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Supporting information

Dithiocarbamate mediated thioamidation *via* C-C single bond cleavage of styrene: Study of the protocol on decarbonylative and decarboxylative thioamidations

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A. General information:

General Information. All the commercial starting materials and reagents were used without further purification. Silica gel (silica gel, f24), TLC plates were purchased from Merck. In column chromatographic purification process, silica gel 60-120 mesh has been used. ^{1}H NMR spectra were recorded using Brucker Spectrometer at 300 MHz, 400 MHz. The ^{19}F spectra of synthesized fluorinated product was recorded in $CDCl_3$ on Brucker Spectrometer, 300 MHz. ^{13}C NMR spectra were recorded at 75 MHz, 100 MHz. In all NMR, $CDCl_3$ and TMS have been used as solvent and internal standard respectively. The chemical shifts are reported in ppm scale considering standard signal of TMS at 0.00 ppm. The coupling constants (J values) are measured in Hz and splitting patterns of the proton are described as s (singlet), d (doublet), t (triplet), and m (multiplet). In NMR data, the rotamers are mentioned as #1 and #2. HRMS were measured in methanol solvent on a waters Micromass Q-tofMicromass spectrometer. GC-MS data were collected from PerkinElmer Clarus SQ 8 C Mass spectrometer. Melting points were determined by a PerkinElmer digital melting point apparatus.

B. General Experimental Procedure for the Preparation of Thioamides (3). CS_2 (0.1 mL, 1.5 mmol) was added drop wise to a solution of secondary amine (1 mmol) and K_2CO_3 (276 mg, 2 mmol) in DMSO (2 ml) at 5 ^{o}C. The resulting solution was stirred at room temperature for 5 min. Styrene (**2**) (0.8 mmol), and $(NH_4)_2S_2O_8$ (1.2 mmol, 273 mg), were added to the solution of dithiocarbamate anion (**1**) containing K_2CO_3. The reaction mixture was allowed to stir at 80 ^{o}C for a certain time period under open air/zero air-balloon. The progress of the reaction was monitored by TLC. After completion of the reaction, the crude product was obtained by usual work-up using EtOAc. The crude product was purified by column chromatography over silica gel using petroleum ether-ethyl acetate solvent mixture.

Similar procedure was followed for the synthesis of thioamide compounds from benzaldehyde derivatives (**2'**). In this case, all the reactions were carried out in DMSO solvent under open air atmosphere (Scheme 2a). [For operational simplicity, all the reactions with benzaldehyde derivatives were performed under open air, although molecular oxygen does not have any role in the thioamidation of benzaldehyde.]

In case of toluene derivative (**2''**), similar experimental procedure was followed. Here, all the reactions were performed in seal tube (Scheme 2b).

Thioamides have been synthesized from benzoic acid derivatives (**2'''**) following similar experimental procedure using Et_3N base (instead of K_2CO_3) and DMSO solvent under open air atmosphere (Scheme 2c). [For operational simplicity, the reactions with benzoic acid derivatives were performed under open air, although molecular oxygen does not have any role in the thioamidation of benzoic acid.]

C. Characterization data of all synthesized products

phenyl(piperidin-1-yl)methanethione[1] **(3a, Table 2)**: White solid; Yield: 88% (145 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.22 (5H, m), 4.35-4.32 (2H, m), 3.51-3.47 (2H, m), 1.81-1.70 (4H, m), 1.56-1.53 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.49, 143.44, 128.37, 128.33, 125.43, 53.17, 50.60, 26.89, 25.50, 24.13.

phenyl(pyrrolidin-1-yl)methanethione methanethione[1] **(3b, Table 2)**: White solid; Yield: 85% (129 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.30 (5H, m), 3.93 (2H, t, *J*=6.2 Hz), 3.42 (2H, t, *J*=6 Hz), 2.05-2.00 (2H, m), 1.95-1.89 (2H, m). ^{13}C NMR (75 MHz, CDCl3): δ 197.21, 144.04, 128.66, 128.26, 125.63, 53.77, 53.40, 26.47, 24.63.

morpholino(phenyl)methanethione[1] (3c, Table 2): White solid; Yield: 87% (144 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.29 (3H, m), 7.24-7.22 (2H,m), 4.38 (2H, t, *J*=5Hz), 3.82 (2H, t, *J*=5Hz), 3.59-3.52 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.96, 142.53, 128.84, 128.52, 125.90, 66.72, 66.49, 52.52, 49.56.

(4-fluorophenyl)(piperidin-1-yl)methanethione[1] (3d, Table 2): Pale yellow solid; Yield: 82% (146 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.26 (2H, m), 7.07-7.01 (2H, m), 4.37-4.33 (2H, m), 3.55-3.51 (2H, m), 1.84-1.74 (4H, m), 1.63-1.56 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.55, 162.56 (d, J_{C-F}= 240Hz), 139.46 (d, J_{C-F}= 4Hz), 127.64 (d, J_{C-F}= 4Hz), 115.41 (d, J_{C-F}= 48Hz), 53.31, 50.88, 26.92, 25.49, 24.13. ^{19}F NMR (282 MHz, $CDCl_3$): -112.65.

(4-fluorophenyl)(pyrrolidin-1-yl)methanethione[3] (3e, Table 2): White solid; Yield: 88% (146 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.30 (2H, m), 6.99-6.94 (2H, m), 3.89 (2H, t, *J*=5.4Hz), 3.42 (2H, t, *J*=5.4Hz), 2.04-1.99 (2H, m), 1.95-1.90 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.01, 162.68, (d, J_{C-F}= 220Hz), 140.12 (d, J_{C-F}= 3Hz), 127.9 (d, J_{C-F}= 4Hz), 115.17 (d, J_{C-F}= 18Hz), 53.89, 53.62, 26.51, 24.62. ^{19}F NMR (282 MHz, $CDCl_3$): -112.23

(4-fluorophenyl)(morpholino) methanethione[4] (3f, Table 2): White solid; Yield: 86% (155 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.24 (2H, m), 7.04-6.99 (2H, m), 4.38 (2H, t, *J*=5.2Hz), 3.84 (2H, t, *J*=5Hz), 3.62-3.52 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.89, 162.8 (d, J_{C-F}= 241Hz), 138.60 (d, J_{C-F}= 3Hz), 128.17 (d, J_{C-F}= 4Hz), 115.53 (d, J_{C-F}= 37Hz), 66.65, 66.46, 52.64, 49.77. ^{19}F NMR (376 MHz, $CDCl_3$): -111.64.

piperidin-1-yl(p-tolyl)methanethione[1] (3g, Table 2): White solid; Yield: 78% (102 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.07 (4H, m), 4.29-4.27 (2H, m), 3.49-3.46 (2H, m), 2.28 (3H, s), 1.75-1.69 (4H, m), 1.67-1.48 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.82, 140.70, 138.32, 128.91, 125.57, 53.17, 50. 69, 26.90, 25.50, 24.15, 21.23.

pyrrolidin-1-yl(p-tolyl)methanethione[1] (3h, Table 2): White solid; Yield: 80% (130 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (2H, d, *J*= 8 Hz), 7.10 (2H, d, *J*=8 Hz), 3.91 (2H, t, *J*=5.4 Hz), 3.43 (2H, t, *J*=5Hz), 2.30 (3H, s), 2.03-1.98 (2H, m), 1.93-1.88 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.44, 141.29, 138.71, 128.79, 125.76, 53.80, 53.47, 26.48, 24.65, 21.25.

morpholino(p-tolyl)methanethione[1] (3i, Table 2): White solid; Yield: 77% (136 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.13 (4H, m), 4.42-4.39 (2H, m), 3.83 (2H, t, *J*=4.8Hz), 3.6o-3.61 (4H, m), 2.33 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.41, 139.75, 139.06, 129.09, 129.06, 66.75, 66.52, 52.59, 49.70, 21.25.

N,N,4-trimethylbenzothioamide[1] (3j, Table 2): Pale yellow liquid; Yield: 72% (103 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.29 (4H, m), 3.72 (3H, s), 3.31(3H, s), 2.48 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.66, 140.60, 138.71, 128.90, 125.91, 44.20, 43.35, 21.26.

(4-chlorophenyl)(piperidin-1-yl)methanethione[1] (3k, Table 2): White solid; Yield: 82% (157 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (2H, d, *J*=7.8 Hz), 7.18 (2H, d, *J*=8 Hz), 4.29-4.26 (2H, m), 3.48-3.45 (2H, m), 1.77-1.68 (4H, m), 1.53-1.50 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.96, 141.76, 134.20, 128.57, 127.01, 53.25, 50.66, 26.88, 25.45, 24.06.

(4-chlorophenyl)(pyrrolidin-1-yl)methanethione[1] **(3l, Table 2)**: White solid; Yield: 78% (141 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.28 (4H, m), 3.90 (2H, t, *J*=5.8Hz), 3.42 (2H, t, *J*=5.6Hz), 2.06-2.00 (2H, m), 1.97-1.92 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.67, 142.32, 134.56, 128.44, 127.24, 53.82, 53.53, 26.51, 24.60.

(4-chlorophenyl)(morpholino)methanethione[1] **(3m, Table 2)**: White solid; Yield: 84% (161 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (2H, m), 7.22-7.19 (2H, m), 4.39-4.36 (2H, m), 3.85-3.82 (2H, m), 3.61-3.55 (4H,m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.50, 140.81, 134.86, 128.75, 127.46, 66.65, 66.46, 52.60, 49.62.

4-chloro-N,N-diethylbenzothioamide[5] **(3n, Table 2)**: Yellow liquid; Yield: 86% (155 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 78.32-7.30 (2H, m), 7.19-7.18 (2H, m), 4.10 (2H, q, *J*=3.6Hz), 3.45 (2H, q, *J*=3.4) 1.37 (3H, t, *J*=3 Hz), 1.14 (3H, t, *J*=3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.95, 142.25, 133.97, 128.60, 126.54, 47.87, 46.21, 13.86, 11.26.

4-chloro-N,N-dimethylbenzothioamide[1] **(3o, Table 2)**:Pale yellow liquid; Yield: 80% (127 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.26 (4H, m), 3.60 (3H, s), 3.19 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.78, 141.68, 134.54, 128.57, 127.31, 44.21, 43.33.

(4-bromophenyl)(piperidin-1-yl)methanethione[1] **(3p, Table 2)**: White solid; Yield: 70% (158 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (2H, m), 7.08-7.06 (2H, m), 4.23-4.20 (2H, m), 3.42-3.39 (2H, m), 1.73-1.60 (4H, m), 1.48-1.42 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.72, 142.20, 131.48, 127.27, 122.32, 53.25, 50.61, 26.90, 25.46, 24.05.

(4-bromophenyl)(pyrrolidin-1-yl)methanethione[1] **(3q, Table 2)**: White solid; Yield: 75% (172 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.43 (2H, m), 7.22-7.20 (2H, m), 3.90 (2H, t, *J*=4.8Hz), 3.42 (2H, t, *J*=4.8 Hz), 2.06-2.01 (2H, m), 1.97-1.92 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.57, 142.74, 131.42, 127.45, 122.82, 53.83, 53.52, 26.52, 24.61.

4-bromo-N,N-dimethylbenzothioamide[1] **(3r, Table 2)**: Pale yellow liquid; Yield: 70% (136 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.47 (2H, m), 7.20-7.17 (2H, m), 3.58 (3H, s), 3.17 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.95, 142.15, 131.54, 127.52, 122.76, 44.15, 43.29.

(4-methoxyphenyl)(piperidin-1-yl)methanethione[1] **(3s, Table 2)**: White solid; Yield: 57% (106 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.16 (2H, m), 6.78-6.76 (2H, m), 4.24-4.23 (2H, m), 3.72 (3H, s), 3.50-3.48 (2H, m), 1.73-1.66 (4H, m), 1.49-1.46 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.65, 159.86, 135.93, 127.52, 113.57, 55.40, 53.32, 51.00, 26.91, 25.48, 24.15.

(4-methoxyphenyl)(pyrrolidin-1-yl)methanethione[1] **(3t, Table 2)**: White solid; Yield: 51% (89 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (2H, m), 6.85-6.83 (2H, m), 3.95 (2H, t, *J*=5.6Hz), 3.80 (3H, s), 3.51(2H, t, *J*=5.2Hz), 2.09-2.02 (2H, m), 1.98-1.91 (2H, m), ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.20, 160.11, 136.58, 127.74, 113.45, 53.39, 53.96, 53.71, 26.55, 24.70.

(4-methoxyphenyl)(morpholino)methanethione[9] **(3u, Table 2)**: White solid; Yield: 62% (116 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.22 (2H, m), 6.83-6.81 (2H, m), 4.36 (2H, m), 3.81 (2H, t, *J*=4Hz), 3.76 (3H, s), 3.60 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.14, 160.29, 134.95, 128.09, 113.73, 66.69, 66.53, 55.44, 52.80, 50.02.

(4-nitrophenyl)(piperidin-1-yl)methanethione[5] **(3v, Table 2)**: White solid; Yield: 68% (136 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.19 (2H, m), 7.42-7.38 (2H, m), 4.34-4.32 (2H, m), 3.48-3.45 (2H, m), 1.84-1.75

(4H, m), 1.61-1.56 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.13, 148.93, 147.26, 126.25, 124.00, 53.28, 50.31, 26.87, 25.41, 24.01.

N,N-dimethyl-4-nitrobenzothioamide[6] **(3w, Table 2)**: Yellow liquid; Yield: 68% (114 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.16 (2H, m), 7.43-7.41 (2H, m), 3.57 (3H, s), 3.14, (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.92, 148.95, 147.34, 126.61, 123.92, 44.04, 42.98.

methyl (phenylcarbonothioyl)-L-prolinate (3x, Table 2): Colorless viscous liquid at room temperature; Yield: 65% (129 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.37 (5H, m, #1), 7.35-7.27 (0.87H, m, #2), 7.26-7.24 (0.52, m, #2), 5.17-5.13 (1H, m, #1), 4.52-4.48 (0.28H, m, #2), 4.16-4.14 (0.54H, m, #2), 3.84 (3H, s, #1), 3.72-3.64 (2H, m, #1),3.61-3.59 (0.74, m, #2), 2.52-2.48 (1H, m, #1), 2.47-2.45 (0.34H, m, #2), 2.23-2.08 (3H, m, #1), 2.07-1.96 (0.89H, m, #2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.75 (C=S, #2), 199.41 (C=S, #1), 171.10 (CO_2Me, #2), 170.93 (CO_2Me, #1), 143.82(C, #2), 143.46 (C, #1), 129.00 (CH, #1), 128.65 (CH, #2), 128.35 (CH, #2), 128.30 (CH, #1), 125.69 (CH, #1), 125.28 (CH, #2), 64.81 (2-CH, #1), 64.51(2-CH, #2), 54.14 (5-CH_2, #1), 53.46 (5-CH_2, #2), 52.51 (OCH_3, #2), 52.46 (OCH_3, #1), 31.51 (3-CH_2, #2), 29.73 (3-CH_2, #1), 25.22 (4-CH_2, #1), 22.89 (4-CH_2, #2). HRMS (ESI) m/z calcd for $C_{13}H_{15}NO_2S$ $[M + H]^+$ 250.082, found 250.146.

4-methyl-N-phenylbenzothioamide[1] **(3y, Table 2)**: Yellow solid; Yield: 56% (95 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (1H, brs), 7.75-7.71 (4H, m), 7.42-7.39 (2H, m), 7.29-7.19 (3H, m), 2.39 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.31, 141.85, 139.21, 129.29, 129.19, 129.03, 128.99, 126.84, 123.90, 21.40.

N-benzyl-4-methylbenzothioamide[1] **(3z, Table 2)**: White solid; Yield: 74% (149 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (1H, brs), 7.66-7.63 (2H, m), 7.37-7.35 (5H, m), 7.14-7.12 (2H, m), 4.96-4.95 (2H, m), 2.36 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.90, 141.75, 138.72, 136.47, 129.13, 1278.97, 128.30, 128.08, 126.87, 50.75, 21.41.

piperidin-1-yl(pyridin-3-yl)methanethione[11] **(3zz, Table 2)**: Yellow solid; Yield: 51% (98 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52-8.47 (2H, m), 7.63-7.59 (1H, m), 7.29-7.24 (1H, m), 4.32-4.29 (2H, m), 3.51-3.47 (2H, m), 1.81-1.70 (4H, m), 1.57-1.53 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.63, 149.21, 145.62, 139.21, 133.63, 123.35, 53.39, 50.70, 26.97, 25.45, 24.01.

4-(piperidine-1-carbonothioyl)benzonitrile[7] **(3aa)**: Yellow solid; Yield: 74% (170 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (2H, d, *J*=8Hz), 7.31 (2H, d, *J*=8Hz), 4.29-4.26 (2H, m), 3.43-3.40 (2H, m), 1.80-1.68 (4H, m), 1.54-1.49 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.39, 147.21, 132.41, 126.09, 118.31, 118.81, 53.27, 50.34, 26.85, 25.40, 23.97.

4-(pyrrolidine-1-carbonothioyl)benzonitrile[4] **(3ab)**: Pale yellow solid; Yield: 75% (161 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (2H, d, *J*=8.2Hz), 7.38 (2H, d, *J*=8Hz), 3.88 (2H, t, *J*=4.8Hz), 3.35 (2H, t, *J*=4.8Hz), 2.05-2.00 (2H, m), 1.97-1.92 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.51, 145.80, 130.45, 124.48, 116.41, 110.31, 51.82, 51.49, 24.60, 22.61.

piperidin-1-yl(o-tolyl)methanethione[8] **(3ac)**: Yellow liquid; Yield: 58% (126 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.11 (3H, m), 7.07-7.04 (1H, m), 4.63-4.57 (1H, m), 4.12-4.08 (1H, m), 3.41-3.36 (1H, m), 3.32-3.29 (1H, m), 2.24 (3H, s), 1.79-1.68 (4H,m), 1.51-1.48 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.83, 143.02, 131.46, 130.40, 127.82, 126.10, 124.95, 52.15, 49.51, 26.67, 25.51, 24.11, 18.93.

(3-nitrophenyl)(piperidin-1-yl)methanethione[1] **(3ad)**: Yellow solid; Yield: 61% (152 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.90 (2H, m), 7.41-7.32 (2H, m), 4.16-4.13 (2H, m), 3.35-3.31(2H, m), 1.66-1.55 (4H,

m), 1.41-1.38 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.57, 147.92, 144.50, 131.35, 129.71, 122.99, 120.60, 53.46, 50.65, 26.88, 25.42, 23.93.

morpholino(o-tolyl)methanethione (3ae): Pale yellow solid; m.p. 105-110 ^{o}C. Yield: 59% (130 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.14 (3H, m), 7.08-7.05 (1H, m), 4.58-4.53 (1H, m), 4.33-4.27 (1H, m), 3.86-3.83 (2H, m), 3.60-3.56 (2H, m), 3.42-3.37, (2H, m), 2.25 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.30, 142.21, 131.61, 130.54, 128.25, 126.30, 125.29, 66.60, 66.51, 51.38, 48.45, 18.98. HRMS (ESI) m/z calcd for $C_{12}H_{15}NOS$ $[M + H]^+$ 222.087, found 222.096.

2,2,6,6-tetramethylpiperidin-1-yl benzoate[9] : Crystalline solid; Yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.06 (2H, m), 7.57-7.55 (1H, m), 7.48-7.43 (2H, m), 1.79-1.60 (4H, m), 1.61-1.55 (2H, m), 1.27 (6H, s), 1.12 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.46, 132.89, 129.71, 129.59, 128.48, 60.44, 39.06, 31.97, 20.88, 17.02.

Isothiocyanatobenzene[10] : Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.31 (2H, m), 7.30-7.26 (1H, m), 7.24-7.19 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.29, 131.25, 129.59, 127.36, 125.79.

Benzophenone[9] : White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.79 (4H, m), 7.61-7.56 (2H, m), 7.51-7.45 (4H, m).^{13}C NMR (100 MHz, $CDCl_3$): δ 196.76, 137.63, 132.44, 130.07, 128.30.

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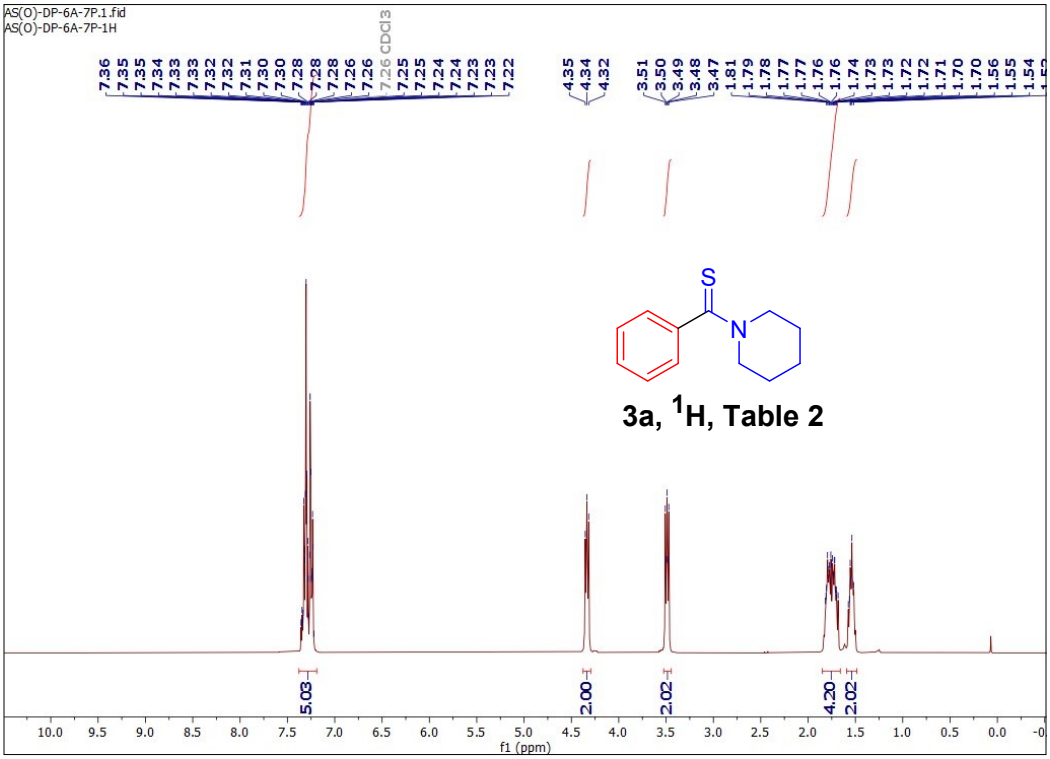
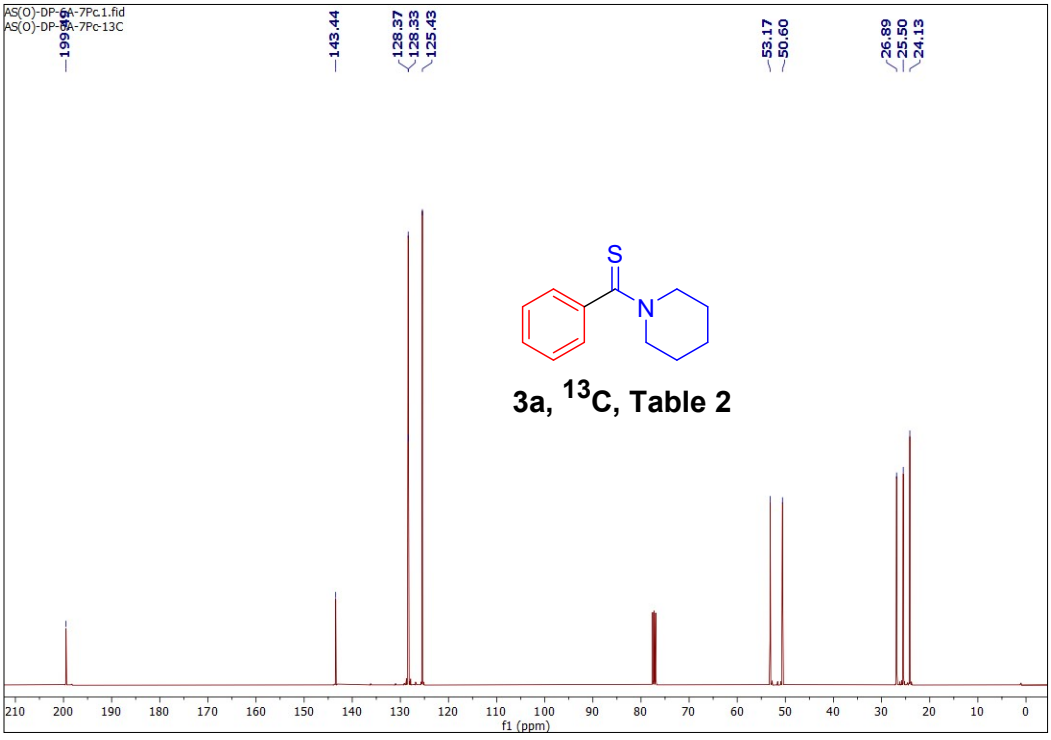
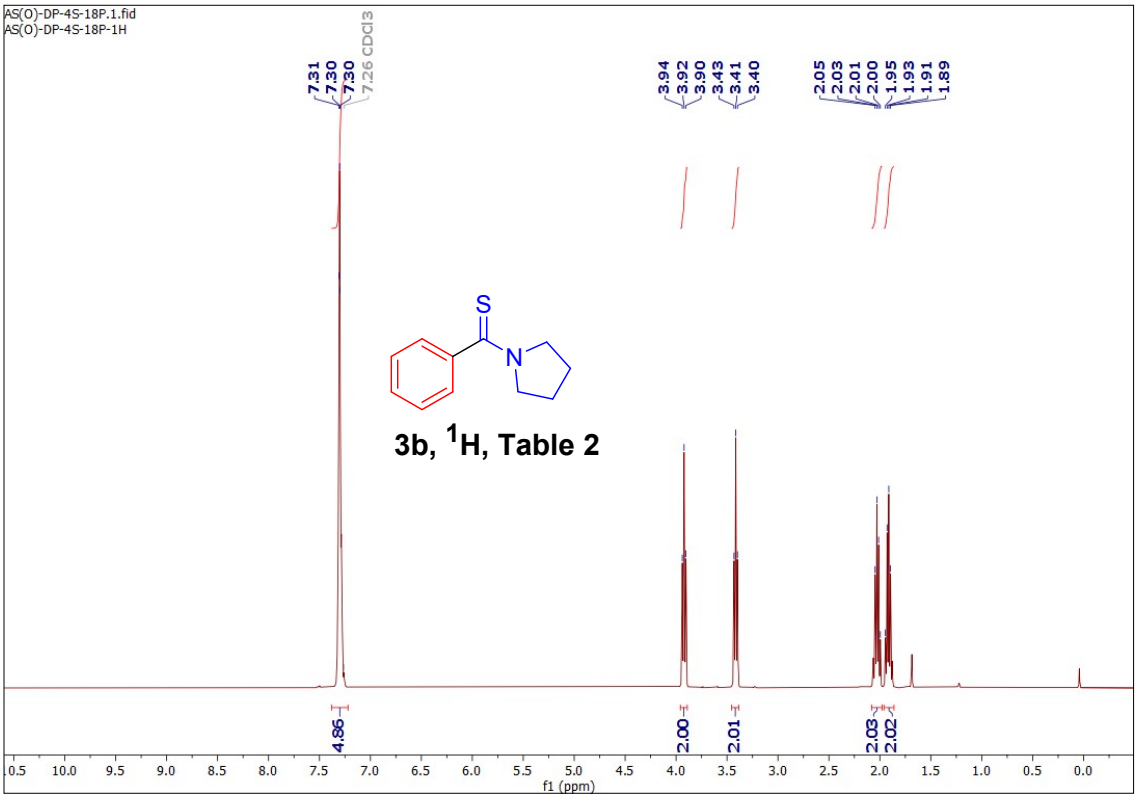
E. ^{1}H and ^{13}C NMR spectra of all products:

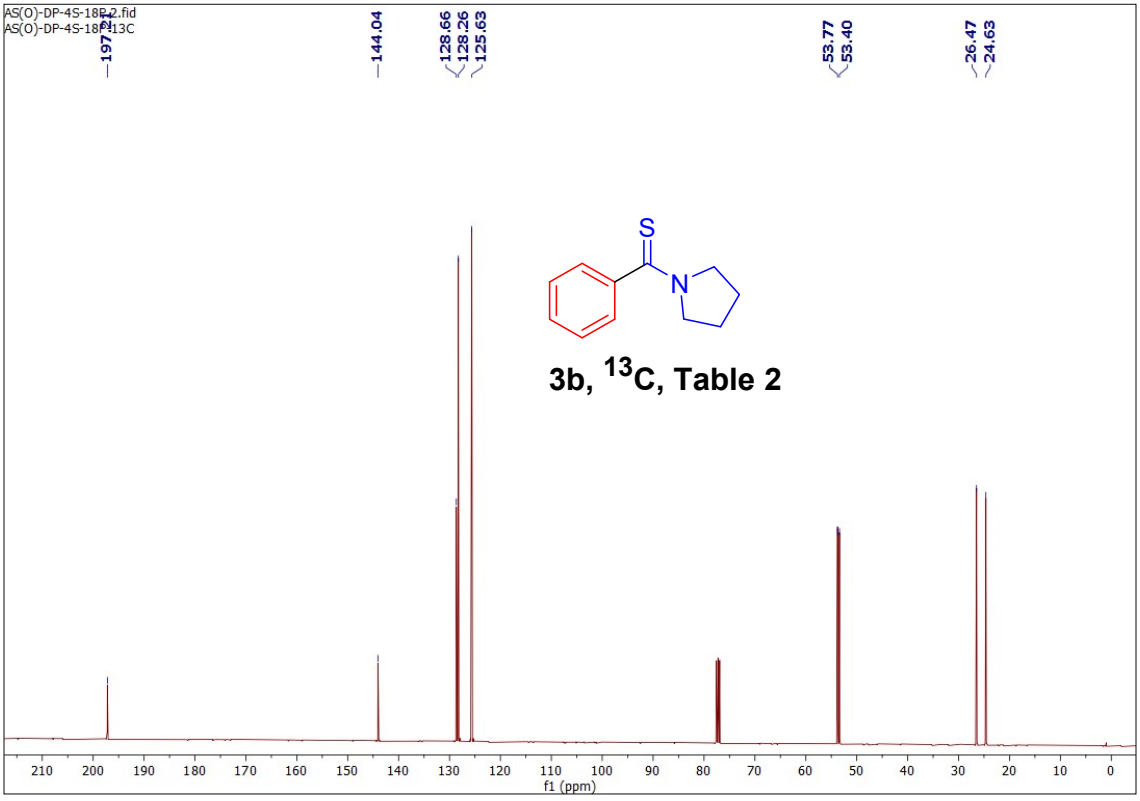
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3a



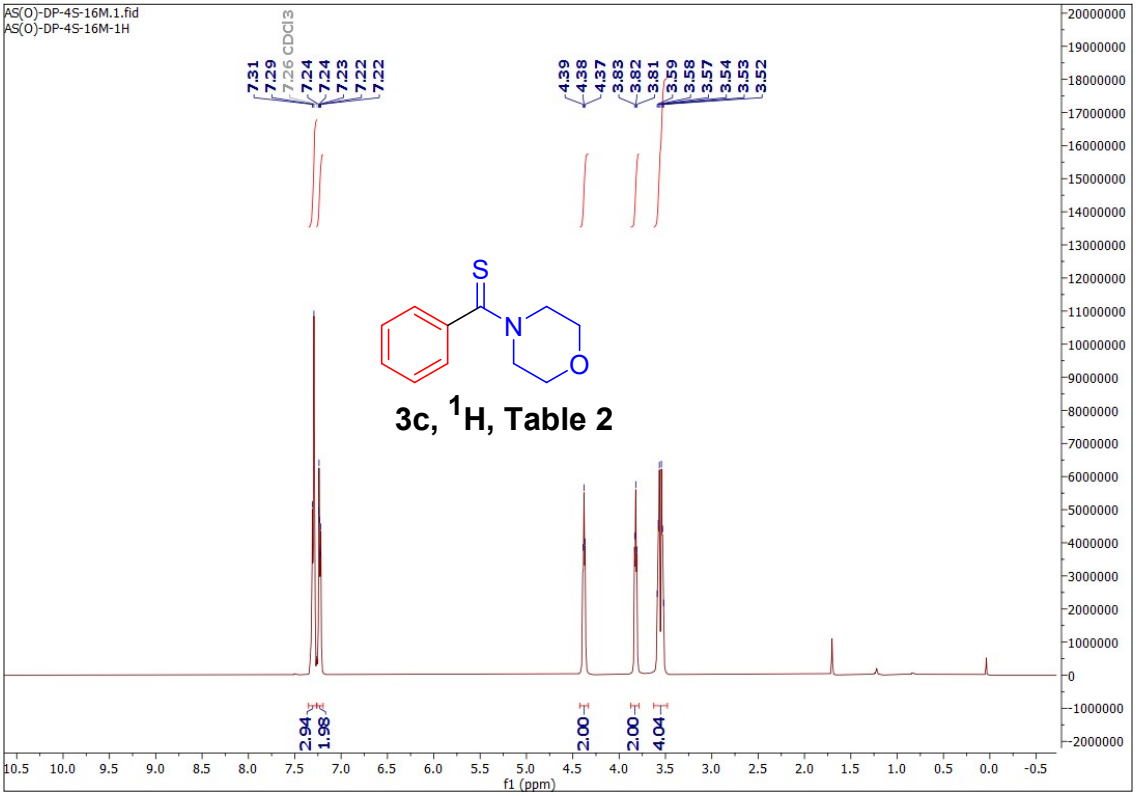


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3b

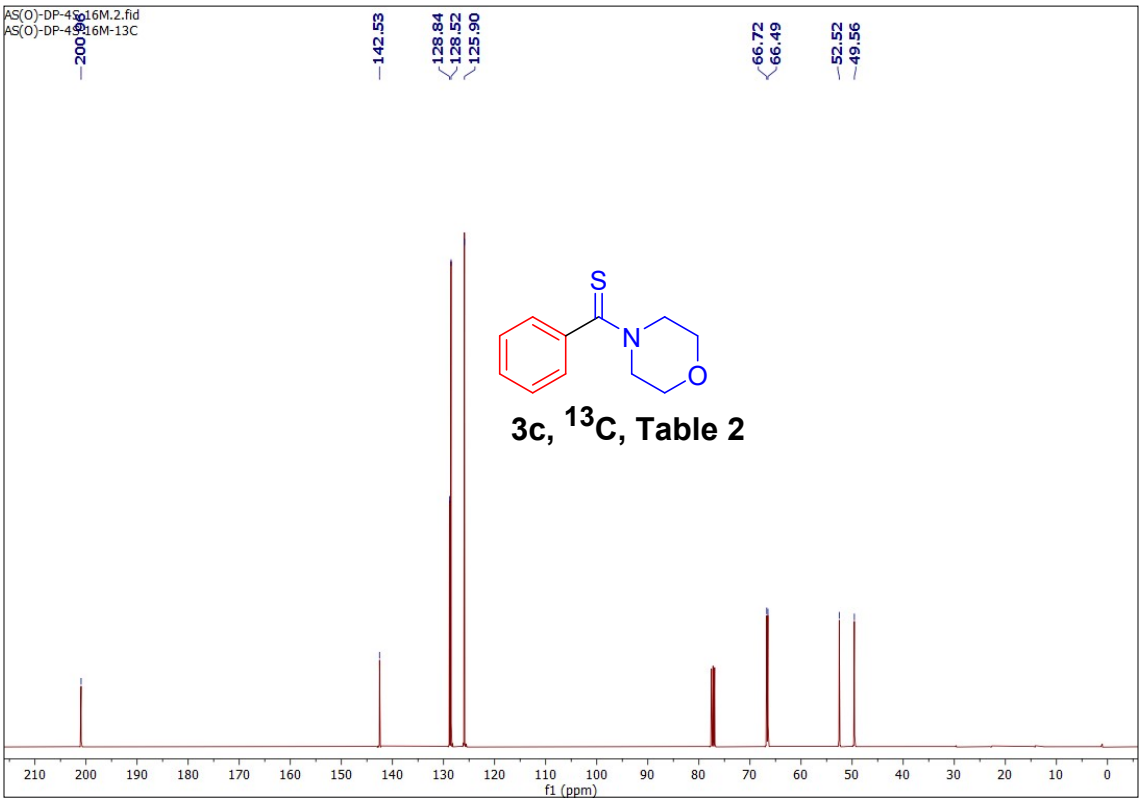




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3c

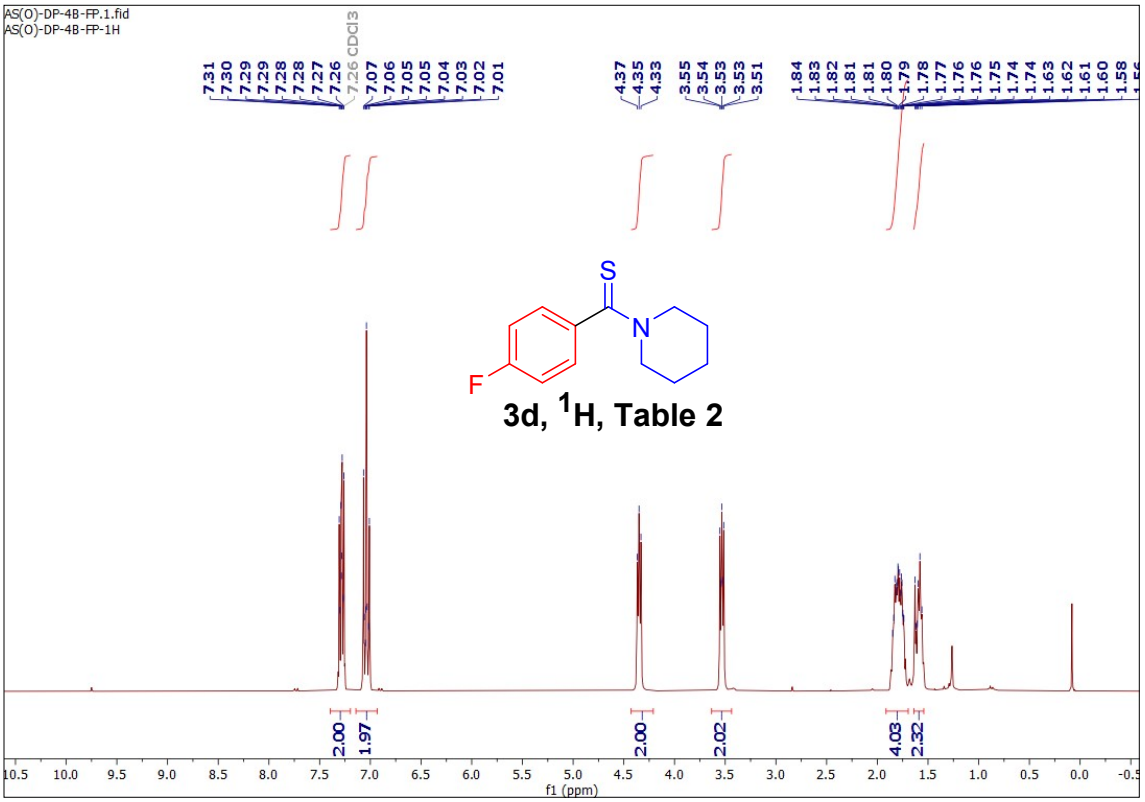


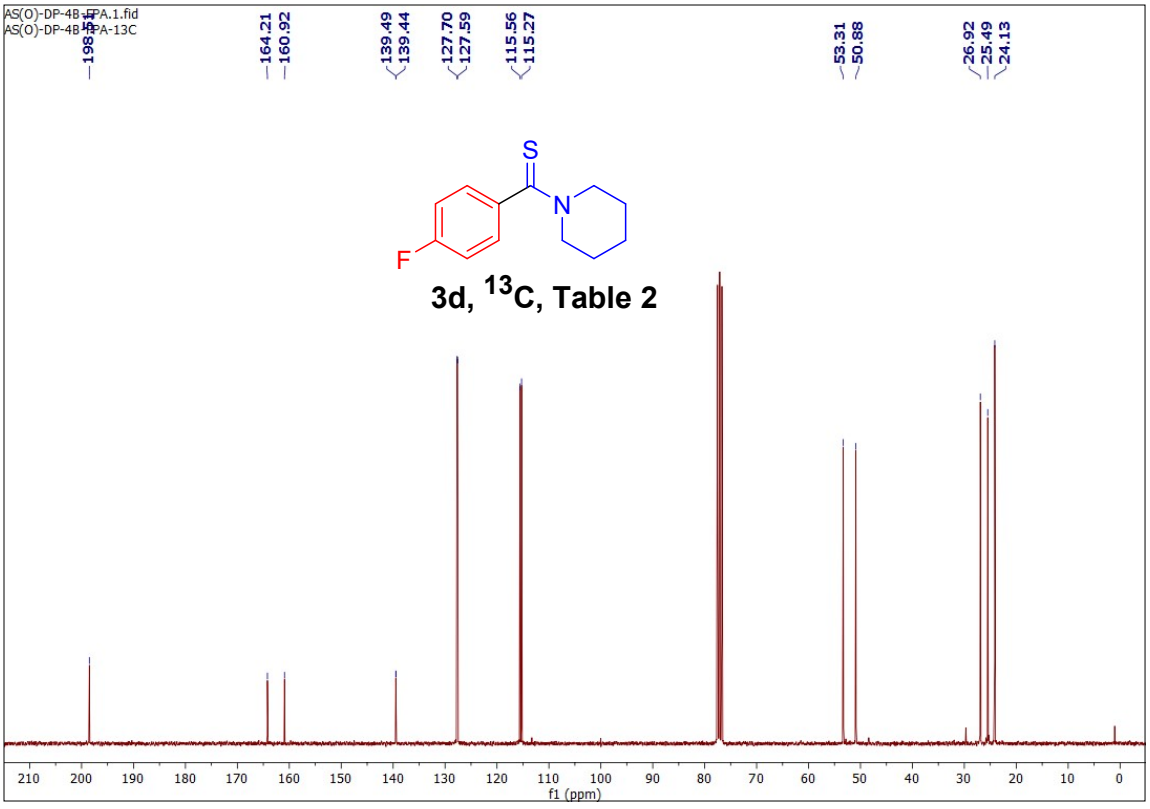
3c, ^{1}H, Table 2



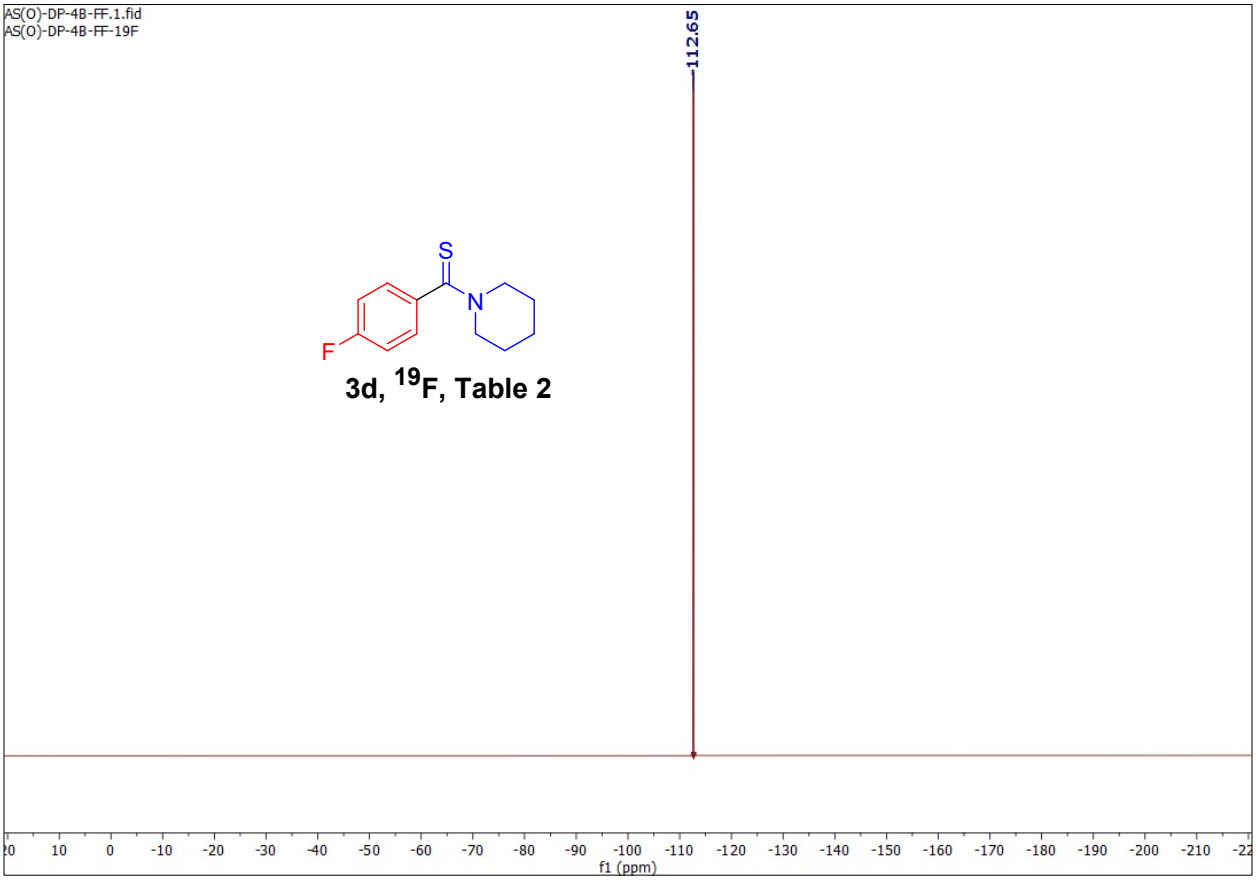
3c, ^{13}C, Table 2

^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3d

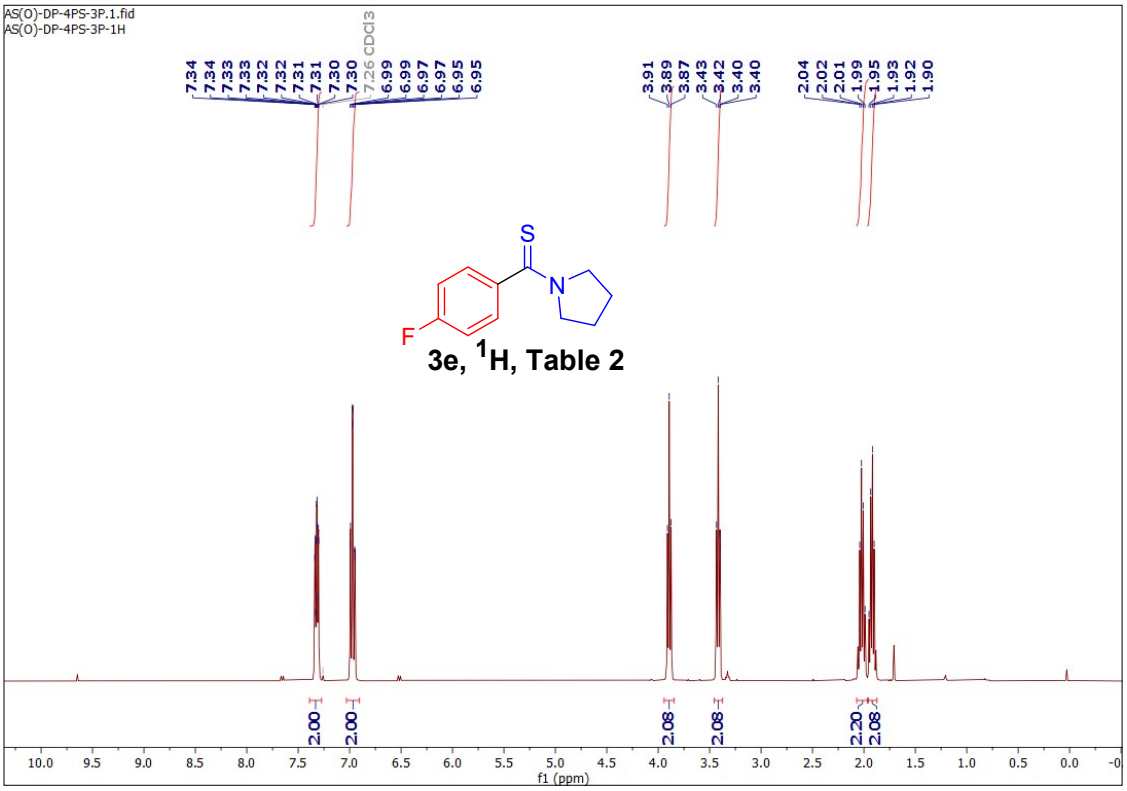


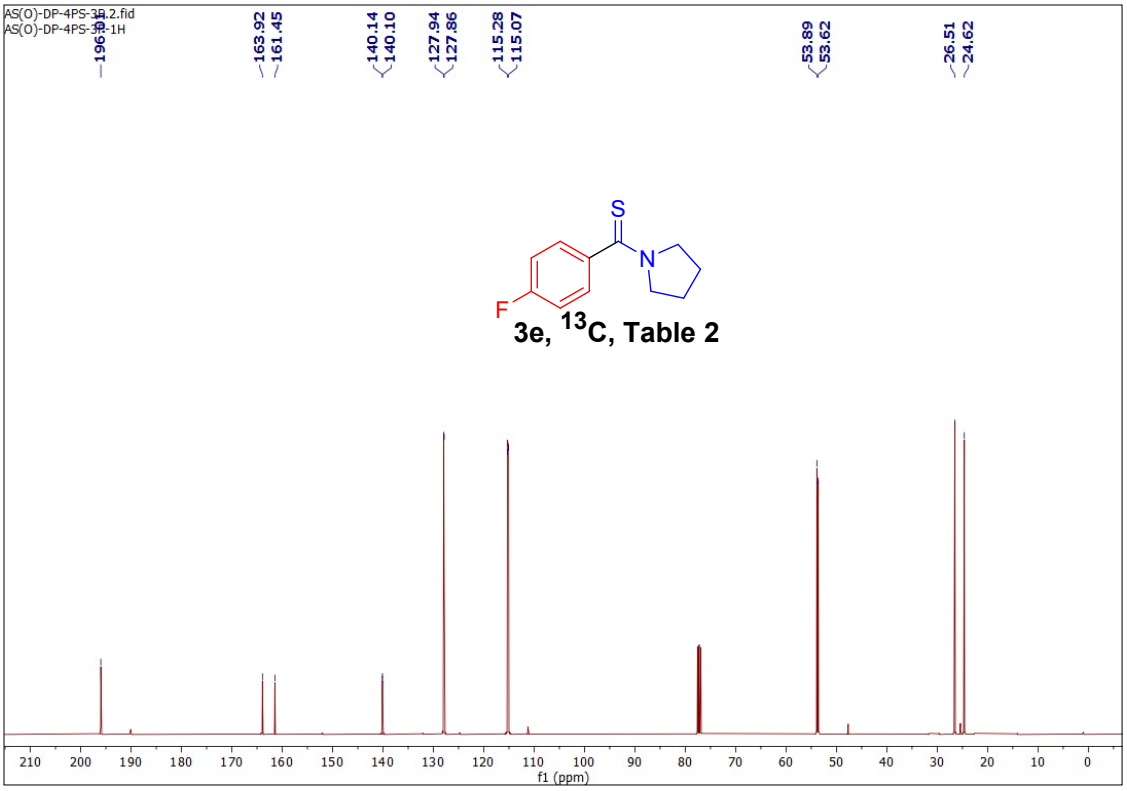


^{19} F NMR (282 MHz, $CDCl_3$) spectrum of 3d

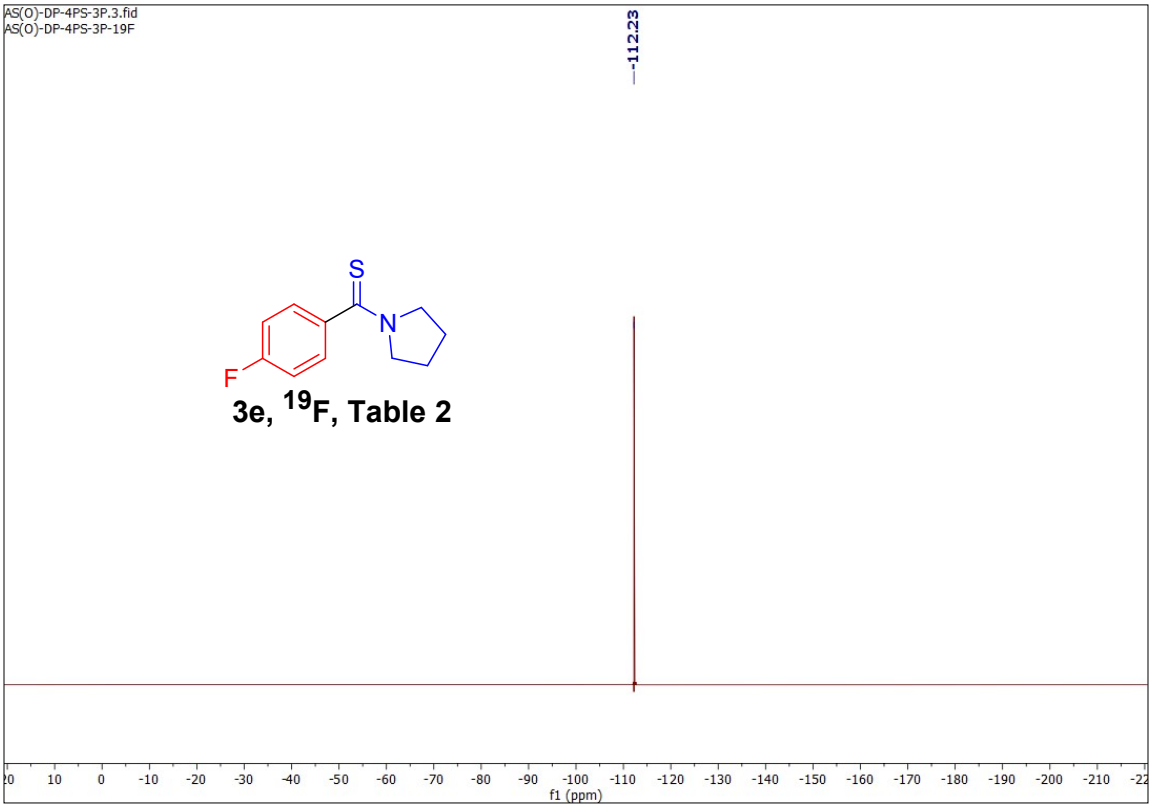


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3e

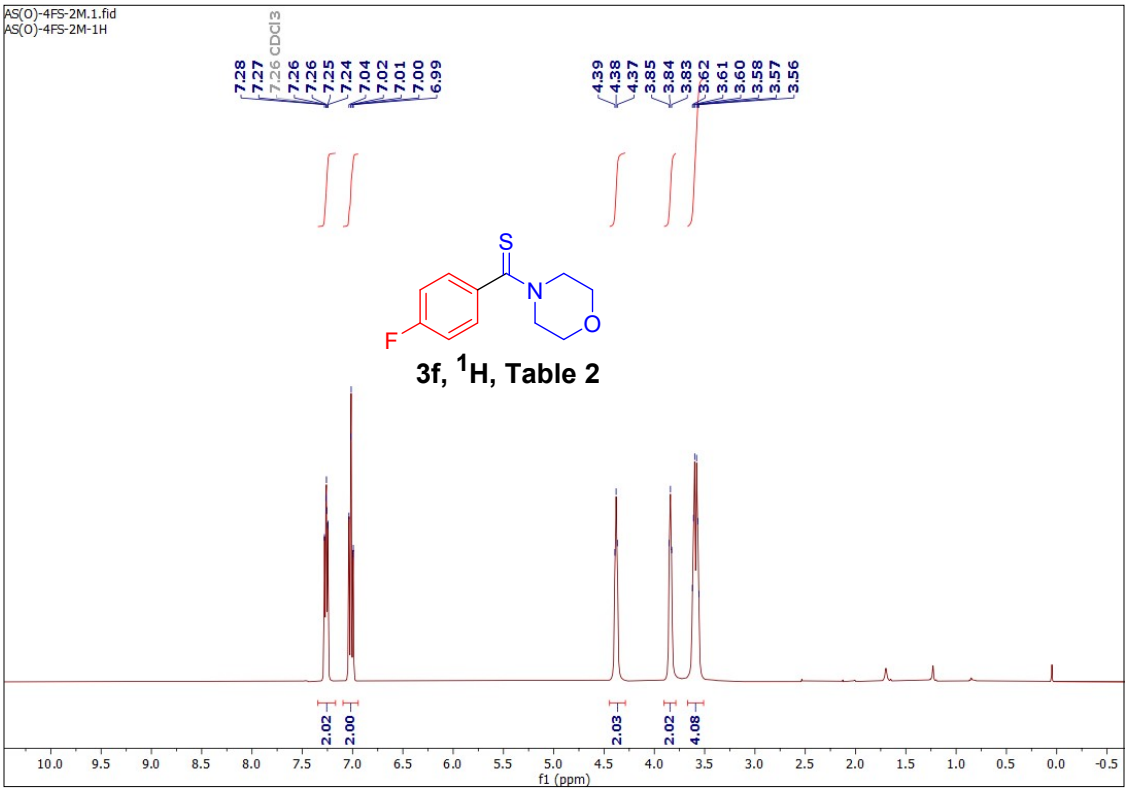


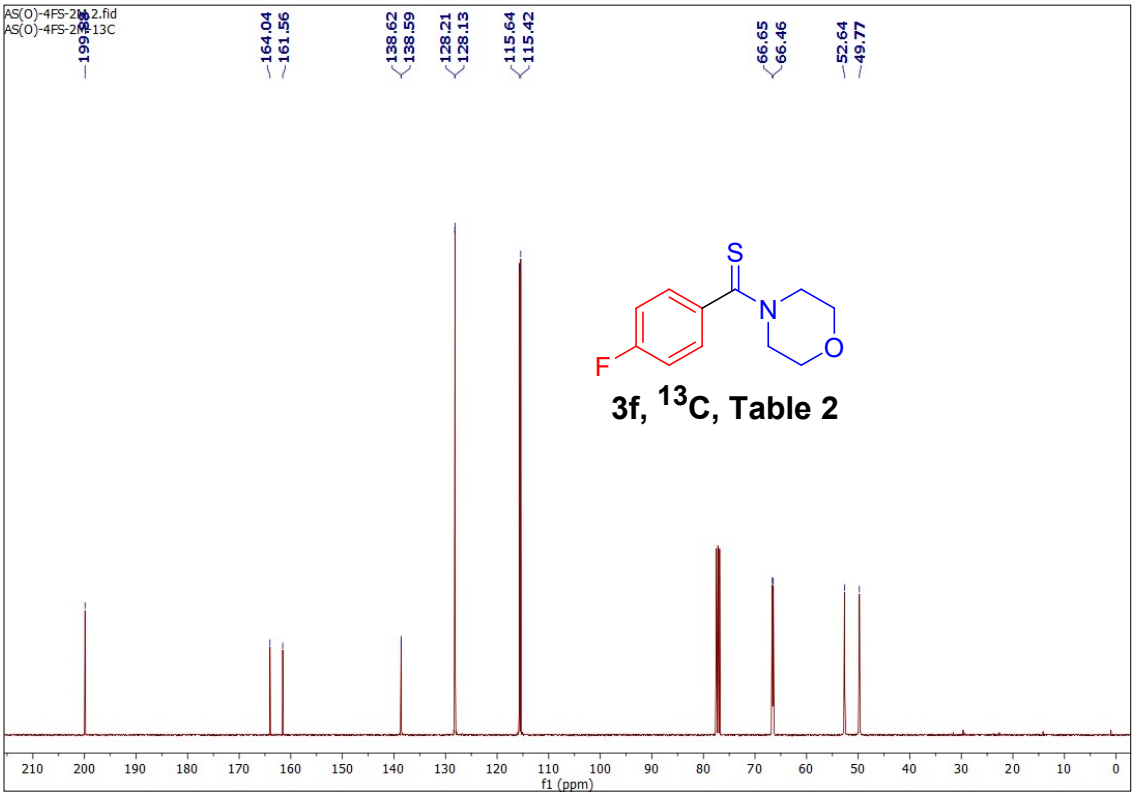


^{19} F NMR (282 MHz, $CDCl_3$) spectrum of 3e

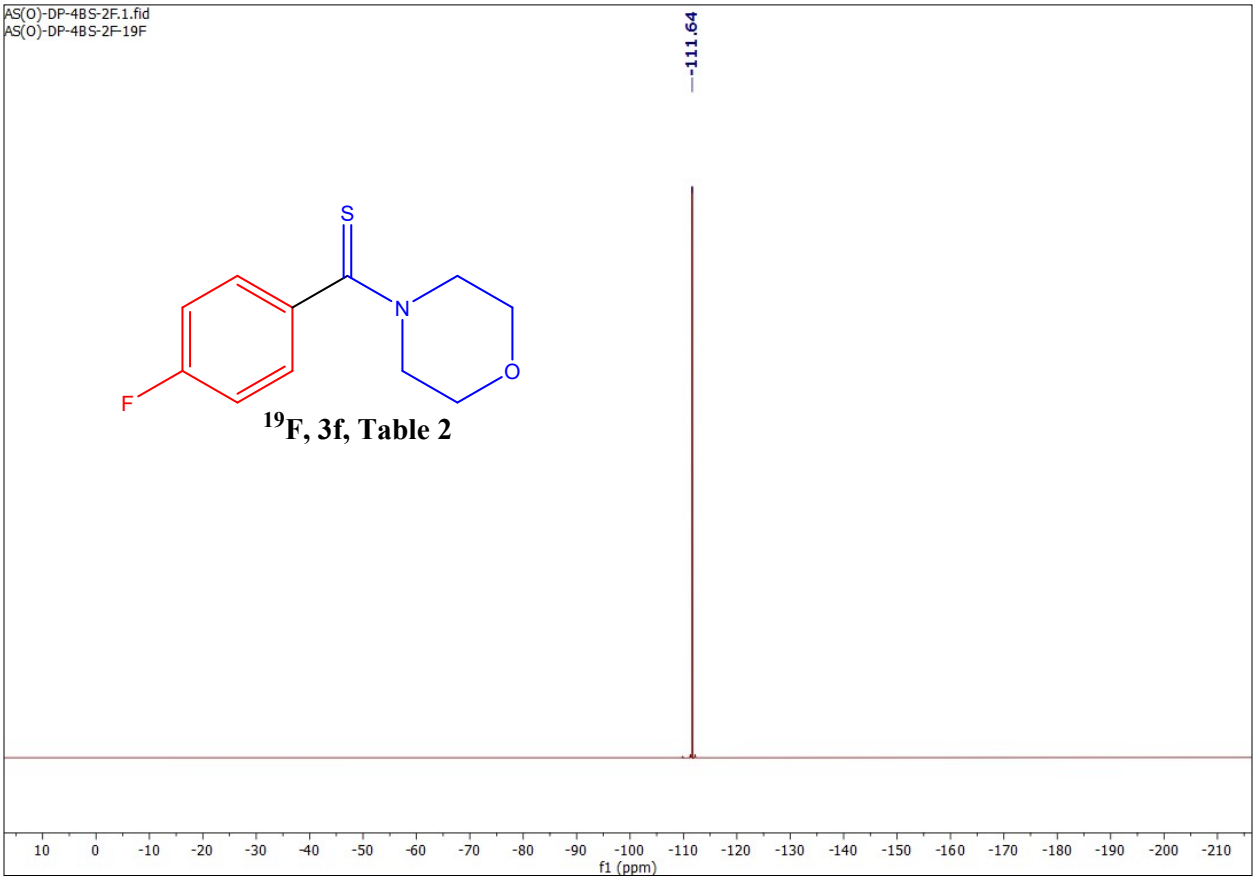


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3f



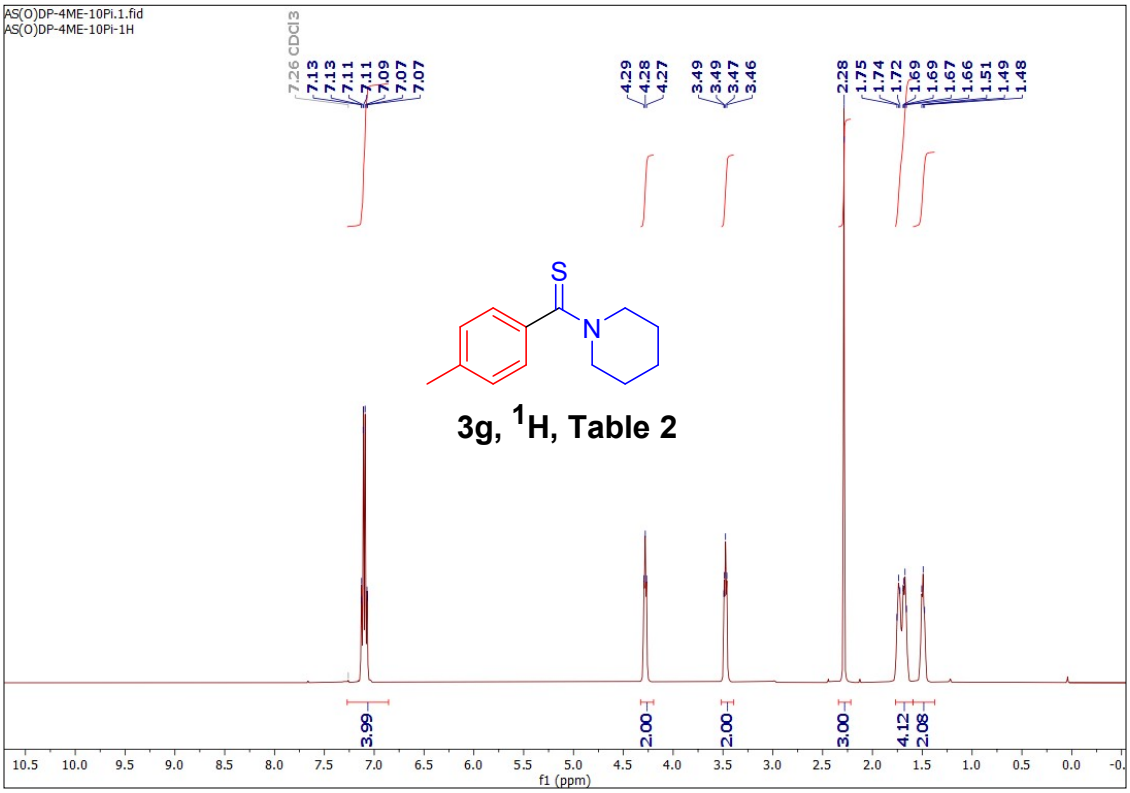


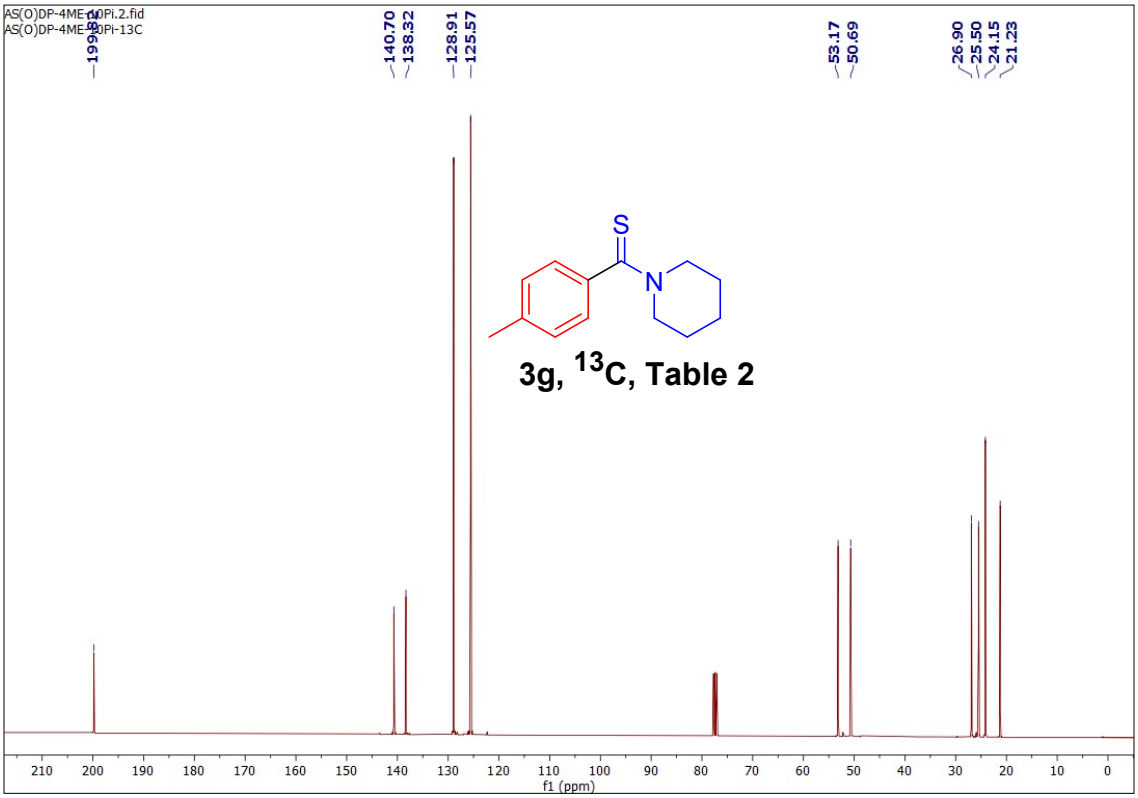
^{19} F NMR (376 MHz, $CDCl_3$) spectrum of 3f



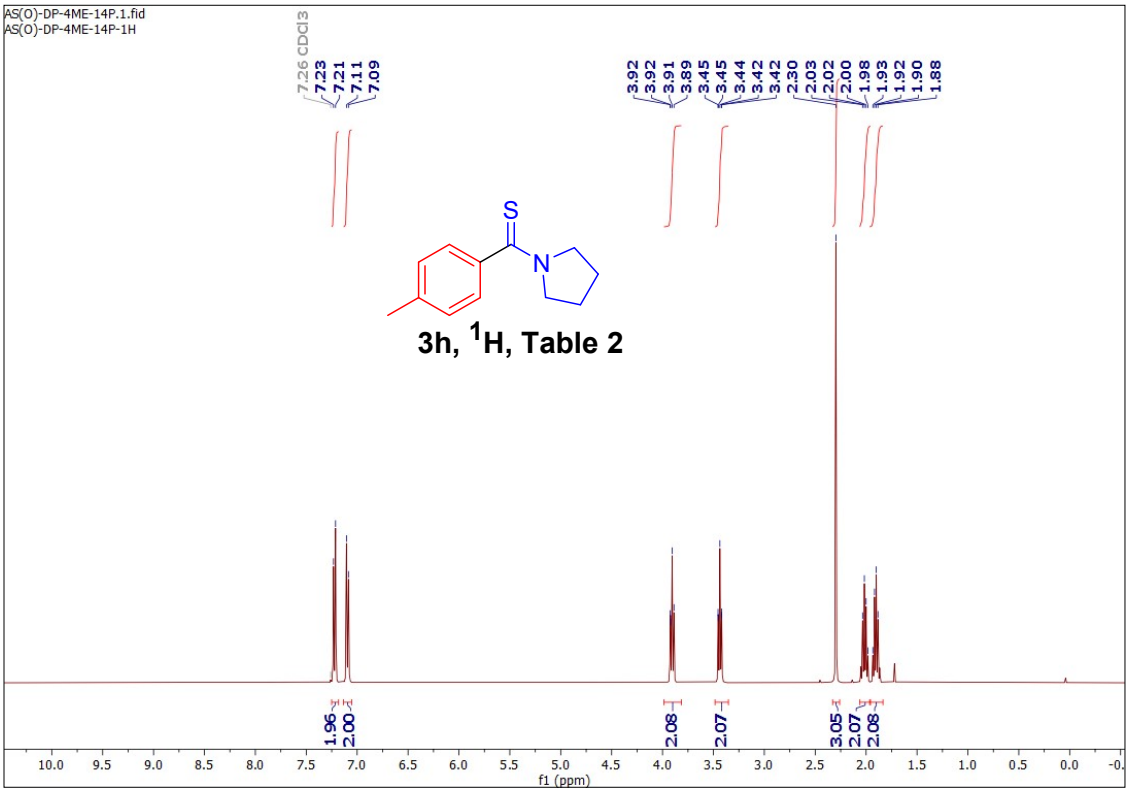
^{19}F, 3f, Table 2

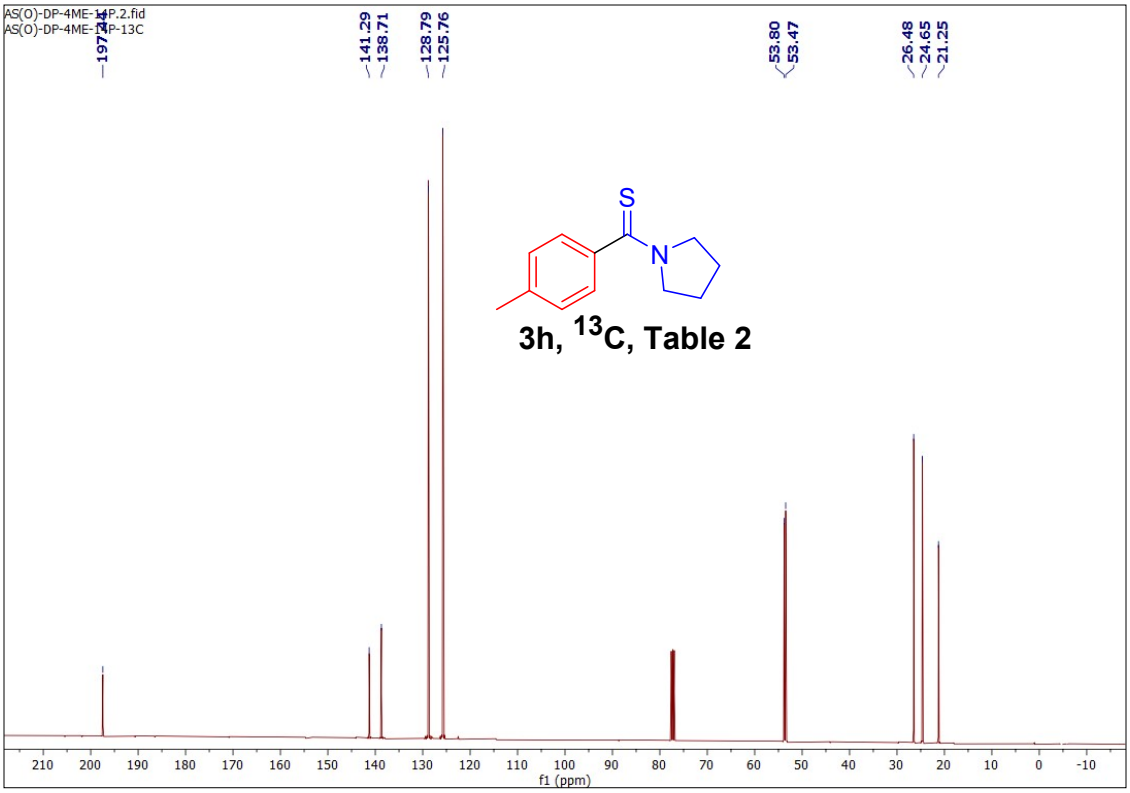
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3g



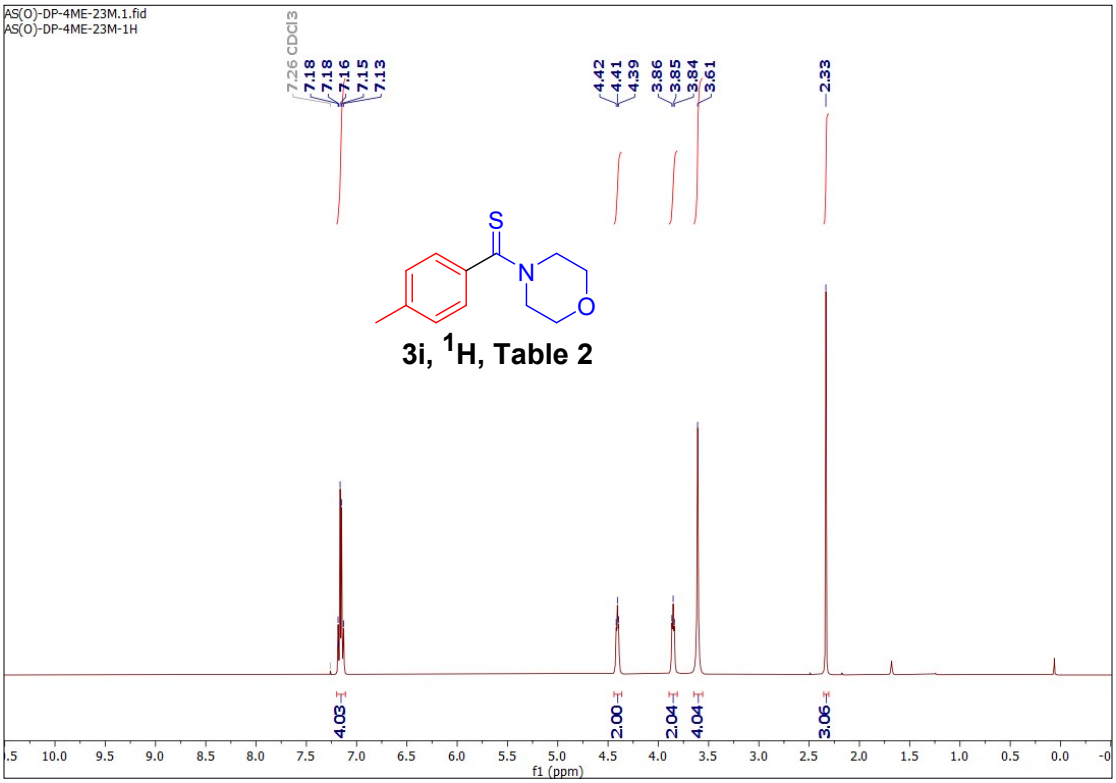


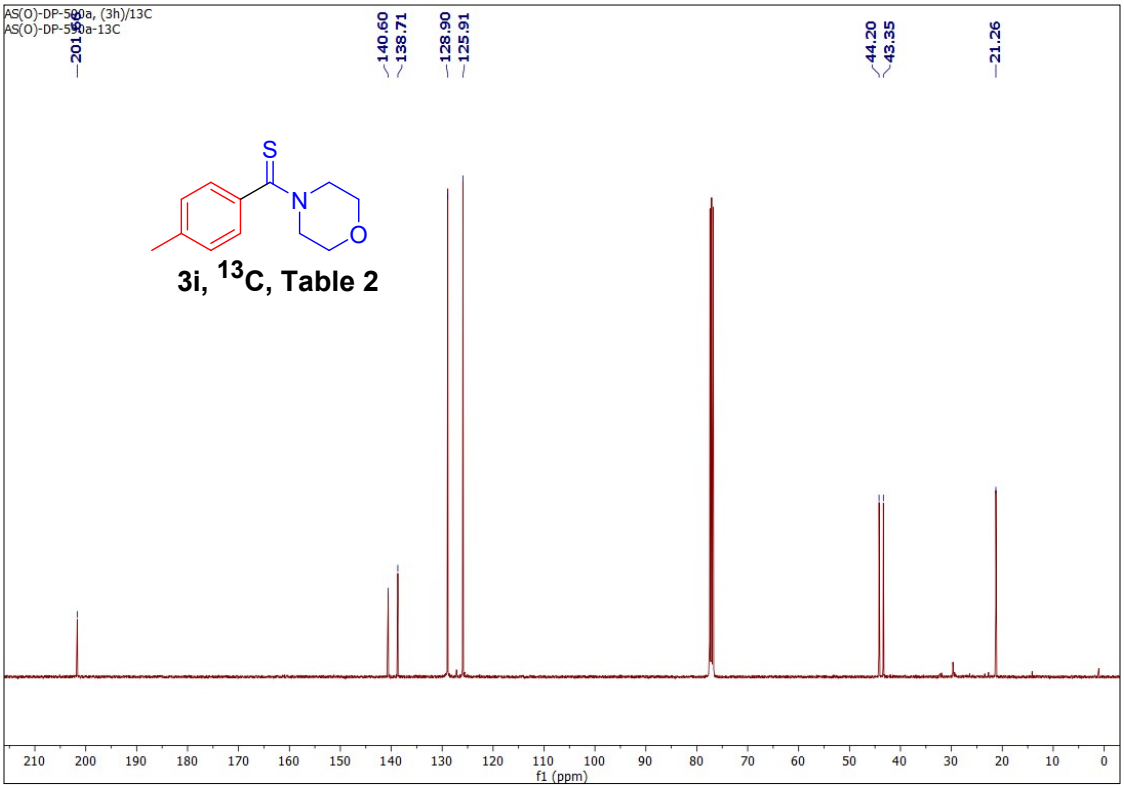
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3h



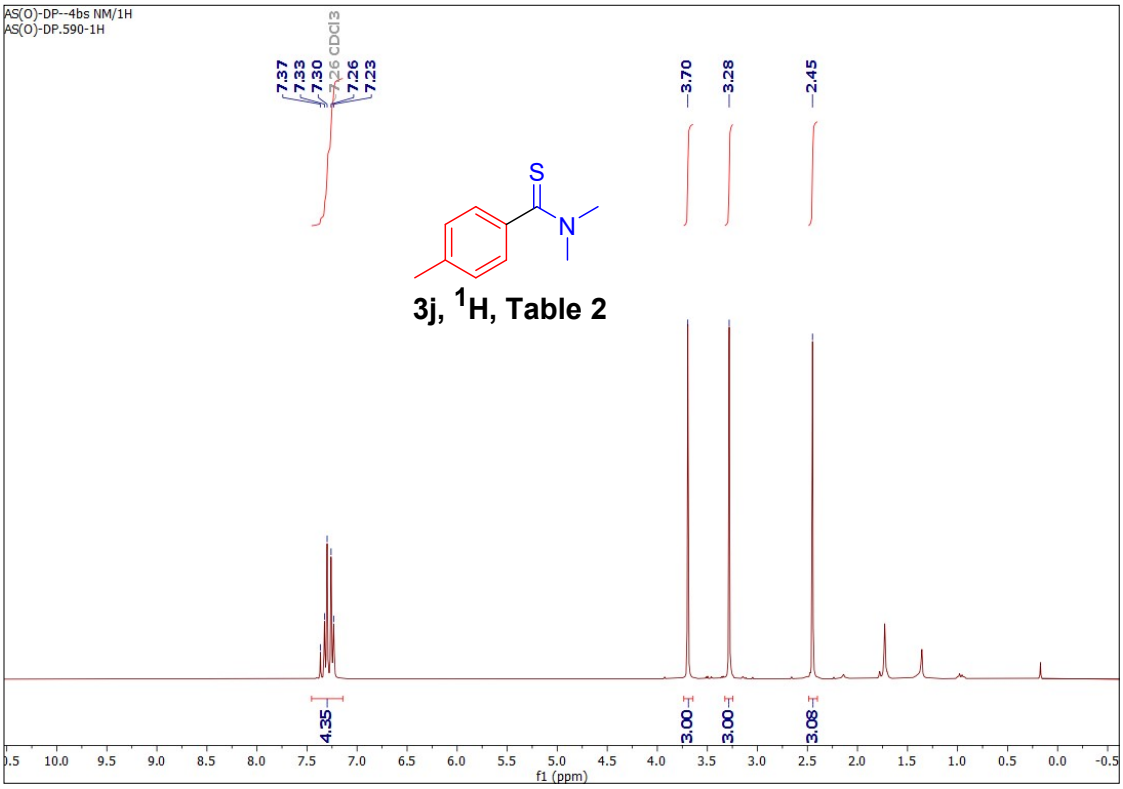


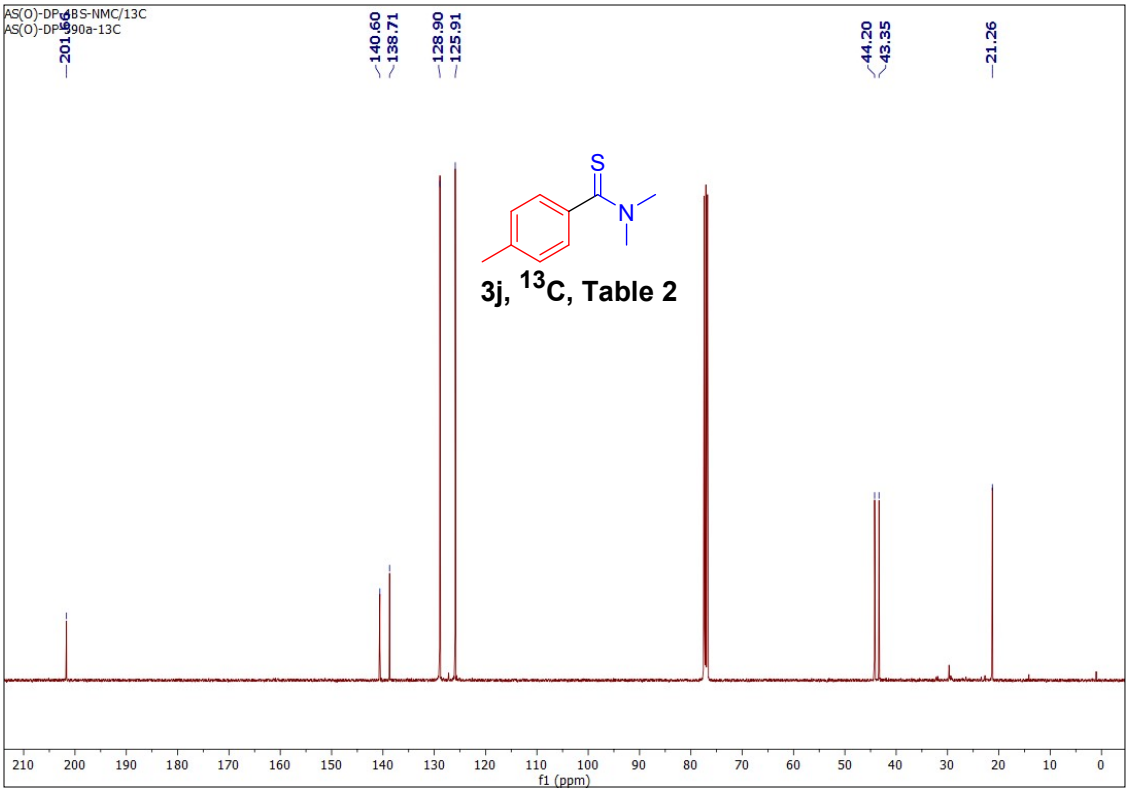
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3i



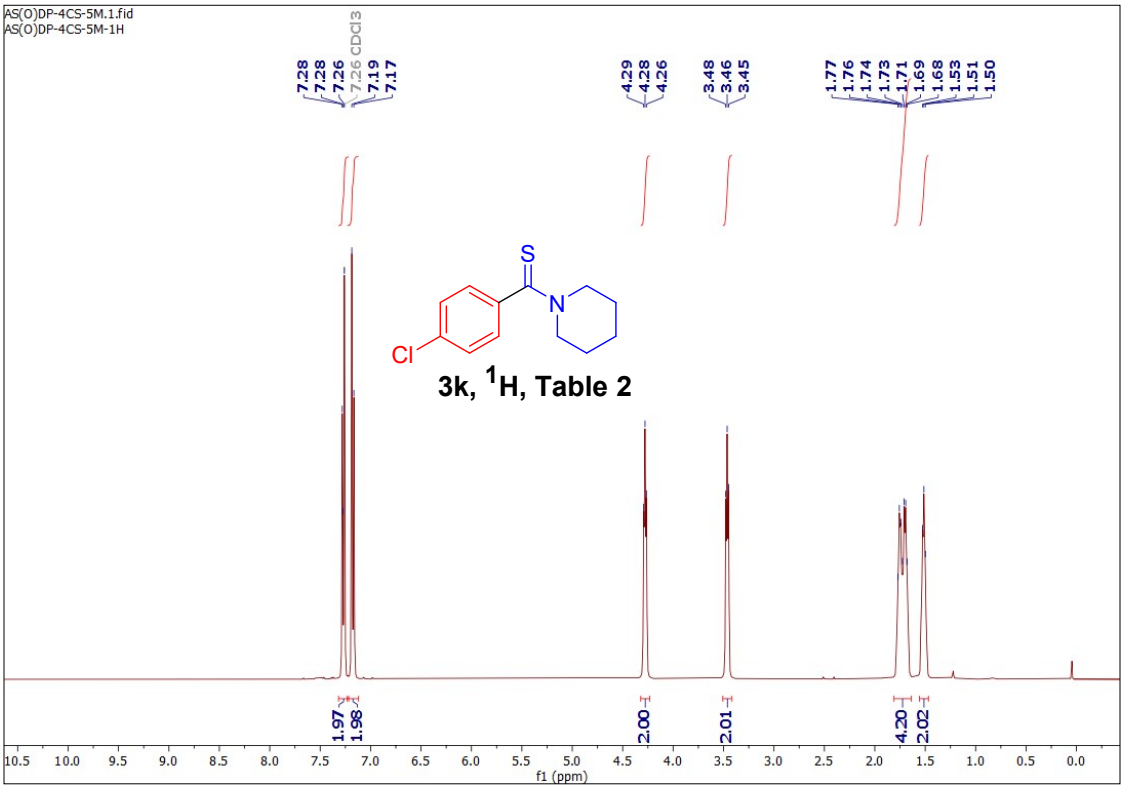


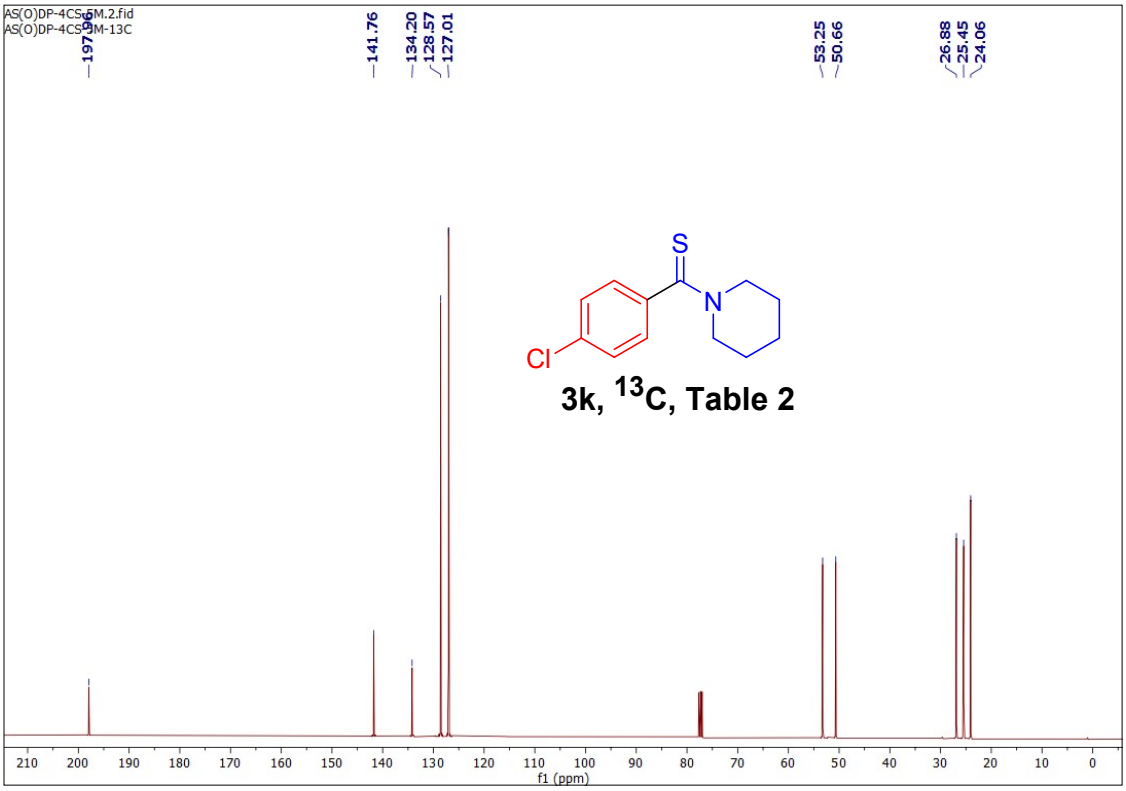
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3j



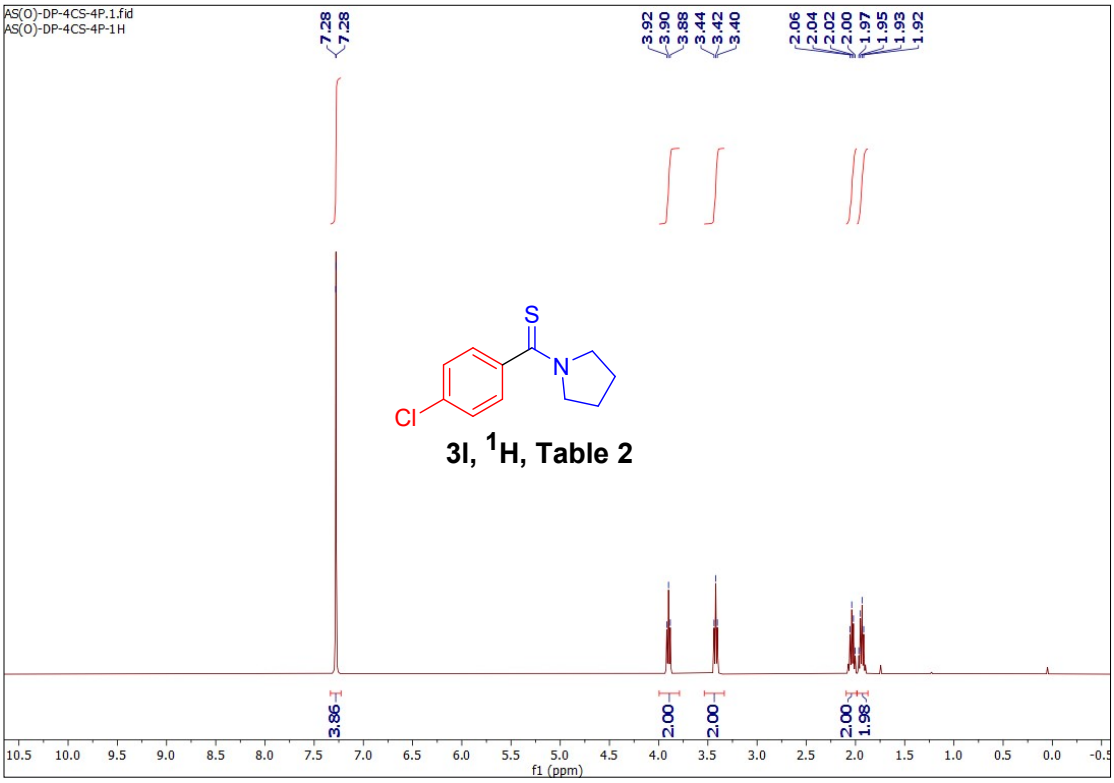


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3k

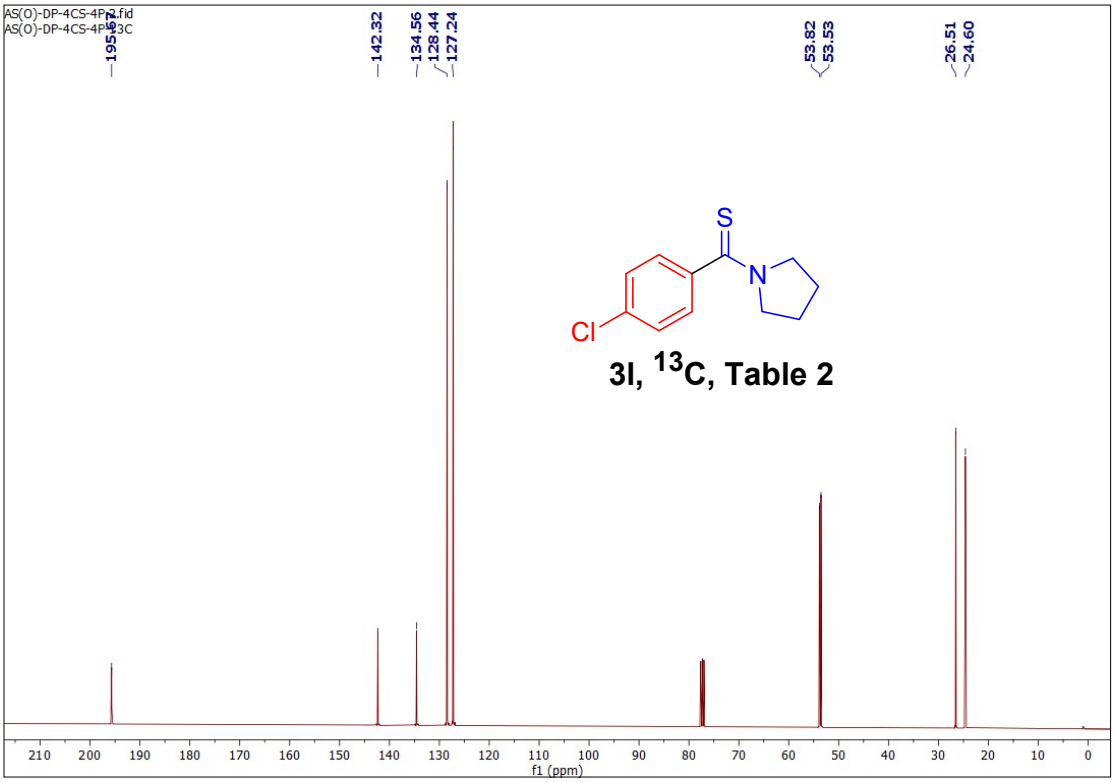




^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3l

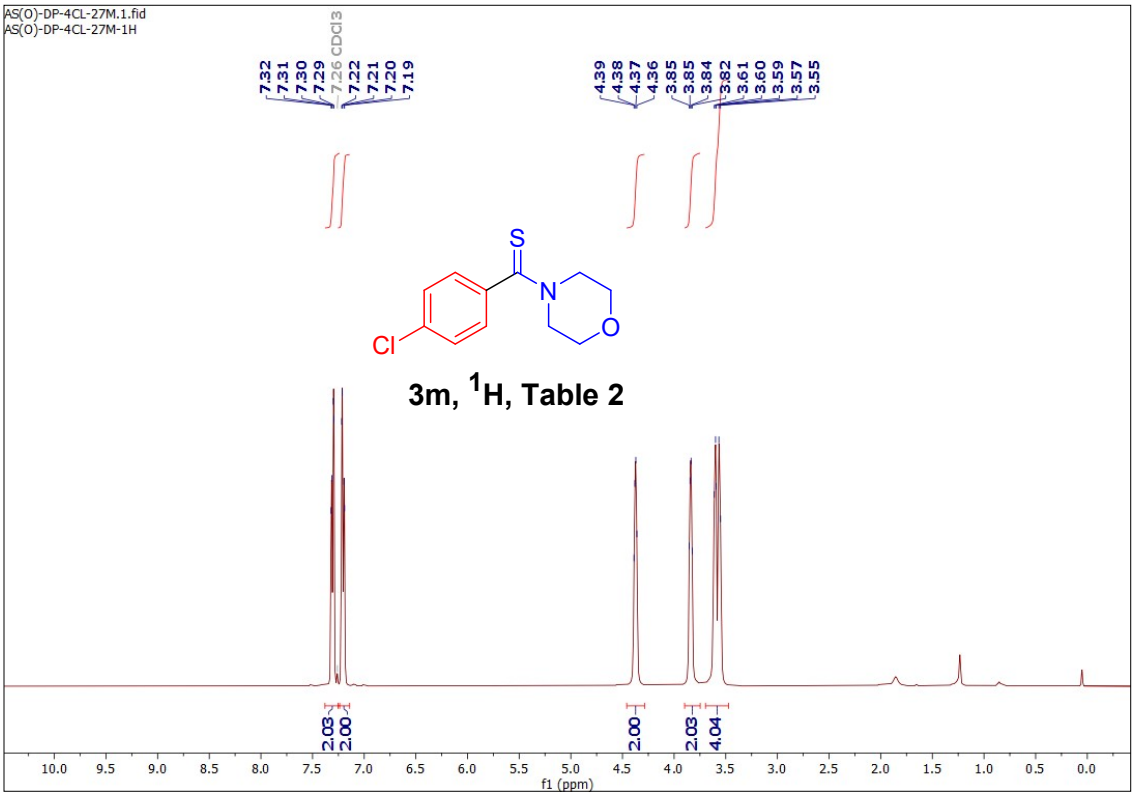


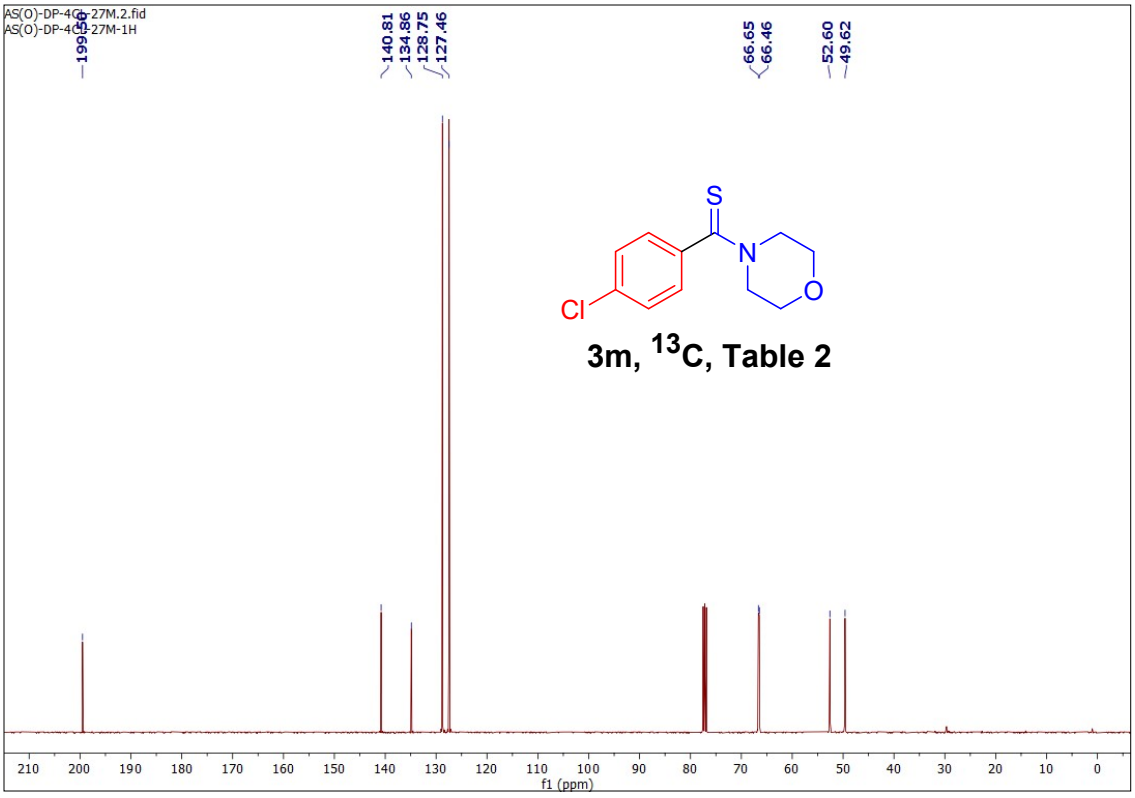
3l, ^{1}H, Table 2



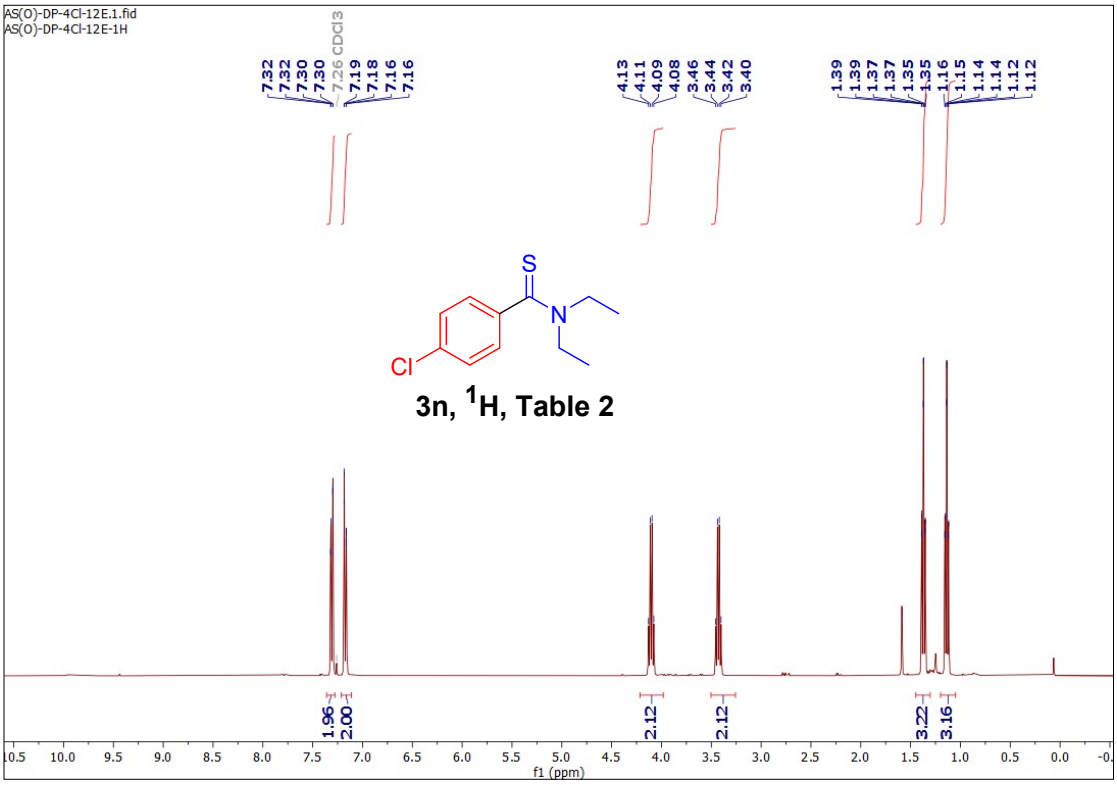
3l, ^{13}C, Table 2

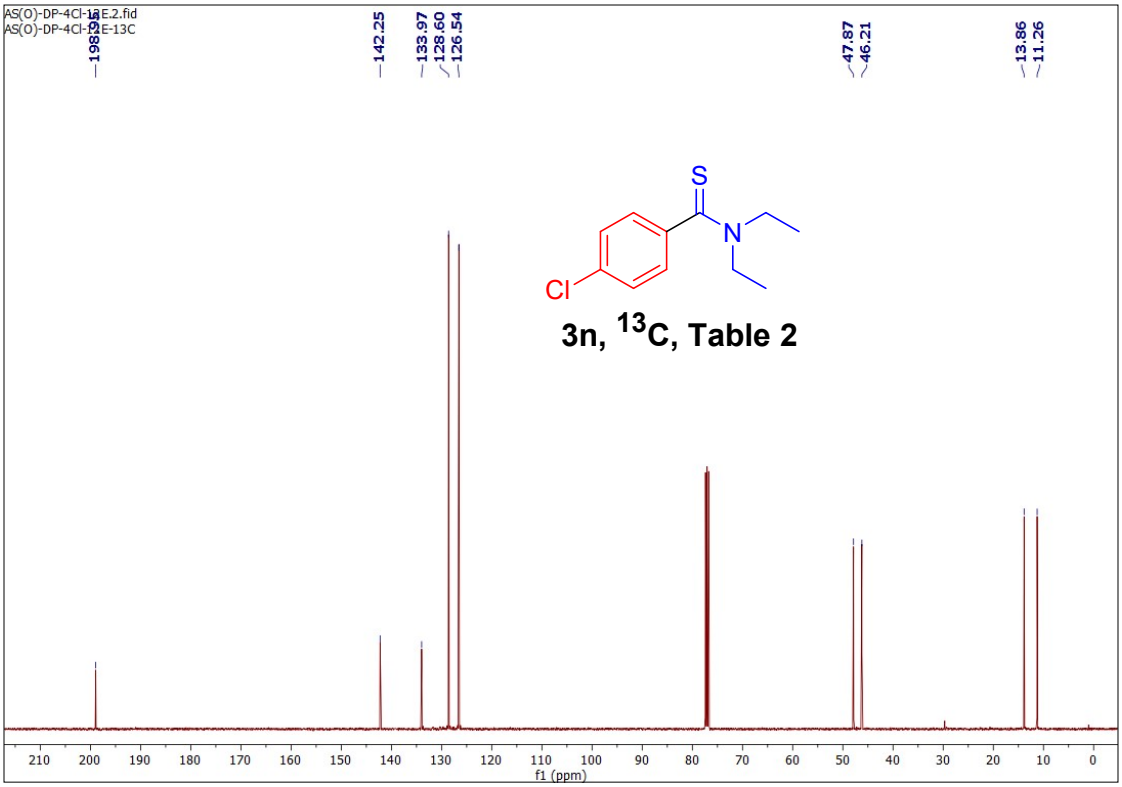
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3m



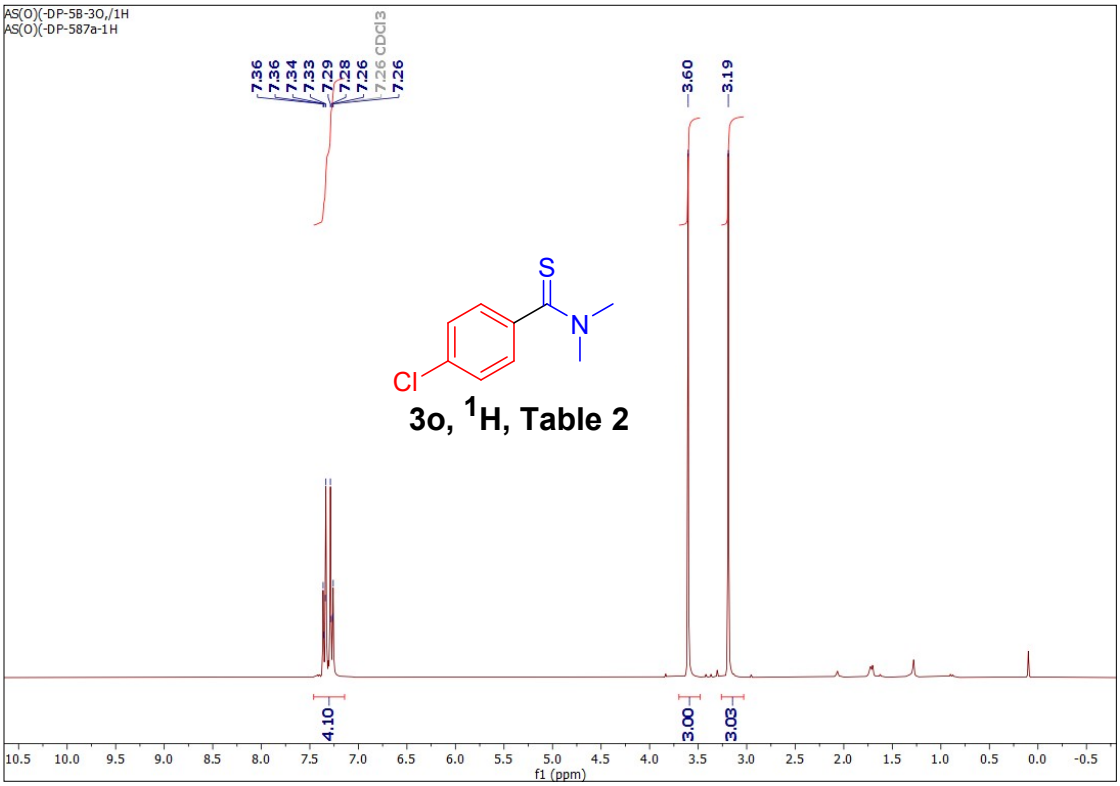


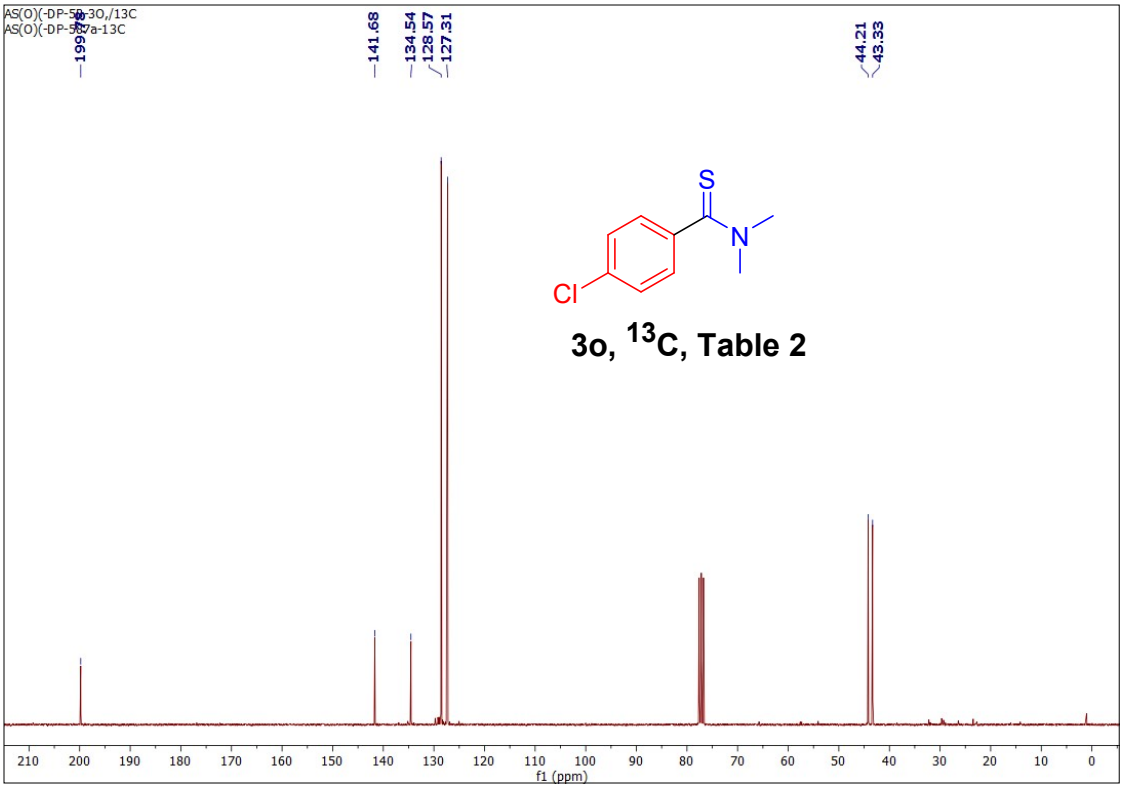
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3n



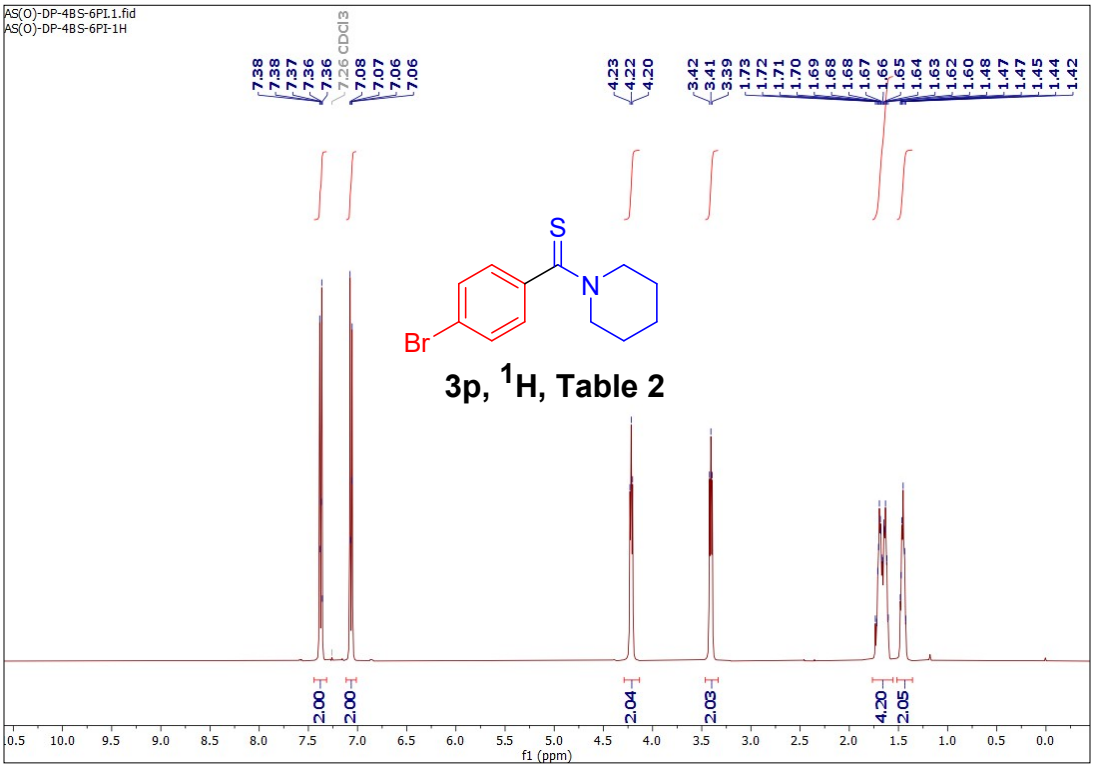


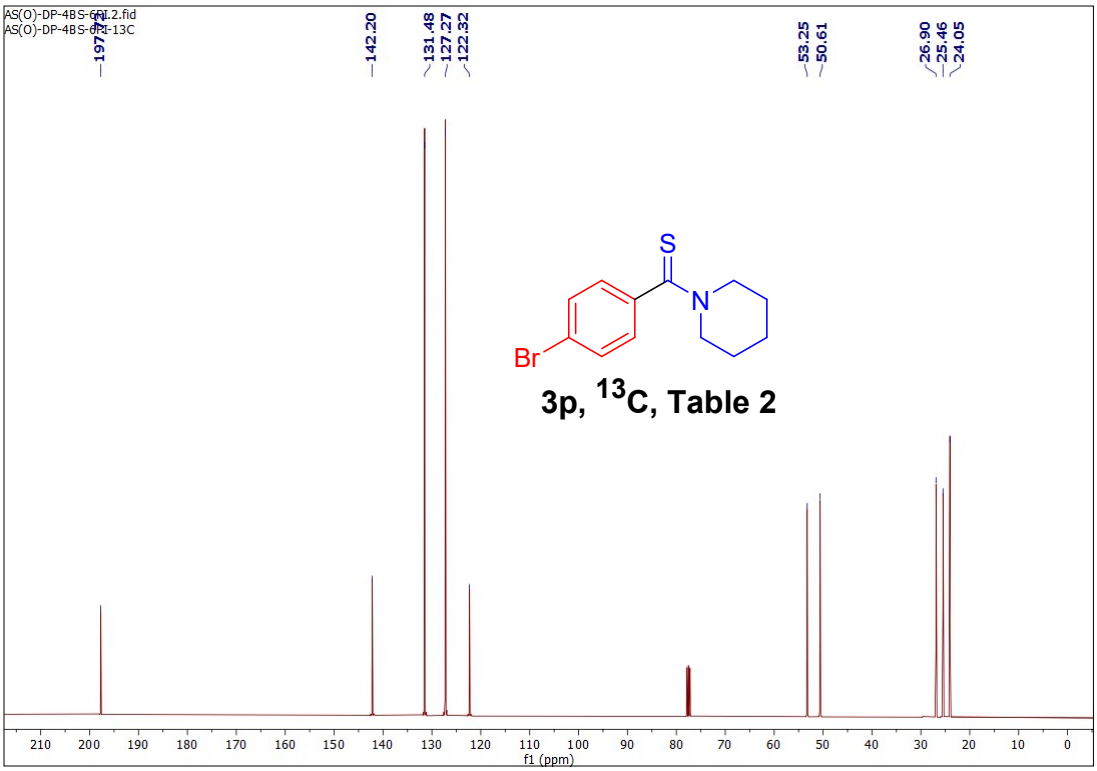
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3o



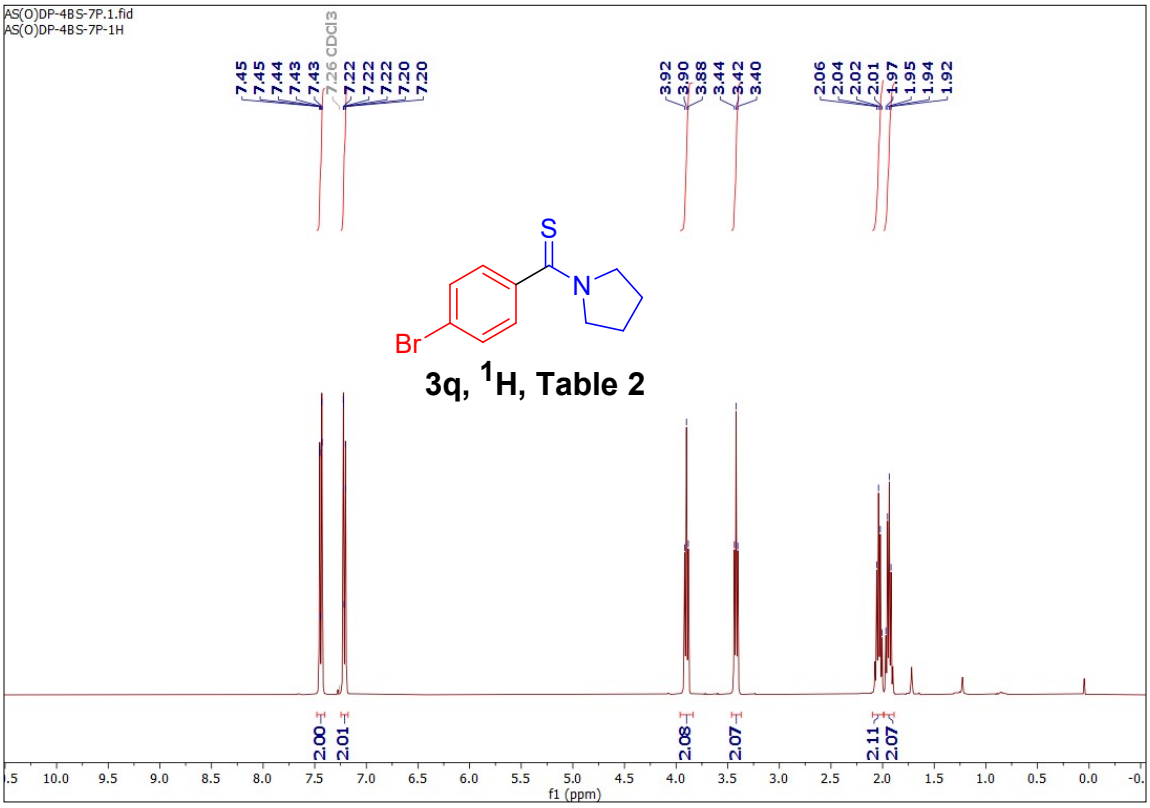


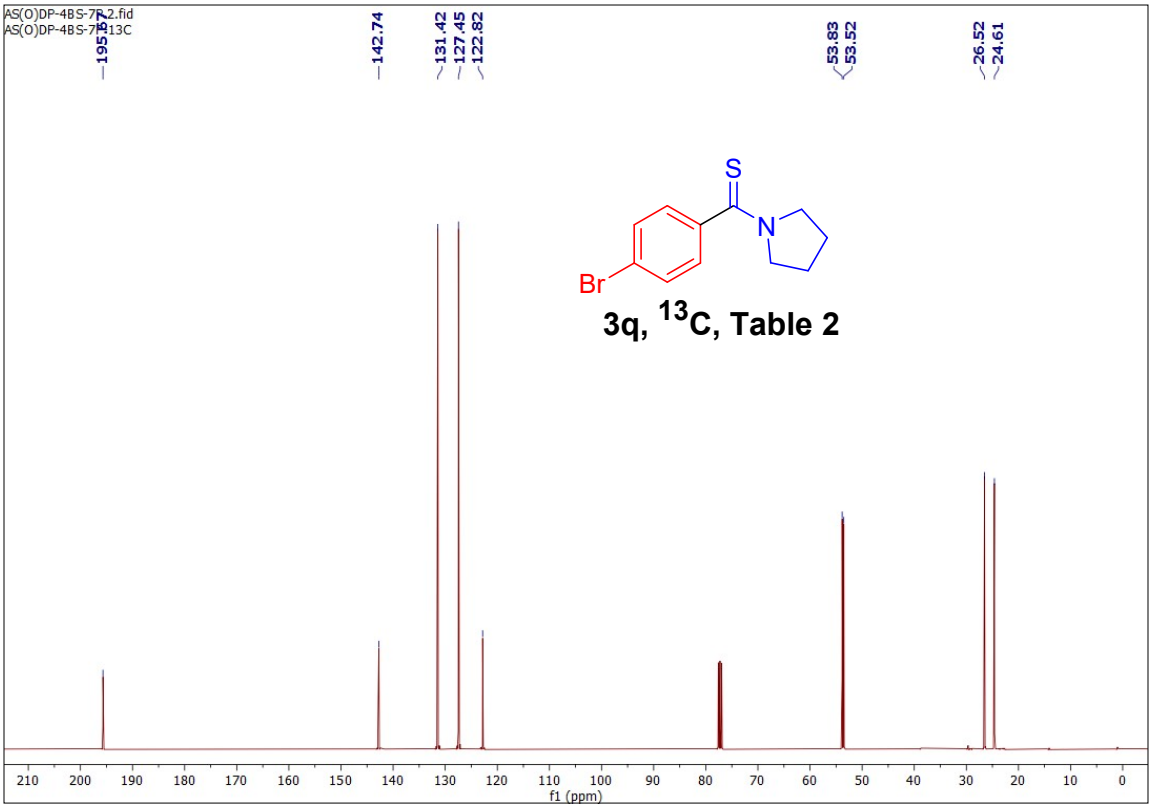
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3p



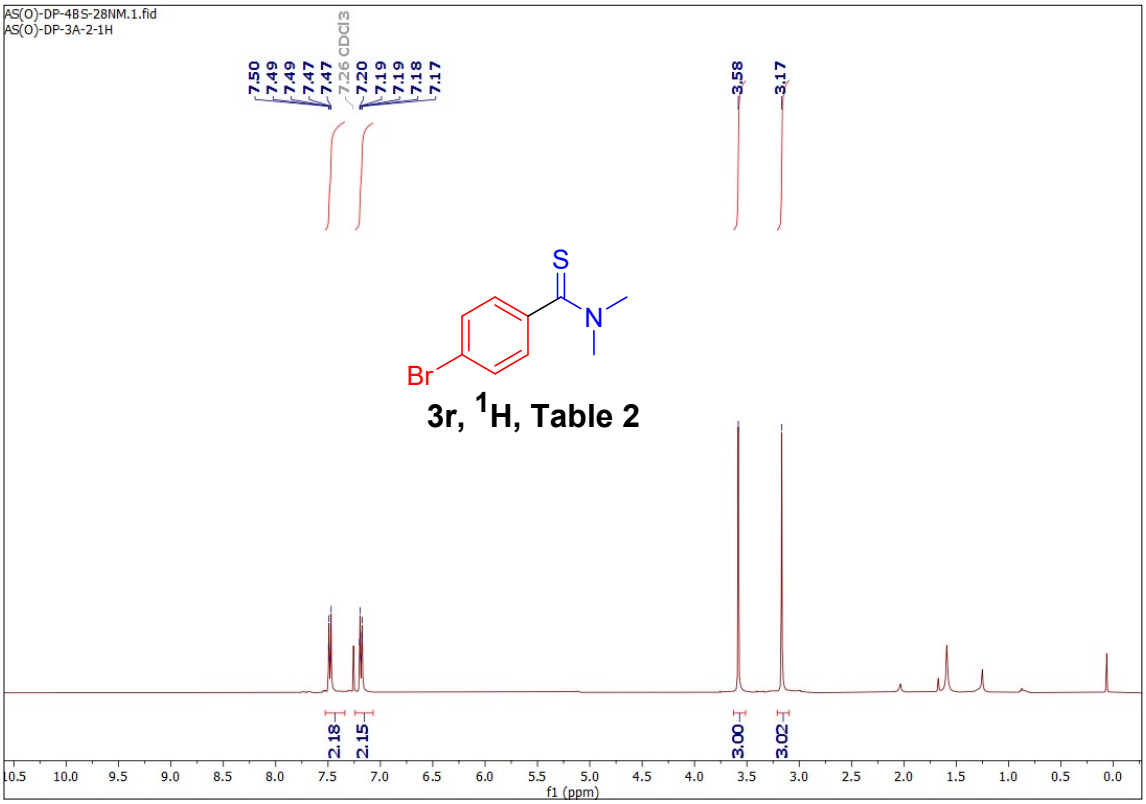


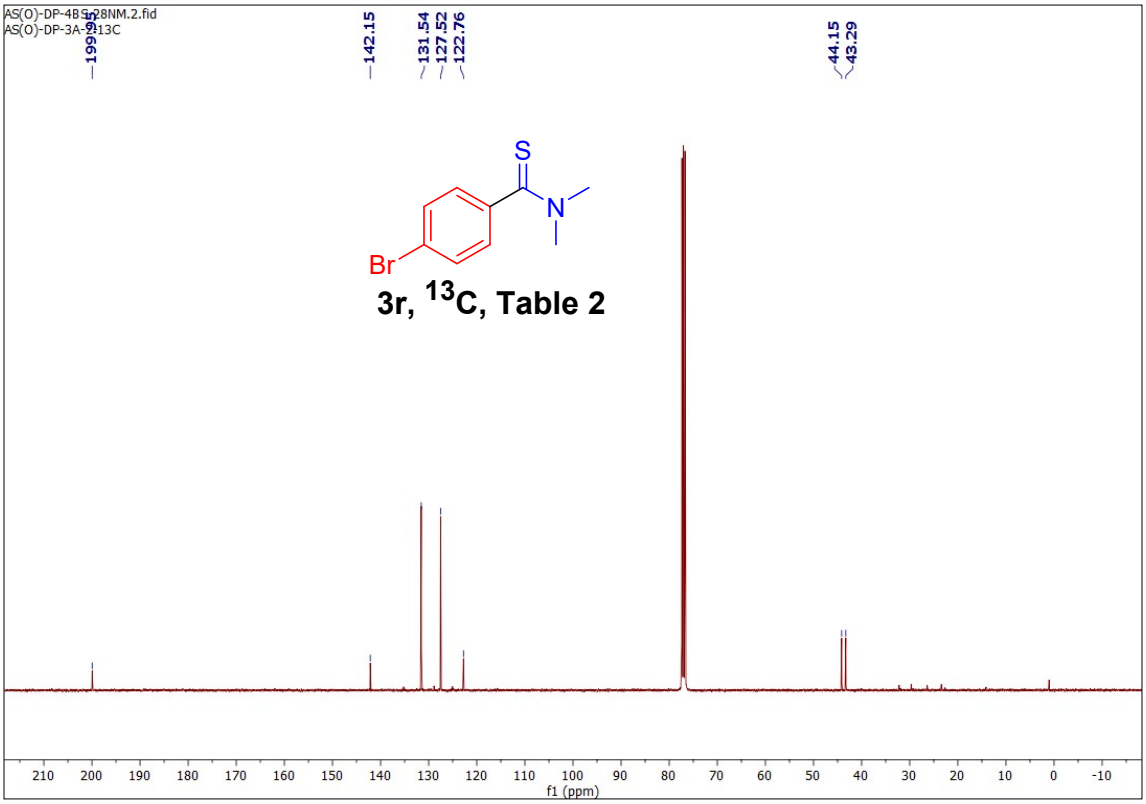
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3q



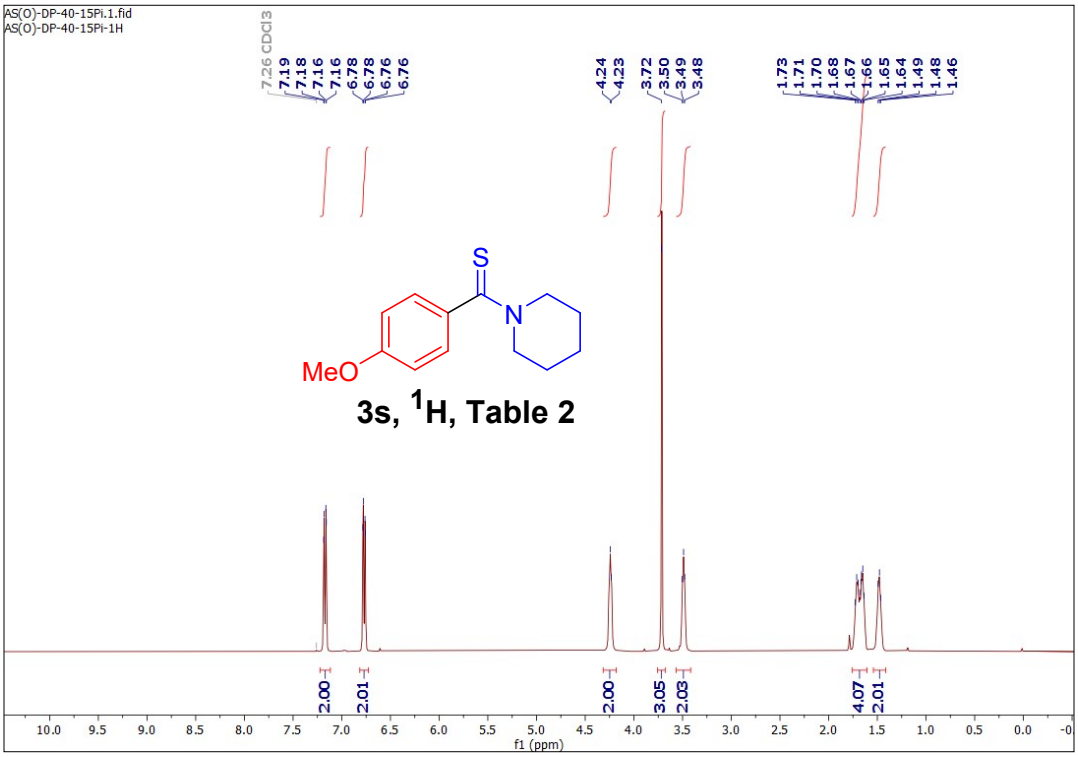


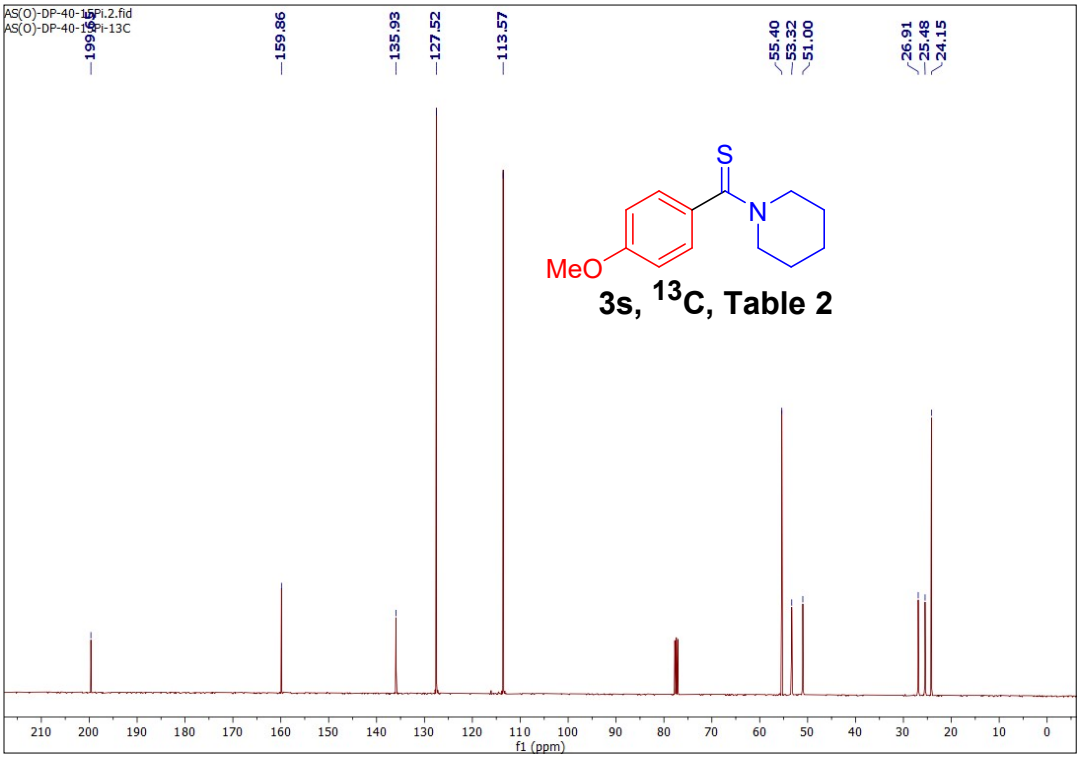
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3r



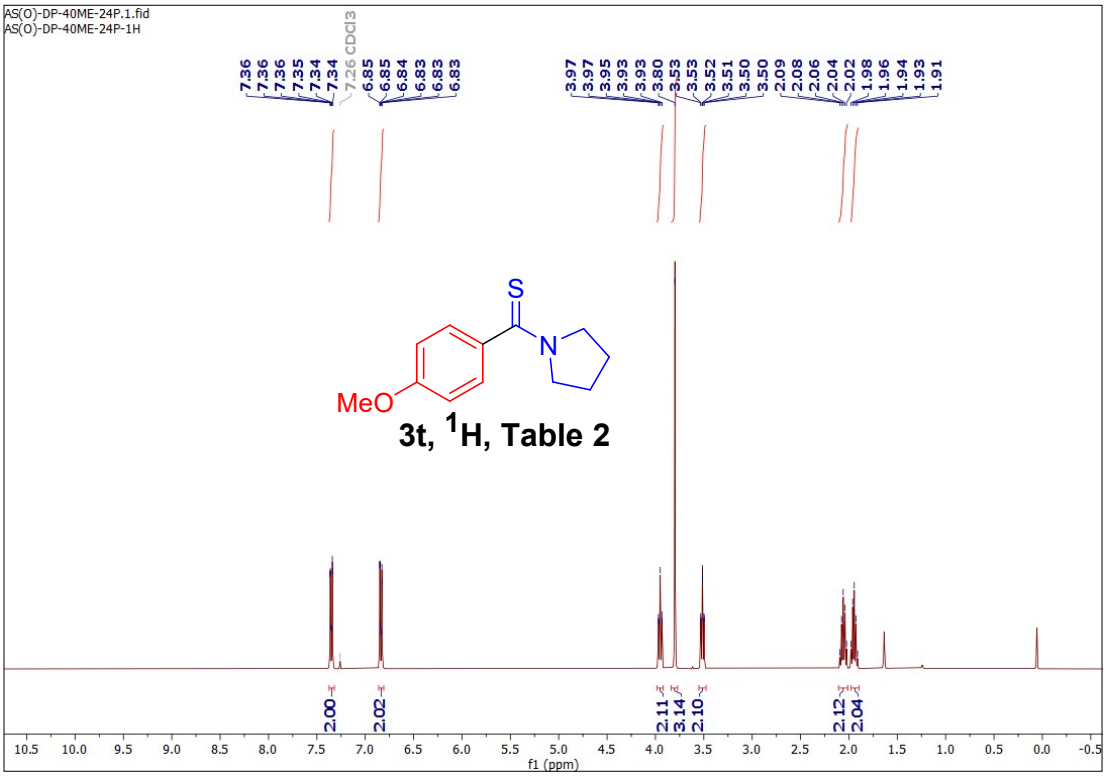


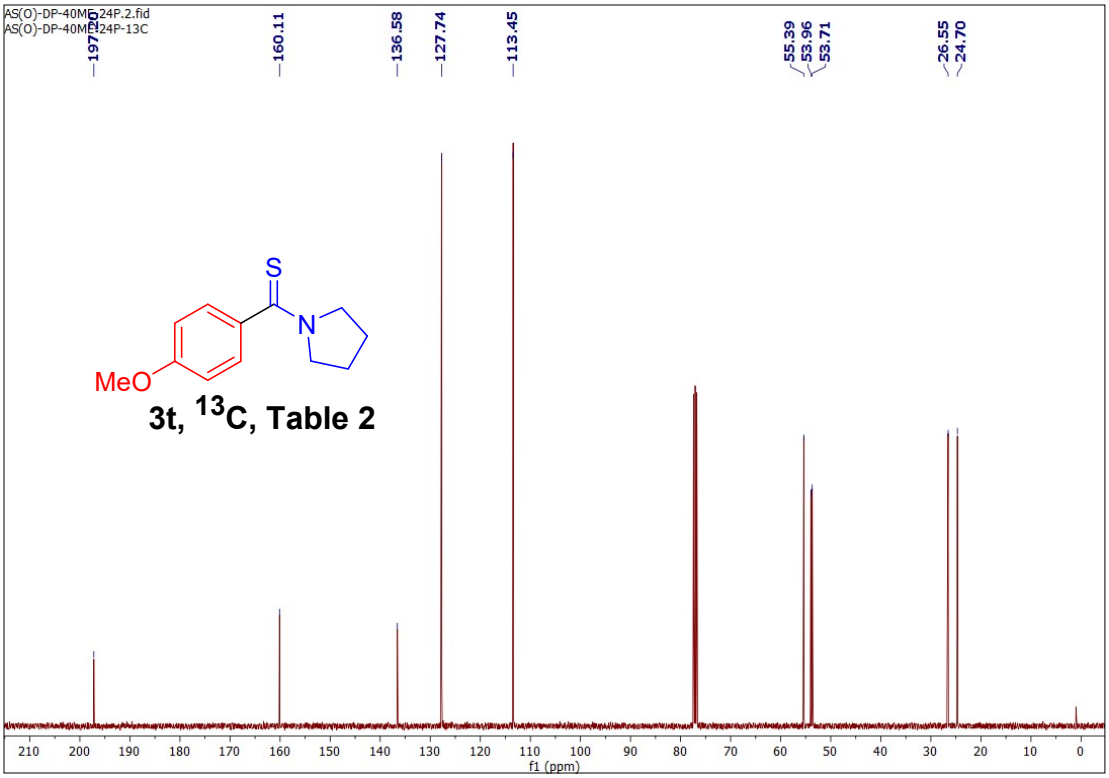
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3s



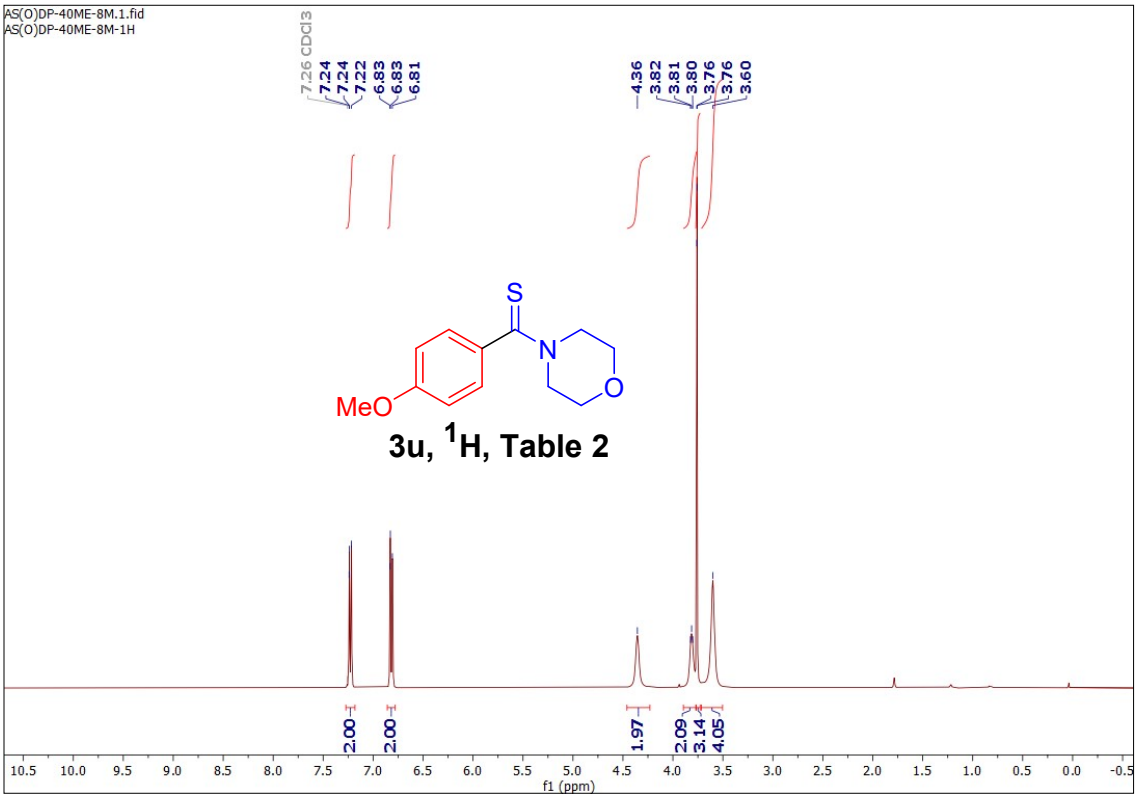


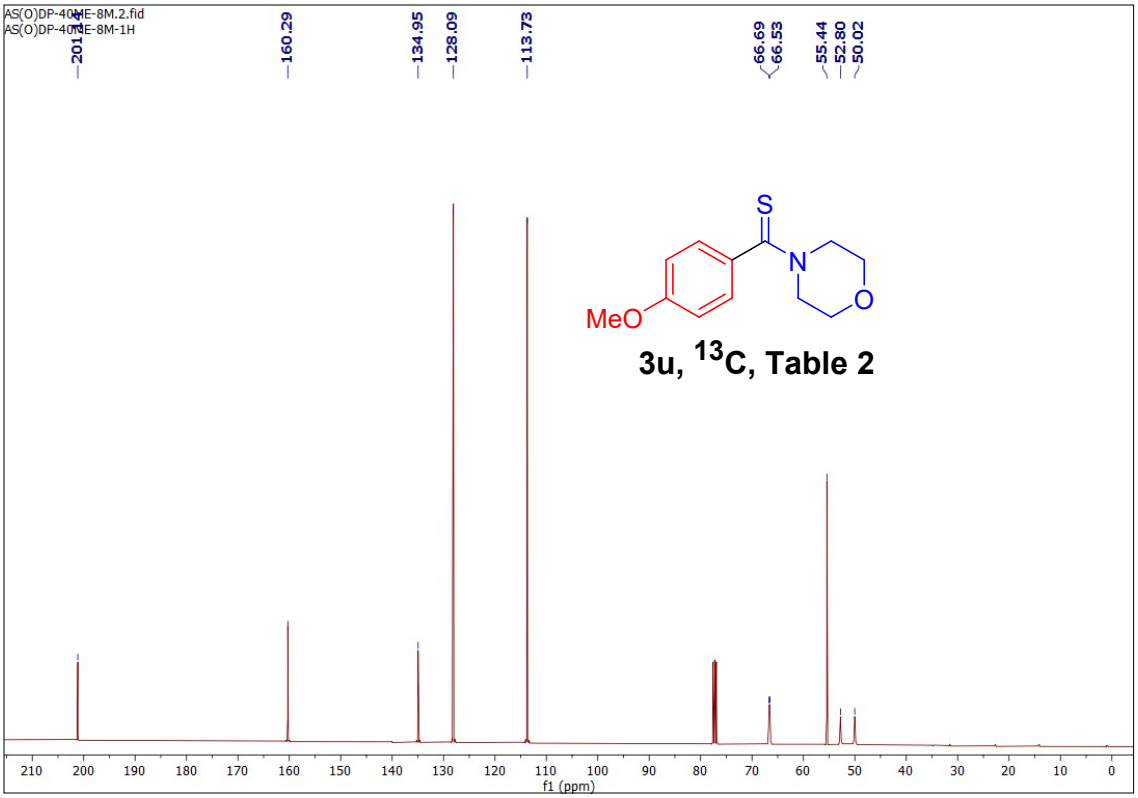
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3t



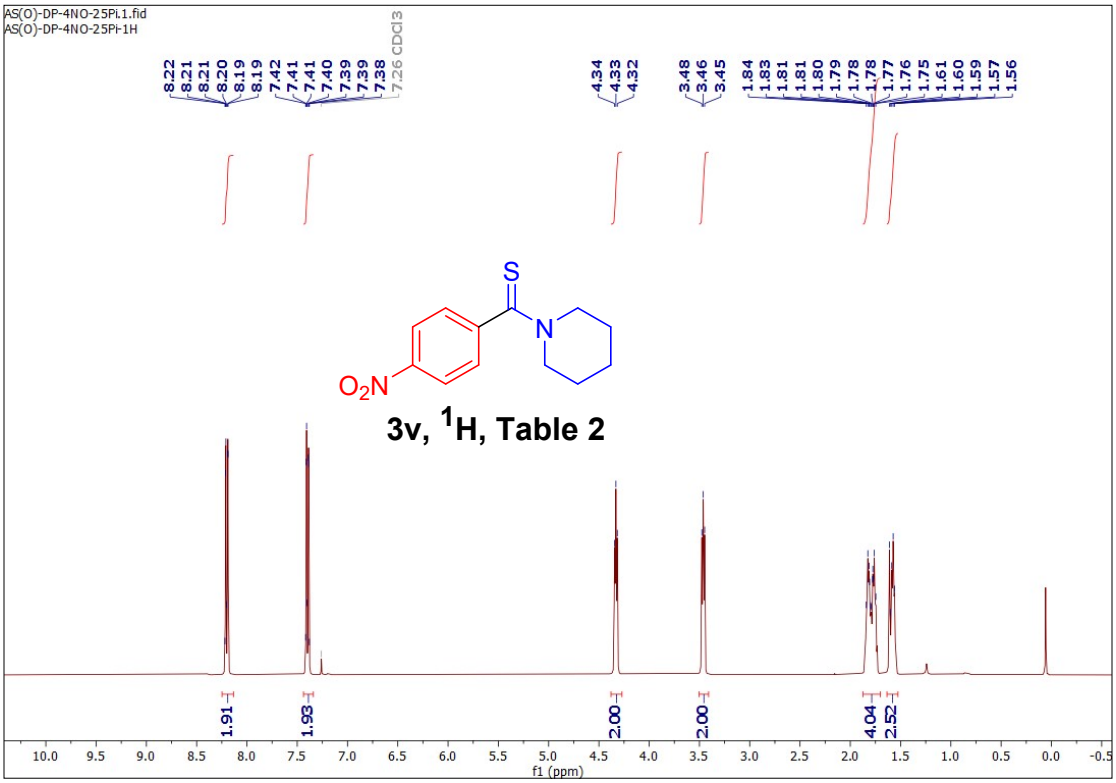


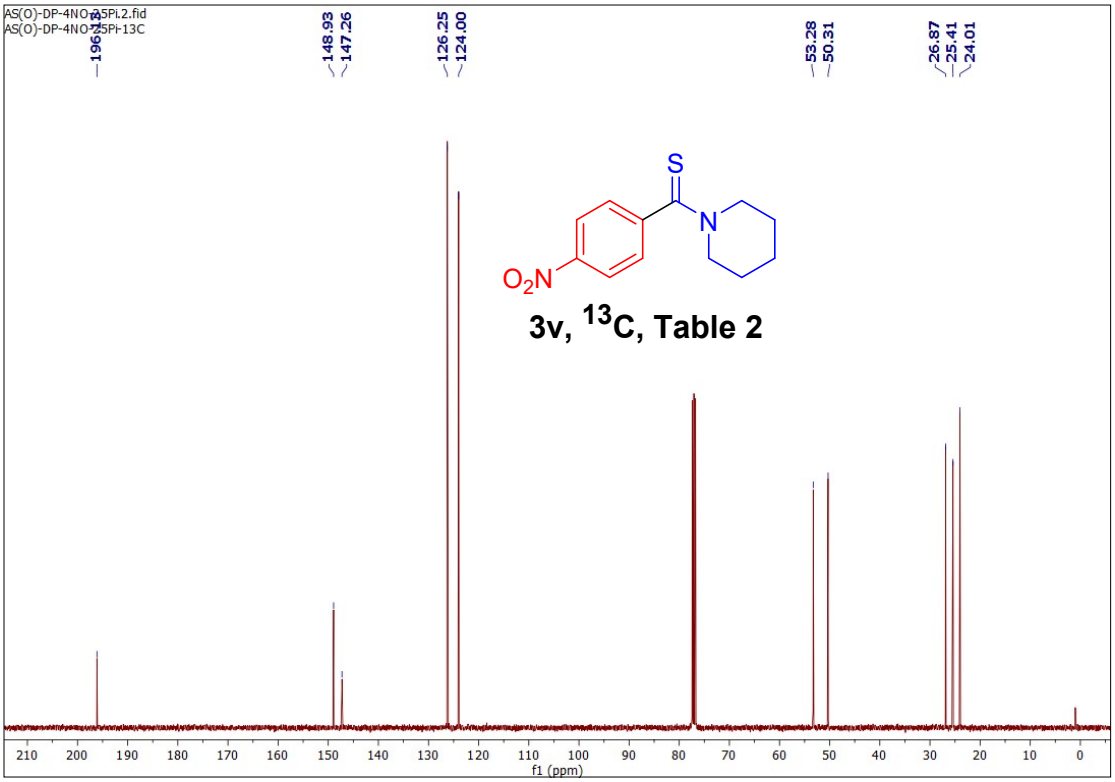
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3u



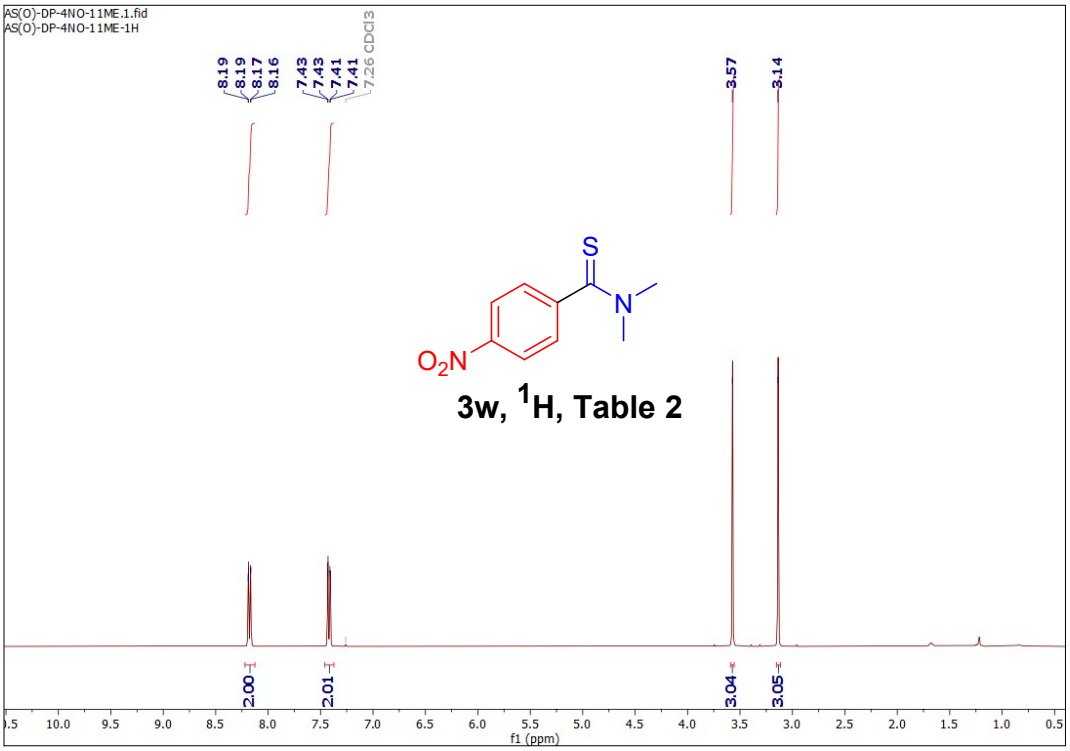


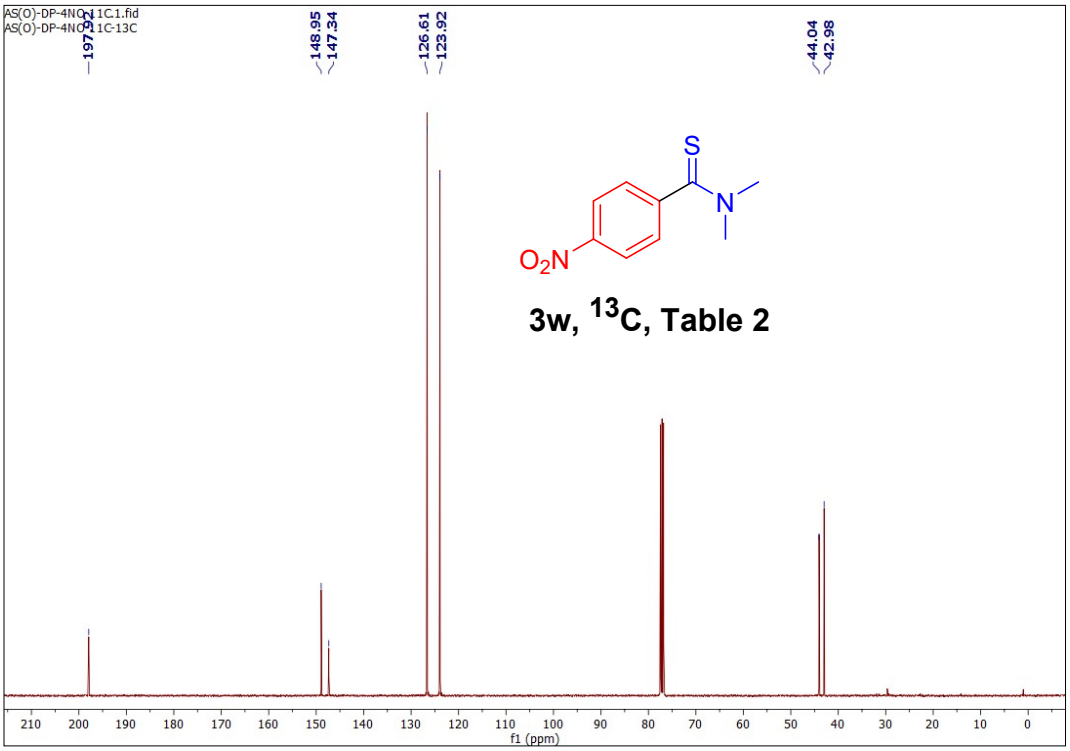
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3v



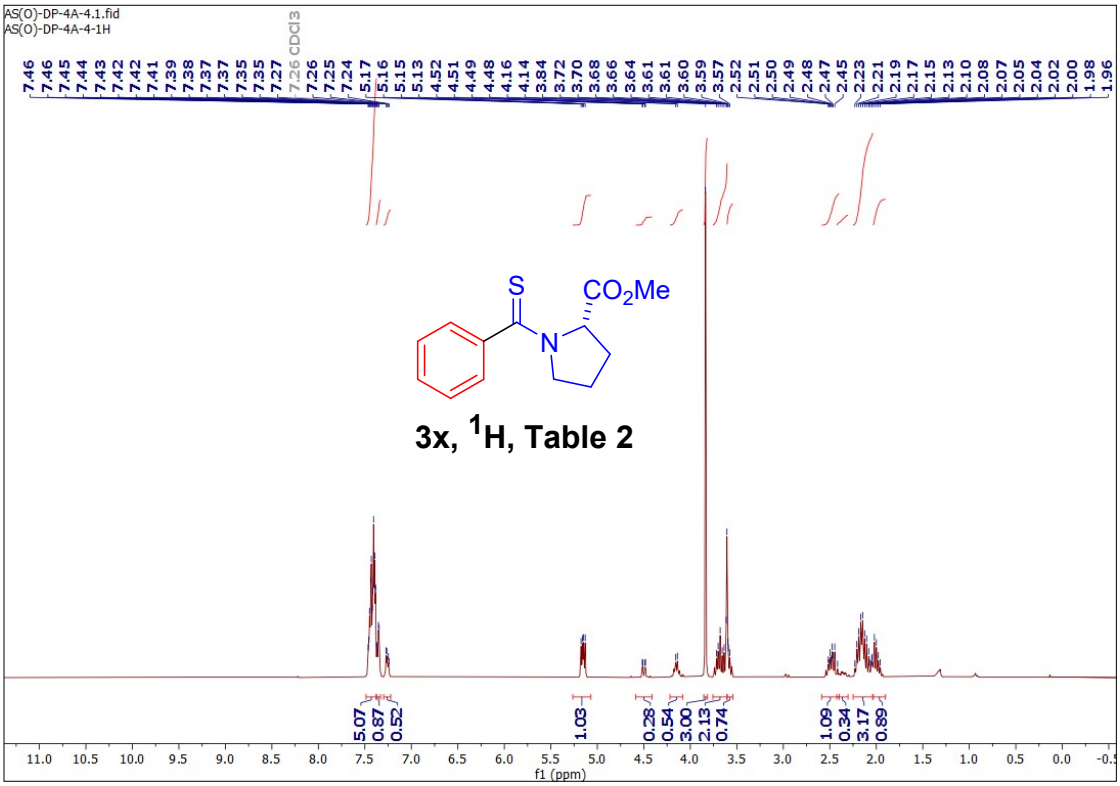


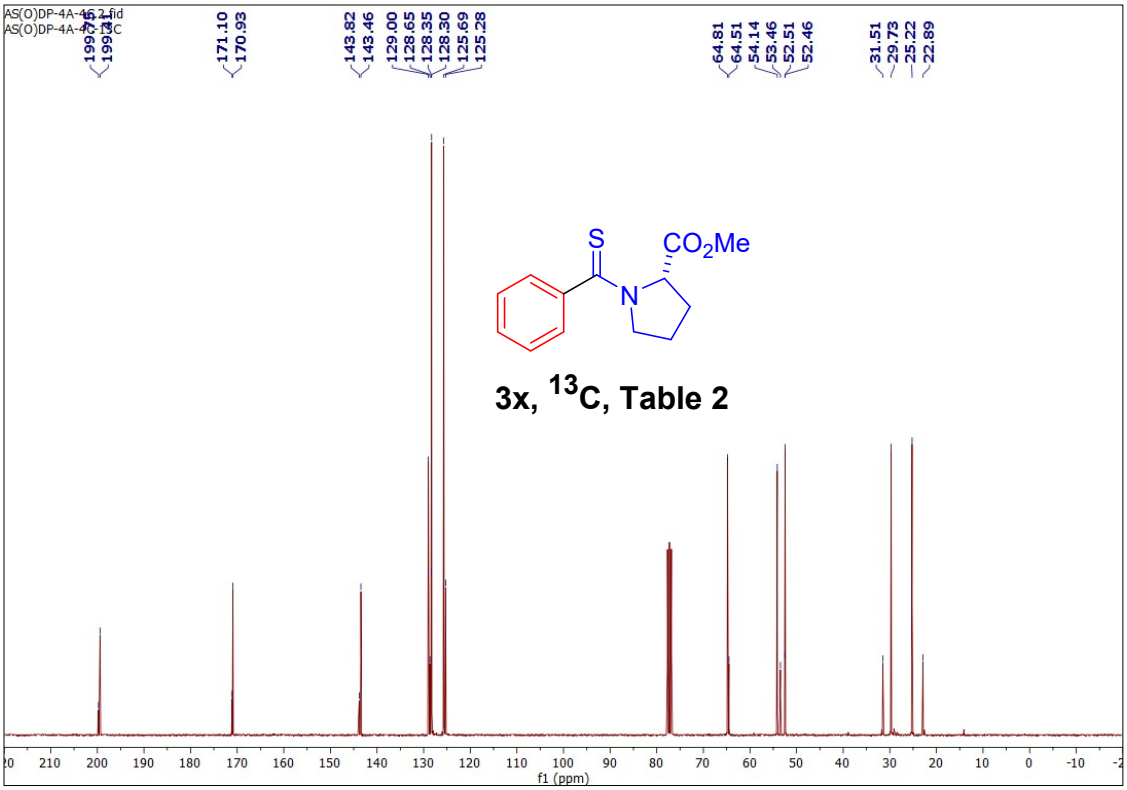
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3w



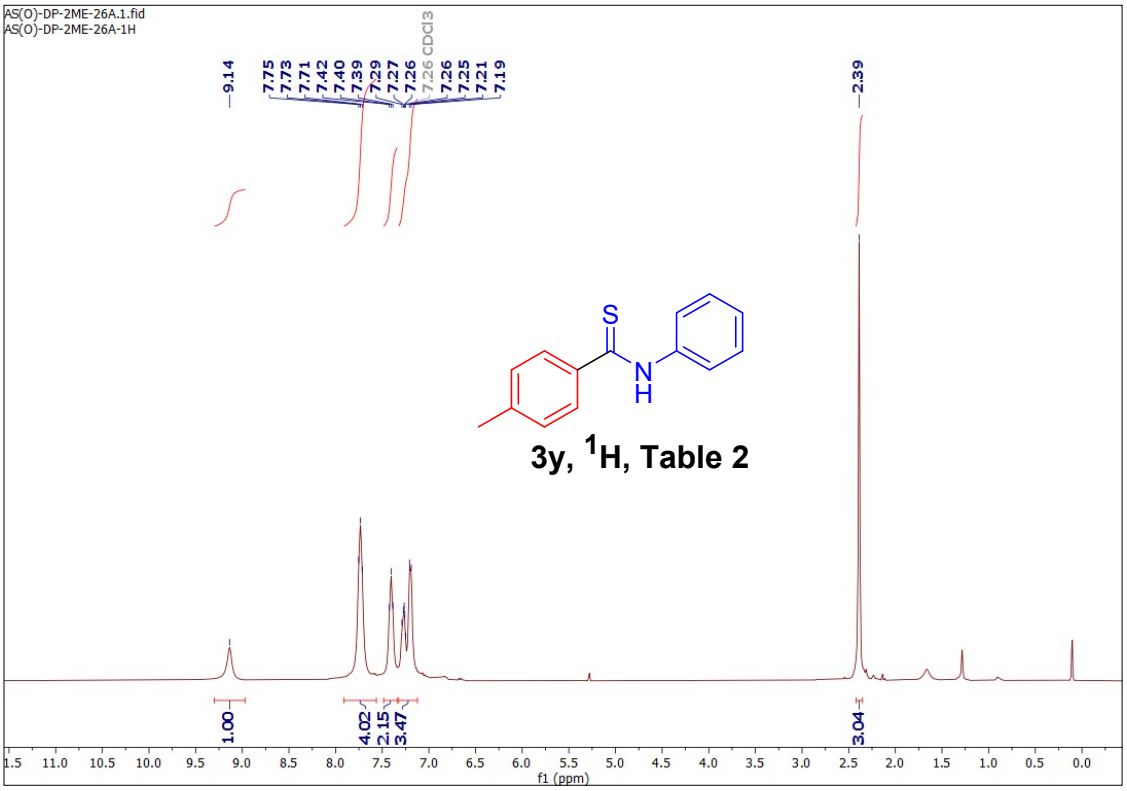


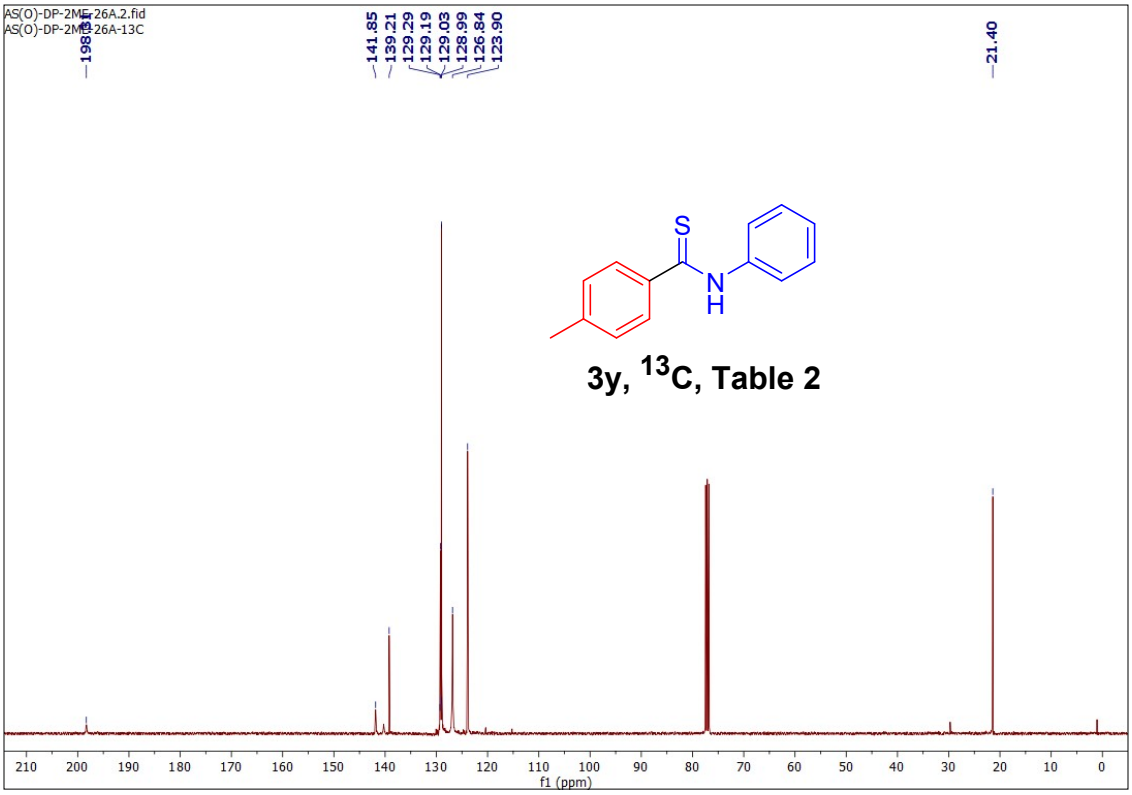
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3x



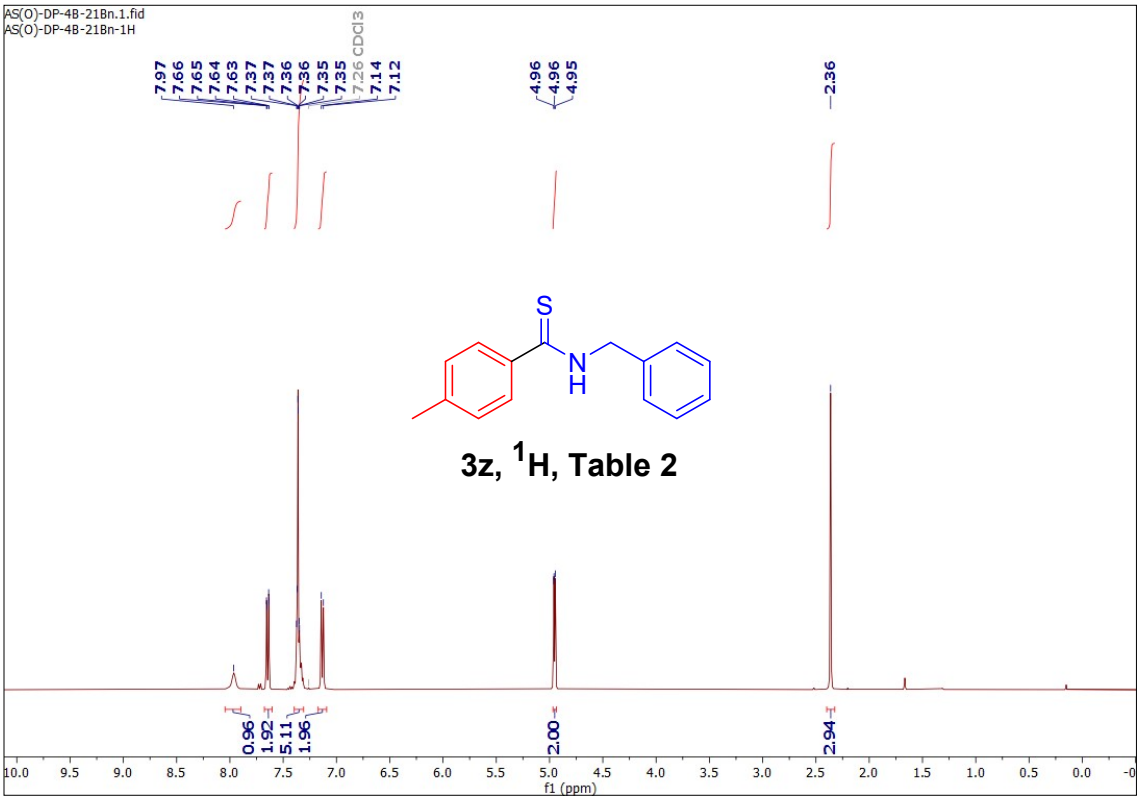


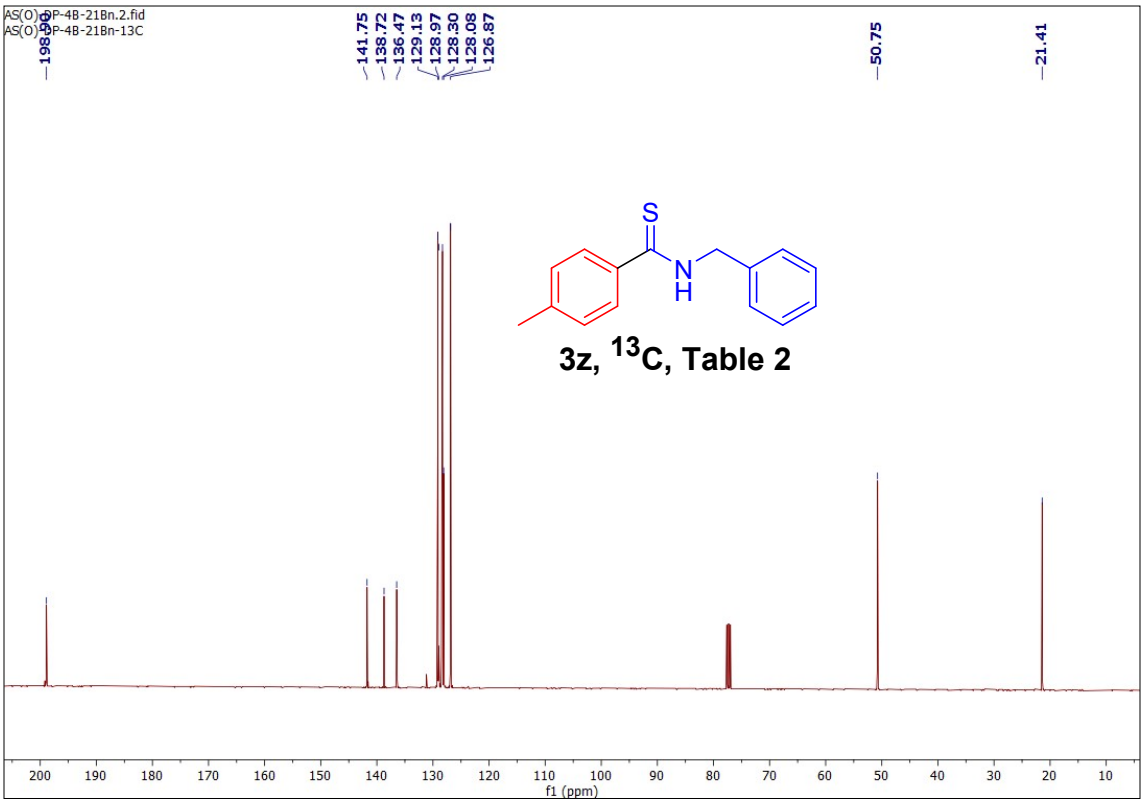
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3y



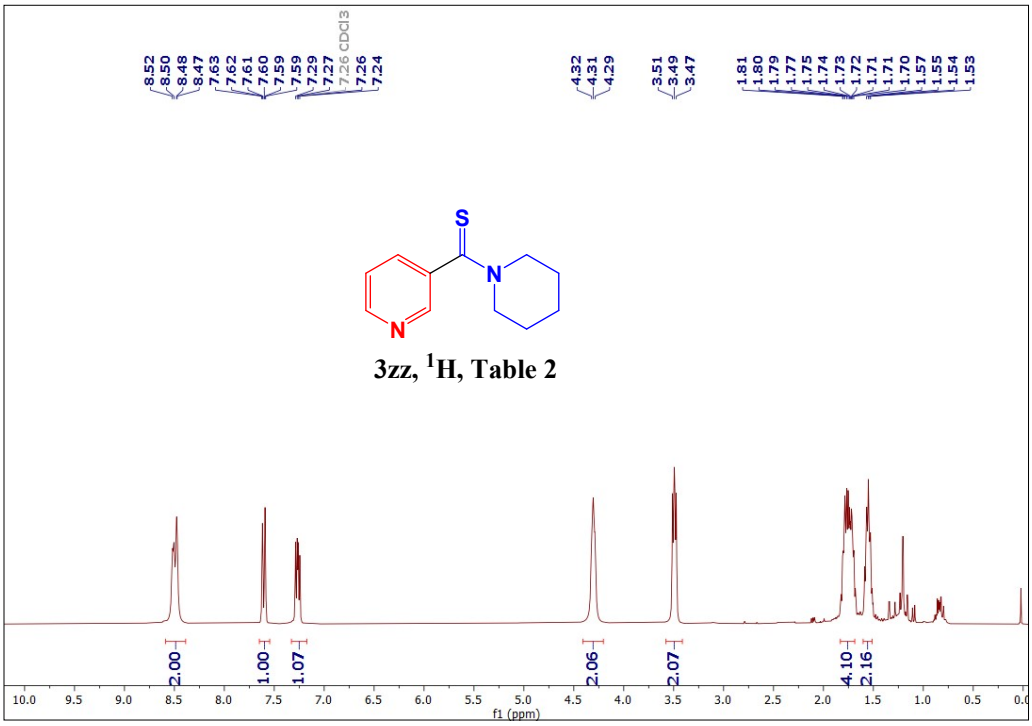


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3z

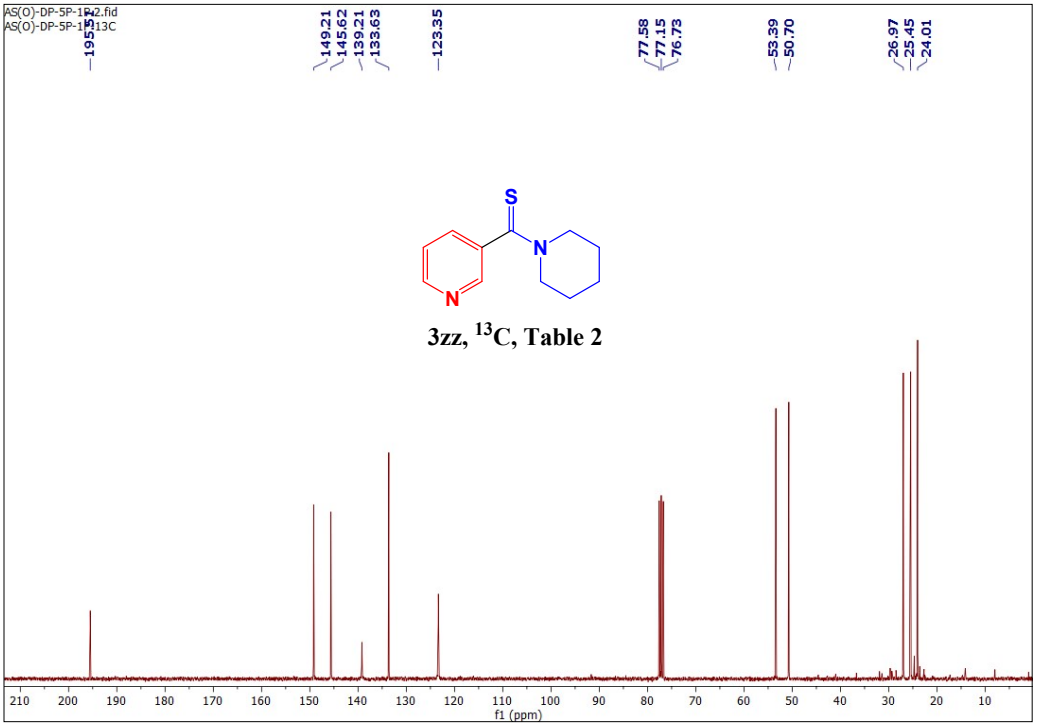




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3zz

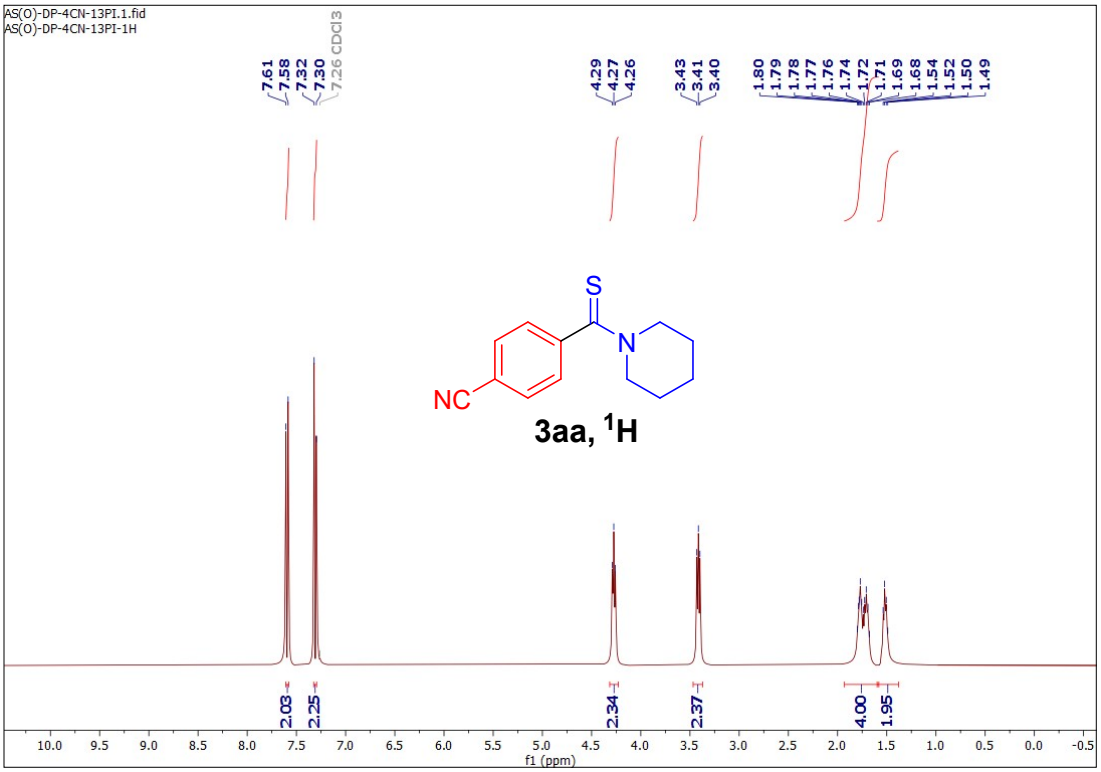


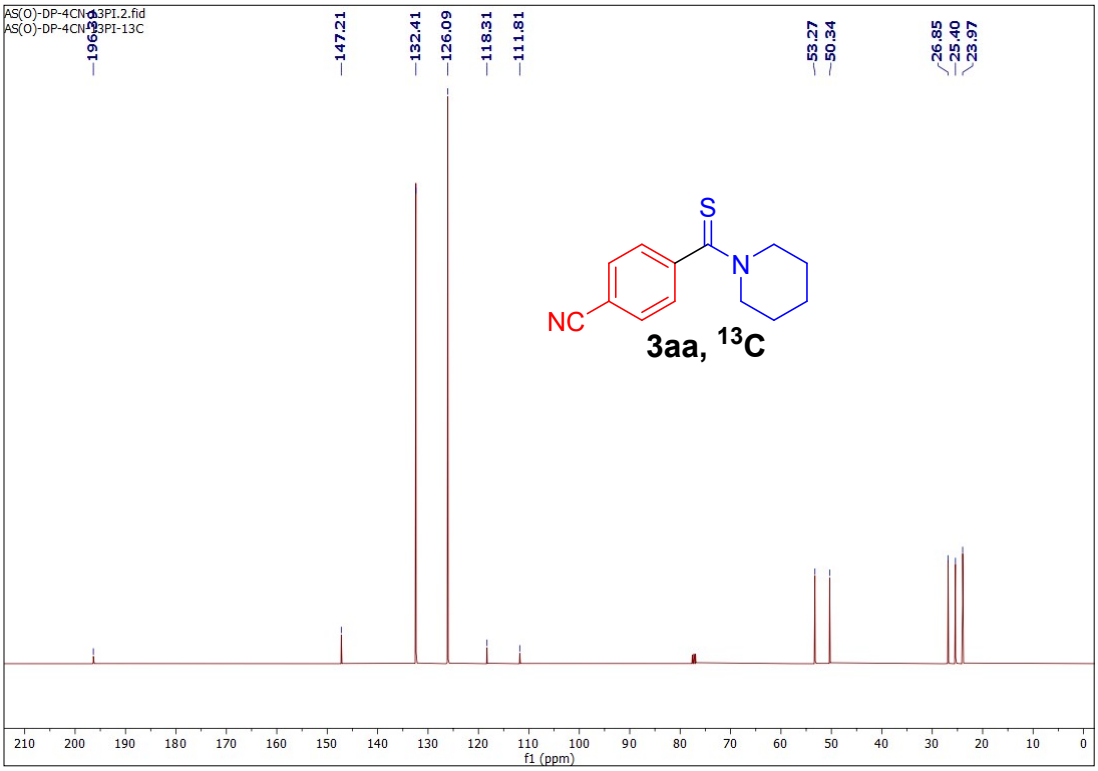
3zz, ^{1}H, Table 2



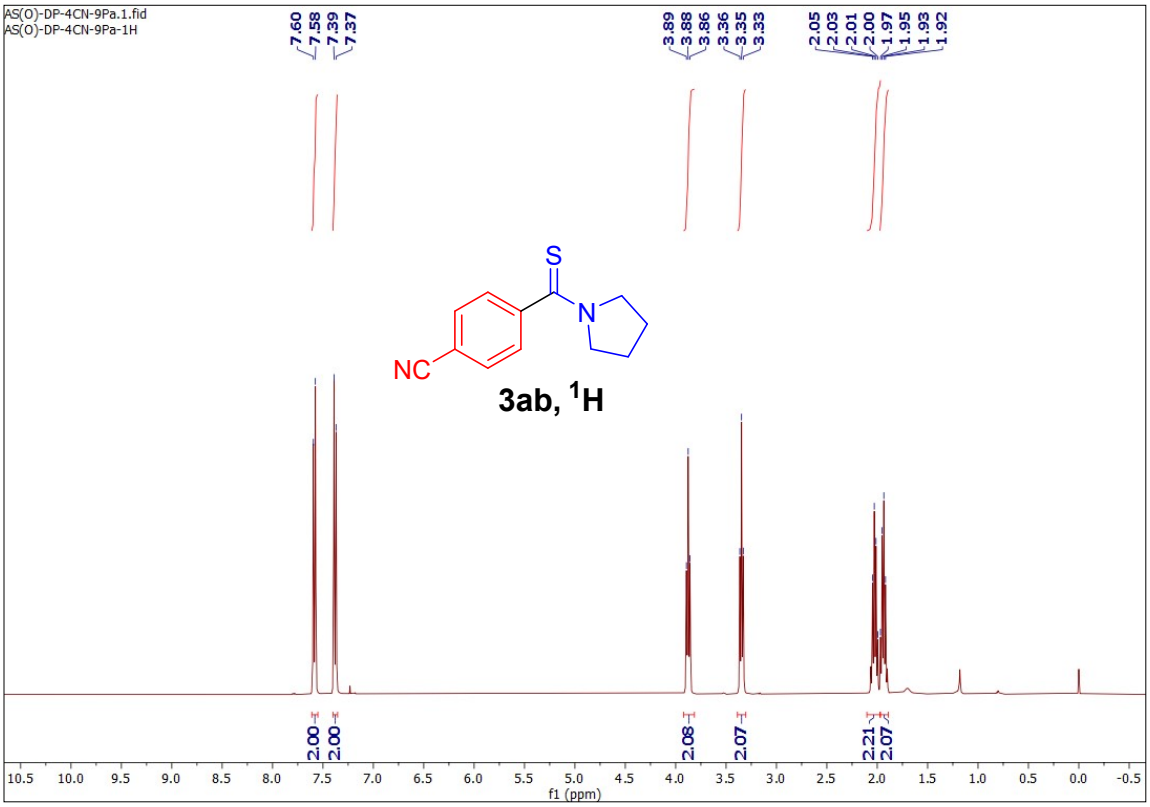
3zz, ^{13}C, Table 2

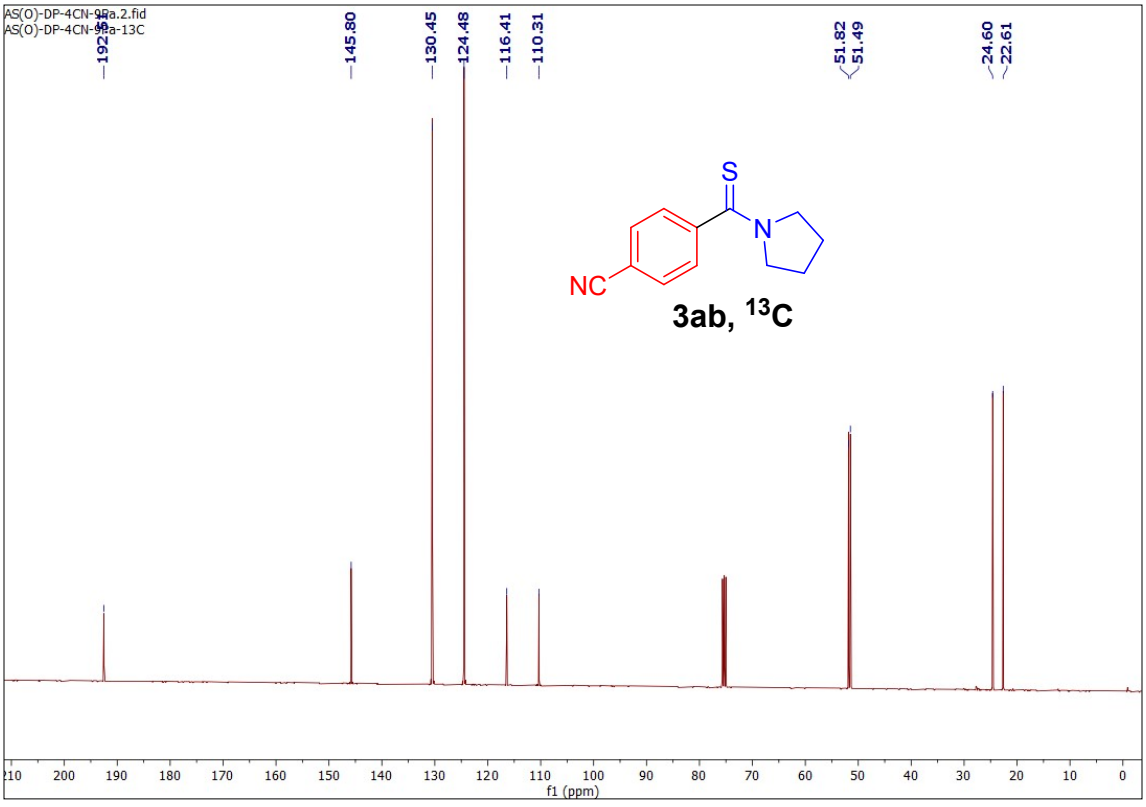
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3aa



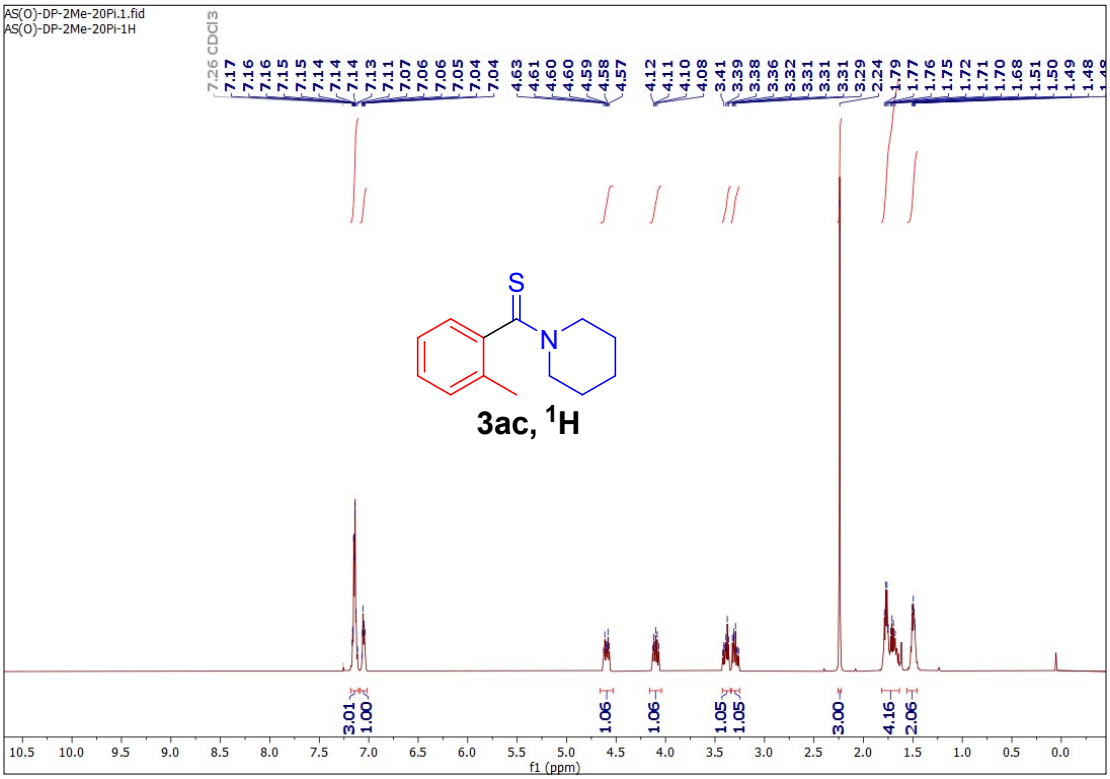


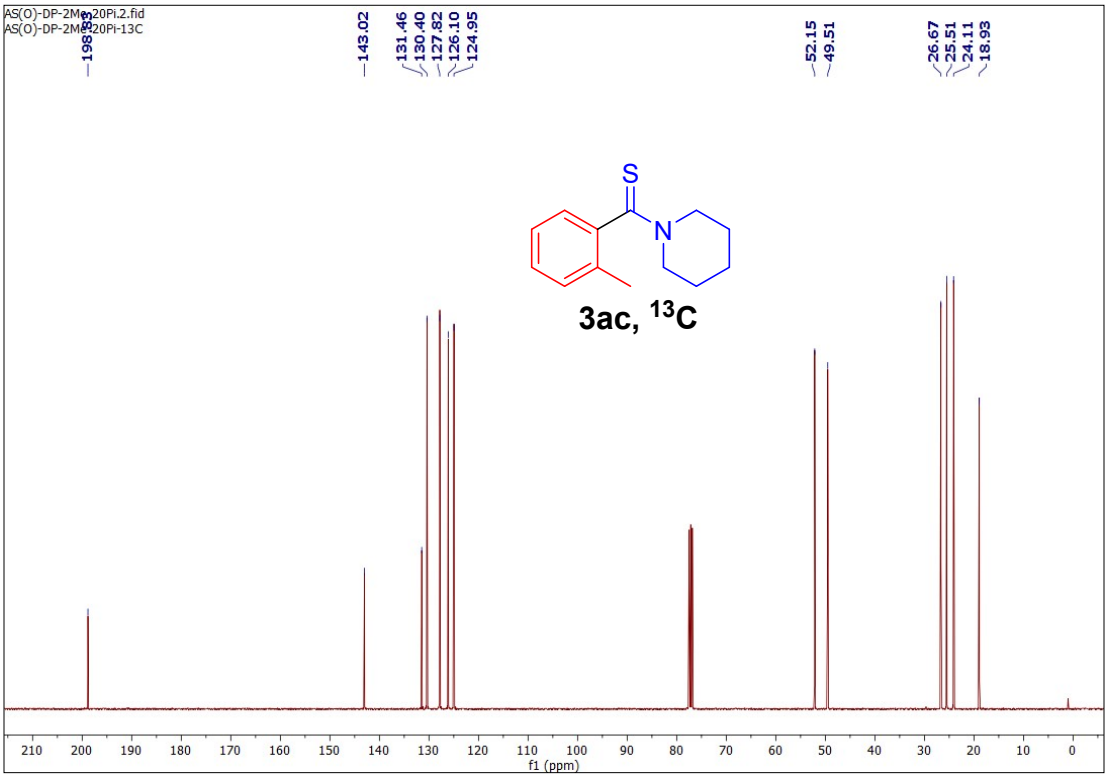
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ab



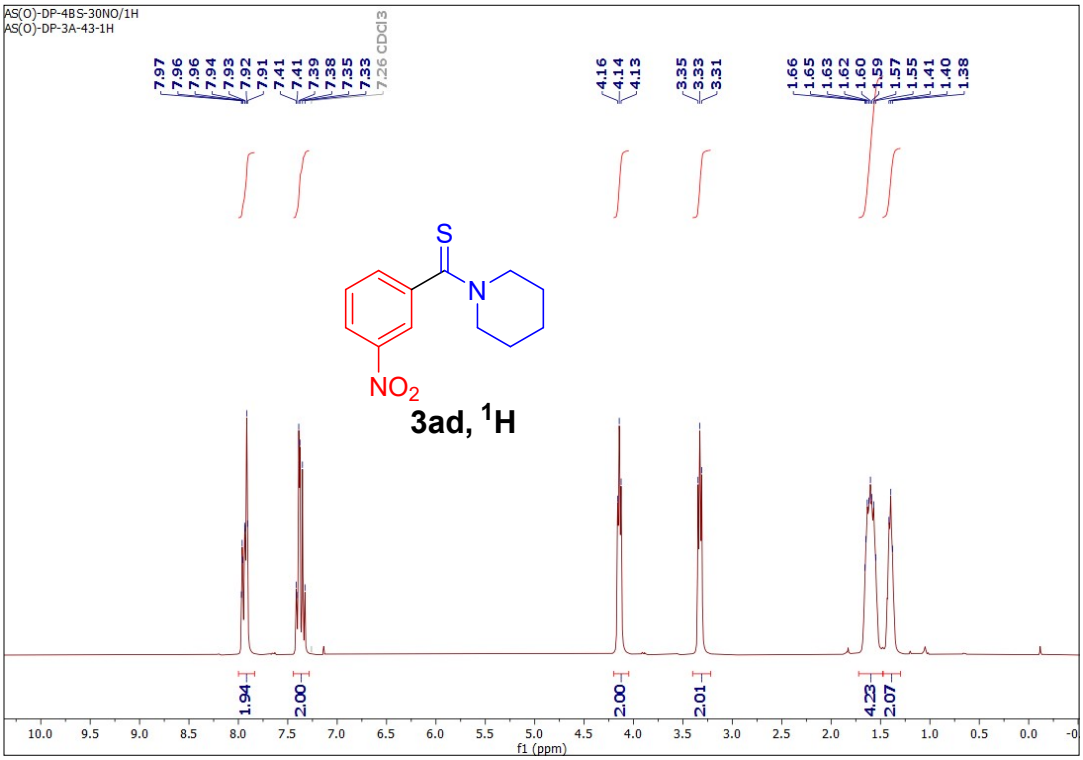


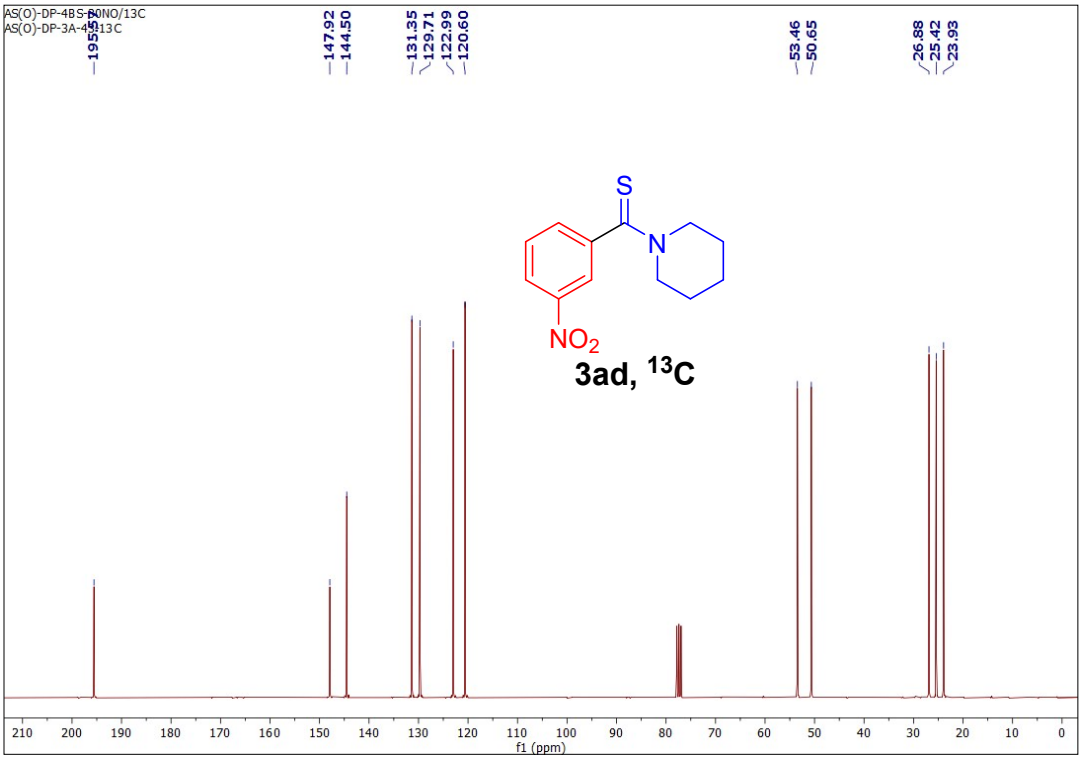
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ac



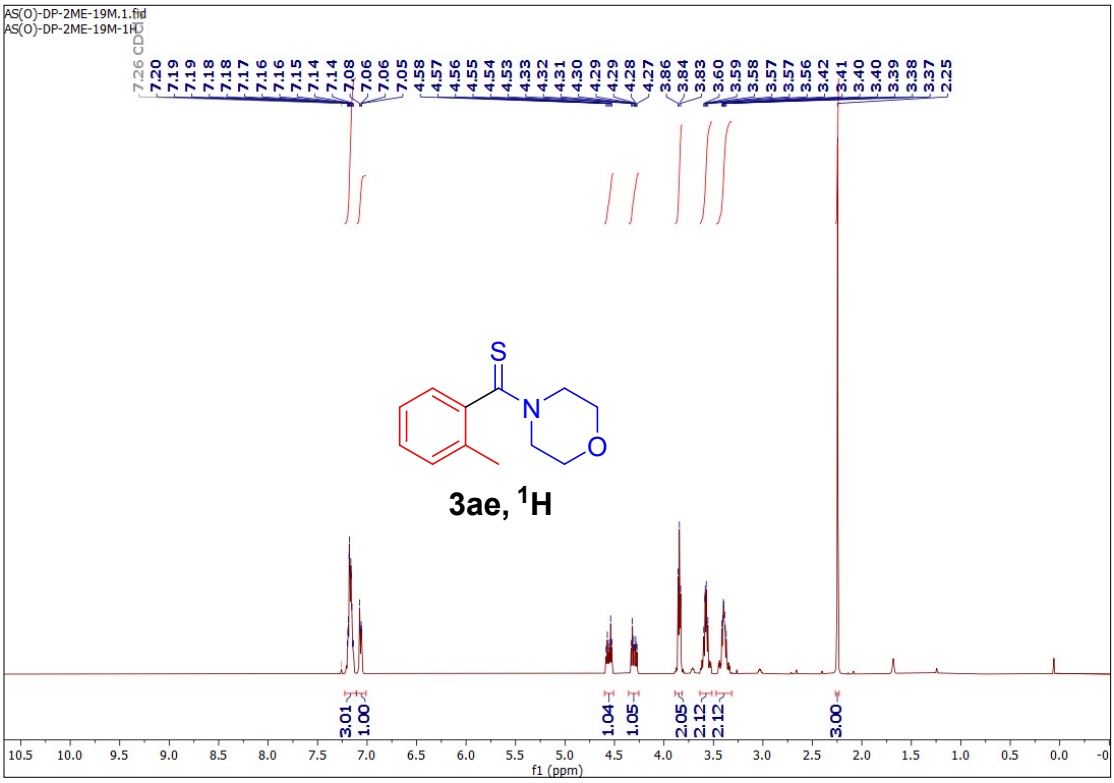


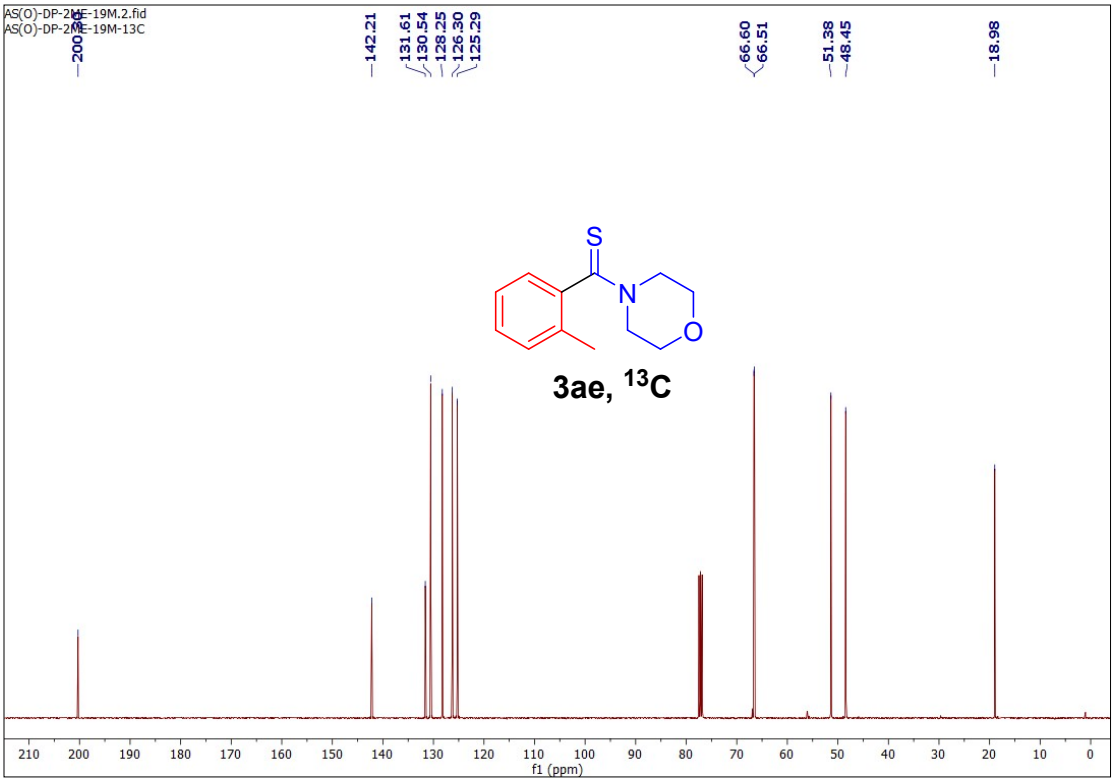
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ad



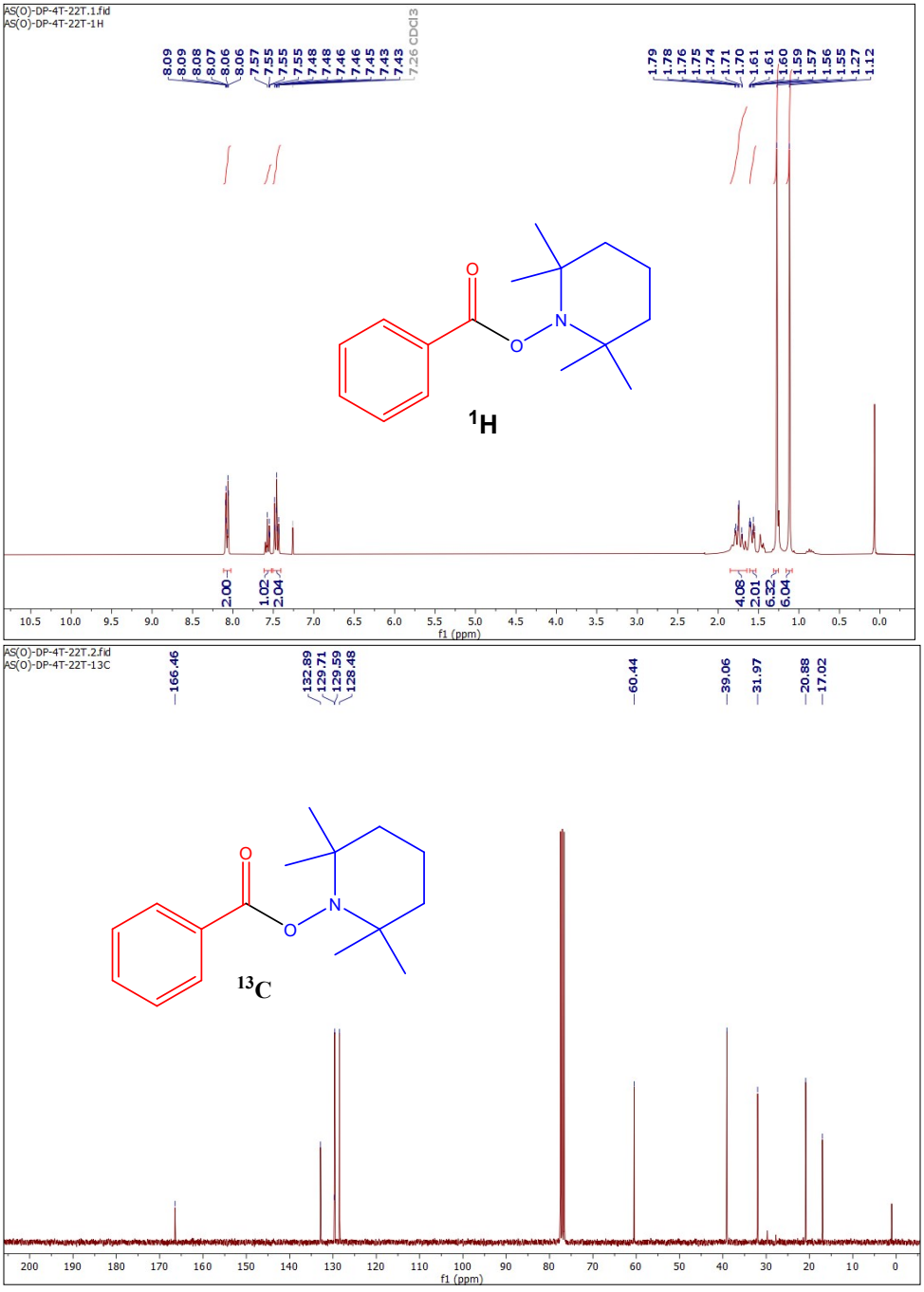


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ae

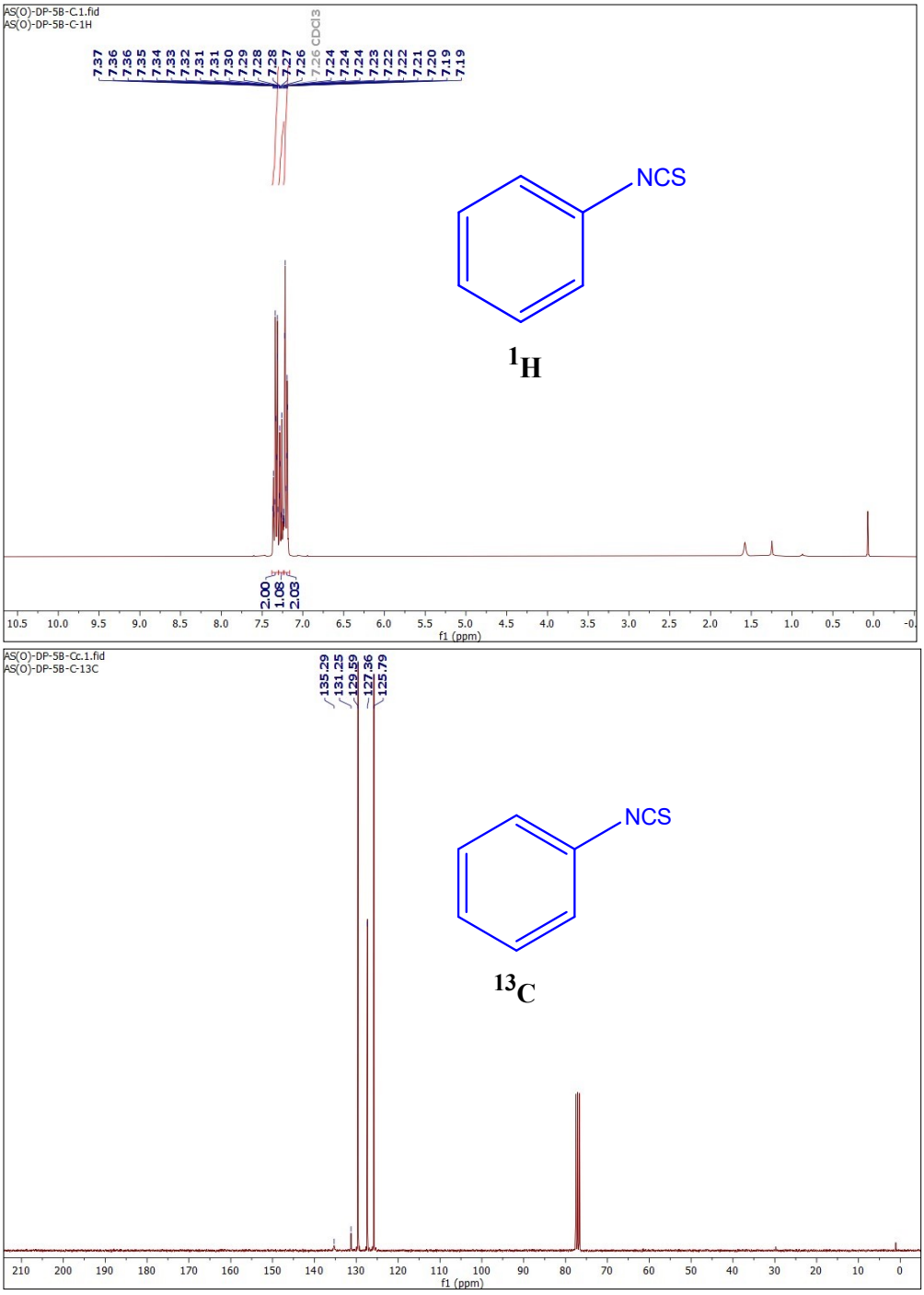




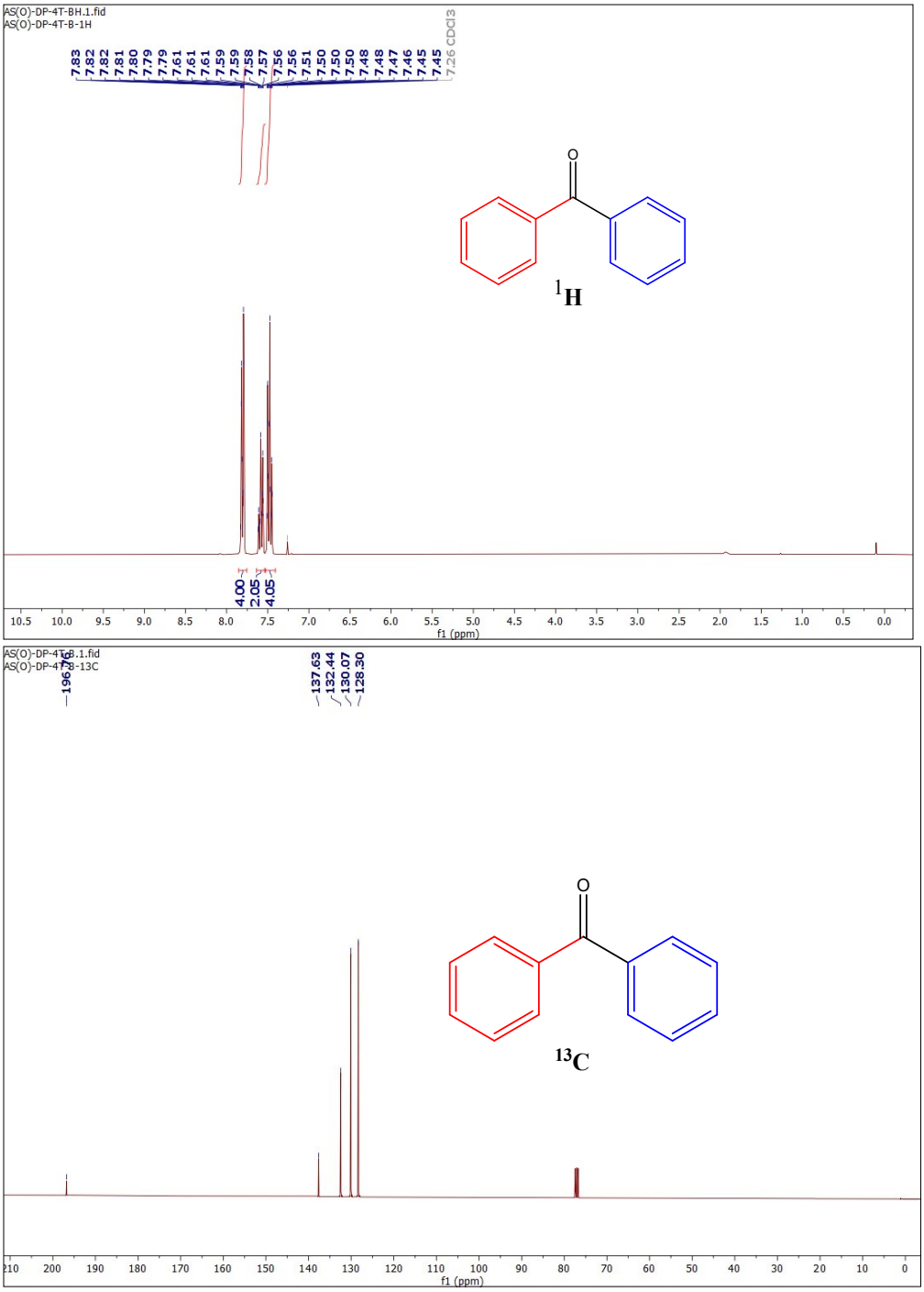
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of O-benzoylated-TEMPO



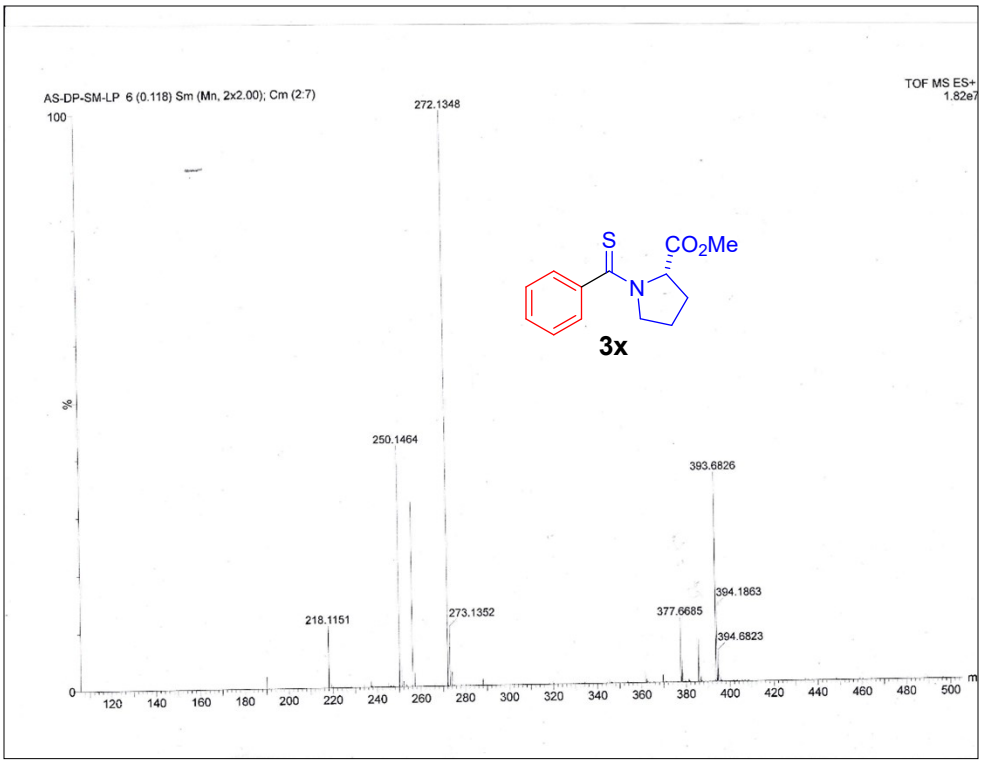
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of isothiocyanatobenzene

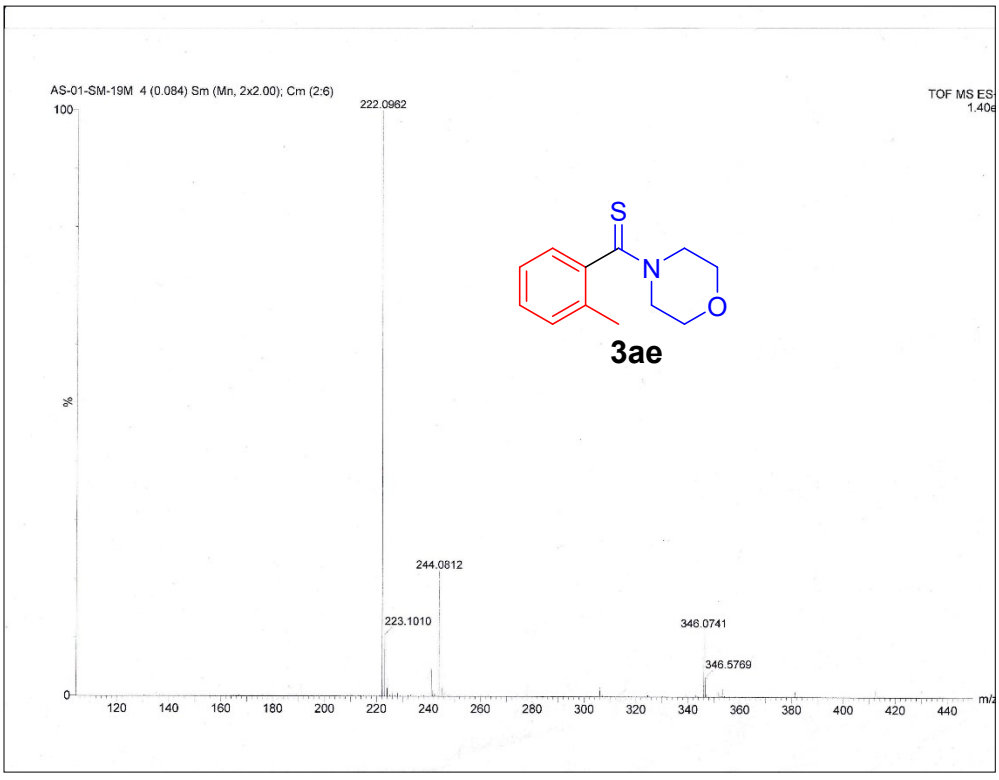


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Benzophenone



F. Mass spectra of products (3x, 3ae)





G. Gas chromatograms:

GC-MS data were collected from PerkinElmer Clarus SQ 8 C Mass spectrometer.

Column specification (COL-Elite-5mS-30).

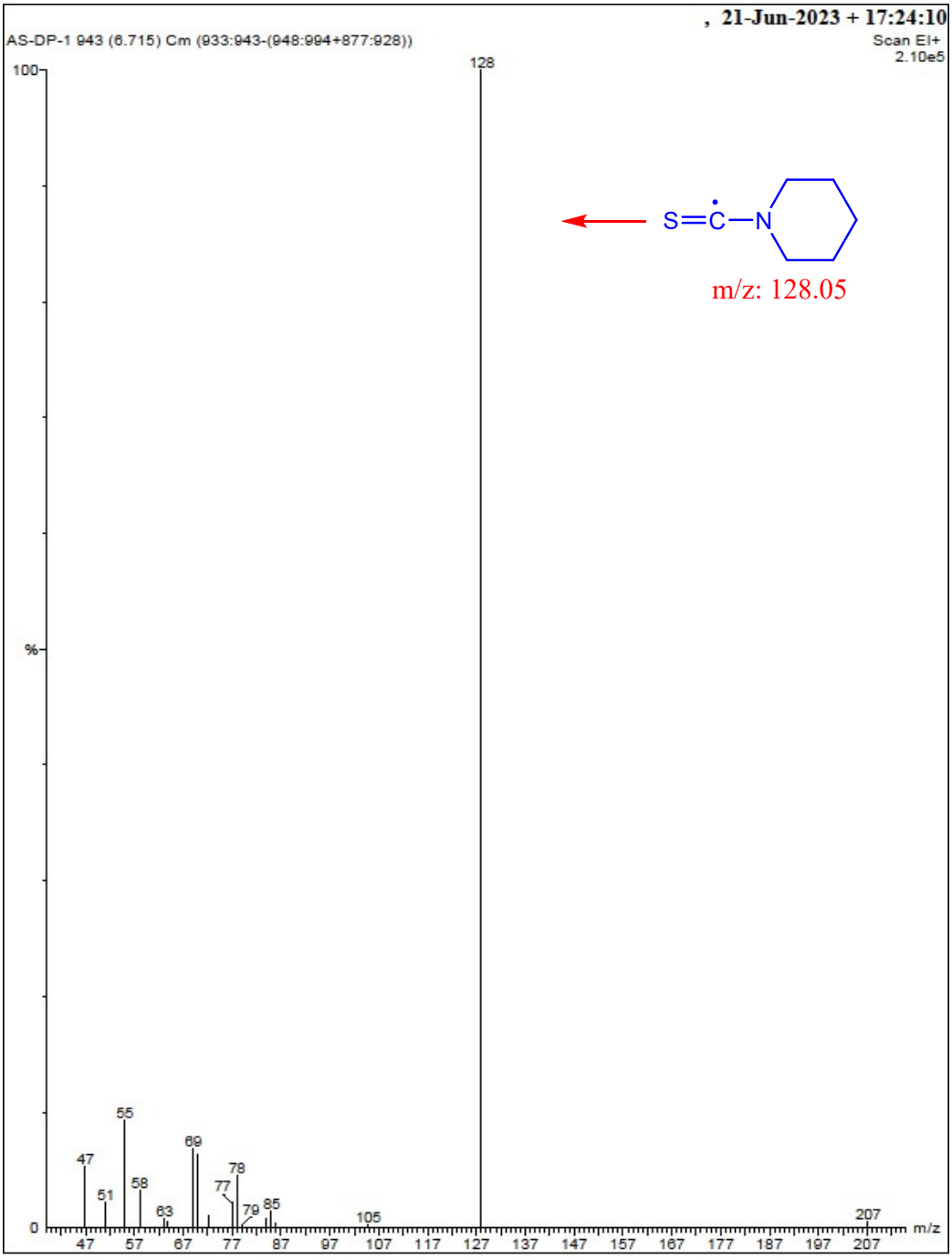


Fig. 1 GC spectrum of the reaction mixture described in 3a product.

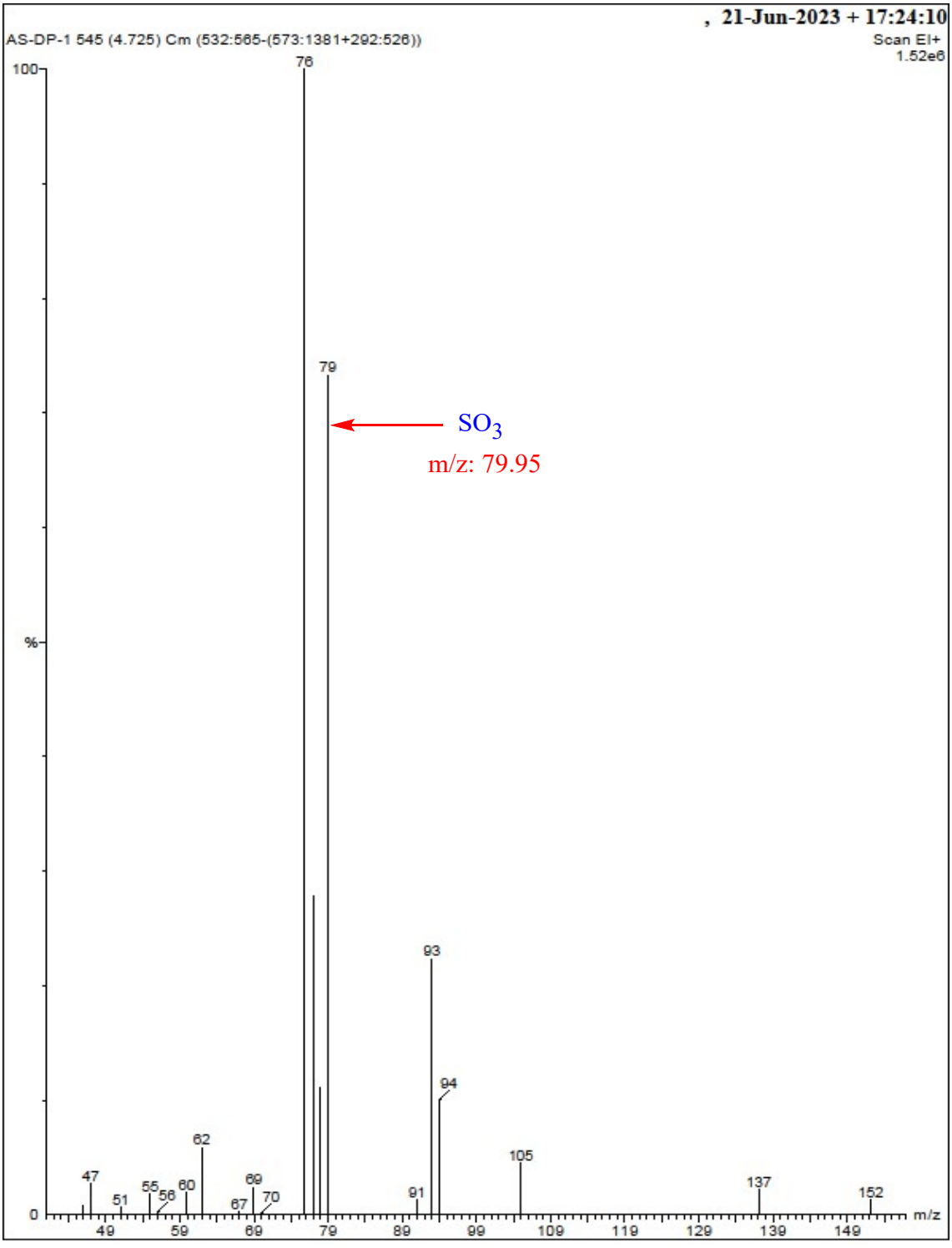


Fig. 2 GC spectrum of the reaction mixture described in 3a product.

H. ^{1}H NMR Spectra of crude reaction mixtures (in $CDCl_3$):

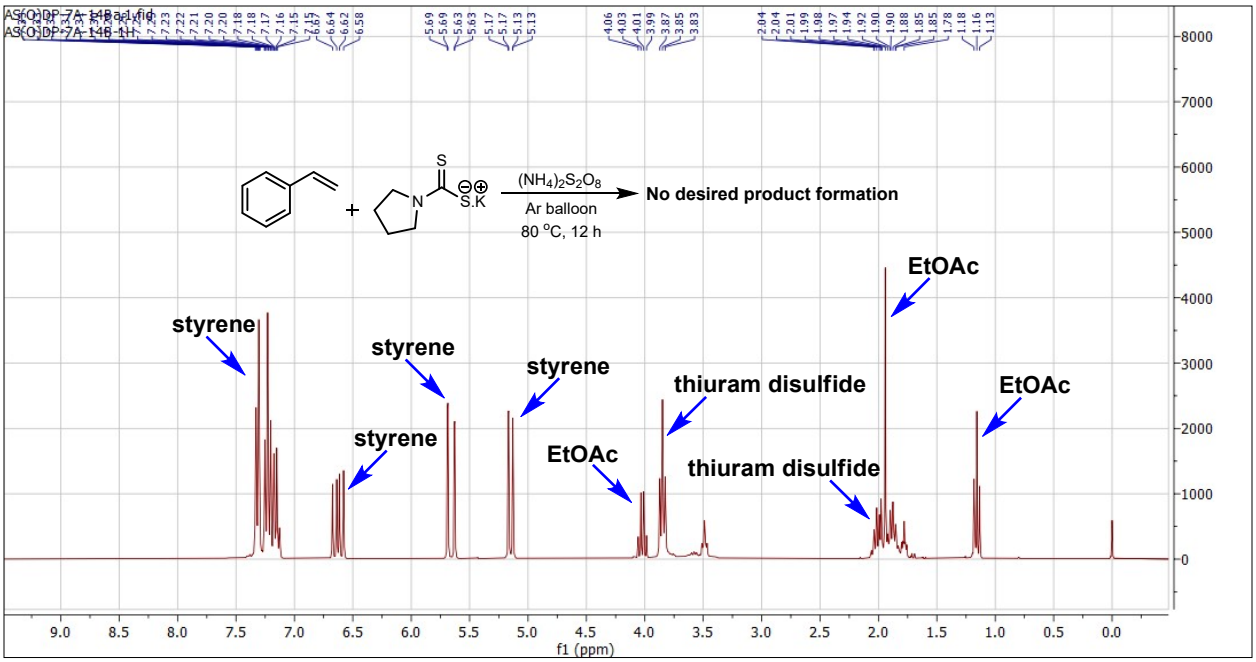


Fig. 3 ^{1}H NMR of crude reaction mixture for the reaction between styrene and pyrrolidine-dithiocarbamate performed in argon atmosphere (Ar balloon).

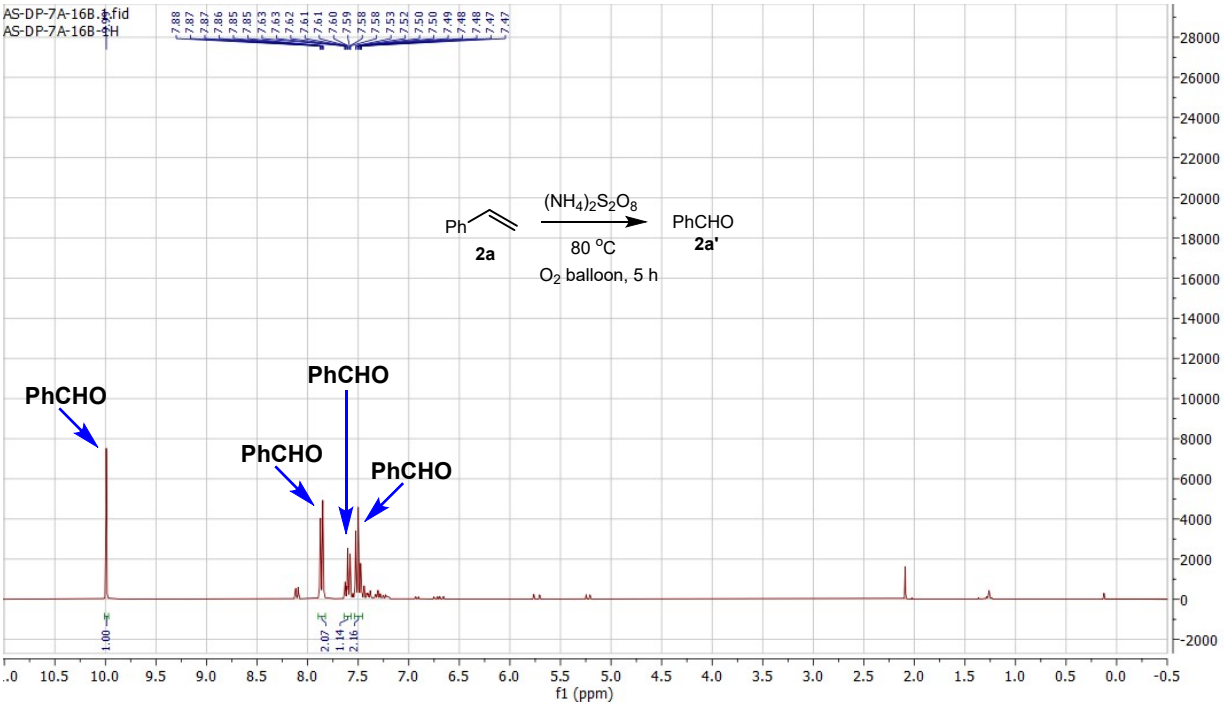


Fig. 4 ^{1}H NMR of crude reaction mixture for the reaction between styrene and persulfate performed using O_2 balloon for 5 h of time period.

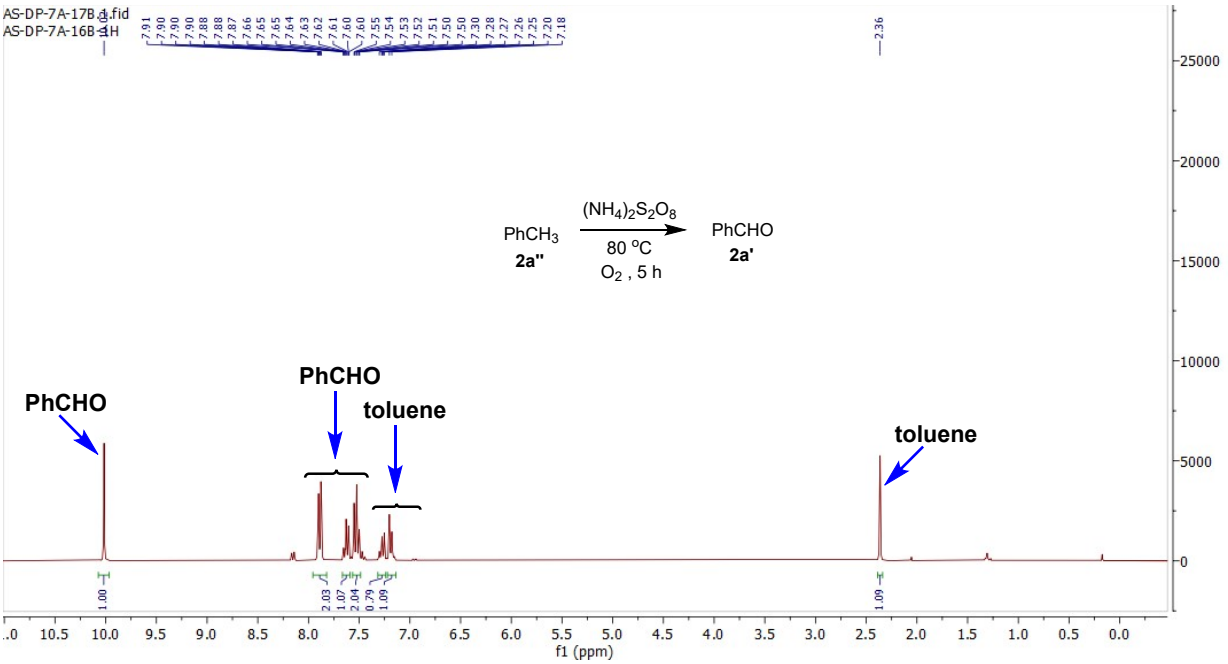


Fig. 5 ^{1}H NMR of crude reaction mixture for the reaction between toluene and persulfate performed in O_2 for 5 h of time period.