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Supporting information

Facile access to S-methyl dithiocarbamates with sulfonium or sulfoxonium iodides as methylation reagent

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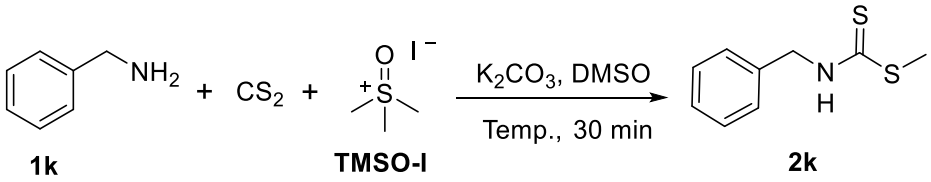
Table S1 TMSO-I-mediated thiolmethylation of benzylamine (**1k**)[a]



1k **TMSO-I** **2k**

Entry	TMSO-I (equiv)	Temp. (℃)	Yield (%)[a]
1	2.0 equiv	65	39
2	**1.5 equiv**	**65**	**88**
3	1.1 equiv	65	78
4	1.5 equiv	80	66
5	1.5 equiv	120	26
6	1.5 equiv	120	89[b]

[a] Reaction condition: **1k (**1.0 equiv), CS_2 (1.2 equiv), TMSO-I (1.1 – 2.0 equiv), K_2CO_3 (4.0 equiv), DMSO, 30 min; [b] K_2CO_3 was replaced with DIPEA.

Experimental procedure

1. General Information

All chemicals were used as received unless otherwise stated. Trimethylsulfonium iodide and trimethylsulfoxonium iodide were purchased from Bide Pharmatech Ltd. (Shanghai, China). D_6-DMSO were purchased from Shanghai Titan Scientific Co., Ltd. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on Bruker 400 NMR spectrometer. Proton chemical shifts of NMR spectra were calibrated with TMS as internal reference. HR-MS spectral data were recorded on Agilent 6550 Q-TOF or Thermo Fisher Q Exactive Orbitrap mass spectrometer. Analytical thin-layer chromatography (TLC) analysis was performed on TLC silica gel plates (0.2 ± 0.03 mm) and visualized with ultraviolet light (254 nm) to monitor the reaction progression.

2. Synthetic procedure and spectroscopic data with trimethylsulfonium iodide as methylation reagent

General procedure: A solution of trimethylsulfonium iodide (3.0 equiv) in ddH_2O (1 mL) was added to a mixture of amine (1.0 equiv), carbondisulfide (1.2 equiv), and 28% ammonium hydroxide solution (1 mL) in ethanol (6 mL) in a sealed tube, and it was stirred at 120 °C for 30 min. Then the mixture was cooled to room temperature, and extracted with DCM or ethyl ether twice. After being washed with H_2O and brine, the combined organic was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The desired compound could be obtained directly for characterization or after purification by silica gel column chromatography.

Compound **2a** was obtained as a yellow solid in 70% yield (195 mg, 1.11 mmol) after extraction with ethyl ether without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (s, 2H), 3.89 (s, 2H), 2.66 (s, 3H), 1.69 (m, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 196.9, 53.0, 51.2, 25.7, 24.3, 20.1. Data are consistent with previous reports[1].

Compound **2b** was obtained as a colorless liquid in 76% yield (150 mg, 0.93 mmol) after extraction with ethyl ether without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (t, *J* = 7.2 Hz, 2H), 3.65 (t, *J* = 6.4 Hz, 2H), 2.66 (s, 3H), 2.09 (p, *J* = 7.2 Hz, 2H), 1.99 (p, *J* = 7.2 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 193.9, 55.0, 50.5, 26.1, 24.4, 19.4. Data are consistent with previous reports[1].

Compound **2c** was obtained as a yellow liquid in 59% yield (120 mg, 0.68 mmol) after purification with silica gel column chromatography (PE/EtOAc 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (brs, 4H), 3.77 (t, *J* = 4.8 Hz, 4H), 2.68 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 198.9, 66.3, 50.6, 19.9. Data are consistent with previous reports[2].

Compound **2d** was obtained as a yellow liquid in 60% yield (140 mg, 0.86 mmol) after extraction with ethyl ether without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (q, *J* = 7.2 Hz, 2H), 3.75 (q, *J* = 7.2 Hz, 2H), 2.64 (s, 3H), 1.29 (m, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 196.8, 49.5, 46.7, 20.0, 12.4, 11.6. Data are consistent with previous reports[1].

Compound **2e** was obtained as a colorless liquid in 72% yield (220 mg, 1.17 mmol) after extraction with ethyl ether without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (m, 2H), 5.23 (m, 4H), 4.67 (s, 2H), 4.30 (s, 2H), 2.65 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 199.3, 131.1 130.4, 118.5, 118.4, 56.5, 53.6, 20.4. Data are consistent with previous reports[3].

Compound **2f** was obtained as a yellow liquid in 91% yield (150 mg, 0.71 mmol) as a mixture of isomers with a ratio of ca. 2:1 after purification through silica gel column chromatography (PE/EtOAc 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 5H), 5.39 [5.00] (s, 2H), 3.29 [3.48] (s, 3H), 2.69 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.1 [199.0], 135.7 [134.9], [128.9] 128.8, [128.0] 127.7, 127.1, 59.5 [57.6], [43.5] 38.8, 20.7 [20.1]. The data of minor isomer are given in square brackets. Data are consistent with previous reports[4].

Compound **2g** was obtained as a colorless liquid in 70% yield (220 mg, 0.92 mmol) as a mixture of isomers with a ratio of 1:1 after purification through silica gel column chromatography (PE/EtOAc 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 5H), [6.05] 5.00 (s, 1H), [5.32] 4.93 (s, 2H), 2.71 [2.63] (s, 3H), 1.22 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.2 [199.9], 137.4 [136.5], 128.6 [128.4], 127.2 [126.8],

[126.5] 126.1, 55.1 [53.9], 52.3 [50.2], 20.7, [20.3] 19.8. The data of the other isomer are given in square brackets. Data are consistent with previous reports[5].

Compound **2h** was obtained as a colorless liquid in 93% yield (273 mg, 0.95 mmol) after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 10H), 5.35 (s, 2H), 4.95 (s, 2H), 2.72 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.9, 139.4, 135.7, 134.8, 129.0, 128.9, 128.3, 127.9, 127.2, 127.0, 61.3, 56.4, 54.0, 42.3, 20.8. Data are consistent with previous reports[6].

Compound **2i** was obtained as a white solid in 73% yield (307 mg, 1.45 mmol) after purification through silica gel column chromatography (PE/DCM 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.13 (m, 2H), 3.76 (s, 3H), 2.53 (s, 3H), 2.41 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.5, 142.3, 139.2, 130.4, 126.6, 46.2, 21.3, 20.8. Data are consistent with previous reports[7].

Compound **2j** was obtained as a yellow liquid in 63% yield (140 mg, 0.67 mmol) after purification through silica gel column chromatography (PE/EtOAc 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 3H), 7.12 (t, J = 7.4 Hz, 1H), 4.51 (t, J = 8.4 Hz, 2H), 3.21 (t, J = 8.4 Hz, 2H), 2.71 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 193.5, 144.1, 134.6, 126.8, 125.3, 125.2, 118.5, 54.3, 27.4, 19.6. Data are consistent with previous reports[6].

3. Synthetic procedure and spectroscopic data with trimethylsulfoxonium iodide as methylation reagent

General procedure: amine (1.0 equiv), carbondisulfide (1.2 equiv), trimethylsulfoxonium iodide (1.5 equiv), K_2CO_3 (4.0 equiv) was added to DMSO (8 mL) in a sealed tube, then the mixture was stirred at 65 °C for 30 min. The reaction mixture was cooled down, diluted with H_2O, and extracted with DCM or ethyl ether twice. After being washed with H_2O and brine, the organic was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The desired compound could be obtained directly for characterization or after purification by silica gel column chromatography.

Compound **3a** was obtained as a yellow liquid in 61% yield (138 mg, 0.61 mmol) as a mixture of isomers in the ratio of 3:1 after purification through silica gel column chromatography (PE/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 9.2 Hz 2H), 6.90 (d, J = 8.8 Hz 2H), 4.84 [4.55] (d, J = 5.2 Hz, 2H), 3.81 (s, 3H), [2.70] 2.65 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ [201.6] 198.8, 159.5, 129.7 [129.4], 128.3 [127.2], 114.3, 55.4, 50.9 [49.9], [19.1] 18.3; HRMS-ESI (m/z): calcd for $C_{10}H_{14}NOS_2^+$ $[M+H]^+$ 228.0511, found 228.0513.

Compound **3b** was obtained as a white solid in 64% yield (142 mg, 0.64 mmol) as a mixture of isomers in the ratio of 17:1 after purification through silica gel column chromatography (PE/EtOAc 9:1). ^{1}H NMR (400 MHz, d_6-DMSO) δ 10.47 (s, 1H), 7.80 (m, 2H), 7.45 (d, J = 8.0 Hz 2H), 4.91 [4.67] (s, 2H), 2.55 [2.52] (s, 3H);

$^{13}C\{^{1}H\}$ NMR (101 MHz, d_6-DMSO) δ [200.7] 199.2, 143.8 [143.2], [133.0] 132.8, 128.7 [128.5], 119.5, [110.6] 110.3, 49.4 [48.9], [18.6] 18.0; HRMS-ESI (m/z): calcd for $C_{10}H_{11}N_2S_2^+$ $[M+H]^+$ 223.0358, found 223.0359.

Compound **3c** was obtained as a yellow liquid in 61% yield (197 mg, 0.92 mmol) as a mixture of isomers in the ratio of 5:1 after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.05 (m, 2H), 4.90 [4.60] (d, J = 5.2 Hz, 2H), [2.70] 2.86 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ [202.0] 199.4, 162.5 (d, J = 247.4 Hz), 132.1 [131.1] (d, J = 3.0 Hz), 130.0 [129.8] (d, J = 8.1 Hz), [116.1] 115.8 (d, J = 21.2 Hz), 50.3 [49.6], [19.1] 18.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ [-113.3] -113.8 (s, 1F); HRMS-ESI (m/z): calcd for $C_9H_{11}FNS_2^+$ $[M+H]^+$ 216.0311, found 216.0309.

Compound **3d** was obtained as a yellow liquid in 69% yield (240 mg, 1.04 mmol) as a mixture of isomers in the ratio of 5:1 after purification through silica gel column chromatography (PE/EtOAc 10:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz 2H), 7.26 (d, J = 8.4 Hz 2H), 4.91 [4.61] (d, J = 5.6 Hz 2H), 2.67 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 199.7, 134.8, 133.9, 129.5, [129.2] 129.0, 50.3 [49.6], [19.1] 18.4; HRMS-ESI (m/z): calcd for $C_9H_{11}ClNS_2^+$ $[M+H]^+$ 232.0016, found 232.0017.

Compound **3e** was obtained as a yellow liquid in 53% yield (147 mg, 0.53 mmol) as a mixture of isomers in the ratio of 4:1 after purification through silica gel column chromatography (PE/EtOAc 10:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.87 [4.57] (d, J = 5.6 Hz, 2H), 2.65 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 199.7, 135.4, 132.0, 129.8 [129.5], 122.0, 50.3 [49.6], [19.1] 18.4; HRMS-ESI (m/z): calcd for $C_9H_{11}BrNS_2^+$ $[M+H]^+$ 275.9511, found 275.9509.

Compound **3f** was obtained as a yellow solid in 75% yield (269 mg, 0.83 mmol) as a mixture of isomers in the ratio of 4:1 after purification through silica gel column chromatography (PE/EtOAc 10:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 4.88 [4.58] (d, J = 5.2 Hz, 2H), 2.66 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 199.7, 138.0, 136.0, 130.0 [129.7], 93.6, 50.4 [49.7], [19.6] 18.4. HRMS-ESI (m/z): calcd for $C_9H_{11}INS_2^+$ $[M+H]^+$ 323.9372, found 323.9371.

Compound **3g** was obtained as a white solid in 51% yield (170 mg, 0.80 mmol) as a mixture of isomers in the ratio of 3:1 after purification through silica gel column chromatography (PE/EtOAc 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 2H), 7.27 (m, 1H), 7.22 (m,2H), 6.92 (s, 1H), 4.01 [3.72] (q, J= 7.2, 12.8 Hz, 2H), 2.98 (m, 2H), [2.69] 2.61 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ [201.9] 199.1, 138.2 [137.3], [129.0] 128.8, 128.8 [128.7], [127.1] 126.8, 48.0 [47.3], [34.9] 34.3, [19.0] 18.1. The data of minor isomer are given in square brackets. Data are consistent with previous reports[8].

Compound **3h** was obtained as a yellow liquid in 66% yield (120 mg, 0.80 mmol) as a mixture of isomers with a ratio of 2:1 after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ [7.63] 6.94 (s, 1H) 3.71 [3.41] (q, *J* = 5.2, 12.4 Hz, 2H), [2.68] 2.64 (s, 3H), 1.69 (m, 2H), 0.99 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ [201.8] 198.9, 49.0 [48.1], [22.1] 21.7, [18.9] 18.2, 11.4. The data of minor isomer are given in square brackets. Data are consistent with previous reports[9].

Compound **3i** was obtained as a yellow liquid in 46% yield (50 mg, 0.31 mmol) as a mixture of isomers with a ratio of 2:1 after purification through silica gel column chromatography (PE/DCM 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 [3.44] (m, 2H), [2.68] 2.64 (s, 3H), 1.65 (m, 2H), 1.41 (m, 2H), 0.96 (q, J= 7.2 Hz 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ [201.8] 198.8, 47.1 [46.1], [30.7] 30.4, 20.1 [20.0], [18.9] 18.2, 13.7 [13.6]. The data of minor isomer are given in square brackets. Data are consistent with previous reports[1].

Compound **2k** was obtained as a yellow liquid in 88% yield (160 mg, 0.81 mmol) as a mixture of isomers with a ratio of 4:1 after purification through silica gel column chromatography (PE/EtOAc 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.10 (s, 1H), 4.92 [4.62] (d, *J* = 5.2 Hz, 2H), [2.70] 2.66 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ [202.0] 199.2, 136.3 [135.3], [129.0] 128.9, 128.3 [128.3], 128.1 [127.9], 51.3 [50.4], [19.1] 18.4. The data of minor isomer are given in square brackets. Data are consistent with previous reports[10].

Compound **2l** was obtained as a yellow liquid in 73% yield (120 mg, 0.53 mmol) as a mixture of isomers with a ratio of 2:1 after purification through silica gel column chromatography (PE/EtOAc 12:1). ^{1}H NMR (400 Hz, $CDCl_3$) δ 7.30 (t, J= 7.6 Hz, 2H),7.20 (m, 3H), 3.78 [3.46] (q, J= 6.8, 13.2 Hz, 2H), 2.70 (m, 2H),2.60 (s, 3H), 2.02 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ [201.9] 198.9, 141.1 [140.5], 128.6, 128.4, 126.3 [126.2], 47.0 [45.9], 33.3 [33.0], [30.1] 29.8, [18.9] 18.2. The data of minor isomer are given in square brackets. Data are consistent with previous reports[11].

4. General procedure for synthesis of S-trideuteromethyl dithiocarbamates with DMSO-d_6 as deuterium source

General procedure: A mixture of trimethylsulfoxonium iodide (1.5 equiv) and DMSO-d_6 (80.0 equiv) in sealed tube was stirred at 120 ºC for 2 h, then it was cooled down. After that, amine (1.0 equiv) and K_2CO_3 (4.0 equiv) was added in, and the mixture was further stirred at 65 ºC for 30 min. After being cooled to room temperature, the reaction mixture was diluted with H_2O and extracted with DCM twice. The combined organic was washed with H_2O and brine, and dried over anhydrous Na_2SO_4. The obtained crude was concentrated under vacuum, and purified by silica gel column chromatography. The level of deuterium incorporation was determined by ^{1}H NMR spectrometry of the S-CH_3 signal based on the following equation:

$$Deuteration\ (\%)\ = (1 - \frac{Normalized\ residual\ \ integral}{3}) \times 100\%$$

Compound **4a** was obtained as a yellow solid in 96% yield and 93% deuterium incorporation (40 mg, 0.22 mmol) after purification through silica gel column chromatography (PE/EtOAc 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (s, 2H), 3.90 (m, 2H), 2.66 (s, 0.21H), 1.71 (m, 6H).

Compound **4b** was obtained as a colorless liquid in 93% yield and 96% deuterium incorporation (120 mg, 0.43 mmol) after purification through silica gel column chromatography (PE/DCM 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 10H), 5.36 (s, 2H), 4.98 (s, 2H), 2.73 (s, 0.12H).

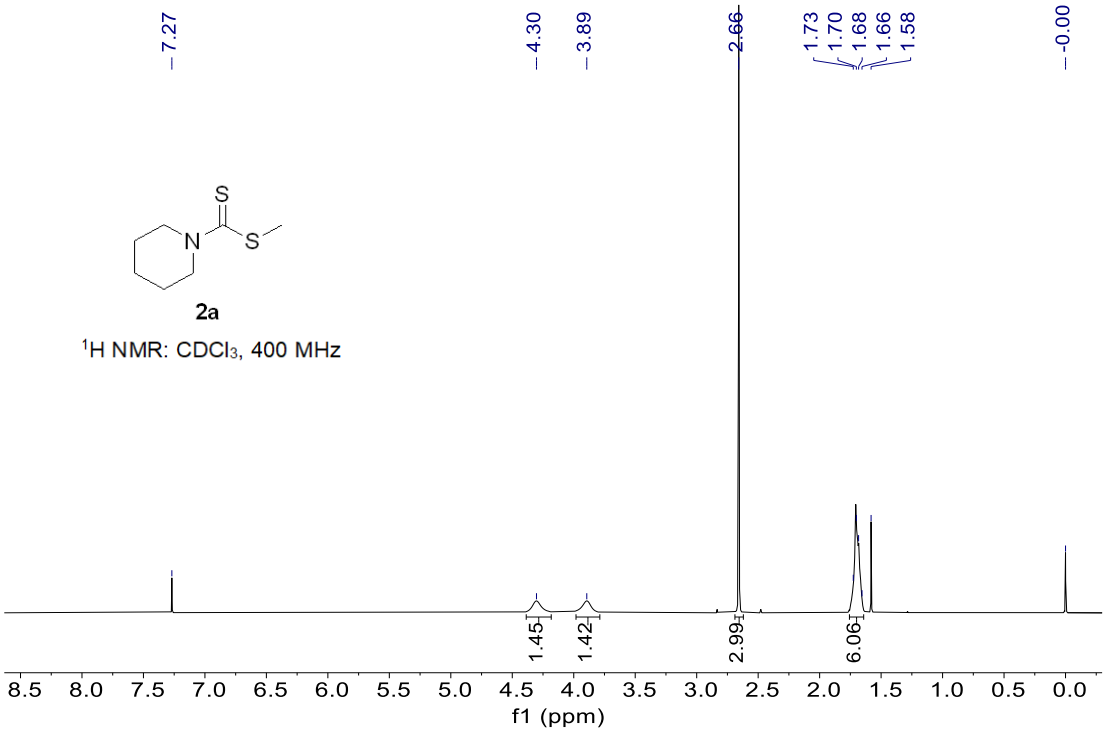
Compound **4c** was obtained as a colorless liquid in 98% yield and 95% deuterium incorporation (60 mg, 0.80 mmol) after purification through silica gel column chromatography (PE/EtOAc 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (m, 2H), 5.40 (s, 1H), 5.23 (m, 4H), 4.65 (d, J = 6.0 Hz, 2H), 4.28 (d, J = 5.2 Hz, 2H), 2.65 (s, 0.14H).

Compound **4d** was obtained as a yellow liquid in 85% yield and 96% deuterium incorporation (170 mg, 0.97 mmol) as a mixture of isomers in the ratio of 2:1 after extraction with ethyl ether without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 5H), 5.38 [5.00] (s, 2H), [3.48] 3.26 (s, 3H), 2.69 (s, 0.12H).

Compound **4e** was obtained as a colorless liquid in 76% yield and 89% deuterium incorporation (35 mg, 0.16 mmol) as a mixture of isomers with a ratio of 2:1 after purification through silica gel column chromatography (PE/EtOAc 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.23 (m, 3H), 3.78 [3.46] (m, 2H), 2.71 (t, J = 7.6 Hz, 2H), 2.60 (s, 0.32H), 2.03 (m, 2H).

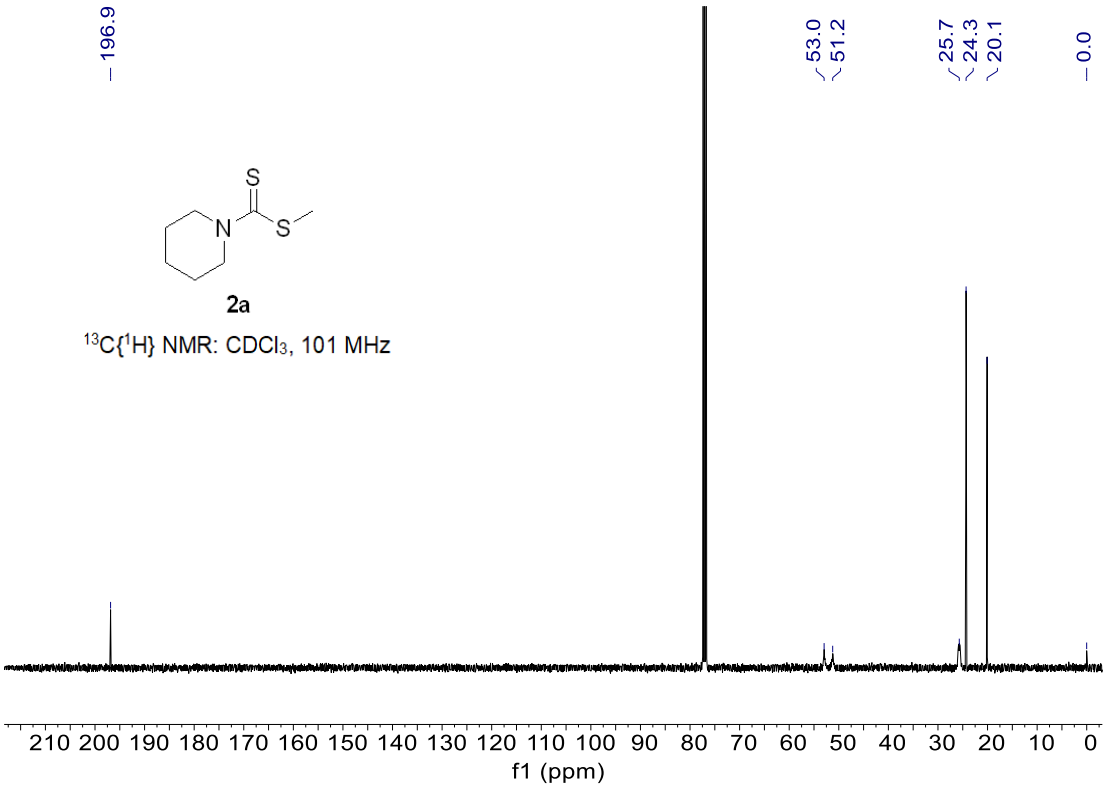
Compound **4f** was obtained as a colorless liquid in 93% yield and 77% deuterium incorporation (43 mg, 0.24 mmol) as a mixture of isomers with a ratio of 2:1 after purification through silica gel column chromatography (PE/EtOAc 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 [3.44] (p, J = 7.2 Hz, 2H), [2.68] 2.64 (s, 0.70H), 1.64 (m, 2H), 1.41 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H).

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



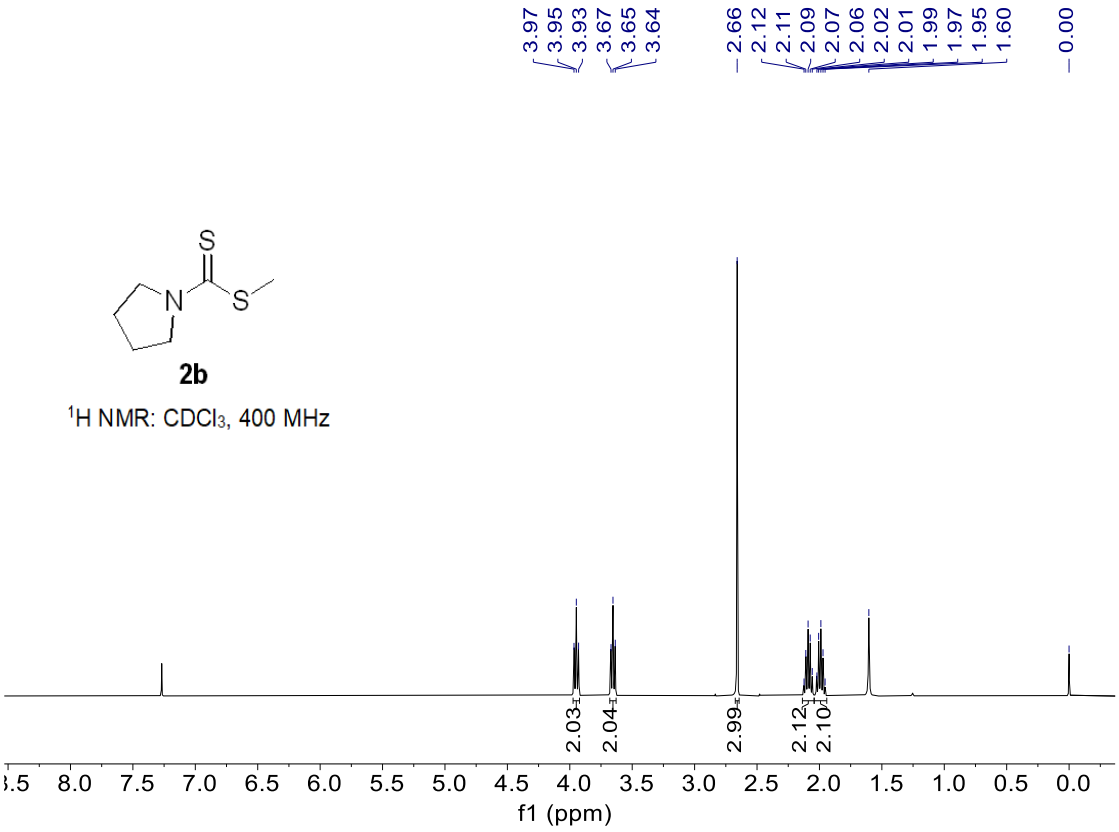
2a

^{1}H NMR: $CDCl_3$, 400 MHz



2a

$^{13}C\{^{1}H\}$ NMR: $CDCl_3$, 101 MHz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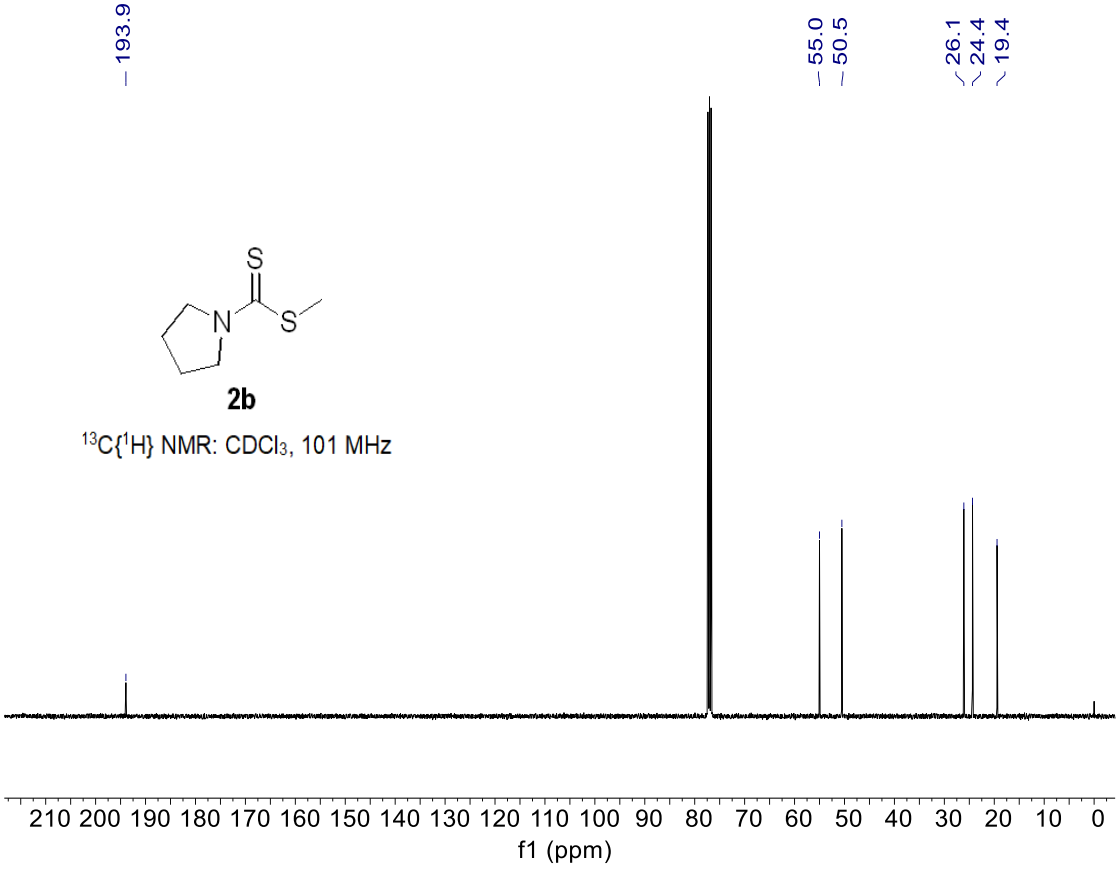
f1 (ppm)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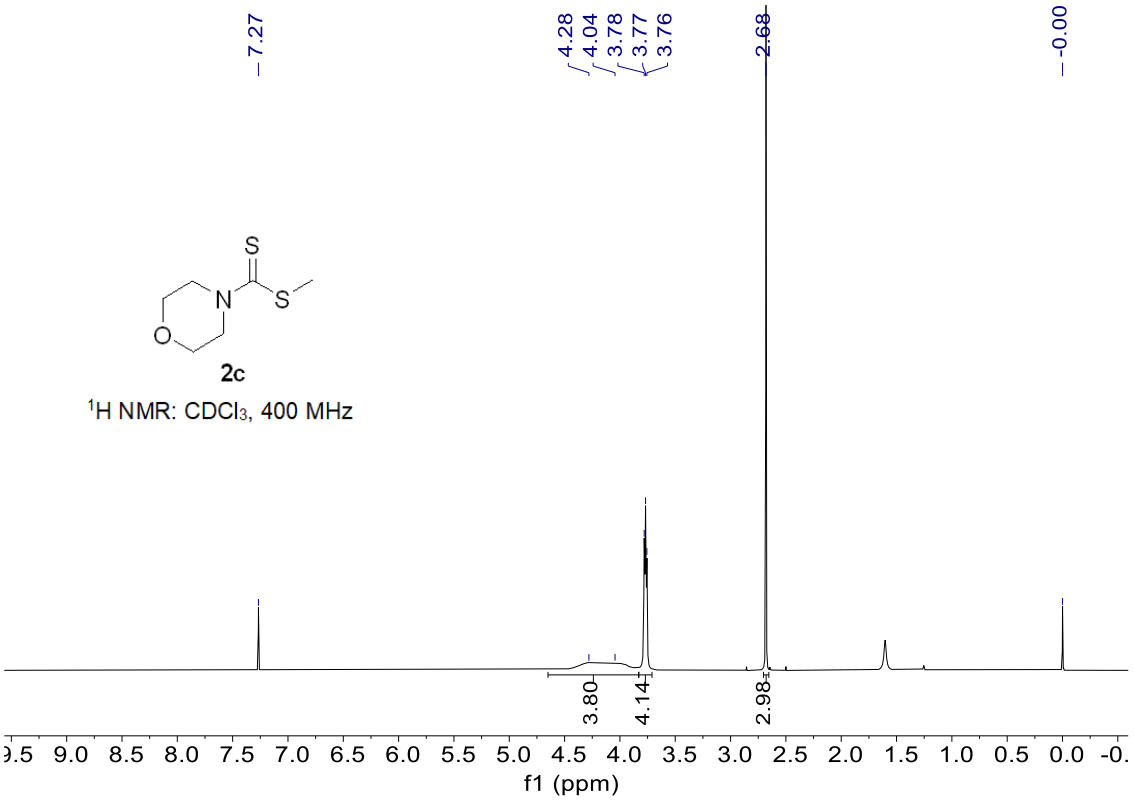
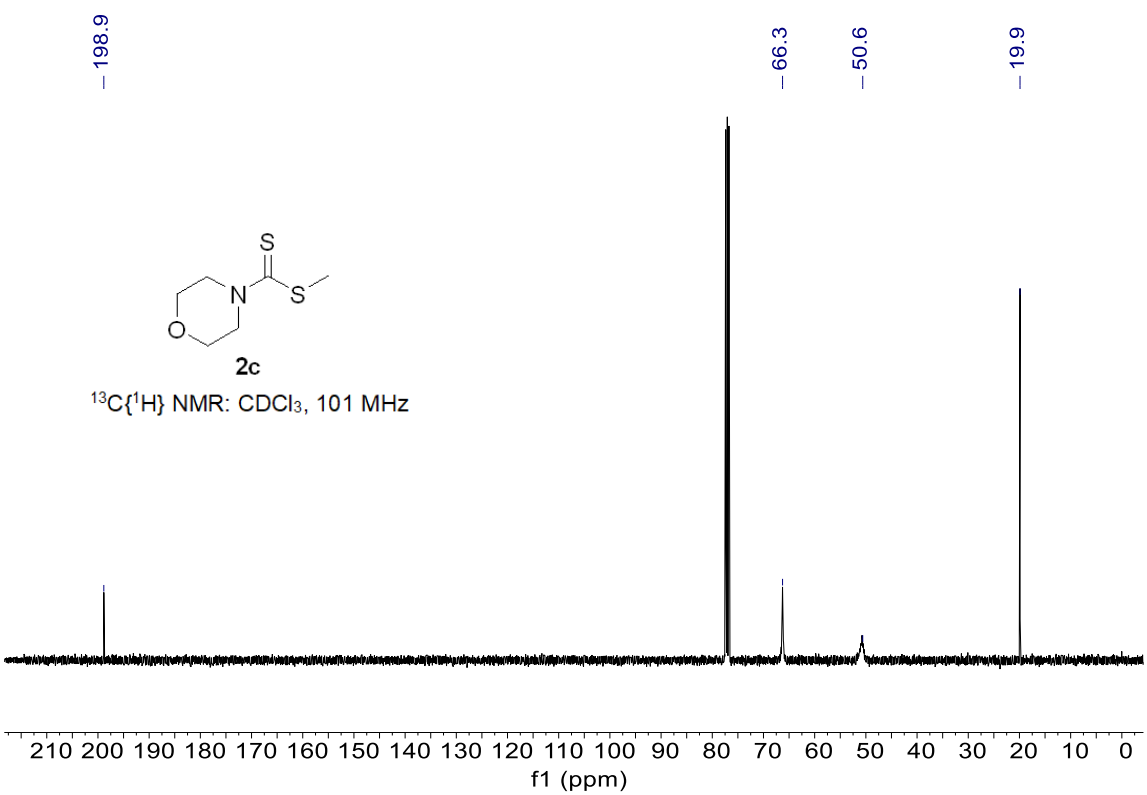
f1 (ppm)



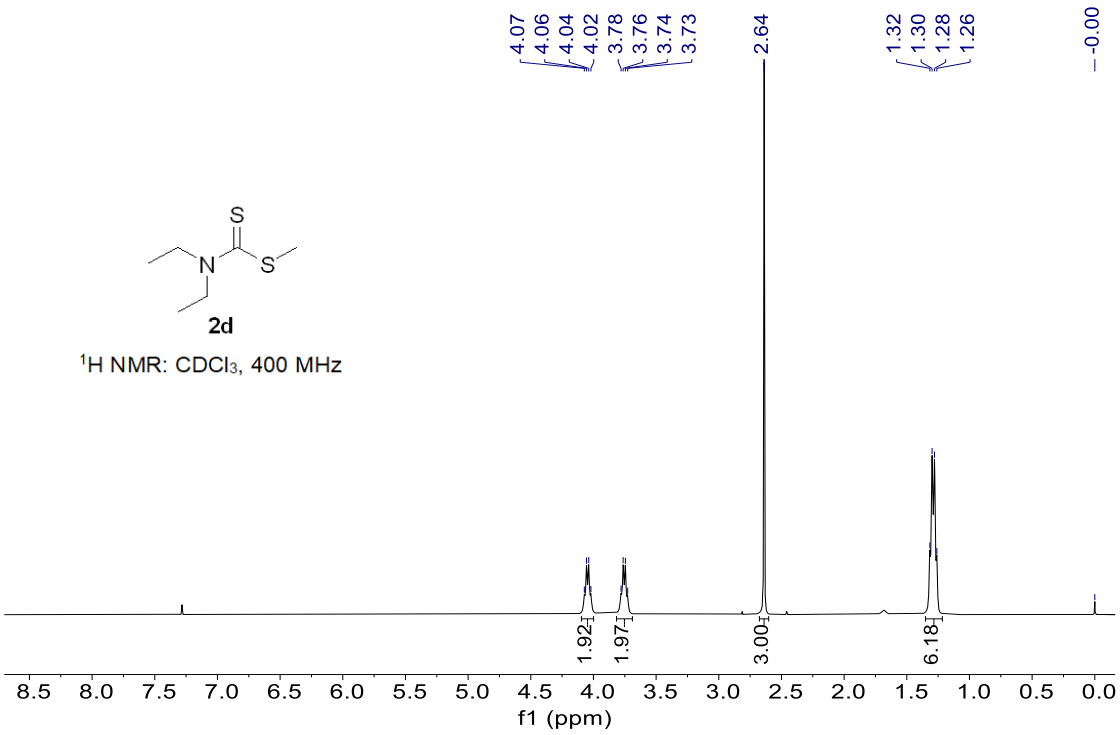
2c

^{1}H NMR: $CDCl_3$, 400 MHz



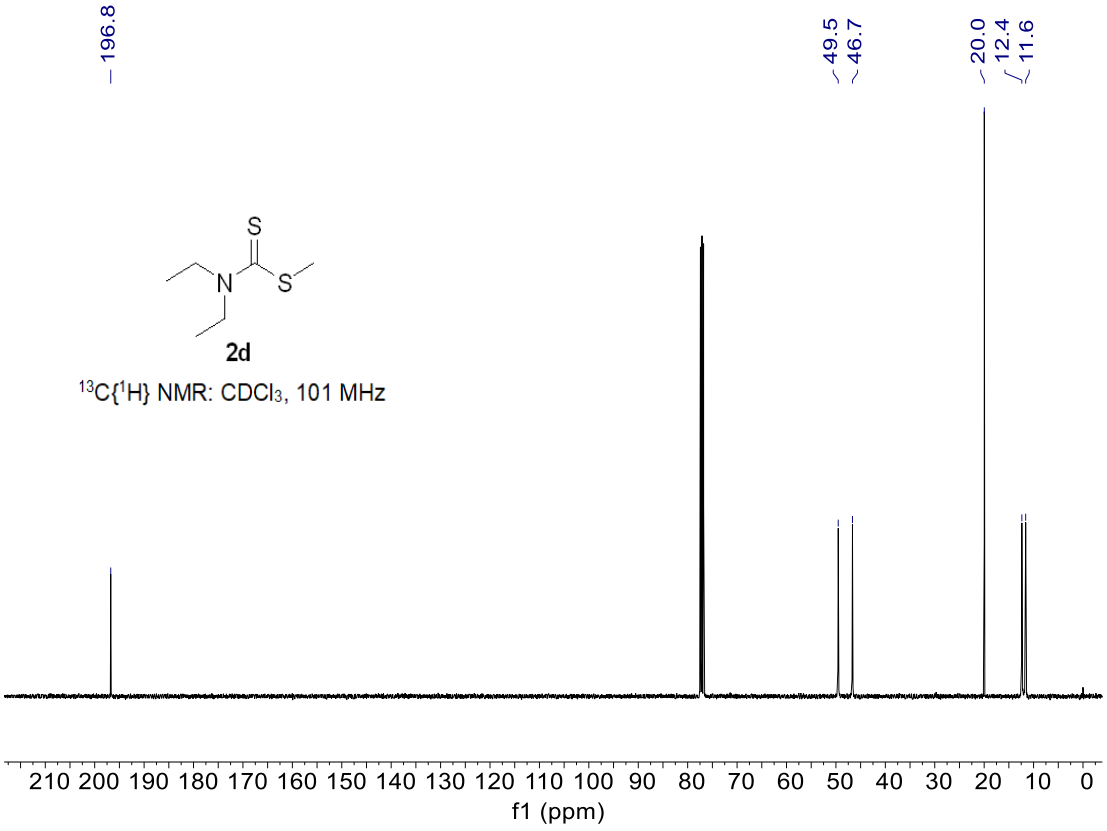
2c

$^{13}C\{^{1}H\}$ NMR: $CDCl_3$, 101 MHz



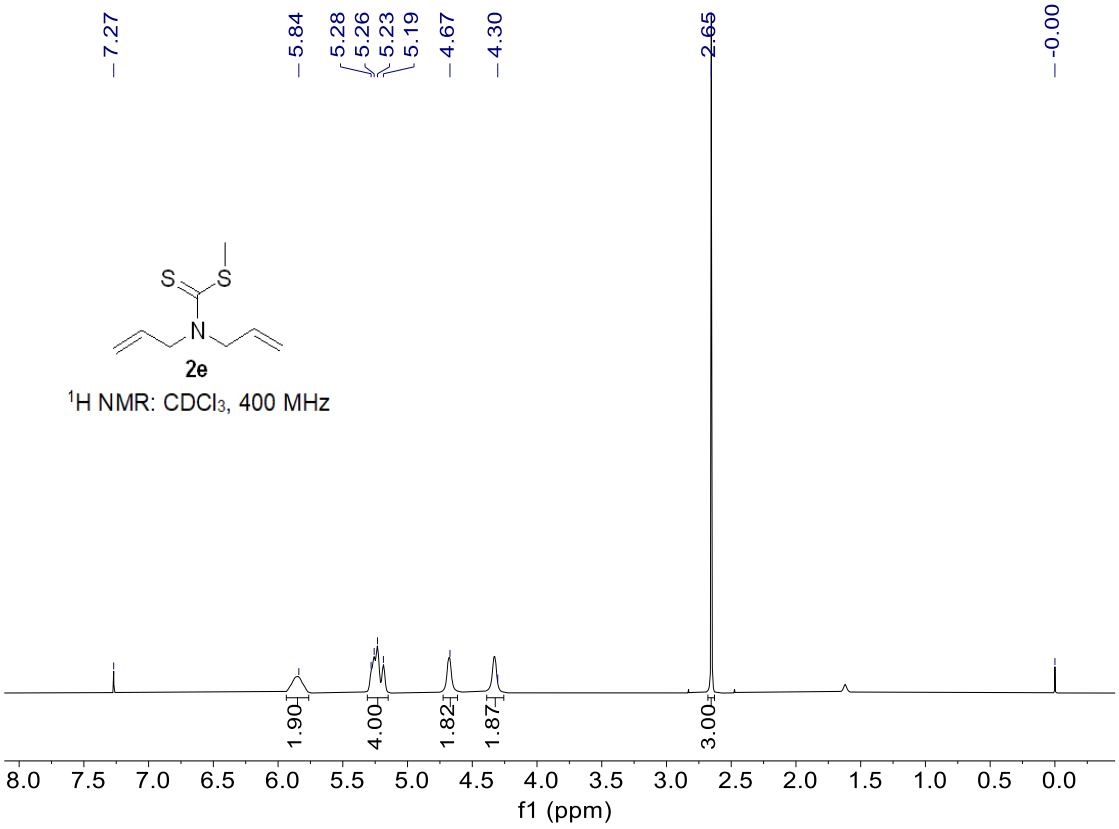
2d

^{1}H NMR: $CDCl_3$, 400 MHz



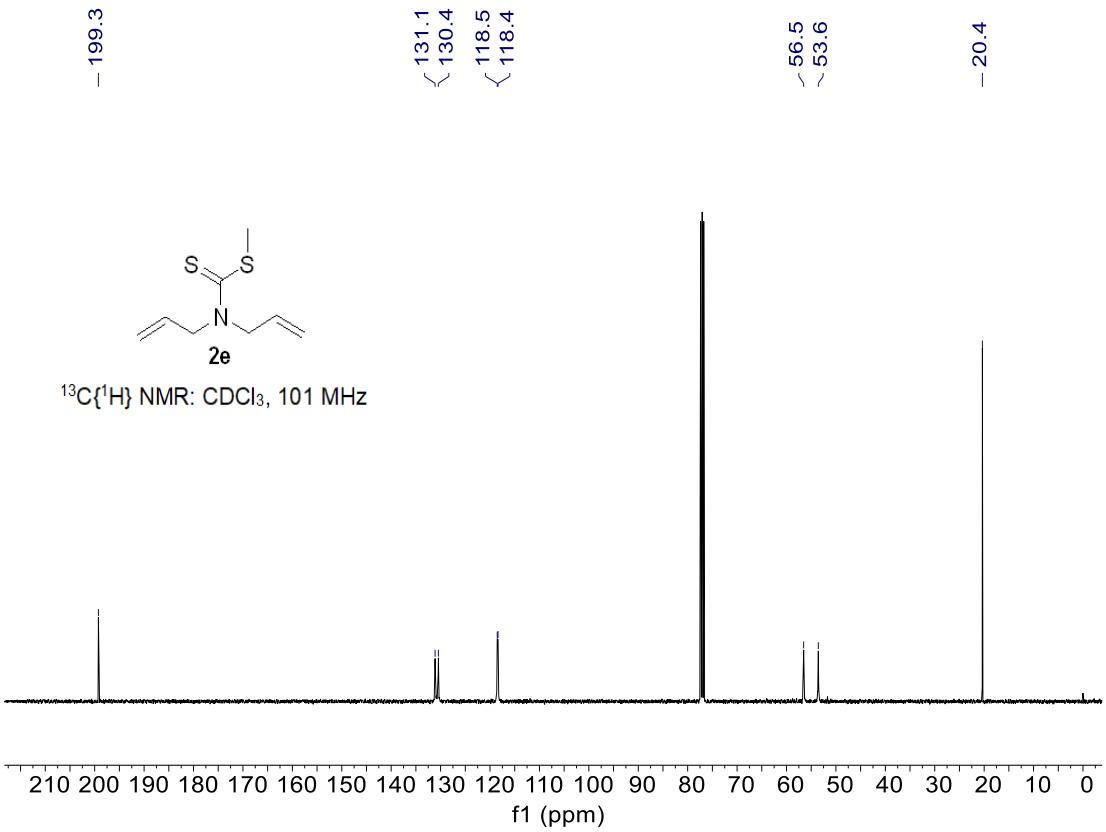
2d

$^{13}C\{^{1}H\}$ NMR: $CDCl_3$, 101 MHz



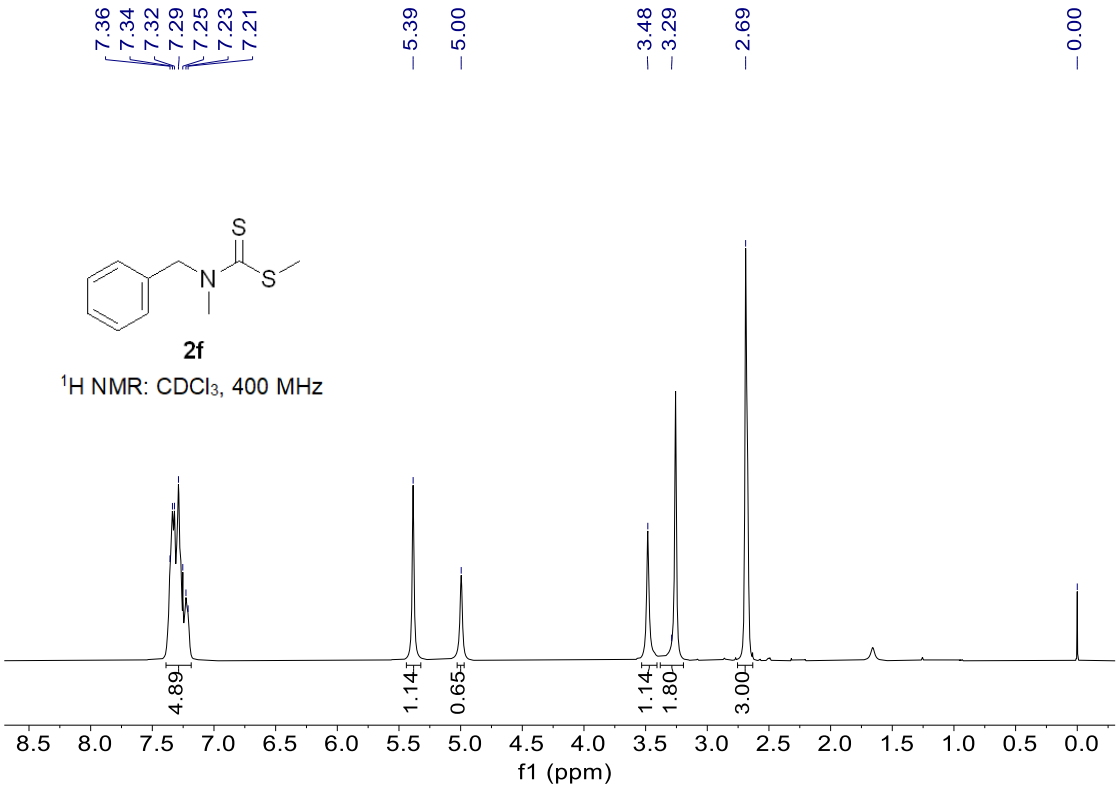
2e

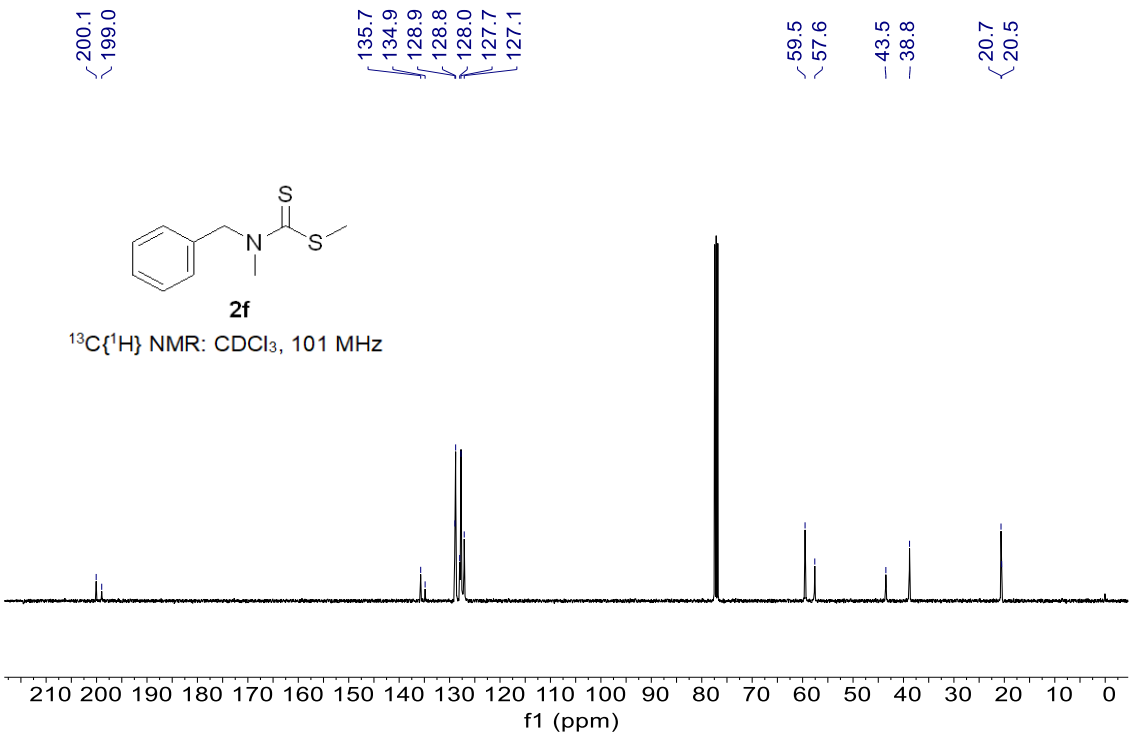
^{1}H NMR: $CDCl_3$, 400 MHz

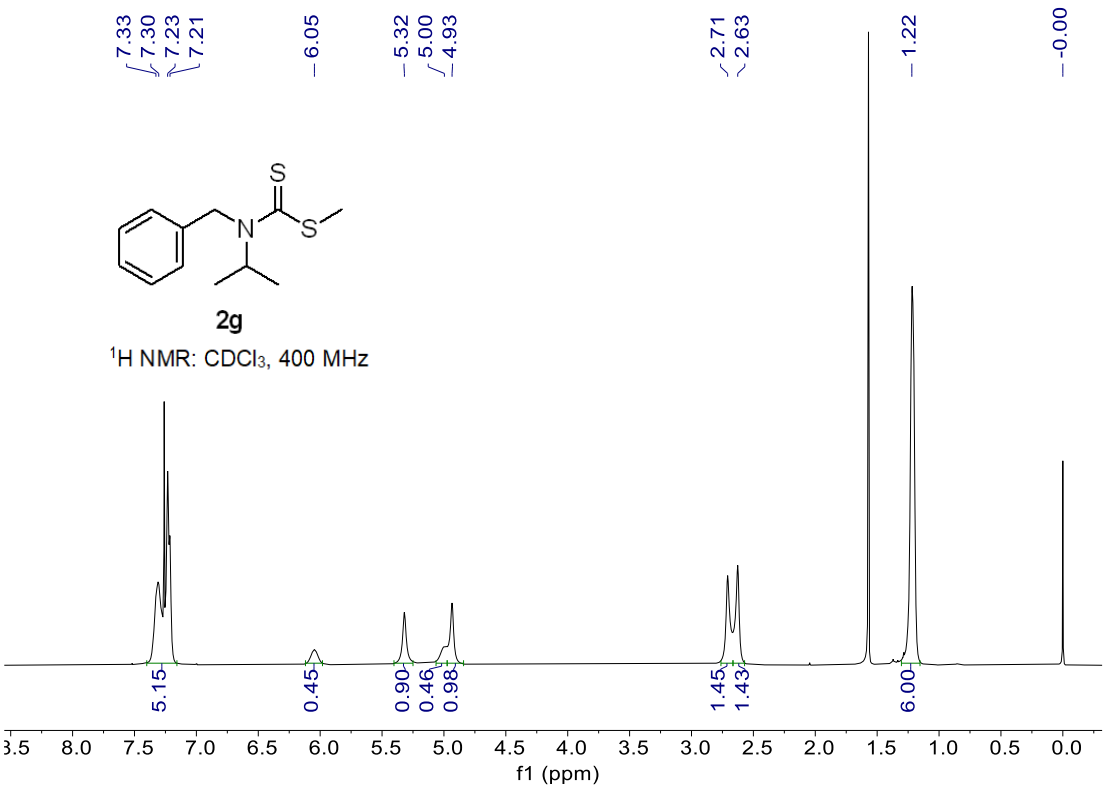


2e

$^{13}C\{^{1}H\}$ NMR: $CDCl_3$, 101 MHz

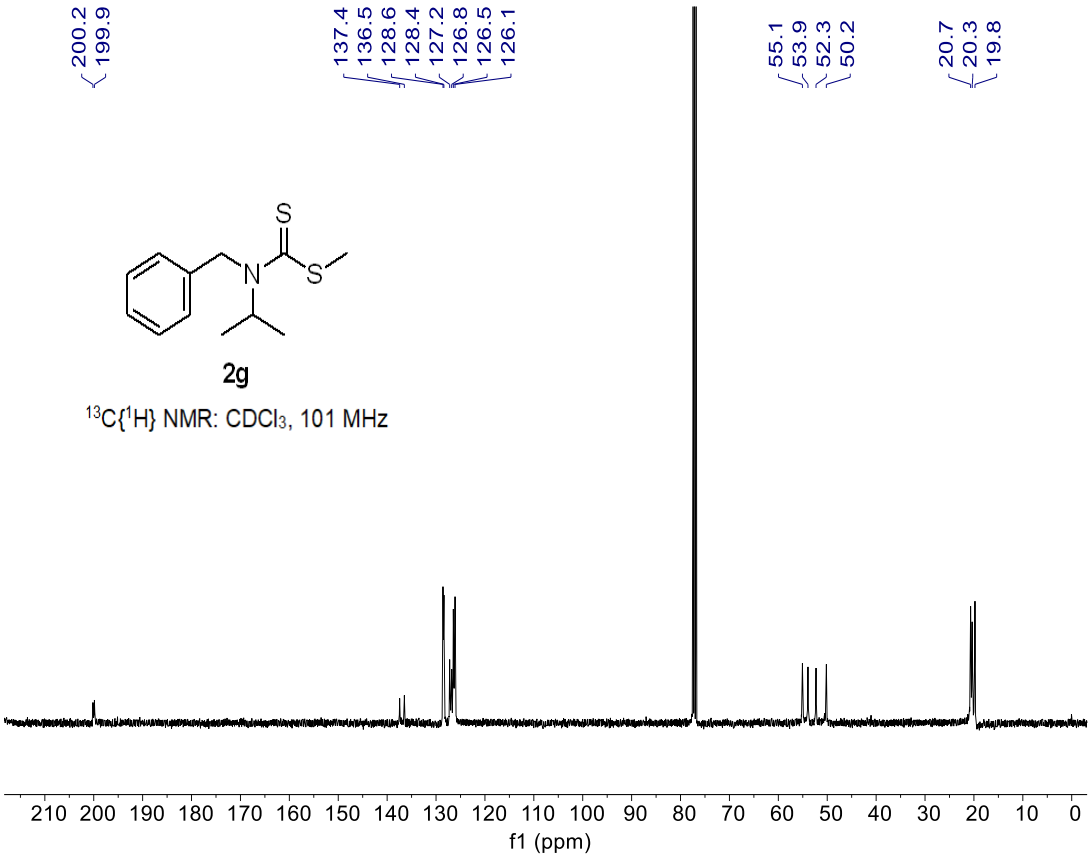

7.36
7.34
7.32
7.29
7.25
7.23
7.21
5.39
5.00
3.48
3.29
2.69
0.00
S
N
S
2f
1H NMR: CDCl3, 400 MHz
4.89
1.14
0.65
1.14
1.80
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


200.1
199.0
135.7
134.9
128.9
128.8
128.0
127.7
127.1
59.5
57.6
43.5
38.8
20.7
20.5
S
N
S
2f
13C{1H} NMR: CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



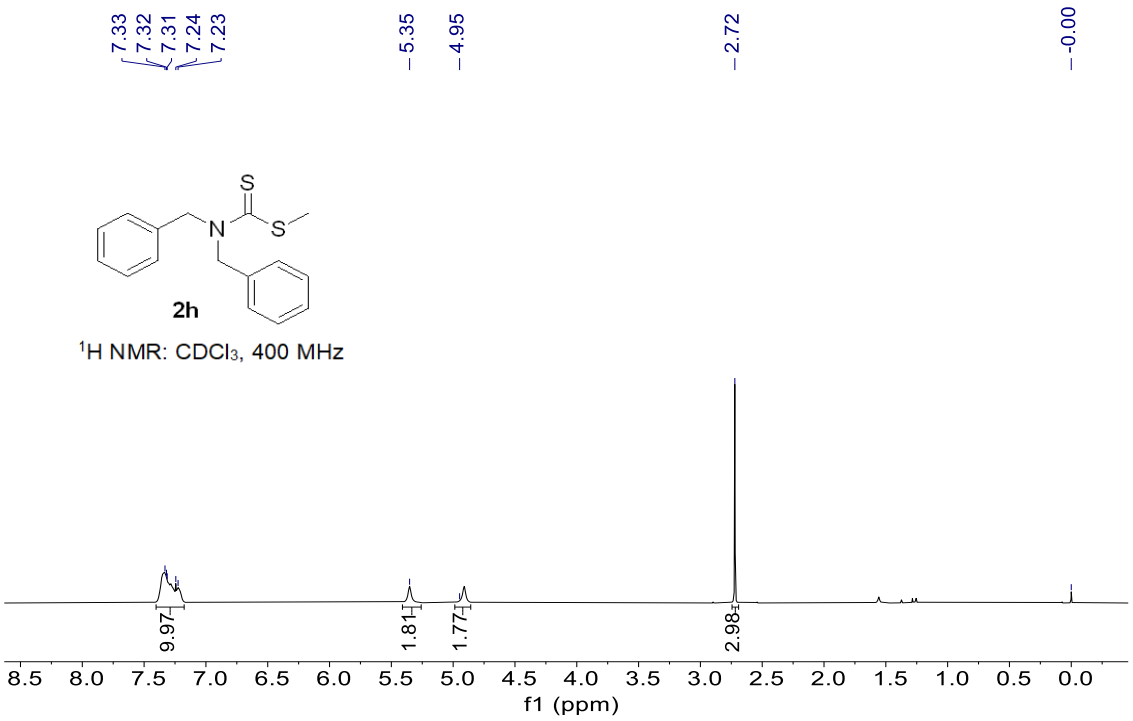
2g

^{1}H NMR: $CDCl_3$, 400 MHz

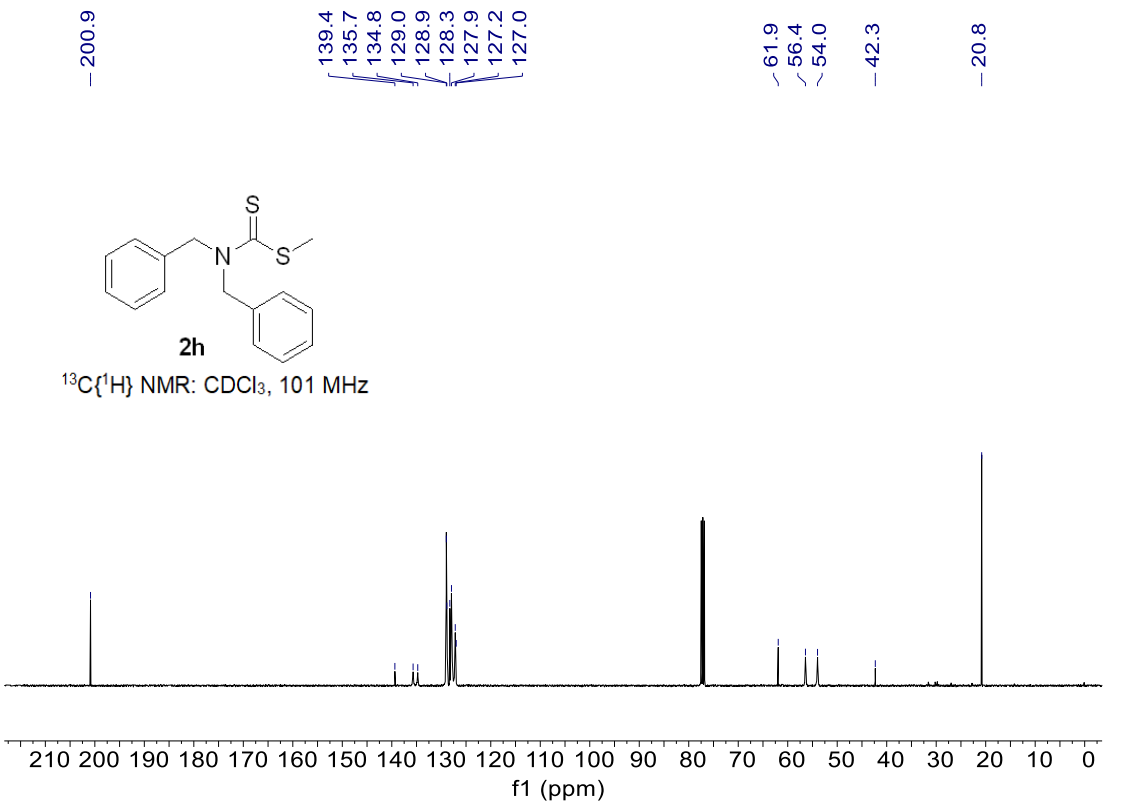


2g

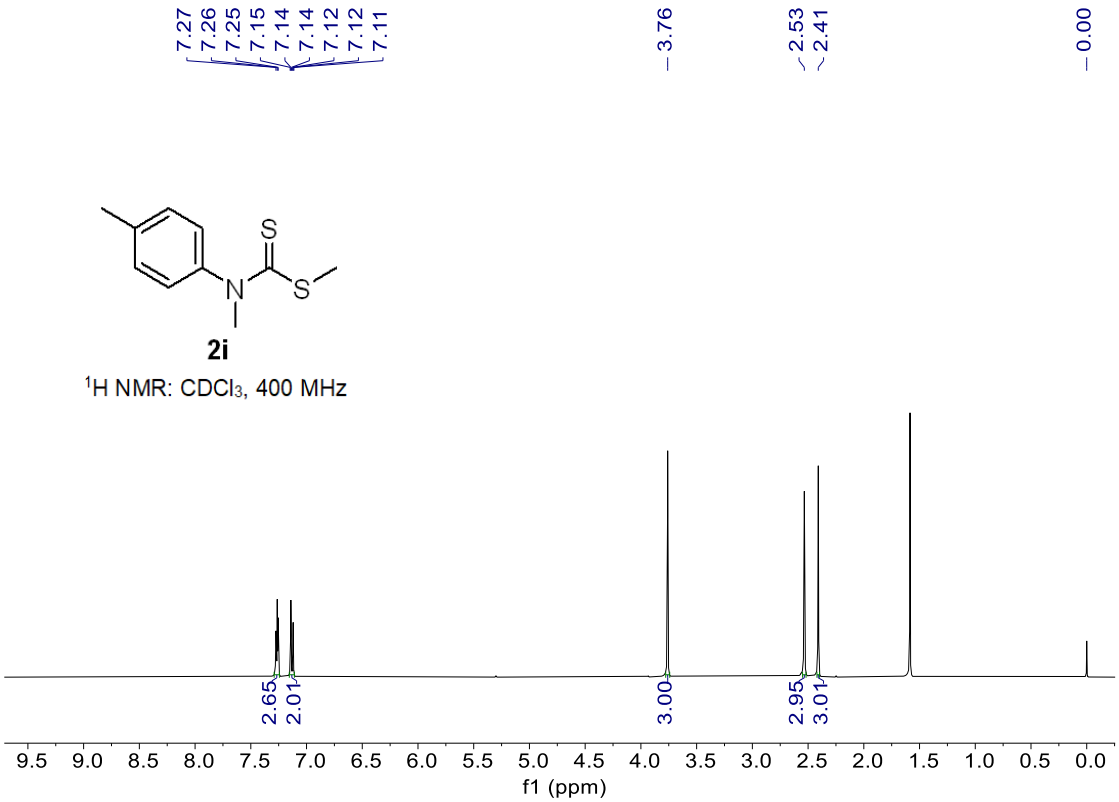
$^{13}C\{^{1}H\}$ NMR: $CDCl_3$, 101 MHz

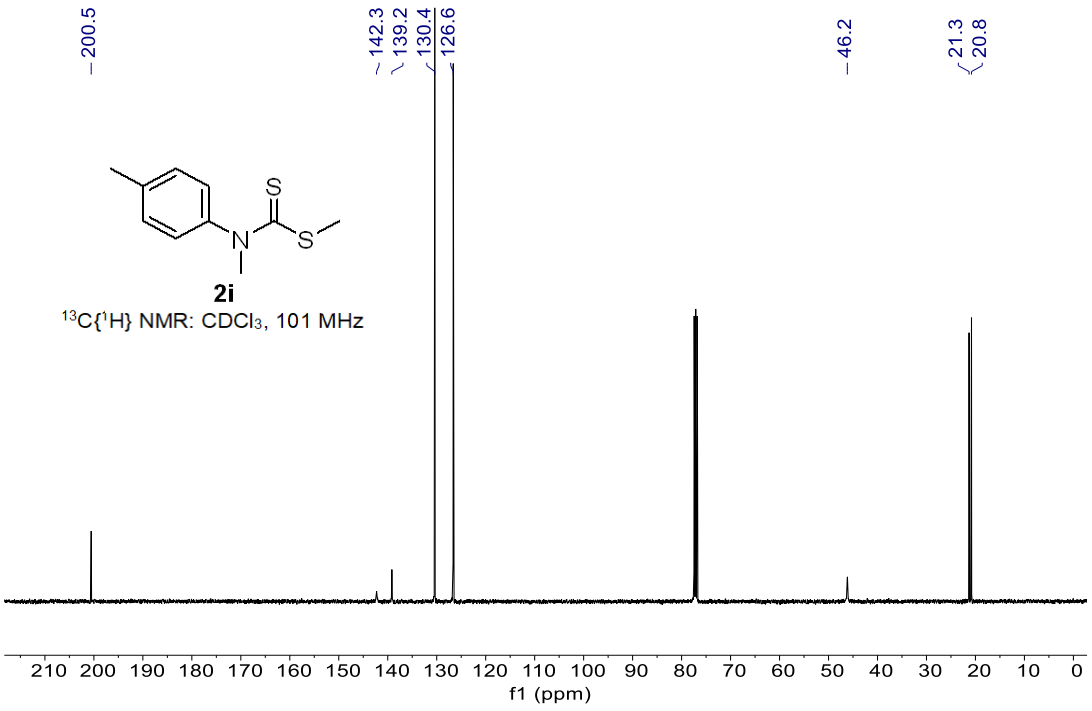


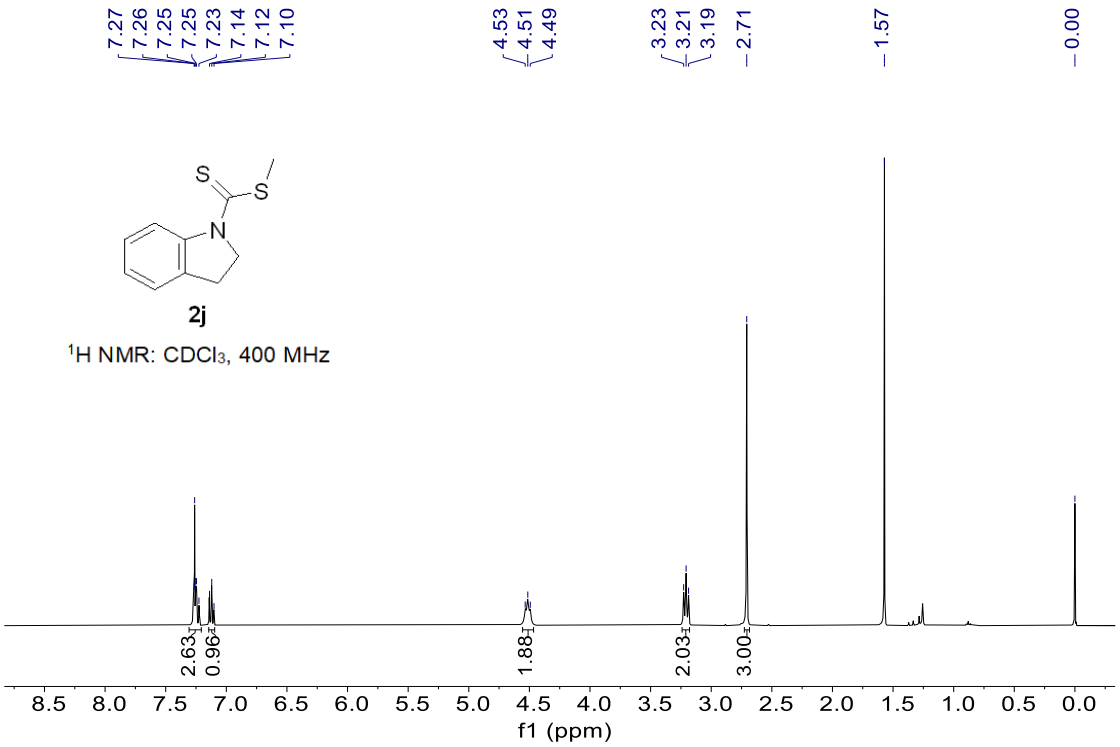
^{1}H NMR: $CDCl_3$, 400 MHz

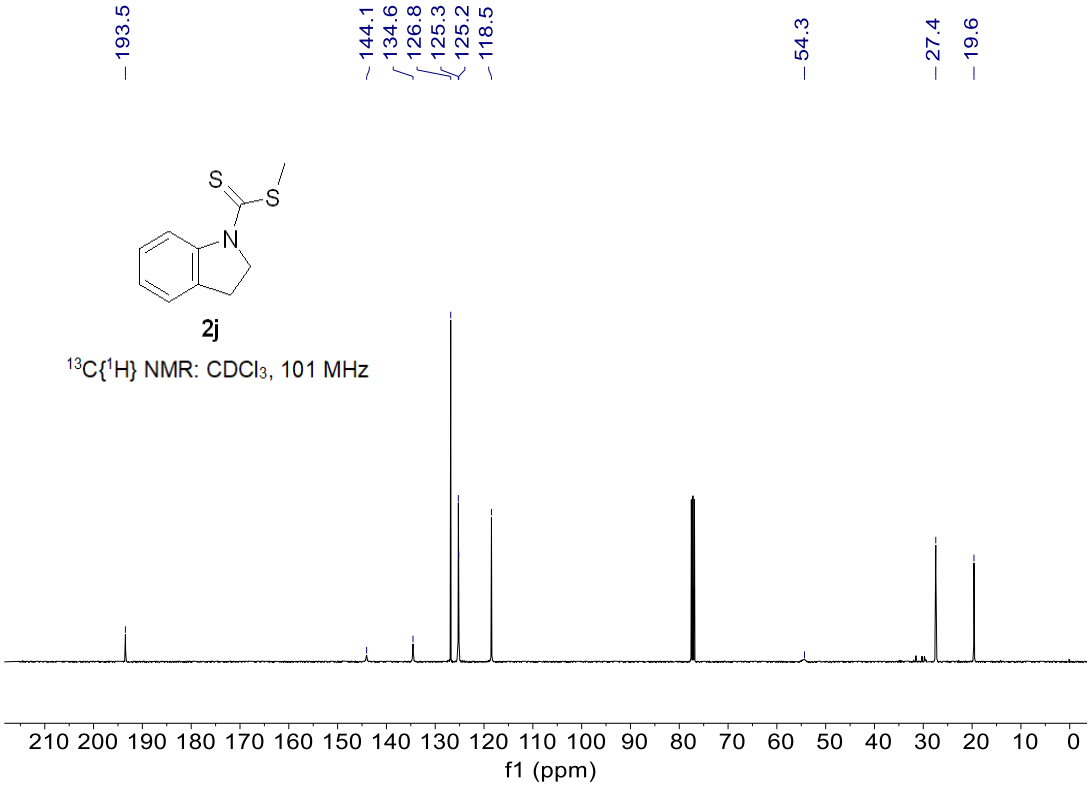


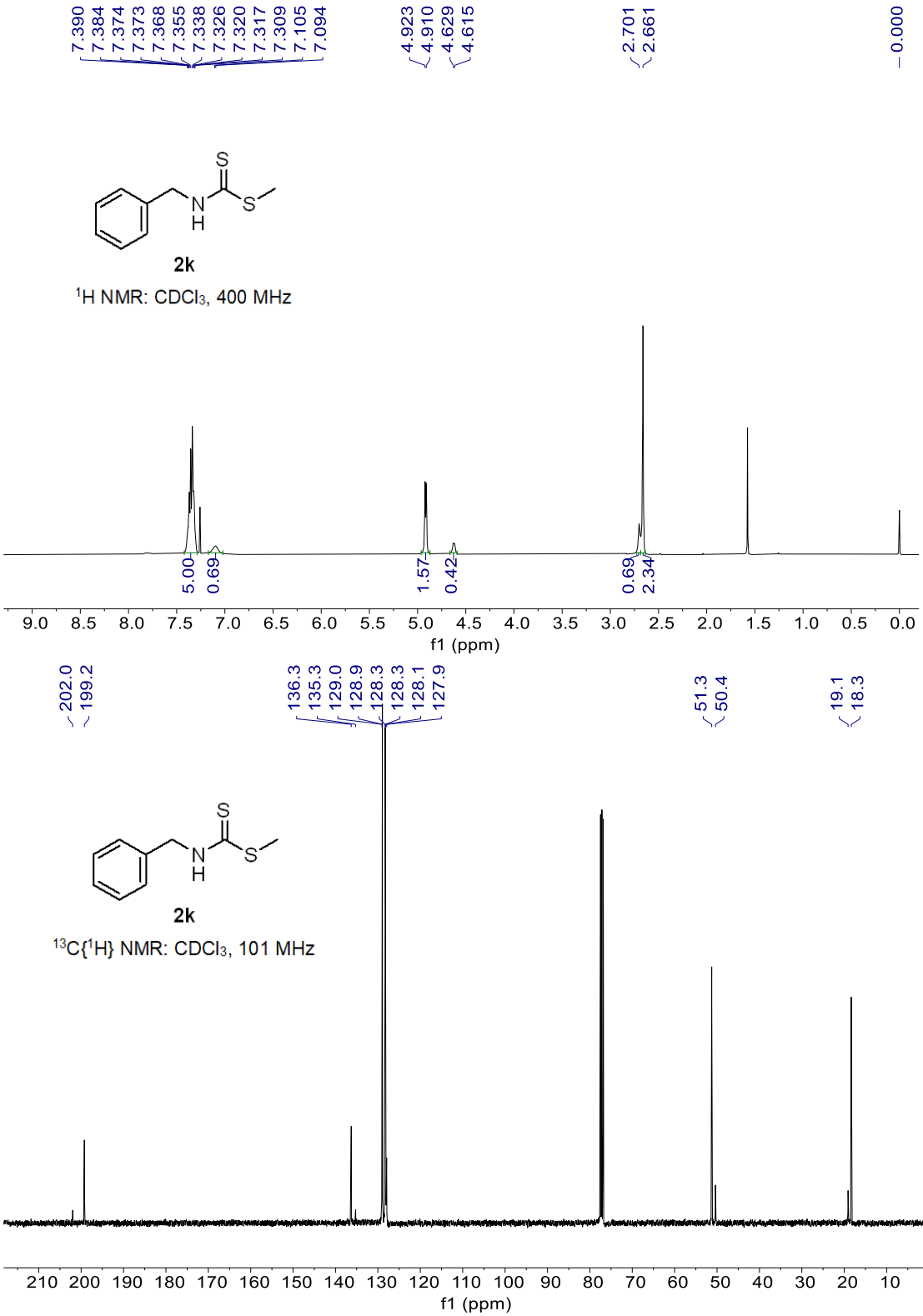
$^{13}C\{^{1}H\}$ NMR: $CDCl_3$, 101 MHz

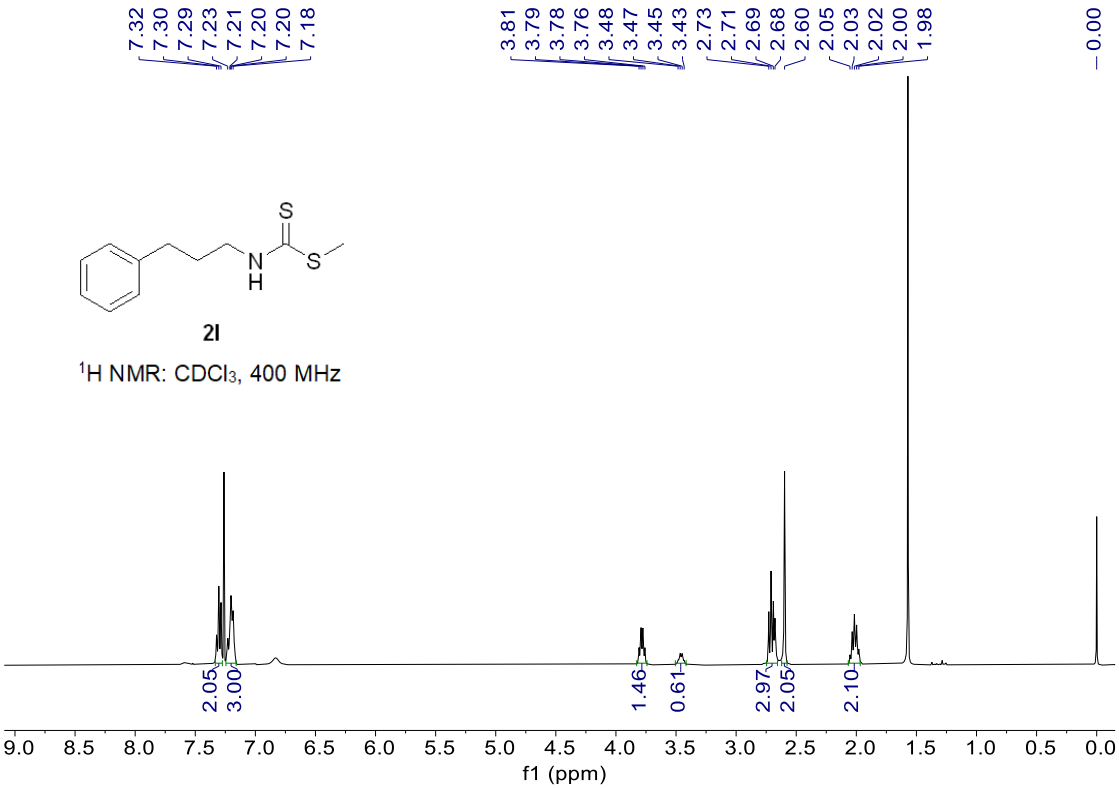

7.27
7.26
7.25
7.15
7.14
7.14
7.12
7.12
7.11
3.76
2.53
2.41
0.00
S
N
S
2i
1H NMR: CDCl3, 400 MHz
2.65
2.01
3.00
2.95
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


200.5
142.3
139.2
130.4
126.6
46.2
21.3
20.8
S
N
S
2i
13C{1H} NMR: CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.27
7.26
7.25
7.25
7.23
7.14
7.12
7.10
4.53
4.51
4.49
3.23
3.21
3.19
2.71
1.57
0.00
S
S
N
2j
1H NMR: CDCl3, 400 MHz
2.63
0.96
1.88
2.03
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

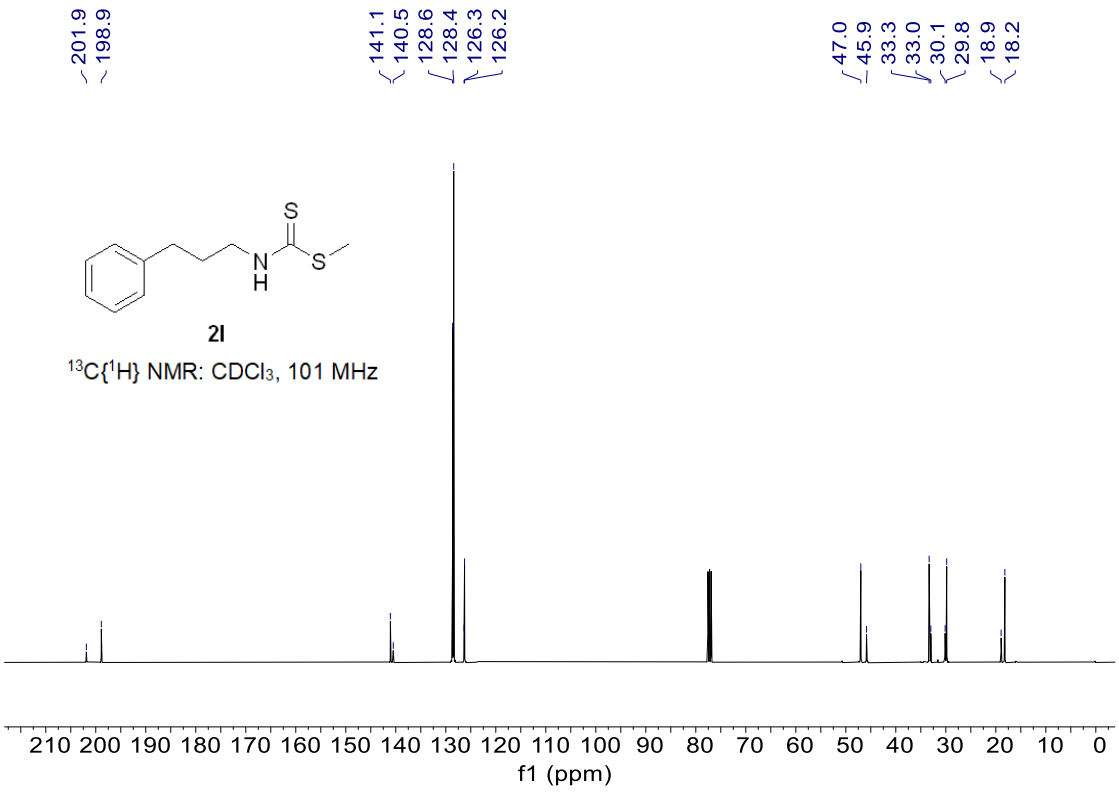

193.5
144.1
134.6
126.8
125.3
125.2
118.5
54.3
27.4
19.6
S
S
N
2j
13C{1H} NMR: CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.390
7.384
7.374
7.373
7.368
7.355
7.338
7.326
7.320
7.317
7.309
7.105
7.094
4.923
4.910
4.629
4.615
2.701
2.661
0.000
S
N
H
S
2k
1H NMR: CDCl3, 400 MHz
5.00
0.69
1.57
0.42
0.69
2.34
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
202.0
199.2
136.3
135.3
129.0
128.9
128.3
128.3
128.1
127.9
51.3
50.4
19.1
18.3
S
N
H
S
2k
13C{1H} NMR: CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



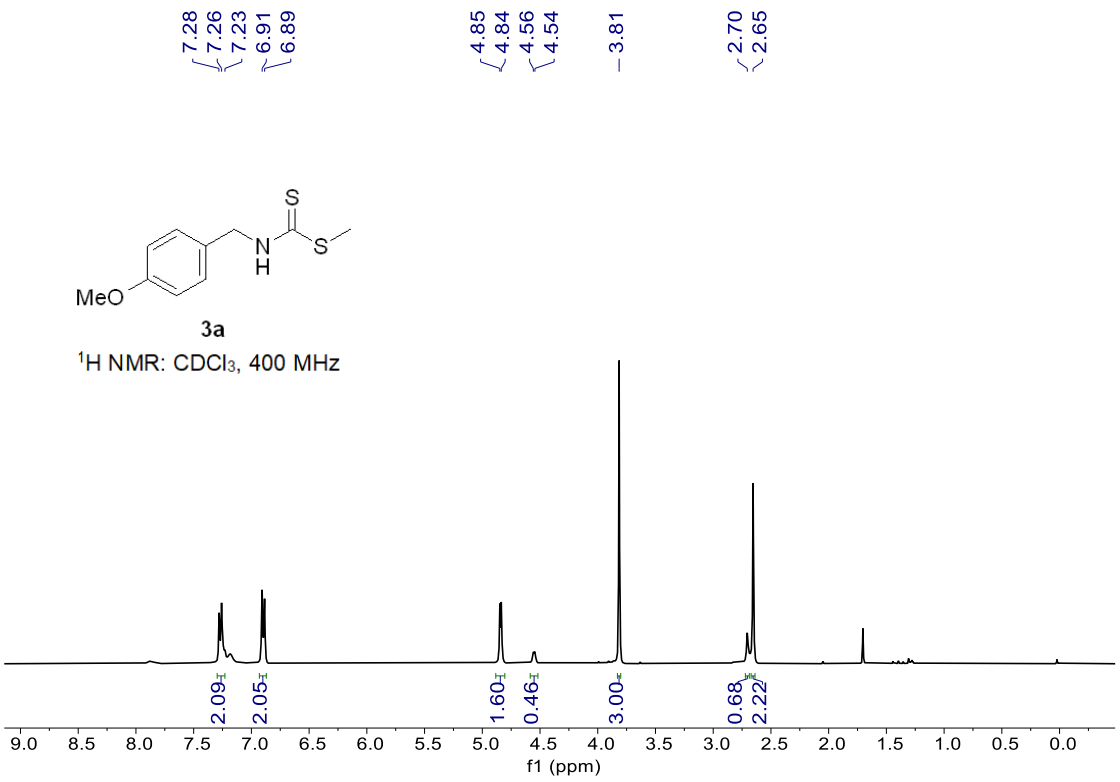
2l

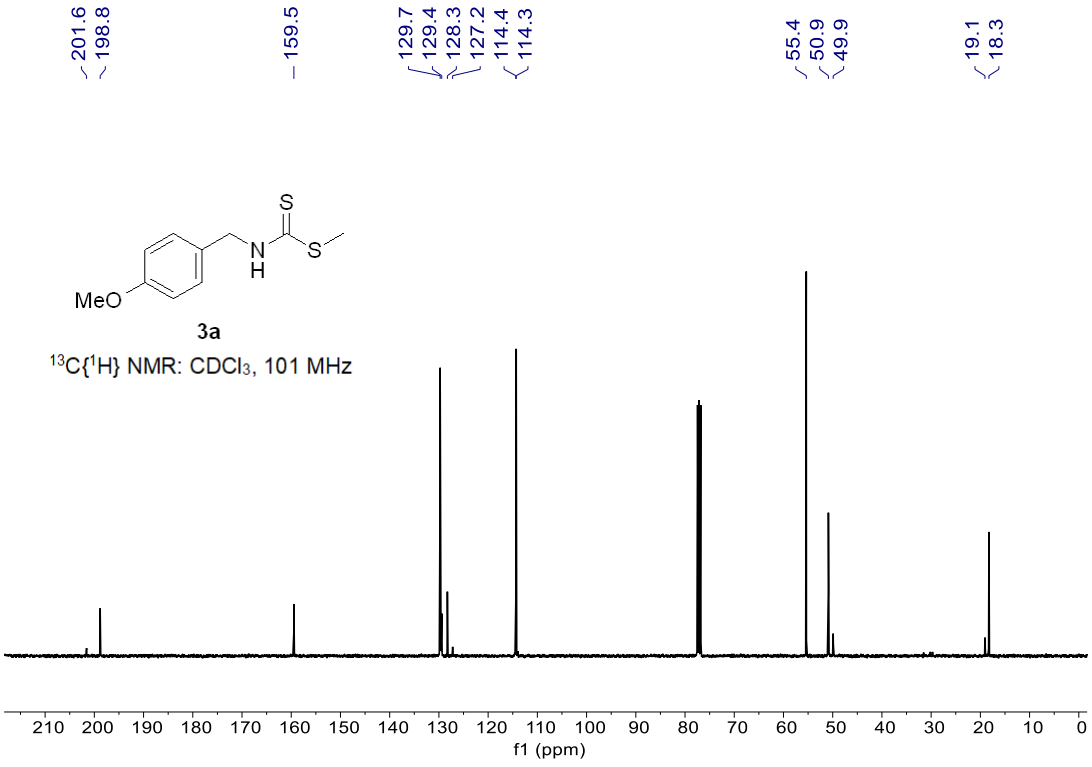
^{1}H NMR: $CDCl_3$, 400 MHz

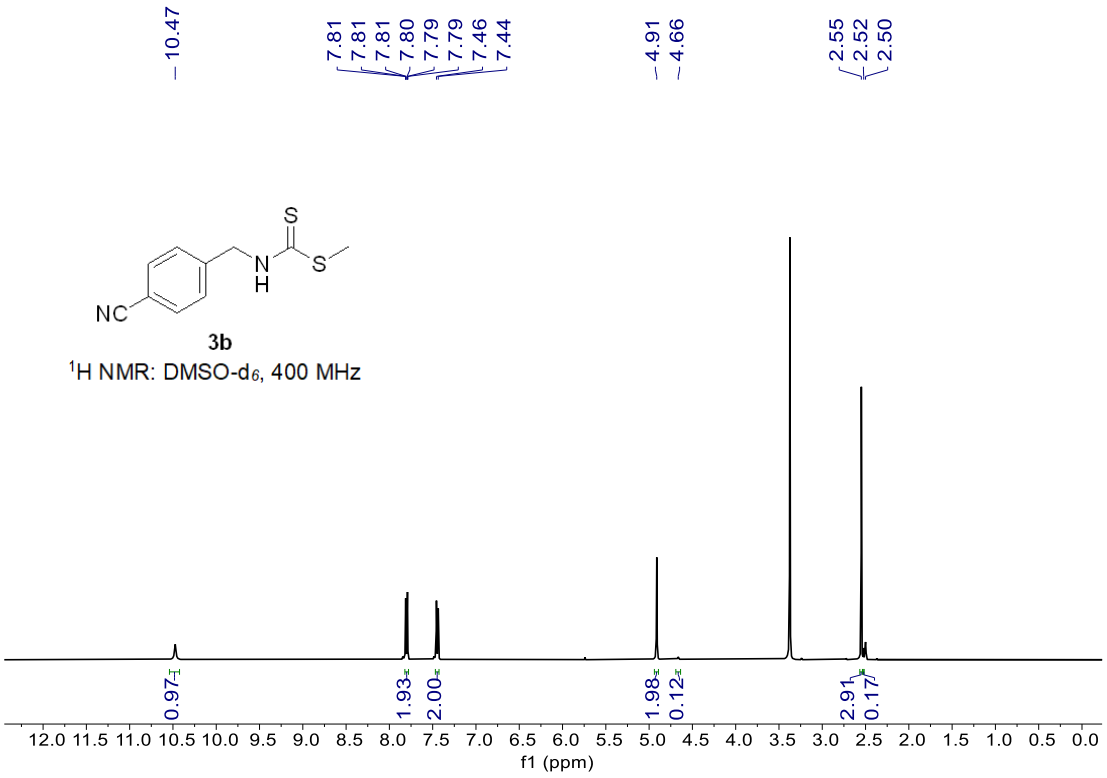


2l

$^{13}C\{^{1}H\}$ NMR: $CDCl_3$, 101 MHz

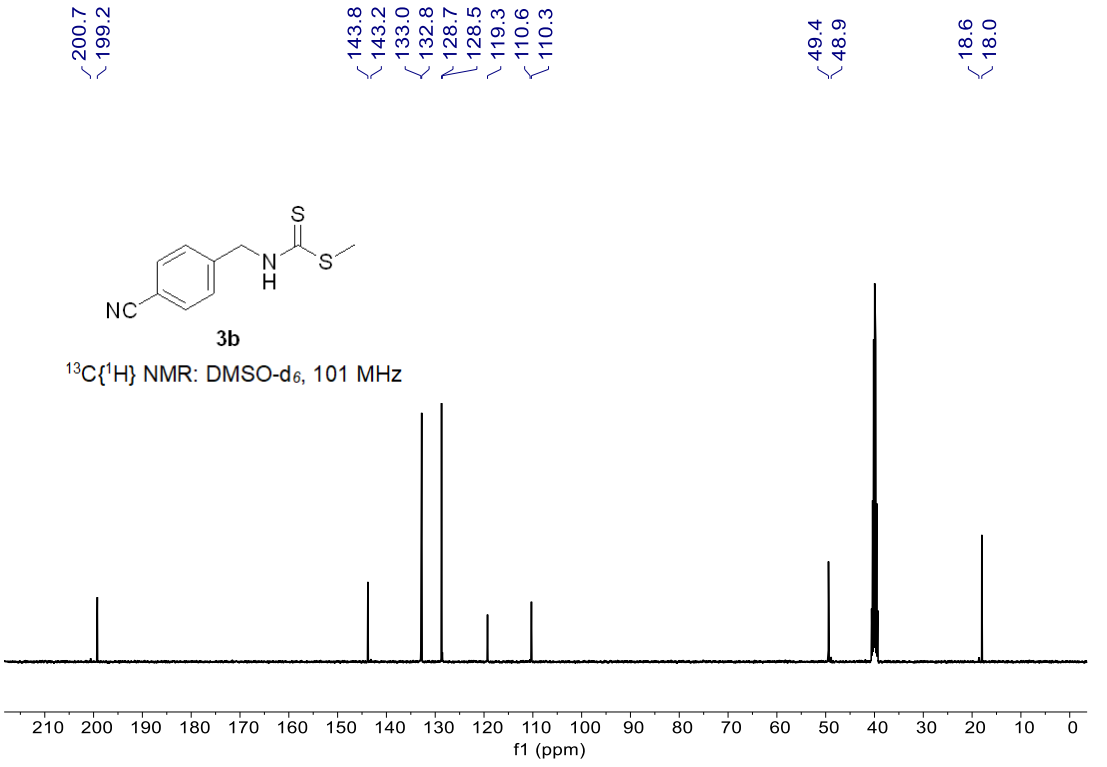

7.28
7.26
7.23
6.91
6.89
4.85
4.84
4.56
4.54
3.81
2.70
2.65
MeO
3a
1H NMR: CDCl3, 400 MHz
2.09
2.05
1.60
0.46
3.00
0.68
2.22
f1 (ppm)


201.6
198.8
159.5
129.7
129.4
128.3
127.2
114.4
114.3
55.4
50.9
49.9
19.1
18.3
MeO
3a
13C{1H} NMR: CDCl3, 101 MHz
f1 (ppm)



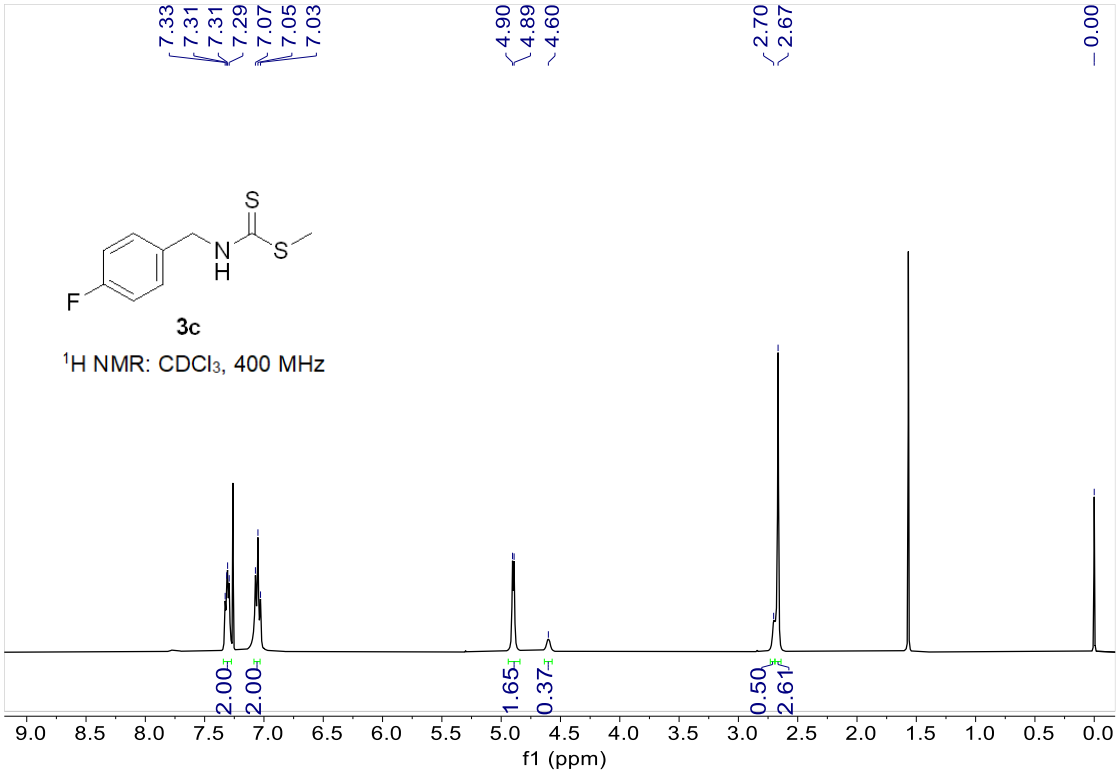
3b

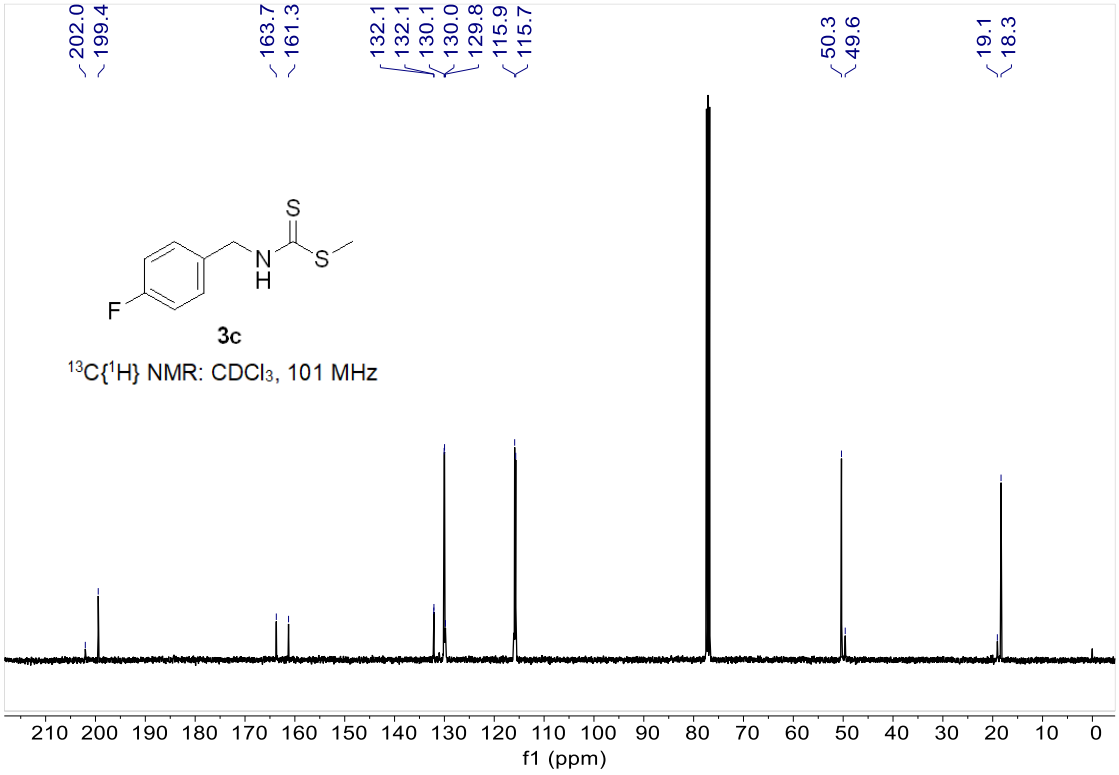
^{1}H NMR: DMSO-d$_6$, 400 MHz

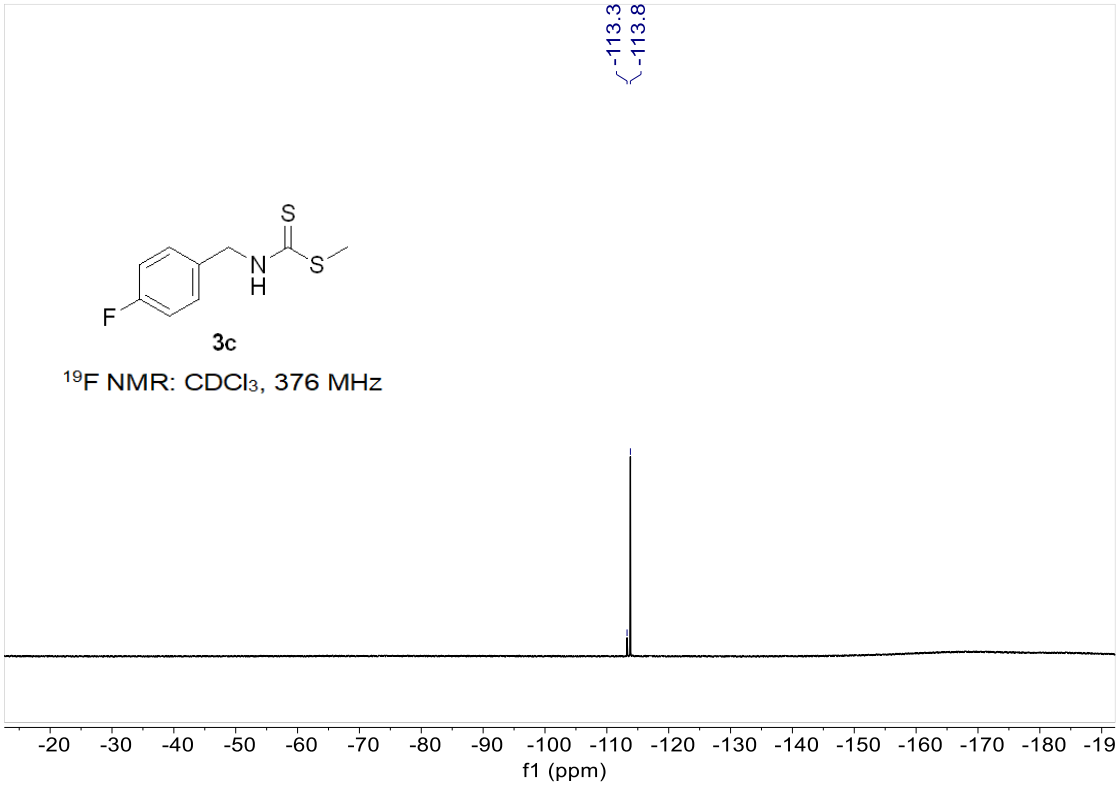


3b

^{13}C{^{1}H} NMR: DMSO-d$_6$, 101 MHz

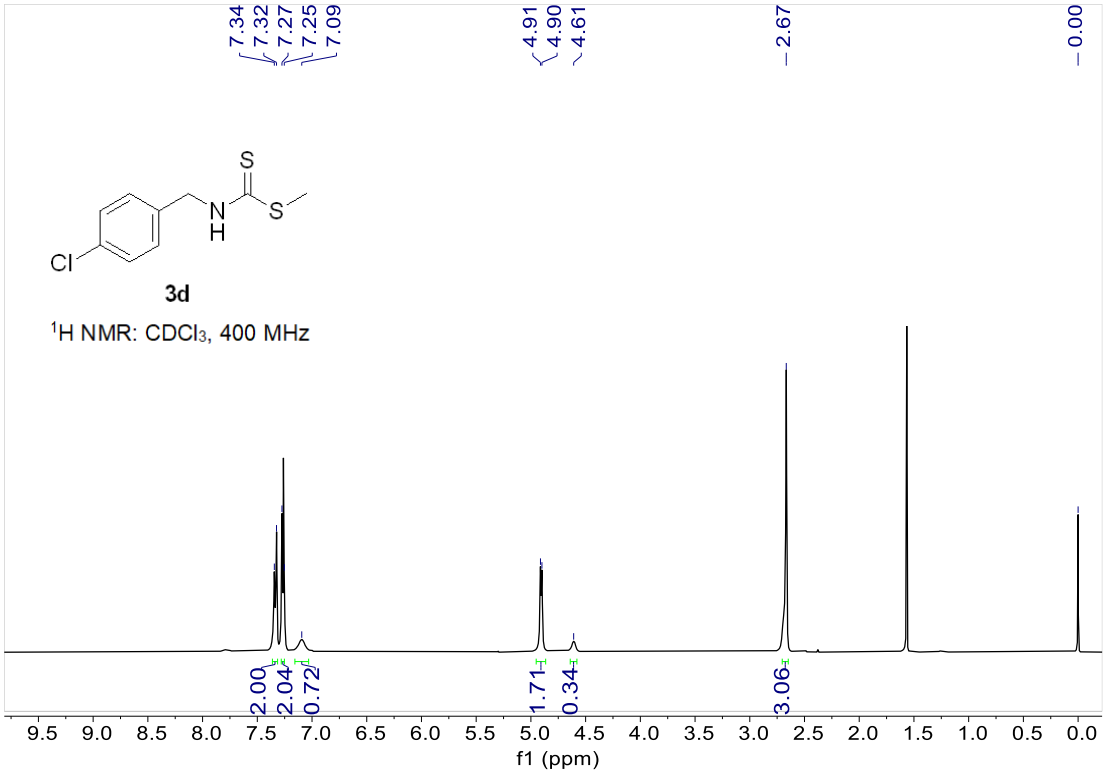

7.33
7.31
7.31
7.29
7.07
7.05
7.03
4.90
4.89
4.60
2.70
2.67
0.00
S
N
H
S
F
3c
1H NMR: CDCl3, 400 MHz
2.00
2.00
1.65
0.37
0.50
2.61
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

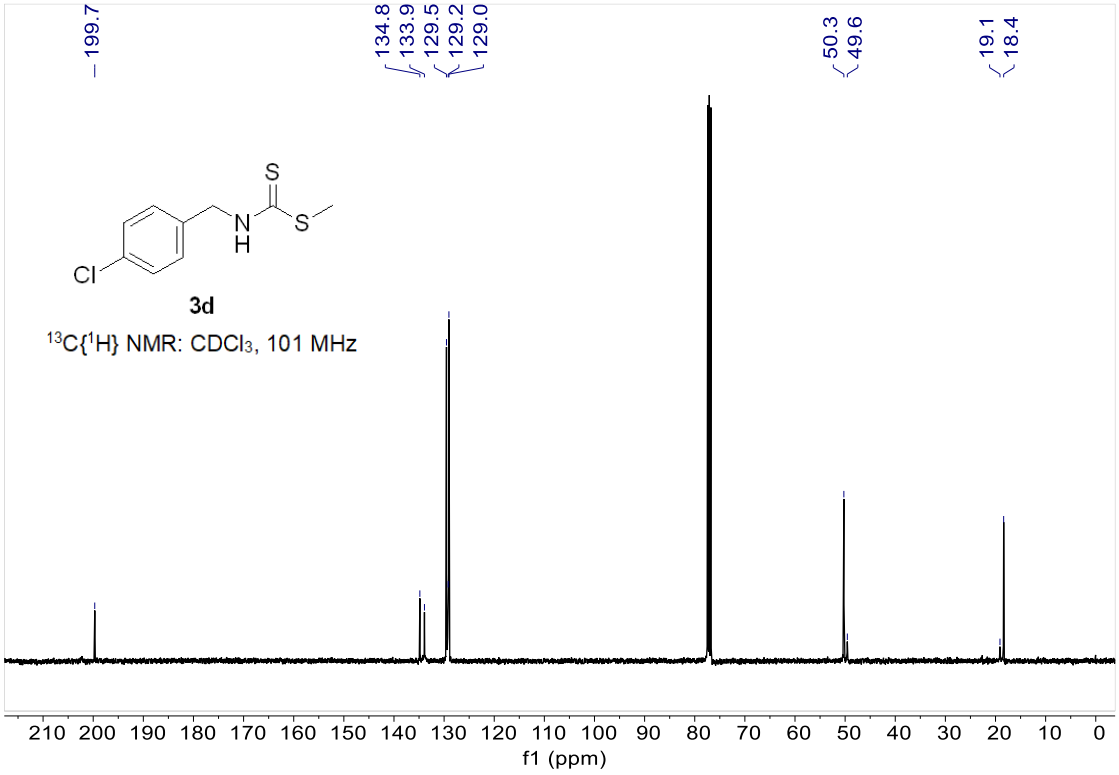

202.0
199.4
163.7
161.3
132.1
132.1
130.1
130.0
129.8
115.9
115.7
50.3
49.6
19.1
18.3
S
N
H
S
F
3c
13C{1H} NMR: CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

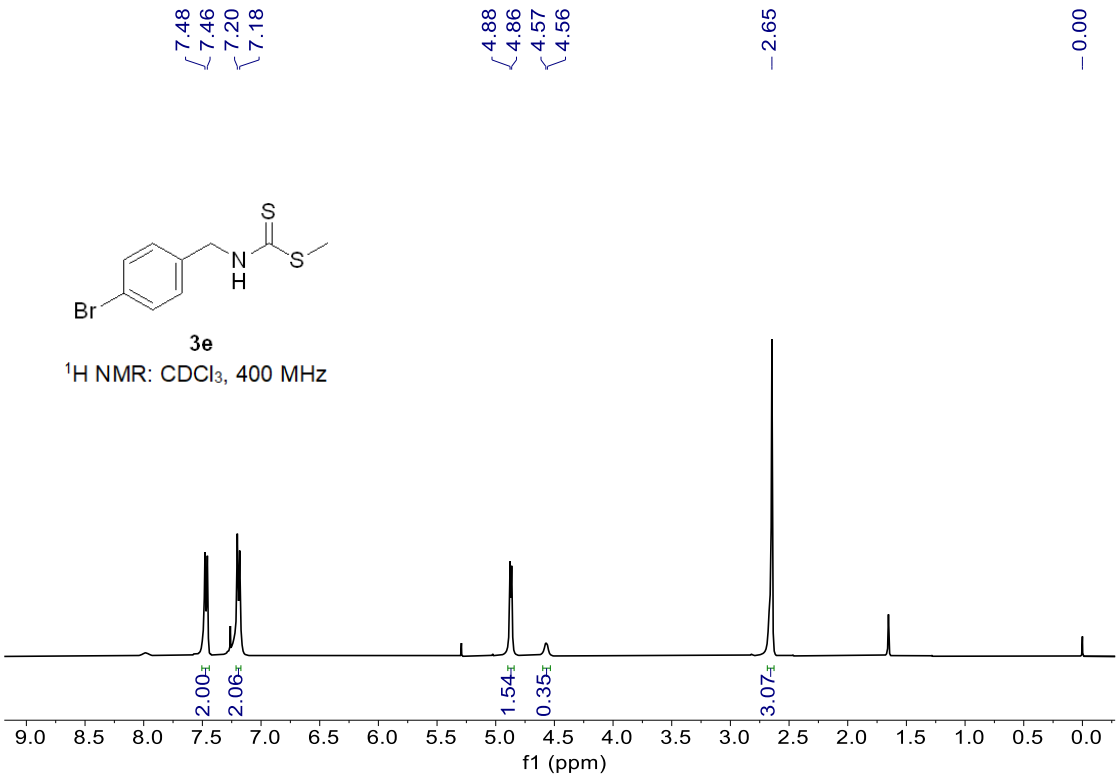


3c

^{19}F NMR: $CDCl_3$, 376 MHz

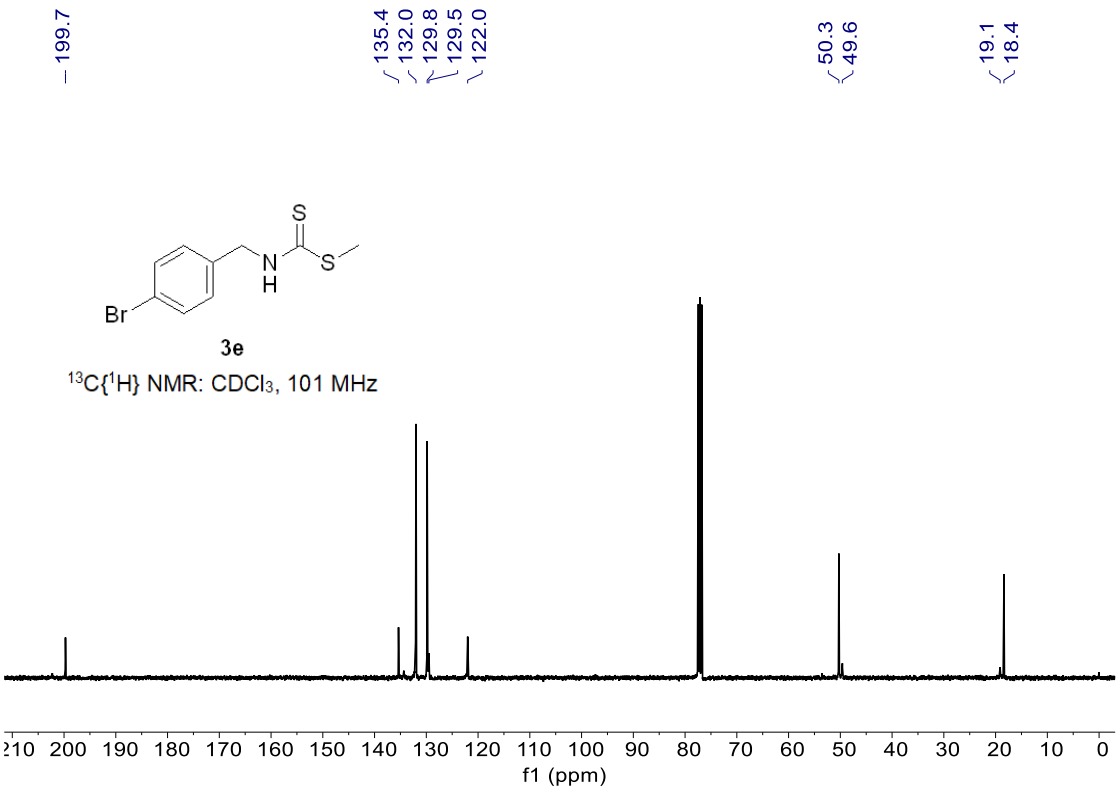

7.34
7.32
7.27
7.25
7.09
4.91
4.90
4.61
2.67
0.00
S
N
H
S
Cl
3d
^{1}H NMR: $CDCl_3$, 400 MHz
2.00
2.04
0.72
1.71
0.34
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


199.7
134.8
133.9
129.5
129.2
129.0
50.3
49.6
19.1
18.4
S
N
H
S
Cl
3d
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



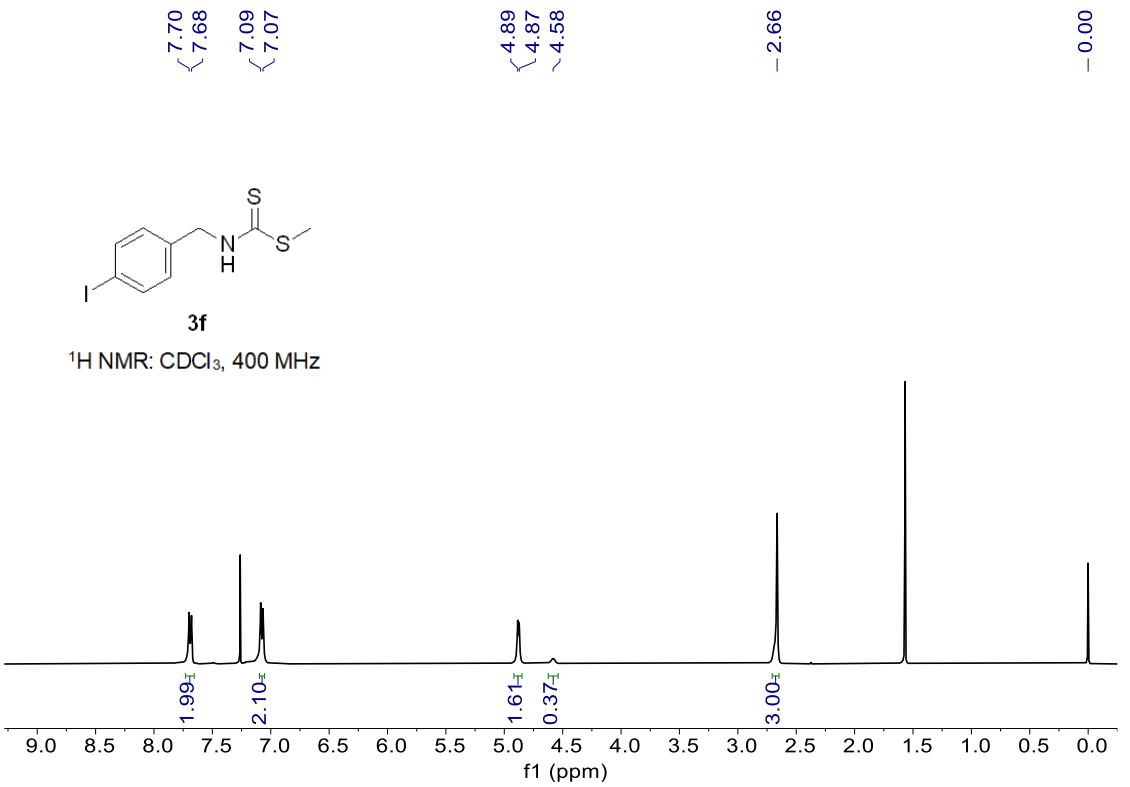
3e

^{1}H NMR: $CDCl_3$, 400 MHz



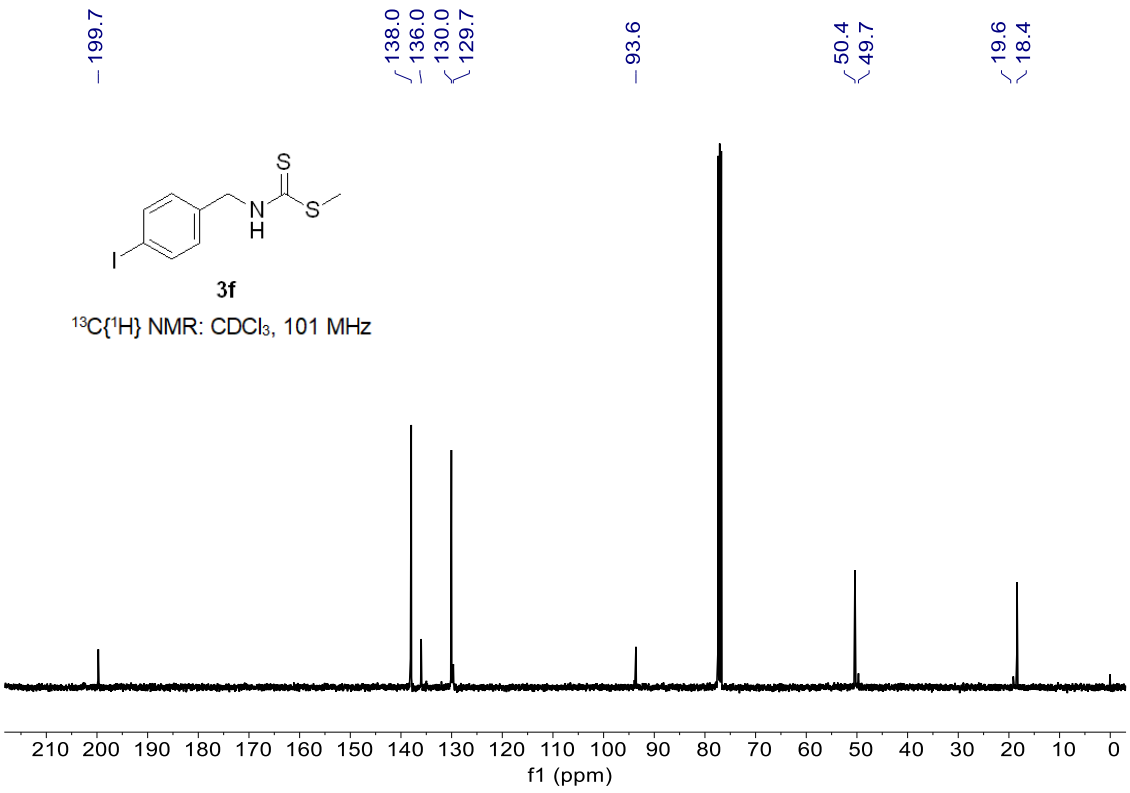
3e

^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz



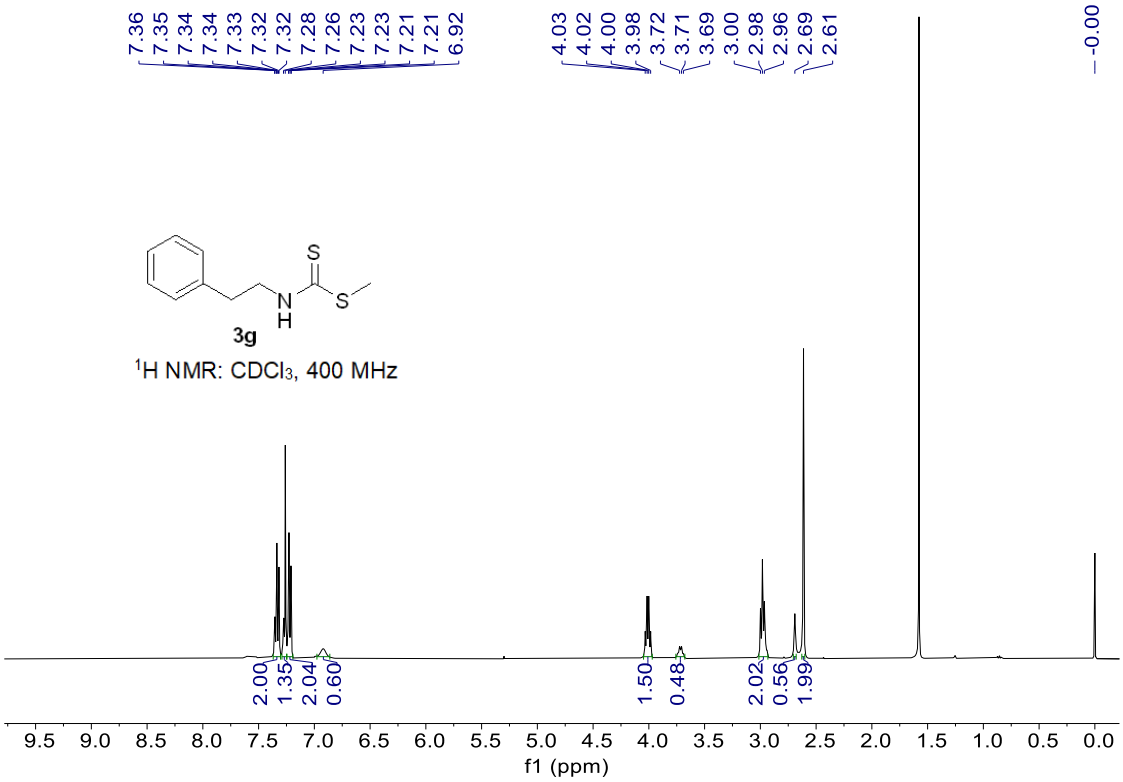
3f

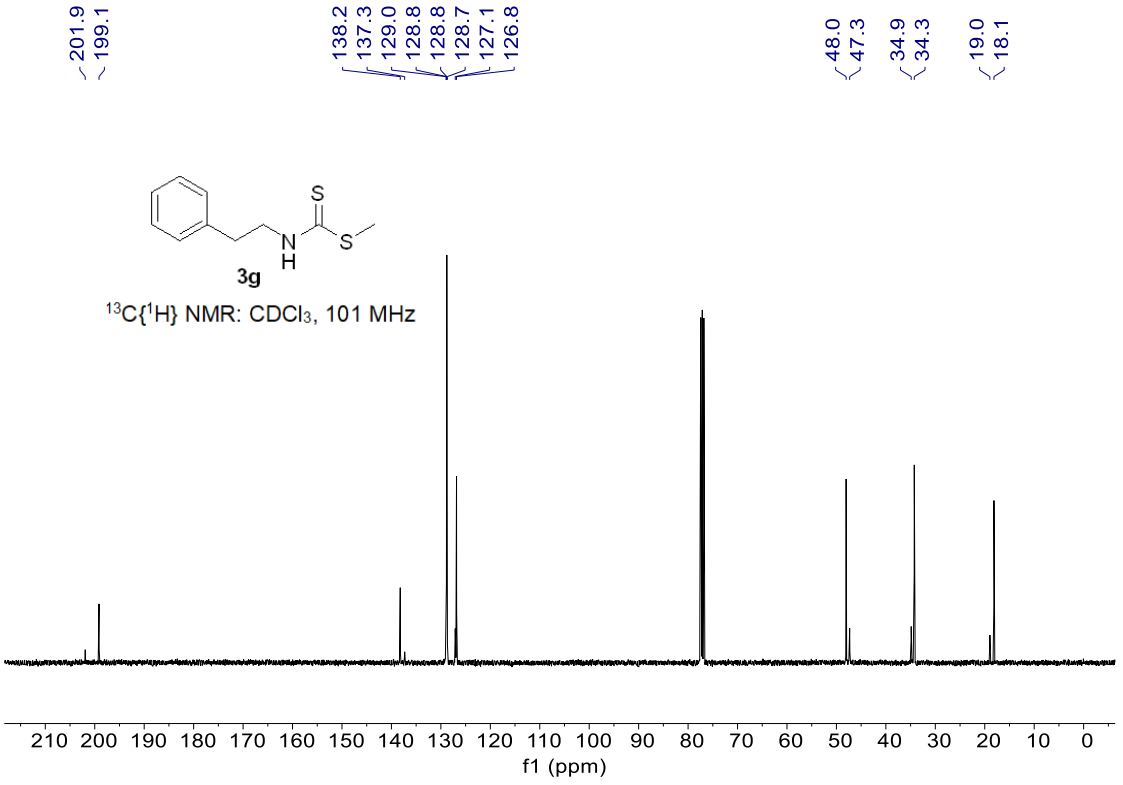
^{1}H NMR: $CDCl_3$, 400 MHz

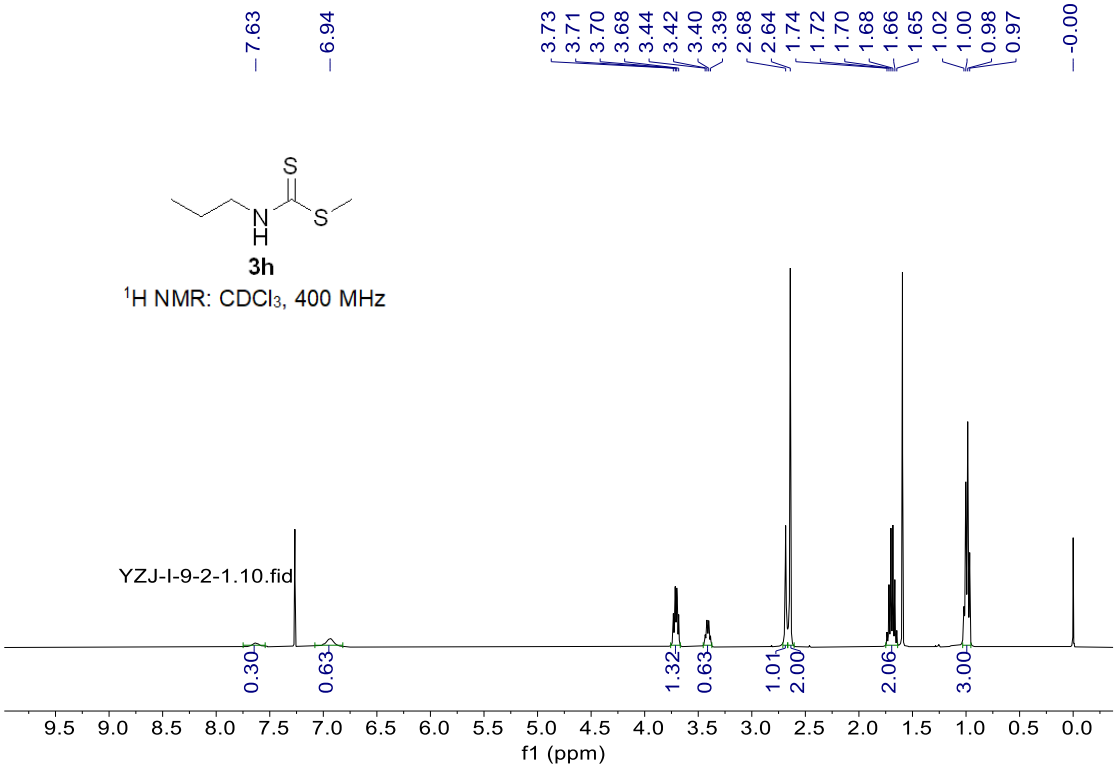


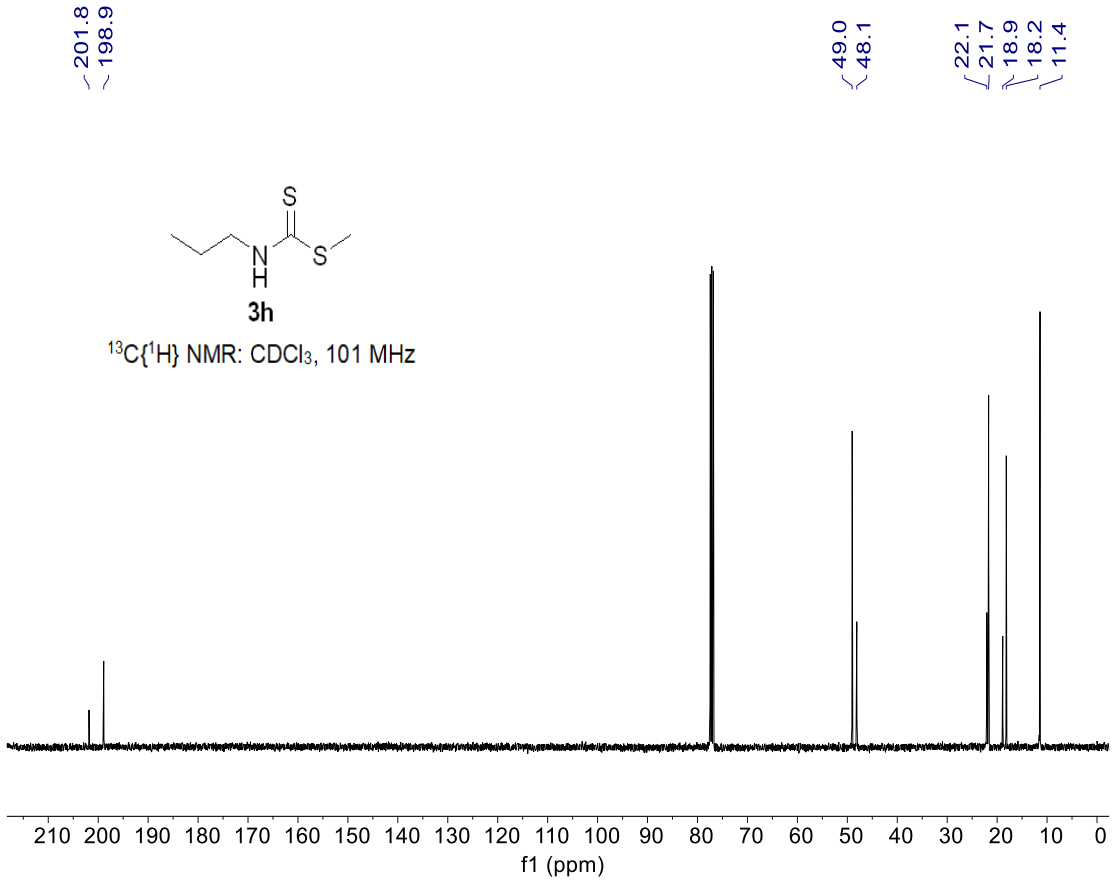
3f

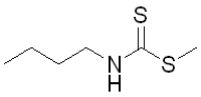
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz


7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.28
7.26
7.23
7.23
7.21
7.21
6.92
4.03
4.02
4.00
3.98
3.72
3.71
3.69
3.00
2.98
2.96
2.69
2.61
-0.00
S
N
H
S
3g
1H NMR: CDCl3, 400 MHz
2.00
1.35
2.04
0.60
1.50
0.48
2.02
0.56
1.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


201.9
199.1
138.2
137.3
129.0
128.8
128.8
128.7
127.1
126.8
48.0
47.3
34.9
34.3
19.0
18.1
S
N
H
S
3g
13C{1H} NMR: CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

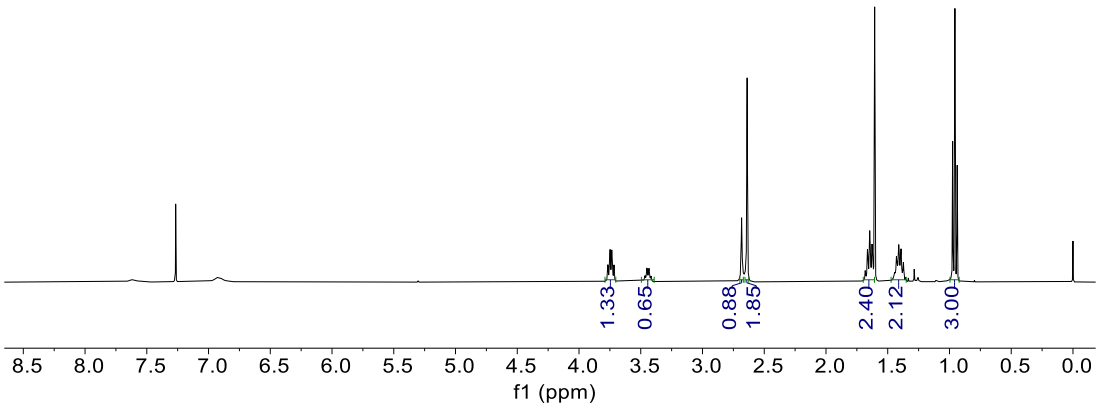

7.63
6.94
3.73
3.71
3.70
3.68
3.44
3.42
3.40
3.39
2.68
2.64
1.74
1.72
1.70
1.68
1.66
1.65
1.02
1.00
0.98
0.97
-0.00
S
N
H
S
3h
1H NMR: CDCl3, 400 MHz
YZJ-I-9-2-1.10.fid
0.30
0.63
1.32
0.63
1.01
2.00
2.06
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

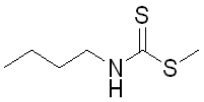

201.8
198.9
49.0
48.1
22.1
21.7
18.9
18.2
11.4
S
N
H
S
3h
13C{1H} NMR: CDCl3, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3i

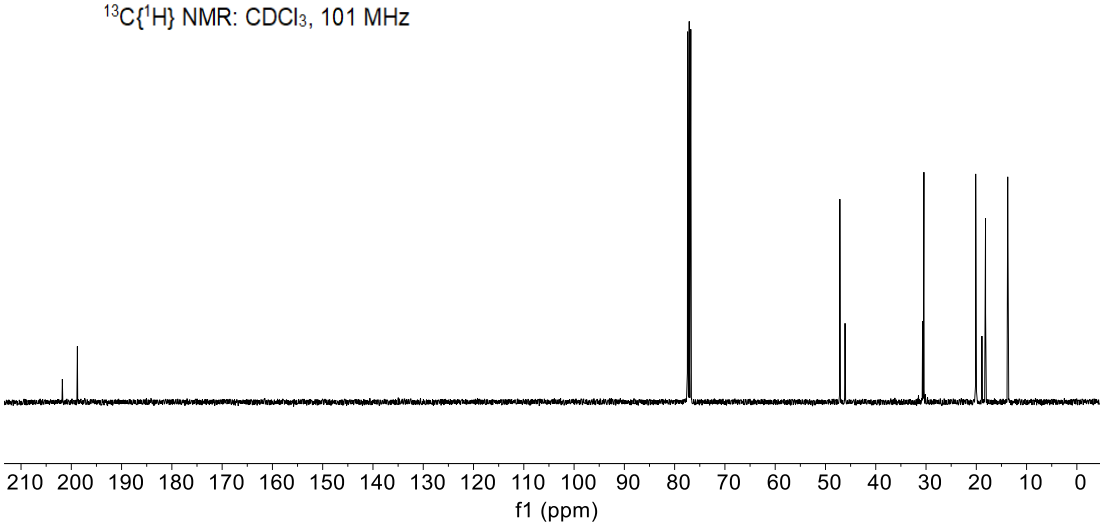
^{1}H NMR: $CDCl_3$, 400 MHz

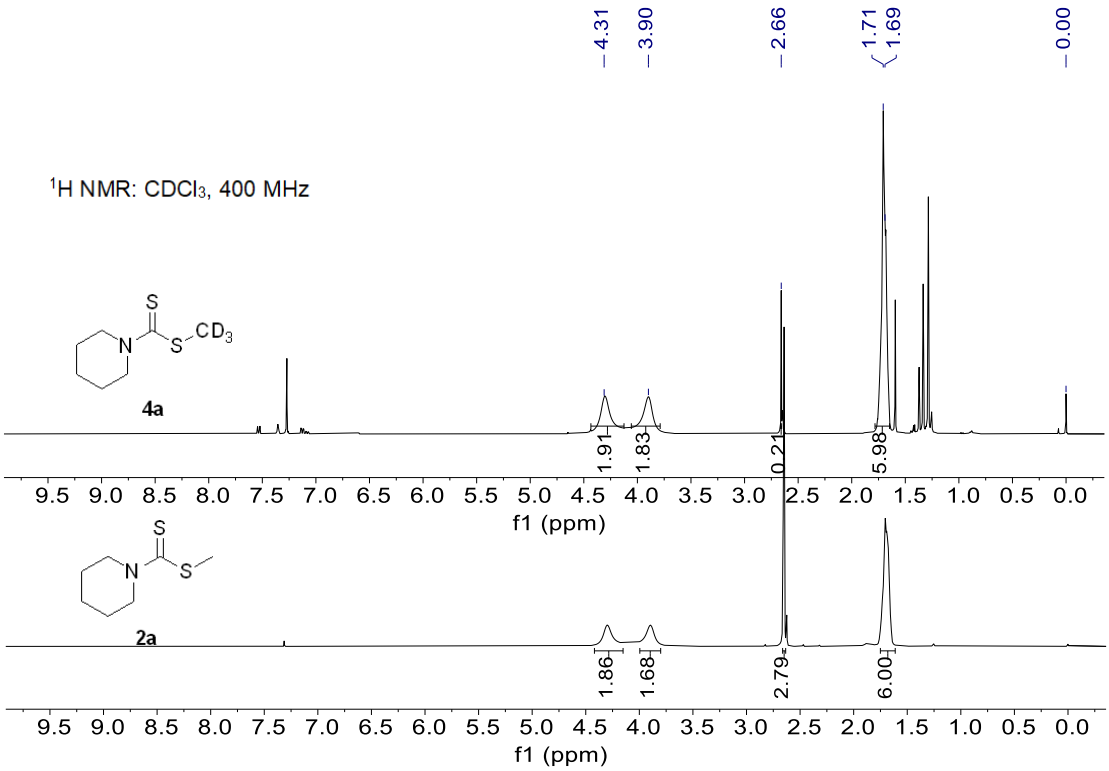


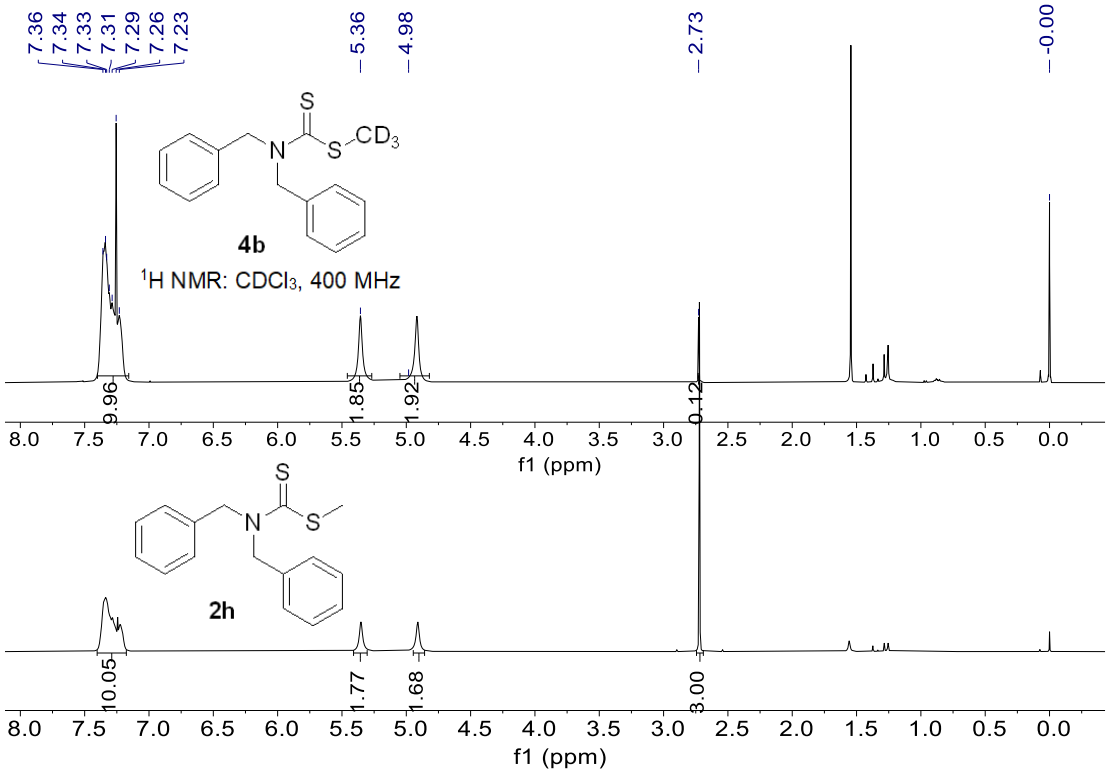


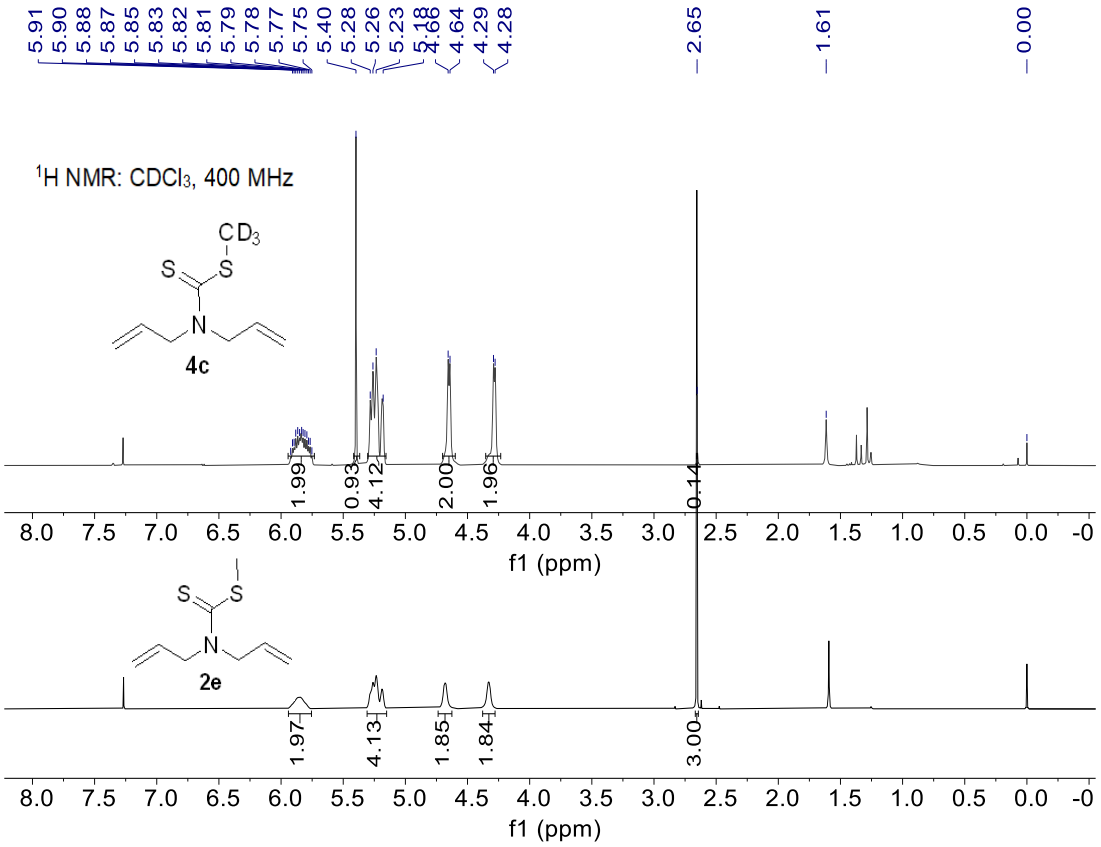
3i

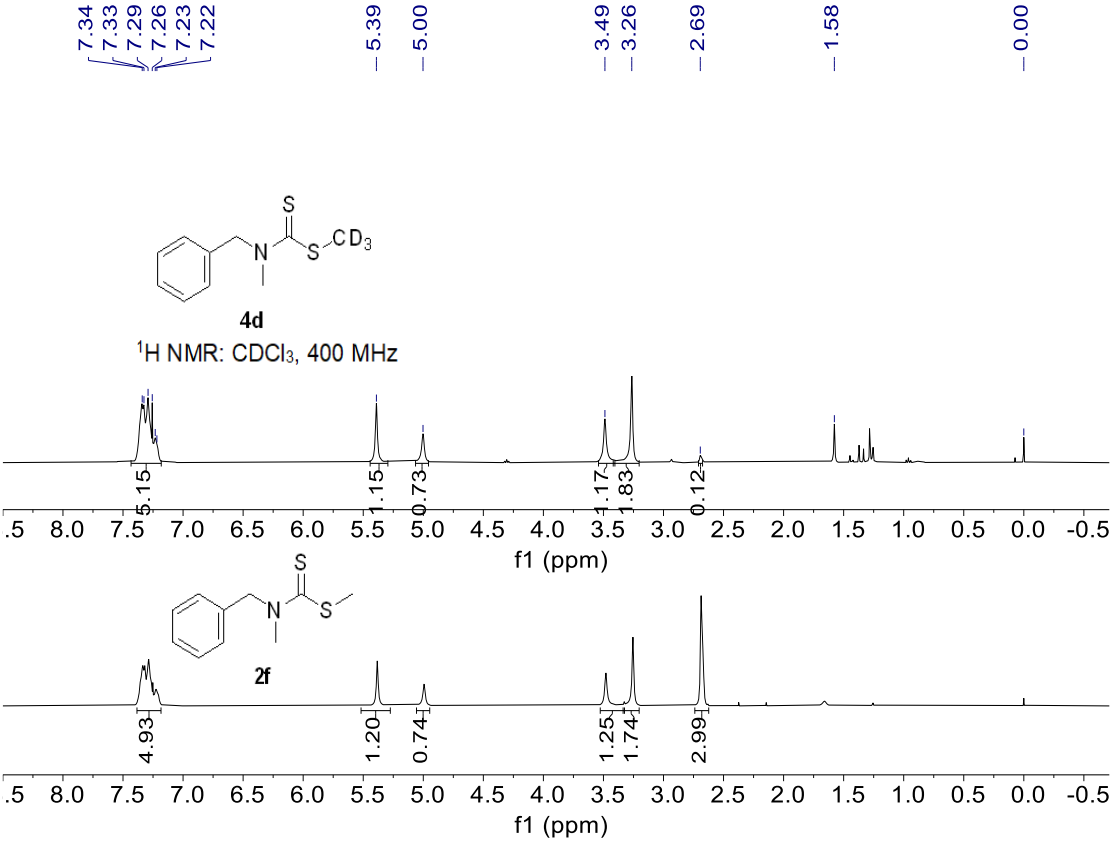
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz

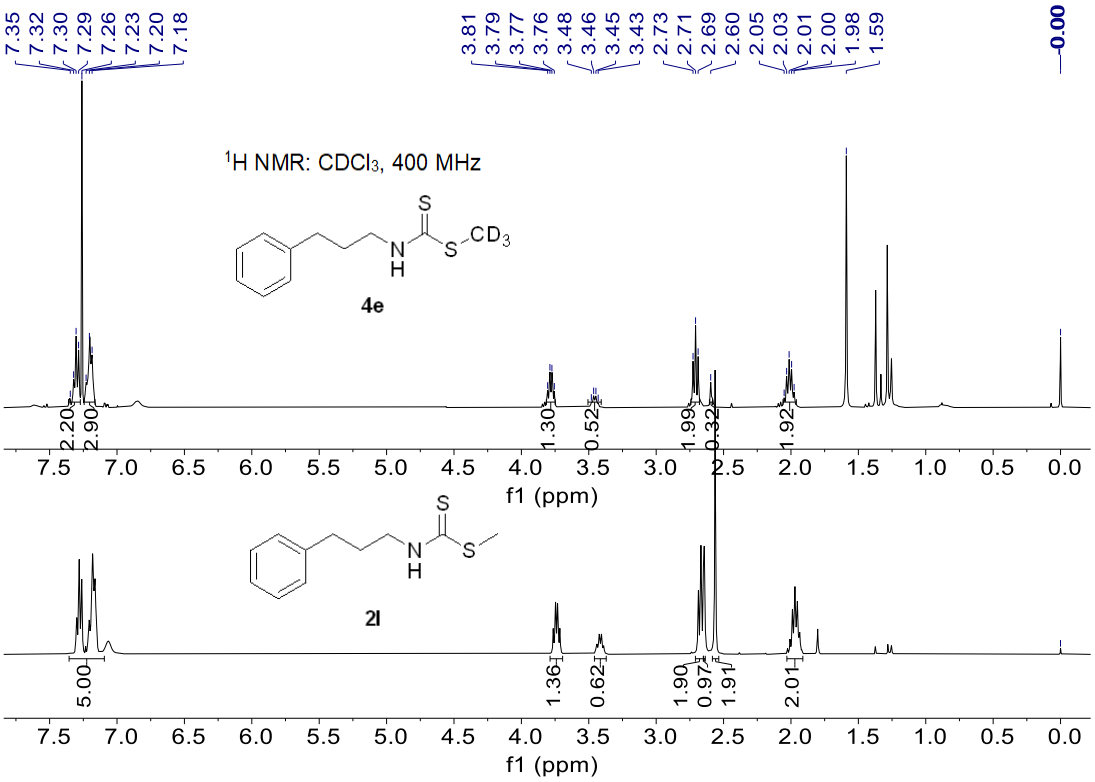


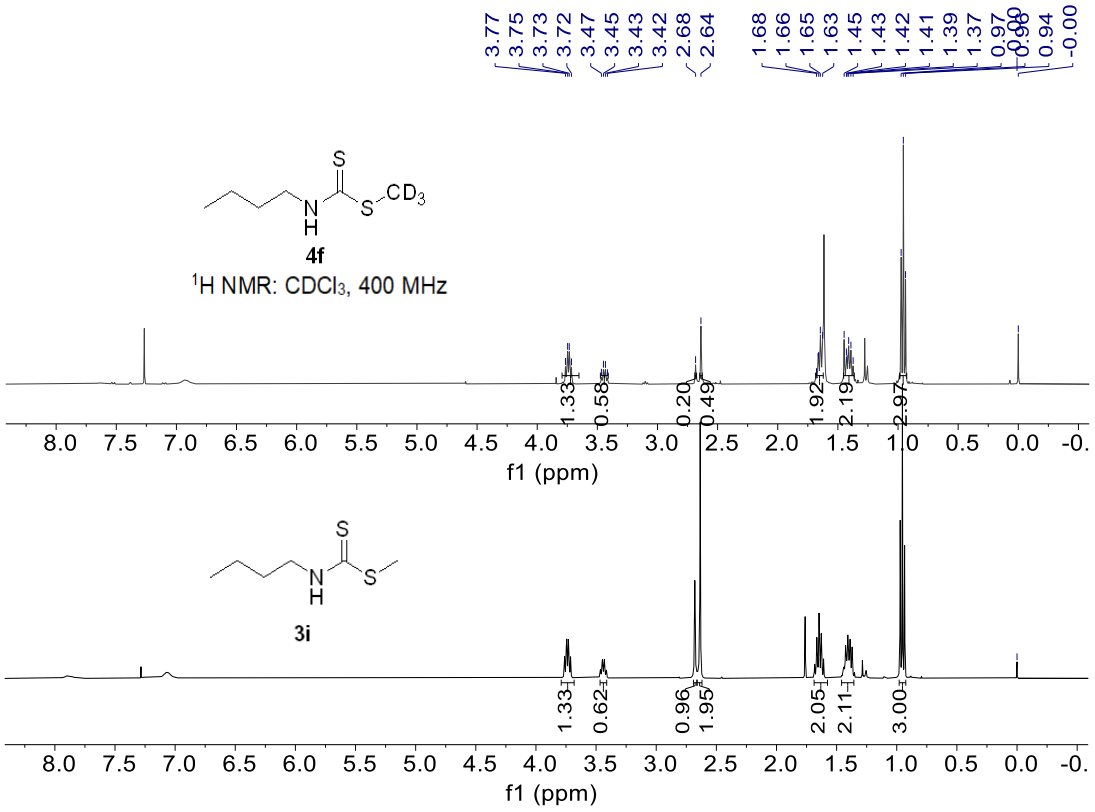

4.31
3.90
2.66
1.71
1.69
0.00
1H NMR: CDCl3, 400 MHz
4a
1.91
1.83
0.21
5.98
f1 (ppm)
2a
1.86
1.68
2.79*
6.00
f1 (ppm)


7.36
7.34
7.33
7.31
7.29
7.26
7.23
5.36
4.98
2.73
0.00
4b
1H NMR: CDCl3, 400 MHz
9.96
1.85
1.92
0.12
f1 (ppm)
2h
10.05
1.77
1.68
3.00
f1 (ppm)


5.91
5.90
5.88
5.87
5.85
5.83
5.82
5.81
5.79
5.78
5.77
5.75
5.40
5.28
5.26
5.23
4.64
4.29
4.28
2.65
1.61
0.00
1H NMR: CDCl3, 400 MHz
CD3
S
S
N
4c
1.99
0.93
4.12
2.00
1.96
0.14
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)
S
S
N
2e
1.97
4.13
1.85
1.84
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


7.34
7.33
7.29
7.26
7.23
7.22
5.39
5.00
3.49
3.26
2.69
1.58
0.00
S
N
S
CD3
4d
1H NMR: CDCl3, 400 MHz
5.15
1.15
0.73
1.17
1.83
0.12
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
S
N
S
2f
4.93
1.20
0.74
1.25
1.74
2.99
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


7.35
7.32
7.30
7.29
7.26
7.23
7.20
7.18
3.81
3.79
3.77
3.76
3.48
3.46
3.45
3.43
2.73
2.71
2.69
2.60
2.05
2.03
2.01
2.00
1.98
1.59
0.00
1H NMR: CDCl3, 400 MHz
S
N
H
S
CD3
4e
2.20
2.90
1.30
0.52
1.99
0.32
1.92
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
S
N
H
S
2l
5.00
1.36
0.62
1.90
0.97
1.91
2.01
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


3.77
3.75
3.73
3.72
3.47
3.45
3.43
3.42
2.68
2.64
1.68
1.66
1.65
1.63
1.45
1.43
1.42
1.41
1.39
1.37
0.97
0.94
-0.00
S
N
H
S
CD3
4f
1H NMR: CDCl3, 400 MHz
1.33
0.58
0.20
0.49
1.92
2.19
2.97
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)
S
N
H
S
3i
1.33
0.62
0.96
1.95
2.05
2.11
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

6. Reference

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