Supporting Information

Cp*Co(III)-Catalyzed Thiocarbamate Directed C−H Aminocarbonylation, Amination and Cascade Annulation of Pyrroles

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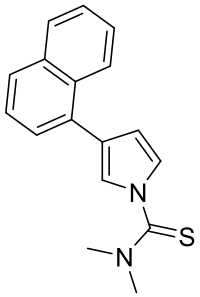
Experimental Section:

General: All reactions involving air or moisture sensitive reagents were carried out in flame dried glassware under nitrogen/argon atmosphere. 1,1,2,2-Tetrachloroethane was obtained from SRL India and used as received. Other solvents were obtained from Merck India and dried according to the standard literature procedure. Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 pre-coated plates (0.25 mm), and visualized under UV light or by dipping into $KMnO_4$ or DNP solution. Silica gel (particle size 100-200 mesh) was purchased from SRL India for performing column chromatography by using mixture of hexanes and ethylacetate as eluent. The ^{1}H NMR spectroscopic data were recorded with a Bruker 400 or 500 MHz instruments. Proton decoupled ^{13}C NMR spectra, $^{13}C\{^{1}H\}$, were similarly recorded by using a broadband decoupled mode. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton or carbon signals in $CDCl_3$ (δ = 7.26, 77.16) or DMSO-d_6 (δ= 2.50, 39.52). Coupling constants (*J*) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, dd: doublet of doublets, m: multiplet, br: broad. Infrared (IR) spectra were recorded by Perkin Elmer FTIR-ATR spectrometer, and reported in terms of wave number (cm^{-1}). High resolution mass spectra (HRMS) were recorded in ESI (+Ve) method using a time-of-flight (TOF) mass analyzer.

General Procedure for the Preparation of Pyrrolyl Thiocarbamates (GP I):[1]

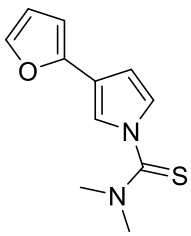
In an oven-dried 25 mL round bottom flask, pyrrole (1.0 equiv) was taken and dissolved in anhydrous THF (2.5 mL/mmol). The resulting solution was cooled down to 0 °C and sodium hydride (1.2 equiv, 60% in mineral oil) was added in small portions. After hydrogen evolution was ceased, dimethylthiocarbamoyl chloride (1.2 equiv) was added to the solution and resulting mixture was stirred at the room temperature for 6 h. On complete consumption of starting material as indicated by TLC, the reaction mixture was quenched by adding saturated aq. NH_4Cl solution. The aqueous layer was extracted with ethylacetate (2 x 10 mL), the combined organic layers were dried over Na_2SO_4, and evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography using 2-5% ethylacetate in hexane as eluent to afford the products **1**.

***N*,*N*-Dimethyl-3-(naphthalen-1-yl)-1*H*-pyrrole-1-carbothioamide (1b):**



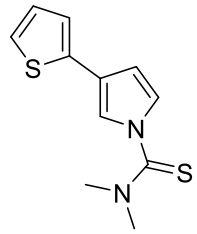
The titled compound **1b** was synthesized according to the **GP I** by using 3-(naphthalen-1-yl)-1*H*-pyrrole (2.0 mmol, 386 mg) and isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent (512 mg, 91%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.31-8.29 (m, 1H), 7.90-7.89 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.52-7.47 (m, 4H), 7.32-7.29 (m, 1H), 7.23-7.20 (m, 1H), 6.57 (d, *J* = 1.0 Hz, 1H), 3.41 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 183.5, 134.0, 133.1, 131.8, 128.4, 127.4, 126.7, 126.1, 126.0, 125.8, 125.6, 122.5, 120.8, 113.2, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2922, 1592, 1485, 1389, 1325, 1259, 1123, 1069, 937, 785. **HRMS (ESI)**: calculated for $C_{17}H_{17}N_2S$ (**[M+H]$^+$**): 281.1107; found 281.1085.

3-(Furan-2-yl)-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (1c):



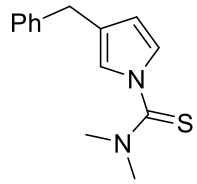
The titled compound **1c** was synthesized according to the **GP I** by using 3-(furan-2-yl)-1*H*-pyrrole (1.0 mmol, 133 mg) and isolated as yellow liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent (143 mg, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.39-7.35 (m, 1H), 7.30-7.27 (m, 1H), 7.10-7.03 (m, 1H), 6.45 (d, *J* = 1.0 Hz, 1H), 6.40-6.37 (m, 1H), 6.36-6.32 (m, 1H), 3.35 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 183.2, 149.9, 140.8, 123.1, 118.3, 117.5, 111.3, 108.6, 104.0, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2925, 1515, 1387, 1328, 1248, 1146, 1086, 1005, 941, 781. **HRMS (ESI)**: calculated for $C_{11}H_{13}N_2OS$ (**[M+H]$^+$**): 221.0743; found 221.0747.

***N*,*N*-Dimethyl-3-(thiophen-2-yl)-1*H*-pyrrole-1-carbothioamide (1d):**



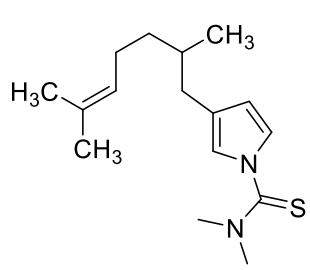
The titled compound **1d** was synthesized according to the **GP I** by using 3-(thiophen-2-yl)-1*H*-pyrrole (2.0 mmol, 298 mg) and isolated as yellow liquid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent (436 mg, 92%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.27 (t, *J* = 1.8 Hz, 1H), 7.14 (d, *J* = 5.0 Hz, 1H), 7.09 (d, *J* = 3.5 Hz, 1H), 7.06 (t, *J* = 2.5 Hz, 1H), 7.00 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.46 (dd, *J* = 3.0, 1.5 Hz, 1H), 3.37 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 183.2, 137.7, 127.7, 123.1, 123.0, 122.5, 121.3, 118.1, 110.1, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2932, 1515, 1391, 1324, 1258, 1146, 1077, 941, 839, 777. **HRMS (ESI)**: calculated for $C_{11}H_{12}N_2NaS_2$ (**[M+Na]$^+$**): 259.0334; found 259.0340.

3-Benzyl-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (1e):



The titled compound **1e** was synthesized according to the **GP I** by using 3-benzyl-1*H*-pyrrole (2.0 mmol, 314 mg) and isolated as yellow sticky liquid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent (414 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.39-7.28 (m, 5H), 7.11-7.04 (m, 1H), 6.91-6.83 (m, 1H), 6.19-6.12 (m, 1H), 3.87 (s, 2H), 3.40 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 183.7, 141.0, 128.8, 128.4, 126.08, 126.05, 122.7, 119.9, 112.2, 43.9, 33.4. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2932, 1515, 1382, 1323, 1142, 1067, 938, 852, 777. **HRMS (ESI)**: calculated for $C_{14}H_{17}N_2S$ (**[M+H]$^+$**): 245.1107; found 245.1109.

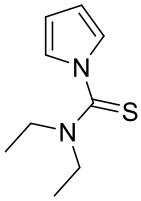
3-(2,6-Dimethylhept-5-en-1-yl)-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (1f):



The titled compound **1f** was synthesized according to the **GP I** by using 3-(2,6-dimethylhept-5-en-1-yl)-1*H*-pyrrole (2.0 mmol, 383 mg) and isolated as yellow liquid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent (484 mg, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.99 (t, *J* = 2.0 Hz, 1H), 6.82-6.76 (m, 1H), 6.09-6.02 (m, 1H), 5.08 (t, *J* = 6.8 Hz, 1H), 3.33 (s, 6H), 2.41 (dd, *J* = 14.2, 5.8 Hz, 1H), 2.20 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.08-1.90 (m, 2H), 1.67 (s, 3H), 1.64-1.61 (m, 1H), 1.59 (s, 3H), 1.43-1.33 (m, 1H), 1.19-1.10 (m, 1H), 0.87 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 183.8, 131.2, 125.8, 124.9, 122.2, 119.9, 112.7, 43.9, 36.8, 34.4, 33.6, 25.8, 25.7, 19.6, 17.8. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2912, 1514, 1381, 1326, 1146, 1062, 940, 853, 774. **HRMS (ESI)**: calculated for $C_{16}H_{27}N_2S$ (**[M+H]$^+$**): 279.1889; found 279.1884.

***N*,*N*-Diethyl-1*H*-pyrrole-1-carbothioamide (1g):**

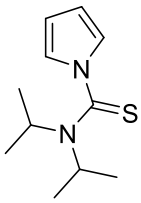
In an oven-dried 25 mL round bottom flask, pyrrole (134 mg, 2.0 mmol, 1.0 equiv) was taken



and dissolved in 5 mL of anhydrous THF. The resulting solution was cooled down to 0 °C and sodium hydride (96 mg, 2.4 mmol, 1.2 equiv, 60% in mineral oil) was added in small portions. After hydrogen evolution was ceased, diethylcarbamoyl chloride (0.30 mL, 2.4 mmol, 1.2 equiv) was added to the solution and resulting mixture was stirred at the room temperature for 6 h. On complete consumption of starting material as indicated by TLC, the reaction mixture was quenched by adding saturated aq. NH_4Cl solution. The aqueous layer was extracted with ethylacetate (2 x 10 mL), the combined organic layers were dried over Na_2SO_4, and evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography using hexane-ethylacetate as eluent. Next, in an oven-dried 10 mL Schlenk tube, the isolated carbonate compound and Lawesson reagent (1.2 g, 3.0 mmol, 1.5 equiv) were taken, and dissolved in 4 mL of anhydrous toluene. The resulting mixture was allowed to stir in a preheated oil bath at 120 ^oC until complete consumption of the starting material (monitored by TLC). The mixture was cooled down to room temperature and solvent was evaporated under *vacuo*. The product **1g** (311 mg, 1.7 mmol, 85%) was isolated as a yellow liquid after column chromatography on silica gel by using 3% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.98 (t, *J* = 2.0 Hz, 2H), 6.23 (t, *J* = 2.0 Hz, 2H), 3.75 (q, *J* = 7.1 Hz, 4H), 1.30 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 183.3, 121.7, 110.8, 47.4, 12.7. **HRMS (ESI)**: calculated for $C_9H_{15}N_2S$ (**$[M+H]^+$**): 183.0950; found 183.0946.

***N*,*N*-Diisopropyl-1*H*-pyrrole-1-carbothioamide (1h):**

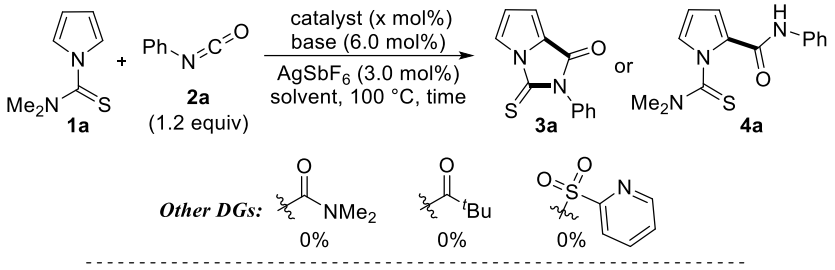
In an oven-dried 25 mL round bottom flask, pyrrole (134 mg, 2.0 mmol, 1.0 equiv) was taken



and dissolved in 5 mL of anhydrous THF. The resulting solution was cooled down to 0 °C and sodium hydride (96 mg, 2.4 mmol, 1.2 equiv, 60% in mineral oil) was added in small portions. After hydrogen evolution was ceased, diisopropylcarbamoyl chloride (393 mg, 2.4 mmol, 1.2 equiv) was added to the solution and resulting mixture was stirred at the room temperature for 6 h. On complete consumption of starting material as indicated by TLC, the reaction mixture was quenched by adding saturated aq. NH_4Cl solution. The aqueous layer was extracted with ethylacetate (2 x 10 mL), the combined organic layers were dried over Na_2SO_4, and evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography using hexane-ethylacetate as eluent. Next, in an oven-dried 10 mL Schlenk tube, the isolated carbonate

compound and Lawesson reagent (1.2 g, 3.0 mmol, 1.5 equiv) were taken, and dissolved in 4 mL of anhydrous toluene. The resulting mixture was allowed to stir in a preheated oil bath at 120 °C until complete consumption of the starting material (monitored by TLC). The mixture was cooled down to room temperature and solvent was evaporated under *vacuo*. The product **1h** (317 mg, 1.5 mmol, 75%) was isolated as a yellow liquid after column chromatography on silica gel by using 3% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.93 (t, *J* = 2.2 Hz, 2H), 6.21 (t, *J* = 2.2 Hz, 2H), 4.14 (sept, *J* = 6.7 Hz, 2H), 1.45 (d, *J* = 6.8 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 182.5, 121.6, 110.3, 53.4, 20.8. **HRMS (ESI)**: calculated for $C_{11}H_{19}N_2S$ (**$[M+H]^+$**): 211.1263; found 211.1266.

Table S1. Optimization Table for C−H Aminocarbonylation[a,b]



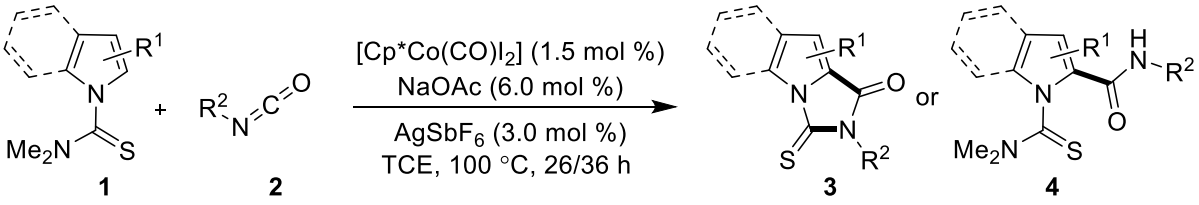
entry	catalyst (mol %)	base (mol %)	solvent	time (h)	yield **4a**/**3a** (%)
1	$Cp^*Co(CO)I_2$ (1.5)	NaOAc (6)	DCE	26	50/<5
2	$Cp^*Co(CO)I_2$ (1.5)	NaOAc (6)	C_6H_5Cl	26	73/0
3	$Cp^*Co(CO)I_2$ (1.5)	NaOAc (6)	$CHCl_3$	26	20/0
4	$Cp^*Co(CO)I_2$ (1.5)	NaOAc (6)	TFE	26	0/0
5	$Cp^*Co(CO)I_2$ (1.5)	NaOAc (6)	THF	26	61/<5
6	$Cp^*Co(CO)I_2$ (1.5)	NaOAc (6)	toluene	26	43/<5
7	$Cp^*Co(CO)I_2$ (1.5)	NaOAc (6)	TCE	26	88/0
8	$Cp^*Co(CO)I_2$ (1.0)	NaOAc (6)	TCE	48	55/10
9	$Cp^*Co(CO)I_2$ (1.5)	KOAc (6)	TCE	26	45/<5
10	$Cp^*Co(CO)I_2$ (1.5)	NaOPiv (6)	TCE	26	82/0
11	$[Cp^*CoCl_2]_2$(0.75)	NaOAc (6)	TCE	26	46/0
12	$[Cp^*RhCl_2]_2$ (0.75)	NaOAc (6)	TCE	26	<5/0
13	$[Cp^*IrCl_2]_2$ (0.75)	NaOAc (6)	TCE	26	0/0
14	[Ru(*p*-cymene)$Cl_2]_2$ (0.75)	NaOAc (6)	TCE	26	0/0
15	$Cp^*Co(CO)I_2$ (1.5)	NaOAc (6)	TCE	36	0/87

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), cat. (0.75-1.5 mol %), base (6.0 mol %), $AgSbF_6$ (3.0 mol %), solvent (1.5 mL), 100 °C, time. [b]Isolated yield.

The optimization study was initiated on the substrate **1a** by employing 1.5 mol % of $Cp^*Co(CO)I_2$ as catalyst, 3.0 mol % of $AgSbF_6$ as additive, 6.0 mol % of NaOAc as base, and phenyl isocyanate **2a** as aminocarbonylating agent in 1.5 mL of DCE solvent. To our delight in our first attempt aminocarbonylated product **4a** was isolated in 50%

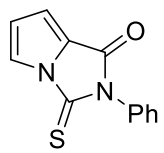
yield along with a trace amount of cyclized product **3a** (Table 1, entry 1). At first, screening of both polar and non-polar solvents led to the identification of 1,1,2,2-tetrachloroethane (TCE) as the optimal solvent to provide **4a** exclusively in 88% yield (entries 2-7). Upon decreasing the catalyst loading yield of **4a** was reduced to 55%, and formation of **3a** was also observed (entry 8). Changing the base has a detrimental effect on yield (entries 9-10). Employment of other congeners of cobalt-catalyst and Ru(II)-based catalyst found to be ineffective (entries 11-14). To our elation, exclusive formation of **3a** was observed by extending the reaction time to 36 h (87% yield). Furthermore, other directing groups, viz, carbamate, pivaloyl, and sulfonyl-pyridine failed to provide any product under the optimized conditions.

General Procedure II (GP II):



The pyrrolyl/indolyl thiocarbamates **1** (0.20 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube. Then catalyst $Cp^*Co(CO)I_2$ (1.4 mg, 0.003 mmol, 1.5 mol %), NaOAc (1.0 mg, 0.012 mmol, 6.0 mol %), and $AgSbF_6$ (2.1 mg, 0.006 mmol, 3.0 mol %) were added successively to the reaction mixture. After that, the isocyanate **2** (0.24 mmol, 1.2 equiv) followed by 1.5 mL of 1,1,2,2-tetrachloroethane were added to the reaction mixture and allowed to stir in a preheated oil bath at 100 °C. In general, to get the product **3** reaction was conducted over 36 h and for product **4** reaction time is 26 h. On completion of the reaction as indicated by TLC, the crude residue was diluted with ethylacetate, and carefully transferred to a round bottom flask. After evaporating the solvent in *vacuo*, the crude product **3/4** was purified by silica gel column chromatography by using 1-22% ethylacetate in hexane as eluent.

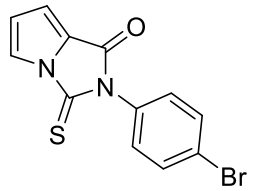
2-Phenyl-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3a):



The titled compound **3a** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **3a** (39.9 mg, 0.17 mmol, 87%) was isolated as a yellow solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.55-7.46 (m, 4H), 7.38 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 2.8 Hz, 1H), 6.49 (t, *J* = 3.2 Hz,

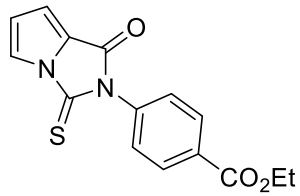
1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 174.4, 158.2, 132.5, 129.42, 129.35, 128.5, 122.9, 120.2, 117.9, 114.6. **FTIR**: ν_{max} (neat)/ cm^{-1} = 1755, 1557, 1501, 1421, 1342, 1236, 1143, 1046, 828, 725. **HRMS (ESI)**: calculated for $C_{12}H_9N_2OS$ (**[M+H]$^+$**): 229.0430; found 229.0431.

2-(4-Bromophenyl)-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3b):



The titled compound **3b** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 1-bromo-4-isocyanatobenzene (47.5 mg, 0.24 mmol, 1.2 equiv). The product **3b** (40 mg, 0.13 mmol, 65%) was isolated as a yellow solid after column chromatography on silica gel by using 3% ethylacetate in hexane as eluent. Here reaction was conducted over 24 h. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.63 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 3.0 Hz, 1H), 6.47 (t, *J* = 3.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 173.9, 157.8, 132.6, 131.5, 130.0, 123.5, 122.8, 120.3, 118.1, 114.8. **FTIR**: ν_{max} (neat)/ cm^{-1} = 1760, 1556, 1492, 1413, 1339, 1235, 1133, 1037, 815, 745. **HRMS (ESI)**: calculated for $C_{12}H_8BrN_2OS$ (**[M+H]$^+$**): 306.9535; found 306.9538.

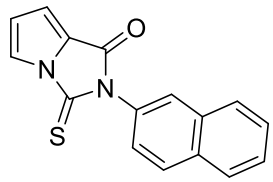
Ethyl 4-(1-oxo-3-thioxo-1*H*-pyrrolo[1,2-*c*]imidazol-2(3*H*)-yl)benzoate (3c):



The titled compound **3c** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and ethyl 4-isocyanatobenzoate (45.9 mg, 0.24 mmol, 1.2 equiv). The product **3c** (45 mg, 0.15 mmol, 75%) was isolated as a yellow solid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent. Here reaction was conducted over 24 h. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.20 (d, *J* = 8.0 Hz, 2H), 7.54-7.52 (m, 1H), 7.49 (d, *J* = 7.5 Hz, 2H), 6.92-6.89 (m, 1H), 6.53-6.48 (m, 1H), 4.41 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 173.7, 165.8, 157.7, 136. 3, 131.2, 130.6, 128.4, 122.8, 120.3, 118.1, 114.9, 61.5, 14.5. **FTIR**: ν_{max} (neat)/ cm^{-1} = 1754, 1708, 1608, 1556, 1509, 1424, 1336, 1280, 1106, 1049, 819, 743. **HRMS (ESI)**: calculated for $C_{15}H_{12}N_2NaO_3S$ (**[M+Na]$^+$**): 323.0461; found 323.0463.

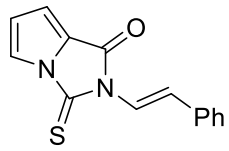
2-(Naphthalen-2-yl)-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3d):

The titled compound **3d** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 2-isocyanatonaphthalene (40.6 mg, 0.24 mmol, 1.2 equiv). The product **3d** (47.5 mg, 0.17 mmol, 85%) was isolated as a yellow solid after column chromatography on silica gel by using 3% ethylacetate in hexane as eluent.



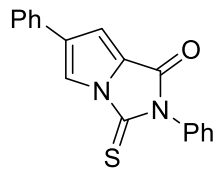
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.98 (d, *J* = 9.0 Hz, 1H), 7.92-7.89 (m, 3H), 7.59-7.55 (m, 2H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.91 (d, *J* = 3.5 Hz, 1H), 6.50 (t, *J* = 3.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 174.5, 158.3, 133.33, 133.30, 129.9, 129.3, 128.4, 128.0, 127.9, 127.4, 126.9, 125.5, 123.1, 120.2, 117. 9, 114.6. **FTIR**: ν_{max} (neat)/ cm^{-1} = 1748, 1556, 1421, 1325, 1127, 1041, 824, 781, 741. **HRMS (ESI)**: calculated for $C_{16}H_{10}N_2NaOS$ (**[M+Na]$^+$**): 301.0406; found 301.0401.

(*E*)-2-Styryl-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3e):



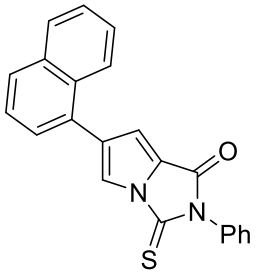
The titled compound **3e** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and (*E*)-(2-isocyanatovinyl)benzene (34.8 mg, 0.24 mmol, 1.2 equiv). The product **3e** (41.3 mg, 0.16 mmol, 81%) was isolated as a yellow sticky solid after column chromatography on silica gel by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 15.0 Hz, 1H), 7.45-7.42 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 3.5 Hz, 1H), 6.43 (t, *J* = 3.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 172.3, 157.3, 135.6, 128.9, 128.1, 126.6, 122.8, 120.2, 119.9, 118.1, 114.9. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2923, 1747, 1557, 1419, 1347, 1235, 1130, 1008, 949, 884, 740. **HRMS (ESI)**: calculated for $C_{14}H_{11}N_2OS$ (**[M+H]$^+$**): 255.0587; found 255.0584.

2,6-Diphenyl-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3f):



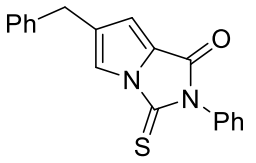
The titled compound **3f** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-3-phenyl-1*H*-pyrrole-1-carbothioamide (46.0 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **3f** (39.6 mg, 0.13 mmol, 65%) was isolated as a yellow solid after column chromatography on silica gel by using 3% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.76 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.46-7.39 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.18 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 174.1, 158.3, 134.1, 132.53, 132.48, 129.5, 129.4, 129.2, 128.5, 128.1, 125.9, 123.5, 115.6, 112.4. **FTIR**: ν_{max} (neat)/ cm^{-1} = 1740, 1567, 1451, 1366, 1284, 1177, 1095, 1022, 826, 755. **HRMS (ESI)**: calculated for $C_{18}H_{13}N_2OS$ (**[M+H]$^+$**): 305.0743; found 305.0734.

6-(Naphthalen-1-yl)-2-phenyl-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3g):



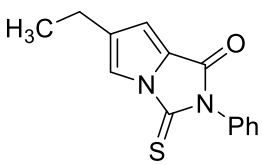
The titled compound **3g** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-3-(naphthalen-1-yl)-1*H*-pyrrole-1-carbothioamide (56.1 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **3g** (50.3 mg, 0.14 mmol, 71%) was isolated as a yellow solid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.15-8.13 (m, 1H), 7.95-7.93 (m, 1H), 7.90 (t, *J* = 4.8 Hz, 1H), 7.72 (s, 1H), 7.58-7.51 (m, 7H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.16 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 174.3, 158.4, 134.1, 132.8, 132.7, 131.5, 131.0, 129.5, 129.4, 128.9, 128.8, 128.5, 127.2, 126.9, 126.4, 125.6, 125.3, 123.0, 118.5, 115.9. **FTIR**: ν_{max} (neat)/ cm^{-1} = 1748, 1570, 1496, 1380, 1284, 1079, 998, 919, 790, 727. **HRMS (ESI)**: calculated for $C_{22}H_{15}N_2OS$ (**[M+H]$^+$**): 355.0900; found 355.0907.

6-Benzyl-2-phenyl-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3h):



The titled compound **3h** was synthesized according to the **GP II** by using 3-benzyl-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (48.9 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **3h** (43.4 mg, 0.14 mmol, 68%) was isolated as a yellow solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. Here reaction was conducted over 48 h. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.50 (t, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.35-7.33 (m, 3H), 7.31 (s, 1H), 7.25-7.23 (m, 4H), 6.69 (s, 1H), 3.85 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 174.3, 158.2, 139.4, 133.6, 132.6, 129.3, 128.9, 128.7, 128.5, 126.8, 123.1, 117.9, 115.2, 33.5. **FTIR**: ν_{max} (neat)/ cm^{-1} = 1738, 1495, 1389, 1345, 1273, 1122, 1071, 786, 730. **HRMS (ESI)**: calculated for $C_{19}H_{15}N_2OS$ (**[M+H]$^+$**): 319.0900; found 319.0897.

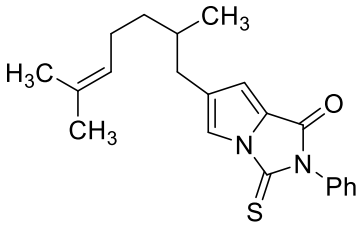
6-Ethyl-2-phenyl-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3i):



The titled compound **3i** was synthesized according to the **GP II** by using 3-ethyl-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (36.5 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **3i** (45 mg, 0.18 mmol, 88%) was isolated as a yellow solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.52 (t, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H),

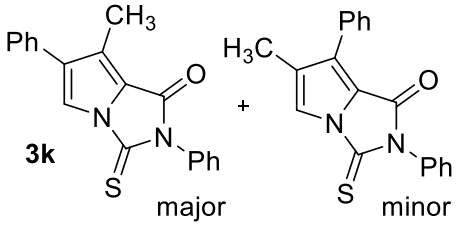
7.37 (d, *J* = 7.2 Hz, 2H), 7.29 (s, 1H), 6.75 (s, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 174.4, 158.4, 136.3, 132.7, 129.3, 128.5, 122.9, 117.0, 115.0, 20.4, 14.5. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2963, 1749, 1589, 1496, 1345, 1129, 1070, 834, 726. **HRMS (ESI)**: calculated for $C_{14}H_{12}N_2NaOS$ (**[M+Na]$^+$**): 279.0563; found 279.0571.

6-(2,6-Dimethylhept-5-en-1-yl)-2-phenyl-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3j):



The titled compound **3j** was synthesized according to the **GP II** by using 3-(2,6-dimethylhept-5-en-1-yl)-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (55.7 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **3j** (50.3 mg, 0.14 mmol, 71%) was isolated as a yellow liquid after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.52 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.27 (s, 1H), 6.71 (s, 1H), 5.11 (t, *J* = 7.0 Hz, 1H), 2.52 (dd, *J* = 14.5, 6.0 Hz, 1H), 2.33 (dd, *J* = 14.3, 7.8 Hz, 1H), 2.12-2.05 (m, 1H), 2.04-1.96 (m, 1H), 1.75-1.72 (m, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.46-1.39 (m, 1H), 1.27-1.18 (m, 1H), 0.95 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 174.4, 158.3, 133.3, 132.7, 131.7, 129.29, 129.27, 128.5, 124.6, 122.8, 118.1, 115.8, 36.6, 34.6, 33.7, 25.8, 25.7, 19.5, 17.8. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2913, 1746, 1575, 1489, 1392, 1337, 1270, 1125, 1075, 986, 874, 724. **HRMS (ESI)**: calculated for $C_{21}H_{25}N_2OS$ (**[M+H]$^+$**): 353.1682; found 353.1684.

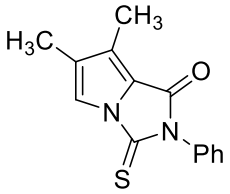
7-Methyl-2,6-diphenyl-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3k):



The titled compound **3k** was synthesized according to the **GP II** by using *N*,*N*,3-trimethyl-4-phenyl-1*H*-pyrrole-1-carbothioamide (48.9 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **3k** (45.9 mg, 0.14 mmol, 72%, as an inseparable mixture of regioisomer in 7.1:1 ratio) was isolated as a yellow solid after column chromatography on silica gel by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.55 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.49-7.44 (m, 5H), 7.41-7.38 (m, 3H), 2.44 (s, 3H) (**Major Isomer**). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 173.8, 158.7, 134.8, 132.77, 132.76, 129.30, 129.25, 129.0, 128.5, 128.2, 128.0, 127.6, 121.0, 117.2, 11.3 (**Major**

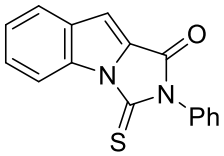
Isomer). **FTIR**: ν_{max} (neat)/ cm^{-1} = 1736, 1594, 1498, 1393, 1279, 1192, 1022, 735. **HRMS (ESI)**: calculated for $C_{19}H_{15}N_2OS$ (**[M+H]**$^+$): 319.0900; found 319.0907.

6,7-Dimethyl-2-phenyl-3-thioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one (3l):



The titled compound **3l** was synthesized according to the **GP II** by using *N*,*N*,3,4-tetramethyl-1*H*-pyrrole-1-carbothioamide (36.5 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **3l** (40.2 mg, 0.16 mmol, 78%) was isolated as a yellow solid after column chromatography on silica gel by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.50 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.23 (s, 1H), 2.25 (s, 3H), 2.07 (d, *J* = 0.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 173.9, 158.6, 132.9, 129.5, 129.4, 129.2, 129.1, 128.6, 120.4, 117.8, 10.3, 10.1. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3130, 1744, 1594, 1498, 1415, 1365, 1273, 1215, 1117, 1019, 793, 742. **HRMS (ESI)**: calculated for $C_{14}H_{12}N_2NaOS$ (**[M+Na]**$^+$): 279.0563; found 279.0557.

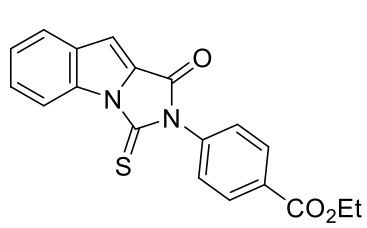
2-Phenyl-3-thioxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-one (3m):



The titled compound **3m** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-indole-1-carbothioamide (40.9 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **3m** (30.1 mg, 0.11 mmol, 54%) was isolated as a yellow solid after column chromatography on silica gel by using 3% ethylacetate in hexane as eluent. Here 3.0 mol % of Cp*Co(CO)I_2, 6.0 mol % $AgSbF_6$, 12.0 mol % NaOAc were used and reaction was conducted over 48 h. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.48 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.59-7.54 (m, 3H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.43-7.41 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.21 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 173.2, 158.8, 134.4, 132.8, 132.5, 130.0, 129.6, 129.4, 128.8, 128.1, 125.3, 124.7, 114.8, 109.7. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2922, 1732, 1568, 1492, 1439, 1386, 1323, 1255, 1145, 1080, 961, 825, 729. **HRMS (ESI)**: calculated for $C_{16}H_{11}N_2OS$ (**[M+H]**$^+$): 279.0587; found 279.0586.

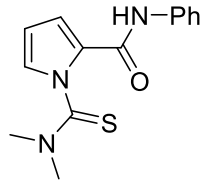
Ethyl 4-(1-oxo-3-thioxo-1*H*-imidazo[1,5-*a*]indol-2(3*H*)-yl)benzoate (3n):

The titled compound **3n** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-indole-1-carbothioamide (40.9 mg, 0.20 mmol, 1.0 equiv) and ethyl 4-isocyanatobenzoate (46 mg, 0.24 mmol, 1.2 equiv). The product **3n** (44.2 mg, 0.13 mmol, 63%) was isolated as a yellow solid after column chromatography on silica gel by using 8% ethylacetate in hexane as eluent.



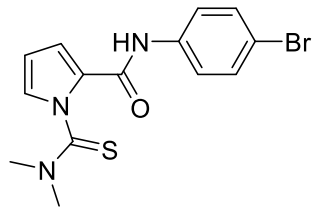
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.47 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 172.4, 165.8, 158.3, 136.2, 134.4, 132.8, 131.4, 130.6, 130.1, 128.7, 127.9, 125.4, 124.8, 114.8, 110.0, 61.5, 14.5. **FTIR**: ν_{max} (neat)/ cm^{-1} = 1746, 1722, 1608, 1563, 1404, 1325, 1277, 1126, 1080, 1026, 960, 828, 745. **HRMS (ESI)**: calculated for $C_{19}H_{15}N_2O_3S$ (**[M+H]$^+$**): 351.0798; found 351.0806.

1-(Dimethylcarbamothioyl)-*N*-phenyl-1*H*-pyrrole-2-carboxamide (4a):



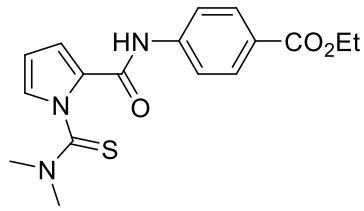
The titled compound **4a** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **4a** (48.2 mg, 0.18 mmol, 88%) was isolated as a white solid after column chromatography on silica gel by using 15% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.75 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.97 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.79 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.30 (t, *J* = 3.2 Hz, 1H), 3.56 (s, 3H), 2.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 182.3, 158.2, 137.9, 129.2, 126.8, 125.8, 124.5, 120.2, 113.6, 110.3, 44.3, 42.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3291, 2924, 1720, 1596, 1535, 1440, 1389, 1243, 1117, 975, 746. **HRMS (ESI)**: calculated for $C_{14}H_{15}N_3NaOS$ (**[M+Na]$^+$**): 296.0828; found 296.0828.

***N*-(4-Bromophenyl)-1-(dimethylcarbamothioyl)-1*H*-pyrrole-2-carboxamide (4b):**



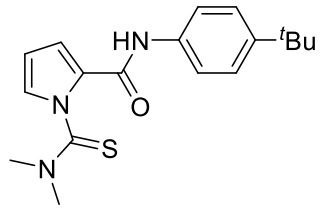
The titled compound **4b** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 1-bromo-4-isocyanatobenzene (47.5 mg, 0.24 mmol, 1.2 equiv). The product **4b** (55.8 mg, 0.16 mmol, 79%) was isolated as a white solid after column chromatography on silica gel by using 16% ethylacetate in hexane as eluent. Here reaction was conducted over 8 h. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.01 (s, 1H), 7.46 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 2H), 6.85 (dd, *J* = 2.8, 1.8 Hz, 1H), 6.81 (dd, *J* = 3.5, 1.5 Hz, 1H), 6.21 (dd, *J* = 3.5, 3.0 Hz, 1H), 3.55 (s, 3H), 2.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 182.3, 158.1, 137.2, 131.9, 126.3, 125.7, 121.8, 116.8, 114.0, 110.4, 44.2, 42.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3305, 1765, 1659, 1590, 1534, 1440, 1390, 1297, 1234, 1162, 1090, 904, 824, 722. **HRMS (ESI)**: calculated for $C_{14}H_{15}BrN_3OS$ (**[M+H]$^+$**): 352.0114; found 352.0108.

Ethyl 4-(1-(dimethylcarbamothioyl)-1*H*-pyrrole-2-carboxamido)benzoate (4c):



The titled compound **4c** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and ethyl 4-isocyanatobenzoate (46 mg, 0.24 mmol, 1.2 equiv). The product **4c** (49.8 mg, 0.14 mmol, 72%) was isolated as a white solid after column chromatography on silica gel by using 22% ethylacetate in hexane as eluent. Here reaction was conducted over 6 h. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.27 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 3.5 Hz, 1H), 6.85-6.80 (m, 1H), 6.20 (t, *J* = 3.3 Hz, 1H), 4.33 (q, *J* = 7.0 Hz, 2H), 3.56 (s, 3H), 2.93 (s, 3H), 1.36 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 182.3, 166.3, 158.1, 142.4, 130.7, 126.2, 125.9, 125.7, 119.2, 114.4, 110.4, 60.9, 44.2, 42.0, 14.4. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3270, 1709, 1663, 1593, 1520, 1439, 1393, 1350, 1271, 1167, 1096, 854, 733. **HRMS (ESI)**: calculated for $C_{17}H_{19}N_3NaO_3S$ (**[M+Na]$^+$**): 368.1039; found 368.1039.

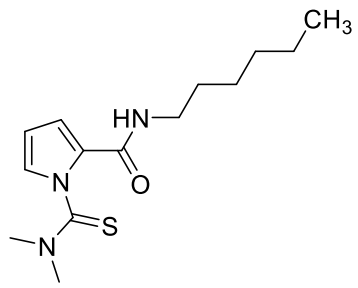
***N*-(4-(*tert*-Butyl)phenyl)-1-(dimethylcarbamothioyl)-1*H*-pyrrole-2-carboxamide (4d):**



The titled compound **4d** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 1-(*tert*-butyl)-4-isocyanatobenzene (42 mg, 0.24 mmol, 1.2 equiv). The product **4d** (43 mg, 0.13 mmol, 65%) was isolated as a white solid after column chromatography on silica gel by using 13% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.78 (s, 1H), 7.46 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.00-6.93 (m, 1H), 6.78 (dd, *J* = 3.5, 1.5 Hz, 1H), 6.27 (t, *J* = 3.3 Hz, 1H), 3.54 (s, 3H), 2.95 (s, 3H), 1.29 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 182.3, 158.2, 147.5, 135.2, 127.0, 126.0, 125.7, 120.2, 113.5, 110.2, 44.2, 41.9, 34.5, 31.5. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3279, 2963, 1653, 1594, 1520, 1441, 1392, 1297, 1245, 1155, 1086, 979, 832, 733. **HRMS (ESI)**: calculated for $C_{18}H_{23}N_3NaOS$ (**[M+Na]$^+$**): 352.1454; found 352.1442.

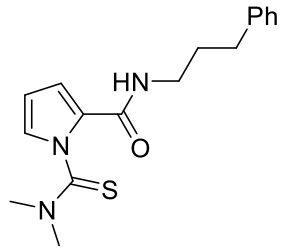
1-(Dimethylcarbamothioyl)-*N*-hexyl-1*H*-pyrrole-2-carboxamide (4e):

The titled compound **4e** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 1-isocyanatohexane (30.5 mg, 0.24 mmol, 1.2 equiv). The product **4e** (29 mg, 0.10 mmol, 51%) was isolated as a white solid after column chromatography on silica gel by using 15% ethylacetate in hexane as eluent. Here 3.0 mol % of Cp*Co(CO)I_2, 6.0 mol % $AgSbF_6$, 12.0 mol % NaOAc were used and reaction



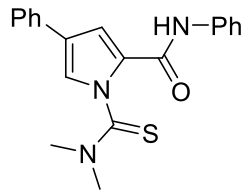
was conducted over 30 h. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.93-6.88 (m, 1H), 6.60-6.56 (m, 1H), 6.26-6.20 (m, 1H), 5.93 (s, 1H), 3.56 (s, 3H), 3.38-3.32 (m, 2H), 2.95 (s, 3H), 1.56-1.51 (m, 2H), 1.37-1.25 (m, 6H), 0.91-0.84 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 182.7, 160.4, 127.1, 124.8, 112.4, 110.0, 44.2, 41.9, 39.7, 31.6, 29.9, 26.8, 22.7, 14.1. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3321, 2927, 1633, 1544, 1439, 1392, 1287, 1152, 1088, 968, 728. **HRMS (ESI)**: calculated for $C_{14}H_{23}N_3NaOS$ (**[M+Na]$^{+}$**): 304.1454; found 304.1459.

1-(Dimethylcarbamothioyl)-*N*-(3-phenylpropyl)-1*H*-pyrrole-2-carboxamide (4f):



The titled compound **4f** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and (3-isocyanatopropyl)benzene (38.7 mg, 0.24 mmol, 1.2 equiv). The product **4f** (31.2 mg, 0.10 mmol, 49%) was isolated as a yellow sticky solid after column chromatography on silica gel by using 30% ethylacetate in hexane as eluent. Here 3.0 mol % of $Cp^*Co(CO)I_2$, 6.0 mol % $AgSbF_6$, 12.0 mol % NaOAc were used and reaction was conducted over 30 h. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.28 (t, *J* = 7.6 Hz, 2H), 7.21-7.18 (m, 3H), 6.89-6.88 (m, 1H), 6.48 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.21 (t, *J* = 3.2 Hz, 1H), 6.03-5.94 (m, 1H), 3.55 (s, 3H), 3.39 (q, *J* = 6.7 Hz, 2H), 2.93 (s, 3H), 2.68 (t, *J* = 7.8 Hz, 2H), 1.89 (quint, *J* = 7.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 182.6, 160.3, 141.5, 128.6, 128.5, 126.8, 126.2, 124.8, 112.5, 110.0, 44.2, 41.9, 39.4, 33.6, 31.4. **HRMS (ESI)**: calculated for $C_{17}H_{22}N_3OS$ (**[M+H]$^{+}$**): 316.1478; found 316.1481.

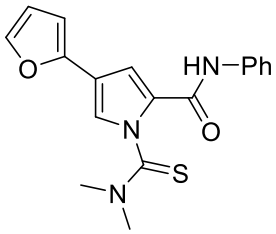
1-(Dimethylcarbamothioyl)-*N*,4-diphenyl-1*H*-pyrrole-2-carboxamide (4g):



The titled compound **4g** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-3-phenyl-1*H*-pyrrole-1-carbothioamide (46 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **4g** (45.6 mg, 0.13 mmol, 65%) was isolated as a white solid after column chromatography on silica gel by using 15% ethylacetate in hexane as eluent. Here reaction was conducted over 30 h. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.95 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.29-7.26 (m, 2H), 7.15-7.12 (m, 2H), 3.61 (s, 3H), 3.07 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 182.0, 158.1, 137.9, 133.5, 129.2, 129.0, 127.6, 127.0, 126.5, 125.5, 124.5, 122.0, 120.3, 111.3, 44.3, 42.2. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3243, 3117, 1662, 1596, 1536, 1391,

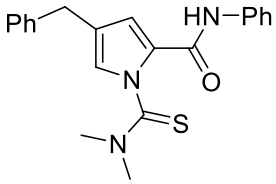
1314, 1249, 988, 819, 751. **HRMS (ESI)**: calculated for $C_{20}H_{19}N_3NaOS$ (**[M+Na]**$^+$): 372.1141; found 372.1144.

1-(Dimethylcarbamothioyl)-4-(furan-2-yl)-*N*-phenyl-1*H*-pyrrole-2-carboxamide (4h):



The titled compound **4h** was synthesized according to the **GP II** by using 3-(furan-2-yl)-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (44 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **4h** (41.7 mg, 0.12 mmol, 61%) was isolated as a white solid after column chromatography on silica gel by using 15% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.86 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.39-7.34 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.23-7.17 (m, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.02-6.97 (m, 1H), 6.45-6.39 (m, 1H), 6.37 (d, *J* = 3.0 Hz, 1H), 3.56 (s, 3H), 3.04 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.6, 158.0, 148.9, 141.2, 137.7, 129.2, 127.4, 124.6, 121.3, 120.3, 117.7, 111.4, 110.1, 104.3, 44.3, 42.2. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3297, 2924, 1647, 1596, 1531, 1442, 1380, 1314, 1249, 1154, 954, 753. **HRMS (ESI)**: calculated for $C_{18}H_{18}N_3O_2S$ (**[M+H]**$^+$): 340.1114; found 340.1109.

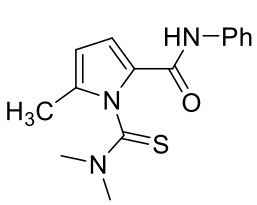
4-Benzyl-1-(dimethylcarbamothioyl)-*N*-phenyl-1*H*-pyrrole-2-carboxamide (4i):



The titled compound **4i** was synthesized according to the **GP II** by using 3-benzyl-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (49 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **4i** (55.5 mg, 0.15 mmol, 76%) was isolated as a white solid after column chromatography on silica gel by using 12% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.69 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.32-7.28 (m, 4H), 7.24-7.22 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.77 (s, 1H), 6.59 (s, 1H), 3.81 (s, 2H), 3.53 (s, 3H), 2.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 182.3, 158.1, 140.6, 137.9, 129.1, 128.8, 128.7, 126.9, 126.4, 125.3, 124.4, 124.0, 120.2, 114.0, 44.2, 42.0, 33.1. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3232, 2926, 1744, 1640, 1599, 1524, 1453, 1390, 1318, 1275, 1147, 973, 754. **HRMS (ESI)**: calculated for $C_{21}H_{21}N_3NaOS$ (**[M+Na]**$^+$): 386.1298; found 386.1287.

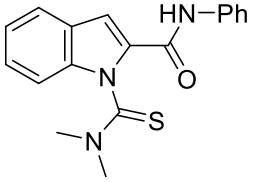
1-(Dimethylcarbamothioyl)-5-methyl-*N*-phenyl-1*H*-pyrrole-2-carboxamide (4j):

The titled compound **4j** was synthesized according to the **GP II** by using *N*,*N*,2-trimethyl-1*H*-pyrrole-1-carbothioamide (33.7 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **4j** (24.3 mg, 0.08 mmol, 42%) was isolated as a white solid after column chromatography on silica gel by using 12% ethylacetate in hexane as eluent. Here 3.0 mol % of Cp*Co(CO)I_2, 6.0 mol % $AgSbF_6$, 12.0 mol % NaOAc were used and reaction



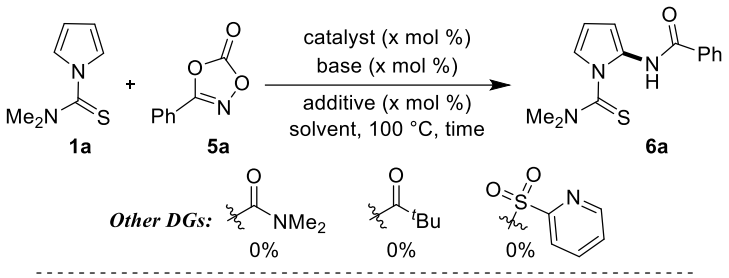
was conducted over 36 h. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.78 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 3.6 Hz, 1H), 5.99 (d, *J* = 3.6 Hz, 1H), 3.59 (s, 3H), 2.98 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 182.1, 158.4, 138.0, 133.4, 129.1, 126.1, 124.1, 120.3, 113.5, 109.0, 43.9, 41.9, 12.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3268, 1648, 1596, 1523, 1393, 1304, 1249, 1156, 989, 747. **HRMS (ESI)**: calculated for $C_{15}H_{17}N_3NaOS$ (**[M+Na]$^+$**): 310.0985; found 310.0971.

1-(Dimethylcarbamothioyl)-*N*-phenyl-1*H*-indole-2-carboxamide (4k):



The titled compound **4k** was synthesized according to the **GP II** by using *N*,*N*-dimethyl-1*H*-indole-1-carbothioamide (41.0 mg, 0.20 mmol, 1.0 equiv) and isocyanatobenzene (28.6 mg, 0.24 mmol, 1.2 equiv). The product **4k** (49.0 mg, 0.15 mmol, 76%) was isolated as a white solid after column chromatography on silica gel by using 15% ethylacetate in hexane as eluent. Here 3.0 mol % of $Cp^*Co(CO)I_2$, 6.0 mol % $AgSbF_6$, 12.0 mol % NaOAc were used. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.10 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.39-7.32 (m, 3H), 7.29-7.25 (m, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.15-7.13 (m, 2H), 3.68 (s, 3H), 3.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 181.8, 159.2, 137.6, 136.9, 133.4, 129.2, 127.0, 126.2, 124.8, 122.6, 122.5, 120.3, 111.2, 108.2, 44.1, 42.4. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3301, 2924, 1651, 1597, 1532, 1442, 1376, 1312, 1243, 1145, 984, 815, 740. **HRMS (ESI)**: calculated for $C_{18}H_{17}N_3NaOS$ (**[M+Na]$^+$**): 346.0985; found 346.0985.

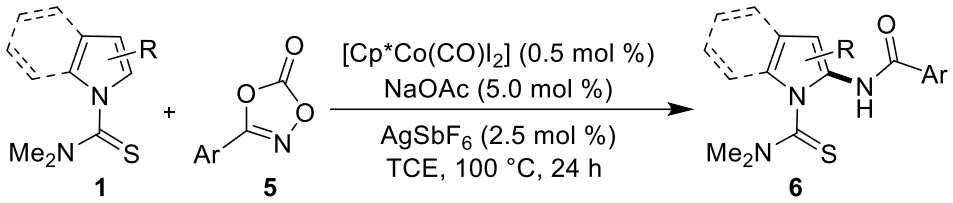
Table S2. Optimization Table for C−H Amidation[a,b]



entry	catalyst (mol %)	base (mol %)	additive (mol %)	solvent	time (h)	yield **6a** (%)
1[c]	Cp*Co(CO)I_2 (5.0)	NaOAc(30)	$AgSbF_6$ (15)	DCE	18	51
2	Cp*Co(CO)I_2 (5.0)	NaOAc(30)	$AgSbF_6$ (15)	DCE	18	63
3	Cp*Co(CO)I_2 (1.0)	NaOAc(10)	$AgSbF_6$ (5.0)	DCE	18	52
4	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	$AgSbF_6$ (2.5)	DCE	18	68
5	0	NaOAc(5)	$AgSbF_6$ (2.5)	DCE	18	0
6	Cp*Co(CO)I_2 (0.5)	0	$AgSbF_6$ (2.5)	DCE	18	0
7	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	0	DCE	18	0
8	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	$AgSbF_6$ (2.5)	DCE	24	73
9	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	$AgSbF_6$ (2.5)	$CHCl_3$	24	66
10	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	$AgSbF_6$ (2.5)	C_6H_5Cl	24	63
11	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	$AgSbF_6$ (2.5)	$C_6H_5CF_3$	24	70
12	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	$AgSbF_6$ (2.5)	THF	24	0
13	**Cp*Co(CO)I_2 (0.5)**	**NaOAc(5)**	**$AgSbF_6$ (2.5)**	**TCE**	**24**	**95**[d]
14	Cp*Co(CO)I_2 (0.5)	KOAc(5)	$AgSbF_6$ (2.5)	TCE	24	81
15	Cp*Co(CO)I_2 (0.5)	$Cu(OAc)_2$(5)	$AgSbF_6$ (2.5)	TCE	24	0
16	Cp*Co(CO)I_2 (0.5)	AgOAc(5)	$AgSbF_6$ (2.5)	TCE	24	0
17	Cp*Co(CO)I_2 (0.5)	NaOBz(5)	$AgSbF_6$ (2.5)	TCE	24	91
18	Cp*Co(CO)I_2 (0.5)	NaOPiv(5)	$AgSbF_6$ (2.5)	TCE	24	90
19	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	AgOTf(5.0)	TCE	24	80
20	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	$AgBF_4$(5.0)	TCE	24	67
21	Cp*Co(CO)I_2 (0.5)	NaOAc(5)	$AgSbF_6$ (2.5)	TFE	24	<5
22	**Cp*Co(CO)I_2 (0.3)**	**NaOAc(3)**	**$AgSbF_6$ (1.5)**	**TCE**	**31**	**75**[e]
23	$[Cp^*CoCl_2]_2$(0.25)	NaOAc(5)	$AgSbF_6$ (2.5)	TCE	24	0
24	$[Cp^*RhCl_2]_2$ (0.25)	NaOAc(5)	$AgSbF_6$ (2.5)	TCE	24	0
25	$[Cp^*IrCl_2]_2$ (0.25)	NaOAc(5)	$AgSbF_6$ (2.5)	TCE	24	0
26	CoI_2 (0.5)	NaOAc(5)	$AgSbF_6$ (2.5)	TCE	24	0

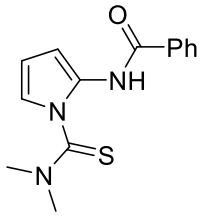
[a]Reaction conditions: **1a** (0.20 mmol), **5a** (0.30 mmol), cat. (0.25-5.0 mol %), additive (1.5-15 mol %), base (3.0-30 mol %), solvent (1.5 mL), 100 °C, time. [b]Isolated yield. [c]Reaction was performed at 90 °C. [d]Average yield of four reactions conducted separately. [e]Average yield of three reactions conducted separately.

General Procedure III (GP III):



The pyrrolyl/indolyl thiocarbamates **1** (0.20 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube. Then catalyst Cp*Co(CO)I_2 (0.5 mg, 0.001 mmol, 0.5 mol %), NaOAc (0.8 mg, 0.010 mmol, 5.0 mol %), and $AgSbF_6$ (1.7 mg, 0.005 mmol, 2.5 mol %) were added successively to the reaction mixture. After that, the dioxazolone **5** (0.30 mmol, 1.5 equiv) followed by 1.5 mL of 1,1,2,2-tetrachloroethane were added to the reaction mixture, and the resulting mixture was allowed to stir in a preheated oil bath at 100 °C for 24 h. On completion of the reaction as indicated by TLC, the crude residue was diluted with ethylacetate, and carefully transferred to a round bottom flask. After evaporating the solvent under *vacuo*, the crude product **6** was purified by silica gel column chromatography by using 12-22% ethylacetate in hexane as eluent.

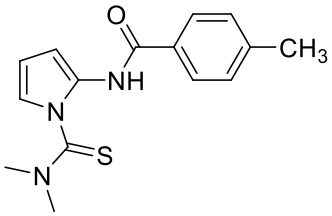
***N*-(1-(Dimethylcarbamothioyl)-1*H*-pyrrol-2-yl)benzamide (6a):**



The titled compound **6a** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6a** (52.2 mg, 0.19 mmol, 95%) was isolated as a white solid after column chromatography on silica gel by using 22% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.87 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.55-7.45 (m, 3H), 6.65-6.64 (m, 1H), 6.49 (dd, *J* = 3.0, 1.4 Hz, 1H), 6.24 (t, *J* = 3.4 Hz, 1H), 3.37 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 181.4, 164.2, 134.0, 132.1, 128.9, 127.8, 127.3, 116.4, 109.8, 103.8, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3257, 1665, 1576, 1504, 1387, 1273, 1141, 1083, 797. **HRMS (ESI)**: calculated for $C_{14}H_{16}N_3OS$ (**[M+H]$^+$**): 274.1009; found 274.1014.

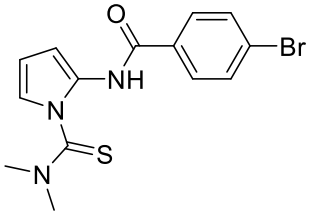
***N*-(1-(Dimethylcarbamothioyl)-1*H*-pyrrol-2-yl)-4-methylbenzamide (6b):**

The titled compound **6b** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (53 mg, 0.30 mmol, 1.5 equiv). The product **6b** (55.8 mg, 0.19 mmol, 97%) was isolated as a white solid after column chromatography on silica gel by using 20% ethylacetate in hexane



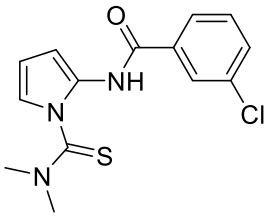
as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 9.75 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 6.63-6.62 (m, 1H), 6.48 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.23 (t, *J* = 3.5 Hz, 1H), 3.37 (s, 6H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.6, 164.3, 142.6, 131.3, 129.6, 127.9, 127.3, 116.3, 109.8, 103.7, 43.9, 21.6. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3253, 2921, 1663, 1492, 1392, 1305, 1148, 1079, 889, 713. **HRMS (ESI)**: calculated for $C_{15}H_{17}N_3NaOS$ (**[M+Na]$^+$**): 310.0985; found 310.0990.

4-Bromo-*N*-(1-(dimethylcarbamothioyl)-1*H*-pyrrol-2-yl)benzamide (6c):



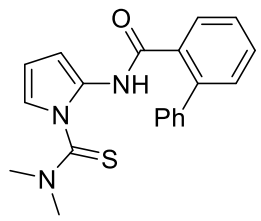
The titled compound **6c** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 3-(4-bromophenyl)-1,4,2-dioxazol-5-one (72.6 mg, 0.30 mmol, 1.5 equiv). The product **6c** (62 mg, 0.18 mmol, 88%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 20% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 9.87 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 6.66-6.62 (m, 1H), 6.49 (dd, *J* = 3.0, 1.5 Hz, 1H), 6.24 (t, *J* = 3.5 Hz, 1H), 3.38 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.4, 163.3, 132.9, 132.1, 128.9, 127.7, 126.8, 116.6, 109.8, 103.9, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3281, 2924, 1861, 1673, 1518, 1388, 1300, 1146, 1009, 842, 735. **HRMS (ESI)**: calculated for $C_{14}H_{14}BrN_3NaOS$ (**[M+Na]$^+$**): 375.9913; found 375.9919.

3-Chloro-*N*-(1-(dimethylcarbamothioyl)-1H-pyrrol-2-yl)benzamide (6d):



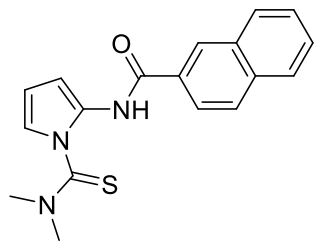
The titled compound **6d** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 3-(3-chlorophenyl)-1,4,2-dioxazol-5-one (59.3 mg, 0.30 mmol, 1.5 equiv). The product **6d** (56.2 mg, 0.18 mmol, 91%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 20% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 9.86 (s, 1H), 7.94-7.91 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 6.64-6.63 (m, 1H), 6.50 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.25 (t, *J* = 3.5 Hz, 1H), 3.38 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.5, 163.0, 135.9, 135.2, 132.1, 130.2, 128.0, 127.6, 125.1, 116.7, 109.8, 104.1, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3275, 2930, 1671, 1515, 1388, 1299, 1148, 1081, 990, 794. **HRMS (ESI)**: calculated for $C_{14}H_{15}ClN_3OS$ (**[M+H]$^+$**): 308.0619; found 308.0605.

***N*-(1-(Dimethylcarbamothioyl)-1*H*-pyrrol-2-yl)-[1,1'-biphenyl]-2-carboxamide (6e):**



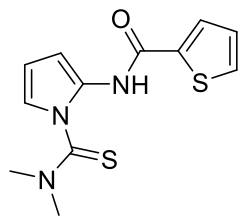
The titled compound **6e** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 3-([1,1'-biphenyl]-2-yl)-1,4,2-dioxazol-5-one (71.8 mg, 0.30 mmol, 1.5 equiv). The product **6e** (53.3 mg, 0.15 mmol, 76%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 20% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.46 (s, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.46-7.42 (m, 3H), 7.41-7.37 (m, 3H), 7.32 (t, *J* = 7.3 Hz, 1H), 6.50-6.44 (m, 1H), 6.36-6.29 (m, 1H), 6.17-6.11 (m, 1H), 3.17 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 180.7, 166.7, 140.2, 139.7, 135.5, 130.7, 130.6, 129.4, 129.3, 128.5, 127.8, 127.5, 127.0, 116.2, 109.5, 103.3, 43.6. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3301, 2925, 1669, 1516, 1389, 1302, 1147, 1081, 879, 741. **HRMS (ESI)**: calculated for $C_{20}H_{19}N_3NaOS$ (**[M+Na]**$^{+}$): 372.1141; found 372.1147.

***N*-(1-(Dimethylcarbamothioyl)-1*H*-pyrrol-2-yl)-2-naphthamide (6f):**



The titled compound **6f** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 3-(naphthalen-2-yl)-1,4,2-dioxazol-5-one (64.0 mg, 0.30 mmol, 1.5 equiv). The product **6f** (57 mg, 0.18 mmol, 88%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 20% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 9.99 (s, 1H), 8.44 (s, 1H), 7.97-7.91 (m, 3H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.58-7.53 (m, 2H), 6.72-6.65 (m, 1H), 6.54-6.45 (m, 1H), 6.29-6.24 (m, 1H), 3.37 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.5, 164.4, 135.1, 132.8, 131.2, 129.3, 128.8, 128.2, 128.0, 127.9, 127.8, 126.9, 123.6, 116.5, 109.8, 103.8, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3281, 2931, 1665, 1517, 1389, 1299, 1146, 1081, 864, 760. **HRMS (ESI)**: calculated for $C_{18}H_{18}N_3OS$ (**[M+H]**$^{+}$): 324.1165; found 324.1152.

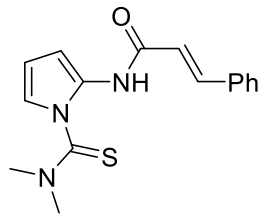
***N*-(1-(Dimethylcarbamothioyl)-1*H*-pyrrol-2-yl)thiophene-2-carboxamide (6g):**



The titled compound **6g** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 3-(thiophen-2-yl)-1,4,2-dioxazol-5-one (50.7 mg, 0.30 mmol, 1.5 equiv). The product **6g** (51.5 mg, 0.18 mmol, 92%) was isolated as a white solid after column chromatography on silica gel by using 20% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 9.73 (s, 1H), 7.60 (dd,

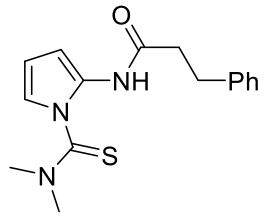
J = 3.5, 1.0 Hz, 1H), 7.52 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.10 (dd, *J* = 4.8, 3.8 Hz, 1H), 6.57 (dd, *J* = 3.3, 1.3 Hz, 1H), 6.48 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.22 (t, *J* = 3.5 Hz, 1H), 3.36 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.4, 158.9, 139.0, 131.0, 128.6, 127.9, 127.3, 116.5, 109.8, 104.0, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3228, 3102, 2924, 1655, 1495, 1415, 1276, 1144, 716. **HRMS (ESI)**: calculated for $C_{12}H_{14}N_3OS_2$ (**[M+H]$^+$**): 280.0573; found 280.0561.

***N*-(1-(Dimethylcarbamothioyl)-1*H*-pyrrol-2-yl)cinnamamide (6h):**



The titled compound **6h** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and (*E*)-3-styryl-1,4,2-dioxazol-5-one (56.8 mg, 0.30 mmol, 1.5 equiv). The product **6h** (58 mg, 0.19 mmol, 97%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 22% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 9.07 (s, 1H), 7.69 (d, *J* = 15.5 Hz, 1H), 7.59-7.47 (m, 2H), 7.42-7.31 (m, 3H), 6.61-6.56 (m, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.48-6.44 (m, 1H), 6.22 (t, *J* = 3.3 Hz, 1H), 3.36 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.4, 163.2, 142.3, 134.8, 130.1, 129.0, 128.1, 127.4, 120.7, 116.5, 109.7, 104.2, 43.8. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3255, 2924, 2853, 1666, 1625, 1519, 1390, 1301, 1148, 976, 763. **HRMS (ESI)**: calculated for $C_{16}H_{17}N_3NaOS$ (**[M+Na]$^+$**): 322.0985; found 322.0990.

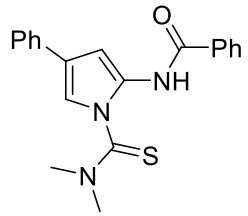
***N*-(1-(Dimethylcarbamothioyl)-1*H*-pyrrol-2-yl)-3-phenylpropanamide (6i):**



The titled compound **6i** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (30.8 mg, 0.20 mmol, 1.0 equiv) and 3-phenethyl-1,4,2-dioxazol-5-one (57.4 mg, 0.30 mmol, 1.5 equiv). The product **6i** (50.7 mg, 0.17 mmol, 84%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 22% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.48 (s, 1H), 7.30-7.27 (m, 2H), 7.23-7.18 (m, 3H), 6.46-6.41 (m, 1H), 6.40-6.34 (m, 1H), 6.20-6.13 (m, 1H), 3.29 (s, 6H), 3.02 (t, *J* = 7.8 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.2, 170.2, 140.7, 128.6, 128.5, 126.6, 126.3, 116.6, 109.4, 104.5, 43.7, 38.7, 31.4. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3275, 2931, 1671, 1518, 1390, 1301, 1146, 1080, 974, 860. **HRMS (ESI)**: calculated for $C_{16}H_{19}N_3NaOS$ (**[M+Na]$^+$**): 324.1141; found 324.1147.

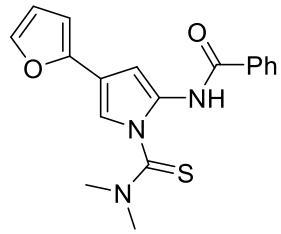
***N*-(1-(Dimethylcarbamothioyl)-4-phenyl-1*H*-pyrrol-2-yl)benzamide (6j):**

The titled compound **6j** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-3-phenyl-1*H*-pyrrole-1-carbothioamide (46 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-



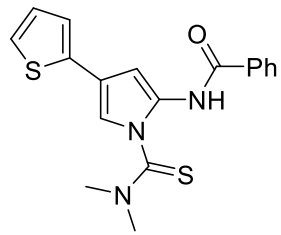
dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6j** (47 mg, 0.13 mmol, 67%) was isolated as a white solid after column chromatography on silica gel by using 12% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 10.00 (s, 1H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.56-7.53 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.26-7.23 (m, 1H), 7.05 (d, *J* = 1.5 Hz, 1H), 6.79 (d, *J* = 1.5 Hz, 1H), 3.42 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.2, 164.2, 134.1, 134.0, 132.2, 129.0, 128.9, 127.4, 126.9, 125.7, 125.6, 112.2, 102.2, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3194, 2924, 1664, 1530, 1454, 1389, 1321, 1275, 1145, 907. **HRMS (ESI)**: calculated for $C_{20}H_{19}N_3NaOS$ (**[M+Na]$^+$**): 372.1141; found 372.1147.

***N*-(1-(Dimethylcarbamothioyl)-4-(furan-2-yl)-1*H*-pyrrol-2-yl)benzamide (6k):**



The titled compound **6k** was synthesized according to the **GP III** by using 3-(furan-2-yl)-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (44.1 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6k** (28 mg, 0.08 mmol, 41%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 15% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 10.09 (s, 1H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.37-7.33 (m, 1H), 6.95-6.91 (m, 1H), 6.80-6.76 (m, 1H), 6.44-6.39 (m, 2H), 3.42 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 180.9, 164.1, 149.6, 141.0, 133.8, 132.2, 130.3, 129.0, 127.4, 116.8, 111.6, 111.5, 104.9, 100.8, 44.1. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3287, 2925, 1665, 1523, 1393, 1320, 1268, 1153, 798, 709. **HRMS (ESI)**: calculated for $C_{18}H_{18}N_3O_2S$ (**[M+H]$^+$**): 340.1114; found 340.1118.

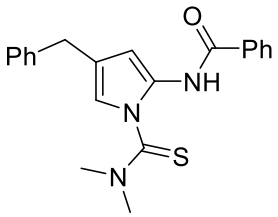
***N*-(1-(Dimethylcarbamothioyl)-4-(thiophen-2-yl)-1*H*-pyrrol-2-yl)benzamide (6l):**



The titled compound **6l** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-3-(thiophen-2-yl)-1*H*-pyrrole-1-carbothioamide (47.3 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6l** (45 mg, 0.13 mmol, 63%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 15% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 10.02 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 5.0 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 7.01 (t, *J* = 4.3 Hz, 1H), 6.99-6.94 (m, 1H), 6.74-6.69 (m, 1H), 3.41 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm)

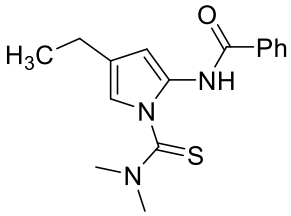
180.9, 164.1, 137.3, 133.9, 132.2, 128.9, 127.8, 127.4, 123.2, 123.0, 119.9, 112.0, 102.4, 44.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3281, 2928, 1670, 1515, 1389, 1316, 1265, 1141, 840, 793. **HRMS (ESI)**: calculated for $C_{18}H_{17}N_3NaOS_2$ (**[M+Na]**$^+$): 378.0705; found 378.0695.

***N*-(4-Benzyl-1-(dimethylcarbamothioyl)-1*H*-pyrrol-2-yl)benzamide (6m):**



The titled compound **6m** was synthesized according to the **GP III** by using 3-benzyl-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (49 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6m** (47.4 mg, 0.13 mmol, 65%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 12% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 10.01 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.26-7.20 (m, 4H), 7.16 (t, *J* = 7.0 Hz, 1H), 6.58-6.51 (m, 1H), 6.14-6.07 (m, 1H), 3.75 (s, 2H), 3.28 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.5, 164.0, 140.6, 134.0, 132.0, 128.90, 128.85, 128.5, 128.3, 127.3, 126.2, 124.9, 114.1, 104.8, 43.9, 33.6. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3287, 2928, 1672, 1516, 1387, 1318, 1264, 1148, 986, 794, 732. **HRMS (ESI)**: calculated for $C_{21}H_{22}N_3OS$ (**[M+H]**$^+$): 364.1478; found 364.1468.

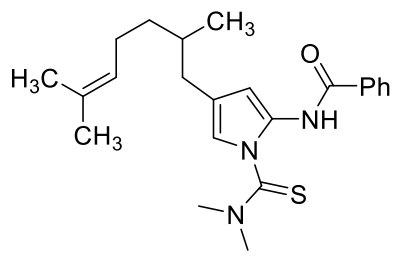
***N*-(1-(Dimethylcarbamothioyl)-4-ethyl-1*H*-pyrrol-2-yl)benzamide (6n):**



The titled compound **6n** was synthesized according to the **GP III** by using 3-ethyl-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (36.5 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6n** (32 mg, 0.11 mmol, 53%) was isolated as a yellow liquid after column chromatography on silica gel by using 12% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 10.07 (s, 1H), 7.90 (d, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 6.59 (d, *J* = 1.5 Hz, 1H), 6.25 (d, *J* = 1.0 Hz, 1H), 3.37 (s, 6H), 2.47 (d, *J* = 7.5 Hz, 2H), 1.19 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 181.5, 163.9, 134.0, 132.0, 128.9, 128.1, 127.5, 127.3, 112.7, 104.4, 44.0, 20.2, 14.4. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3295, 2929, 1666, 1522, 1390, 1306, 1152, 1069, 801, 708. **HRMS (ESI)**: calculated for $C_{16}H_{20}N_3OS$ (**[M+H]**$^+$): 302.1322; found 302.1314.

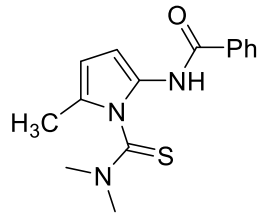
***N*-(1-(Dimethylcarbamothioyl)-4-(2,6-dimethylhept-5-en-1-yl)-1*H*-pyrrol-2-yl)benzamide (6o):**

The titled compound **6o** was synthesized according to the **GP III** by using 3-(2,6-dimethylhept-5-en-1-yl)-*N*,*N*-dimethyl-1*H*-pyrrole-1-carbothioamide (55.7 mg, 0.20 mmol, 1.0 equiv) and



3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6o** (55.8 mg, 0.14 mmol, 70%) was isolated as a yellow liquid after column chromatography on silica gel by using 13% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 10.12 (s, 1H), 7.90 (d, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 6.57 (s, 1H), 6.23 (s, 1H), 5.10 (t, *J* = 7.0 Hz, 1H), 3.36 (s, 6H), 2.45 (dd, *J* = 14.3, 5.8 Hz, 1H), 2.21 (dd, *J* = 14.3, 8.0 Hz, 1H), 2.08-2.01 (m, 1H), 1.99-1.94 (m, 1H), 1.73-1.70 (m, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.45-1.38 (m, 1H), 1.22-1.15 (m, 1H), 0.90 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.7, 163.9, 134.2, 131.9, 131.3, 128.9, 128.1, 127.3, 125.0, 124.3, 114.0, 105.1, 44.0, 37.0, 34.7, 33.5, 25.83, 25.79, 19.7, 17.8. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3284, 2914, 1670, 1515, 1387, 1315, 1133, 987, 752, 704. **HRMS (ESI)**: calculated for $C_{23}H_{32}N_3OS$ (**[M+H]**$^+$): 398.2261; found 398.2265.

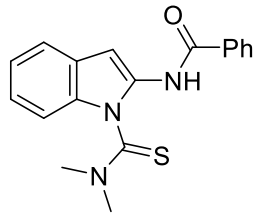
***N*-(1-(Dimethylcarbamothioyl)-5-methyl-1*H*-pyrrol-2-yl)benzamide (6p):**



The titled compound **6p** was synthesized according to the **GP III** by using *N*,*N*,2-trimethyl-1*H*-pyrrole-1-carbothioamide (33.7 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6p** (20.3 mg, 0.07 mmol, 35%) was isolated as a white solid after column chromatography on silica gel by using 15% ethylacetate in hexane as eluent. Here 2.0 mol % of $Cp^*Co(CO)I_2$ was used and reaction was conducted over 48 h. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.44 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 6.32 (d, *J* = 3.0 Hz, 1H), 5.96 (d, *J* = 3.0 Hz, 1H), 3.50 (s, 3H), 3.05 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 181.2, 165.7, 134.1, 132.1, 128.9, 127.4, 124.4, 124.3, 107.9, 104.3, 43.7, 42.3, 12.3. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3233, 2924, 1669, 1585, 1528, 1471, 1377, 1307, 1152, 968, 724. **HRMS (ESI)**: calculated for $C_{15}H_{17}N_3NaOS$ (**[M+Na]**$^+$): 310.0985; found310.0990.

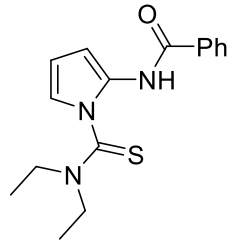
***N*-(1-(Dimethylcarbamothioyl)-1*H*-indol-2-yl)benzamide (6q):**

The titled compound **6q** was synthesized according to the **GP III** by using *N*,*N*-dimethyl-1*H*-indole-1-carbothioamide (40.9 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6q** (51.9 mg, 0.16 mmol, 80%) was isolated as a white solid after column chromatography on silica gel by using 22% ethylacetate in hexane as



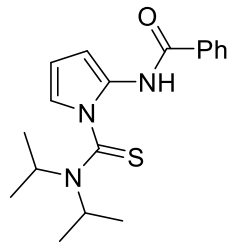
eluent. Here 1.0 mol % of Cp*Co(CO)I_2 was used. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 10.17 (s, 1H), 7.98-7.96 (m, 2H), 7.59-7.55 (m, 2H), 7.52-7.49 (m, 2H), 7.24-7.17 (m, 2H), 7.16 (s, 1H), 6.97 (d, *J* = 8.8 Hz, 1H), 3.63 (s, 3H), 3.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 180.0, 164.1, 133.7, 132.9, 132.4, 131.5, 129.0, 128.1, 127.4, 122.8, 122.5, 121.1, 110.7, 97.1, 43.7. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3223, 2926, 1673, 1590, 1526, 1465, 1395, 1310, 1151, 1020, 856. **HRMS (ESI)**: calculated for $C_{18}H_{17}N_3NaOS$ (**[M+Na]$^+$**): 346.0985; found 346.0992.

***N*-(1-(Diethylcarbamothioyl)-1*H*-pyrrol-2-yl)benzamide (6r):**



The titled compound **6r** was synthesized according to the **GP III** by using *N*,*N*-diethyl-1*H*-pyrrole-1-carbothioamide (36.5 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6r** (34 mg, 0.11 mmol, 56%) was isolated as a white solid after column chromatography on silica gel by using 15% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.47 (s, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 6.60-6.59 (m, 1H), 6.48 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.24 (t, *J* = 3.4 Hz, 1H), 3.87-3.69 (m, 4H), 1.28 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 180.7, 164.5, 133.9, 132.1, 128.9, 127.3, 127.1, 116.0, 109.6, 103.9, 47.7, 13.3. **HRMS (ESI)**: calculated for $C_{16}H_{20}N_3OS$ (**[M+H]$^+$**): 302.1322; found 302.1323.

***N*-(1-(Diisopropylcarbamothioyl)-1*H*-pyrrol-2-yl)benzamide (6s):**



The titled compound **6s** was synthesized according to the **GP III** by using *N*,*N*-diisopropyl-1*H*-pyrrole-1-carbothioamide (42.1 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The product **6s** (20.5 mg, 0.06 mmol, 31%, as an inseparable mixture of rotamer in 3.3:1 ratio) was isolated as a yellow sticky solid after column chromatography on silica gel by using 10% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.15 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.54-7.53 (m, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 6.56-6.54 (m, 1H), 6.46 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.22 (t, *J* = 3.4 Hz, 1H), 4.25-4.11 (m, 2H), 1.52-1.43 (m, 6H), 1.37 (d, *J* = 6.8 Hz, 6H) (**Major Isomer**). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 179.8, 164.4, 133.9, 132.0, 128.8, 127.2, 126.5, 116.2, 109.0, 103.8, 53.8, 21.0, 20.7 (**Major Isomer**). **HRMS (ESI)**: calculated for $C_{18}H_{24}N_3OS$ (**[M+H]$^+$**): 330.1635; found 330.1635.

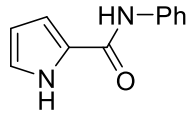
Gram-Scale Synthesis:

The pyrrolyl thiocarbamate **1a** (463 mg, 3.0 mmol, 1.0 equiv) was taken in a 30.0 mL screw capped sealed tube. Then catalyst Cp*Co(CO)I_2 (21.4 mg, 0.045 mmol, 1.5 mol %), NaOAc (14.8 mg, 0.18 mmol, 6.0 mol %), and $AgSbF_6$ (30.9 mg, 0.09 mmol, 3.0 mol %) were added successively to the reaction mixture. After that, phenyl isocyanate **2a** (631 mg, 3.6 mmol, 1.2 equiv), 5.0 mL of 1,1,2,2-tetrachloroethane were added to the reaction mixture and allowed to stir in a preheated oil bath at 100 °C for 26 h (to get **4a**) or 36 h (to get **3a**). On complete consumption of all the starting material as indicated by TLC, solvent was evaporated under *vacuo*. Ethylacetate was subsequently added to the black crude residue and filtered over a pad of celite. The filtrate was collected and solvent was evaporated under reduced pressure. The cyclic amide **3a** (2.49 mmol, 0.57 g, 83%) was isolated as a yellow solid, and for a second reaction, acyclic amide **4a** (2.43 mmol, 0.67 g, 81%) was isolated as a white solid after column chromatography on silica gel by using ethylacetate in hexane as eluent.

Removal of Directing Group:

***N*-Phenyl-1*H*-pyrrole-2-carboxamide (7):[2]**

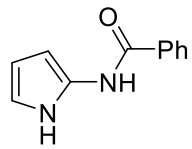
In an oven-dried 100 mL round bottom flask, **4a** (41.0 mg, 0.15 mmol, 1.0 equiv) and



$NiCl_2 \cdot 6H_2O$ (285 mg, 1.20 mmol, 8.0 equiv) were taken, and dissolved in 40 mL of MeOH-THF (1:1 v/v). The resulting solution was cooled down to 0 ^oC and $NaBH_4$ (85 mg, 2.25 mmol, 15.0 equiv) was added slowly in portions. The reaction mixture was stirred at the same temperature for 2 h. On complete consumption of all the starting material as indicated by TLC, solvent was evaporated under *vacuo*. Ethylacetate was subsequently added to the black crude residue and filtered over a pad of celite. The filtrate was collected and solvent was evaporated under reduced pressure. The product **7** (20.2 mg, 0.11 mmol, 72%) was isolated as a white solid after column chromatography on silica gel by using 10% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 9.96 (br s, 1H), 7.68 (s, 1H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.01-6.95 (m, 1H), 6.77-6.71 (m, 1H), 6.30-6.28 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 159.3, 137.9, 129.2, 126.1, 124.4, 122.7, 120.2, 110.2, 109.8. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3318, 1633, 1524, 1442, 1332, 1238, 1122, 1045, 732. **HRMS (ESI)**: calculated for $C_{11}H_{11}N_2O$ (**[M+H]$^+$**): 187.0866; found 187.0862.

***N*-(1*H*-Pyrrol-2-yl)benzamide (8):[1]**

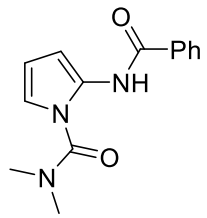
***Method a*:** In an oven-dried 25 mL round bottom flask, **6a** (54.7 mg, 0.20 mmol, 1.0 equiv) was taken and dissolved in 5 mL of anhydrous THF. The resulting solution was cooled down to 0 °C and lithium aluminium hydride (22.8 mg, 0.60 mmol, 3.0 equiv) was added in portions. Then the reaction mixture was stirred at the same temperature for 45 minutes. On complete consumption of all the starting material as indicated by TLC, the reaction mixture was quenched by adding saturated aq. NH_4Cl solution. The aqueous layer was extracted with ethylacetate (2 x 10 mL), the combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The product **8** (34.4 mg, 0.18 mmol, 92%) was isolated as a white solid after column chromatography on silica gel by using 10% ethylacetate in hexane as eluent.



***Method b*:** To a stirred solution of **6a** (109 mg, 0.4 mmol, 1.0 equiv) in MeOH (5.0 mL) was added NaOH (112 mg, 2.8 mmol, 7.0 equiv). The resulting mixture was refluxed until complete consumption of the starting material (monitored by TLC). The mixture was cooled to room temperature and then quenched by dropwise addition of 6 N HCl. After evaporation of MeOH under *vacuo*, the aqueous layer was extracted with ethylacetate (2 x 10 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The product **8** (65 mg, 0.35 mmol, 87%) was isolated as a white solid after column chromatography on silica gel by using 10% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, DMSO-d_6): δ (ppm) 10.72 (br s, 1H), 10.54 (s, 1H), 7.96 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 6.49 (d, J = 2.0 Hz, 1H), 5.95 (d, J = 3.0 Hz, 1H), 5.91-5.84 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6): δ (ppm) 163.8, 134.1, 131.4, 128.4, 127.9, 127.3, 112.7, 106.3, 96.2. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3416, 3298, 1593, 1523, 1431, 1298, 1079, 1024, 899, 787. **HRMS (ESI)**: calculated for $C_{11}H_{11}N_2O$ (**$[M+H]^+$**): 187.0866; found 187.0870.

2-Benzamido-*N*,*N*-dimethyl-1*H*-pyrrole-1-carboxamide (9):[2]

In an oven-dried 25 mL round bottom flask, **6a** (82.0 mg, 0.30 mmol, 1.0 equiv) and Ag_2CO_3 (166 mg, 0.60 mmol, 2.0 equiv) were taken, and 5 mL of anhydrous dichloromethane was added. The reaction mixture was stirred at rt for 10 h. On complete consumption of all the starting material as indicated by TLC, dichloromethane was subsequently added to the black crude residue and filtered over a pad of celite. The filtrate was collected and solvent was evaporated under *vacuo*. The product **9** (73.5 mg, 0.29 mmol, 95%) was isolated as a white solid after column chromatography on silica gel by using 25% ethylacetate in hexane as eluent.



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.13 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 6.74-6.66 (m, 1H), 6.63-6.56 (m, 1H), 6.24-6.16 (m, 1H), 3.10 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 163.5, 155.7, 133.9, 131.9, 129.8, 128.8, 127.1, 115.1, 110.1, 100.9, 39.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3336, 1669, 1523, 1488, 1384, 1266, 1104, 1052, 876, 800, 715. **HRMS (ESI)**: calculated for $C_{14}H_{15}N_3NaO_2$ (**[M+Na]$^+$**): 280.1056; found 280.1046.

2-Phenyl-1*H*-pyrrolo[1,2-*c*]imidazole-1,3(2*H*)-dithione (10):[2]

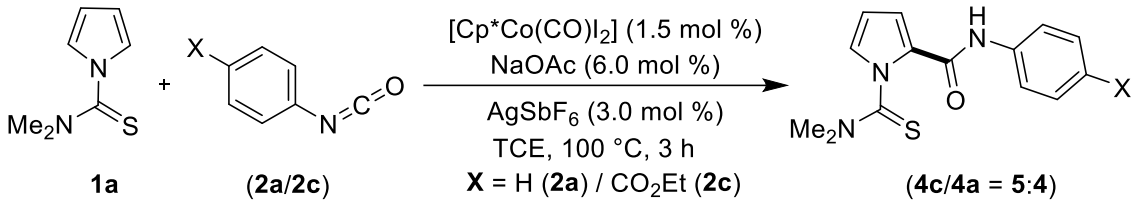
In an oven-dried 10 mL Schlenk tube, **3a** (45.7 mg, 0.20 mmol, 1.0 equiv) and Lawesson reagent (323.6 mg, 0.80 mmol, 4.0 equiv) were taken, and dissolved in 3 mL of anhydrous toluene. The resulting mixture was allowed to stir in a preheated oil bath at 120 °C until complete consumption of the starting material (monitored by TLC). The mixture was cooled down to room temperature and solvent was evaporated under *vacuo*. The product **10** (40.2 mg, 0.16 mmol, 82%) was isolated as a reddish solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.57-7.51 (m, 3H), 7.37 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.34-7.32 (m, 2H), 6.99 (dd, *J* = 3.5, 0.5 Hz, 1H), 6.45 (t, *J* = 3.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 182.9, 174.0, 134.9, 134.8, 129.9, 129.5, 129.3, 118.4, 114.1. **FTIR**: ν_{max} (neat)/ cm^{-1} = 1553, 1496, 1417, 1332, 1285, 1230, 1119, 1041, 918. **HRMS (ESI)**: calculated for $C_{12}H_9N_2S_2$ (**[M+H]$^+$**): 245.0202; found 245.0205.

2-Phenyl-1*H*-pyrrolo[1,2-*c*]imidazole-1,3(2*H*)-dione (11):

In an oven-dried 10 mL screw capped sealed tube, **4a** (54.7 mg, 0.20 mmol, 1.0 equiv) and Cp*Co(CO)I_2 (1.4 mg, 0.003 mmol, 1.5 mol %) were taken, and dissolved in 1.5 mL of TCE. The resulting mixture was allowed to stir in a preheated oil bath at 100 °C for 48 h. On complete consumption of all the starting material as indicated by TLC, the mixture was cooled down to room temperature and solvent was evaporated under *vacuo*. The product **11** (10.7 mg, 0.05 mmol, 25%) was isolated as a white solid after column chromatography on silica gel by using 4% ethylacetate in hexane as eluent. In second fraction, **3a** was also isolated in 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.51 (t, *J* = 7.6 Hz, 2H), 7.44-7.40 (m, 3H), 7.37 (d, *J* = 1.6 Hz, 1H), 6.91 (d, *J* = 2.8 Hz, 1H), 6.55-6.51 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 157.5, 147.9, 131.1, 129.4, 128.6, 126.5, 125.0, 119.5, 118.1, 114.5. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2922, 1800, 1715, 1562, 1491, 1416, 1372, 1276, 1141, 1093, 815, 737. **HRMS (ESI)**: calculated for $C_{12}H_9N_2O_2$ (**[M+H]$^+$**): 213.0659; found 213.0653.

Mechanistic Studies:

Competition experiment:



The pyrrolyl thiocarbamate **1a** (0.20 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube. Then catalyst $Cp^*Co(CO)I_2$ (1.4 mg, 0.003 mmol, 1.5 mol %), NaOAc (1.0 mg, 0.012 mmol, 6.0 mol %), and $AgSbF_6$ (2.1 mg, 0.006 mmol, 3.0 mol %) were added successively to the reaction mixture. After that, **2a** (0.24 mmol, 1.2 equiv), **2c** (0.24 mmol, 1.2 equiv) and 1.5 mL of 1,1,2,2-tetrachloroethane were added to the reaction mixture, and allowed to stir in a preheated oil bath at 100 °C for 12 h. Then the crude residue was diluted with ethylacetate, and carefully transferred to a round bottom flask. After evaporating the solvent under *vacuo*, the crude product flash through a silica gel column by using hexane-ethylacetate as eluent. The ratio of **4c**:**4a** = 5:4 is being calculated by ^{1}H NMR analysis (Figure S1).

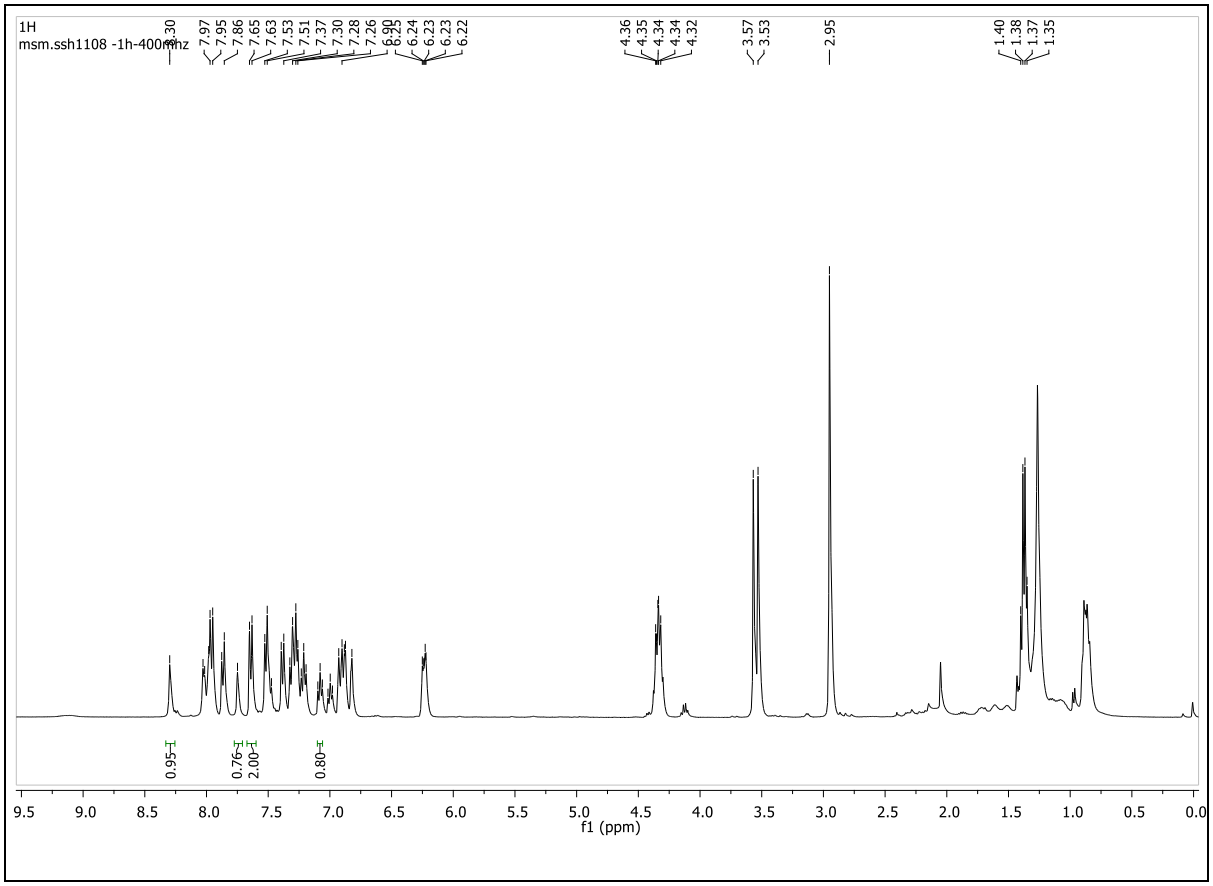
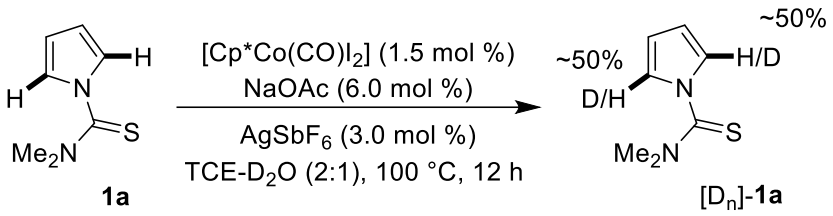


Figure S1: ^{1}H NMR spectra of competition experiment between isocyanates **2a** and **2c**.

Deuterium labelling experiments using deuterated solvent as a co-solvent:



The pyrrolyl thiocarbamate **1a** (0.20 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube. Then catalyst Cp*Co(CO)I_2 (1.4 mg, 0.003 mmol, 1.5 mol %), NaOAc (1.0 mg, 0.012 mmol, 6.0 mol %), and $AgSbF_6$ (2.1 mg, 0.006 mmol, 3.0 mol %) were added successively to the reaction mixture. After that, TCE and deuterated solvent were added (total volume 1.5 mL) while maintaining the required ratio and allowed to stir in a preheated oil bath at 100 °C for 12 h. Purification by silica gel column chromatography using hexane-ethylacetate as eluent provided mixture of **1a** and [D_n]-**1a**. The D-incorporation in [D_n]-**1a** was estimated by ^{1}H-NMR spectroscopy (Figure S2).

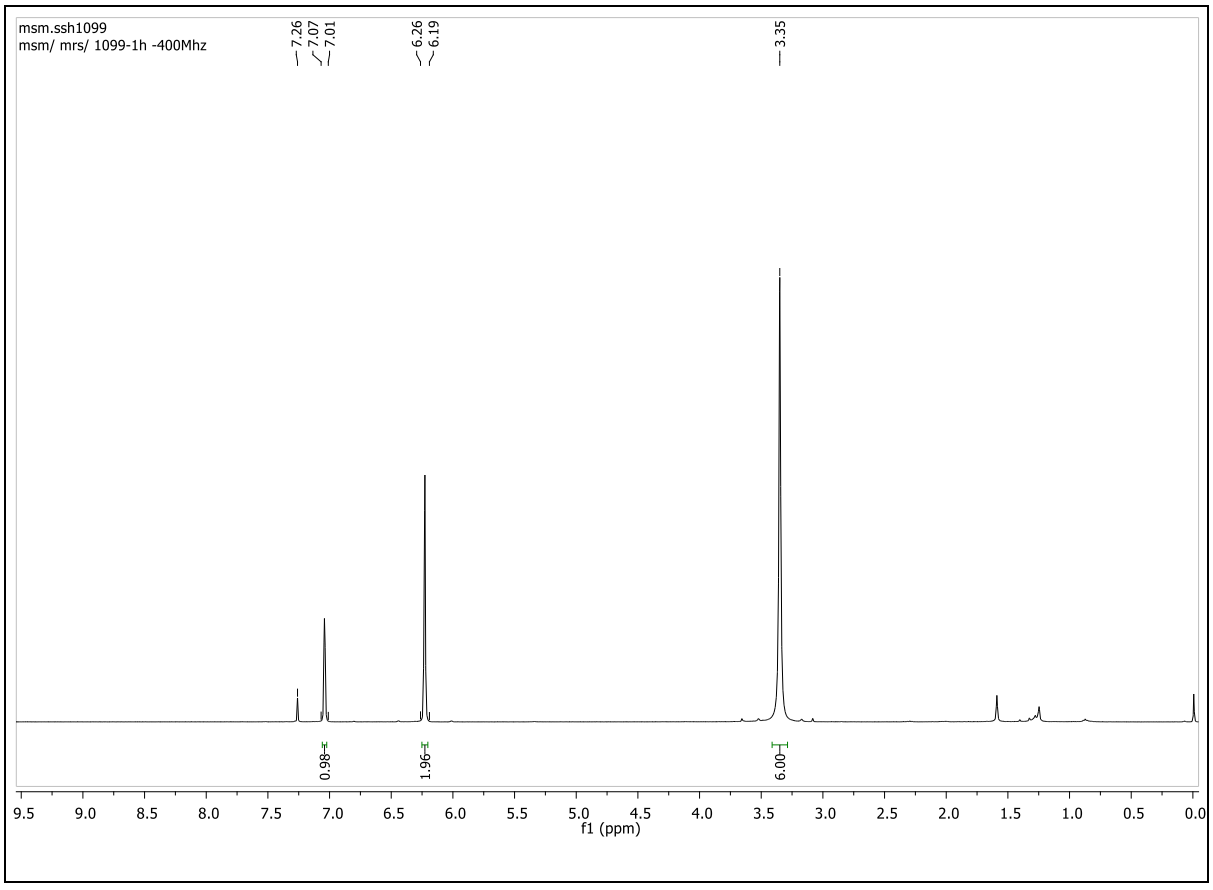
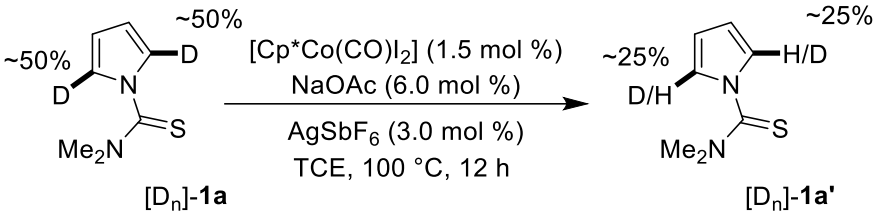


Figure S2: ^{1}H NMR spectra of deuterium labelling experiment.



The pyrrolyl thiocarbamate [D_n]-**1a** (0.20 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube. Then catalyst Cp*Co(CO)I_2 (1.4 mg, 0.003 mmol, 1.5 mol %), NaOAc (1.0 mg, 0.012 mmol, 6.0 mol %), and $AgSbF_6$ (2.1 mg, 0.006 mmol, 3.0 mol %) were added successively to the reaction mixture. After that, 1.5 mL of TCE was added to the reaction mixture and allowed to stir in a preheated oil bath at 100 °C for 12 h. Purification by silica gel column chromatography using hexane-ethylacetate as eluent provided mixture of **1a** and [D_n]-**1a'**. The D-incorporation in [D_n]-**1a'** was estimated by ^{1}H-NMR spectroscopy (Figure S3).

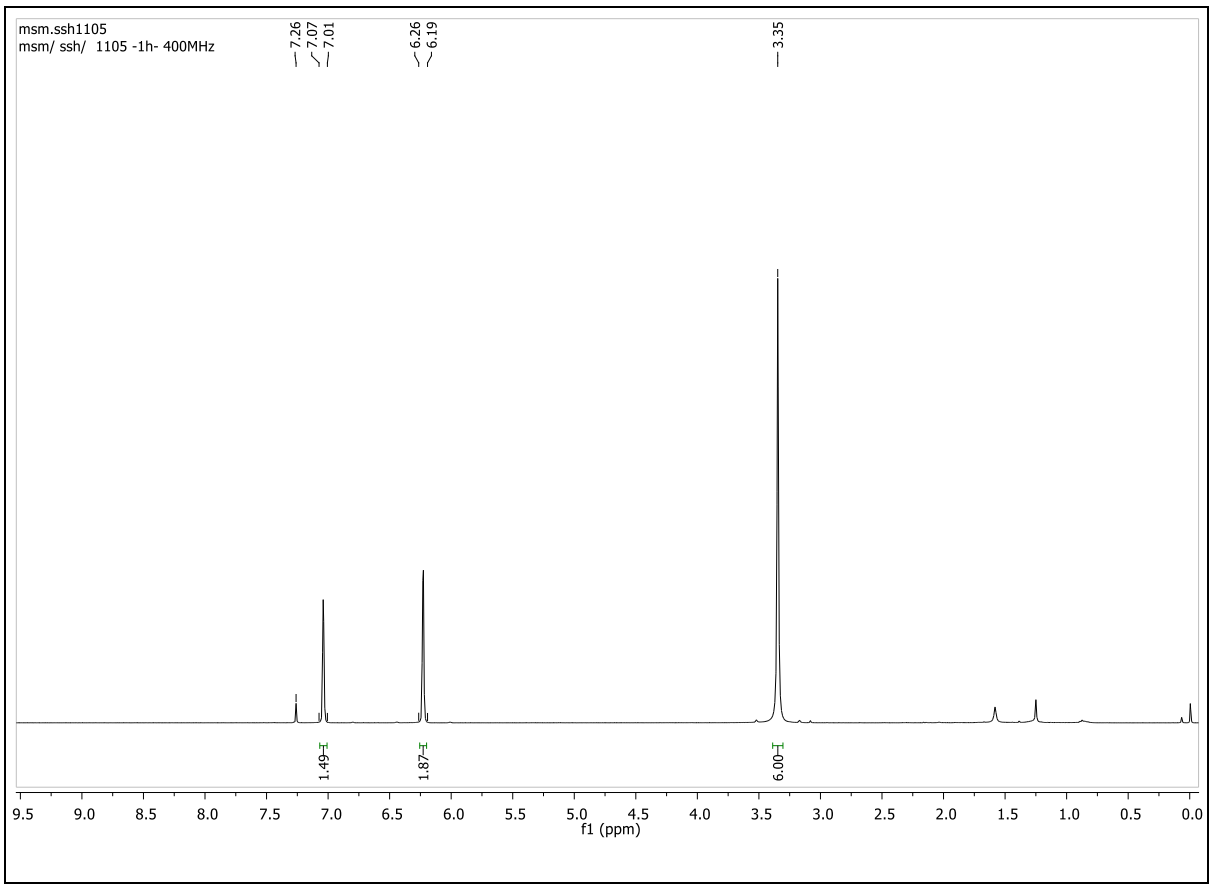
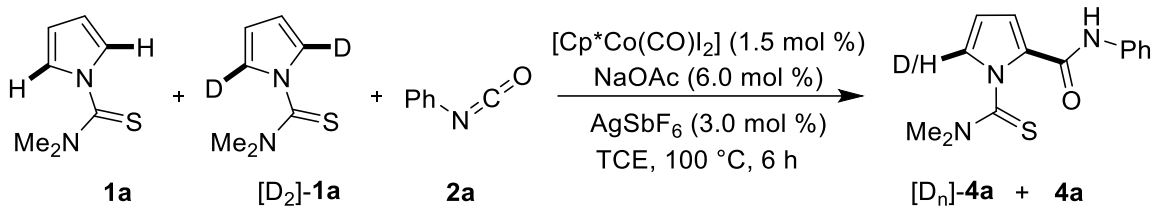


Figure S3: ^{1}H NMR spectra of deuterium labelling experiment.

Determination of k_H/k_D from intermolecular competition experiment:



1a [D$_2$]-**1a** **2a** [D$_n$]-**4a** + **4a**

The pyrrolyl thiocarbamate **1a** (0.20 mmol, 1.0 equiv) and deuterio-pyrrolyl thiocarbamate [D$_2$]-**1a** (0.20 mmol, 1.0 equiv) were taken in a 15.0 mL screw capped sealed tube. Then catalyst Cp*Co(CO)I$_2$ (1.4 mg, 0.003 mmol, 1.5 mol %), NaOAc (1.0 mg, 0.012 mmol, 6.0 mol %), and AgSbF$_6$ (2.1 mg, 0.006 mmol, 3.0 mol %) were added successively to the reaction mixture. After that, phenyl isocyanate **2a** (0.24 mmol, 1.2 equiv) and 1.5 mL of TCE were added to the reaction mixture and allowed to stir in a preheated oil bath at 100 °C for 6 h. Purification by silica gel column chromatography using hexane-ethylacetate as eluent, provided the mixture of **4a** and [D$_n$]-**4a**. The ratio of **4a**:[D$_n$]-**4a** was determined by ^{1}H NMR analysis to obtain a k_H/k_D value of approximately 1.5 (Figure S4).

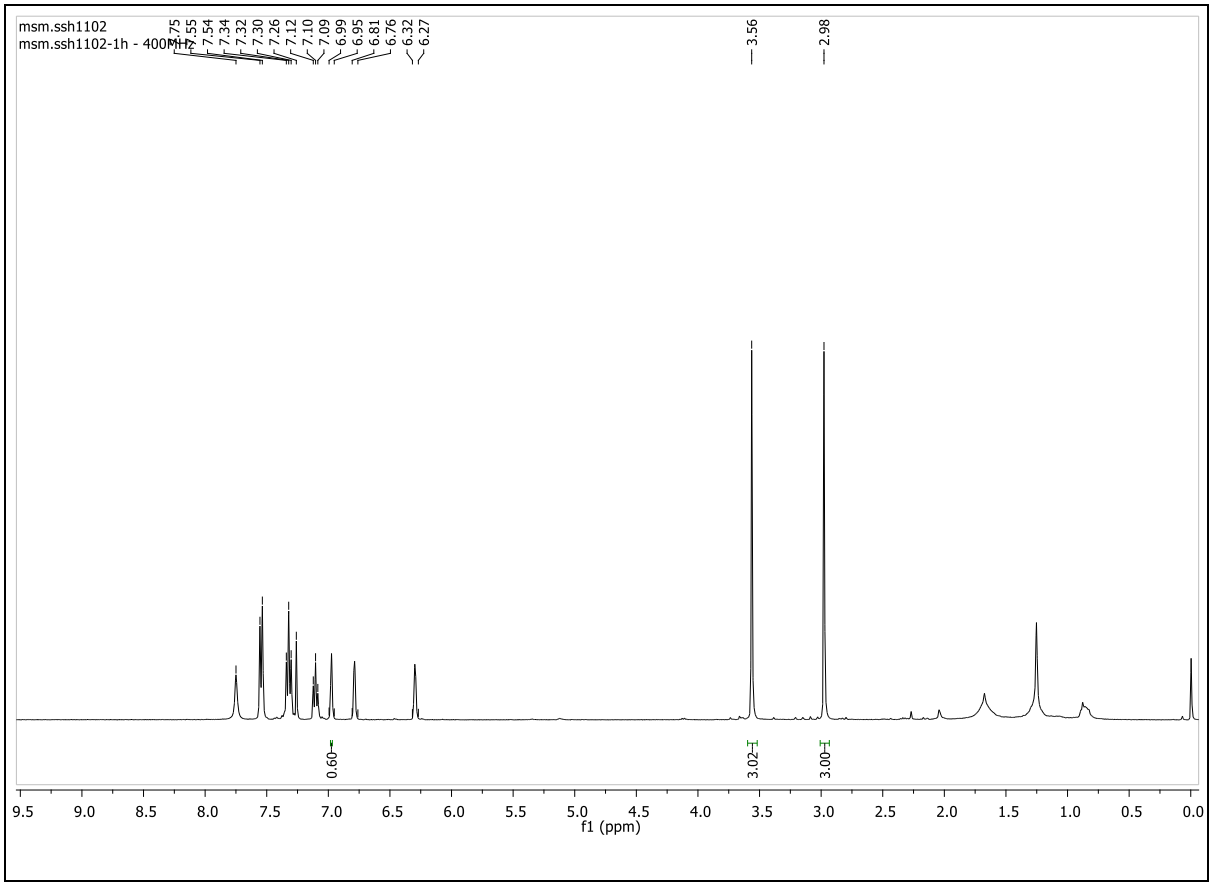
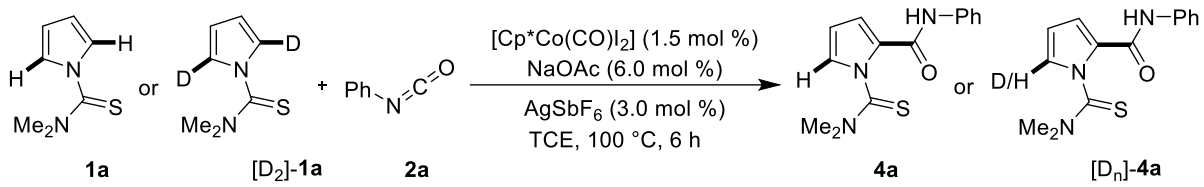


Figure S4: ^{1}H NMR spectra for determination of k_H/k_D value by intermolecular competition experiment.

Determination of k_H/k_D from parallel experiments:



The pyrrolyl thiocarbamate **1a** (0.20 mmol, 1.0 equiv) and deuterio-pyrrolyl thiocarbamate [D_2]-**1a** (0.20 mmol, 1.0 equiv) were taken separately in a 15.0 mL screw capped sealed tube. Then catalyst Cp*Co(CO)I_2 (1.4 mg, 0.003 mmol, 1.5 mol %), NaOAc (1.0 mg, 0.012 mmol, 6.0 mol %), and $AgSbF_6$ (2.1 mg, 0.006 mmol, 3.0 mol %) were added successively to both the reaction mixture. After that, phenyl isocyanate **2a** (0.24 mmol, 1.2 equiv) and 1.5 mL of TCE were added to each reaction mixture and allowed to stir in a preheated oil bath at 100 °C for 6 h. Finally, both the reaction mixtures were mixed together and purified by silica gel column chromatography using hexane-ethylacetate as eluent. The ratio of **4a**:[D_n]-**4a** was determined by ^{1}H NMR analysis to obtain a k_H/k_D value of approximately 1.6 (Figure S5).

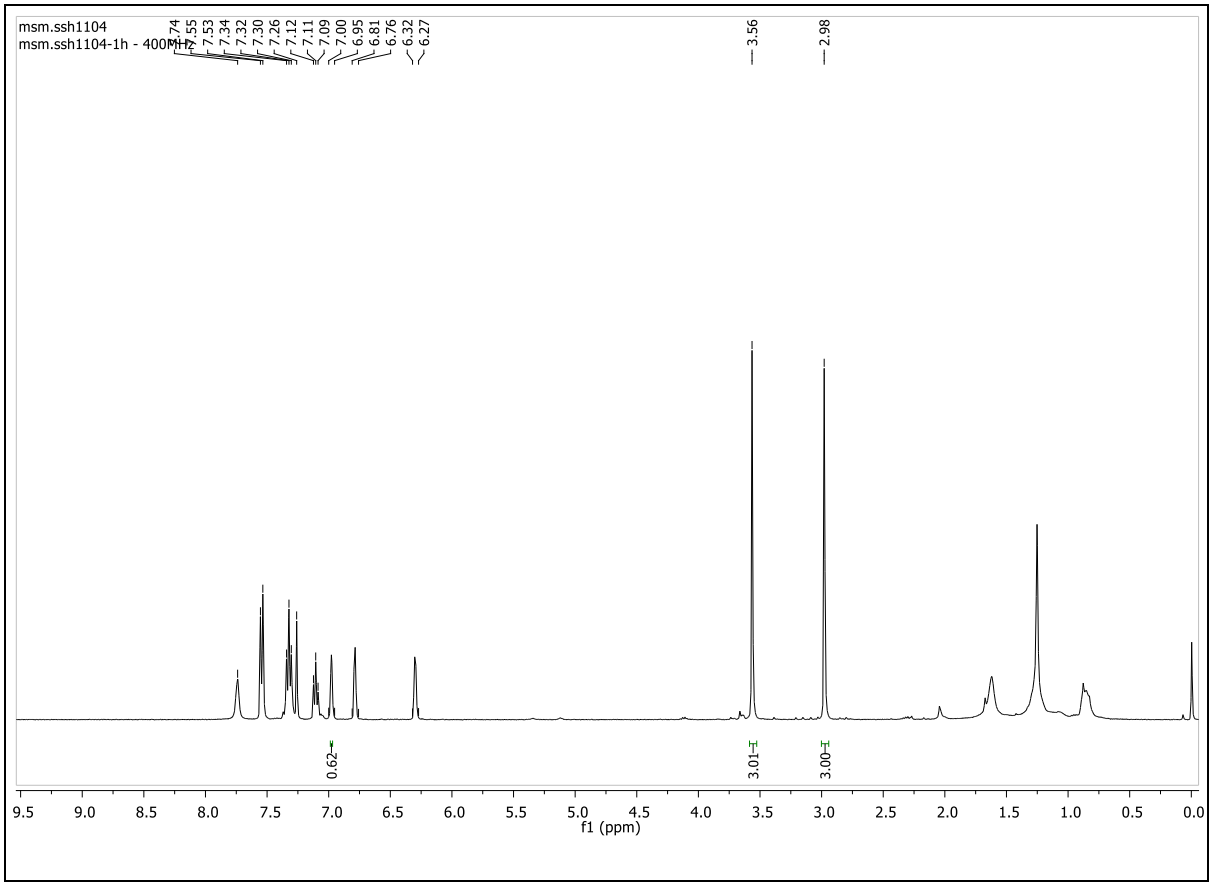
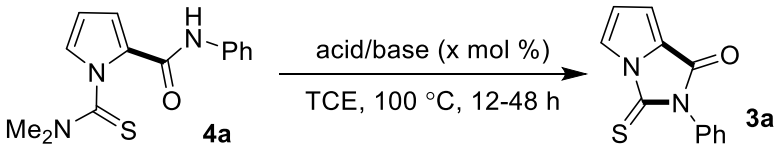


Figure S5: ^{1}H NMR spectra for determination of k_H/k_D value from parallel experiments.

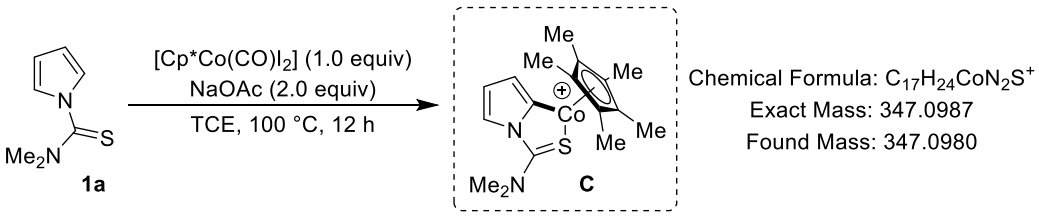
Control experiments for the cyclization step:



In an oven-dried 10 mL screw capped sealed tube, **4a** (54.7 mg, 0.20 mmol, 1.0 equiv) and acid/base (x mol %) were taken, and dissolved in 1.5 mL of TCE. The resulting mixture was allowed to stir in a preheated oil bath at 100 ^{o}C for 12-48 h. Next, progress of the reaction was monitored by TLC, the mixture was cooled down to room temperature and solvent was evaporated under *vacuo*. The product **3a** was isolated as a yellow solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent.

entry	acid/base (mol %)	time (h)	yield **3a** (%)
1	na	12	0
2	NaOAc(6.0)	12	95
3	Et_3N (6.0)	12	46
4	$AgSbF_6$ (3.0)	12	81
5	$Sc(OTf)_3$ (3.0)	12	15
6	$Cp^*Co(CO)I_2$ (1.5)	48	61

Detection of complex C in HRMS:



The pyrrolyl thiocarbamate **1a** (0.20 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube. Then catalyst $Cp^*Co(CO)I_2$ (95.2 mg, 0.20 mmol, 1.0 equiv) and NaOAc (164.1 mg, 0.04 mmol, 2.0 equiv) were added successively to the reaction mixture. After that, 1.5 mL of TCE was added to the reaction mixture and allowed to stir in a preheated oil bath at 100 °C for 12 h. Then, the reaction was cooled to room temperature, and the crude mixture was analyzed by HRMS, which was in complete agreement with the molecular formula related to species **C**.

Target Screening Report

Agilent | Trusted Answers

Sample Information

Name	MSM_SSH_1116	**Data File Path**	D:\MassHunter\Data\AUG2022\04-08-2022\MSM_SSH_1116_POS_01.d
Sample ID		**Acq. Time (Local)**	8/4/2022 12:10:14 PM (UTC+05:30)
Instrument	IITKGP	**Method Path (Acq)**	D:\MassHunter\Methods\TRAINING\MS SCAN POS_ORGANOMETALLICS_03.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.09.00 (B9044.1 SP1)
Inj. Vol. (ul)	2	**IRM Status**	Success
Position	P1-D9	**Method Path (DA)**	D:\MassHunter\Methods\TARGETED ANALYSIS ORGANOMETALLICS REPORTING_01.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Compound Summary

Cpd	Name	Formula	CAS	RT	Mass	Mass (Tgt)	Diff (Tgt, ppm)	Score	Algorithm
1		C17 H24 Co N2 S		0.264	347.0986	347.0992	-1.90	97.25	FBF

Compound Details

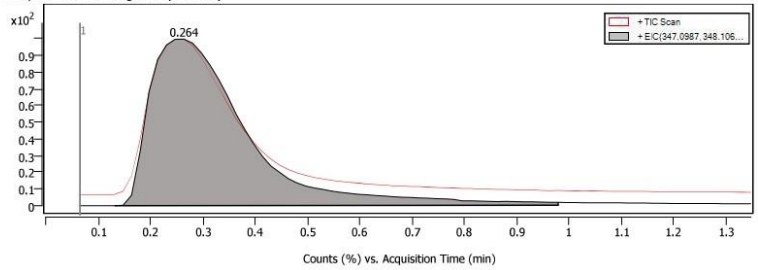
Cpd. 1: C17 H24 Co N2 S

Name	Formula	RT	RI	Mass	Diff (Tgt, ppm)	CAS	ID Source	Score	Algorithm
	C17 H24 Co N2 S	0.264		347.0986	-1.90		FBF	97.25	FBF

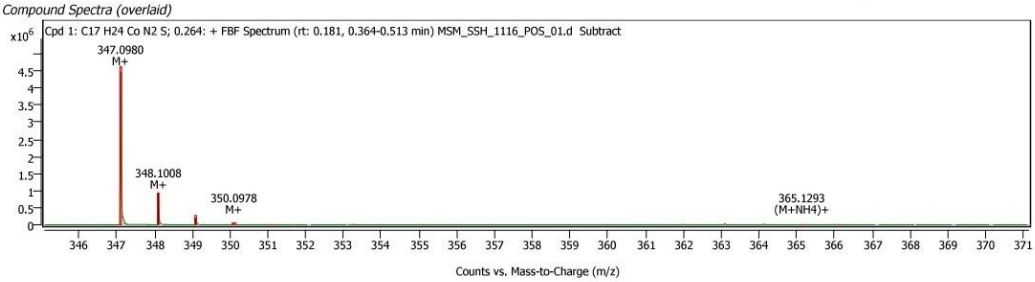
Species	m/z	Score (Tgt)	Score (Lib)	Score (DB)	Score (MFG)	Score (RT)
M+ (M+NH4)+	347.0980 365.1293	97.25				

Compound Chromatograms (overlaid)

Structure



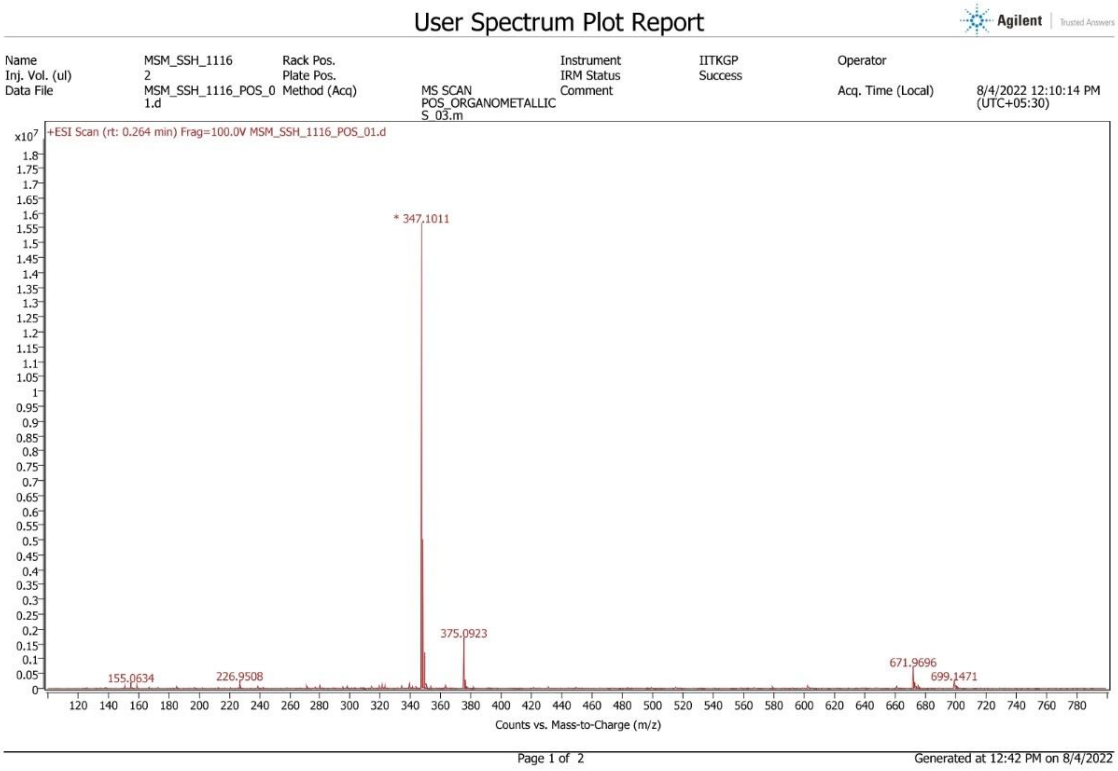
Compound Spectra (overlaid)



Compound ID Table

Name	Formula	Species	RT	RT Diff	Mass	CAS	ID Source	Score	Score (Lib)	Score (Tgt)
	C17 H24 Co N2 S	M+ (M+NH4)+	0.264		347.0986		FBF	97.25		97.25

MassHunter Qual 10.0
(End of Report)



Single Crystal X-ray Diffraction:

Single crystals of **6a** and **4a** were grown by slow evaporation of their saturated ethylacetate solution. Single crystal X-ray data were collected at 150 K on a Bruker SMART APEX II CCD diffractometer using graphite-monochromated Mo-K_α radiation (0.71073 Å). The data collection was evaluated by using the Crystal Clear-SM Expert software. The data were collected by the standard ω-scan technique. The structure was solved by direct method using SHELXS-97 and refined by full matrix least-squares with SHELXL-2018, refining on F^2.[3] All data were corrected for Lorentz and polarization effects and all non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms. Hydrogen atoms were included in the refinement process as per the riding model. Supplementary crystallographic data for the compounds mentioned in the paper may be obtained free of charge from the Crystallographic Data Center (www.ccdc.cam.ac.uk/data_request/cif) using CCDC numbers 2131973 (**6a**), 2131974 (**4a**). The alert B in the checkCIF of **4a** was developed due to the weakly diffracting nature of the crystal.

Table S3. Selected Crystallographic Parameters

complex	**4a**	**6a**
CCDC	**2131974**	**2131973**
empirical formula	$C_{14}H_{15}N_3OS$	$C_{14}H_{15}N_3OS$
formula weight	273.35	273.35
crystal system	Triclinic	Triclinic
space group	P-1	P-1
a (Å)	9.1959(7)	9.831(4)
b (Å)	9.4051(6)	9.988(7)
c (Å)	17.0462(15)	14.908(7)
α (deg)	81.503(6)	91.97(2)
β(deg)	82.539(7)	97.090(12)
γ (deg)	82.743(6)	103.993(18)
V (Å^3)	1437.12(19)	1406.3(13)
Z	4	4
μ (mm^{-1})	0.221	0.226
ρ_{calcd} (g cm^{-3})	1.263	1.291
T (K)	150(2)	150(2)
F (000)	576	576
θ range (deg)	2.187 to 27.248	2.396 to 26.666
data/restraints /parameters	12300/0/348	5968/0/343
R_1,wR_2[$I > 2\sigma(I)$]	0.0679, 0.1571	0.0473, 0.1285
R_1, wR_2 (all data)	0.2145, 0.2289	0.0653, 0.1451
GOF on F^2	0.934	1.049
largest difference in peak and hole (e Å^{-3})	0.204, -0.209	0.389, -0.291

Table S4. Selected Experimental Bond Lengths (Å)

Bond lengths	**4a**	Bond lengths	**6a**
C1-N1	1.403(3)	C1-N1	1.388(3)
C1-C5	1.450(3)	C1-N2	1.395(3)
C5-N2	1.354(3)	C5-N2	1.362(3)
C5-O1	1.232(2)	C5-O1	1.225(3)
C12-N1	1.441(3)	C12-N1	1.418(3)
C12-S1	1.645(3)	C12-S1	1.661(2)
C12-N3	1.323(3)	C12-N3	1.326(3)
C4-N1	1.362(3)	C4-N1	1.384(3)
C1-C2	1.380(3)	C1-C2	1.358(3)
C2-C3	1.401(3)	C2-C3	1.409(4)
C3-C4	1.364(4)	C3-C4	1.351(4)

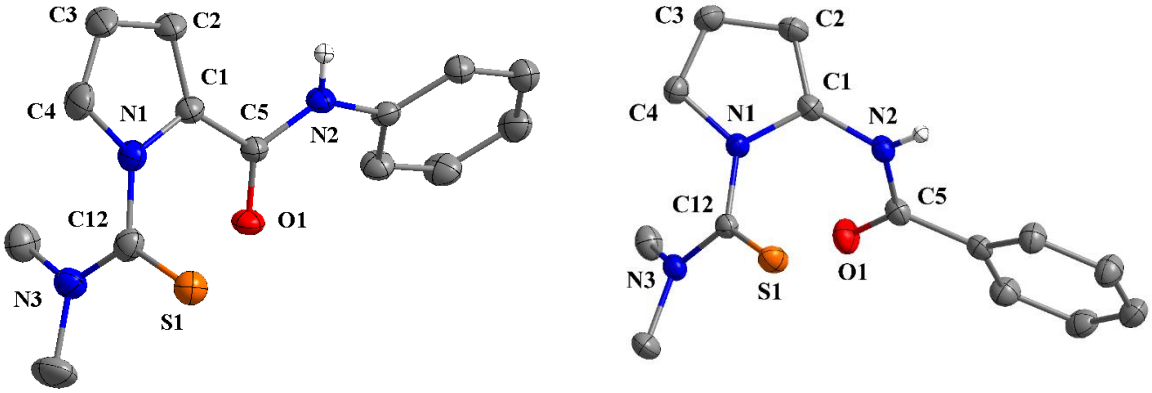
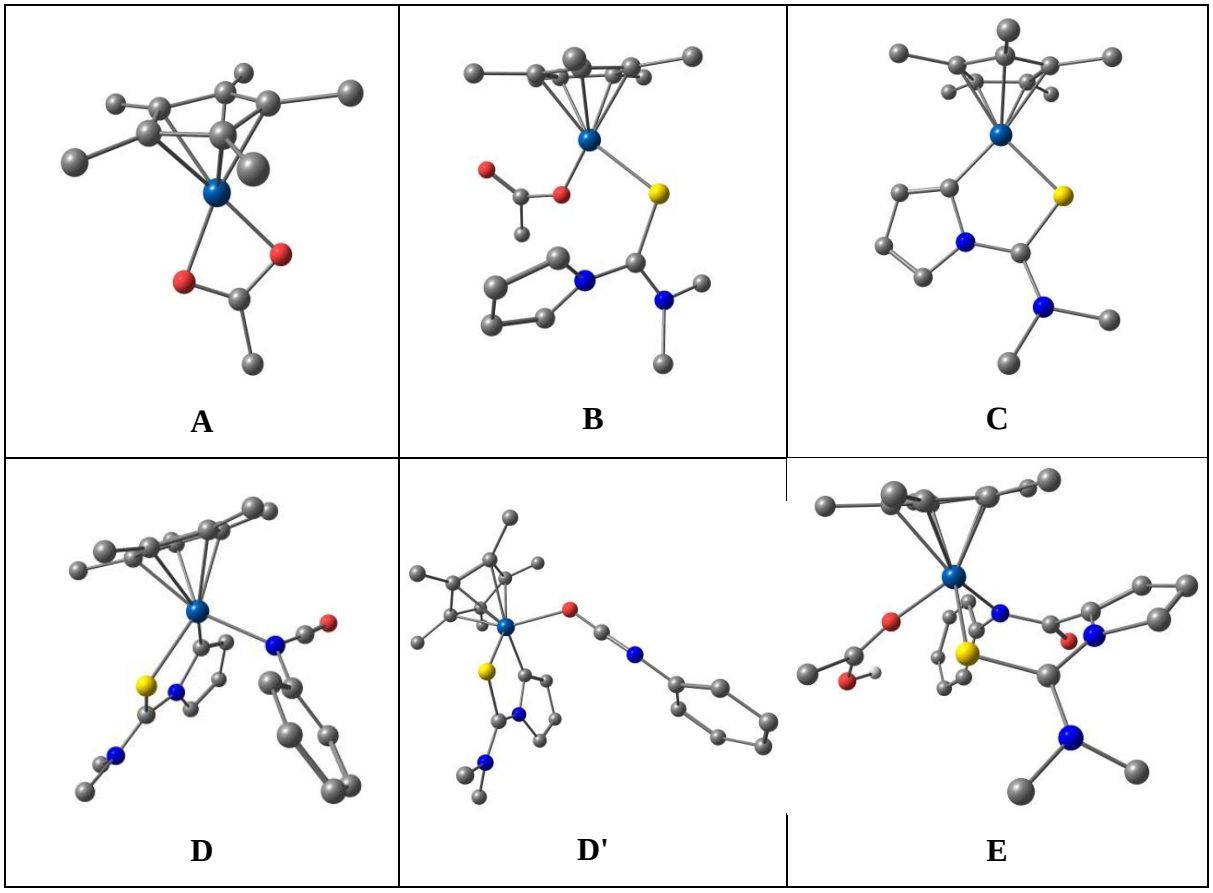


Figure S6. Perspective views at 25% probability level of **4a** and **6a**. Hydrogen atoms (except the N-H) are omitted for clarity.

Computational Studies:

All the calculations were performed with the Gaussian 16, Revision B.01 program package.[4] Geometry optimization and frequency analysis were conducted using B3LYP function.[5] During geometry optimization we used TZVP basis set for non-metal atoms and the SDD basis set for cobalt. In all cases, ultrafine integral grid was employed. To refine the computed energy, single point calculations were performed using the B3LYP functional with the Def2-TZVP basis set for non-metal atoms and the SDD basis set for cobalt with considering the Grimme's D3 (BJ-damping) dispersion effect. The SMD solvent model[6] was used to simulate the implicit solvent effect (due to similar dielectric constant we have used 1,1,2-

trichloroethane instead of our experimentally used solvent 1,1,2,2-tetrachloroethane). Transition state optimizations were performed starting from infinitely separated substrates. Single imaginary frequency for the transition states (TSs) and real frequencies for local minima were obtained. The connectivity of each TS was validated through a relaxed potential energy surface scan for the corresponding reaction coordinate, and was found to be the highest-energy point that connected the relevant reactant and product. The geometries were optimized without any symmetry constraints. The zero-point vibrational energies (ZPVE), thermal corrections were obtained by using the temperature 373.15 K and 1 atm pressure. Unless otherwise specified, the ΔG was used throughout the text. All calculated structures were visualized with ChemCraft.[7]



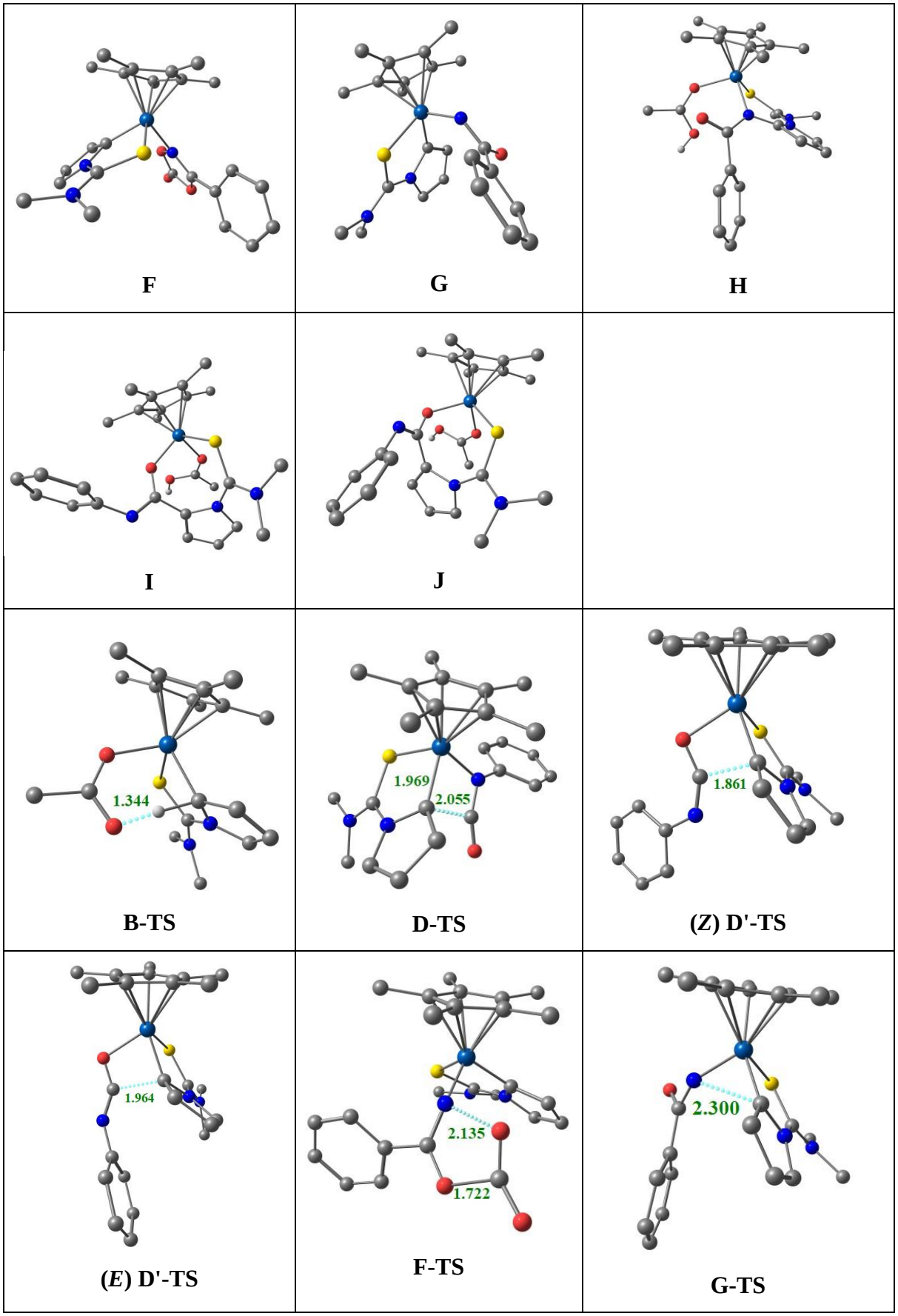


Figure S7. DFT optimized structures. Hydrogen atoms are removed for clarity.

Table S5. Electronic and Gibbs free energies (in Hartree) at the at B3LYP(SMD)/Def2-TZVP/SDD//B3LYP/TZVP/SDD level of theory (Substrate is **1a**).

Structures	*E*	*G*	Structures	*E*	*G*
CO_2	-188.657331	-188.688910	**F**	-1904.086925	-1904.229991
AcOH	-229.133340	-229.176376	**G**	-1715.421784	-1715.560058
1a	-780.477221	-780.540688	**H**	-1944.643375	-1944.796129
2a	-399.803920	-399.858622	**I**	-1944.634086	-1944.788515
5a	-588.388910	-588.449822	**J**	-1944.630074	-1944.787704
A	-764.312618	-764.405933	**B-TS**	-1544.823784	-1544.949327
B	-1544.820162	-1544.952278	**D-TS**	-1715.484643	-1715.618908
C	-1315.672132	-1315.782421	**(*Z*) D'-TS**	-1715.460538	-1715.594062
D	-1715.492516	-1715.630095	**(*E*) D'-TS**	-1715.471595	-1715.606005
D'	-1715.486681	-1715.629715	**F-TS**	-1904.056098	-1904.200931
E	-1944.644009	-1944.798107	**G-TS**	-1715.418419	-1715.554620

G = Sum of electronic and thermal free energies.

Table S6. Cartesian coordinates (Å) of the optimized structures of all intermediates and transition states involved in the C−H amidation of pyrrole at B3LYP/TZVP/SDD level of theory.

CO_2

C	-8.657806000	0.707085000	-4.943568000
O	-8.232219000	1.779047000	-4.815109000
O	-9.083393000	-0.364876000	-5.072028000

AcOH

O	-5.446721000	-5.792465000	-9.011001000
C	-4.334769000	-6.562618000	-9.140134000
O	-3.222815000	-6.108175000	-9.057569000
C	-4.687035000	-8.002135000	-9.390197000
H	-5.291468000	-8.385477000	-8.566524000
H	-5.283967000	-8.086134000	-10.299793000
H	-3.776777000	-8.587025000	-9.487316000
H	-5.146988000	-4.883540000	-8.852450000

1a

C	-7.566551000	-4.818836000	-9.830768000
C	-4.221517000	-5.345795000	-11.025270000
C	-5.106876000	-4.752366000	-10.172351000
N	-6.386633000	-5.145127000	-10.534069000
C	-6.290852000	-6.022191000	-11.612347000
C	-4.970420000	-6.159919000	-11.929810000
H	-3.151416000	-5.219357000	-11.006999000
H	-7.167725000	-6.496622000	-12.015411000
H	-4.575626000	-6.787336000	-12.712614000
S	-7.577553000	-4.736445000	-8.162450000
N	-8.654616000	-4.618142000	-10.614218000
C	-8.587638000	-4.069982000	-11.973030000
H	-9.083933000	-4.733860000	-12.684607000
H	-7.558493000	-3.927571000	-12.282951000
H	-9.097877000	-3.102686000	-11.988373000
C	-9.975051000	-4.526946000	-10.000930000
H	-10.061827000	-5.254313000	-9.198200000
H	-10.722812000	-4.729685000	-10.768436000
H	-10.150258000	-3.532544000	-9.579168000
H	-4.964176000	-4.089535000	-9.338189000

2a

C	-8.244533000	-9.574833000	-7.821869000
C	-8.158885000	-8.446254000	-7.012503000
C	-7.231554000	-9.841569000	-8.738885000
H	-8.942048000	-8.230749000	-6.296316000
H	-7.289420000	-10.717571000	-9.373104000
C	-7.071654000	-7.587470000	-7.114616000
C	-6.139827000	-8.990688000	-8.850255000
H	-6.994231000	-6.707052000	-6.490702000

H	-5.351780000	-9.198170000	-9.563641000
C	-6.058398000	-7.857855000	-8.034742000
H	-9.093237000	-10.241786000	-7.739528000
N	-4.980037000	-6.975983000	-8.113003000
C	-3.947205000	-6.782120000	-8.689960000
O	-2.926414000	-6.495440000	-9.186915000

5a

C	-9.622337000	-7.151444000	-7.266909000
C	-9.091775000	-5.983751000	-6.720618000
C	-8.820824000	-7.986998000	-8.037133000
H	-9.715588000	-5.333108000	-6.121027000
H	-9.230870000	-8.894209000	-8.462249000
C	-7.765175000	-5.649946000	-6.941738000
C	-7.489365000	-7.662119000	-8.265278000
H	-7.346412000	-4.745261000	-6.521085000
H	-6.863831000	-8.310325000	-8.863973000
C	-6.957509000	-6.491157000	-7.717333000
H	-10.659688000	-7.407622000	-7.091022000
C	-5.562772000	-6.140729000	-7.950011000
N	-4.949643000	-5.101612000	-7.508121000
O	-3.623968000	-5.227382000	-8.011639000
O	-4.780839000	-6.961023000	-8.706183000
C	-3.529587000	-6.366641000	-8.742786000
O	-2.577355000	-6.785873000	-9.306777000

A

Co	-5.477637000	-4.221522000	-8.093594000
C	-5.827346000	-2.464898000	-7.038095000
C	-5.199075000	-3.498936000	-6.239440000
C	-3.899171000	-3.790240000	-6.811440000
C	-3.773660000	-3.021803000	-7.987349000
C	-4.974084000	-2.196808000	-8.128514000
C	-7.169638000	-1.873205000	-6.768625000
H	-7.888112000	-2.630736000	-6.455590000
H	-7.574012000	-1.365495000	-7.641526000
H	-7.090651000	-1.139515000	-5.960827000
C	-5.754901000	-4.094745000	-4.994693000
H	-5.391357000	-5.107885000	-4.829598000
H	-6.843802000	-4.107620000	-4.999206000
H	-5.438827000	-3.490351000	-4.136683000
C	-2.930785000	-4.787386000	-6.270703000
H	-2.185470000	-5.073984000	-7.009400000
H	-3.433345000	-5.692402000	-5.929558000
H	-2.404615000	-4.358586000	-5.412594000
C	-2.637690000	-3.032343000	-8.952802000
H	-2.980811000	-2.976545000	-9.986570000
H	-2.016899000	-3.919204000	-8.844964000
H	-2.002906000	-2.157251000	-8.779270000
C	-5.223788000	-1.255060000	-9.256979000
H	-6.276049000	-0.993987000	-9.347322000
H	-4.888017000	-1.663816000	-10.210733000
H	-4.663097000	-0.329359000	-9.091006000
O	-7.200801000	-4.905013000	-8.617461000
C	-6.670795000	-6.066369000	-8.731911000
O	-5.432131000	-6.121748000	-8.407239000
C	-7.433935000	-7.254146000	-9.185213000
H	-7.864781000	-7.741229000	-8.305175000
H	-8.249488000	-6.954346000	-9.840694000
H	-6.772540000	-7.965640000	-9.676286000

B

Co	0.920306000	-0.191459000	-0.126030000
C	2.343004000	-1.564530000	0.571033000
C	2.748516000	-0.975852000	-0.668961000
C	2.903039000	0.446973000	-0.475590000
C	2.535970000	0.738836000	0.863483000
C	2.162716000	-0.504442000	1.505015000
C	-2.289919000	-0.926517000	-0.020737000
C	2.182588000	-3.026045000	0.839047000
H	1.846288000	-3.571809000	-0.041749000
H	1.477689000	-3.220313000	1.645627000
H	3.147744000	-3.447150000	1.135875000
C	3.020520000	-1.706325000	-1.939936000
H	2.768975000	-1.105970000	-2.813506000
H	2.474272000	-2.646509000	-1.996237000
H	4.088313000	-1.941438000	-2.004066000
C	3.434948000	1.400184000	-1.491425000
H	3.105326000	2.416803000	-1.297768000
H	3.127298000	1.130192000	-2.501665000
H	4.529412000	1.375117000	-1.467288000
C	2.563044000	2.068874000	1.532505000
H	1.772073000	2.161462000	2.276380000
H	2.446749000	2.876912000	0.817163000
H	3.518968000	2.184523000	2.055442000
C	1.746204000	-0.640781000	2.930948000
H	1.176590000	-1.552187000	3.103862000
H	1.150160000	0.209687000	3.260059000
H	2.634658000	-0.679596000	3.569639000
C	-2.468357000	1.606151000	2.478998000
C	-2.048190000	0.384789000	2.058672000

N	-2.551041000	0.173603000	0.768486000
C	-3.276555000	1.313726000	0.391111000
C	-3.229586000	2.200009000	1.418709000
H	-2.275122000	2.038881000	3.446812000
H	-3.697177000	1.398040000	-0.594191000
H	-3.674391000	3.181717000	1.420209000
S	-0.756334000	-1.732548000	0.064046000
N	-3.263497000	-1.403959000	-0.785903000
C	-4.697272000	-1.171102000	-0.533421000
H	-5.126636000	-0.538213000	-1.310908000
H	-4.847270000	-0.708967000	0.435906000
H	-5.198026000	-2.139440000	-0.554237000
C	-3.002430000	-2.372002000	-1.860183000
H	-1.997425000	-2.236498000	-2.245981000
H	-3.730087000	-2.199634000	-2.652104000
H	-3.111973000	-3.392919000	-1.489571000
O	-0.188786000	0.934193000	-1.069923000
C	0.008266000	2.200573000	-1.423321000
O	0.821022000	2.939065000	-0.903576000
C	-0.915534000	2.657855000	-2.532221000
H	-0.914098000	1.942308000	-3.355256000
H	-1.936404000	2.719621000	-2.150236000
H	-0.611757000	3.639819000	-2.886232000
H	-1.493557000	-0.390359000	2.554332000

C

Co	-5.587935000	-3.911288000	-8.220358000
C	-5.672261000	-2.714571000	-6.469565000
C	-4.980518000	-3.916920000	-6.206231000
C	-3.832021000	-3.991772000	-7.096879000
C	-3.825747000	-2.828849000	-7.905181000
C	-5.000880000	-2.063725000	-7.565750000
C	-7.733732000	-4.847494000	-10.133238000
C	-6.882267000	-2.196429000	-5.758969000
H	-7.454194000	-2.996175000	-5.290286000
H	-7.548410000	-1.656492000	-6.431146000
H	-6.580897000	-1.502317000	-4.969141000
C	-5.327802000	-4.951996000	-5.187893000
H	-5.184383000	-5.962036000	-5.573378000
H	-6.357819000	-4.861373000	-4.848142000
H	-4.678884000	-4.845138000	-4.312796000
C	-2.819417000	-5.088988000	-7.078307000
H	-2.203587000	-5.092372000	-7.975292000
H	-3.286729000	-6.069670000	-6.985647000
H	-2.152958000	-4.964082000	-6.219015000
C	-2.779383000	-2.406916000	-8.884520000
H	-3.213169000	-1.980843000	-9.788339000
H	-2.134558000	-3.233804000	-9.175156000
H	-2.142318000	-1.641712000	-8.430917000
C	-5.392782000	-0.763753000	-8.182787000
H	-6.467903000	-0.597565000	-8.132425000
H	-5.083308000	-0.701887000	-9.225362000
H	-4.907771000	0.059630000	-7.647163000
C	-4.280702000	-5.048982000	-10.712616000
C	-5.347236000	-4.621646000	-9.961096000
N	-6.501860000	-5.033795000	-10.690318000
C	-6.105130000	-5.747810000	-11.839183000
C	-4.749399000	-5.756415000	-11.866582000
H	-3.243312000	-4.901109000	-10.463158000
H	-6.805300000	-6.219164000	-12.500784000
H	-4.144964000	-6.232997000	-12.621817000
S	-7.738699000	-4.312327000	-8.467027000
N	-8.871275000	-5.013427000	-10.795495000
C	-8.991462000	-5.021871000	-12.261531000
H	-9.064936000	-6.039999000	-12.648248000
H	-8.150681000	-4.509231000	-12.718989000
H	-9.904472000	-4.487482000	-12.519281000
C	-10.161330000	-5.011899000	-10.086746000
H	-10.042667000	-5.399611000	-9.079925000
H	-10.846923000	-5.655075000	-10.635578000
H	-10.571654000	-4.001041000	-10.040772000

D

Co	-5.368457000	-4.544713000	-8.346869000
C	-5.987910000	-3.456124000	-6.557351000
C	-4.935952000	-4.313458000	-6.197888000
C	-3.781612000	-3.988005000	-7.017229000
C	-4.122460000	-2.877377000	-7.832971000
C	-5.511242000	-2.597414000	-7.628104000
C	-7.150605000	-4.446417000	-10.841048000
C	-7.340709000	-3.360977000	-5.927138000
H	-7.592959000	-4.253442000	-5.356129000
H	-8.124380000	-3.199870000	-6.667684000
H	-7.368149000	-2.512924000	-5.236336000
C	-4.927104000	-5.332683000	-5.104007000
H	-4.502212000	-6.283392000	-5.428145000
H	-5.923934000	-5.524588000	-4.711684000
H	-4.313230000	-4.973735000	-4.272634000
C	-2.412791000	-4.567348000	-6.840737000
H	-1.830396000	-4.539003000	-7.760931000

H	-2.443083000	-5.599717000	-6.493820000
H	-1.860459000	-3.994364000	-6.089045000
C	-3.186264000	-2.071857000	-8.670797000
H	-3.670326000	-1.667462000	-9.557235000
H	-2.320802000	-2.647445000	-8.991951000
H	-2.818592000	-1.229037000	-8.076204000
C	-6.265200000	-1.451118000	-8.220572000
H	-7.332221000	-1.658786000	-8.282330000
H	-5.907705000	-1.209333000	-9.220991000
H	-6.135794000	-0.557685000	-7.601132000
C	-3.644489000	-4.596871000	-10.859678000
C	-4.828688000	-4.468154000	-10.192897000
N	-5.835034000	-4.449253000	-11.202264000
C	-5.233682000	-4.617890000	-12.469109000
C	-3.897060000	-4.700943000	-12.271242000
H	-2.667124000	-4.645112000	-10.408578000
H	-5.803846000	-4.707917000	-13.372333000
H	-3.160005000	-4.839767000	-13.046420000
S	-7.482739000	-4.670142000	-9.156991000
N	-8.142433000	-4.271961000	-11.716391000
C	-8.002931000	-3.582750000	-13.008046000
H	-8.002617000	-4.289668000	-13.839931000
H	-7.097331000	-2.985138000	-13.031523000
H	-8.857634000	-2.916404000	-13.121281000
C	-9.532116000	-4.530564000	-11.318272000
H	-9.578172000	-5.366954000	-10.626452000
H	-10.098533000	-4.781127000	-12.213557000
H	-9.974649000	-3.649343000	-10.847262000
C	-8.129788000	-9.620584000	-7.767865000
C	-8.120674000	-8.478006000	-6.974313000
C	-7.155908000	-9.787856000	-8.746812000
H	-8.876417000	-8.340784000	-6.211458000
H	-7.156907000	-10.671491000	-9.372020000
C	-7.142999000	-7.505762000	-7.150875000
C	-6.176126000	-8.819767000	-8.934439000
H	-7.133692000	-6.617436000	-6.537039000
H	-5.428617000	-8.946806000	-9.708623000
C	-6.170390000	-7.685547000	-8.125970000
H	-8.891562000	-10.375799000	-7.624845000
N	-5.146313000	-6.677361000	-8.293961000
C	-3.998295000	-6.957407000	-8.639326000
O	-2.901533000	-7.162935000	-8.938494000

D'

Co	-5.606177000	-4.107446000	-7.775544000
C	-5.625619000	-2.238335000	-6.680724000
C	-4.905673000	-3.186260000	-5.937924000
C	-3.795211000	-3.656248000	-6.753463000
C	-3.823009000	-2.956475000	-7.982936000
C	-5.013327000	-2.148609000	-7.994929000
C	-7.700100000	-4.543660000	-9.962006000
C	-6.796754000	-1.431356000	-6.221227000
H	-7.312518000	-1.898433000	-5.383353000
H	-7.521182000	-1.274268000	-7.019725000
H	-6.456172000	-0.445495000	-5.890271000
C	-5.174021000	-3.635795000	-4.538610000
H	-5.068860000	-4.716157000	-4.438545000
H	-6.174113000	-3.361360000	-4.207145000
H	-4.458833000	-3.172541000	-3.852215000
C	-2.756777000	-4.625855000	-6.290419000
H	-2.172941000	-5.023538000	-7.119089000
H	-3.203112000	-5.464944000	-5.756305000
H	-2.060815000	-4.134702000	-5.603280000
C	-2.782505000	-2.979532000	-9.052955000
H	-3.214205000	-2.882303000	-10.047047000
H	-2.188618000	-3.891109000	-9.030861000
H	-2.098252000	-2.138497000	-8.901612000
C	-5.404233000	-1.188149000	-9.071186000
H	-6.480496000	-1.021285000	-9.089266000
H	-5.098708000	-1.542581000	-10.055121000
H	-4.922712000	-0.218749000	-8.906661000
C	-4.430664000	-5.811351000	-10.000766000
C	-5.394008000	-5.014335000	-9.452032000
N	-6.509188000	-5.099294000	-10.335575000
C	-6.206809000	-5.985705000	-11.392741000
C	-4.937370000	-6.419041000	-11.201567000
H	-3.447818000	-5.978638000	-9.591147000
H	-6.921614000	-6.255331000	-12.144984000
H	-4.413318000	-7.109045000	-11.844426000
S	-7.794963000	-3.956530000	-8.331955000
N	-8.738077000	-4.438195000	-10.791342000
C	-8.633434000	-4.429031000	-12.257929000
H	-8.967346000	-5.375490000	-12.687512000
H	-7.615290000	-4.220544000	-12.570684000
H	-9.278386000	-3.633793000	-12.630728000
C	-10.060808000	-4.059116000	-10.277548000
H	-10.215068000	-4.473912000	-9.285530000
H	-10.813655000	-4.464274000	-10.951478000
H	-10.164544000	-2.972378000	-10.232322000
C	-8.069728000	-11.705012000	-8.667539000

C	-8.731950000	-11.137768000	-7.582850000
C	-7.033683000	-11.013561000	-9.289711000
H	-9.536639000	-11.673560000	-7.096202000
H	-6.516254000	-11.453740000	-10.132517000
C	-8.364985000	-9.882472000	-7.115316000
C	-6.653109000	-9.758357000	-8.834034000
H	-8.869763000	-9.431027000	-6.271740000
H	-5.850882000	-9.210558000	-9.310663000
C	-7.322687000	-9.201433000	-7.743041000
H	-8.358621000	-12.684407000	-9.026275000
N	-6.953293000	-7.946116000	-7.268109000
C	-6.371231000	-6.958659000	-7.027676000
O	-5.824655000	-5.941067000	-6.722372000

E

Co	-7.827177000	-3.878020000	-8.764249000
C	-7.280533000	-2.108393000	-7.587046000
C	-7.919137000	-3.047977000	-6.761334000
C	-7.141145000	-4.272250000	-6.805949000
C	-5.997380000	-4.037986000	-7.631249000
C	-6.111853000	-2.727748000	-8.173081000
C	-7.671908000	-0.685029000	-7.802931000
H	-8.719297000	-0.501782000	-7.569198000
H	-7.476973000	-0.360449000	-8.824346000
H	-7.076702000	-0.044983000	-7.143589000
C	-9.107237000	-2.814346000	-5.885203000
H	-9.749188000	-3.692321000	-5.828476000
H	-9.712007000	-1.976369000	-6.230113000
H	-8.777152000	-2.581048000	-4.868245000
C	-7.354931000	-5.439500000	-5.902359000
H	-6.918640000	-6.352741000	-6.298201000
H	-8.411985000	-5.618366000	-5.712642000
H	-6.881412000	-5.236441000	-4.935692000
C	-4.863118000	-4.983498000	-7.835829000
H	-4.392829000	-4.858167000	-8.808561000
H	-5.180267000	-6.019622000	-7.744489000
H	-4.101782000	-4.800038000	-7.070587000
C	-5.114430000	-1.999804000	-9.015393000
H	-5.562544000	-1.593545000	-9.923124000
H	-4.287458000	-2.641758000	-9.308765000
H	-4.694661000	-1.161877000	-8.451108000
C	-10.009258000	-6.461980000	-8.623236000
S	-9.955452000	-4.750835000	-8.714338000
N	-11.166461000	-7.103282000	-8.788421000
C	-12.433718000	-6.368810000	-8.852565000
H	-12.578691000	-5.934110000	-9.844377000
H	-13.241520000	-7.067407000	-8.645471000
H	-12.446377000	-5.572261000	-8.112354000
C	-11.265010000	-8.524254000	-9.173327000
H	-10.286741000	-8.932066000	-9.399927000
H	-11.891923000	-8.582551000	-10.063884000
C	-6.913985000	-8.242847000	-8.317105000
C	-7.623903000	-7.228115000	-8.900208000
N	-8.899984000	-7.235181000	-8.308024000
C	-8.936834000	-8.247789000	-7.337620000
C	-7.722600000	-8.859186000	-7.319262000
H	-5.922616000	-8.537649000	-8.619333000
H	-9.814460000	-8.391355000	-6.732142000
H	-7.434184000	-9.660219000	-6.658126000
H	-11.727759000	-9.106691000	-8.376108000
C	-7.207128000	-6.488589000	-10.140439000
O	-6.785428000	-7.185828000	-11.062454000
N	-7.264252000	-5.135577000	-10.172477000
C	-6.954449000	-4.585782000	-11.461002000
C	-5.696617000	-4.059448000	-11.742599000
C	-7.922870000	-4.579980000	-12.470014000
H	-4.921815000	-4.110831000	-10.991279000
H	-8.889181000	-5.028142000	-12.273717000
C	-5.418518000	-3.500202000	-12.986878000
C	-7.647954000	-4.026549000	-13.716313000
H	-4.431639000	-3.102055000	-13.188488000
H	-8.402269000	-4.049555000	-14.494092000
C	-6.394677000	-3.470413000	-13.975974000
H	-6.177110000	-3.044958000	-14.947315000
O	-8.481401000	-2.576169000	-10.208572000
C	-9.389852000	-1.958646000	-10.753121000
O	-9.342077000	-1.688455000	-12.046140000
H	-8.590713000	-2.166557000	-12.456346000
C	-10.619386000	-1.426867000	-10.087015000
H	-10.694774000	-0.352896000	-10.265189000
H	-11.500716000	-1.889243000	-10.534165000
H	-10.599553000	-1.629791000	-9.020944000

F

Co	-5.441918000	-4.694042000	-8.423001000
C	-6.100593000	-3.638920000	-6.624915000
C	-5.027518000	-4.479509000	-6.280699000
C	-3.879021000	-4.103720000	-7.085208000
C	-4.248495000	-2.982123000	-7.875541000
C	-5.641173000	-2.740938000	-7.667264000

C	-7.144923000	-4.366201000	-10.956956000
C	-7.456925000	-3.588472000	-5.996459000
H	-7.669860000	-4.478373000	-5.405319000
H	-8.246985000	-3.473818000	-6.739571000
H	-7.520654000	-2.729686000	-5.321599000
C	-5.003799000	-5.528244000	-5.214855000
H	-4.464178000	-6.421649000	-5.530392000
H	-6.003796000	-5.826823000	-4.904276000
H	-4.490270000	-5.143071000	-4.328893000
C	-2.494515000	-4.646234000	-6.921790000
H	-1.917539000	-4.576310000	-7.842704000
H	-2.496160000	-5.689028000	-6.610408000
H	-1.959907000	-4.075660000	-6.155480000
C	-3.330538000	-2.142687000	-8.699945000
H	-3.834144000	-1.704567000	-9.559303000
H	-2.474393000	-2.706111000	-9.064170000
H	-2.949840000	-1.322979000	-8.081700000
C	-6.424722000	-1.599696000	-8.231335000
H	-7.483700000	-1.839789000	-8.314349000
H	-6.062888000	-1.312280000	-9.218153000
H	-6.332737000	-0.723310000	-7.581806000
C	-3.659653000	-4.720767000	-10.896182000
C	-4.850435000	-4.559091000	-10.253130000
N	-5.822015000	-4.378331000	-11.280994000
C	-5.192981000	-4.474253000	-12.543729000
C	-3.873181000	-4.674001000	-12.317467000
H	-2.708221000	-4.895504000	-10.422055000
H	-5.739305000	-4.442942000	-13.465542000
H	-3.123085000	-4.798065000	-13.082749000
S	-7.536886000	-4.779894000	-9.319754000
N	-8.101075000	-4.052336000	-11.833147000
C	-7.889286000	-3.232052000	-13.034974000
H	-7.900439000	-3.841190000	-13.940822000
H	-6.953154000	-2.686902000	-12.970023000
H	-8.705097000	-2.511754000	-13.092567000
C	-9.511904000	-4.296125000	-11.510019000
H	-9.613187000	-5.198184000	-10.913193000
H	-10.054787000	-4.427893000	-12.444520000
H	-9.939228000	-3.452836000	-10.961839000
C	-9.652142000	-9.000343000	-7.615040000
C	-9.124990000	-7.861464000	-7.010539000
C	-8.877215000	-9.746247000	-8.498657000
H	-9.724165000	-7.292514000	-6.311539000
H	-9.284083000	-10.635473000	-8.962068000
C	-7.828939000	-7.460395000	-7.293244000
C	-7.575244000	-9.359801000	-8.780139000
H	-7.413581000	-6.585878000	-6.814750000
H	-6.967824000	-9.946569000	-9.455723000
C	-7.049208000	-8.204185000	-8.185841000
H	-10.664064000	-9.311882000	-7.389020000
C	-5.670745000	-7.840995000	-8.469121000
N	-5.079310000	-6.686448000	-8.430744000
O	-3.706326000	-6.956603000	-8.703613000
O	-4.822155000	-8.840845000	-8.807328000
C	-3.564577000	-8.282941000	-8.972307000
O	-2.576393000	-8.850060000	-9.269763000

G

Co	-0.870107000	-0.506396000	0.000792000
C	-2.004271000	-1.494365000	-1.593560000
C	-1.951897000	-2.372496000	-0.478901000
C	-2.547934000	-1.700523000	0.635198000
C	-3.063481000	-0.431370000	0.170610000
C	-2.710403000	-0.294078000	-1.189993000
C	0.341872000	2.283382000	-0.476414000
C	-1.544513000	-1.786974000	-2.983550000
H	-0.780647000	-2.562087000	-3.006653000
H	-1.147299000	-0.898842000	-3.475092000
H	-2.389618000	-2.137211000	-3.584777000
C	-1.367153000	-3.741597000	-0.425349000
H	-0.611833000	-3.806013000	0.360256000
H	-0.903621000	-4.025869000	-1.368068000
H	-2.147143000	-4.473819000	-0.200944000
C	-2.756455000	-2.296122000	1.986905000
H	-2.906352000	-1.534727000	2.750115000
H	-1.914307000	-2.919197000	2.284340000
H	-3.651114000	-2.927804000	1.976379000
C	-3.939164000	0.486233000	0.953870000
H	-3.886378000	1.510901000	0.590574000
H	-3.684922000	0.492041000	2.011328000
H	-4.978054000	0.152697000	0.862004000
C	-3.118851000	0.815085000	-2.102059000
H	-2.375032000	1.000008000	-2.875514000
H	-3.283575000	1.744919000	-1.558992000
H	-4.058214000	0.556657000	-2.601119000
C	-0.960247000	1.097087000	2.551846000
C	-0.740908000	0.973651000	1.218085000
N	-0.148296000	2.193578000	0.787261000
C	0.006307000	3.044022000	1.908185000
C	-0.495307000	2.387938000	2.980028000

H	-1.341773000	0.329515000	3.202950000
H	0.488718000	3.998560000	1.846543000
H	-0.509764000	2.767048000	3.989588000
S	0.293277000	0.818282000	-1.410147000
N	0.831275000	3.403040000	-1.004516000
C	0.514862000	4.757539000	-0.526347000
H	1.326798000	5.166032000	0.078078000
H	-0.409135000	4.759198000	0.043442000
H	0.379855000	5.392705000	-1.400743000
C	1.570154000	3.362577000	-2.274372000
H	2.135105000	2.437718000	-2.355063000
H	2.266390000	4.199096000	-2.286391000
H	0.889680000	3.448535000	-3.124855000
C	5.372230000	-1.475581000	-0.664533000
C	4.219301000	-1.851613000	-1.349780000
C	5.288197000	-1.009150000	0.645499000
H	4.289618000	-2.227015000	-2.362892000
H	6.186578000	-0.724562000	1.178366000
C	2.981392000	-1.755588000	-0.728453000
C	4.053453000	-0.918070000	1.272965000
H	2.086727000	-2.063604000	-1.254856000
H	3.970866000	-0.570834000	2.294830000
C	2.893668000	-1.286436000	0.585208000
H	6.337529000	-1.554410000	-1.149019000
C	1.599169000	-1.180050000	1.296812000
N	0.421676000	-1.423635000	0.665339000
O	1.481083000	-0.980170000	2.508646000

H

Co	-6.989022000	-3.885019000	-7.837915000
C	-7.518944000	-2.003955000	-6.895241000
C	-6.311606000	-2.464581000	-6.336876000
C	-5.335456000	-2.581918000	-7.404664000
C	-5.953220000	-2.179677000	-8.610563000
C	-7.335556000	-1.895990000	-8.326504000
C	-8.763584000	-1.645207000	-6.153359000
H	-8.856094000	-2.192357000	-5.216279000
H	-9.658586000	-1.835607000	-6.742937000
H	-8.746236000	-0.577472000	-5.912809000
C	-6.031735000	-2.732025000	-4.894531000
H	-5.483391000	-3.664661000	-4.764761000
H	-6.945798000	-2.791270000	-4.305932000
H	-5.419078000	-1.928373000	-4.475439000
C	-3.905579000	-2.971723000	-7.232551000
H	-3.560240000	-3.572213000	-8.071792000
H	-3.757872000	-3.547730000	-6.320556000
H	-3.280628000	-2.075654000	-7.161865000
C	-5.289908000	-2.055426000	-9.939970000
H	-5.986972000	-2.231011000	-10.758175000
H	-4.457893000	-2.750168000	-10.035920000
H	-4.898467000	-1.039510000	-10.055740000
C	-8.325417000	-1.326681000	-9.291383000
H	-9.351019000	-1.518772000	-8.977298000
H	-8.193784000	-1.733429000	-10.293362000
H	-8.203960000	-0.240777000	-9.357906000
C	-9.929871000	-4.867416000	-8.954770000
S	-9.047987000	-4.765420000	-7.479161000
N	-6.956868000	-4.808769000	-9.542229000
N	-11.263155000	-5.105979000	-8.860103000
C	-11.795325000	-5.724228000	-7.639965000
H	-11.924628000	-4.994229000	-6.835761000
H	-12.764062000	-6.155753000	-7.889012000
H	-11.137088000	-6.517815000	-7.297646000
C	-12.287450000	-4.333277000	-9.589780000
H	-11.846722000	-3.498465000	-10.124806000
H	-12.983139000	-3.929219000	-8.852702000
C	-5.836770000	-5.539735000	-9.867109000
O	-4.775270000	-5.374416000	-9.263653000
C	-4.766808000	-7.914159000	-12.604963000
C	-4.784163000	-6.864311000	-11.694288000
C	-5.863197000	-8.764581000	-12.710733000
H	-3.922641000	-6.218453000	-11.585012000
H	-5.846707000	-9.588256000	-13.413511000
C	-6.978936000	-8.557531000	-11.903835000
H	-7.828920000	-9.225337000	-11.973053000
C	-7.006854000	-7.493319000	-11.010650000
H	-7.877601000	-7.340606000	-10.386139000
H	-3.893795000	-8.074721000	-13.225246000
C	-5.910922000	-6.632813000	-10.902191000
C	-7.821164000	-4.399516000	-11.820929000
C	-7.938257000	-4.595417000	-10.473457000
N	-9.350786000	-4.712210000	-10.186058000
C	-10.022951000	-4.697705000	-11.437088000
C	-9.113913000	-4.495028000	-12.415920000
H	-6.885576000	-4.289769000	-12.341711000
H	-11.079705000	-4.833131000	-11.515911000
H	-9.340866000	-4.427440000	-13.467583000
H	-12.848971000	-4.962155000	-10.282992000
O	-6.092182000	-5.356926000	-6.727945000
C	-5.857349000	-6.550128000	-6.833630000

O	-6.624718000	-7.306932000	-7.614805000
H	-6.296593000	-8.215910000	-7.662974000
C	-4.713366000	-7.207916000	-6.122077000
H	-4.355890000	-6.568141000	-5.320440000
H	-4.991570000	-8.183380000	-5.720214000
H	-3.904575000	-7.345693000	-6.845395000

I

Co	-6.155603000	-3.421197000	-7.884827000
C	-6.932031000	-1.888980000	-6.593455000
C	-6.130763000	-2.762948000	-5.824240000
C	-4.819046000	-2.790790000	-6.414993000
C	-4.790657000	-1.802020000	-7.466326000
C	-6.101946000	-1.300557000	-7.630149000
C	-5.177069000	-5.409463000	-10.453905000
C	-8.352461000	-1.515937000	-6.322139000
H	-8.899051000	-2.320450000	-5.835398000
H	-8.882066000	-1.239836000	-7.233627000
H	-8.380009000	-0.643589000	-5.661355000
C	-6.550121000	-3.589613000	-4.661493000
H	-6.475701000	-4.651627000	-4.908258000
H	-7.572455000	-3.374527000	-4.356551000
H	-5.892825000	-3.398731000	-3.809682000
C	-3.662566000	-3.573586000	-5.887093000
H	-2.884172000	-3.704688000	-6.637697000
H	-3.979776000	-4.561139000	-5.553126000
H	-3.214630000	-3.056933000	-5.032188000
C	-3.575238000	-1.363243000	-8.212395000
H	-3.810597000	-0.997495000	-9.210718000
H	-2.835327000	-2.157048000	-8.301447000
H	-3.104535000	-0.542386000	-7.661872000
C	-6.546325000	-0.257007000	-8.603461000
H	-7.546857000	-0.461395000	-8.984560000
H	-5.873419000	-0.187084000	-9.456716000
H	-6.573925000	0.725249000	-8.121922000
C	-8.200800000	-7.091432000	-9.533647000
C	-7.037607000	-6.480604000	-9.157665000
N	-6.431787000	-5.995514000	-10.325388000
C	-7.255310000	-6.298649000	-11.417859000
C	-8.346928000	-6.960971000	-10.949009000
H	-8.861199000	-7.609066000	-8.857627000
H	-6.982732000	-5.987556000	-12.410770000
H	-9.165580000	-7.322719000	-11.550491000
S	-4.640406000	-4.113532000	-9.478577000
N	-4.389315000	-5.884414000	-11.422385000
C	-4.481628000	-7.261854000	-11.941939000
H	-4.741175000	-7.255048000	-13.001052000
H	-5.218063000	-7.835092000	-11.390849000
H	-3.503475000	-7.729323000	-11.820490000
C	-3.175576000	-5.169317000	-11.827512000
H	-3.361542000	-4.098324000	-11.853636000
H	-2.896013000	-5.513832000	-12.821145000
H	-2.356026000	-5.369900000	-11.133276000
C	-4.733229000	-7.760803000	-3.262983000
C	-6.101968000	-7.733943000	-3.515060000
C	-3.843901000	-7.671542000	-4.329932000
H	-6.805130000	-7.820042000	-2.695122000
H	-2.776134000	-7.710387000	-4.149210000
C	-6.578879000	-7.611010000	-4.815388000
C	-4.314022000	-7.548579000	-5.633139000
H	-7.644256000	-7.611993000	-5.010910000
H	-3.621530000	-7.504604000	-6.464934000
C	-5.688718000	-7.508376000	-5.890204000
H	-4.364924000	-7.868482000	-2.250725000
N	-6.163287000	-7.470441000	-7.216170000
C	-6.466634000	-6.362614000	-7.781764000
O	-6.423982000	-5.182980000	-7.213697000
O	-7.744482000	-3.385264000	-9.155337000
C	-8.911890000	-3.733408000	-9.047138000
O	-9.357326000	-4.188905000	-7.880106000
H	-10.279975000	-4.475358000	-7.937018000
C	-9.885629000	-3.632696000	-10.183622000
H	-9.391887000	-3.221005000	-11.058465000
H	-10.274584000	-4.623685000	-10.425225000
H	-10.725981000	-2.993227000	-9.902264000

J

Co	-6.299185000	-3.800877000	-8.053090000
C	-7.293429000	-2.430761000	-6.744460000
C	-6.410362000	-3.231403000	-5.983395000
C	-5.087207000	-3.070740000	-6.529718000
C	-5.155362000	-2.044894000	-7.539625000
C	-6.516995000	-1.705345000	-7.732249000
C	-4.915481000	-5.508340000	-10.754260000
C	-8.759875000	-2.262771000	-6.519316000
H	-9.204910000	-3.144697000	-6.064366000
H	-9.290413000	-2.048079000	-7.446633000
H	-8.931242000	-1.414861000	-5.848505000
C	-6.753271000	-4.147688000	-4.862179000
H	-6.517372000	-5.176718000	-5.141080000

H	-7.806831000	-4.090478000	-4.595697000
H	-6.163885000	-3.890924000	-3.978258000
C	-3.863443000	-3.748254000	-6.006180000
H	-3.006956000	-3.599304000	-6.661644000
H	-4.028331000	-4.822196000	-5.907661000
H	-3.601105000	-3.349943000	-5.021208000
C	-3.987376000	-1.426613000	-8.231598000
H	-4.241685000	-1.054140000	-9.222761000
H	-3.150204000	-2.115776000	-8.326639000
H	-3.642519000	-0.574342000	-7.637236000
C	-7.061098000	-0.687534000	-8.682270000
H	-8.025203000	-0.992786000	-9.089012000
H	-6.386706000	-0.515401000	-9.519796000
H	-7.208455000	0.269998000	-8.173369000
C	-7.369511000	-7.851646000	-9.623465000
C	-6.344653000	-6.991750000	-9.349996000
N	-5.907349000	-6.463781000	-10.568993000
C	-6.689498000	-7.004039000	-11.600359000
C	-7.588431000	-7.854994000	-11.037310000
H	-7.892476000	-8.442800000	-8.889796000
H	-6.542382000	-6.697913000	-12.620515000
H	-8.325029000	-8.431387000	-11.574139000
S	-4.737227000	-4.127202000	-9.756058000
N	-4.086837000	-5.695452000	-11.784442000
C	-3.777927000	-7.023947000	-12.346749000
H	-4.115907000	-7.089788000	-13.381687000
H	-4.238042000	-7.809100000	-11.758365000
H	-2.695629000	-7.153128000	-12.318145000
C	-3.192259000	-4.627909000	-12.240123000
H	-3.701416000	-3.668235000	-12.200168000
H	-2.904136000	-4.844570000	-13.267020000
H	-2.295625000	-4.579885000	-11.617668000
C	-2.516398000	-10.340517000	-9.133180000
C	-3.820273000	-10.536727000	-8.689237000
C	-1.951771000	-9.070367000	-9.046383000
H	-4.262717000	-11.524797000	-8.729532000
H	-0.927777000	-8.910411000	-9.362910000
C	-4.562217000	-9.476338000	-8.180178000
C	-2.682794000	-8.008732000	-8.527173000
H	-5.565677000	-9.643309000	-7.810931000
H	-2.235048000	-7.027946000	-8.423035000
C	-4.007247000	-8.193130000	-8.106932000
H	-1.939853000	-11.170694000	-9.520763000
N	-4.687425000	-7.104613000	-7.534701000
C	-5.732411000	-6.577708000	-8.044463000
O	-6.380874000	-5.607672000	-7.441241000
O	-7.869880000	-4.009246000	-9.340197000
C	-8.938970000	-4.597837000	-9.264276000
O	-9.345169000	-5.082785000	-8.095404000
H	-10.185675000	-5.554865000	-8.177949000
C	-9.827782000	-4.790397000	-10.457629000
H	-9.766513000	-5.834727000	-10.773902000
H	-10.867811000	-4.560927000	-10.218239000
H	-9.489966000	-4.159213000	-11.274417000

B-TS

Co	-5.372377000	-4.126903000	-7.944069000
C	-5.840753000	-2.593333000	-6.491697000
C	-4.968782000	-3.594502000	-5.949896000
C	-3.734341000	-3.537189000	-6.685560000
C	-3.879772000	-2.588791000	-7.726976000
C	-5.206017000	-2.017655000	-7.626699000
C	-7.977174000	-4.568963000	-9.554405000
C	-7.160908000	-2.186934000	-5.926571000
H	-7.662085000	-3.006854000	-5.415104000
H	-7.833382000	-1.797978000	-6.689188000
H	-7.000415000	-1.391230000	-5.191698000
C	-5.216797000	-4.446475000	-4.747113000
H	-6.280399000	-4.554359000	-4.537993000
H	-4.750927000	-4.004017000	-3.861229000
H	-4.797422000	-5.443594000	-4.879235000
C	-2.518411000	-4.343726000	-6.381176000
H	-2.778276000	-5.375354000	-6.147940000
H	-2.008510000	-3.921988000	-5.509363000
H	-1.811200000	-4.345451000	-7.208980000
C	-2.791205000	-2.138494000	-8.648370000
H	-3.179978000	-1.573783000	-9.492548000
H	-2.204191000	-2.972813000	-9.033275000
H	-2.102734000	-1.482830000	-8.106477000
C	-5.735346000	-0.880005000	-8.439876000
H	-6.823451000	-0.895454000	-8.496636000
H	-5.347972000	-0.892104000	-9.456815000
H	-5.446477000	0.073162000	-7.986267000
C	-4.983781000	-3.330459000	-10.988916000
C	-5.628472000	-4.083665000	-10.014656000
N	-7.013373000	-3.987313000	-10.357961000
C	-7.171961000	-3.165021000	-11.455261000
C	-5.930992000	-2.754894000	-11.867104000
H	-3.913174000	-3.244292000	-11.081407000
H	-8.142158000	-2.906663000	-11.841125000

H	-5.734072000	-2.113039000	-12.710910000
S	-7.536874000	-4.877952000	-7.927595000
N	-9.172093000	-4.889952000	-10.046092000
C	-9.435822000	-5.164604000	-11.469107000
H	-8.508411000	-5.248079000	-12.025884000
H	-10.064780000	-4.388113000	-11.907752000
H	-9.963134000	-6.116450000	-11.532360000
C	-10.254114000	-5.296897000	-9.140492000
H	-10.174861000	-6.358653000	-8.895251000
H	-11.202985000	-5.112561000	-9.640660000
H	-10.213751000	-4.716026000	-8.222739000
O	-4.724359000	-5.959120000	-7.728570000
C	-4.626852000	-6.826759000	-8.654293000
O	-4.915475000	-6.594923000	-9.859101000
C	-4.121244000	-8.196830000	-8.285674000
H	-3.126877000	-8.332457000	-8.716171000
H	-4.069622000	-8.319738000	-7.207014000
H	-4.770187000	-8.955062000	-8.723544000
H	-5.241594000	-5.292659000	-9.919500000

D-TS

Co	-7.270181000	-3.903429000	-8.196655000
C	-7.425274000	-2.183585000	-6.929905000
C	-7.876827000	-3.365251000	-6.215563000
C	-6.789189000	-4.266258000	-6.118945000
C	-5.676045000	-3.693376000	-6.822814000
C	-6.063978000	-2.376896000	-7.258100000
C	-8.228338000	-0.937177000	-7.132874000
H	-9.277007000	-1.154634000	-7.337360000
H	-7.842059000	-0.335594000	-7.954433000
H	-8.197467000	-0.318389000	-6.230784000
C	-9.207797000	-3.522082000	-5.553802000
H	-9.498429000	-4.568481000	-5.466935000
H	-9.996097000	-2.996916000	-6.090462000
H	-9.166061000	-3.107856000	-4.541273000
C	-6.789650000	-5.540919000	-5.338923000
H	-7.747464000	-6.056783000	-5.395671000
H	-6.599159000	-5.318860000	-4.284262000
H	-6.016204000	-6.229452000	-5.671609000
C	-4.289232000	-4.248019000	-6.906772000
H	-3.829923000	-4.046522000	-7.874928000
H	-4.269274000	-5.323965000	-6.740471000
H	-3.650310000	-3.792557000	-6.143887000
C	-5.147266000	-1.381660000	-7.888174000
H	-5.682276000	-0.636576000	-8.472934000
H	-4.410650000	-1.853320000	-8.536650000
H	-4.599410000	-0.854695000	-7.100222000
C	-9.582082000	-5.463198000	-9.527394000
S	-9.413829000	-3.827725000	-9.025667000
N	-10.633733000	-5.882434000	-10.229625000
C	-11.813747000	-5.017984000	-10.363722000
H	-11.675787000	-4.296197000	-11.172344000
H	-12.671707000	-5.649636000	-10.585832000
H	-11.995689000	-4.483015000	-9.435546000
C	-10.614773000	-7.030259000	-11.152965000
H	-9.596138000	-7.331571000	-11.375900000
H	-11.087636000	-6.713645000	-12.082091000
C	-6.540833000	-6.906424000	-8.425044000
C	-7.301708000	-5.792497000	-8.751281000
N	-8.552160000	-6.322063000	-9.192315000
C	-8.526449000	-7.703870000	-9.106850000
C	-7.293726000	-8.081899000	-8.643839000
H	-5.515271000	-6.873279000	-8.095261000
H	-9.380288000	-8.312752000	-9.339590000
H	-6.978069000	-9.099138000	-8.475562000
H	-11.176550000	-7.874093000	-10.748394000
C	-6.475066000	-4.964815000	-10.441241000
O	-6.328241000	-5.739930000	-11.314712000
N	-6.449623000	-3.772164000	-9.986750000
C	-6.060189000	-2.689370000	-10.853879000
C	-4.842247000	-2.729445000	-11.529846000
C	-6.909666000	-1.595847000	-10.999868000
H	-4.185358000	-3.582627000	-11.415340000
H	-7.860928000	-1.583407000	-10.484786000
C	-4.480397000	-1.671892000	-12.357446000
C	-6.536557000	-0.540449000	-11.824817000
H	-3.535658000	-1.707090000	-12.885010000
H	-7.201072000	0.306313000	-11.943276000
C	-5.322293000	-0.574225000	-12.504028000
H	-5.036090000	0.247858000	-13.147227000

(Z) D'-TS

Co	-5.404771000	-3.943654000	-7.691771000
C	-5.669386000	-2.128911000	-6.593604000
C	-4.730750000	-2.947212000	-5.933927000
C	-3.633537000	-3.200299000	-6.844863000
C	-3.880086000	-2.465759000	-8.044310000
C	-5.162561000	-1.859886000	-7.931037000
C	-7.354478000	-4.824367000	-9.938245000
C	-6.931637000	-1.565668000	-6.022822000

H	-7.309953000	-2.166423000	-5.197090000
H	-7.719363000	-1.486488000	-6.771982000
H	-6.747014000	-0.557423000	-5.639650000
C	-4.824665000	-3.505064000	-4.552105000
H	-4.614139000	-4.575304000	-4.542678000
H	-5.809718000	-3.349871000	-4.116050000
H	-4.091937000	-3.018476000	-3.901794000
C	-2.406966000	-3.980370000	-6.496209000
H	-1.817543000	-4.230825000	-7.377395000
H	-2.658123000	-4.906895000	-5.978835000
H	-1.762371000	-3.398090000	-5.830817000
C	-2.949830000	-2.321070000	-9.204392000
H	-3.482957000	-2.245771000	-10.151338000
H	-2.246723000	-3.148898000	-9.275069000
H	-2.362956000	-1.404947000	-9.086022000
C	-5.795460000	-0.940642000	-8.926064000
H	-6.882843000	-0.996518000	-8.893869000
H	-5.476182000	-1.163873000	-9.943810000
H	-5.512845000	0.095475000	-8.714725000
C	-3.902760000	-5.659387000	-9.776695000
C	-5.071000000	-5.138099000	-9.206126000
N	-6.066668000	-5.250855000	-10.234739000
C	-5.519124000	-5.932484000	-11.299351000
C	-4.186355000	-6.165241000	-11.051697000
H	-2.962394000	-5.746188000	-9.255849000
H	-6.081128000	-6.221645000	-12.164641000
H	-3.513585000	-6.679588000	-11.718866000
S	-7.570638000	-4.077009000	-8.398251000
N	-8.384638000	-4.970106000	-10.770240000
C	-8.286737000	-5.258308000	-12.208991000
H	-8.228584000	-6.331332000	-12.401414000
H	-7.436439000	-4.745451000	-12.652389000
H	-9.185511000	-4.874785000	-12.684023000
C	-9.743411000	-4.665846000	-10.287559000
H	-9.866987000	-5.018737000	-9.267179000
H	-10.452195000	-5.182904000	-10.929316000
H	-9.935947000	-3.591237000	-10.320416000
C	-7.444791000	-10.856447000	-6.441193000
C	-7.213612000	-9.697626000	-5.705454000
C	-7.119064000	-10.890061000	-7.794007000
H	-7.461786000	-9.667115000	-4.651686000
H	-7.291540000	-11.789432000	-8.371925000
C	-6.661518000	-8.574585000	-6.310026000
C	-6.568842000	-9.772522000	-8.407921000
H	-6.479194000	-7.679004000	-5.731391000
H	-6.305513000	-9.786378000	-9.457667000
C	-6.335217000	-8.609581000	-7.670684000
H	-7.872653000	-11.727930000	-5.962358000
N	-5.770693000	-7.512030000	-8.361831000
C	-5.472147000	-6.405667000	-7.903430000
O	-5.372560000	-5.724132000	-6.849010000

(*E*) D'-TS

Co	-5.925368000	-4.059056000	-7.957290000
C	-5.487468000	-2.426412000	-6.660058000
C	-4.976841000	-3.617823000	-6.101379000
C	-4.038884000	-4.190219000	-7.039883000
C	-3.914376000	-3.284872000	-8.141629000
C	-4.847794000	-2.232339000	-7.952872000
C	-8.027261000	-3.910449000	-10.209391000
C	-6.443066000	-1.471690000	-6.018827000
H	-7.085443000	-1.964269000	-5.290400000
H	-7.080461000	-0.977930000	-6.751959000
H	-5.887532000	-0.688933000	-5.493239000
C	-5.351012000	-4.237969000	-4.796191000
H	-5.638276000	-5.282937000	-4.922411000
H	-6.178290000	-3.716030000	-4.319446000
H	-4.498365000	-4.208450000	-4.111867000
C	-3.234381000	-5.425285000	-6.789696000
H	-2.808887000	-5.829545000	-7.707498000
H	-3.836296000	-6.204336000	-6.321209000
H	-2.400867000	-5.207018000	-6.114977000
C	-2.937482000	-3.380865000	-9.267491000
H	-3.365280000	-3.052631000	-10.213980000
H	-2.556060000	-4.391304000	-9.397850000
H	-2.080705000	-2.734148000	-9.053705000
C	-5.009726000	-1.032726000	-8.830146000
H	-6.022057000	-0.633455000	-8.788660000
H	-4.778843000	-1.258960000	-9.870751000
H	-4.328814000	-0.238310000	-8.508355000
C	-5.024792000	-5.786052000	-10.366213000
C	-6.029093000	-5.173043000	-9.620686000
N	-6.961123000	-4.702403000	-10.596601000
C	-6.479189000	-4.969054000	-11.868943000
C	-5.296338000	-5.644743000	-11.747604000
H	-4.164901000	-6.279966000	-9.944352000
H	-6.991071000	-4.644169000	-12.756330000
H	-4.693616000	-5.997832000	-12.568782000
S	-7.931378000	-3.194121000	-8.652685000
N	-9.080771000	-3.744737000	-11.006302000

C	-9.474152000	-4.682932000	-12.070348000
H	-8.940599000	-5.623456000	-11.975431000
H	-9.300923000	-4.252152000	-13.058264000
H	-10.540635000	-4.879513000	-11.961791000
C	-10.096261000	-2.734859000	-10.679726000
H	-10.819772000	-3.131177000	-9.963427000
H	-10.610531000	-2.461524000	-11.599054000
H	-9.625060000	-1.851580000	-10.256930000
C	-7.453165000	-9.812429000	-12.090291000
C	-8.606602000	-9.144540000	-11.680526000
C	-6.281777000	-9.680423000	-11.352464000
H	-9.529496000	-9.271540000	-12.232890000
H	-5.391351000	-10.221251000	-11.647911000
C	-8.587072000	-8.337179000	-10.552692000
C	-6.248631000	-8.871679000	-10.222536000
H	-9.485586000	-7.843881000	-10.204176000
H	-5.350641000	-8.798395000	-9.623782000
C	-7.397976000	-8.174925000	-9.829432000
H	-7.476981000	-10.451732000	-12.963334000
N	-7.397303000	-7.388509000	-8.689529000
C	-6.876967000	-6.350098000	-8.296787000
O	-6.727033000	-5.694007000	-7.248676000

F-TS

C	-1.523375000	-0.761638000	-1.806899000
C	-1.947514000	-1.625009000	-0.761261000
C	-0.930753000	-2.623369000	-0.582844000
C	-0.242583000	-1.221385000	-2.291038000
C	0.104343000	-2.381921000	-1.555370000
C	-1.019372000	-3.823814000	0.296885000
H	-1.374902000	-4.674569000	-0.294711000
H	-0.051697000	-4.088740000	0.717553000
H	-1.725137000	-3.677804000	1.111718000
C	-3.275896000	-1.595840000	-0.079702000
H	-3.978703000	-2.237365000	-0.620334000
H	-3.211890000	-1.956763000	0.944593000
H	-3.698955000	-0.592421000	-0.058319000
C	-2.328778000	0.331664000	-2.422342000
H	-2.928694000	-0.086624000	-3.237752000
H	-3.015975000	0.785667000	-1.710455000
H	-1.703761000	1.117171000	-2.843073000
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C	1.302711000	-3.246461000	-1.748843000
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Co	-0.073686000	-0.710882000	-0.157310000
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H	-1.677825000	1.735627000	3.982145000
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G-TS

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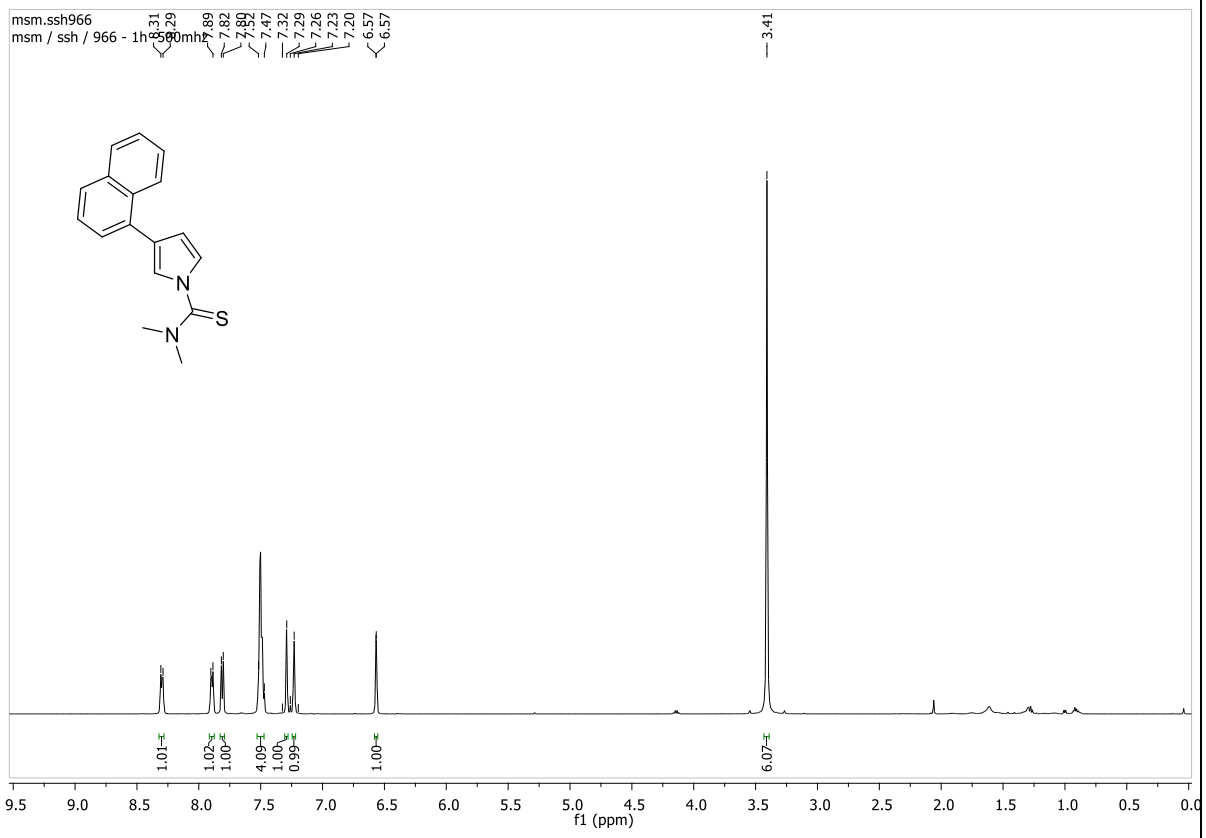
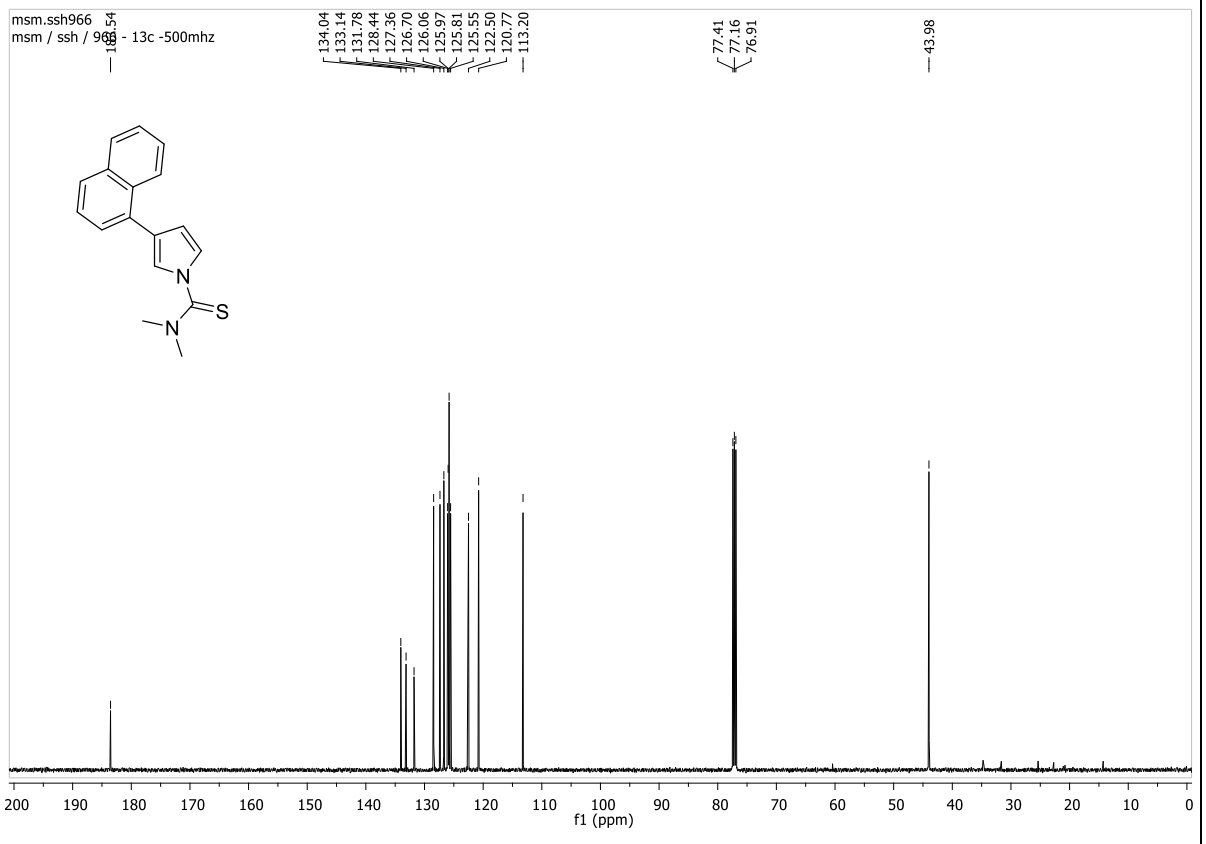
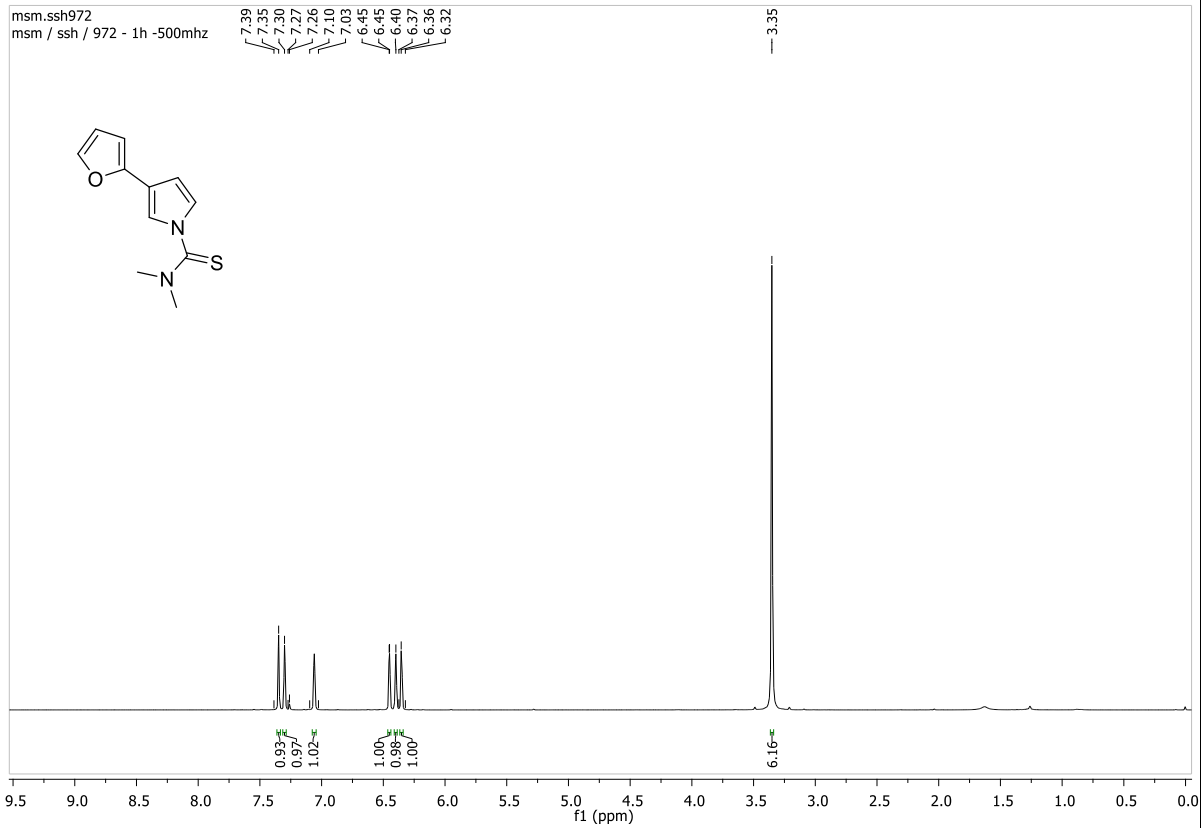
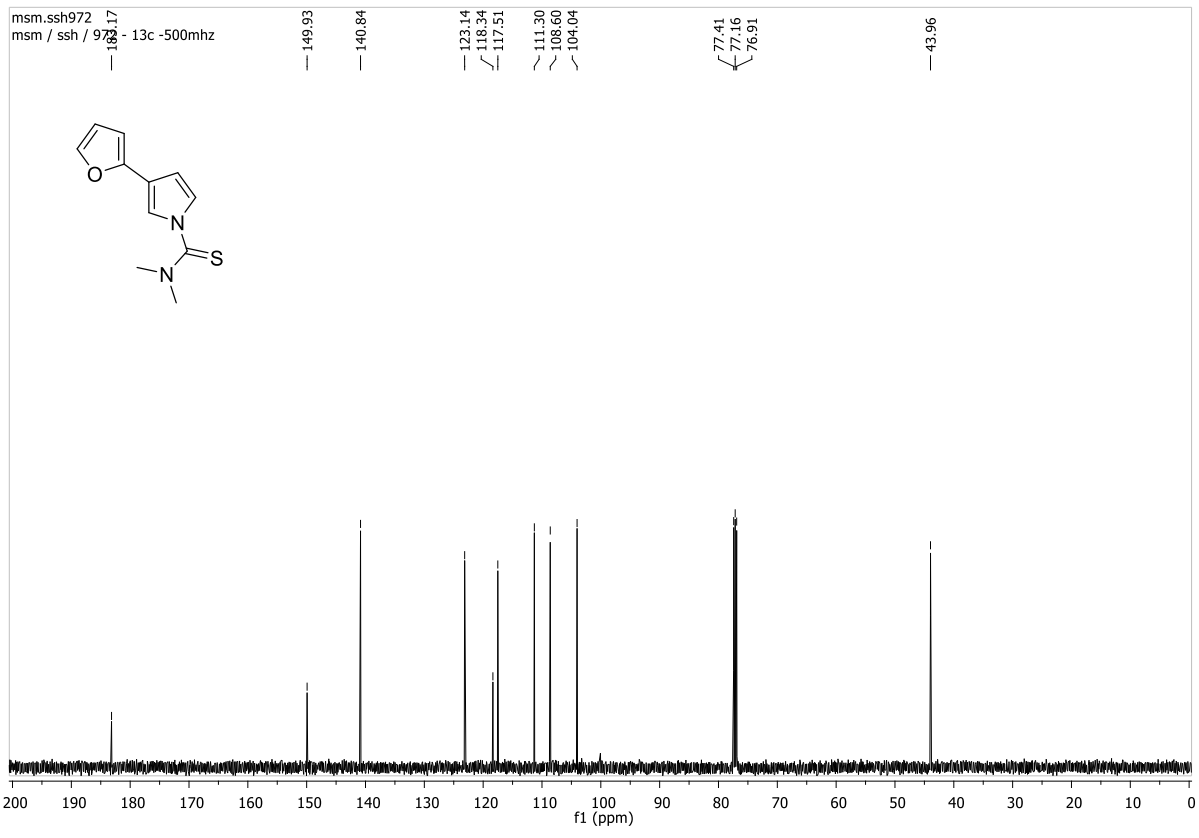
^{1}H NMR and ^{13}C NMR Spectra of Compound **1b**





^{1}H NMR and ^{13}C NMR Spectra of Compound **1c**





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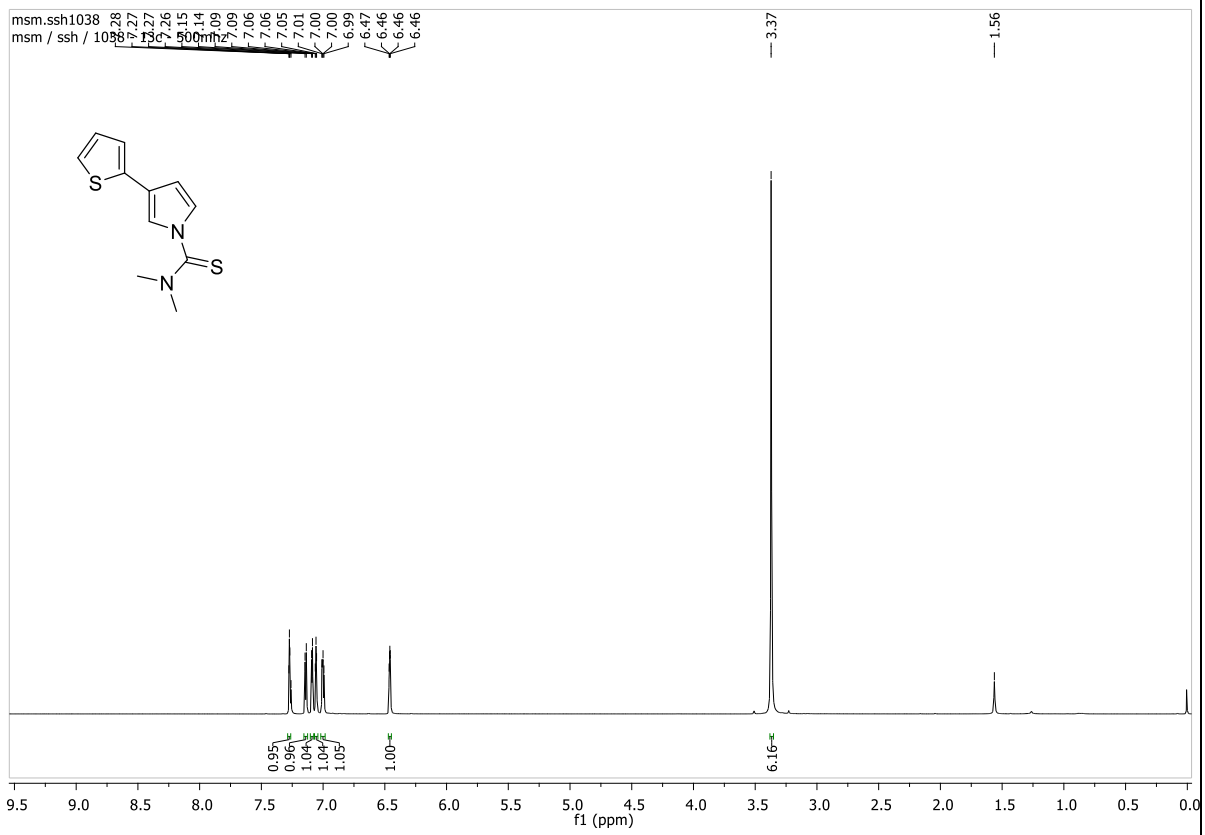
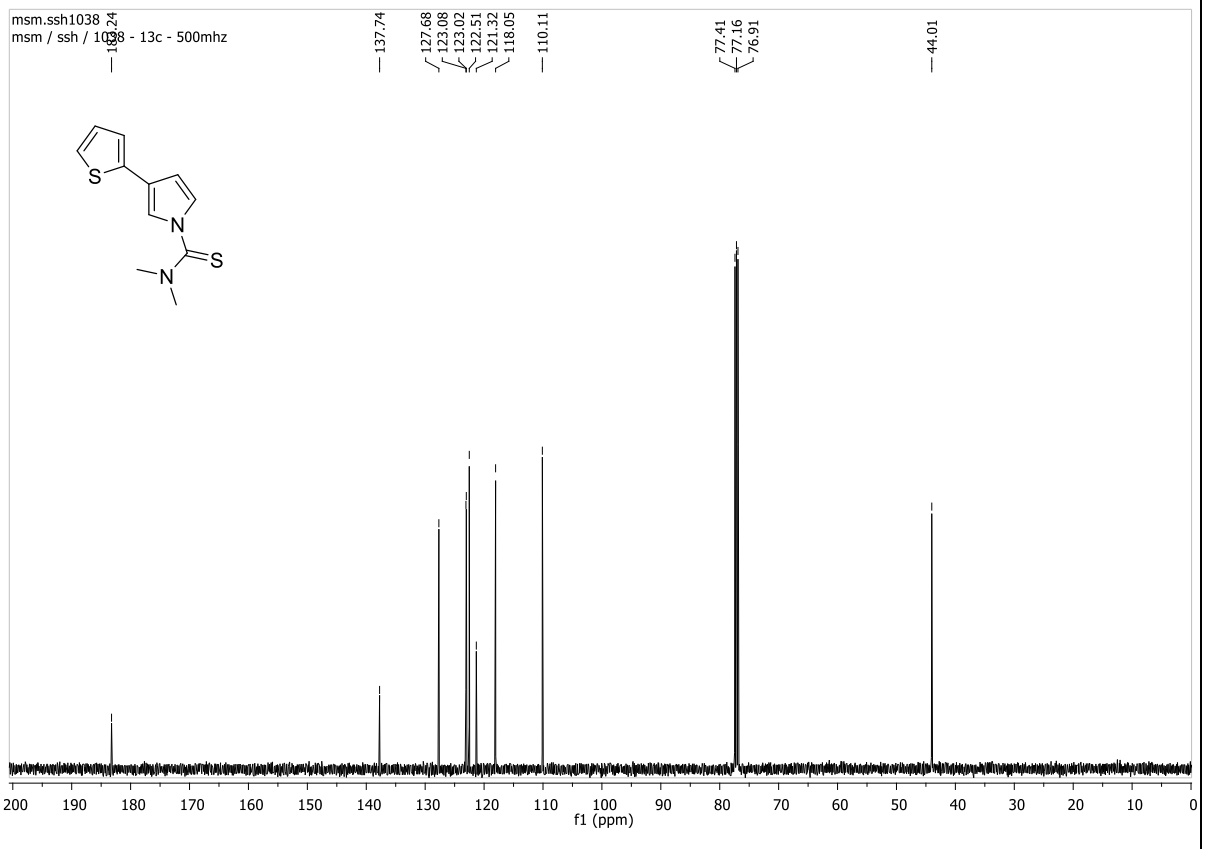
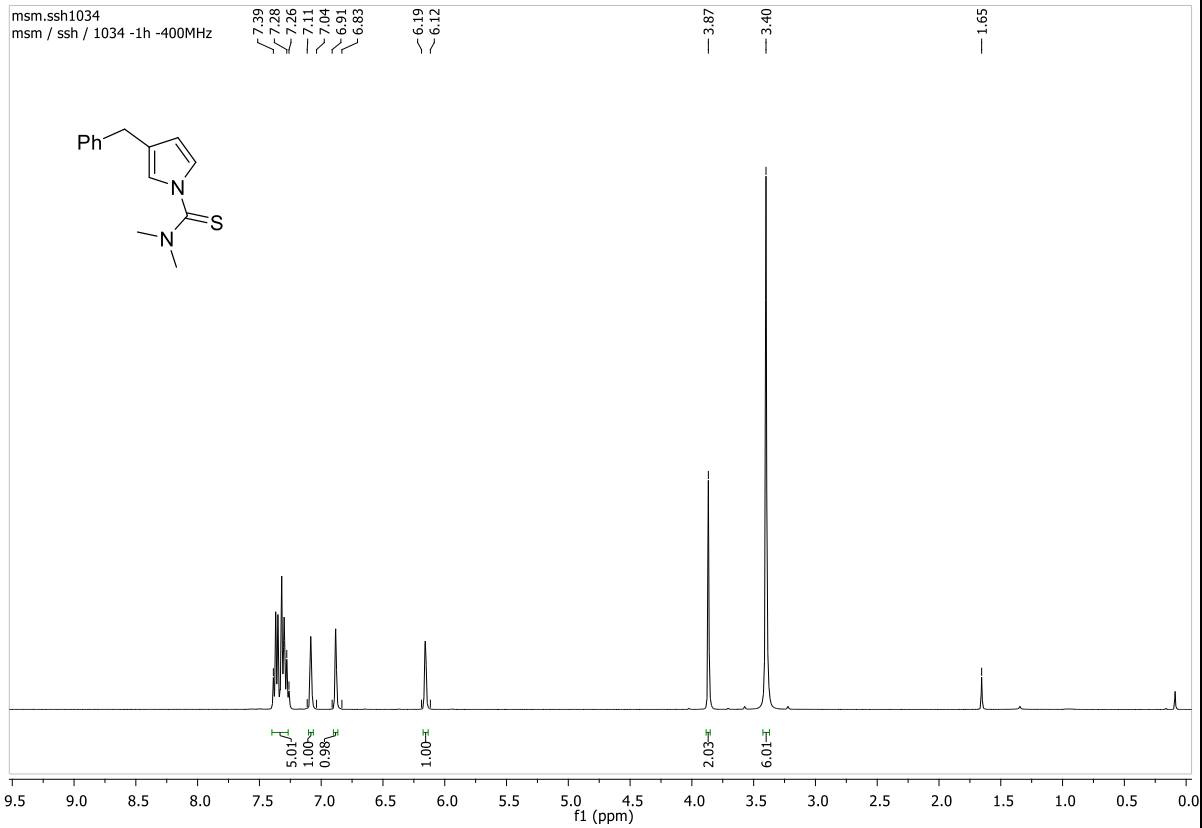
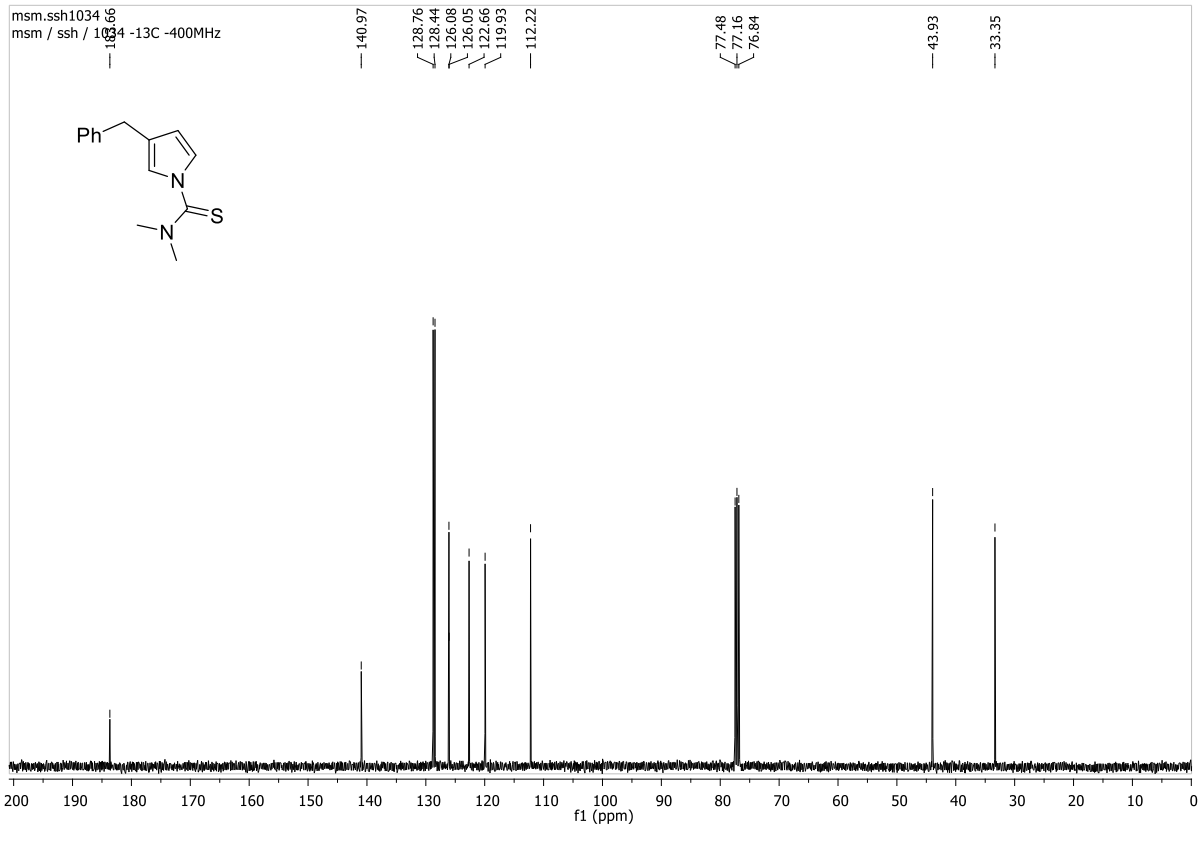


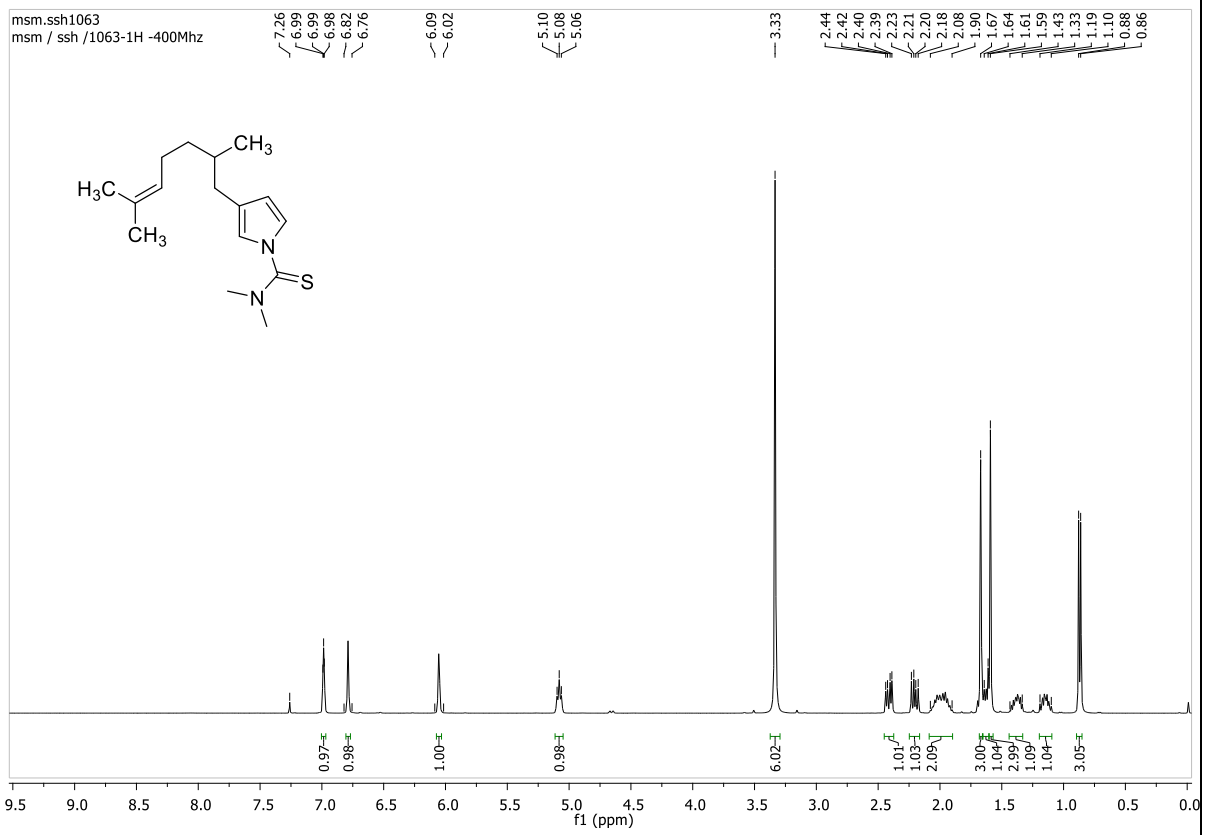


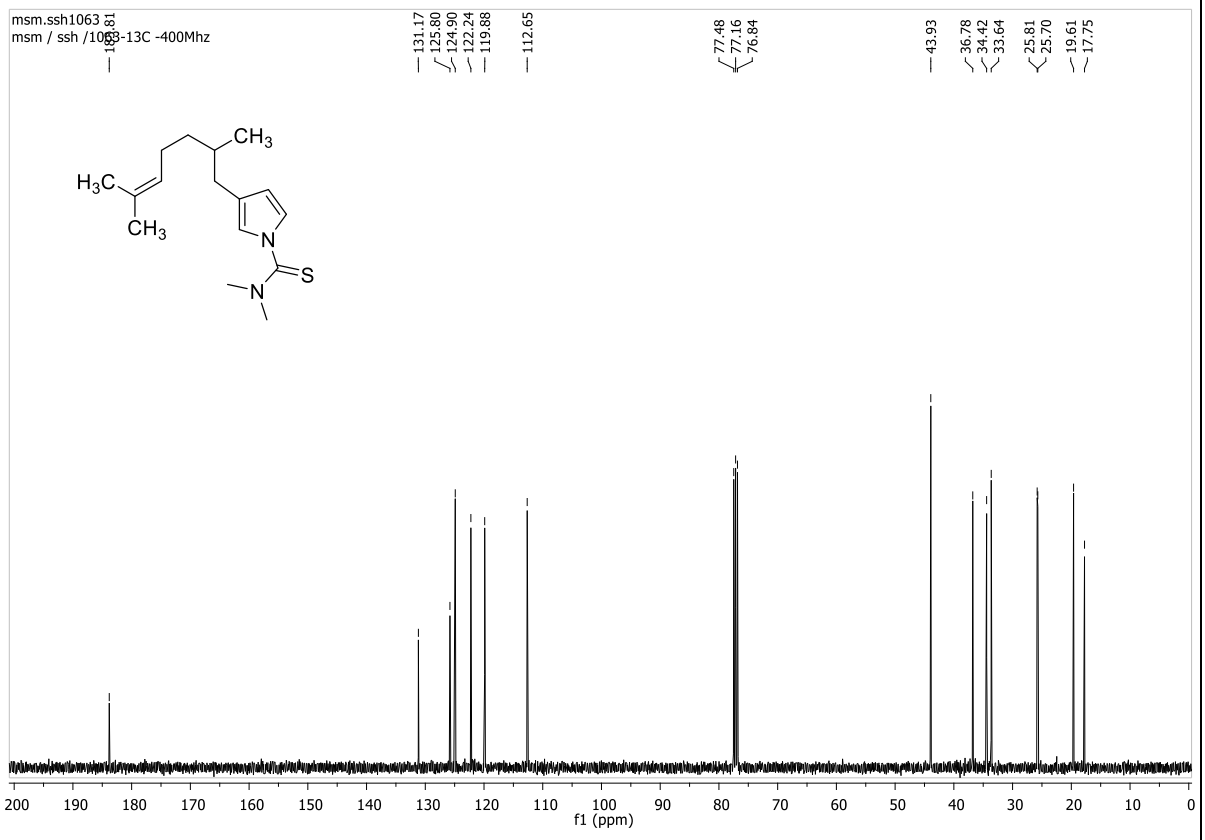
^{1}H NMR and ^{13}C NMR Spectra of Compound **1e**





^{1}H NMR and ^{13}C NMR Spectra of Compound **1f**





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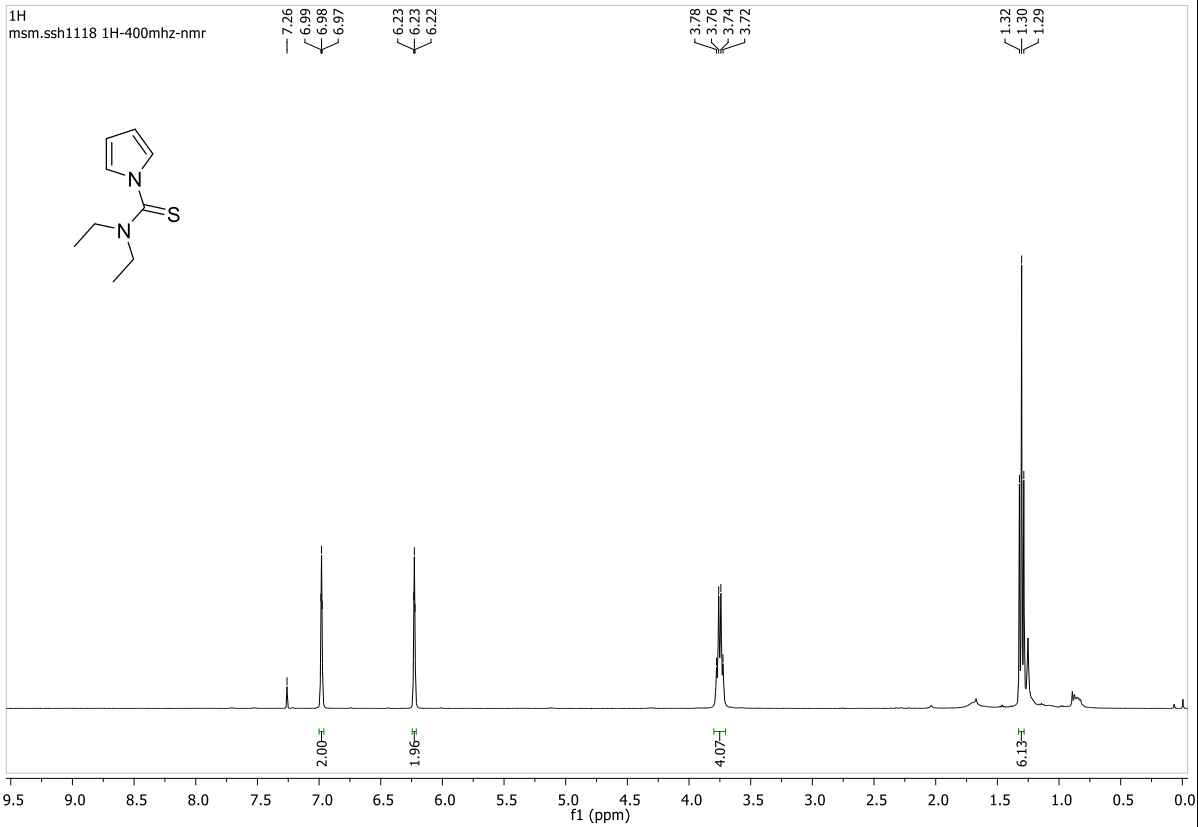

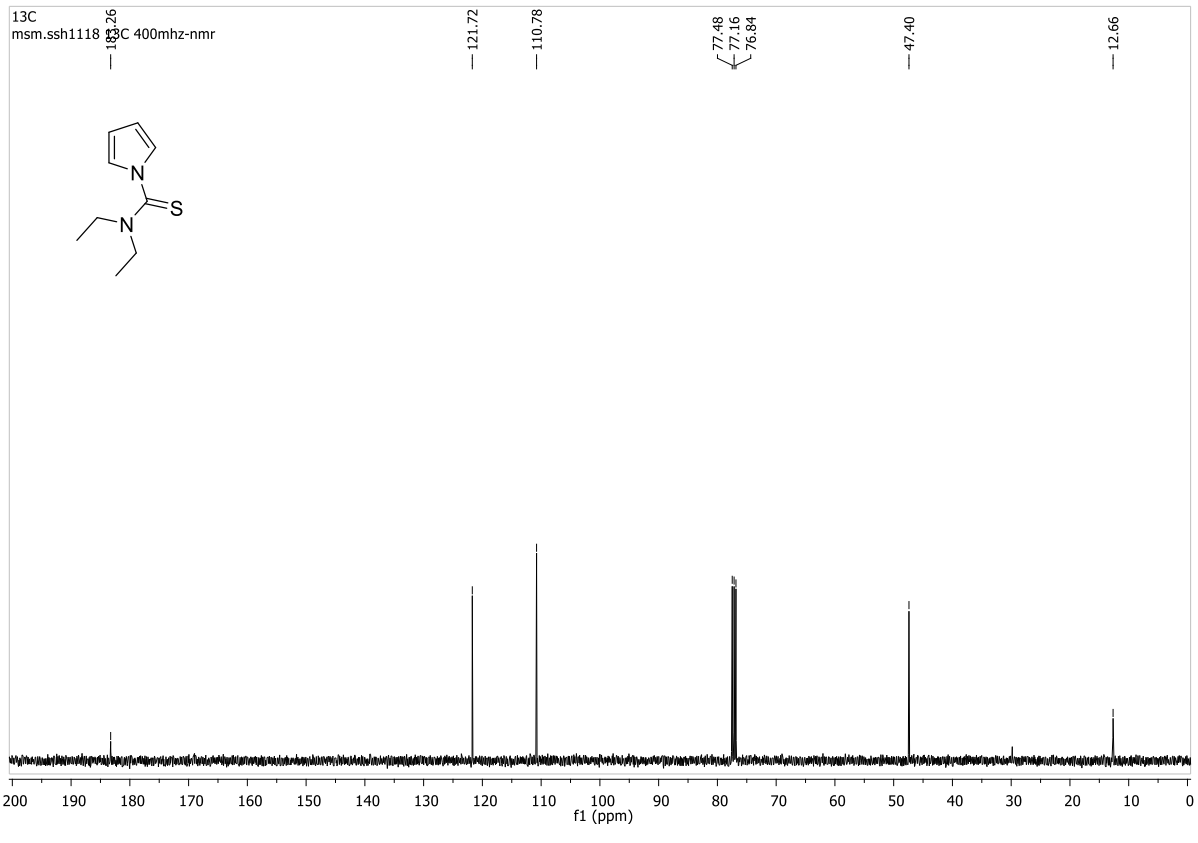

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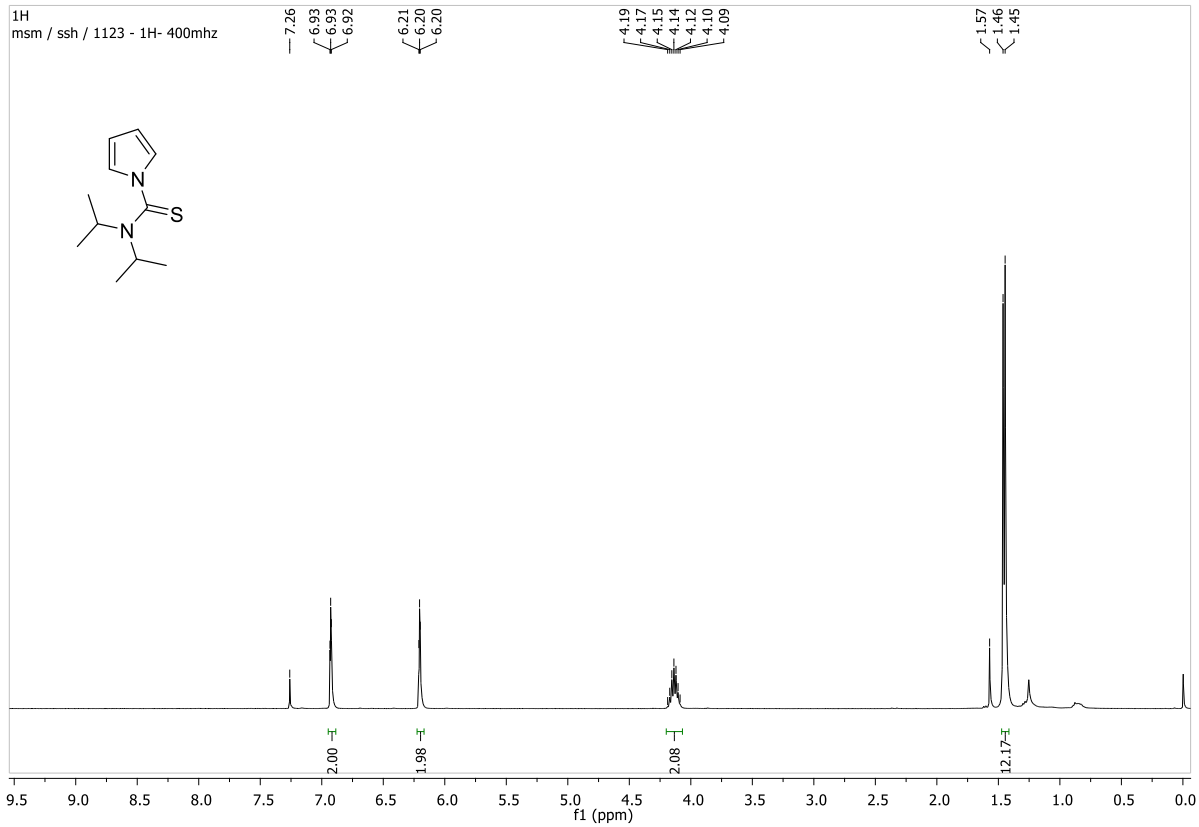
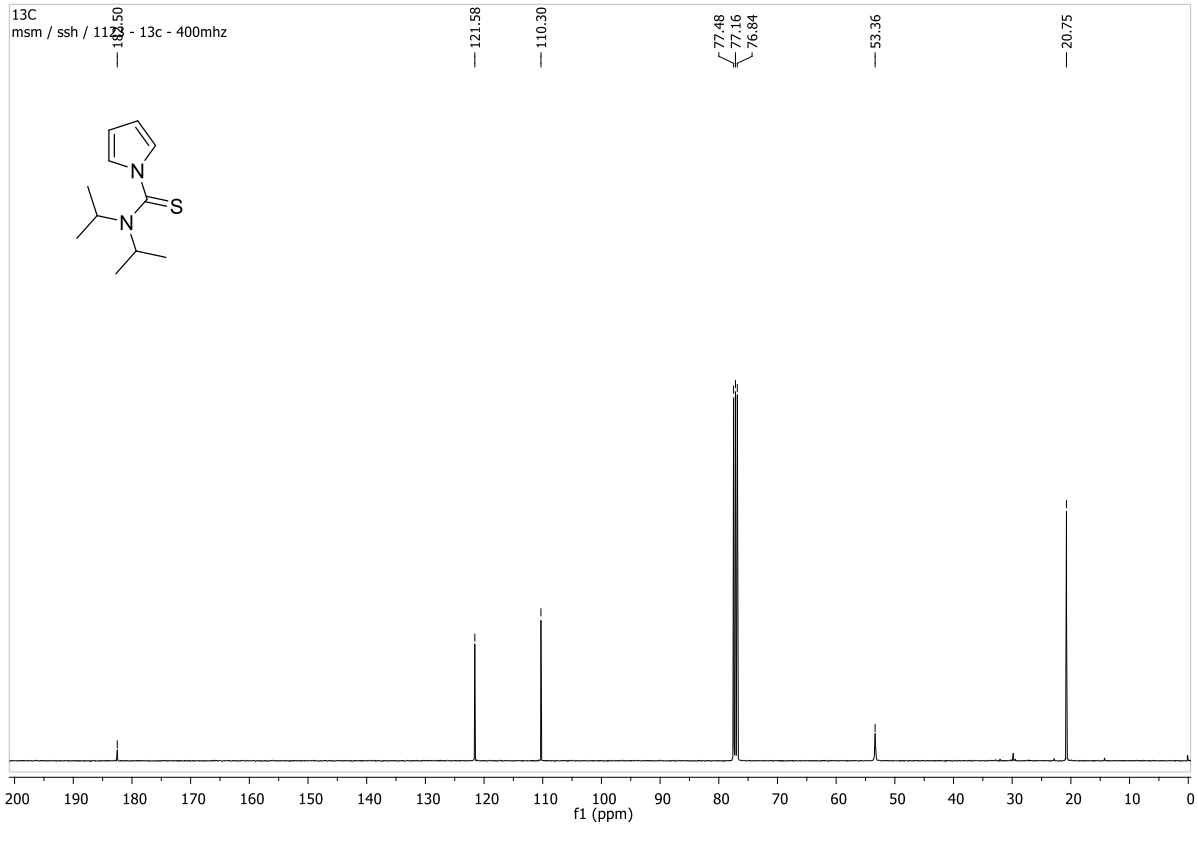
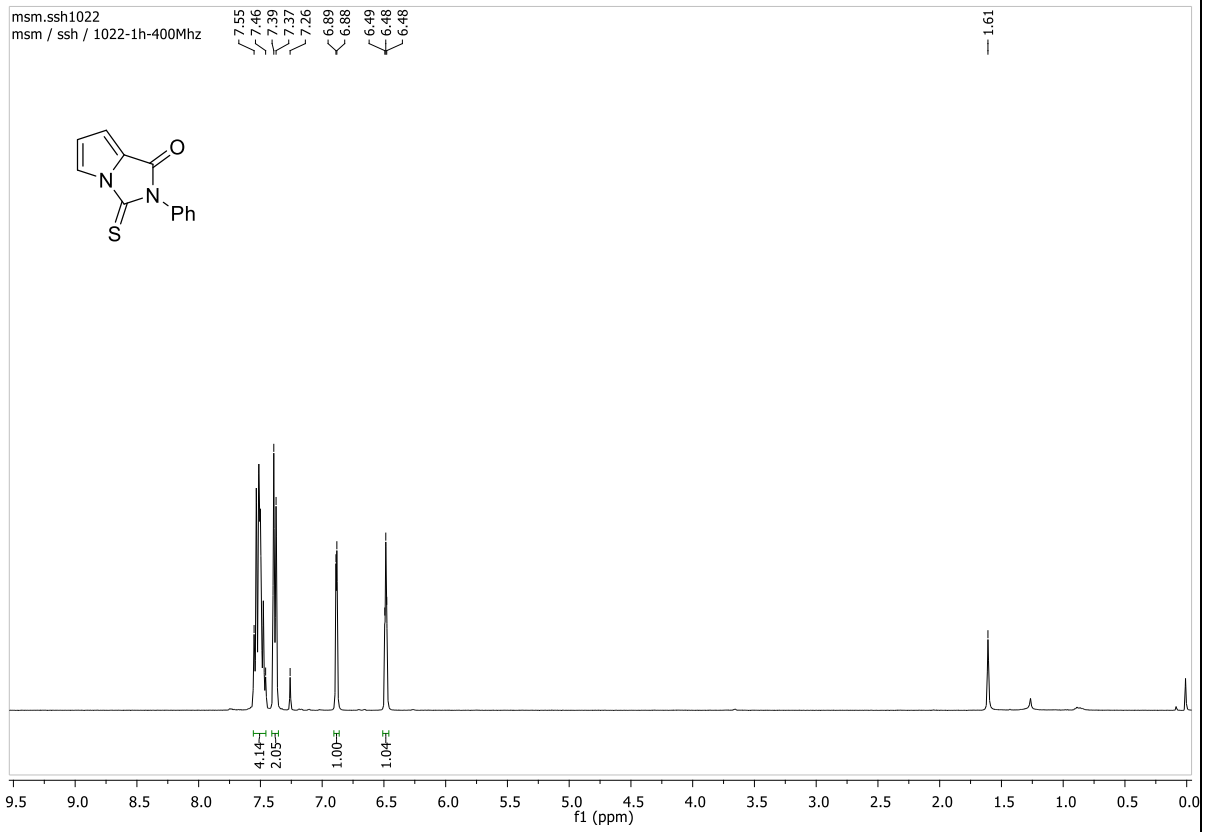
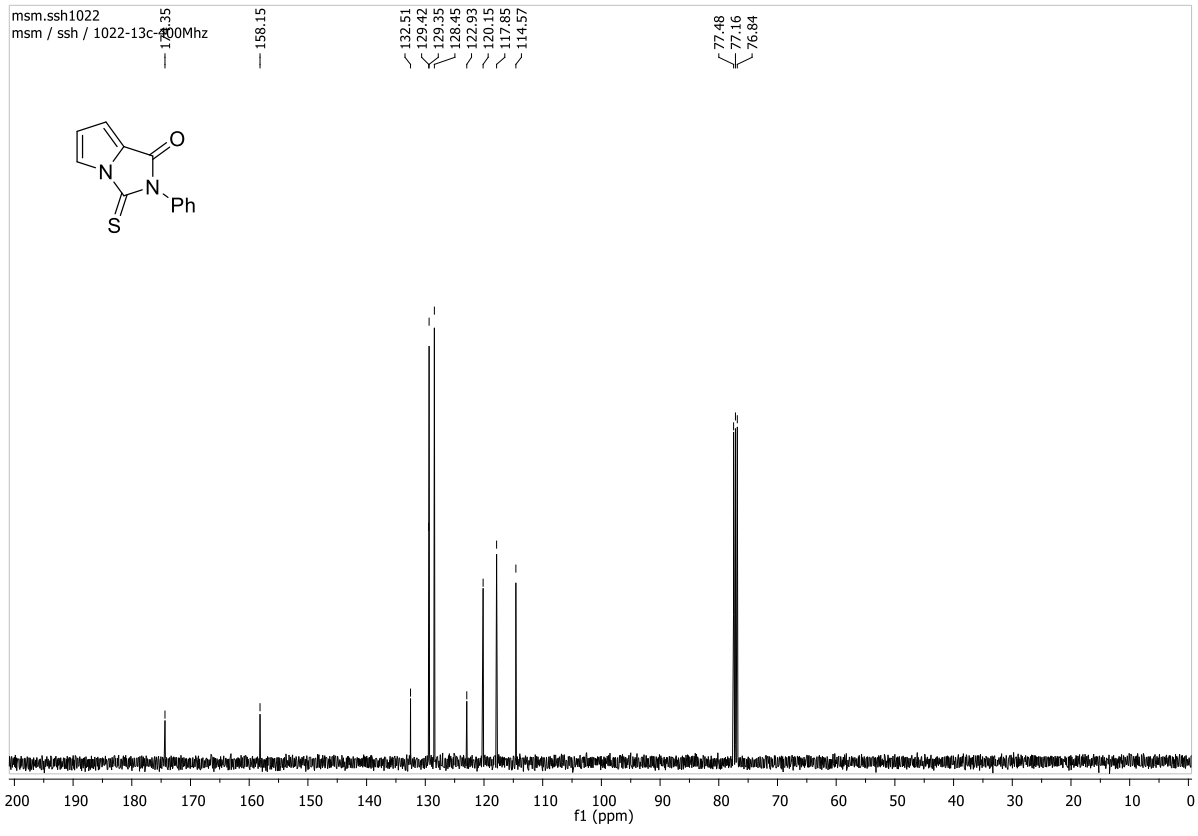


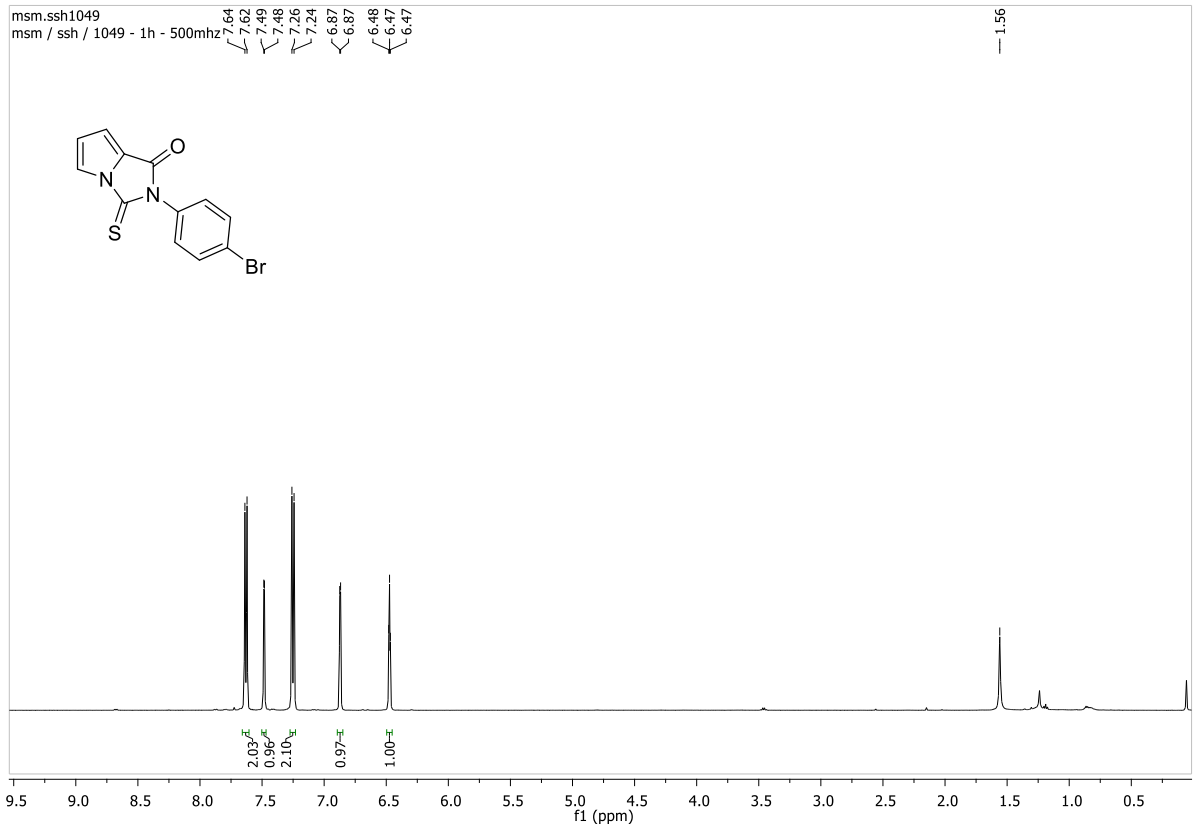


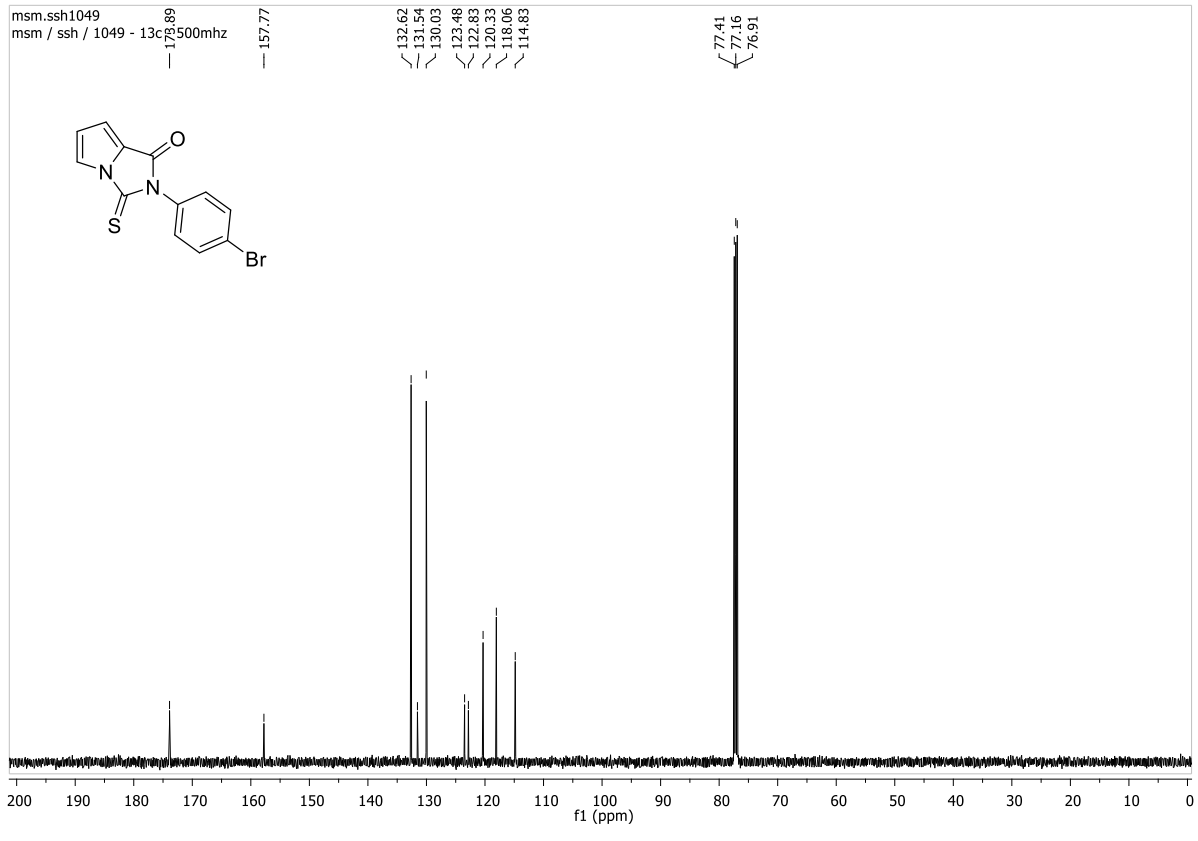
^{1}H NMR and ^{13}C NMR Spectra of Compound **3a**





^{1}H NMR and ^{13}C NMR Spectra of Compound **3b**





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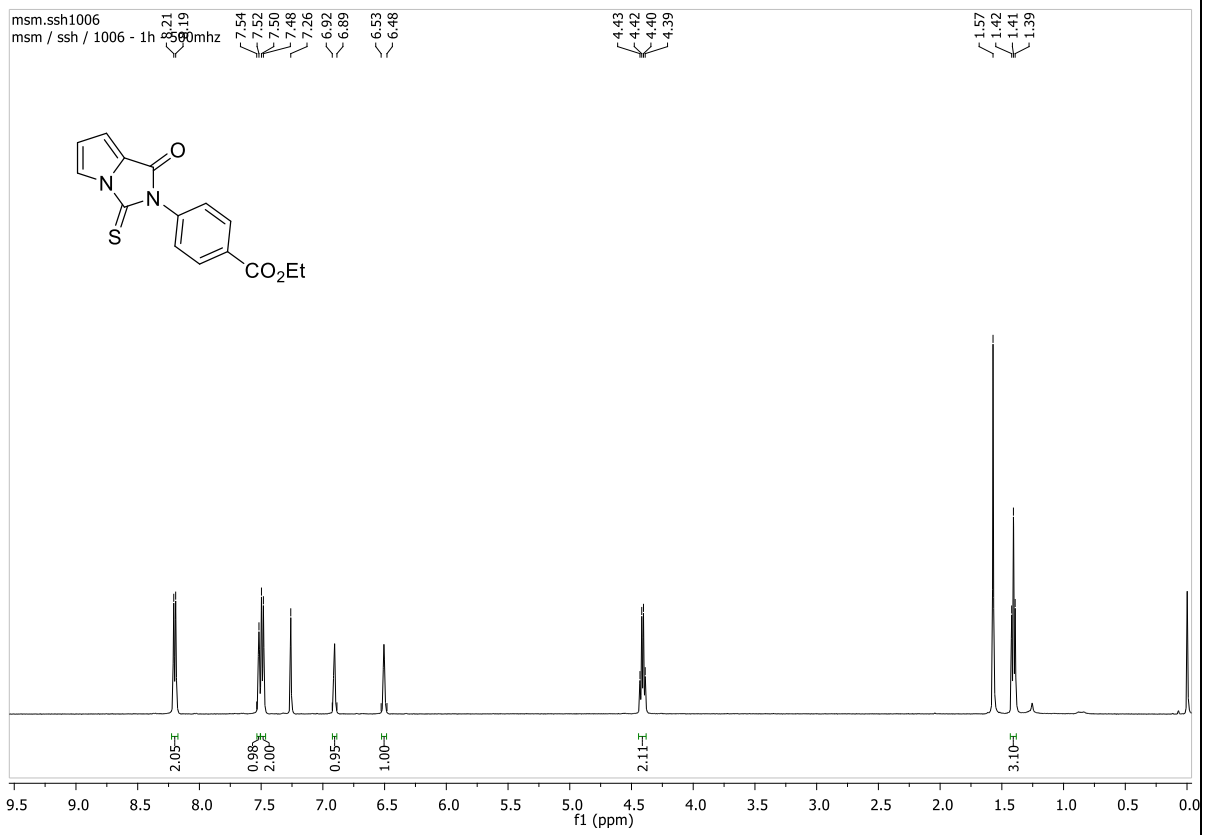

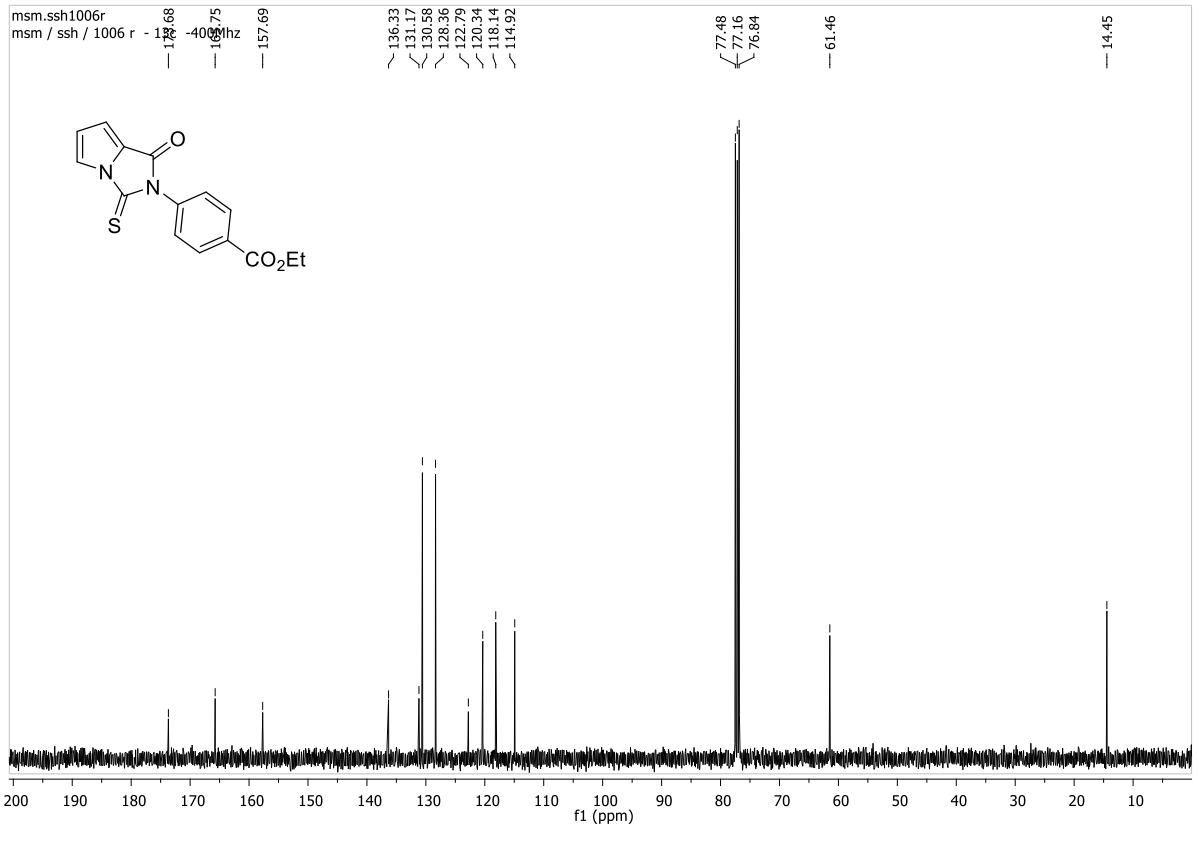

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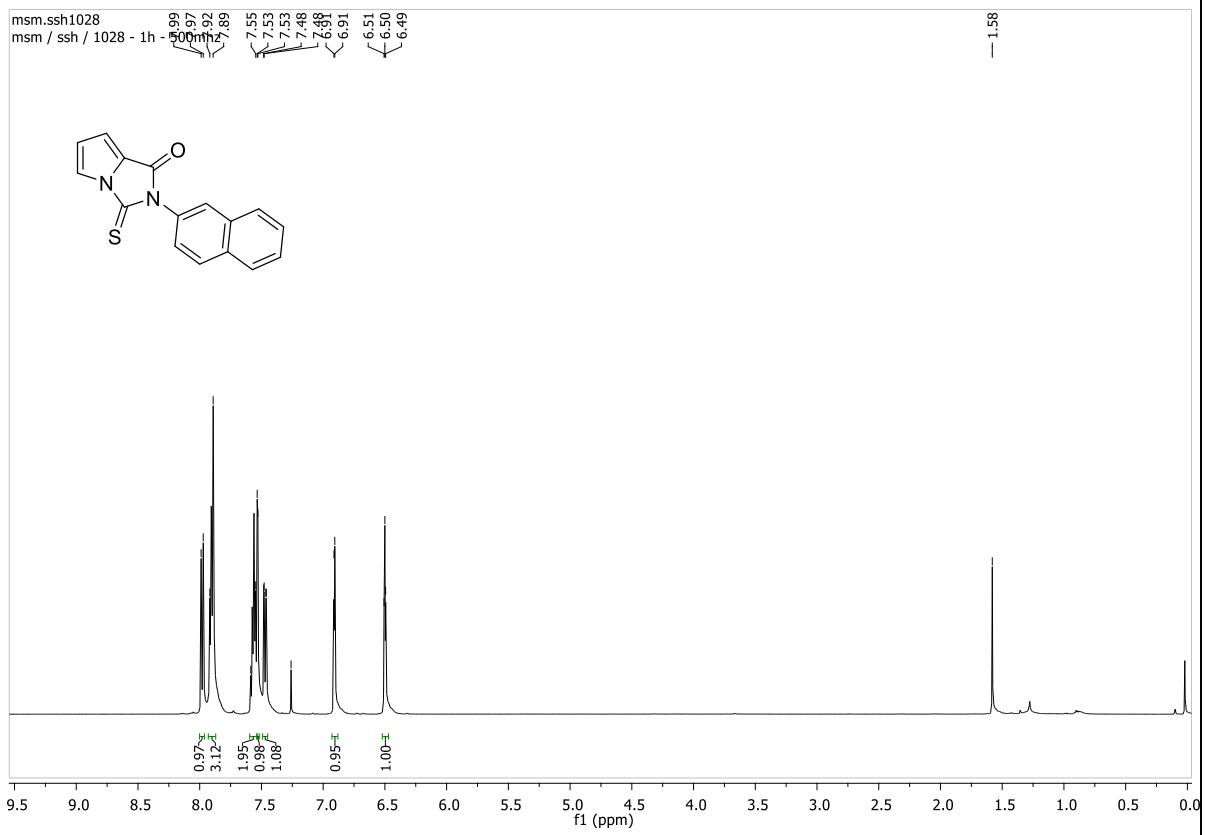

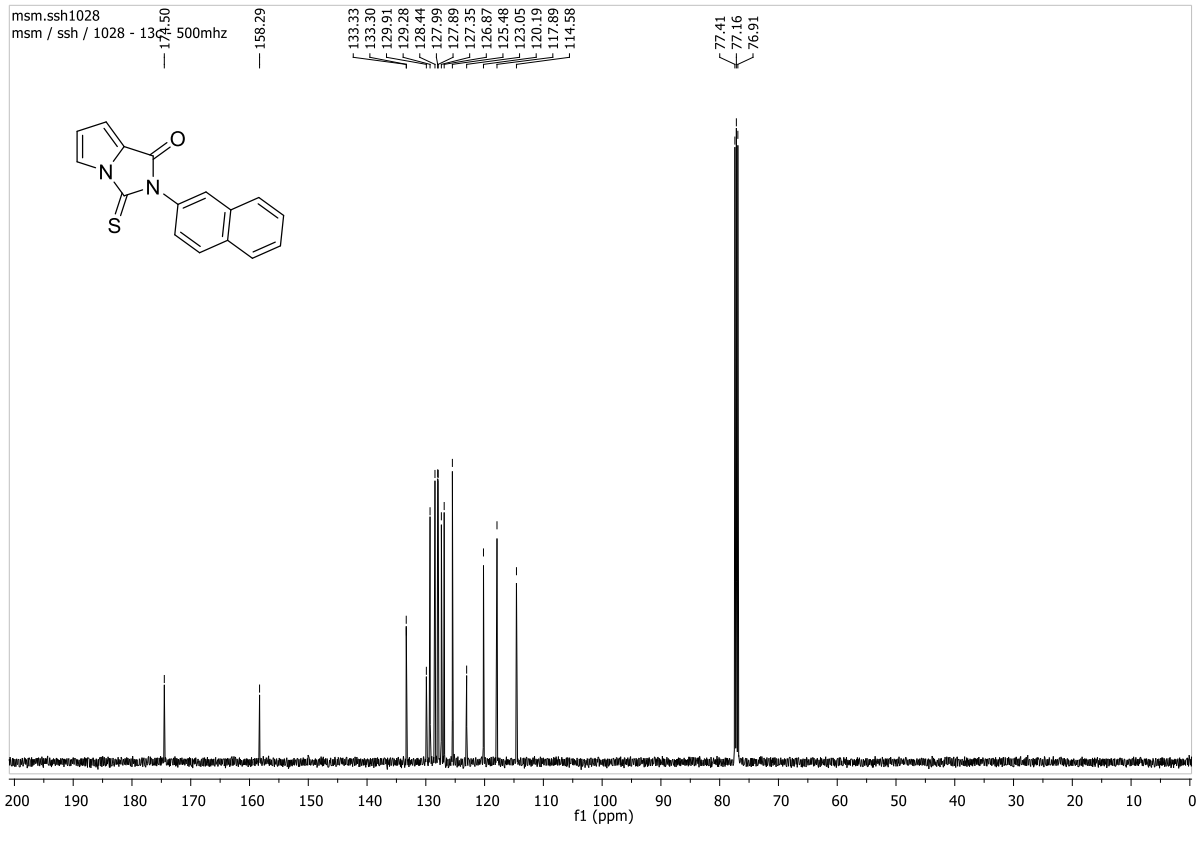

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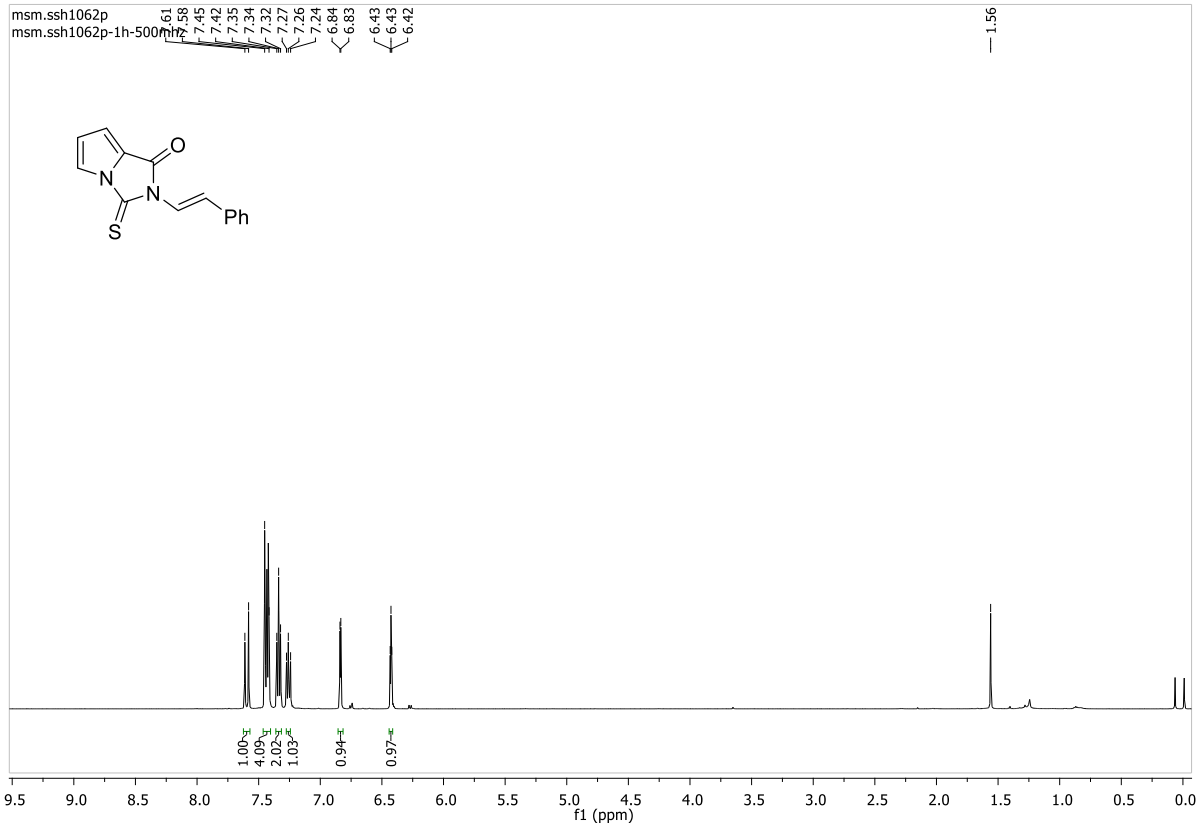
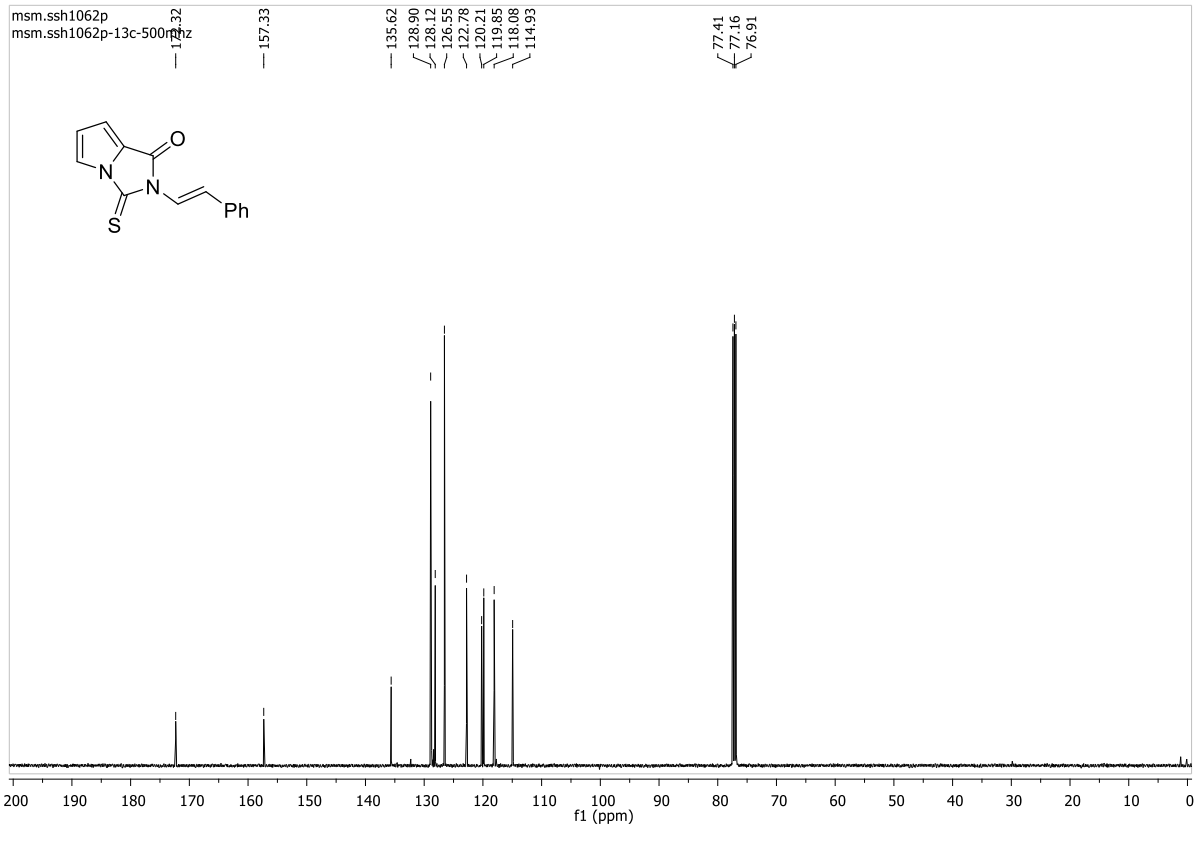
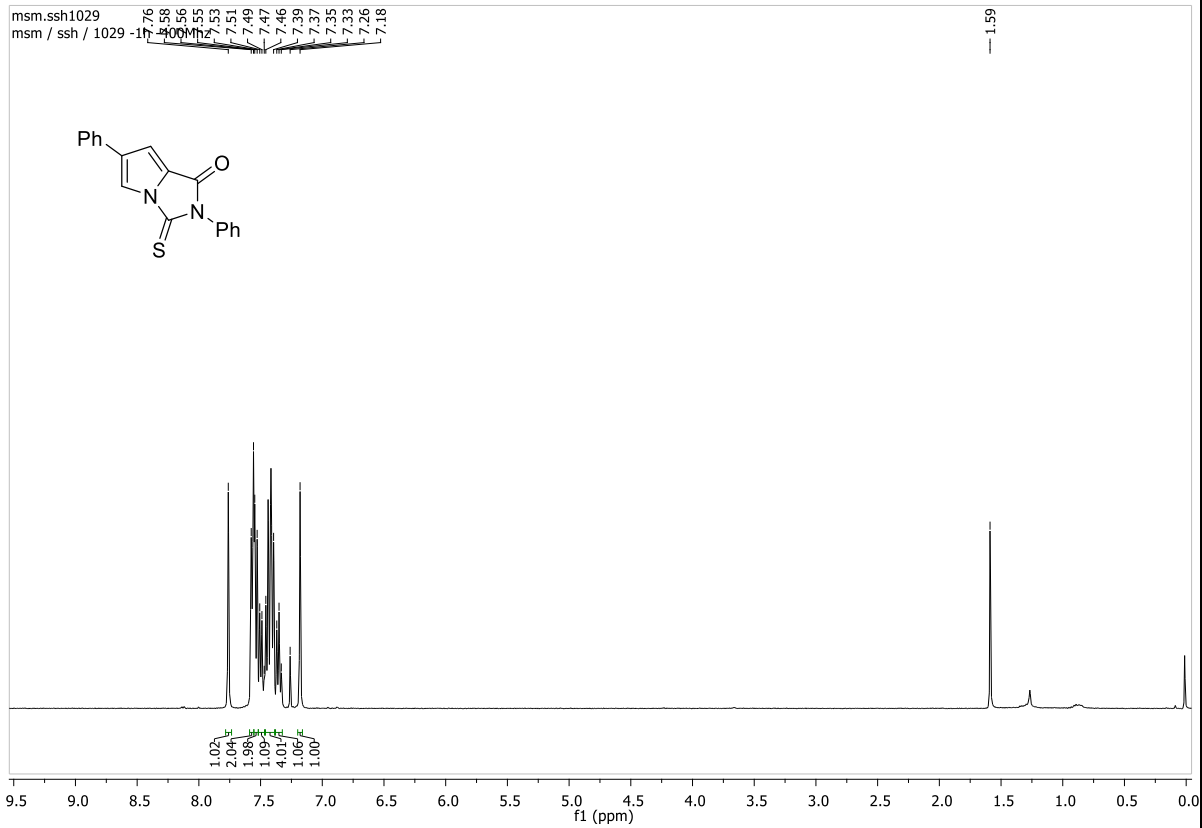
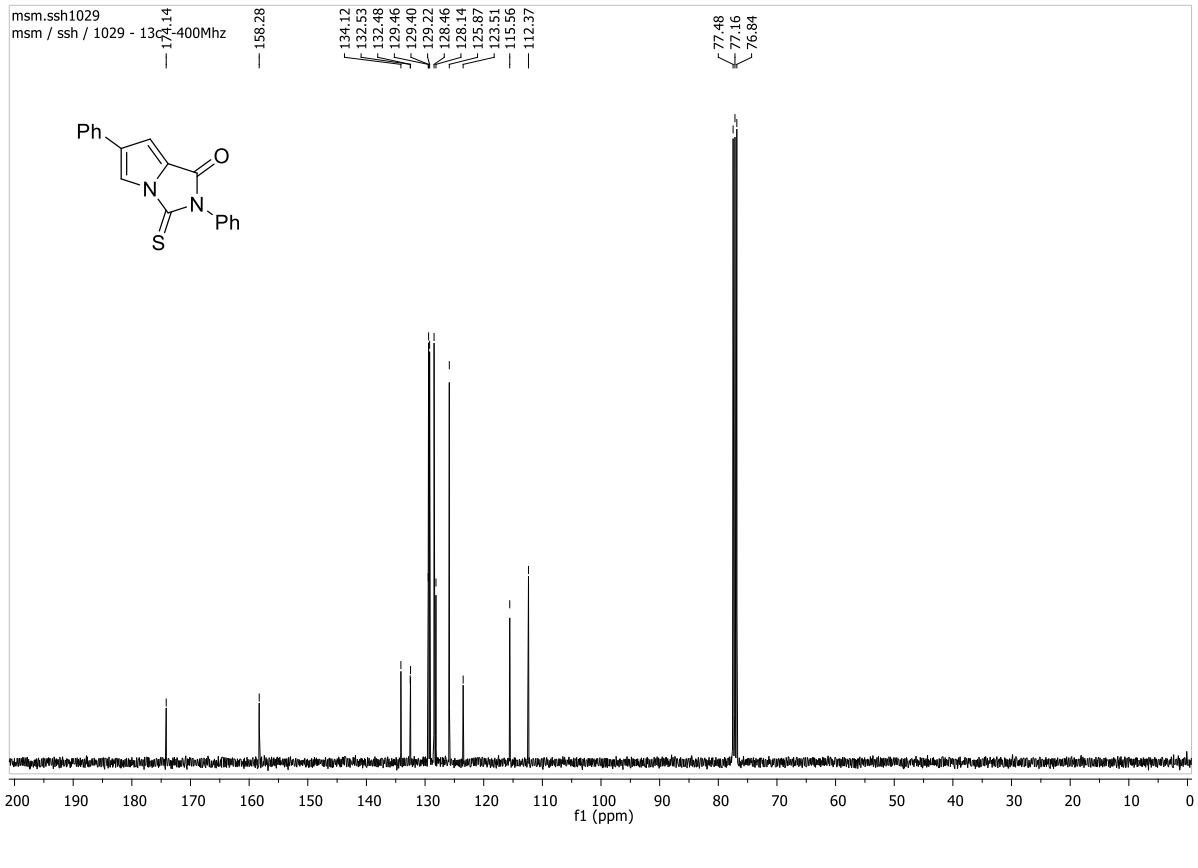


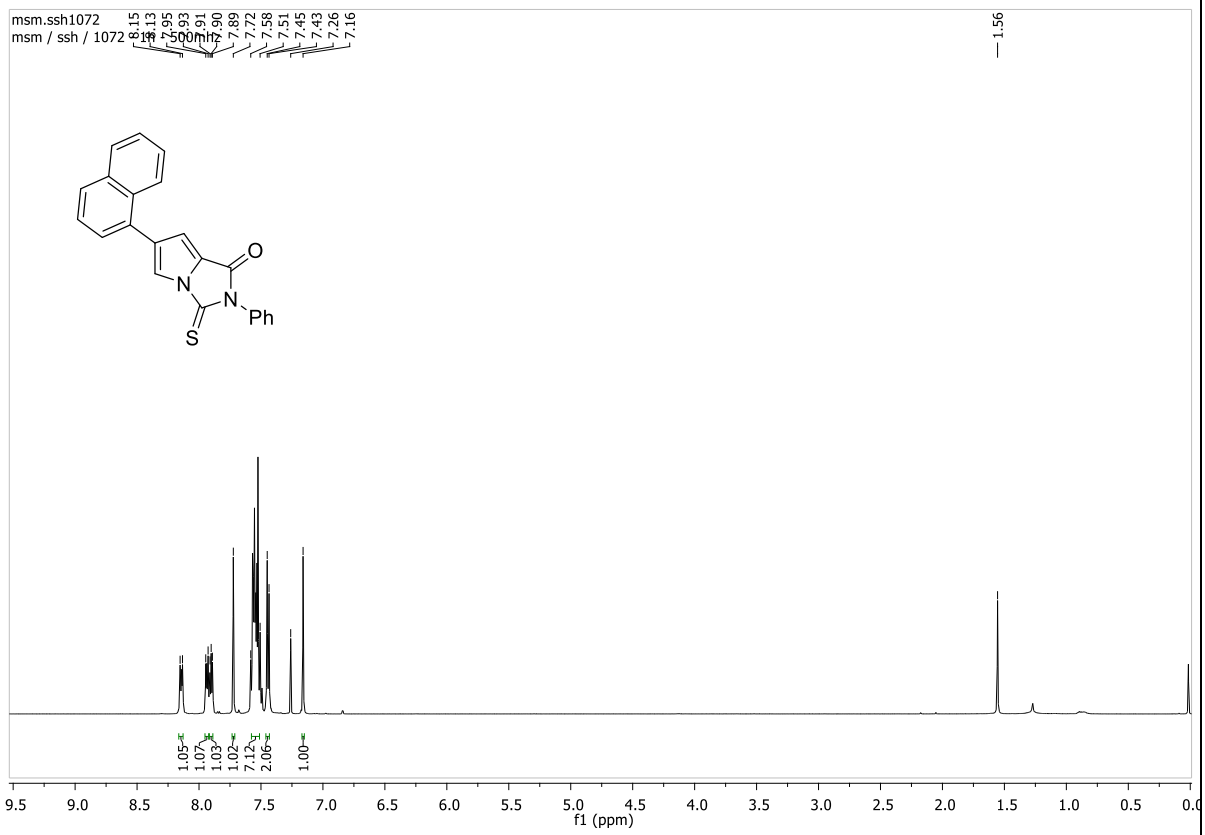


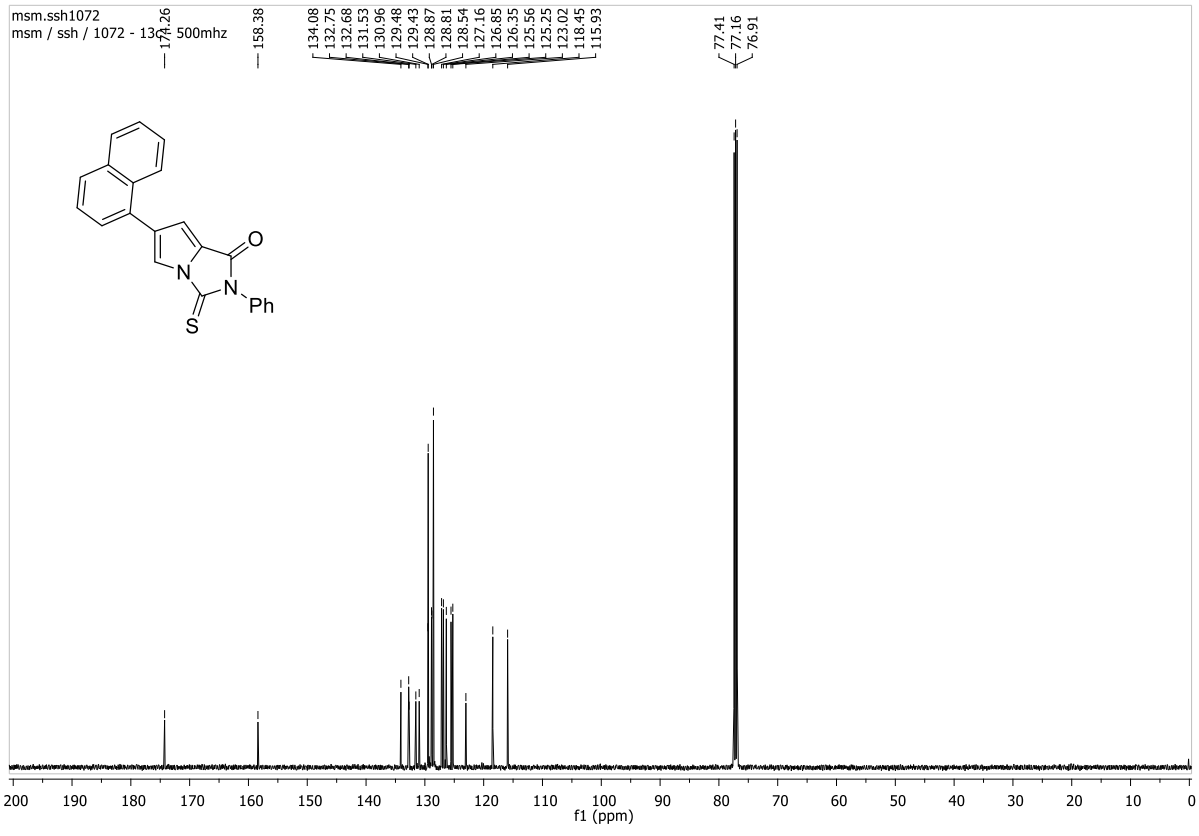
^{1}H NMR and ^{13}C NMR Spectra of Compound **3f**





^{1}H NMR and ^{13}C NMR Spectra of Compound **3g**





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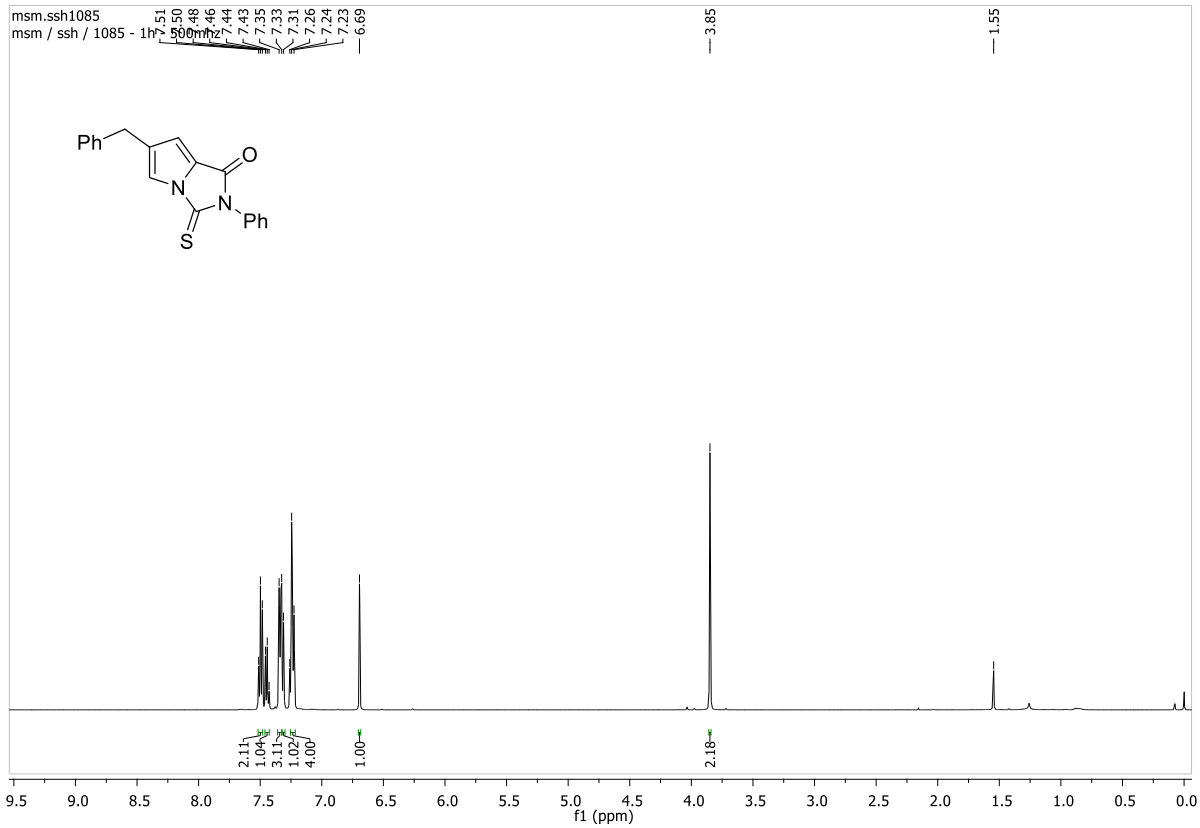
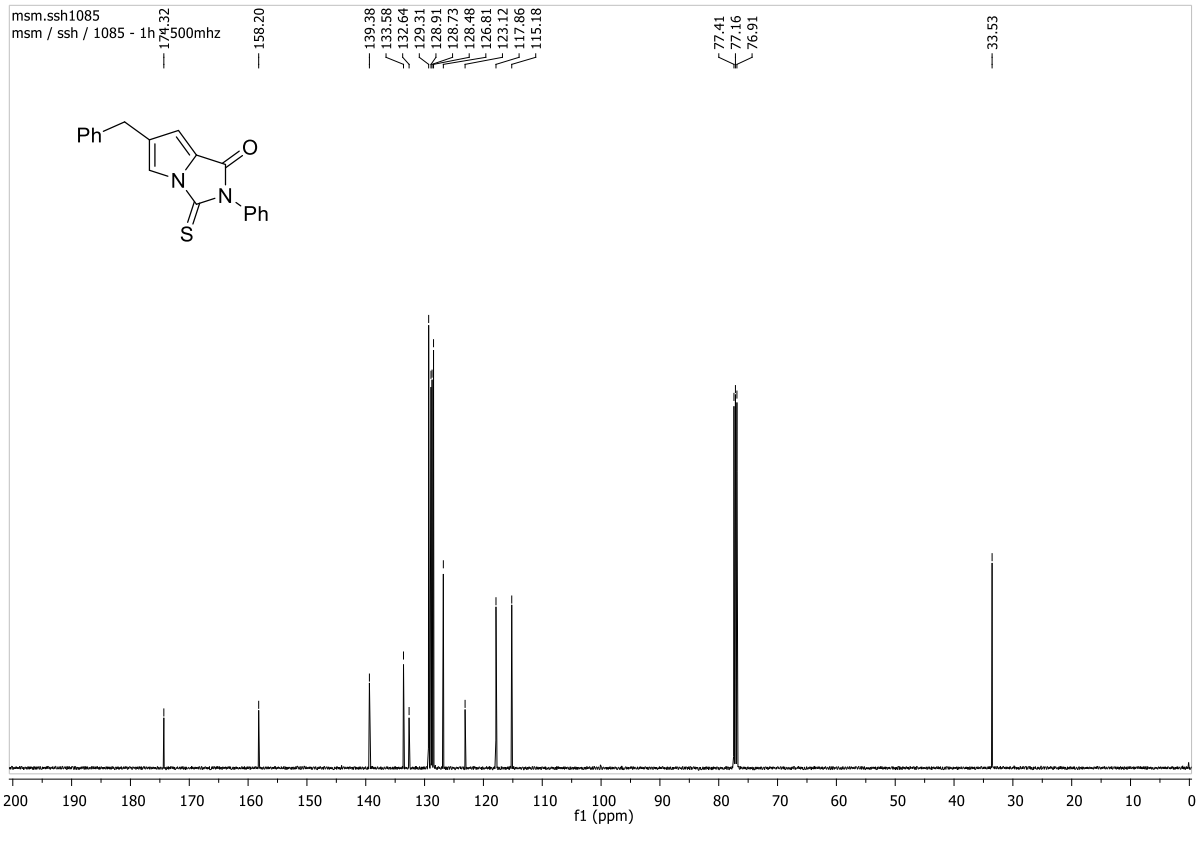
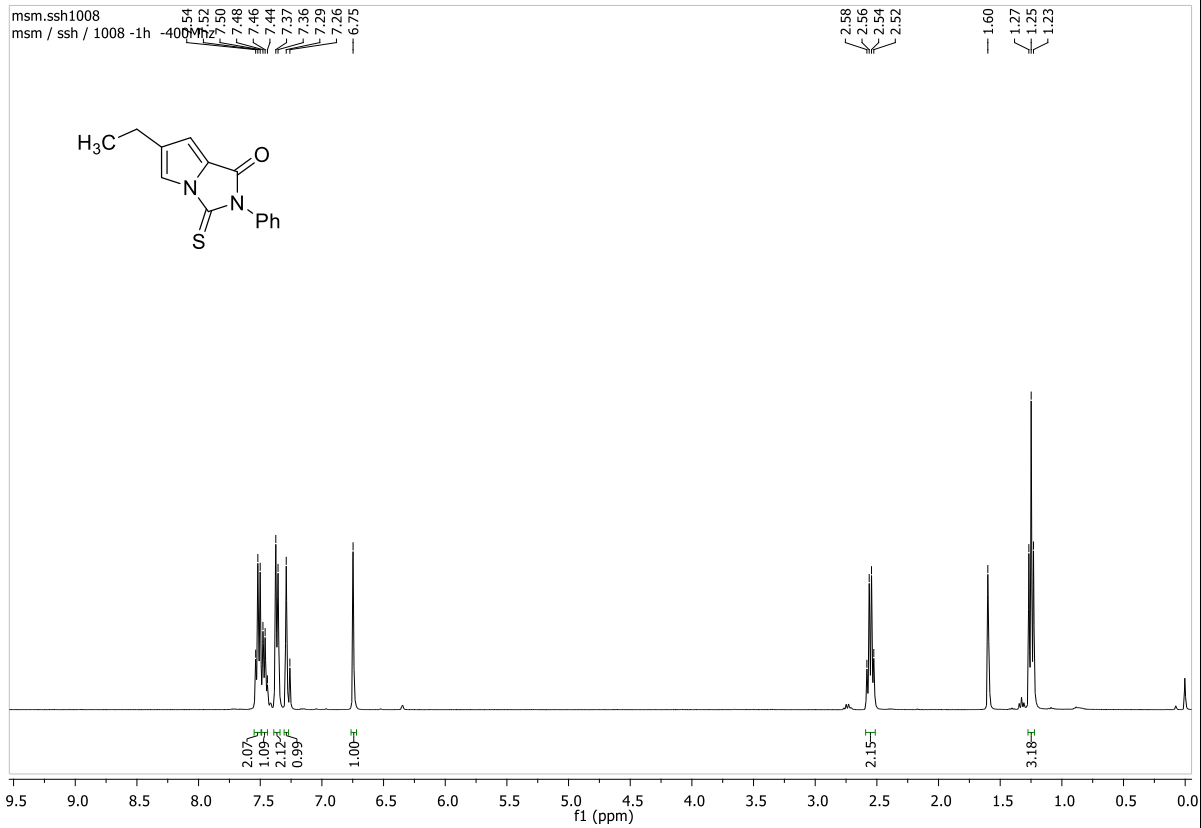
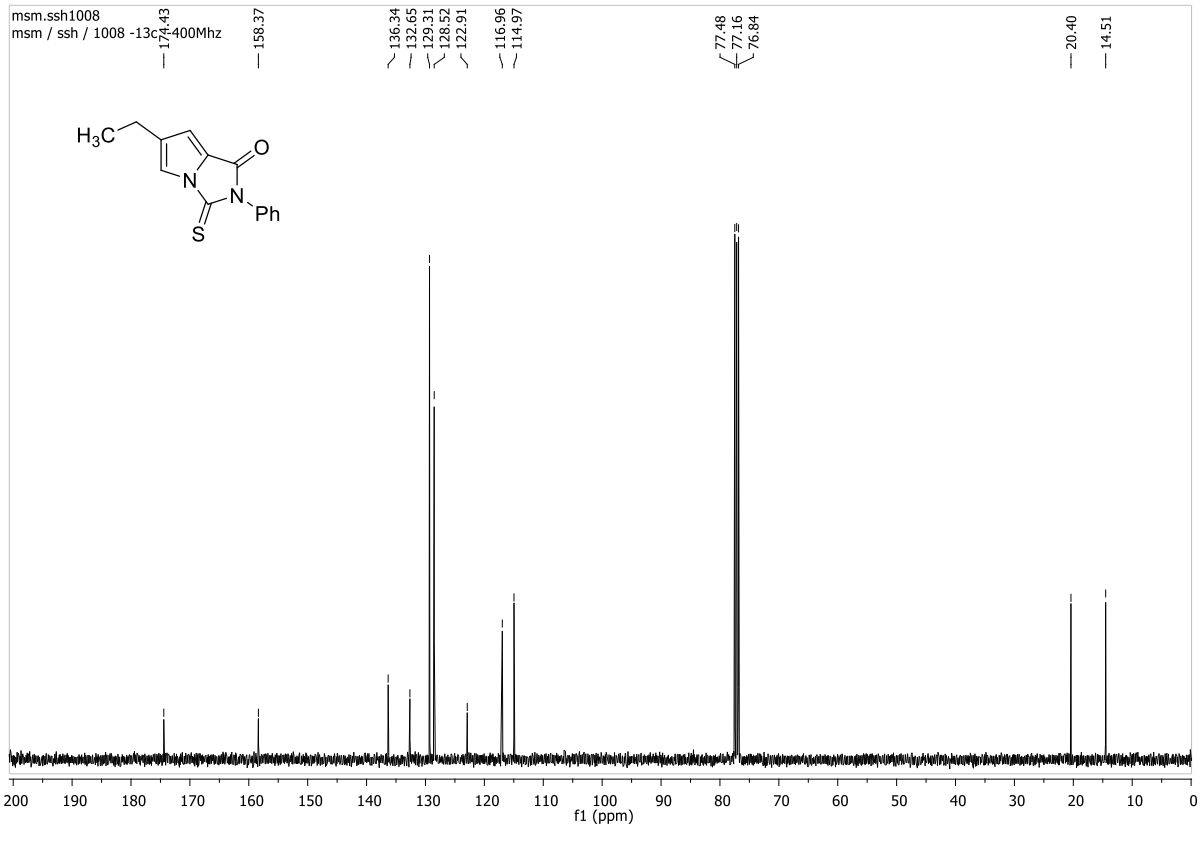


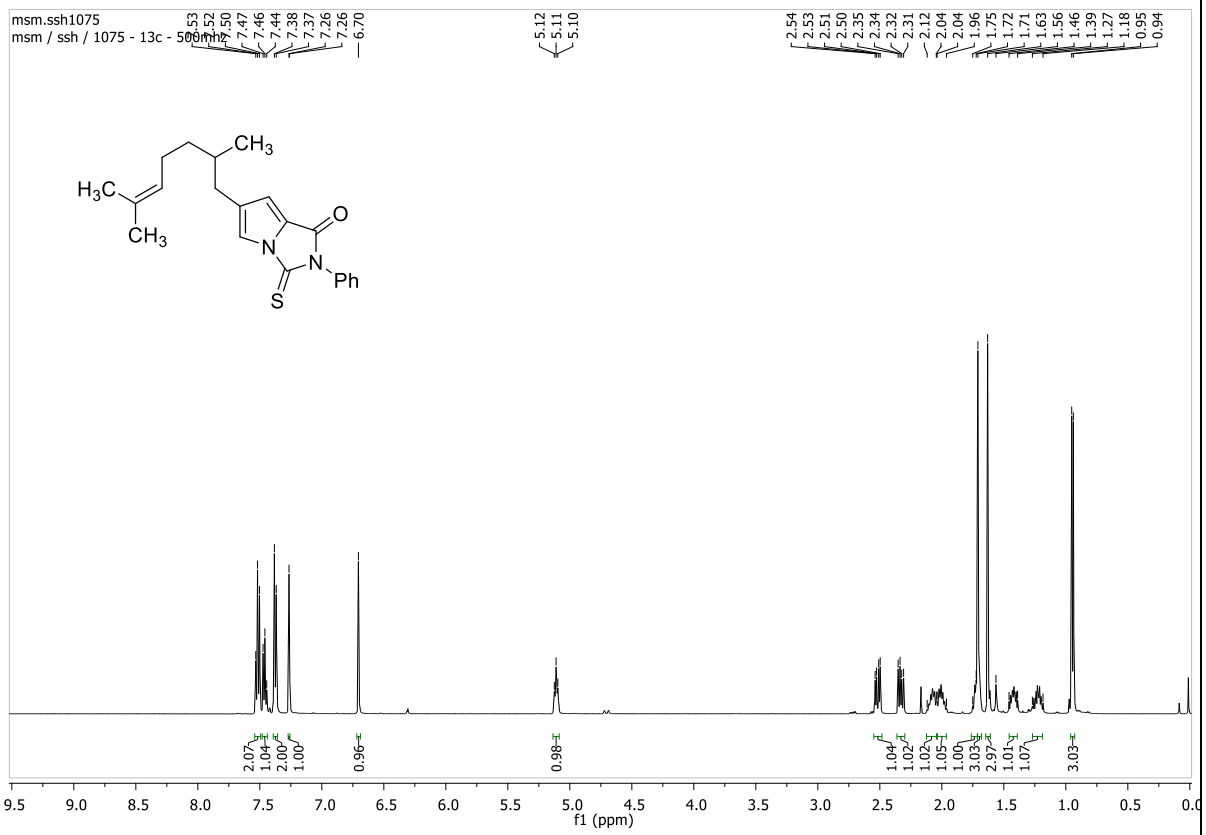


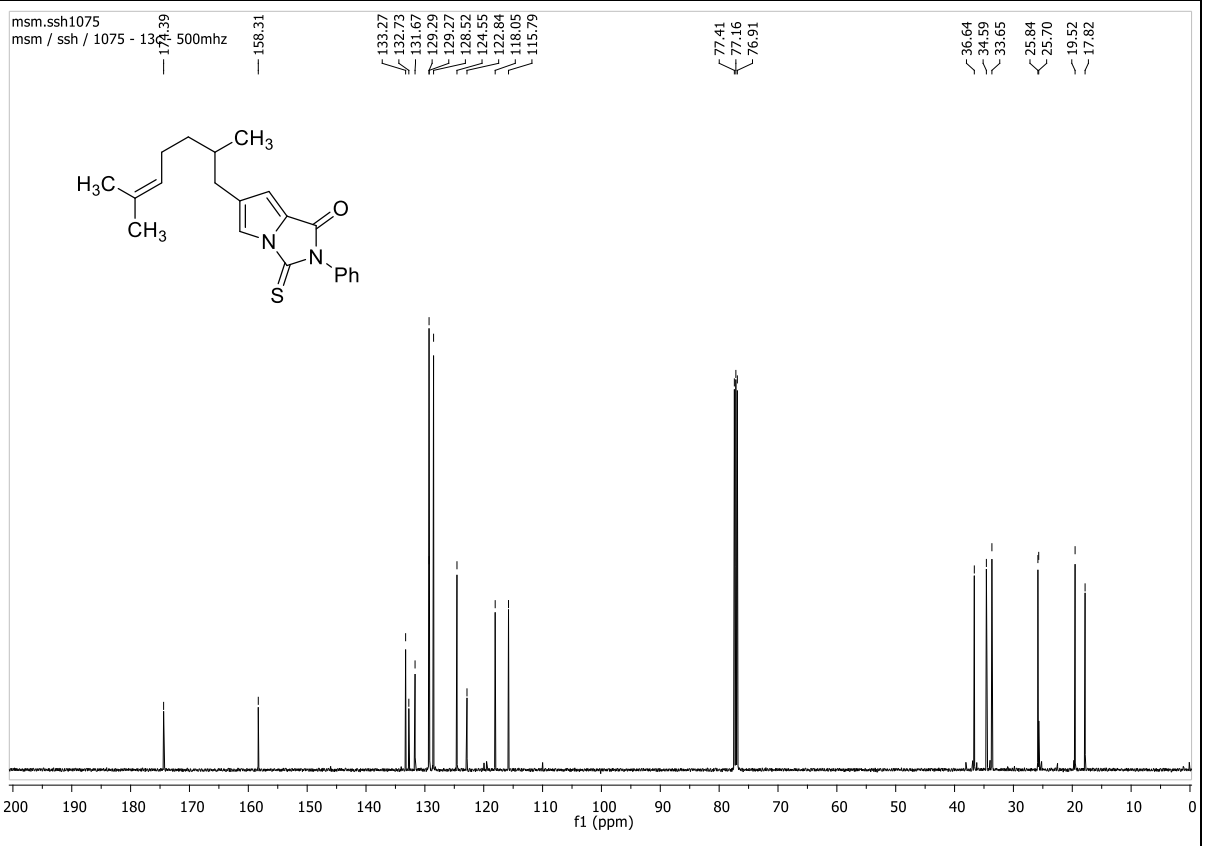
^{1}H NMR and ^{13}C NMR Spectra of Compound **3i**



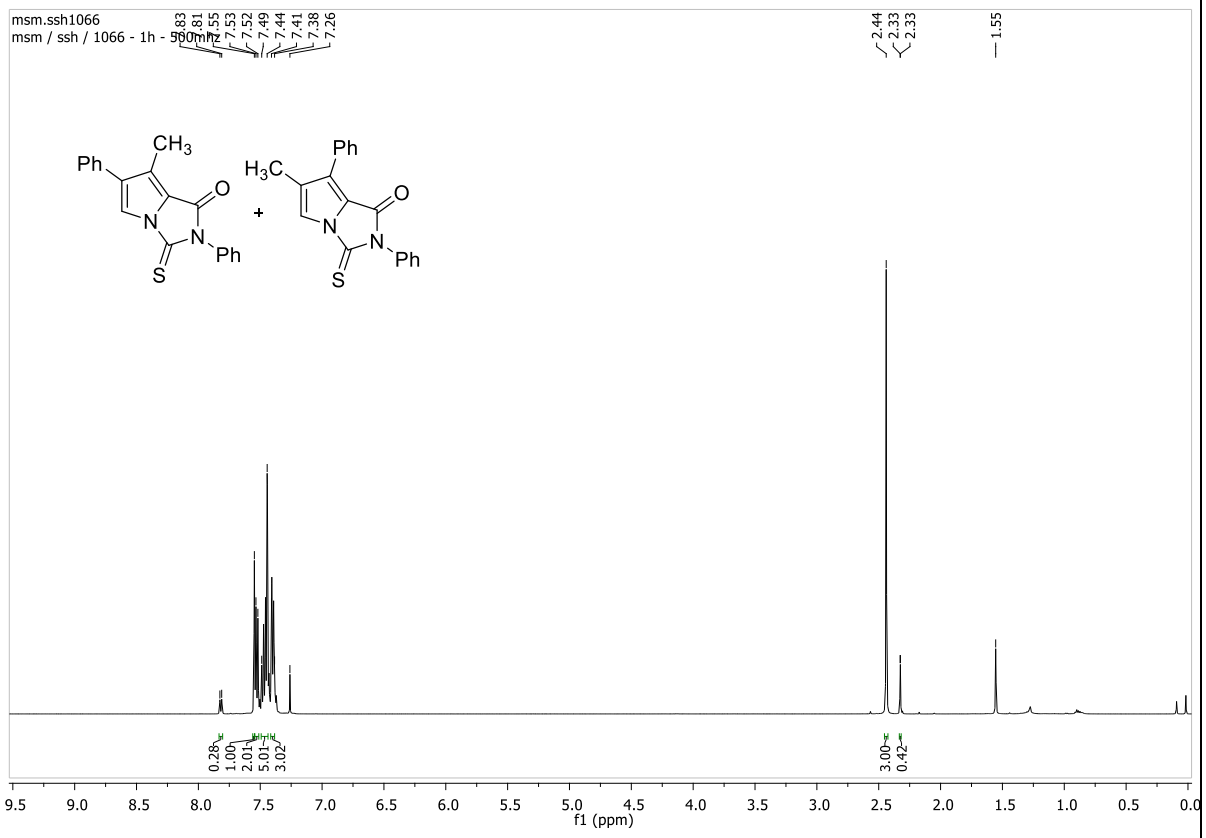


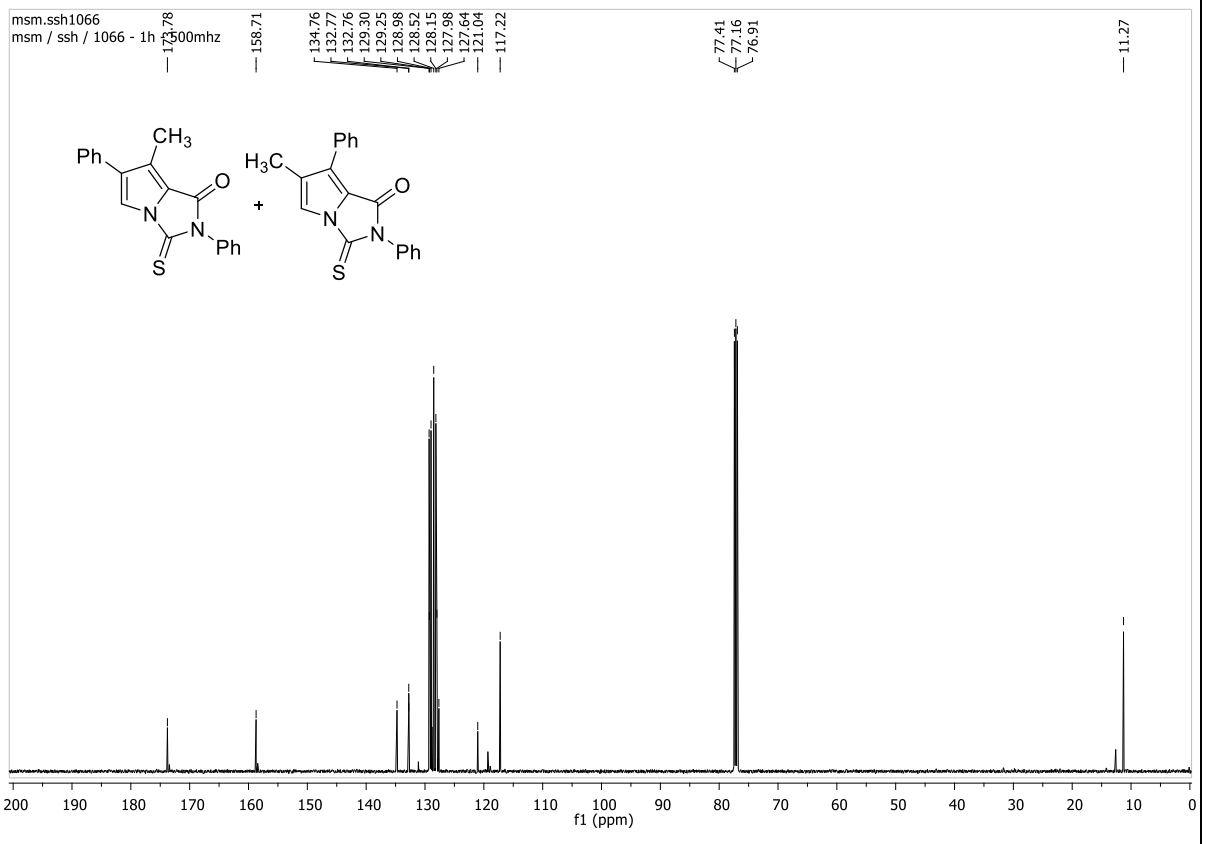
^{1}H NMR and ^{13}C NMR Spectra of Compound **3j**



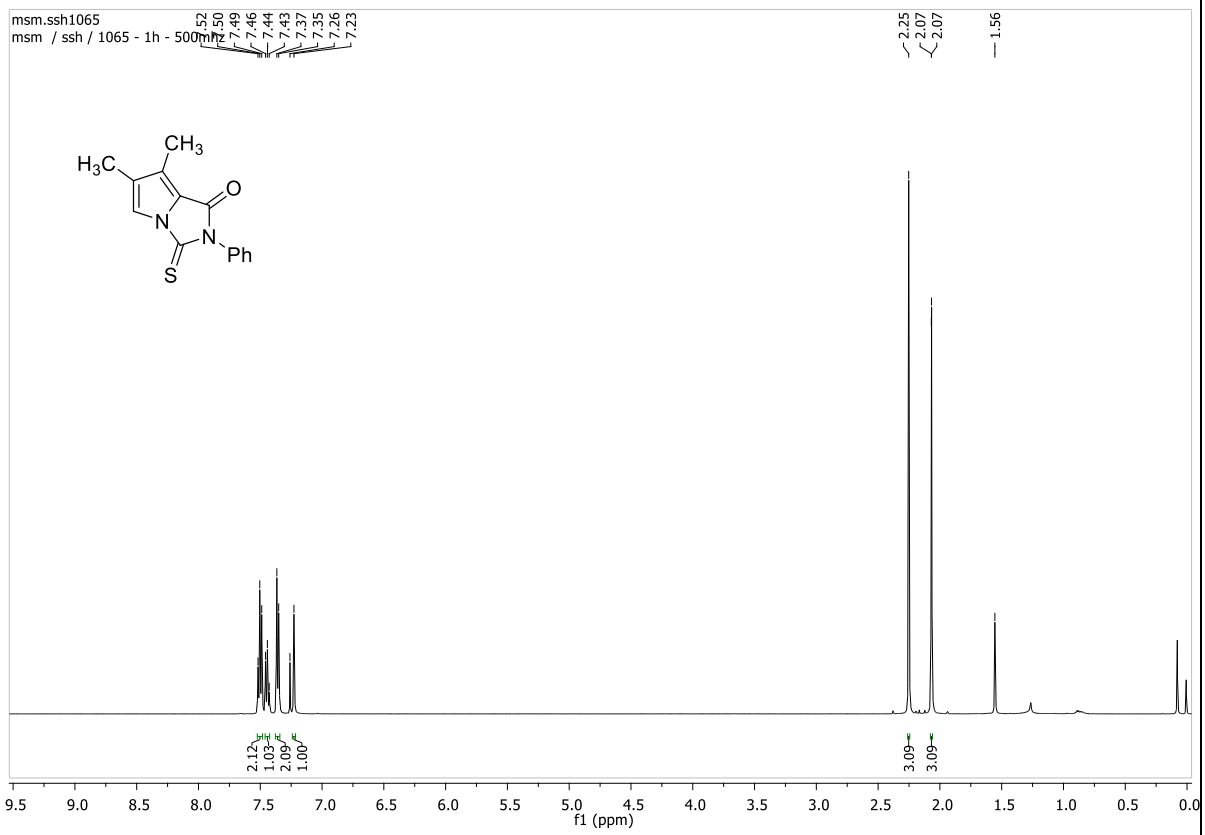


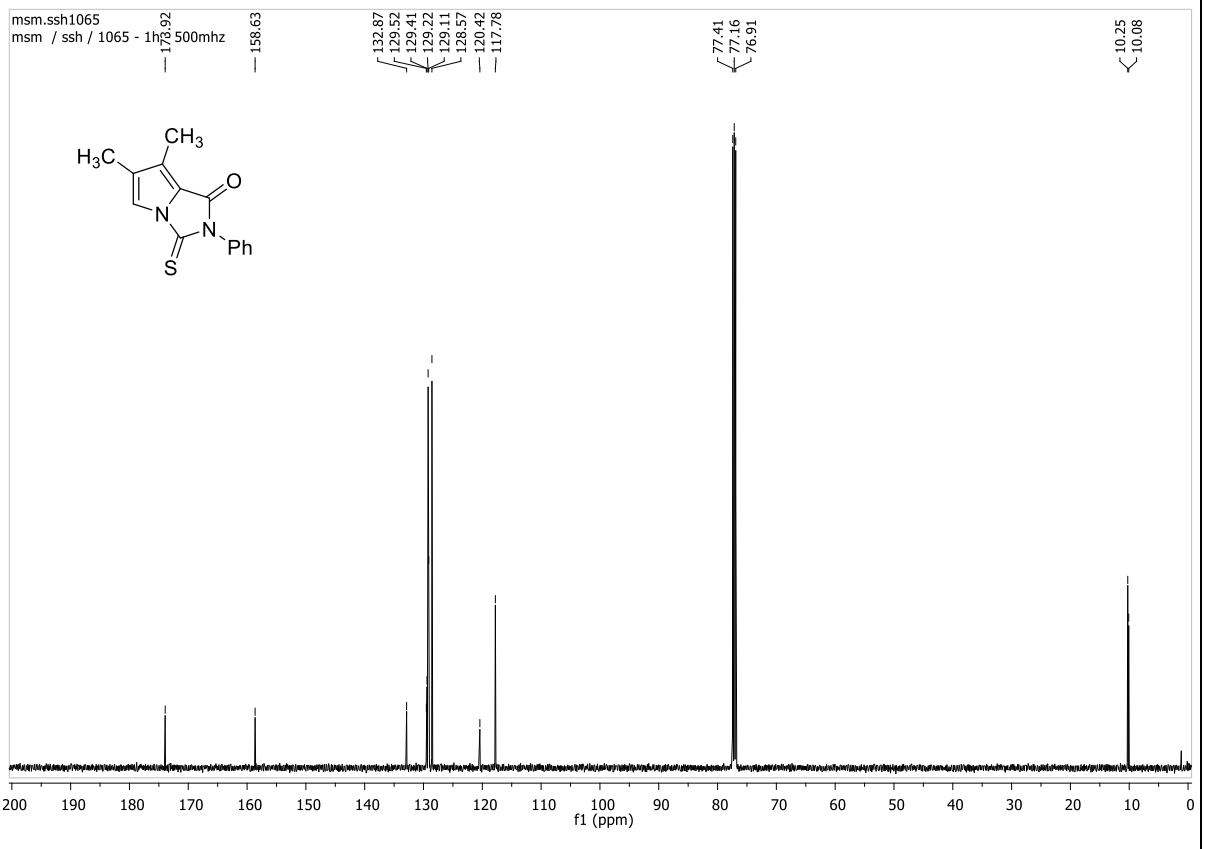
^{1}H NMR and ^{13}C NMR Spectra of Compound **3k**



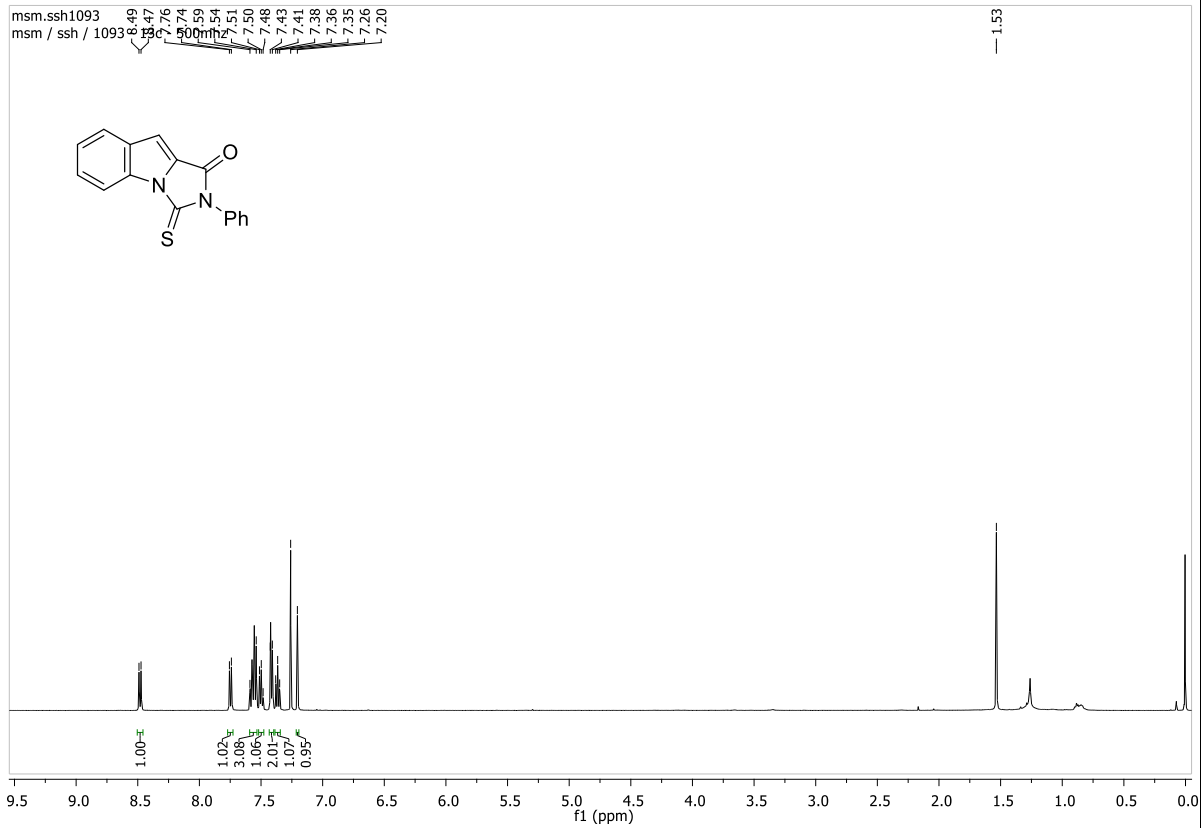


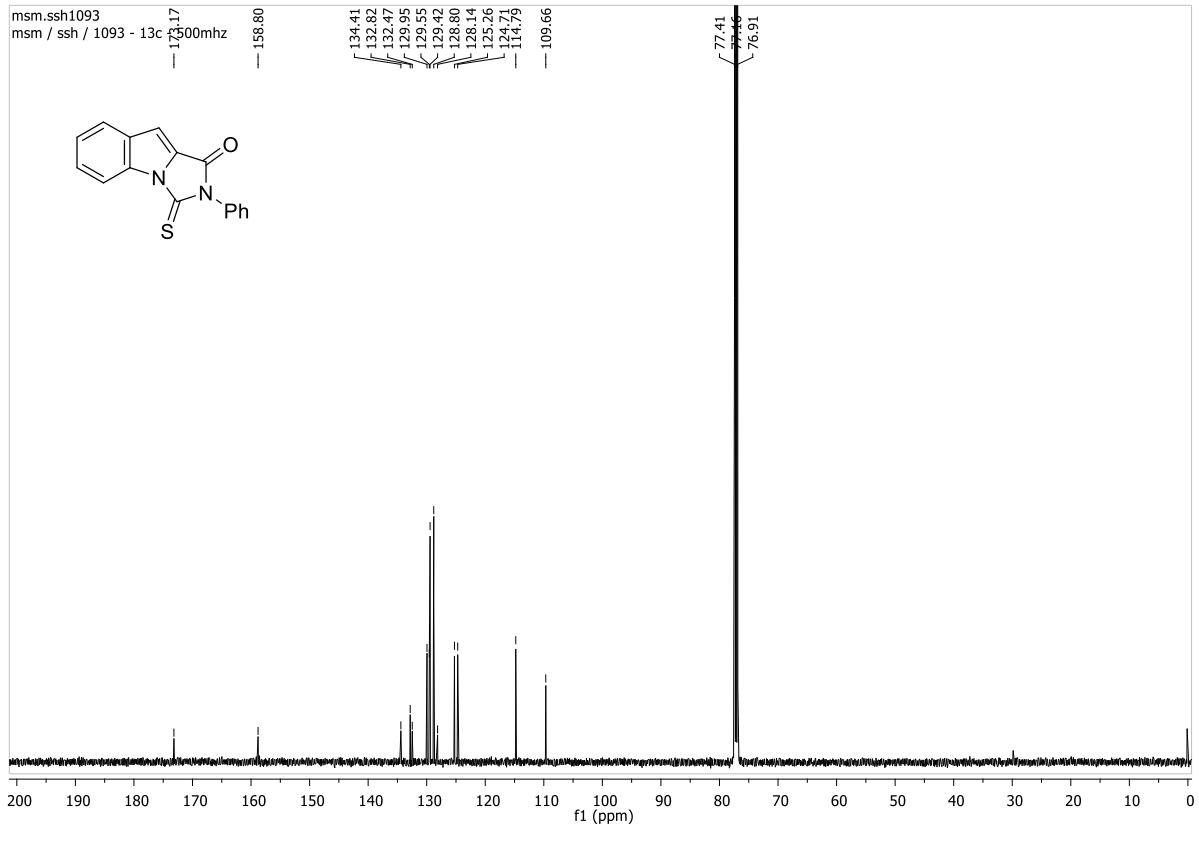
^{1}H NMR and ^{13}C NMR Spectra of Compound **3l**



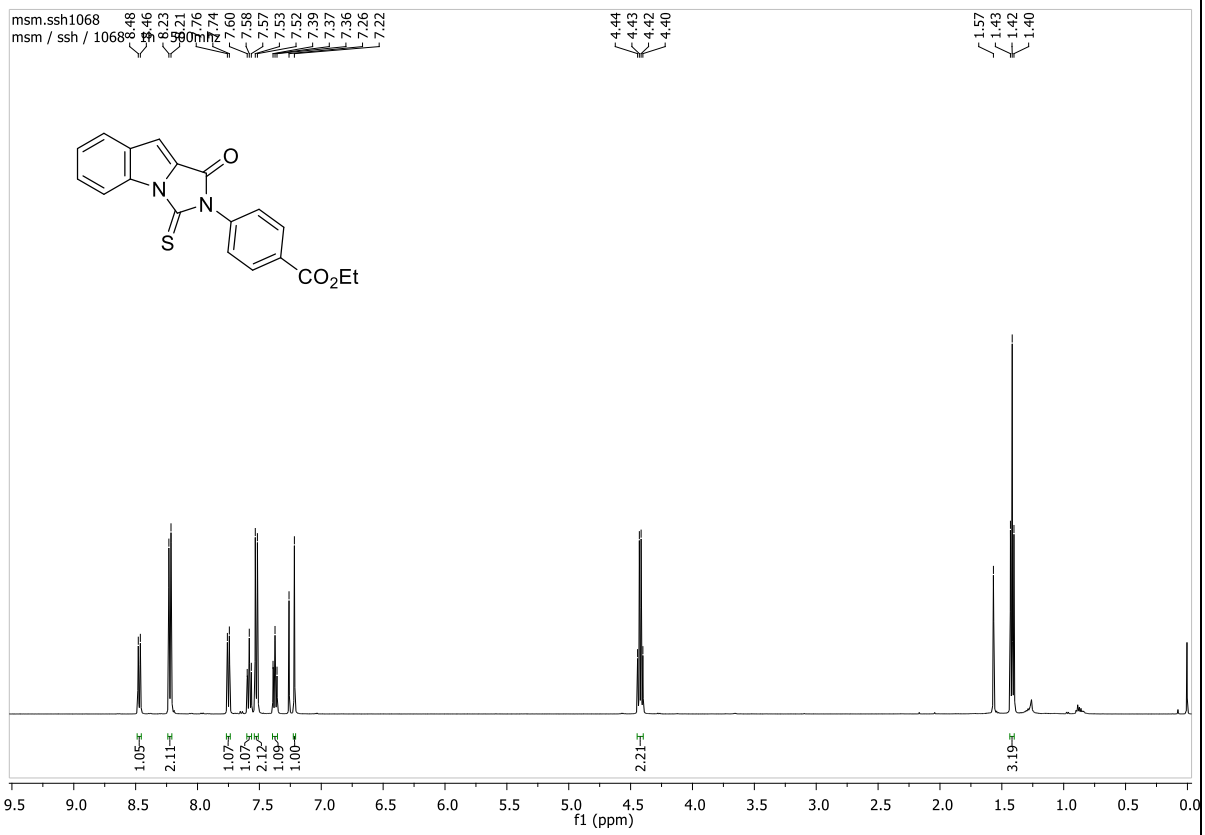


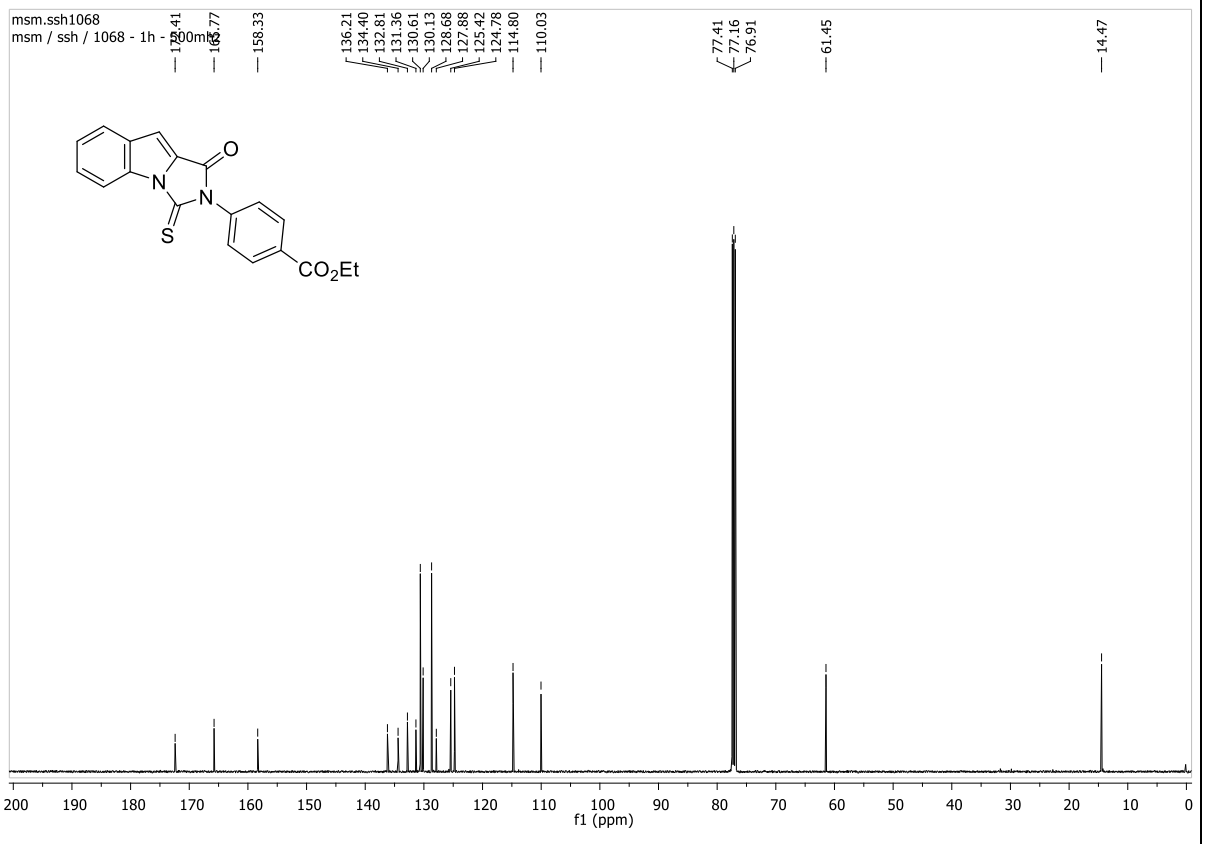
^{1}H NMR and ^{13}C NMR Spectra of Compound **3m**



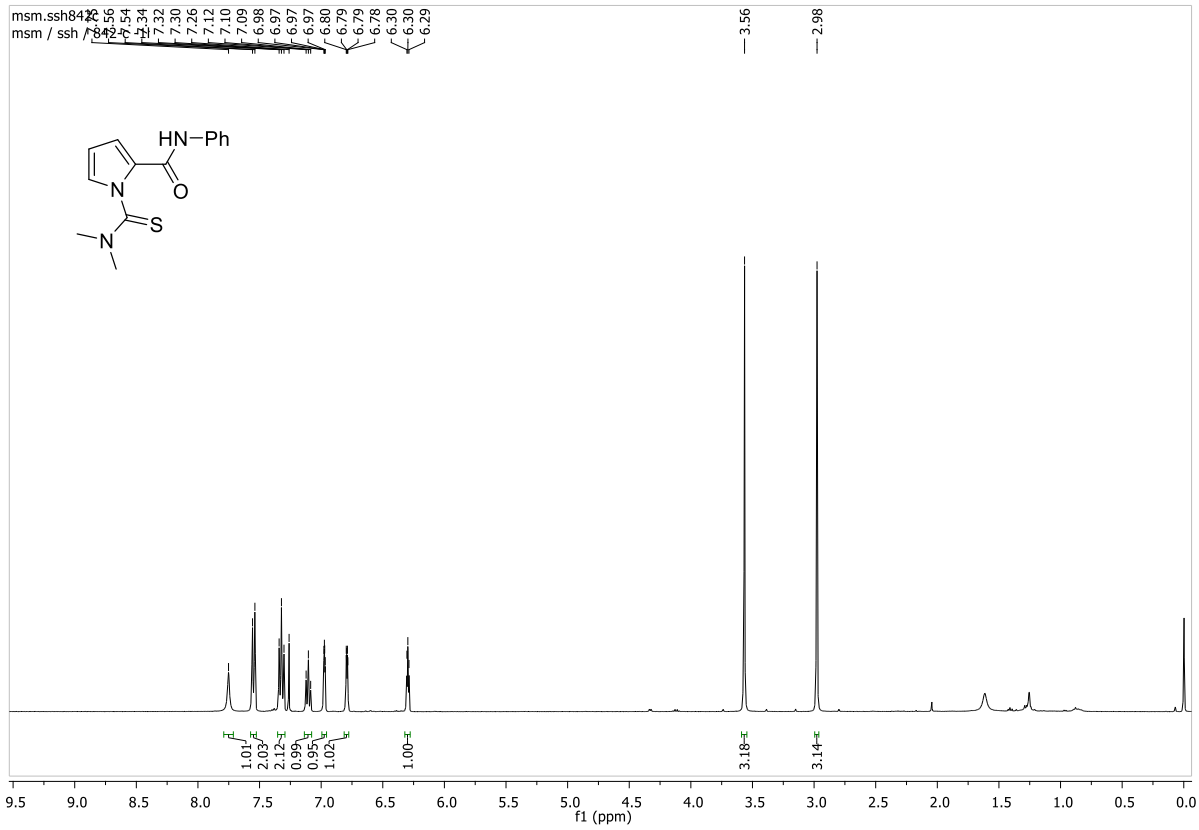


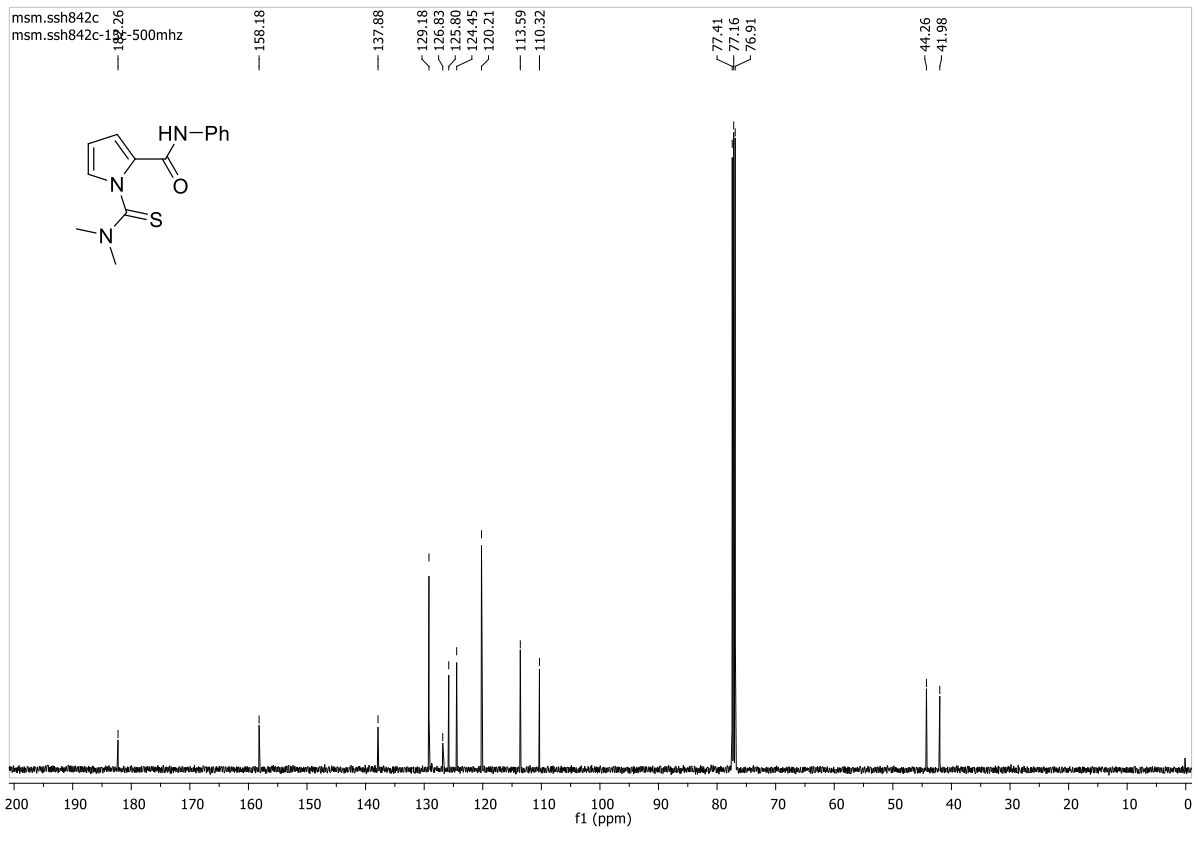
[1]H NMR and [13]C NMR Spectra of Compound **3n**



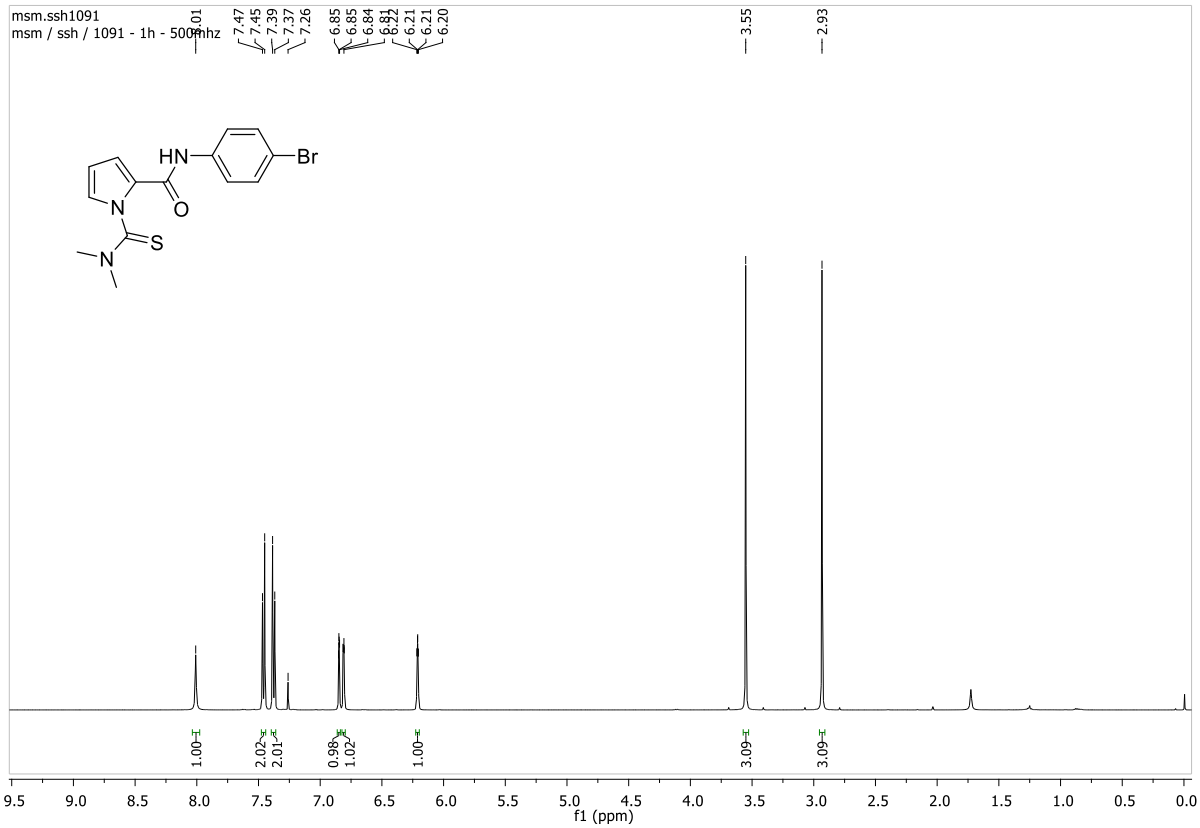


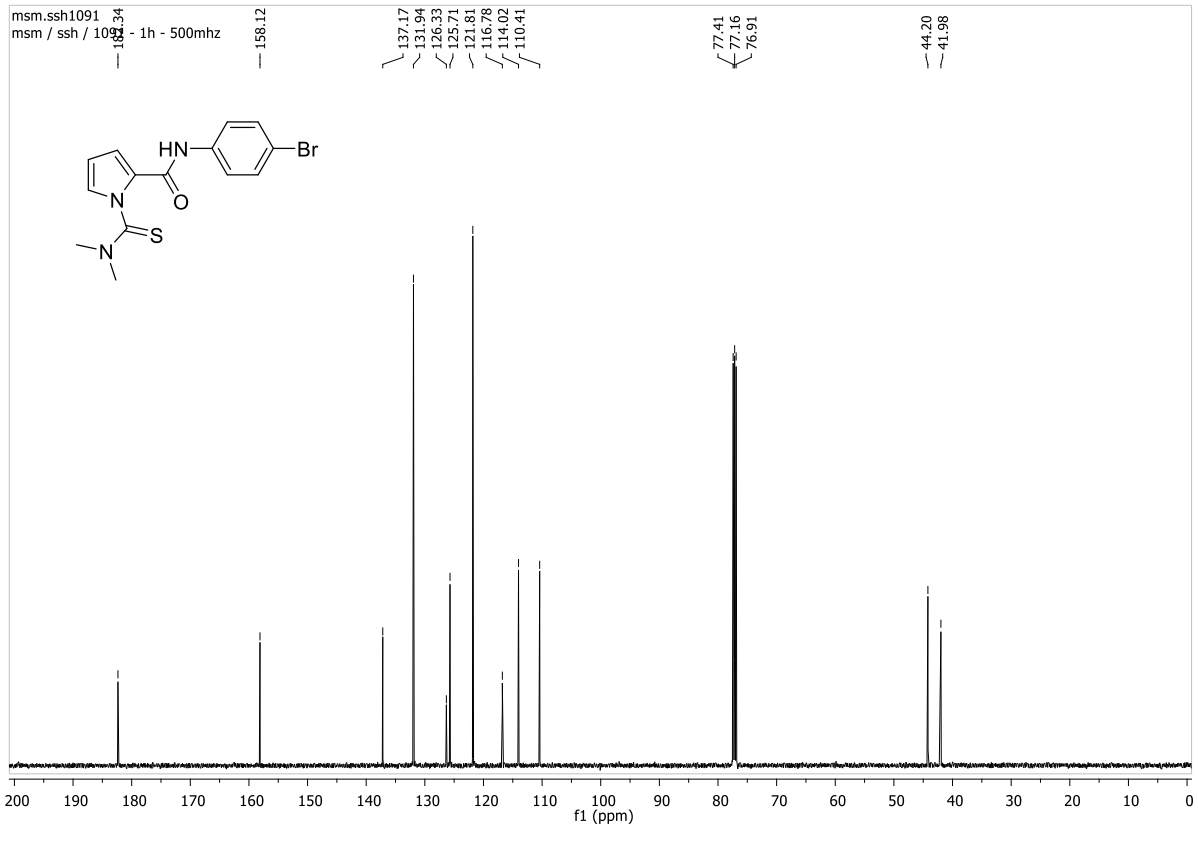
^{1}H NMR and ^{13}C NMR Spectra of Compound **4a**



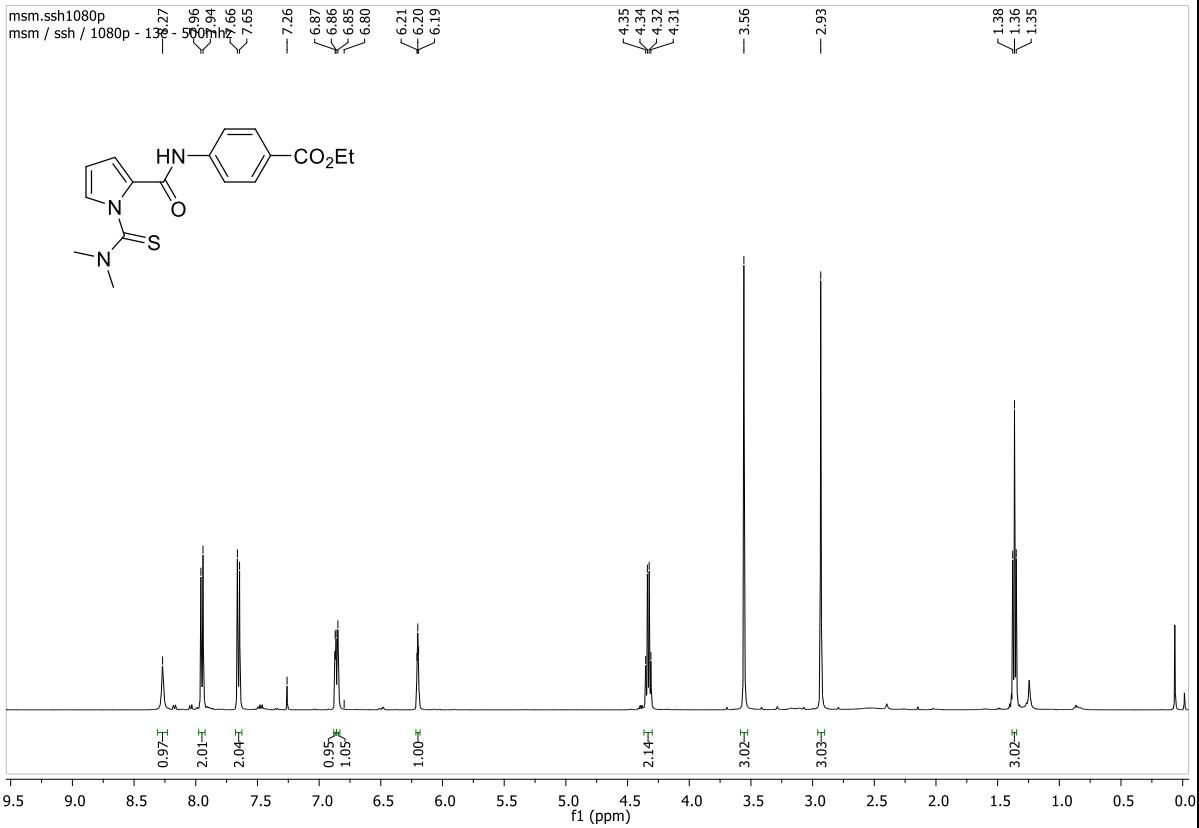


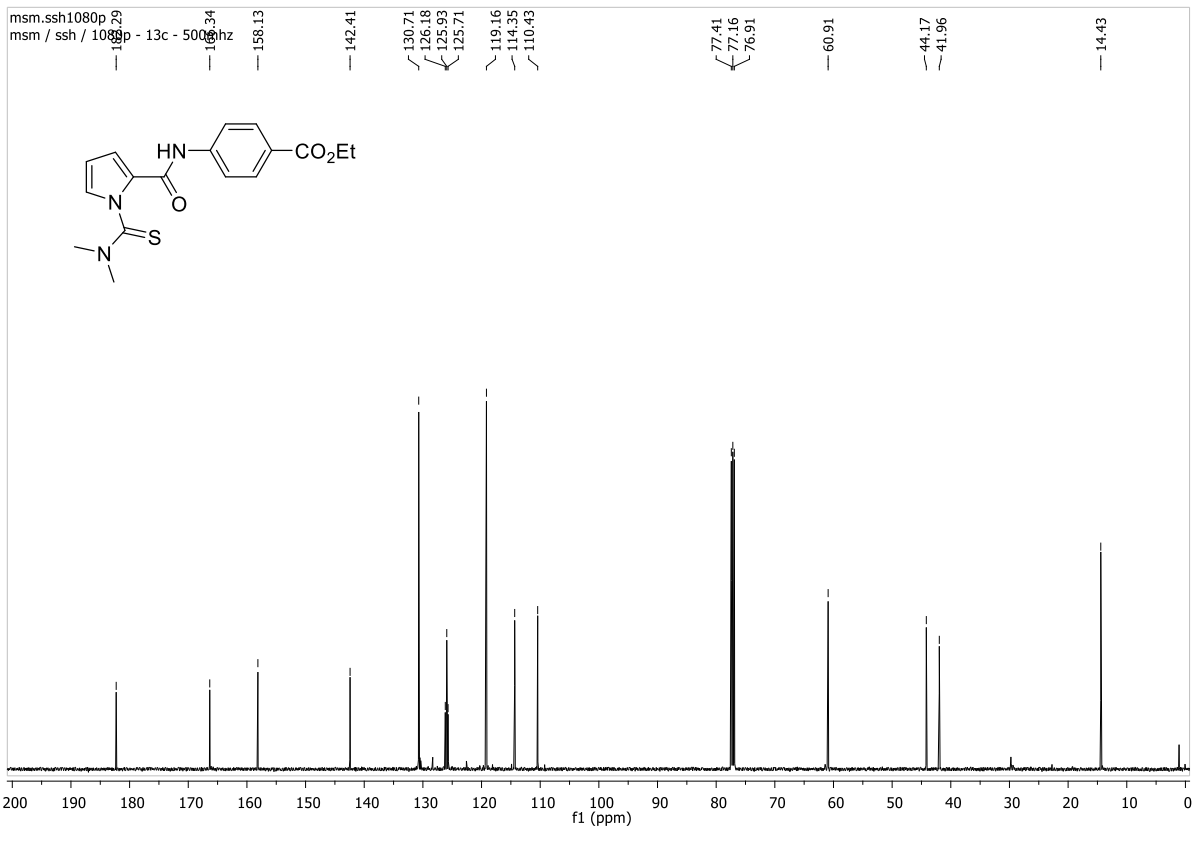
^{1}H NMR and ^{13}C NMR Spectra of Compound **4b**



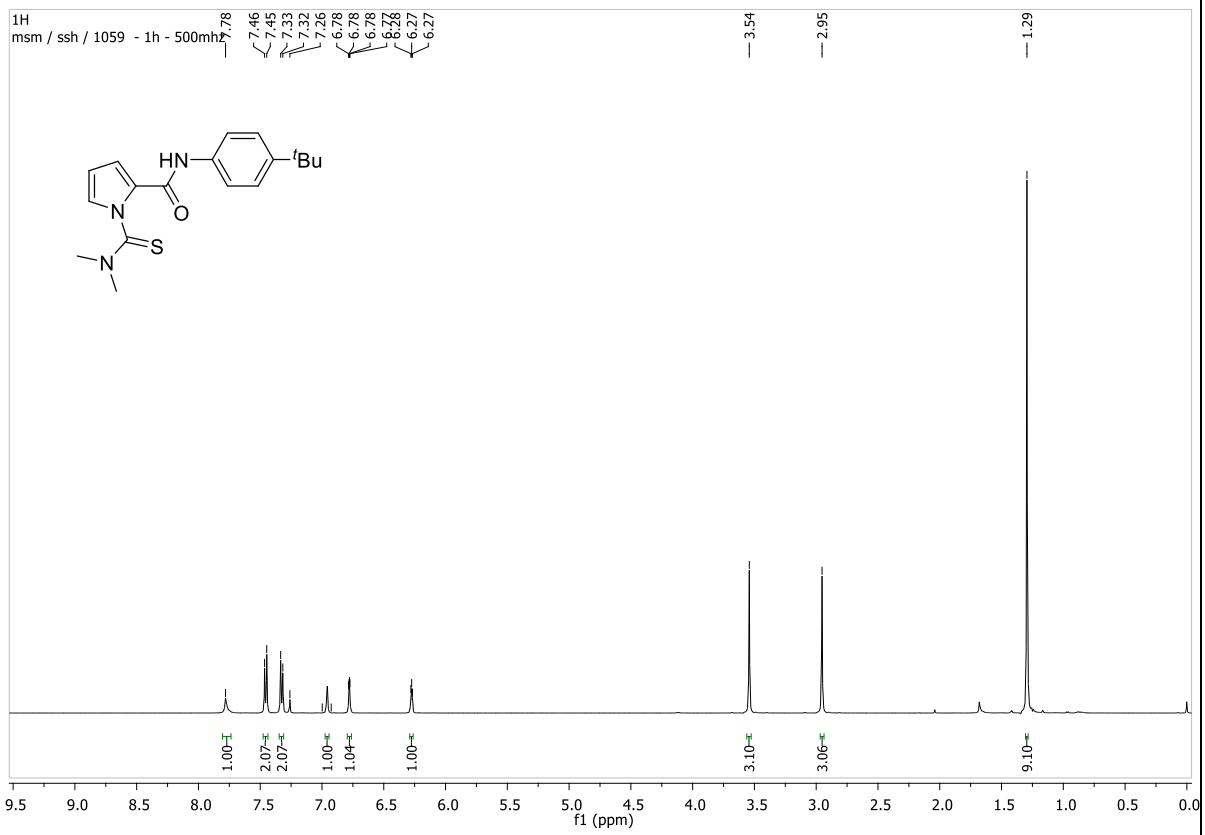


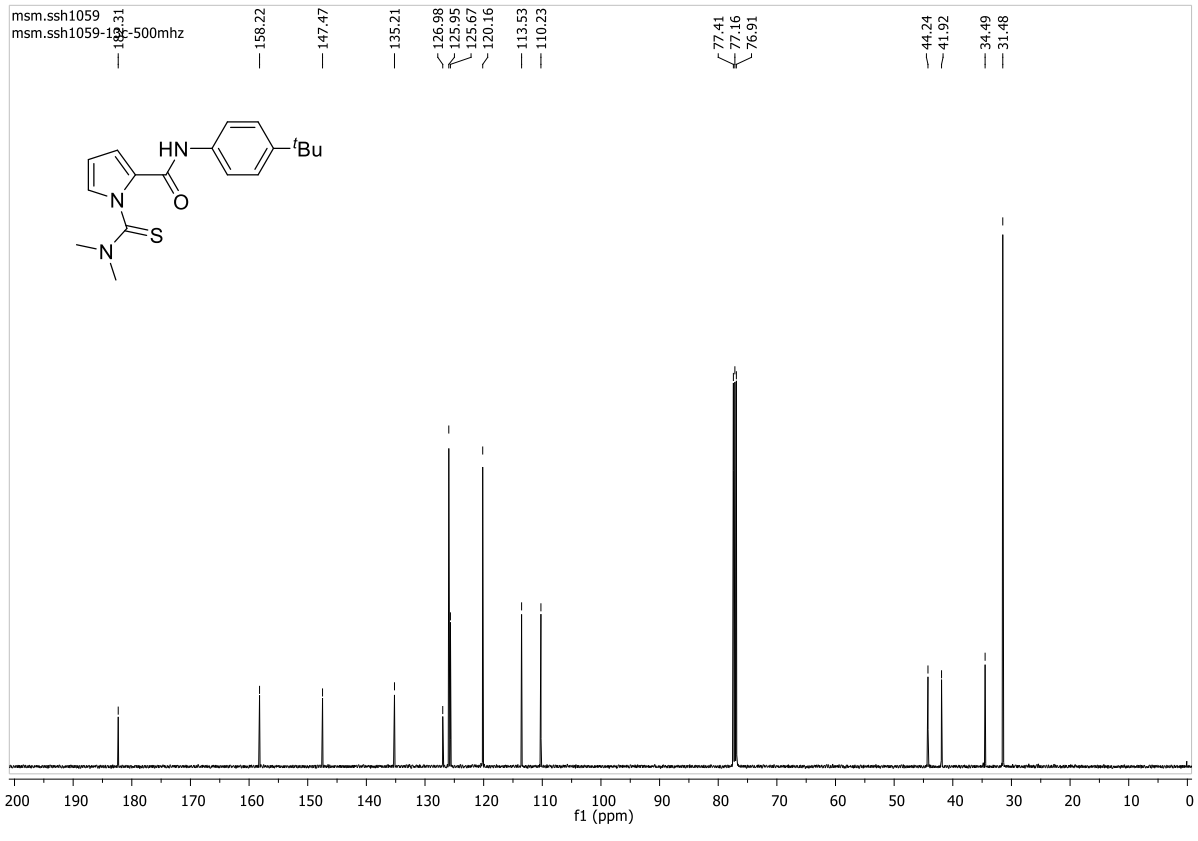
^{1}H NMR and ^{13}C NMR Spectra of Compound **4c**



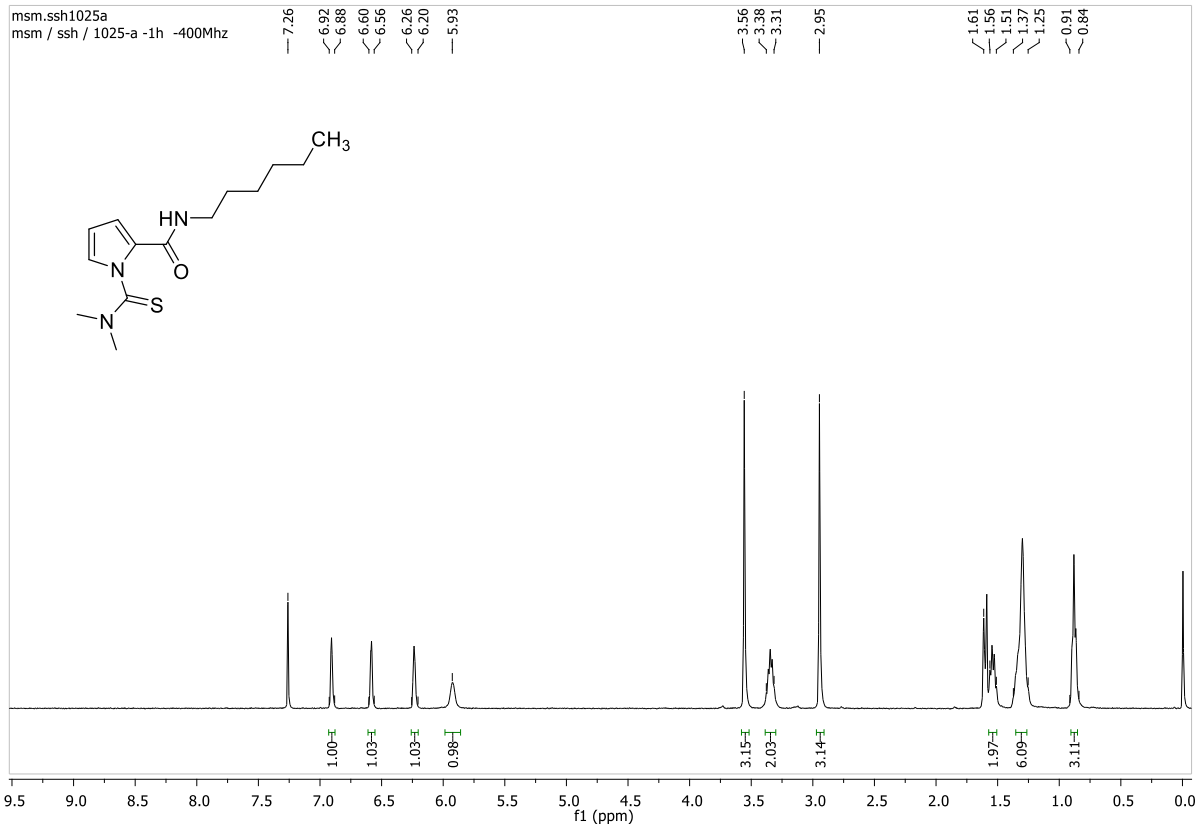


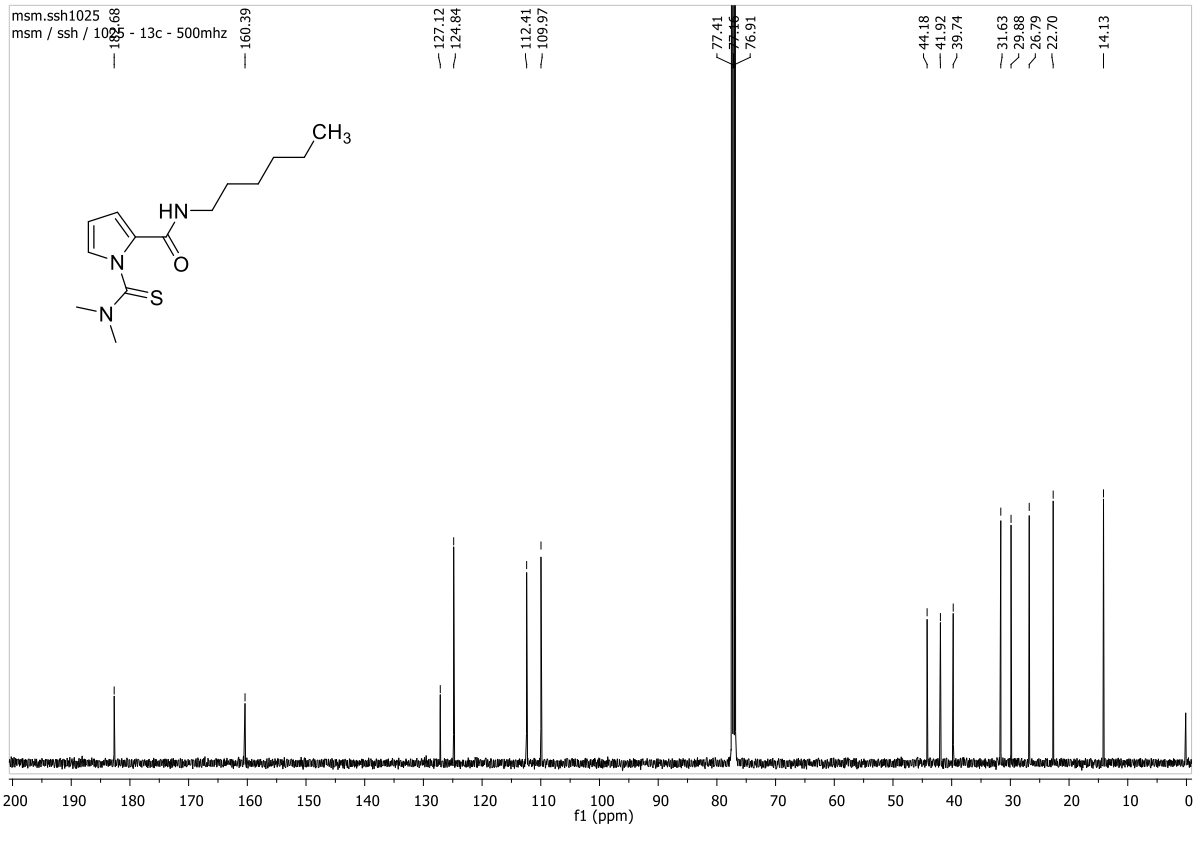
^{1}H NMR and ^{13}C NMR Spectra of Compound **4d**



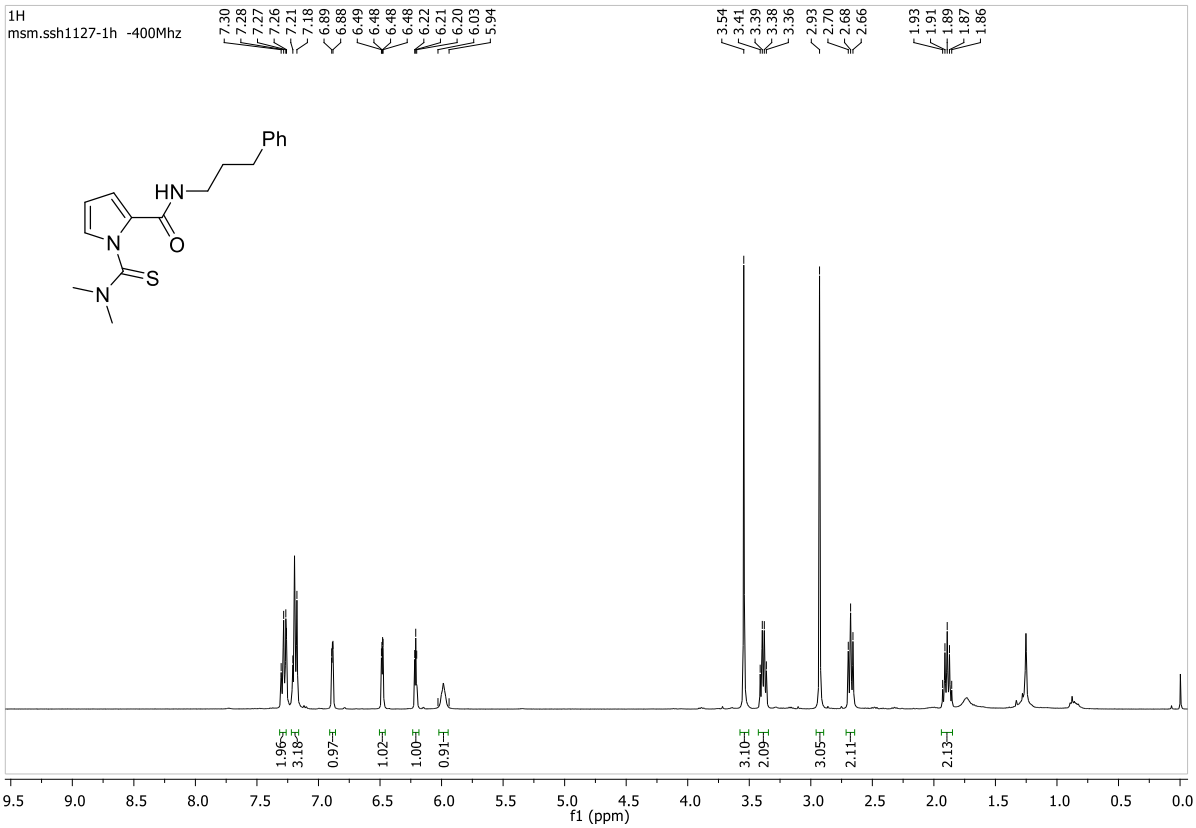


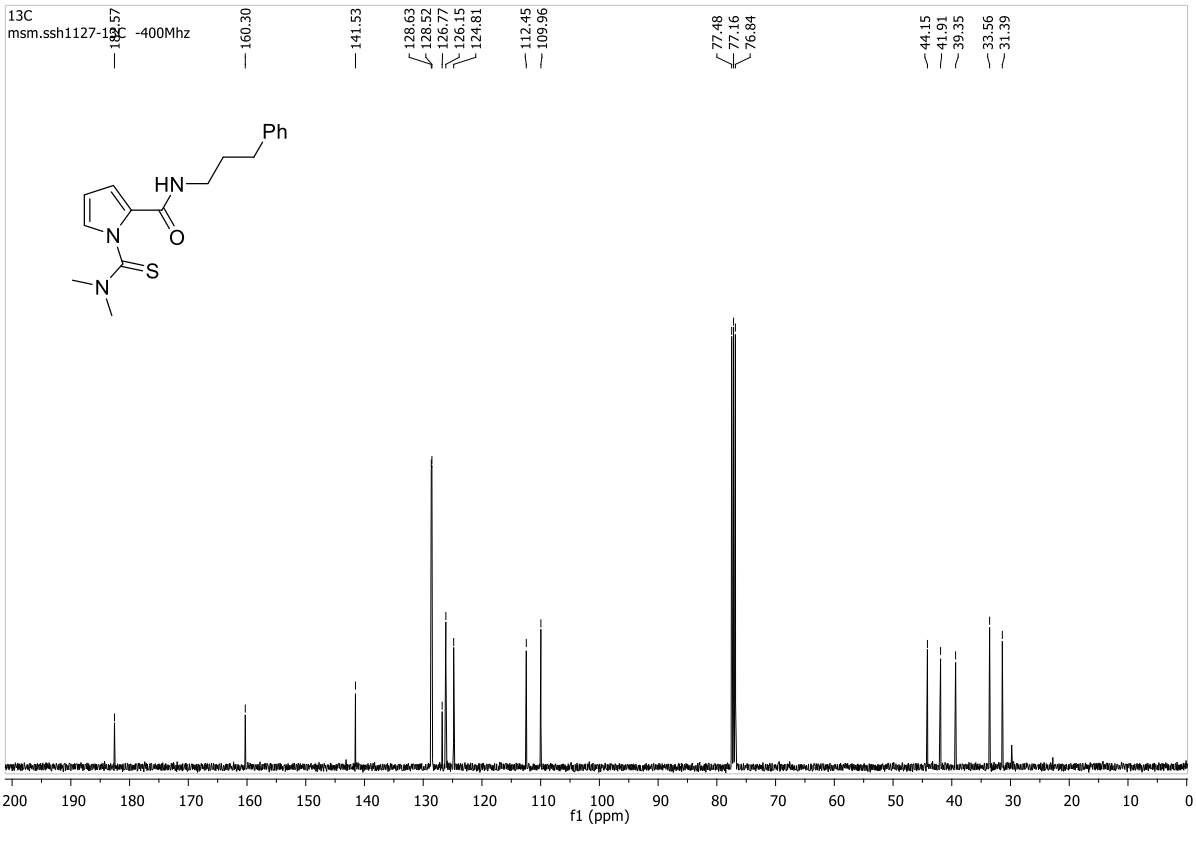
^{1}H NMR and ^{13}C NMR Spectra of Compound **4e**



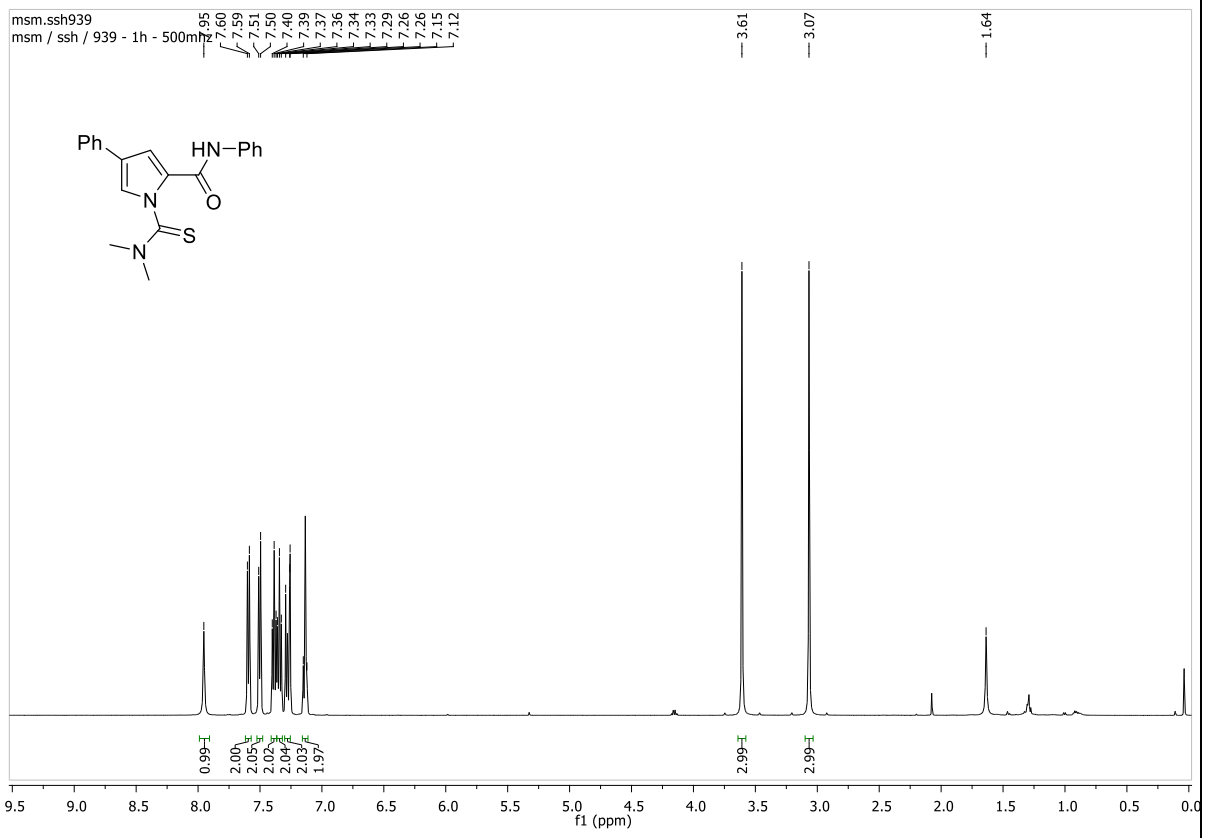


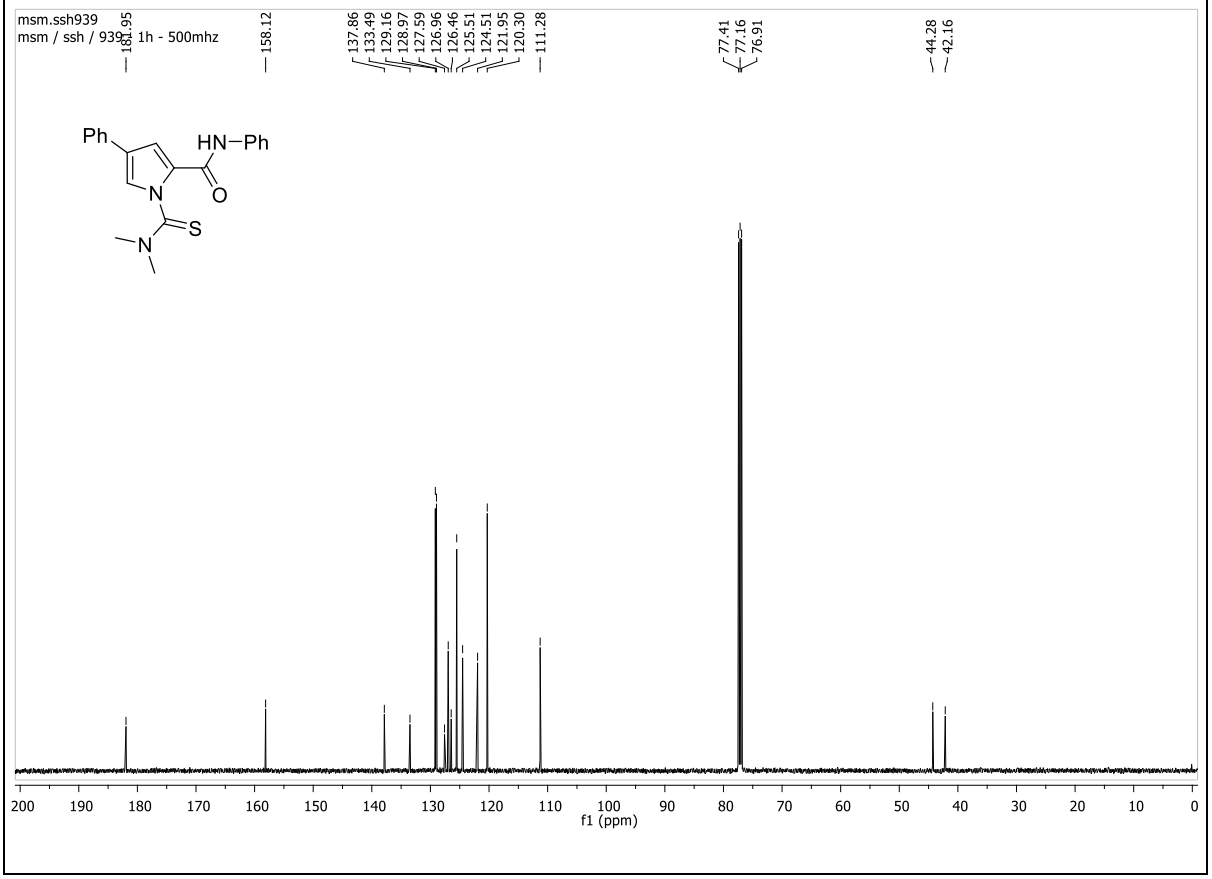
^{1}H NMR and ^{13}C NMR Spectra of Compound **4f**



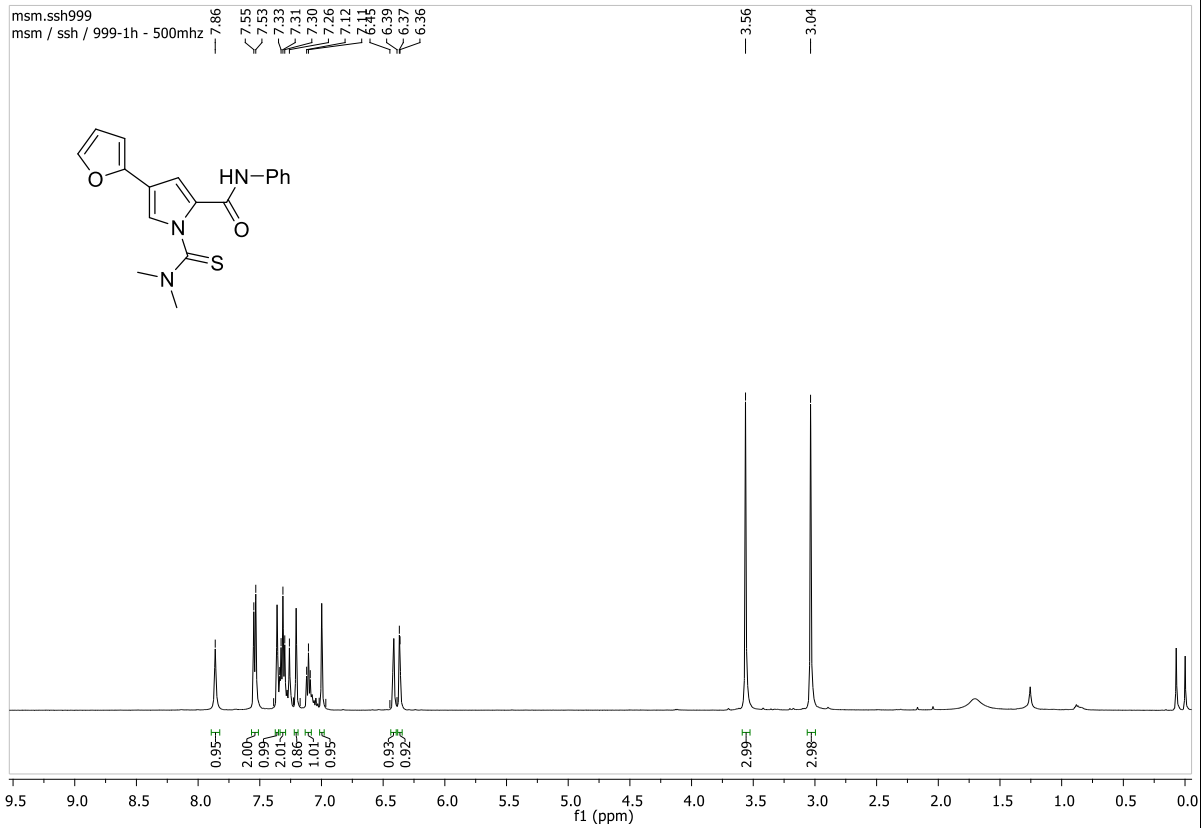


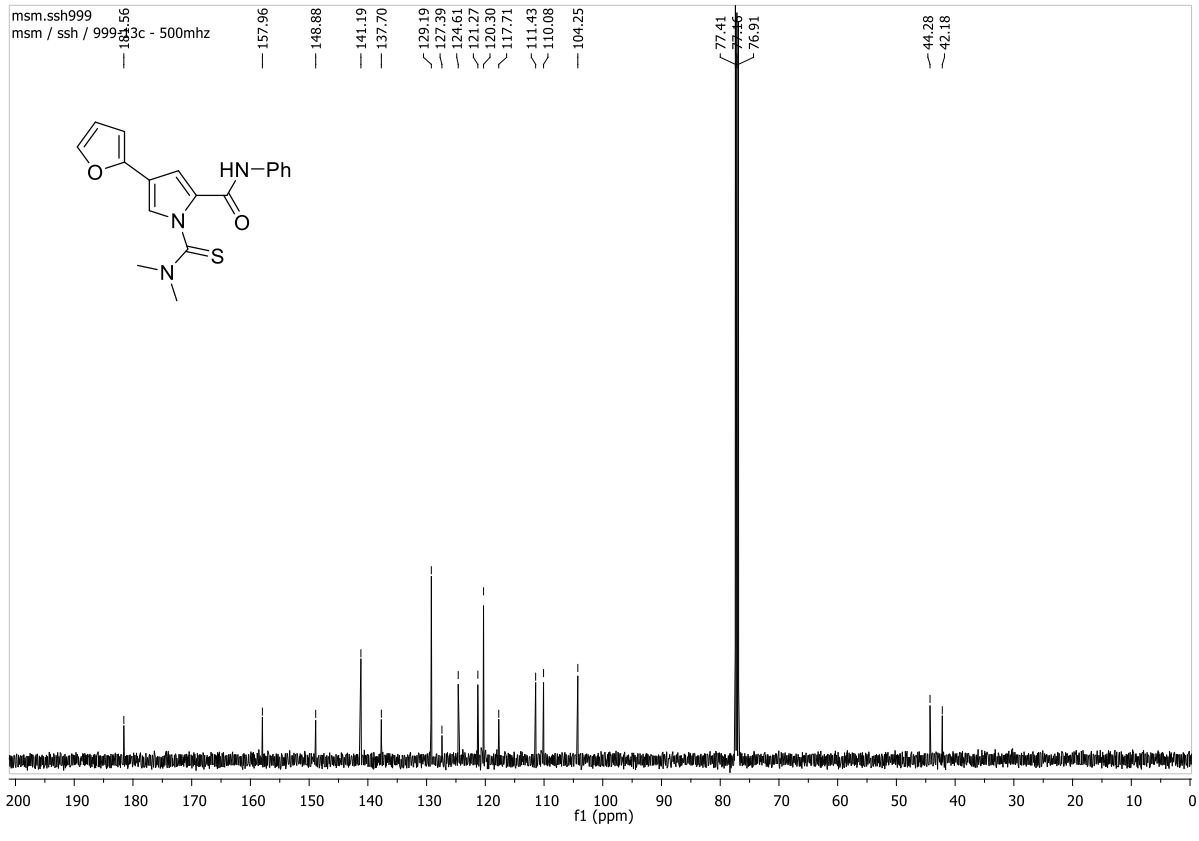
^{1}H NMR and ^{13}C NMR Spectra of Compound **4g**



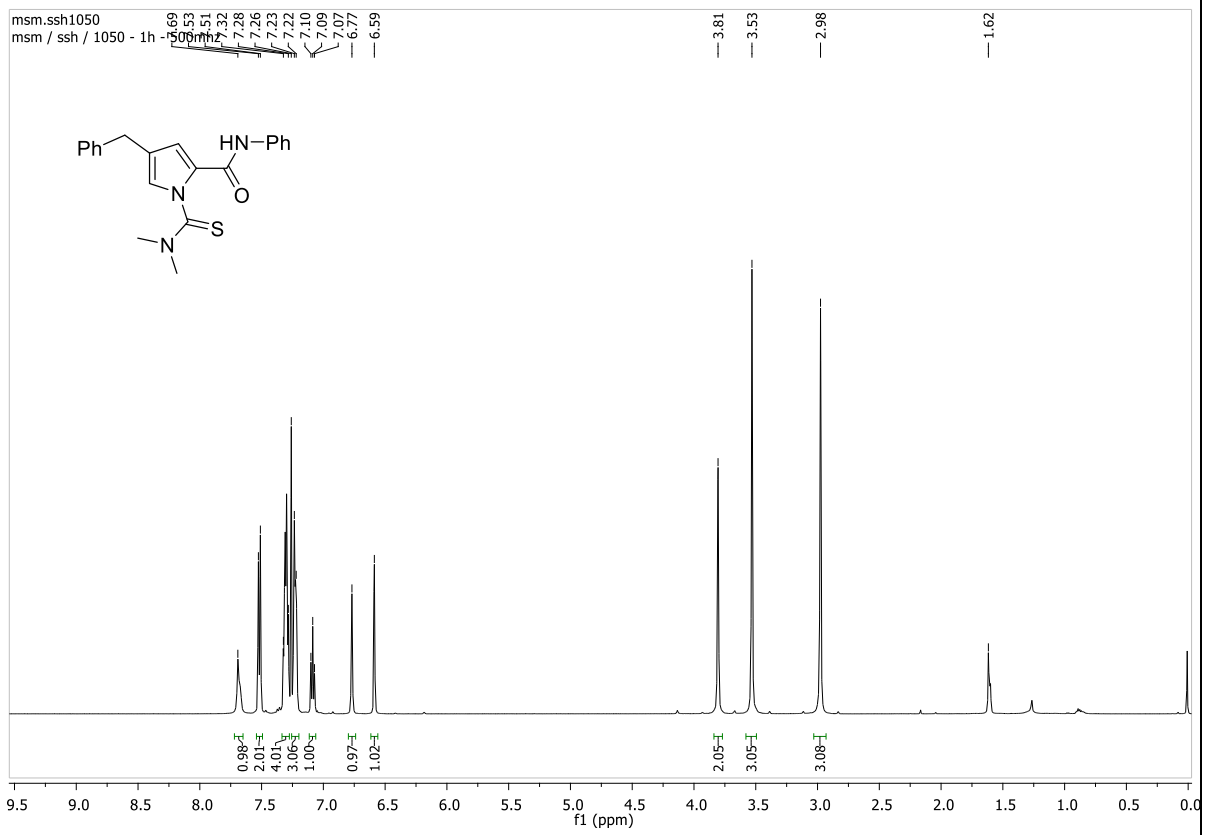


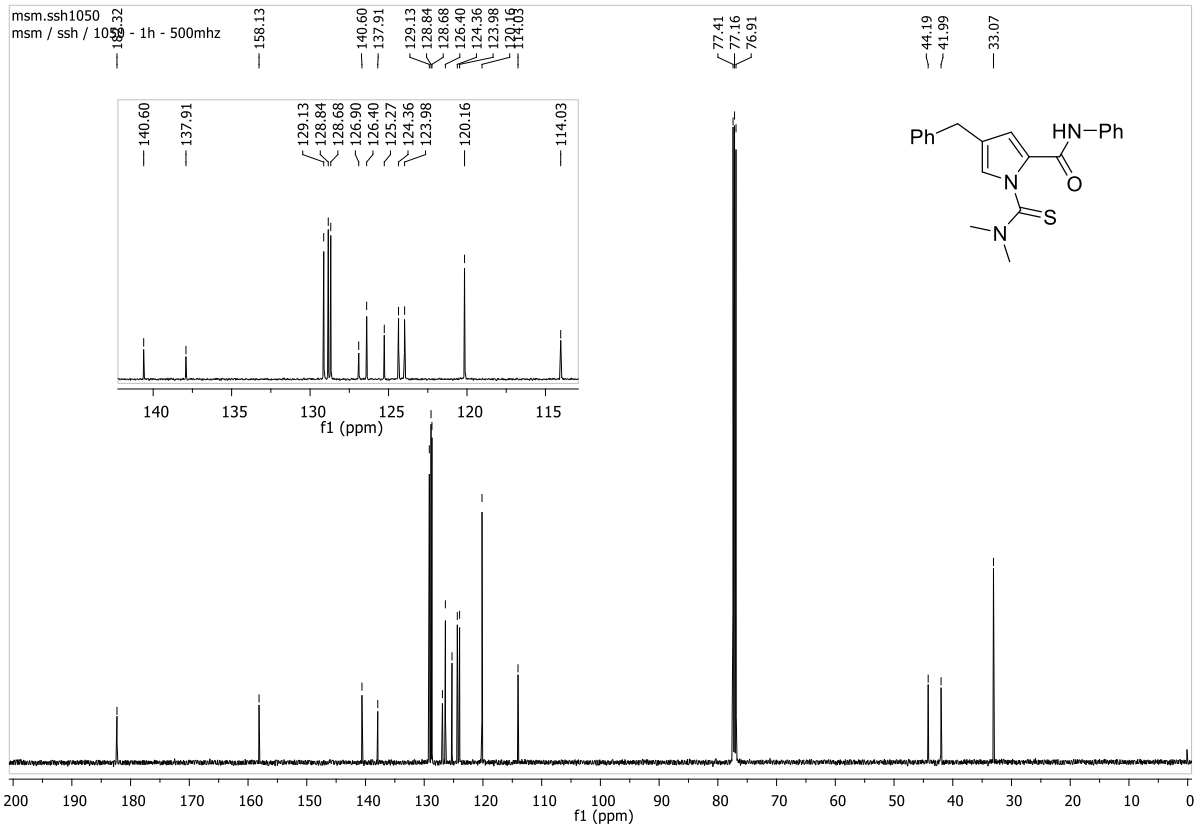
^{1}H NMR and ^{13}C NMR Spectra of Compound **4h**



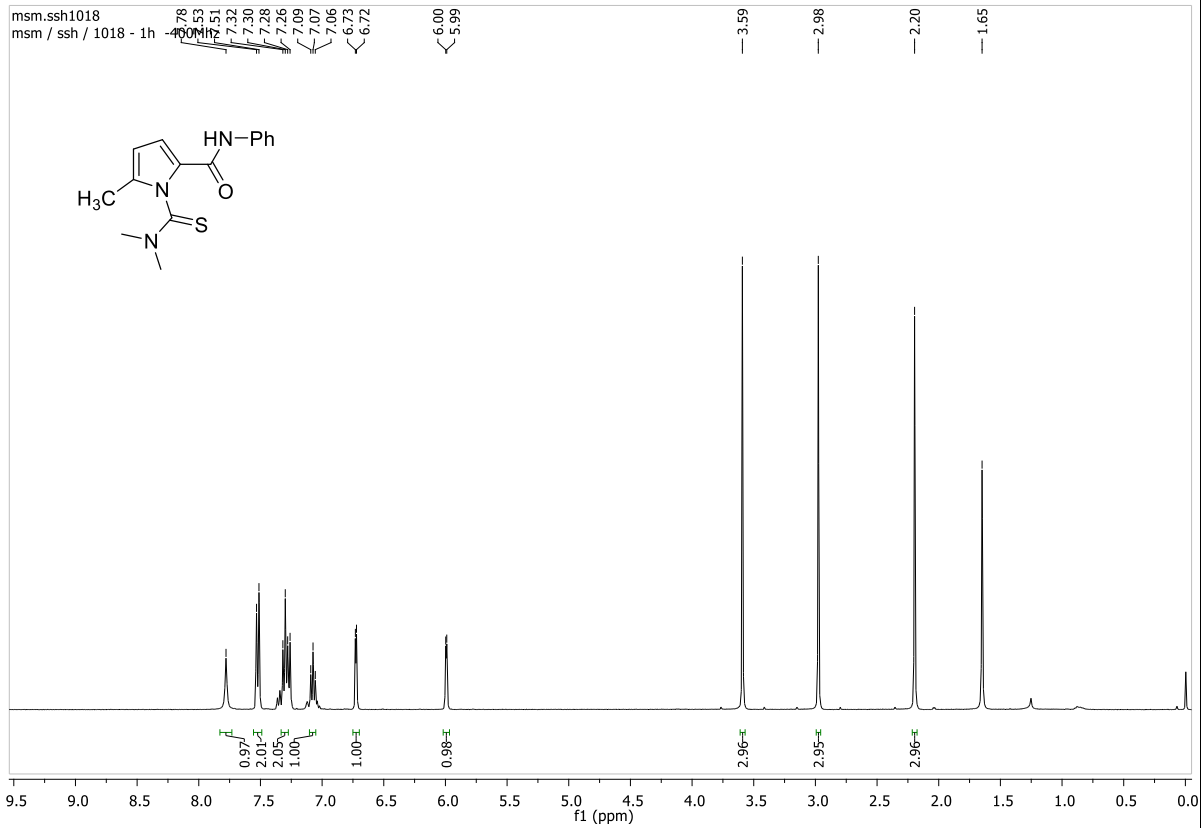


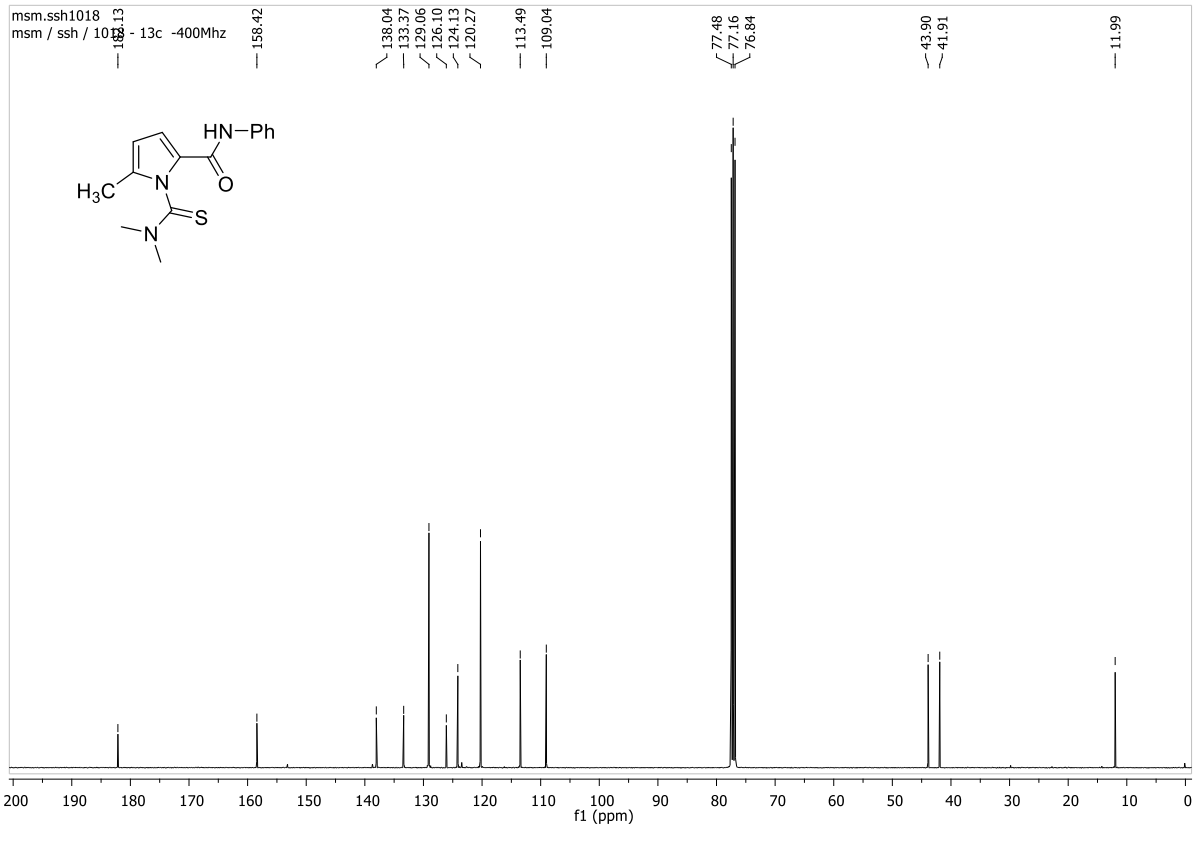
^{1}H NMR and ^{13}C NMR Spectra of Compound **4i**



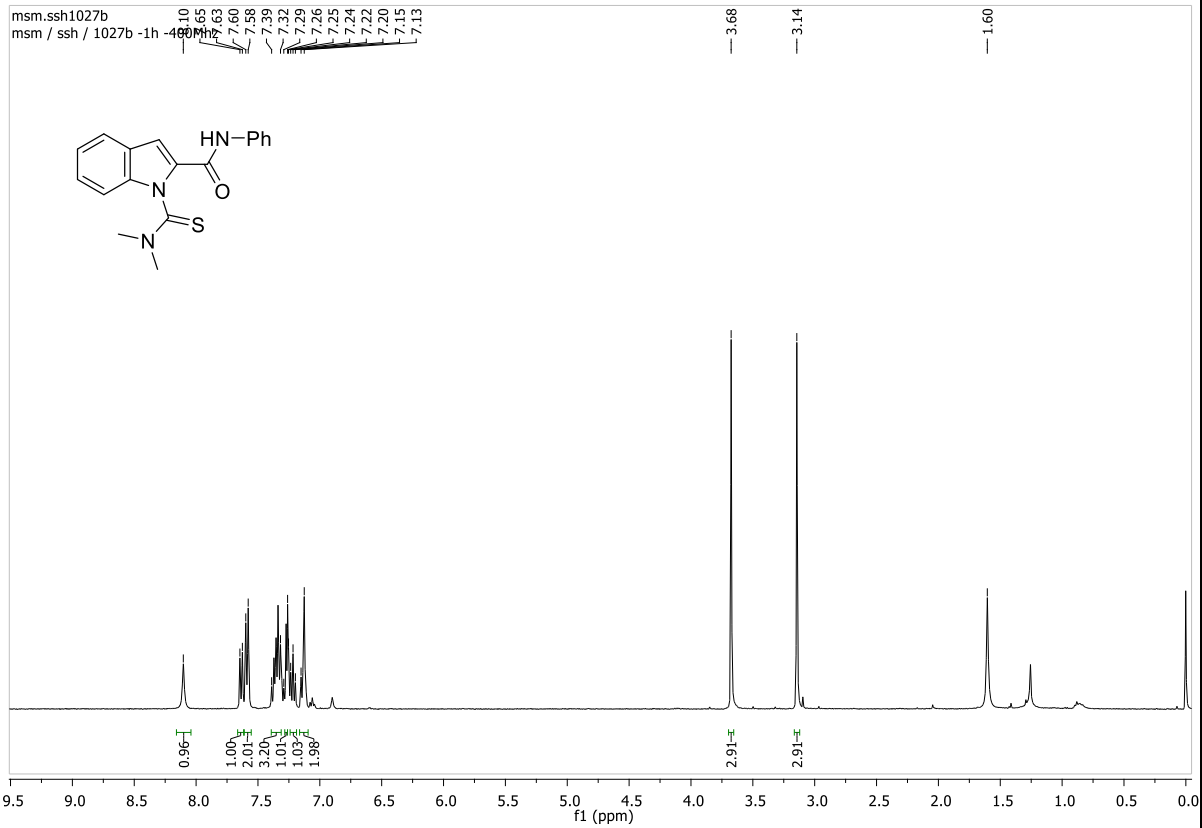


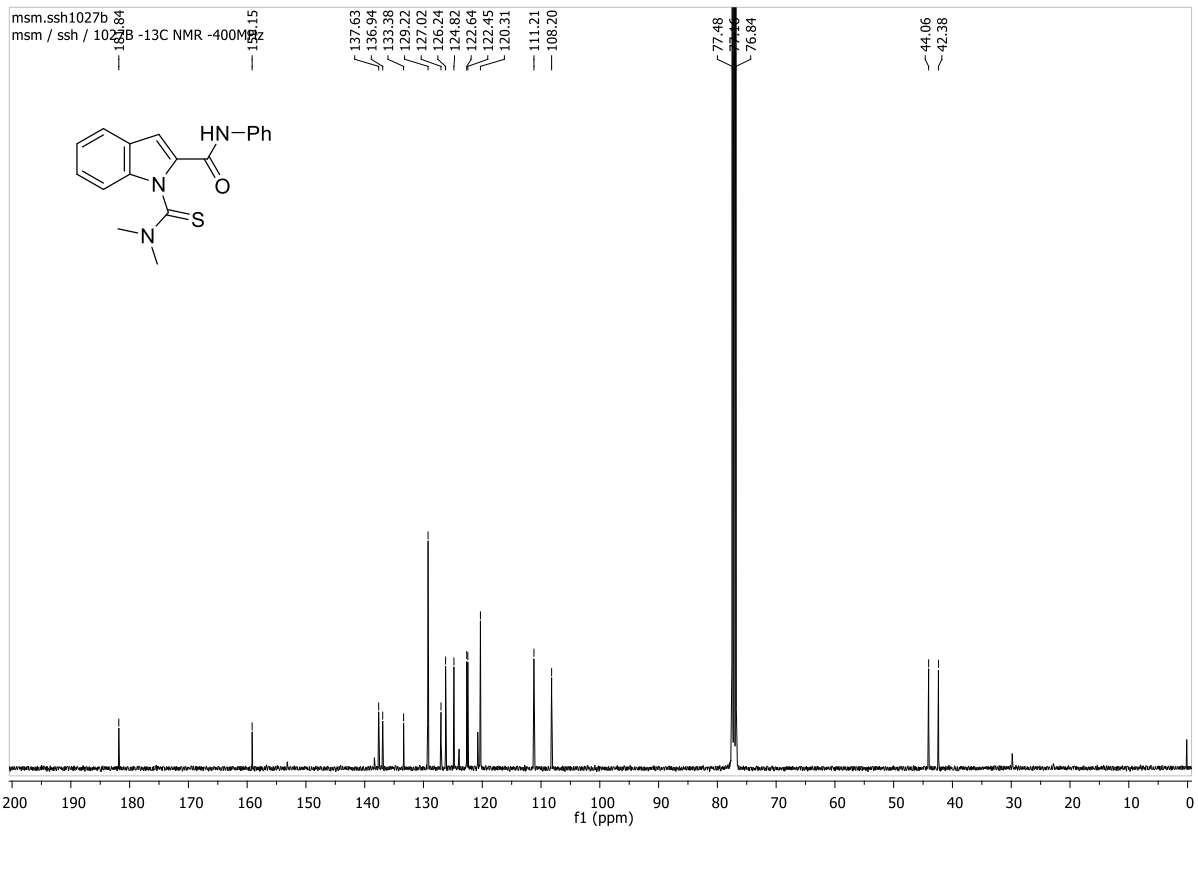
^{1}H NMR and ^{13}C NMR Spectra of Compound **4j**



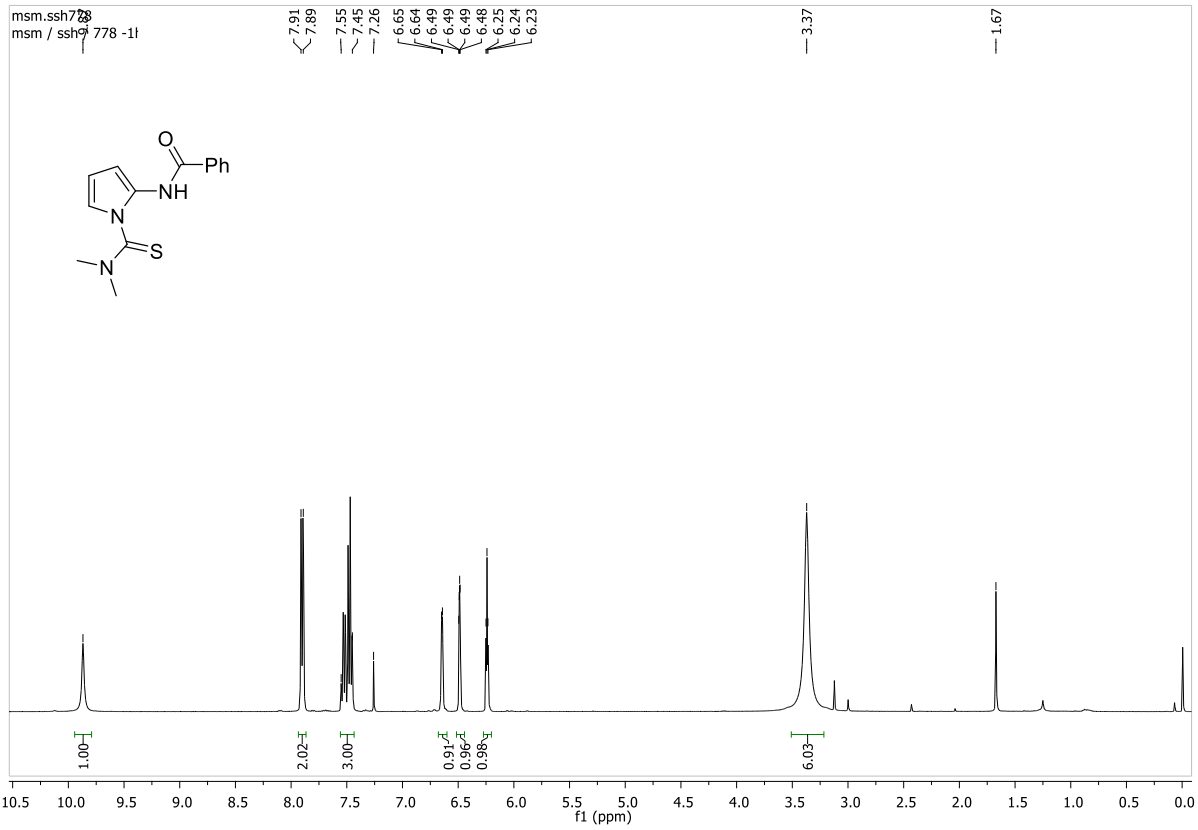


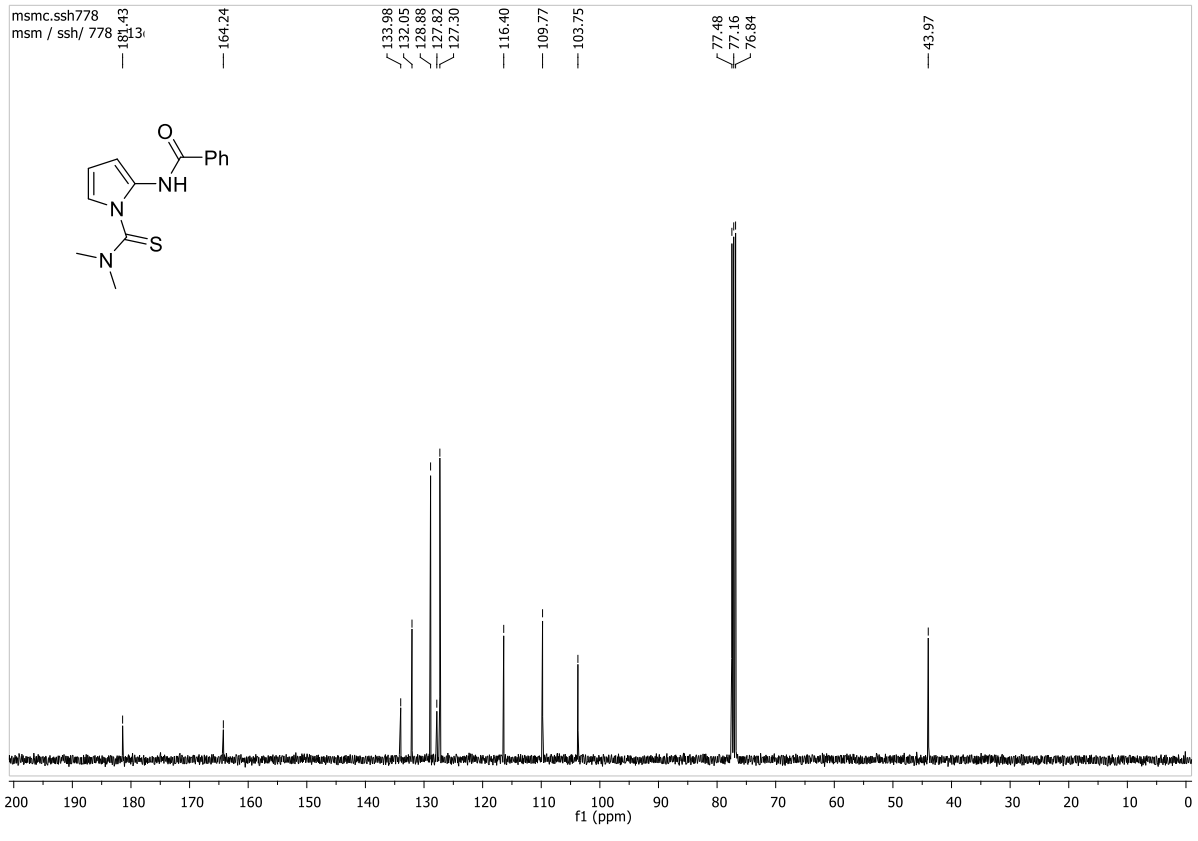
^{1}H NMR and ^{13}C NMR Spectra of Compound **4k**



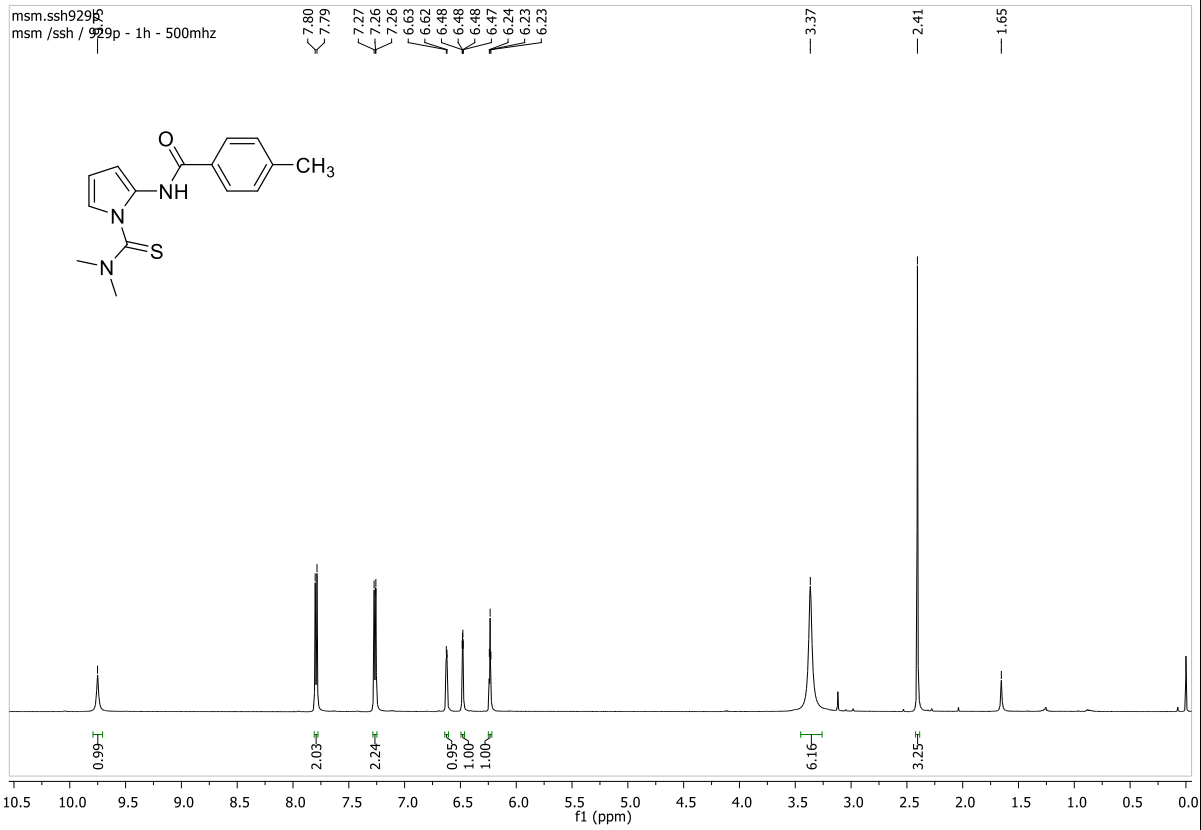


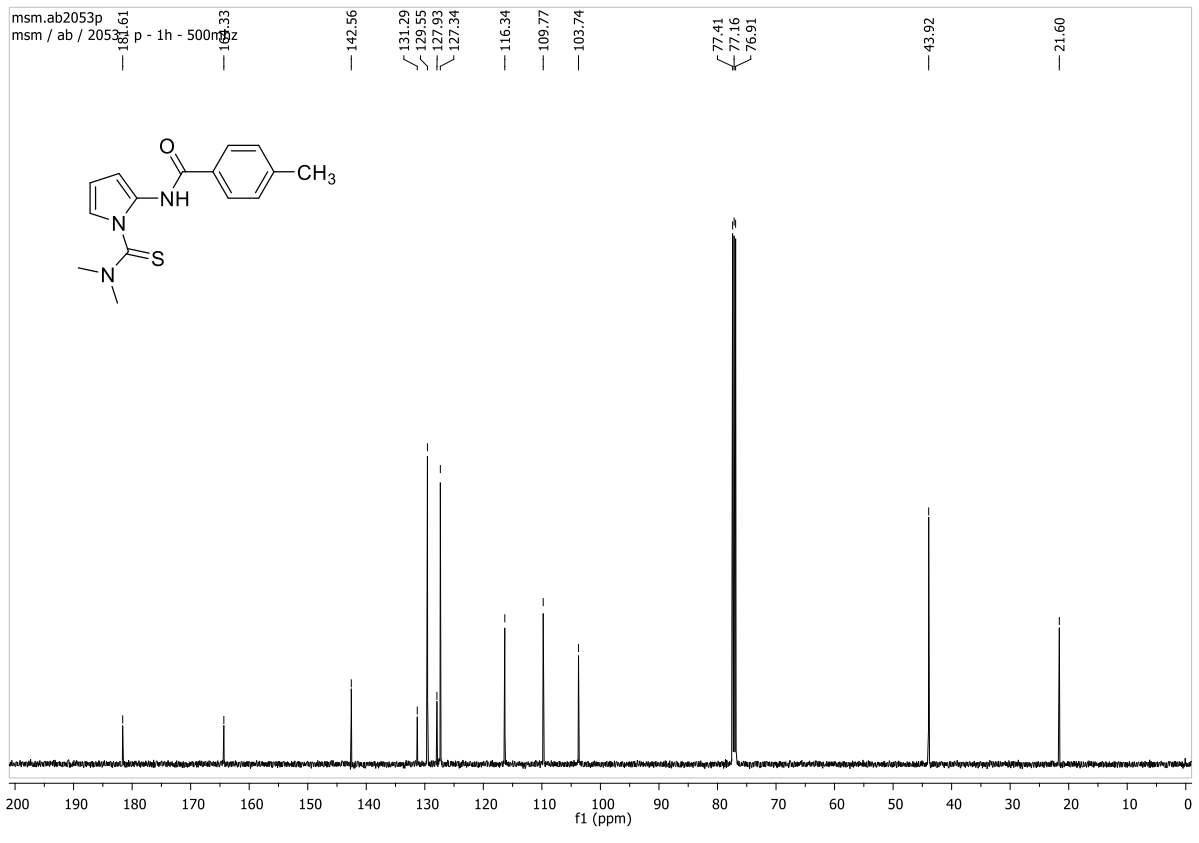
^{1}H NMR and ^{13}C NMR Spectra of Compound **6a**



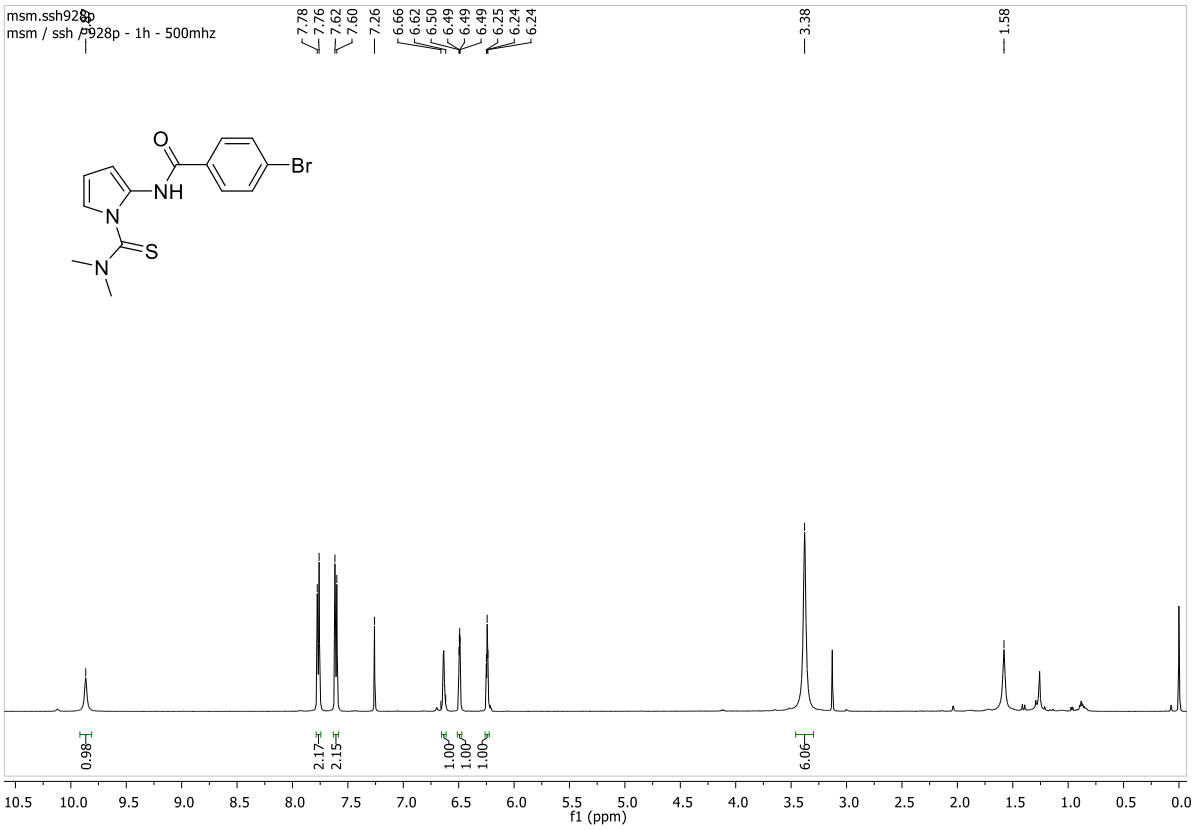


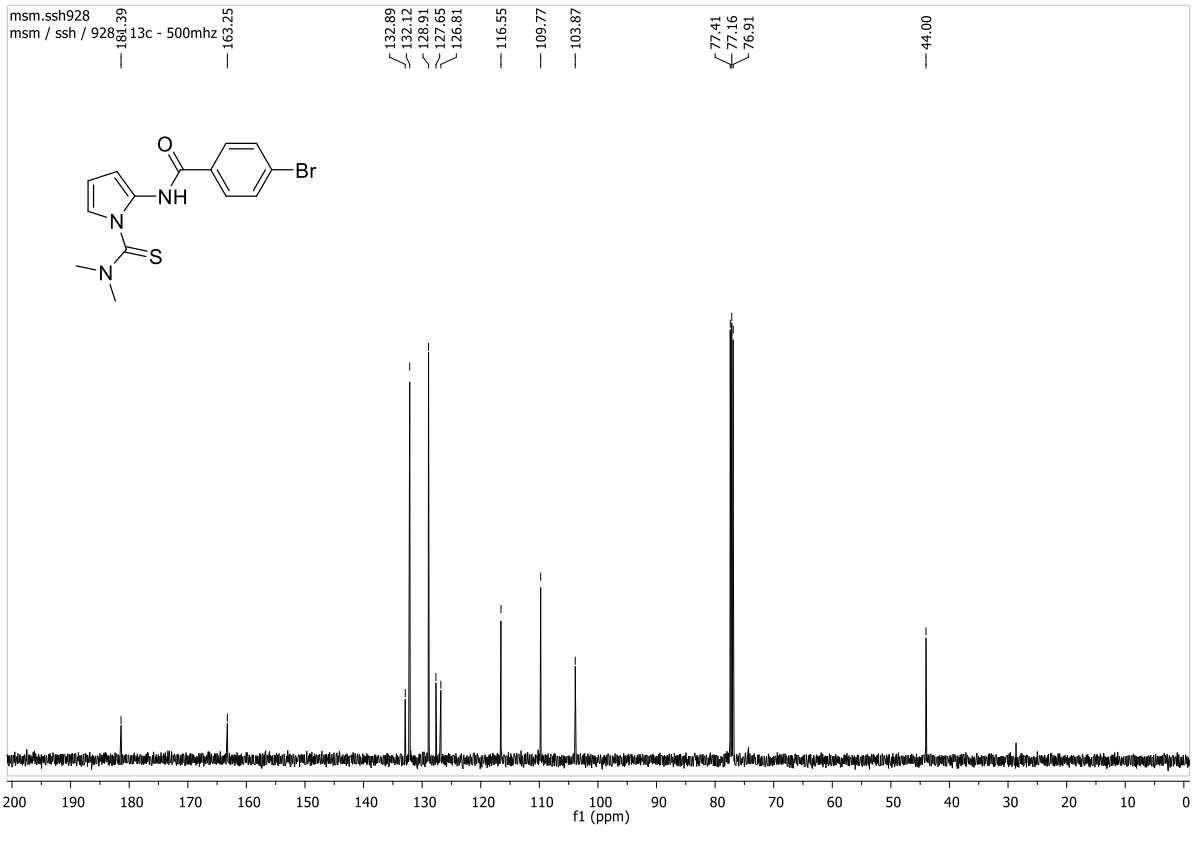
^{1}H NMR and ^{13}C NMR Spectra of Compound **6b**



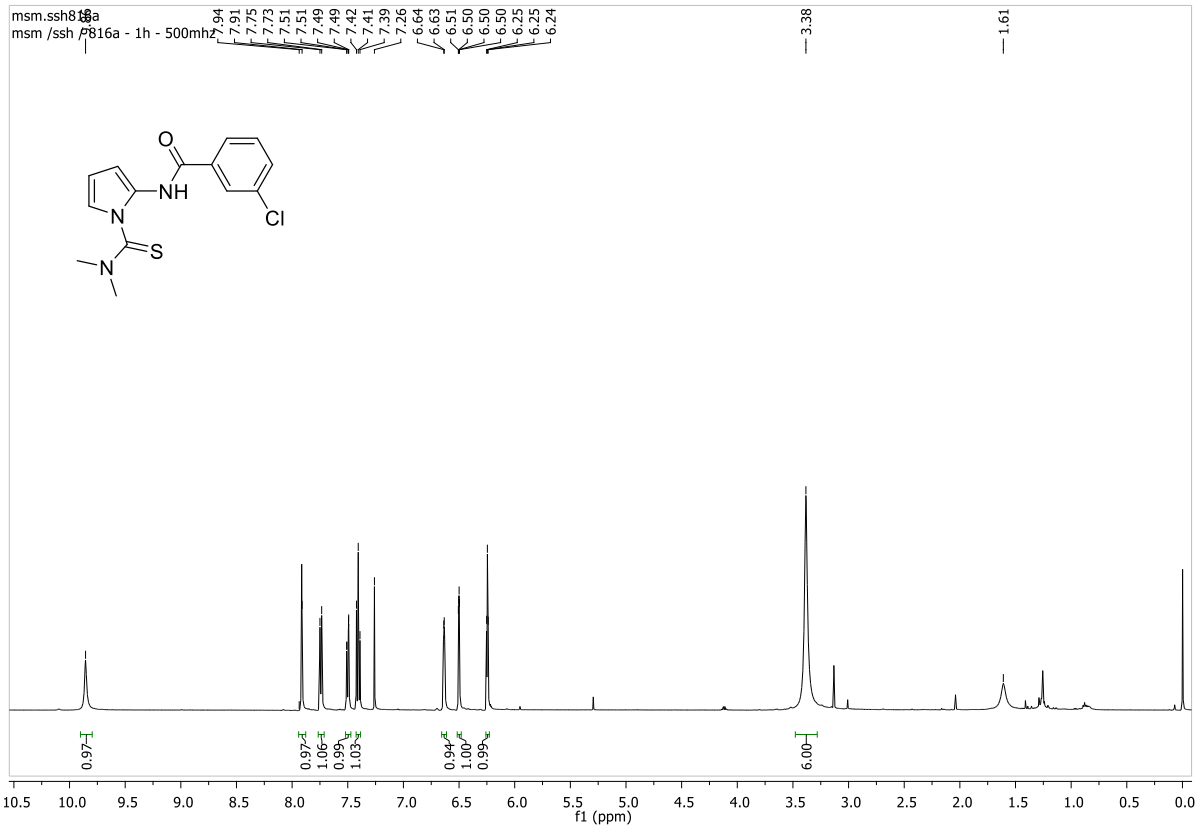


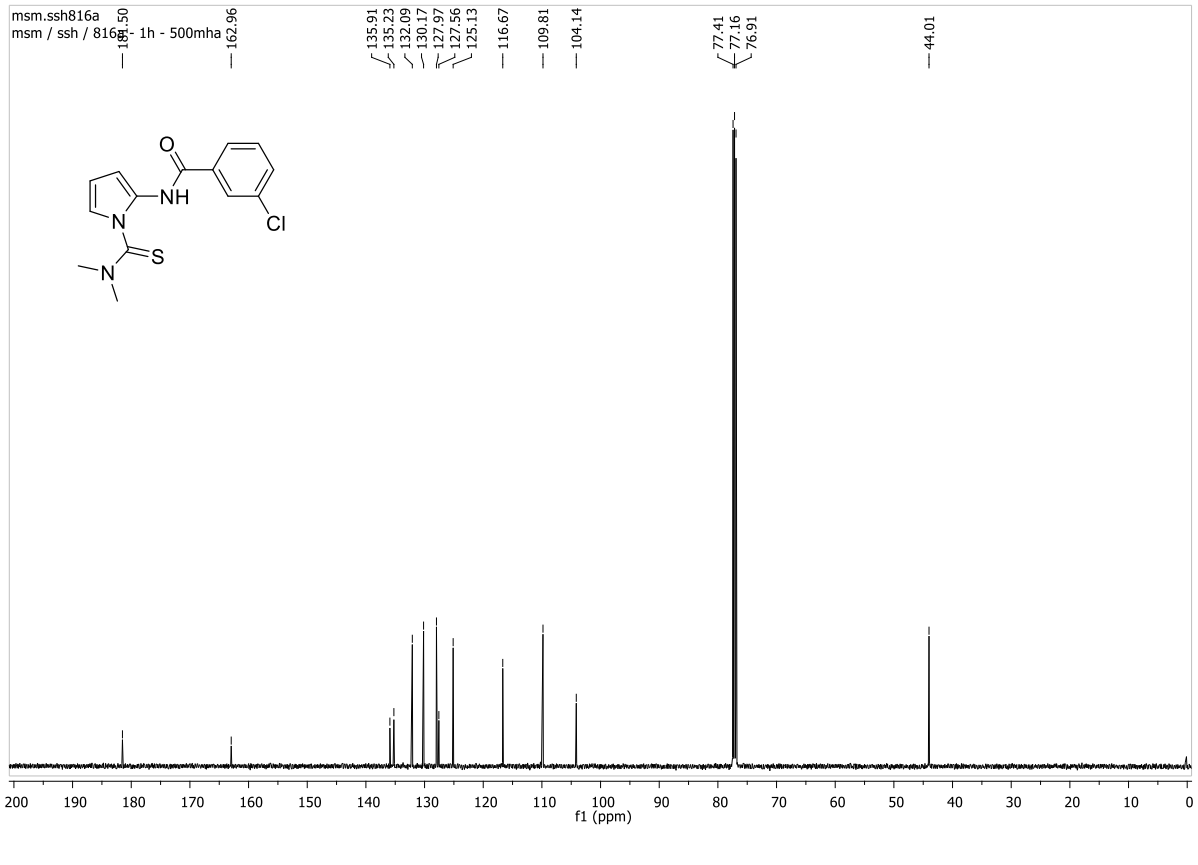
^{1}H NMR and ^{13}C NMR Spectra of Compound **6c**



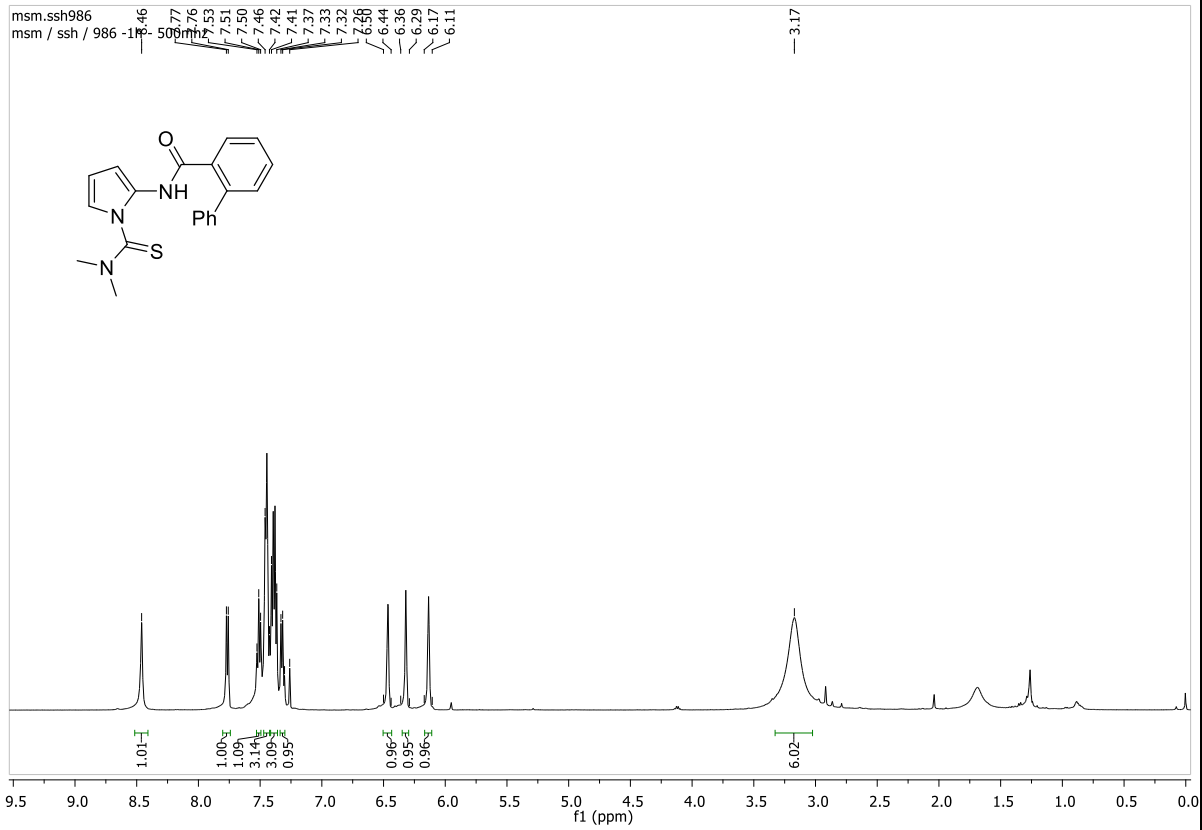


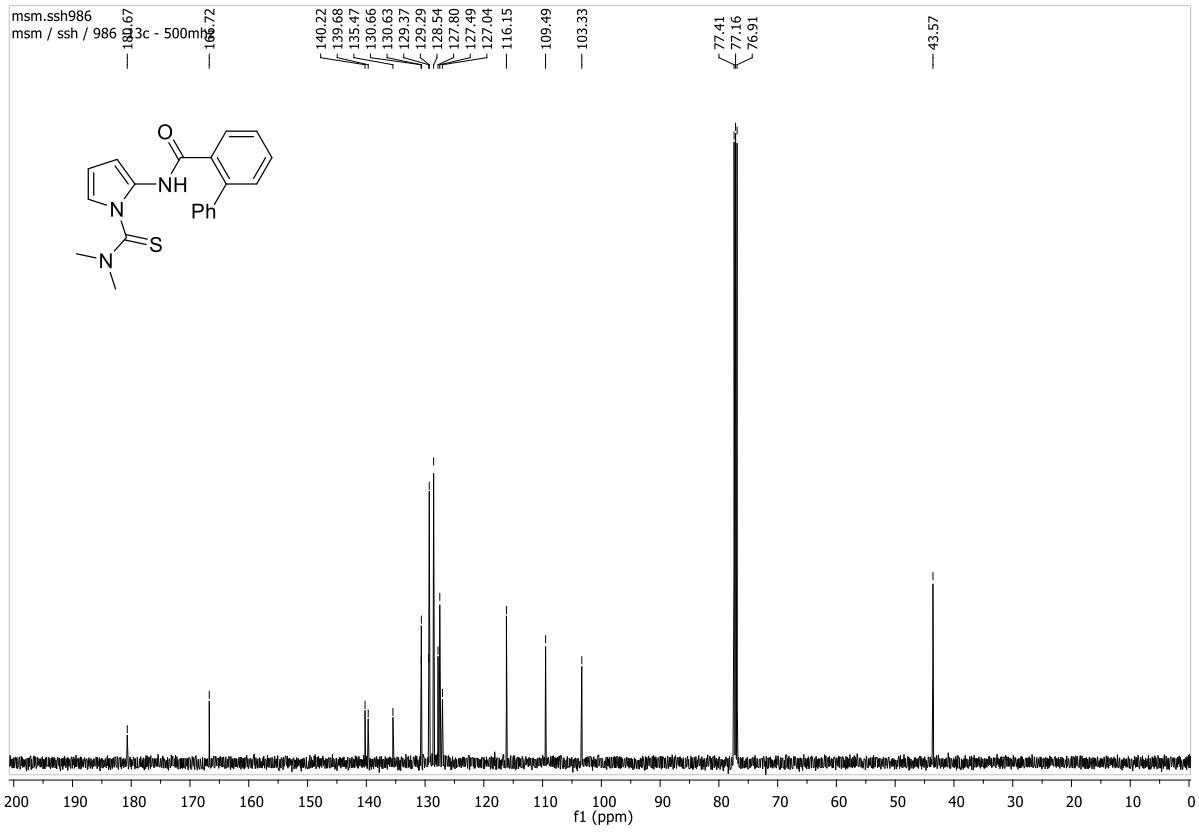
^{1}H NMR and ^{13}C NMR Spectra of Compound **6d**



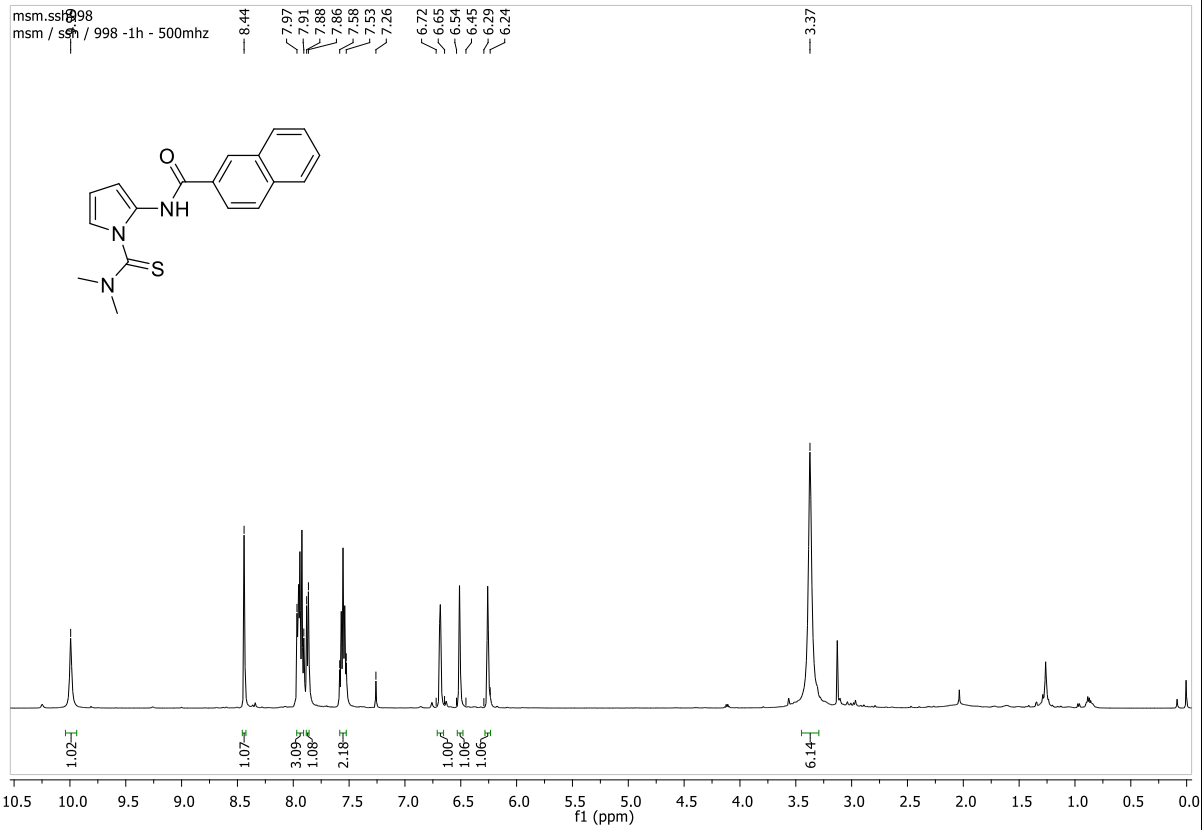


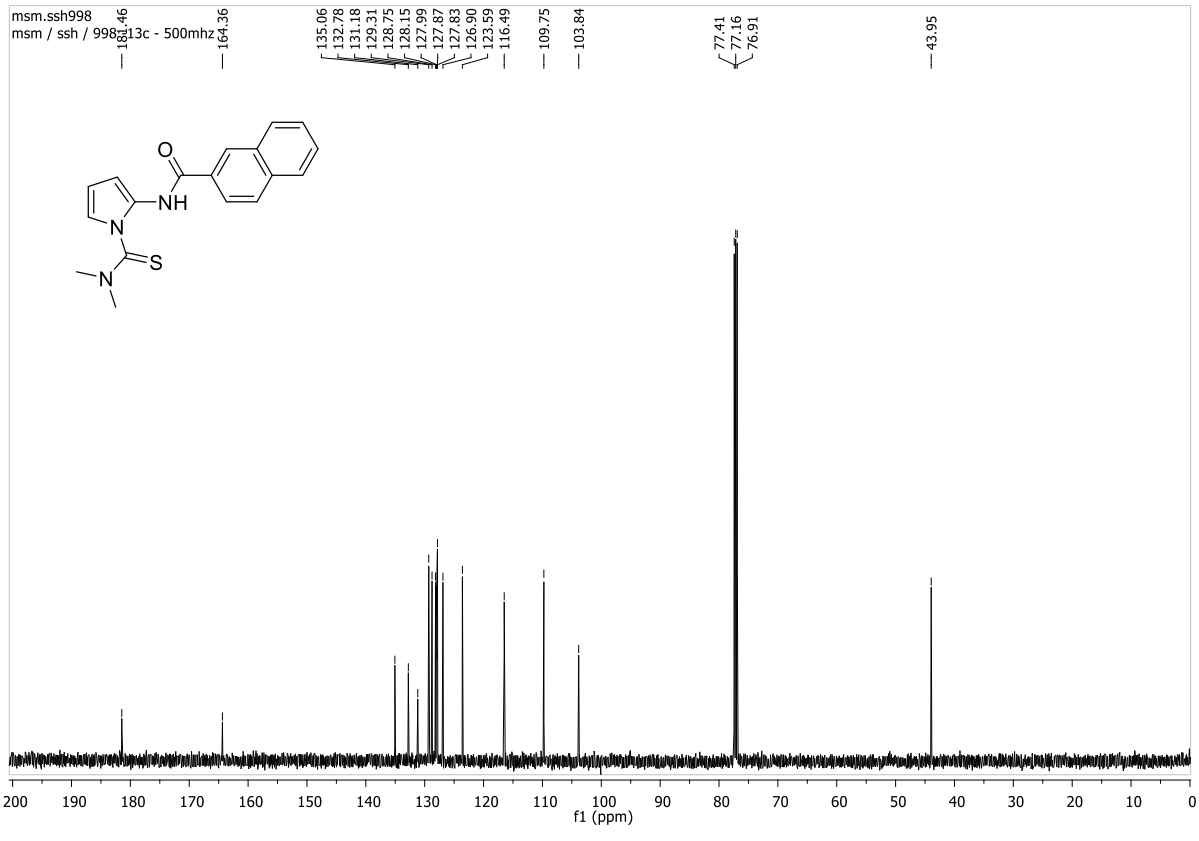
^{1}H NMR and ^{13}C NMR Spectra of Compound **6e**



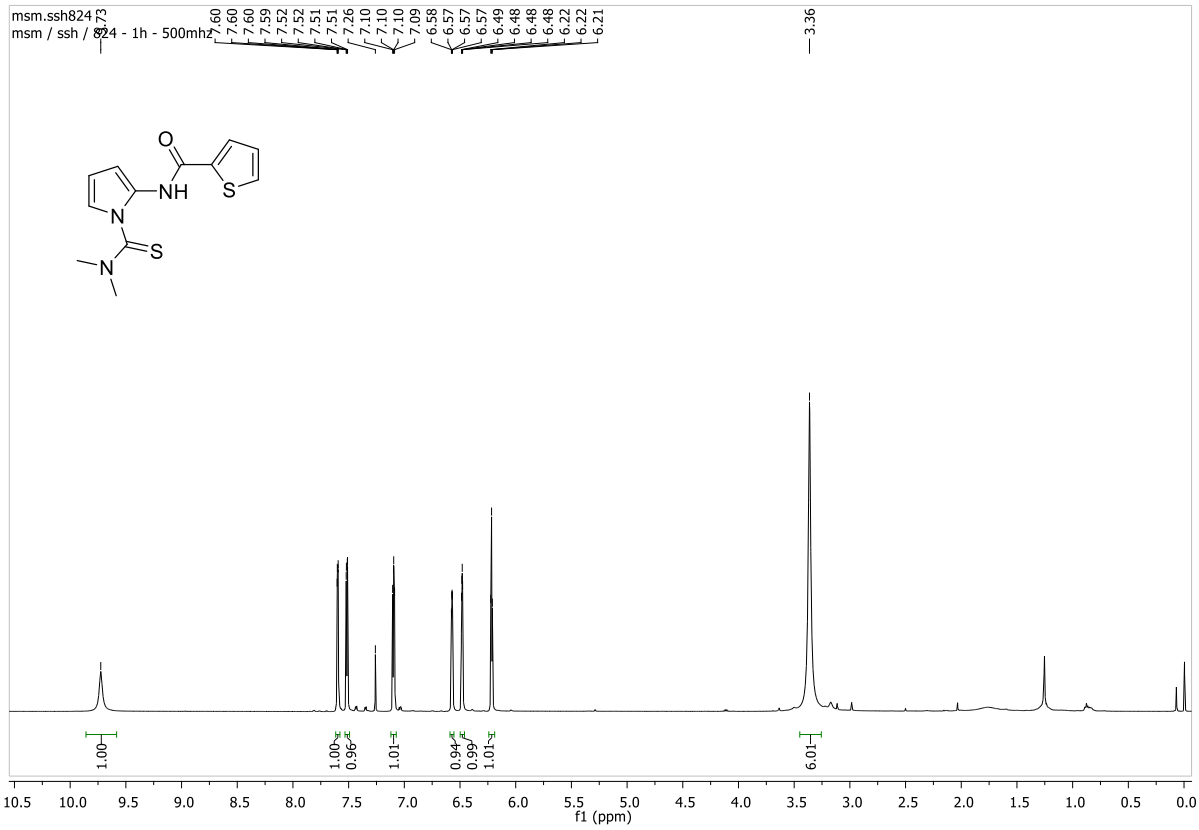


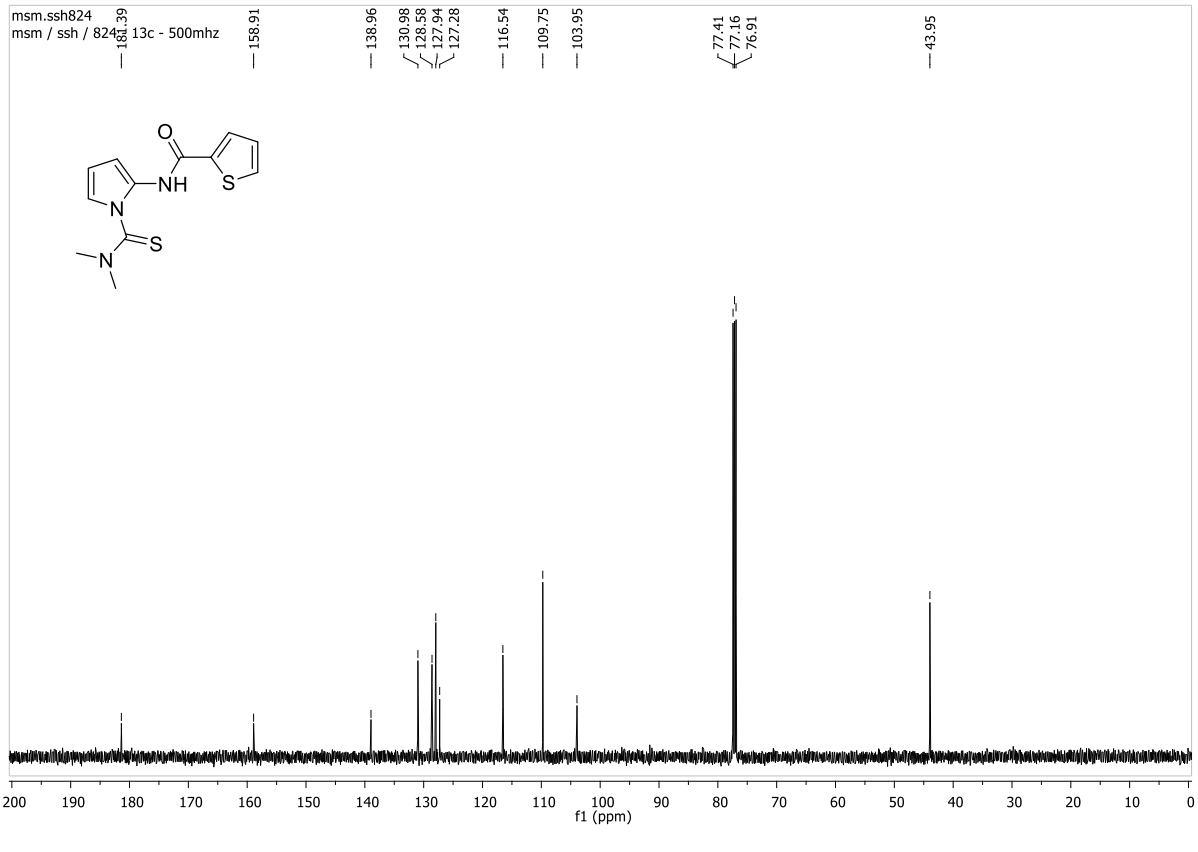
^{1}H NMR and ^{13}C NMR Spectra of Compound **6f**



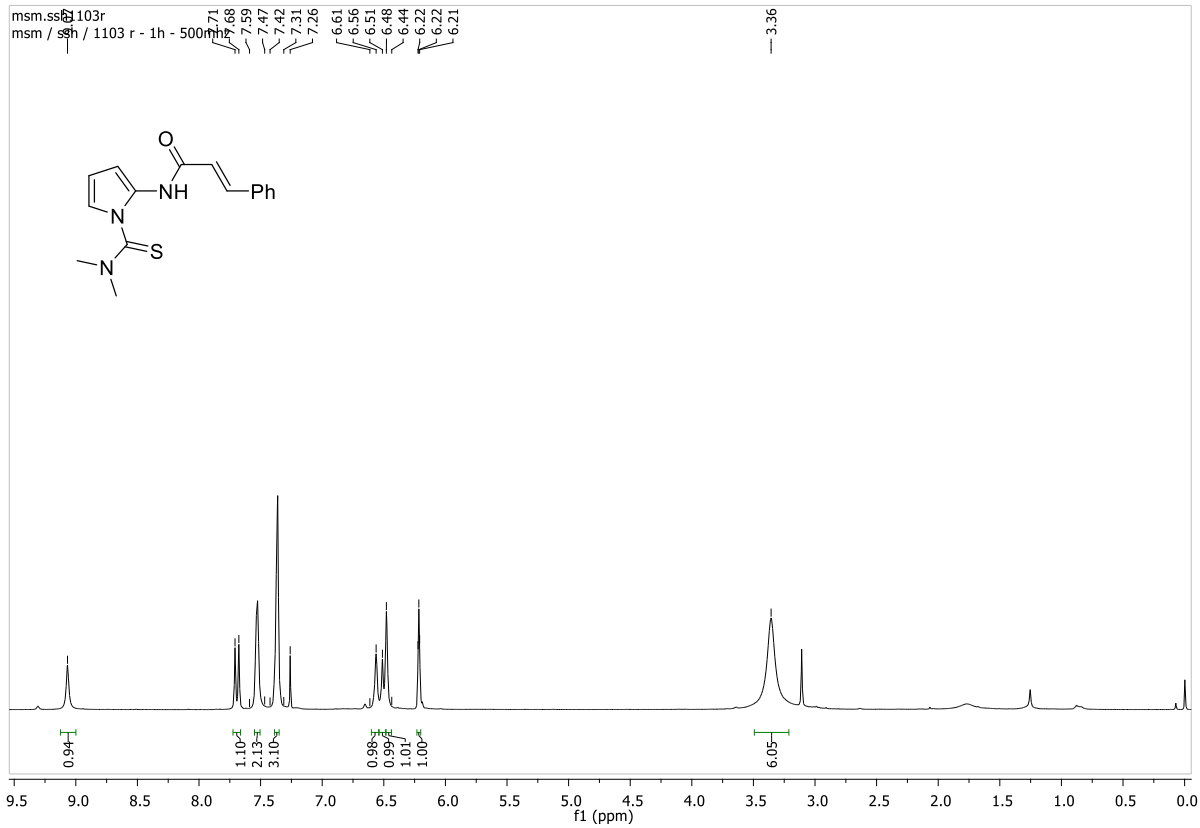


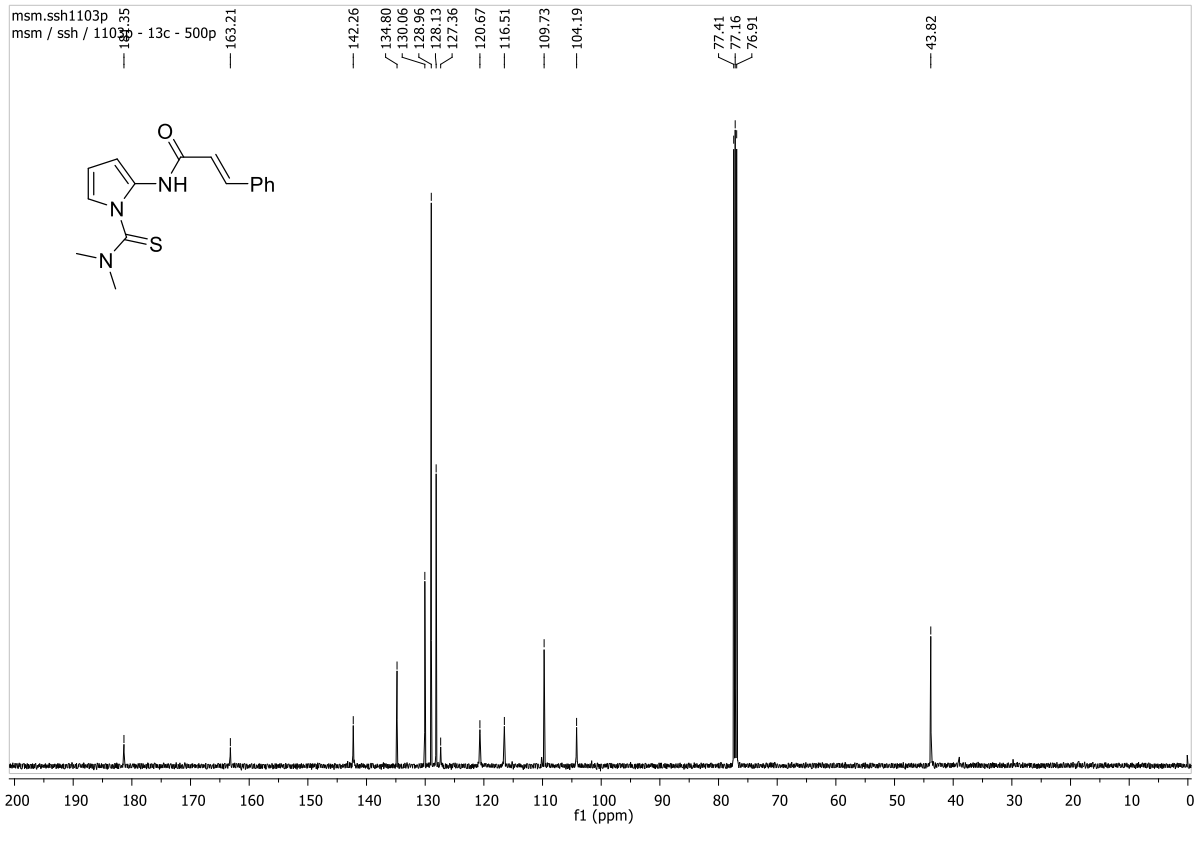
^{1}H NMR and ^{13}C NMR Spectra of Compound **6g**



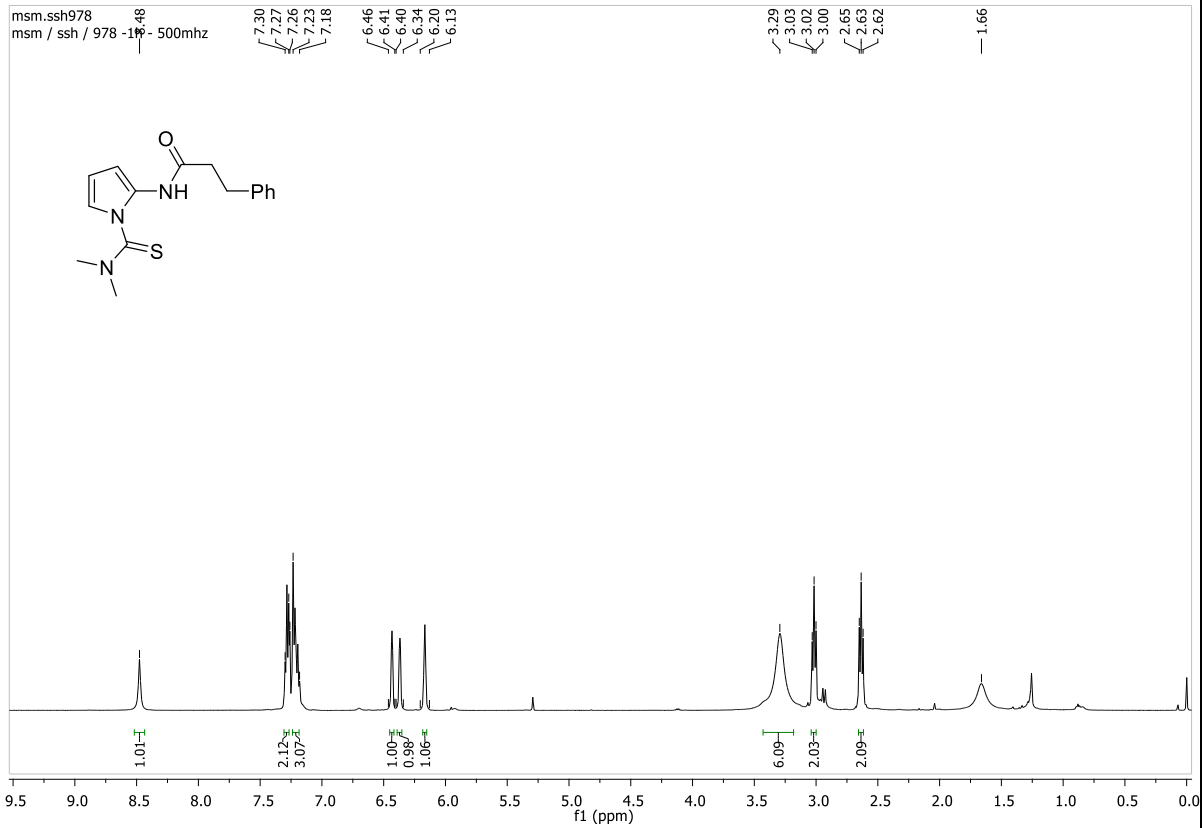


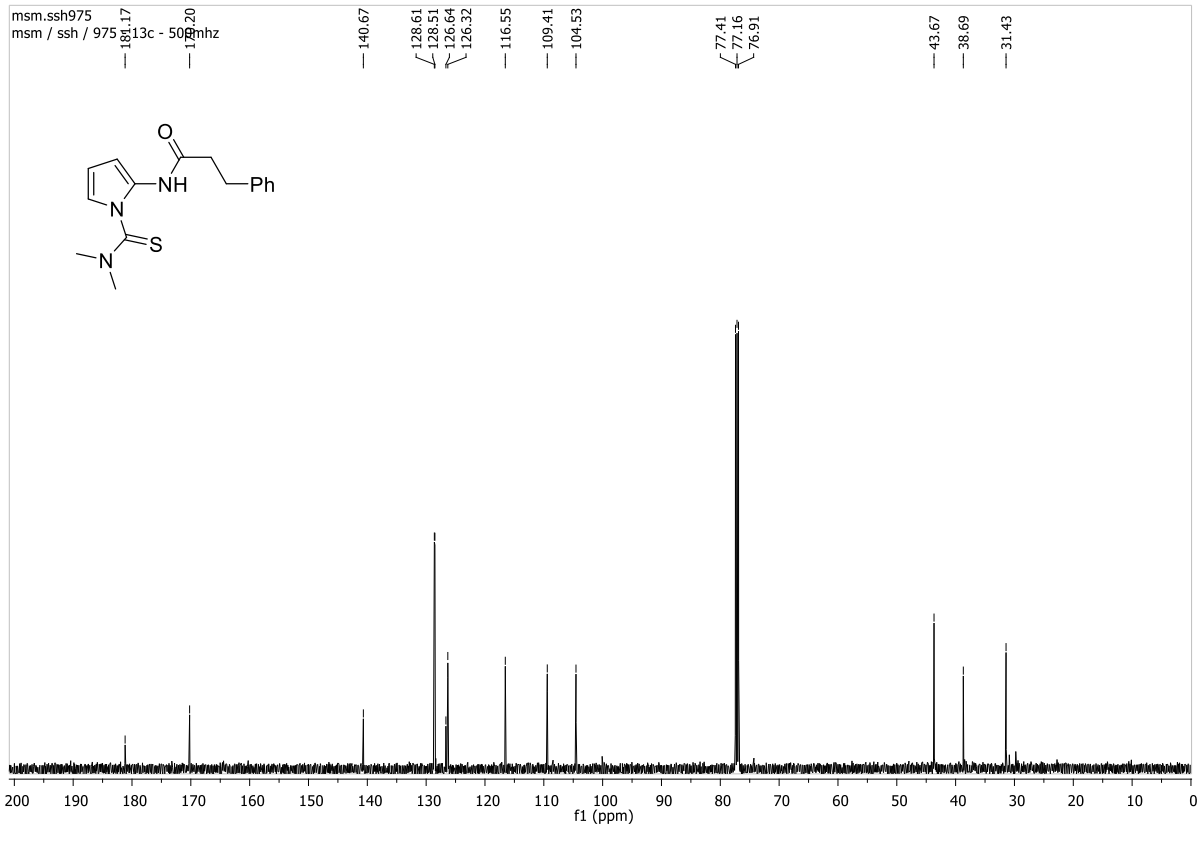
^{1}H NMR and ^{13}C NMR Spectra of Compound **6h**



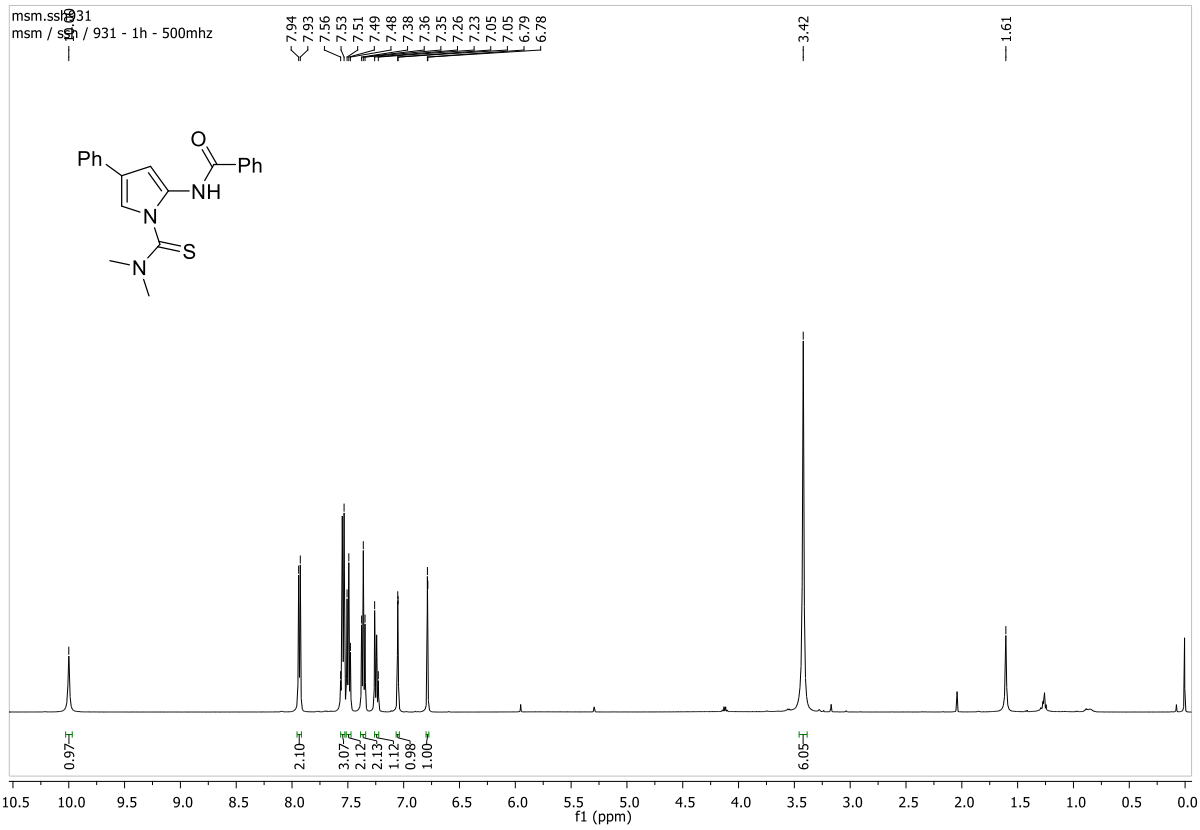


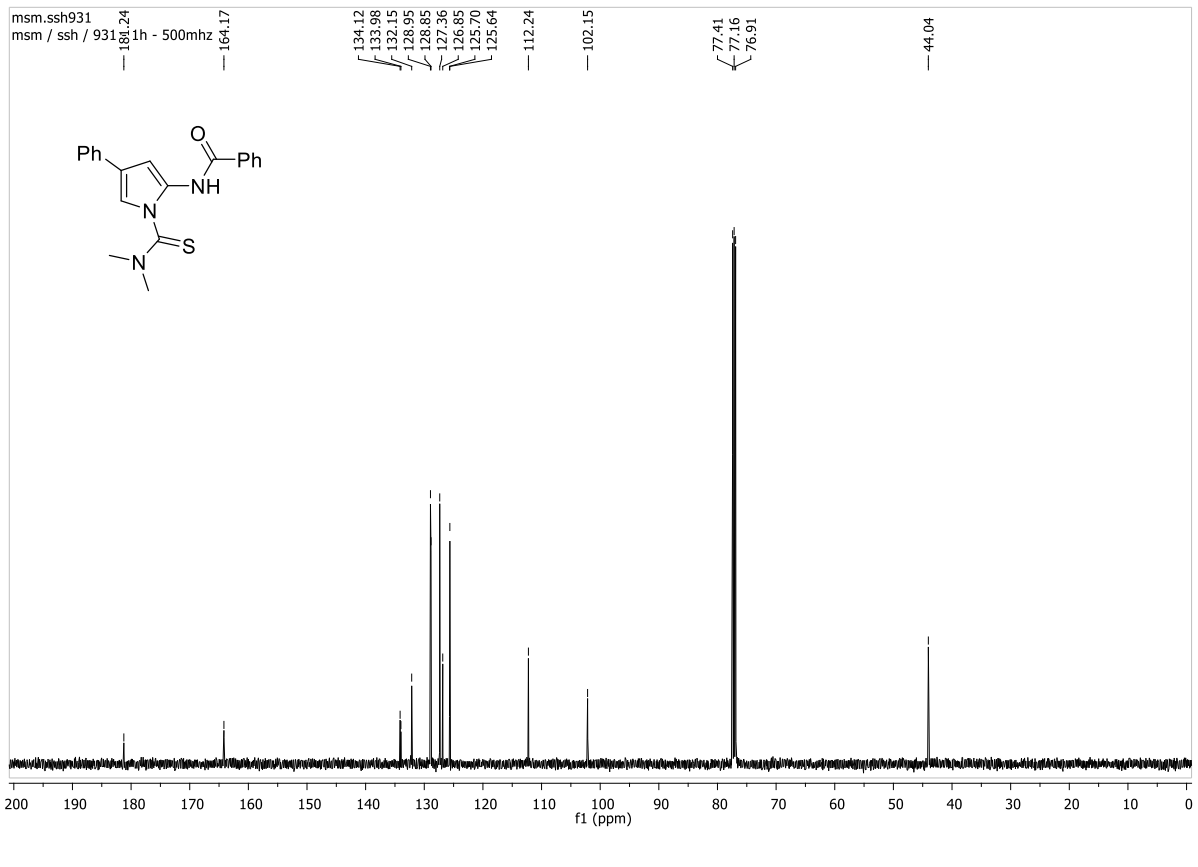
^{1}H NMR and ^{13}C NMR Spectra of Compound **6i**



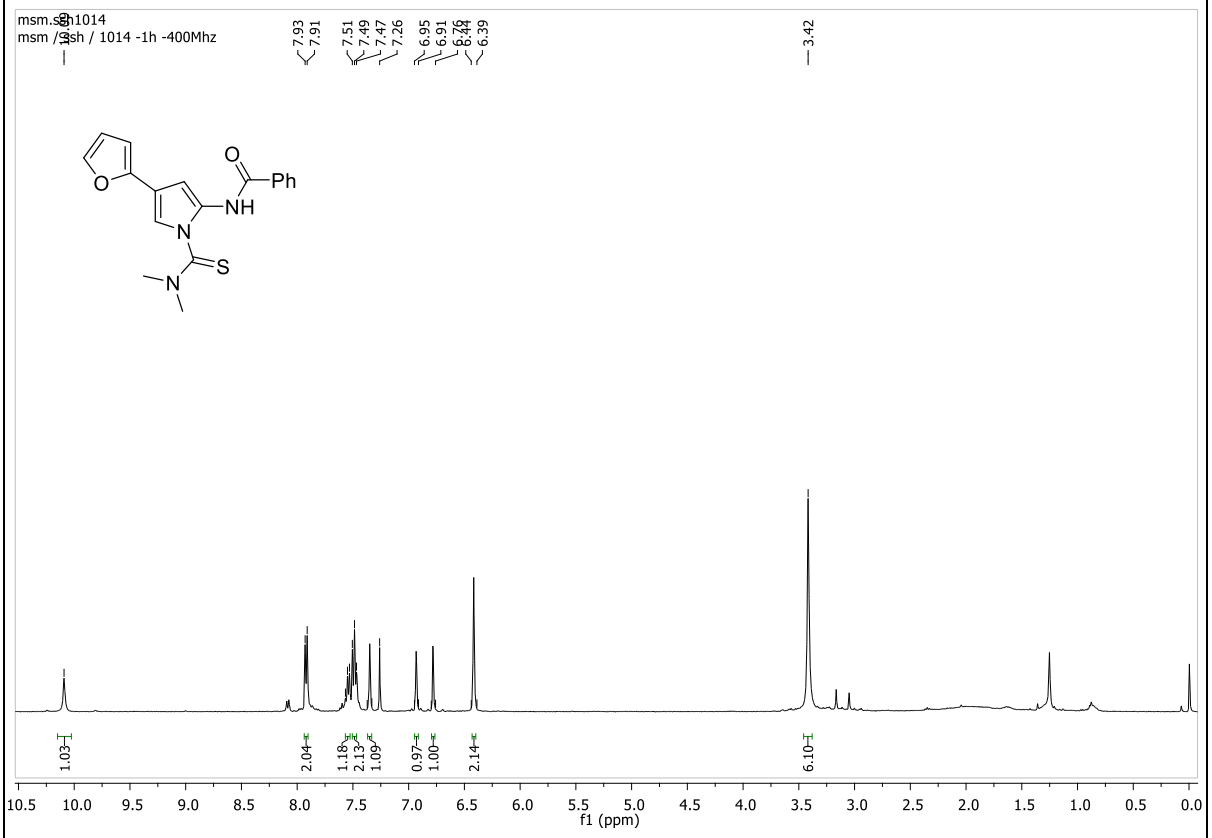


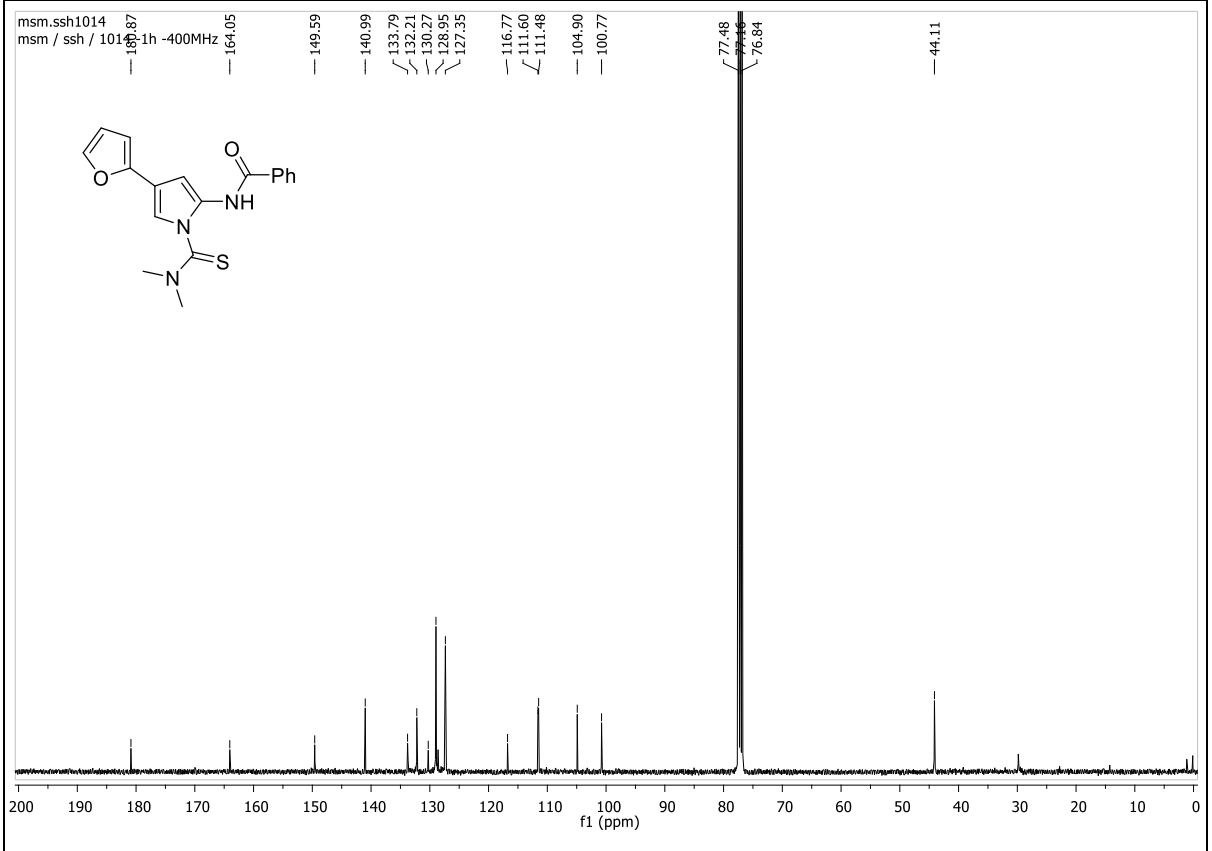
^{1}H NMR and ^{13}C NMR Spectra of Compound **6j**



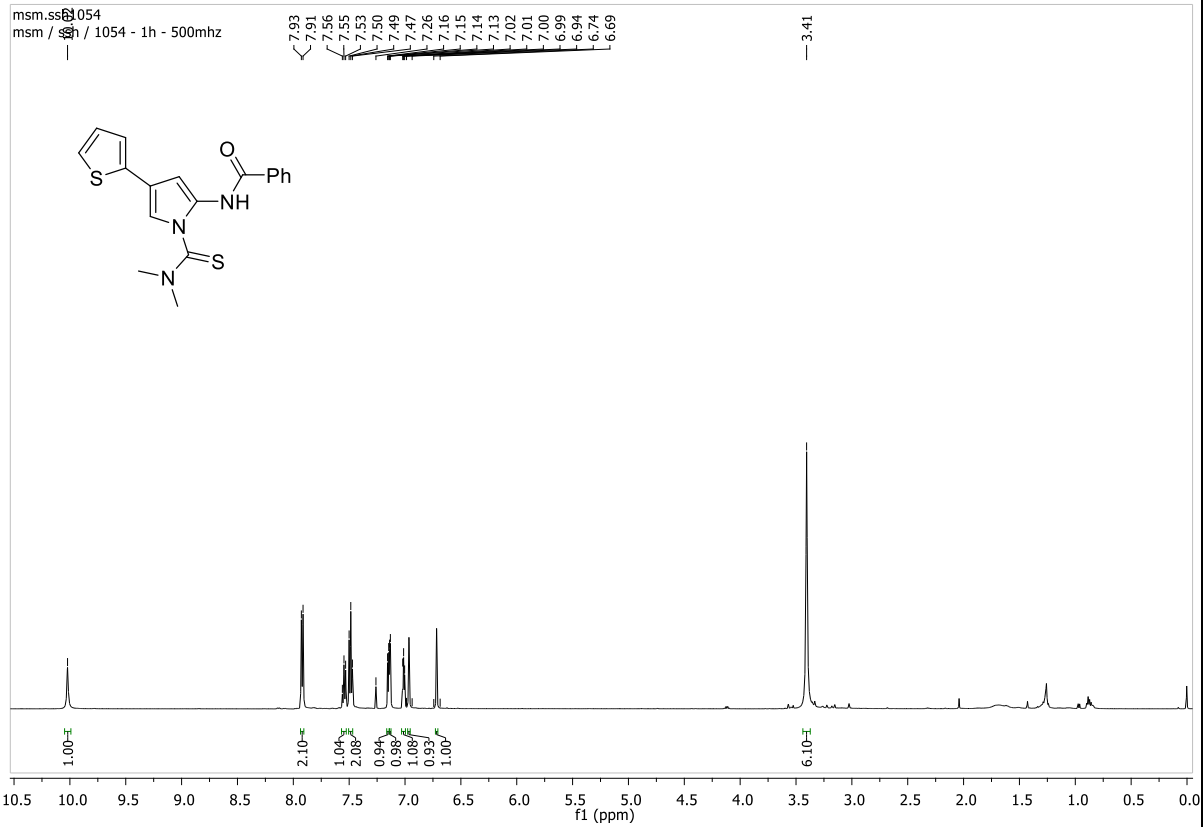


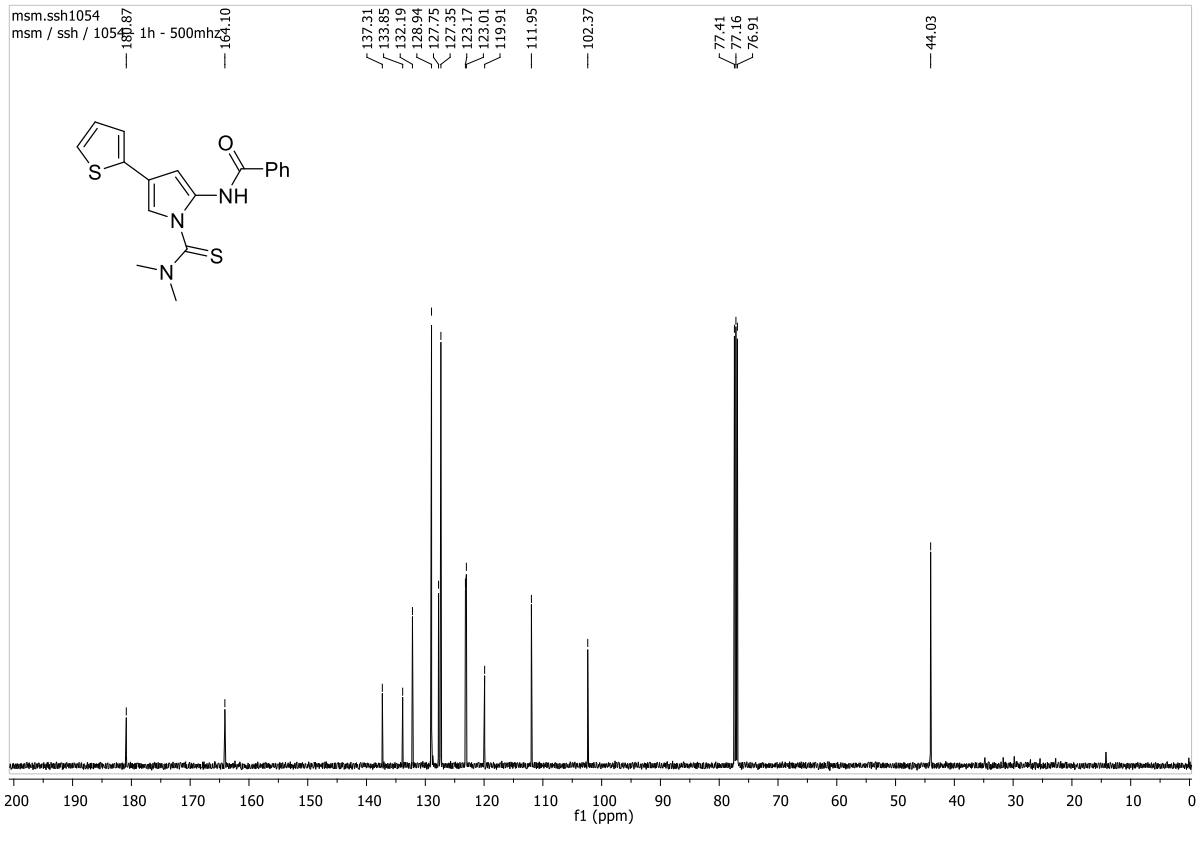
^{1}H NMR and ^{13}C NMR Spectra of Compound **6k**



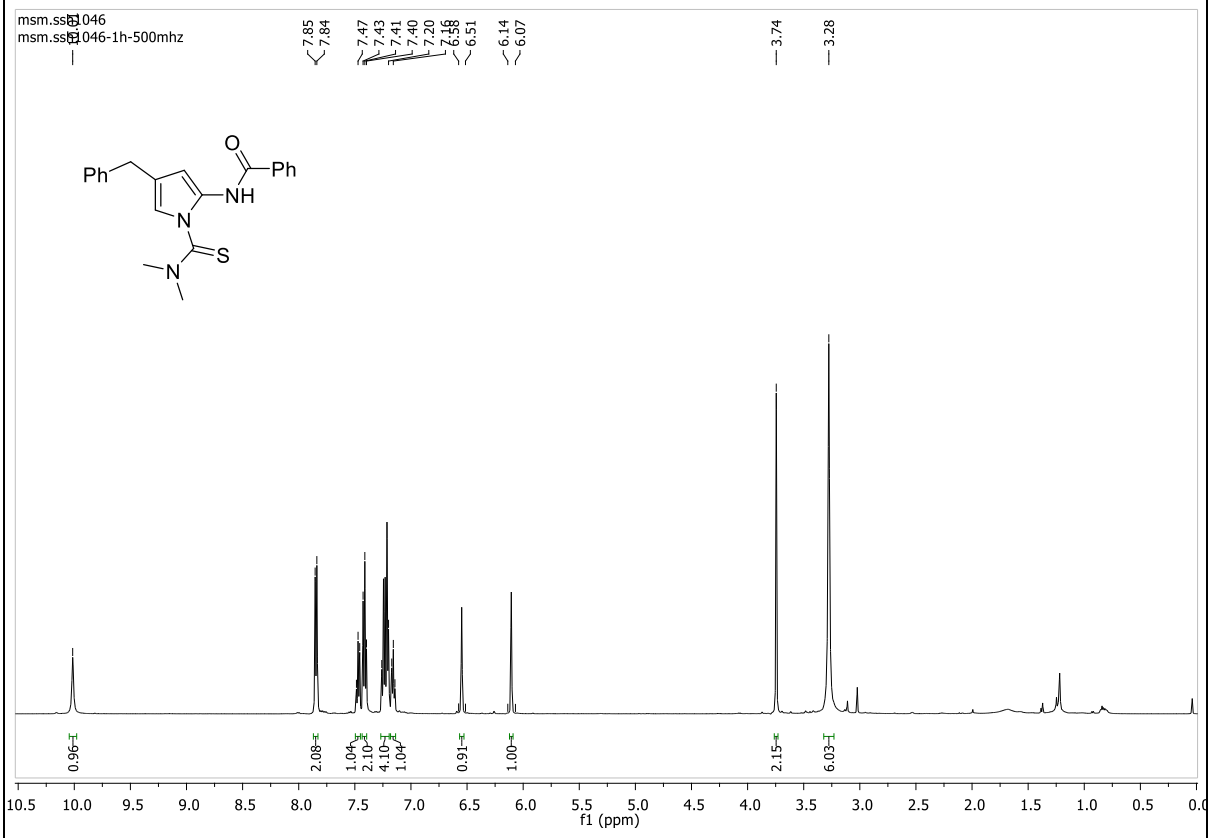


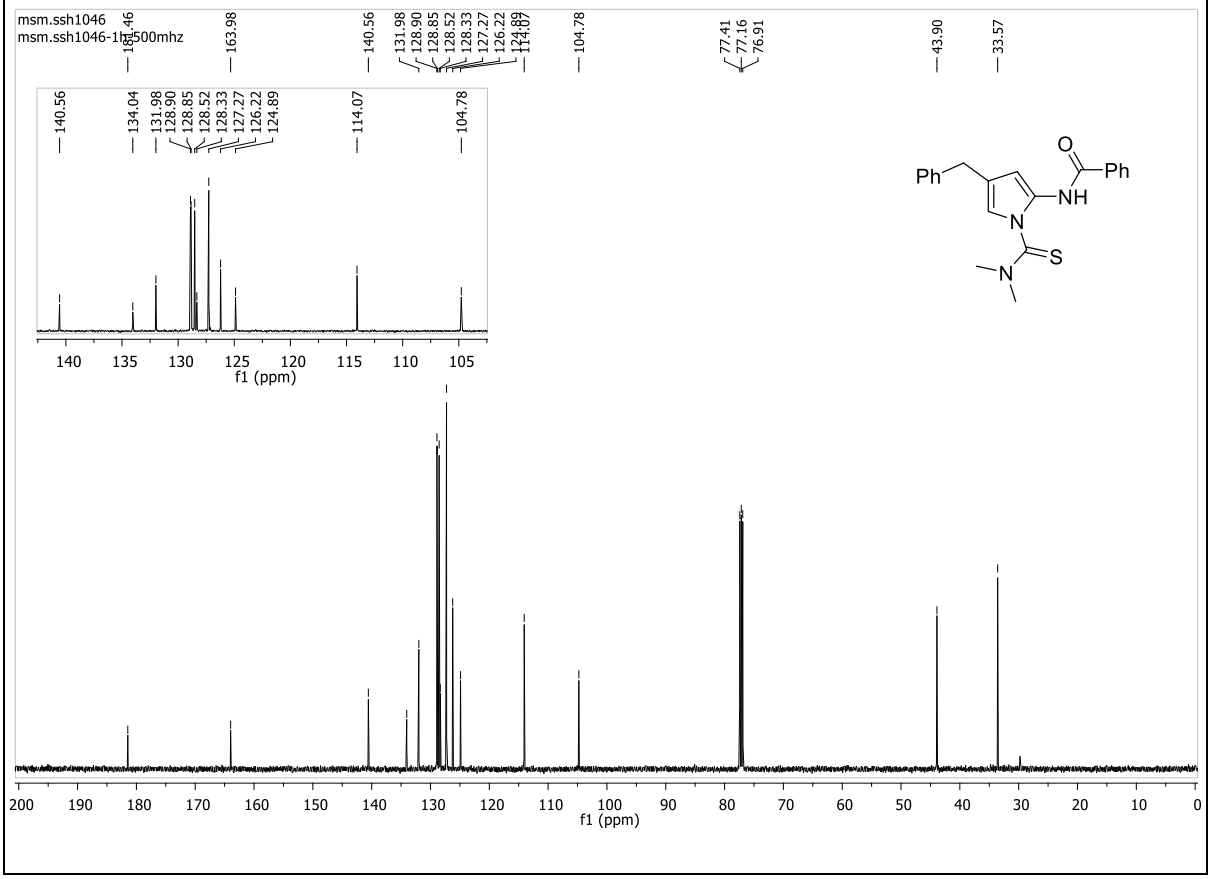
^{1}H NMR and ^{13}C NMR Spectra of Compound **6l**



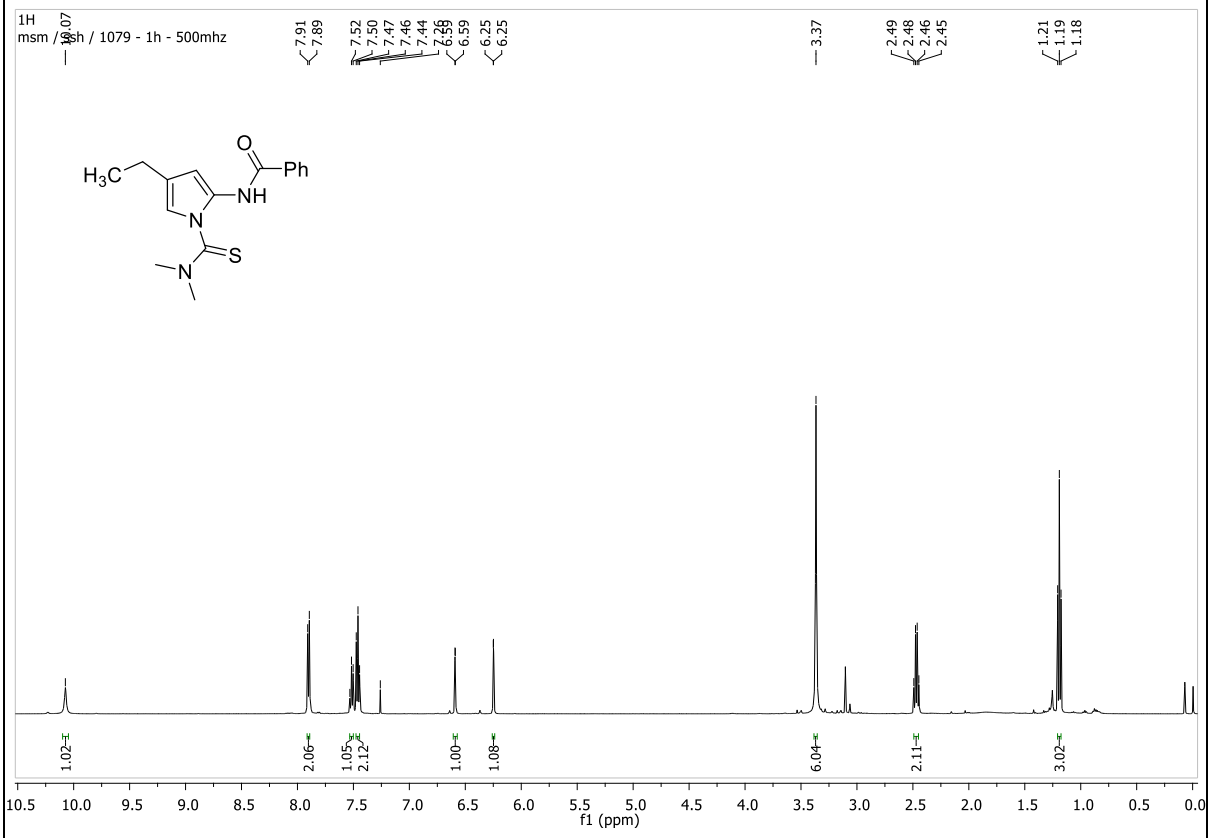


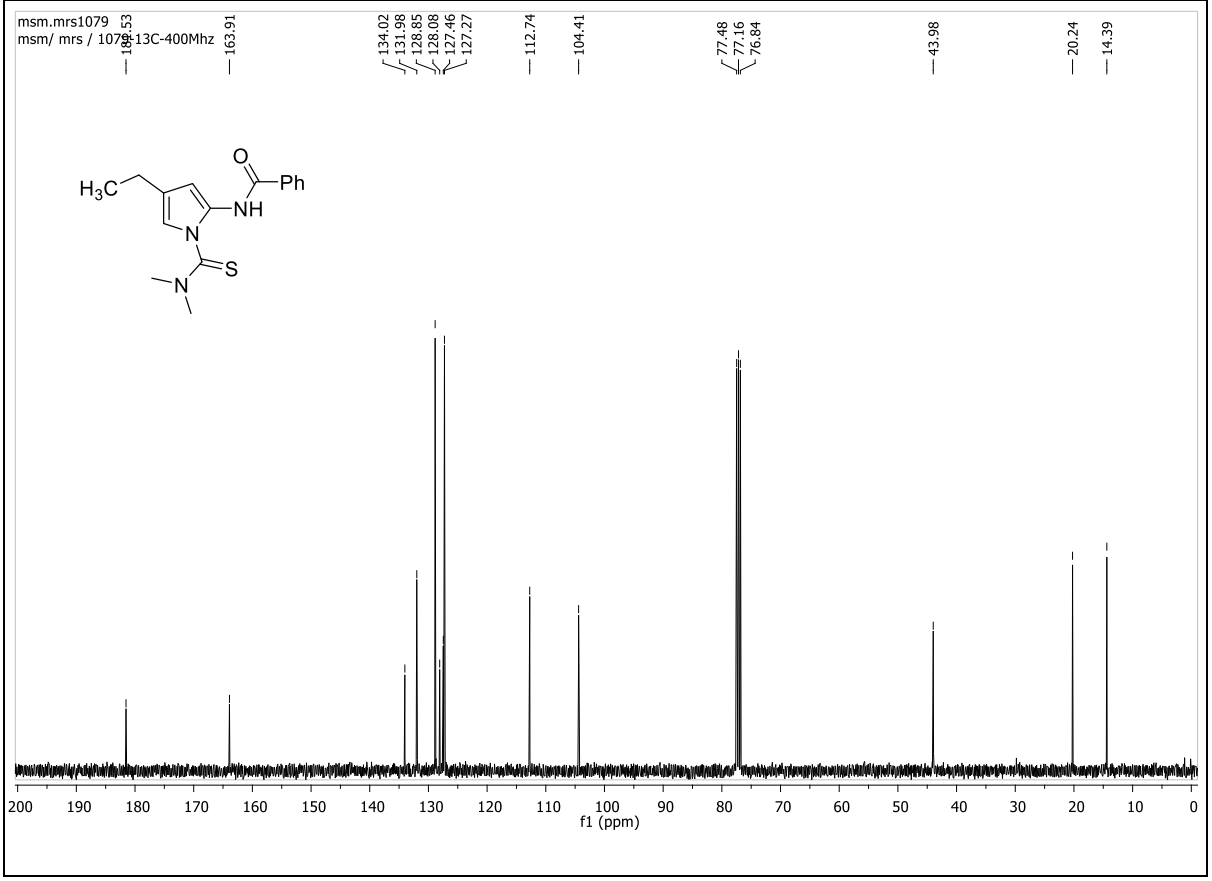
^{1}H NMR and ^{13}C NMR Spectra of Compound **6m**



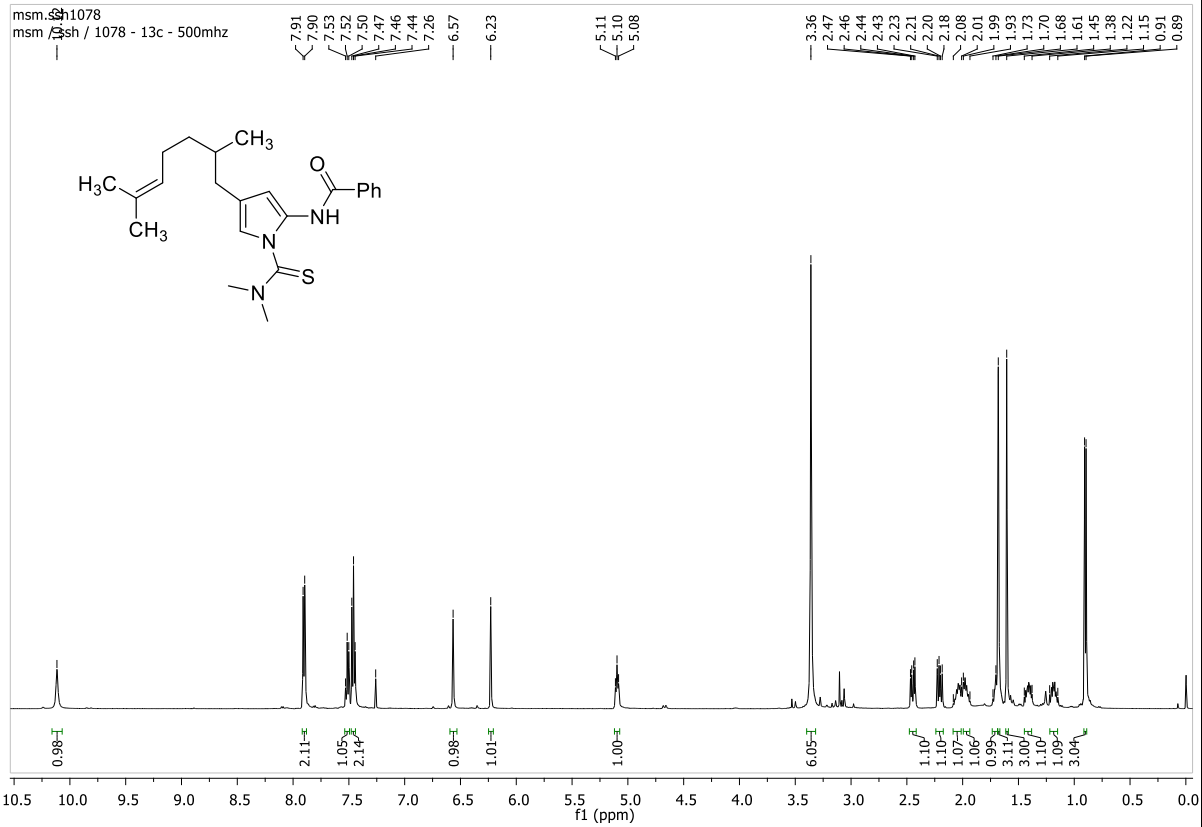


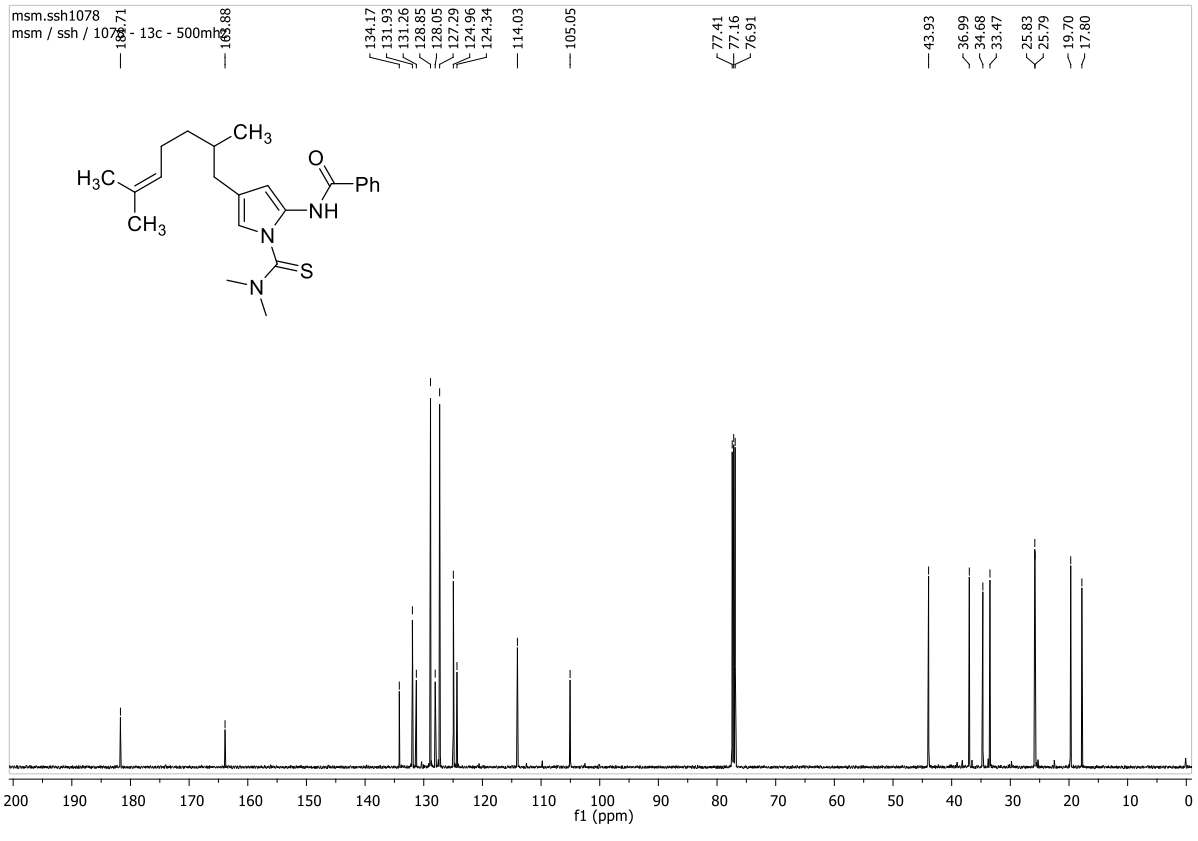
[1]H NMR and [13]C NMR Spectra of Compound **6n**



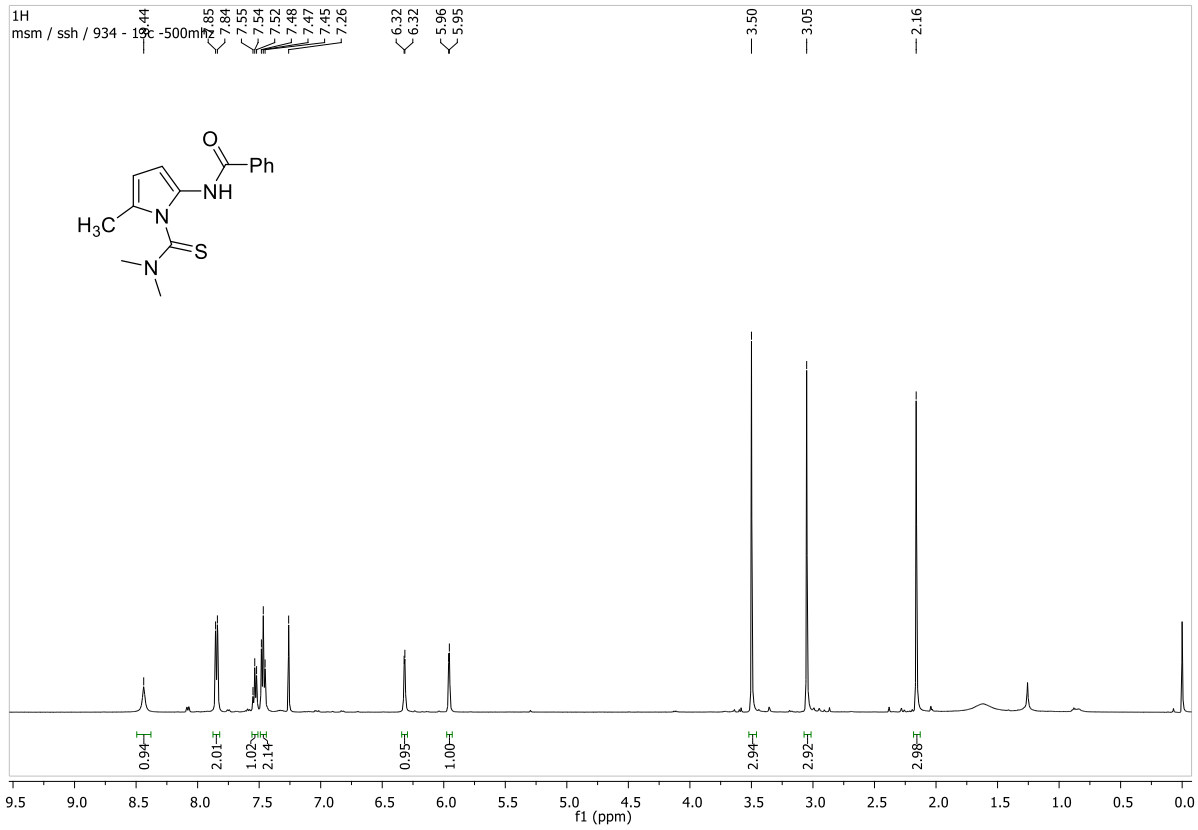


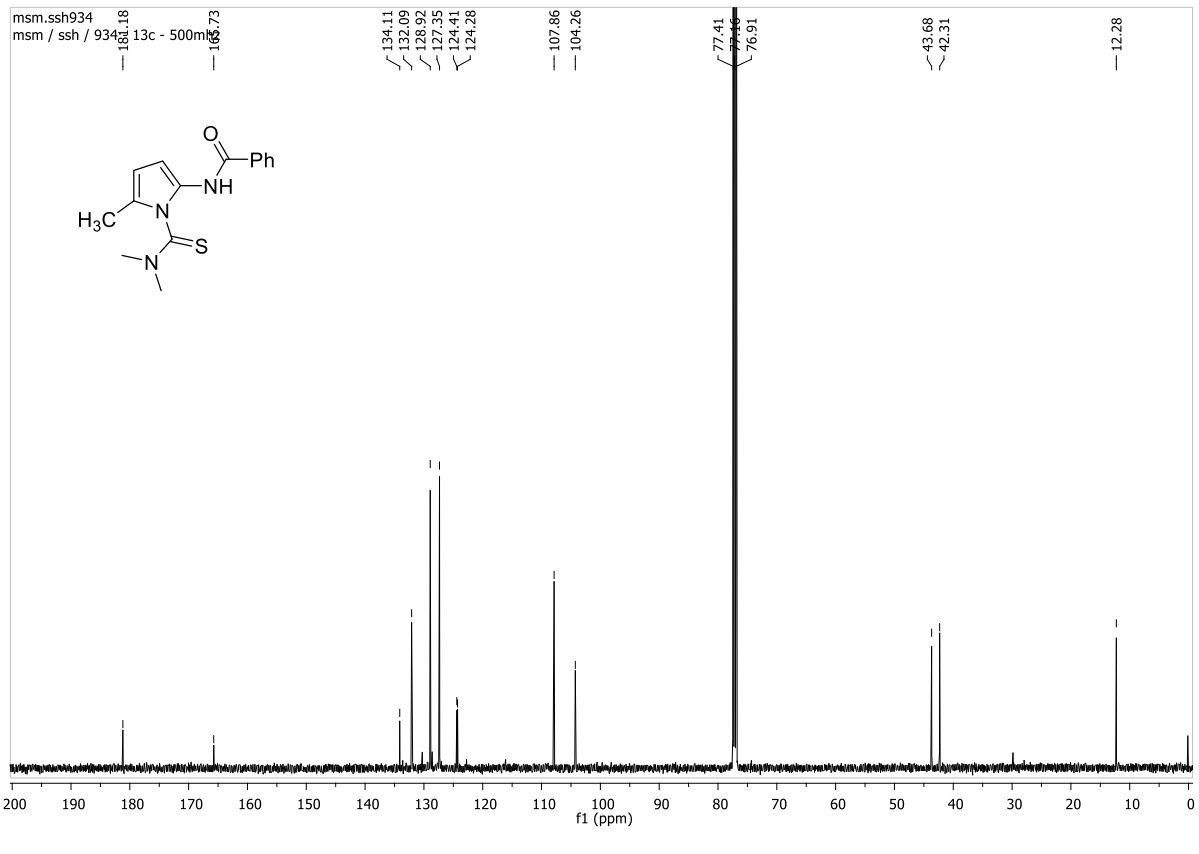
^{1}H NMR and ^{13}C NMR Spectra of Compound **6o**



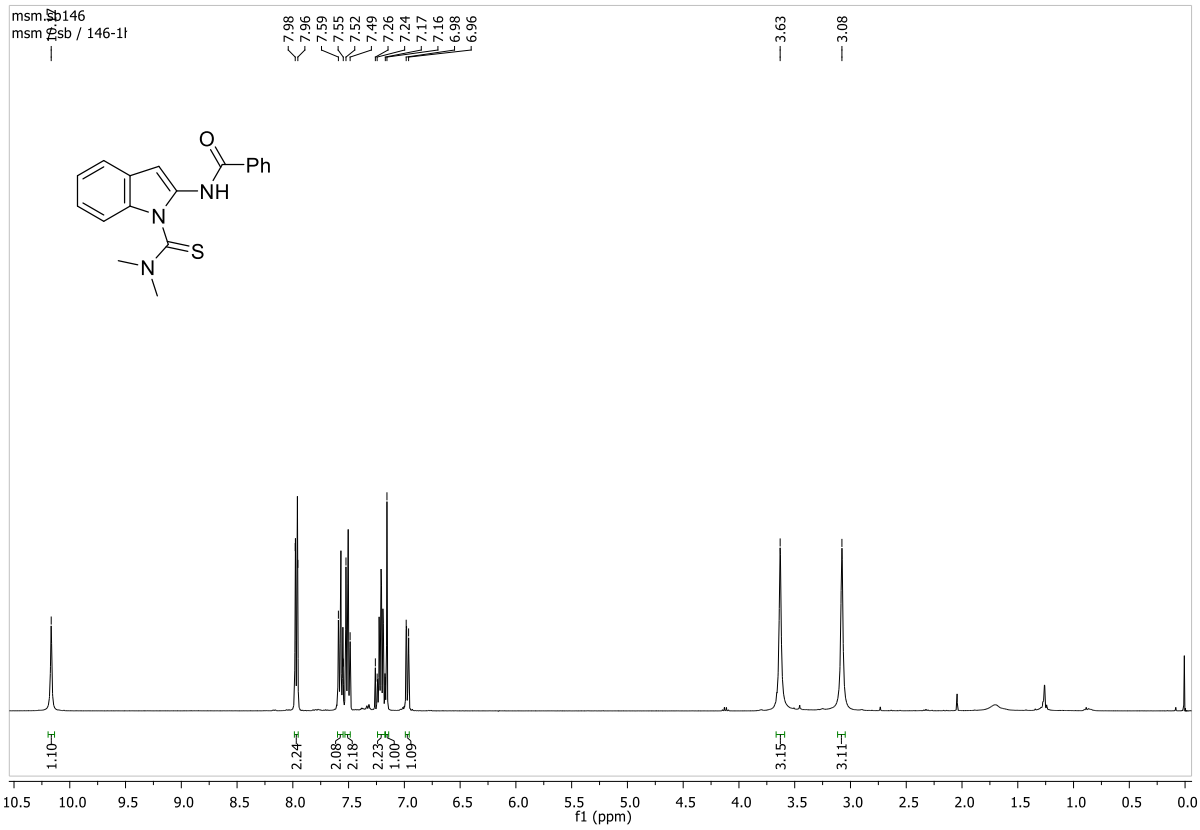


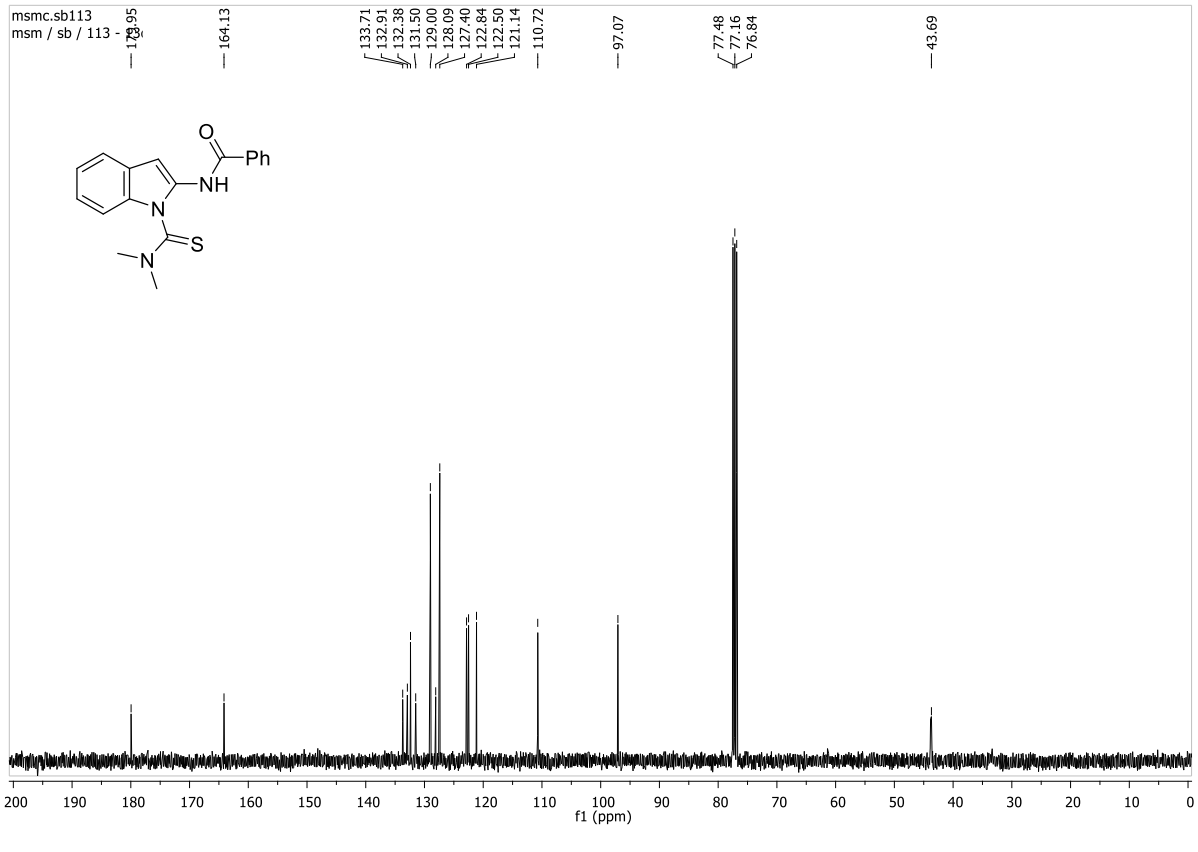
^{1}H NMR and ^{13}C NMR Spectra of Compound **6p**



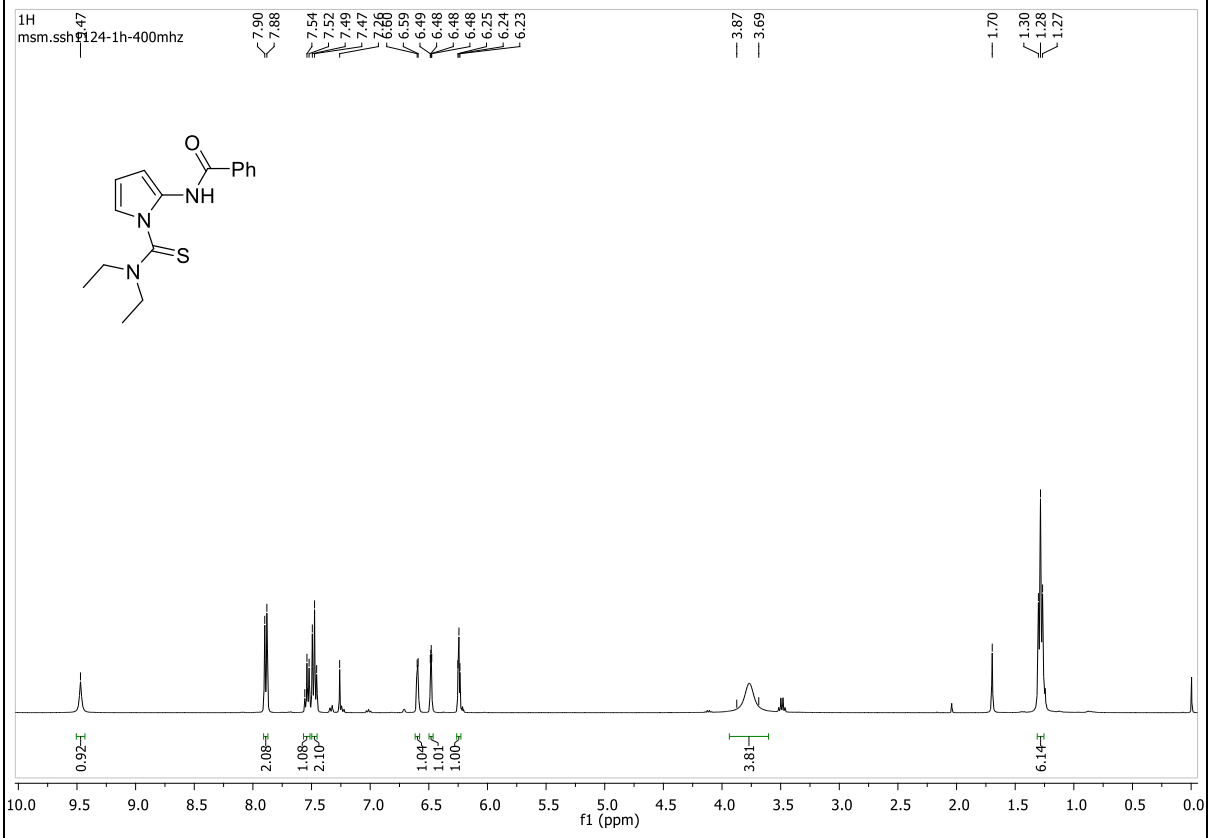


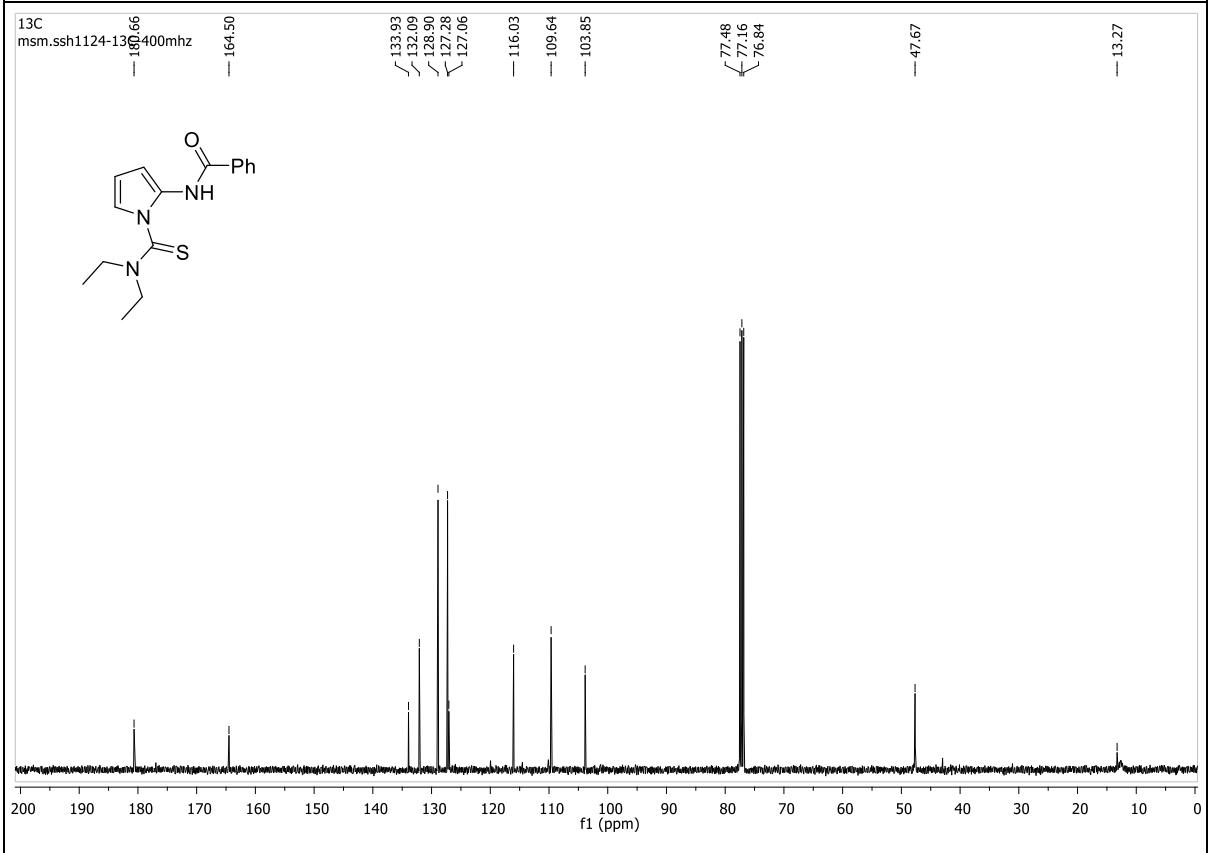
^{1}H NMR and ^{13}C NMR Spectra of Compound **6q**



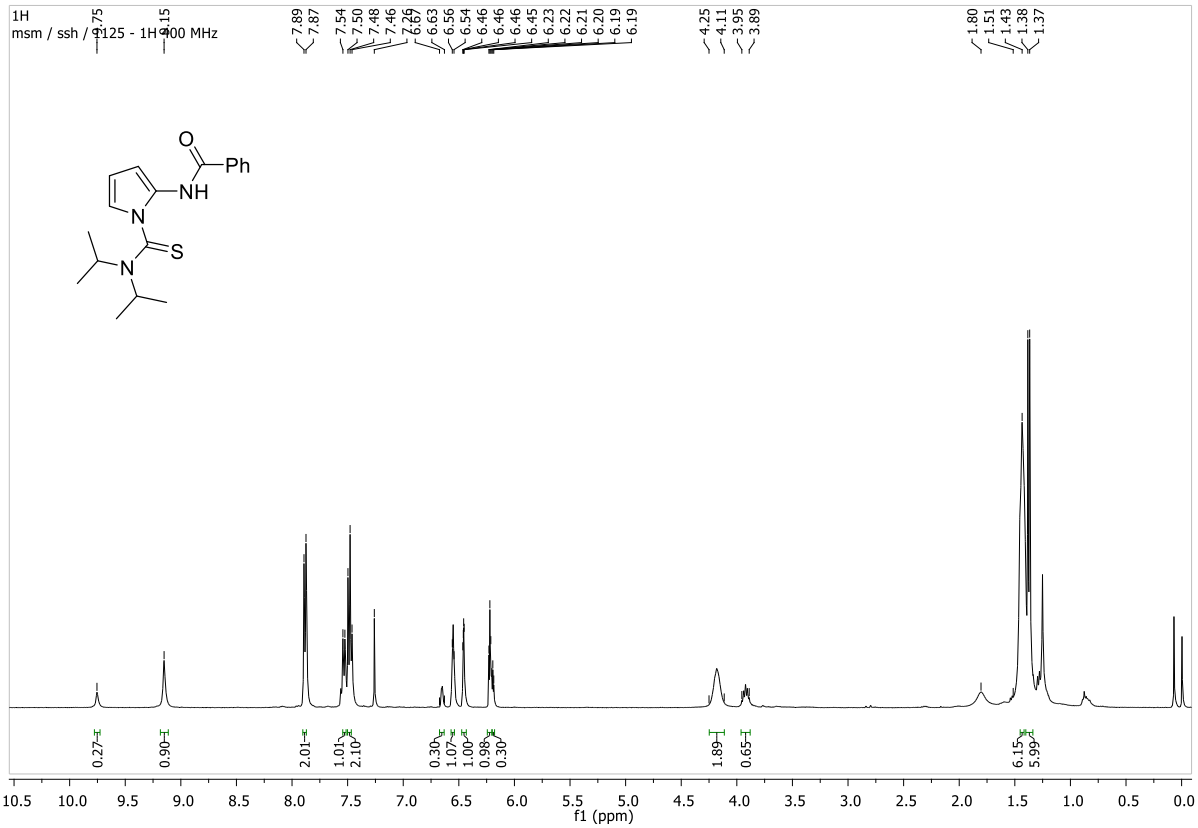


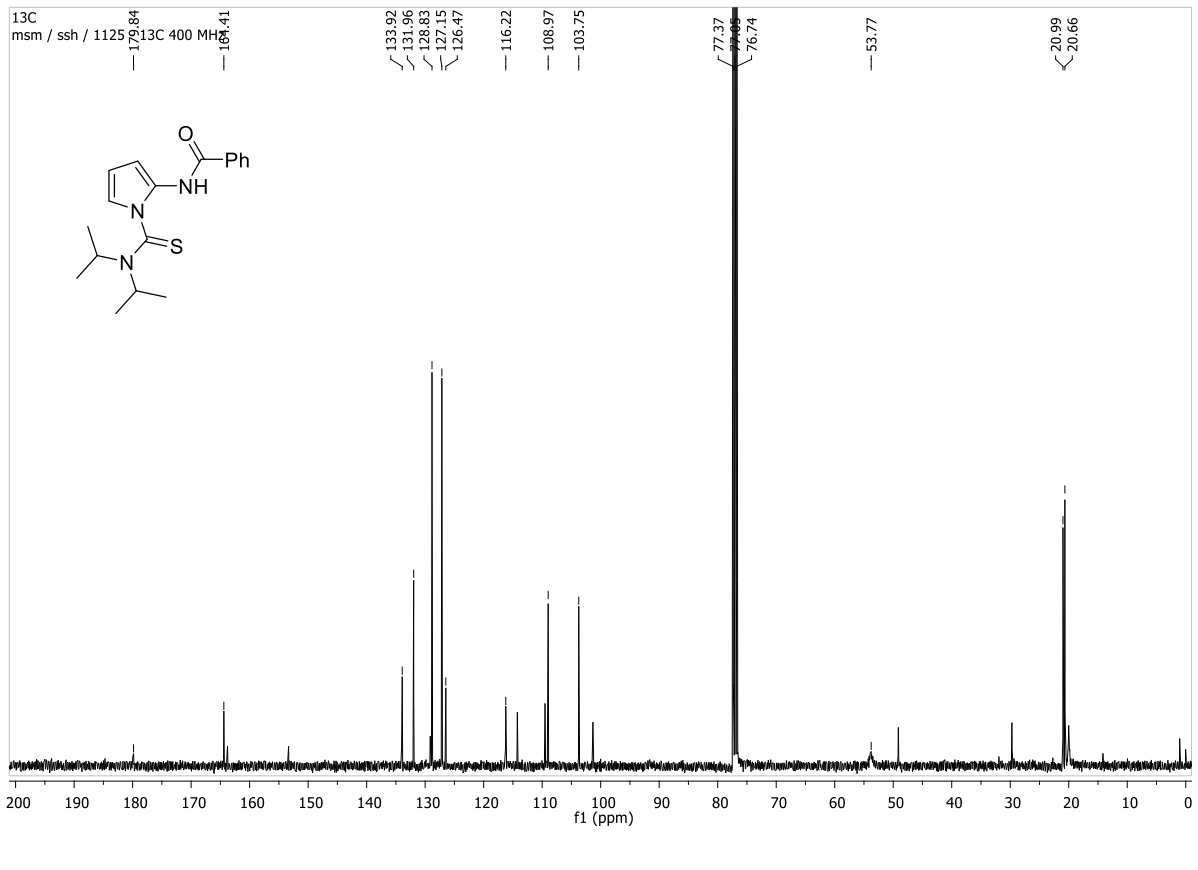
^{1}H NMR and ^{13}C NMR Spectra of Compound **6r**



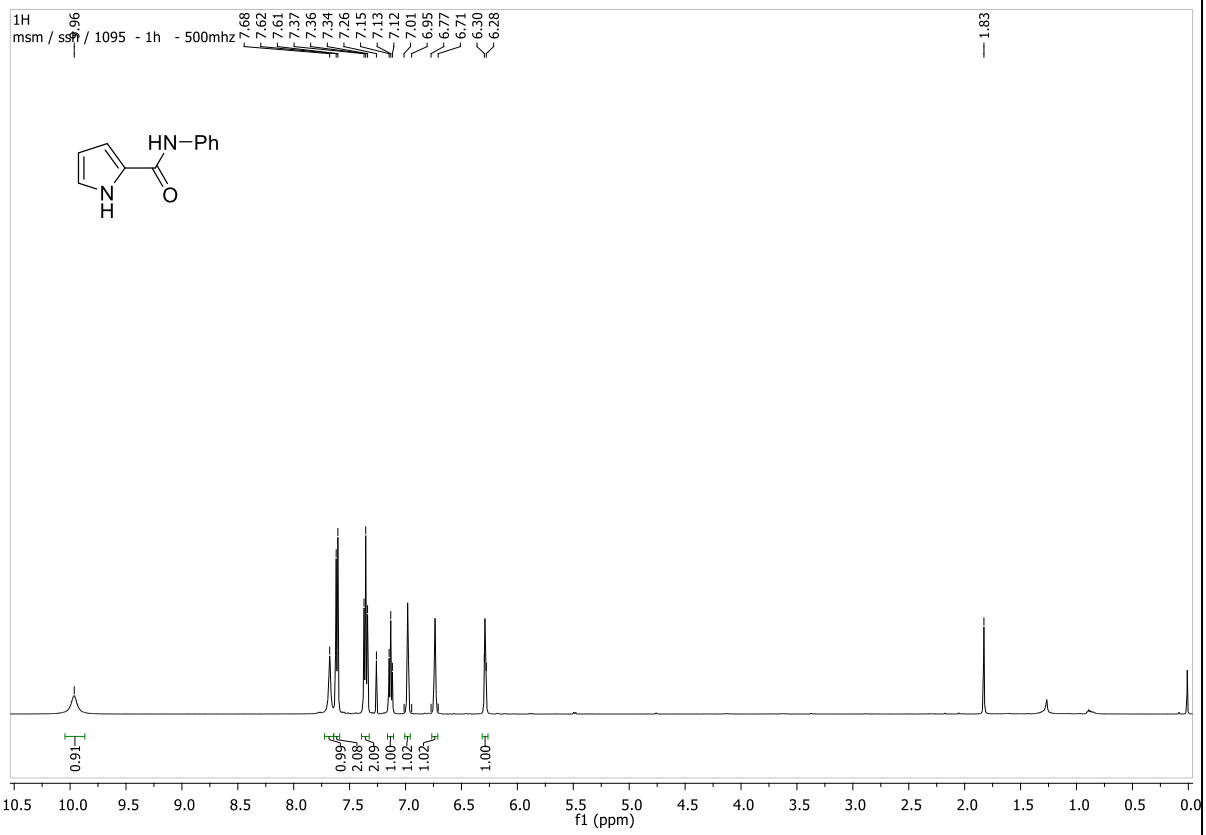


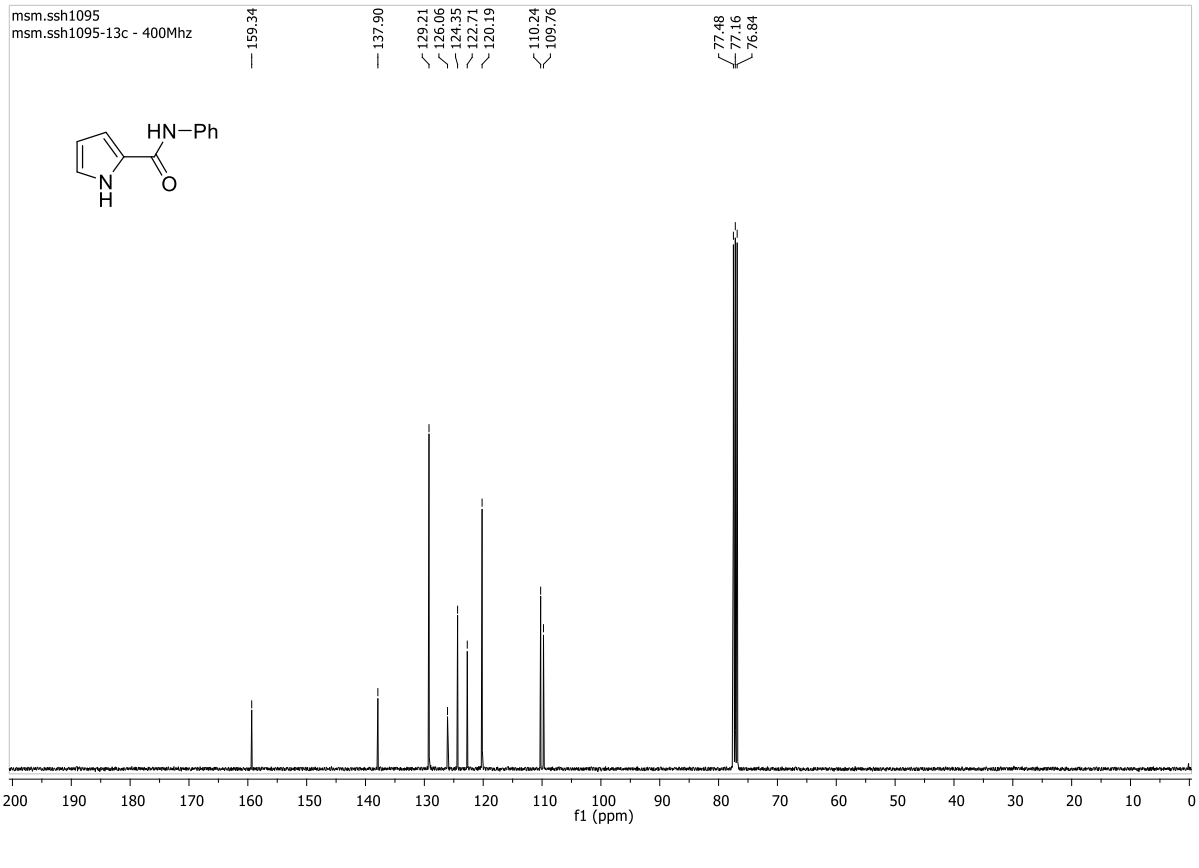
^{1}H NMR and ^{13}C NMR Spectra of Compound **6s**



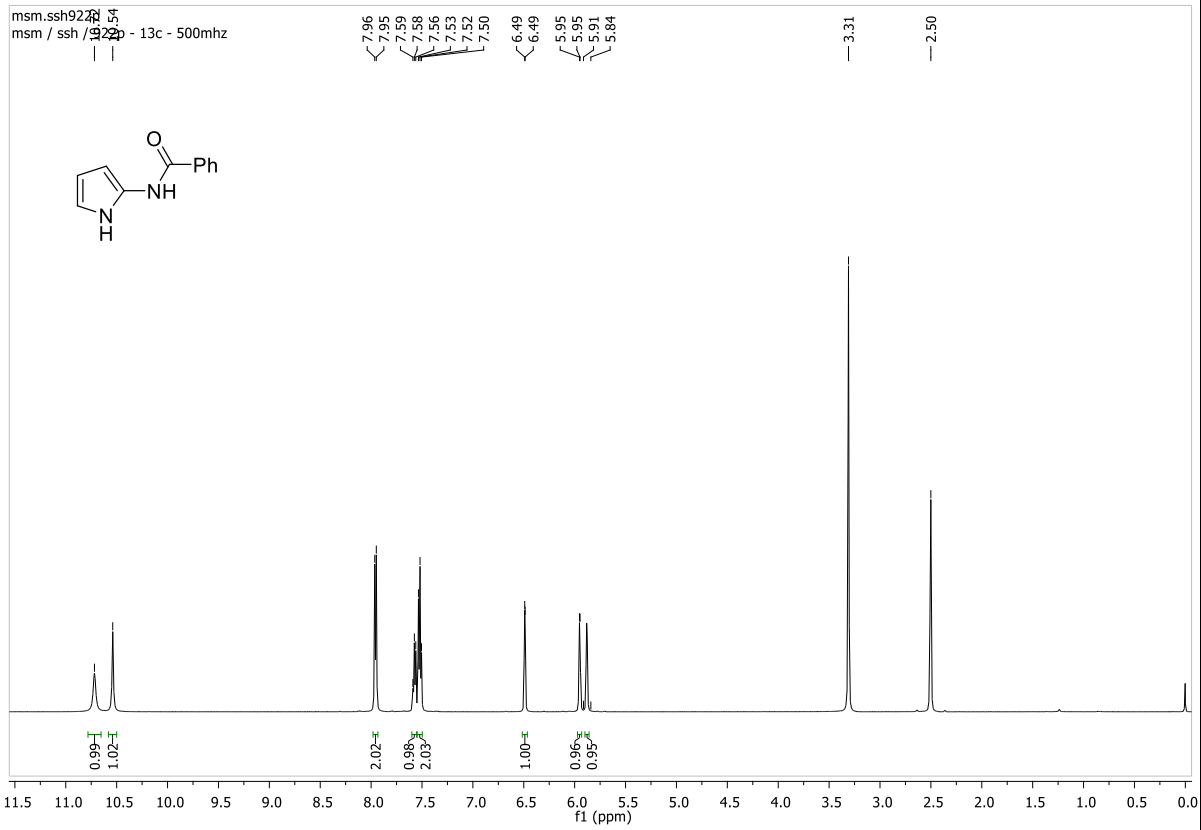


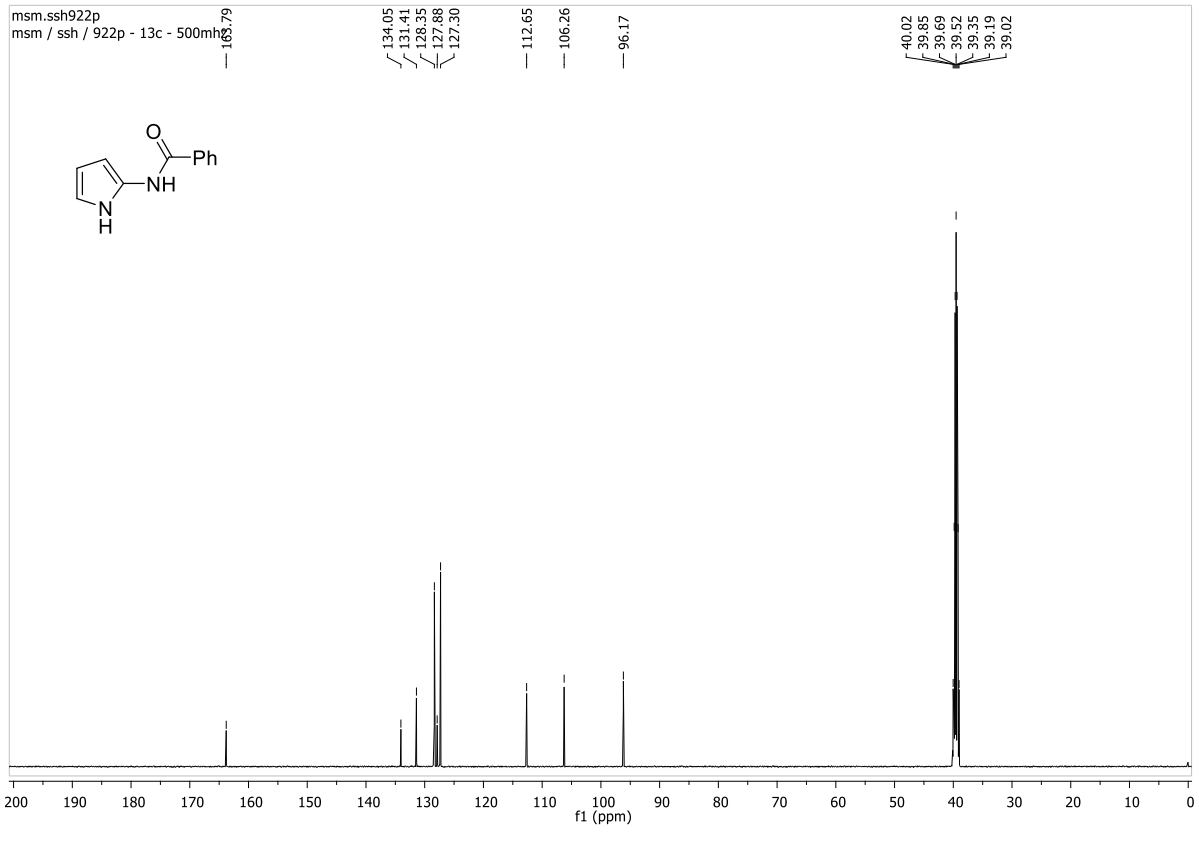
^{1}H NMR and ^{13}C NMR Spectra of Compound **7**



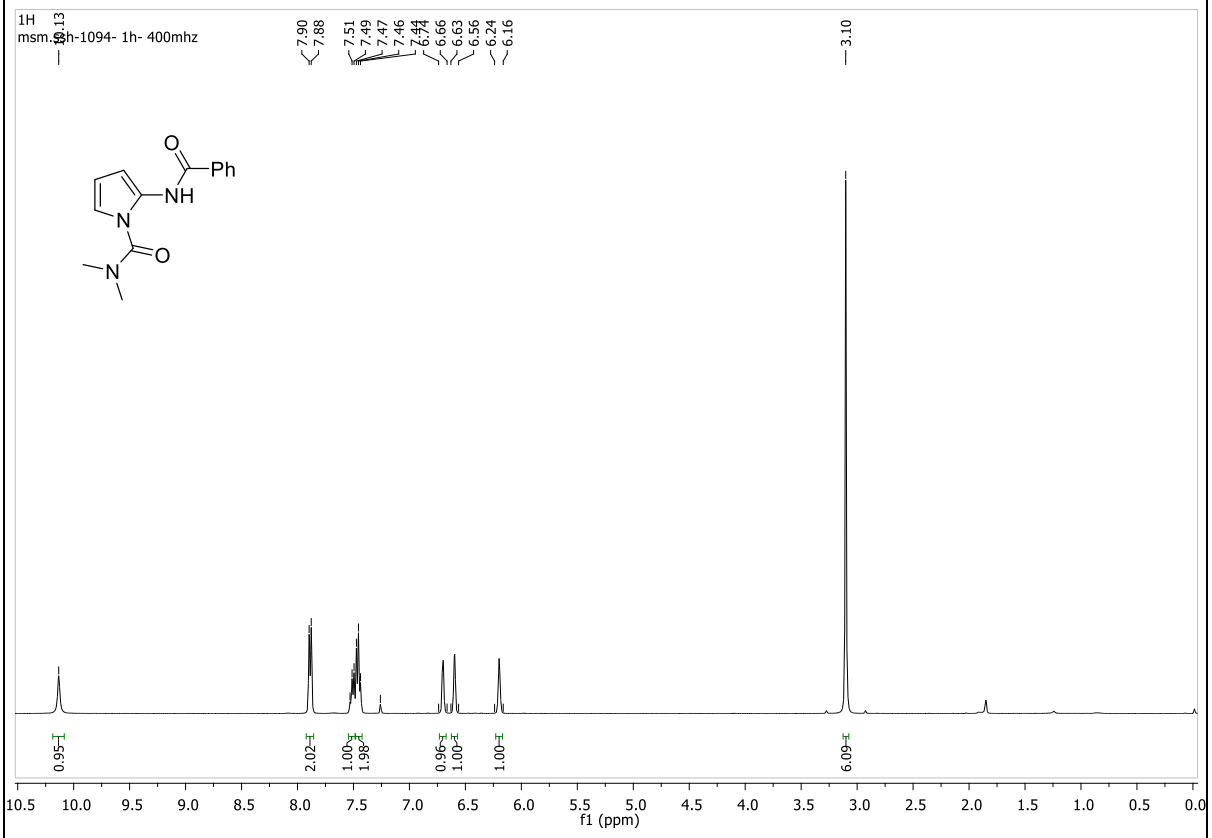


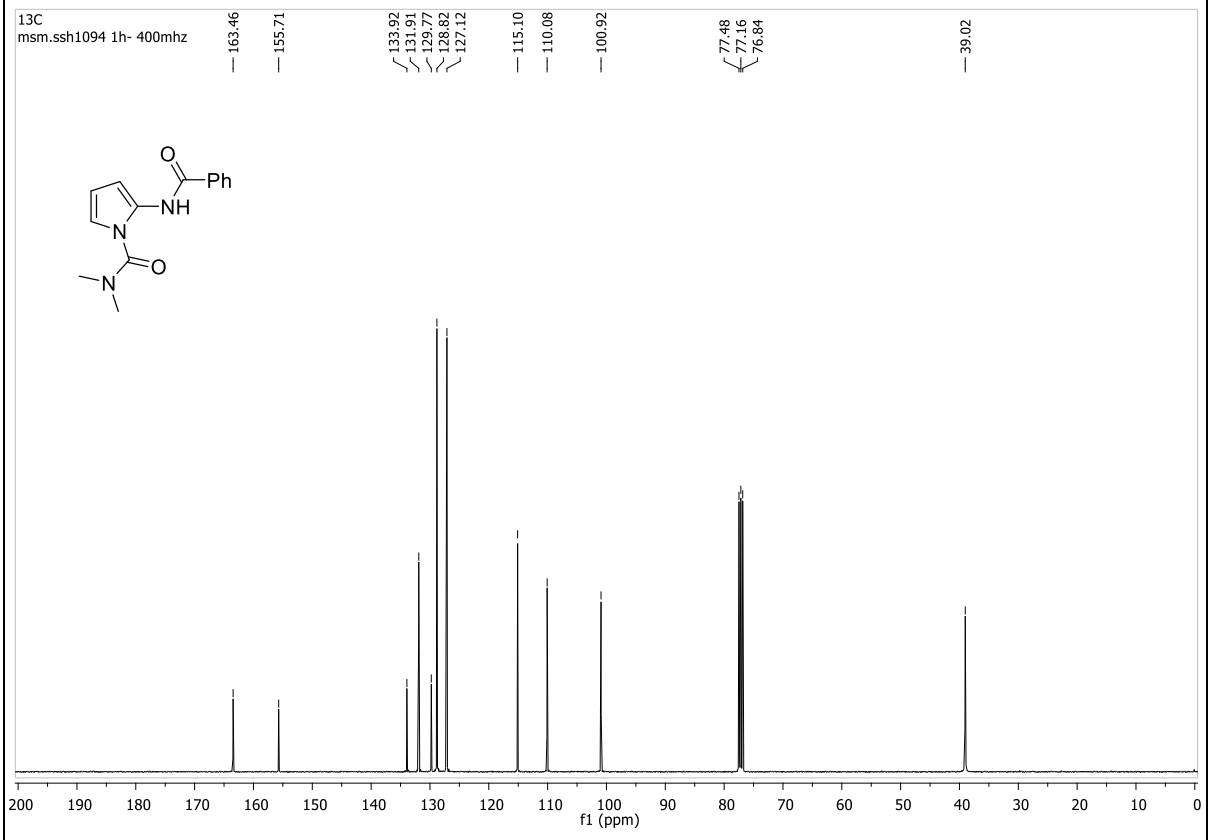
[1]H NMR and [13]C NMR Spectra of Compound **8**



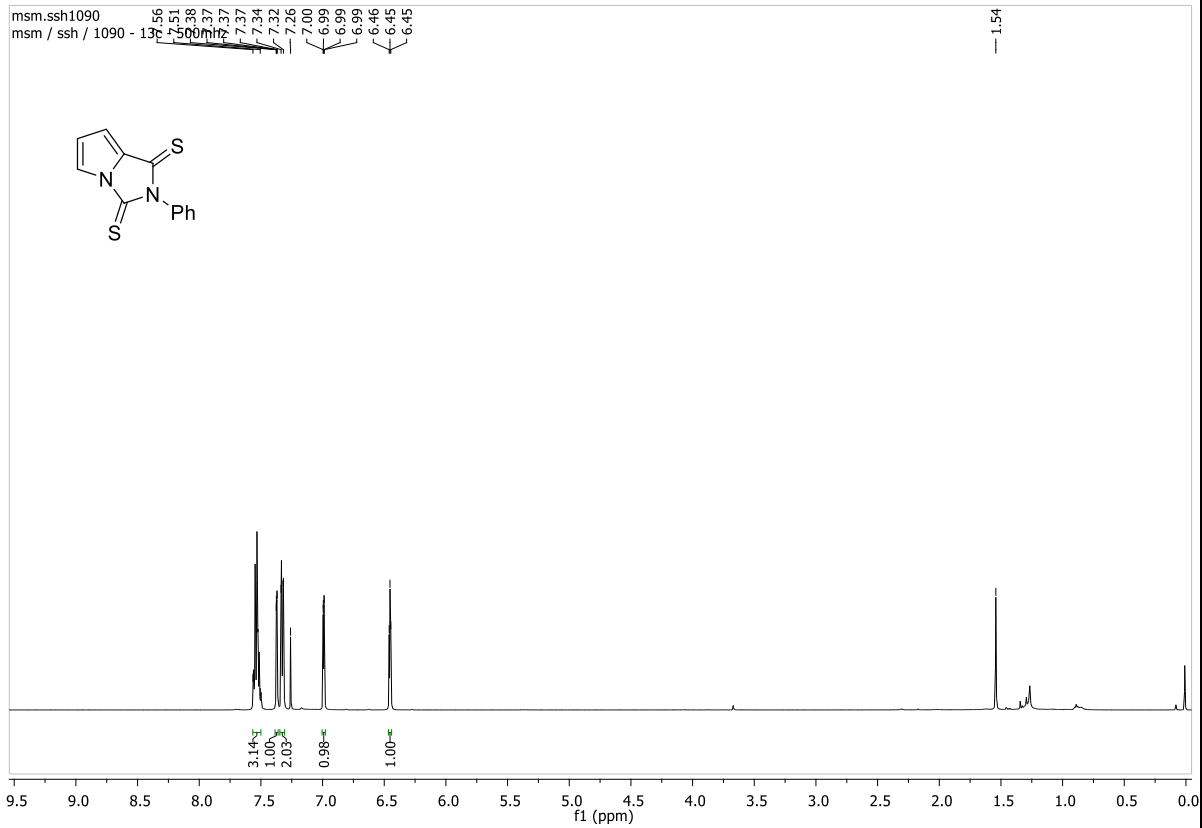


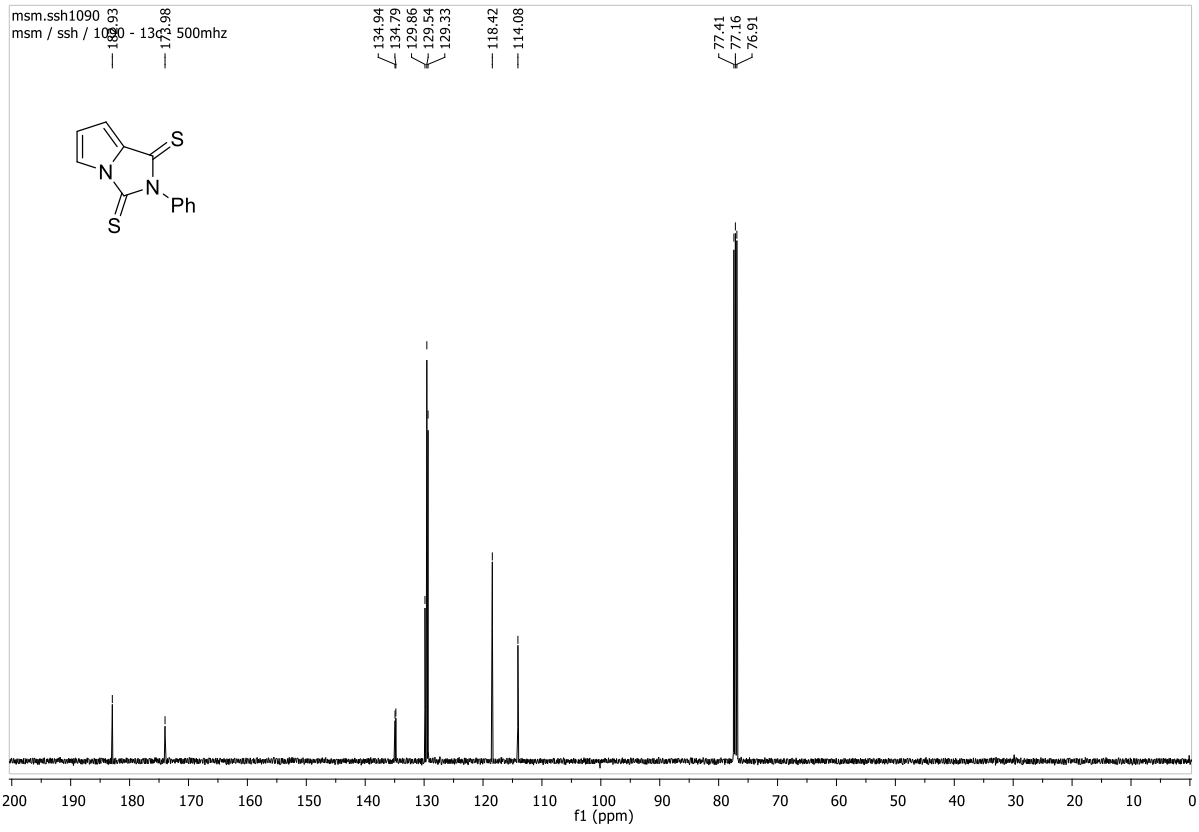
^{1}H NMR and ^{13}C NMR Spectra of Compound **9**





^{1}H NMR and ^{13}C NMR Spectra of Compound **10**





^{1}H NMR and ^{13}C NMR Spectra of Compound **11**