Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Selectfluor-promoted oxidative reaction of disulfides and amines: access to sulfinamides

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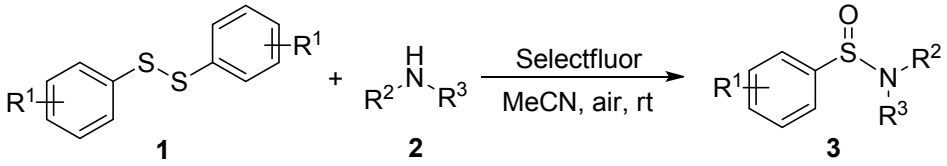
1. General information

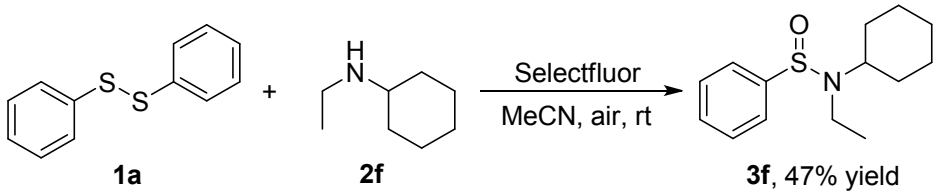
All the commercial reagents including solvents were used directly without further purification. All the experiments were monitored by thin layer chromatography (TLC) with UV light. The TLC employed 0.25 mm silica gel coated on glass plates. Column chromatography was performed with silica gel 60 (300-400 mesh). NMR spectra were recorded on Bruker 600MHz and 400MHz spectrometers. High resolution mass spectra (HRMS) were measured on Agilent 6210 ESI/TOF MS instrument.

2. Typical procedure of the reaction of disulfides and amines



Into a 10 mL vial were taken disulfide **1** (0.2 mmol), Selectfluor (4 equiv) and acetonitrile (3 mL). The mixture was stirred at room temperature for 5 minutes. Then, amine **2** (10 equiv) dissolved in acetonitrile (2 mL) was added dropwise within 30 minutes. After stirred for another 15 minutes, the mixture was concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc (4:1, v/v) as eluent to afford the desired product **3**.

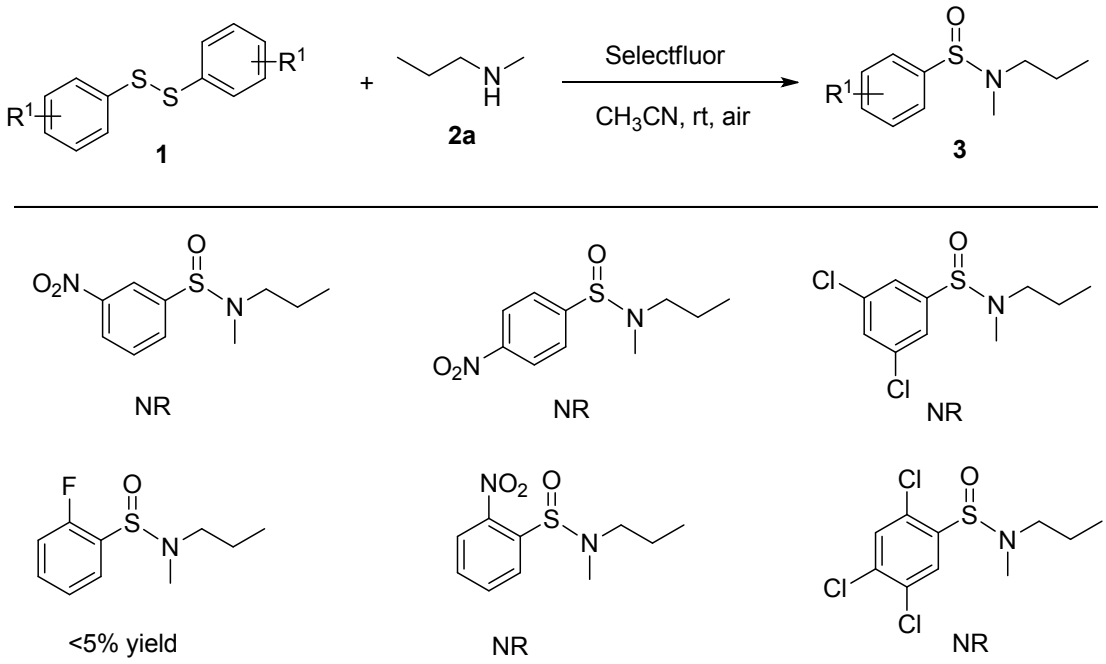
3. Procedure for the large-scale synthesis



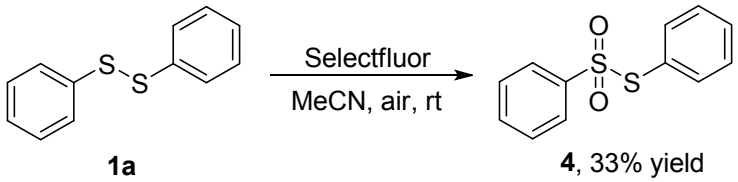
Into a 250 mL vial were taken disulfide **1a** (4 mmol), Selectfluor (4 equiv) and acetonitrile (50

mL). The mixture was stirred at room temperature for 5 minutes. Then, amine **2f** (10 equiv) dissolved in acetonitrile (25 mL) was added dropwise within 40 minutes. After stirred for another 20 minutes, the mixture was concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc (4:1, v/v) as eluent to afford the desired product **3f**.

4. Disulfides tried in this reaction with negative results (Scheme S1)

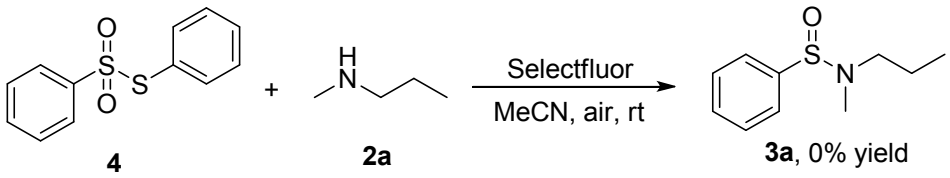


5. Control experiments



Into a 25 mL vial were taken disulfide **1a** (1 mmol), Selectfluor (4 equiv) and acetonitrile (15 mL). The mixture was stirred at room temperature for 30 minutes. Then, the reaction was diluted with

H_2O (30 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc (4:1, v/v) as eluent to afford the compound **4**.



4 **2a** **3a**, 0% yield

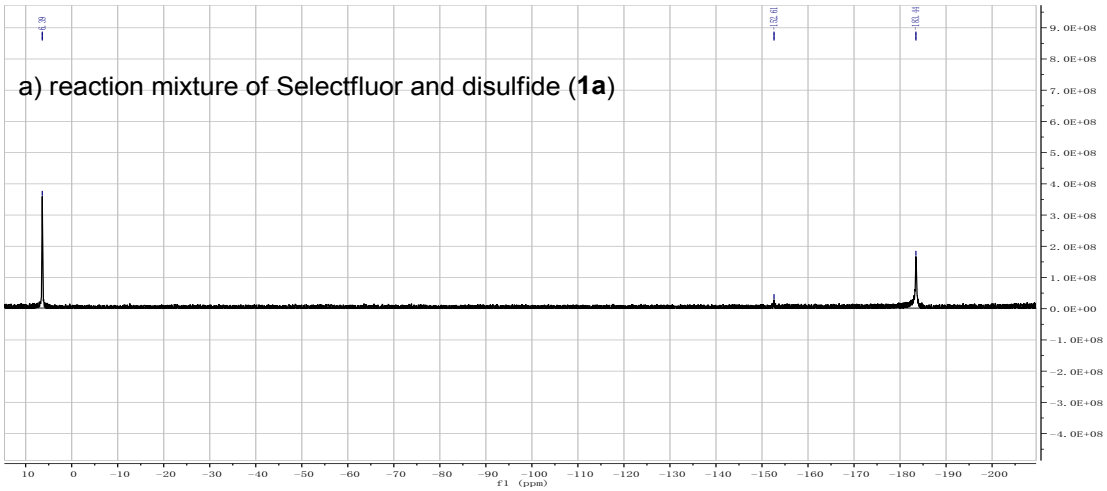
Into a 10 mL vial were taken compound **4** (0.2 mmol), Selectfluor (4 equiv) and acetonitrile (3 mL). The mixture was stirred at room temperature for 5 minutes. Then, amine **2a** (10 equiv) dissolved in acetonitrile (2 mL) was added dropwise within 30 minutes. The reaction was monitored by thin layer chromatography.

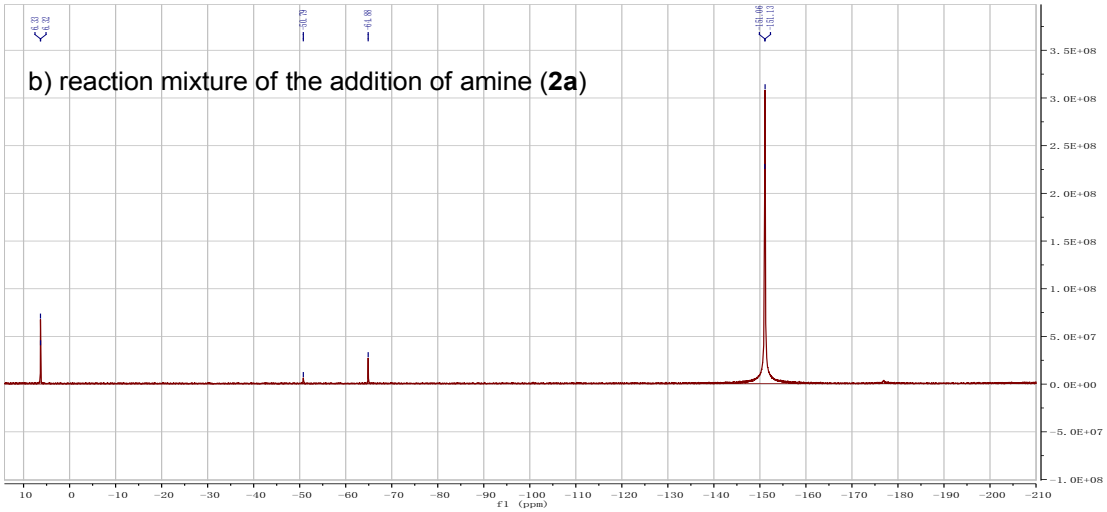
6. ^{19}F NMR detection of the process (Figure S1)

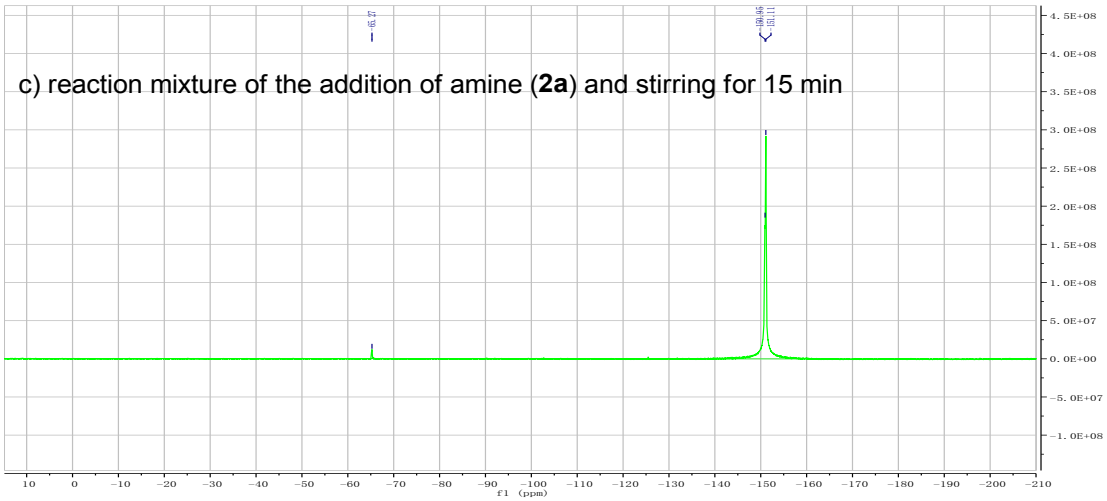
a) Into a 10 mL vial were taken disulfide **1a** (0.2 mmol), Selectfluor (4 equiv) and acetonitrile (3 mL). The mixture was stirred at room temperature for 5 minutes.

b) After addition of amine **2a** (5 equiv) dissolved in acetonitrile (1 mL).

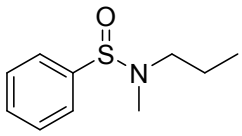
c) After addition of another amine **2a** (5 equiv) dissolved in acetonitrile (1 mL) was added. Then, stirred for another 15 minutes.



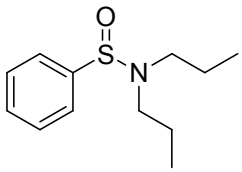




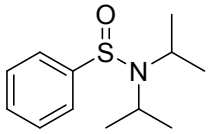
7. Characterization of product 3



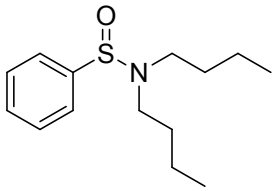
Compound **3a**: colorless oil, 75% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67-7.65 (m, 2H), 7.52-7.48 (m, 3H), 3.19-3.14 (m, 1H), 3.07-3.02 (m, 1H), 3.27 (s, 3H), 1.67-1.59 (m, 2H), 0.94 (t, *J* = 7.35 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.0, 130.7, 128.8, 126.2, 54.3, 32.3, 21.4, 11.3. HRMS (ESI): calculated for $C_{10}H_{15}NNaOS^+$ $[M+Na]^+$ 220.0767, found 220.0769.



Compound **3b**: colorless oil, 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67-7.65 (m, 2H), 7.50-7.44 (m, 3H), 3.03-2.95 (m, 4H), 1.61-1.55 (m, 2H), 1.50-1.44 (m, 2H), 0.82 (t, *J* = 7.38 Hz, 6H). HRMS (ESI): calculated for $C_{12}H_{19}NNaOS^+$ $[M+Na]^+$ 248.1080, found 248.1083.

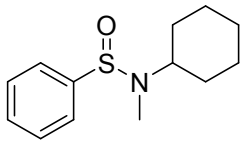


Compound **3c**: colorless oil, 40% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67-7.65 (m, 2H), 7.50-7.47 (m, 2H), 7.45-7.43 (m, 1H), 3.60-3.53 (m, 2H), 1.42 (d, *J* = 6.72 Hz, 6H), 1.13 (d, *J* = 6.84 Hz, 6H). HRMS (ESI): calculated for $C_{12}H_{19}NNaOS^+$ $[M+Na]^+$ 248.1080, found 248.1084.

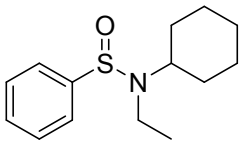


Compound **3d**: colorless oil, 47% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67-7.66 (m, 2H), 7.51-7.45 (m, 3H), 3.05 (t, *J* = 7.59 Hz, 4H), 1.58-1.51 (m, 2H), 1.47-1.39 (m, 2H), 1.29-1.19 (m,

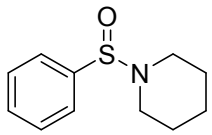
4H), 0.85 (t, J = 7.41 Hz, 6H). HRMS (ESI): calculated for $C_{14}H_{23}NNaOS^+$ $[M+Na]^+$ 276.1393, found 276.1397.



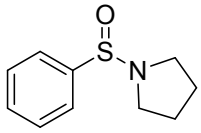
Compound **3e**: colorless oil, 67% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63-7.62 (m, 2H), 7.49-7.43 (m, 3H), 3.29-3.23 (m, 1H), 2.40 (s, 3H), 2.04-2.00 (m, 1H), 1.97-1.94 (m, 1H), 1.87-1.80 (m, 2H), 1.66-1.63 (m, 1H), 1.62-1.50 (m, 2H), 1.37-1.27 (m, 2H), 1.16-1.08 (m, 1H). HRMS (ESI): calculated for $C_{13}H_{19}NNaOS^+$ $[M+Na]^+$ 260.1080, found 260.1082.



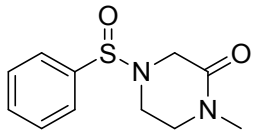
Compound **3f**: colorless oil, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65-7.64 (m, 2H), 7.47-7.42 (m, 3H), 3.12-3.07 (m, 2H), 2.92-2.86 (m, 1H), 2.15-2.11 (m, 1H), 1.84-1.78 (m, 3H), 1.66-1.57 (m, 3H), 1.29-1.22 (m, 2H), 1.16-1.09 (m, 1H), 0.89 (t, J = 7.14 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.7, 130.3, 128.5, 126.4, 59.8, 37.9, 33.7, 33.2, 26.3, 26.2, 25.6, 15.8. HRMS (ESI): calculated for $C_{14}H_{21}NNaOS^+$ $[M+Na]^+$ 274.1236, found 274.1239.



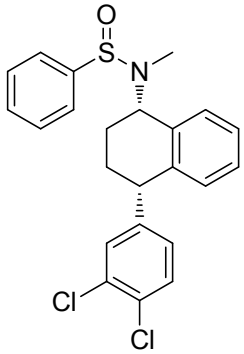
Compound **3g**: white solid, 58% yield, mp 78-79 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67-7.66 (m, 2H), 7.51-7.47 (m, 3H), 3.14-3.10 (m, 2H), 2.98-2.94 (m, 2H), 1.66-1.57 (m, 4H), 1.55-1.51 (m, 2H). HRMS (ESI): calculated for $C_{11}H_{15}NNaOS^+$ $[M+Na]^+$ 232.0767, found 232.0770.



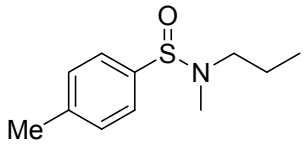
Compound **3h**: colorless oil, 37% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69-7.67 (m, 2H), 7.50-7.45 (m, 3H), 3.37-3.33 (m, 2H), 3.03-2.99 (m, 2H), 1.87-1.84 (m, 4H). HRMS (ESI): calculated for $C_{10}H_{13}NNaOS^+$ $[M+Na]^+$ 218.0610, found 218.0614.



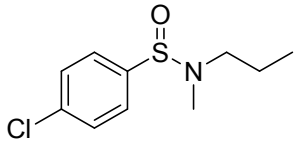
Compound **3i**: colorless oil, 49% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65-7.63 (m, 2H), 7.52-7.50 (m, 3H), 3.76 (d, *J* = 16.8 Hz, 1H), 3.52-3.45 (m, 2H), 3.38-3.32 (m, 3H), 2.95 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.3, 141.7, 131.5, 129.1, 125.9, 48.9, 46.6, 44.7, 34.2. HRMS (ESI): calculated for $C_{11}H_{14}N_2NaO_2S^+$ $[M+Na]^+$ 261.0668, found 261.0670.



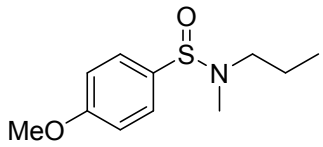
Compound **3j**: colorless oil, 48% yield (dr = 3:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80-7.78 (m, 0.8H), 7.73-7.72 (m, 1.8H), 7.69-7.67 (m, 0.4H), 7.58-7.47 (m, 3H), 7.36-7.32 (m, 2H), 7.24-7.20 (m, 1H), 7.14-7.13 (m, 0.6H), 7.09-7.08 (m, 0.4H), 6.97-6.94 (m, 1H), 6.87-6.85 (m, 0.6H), 6.84-6.82 (m, 0.4H), 4.91-4.88 (m, 0.4H), 4.85-4.83 (m, 0.6H), 4.18-4.12 (m, 1H), 2.42 (s, 1.8H), 2.39 (m, 1.2H), 2.31-2.21 (m, 1H), 2.16-2.07 (m, 1H), 2.04-1.89 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.9, 146.8, 144.2, 144.1, 138.6, 138.5, 136.1, 135.8, 132.3, 132.2, 130.9, 130.8, 130.73, 130.70, 130.6, 130.5, 130.2, 130.1, 129.1, 129.0, 128.9, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6, 127.4, 126.2, 126.1, 61.9, 61.7, 60.4, 43.4, 43.2, 29.9, 29.8, 28.0, 27.1, 24.3, 23.4, 14.2. HRMS (ESI): calculated for $C_{23}H_{21}Cl_2NNaOS^+$ $[M+Na]^+$ 452.0613, found 452.0615.



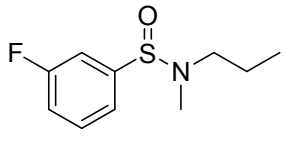
Compound **3k**: colorless oil, 74% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.53-7.51 (m, 2H), 7.30-7.28 (m, 2H), 3.15-3.11 (m, 1H), 3.04-2.99 (m, 1H), 2.50 (s, 3H), 2.40 (s, 3H), 1.66-1.56 (m, 2H), 0.92 (t, *J* = 7.38 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.0, 140.9, 129.4, 126.1, 54.1, 32.2, 21.4, 21.3, 11.3. HRMS (ESI): calculated for $C_{11}H_{17}NNaOS^+$ $[M+Na]^+$ 234.0923, found 234.0925.



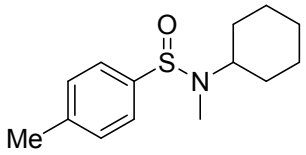
Compound **3l**: colorless oil, 53% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60-7.57 (m, 2H), 7.48-7.46 (m, 2H), 3.16-3.12 (m, 1H), 3.05-3.00 (m, 1H), 2.52 (s, 3H), 1.67-1.57 (m, 2H), 0.93 (t, *J* = 7.38 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.6, 137.0, 129.0, 127.6, 54.3, 32.3, 21.4, 11.3. HRMS (ESI): calculated for $C_{10}H_{14}ClNNaOS^+$ $[M+Na]^+$ 254.0377, found 254.0381.



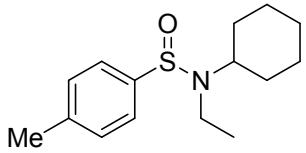
Compound **3m**: colorless oil, 41% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57-7.54 (m, 2H), 7.01-6.98 (m, 2H), 3.85 (s, 3H), 3.14-3.09 (m, 1H), 3.03-2.98 (m, 1H), 2.50 (s, 3H), 1.65-1.56 (m, 2H), 0.92 (t, *J* = 7.38 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.6, 135.3, 127.7, 114.2, 55.5, 53.9, 32.1, 21.4, 11.3. HRMS (ESI): calculated for $C_{11}H_{18}NO_2S^+$ $[M+H]^+$ 228.1053, found 228.1056.



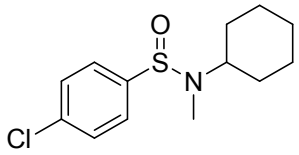
Compound **3n**: colorless oil, 41% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49-7.46 (m, 1H), 7.44-7.42 (m, 1H), 7.39-7.37 (m, 1H), 7.18-7.14 (m, 1H), 3.18-3.13 (m, 1H), 3.06-3.01 (m, 1H), 2.53 (s, 3H), 1.67-1.60 (m, 2H), 0.93 (t, *J* = 7.38 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.7 (d, *J* = 249.3 Hz), 146.8 (d, *J* = 5.8 Hz), 130.4 (d, *J* = 7.7 Hz), 121.9 (d, *J* = 3.4 Hz), 117.9 (d, *J* = 21.4 Hz), 113.5 (d, *J* = 23.6 Hz), 54.4, 32.4, 21.4, 11.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -110.9. HRMS (ESI): calculated for $C_{10}H_{14}FNNaOS^+$ $[M+Na]^+$ 238.0672, found 238.0675.



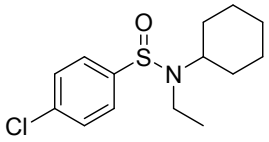
Compound **3o**: colorless oil, 45% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.28 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.28-3.23 (m, 1H), 2.40 (s, 6H), 2.03-2.00 (m, 1H), 1.97-1.94 (m, 1H), 1.87-1.80 (m, 2H), 1.67-1.63 (m, 1H), 1.62-1.50 (m, 2H), 1.37-1.28 (m, 2H), 1.16-1.09 (m, 1H). HRMS (ESI): calculated for $C_{14}H_{21}NNaOS^+$ $[M+Na]^+$ 274.1236, found 274.1239.



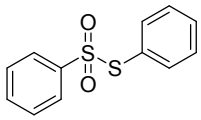
Compound **3p**: colorless oil, 79% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.16 Hz, 2H), 7.26 (d, *J* = 7.92 Hz, 2H), 3.12-3.05 (m, 2H), 2.92-2.86 (m, 1H), 2.39 (s, 3H), 2.14-2.11 (m, 1H), 1.84-1.78 (m, 3H), 1.66-1.55 (m, 3H), 1.29-1.22 (m, 2H), 1.17-1.09 (m, 1H), 0.91 (t, *J* = 7.17 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.5, 140.5, 129.3, 126.4, 59.7, 37.8, 33.7, 33.3, 26.3, 26.2, 25.6, 21.3, 15.8. HRMS (ESI): calculated for $C_{15}H_{23}NNaOS^+$ $[M+Na]^+$ 288.1393, found 288.1395.



Compound **3q**: white solid, 54% yield, mp 59-60 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57-7.55 (m, 2H), 7.46-7.44 (m, 2H), 3.27-3.22 (m, 1H), 2.40 (s, 3H), 2.02-1.99 (m, 1H), 1.95-1.92 (m, 1H), 1.87-1.80 (m, 2H), 1.67-1.63 (m, 1H), 1.61-1.49 (m, 2H), 1.36-1.27 (m, 2H), 1.16-1.08 (m, 1H). HRMS (ESI): calculated for $C_{13}H_{18}ClNNaOS^+$ $[M+Na]^+$ 294.0690, found 294.0693.



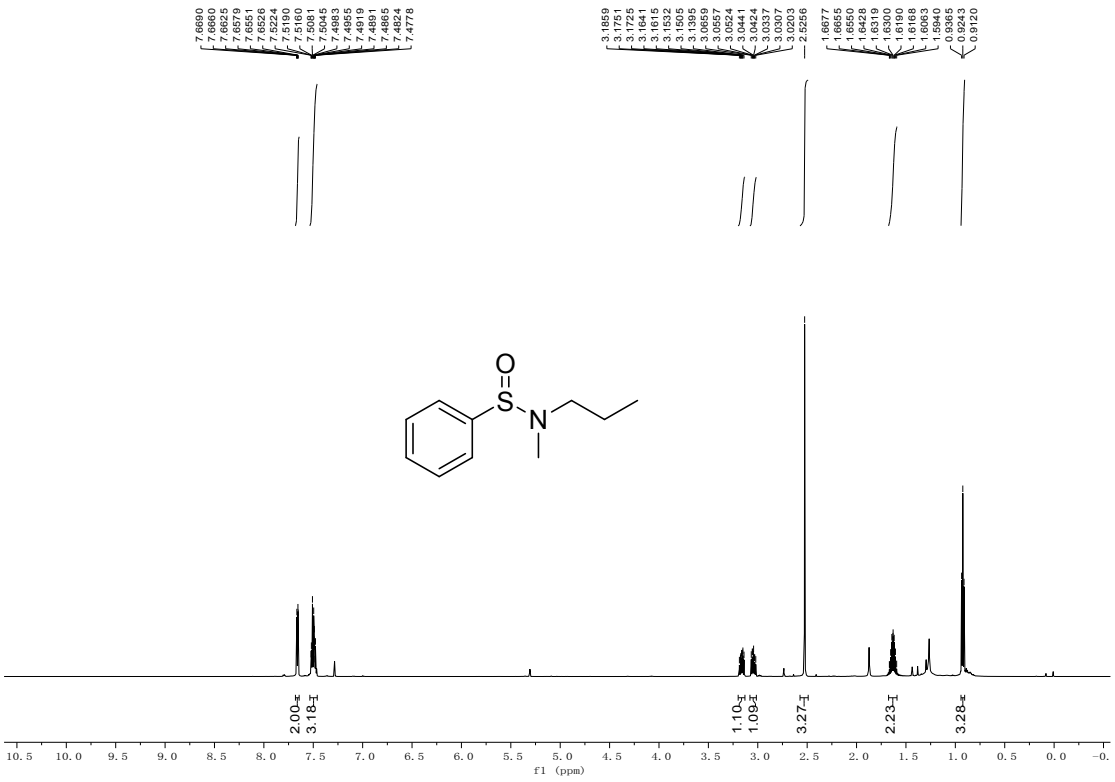
Compound **3r**: colorless oil, 47% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60-7.58 (m, 2H), 7.46-7.43 (m, 2H), 3.12-3.05 (m, 2H), 2.94-2.88 (m, 1H), 2.15-2.11 (m, 1H), 1.86-1.80 (m, 3H), 1.66-1.55 (m, 3H), 1.31-1.23 (m, 2H), 1.18-1.12 (m, 1H), 0.93 (t, *J* = 7.17 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.3, 136.6, 128.8, 127.9, 59.8, 38.0, 33.7, 33.2, 26.2, 26.1, 25.5, 15.8. HRMS (ESI): calculated for $C_{18}H_{20}ClNNaOS^+$ $[M+Na]^+$ 308.0846, found 308.0847.



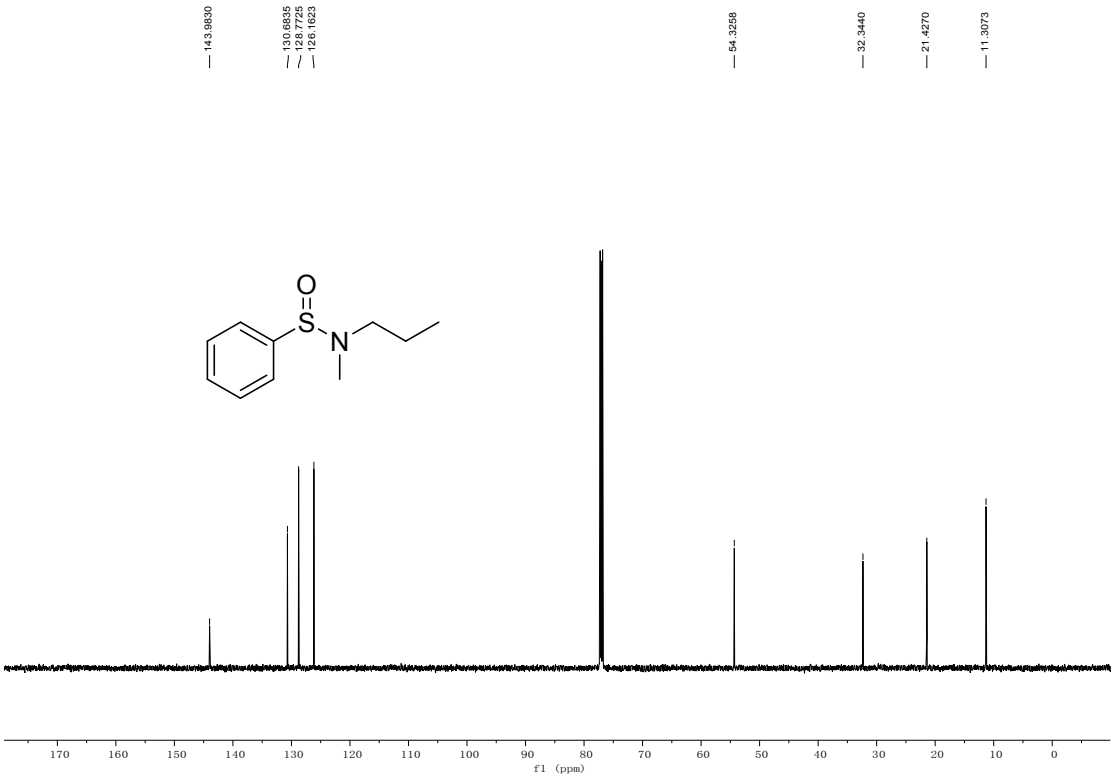
*S-phenyl benzenesulfonothioate (**4**)*: yellow oil, 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.56 (m, 3H), 7.50-7.46 (m, 1H), 7.45-7.41 (m, 2H), 7.37-7.32 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9, 136.6, 133.8, 131.5, 129.5, 128.9, 127.8, 127.6. HRMS (ESI): calculated for $C_{12}H_{11}O_2S_2^+$ $[M+H]^+$ 251.0195, found 251.0196.

8. ^{1}H, ^{13}C and ^{19}F NMR spectra

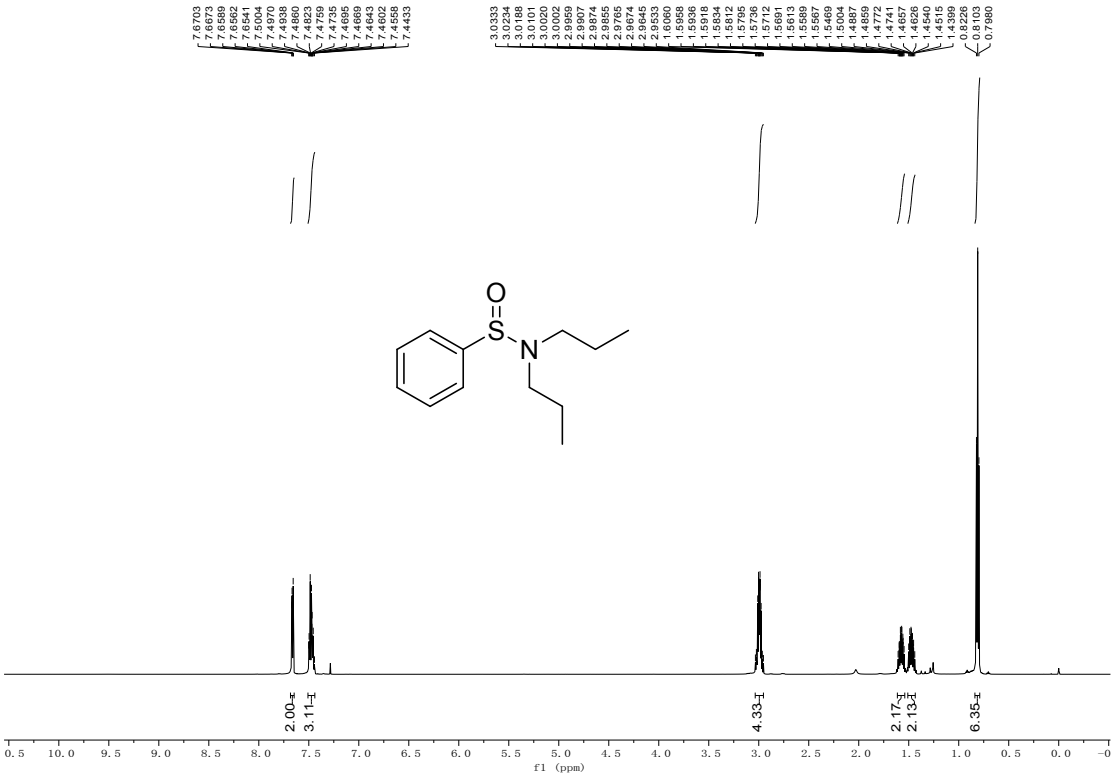
^{1}H NMR (600 MHz, $CDCl_3$) of **3a**:



^{13}C NMR (150 MHz, $CDCl_3$) of **3a**:

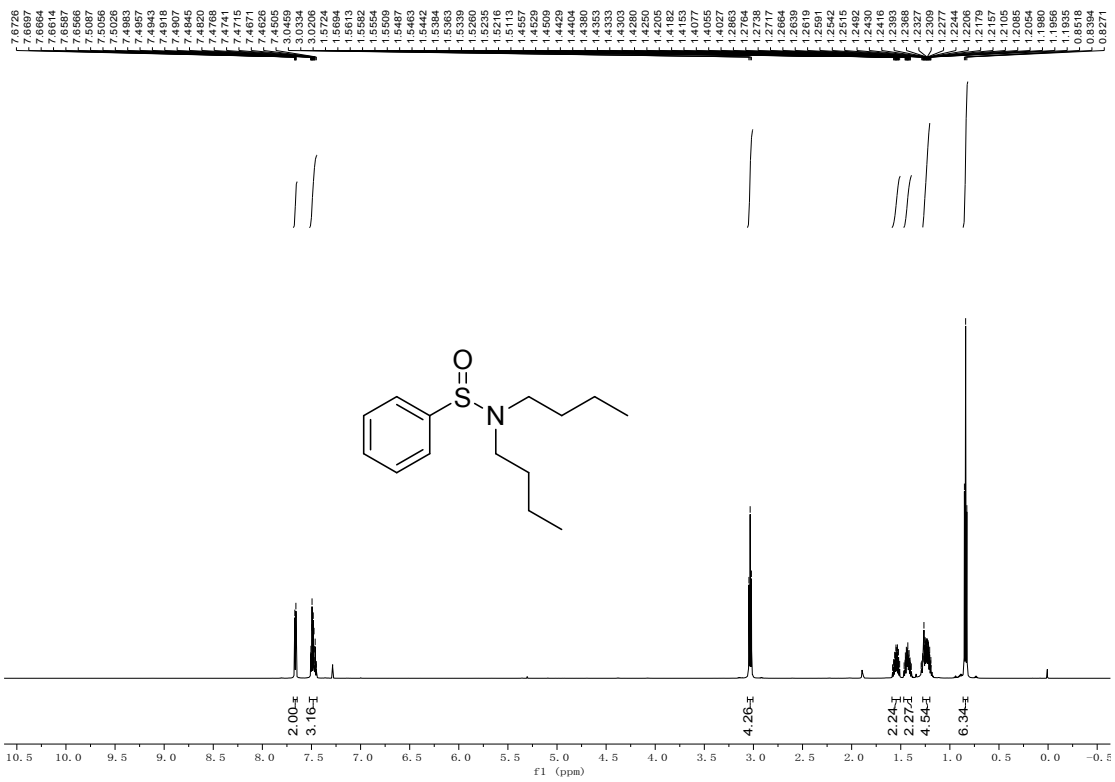


^{1}H NMR (600 MHz, $CDCl_3$) of **3b**:

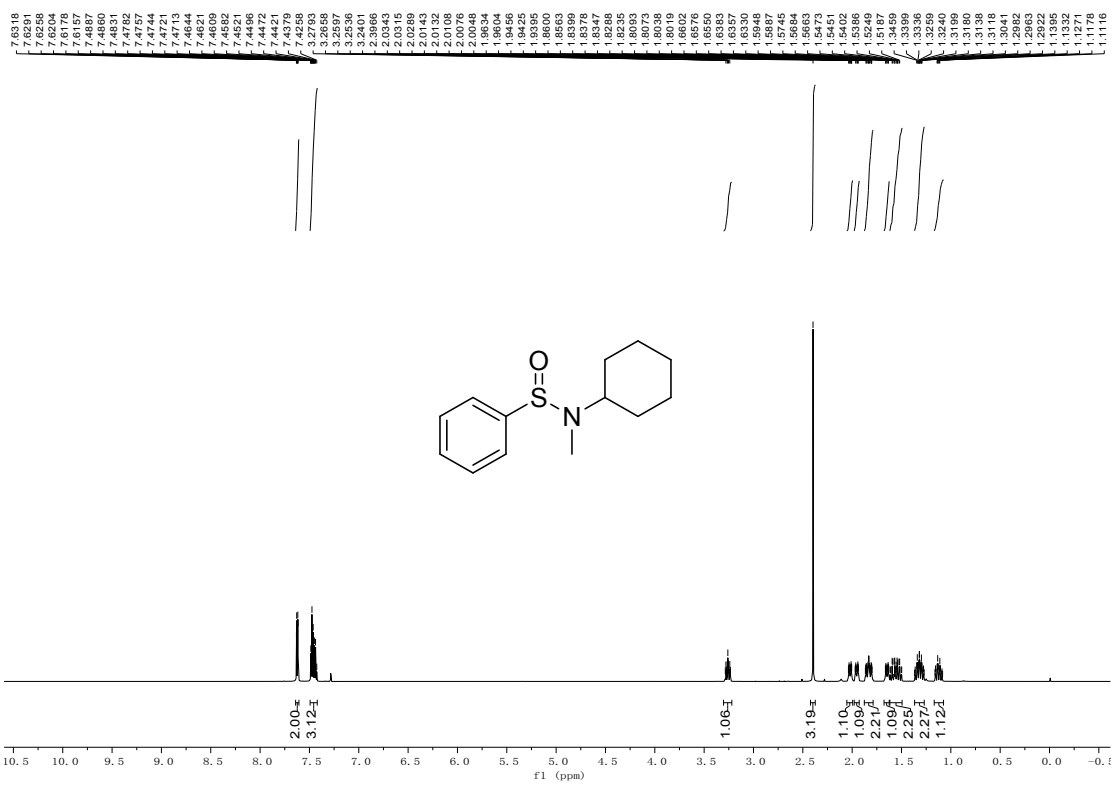


^{1}H NMR (600 MHz, $CDCl_3$) of **3c**:

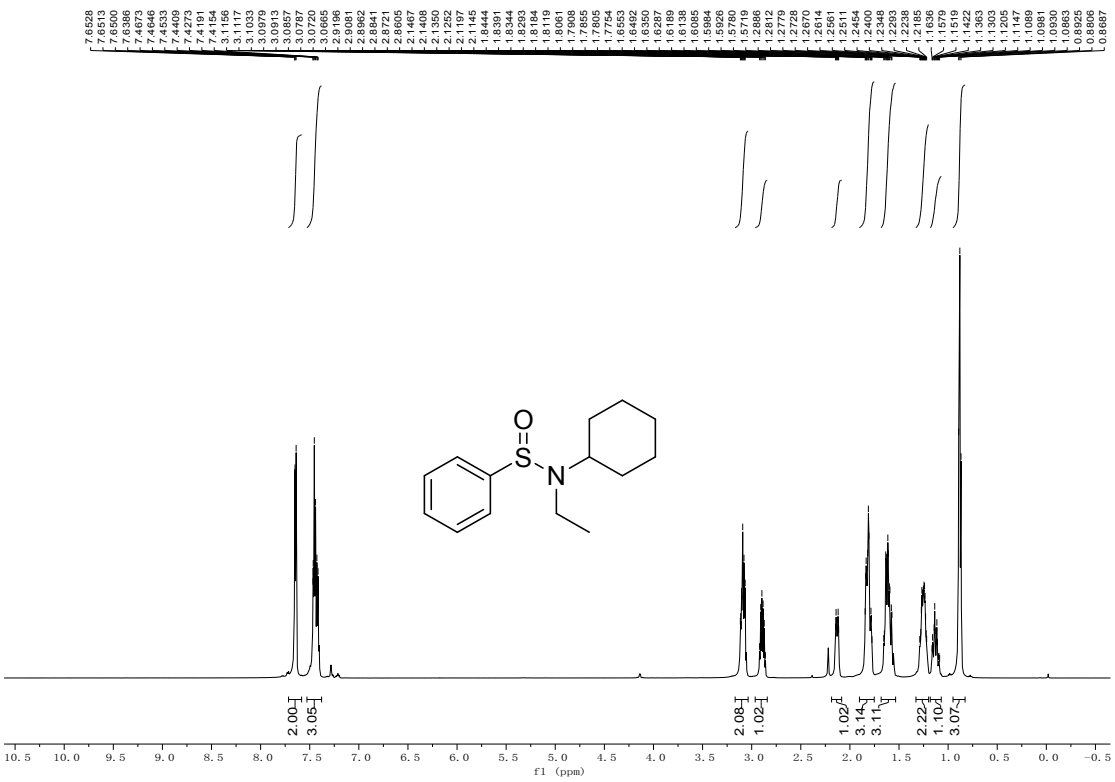
^{1}H NMR (600 MHz, $CDCl_3$) of **3d**:



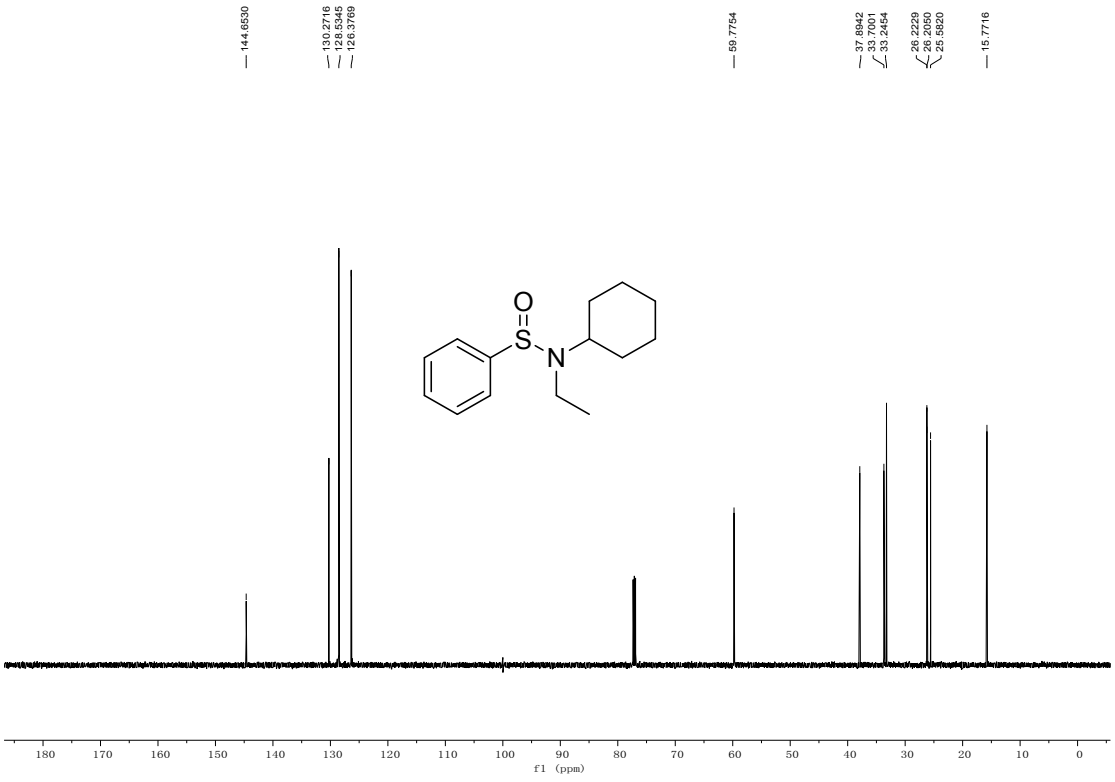
^{1}H NMR (600 MHz, $CDCl_3$) of **3e**:



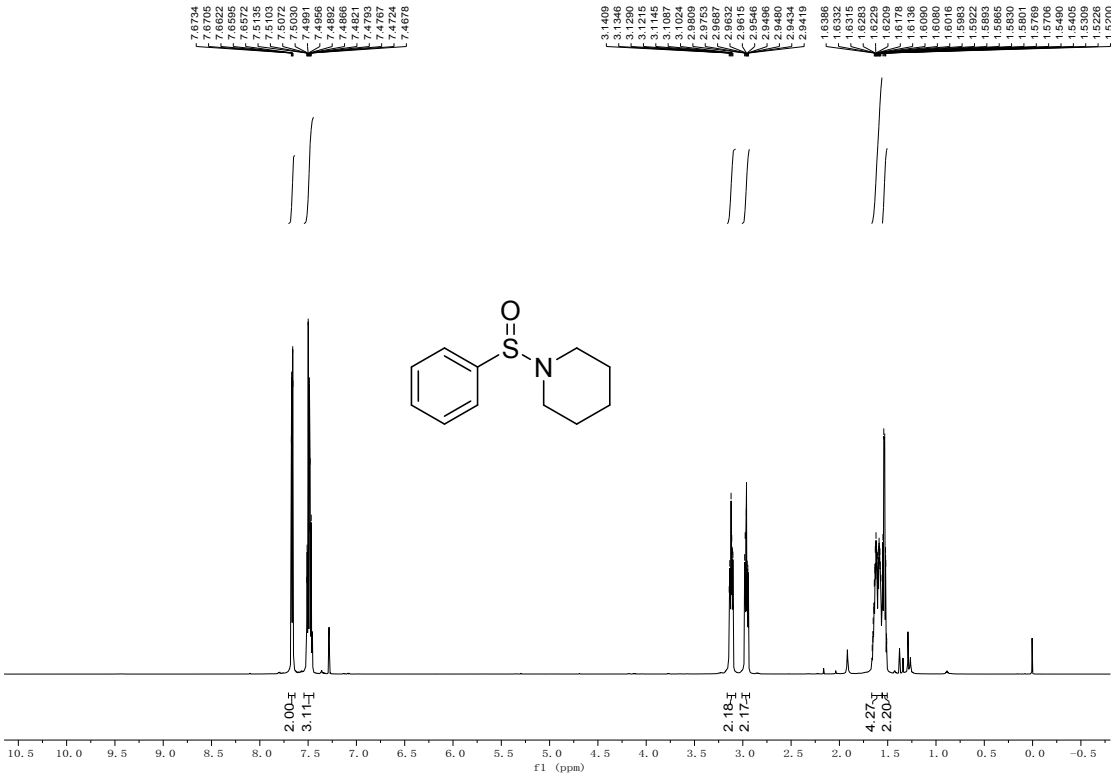
^{1}H NMR (600 MHz, $CDCl_3$) of **3f**:



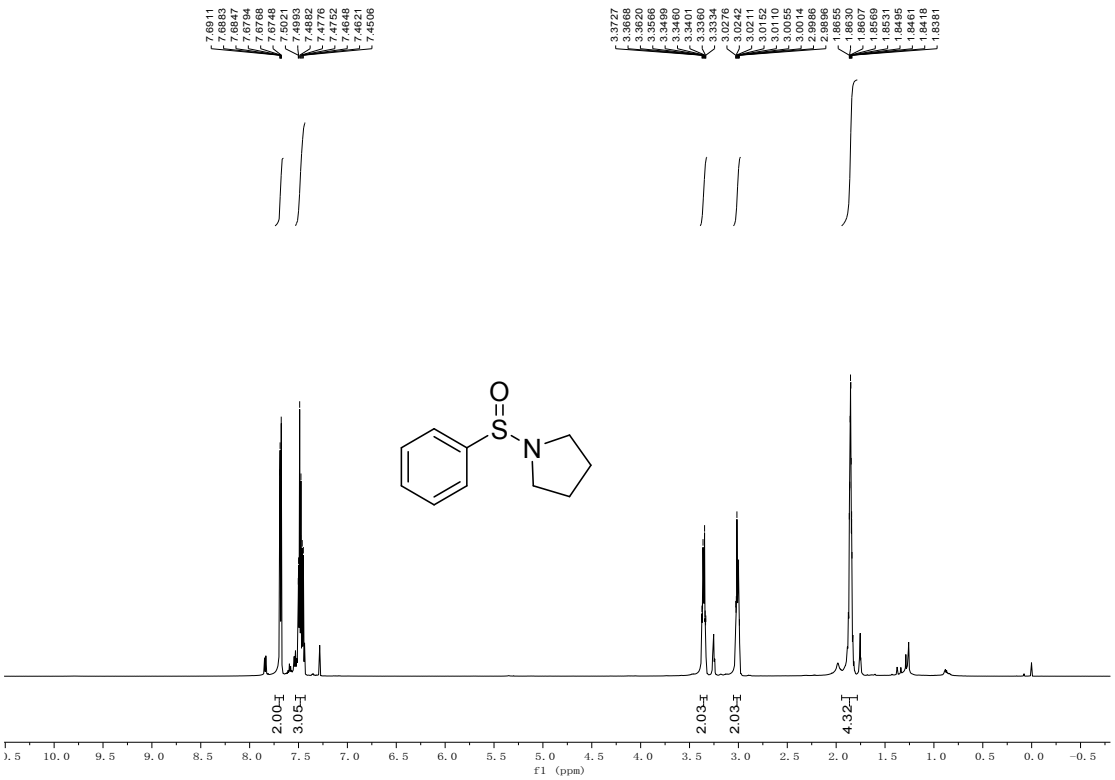
^{13}C NMR (150 MHz, $CDCl_3$) of **3f**:



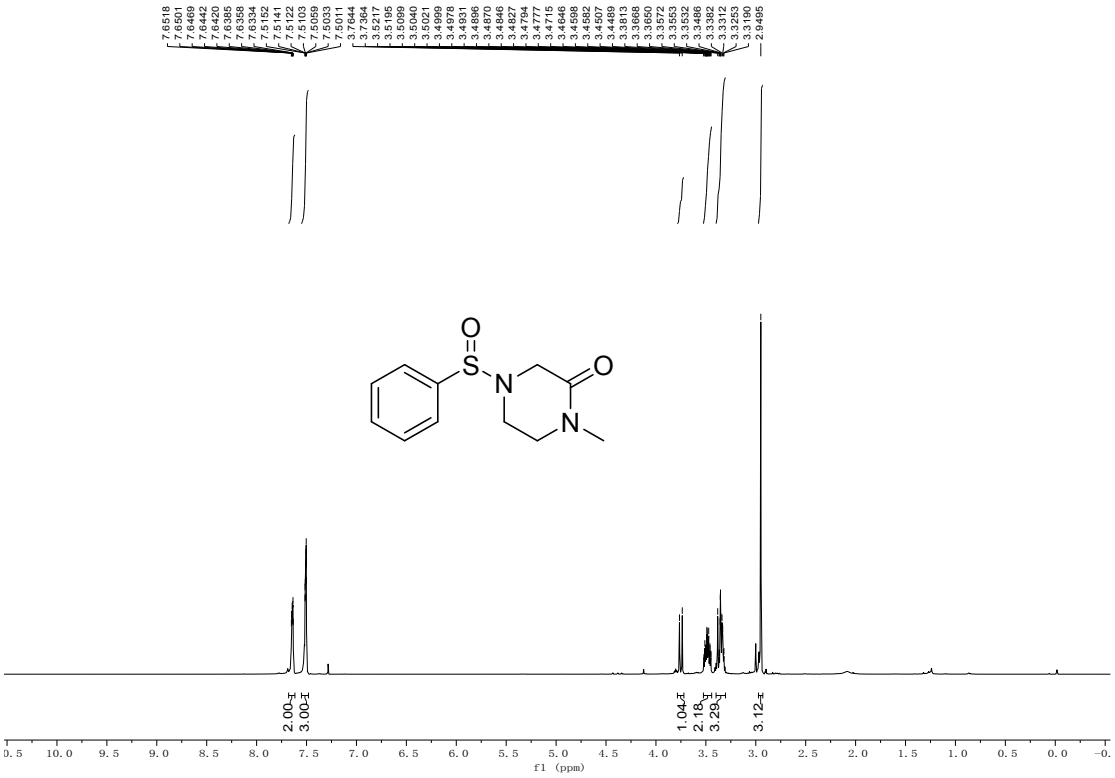
^{1}H NMR (600 MHz, $CDCl_3$) of **3g**:



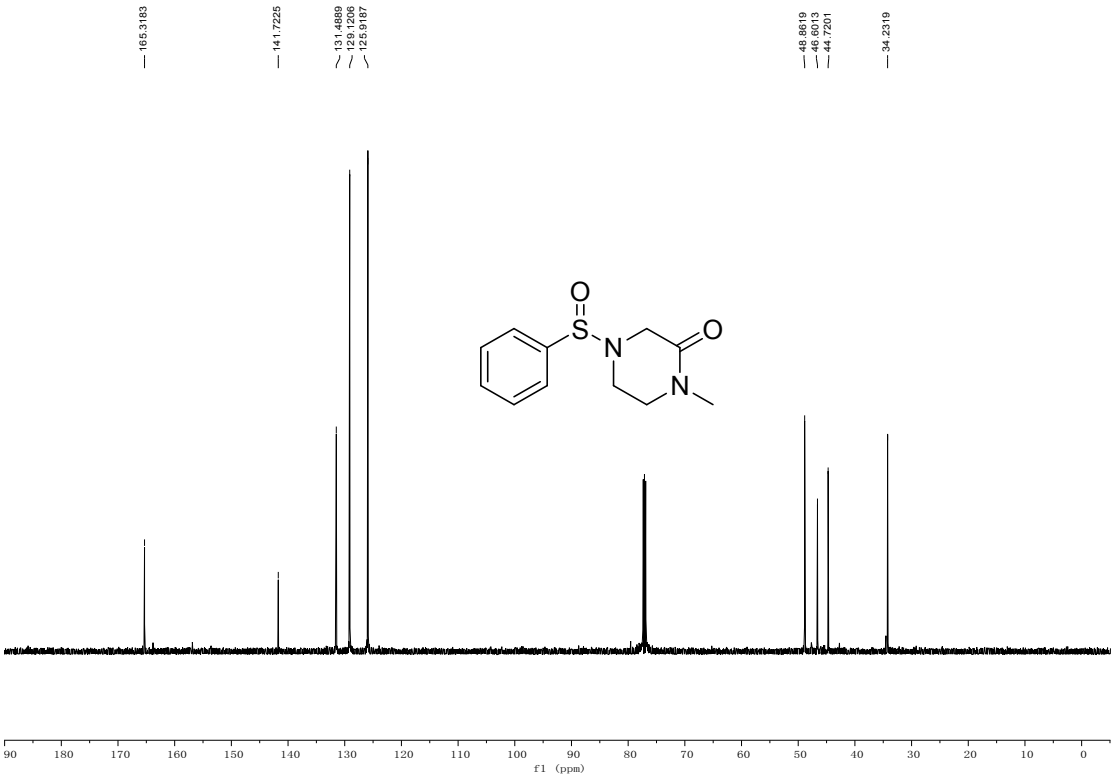
^{1}H NMR (600 MHz, $CDCl_3$) of **3h**:



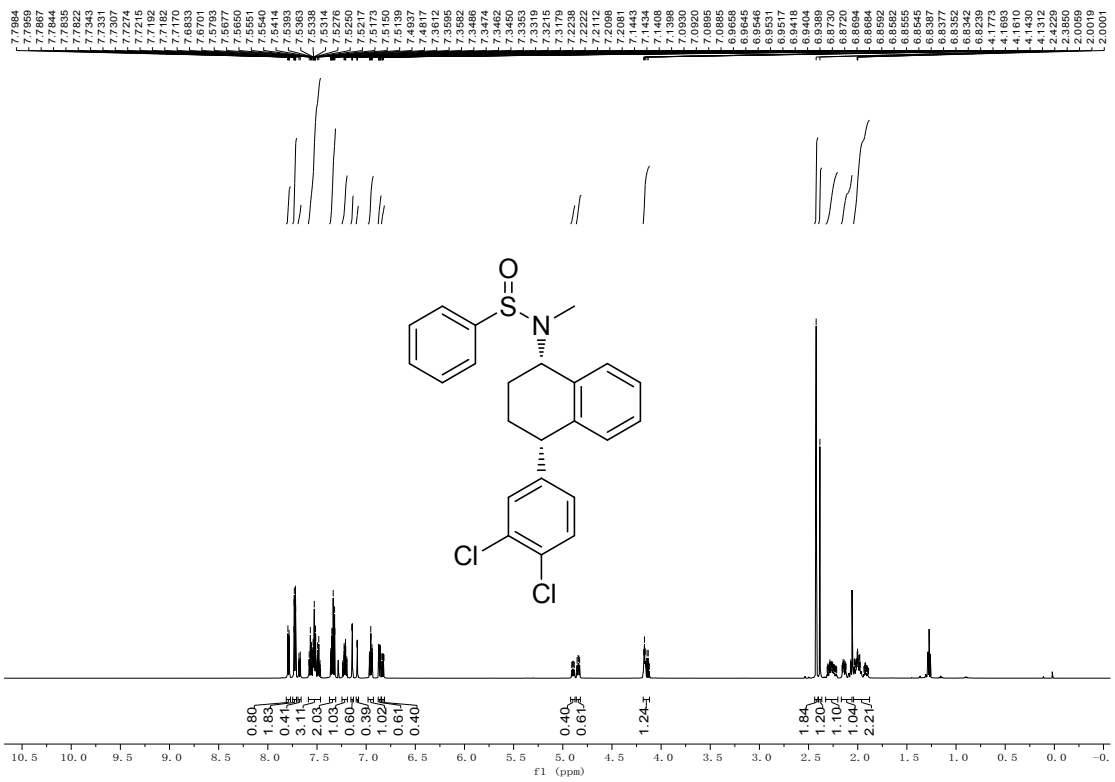
^{1}H NMR (600 MHz, $CDCl_3$) of **3i**:



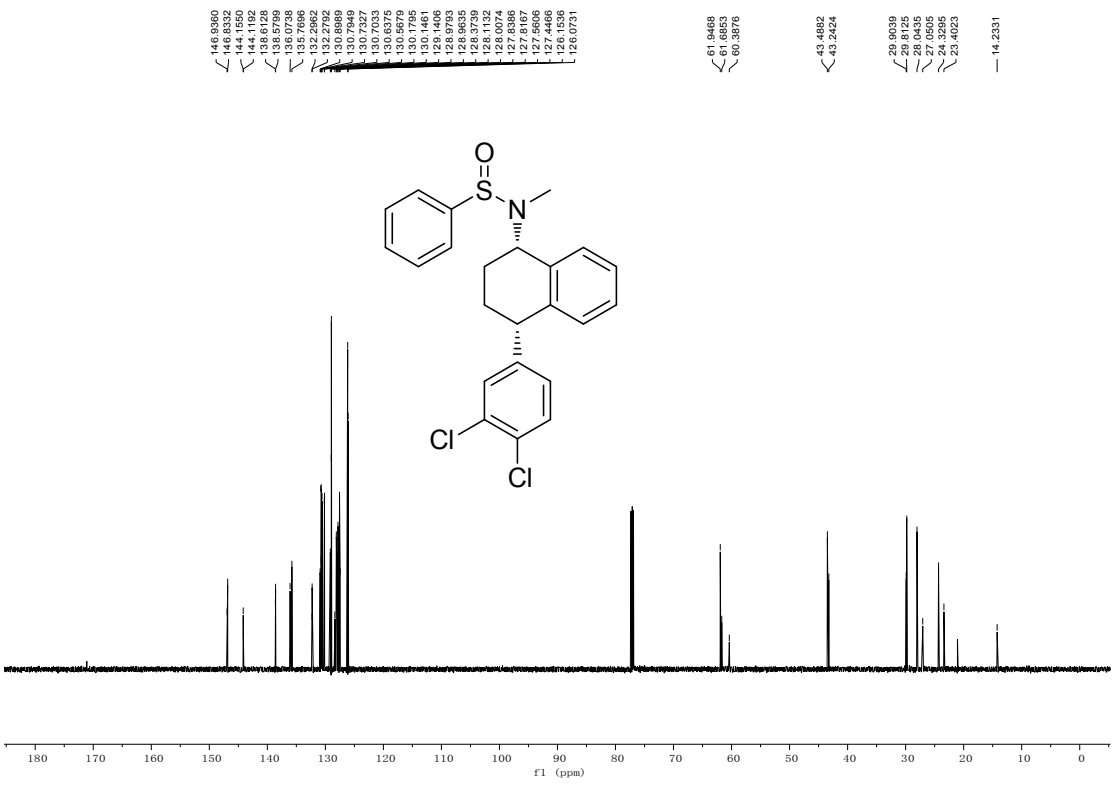
^{13}C NMR (150 MHz, $CDCl_3$) of **3i**:



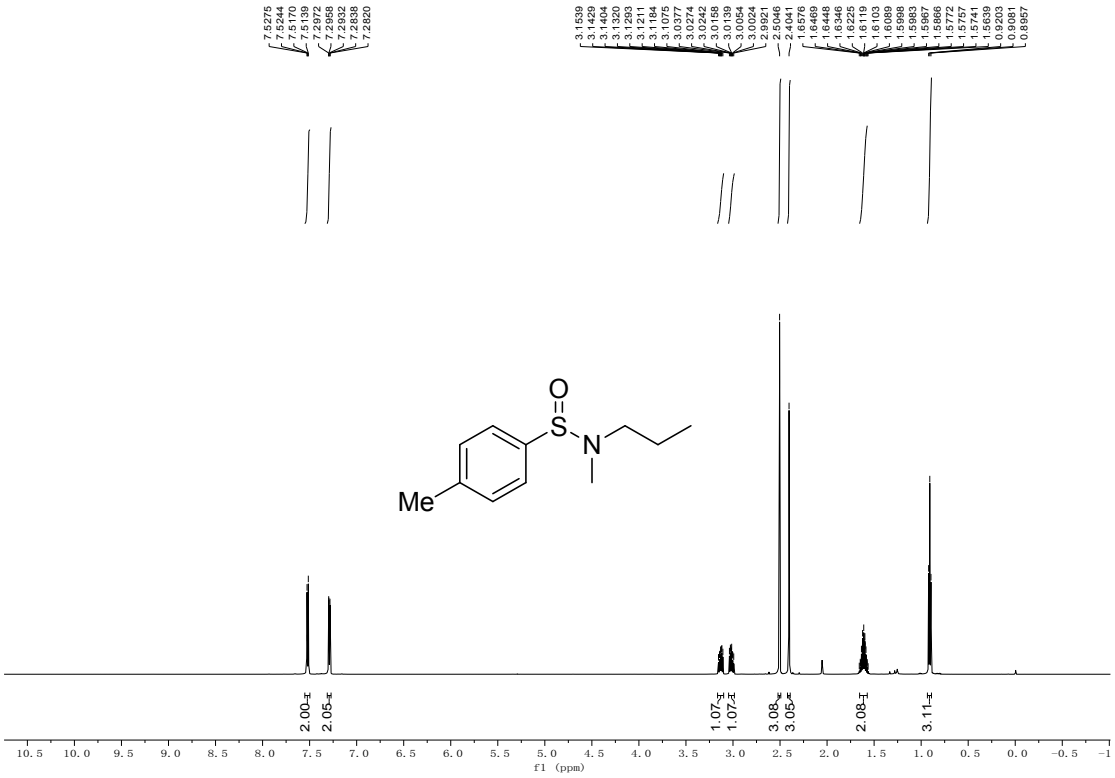
^{1}H NMR (600 MHz, $CDCl_3$) of **3j**:



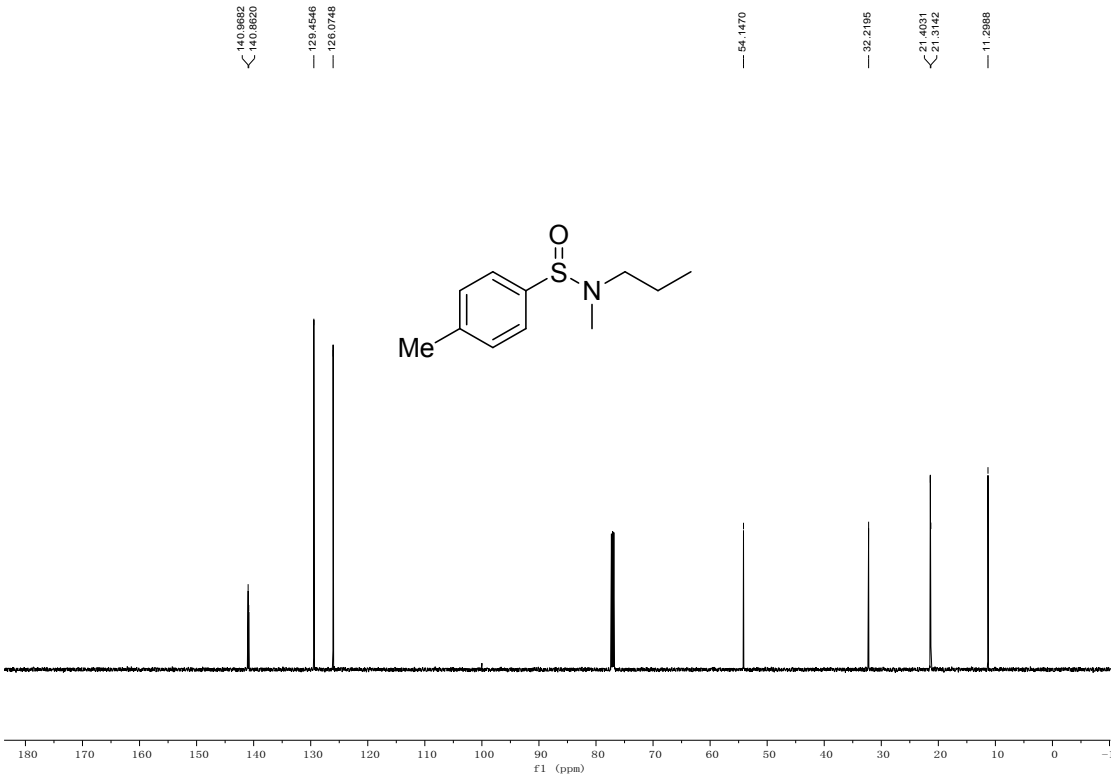
^{13}C NMR (150 MHz, $CDCl_3$) of **3j**:



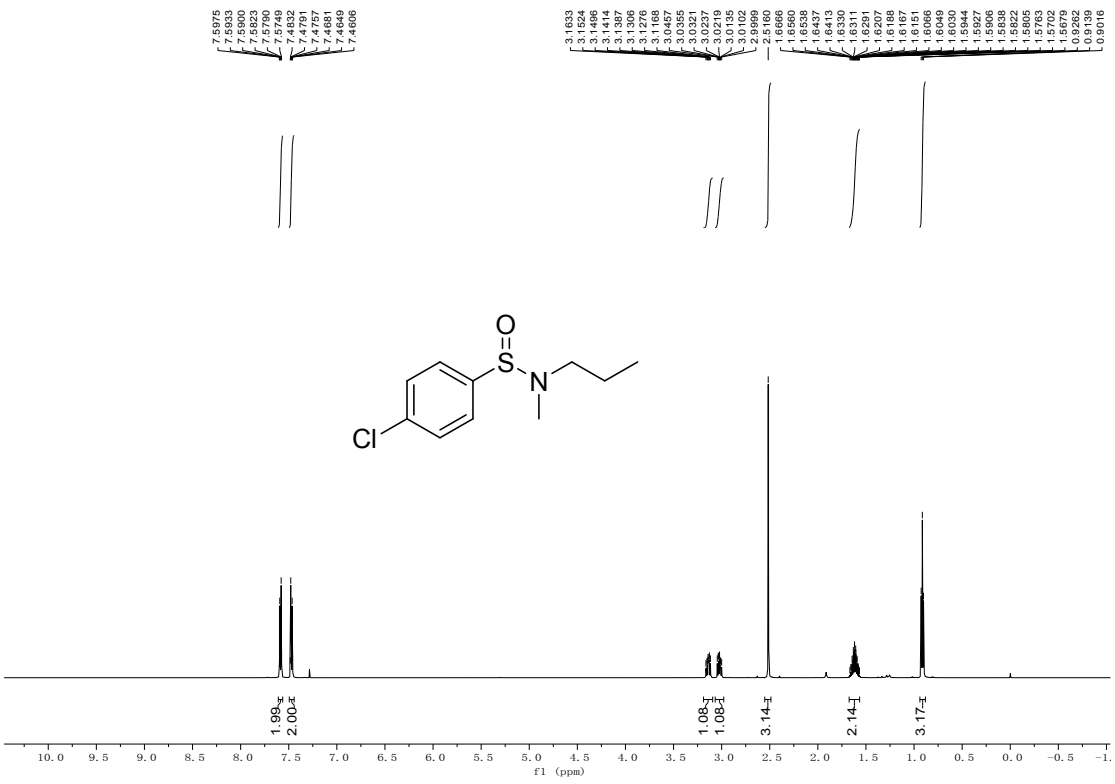
^{1}H NMR (600 MHz, $CDCl_3$) of **3k**:



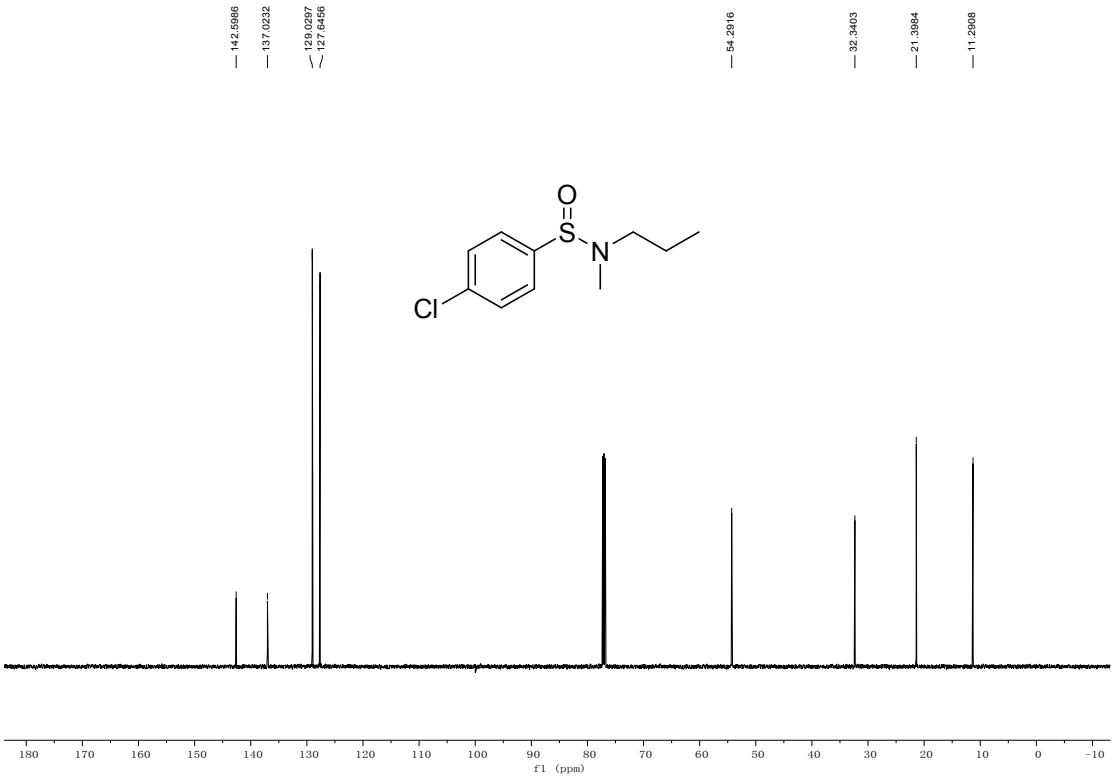
^{13}C NMR (150 MHz, $CDCl_3$) of **3k**:



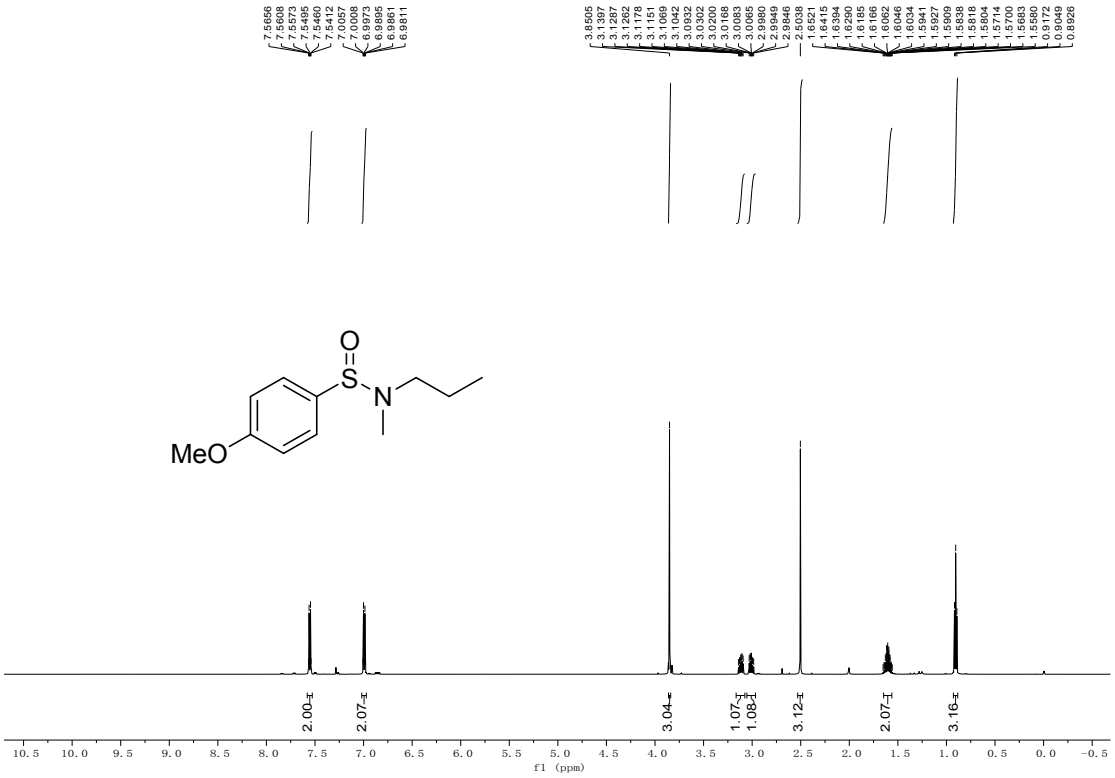
^{1}H NMR (600 MHz, $CDCl_3$) of **3l**:



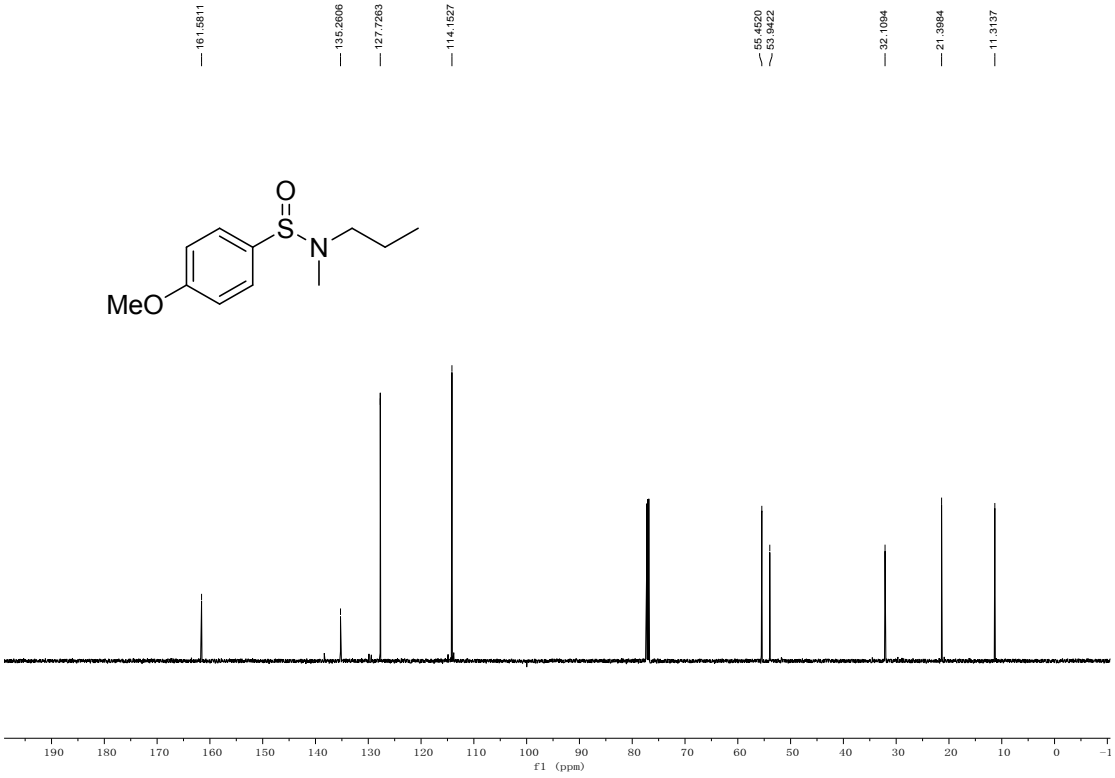
^{13}C NMR (150 MHz, $CDCl_3$) of **3l**:



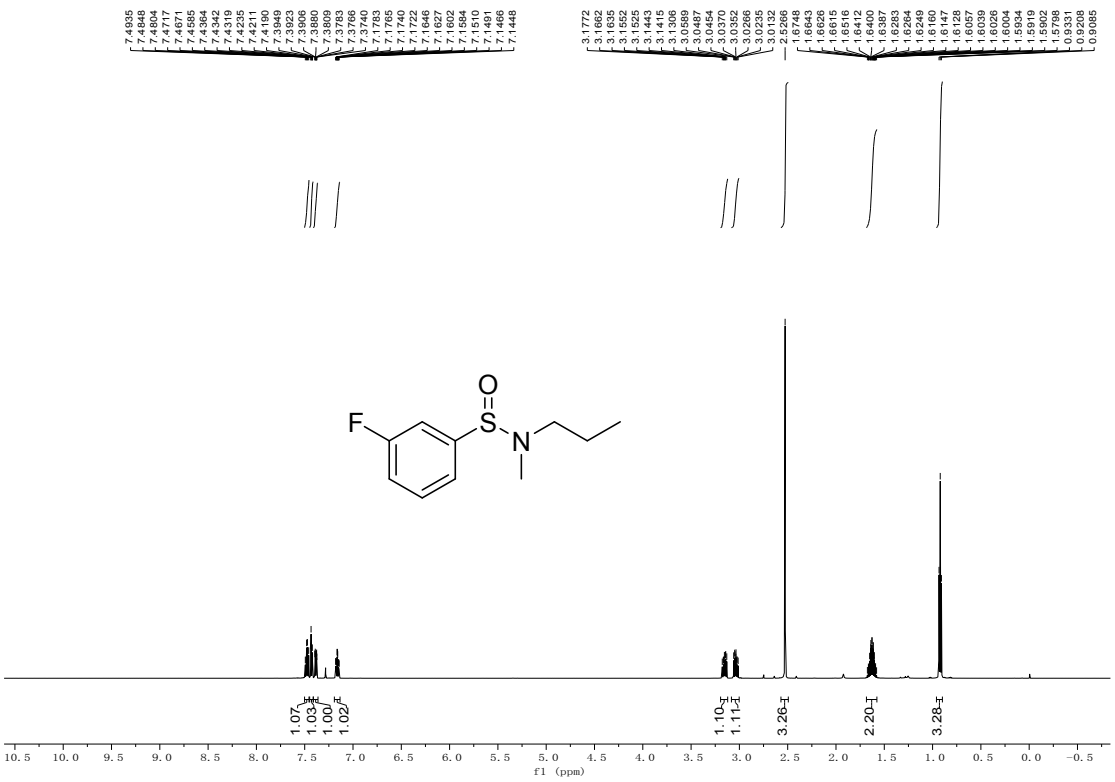
^{1}H NMR (600 MHz, $CDCl_3$) of **3m**:



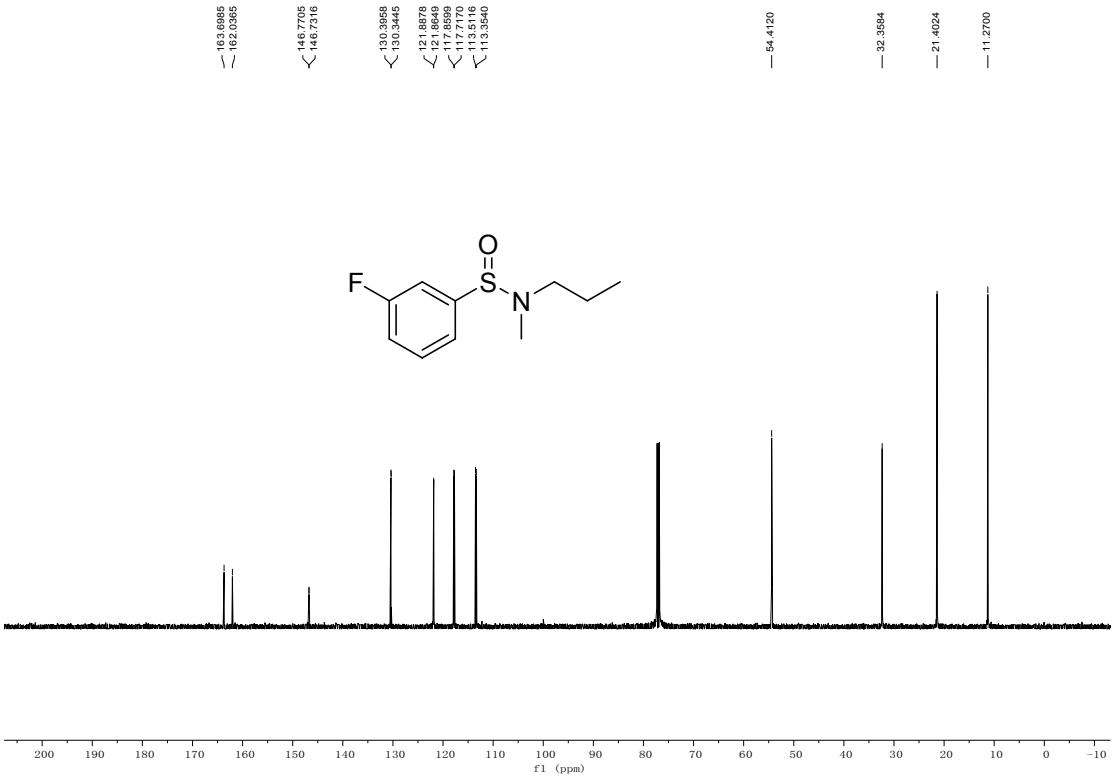
^{13}C NMR (150 MHz, $CDCl_3$) of **3m**:



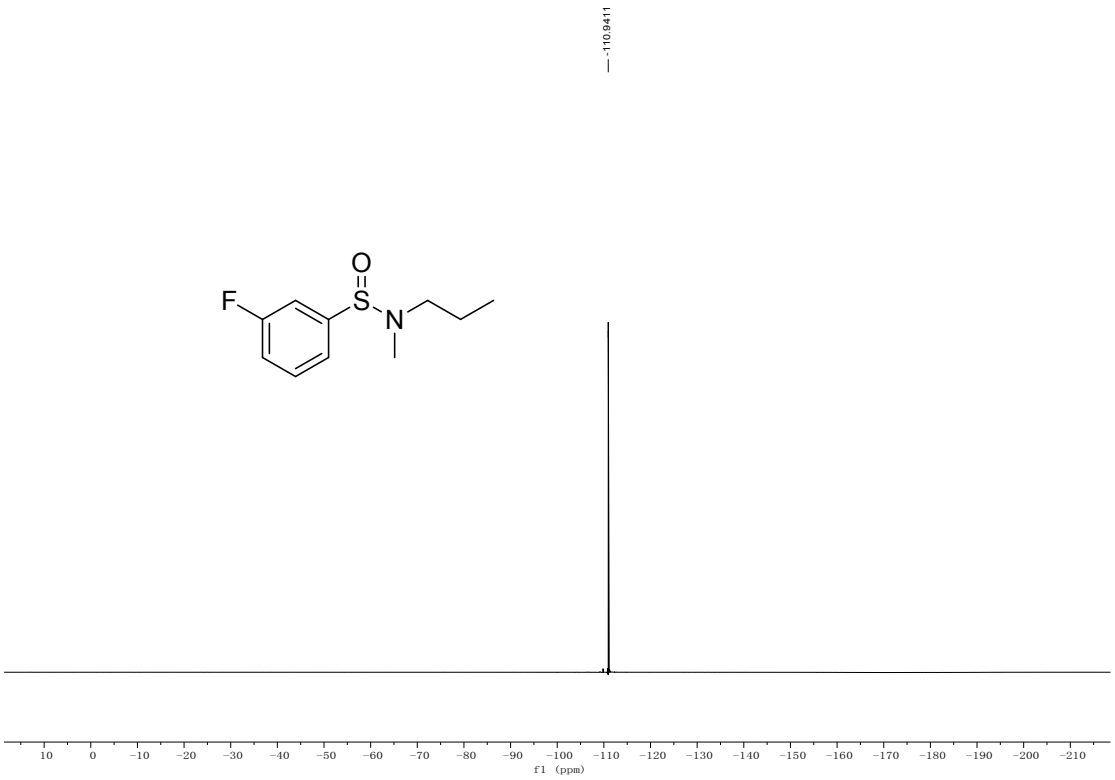
^{1}H NMR (600 MHz, $CDCl_3$) of **3n**:



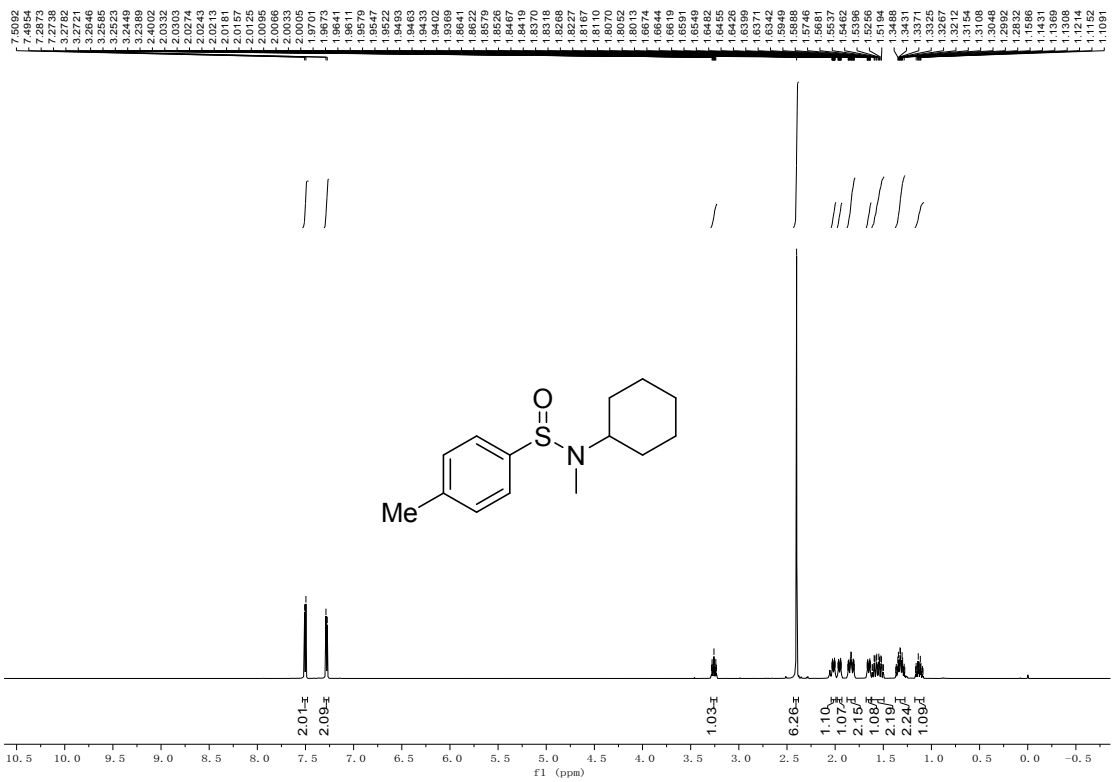
^{13}C NMR (150 MHz, $CDCl_3$) of **3n**:



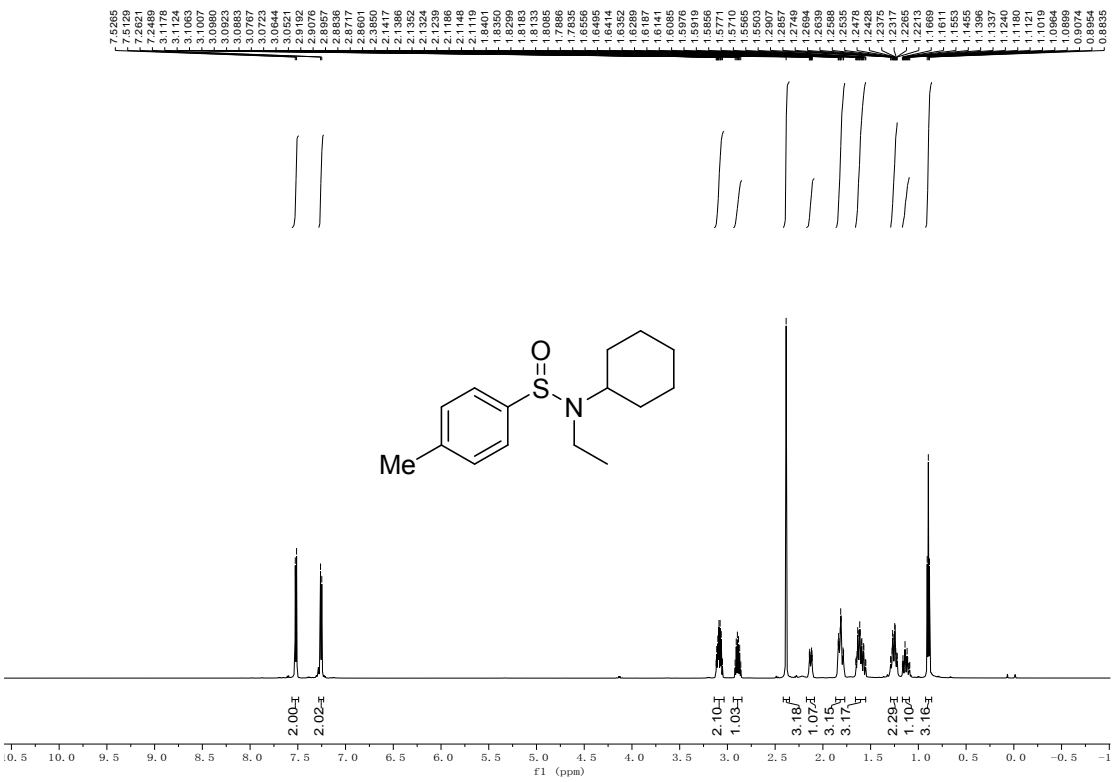
^{19}F NMR (565 MHz, $CDCl_3$) of **3n**:



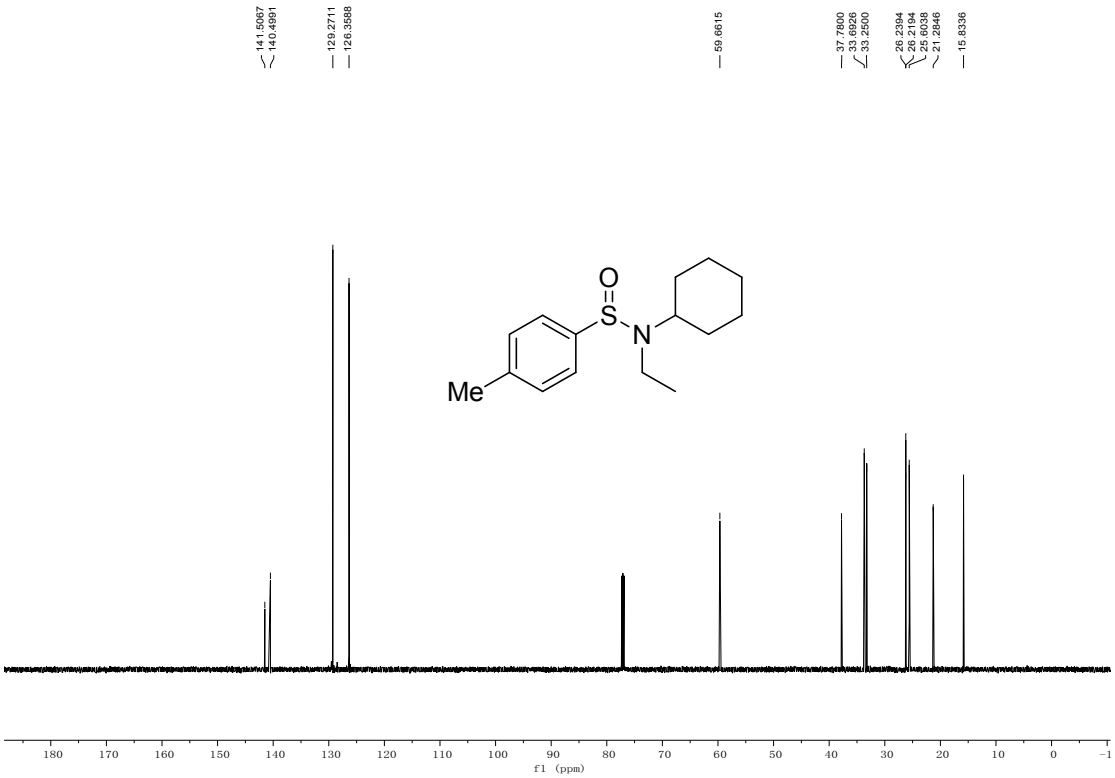
^{1}H NMR (600 MHz, $CDCl_3$) of **3o**:



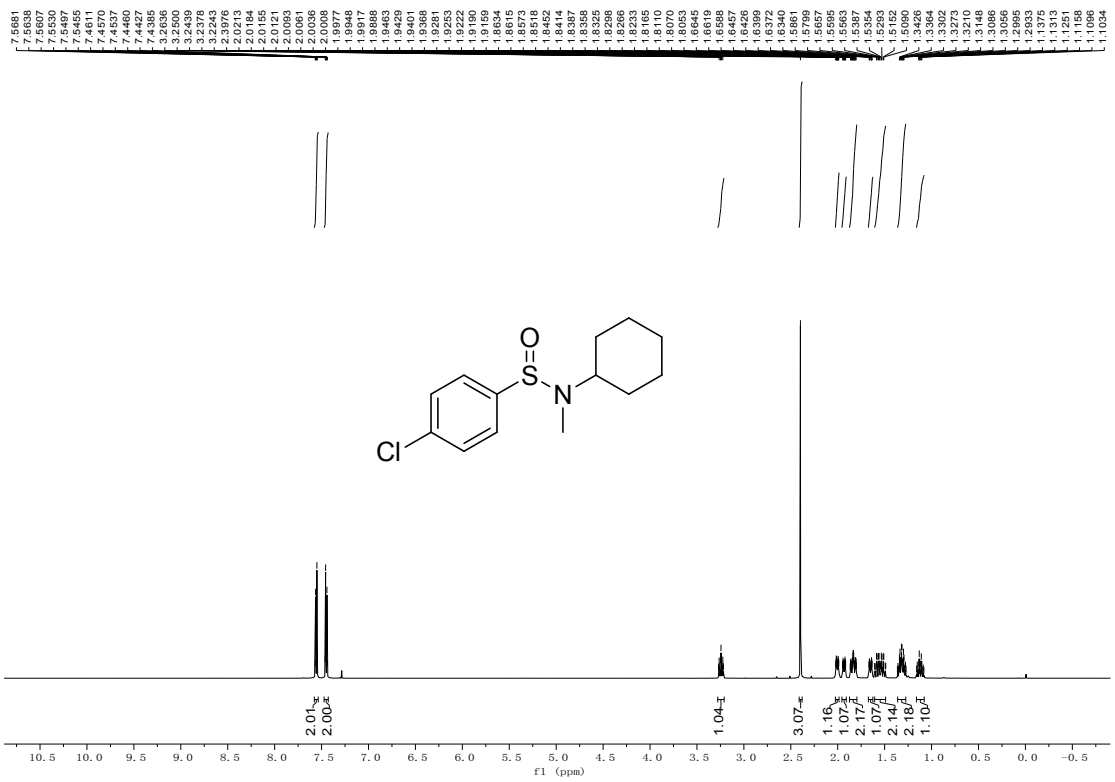
^{1}H NMR (600 MHz, $CDCl_3$) of **3p**:



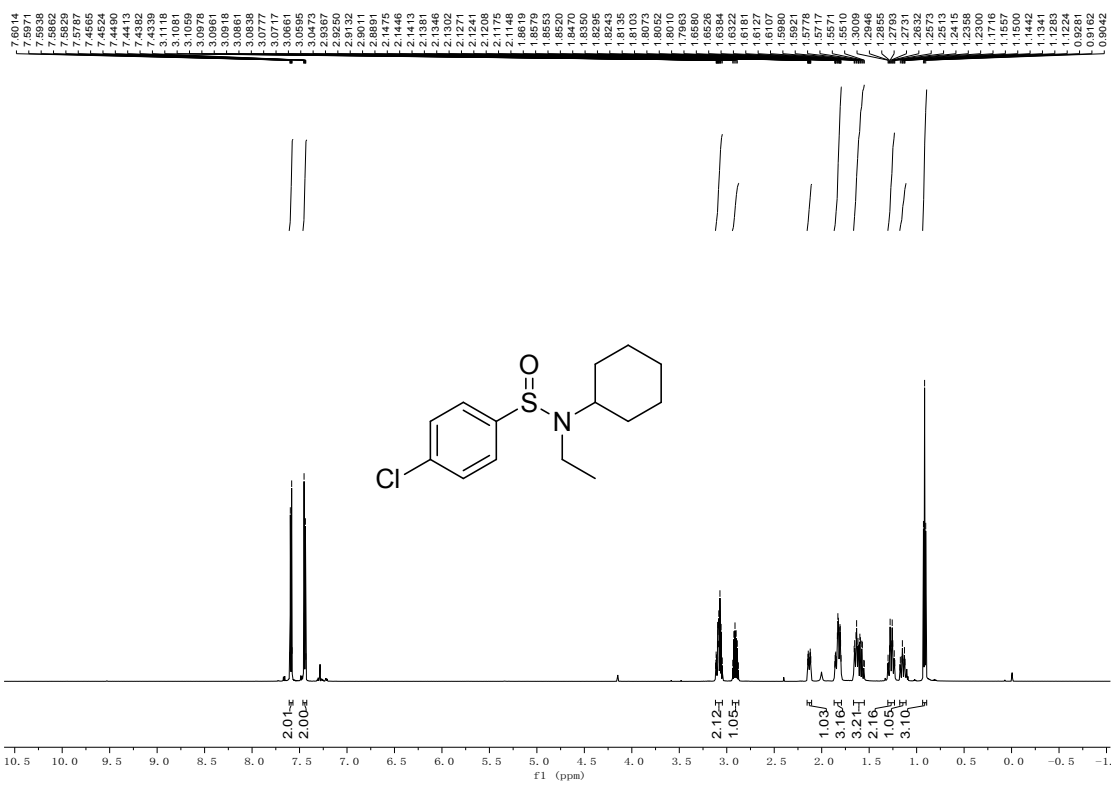
^{13}C NMR (150 MHz, $CDCl_3$) of **3p**:



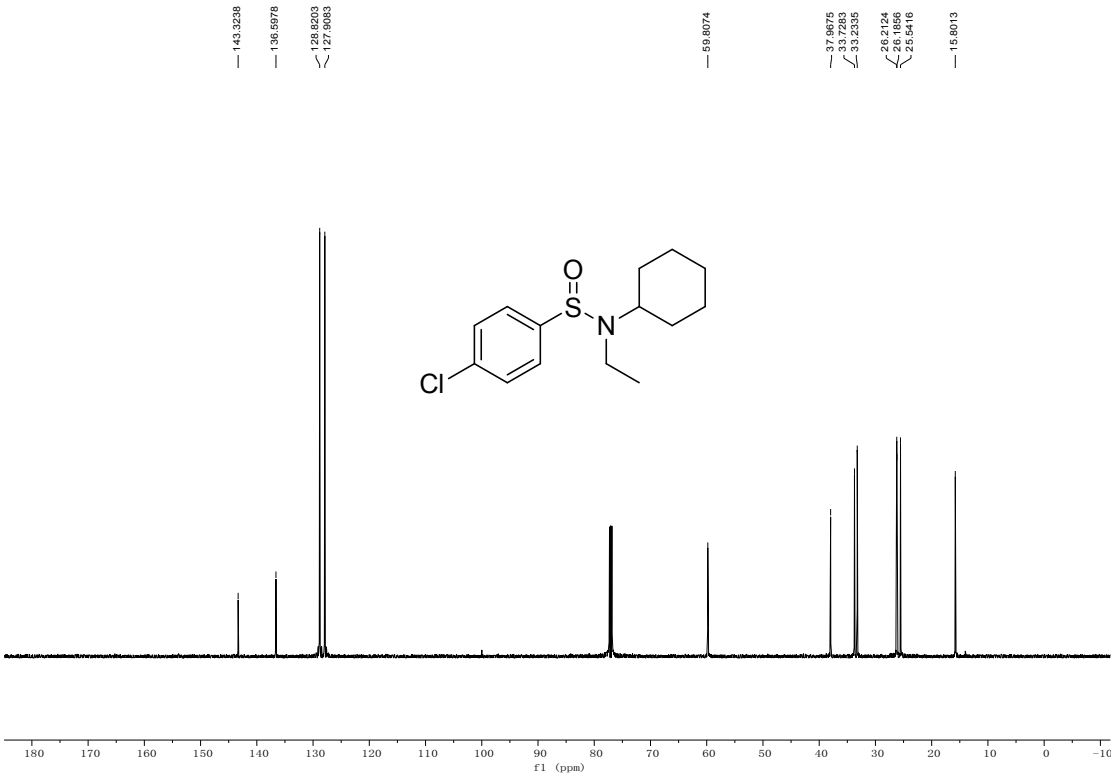
^{1}H NMR (600 MHz, $CDCl_3$) of **3q**:



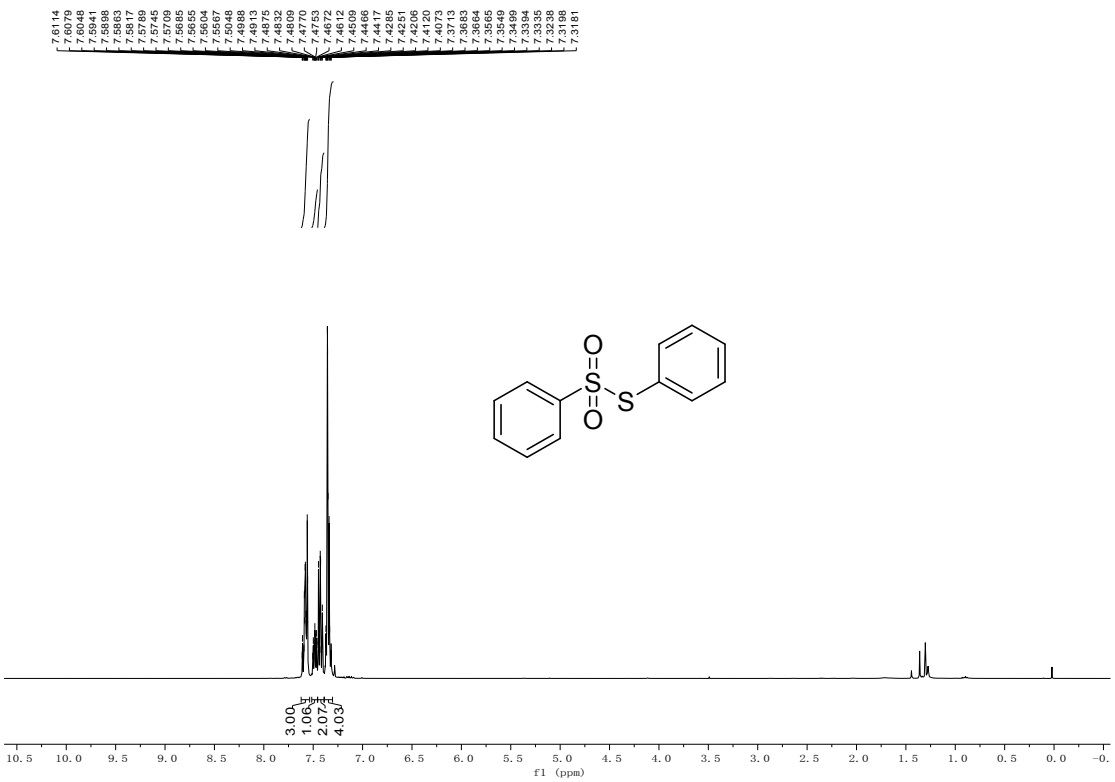
^{1}H NMR (600 MHz, $CDCl_3$) of **3r**:



^{13}C NMR (150 MHz, $CDCl_3$) of **3r**:



^{1}H NMR (400 MHz, $CDCl_3$) of **4**:



^{13}C NMR (100 MHz, $CDCl_3$) of **4**: