Supporting Information

Palladium-catalyzed Synthesis of *S*-Aryl Thiocarbamate *via* Desulfurative C-S Cross-coupling Reaction of Dithiocarbamates

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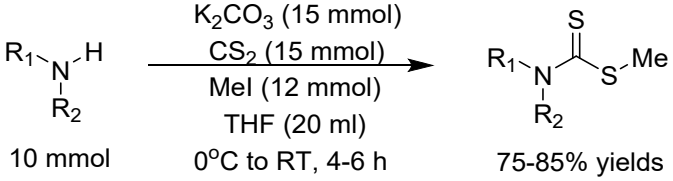
1. General information:

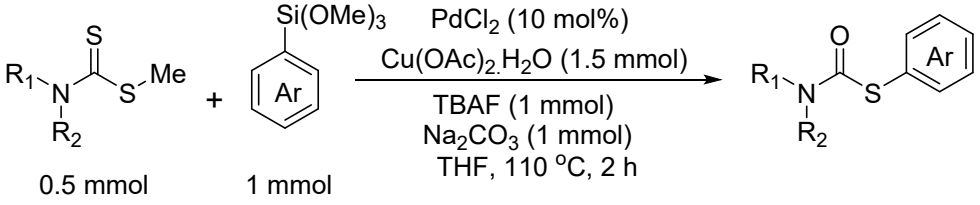
NMR spectra were recorded on a Bruker-Daltonics Avance-300 & 400 spectrometer operating at 300 MHz, 400 MHz (^{1}H), or 75 MHz, 100 MHz (^{13}C), with the residual protic solvent used as the internal standard. Silica gel (60 - 120 mesh) and (100 - 200 mesh) were used for chromatographic separation. Petroleum ether refers to the fraction between 60°C and 80°C.

2. General experimental procedure for synthesis of methyl dialkylcarbamodithioates (1):



CS_2 (0.95 ml, 15 mmol) was added drop wise to a mixture of secondary amine (10 mmol) and K_2CO_3 (2.07 g, 15 mmol) in THF (20 mL) at 0 °C. After completion of addition, the reaction mixture was allowed to stir for 20 min. Then MeI (0.65 mL, 12 mmol) was added slowly into the reaction mixture. The reaction mixture was allowed to stir at room temperature. After completion of reaction (checked by TLC), the solvent was evaporated under reduced pressure. The crude product was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and purified by column chromatography to obtain the desired products up to 85% yield.

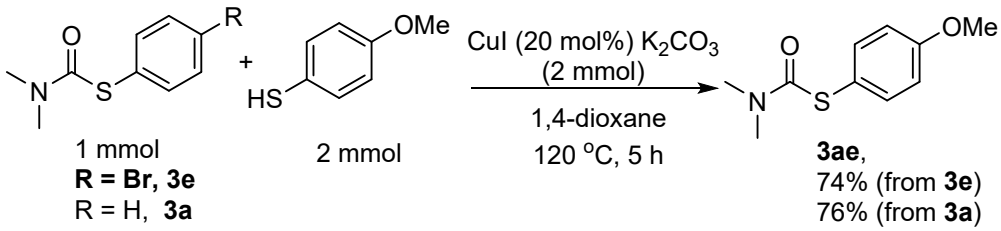
3. General experimental procedure for synthesis of *S*-thiocarbamates (3):



An oven-dried sealed tube (15 mL) equipped with a stir bar was charged with dithiocarbamate ester (0.5 mmol, 1.0 equiv.), $PdCl_2$ (0.05 mmol, 10 mol%), $Cu(OAc)_2.H_2O$ (1.5 mmol, 3 equiv.), Na_2CO_3 (1 mmol, 2 equiv.), silane (1 mmol, 2 equiv.), TBAF (0.5 mmol, 1 equiv.) and 5 mL THF solvent. Then, reaction mixture was stirred and heated in an oil bath at 110 °C for 2 hr. After completion of the reaction (checked by TLC), the resulting mixture was cooled to room temperature and evaporated under reduced pressure. The crude product was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and purified by column chromatography to obtain the desired products.

4. Experimental Procedure of Post-functionalization:

(i) Synthesis of *S*-(4-methoxyphenyl) dimethylcarbamothioate (3ae):



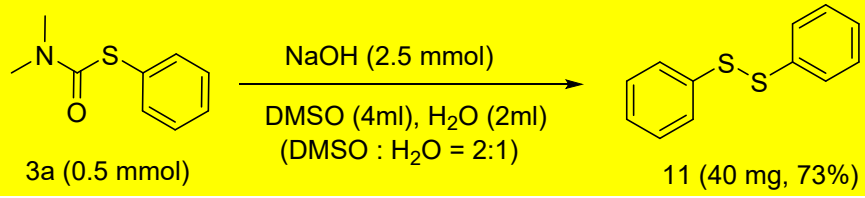
1 mmol
R = Br, 3e
R = H, **3a**

2 mmol

3ae,
74% (from **3e**)
76% (from **3a**)

A 10 mL round bottom flask was charged with *S*-aryl dimethylcarbamothioate (1 mmol), K_2CO_3 (276mg, 2 mmol), CuI (19 mg, 0.1 mmol), 4-Methoxy thiophenol (1.8 ml, 2 mmol) and 1,4-dioxane (5 mL). The resulting solution was stirred in an oil bath at 120°C for 5 h. After completion of the reaction (checked by TLC), the resulting mixture was cooled to room temperature and cold water was added to this solution. The crude product was extracted with ethyl acetate and purified by column chromatography to obtain the desired product (156.3 mg, 74% (from 3e) & 160.5 mg, 76% (from 3a)).

(ii) Synthesis of diphenyl disulfide (11):

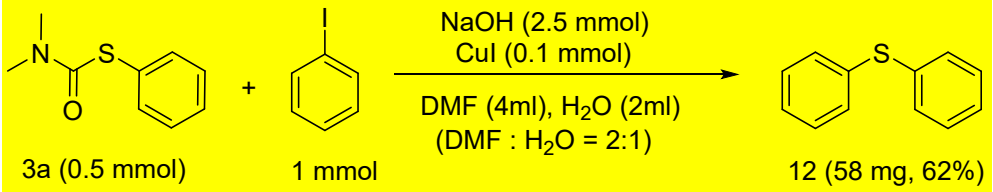


3a (0.5 mmol)

11 (40 mg, 73%)

100 mg (2.5 mmol) of NaOH was taken in an oven-dried sealed tube (15 mL) equipped with a stir bar and dissolved it in a mixture of DMSO (4ml) and distilled water (2ml) (DMSO : H_2O = 2:1) by stirring. Then S-phenyl dimethylcarbamothioate (0.5 mmol) was added to it. The resulting solution was stirred in an oil bath at 120 °C for 5 h. After completion of the reaction (checked by TLC), the resulting mixture was cooled to room temperature and cold water was added to this solution. The crude product was extracted with ethyl acetate and purified by column chromatography to obtain the desired product (40mg, 73%).

(iii) Synthesis of diphenyl sulfide (12) :



3a (0.5 mmol)

1 mmol

12 (58 mg, 62%)

100 mg (2.5 mmol) of NaOH was taken in an oven-dried sealed tube (15 mL) equipped with a stir bar and dissolved it in a mixture of DMF (4ml) and distilled water (2ml) (DMF : H_2O = 2:1) by stirring. Then S-phenyl dimethylcarbamothioate (0.5 mmol), CuI (19 mg, 0.1 mmol), phenyl iodide (1 mmol) were added to it. The resulting solution was stirred in an oil bath at 120°C for 5 h. After completion of the reaction (checked by TLC), the resulting mixture was cooled to room temperature and cold water was added to this solution. The crude product was extracted with ethyl acetate and purified by column chromatography to obtain the desired product (58 mg, 62%).

5. Characterization Data of Synthesized Compounds:

1. S-phenyl dimethylcarbamothioate (3a). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 97/3 mixture as the eluent solvent to afford colourless solid (56.2 mg, 62%), m.p – 31-33 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.39 (dt, *J* = 5.0, 1.6 Hz, 3H), 3.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.91, 135.74, 129.16, 128.93, 128.81, 36.91; IR (cm^{-1}) : 3052, 2924, 1651, 1474, 1438, 1361, 1255, 1098,1084, 1070, 746, 707, 683, 651, 523. HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_9H_{12}NOS$, 182.0640; found, 182.0641.

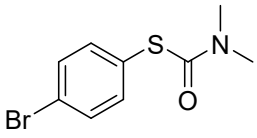
2. S-(p-tolyl) dimethylcarbamothioate (3b). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 98/2 mixture as the eluent solvent to afford pale yellow liquid (56.6 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.05 (s, 6H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.32, 139.38, 135.72, 129.79, 125.23, 36.89, 21.34; IR (cm^{-1}) : 2940, 2857, 1651, 1587, 1397, 1207, 1002; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{10}H_{14}NOS$, 196.0796; found, 195.0794.

3. S-(4-methoxyphenyl) dimethylcarbamothioate (3c). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 95/5 mixture as the eluent solvent to afford white solid (67.8 mg, 64%), m.p – 94-96 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.65, 160.57, 137.35, 119.45, 114.63, 55.36, 36.87; IR (cm^{-1}) : 2968, 1666, 1651, 1592, 1363, 1245, 1105, 1093, 1022, 829, 819, 686, 657, 535; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{10}H_{14}NO_2S$, 212.0745; found, 212.0744.

4. S-(4-chlorophenyl) dimethylcarbamothioate (3d). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 98/2

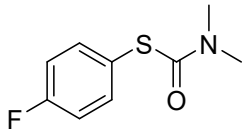
mixture as the eluent solvent to afford colourless solid (71.3 mg, 66%), m.p – 77-79 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 3.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.26, 136.92, 135.52, 129.11, 127.40, 36.92; IR (cm^{-1}) : 2931, 1663, 1361, 1220, 1086, 829, 525; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_9H_{11}ClNOS$, 216.0250; found, 216.0252.

5. S-(4-bromophenyl) dimethylcarbamothioate (3e). This product was synthesized by general procedure



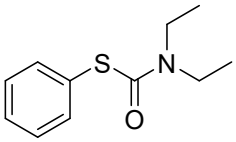
for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 98/2 mixture as the eluent solvent to afford white solid (76.5 mg, 59%), m.p – 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.23, 137.19, 132.11, 127.97, 123.87, 37.07; IR (cm^{-1}) : 2937, 1660, 1470, 1357, 1254, 1101, 1078, 1064, 1007, 905, 830, 733, 703, 679, 652, 539; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_9H_{11}BrNOS$, 259.9745; found, 259.9742.

6. S-(4-fluorophenyl) dimethylcarbamothioate (3f). This product was synthesized by general procedure



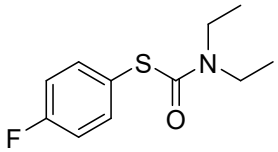
for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 97/3 mixture as the eluent solvent to afford pale yellow liquid (60.8 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 2H), 7.12 – 7.01 (m, 2H), 3.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.74, 163.45 (d, *J* = 249.4 Hz), 137.77 (d, *J* = 8.6 Hz), 124.15 (d, *J* = 3.5 Hz), 116.10 (d, *J* = 22.1 Hz). 36.89; IR (cm^{-1}) : 2933, 1663, 1590, 1489, 1220, 1104, 829, 684, 526; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_9H_{11}FNOS$, 200.0545; found, 200.0547.

7. S-phenyl diethylcarbamothioate (3g). This product was synthesized by general procedure for the

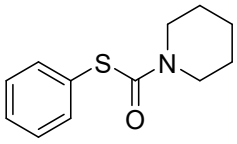


synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 97/3 mixture as the eluent solvent to afford colourless liquid (71.2 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.41 – 7.35 (m, 3H), 3.44 (q, *J* = 7.1 Hz, 4H), 1.30 – 1.13 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.74, 135.78, 129.02, 128.87, 128.84, 42.36; ; IR (cm^{-1}) : 3053, 2924, 1651, 1402, 1361, 1099, 684; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{11}H_{16}NOS$, 210.0953; found, 210.0956.

8. S-(4-fluorophenyl) diethylcarbamothioate (3h). This product was synthesized by general procedure for

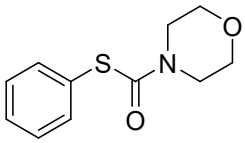


the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 97/3 mixture as the eluent solvent to afford pale yellow liquid (68.5 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 6.7 Hz, 2H), 7.10 – 7.04 (m, 2H), 3.42 (d, *J* = 7.4 Hz, 4H), 1.21 (dd, *J* = 40.8, 11.2 Hz, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.61, 163.42 (d, *J* = 249.3 Hz), 137.83 (d, *J* = 8.4 Hz), 124.13 (d, *J* = 3.4 Hz), 123.17 (d, *J* = 8.4 Hz), 116.08 (d, *J* = 22.0 Hz), 115.78 (d, *J* = 23.4 Hz), 42.40, 13.84, 13.16. HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{11}H_{15}ClNOS$, 228.0858; found, 228.0861.

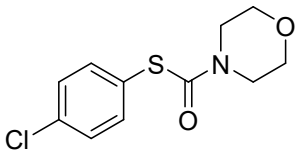


9. S-phenyl piperidine-1-carbothioate (3i). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 98/2 mixture as the eluent solvent to afford white solid (74.3 mg, 67%), m.p – 57-59 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.41 – 7.34 (m, 3H), 3.54 (t, *J* = 5.1 Hz, 4H), 1.64 (h, *J* = 6.6, 5.0 Hz, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.47, 135.86, 129.09, 128.88, 128.84, 25.77, 24.52; IR (cm^{-1}) : 2973, 2928, 1658, 1276, 1034, 748, 622; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{12}H_1NOS$, 222.0953; found, 222.0955.

10. S-(4-fluorophenyl) piperidine-1-carbothioate (3j). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 97/3 mixture as the eluent solvent to afford pale yellow solid (67.1 mg, 56%), m.p – 65-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 8.5 Hz, 2H), 3.52 (s, 4H), 1.63 (d, *J* = 16.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.27 (d, *J* = 1.3 Hz), 163.46 (d, *J* = 249.3 Hz), 137.87 (d, *J* = 8.5 Hz), 124.18 (d, *J* = 3.4 Hz), 116.07 (d, *J* = 22.1 Hz), 46.57, 25.73, 24.48; IR (cm^{-1}) : 2940, 2857, 1650, 1586, 1488, 1397, 1246, 1222, 1207, 1088, 1001, 832, 821, 673, 651, 640, 557, 516; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{12}H_{15}FNOS$, 240.0858 ; found, 240.0857.



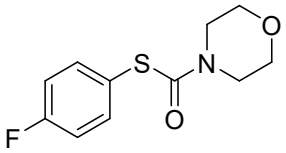
11. S-phenyl morpholine-4-carbothioate (3k). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 95/5 mixture as the eluent solvent to afford pale yellow solid (70.3 mg, 63%), m.p – 106-108 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.44 – 7.36 (m, 3H), 3.73 (dd, *J* = 5.7, 3.7 Hz, 4H), 3.61 (dd, *J* = 5.7, 3.8 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.38, 135.83, 129.40, 129.04, 127.96, 66.55, 45.34; IR (cm^{-1}) : 2974, 2917, 2857, 1652, 1401, 1269, 1208, 1191, 1107, 1013, 836, 765, 756, 649, 597; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{11}H_{14}NO_2S$, 224.0745 ; found, 224.0744.



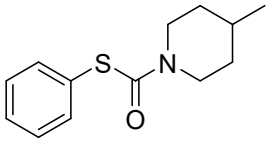
12. S-(4-chlorophenyl) morpholine-4-carbothioate (3l). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 95/5 mixture as the eluent solvent to afford pale yellow solid (91.6 mg, 71%), m.p – 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 3.73 (t, *J* = 4.9 Hz, 4H), 3.59 (t, *J* = 4.8 Hz, 4H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.75, 137.00, 135.89, 129.26, 126.49, 66.51, 45.35; IR (cm^{-1}) : 2963,

2919, 2858, 1646, 1389, 1404, 1271, 1210, 1192, 1108, 1092, 1083, 1018, 1009, 821, 513; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{11}H_{13}ClNO_2S$, 258.0356 ; found, 258.0355.

13. S-(4-fluorophenyl) morpholine-4-carbothioate (3m). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 93/7 mixture as the eluent solvent to afford pale yellow liquid (73.6 mg, 61%) .

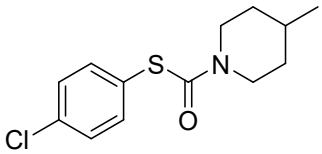


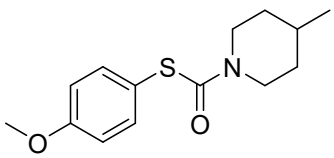
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 2H), 7.09 (td, *J* = 8.8, 2.8 Hz, 2H), 3.75 – 3.57 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.24, 163.61 (d, *J* = 250.0 Hz), 137.89 (d, *J* = 8.5 Hz), 123.24 (d, *J* = 3.6 Hz), 116.29 (d, *J* = 22.2 Hz), 66.53, 45.84, 44.61; IR (cm^{-1}) : 2934, 1663, 1490, 1361, 1086, 526;HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{11}H_{13}FNO_2S$, 242.0651 ; found, 242.0653.



14. S-phenyl 4-methylpiperidine-1-carbothioate (3n). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 98/2 mixture as the eluent solvent to afford pale yellow liquid (76.5 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.42 – 7.35 (m, 3H), 4.25 (s, 2H), 2.89 (s, 2H), 1.75 – 1.60 (m, 3H), 1.27 – 1.16 (m, 2H), 0.98 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.43, 135.85, 129.09, 128.89, 128.86, 45.23, 33.92, 31.11, 21.72; IR (cm^{-1}) : 2918, 2944, 2852, 1654, 1396, 1263, 1213, 1201, 1125, 1084, 752, 686, 584; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{13}H_{18}NOS$, 236.1109 ; found, 236.1106.

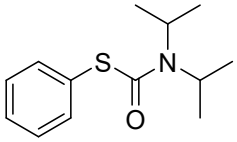
15. S-(4-chlorophenyl) 4-methylpiperidine-1-carbothioate (3o). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 97/3 mixture as the eluent solvent to afford pale yellow solid (77.2 mg, 57%), m.p – 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.6, 2.0 Hz, 2H), 7.34 (dd, *J* = 8.5, 1.9 Hz, 2H), 4.17 (d, *J* = 179.9 Hz, 2H), 2.89 (d, *J* = 114.9 Hz, 2H), 1.70 (d, *J* = 13.9 Hz, 2H), 1.23 (d, *J* = 19.4 Hz, 3H), 0.98 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.79, 137.02, 135.53, 129.09, 127.41, 33.90, 31.08, 21.68; IR (cm^{-1}) : 2918, 2851, 1651,1398, 1261, 1213, 1126, 1083, 1008, 964, 820, 797, 681, 509; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{13}H_{17}ClNOS$, 270.0719 ; found, 270.0717.



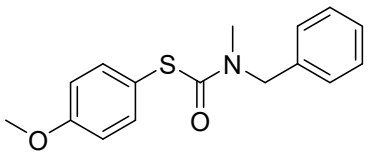


16. S-(4-methoxyphenyl) 4-methylpiperidine-1-carbothioate (3p). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 95/5 mixture as the eluent solvent to afford pale yellow liquid (82.3 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.35 (s, 2H), 3.81 (s,

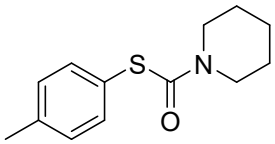
3H), 2.93 (s, 2H), 1.71 (s, 1H), 1.65 – 1.52 (m, 2H), 1.24 – 1.10 (m, 2H), 0.97 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.19, 160.53, 137.44, 119.50, 114.60, 55.36, 44.94, 33.91, 31.11, 21.71; IR (cm^{-1}) : 2968, 1651, 1245, 1022, 819, 535, HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{14}H_{20}NO_2S$, 266.1215 ; found, 266.1216.



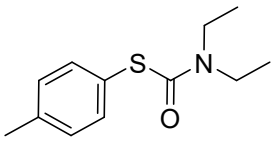
17. S-phenyl diisopropylcarbamothioate (3q). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 98/2 mixture as the eluent solvent to afford white solid (63.1 mg, 53%), m.p – 102-104 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.38 (dd, *J* = 5.0, 1.8 Hz, 3H), 4.17 (s, 1H), 3.52 (s, 1H), 1.33 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.87, 135.91, 129.27, 128.90, 128.85, 20.67; IR (cm^{-1}) : 2973, 2929, 1658, 1418, 1277, 1205,1036, 812, 748, 688, 622, 553, 504 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{13}H_{20}NOS$, 238.1266 ; found, 238.1268.



18. S-(4-methoxyphenyl) benzyl methyl carbamothioate (3r). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 95/5 mixture as the eluent solvent to afford pale yellow liquid (69.3 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dt, *J* = 8.7, 1.7 Hz, 2H), 7.41 – 7.26 (m, 5H), 6.97 – 6.90 (m, 2H), 4.61 (s, 2H), 3.82 (s, 3H), 2.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.64, 137.39, 128.74, 128.15, 127.69, 119.30, 114.69, 55.38, 52.84, 34.52; IR (cm^{-1}) : 2923, 2852, 1666, 1494, 1380, 1244, 1199, 1174, 1029, 826, 748, 695, 533, 461; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{16}H_{18}NO_2S$, 288.1058 ; found, 288.1061.



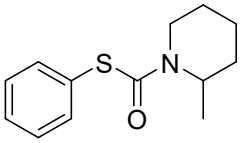
19. S-(4-methylphenyl) piperidine-1-carbothioate (3s). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 98/2 mixture as the eluent solvent to afford colourless liquid (68 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.1, 2.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 3.53 (s, 4H), 2.38 – 2.34 (m, 3H), 1.70 – 1.60 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.84, 139.31, 135.83, 129.75, 125.28, 24.54, 21.33; IR (cm^{-1}) : 2922, 2854, 1657, 1399, 1243, 1243, 1202, 1114, 999, 808, 670, 650, 512; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{13}H_{18}NOS$, 236.1109 ; found, 236.1108.



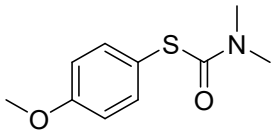
20. S-(4-methylphenyl) diethylcarbamothioate (3t). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 97/3 mixture as the eluent solvent to afford colourless liquid (61 mg, 55%). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.13, 139.25, 135.77, 129.73, 125.27, 42.33, 21.31; IR

(cm^{-1}) : 2963, 2921, 2856, 1644, 1211, 1107, 1011, 822; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{12}H_{18}NOS$, 224.1109 ; found, 224.1107.

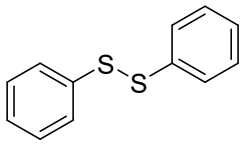
21. S-phenyl 2-methylpiperidine-1-carbothioate (3u). This product was synthesized by general procedure for the synthesis of S-thiocarbamate compounds. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 99/1 mixture as the eluent solvent to afford pale yellow liquid (60 mg, 52%); ^{1}H NMR (300 MHz, DMSO) δ 7.42 (d, *J* = 3.2 Hz, 5H), 4.37 (s, 1H), 3.89 (s, 1H), 3.02 (s, 1H), 1.62 – 1.53 (m, 4H), 1.23 – 1.16 (m, 5H); ^{13}C NMR (75 MHz, DMSO) δ 164.19, 136.08, 129.49, 129.33, 129.03, 30.19, 29.71, 25.74, 18.80, 16.23; IR (cm^{-1}) : 2929, 1660, 1356, 1007, 830, 679 ; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{13}H_{18}NOS$, 236.1109 ; found, 236.1108.



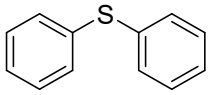
22. S-(4-methoxyphenyl) dimethylcarbamothioate (3ae). This product was synthesized by experimental procedure for post-functionalization. The crude product was purified by (60-120) mesh silica gel chromatography and hexane/ethyl acetate 95/5 mixture as the eluent solvent to afford white solid (156.3 mg, 74% (from 3e) & 160.5 mg, 76% (from 3a)), m.p – 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.6, 1.5 Hz, 2H), 6.91 (dd, *J* = 8.6, 1.5 Hz, 2H), 3.80 (d, *J* = 1.6 Hz, 3H), 3.03 (d, *J* = 14.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.69, 160.57, 137.35, 119.43, 114.63, 55.36, 36.88; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{10}H_{14}NO_2S$, 212.0745; found, 212.0744.



23. diphenyl disulfide (11). This product was synthesized by experimental procedure for post-functionalization. The crude product was purified by (60-120) mesh silica gel chromatography and hexane as the eluent solvent to afford colorless solid (40 mg, 73%),), m.p – 59-61 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 4H), 7.35 – 7.20 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.08, 129.12, 127.56, 127.21; HRMS (ESI-TOF) *m/z*: [M+H]+ calcd for $C_{12}H_{11}S_2$, 219.0302 ; found, 219.0305.

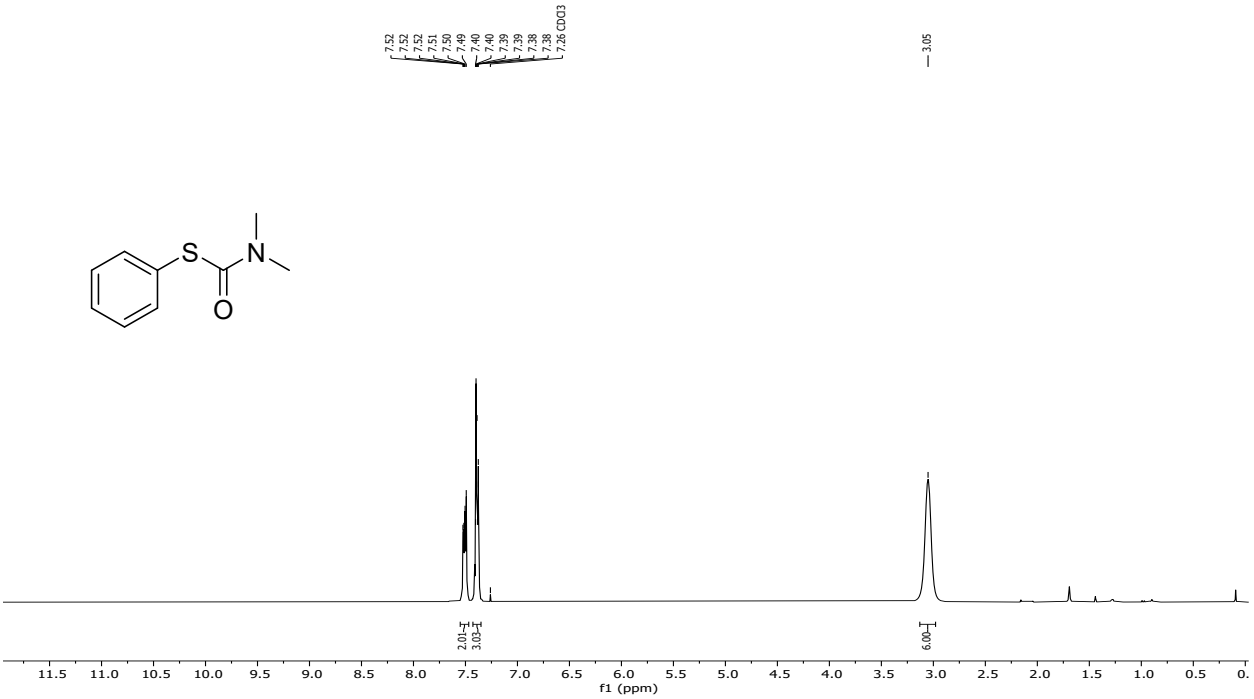


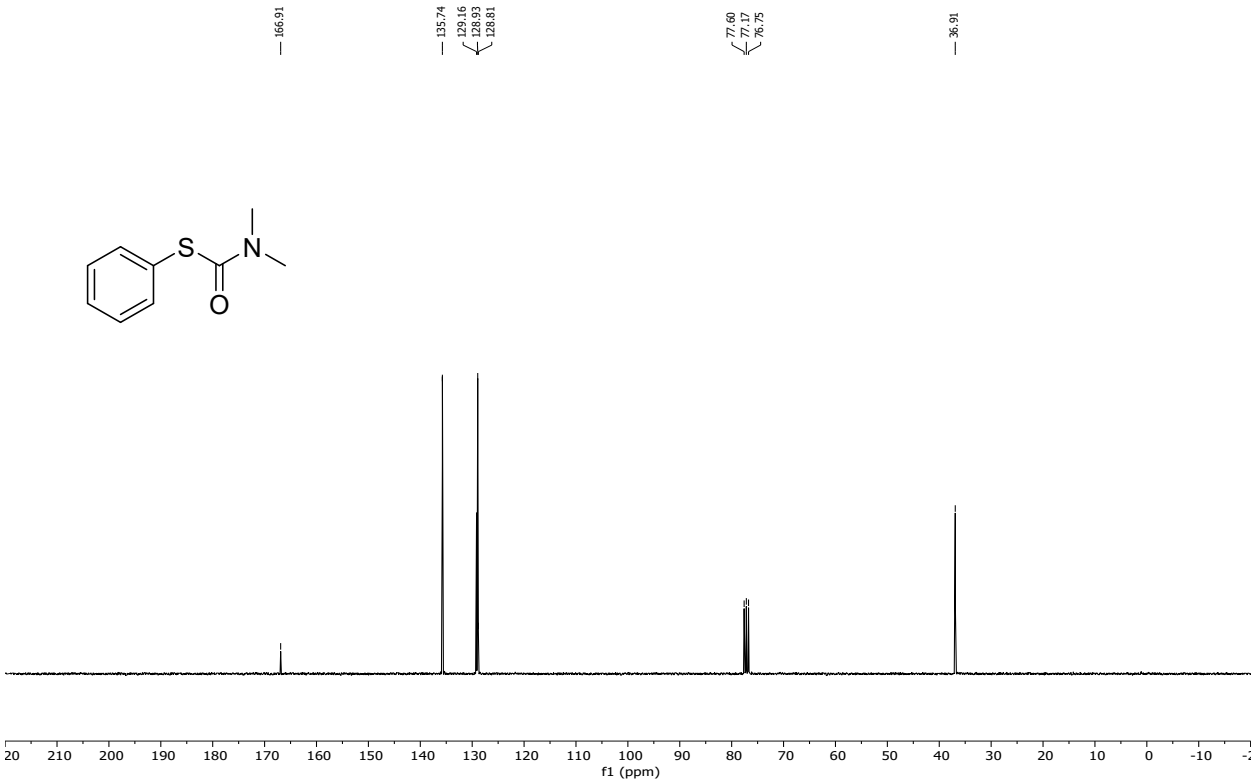
24. diphenyl sulfide (12). This product was synthesized by experimental procedure for post-functionalization. The crude product was purified by (60-120) mesh silica gel chromatography and hexane as the eluent solvent to afford pale yellow liquid (58 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.84, 131.09, 129.24, 127.08; ; HRMS (ESI-TOF) *m/z*: [M+K]+ calcd for $C_{12}H_{11}S_1$, 225.0140 ; found, 225.0142.



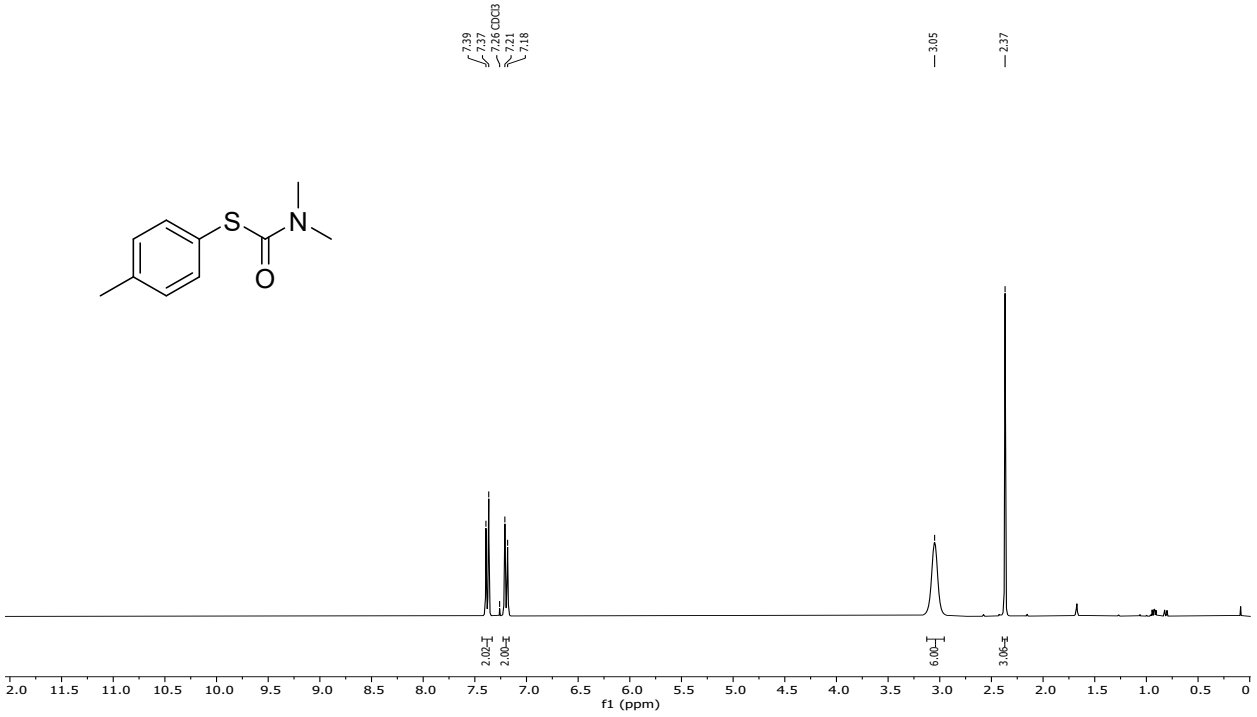
6. ^{1}H and ^{13}C Spectra of All Compounds

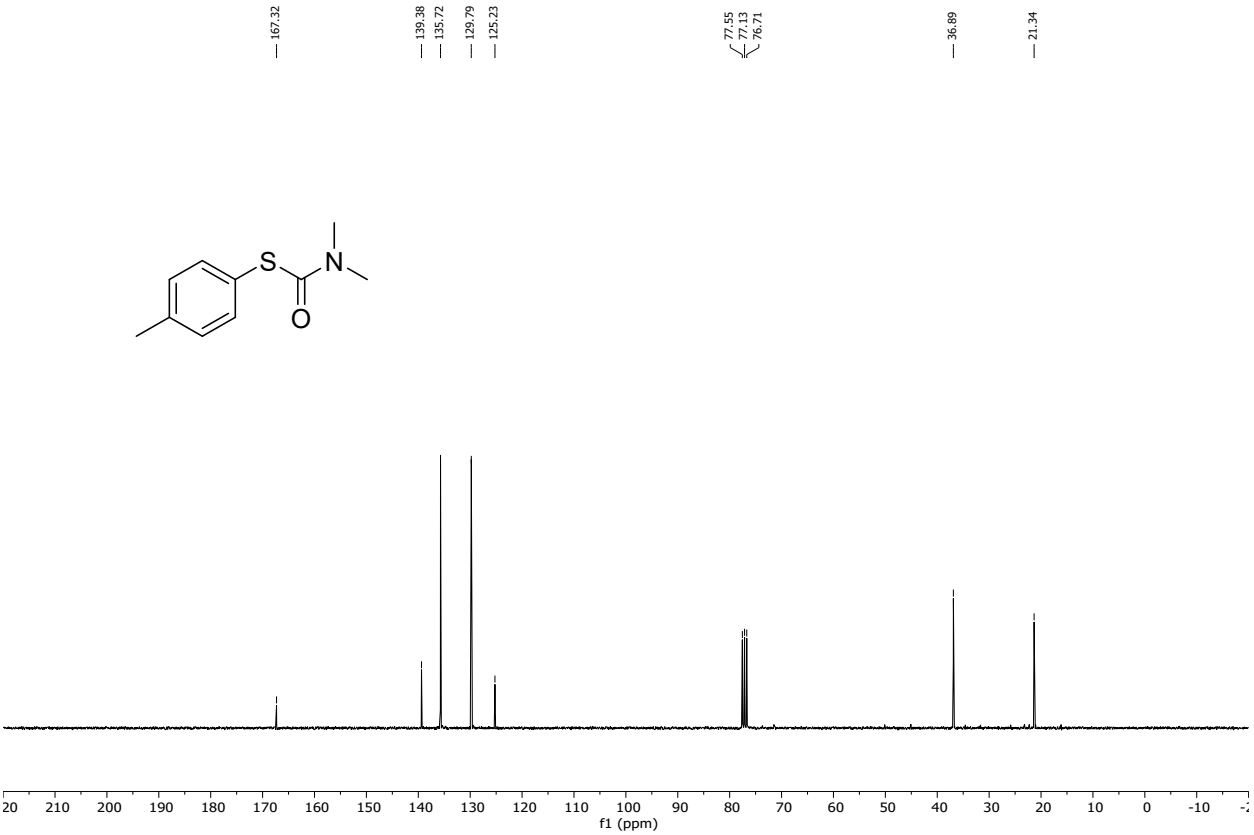
1. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) spectra of **3a**



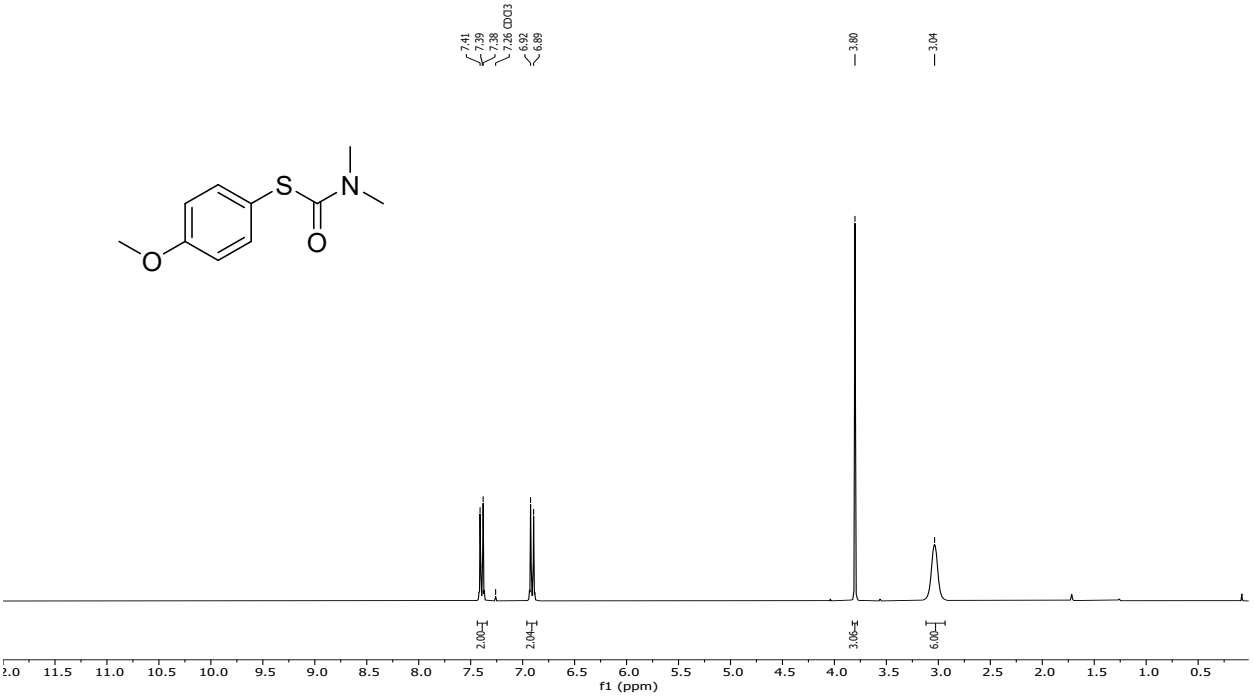


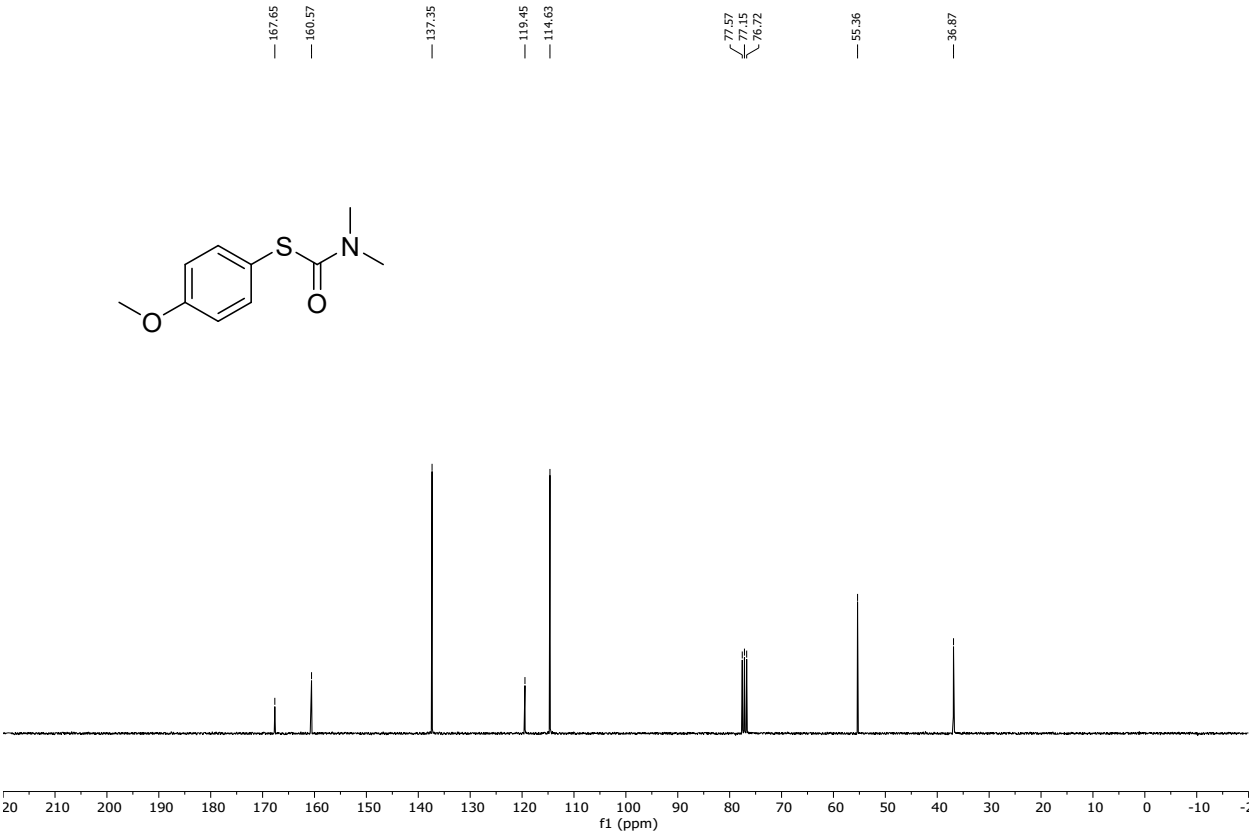
2. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3b**



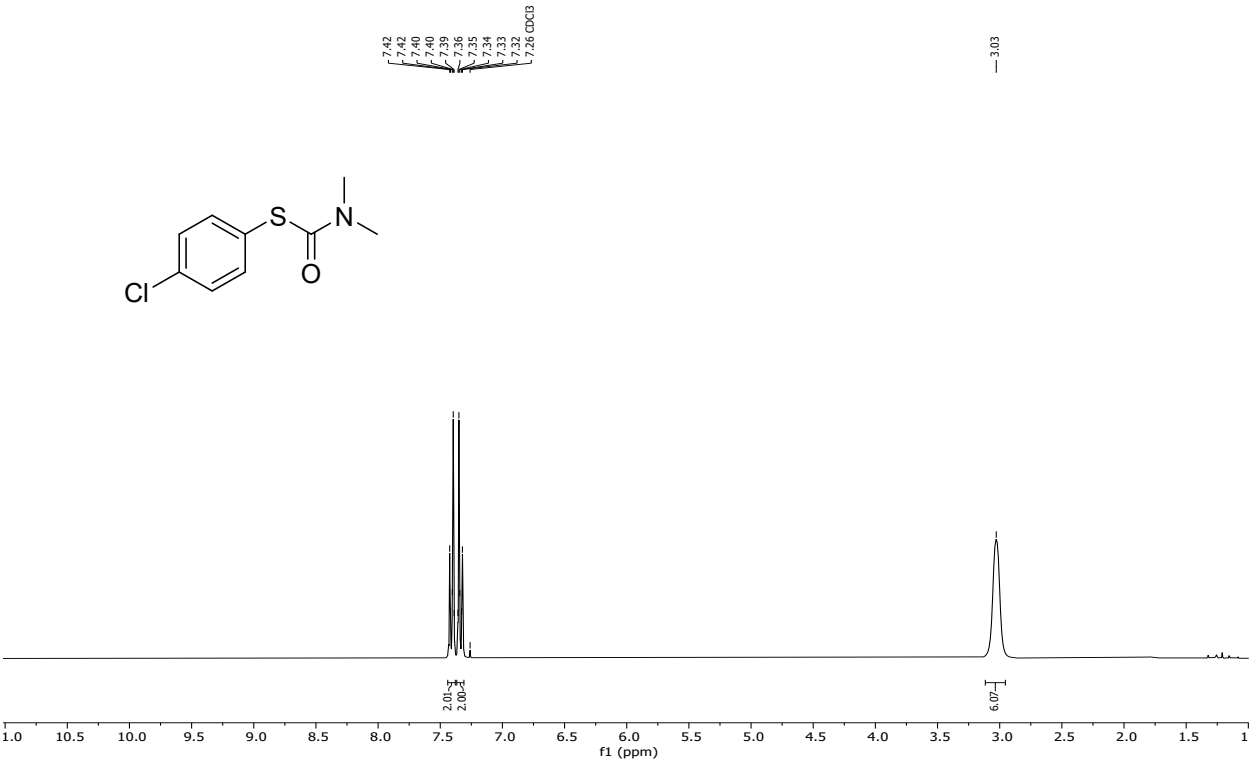


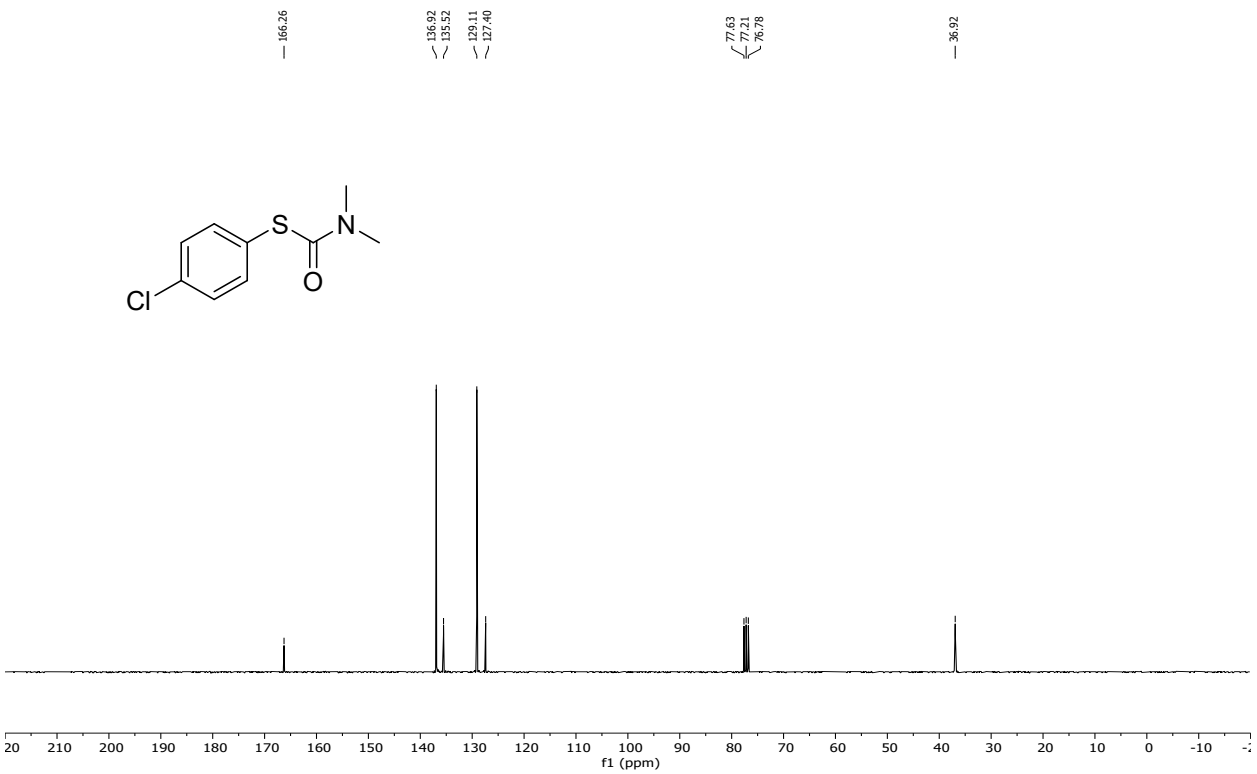
3. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3c**



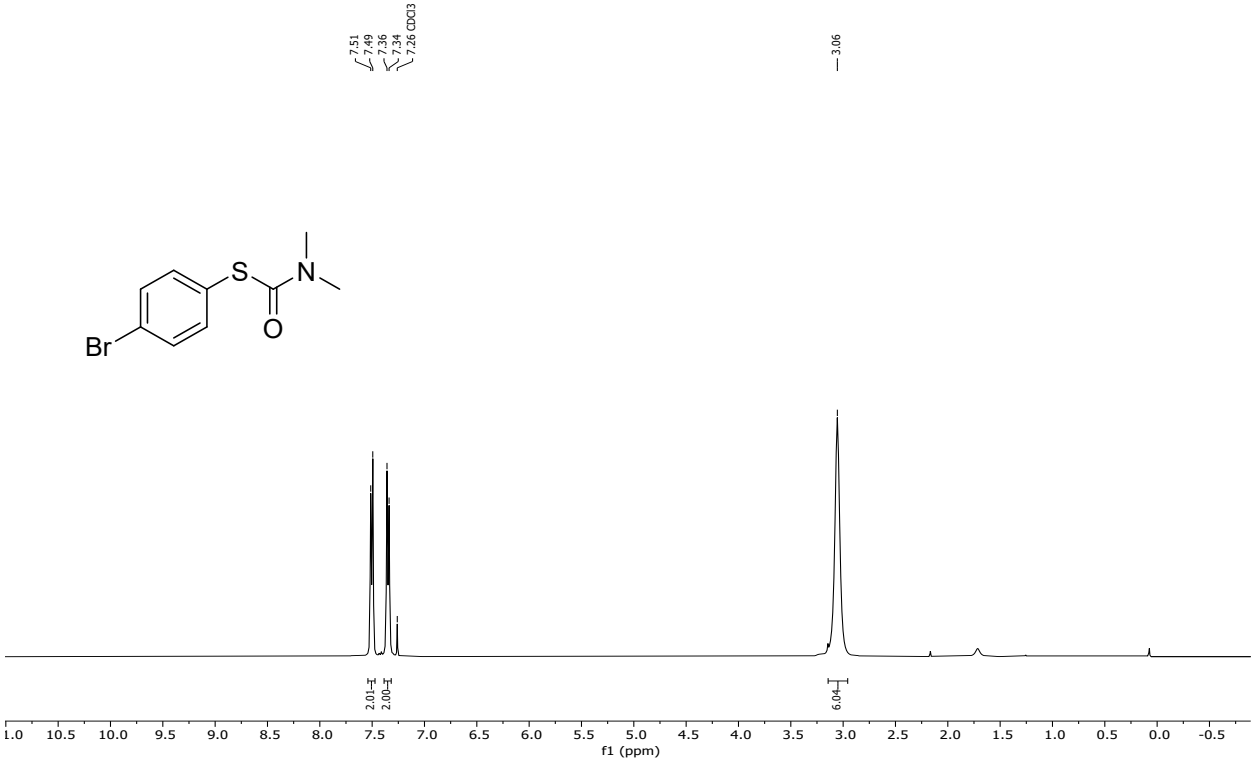


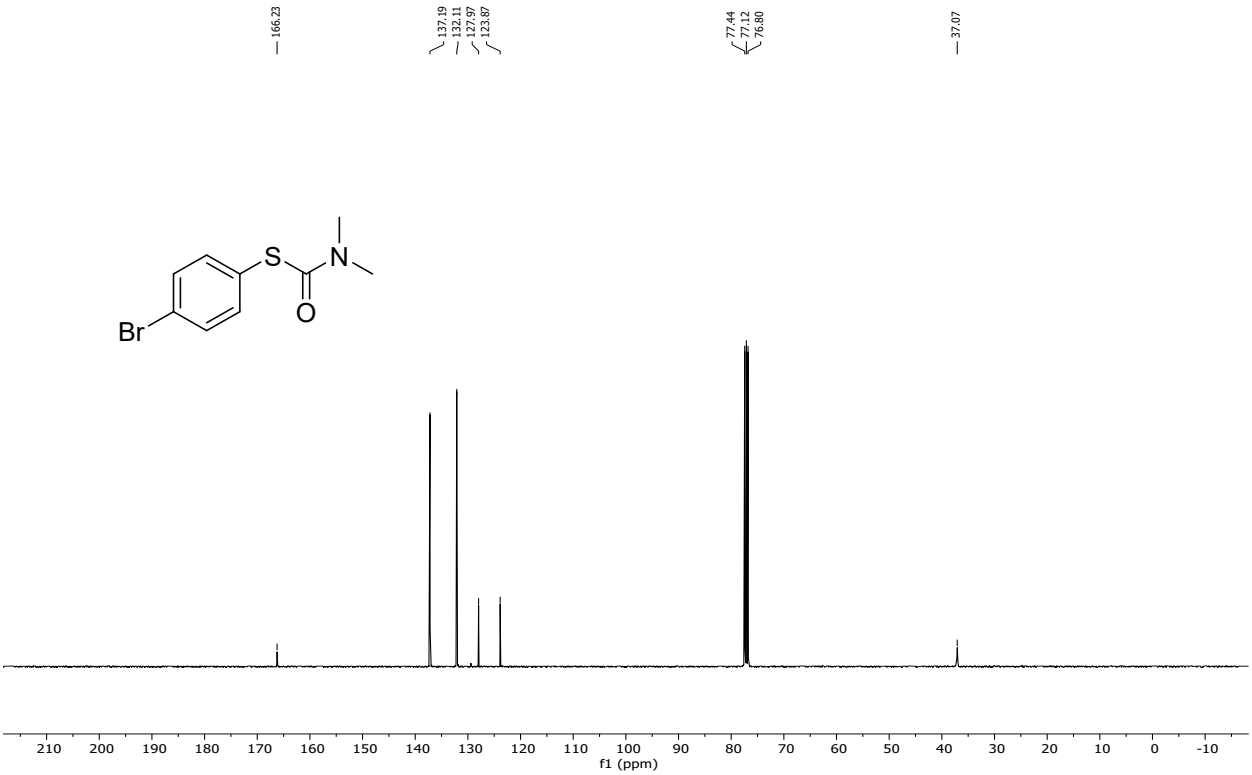
4. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3d**



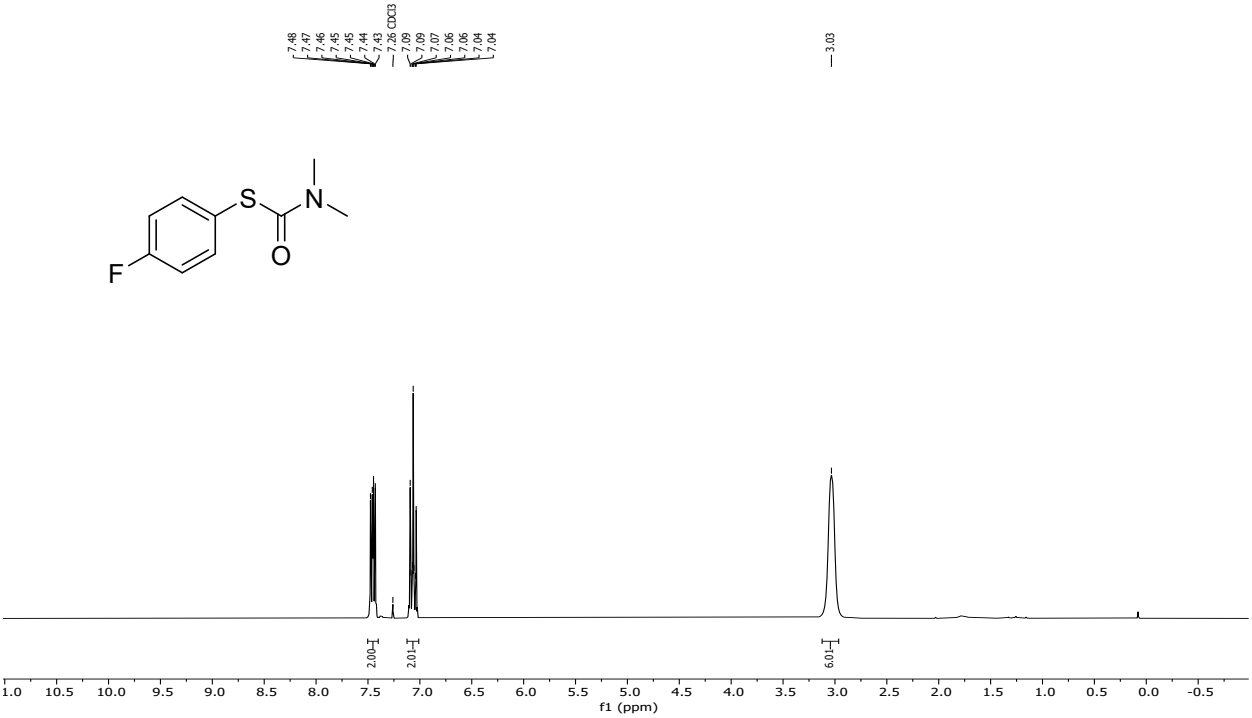


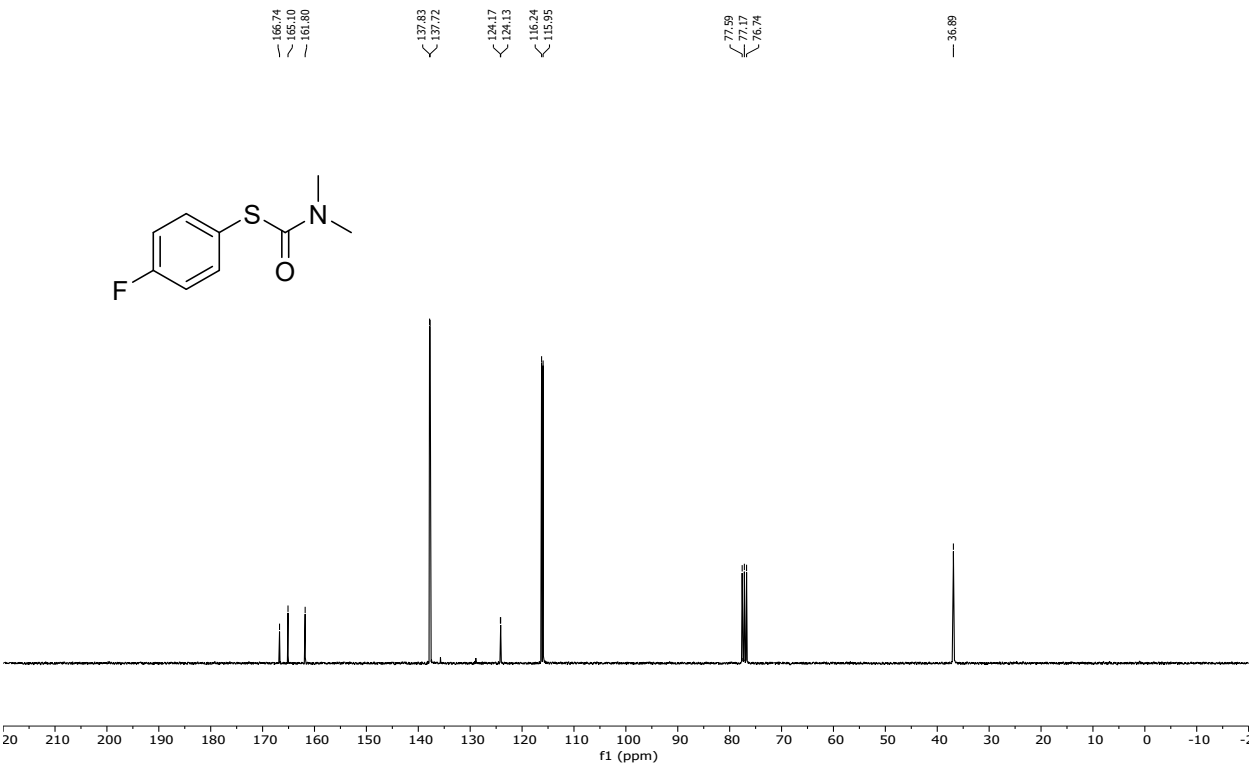
5. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3e**



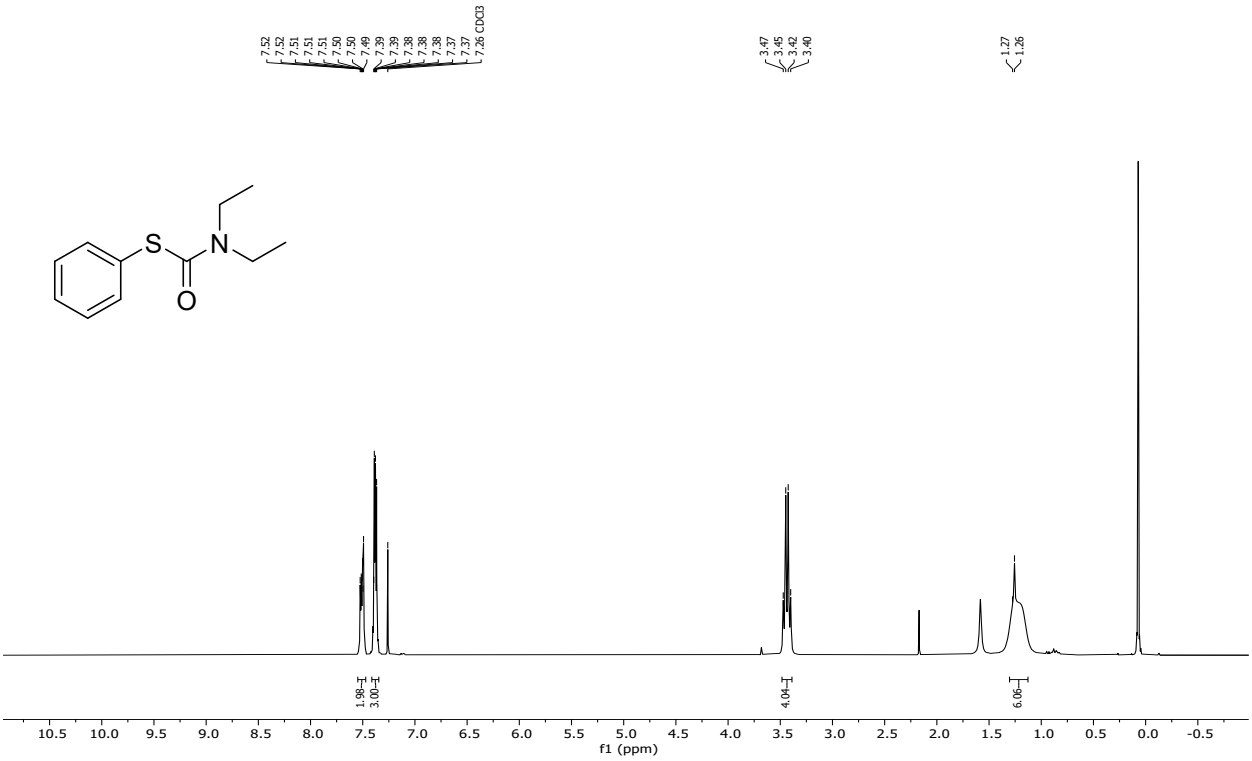


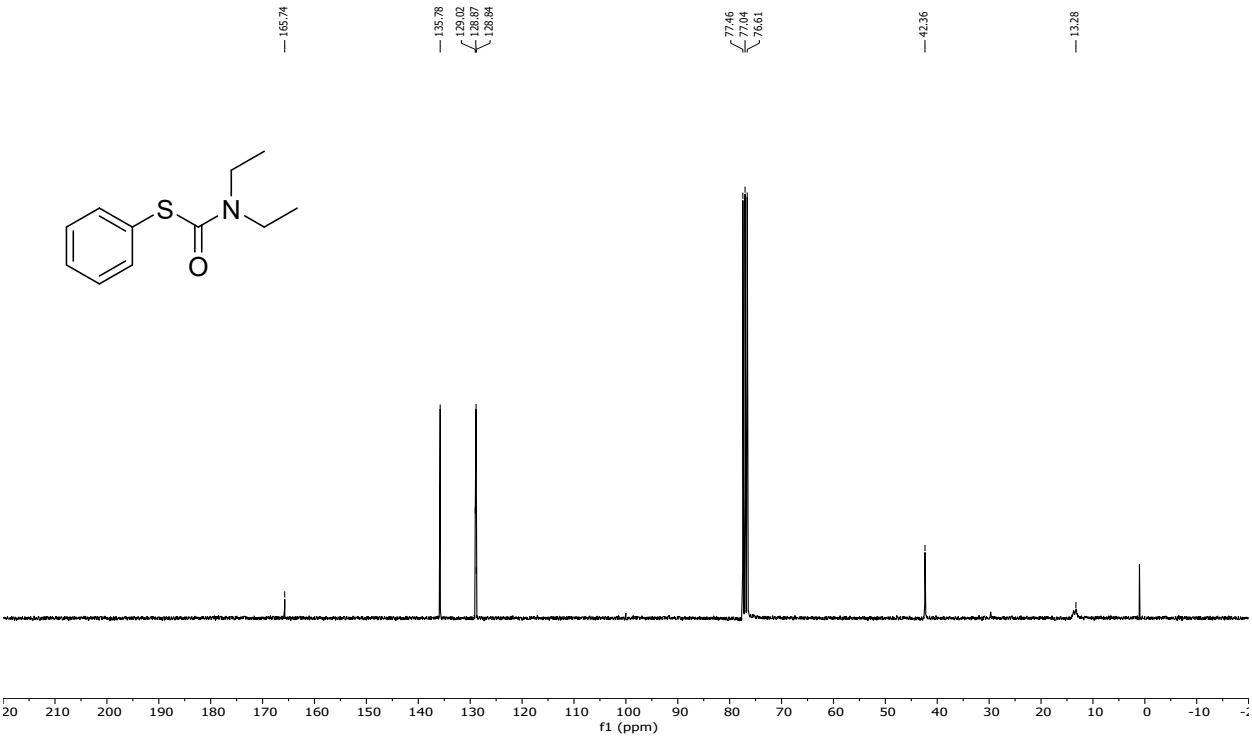
6. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3f**



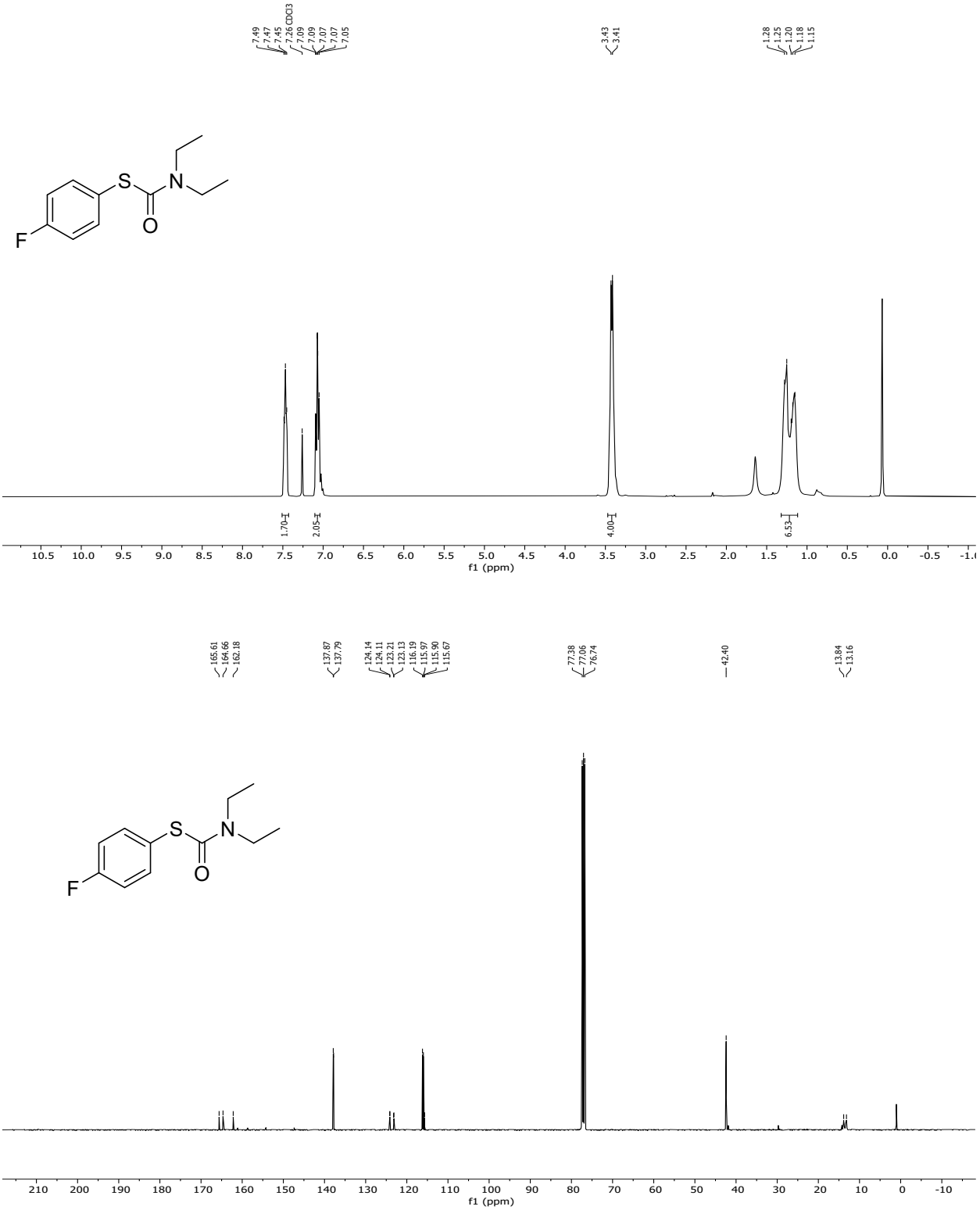


7. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) spectra of **3g**

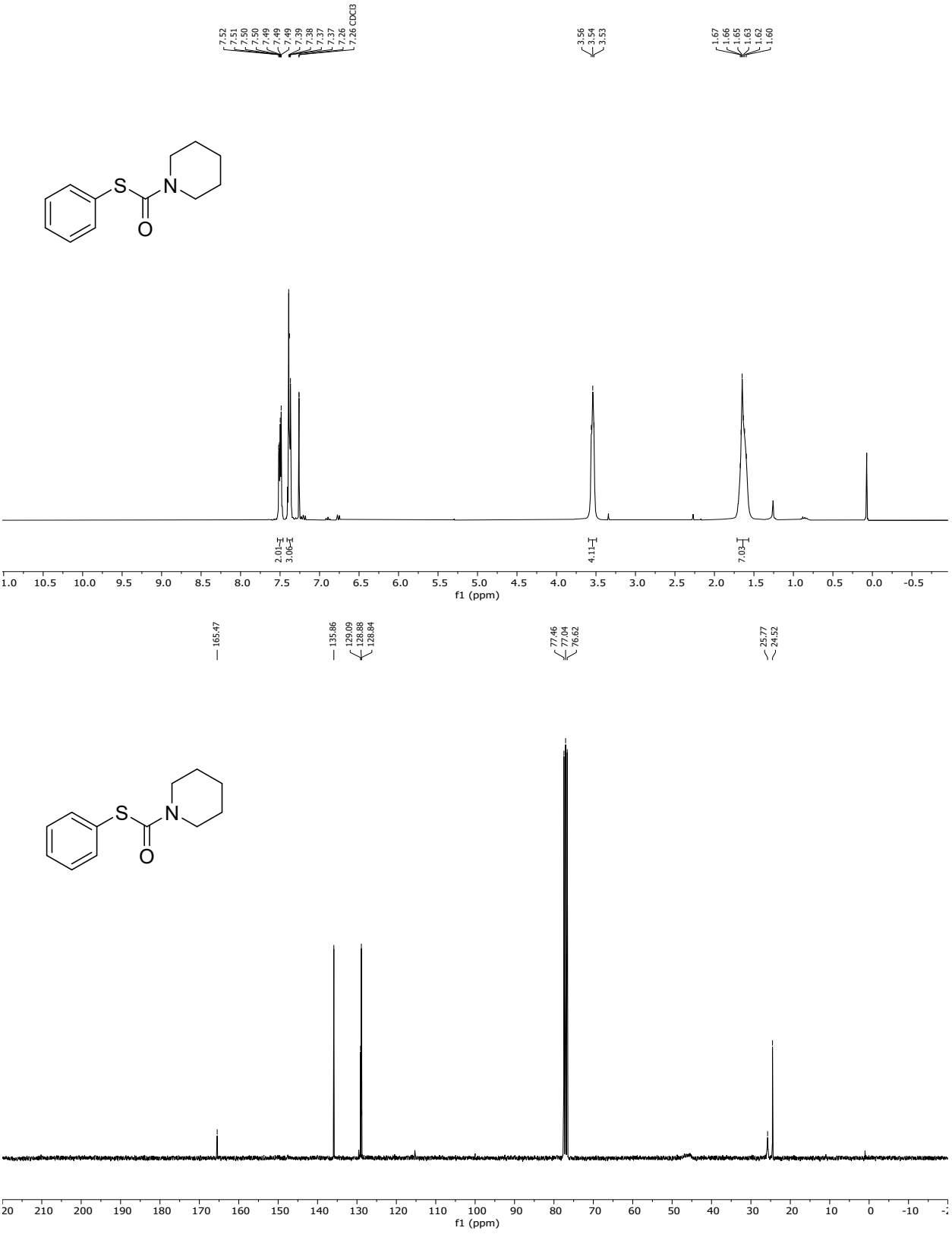




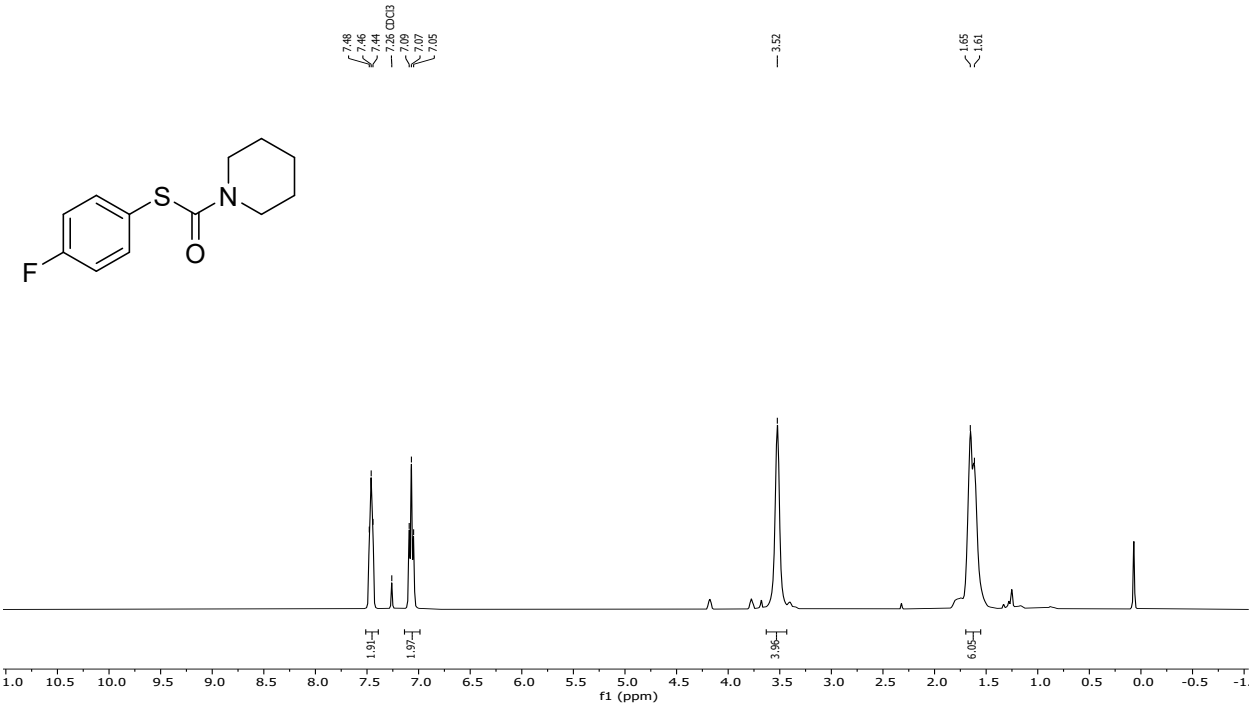
8. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3h**

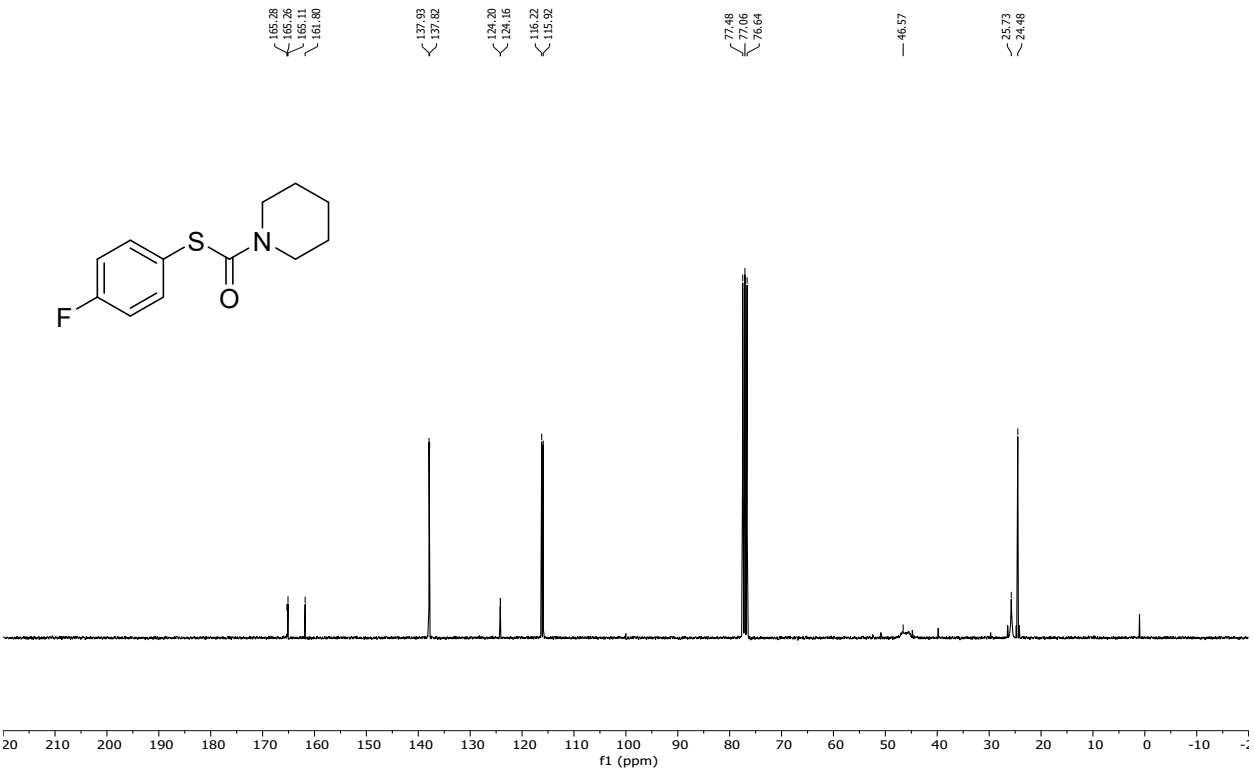


9. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3i**

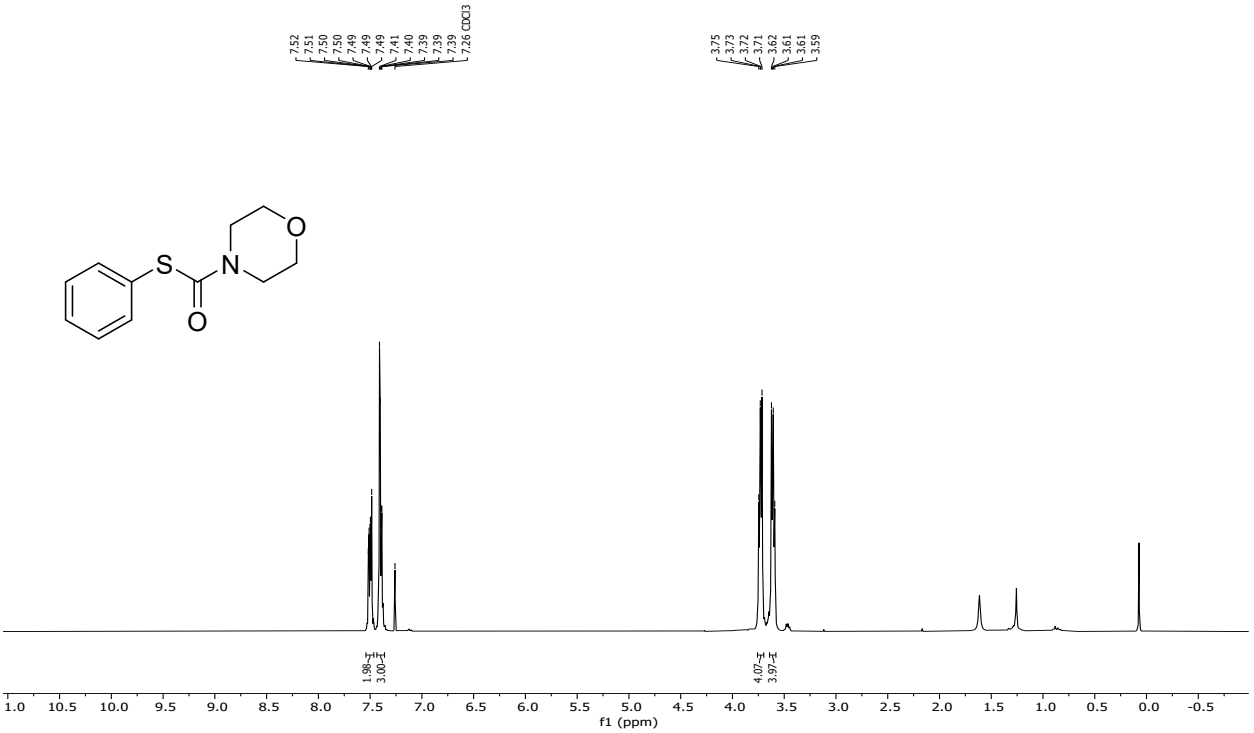


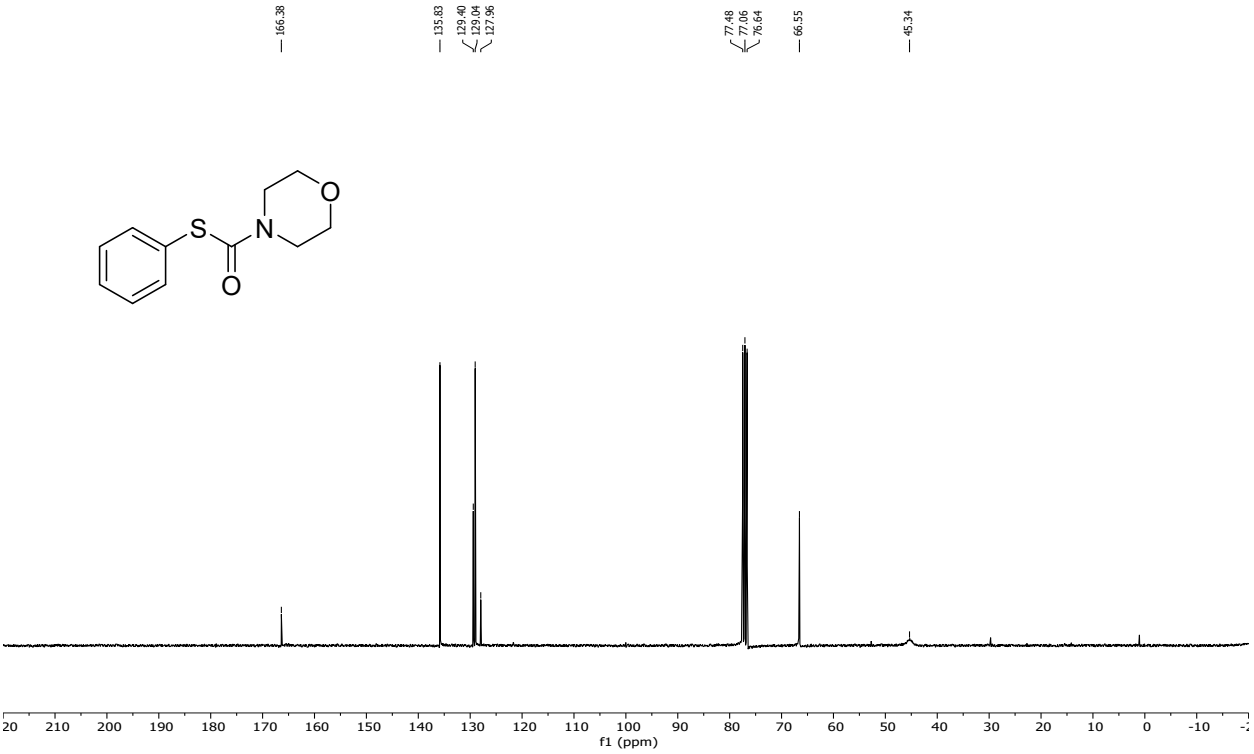
10. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3j**


7.48
7.46
7.44
7.26 CDCl3
7.09
7.07
7.05
3.52
1.65
1.61
S
N
O
F
1.91
1.97
3.96
6.05
f1 (ppm)

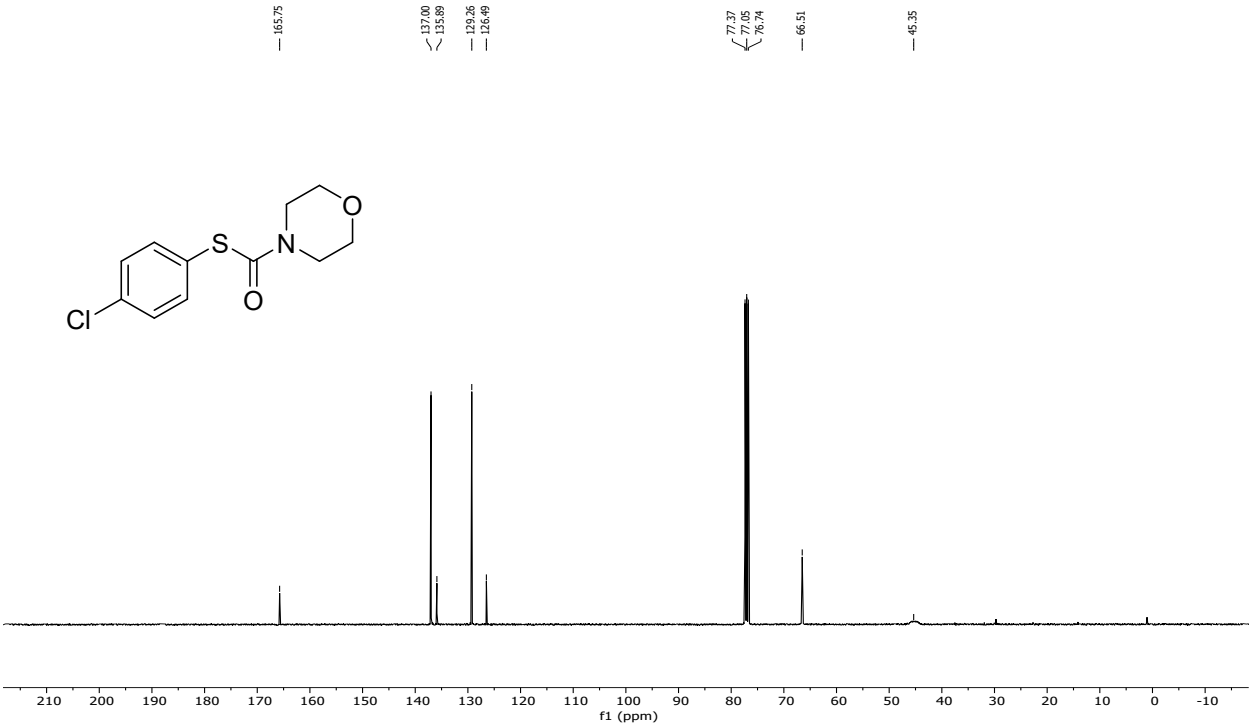

165.28
165.26
165.11
161.80
137.93
137.82
124.20
124.16
116.22
115.92
77.48
77.06
76.64
46.57
25.73
24.48
S
N
O
F
f1 (ppm)

11. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3k**

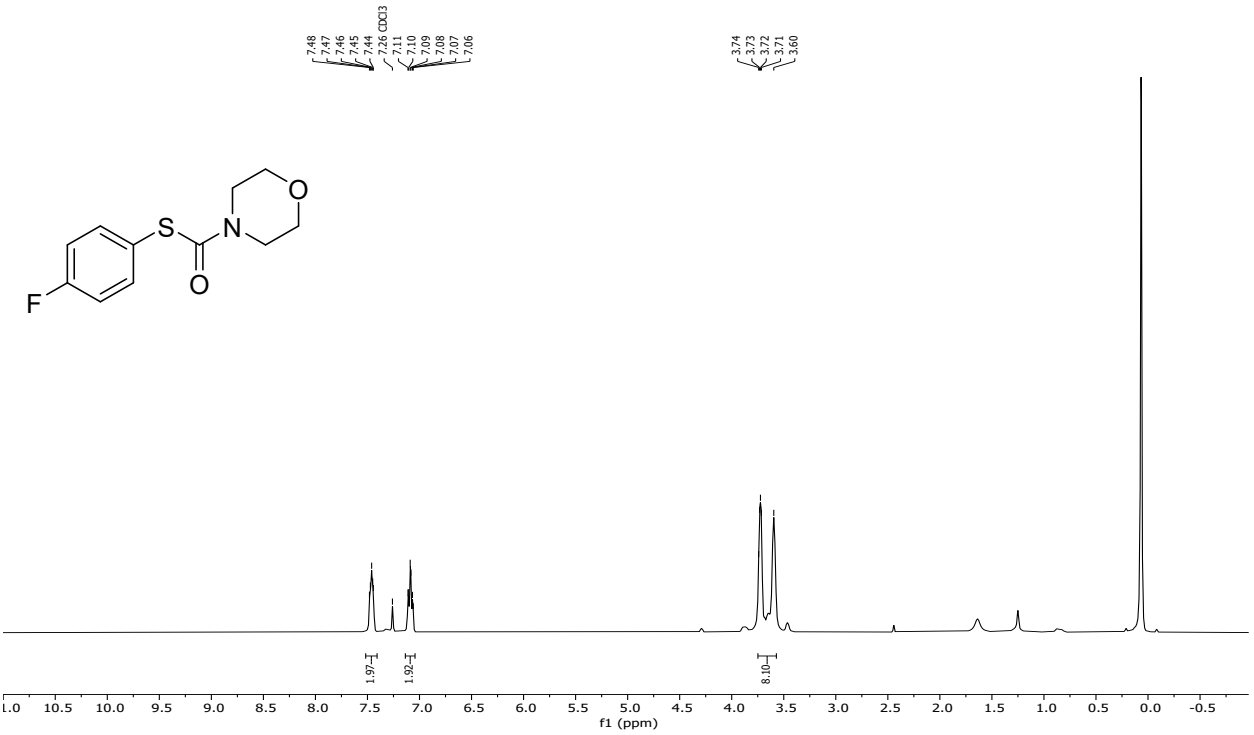


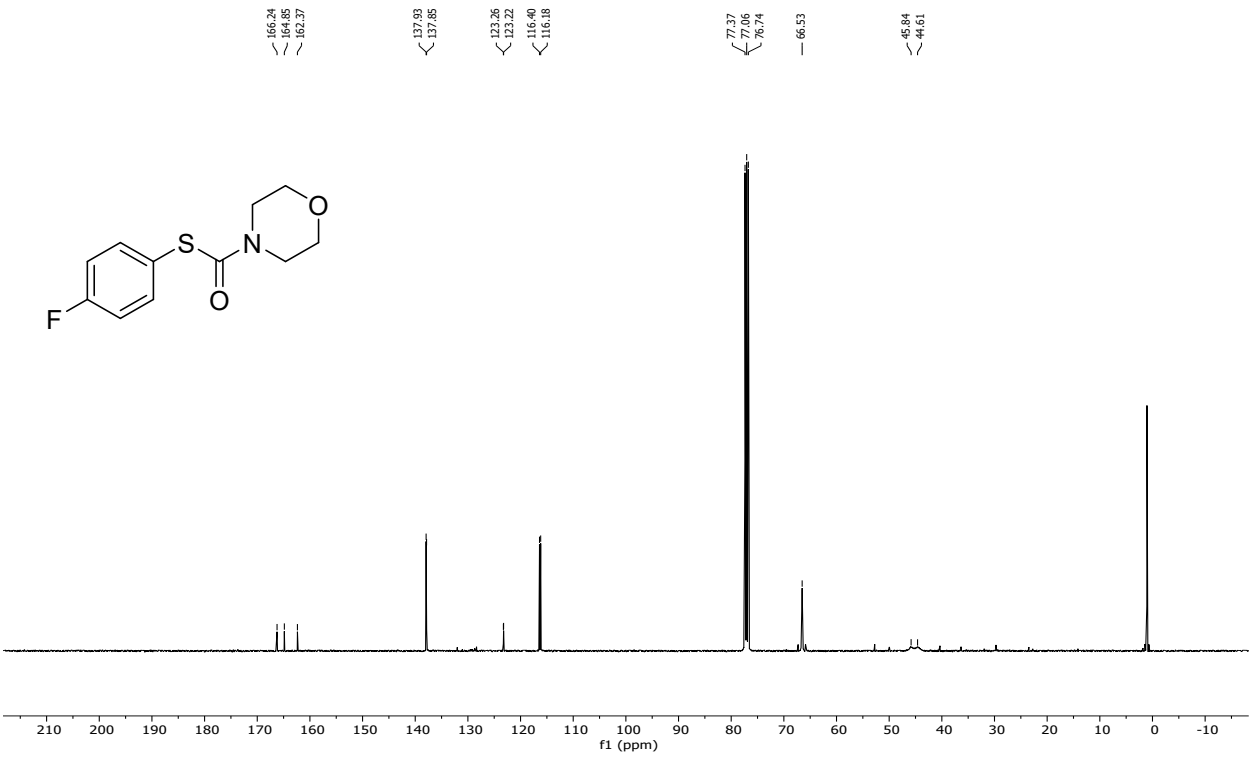


12. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3l**

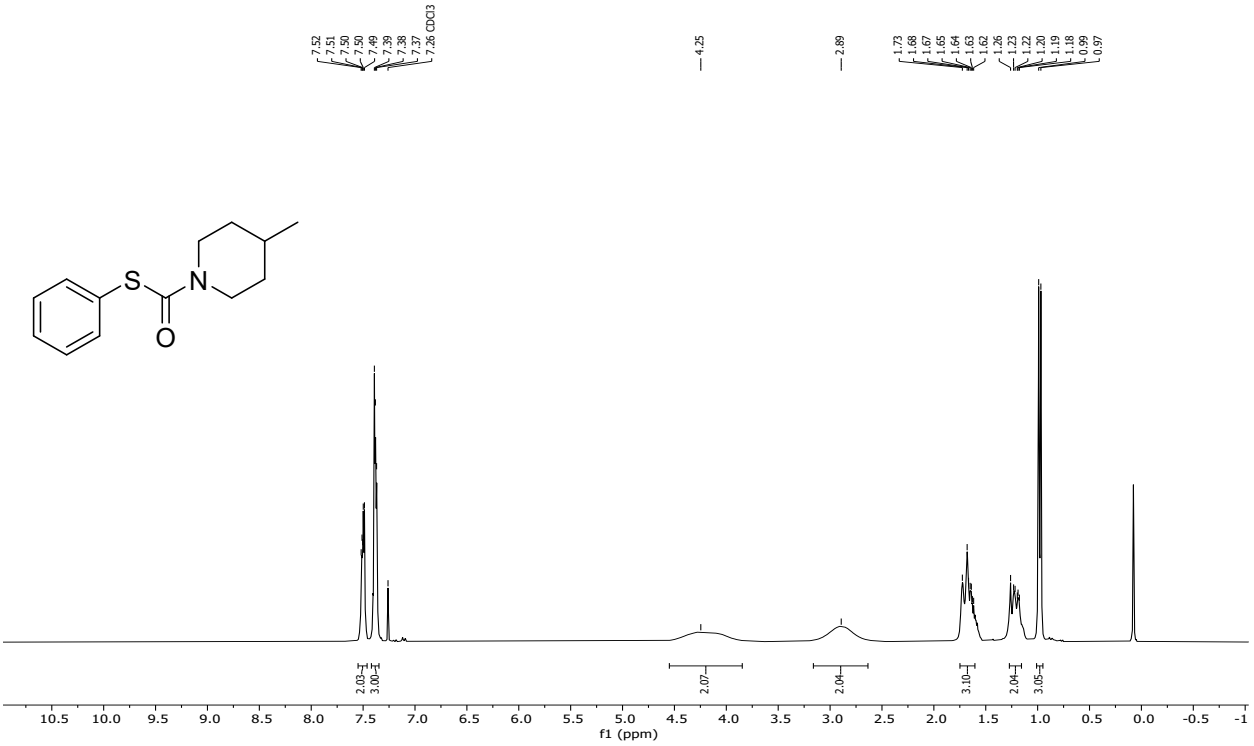


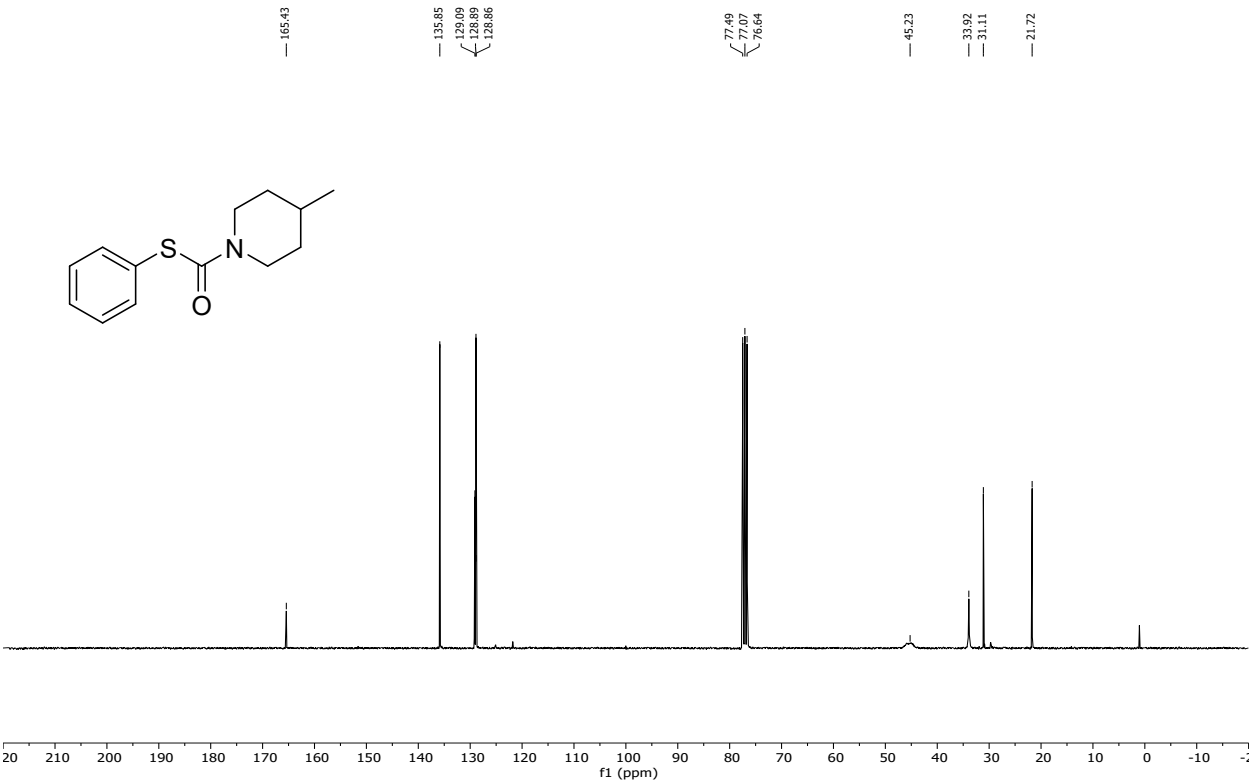
13. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3m**



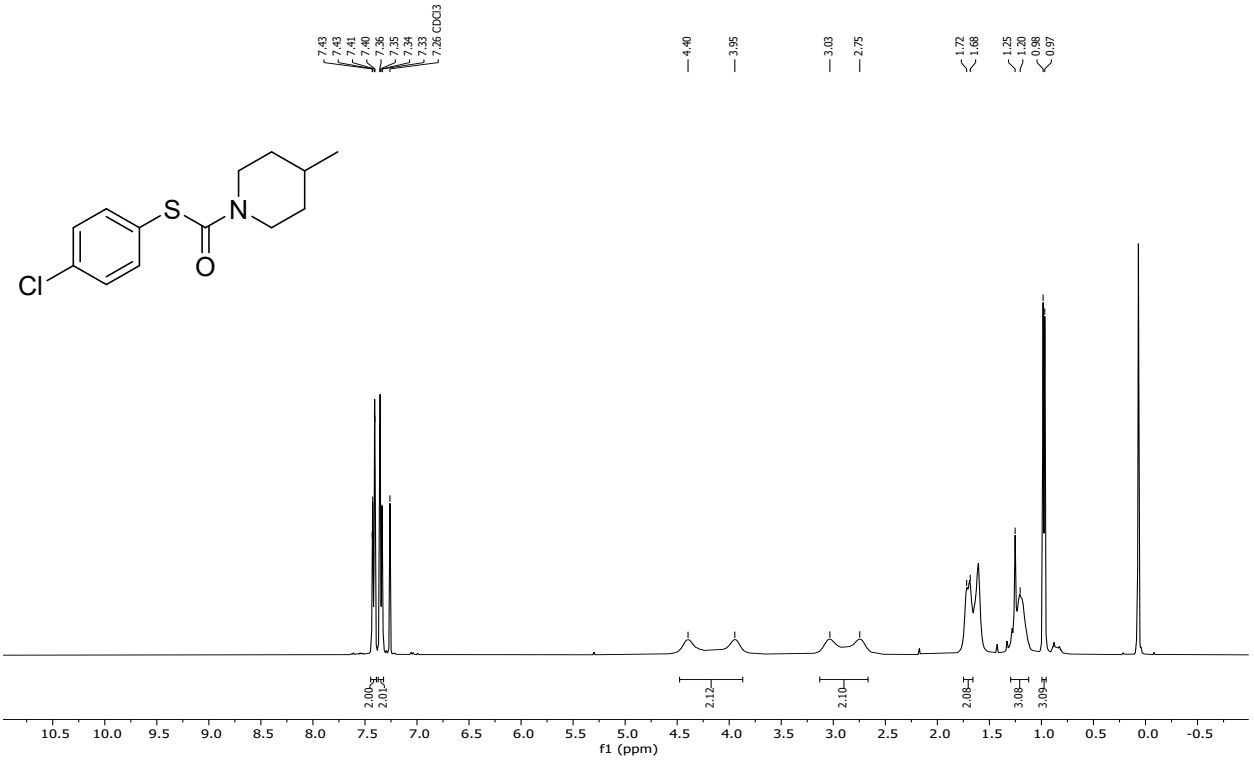


14. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3n**

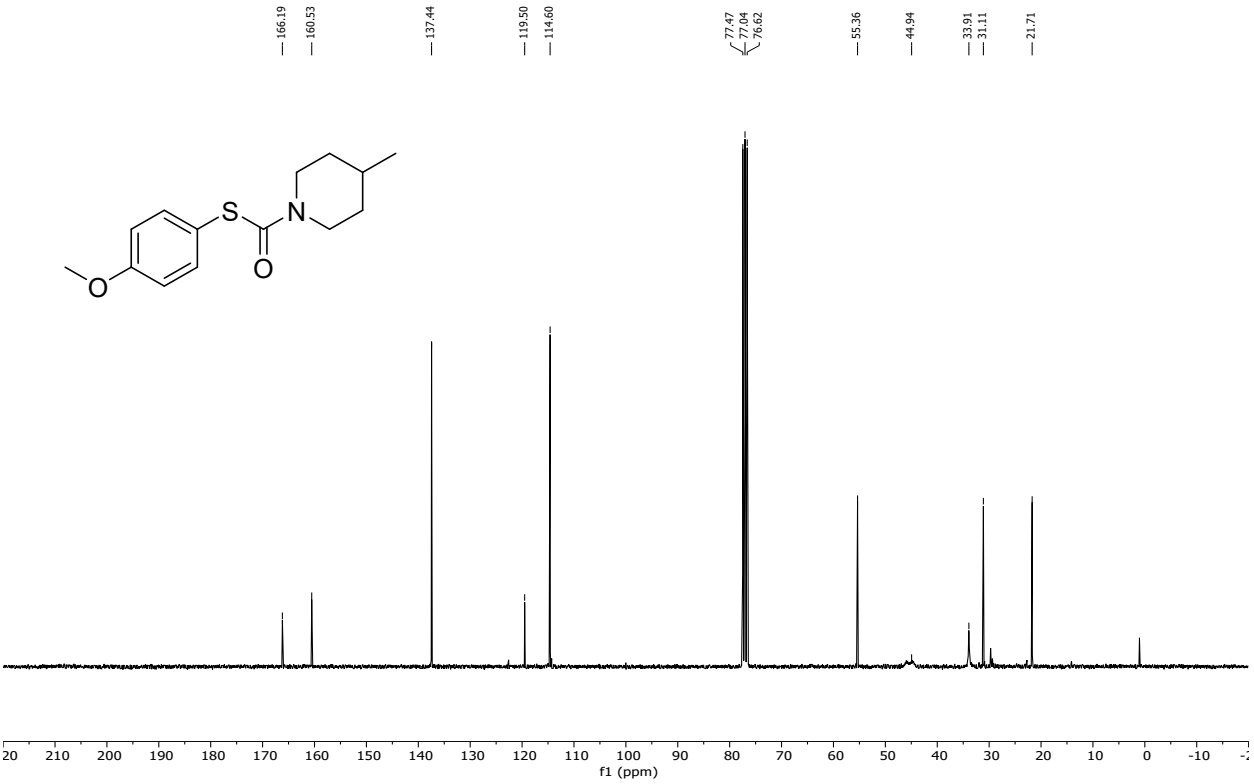




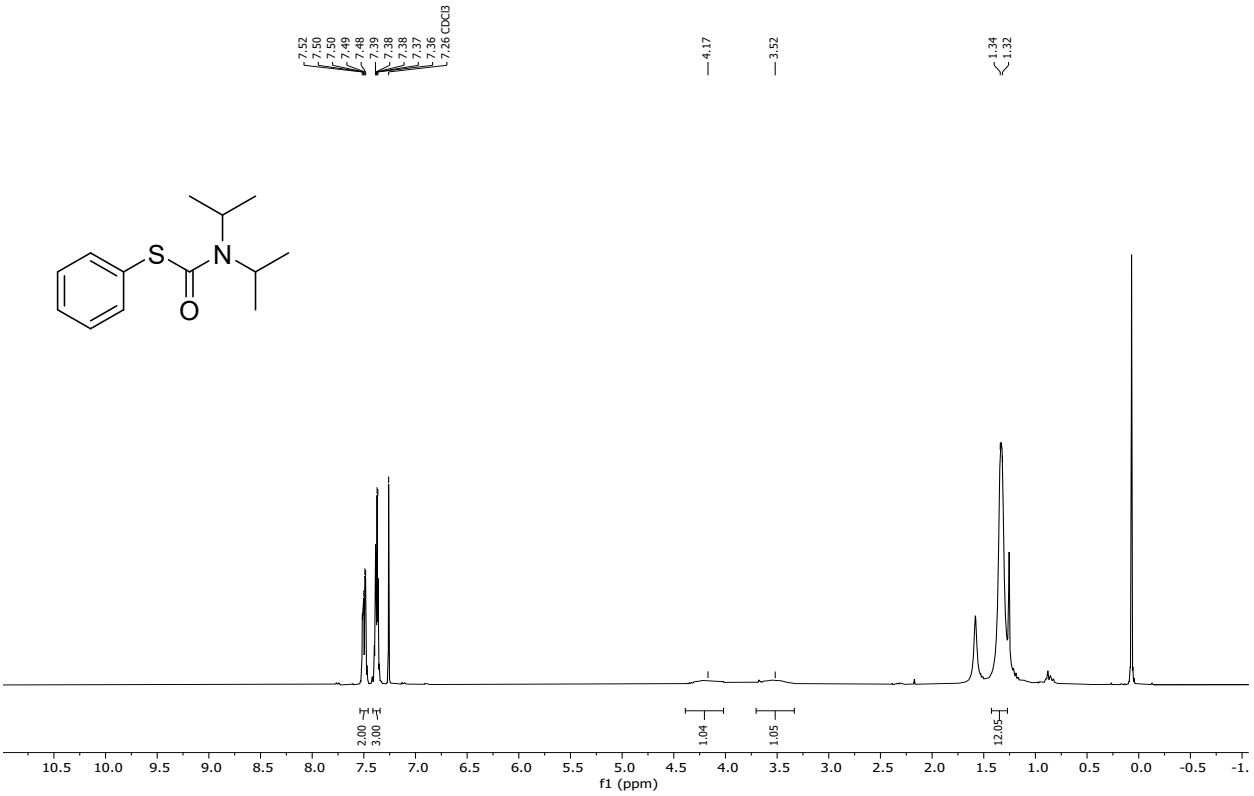
15. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3o**

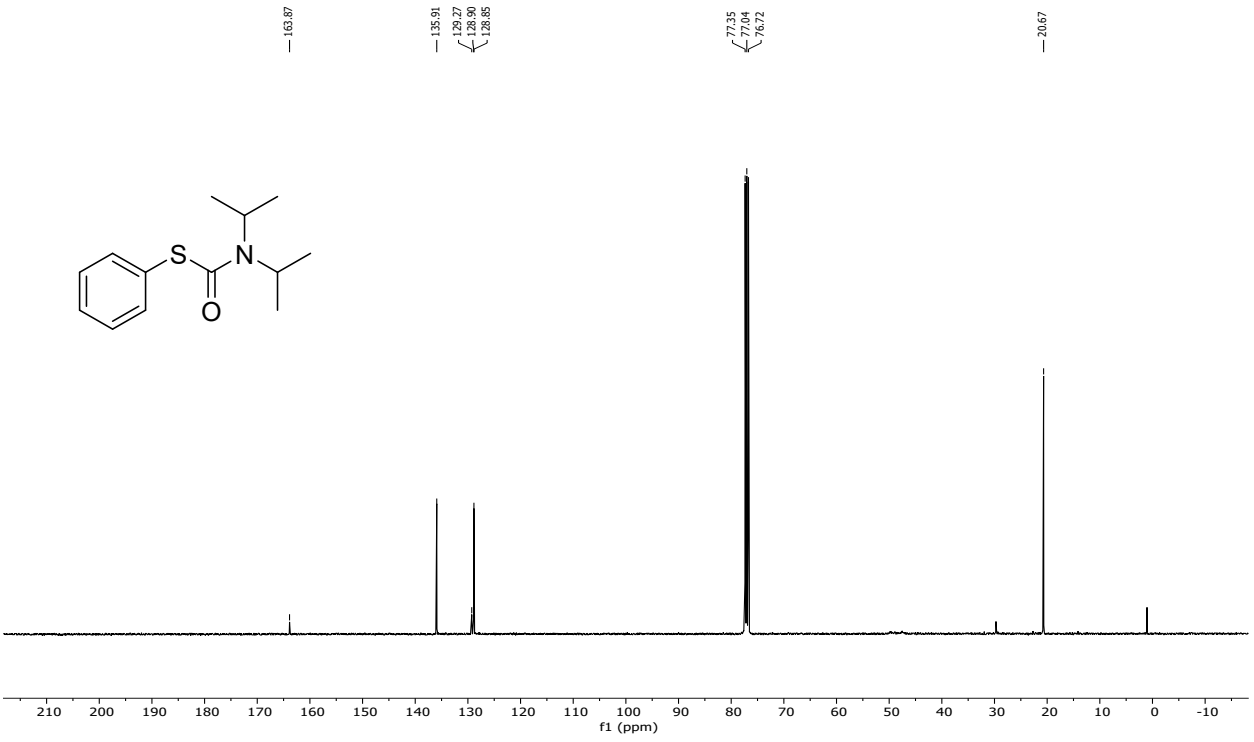


16. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3p**

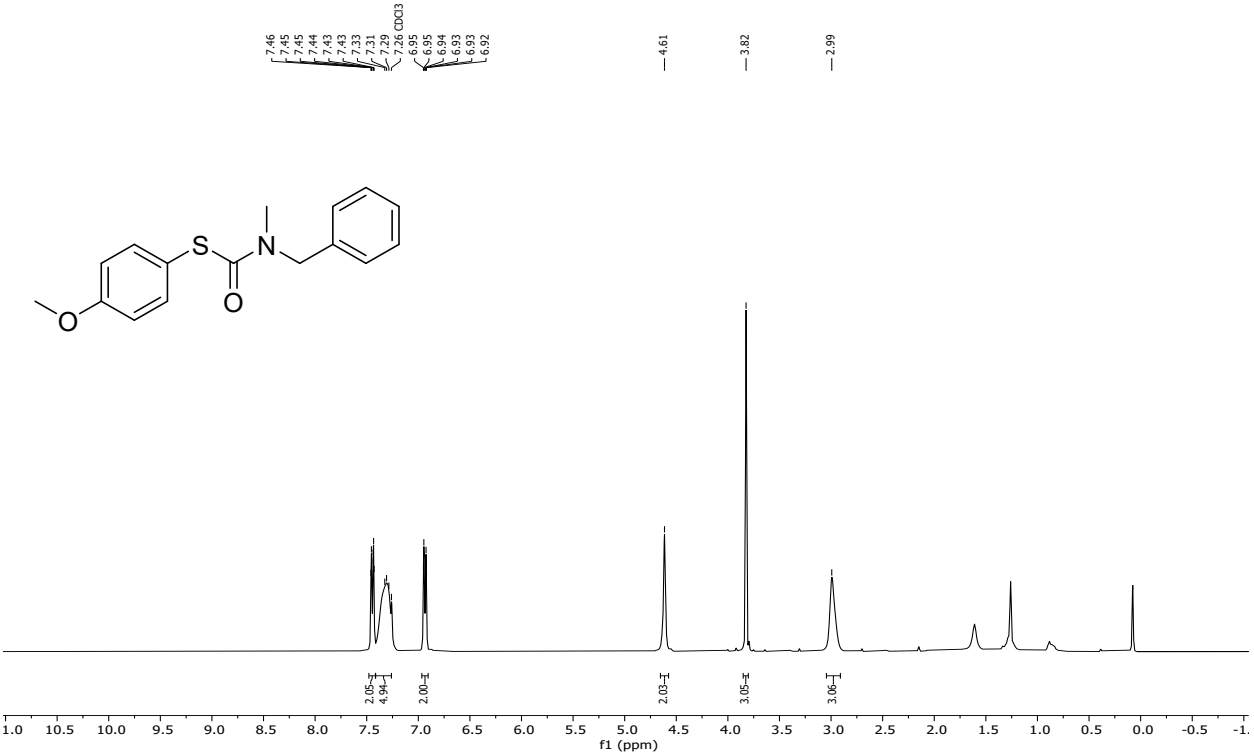


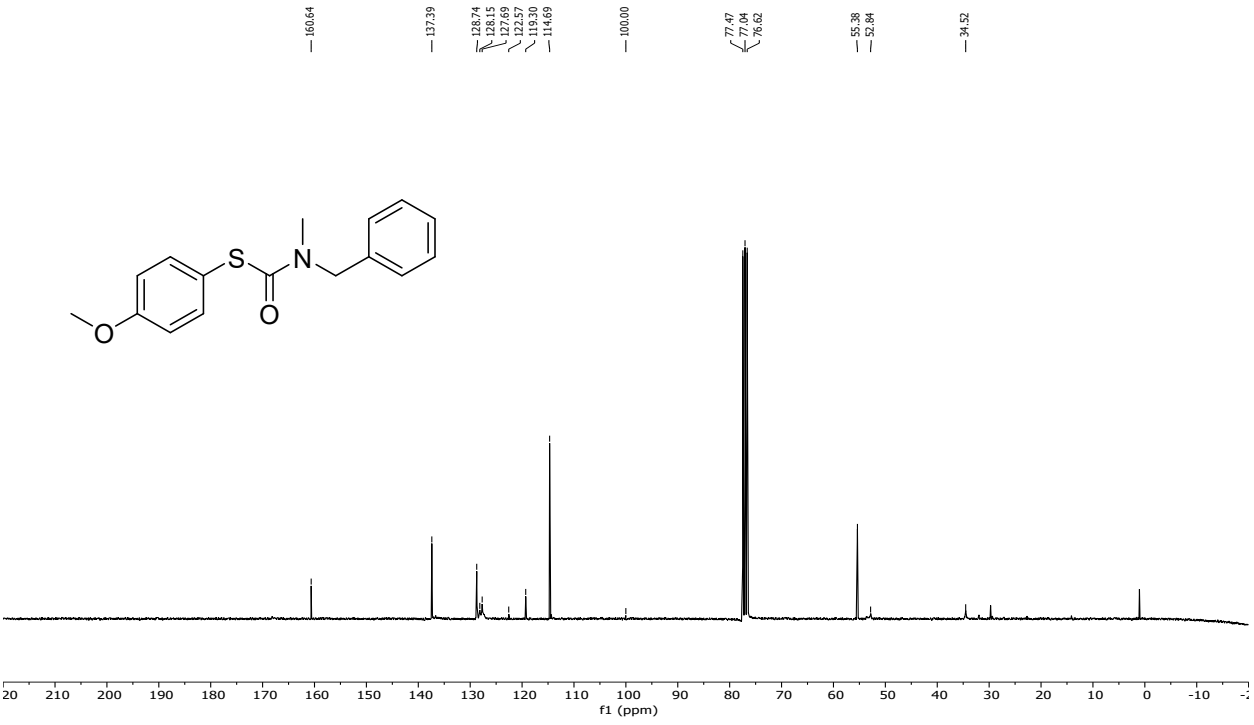
17. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3q**



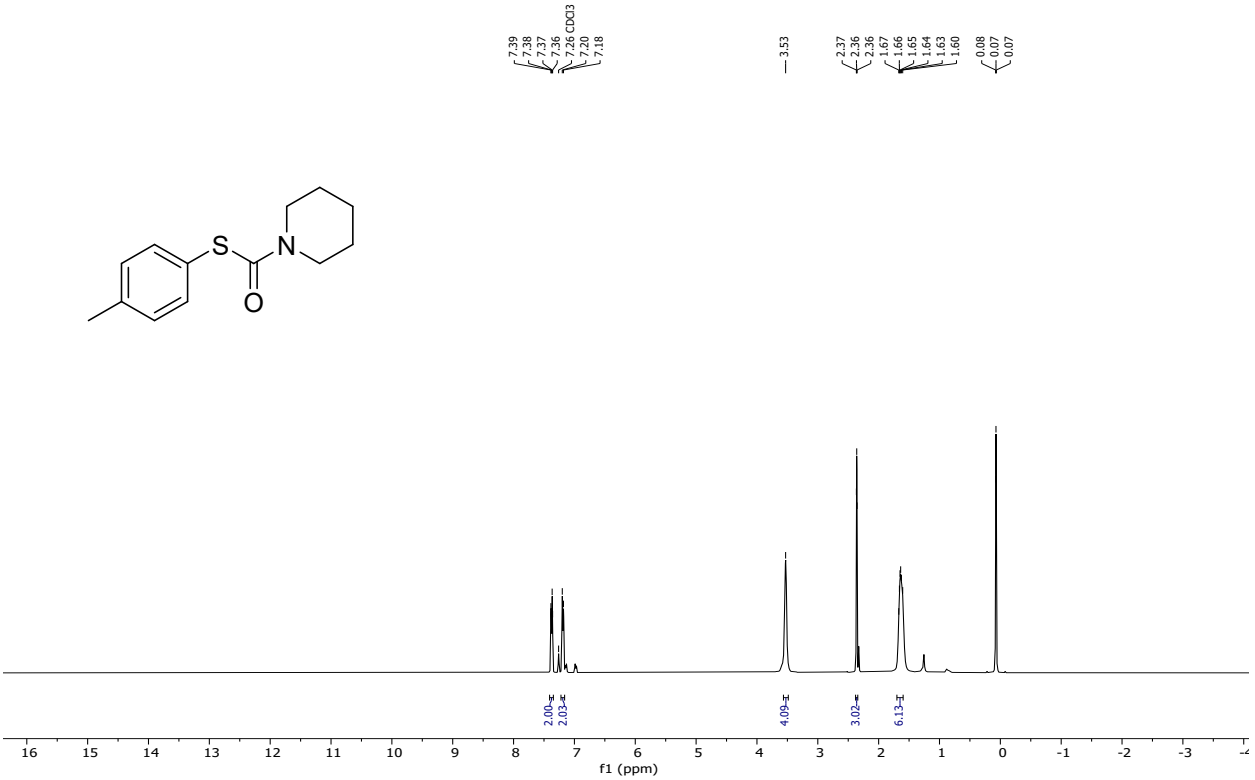


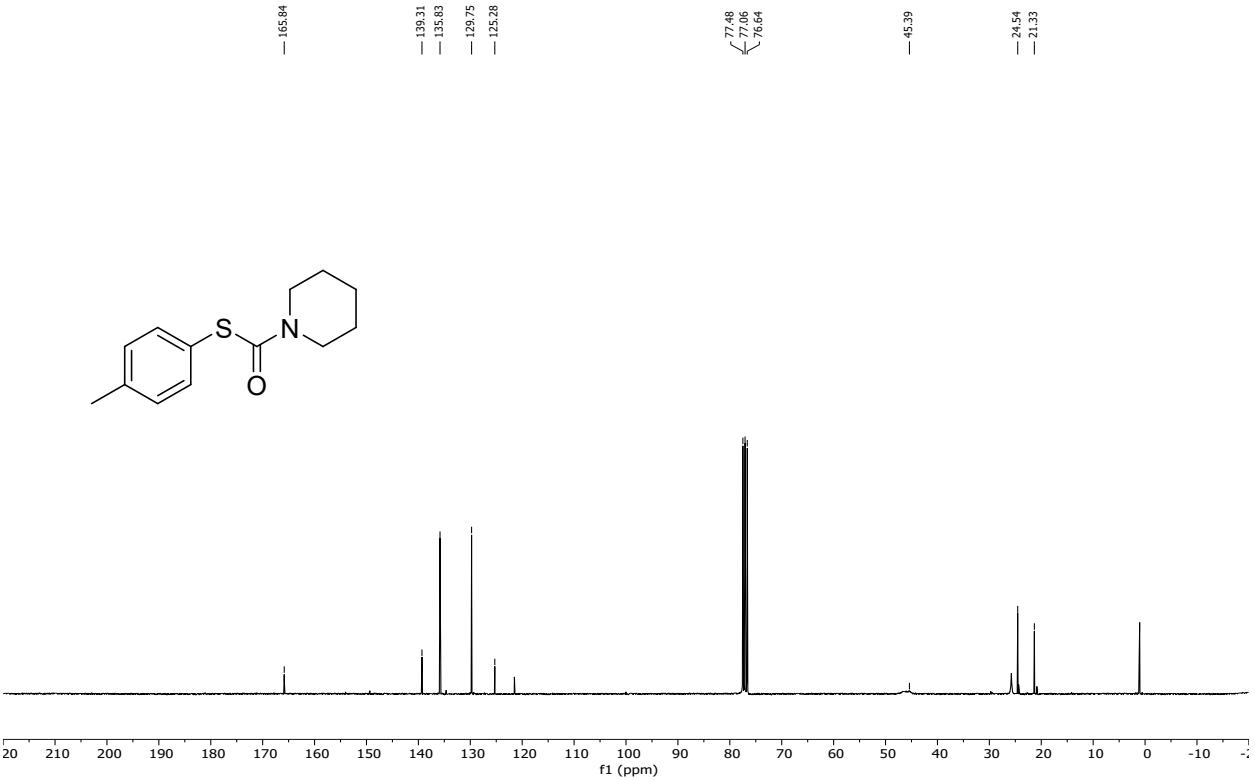
18. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3r**



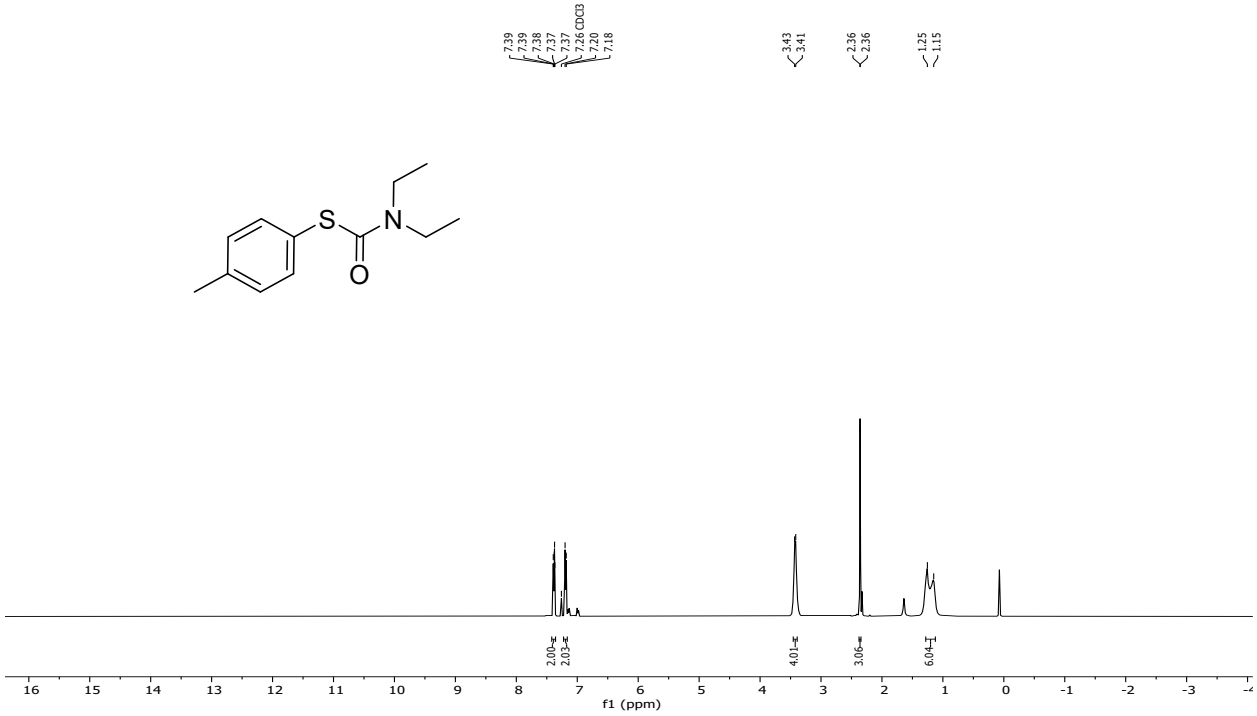


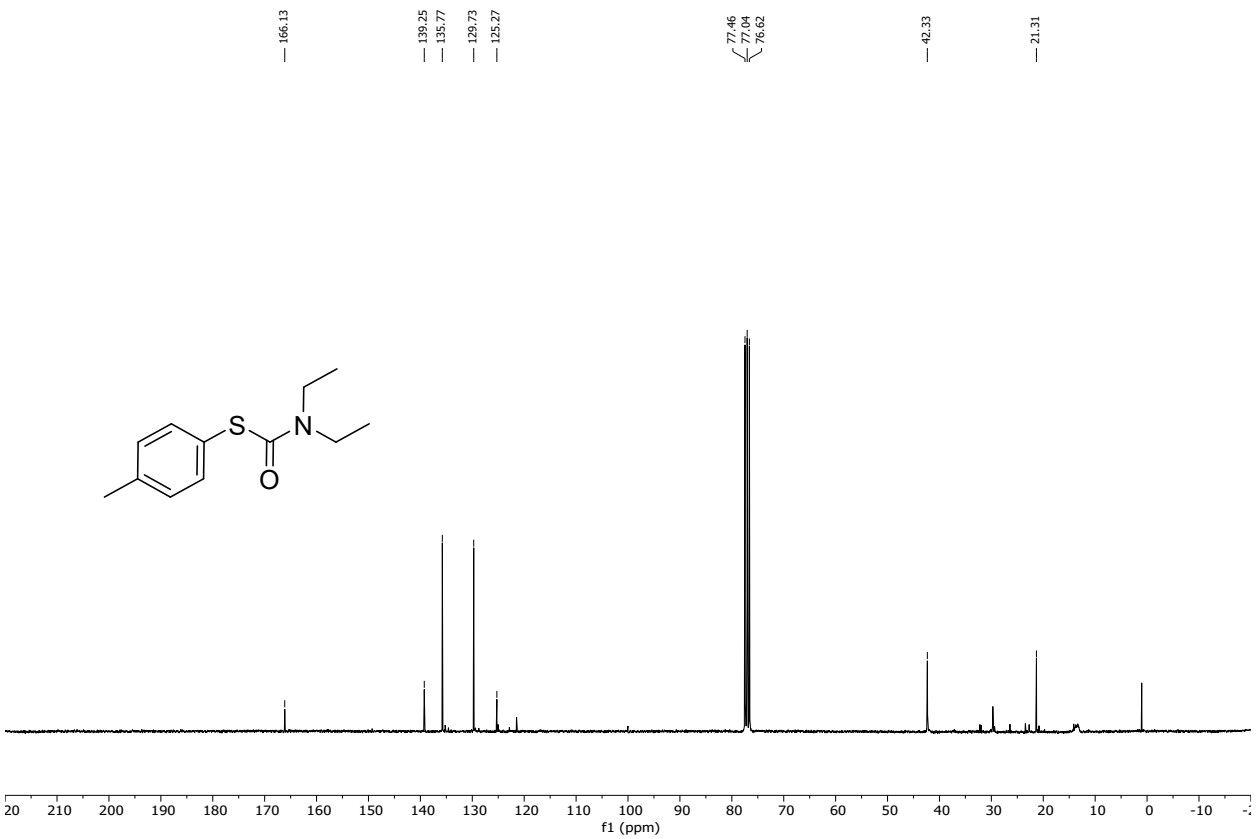
19. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) spectra of **3s**



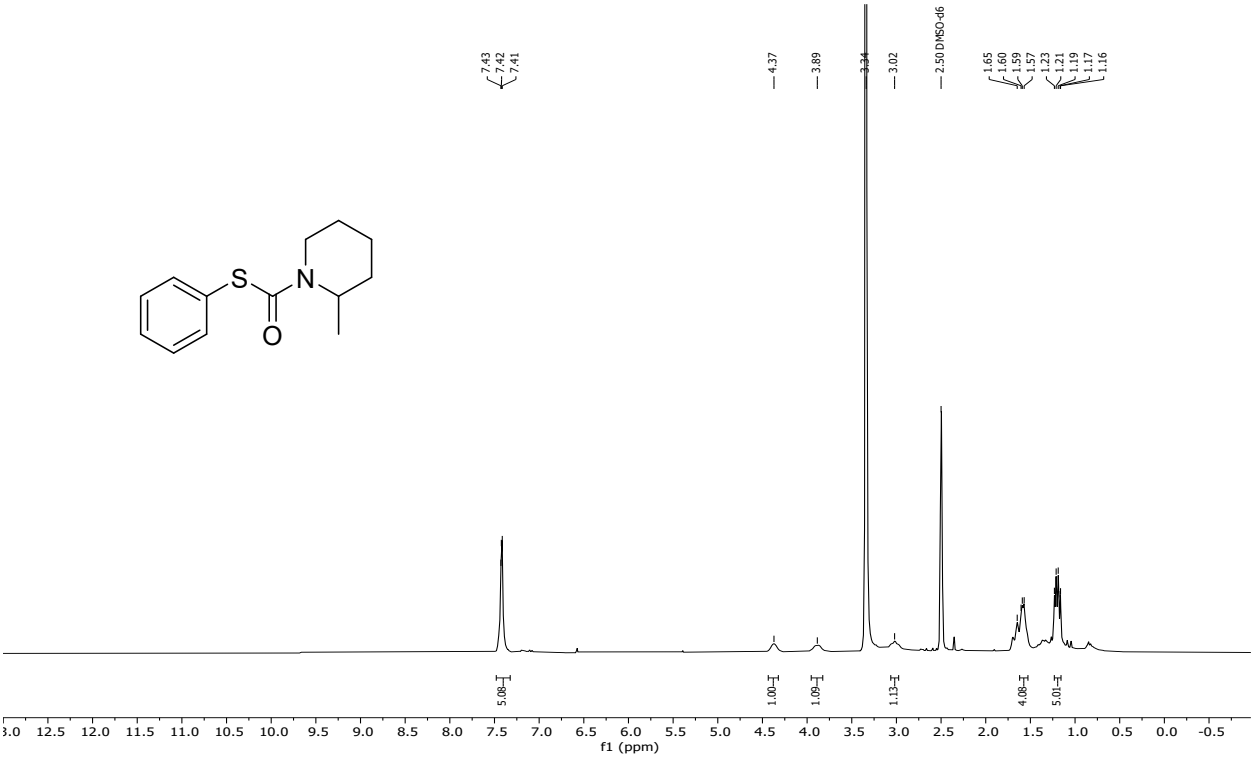


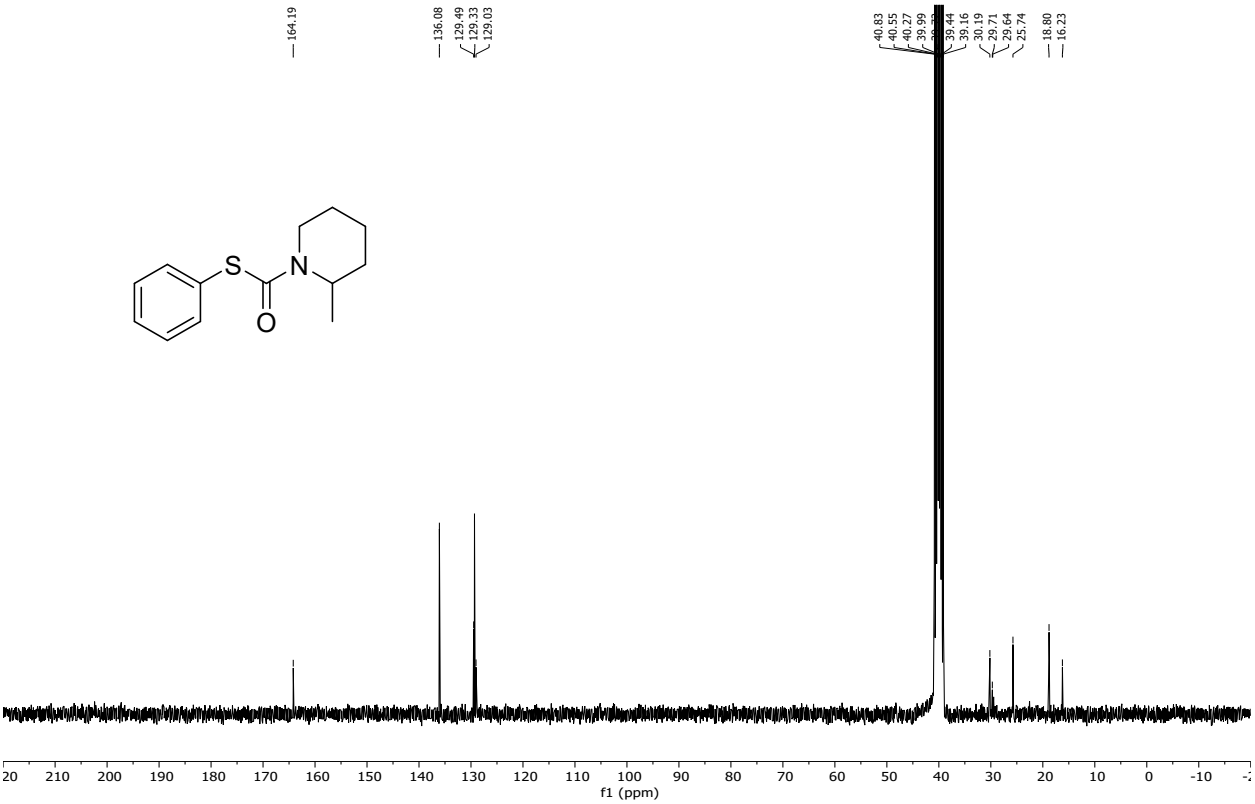
20. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3t**



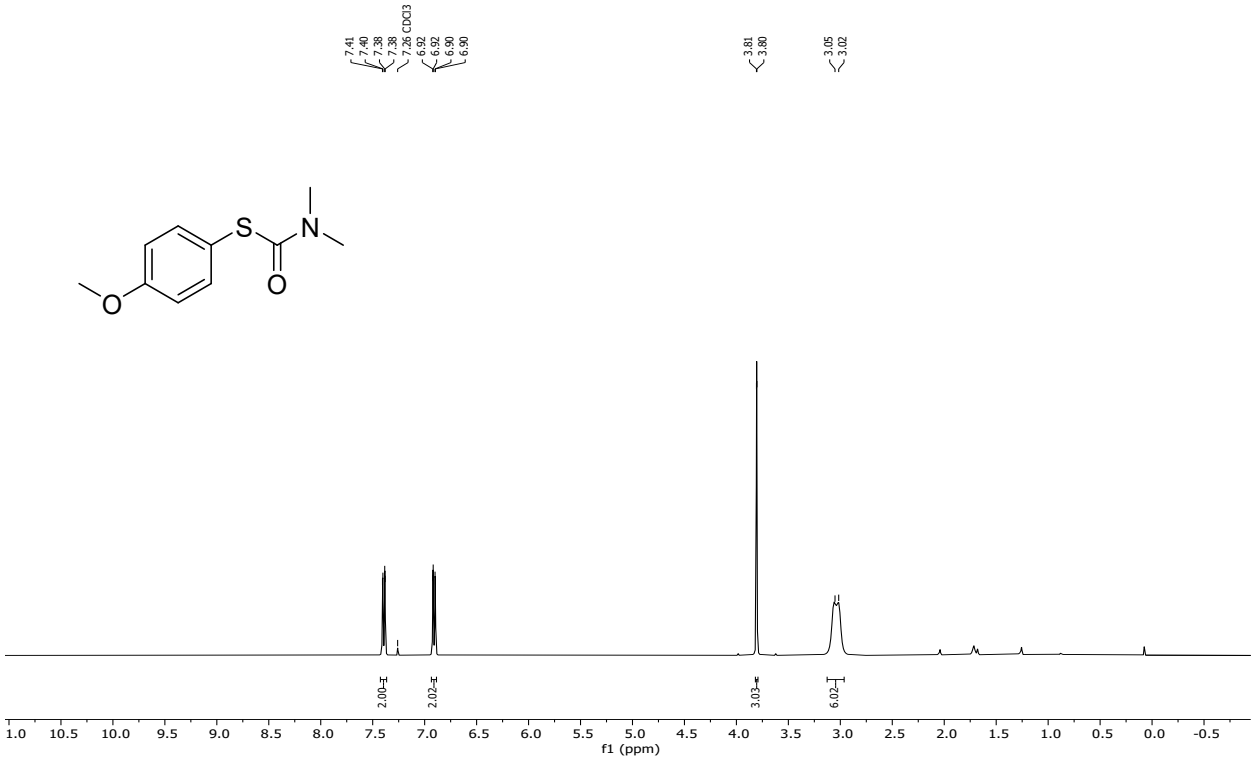


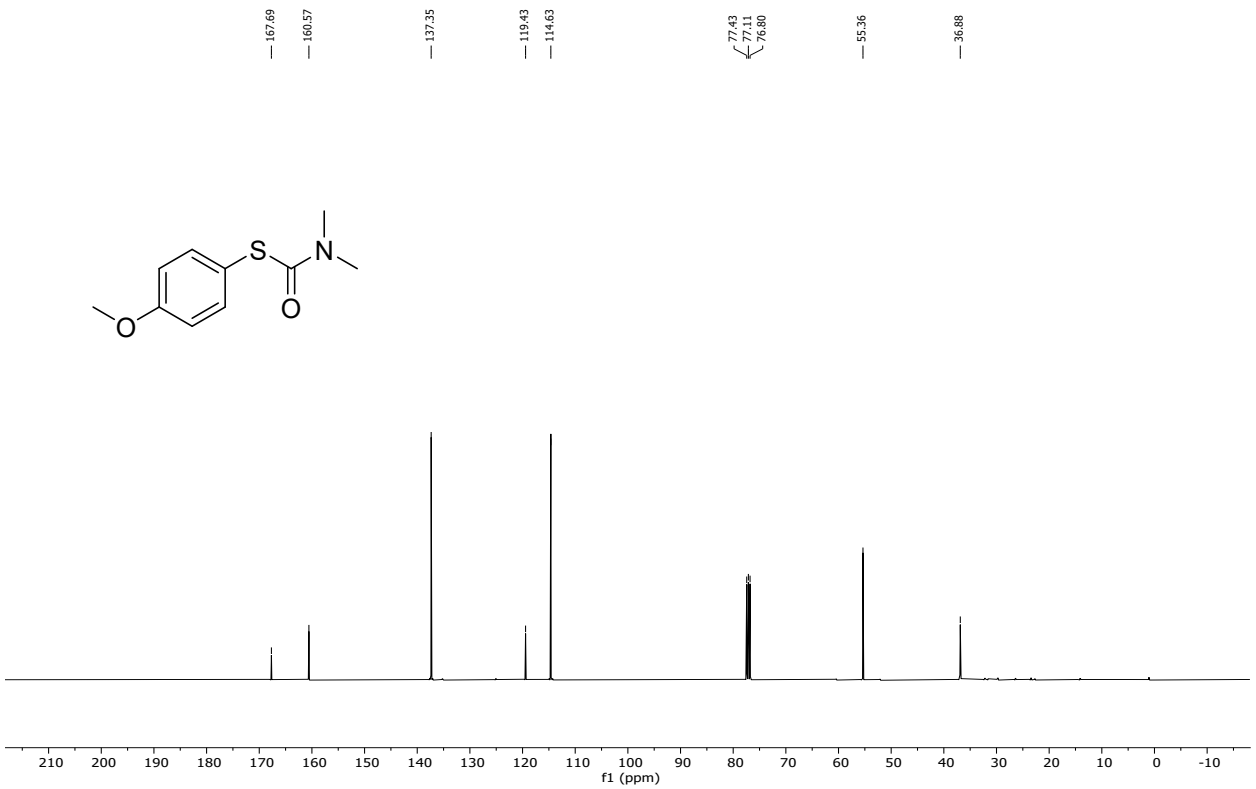
21. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3u**



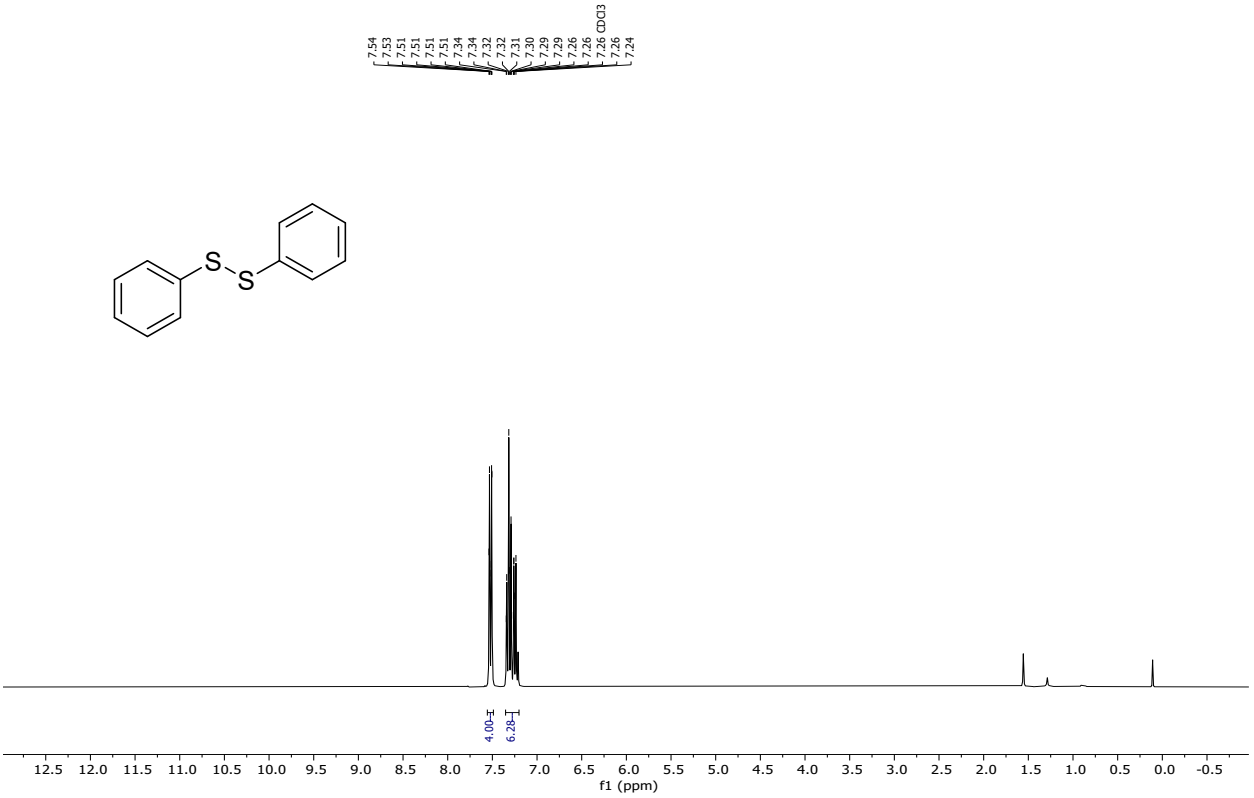


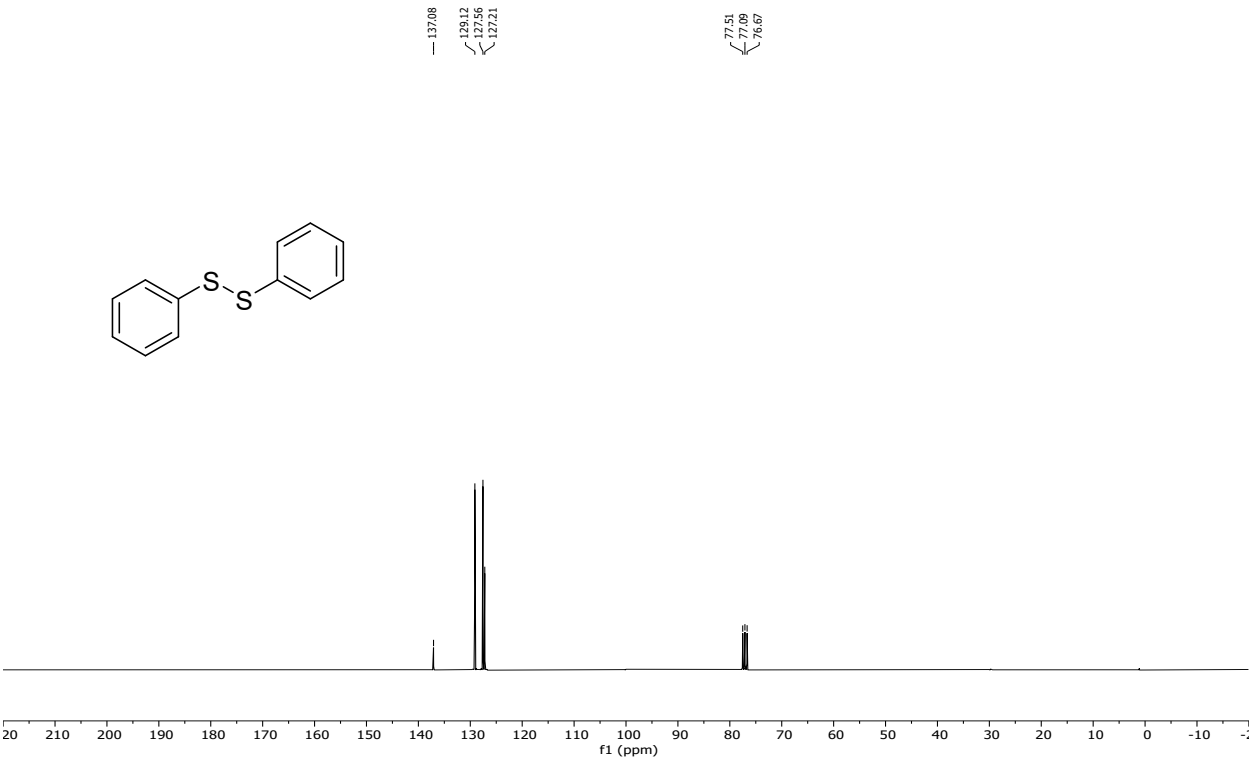
22. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **3ae**



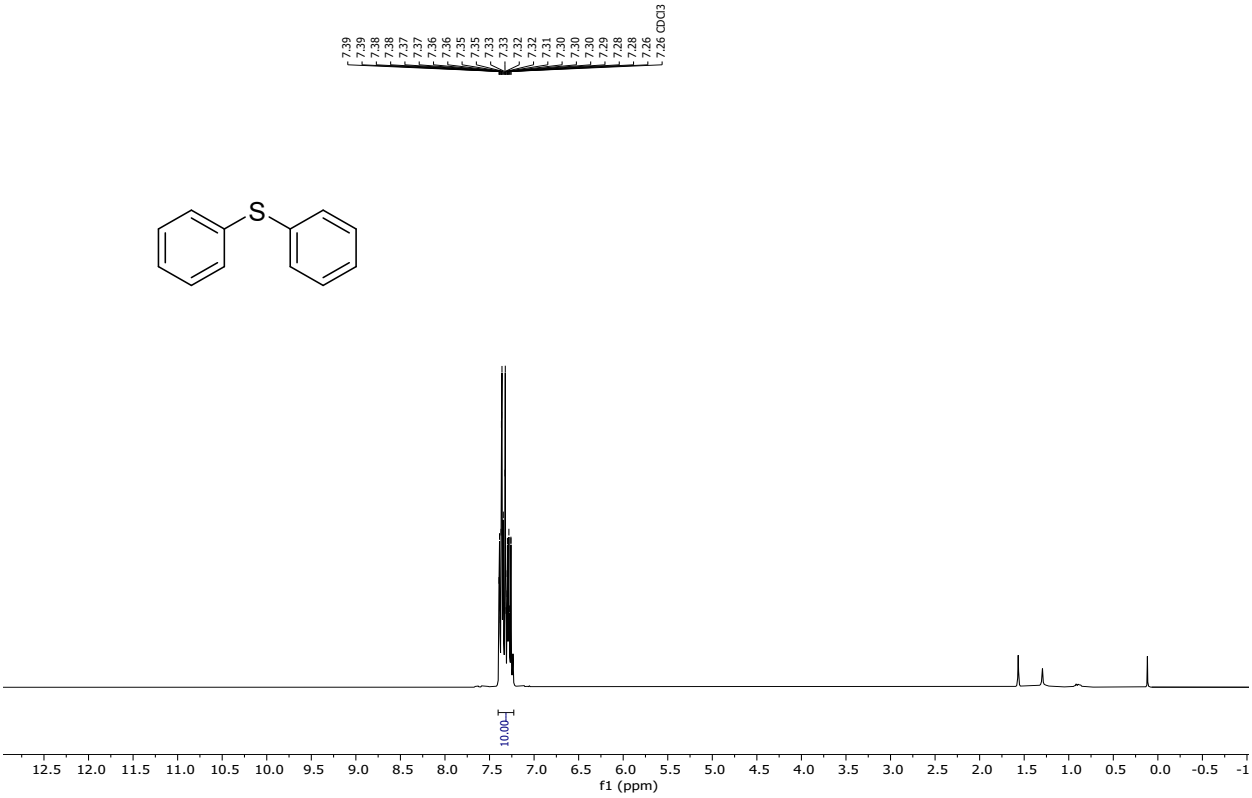


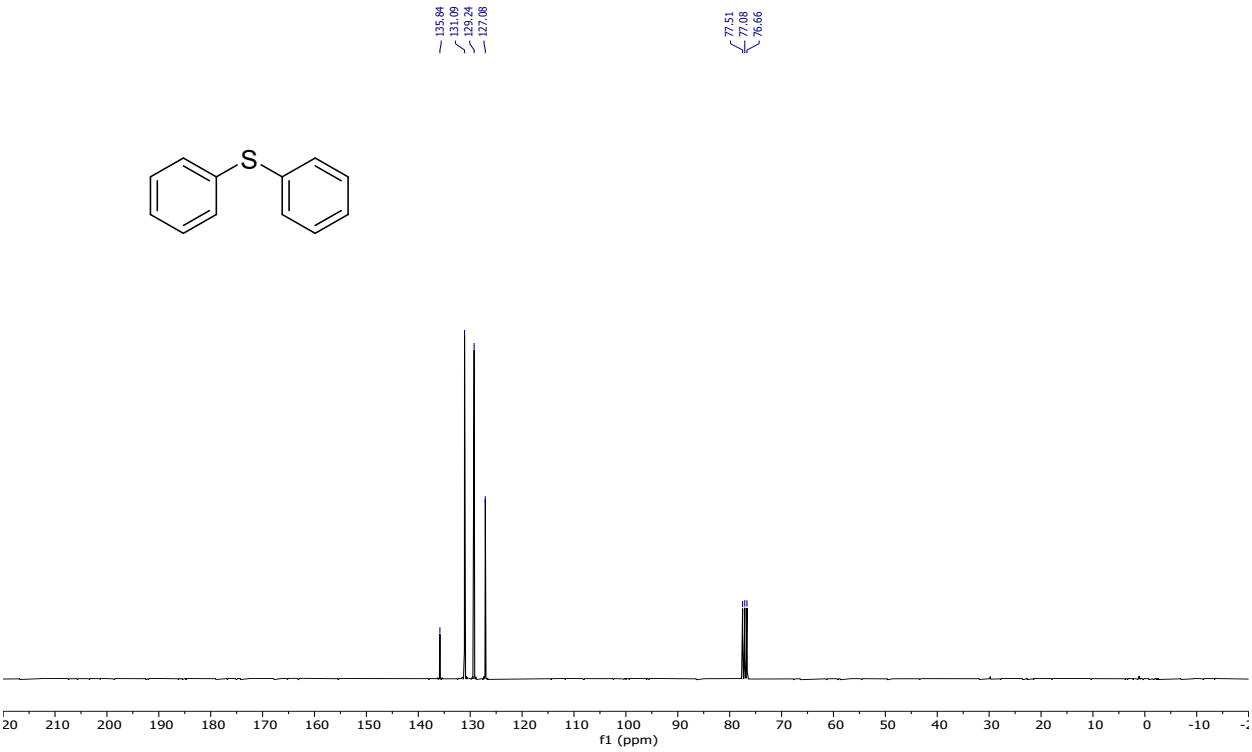
23. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **(11)**



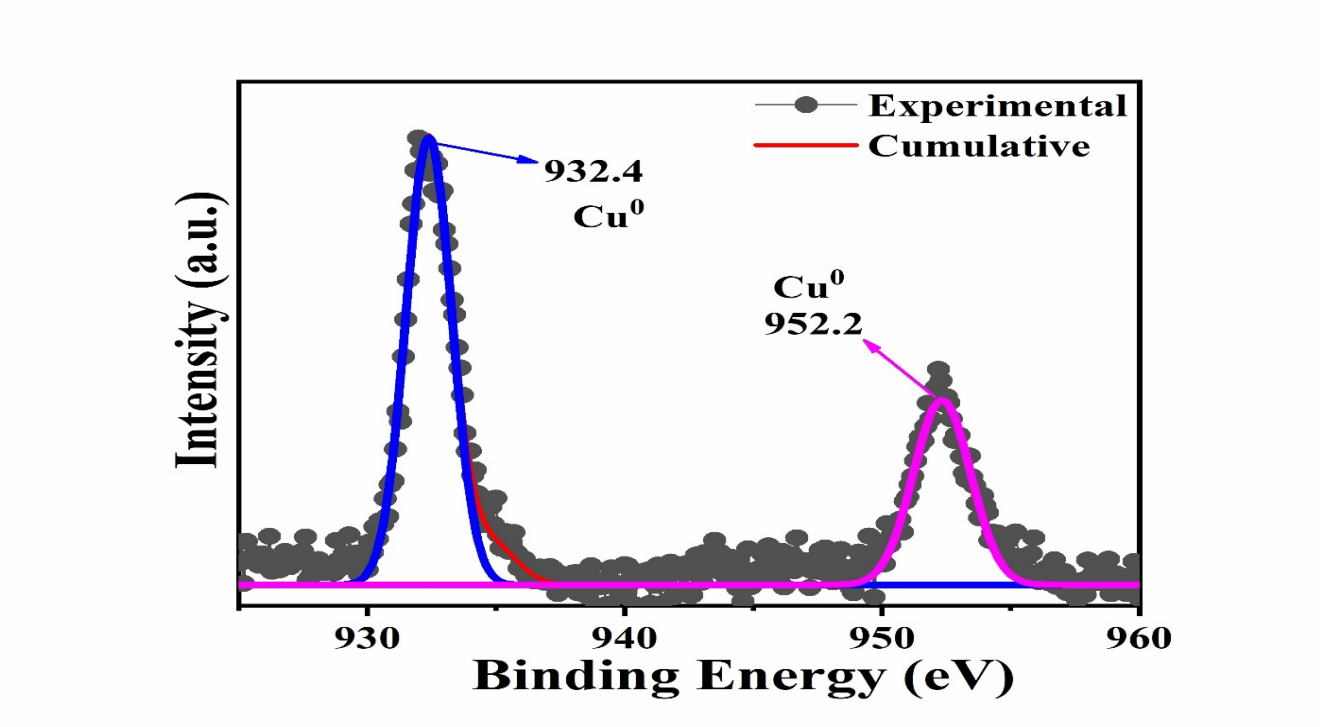


24. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of **(12)**

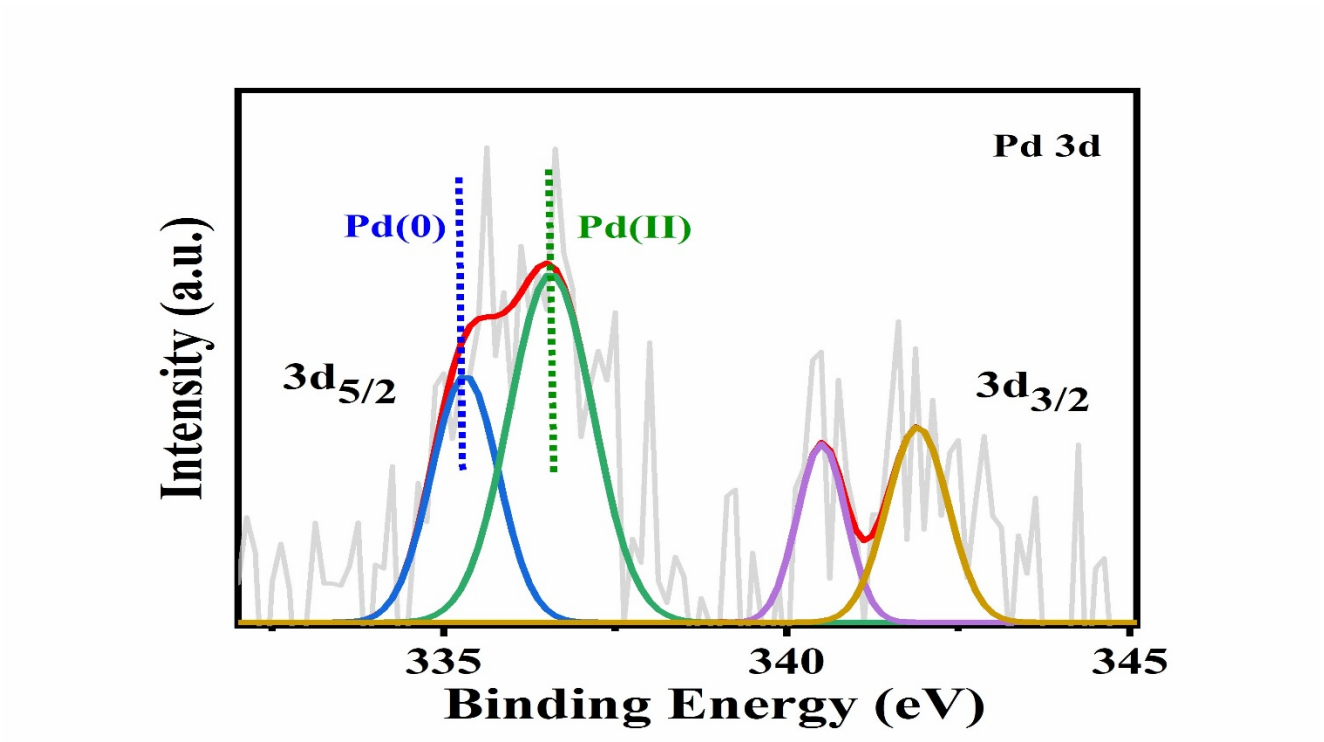




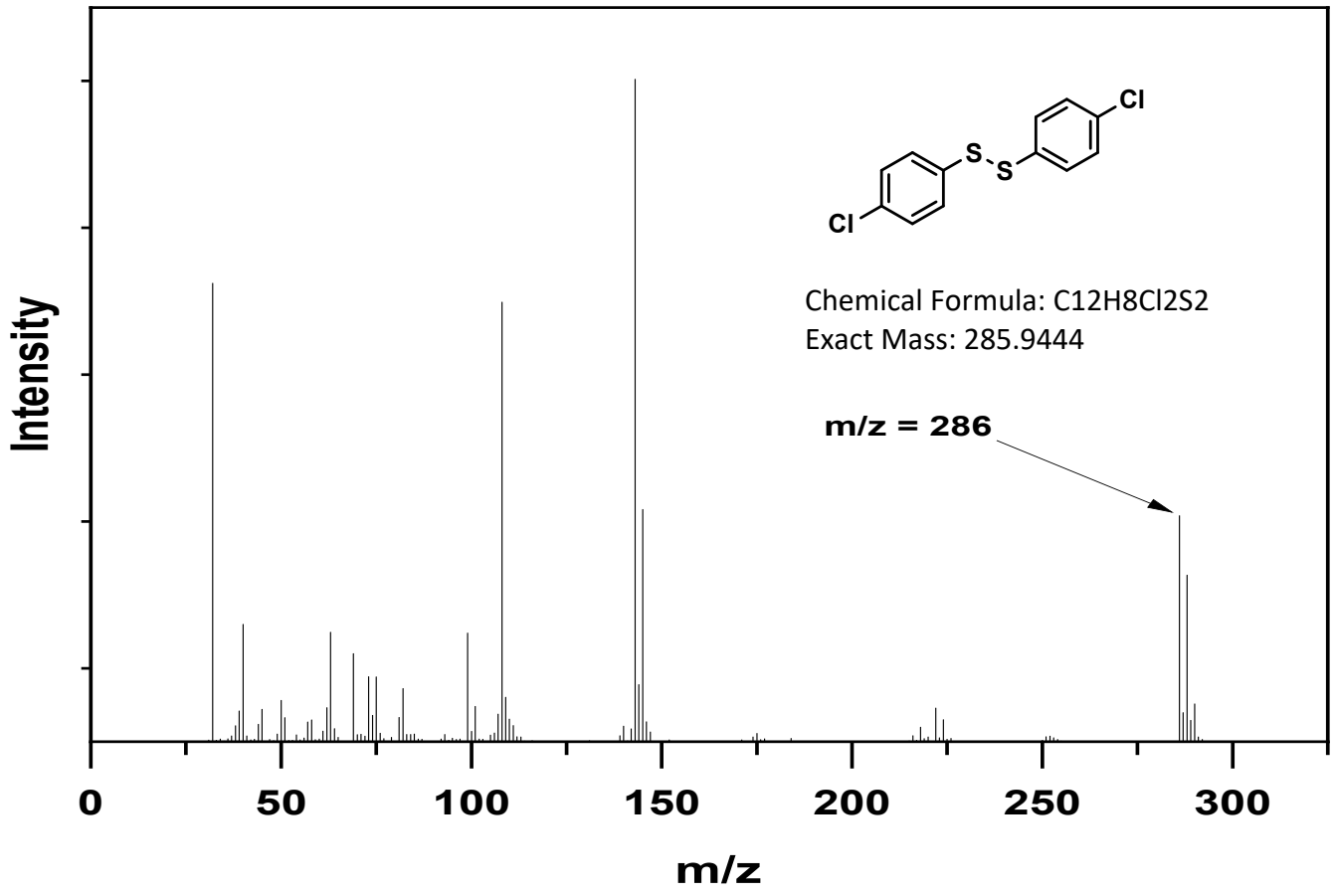
7. XPS data: Evidence of Cu(0) metal state :

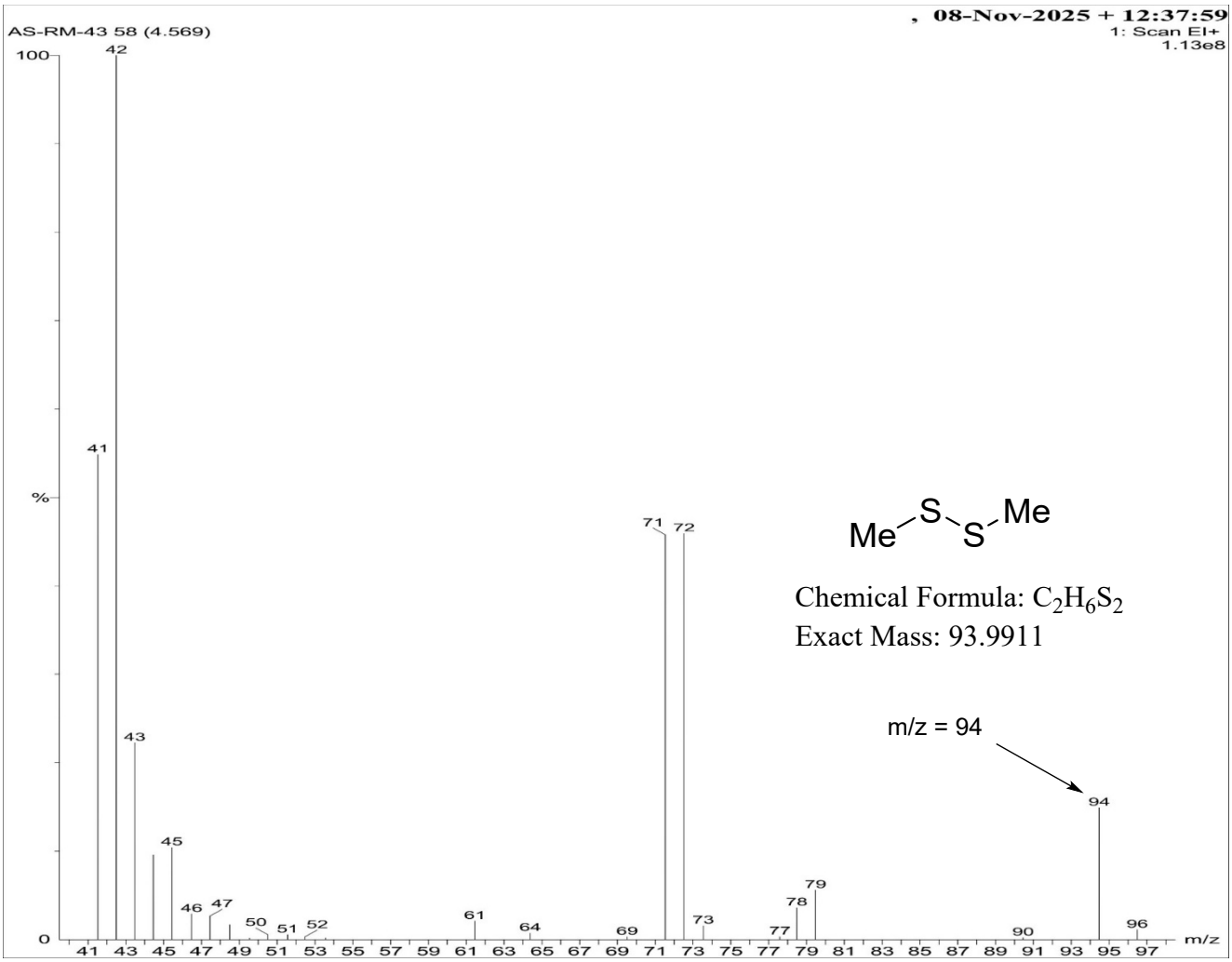


G. XPS data: Evidence of Pd(0) & Pd(II) :



8. GC-MS data:


Intensity
0
50
100
150
200
250
300
m/z
Cl
S
S
Cl
Chemical Formula: C12H8Cl2S2
Exact Mass: 285.9444
m/z = 286


AS-RM-43 58 (4.569)
, 08-Nov-2025 + 12:37:59
1: Scan EI+
1.13e8
100
%
0
m/z
Me S S Me
Chemical Formula: $C_2H_6S_2$
Exact Mass: 93.9911
m/z = 94

9. XRD Data of compounds 3c

The X-ray single-crystal data for compound **3c** has been collected at room temperature in a Bruker-made APEX III diffractometer. At first, single crystals of the compound **3c** have been isolated and then mounted on the glass fiber tip using commercial super glue. Mo−Kα radiation (λ = 0.71073 Å) from a sealed tube X-ray source has been used. The raw data have been integrated using the SAINT program and by utilizing SADABS, the absorption corrections were performed. The structures have been solved by SHELXL-2016/6, and full-matrix least-squares refinements on F^2 for all non-hydrogen atoms were performed by SHELXL-2016/6, with anisotropic displacement parameters. All the calculations and molecular graphics were done by SHELXL-2016/6, PLATON v1.15, WinGX system Ver-1.80, Mercury. The crystallographic data and structural refinement parameters for the compound **3c** have been mentioned.

X-Ray single-crystal data for compound 3c

```
Bond precision:   C-C = 0.0102 A          Wavelength=0.71073

Cell:               a=5.8153(4)      b=7.8399(6)      c=23.7777(17)
                    alpha=90         beta=90          gamma=90
Temperature:        273 K

                  Calculated                  Reported
Volume            1084.06(14)                 1084.06(14)
Space group       P 21 21 21                  P 21 21 21
Hall group        P 2ac 2ab                   P 2ac 2ab
Moiety formula    C10 H13 N O2 S              C10 H13 N O2 S
Sum formula       C10 H13 N O2 S              C10 H13 N O2 S
Mr                211.27                      211.27
Dx,g cm-3         1.294                       1.294
Z                 4                           4
Mu (mm-1)         0.273                       0.273
F000              448.0                       448.0
F000'             448.68
h,k,lmax          7,10,30                     7,10,30
Nref              2410[ 1433]                 2405
Tmin,Tmax                                     0.000,1.000
Tmin'

Correction method= # Reported T Limits: Tmin=0.000 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.68/1.00        Theta(max)= 27.162

R(reflections)= 0.0837( 1547)                wR2(reflections)=
                                             0.3092( 2405)
S = 1.204                 Npar= 130
```

Thermal ellipsoidal (50% ellipsoid probability) structure of compound 3c