

# Supporting Information

## **Buchwald-Hartwig Amination of Aryl Esters and Chlorides catalyzed by Dianisole-decorated Pd-NHC complex**

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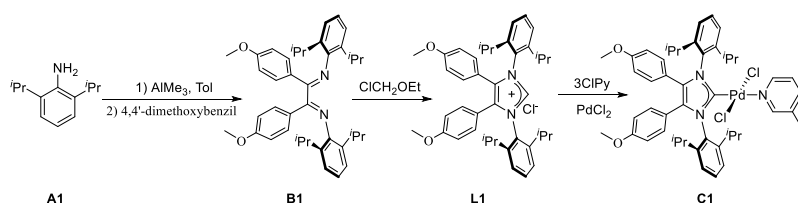
## 1. General experimental information

**Physical Measurements and Materials.** All aryl esters, amines and chlorides were purchased from Aldrich Chemical. 1,2-bis(4-methoxyphenyl)ethane-1,2-dione, chloromethyl ethyl ether, palladium chloride, trimethylaluminum (2 M, hexane), and inorganic bases were also commercially obtained from Aldrich Chemical. 2,6-diisopropylaniline was distilled under reduced pressure before being used. 3-chloropyridine, toluene, 1,4-dioxane and other solvents were purchased from Guangzhou Chemical Reagent Factory and used as received. Complexes PEPPSI-IPr,<sup>1</sup> PEPPSI-IPr<sup>An</sup>,<sup>2</sup> and **C1**<sup>3</sup> were prepared according to the previously reported procedures.

The NMR data of the compounds were obtained on a Varian Mercury-Plus 400 MHz spectrometer at ambient temperature with the decoupled nucleus, using the CDCl<sub>3</sub> as solvent and referenced versus TMS as the standard. *J* values are given in Hz. GC yields for optimization studies were obtained using a Shimadzu GC-2010 Plus instrument. Unless otherwise indicated, all reactions have been carried out with parallel reactors under an air atmosphere. All work-up and purification procedures were carried out with reagent-grade solvents (purchased from Guangzhou Chemical Reagent Factory) in air. Standard column chromatography techniques using silica gel were used for purification.

## 2. Preparation of Catalyst C1

**Preparation of Catalyst C1:** The complex **C1** was prepared according to previously reported procedure (as shown below).<sup>3</sup>



**Procedure for the Synthesis of  $\alpha$ -Diimine Compound B1.** 2,6-diisopropylaniline (3.55g, 20 mmol), trimethylaluminum (10 mL, 2 M) and toluene (10 mL), a stir bar were added into a flask under N<sub>2</sub> atmosphere and the resulting mixture was refluxed for 2 h. After the mixture was cooled to room temperature, 4,4'-dimethoxybenzil (10 mmol) was carefully added. Then the resulted mixture was heated under reflux for another 6 h. After completion of the reaction, the reaction mixture was cooled to room temperature, hydrolyzed with 5% aqueous NaOH solution, and then stirred for another 1 h. After stirring was stopped for a moment, the mixture was layered, the aqueous layer was extracted three times with ethyl acetate, and then the organic layers were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The resulting crude compound was purified by column chromatography to give the titled product **B1** in 35% yield as yellow solids.

**B1:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (1H, s, Ar-H), 7.31 (2H, d,  $J = 41.2$  Hz, Ar-H), 7.02 (8H, t,  $J = 33.1$  Hz, Ar-H), 6.68 (3H, d,  $J = 68.4$  Hz, Ar-H), 3.91 – 3.66 (6H, m, OCH<sub>3</sub>), 3.07 (3H, d,  $J = 55.4$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.32 (1H, s, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 – 0.57 (24H, m, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  160.5, 145.5, 135.2, 131.4, 131.1, 130.3, 123.4, 123.1, 122.4, 113.7, 113.3, 55.2, 28.8, 28.4, 27.6, 23.5, 22.6, 22.0. ESI-MS  $m/z$ : 589.65, [**B1+H**]<sup>+</sup> (C<sub>40</sub>H<sub>49</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, calcd 589.38).

**Procedure for the Synthesis of Imidazolium Salt L1.**  $\alpha$ -Diimine compound **B1** (1.17g, 2 mmol) and chloromethyl ethyl ether (75 mmol, 7 mL) were added to a thick-walled reaction vessel under a nitrogen atmosphere. The vessel was sealed and the mixture was allowed to heat at 100 °C for 16 h. After cooled to room temperature, the reaction

mixture was treated with anhydrous Et<sub>2</sub>O and stirred for another 1 h, causing the formation of a great deal of precipitate. The solid was isolated by filtration and washed three times with anhydrous Et<sub>2</sub>O. The resulting product was obtained as yellowish powder in 92% yield.

**L1:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.99 (1H, s, NCHN), 7.53 (2H, t, *J* = 7.8 Hz, Ar-H), 7.30 – 7.27 (4H, m, Ar-H), 6.96 – 6.91 (4H, m, Ar-H), 6.74 – 6.70 (4H, m, Ar-H), 3.74 (6H, s, OCH<sub>3</sub>), 2.51 (4H, dt, *J* = 13.5, 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.32 (12H, d, *J* = 6.8 Hz, CH<sub>3</sub>), 1.09 (12H, d, *J* = 6.8 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.7, 145.1, 139.1, 132.1, 132.0, 131.3, 128.4, 124.7, 116.4, 114.4, 55.3, 29.4, 25.5, 22.6. ESI-MS *m/z*: 601.78, [L1- Cl]<sup>+</sup> (C<sub>41</sub>H<sub>49</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, calcd 601.38).

**Procedures for the Synthesis of Pd-PEPPSI complex C1.** A mixture of imidazolium salt **L1** (0.637g, 1 mmol), palladium dichloride (0.195 g, 1.1 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.382 g, 10 mmol) in 3-chloropyridine (4 mL) was allowed to stir at 90 °C for 24 h. After the solution was cooled to room temperature, 20 mL of dichloromethane was added, and then the resulting mixture was placed on a short silica gel column and eluted with substantial dichloromethane. Evaporation of the filtrate provided a yellow-brown solid. The yellow-brown solid was dissolved in the right amount of DCM and then the resulting DCM solution was dropped into a large amount of vigorously stirring hexane, resulting in the formation of a yellow precipitate. The suspension was filtered and dried in vacuo to afford the desired Pd-PEPPSI complex **C1** in 92% yield.

**C1:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.66 (1H, d, *J* = 2.2 Hz, Ar-H), 8.58 (1H, dd, *J* = 5.5, 1.0 Hz, Ar-H), 7.57 – 7.53 (1H, m, Ar-H), 7.47 (2H, t, *J* = 7.7 Hz, Ar-H), 7.28

(4H, d,  $J = 7.8$  Hz, Ar-H), 7.07 (1H, dd,  $J = 8.1, 5.6$  Hz, Ar-H), 6.72 (4H, d,  $J = 8.9$  Hz, Ar-H), 6.57 (4H, d,  $J = 8.9$  Hz, Ar-H), 3.70 (6H, d,  $J = 5.9$  Hz, OCH<sub>3</sub>), 3.24 (4H, dt,  $J = 13.1, 6.5$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.56 (12H, d,  $J = 6.5$  Hz, CH<sub>3</sub>), 0.70 (12H, d,  $J = 6.7$  Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.3, 153.9, 150.5, 149.5, 146.8, 137.3, 134.2, 133.6, 132.1, 131.8, 130.0, 124.8, 124.2, 120.7, 113.6, 55.1, 28.7, 25.9, 24.8. ESI-MS  $m/z$ :  $m/z$ : 707.61, [C1 - (3ClPy + 2Cl)+H]<sup>+</sup> (C<sub>41</sub>H<sub>49</sub>N<sub>2</sub>O<sub>2</sub>Pd<sup>+</sup>, calcd 707.28). Anal. calcd for C<sub>46</sub>H<sub>52</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>2</sub>Pd: C, 61.96; H, 5.88; N, 4.71. Found: C, 61.62; H, 5.94; N, 4.63.

### 3. General procedure for aryl ester amination reactions

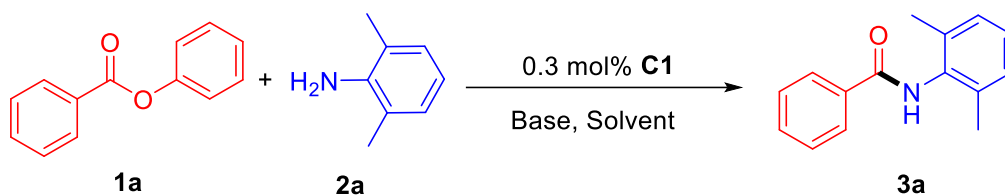
Under an air atmosphere, Pd-PEPPSI complex (0.003 mmol, 0.30 mol%), aryl ester (1.00 mmol), amine (1.20 mmol), base (1.50 mmol), H<sub>2</sub>O (0.10 mmol, 10 mol%) and solvent (3 mL) were added into a sealable vial which equipped with a magnetic stir bar. The reaction mixture was allowed to stir at 110 °C for 16 h. After the indicated time, the reaction solution was cooled to room temperature, and 20 mL of water and 20 mL of dichloromethane were added into the vial. The resulting mixture was then allowed to stir for another several minutes, followed by extraction with dichloromethane three times (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The resulting residue was then purified by silica-gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford corresponding products **3-7**. The observed characterization data (<sup>1</sup>H NMR and <sup>13</sup>C NMR) were consistent with that previously reported in the literature.<sup>4-20</sup> The isolated yields of products were calculated based on the feedings of the aryl esters.

### 4. General procedure for aryl chloride amination reactions

Under an air atmosphere, Pd-PEPPSI complex (0.001 mmol, 0.10 mol%), aryl

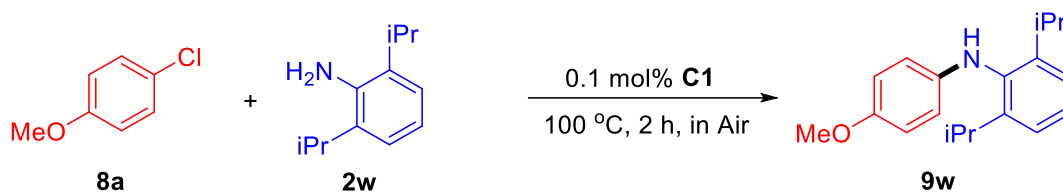
chloride (1.00 mmol), amine (1.20 mmol), base (1.50 mmol), and solvent (4 mL) were added into a sealable vial which equipped with a magnetic stir bar. The reaction mixture was allowed to stir at 100 °C for 2 h. After cooled to room temperature, 20 mL of water and 20 mL of dichloromethane were added into the vial. The resulting mixture was then allowed to vigorously stir for another few minutes, followed by extraction with dichloromethane three times (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The resulting residue was then purified by silica-gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford corresponding products **9-18**. The observed characterization data (<sup>1</sup>H NMR and <sup>13</sup>C NMR) were consistent with that previously reported in the literature.<sup>21-31</sup> The isolated yields of products were calculated based on the amounts of aryl chlorides.

## **5. Tables of reaction optimization.**

**Table S1.** Optimization of **C1** catalyzed Aryl Ester Amination.<sup>a</sup>

Run	Base	Solvent	Additives	Yield(%) <sup>b</sup>
1	K <sub>2</sub> CO <sub>3</sub>	Toluene	None	0
2 <sup>c</sup>	K <sub>2</sub> CO <sub>3</sub>	Toluene	H <sub>2</sub> O	86
<b>3</b>	<b>K<sub>2</sub>CO<sub>3</sub></b>	<b>Toluene</b>	<b>H<sub>2</sub>O</b>	<b>97(93)<sup>d</sup></b>
4	K <sub>3</sub> PO <sub>4</sub>	Toluene	H <sub>2</sub> O	31
5	Na <sub>2</sub> CO <sub>3</sub>	Toluene	H <sub>2</sub> O	95
6	KO <sup>t</sup> Bu	Toluene	H <sub>2</sub> O	88
7	KO <sup>i</sup> Am	Toluene	H <sub>2</sub> O	92
8	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	H <sub>2</sub> O	96
9	NaOH	Toluene	H <sub>2</sub> O	94
10	K <sub>2</sub> CO <sub>3</sub>	THF	H <sub>2</sub> O	36
11	K <sub>2</sub> CO <sub>3</sub>	DMF	H <sub>2</sub> O	0
12	K <sub>2</sub> CO <sub>3</sub>	DMAc	H <sub>2</sub> O	0
13	K <sub>2</sub> CO <sub>3</sub>	DMSO	H <sub>2</sub> O	0
14	K <sub>2</sub> CO <sub>3</sub>	dioxane	H <sub>2</sub> O	26
15	K <sub>2</sub> CO <sub>3</sub>	NMP	H <sub>2</sub> O	0
16	K <sub>2</sub> CO <sub>3</sub>	xylene	H <sub>2</sub> O	2
17 <sup>e</sup>	K <sub>2</sub> CO <sub>3</sub>	Toluene	H <sub>2</sub> O	0

<sup>a</sup>Reagents and conditions: Phenyl benzoate (1 mmol), 2,6-dimethylaniline (1.2 mmol), Pd-PEPPSI<sup>(PhOMe)<sub>2</sub></sup> (0.3% mmol, 0.3 mol%), base (1.5 mmol), H<sub>2</sub>O (0.1 mmol, 10 mol%), and solvent (3 mL) in air. <sup>b</sup>GC yield, average of two runs. <sup>c</sup>The reaction was performed with 3 eq H<sub>2</sub>O. <sup>d</sup>Isolated yields in parentheses. <sup>e</sup>The reaction was performed without the presence of precatalyst **C1**.

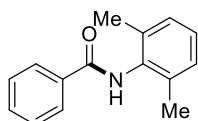
**Table S2.** Optimization of **C1** catalyzed Aryl Chloride Amination.<sup>a</sup>

Run	Base	Solvent	Yield(%) <sup>b</sup>
<b>1</b>	<b>KO<sup>t</sup>Am</b>	<b>1,4-dioxane</b>	<b>93(90)<sup>c</sup></b>
2	KO <sup>t</sup> Bu	1,4-dioxane	87
3	NaO <sup>t</sup> Bu	1,4-dioxane	51
4	KOH	1,4-dioxane	22
5	KO <sup>t</sup> Am	Toluene	45
6	KO <sup>t</sup> Am	DME	82
7	KO <sup>t</sup> Am	THF	39

<sup>a</sup>Reagents and conditions: 4-chloroanisole (1 mmol), 2,6-diisopropylaniline (1.2 mmol), Pd-PEPPSI<sup>(PhOMe)<sub>2</sub></sup> (0.1% mmol), base (1.5 mmol), and solvent (4 mL) in air. <sup>b</sup>GC yield, average of two runs. <sup>c</sup>Isolated yields in parentheses.

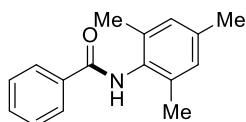
## 6. Characterization data of aryl ester amination products

**N-(2,6-dimethylphenyl)benzamide (3a, 209 mg, 93%)<sup>4</sup>**



White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (2H, d, *J* = 7.0 Hz, Ar-H), 7.75 (1H, s, NH-H), 7.50 (3H, dt, *J* = 8.5, 7.1 Hz, Ar-H), 7.29 (2H, s, Ar-H), 6.80 (1H, s, Ar-H), 2.33 (6H, s, CH<sub>3</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.6, 156.6, 135.0, 131.7, 131.0, 128.7, 127.0, 122.1, 114.2, 55.5.

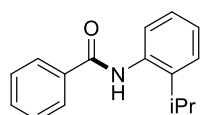
**N-mesitylbenzamide (3b, 213 mg, 89%)<sup>5</sup>**



Colorless solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (2H, d, *J* = 7.9 Hz, Ar-H), 7.54 (1H, d, *J* = 7.2 Hz, Ar-H), 7.49 (2H, d, *J* = 7.1 Hz, Ar-H), 7.39 (1H, s, NH-H), 6.93 (2H, s, Ar-H), 2.29 (3H, s, CH<sub>3</sub>-H), 2.23 (6H, s, CH<sub>3</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.1, 137.1, 135.3, 134.6, 131.7, 131.2, 129.0, 128.7, 127.2, 20.9, 18.3.

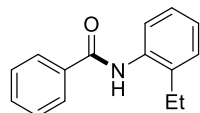
**N-(2-isopropylphenyl)benzamide (3c, 232 mg, 97%)<sup>6</sup>**





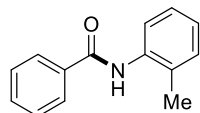
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (2H, d,  $J = 7.4$  Hz, Ar-H), 7.80 (2H, s, Ar-H, NH-H), 7.52 (3H, dt,  $J = 27.7, 7.2$  Hz, Ar-H), 7.32 (1H, d,  $J = 2.6$  Hz, Ar-H), 7.26 – 7.20 (2H, m, Ar-H), 3.17 – 3.05 (1H, m, CH-H), 1.28 (6H, d,  $J = 6.8$  Hz,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 140.6, 134.9, 134.1, 131.8, 128.8, 127.0, 126.5, 126.2, 125.7, 124.8, 28.2, 23.0.

**N-(2-ethylphenyl)benzamide (3d)**, 221 mg, 98%<sup>7</sup>



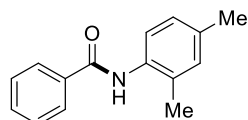
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.74 (3H, m, Ar-H), 7.82 (1H, s, NH-H), 7.58 – 7.52 (1H, m, Ar-H), 7.47 (2H, t,  $J = 7.6$  Hz, Ar-H), 7.27 – 7.14 (3H, m, Ar-H), 2.67 (2H, d,  $J = 7.6$  Hz,  $\text{CH}_2$ -H), 1.26 (3H, t,  $J = 7.6$  Hz,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 135.3, 135.0, 134.9, 131.8, 128.8, 128.5, 127.0, 126.7, 125.7, 123.8, 24.3, 13.9.

**N-(o-tolyl)benzamide (3e)**, 198 mg, 94%<sup>4</sup>



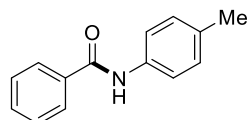
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (1H, m, Ar-H), 7.89 (2H, dd,  $J = 5.3, 3.3$  Hz, Ar-H), 7.68 (1H, s, NH-H), 7.53 (3H, ddd,  $J = 13.2, 7.9, 6.4$  Hz, Ar-H), 7.27 (1H, s, Ar-H), 7.24 (1H, d,  $J = 7.2$  Hz, Ar-H), 7.13 (1H, dd,  $J = 7.5, 1.1$  Hz, Ar-H), 2.34 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 135.8, 135.0, 131.8, 130.6, 129.2, 128.8, 127.0, 126.9, 125.4, 123.1, 17.8.

**N-(2,4-dimethylphenyl)benzamide (3f)**, 214 mg, 95%<sup>8</sup>



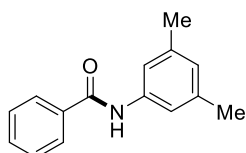
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (2H, d,  $J = 7.2$  Hz, Ar-H), 7.75 (1H, d,  $J = 7.6$  Hz, Ar-H), 7.62 (1H, s, NH-H), 7.58 – 7.54 (1H, m, Ar-H), 7.49 (2H, t,  $J = 7.3$  Hz, Ar-H), 7.06 (2H, d,  $J = 8.0$  Hz, Ar-H), 2.32 (3H, s,  $\text{CH}_3$ -H), 2.30 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 135.2, 135.0, 133.1, 131.7, 131.2, 129.6, 128.8, 127.4, 127.0, 123.4, 20.9, 17.8.

**N-(p-tolyl)benzamide (3g)**, 209 mg, 99%<sup>8</sup>



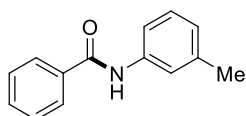
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (1H, s, NH-H), 7.85 (2H, dd,  $J = 5.3, 3.3$  Hz, Ar-H), 7.53 (3H, t,  $J = 6.7$  Hz, Ar-H), 7.48 – 7.43 (2H, m, Ar-H), 7.16 (2H, d,  $J = 8.2$  Hz, Ar-H), 2.34 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 135.4, 135.1, 134.2, 131.7, 129.5, 128.7, 127.0, 120.3, 20.9.

**N-(3,5-dimethylphenyl)benzamide (3h)**, 216 mg, 96%<sup>8</sup>



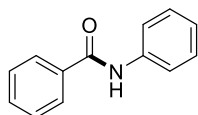
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.83 (3H, m, Ar-H, NH-H), 7.52 (1H, d,  $J = 7.3$  Hz, Ar-H), 7.46 (2H, dd,  $J = 8.1, 6.7$  Hz, Ar-H), 7.28 (2H, s, Ar-H), 6.79 (1H, s, Ar-H), 2.31 (6H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 138.7, 137.7, 135.1, 131.7, 128.7, 127.0, 126.3, 117.9, 21.4.

**N-(*m*-tolyl)benzamide (3i, 209 mg, 99%)<sup>9</sup>**



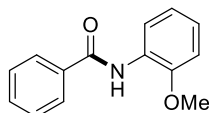
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (1H, s, NH-H), 7.65 (2H, dd,  $J = 5.2, 3.3$  Hz, Ar-H), 7.36 – 7.27 (3H, m, Ar-H), 7.26 – 7.20 (2H, m, Ar-H), 7.07 – 7.00 (1H, m, Ar-H), 6.77 (1H, d,  $J = 7.5$  Hz, Ar-H), 2.15 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 139.1, 137.8, 135.1, 131.8, 128.9, 128.8, 127.0, 125.4, 120.8, 117.3, 21.5.

**N-phenylbenzamide (3j, 195 mg, 99%)<sup>4</sup>**



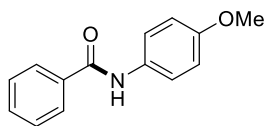
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (3H, dd,  $J = 8.3, 1.3$  Hz, Ar-H), 7.65 (2H, d,  $J = 7.6$  Hz, Ar-H), 7.55 (1H, s, NH-H), 7.49 (2H, d,  $J = 7.7$  Hz, Ar-H), 7.40 – 7.32 (2H, m, Ar-H), 7.16 (1H, s, Ar-H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 137.9, 135.0, 131.8, 129.1, 128.8, 127.0, 124.6, 120.2.

**N-(2-methoxyphenyl)benzamide (3k, 141 mg, 62%)<sup>10</sup>**



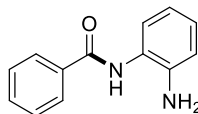
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (3H, dd,  $J = 12.8, 5.5$  Hz, Ar-H), 7.75 (1H, s, NH-H), 7.57 – 7.53 (1H, m, Ar-H), 7.50 – 7.45 (2H, m, Ar-H), 7.25 – 7.20 (2H, m, Ar-H), 7.11 (1H, td,  $J = 7.5, 1.1$  Hz, Ar-H), 2.32 (3H, s,  $\text{OCH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 135.7, 135.0, 131.8, 130.5, 129.4, 128.8, 127.0, 126.8, 125.4, 123.2, 17.8.

**N-(4-methoxyphenyl)benzamide (3l, 213 mg, 94%)<sup>10</sup>**



White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (2H, d,  $J = 7.2$  Hz, Ar-H), 7.80 (1H, s, NH-H), 7.56 – 7.52 (3H, m, Ar-H), 7.49 – 7.45 (2H, m, Ar-H), 6.92 – 6.89 (2H, m, Ar-H), 3.81 (3H, s,  $\text{OCH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 156.6, 135.0, 131.7, 130.9, 128.7, 127.0, 122.1, 114.2, 55.5.

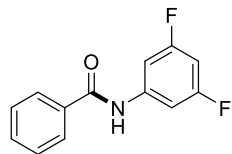
**N-(2-aminophenyl)benzamide (3m, 167 mg, 79%)<sup>11</sup>**



Brown solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (1H, s, NH-H), 7.89 (2H, d,  $J = 4.0$  Hz, Ar-H), 7.56 (1H, t,  $J = 7.4$  Hz, Ar-H), 7.48 (2H, t,  $J = 7.5$  Hz, Ar-H), 7.31 (1H, d,  $J = 7.9$  Hz, Ar-H), 7.09 (1H, td,  $J$

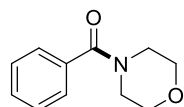
= 7.8, 1.4 Hz, Ar-H), 6.86 – 6.82 (2H, m, Ar-H), 3.87 (2H, s, NH<sub>2</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 140.7, 134.1, 131.9, 128.7, 127.3, 127.2, 125.2, 124.5, 119.8, 118.4.

**N-(3,5-difluorophenyl)benzamide (3n)**, 228 mg, 98%<sup>8</sup>



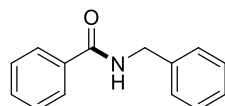
White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (1H, s, NH-H), 7.83 (2H, d, *J* = 7.3 Hz, Ar-H), 7.52 (3H, dt, *J* = 14.8, 7.2 Hz, Ar-H), 7.27 (2H, d, *J* = 9.0 Hz, Ar-H), 6.59 (1H, t, *J* = 8.8 Hz, Ar-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 164.5, 164.3, 162.0, 161.9, 140.2, 140.1, 139.9, 134.2, 132.3, 128.9, 127.0, 103.3, 103.2, 103.1, 103.0, 100.0, 99.8, 99.5.

**morpholino(phenyl)methanone (3o)**, 183 mg, 96%<sup>12</sup>



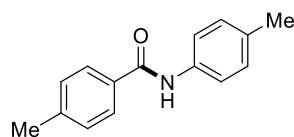
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 (5H, d, *J* = 1.4 Hz, Ar-H), 3.77 – 3.31 (8H, m, CH<sub>2</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.4, 135.3, 129.9, 128.5, 127.1, 66.9, 30.9.

**N-benzylbenzamide (3p)**, 192 mg, 91%<sup>8</sup>



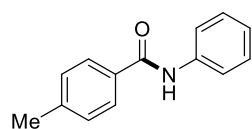
White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 – 7.76 (2H, m, Ar-H), 7.53 – 7.47 (1H, m, Ar-H), 7.42 (2H, dd, *J* = 8.1, 6.7 Hz, Ar-H), 7.33 (5H, dd, *J* = 21.3, 4.5 Hz, Ar-H), 6.50 (1H, s, NH-H), 4.64 (2H, d, *J* = 5.7 Hz, CH<sub>2</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 138.2, 134.4, 131.5, 128.8, 128.6, 127.9, 127.6, 126.9, 44.1.

**4-methyl-N-(p-tolyl)benzamide (4g)**, 221 mg, 98%<sup>9</sup>



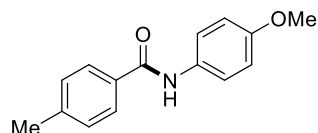
White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (1H, s, NH-H), 7.76 (2H, d, *J* = 8.2 Hz, Ar-H), 7.52 (2H, d, *J* = 8.4 Hz, Ar-H), 7.30 – 7.26 (2H, m, Ar-H), 7.16 (2H, d, *J* = 8.2 Hz, Ar-H), 2.42 (3H, s, CH<sub>3</sub>-H), 2.34 (3H, s, CH<sub>3</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.6, 142.2, 135.4, 134.0, 132.2, 129.5, 129.4, 127.0, 120.2, 21.5, 20.9.

**4-methyl-N-phenylbenzamide (4j)**, 209 mg, 99%<sup>12</sup>



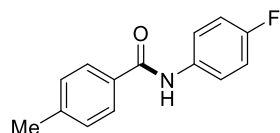
White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 (1H, s, NH-H), 7.77 (2H, d, *J* = 8.2 Hz, Ar-H), 7.64 (2H, d, *J* = 7.6 Hz, Ar-H), 7.38 (2H, d, *J* = 7.5 Hz, Ar-H), 7.29 (2H, d, *J* = 7.9 Hz, Ar-H), 7.15 (1H, s, Ar-H), 2.43 (3H, s, CH<sub>3</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.6, 142.4, 138.0, 132.1, 129.4, 129.1, 127.0, 124.4, 120.1, 21.5.

**N-(4-methoxyphenyl)-4-methylbenzamide (4l)**, 236 mg, 98%<sup>4</sup>



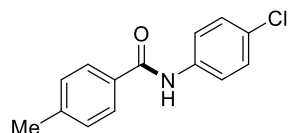
Beige solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (1H, s, NH-H), 7.75 (2H, d,  $J = 8.1$  Hz, Ar-H), 7.53 (2H, d,  $J = 8.9$  Hz, Ar-H), 7.27 (1H, s, Ar-H), 7.25 (1H, s, Ar-H), 6.92 – 6.87 (2H, m, Ar-H), 3.80 (3H, s,  $\text{OCH}_3$ -H), 2.41 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 156.6, 142.2, 132.2, 131.1, 129.4, 127.0, 122.1, 114.2, 55.5, 21.5.

**N-(4-fluorophenyl)-4-methylbenzamide (4q)**, 218 mg, 95%)<sup>13</sup>



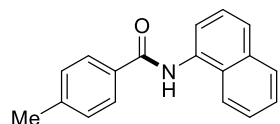
White solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (1H, s, NH-H), 7.76 (2H, d,  $J = 8.2$  Hz, Ar-H), 7.62 – 7.56 (2H, m, Ar-H), 7.30 (2H, s, Ar-H), 7.09 – 7.03 (2H, m, Ar-H), 2.43 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 160.7, 158.3, 142.5, 134.0, 131.8, 129.5, 127.0, 122.1, 122.0, 115.8, 115.6, 21.5.

**N-(4-chlorophenyl)-4-methylbenzamide (4r)**, 162 mg, 66%)<sup>14</sup>



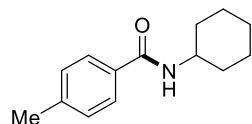
White solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (2H, m, Ar-H, NH-H), 7.75 (1H, s, Ar-H), 7.60 (2H, d,  $J = 8.9$  Hz, Ar-H), 7.31 (4H, dd,  $J = 14.8, 8.4$  Hz, Ar-H), 2.43 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 142.7, 136.6, 131.7, 129.5, 129.4, 129.1, 127.0, 121.3, 21.3.

**4-methyl-N-(naphthalen-1-yl)benzamide (4s)**, 144 mg, 55%)<sup>15</sup>



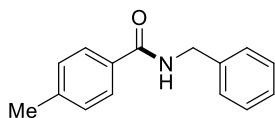
White solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (1H, s, NH-H), 8.04 (1H, d,  $J = 7.4$  Hz, Ar-H), 7.92 – 7.87 (4H, m, Ar-H), 7.74 (1H, d,  $J = 8.3$  Hz, Ar-H), 7.56 – 7.49 (3H, m, Ar-H), 7.33 (2H, d,  $J = 7.9$  Hz, Ar-H), 2.45 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.5, 134.2, 132.5, 132.0, 129.5, 128.9, 127.4, 127.2, 126.4, 126.0, 126.0, 125.8, 121.1, 120.6, 21.5.

**N-cyclohexyl-4-methylbenzamide (4t)**, 204 mg, 94%)<sup>15</sup>



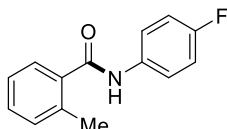
White solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (2H, d,  $J = 8.2$  Hz, Ar-H), 7.22 – 7.18 (2H, m, Ar-H), 6.11 (1H, s, NH-H), 4.01 – 3.91 (1H, m, CH-H), 2.38 (3H, s,  $\text{CH}_3$ -H), 2.04 – 1.98 (2H, m,  $\text{CH}_2$ -H), 1.78 – 1.71 (2H, m,  $\text{CH}_2$ -H), 1.68 – 1.59 (1H, m,  $\text{CH}_2$ -H), 1.46 – 1.34 (2H, m,  $\text{CH}_2$ -H), 1.28 – 1.16 (3H, m,  $\text{CH}_2$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 141.5, 132.2, 129.1, 126.8, 48.8, 48.5, 33.2, 25.6, 24.9, 21.4.

**N-benzyl-4-methylbenzamide (4p)**, 140 mg, 62%)<sup>15</sup>



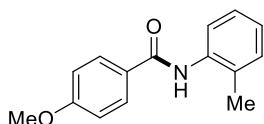
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (2H, d,  $J = 8.2$  Hz, Ar-H), 7.36 (4H, d,  $J = 4.5$  Hz, Ar-H), 7.30 (1H, dd,  $J = 8.4, 3.5$  Hz, Ar-H), 7.23 (2H, d,  $J = 7.9$  Hz, Ar-H), 6.40 (1H, s, NH-H), 4.64 (2H, d,  $J = 5.7$  Hz,  $\text{CH}_2$ -H), 2.39 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 141.9, 138.3, 131.5, 129.2, 128.7, 127.8, 127.5, 126.9, 44.0, 21.4.

**N-(4-fluorophenyl)-2-methylbenzamide (5q)**, 218 mg, 95%)<sup>16</sup>



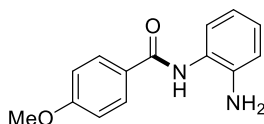
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (3H, m, Ar-H, NH-H), 7.46 (1H, d,  $J = 7.5$  Hz, Ar-H), 7.37 (1H, t,  $J = 7.0$  Hz, Ar-H), 7.29 – 7.24 (2H, m, Ar-H), 7.05 (2H, t,  $J = 8.6$  Hz, Ar-H), 2.49 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 136.5, 136.1, 133.93, 131.3, 130.4, 126.6, 125.9, 121.7, 121.6, 115.8, 115.6, 19.8.

**4-methoxy-N-(o-tolyl)benzamide (6e)**, 234 mg, 97%)<sup>17</sup>



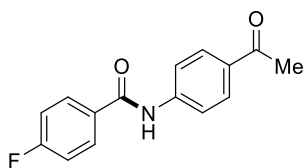
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (1H, d,  $J = 7.9$  Hz, Ar-H), 7.87 – 7.84 (2H, m, Ar-H), 7.60 (1H, s, NH-H), 7.26 – 7.21 (2H, m, Ar-H), 7.11 (1H, dt,  $J = 7.4, 3.7$  Hz, Ar-H), 6.99 (2H, d,  $J = 8.9$  Hz, Ar-H), 3.88 (3H, s,  $\text{OCH}_3$ -H), 2.34 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 162.5, 135.9, 130.5, 129.0, 128.9, 127.2, 126.9, 125.1, 123.0, 114.0, 55.5, 17.8.

**N-(2-aminophenyl)-4-methoxybenzamide (6m)**, 232 mg, 96%)<sup>18</sup>



White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (1H, s, Ar-H), 7.86 (1H, s, Ar-H), 7.77 (1H, s, NH-H), 7.30 (1H, d,  $J = 7.6$  Hz, Ar-H), 7.08 (1H, dt,  $J = 7.9, 3.8$  Hz, Ar-H), 6.98 – 6.96 (2H, m, Ar-H), 6.86 – 6.82 (3H, m, Ar-H,  $\text{NH}_2$ -H), 5.30 (1H, s,  $\text{NH}_2$ -H), 3.88 (3H, s,  $\text{OCH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6, 140.7, 129.2, 127.1, 126.4, 125.2, 124.8, 119.8, 118.4, 116.7, 114.0, 55.47.

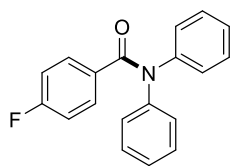
**N-(4-acetylphenyl)-4-fluorobenzamide (7u)**, 193 mg, 75%)<sup>19</sup>



Pale yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (1H, s, NH-H), 7.98 (2H, m, Ar-H), 7.91 (2H, dd,  $J = 8.9, 5.2$  Hz, Ar-H), 7.75 (2H, d,  $J = 8.8$  Hz, Ar-H), 7.19 (2H, t,  $J = 8.6$  Hz, Ar-H), 2.60 (3H, s,  $\text{CH}_3$ -

H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.0, 142.1, 133.2, 130.6, 129.9, 129.6, 129.5, 119.3, 116.2, 116.0, 26.5.

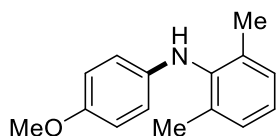
**4-fluoro-N,N-diphenylbenzamide (7v, 274 mg, 94%)<sup>20</sup>**



White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.44 (2H, m, Ar-H), 7.30 (4H, t,  $J = 7.7$  Hz, Ar-H), 7.20 (2H, t,  $J = 7.4$  Hz, Ar-H), 7.14 (4H, d,  $J = 7.7$  Hz, Ar-H), 6.89 (2H, t,  $J = 8.7$  Hz, Ar-H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 143.8, 131.6, 131.5, 129.2, 127.42, 126.5, 115.1, 114.9, 100.0.

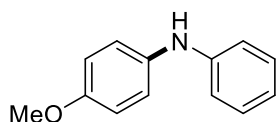
## 7. Characterization data of aryl chloride amination products

**N-(4-methoxyphenyl)-2,6-dimethylaniline (9a, 214 mg, 94%)<sup>21</sup>**



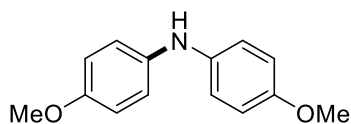
Brown solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15 – 6.98 (3H, m, Ar-H), 6.75 (2H, d,  $J = 8.3$  Hz, Ar-H), 6.49 (2H, d,  $J = 8.1$  Hz, Ar-H), 5.02 (1H, s, NH-H), 3.74 (3H, s,  $\text{OCH}_3$ -H), 2.19 (6H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 139.3, 137.3, 134.9, 128.6, 125.0, 115.3, 114.7, 55.7, 18.4.

**4-methoxy-N-phenylaniline (9j, 171 mg, 86%)<sup>21</sup>**



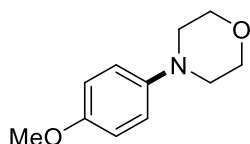
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 – 7.18 (2H, m, Ar-H), 7.08 – 7.04 (2H, m, Ar-H), 6.91 – 6.88 (2H, m, Ar-H), 6.87 – 6.84 (2H, m, Ar-H), 6.82 (1H, t,  $J = 4.2$  Hz, Ar-H), 5.48 (1H, s, NH-H), 3.79 (3H, s,  $\text{OCH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 145.1, 135.6, 129.3, 122.1, 119.5, 115.6, 114.6, 55.5.

**bis(4-methoxyphenyl)amine (9l, 209 mg, 91%)<sup>22</sup>**



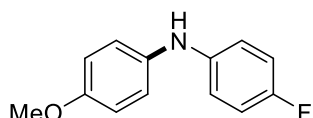
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.95 (4H, d,  $J = 9.0$  Hz, Ar-H), 6.83 (4H, d,  $J = 9.0$  Hz, Ar-H), 5.29 (1H, s, NH-H), 3.79 (6H, s,  $\text{OCH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 137.9, 119.5, 114.7, 55.6.

**4-(4-methoxyphenyl)morpholine (9o, 178 mg, 92%)<sup>22</sup>**



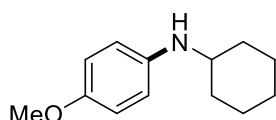
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.87 (4H, q,  $J = 9.2$  Hz, Ar-H), 3.91 – 3.82 (4H, m,  $\text{OCH}_2\text{-H}$ ), 3.77 (3H, s,  $\text{CH}_3\text{-H}$ ), 3.11 – 3.01 (4H, m,  $\text{NCH}_2\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 145.6, 117.8, 114.5, 67.0, 55.5, 50.8.

**4-fluoro-N-(4-methoxyphenyl)aniline (9q)**, 187 mg, 86%)<sup>21</sup>



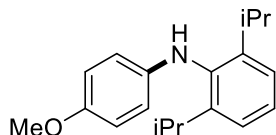
Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.03 – 6.86 (8H, m, Ar-H), 5.42 (1H, s, NH-H), 3.81 (3H, s,  $\text{OCH}_3\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 155.9, 154.9, 141.0, 141.0, 136.4, 121.1, 117.7, 117.6, 115.8, 115.6, 114.7, 55.5.

**N-cyclohexyl-4-methoxyaniline (9t)**, 187 mg, 91%)<sup>22</sup>



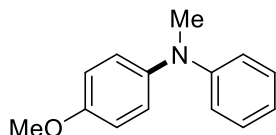
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.78 (2H, d,  $J = 8.9$  Hz, Ar-H), 6.59 (2H, d,  $J = 8.9$  Hz, Ar-H), 3.75 (3H, s,  $\text{OCH}_3\text{-H}$ ), 3.18 (1H, ddd,  $J = 13.7, 10.1, 3.5$  Hz, CH-H), 3.07 (1H, s, NH-H), 2.06 (2H, d,  $J = 10.4$  Hz,  $\text{CH}_2\text{-H}$ ), 1.77 (2H, d,  $J = 13.3$  Hz,  $\text{CH}_2\text{-H}$ ), 1.66 – 1.07 (6H, m,  $\text{CH}_2\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.8, 141.5, 114.8, 114.8, 55.7, 52.7, 33.5, 25.9, 25.0.

**2-isopropyl-N-(4-methoxyphenyl)-6-propylaniline (9w)**, 255 mg, 90%)<sup>22</sup>



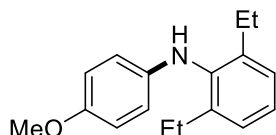
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.16 (3H, m, Ar-H), 6.79 (2H, d,  $J = 8.2$  Hz, Ar-H), 6.50 (2H, d,  $J = 8.2$  Hz, Ar-H), 5.02 (1H, s, NH-H), 3.79 (3H, s,  $\text{OCH}_3\text{-H}$ ), 3.26 (2H, dt,  $J = 13.6, 6.8$  Hz, CH-H), 1.20 (12H, d,  $J = 6.9$  Hz,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 147.1, 142.3, 136.1, 126.7, 123.8, 114.7, 114.2, 55.7, 28.1, 23.8.

**4-methoxy-N-methyl-N-phenylaniline (9x)**, 200 mg, 94%)<sup>22</sup>



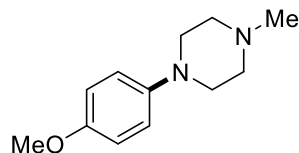
Orange oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (2H, t,  $J = 7.5$  Hz, Ar-H), 7.07 (2H, d,  $J = 8.2$  Hz, Ar-H), 6.87 (2H, d,  $J = 8.0$  Hz, Ar-H), 6.77 (3H, t,  $J = 7.7$  Hz, Ar-H), 3.78 (3H, s,  $\text{OCH}_3\text{-H}$ ), 3.24 (3H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 149.7, 142.2, 128.8, 126.1, 118.3, 115.7, 114.7, 55.4, 40.4.

**2,6-diethyl-N-(4-methoxyphenyl)aniline (9y)**, 235 mg, 92%)<sup>22</sup>



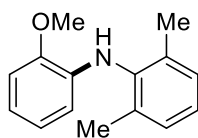
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (3H, s, Ar-H), 6.74 (2H, d,  $J = 8.3$  Hz, Ar-H), 6.47 (2H, d,  $J = 8.3$  Hz, Ar-H), 5.01 (1H, s, NH-H), 3.74 (3H, s,  $\text{OCH}_3$ -H), 2.57 (4H, q,  $J = 7.5$  Hz,  $\text{CH}_2$ -H), 1.15 (6H, t,  $J = 7.5$  Hz,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 141.5, 141.3, 137.9, 126.7, 125.9, 114.8, 114.7, 55.7, 24.7, 14.6.

**1-(4-methoxyphenyl)-4-methylpiperazine (9z, 171 mg, 83%)<sup>22</sup>**



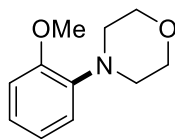
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.90 (2H, d,  $J = 9.1$  Hz, Ar-H), 6.85 – 6.81 (2H, m, Ar-H), 3.75 (3H, s,  $\text{OCH}_3$ -H), 3.12 – 3.07 (4H, m,  $\text{NCH}_2$ -H), 2.60 – 2.55 (4H, m,  $\text{NMe-CH}_2$ -H), 2.34 (3H, s,  $\text{NCH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7, 145.6, 118.1, 114.3, 55.5, 55.2, 50.5, 46.1.

**N-(2-methoxyphenyl)-2,6-dimethylaniline (10a, 204 mg, 90%)<sup>21</sup>**



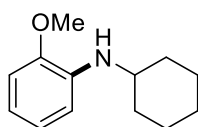
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 (3H, q,  $J = 5.8$  Hz, Ar-H), 6.96 – 6.83 (1H, m, Ar-H), 6.74 (2H, dd,  $J = 6.1, 3.7$  Hz, Ar-H), 6.15 (1H, dd,  $J = 7.1, 2.0$  Hz, Ar-H), 5.67 (1H, s, NH-H), 3.97 (3H, s,  $\text{OCH}_3$ -H), 2.23 (6H, s,  $\text{CH}_3$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 138.4, 136.1, 135.9, 128.4, 125.7, 121.1, 117.3, 111.1, 109.9, 55.6, 18.3.

**4-(2-methoxyphenyl)morpholine (10o, 179 mg, 93%)<sup>21</sup>**



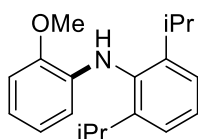
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06–6.78 (4H, m, Ar-H), 3.88 (7H, d,  $J = 11.3$  Hz,  $\text{OCH}_3$ -H,  $\text{OCH}_2$ -H), 3.07 (4H, s,  $\text{NCH}_2$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 141.0, 123.1, 120.9, 117.9, 111.2, 67.1, 55.3, 51.1.

**N-cyclohexyl-2-methoxyaniline (10t, 172 mg, 84%)<sup>21</sup>**



White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.94 (1H, t,  $J = 7.1$  Hz, Ar-H), 6.84 (1H, d,  $J = 7.4$  Hz, Ar-H), 6.72 (2H, d,  $J = 7.5$  Hz, Ar-H), 4.08 (1H, s, NH-H), 3.90 (3H, s,  $\text{OCH}_3$ -H), 3.35 (1H, t,  $J = 9.9$  Hz, CH-H), 2.16 (2H, d,  $J = 12.1$  Hz,  $\text{CH}_2$ -H), 1.86 (2H, d,  $J = 12.8$  Hz,  $\text{CH}_2$ -H), 1.58 – 1.18 (6H, m,  $\text{CH}_2$ -H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 137.1, 121.1, 115.7, 110.1, 109.4, 55.2, 51.2, 33.3, 25.9, 25.0.

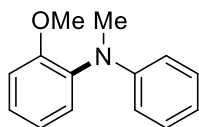
**2-isopropyl-N-(2-methoxyphenyl)-6-propylaniline (10w, 255 mg, 90%)<sup>21</sup>**





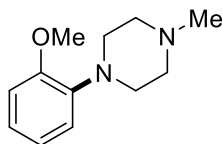
Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (1H, dd,  $J = 8.9, 6.1$  Hz, Ar-H), 7.52 – 7.49 (2H, m, Ar-H), 7.10 (1H, dd,  $J = 7.7, 1.5$  Hz, Ar-H), 7.01 – 6.92 (2H, m, Ar-H), 6.43 (1H, dd,  $J = 7.6, 1.8$  Hz, Ar-H), 5.96 (1H, s, NH-H), 4.15 (3H, s,  $\text{OCH}_3$ -H), 3.52 – 3.44 (2H, m, CH-H), 1.43 (12H, d,  $J = 7.0$  Hz,  $\text{CH}_3$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.4, 146.1, 137.8, 135.3, 127.0, 123.6, 121.0, 116.7, 110.8, 109.5, 55.4, 28.0, 23.7.

**4-methoxy-N-methyl-N-phenylaniline (10x)**, 185 mg, 87%)<sup>21</sup>



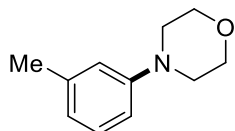
Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (2H, t,  $J = 7.5$  Hz, Ar-H), 7.07 (2H, d,  $J = 8.2$  Hz, Ar-H), 6.87 (2H, d,  $J = 8.0$  Hz, Ar-H), 6.77 (3H, t,  $J = 7.7$  Hz, Ar-H), 3.78 (3H, s,  $\text{OCH}_3$ -H), 3.24 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 149.7, 142.2, 128.8, 126.1, 118.3, 115.7, 114.7, 55.4, 40.4.

**1-(2-methoxyphenyl)-4-methylpiperazine (10z)**, 183 mg, 89%)<sup>21</sup>



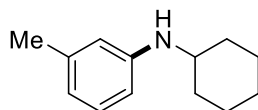
Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.00 – 6.62 (4H, m, Ar-H), 3.77 (3H, s,  $\text{OCH}_3$ -H), 3.04 (4H, s,  $\text{NCH}_2$ -H), 2.56 (4H, s,  $\text{NMe-CH}_2$ -H), 2.29 (3H, s,  $\text{NCH}_3$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 141.1, 123.0, 120.9, 118.2, 111.1, 55.3, 55.1, 50.3, 45.8.

**4-(m-tolyl)morpholine (11o)**, 163 mg, 92%)<sup>23</sup>



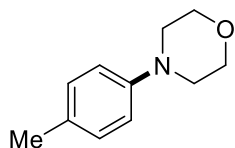
Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (1H, t,  $J = 7.6$  Hz, Ar-H), 6.84 – 6.62 (3H, m, Ar-H), 3.95 – 3.75 (4H, m,  $\text{OCH}_2$ -H), 3.16 (4H, d,  $J = 4.0$  Hz,  $\text{NCH}_2$ -H), 2.34 (3H, s,  $\text{CH}_3$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3, 138.9, 129.0, 120.9, 116.5, 112.8, 67.0, 49.5, 21.8.

**N-cyclohexyl-3-methylaniline (11t)**, 170 mg, 90%)<sup>24</sup>



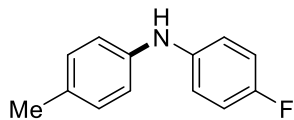
Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06 – 7.01 (1H, m, Ar-H), 6.48 (1H, d,  $J = 7.7$  Hz, Ar-H), 6.39 (2H, d,  $J = 6.4$  Hz, Ar-H), 3.26 (1H, s, NH-H), 3.22 (1H, dd,  $J = 8.8, 5.1$  Hz, CH-H), 2.26 (3H, s,  $\text{CH}_3$ -H), 2.07 – 2.01 (2H, m,  $\text{CH}_2$ -H), 1.78 – 1.71 (2H, m,  $\text{CH}_2$ -H), 1.35 (2H, dt,  $J = 14.9, 7.8$  Hz,  $\text{CH}_2$ -H), 1.30 – 1.02 (4H, m,  $\text{CH}_2$ -H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.3, 138.9, 129.1, 117.7, 113.8, 110.2, 51.5, 33.5, 25.9, 25.0, 21.6.

**4-(p-tolyl)morpholine (12o)**, 161 mg, 91%)<sup>25</sup>



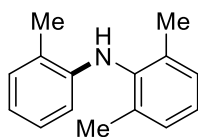
Off-white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (2H, d,  $J = 8.2$  Hz, Ar-H), 6.85 (2H, d,  $J = 8.2$  Hz, Ar-H), 4.04 – 3.65 (4H, m,  $\text{OCH}_2\text{-H}$ ), 3.46 – 2.92 (4H, m,  $\text{NCH}_2\text{-H}$ ), 2.29 (3H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.2, 129.7, 129.5, 116.0, 67.0, 49.9, 20.4.

**4-fluoro-N-(p-tolyl)aniline (12q)**, 173 mg, 86%)<sup>26</sup>



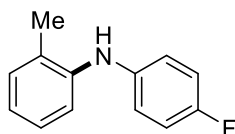
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06 (2H, d,  $J = 8.1$  Hz, Ar-H), 6.98 – 6.87 (6H, m, Ar-H), 5.46 (1H, s, NH-H), 2.28 (3H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 156.4, 141.0, 139.7, 139.7, 130.4, 129.9, 119.3, 119.3, 117.8, 115.9, 115.7, 20.6.

**2,6-dimethyl-N-(o-tolyl)aniline (13a)**, 165 mg, 78%)<sup>21</sup>



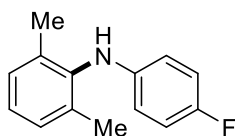
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 – 7.08 (4H, m, Ar-H), 6.99 (1H, t,  $J = 7.6$  Hz, Ar-H), 6.73 (1H, t,  $J = 7.3$  Hz, Ar-H), 6.17 (1H, d,  $J = 8.0$  Hz, Ar-H), 4.95 (1H, s, NH-H), 2.35 (3H, s,  $\text{CH}_3\text{-H}$ ), 2.21 (6H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 138.7, 135.5, 130.2, 128.5, 126.9, 125.5, 122.4, 118.1, 111.7, 18.3, 17.6.

**N-(4-fluorophenyl)-2-methylaniline (13q)**, 191 mg, 95%)<sup>27</sup>



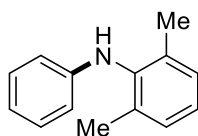
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (1H, d,  $J = 7.4$  Hz, Ar-H), 7.12 (2H, q,  $J = 8.0$  Hz, Ar-H), 7.04 – 6.88 (5H, m, Ar-H), 5.29 (1H, s, NH-H), 2.26 (3H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 156.6, 142.0, 139.7, 130.9, 127.2, 126.8, 121.4, 120.2, 120.1, 117.3, 116.0, 115.7, 17.8.

**N-(4-fluorophenyl)-2,6-dimethylaniline (14q)**, 189 mg, 88%)<sup>22</sup>



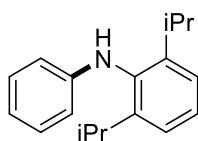
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (3H, dd,  $J = 14.2, 5.8$  Hz, Ar-H), 6.89 (2H, t,  $J = 8.4$  Hz, Ar-H), 6.56 – 6.40 (2H, m, Ar-H), 5.13 (1H, s, NH-H), 2.24 (6H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4, 155.1, 142.5, 138.5, 135.5, 128.6, 125.6, 115.7, 115.5, 114.5, 114.4, 18.2.

**2,6-dimethyl-N-phenylaniline (15a)**, 195 mg, 99%)<sup>21</sup>



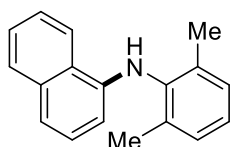
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 – 7.06 (5H, m, Ar-H), 6.76 – 6.71 (1H, m, Ar-H), 6.51 – 6.47 (2H, m, Ar-H), 5.15 (1H, s, NH-H), 2.20 (6H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.2, 138.1, 135.9, 129.2, 128.5, 125.7, 118.1, 113.4, 18.3.

**2-isopropyl-N-phenyl-6-propylaniline (15w, 233 mg, 92%)<sup>21</sup>**



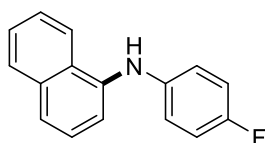
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 (3H, dt, *J* = 17.7, 7.7 Hz, Ar-H), 7.17 (2H, t, *J* = 7.7 Hz, Ar-H), 6.74 (1H, t, *J* = 7.3 Hz, Ar-H), 6.51 (2H, d, *J* = 7.9 Hz, Ar-H), 5.14 (1H, s, NH-H), 3.23 (2H, dt, *J* = 13.7, 6.8 Hz, CH-H), 1.17 (12H, d, *J* = 6.9 Hz, CH<sub>3</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.1, 147.6, 135.1, 129.2, 127.2, 123.8, 117.7, 112.9, 28.2, 23.8.

**N-(2,6-dimethylphenyl)naphthalen-1-amine (16a, 175 mg, 71%)<sup>21</sup>**



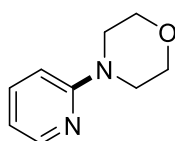
Colorless solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (1H, d, *J* = 7.8 Hz, Ar-H), 7.91 (1H, d, *J* = 5.9 Hz, Ar-H), 7.61 – 7.51 (2H, m, Ar-H), 7.37 (1H, d, *J* = 7.6 Hz, Ar-H), 7.32 – 7.14 (4H, m, Ar-H), 6.28 (1H, d, *J* = 7.1 Hz, Ar-H), 5.76 (1H, s, NH-H), 2.26 (6H, s, CH<sub>3</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.2, 138.7, 135.1, 134.5, 128.7, 128.7, 126.5, 125.8, 125.5, 125.0, 124.0, 120.4, 118.8, 107.3, 18.2.

**N-(4-fluorophenyl)naphthalen-1-amine (16q, 223 mg, 94%)<sup>28</sup>**



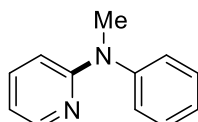
Brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (1H, d, *J* = 8.0 Hz, Ar-H), 7.91 (1H, d, *J* = 7.2 Hz, Ar-H), 7.55 (3H, ddd, *J* = 12.9, 10.9, 7.0 Hz, Ar-H), 7.42 (1H, t, *J* = 7.8 Hz, Ar-H), 7.27 (1H, t, *J* = 5.4 Hz, Ar-H), 7.11 – 6.93 (4H, m, Ar-H), 5.89 (1H, s, NH-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.9, 156.6, 140.4, 139.6, 134.6, 128.6, 127.0, 126.1, 126.0, 125.6, 122.4, 121.4, 119.9, 119.8, 116.0, 115.8, 114.2.

**4-(pyridin-2-yl)morpholine (17o, 144 mg, 88%)<sup>21</sup>**



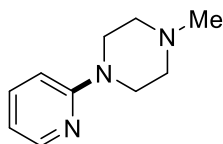
Pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (1H, d, *J* = 4.1 Hz, Ar-H), 7.45 (1H, t, *J* = 7.8 Hz, Ar-H), 6.61 (2H, dd, *J* = 13.5, 7.4 Hz, Ar-H), 3.90 – 3.68 (4H, m, CH<sub>2</sub>-H), 3.64 – 3.38 (4H, m, CH<sub>2</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.6, 147.9, 137.5, 113.8, 106.9, 66.7, 45.6.

**N-methyl-N-phenylpyridin-2-amine (17x, 180 mg, 98%)<sup>29</sup>**



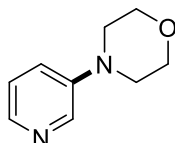
Orange oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (1H, d, *J* = 4.6 Hz, Ar-H), 7.32 (6H, ddt, *J* = 32.6, 25.3, 7.4 Hz, Ar-H), 6.67 – 6.51 (2H, m, Ar-H), 3.51 (3H, s, CH<sub>3</sub>-H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.9, 147.8, 146.9, 136.5, 129.7, 126.3, 125.4, 113.1, 109.2, 38.4.

**1-methyl-4-(pyridin-2-yl)piperazine (17z, 170 mg, 96%)<sup>30</sup>**



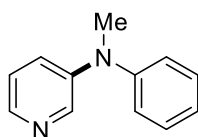
Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 – 8.16 (1H, m, Ar-H), 7.46 (1H, ddd,  $J = 8.7, 7.1, 2.0$  Hz, Ar-H), 6.61 (2H, ddd,  $J = 7.3, 5.5, 4.6$  Hz, Ar-H), 3.57 – 3.53 (4H, m,  $\text{NCH}_2\text{-H}$ ), 2.53 – 2.50 (4H, m,  $\text{NMe-CH}_2\text{-H}$ ), 2.34 (3H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 147.9, 137.4, 113.3, 107.1, 54.9, 46.2, 45.1.

**4-(pyridin-3-yl)morpholine (18o)**, 157 mg, 96%)<sup>30</sup>



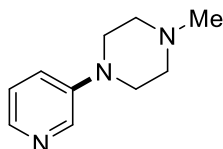
Yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (1H, s, Ar-H), 8.12 (1H, s, Ar-H), 7.17 (2H, s, Ar-H), 3.92 – 3.79 (4H, m,  $\text{OCH}_2\text{-H}$ ), 3.40 – 3.00 (4H, m,  $\text{NCH}_2\text{-H}$ ).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 141.1, 138.3, 123.5, 122.1, 66.7, 48.6.

**N-methyl-N-phenylpyridin-3-amine (18x)**, 177 mg, 96%)<sup>21</sup>



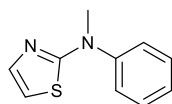
Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (1H, d,  $J = 1.5$  Hz, Ar-H), 8.15 (1H, d,  $J = 4.4$  Hz, Ar-H), 7.47 – 6.94 (7H, m, Ar-H), 3.35 (3H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.9, 145.1, 141.1, 140.5, 129.6, 124.8, 123.4, 123.3, 122.4, 40.0.

**1-methyl-4-(pyridin-3-yl)piperazine (18z)**, 156 mg, 89%)<sup>31</sup>



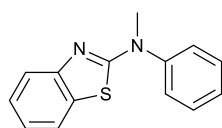
Orange oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (1H, d,  $J = 1.8$  Hz, Ar-H), 8.09 (1H, dd,  $J = 4.0, 1.5$  Hz, Ar-H), 7.24 – 7.05 (2H, m, Ar-H), 3.35 – 3.09 (4H, m,  $\text{NCH}_2\text{-H}$ ), 2.70 – 2.50 (4H, m,  $\text{NMe-CH}_2\text{-H}$ ), 2.36 (3H, s,  $\text{CH}_3\text{-H}$ ).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 140.5, 138.4, 123.4, 122.3, 54.7, 48.2, 46.0.

**N-methyl-N-phenylthiazol-2-amine (19x)**, 103 mg, 54%)<sup>29</sup>



Yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.29 (4H, m, Ar-H), 7.18 (2H, dd,  $J = 12.8, 4.2$  Hz, Ar-H), 6.41 (1H, d,  $J = 3.6$  Hz, Ar-H), 3.47 (3H, s,  $\text{NMe}$ ).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 146.5, 139.3, 129.7, 126.3, 124.9, 107.5, 77.3, 77.0, 76.7, 40.4.

**N-methyl-N-phenylbenzo[d]thiazol-2-amine (20x)**, 161 mg, 67%)<sup>29</sup>



Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (1H, d,  $J = 8.1$  Hz, Ar-H), 7.38 (5H, dt,  $J = 13.5, 7.5$  Hz, Ar-H), 7.29 – 7.18 (2H, m, Ar-H), 6.99 (1H, t,  $J = 7.6$  Hz, Ar-H), 3.57 (3H, s, *NMe*).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 152.6, 145.8, 131.1, 129.9, 127.4, 125.9, 121.7, 120.4, 119.1, 77.3, 77.0, 76.7, 40.4.

## 8. NMR spectrums in the preparation of C1

Figure S1. The  $^1\text{H}$  NMR spectrum of B1.

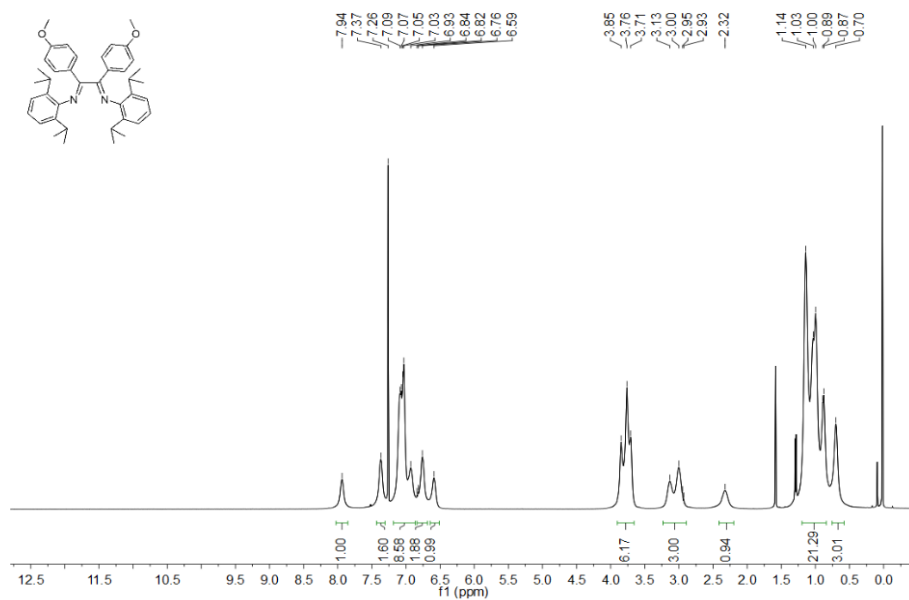


Figure S2. The  $^{13}\text{C}$  NMR spectrum of B1.

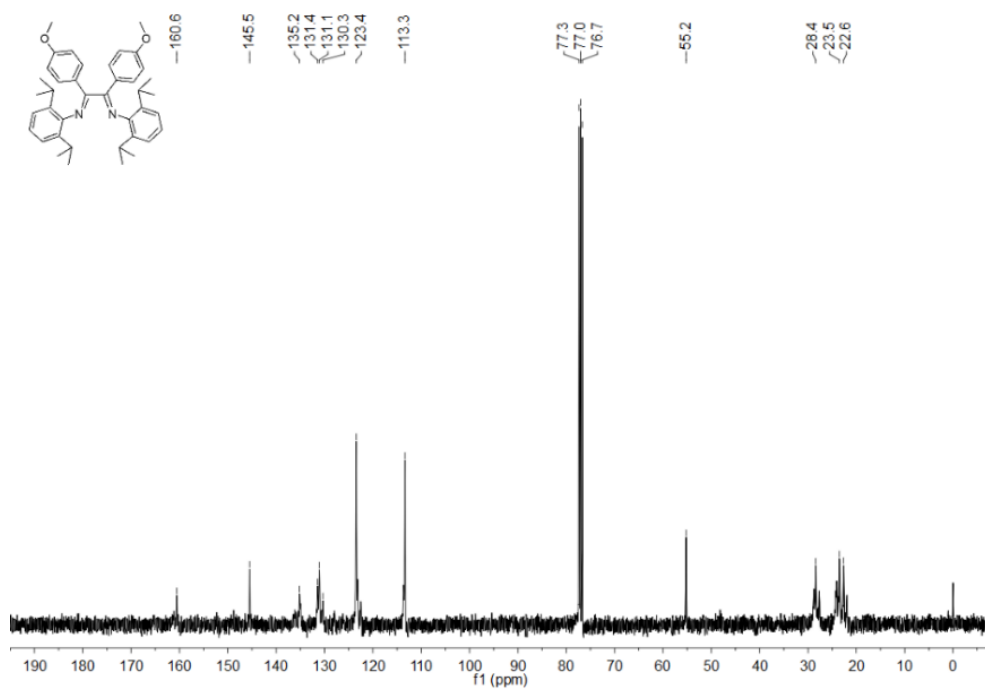


Figure S3. The  $^1\text{H}$  NMR spectrum of L1.

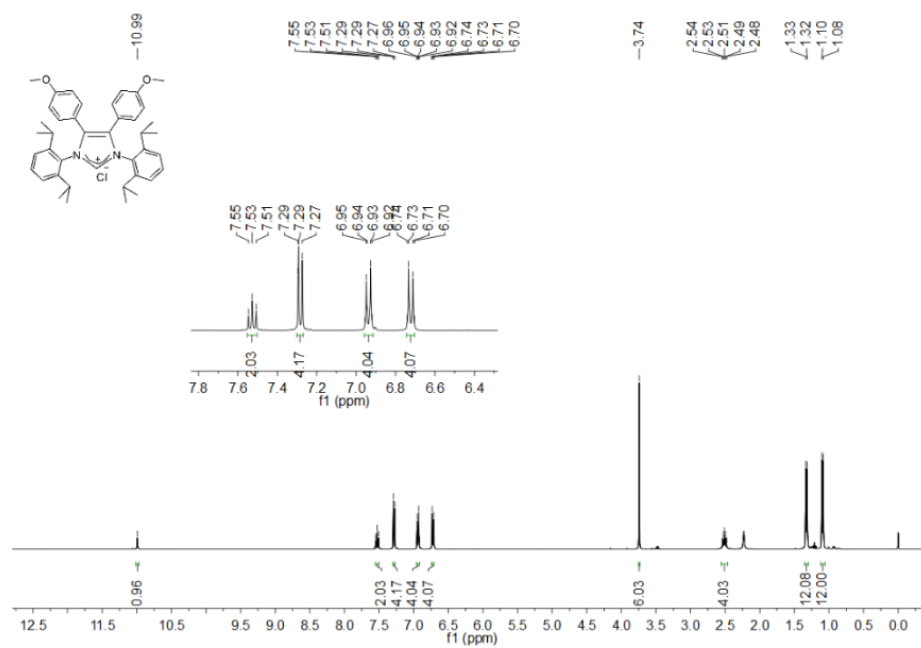


Figure S4. The  $^{13}\text{C}$  NMR spectrum of L1.

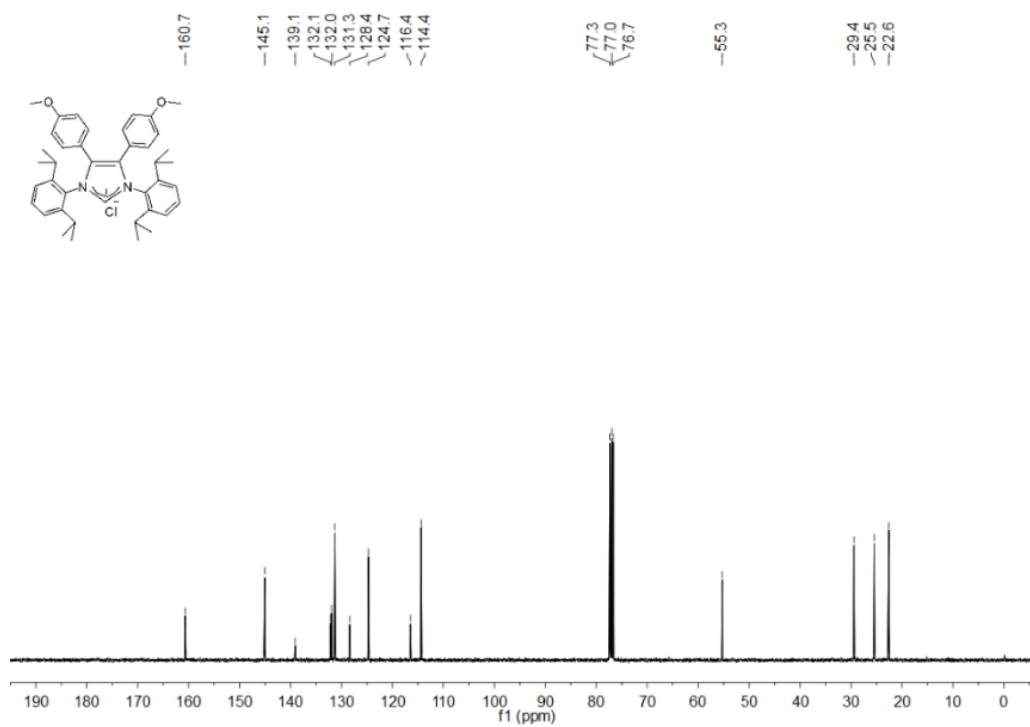


Figure S5. The  $^1\text{H}$  NMR spectrum of C1.

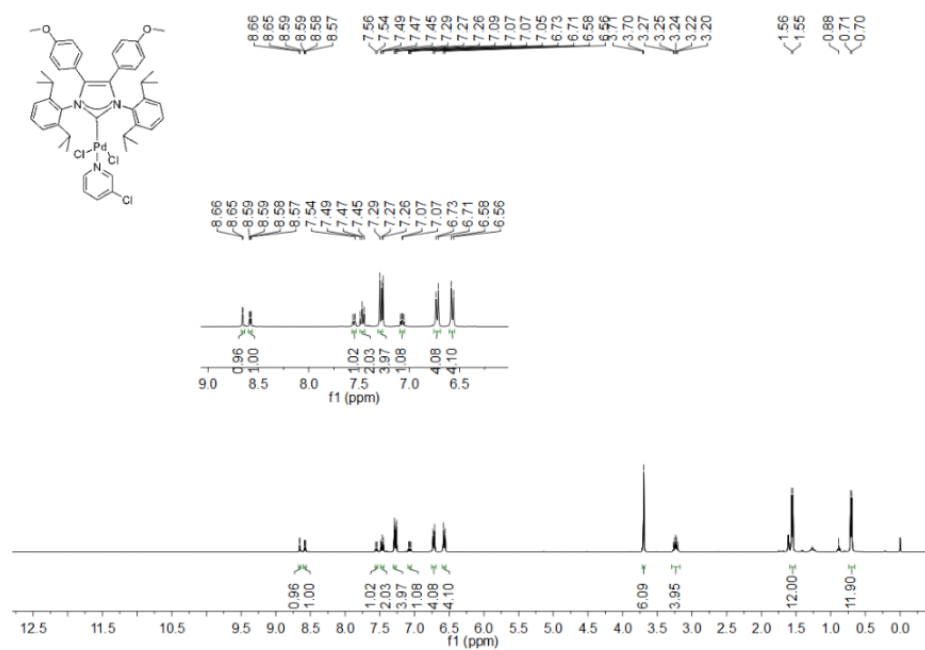
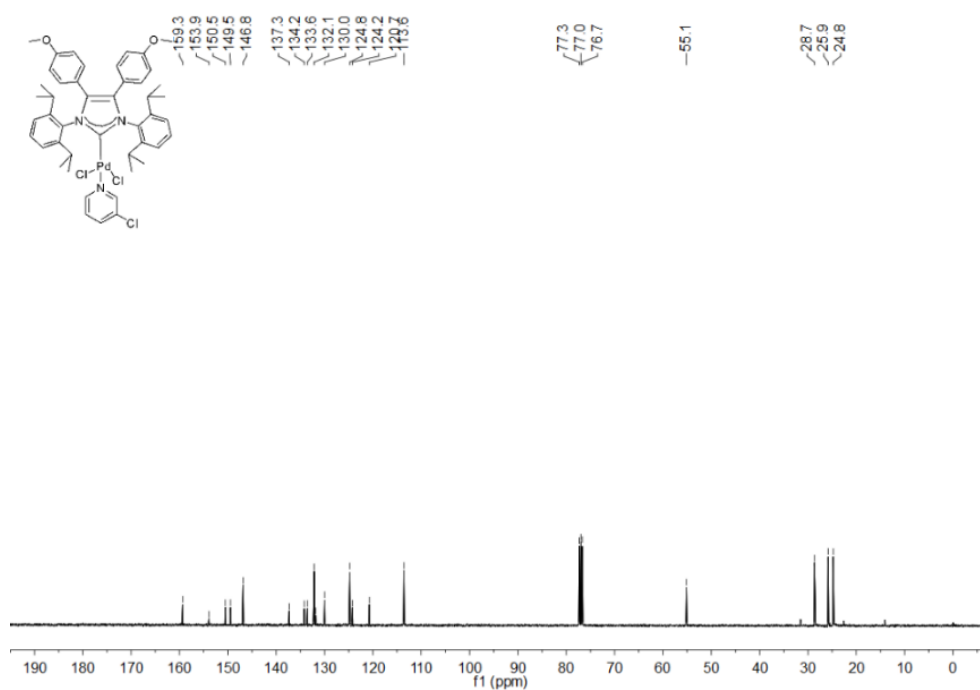


Figure S6. The  $^{13}\text{C}$  NMR spectrum of C1.





## 9. NMR spectra of the aryl ester amination products

Figure S7. The  $^1\text{H}$  NMR spectrum of N-(2,6-dimethylphenyl)benzamide (3a).

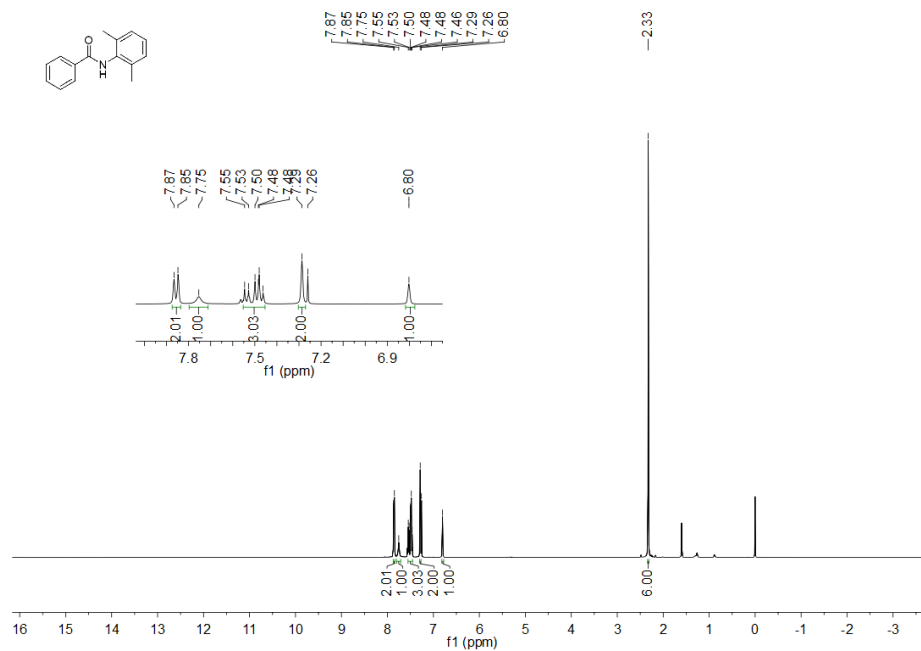


Figure S8. The  $^{13}\text{C}$  NMR spectrum of N-(2,6-dimethylphenyl)benzamide (3a).

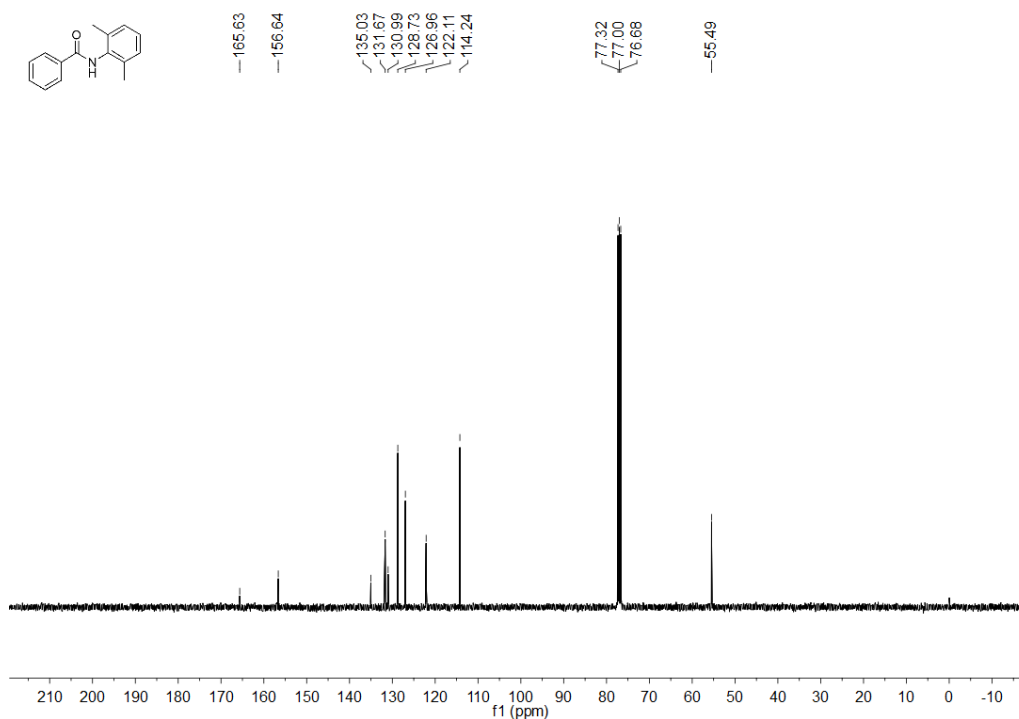


Figure S9. The  $^1\text{H}$  NMR spectrum of N-mesitylbenzamide (3b).

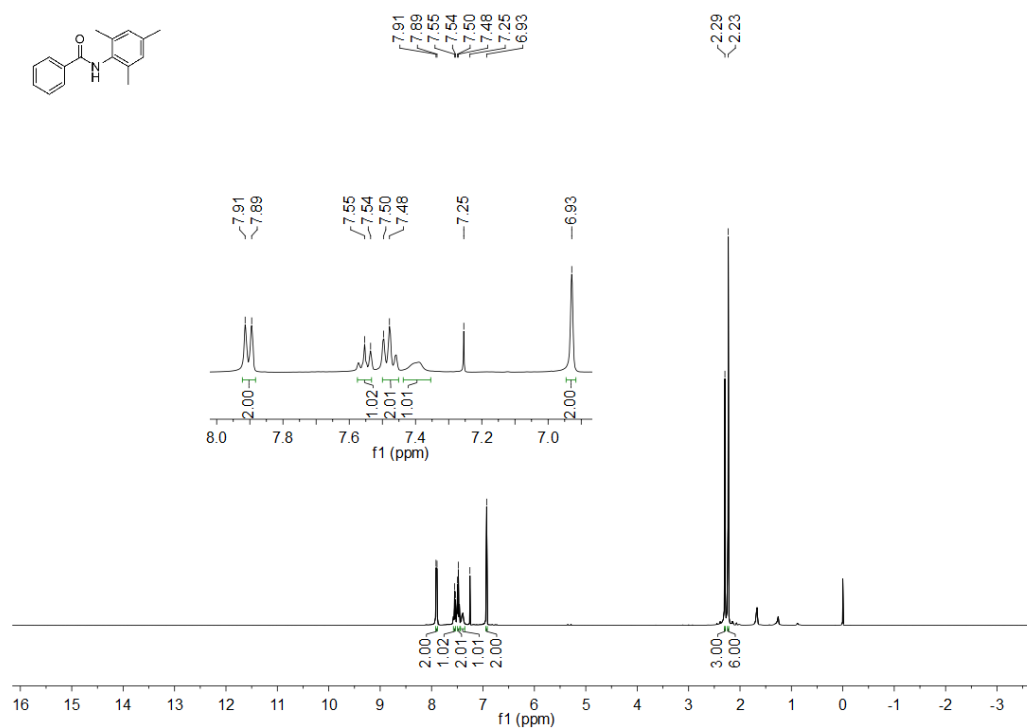


Figure S10. The  $^{13}\text{C}$  NMR spectrum of N-mesitylbenzamide (3b).

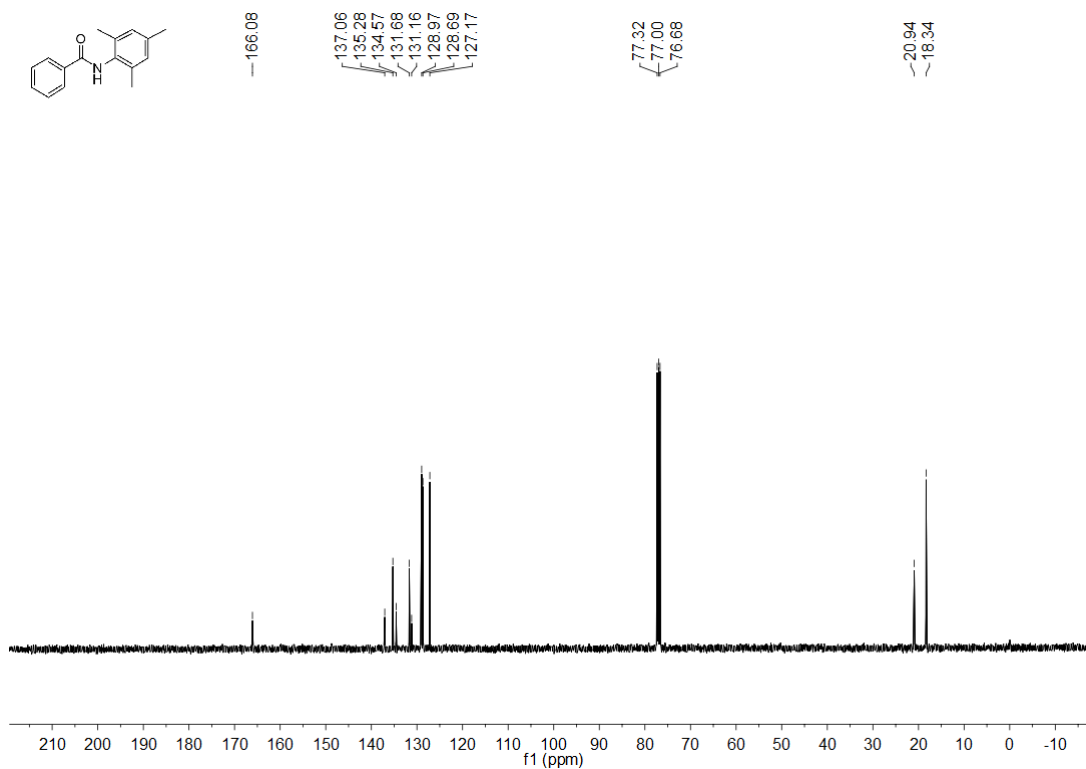


Figure S11. The  $^1\text{H}$  NMR spectrum of N-(2-isopropylphenyl)benzamide (3c).

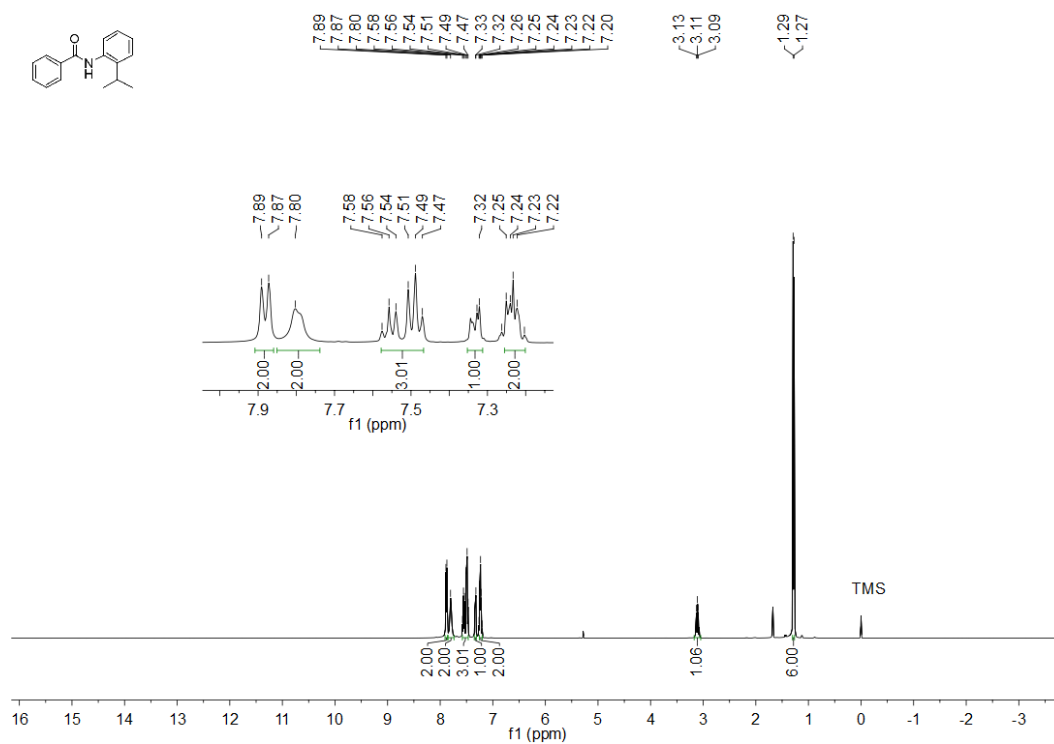


Figure S12. The  $^{13}\text{C}$  NMR spectrum of N-(2-isopropylphenyl)benzamide (3c).

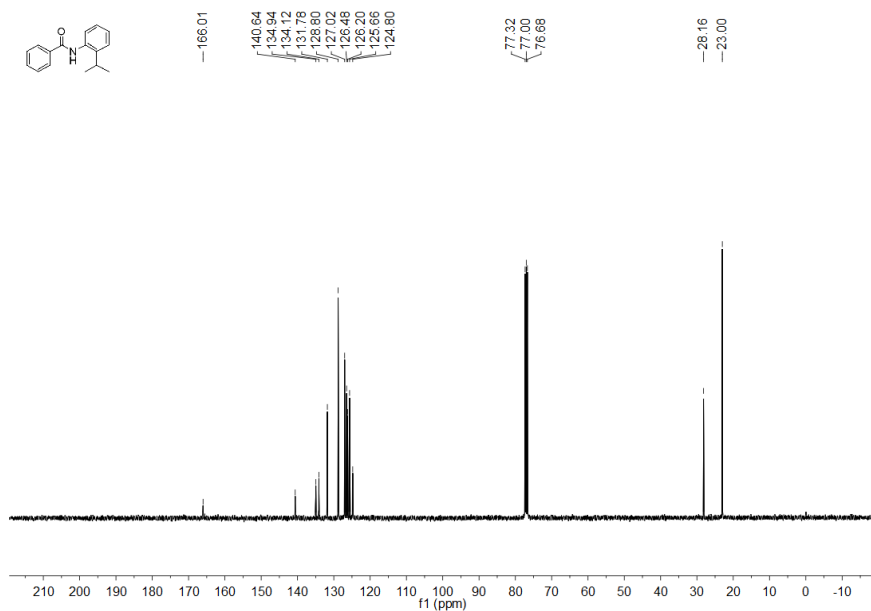


Figure S13. The  $^1\text{H}$  NMR spectrum of N-(2-ethylphenyl)benzamide (3d).

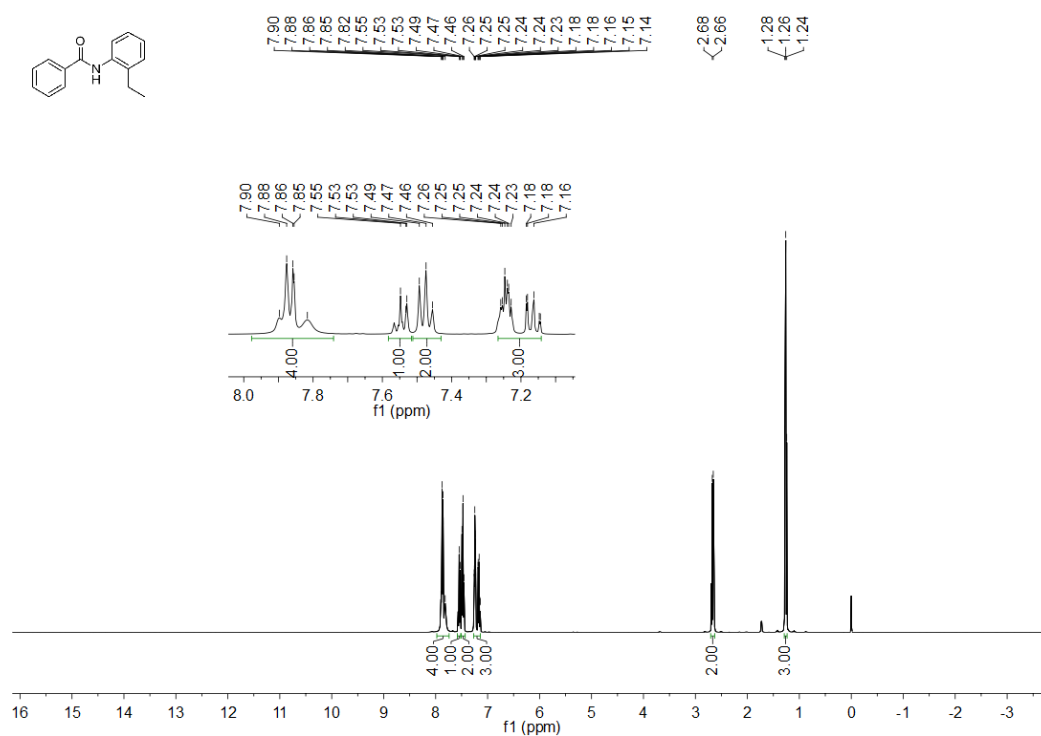


Figure S14. The  $^{13}\text{C}$  NMR spectrum of N-(2-ethylphenyl)benzamide (3d).

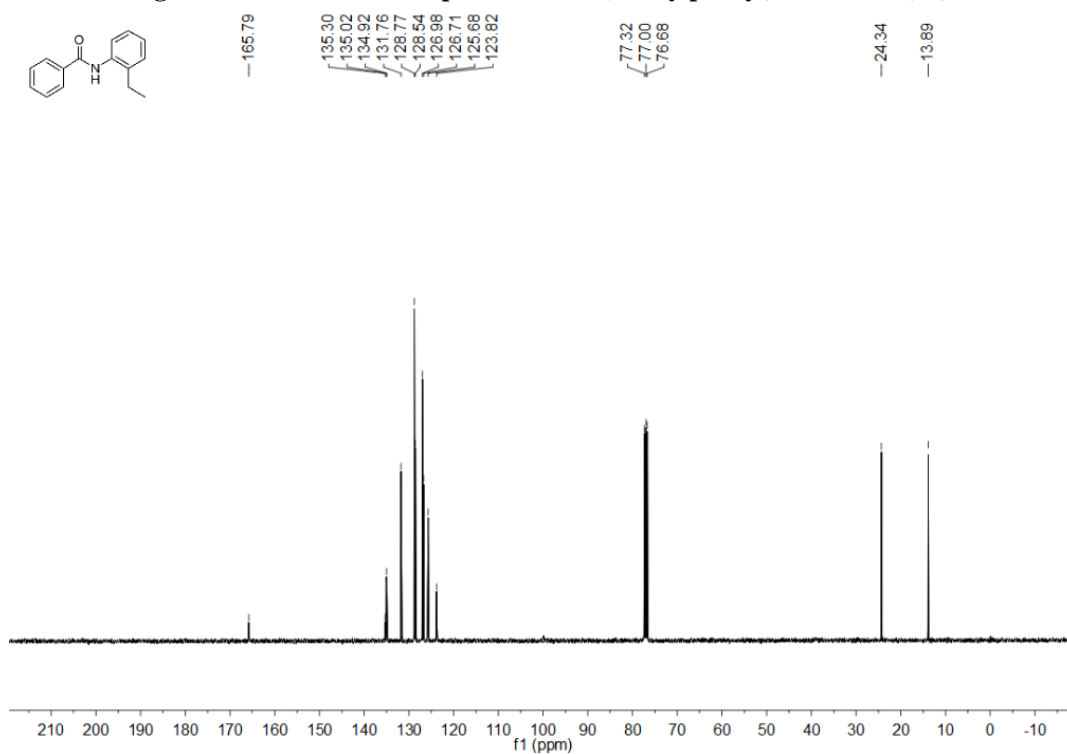


Figure S15. The  $^1\text{H}$  NMR spectrum of N-(o-tolyl)benzamide (3e).

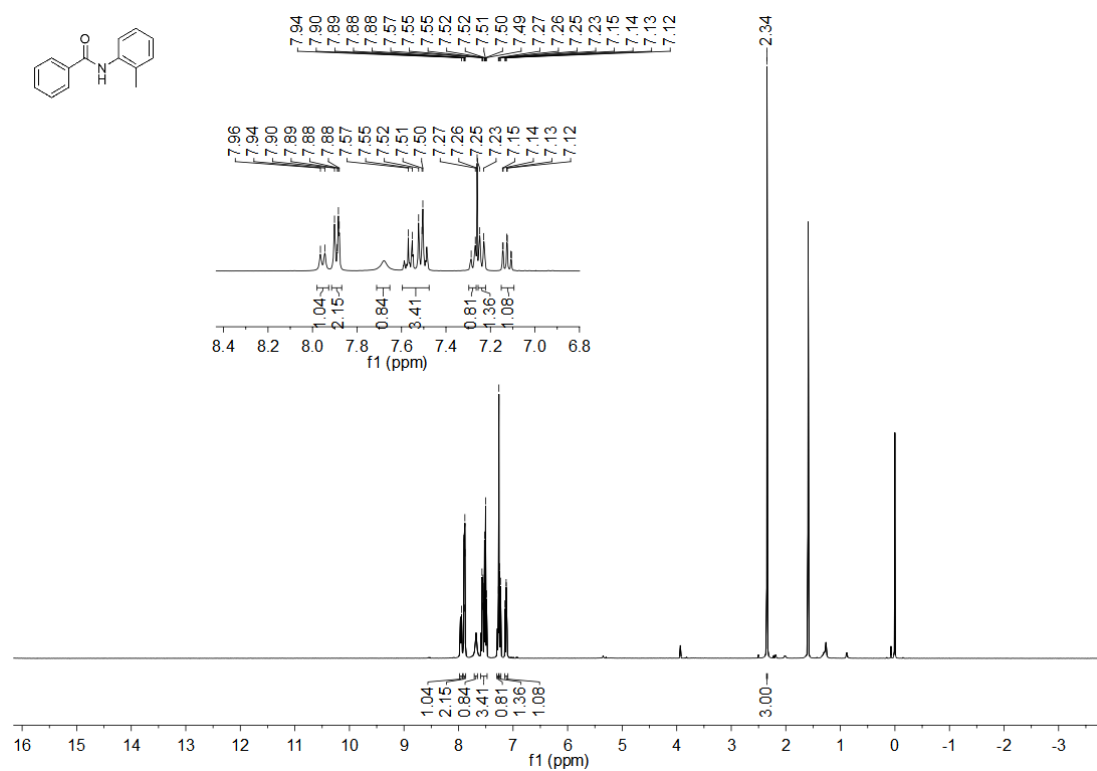


Figure S16. The  $^{13}\text{C}$  NMR spectrum of N-(o-tolyl)benzamide (3e).

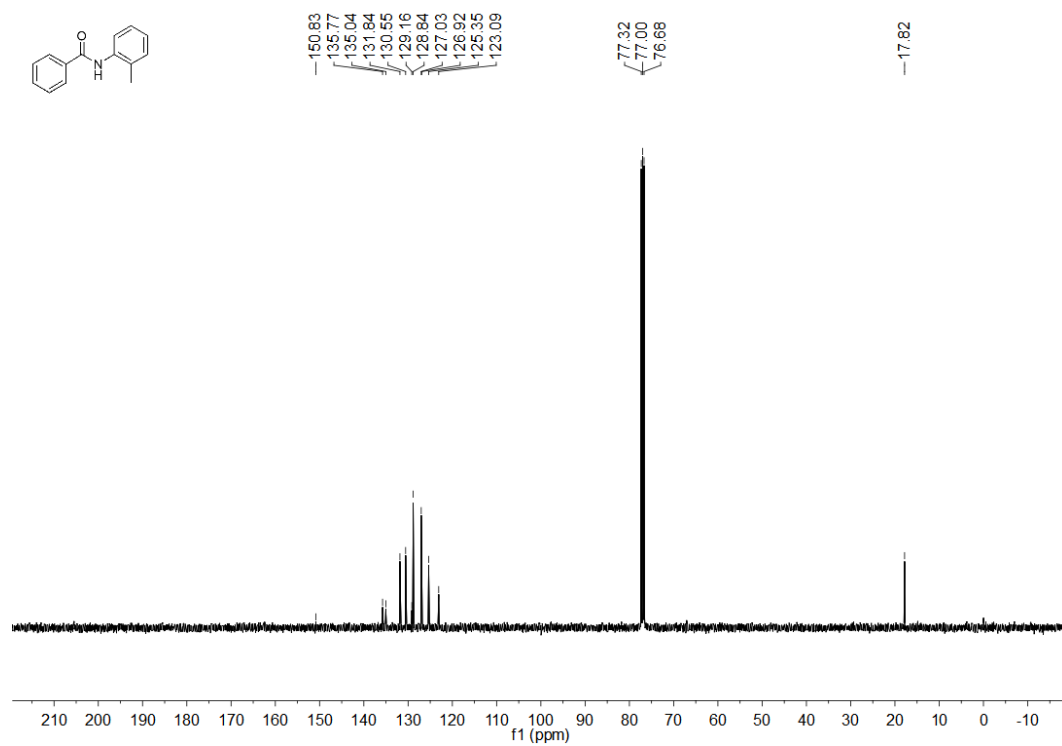


Figure S17. The  $^1\text{H}$  NMR spectrum of N-(2,4-dimethylphenyl)benzamide (3f).

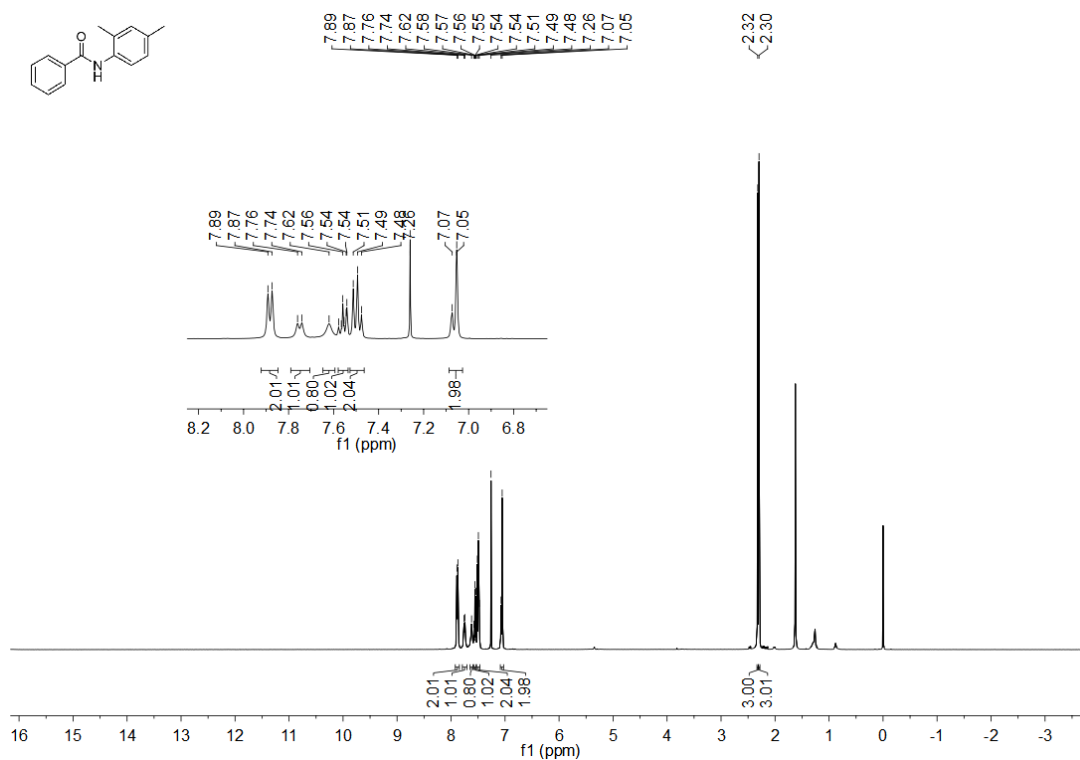


Figure S18. The  $^{13}\text{C}$  NMR spectrum of N-(2,4-dimethylphenyl)benzamide (3f).

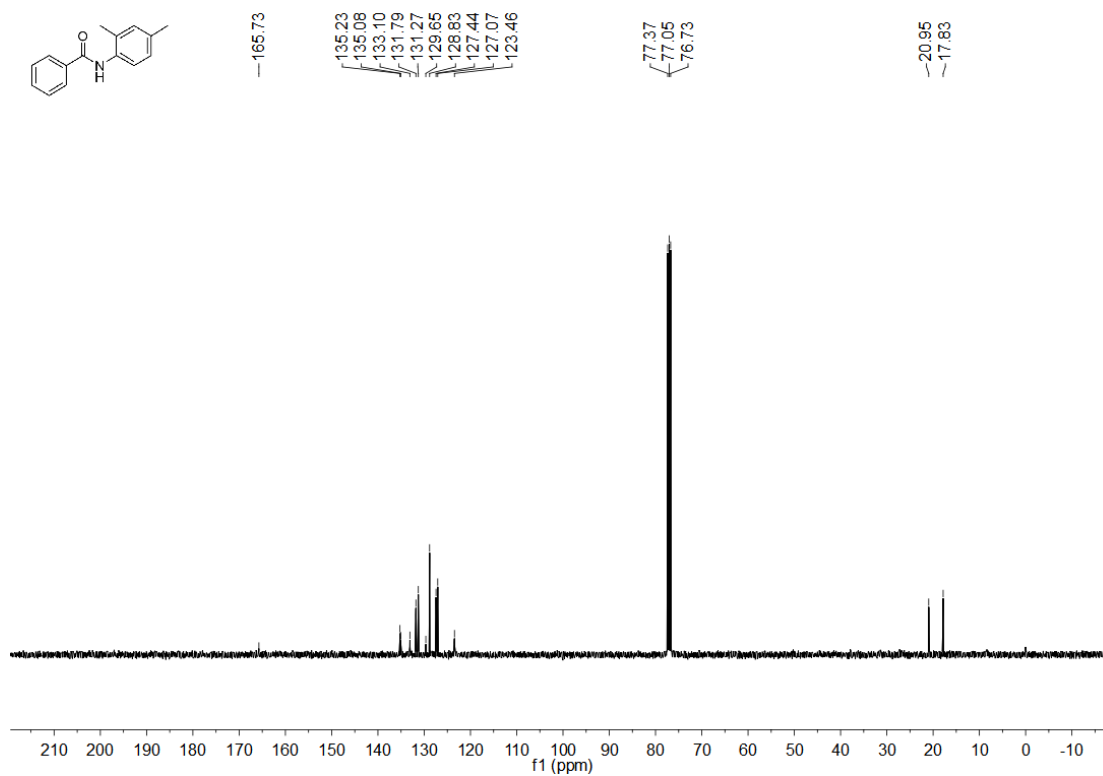


Figure S19. The  $^1\text{H}$  NMR spectrum of N-(p-tolyl)benzamide (3g).

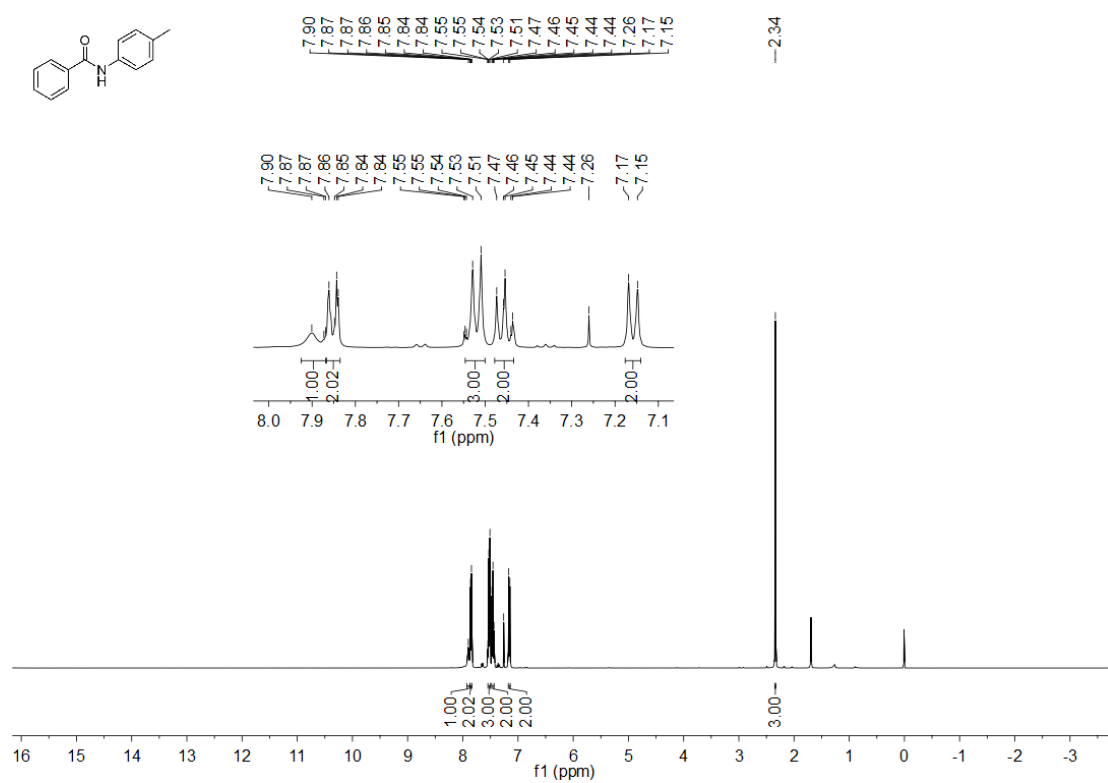


Figure S20. The  $^{13}\text{C}$  NMR spectrum of N-(p-tolyl)benzamide (3g).

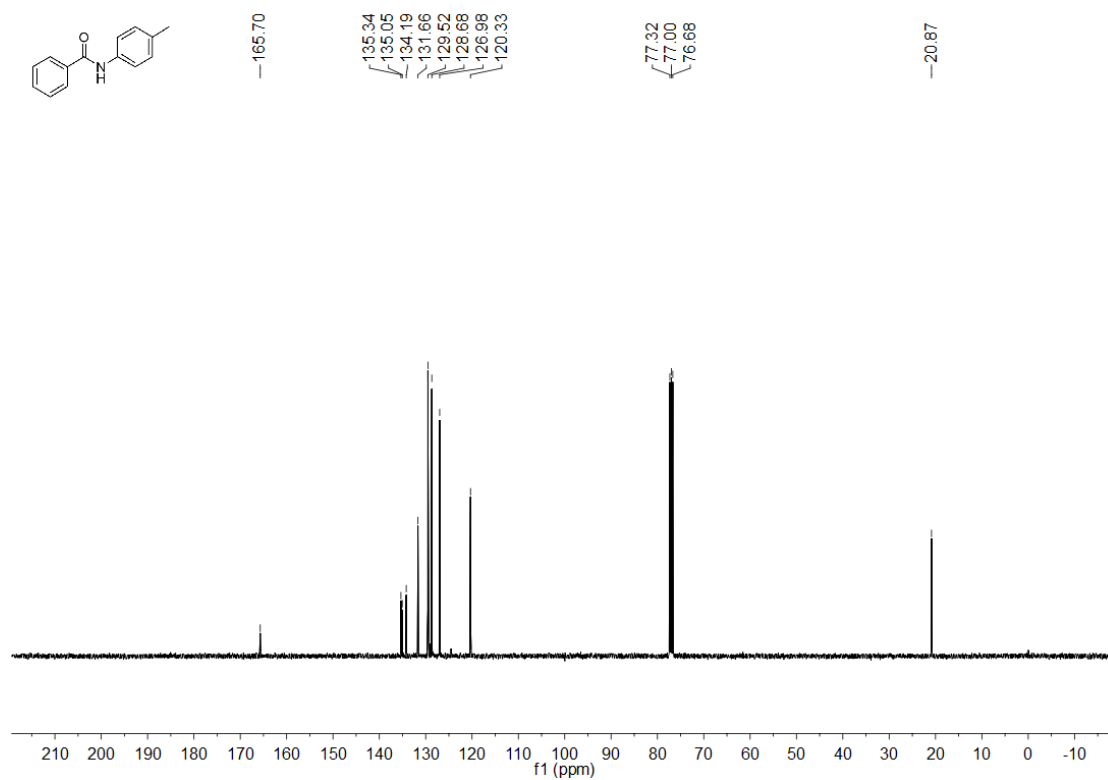


Figure S21. The  $^1\text{H}$  NMR spectrum of N-(3,5-dimethylphenyl)benzamide (3h).

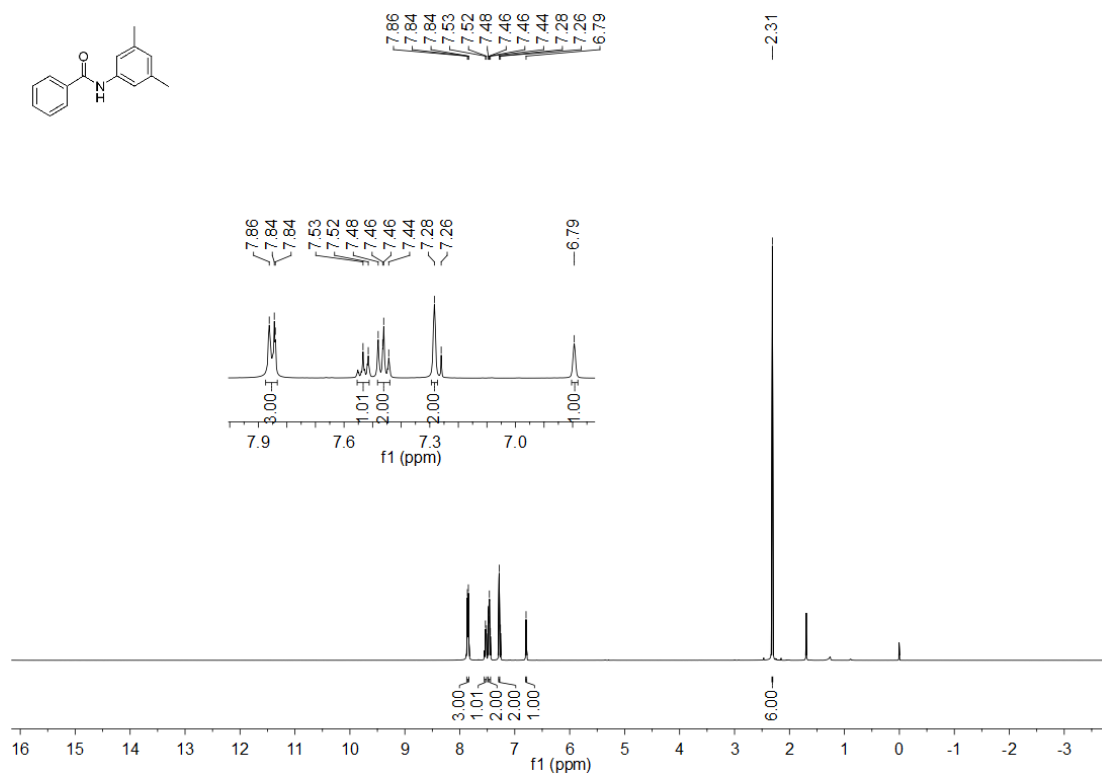


Figure S22. The  $^{13}\text{C}$  NMR spectrum of N-(3,5-dimethylphenyl)benzamide (3h).

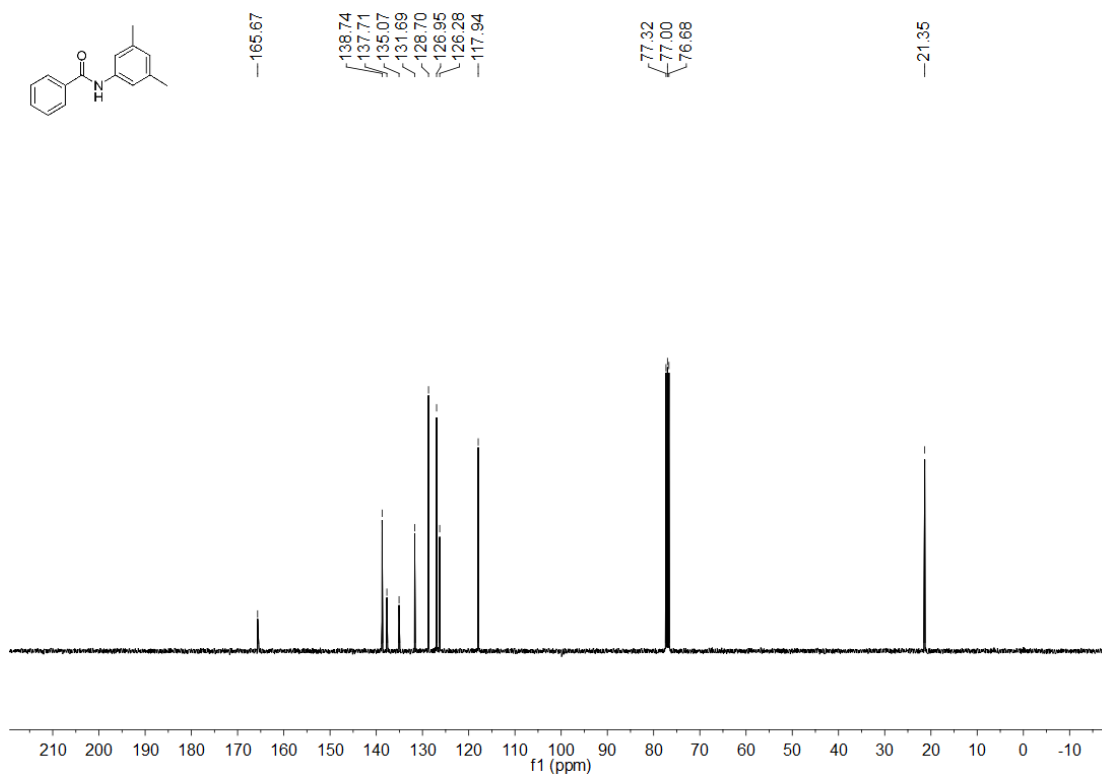




Figure S23. The  $^1\text{H}$  NMR spectrum of N-(m-tolyl)benzamide (3i).

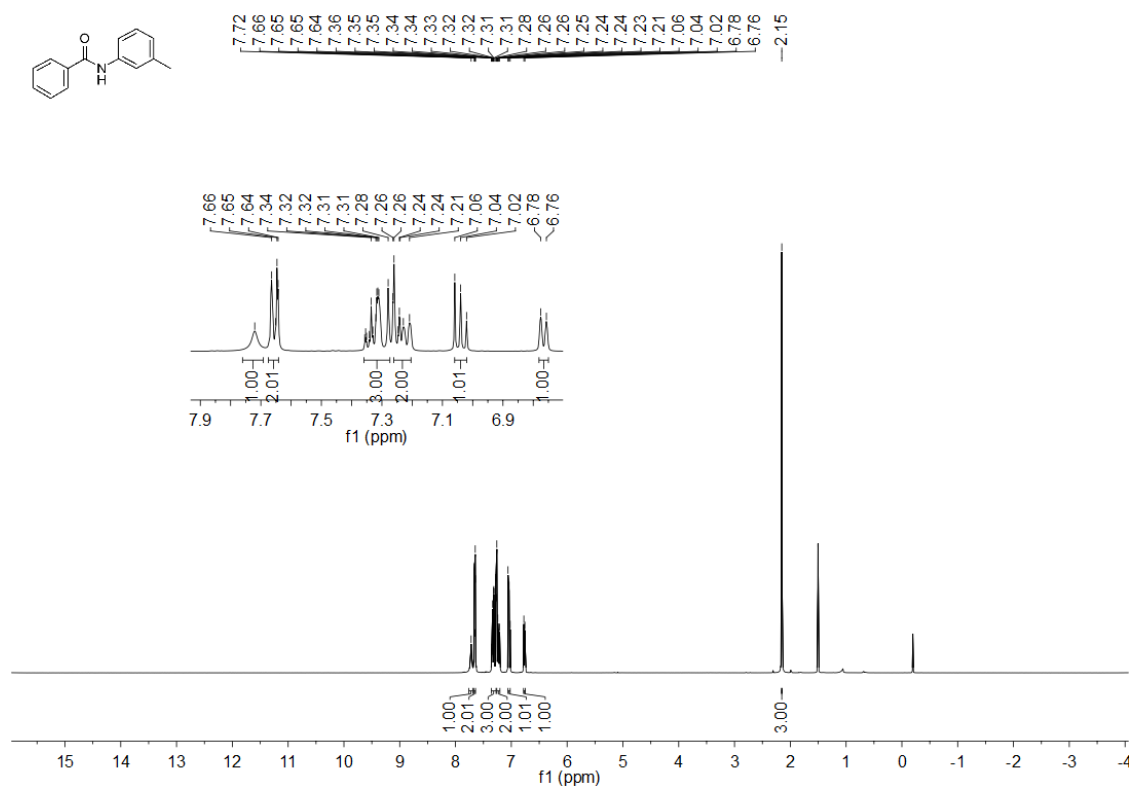


Figure S24. The  $^{13}\text{C}$  NMR spectrum of N-(m-tolyl)benzamide (3i).

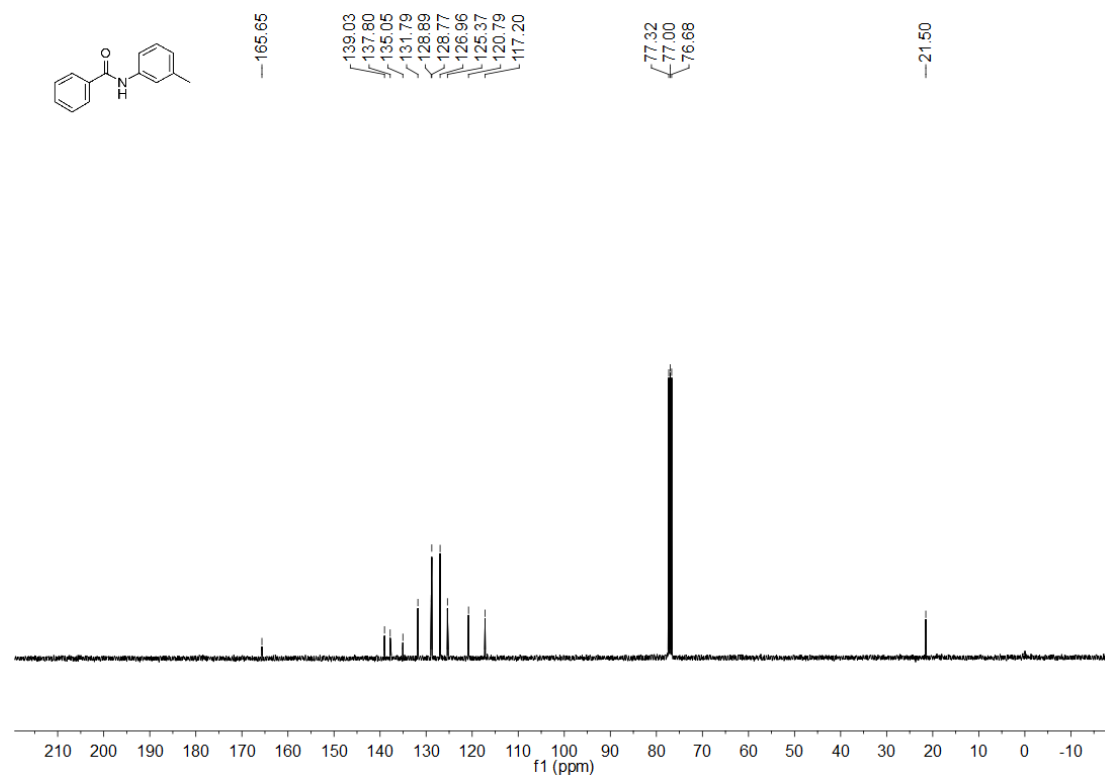


Figure S25. The  $^1\text{H}$  NMR spectrum of N-phenylbenzamide (3j).

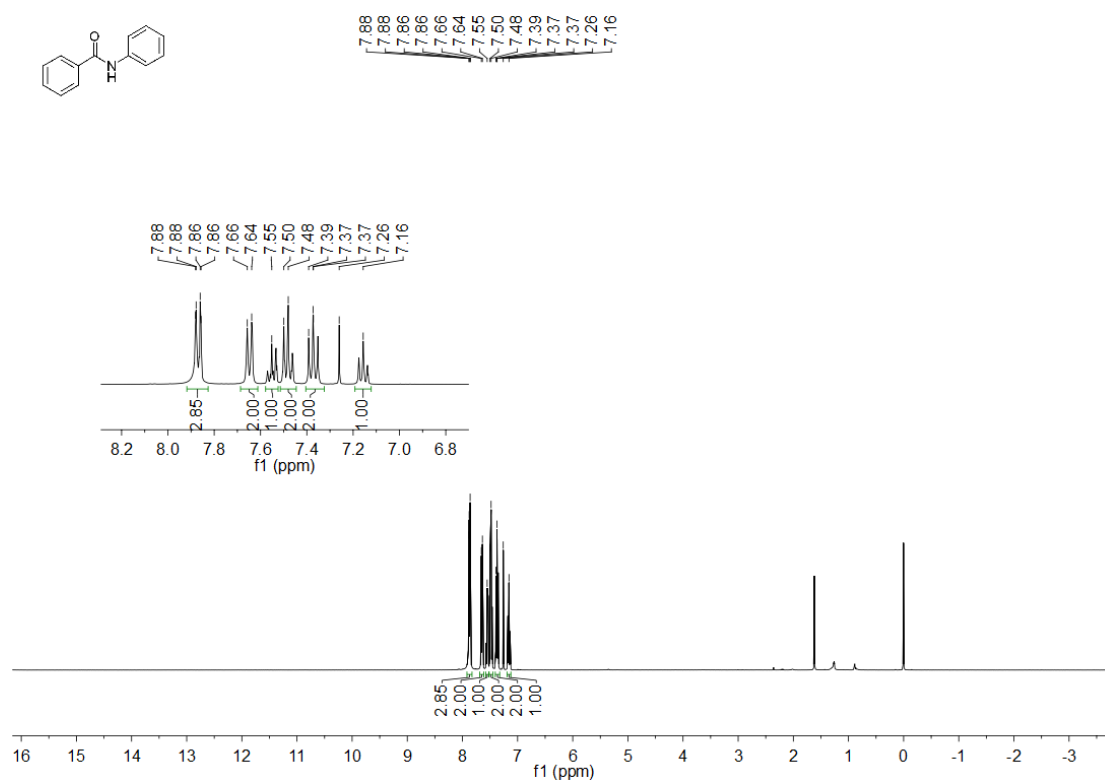


Figure S26. The  $^{13}\text{C}$  NMR spectrum of N-phenylbenzamide (3j).

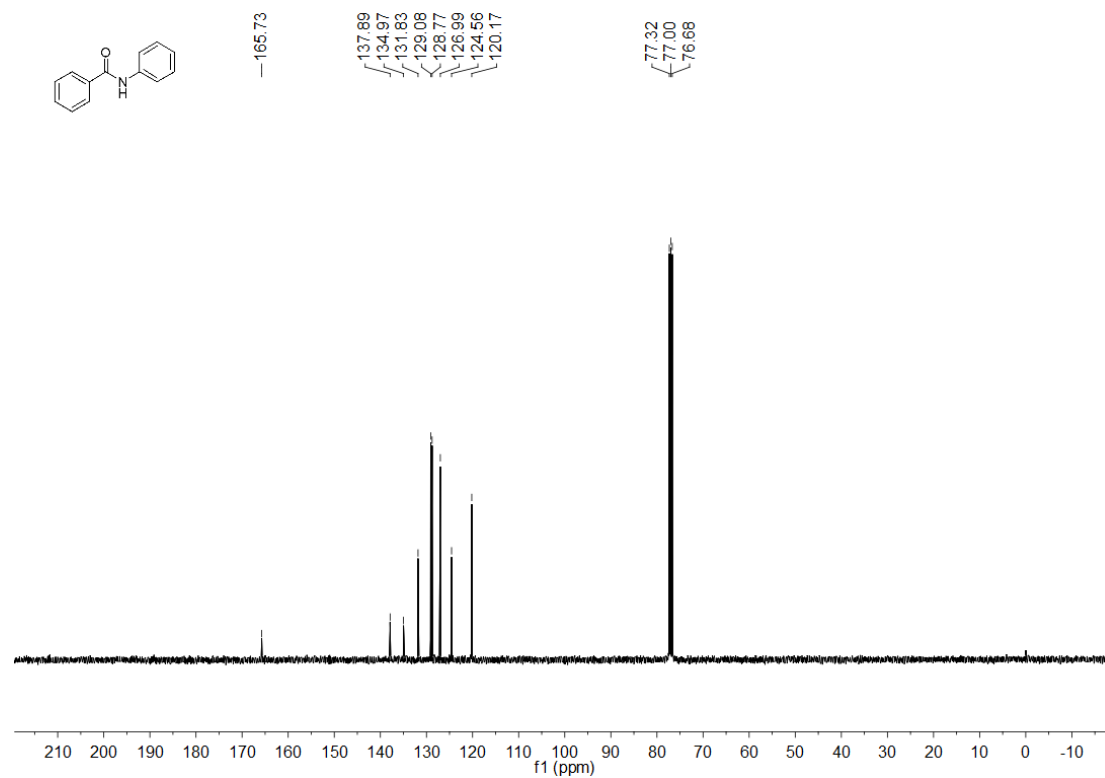


Figure S27. The  $^1\text{H}$  NMR spectrum of N-(2-methoxyphenyl)benzamide (3k).

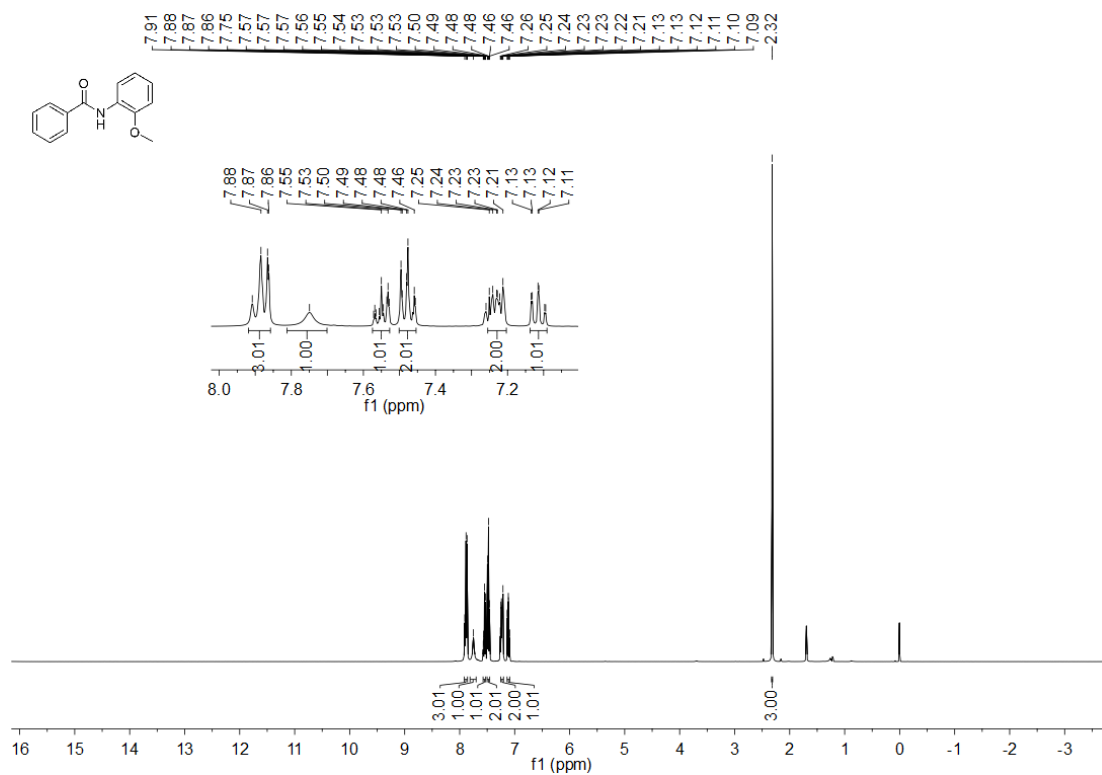


Figure S28. The  $^{13}\text{C}$  NMR spectrum of N-(2-methoxyphenyl)benzamide (3k).

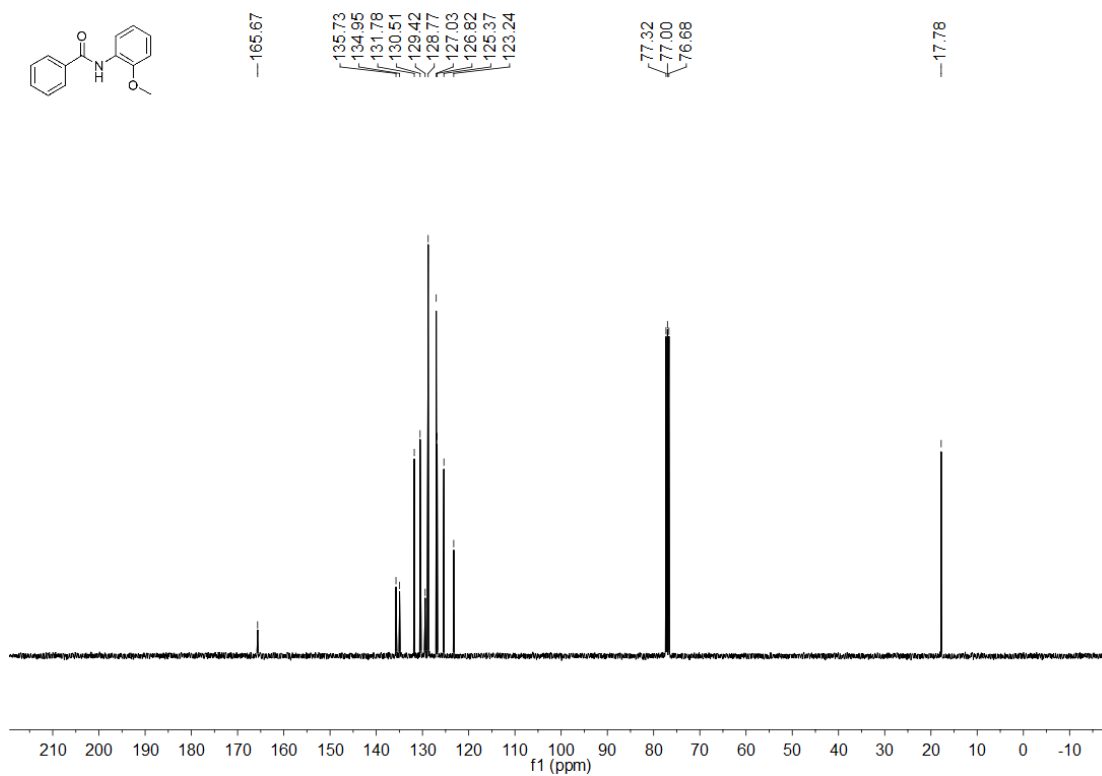


Figure S29. The  $^1\text{H}$  NMR spectrum of N-(4-methoxyphenyl)benzamide (3l).

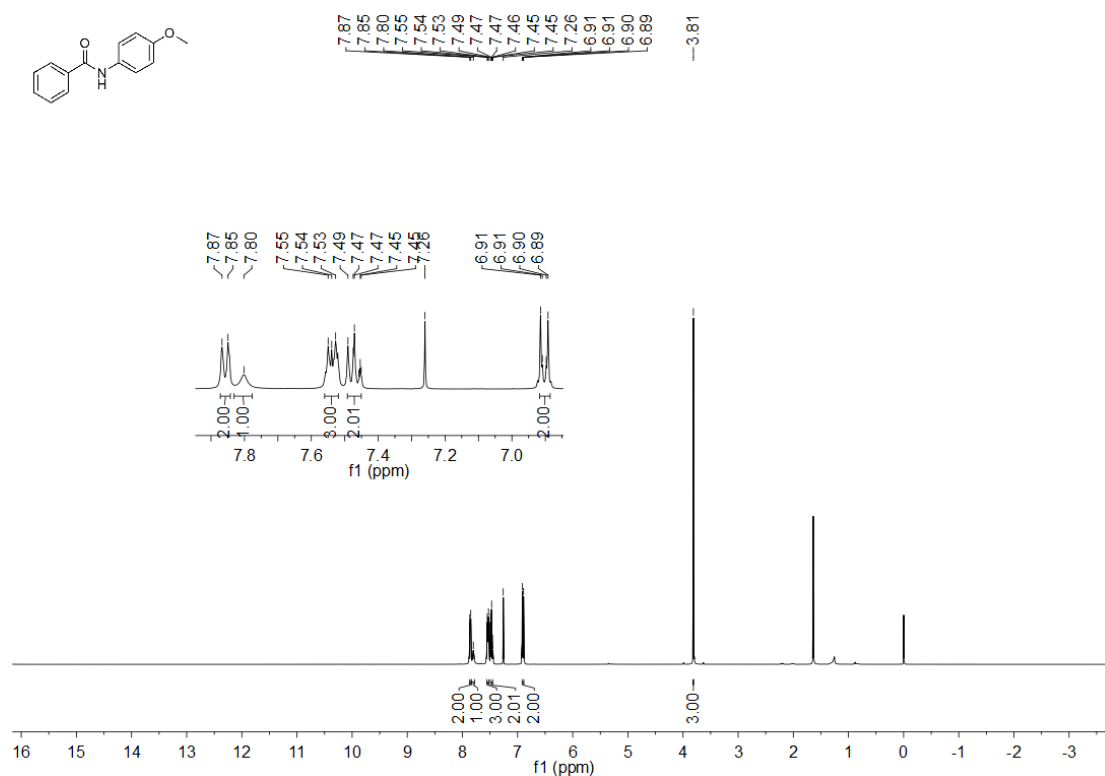


Figure S30. The  $^{13}\text{C}$  NMR spectrum of N-(4-methoxyphenyl)benzamide (3l).

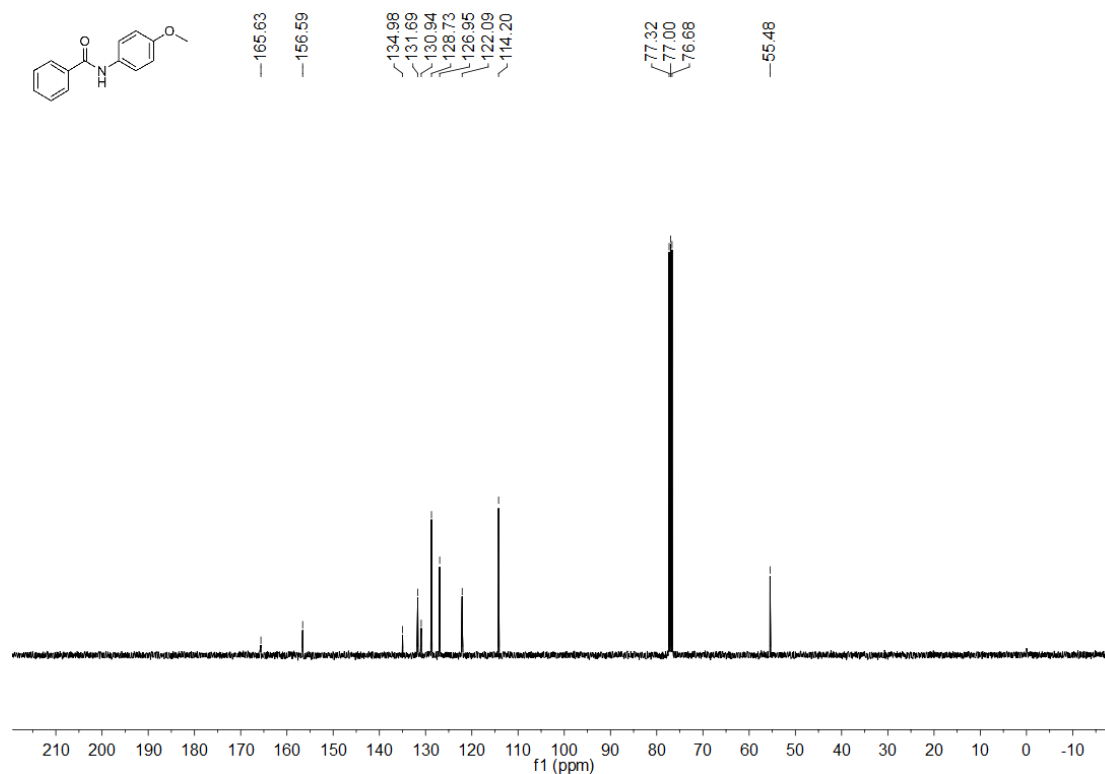


Figure S31. The <sup>1</sup>H NMR spectrum of N-(2-aminophenyl)benzamide (3m).

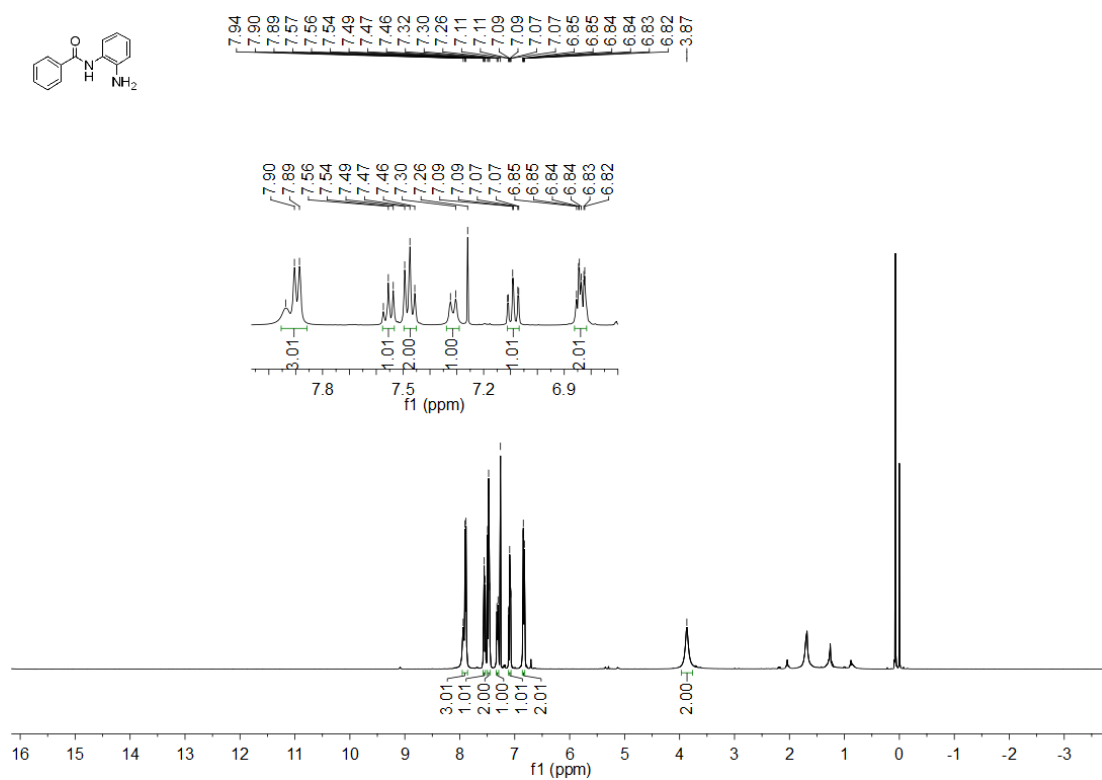


Figure S32. The <sup>13</sup>C NMR spectrum of N-(2-aminophenyl)benzamide (3m).

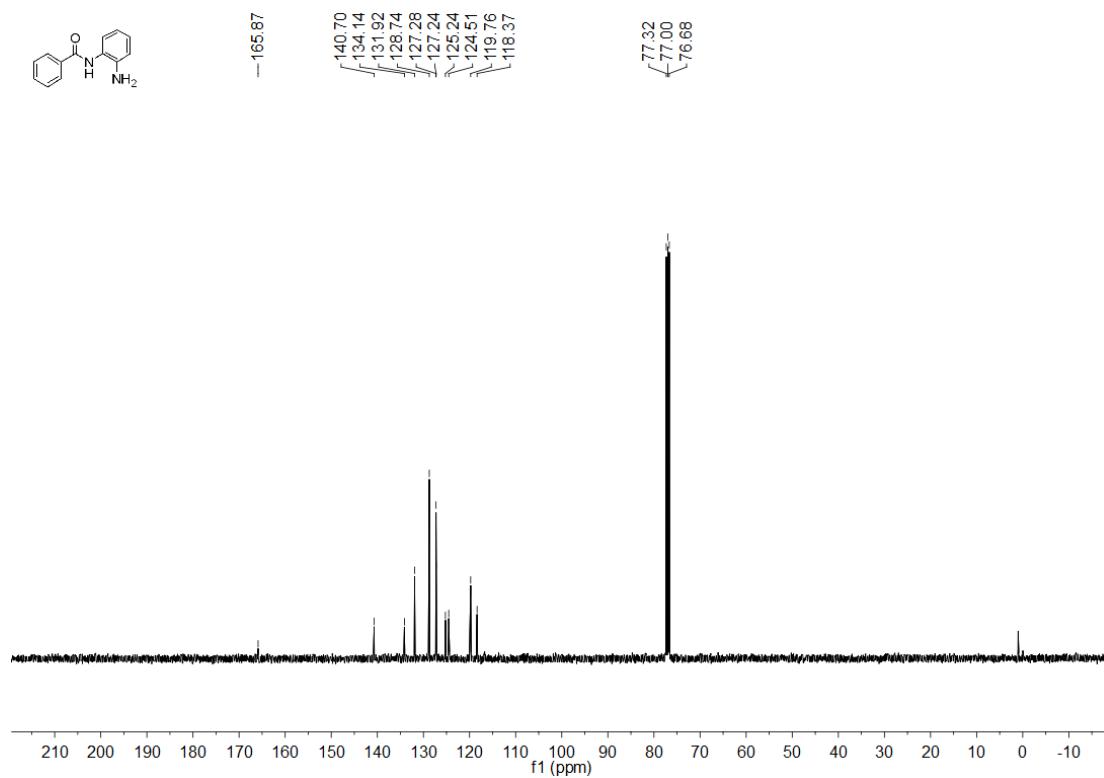


Figure S33. The  $^1\text{H}$  NMR spectrum of N-(3,5-difluorophenyl)benzamide (3n).

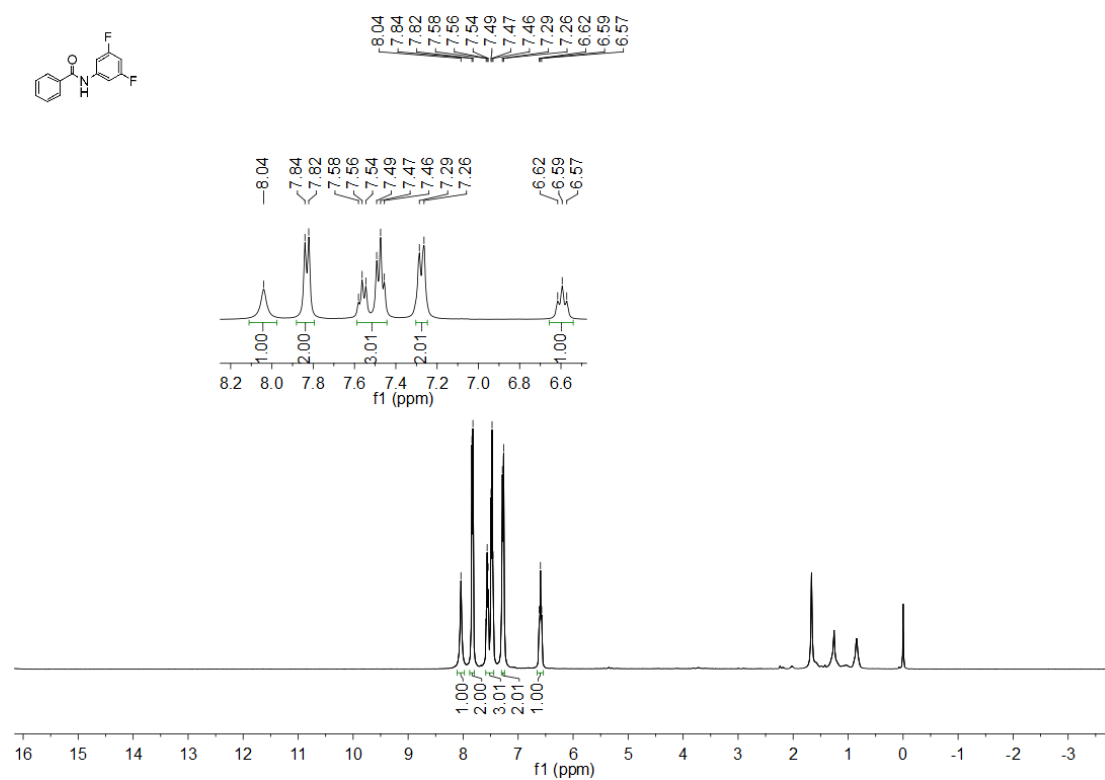


Figure S34. The  $^{13}\text{C}$  NMR spectrum of N-(3,5-difluorophenyl)benzamide (3n).

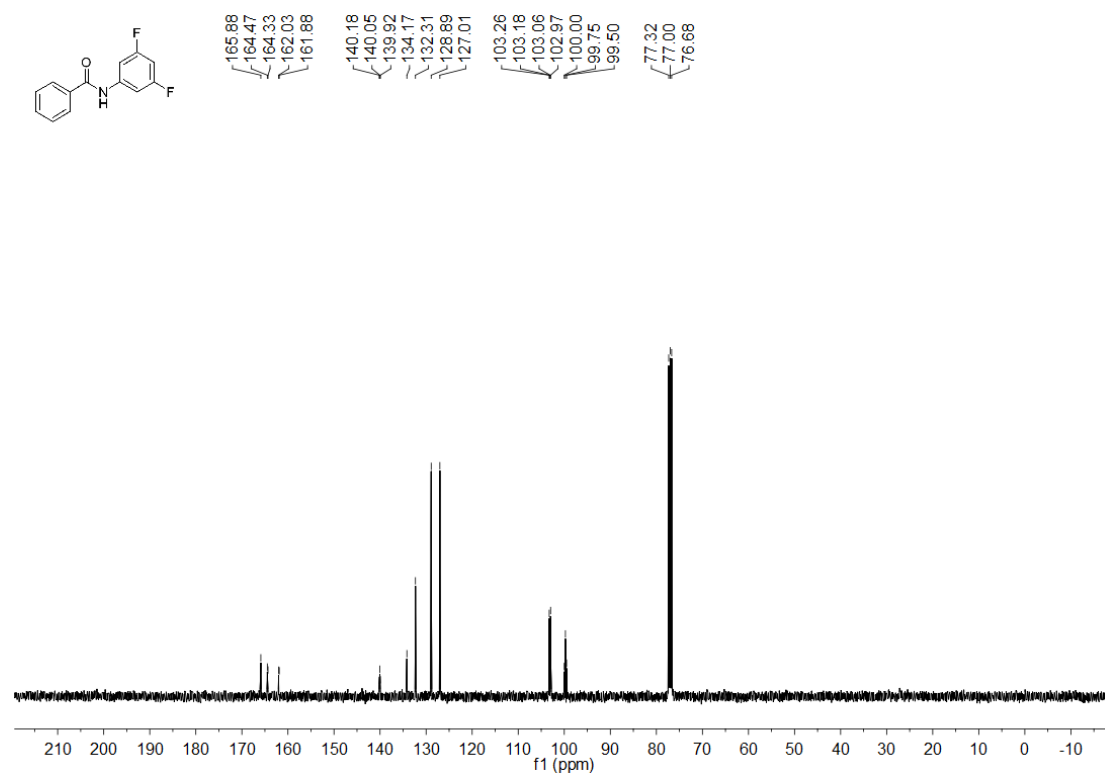


Figure S35. The  $^1\text{H}$  NMR spectrum of morpholino(phenyl)methanone (3o).

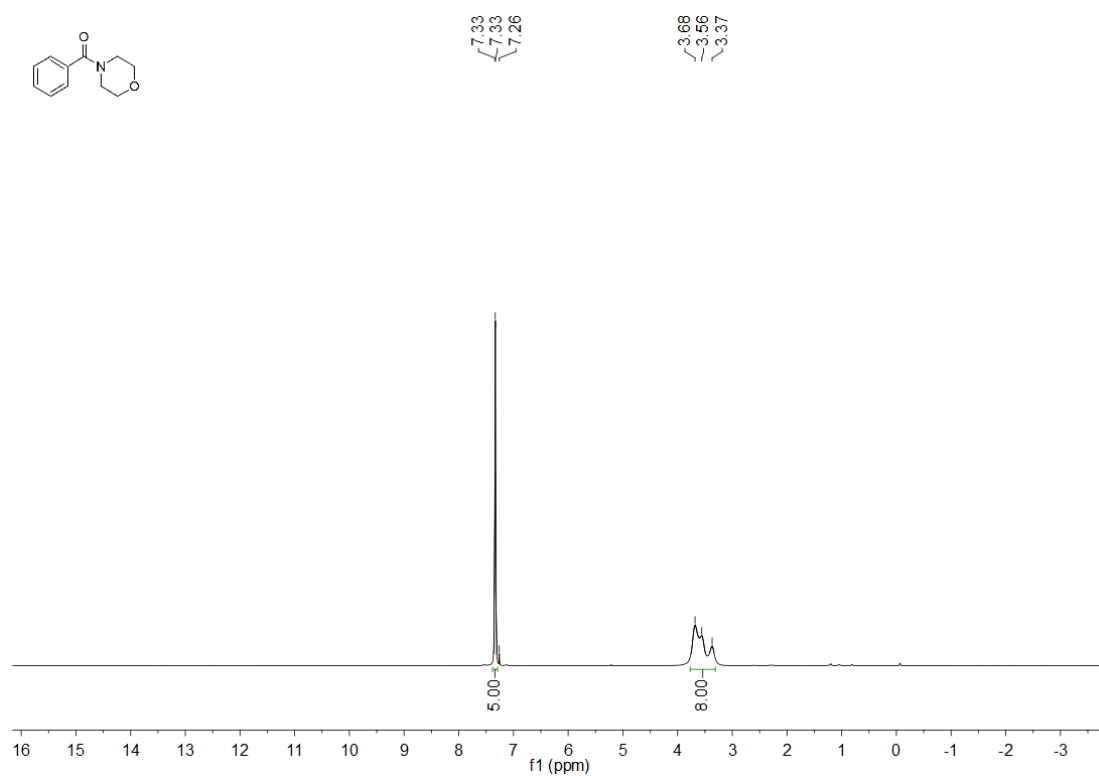


Figure S36. The  $^{13}\text{C}$  NMR spectrum of morpholino(phenyl)methanone (3o).

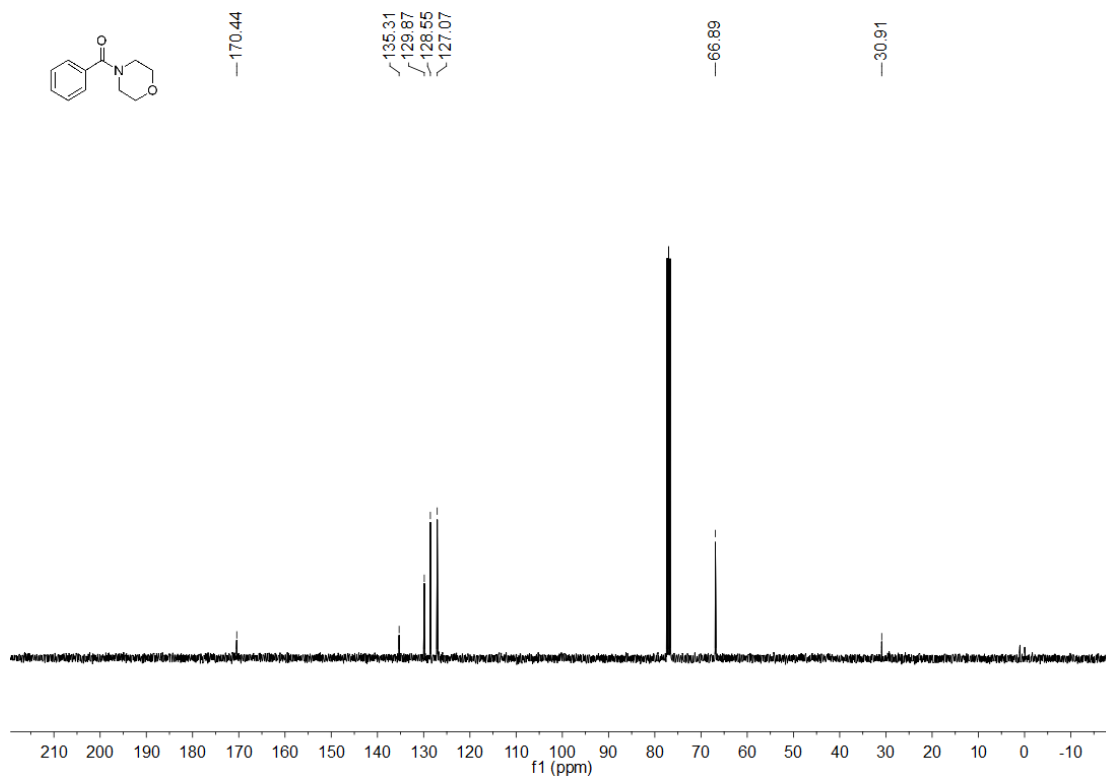


Figure S37. The  $^1\text{H}$  NMR spectrum of N-benzylbenzamide (3p).

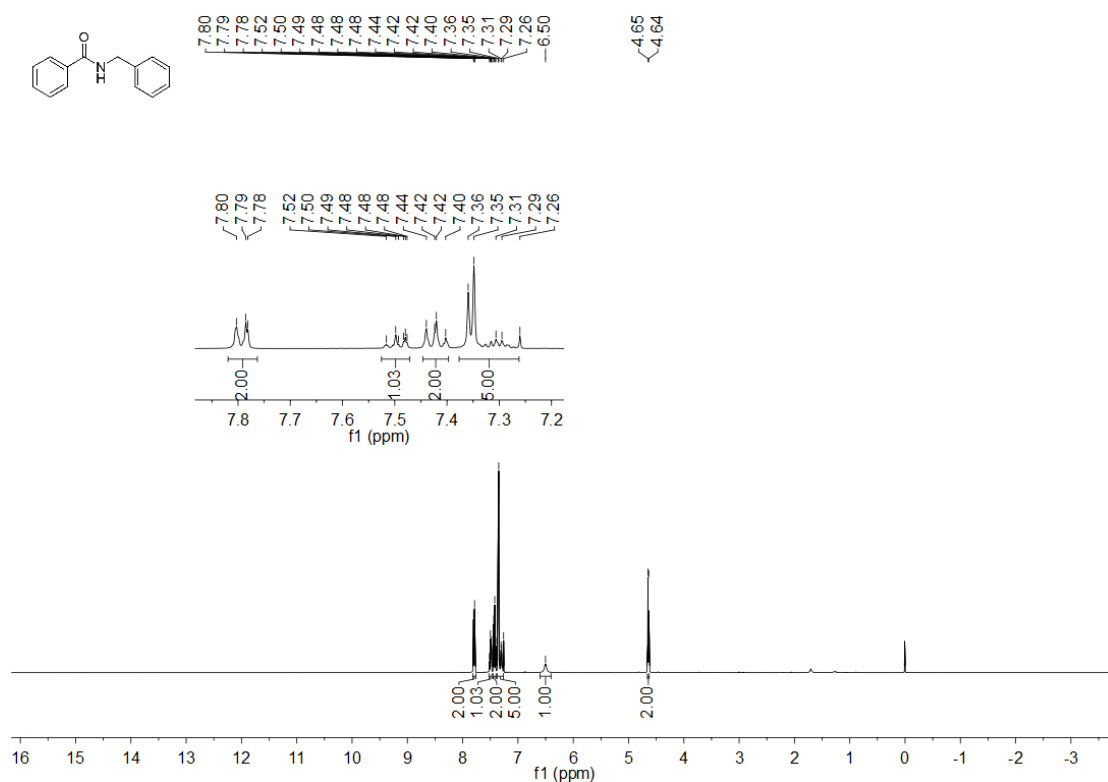


Figure S38. The  $^{13}\text{C}$  NMR spectrum of N-benzylbenzamide (3p).

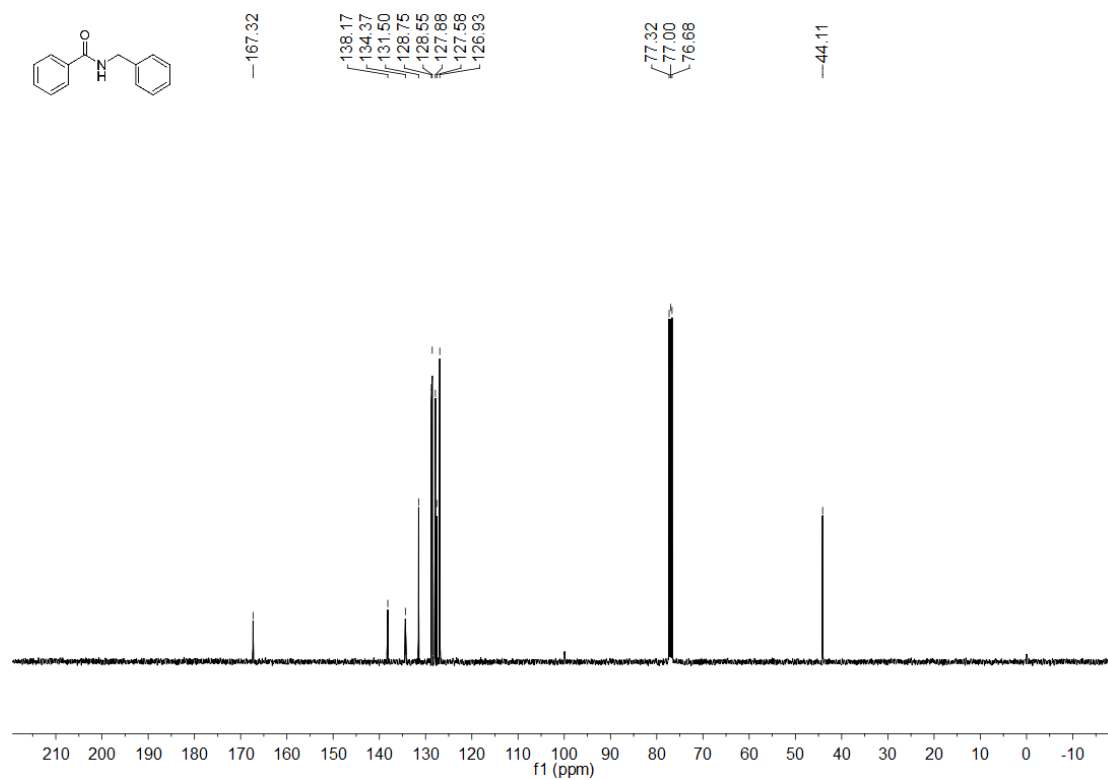




Figure S39. The  $^1\text{H}$  NMR spectrum of 4-methyl-N-(p-tolyl)benzamide (4g).

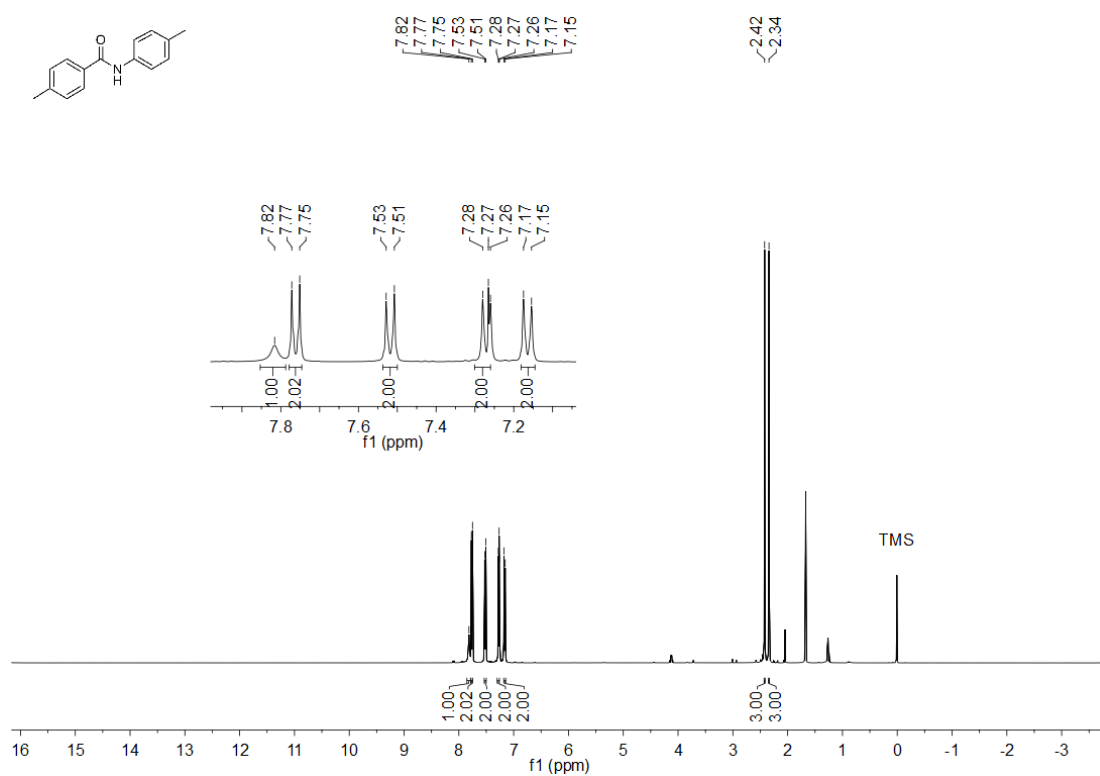


Figure S40. The  $^{13}\text{C}$  NMR spectrum of 4-methyl-N-(p-tolyl)benzamide (4g).

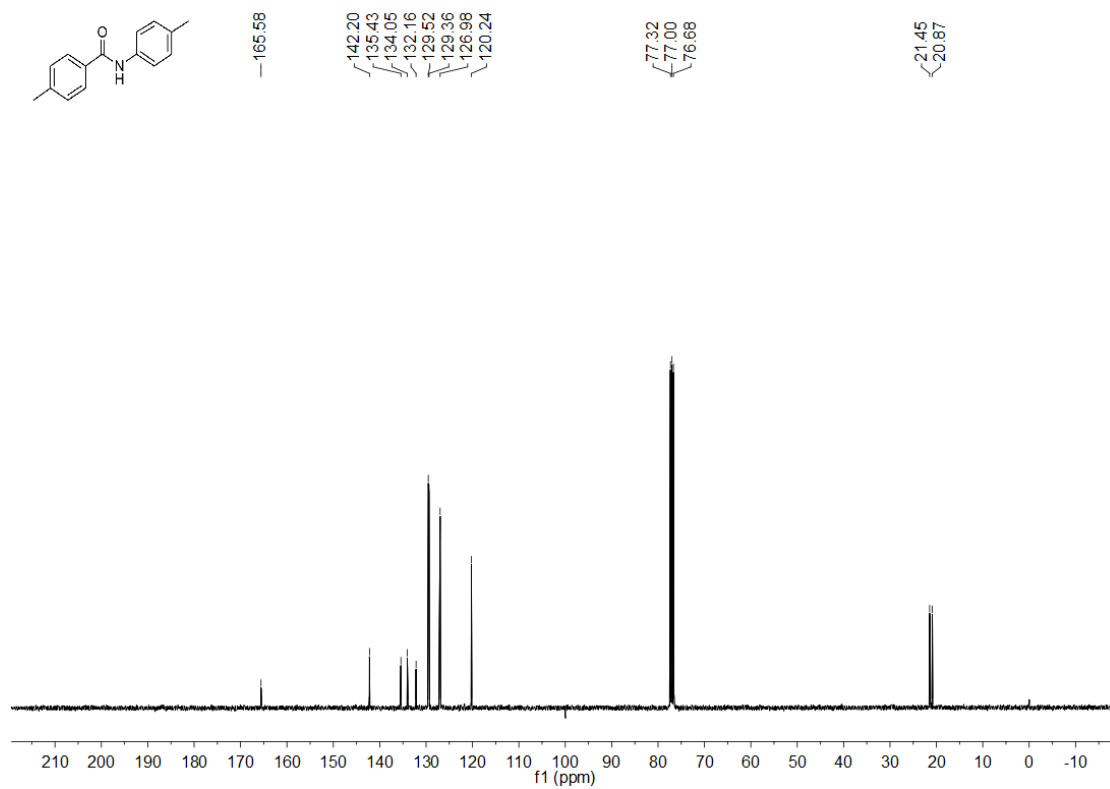


Figure S41. The  $^1\text{H}$  NMR spectrum of 4-methyl-N-phenylbenzamide (4j).

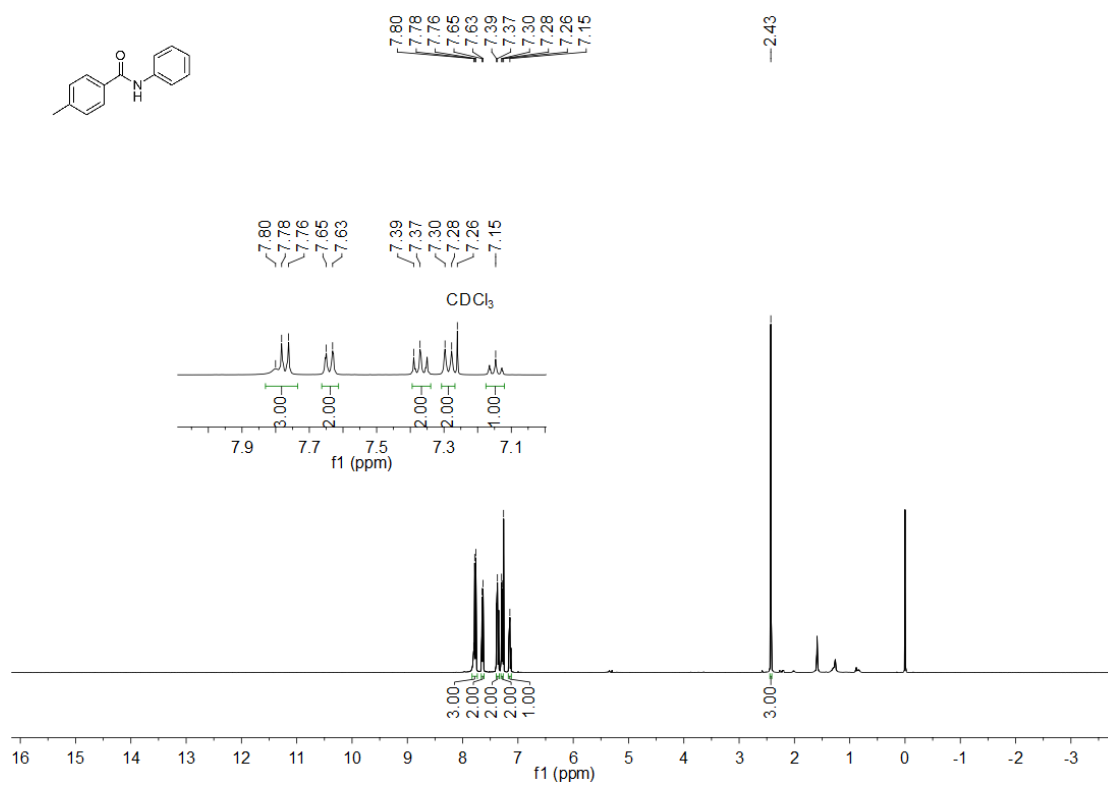


Figure S42. The  $^{13}\text{C}$  NMR spectrum of 4-methyl-N-phenylbenzamide (4j).

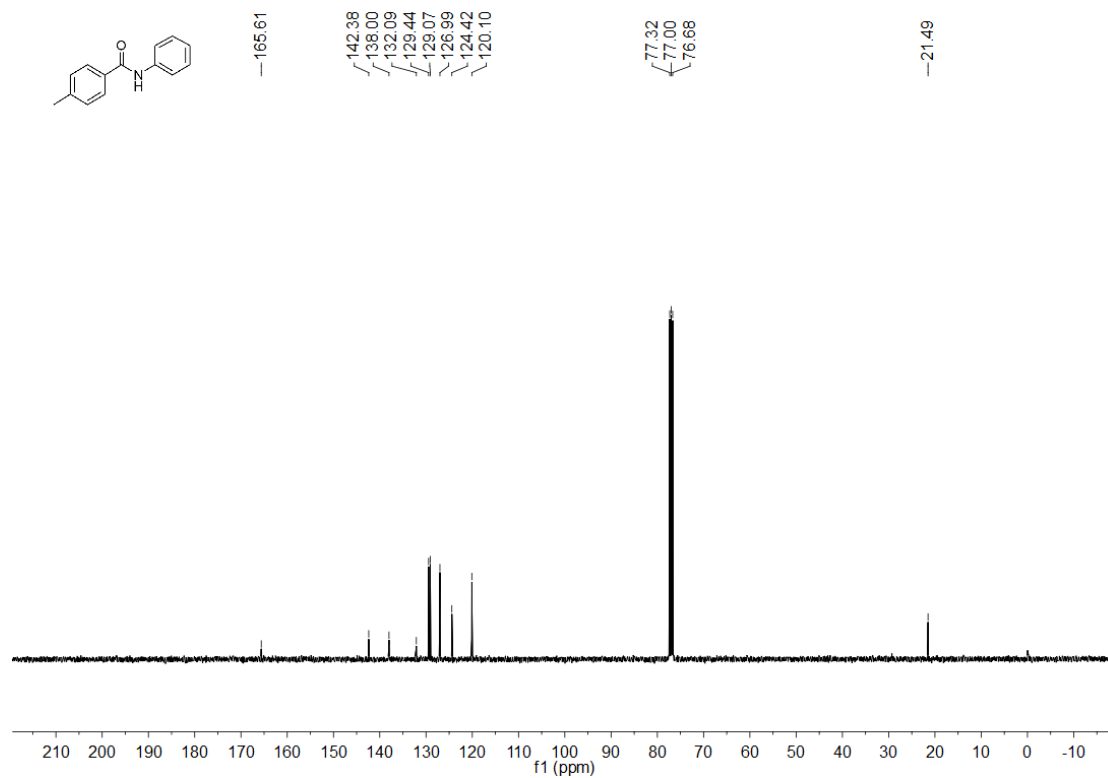


Figure S43. The  $^1\text{H}$  NMR spectrum of N-(4-methoxyphenyl)-4-methylbenzamide (4l).

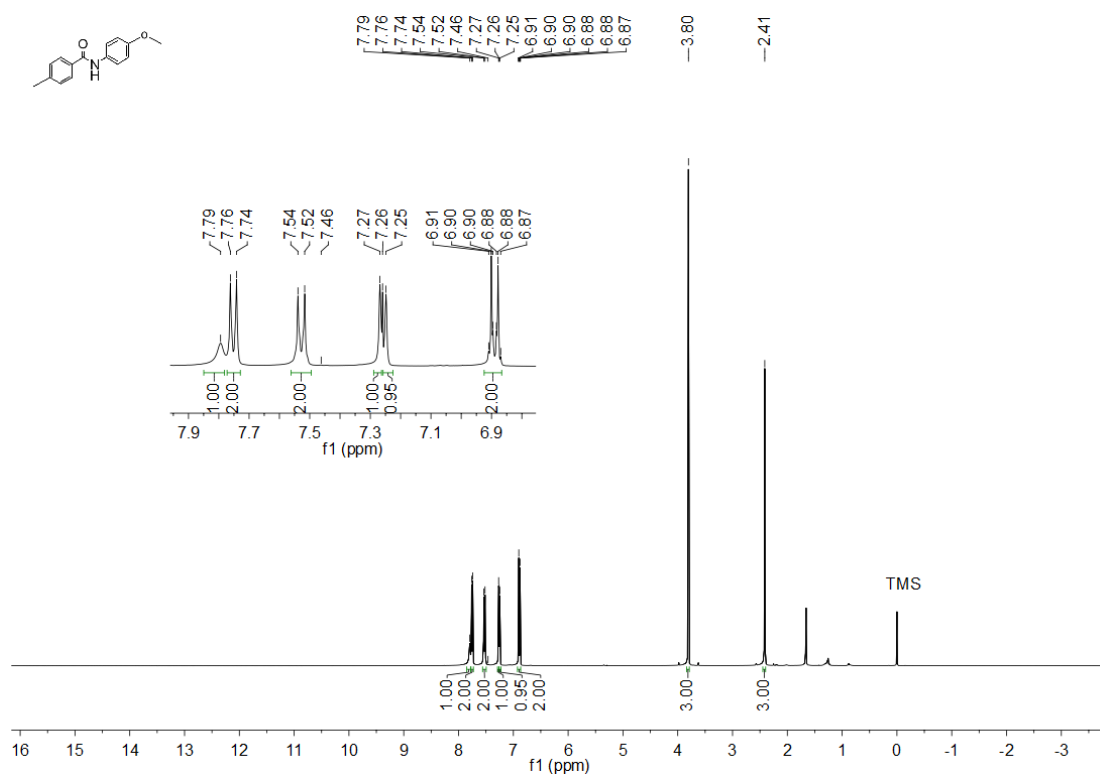


Figure S44. The  $^{13}\text{C}$  NMR spectrum of N-(4-methoxyphenyl)-4-methylbenzamide (4l).

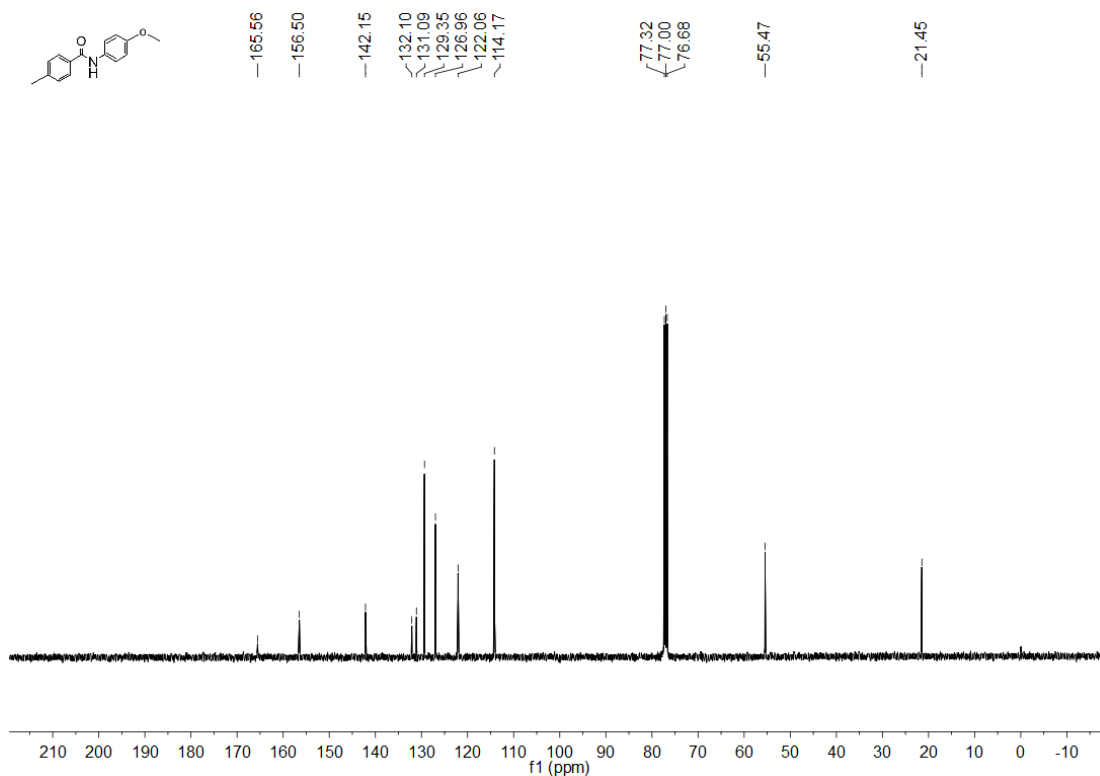


Figure S45. The  $^1\text{H}$  NMR spectrum of N-(4-fluorophenyl)-4-methylbenzamide (4q).

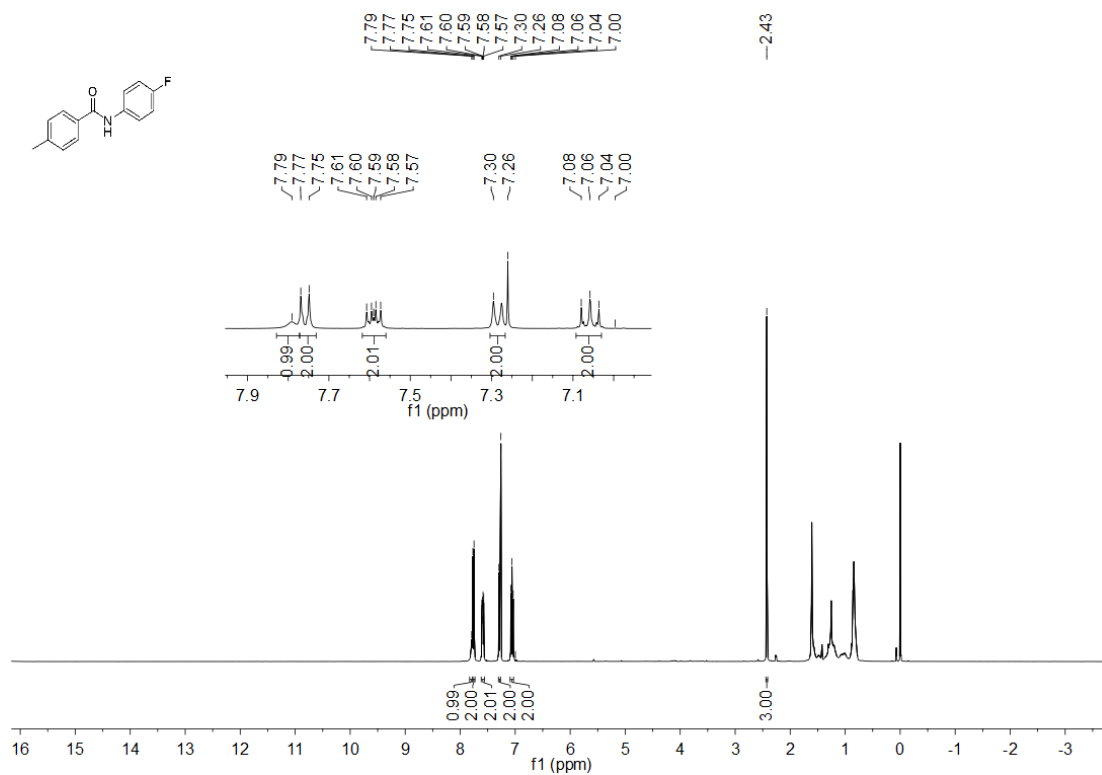


Figure S46. The  $^{13}\text{C}$  NMR spectrum of N-(4-fluorophenyl)-4-methylbenzamide (4q).

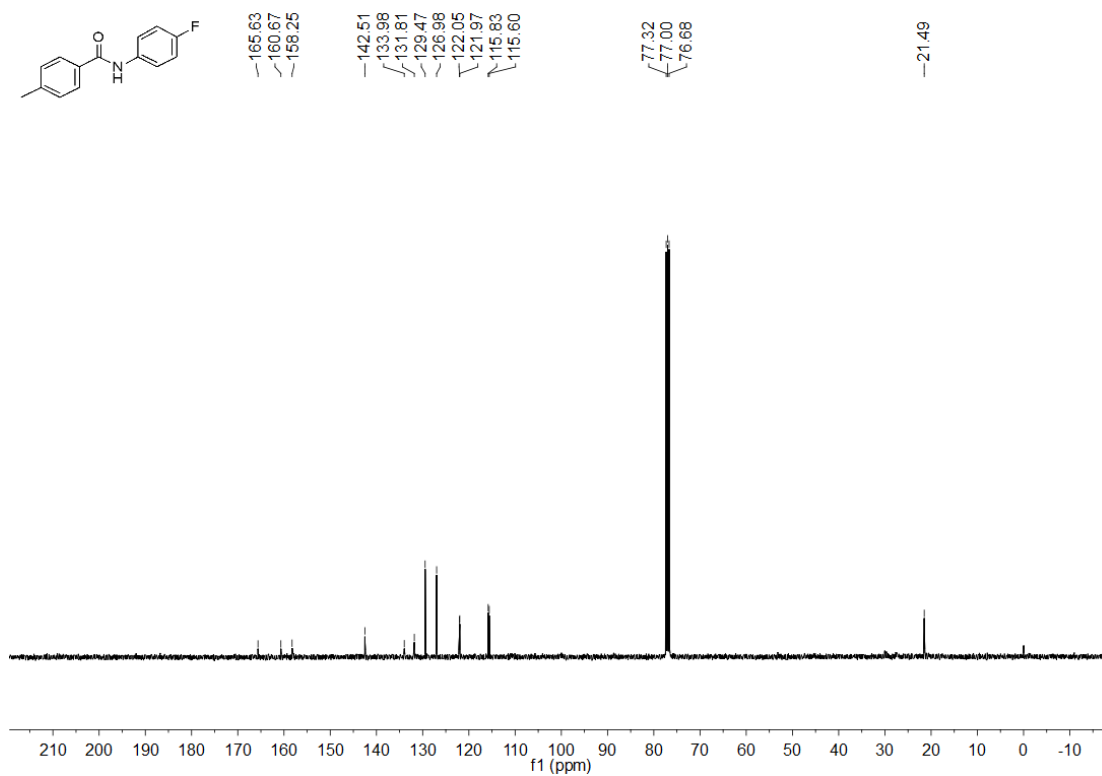


Figure S47. The  $^1\text{H}$  NMR spectrum of N-(4-chlorophenyl)-4-methylbenzamide (4r).

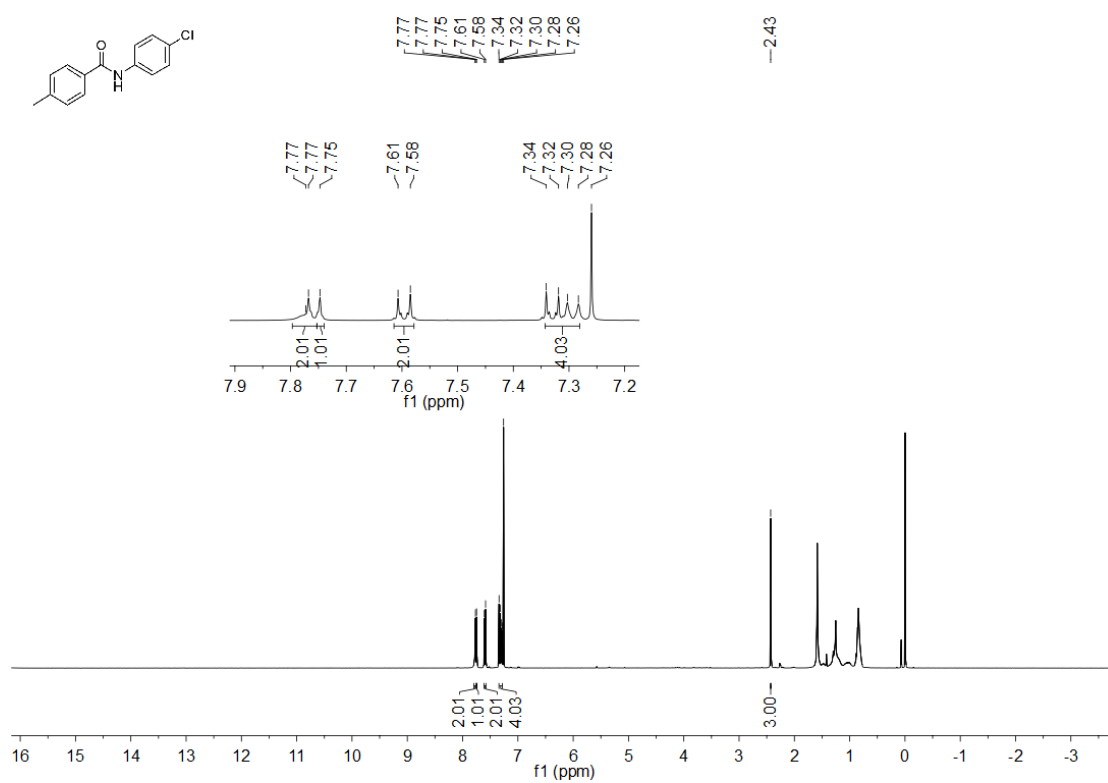


Figure S48. The  $^{13}\text{C}$  NMR spectrum of N-(4-chlorophenyl)-4-methylbenzamide (4r).

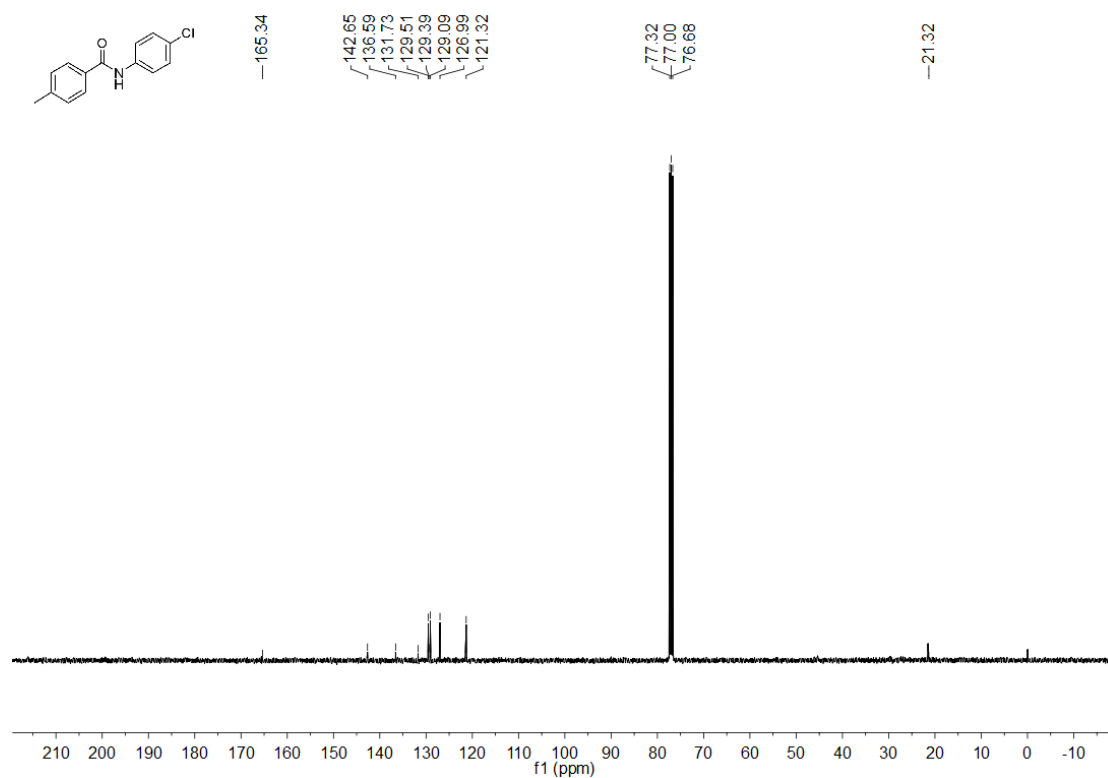


Figure S49. The  $^1\text{H}$  NMR spectrum of 4-methyl-N-(naphthalen-1-yl)benzamide (4s).

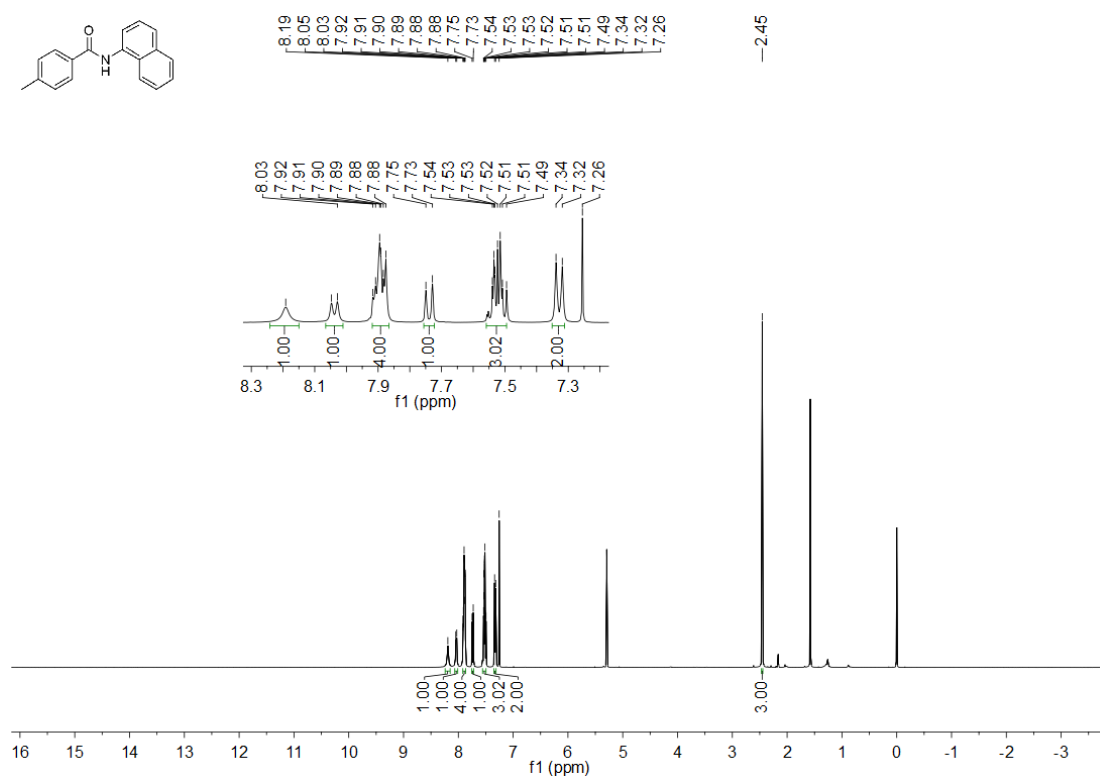


Figure S50. The  $^{13}\text{C}$  NMR spectrum of 4-methyl-N-(naphthalen-1-yl)benzamide (4s).

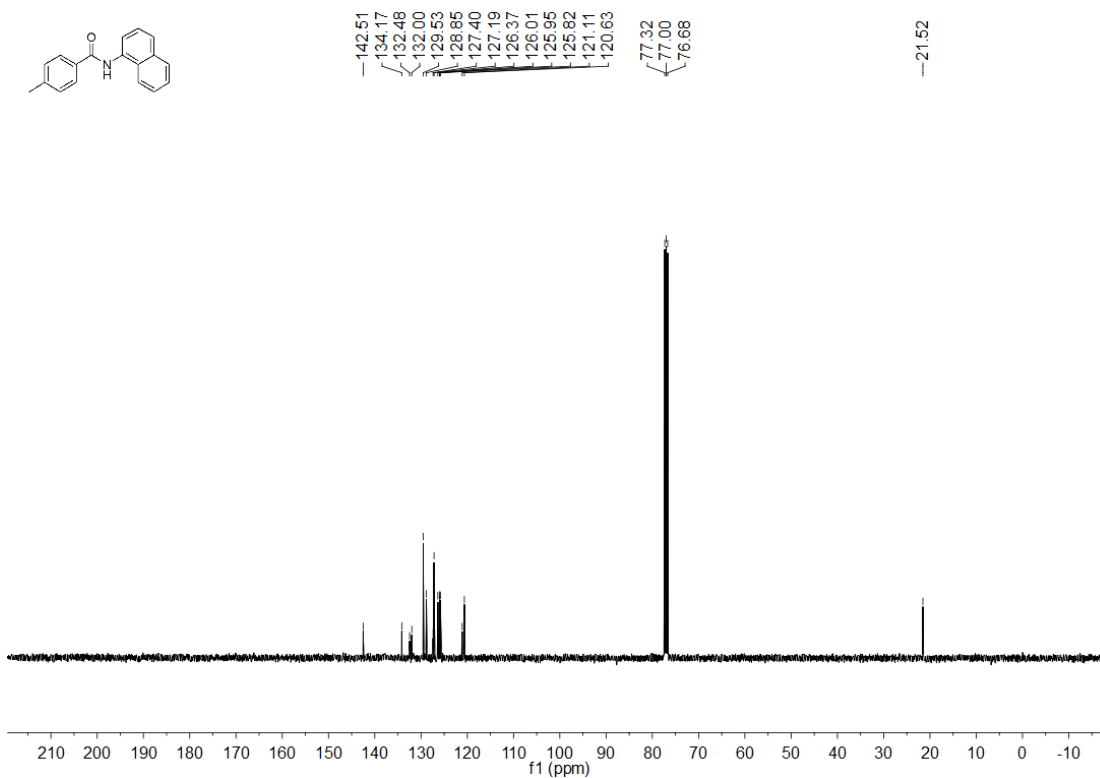


Figure S51. The  $^1\text{H}$  NMR spectrum of N-cyclohexyl-4-methylbenzamide (4t).

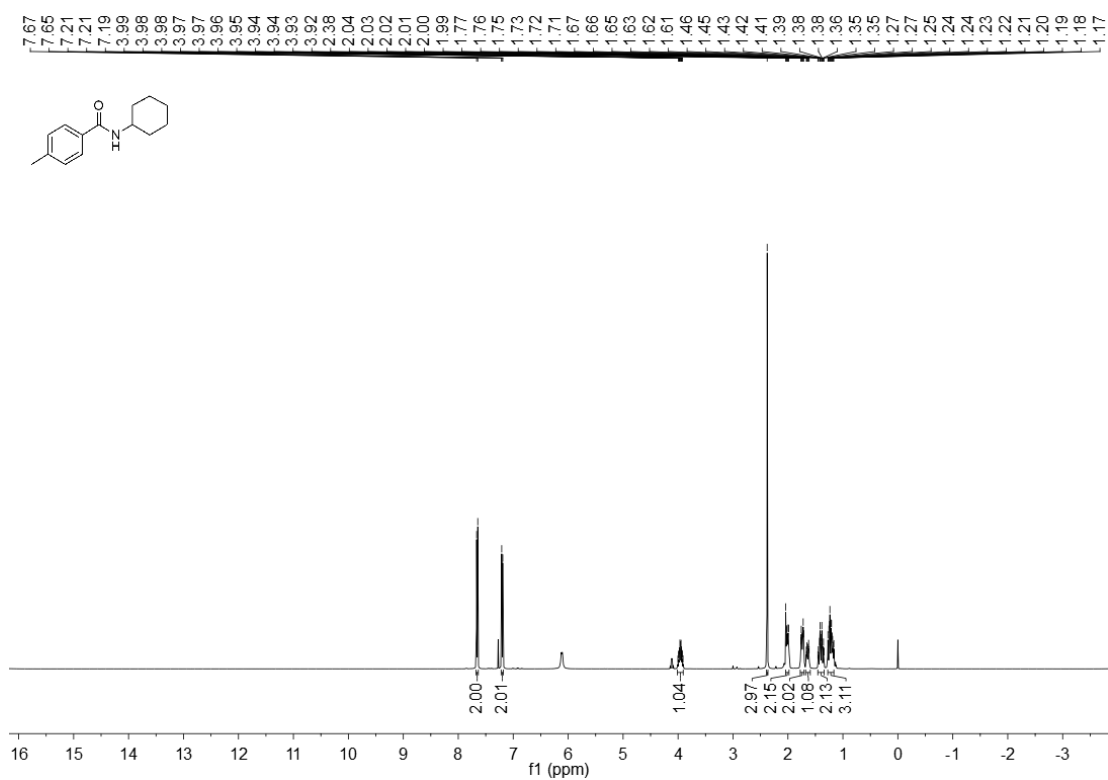


Figure S52. The  $^{13}\text{C}$  NMR spectrum of N-cyclohexyl-4-methylbenzamide (4t).

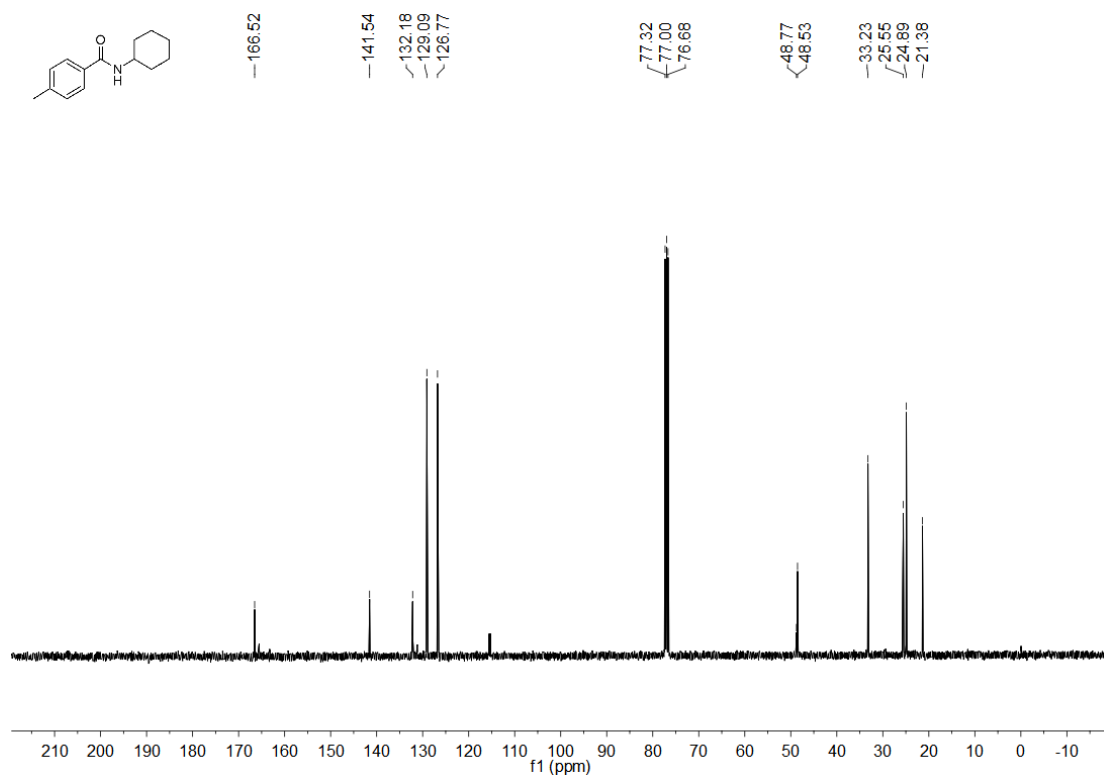


Figure S53. The  $^1\text{H}$  NMR spectrum of N-benzyl-4-methylbenzamide (4p).

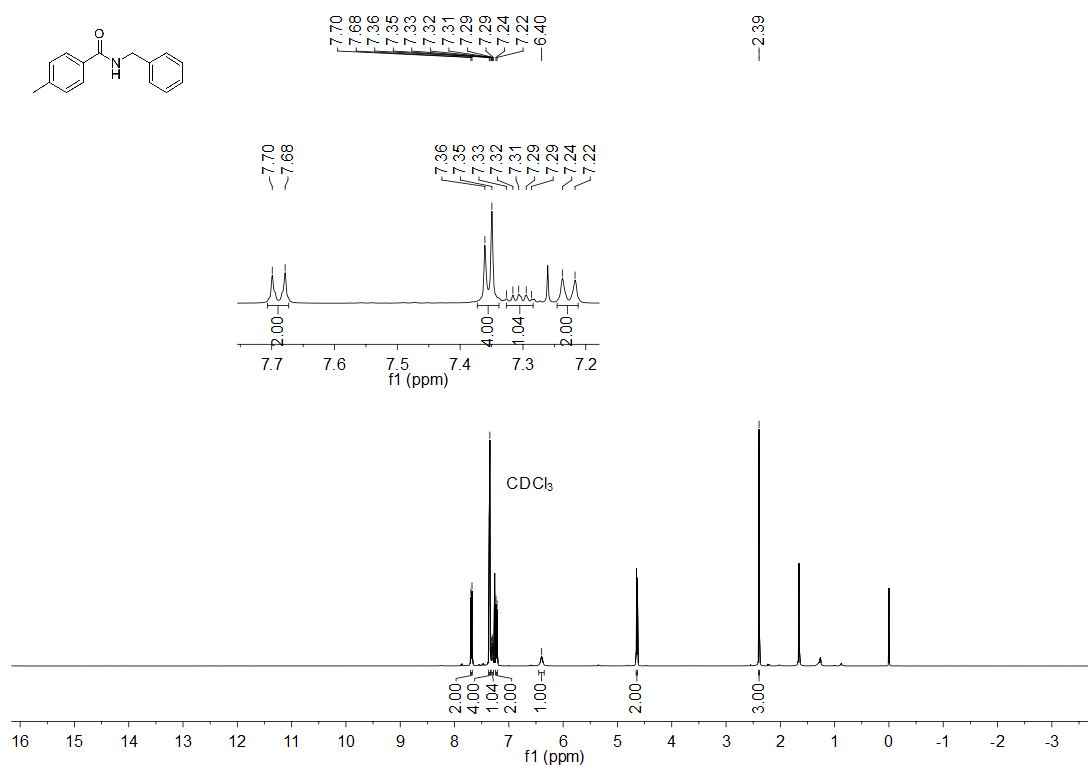


Figure S54. The  $^{13}\text{C}$  NMR spectrum of N-benzyl-4-methylbenzamide (4p).

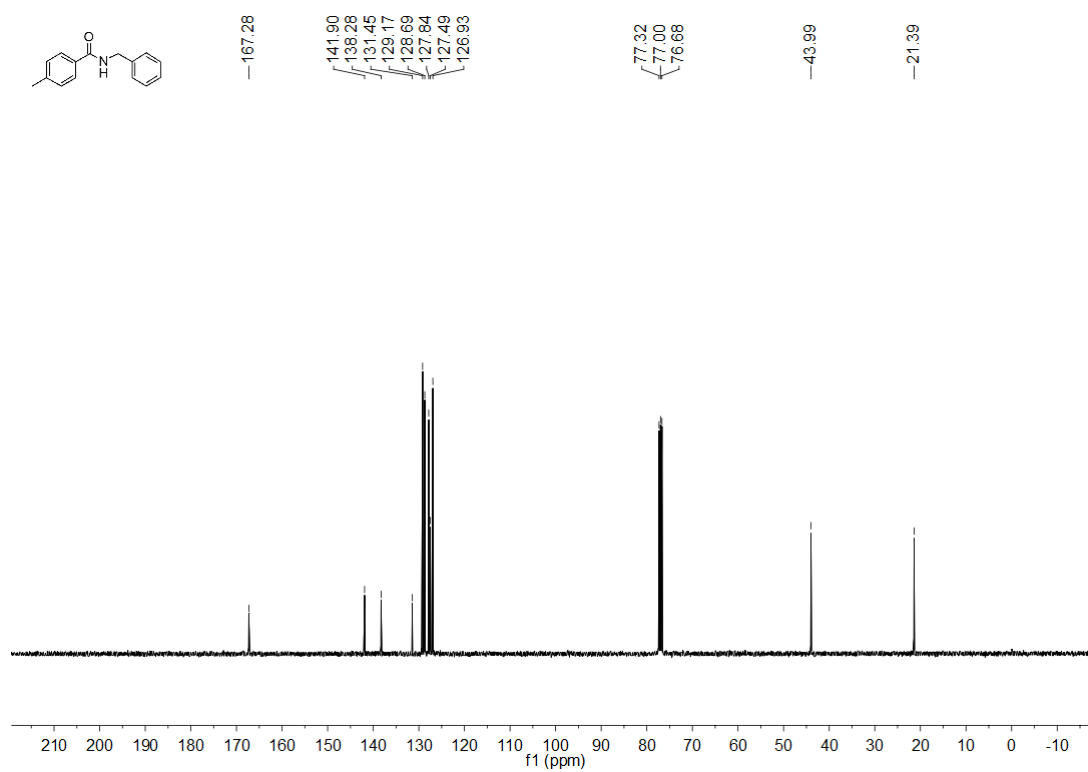




Figure S55. The  $^1\text{H}$  NMR spectrum of N-(4-fluorophenyl)-2-methylbenzamide (5q).

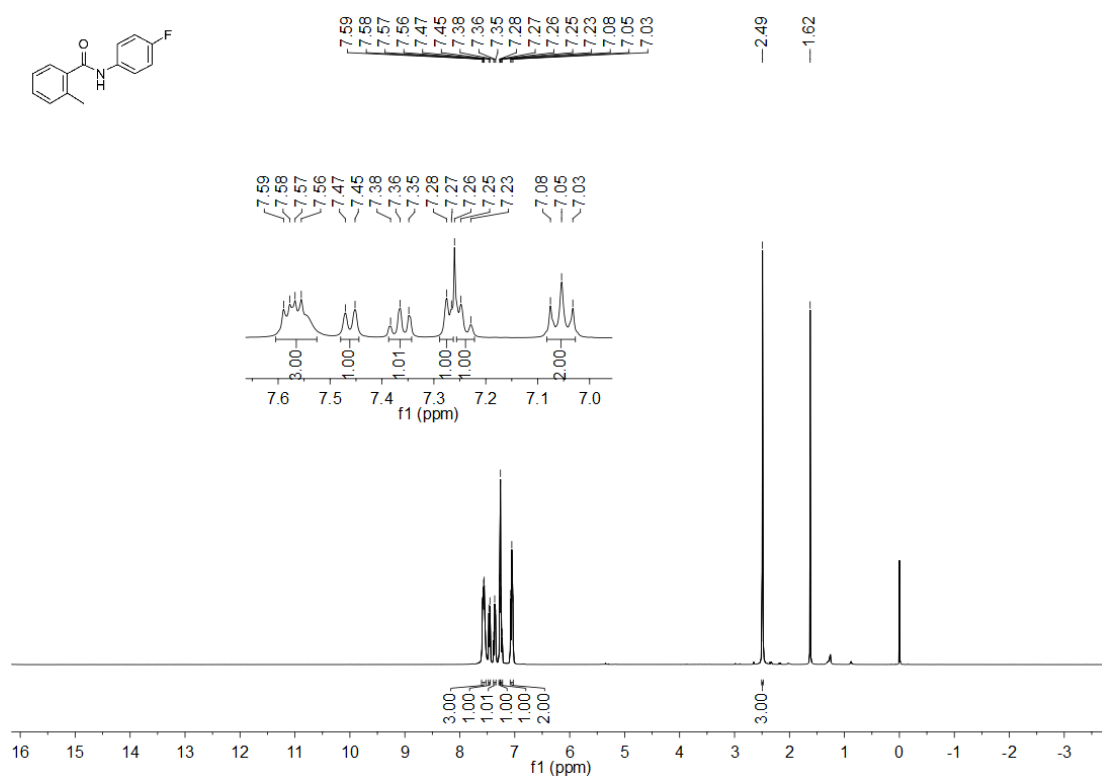


Figure S56. The  $^{13}\text{C}$  NMR spectrum of N-(4-fluorophenyl)-2-methylbenzamide (5q).

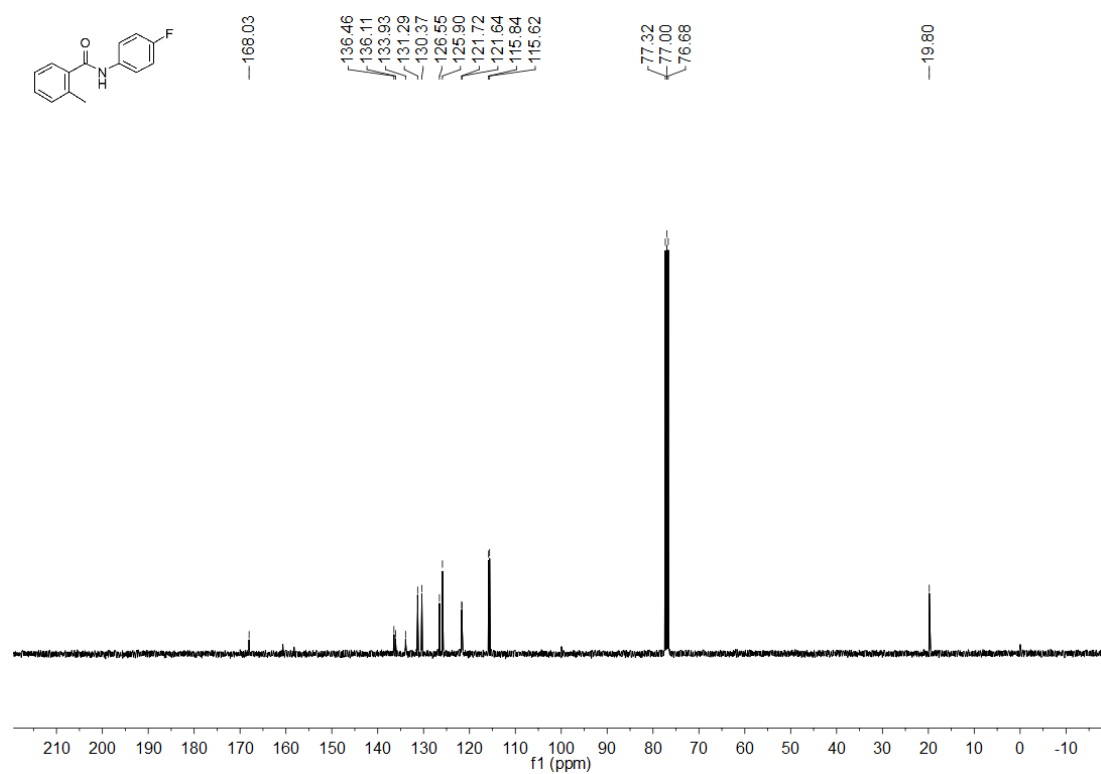


Figure S57. The  $^1\text{H}$  NMR spectrum of 4-methoxy-N-(o-tolyl)benzamide (6e).

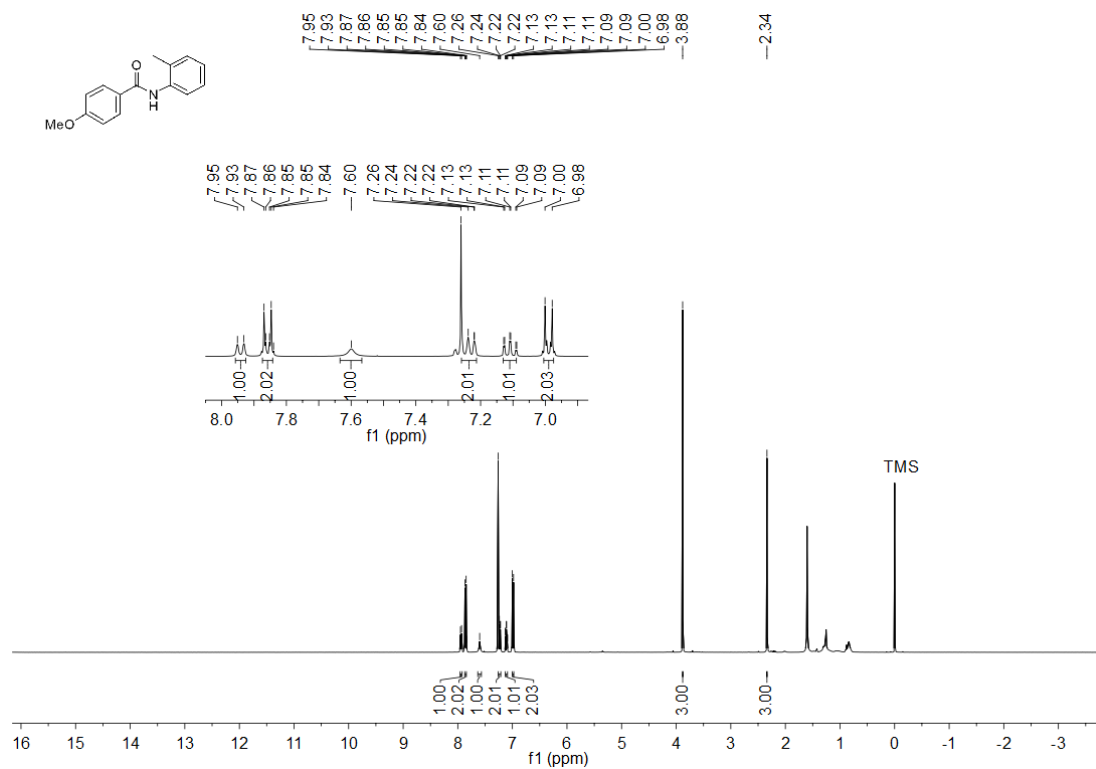


Figure S58. The  $^{13}\text{C}$  NMR spectrum of 4-methoxy-N-(o-tolyl)benzamide (6e).

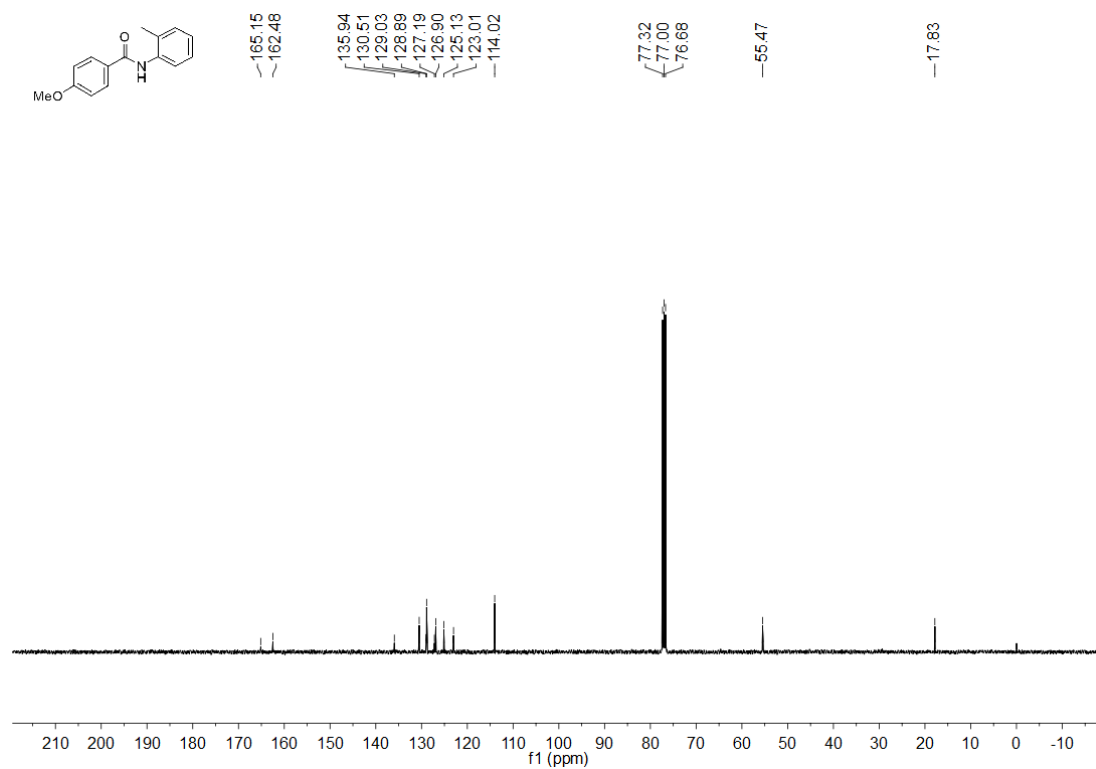


Figure S59. The  $^1\text{H}$  NMR spectrum of N-(2-aminophenyl)-4-methoxybenzamide (6m).

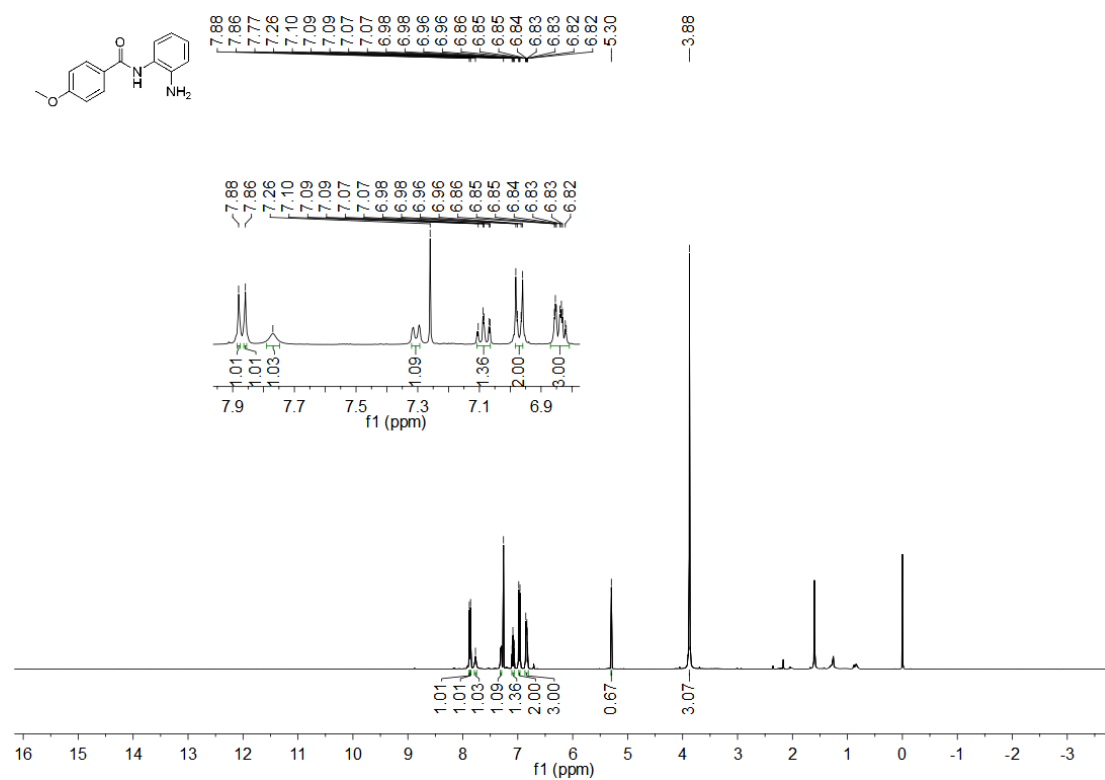


Figure S60. The  $^{13}\text{C}$  NMR spectrum of N-(2-aminophenyl)-4-methoxybenzamide (6m).

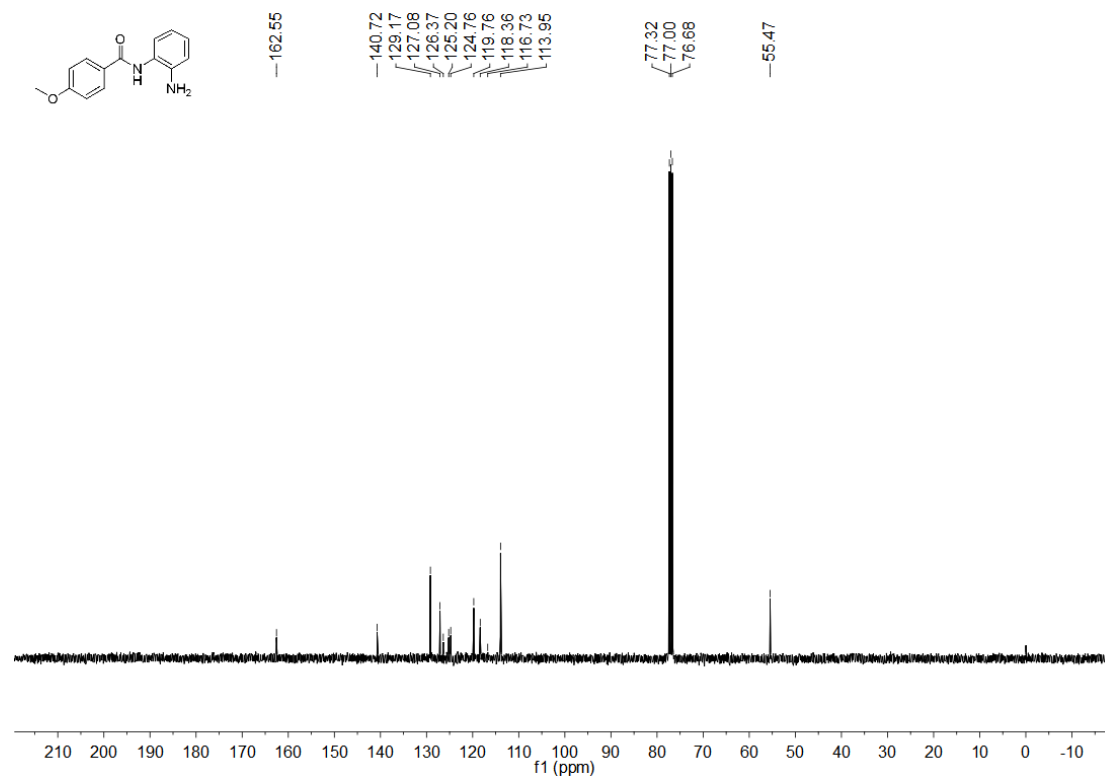


Figure S61. The  $^1\text{H}$  NMR spectrum of N-(4-acetylphenyl)-4-fluorobenzamide (7u).

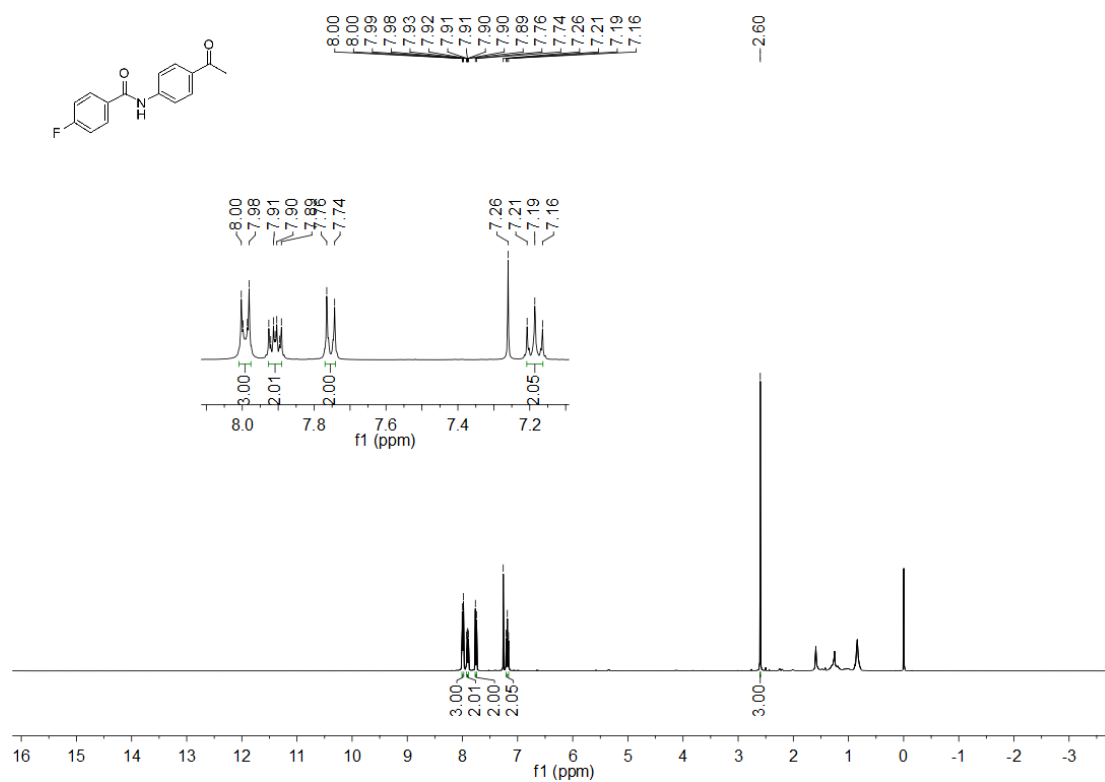


Figure S62. The  $^{13}\text{C}$  NMR spectrum of N-(4-acetylphenyl)-4-fluorobenzamide (7u).

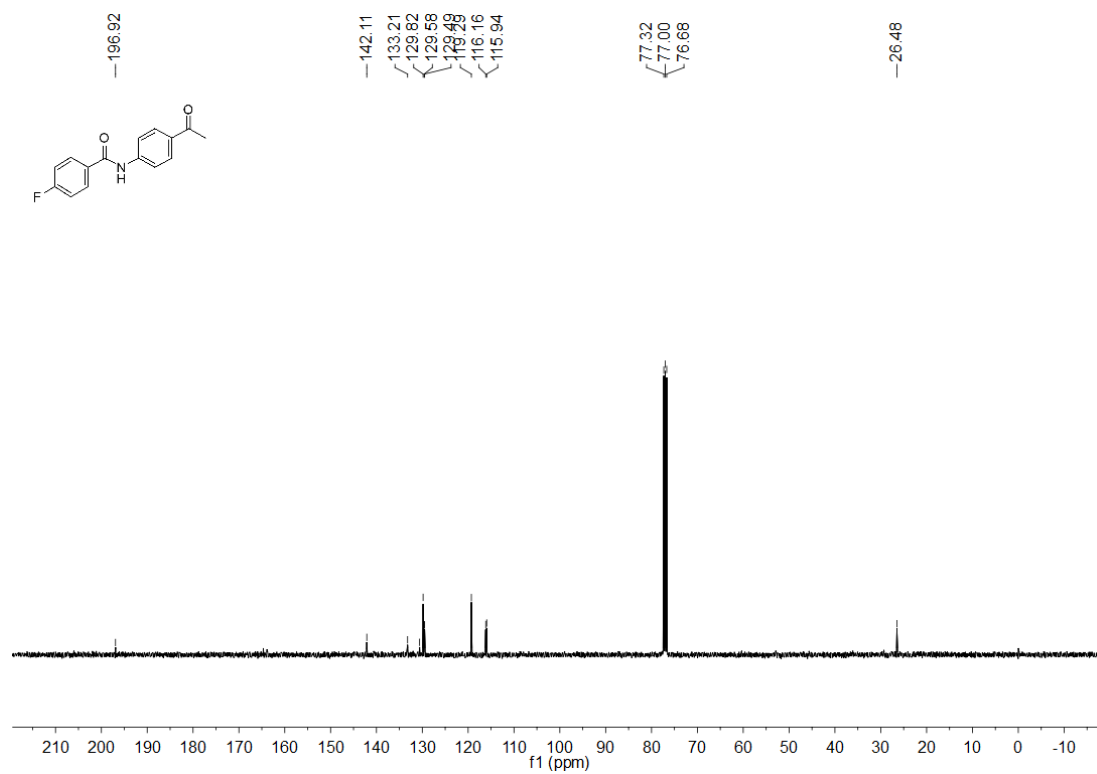


Figure S63. The  $^1\text{H}$  NMR spectrum of 4-fluoro-N,N-diphenylbenzamide (7v).

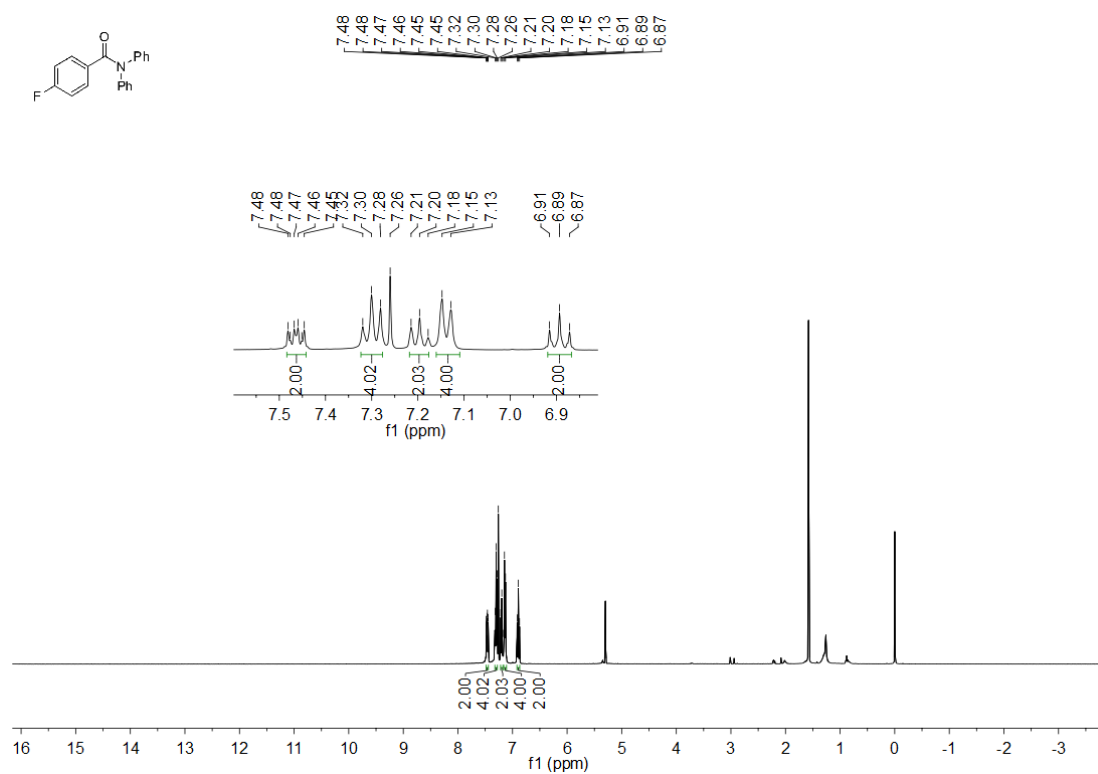
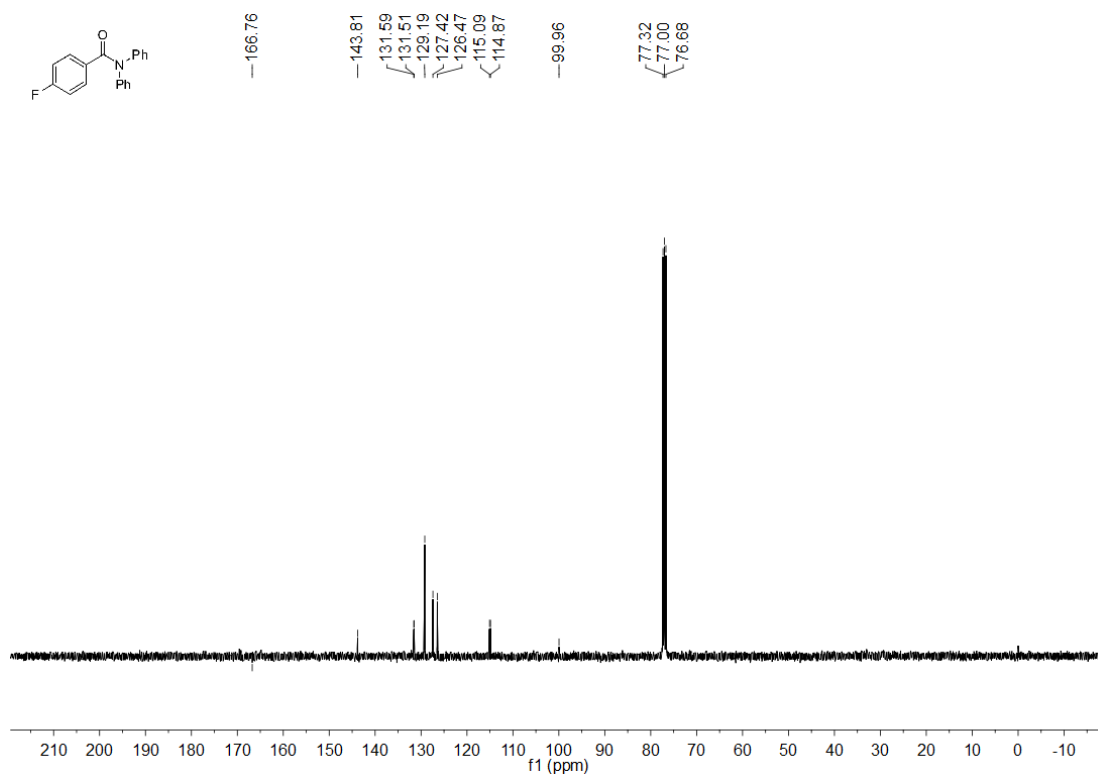


Figure S64. The  $^{13}\text{C}$  NMR spectrum of 4-fluoro-N,N-diphenylbenzamide (7v).



## 10. NMR spectrums of the aryl chloride amination products

Figure S65. The  $^1\text{H}$  NMR spectrum of N-(4-methoxyphenyl)-2,6-dimethylaniline (9a).

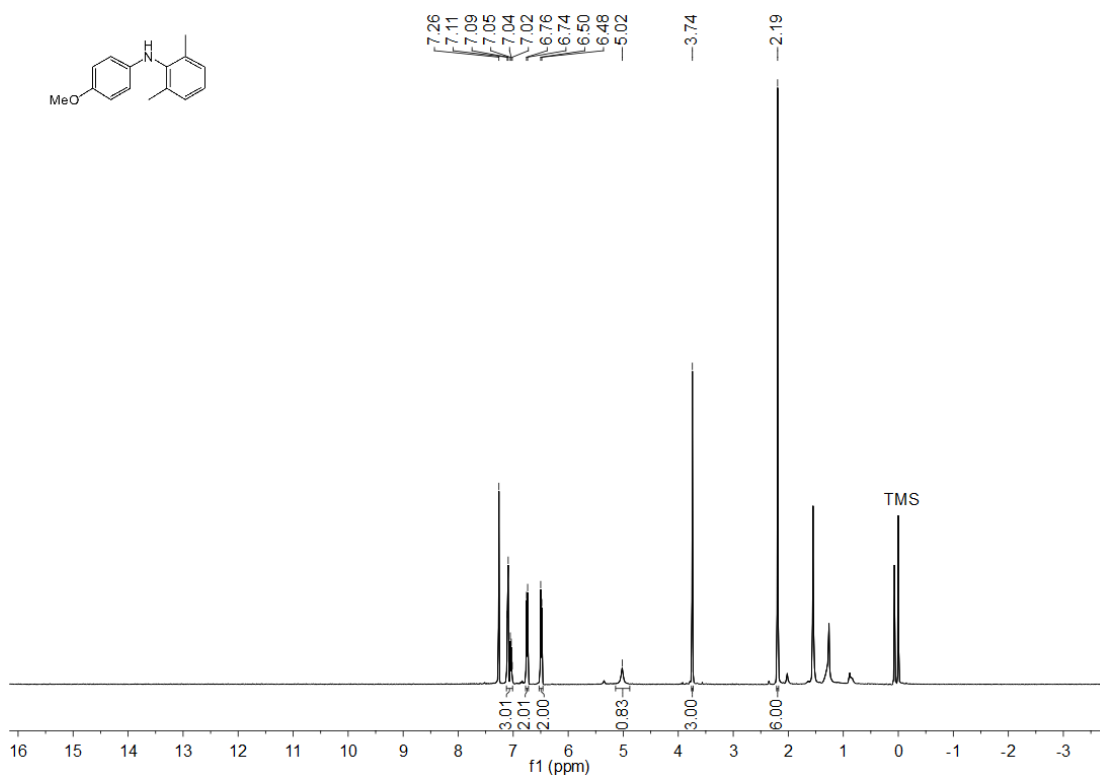


Figure S66. The  $^{13}\text{C}$  NMR spectrum of N-(4-methoxyphenyl)-2,6-dimethylaniline (9a).

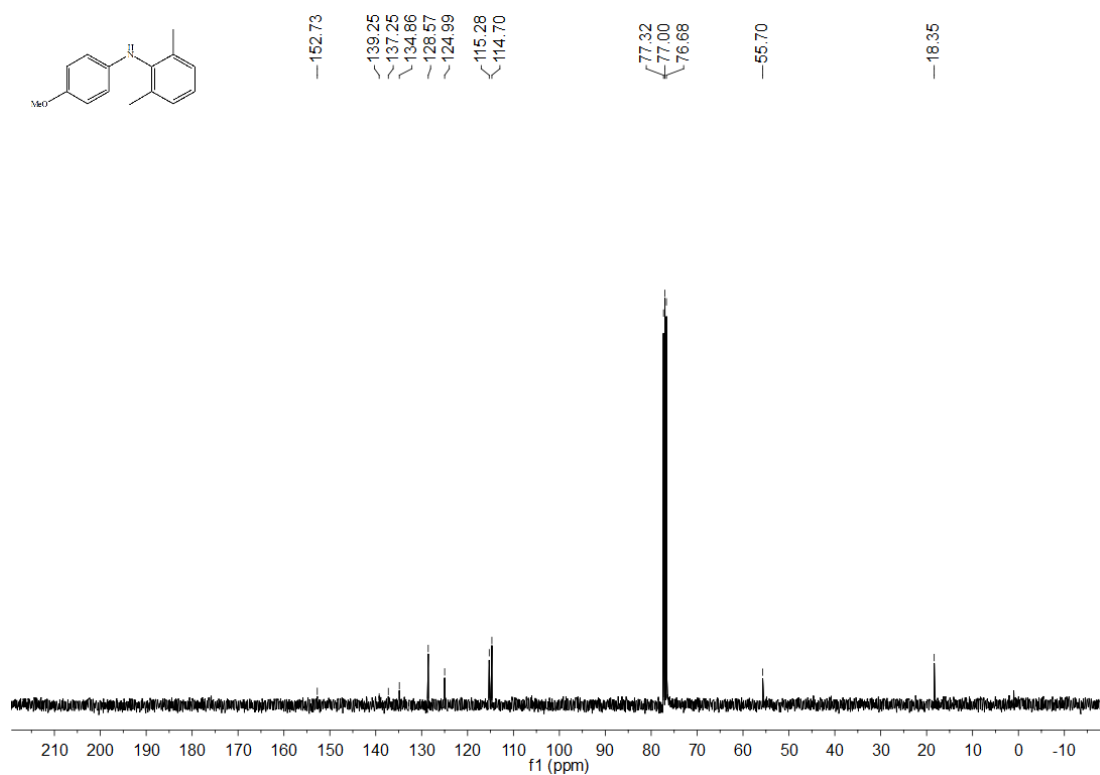


Figure S67. The <sup>1</sup>H NMR spectrum of 4-methoxy-N-phenylaniline (9j).

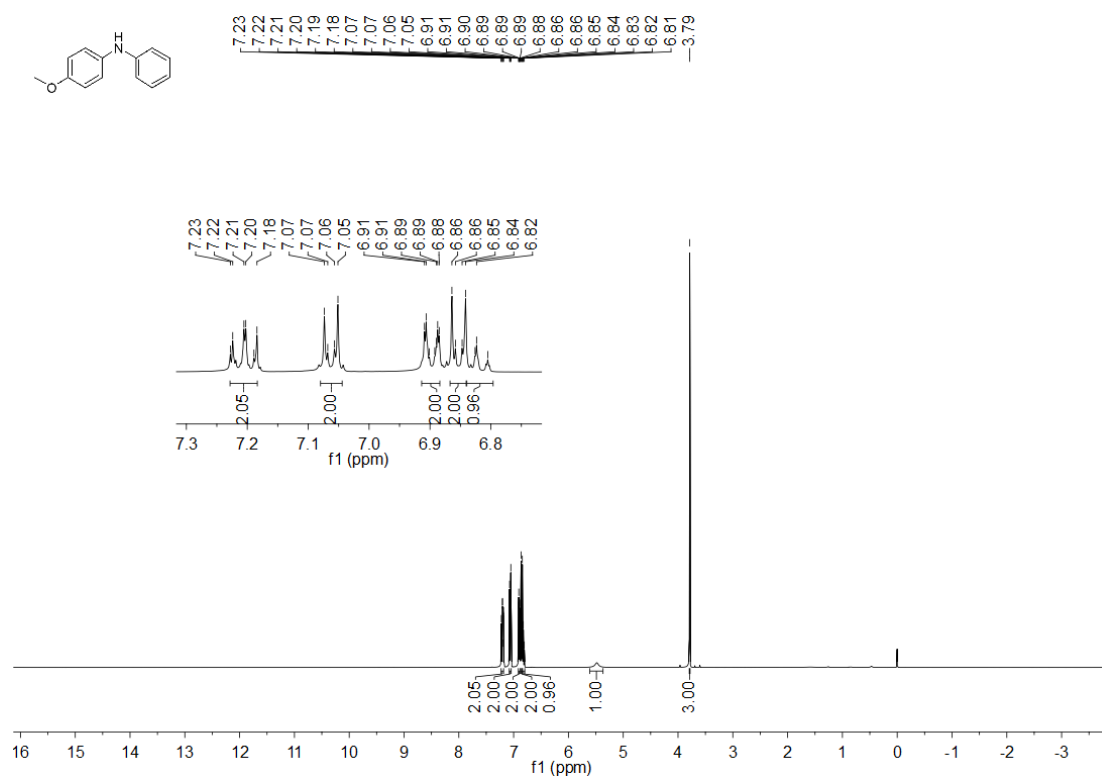


Figure S68. The <sup>13</sup>C NMR spectrum of 4-methoxy-N-phenylaniline (9j).

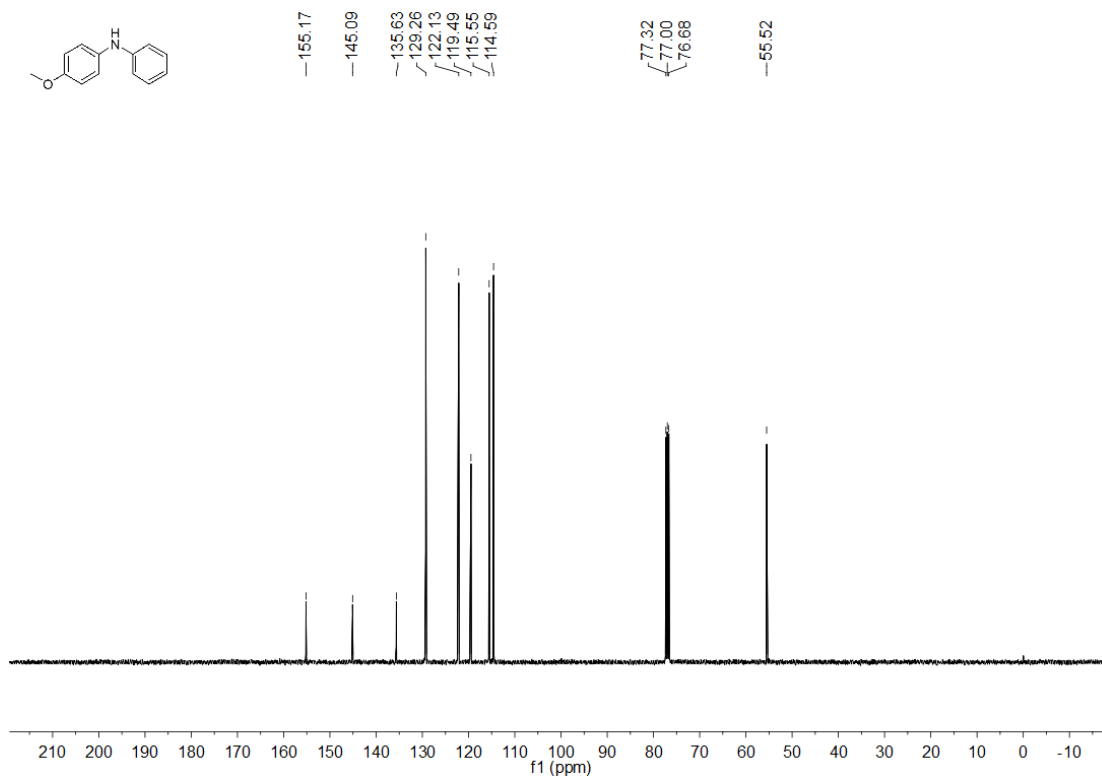


Figure S69. The  $^1\text{H}$  NMR spectrum of bis(4-methoxyphenyl)amine (91).

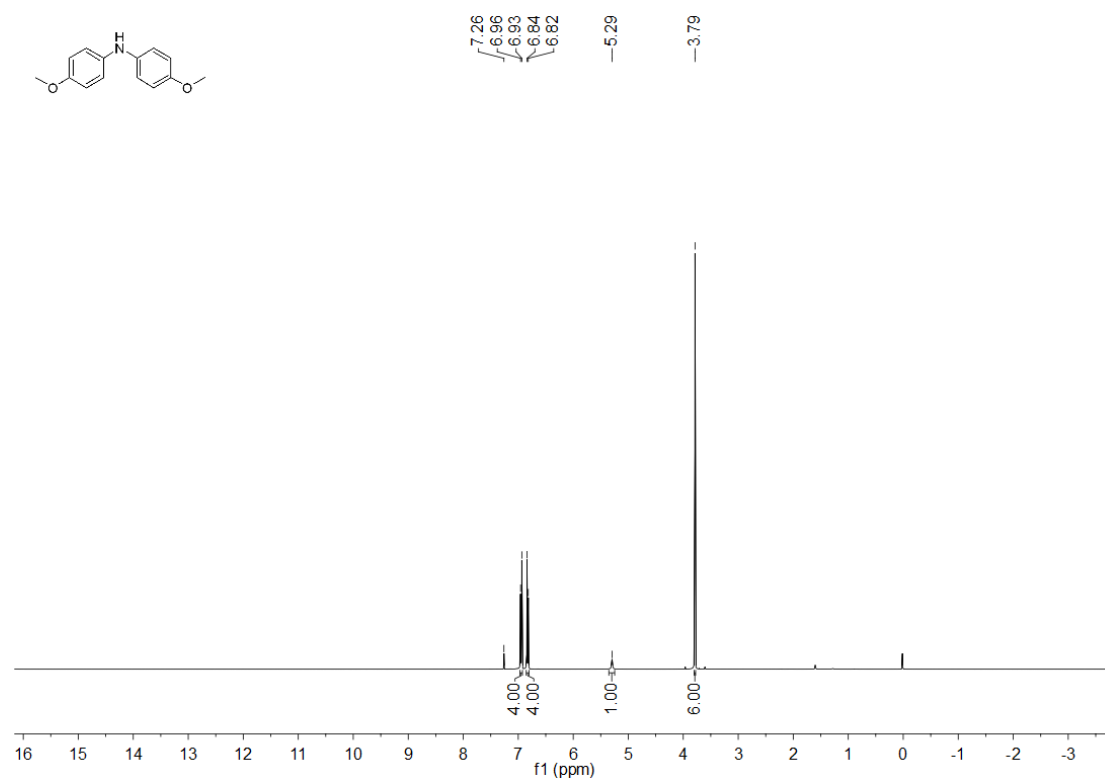


Figure S70. The  $^{13}\text{C}$  NMR spectrum of bis(4-methoxyphenyl)amine (91).

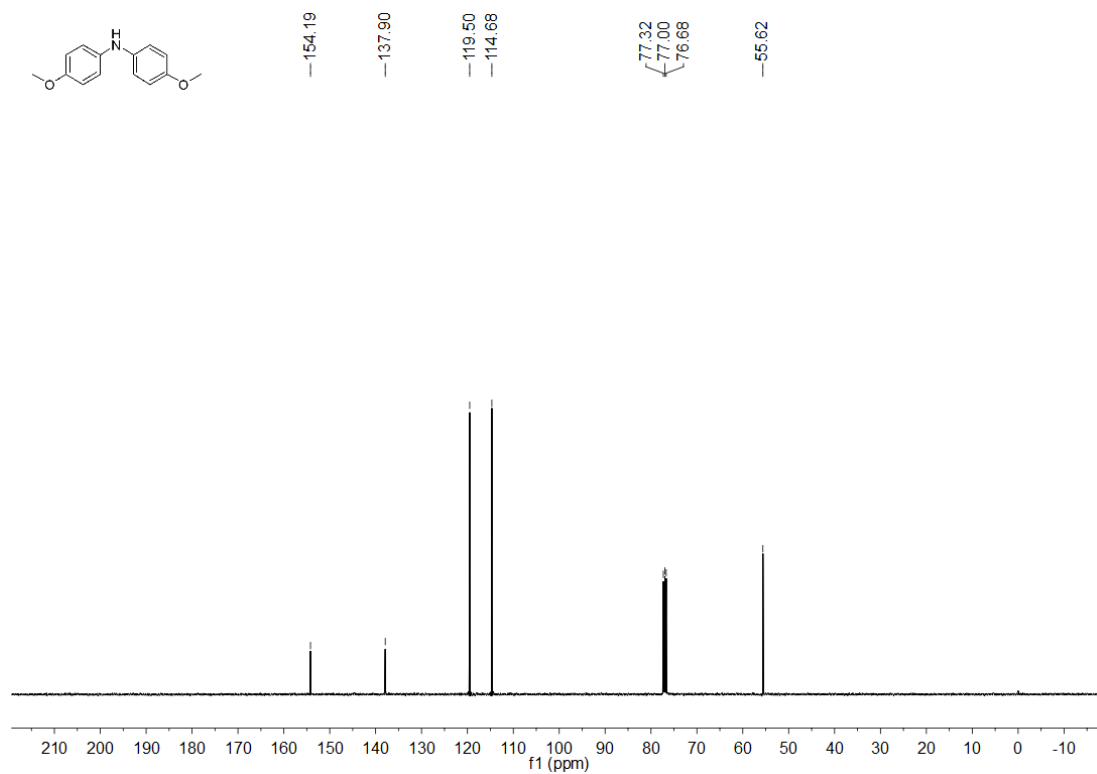




Figure S71. The  $^1\text{H}$  NMR spectrum of 4-(4-methoxyphenyl)morpholine (9o).

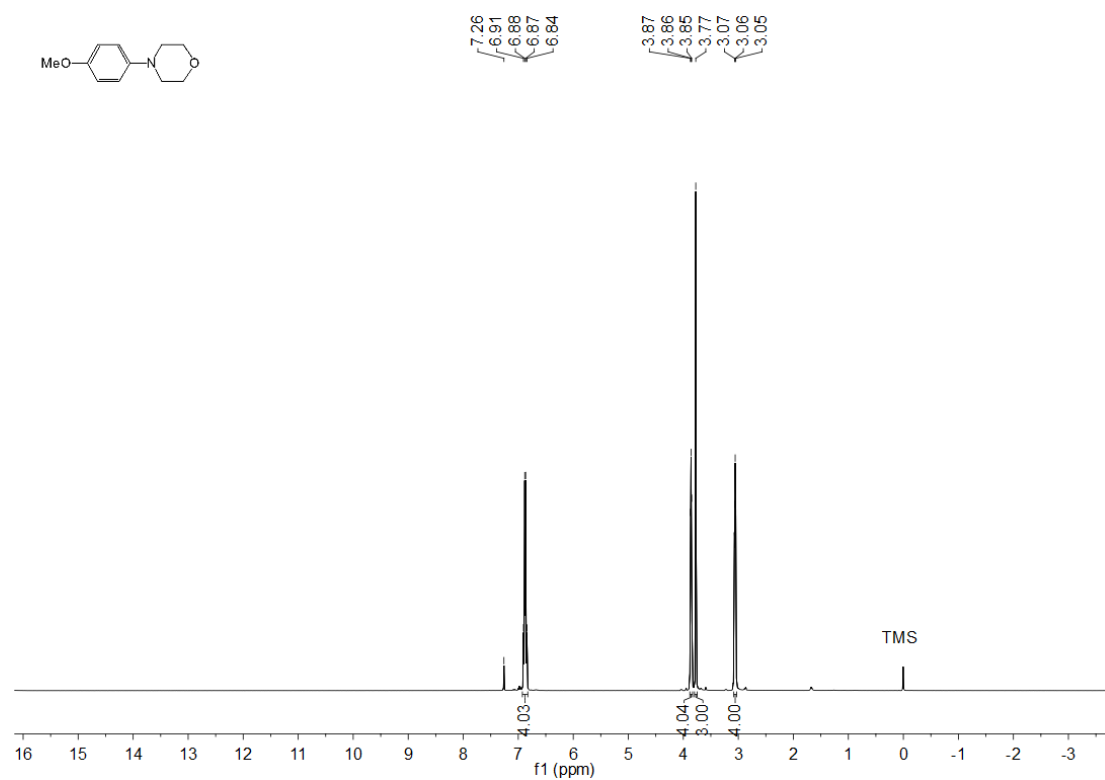


Figure S72. The  $^{13}\text{C}$  NMR spectrum of 4-(4-methoxyphenyl)morpholine (9o).

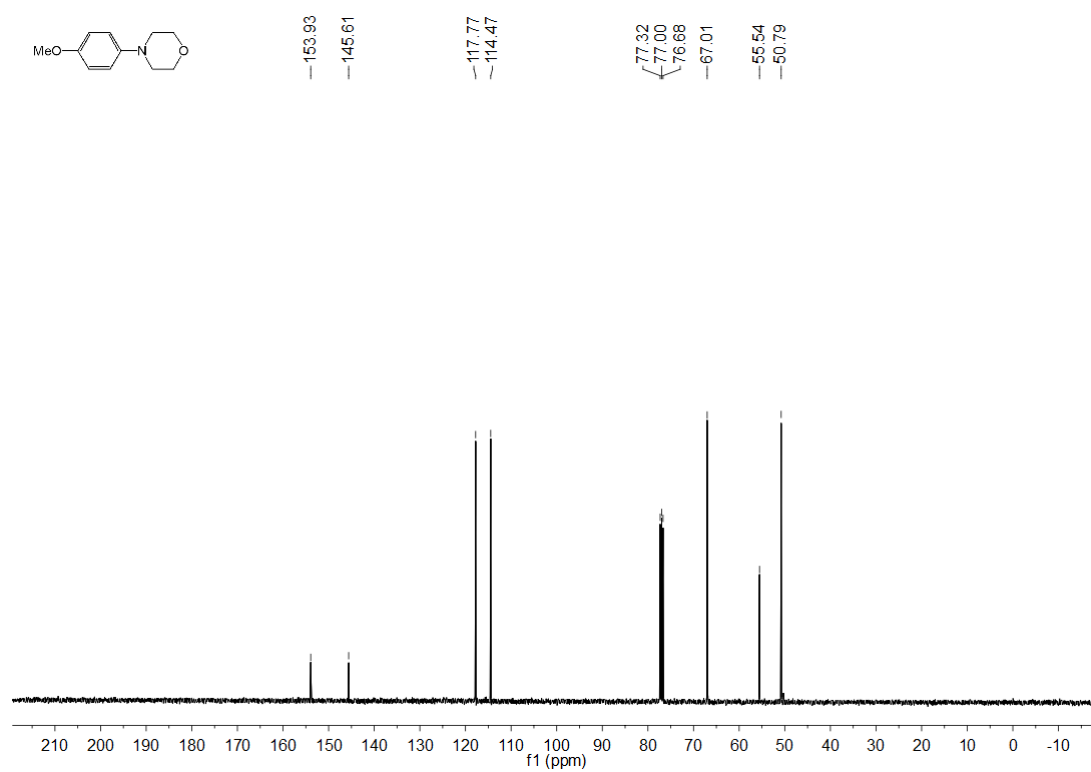


Figure S73. The  $^1\text{H}$  NMR spectrum of 4-fluoro-N-(4-methoxyphenyl)aniline (9q).

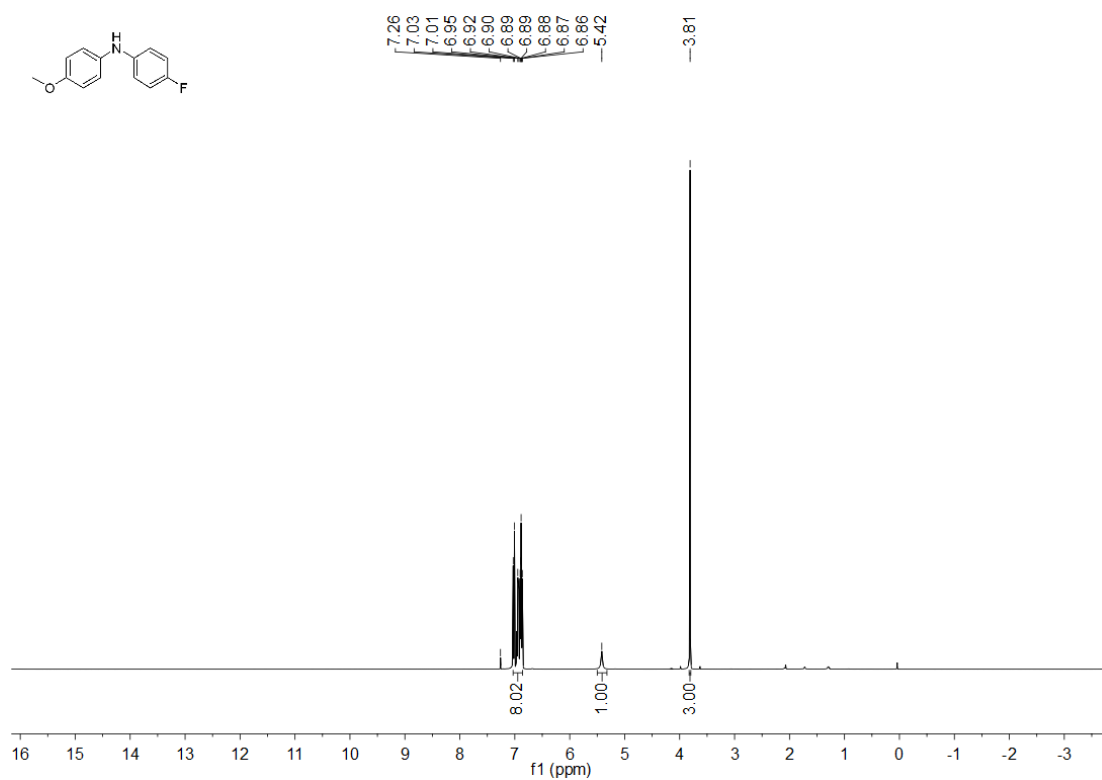


Figure S74. The  $^{13}\text{C}$  NMR spectrum of 4-fluoro-N-(4-methoxyphenyl)aniline (9q).

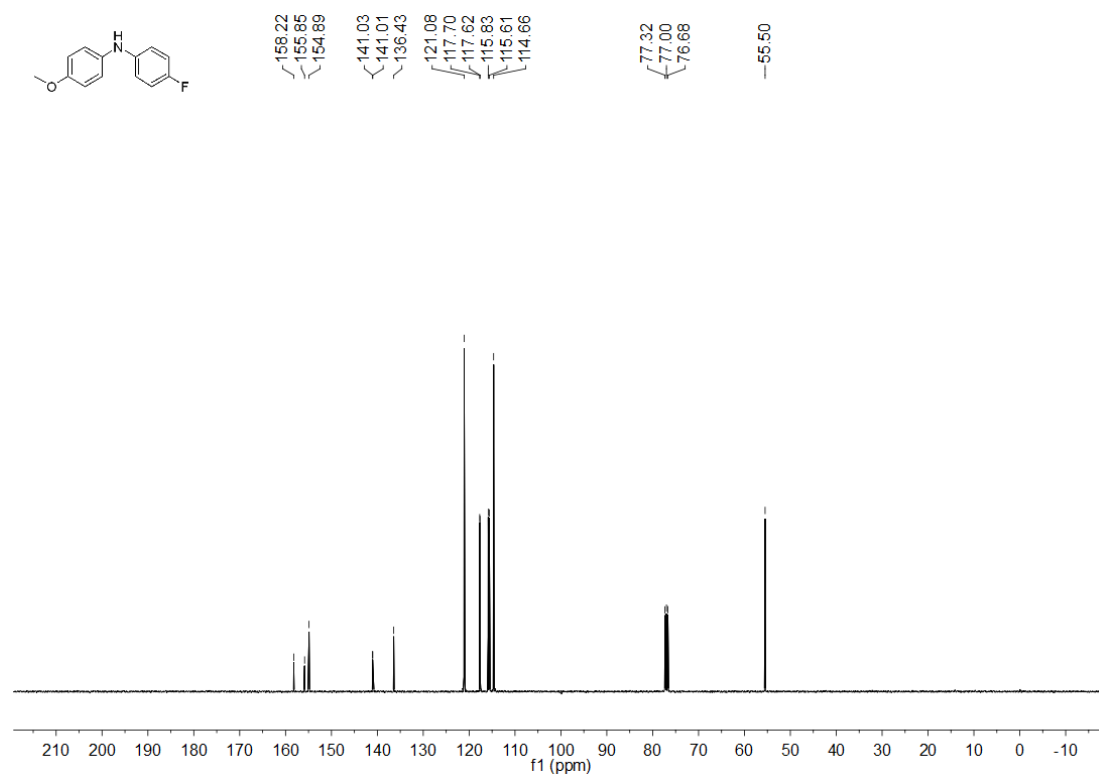


Figure S75. The  $^1\text{H}$  NMR spectrum of N-cyclohexyl-4-methoxyaniline (9t).

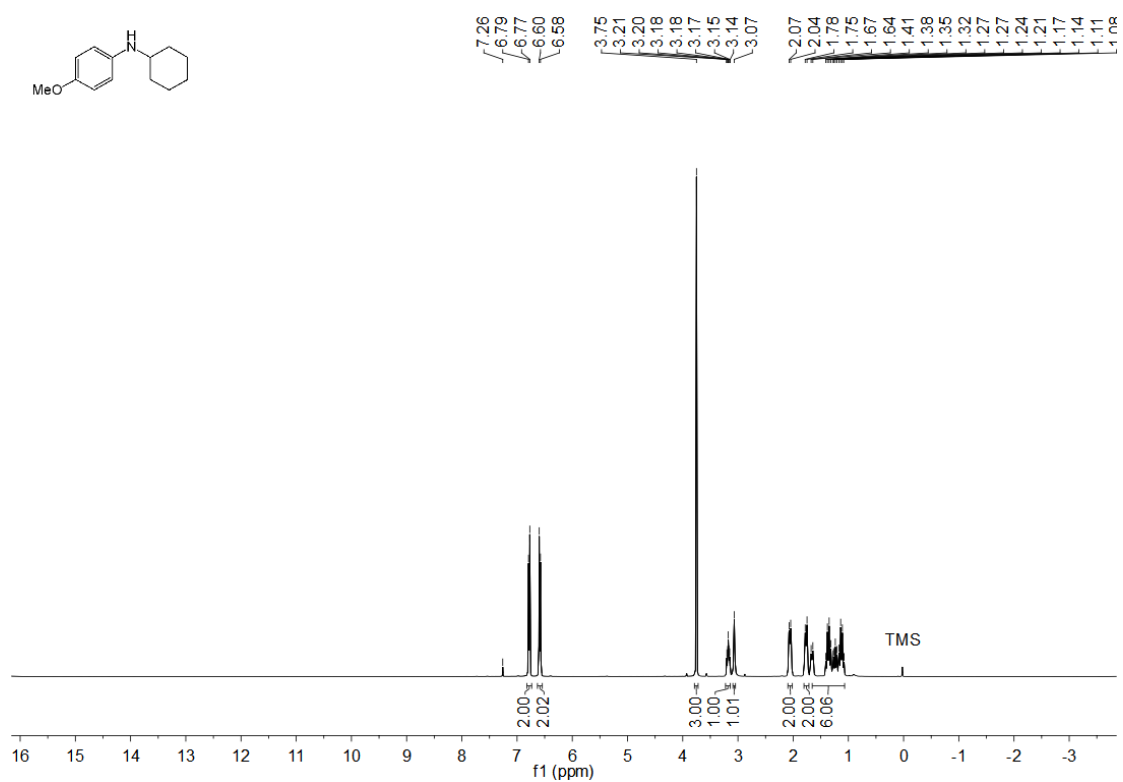


Figure S76. The  $^{13}\text{C}$  NMR spectrum of N-cyclohexyl-4-methoxyaniline (9t).

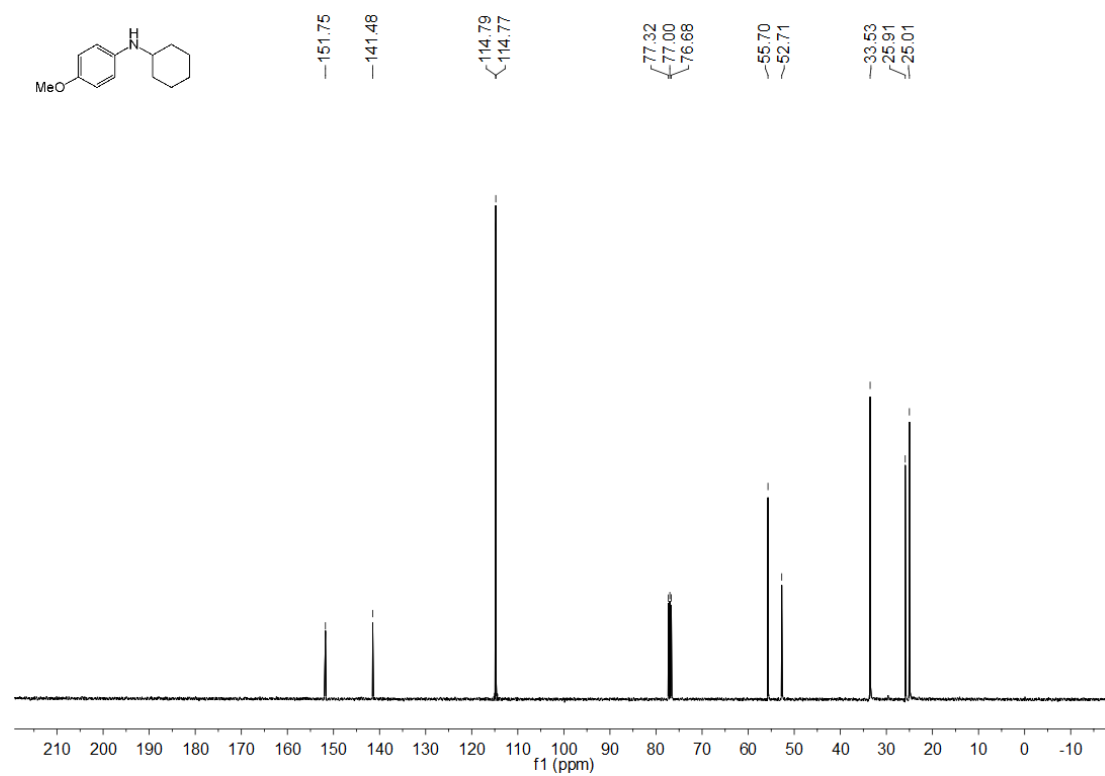


Figure S77. The  $^1\text{H}$  NMR spectrum of 2-isopropyl-N-(4-methoxyphenyl)-6-propylaniline (9w).

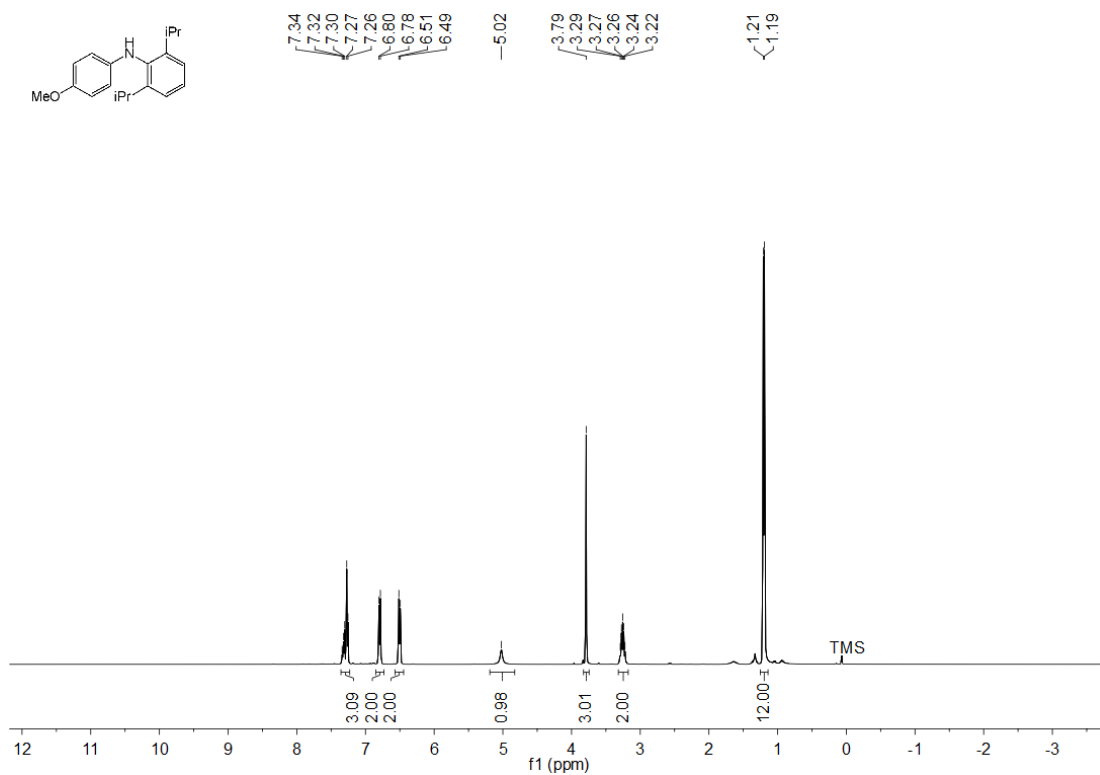


Figure S78. The  $^{13}\text{C}$  NMR spectrum of 2-isopropyl-N-(4-methoxyphenyl)-6-propylaniline (9w).

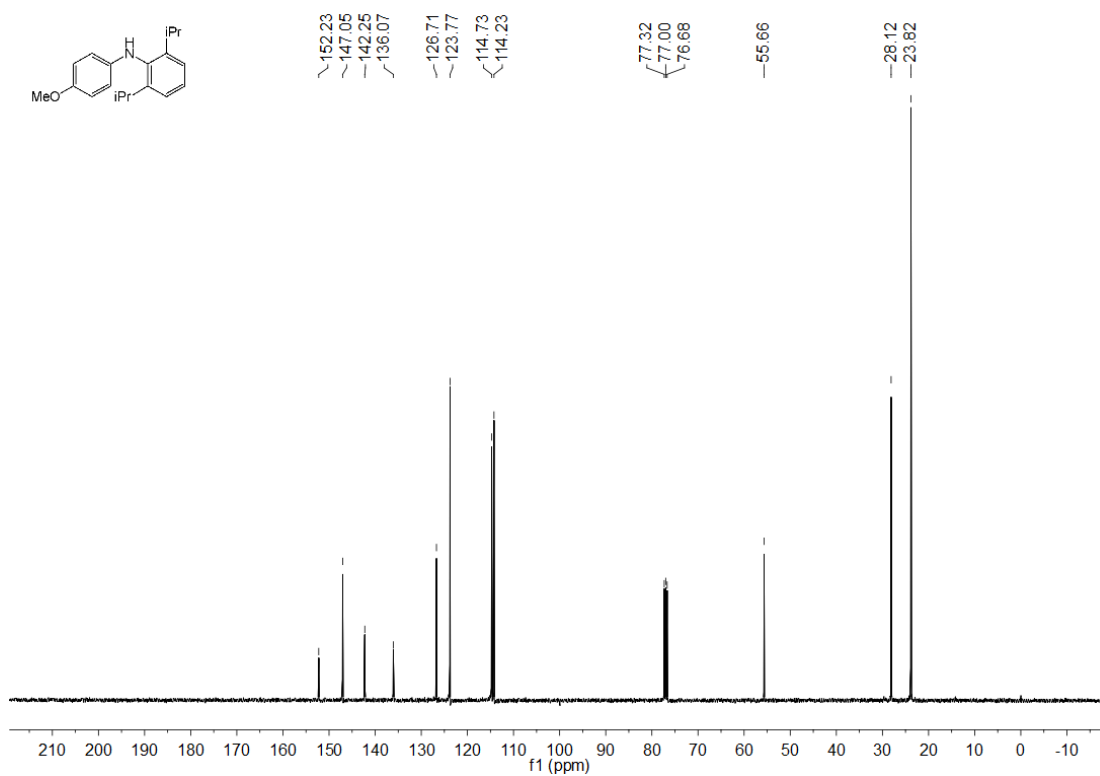


Figure S79. The  $^1\text{H}$  NMR spectrum of 4-methoxy-N-methyl-N-phenylaniline (9x).

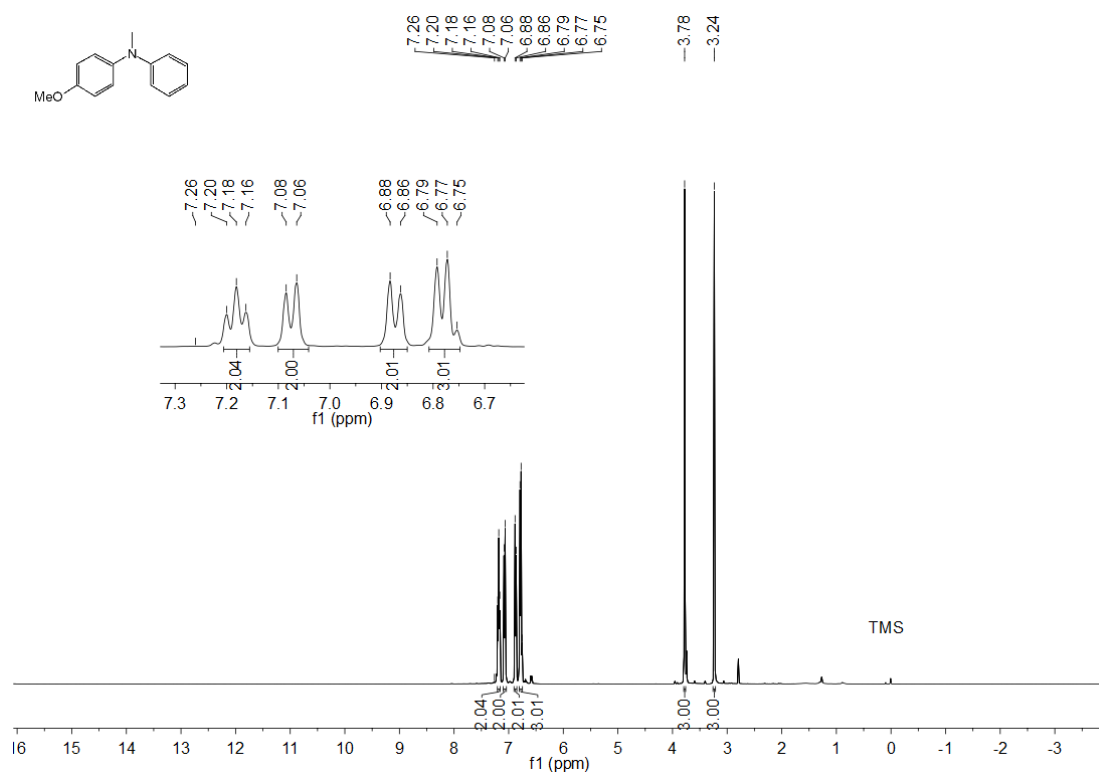


Figure S80. The  $^{13}\text{C}$  NMR spectrum of 4-methoxy-N-methyl-N-phenylaniline (9x).

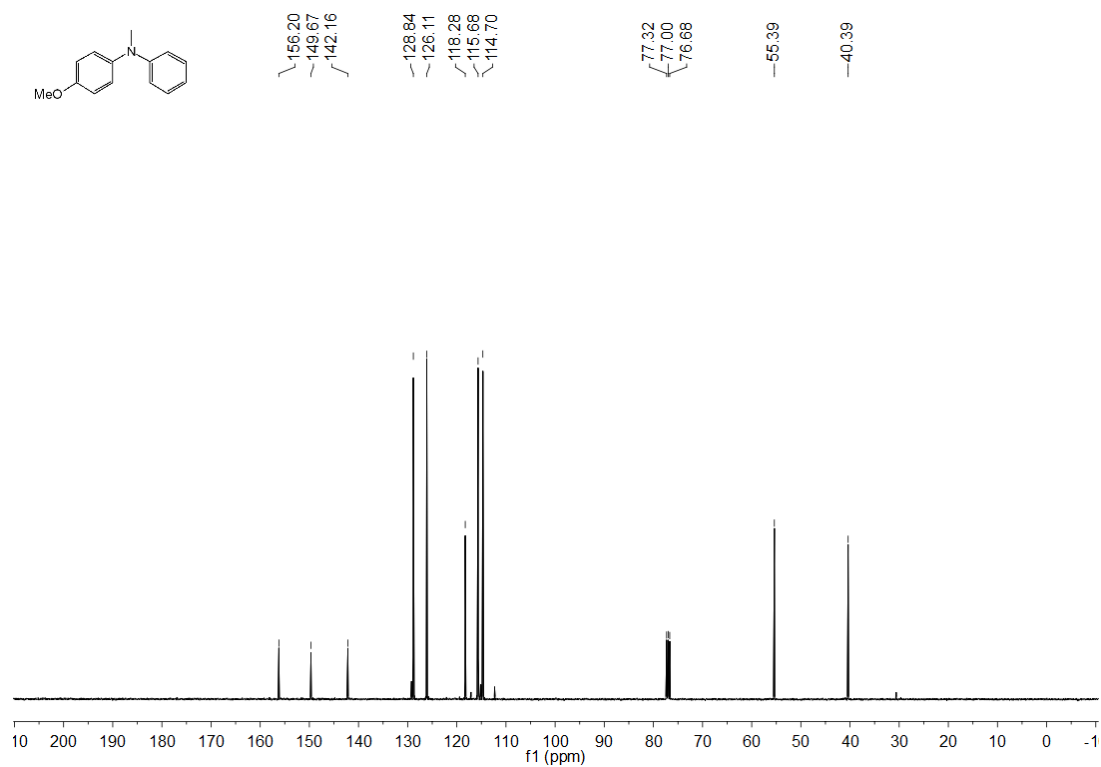


Figure S81. The  $^1\text{H}$  NMR spectrum of 2,6-diethyl-N-(4-methoxyphenyl)aniline (**9y**).

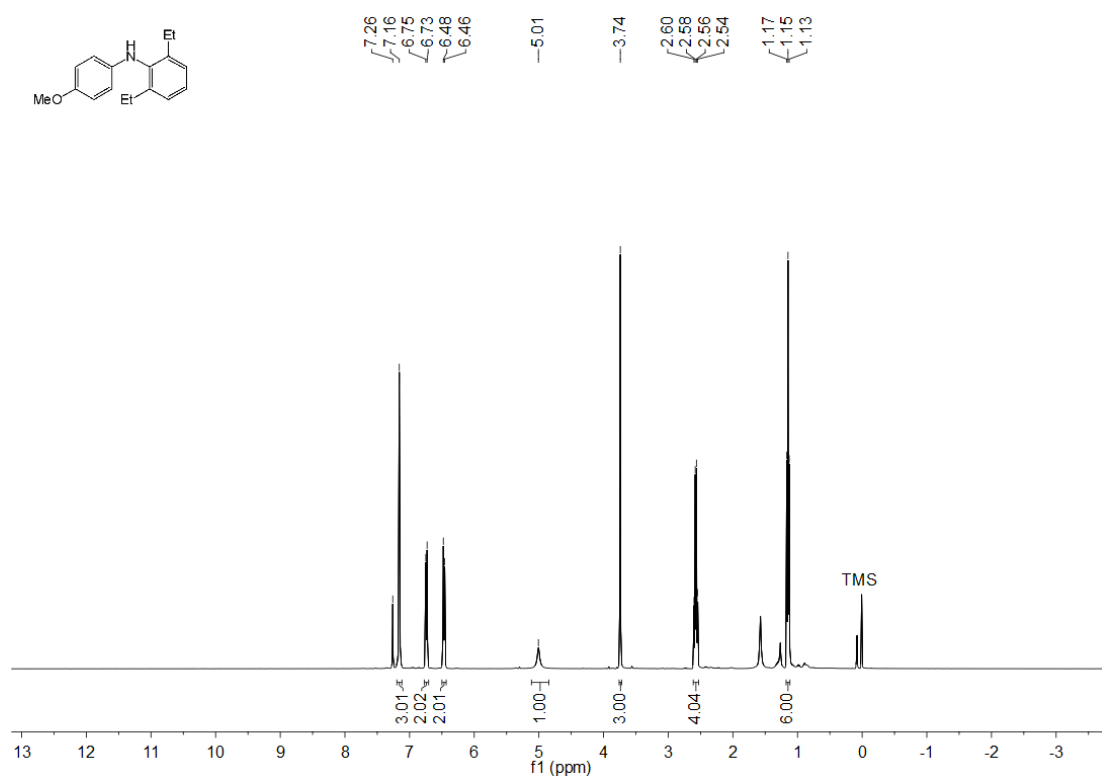


Figure S82. The  $^{13}\text{C}$  NMR spectrum of 2,6-diethyl-N-(4-methoxyphenyl)aniline (**9y**).

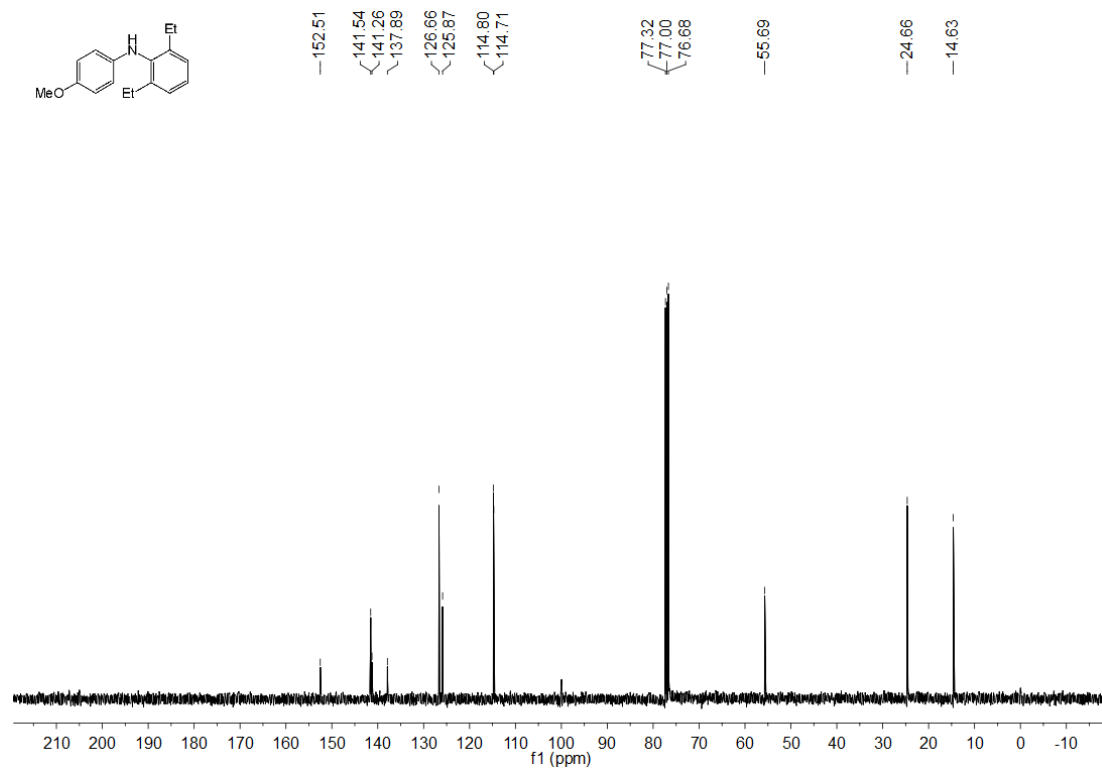


Figure S83. The  $^1\text{H}$  NMR spectrum of 1-(4-methoxyphenyl)-4-methylpiperazine (**9z**).

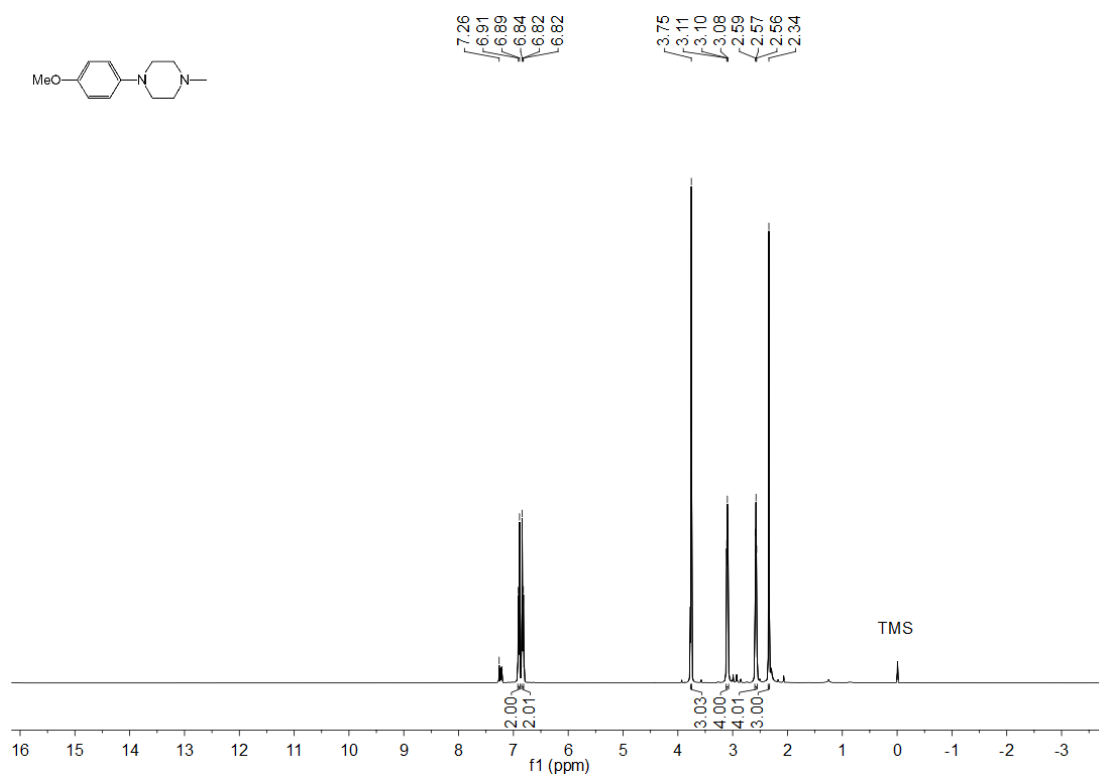


Figure S84. The  $^{13}\text{C}$  NMR spectrum of 1-(4-methoxyphenyl)-4-methylpiperazine (**9z**).

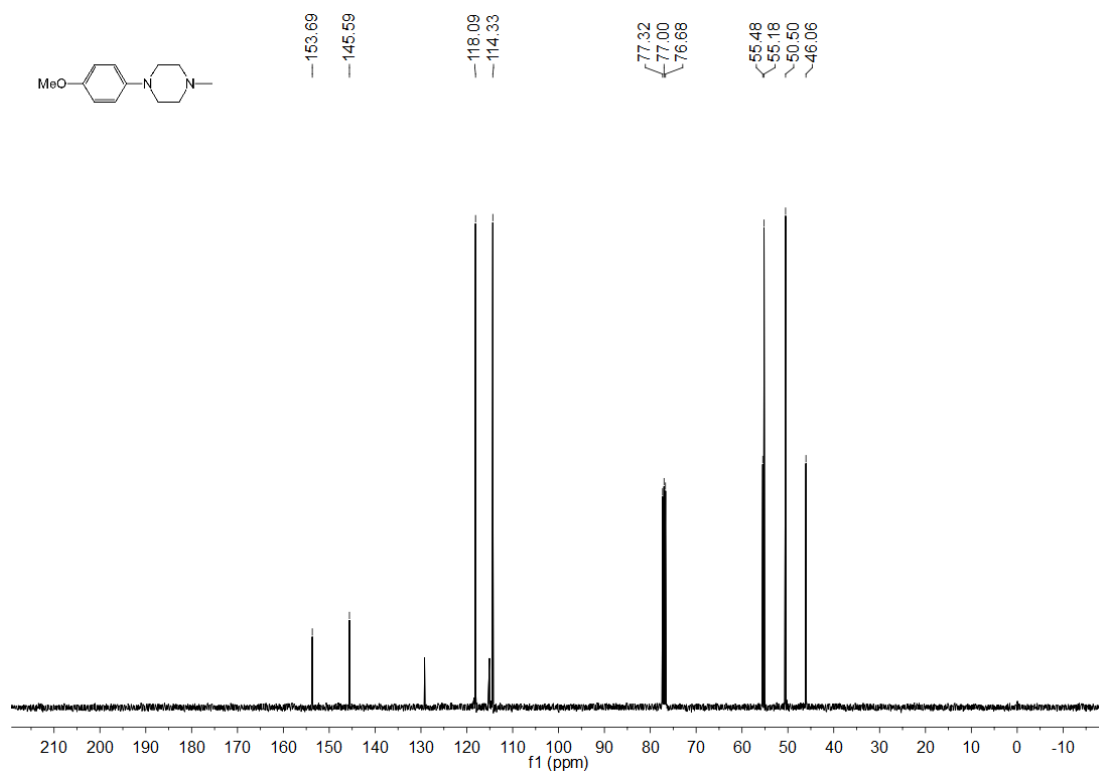


Figure S85. The  $^1\text{H}$  NMR spectrum of N-(2-methoxyphenyl)-2,6-dimethylaniline (10a).

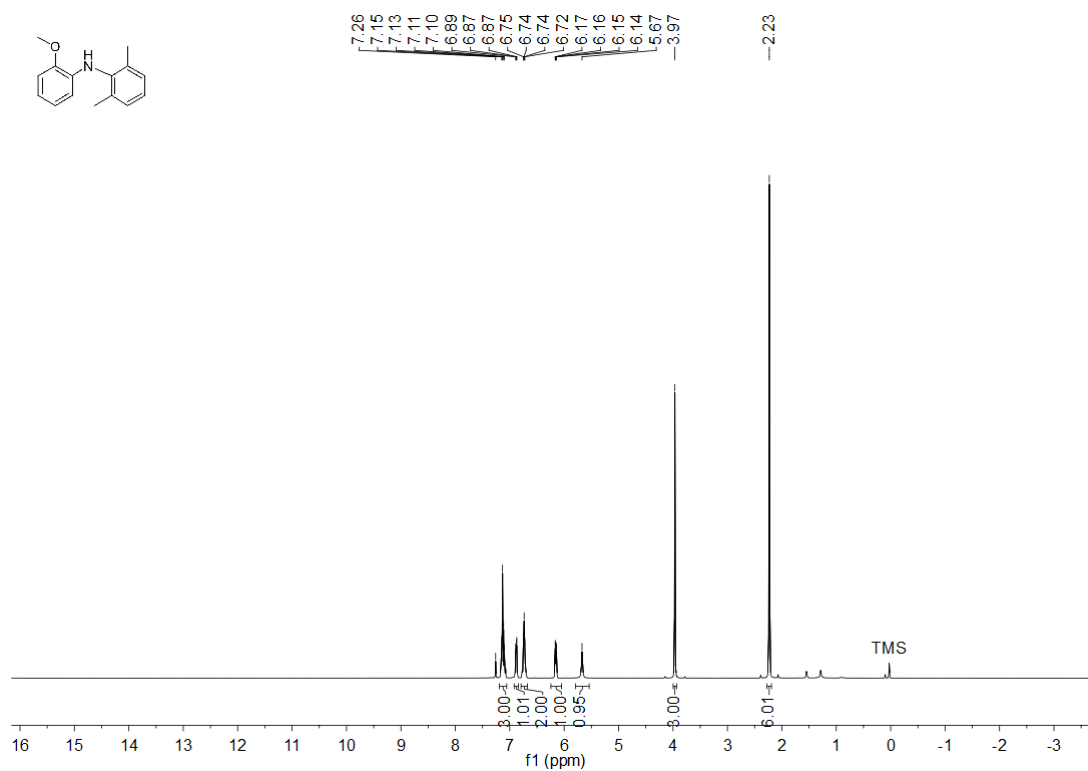


Figure S86. The  $^{13}\text{C}$  NMR spectrum of N-(2-methoxyphenyl)-2,6-dimethylaniline (10a).

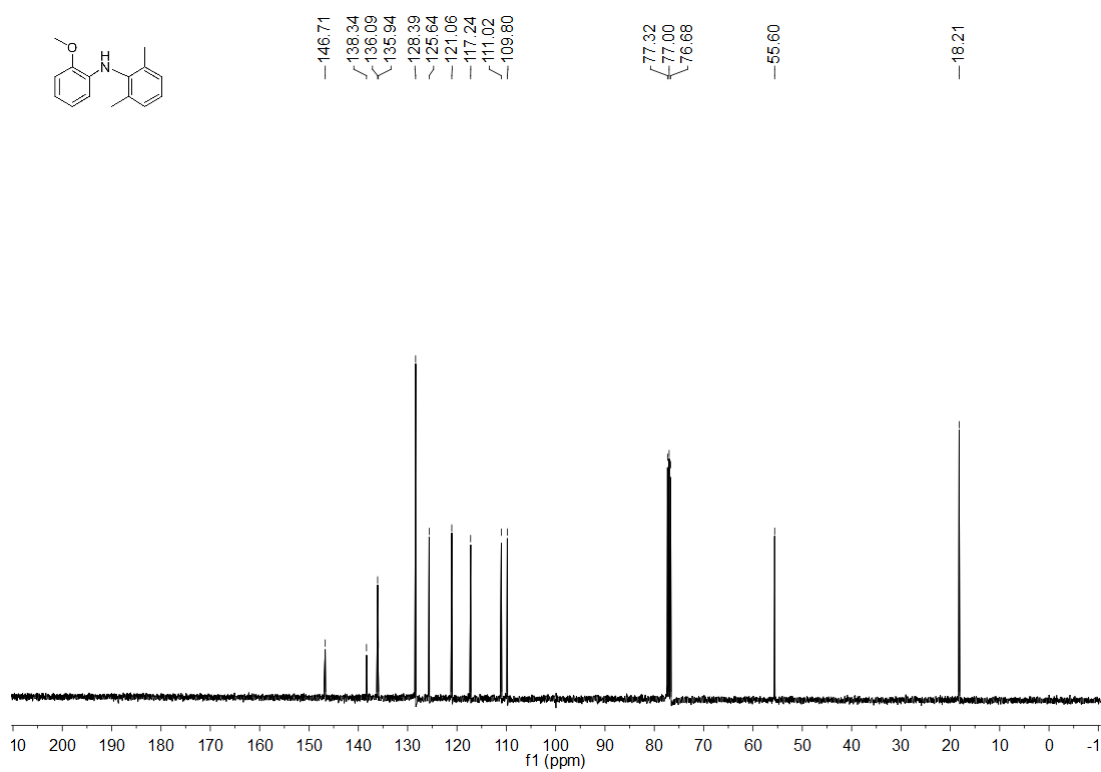




Figure S87. The  $^1\text{H}$  NMR spectrum of 4-(2-methoxyphenyl)morpholine (10o).

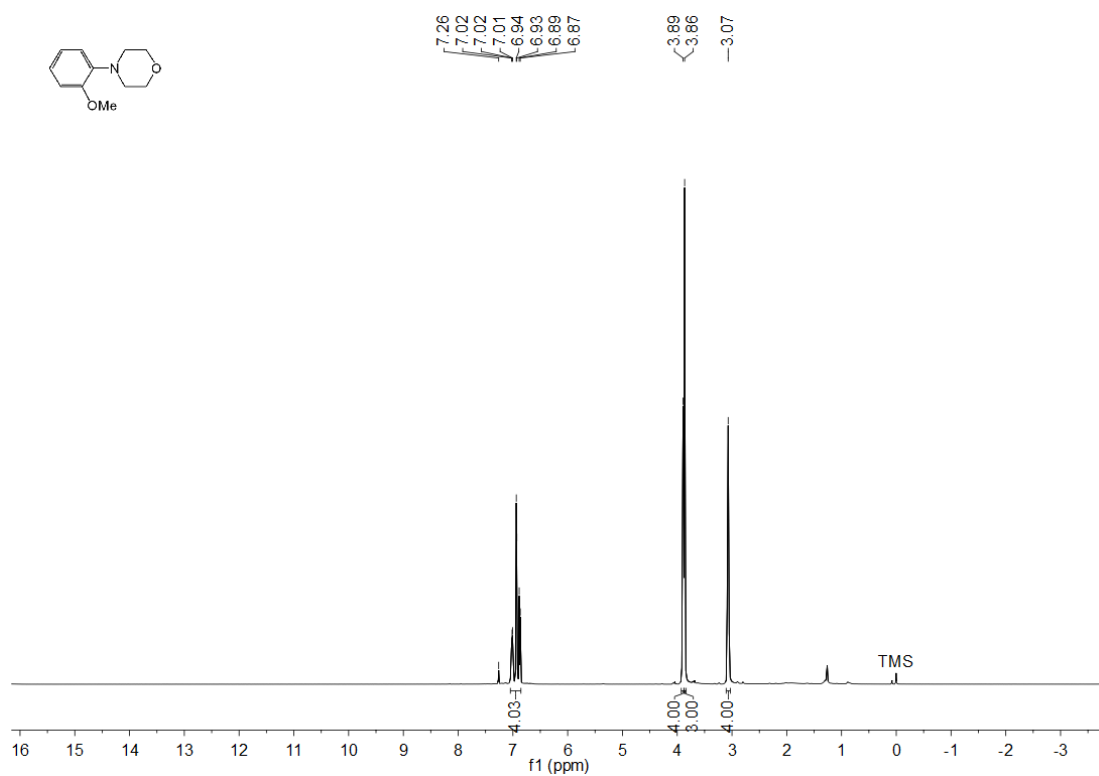


Figure S88. The  $^{13}\text{C}$  NMR spectrum of 4-(2-methoxyphenyl)morpholine (10o).

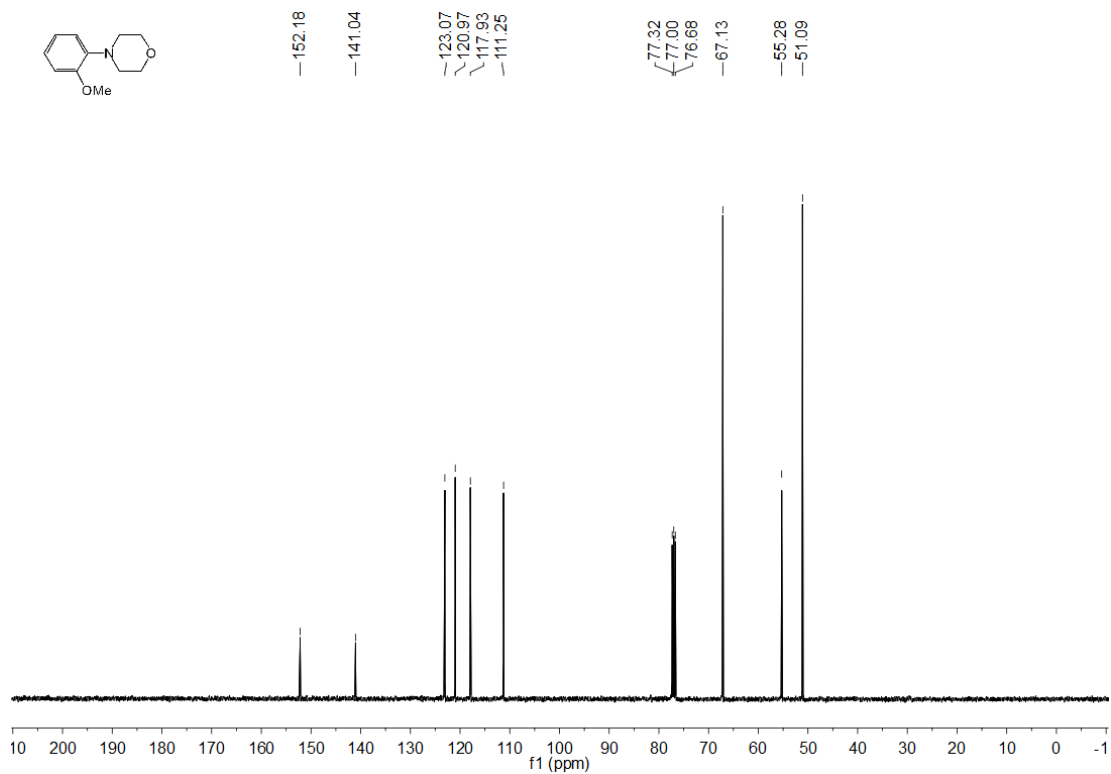


Figure S89. The  $^1\text{H}$  NMR spectrum of N-cyclohexyl-2-methoxyaniline (10t).

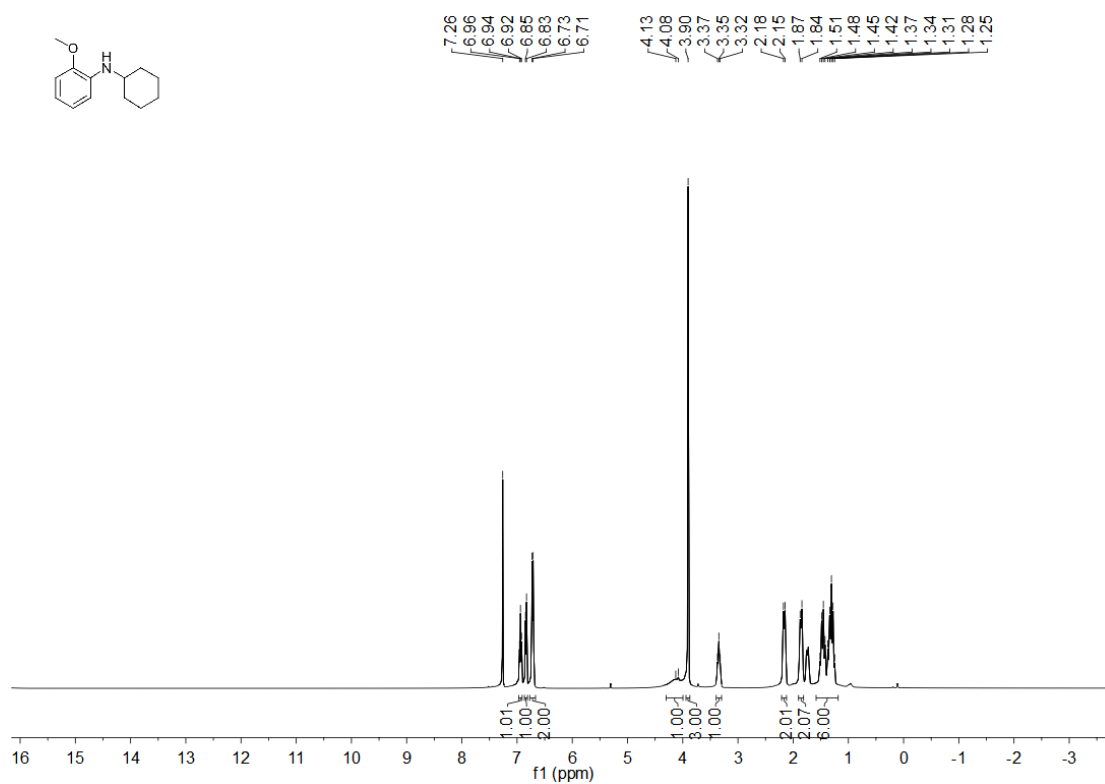


Figure S90. The  $^{13}\text{C}$  NMR spectrum of N-cyclohexyl-2-methoxyaniline (10t).

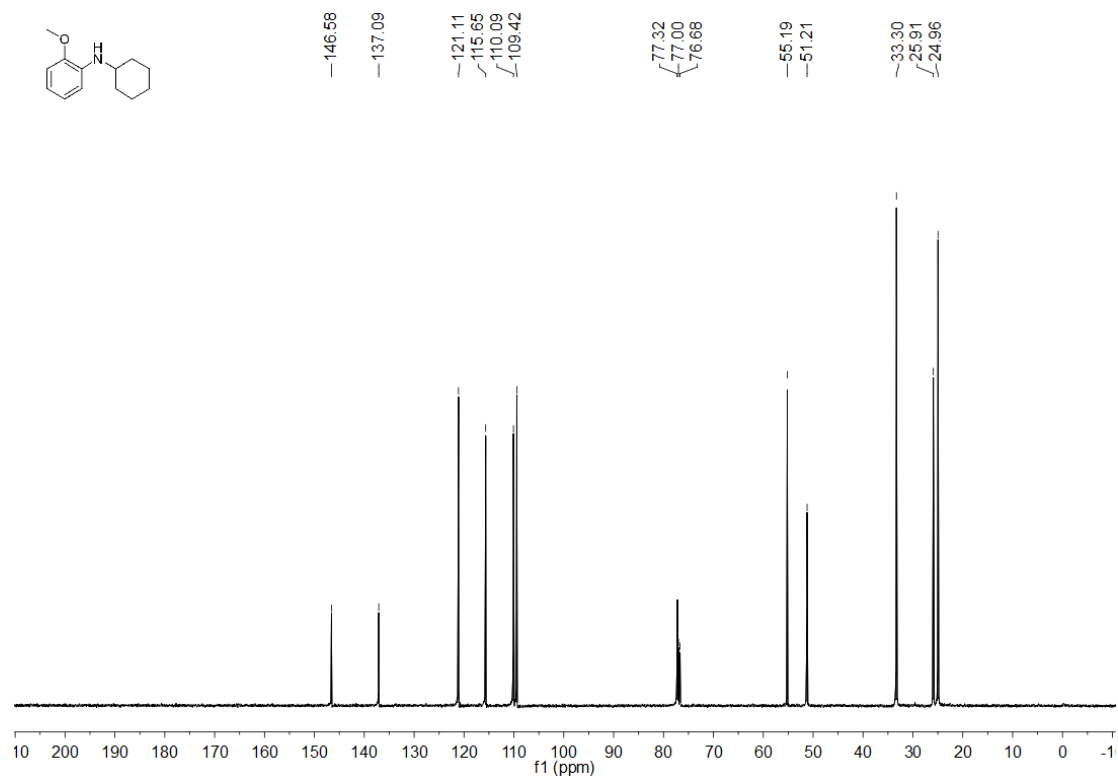


Figure S91. The  $^1\text{H}$  NMR spectrum of 2-isopropyl-N-(2-methoxyphenyl)-6-propylaniline (10w).

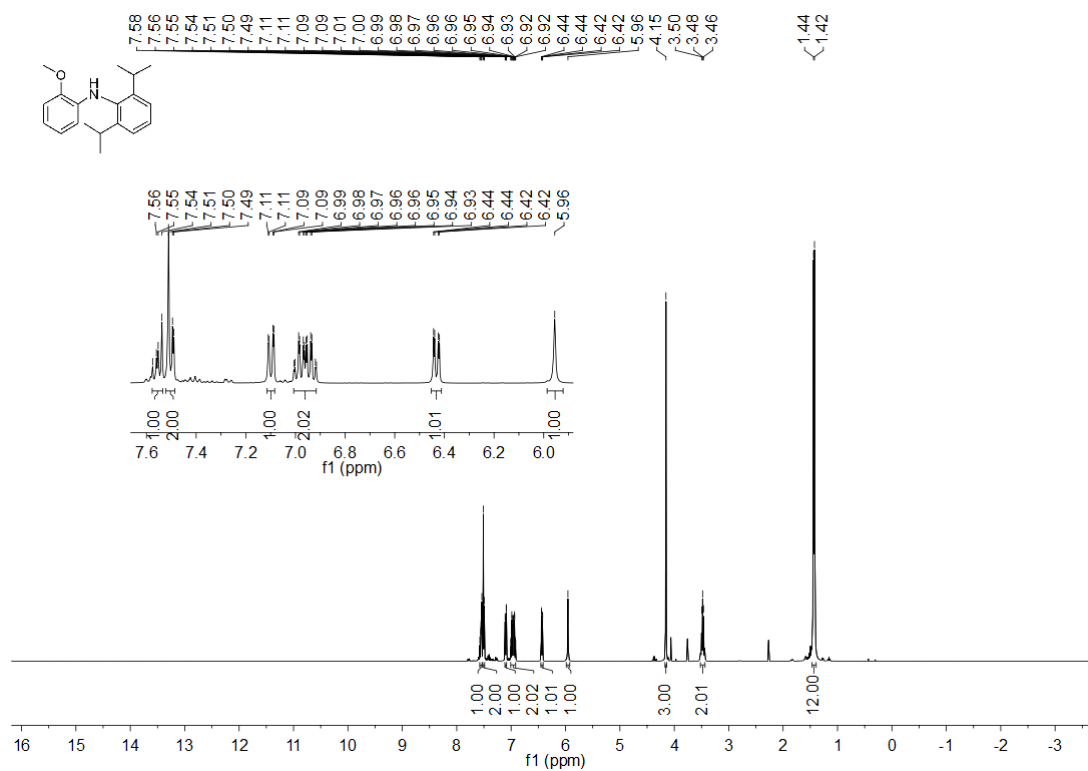


Figure S92. The  $^{13}\text{C}$  NMR spectrum of 2-isopropyl-N-(2-methoxyphenyl)-6-propylaniline (10w).

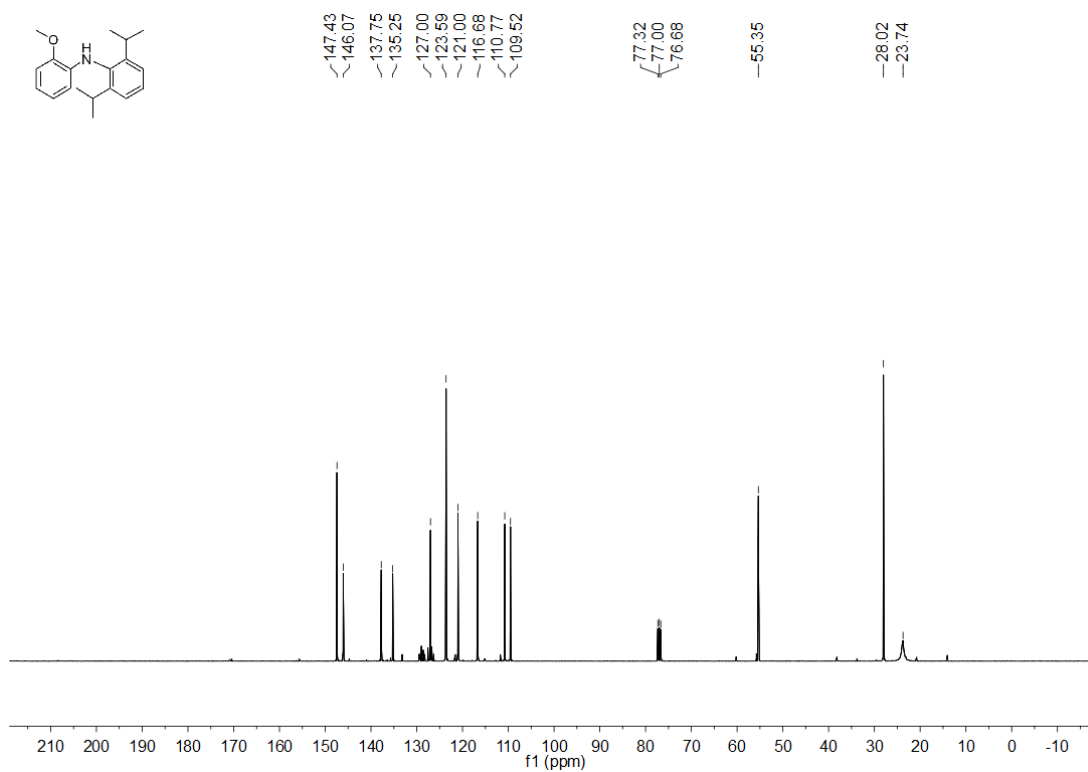


Figure S93. The  $^1\text{H}$  NMR spectrum of 4-methoxy-N-methyl-N-phenylaniline (10x).

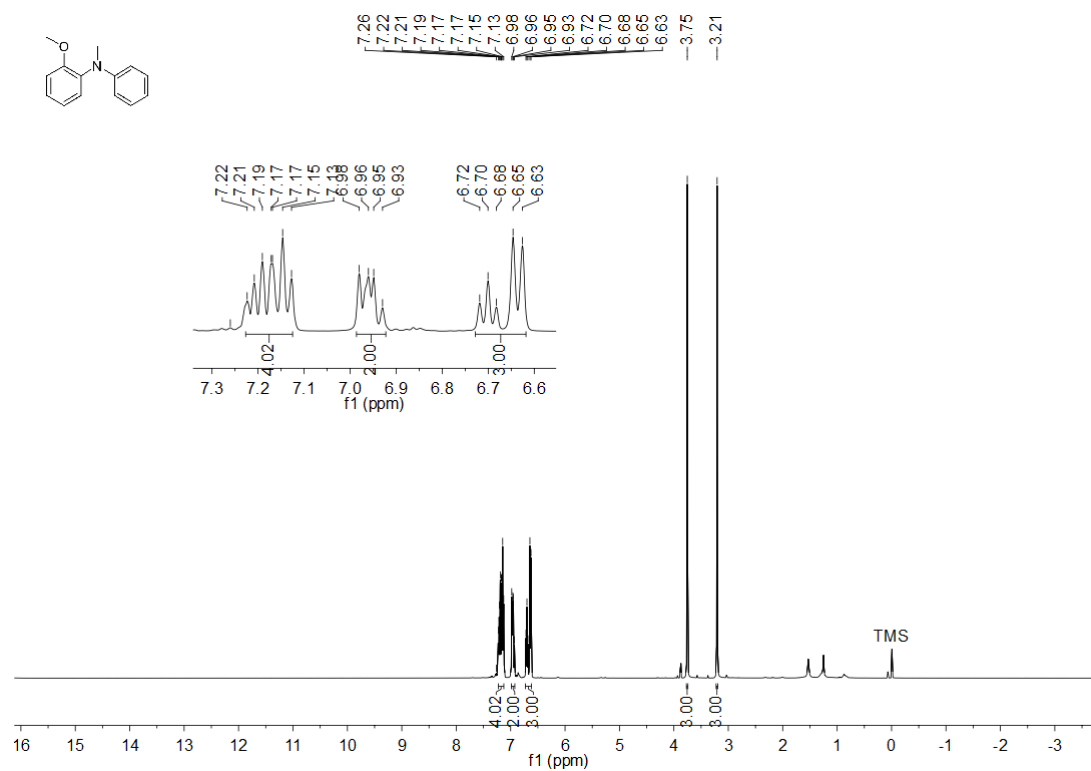


Figure S94. The  $^{13}\text{C}$  NMR spectrum of 4-methoxy-N-methyl-N-phenylaniline (10x).

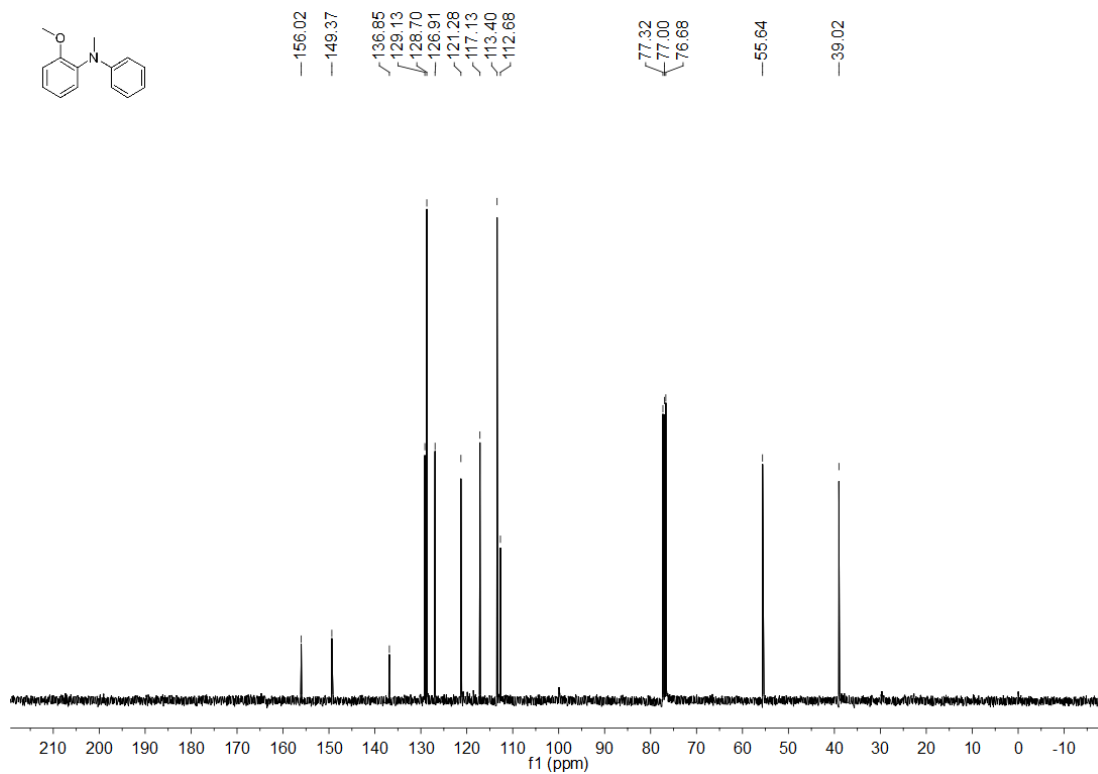


Figure S95. The  $^1\text{H}$  NMR spectrum of 1-(2-methoxyphenyl)-4-methylpiperazine (10z).

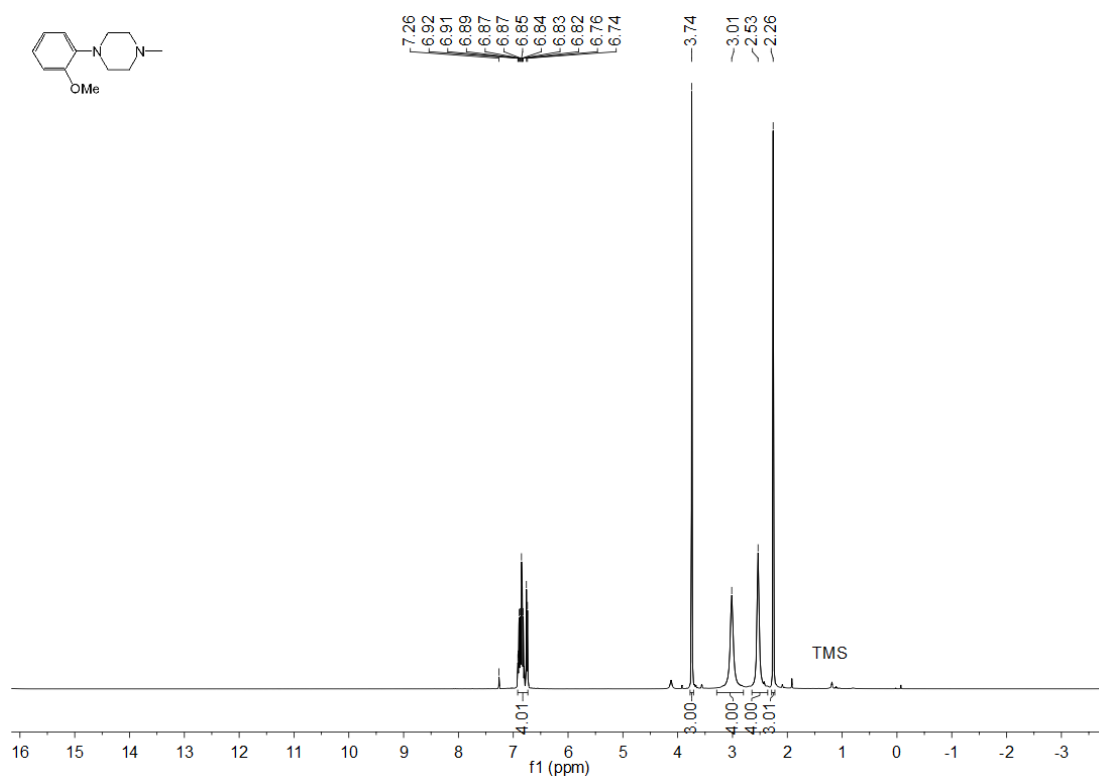


Figure S96. The  $^{13}\text{C}$  NMR spectrum of 1-(2-methoxyphenyl)-4-methylpiperazine (10z).

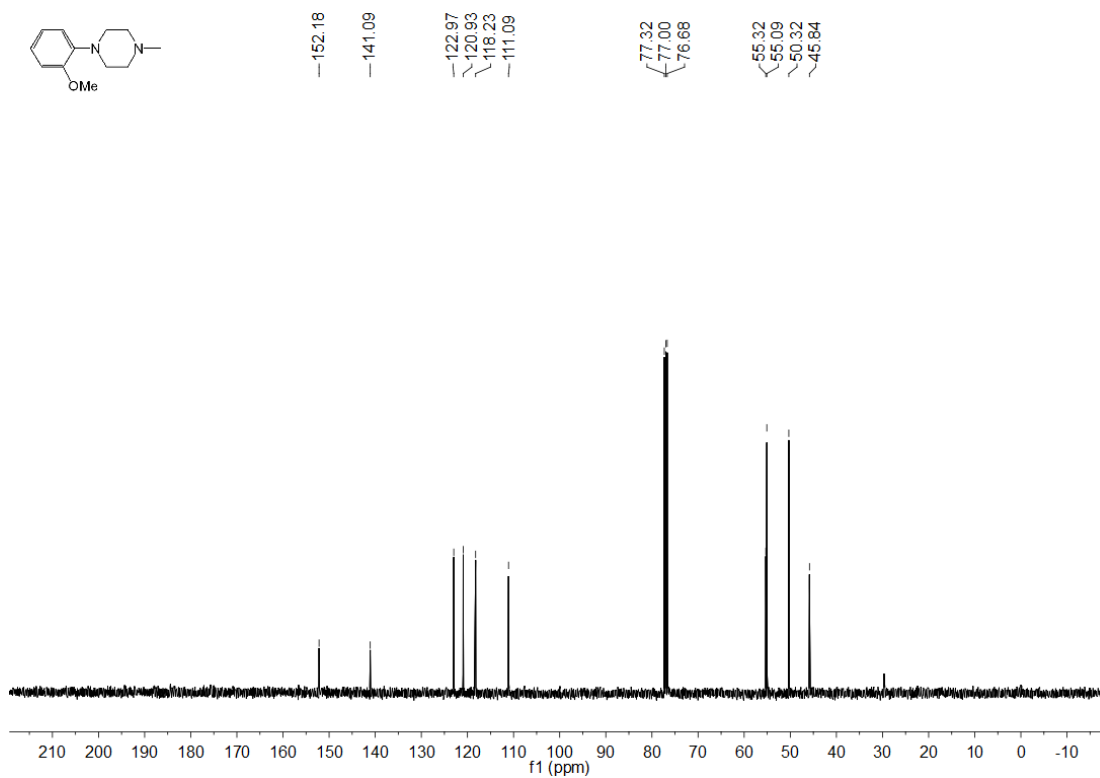


Figure S97. The  $^1\text{H}$  NMR spectrum of 4-(m-tolyl)morpholine (11o).

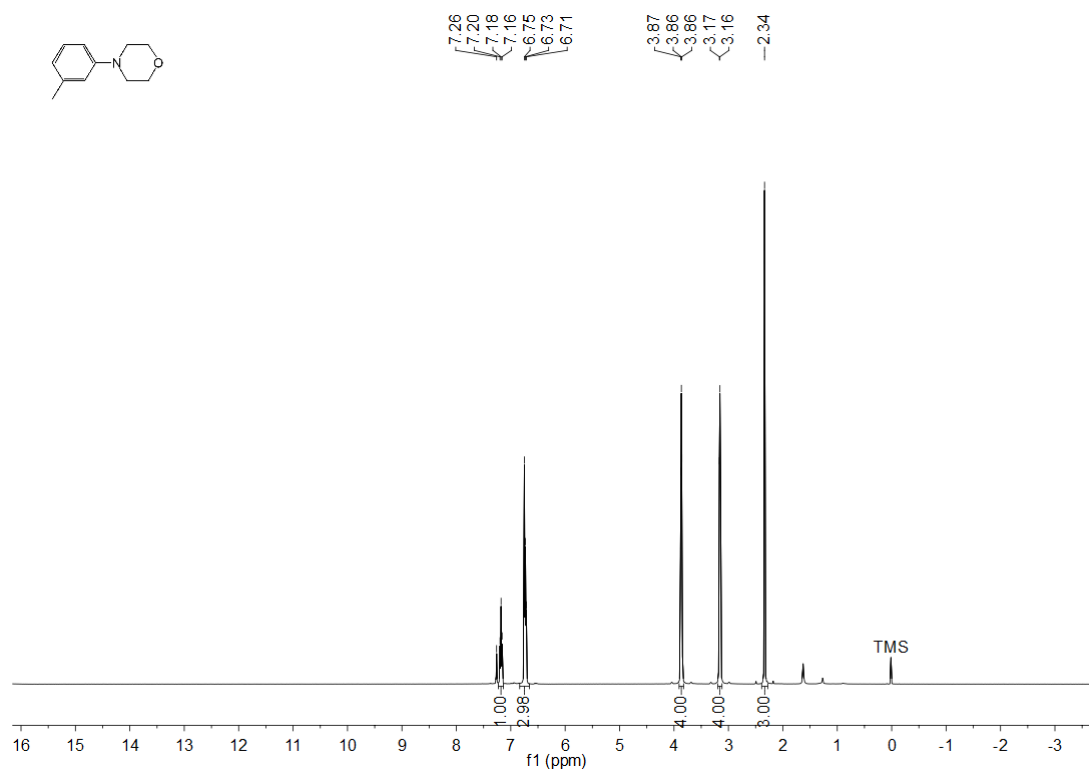


Figure S98. The  $^{13}\text{C}$  NMR spectrum of 4-(m-tolyl)morpholine (11o).

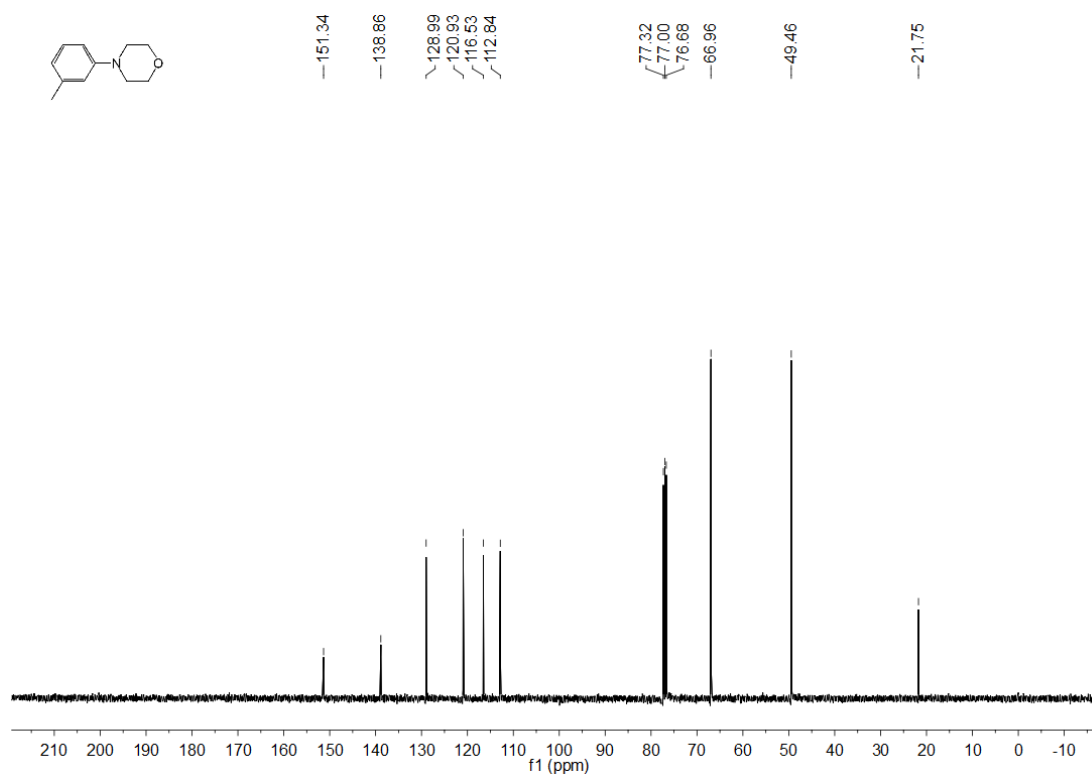


Figure S99. The  $^1\text{H}$  NMR spectrum of N-cyclohexyl-3-methylaniline (11t).

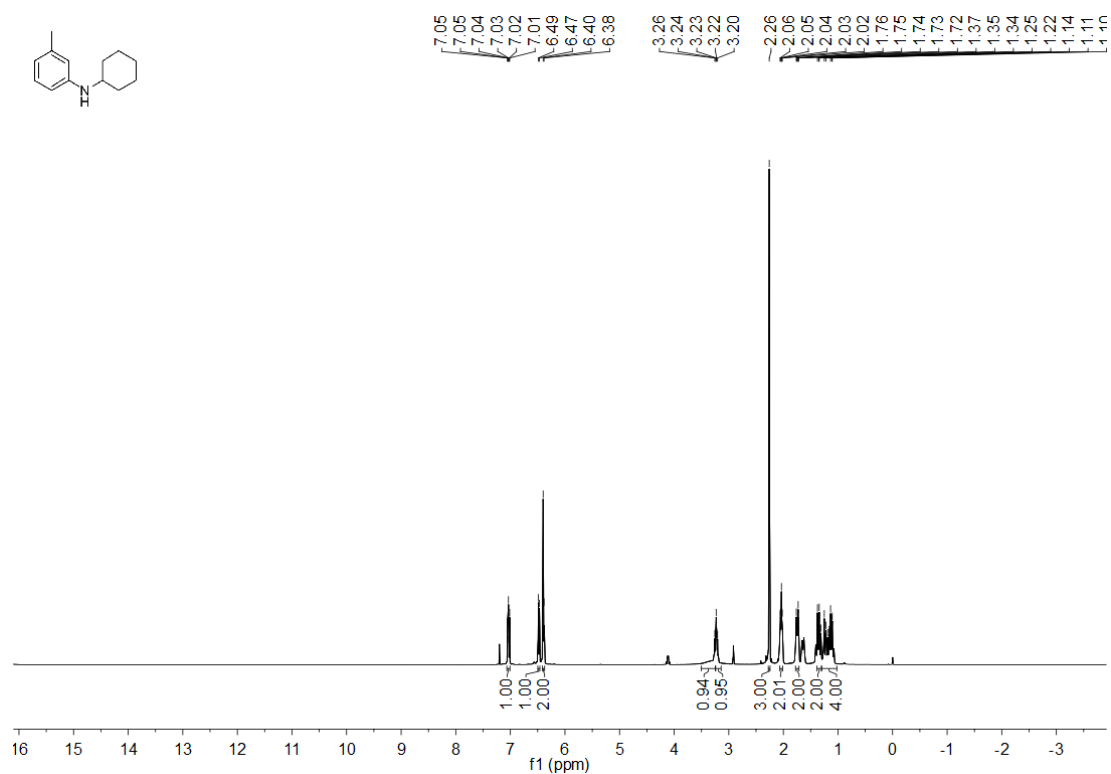


Figure S100. The  $^{13}\text{C}$  NMR spectrum of N-cyclohexyl-3-methylaniline (11t).

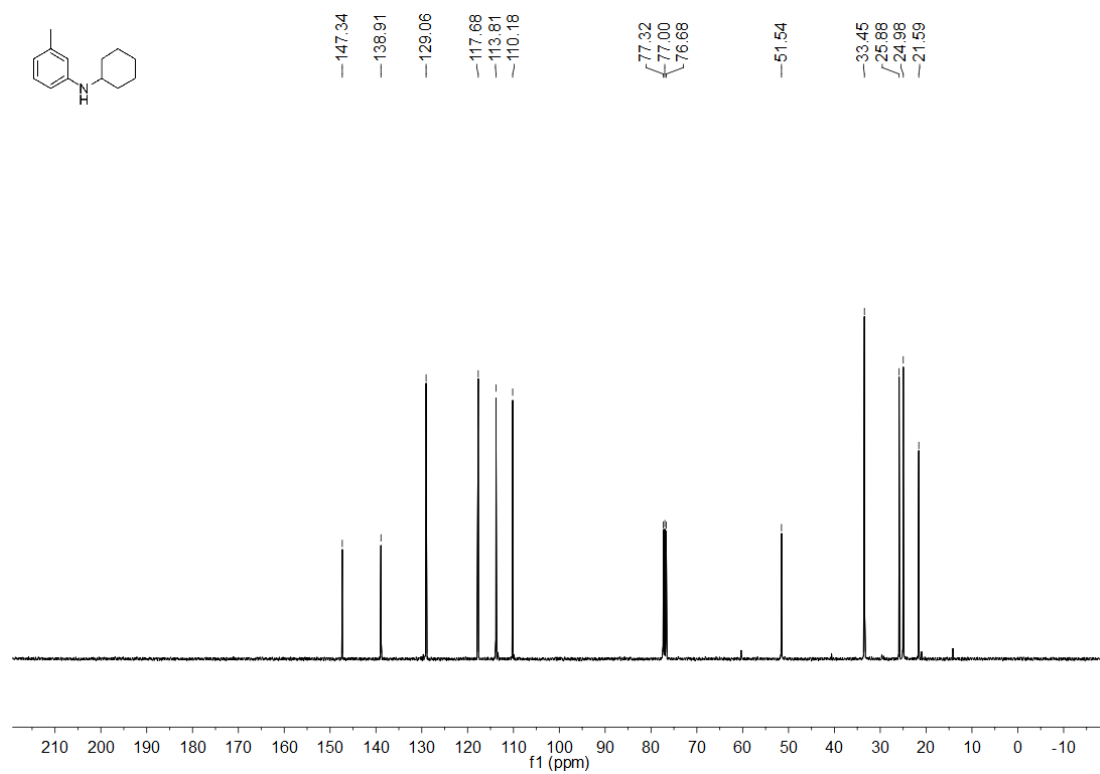


Figure S101. The  $^1\text{H}$  NMR spectrum of 4-(p-tolyl)morpholine (12o).

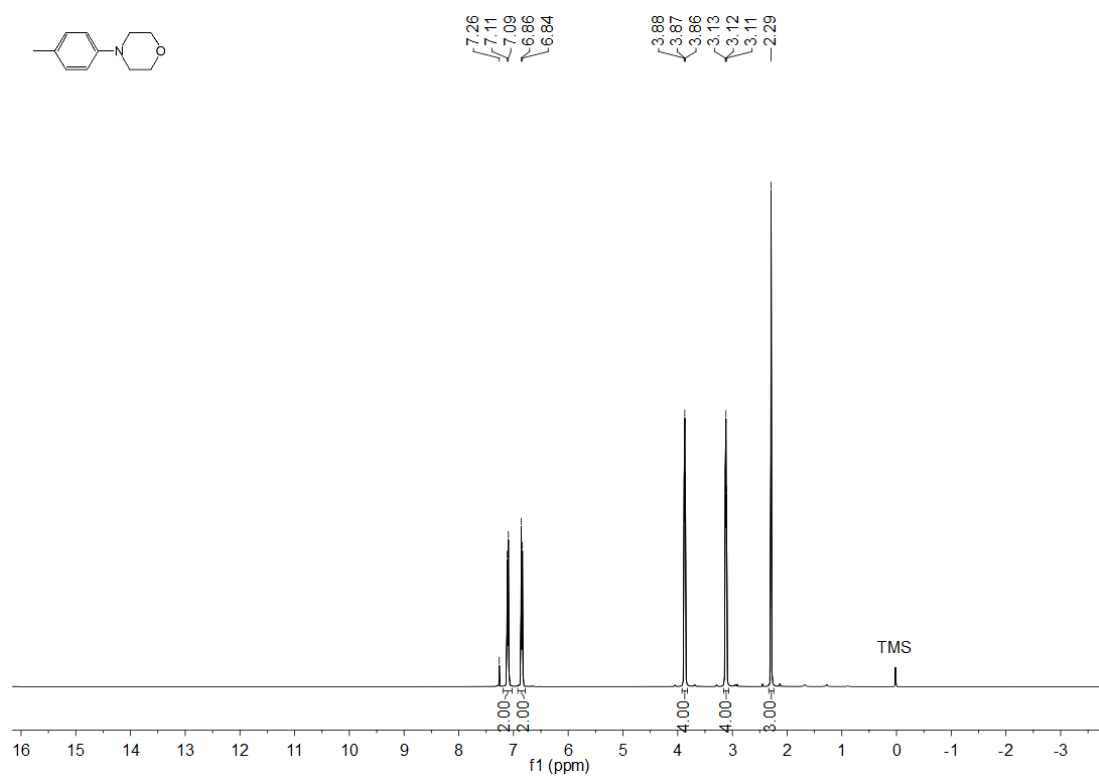


Figure S102. The  $^{13}\text{C}$  NMR spectrum of 4-(p-tolyl)morpholine (12o).

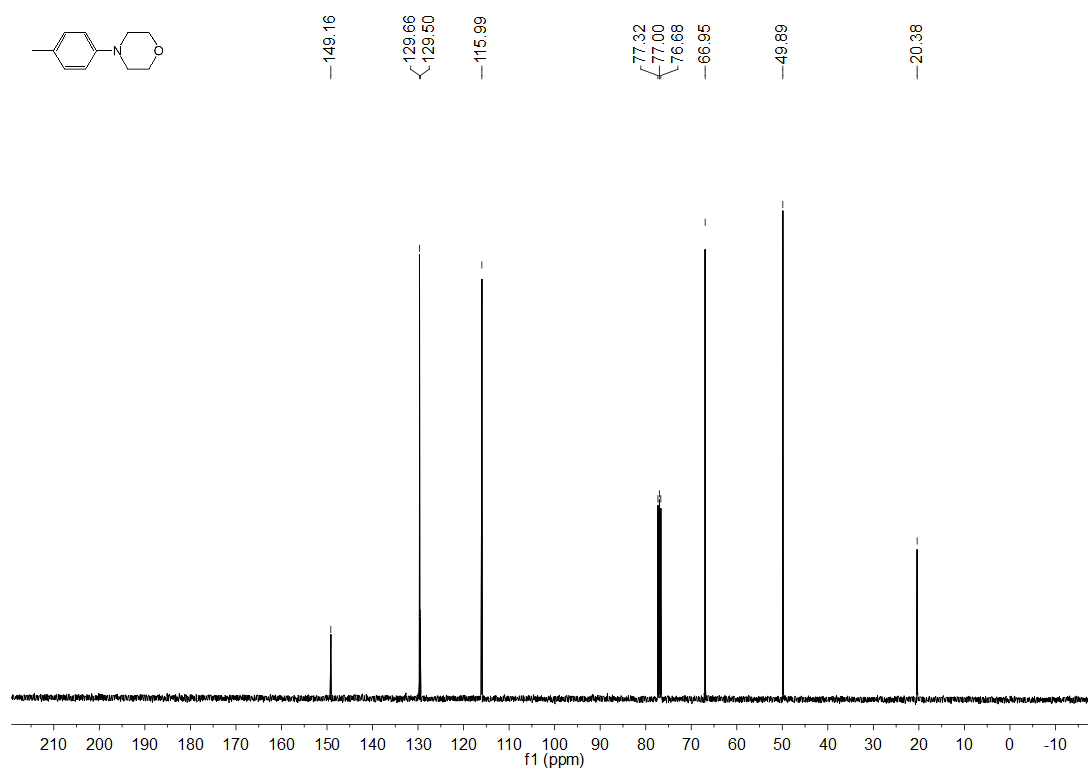




Figure S103. The  $^1\text{H}$  NMR spectrum of 4-fluoro-N-(p-tolyl)aniline (12q).

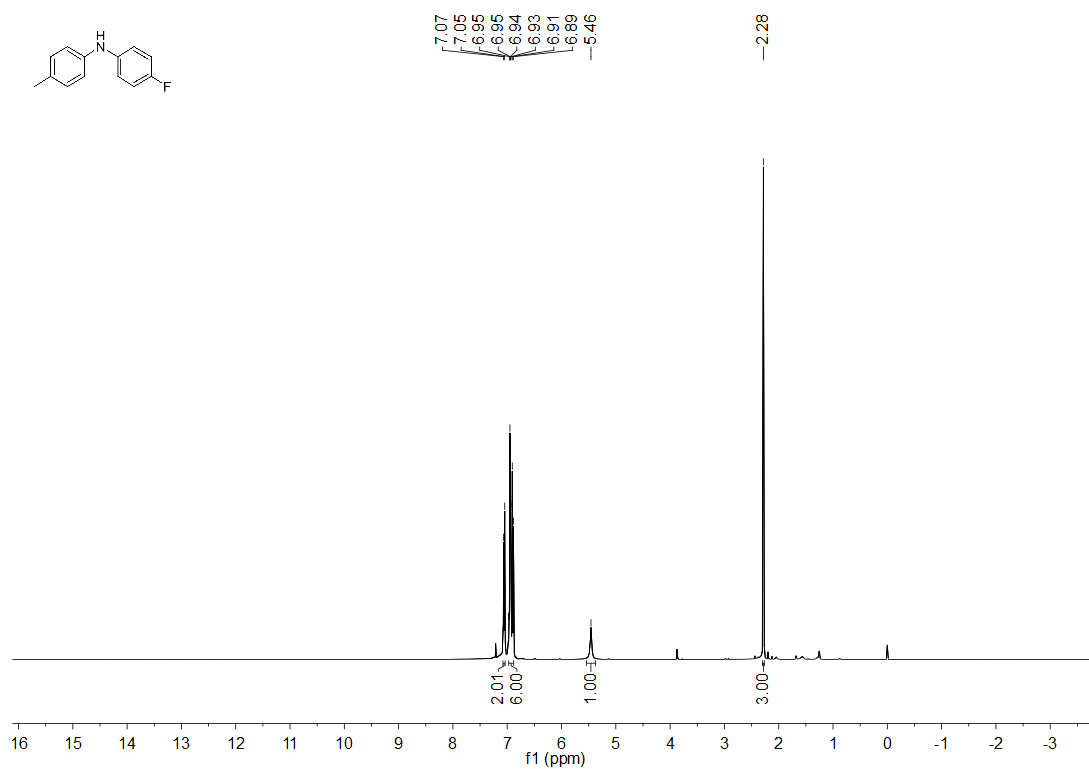


Figure S104. The  $^{13}\text{C}$  NMR spectrum of 4-fluoro-N-(p-tolyl)aniline (12q).

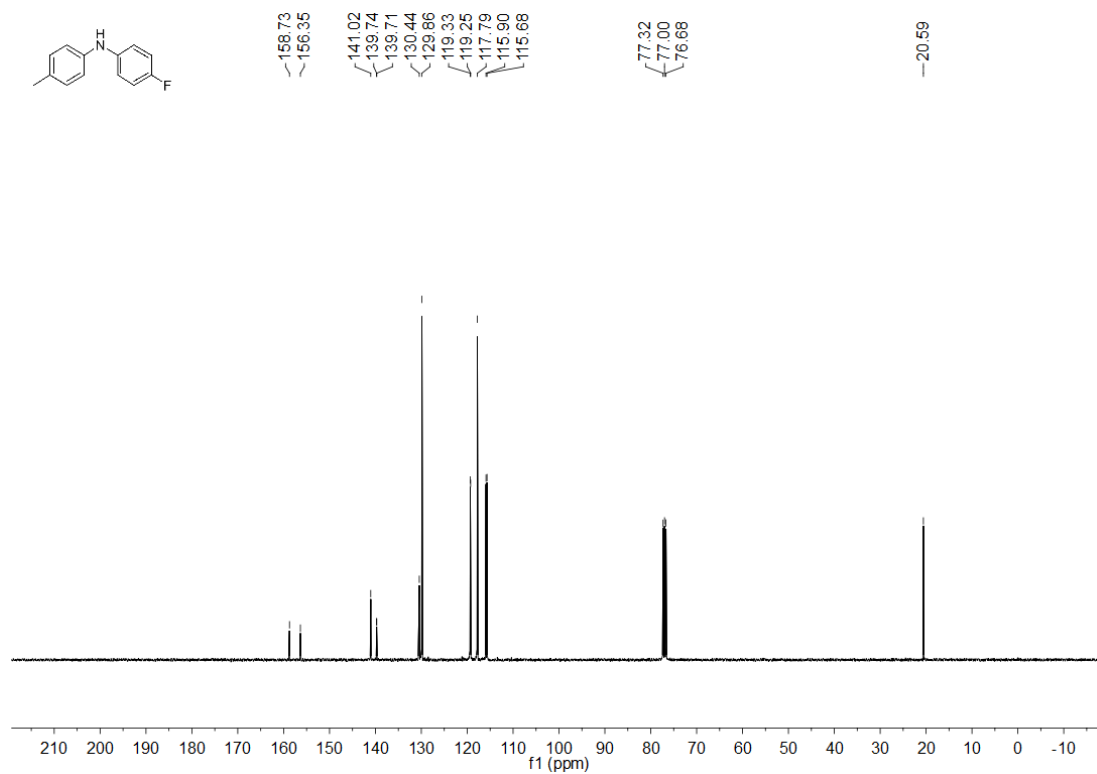


Figure S105. The  $^1\text{H}$  NMR spectrum of 2,6-dimethyl-N-(o-tolyl)aniline (13a).

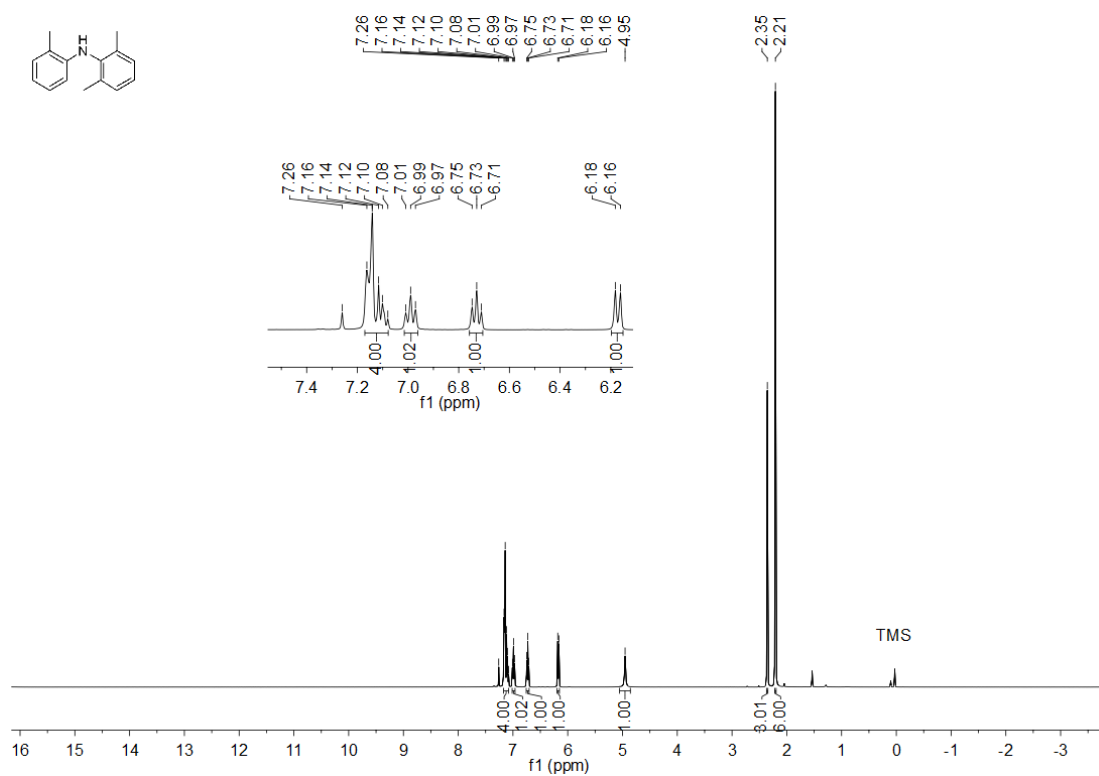


Figure S106. The  $^{13}\text{C}$  NMR spectrum of 2,6-dimethyl-N-(o-tolyl)aniline (13a).

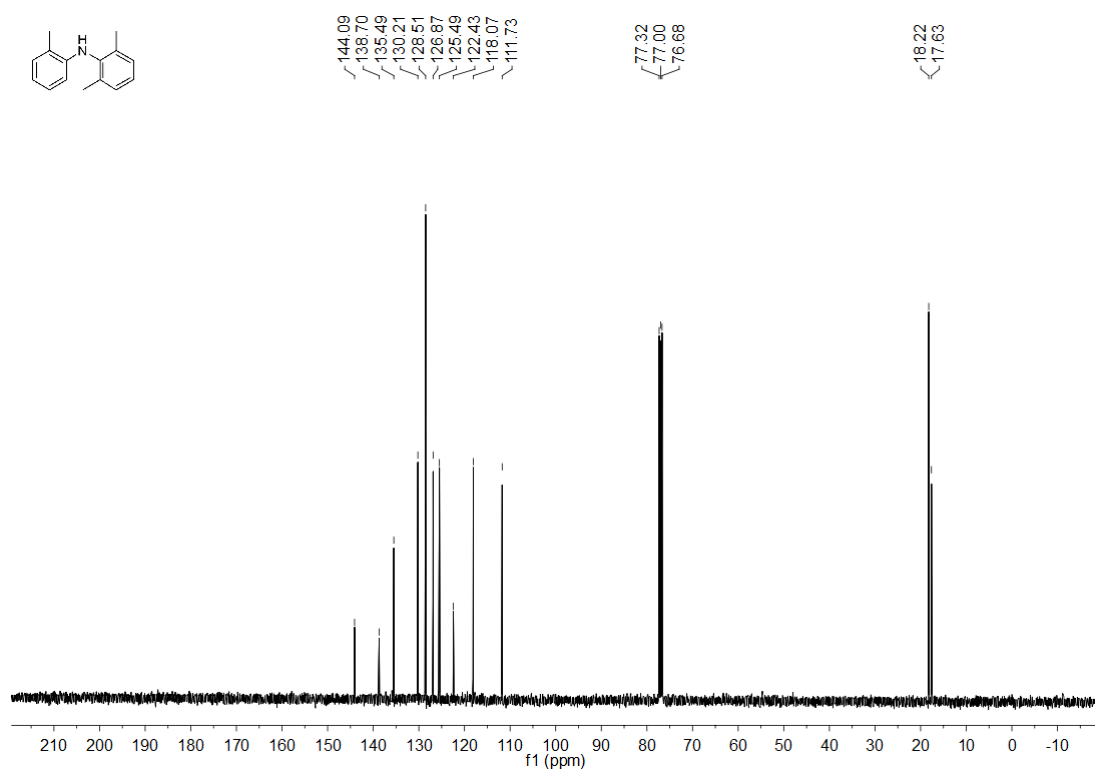


Figure S107. The  $^1\text{H}$  NMR spectrum of N-(4-fluorophenyl)-2-methylaniline (13q).

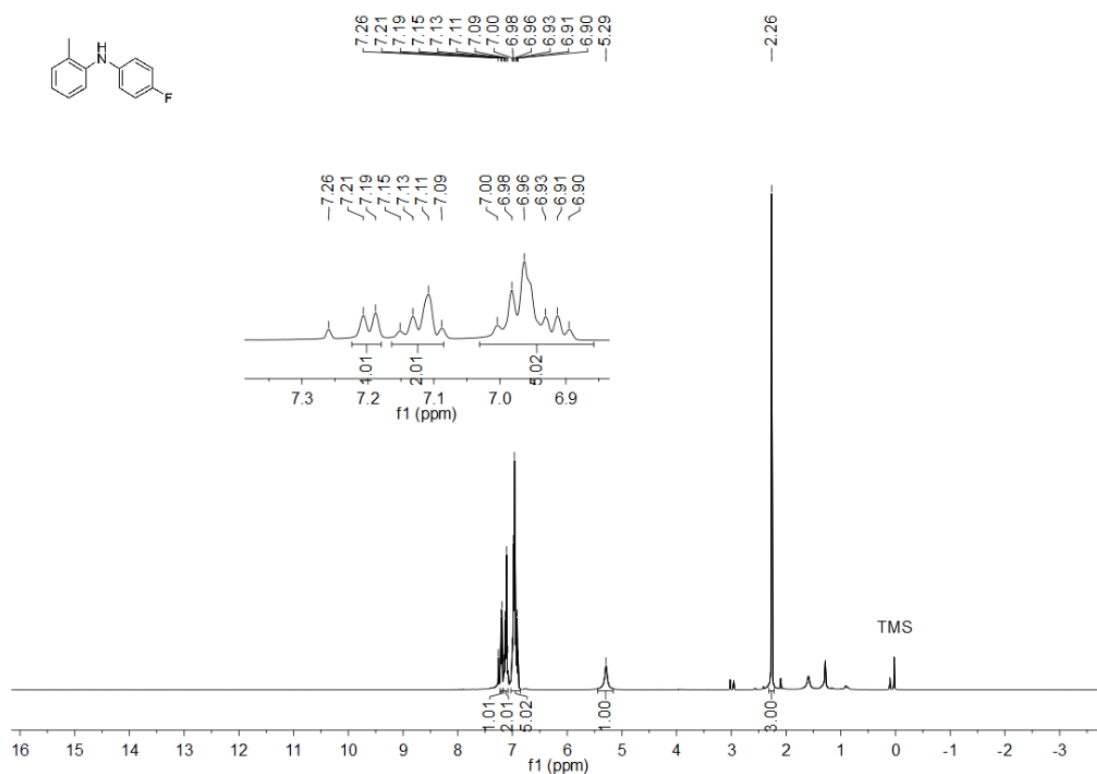


Figure S108. The  $^{13}\text{C}$  NMR spectrum of N-(4-fluorophenyl)-2-methylaniline (13q).

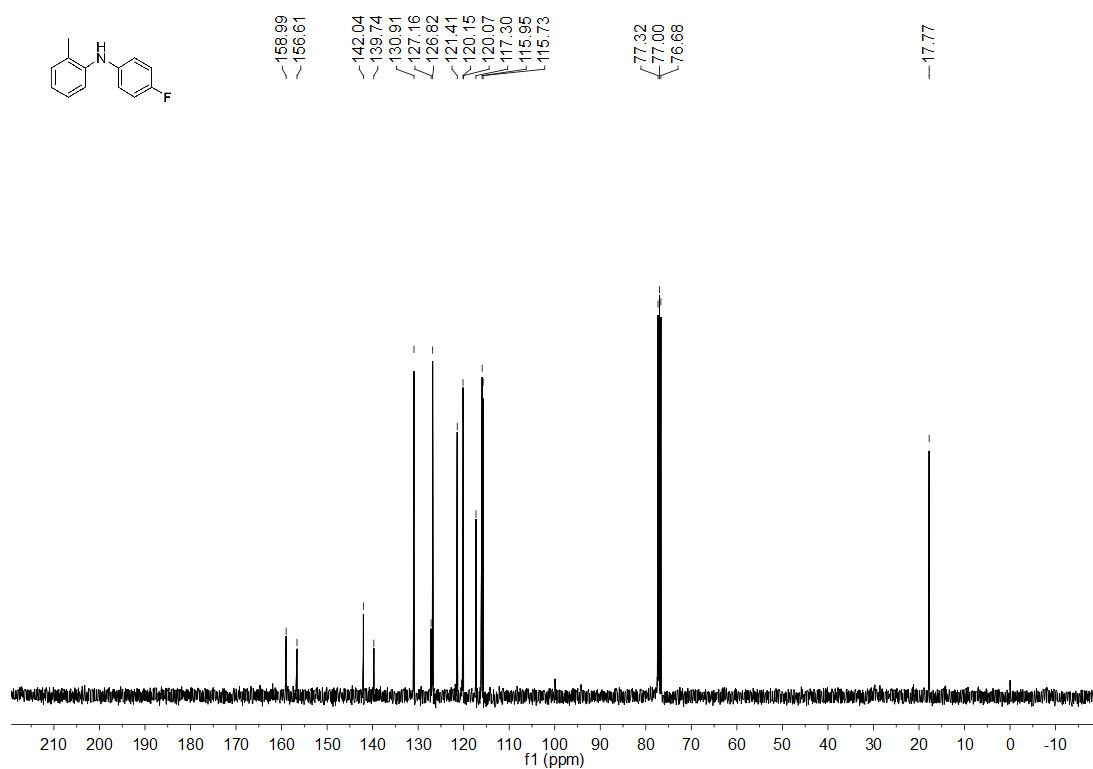


Figure S109. The  $^1\text{H}$  NMR spectrum of N-(4-fluorophenyl)-2,6-dimethylaniline (14q).

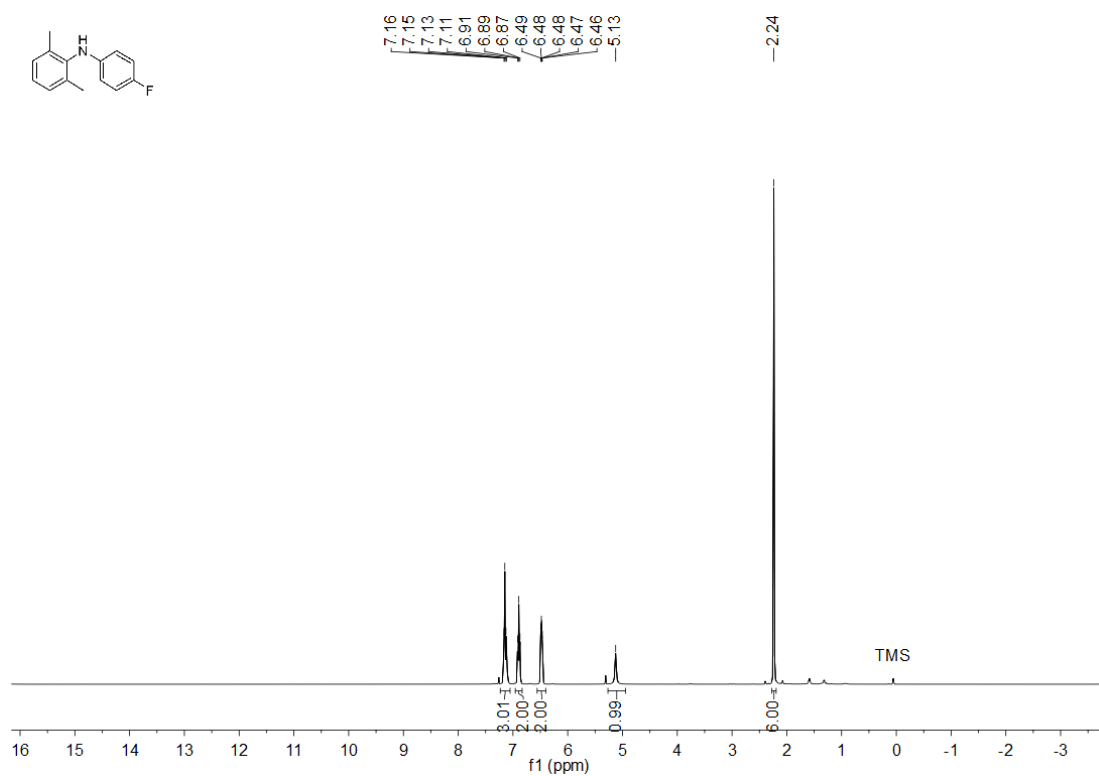


Figure S110. The  $^{13}\text{C}$  NMR spectrum of N-(4-fluorophenyl)-2,6-dimethylaniline (14q).

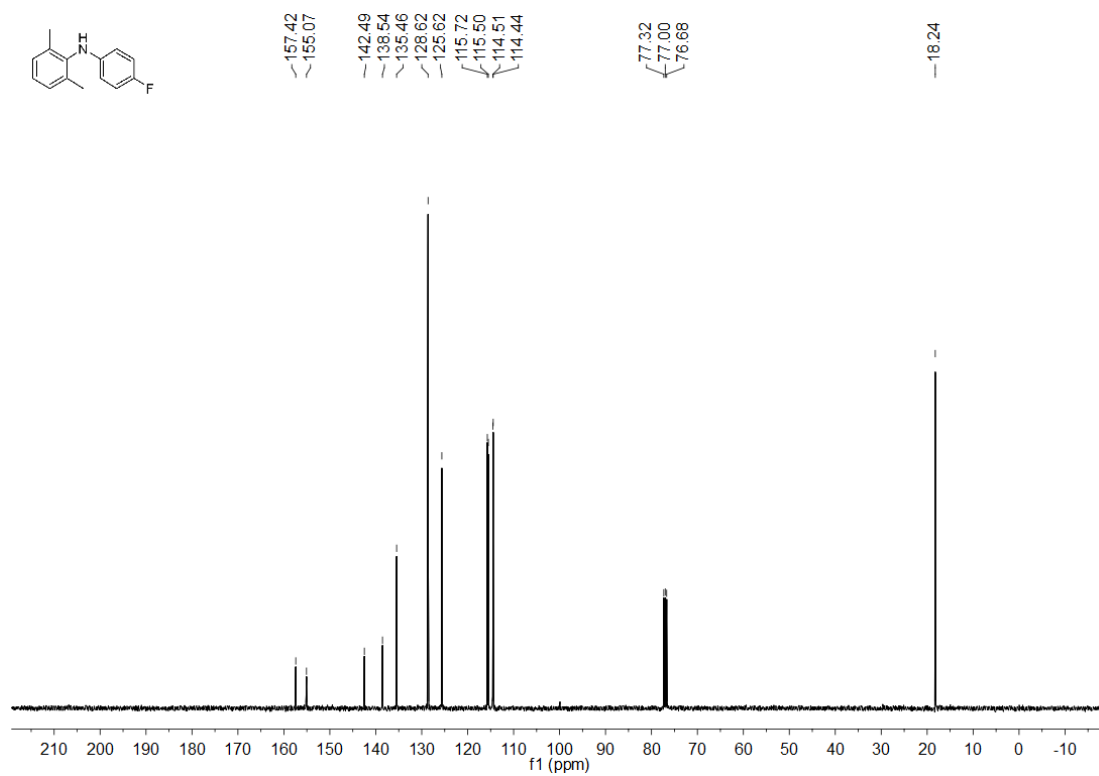


Figure S111. The  $^1\text{H}$  NMR spectrum of 2,6-dimethyl-N-phenylaniline (15a).

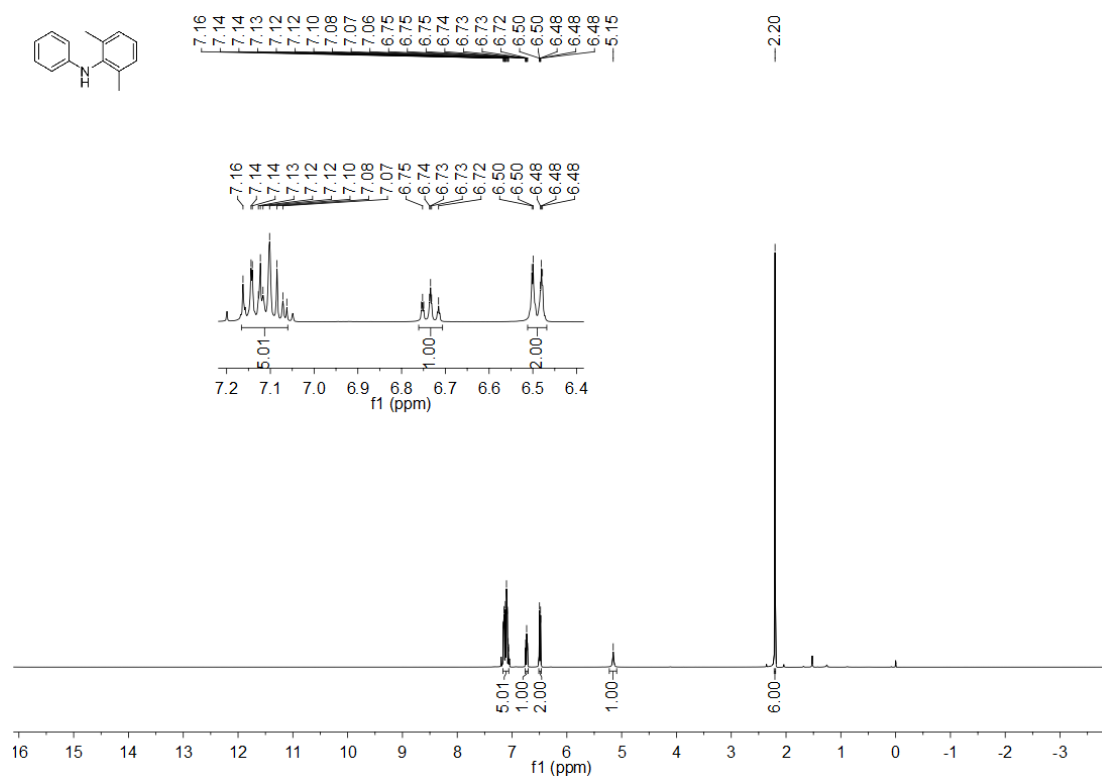


Figure S112. The  $^{13}\text{C}$  NMR spectrum of 2,6-dimethyl-N-phenylaniline (15a).

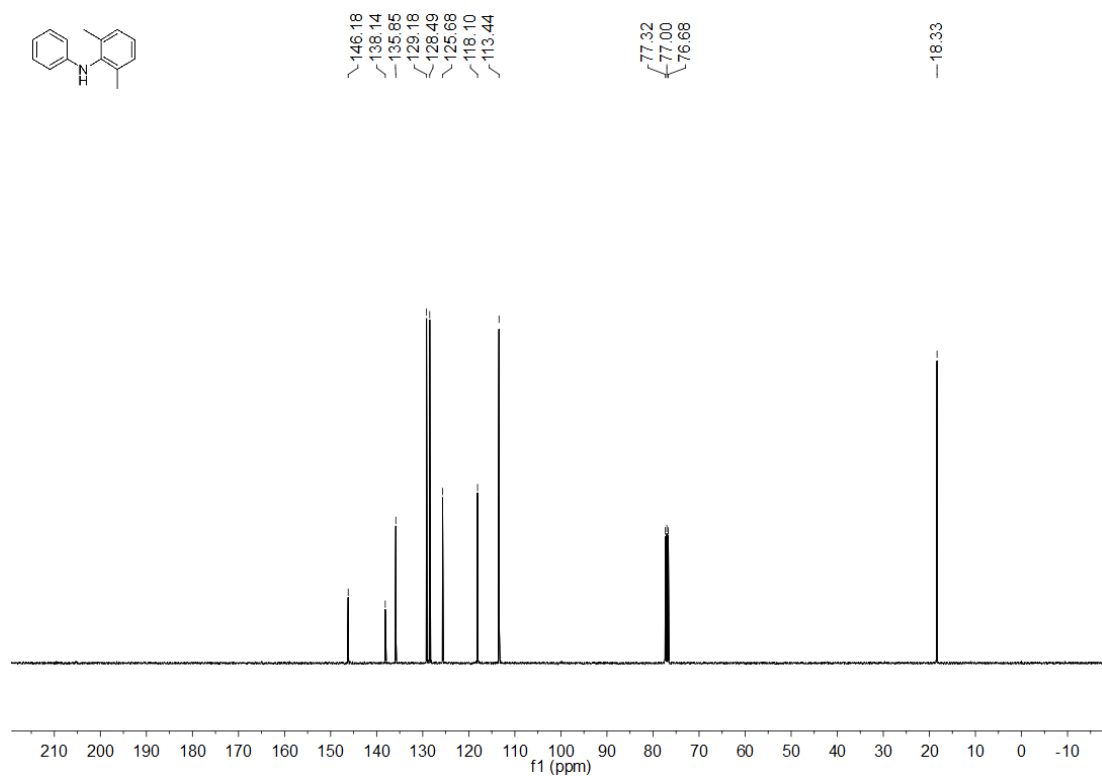


Figure S113. The  $^1\text{H}$  NMR spectrum of 2-isopropyl-N-phenyl-6-propylaniline (15w).

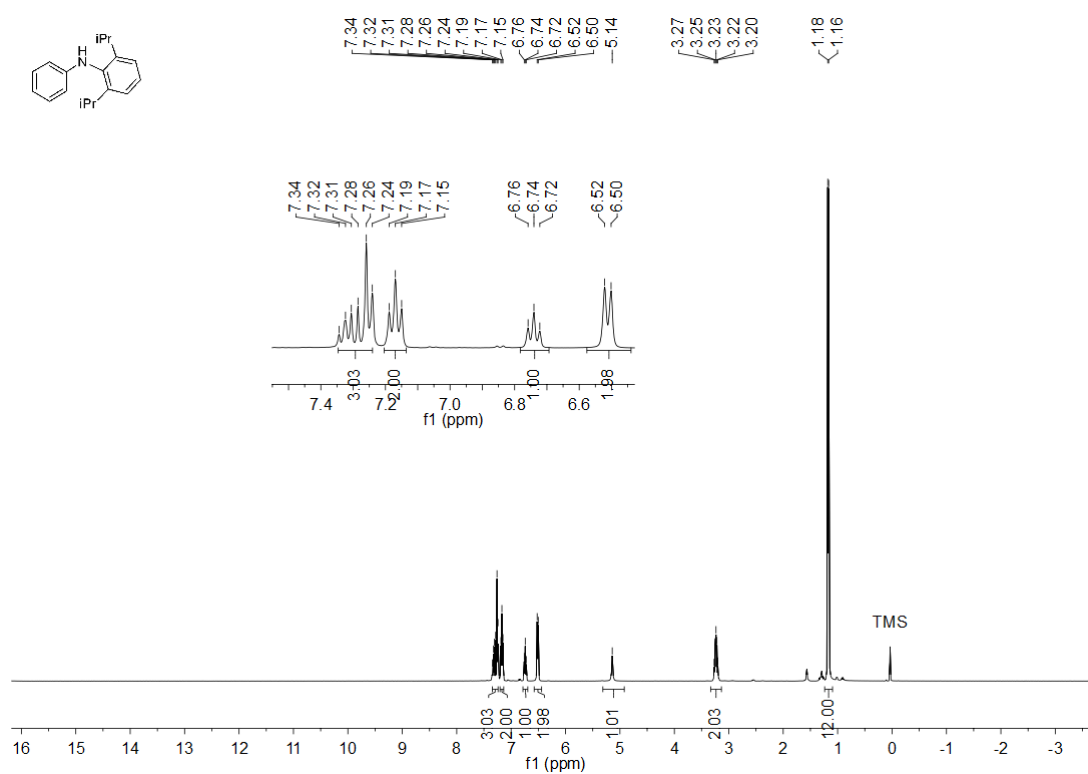


Figure S114. The  $^{13}\text{C}$  NMR spectrum of 2-isopropyl-N-phenyl-6-propylaniline (15w).

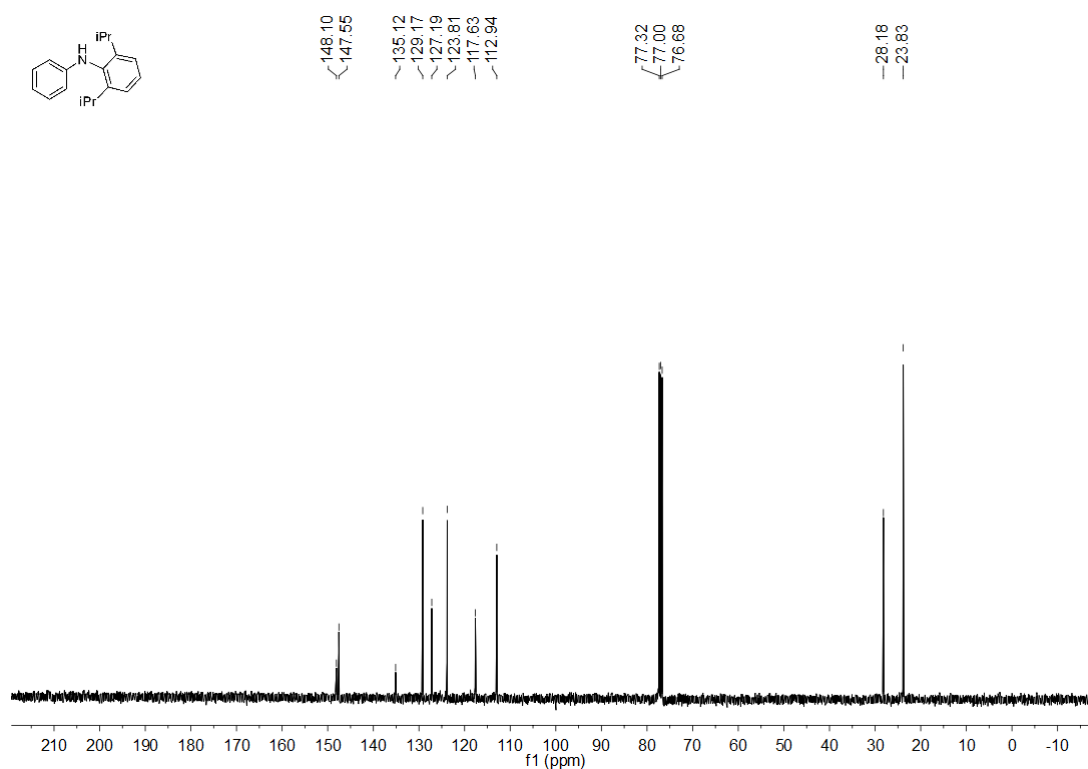


Figure S115. The  $^1\text{H}$  NMR spectrum of N-(2,6-dimethylphenyl)naphthalen-1-amine (16a).

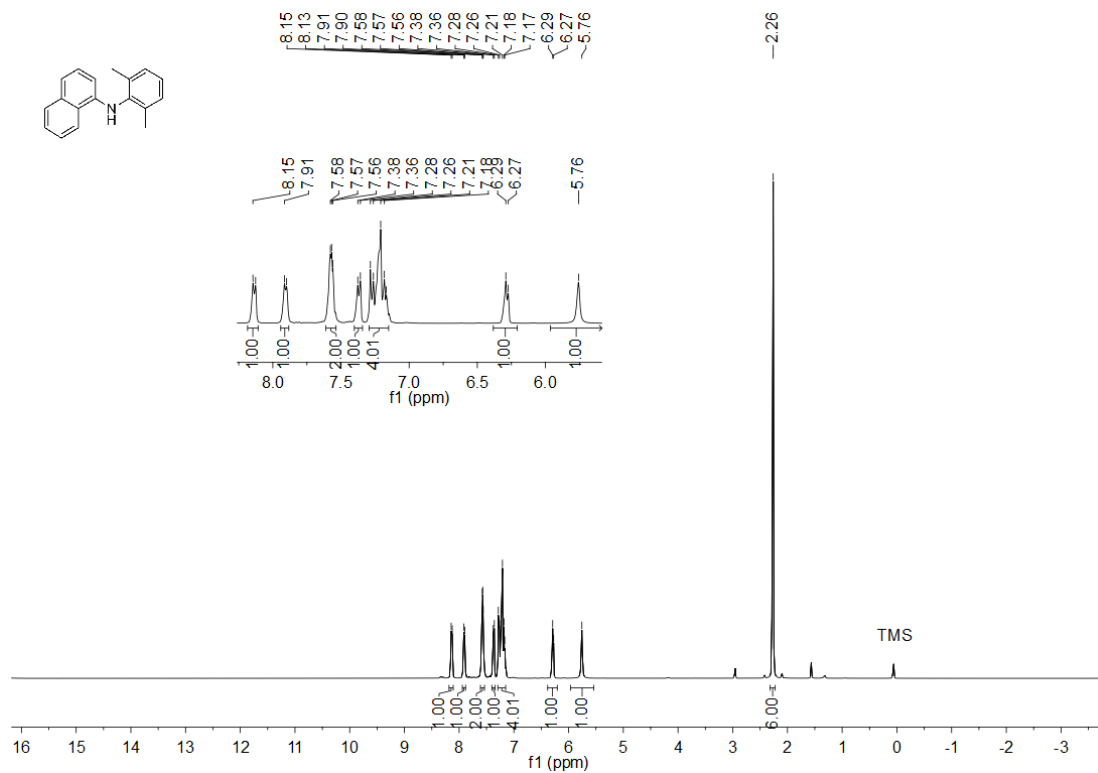


Figure S116. The  $^{13}\text{C}$  NMR spectrum of N-(2,6-dimethylphenyl)naphthalen-1-amine (16a).

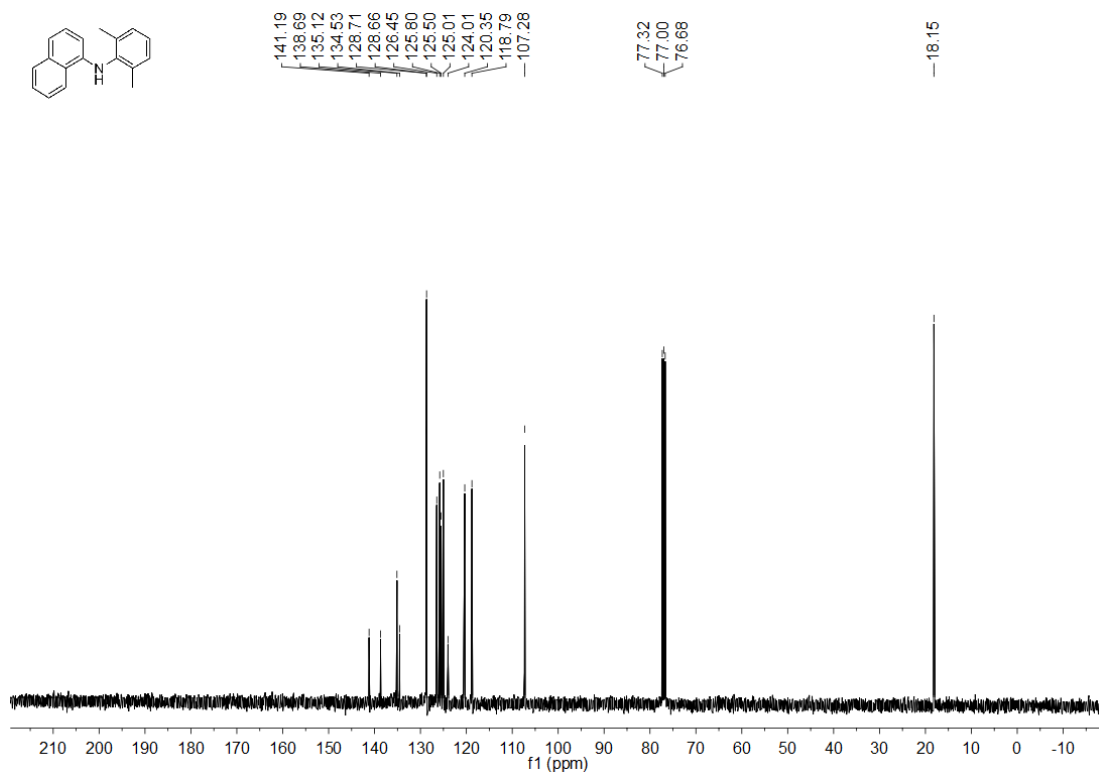


Figure S117. The  $^1\text{H}$  NMR spectrum of N-(4-fluorophenyl)naphthalen-1-amine (16q).

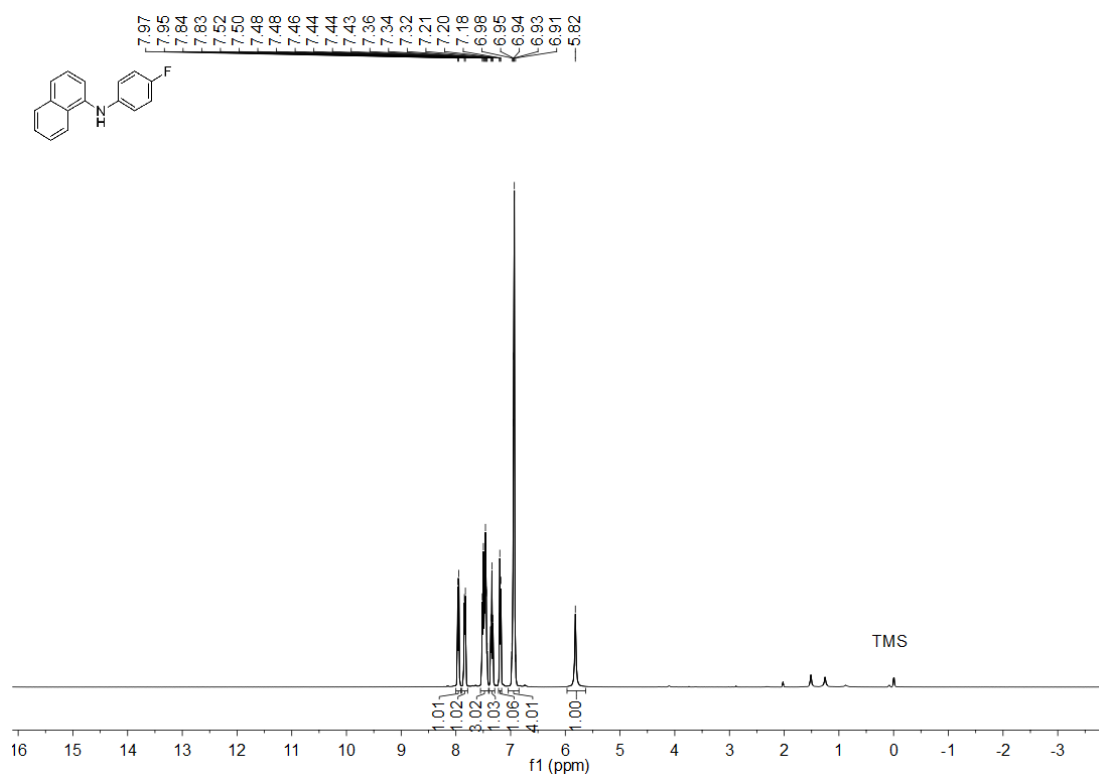


Figure S118. The  $^{13}\text{C}$  NMR spectrum of N-(4-fluorophenyl)naphthalen-1-amine (16q).

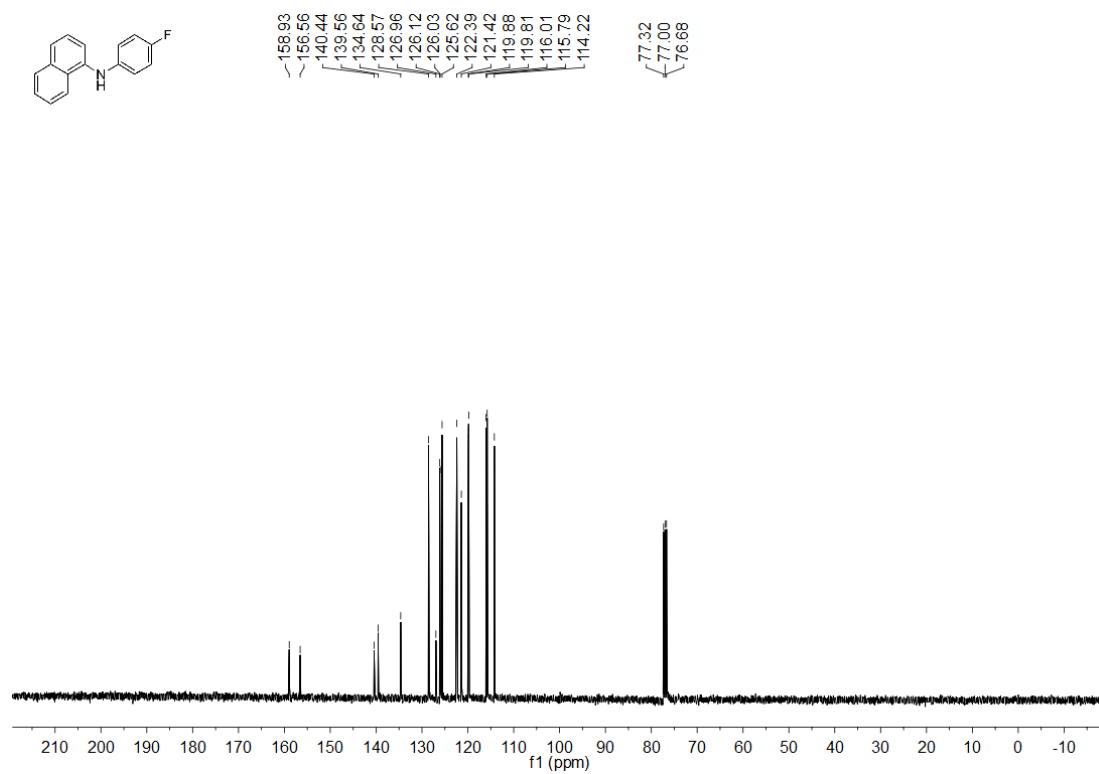




Figure S119. The  $^1\text{H}$  NMR spectrum of 4-(pyridin-2-yl)morpholine (17o).

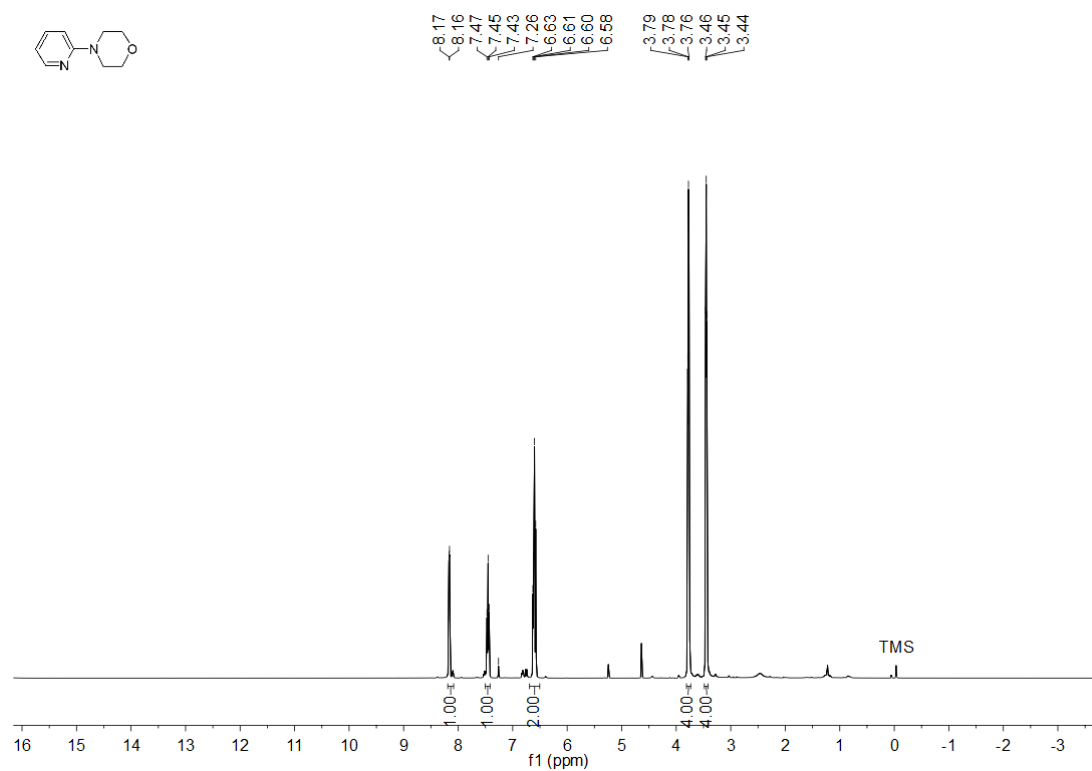


Figure S120. The  $^{13}\text{C}$  NMR spectrum of 4-(pyridin-2-yl)morpholine (17o).

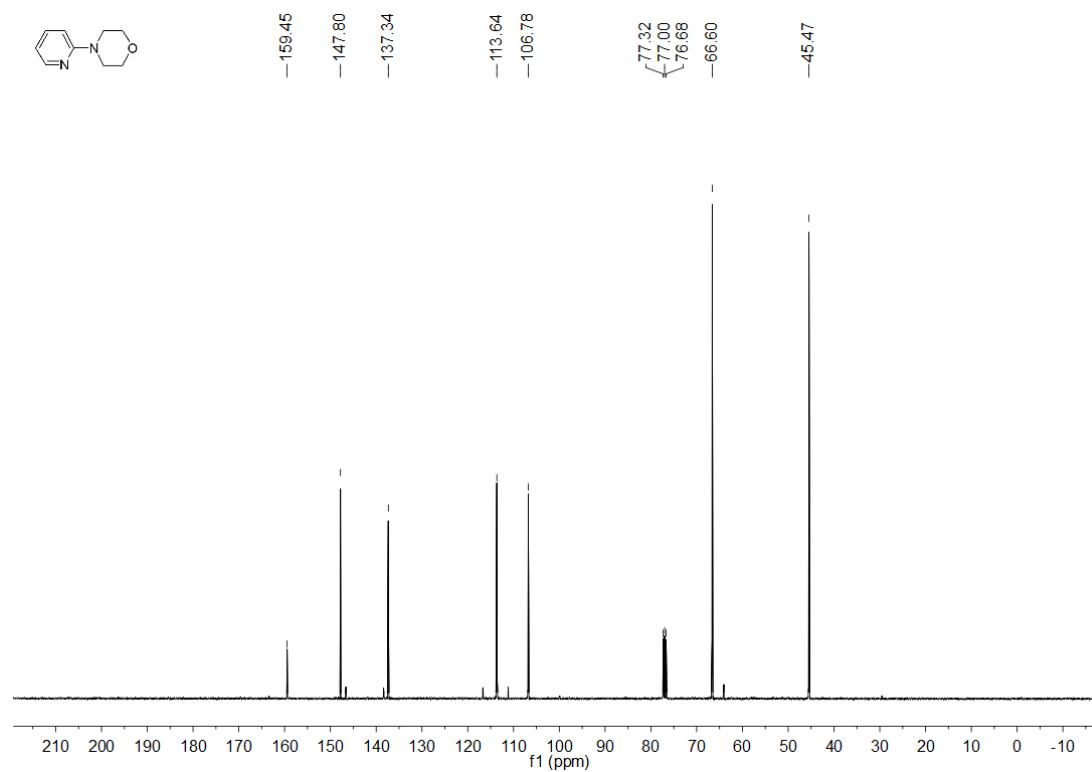


Figure S121. The  $^1\text{H}$  NMR spectrum of N-methyl-N-phenylpyridin-2-amine (17x).

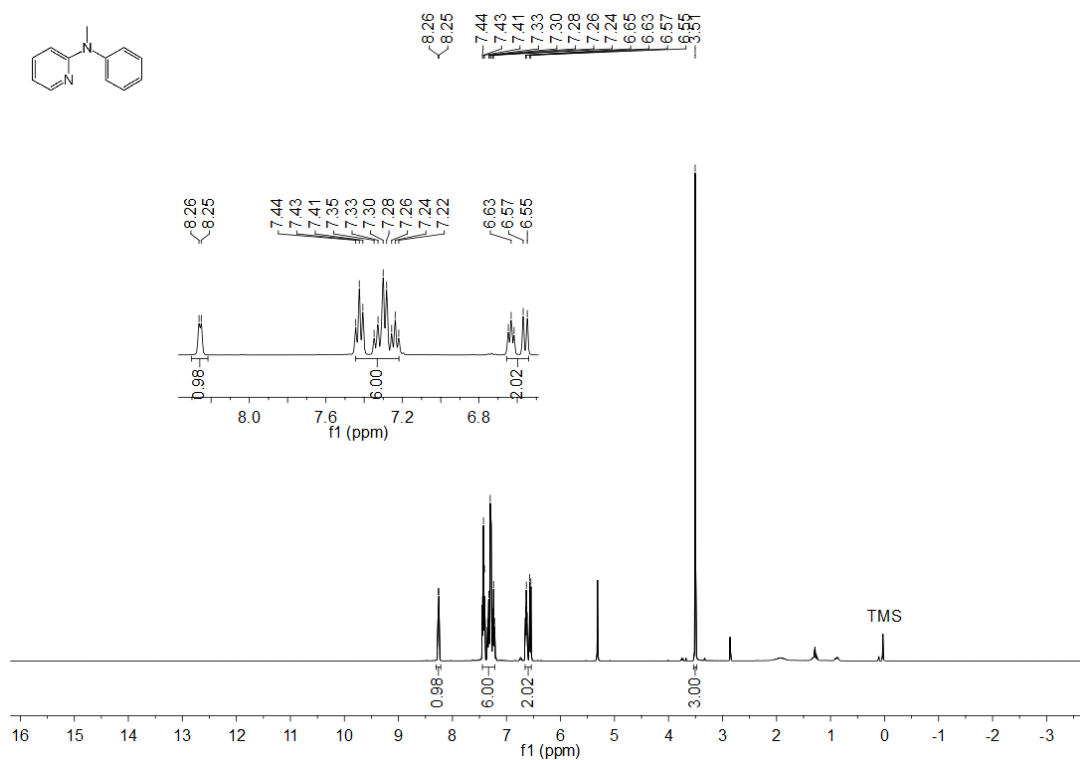


Figure S122. The  $^{13}\text{C}$  NMR spectrum of N-methyl-N-phenylpyridin-2-amine (17x).

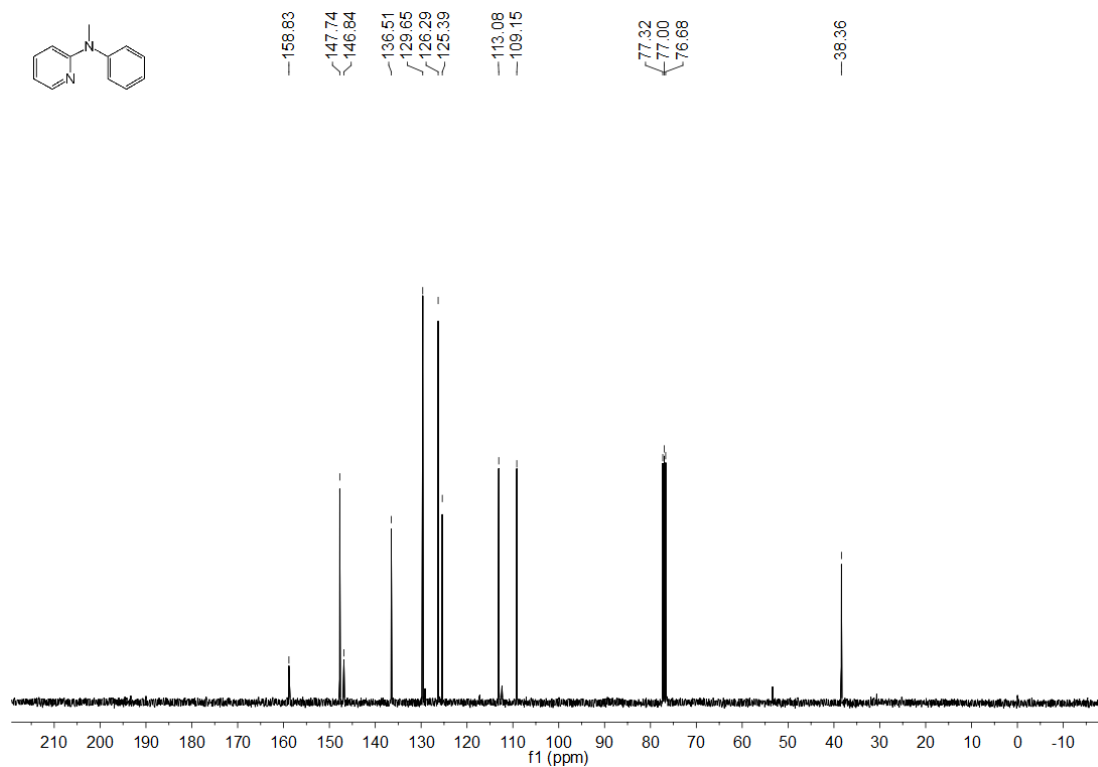


Figure S123. The  $^1\text{H}$  NMR spectrum of 1-methyl-4-(pyridin-2-yl)piperazine (17z).

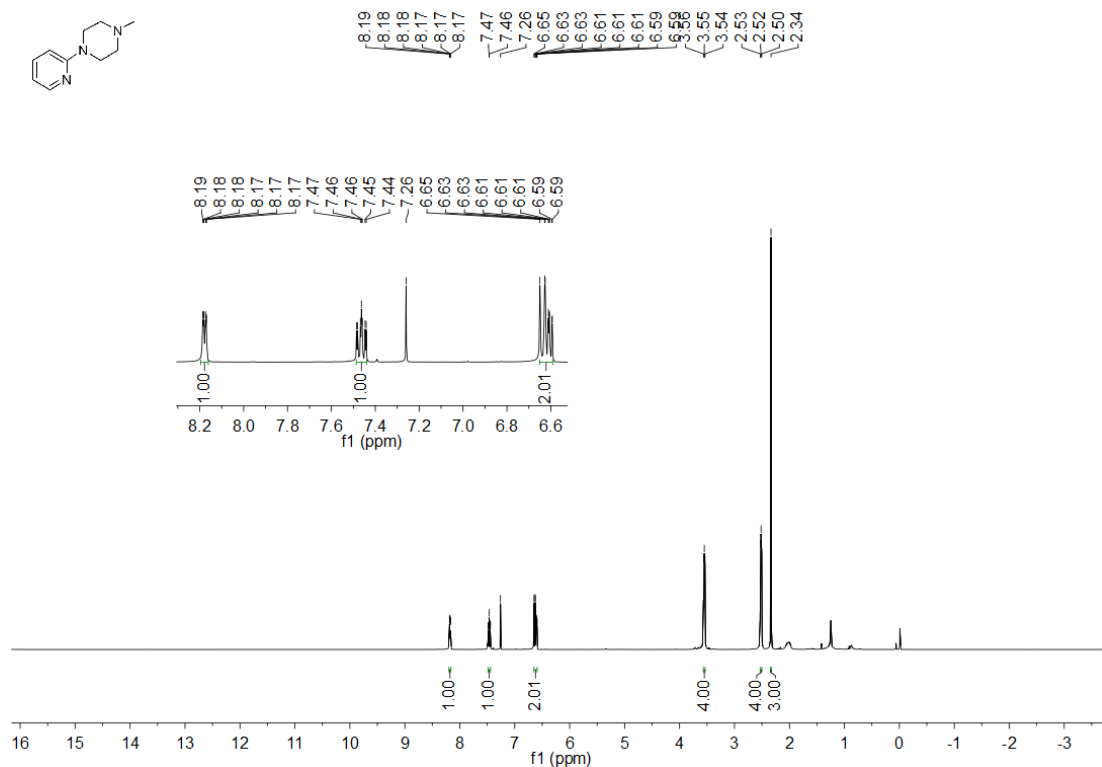


Figure S124. The  $^{13}\text{C}$  NMR spectrum of 1-methyl-4-(pyridin-2-yl)piperazine (17z).

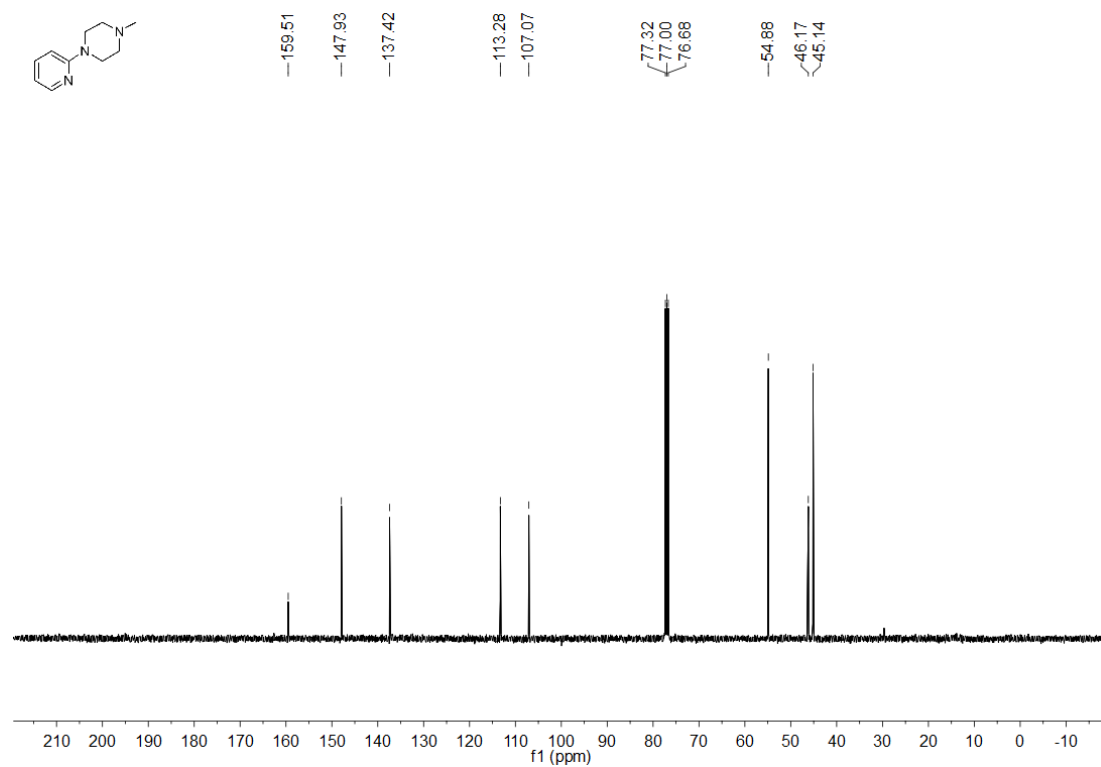


Figure S125. The  $^1\text{H}$  NMR spectrum of 4-(pyridin-3-yl)morpholine (18o).

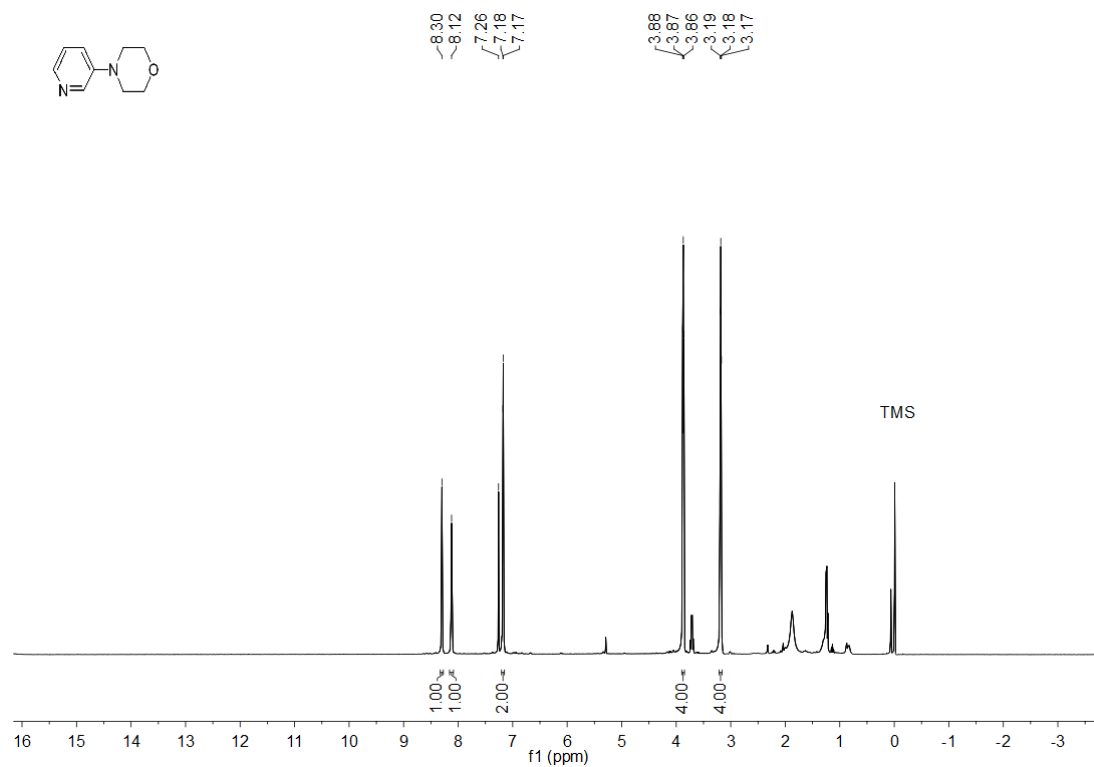


Figure S126. The  $^{13}\text{C}$  NMR spectrum of 4-(pyridin-3-yl)morpholine (18o).

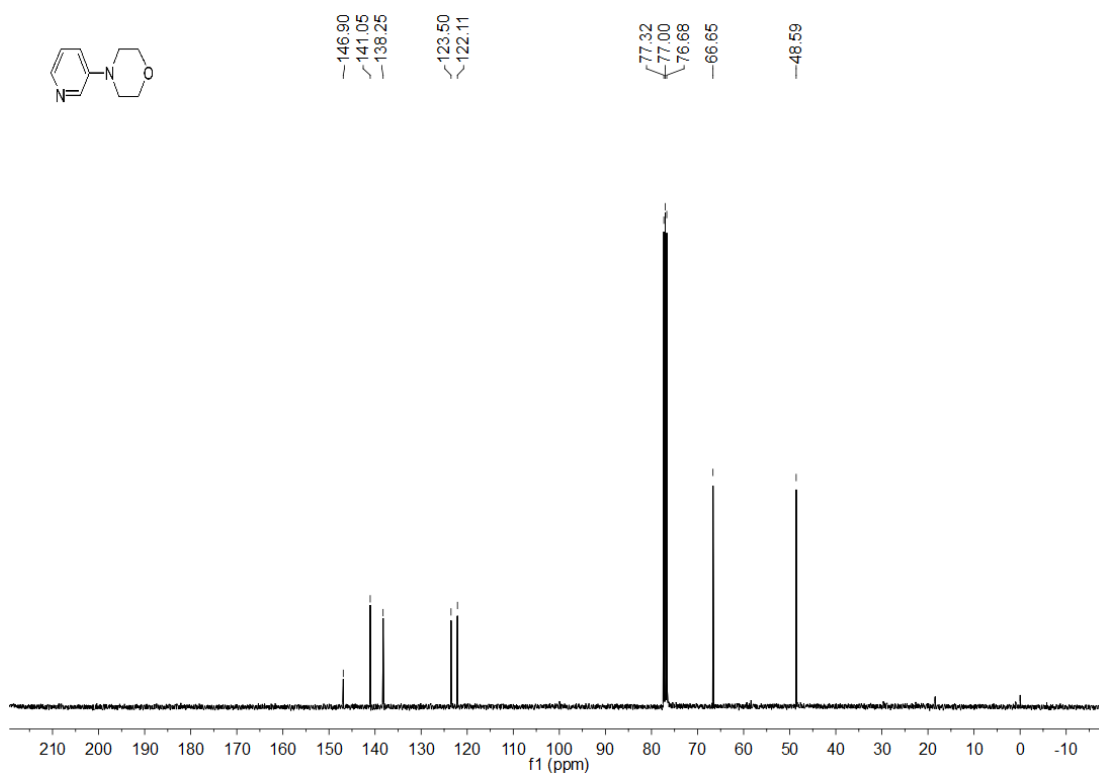


Figure S127. The  $^1\text{H}$  NMR spectrum of N-methyl-N-phenylpyridin-3-amine (18x).

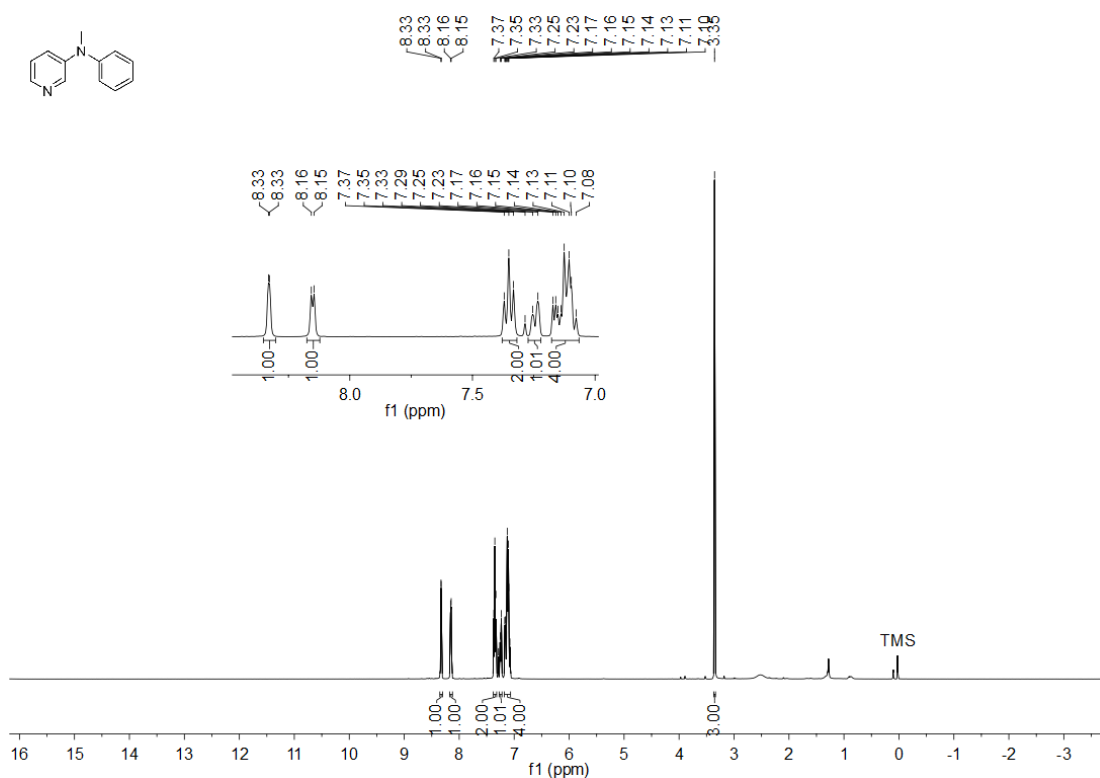


Figure S128. The  $^{13}\text{C}$  NMR spectrum of N-methyl-N-phenylpyridin-3-amine (18x).

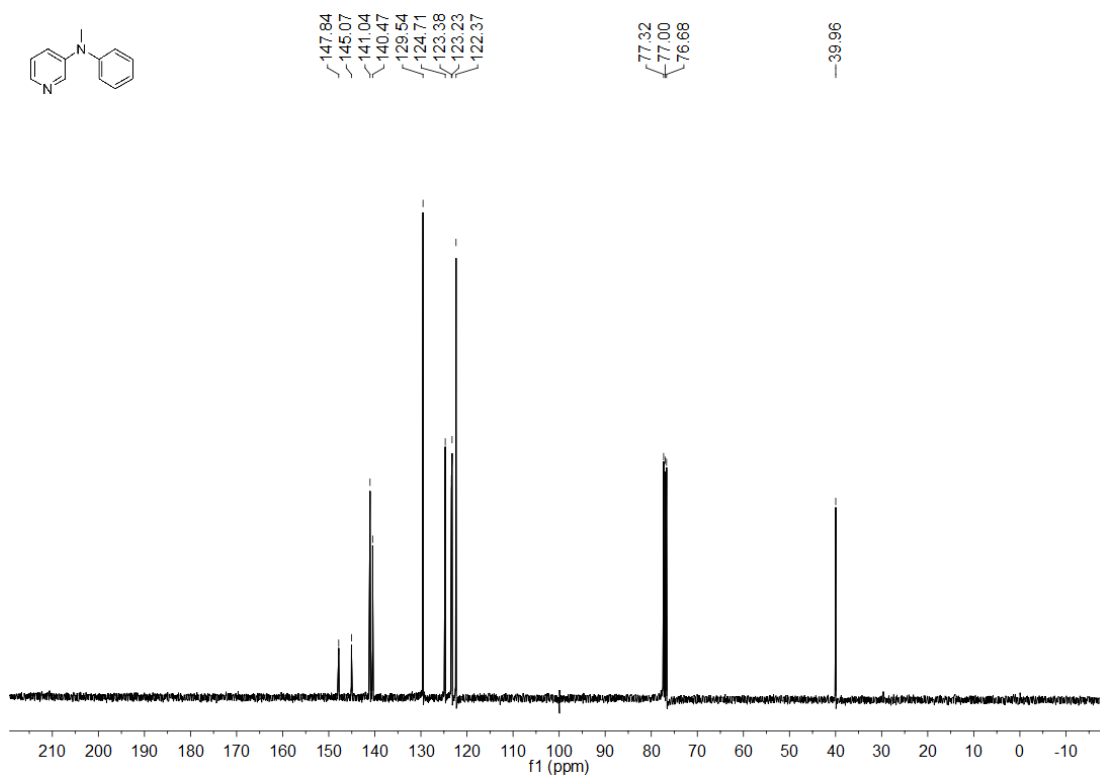


Figure S129. The  $^1\text{H}$  NMR spectrum of 1-methyl-4-(pyridin-3-yl)piperazine (18z).

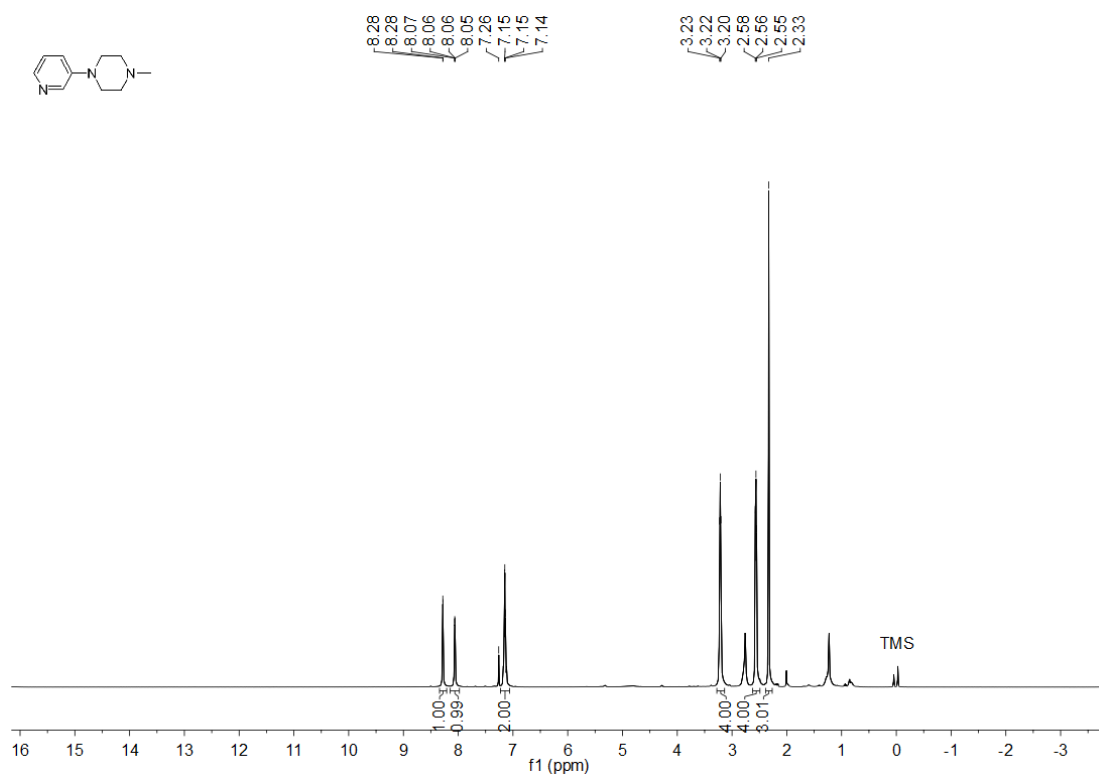


Figure S130. The  $^{13}\text{C}$  NMR spectrum of 1-methyl-4-(pyridin-3-yl)piperazine (18z).

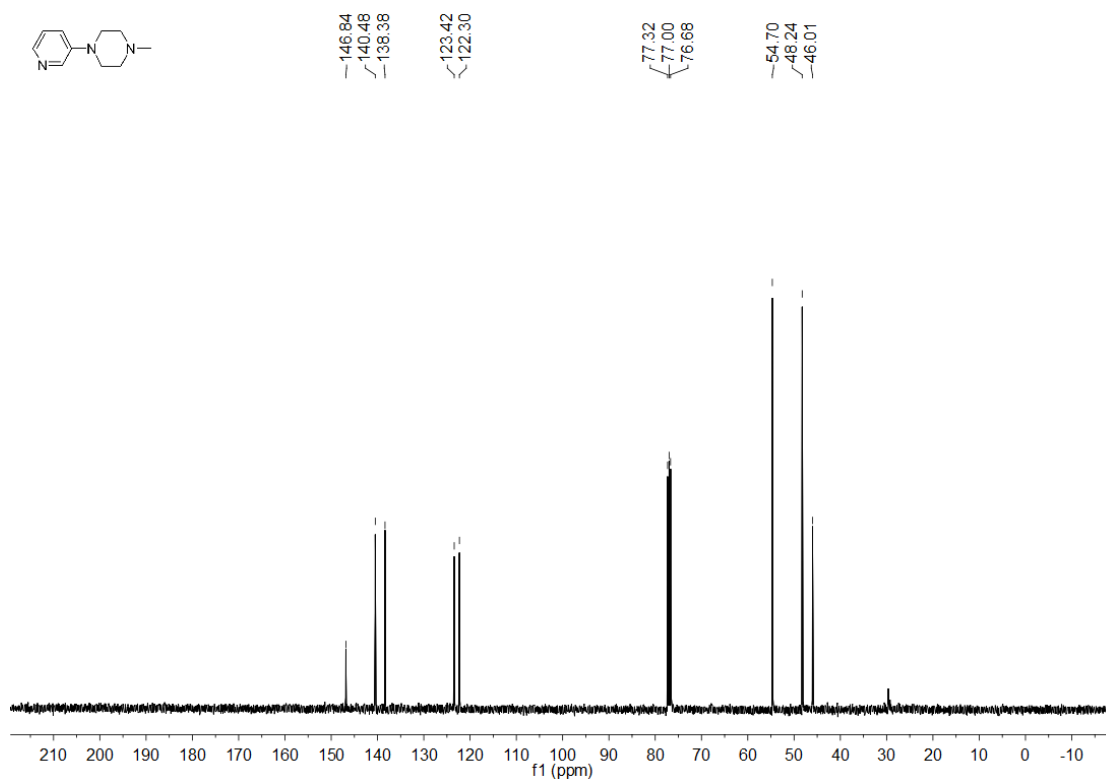


Figure S131. The  $^1\text{H}$  NMR spectrum of *N*-methyl-*N*-phenylthiazol-2-amine (19x).

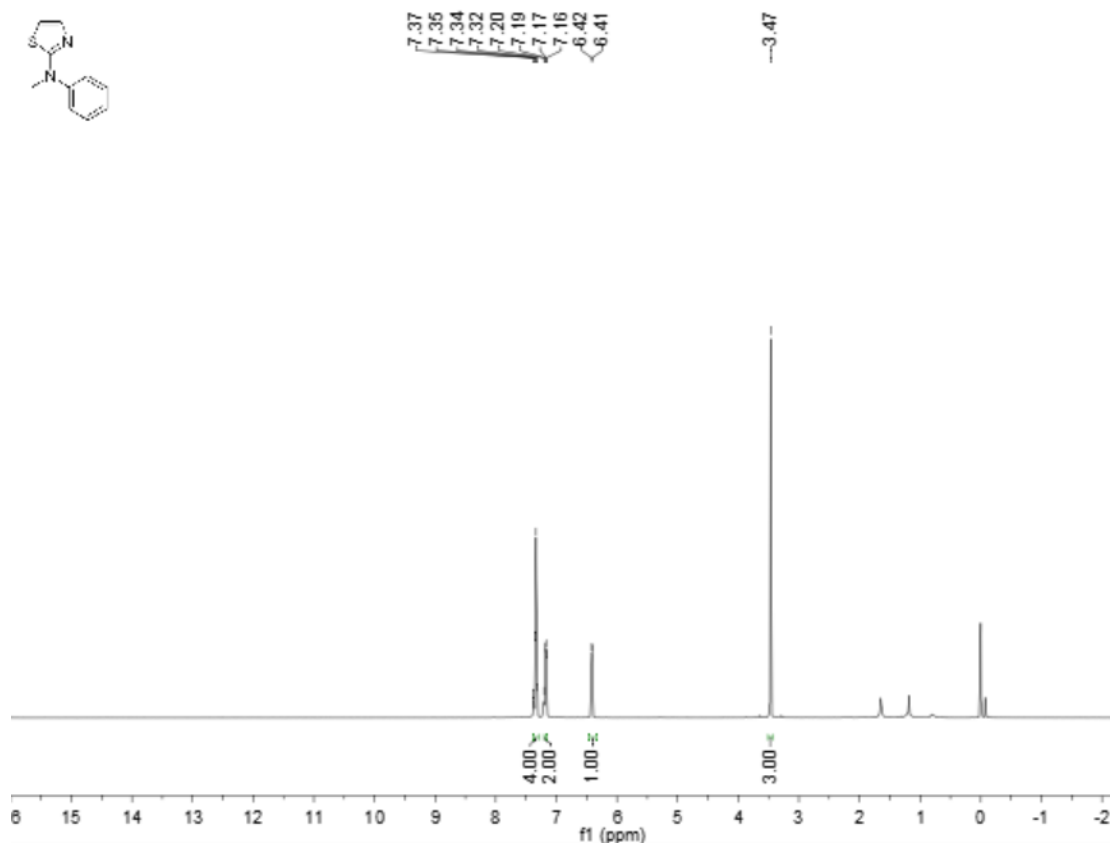


Figure S132. The  $^{13}\text{C}$  NMR spectrum of *N*-methyl-*N*-phenylthiazol-2-amine (19x).

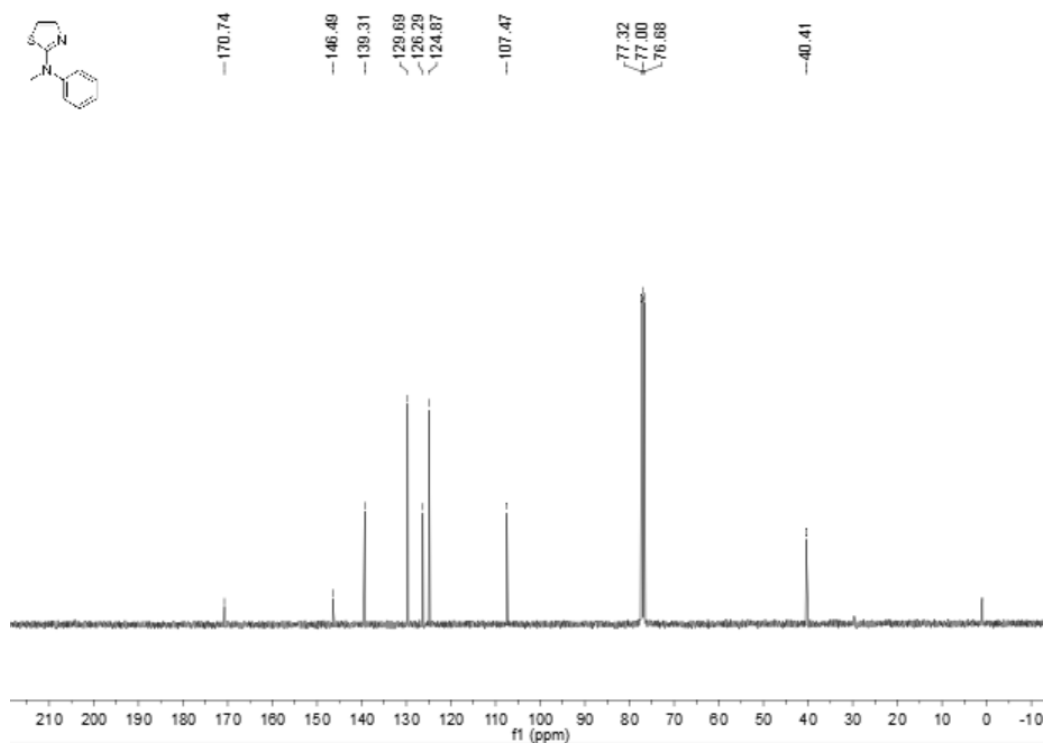


Figure S133. The  $^1\text{H}$  NMR spectrum of *N*-methyl-*N*-phenylbenzo[d]thiazol-2-amine (20x).

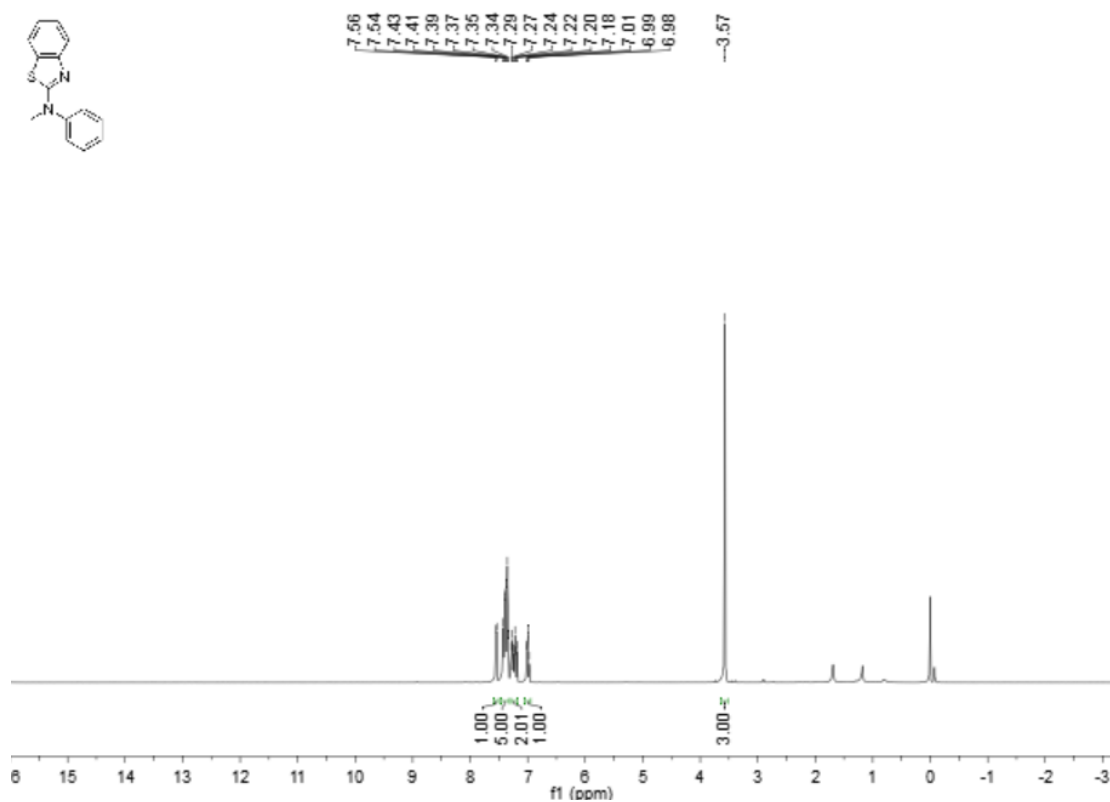
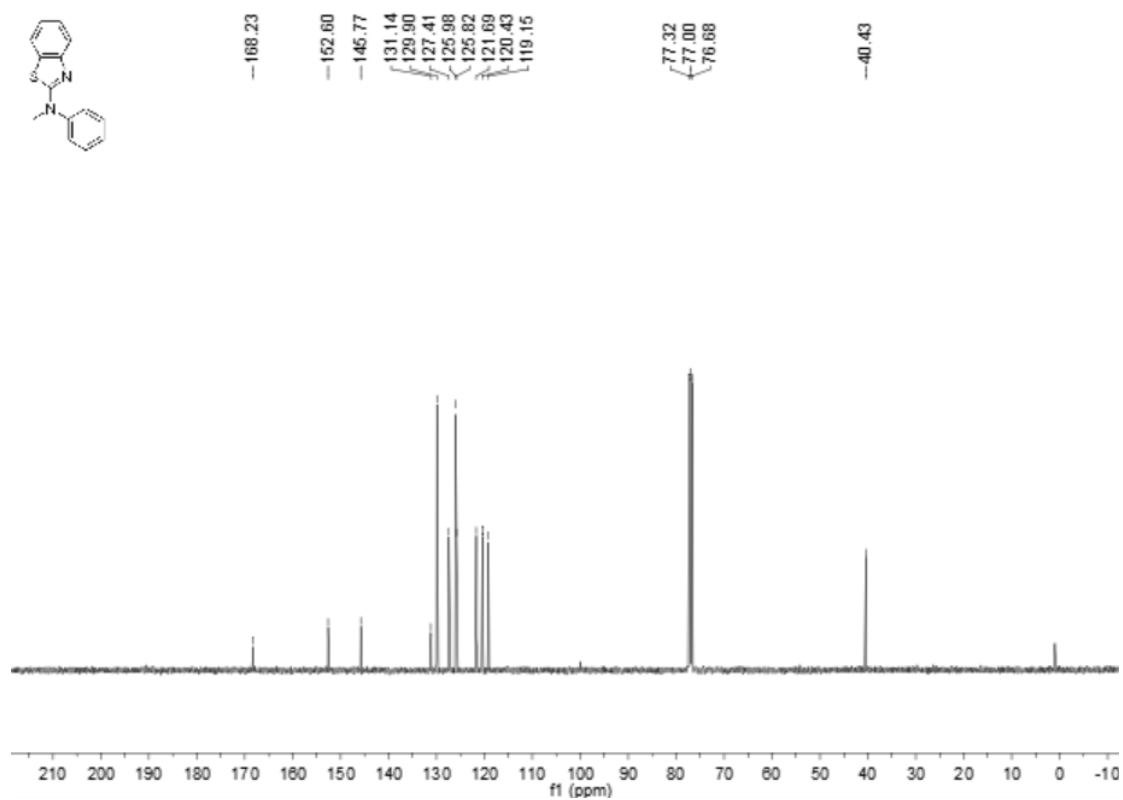


Figure S134. The  $^{13}\text{C}$  NMR spectrum of *N*-methyl-*N*-phenylbenzo[d]thiazol-2-amine (20x).





## 11. References

1. C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson and M. G. Organ, Easily Prepared Air- and Moisture-Stable Pd–NHC (NHC=N-Heterocyclic Carbene) Complexes: A Reliable, User-Friendly, Highly Active Palladium Precatalyst for the Suzuki–Miyaura Reaction, *Chemistry – A European Journal*, 2006, **12**, 4743-4748.
2. T. Tu, W. Fang and J. Jiang, A highly efficient precatalyst for amination of aryl chlorides: synthesis, structure and application of a robust acenaphthoimidazolylidene palladium complex, *Chemical Communications*, 2011, **47**, 12358-12360.
3. X.-X. He, Y. Li, B.-B. Ma, Z. Ke and F.-S. Liu, Sterically Encumbered Tetraarylimidazolium Carbene Pd-PEPPSI Complexes: Highly Efficient Direct Arylation of Imidazoles with Aryl Bromides under Aerobic Conditions, *Organometallics*, 2016, **35**, 2655-2663.
4. A. H. Dardir, P. R. Melvin, R. M. Davis, N. Hazari and M. Mohadjer Beromi, Rapidly Activating Pd-Precatalyst for Suzuki–Miyaura and Buchwald–Hartwig Couplings of Aryl Esters, *The Journal of Organic Chemistry*, 2018, **83**, 469-477
5. C. D. Irving, J. T. Floreancig and S. Laulhé, Amide Synthesis through the In Situ Generation of Chloro- and Imido-Phosphonium Salts, *ACS Omega*, 2020, **5**, 15734-15745.
6. S. Sharif, J. Day, H. N. Hunter, Y. Lu, D. Mitchell, M. J. Rodriguez and M. G. Organ, Cross-Coupling of Primary Amides to Aryl and Heteroaryl Partners Using (DiMeIHept<sup>Cl</sup>)Pd Promoted by Trialkylboranes or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, *Journal of the American Chemical Society*, 2017, **139**, 18436-18439.
7. Z. Tan, Z. Li, Y. Ma, J. Qin and C. Yu, Potassium tert-Butoxide Prompted Highly Efficient Transamidation and Its Coordination Radical Mechanism, *European Journal of Organic Chemistry*, 2019, **2019**, 4538-4545.
8. S. A. Rzhavskiy, A. A. Ageshina, G. A. Chesnokov, P. S. Gribanov, M. A. Topchiy, M. S. Nechaev and A. F. Asachenko, Solvent- and transition metal-free amide synthesis from phenyl esters and aryl amines, *RSC Advances*, 2019, **9**, 1536-1540.
9. A. Sen, R. N. Dhital, T. Sato, A. Ohno and Y. M. A. Yamada, Switching from Biaryl Formation to Amidation with Convuluted Polymeric Nickel Catalysis, *ACS Catalysis*, 2020, **10**, 14410-14418.
10. S. Shi and M. Szostak, Pd–PEPPSI: a general Pd–NHC precatalyst for Buchwald–Hartwig cross-coupling of esters and amides (transamidation) under the same reaction conditions, *Chemical Communications*, 2017, **53**, 10584-10587.
11. M. D. Reddy, A. N. Blanton and E. B. Watkins, Palladium-Catalyzed, N-(2-Aminophenyl)acetamide-Assisted Ortho-Arylation of Substituted Benzamides: Application to the Synthesis of Urolithins B, M6, and M7, *The Journal of Organic Chemistry*, 2017, **82**, 5080-5095.
12. G. Li and M. Szostak, Highly selective transition-metal-free transamidation of amides and amidation of esters at room temperature, *Nature Communications*, 2018, **9**, 4165.
13. N. Shen, C. W. Cheung and J.-A. Ma, Direct amide synthesis via Ni-mediated aminocarbonylation of arylboronic acids with CO and nitroarenes, *Chemical Communications*, 2019, **55**, 13709-13712.
14. J. Zhang, Y. Ma and Y. Ma, Synthesis of Secondary Amides through the Palladium(II)-Catalyzed Aminocarbonylation of Arylboronic Acids with Amines or Hydrazines and Carbon Monoxide, *European Journal of Organic Chemistry*, 2018, **2018**, 1720-1725.
15. L. Zhu, L. Le, M. Yan, C.-T. Au, R. Qiu and N. Kambe, Carbon–Carbon Bond Formation of Trifluoroacetyl Amides with Grignard Reagents via C(O)–CF<sub>3</sub> Bond Cleavage, *The Journal of Organic Chemistry*, 2019, **84**, 5635-5644.
16. K. Nozawa-Kumada, J. Kadokawa, T. Kameyama and Y. Kondo, Copper-Catalyzed sp<sup>3</sup> C–H Aminative Cyclization of 2-Alkyl-N-arylbenzamides: An Approach for the Synthesis of N-Aryl-isoindolinones, *Organic Letters*, 2015, S89

- 17, 4479-4481.
17. B. A. Mair, M. H. Fouad, U. S. Ismailani, M. Munch and B. H. Rotstein, Rhodium-Catalyzed Addition of Organozinc Iodides to Carbon-11 Isocyanates, *Organic Letters*, 2020, **22**, 2746-2750.
  18. M. Kortelainen, A. Suhonen, A. Hamza, I. Pápai, E. Nauha, S. Yliniemelä-Sipari, M. Nissinen and P. M. Pihko, Folding Patterns in a Family of Oligoamide Foldamers, *Chemistry – A European Journal*, 2015, **21**, 9493-9504.
  19. R. Zhao, W. Dong, J. Teng, Z. Wang, Y. Wang, J. Yang, Q. Jia and C. Chu, Activated charcoal supported copper nanoparticles: A readily available and inexpensive heterogeneous catalyst for the N-arylation of primary amides and lactams with aryl iodides, *Tetrahedron*, 2021, **79**, 131858.
  20. N. M. Rezaee, D. C. Samblanet and M. S. Sanford, Iron-Catalyzed Hydrogenation of Amides to Alcohols and Amines, *ACS Catal.*, 2016, **6**, 6377-6383.
  21. X.-B. Lan, Y. Li, Y.-F. Li, D.-S. Shen, Z. Ke and F.-S. Liu, Flexible Steric Bulky Bis(Imino)acenaphthene (BIAN)-Supported N-Heterocyclic Carbene Palladium Precatalysts: Catalytic Application in Buchwald–Hartwig Amination in Air, *The Journal of Organic Chemistry*, 2017, **82**, 2914-2925.
  22. F.-Y. Zhang, X.-B. Lan, C. Xu, H.-G. Yao, T. Li and F.-S. Liu, Rigid hindered N-heterocyclic carbene palladium precatalysts: synthesis, characterization and catalytic amination, *Organic Chemistry Frontiers*, 2019, **6**, 3292-3299.
  23. M. Kim, T. Shin, A. Lee and H. Kim, Synergistic Ligand Effect between N-Heterocyclic Carbene (NHC) and Bicyclic Phosphoramidite (Briphos) Ligands in Pd-Catalyzed Amination, *Organometallics*, 2018, **37**, 3253-3258.
  24. S. S. Kampmann, B. W. Skelton, D. A. Wild, G. A. Koutsantonis and S. G. Stewart, An Air-Stable Nickel(0) Phosphite Precatalyst for Primary Alkylamine C–N Cross-Coupling Reactions, *European Journal of Organic Chemistry*, 2015, 2015, 5995-6004.
  25. A. Cook, S. Prakash, Y.-L. Zheng and S. G. Newman, Exhaustive Reduction of Esters Enabled by Nickel Catalysis, *Journal of the American Chemical Society*, 2020, **142**, 8109-8115.
  26. R. N. Dhital, A. Sen, T. Sato, H. Hu, R. Ishii, D. Hashizume, H. Takaya, Y. Uozumi and Y. M. A. Yamada, Activator-Promoted Aryl Halide-Dependent Chemoselective Buchwald–Hartwig and Suzuki–Miyaura Type Cross-Coupling Reactions, *Organic Letters*, 2020, **22**, 4797-4801.
  27. F. Liu, Y.-Y. Hu, D. Li, Q. Zhou and J.-M. Lu, N-Heterocyclic carbene-palladacyclic complexes: synthesis, characterization and their applications in the C–N coupling and  $\alpha$ -arylation of ketones using aryl chlorides, *Tetrahedron*, 2018, **74**, 5683-5690.
  28. J. Mao, J. Zhang, S. Zhang and P. J. Walsh, NIXANTPHOS: a highly active ligand for palladium catalyzed Buchwald–Hartwig amination of unactivated aryl chlorides, *Dalton Transactions*, 2018, **47**, 8690-8696.
  29. F.-D. Huang, C. Xu, D.-D. Lu, D.-S. Shen, T. Li and F.-S. Liu, Pd-PEPPSI-IPent<sup>An</sup> Promoted Deactivated Amination of Aryl Chlorides with Amines under Aerobic Conditions, *The Journal of Organic Chemistry*, 2018, **83**, 9144-9155.
  30. Á. Sinai, D. C. Simkó, F. Szabó, A. Paczal, T. Gáti, A. Bényei, Z. Novák and A. Kotschy, Aryl-Diadamantyl Phosphine Ligands in Palladium-Catalyzed Cross-Coupling Reactions: Synthesis, Structural Analysis, and Application, *European Journal of Organic Chemistry*, 2020, **2020**, 1122-1128.
  31. A. Chartoire, X. Frogneux and S. P. Nolan, An Efficient Palladium-NHC (NHC=N-Heterocyclic Carbene) and Aryl Amination Pre-Catalyst: [Pd(IPr\*)(cinnamyl)Cl], *Advanced Synthesis & Catalysis*, 2012, **354**, 1897-1901.