

## Supporting Information

### Manganese-Catalyzed Directed Methylation of C(sp<sup>2</sup>)-H Bonds at 25 °C with High Catalytic Turnover

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## 1. Materials and Methods

**General.** All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under an atmosphere of nitrogen. Gas-liquid chromatographic (GC) analysis was performed on a Shimadzu GC-2025 machine equipped with glass capillary column HR-1 (0.25-mm i.d.  $\times$  25 m). Flash silica gel column chromatography was performed on silica gel 60N (Kanto, spherical and neutral, 140–325 mesh) as described by Still.<sup>1</sup> Gel permeation column chromatography was performed on a Japan Analytical Industry LC-92XX II (eluent: chloroform) with JAIGEL 1H and 2H polystyrene columns. Melting points were determined by MEL-TEMP II. IR spectra were recorded on JACSO FT/IR-6100 equipped with an attenuated total reflection (ATR) and are reported as wavenumber ( $\nu$ )  $\text{cm}^{-1}$ . NMR spectra were measured on JEOL ECZ-500 spectrometer and reported in parts per million from tetramethylsilane or DMSO.  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  or DMSO were referenced internally to tetramethylsilane (0.0 ppm) or DMSO (2.49 ppm) as a standard, respectively.  $^{13}\text{C}$  NMR spectra in  $\text{CDCl}_3$  or DMSO were referenced to  $\text{CDCl}_3$  (77.0 ppm) or DMSO (39.5 ppm) as a standard, respectively.  $^{19}\text{F}$  NMR spectra were referenced to  $\text{C}_6\text{F}_6$  (–164.9 ppm) as a standard. Mass spectra (GC MS) are taken at SHIMADZU Parvum 2 gas chromatograph mass spectrometer. High resolution mass spectra were acquired by atmospheric pressure ionization (APCI) using a time-of-flight mass analyzer on Bruker micrOTF II with a calibration standard of polyethylene glycol (MW 600) or JEOL JMS-T100LC (AccuTOF) spectrometer with a calibration standard of Reserpine (MW 609).

**Materials.** Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and used without further purification. Anhydrous ethereal solvents (stabilizer-free) were purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour)<sup>2</sup> equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use. The water content was determined with a Karl-Fischer moisture titrator (MKC-210, Kyoto Electronics Company) to be less than 30 ppm. Manganese(II) chloride (99.99%) was purchased from Alfa Aesar. Manganese ate complex ( $\text{MnCl}_2 \cdot 2\text{LiCl}$ ) was prepared from

manganese(II) chloride and anhydrous lithium chloride in THF.<sup>3</sup> Methylmagnesium bromide in THF was purchased from TCI and titrated prior to use.

## 2. Preparation of Substrates

The following compounds were prepared according to the literature procedures. The spectral data showed good agreement with the literature data.

*N*,3-dimethylbenzamide<sup>4</sup>

*N*-methyl-3-(trifluoromethyl)benzamide<sup>4</sup>

3-fluoro-*N*-methylbenzamide<sup>4</sup>

3-bromo-*N*-methylbenzamide<sup>5</sup>

3-methoxy-*N*-methylbenzamide<sup>6</sup>

*N*-methyl-1-naphthamide<sup>4</sup>

*N*-methyl-2-thiophenecarboxamide<sup>6</sup>

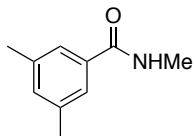
*N*,1-dimethyl-1*H*-indole-2-carboxamide<sup>6</sup>

*N*-(1-naphthyl)picolinamide<sup>7</sup>

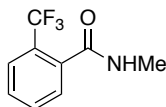
*N*-methyl-1-cyclohexene-1-carboxamide<sup>8</sup>

*N*-methyl-2,3,4,5,6-pentadeuteriobenzamide<sup>4</sup>

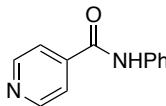
### ***N*,3,5-Trimethylbenzamide:**



To a solution of 3,5-dimethylbenzoyl chloride (0.74 mL, 5.0 mmol) and  $\text{MeNH}_2 \cdot \text{HCl}$  (0.51 g, 7.5 mmol) in THF (10 mL) was added  $\text{Et}_3\text{N}$  (2.8 mL, 20 mmol). The mixture was stirred at 25 °C overnight, diluted with EtOAc (20 mL) and washed with  $\text{H}_2\text{O}$  (3 × 10 mL). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and the crude product was purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane to afford the desired product as white needles (0.50 g, 61%). Melting Point: 80-81 °C ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3297, 3001, 2952, 2924, 2857, 1637, 1601, 1541, 1457, 1396, 1328  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 (s, 2H), 7.12 (s, 1H), 6.10 (br, 1H), 3.00 (d,  $J = 4.8$  Hz, 3H), 2.35 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 138.1, 134.6, 132.9, 124.6, 26.7, 21.2; HRMS (APCI) Calcd for  $\text{C}_{10}\text{H}_{14}\text{NO}^+$  [ $\text{M} + \text{H}$ ]<sup>+</sup> 164.1075, found, 164.1072.

***N*-Methyl-2-(trifluoromethyl)benzamide:**

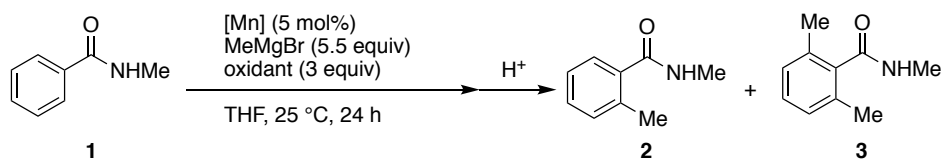
To a solution of 2-(trifluoromethyl)benzoyl chloride (1.5 mL, 10 mmol) and MeNH<sub>2</sub>•HCl (1.0 g, 15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added Et<sub>3</sub>N (5.6 mL, 40 mmol). The mixture was stirred at 25 °C for 30 min, diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and washed with H<sub>2</sub>O (3 × 15 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the crude product was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane to afford the desired product as white needles (1.1 g, 53%). Melting Point: 114-115 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (ATR): 3284, 3083, 1636, 1558, 1315, 1138, 775 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.57–7.47 (m, 3H), 6.03 (s, 1H), 2.96–2.95 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.5, 135.8 (q, *J*<sub>C-F</sub> = 1.8 Hz), 131.9, 129.7, 128.5, 127.1 (q, *J*<sub>C-F</sub> = 31.8 Hz), 126.2 (q, *J*<sub>C-F</sub> = 5.4 Hz), 123.5 (q, *J*<sub>C-F</sub> = 271.8 Hz), 26.8; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -62.3; HRMS (APCI) Calcd for C<sub>9</sub>H<sub>9</sub>F<sub>3</sub>NO<sup>+</sup> [*M* + *H*]<sup>+</sup> 204.0636, found, 204.0632.

***N*-Phenyl-4-pyridinecarboxamide:**

To a solution of isonicotinoyl chloride hydrochloride (1.8 g, 10 mmol) and aniline (1.0 mL, 11 mmol) in THF (30 mL) was added Et<sub>3</sub>N (4.2 mL, 30 mmol). The mixture was stirred at 25 °C overnight, diluted with EtOAc (20 mL) and washed with H<sub>2</sub>O (3 × 15 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the crude product was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane to afford the desired product as a white granular solid (1.3 g, 60%). Melting Point: 169-170 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (ATR): 3337, 2989, 2955, 1653, 1600, 1542, 746, 687 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.77 (dd, *J* = 4.6, 1.4 Hz, 2H), 8.06 (br, 1H), 7.70 (d, *J* = 6.0 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 163.8, 150.7, 142.1, 137.2, 129.2, 125.3, 120.9, 120.4; HRMS (APCI) Calcd for C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>O<sup>+</sup> [*M* + *H*]<sup>+</sup> 199.0871, found, 199.0876.

### 3. Investigation of the Key Reaction Parameters

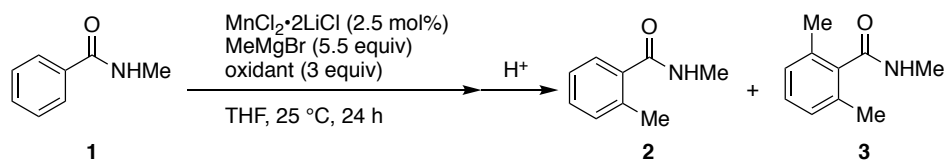
#### 3.1. Investigation of manganese catalyst



entry	[Mn]	GC yield (%)		
		2	3	1
1	MnCl <sub>2</sub> ·2LiCl	<5	77	<5
2	MnCl <sub>2</sub>	<5	74	<5
3	MnBr <sub>2</sub>	<5	73	<5
4	Mn(acac) <sub>2</sub>	<5	70	<5
5	Mn(acac) <sub>3</sub>	<5	79	<5
6	Mn(OAc) <sub>2</sub>	<5	77	<5
7	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	<5	78	<5
8	MnF <sub>2</sub>	38	n.d.	60
9	MnF <sub>3</sub>	32	n.d.	44
10	none	n.d.	n.d.	80

In an oven-dried Schlenk tube were placed *N*-methylbenzamide (27 mg, 0.20 mmol) and the manganese catalyst (0.010 mmol). MeMgBr in THF (1.1 mL, 1.00 M, 1.1 mmol) and 1-bromo-2-chloroethane (50  $\mu$ L, 0.60 mmol) were sequentially added. The reaction mixture was stirred at 25 °C for 24 h, and then it was quenched by the addition of a saturated aqueous solution of NH<sub>4</sub>Cl (1 mL) and small amount of water. The crude mixture was analyzed by GC in the presence of tridecane as an internal standard.

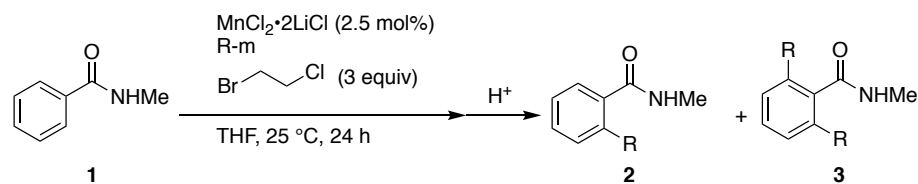
### 3.2. Investigation of oxidant



entry	oxidant	GC yield (%)		
		2	3	1
1		<5	86	<5
2		n.d.	n.d.	85
3		n.d.	n.d.	91
4		n.d.	n.d.	80
5		19	26	<5
6		15	25	<5
7		32	18	<5
8	none	n.d.	n.d.	82

In an oven-dried Schlenk tube were placed *N*-methylbenzamide (27 mg, 0.20 mmol) and a solution of  $\text{MnCl}_2 \cdot 2\text{LiCl}$  in THF (50  $\mu\text{L}$ , 0.10 M, 0.0050 mmol).  $\text{MeMgBr}$  in THF (1.1 mL, 1.00 M, 1.1 mmol) and 1-bromo-2-chloroethane (50  $\mu\text{L}$ , 0.60 mmol) were sequentially added. The reaction mixture was stirred at 25 °C for 24 h, and then it was quenched by the addition of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (1 mL) and small amount of water. The crude mixture was analyzed by GC in the presence of tridecane as an internal standard.

### 3.3. Investigation of organometallic reagent



entry	R-m	GC yield (%)			others
		2	3	1	
1	MeMgBr (5.5 equiv)	<5	86	<5	
2	MeMgBr (5.5 equiv) + ZnCl <sub>2</sub> •TMEDA (4.5 equiv) <sup>a</sup>	n.d.	n.d.	96	
3	MeMgBr (10 equiv) + ZnCl <sub>2</sub> •TMEDA (4.5 equiv) <sup>a</sup>	n.d.	n.d.	91	
4	MeLi (5.5 equiv)	8	n.d.	58	
5	OctylMgBr (5.5 equiv)	n.d.	n.d.	64	octene (173%), octane (276%)
6	PhMgBr (5.5 equiv)	n.d.	n.d.	64	Ph-Ph (280%)

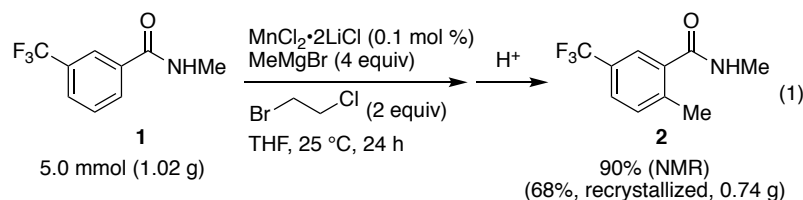
<sup>a</sup>TMEDA = *N,N,N',N'*-tetramethylethylenediamine.

In an oven-dried Schlenk tube were placed *N*-methylbenzamide (27 mg, 0.20 mmol) and the organometallic reagent was added. The solvent was removed in *vacuo*, and then THF (1.1 mL) was added if necessary. A solution of MnCl<sub>2</sub>•2LiCl in THF (50 μL, 0.10 M, 0.0050 mmol) and 1-bromo-2-chloroethane (50 μL, 0.60 mmol) were sequentially added. The reaction mixture was stirred at 25 °C for 24 h, and then it was quenched by the addition of a saturated aqueous solution of NH<sub>4</sub>Cl (1 mL) and small amount of water. The crude mixture was analyzed by GC in the presence of tridecane as an internal standard.



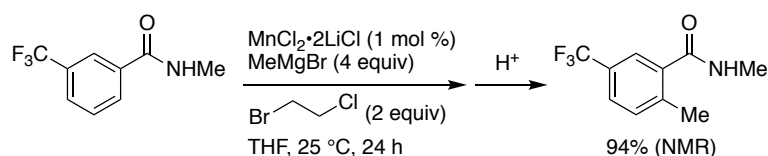
#### 4. Manganese-Catalyzed Directed Methylation of *N*-Methyl-3-(trifluoromethyl)benzamide

Reaction on gram scale (eq 1):



In a 100 mL oven-dried two-necked round bottom flask were placed *N*-methyl-3-(trifluoromethyl)benzamide (1.02 g, 5.0 mmol) and  $\text{MeMgBr}$  in THF (20 mL, 1.00 M, 20 mmol) was added at 0 °C. A solution of  $\text{MnCl}_2 \cdot 2\text{LiCl}$  in THF (10  $\mu\text{L}$ , 0.50 M, 0.0050 mmol) and 1-bromo-2-chloroethane (0.83 mL, 10 mmol) were sequentially added at 25 °C. The reaction mixture was stirred at 25 °C for 24 h, and then it was quenched by the addition of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (30 mL) and a small amount of water. After extraction with ethyl acetate ( $3 \times 50$  mL), the combined organic layers were passed over a silica gel pad with ethyl acetate, and the resulting solution was concentrated under reduced pressure. The crude mixture was analyzed by  $^1\text{H}$  NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard (product: 90%, recovery: 10%). The crude product was purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane to afford the desired product as a white solid (0.74 g, 68%).

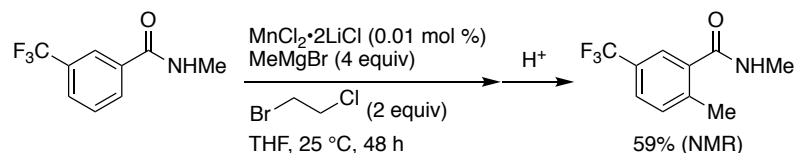
Reaction with 1 mol % of catalyst:



In an oven-dried Schlenk tube were placed *N*-methyl-3-(trifluoromethyl)benzamide (41 mg, 0.20 mmol) and a solution of  $\text{MnCl}_2 \cdot 2\text{LiCl}$  in THF (20  $\mu\text{L}$ , 0.10 M, 0.0020 mmol).  $\text{MeMgBr}$  in THF (0.80 mL, 1.00 M, 0.80 mmol) and 1-bromo-2-chloroethane (33  $\mu\text{L}$ , 0.40 mmol) were sequentially added. The reaction mixture was stirred at 25 °C for 24 h, and then it was quenched by the addition of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (1 mL) and small amount of water. After extraction with ethyl acetate ( $3 \times 3$  mL), the

combined organic layers were passed over a silica gel pad with ethyl acetate, and the resulting solution was concentrated under reduced pressure. The crude mixture was analyzed by  $^1\text{H}$  NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard (product: 94%, recovery: 6%).

#### Reaction with 0.01 mol % of catalyst:



In an oven-dried Schlenk tube were placed *N*-Methyl-3-(trifluoromethyl)benzamide (102 mg, 0.50 mmol) and a solution of  $\text{MnCl}_2 \cdot 2\text{LiCl}$  in THF (5.0  $\mu\text{L}$ , 0.10 M, 0.00050 mmol).  $\text{MeMgBr}$  in THF (2.00 mL, 1.00 M, 2.00 mmol) and 1-bromo-2-chloroethane (83  $\mu\text{L}$ , 1.0 mmol) were sequentially added. The reaction mixture was stirred at 25 °C for 48 h, and then it was quenched by the addition of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (3 mL) and small amount of water. After extraction with ethyl acetate ( $3 \times 5$  mL), the combined organic layers were passed over a silica gel pad with ethyl acetate, and the resulting solution was concentrated under reduced pressure. The crude mixture was analyzed by  $^1\text{H}$  NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard (product: 59%, recovery: 41%).

#### 5. Stoichiometric Reaction (eq 2)

In an oven-dried Schlenk tube were placed *N*-methyl-3-(trifluoromethyl)benzamide (41 mg, 0.20 mmol) and a manganese salt (0.20 mmol).  $\text{MeMgBr}$  in THF (0.84 mL, 0.95 M, 0.80 mmol) was added. 1-Bromo-2-chloroethane (33  $\mu\text{L}$ , 0.40 mmol) was added if necessary. The reaction mixture was stirred at 25 °C for 30 min, and then it was quenched by the addition of  $\text{D}_2\text{O}$  (1 mL). After extraction with ethyl acetate ( $3 \times 3$  mL), the combined organic layers were passed over a silica gel pad with ethyl acetate, and the resulting solution was concentrated under reduced pressure. The crude mixture was analyzed by  $^1\text{H}$  NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard. Deuterium was not incorporated in all cases.

## 6. General Procedure of Manganese-Catalyzed Directed Methylation

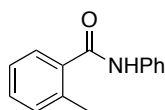
### General Procedure A (Table 1):

In an oven-dried Schlenk tube were placed the substrate (0.50 mmol) and a solution of  $\text{MnCl}_2 \cdot 2\text{LiCl}$  in THF (50  $\mu\text{L}$ , 0.10 M, 0.0050 mmol).  $\text{MeMgBr}$  in THF (2.00 mL, 1.00 M, 2.00 mmol) and 1-bromo-2-chloroethane (83  $\mu\text{L}$ , 1.0 mmol) were sequentially added. The reaction mixture was stirred at 25  $^\circ\text{C}$  for 24 h, and then it was quenched by the addition of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (3 mL) and small amount of water. After extraction with ethyl acetate ( $3 \times 5$  mL), the combined organic layers were passed over a silica gel pad with ethyl acetate, and the resulting solution was concentrated under reduced pressure. The crude mixture was analyzed by  $^1\text{H}$  NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by gel permeation column chromatography (eluent:  $\text{CHCl}_3$ ) to afford the desired product.

### General Procedure B (Table 2):

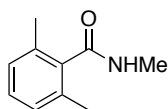
In an oven-dried Schlenk tube were placed the substrate (0.50 mmol) and a solution of  $\text{MnCl}_2 \cdot 2\text{LiCl}$  in THF (50  $\mu\text{L}$ , 0.50 M, 0.025 mmol).  $\text{MeMgBr}$  in THF (2.25 mL, 1.00 M, 2.25 mmol) and 1-bromo-2-chloroethane (124  $\mu\text{L}$ , 1.50 mmol) were sequentially added. The reaction mixture was stirred at 25  $^\circ\text{C}$  for 48 h, and then it was quenched by the addition of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (3 mL) and small amount of water. After extraction with ethyl acetate ( $3 \times 5$  mL), the combined organic layers were passed over a silica gel pad with ethyl acetate, and the resulting solution was concentrated under reduced pressure. The crude mixture was analyzed by  $^1\text{H}$  NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified by gel permeation column chromatography (eluent:  $\text{CHCl}_3$ ) to afford the desired product.

### 2-Methyl-*N*-phenylbenzamide (Table 1, entry 1):



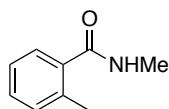
The general procedure A was applied to *N*-phenylbenzamide (99 mg, 0.50 mmol) for 48 h. The title compound was obtained (104 mg, 98%) ( $^1\text{H}$  NMR yield: 99%). The analytically pure product was obtained after a short pass over a silica gel column. The title compound was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 126-127 °C ( $\text{CH}_2\text{Cl}_2$ /hexane);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78 (br, 1H), 7.58 (d,  $J$  = 7.7 Hz, 2H), 7.39 (d,  $J$  = 7.7 Hz, 1H), 7.33–7.30 (m, 3H), 7.21–7.16 (m, 2H), 7.12 (t,  $J$  = 7.4 Hz, 1H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 138.0, 136.3, 136.2, 131.1, 130.1, 128.9, 126.6, 125.7, 124.4, 119.9, 19.7; HRMS (APCI) Calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}^+$   $[\text{M} + \text{H}]^+$  212.1070, found, 212.1072. The compound data was in good agreement with the literature data.<sup>9</sup>

***N*,2,6-Trimethylbenzamide (Table 1, entry 2):**



The general procedure A was applied to *N*-methylbenzamide (68 mg, 0.50 mmol) using  $\text{MeMgBr}$  in THF (2.75 mL, 1.00 M, 2.75 mmol) and 1-bromo-2-chloroethane (124  $\mu\text{L}$ , 1.50 mmol) for 48 h. The title compound was obtained (62 mg, 83%) ( $^1\text{H}$  NMR yield: 89%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 146-147 °C ( $\text{CH}_2\text{Cl}_2$ /hexane);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.13 (t,  $J$  = 7.8 Hz, 1H), 6.99 (d,  $J$  = 7.4 Hz, 2H), 5.81 (br, 1H), 2.97 (d,  $J$  = 5.0 Hz, 3H), 2.28 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 137.6, 134.1, 128.6, 127.3, 26.2, 19.1; HRMS (APCI) Calcd for  $\text{C}_{10}\text{H}_{14}\text{NO}^+$   $[\text{M} + \text{H}]^+$  164.1070, found, 164.1077. The compound data was in good agreement with the literature data.<sup>10</sup>

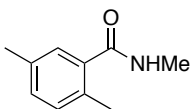
***N*,2-Dimethylbenzamide (Table 1, entry 3):**



The general procedure A was applied to *N*-methylbenzamide (68 mg, 0.50 mmol) using  $\text{MeMgBr}$  in THF (1.55 mL, 1.00 M, 1.55 mmol). The title compound was obtained (45 mg, 60%) ( $^1\text{H}$  NMR yield: 69%). A dimethylated product was also obtained (11 mg, 13%) ( $^1\text{H}$  NMR yield: 16%). The title compound was further purified by

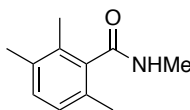
recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane as white needles. Melting Point: 63-64 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.28–7.25 (m, 2H), 7.18–7.12 (m, 2H), 6.14 (br, 1H), 2.91 (dd, *J* = 5.1, 1.4 Hz, 3H), 2.38 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.8, 136.4, 135.8, 130.8, 129.6, 126.6, 125.5, 26.4, 19.6; HRMS (APCI) Calcd for C<sub>9</sub>H<sub>12</sub>NO<sup>+</sup> [*M* + *H*]<sup>+</sup> 150.0913, found, 150.0918. The compound data was in good agreement with the literature data.<sup>6</sup>

***N*,2,5-Trimethylbenzamide (Table 1, entry 4):**



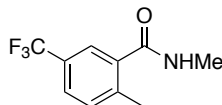
The general procedure A was applied to *N*,3-dimethylbenzamide (75 mg, 0.50 mmol). The title compound was obtained (56 mg, 69%) (<sup>1</sup>H NMR yield: 81%). Dimethylated product was also obtained (5.3 mg, 6%) (<sup>1</sup>H NMR yield: 9%). The title compound was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane as white needles. Melting Point: 122-123 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.11 (s, 1H), 7.09–7.05 (m, 2H), 6.05 (s, 1H), 2.92 (dd, *J* = 4.8, 1.1 Hz, 3H), 2.34 (s, 3H), 2.28 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.9, 136.2, 135.0, 132.6, 130.7, 130.3, 127.4, 26.4, 20.7, 19.1; HRMS (APCI) Calcd for C<sub>10</sub>H<sub>14</sub>NO<sup>+</sup> [*M* + *H*]<sup>+</sup> 164.1070, found, 164.1077. The compound data was in good agreement with the literature data.<sup>10</sup>

***N*,2,3,6-Tetramethylbenzamide (Table 1, entry 4):**



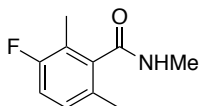
The title compound was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane as a white amorphous solid. Melting Point: 139-140 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (ATR): 3254, 3086, 2924, 2852, 1634, 1568, 1559, 1508, 1457, 1316, 816 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.04 (d, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 5.65 (br, 1H), 3.01 (d, *J* = 4.9 Hz, 3H), 2.26 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.7, 137.9, 134.3, 132.5, 131.6, 130.0, 127.3, 26.4, 19.8, 19.0, 16.4; HRMS (APCI) Calcd for C<sub>11</sub>H<sub>16</sub>NO<sup>+</sup> [*M* + *H*]<sup>+</sup> 178.1232, found, 178.1225.

***N*,2-Dimethyl-5-(trifluoromethyl)benzamide (Table 1, entry 5):**



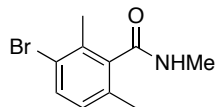
The general procedure A was applied to *N*-methyl-3-(trifluoromethyl)benzamide (102 mg, 0.50 mmol) using  $\text{MnCl}_2 \cdot 2\text{LiCl}$  in THF (5.0  $\mu\text{L}$ , 0.10 M, 0.00050 mmol). The title compound was obtained (82 mg, 75%) ( $^1\text{H}$  NMR yield: 90%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 122-123  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3292, 3095, 2925, 2875, 1643, 1556, 1541, 1408, 1342, 1111, 712  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.52–7.50 (m, 2H), 7.27 (d,  $J = 7.7$  Hz, 1H), 6.46 (br, 1H), 2.91 (d,  $J = 4.9$  Hz, 3H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 140.2, 136.9, 131.3, 128.0 (q,  $J_{\text{C-F}} = 32.4$  Hz), 126.2 (q,  $J_{\text{C-F}} = 4.2$  Hz), 123.8 (q,  $J_{\text{C-F}} = 270.0$  Hz), 123.6 (q,  $J_{\text{C-F}} = 3.6$  Hz), 26.5, 19.6;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  –65.7; HRMS (APCI) Calcd for  $\text{C}_{10}\text{H}_{11}\text{F}_3\text{NO}^+$   $[\text{M} + \text{H}]^+$  218.0793, found, 218.0793.

**3-Fluoro-*N*,2,6-trimethylbenzamide (Table 1, entry 6):**



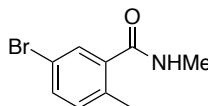
The general procedure A was applied to 3-fluoro-*N*-methylbenzamide (77 mg, 0.50 mmol) using  $\text{MeMgBr}$  in THF (2.75 mL, 1.00 M, 2.75 mmol) and 1-bromo-2-chloroethane (124  $\mu\text{L}$ , 1.50 mmol) for 48 h. The title compound was obtained (66 mg, 73%) ( $^1\text{H}$  NMR yield: 79%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 133-134  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3280, 2989, 2957, 1652, 1636, 1558, 1542, 1409, 1320, 1242, 820  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.94–6.86 (m, 2H), 6.04 (br, 1H), 2.94 (d,  $J = 4.9$  Hz, 3H), 2.20 (s, 3H), 2.14 (d,  $J = 2.3$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8 (d,  $J_{\text{C-F}} = 3.0$  Hz), 159.2 (d,  $J_{\text{C-F}} = 241.8$  Hz), 139.2 (d,  $J_{\text{C-F}} = 3.6$  Hz), 129.5 (d,  $J_{\text{C-F}} = 4.2$  Hz), 128.5 (d,  $J_{\text{C-F}} = 7.8$  Hz), 121.3 (d,  $J_{\text{C-F}} = 18.0$  Hz), 115.1 (d,  $J_{\text{C-F}} = 22.2$  Hz), 26.2, 18.5, 11.4;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  –123.3; HRMS (APCI) Calcd for  $\text{C}_{10}\text{H}_{13}\text{FNO}^+$   $[\text{M} + \text{H}]^+$  182.0981, found, 182.0973.

**3-Bromo-*N*,2,6-trimethylbenzamide (Table 1, entry 7):**



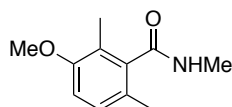
The general procedure A was applied to 3-bromo-*N*-methylbenzamide (107 mg, 0.50 mmol) using MeMgBr in THF (2.75 mL, 1.00 M, 2.75 mmol) and 1-bromo-2-chloroethane (124  $\mu$ L, 1.50 mmol) for 48 h. The title compound was obtained (77 mg, 64%) ( $^1\text{H}$  NMR yield: 70%). Monomethylated product was also obtained (19 mg, 16%) ( $^1\text{H}$  NMR yield: 21%). The title compound was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 174-175  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3283, 2998, 2954, 2922, 1653, 1557, 1542, 1412, 1311, 822  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 (d,  $J$  = 8.0 Hz, 1H), 6.85 (d,  $J$  = 8.3 Hz, 1H), 6.05 (br, 1H), 2.94 (d,  $J$  = 5.1 Hz, 3H), 2.29 (s, 3H), 2.19 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 139.1, 133.7, 133.5, 132.5, 128.9, 122.6, 26.3, 19.9, 18.8; HRMS (APCI) Calcd for  $\text{C}_{10}\text{H}_{13}^{79}\text{BrNO}^+ [\text{M} + \text{H}]^+$  242.0175, found, 242.0170.

**5-Bromo-*N*,2-dimethylbenzamide (Table 1, entry 7):**



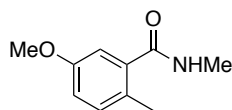
The title compound was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 139-140  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3284, 3001, 2953, 2924, 1645, 1550, 1542, 1404, 1319, 1038, 819  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47 (d,  $J$  = 2.2 Hz, 1H), 7.41 (dd,  $J$  = 8.0, 2.0 Hz, 1H), 7.09 (d,  $J$  = 8.0 Hz, 1H), 5.81 (br, 1H), 2.98 (d,  $J$  = 4.1 Hz, 3H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 138.2, 135.1, 132.7, 132.6, 129.6, 119.1, 26.7, 19.3; HRMS (APCI) Calcd for  $\text{C}_9\text{H}_{11}^{79}\text{BrNO}^+ [\text{M} + \text{H}]^+$  228.0024, found, 228.0023.

**3-Methoxy-*N*,2,6-trimethylbenzamide (Table 1, entry 8):**



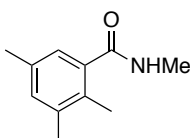
The general procedure A was applied to 3-methoxy-*N*-methylbenzamide (83 mg, 0.50 mmol) using MeMgBr in THF (2.75 mL, 1.00 M, 2.75 mmol) and 1-bromo-2-chloroethane (124  $\mu$ L, 1.50 mmol) for 48 h. After purification, a mixture of di- and monomethylated product was obtained (78 mg; di-: 48%, mono-: 37%). The title compound was isolated after further purification by using gel permeation column chromatography ( $^1\text{H}$  NMR yield: 49%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 133-134  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3245, 2955, 2924, 2838, 1635, 1588, 1558, 1457, 1403, 1316, 1099, 811  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.98 (d,  $J$  = 8.3 Hz, 1H), 6.74 (d,  $J$  = 8.3 Hz, 1H), 5.63 (br, 1H), 3.80 (s, 3H), 3.01 (d,  $J$  = 4.8 Hz, 3H), 2.24 (s, 3H), 2.16 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 155.7, 138.8, 128.0, 125.8, 123.0, 110.5, 55.6, 26.4, 18.4, 12.8; HRMS (APCI) Calcd for  $\text{C}_{11}\text{H}_{16}\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  194.1181, found, 194.1181.

**5-Methoxy-*N*,2-dimethylbenzamide (Table 1, entry 8):**



The title compound was isolated after further purification by using gel permeation column chromatography as a white amorphous solid ( $^1\text{H}$  NMR yield: 37%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 99-100  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3274, 2958, 2922, 2835, 1636, 1596, 1557, 1457, 1397, 1317, 1033, 824  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.08 (d,  $J$  = 8.3 Hz, 1H), 6.85 (d,  $J$  = 2.5 Hz, 1H), 6.82 (dd,  $J$  = 8.3, 2.8 Hz, 1H), 6.05 (br, 1H), 3.76 (s, 3H), 2.93 (d,  $J$  = 4.8 Hz, 3H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 157.3, 137.2, 131.8, 127.4, 115.3, 112.1, 55.3, 26.5, 18.7; HRMS (APCI) Calcd for  $\text{C}_{10}\text{H}_{14}\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  180.1025, found, 180.1018.

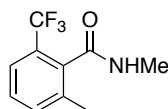
***N*,2,3,5-Tetramethylbenzamide (Table 1, entry 9):**





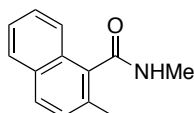
The general procedure A was applied to *N*,3,5-trimethylbenzamide (82 mg, 0.50 mmol). The title compound was obtained (74 mg, 84%) ( $^1\text{H}$  NMR yield: 90%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 142-143 °C ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3307, 3010, 2950, 2924, 2857, 1635, 1604, 1541, 1457, 1324  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.98 (s, 1H), 6.93 (s, 1H), 5.97 (br, 1H), 2.92 (d,  $J$  = 4.8 Hz, 3H), 2.25–2.21 (m, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.7, 137.5, 137.2, 134.7, 131.7, 130.6, 124.7, 26.4, 20.6, 20.0, 15.7; HRMS (APCI) Calcd for  $\text{C}_{11}\text{H}_{16}\text{NO}^+$  [ $\text{M} + \text{H}$ ] $^+$  178.1232, found, 178.1225.

***N*,6-Dimethyl-2-(trifluoromethyl)benzamide (Table 1, entry 10):**



The general procedure A was applied to *N*-methyl-2-(trifluoromethyl)benzamide (102 mg, 0.50 mmol) for 48 h. The title compound was obtained in (87 mg, 81%) ( $^1\text{H}$  NMR yield: 92%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 148-149 °C ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3272, 3090, 2918, 2858, 1646, 1557, 1542, 1318, 1116, 801  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45–7.42 (m, 1H), 7.36–7.34 (m, 1H), 6.13 (s, 1H), 2.93 (d,  $J$  = 5.1 Hz, 3H), 2.30 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 136.5, 135.2 (d,  $J_{\text{C-F}}$  = 2.4 Hz), 133.7, 128.8, 126.9 (q,  $J_{\text{C-F}}$  = 30.6 Hz), 123.7 (q,  $J_{\text{C-F}}$  = 272.4 Hz), 123.3 (q,  $J_{\text{C-F}}$  = 10.2 Hz), 26.4, 18.9;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.4; HRMS (APCI) Calcd for  $\text{C}_{10}\text{H}_{11}\text{F}_3\text{NO}^+$  [ $\text{M} + \text{H}$ ] $^+$  218.0793, found, 218.0797.

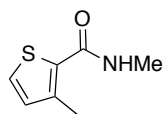
***N*,2-Dimethyl-1-naphthalenecarboxamide (Table 1, entry 11):**



The general procedure A was applied to *N*-methyl-1-naphthalenecarboxamide (93 mg, 0.50 mmol). The title compound was obtained (78 mg, 78%) ( $^1\text{H}$  NMR yield: 89%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 188-189 °C ( $\text{CH}_2\text{Cl}_2$ /hexane);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):

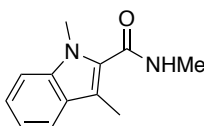
$\delta$  7.75 (d,  $J$  = 7.7 Hz, 1H), 7.70 (t,  $J$  = 9.1 Hz, 2H), 7.44–7.38 (m, 2H), 7.21 (d,  $J$  = 8.3 Hz, 1H), 6.07 (br, 1H), 2.95 (d,  $J$  = 4.8 Hz, 3H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 133.8, 131.9, 131.5, 130.0, 128.6, 128.2, 127.8, 126.6, 125.2, 124.4, 26.3, 19.4; HRMS (APCI) Calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}^+$   $[\text{M} + \text{H}]^+$  200.1070, found, 200.1072. The compound data was in good agreement with the literature data.<sup>11</sup>

***N*,3-Dimethyl-2-thiophenecarboxamide (Table 1, entry 12):**



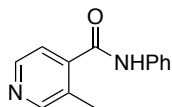
The general procedure A was applied to *N*-methyl-2-thiophenecarboxamide (71 mg, 0.50 mmol). The title compound was obtained (46 mg, 60%) as a yellow oil ( $^1\text{H}$  NMR yield: 68%). IR (ATR): 3307, 3102, 2935, 1626, 1543, 1518, 1408, 1287  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.24 (d,  $J$  = 5.1 Hz, 1H), 6.87 (d,  $J$  = 4.9 Hz, 1H), 6.02 (br, 1H), 2.95 (d,  $J$  = 4.8 Hz, 3H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 140.7, 131.8, 130.9, 126.1, 26.6, 15.5; HRMS (APCI) Calcd for  $\text{C}_7\text{H}_{10}\text{NOS}^+$   $[\text{M} + \text{H}]^+$  156.0478, found, 156.0484.

***N*,1,3-Trimethyl-1*H*-indole-2-carboxamide (Table 1, entry 13):**



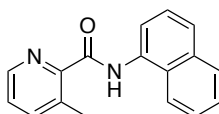
The general procedure A was applied to *N*,1-dimethyl-1*H*-indole-2-carboxamide (93 mg, 0.50 mmol). The title compound was obtained (61 mg, 61%) ( $^1\text{H}$  NMR yield: 70%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 188-189  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3306, 3003, 2924, 2853, 1608, 1541, 1457, 1360, 738  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55 (d,  $J$  = 8.0 Hz, 1H), 7.31–7.26 (m, 2H), 7.14–7.10 (m, 1H), 5.97 (br, 1H), 3.81 (s, 3H), 3.02 (d,  $J$  = 4.8 Hz, 3H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 137.7, 130.3, 127.1, 123.8, 119.8, 119.4, 111.6, 109.7, 31.1, 26.4, 10.0; HRMS (APCI) Calcd for  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}^+$   $[\text{M}]^+$  202.1101, found, 202.1110.

### 3-Methyl-*N*-phenyl-4-pyridinecarboxamide (Table 1, entry 14):



The general procedure A was applied to *N*-phenyl-4-pyridinecarboxamide (99 mg, 0.50 mmol). The title compound was obtained (84 mg, 79%) (<sup>1</sup>H NMR yield: 89%). The product was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane as yellow needles. Melting Point: 108-109 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (ATR): 3293, 2989, 2955, 1654, 1558, 1542, 1406, 1321, 747, 689 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO): δ 10.5 (br, 1H), 8.56 (br, 2H), 7.71 (d, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 4.6 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.11 (t, *J* = 7.1 Hz, 1H), 2.35 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 165.7, 151.9, 147.4, 143.3, 137.5, 130.7, 129.2, 125.1, 120.4, 120.1, 16.5; HRMS (APCI) Calcd for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O<sup>+</sup> [M + H]<sup>+</sup> 213.1028, found, 213.1031.

### 3-Methyl-*N*-(naphthalen-1-yl)picolinamide (Table 1, entry 15):



In an oven-dried Schlenk tube were placed *N*-(1-naphthyl)picolinamide (50 mg, 0.20 mmol) and a solution of MnCl<sub>2</sub>•2LiCl in THF (40 μL, 0.50 M, 0.020 mmol). MeMgBr in THF (0.77 mL, 1.04 M, 0.80 mmol) and 1-bromo-2-chloroethane (33 μL, 0.4 mmol) were sequentially added. The reaction mixture was stirred at 25 °C for 24 h, and then it was quenched by the addition of a saturated aqueous solution of NH<sub>4</sub>Cl (1 mL) and small amount of water. After extraction with ethyl acetate (3 × 3 mL), the combined organic layers were passed over a silica gel pad with ethyl acetate, and the resulting solution was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 5:1) to afford the title compound (49 mg, 92%). The product was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane as white needles. Melting Point: 143-144 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (ATR): 3328, 3011, 2924, 2853, 1688, 1525, 1497, 1340, 792, 772 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 11.0 (br, 1H), 8.56 (dd, *J* = 4.3, 0.8 Hz, 1H), 8.36 (d, *J* = 7.4 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.70–7.69 (m, 2H), 7.60–7.51 (m,

3H), 7.42 (dd,  $J = 7.7, 4.6$  Hz, 1H), 2.87 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 147.0, 145.5, 141.4, 136.3, 134.1, 132.7, 128.8, 126.6, 126.1 (2C), 126.0, 125.9, 124.8, 120.7, 118.6, 20.9; HRMS (APCI) Calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}^+$   $[\text{M} + \text{H}]^+$  263.1184, found, 263.1186.

#### • X-ray crystallographic analysis

The diffraction images for X-ray crystallographic analysis were collected on a Rigaku Rapid II diffractometer equipped with an imaging plate (IP) using Cu  $\text{K}\alpha$  ( $\lambda = 1.5419$  Å) radiation. The positional and thermal parameters were refined by the full-matrix least-squares method using SHELXL-2014/7 program.<sup>12</sup> The Yadokari-XG software was used for refinement of the structure.<sup>13</sup>

CCDC 1560075 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

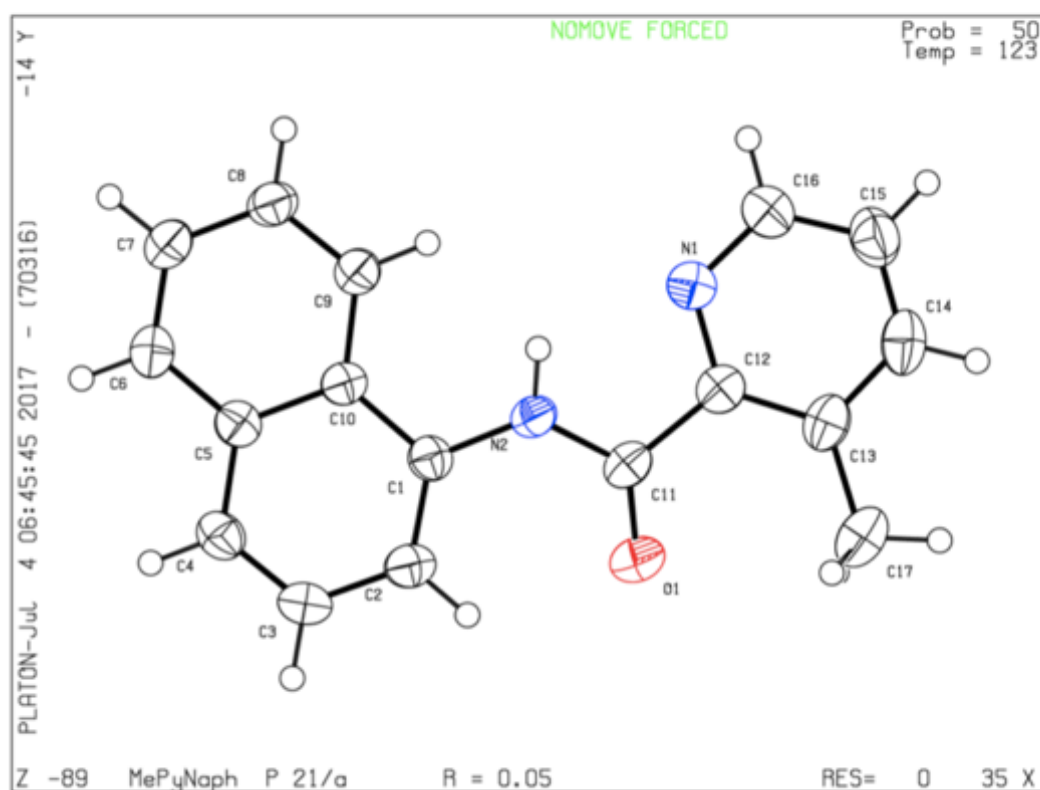
#### Crystal data for X (CCDC 1560075)

Formula	$\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$
Formula weight	262.30
Measurement temperature	123(2) K
Crystal system	monoclinic
Space group	P 21/a
Lattice parameters	$a = 14.4154(6)$ Å $b = 6.0240(2)$ Å $c = 15.0935(6)$ Å $\alpha = 90^\circ$ $\beta = 94.616(7)^\circ$ $\gamma = 90^\circ$
Volume	$1306.44(9)$ Å <sup>3</sup>
Z value	4
Density (calculated)	$1.334$ g/cm <sup>3</sup>
$F(000)$	552.0
Number of reflections measured	13222
Number of unique reflections	2385
$R_{\text{int}}$	0.0514
Number of observed reflections ( $I > 2\sigma(I)$ )	1615

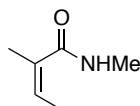
Goodness of fit indicator	1.040
Final $R_1$ indices [ $I > 2\sigma(I)$ ] ( $R_{\text{obs}}$ , $wR_{\text{obs}}$ )	0.0517, 0.1215
R indices [all data] ( $R_{\text{all}}$ , $wR_{\text{all}}$ )	0.0846, 0.1370
Largest diff peak and hole	0.171/-0.197 e $\cdot\text{\AA}^{-3}$

PLATON version of 27/03/2017; check.def file version of 24/03/2017

Datablock MePyNaph - ellipsoid plot

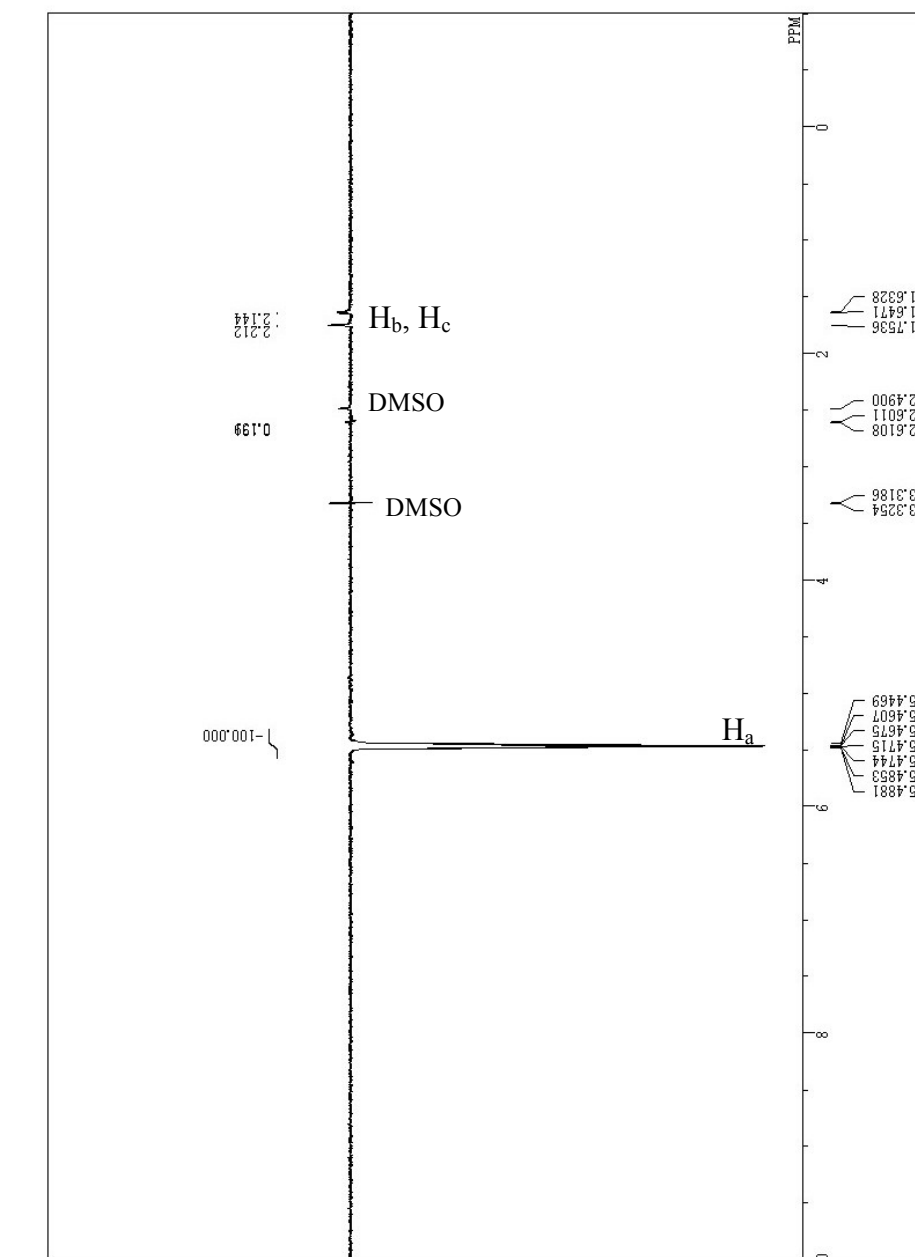
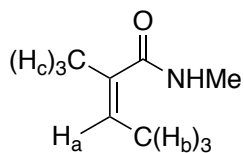


**(Z)-N,2-Dimethyl-2-butenamide (Table 1, entry 16):**

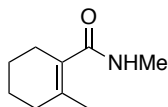


The general procedure A was applied to *N*-methylmethacrylamide (50 mg, 0.50 mmol). The title compound was obtained (37 mg, 65%) as a colorless oil ( $^1\text{H}$  NMR yield: 80%). IR (ATR): 3291, 3079, 2945, 1626, 1523, 1456, 1407, 829  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, DMSO):  $\delta$  7.65 (br, 1H), 5.47 (qd,  $J = 6.9, 1.4$  Hz, 1H), 2.61 (dd,  $J = 4.5, 1.1$  Hz, 3H), 1.76 (d,  $J = 1.4$  Hz, 3H), 1.64 (d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 132.7, 127.4, 25.9, 20.7, 15.0; HRMS (APCI) Calcd for  $\text{C}_6\text{H}_{12}\text{NO}^+$  [ $\text{M} + \text{H}$ ] $^+$  114.0919,

found, 114.0915. The stereochemistry of the compound was determined by NOE experiments, using CDCl<sub>3</sub> as a solvent. When signal H<sub>a</sub> at  $\delta = 5.47$  (qd,  $J = 6.9, 1.4$  Hz, 1H) was irradiated, the two methyl signals H<sub>b</sub> and H<sub>c</sub> at  $\delta = 1.76$  (d,  $J = 1.4$  Hz, 3H) and  $\delta = 1.64$  (d,  $J = 6.9$  Hz, 3H) exhibited an enhancement by 2.1% and 2.2%.

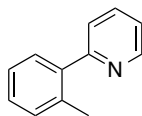


***N*,2-Dimethyl-1-cyclohexene-1-carboxamide (Table 1, entry 17):**



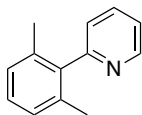
The general procedure A was applied to *N*-methyl-1-cyclohexene-1-carboxamide (70 mg, 0.50 mmol). The title compound was obtained (68 mg, 88%) ( $^1\text{H}$  NMR yield: 93%). The product was further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane as white needles. Melting Point: 63-64 °C ( $\text{CH}_2\text{Cl}_2$ /hexane); IR (ATR): 3299, 2929, 2856, 1616, 1522, 1473, 1457, 1397  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.82 (br, 1H), 2.85 (d,  $J$  = 4.8 Hz, 3H), 2.20–2.19 (m, 2H), 1.99–1.97 (br, 2H), 1.75 (s, 3H), 1.61–1.60 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.6, 134.0, 129.3, 31.1, 26.8, 25.9, 22.3, 22.1, 20.7; HRMS (APCI) Calcd for  $\text{C}_9\text{H}_{16}\text{NO}^+$  [ $\text{M} + \text{H}$ ] $^+$  154.1226, found, 154.1232.

**2-(2-Methylphenyl)pyridine (Table 2, entry 1):**



The general procedure B was applied to 2-phenylpyridine (78 mg, 0.50 mmol). The title compound was obtained (54 mg, 64%) as a yellow oil ( $^1\text{H}$  NMR yield: 80%). A dimethylated product was also obtained (7.4 mg, 8%) as a yellow oil ( $^1\text{H}$  NMR yield: 10%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.69 (d,  $J$  = 4.6 Hz, 1H), 7.73 (td,  $J$  = 7.2, 1.7 Hz, 1H), 7.39 (d,  $J$  = 6.8 Hz, 2H), 7.31–7.21 (m, 4H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 149.1, 140.3, 136.1, 135.6, 130.6, 129.5, 128.2, 125.8, 124.0, 121.5, 20.2; HRMS (APCI) Calcd for  $\text{C}_{12}\text{H}_{12}\text{N}^+$  [ $\text{M} + \text{H}$ ] $^+$  170.0964, found, 170.0964. The compound data was in good agreement with the literature data.<sup>14</sup>

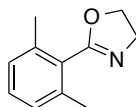
**2-(2,6-Dimethylphenyl)pyridine (Table 2, entry 1):**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.72 (d,  $J$  = 4.8 Hz, 1H), 7.76 (td,  $J$  = 7.7, 1.7 Hz, 1H), 7.27–7.09 (m, 3H), 7.10 (d,  $J$  = 7.7 Hz, 2H), 2.04 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 149.7, 140.5, 136.2, 135.7, 127.8, 127.5, 124.4, 121.6, 20.2; HRMS (APCI)

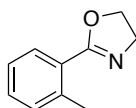
Calcd for  $C_{13}H_{14}N^+$   $[M + H]^+$  184.1126, found, 184.1134. The compound data was in good agreement with the literature data.<sup>14</sup>

**2-(2,6-Dimethylphenyl)-4,5-dihydrooxazole (Table 2, entry 2):**



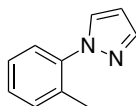
The general procedure B was applied to 2-phenyl-4,5-dihydrooxazole (74 mg, 0.50 mmol) at 40 °C. The title compound was obtained (23 mg, 26%) as a yellow oil ( $^1H$  NMR yield: 41%). A dimethylated product was also obtained (11 mg, 14%) as a yellow oil ( $^1H$  NMR yield: 19%). IR (ATR): 2965, 1660, 1465, 1349, 1239, 1047, 774  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.18 (t,  $J$  = 7.4 Hz, 1H), 7.03 (d,  $J$  = 7.7 Hz, 2H), 4.41 (t,  $J$  = 9.4 Hz, 2H), 4.09 (t,  $J$  = 9.7 Hz, 2H), 2.32 (s, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  164.8, 136.9, 129.3, 128.9, 127.3, 67.1, 55.1, 19.7; HRMS (APCI) Calcd for  $C_{11}H_{14}NO^+$   $[M + H]^+$  176.1070, found, 176.1070.

**2-(2-Methylphenyl)-4,5-dihydrooxazole (Table 2, entry 2):**



$^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.80 (dd,  $J$  = 7.4, 0.8 Hz, 1H), 7.33 (td,  $J$  = 7.4, 1.1 Hz, 1H), 7.24–7.20 (m, 2H), 4.38 (t,  $J$  = 9.7 Hz, 2H), 4.10 (t,  $J$  = 9.7 Hz, 2H), 2.59 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  165.0, 138.7, 131.1, 130.5, 129.8, 127.1, 125.5, 66.8, 55.4, 21.7; HRMS (APCI) Calcd for  $C_{10}H_{12}NO^+$   $[M + H]^+$  162.0919, found, 162.0916. The compound data was in good agreement with the literature data.<sup>15</sup>

**1-(2-Methylphenyl)pyrazole (Table 2, entry 3):**

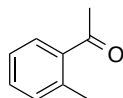


The general procedure B was applied to 1-phenylpyrazole (72 mg, 0.50 mmol) at 40 °C. The title compound was obtained (25 mg, 32%) as a yellow oil ( $^1H$  NMR yield: 47%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.72 (d,  $J$  = 1.7 Hz, 1H), 7.60 (d,  $J$  = 2.3 Hz, 1H), 7.33–



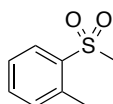
7.26 (m, 4H), 6.44 (t,  $J = 2.0$  Hz, 1H), 2.24 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 134.0, 133.7, 131.2, 130.5, 128.3, 126.5, 126.1, 106.1, 18.0; HRMS (APCI) Calcd for  $\text{C}_{10}\text{H}_{11}\text{N}_2^+$   $[\text{M} + \text{H}]^+$  159.0917, found, 159.0918. The compound data was in good agreement with the literature data.<sup>16</sup>

**1-(2-Methylphenyl)ethanone (Table 2, entry 4):**



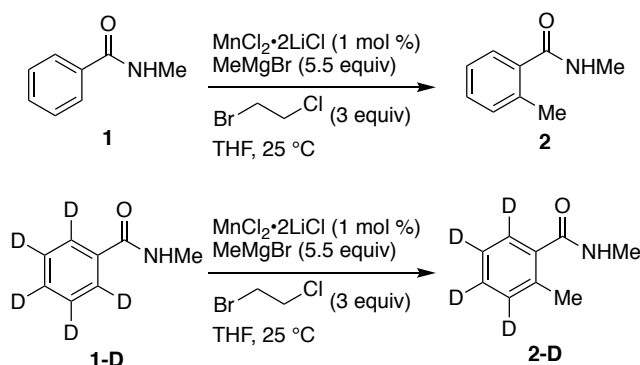
The general procedure B was applied to benzonitrile (52 mg, 0.50 mmol) using  $\text{MeMgBr}$  in THF (2.75 mL, 1.00 M, 2.75 mmol). The reaction was quenched by the addition of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (1 mL) and a 3M aqueous solution of  $\text{HCl}$  (2 mL). The resulting mixture was stirred for 1 h. After extraction, the combined organic layers were passed over a Florisil pad. The title compound was obtained (33 mg, 50%) as a yellow oil ( $^1\text{H}$  NMR yield: 67%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69 (d,  $J = 7.7$  Hz, 1H), 7.38 (t,  $J = 7.7$  Hz, 1H), 7.28–7.24 (m, 2H), 2.58 (s, 3H), 2.53 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  201.4, 138.1, 137.3, 131.7, 131.2, 129.1, 125.4, 29.3, 21.3; HRMS (APCI) Calcd for  $\text{C}_9\text{H}_{11}\text{O}^+$   $[\text{M} + \text{H}]^+$  135.0804, found, 135.0798. The compound data was in good agreement with the literature data.<sup>17</sup>

**1-Methyl-2-(methylsulfonyl)benzene (Table 2, entry 5):**



The general procedure B was applied to methyl phenyl sulfone (78 mg, 0.50 mmol) using  $\text{MeMgBr}$  in THF (2.75 mL, 1.00 M, 2.75 mmol) and 2,3-dibromobutane (184  $\mu\text{L}$ , 1.50 mmol) instead of 1-bromo-2-chloroethane. The title compound was obtained (19 mg, 22%) as a yellow oil ( $^1\text{H}$  NMR yield: 34%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04 (dd,  $J = 7.7, 0.9$  Hz, 1H), 7.53 (td,  $J = 7.4, 1.1$  Hz, 1H), 7.04–7.34 (m, 2H), 3.08 (s, 1H), 2.72 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6, 137.5, 133.7, 132.7, 129.2, 126.7, 43.6, 20.3; HRMS (APCI) Calcd for  $\text{C}_8\text{H}_{11}\text{O}_2\text{S}^+$   $[\text{M} + \text{H}]^+$  171.0474, found, 171.0482. The compound data was in good agreement with the literature data.<sup>18</sup>

## 7. KIE Experiment



time (h)	1.5	2	2.5	3
yield of <b>2</b> (%)	9	14	20	25
yield of <b>2-D</b> (%)	5	7	9	12

$$k_{\text{H}}/k_{\text{D}} = 2.0 \pm 0.1$$

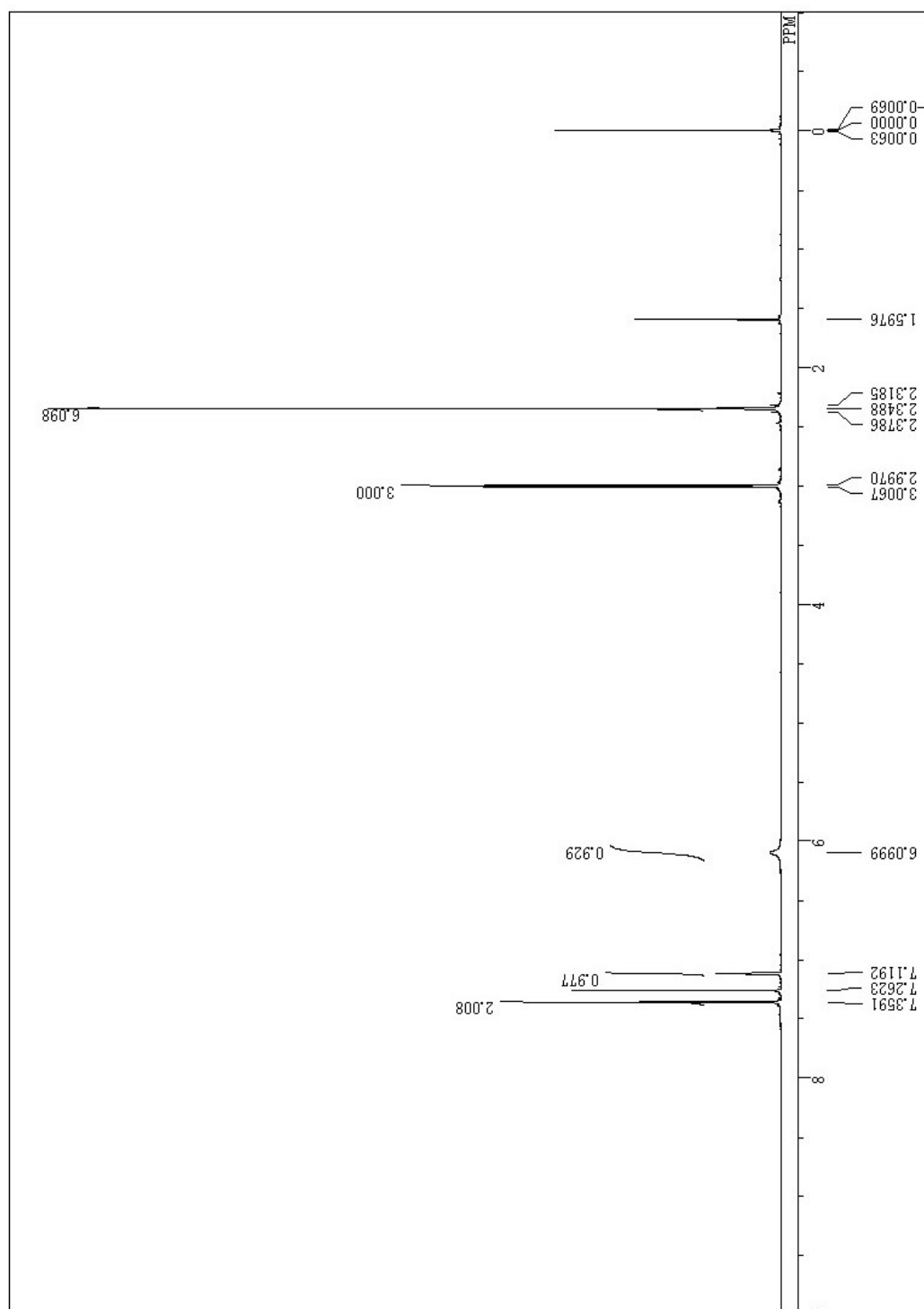
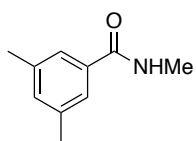
In two oven-dried Schlenk tubes were placed *N*-methylbenzamide (27 mg, 0.20 mmol) and *N*-methyl-2,3,4,5,6-pentadeuteriobenzamide (28 mg, 0.20 mmol), respectively. A solution of  $\text{MnCl}_2 \cdot 2\text{LiCl}$  in THF (20  $\mu\text{L}$ , 0.10 M, 0.0020 mmol), tridecane (36 mg, 0.20 mmol),  $\text{MeMgBr}$  in THF (1.1 mL, 1.00 M, 1.1 mmol), and 1-bromo-2-chloroethane (50  $\mu\text{L}$ , 0.60 mmol) were sequentially added to each reaction tube. The two reaction mixtures were stirred at 25 °C and sampled after 1.5 h, 2 h, 2.5 h, and 3 h. The samples were analyzed by GC analysis in the presence of tridecane as an internal standard.

## 8. References

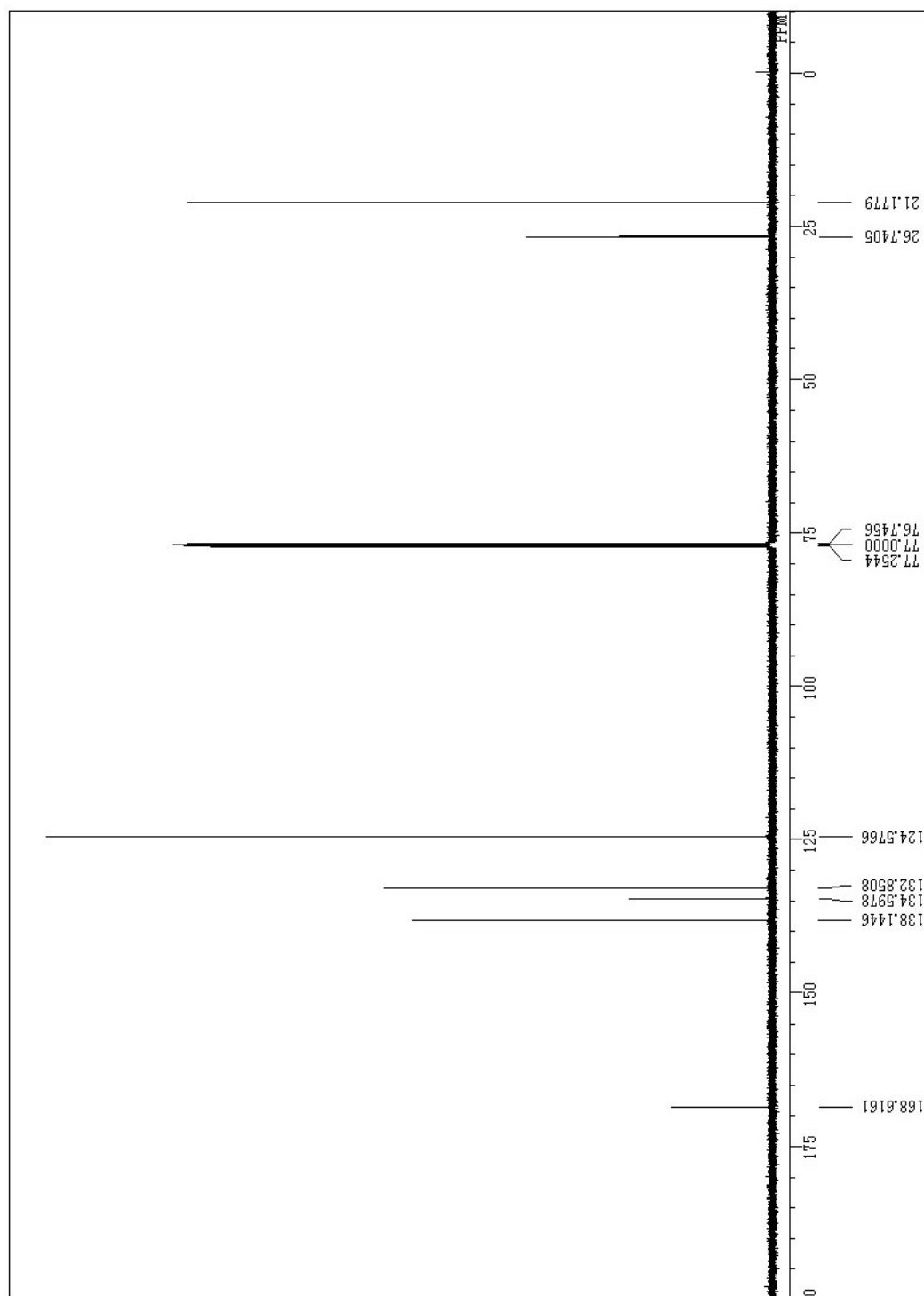
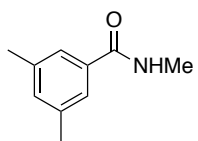
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## 9. $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ Spectra

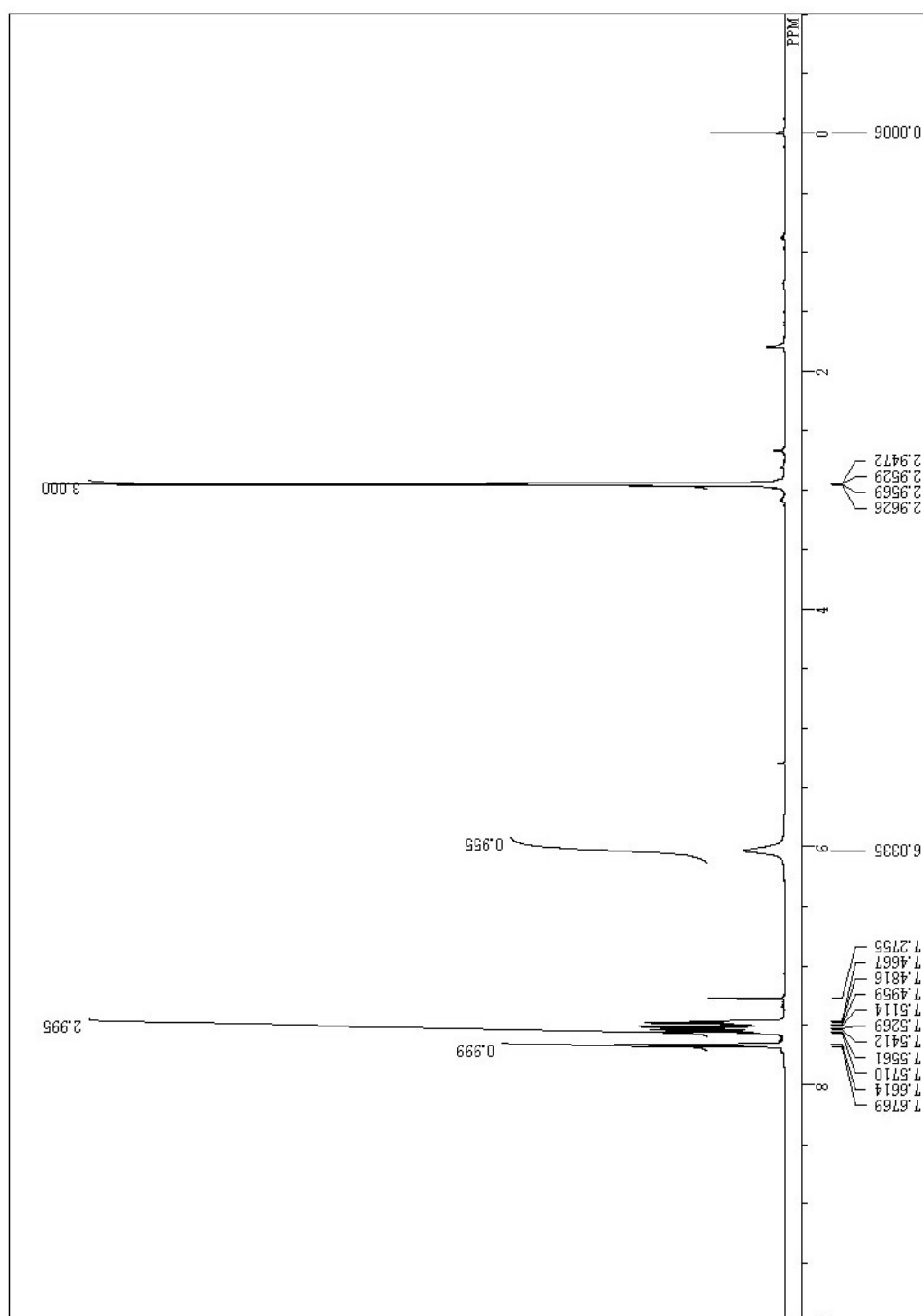
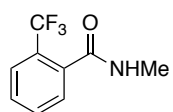
$^1\text{H}$  NMR of *N*,3,5-Trimethylbenzamide



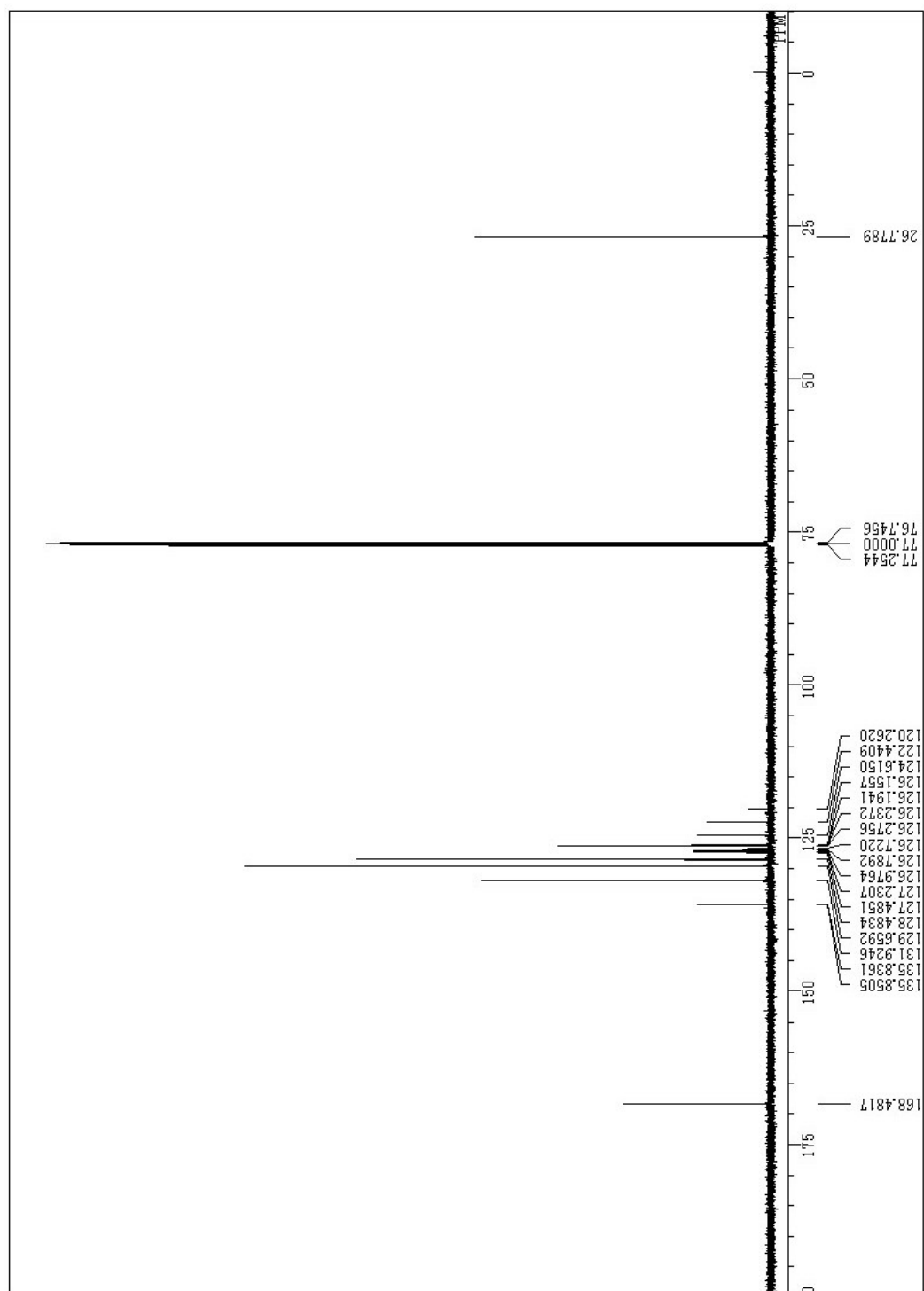
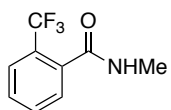
$^{13}\text{C}$  NMR of *N*,3,5-Trimethylbenzamide



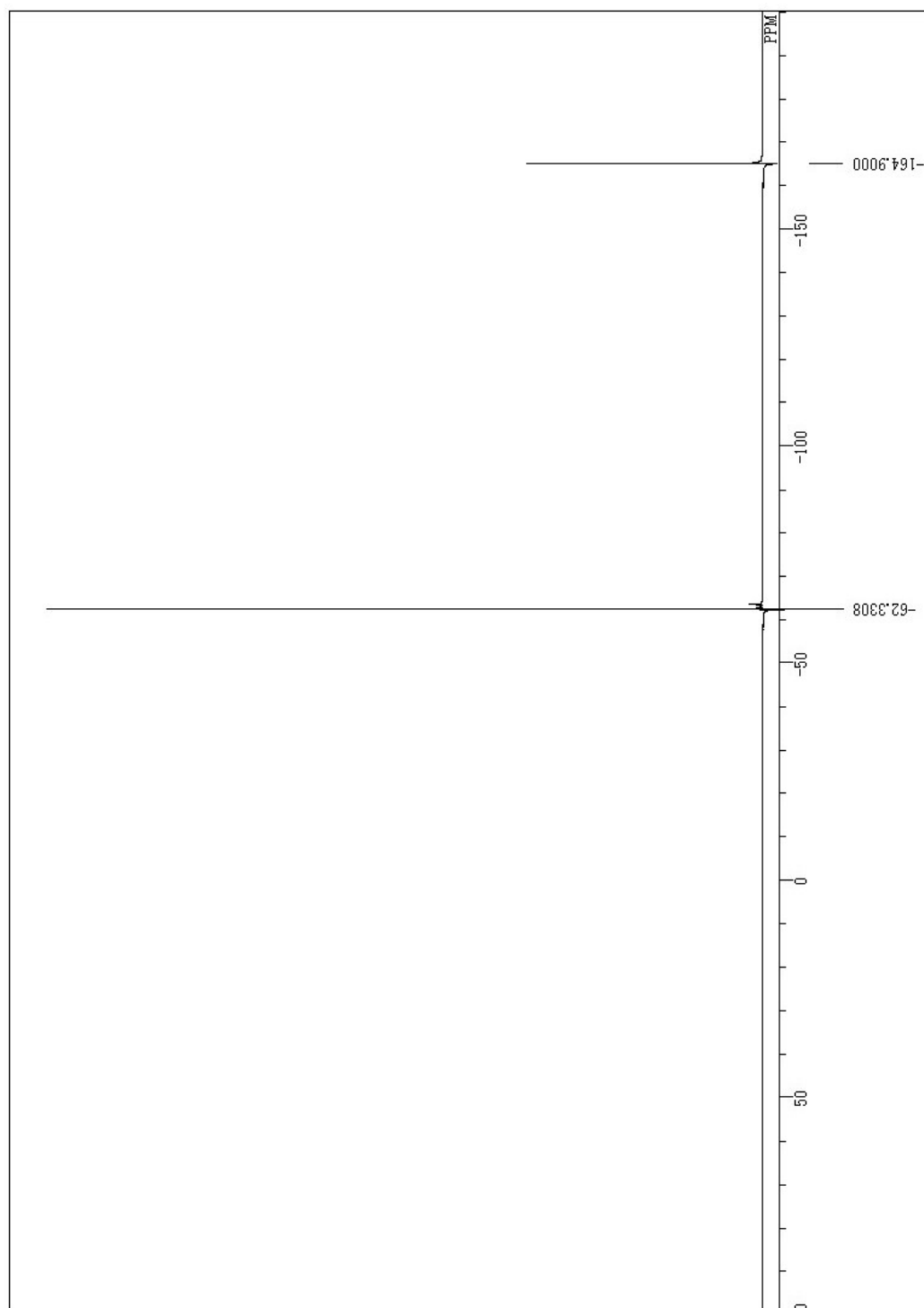
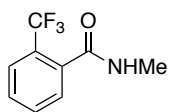
<sup>1</sup>H NMR of *N*-Methyl-2-(trifluoromethyl)benzamide



$^{13}\text{C}$  NMR of *N*-Methyl-2-(trifluoromethyl)benzamide

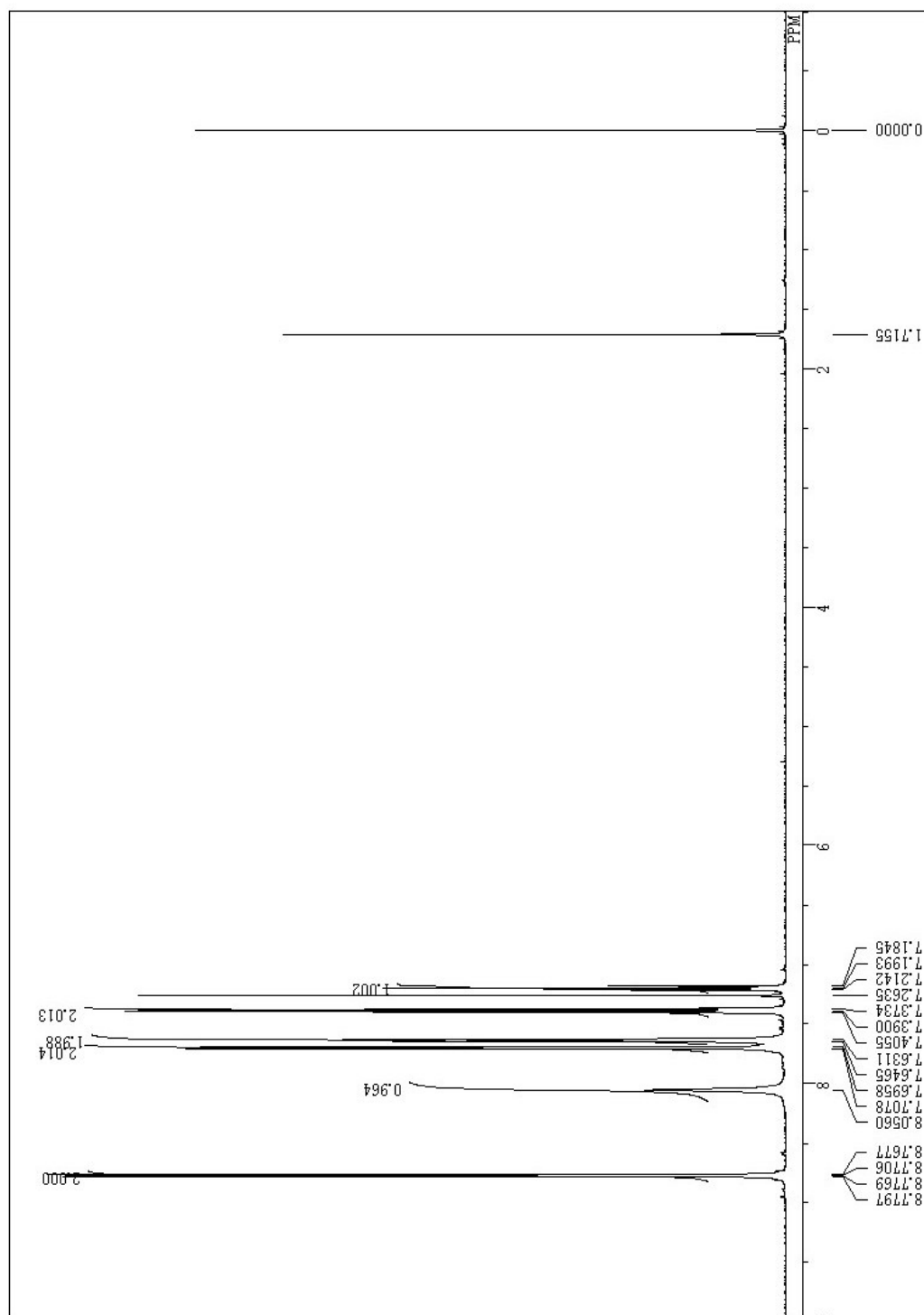
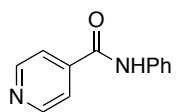


$^{19}\text{F}$  NMR of *N*-Methyl-2-(trifluoromethyl)benzamide

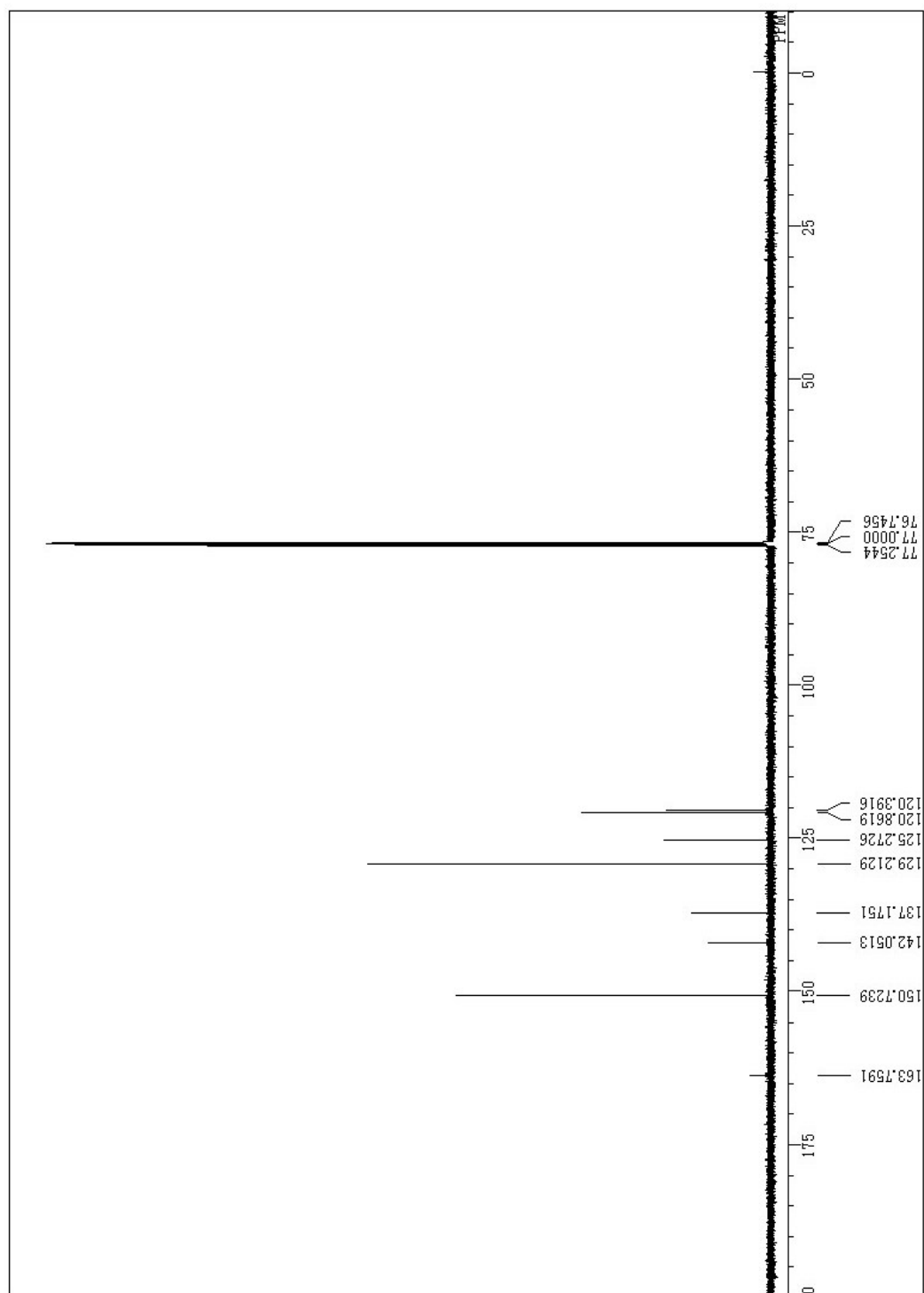
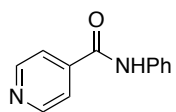




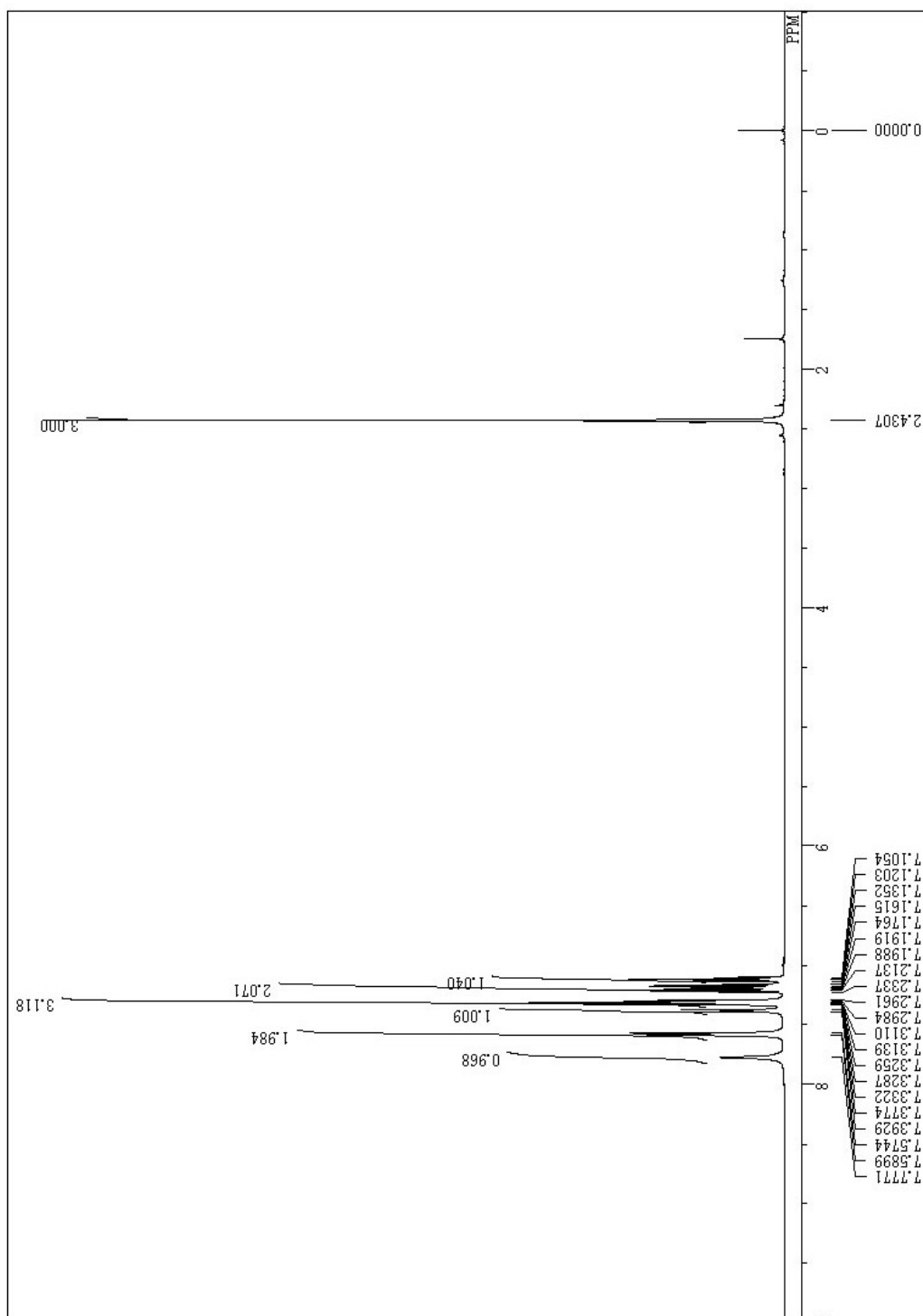
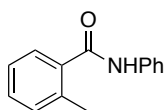
$^1\text{H}$  NMR of *N*-Phenyl-4-pyridinecarboxamide



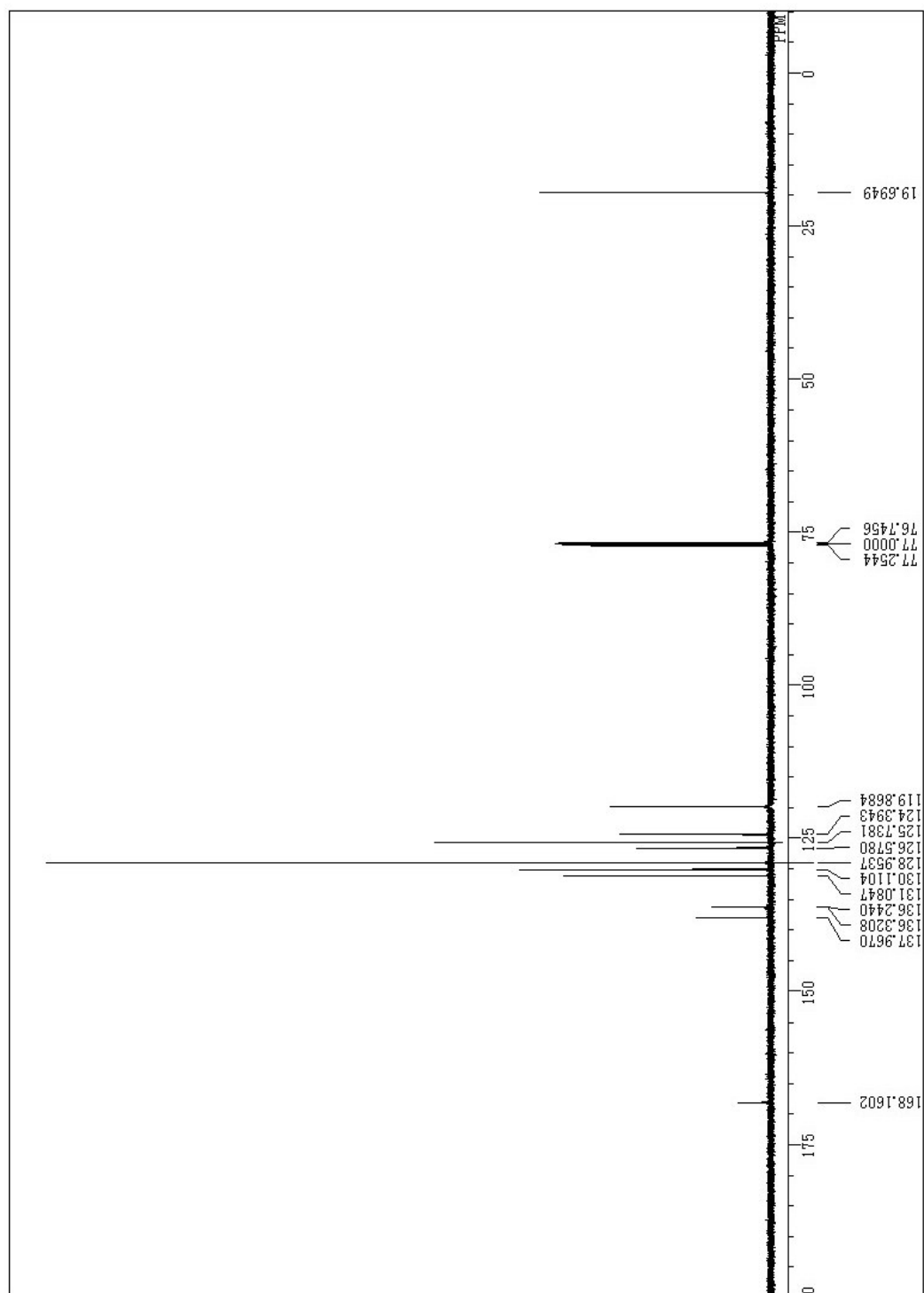
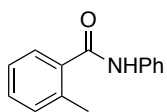
$^{13}\text{C}$  NMR of *N*-Phenyl-4-pyridinecarboxamide



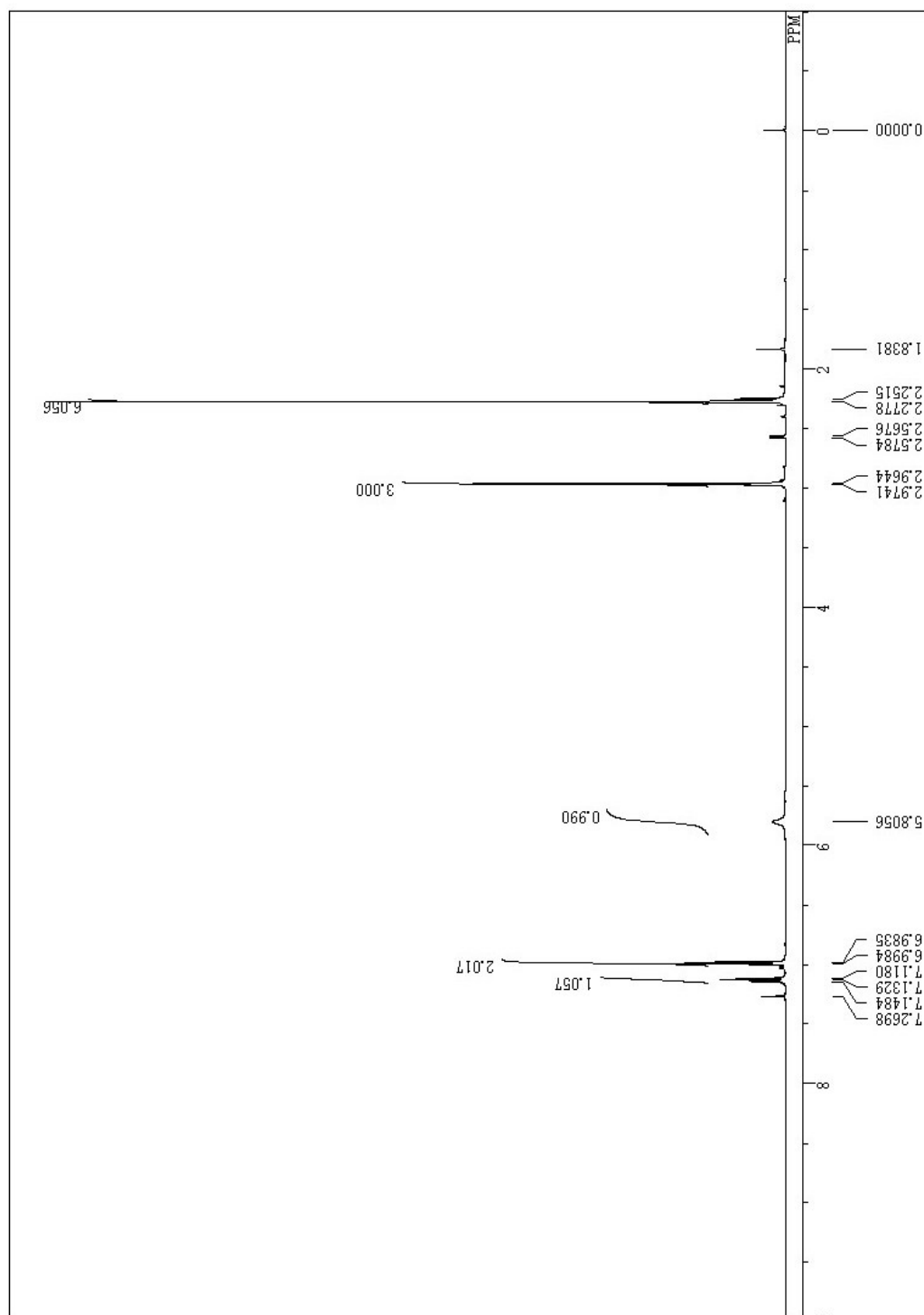
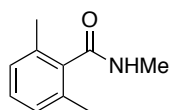
$^1\text{H}$  NMR of 2-Methyl-*N*-phenylbenzamide (Table 1, entry 1)



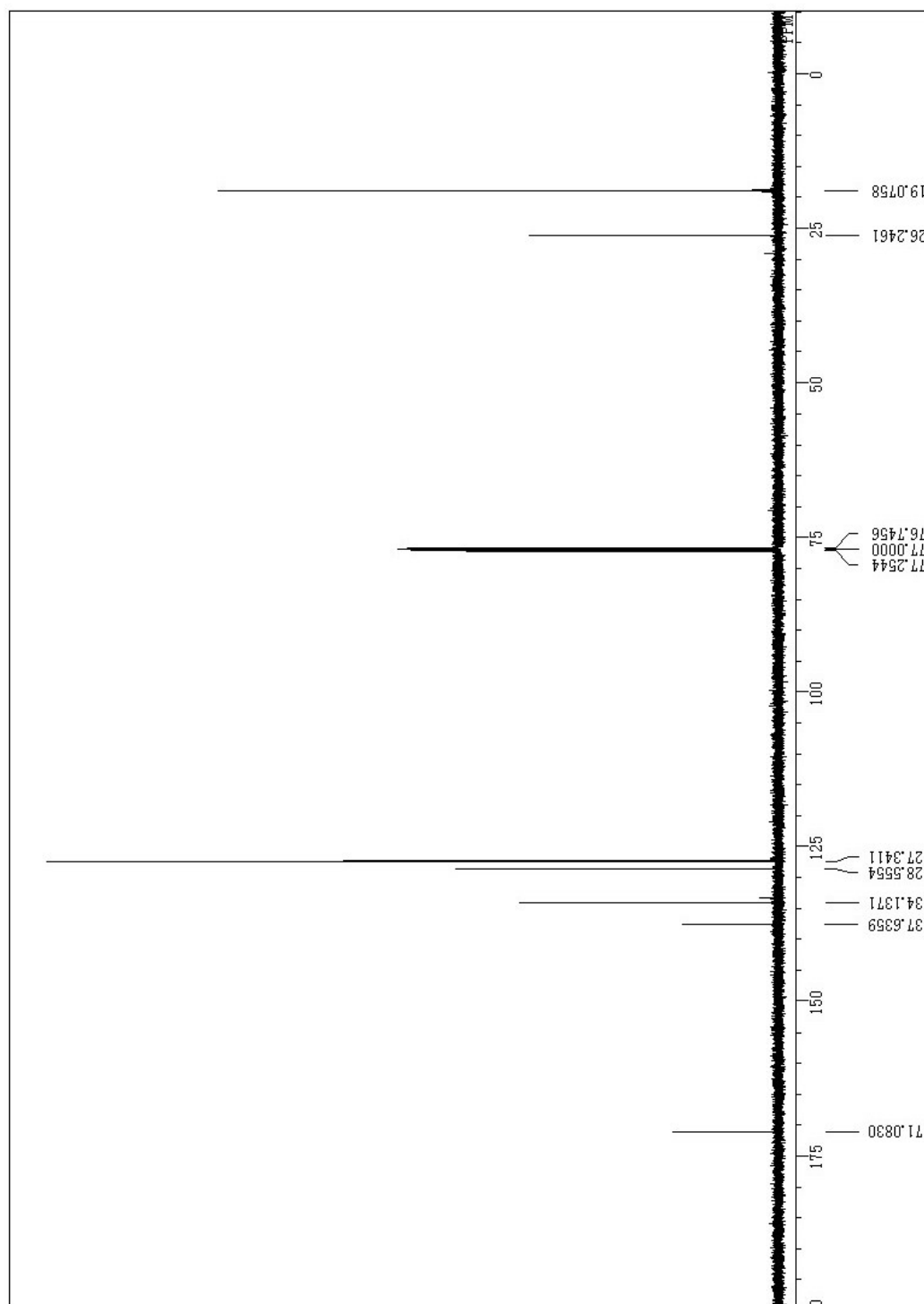
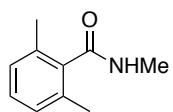
<sup>13</sup>C NMR of 2-Methyl-*N*-phenylbenzamide (Table 1, entry 1)



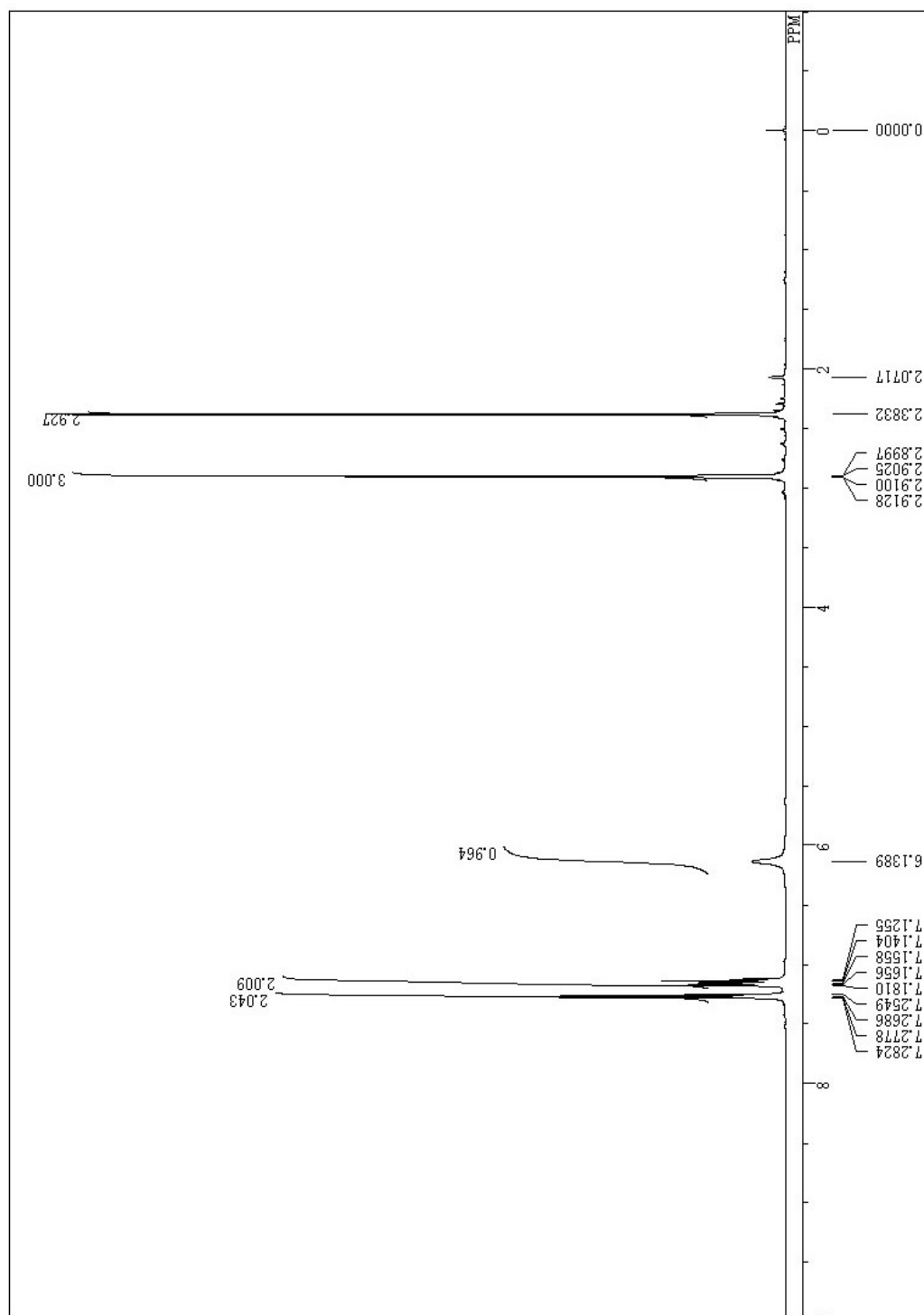
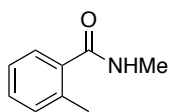
$^1\text{H}$  NMR of *N*,2,6-Trimethylbenzamide (Table 1, entry 2)



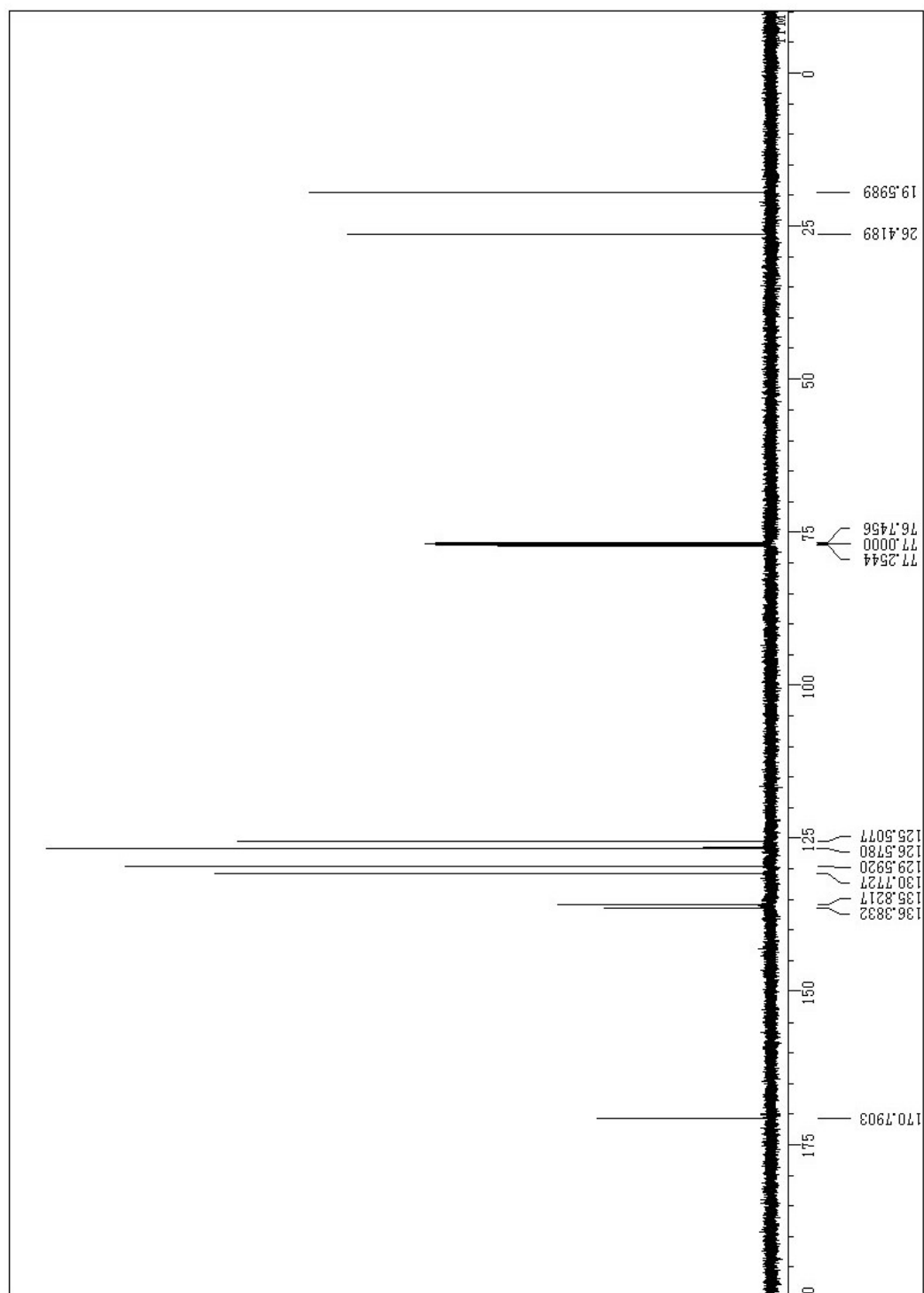
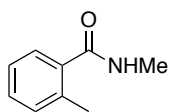
$^{13}\text{C}$  NMR of *N*,2,6-Trimethylbenzamide (Table 1, entry 2)



$^1\text{H}$  NMR of *N*,2-Dimethylbenzamide (Table 1, entry 3)

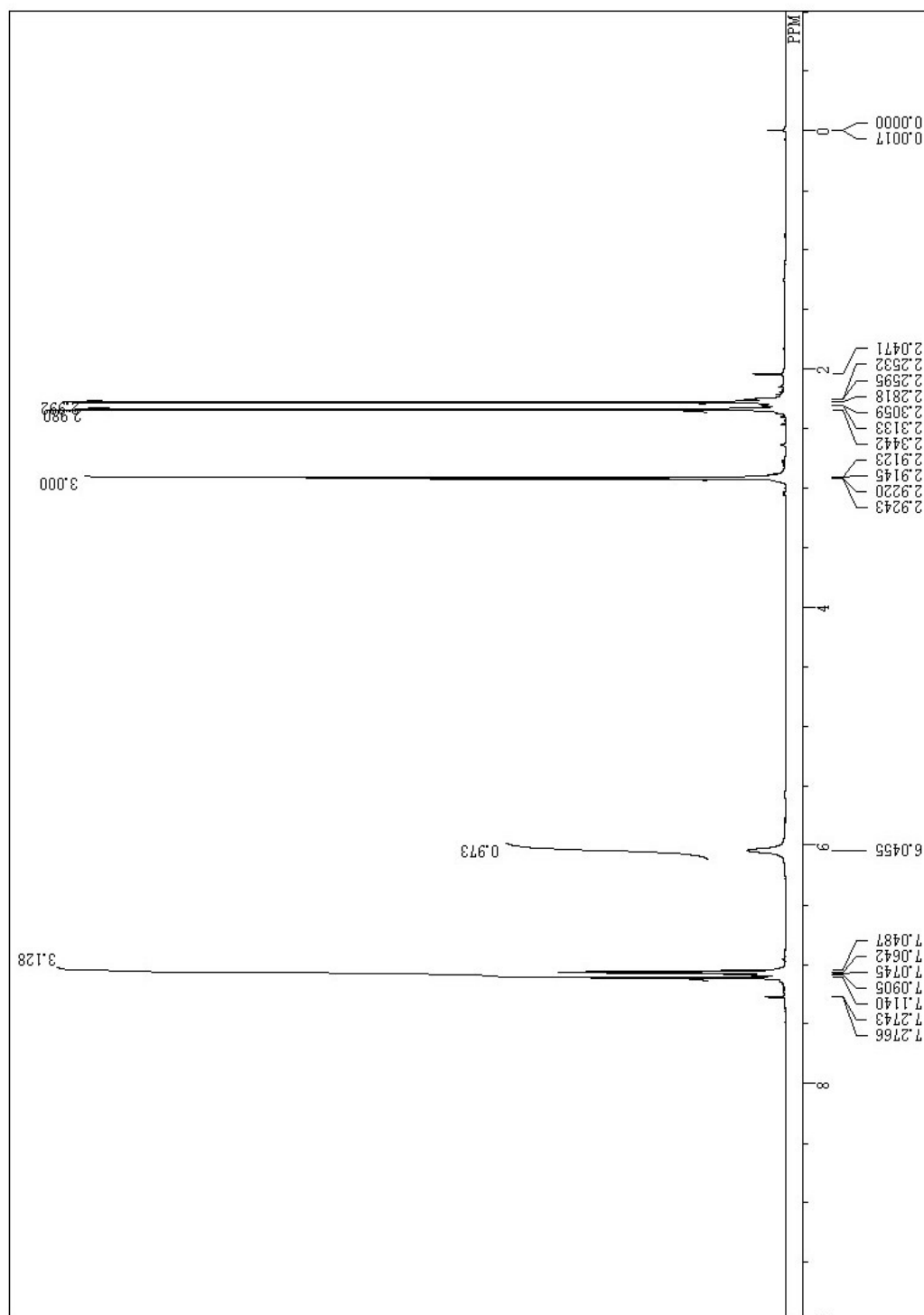
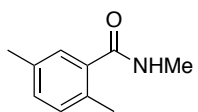


$^{13}\text{C}$  NMR of *N*,2-Dimethylbenzamide (Table 1, entry 3)

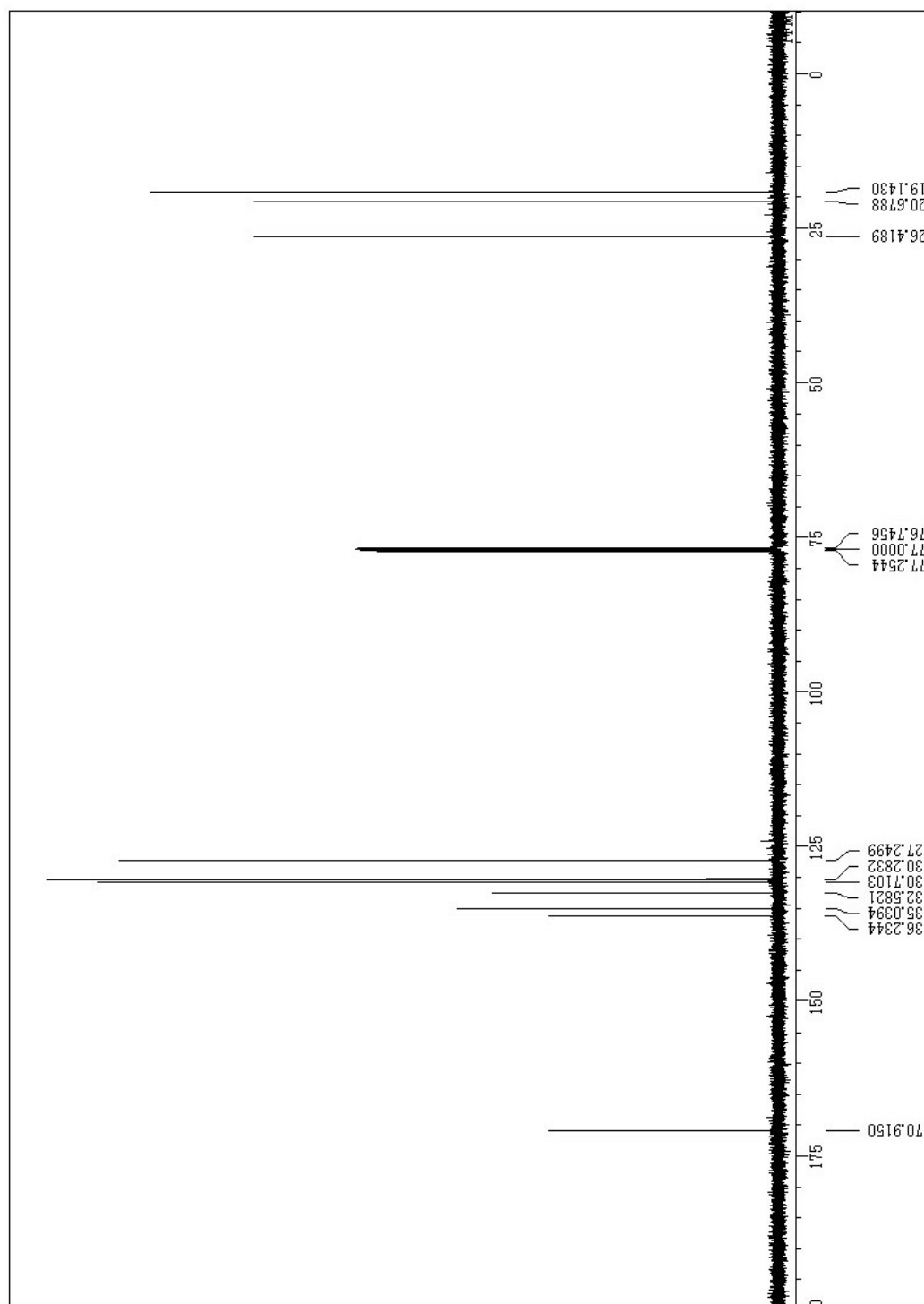
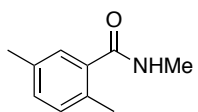




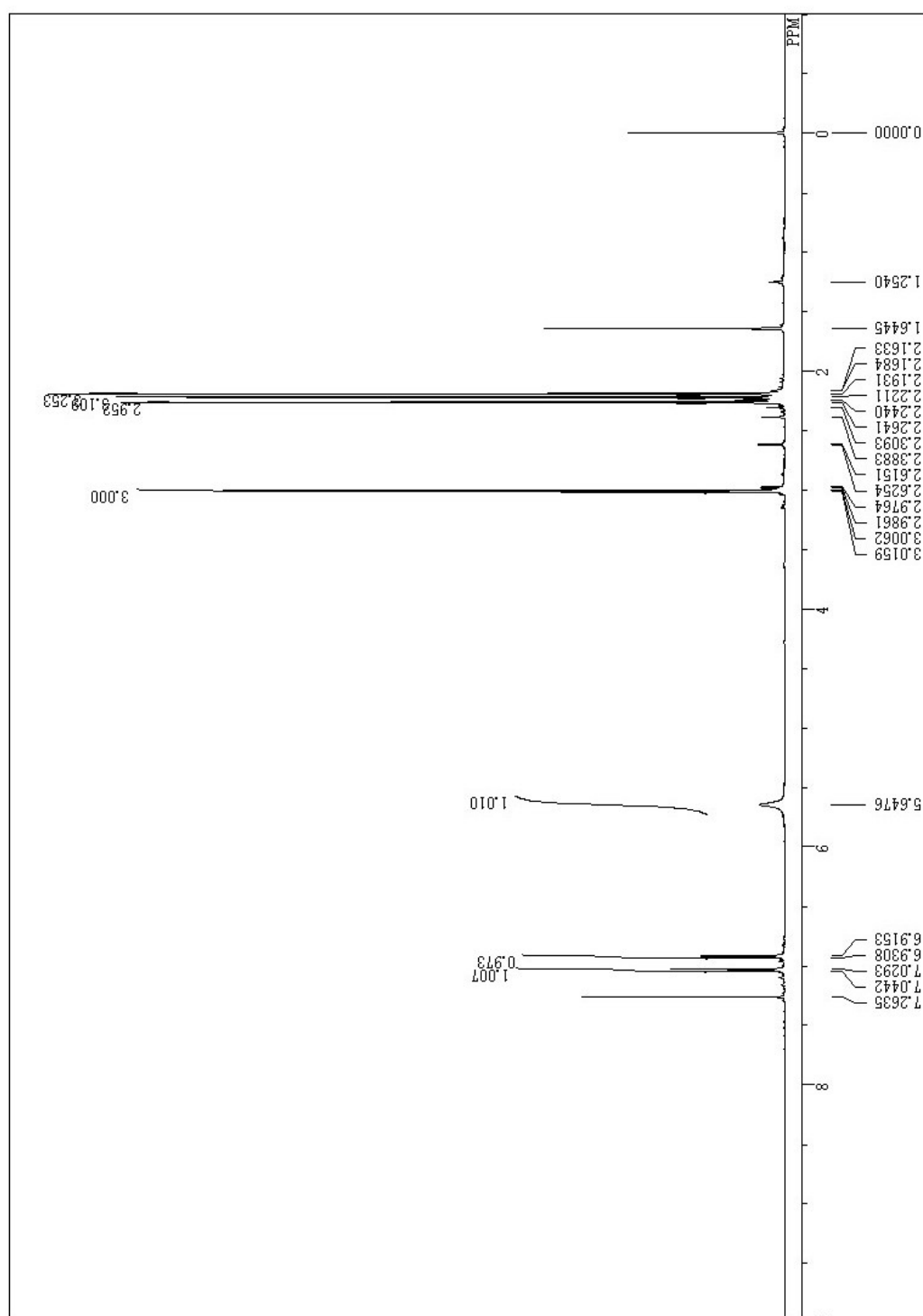
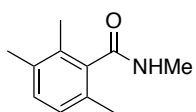
$^1\text{H}$  NMR of *N*,2,5-Trimethylbenzamide (Table 1, entry 4)



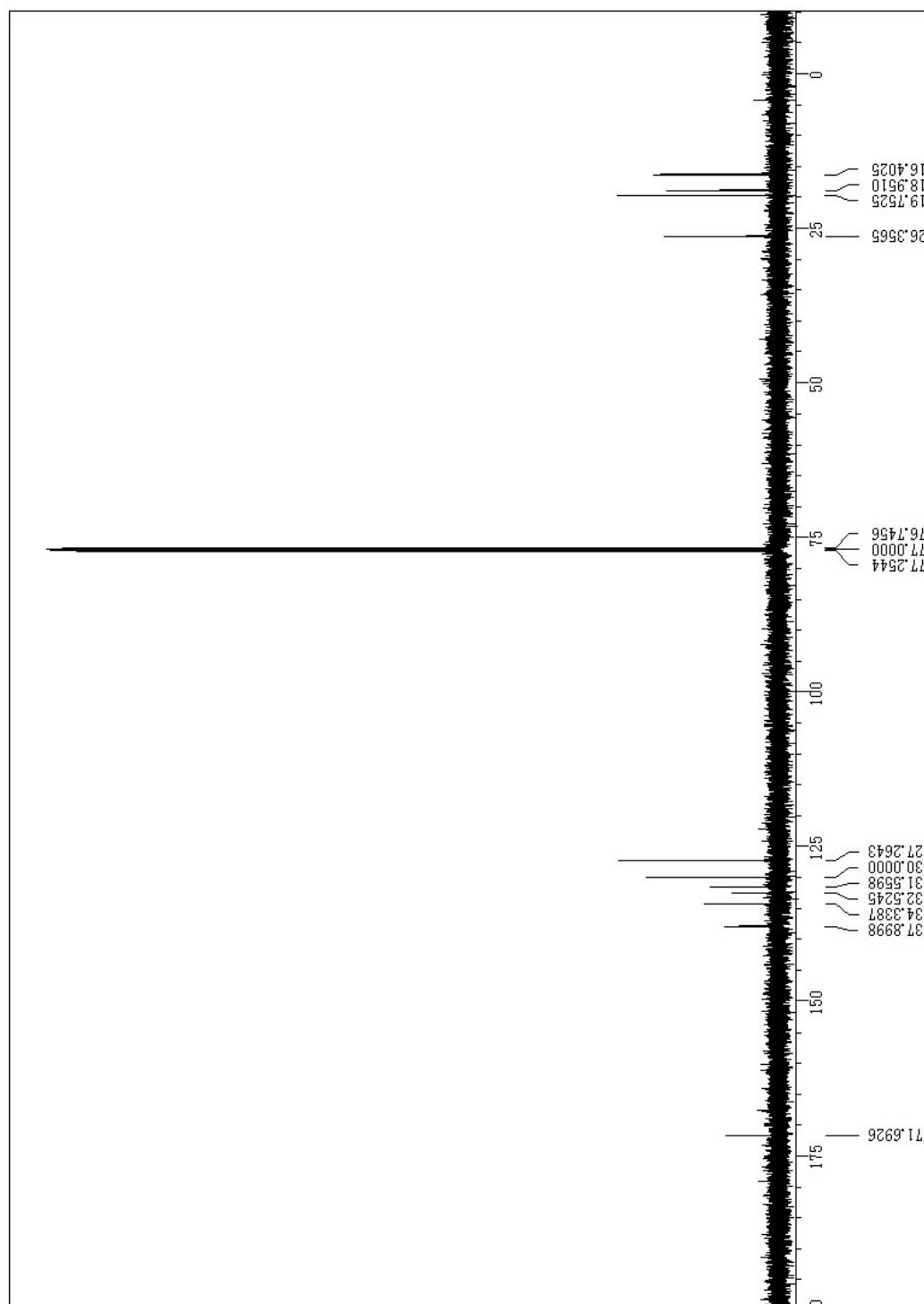
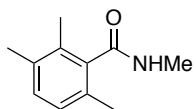
$^{13}\text{C}$  NMR of *N*,2,5-Trimethylbenzamide (Table 1, entry 4)



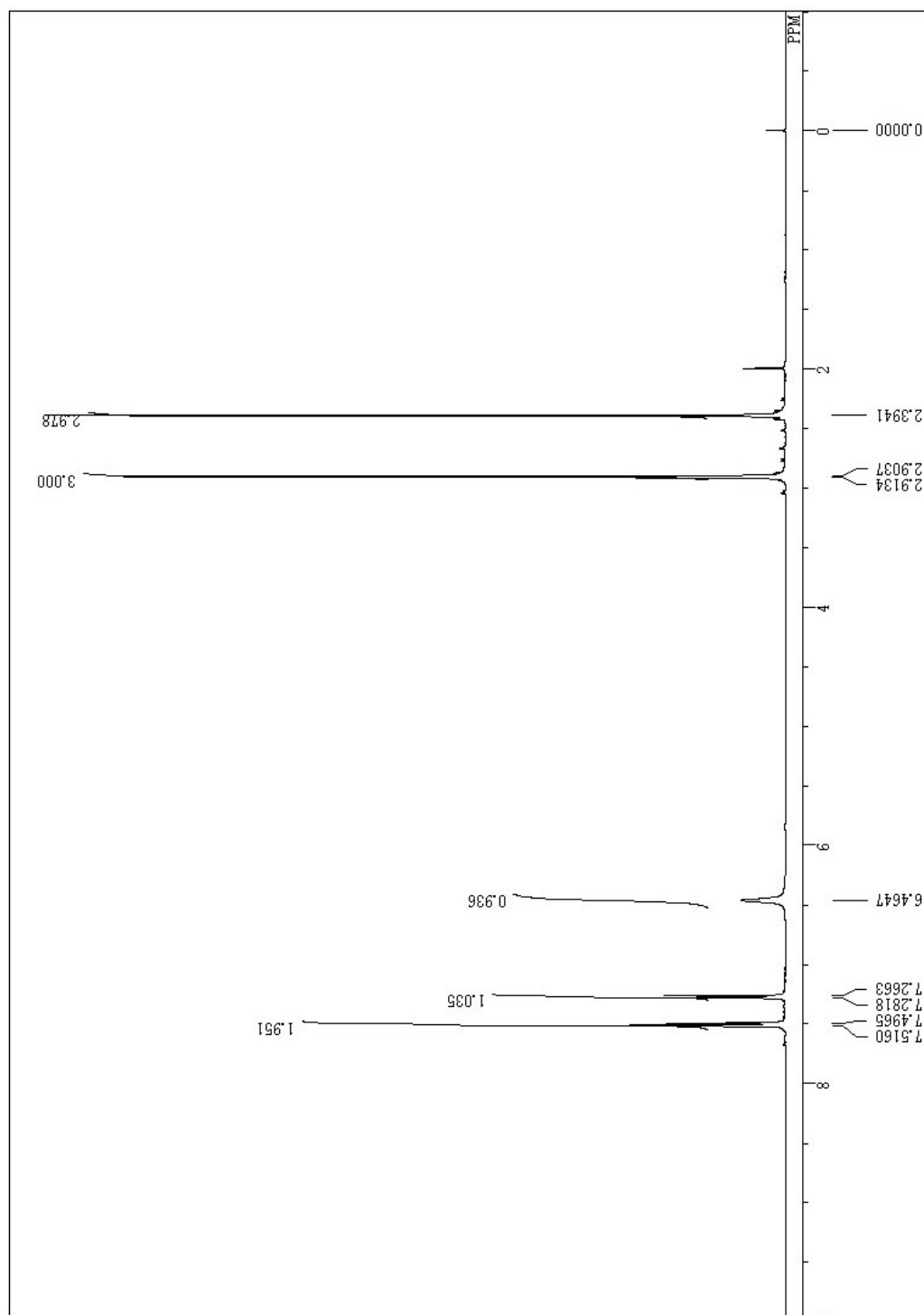
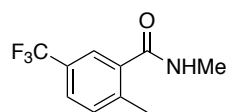
$^1\text{H}$  NMR of *N*,2,3,6-Tetramethylbenzamide (Table 1, entry 4)



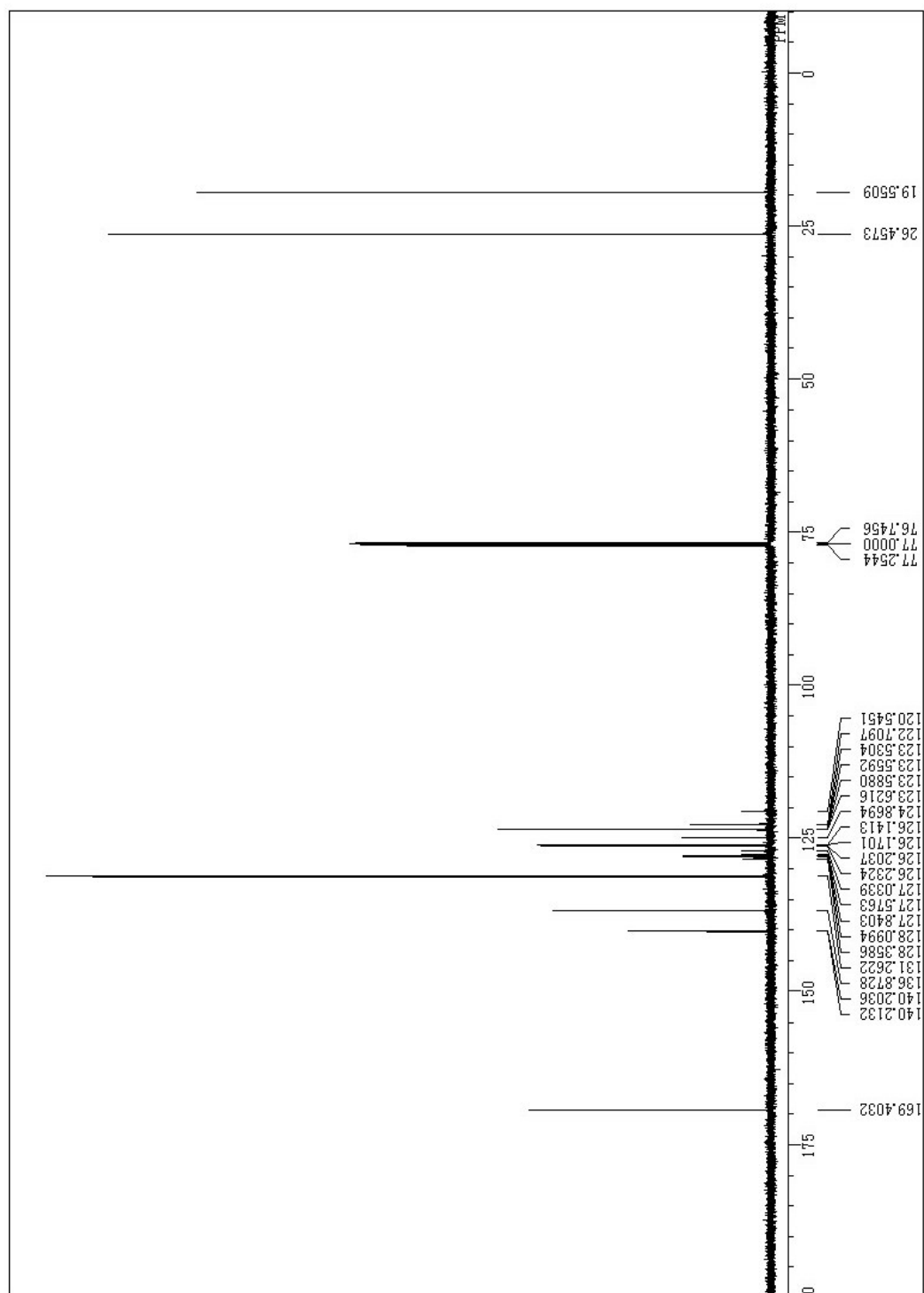
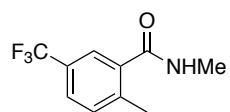
$^{13}\text{C}$  NMR of *N*,2,3,6-Tetramethylbenzamide (Table 1, entry 4)



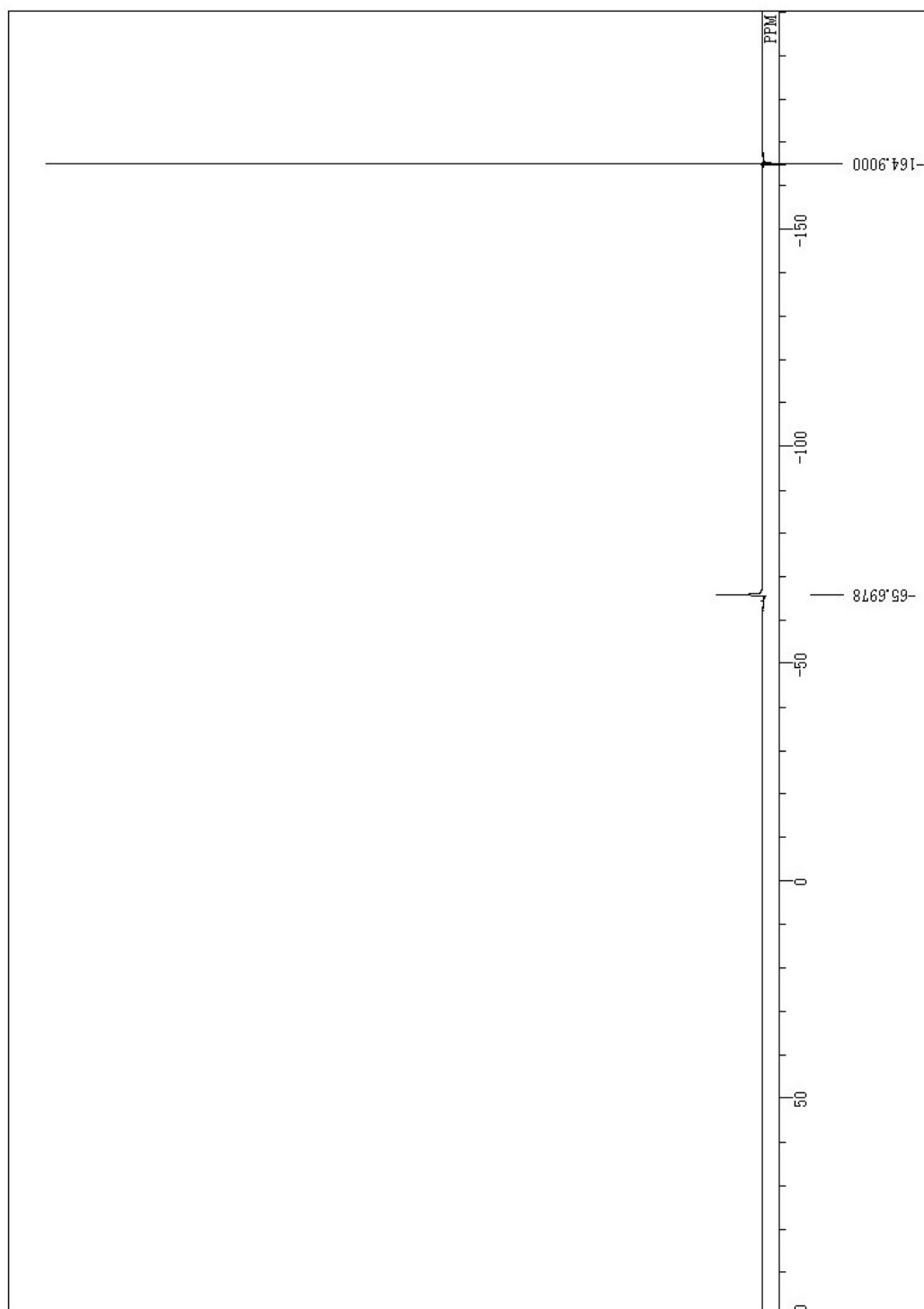
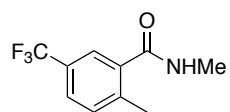
$^1\text{H}$  NMR of *N*,2-Dimethyl-5-(trifluoromethyl)benzamide (Table 1, entry 5)



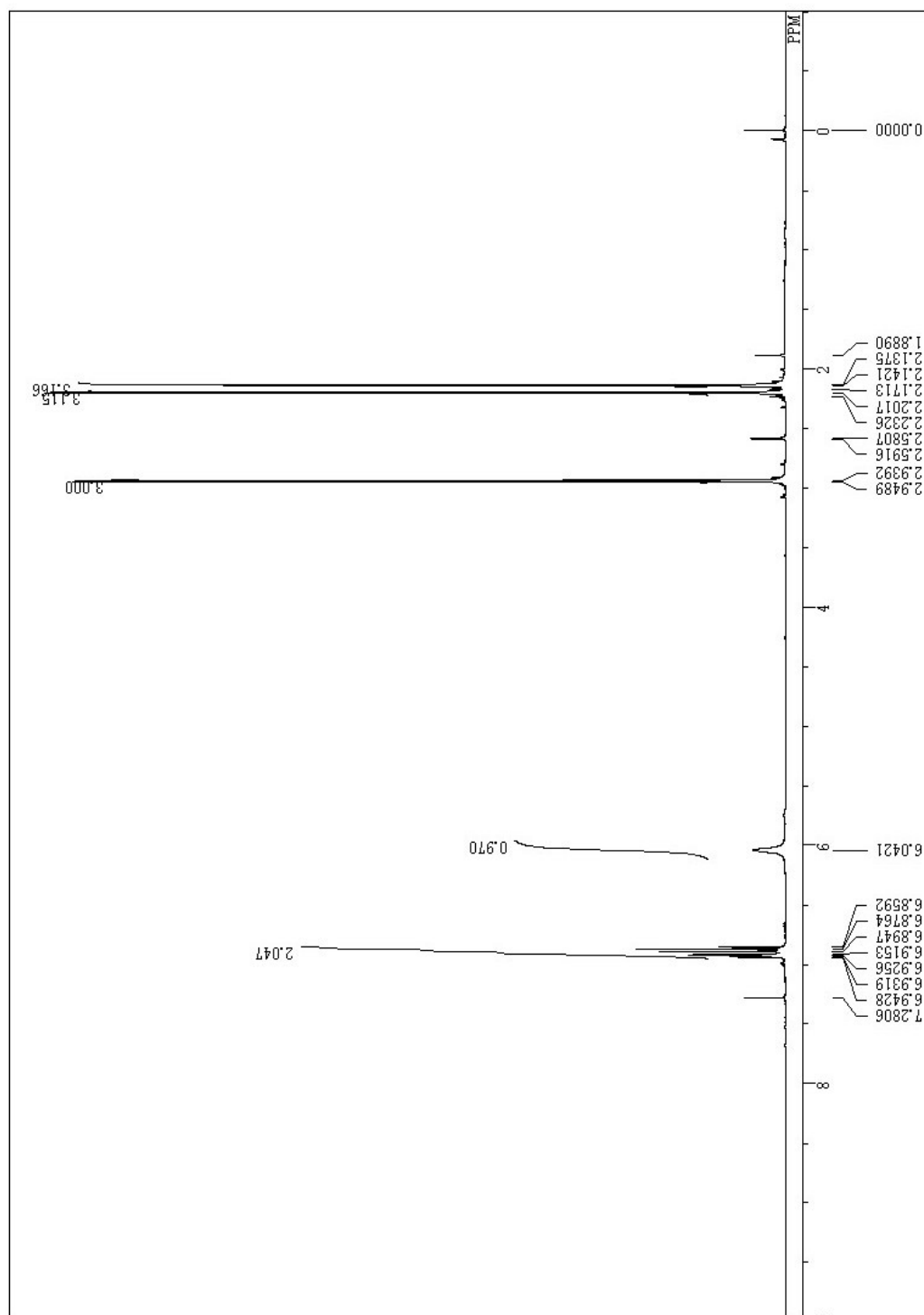
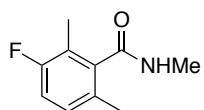
$^{13}\text{C}$  NMR of *N*,2-Dimethyl-5-(trifluoromethyl)benzamide (Table 1, entry 5)



$^{19}\text{F}$  NMR of *N*,2-Dimethyl-5-(trifluoromethyl)benzamide (Table 1, entry 5)

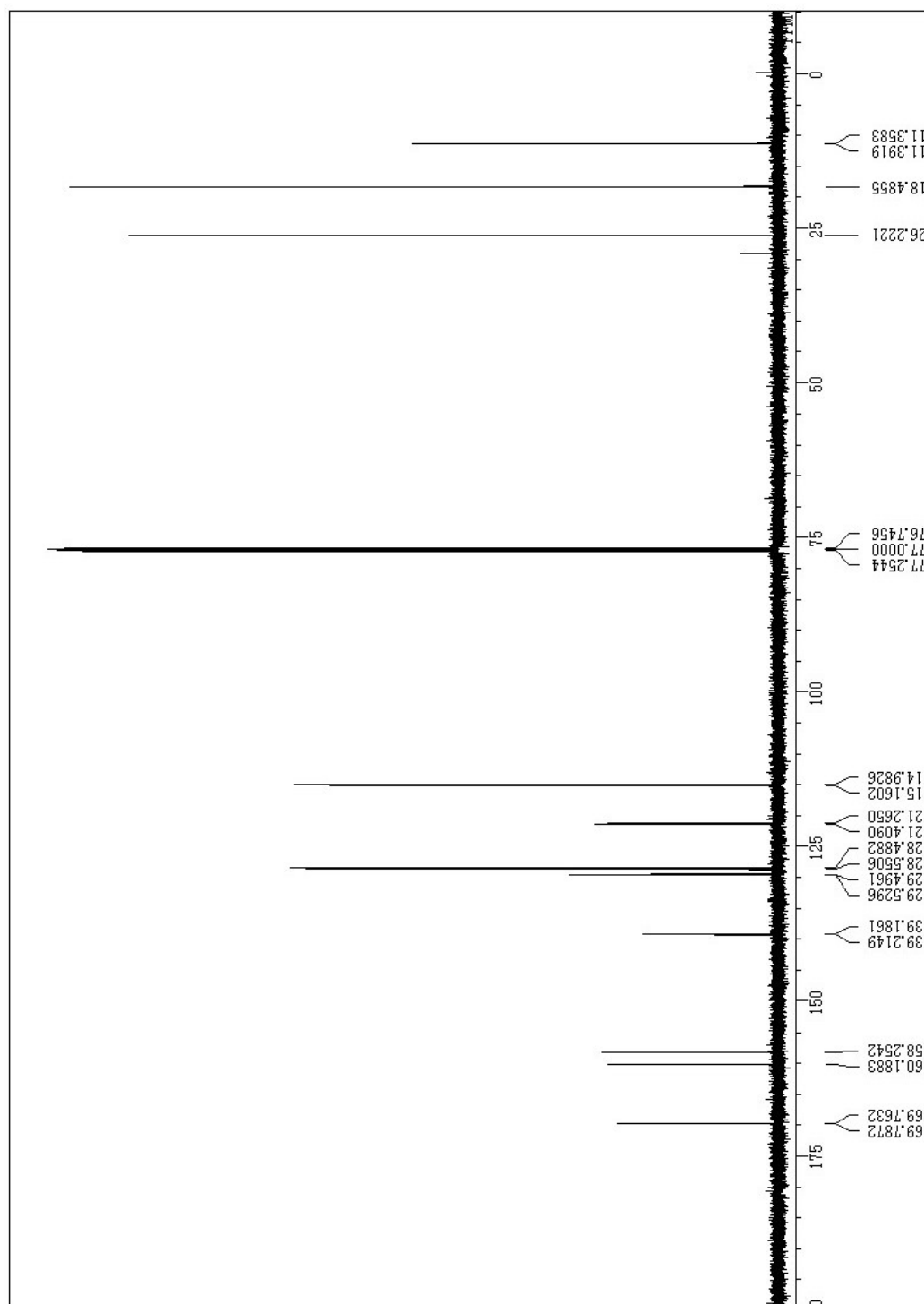
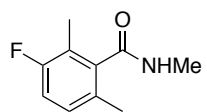


$^1\text{H}$  NMR of 3-Fluoro-*N*,2,6-trimethylbenzamide (Table 1, entry 6)

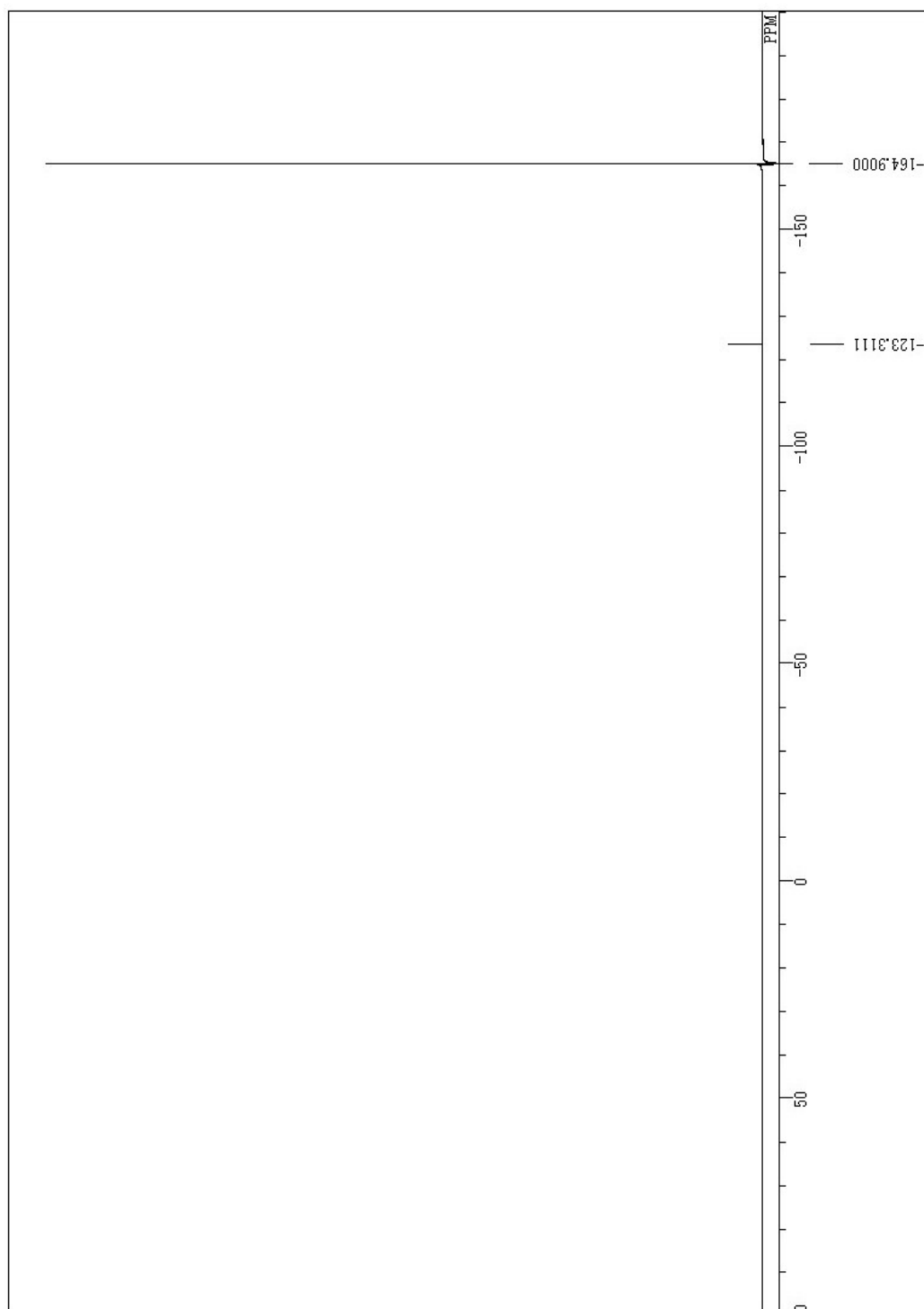
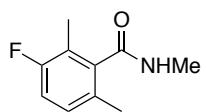




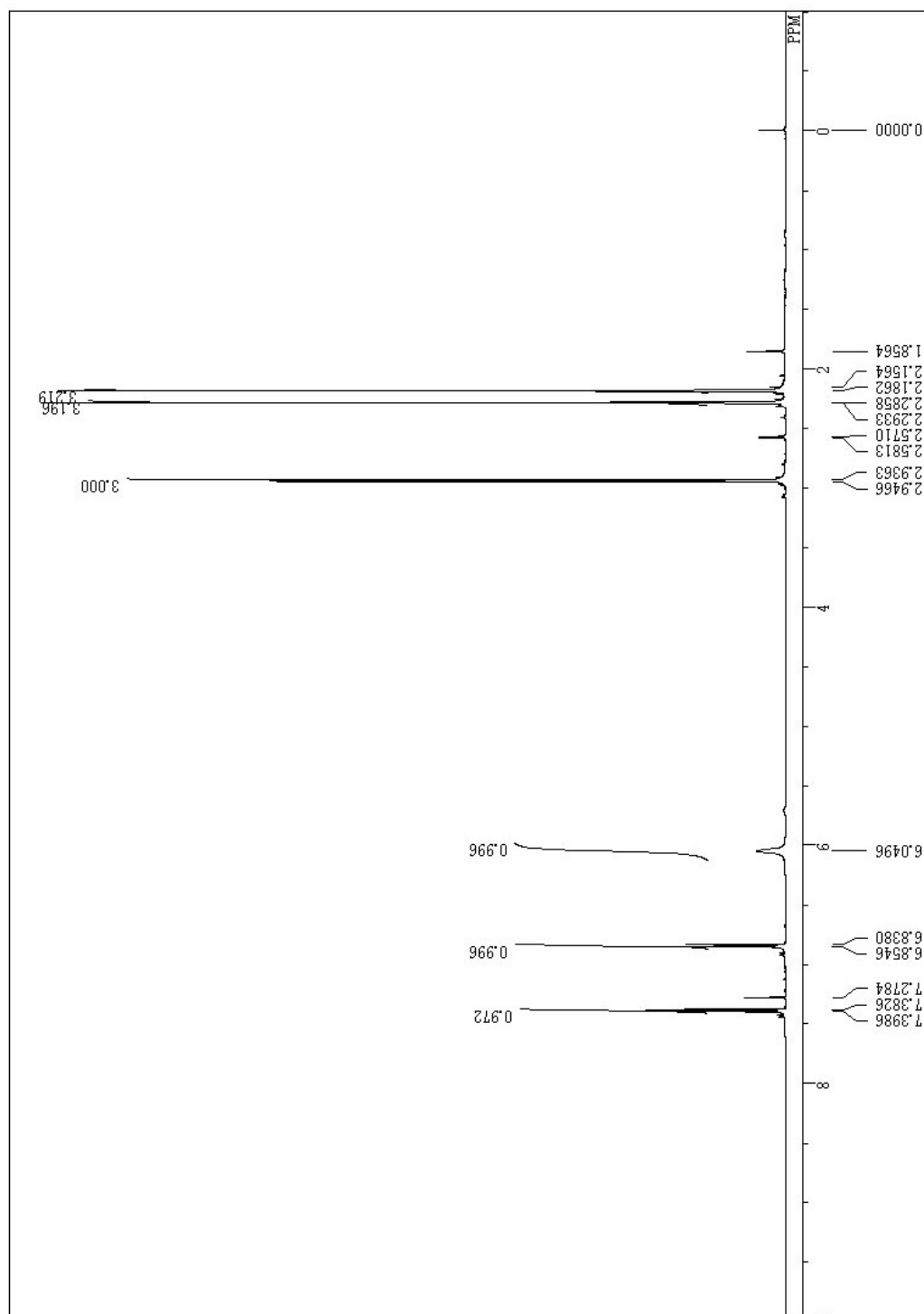
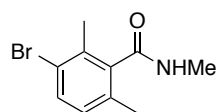
<sup>13</sup>C NMR of 3-Fluoro-*N*,2,6-trimethylbenzamide (Table 1, entry 6)



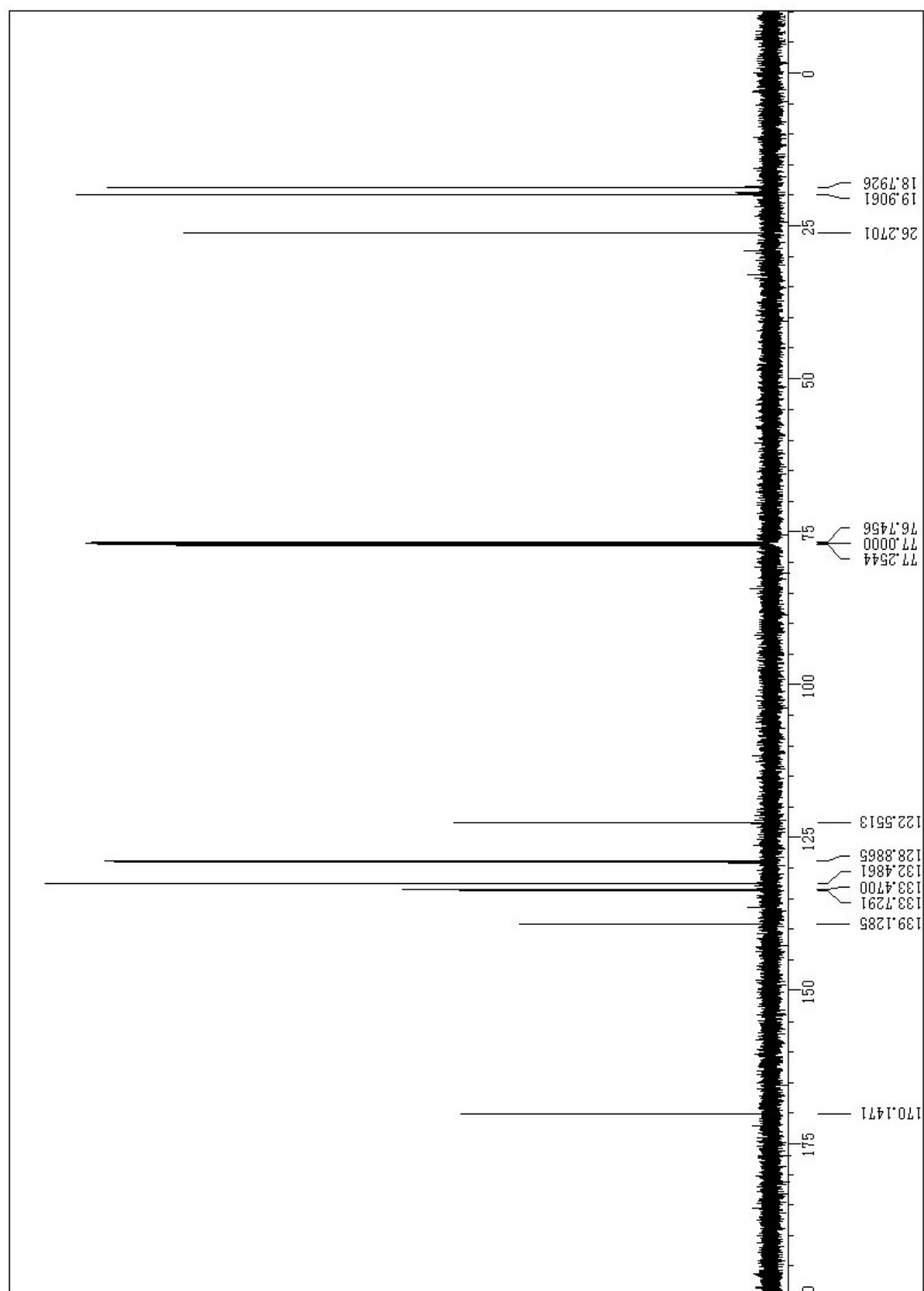
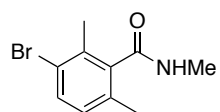
$^{19}\text{F}$  NMR of 3-Fluoro-*N*,2,6-trimethylbenzamide (Table 1, entry 6)



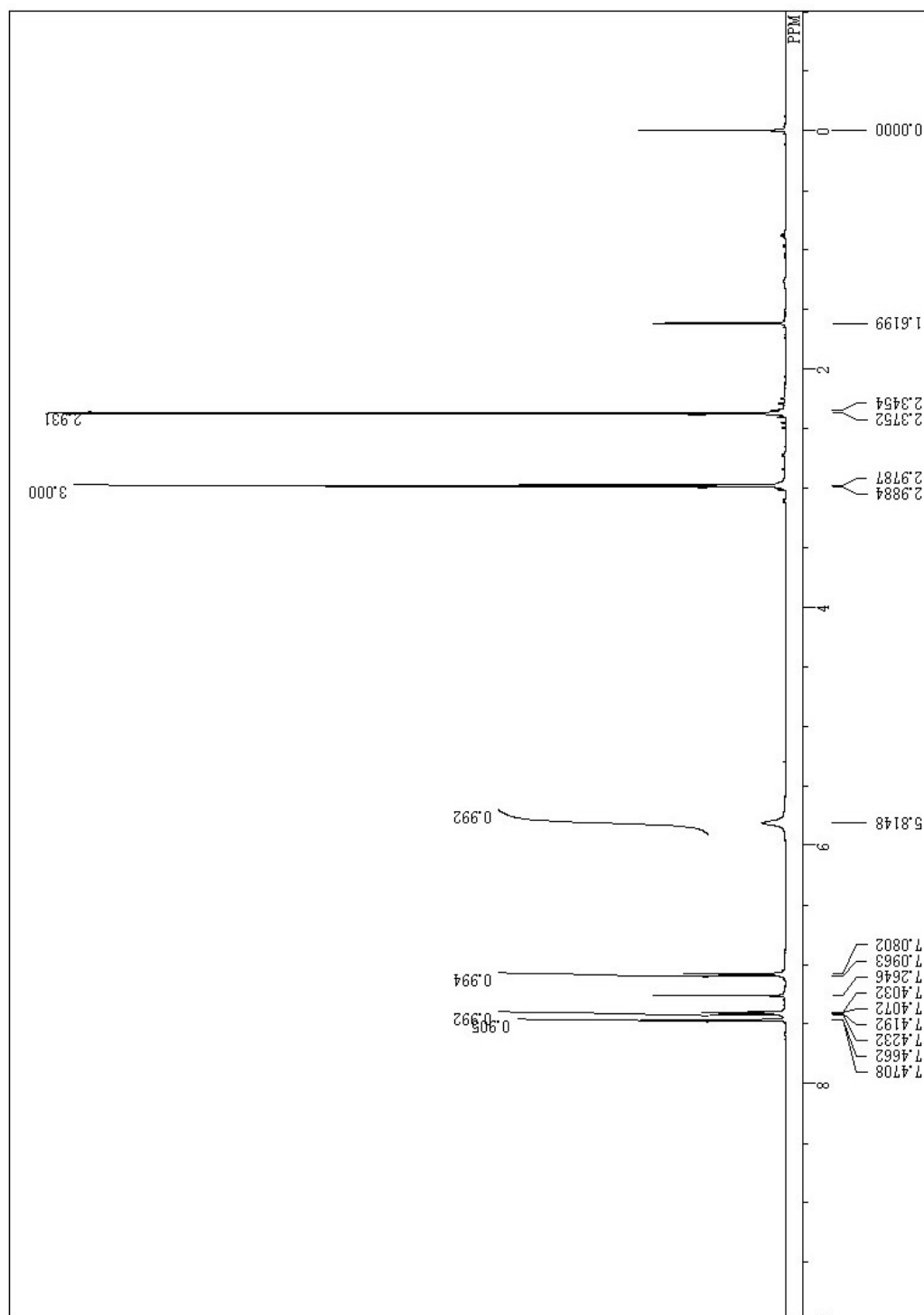
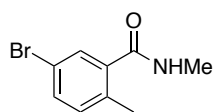
<sup>1</sup>H NMR of 3-Bromo-*N*,2,6-trimethylbenzamide (Table 1, entry 7)



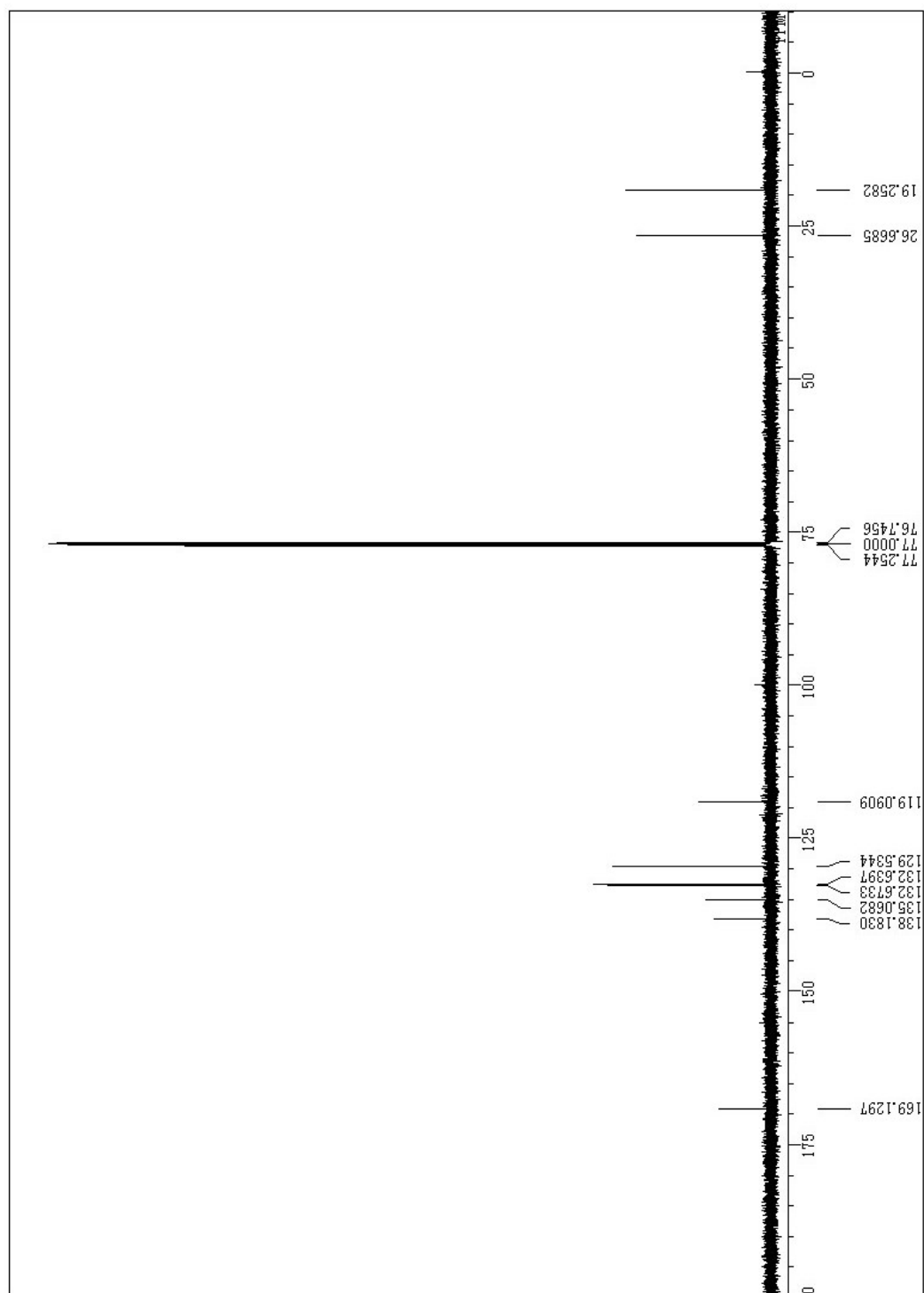
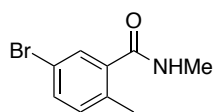
<sup>13</sup>C NMR of 3-Bromo-*N*,2,6-trimethylbenzamide (Table 1, entry 7)



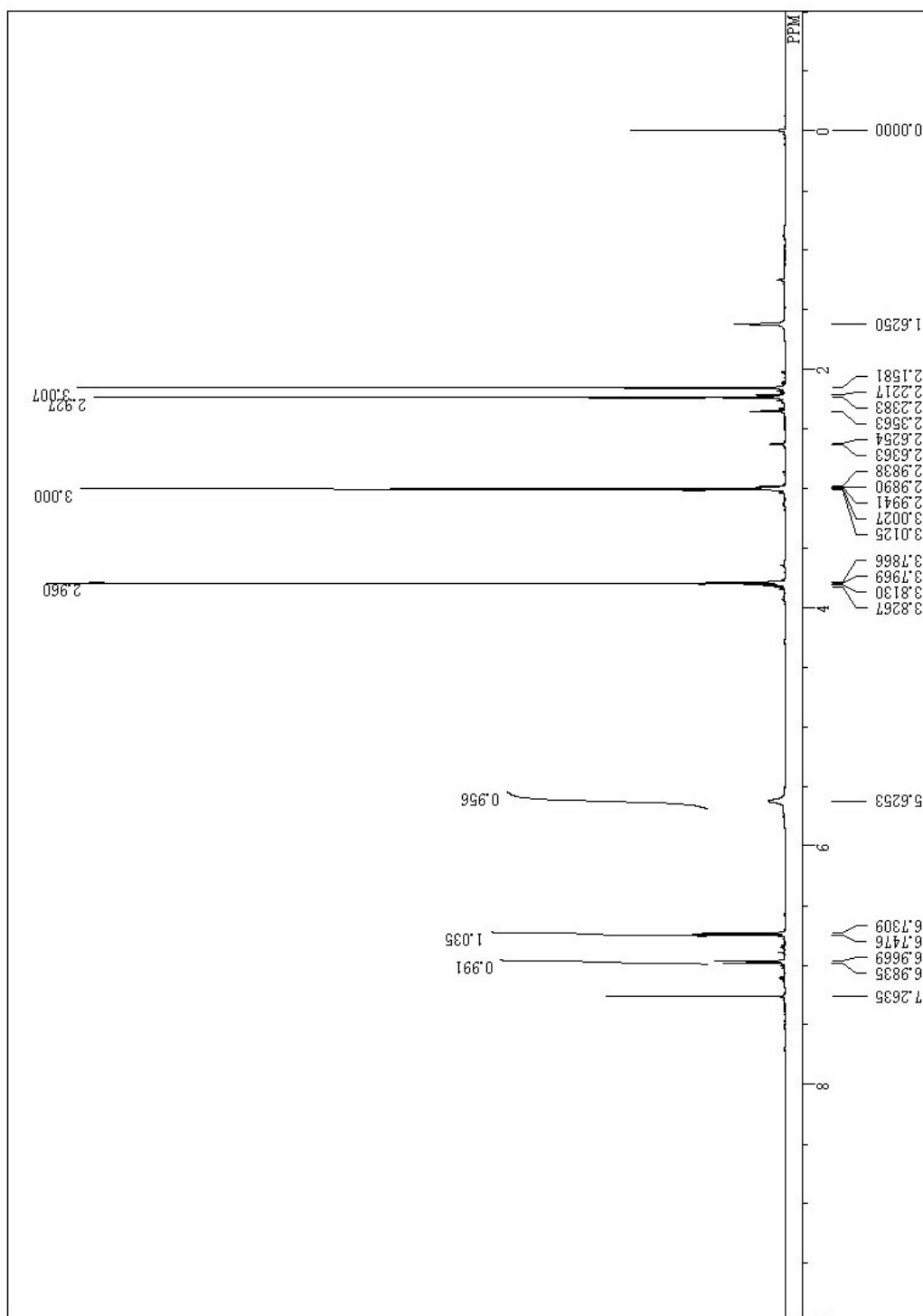
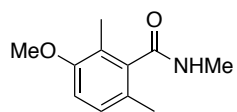
<sup>1</sup>H NMR of 5-Bromo-*N*,2-dimethylbenzamide (Table 1, entry 7)



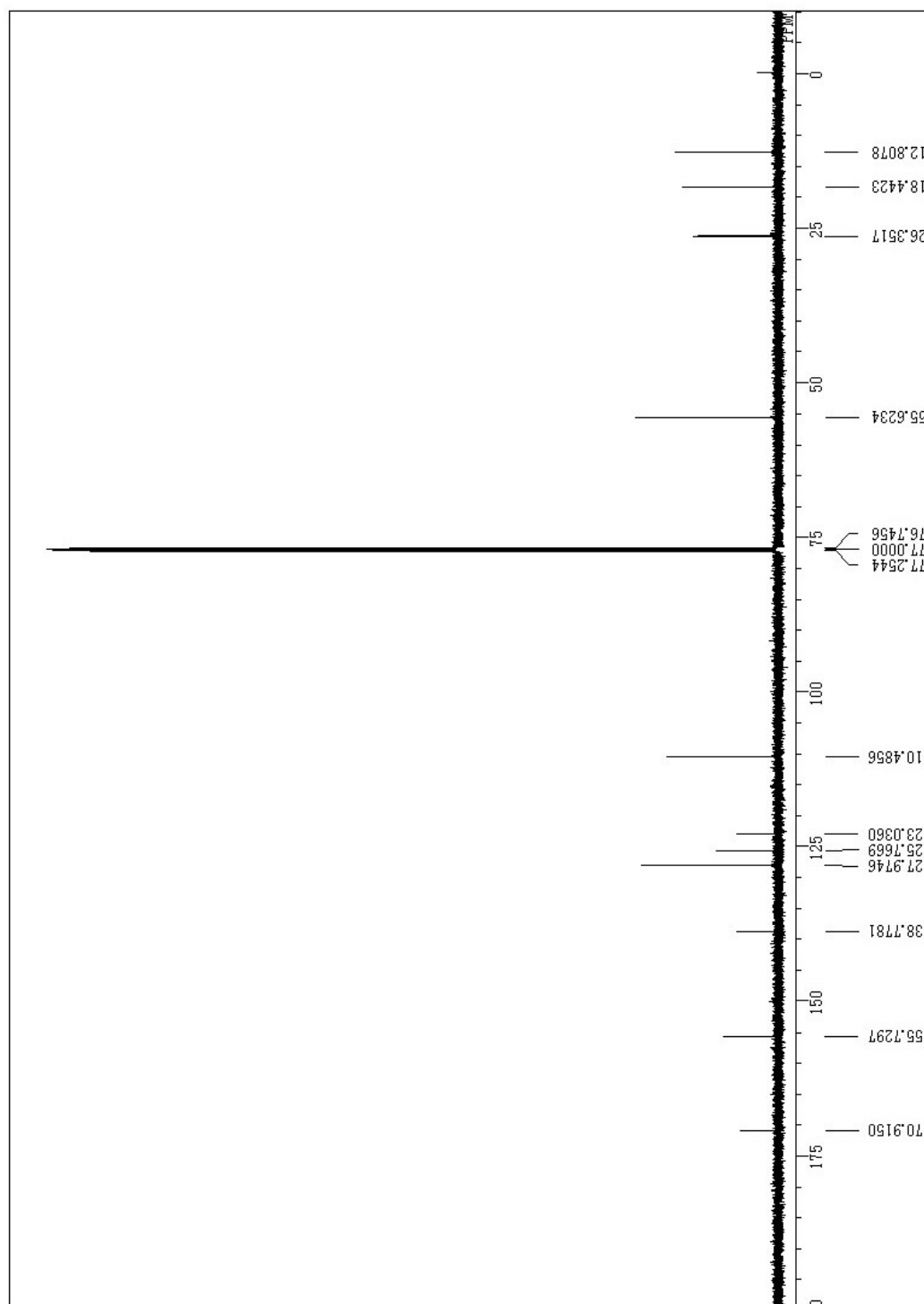
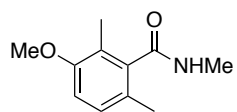
$^{13}\text{C}$  NMR of 5-Bromo-*N*,2-dimethylbenzamide (Table 1, entry 7)



<sup>1</sup>H NMR of 3-Methoxy-*N*,2,6-trimethylbenzamide (Table 1, entry 8)

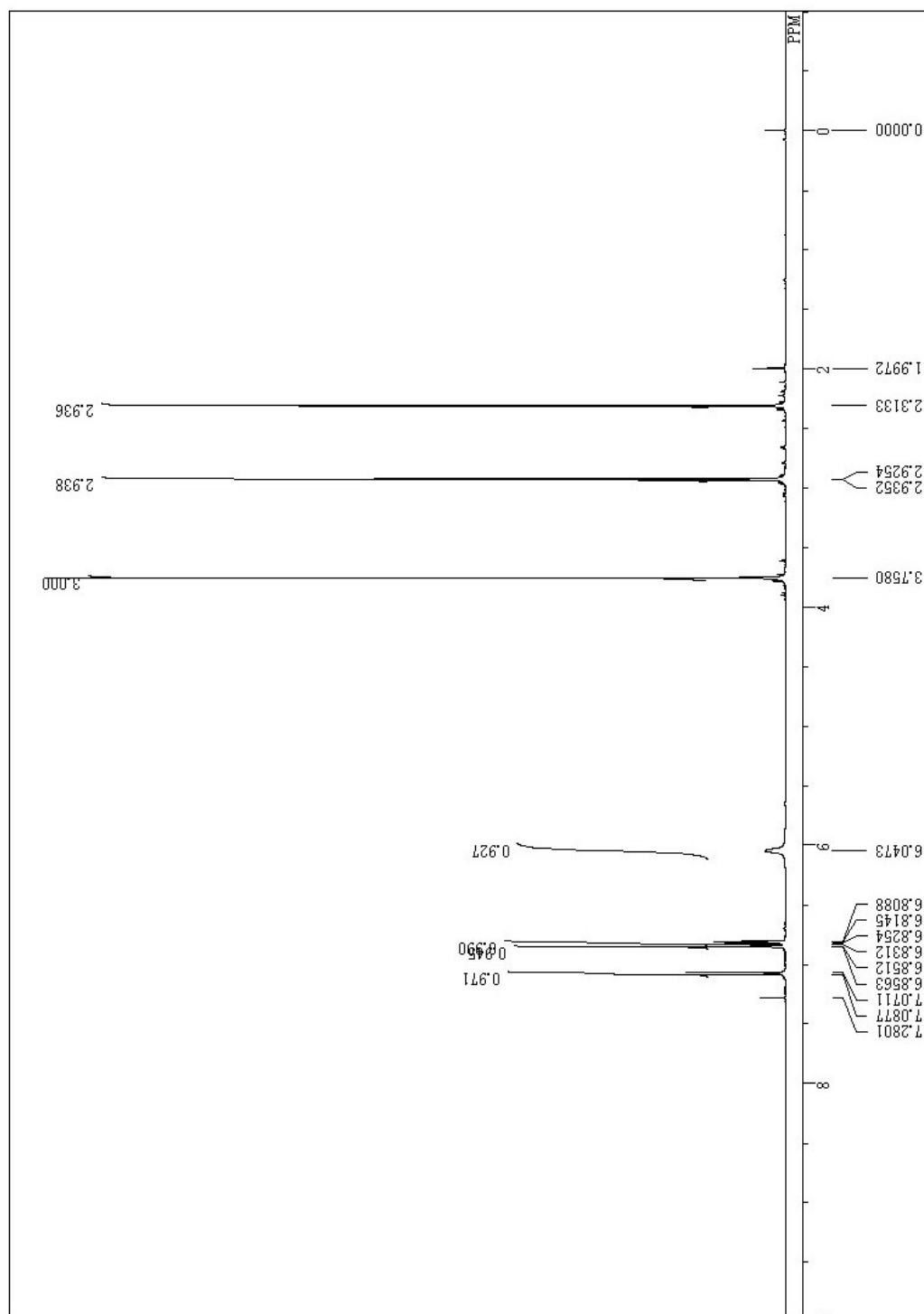
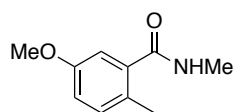


$^{13}\text{C}$  NMR of 3-Methoxy-*N*,2,6-trimethylbenzamide (Table 1, entry 8)

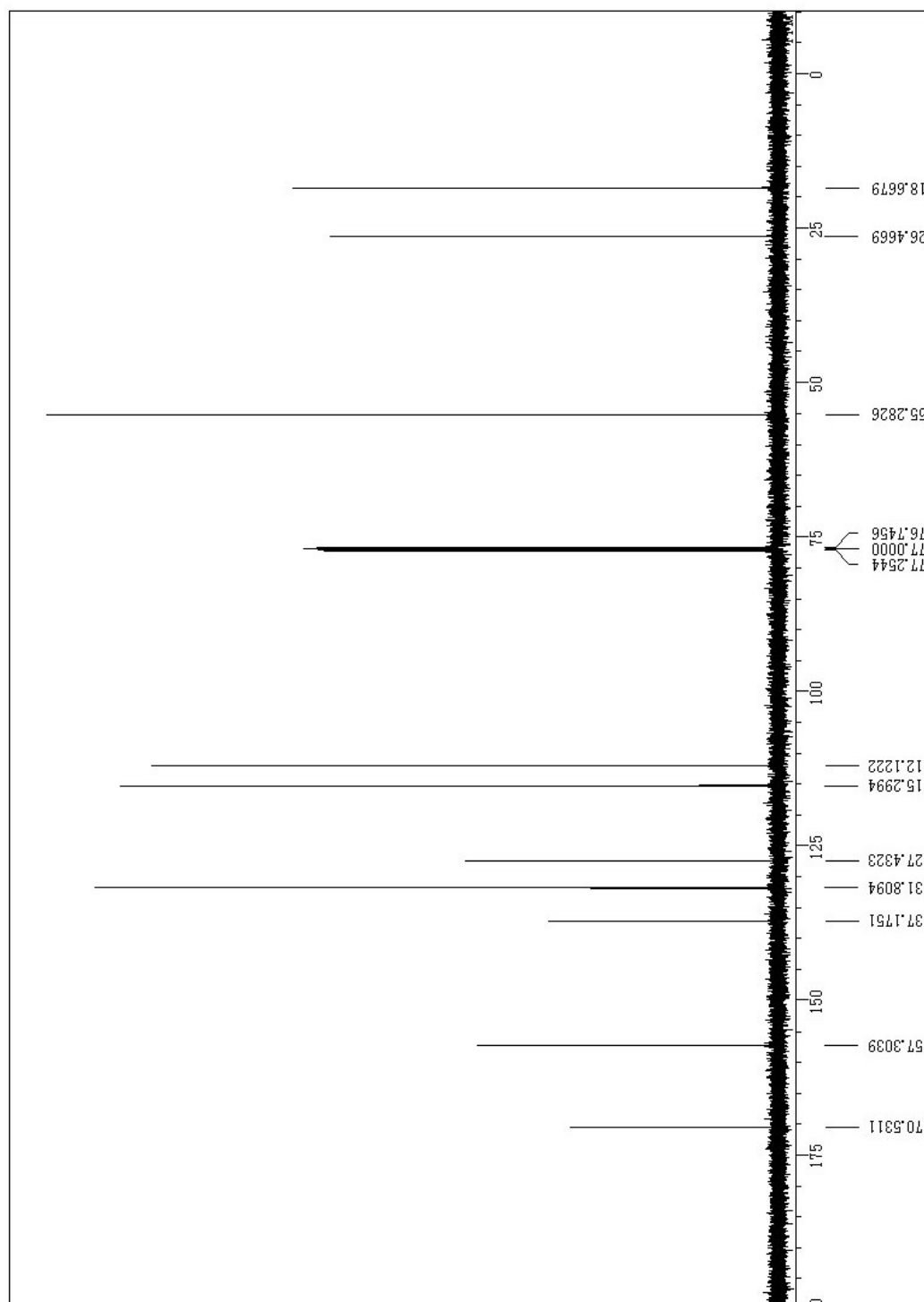
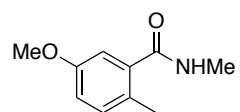




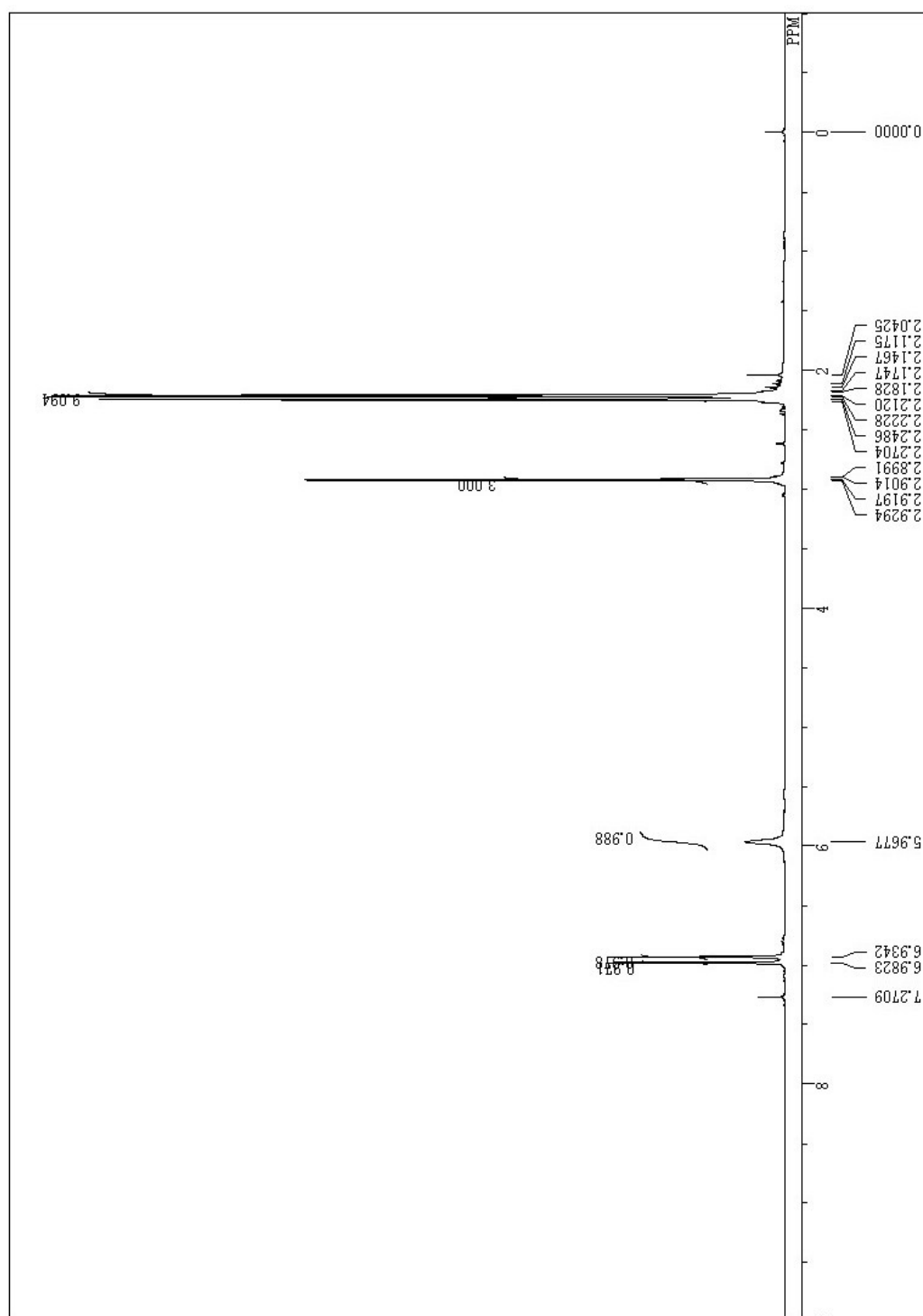
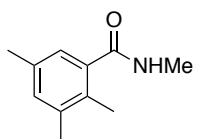
<sup>1</sup>H NMR of 5-Methoxy-*N*,2-dimethylbenzamide (Table 1, entry 8)



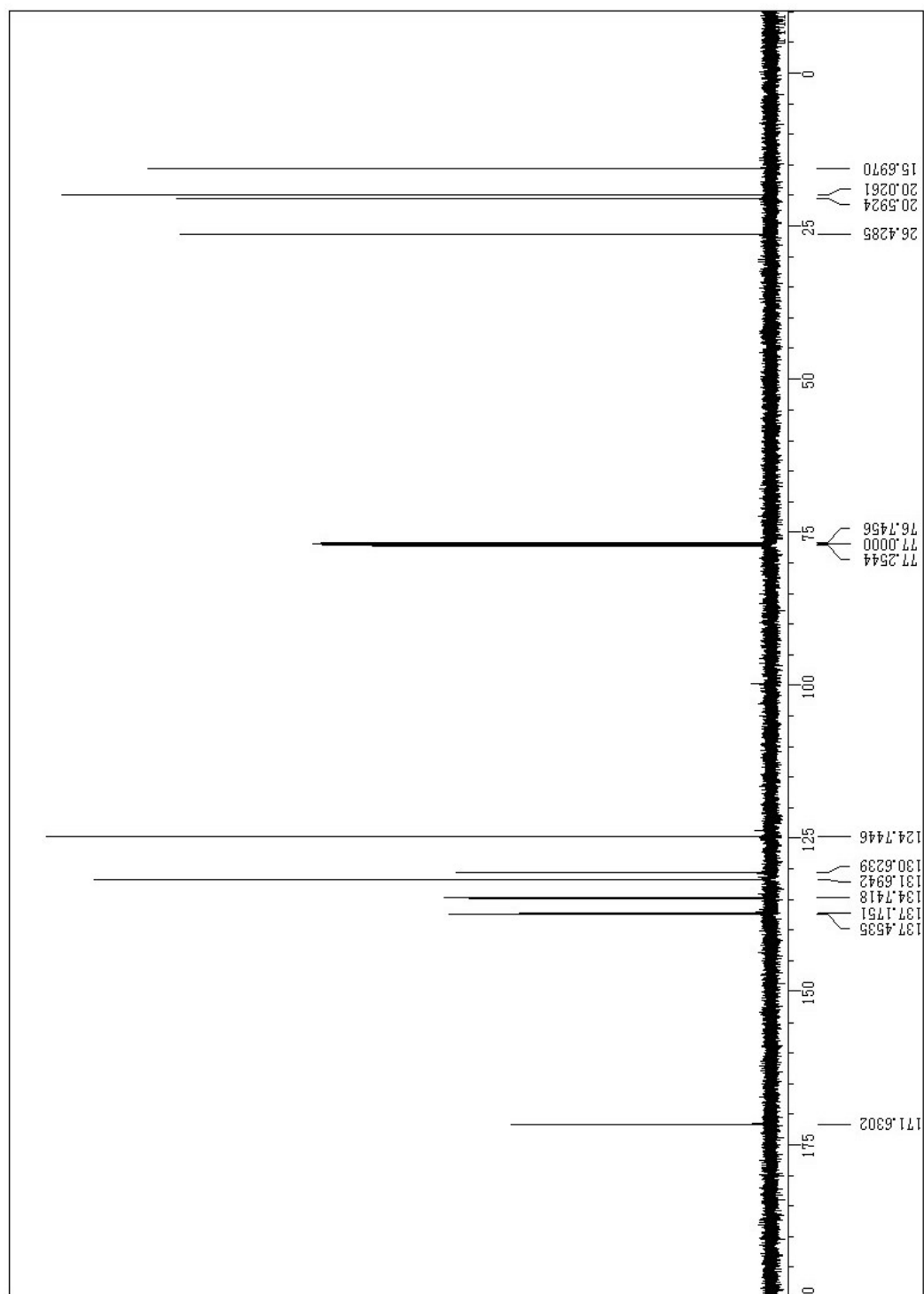
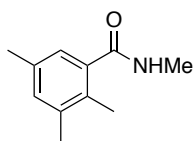
$^{13}\text{C}$  NMR of 5-Methoxy-*N*,2-dimethylbenzamide (Table 1, entry 8)



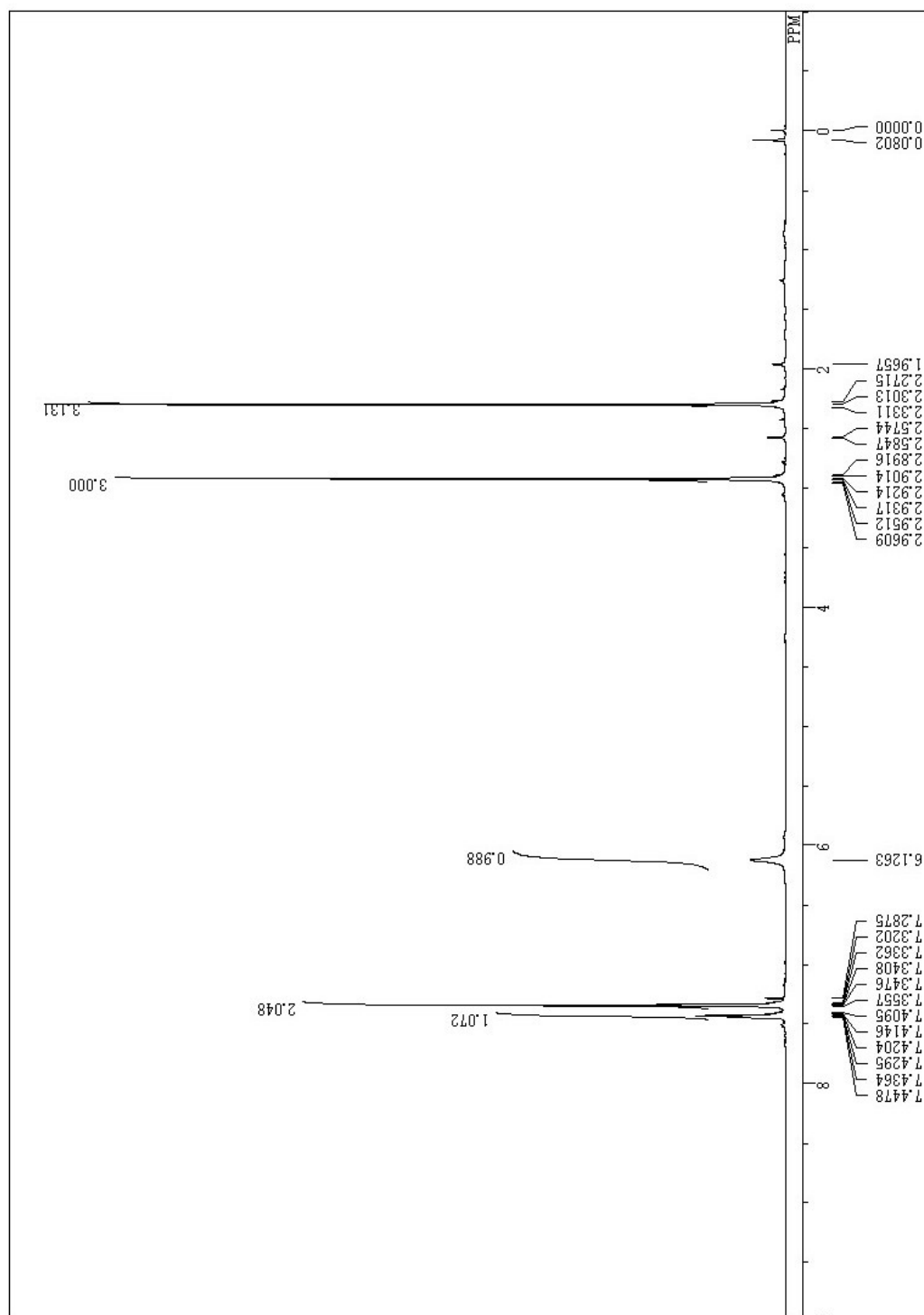
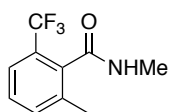
$^1\text{H}$  NMR of *N*,2,3,5-Tetramethylbenzamide (Table 1, entry 9)



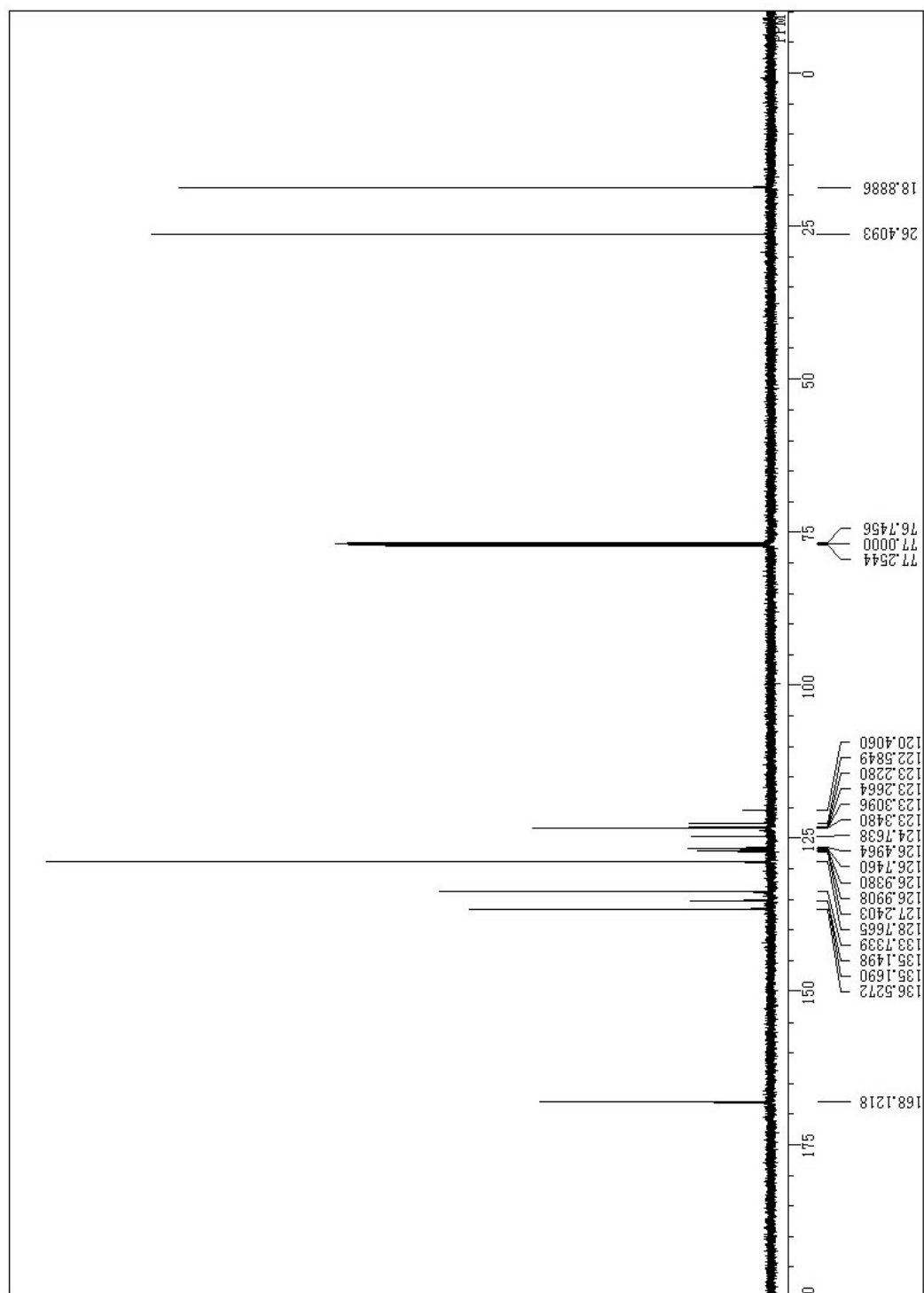
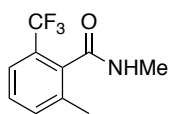
$^{13}\text{C}$  NMR of *N*,2,3,5-Tetramethylbenzamide (Table 1, entry 9)



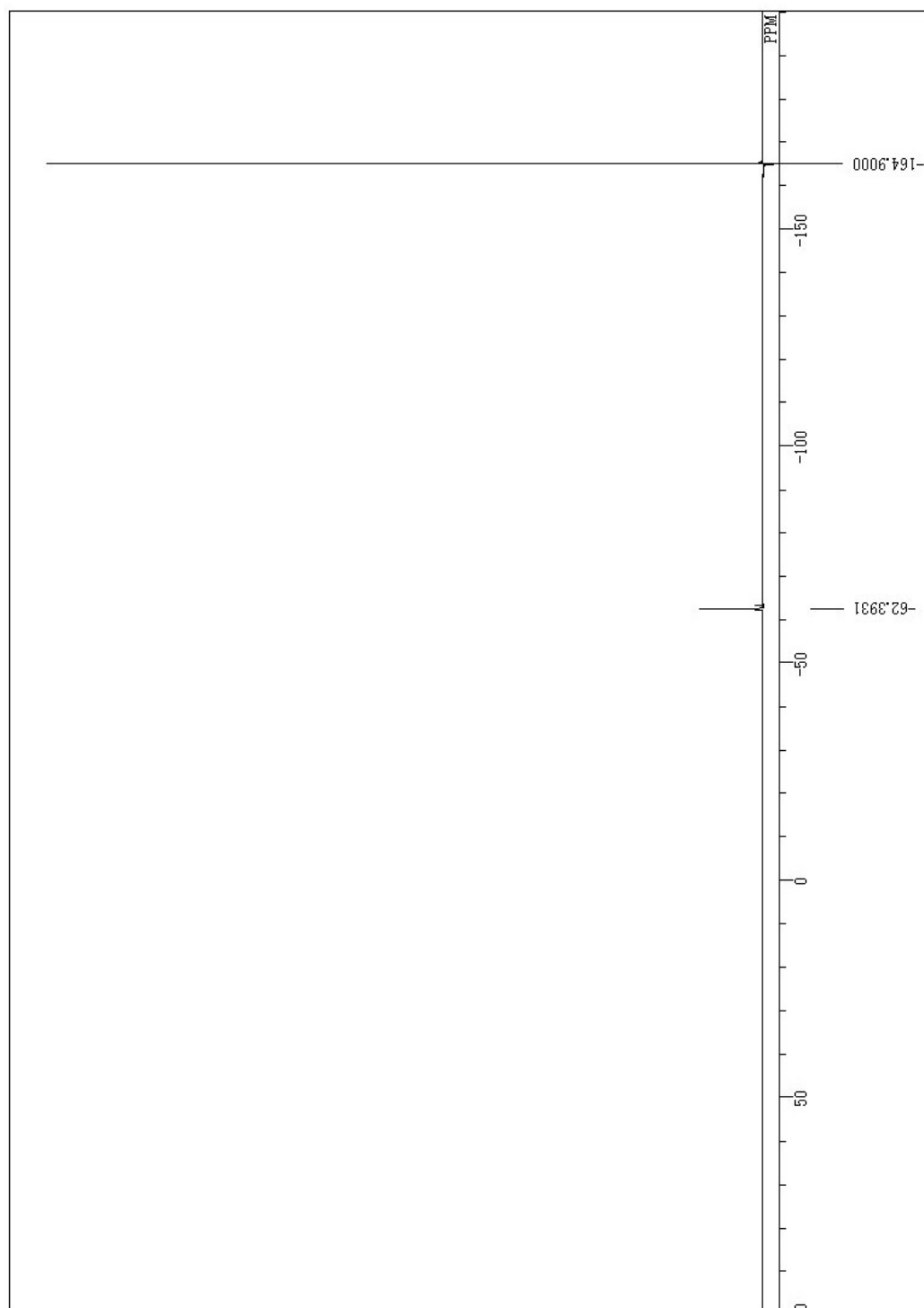
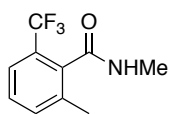
$^1\text{H}$  NMR of *N*,6-Dimethyl-2-(trifluoromethyl)benzamide (Table 1, entry 10)



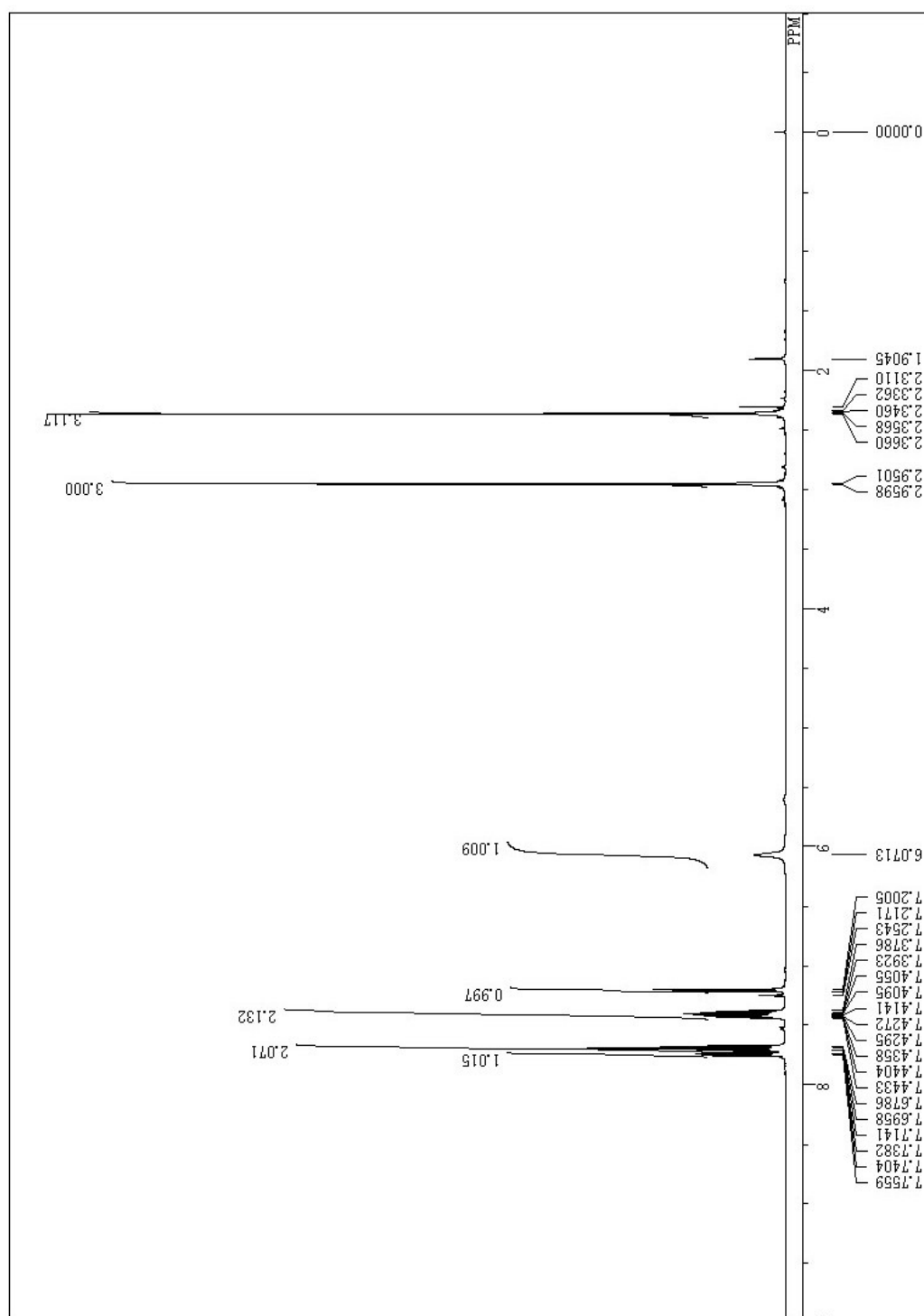
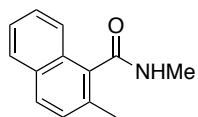
$^{13}\text{C}$  NMR of *N*,6-Dimethyl-2-(trifluoromethyl)benzamide (Table 1, entry 10)



$^{19}\text{F}$  NMR of *N*,6-Dimethyl-2-(trifluoromethyl)benzamide (Table 1, entry 10)

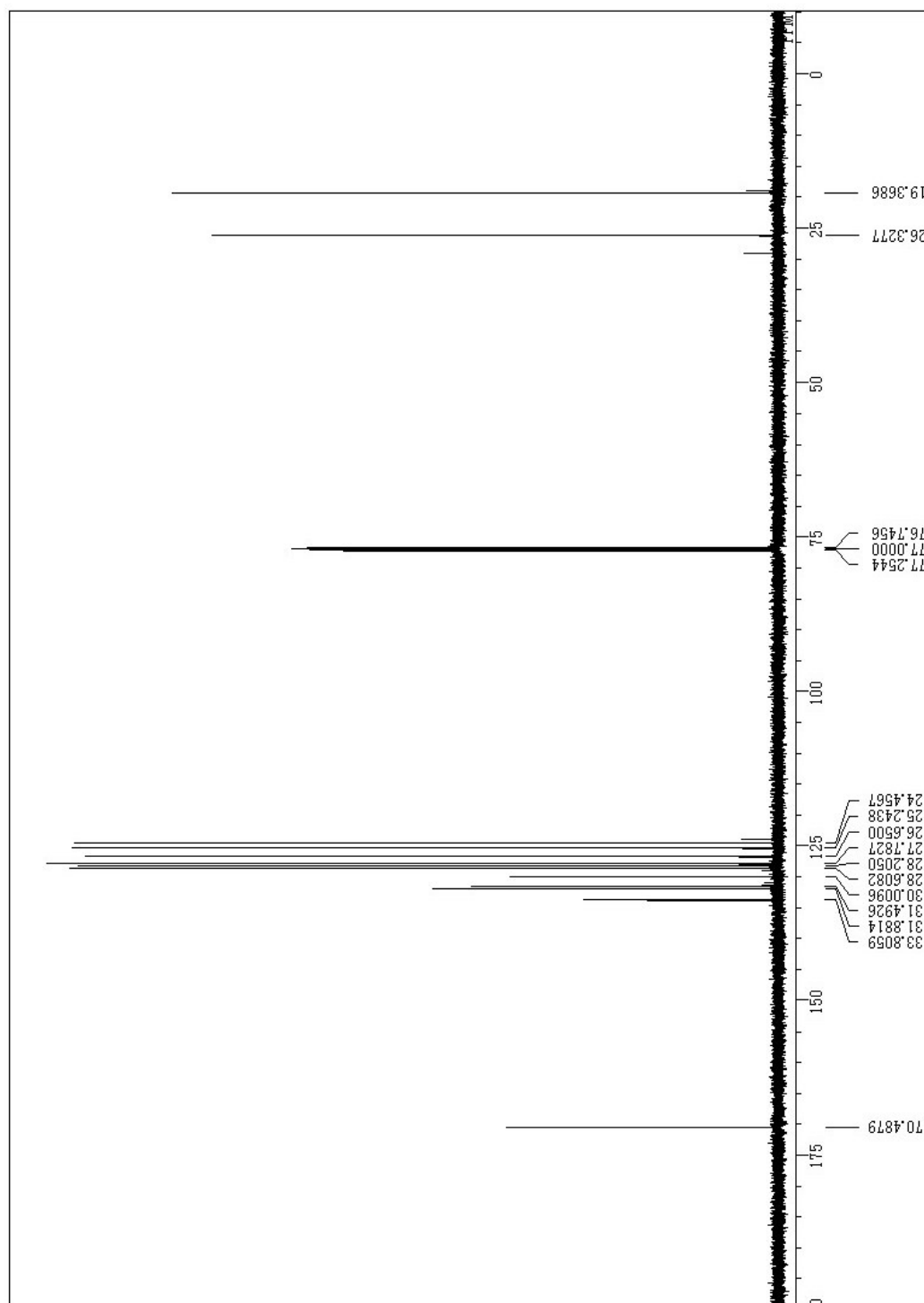
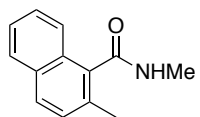


<sup>1</sup>H NMR of *N*,2-Dimethyl-1-naphthalenecarboxamide (Table 1, entry 11)

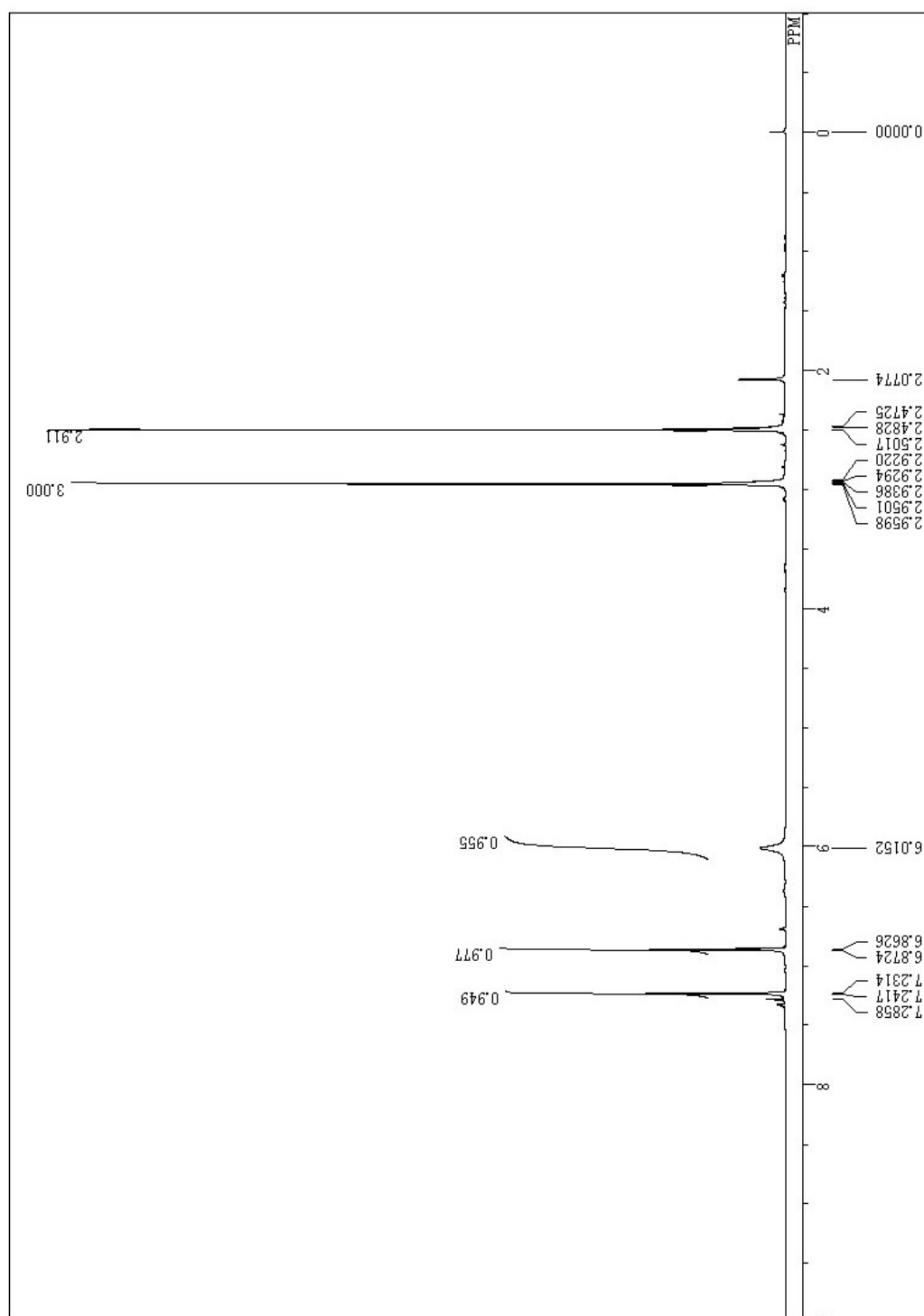
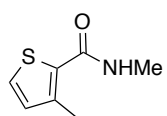




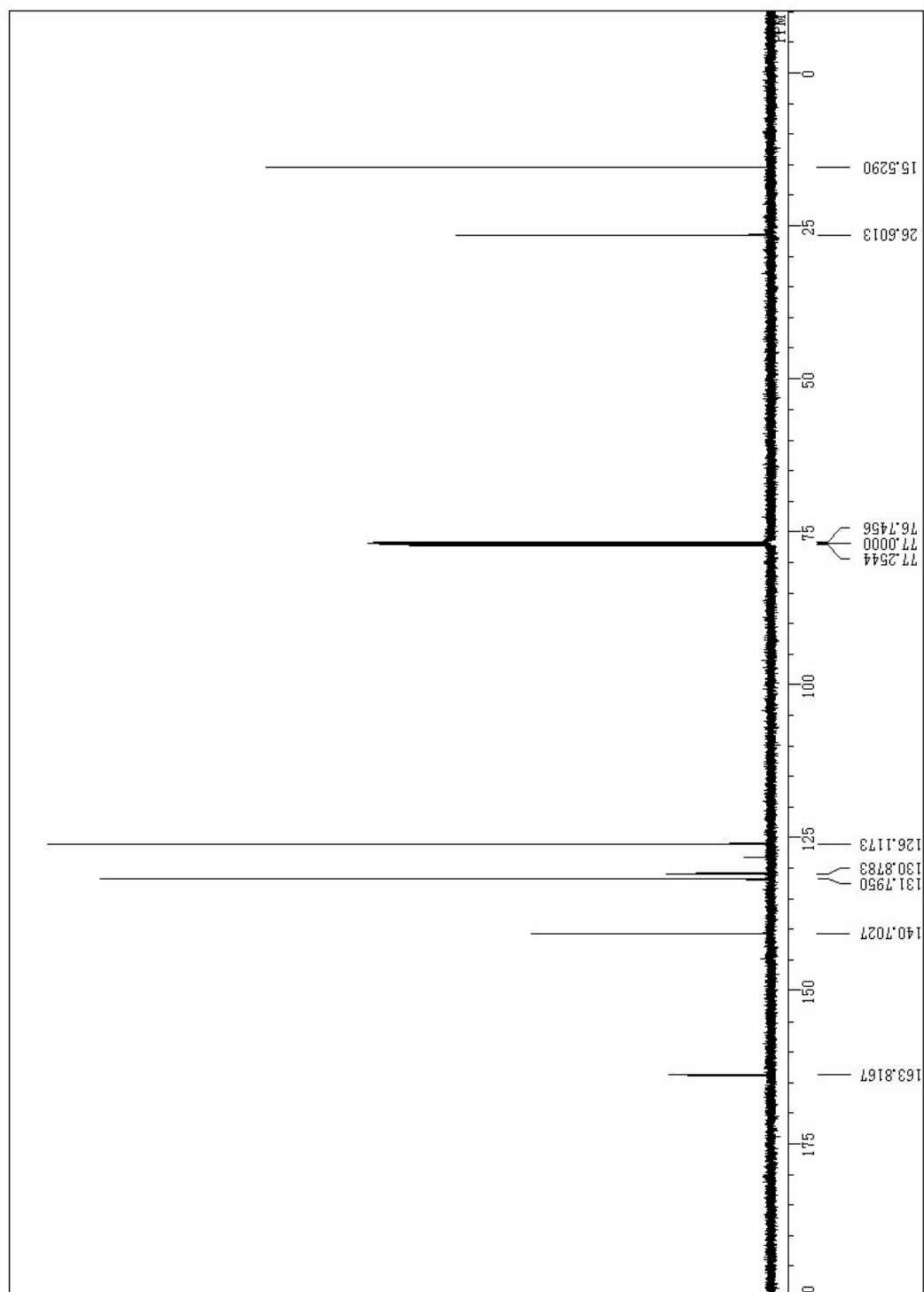
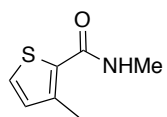
$^{13}\text{C}$  NMR of *N*,2-Dimethyl-1-naphthalenecarboxamide (Table 1, entry 11)



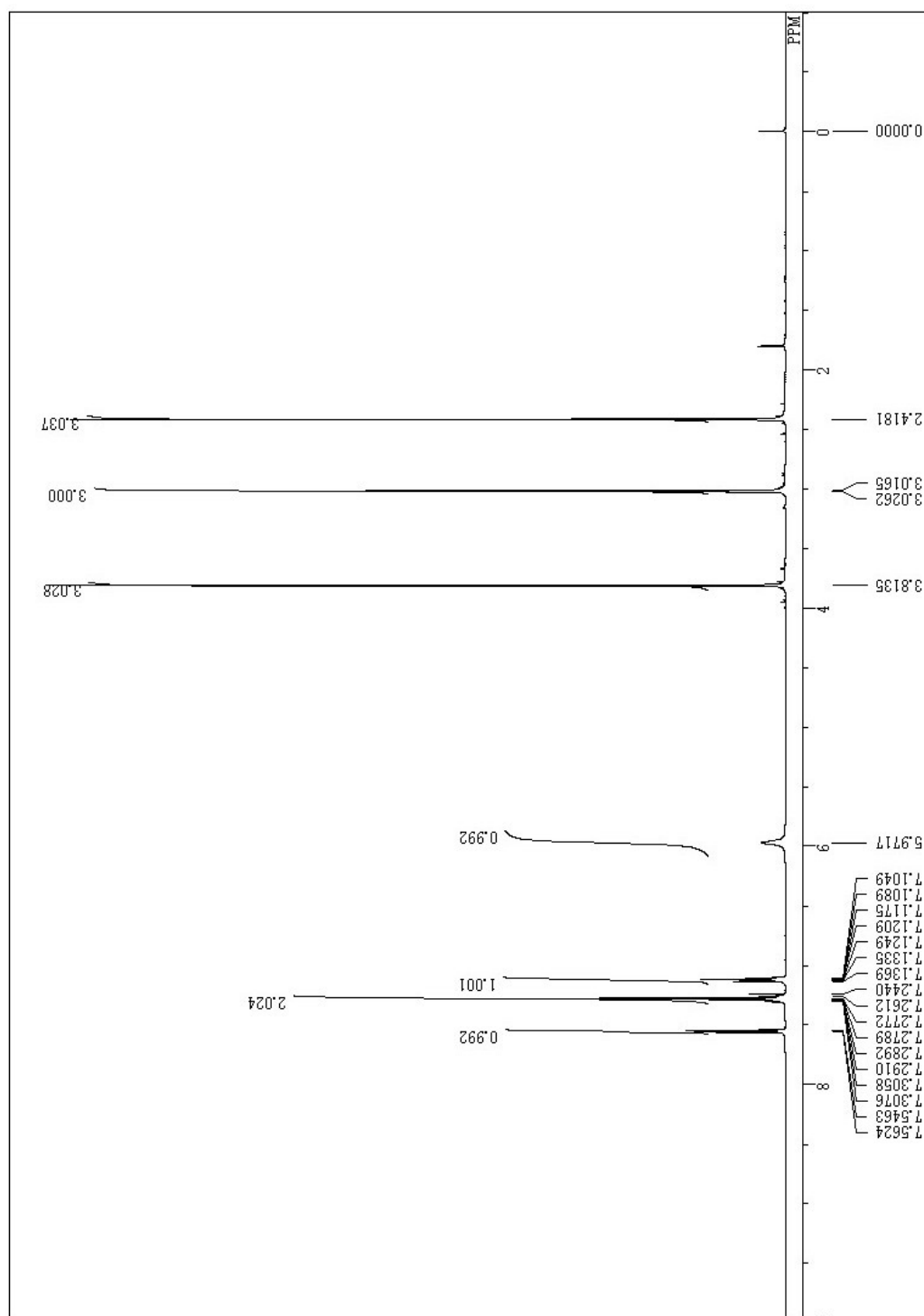
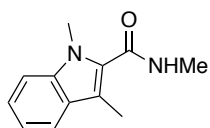
$^1\text{H}$  NMR of *N*,3-Dimethyl-2-thiophenecarboxamide (Table 1, entry 12)



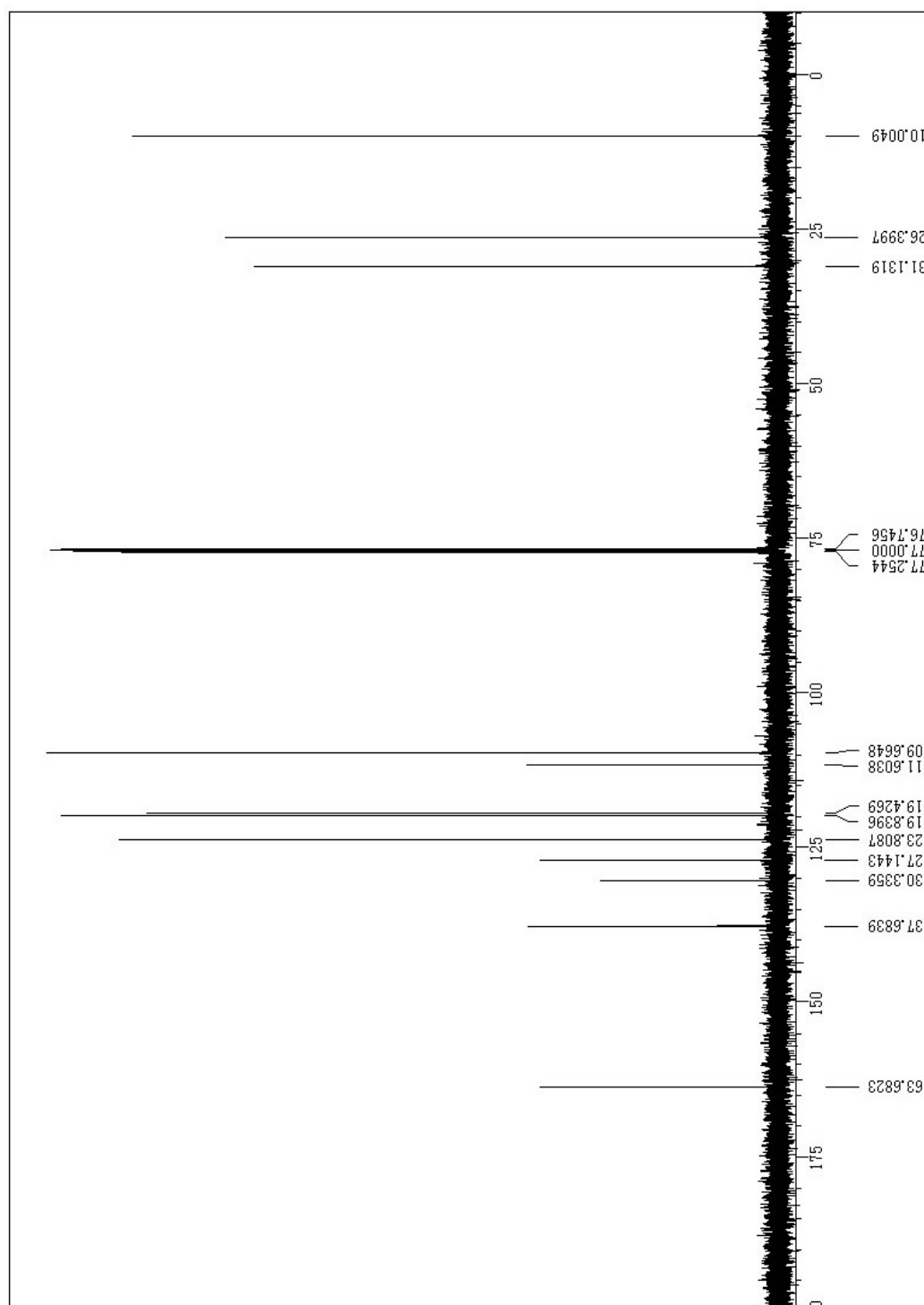
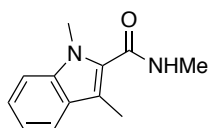
$^{13}\text{C}$  NMR of *N*,3-Dimethyl-2-thiophenecarboxamide (Table 1, entry 12)



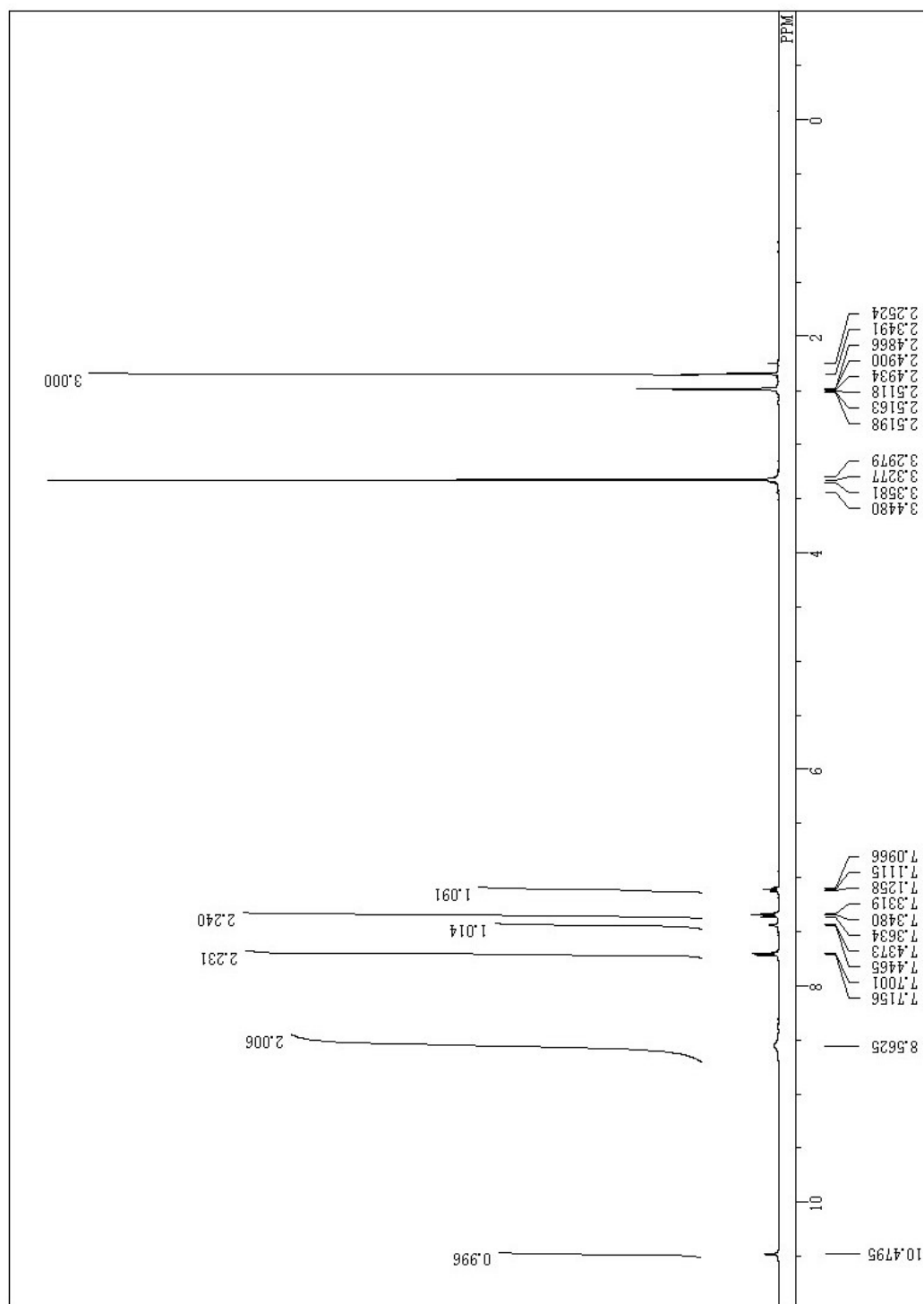
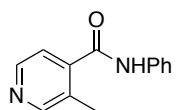
$^1\text{H}$  NMR of *N*,1,3-Trimethyl-1*H*-indole-2-carboxamide (Table 1, entry 13)



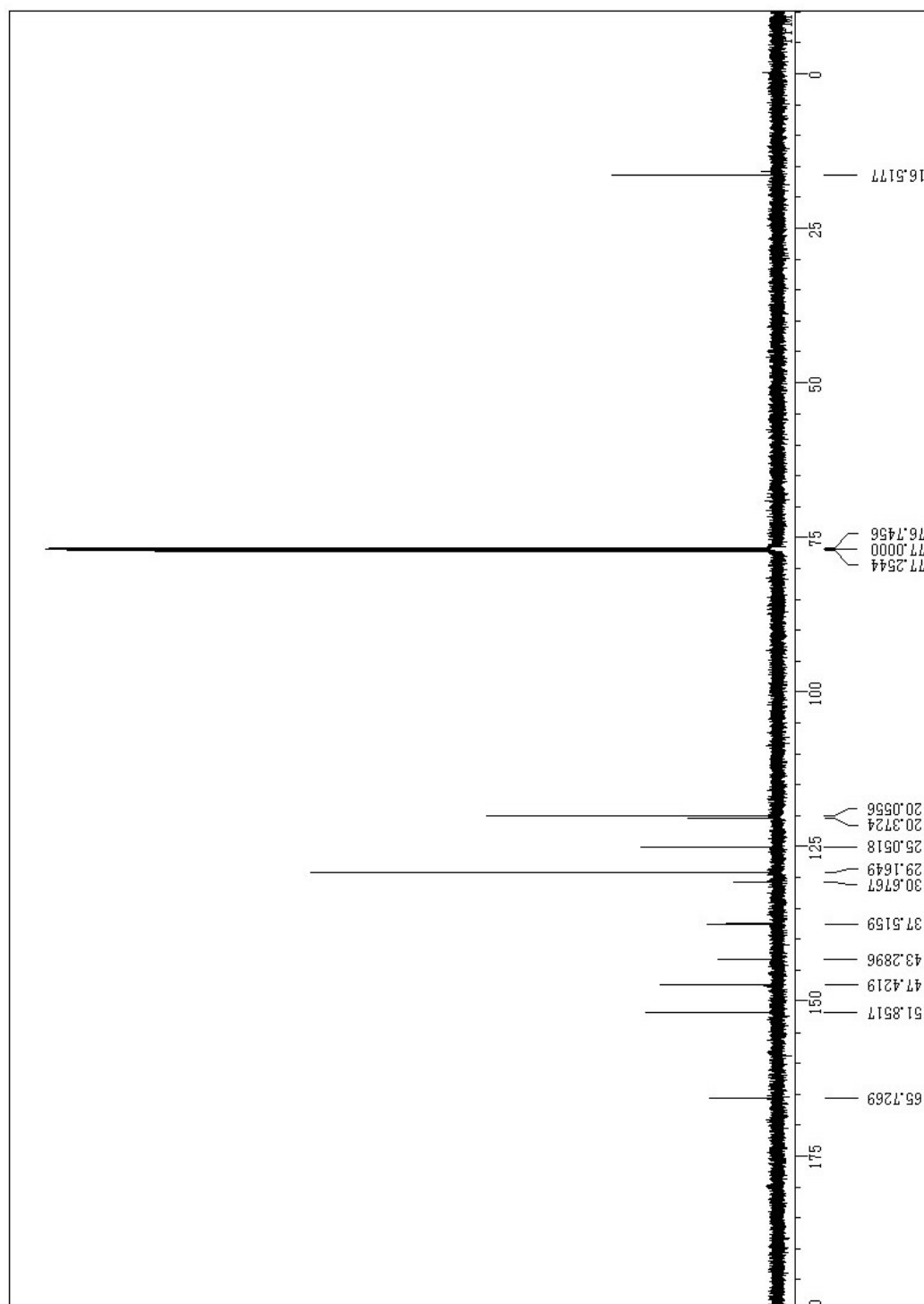
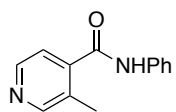
$^{13}\text{C}$  NMR of *N*,1,3-Trimethyl-1*H*-indole-2-carboxamide (Table 1, entry 13)



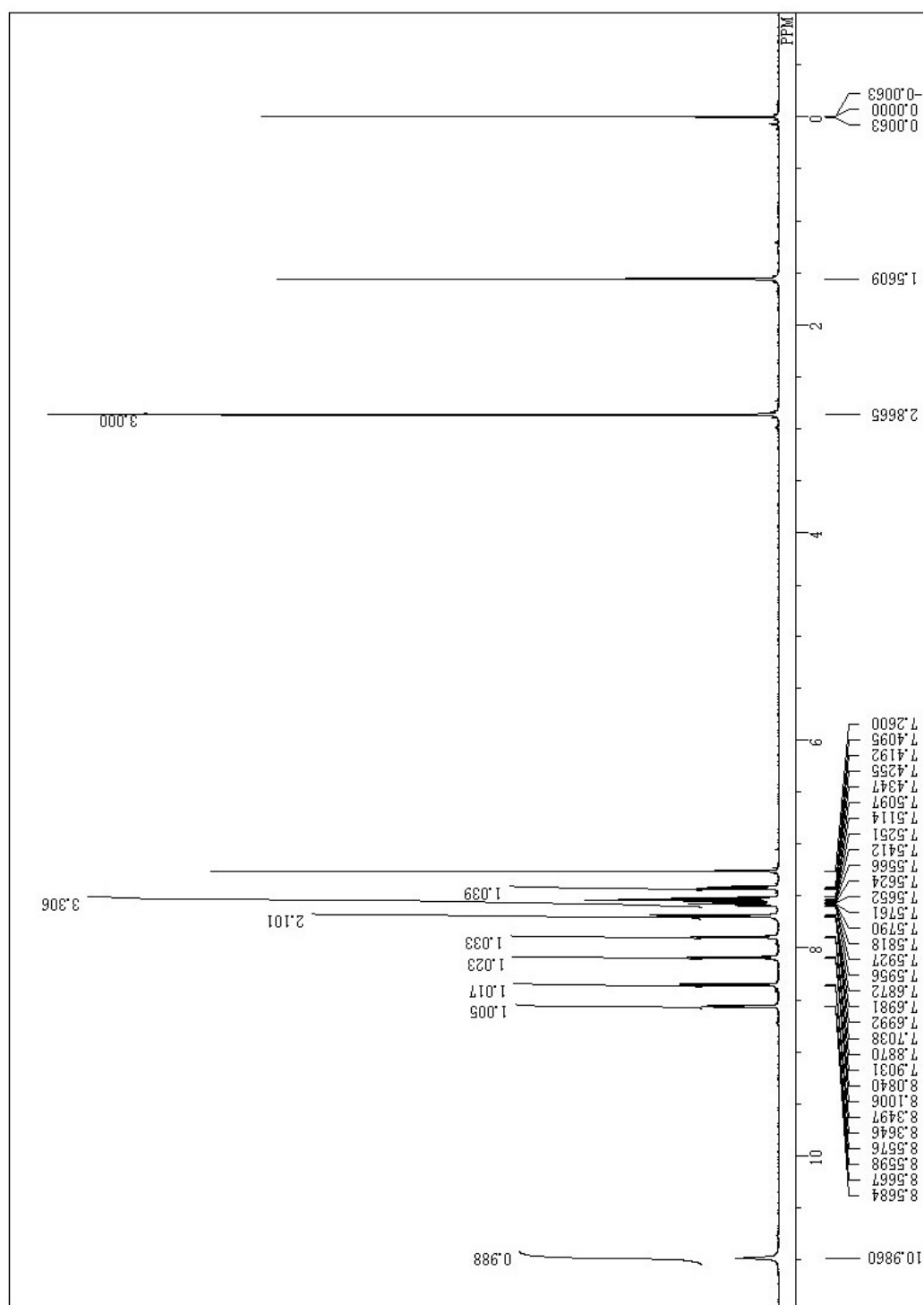
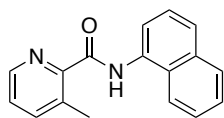
<sup>1</sup>H NMR of 3-Methyl-*N*-phenyl-4-pyridinecarboxamide (Table 1, entry 14)



$^{13}\text{C}$  NMR of 3-Methyl-*N*-phenyl-4-pyridinecarboxamide (Table 1, entry 14)

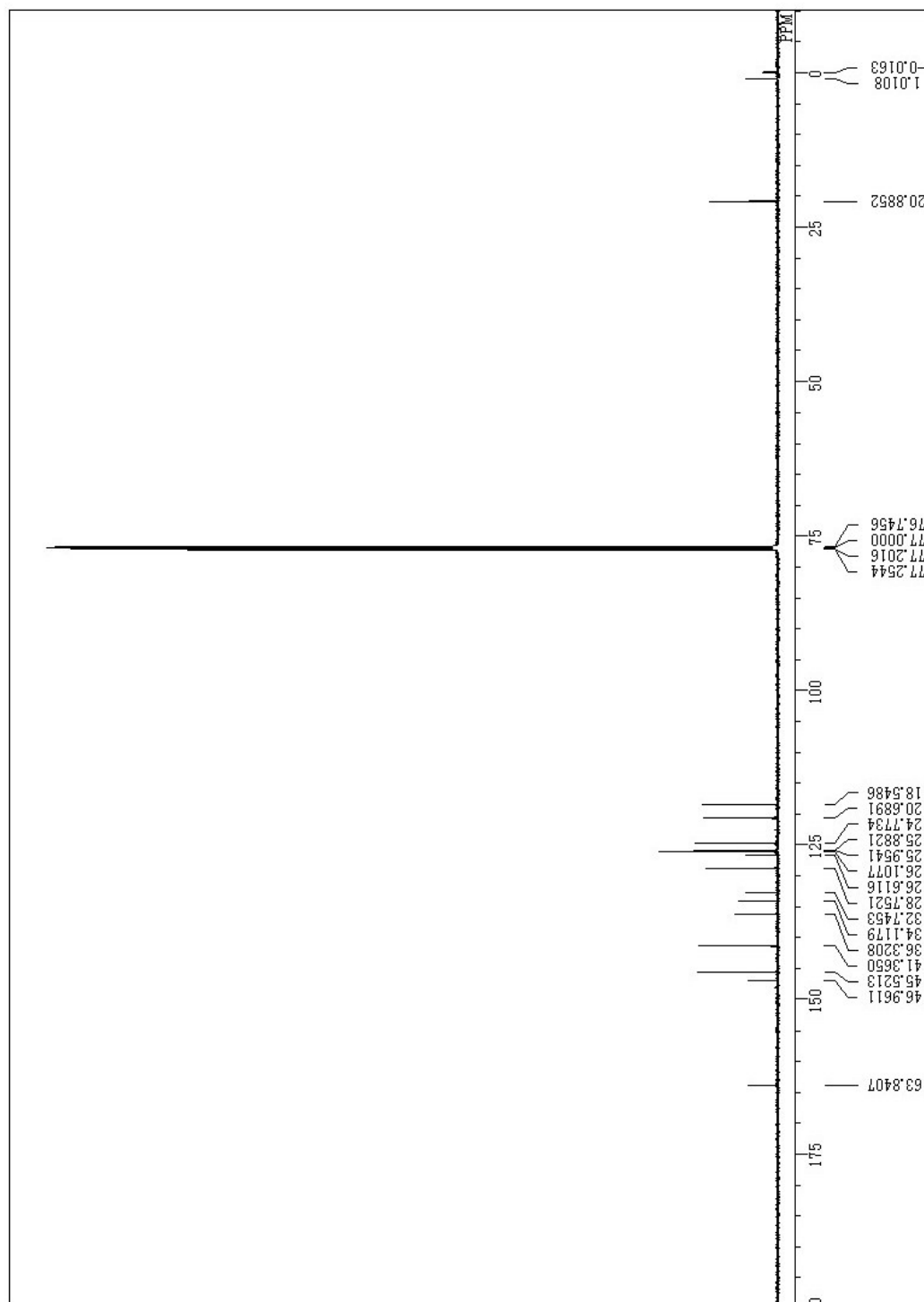
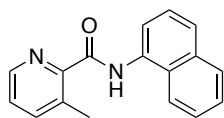


<sup>1</sup>H NMR of 3-Methyl-*N*-(naphthalen-1-yl)picolinamide (Table 1, entry 15)

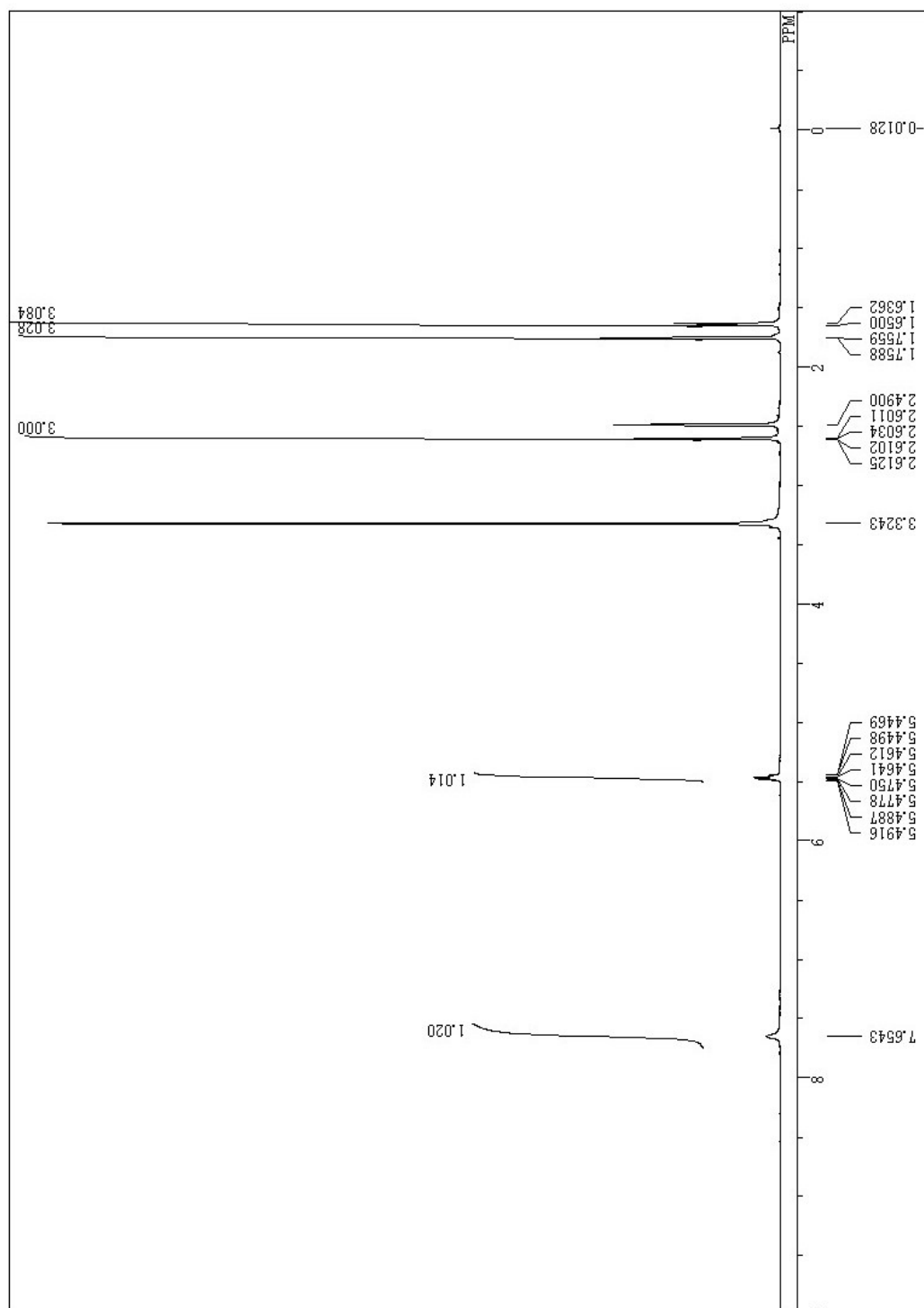
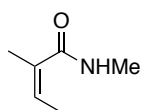




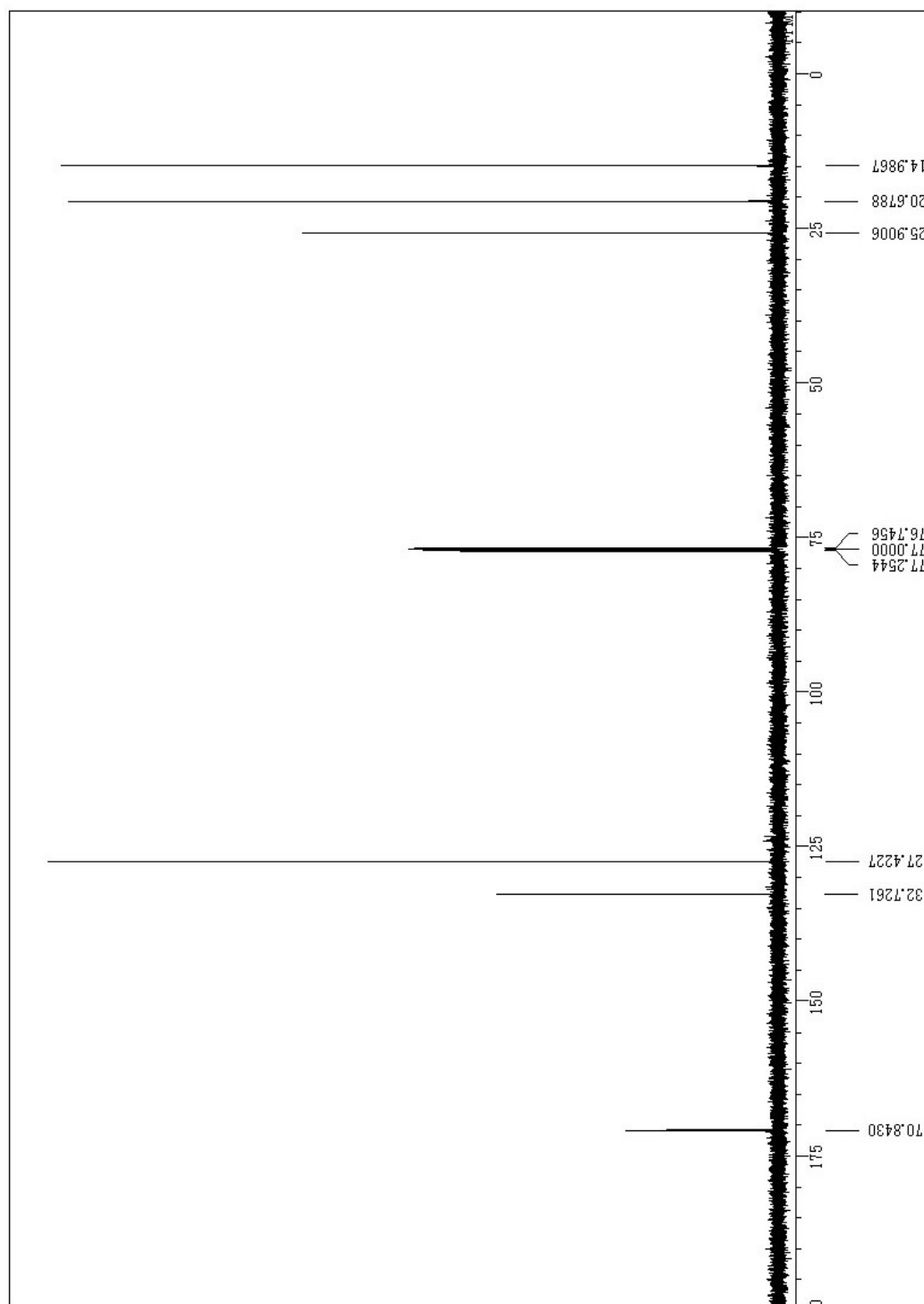
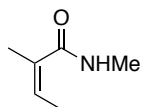
$^{13}\text{C}$  NMR of 3-Methyl-*N*-(naphthalen-1-yl)picolinamide (Table 1, entry 15)



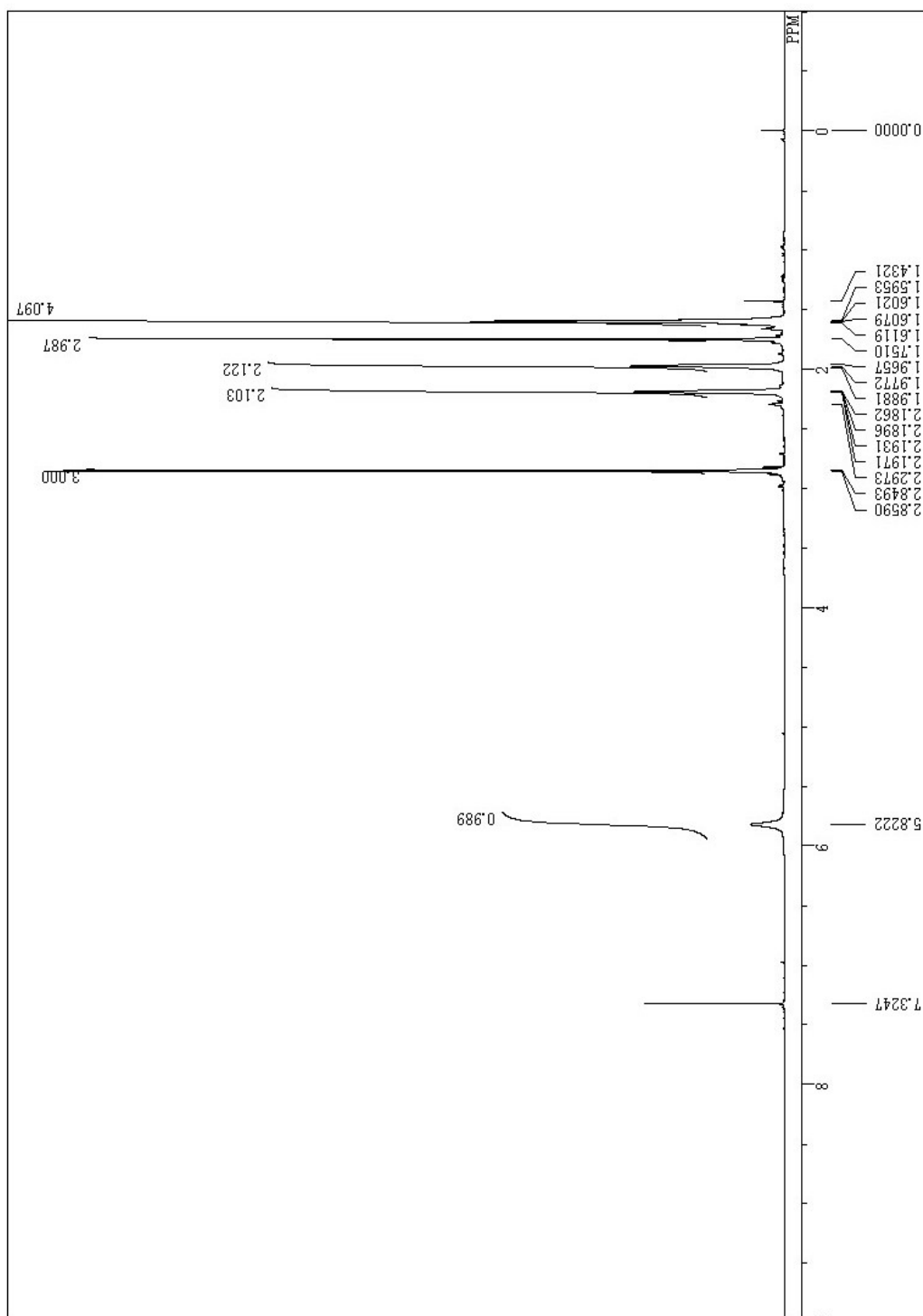
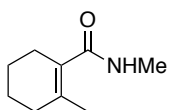
$^1\text{H}$  NMR of (Z)-N,2-Dimethyl-2-butenamide (Table 1, entry 16)



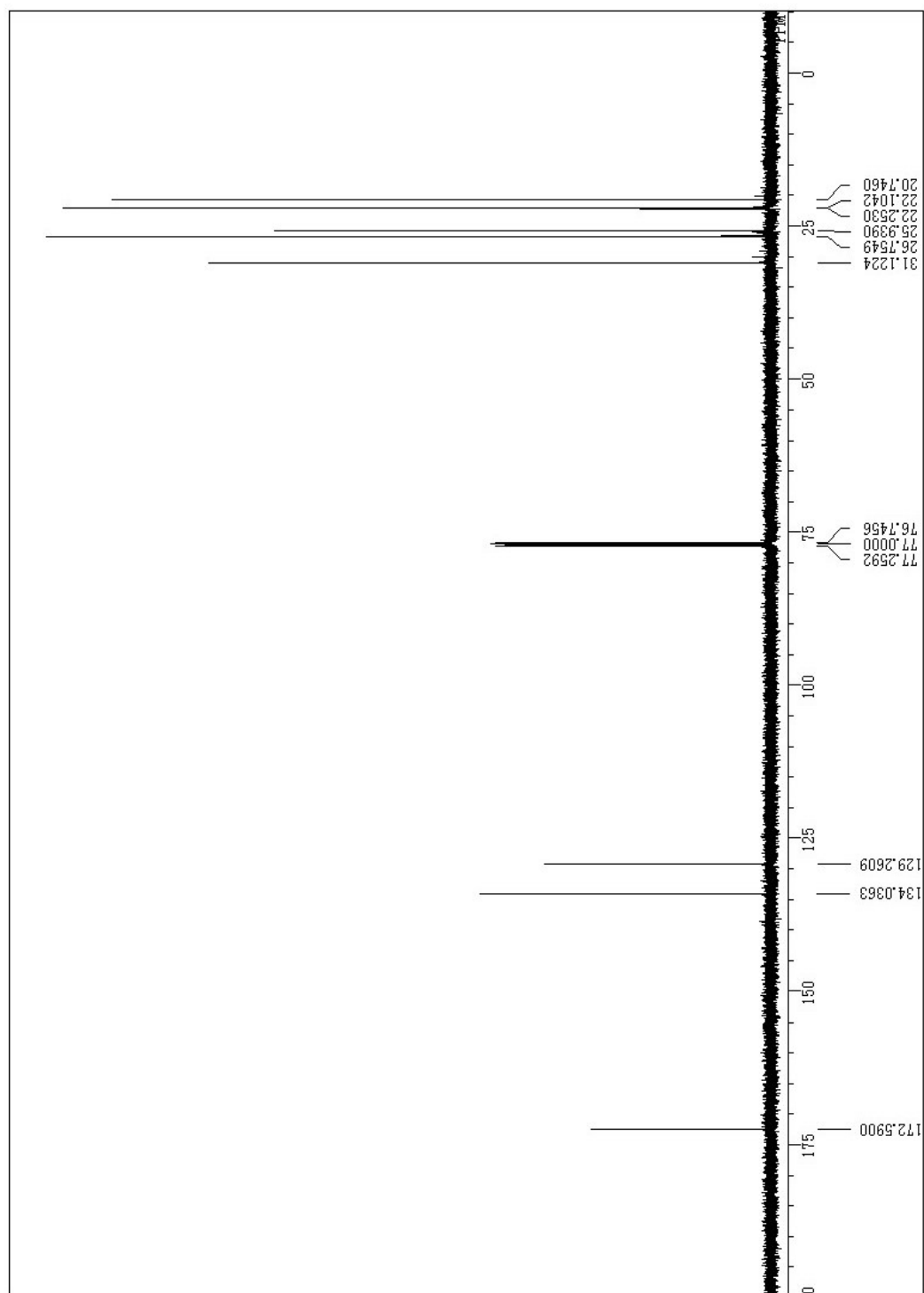
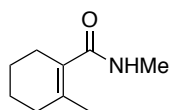
$^{13}\text{C}$  NMR of (*Z*)-*N*,2-Dimethyl-2-butenamide (Table 1, entry 16)



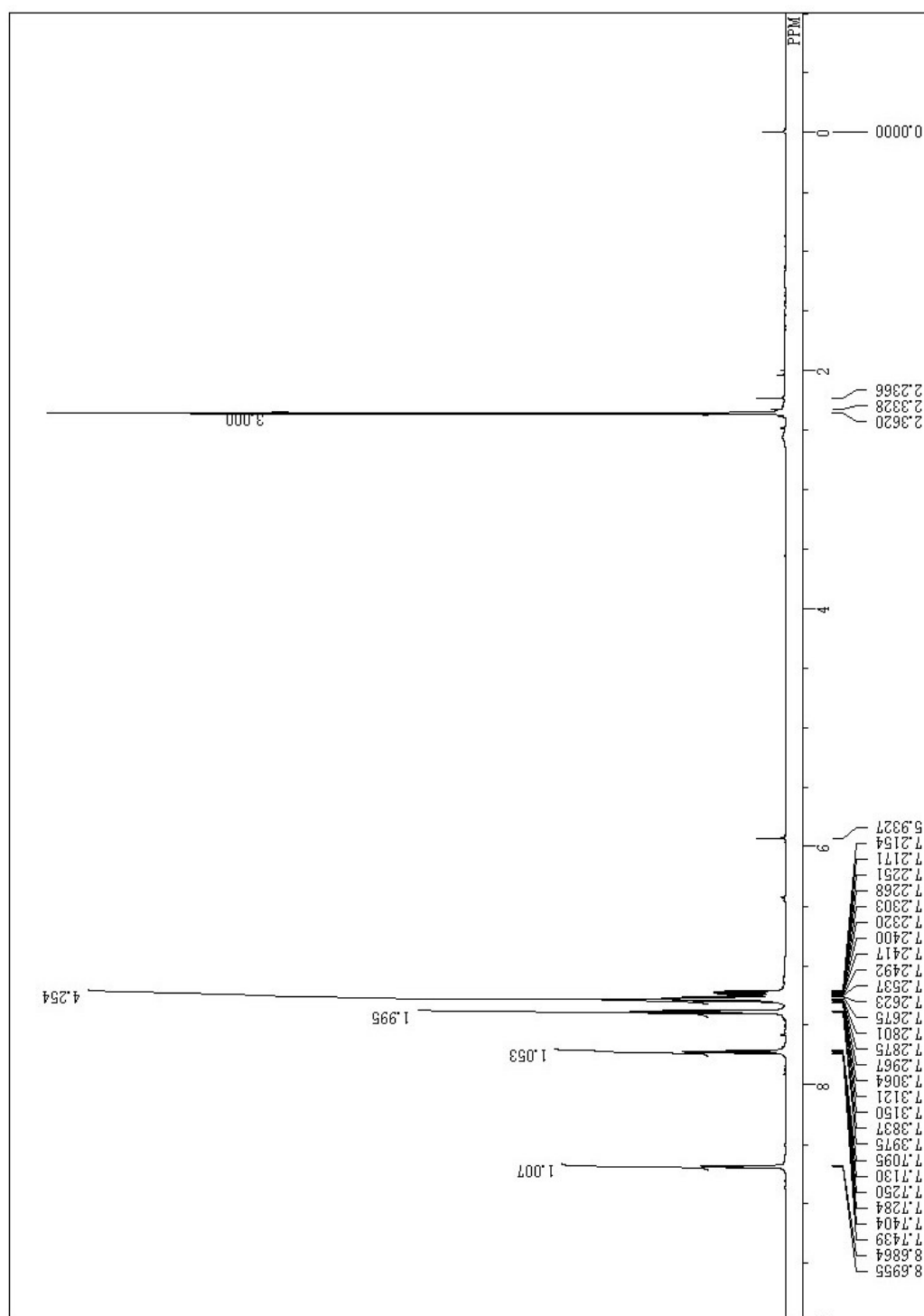
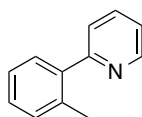
<sup>1</sup>H NMR of *N*,2-Dimethyl-1-cyclohexene-1-carboxamide (Table 1, entry 17)



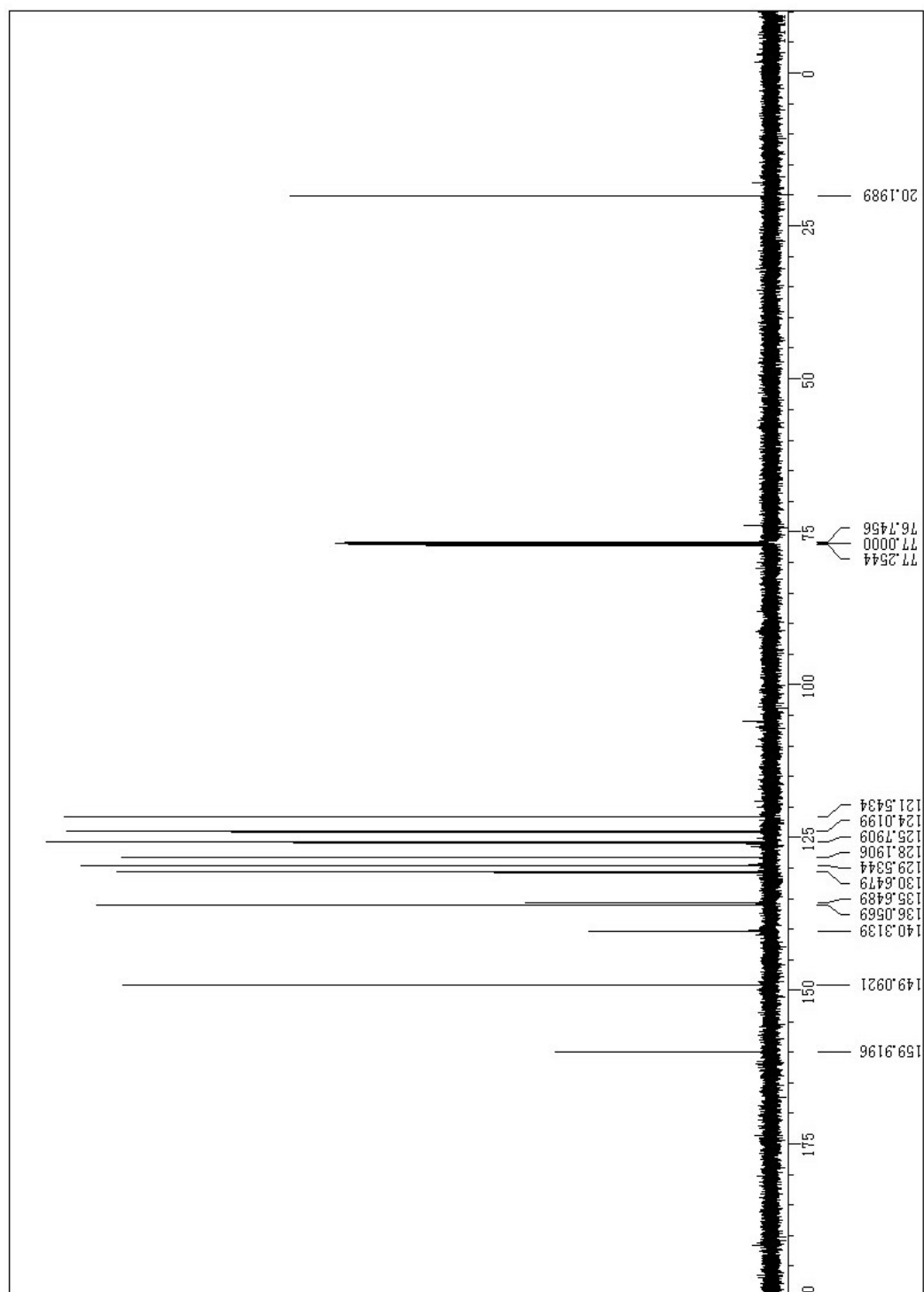
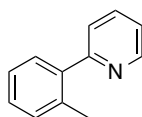
$^{13}\text{C}$  NMR of *N*,2-Dimethyl-1-cyclohexene-1-carboxamide (Table 1, entry 17)



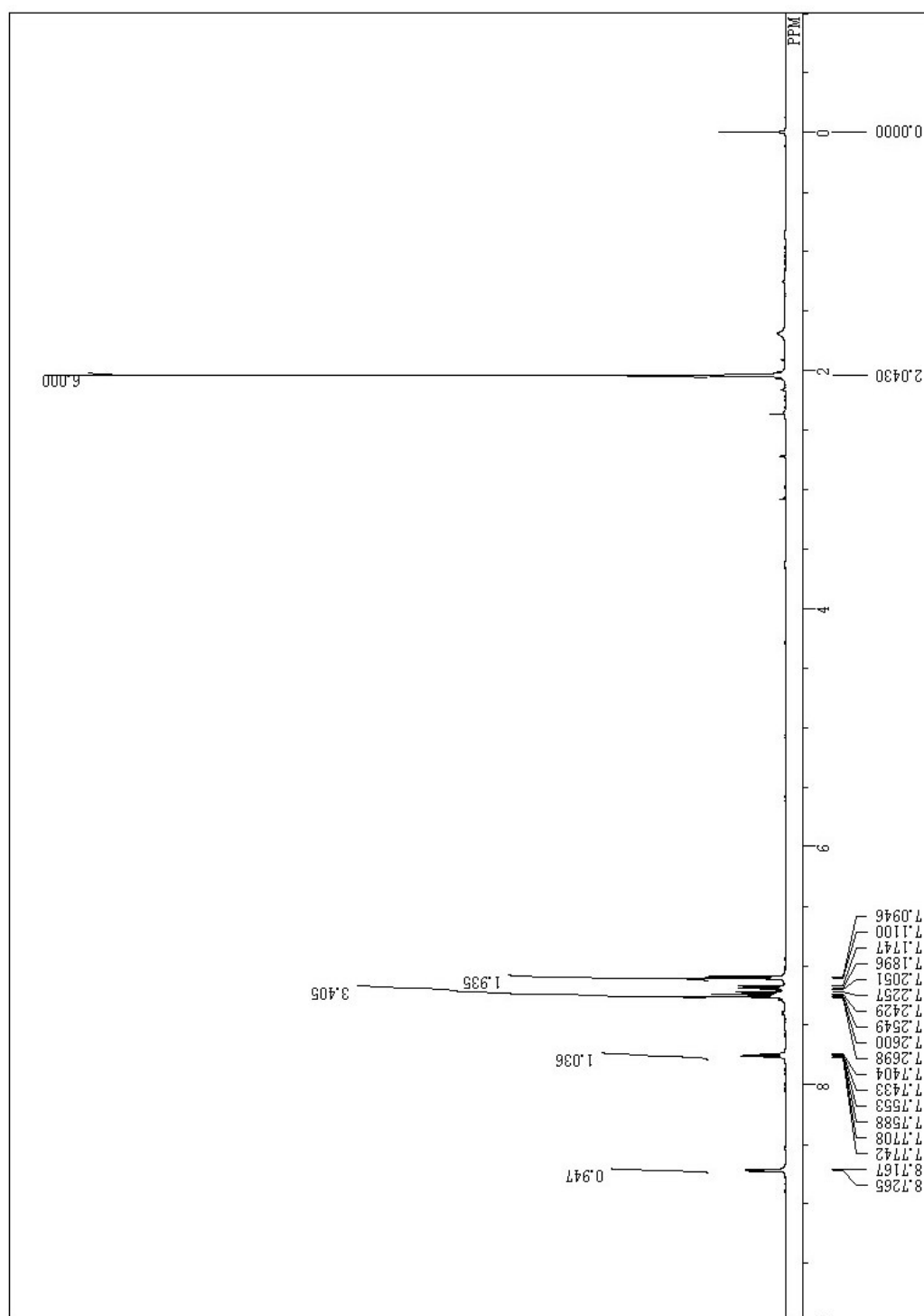
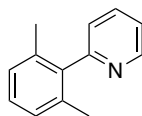
$^1\text{H}$  NMR of 2-(2-Methylphenyl)pyridine (Table 2, entry 1)



<sup>13</sup>C NMR of 2-(2-Methylphenyl)pyridine (Table 2, entry 1)

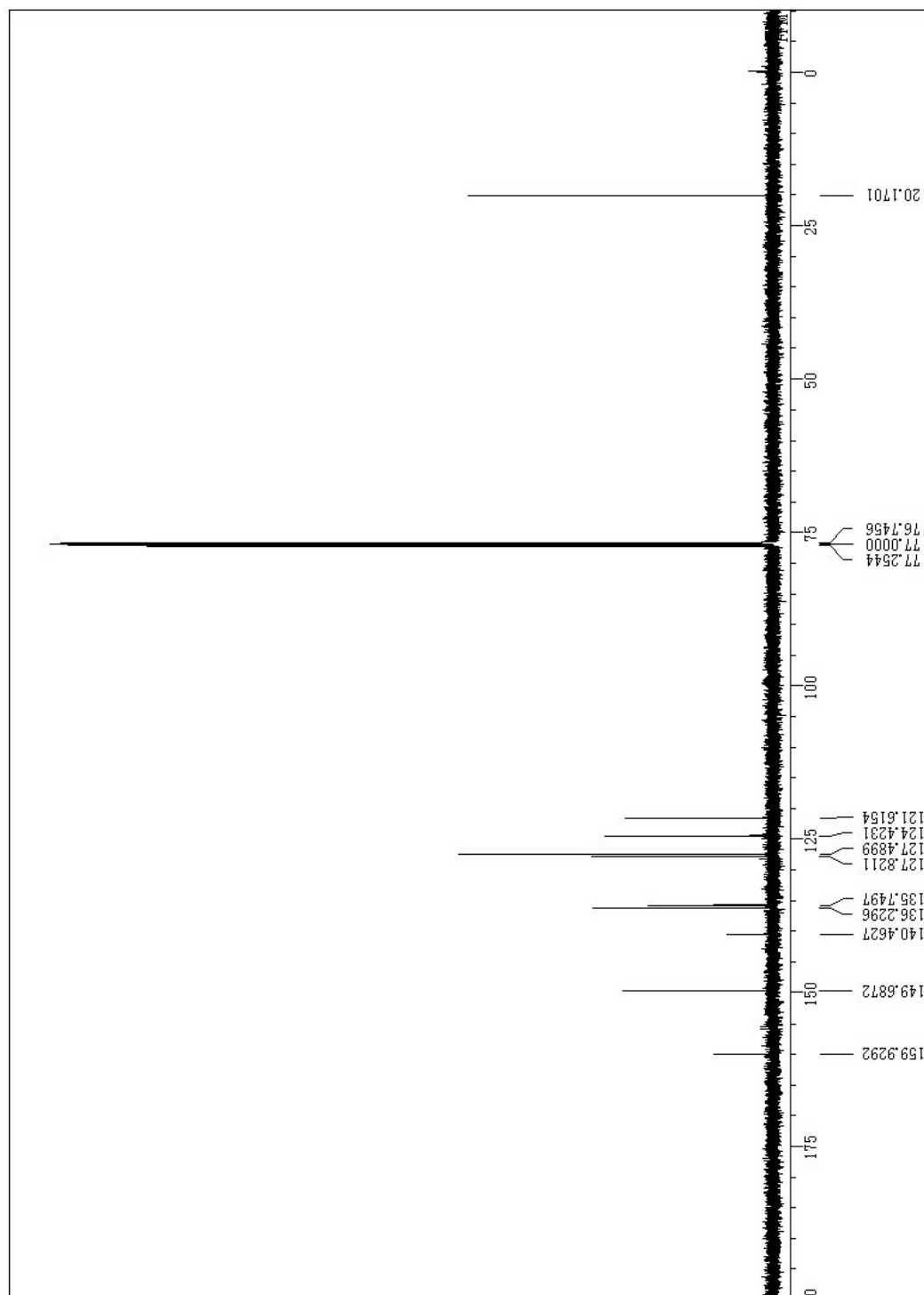
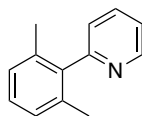


<sup>1</sup>H NMR of 2-(2,6-Dimethylphenyl)pyridine (Table 2, entry 1)

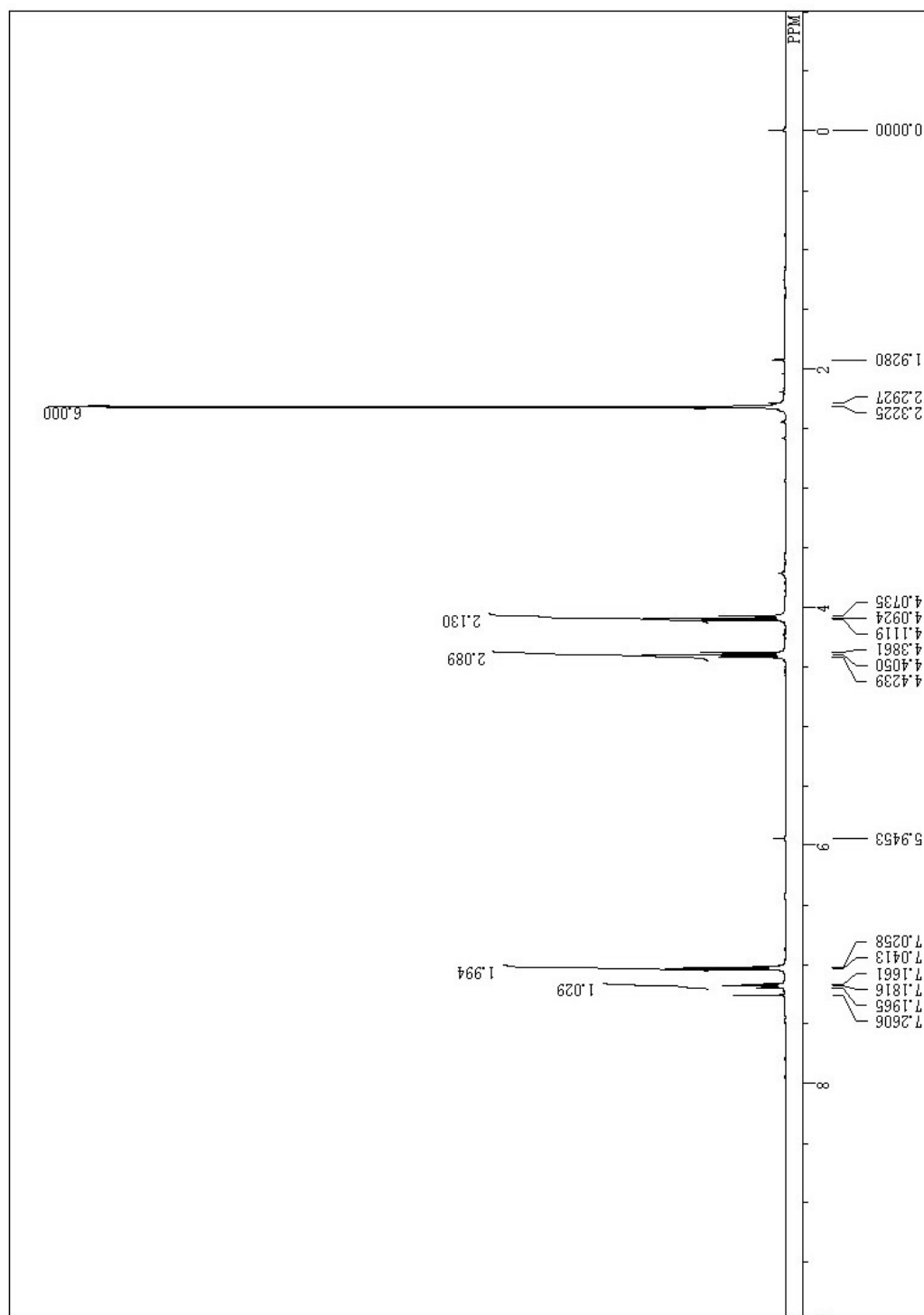
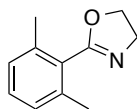




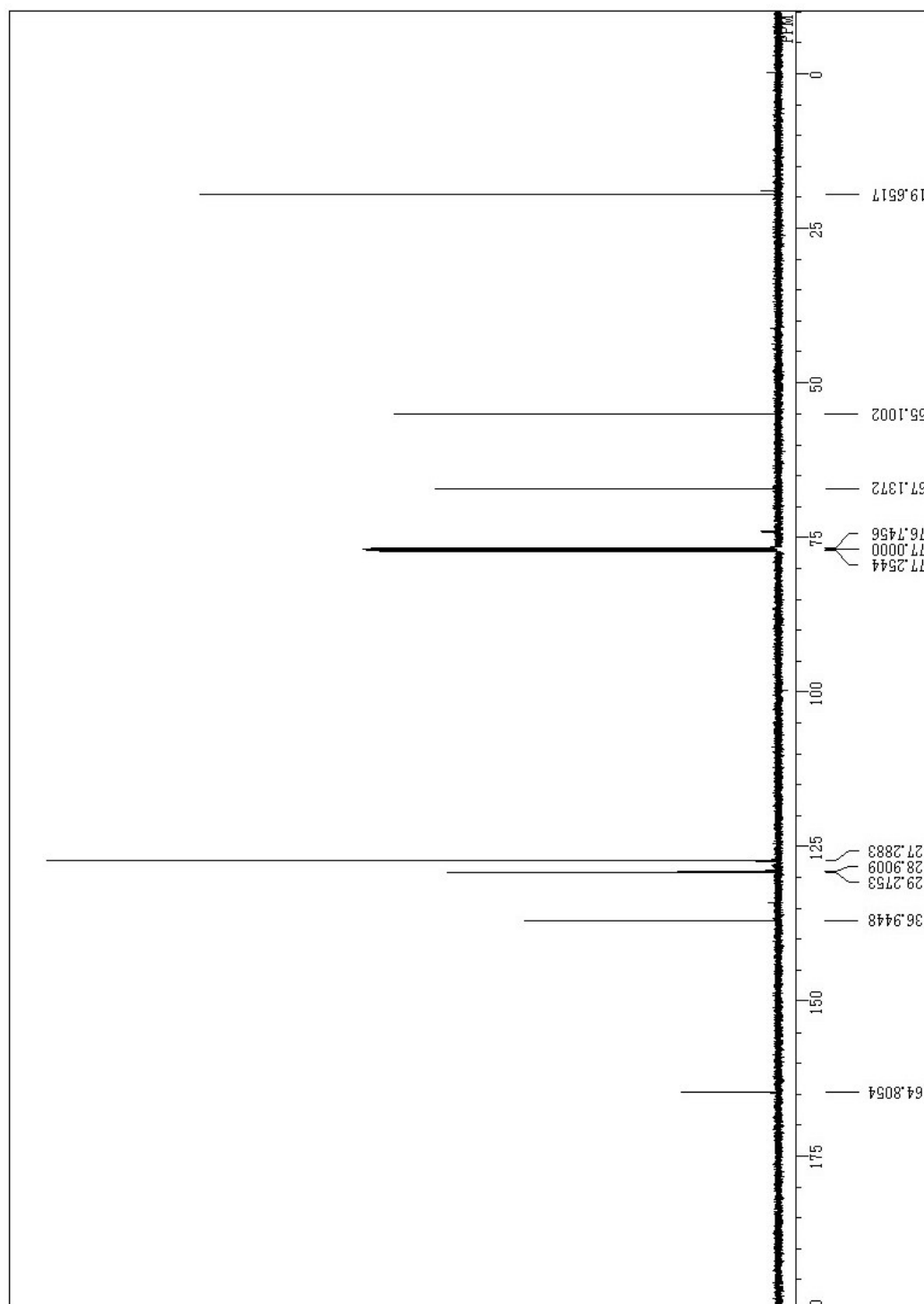
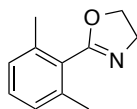
$^{13}\text{C}$  NMR of 2-(2,6-Dimethylphenyl)pyridine (Table 2, entry 1)



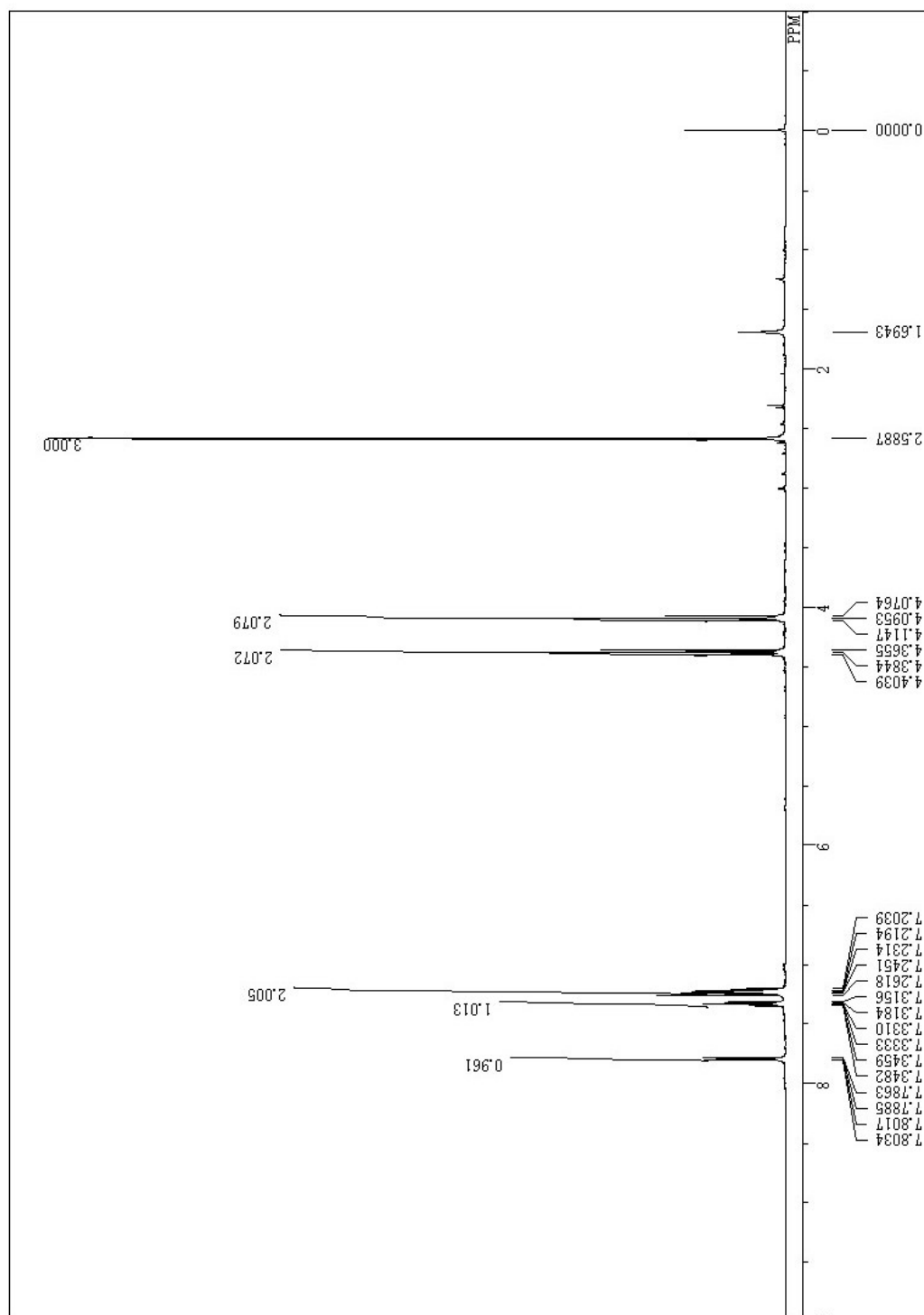
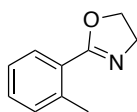
$^1\text{H}$  NMR of 2-(2,6-Dimethylphenyl)-4,5-dihydrooxazole (Table 2, entry 2)



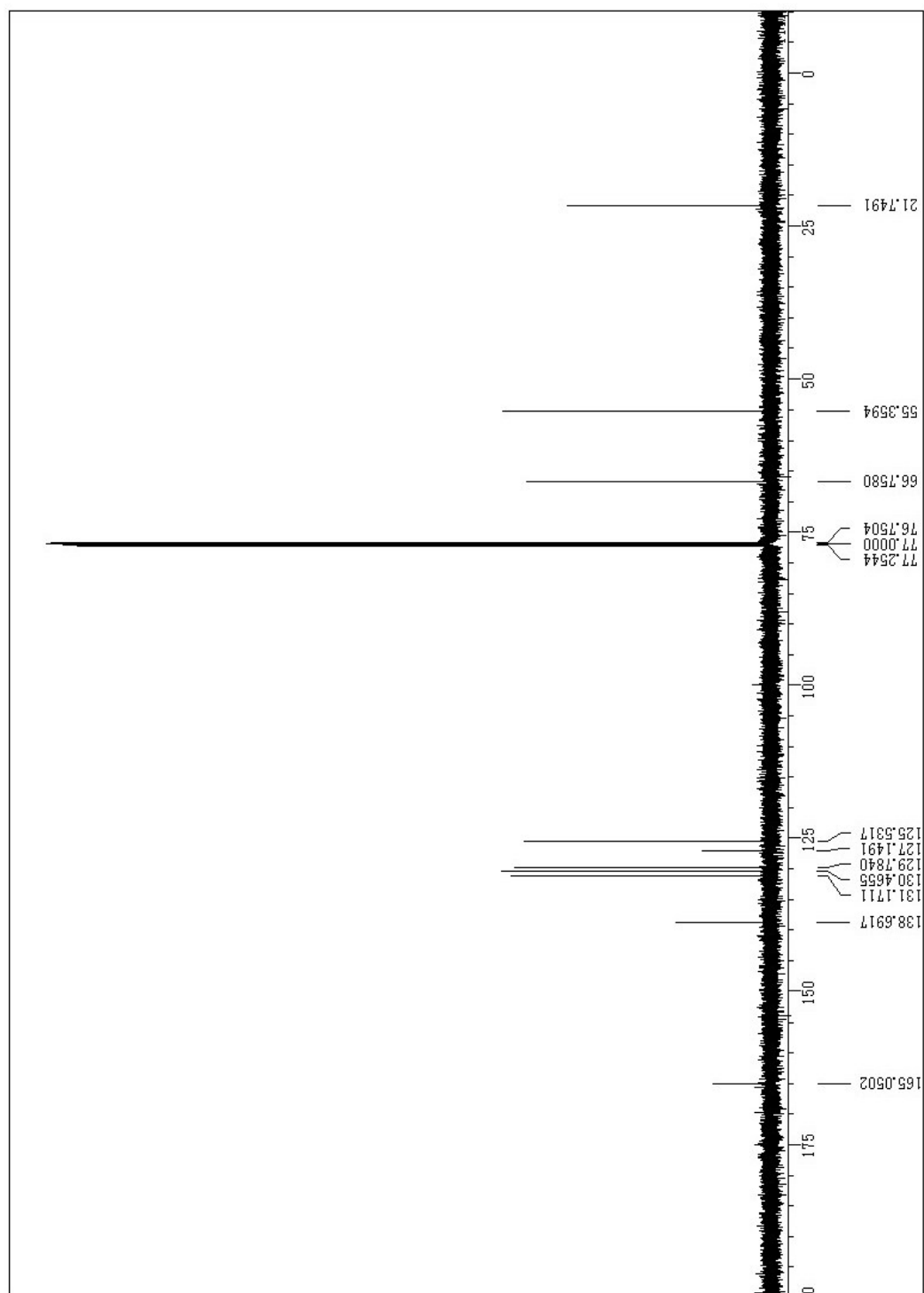
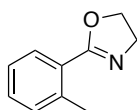
$^{13}\text{C}$  NMR of 2-(2,6-Dimethylphenyl)-4,5-dihydrooxazole (Table 2, entry 2)



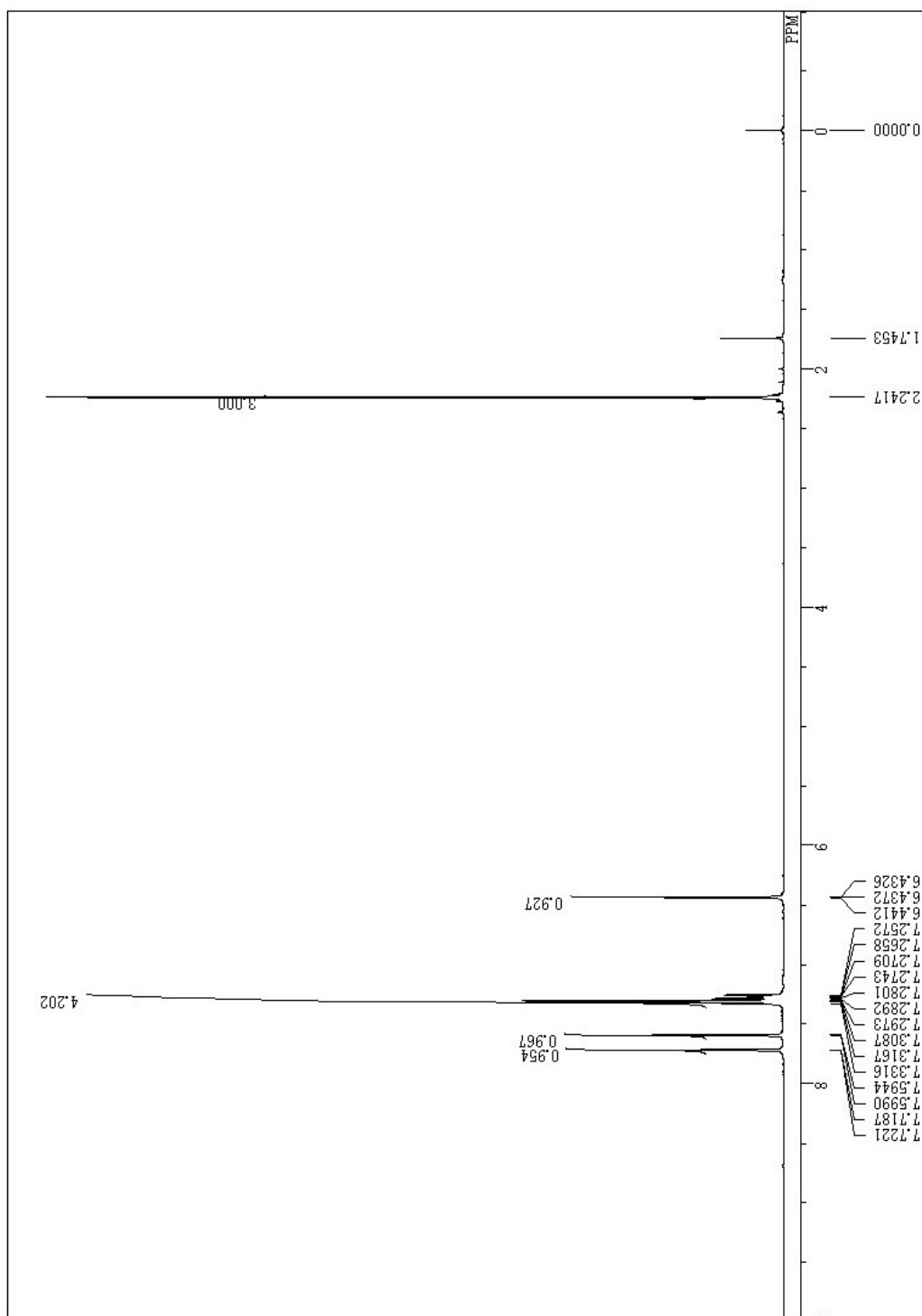
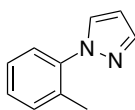
<sup>1</sup>H NMR of 2-(2-Methylphenyl)-4,5-dihydrooxazole (Table 2, entry 2)



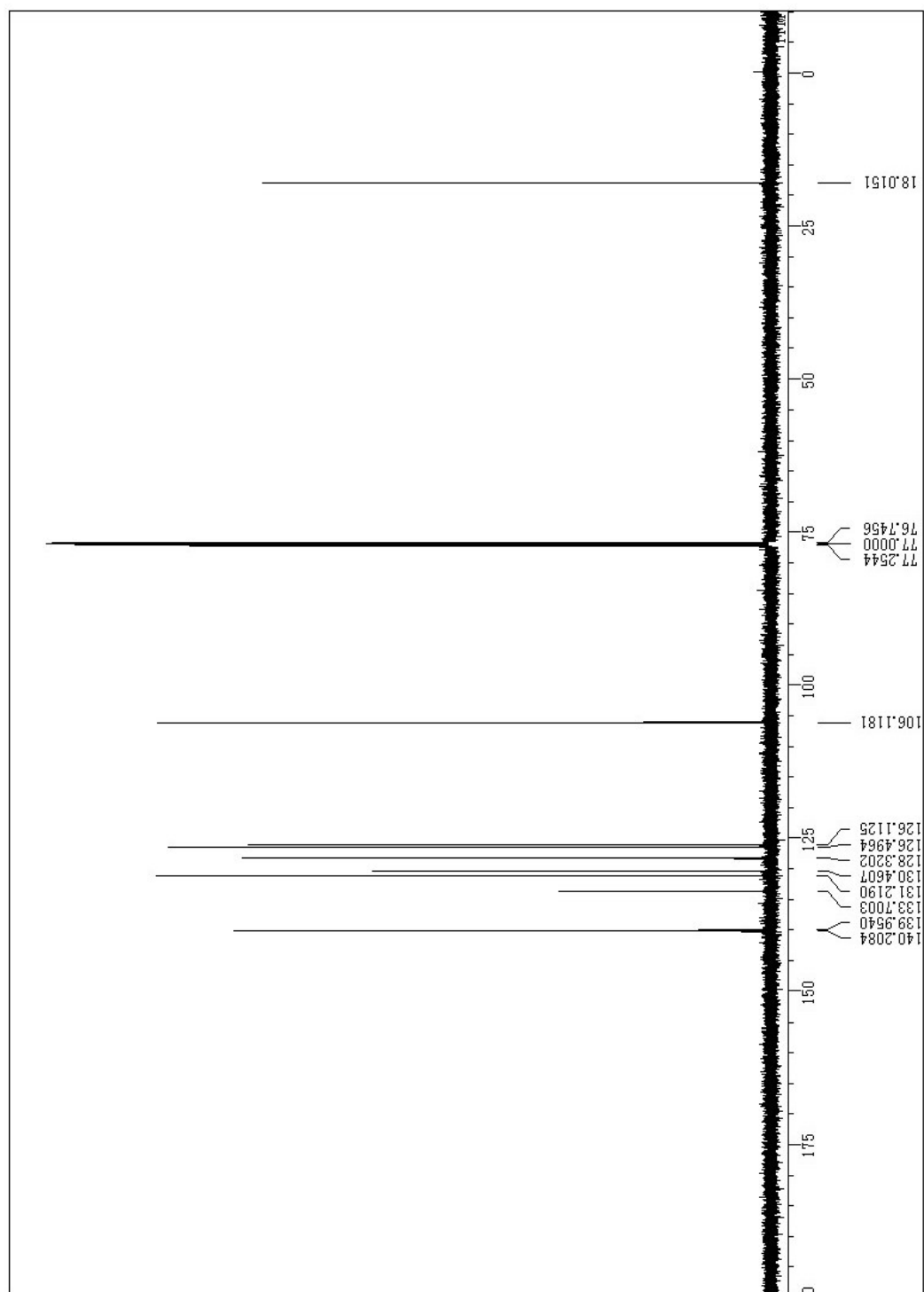
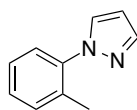
$^{13}\text{C}$  NMR of 2-(2-Methylphenyl)-4,5-dihydrooxazole (Table 2, entry 2)



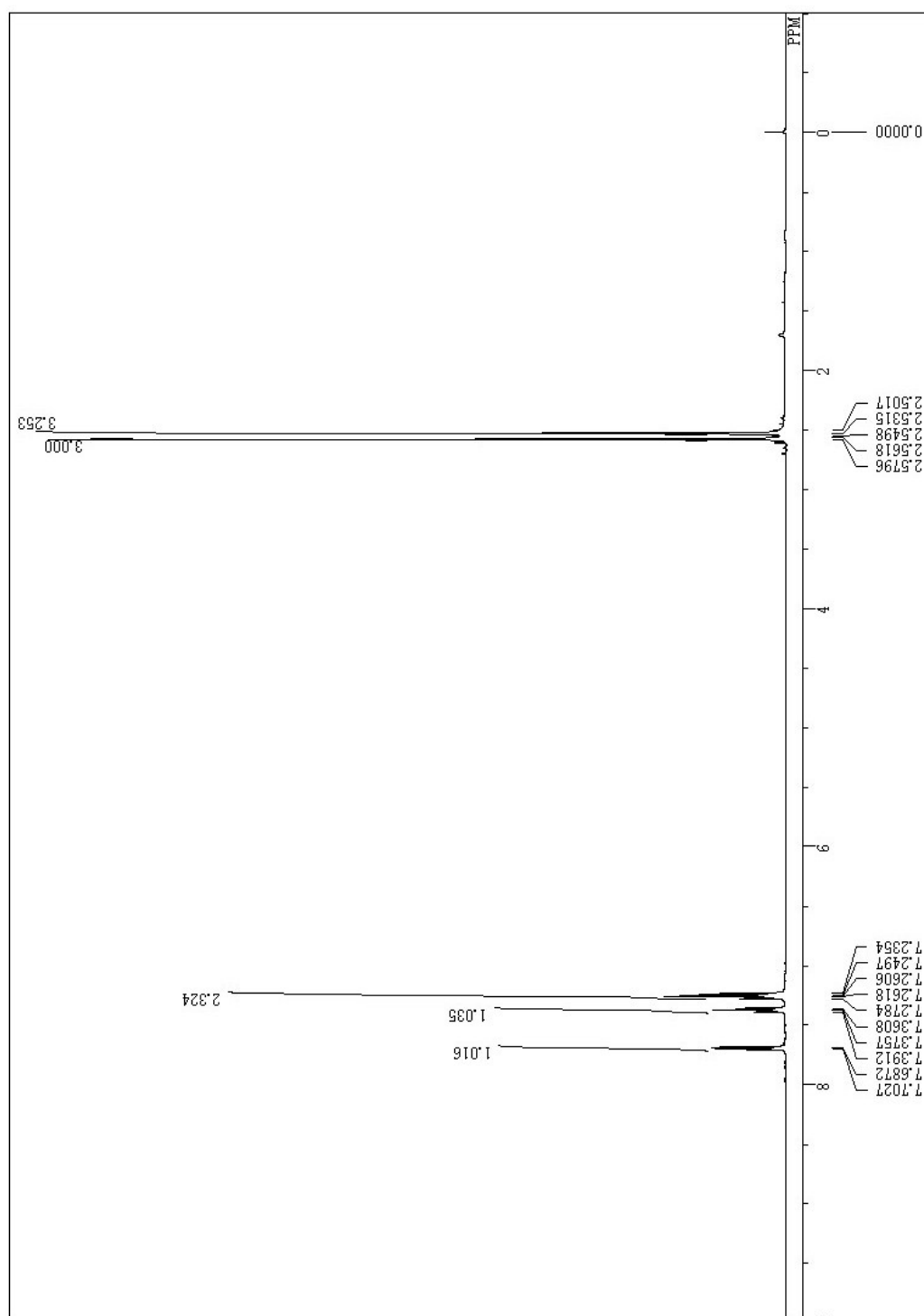
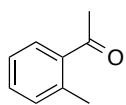
<sup>1</sup>H NMR of 1-(2-Methylphenyl)pyrazole (Table 2, entry 3)



<sup>13</sup>C NMR of 1-(2-Methylphenyl)pyrazole (Table 2, entry 3)

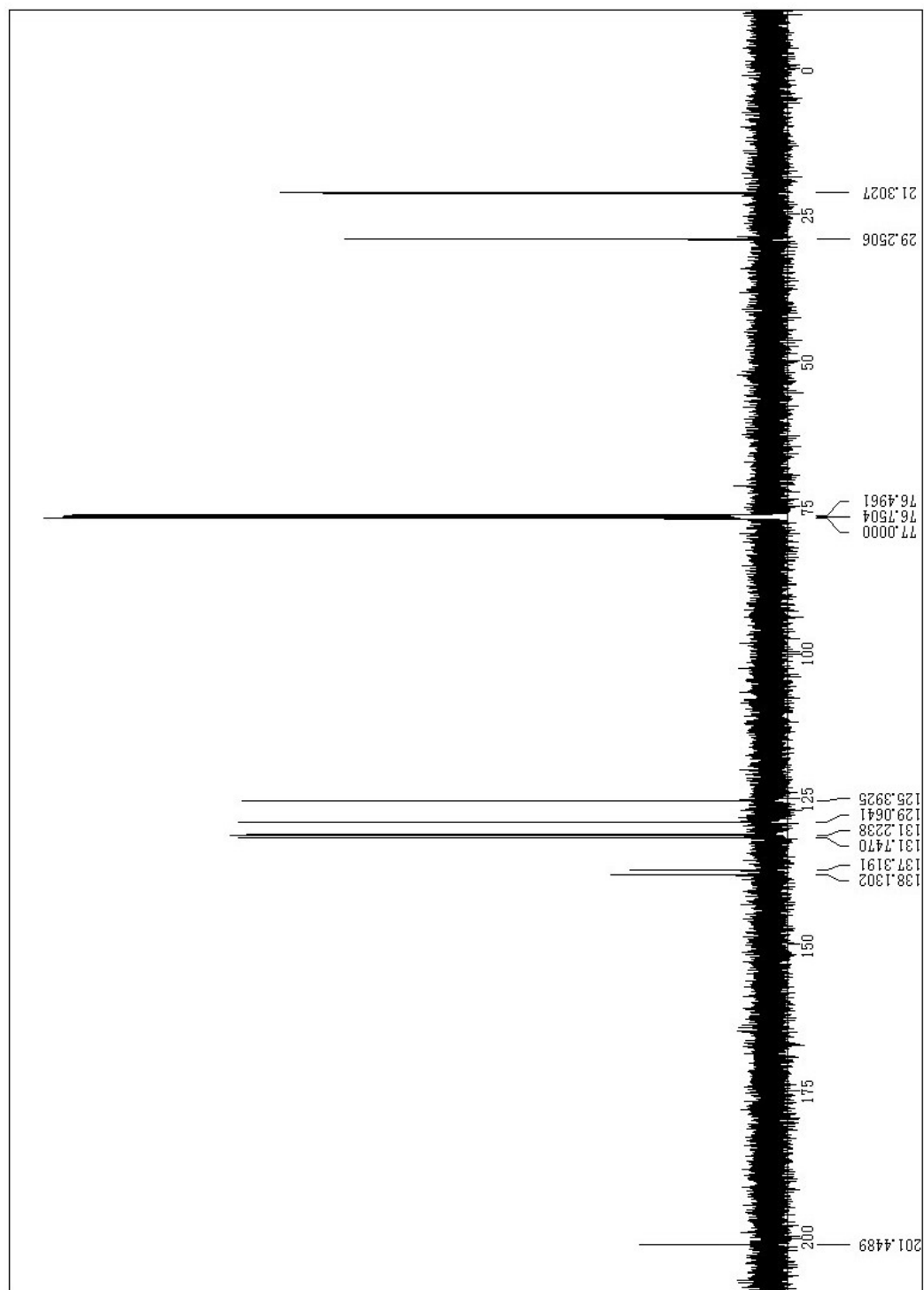
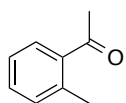


$^1\text{H}$  NMR of 1-(2-Methylphenyl)ethanone (Table 2, entry 4)

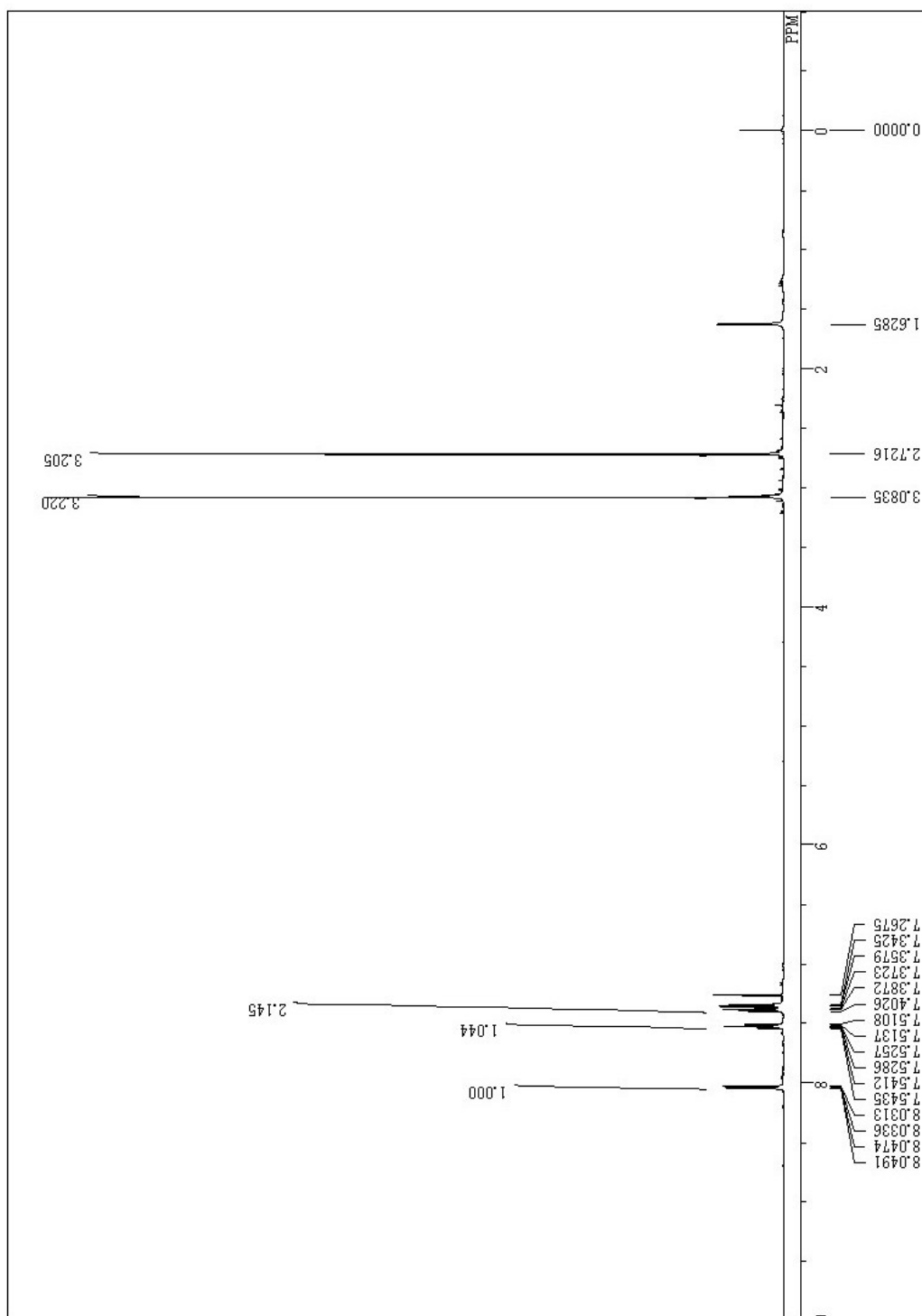
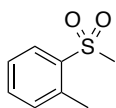




$^{13}\text{C}$  NMR of 1-(2-Methylphenyl)ethanone (Table 2, entry 4)



<sup>1</sup>H NMR of 1-Methyl-2-(methylsulfonyl)benzene (Table 2, entry 5)



$^{13}\text{C}$  NMR of 1-Methyl-2-(methylsulfonyl)benzene (Table 2, entry 5)

