Supplementary Information

Iodine-Promoted Ring-Opening Methylation of Benzothiazoles with Dimethyl Sulfite

Ying-Qiong Guo,[a] Fan Chen,*[a] Chen-Liang Deng,[a] and Xing-Guo Zhang*[a,b]

[a]College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China;

[b]Guangxi Key Laboratory of Calcium Carbonate Resources Comprehensive Utilization, Hezhou University, Hezhou 542899, China

E-mail: zxg@wzu.edu.cn

Supplementary data

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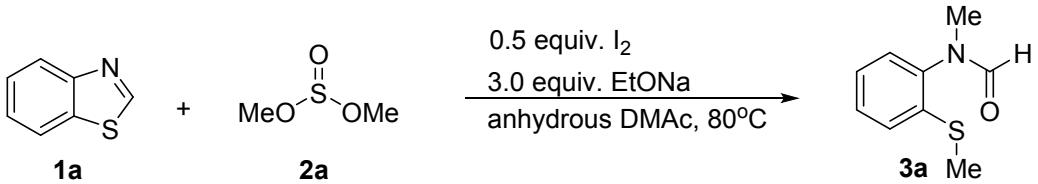
1. General Information

Chemicals were either purchased or purified by standard techniques. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were measured on a 500 MHz spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) or a 400 MHz spectrometer (400 MHz for ^{1}H), using $CDCl_3$ or DMSO-d_6 as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometry. All reactions under air atmosphere were conducted using standard Schlenk techniques. Melting points were measured on X4 melting point apparatus and uncorrected. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

2. Experimental procedures

2.1 The optimization of H_2O equivalent

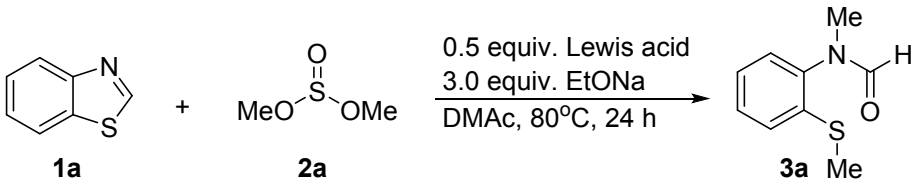


1a **2a** **3a**

Entry	H_2O (equiv.)	Yield (%)
1	0	NR
2	0.5	Trace
3	1	13
4	2	30
5	3	51
6	4	64
7	5	78
8	10	52
9	0	81[b]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2 mmol), Lewis acid (50 mol%), EtONa (3.0 equiv.), dry DMAc (2.0 mL) at 80 °C for 24 h, isolated yield. [b] not dry DMAc

2.2 Screening for Reactionof Lewis acid

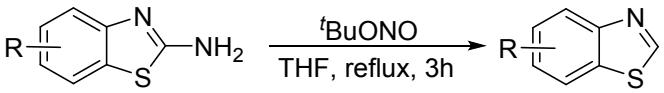


1a **2a** **3a**

Entry	Lewis acid	Yield (%)
1	ZnI_2	43
2	$ZnCl_2$	Trace
3	$Zn(OTf)_2$	Trace
4	$MgBr_2$	26
5	$FeCl_3$	Trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2 mmol), Lewis acid (50 mol%), EtONa (3.0 equiv.), DMAc (2.0 mL) at 80 °C for 24 h, isolated yield

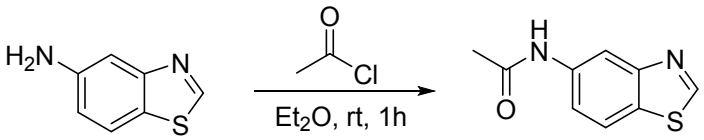
2.3 General Procedure for the Synthesis of Benzothiazole 1b, 1c, 1l:[1]



R = 4-Me, 6-Me, 6-OMe

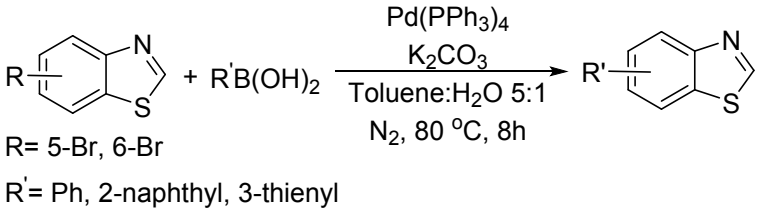
To a solution containing ^{t}BuONO (10 mmol) in 15 mL of THF was added 2-Amino-benzothiazole (5 mmol) dropwise at room temperature. The reaction was refluxed for 3 h and then allowed to cool to room temperature. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the benzothiazole **1b**, **1c**, **1l**.

2.4 General Procedure for the Synthesis of Benzothiazole 1d:[2]



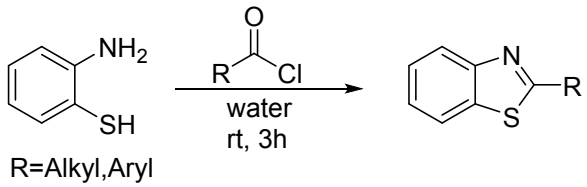
To a solution containing 1,3-benzothiazol-5-amine (5 mmol) in 10ml of diethyl ether was added Acetyl chloride (6 mmol) dropwise at room temperature. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 1 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give benzothiazole **1d**.

2.5 General Procedure for the Synthesis of Benzothiazole 1e-1h:[3]



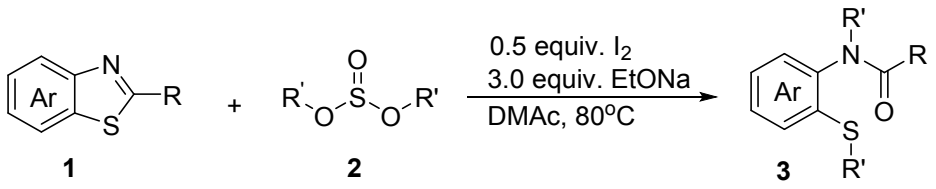
To a mixture of the benzothiazole (2 mmol,), boronic acid (3 mmol), tetrakis(triphenylphosphine)palladium (0.1 mmol), potassium carbonate (8.0 mmol) was added toluene (10 mL) and water (2 mL) under a nitrogen atmosphere. The mixture was stirred heated at 80 °C. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to afford the benzothiazole **1e-1h**.

2.6 General Procedure for the Synthesis of Benzothiazole 1o-1q, 1s-1v:[4]



To a mixture of the 2-aminobenzenethiol (5 mmol) and corresponding acyl chlorides (6 mmol) was added water (10 mL) at room temperature. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 3 h. then washed with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated to afford residue, which was purified by flash column chromatography on silica gel to give the benzothiazole **1o-1q**, **1s-1v**.

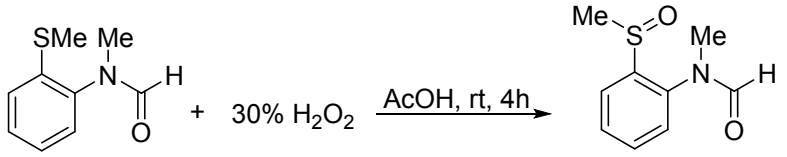
2.7 General Procedure for the Synthesis of *N*-methyl-*N*-(*o*-methylthio)phenyl 3



To a Schlenk tube with a magnetic stirring bar were charged with **1** (0.2 mmol, 1.0 equiv.), **2** (2mmol, 10.0 equiv.), I_2 (25.4 mg, 0.1 mmol, 0.5 equiv.), EtONa (40.9 mg, 0.6 mmol, 3.0 equiv.) in DMAc (2 mL). The mixture was stirred under air atmosphere and heated at 80 °C. After 24 h, washed with water (15 mL) and saturated

solution $Na_2S_2O_3$ (15 mL). The organic layer was dried over Na_2SO_4 and evaporated to afford residue, which was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford *N*-methyl-*N*-(*o*-methylthio)phenyl **3**.

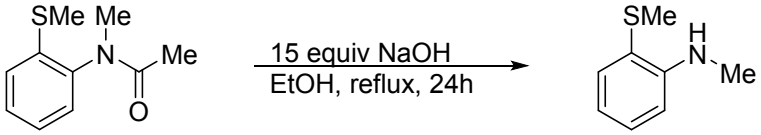
2.8 General Procedure for the Synthesis of *N*-methyl-*N*-(2-(methylsulfinyl)-phenyl)formamide 5



3a **5**, 67%

To a solution containing 3a (0.2 mmol) in 1 mL of glacial acetic acid was added 30% hydrogen peroxide (0.11 mL) dropwise at room temperature. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 4 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the product **5.**

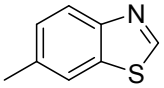
2.9 General Procedure for the Synthesis of *N*-methyl-2-(methylthio)aniline 4



3r **6**, 60%

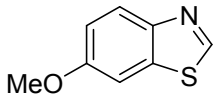
To a mixture of the **3r** (0.2 mmol), NaOH (120 mg, 15 mmol) was added EtOH (1 mL) at room temperature. The reaction was refluxed for 24 h and then allowed to cool to room temperature, diluted with 10 mL of EtOAc and washed with HCl (1 M, 3 × 4 mL). The residue was purified by flash column chromatography on silica gel to give the product **6**.

3. Characterization of starting materials



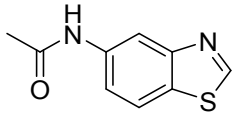
6-methylbenzo[*d*]thiazole (1b)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 521.6 mg, yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.74 (s, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 2.51 (s, 3H).



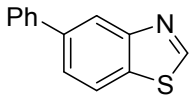
6-methoxybenzo[*d*]thiazole (1c)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 618.9 mg, yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.38 (s, 1H), 7.13 – 7.10 (m, 1H), 3.87 (s, 3H).



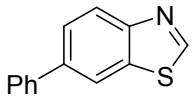
***N*-(benzo[*d*]thiazol-5-yl)acetamide (1d)**

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 2:1), 844.9 mg, yield: 88%; mp 185–187^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.18 (s, 1H), 9.36 (s, 1H), 8.47 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.60-7.58(m, 1H), 2.10 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.6, 156.9, 153.7, 138.0, 127.7, 122.3, 118.0, 112.6, 24.0.HRMS (ESI) Calcd for $C_9H_8N_2OSNa^+$([M + Na]$^+$) 215.0250, found: 215.0253.



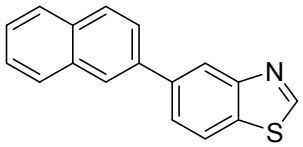
5-Phenyl benzothiazole (1e)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 274.3 mg, yield: 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.35 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.67 (m, 3H), 7.50 – 7.46 (m, 2H), 7.40 – 7.36 (m, 1H).



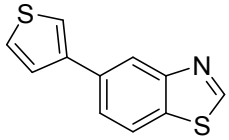
6-Phenyl benzothiazole (1f)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 227.9 mg, yield: 54%; mp 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.19 – 8.14 (m, 2H), 7.76 – 7.74 (m, 1H), 7.64 (d, *J* = 6.0 Hz, 2H), 7.49 – 7.46 (m, 2H), 7.37 – 7.40 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 152.7, 140.7, 139.3, 134.7, 129.1, 127.7, 127.6, 126.1, 123.8, 120.3.HRMS (ESI) Calcd for $C_{13}H_{10}NS^+$([M + H]$^+$) 212.0528, found: 212.0521.



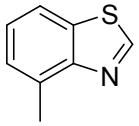
5-(naphthalen-2-yl)benzo[*d*]thiazole (1g)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 423.0 mg, yield: 81%; mp 112–114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.28 (s, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.93 – 7.89 (m, 3H), 7.59 – 7.54 (m, 2H), 7.52 – 7.49 (m, 2H), 7.44 – 7.41 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 153.7, 139.5, 139.3, 133.9, 132.8, 131.8, 128.5, 128.11, 128.08, 127.5, 126.4, 126.0, 125.9, 125.5, 125.0, 121.6. HRMS (ESI) Calcd for $C_{17}H_{12}NS^+$ ([M + H]$^+$) 262.0685, found: 262.0679.



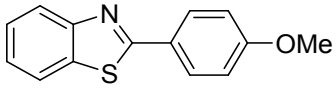
5-(thiophen-3-yl)benzo[*d*]thiazole (1h)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 423.0 mg, yield: 81%; mp 92–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.35 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.54 (s, 1H), 7.49 – 7.40 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 154.1, 141.8, 134.5, 132.4, 126.7, 126.6, 124.6, 122.1, 121.2, 120.9. HRMS (ESI) Calcd for $C_{11}H_8NS_2^+$ ([M + H]$^+$) 218.0093, found: 218.0093.



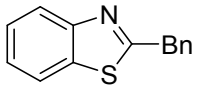
4-methylbenzo[*d*]thiazole (1i)

Yellow oilobtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 484.3 mg, yield:65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.75 – 7.73 (m, 1H), 7.31-7.26 (m, 2H), 2.78 (s, 3H).



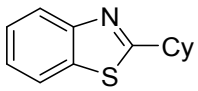
2-(4-methoxyphenyl)benzo[*d*]thiazole (1o)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 928.2 mg, yield: 77%; mp 133–134 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.01 (m, 3H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.35 – 7.31 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H).



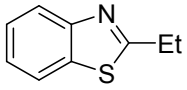
2-benzylbenzo[*d*]thiazole (1p)

White oil obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 787.7 mg, yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.36 – 7.27 (m, 6H), 4.43 (s, 2H).



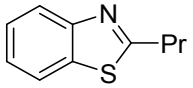
2-cyclohexylbenzo[*d*]thiazole (1q)

White oil obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 651.3 mg, yield:60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.15 (m, 1H), 7.34 – 7.30 (m, 1H), 3.14 – 3.06 (m, 1H), 2.20 (d, *J* = 11.6 Hz, 2H), 1.90 – 1.86 (m, 2H), 1.78 – 1.59 (m, 3H), 1.48 – 1.38 (m, 2H), 1.36 – 1.25 (m, 1H).



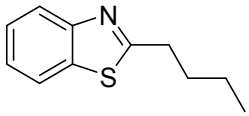
2-ethylbenzo[*d*]thiazole (1s)

Yellow oilobtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 546.2 mg, yield: 67%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.36 – 7.32 (m, 1H), 3.15 (q, *J* = 7.6 Hz, 2H), 1.47 (t, *J* = 7.6 Hz, 3H).



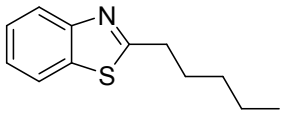
2-propylbenzo[*d*]thiazole (1t)

Yellow oilobtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 540.1 mg, yield: 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.35 – 7.31 (m, 1H), 3.09 (t, *J* = 7.6 Hz, 2H), 1.96-1.86 (m, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).



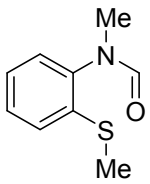
2-butylbenzo[*d*]thiazole (1u)

White oil obtained by column chromatography (petroleum ether/ethyl acetate = 20:1), 697.5 mg, yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.35 – 7.31 (m, 1H), 3.11 (t, *J* = 7.6 Hz, 2H), 1.90 – 1.82 (m, 2H),, 1.51 – 1.42 (m, 2H), 1.00 – 0.94 (m, 3H).



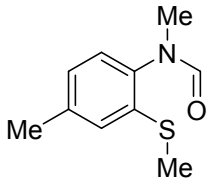
2-pentylbenzo[*d*]thiazole (1v)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 20:1),563.9 mg, yield:55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.35-7.31 (m, 1H), 3.10 (t, *J* = 7.6 Hz,, 2H), 1.92-1.84 (m, 2H), 1.44-1.35 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H).



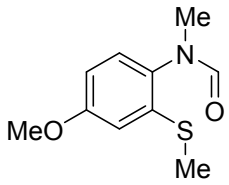
***N*-methyl-*N*-(2-(methylthio)phenyl)formamide (3a)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 29.3 mg, yield: 81%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.39 – 7.36 (m, 1H), 7.27 – 7.19 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 1H), 3.21 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 139.1, 138.4, 129.1, 128.3, 126.0, 125.6, 32.5, 14.9. HRMS (ESI) Calcd for $C_9H_{11}NOSK^+$([M + K]$^+$) 220.0193, found: 220.0199.



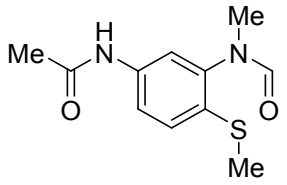
***N*-methyl-*N*-(4-methyl-2-(methylthio)phenyl)formamide (3b)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 33.9 mg, yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.04 – 6.98 (m, 2H), 3.19 (s, 3H), 2.44 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 139.3, 138.0, 136.8, 128.2, 126.6, 126.2, 32.7, 21.3, 15.0. HRMS (ESI) Calcd for $C_{10}H_{13}NOSNa^+$([M + Na]$^+$) 218.0610, found: 218.0614.



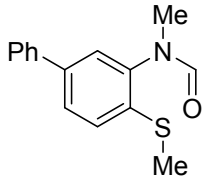
***N*-(4-methoxy-2-(methylthio)phenyl)-*N*-methylformamide (3c)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 35.0 mg, yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 6.97 (d, *J*= 8.4 Hz, 1H), 6.65 (s, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 3.07 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 160.1, 140.1, 132.1, 129.5, 112.0, 109.9, 55.7, 32.8, 14.9. HRMS (ESI) Calcd for $C_{10}H_{13}NO_2SNa^+$([M + Na]$^+$) 234.0559, found: 234.0558.



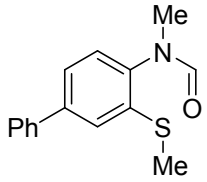
***N*-(3-(*N*-methylformamido)-4-(methylthio)phenyl)acetamide (3d)**

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1), 32.4 mg, yield: 68%; mp 134–135°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.10 (s, 1H), 7.54 – 7.36 (m, 2H), 7.22 – 7.12 (m, 1H), 3.20 (s, 3H), 2.42 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 163.4, 139.6, 136.9, 132.3, 127.5, 120.6, 119.8, 32.8, 24.5, 15.8.HRMS (ESI) Calcd for $C_{11}H_{15}N_2O_2S^+$([M + H]$^+$) 239.0849, found: 239.0844.



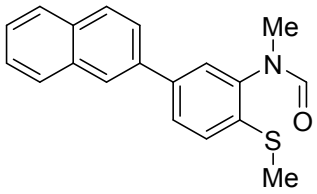
***N*-methyl-*N*-(4-(methylthio)-[1,1'-biphenyl]-3-yl)formamide (3e)**

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 45.8 mg, yield: 89%; mp 106-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.62 – 7.57 (m, 3H), 7.55 – 7.43 (m, 2H), 7.39 – 7.31 (m, 3H), 3.26 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 139.6, 139.3, 139.1, 137.3, 129.1, 127.9, 127.6, 127.0, 126.8, 126.6, 32.7, 15.2.HRMS (ESI) Calcd for $C_{15}H_{15}NOSNa^+$([M + Na]$^+$) 280.0767, found: 280.0769.



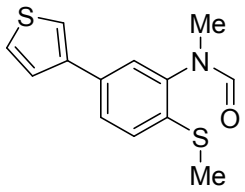
***N*-methyl-*N*-(3-(methylthio)-[1,1'-biphenyl]-4-yl)formamide (3f)**

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 47.3 mg, yield: 92%; mp 109–111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.38 (m, 2H), 7.32 – 7.26 (m, 3H), 7.10 – 7.08 (m, 1H), 3.14 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 142.3, 140.0, 138.7, 138.2, 129.0, 128.6, 128.0, 127.2, 124.7, 124.5, 32.6, 15.0. HRMS (ESI) Calcd for $C_{15}H_{16}NOS^+$([M + H]$^+$) 258.0947, found: 258.0946.



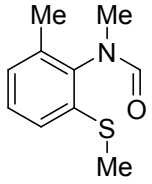
***N*-methyl-*N*-(2-(methylthio)-5-(naphthalen-2-yl)phenyl)formamide (3g)**

White oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 57.1 mg, yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.92 – 7.87 (m, 3H), 7.54 – 7.44 (m, 4H), 7.41 – 7.35 (m, 2H), 7.30 (s, 1H), 3.27 (s, 3H), 2.52 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 139.0, 138.5, 138.2, 137.3, 133.9, 131.4, 130.7, 129.8, 128.6, 128.3, 127.1, 126.5, 126.1, 125.9, 125.5, 125.4, 32.7, 15.1. HRMS (ESI) Calcd for $C_{19}H_{18}NOS^{+}$ ([M + H]$^{+}$) 308.1104, found: 308.1110.



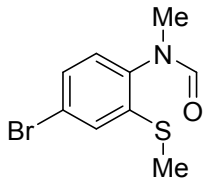
***N*-methyl-*N*-(2-(methylthio)-5-(thiophen-3-yl)phenyl)formamide (3h)**

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 38.4 mg, yield: 73%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.58 – 7.56 (s, 1H), 7.45 – 7.40 (m, 2H), 7.37 – 7.34 (m, 2H), 7.28 – 7.24 (m, 1H), 3.24 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 140.4, 139.4, 136.9, 133.7, 126.9, 126.8, 126.4, 126.3, 125.9, 120.6, 32.6, 15.1. HRMS (ESI) Calcd for $C_{13}H_{13}NOS_2Na^{+}$ ([M + Na]$^{+}$) 286.0331, found: 286.0337.



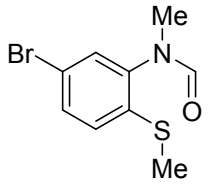
***N*-methyl-*N*-(2-methyl-6-(methylthio)phenyl)formamide (3i)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 12.9 mg, yield: 33%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.28 – 7.26(m,1H), 7.07 – 7.04 (m, 2H), 3.14 (s, 3H), 2.42 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 140.1, 137.5, 137.2, 129.3, 127.1, 122.8, 31.2, 17.7, 14.8. HRMS (ESI) Calcd for $C_{10}H_{13}NOSNa^{+}$([M + Na]$^{+}$) 218.0610, found: 218.0619.



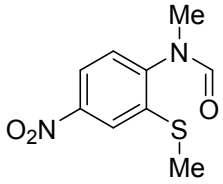
***N*-(4-bromo-2-(methylthio)phenyl)-*N*-methylformamide (3j)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 40.9 mg, yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.24 – 7.22 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.10 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 141.1, 137.8, 129.7, 128.4, 128.1, 123.1, 32.3, 14.8. HRMS (ESI) Calcd for $C_9H_{11}BrNOS^+$([M + H]$^+$) 259.9739, found: 259.9729.



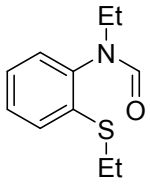
***N*-(5-bromo-2-(methylthio)phenyl)-*N*-methylformamide (3k)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 43.0 mg, yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.52 – 7.48 (m, 1H), 7.31 (s, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 3.20 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 140.2, 138.0, 132.2, 131.4, 127.4, 118.4, 32.6, 15.1. HRMS (ESI) Calcd for $C_9H_{11}BrNOS^+$([M + H]$^+$) 259.9739, found: 259.9746.



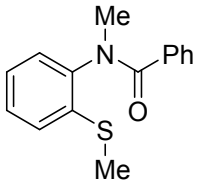
***N*-methyl-*N*-(2-(methylthio)-4-nitrophenyl)formamide (3l)**

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 29.4 mg, yield: 65%; mp 82–83 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.09-8.04 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 3.25 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 148.1, 144.1, 141.5, 128.8, 120.5, 120.4, 32.5, 15.0. HRMS (ESI) Calcd for $C_9H_{11}N_2O_3S^+$([M + H]$^+$) 227.0485, found: 227.0482.



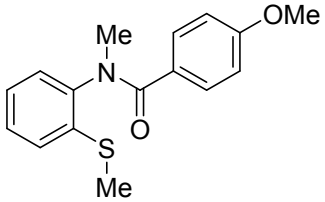
***N*-ethyl-*N*-(2-(ethylthio)phenyl)formamide (3m)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 12.5 mg, yield: 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.37 – 7.32 (m, 2H), 7.23 – 7.19 (m, 1H), 7.14 – 7.12 (m, 1H), 3.77 (q, *J* = 7.2 Hz, 2H), 2.94 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz,3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 138.4, 137.7, 129.8, 129.0, 127.8, 125.8, 40.2, 26.5, 13.9, 13.0. HRMS (ESI) Calcd for $C_{11}H_{15}NOSNa^{+}$([M + Na]$^{+}$) 232.0767, found: 232.0765.



***N*-methyl-*N*-(2-(methylthio)phenyl)benzamide (3n)**

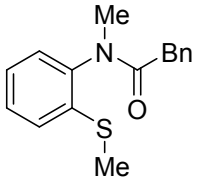
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 16.0 mg, yield: 31%; mp 100–101 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.22 – 7.10 (m, 5H), 6.98 – 6.89 (m, 2H), 3.36 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 141.8, 137.7, 136.0, 129.8, 129.4, 128.3, 128.0, 127.9, 127.6, 125.3, 36.7, 14.7. HRMS (ESI) Calcd for $C_{15}H_{16}NOS^{+}$ ([M + H]$^{+}$) 258.0947, found: 258.0947.



4-methoxy-*N*-methyl-*N*-(2-(methylthio)phenyl)benzamide (3o)

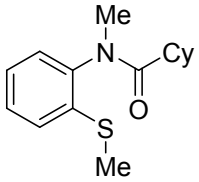
White oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 24.1 mg, yield: 42%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.11 (m, 2H), 7.02 – 6.87 (m, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 3.71 (s, 3H), 3.33 (s, 3H), 2.45 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 160.8, 142.3, 137.6, 130.2, 129.2,

128.1, 125.4, 112.9, 55.2, 37.0, 14.7. HRMS (ESI) Calcd for $C_{16}H_{18}NO_2S^+$ ([M + H]$^+$) 288.1053, found: 288.1052.



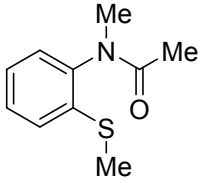
***N*-methyl-*N*-(2-(methylthio)phenyl)-2-phenylacetamide (3p)**

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 31.2 mg, yield: 59%; mp 90–92 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 1H), 7.23 – 7.10 (m, 5H), 7.06 (d, *J* = 7.0 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 3.41 (d, *J* = 15.0 Hz, 1H), 3.31 (d, *J* = 15.0 Hz, 1H), 3.19 (s, 3H), 2.43 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 140.2, 138.7, 135.4, 129.3, 129.0, 128.8, 128.1, 126.5, 125.3, 124.8, 40.7, 35.4, 14.1. HRMS (ESI) Calcd for $C_{16}H_{18}NOS^+$ ([M + H]$^+$) 272.1104, found: 272.1105.



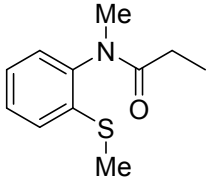
***N*-methyl-*N*-(2-(methylthio)phenyl)cyclohexanecarboxamide (3q)**

White oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 26.3 mg, yield: 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 1H), 7.23-7.16 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 3.16 (s, 3H), 2.45 (s, 3H), 1.98 – 1.91 (m, 1H), 1.79 – 1.75 (m, 1H), 1.69 – 1.57 (m, 4H), 1.55 – 1.51 (m, 1H), 1.48 – 1.38 (m, 1H), 1.22 – 1.12 (m, 1H), 1.06 – 0.85 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 140.6, 138.8, 128.8, 128.2, 125.3, 124.9, 41.9, 35.3, 29.9, 29.4, 25.8, 25.7, 25.5, 14.3. HRMS (ESI) Calcd for $C_{15}H_{21}NOSNa^+$ ([M + Na]$^+$) 286.1236, found: 286.1245.



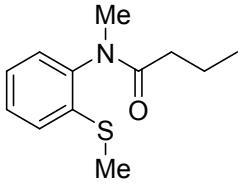
***N*-methyl-*N*-(2-(methylthio)phenyl)acetamide (3r)[5]**

White solidobtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 28.5 mg, yield: 73%; mp 76–78 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 1H), 7.22 – 7.17 (m, 2H), 7.13 (d, *J* = 6.0 Hz, 1H), 3.18 (s, 3H), 2.46 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 141.0, 138.6, 129.0, 128.3, 125.6, 125.1, 35.2, 21.9, 14.2.



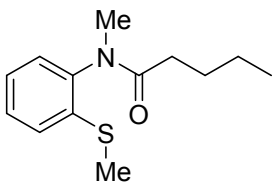
***N*-methyl-*N*-(2-(methylthio)phenyl)propionamide (3s)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 25.9 mg, yield: 62%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 1H), 7.22 – 7.16 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 3.18 (s, 3H), 2.44 (s, 3H), 2.00 (q, *J* = 7.5 Hz, 2H), 1.05 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 140.6, 138.7, 128.9, 128.4, 125.5, 124.9, 35.3, 27.1, 14.2, 9.6. HRMS (ESI) Calcd for $C_{11}H_{15}NOSNa^+$([M + Na]$^+$) 232.0767, found: 232.0776.



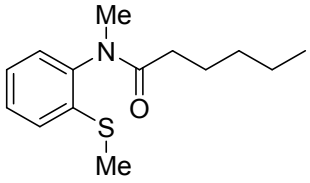
***N*-methyl-*N*-(2-(methylthio)phenyl)butyramide (3t)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 29.4 mg, yield: 66%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 1H), 7.22 – 7.16 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H), 2.45 (s, 3H), 1.99 – 1.92 (m, 2H), 1.65 – 1.55 (m, 2H), 0.82 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 140.6, 138.7, 128.9, 128.4, 125.4, 124.9, 35.6, 35.2, 18.7, 14.1, 14.0. HRMS (ESI) Calcd for $C_{12}H_{18}NOS^+$([M + H]$^+$) 224.1104, found: 224.1103.



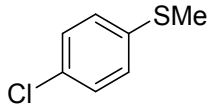
***N*-methyl-*N*-(2-(methylthio)phenyl)pentanamide (3u)**

White oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 29.4 mg, yield: 62%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 1H), 7.22 – 7.16 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 3.17 (s, 3H), 2.45 (s, 3H), 2.00 – 1.96 (m, 2H), 1.59 – 1.52 (m, 2H), 1.25 – 1.18 (m, 2H), 0.80 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 140.6, 138.7, 128.9, 128.4, 125.4, 124.9, 35.2, 33.4, 27.4, 22.5, 14.2, 13.9. HRMS (ESI) Calcd for $C_{13}H_{20}NOS^+$ ($[M + H]^+$) 238.1260, found: 238.1263.



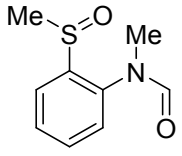
***N*-methyl-*N*-(2-(methylthio)phenyl)hexanamide (3v)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 6:1), 30.6 mg, yield: 61%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 1H), 7.22 – 7.16 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 3.17 (s, 3H), 2.44 (s, 3H), 1.97 (t, *J* = 8.0 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.23 – 1.14 (m, 4H), 0.82 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 140.6, 138.7, 128.9, 128.4, 125.4, 124.9, 35.2, 33.7, 31.6, 25.0, 22.5, 14.2, 14.0. HRMS (ESI) Calcd for $C_{14}H_{22}NOS^+$($[M + H]^+$) 252.1417, found: 252.1422.



4-Chlorothioanisole (4)[6]

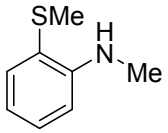
Yellow oil obtained by column chromatography (petroleum ether), 25.0 mg, yield: 79%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 131.0, 129.0, 128.0, 16.2.



***N*-methyl-*N*-(2-(methylsulfinyl)phenyl)formamide (5)**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 1:1), 26.4 mg, yield: 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 0.3H), 8.23 (s, 0.7H), 8.11-8.09 (m, 1H), 7.68-7.60 (m, 2H), 7.26-7.21 (m, 1H), 3.39 (s, 1H), 3.27 (s, 2H),

2.80 (s, 1H), 2.70 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 162.6, 144.0, 143.8, 138.1, 136.8, 132.7, 132.5, 130.0, 129.9, 128.0, 127.2, 125.3, 125.2, 43.2, 42.8, 37.8, 34.0. HRMS (ESI) Calcd for $C_9H_{11}NO_2SK^+$([M + K]$^+$) 236.0142, found: 236.0135.



***N*-methyl-2-(methylthio)aniline (6)[7]**

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 100:1), 18.4mg, yield: 60%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 1H), 7.22 – 7.19 (m, 1H), 6.67 – 6.58 (m, 2H), 4.91 (s, 1H), 2.89 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 133.9, 129.5, 119.8, 116.9, 109.6, 30.7, 18.1.

4. References

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(2)C. Büll, T. Heise, N. V. Hilten, J. F. A. Pijnenborg, V. R. L. J. Bloemendal, L. Gerrits, E. D. Kers-Rebel, T. Ritschel, M. H. D. Brok, G. J. Adema, T. J. Boltje, *Angew. Chem. Int. Ed.*, 2017, **56**, 3309–3313.

(3) S. Wang, S. Xu, C. Yang, H. Sun, J. Wang, *Org. Lett*. 2019, **21**, 1809−1812.

(4) S. B. Yoon, E. J. Chun, Y. R. Noh, Y. J. Yoon, S.-G. Lee, *Bull. Korean Chem. Soc*., 2013, **34**, 2819–2821.

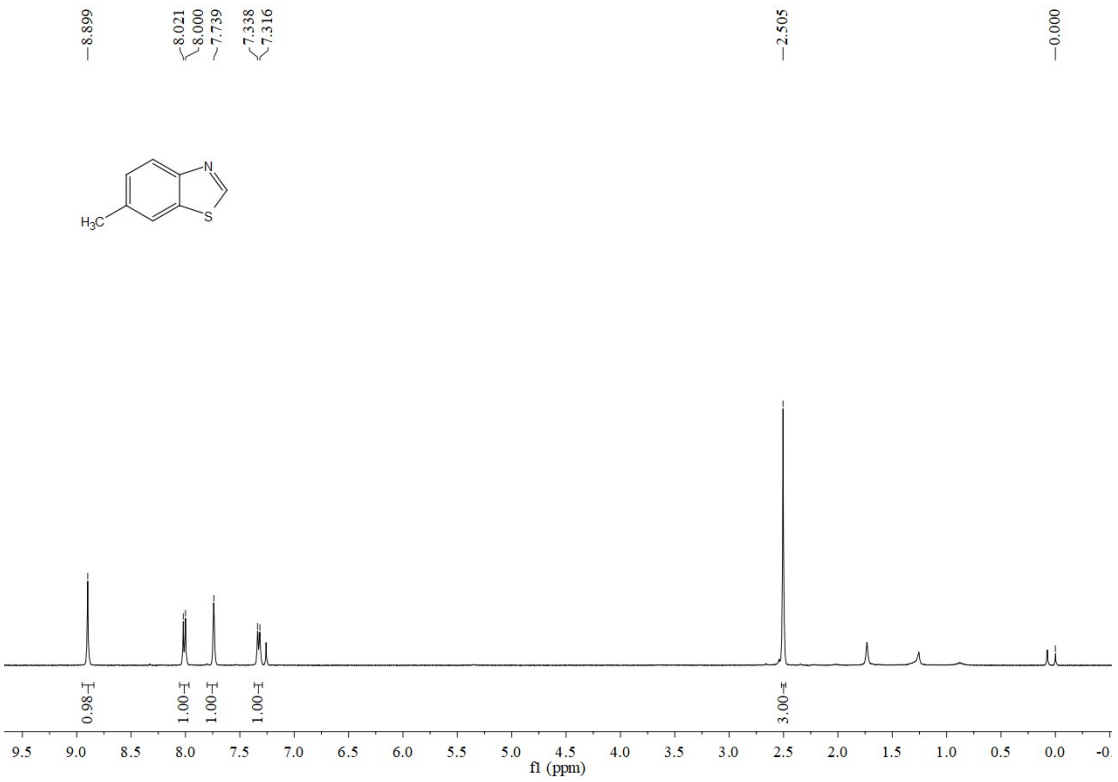
(5)V. Rey, A. B. Pierini, and A. B. Peñéñory, *J. Org. Chem*. 2009, **74**, 1223–1230.

(6) R. Ma, A.-H. Liu, C.-B. Huang, X.-D. Li and L.-N. He, *Green Chem*., 2013, **15**, 1274–1279.

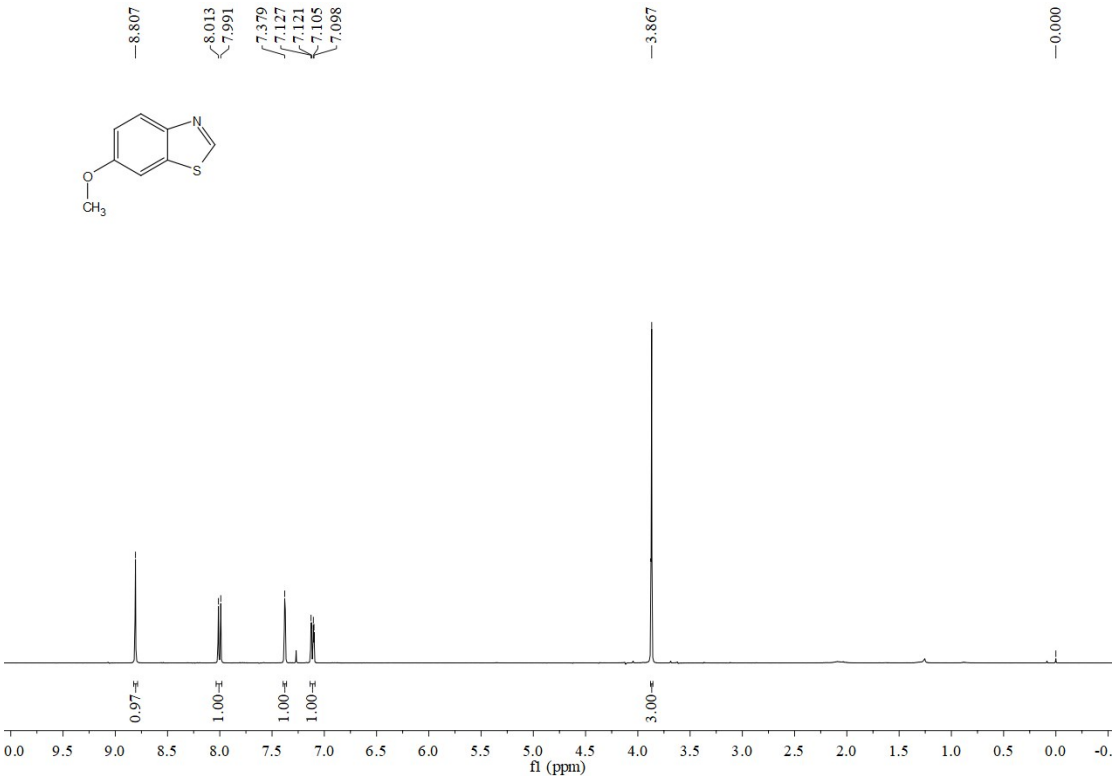
(7) S. Huang, X. Hong, H.-Z. Cui, Q. Zhou, Y.-J. Lina and X.-F. Hou, *Dalton Trans.*, 2019, **48**, 5072–5082.

5. Copies of ^{1}H and ^{13}C NMR SpectraSpectral data

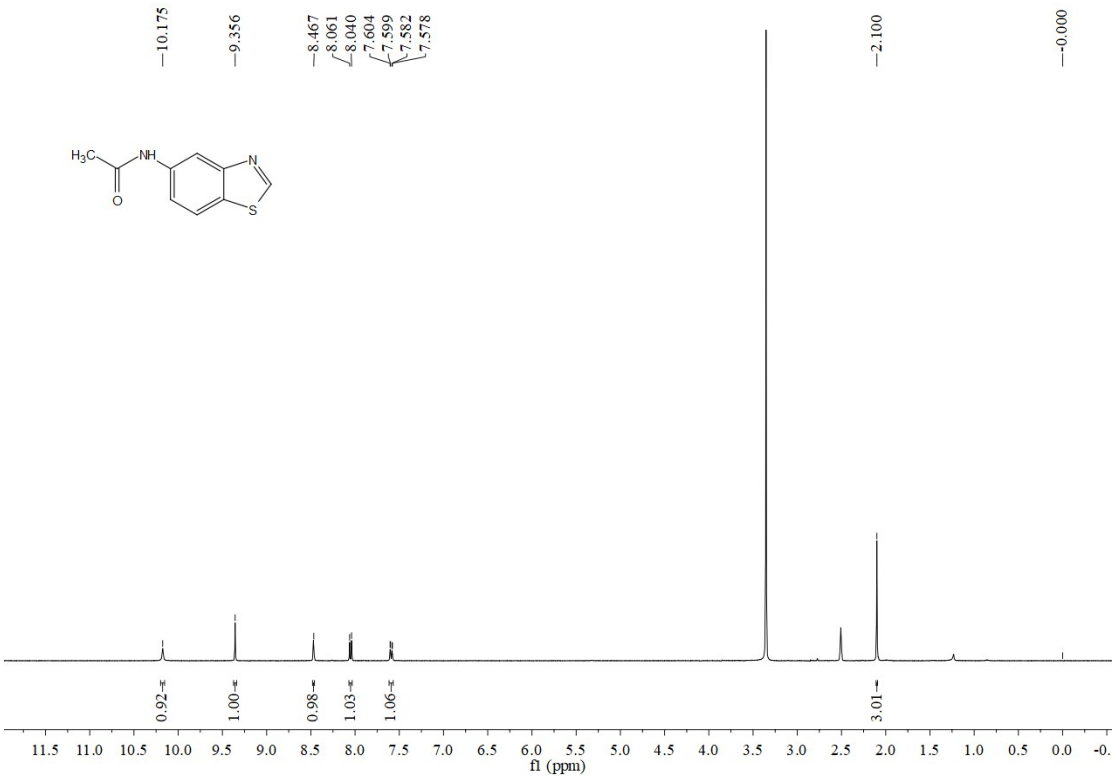
^{1}H NMR (400 MHz, $CDCl_3$) 6-methylbenzo[*d*]thiazole (1b)



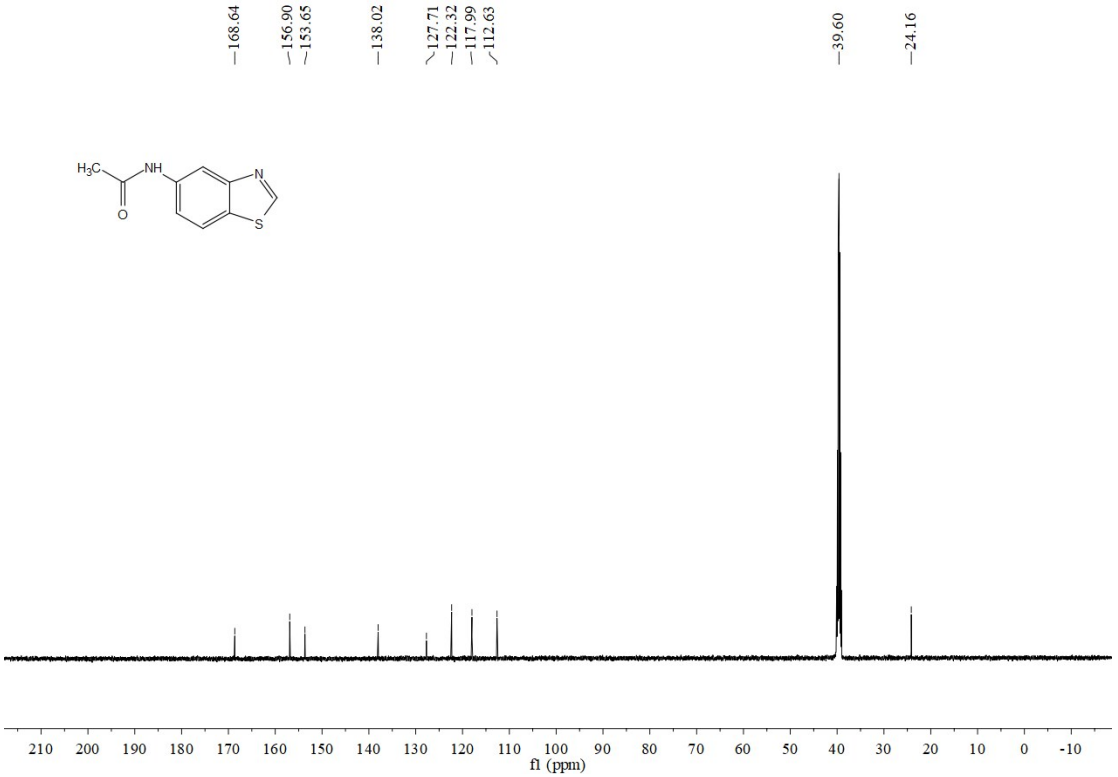
^{1}H NMR (400 MHz, $CDCl_3$) 6-methoxybenzo[*d*]thiazole (1c)



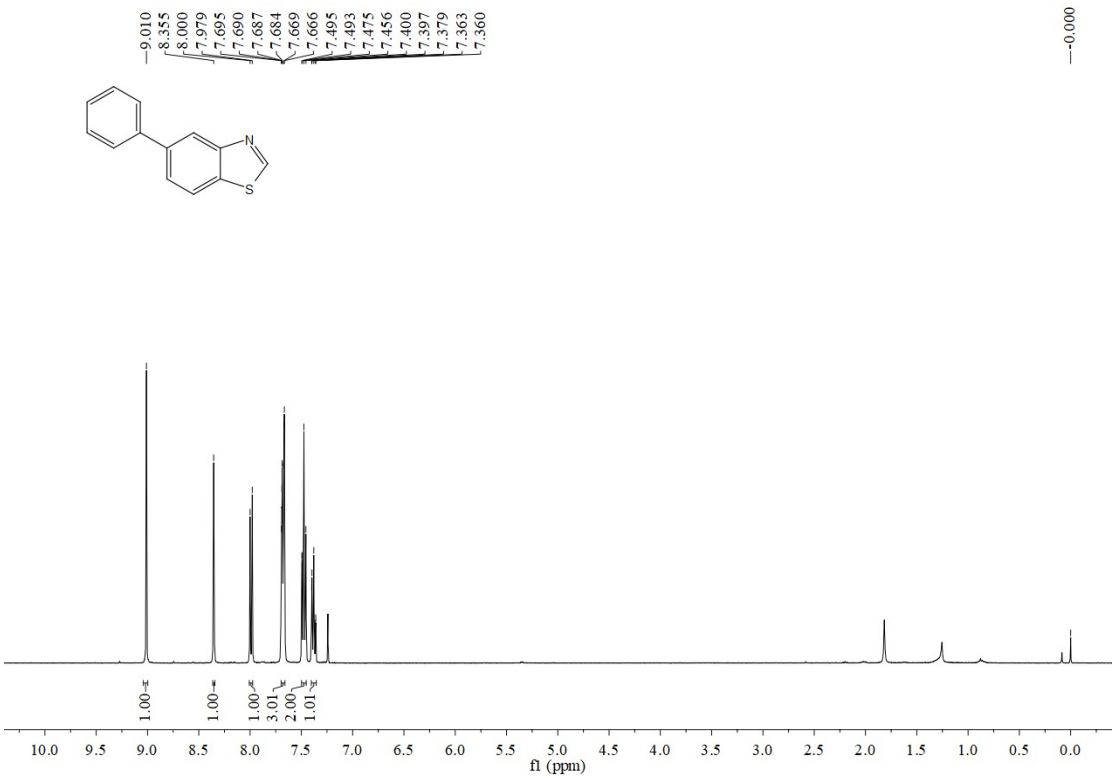
^{1}H NMR (400 MHz, DMSO-d_6) N-(benzo[*d*]thiazol-5-yl)acetamide (1d)



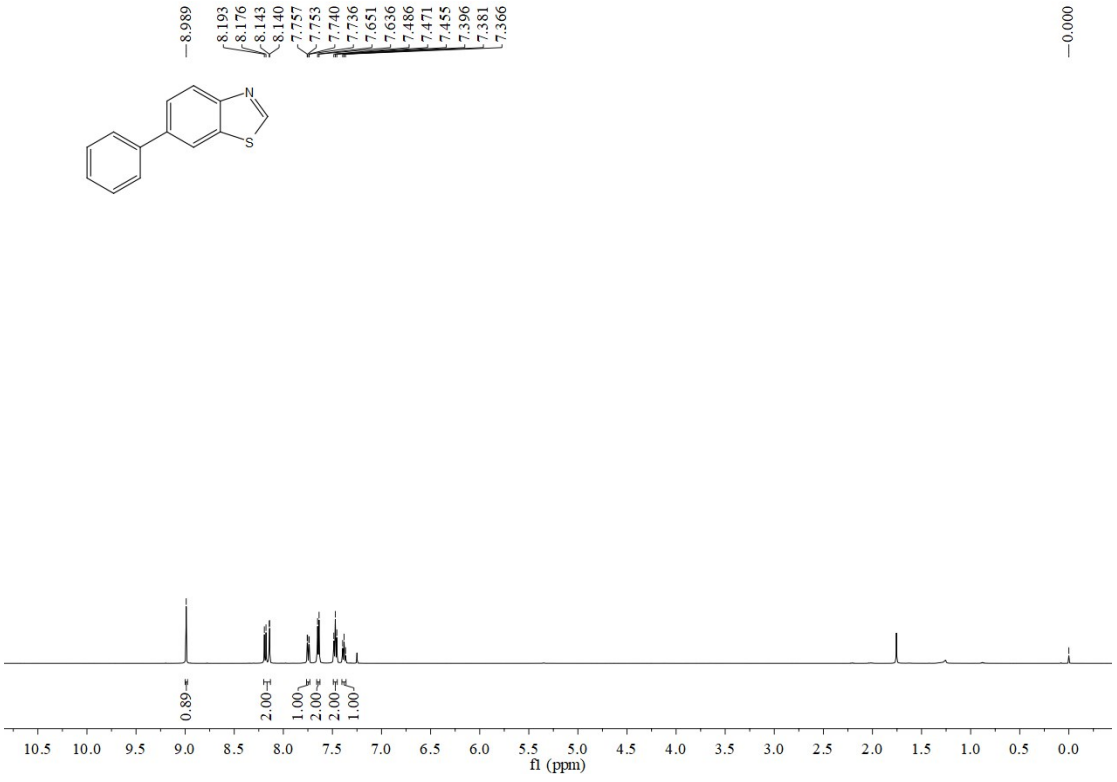
^{13}C NMR (400 MHz, DMSO-d_6) N-(benzo[*d*]thiazol-5-yl)acetamide (1d)



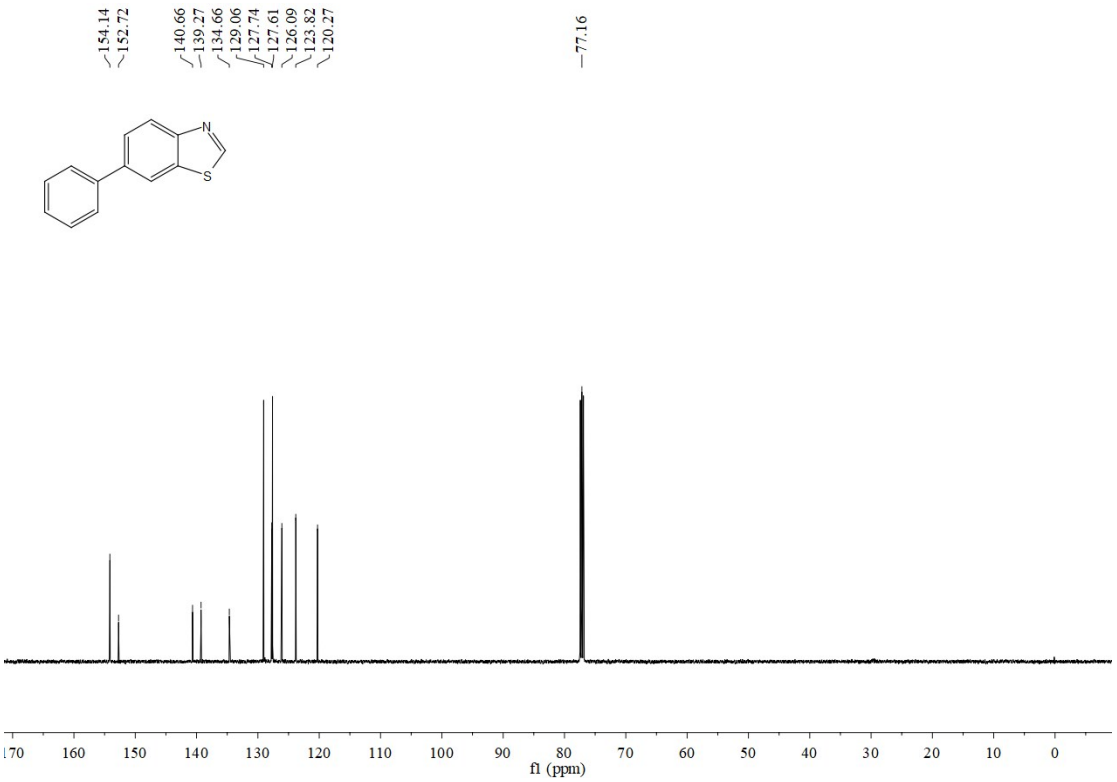
^{1}H NMR (400 MHz, $CDCl_3$) 5-Phenyl benzothiazole (1e)



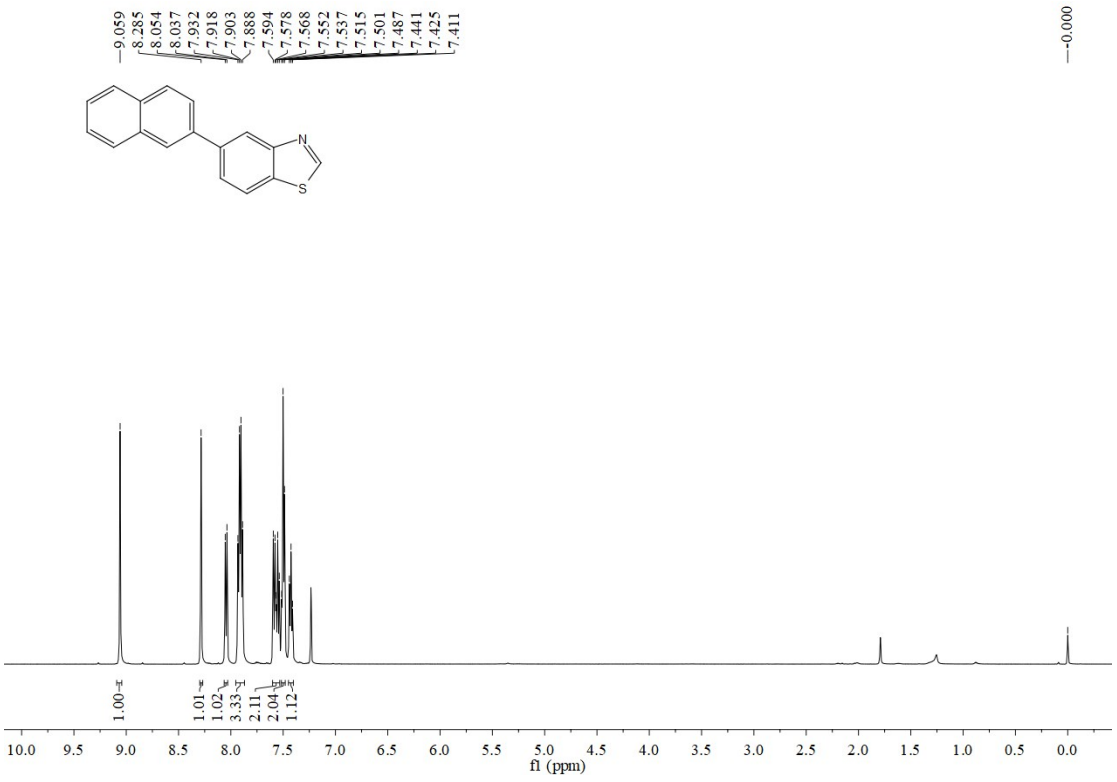
^{1}H NMR (400 MHz, $CDCl_3$) 6-Phenyl benzothiazole (1f)



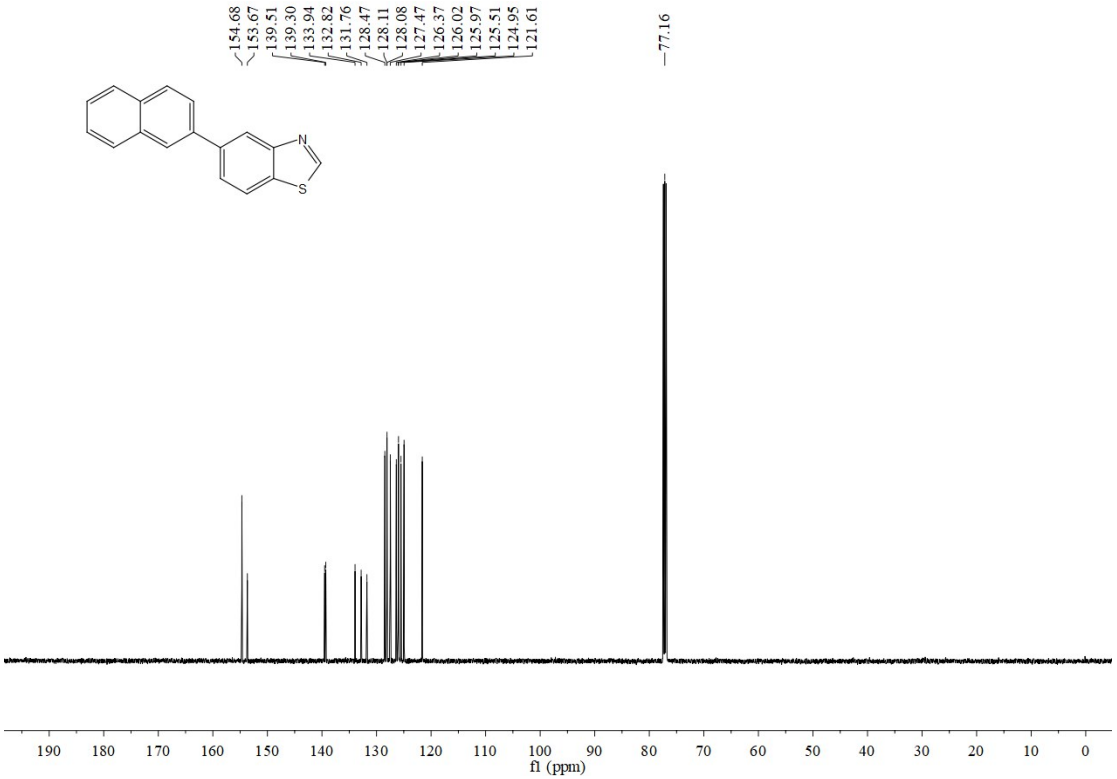
^{13}C NMR (125 MHz, $CDCl_3$)6-Phenyl benzothiazole (1f)



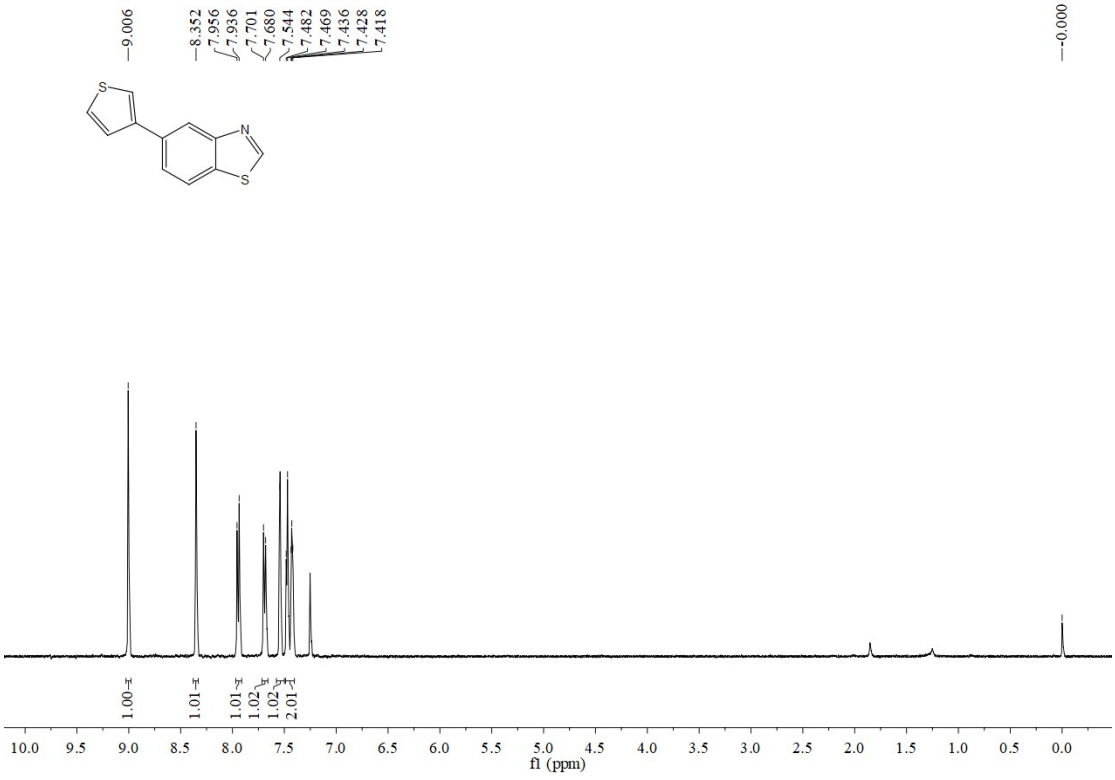
^{1}H NMR (500 MHz, $CDCl_3$) 5-(naphthalen-2-yl)benzo[*d*]thiazole (1g)



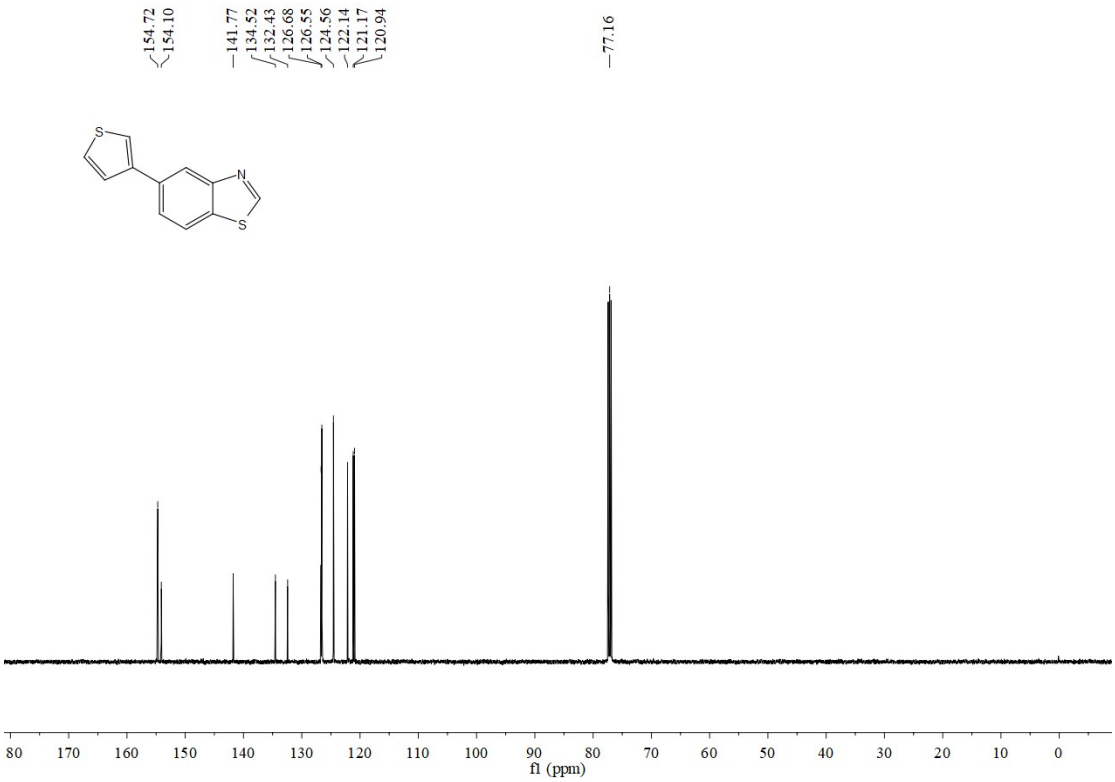
^{13}C NMR (125 MHz, $CDCl_3$) 5-(naphthalen-2-yl)benzo[*d*]thiazole (1g)



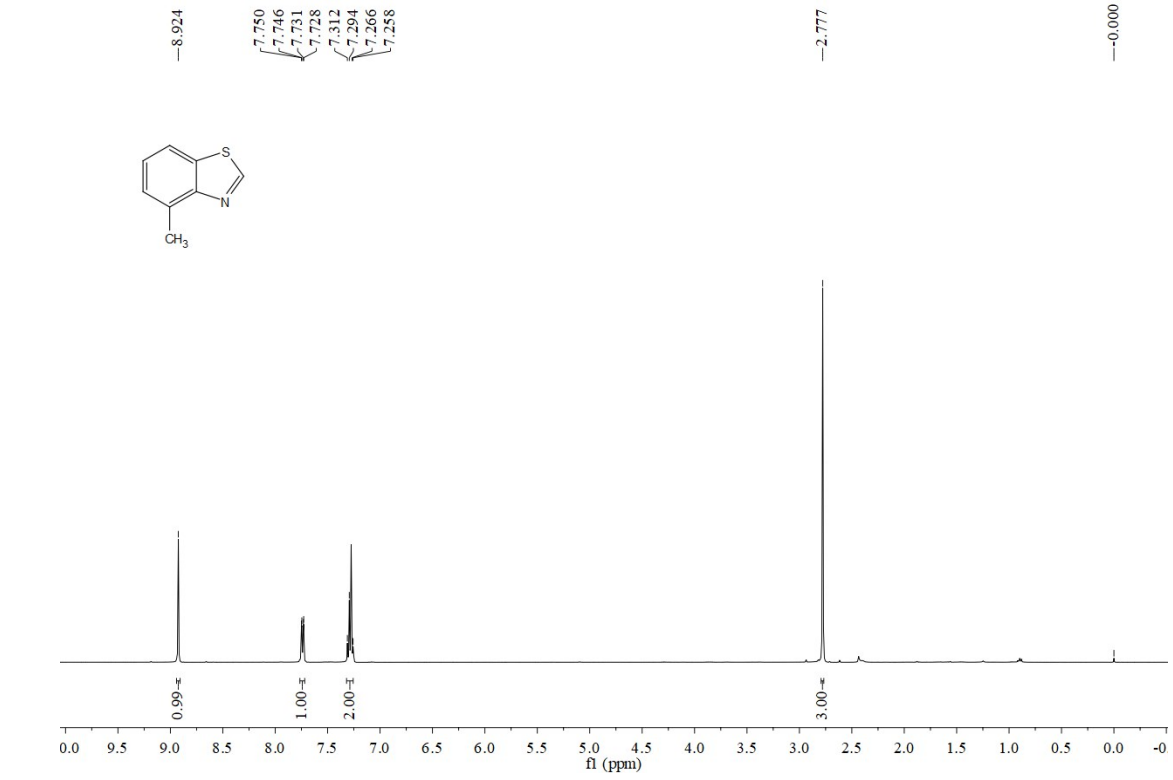
^{1}H NMR (400 MHz, $CDCl_3$) 5-(thiophen-3-yl)benzo[*d*]thiazole (1h)



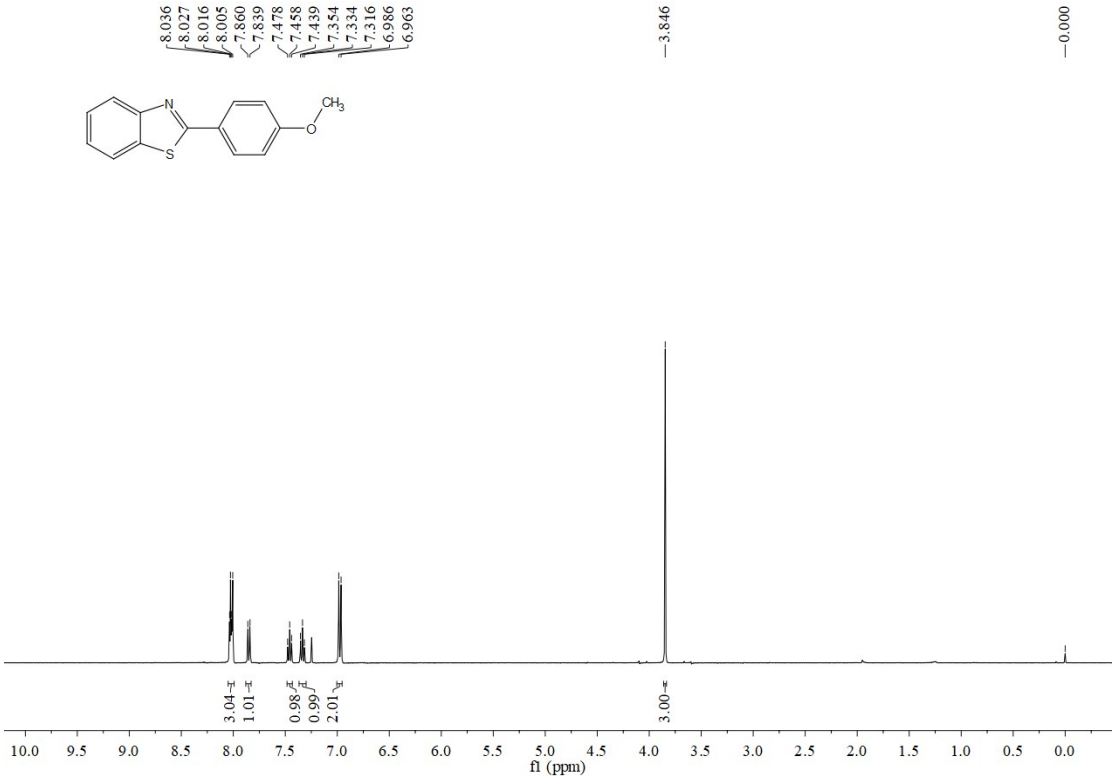
^{13}C NMR (125 MHz, $CDCl_3$) 5-(thiophen-3-yl)benzo[*d*]thiazole (1h)



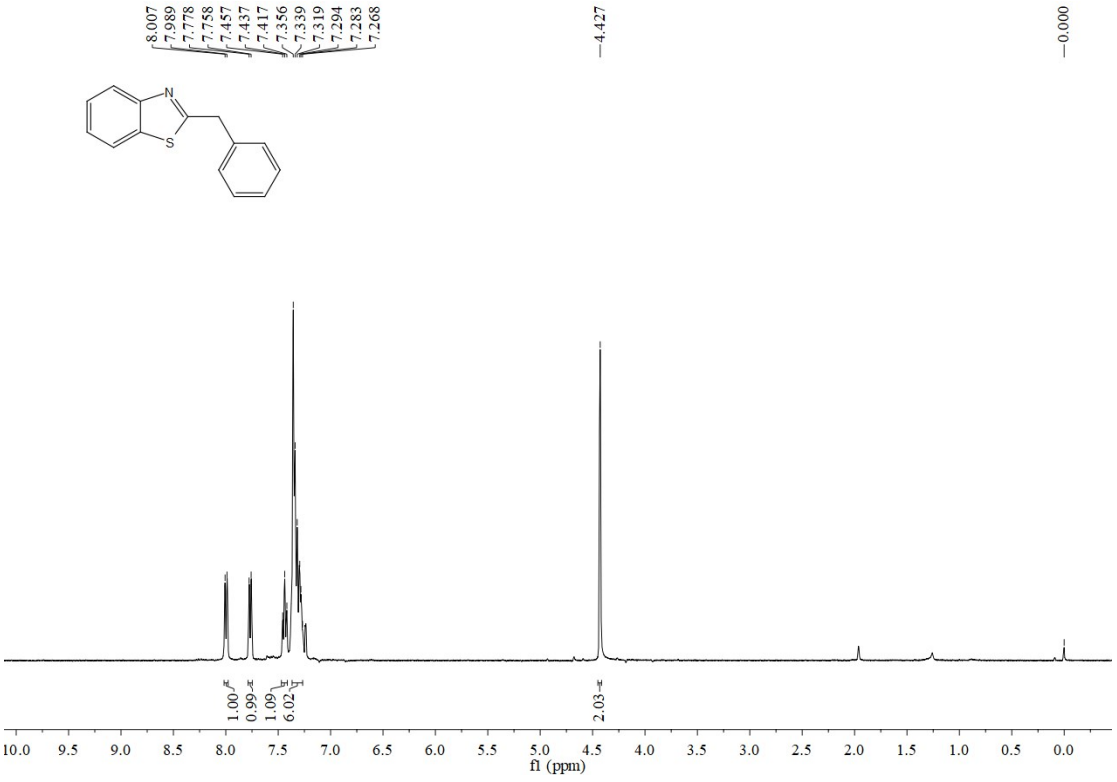
^{1}H NMR (400 MHz, $CDCl_3$) 4-methylbenzo[*d*]thiazole (1i)



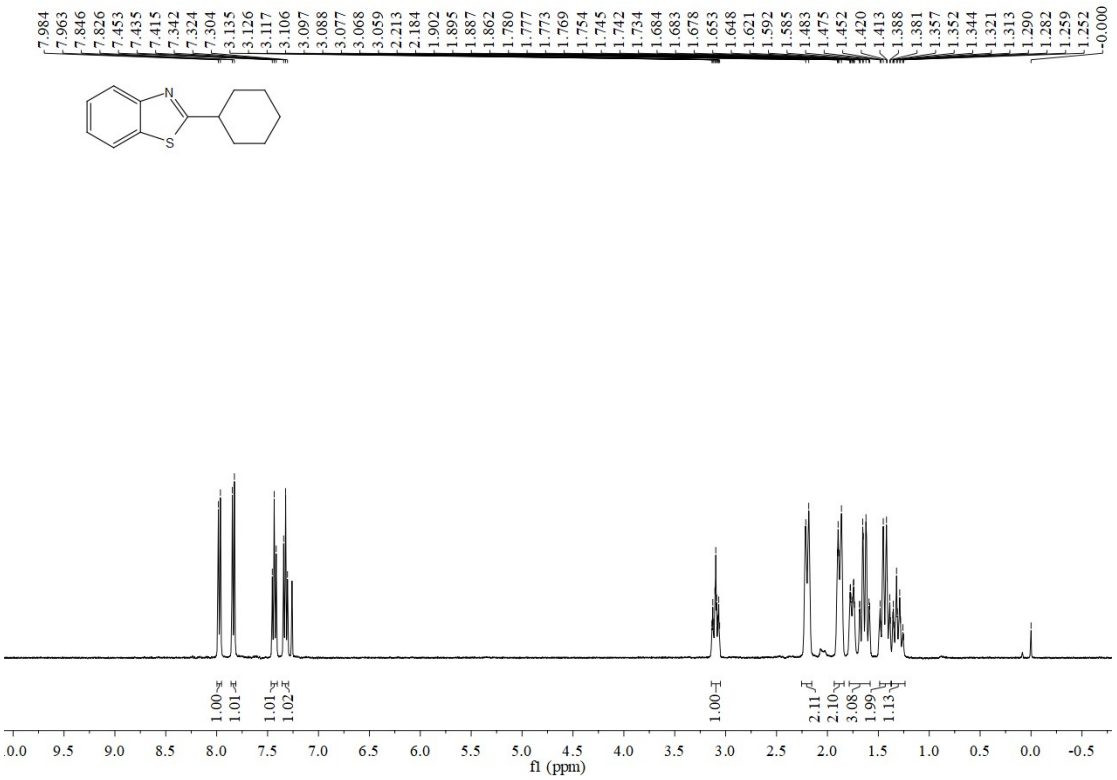
^{1}H NMR (400 MHz, $CDCl_3$) 2-(4-methoxyphenyl)benzo[d]thiazole (1o)



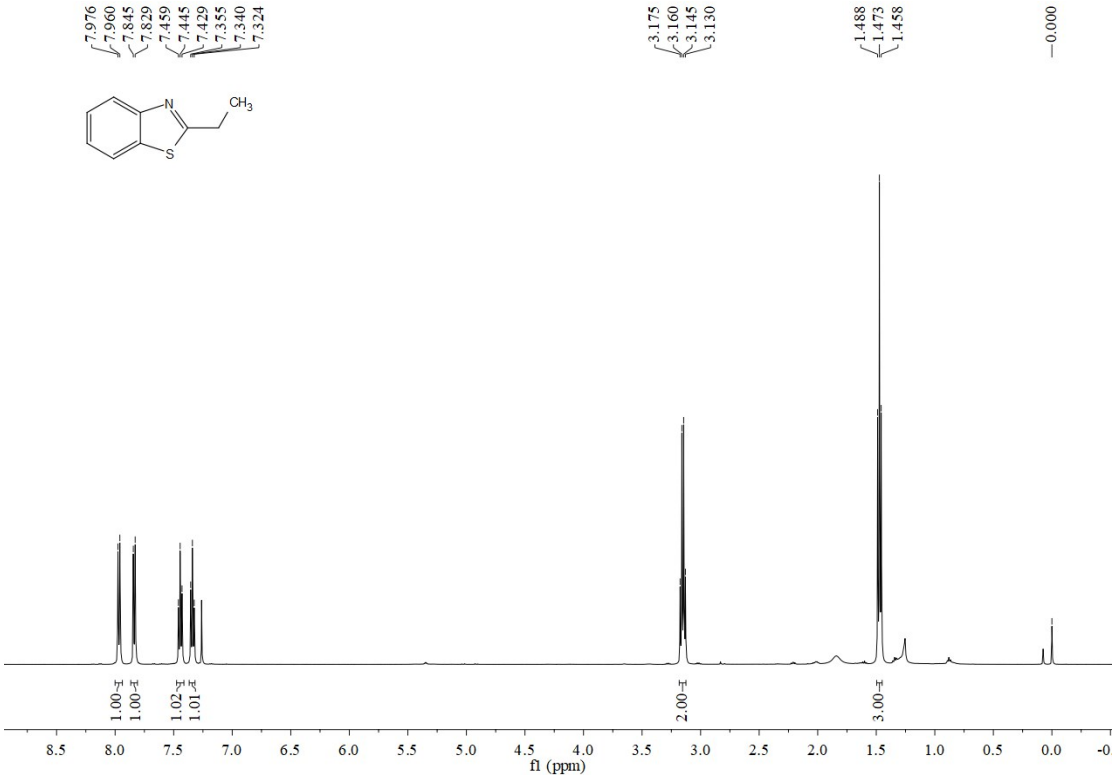
^{1}H NMR (400 MHz, $CDCl_3$) 2-benzylbenzo[*d*]thiazole (1p)



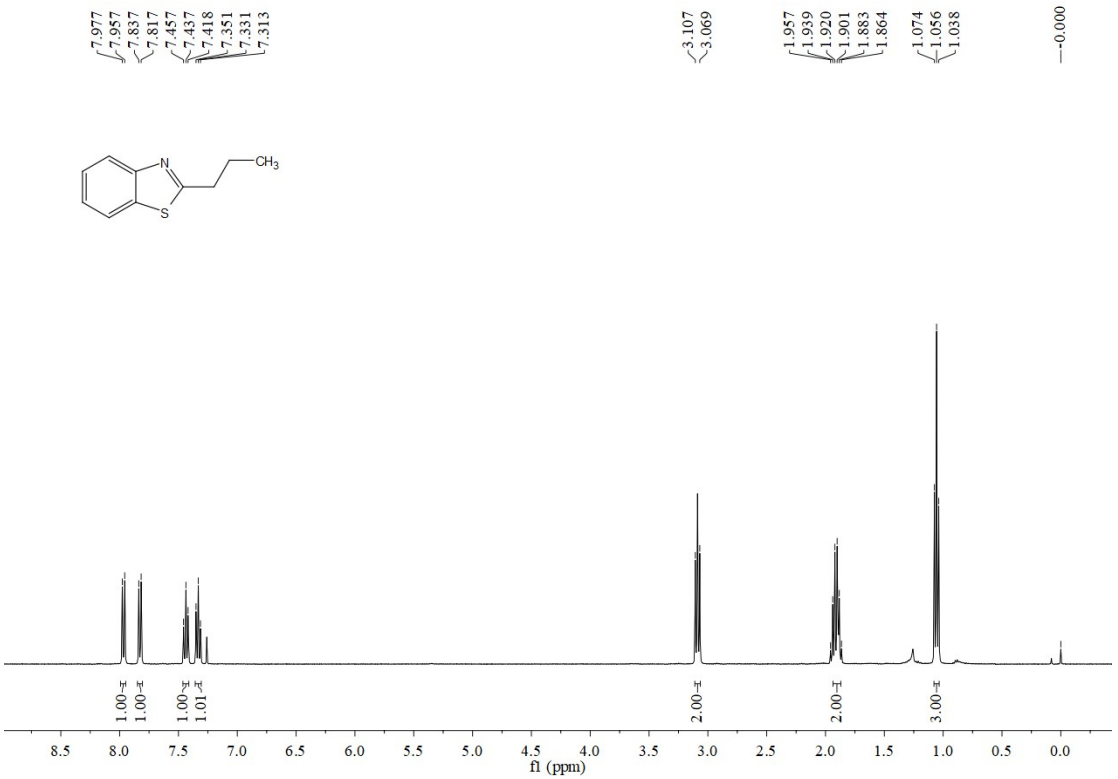
^{1}H NMR (400 MHz, $CDCl_3$) 2-cyclohexylbenzo[*d*]thiazole (1q)



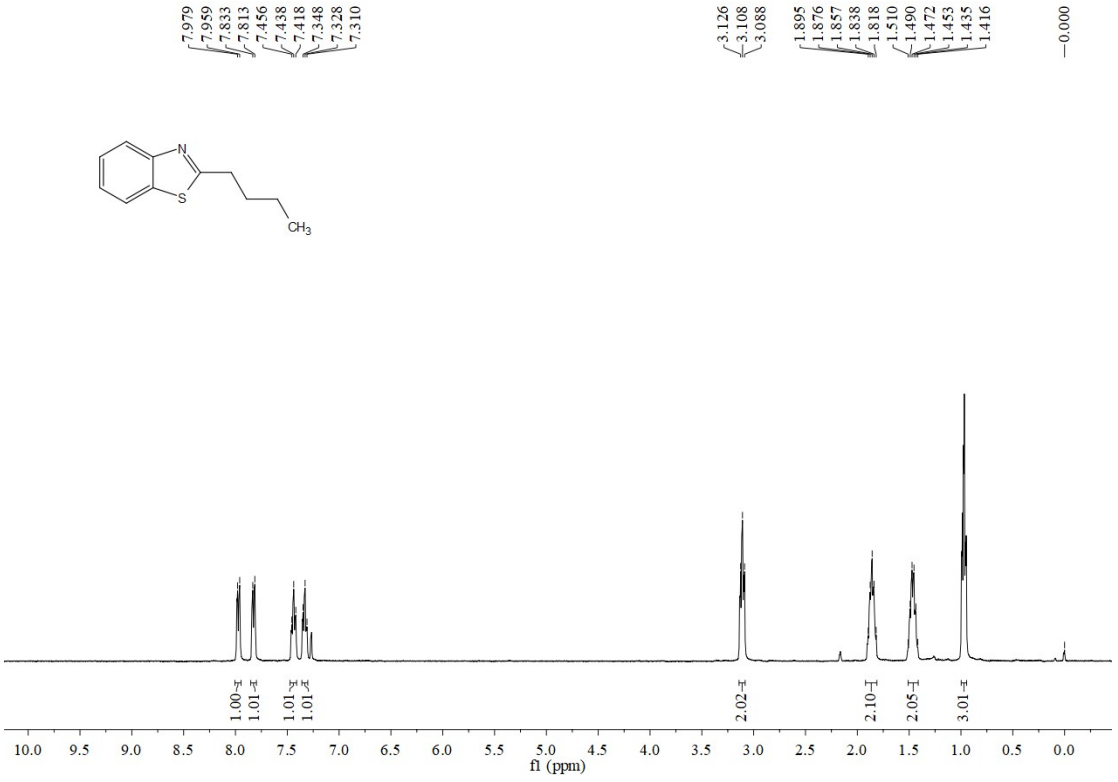
^{1}H NMR (500 MHz, $CDCl_3$) 2-ethylbenzo[*d*]thiazole (1s)



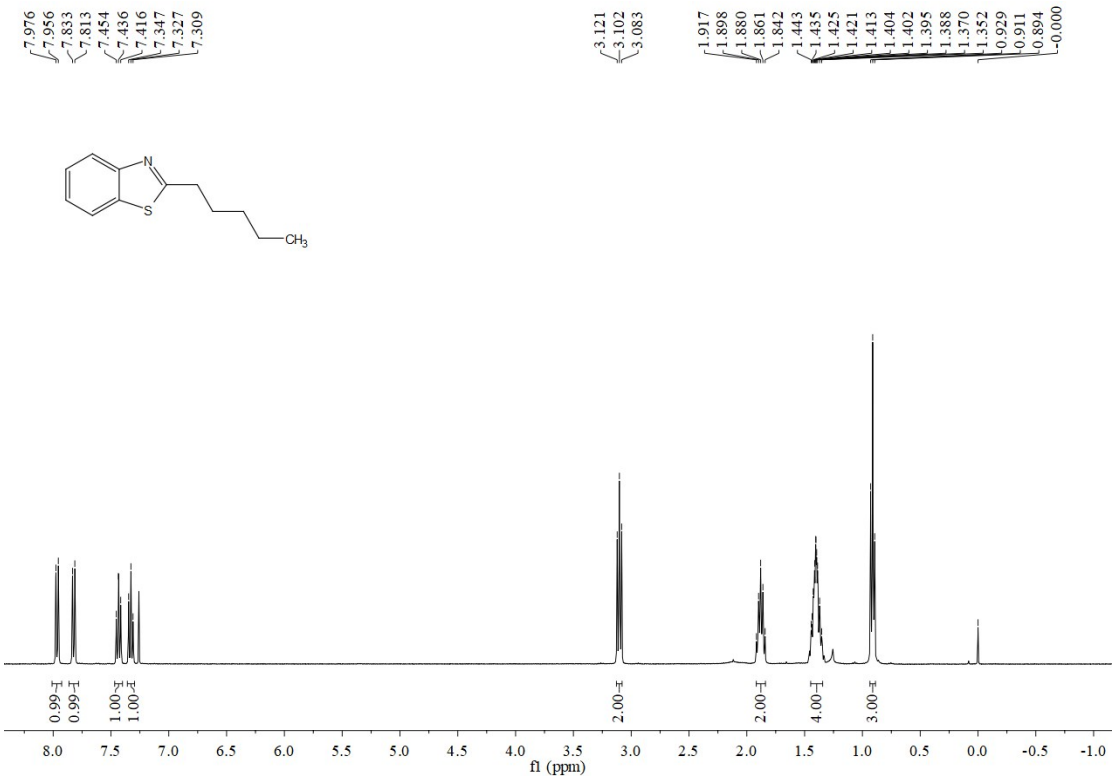
^{1}H NMR (500 MHz, $CDCl_3$) 2-propylbenzo[*d*]thiazole (1t)



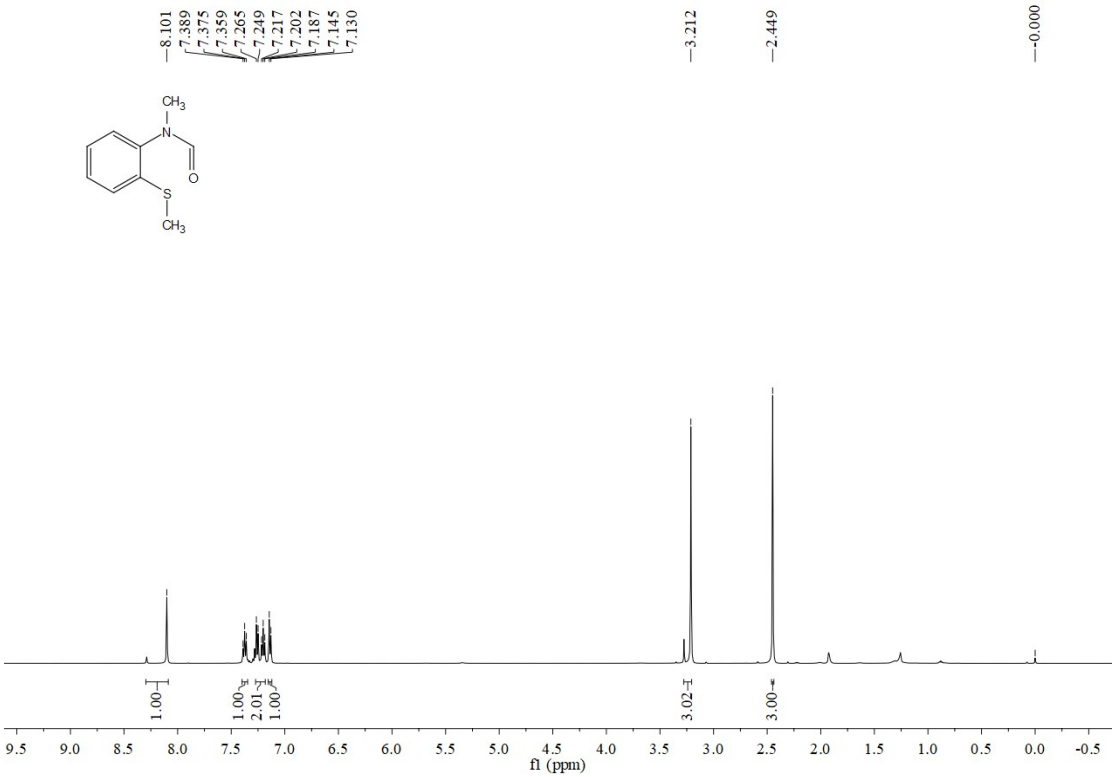
^{1}H NMR (400 MHz, $CDCl_3$) 2-butylbenzo[*d*]thiazole (1u)



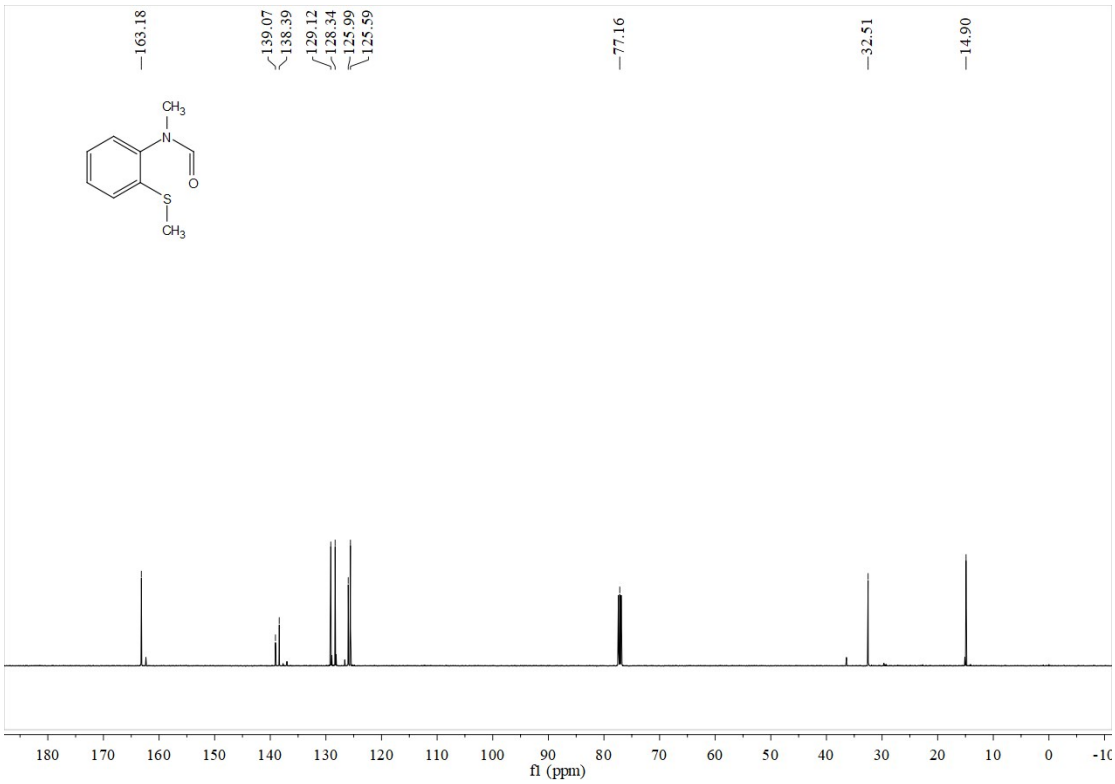
^{1}H NMR (500 MHz, $CDCl_3$) 2-pentylbenzo[*d*]thiazole (1v)



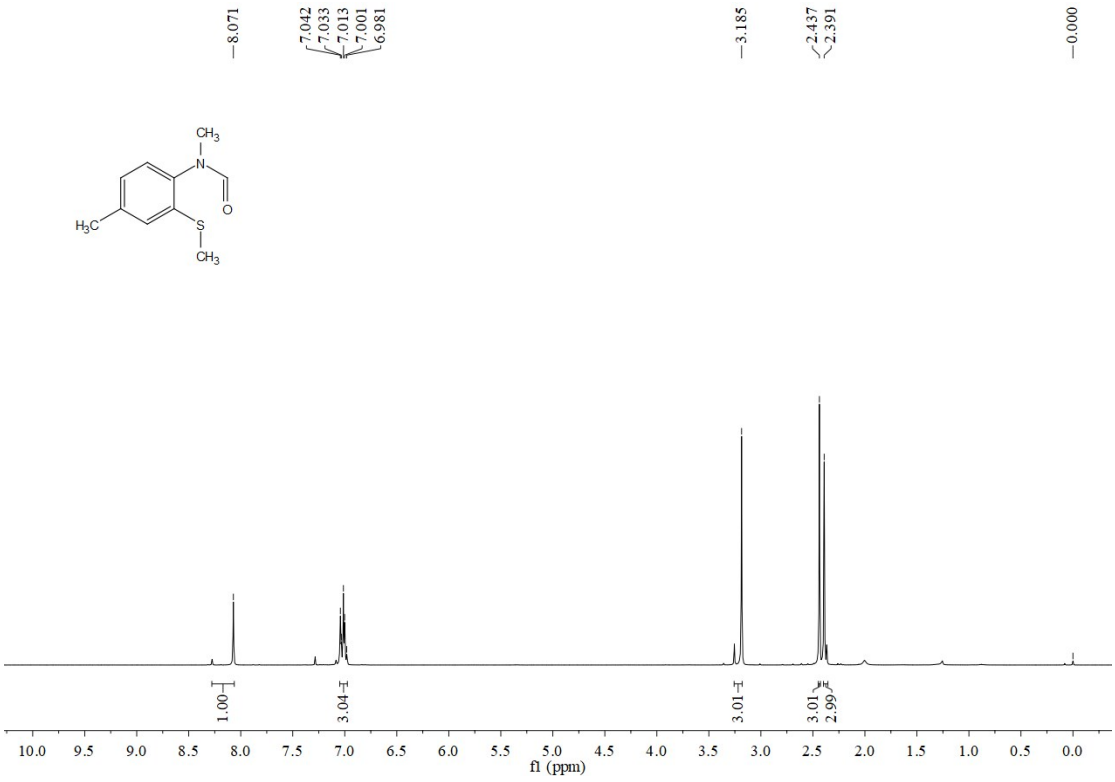
^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)formamide (3a)



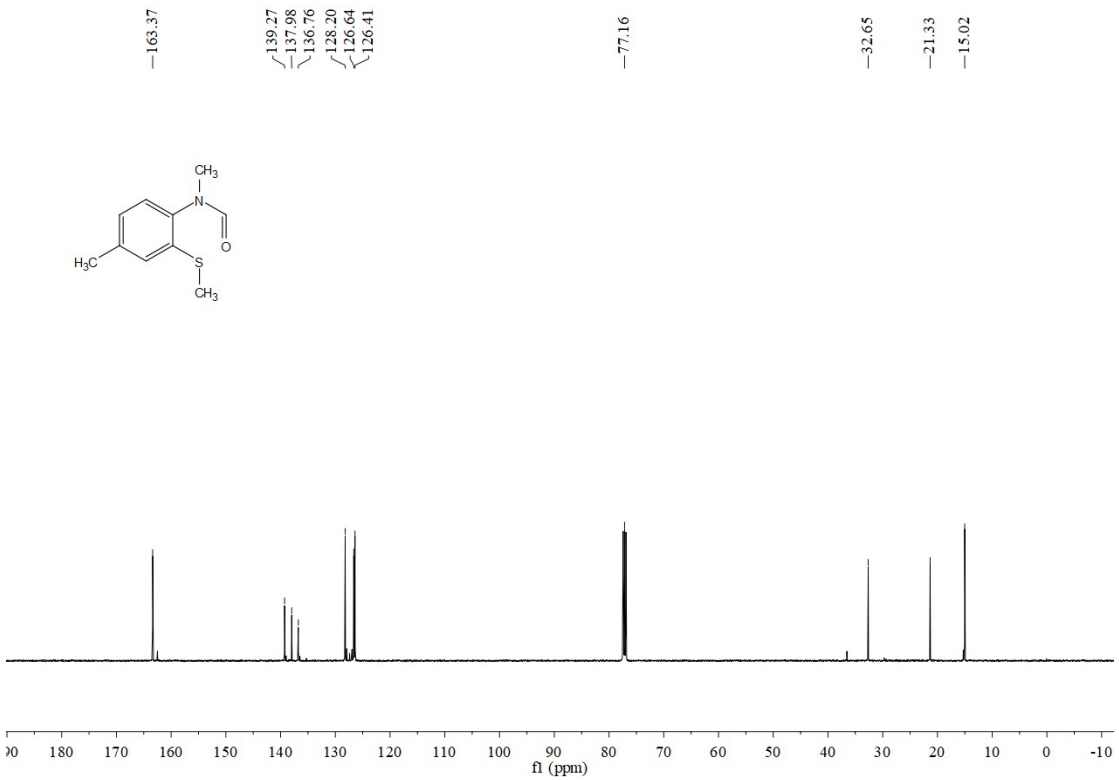
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)formamide (3a)



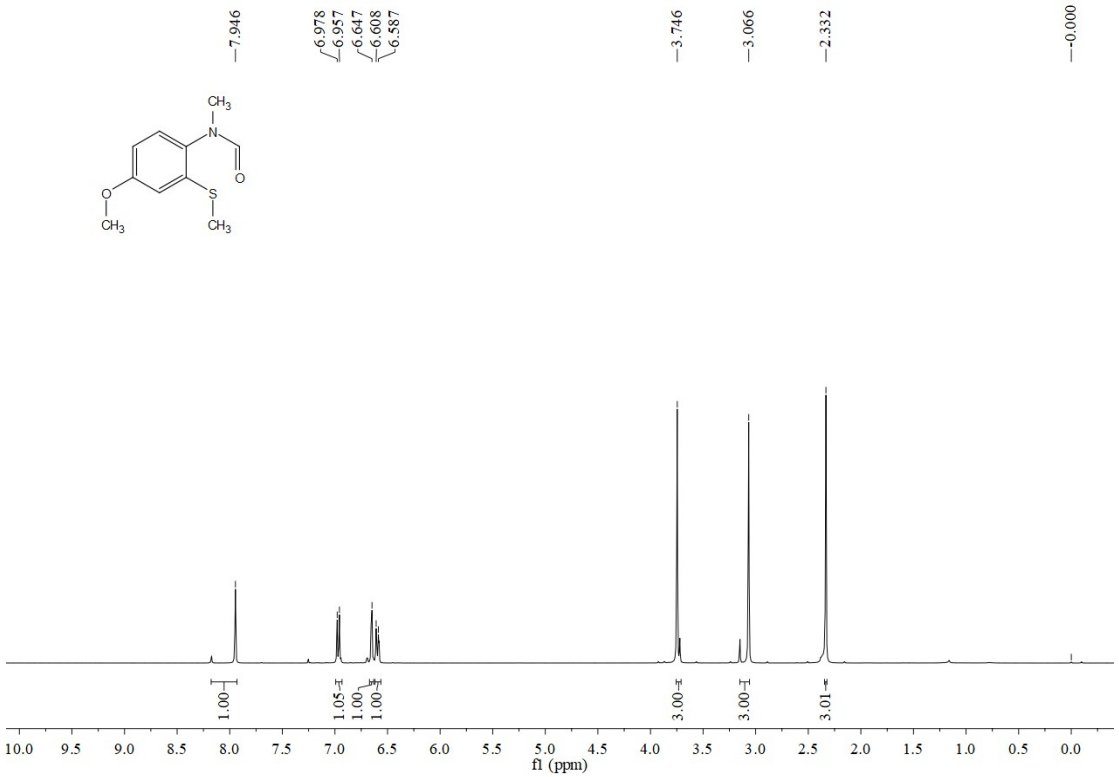
^{1}H NMR (400 MHz, $CDCl_3$) *N*-methyl-*N*-(4-methyl-2-(methylthio)phenyl)formamide (3b)



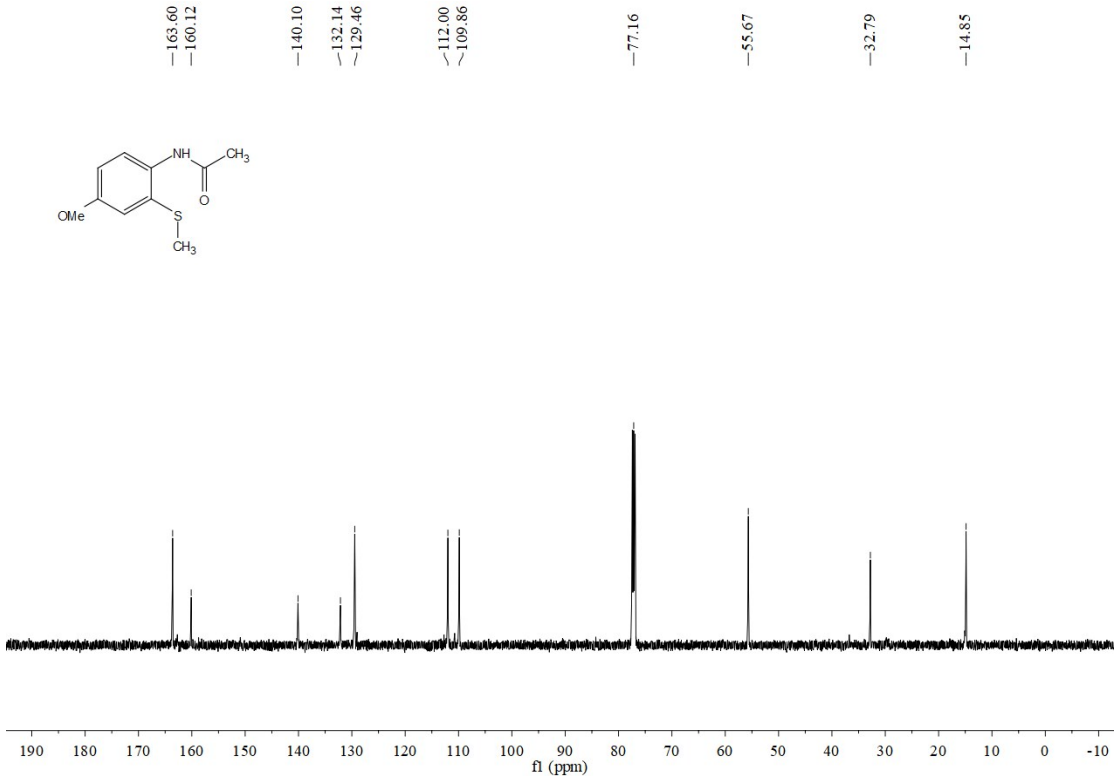
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(4-methyl-2-(methylthio)phenyl)formamide (3b)



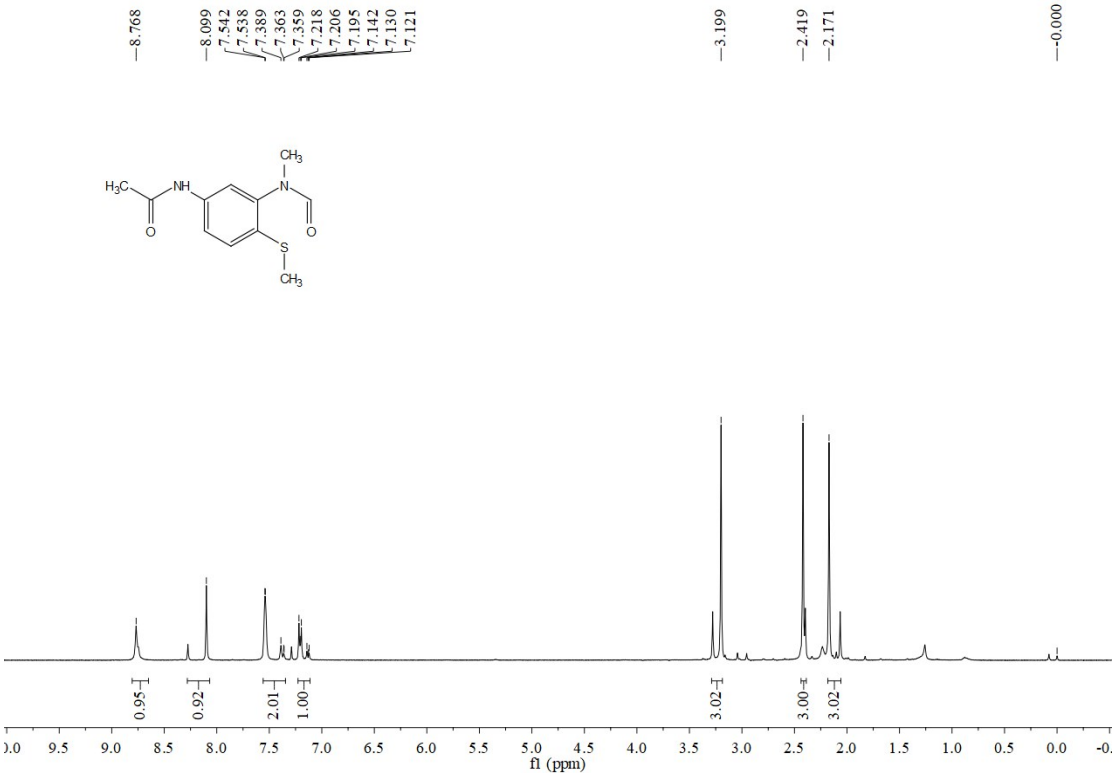
^{1}H NMR (400 MHz, $CDCl_3$) *N*-(4-methoxy-2-(methylthio)phenyl)-*N*-methylformamide (3c)



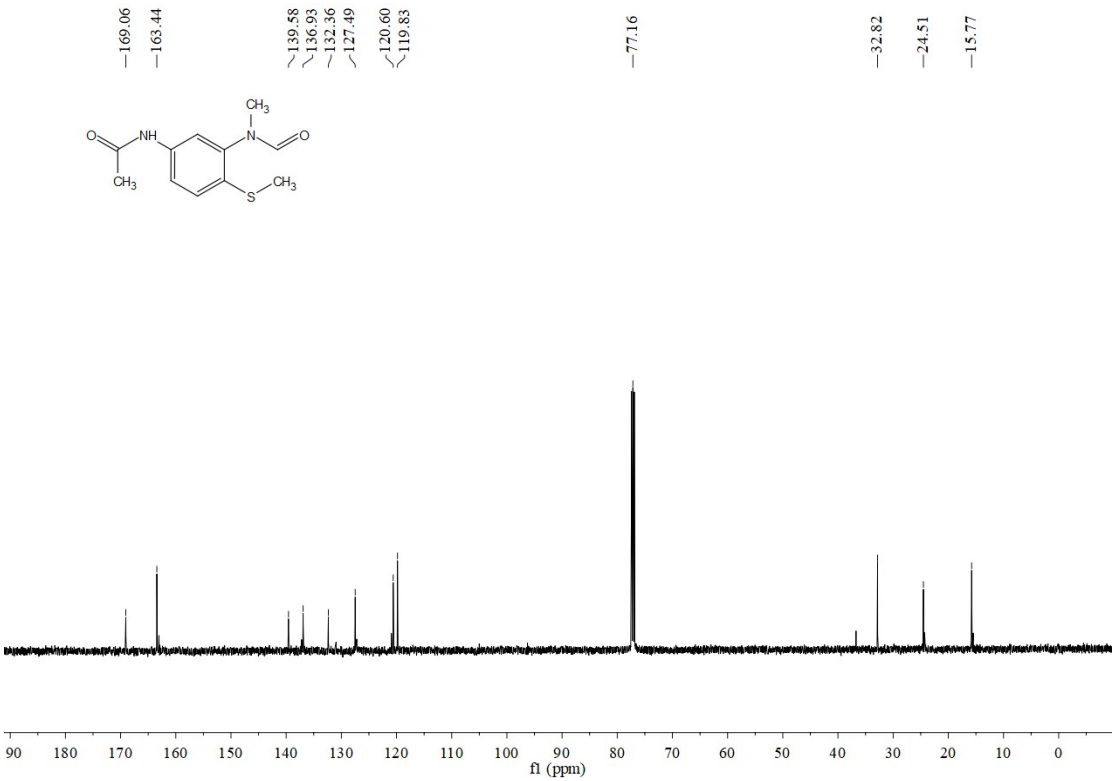
^{13}C NMR (125 MHz, $CDCl_3$) *N*-(4-methoxy-2-(methylthio)phenyl)-*N*-methylformamide (3c)



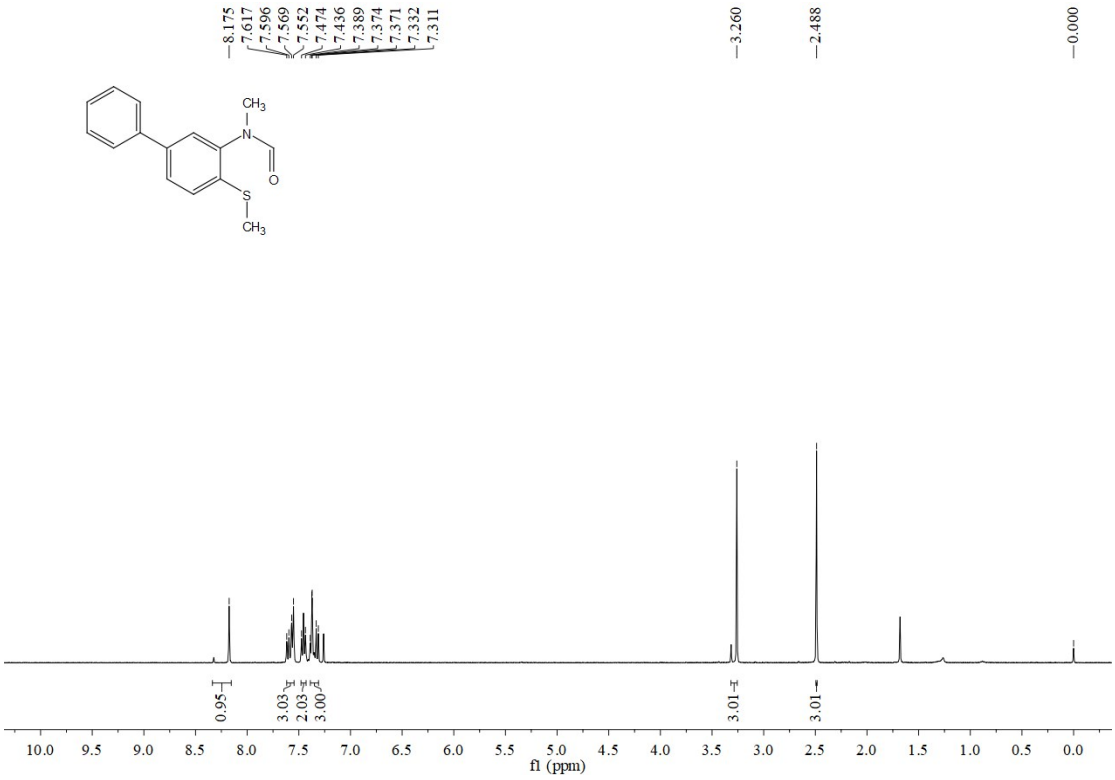
^{1}H NMR (400 MHz, $CDCl_3$) *N*-(3-(*N*-methylformamido)-4-(methylthio)phenyl)acetamide (3d)



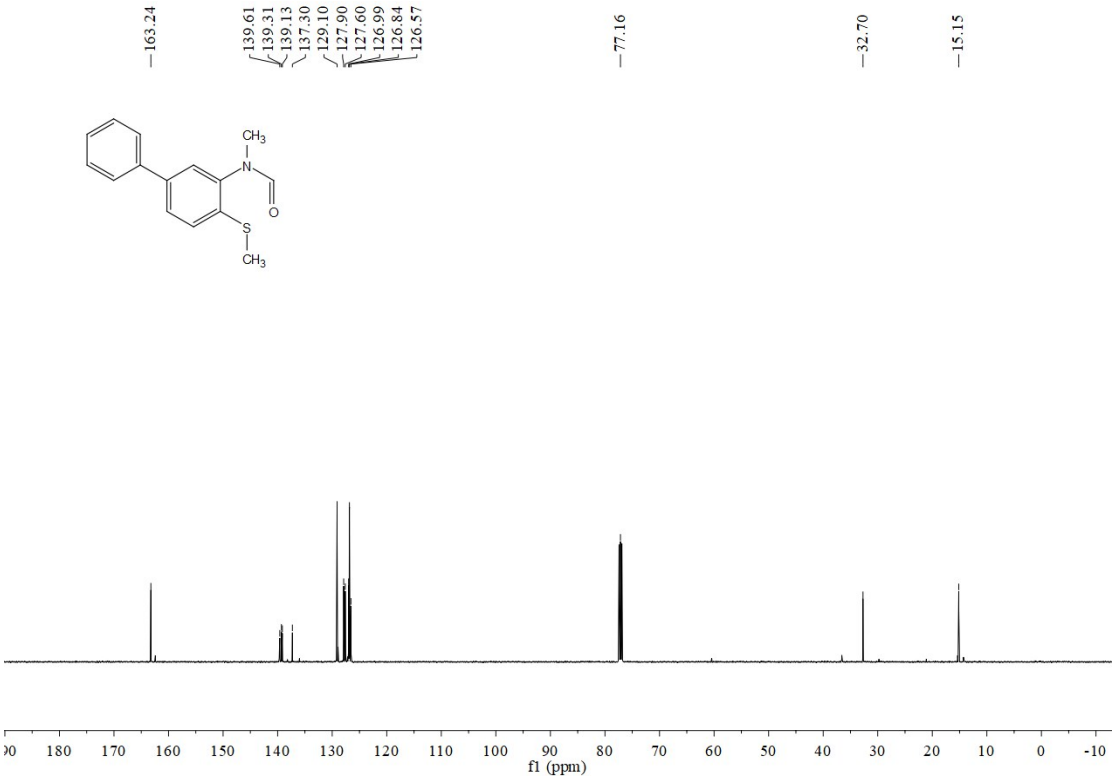
^{13}C NMR (125 MHz, $CDCl_3$) *N*-(3-(*N*-methylformamido)-4-(methylthio)phenyl)acetamide (3d)



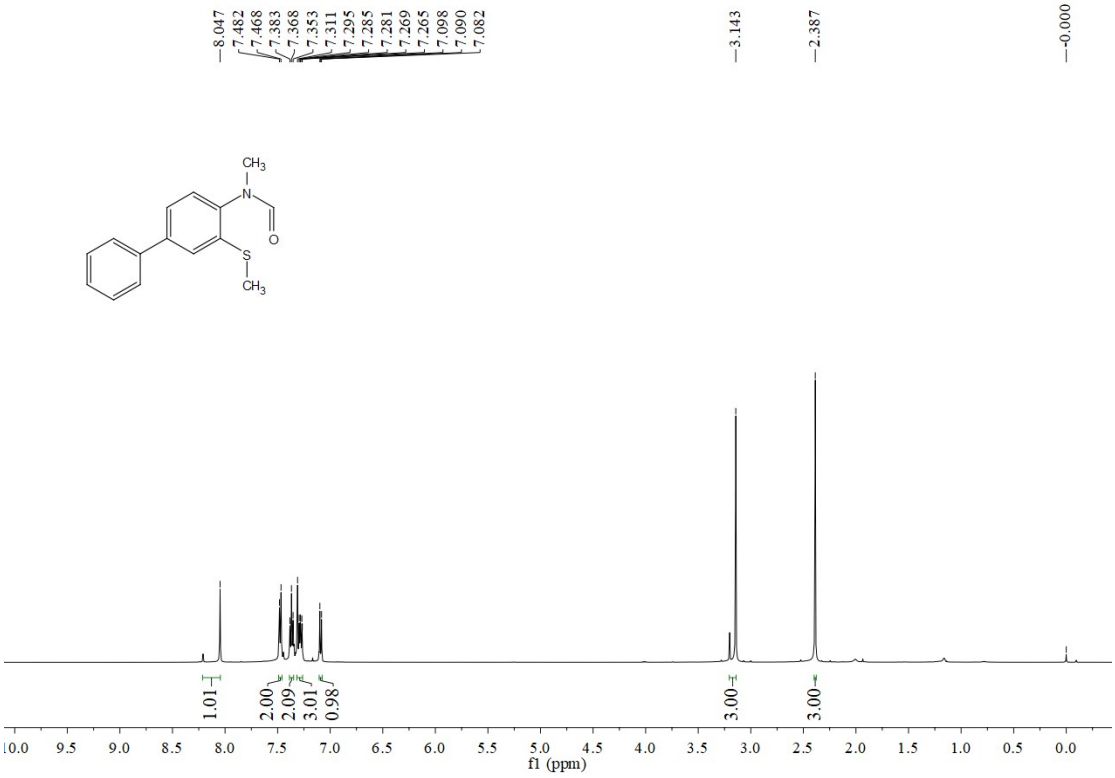
^{1}H NMR (400 MHz, $CDCl_3$) *N*-methyl-*N*-(4-(methylthio)-[1,1'-biphenyl]-3-yl)formamide (3e)



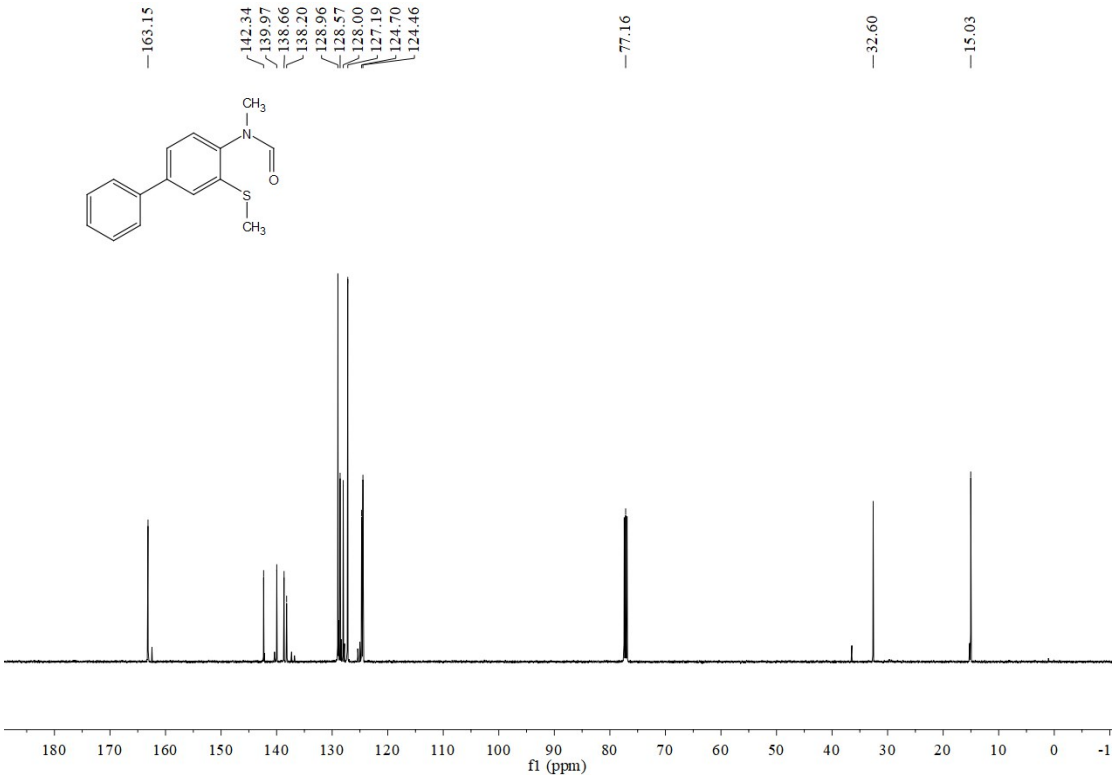
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(4-(methylthio)-[1,1'-biphenyl]-3-yl)formamide (3e)



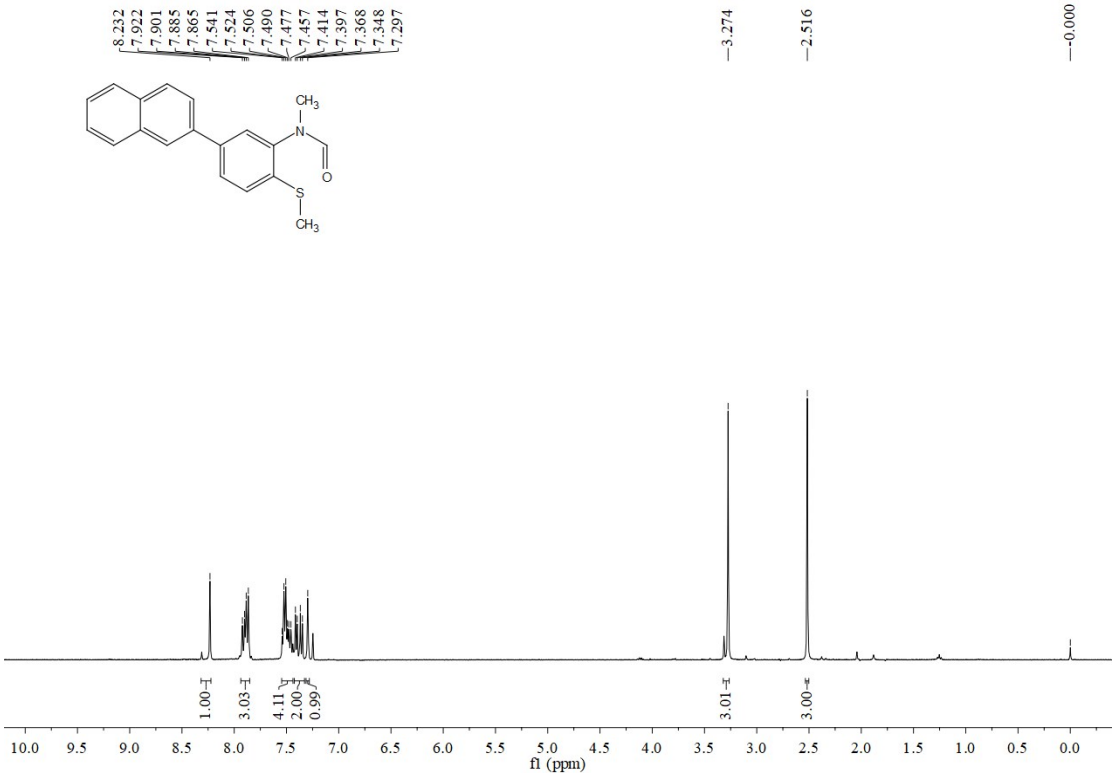
^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-*N*-(3-(methylthio)-[1,1'-biphenyl]-4-yl)formamide (3f)



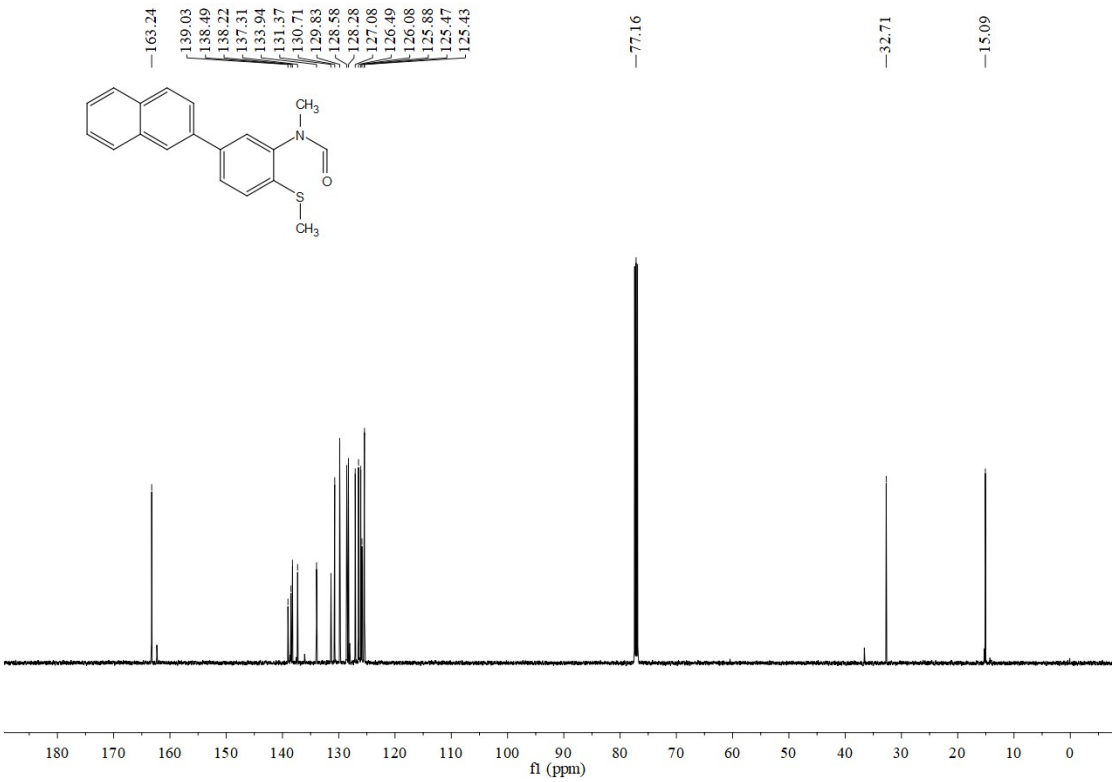
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(3-(methylthio)-[1,1'-biphenyl]-4-yl)formamide (3f)



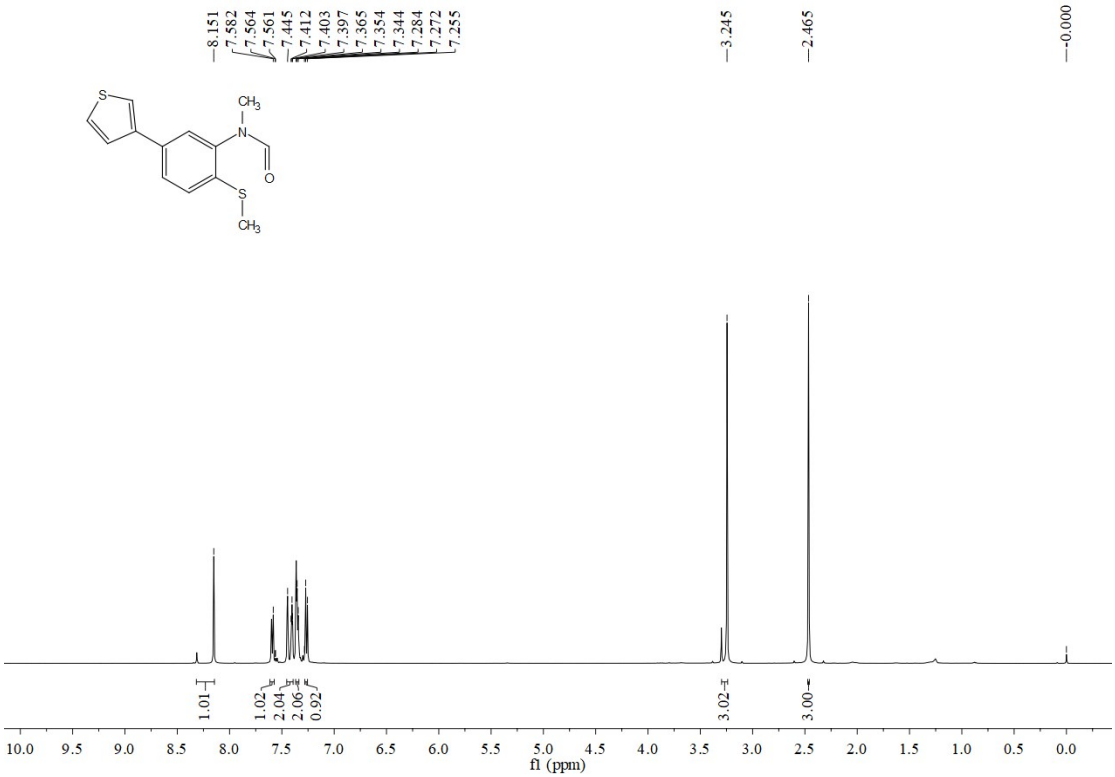
^{1}H NMR (400 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)-5-(naphthalen-2-yl)phenyl)formamide (3g)



^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)-5-(naphthalen-2-yl)phenyl)formamide (3g)

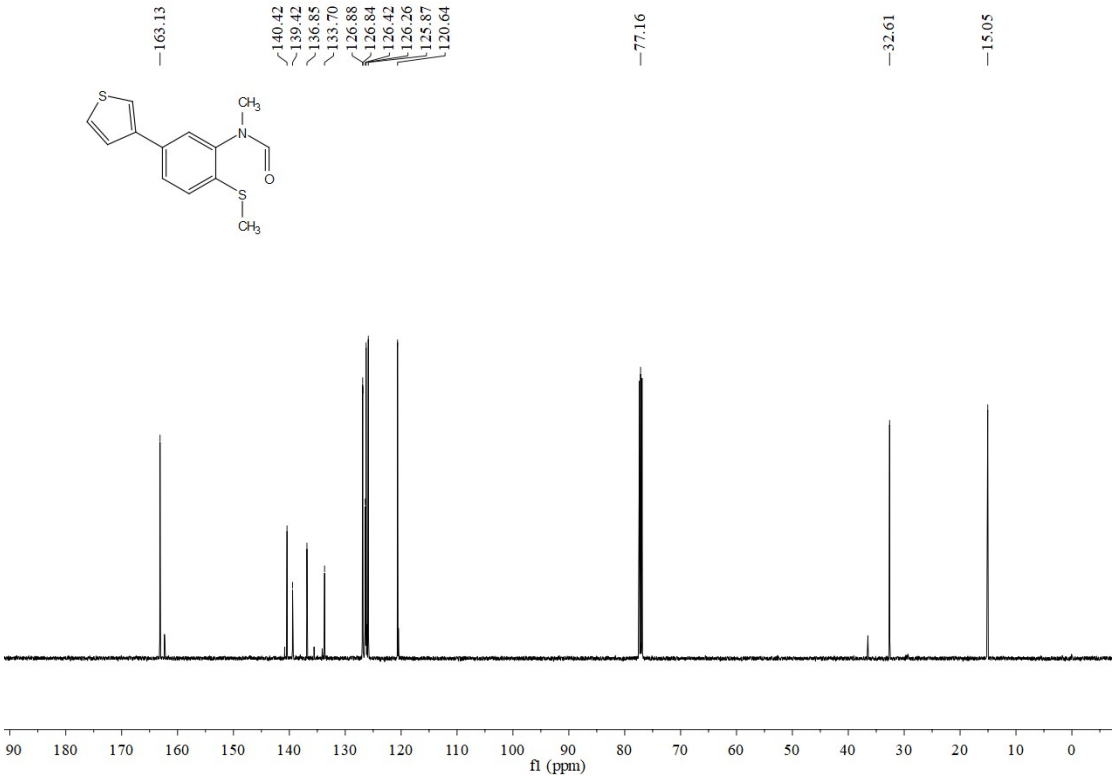


^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)-5-(thiophen-3-yl)phenyl)formamide (3h)

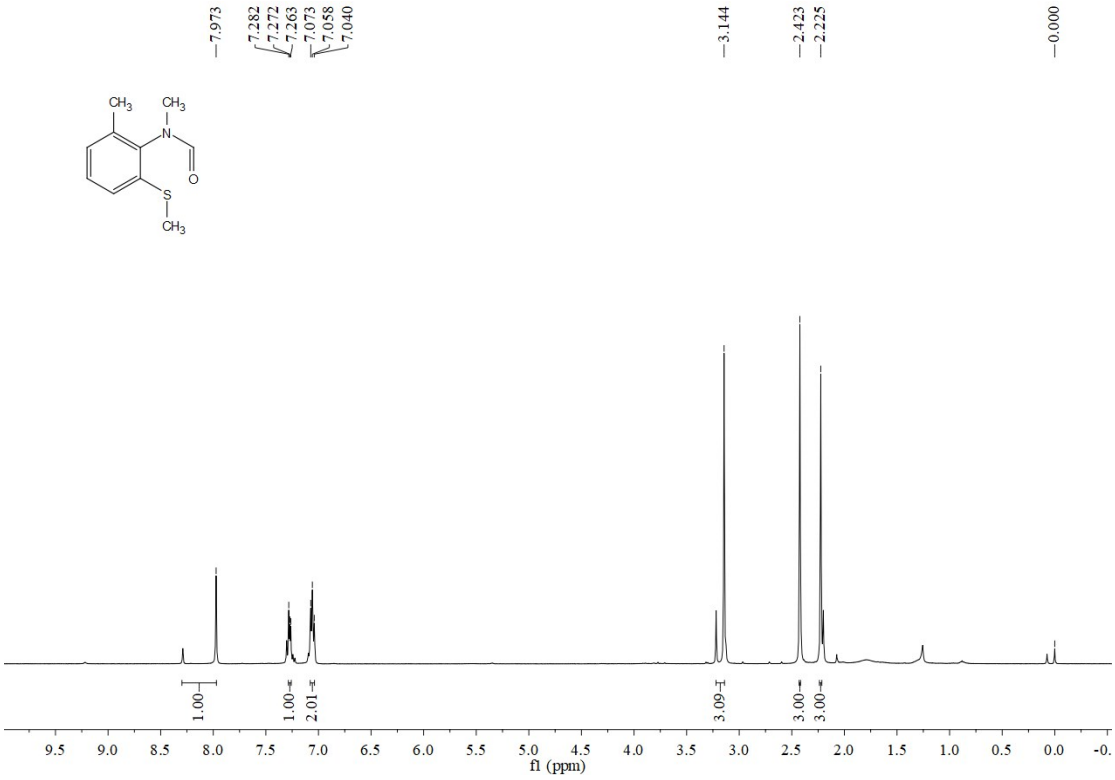


^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)-5-(thiophen-3-

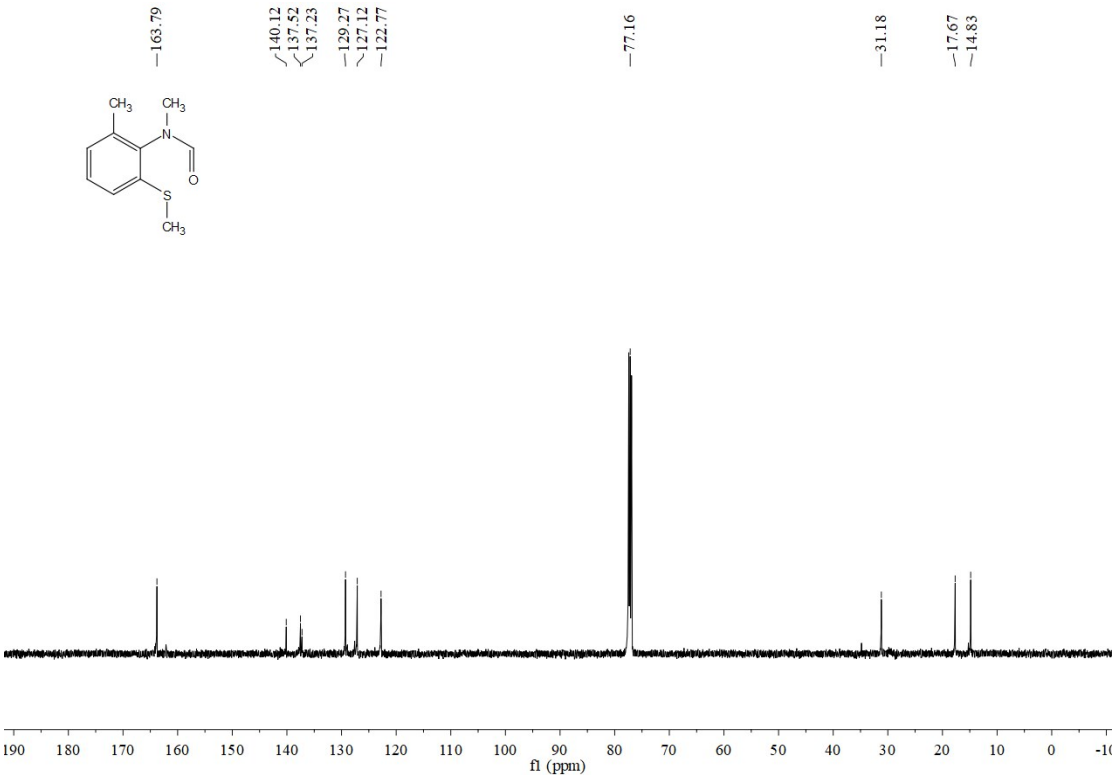
yl)phenyl)formamide (3h)



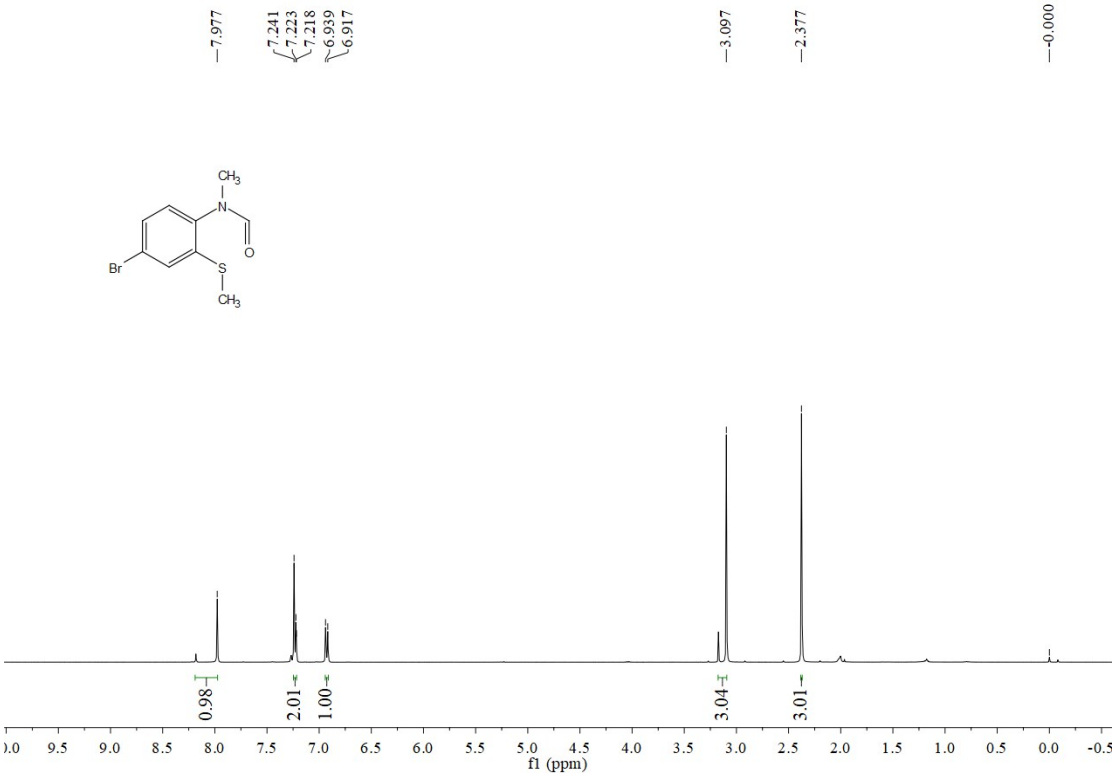
^{1}H NMR (400 MHz, $CDCl_3$) *N*-methyl-*N*-(2-methyl-6-(methylthio)phenyl)formamide (3i)



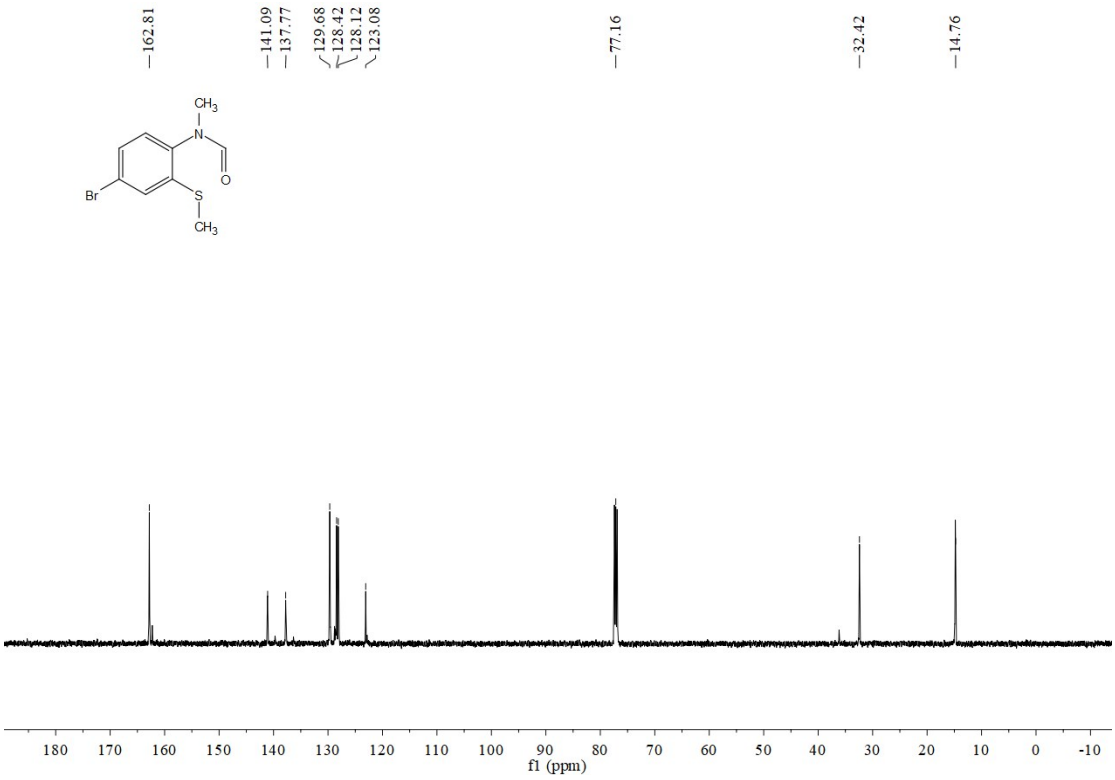
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-methyl-6-(methylthio)phenyl)formamide (3i)



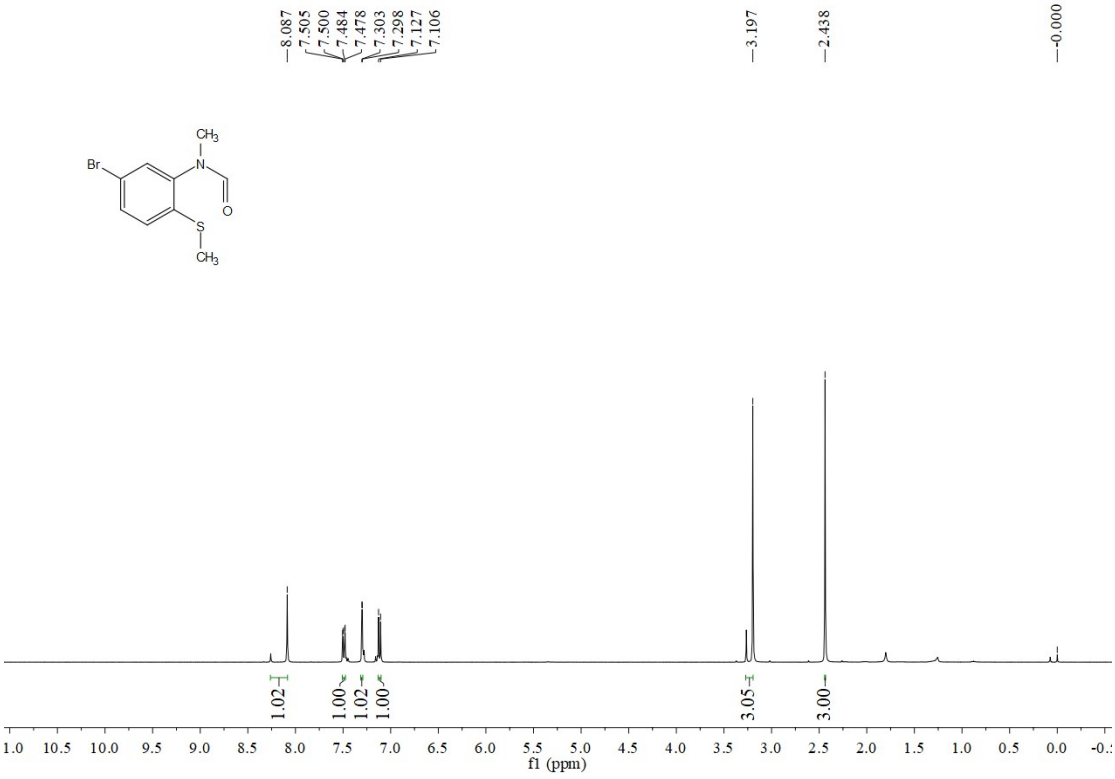
^{1}H NMR (400 MHz, $CDCl_3$) *N*-(4-bromo-2-(methylthio)phenyl)-*N*-methylformamide (3j)



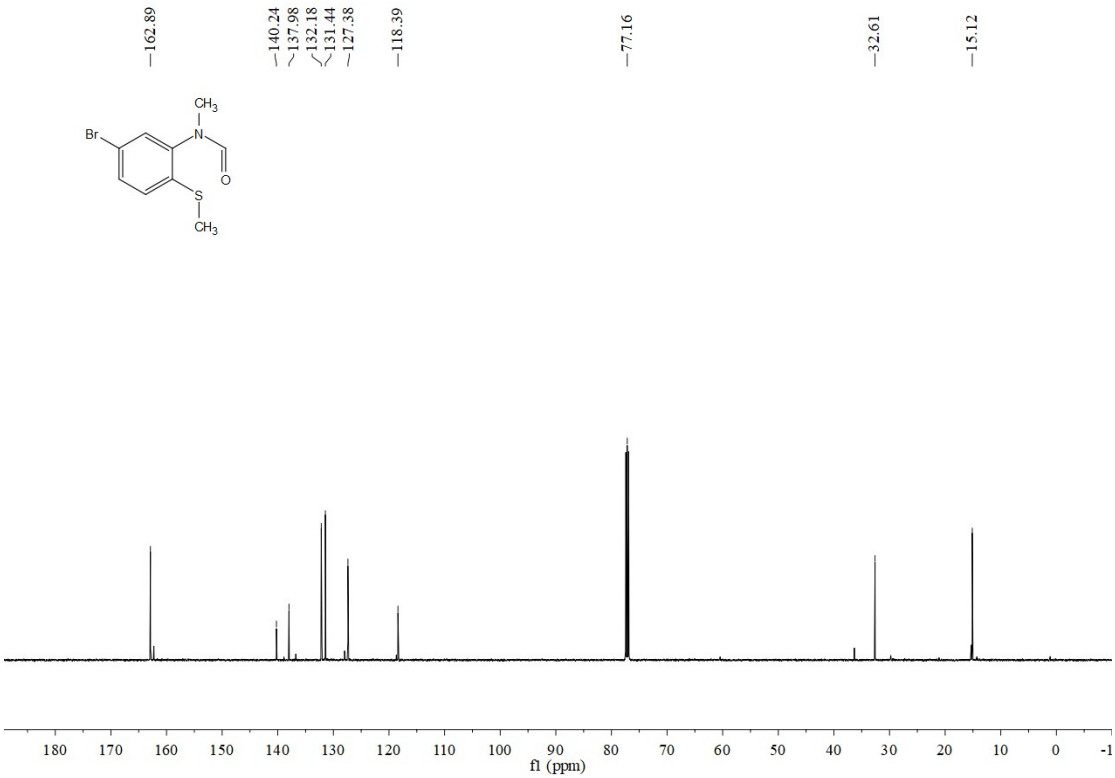
^{13}C NMR (125 MHz, $CDCl_3$) *N*-(4-bromo-2-(methylthio)phenyl)-*N*-methylformamide (3j)



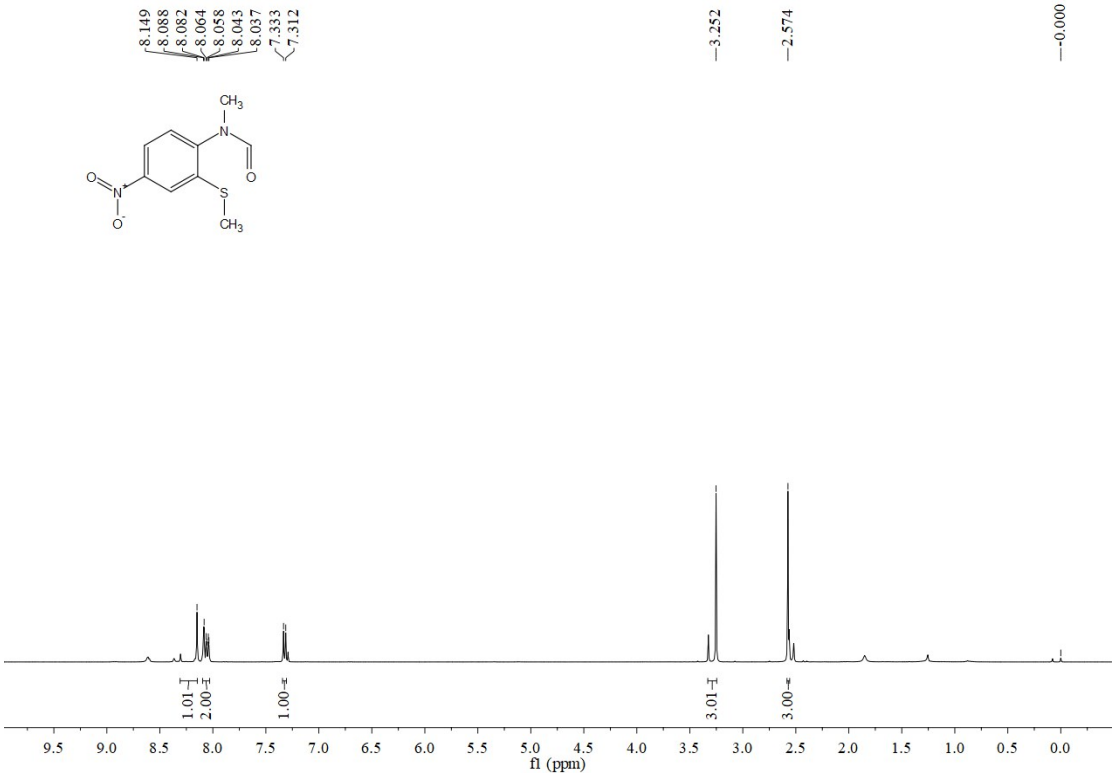
^{1}H NMR (400 MHz, $CDCl_3$) *N*-(5-bromo-2-(methylthio)phenyl)-*N*-methylformamide (3k)



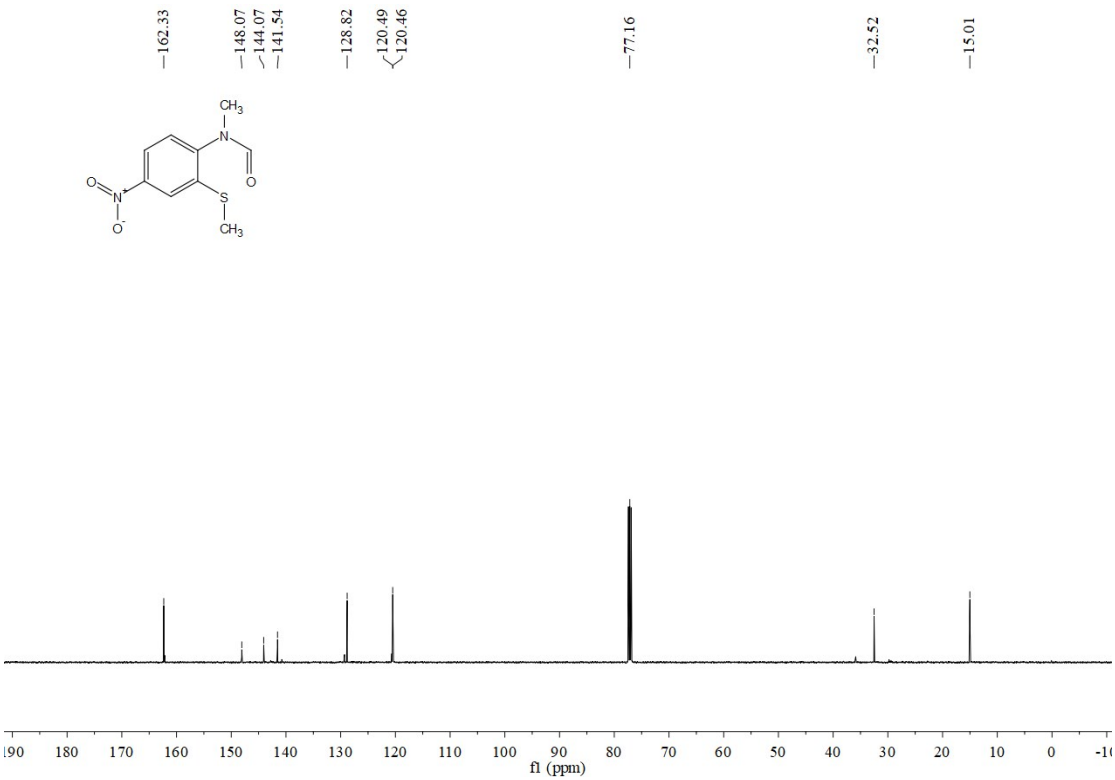
^{13}C NMR (125 MHz, $CDCl_3$) *N*-(5-bromo-2-(methylthio)phenyl)-*N*-methylformamide (3k)



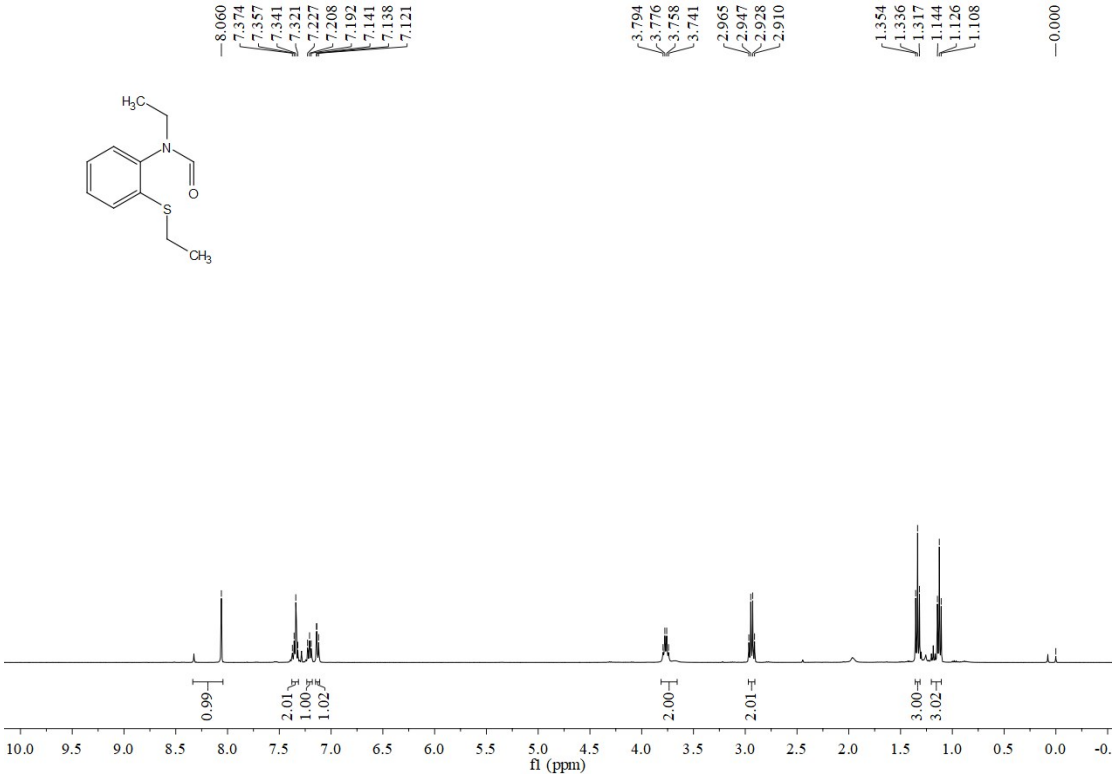
^{1}H NMR (400 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)-4-nitrophenyl)formamide (3l)



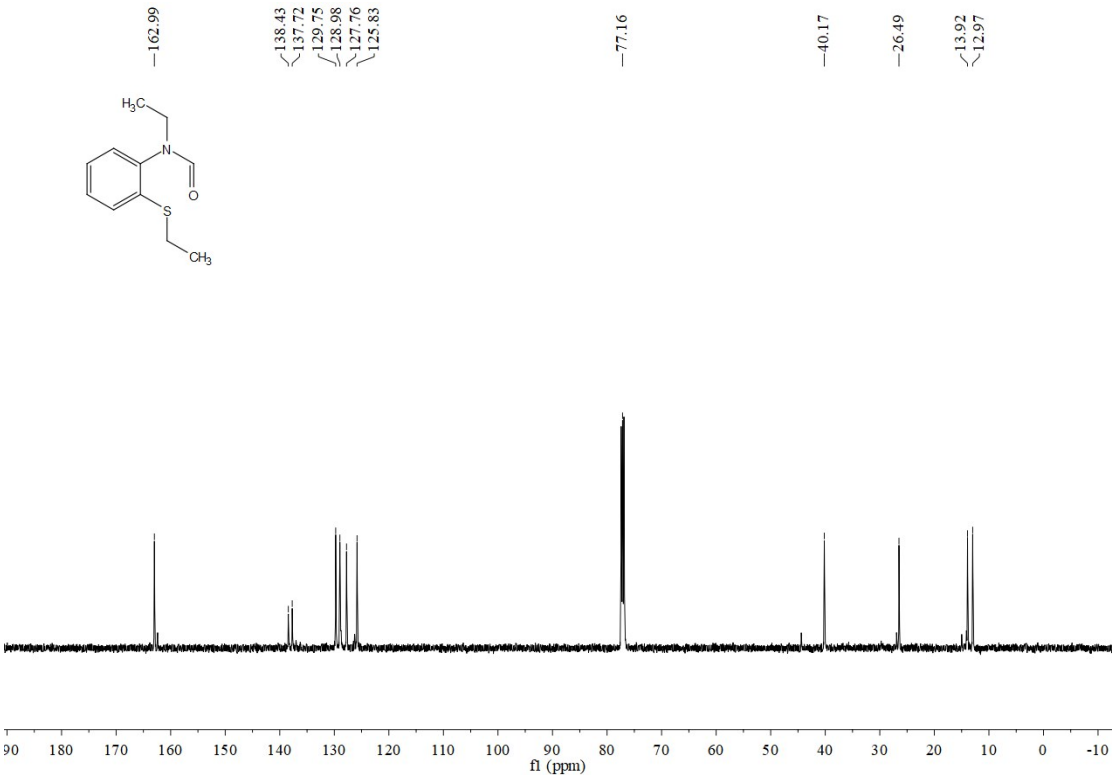
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)-4-nitrophenyl)formamide (3l)



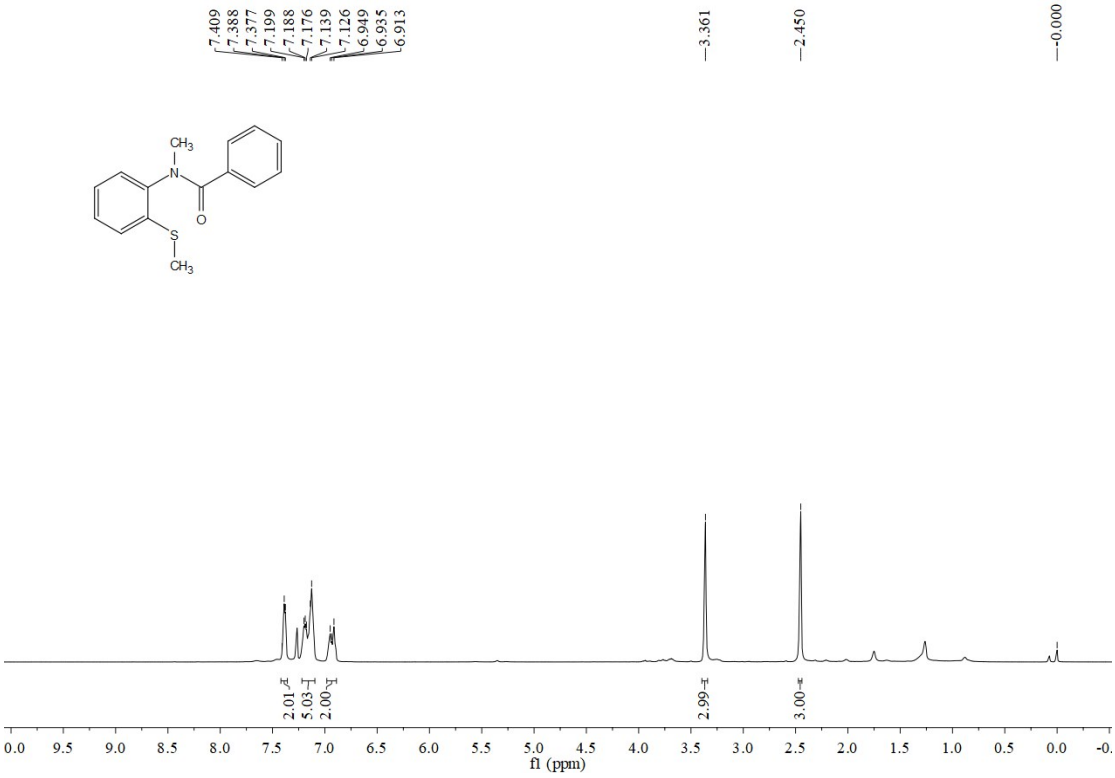
^{1}H NMR (400 MHz, $CDCl_3$) *N*-ethyl-*N*-(2-(ethylthio)phenyl)formamide (3m)



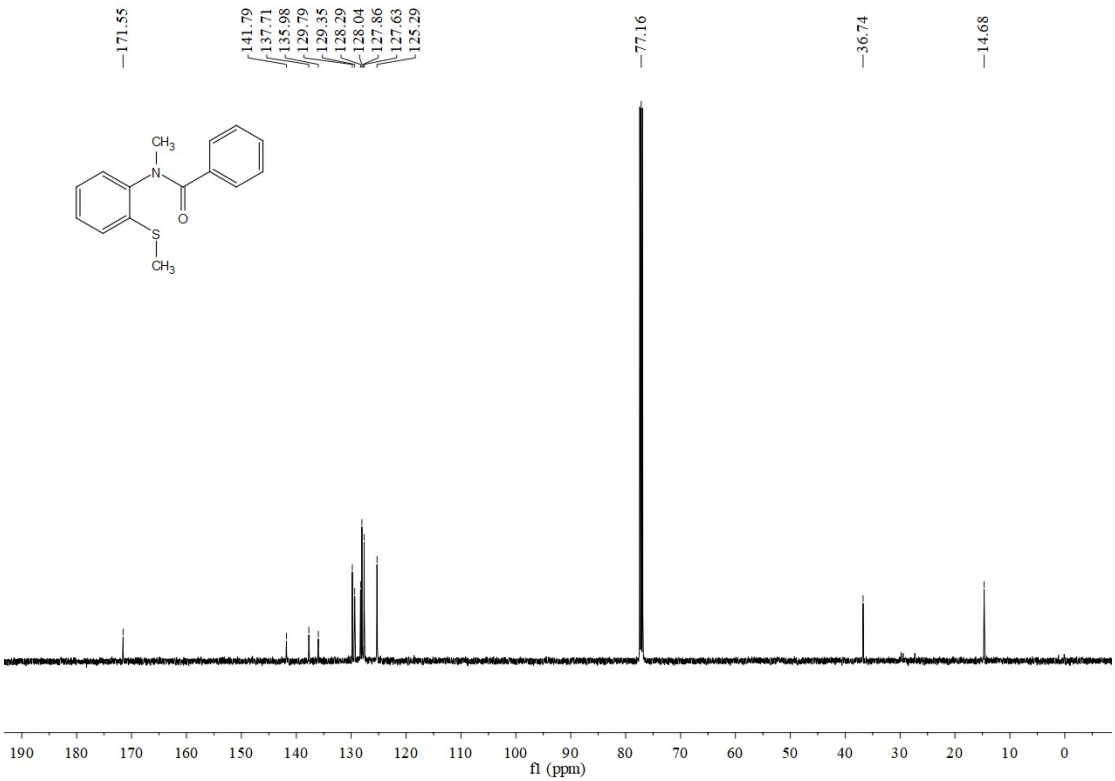
^{13}C NMR (125 MHz, $CDCl_3$) *N*-ethyl-*N*-(2-(ethylthio)phenyl)formamide (3m)



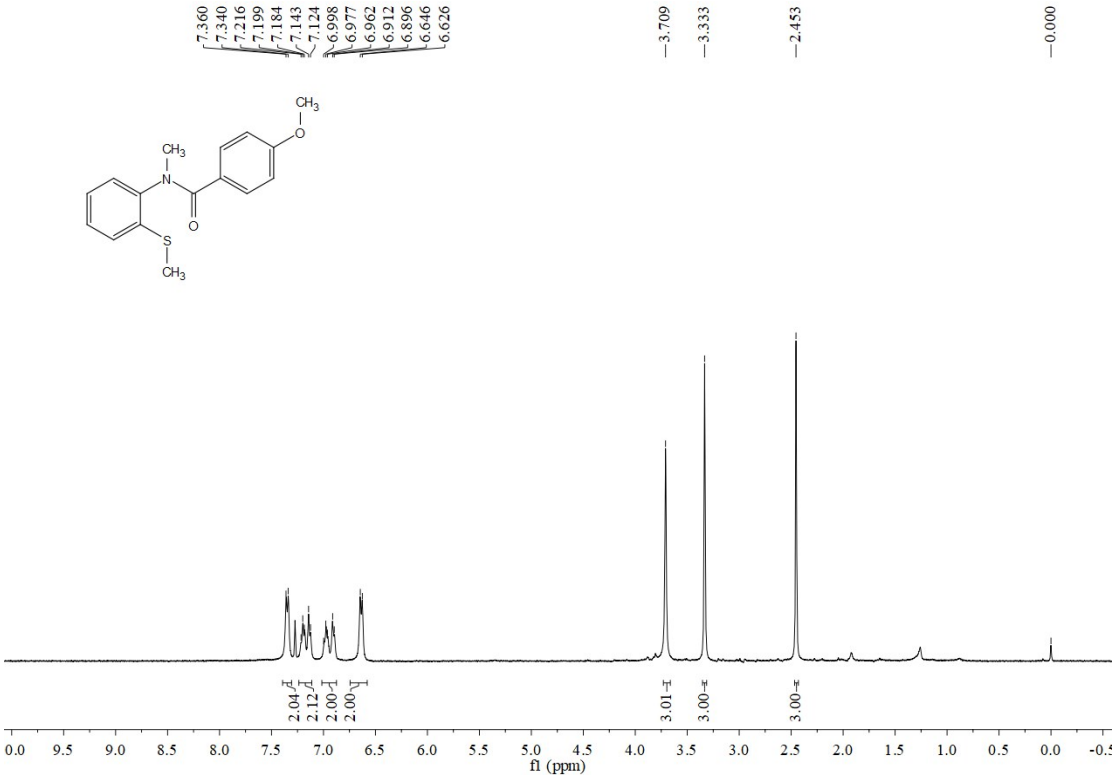
^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)benzamide (3n)



^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)benzamide (3n)

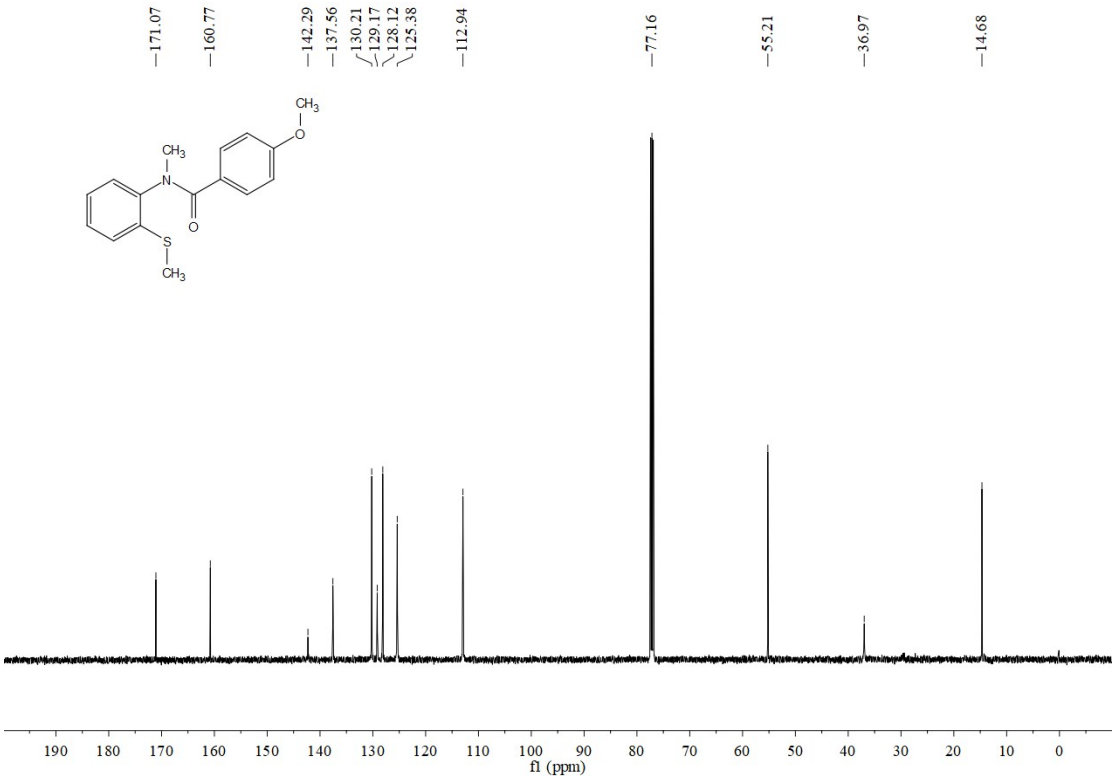


^{1}H NMR (400 MHz, $CDCl_3$) 4-methoxy-*N*-methyl-*N*-(2-(methylthio)phenyl)benzamide (3o)

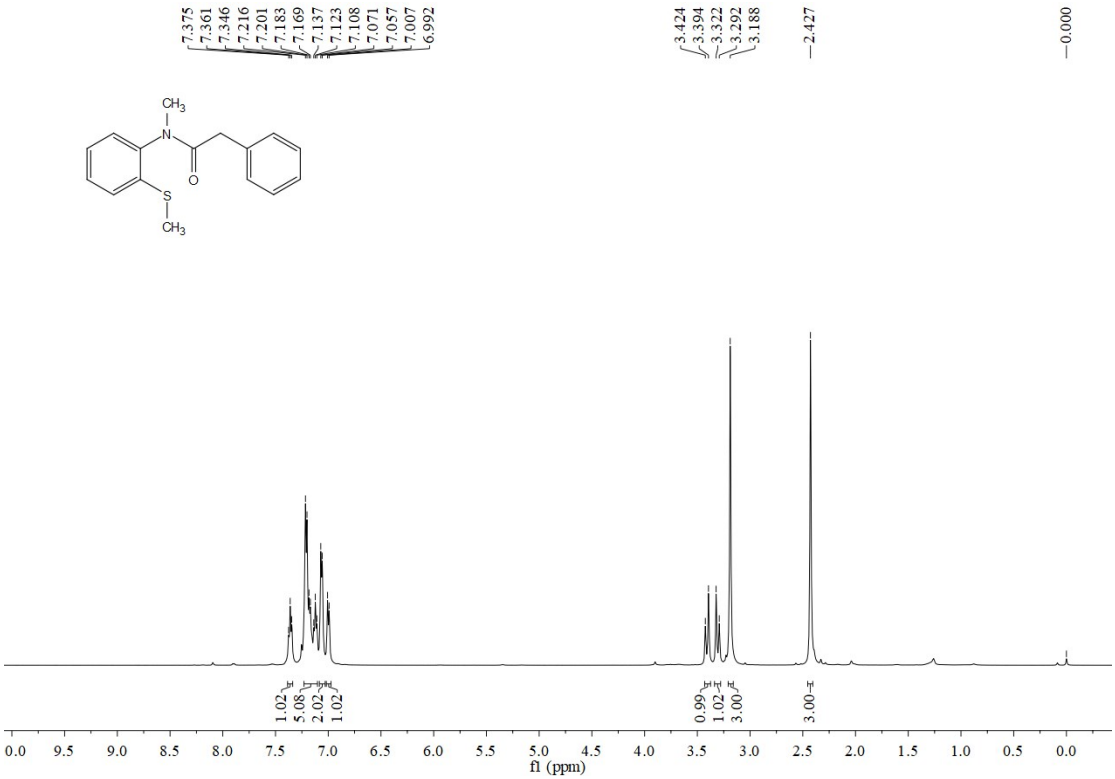


^{13}C NMR (125 MHz, $CDCl_3$) 4-methoxy-*N*-methyl-*N*-(2-

(methylthio)phenyl)benzamide (3o)

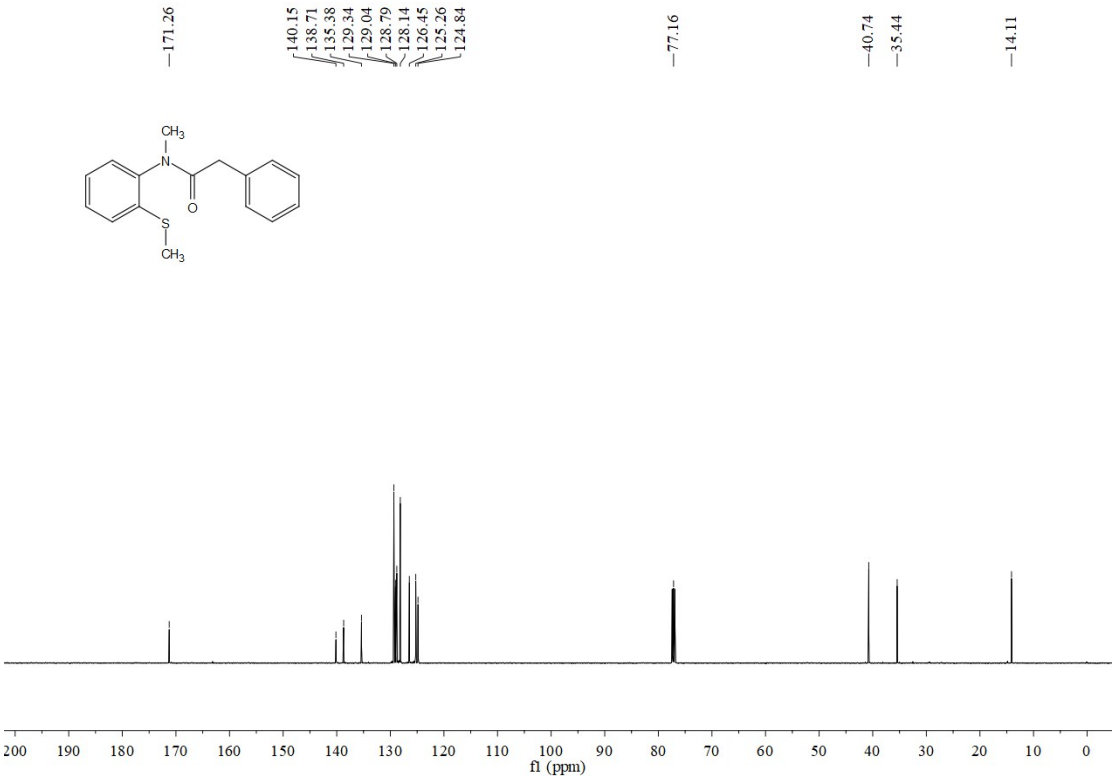


^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)-2-phenylacetamide (3p)

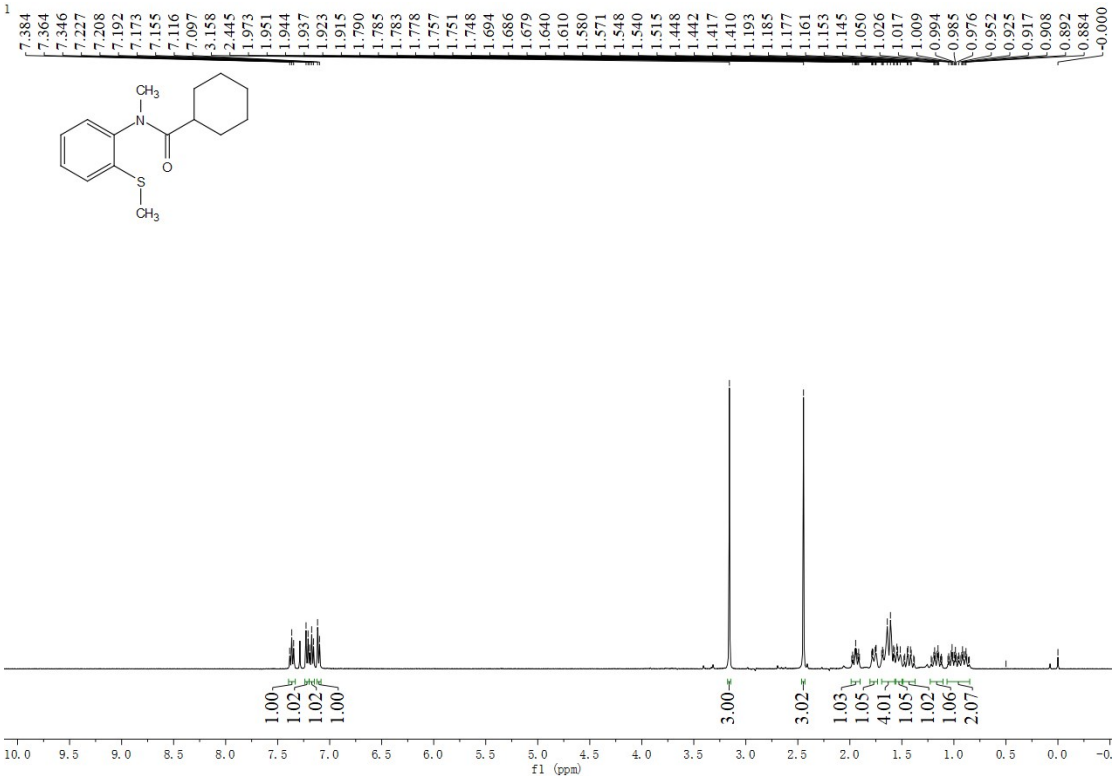


^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)-2-

phenylacetamide (3p)

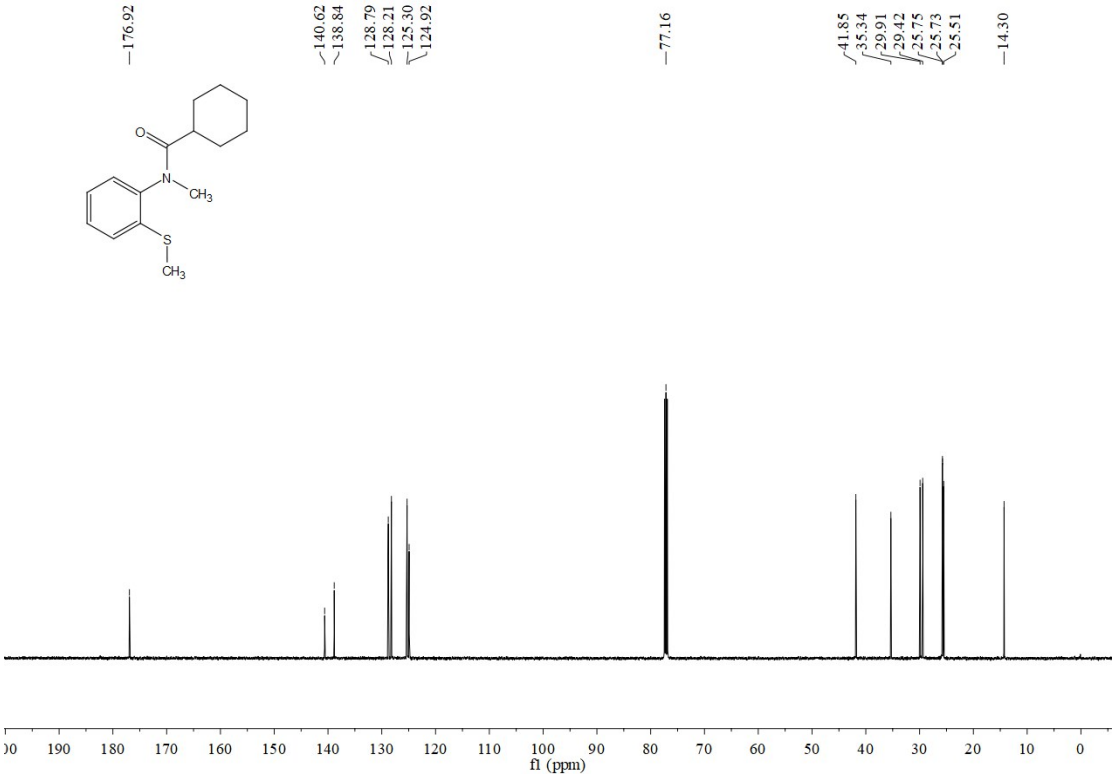


^{1}H NMR (400 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)cyclohexanecarboxamide (3q)

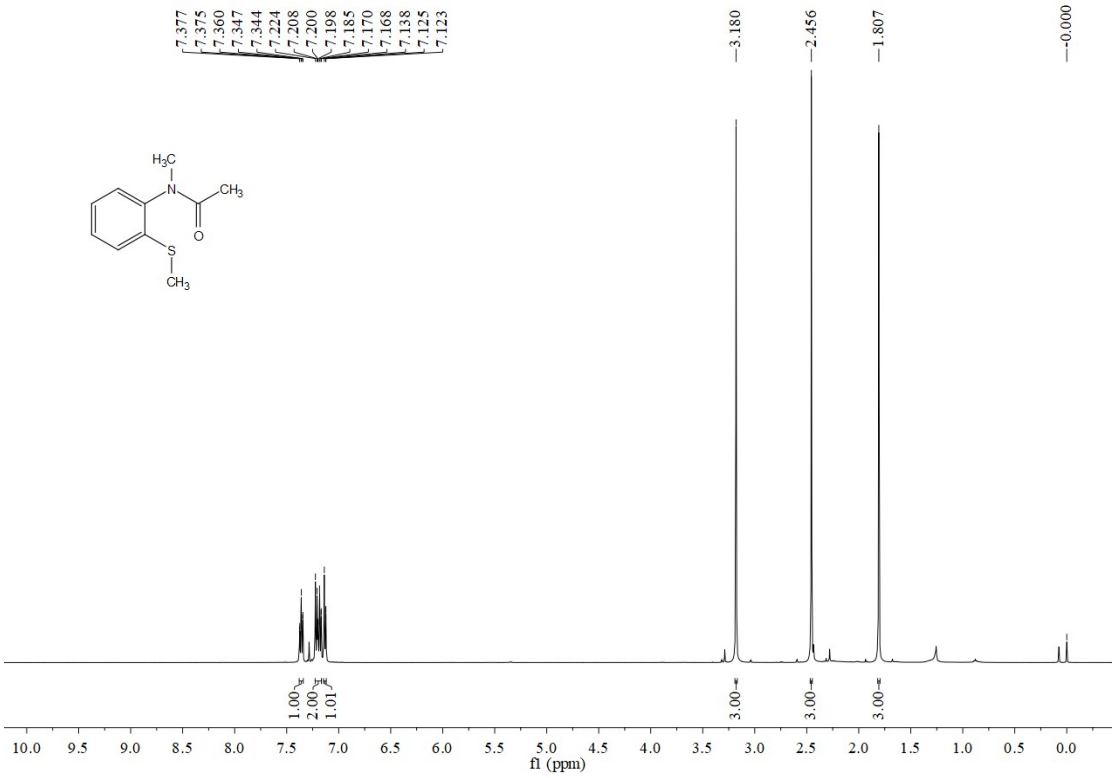


^{1}H NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-

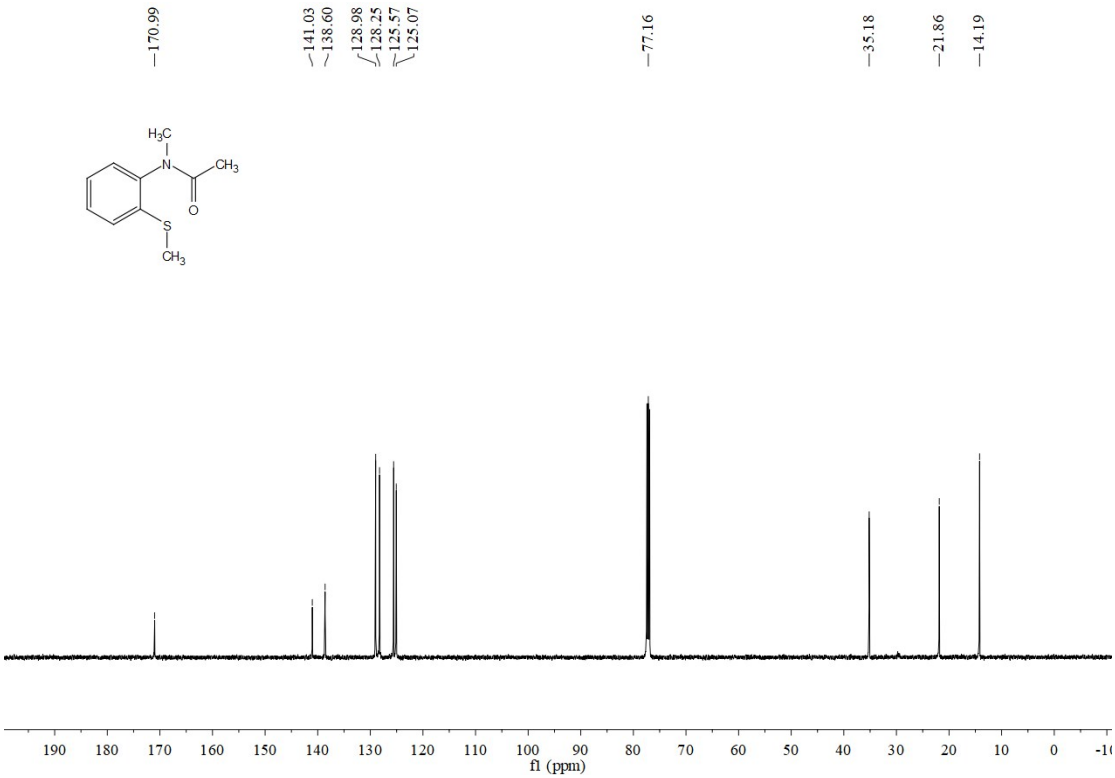
(methylthio)phenyl)cyclohexanecarboxamide (3q)



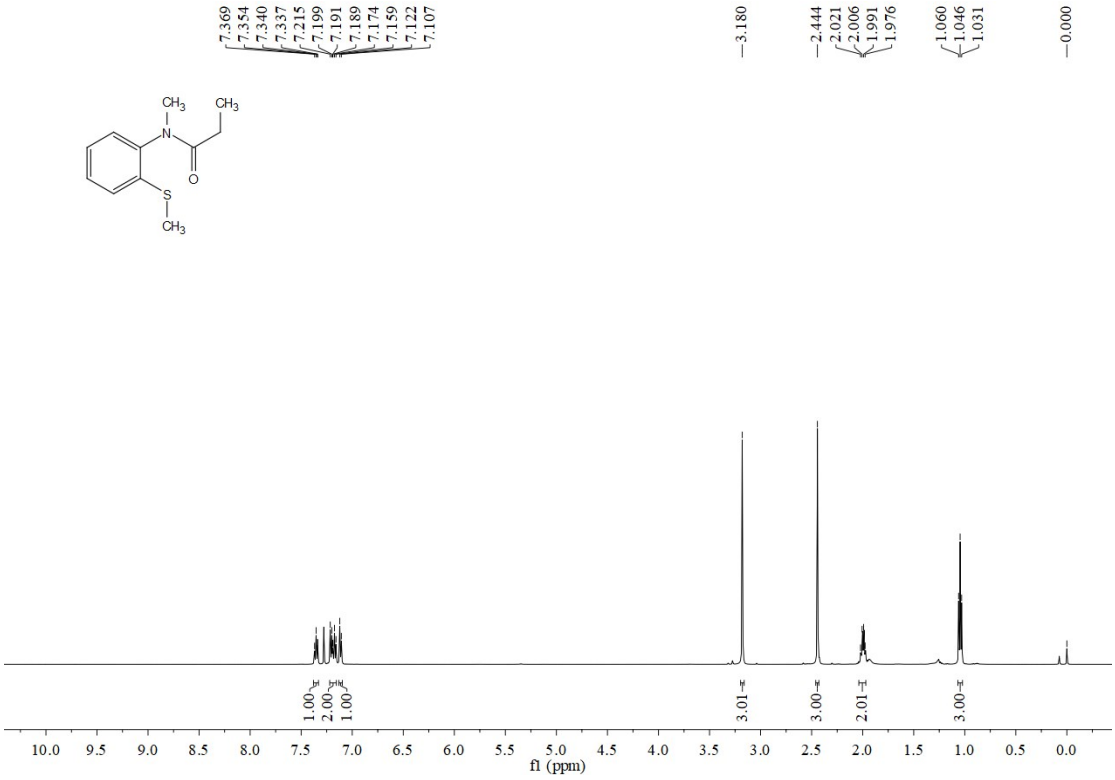
^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)acetamide (3r)



^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)acetamide (3r)

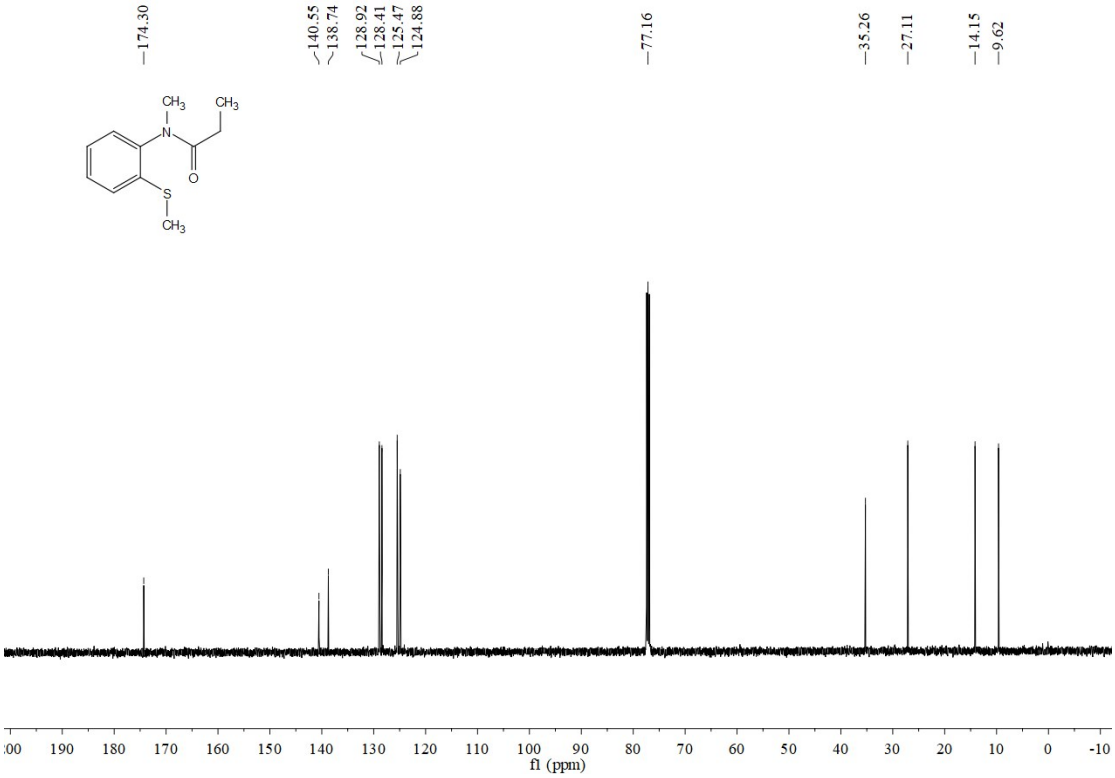


^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)propionamide (3s)

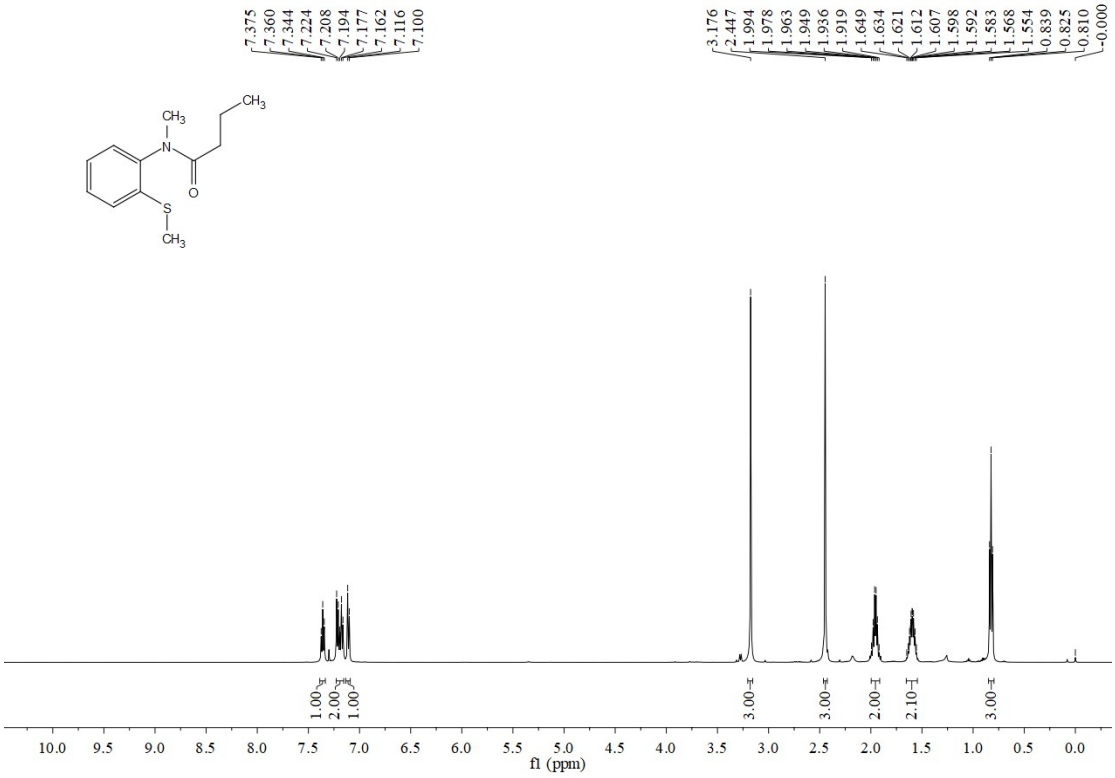


^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)propionamide

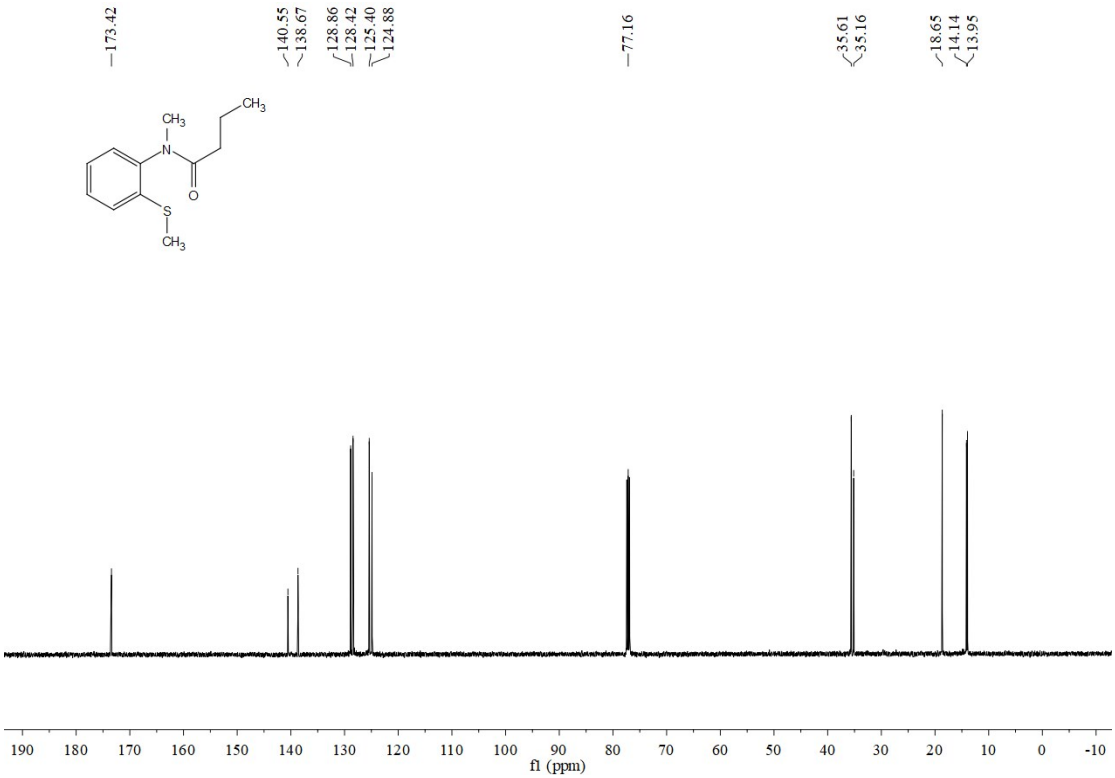
(3s)



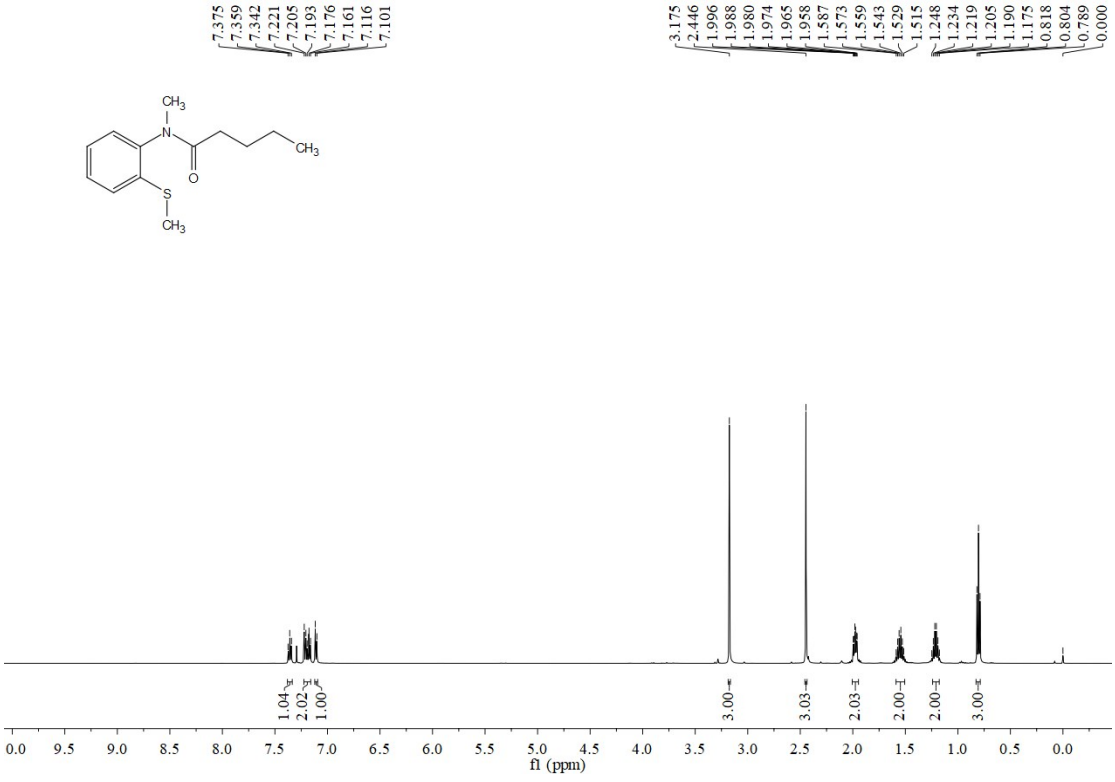
^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)butyramide (3t)



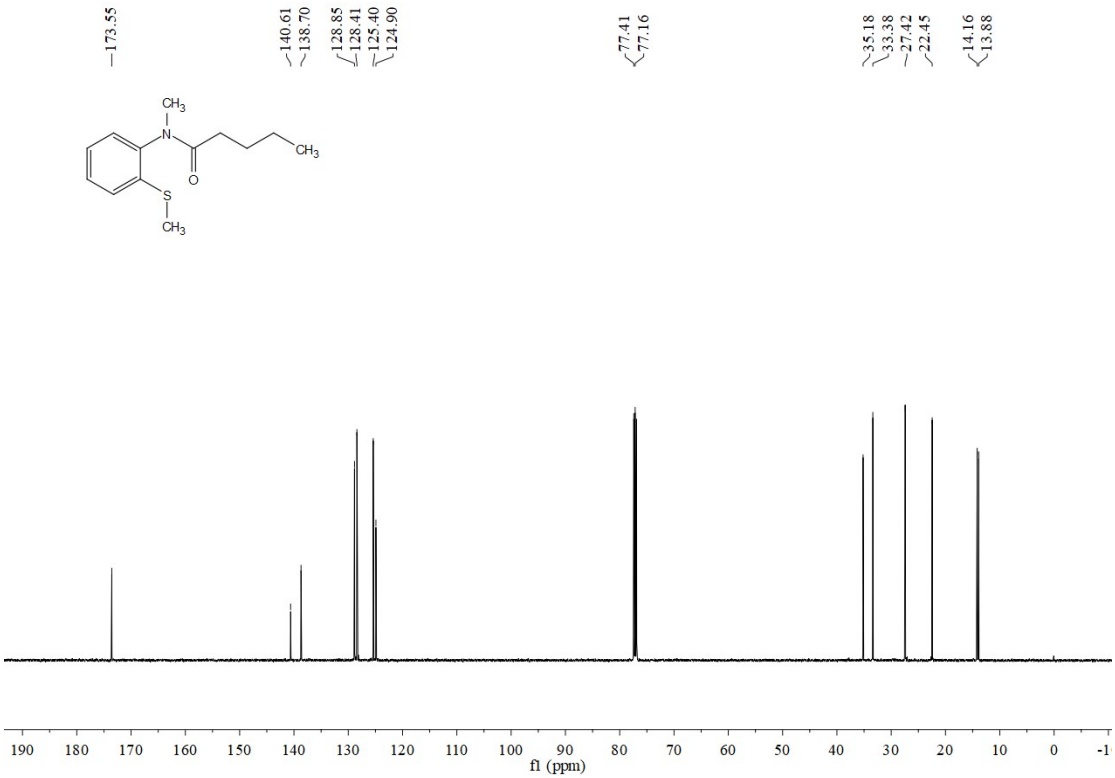
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)butyramide (3t)



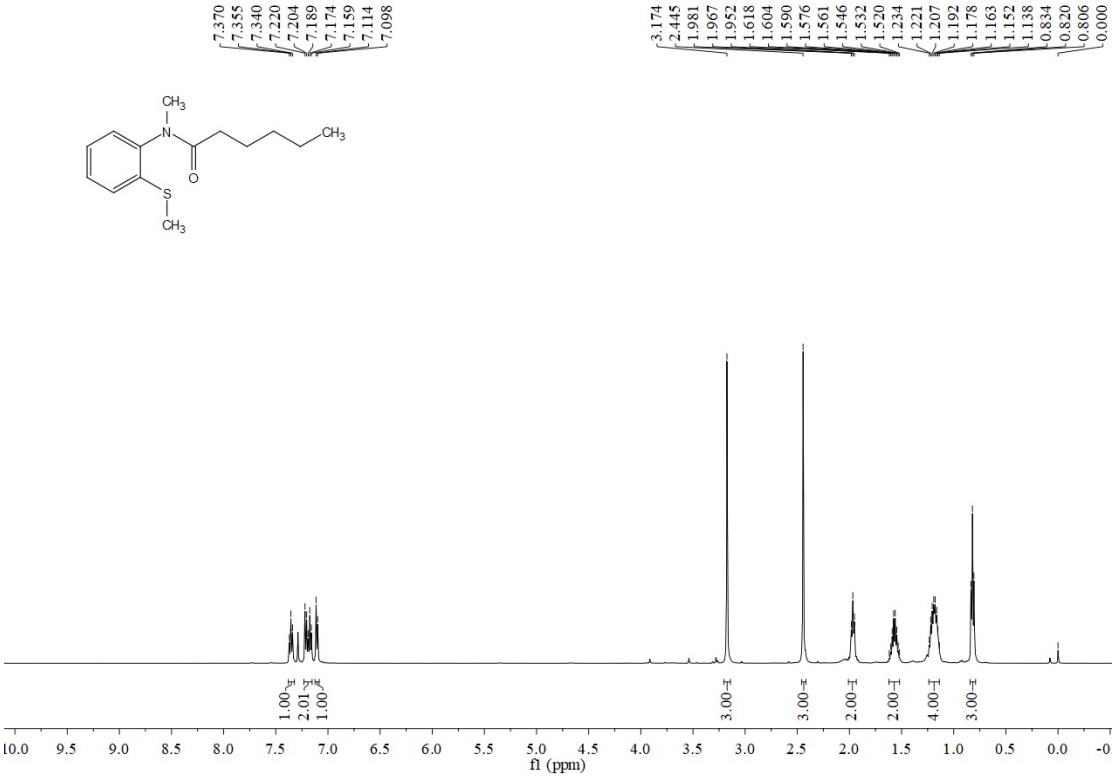
^{1}H NMR (400 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)pentanamide (3u)



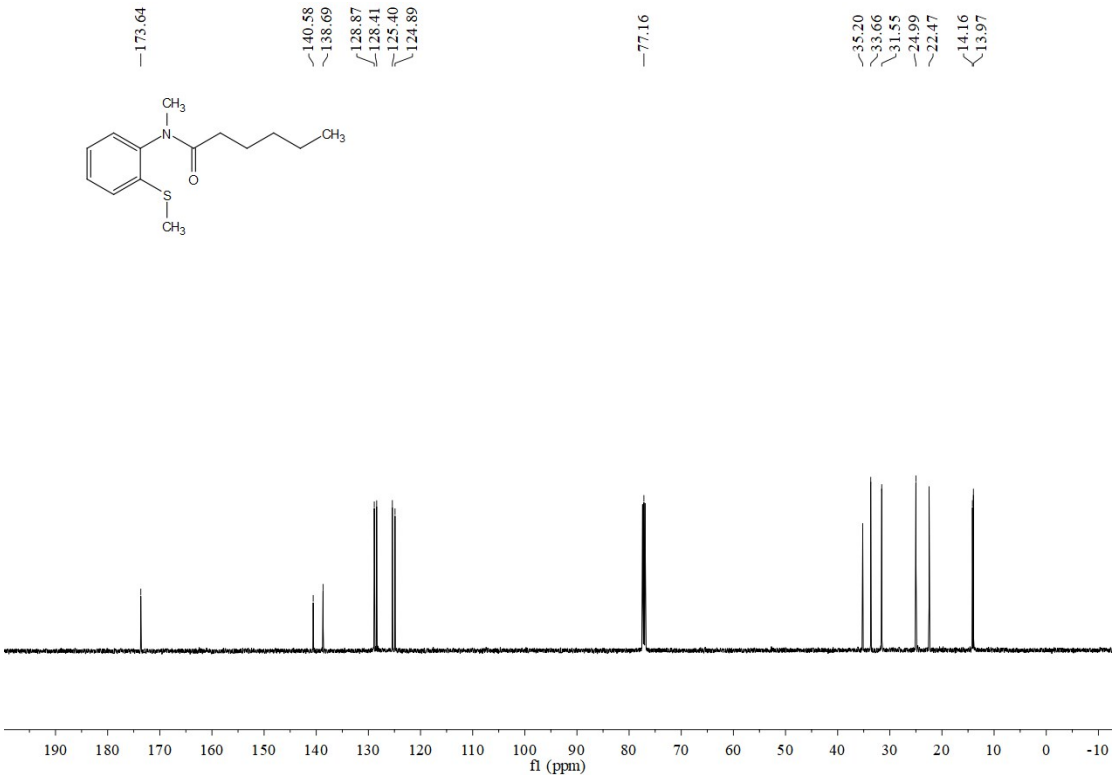
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)pentanamide (3u)



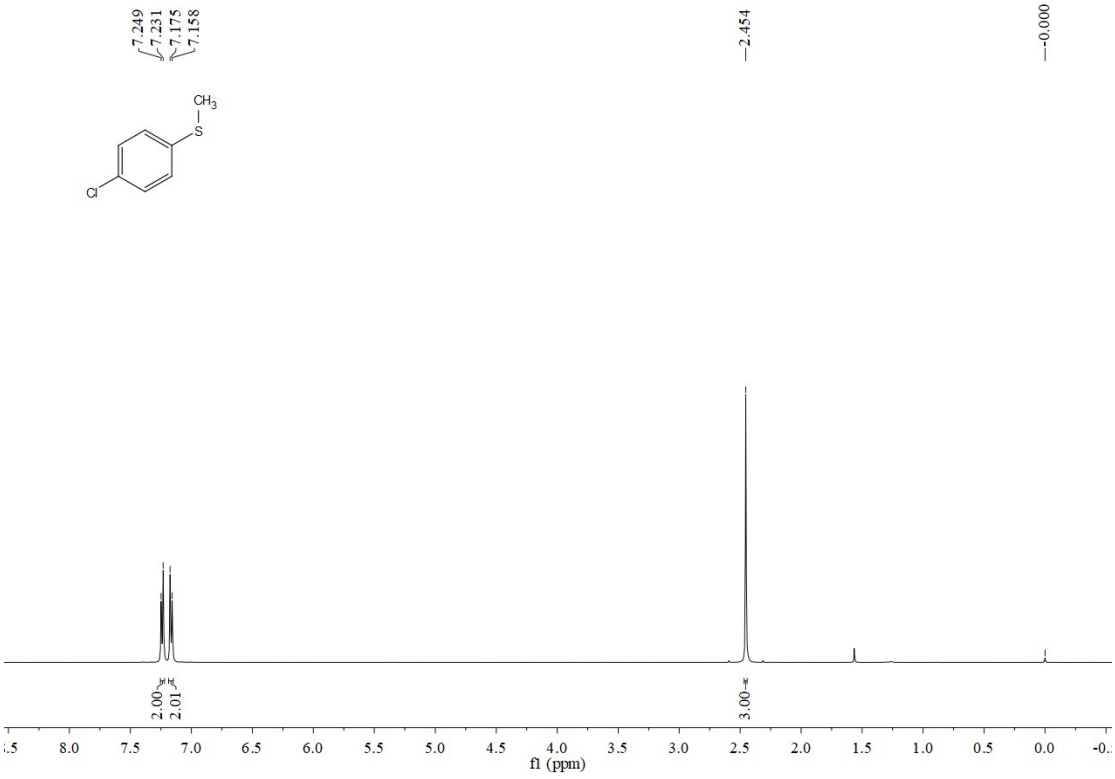
^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)hexanamide (3v)



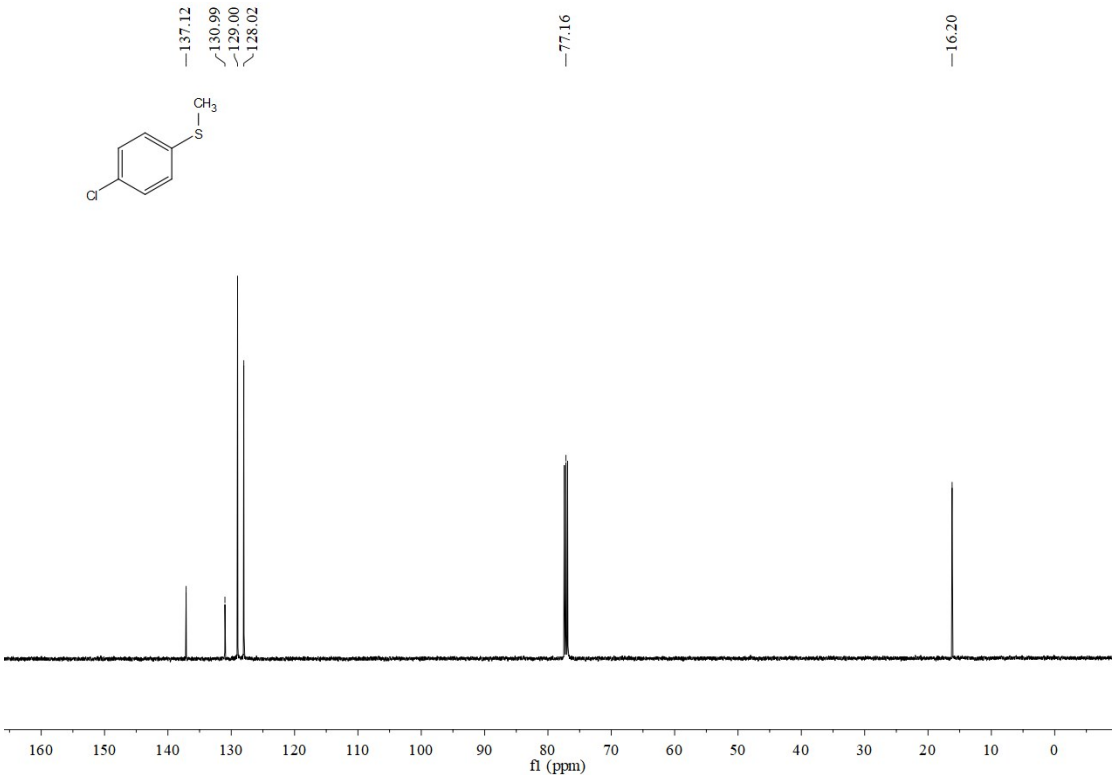
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylthio)phenyl)hexanamide (3v)



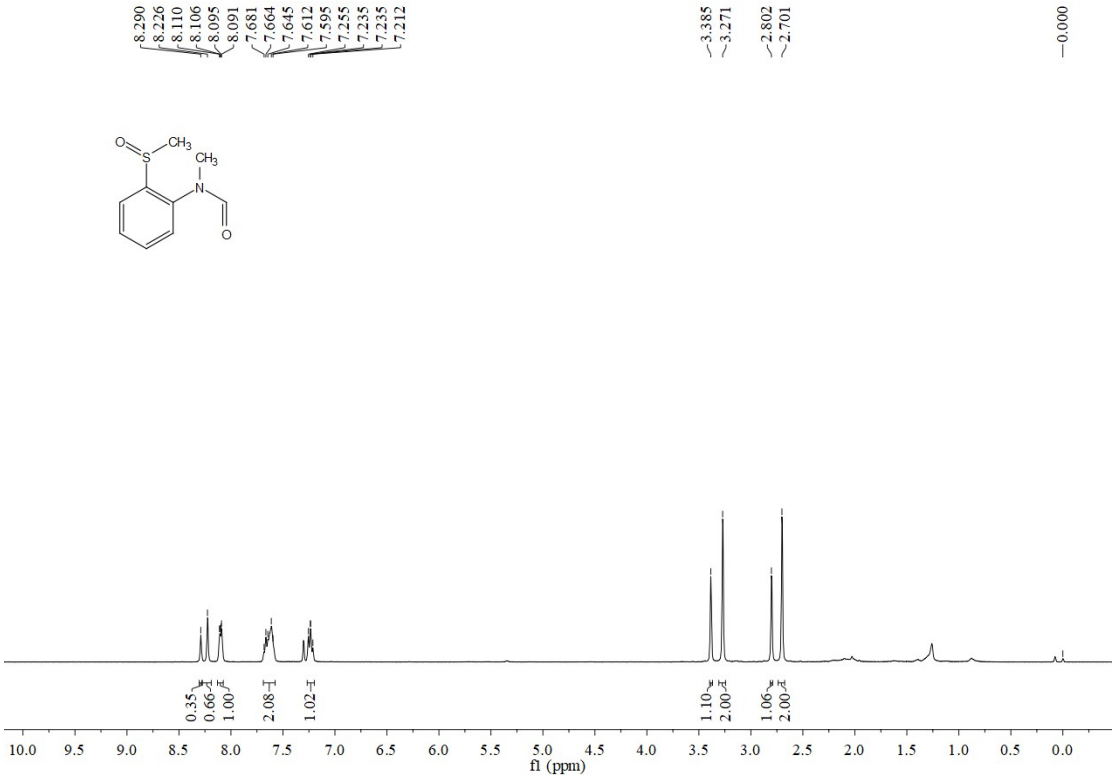
^{1}H NMR (500 MHz, $CDCl_3$) 4-Chlorothioanisole (4)



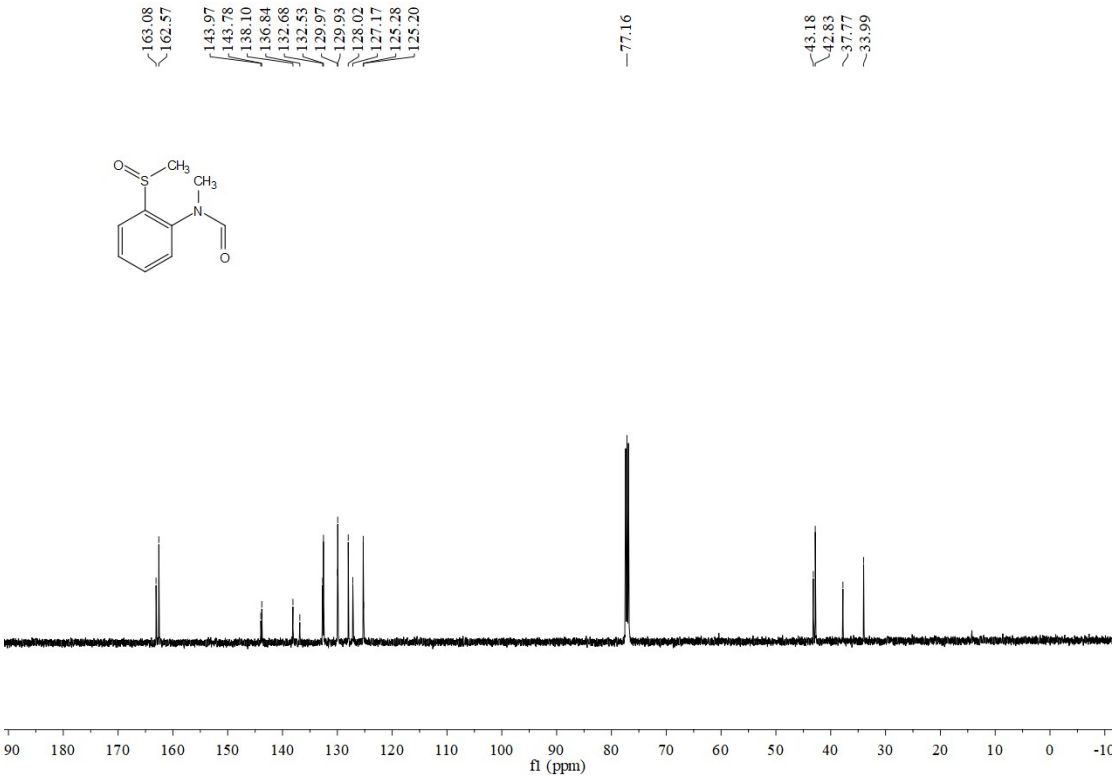
^{13}C NMR (125 MHz, $CDCl_3$) 4-Chlorothioanisole (4)



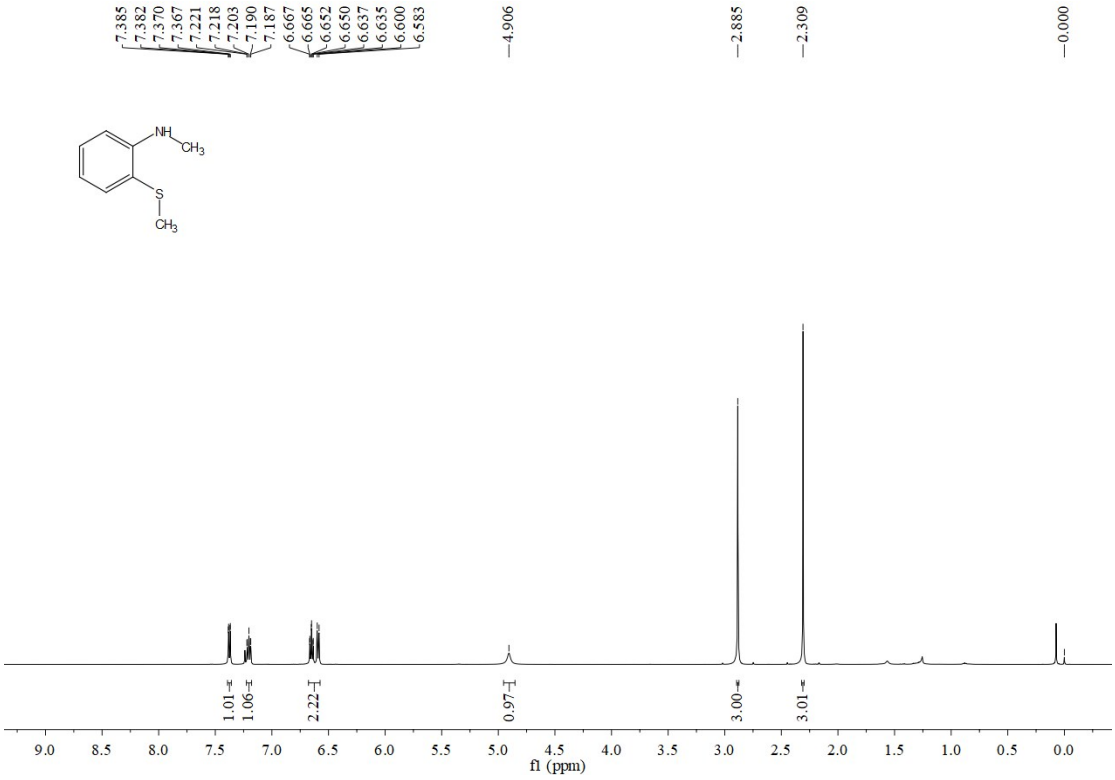
^{1}H NMR (400 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylsulfinyl)phenyl)formamide (5)



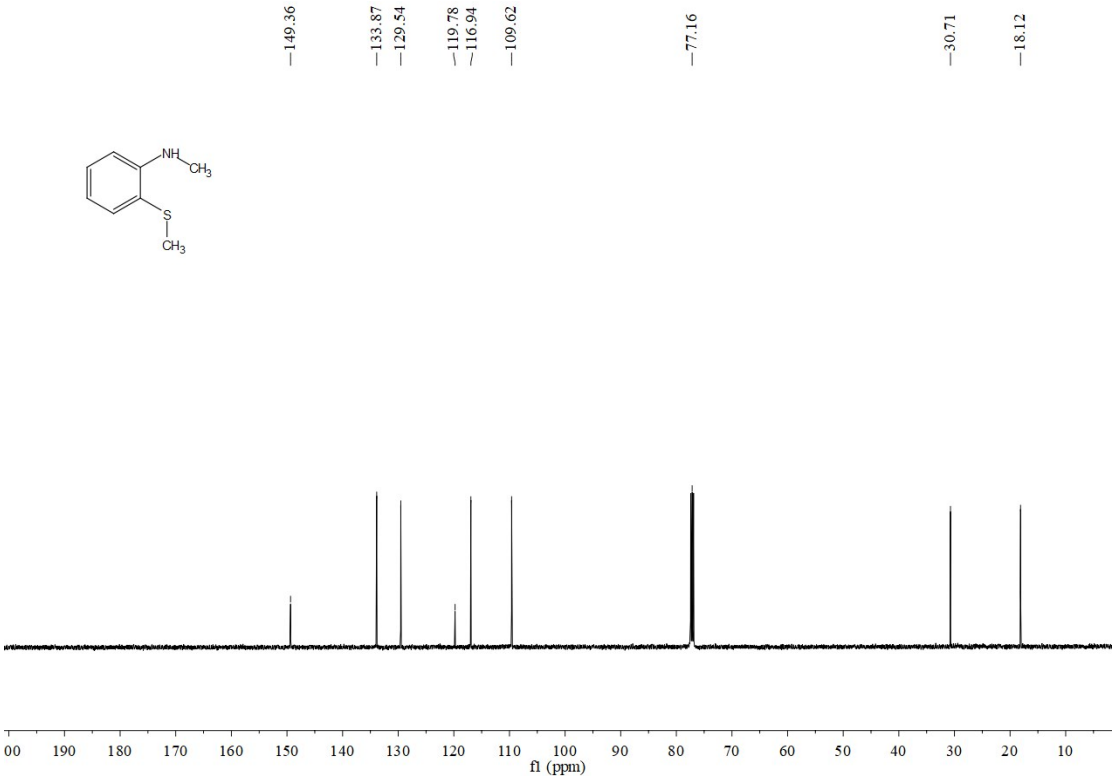
^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-*N*-(2-(methylsulfinyl)phenyl)formamide (5)



^{1}H NMR (500 MHz, $CDCl_3$) *N*-methyl-2-(methylthio)aniline (6)



^{13}C NMR (125 MHz, $CDCl_3$) *N*-methyl-2-(methylthio)aniline (6)



6. O^{18}:O^{16}-3a GC analysis