

## **Supporting Information**

### **Pd Nanoparticles in Ionic Liquid Brush: A Highly active and Reusable Heterogeneous Catalytic Assembly for Solvent-free or On-water Hydrogenation of Nitroarene under Mild Conditions**

**Jing Li, Xian-Ying Shi, Yuan-Yuan Bi, Jun-Fa Wei,\* Zhan-Guo Chen**

School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an,  
710062, P. R. China

#### **Table of Content**

<b>1. Experimental Section.....</b>	<b>P1</b>
<b>2. General procedures.....</b>	<b>P2-P8</b>
<b>2.1. Preparation and characterization of the multiple layer ionic liquids.</b>	
<b>2.2. The procedures for hydrogenation reactions under mild conditions.</b>	
<b>3. Experimental characterization data for products.....</b>	<b>P8-P11</b>
<b>4. Copies of the IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra of the catalysts.....</b>	<b>P12-P16</b>
<b>5. Copies of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products.....</b>	<b>P17-P37</b>
<b>6. References.....</b>	<b>P38</b>

## 1. Experimental Section

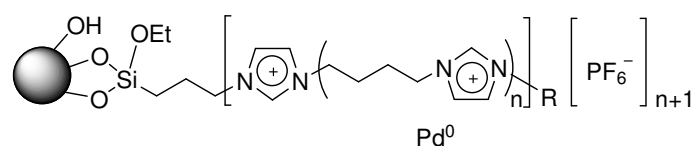
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DRX 300 spectrometer in  $\text{CDCl}_3$ , and tetramethylsilane (TMS) was used as internal standard. The structures of the synthesized materials were confirmed by TEM using a JEM-3010 transmission electron microscope operating at an accelerating voltage of 300kv. Histograms of particle size distribution of Pd nanoparticles were obtained from the TEM images by measuring more than 200 particles in each sample. The surface area of the catalysts was determined from full nitrogen adsorption and desorption isotherms at 77K using a Sorptometer ST-03A. The catalysts were outgassed for four hours at 573K prior to measurements. Infrared spectra were recorded with a FT-IR Bruker EQUINX-55 Spectrometer equipped with a KBr beam splitter and a TGS detector. The chemical analyses of the content of palladium, respectively, were carried out with an ICP-OES (inductively coupled plasma-optical emission spectrometer) Vista (Varian). The samples (amount of about 10 mg) were digested in a mixture of 1.5 mL of HCl (37%), 0.5 mL of  $\text{HNO}_3$  (65%), and 1 mL of HF (40%) by heating. Generally, the solutions were diluted to a volume of 50 mL using a volumetric flask. EDXA measurements were performed on a Philips-FEI Quanta 200 scanning electron microscope. This apparatus was equipped with a Si-Li energy dispersive, quantitative chemical analysis was performed for Si and Pd. C, H and N elemental analysis were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The powder XRD pattern of  $\text{SiO}_2\text{-BisILs}[\text{PF}_6]\text{-Pd}^0$  (**2c**) was recorded on a Rigaku D/Max-3c X-ray diffractometer (Cuka, Ni filter). Gas chromatography was performed on an Agilent GC 6890N with a FID detector equipped with an DB-35 column (30 m long, 0.25 mm inner diameter). Parameters were as follows: initial temperature 70 °C; initial time 3 min; ramp 8 °C·min $^{-1}$ ; final temperature 180 °C; final time 2 min; injector temperature 220 °C; detector temperature 250 °C; injection volume 1.0  $\mu\text{L}$ . The high boiling point substrates and the products were analyzed by using HPLC. All hydrogenated products were initially identified using authentic commercial samples of the expected products. Melting point is uncorrected.

**Materials.**  $\text{PdCl}_2$  (AR grade), imidazole (AR grade), sodium borohydride (AR grade), 1-chlorooctane (AR grade),  $\text{KPF}_6$ , silica gel (surface area, 385  $\text{m}^2\text{g}^{-1}$ ), nitrobenzene, 4-nitrophenol, 2-nitrophenol and other aromatic nitro compounds were used as received. 1,4-dibromobutane and 3-chloropropyltriethoxy silane, purchased from Alfa Aesar. All organic solvents (toluene, methanol, ethanol, and so on.) were dried under standard purification conditions.

## 2. General procedures

### 2.1. Preparation and characterization of the multiple layer ionic liquids.

The  $\text{SiO}_2$  immobilized multiple layer ILs and the Pd nanoparticles catalysts involved in this work are shown in Figure S1 and Table S1. The synthetic route of the catalysts, *e.g.*, the bis-layer ionic liquids catalyst **2c**, is shown in Scheme S1.



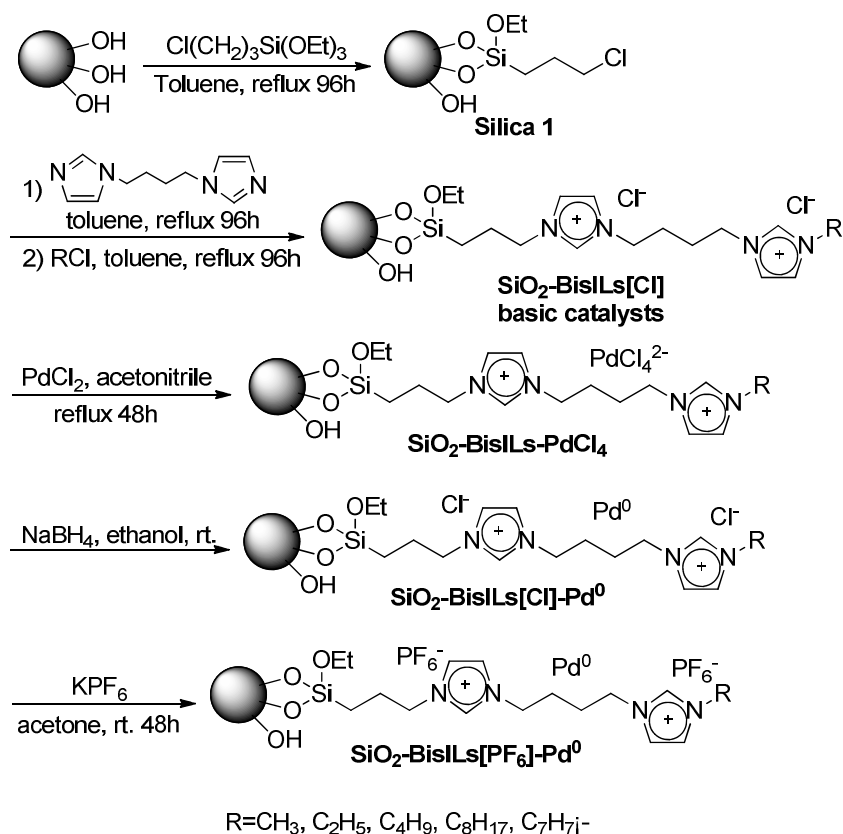
R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>4</sub>H<sub>9</sub>, C<sub>8</sub>H<sub>17</sub>, C<sub>7</sub>H<sub>7</sub>,...

n=0, 1, 2, 3...

**Figure S1.** Silica immobilized multilayer ionic liquids as the catalysts

**Table S1:** The catalysts used in this work

Catalysts	<i>n</i>	<i>R</i>	Constant of Pd(wt.%)	Catalysts	<i>n</i>	<i>R</i>	Constant of Pd(wt.%)
Silica-Pd <sup>0</sup> (0)	-	-	1.0	Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2c-1)	1	C <sub>8</sub> H <sub>17</sub>	1.5
Silica-IL[PF <sub>6</sub> ]-Pd <sup>0</sup> (1)	0	C <sub>8</sub> H <sub>17</sub>	1.0	Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2c-2)	1	C <sub>8</sub> H <sub>17</sub>	2.0
Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2a)	1	C <sub>2</sub> H <sub>5</sub>	1.0	Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2d)	1	C <sub>12</sub> H <sub>25</sub>	1.0
Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2b)	1	C <sub>4</sub> H <sub>9</sub>	1.0	Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2e)	1	C <sub>7</sub> H <sub>7</sub>	1.0
Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2c)	1	C <sub>8</sub> H <sub>17</sub>	1.0	Silica-TriILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (3)	2	C <sub>8</sub> H <sub>17</sub>	1.0

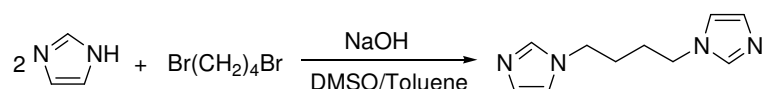


**Scheme S1.** The route of synthesizing the catalyst SiO<sub>2</sub>-BisILs[PF<sub>6</sub>]-Pd<sup>0</sup>

## 2.1.1 Preparation of the multilayer ionic liquids portion.

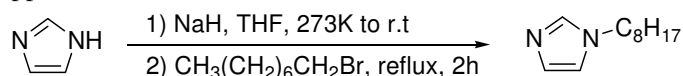
### 2.1.1.1 Synthesis of 1,4-bis(imidazole-1-yl)butane.

1,4-Bis(imidazole-1-yl)butane was synthesized according to the literature.<sup>[S1]</sup> m.p. 61-63°C, <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 1.61 (m, 4H), 3.96 (m, 4H), 6.89 (s, 2H), 7.14 (s, 2H), 7.62 (s, 2H); <sup>13</sup>C NMR (300 MHz, DMSO-*d*<sub>6</sub>, ppm) δ 28.1, 39.4, 39.6, 39.9, 40.2, 40.5, 45.7, 119.7, 128.9, 137.7.



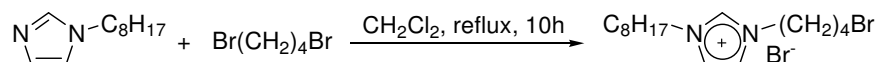
### 2.1.1.2 Synthesis of 1-octylimidazolium.

1-Octylimidazolium was synthesized according to the literature.<sup>[S2]</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 0.42-1.30 (m, 15H), 3.48-3.43 (t, 2H), 6.46 (d, 1H), 6.59 (d, 1H), 7.00 (s, 1H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 13.7, 22.3, 26.2, 28.7, 28.8, 30.8, 31.4, 46.7, 118.5, 128.9, 136.7.



### 2.1.1.3 Synthesis of 1-(4-bromododecyl)-3-octylimidazolium bromide.

1-(4-Bromododecyl)-3-octylimidazolium bromide was synthesized according to the literature.<sup>[S3]</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 0.87-0.85(t, 3H), 1.49-1.13(m, 10H), 2.15-1.79(m, 6H), 4.60-4.37(m, 6H), 7.65-7.33(m, 2H), 10.01(s, 1H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 13.8, 22.3, 26.0, 26.3, 26.7, 28.8, 28.9, 30.1, 31.5, 32.5, 46.6, 50.0, 122.2, 122.3, 136.6.



## 2.1.2 Preparation and characterization of the Catalyst: SiO<sub>2</sub>-BisILs[PF<sub>6</sub>]-Pd<sup>0</sup>.

### 2.1.2.1 Functionalization of silica: Silica 1.

The functionalization of the silica was performed according to the literature,<sup>[S4]</sup> while the white color of the solid support changed to pale yellow, denoted as **Silica 1**. S<sub>BET</sub> (m<sup>2</sup>/g): 385. IR: (KBr disk) 2958, 2930, 2871 cm<sup>-1</sup> ν(C-H, aliphatic).

### 2.1.2.2 Modification of the Silica 1 with 1,4-bis(imidazole-1-yl)butane.

1,4-Bis(imidazole-1-yl)butane (4.3 g, 22.5mmol), synthesized according to the literature,<sup>[S5]</sup> was mixed with **Silica 1** (4.5 g) in 15 mL dry toluene. And then the mixture was refluxed for 96 h. It was then filtered and washed thoroughly with toluene followed by methanol in a Soxhlet apparatus. After drying under high vacuum, 5.1 g of resulting solid was obtained. S<sub>BET</sub> (m<sup>2</sup>/g): 236. IR: (KBr disk) 3155, 3120 cm<sup>-1</sup> ν(C-H, aromatic), 2947, 2871 cm<sup>-1</sup> ν(C-H, aliphatic), 1555, 1456 cm<sup>-1</sup> ν(C=N). Elemental analysis for the resulting solid was found to be (%): C, 14.79; H, 2.574; N, 4.212, revealing that 1.50 mmol of imidazolium /g.

### 2.1.2.3 Alkylation of 1,4-bis (imidazole-1-yl) butane modified Silica 1: Silica 2.

A mixture of the above modified silica (5g, 1.50 mmol of imidazolium /g) and 1-chlorooctane (5 g, 34 mmol) in toluene was refluxed for 24 h under nitrogen atmosphere. After the reaction mixture was cooled to room temperature the solid was filtered off and washed with toluene followed by ethanol in a Soxhlet apparatus., then dried under vacuum, 5.4 g of resulting solid was obtained, denoted as **Silica 2**. S<sub>BET</sub> (m<sup>2</sup>/g): 181. IR: (KBr disk) 3151, 3084 cm<sup>-1</sup> ν(C-H, aromatic), 2936, 2855 cm<sup>-1</sup> ν(C-H, aliphatic), 1568, 1458 cm<sup>-1</sup> ν(C=N). Elemental analysis for **Silica 2** was found to be (%): C, 14.06; H, 2.335; N, 3.545; revealing that 1.27 mmol of imidazolium /g.

### 2.1.2.4 Synthesis of SiO<sub>2</sub>-BisILs-PdCl<sub>4</sub>.

A typical procedure of the catalysts was as follows: to a yellow solution of PdCl<sub>2</sub> (0.017 g, 0.09 mmol) in 10 ml of freshly distilled acetonitrile, the **Silica 2** (1.0 g, 1.27 mmol of ionic liquid portion/g) was added and the suspension was refluxed for 96 h under nitrogen atmosphere. The solid material was filtered off and washed repeatedly with methanol in a Soxhlet apparatus and dried under vacuum, 1.013 g of resulting solid was obtained, denoted as **SiO<sub>2</sub>-BisILs-PdCl<sub>4</sub>**. S<sub>BET</sub> (m<sup>2</sup>/g): 227. Elemental analysis for **SiO<sub>2</sub>-BisILs-PdCl<sub>4</sub>** was found to be (%): C, 13.58; H, 2.39; N,

2.85, revealing that 1.02 mmol of imidazolium /g.

#### 2.1.2.5 Synthesis of $\text{SiO}_2\text{-BisILs[Cl]-Pd}^0$ : Silica 3.

The saffron yellow solid,  $\text{SiO}_2\text{-BisILs-PdCl}_4$  (1 g, 1.02 mmol of imidazolium /g) was suspended in EtOH (10 mL) at 303 K under nitrogen atmosphere. Then, a stoichiometric amount of sodium borohydride ( $\text{NaBH}_4$ ) ethanol solution was added dropwisely, and the reaction mixture changed to black colored indicating a reduction of Pd (II) to Pd (0). The resulting product was filtered, washed with EtOH in a Soxhlet apparatus and dried under vacuum to give 0.96 g  $\text{SiO}_2\text{-BisILs[Cl]-Pd}^0$  as a black solid, denoted as **Silica 3**.  $S_{\text{BET}}$  ( $\text{m}^2/\text{g}$ ): 212. Elemental analysis for  $\text{SiO}_2\text{-BisILs[Cl]-Pd}^0$  was found to be (%): C, 13.85; H, 2.615; N, 3.245, revealing that 1.15 mmol of imidazolium /g.

#### 2.1.2.6 Synthesis of the catalyst with expected anions by exchanging $\text{Cl}^-$ to $\text{PF}_6^-$ : $\text{SiO}_2\text{-BisILs[PF}_6\text{]-Pd}^0$ (2c).

To a solution of  $\text{KPF}_6$  (2.1 g, 11.5 mmol) in acetone (50 mL, 0.1 mol/L), **Silica 3** (1.0 g, 1.15 mmol of imidazolium /g) was added and the mixture was stirred for 48 h under nitrogen atmosphere at room temperature. The solid material was filtered off and washed repeatedly with acetone, distilled water and acetone, followed by extraction with ethanol in a Soxhlet apparatus, and then dried under vacuum to give 1.2 g black solid, which was the expected catalyst, denoted as  $\text{SiO}_2\text{-BisILs[PF}_6\text{]-Pd}^0$  (2c).  $S_{\text{BET}}$  ( $\text{m}^2/\text{g}$ ): 110. IR: (KBr disk)  $3167, 3120\text{ cm}^{-1}$   $\nu(\text{C-H, aromatic})$ ,  $2948, 2876\text{ cm}^{-1}$   $\nu(\text{C-H, aliphatic})$ ,  $1567, 1468\text{ cm}^{-1}$   $\nu(\text{C=N})$ ,  $842\text{ cm}^{-1}$   $\nu(\text{P-F})$ . Elemental analysis for  $\text{SiO}_2\text{-BisILs[PF}_6\text{]-Pd}^0$  (2c) was found to be (%): C, 12.62; H, 2.552; N, 2.946, revealing that 1.05 mmol of imidazolium /g. EDXA: Pd, 1.0 %.

#### 2.1.2.7 Supporting data for structural characteristics of $\text{SiO}_2\text{-BisILs[PF}_6\text{]-Pd}^0$ (2c)

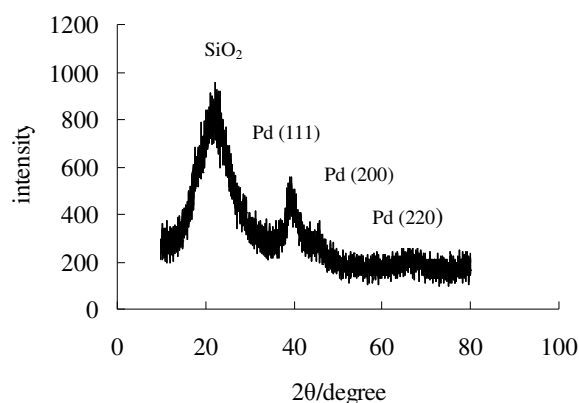


Figure S2. powder XRD pattern of  $\text{SiO}_2\text{-BisILs[PF}_6\text{]-Pd}^0$  (2c)

The powder XRD pattern, shown in the Figure S2, exhibited typical diffused rings, which could be assigned to (111), (200), and (220) reflections of face centered cubic structure corresponding to metallic Pd. The particle size calculated from the line broadening of (111) reflection using the Scherrer formula was 1 nm, which matched very well with TEM data (Figure 2).<sup>[S6]</sup> One broad reflection ( $2\theta=10\text{-}30^\circ$ ) is also observed in the XRD pattern, which is attributed to the reflection of amorphous  $\text{SiO}_2$ .

#### 2.1.3 Synthesis of the other catalysts used in this work.

The other catalysts, as shown in Table S1, were prepared via the same procedure or, if necessary, via those with a slight modification. All the elemental analyses were shown in Table S2.

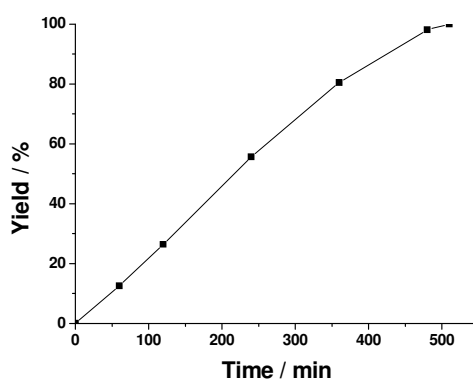
**Table S2:** The elemental analysis of the catalysts used in this work

Catalysts	S <sub>BET</sub> (m <sup>2</sup> /g)	N (wt.%)	C (wt.%)	H (wt.%)	Loading of imidazolium (mmol/g)
Silica-Pd <sup>0</sup> (0)	395	-	-	0.743	-
Silica-IL[PF <sub>6</sub> ]-Pd <sup>0</sup> (1)	241	1.943	11.44	1.734	0.69
Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2a)	173	3.131	11.98	1.760	1.12
Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2b)	136	3.112	12.28	1.520	1.11
Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2c)	110	2.946	12.62	2.552	1.05
Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2d)	35	3.020	19.33	2.656	1.08
Silica-BisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (2e)	127	3.038	12.16	2.368	1.09
Silica-TrisILs[PF <sub>6</sub> ]-Pd <sup>0</sup> (3)	227	1.916	12.23	2.294	0.68

## 2.2. The procedures for hydrogenation reactions under mild conditions.

### 2.2.1 A typical procedure for hydrogenation of nitrobenzene under solvent-free condition.

All hydrogenation reactions were carried out under standard conditions (30 °C, 1 atm of H<sub>2</sub>). A round bottom flask (25 mL), charged with the supported Pd<sup>0</sup> catalyst (10 μmol) and a magnetic stirrer, was connected to a gas burette (500 mL) with a flask to balance the pressure. The flask was closed by a septum, and the system was filled with hydrogen. Nitrobenzene (3.5×10<sup>-2</sup> mol) was injected through the septum, and the mixture was stirred (1500 min<sup>-1</sup>). The reaction was monitored by the volume of gas consumed and by gas chromatography. At the end of the reaction, the two phases were separated by decantation and the solid phase was reused in a second run. The liquid phase was collected and divided into two equal parts. One was used for the determination of the Pd content by ICP analysis and the other one was used for detection. ICP analysis indicated absence of any palladium within the detection limits (i.e., less than 0.1 μg/mL). The rates of the products were determined and checked by GC.



**Figure S3.** The yield against the reaction time in the hydrogenation of nitrobenzene with **2c**

In the course of hydrogenation of nitrobenzene, it was found that the maximal speed could be got with about 50% conversion; but the speed was slower after the conversion reached to 80% and

the speed turned slowest when the conversion exceeded 98%. The results, to our great delight, show that the hydrogenation reaction of nitrobenzene was proceeded smoothly and completely to give aniline in quantitative yields.

Encouraged by these excellent results, we compared the catalyst **2c** with the Pd catalysts reported in literatures<sup>[S8]</sup> for the hydrogenation of nitrobenzene (Table S3). In the result, **2c** has unprecedented activity in nitrobenzene hydrogenation under organic solvent-free, atmospheric pressure and room temperature conditions, while **Pd/SiO<sub>2</sub>** cannot promote the reaction to be complete<sup>[S8a]</sup> and **PS-DVB-Pd** catalyzes the reaction with a rather low rates<sup>[S8b]</sup> even under rigorous conditions. Although **PVPA-Pd** exhibits a higher activity, its catalytic activity decreases significantly after reusing for 4 cycles.<sup>[S8c]</sup> **EnPdCl<sub>2</sub>Cat** could be recycled three times without deactivation, but its catalytic activity was too low.<sup>[S8d]</sup> In addition, all of these Pd catalysts reported must be employed in methanol, ethanol or hexane. The reasons might be that the ionic liquid brushes provide a fence protecting nanoparticles from aggregation and a suitable reaction environment as mentioned above.

**Table S3.** Comparison of standard catalysts versus the catalyst **2c** for the hydrogenation of nitrobenzene

Catalyst	Subs./Pd (mol/g)	Solvent	<i>T</i> (K)	<i>P</i> (atm)	<i>t</i> (h)	Yield (%)	Rate <sup>[S7]</sup> (mol/g·h) <sup>[a]</sup>	Ref.
<b>Pd/SiO<sub>2</sub></b> <sup>[b]</sup>	19.6	ethanol	393	10	4.7	80	3.33	[S8a]
<b>PS-DVB-Pd</b> <sup>[c]</sup>	3.54	methanol	303	1	10.0	100	0.35	[S8b]
<b>PVPA-Pd</b> <sup>[d]</sup>	4.70	ethanol	308	1	1.3	100	3.61	[S8c]
<b>EnPdCl<sub>2</sub>Cat</b> <sup>[e]</sup>	0.78	hexane	303	1	2	100	0.39	[S8d]
<b>SiO<sub>2</sub>-BisILs[PF<sub>6</sub>]-Pd<sup>0</sup> (2c)</b>	33	-	303	1	8.5	100	3.88	This work

[a] The rate based on total metal (mol aniline formed per g Pd per hour). [b] 1.0 g Pd/SiO<sub>2</sub> with Pd loading of 0.5 wt.%, 40 mL ethanol, 10 mL nitrobenzene. [c] Polymer (styrene divinyl benzene co-polymer) anchored 2.58×10<sup>-5</sup> mol Pd, 20 mL methanol, 9.72×10<sup>-3</sup> mol nitrobenzene. [d] Palladium complex of a random copolymer of 4-vinylpyridine with acrylic acid, Reaction conditions: 15 mL of ethanol, 0.1 mol/L of KOH. [e] 1.8×10<sup>-5</sup> mol PdCl<sub>2</sub> loaded on the microcapsule, 5 mL hexane, 1.5×10<sup>-3</sup> mol nitrobenzene.

### 2.2.2 A typical procedure for hydrogenation of various substrates in water.

All hydrogenation reactions were carried out under standard conditions (30 °C, 1 atm of H<sub>2</sub>). A round bottom flask (25 mL), charged with the supported Pd<sup>0</sup> catalyst (10 μmol), 3 mL H<sub>2</sub>O, and a magnetic stirrer, was connected to a gas burette (500 mL) with a flask to balance the pressure. The appropriate substrate (3.5×10<sup>-2</sup> mol) was added, and the flask was closed by a septum, then the mixture was stirred (1500 min<sup>-1</sup>). The reaction was monitored by the volume of gas consumed. At the end of the reaction, the two phases were separated by decantation and the solid phase was reused in a second run. The liquid phase mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10mL×4 times). The organic phase was collected and divided into two equal parts. One was used for the determination of the Pd content by ICP analysis and the other one was used for detection. ICP analysis indicated absence of any palladium within the detection limits (i.e., less than 0.1μg/mL) both organic liquid and the aqueous phase. The products were checked by HPLC.

All hydrogenation of the other aromatic nitro compounds could be carried out according to this process.

### 2.2.3 Recycle and reuse of SiO<sub>2</sub>-BisILs[PF<sub>6</sub>]-Pd<sup>0</sup>

The durability of the catalytic system was investigated by employing it in several successive hydrogenations. For this, nitrobenzene was again selected as a reference substrate. After a first cycle, the solid phase containing the catalysis was separated from the product by filtering, and followed by that either washing with the purpose of quantitative detection or not, then reused in a second run. In the same way, the catalytic suspension was recovered for a third, fourth and fifth hydrogenation cycle. After 15 times of repeated catalytic hydrogenation of nitrobenzene given in entry 14 in Table 1, no deactivation of the catalytic activity was observed (Figure S4).

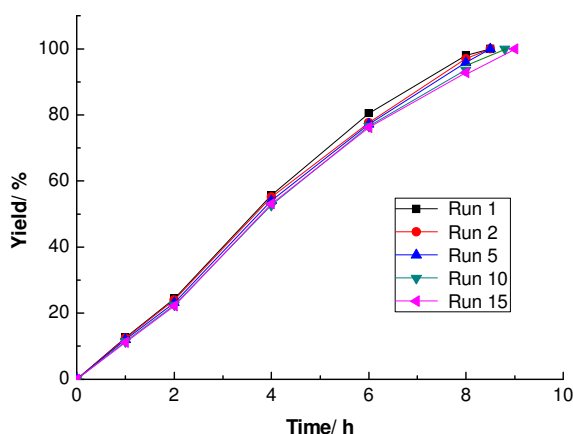
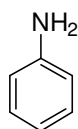


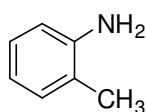
Figure S4. Kinetic data for SiO<sub>2</sub>-BisILs[PF<sub>6</sub>]-Pd<sup>0</sup> (2c) followed by 15 recycles

### 3. Experimental characterization data for products (Table x-y means Entry x, Table y, for example, Table 1-1 = Entry 1, Table 1)



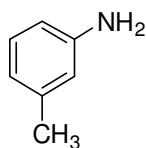
**Aniline:** The reaction of nitrobenzene (2.154 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) at 303 K in distilled water (5 mL) produced 1.6298 g (100%) of aniline.

Colorless oil, bp. 84 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.02-6.97(t, 2H), 6.57-6.48(m, 3H), 4.97(s, 2H), <sup>13</sup>C NMR (75.45 MHz, CDCl<sub>3</sub>) δ(ppm): 149.0, 129.3, 116.2, 114.4.



**2-Toluidine** (Table 3-1): 2-Nitrotoluene (2.400 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 1.8751 g (100%) of 2-toluidine.

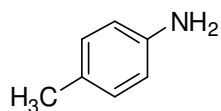
Light yellow oil, bp. 199-200 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 6.99 (d, J = 6.0Hz, 2H), 6.69-6.56 (m, 2H), 3.45 (s, 2H), 2.08(s, 3H), <sup>13</sup>C NMR (75.45 MHz, CDCl<sub>3</sub>) δ(ppm): 144.9, 130.6, 127.1, 122.5, 118.7, 115.1, 17.5.



**3-Toluidine** (Table 3-2): 3-Nitrotoluene (2.400 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 1.8751 g (100%) of 3-toluidine.

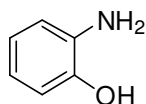
Colorless oil, bp. 203-204 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.06-7.01 (t, 1H), 6.59-6.48 (m, 3H), 3.51 (s, 2H), 2.26(s, 3H), <sup>13</sup>C NMR (75.45 MHz, CDCl<sub>3</sub>) δ(ppm): 146.3, 139.1, 129.2, 119.5, 116.0, 112.3, 21.4.





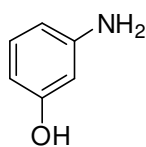
**4-Toluidine** (Table 3-3): 4-Nitrotoluene (2.400 g, 17.5 mmol) and the brush (0.053g, 5  $\mu$ mol) under constant hydrogen pressure (1 atm) produced 1.8751 g (100%) of 4-toluidine.

Colorless plate-like crystal, bp. 200-202 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 6.96-6.94 (d,  $J = 7.8\text{Hz}$ , 2H), 6.59-6.57 (d,  $J = 8.1\text{Hz}$ , 2H), 3.46 (s, 2H), 2.23(s, 3H),  $^{13}\text{C}$  NMR (75.45 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm) 143.9, 129.8 (2), 127.8, 115.3(2), 20.5.



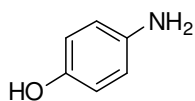
**2-Aminophenol** (Table 3-4): 2-Nitrophenol (2.434 g, 17.5 mmol) and the brush (0.053g, 5  $\mu$ mol) under constant hydrogen pressure (1 atm) produced 1.9098 g (100%) of 2-aminophenol.

Off-white crystal power, mp. 172-177 °C (EtOH).  $^1\text{H}$  NMR (300 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 8.92 (s, 1H), 6.64-6.36 (m, 4H), 4.45 (s, 2H),  $^{13}\text{C}$  NMR (75.45 MHz,  $d_6$ -DMSO)  $\delta$ (ppm): 144.5, 137.0, 120.0, 117.0, 115.0, 114.9.



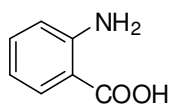
**3-Aminophenol** (Table 3-5): 3-Nitrophenol (2.434 g, 17.5 mmol) and the brush (0.053g, 5  $\mu$ mol) under constant hydrogen pressure (1 atm) produced 1.9098 g (100%) of 3-aminophenol.

White crystal, mp: 120-121 °C (EtOH).  $^1\text{H}$  NMR (300 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 8.87 (s, 1H), 6.82-6.77 (m, 1H), 6.03 (d,  $J = 7.20\text{Hz}$ , 2H), 5.98 (d,  $J = 7.8\text{Hz}$ , 1H), 4.84 (s, 2H),  $^{13}\text{C}$  NMR (75.45 MHz,  $d_6$ -DMSO)  $\delta$ (ppm): 158.5, 150.2, 130.0, 106.0, 104.0, 101.5.



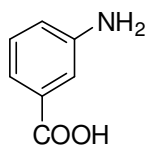
**4-Aminophenol** (Table 3-6): 4-Nitrophenol (2.434 g, 17.5 mmol) and the brush (0.053g, 5  $\mu$ mol) under constant hydrogen pressure (1 atm) produced 1.9098 g (100%) of 4-aminophenol.

White plate-like crystal, bp. 186-189 °C.  $^1\text{H}$  NMR (300 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 8.36 (s, 1H), 6.47 (s, 2H), 6.43(s, 2H), 4.42 (s, 2H),  $^{13}\text{C}$  NMR (75.45 MHz,  $d_6$ -DMSO)  $\delta$ (ppm): 148.8, 141.0, 116.0(2), 115.8(2).



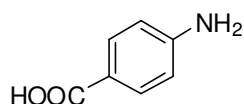
**2-Aminobenzoic acid** (Table 3-7): 2-Nitrobenzoic acid (2.925 g, 17.5 mmol) and the brush (0.053g, 5  $\mu$ mol) under constant hydrogen pressure (1 atm) produced 2.4000 g (100%) of 2-aminobenzoic acid.

White crystal power, mp. 145-147 °C (EtOH).  $^1\text{H}$  NMR (300 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 11.96 (s, 1H), 7.68-7.66 (m, 2H), 6.61-6.58(m, 1H), 6.33 (d,  $J = 7.80\text{Hz}$ , 1H), 5.85 (s, 2H),  $^{13}\text{C}$  NMR (75.45 MHz,  $d_6$ -DMSO)  $\delta$ (ppm): 168.3, 149.3, 131.8, 129.3, 118.5, 117.2, 115.0.



**3-Aminobenzoic acid** (Table 3-8): 3-Nitrobenzoic acid (2.925 g, 17.5 mmol) and the brush (0.053g, 5  $\mu$ mol) under constant hydrogen pressure (1 atm) produced 2.4000 g (100%) of 3-aminobenzoic acid.

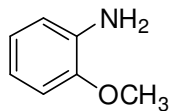
White crystal, mp. 174 °C.  $^1\text{H}$  NMR (300 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 12.52 (s, 1H), 7.09-7.17 (m, 3H), 6.76(s, 1H), 5.33(s, 2H),  $^{13}\text{C}$  NMR (75.45 MHz,  $d_6$ -DMSO)  $\delta$ (ppm): 167.9, 148.8, 131.3, 128.9, 118.0, 116.6, 114.4.



**4-Aminobenzoic acid** (Table 3-9): 2-Nitrobenzoic acid (2.925 g, 17.5 mmol) and the brush (0.053g, 5  $\mu$ mol) under constant hydrogen pressure (1

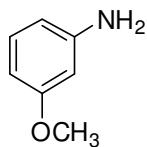
atm) produced 2.4000 g (100%) of 4-aminobenzoic acid.

White crystal, mp. 186-189 °C (EtOH). <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 11.96 (s, 1H), 7.68-7.65 (d, 2H), 6.61-6.58(d, 2H), 5.85 (s, 2H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm):168.0, 153.6, 131.7, 117.5, 113.1.



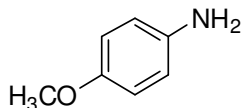
**2-Methoxyaniline** (Table 3-10): 2-Nitroanisole (2.680 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 2.1551 g (100%) of 2-methoxyaniline.

Light yellow oil, bp. 224-225 °C. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 6.78-6.75 (d, 1H), 6.69-6.61(m, 2H), 6.53-6.50(t, 1H), 4.64(s, 2H), 3.74(s, 3H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm): 146.4, 137.6, 120.8, 116.2, 113.8, 110.6, 55.2.



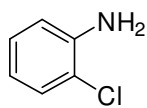
**3-Methoxyaniline** (Table 3-11): 3-Nitroanisole (2.680 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 2.1551 g (100%) of 3-methoxyaniline.

Light yellow oil, bp. 251 °C. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 6.93-6.87(t, 3H), 6.18-6.15(d, 2H), 6.10-6.07(d, 1H), 5.01(s, 2H), 3.64(s, 1H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm): 160.3, 149.9, 129.5, 106.9, 101.5, 99.5, 54.5.



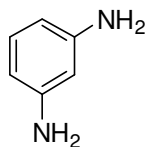
**4-Methoxyaniline** (Table 3-12): 4-Nitroanisole (2.680 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 2.1551 g (100%) of 4-methoxyaniline.

White solid, mp. 57 °C. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 6.65-6.63(d, 2H), 6.53-6.50(d, 2H), 4.57(s, 2H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm): 3.61(s, 3H), 150.7, 142.3, 115.0, 114.5, 55.3.



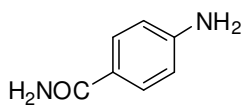
**2-Chloroaniline** (Table 3-13): 2-Chloronitrobenzene (2.757 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 1.6677 g (74.7 %) of 2-chloroaniline.

Amber liquid, bp. 208-211 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.22-7.20 (d, J = 7.8Hz, 1H), 7.05-7.00 (m, 1H), 6.70-6.65 (m, 2H), 3.95 (s, 2H), <sup>13</sup>C NMR (75.45 MHz, CDCl<sub>3</sub>) δ(ppm): 143.1, 129.5, 127.7, 119.3, 119.1, 116.0.



**1,3-Diaminobenzene** (Table 3-14): 1, 3-Dinitrobenzene (2.942 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 1.8925 g (100%) of 1,3-diaminobenzene.

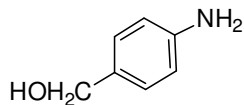
Colorless acicular crystal, mp. 63-65°C (EtOH). <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 6.70-6.68 (m, 1H), 5.80-5.83 (d, J = 7.8Hz, 3H), 4.58(s, 4H); <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm): 149.5, 129.7, 103.7, 100.6.



**4-Aminobenzamide** (Table 3-15): 4-Nitrobenzamide (2.908 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 2.3826 g (100%) of 4-aminobenzamide.

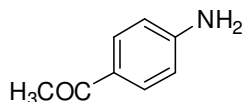
White power, mp. 180-182 °C. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 7.61-7.58(d, 2H),

7.53(s, 1H), 6.85(s, 1H), 6.54-6.51(d, 2H), 5.60(s, 2H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm):167.6, 151.2, 128.6, 120.5, 112.0.



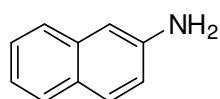
**4-Aminophenyl alcohol** (Table 3-16): 4-Nitrobenzyl alcohol(2.680 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 2.1551 g (100%) of 4-Aminophenyl alcohol.

Yellow solid, mp. 60-63 °C. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 6.97-6.95(d, 2H), 6.52-6.50(d, 2H), 4.91(s, 1H), 4.82-4.79(t, 1H), 4.30-4.28(d, 2H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm): 147.4, 129.7, 127.9, 113.6, 63.1.



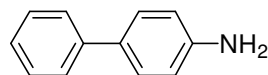
**4'-Aminoacetophenone** (Table 3-17): 4'-Nitroacetophenone (2.890 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 2.3655 g (100%) of 4'-aminoacetophenone.

Yellow acicular crystal, mp. 106 °C. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 7.65-7.63(d, 2H), 6.56-6.52(d, 2H), 6.01(s, 2H), 2.37(s, 3H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm): 194.9, 153.6, 130.5, 124.9, 112.5, 25.8.



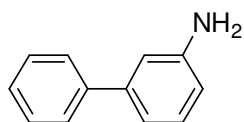
**2-Naphthylamine** (Table 3-18): 2-Nitronaphthalene (3.030 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 2.5058 g (100%) of 2-naphthylamine.

White plate-like crystal, bp. 111-113 °C. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 8.07-8.05(d, 1H), 7.73-7.71(d, 1H), 7.42-7.35(m, 2H), 7.22-7.17(t, 1H), 7.08-7.05(d, 2H), 6.69-6.67(d, 2H), 5.69(s, 2H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm): 145.1, 134.7, 128.3, 127.2, 126.0, 124.1, 123.2, 122.8, 115.8, 107.9.



**4-Aminobiphenyl** (Table 3-19): 4-Nitrobiphenyl (3.486 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 2.9614 g (100%) of 4-aminobiphenyl.

Chocolate brown power, bp. 52-54 °C. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 7.54-7.52(d, 2H), 7.39-7.34(t, 4H), 7.23-7.18(t, 1H), 6.67-6.64(d, 2H), 5.22(s, 2H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm): 148.8, 141.1, 129.2, 128.0, 127.6, 126.1, 125.8, 114.8.



**3-Aminobiphenyl** (Table 3-20): 4-Nitrobiphenyl (3.486 g, 17.5 mmol) and the brush (0.053g, 5 μmol) under constant hydrogen pressure (1 atm) produced 2.9614 g (100%) of 3-aminobiphenyl.

Acicular crystal, bp. 30-32 °C. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ (ppm): 7.56-7.54(d, 2H), 7.45-7.40(m, 2H), 7.36-7.30(m, 1H), 7.13-7.08(t, 1H), 6.86(s, 1H), 6.79-6.77(d, 2H), 6.59-6.57(d, 2H), 5.16(s, 2H), <sup>13</sup>C NMR (75.45 MHz, *d*<sub>6</sub>-DMSO) δ(ppm): 148.6, 140.6, 140.5, 128.9, 128.3, 126.6, 126.0, 113.9, 112.7, 111.7.

#### 4. Copies of the IR, $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of the catalysts.

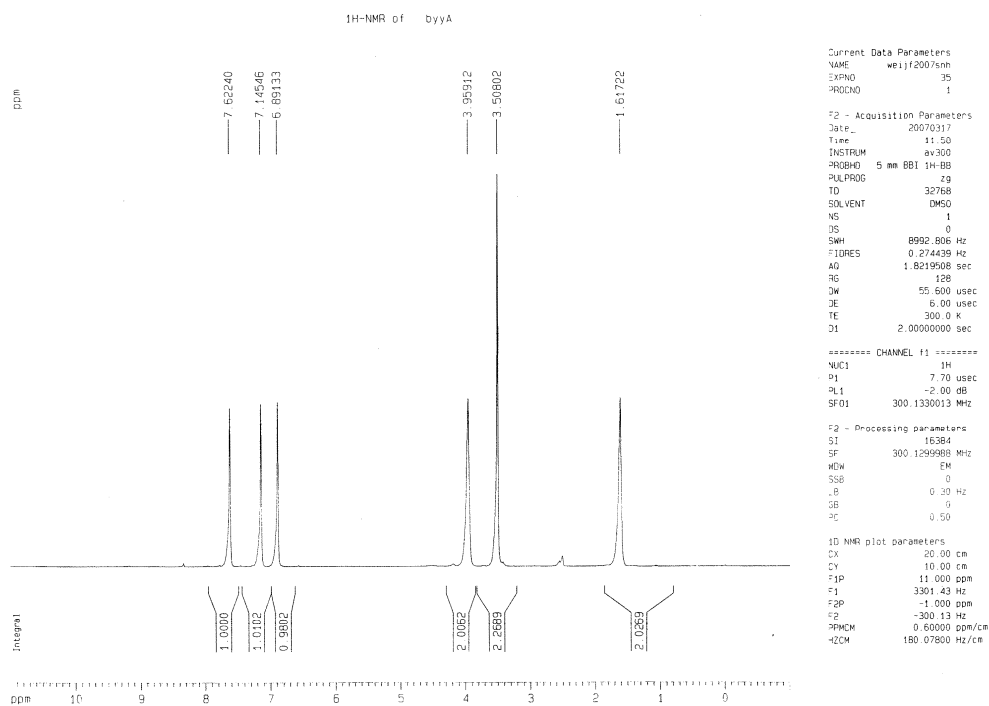


Figure S5  $^1\text{H}$  NMR spectra of 1,4-Bis(imidazole-1-yl)butane

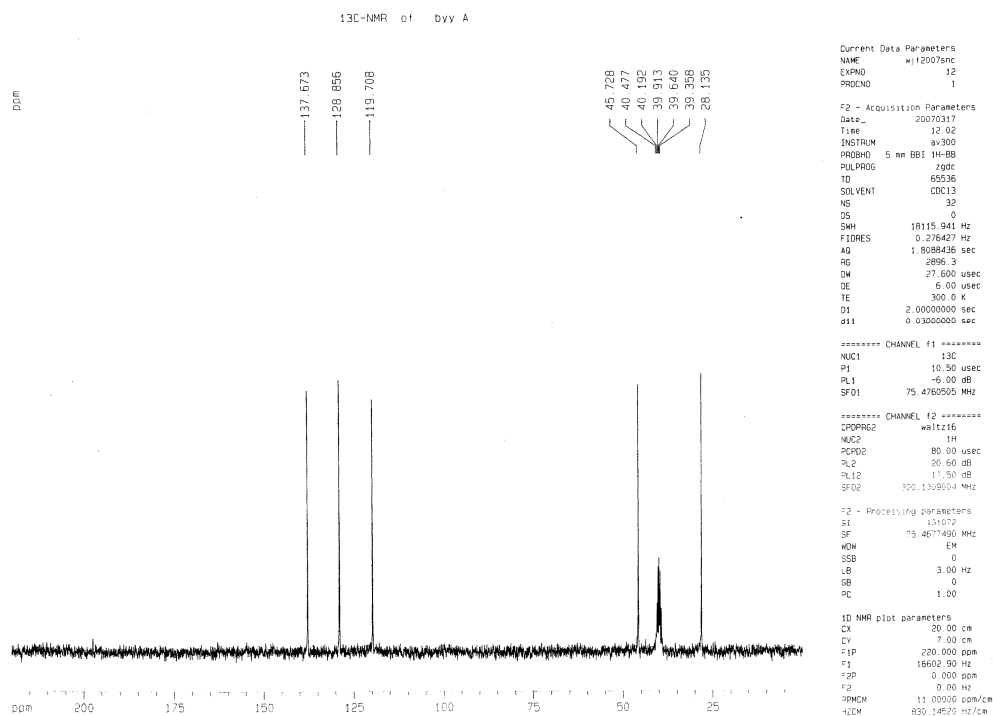


Figure S6  $^{13}\text{C}$  NMR spectra of 1,4-Bis(imidazole-1-yl)butane

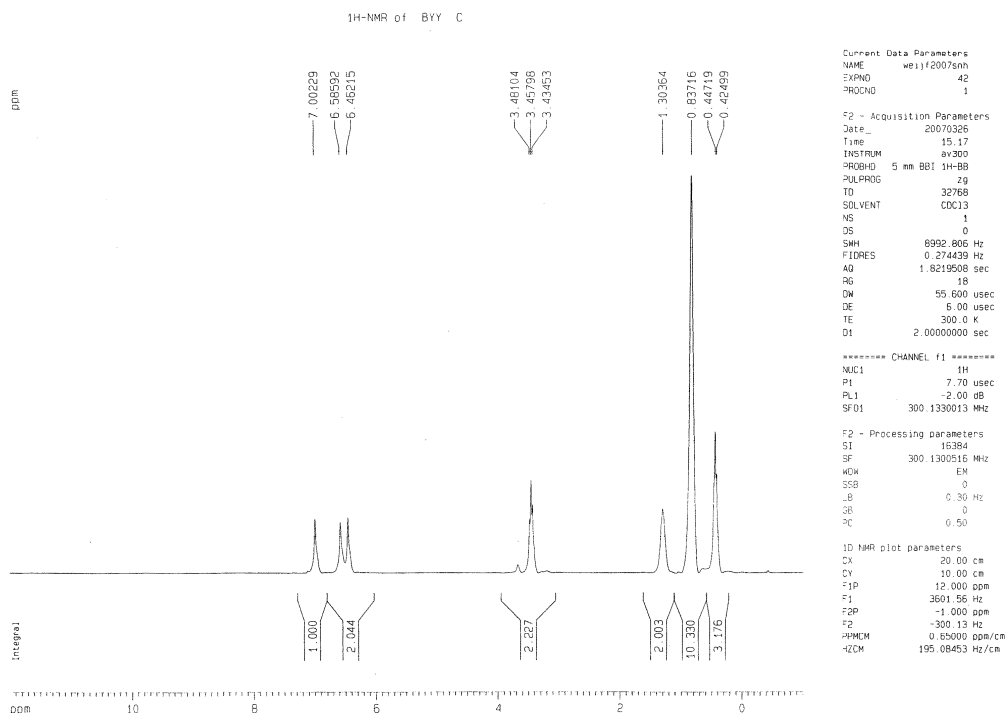


Figure S7  $^1\text{H}$  NMR spectra of 1-octylimidazolium

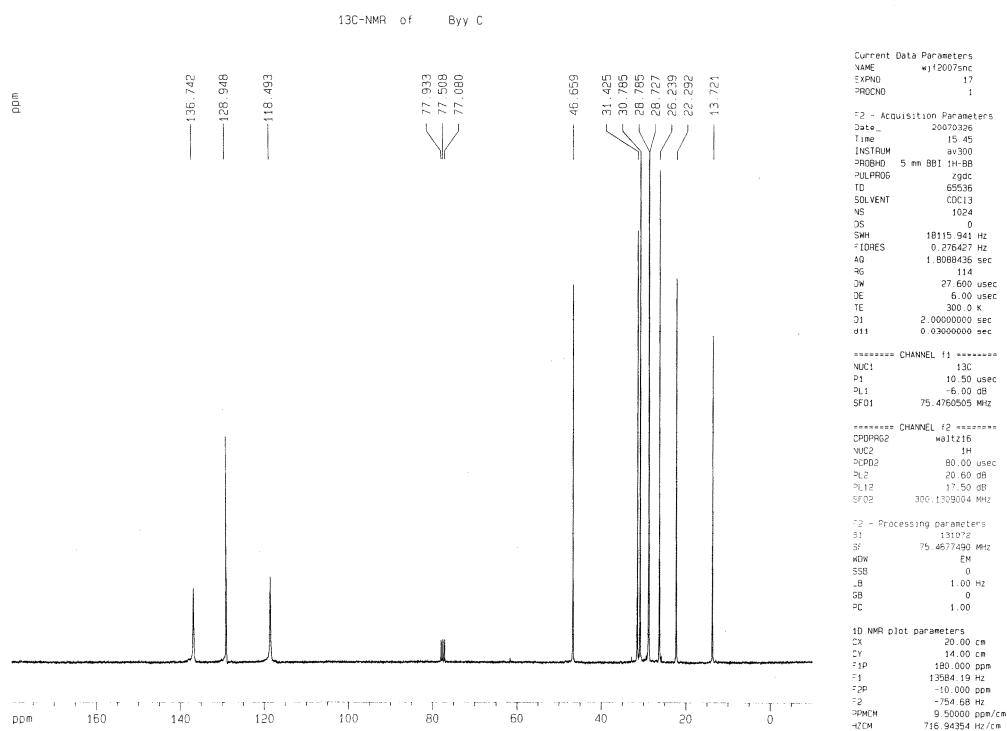


Figure S8  $^{13}\text{C}$  NMR spectra of 1-octylimidazolium

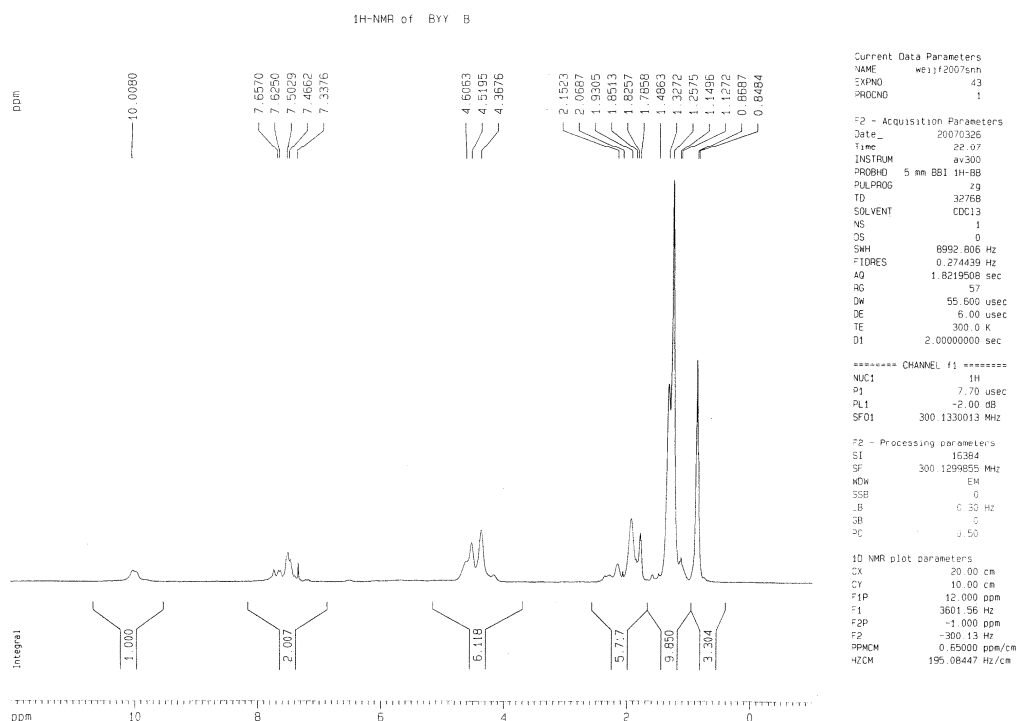


Figure S9  $^1\text{H}$  NMR spectra of 1-(4-Bromododecyl)-3-butylimidazolium bromide

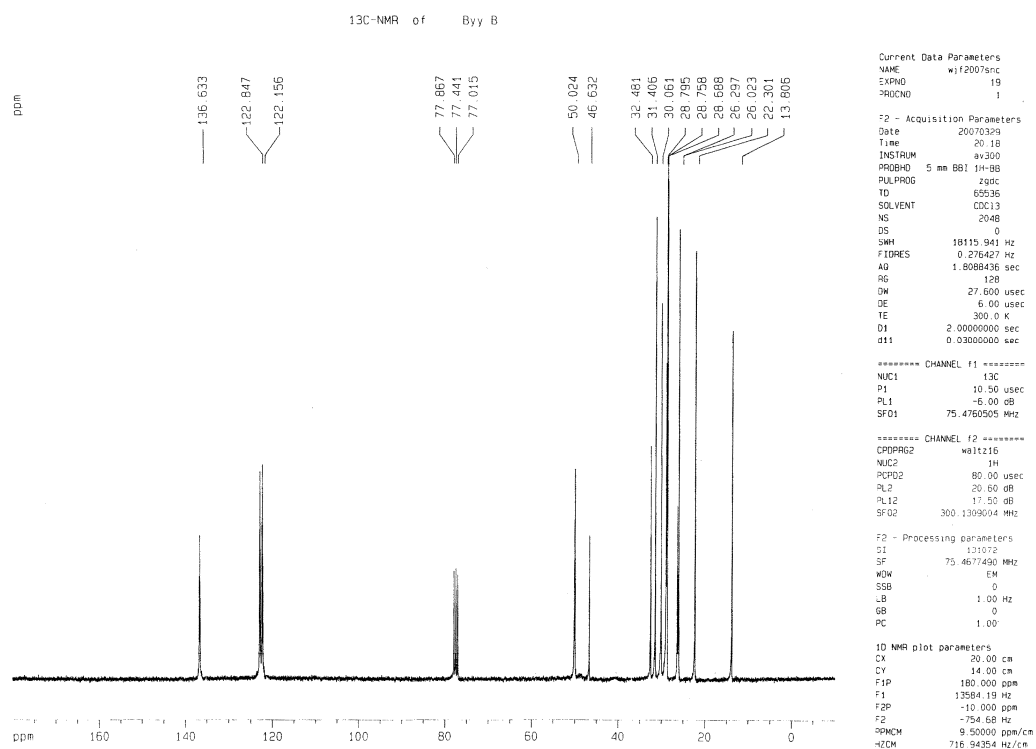


Figure S10  $^{13}\text{C}$  NMR spectra of 1-(4-Bromododecyl)-3-butyliimidazolium bromide

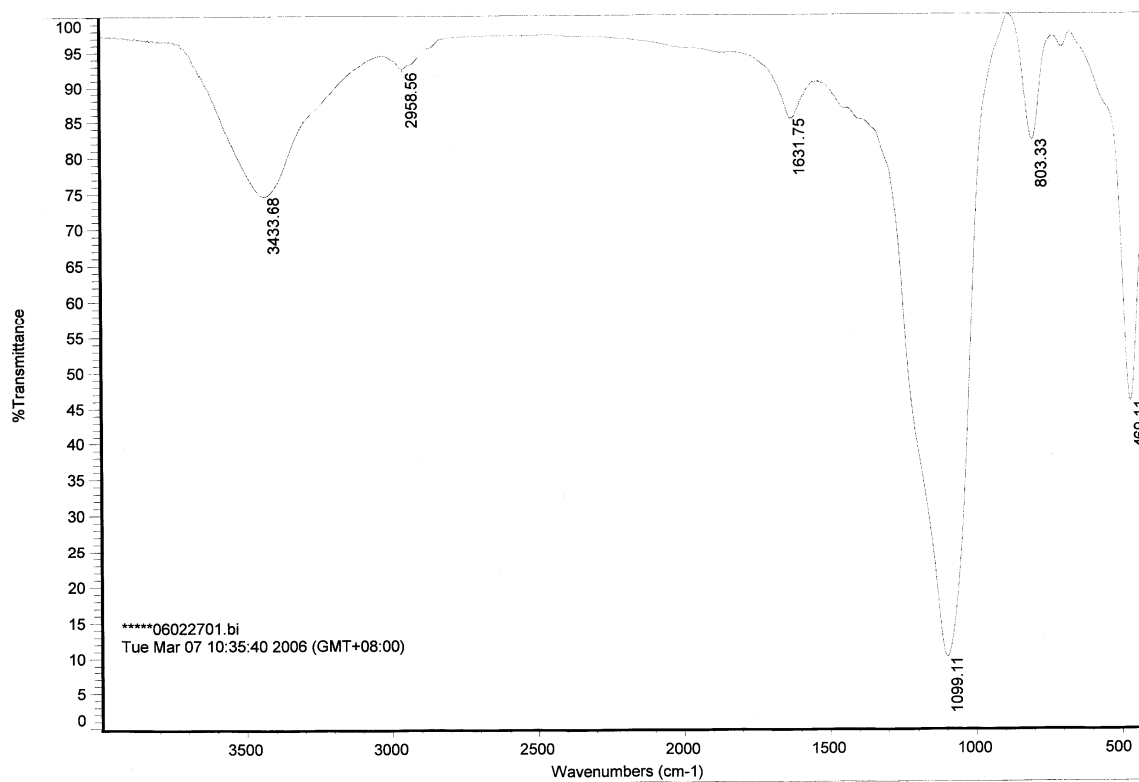
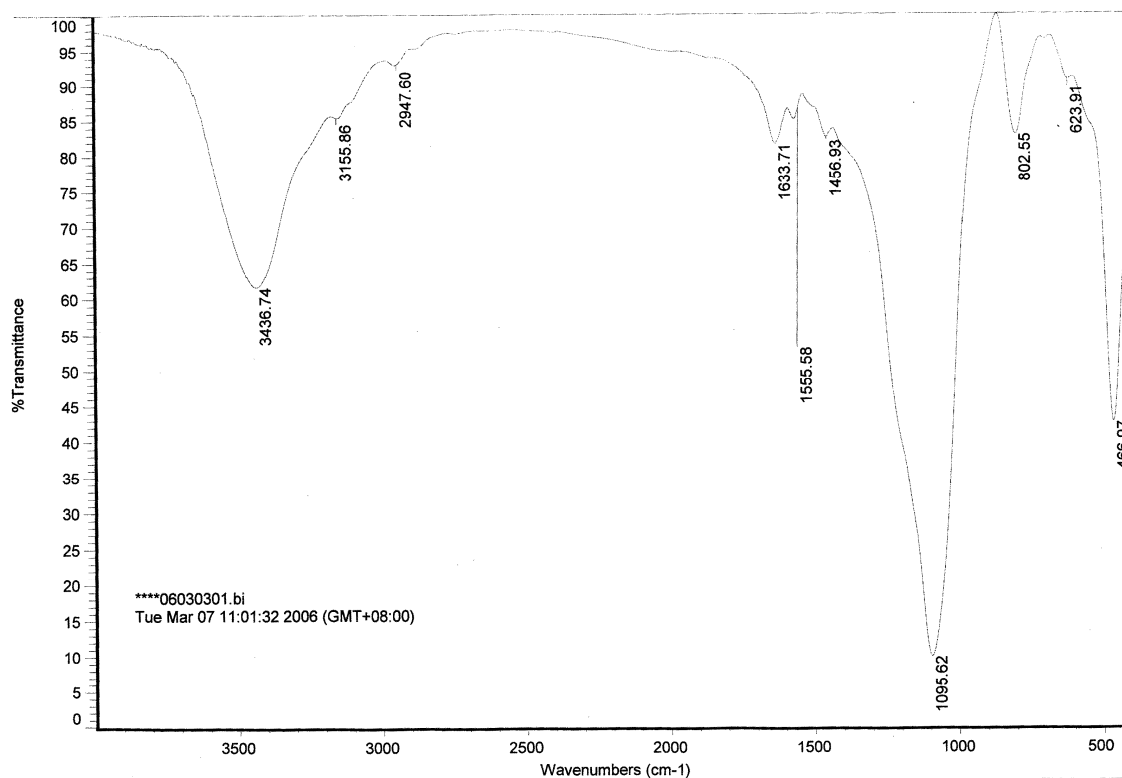
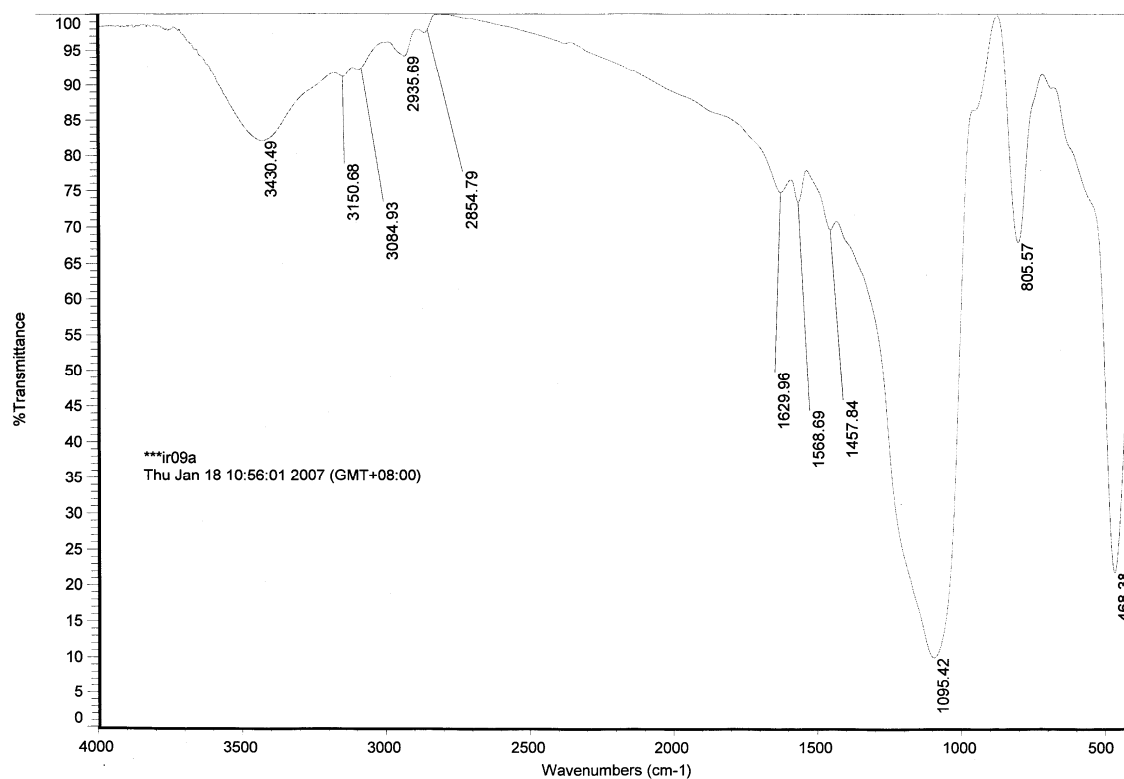


Figure S11 IR spectra of silica 1



**Figure S12** IR spectra of Silica 1 with 1,4-bis(imidazole-1-yl)butane



**Figure S13** IR spectra of Silica 2



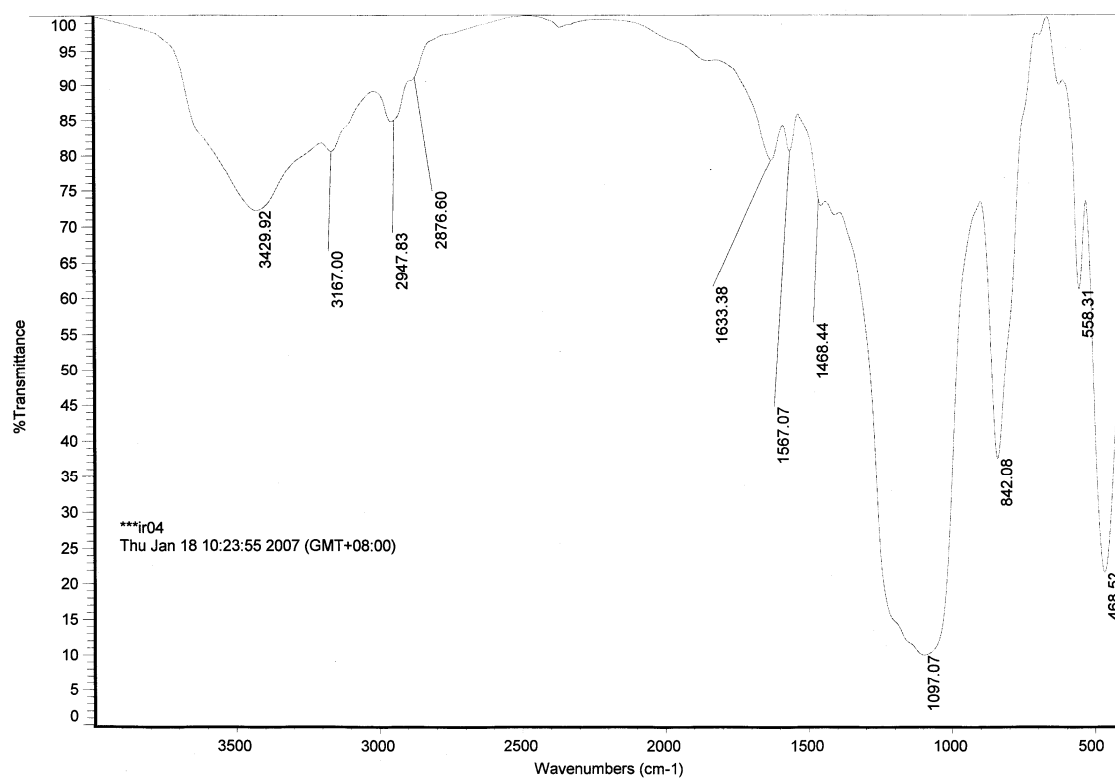
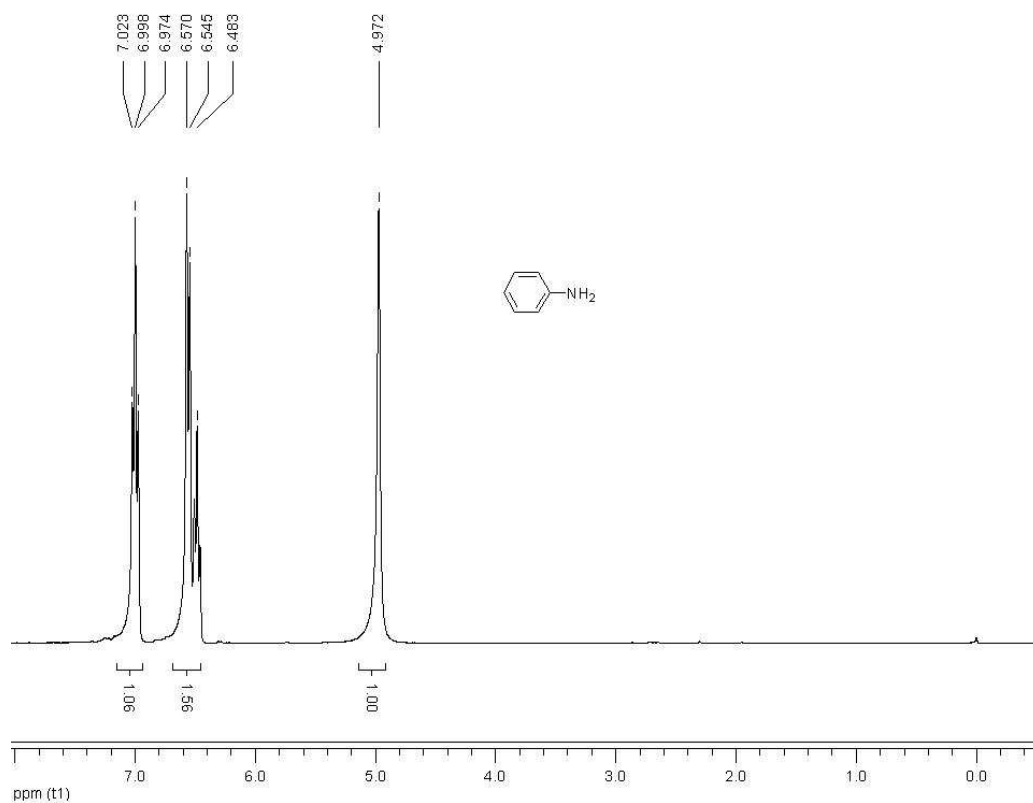
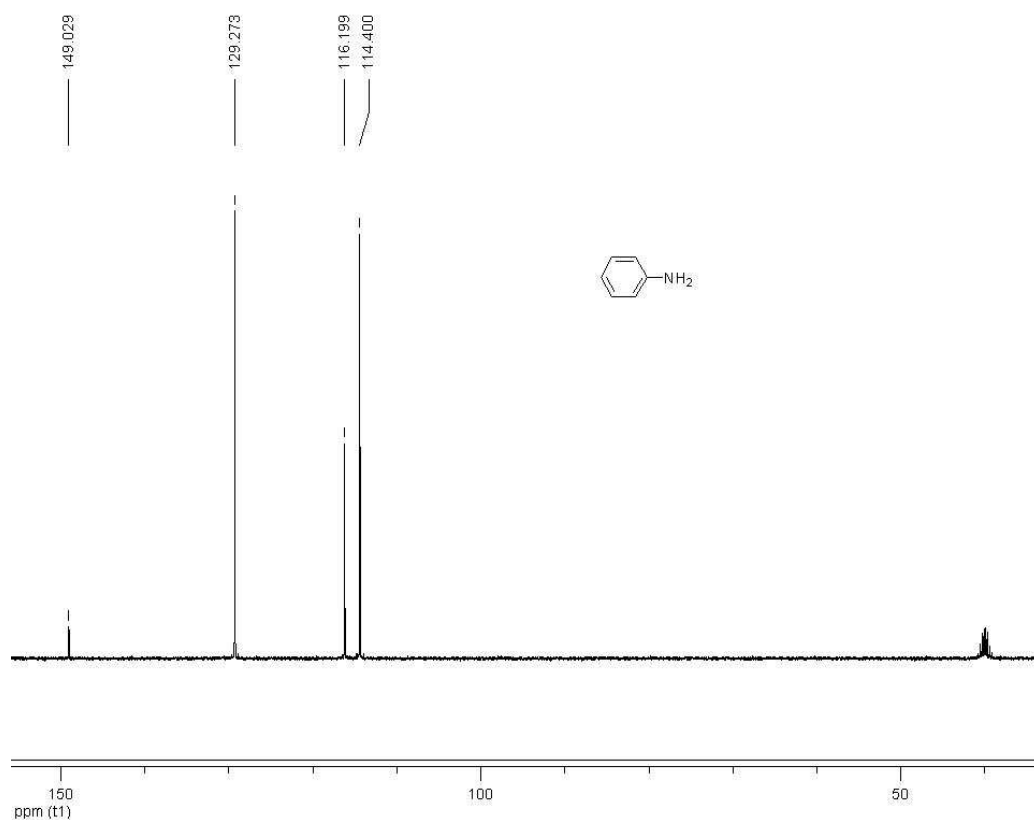


Figure S14 IR spectra of SiO<sub>2</sub>-BisILs[PF<sub>6</sub>]-Pd<sup>0</sup> (2c)

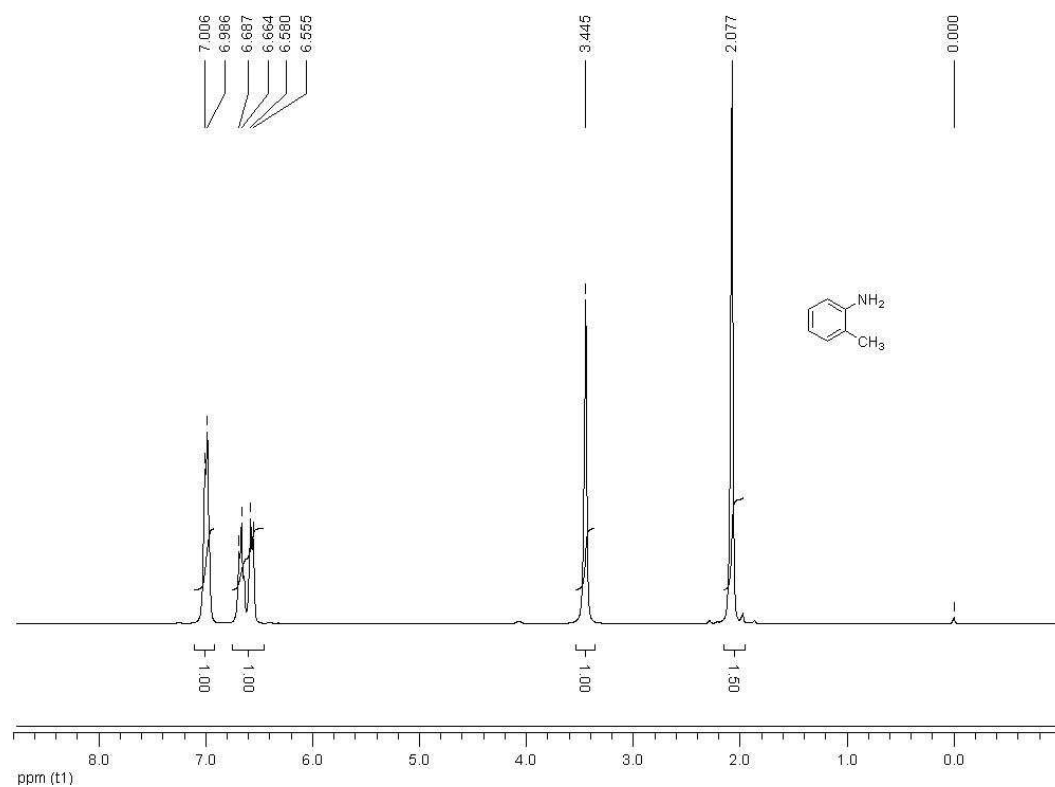
## 5. Copies of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products.



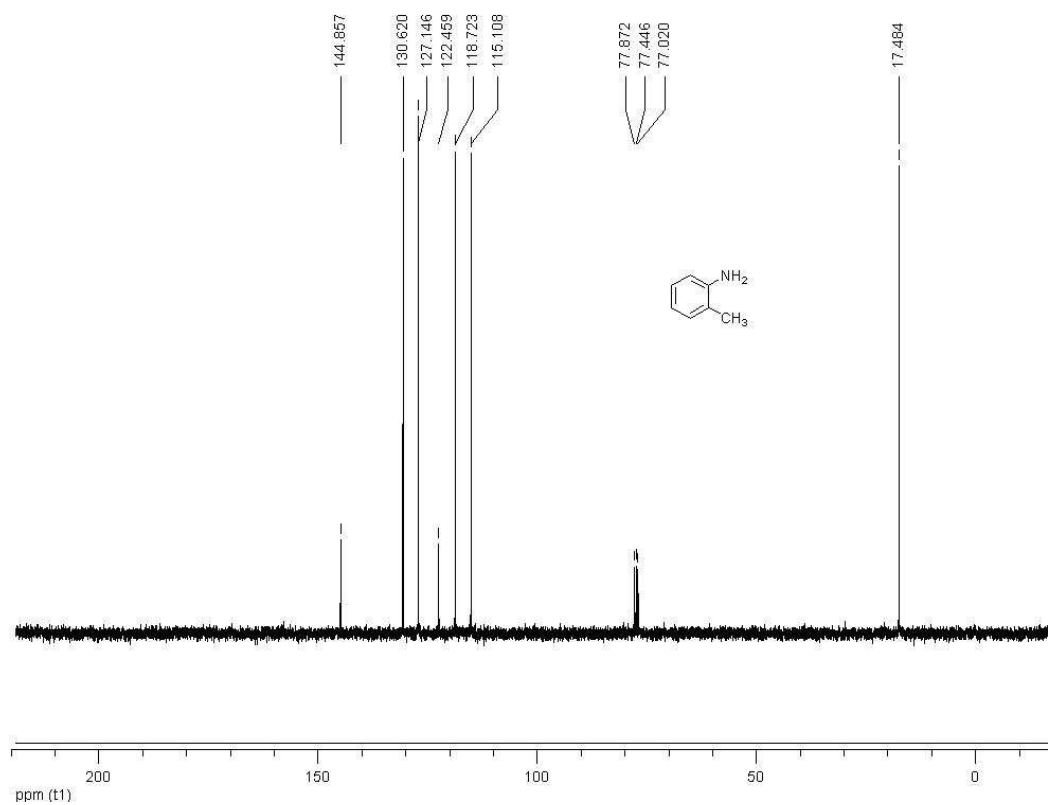
**Figure S15**  $^1\text{H}$  NMR spectra of Aniline



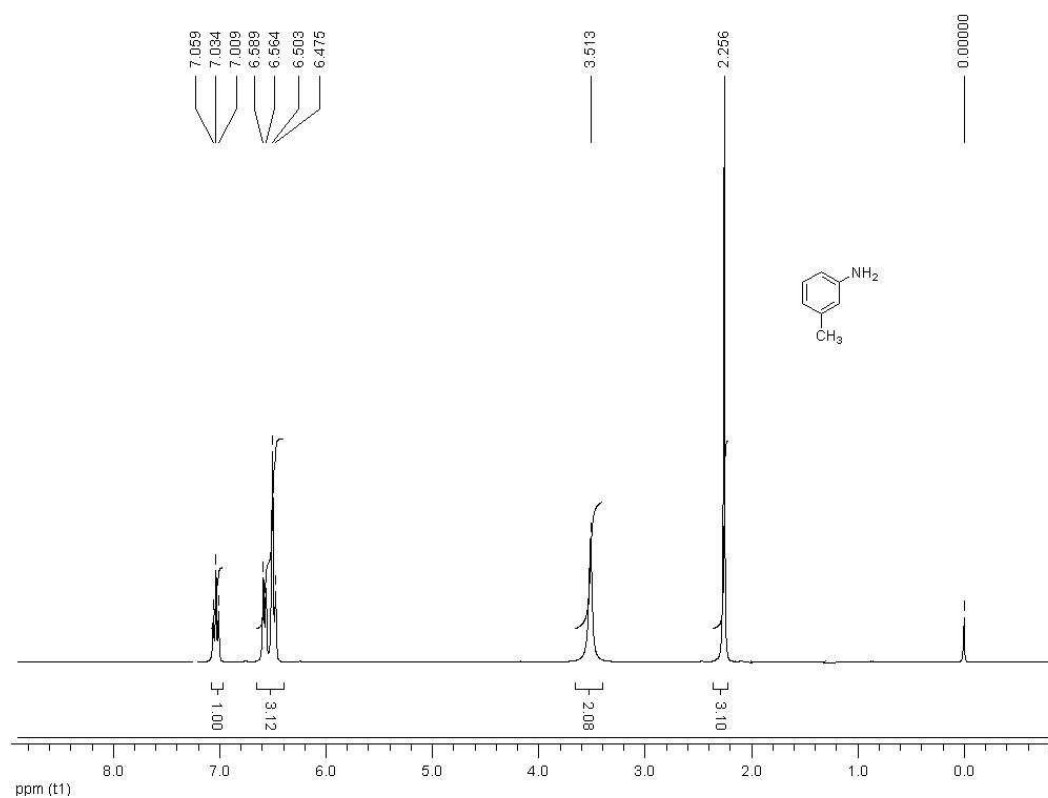
**Figure S16**  $^{13}\text{C}$  NMR spectra of Aniline



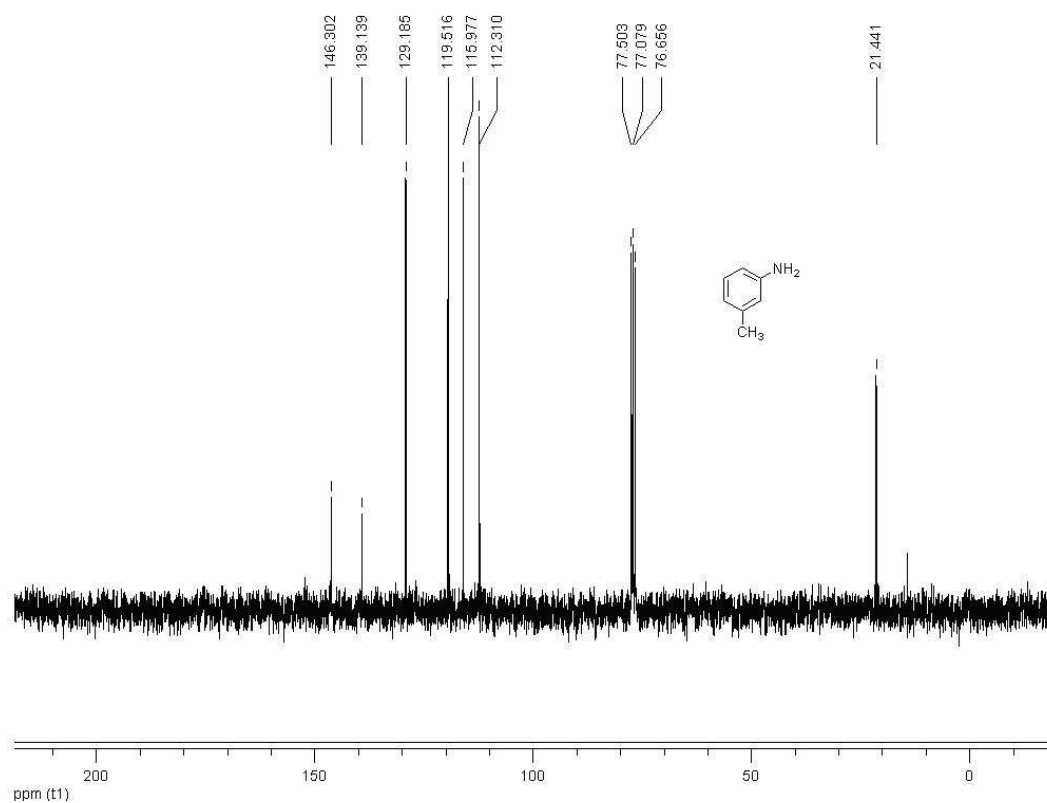
**Figure S17**  $^1\text{H}$  NMR spectra of 2-Toluidine (Table 3-1)



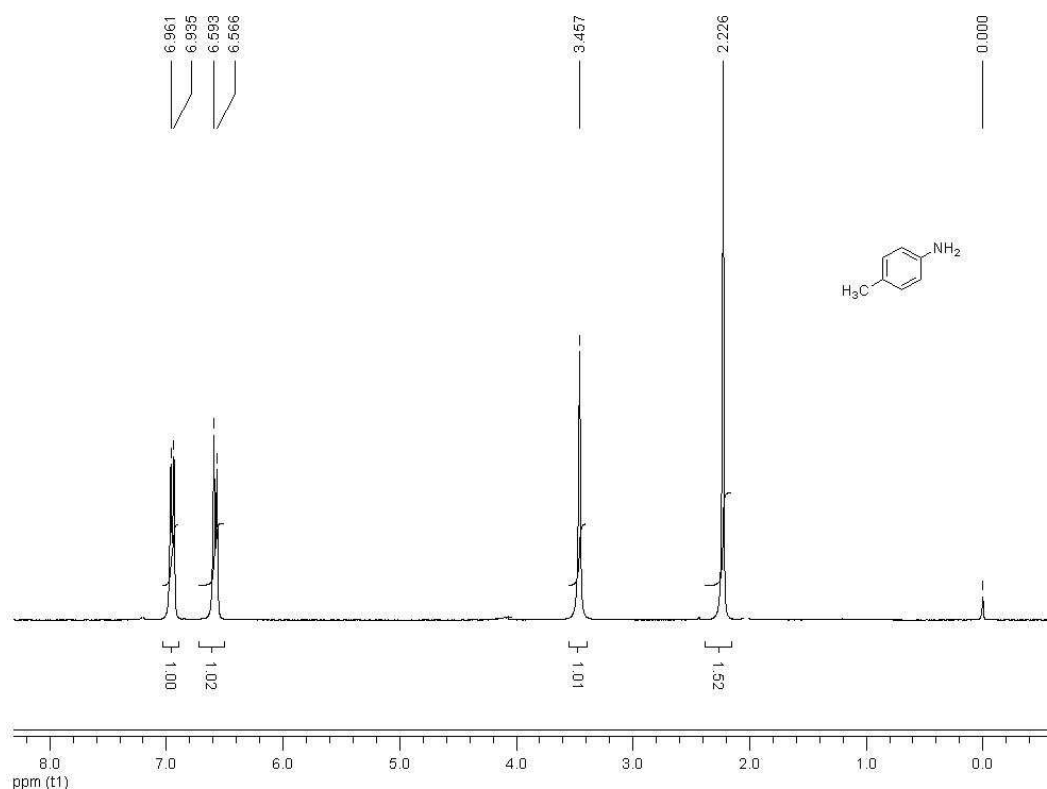
**Figure S18**  $^{13}\text{C}$  NMR spectra of 2-Toluidine (Table 3-1)



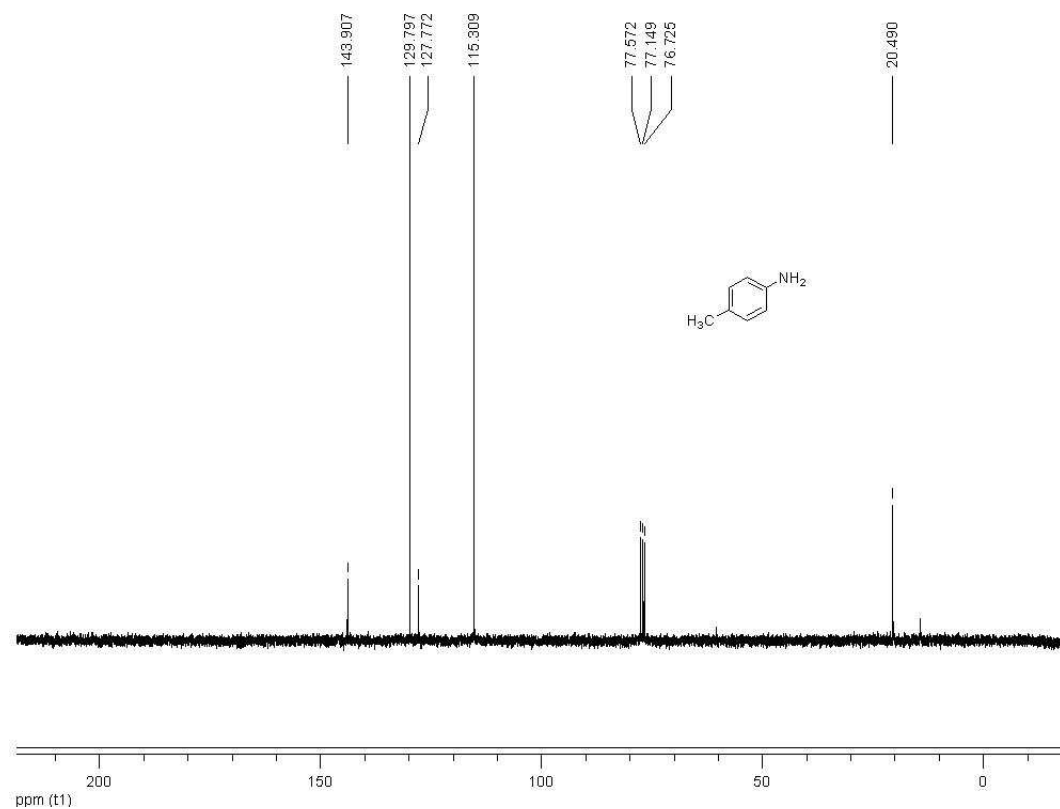
**Figure S19**  $^1\text{H}$  NMR spectra of 3-Toluidine (Table 3-2)



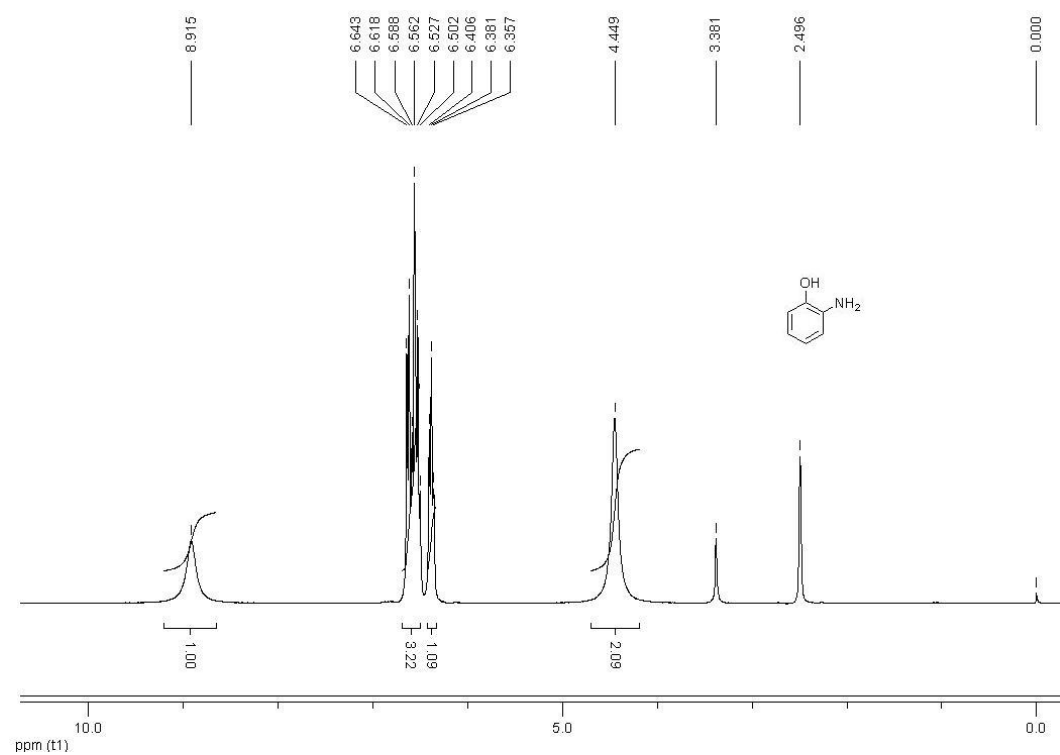
**Figure S20**  $^{13}\text{C}$  NMR spectra of 3-Toluidine (Table 3-2)



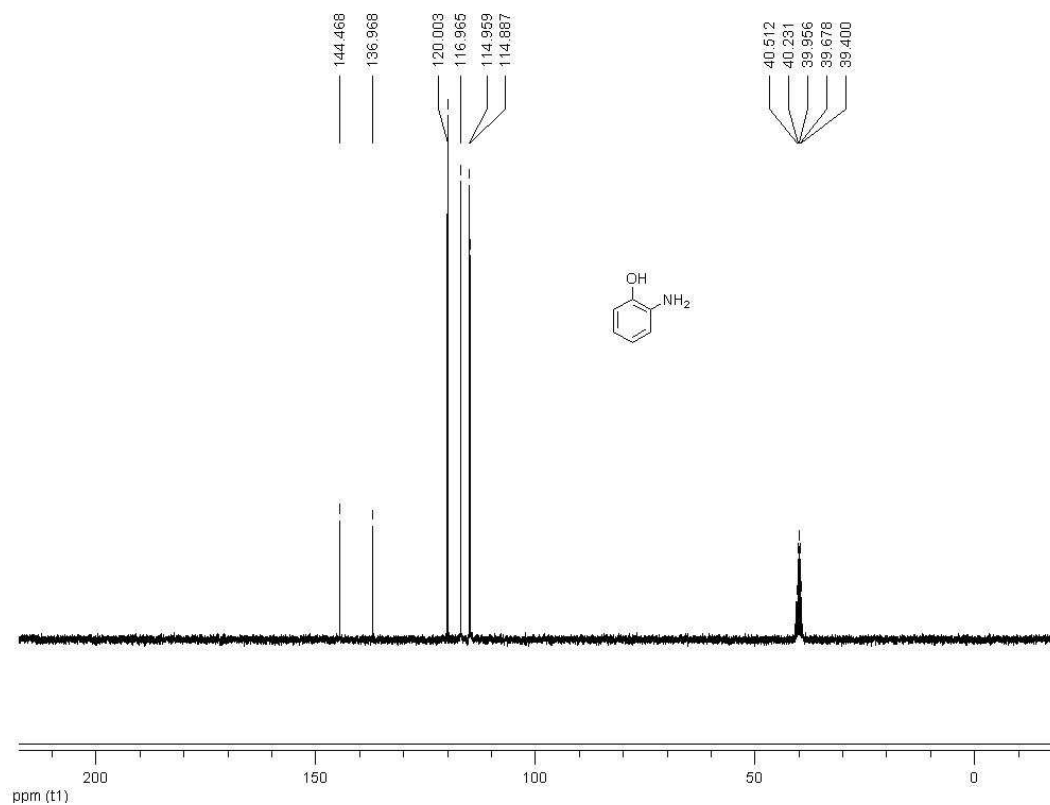
**Figure S21**  $^1\text{H}$  NMR spectra of 4-Toluidine (Table 3-3)



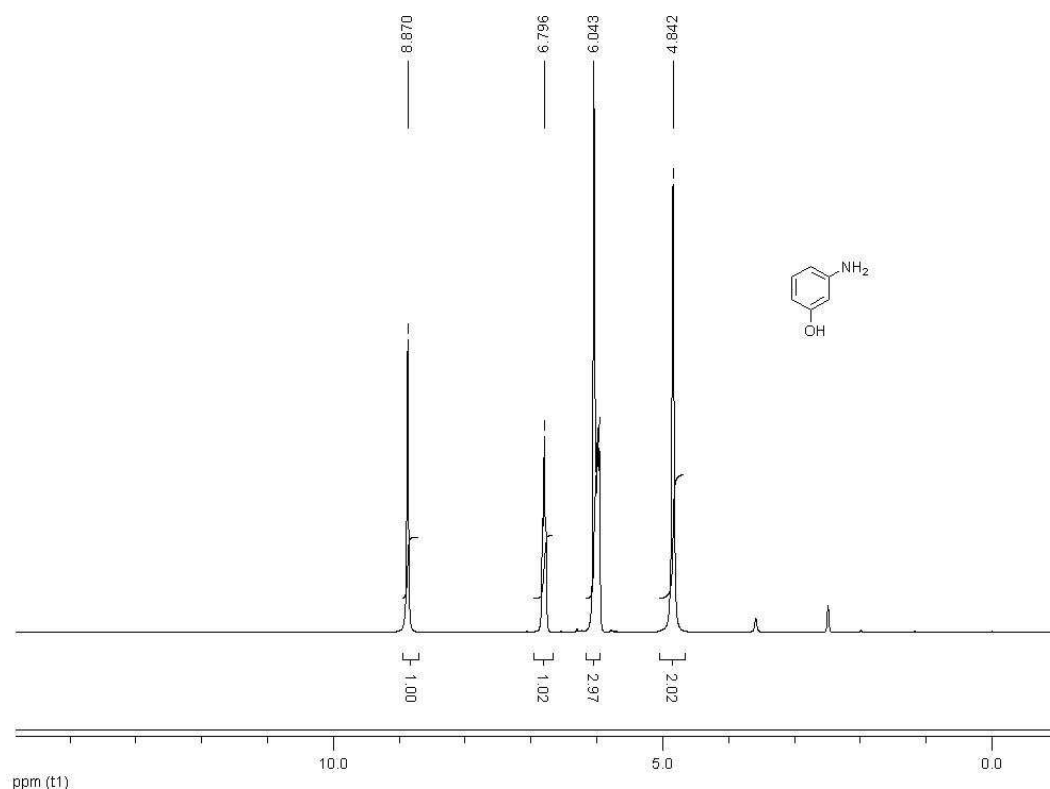
**Figure S22**  $^{13}\text{C}$  NMR spectra of 4-Toluidine (Table 3-3)



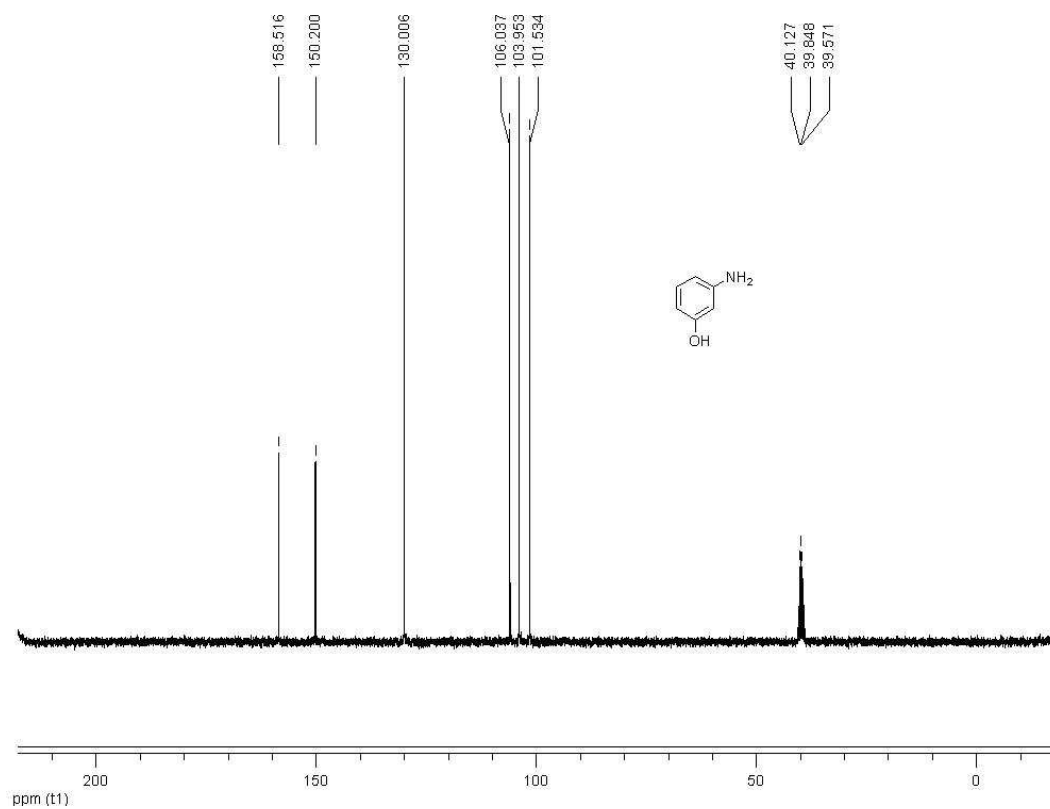
**Figure S23**  $^1\text{H}$  NMR spectra of 2-Aminophenol (Table 3-4)



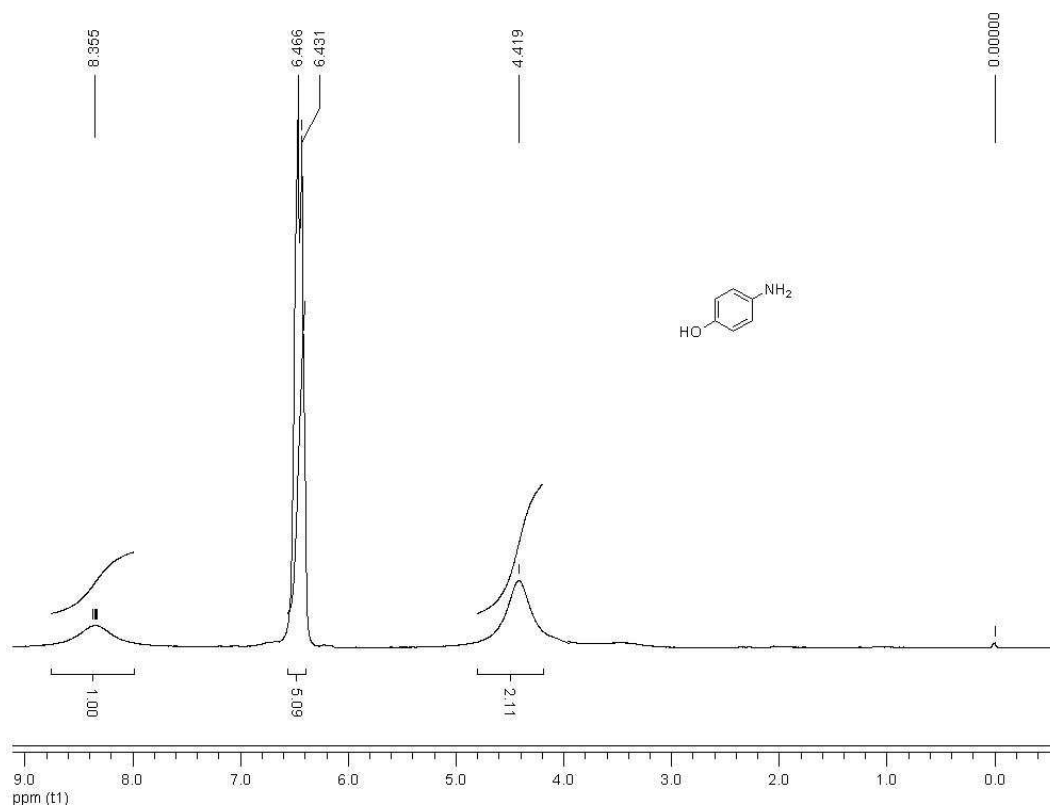
**Figure S24** <sup>13</sup>C NMR spectra of 2-Aminophenol (Table 3-4)



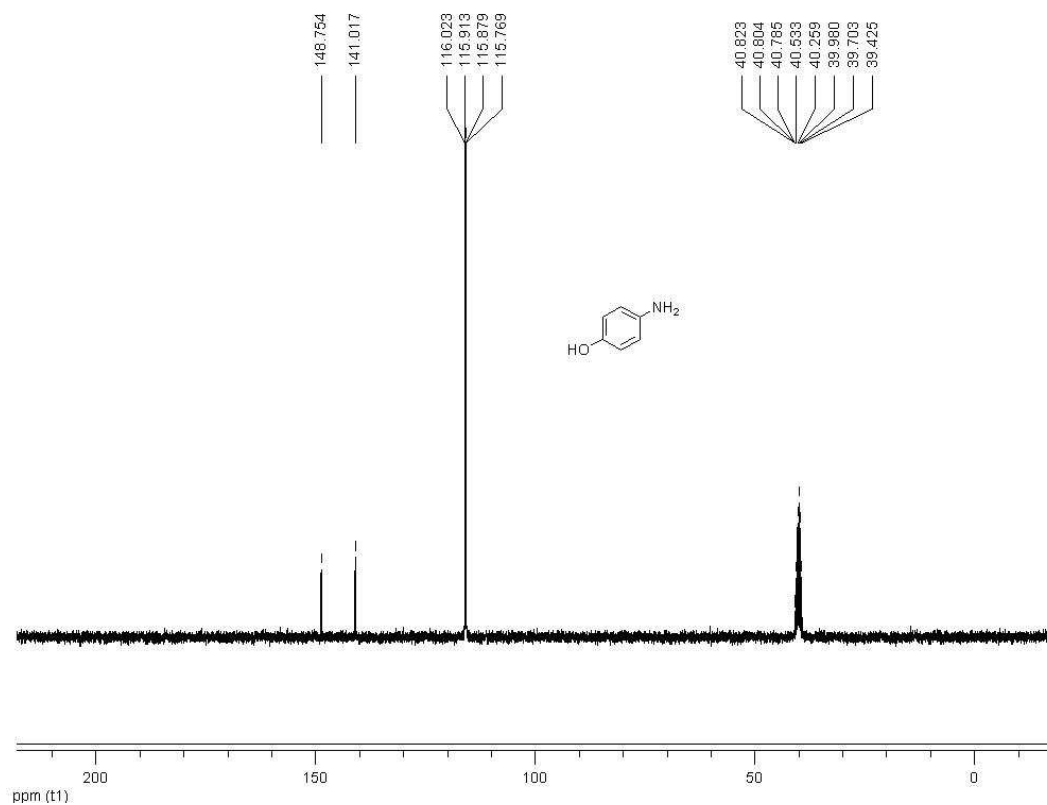
**Figure S25** <sup>1</sup>H NMR spectra of 3-Aminophenol (Table 3-5)



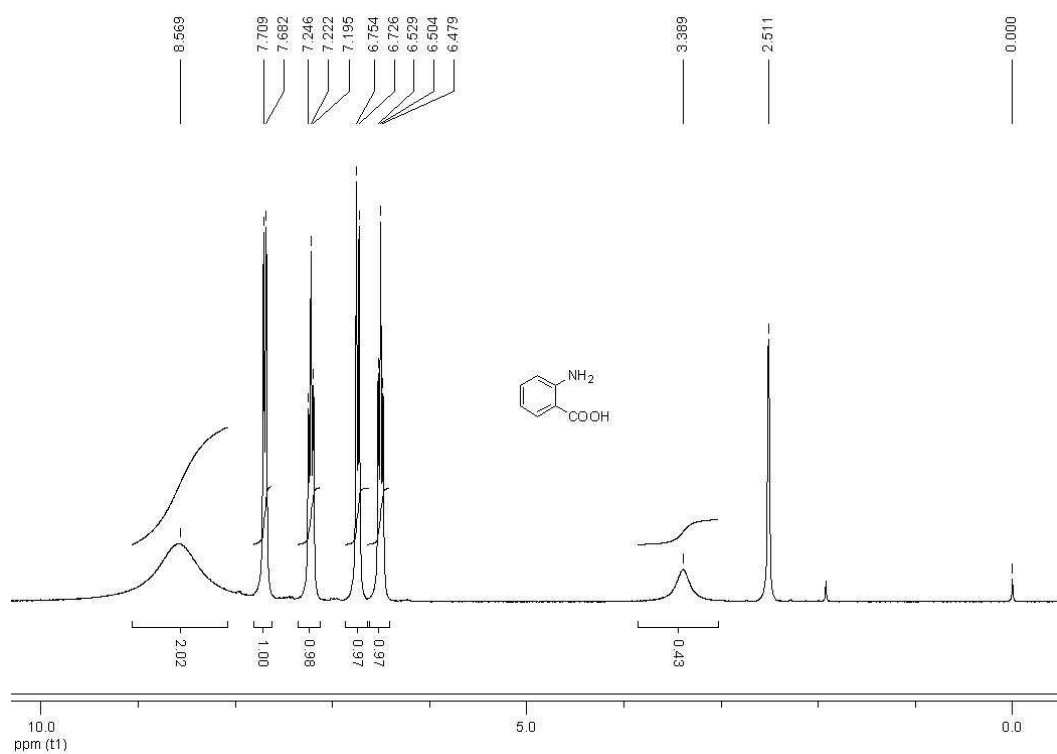
**Figure S26** <sup>13</sup>C NMR spectra of 3-Aminophenol (Table 3-5)



**Figure S27** <sup>1</sup>H NMR spectra of 4-Aminophenol (Table 3-6)

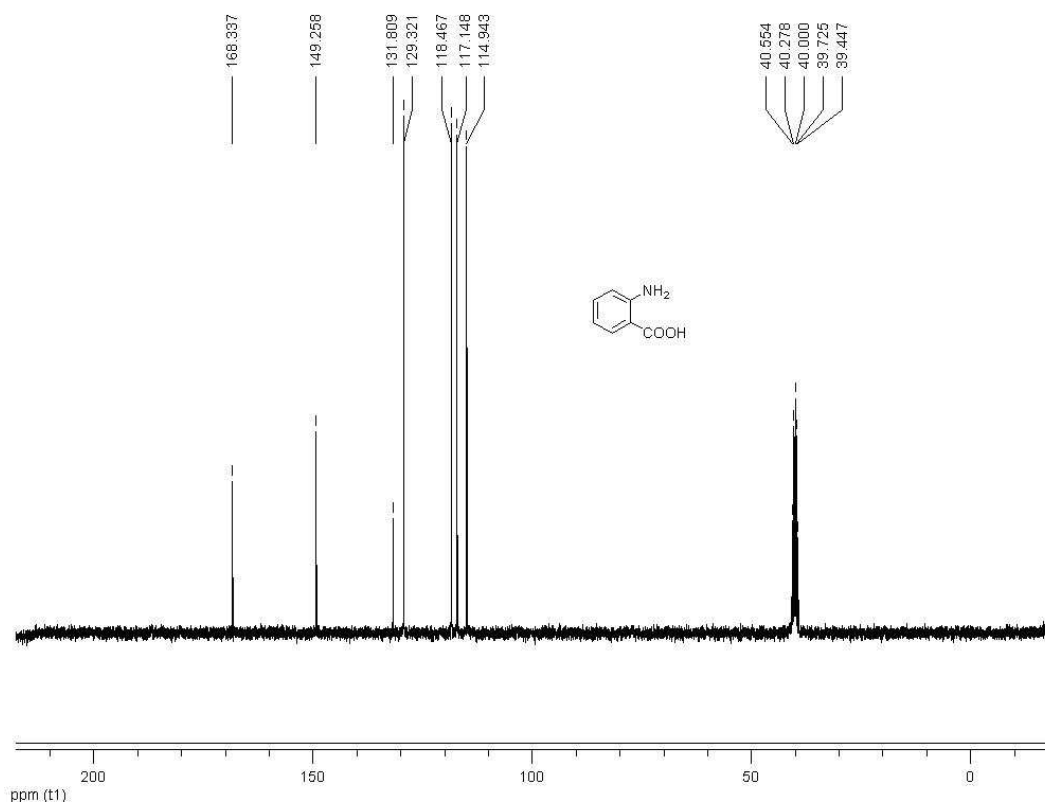


**Figure S28** <sup>13</sup>C NMR spectra of 4-Aminophenol (Table 3-6)

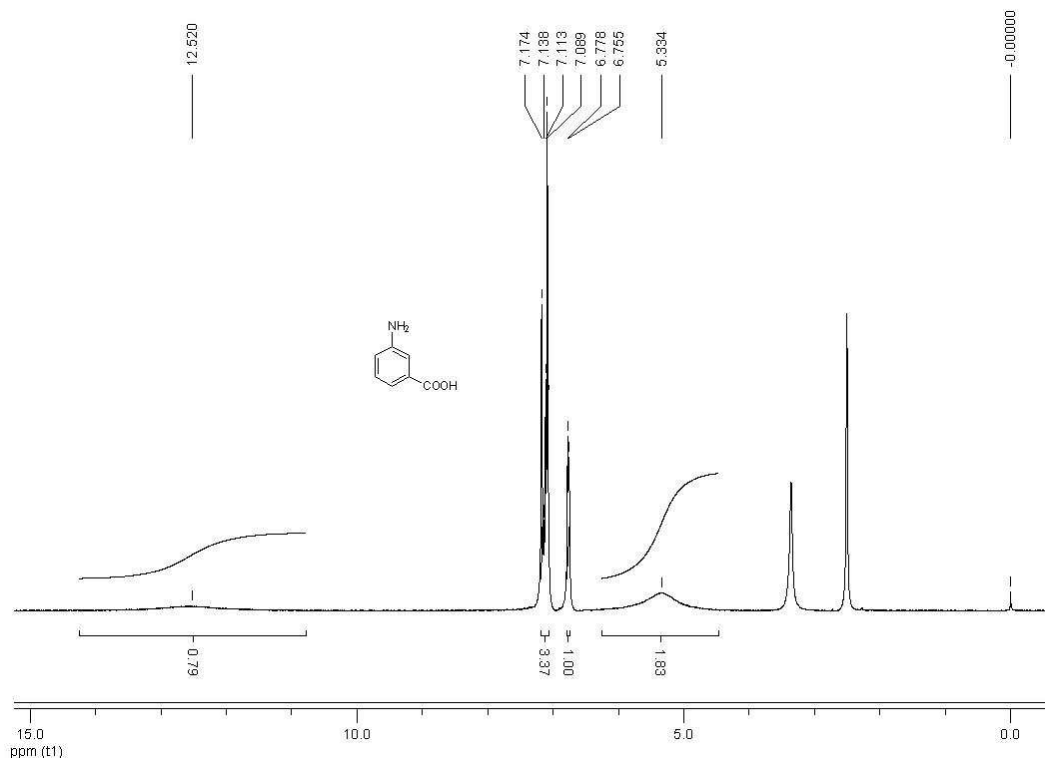


**Figure S29** <sup>1</sup>H NMR spectra of 2-Aminobenzoic acid (Table 3-7)

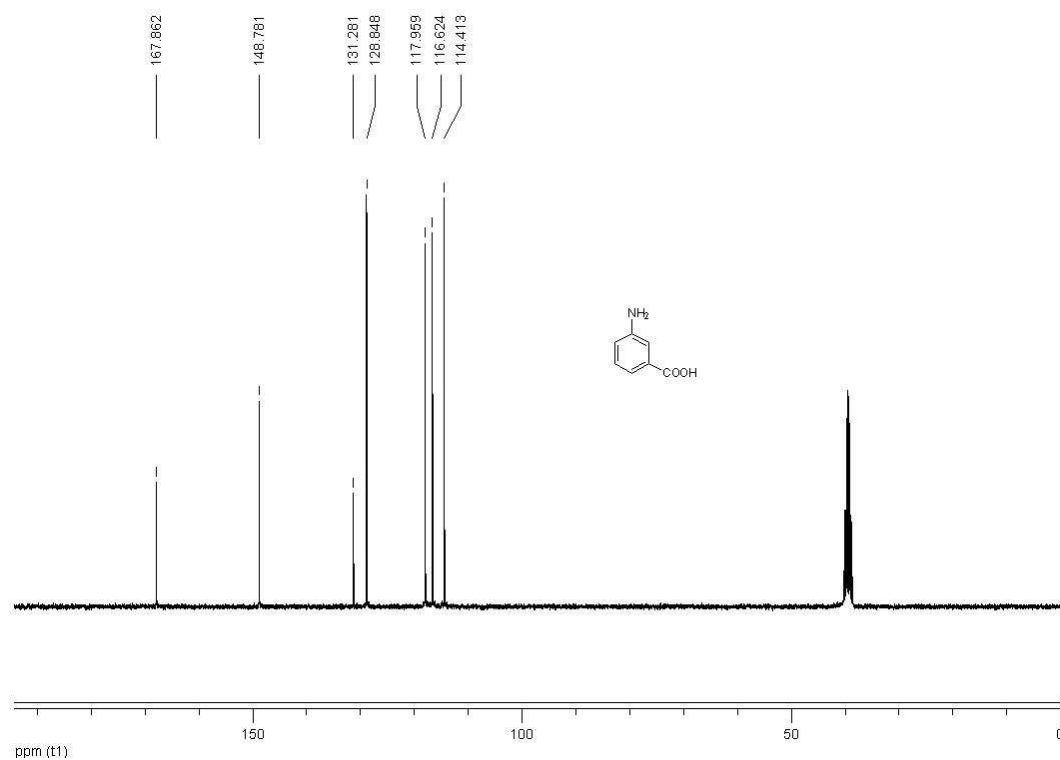




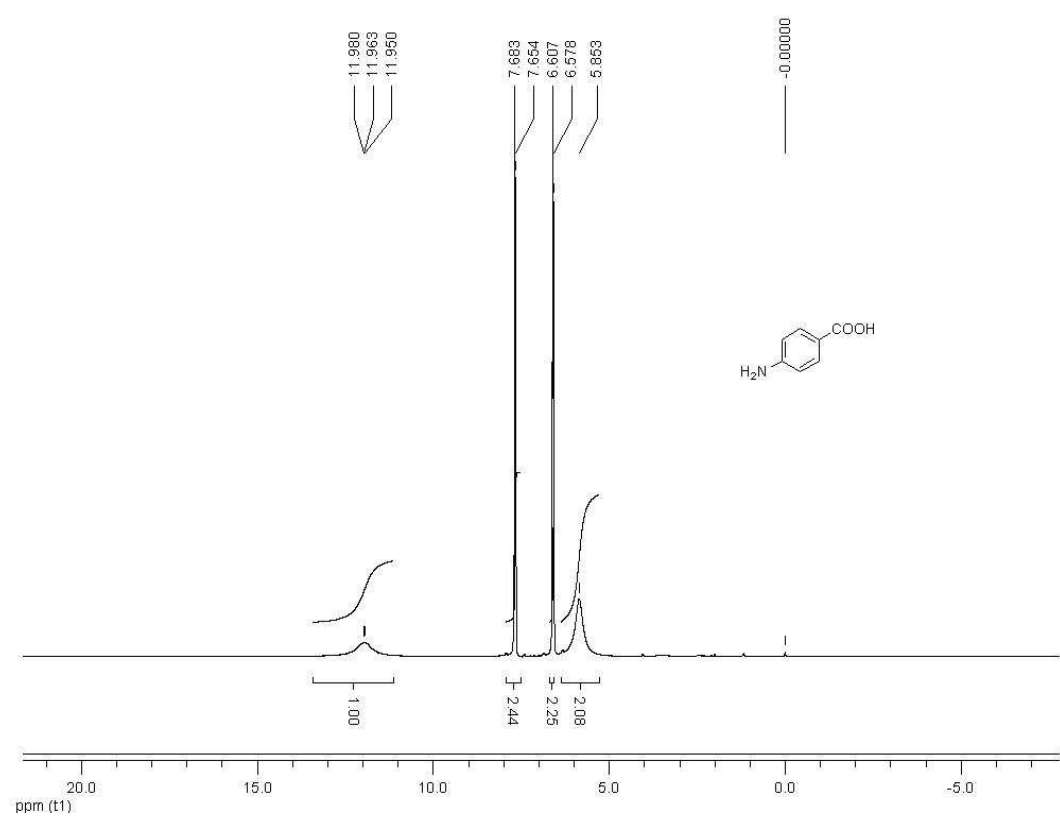
**Figure S30** <sup>13</sup>C NMR spectra of 2-Aminobenzoic acid (Table 3-7)



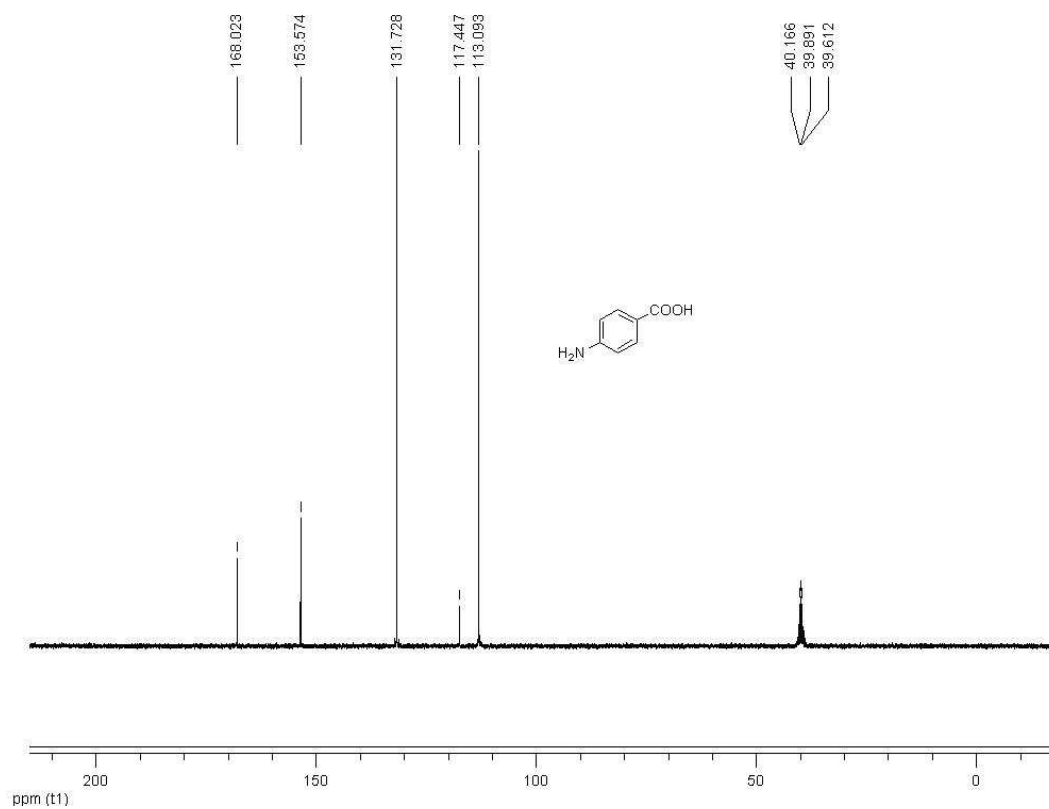
**Figure S31** <sup>1</sup>H NMR spectra of 3-Aminobenzoic acid (Table 3-8)



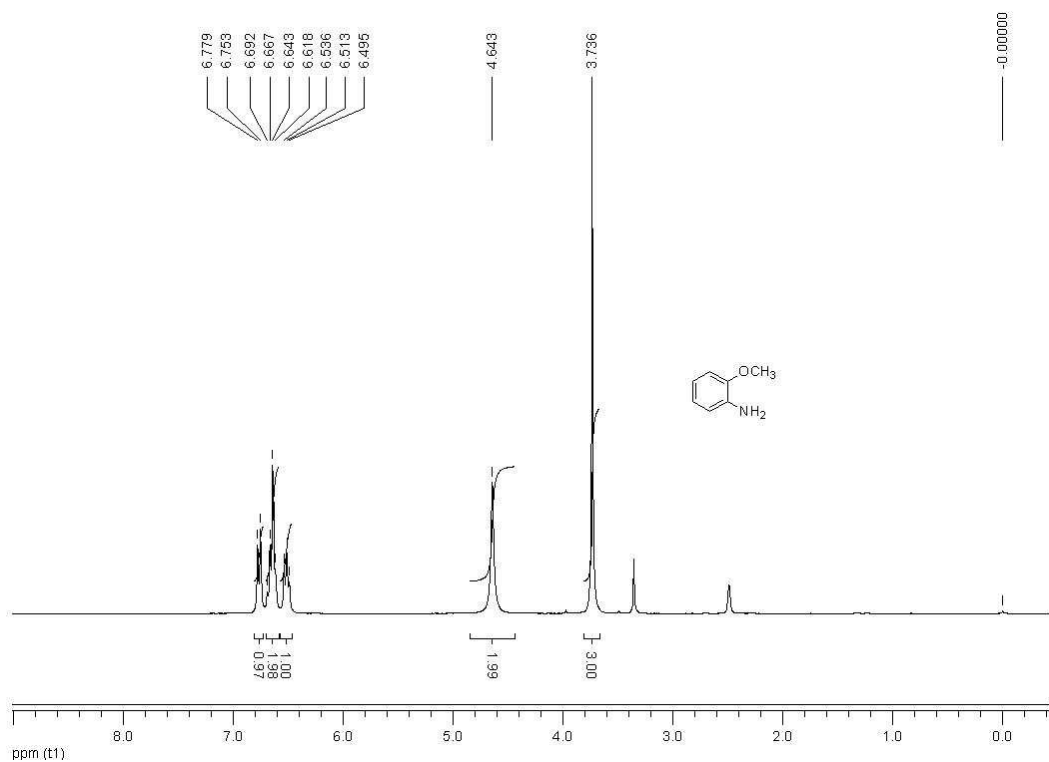
**Figure S32** <sup>13</sup>C NMR spectra of 3-Aminobenzoic acid (Table 3-8)



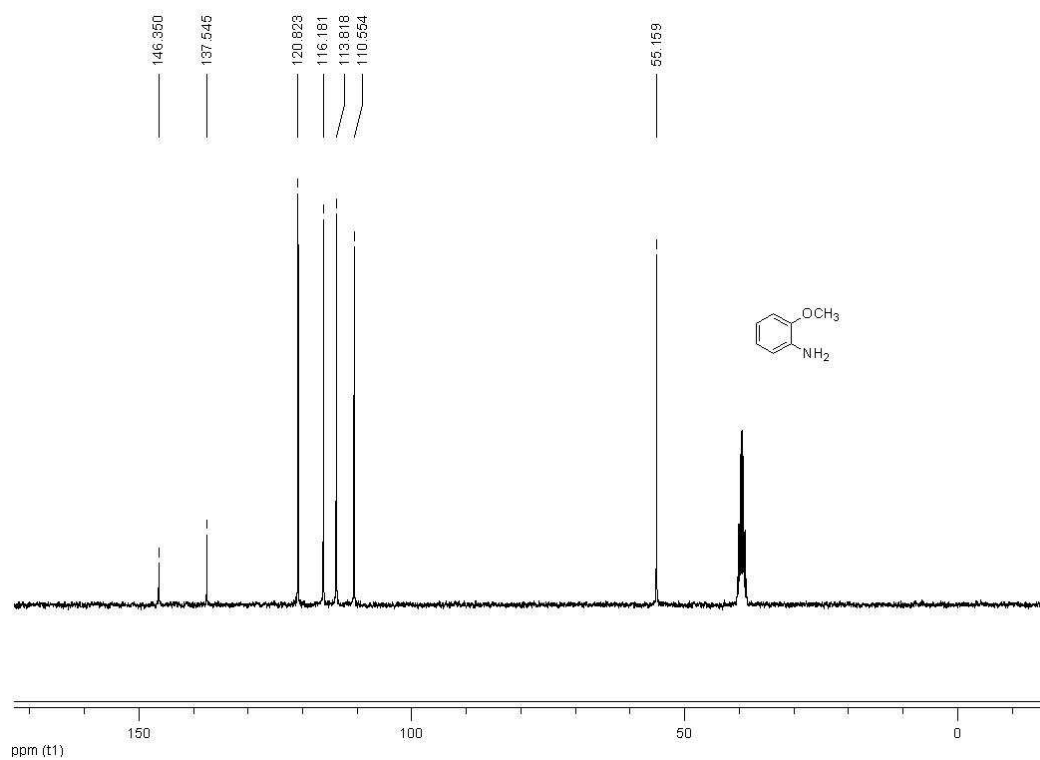
**Figure S33** <sup>1</sup>H NMR spectra of 4-Aminobenzoic acid (Table 3-9)



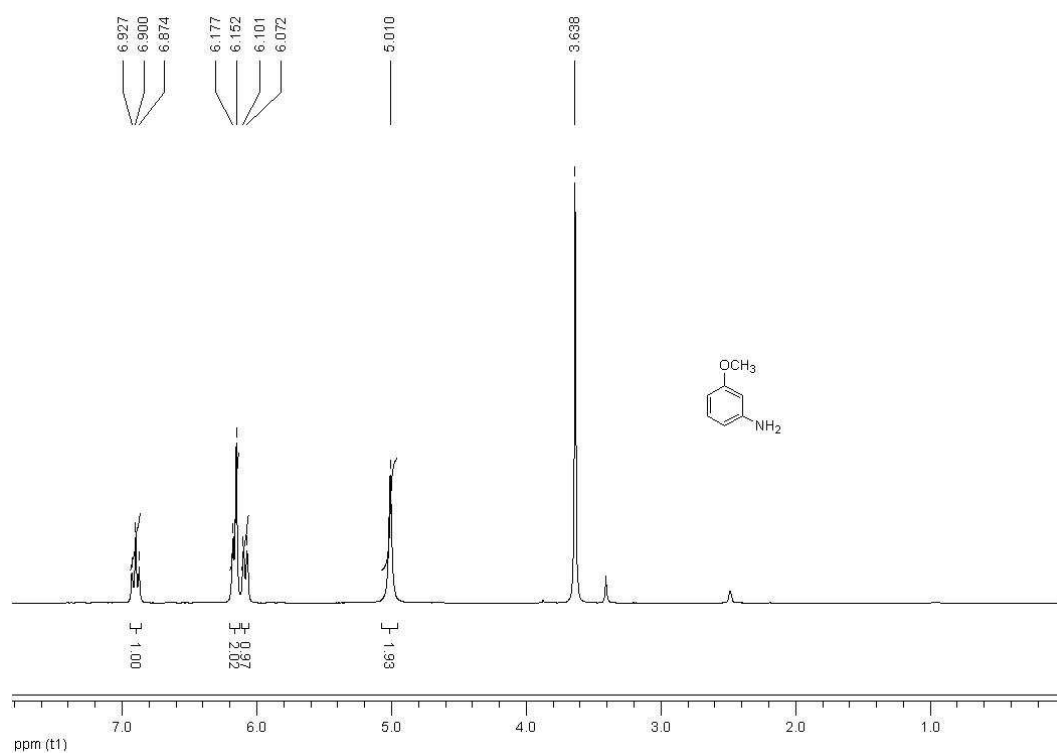
**Figure S34** <sup>13</sup>C NMR spectra of 4-Aminobenzoic acid (Table 3-9)



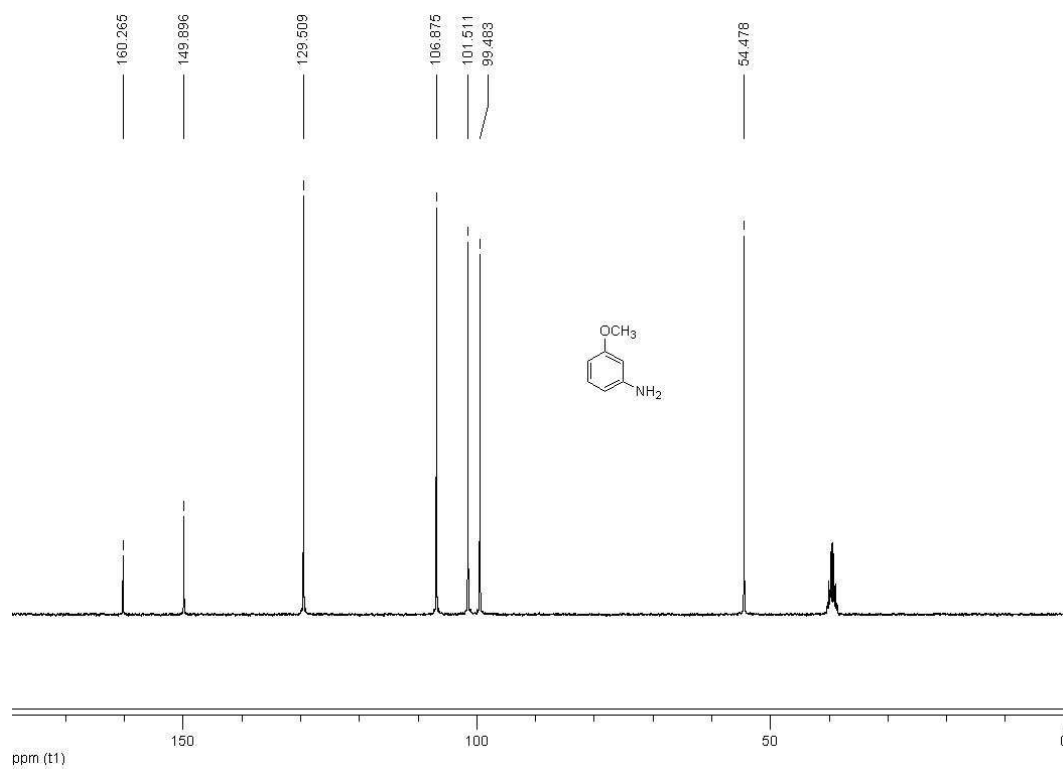
**Figure S35** <sup>1</sup>H NMR spectra of 2-Methoxyaniline (Table 3-10)



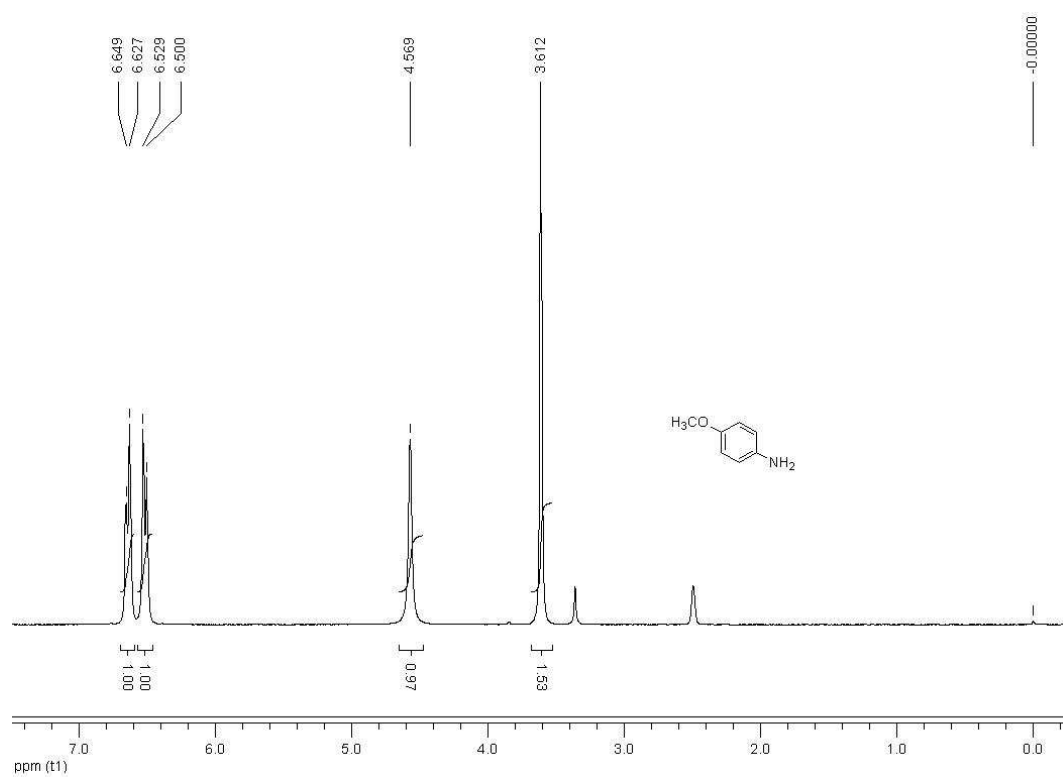
**Figure S36** <sup>13</sup>C NMR spectra of 2-Methoxyaniline (Table 3-10)



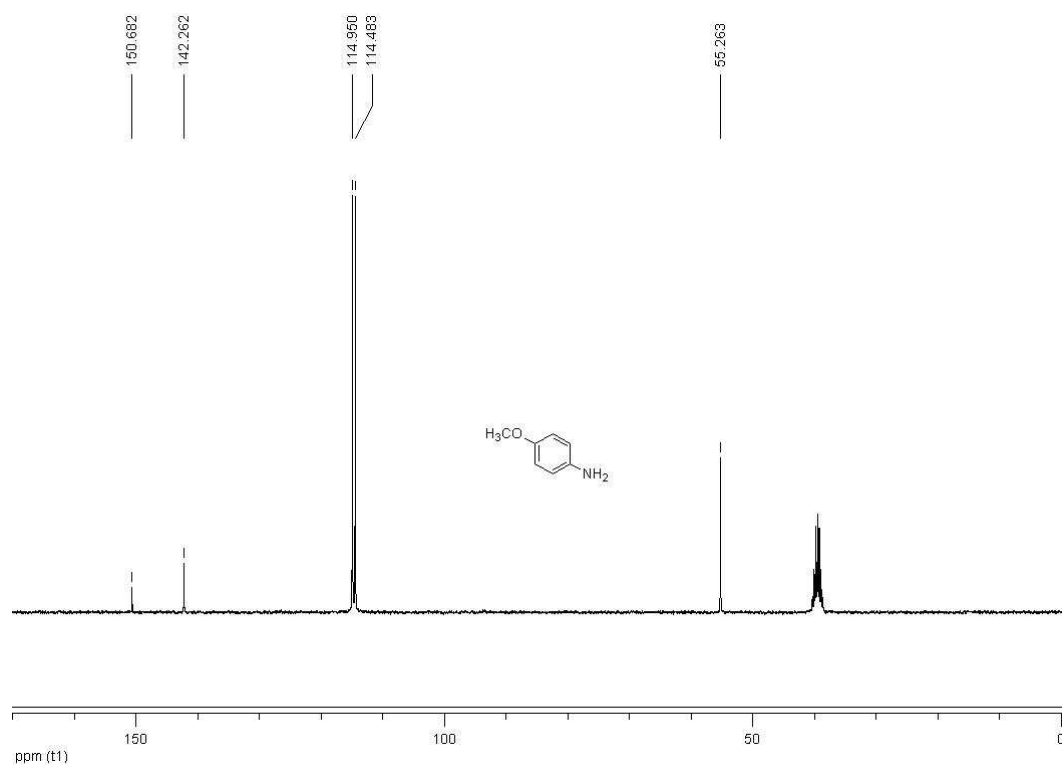
**Figure S37** <sup>1</sup>H NMR spectra of 3-Methoxyaniline (Table 3-11)



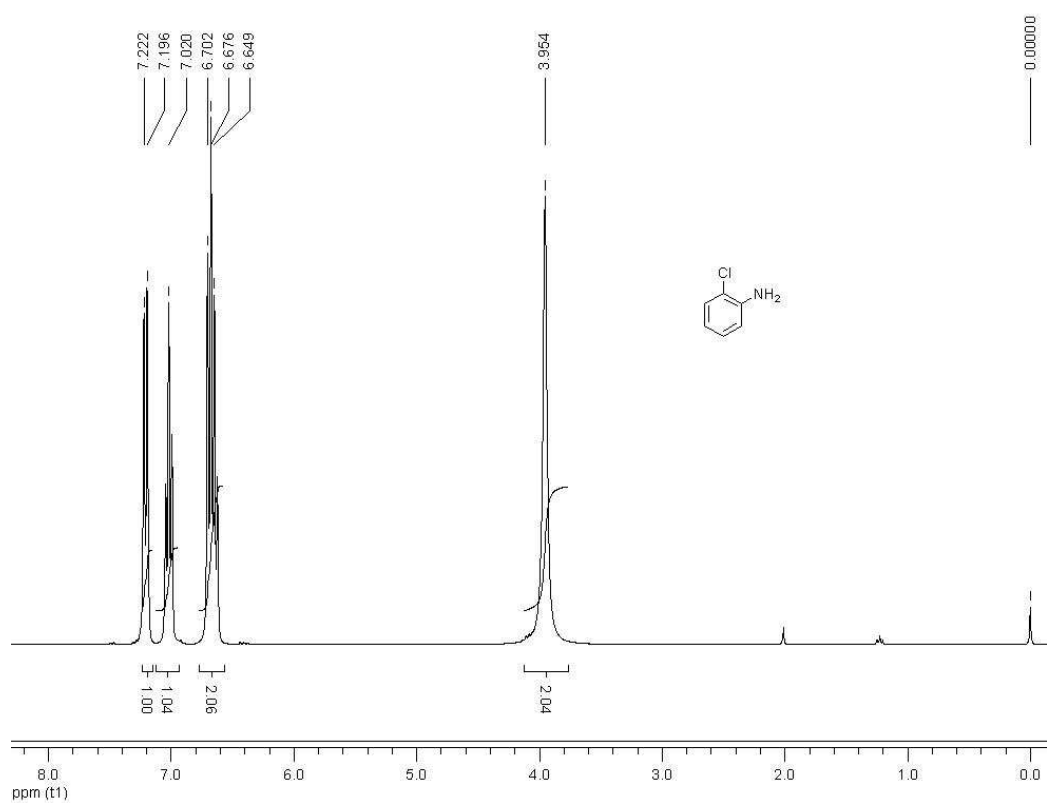
**Figure S38** <sup>13</sup>C NMR spectra of 3-Methoxyaniline (Table 3-11)



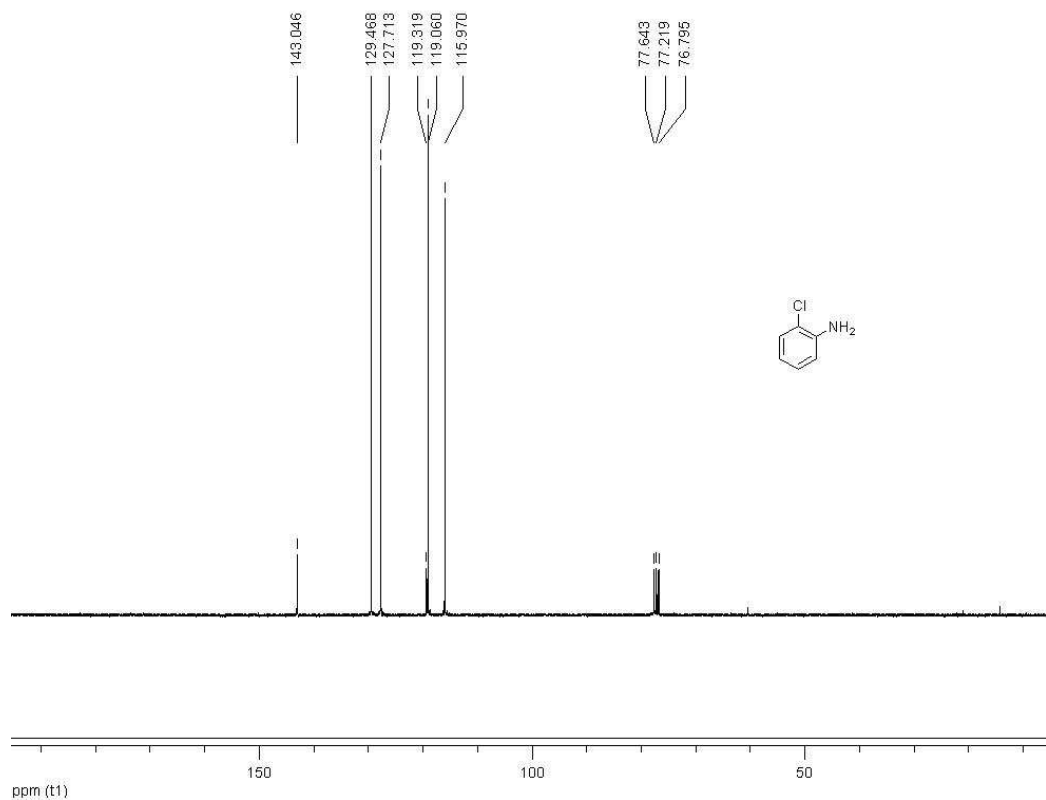
**Figure S39** <sup>1</sup>H NMR spectra of 4-Methoxyaniline (Table 3-12)



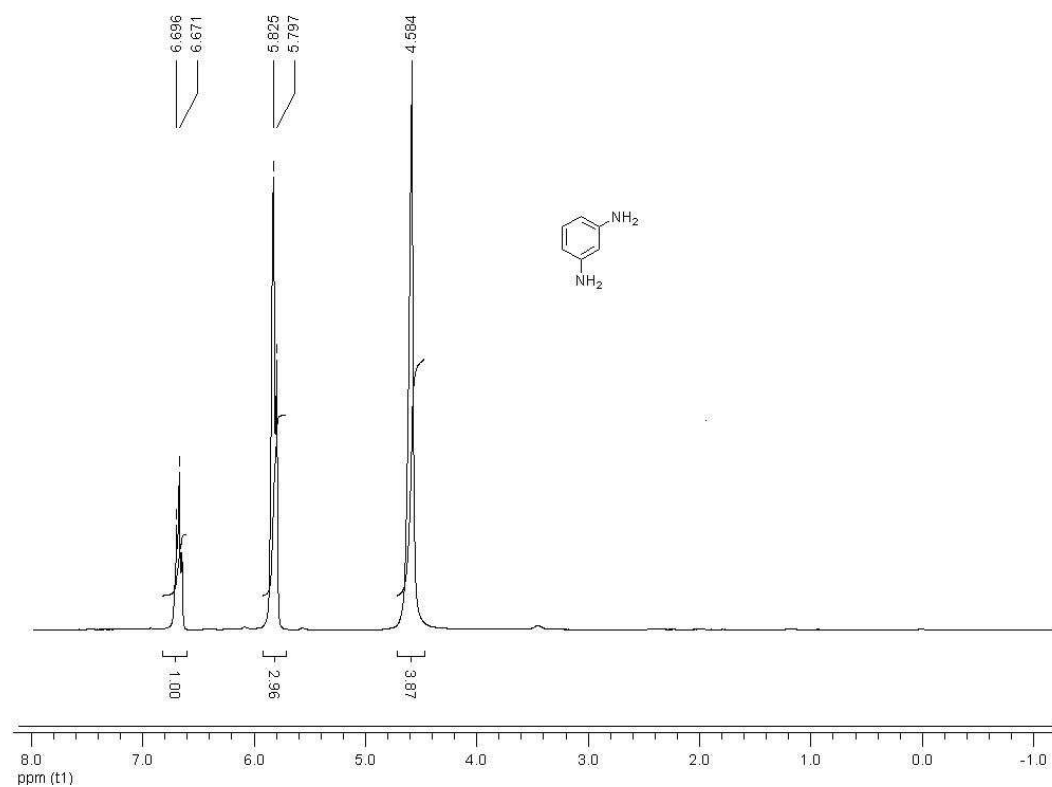
**Figure S40** <sup>13</sup>C NMR spectra of 4-Methoxyaniline (Table 3-12)



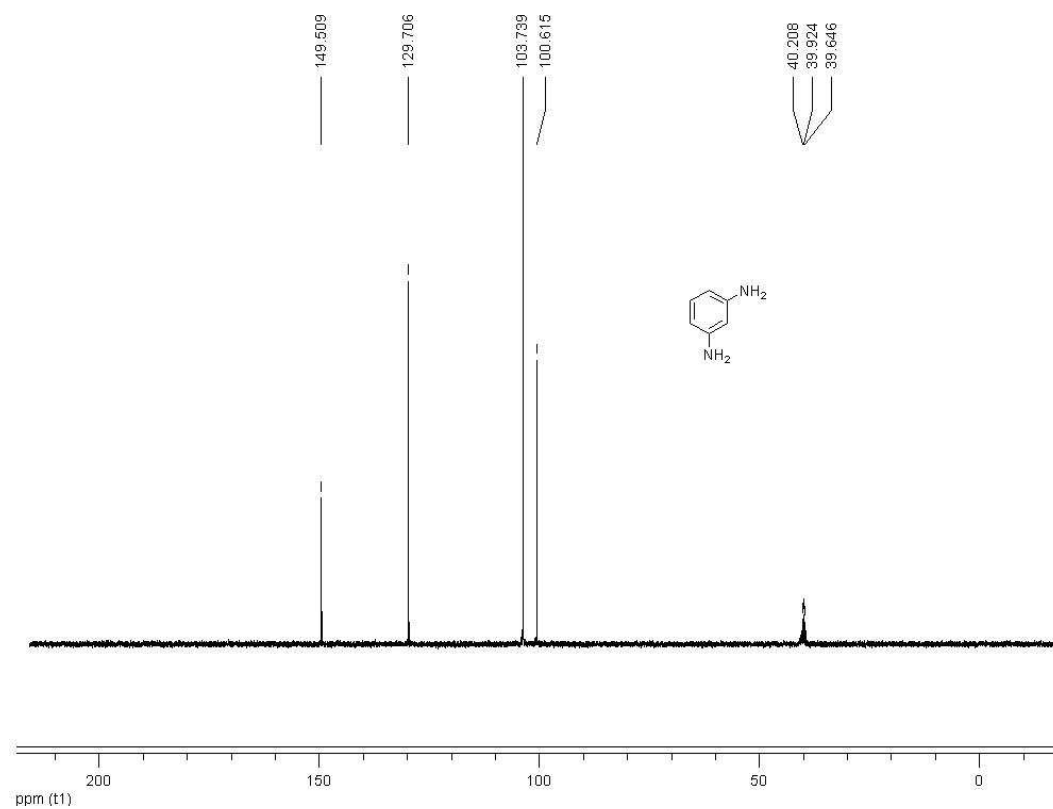
**Figure S41** <sup>1</sup>H NMR spectra of 2-Chloroaniline (Table 3-13)



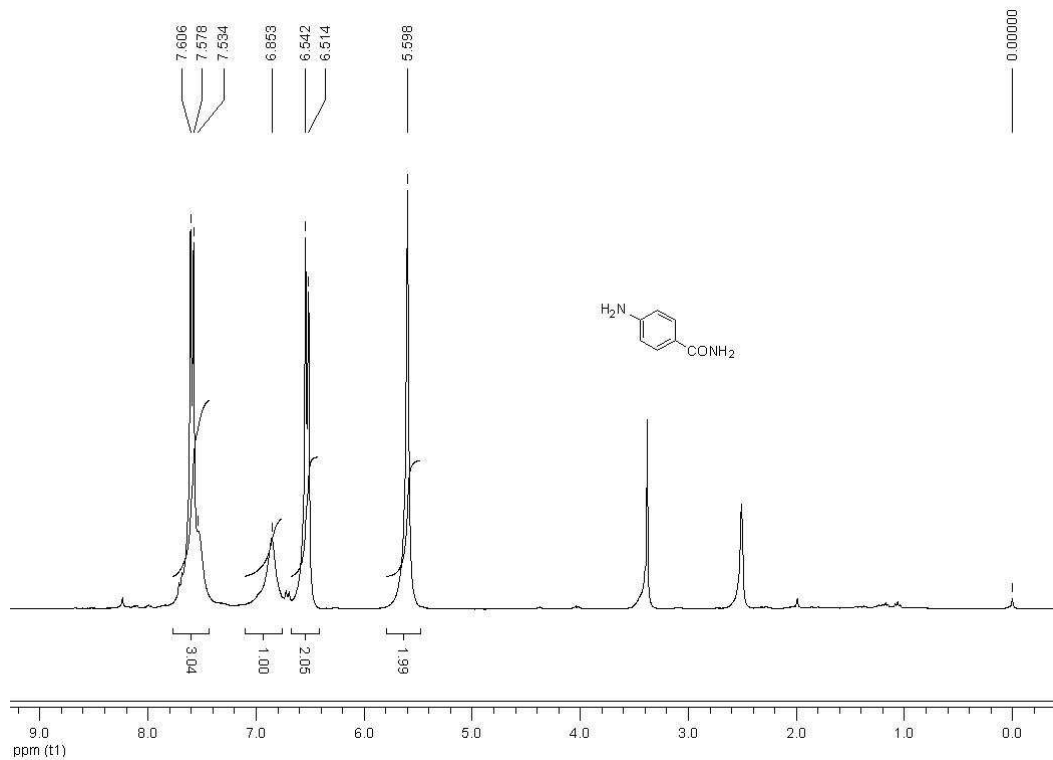
**Figure S42** <sup>13</sup>C NMR spectra of 2-Chloroaniline (Table 3-13)



**Figure S43** <sup>1</sup>H NMR spectra of 1,3-Diaminobenzene (Table 3-14)

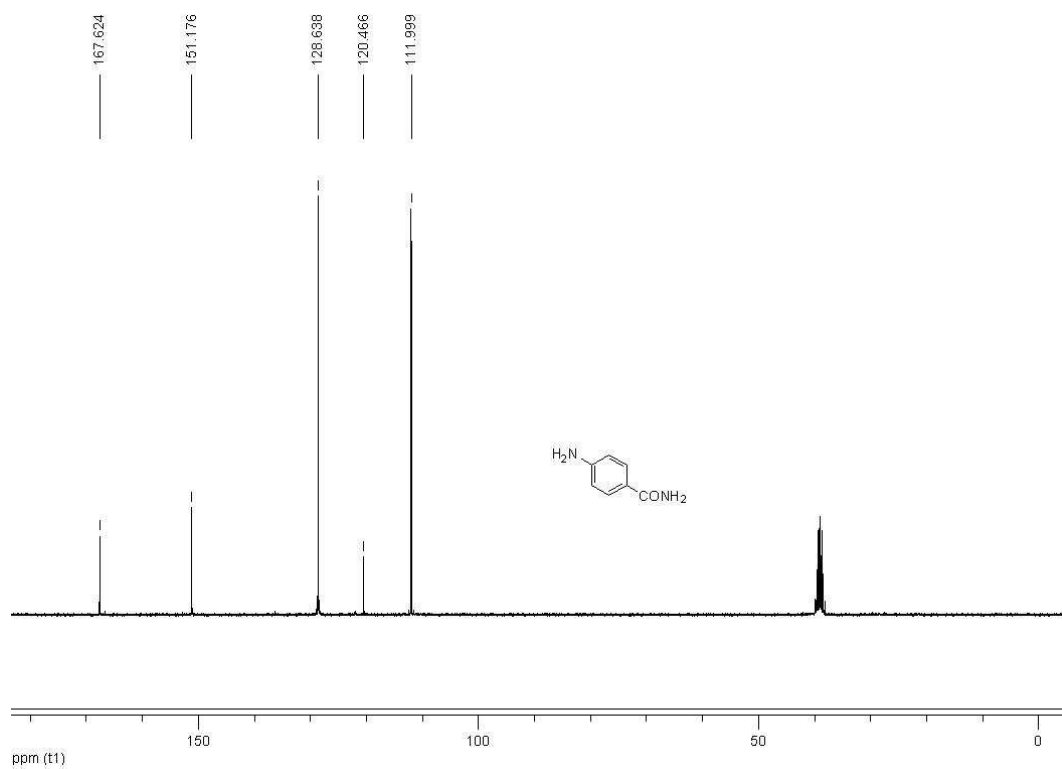


**Figure S44** <sup>13</sup>C NMR spectra of 1,3-Diaminobenzene (Table 3-14)

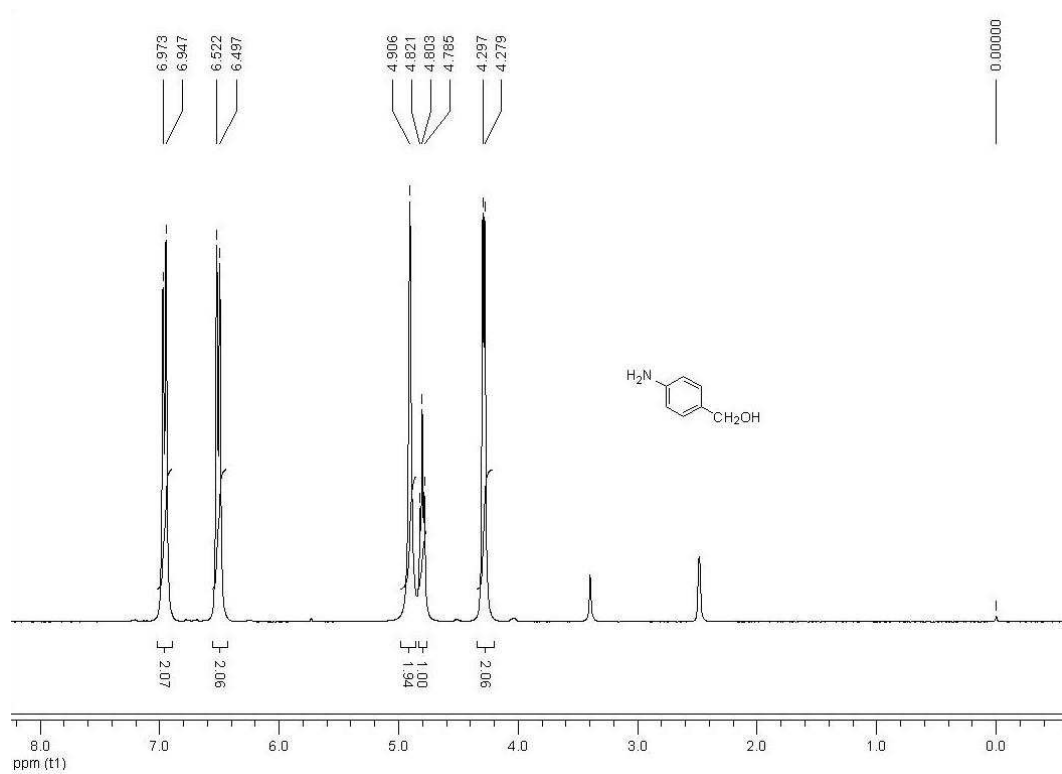


**Figure S45** <sup>1</sup>H NMR spectra of 4'-Aminobenzamide (Table 3-15)

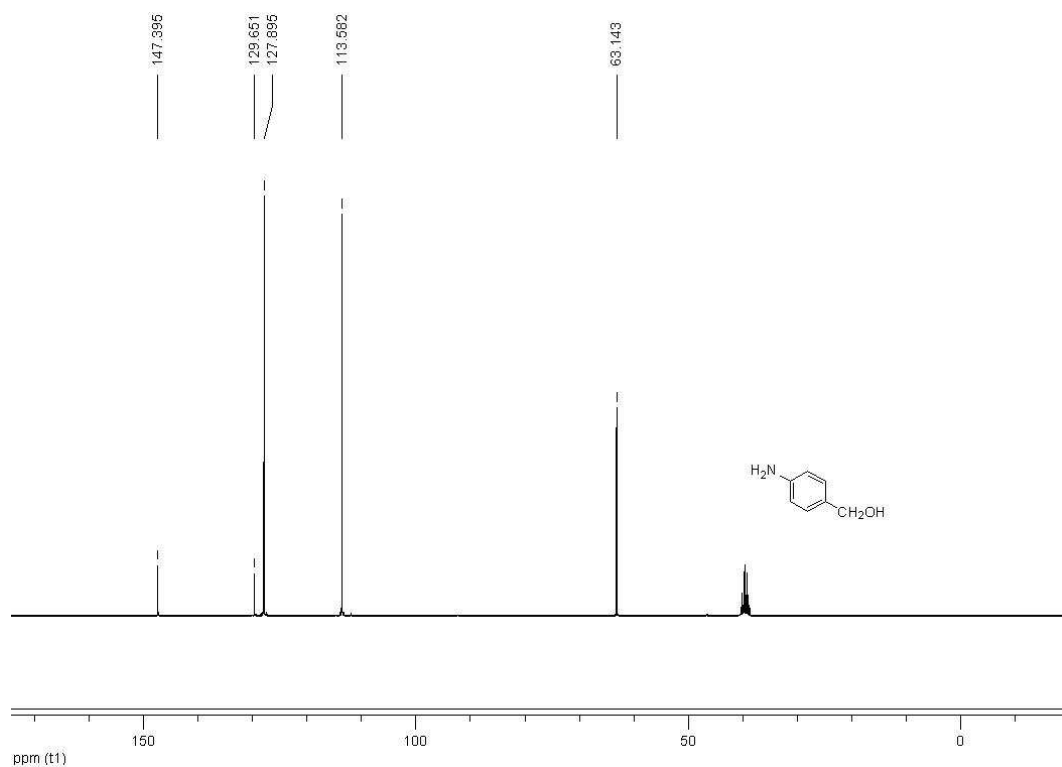




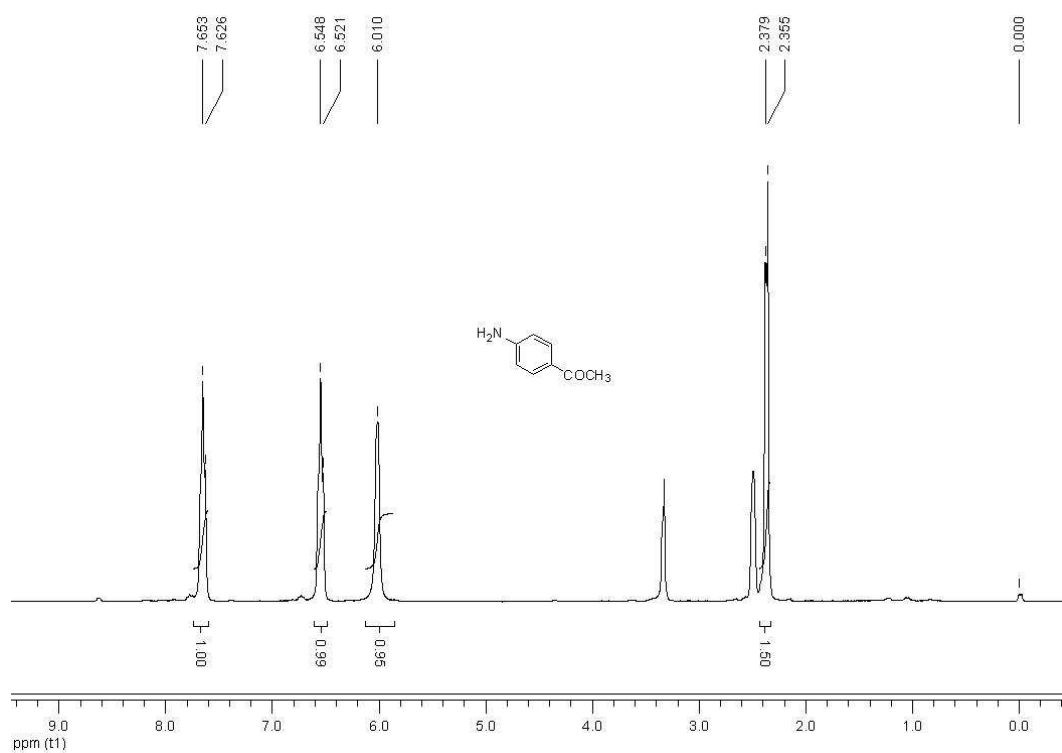
**Figure S46**  $^{13}\text{C}$  NMR spectra of 4-Aminobenzamide (Table 3-15)



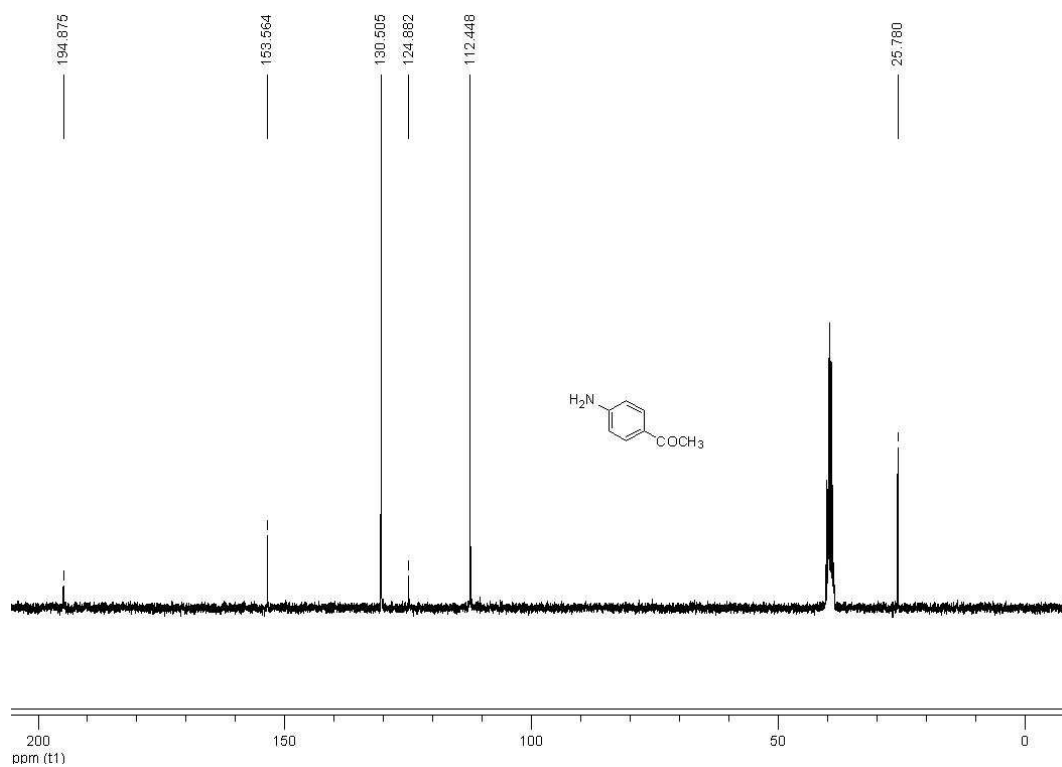
**Figure S47**  $^1\text{H}$  NMR spectra of 4-Aminophenyl alcohol (Table 3-16)



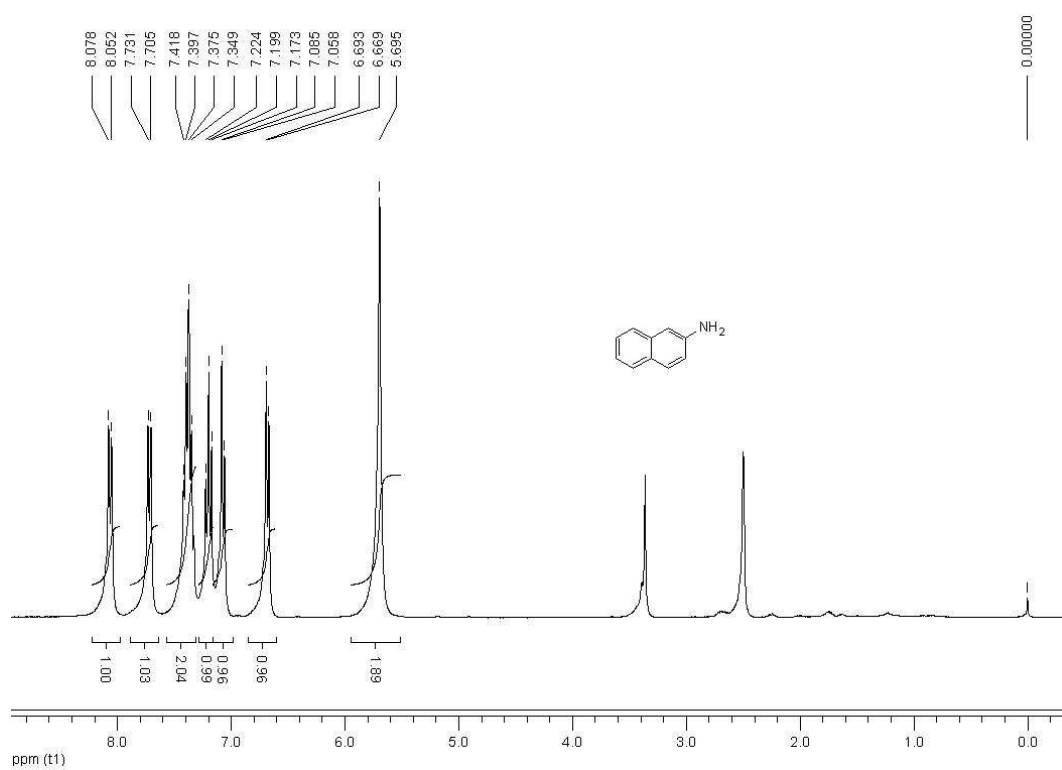
**Figure S48** <sup>13</sup>C NMR spectra of 4-Aminophenyl alcohol (Table 3-16)



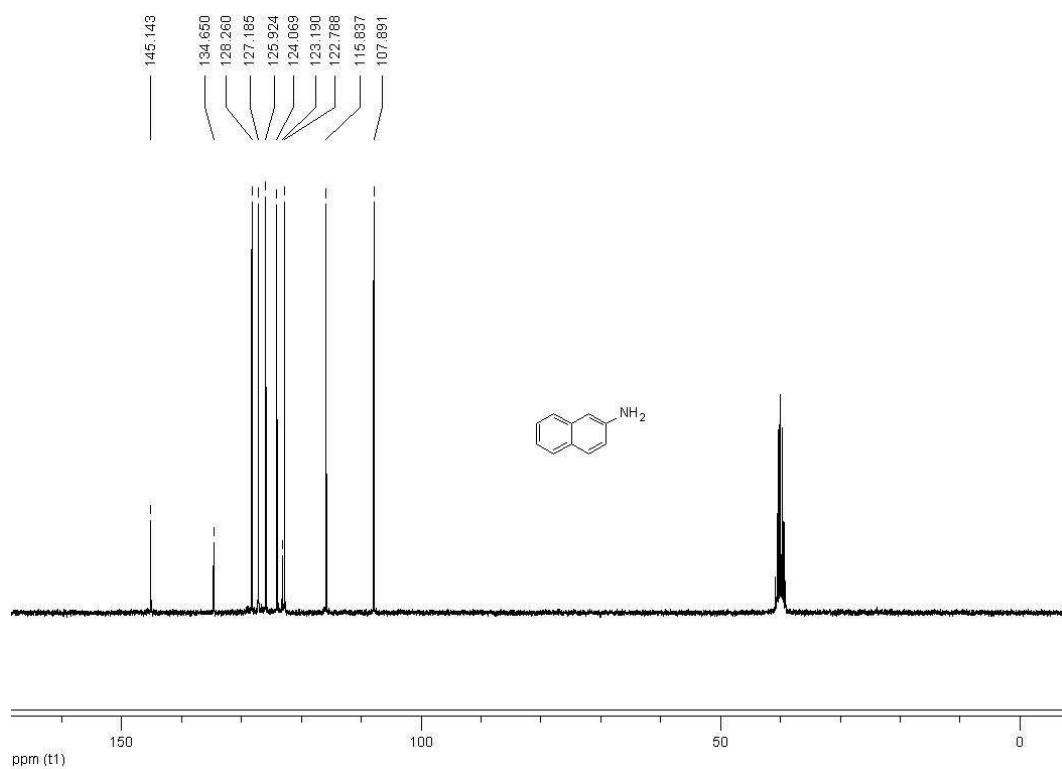
**Figure S49** <sup>1</sup>H NMR spectra of 4'-Aminoacetophenone (Table 3-17)



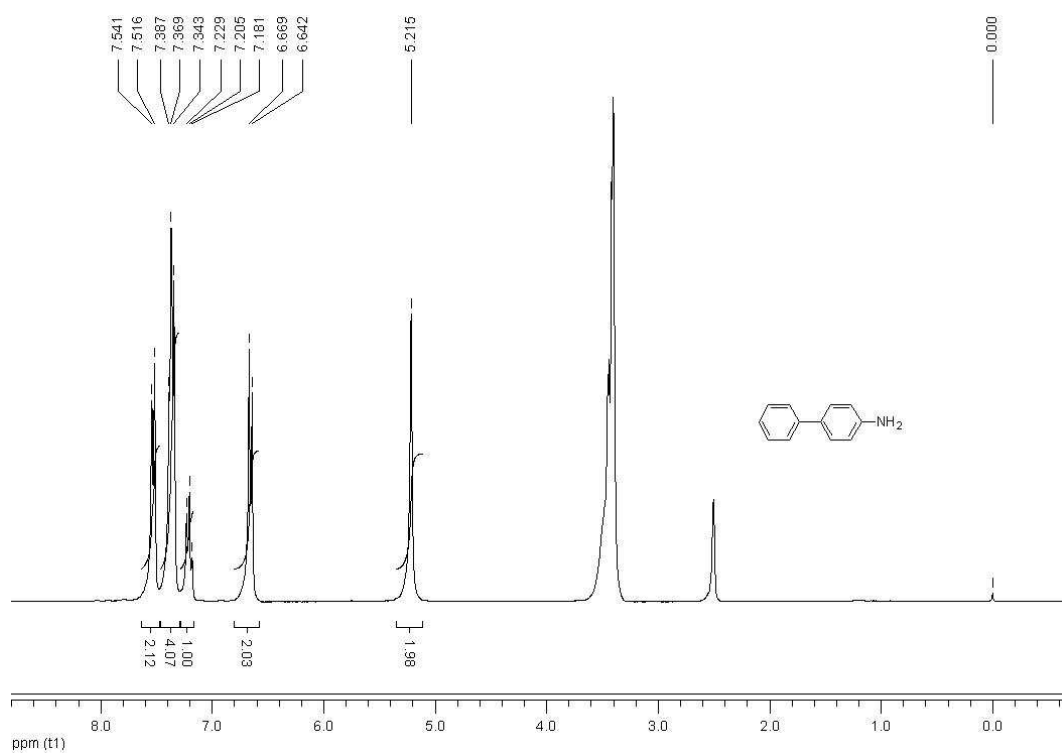
**Figure S50** <sup>13</sup>C NMR spectra of 4'-Aminoacetophenone (Table 3-17)



**Figure S51** <sup>1</sup>H NMR spectra of 2-Naphthylamine (Table 3-18)

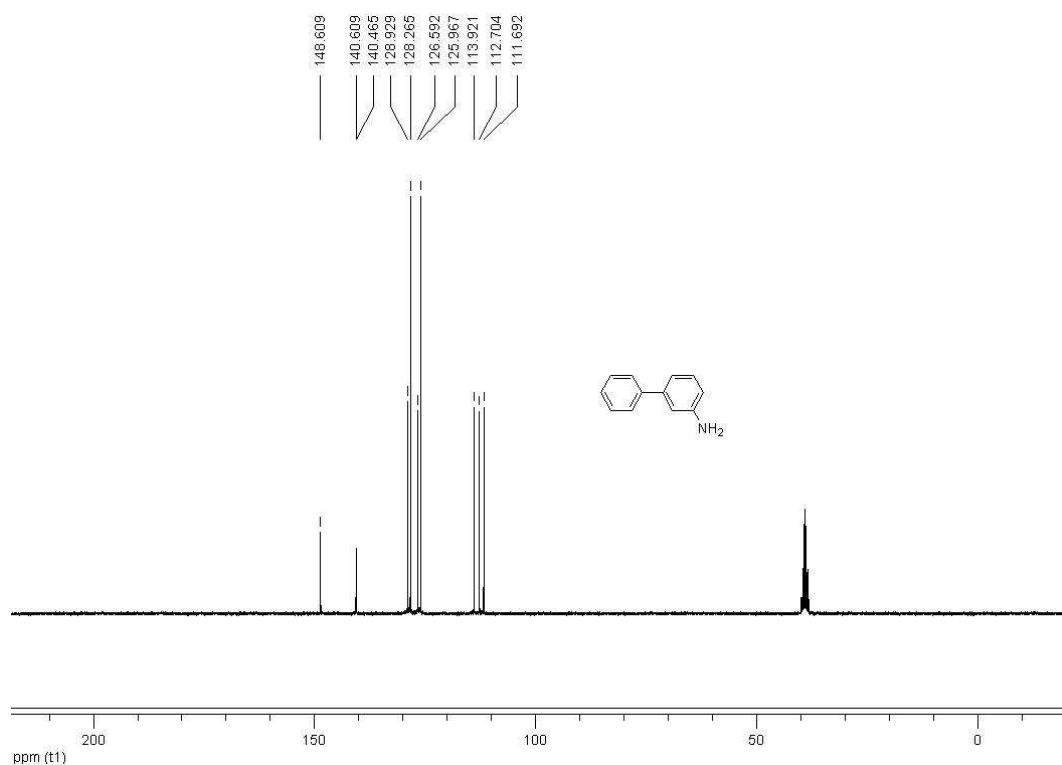


**Figure S52** <sup>13</sup>C NMR spectra of 2-Naphthylamine (Table 3-18)



**Figure S53** <sup>1</sup>H NMR spectra of 4-Aminobiphenyl (Table 3-19)





**Figure S56** <sup>13</sup>C NMR spectra of 3-Aminobiphenyl (Table 3-20)

## 6 References

- [S1] Y. H. So, *Macromolecules* **1992**, 25, 516-520.
- [S2] P. K. Dhal, F. H. Arnold, *Macromolecules* **1992**, 25, 7051-7059.
- [S3] B. S. Lee, Y. S. Chi, J. K. Lee, I. S. Choi, C. E. Song, S. K. Namgoong, S. -g. Lee, *J. Am. Chem. Soc.* **2004**, 126, 480-481.
- [S4] T. Kovalchuk, H. Sfihi, L. Kostenko, V. Zaitsev, J. Fraissard, *J. Colloid Interface Sci.* **2006**, 302, 214-229.
- [S5] Y. H. So, *Macromolecules* **1992**, 25, 516-520.
- [S6] S. -W. Kim, J. Park, Y. J. Jang, Y. H. Chung, S. J Hwang, T. Hyeon, Y. W. Kim, *Nano Lett.* **2003**, 3, 1289-1291.
- [S7] Jones, C. W. *Top Catal.* **2010**, 53, 942.
- [S8] a) X. B. Yu, M. H. Wang, H. X. Li, *Appl. Catal., A* **2000**, 202, 17-22; b) D. R. Patel, R. N. Ram, *J. Mol. Catal. A: Chem.* **1998**, 130, 57-64; c) X. L. Xi, Y. L. Liu, J. Shi, S. K. Cao, *J. Mol. Catal. A: Chem.* **2003**, 192, 1-7; d) Ji, H. B.; Pei, L. X.; Kuang, J. G. CN Patent 1 974 538, 2007.