Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electrooxidation-induced Selective Cleavage of C–N Bonds of Tertiary Amines to Access Thioureas, Selenoureas, and 2-Aminated Benzoselenazoles

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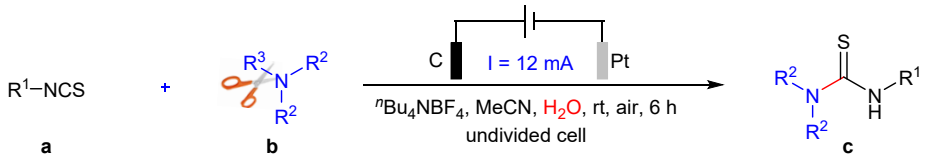
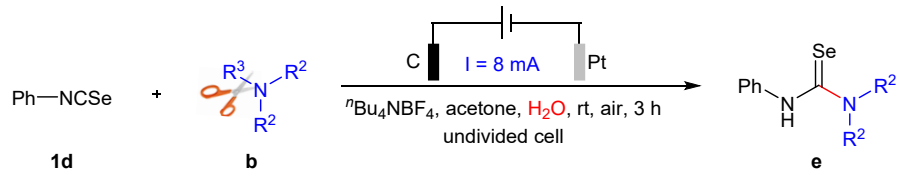
1. General information

All glassware was oven dried at 100 °C for hours and cooled down under vacuum. Isoselenocyanatobenzene and 1-iodo-2-isoselenocyanatobenzene derivatives were prepared according to reported procedures.[1] All the reaction prepared using the solvent of CH_3CN, DCM, and acetone (AR, 99.0%) was purchased from Macklin. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B or SS-L303SPD) (made in China), the carbon rod (ϕ = 6 mm), Pt plates (1 x 1 cm^2), and Ni plates (1 x 1 cm^2) was purchased from Xuzhou Xinke Instrument and Meter Co. LTD. The thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (b. p. 60-90 °C). ^1H, ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (400 or 500 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 (77.00 ppm, chloroform, 40.0 ppm, DMSO-d_6), respectively.

2. General procedure for electrooxidation-induced selective cleavage of C-N bonds of tertiary amines to access asymmetric thioureas, selenoureas, and 2-aminealkylated benzoselenazole derivatives.

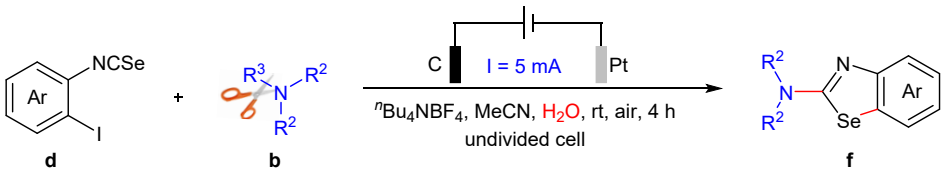


In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **a** (0.5 mmol), **b** (1.5 mmol), and $^nBu_4NBF_4$ (1.0 mmol, 330.0 mg) were combined. The flask was equipped with a carbon rods (ϕ = 6 mm) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, CH_3CN (8.0 mL) and H_2O (0.6 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA under room temperature for 6 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (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.



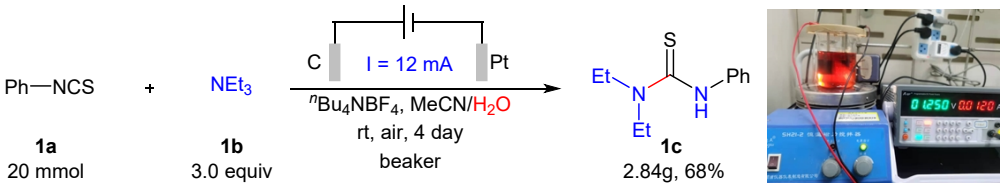
In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1d** (0.5 mmol, 91.5 mg), **b** (1.5 mmol), and $^nBu_4NBF_4$ (1.0 mmol, 330.0 mg) were combined. The flask was equipped with a carbon rods (ϕ = 6 mm) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, acetone

(8.0 mL) and H_2O (0.6 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under room temperature for 3 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (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.

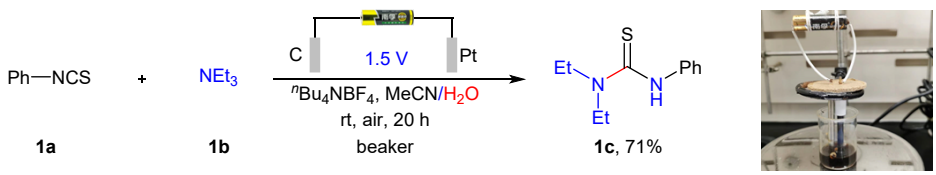


In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **d** (0.5 mmol), **b** (1.5 mmol), and ^{n}Bu$_4$NBF$_4$ (1.0 mmol, 330.0 mg) were combined. The flask was equipped with a carbon rods (ϕ = 6 mm) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, aceton (8.0 mL) and H_2O (0.6 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 4 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (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.

3. Large-scale synthesis of 1c and synthesis with battery



In an oven-dried beaker (500 mL) equipped with a stir bar, **1a** (20.0 mmol, 2.70 g), **1b** (30.0 mmol, 3.03 g), and ^{n}Bu$_4$NBF$_4$ (40.0 mmol, 13.2 g) were combined. The beaker was equipped with a carbon felt (2.0 × 2.0 cm^2) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, CH_3CN (320.0 mL) and H_2O (24.0 mL) were slowly injected into the reaction system. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA under room temperature for 96 h. When the reaction was finished, the reaction mixture was concentrated, and then extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated again. The pure product **1c** was obtained in a yield of 68% by flash column chromatography on silica gel.

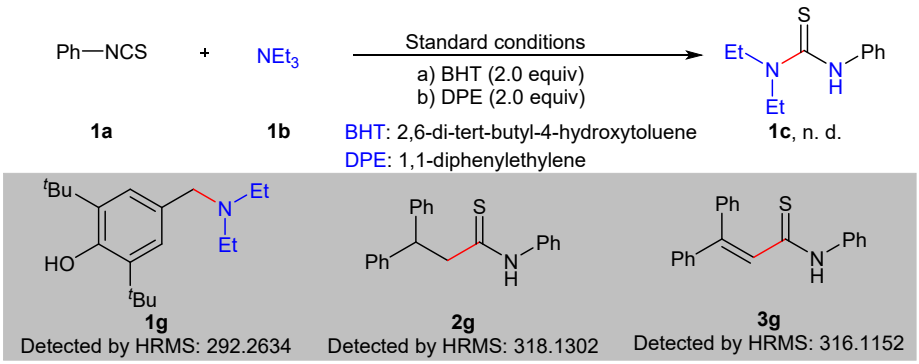


In an oven-dried beaker (25 mL) equipped with a stir bar, **1a** (0.5 mmol, 67.5 mg), **b** (1.5 mmol, 151.1

mg), and $^{n}Bu_4NBF_4$ (1.0 mmol, 330.0 mg) were combined. The beaker was equipped with a carbon rods (ϕ = 6 mm) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, CH_3CN (8.0 mL) and H_2O (0.6 mL) were slowly injected into the reaction system. The reaction mixture was stirred and electrolyzed at 1.5-volt battery as the sole power supply under room temperature for 20 h. When the reaction was finished, the pure product **1c** was obtained in a yield of 71% by flash column chromatography on silica gel.

4. Preliminary mechanistic studies

4.1 Radical trapping experiments



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1a** (0.5 mmol, 67.5 mg), **1b** (1.5 mmol, 151.1 mg) $^{n}Bu_4NBF_4$ (1.0 mmol, 330.0 mg), and BHT (1.5 mmol, 330.0 mg) or DPE (1.5 mmol, 270.0 mg) were combined. The flask was equipped with a carbon rods (ϕ = 6 mm) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, CH_3CN (8.0 mL) and H_2O (0.6 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA under room temperature for 6 h. When the reaction was finished, the solution was concentrated in a vacuum and not detected the desired product **1c**. The compounds **1g-3g** can be detected by HRMS.

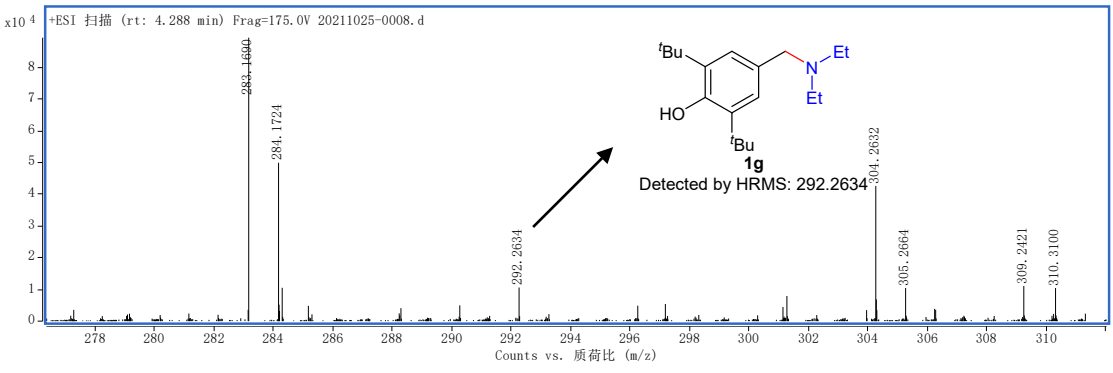


Figure S1. HRMS results of **1g.**

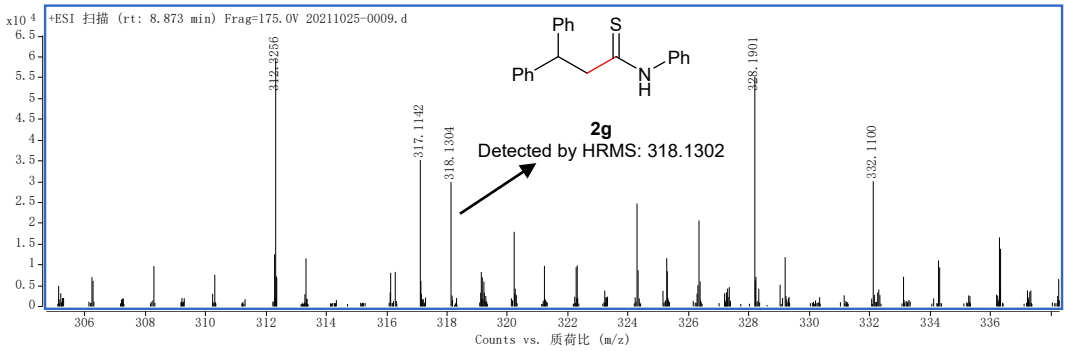


Figure S2. HRMS results of **2g.**

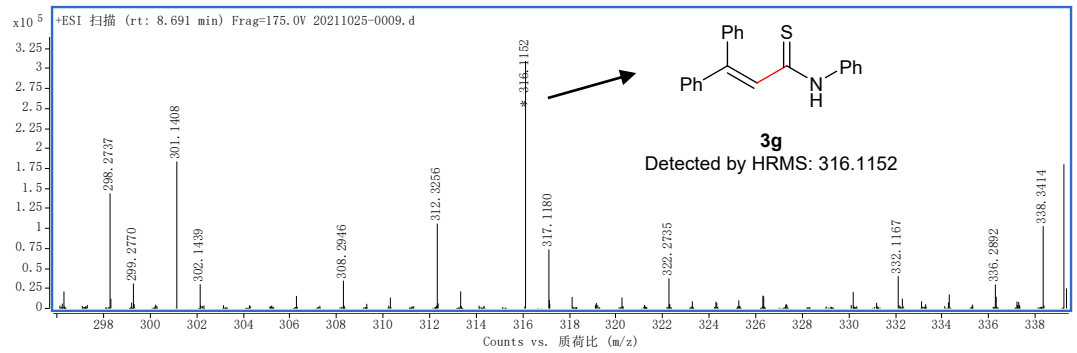


Figure S3. HRMS results of **3g.**

4.2 CV experiments

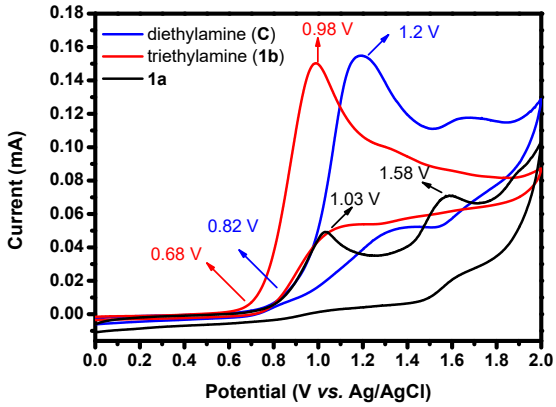


Fig. S4. Cyclic voltammograms at grass carbon as work electrode, Ag/AgCl as the reference electrode, Pt (1 x 1 cm ^{2}) as counter electrode in 0.1 M ^{n}Bu$_4$NBF$_4$, **C** (0.25 mM), **1b** (0.25 mM), **1a** (0.25 mM) in CH_3CN, scan rate 100 mV/s.

5. References

(1) (a) Takemoto, Y.; Nanjo, T.; Tsukano, C, *Synlett.* **2014,** *25*, 1473-1477; (b) Zhou, M.; Ji, S.; Wu, Z.; Li, Y.; Zheng, W.; Zhou, H.; Chen, T., *Eur. J. Med. Chem.* **2015,** *96*, 92-7.

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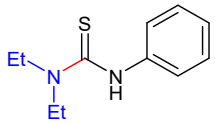
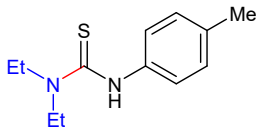
H.; Min, J. K.; Lee, G.-J., *Tetrahedron Lett.* **1999,** *40*, 8201-8204; (g) Koohgard, M.; Sarvestani, A. M.; Hosseini-Sarvari, M., *N. J. Chem.* **2020,** *44*, 14505-14512; (h) Li, L.; Wu, J.; Wei, L.; Lu, J.; Jiang, X., *J Org Chem* **2021,** *86*, 446-454; (i) Ramadas, K.; Srinivasan, N., *Synth. Commun.* **1995,** *25*, 3381-3387; (j) Sudha, L. V.; Sathyanarayana, D. N., *J. Mol. Struct.* **1985,** *127*, 313-317; (k) Sugimoto, H.; Makino, I.; Hirai, K., *J. Org. Chem.* **1988,** *53*, 2263-2267; (l) Tavakol, H.; Mahmoudi, A.; Ranjbari, M.-A., *J. Sulfur Chem.* **2018,** *40*, 113-123; (m) Yonemoto, K.; Shibuya, I., *Chem. Soc.Japan* **1988,** *61*, 4043-4049; (n) Zakrzewski, J.; Krawczyk, M., *Phosphorus, Sulfur, and Silicon and the Related Elements* **2009,** *184*, 1880-1903; (o) Souldozi, A.; Ramazani, A.; Dadrass, A. R.; lepokura, a.; Lis, T., *Helvetica Chimica Acta* **2012,** *95*, 339-348.

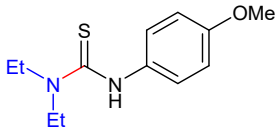
6. Detail descriptions for products



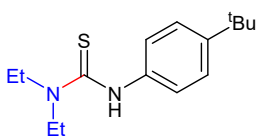
1,1-diethyl-3-phenylthiourea (1c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 85% isolated yield (88.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.09 (s, 1H), 3.73 (q, *J* = 7.1 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.7, 139.8, 128.6, 125.9, 125.8, 45.7, 12.7. 85



1,1-diethyl-3-(p-tolyl)thiourea (2c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 71% isolated yield (78.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (q, *J* = 8.4 Hz, 4H), 6.98 (s, 1H), 3.73 (q, *J* = 7.1 Hz, 4H), 2.32 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.0, 137.2, 135.8, 129.4, 126.3, 45.7, 21.1, 12.7.

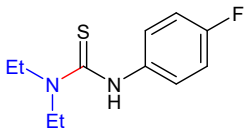


1,1-diethyl-3-(4-methoxyphenyl)thiourea (3c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 69% isolated yield (82.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.8 Hz, 2H), 7.02 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.73 (q, *J* = 7.0 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.0, 157.8, 132.7, 128.2, 113.8, 55.4, 45.6, 12.7.

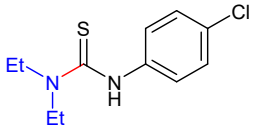


3-(4-(tert-butyl)phenyl)-1,1-diethylthiourea (4c): yellow oil was obtained by column chromatography

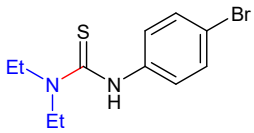
(eluent: EtOAc/petroleum ether = 1/7) with 60% isolated yield (79.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 1H), 7.35 (m, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.22 (d, *J* = 2.1 Hz, 1H),, 6.98 (s, 1H), 3.74 (q, *J* = 7.2 Hz, 4H), 1.30 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.7, 148.7, 137.1, 125.7, 125.4, 45.7, 34.5, 31.4, 12.7. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{15}H_{24}N_2S$: 265.1733; found: 265.1733.



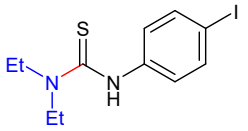
1,1-diethyl-3-(4-fluorophenyl)thiourea (5c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 76% isolated yield (86.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.7, 4.9 Hz, 2H), 7.06 (m, 3H), 3.73 (q, *J* = 7.1 Hz, 4H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.9, 160.7 (d, *J* = 245.5 Hz), 135.8 (d, *J* = 3.1 Hz), 128.4 (d, *J* = 8.3 Hz), 115.5 (d, *J* = 22.6 Hz), 45.7, 12.7. ^{19}FNMR (376 MHz, $CDCl_3$) δ -115.9. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{11}H_{15}FN_2S$: 227.1013; found: 227.1013.



3-(4-chlorophenyl)-1,1-diethylthiourea (6c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 79% isolated yield (95.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 4H), 7.00 (s, 1H), 3.72 (q, *J* = 7.1 Hz, 4H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.5, 138.3, 131.3, 128.7, 127.4, 45.8, 12.7.

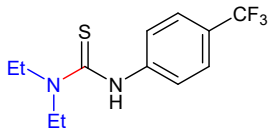


3-(4-bromophenyl)-1,1-diethylthiourea (7c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 84% isolated yield (120.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.19 (m, 2H), 7.02 (s, 1H) , 3.70 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.3, 138.9, 131.6, 127.7, 119.0, 45.8, 12.7. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{11}H_{15}BrN_2S$: 287.0212; found: 287.0212.

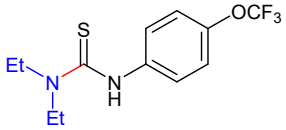


1,1-diethyl-3-(4-iodophenyl)thiourea (8c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 66% isolated yield (110.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.09 (m, 2H), 6.99 (s, 1H), 3.72 (q, *J* = 7.1 Hz, 4H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR

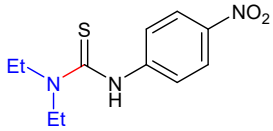
(101 MHz, $CDCl_3$) δ 180.3, 139.6, 137.6, 127.8, 121.9, 45.8, 12.7. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{11}H_{15}IN_2S$: 335.0073; found: 335.0073.



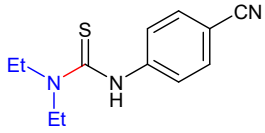
1,1-diethyl-3-(4-(trifluoromethyl)phenyl)thiourea (9c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 63% isolated yield (86.9 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.12 (s, 1H), 3.77 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.1, 143.0, 128.6, 126.9 (q, J = 32.7 Hz), 125.6 (q, J = 3.7 Hz), 124.9, 124.1 (q, J = 271.7 Hz), 119.1, 45.8, 12.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.1. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{12}H_{15}F_3N_2S$: 277.0981; found: 277.0981.



1,1-diethyl-3-(4-(trifluoromethoxy)phenyl)thiourea (10c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 72% isolated yield (105.2 mg). m. p. = 74-76°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, 2H), 7.45 (m, 2H), 7.11 (s, 1H) , 3.75 (q, J = 7.1 Hz, 4H), 1.29 (t, J = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.4, 146.5, 138.3, 127.2, 121.0, 120.4 (q, J = 257.1 Hz), 45.7, 12.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{12}H_{15}F_3N_2OS$: 293.0930; found: 2293.0930.

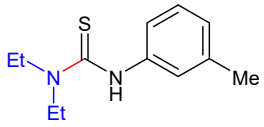


1,1-diethyl-3-(4-nitrophenyl)thiourea (11c): yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 38% isolated yield (48.1 mg). m. p. = 60-62 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, J = 8.5 Hz, 2H), 6.88 (s, 1H), 6.66 (d, J = 8.5 Hz, 2H), 3.76 (q, J = 7.1 Hz, 4H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.4, 144.9, 130.8, 128.1, 115.2, 45.6, 12.7. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{11}H_{15}N_3O_2S$: 254.0958; found: 254.0958.

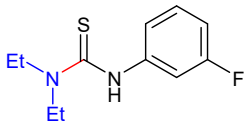


3-(4-cyanophenyl)-1,1-diethylthiourea (12c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 39% isolated yield (45.5 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (m, 2H), 6.97 (s, 1H), 6.89 (m, 2H), 3.75 (q, J = 7.1 Hz, 4H), 1.29 (t, J = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.1, 157.8, 132.7, 128.1, 126.9, 113.9, 45.6, 12.7. HRMS (ESI) *m/z:* $[M+H]^+$

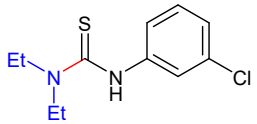
calcd for $C_{12}H_{15}N_3S$: 234.1059; found: 234.1059.



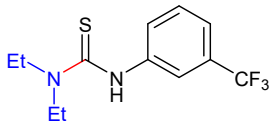
1,1-diethyl-3-(m-tolyl)thiourea (13c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 88% isolated yield (97.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 1H), 7.11 (m, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 3.72 (q, *J* = 7.1 Hz, 4H), 2.32 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.8, 139.7, 138.6, 128.5, 126.7, 126.6, 123.1, 45.7, 21.4, 12.7. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{12}H_{18}N_2S$: 223.1263; found: 223.1263.



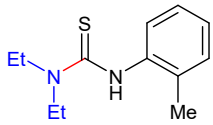
1,1-diethyl-3-(3-fluorophenyl)thiourea (14c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 85% isolated yield (96.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (td, *J* = 8.1, 6.6 Hz, 1H), 7.18 (s, 1H), 7.14 (dt, *J* = 10.4, 2.2 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.85 (td, *J* = 8.3, 2.2 Hz, 1H), 3.71 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 162.4 (d, *J* = 245.2 Hz), 141.4 (d, *J* = 10.5 Hz), 129.4 (d, *J* = 9.3 Hz), 121.2 (d, *J* = 2.4 Hz), 113.1 (d, *J* = 24.1 Hz), 112.2 (d, *J* = 21.1 Hz), 45.7, 12.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.5. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{11}H_{15}FN_2S$: 227.1013; found: 227.1013.



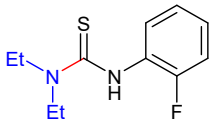
3-(3-chlorophenyl)-1,1-diethylthiourea (15c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 80% isolated yield (97.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 2.0 Hz, 1H), 7.24 (m, 1H), 7.18 (dt, *J* = 8.1, 1.7 Hz, 1H), 7.12 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.07 (s, 1H), 3.70 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.3, 141.0, 133.9, 129.5, 125.9, 125.7, 124.1, 45.8, 12.7. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{11}H_{15}ClN_2S$: 243.0717; found: 243.0717.



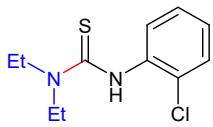
1,1-diethyl-3-(3-(trifluoromethyl)phenyl)thiourea (16c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 62% isolated yield (85.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, 2H), 7.45 (m, 2H), 7.11 (s, 1H), 3.75 (q, *J* = 7.1 Hz, 4H), 1.29 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.3, 140.3, 130.8 (q, *J* = 32.5 Hz), 129.2, 128.9, 123.8 (q, *J* = 272.9 Hz), 122.3 (q, *J* = 3.8 Hz), 122.1 (q, *J* = 3.8 Hz), 45.7, 12.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{12}H_{15}F_3N_2S$: 277.0981; found: 277.0981.



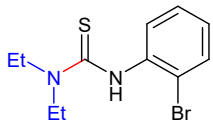
1,1-diethyl-3-(o-tolyl)thiourea (17c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 79% isolated yield (87.7mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 6.8, 4.6 Hz, 2H), 7.19 (m, 2H), 6.86 (s, 1H), 3.72 (q, *J* = 7.0 Hz, 4H), 2.25 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.8, 138.5, 135.1, 130.6, 128.2, 127.0, 126.3, 45.6, 18.2, 12.7. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{12}H_{18}N_2S$: 223.1263; found: 223.1263.



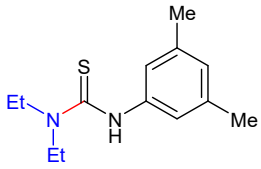
1,1-diethyl-3-(2-fluorophenyl)thiourea (18c): yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 76% isolated yield (85.9mg). m. p. = 42-45°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (m, 1H), 7.16 (m, 3H), 6.95 (s, 1H), 3.77 (q, *J* = 7.2 Hz, 4H), 1.31 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 155.8 (d, *J* = 244.7 Hz), 127.9 (d, *J* = 0.7 Hz), 127.8 (d, *J* = 10.7 Hz), 126.5 (d, *J* = 7.9 Hz), 123.8 (d, *J* = 3.7 Hz), 115.4 (d, *J* = 20.0 Hz), 45.9, 12.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.6. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{11}H_{15}FN_2S$: 227.1013; found: 227.1013.



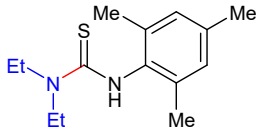
3-(2-chlorophenyl)-1,1-diethylthiourea (19c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/7) with 72% isolated yield (87.4mg). m. p. = 97-99°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.25 (td, *J* = 7.8, 1.5 Hz, 1H), 7.21 (s, 1H), 7.09 (td, *J* = 7.7, 1.6 Hz, 1H), 3.77 (q, *J* = 7.1 Hz, 4H), 1.32 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 136.7, 129.1, 127.4, 127.4, 126.8, 126.0, 45.8, 12.7. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{11}H_{15}ClN_2S$: 243.0717; found: 243.0717.



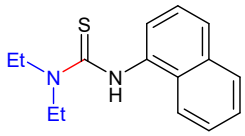
3-(2-bromophenyl)-1,1-diethylthiourea (20c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/7) with 96% isolated yield (118.7mg). m. p. = 102-104°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.28 (q, *J* = 7.8 Hz, 1H), 7.18 (s, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 3.77 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 138.0, 132.3, 127.7, 127.4, 126.5, 118.3, 45.8, 12.8. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{11}H_{15}BrN_2S$: 287.0212; found: 287.0212.



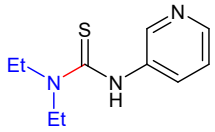
3-(3,5-dimethylphenyl)-1,1-diethylthiourea (21c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/7) with 80% isolated yield (94.4mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.89 (s, 2H), 6.82 (s, 1H), 3.72 (q, *J* = 7.1 Hz, 4H), 2.28 (s, 6H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.9, 139.6, 138.4, 127.8, 123.8, 45.7, 21.3, 12.7. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{13}H_{20}N_2S$: 237.1420; found: 237.1420.



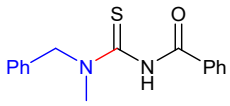
1,1-diethyl-3-mesitylthiourea (22c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/7) with 53% isolated yield (66.2mg). m. p. = 105-107°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 6.52 (s, 1H), 3.78 (q, *J* = 7.1 Hz, 4H), 2.27 (s, 3H), 2.20 (s, 6H), 1.31 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.6, 137.2, 136.3, 134.6, 129.0, 45.6, 21.1, 18.5, 13.0. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{14}H_{22}N_2S$: 251.1576; found: 251.1576.



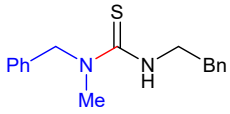
1,1-diethyl-3-(naphthalen-1-yl)thiourea (23c):[2] yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 68% isolated yield (87.7mg). m. p. = 90-92°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (m, 1H), 7.87 (m, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.53 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.43 (m, 1H), 7.17 (s, 1H), 3.77 (q, *J* = 7.1 Hz, 4H), 1.31 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.2, 136.1, 134.3, 130.5, 128.5, 127.4, 126.6, 126.2, 125.5, 125.4, 122.6, 46.0, 12.8.



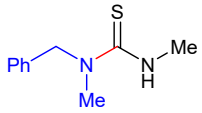
1,1-diethyl-3-(pyridin-3-yl)thiourea (24c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 64% isolated yield (67.0mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 1.8 Hz, 1H), 8.31 (d, *J* = 4.3 Hz, 1H), 7.88 (m, 2H), 7.25 (dd, *J* = 8.1, 4.8 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.4, 146.8, 146.0, 137.1, 134.3, 123.0, 45.8, 12.6.



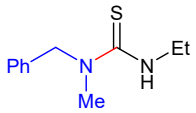
N-(benzyl(methyl)carbamothioyl)benzamide (25c):[2] yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 52% isolated yield (73.8mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 6.0 Hz, 3H), 7.38 – 7.34 (m, 3H), 7.29 (t, *J* = 7.3 Hz, 2H), 5.26 (s, 2H), 3.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.7, 163.8, 134.9, 133.0, 132.4, 129.6, 129.0, 128.8, 128.1, 127.8, 59.4, 40.2.



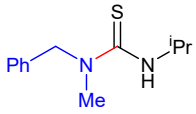
1-benzyl-1-methyl-3-phenethylthiourea (26c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/7) with 88% isolated yield (125.0mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 5H), 7.23 (m, 5H), 5.43 (S, 1H), 4.97 (S, 2H), 4.00 (m, 2H), 3.02 (S, 1H), 2.92 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3, 138.8, 136.4, 128.9, 128.8, 128.8, 127.7, 127.1, 126.6, 56.5, 47.1, 35.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{20}N_2S$: 285.1420; found: 285.1420.



1-benzyl-1,3-dimethylthiourea (27c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 81% isolated yield (78.6mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.28 (m, 3H), 5.64 (S, 1H), 5.04 (S, 2H), 3.13 (d, *J* = 4.5 Hz, 3H), 3.10 (S, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.4, 136.6, 128.9, 127.7, 127.1, 56.7, 37.3, 33.2.

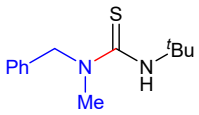


1-benzyl-3-ethyl-1-methylthiourea (28c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) with 95% isolated yield (98.8mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.28 (m, 3H), 5.41 (s, 1H), 5.04 (s, 2H), 3.67 (m, 2H), 3.11 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3, 136.6, 128.9, 127.7, 127.1, 56.6, 41.3, 37.3, 14.7. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{11}H_{16}N_2S$: 209.1107; found: 207.1107.

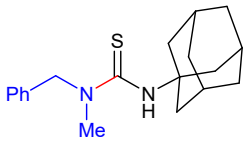


1-benzyl-3-isopropyl-1-methylthiourea (29c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/10 with 95% isolated yield (105.4mg). m. p. = 66-68°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.2 Hz, 2H), 7.30 (m, 3H), 5.22 (s, 1H), 5.04 (s, 2H), 4.70 (m, 1H), 3.13 (s, 3H), 1.22 (s, 3H), 1.21 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.2, 136.6, 128.8, 127.6, 127.0, 56.4,

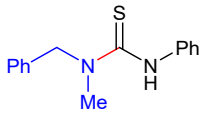
47.8, 37.4, 22.8. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{12}H_{18}N_2S$: 223.1263; found: 223.1263.



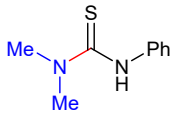
1-benzyl-3-(tert-butyl)-1-methylthiourea (30c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/10 with 71% isolated yield (83.8mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.29 (m, 3H), 5.37 (s, 1H), 4.98 (s, 2H), 3.15 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.1, 136.8, 128.9, 127.7, 127.0, 56.1, 54.3, 38.2, 29.2.



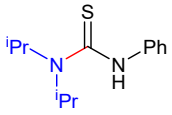
3-((3R,5R)-adamantan-1-yl)-1-benzyl-1-methylthiourea (31c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/20 with 75% isolated yield (117.7mg). m. p. = 49-52°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.28 (m, 3H), 5.23 (s, 1H), 4.96 (s, 2H), 3.13 (s, 3H), 2.22 (d, J = 2.8 Hz, 6H), 2.07 (s, 3H), 1.65 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 136.8, 128.9, 127.6, 127.0, 56.0, 54.9, 41.8, 38.2, 36.4, 29.7. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{19}H_{26}N_2S$: 315.1889; found: 315.1889.



1-benzyl-1-methyl-3-phenylthiourea (32c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5 with 60% isolated yield (77.9mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.31 (dd, J = 9.0, 3.9 Hz, 5H), 7.25 (d, J = 6.7 Hz, 2H), 7.22 (m, 2H), 5.07 (s, 2H), 3.22 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 159.7, 157.3, 152.9, 150.6, 144.6, 131.6, 130.4, 129.4, 128.2, 127.4, 115.4, 114.7, 55.6, 29.7.

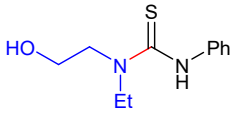


1,1-dimethyl-3-phenylthiourea (33c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3 with 80% isolated yield (72.0mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, J = 7.8 Hz, 2H), 7.25 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 7.4 Hz, 2H), 3.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.4, 139.8, 128.8, 125.5, 124.9, 41.5.

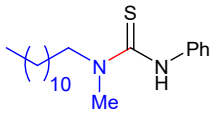


1,1-diisopropyl-3-phenylthiourea (34c):[2] yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/7 with 56% isolated yield (66.2mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, J = 8.6, 1.0 Hz, 2H), 7.29 (m, 2H), 7.03 (m, 1H), 6.20 (s, 1H), 3.99 (dt, J = 13.8, 6.9 Hz, 2H),

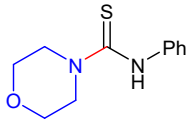
1.34 (s, 6H), 1.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 139.3, 128.8, 122.7, 119.7, 45.4, 21.5.



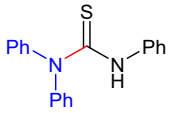
1-ethyl-1-(2-hydroxyethyl)-3-phenylthiourea (35c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1 with 55% isolated yield (61.7mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.48 (s, 1H), 7.29 (m, 4H), 7.08 (t, *J* = 7.1 Hz, 1H), 5.59 (s, 1H), 3.82 (q, *J* = 7.0 Hz, 2H), 3.72 (s, 4H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, DMSO- d_6) δ 181.5, 141.3, 128.3, 125.2, 124.4, 60.4, 52.7, 46.7, 12.5.



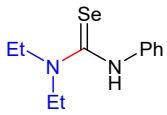
1-dodecyl-1-methyl-3-phenylthiourea (36c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5 with 94% isolated yield (77.9mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.25 (m, 2H), 7.17 (m, 2H), 3.76 (t, *J* = 7.68 Hz, 2H), 3.16 (s, 3H), 1.65 (m, 2H), 1.26 (m, 18H), 0.88 (t, *J* = 7.12 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.7 , 140.0 , 128.7 , 125.6 , 125.4 , 54.2 , 39.1 , 32.0 , 29.7 , 29.7 , 29.6 , 29.6 , 29.5 , 29.4 , 27.3 , 26.9 , 22.7 , 14.2 . HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{20}H_{34}N_2S$: 335.2515; found: 335.2507.



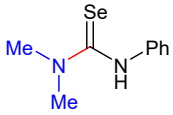
N-phenylmorpholine-4-carbothioamide (37c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3 with 60% isolated yield (66.6mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 5.4 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.15 (dd, *J* = 17.2, 7.8 Hz, 3H), 3.78 (dd, *J* = 6.4, 3.1 Hz, 4H), 3.69 (dd, *J* = 5.6, 3.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.5, 139.8, 129.1, 125.4, 123.3, 66.1, 49.6.



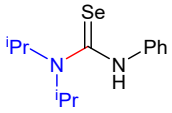
1,1,3-triphenylthiourea (38c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/4 with 24% isolated yield (36.5mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.69 (d, *J* = 10.4 Hz, 1H), 8.32 (s, 1H), 8.08 (d, *J* = 29.3 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.37 (m, 5H), 7.19 (m, 1H), 7.15 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 163.0, 159.6, 159.6, 137.0, 137.0, 136.8, 136.8, 129.7, 129.0, 125.3, 124.8, 120.1, 120.1, 118.8. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{19}H_{16}N_2S$: 305.1107; found: 305.1107.



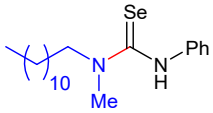
1,1-diethyl-3-phenylselenourea (1e): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2 with 56% isolated yield (71.7mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.28 (m, 2H), 3.82 (d, *J* = 5.2 Hz, 4H), 1.30 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.5, 140.5, 128.7, 126.7, 126.4, 41.6, 12.5. HRMS (ESI) *m/z:* [M+H]$^+$ calcd for $C_{11}H_{16}N_2Se$: 257.0551; found: 257.0551.



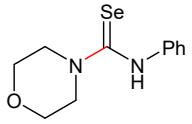
1,1-dimethyl-3-phenylselenourea (2e):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2 with 37% isolated yield (42.0mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 3H), 3.35 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.4, 140.3, 128.9, 126.0, 125.2, 36.4.



1,1-diisopropyl-3-phenylselenourea (3e): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5 with 42% isolated yield (59.4mg). m. p. = 112-114°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.27 (dd, *J* = 9.9, 5.6 Hz, 2H), 6.99 (dd, *J* = 10.8, 3.9 Hz, 1H), 6.22 (s, 1H), 3.98 (dt, *J* = 13.7, 6.9 Hz, 2H), 1.33 (s, 6H), 1.31 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 139.3, 128.8, 122.6, 119.6, 45.4, 21.5. HRMS (ESI) *m/z:* [M+H]$^+$ calcd for $C_{13}H_{20}N_2Se$: 285.0864; found: 285.0864.

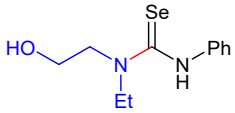


1-dodecyl-1-methyl-3-phenylselenourea (4e): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3 with 88% isolated yield (167.6mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.36 (m, 2H), 7.21 (t, *J* = 8.5 Hz, 3H), 3.84 (s, 2H), 3.20 (s, 3H), 1.73 (m, 2H), 1.28 (d, *J* = 18.3 Hz, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.5, 140.5, 128.7, 126.1, 125.9, 49.1, 34.6, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3., 27.1, 26.8, 22.6, 14.1. HRMS (ESI) *m/z:* [M+H]$^+$ calcd for $C_{20}H_{34}N_2Se$: 383.1960; found: 383.1960.

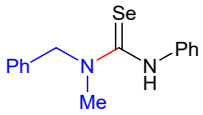


N-phenylmorpholine-4-carboselenoamide (5e):[2] yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2 with 26% isolated yield (34.9mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.35 (dd, *J* = 10.8, 5.0 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 3.90 (m, 4H), 3.74 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.8, 140.0, 129.4, 125.7, 122.9,

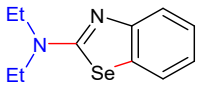
66.0, 52.1.



1-ethyl-1-(2-hydroxyethyl)-3-phenylselenourea (6e): red oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3 with 40% isolated yield (54.2mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.39 (m, 5H), 7.17 (t, *J* = 7.3 Hz, 1H), 3.96 (d, *J* = 6.8 Hz, 2H), 3.86 (m, 2H), 3.74 (d, *J* = 5.0 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.4, 141.0, 128.5, 125.4, 125.2, 61.5, 48.6, 42.6, 12.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{11}H_{16}N_2OSe$: 273.0501; found: 273.0501.



1-benzyl-1-methyl-3-phenylselenourea (7e): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/4 with 33% isolated yield (50.04mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.39 (m, 7H), 7.26 (m, 3H), 5.18 (s, 2H), 3.20 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.0, 140.4, 135.4, 129.0, 128.9, 128.8, 128.0, 127.4, 127.3, 126.4, 126.2, ,123.2, 120.1, 52.3, 34.8. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{15}H_{16}N_2Se$: 305.0551; found: 305.0551.

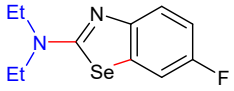


N,N-diethylbenzo[d][1,3]selenazol-2-amine (1f):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/20 with 60% isolated yield (76.2mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.46 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.21 (m, 1H), 6.88 (td, *J* = 7.7, 1.2 Hz, 1H), 3.46 (q, *J* = 7.1 Hz, 4H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 155.1, 133.3, 126.1, 123.8, 120.8, 119.8, 46.5, 13.0.

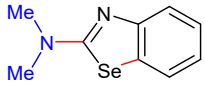
6-chloro-N,N-diethylbenzo[d][1,3]selenazol-2-amine (2f): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/10 with 74% isolated yield (106.43mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.2 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.21 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.52 (q, *J* = 7.1 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 153.7, 134.3, 126.4, 125.7, 123.4, 120.3, 46.6, 12.9. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{11}H_{13}ClN_2Se$: 289.0005; found: 289.0005.

N,N-diethyl-5-methylbenzo[d][1,3]selenazol-2-amine (3f): yellow oil was obtained by column

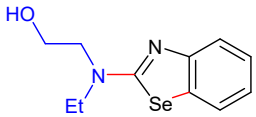
chromatography (eluent: EtOAc/petroleum ether = 1/10 with 64% isolated yield (86.4mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.38 (s, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 3.53 (q, *J* = 7.1 Hz, 4H), 2.37 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H). 13C NMR (126 MHz, CDCl3) δ 167.7, 155.3, 135.9, 129.7, 123.3, 122.0, 120.4, 46.4, 21.4, 13.0. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{12}H_{16}N_2Se$: 269.0551; found: 269.0551.



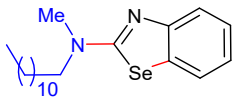
N,N-diethyl-6-fluorobenzo[d][1,3]selenazol-2-amine (4f): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/10 with 65% isolated yield (88.1mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.32 (dd, *J* = 8.0, 2.7 Hz, 1H), 6.98 (td, *J* = 8.9, 2.7 Hz, 1H), 3.52 (q, *J* = 7.1 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 157.5 (d, *J* = 240.4 Hz), 151.5 (d, *J* = 1.6 Hz), 133.7 (d, *J* = 9.6 Hz), 119.9 (d, *J* = 8.3 Hz), 113.4 (d, *J* = 23.4 Hz), 110.5 (d, *J* = 26.1 Hz), 46.4, 13.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -122.6. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{11}H_{13}FN_2Se$: 273.0301; found: 273.0301.



N,N-dimethylbenzo[d][1,3]selenazol-2-amine (5f): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/10 with 34% isolated yield (38.2mg). m. p. = 110-112°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.28 (dd, *J* = 11.9, 4.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 3.19 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 155.0, 133.8, 126.2, 123.9, 121.0, 120.1, 41.0. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_9H_{10}N_2Se$: 227.0082; found: 227.0082.



2-(benzo[d][1,3]selenazol-2-yl(ethyl)amino)ethan-1-ol (6f): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3 with 39% isolated yield (52.4mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.52 (m, 1H), 7.30 (m, 1H), 6.99 (td, *J* = 7.8, 1.0 Hz, 1H), 4.84 (s, 1H), 3.94 (m, 2H), 3.79 (m, 2H), 3.46 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 153.6, 132.8, 126.3, 123.9, 121.5, 119.9, 62.9, 54.1, 50.8, 12.9. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{11}H_{14}N_2OSe$: 271.0344; found: 271.0344.



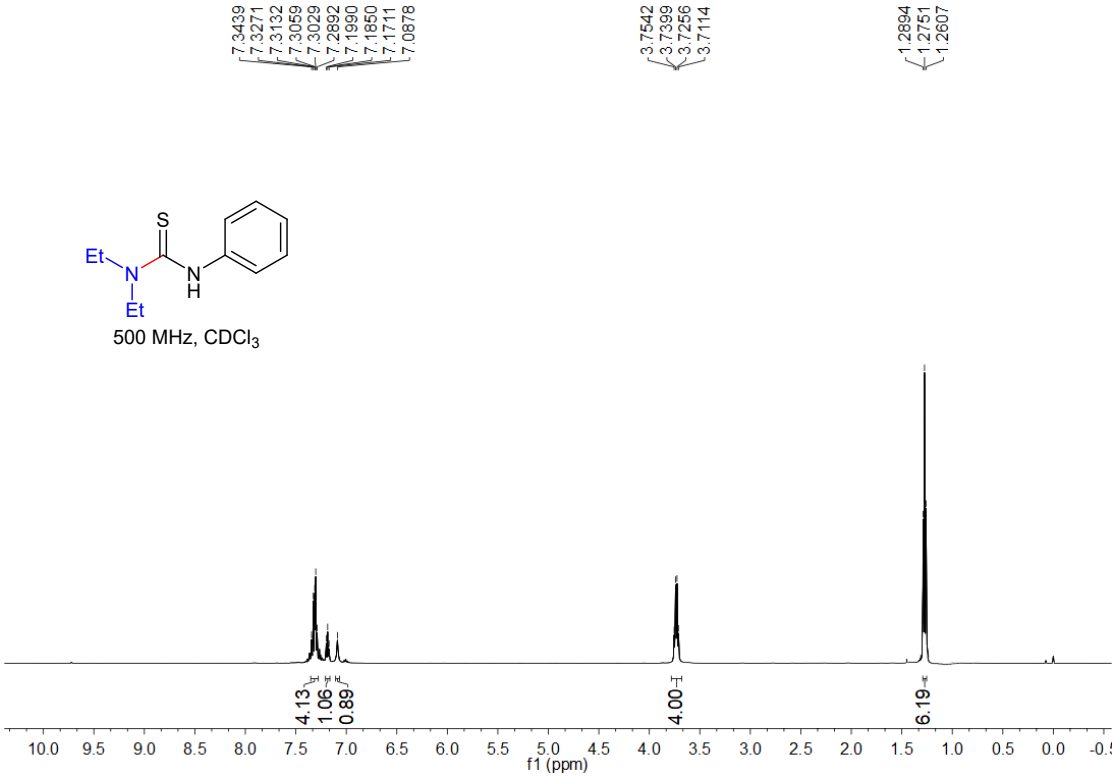
N-dodecyl-N-methylbenzo[d][1,3]selenazol-2-amine (7f): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/10 with 65% isolated yield (123.2mg). ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.62 (td, *J* = 7.9, 1.2 Hz, 1H), 7.5 (m, 1H), 7.28 (m, 1H), 6.96 (td, *J* = 7.7, 1.1 Hz, 1H), 3.48 (m, 2H), 3.17 (s, 3H), 1.72 (m, 2H), 1.32 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 155.0, 139.0, 126.1, 123.8, 120.9, 119.9, 54.9, 38.6, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 27.3, 26.8, 22.7, 14.1. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{20}H_{32}N_2Se$: 381.1803; found: 381.1803.

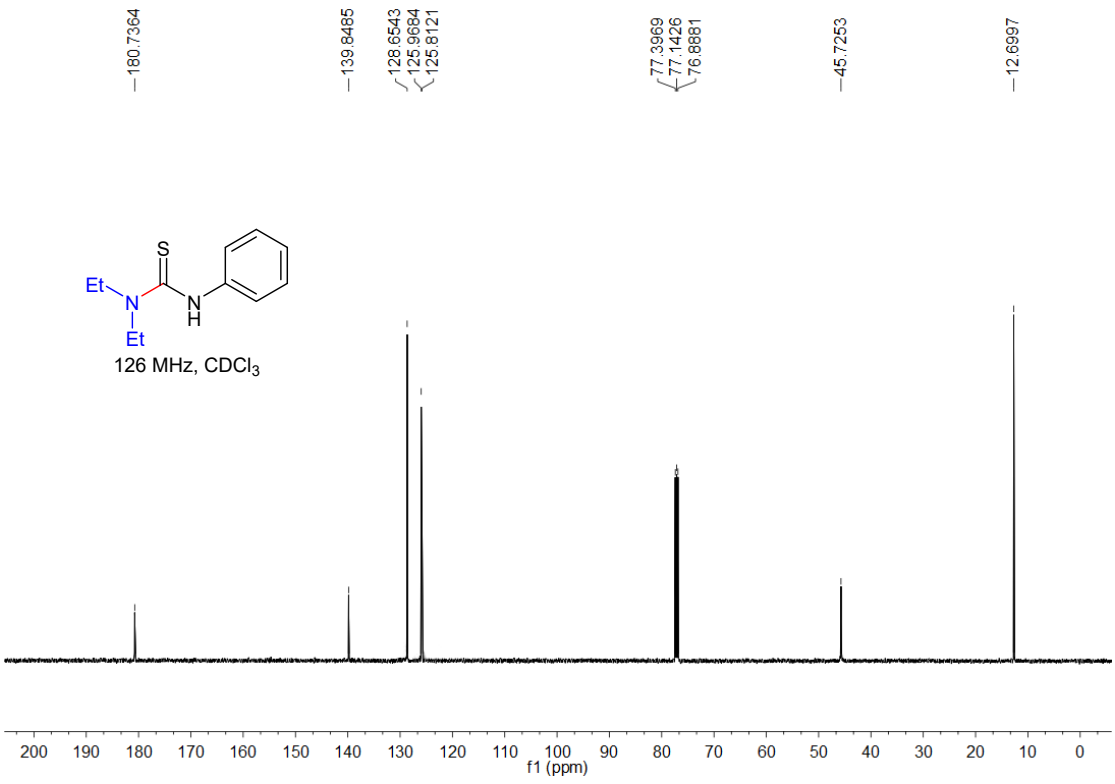
7. Copies of product NMR Spectra

1c

^{1}H NMR

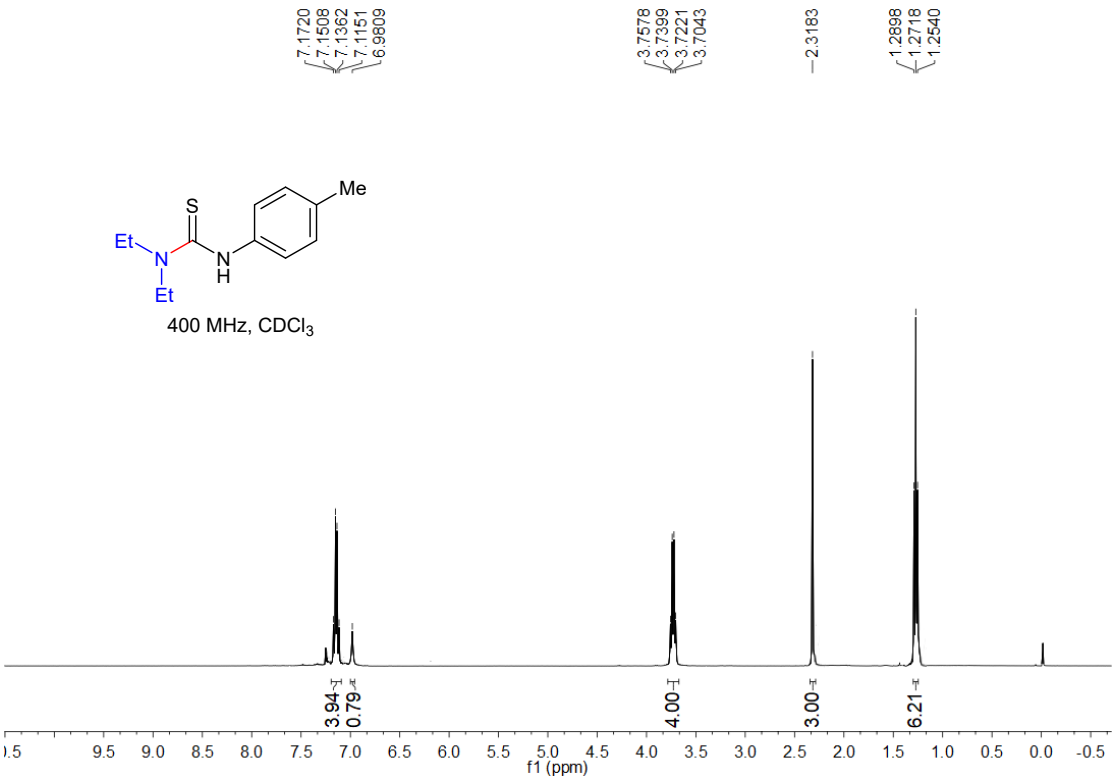


^{13}C NMR

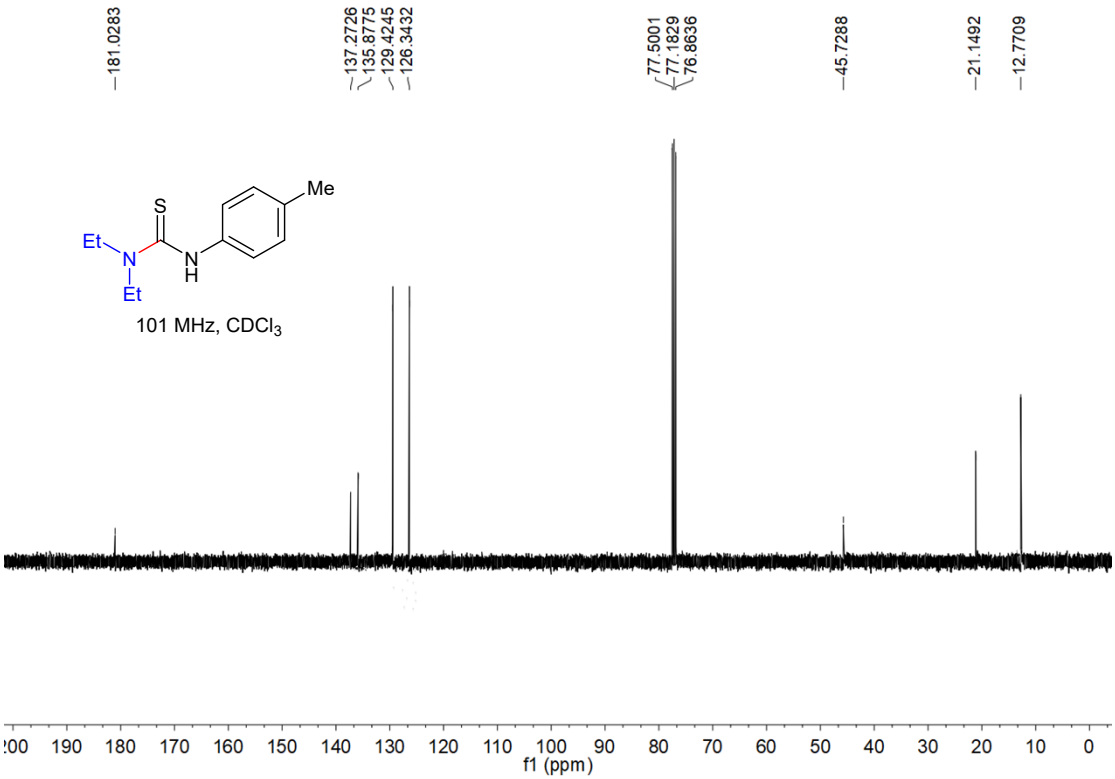


2c

^{1}H NMR

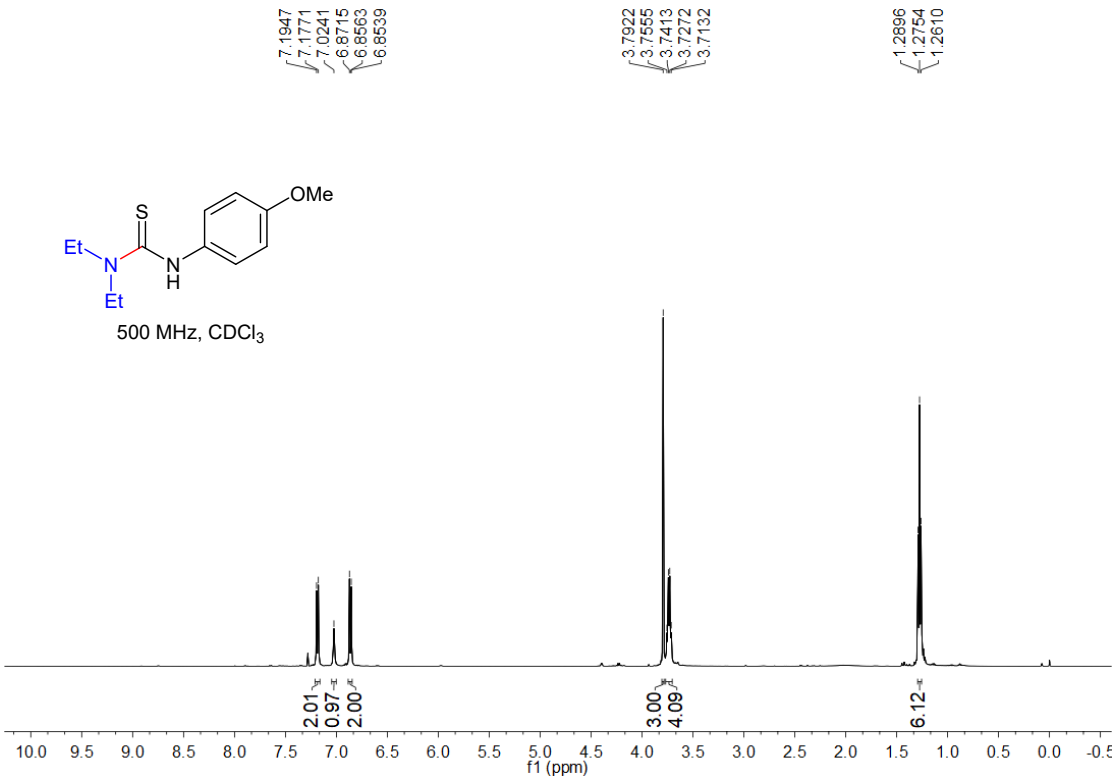


^{13}C NMR

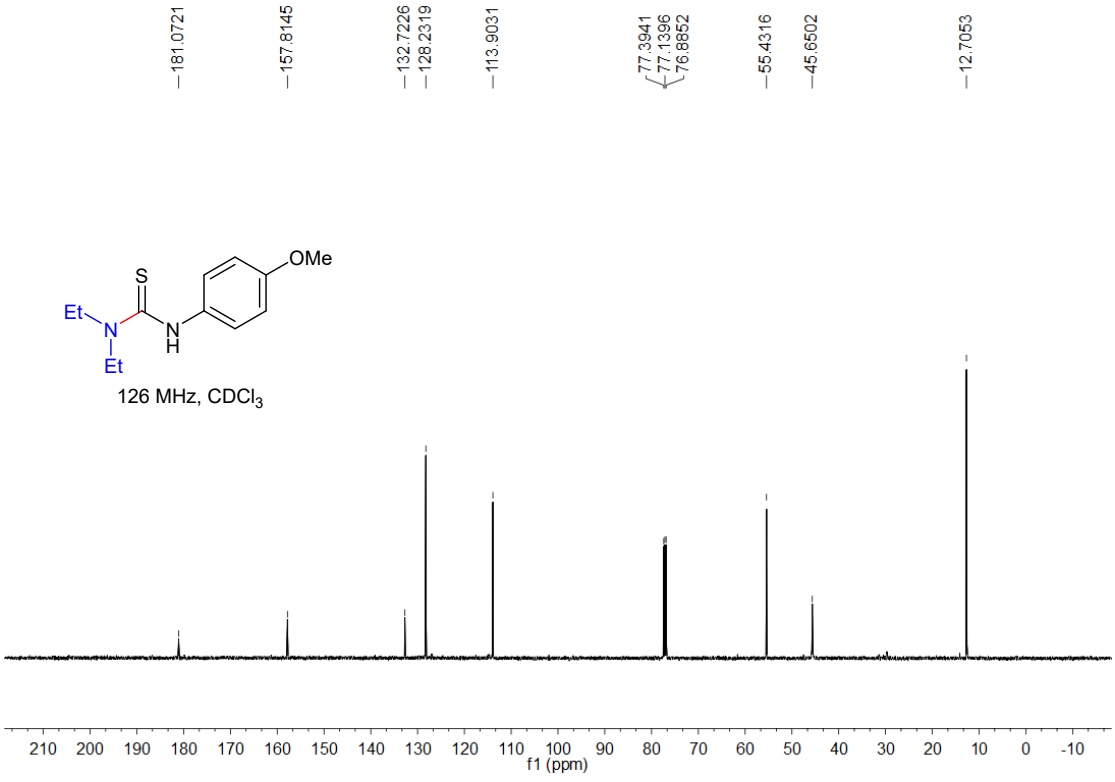


3c

^{1}H NMR

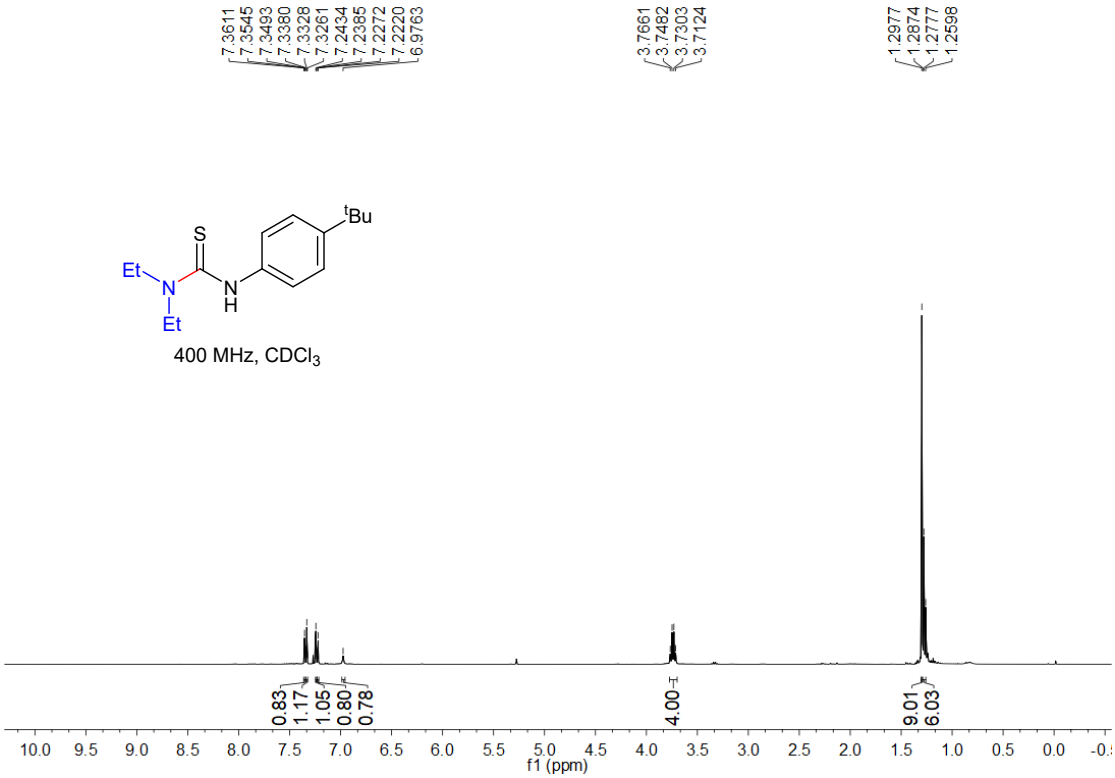


^{13}C NMR

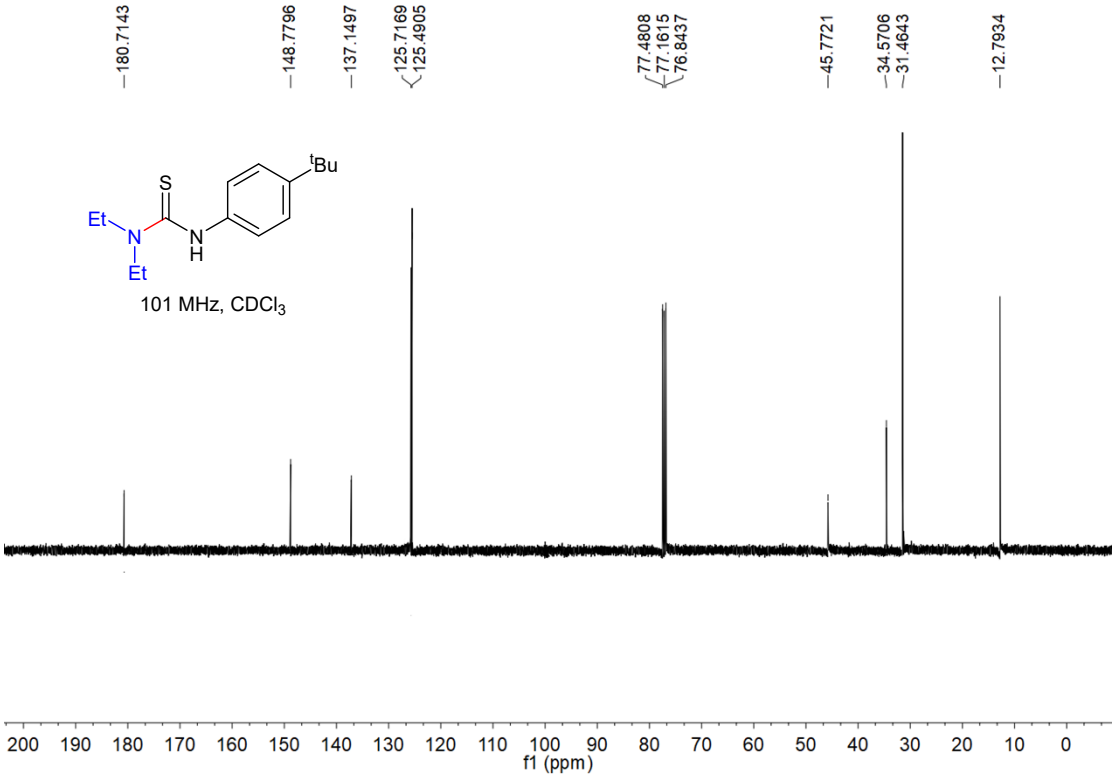


4c

^{1}H NMR

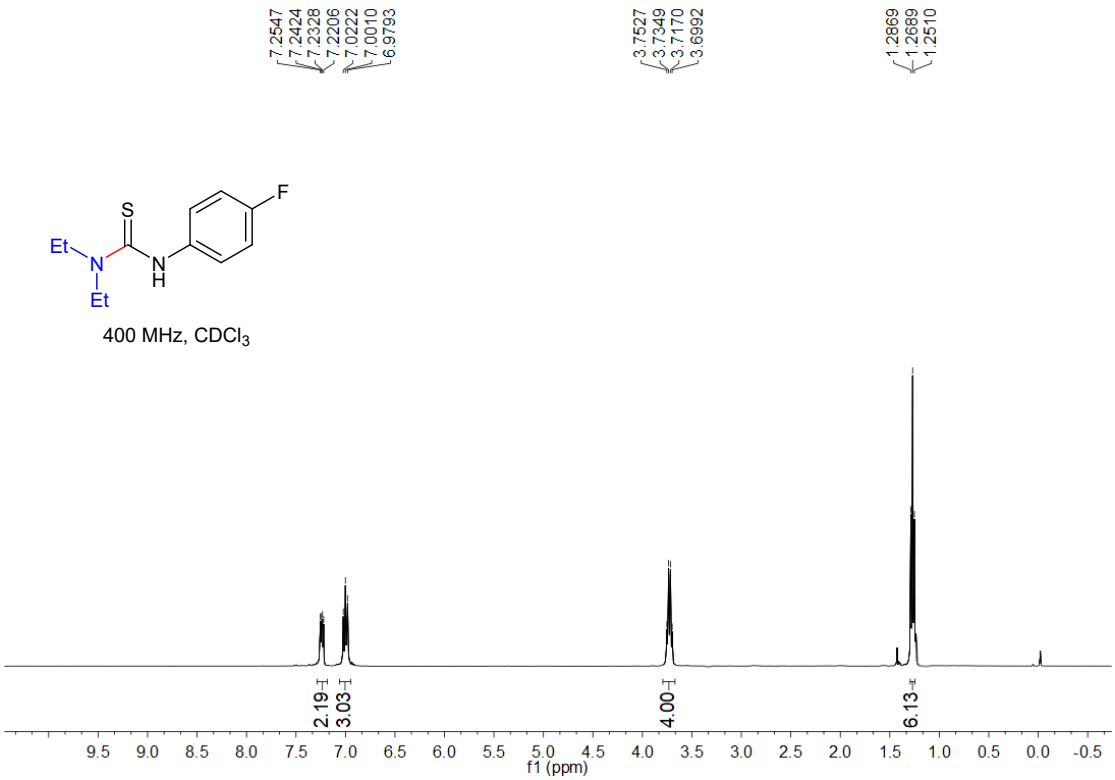


^{13}C NMR

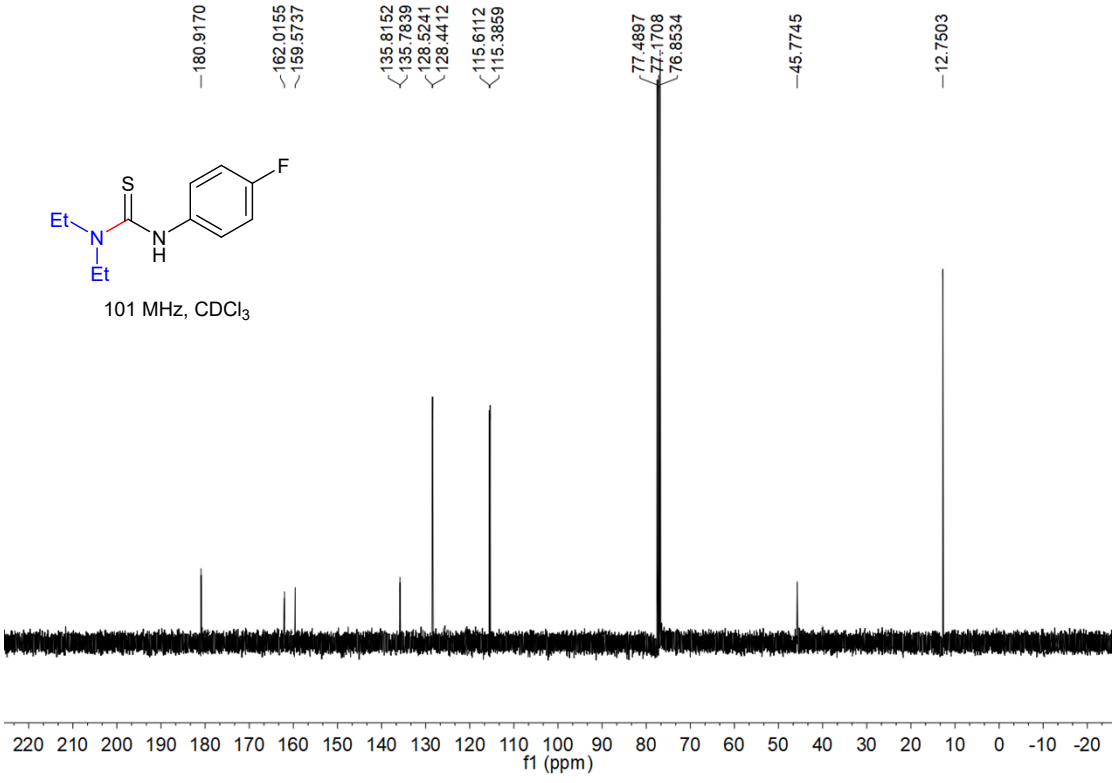


5c

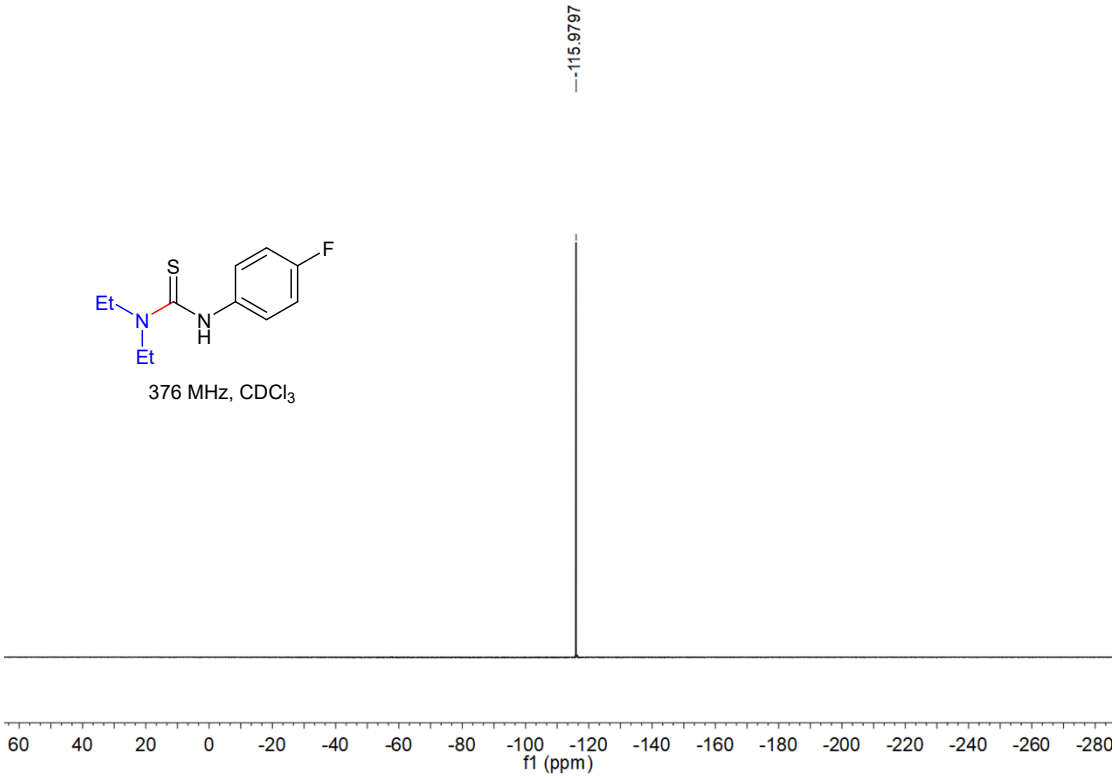
^{1}H NMR



^{13}C NMR

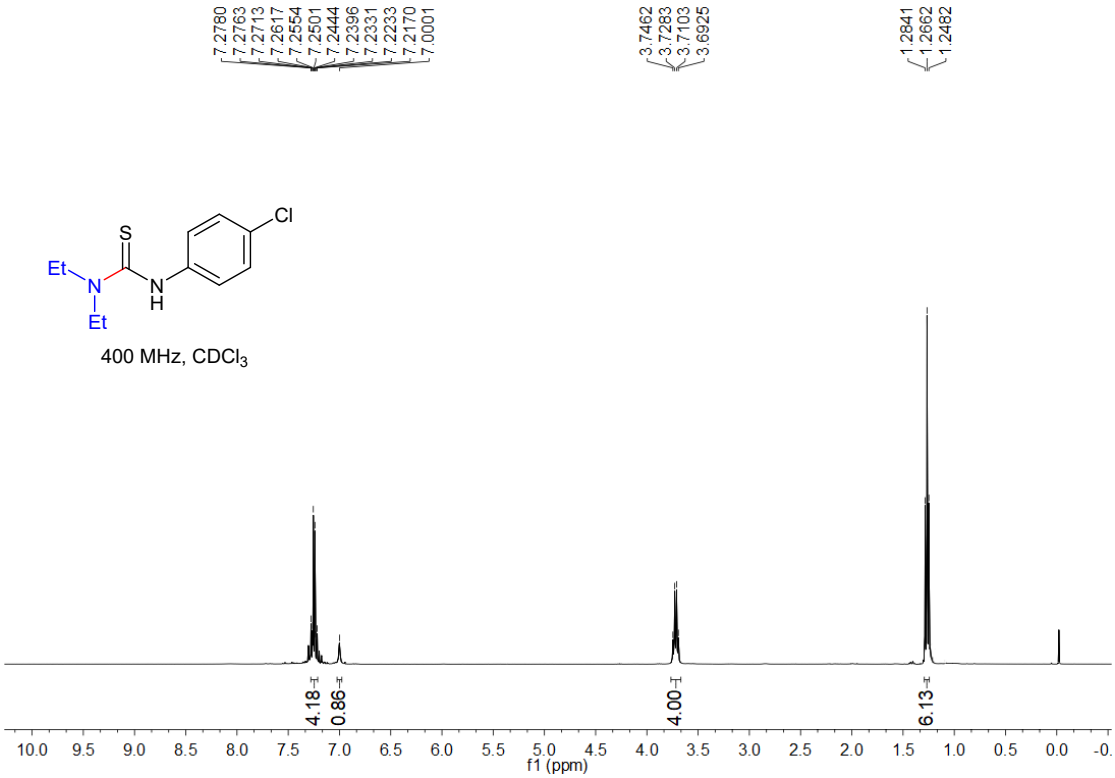


^{19}F NMR

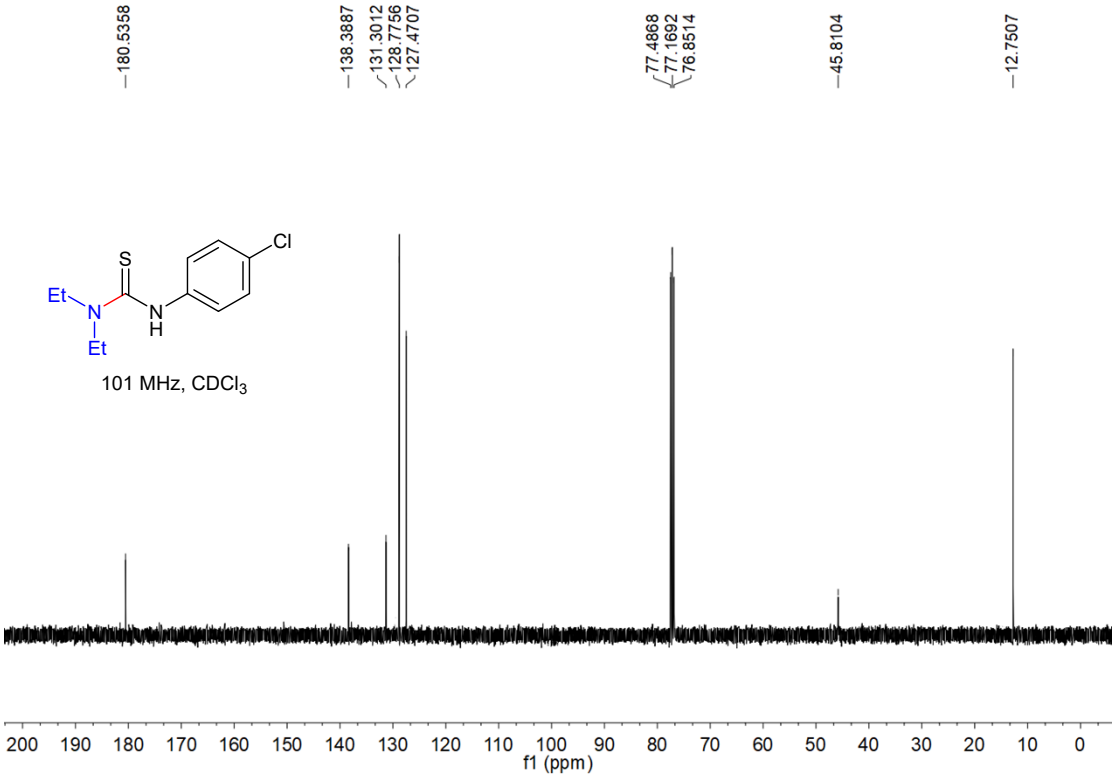

-115.9797
F
S
Et
N
N
H
Et
376 MHz, CDCl3
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

6c

^{1}H NMR

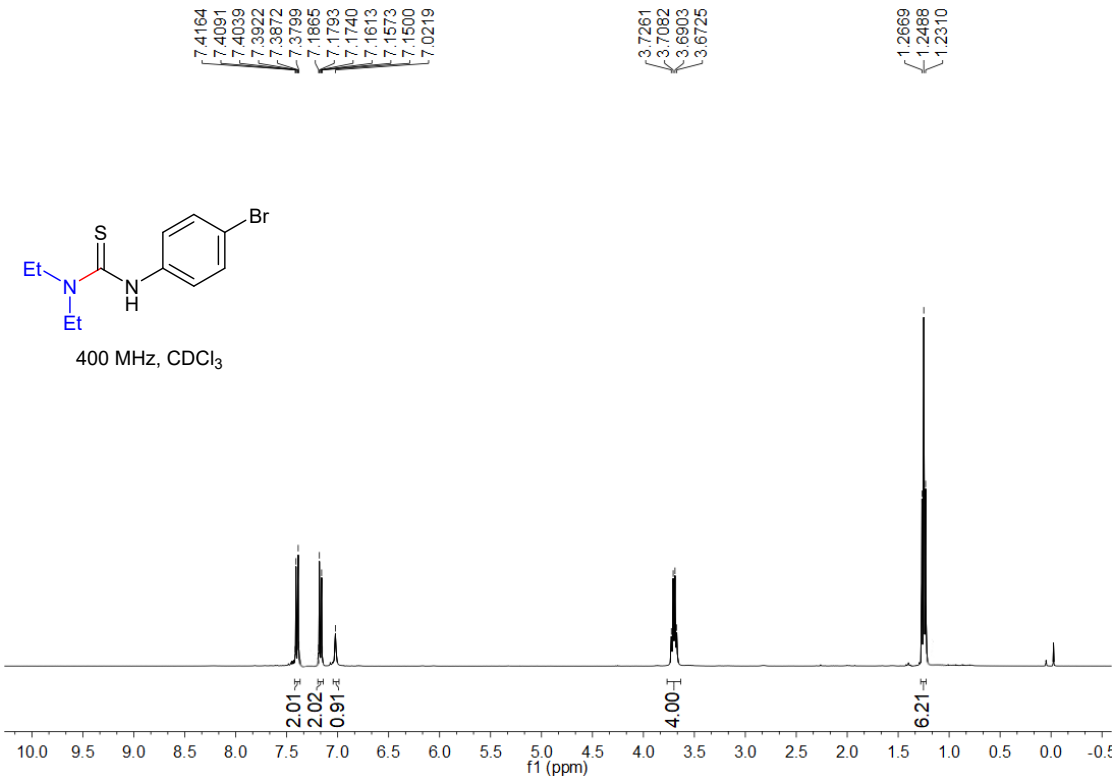


^{13}C NMR

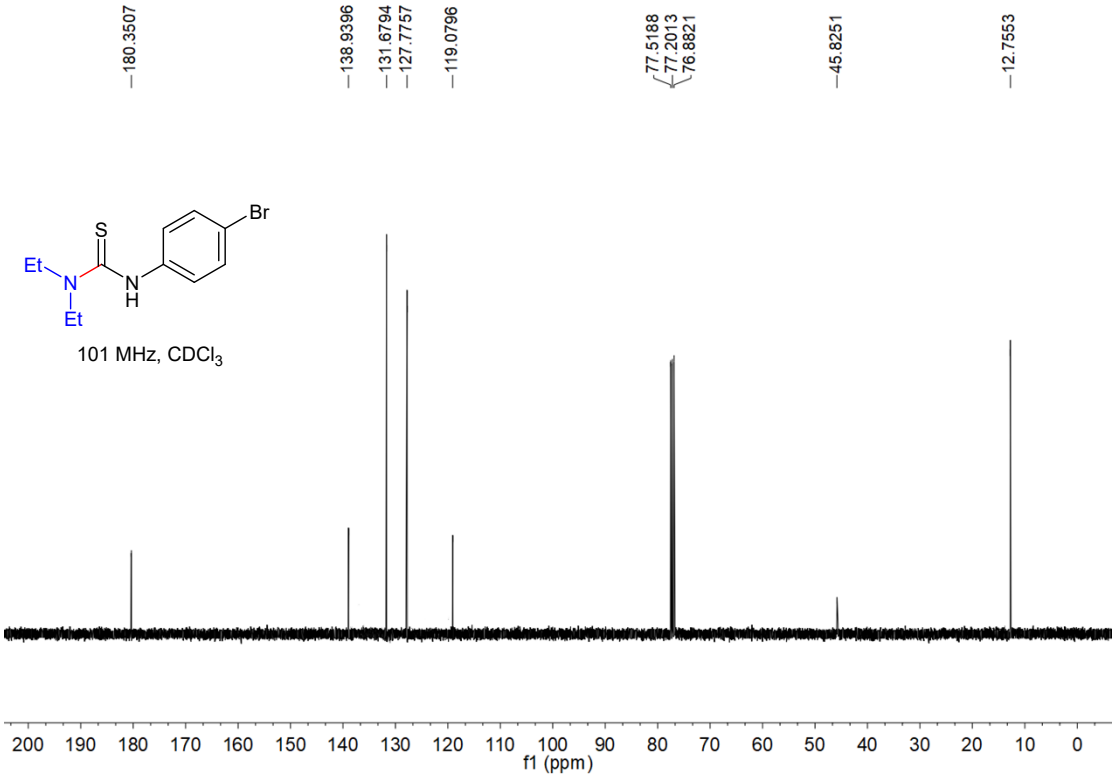


7c

^{1}H NMR

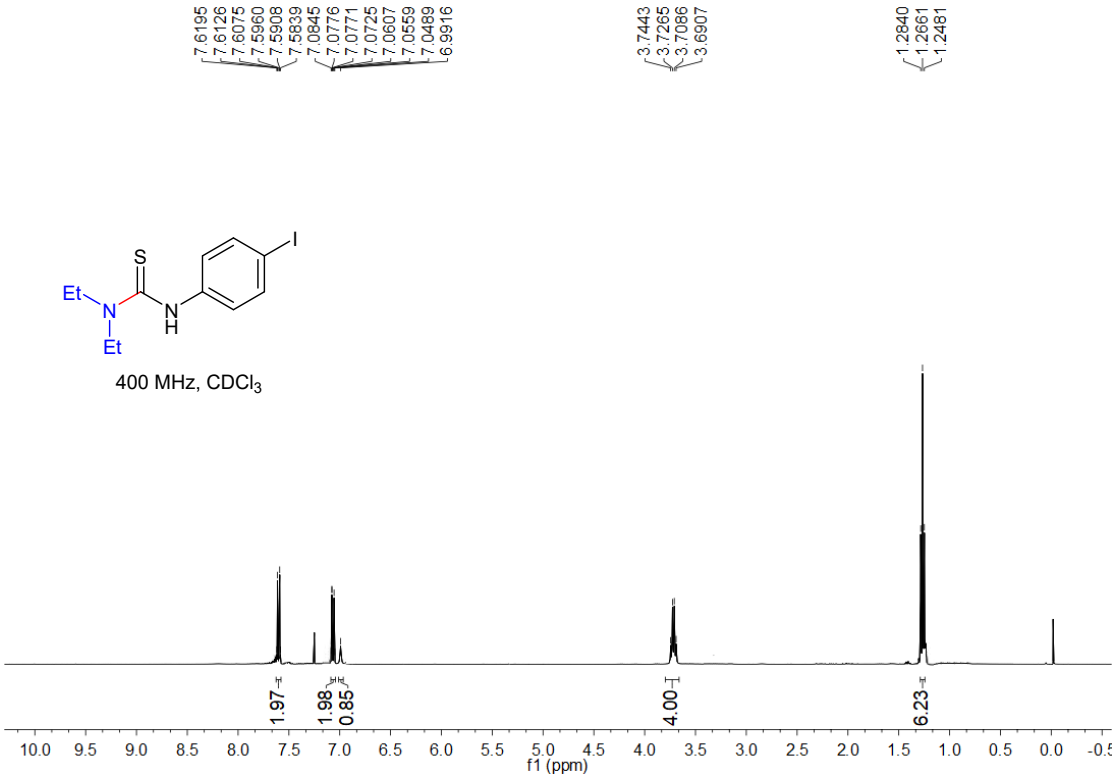


^{13}C NMR

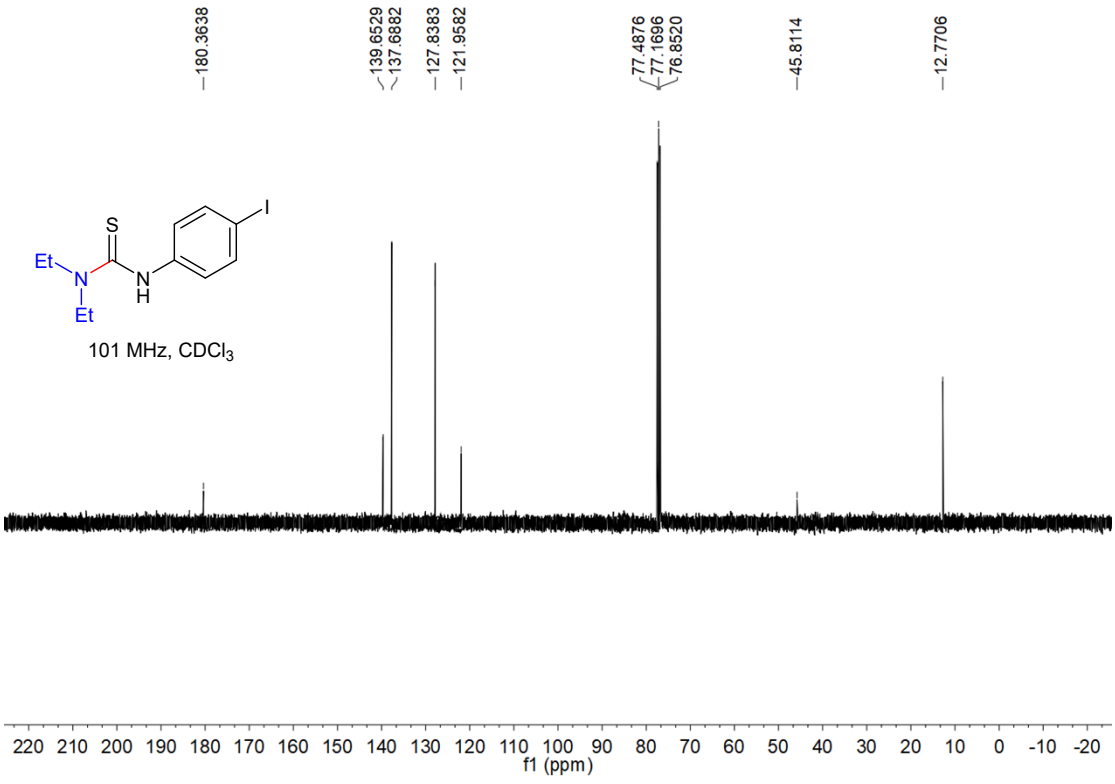


8c

^{1}H NMR

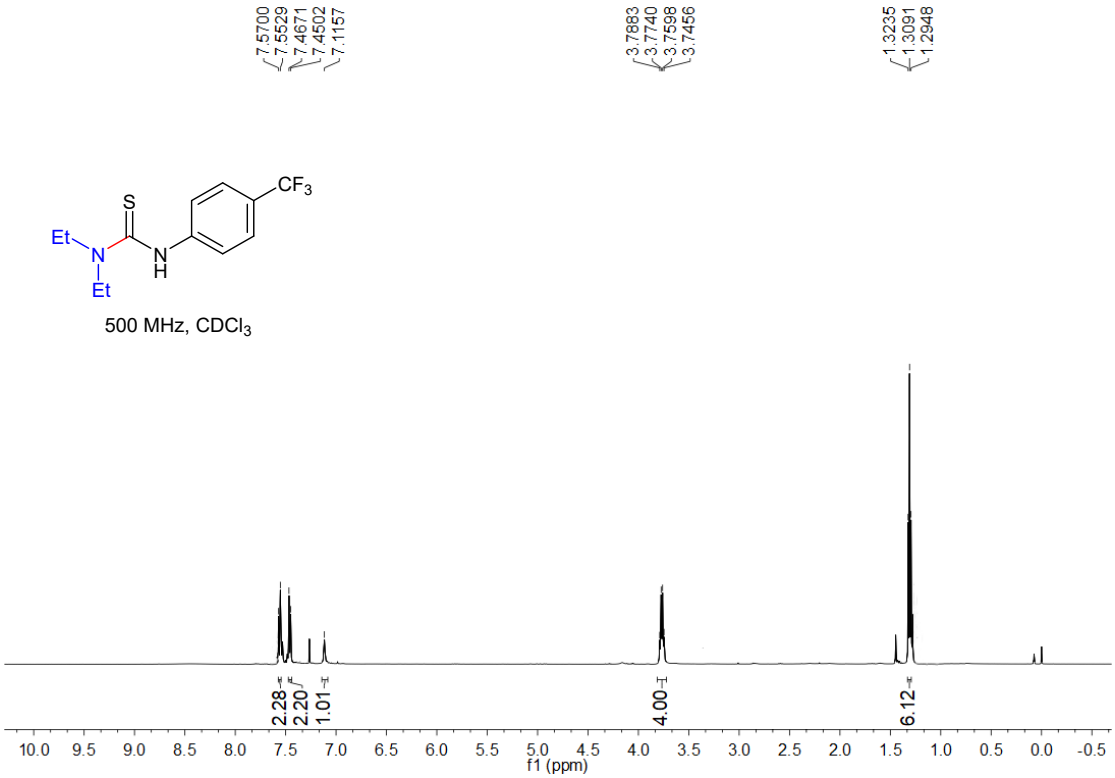


^{13}C NMR

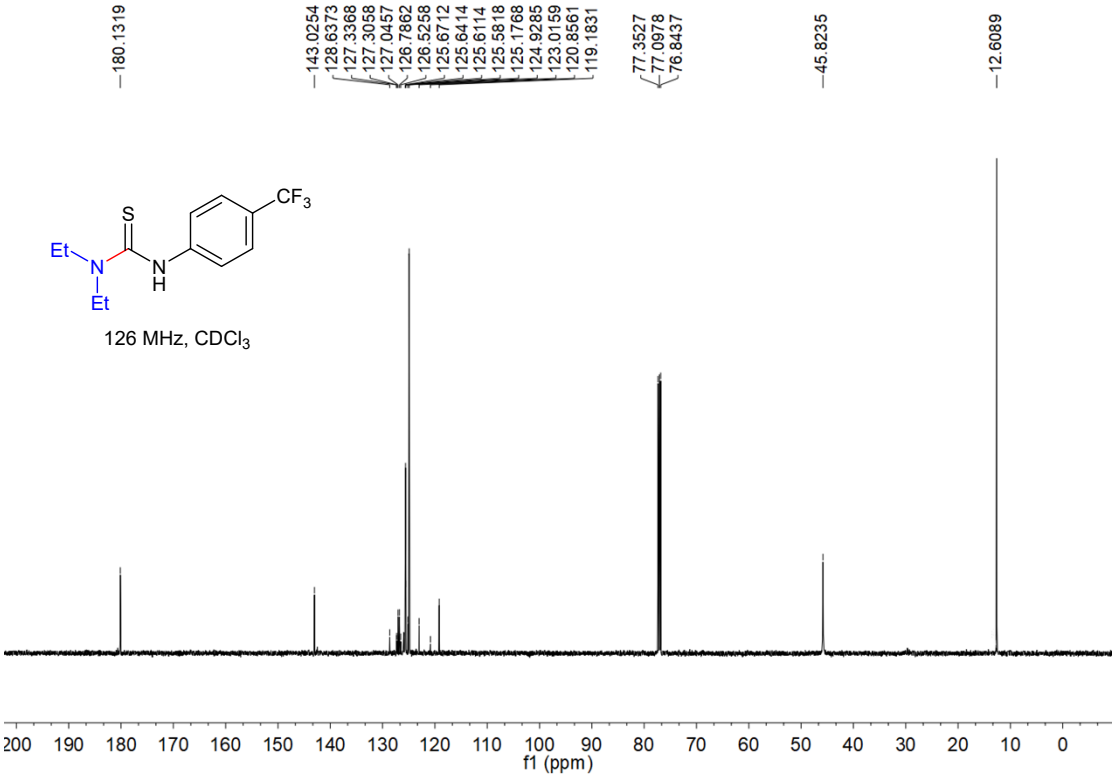


9c

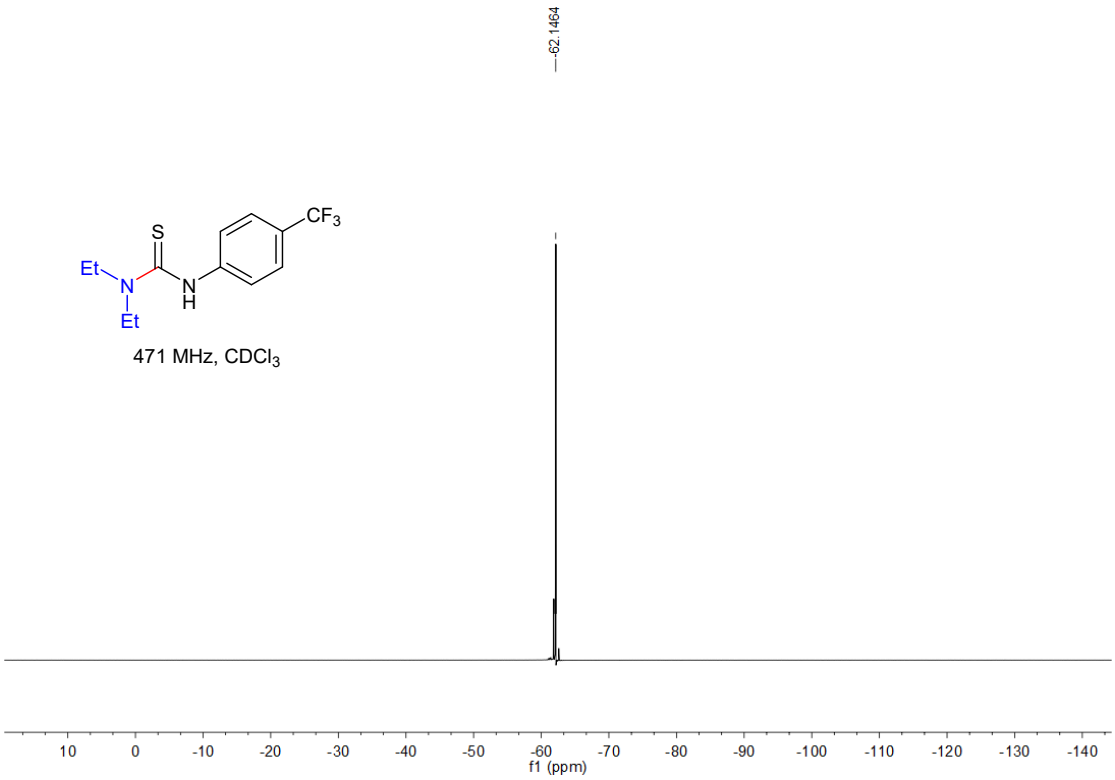
^{1}H NMR



^{13}C NMR

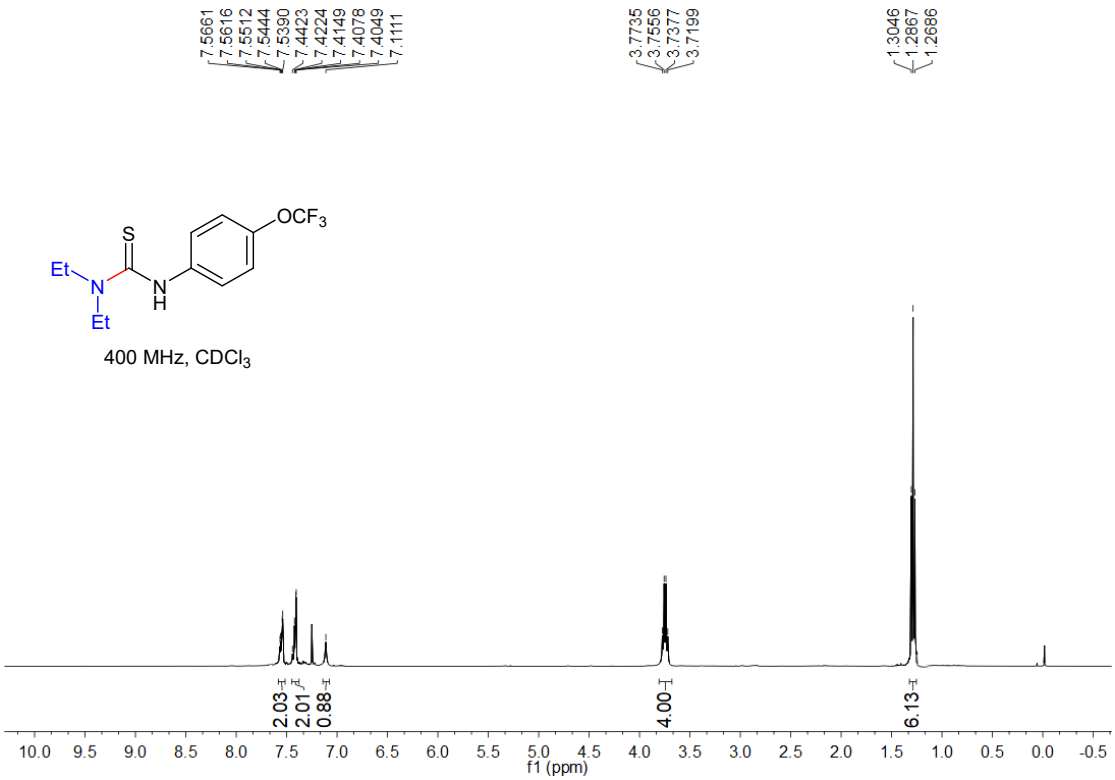


^{19}F NMR

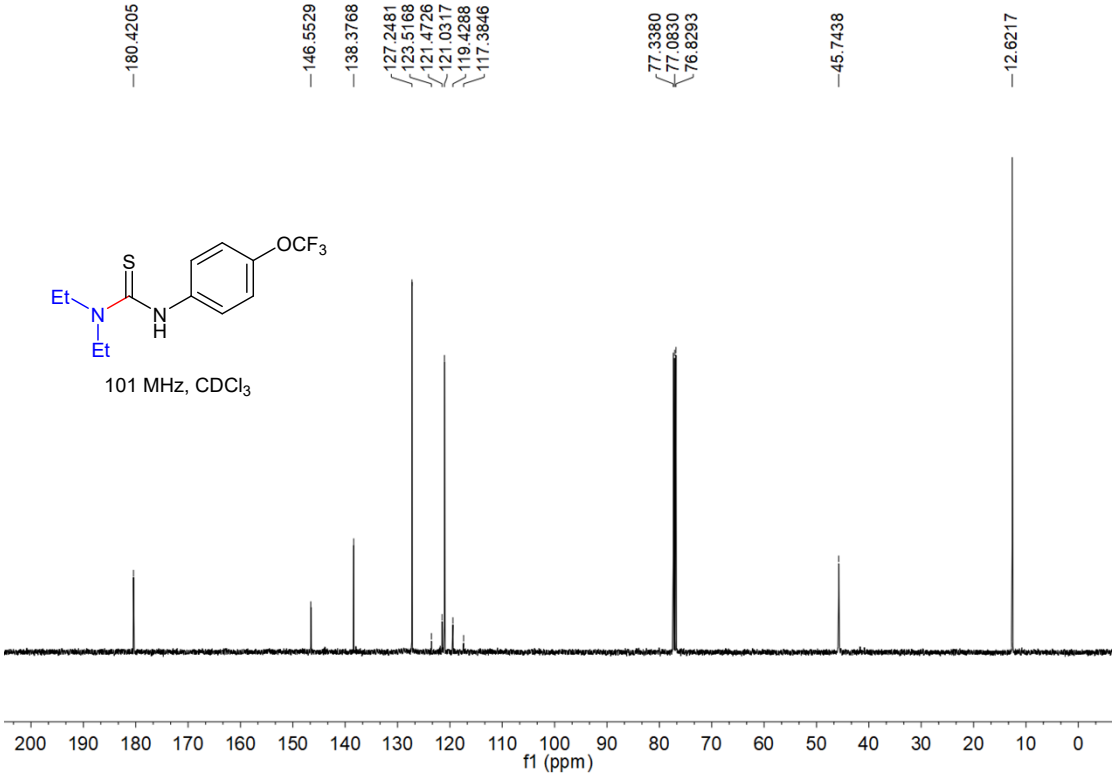

-62.1464
S
Et
N
N
H
Et
CF3
471 MHz, CDCl3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

10c

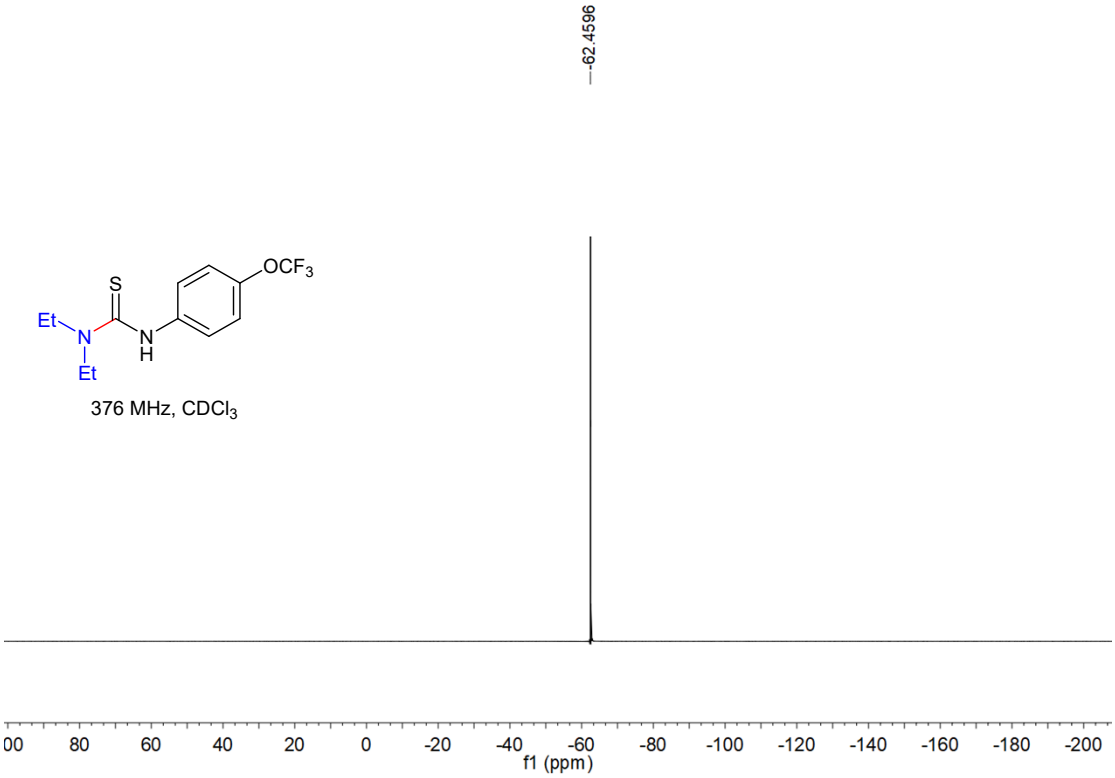
^{1}H NMR



^{13}C NMR

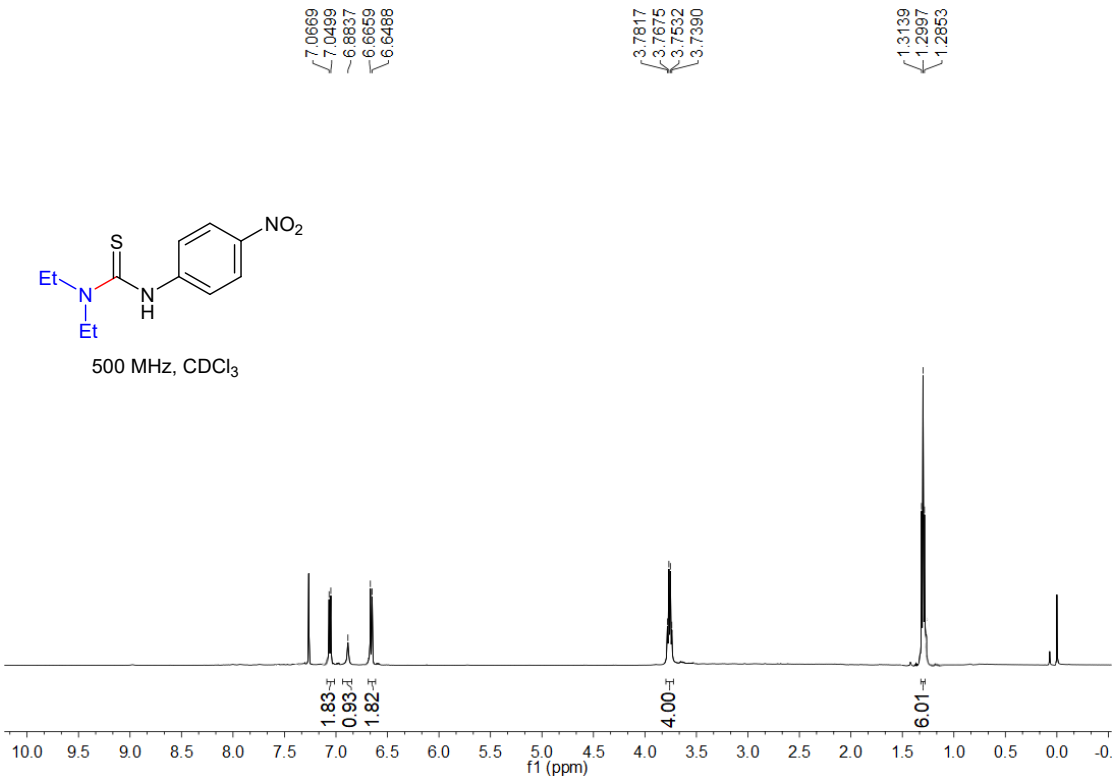


^{19}F NMR

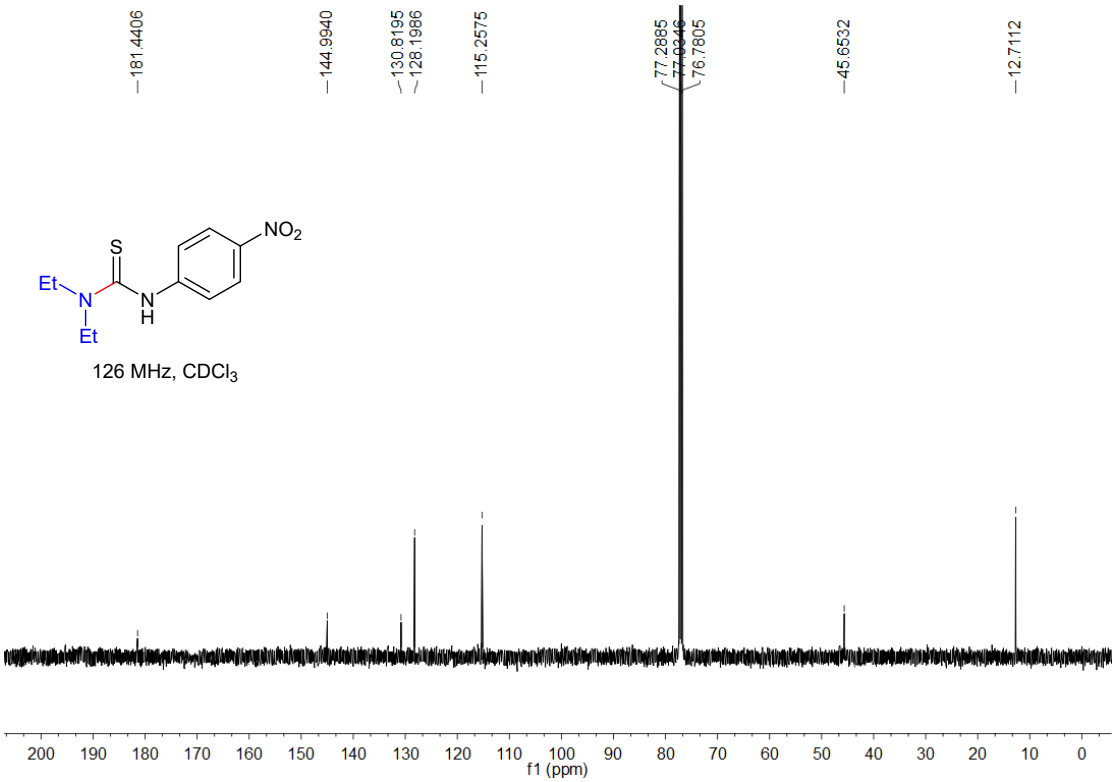

-62.4596
OCF3
S
Et
N
N
H
Et
376 MHz, CDCl3
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

11c

^{1}H NMR

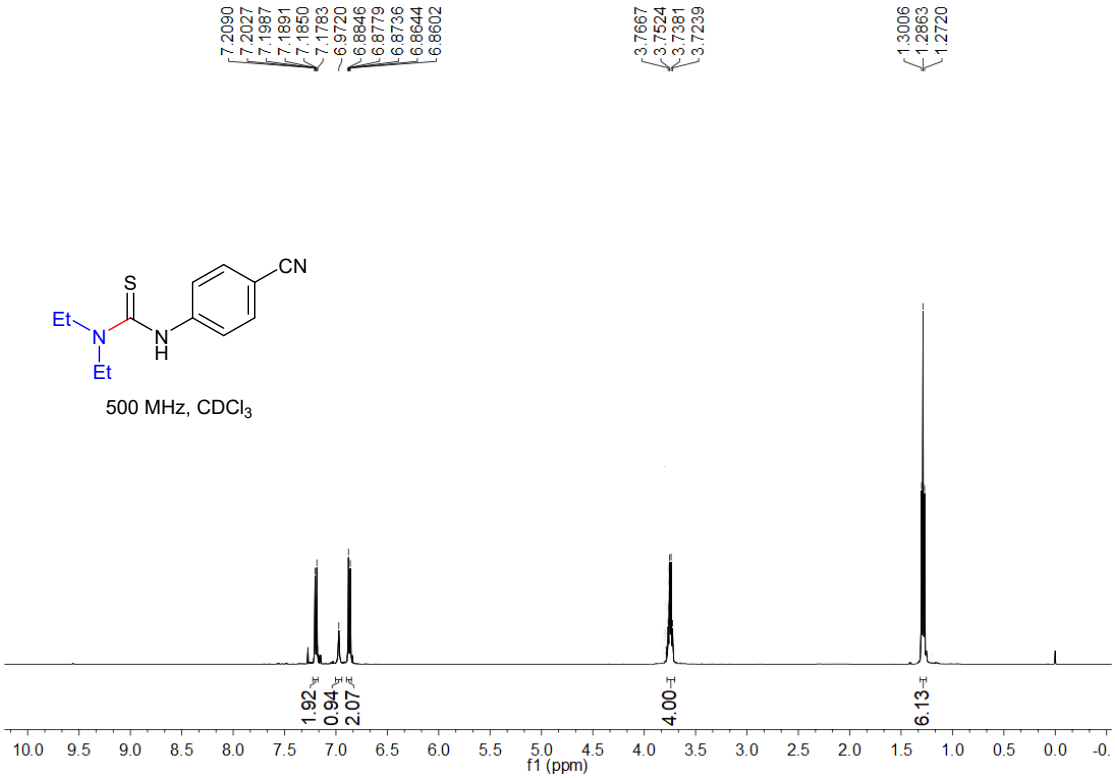


^{13}C NMR

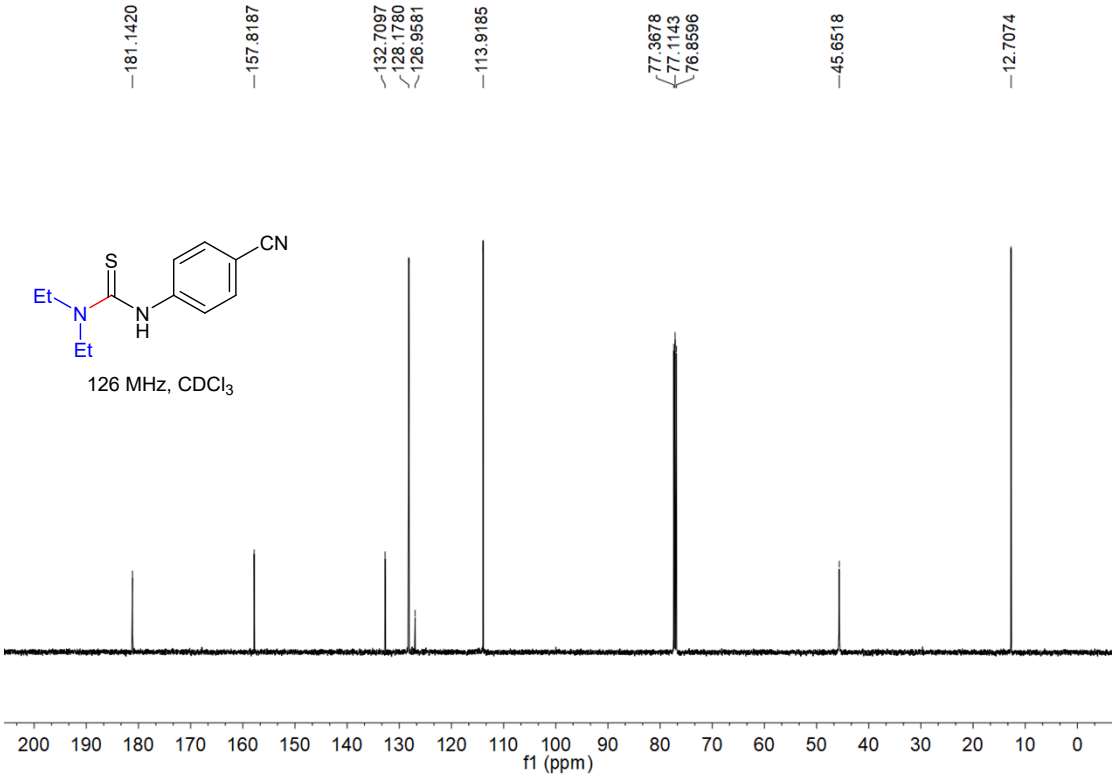


12c

^{1}H NMR

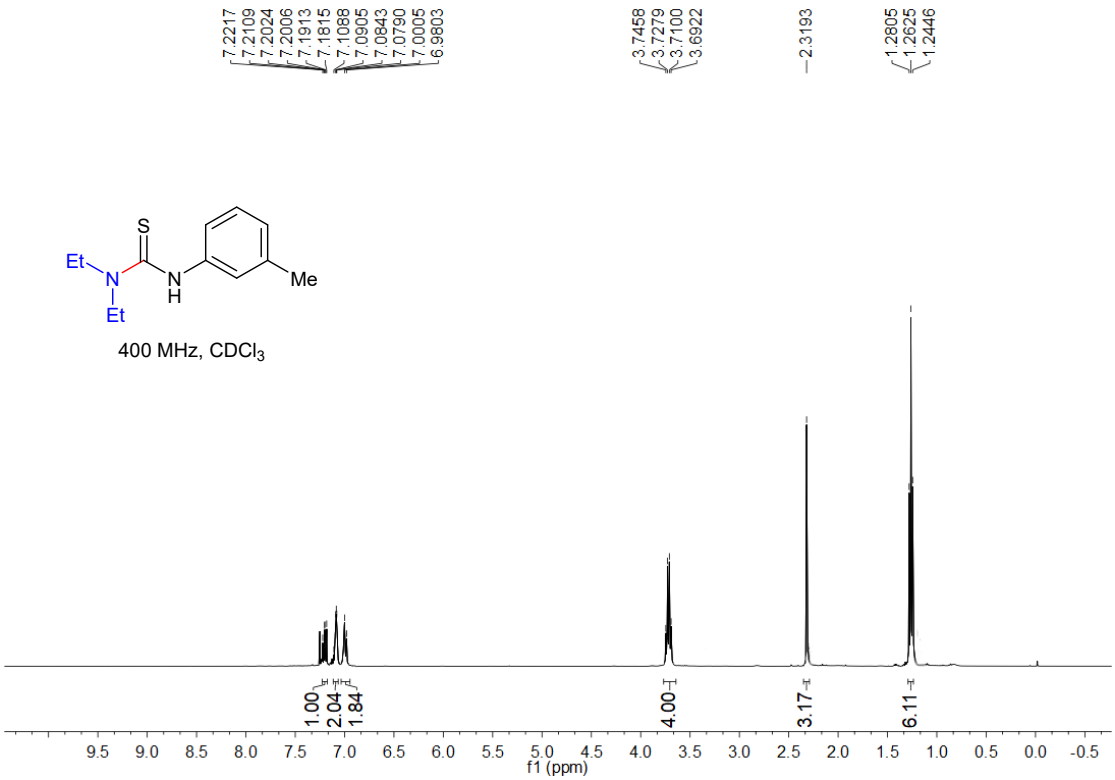


^{13}C NMR

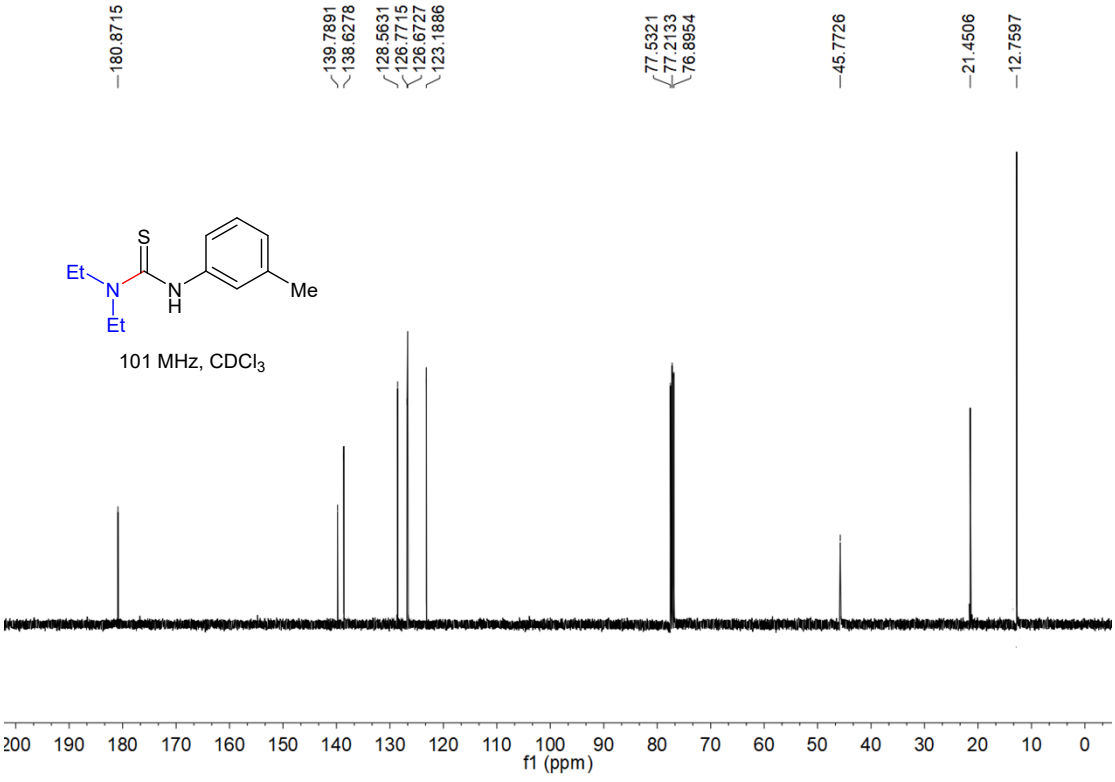


13c

^{1}H NMR

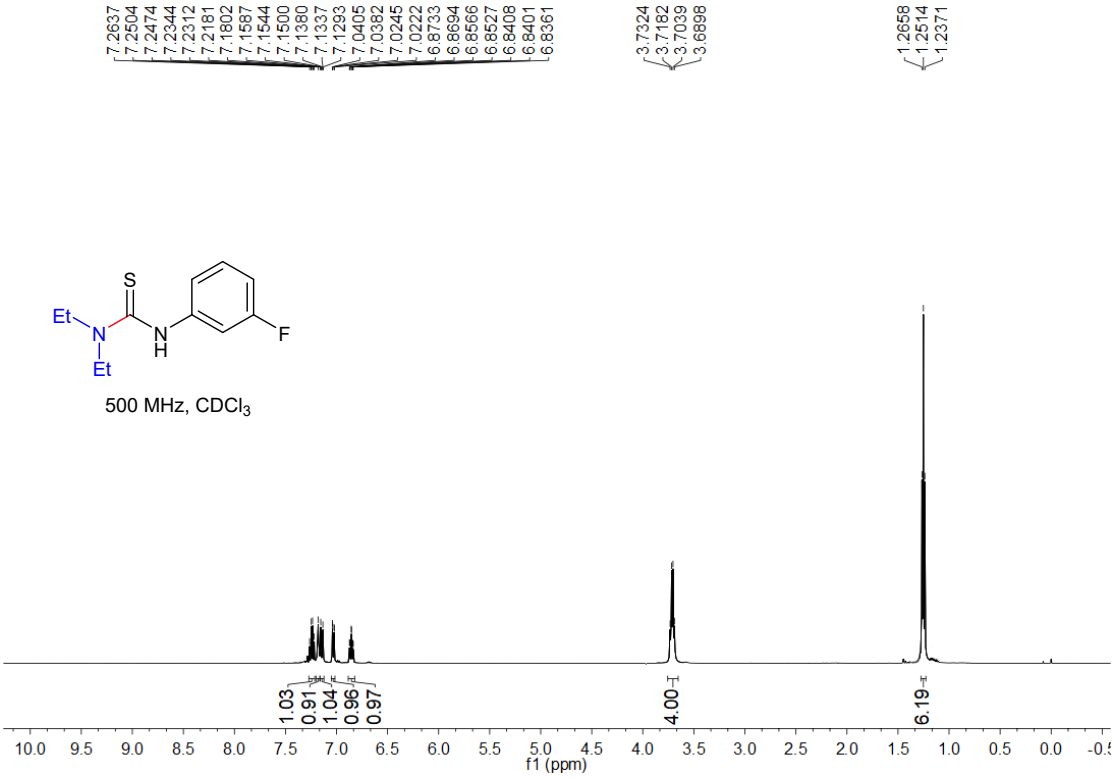


^{13}C NMR

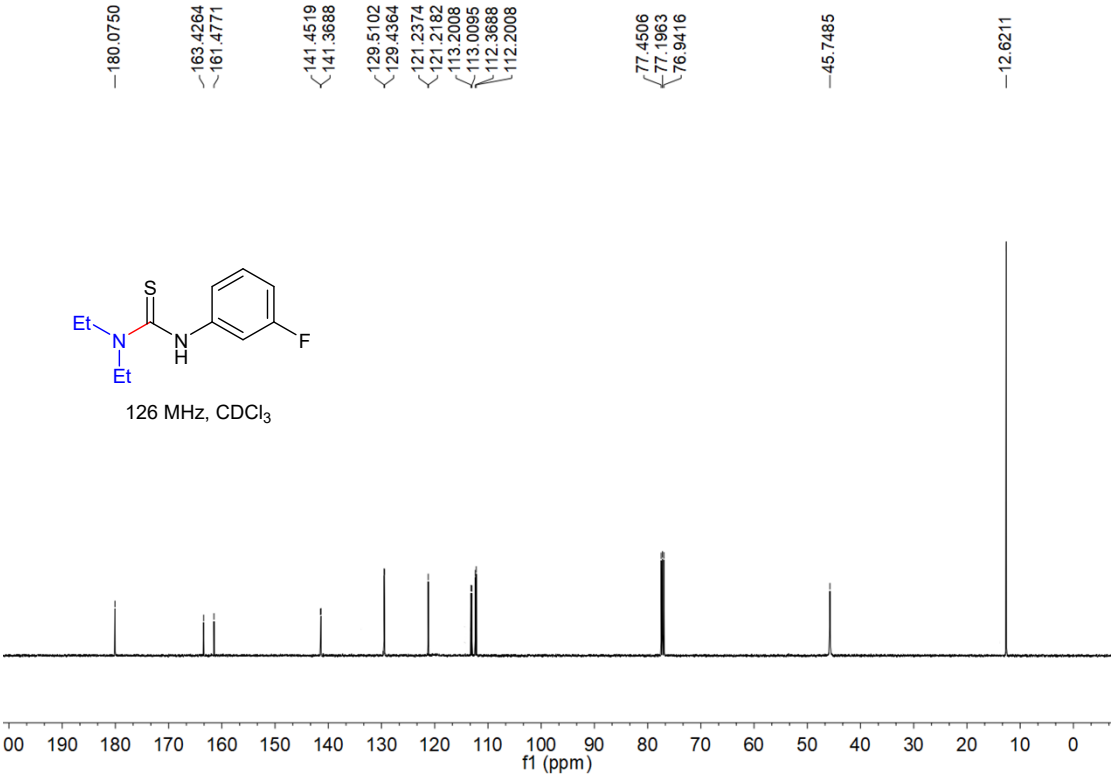


14c

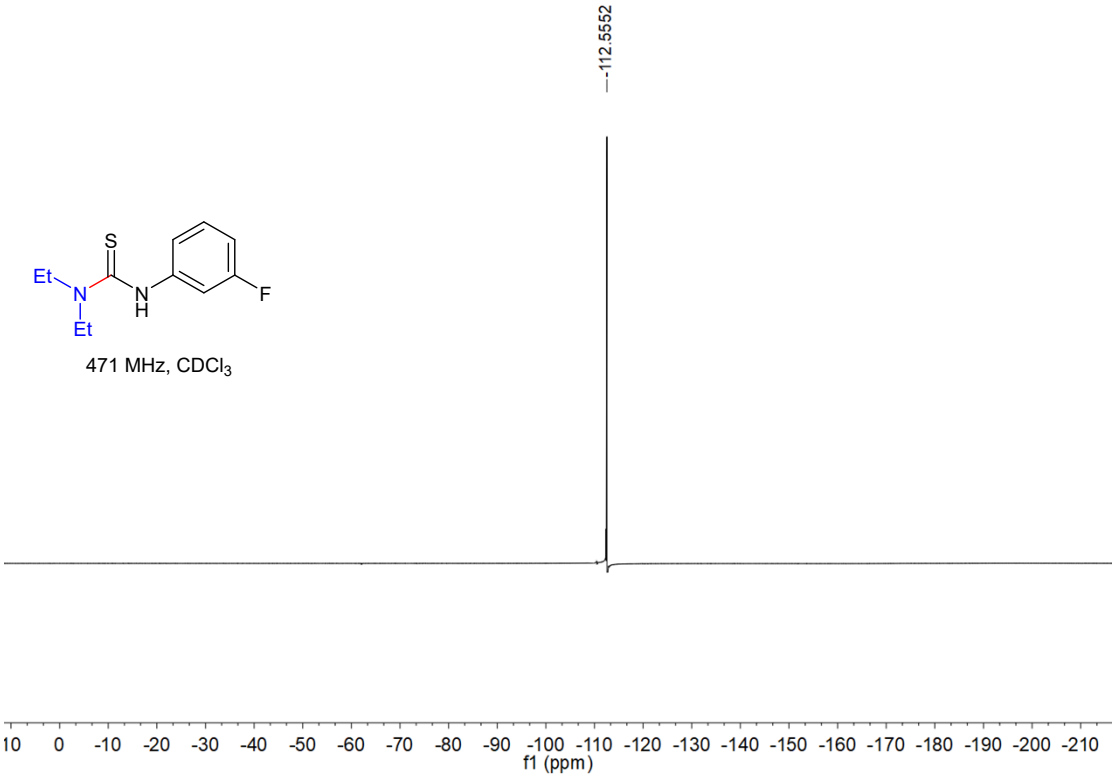
^{1}H NMR



^{13}C NMR

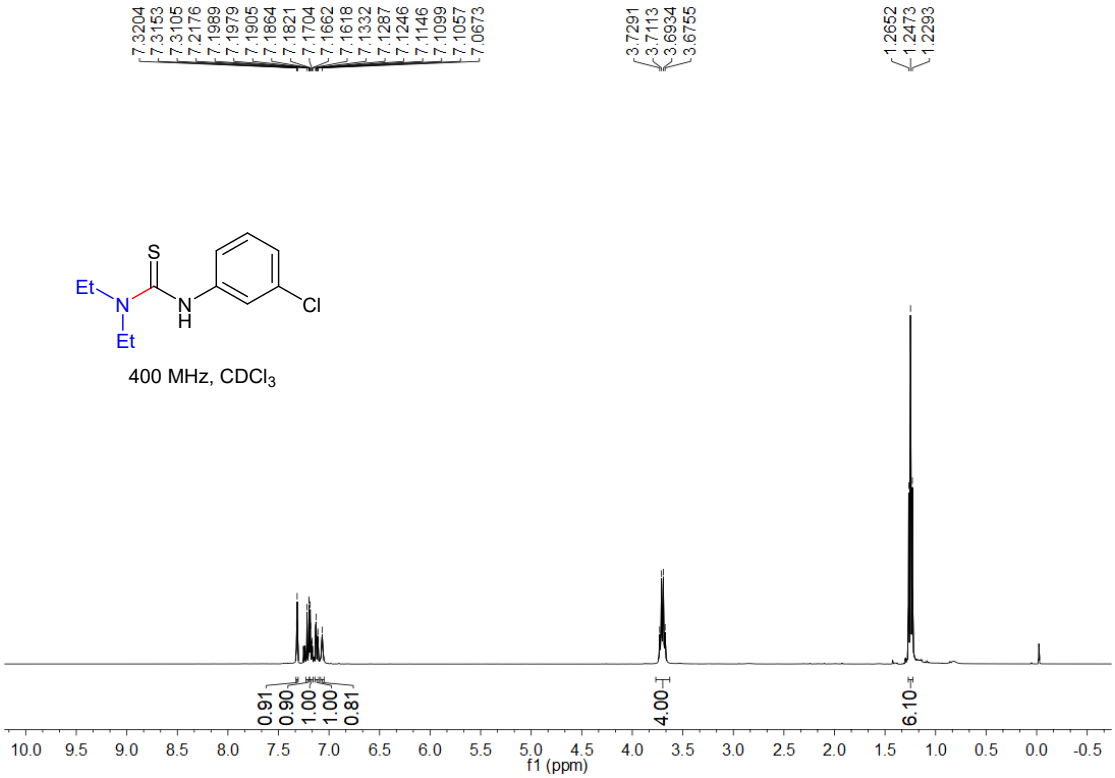


^{19}F NMR

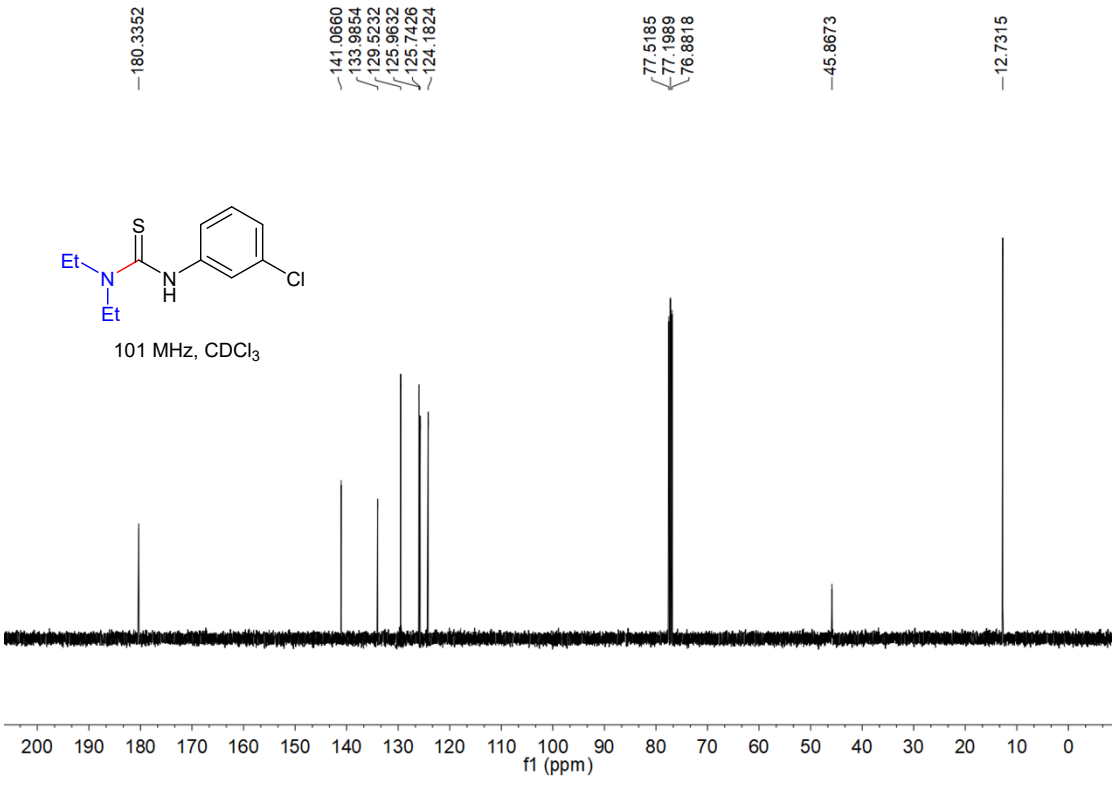

-112.5552
S
Et
N
Et
N
H
F
471 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

15c

^{1}H NMR

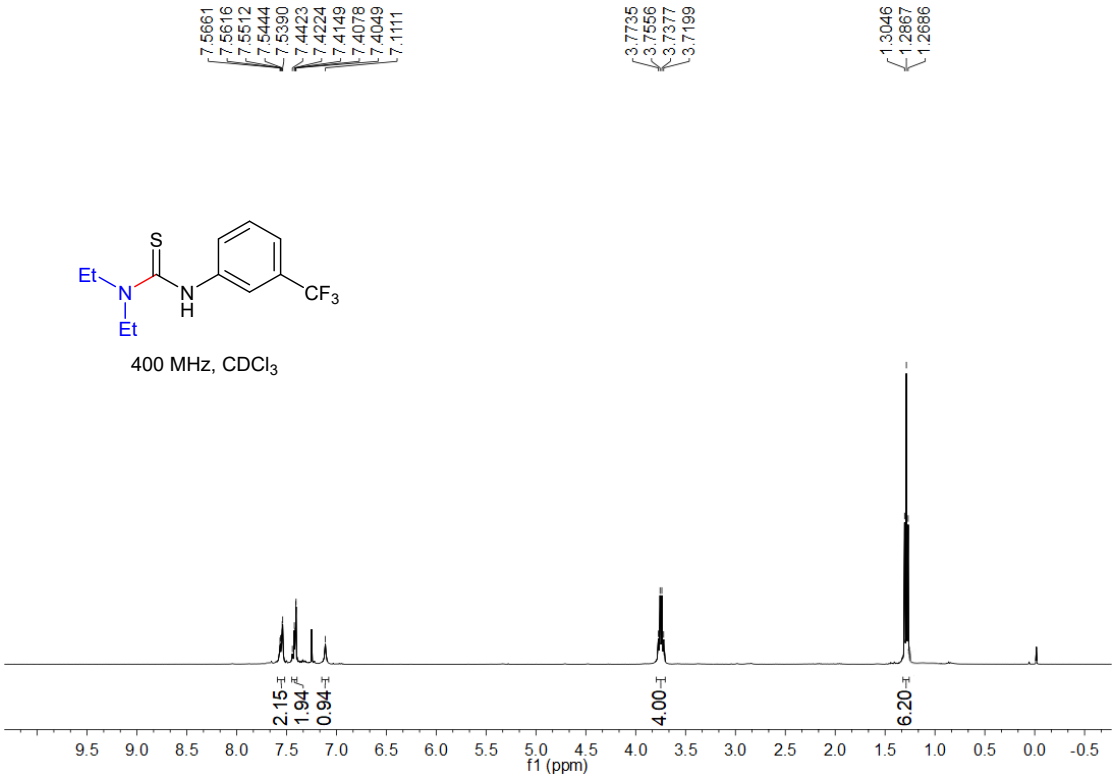


^{13}C NMR

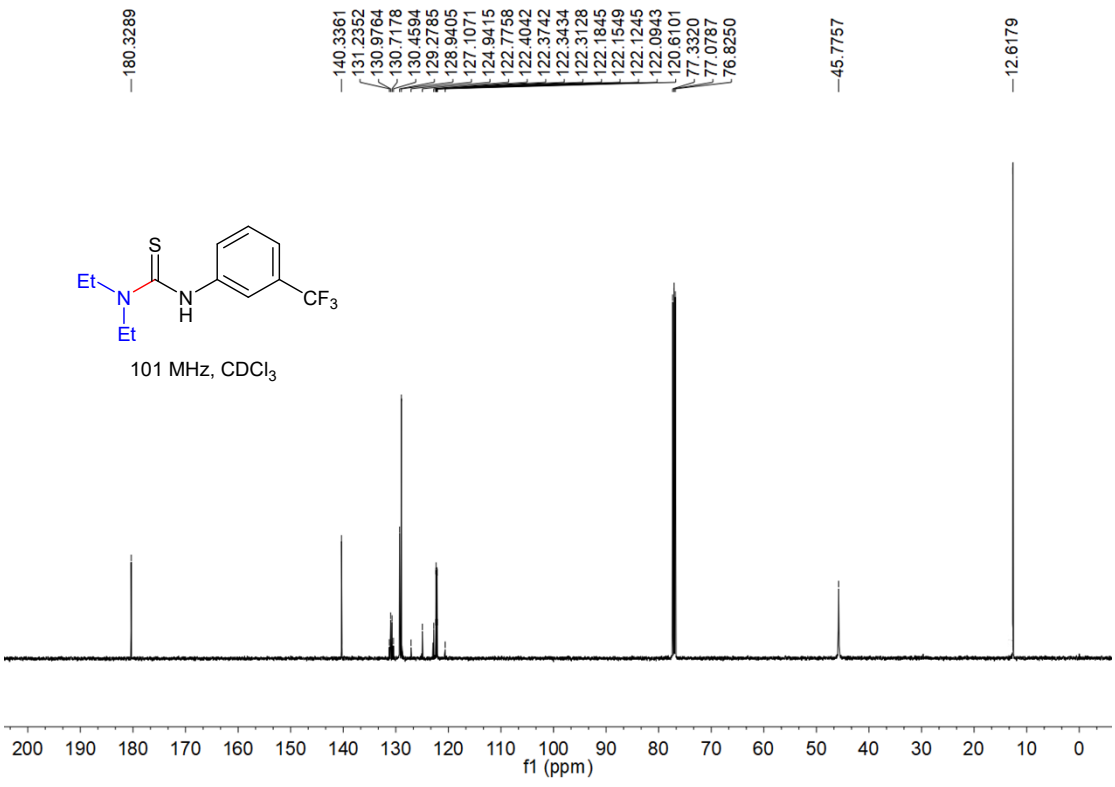


16c

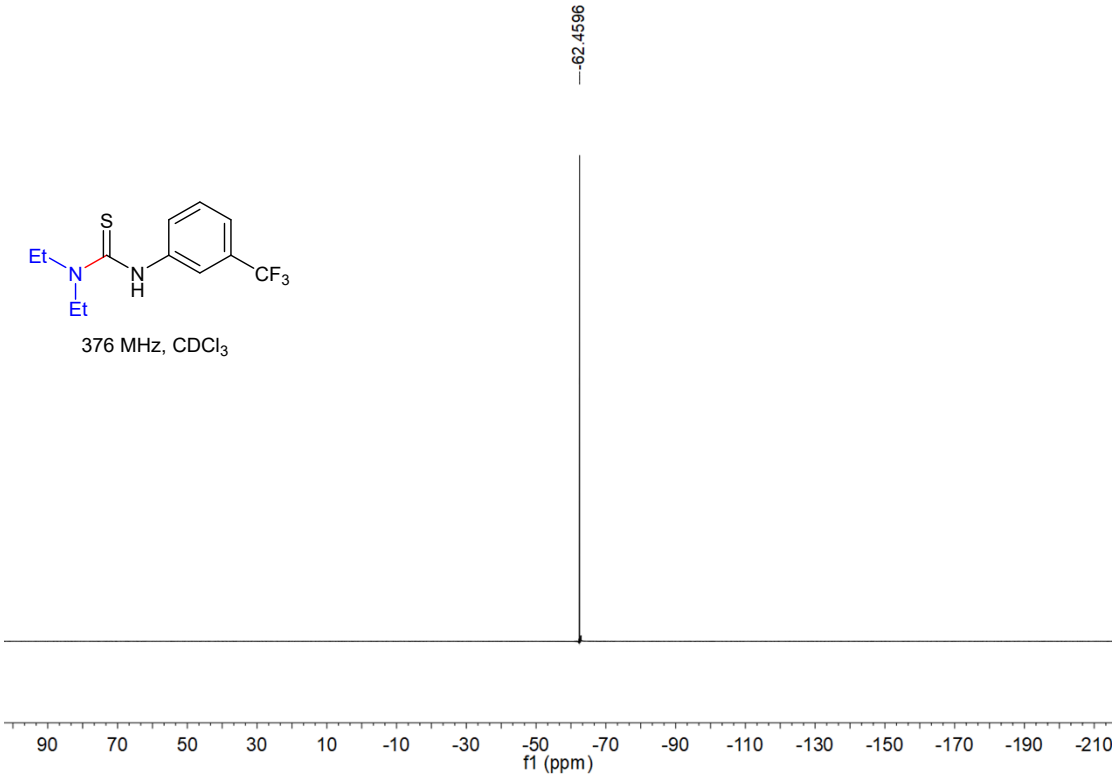
^{1}H NMR



^{13}C NMR

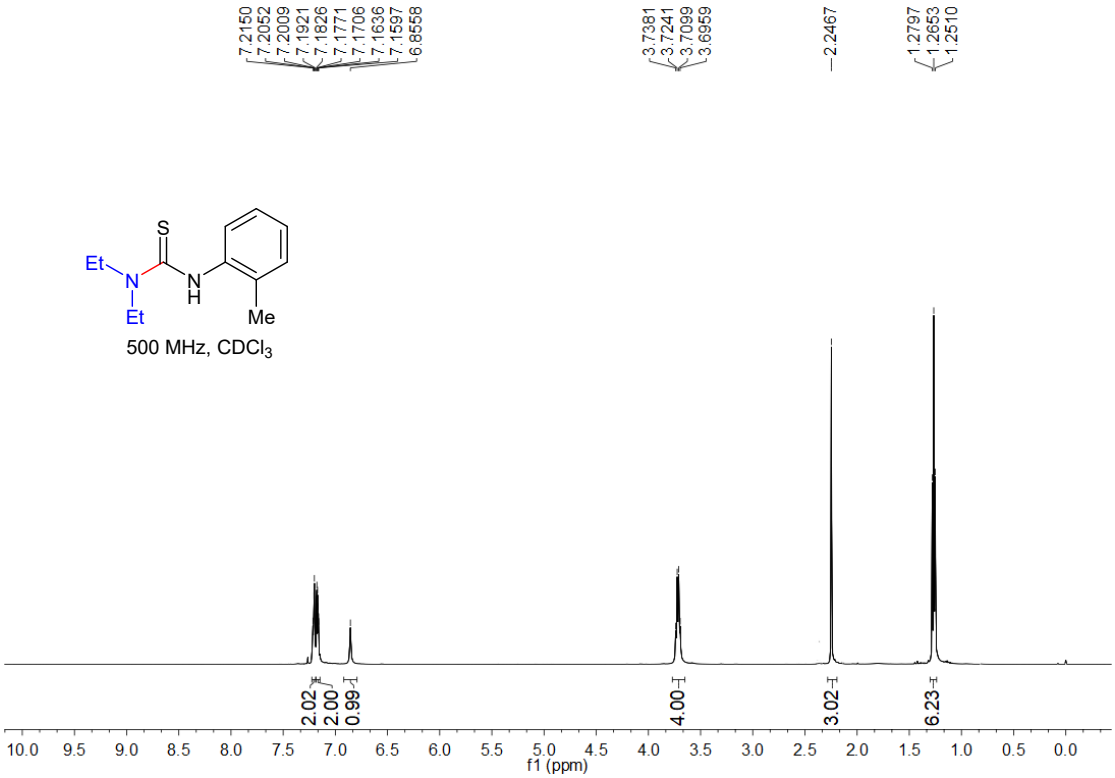


^{19}F NMR

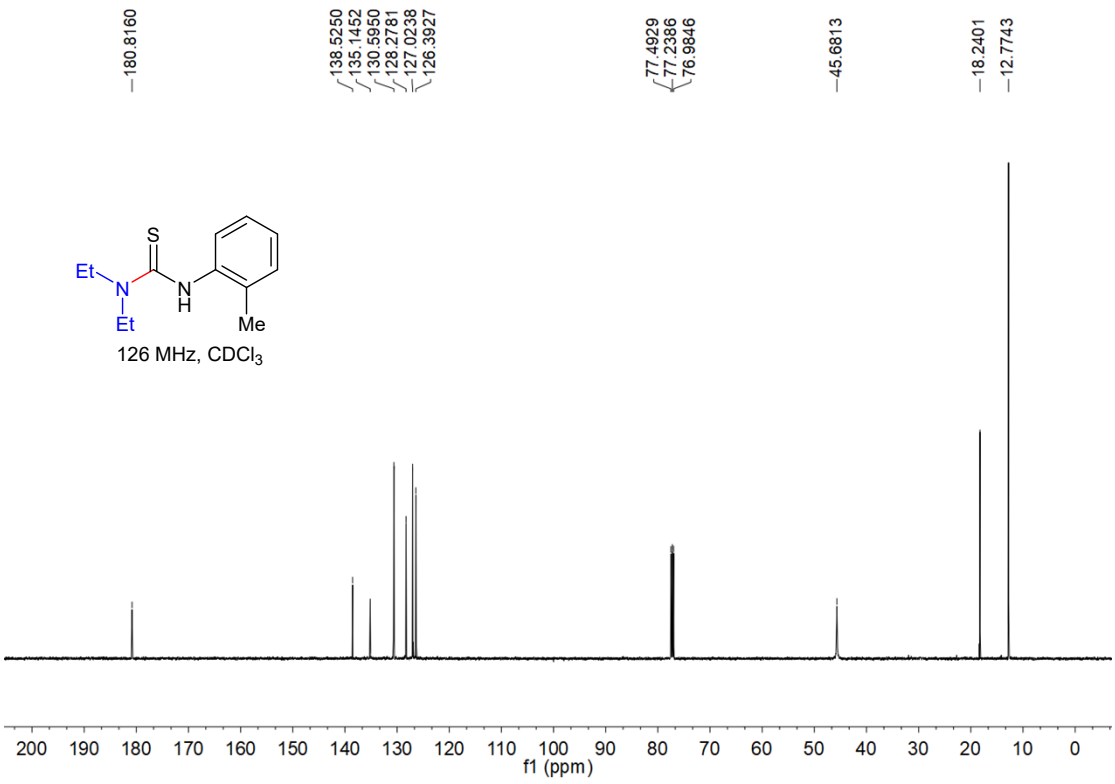

-62.4596
S
Et
N
Et
N
H
CF3
376 MHz, CDCl3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

17c

^{1}H NMR

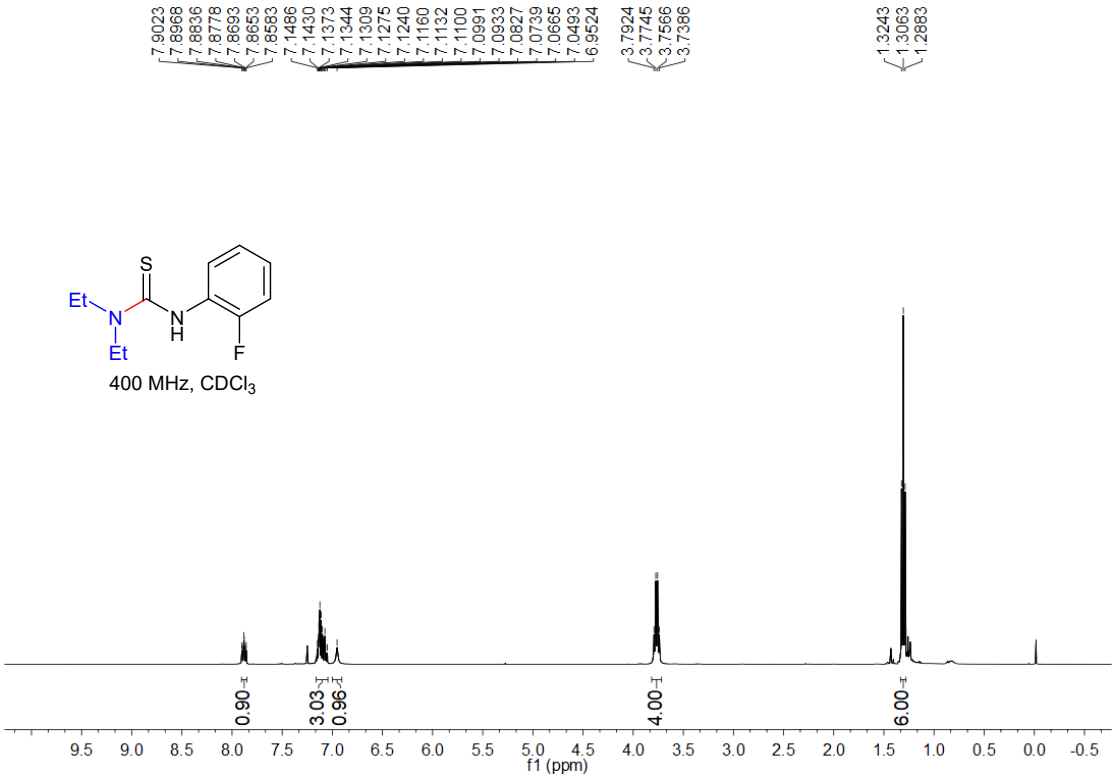


^{13}C NMR

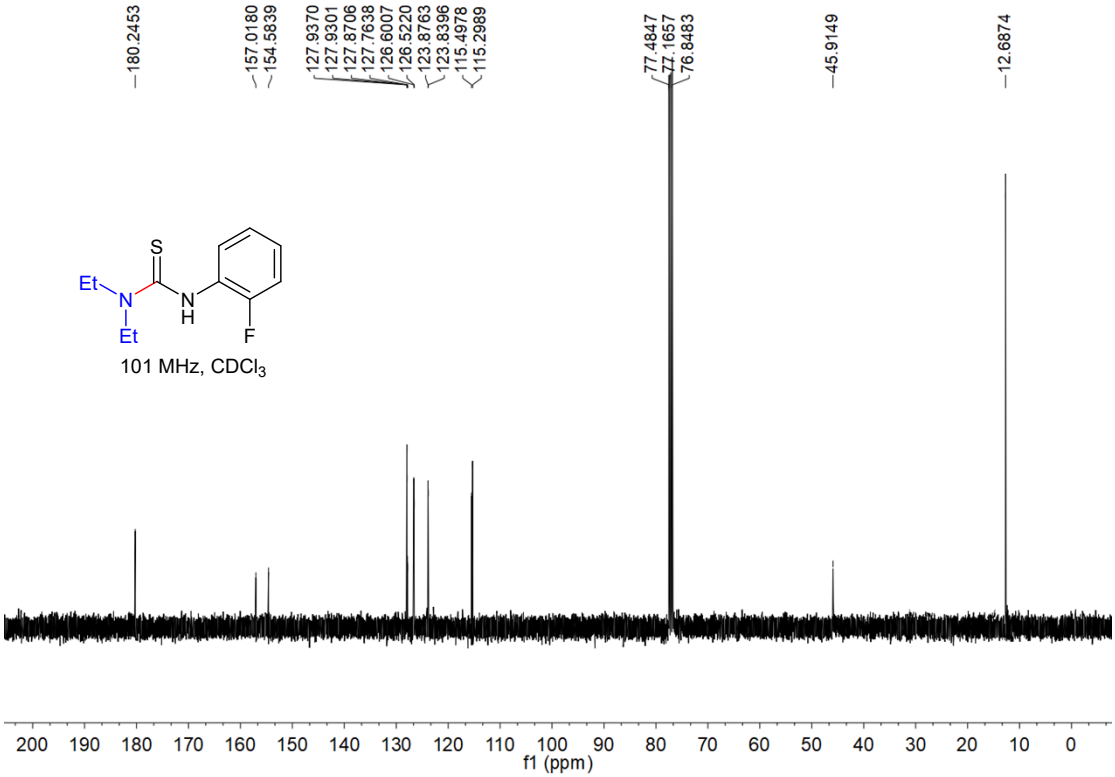


18c

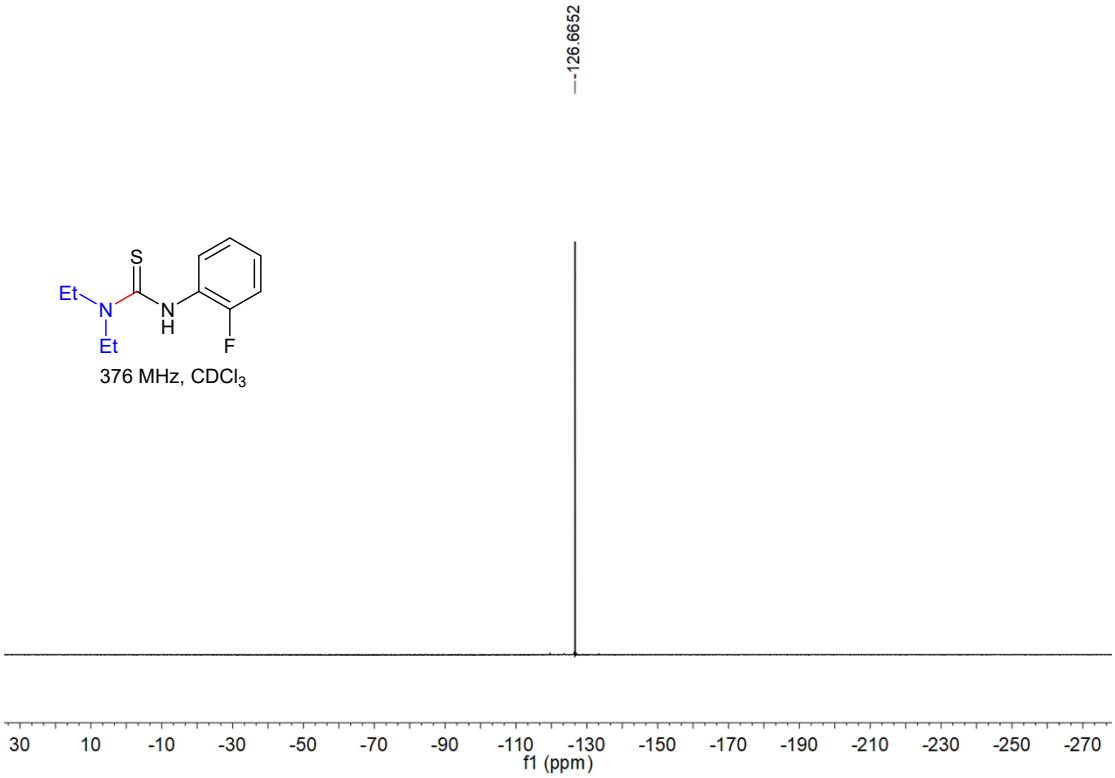
^{1}H NMR



^{13}C NMR

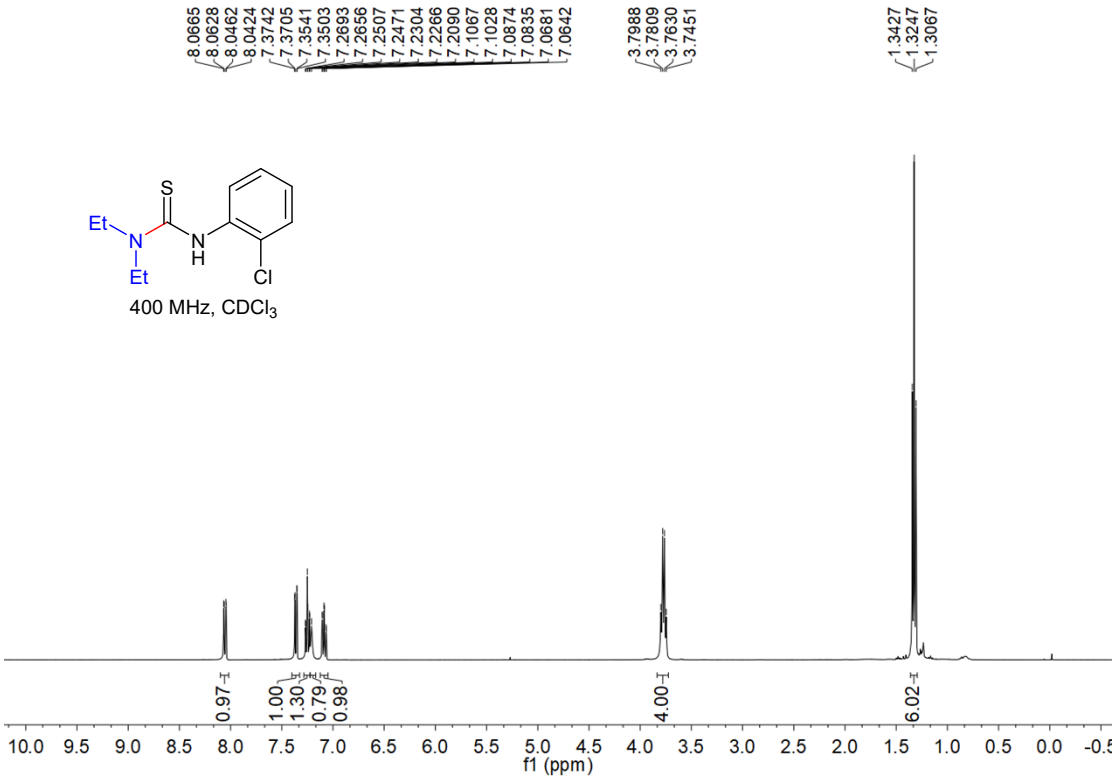


^{19}F NMR

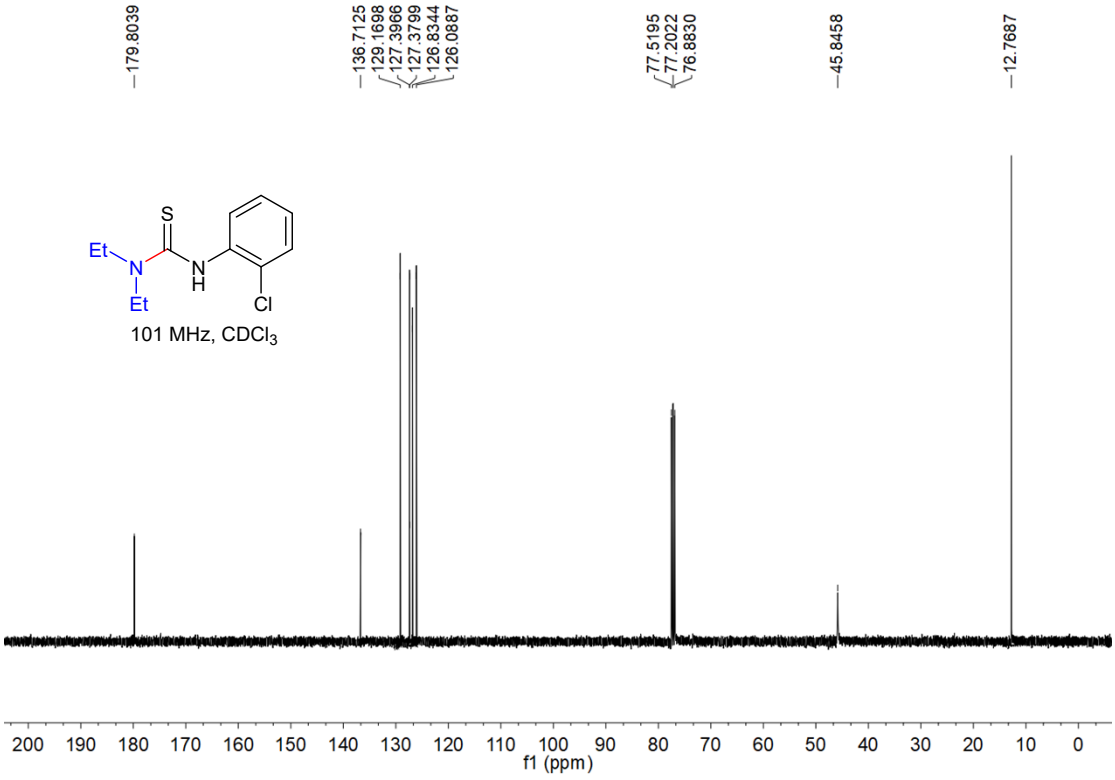

-126.6652
S
Et
N
Et
N
H
F
376 MHz, CDCl3
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
f1 (ppm)

19c

^{1}H NMR

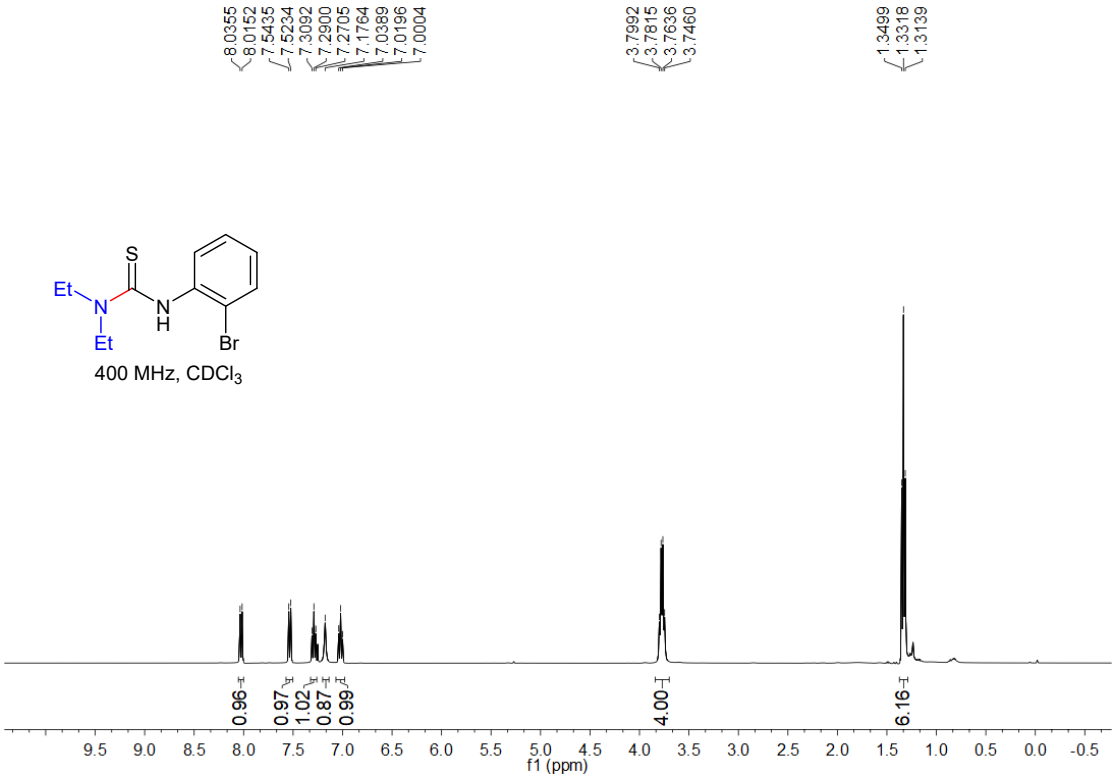


^{13}C NMR

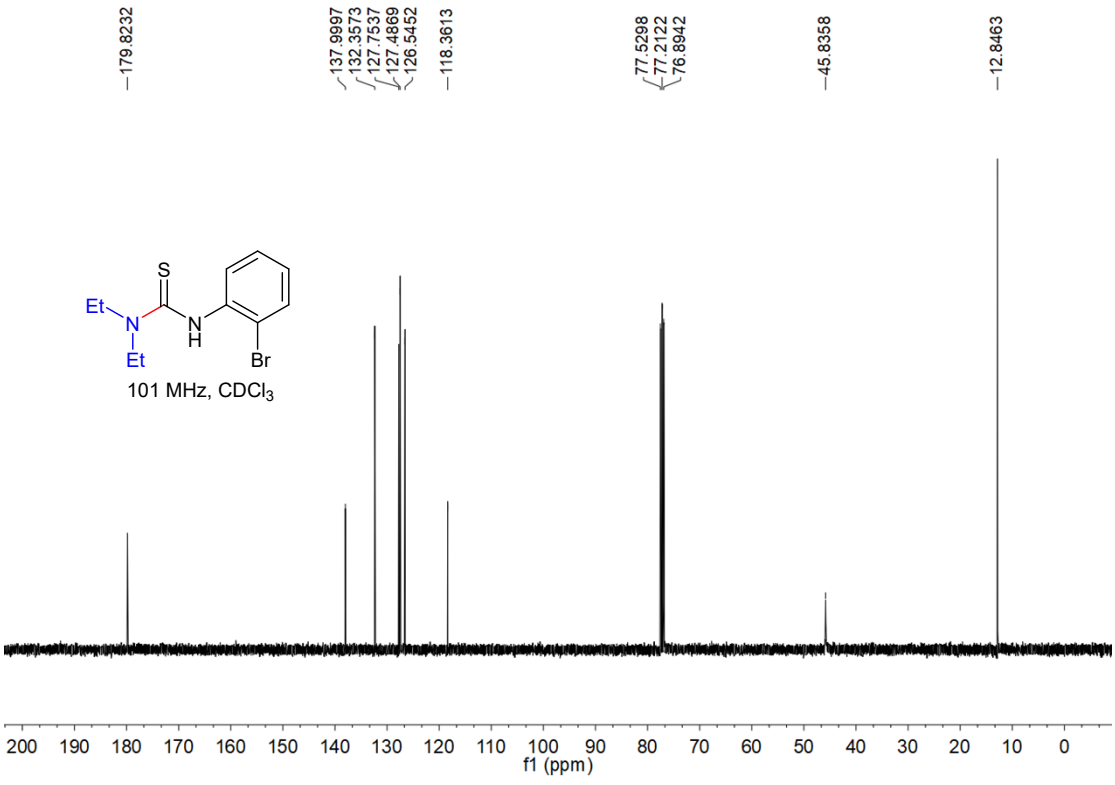


20c

^{1}H NMR

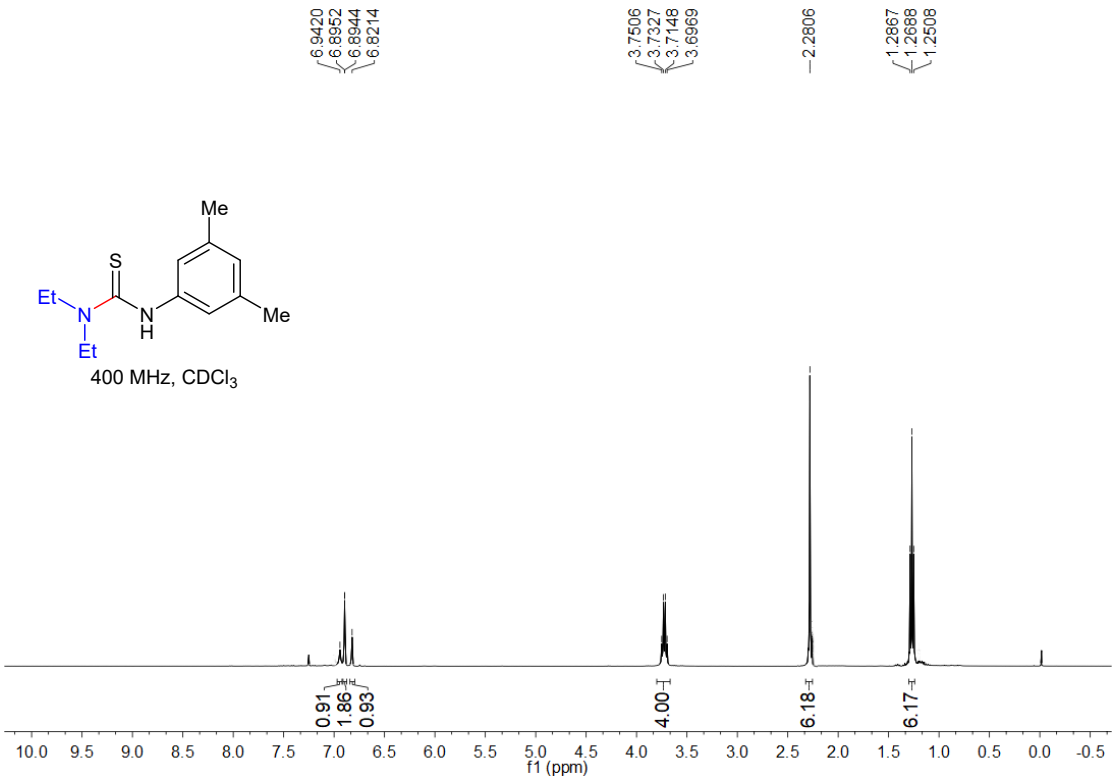


^{13}C NMR

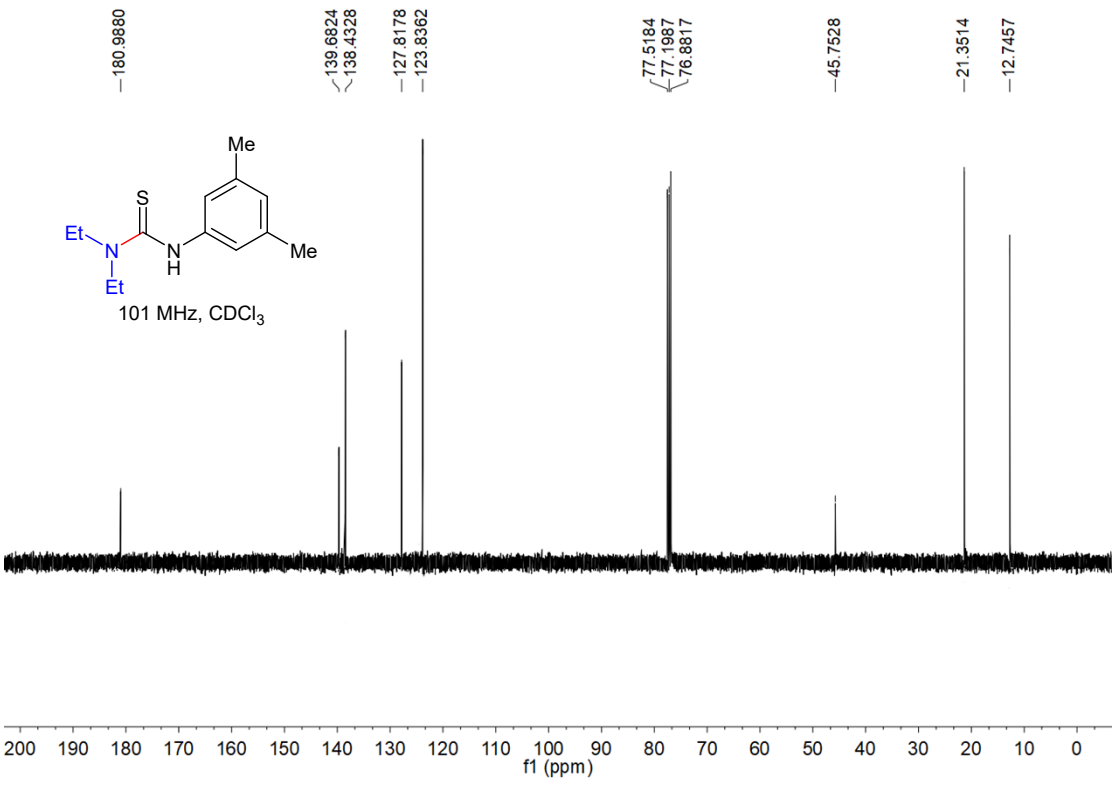


21c

^{1}H NMR

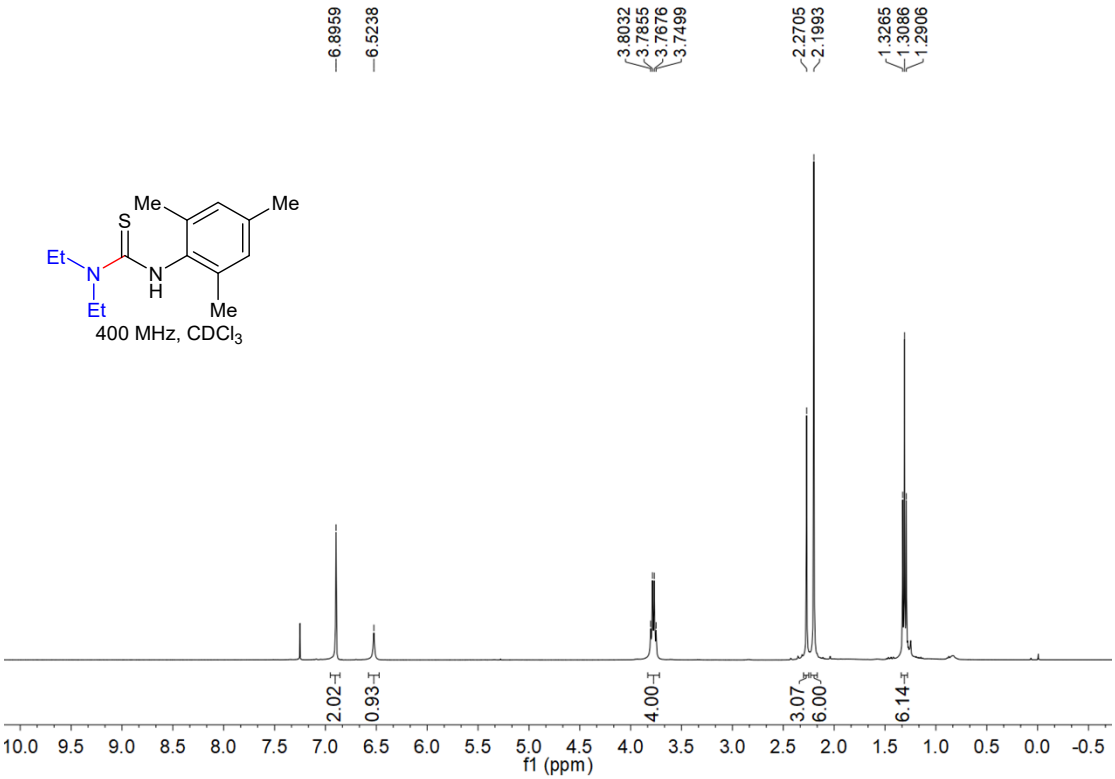


^{13}C NMR

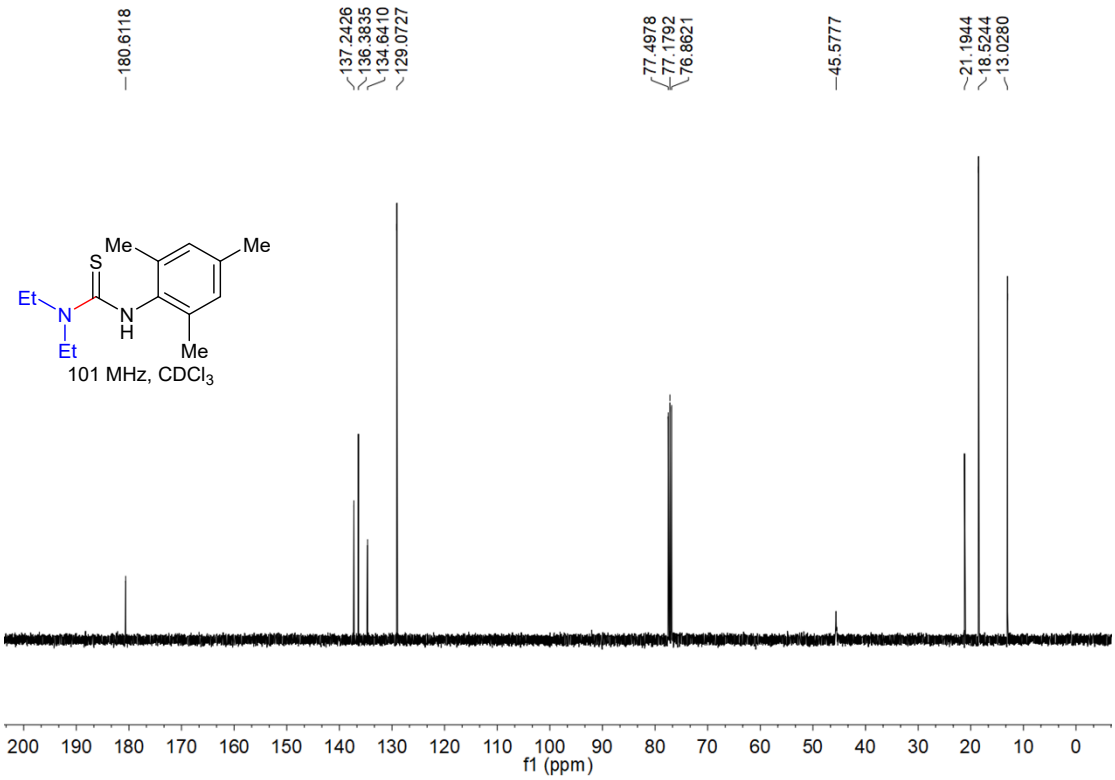


22c

^{1}H NMR

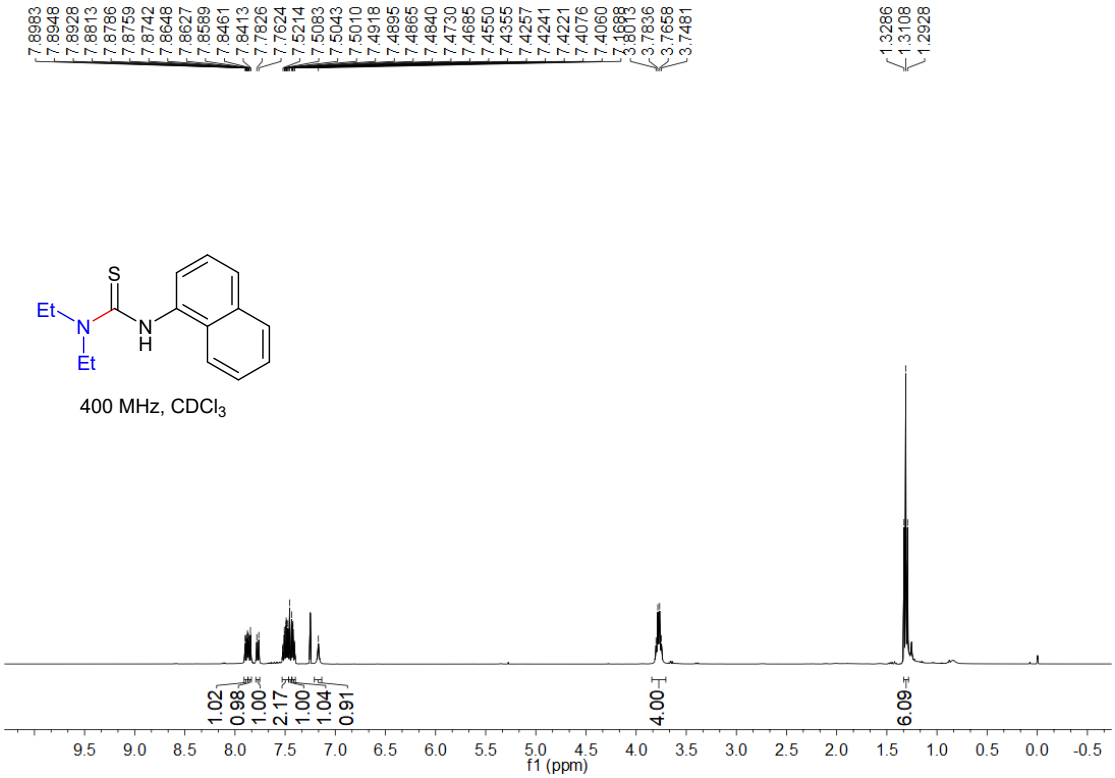


^{13}C NMR

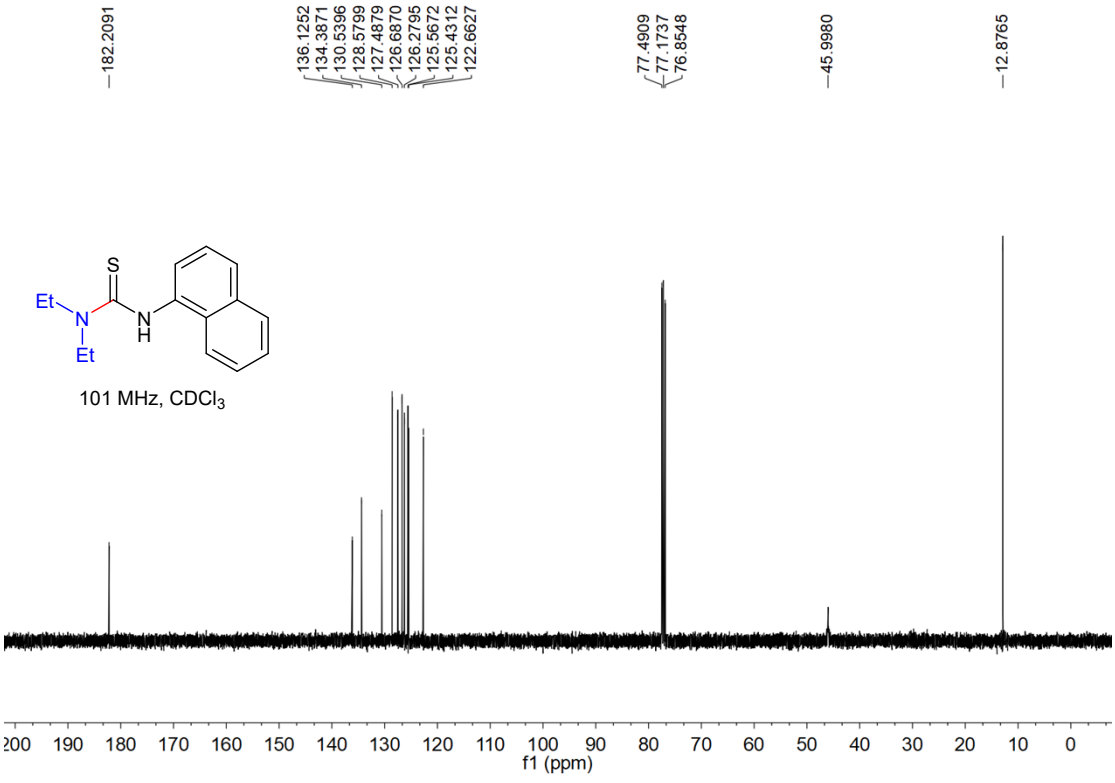


23c

^{1}H NMR

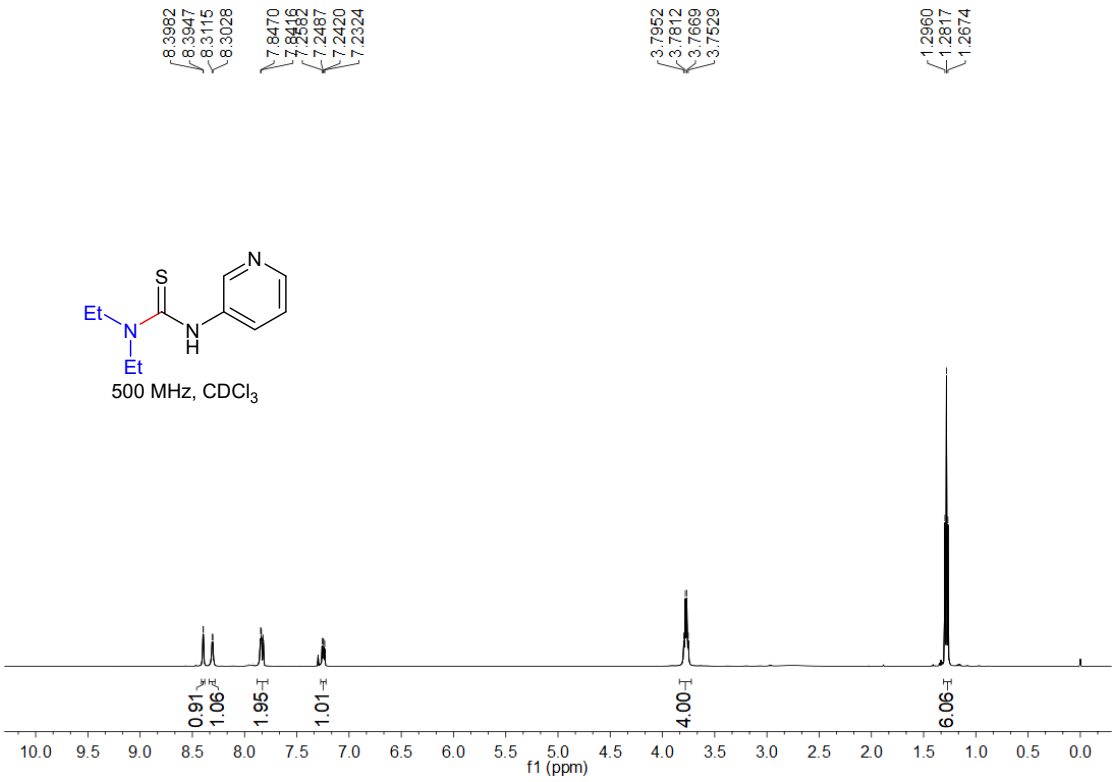


^{13}C NMR

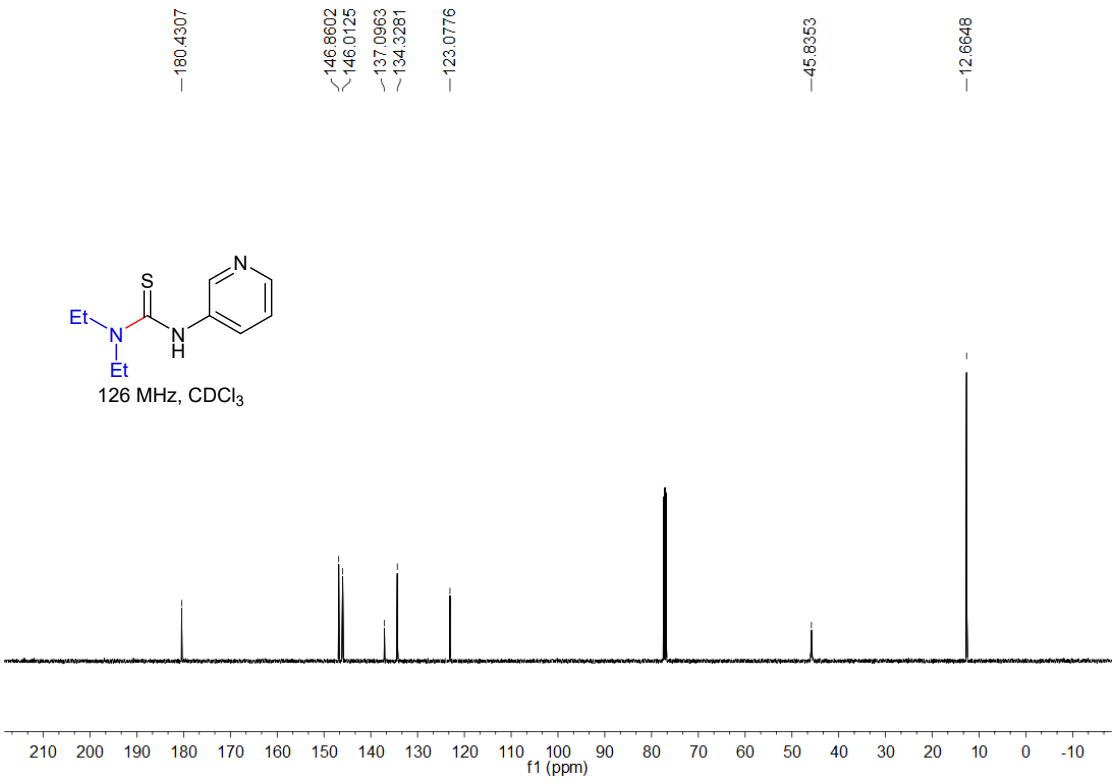


24c

^{1}H NMR

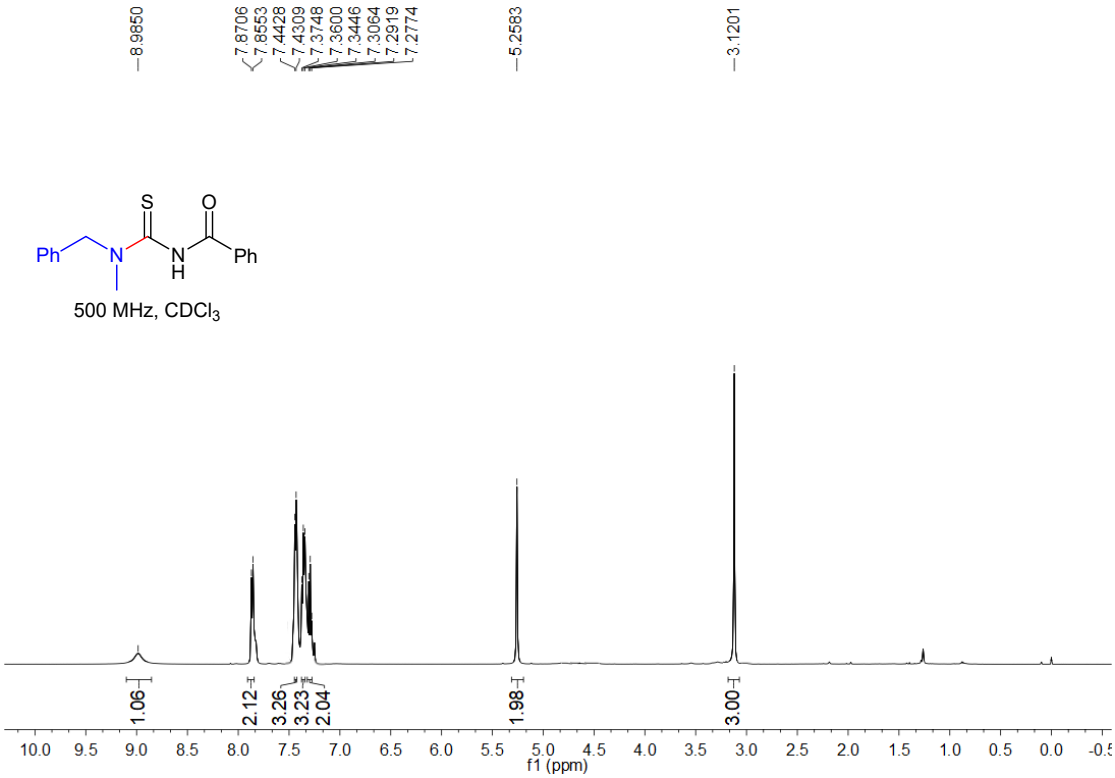


^{13}C NMR

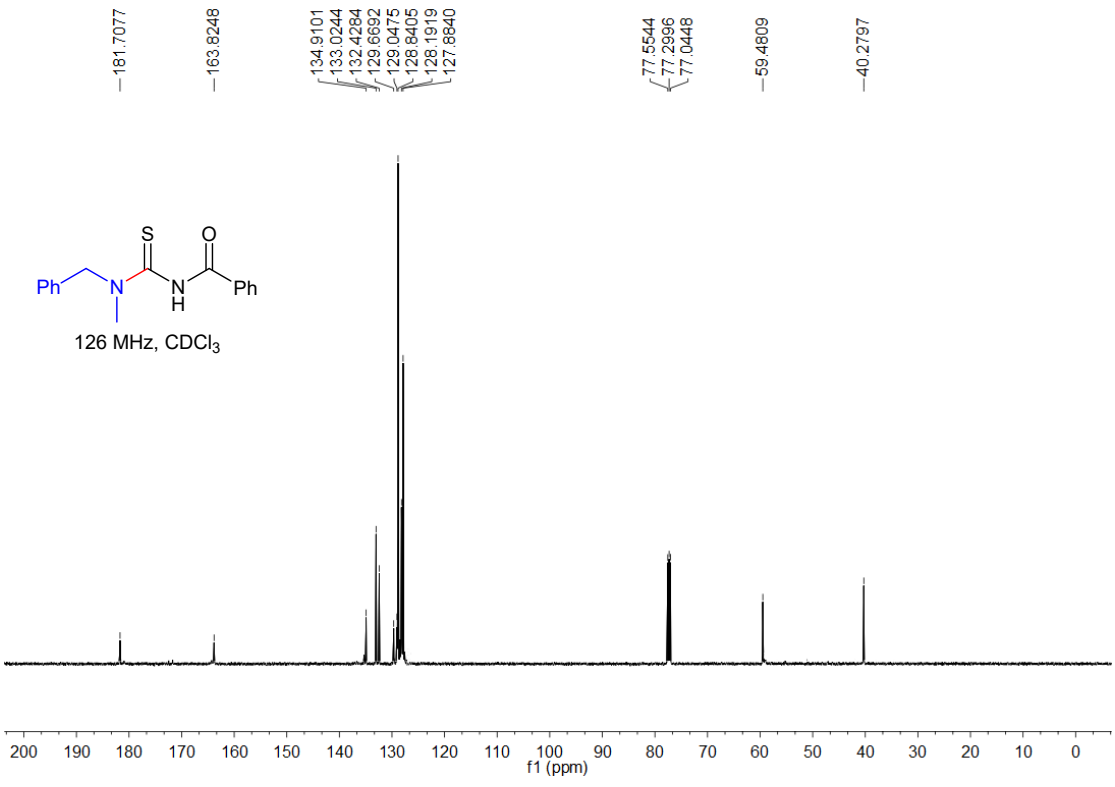


25c

^{1}H NMR

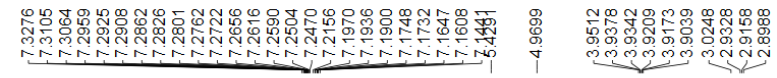


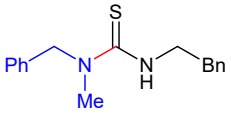
^{13}C NMR



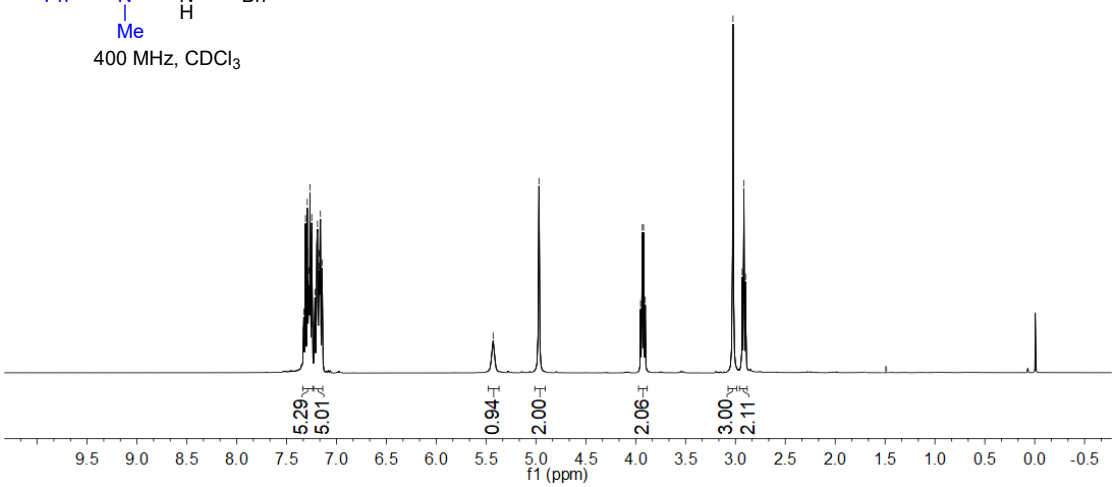
26c

^{1}H NMR

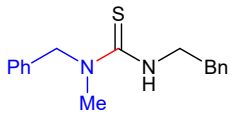




400 MHz, $CDCl_3$



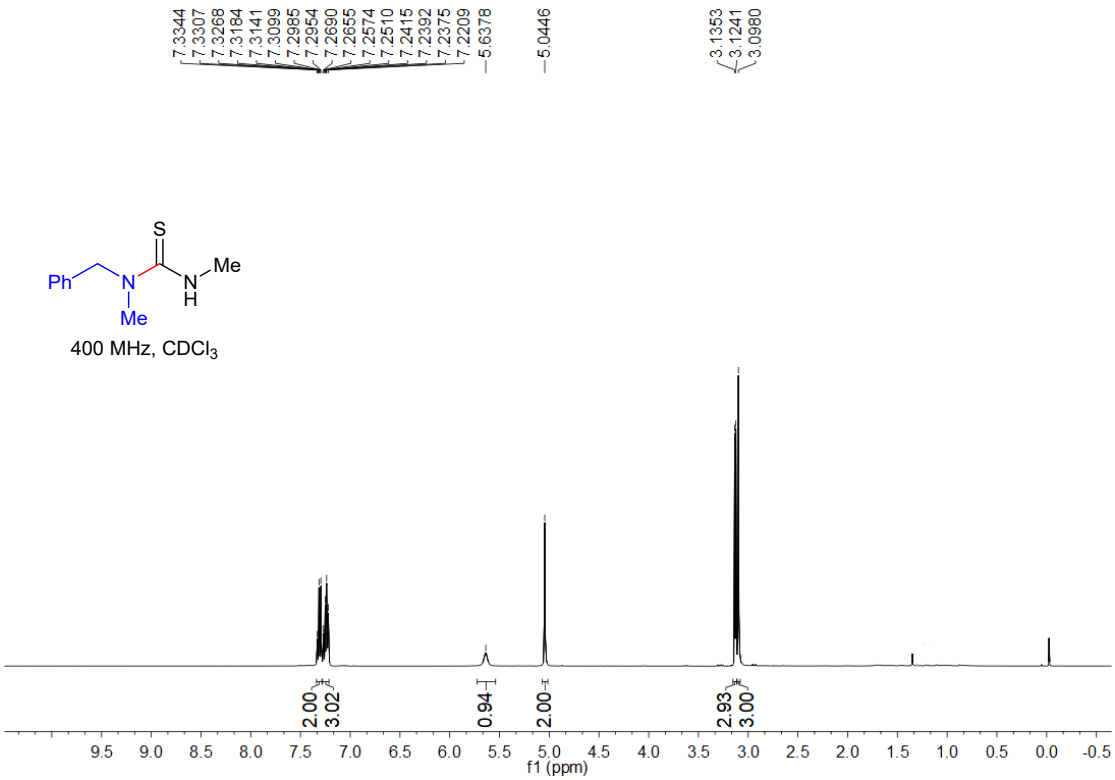
^{13}C NMR



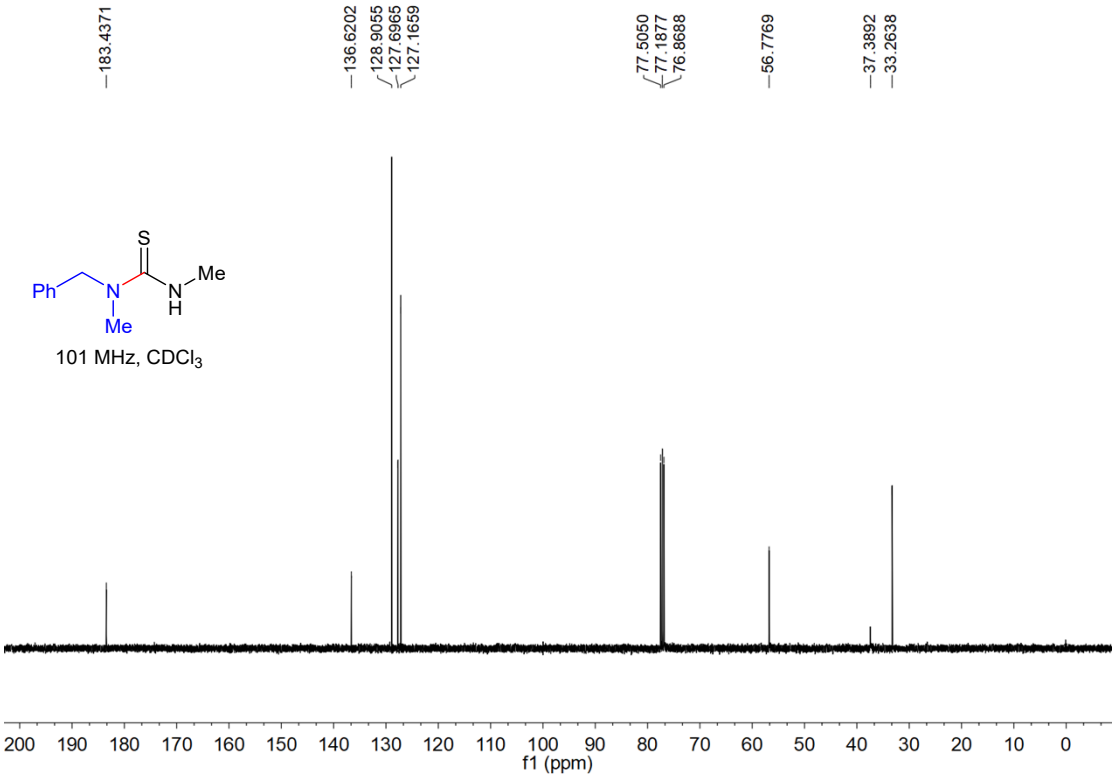
101 MHz, $CDCl_3$

27c

^{1}H NMR

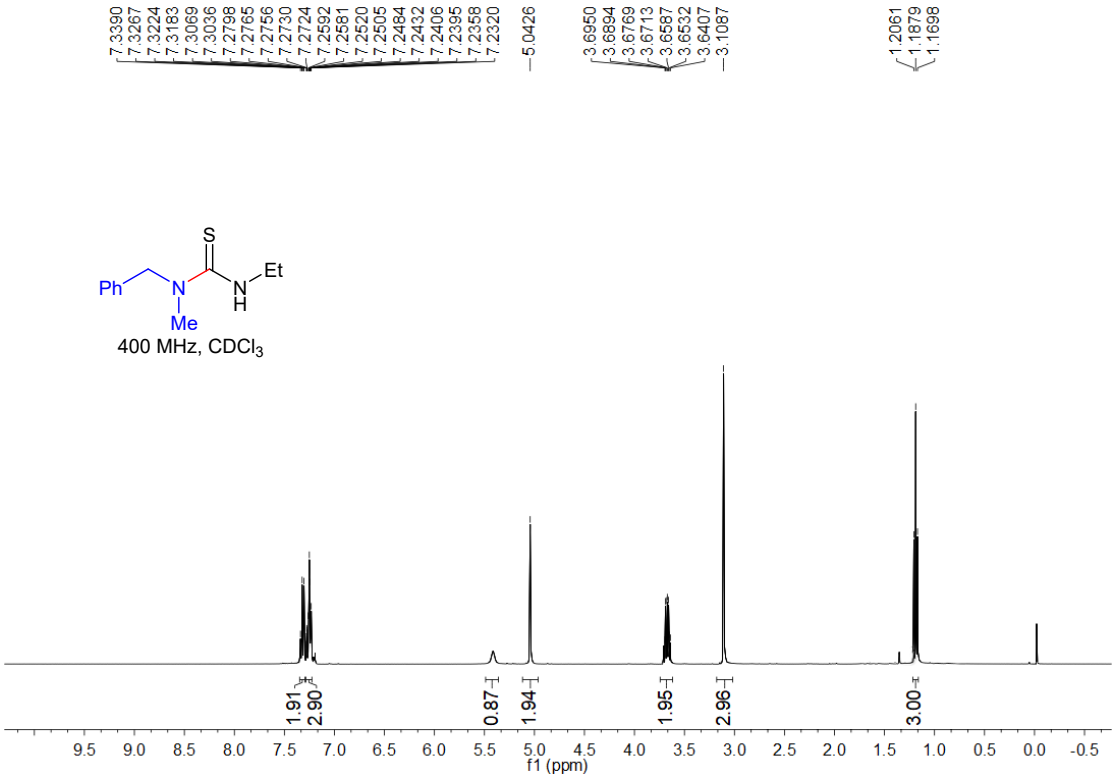


^{13}C NMR



28c

^{1}H NMR



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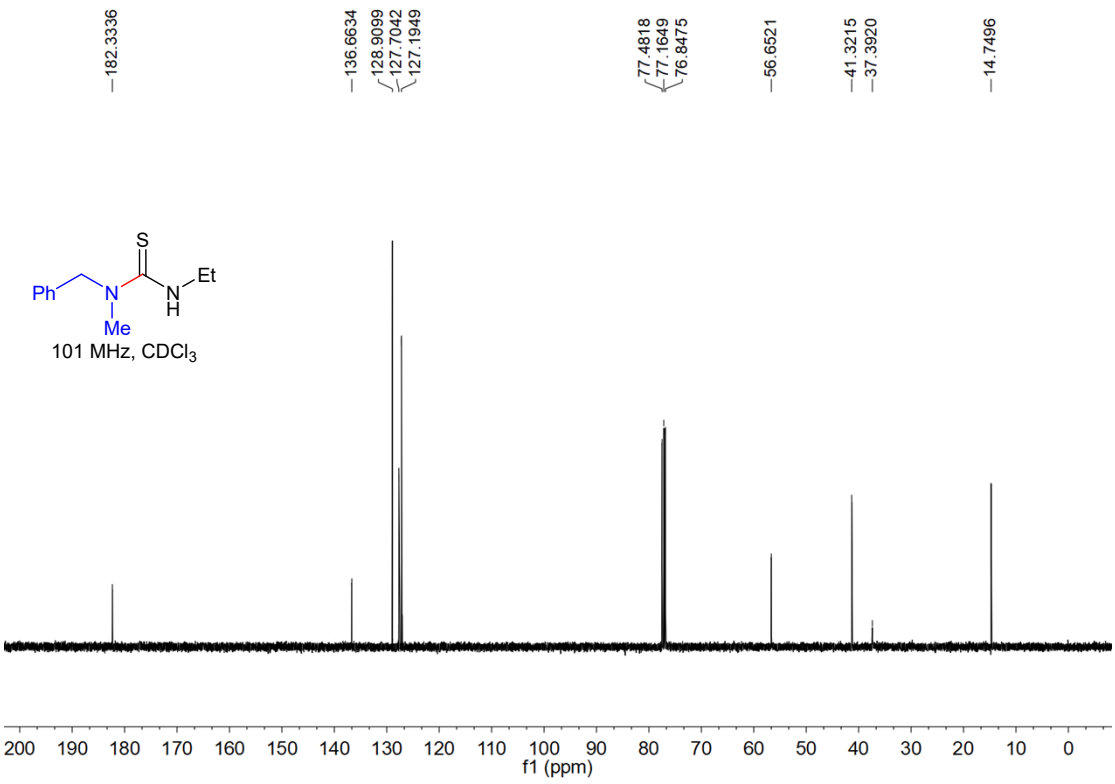

29c

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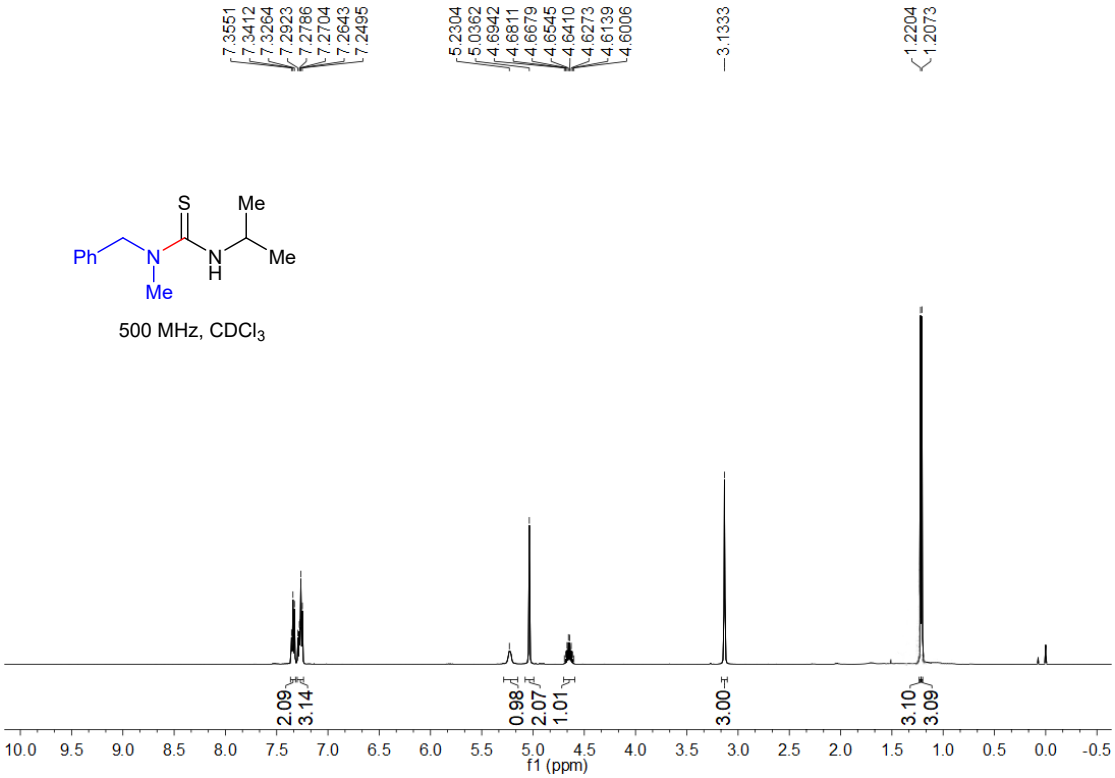
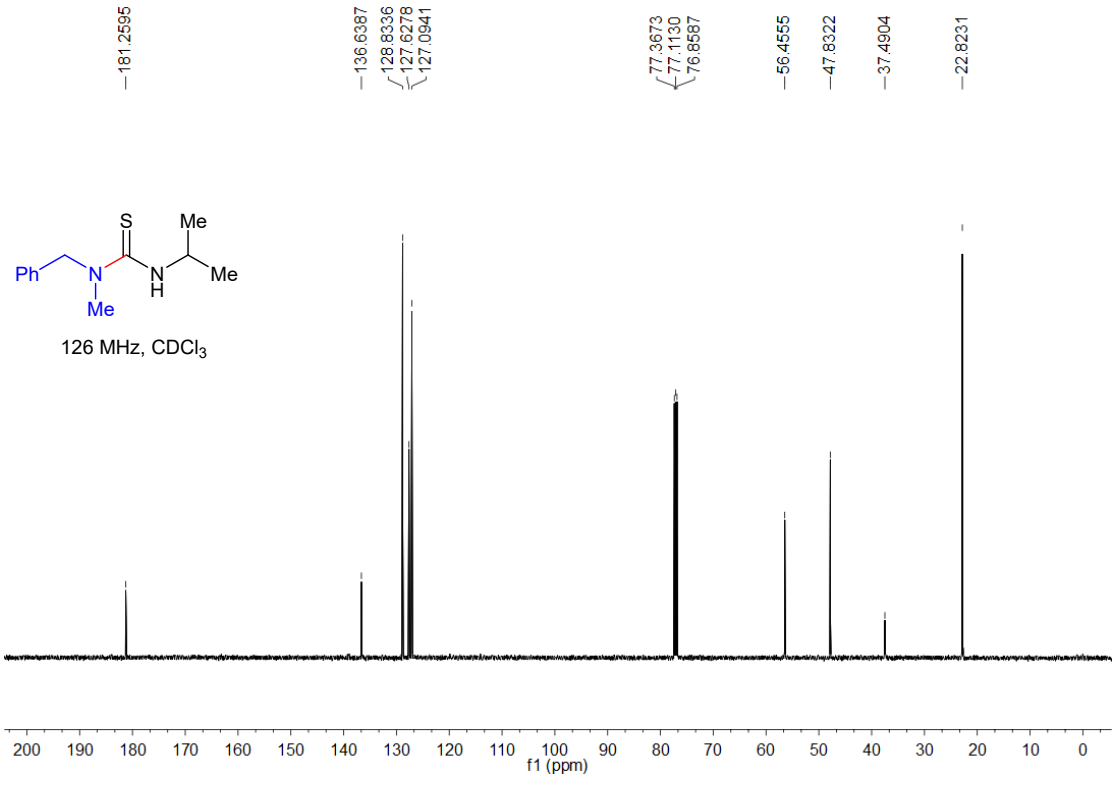
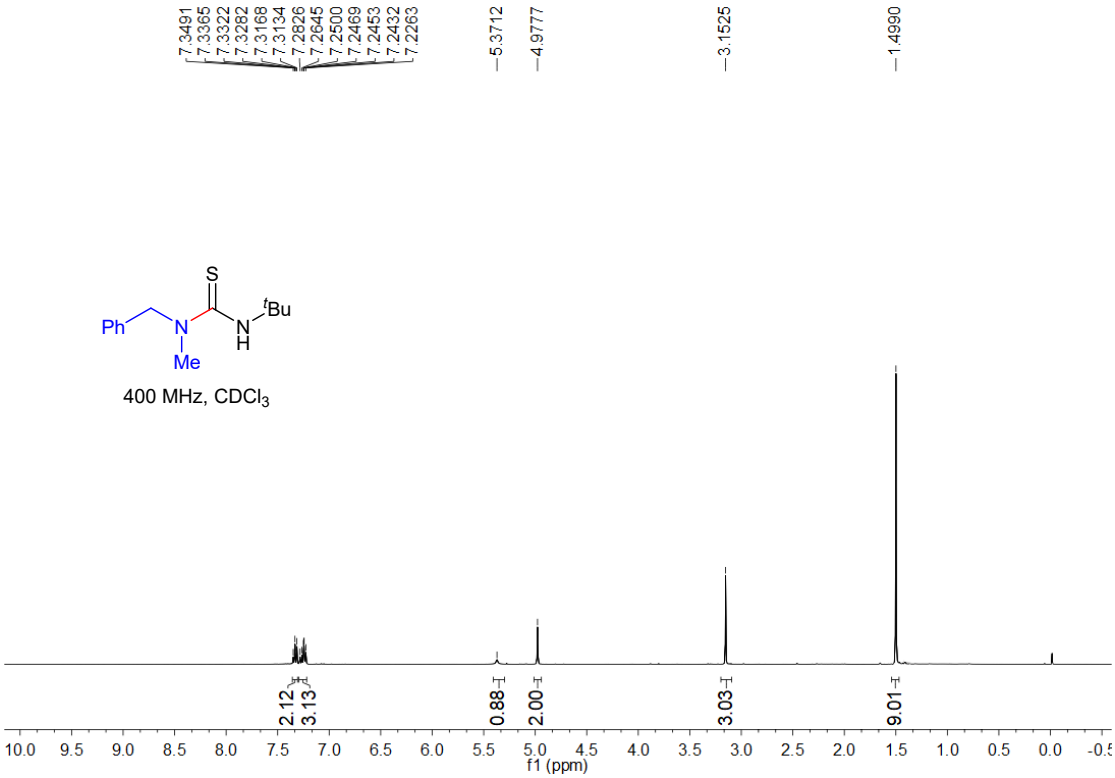


^{13}C NMR

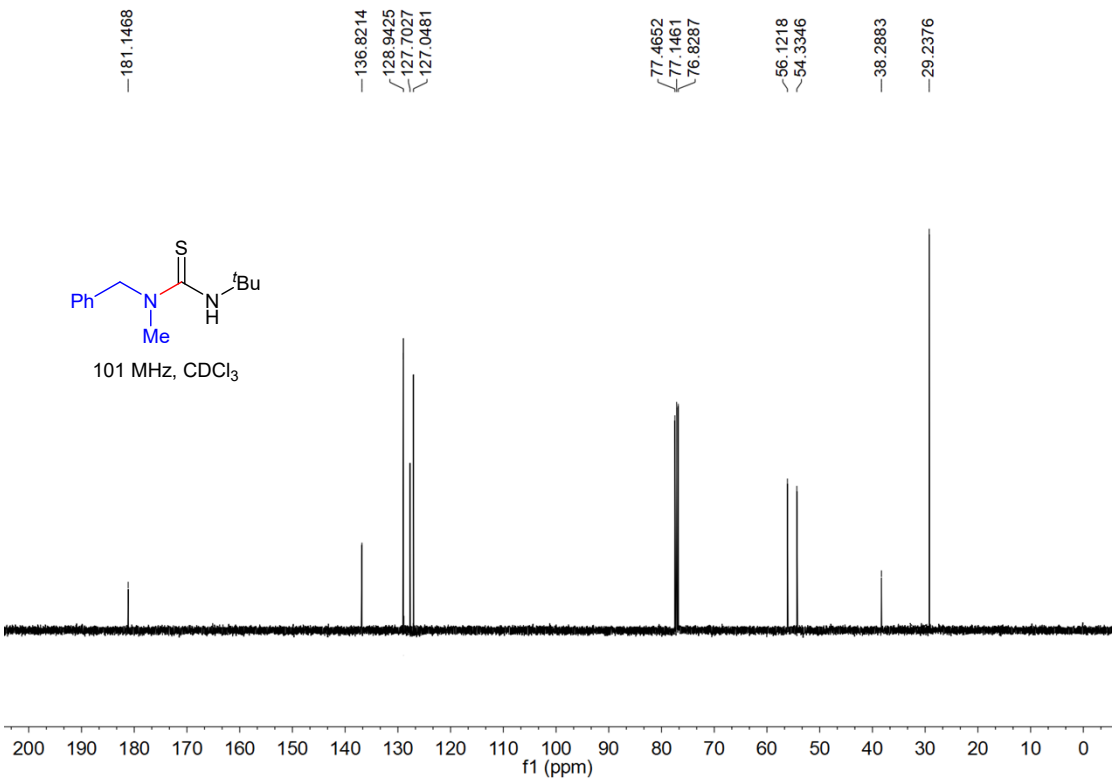


30c

^{1}H NMR

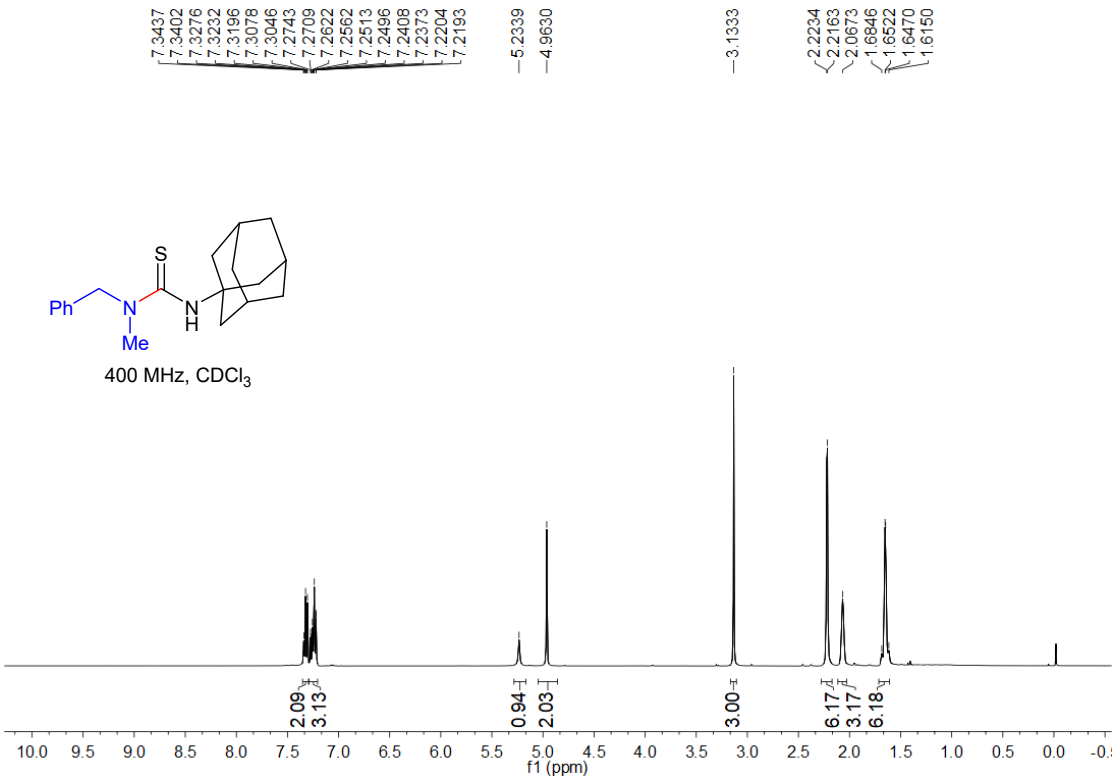


^{13}C NMR

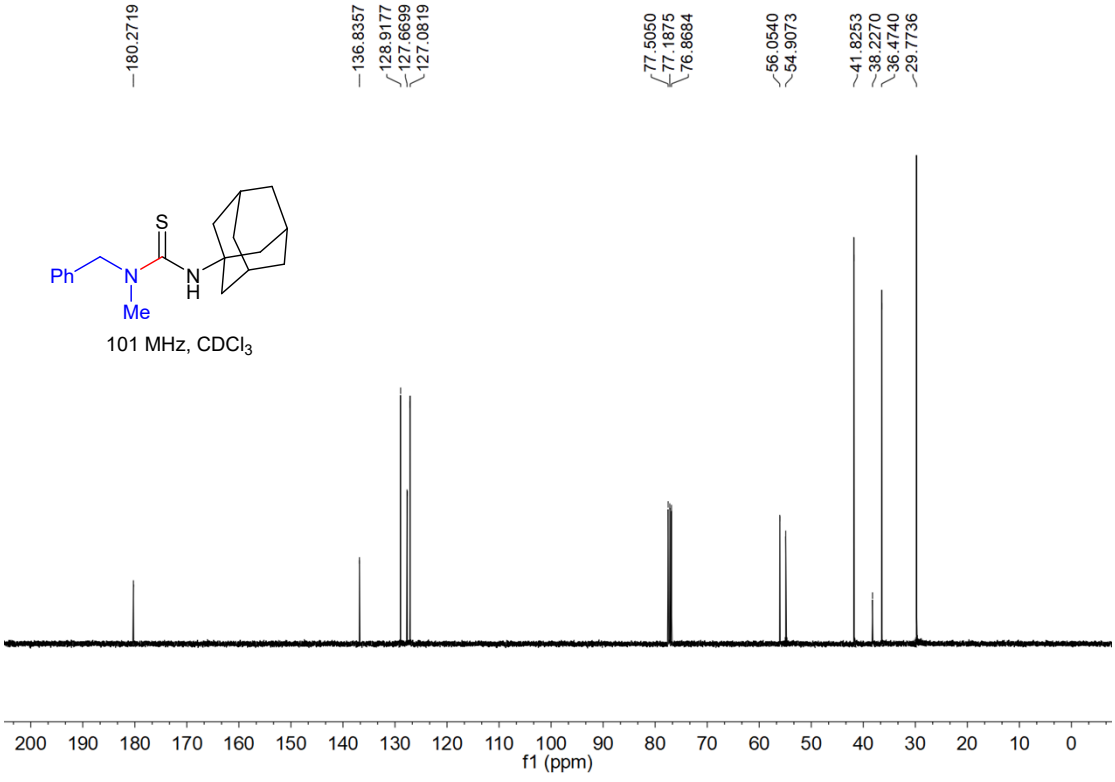


31c

^{1}H NMR

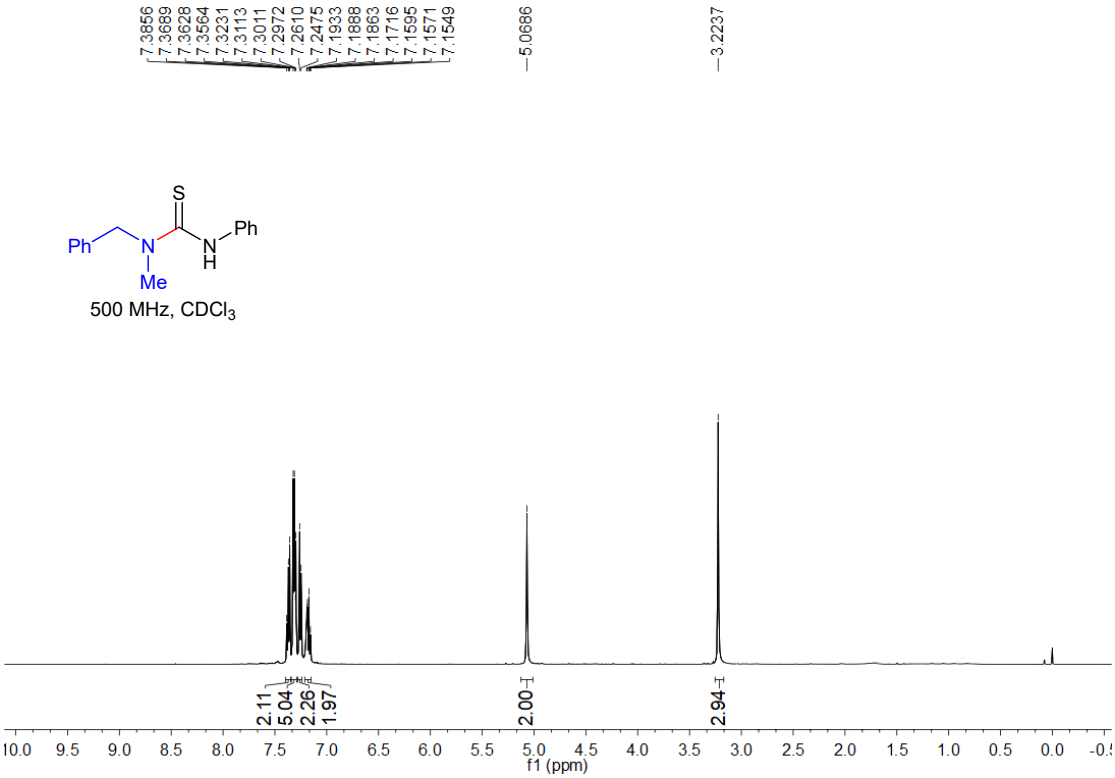


^{13}C NMR

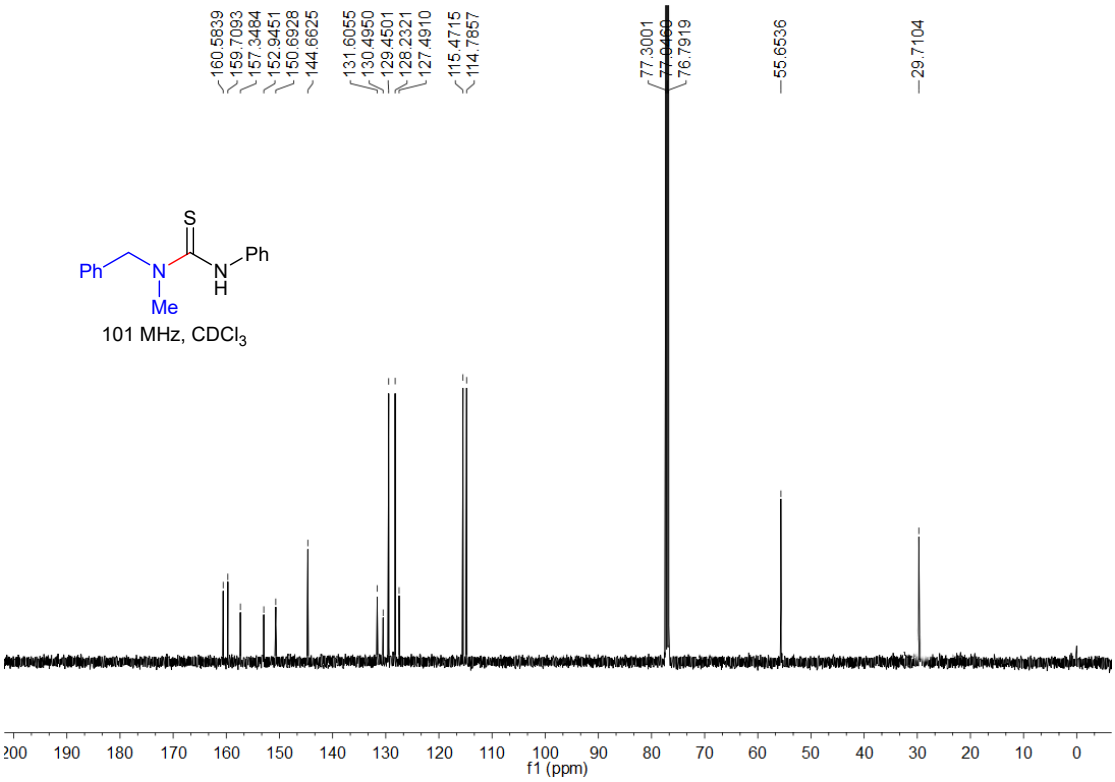


32c

^{1}H NMR



^{13}C NMR



33c

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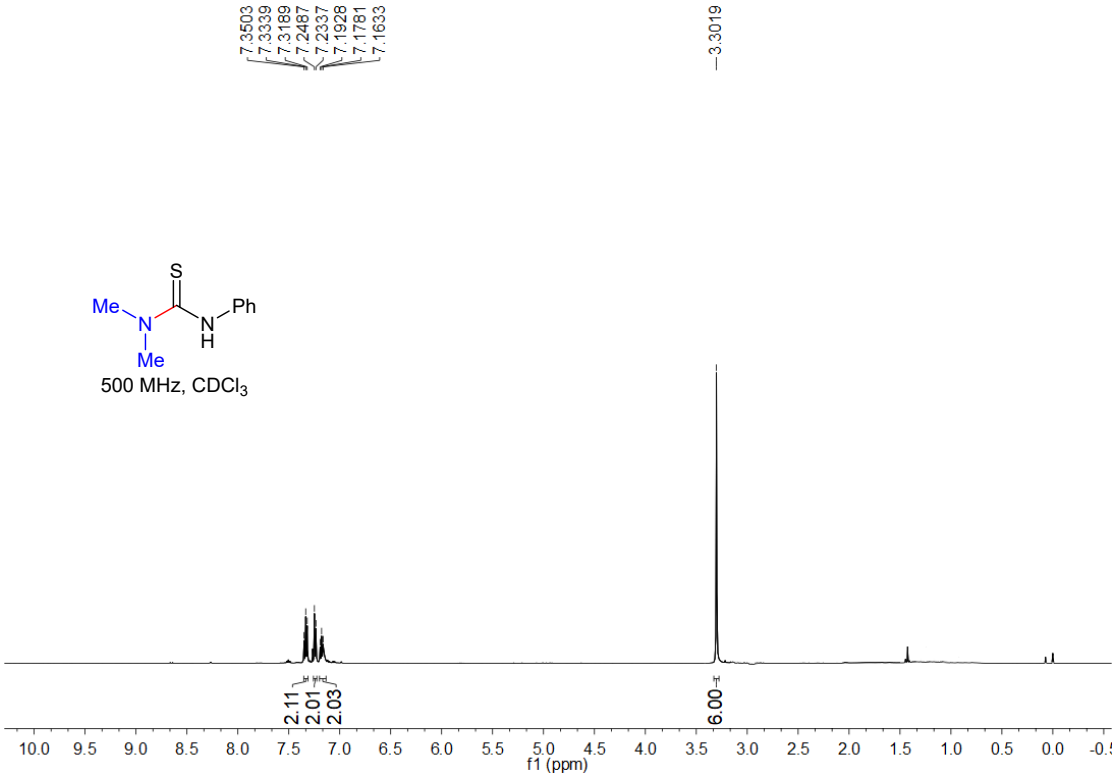
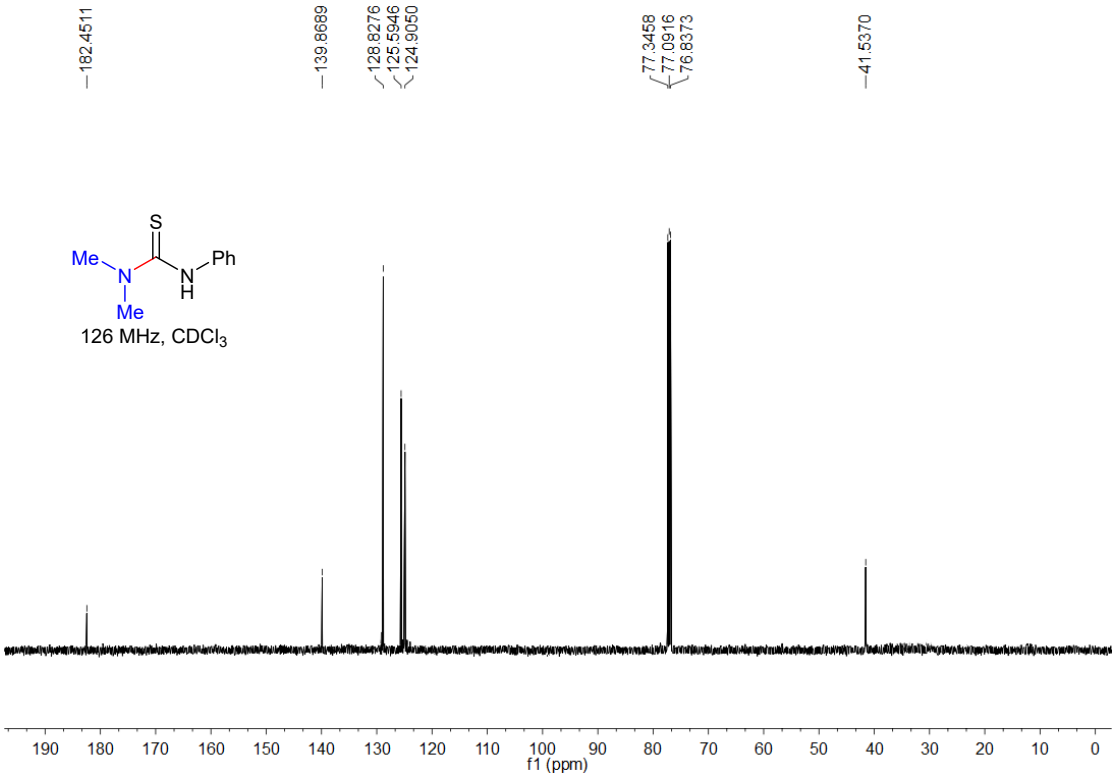
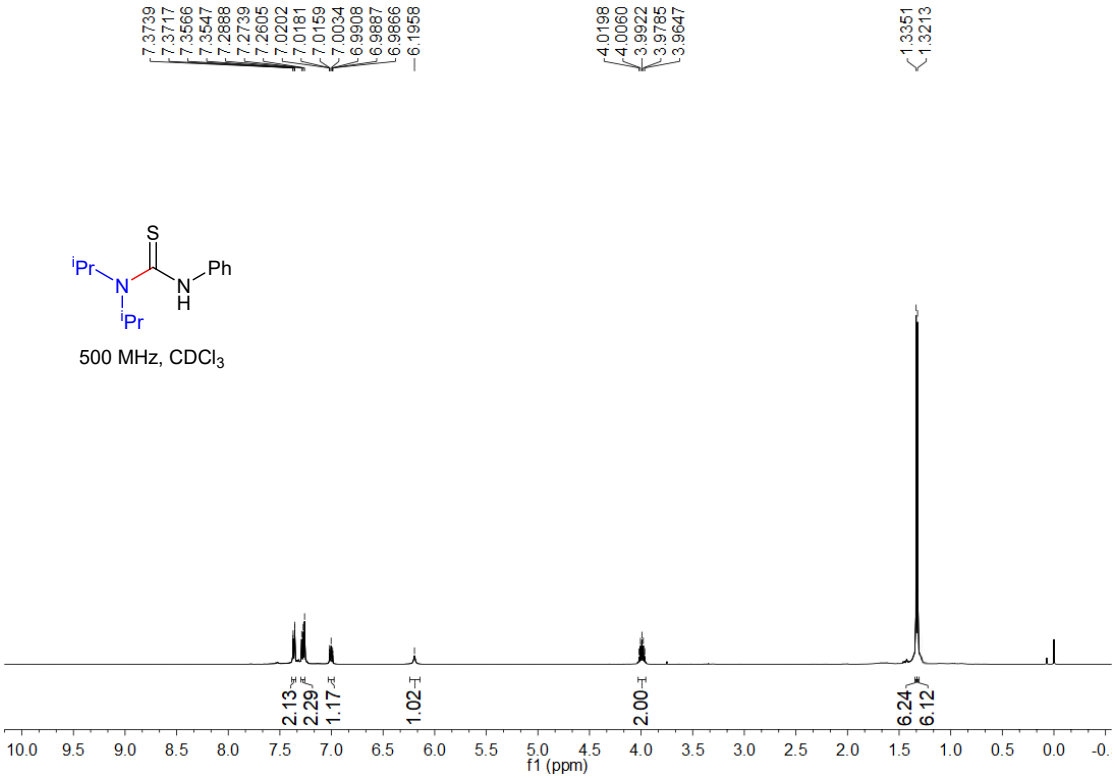


^{13}C NMR

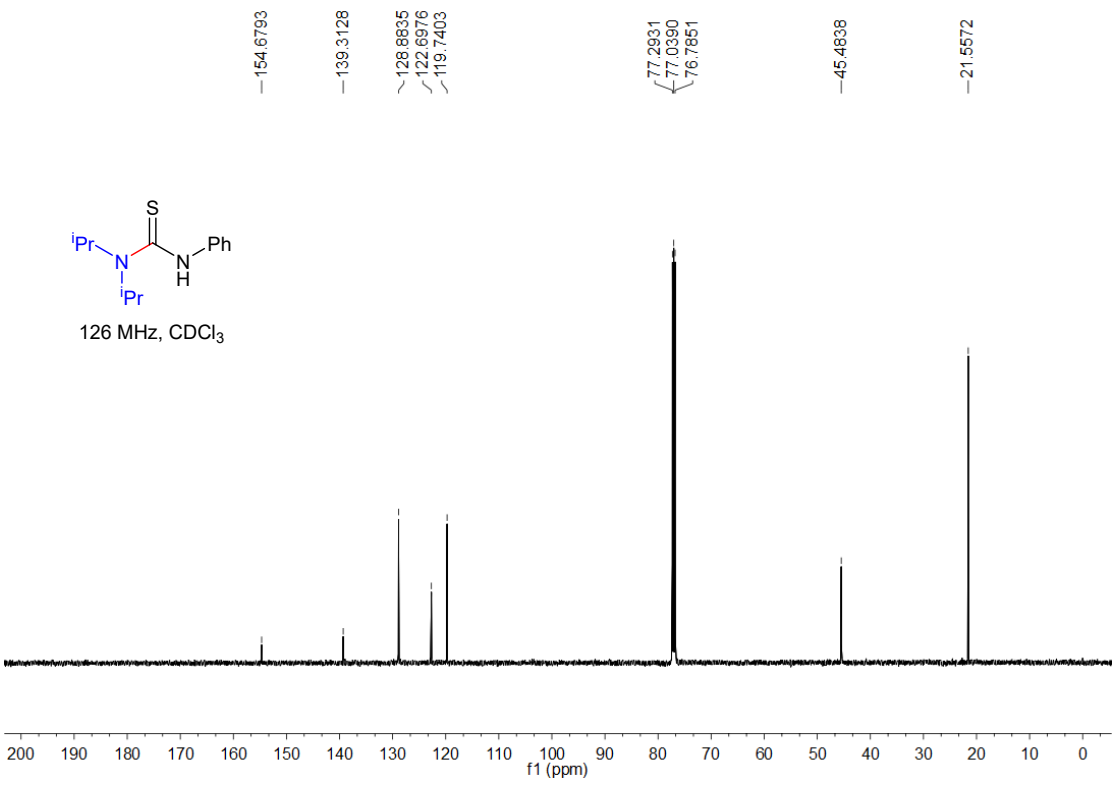


34c

^{1}H NMR

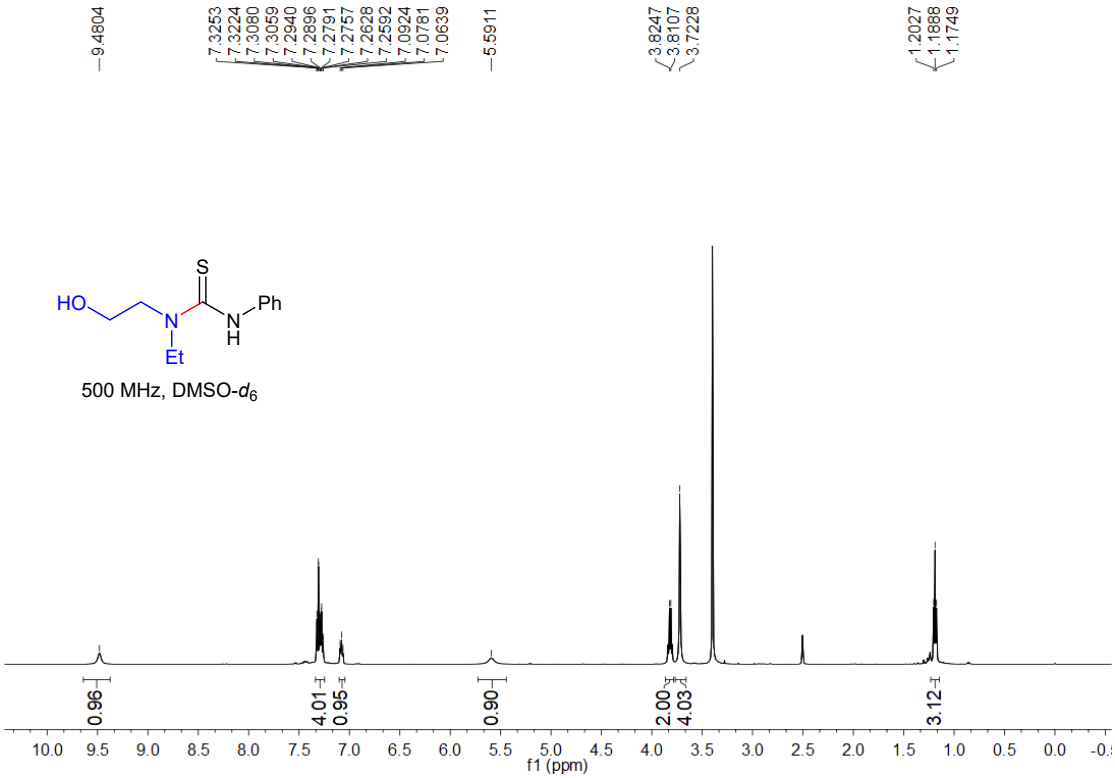


^{13}C NMR

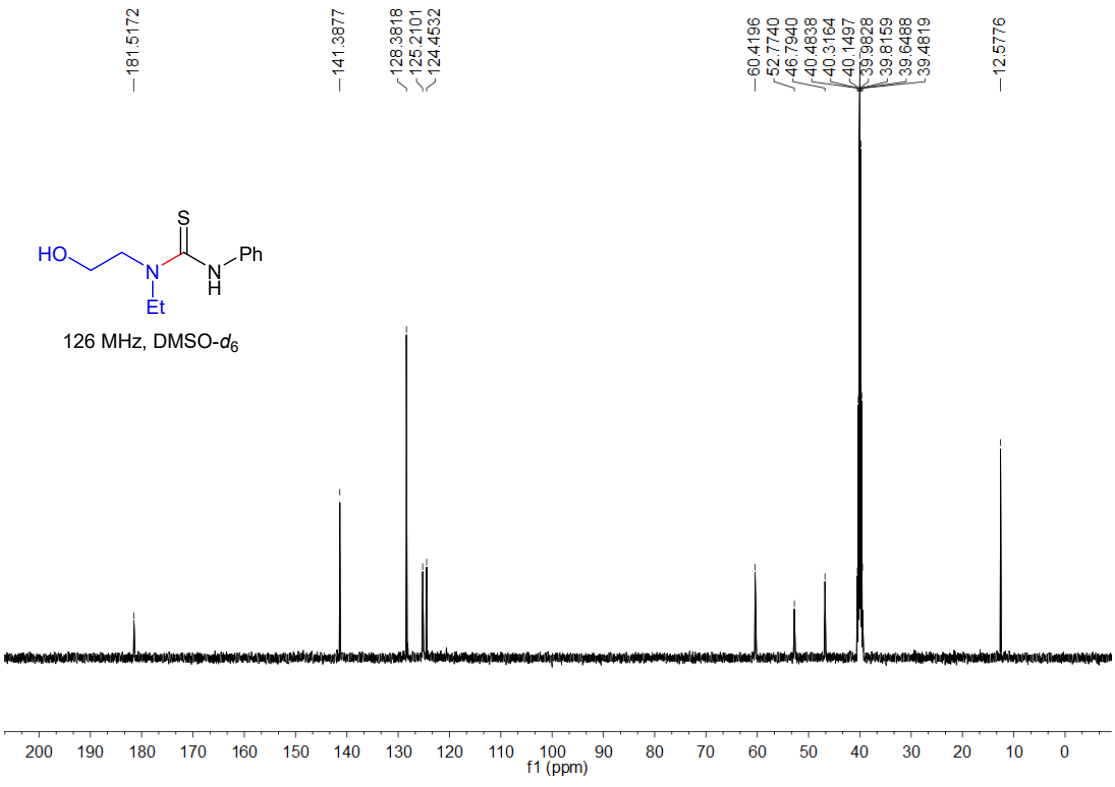


35c

^{1}H NMR

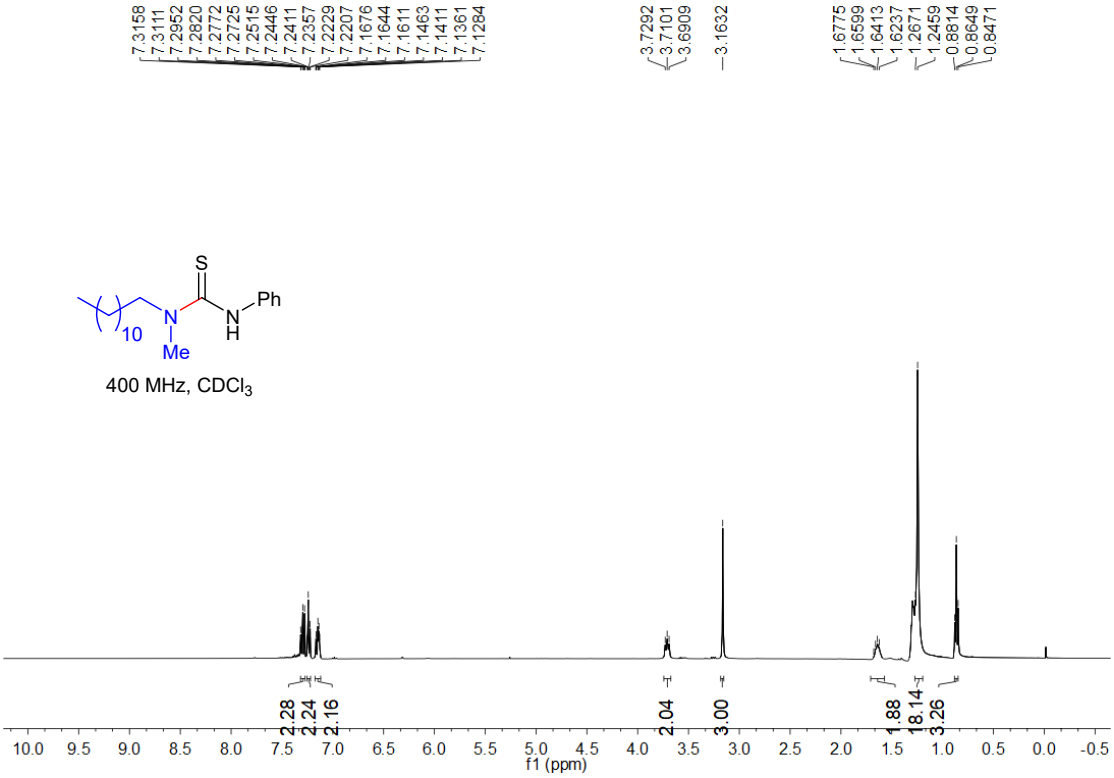


^{13}C NMR

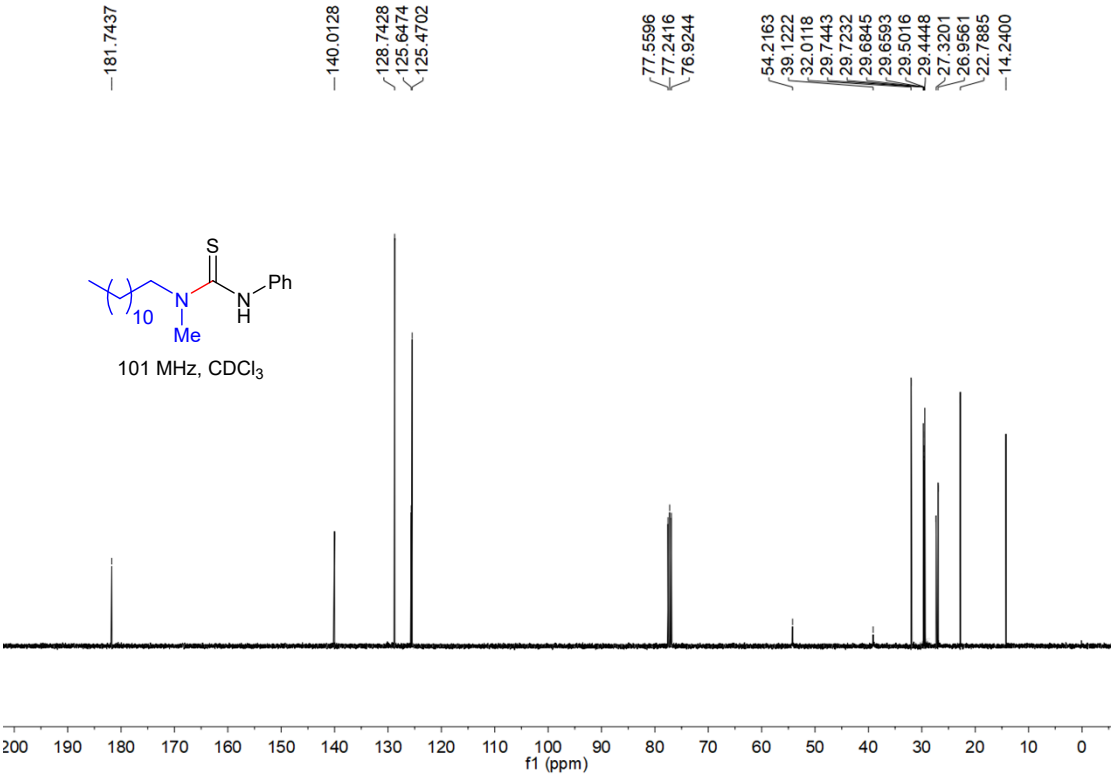


36c

[1]H NMR

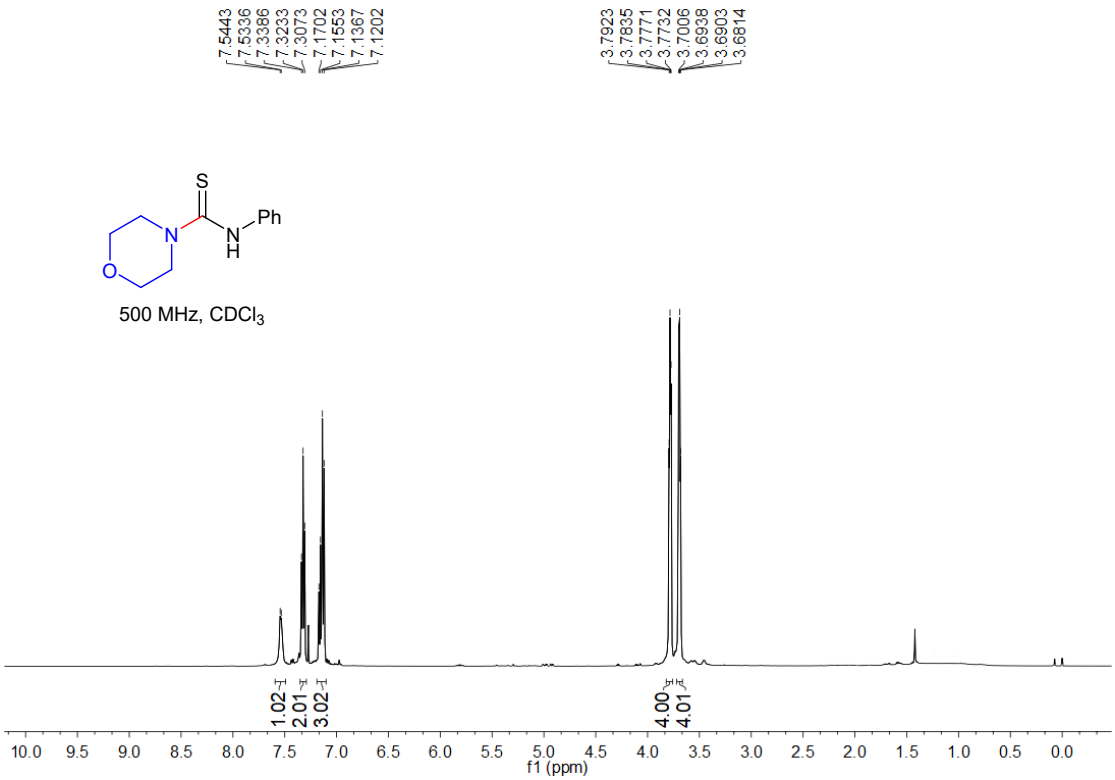


[13]C NMR

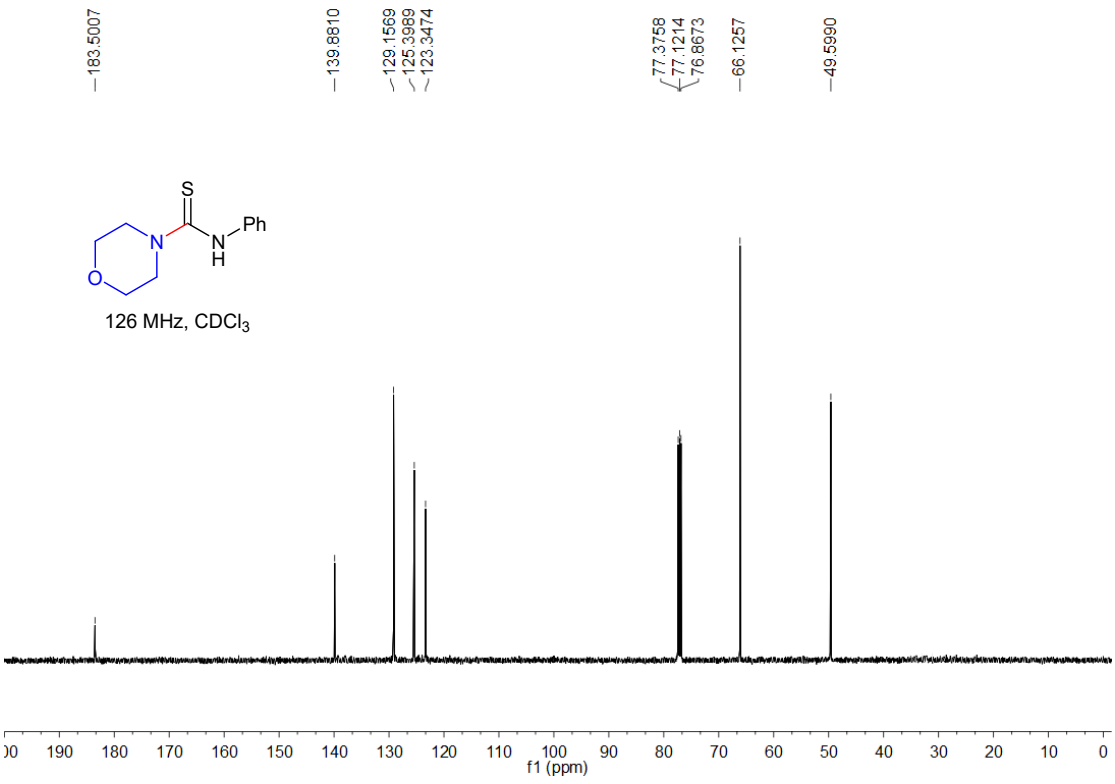


37c

^{1}H NMR

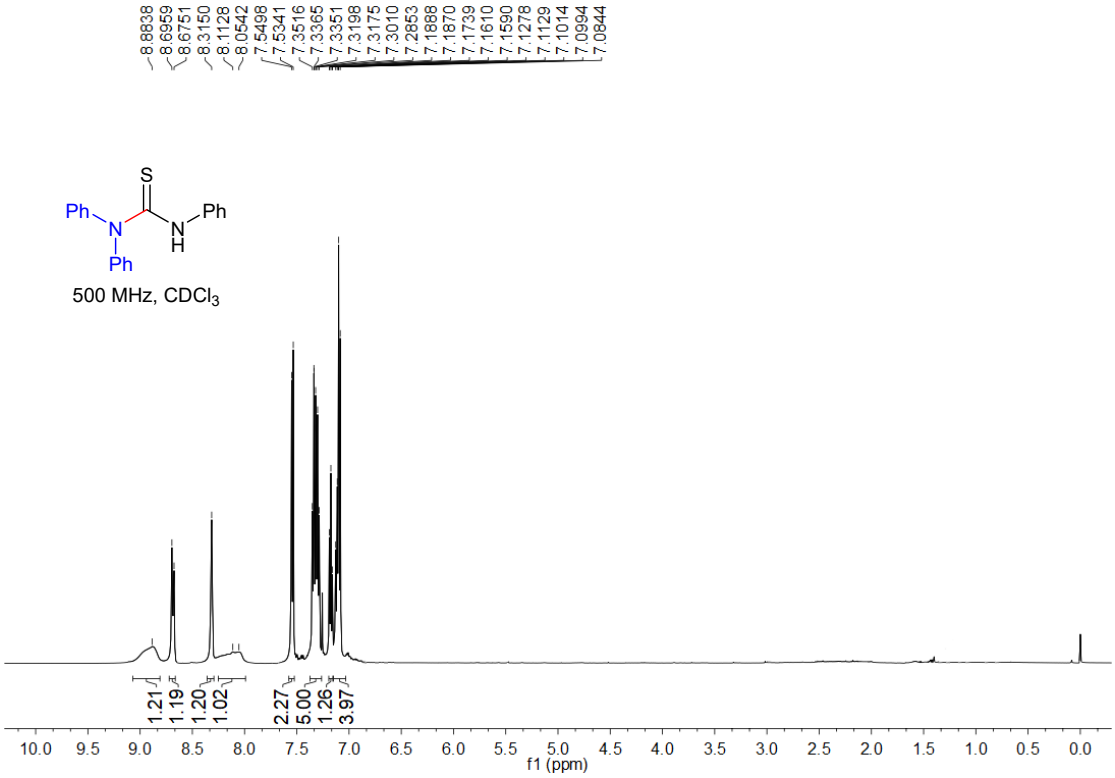


^{13}C NMR

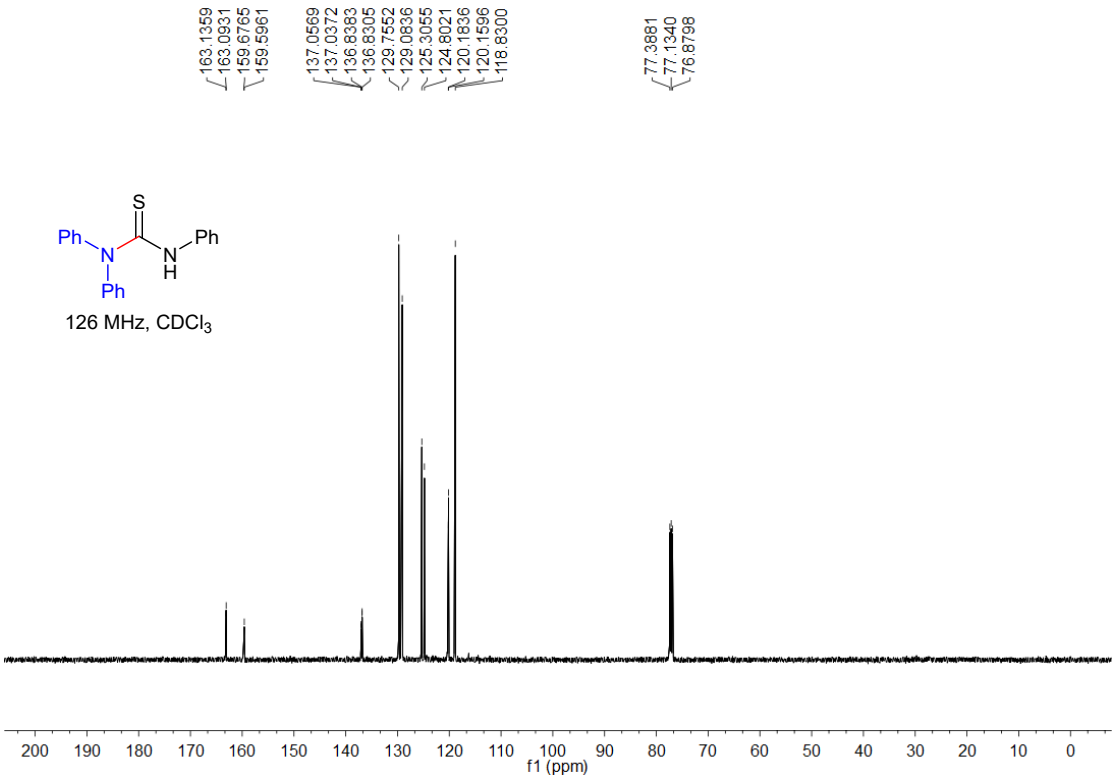


38c

^{1}H NMR

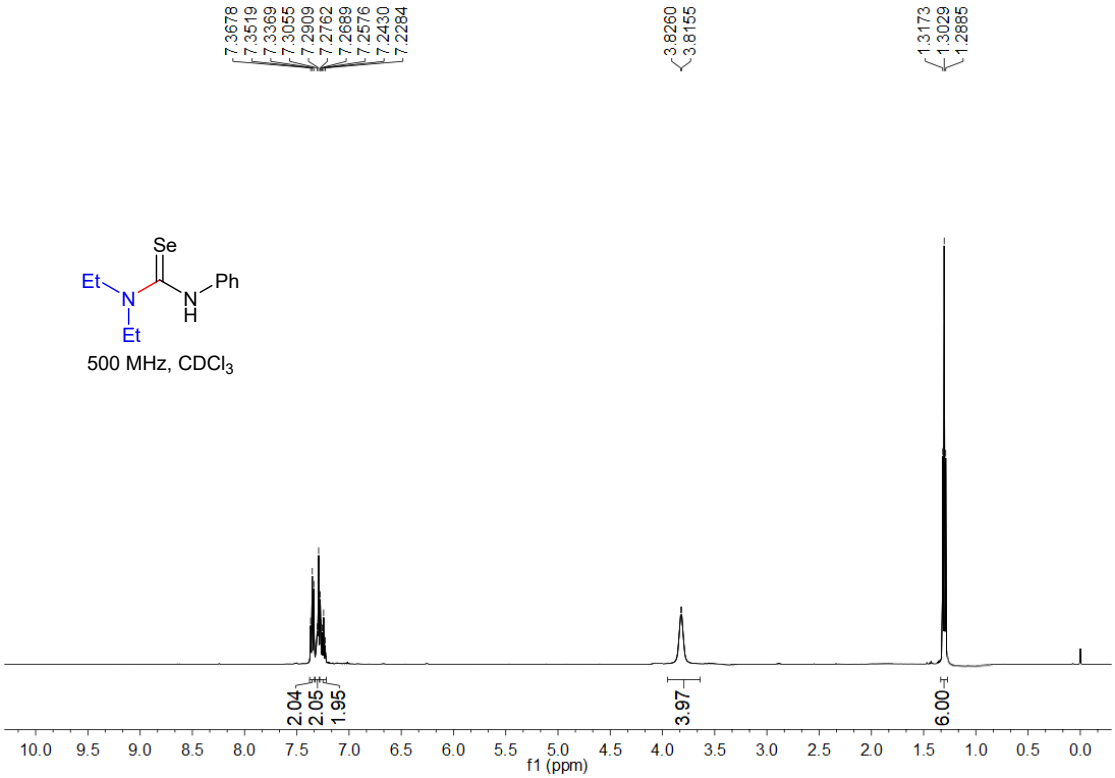


^{13}C NMR

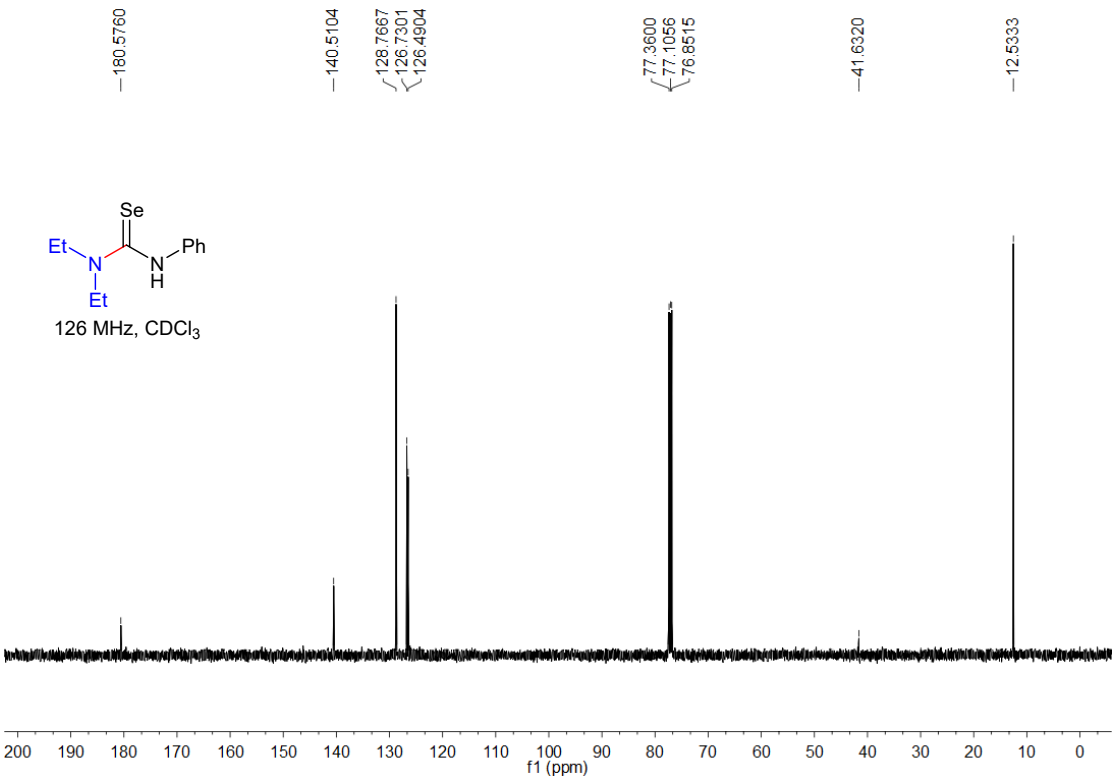


1e

^{1}H NMR

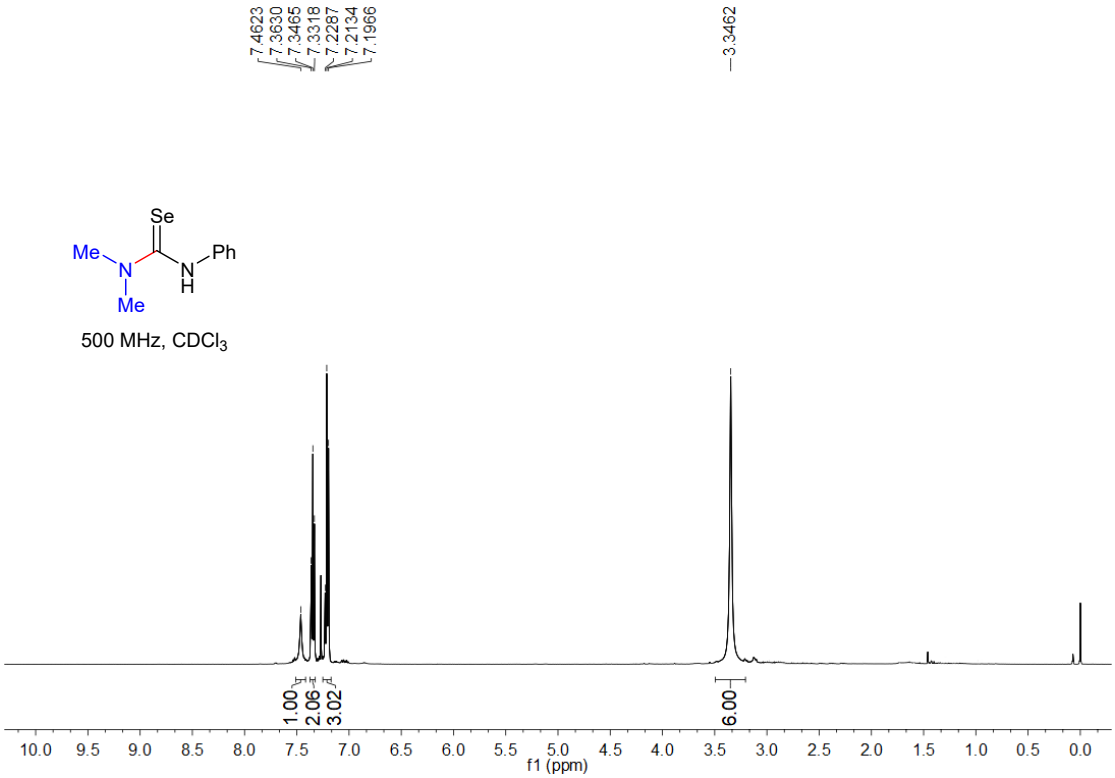


^{13}C NMR

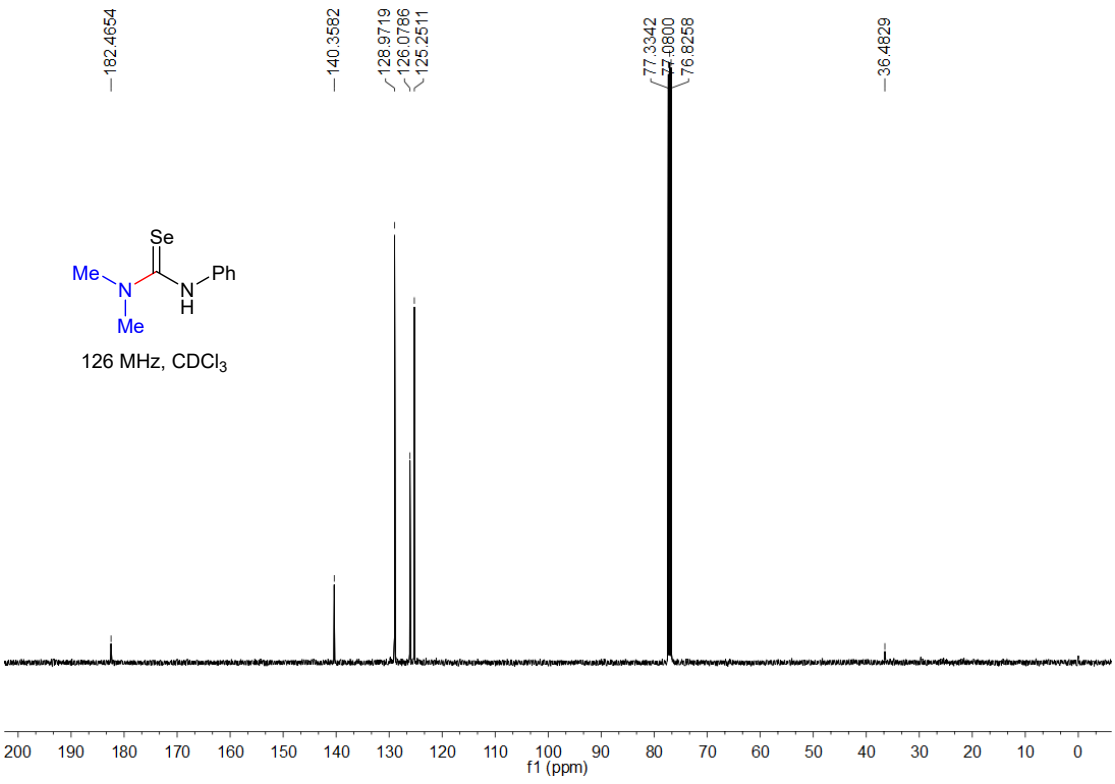


2e

^{1}H NMR

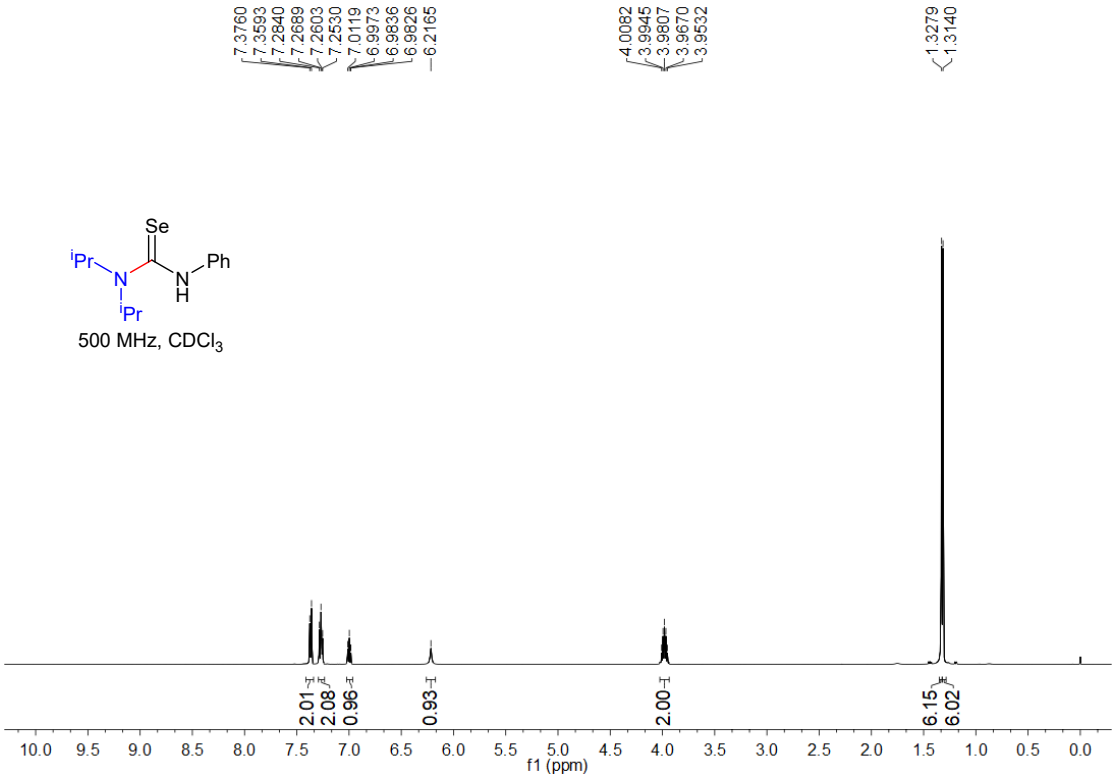


^{13}C NMR

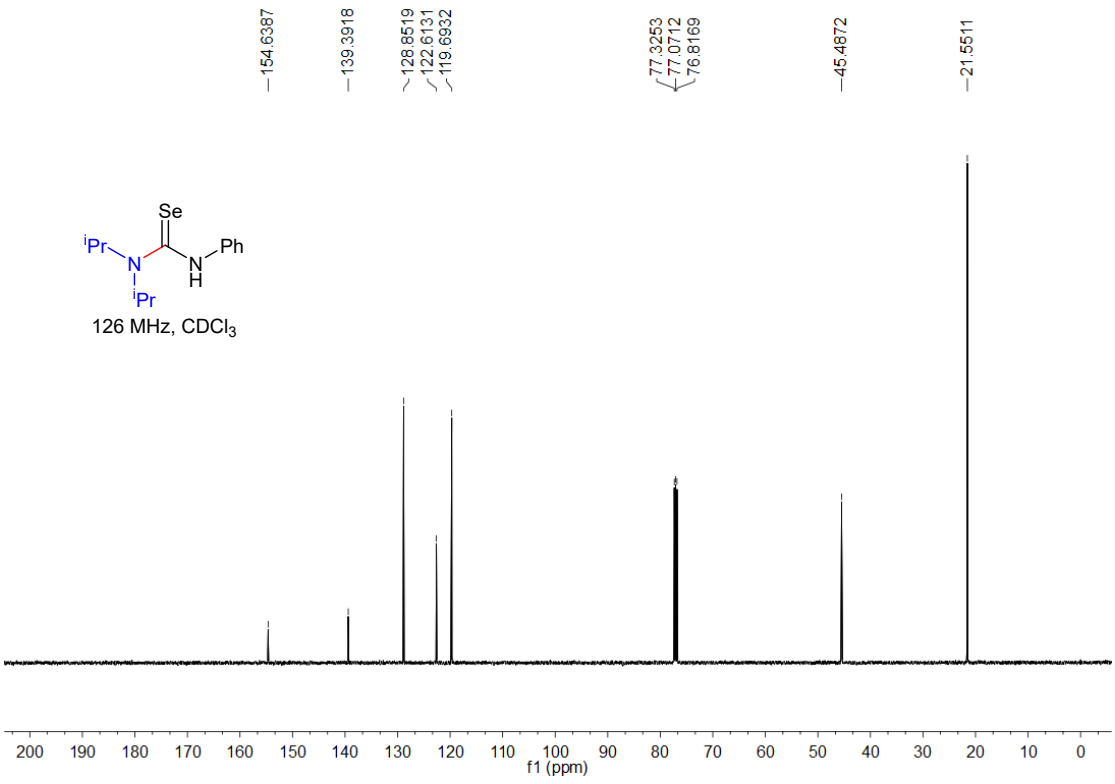


3e

^{1}H NMR

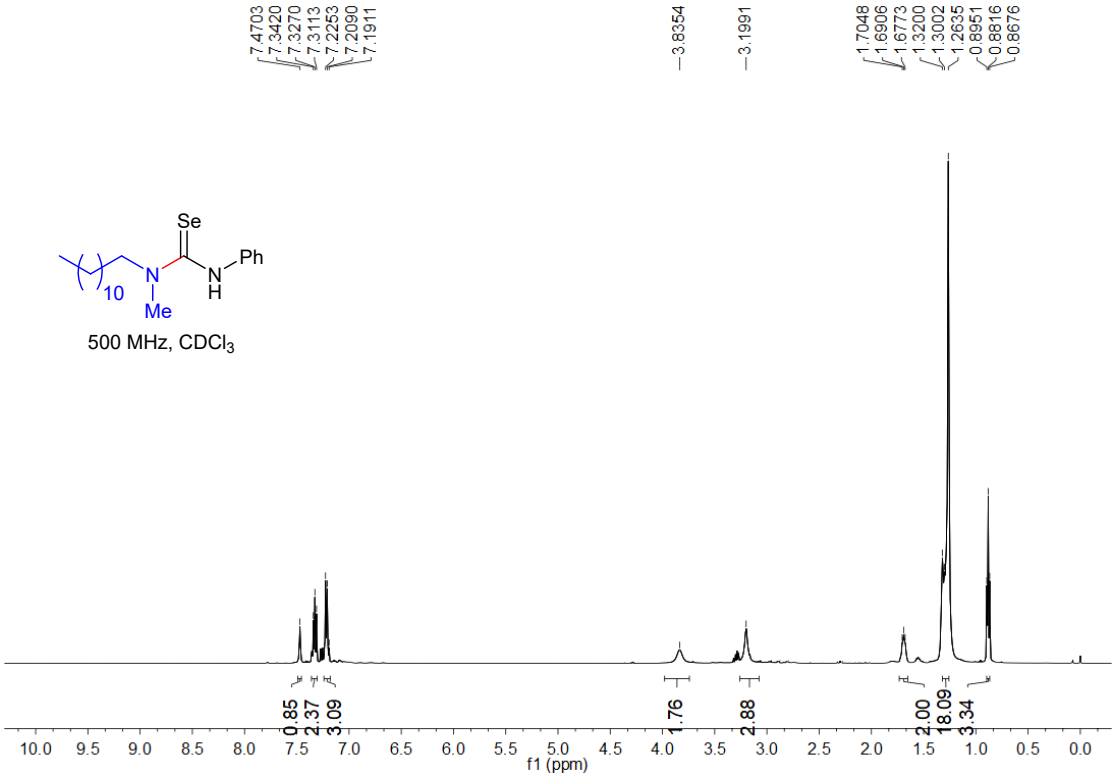


^{13}C NMR

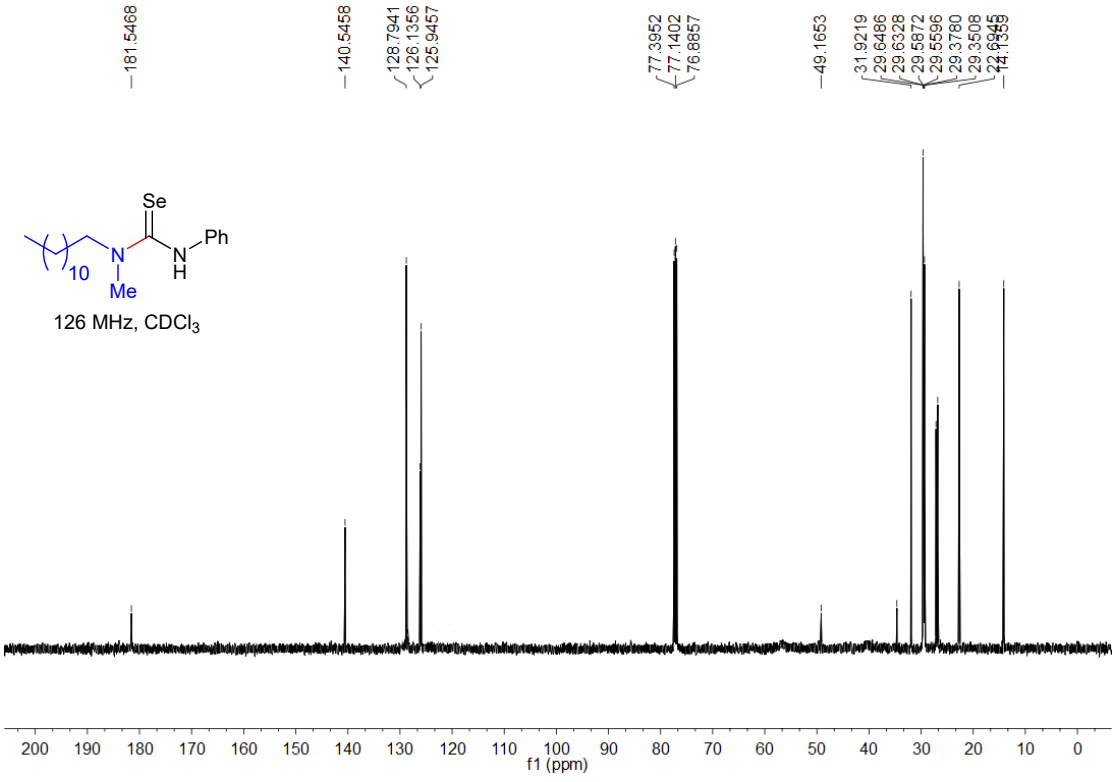


4e

^{1}H NMR

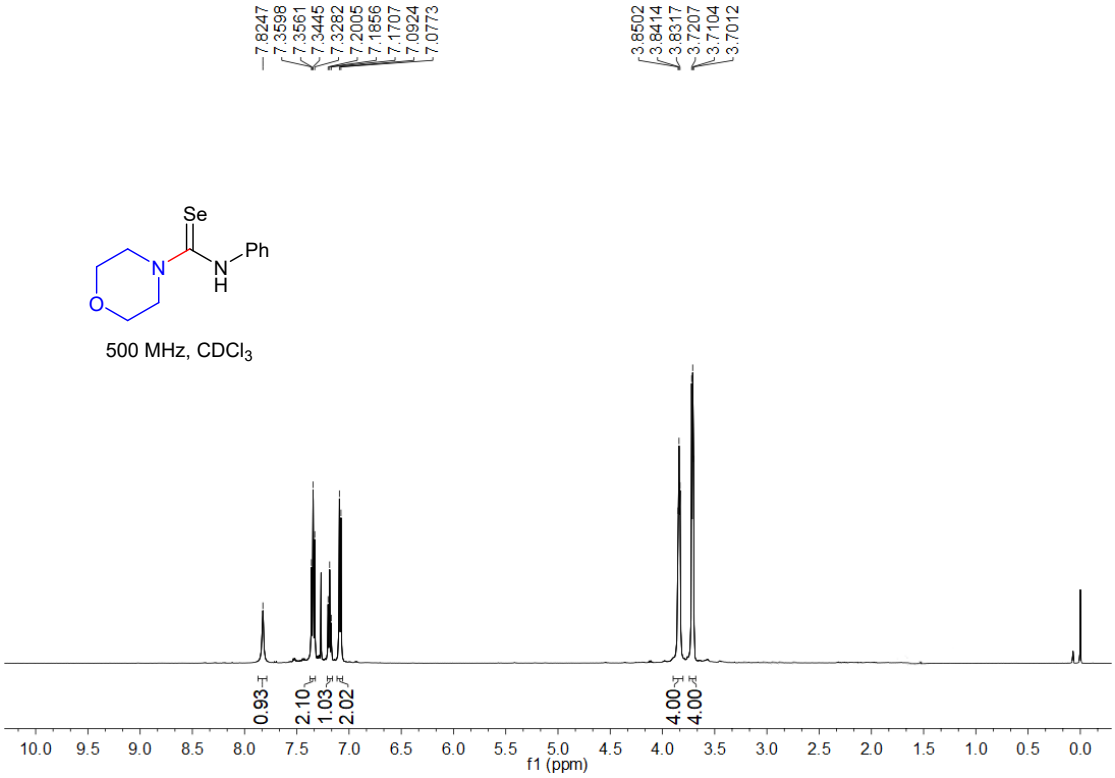


^{13}C NMR

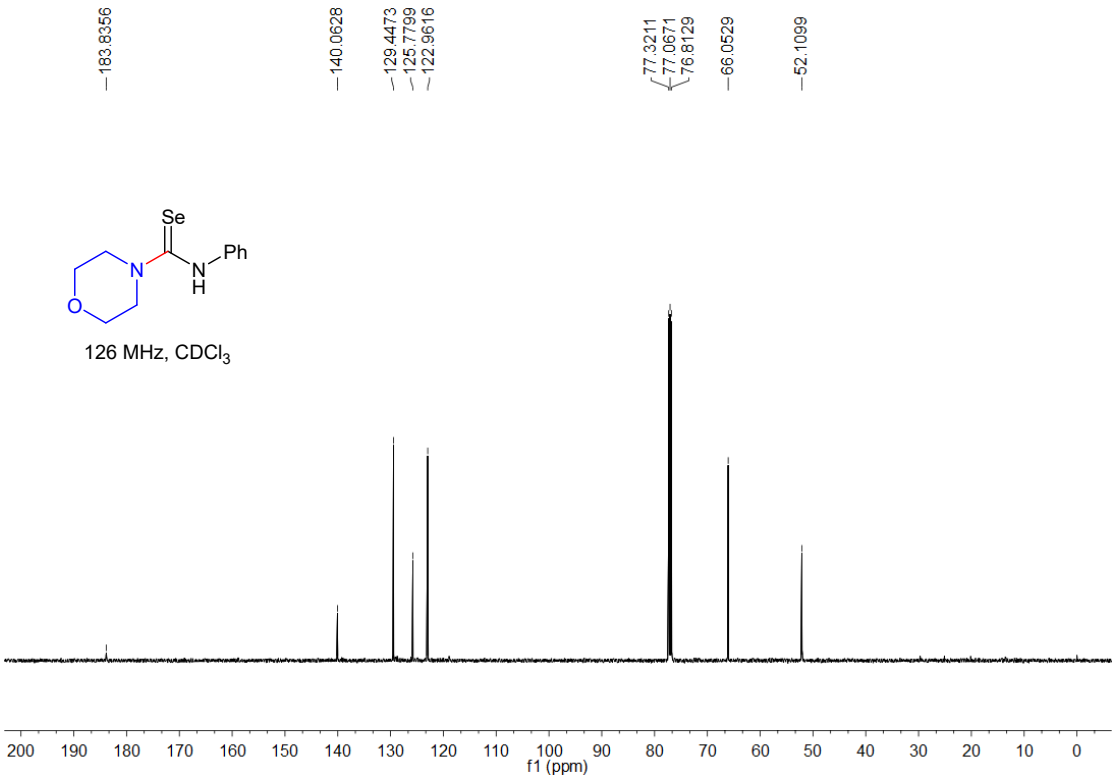


5e

^{1}H NMR

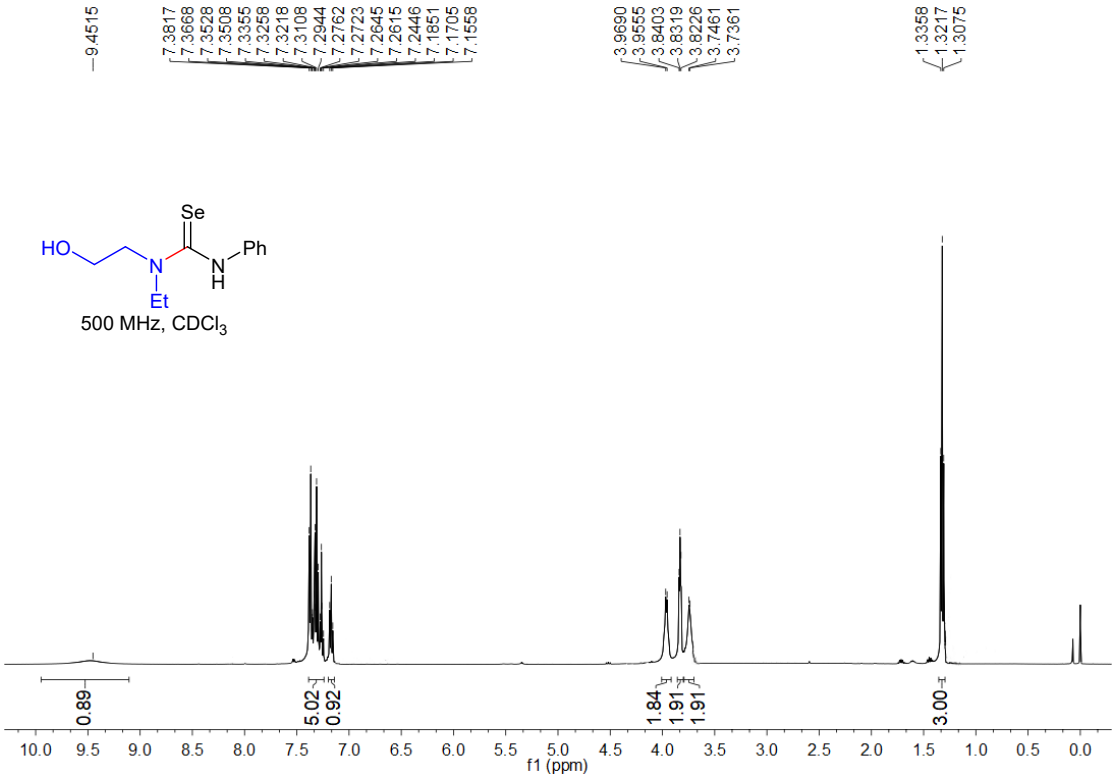


^{13}C NMR

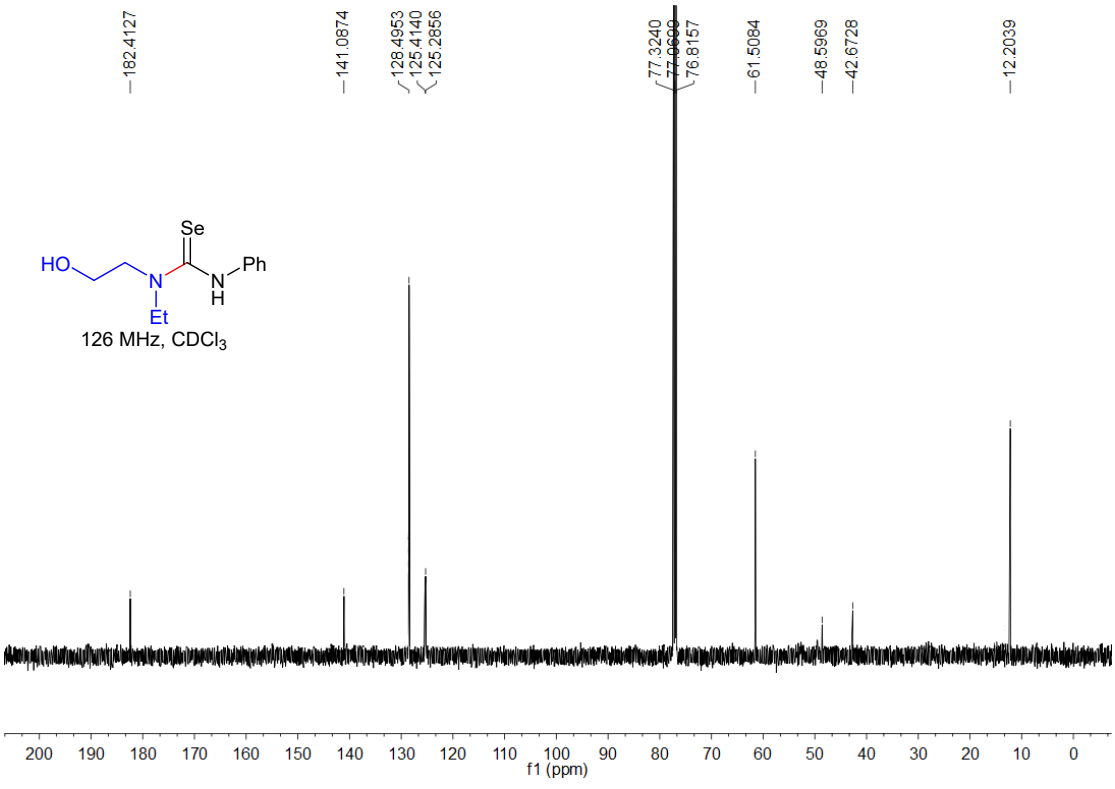


6e

^{1}H NMR

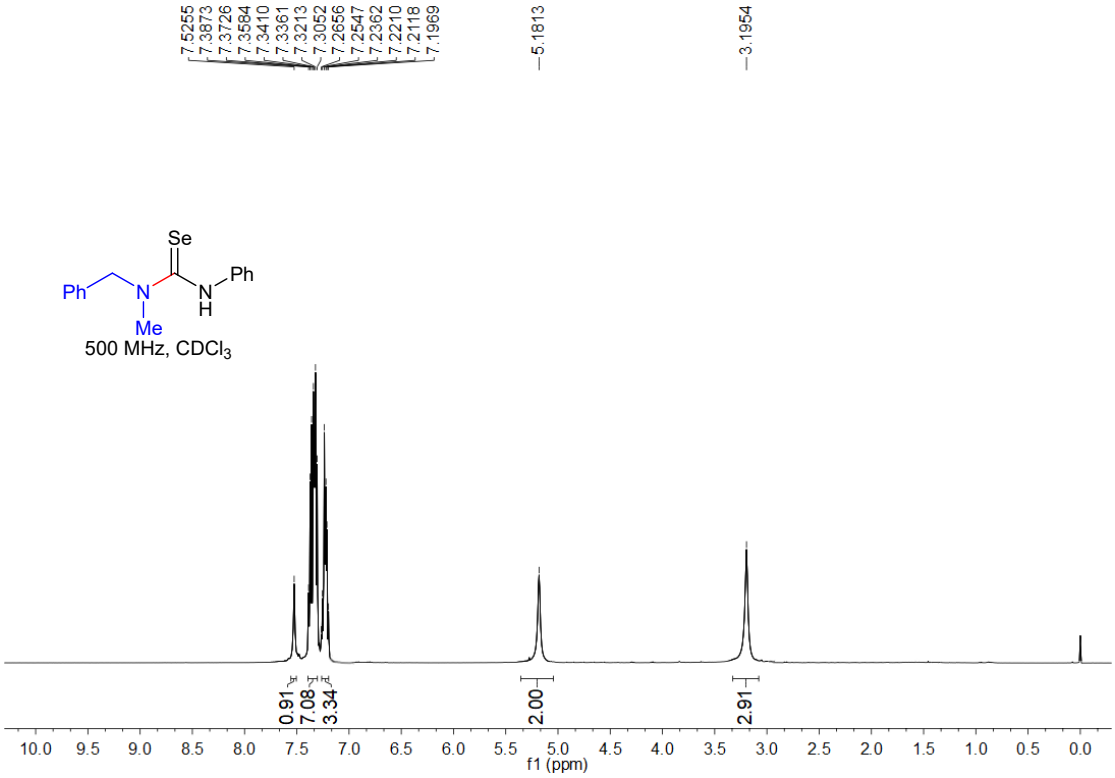


^{13}C NMR

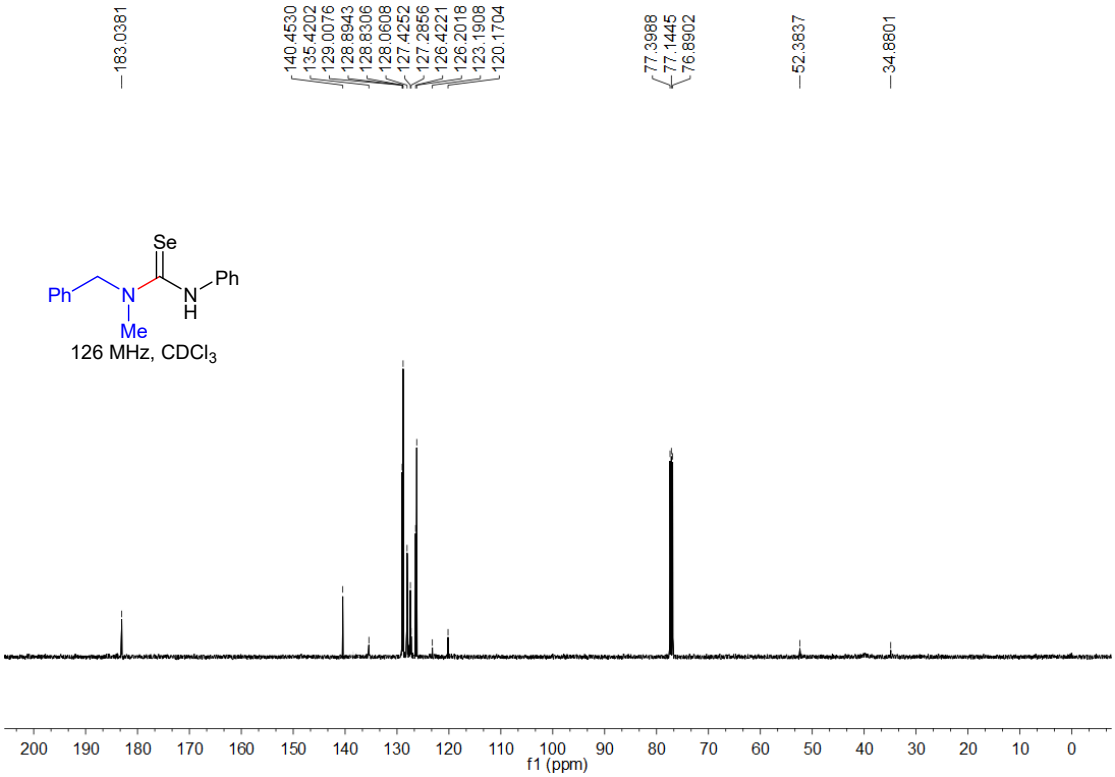


7e

^{1}H NMR

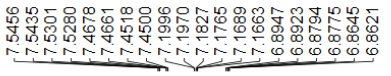


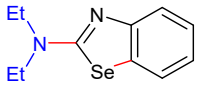
^{13}C NMR



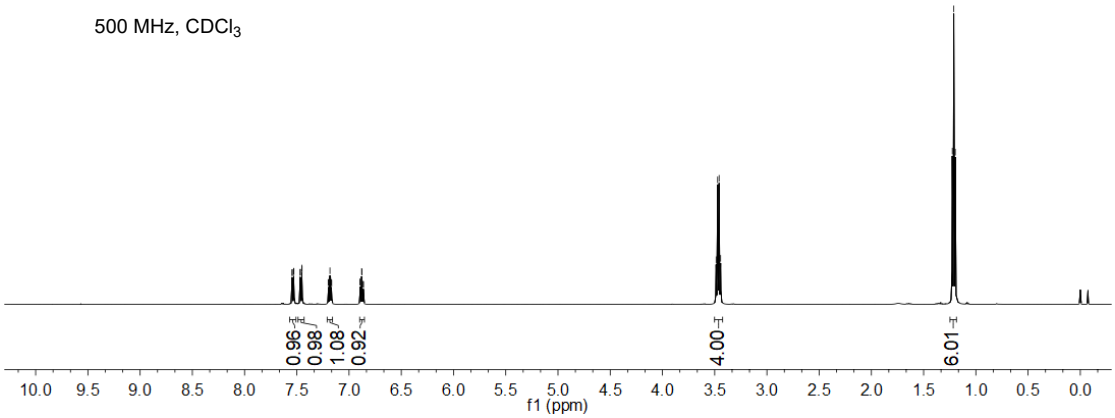
1f

^{1}H NMR

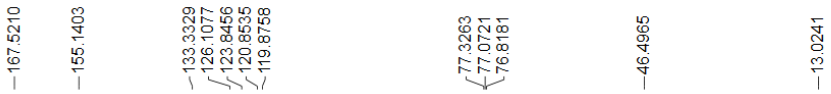


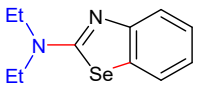


500 MHz, $CDCl_3$

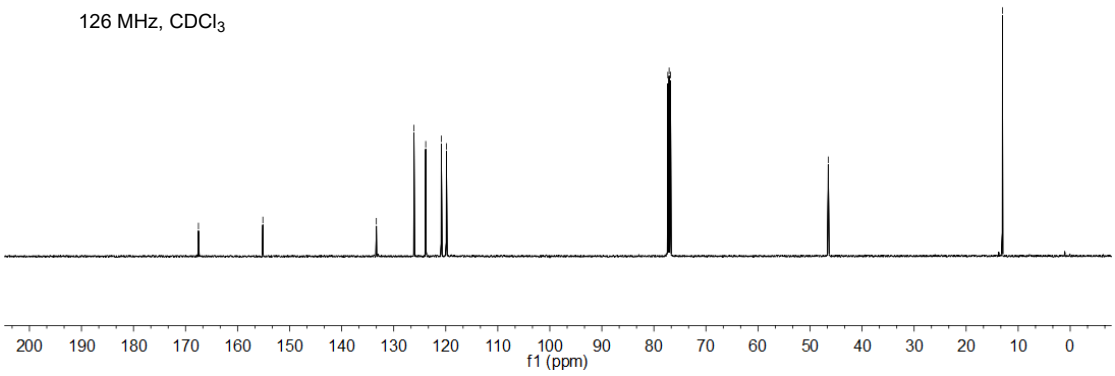


^{13}C NMR



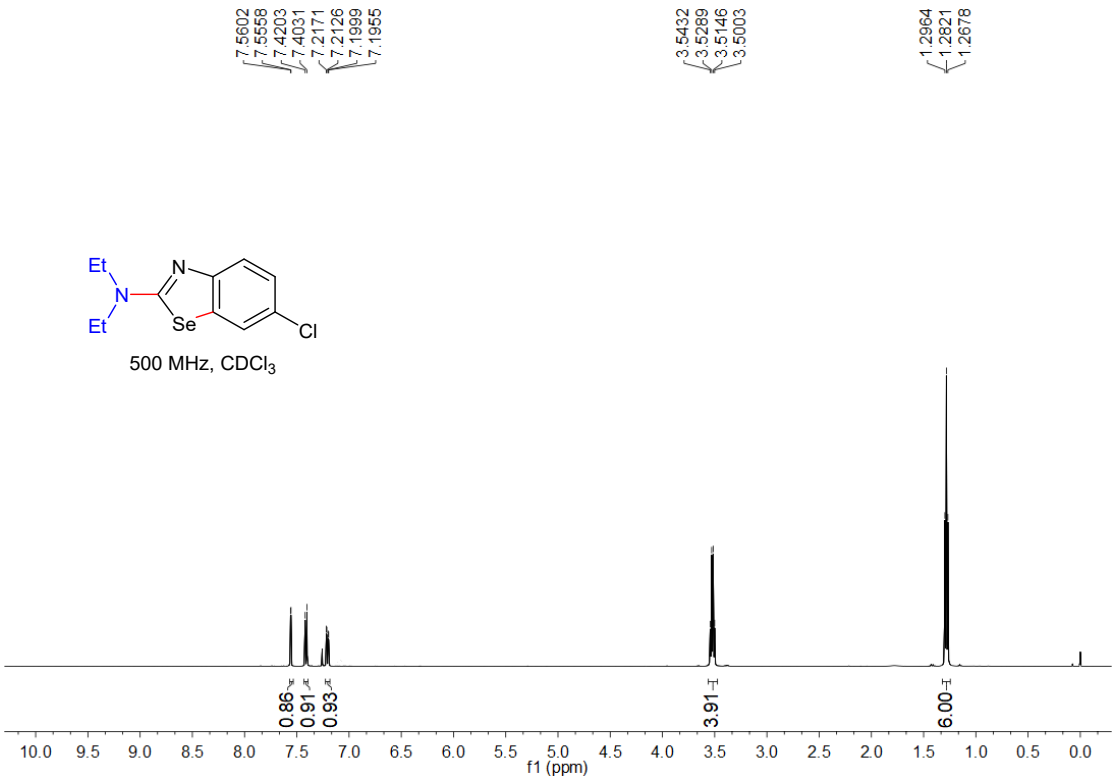


126 MHz, $CDCl_3$

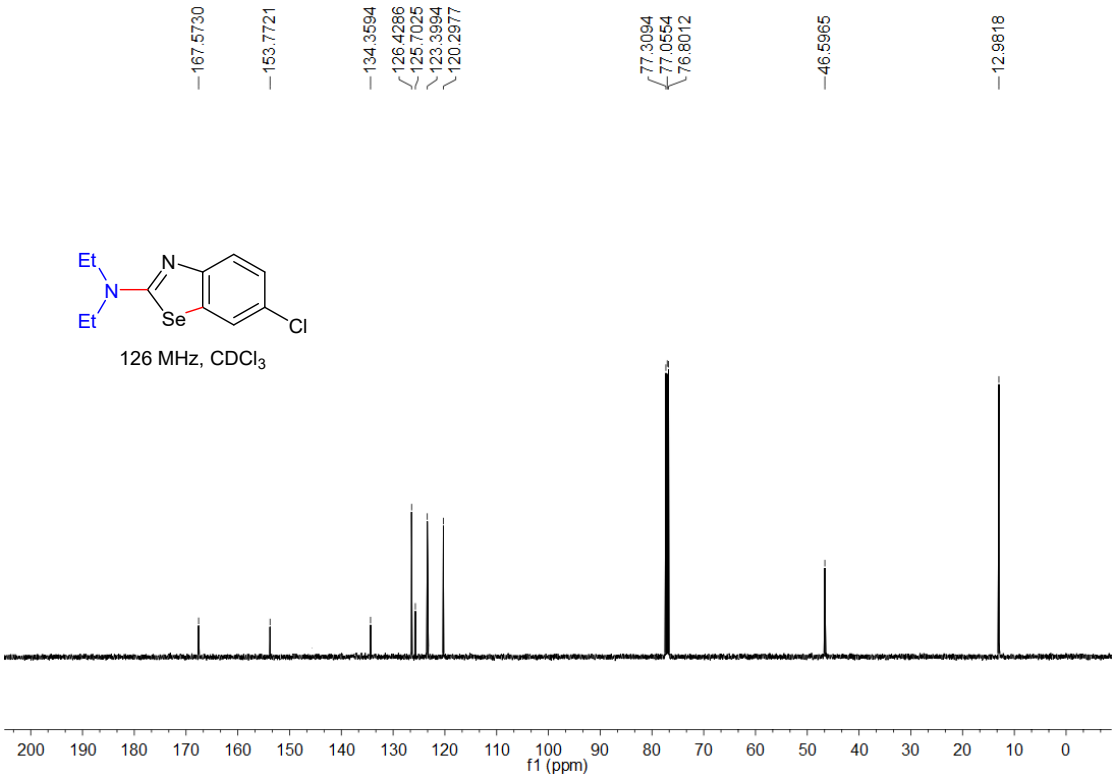


2f

^{1}H NMR



^{13}C NMR



3f

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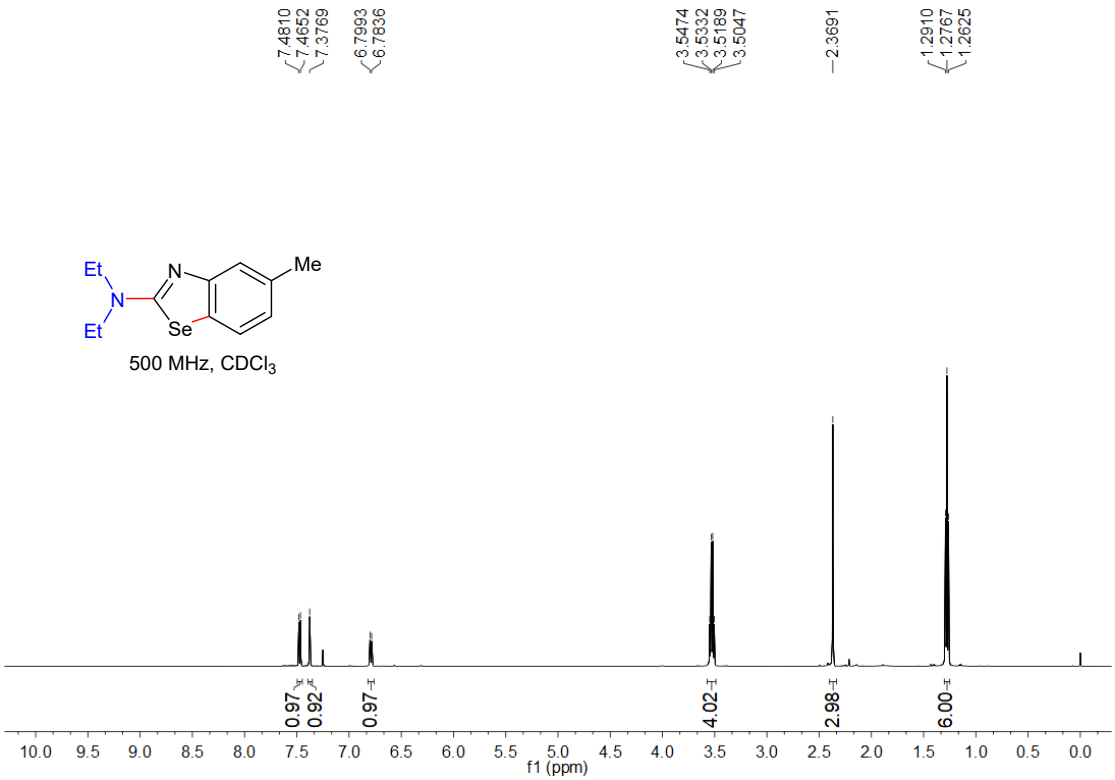
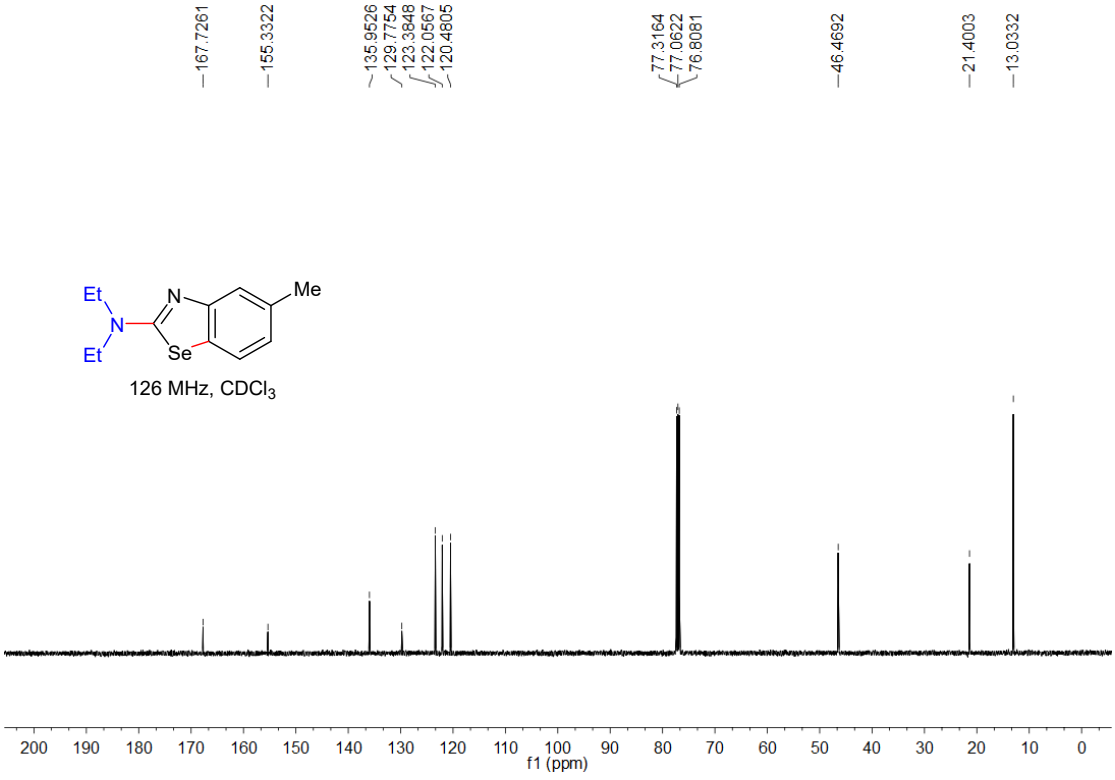
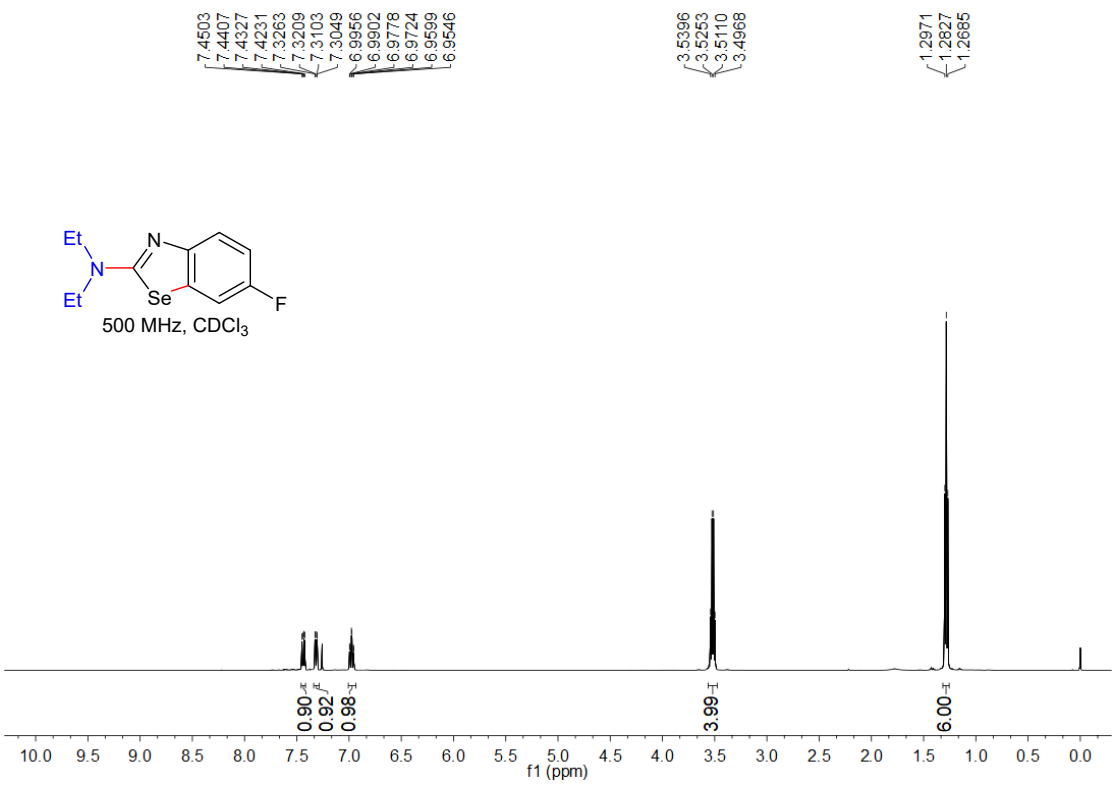


^{13}C NMR

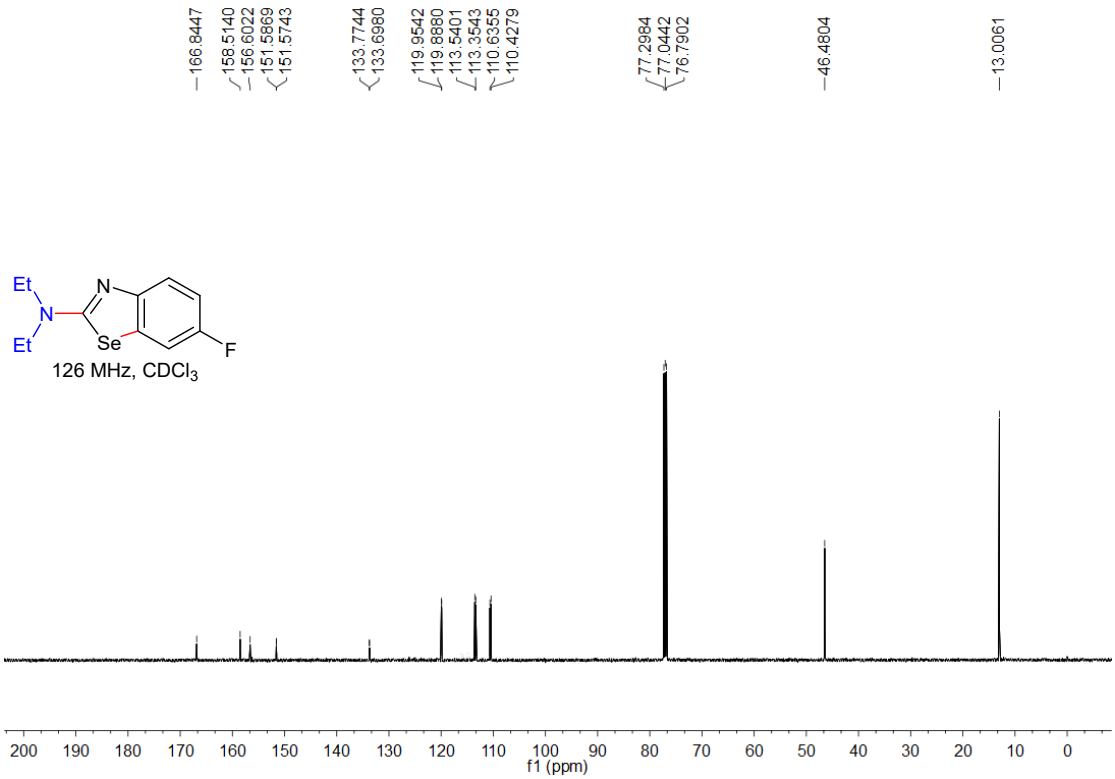


4f

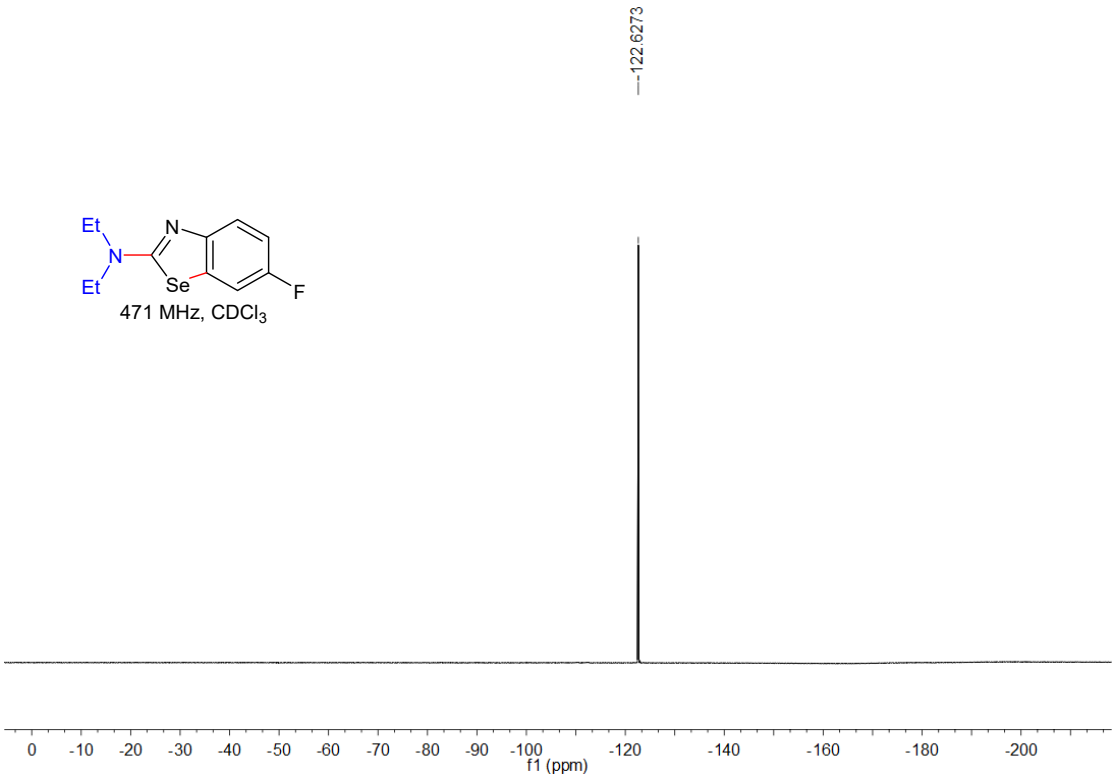
^{1}H NMR



^{13}C NMR

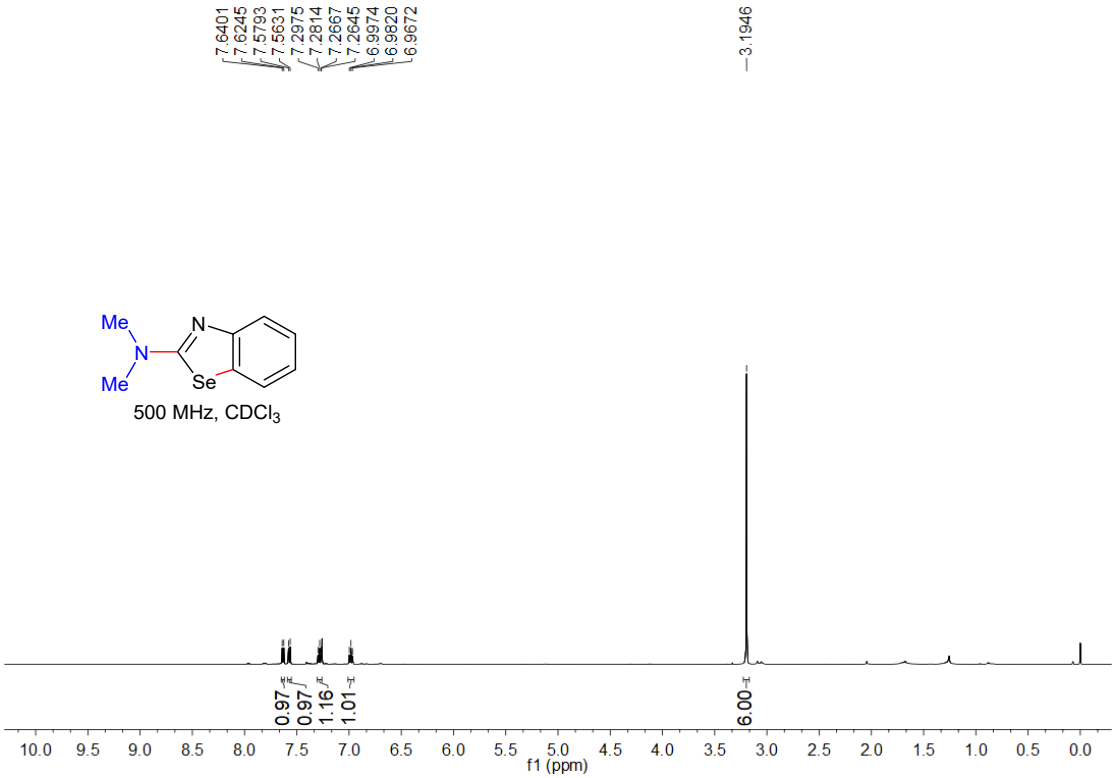


^{19}F NMR

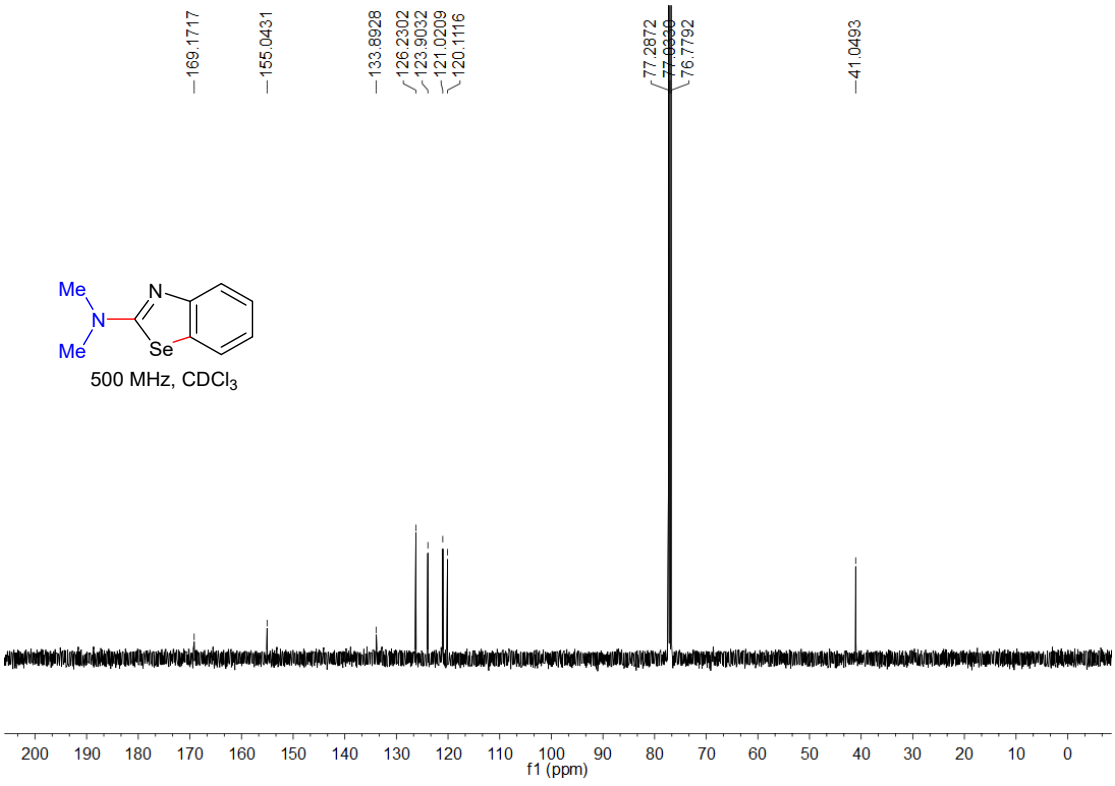

-122.6273
Et
N
Et
N
Se
F
471 MHz, CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

5f

^{1}H NMR

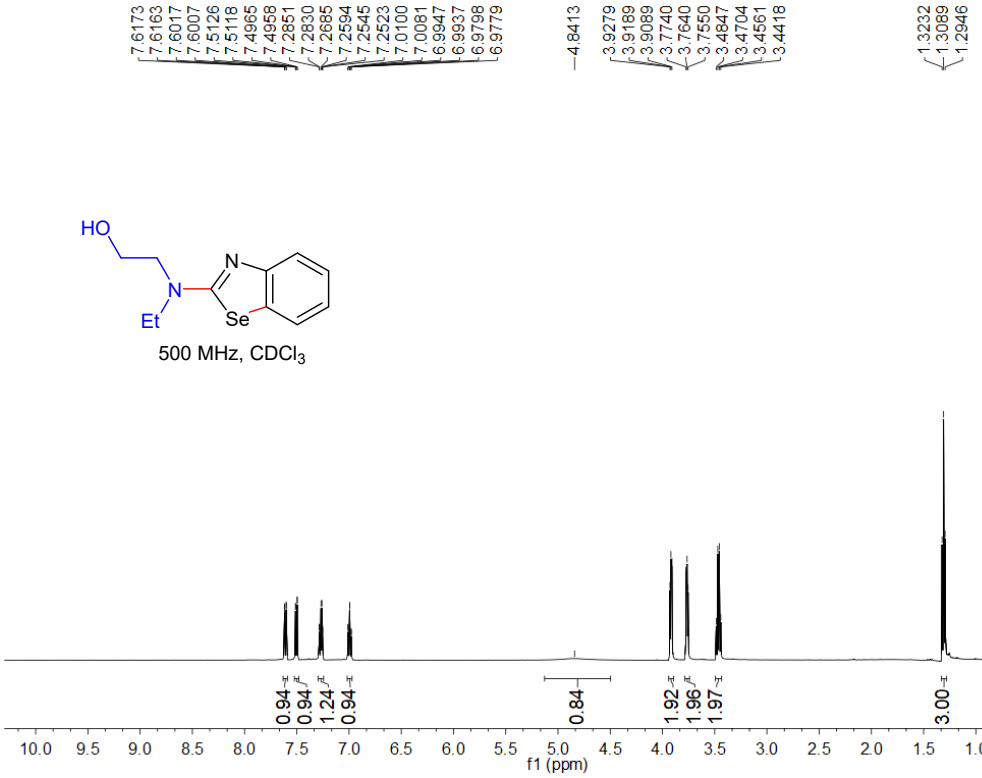


^{13}C NMR

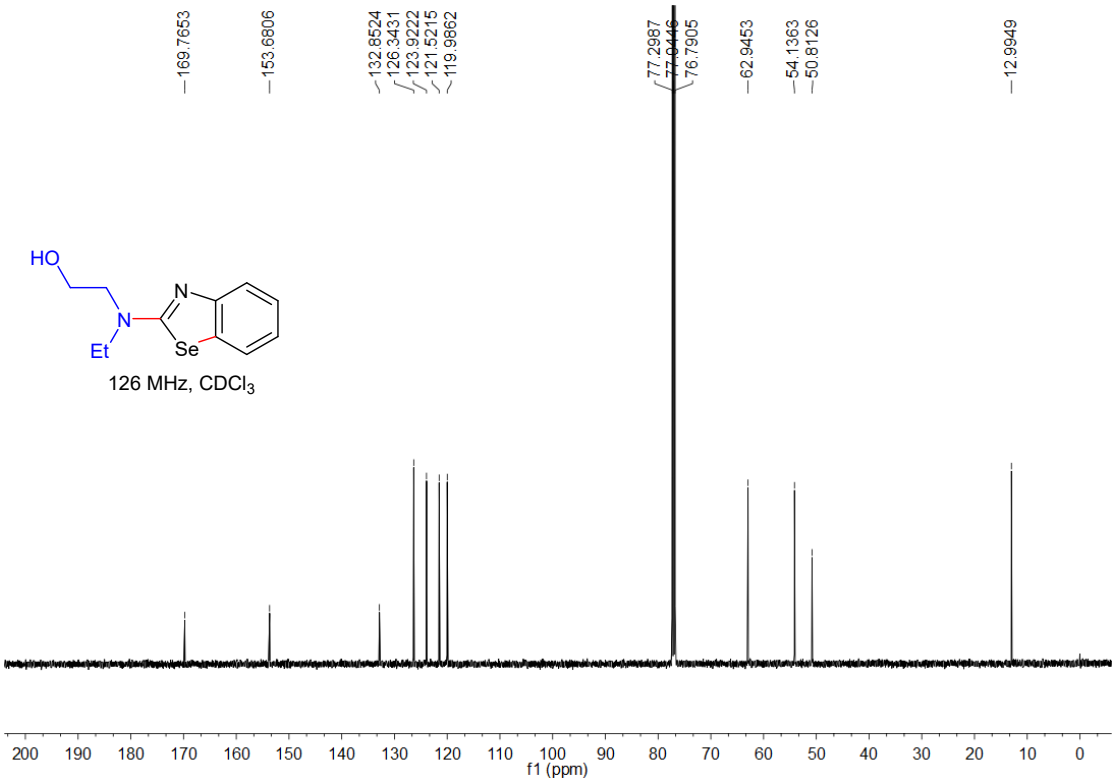


6f

^{1}H NMR

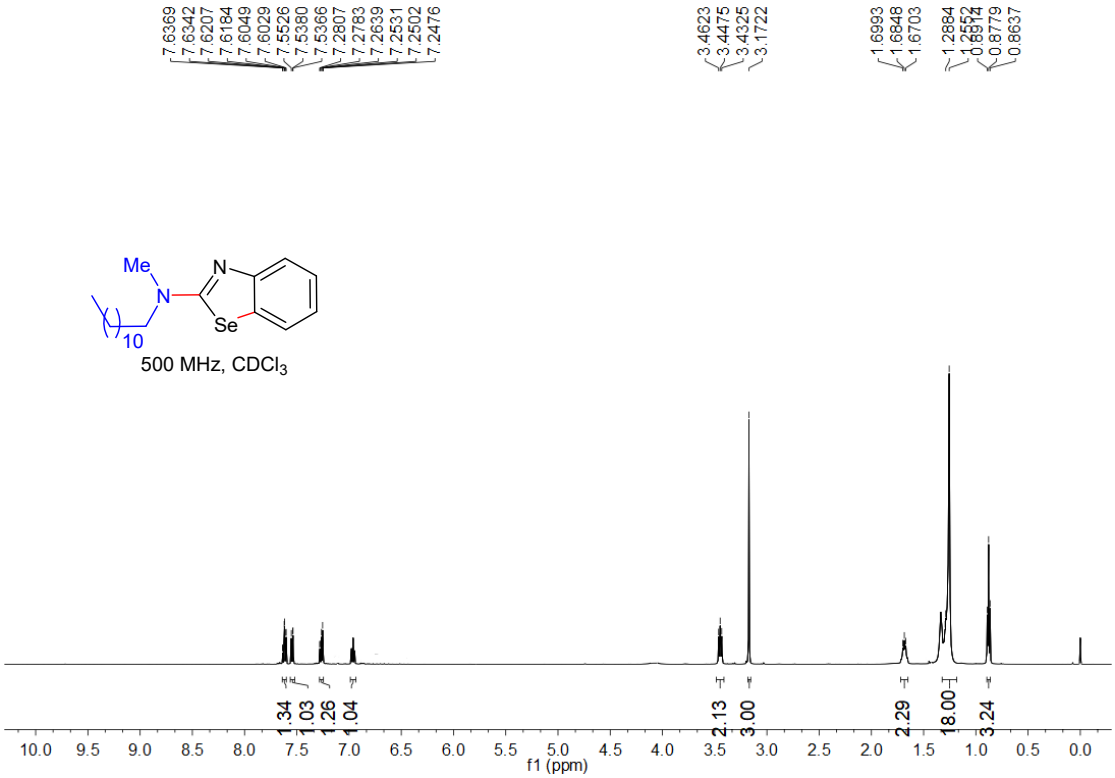


^{13}C NMR



7f

^{1}H NMR



^{13}C NMR