

Supporting information

Dithiocarbamate mediated thioamidation of arylglyoxylic acids by decarboxylative-decarbonylative C-C bond formation reactions

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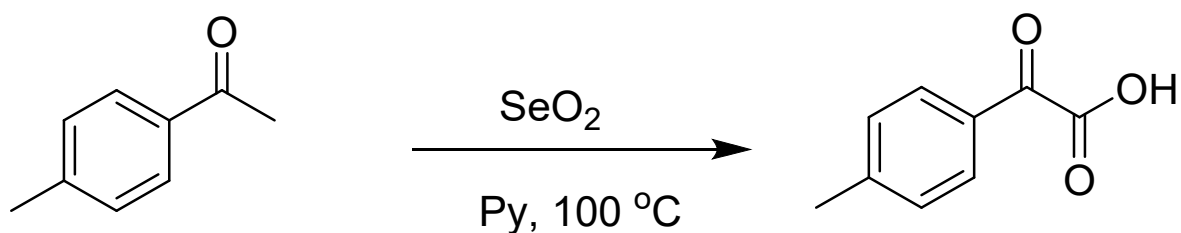
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A. General information:

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. IR spectra were recorded in JASCO FT/IR-4600 in neat condition. ^1H NMR spectra were recorded using Bruker Spectrometer at 300 MHz, 400 MHz. The ^{19}F spectra of synthesized fluorinated product was recorded in CDCl_3 on Bruker Spectrometer, 400 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. Melting points were determined by a LabX India digital melting point apparatus.

B. Representative experimental procedure of α - oxocarboxylic acids:^[1]

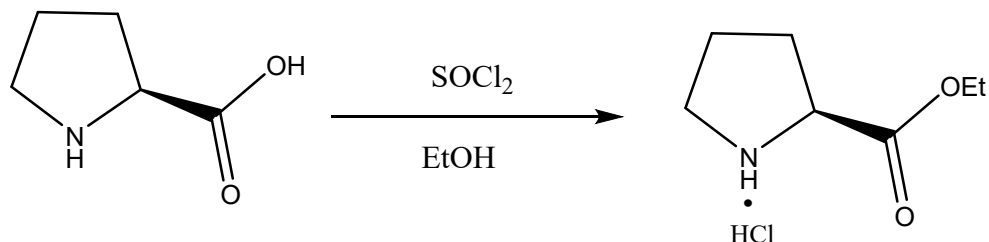
Example for synthesis of 4-methylphenylglyoxalic acid



A mixture of 4-methylacetophenone (10 mmol, 1 eq), SeO_2 (15 mmol, 1.5 eq) and anhydrous Py (4 mL) 500 mL round bottom flask equipped with a magnetic bar. The reaction mixture was heated in an oil bath under Ar at $110\text{ }^\circ\text{C}$ for 4 h. Upon completion (TLC) the reaction mixture was cooled to room temperature and filtered. The residue was washed with EtOAc (50 mL). The combined filtrate was treated with 1N HCL. The organic layer was separated and the aq. layer was extracted with EtOAc then the organic layer as was treated with 1M NaOH and aq. layer was separated. The organic layer was extracted water and the combined aq. layers were added dropwise with 1M HCL until pH = 1-2. The mixture was extracted with EtOAc and the combined organic layer were dried with anhydrous Na_2SO_4 and concentrated in vacuum. The desired product was recrystallized from ethanol. Yield: 74% (555 mg).

This procedure was followed for preparation of other phenylglyoxalic acid derivatives listed in Table 2.

C. Experimental procedure of L- proline ethyl ester^[2]



To a solution of L-proline (10 mmol, 1 eq), in EtOH (10 ml), SOCl_2 (13 mmol, 1.3 eq), was added dropwise at 5 °C and the mixture was stirred for 12 h at room temperature. After completion of the reaction ethanol was removed under reduced pressure. The crude product (L-proline ethyl ester hydrochloride) was obtained as pale yellow viscous oil which was directly used in the reaction without further purification. Yield 78%.

D. General experimental procedure:

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 Et_3N (0.28 mL, 2 mmol) in NMP (2 ml) at 5 °C. The resulting solution was stirred at room temperature for 5 min. Arylglyoxylic acid (**2**) (0.8 mmol), $(\text{dppf})\text{PdCl}_2$ (10 mol %), and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (1 mmol, 228 mg), were added to the solution of dithiocarbamate anion (**1**) containing Et_3N . The reaction mixture was allowed to stir at 70 °C for a certain time period under Ar atmosphere. 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.

E. Characterization data of all synthesized products:

Phenyl(piperidin-1-yl)methanethione^[3] (3a, Table 2): Yellow solid; Yield: 96% (157 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.34-7.24 (5H, m), 4.37-4.33 (2H, m), 3.52-3.48 (2H, m), 1.83-1.70 (4H, m), 1.59-1.51 (2H, m). ¹³C NMR (75 MHz, CDCl₃): δ 199.54, 143.41, 128.42, 128.37, 125.43, 53.20, 50.63, 26.91, 25.52, 24.71.

Phenyl(pyrrolidin-1-yl)methanethione^[3] (3b, Table 2): Yellow liquid; Yield: 90% (137 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.37-7.32 (5H, m), 3.98 (2H, t, J=6Hz), 3.47 (2H, t, J=6 Hz), 2.11-2.04 (2H, m), 2.01-1.95 (2H, m). ¹³C NMR (75 MHz, CDCl₃): δ 197.33, 144.01, 128.75, 128.34, 125.67, 53.82, 53.44, 26.51, 24.70.

Morpholino(phenyl)methanethione^[3] (3c, Table 2): Yellow solid; m.p. 135-137 °C. Yield: 93% (154 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.35-7.31 (3H, m), 7.28-7.24 (2H, m), 4.44-4.40 (2H, m), 3.88-3.85 (2H, m), 3.62-3.57 (4H, m). ¹³C NMR (100 MHz, CDCl₃): δ 200.99, 142.48, 128.89, 128.56, 125.90, 66.75, 66.53, 52.53, 49.56. IR (neat) 2920, 2847, 1720, 1619, 1478, 1433, 1288, cm⁻¹.

N,N-dimethylbenzothioamide^[4] (3d, Table 2): Yellow solid; Yield: 92% (121 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.27 (5H, m), 3.59 (3H, s), 3.15 (3H, s). ¹³C NMR (100 MHz, CDCl₃): δ 201.28, 143.40, 128.59, 128.35, 125.75, 44.19, 43.26.

Piperidin-1-yl(p-tolyl)methanethione^[5] (3e, Table 2): Pale yellow solid; Yield: 92% (161 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.17-7.11 (4H, m), 4.34-4.32 (2H, m), 3.54-3.51 (2H, m), 2.33 (3H, s), 1.80-1.73 (4H, m), 1.72-1.53 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 199.99, 140.65, 138.44, 128.97, 125.58, 53.21, 50.75, 26.91, 25.52, 24.20, 21.25.

Pyrrolidin-1-yl(*p*-tolyl)methanethione^[5] (**3f**, Table 2): White solid; Yield: 89% (145 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.24 (2H, d, J=12 Hz), 7.12 (2H, d, J=8 Hz), 3.93 (2H, t, J=8 Hz), 3.46 (2H, t, J=8 Hz), 2.32 (3H, s), 2.07-2.00 (2H, m), 1.97-1.89 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 197.42, 141.23, 138.79, 128.83, 125.78, 53.87, 53.52, 26.50, 24.69, 21.29.

Morpholino(*p*-tolyl)methanethione^[3] (**3g**, Table 2): Yellow solid; m.p. 126--129 °C. Yield: 90% (159 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.18-7.12 (4H, m), 4.41-4.38 (2H, m), 3.85-3.83 (2H, m), 3.60 (4H, m), 2.32 (3H, s). ¹³C NMR (100 MHz, CDCl₃): δ 201.30, 139.69, 139.07, 129.11, 126.07, 66.76, 66.53, 52.60, 49.70, 21.32. IR (neat) 2980, 2921, 2855, 1474, 1431, 1292, 1256 cm⁻¹.

N,N,4-trimethylbenzothioamide^[4] (**3h**, Table 2): Pale yellow solid; Yield: 88% (126 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.22-7.13 (4H, m), 3.59 (3H,s), 3.18 (3H,s), 2.34 (3H, s). ¹³C NMR (100 MHz, CDCl₃): δ 201.66, 140.60, 138.71, 128.90, 125.91, 44.20, 43.35, 21.26.

(4-chlorophenyl)(piperidin-1-yl)methanethione^[6] (**3i**, Table 2): Yellow liquid; Yield: 91% (175 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.31-7.28 (2H, m), 7.21-7.19 (2H, m), 4.32-4.30 (2H, m), 3.51-3.48 (2H, m), 1.81-1.71 (4H, m), 1.70-1.52 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 198.10, 141.71, 134.32, 128.63, 126.99, 53.27, 50.70, 26.90, 25.47, 24.10.

(4-chlorophenyl)(pyrrolidin-1-yl)methanethione^[6] (**3j**, Table 2): Yellow solid; Yield: 86% (156 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.33-7.28 (4H, m), 3.95-3.92 (2H, m), 3.47-3.43(2H, m), 2.11-2.04 (2H, m), 2.03-1.93 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 195.85, 142.26, 134.71, 128.52, 127.22, 53.85, 53.55, 26.53, 24.64.

4-chloro-N,N-dimethylbenzothioamide^[4] (**3k**, Table 2): Pale yellow solid; Yield: 84% (134 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.32-7.29 (2H, m), 7.24-7.21 (2H, m), 3.56 (3H, s), 3.14 (3H, s). ¹³C NMR (75 MHz, CDCl₃): δ 199.78, 141.68, 134.54, 128.57, 127.31, 44.21, 43.33.

(4-bromophenyl)(piperidin-1-yl)methanethione^[6] (3l, Table 2): White solid; m.p. 118--121 °C. Yield: 86% (195 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.47 (2H, d, J= 9 Hz), 7.15 (2H, d, J= 6 Hz), 4.33 (2H, t, J=6 Hz), 3.51 (2H, t, J=6 Hz), 1.81-1.75 (4H, m), 1.61-1.56 (2H, m). ¹³C NMR (75 MHz, CDCl₃): δ 198.16, 142.16, 131.61, 127.20, 122.50, 53.26, 50.68, 26.90, 25.46, 24.12. IR (neat) 2919, 2855, 1477, 1435, 1237 cm⁻¹.

(4-bromophenyl)(pyrrolidin-1-yl)methanethione^[6] (3m, Table 2): Light brown solid; Yield: 82% (177 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.48 (2H, d, J= 9 Hz), 7.24 (2H, d, J=9 Hz), 3.95 (2H, t, J= 6 Hz), 3.46 (2H, t, J= 6 Hz), 2.11-2.04 (2H, m), 2.02-1.96 (2H, m). ¹³C NMR (75 MHz, CDCl₃): δ 195.90, 142.71, 131.56, 131.50, 127.43, 122.94, 53.83, 53.52, 26.53, 24.64.

4-bromo-N,N-dimethylbenzothioamide^[6] (3n, Table 2): Yellow liquid; Yield: 80% (156 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.50-7.47 (2H, m), 7.20-7.18 (2H, m), 3.59, (3H, s), 3.17 (3H, s). ¹³C NMR (100 MHz, CDCl₃): δ 199.95, 142.15, 131.54, 127.52, 122.76, 44.15, 43.29.

(4-methoxyphenyl)(piperidin-1-yl)methanethione^[3] (3o, Table 2): White solid; Yield: 66% (124 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.27-7.24 (2H, m), 6.86-6.84 (2H, m), 4.33 (2H, t, J=6 Hz), 3.81 (3H, s), 3.57 (2H, t, J=6 Hz), 1.81-1.74 (4H, m), 1.60-1.55 (2H, m). ¹³C NMR (75 MHz, CDCl₃): δ 199.87, 159.92, 135.95, 127.58, 113.63, 55.40, 53.36, 51.09, 26.95, 25.51, 24.23.

(4-methoxyphenyl)(pyrrolidin-1-yl)methanethione^[5] (3p, Table 2): White solid; m.p. 112-114 °C. Yield: 62% (109 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.35 (2H, d, J= 8 Hz), 6.84 (2H, d, J= 8 Hz), 3.95 (2H, t, J= 8 Hz), 3.80 (3H, s), 3.52 (2H, t, J= 4Hz), 2.08-2.04 (2H, m), 1.96-1.93 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 197.14, 160.10, 136.52, 127.76, 113.44, 55.40, 54.02, 53.75, 26.57, 24.72. IR (neat) 2957, 2869, 2822, 1606, 1441, 1236 cm⁻¹.

(3-nitrophenyl)(piperidin-1-yl)methanethione^[6] (3q, Table 2): Yellow solid; Yield: 72% (144 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.09-8.03 (2H, m), 7.54-7.45 (2H, m), 4.28-4.25 (2H, m), 3.47-3.43 (2H, m), 1.78-1.69 (4H, m), 1.54-1.50 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 195.57, 147.92, 144.50, 131.35, 129.72, 122.99, 120.60, 53.46, 50.65, 26.88, 25.42, 23.93.

(3-nitrophenyl)(pyrrolidin-1-yl)methanethione^[6] (3r, Table 2): Yellow solid; Yield: 68% (128 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.11-8.06 (2H, m), 7.61(1H, d, J=8 Hz), 7.49-7.45 (1H, m), 3.86 (2H, t, J=8 Hz), 3.40 (2H, t, J=8Hz), 2.06-1.99 (2H, m), 1.96-1.89 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 193.37, 147.76, 144.99, 131.70, 129.64, 123.30, 120.82, 53.97, 53.86, 26.56, 24.56.

N,N-dimethyl-3-nitrobenzothioamide^[4] (3s, Table 2): Yellow solid; Yield: 65% (109 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.19-8.15 (2H, m), 7.65-7.63 (1H, m), 7.56-7.52 (1H, m), 3.61 (3H, s), 3.19 (3H, s). ¹³C NMR (100 MHz, CDCl₃): δ 197.62, 147.92, 144.53, 131.74, 129.65, 123.26, 120.85, 44.26, 43.31.

N-benzyl-4-methylbenzothioamide^[7] (3t, Table 2): Yellow solid; m.p. 83-85°C. Yield: 85% (164 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.68 (2H, d, J= 8 Hz), 7.41-7.38 (5H, m), 7.18 (2H, d, J= 8 Hz), 5.00 (2H, d, J= 8 Hz), 2.37 (3H, s). ¹³C NMR (100 MHz, CDCl₃): δ 198.94, 141.81, 138.82, 136.34, 129.18, 129.06, 128.41, 128.24, 126.71, 51.09, 21.35. IR (neat) 3313, 3033, 1607, 1518, 1318, 1268 cm⁻¹.

N-phenylbenzothioamide^[8] (3u, Table 2): Yellow solid; Yield: 58% (99 mg); ¹H NMR (400 MHz, CDCl₃): δ 9.09 (1H, br. S), 7.84-7.73 (4H, m), 7.50-7.42 (5H, m), 7.41-7.29 (1H, m), ¹³C NMR (100 MHz, CDCl₃): δ 198.59, 143.15, 139.05, 131.32, 129.08, 128.66, 127.03, 126.77, 123.81.

ethyl (phenylcarbonothioyl)-L-prolinate^[9] (3v, Table 2): Pale yellow solid; Yield: 60% (126 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.29 (5H, m, #1), 7.23-7.22 (1.12H, m, #2), 7.22-7.21 (0.67, m, #2), 5.12-5.09 (1H, m, #1), 4.28-4.23 (0.29H, m, #2), 4.10 (2H, q, J=8 Hz, #1), 4.03-4.00 (0.52H, q, J=7.4 Hz,

#2), 3.67-3.62 (0.67H, m, #2), 3.57-3.54 (1H, m, #1), 3.53-3.51 (1H, m, #1), 2.46-2.43 (1H, m, #1), 2.42-2.40 (0.22H, m, #2), 2.16-2.10 (2.92H, m, #1, #2), 2.09-1.92 (1H, m, #1), 1.32 (3H, t, J=8Hz, #1), 1.14 (0.89H, t, J=7.2 Hz, #2). ¹³C NMR (100 MHz, CDCl₃): δ 199.79 (C=S, #2), 199.47 (C=S, #1), 170.65 (CO₂Et, #2), 170.4 (CO₂Et, #1), 143.85 (C, #2), 143.58 (C, #1), 128.96 (CH, #1), 128.63 (CH, #2), 128.35 (CH, #2), 128.32 (CH, #1), 125.67 (CH, #1), 125.40 (CH, #2), 64.87 (2-CH, #1), 64.67 (2-CH, #2), 61.65 (OCH₂CH₃, #2), 61.45 (OCH₂CH₃, #1), 54.10 (5-CH₂, #1), 53.46 (5-CH₂, #2), 31.52 (3-CH₂, #2), 29.73 (3-CH₂, #1), 25.20 (4-CH₂, #1), 22.84 (4-CH₂, #2), 14.21 (OCH₂CH₃, #1), 14.03 (OCH₂CH₃, #2).

(4-fluorophenyl)(piperidin-1-yl)methanethione^[10] (3W, Table 2): pale yellow liquid; yield: 88% (196 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.21 (2H, m), 7.02-6.96 (2H, m), 4.32-4.28 (2H, m), 3.50-3.47 (2H, m), 1.80-1.71 (4H, m), 1.69-1.51 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 198.46, 164.16, 160.87, 139.51, 139.47, 127.69, 127.58, 115.51, 115.22, 53.29, 50.85, 26.89, 25.47, 24.09. ¹⁹F NMR (100 MHz, CDCl₃) -112.67.

2-phenyl-1-(piperidin-1-yl)ethane-1-thione^[11] (3x, Table 2): Pale yellow liquid; Yield: 64% (140 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.12 (5H, m), 4.25 (2H, s), 4.19-4.16, (2H, m), 3.49-3.46 (2H, m), 1.59-1.49 (4H, m), 1.22-1.17 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 198.35, 136.18, 128.78, 127.87, 126.87, 51.62, 51.59, 51.00, 26.21, 25.25, 23.84.

1-(piperidin-1-yl)ethane-1-thione^[12] (3y, Table 2): white solid; Yield: 32% (45 mg); ¹H NMR (400 MHz, CDCl₃): δ 4.19-4.17 (2H, m), 3.63-3.61 (2H, m), 2.58 (3H, s), 1.65-1.58 (6H, m). ¹³C NMR (100 MHz, CDCl₃): δ 192.14, 51.18, 51.14, 32.39, 26.47, 25.28, 23.93.

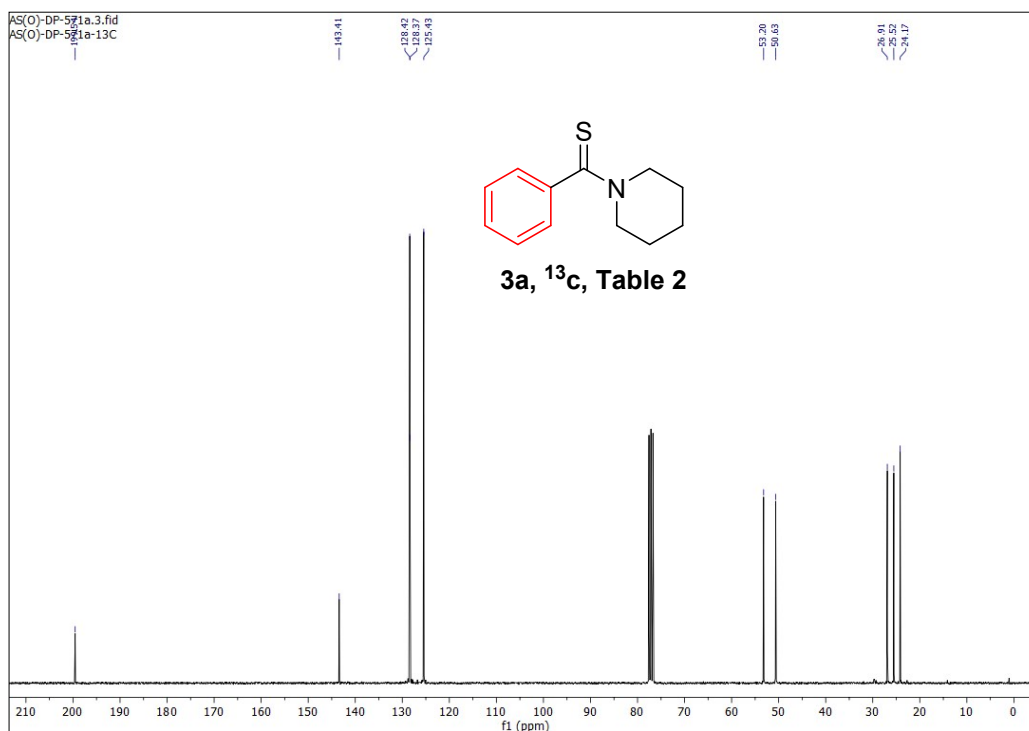
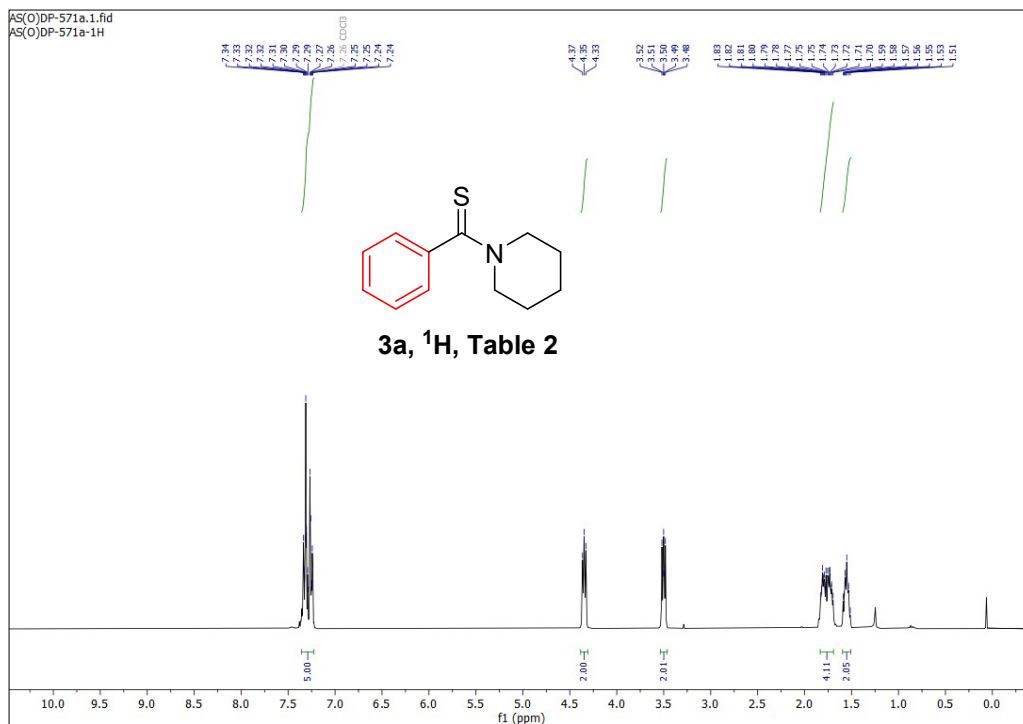
(4-methoxyphenyl)(pyrrolidin-1-yl)methanone^[13] (3p'): Yellow solid; Yield: 80% (164 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.50-7.48 (2H, m), 6.89-6.85 (2H, m), 3.80 (3H, s), 3.62-3.59 (2H, m), 3.47-3.44

(2H, m), 1.94-1.91 (2H, m), 1.87-1.82 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 167.26, 158.57, 127.08, 126.91, 111.17, 53.06, 47.56, 44.10, 24.24, 22.19.

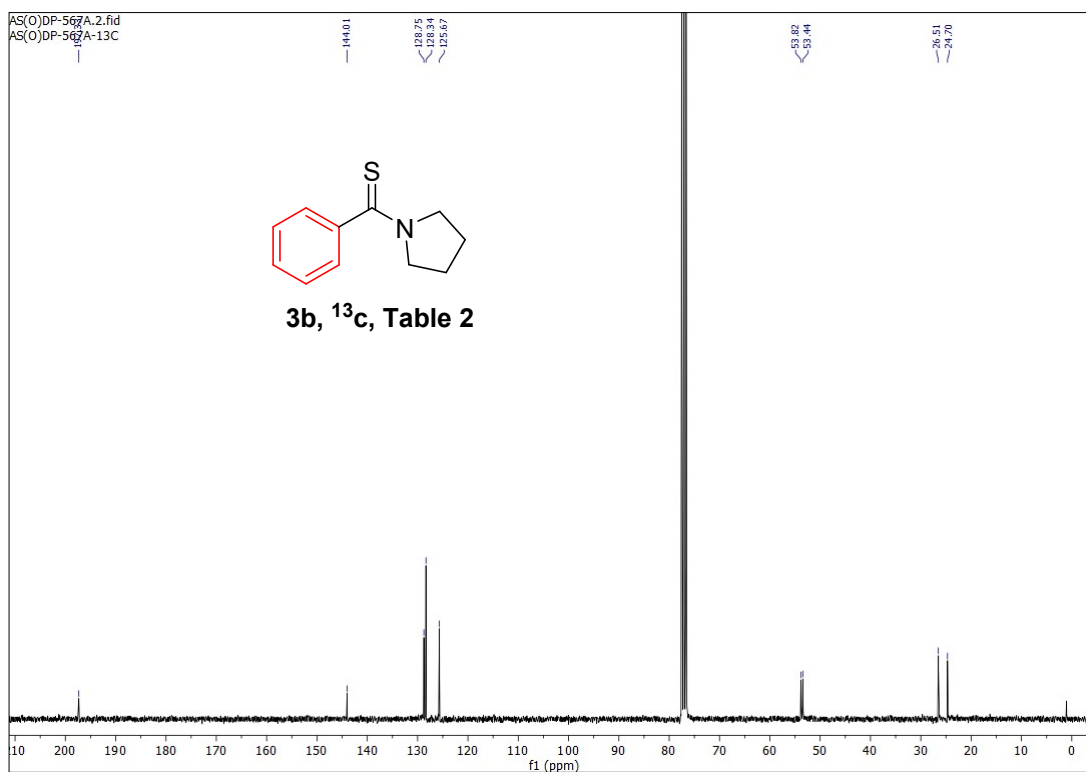
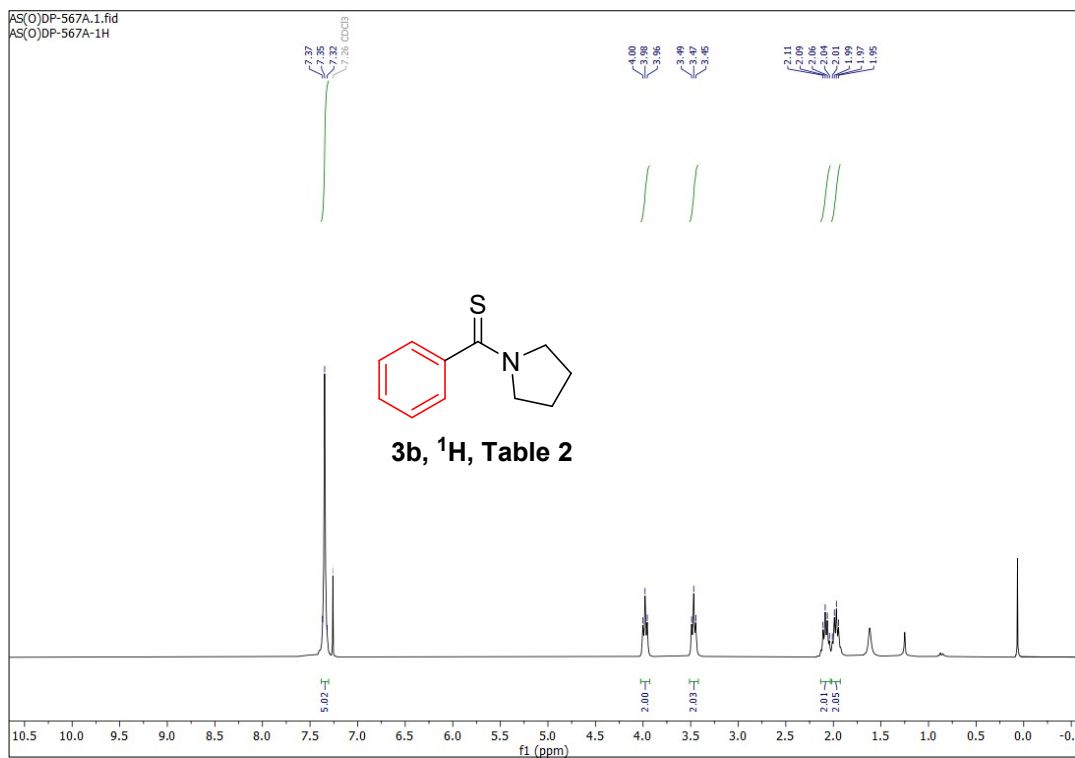
2,2,6,6-tetramethylpiperidin-1-yl benzoate ^[14] (**4**): White solid; ¹H NMR (400 MHz, CDCl₃): δ 8.08-8.06 (2H, m), 7.60-7.56 (1H, m), 7.55-7.44 (2H, m), 1.82-1.48 (6H, m), 1.28 (6H, s), 1.12 (6H, s). ¹³C NMR (100 MHz, CDCl₃): δ 166.44, 132.87, 129.74, 129.59, 128.47, 60.44, 39.08, 32.00, 31.95, 20.89, 20.85, 17.02

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

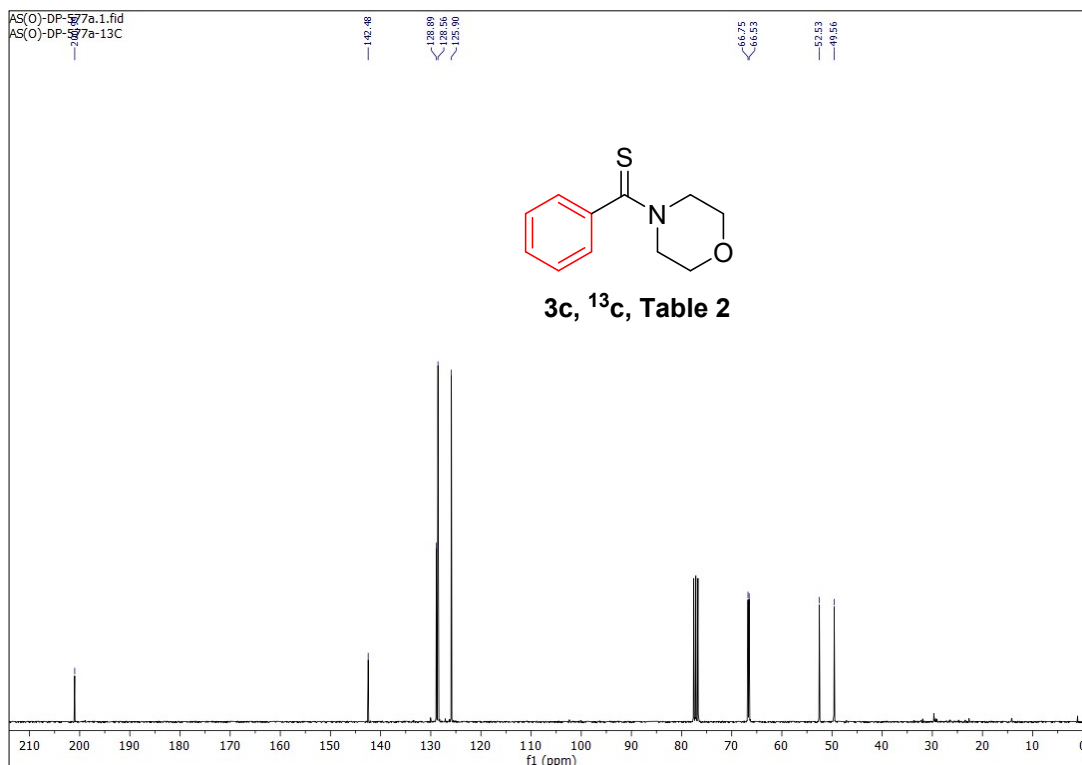
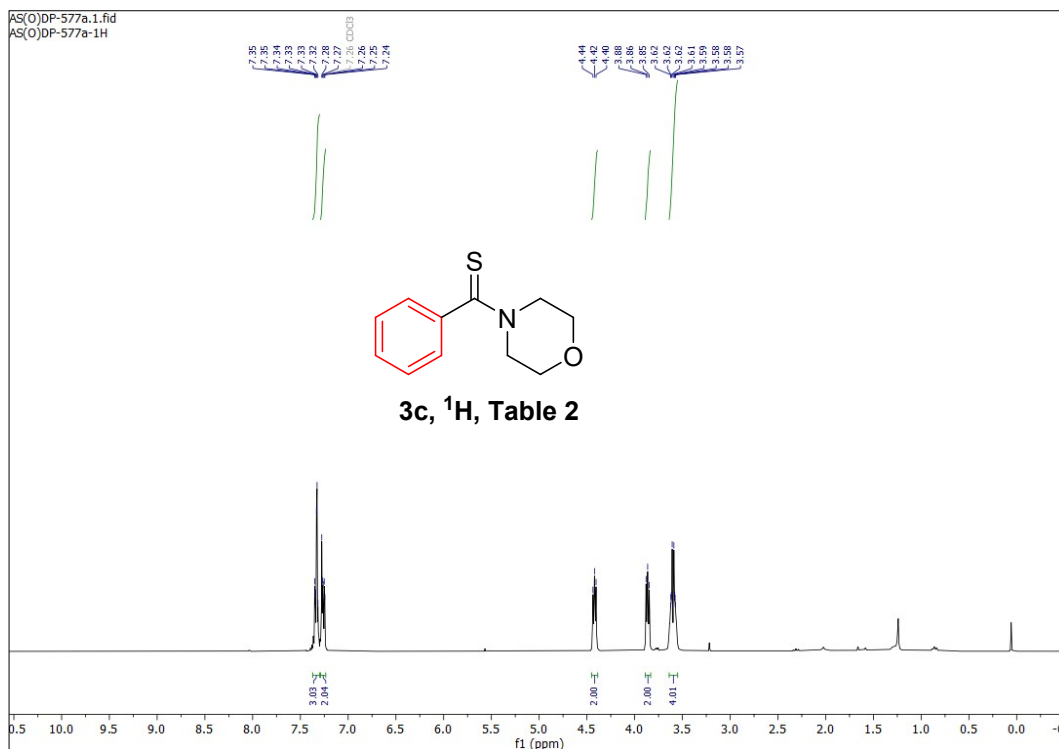
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3a



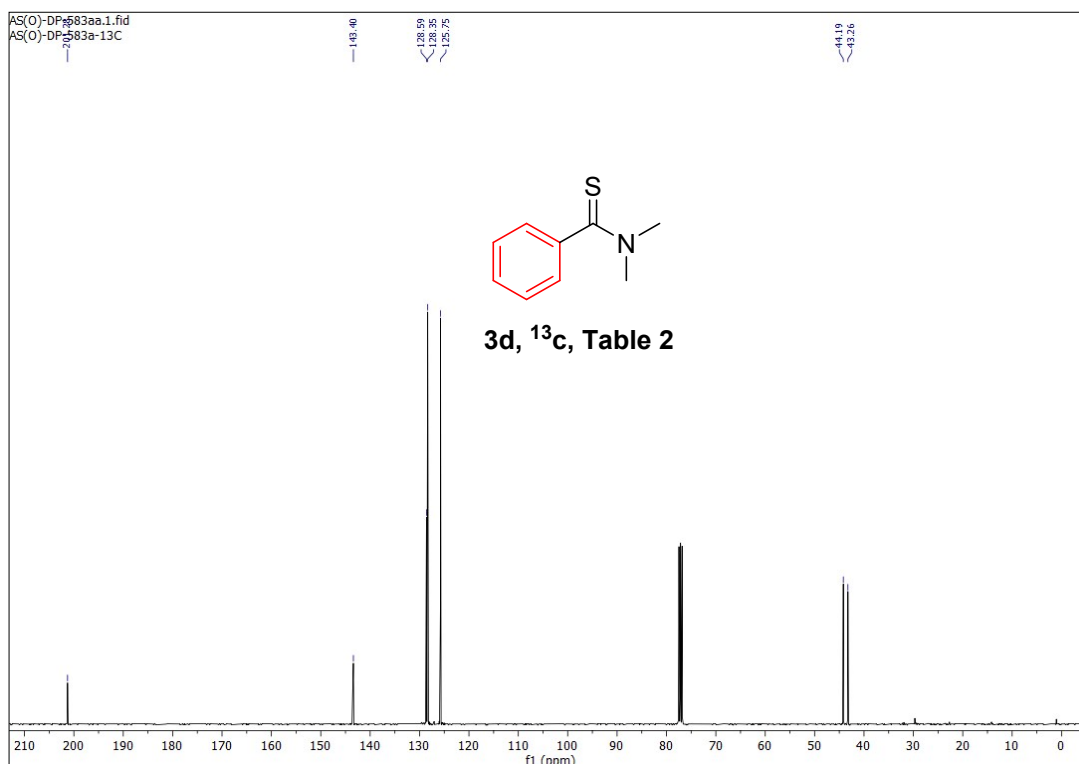
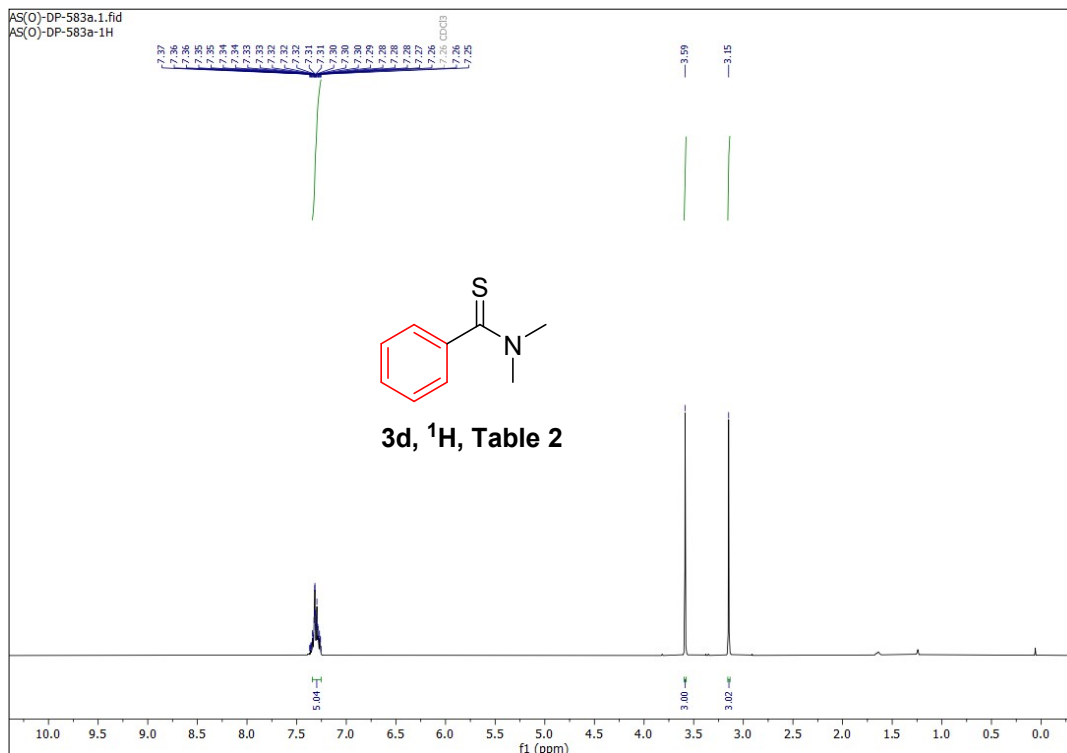
¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectrum of 3b



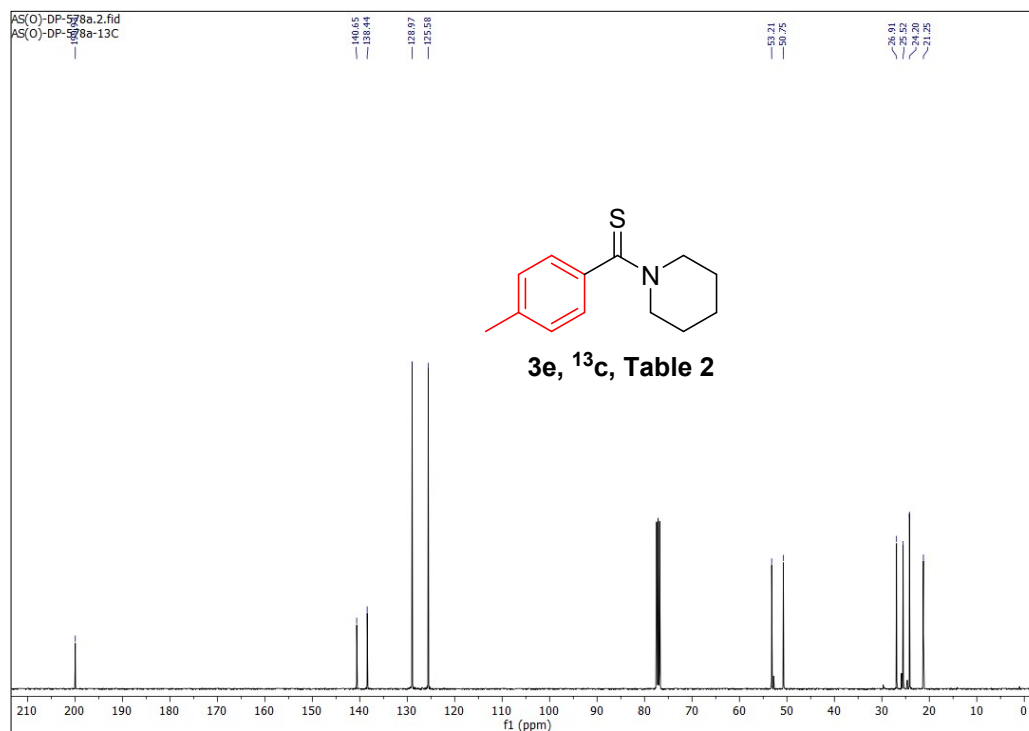
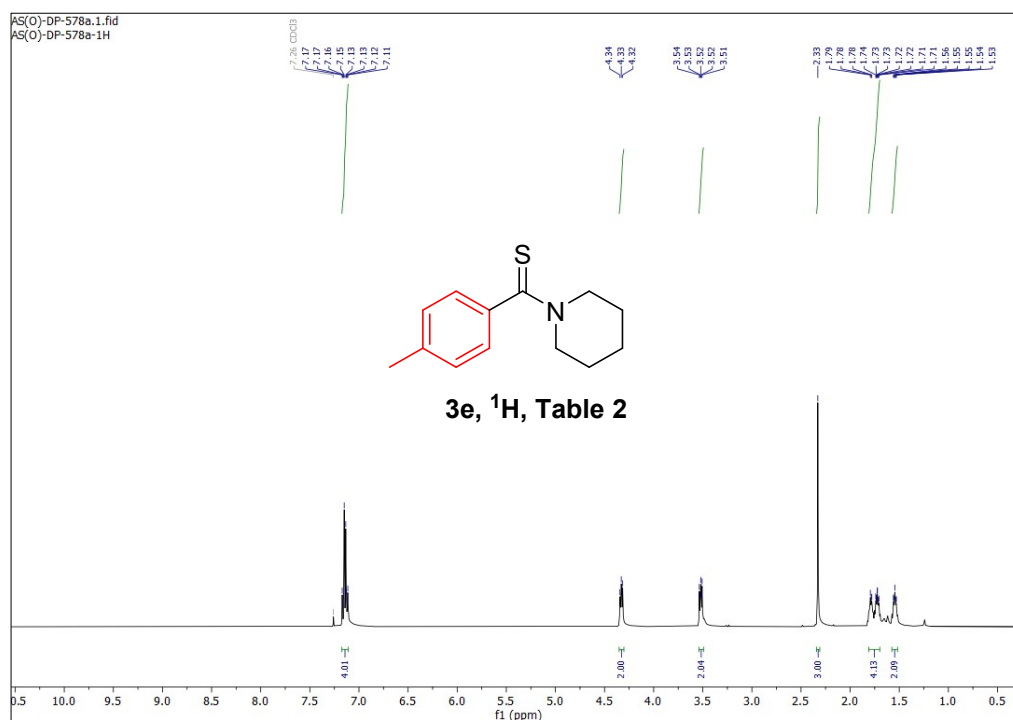
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3c**



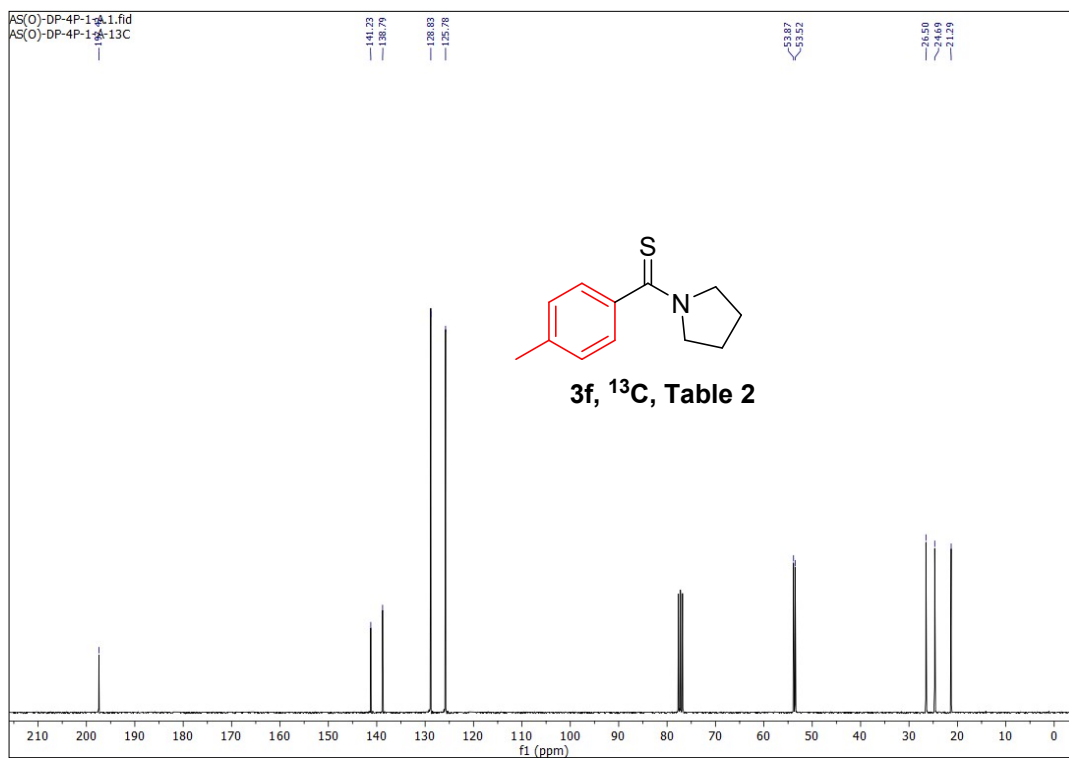
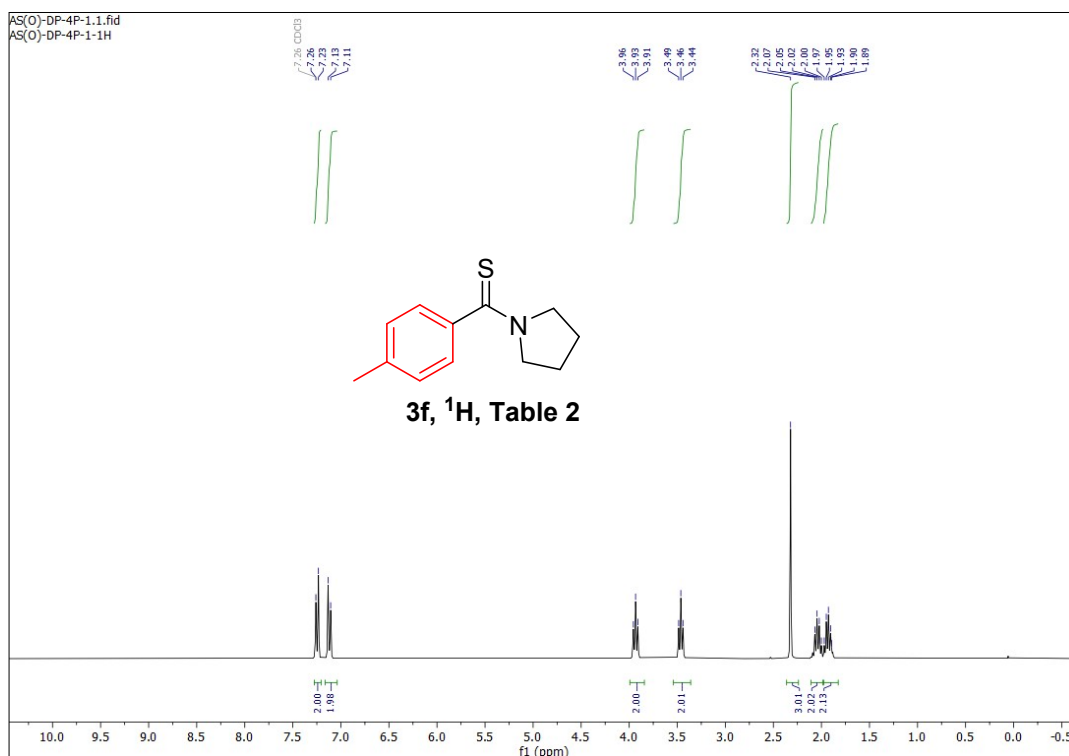
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectrum of 3d



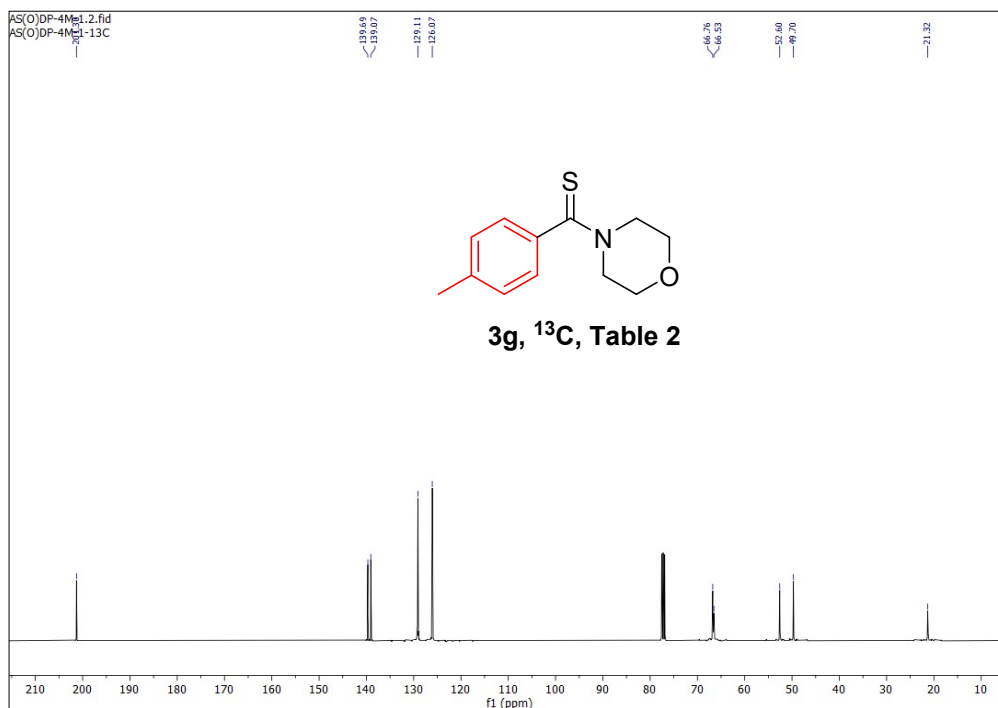
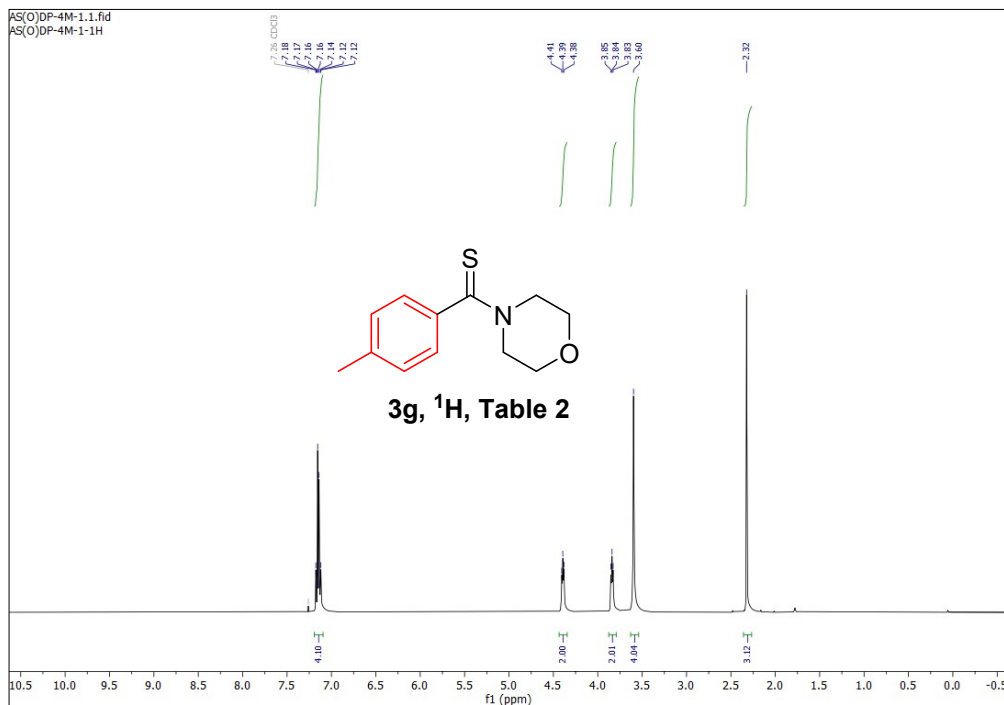
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3e**



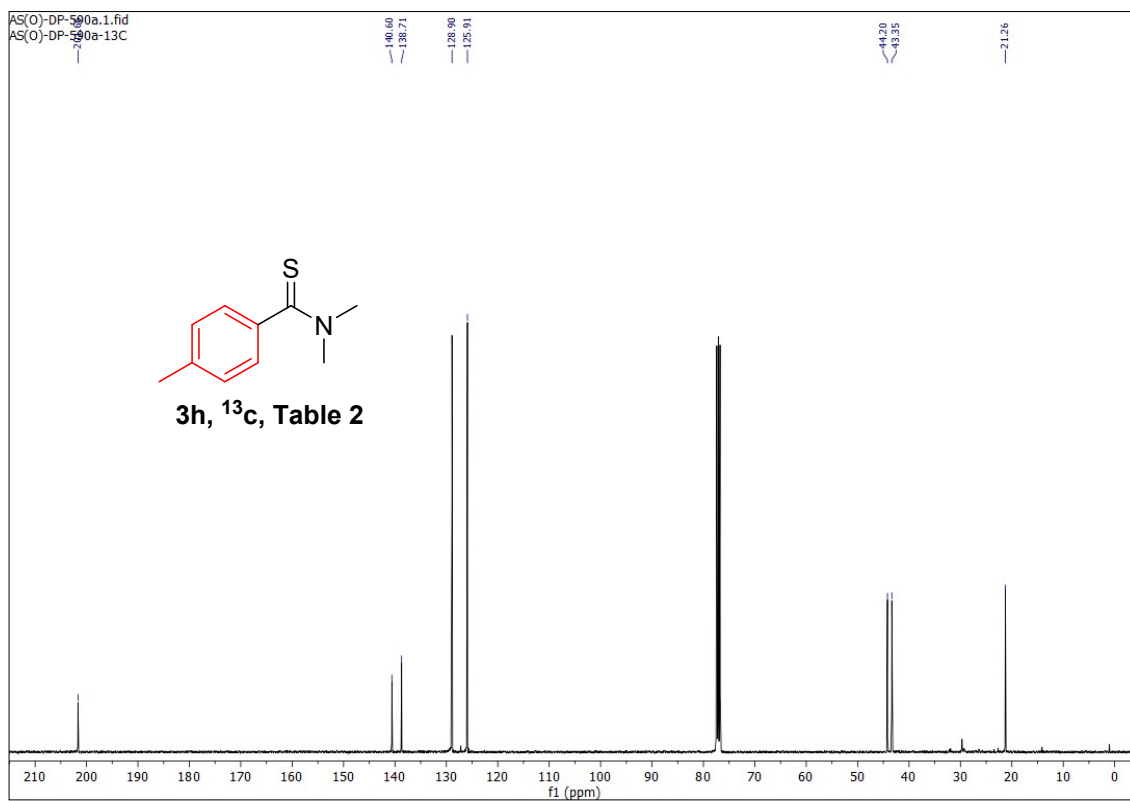
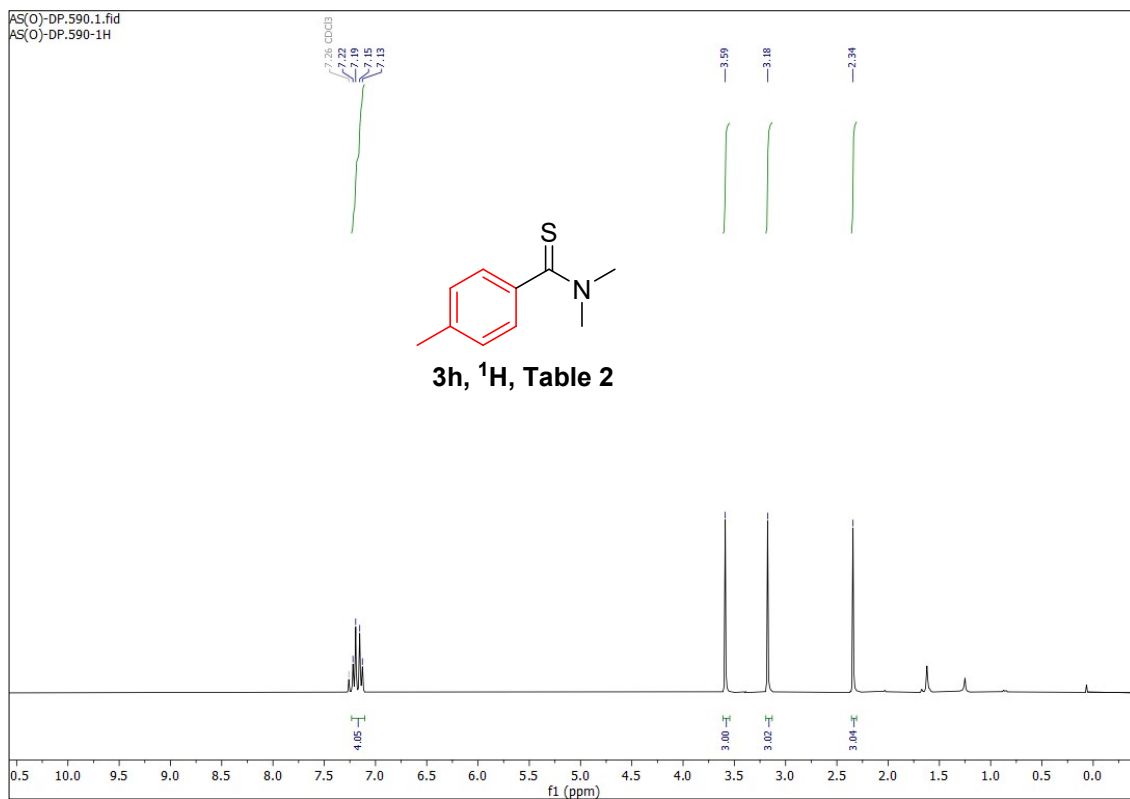
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectrum of 3f



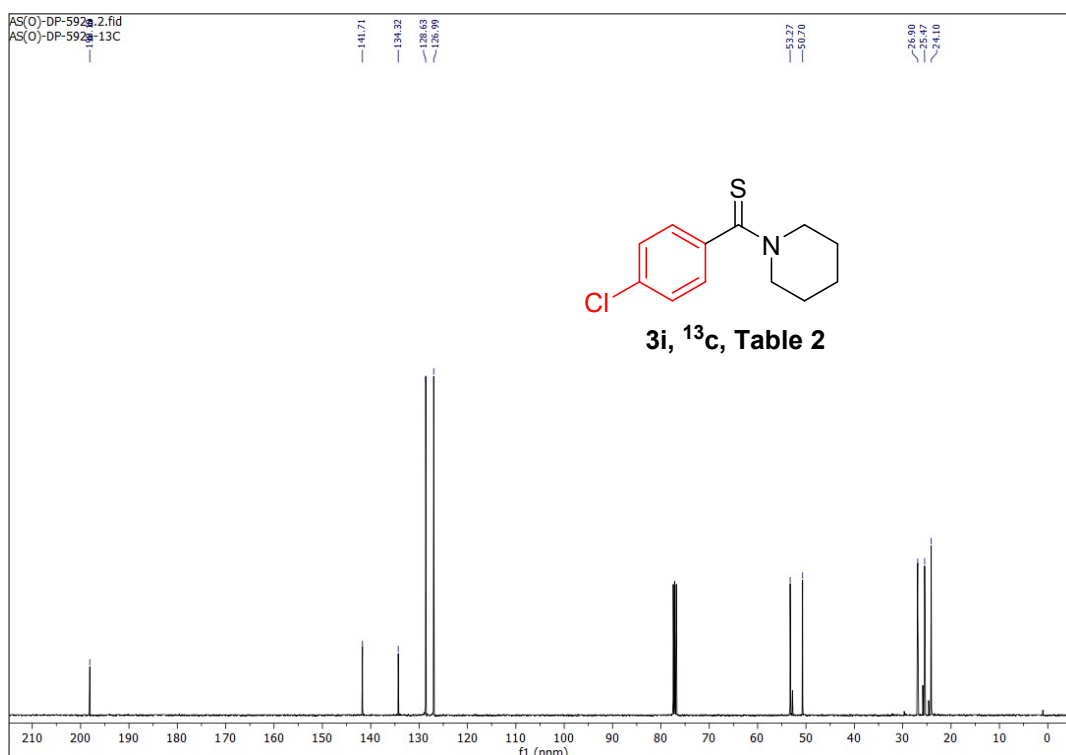
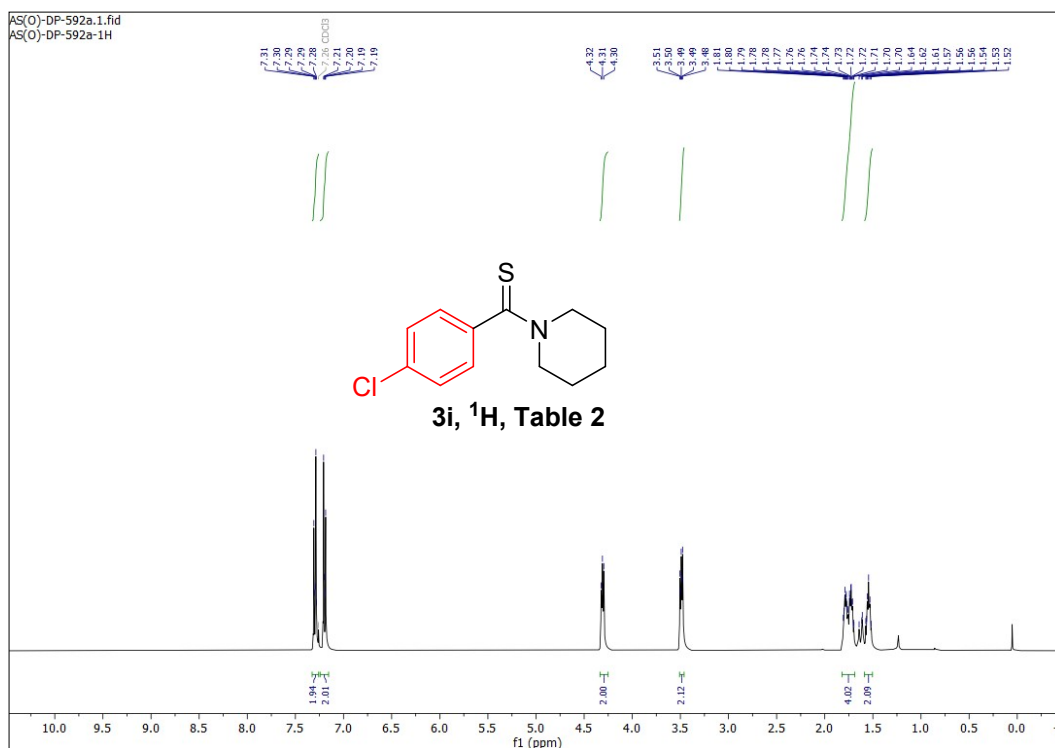
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3g**



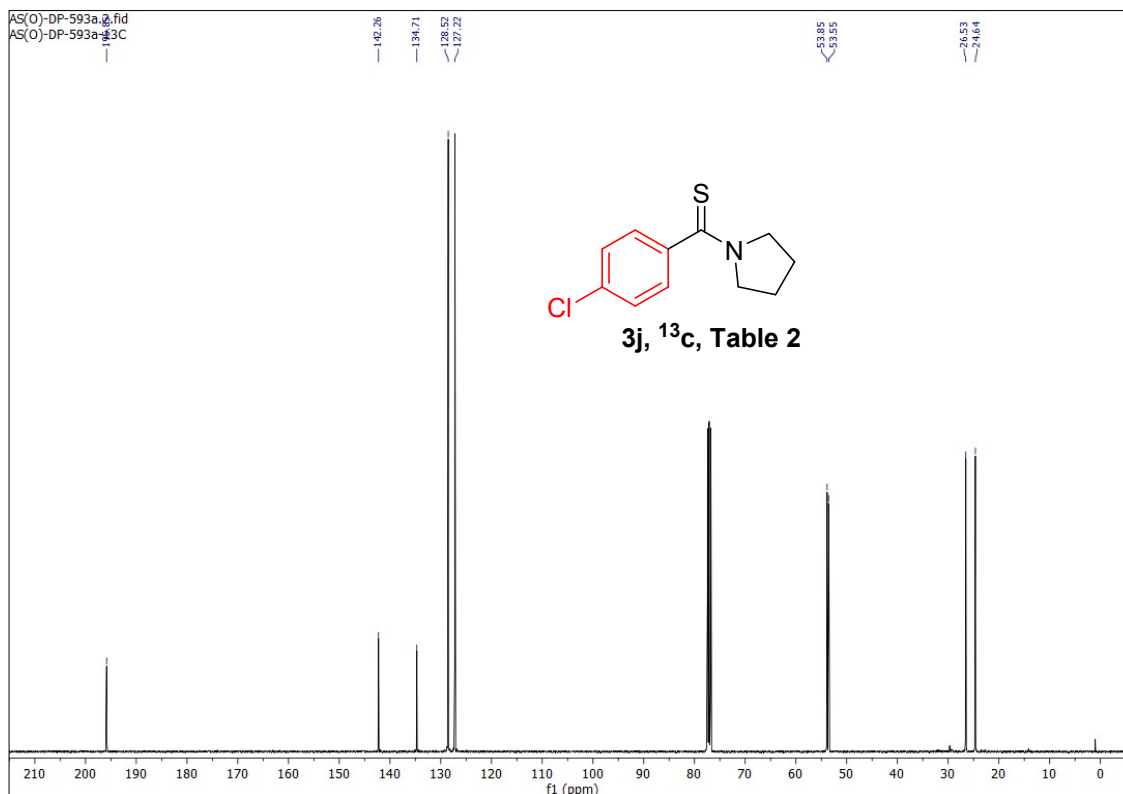
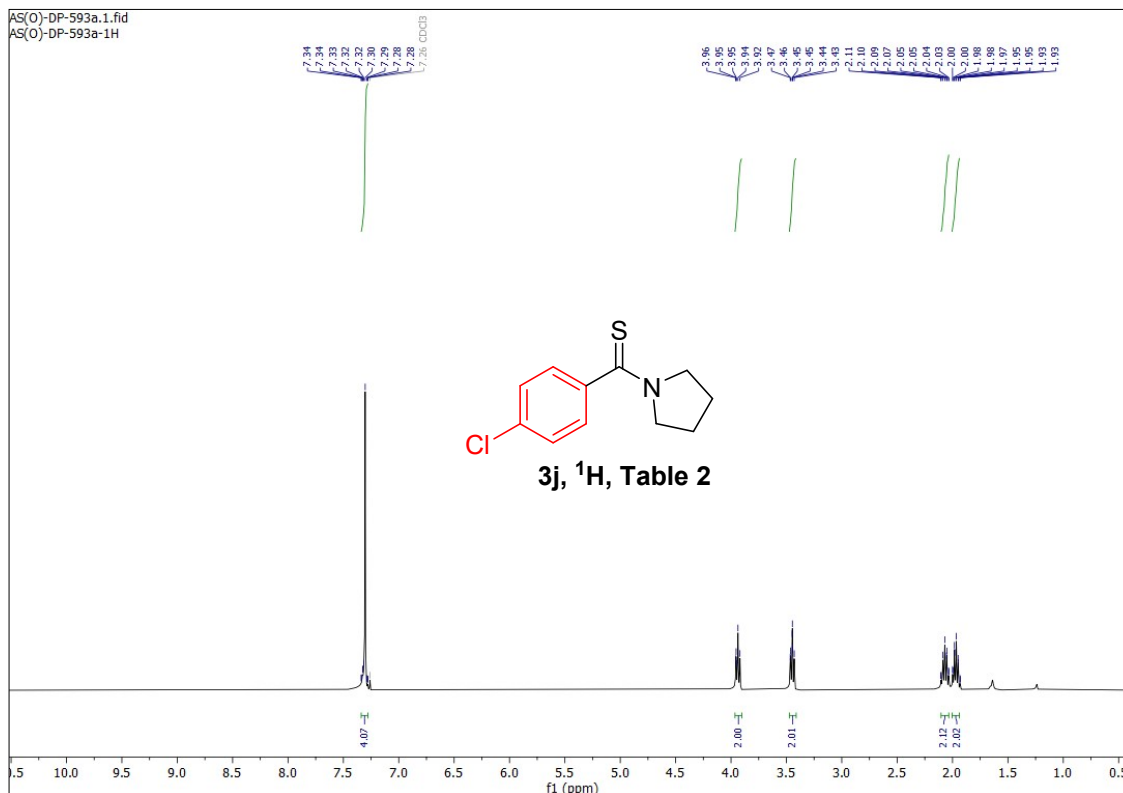
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectrum of 3h



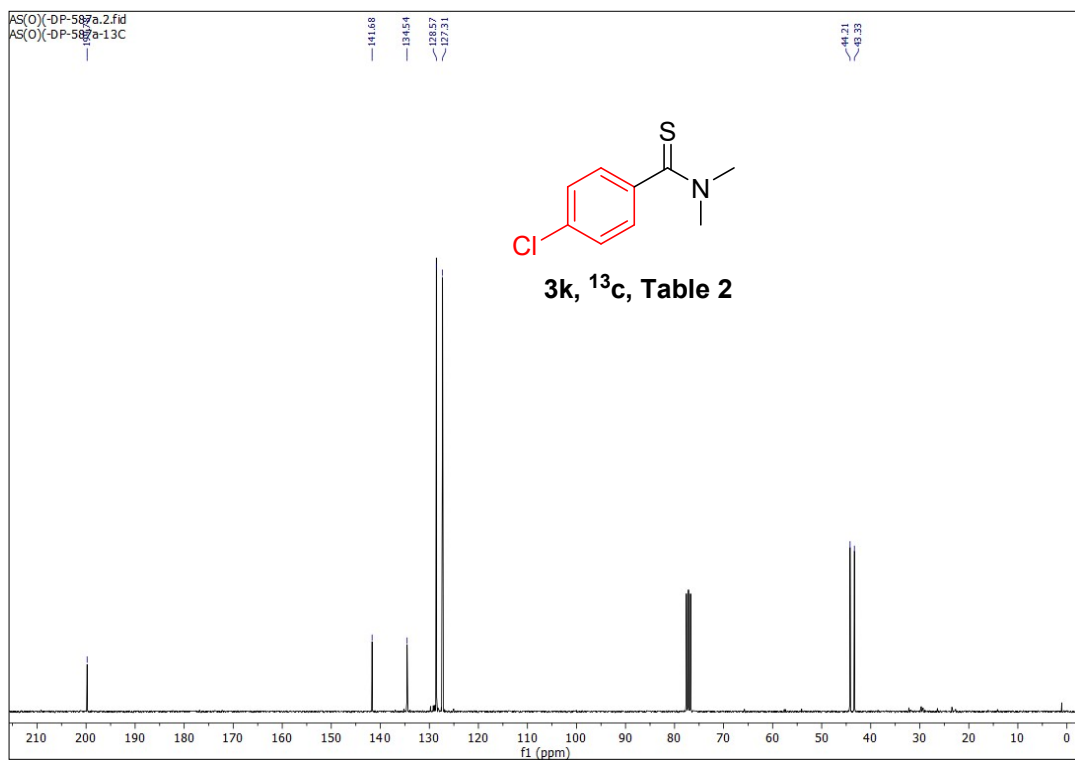
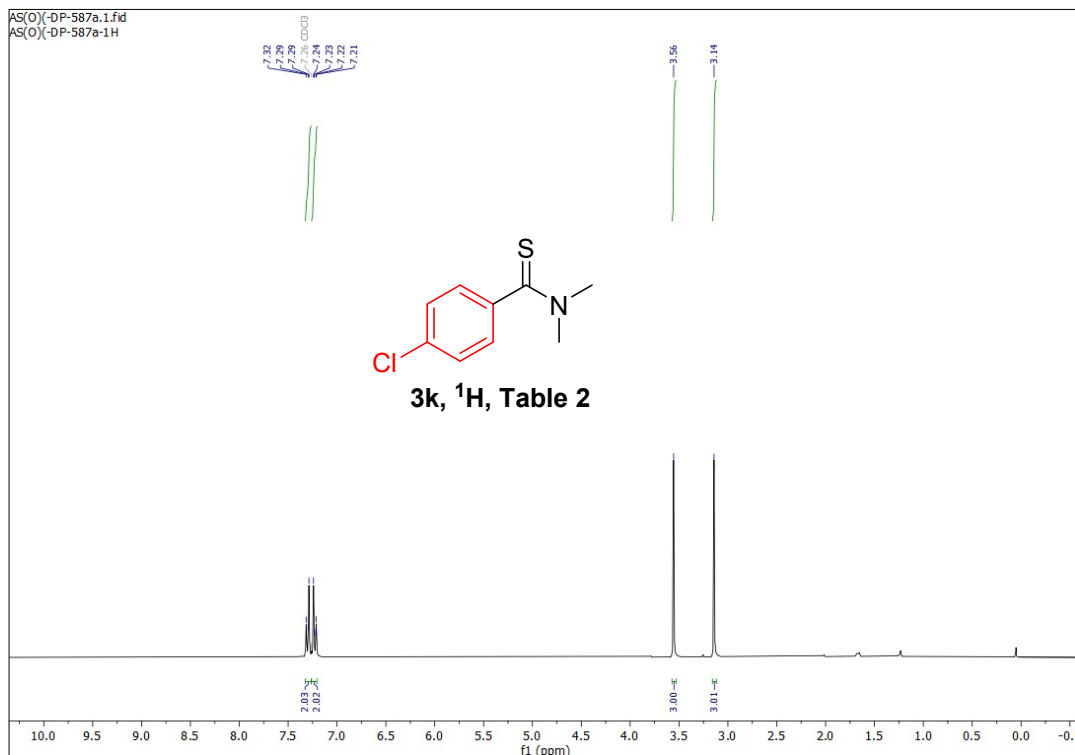
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectrum of 3i



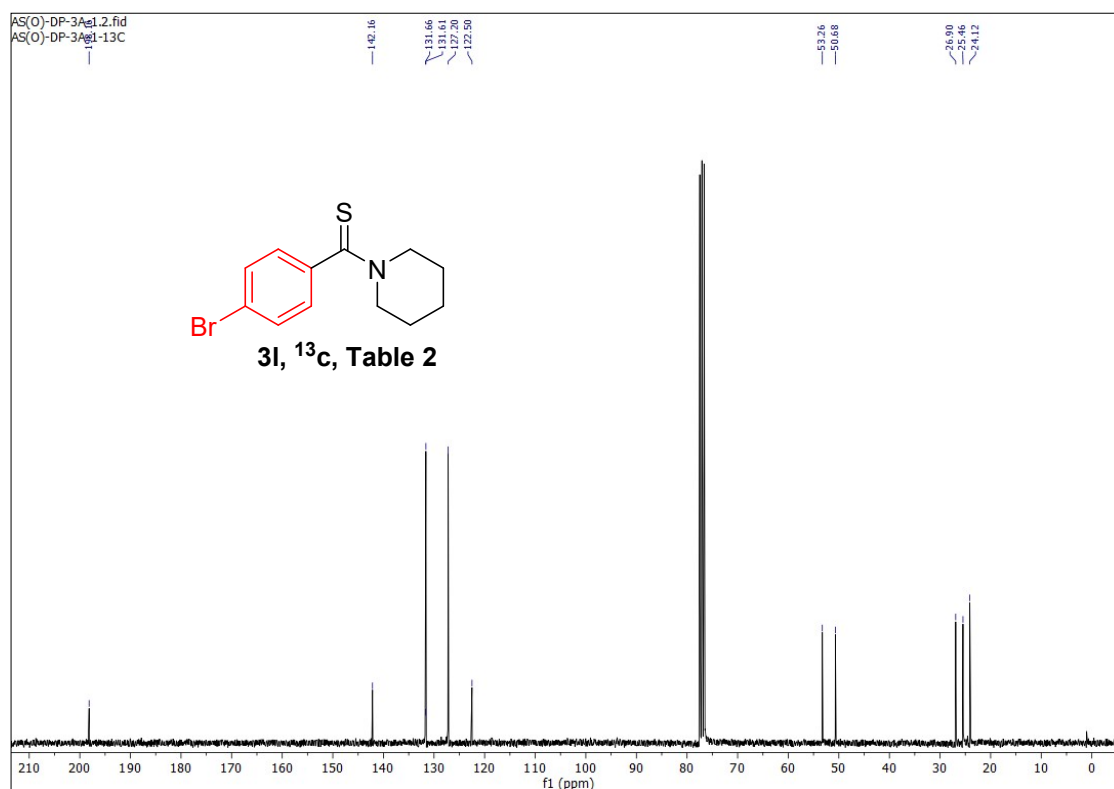
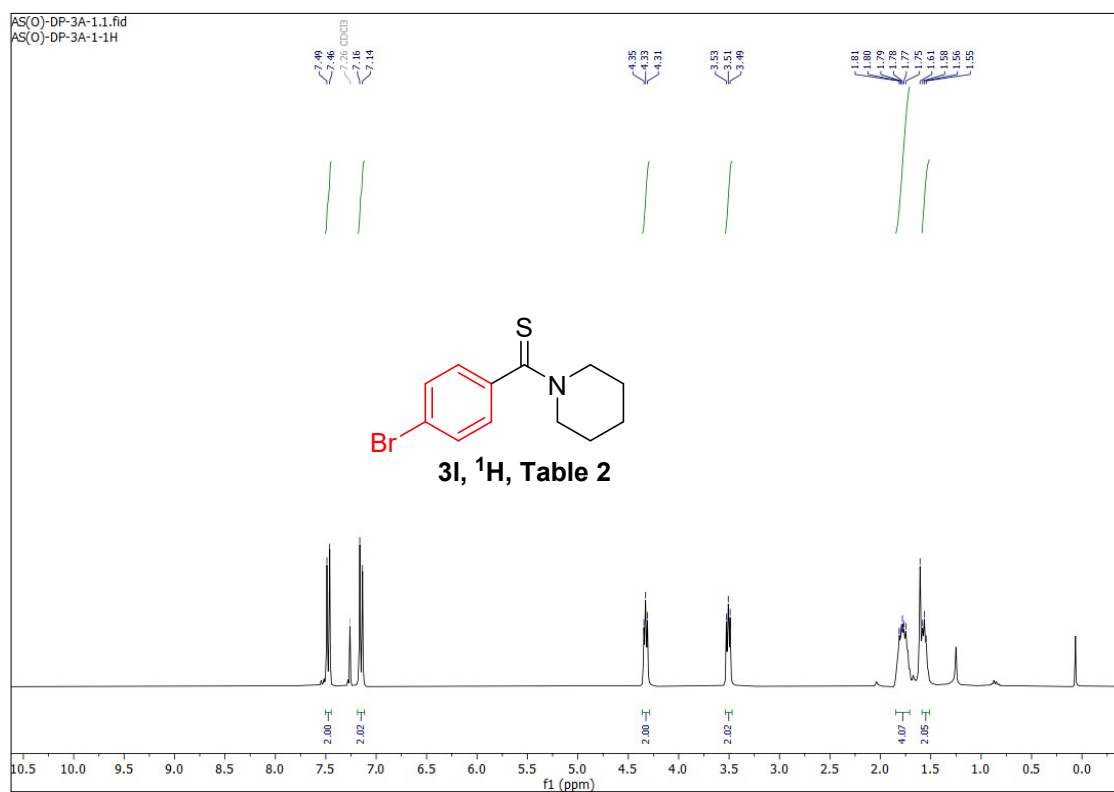
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3j**



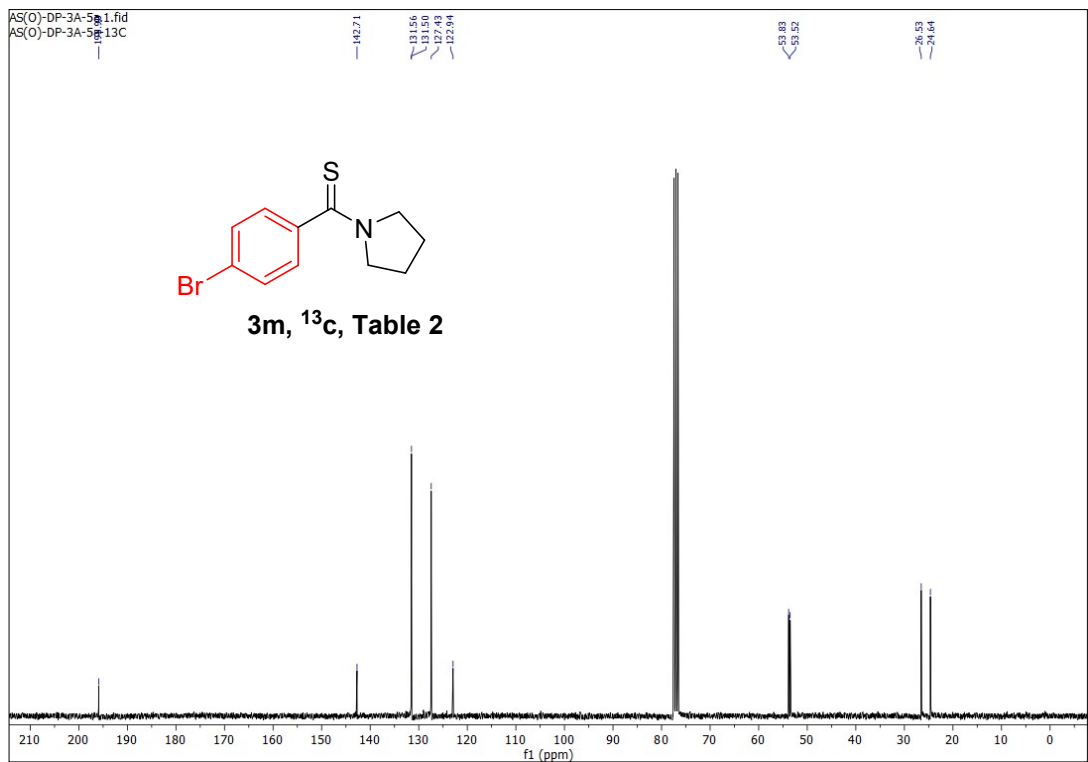
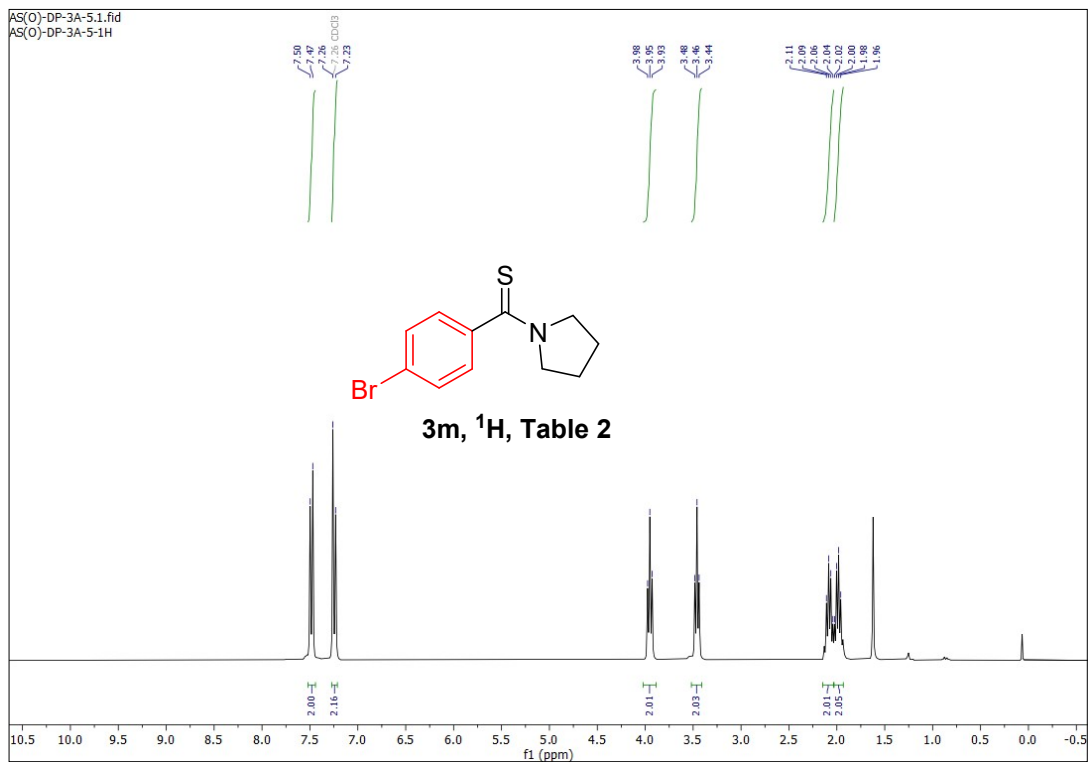
¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectrum of 3k



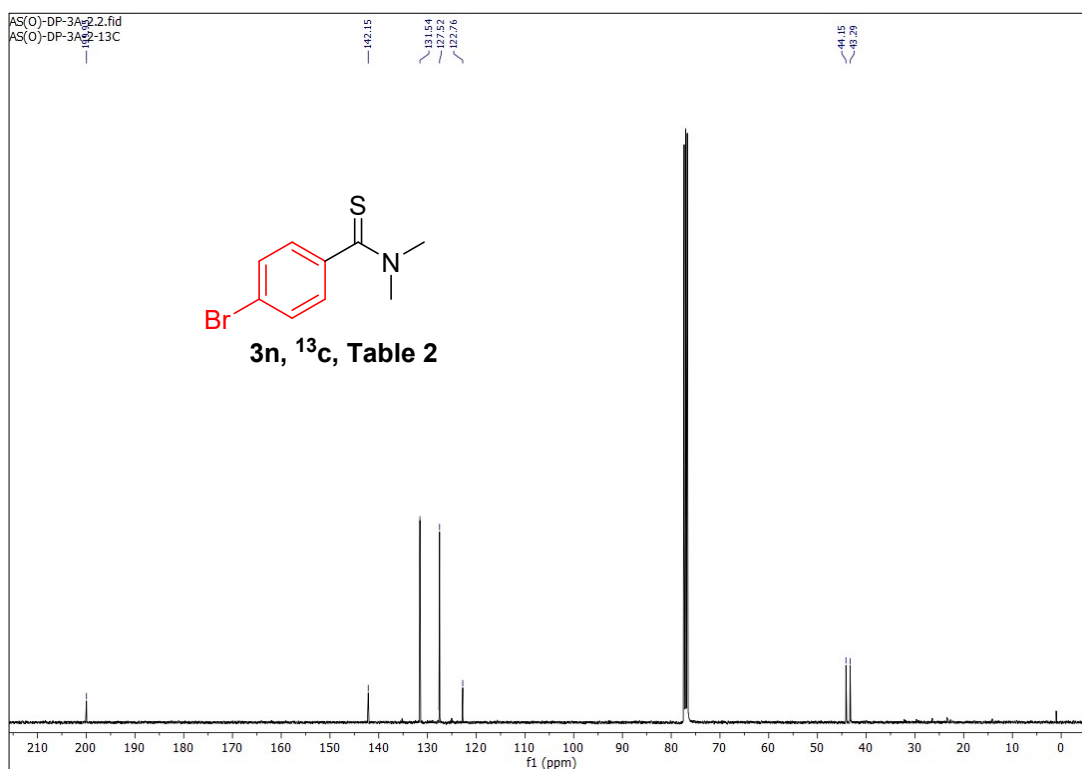
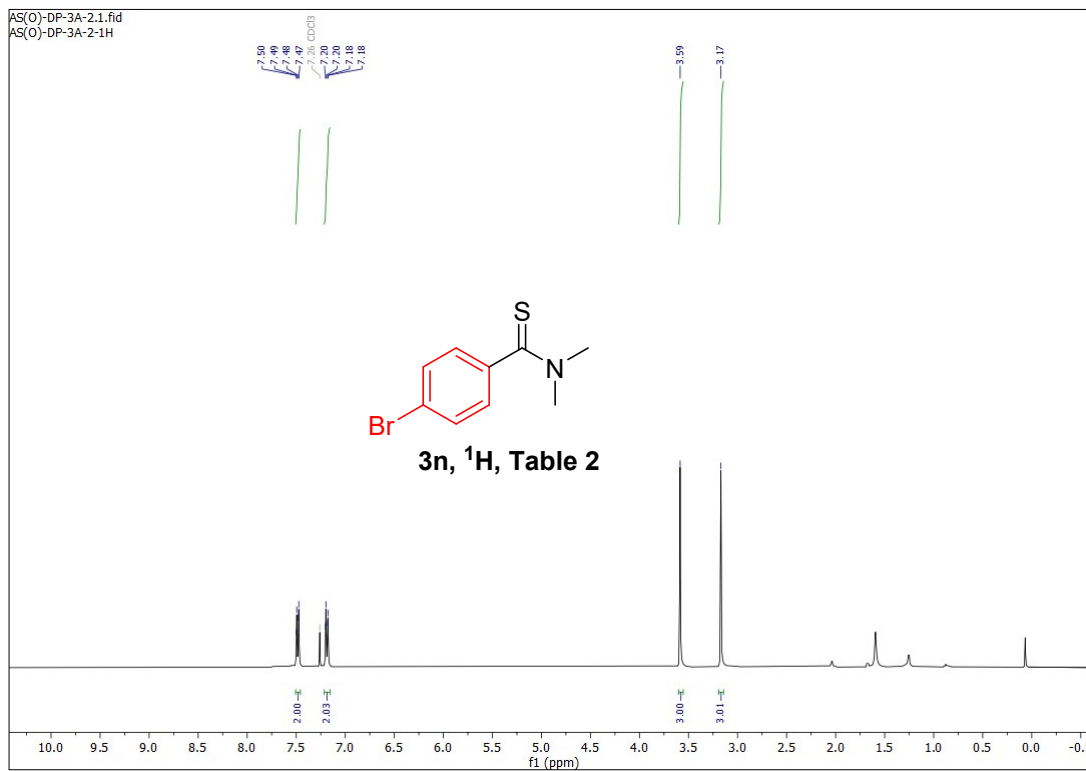
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3l



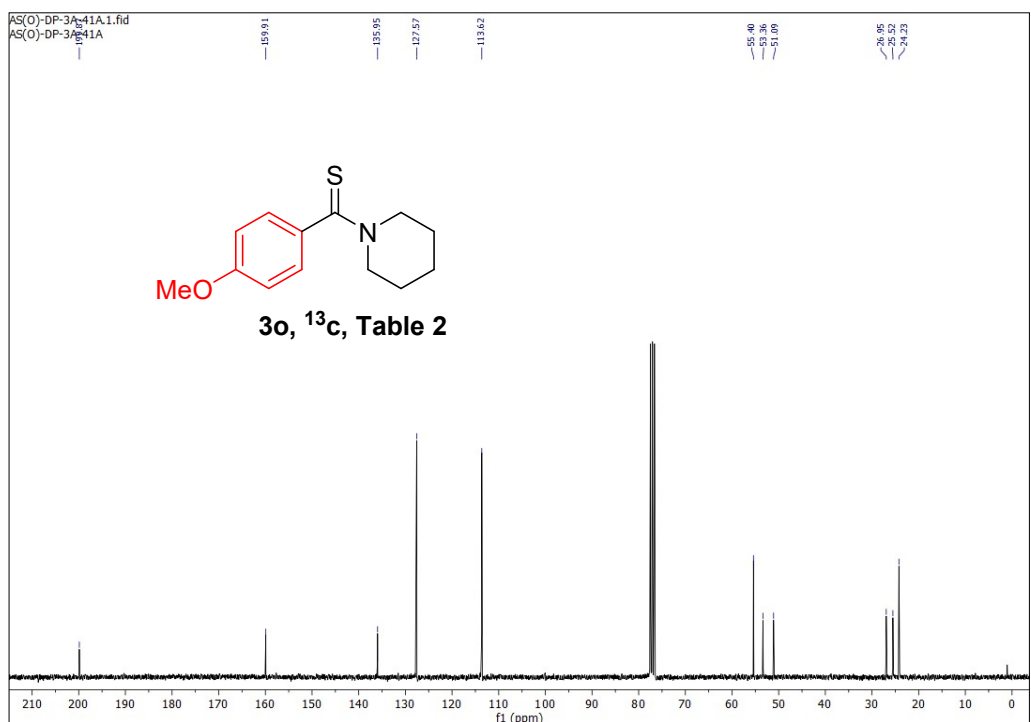
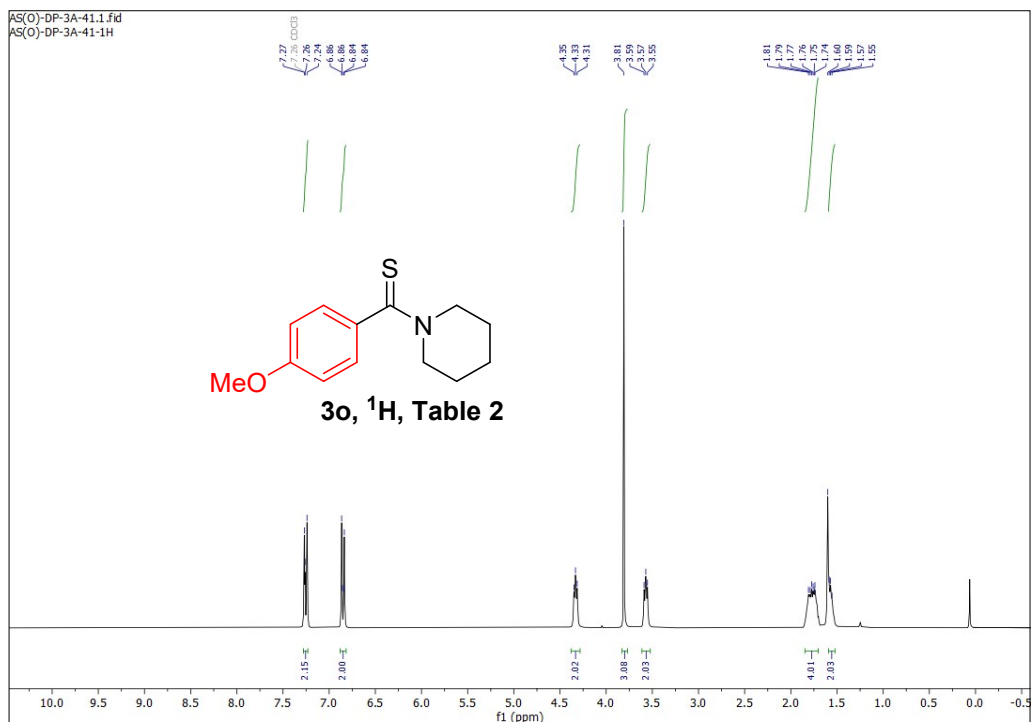
¹H NMR (300 MHz, CDCl₃) and ¹³C NMR (75 MHz, CDCl₃) spectrum of 3m



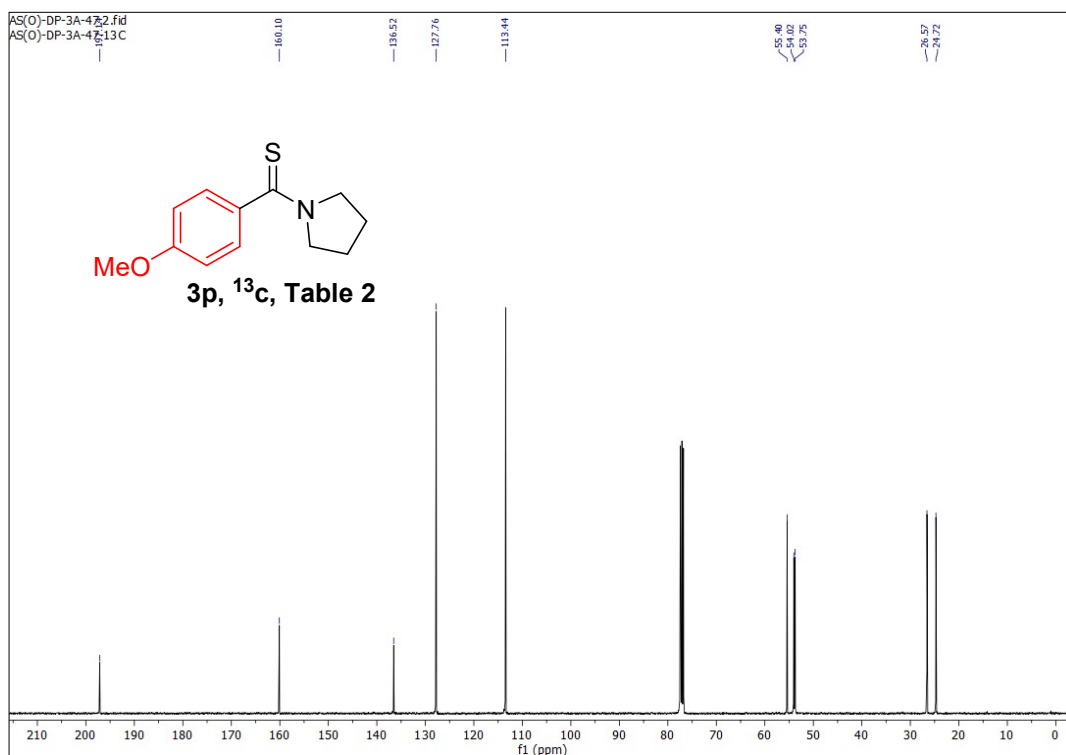
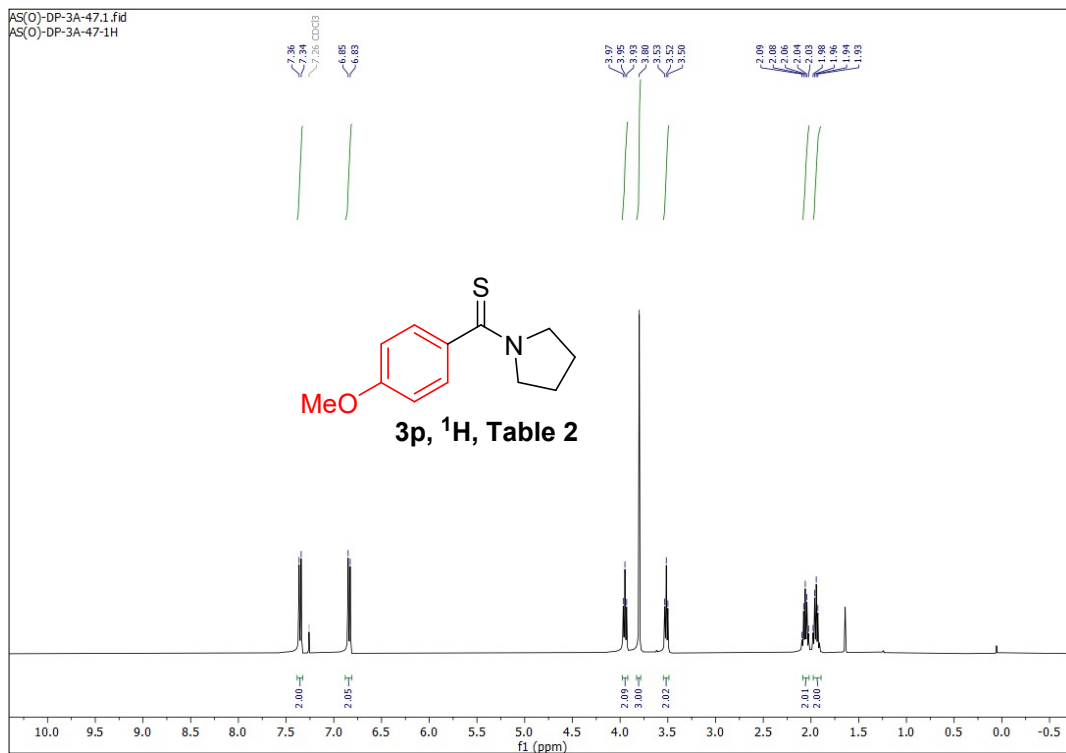
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3n**



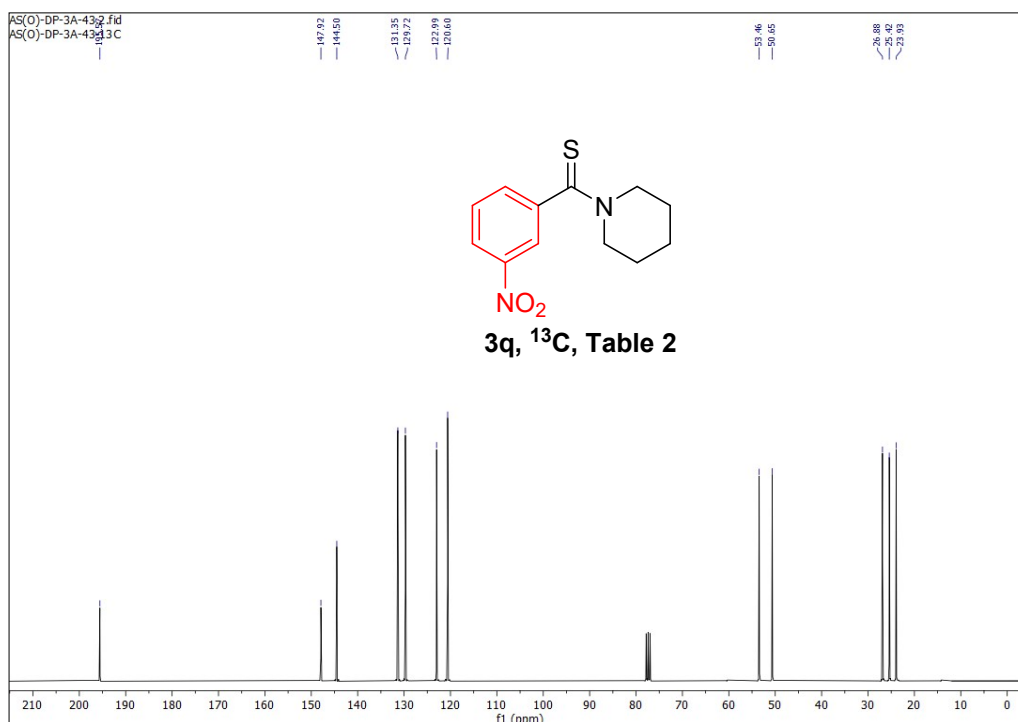
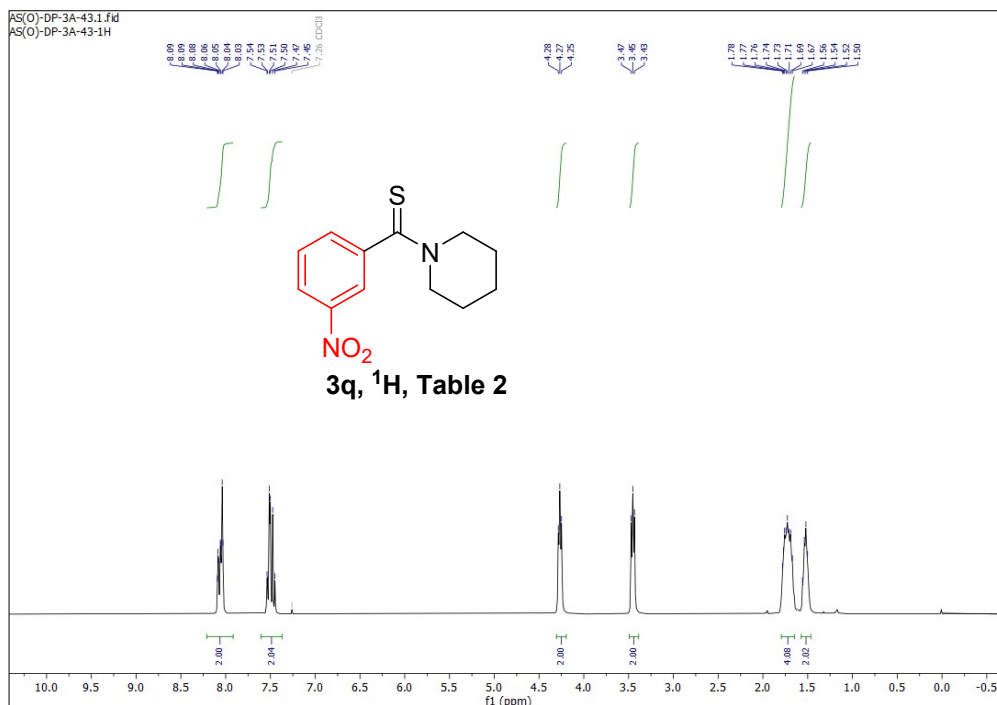
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of **3o**



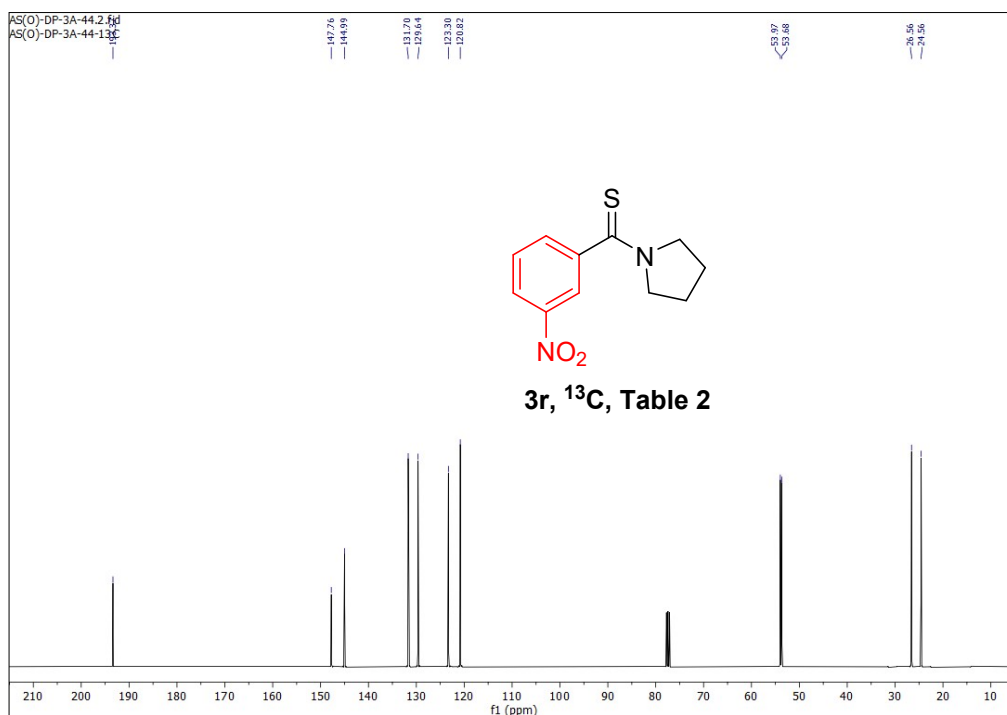
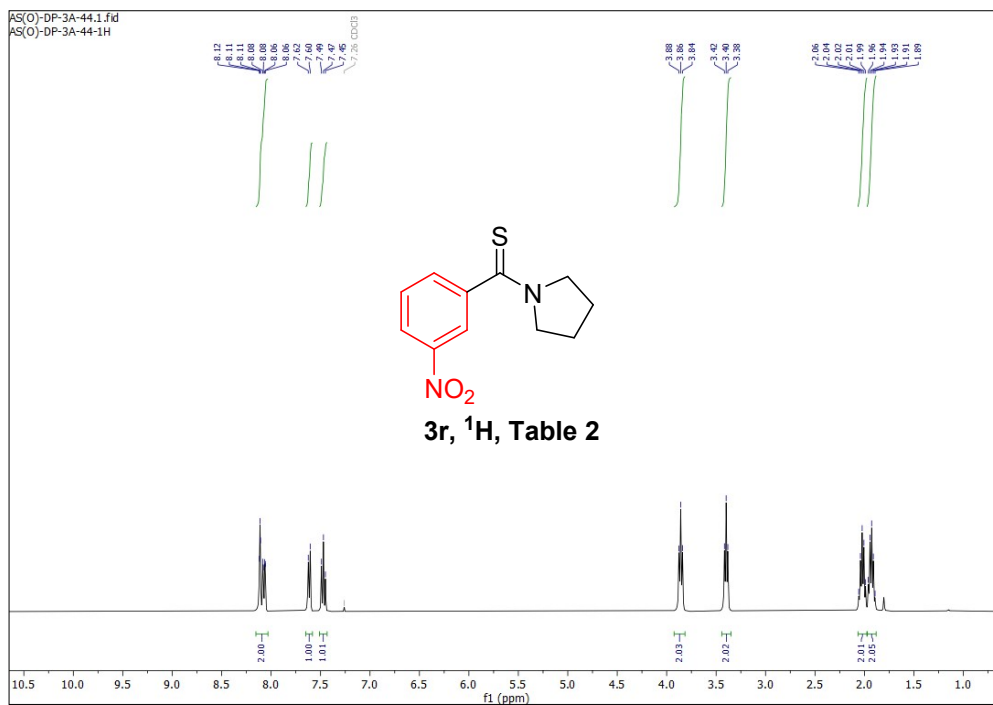
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectrum of 3p



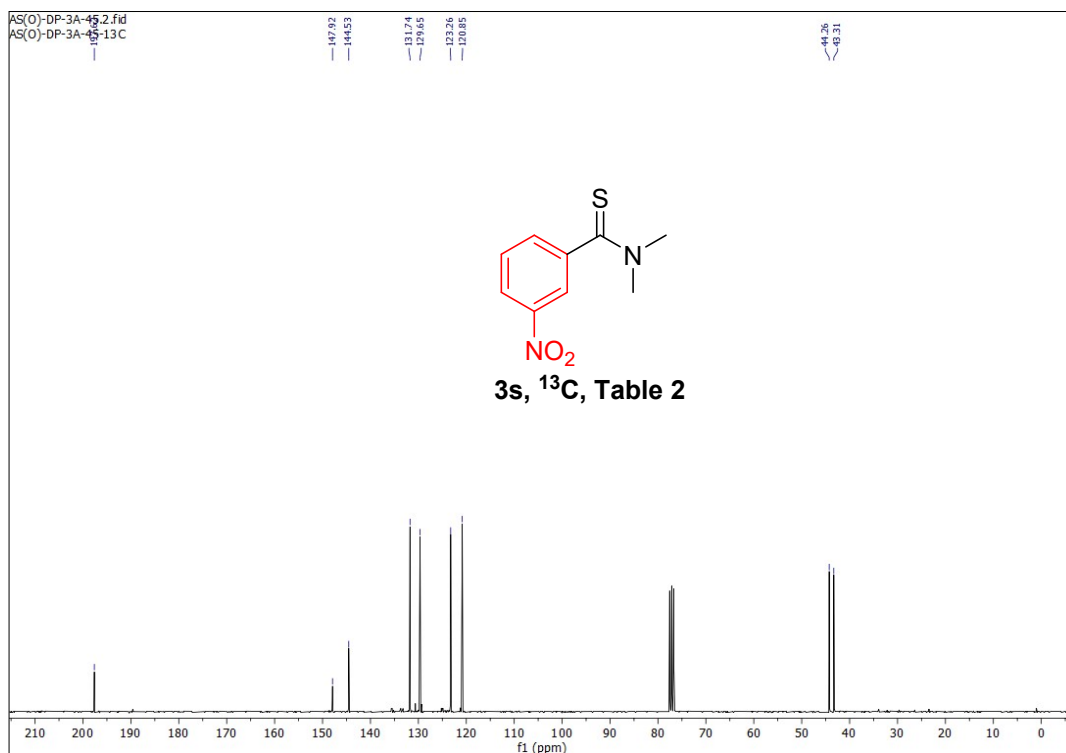
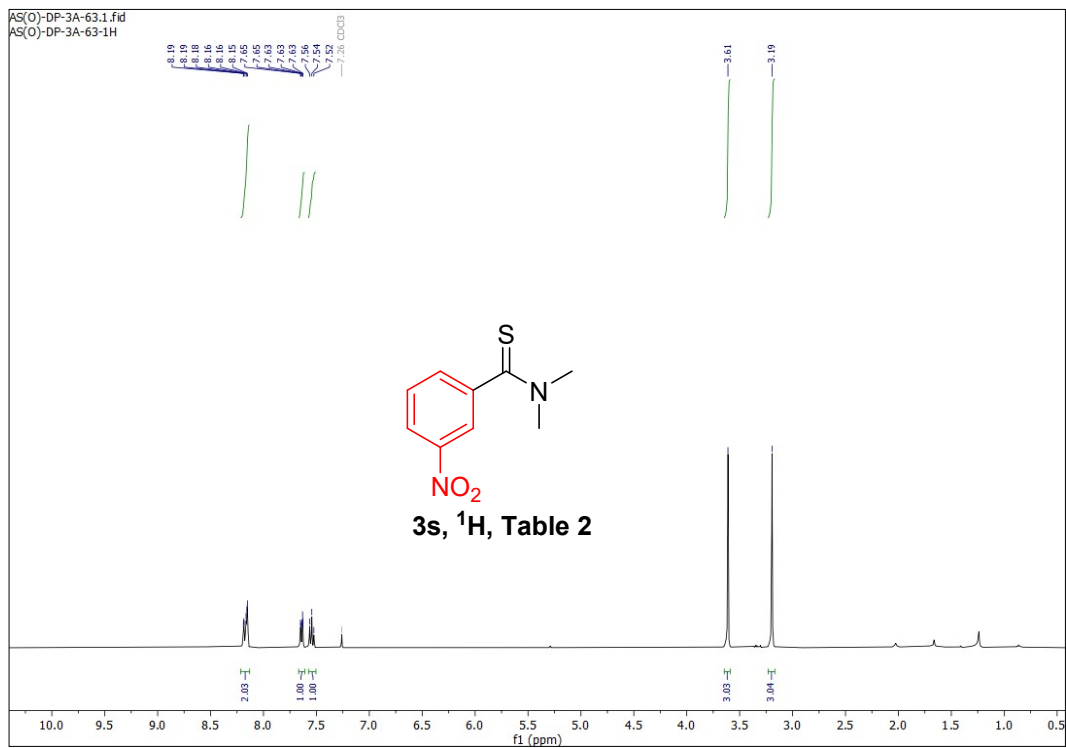
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3q**



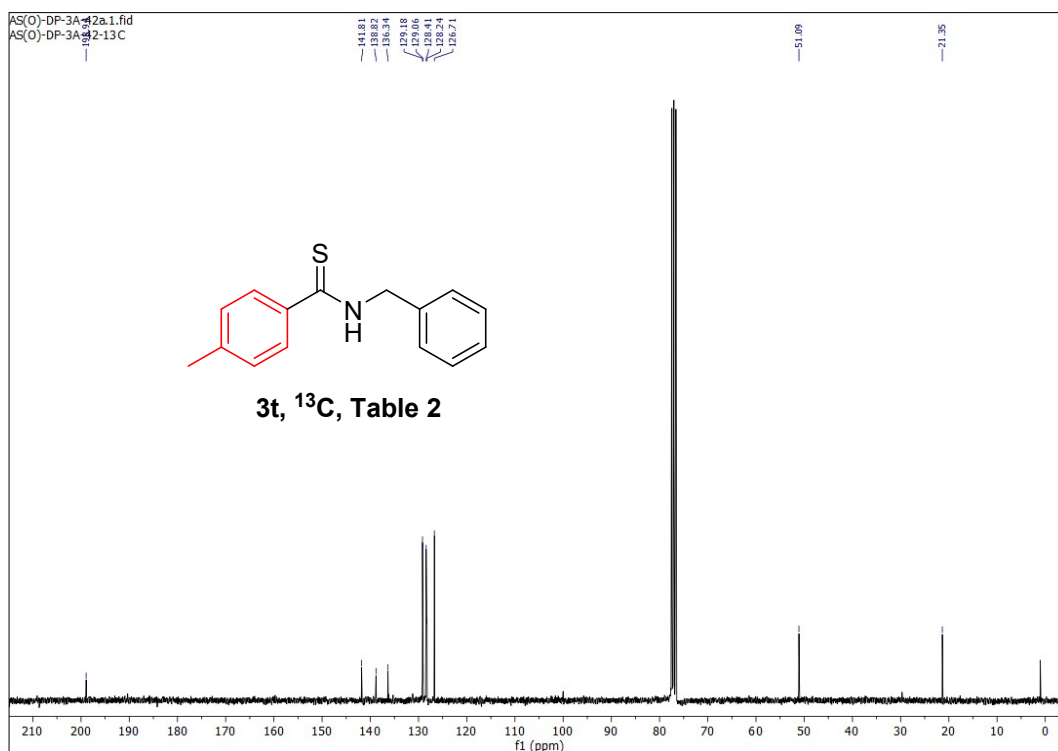
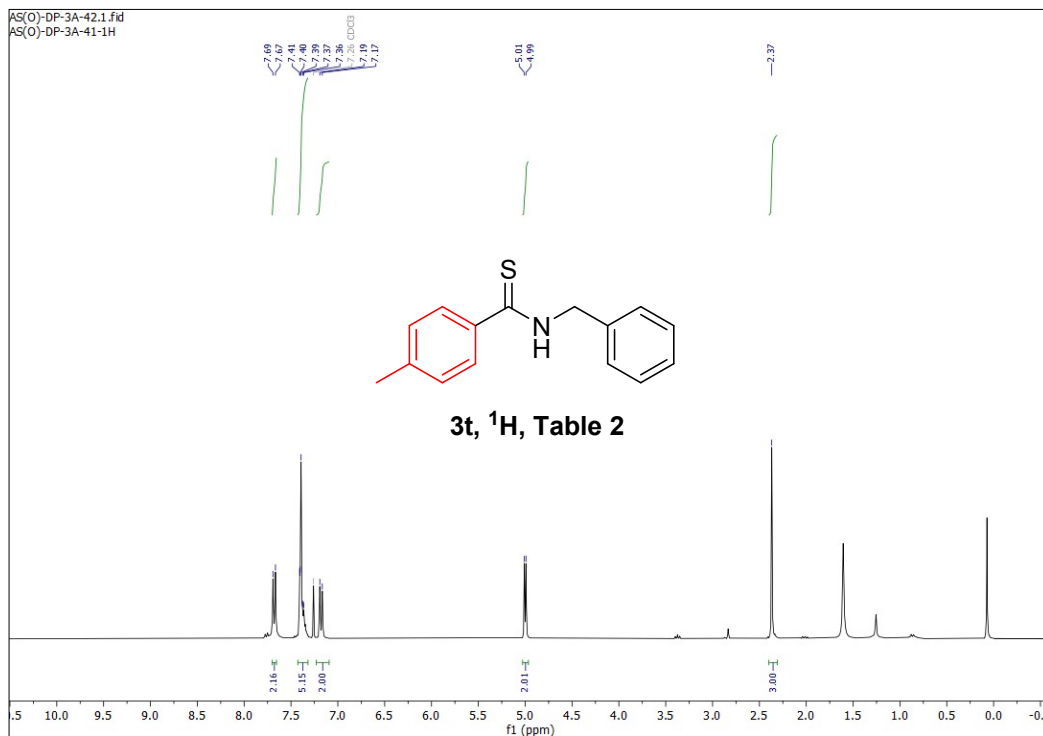
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3r**



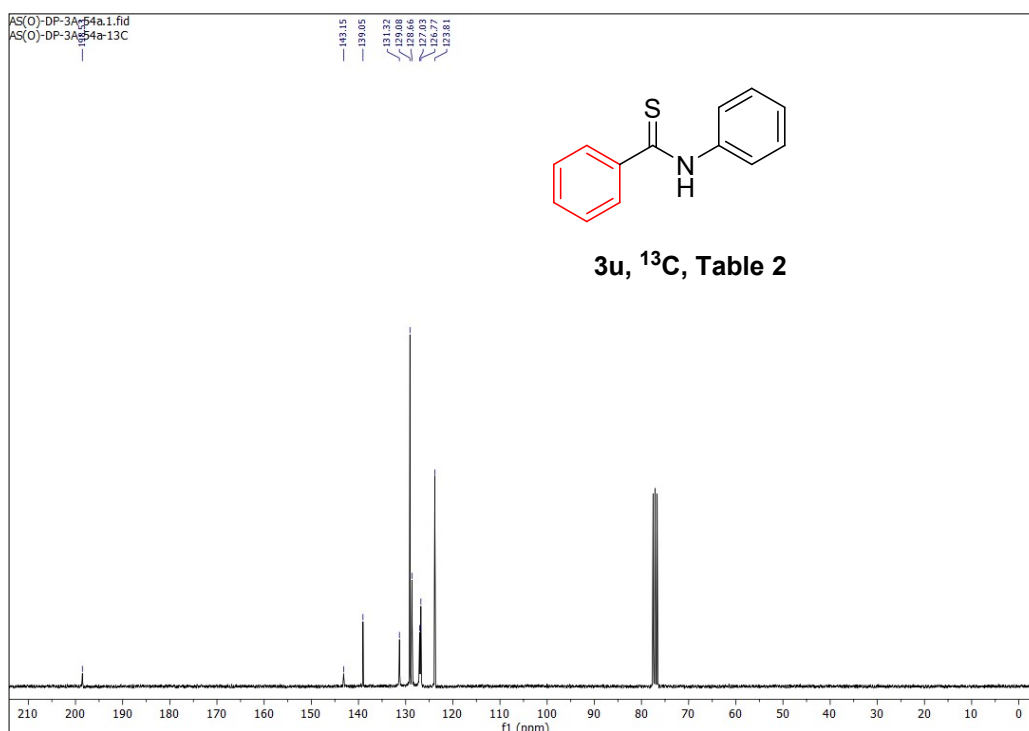
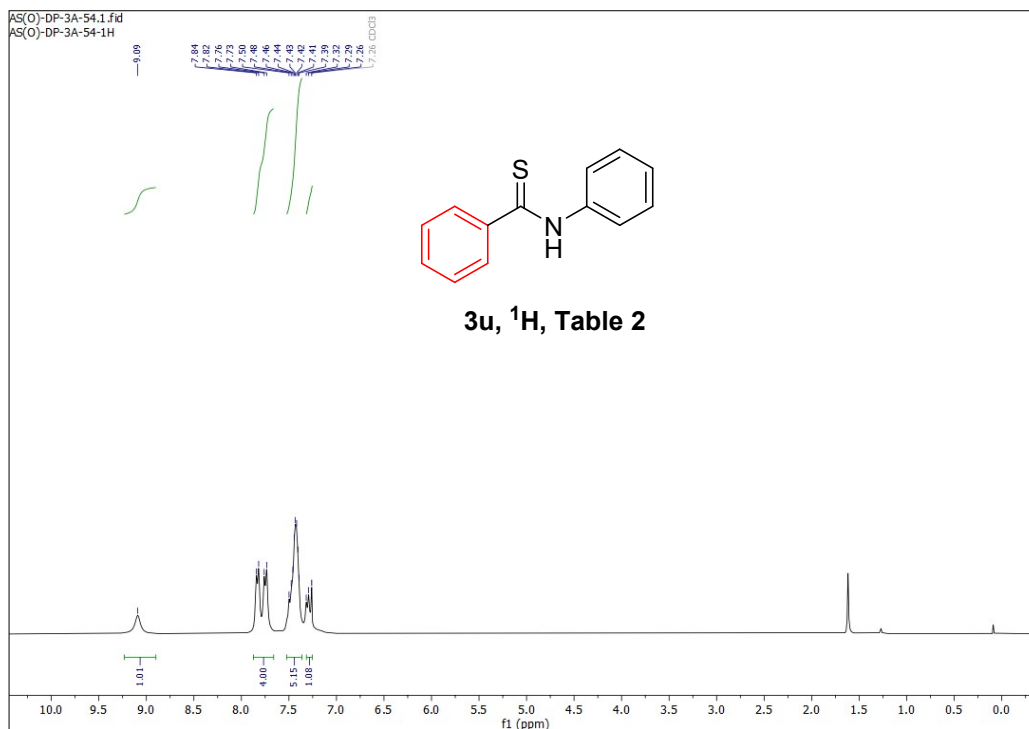
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectrum of 3s



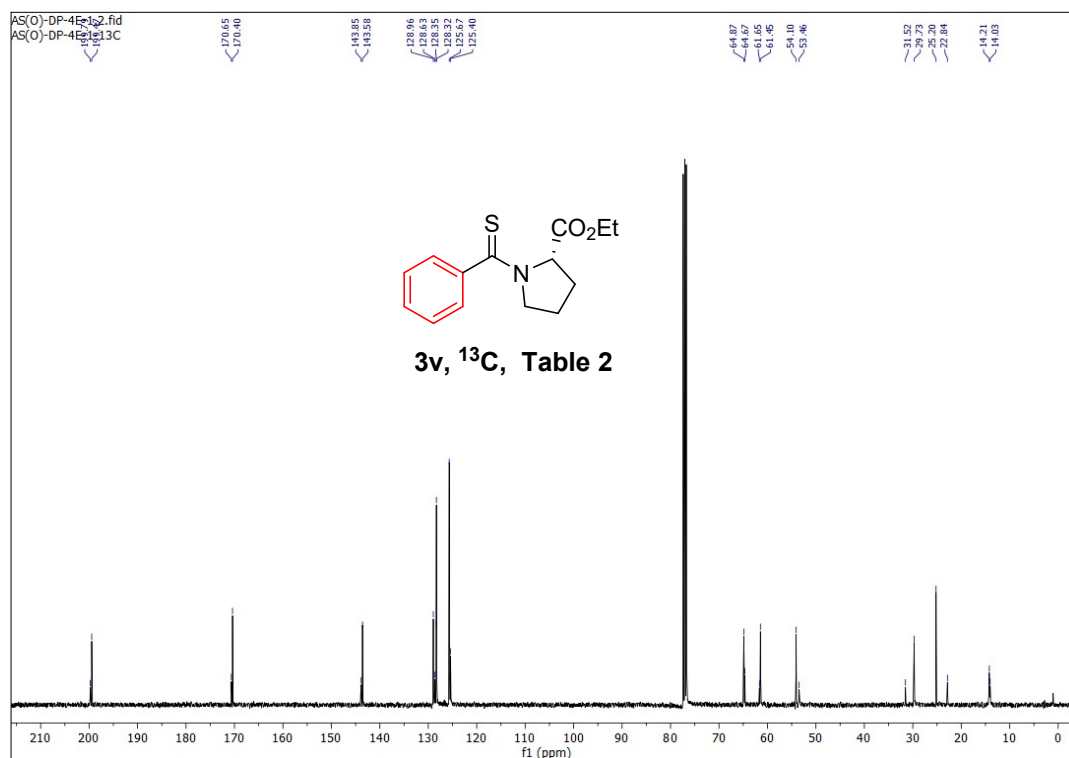
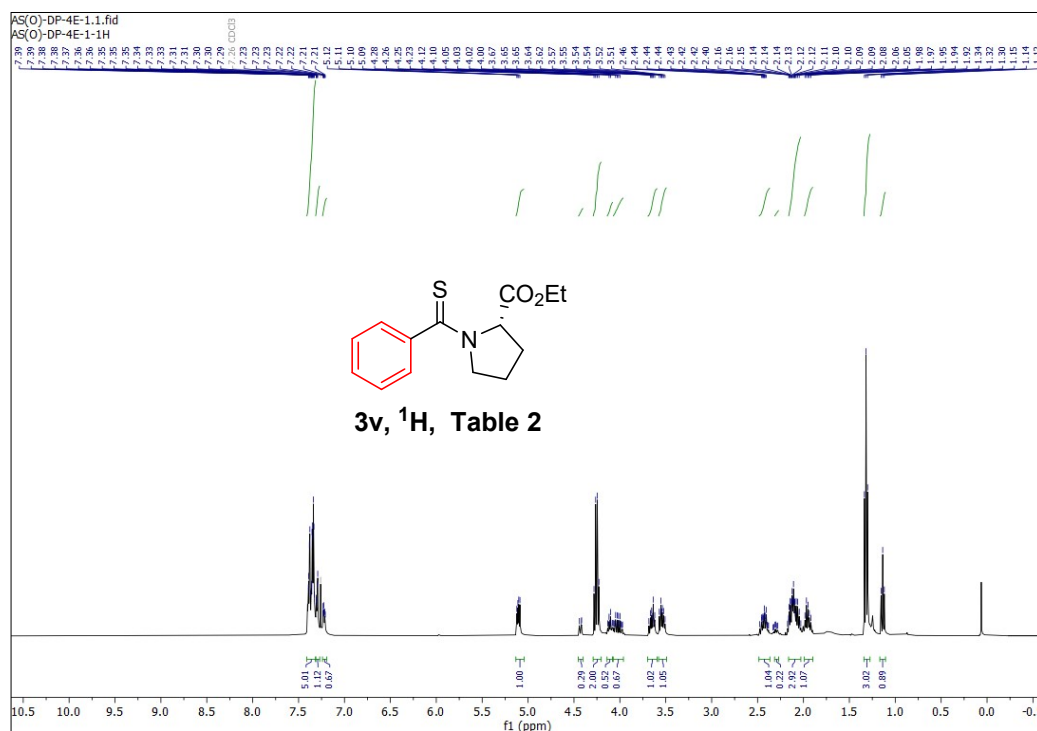
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 3t



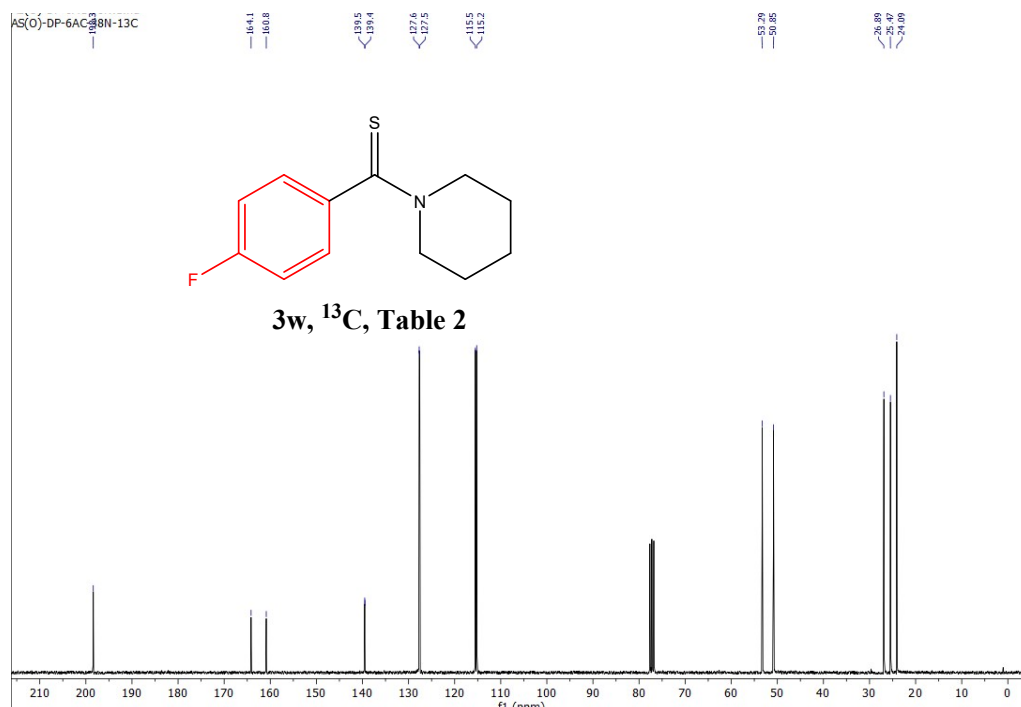
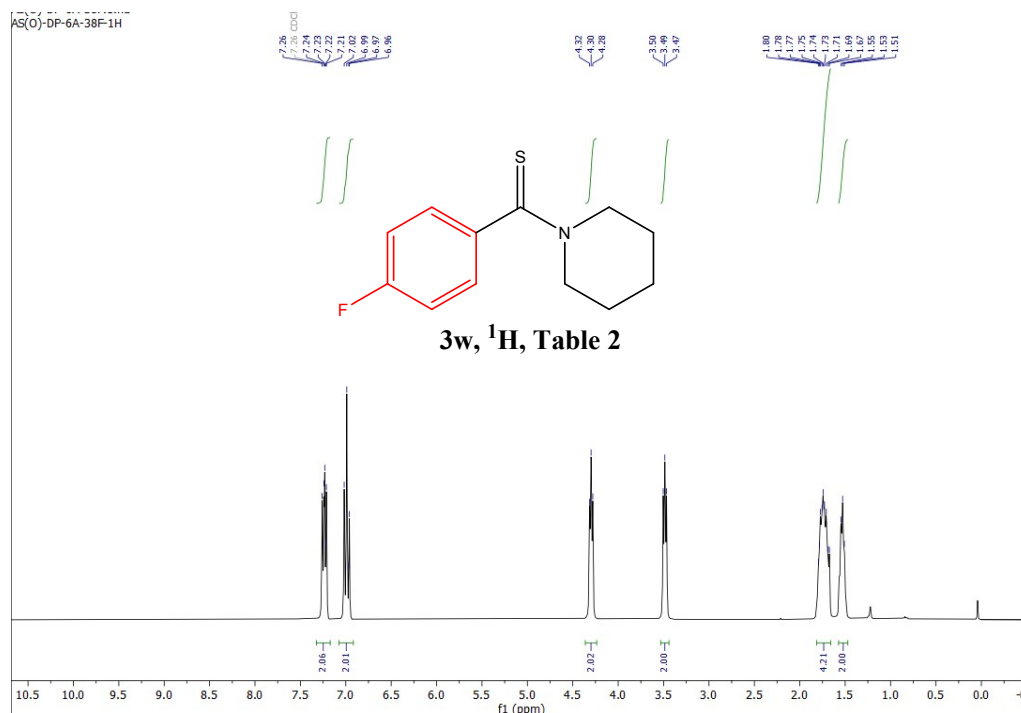
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3u**

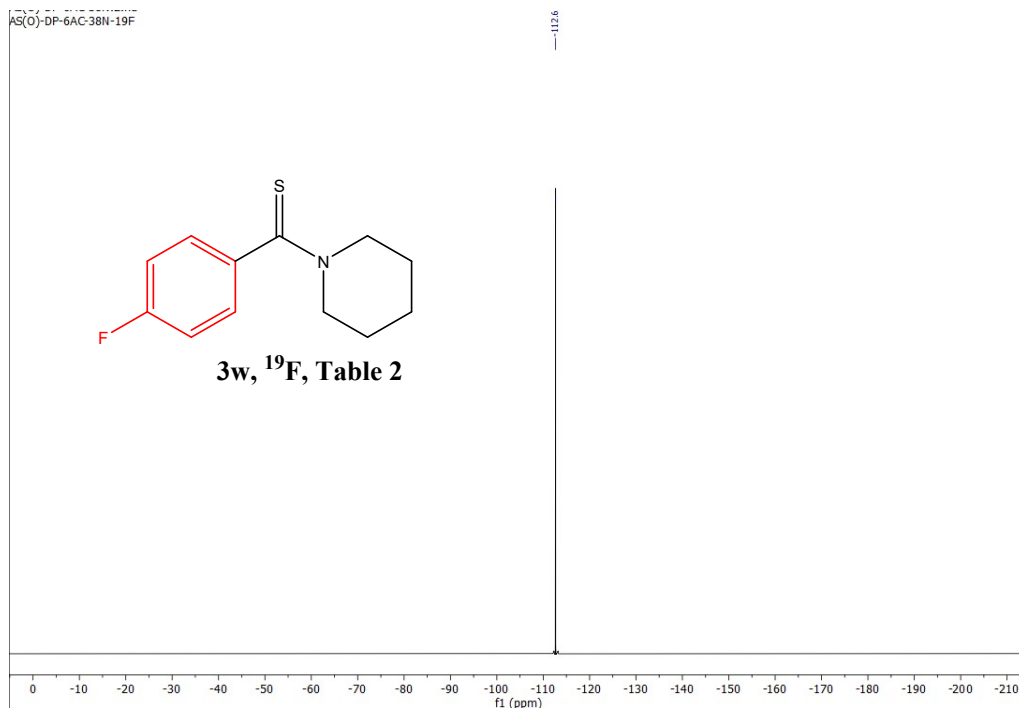


^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3v**

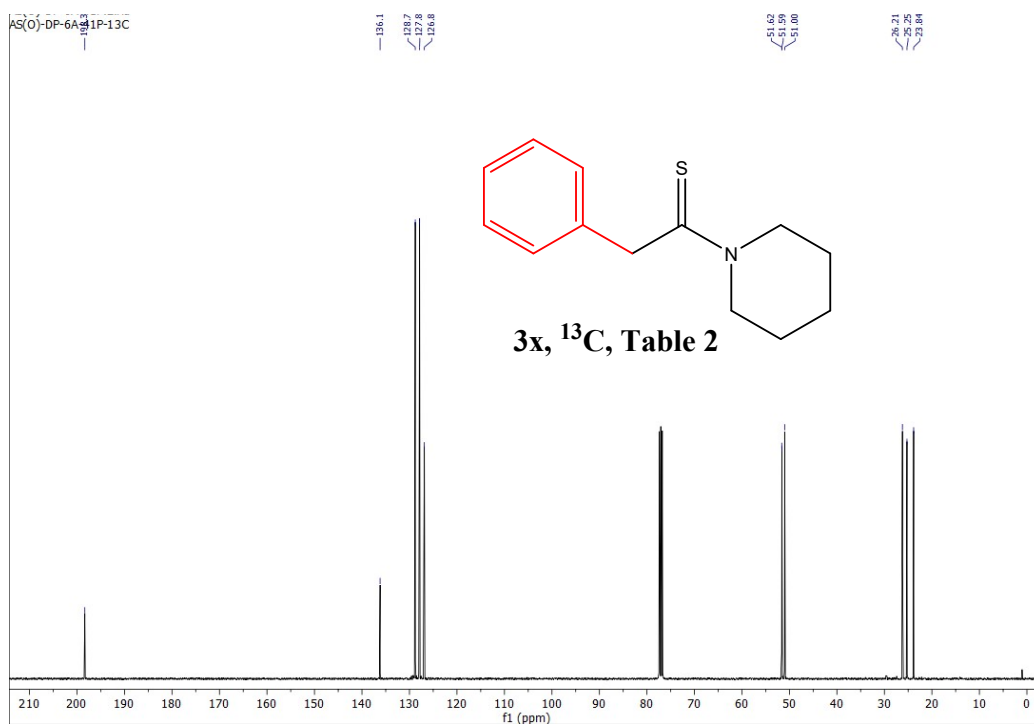
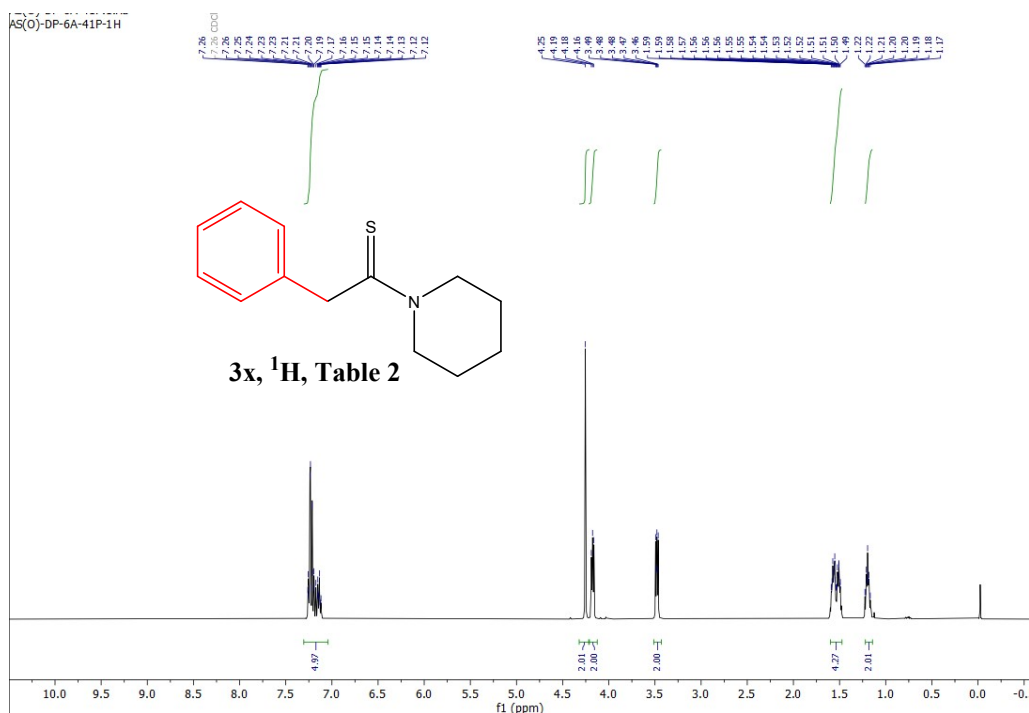


^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) and ^{19}F NMR (400 MHz, CDCl_3) spectrum of 3w

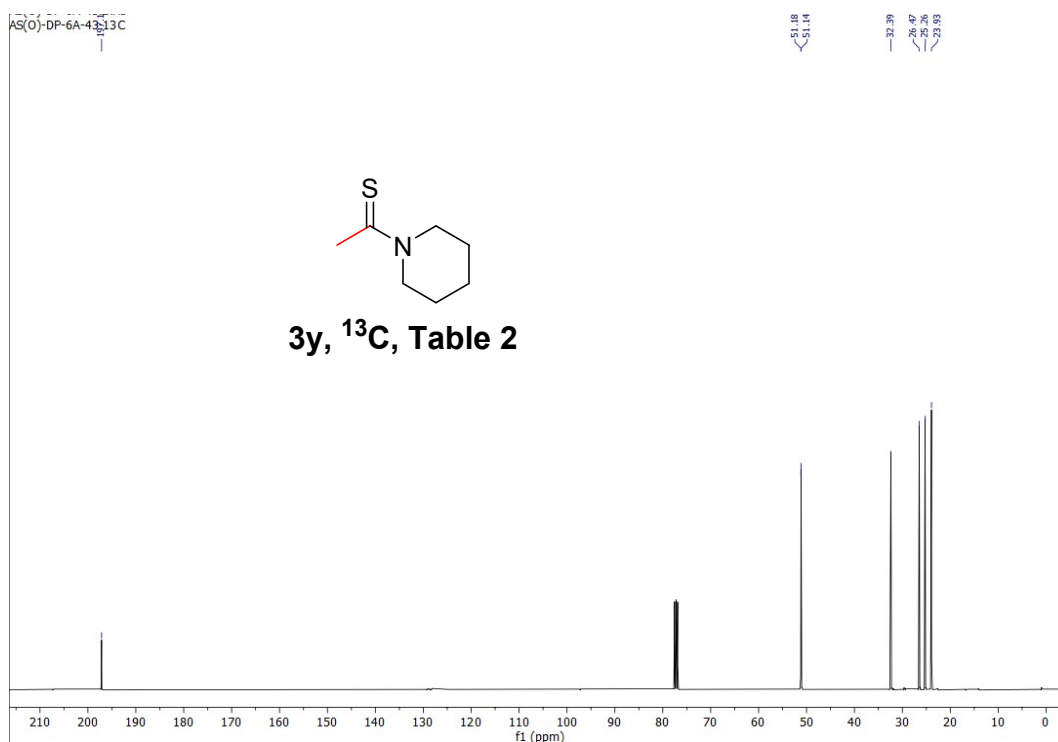
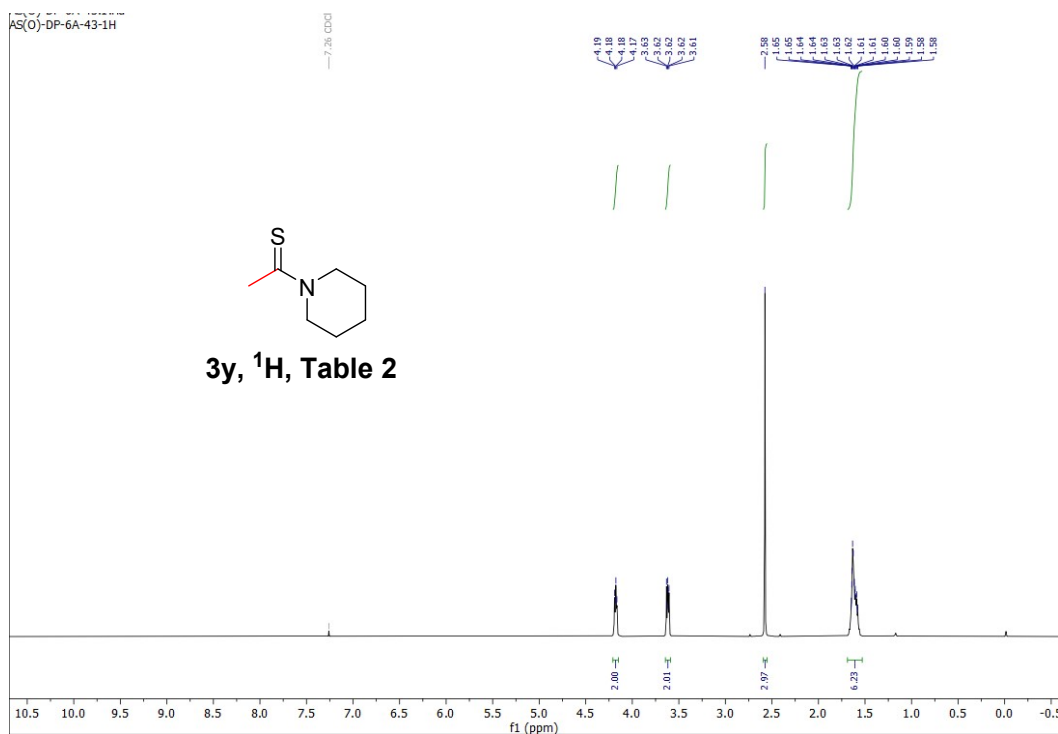




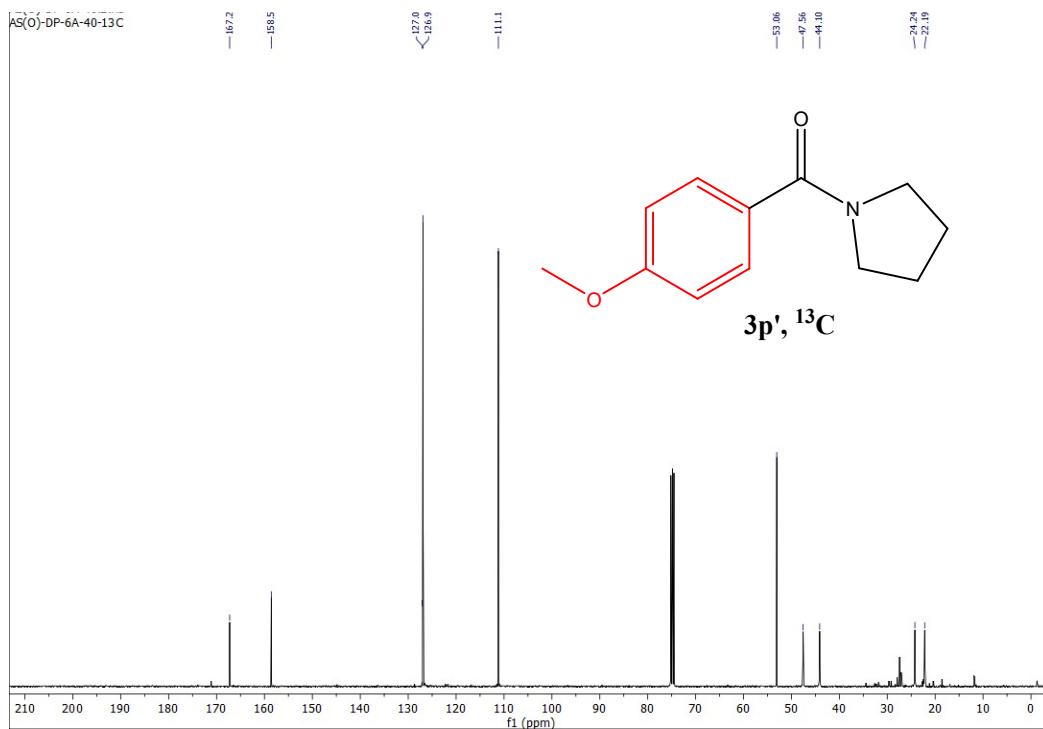
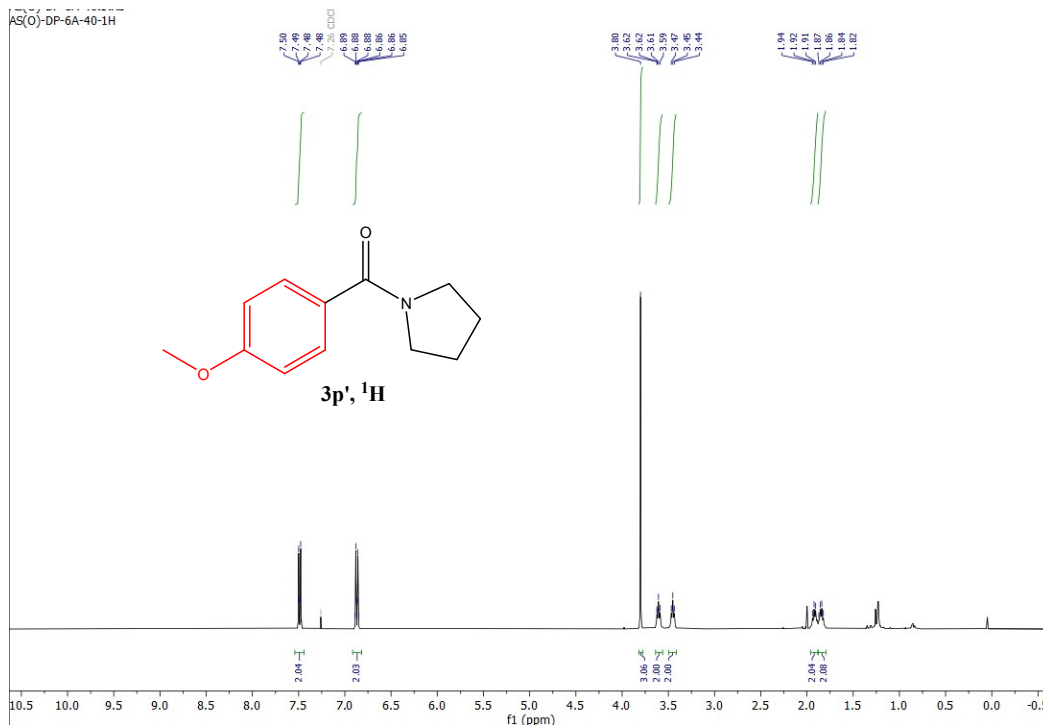
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3x**



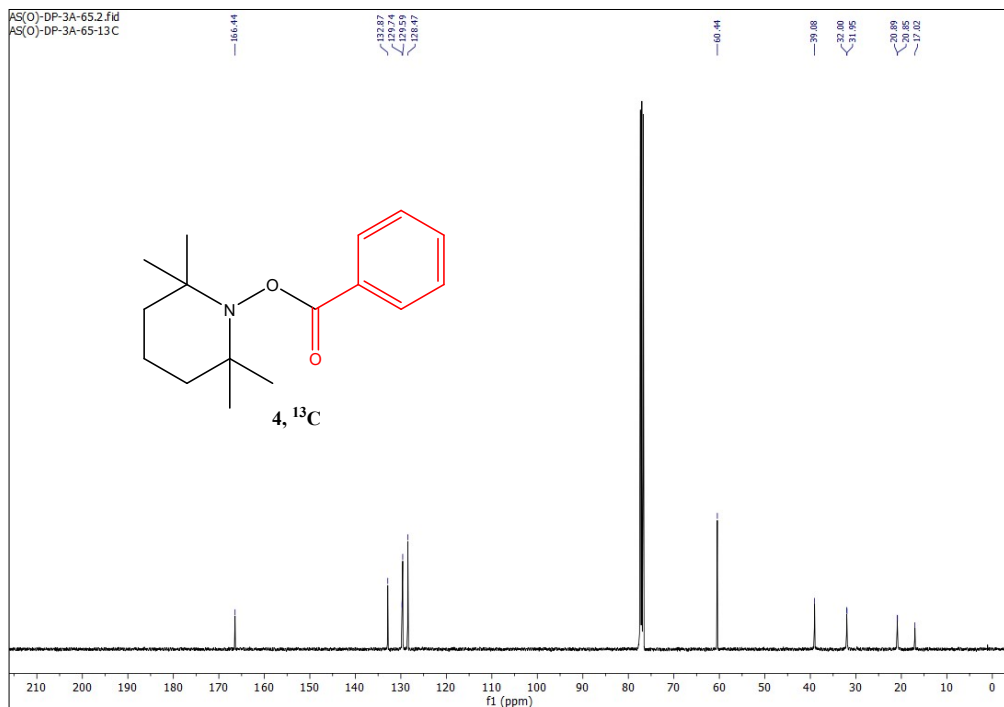
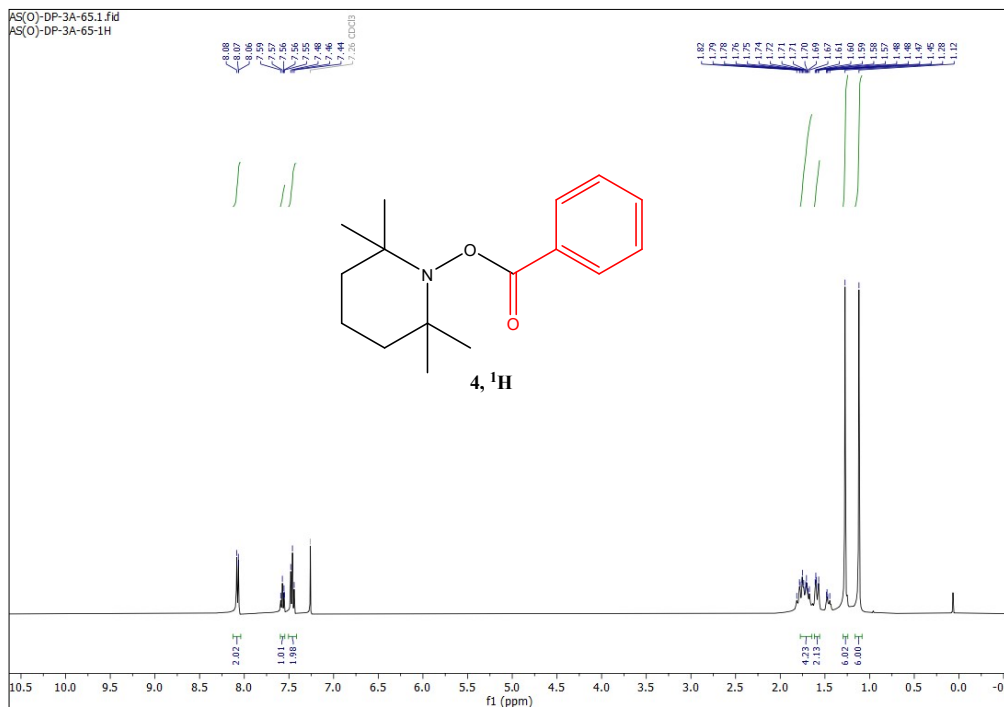
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3y**



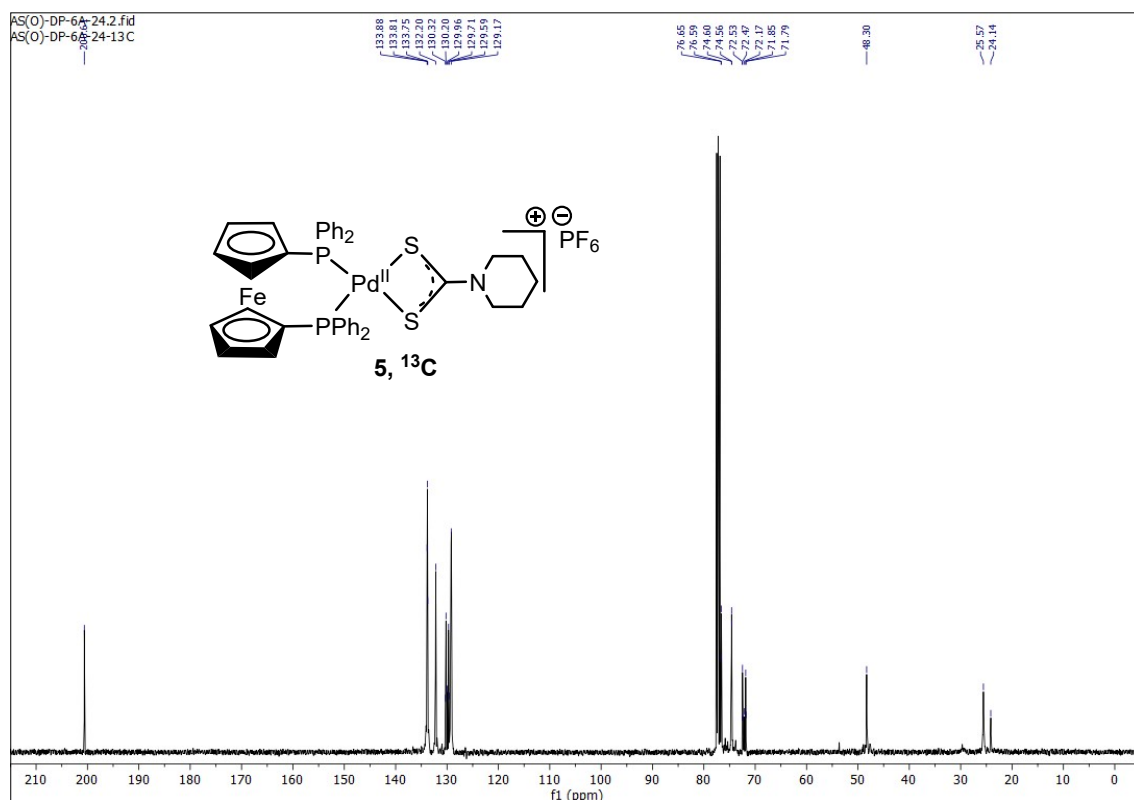
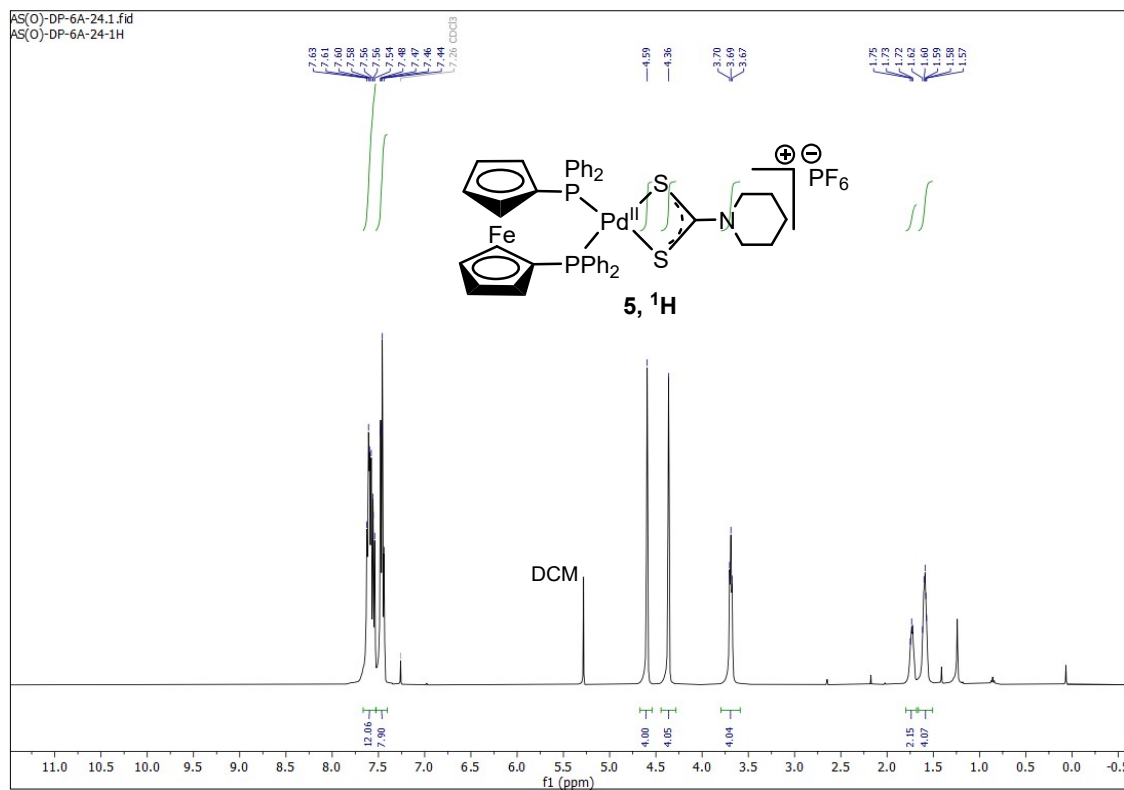
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3p'**



^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 4



^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 5



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