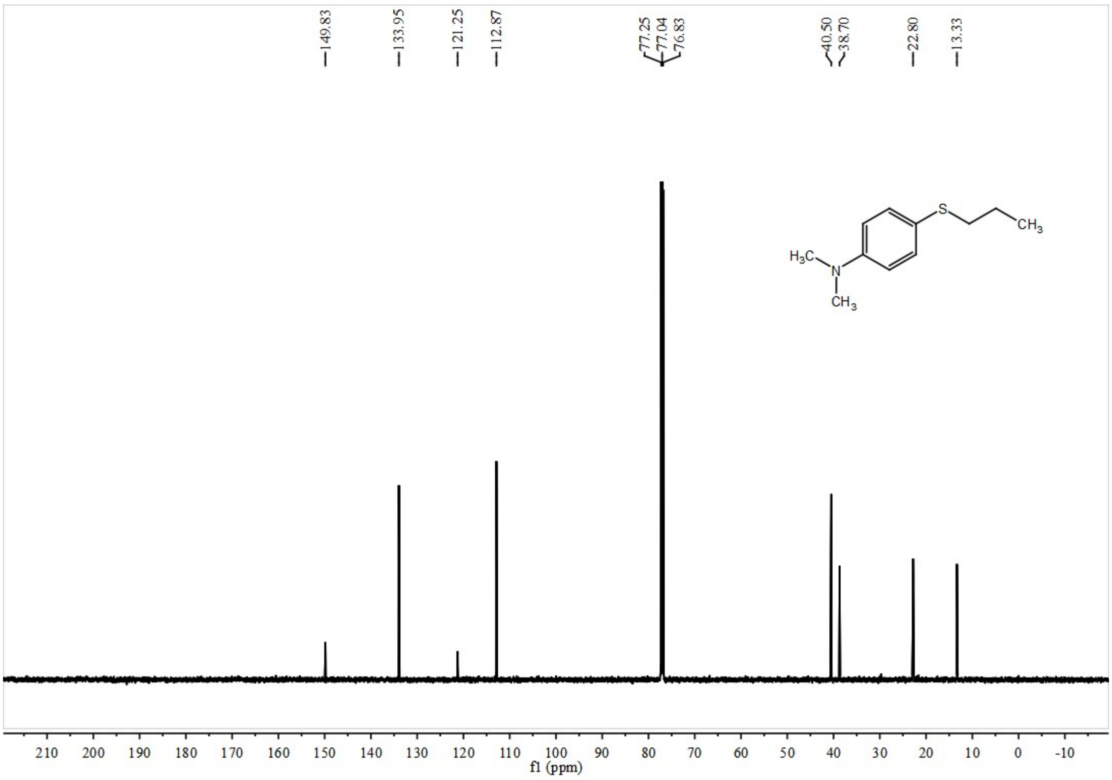

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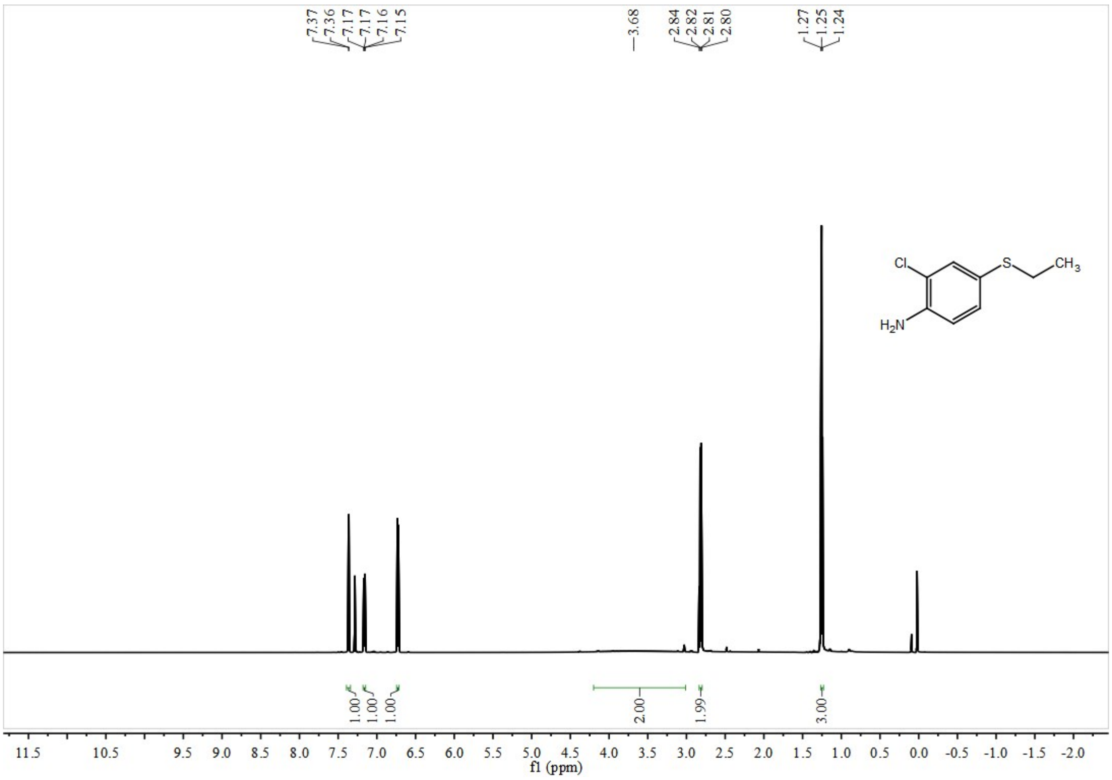

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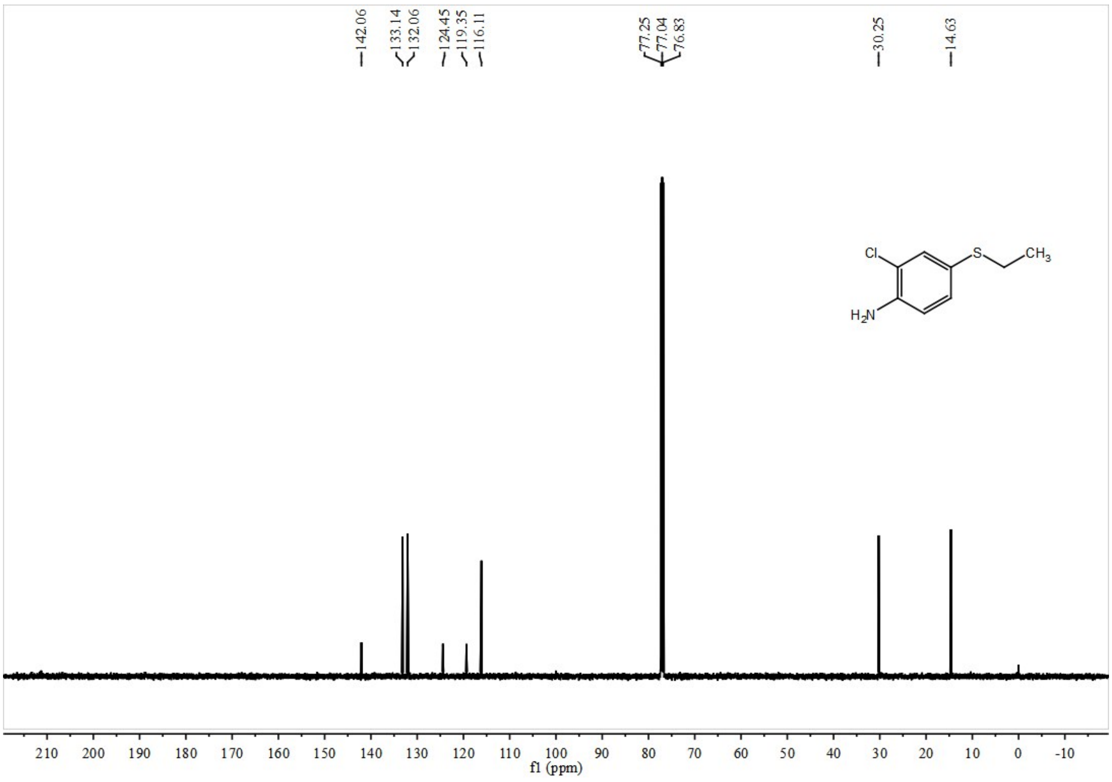
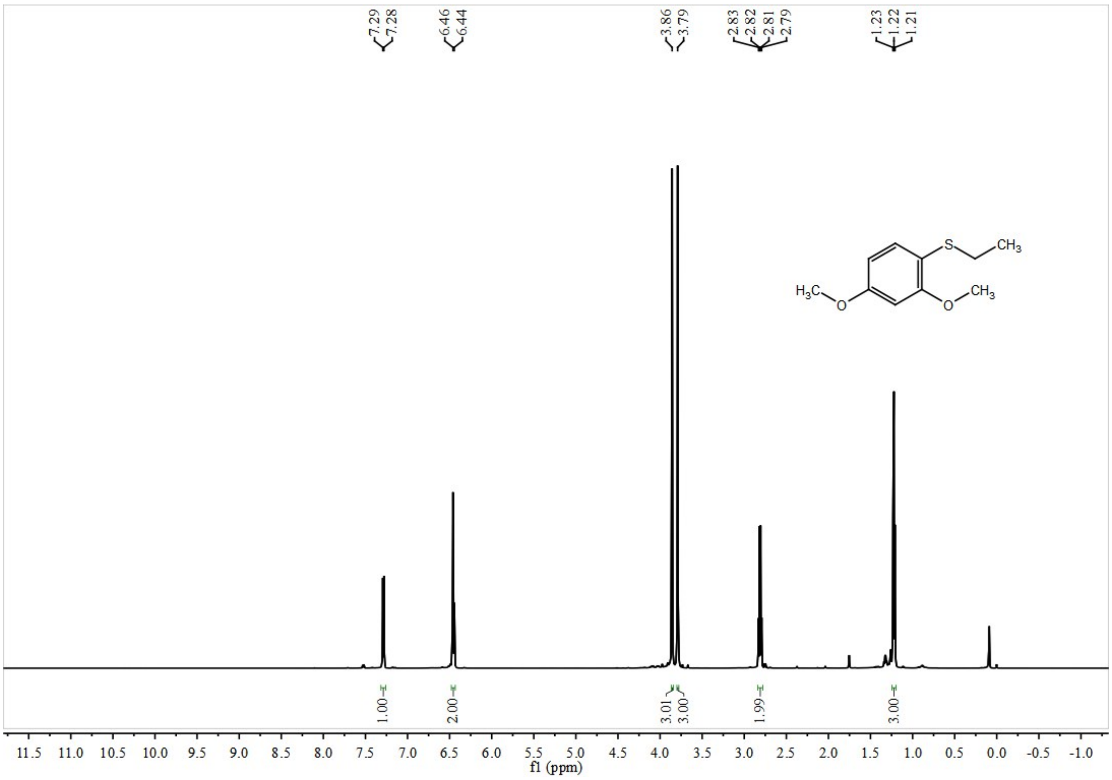
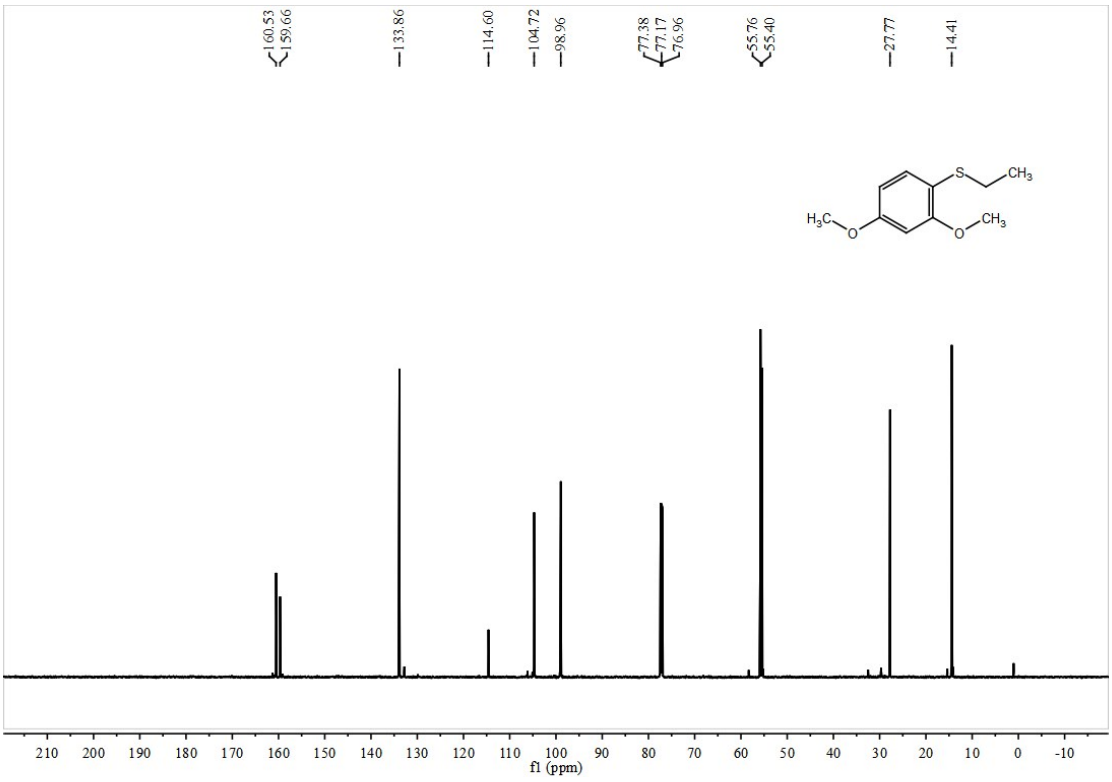


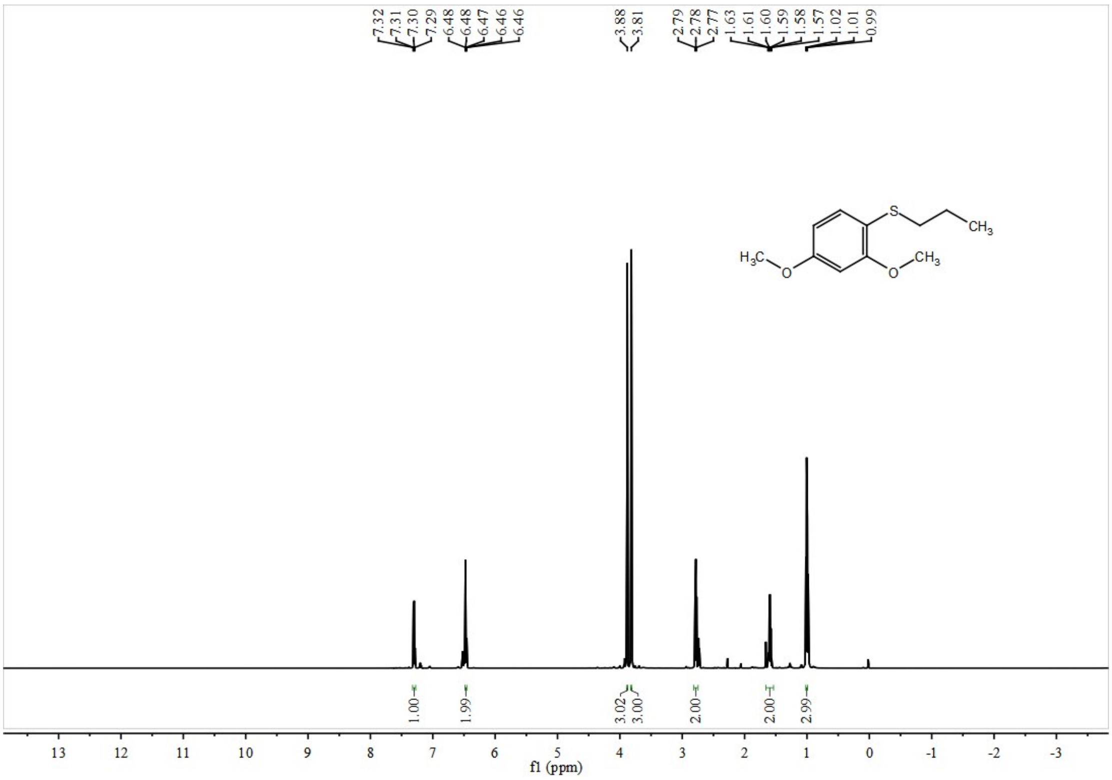
^{1}H NMR **3bd**



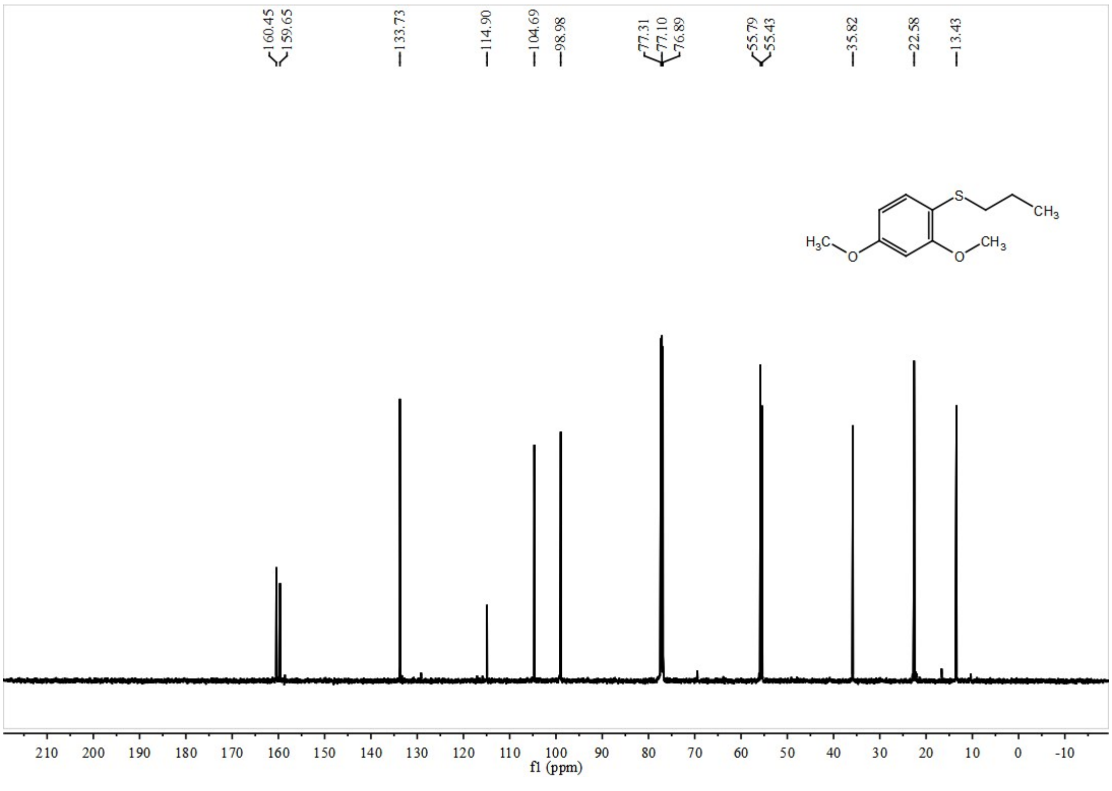
^{13}C NMR



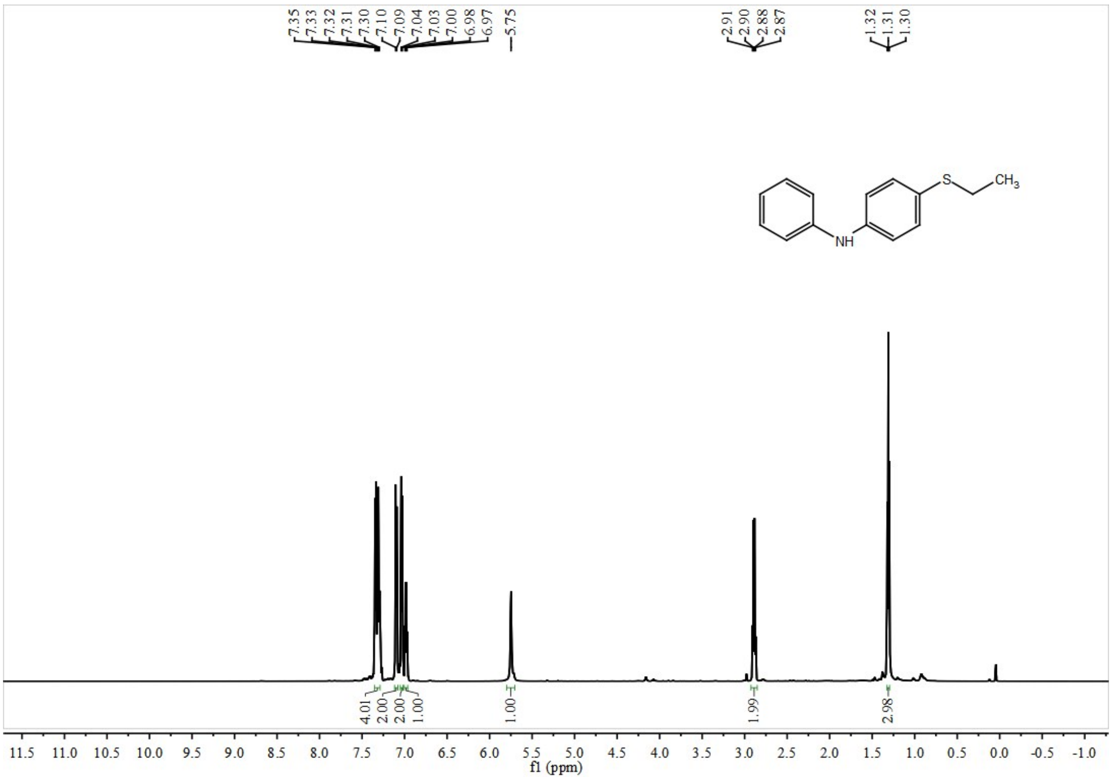
^{1}H NMR **3be**



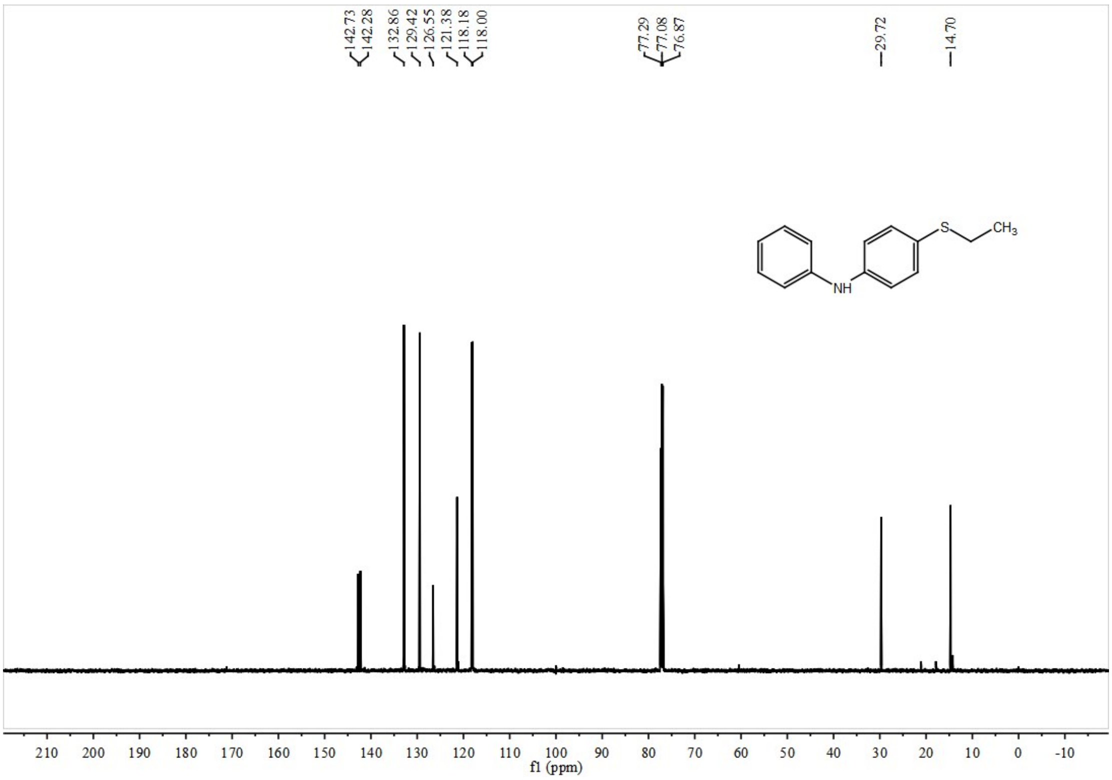
^{13}C NMR



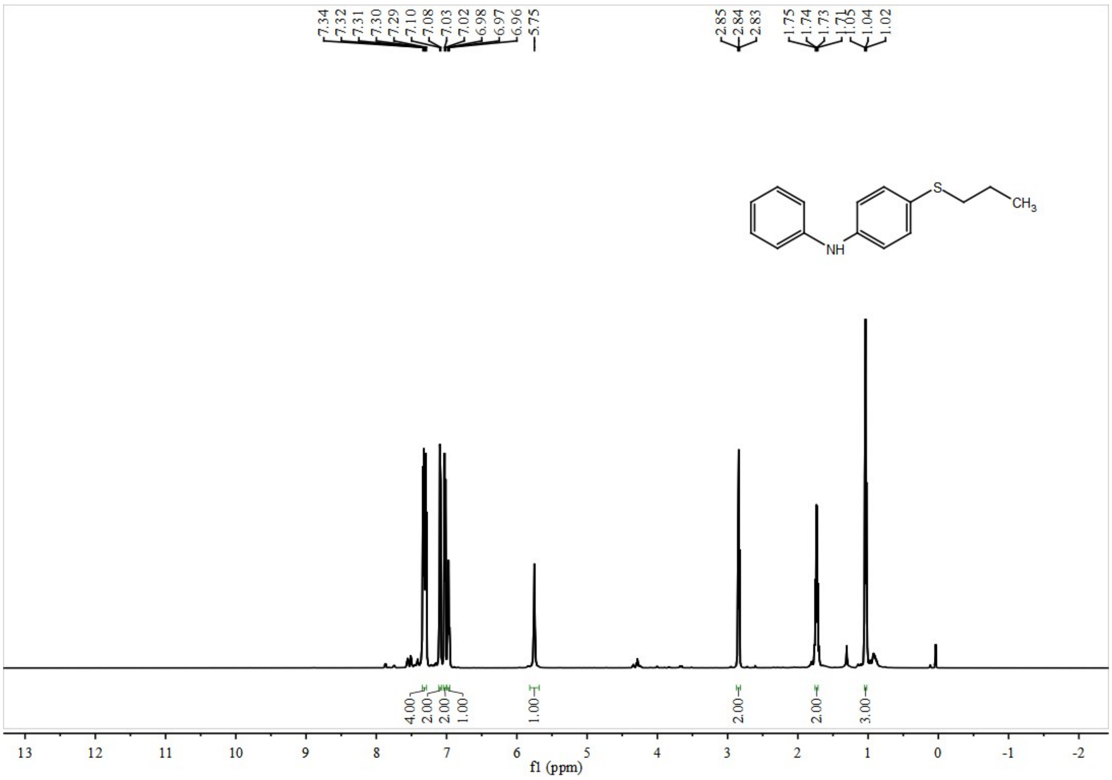
^{1}H NMR **3bf**



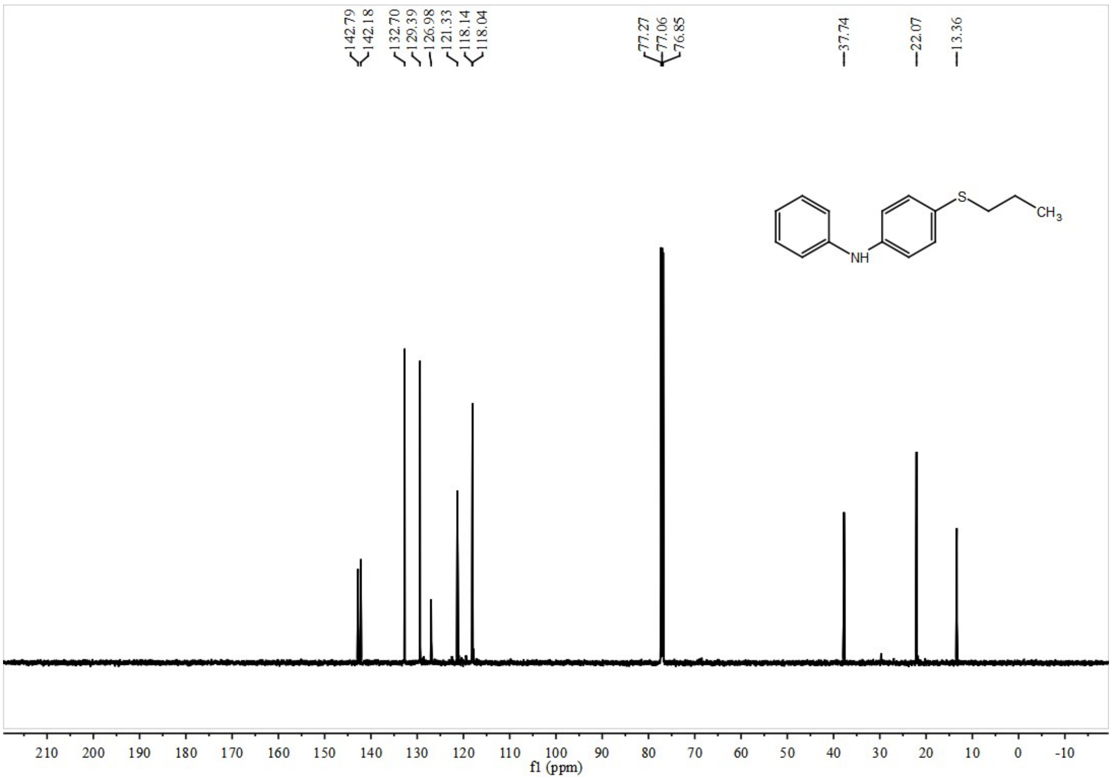
^{13}C NMR



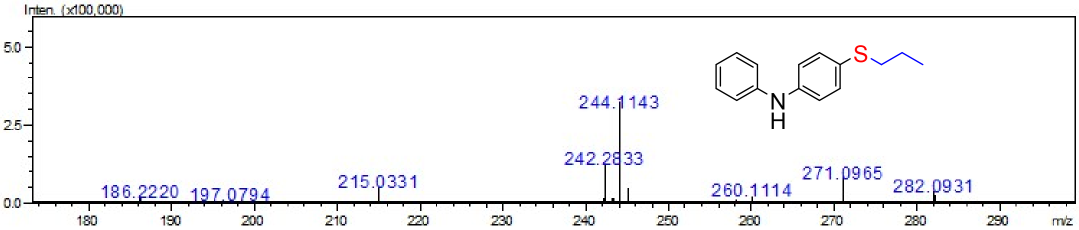
^{1}H NMR **3bg**



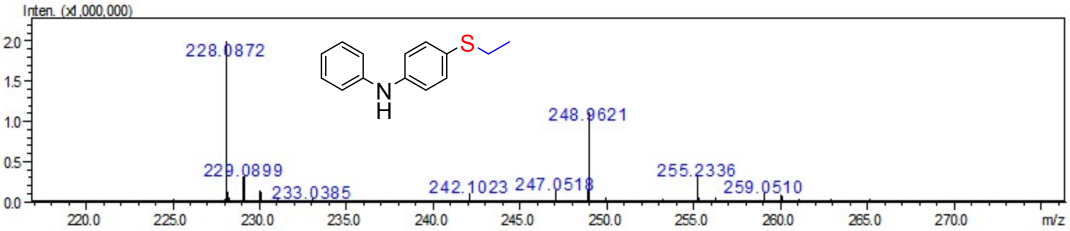
^{13}C NMR



10. Copies of HRMS spectra



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Diff (mDa)	Diff (ppm)	Iso Score	DBE
1	60.24	C15 H17 N S	[M+H]+	244.1143	244.1154	-1.1	-4.51	66.03	8.0



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Diff (mDa)	Diff (ppm)	Iso Score	DBE
1	42.87	C14 H15 N S	[M-H]-	228.0872	228.0852	2.0	8.77	81.96	8.0