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# Green Synthesis of Pdnp's and Its Application Towards Chemoselective Catalytic Transfer Hydrogenation of Nitroarenes

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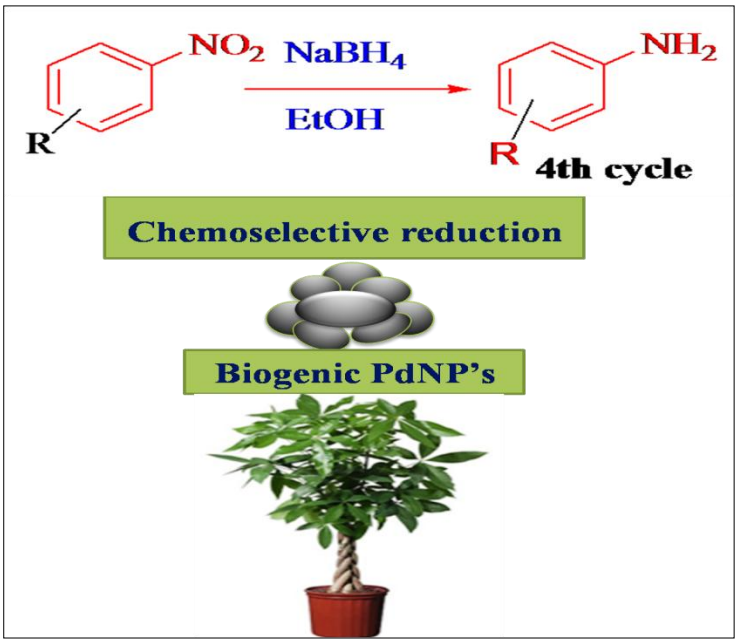
**Graphical Abstract**




**Highlights :**

1. Development of cost effective, green route towards synthesis of PdNP's
2. Bryophylum pinnatum leaf Extract as reducing and stabilizing agent without use of exogenous agent
3. Pd@BrP as green catalyst towards Chemoselective Catalytic Transfer Hydrogenation of nitroarenes

**Keywords:** Palladium nanoparticles, CCTH Chemoselctive Catalytic Transfer Hydrogenation, BPLE Bryophylum Pinnatum Leaves Extract

**Abstract:**

A simple and greener approach towards the synthesis of PdNP's is developed using leaf extract Bryophylum pinnatum (BPLE). The XRD and HRTEM analyses of self assembled Pd@Brp suggest average size 20-30

nm. The Fourier transform infrared spectroscopy FTIR suggest the role of amide and poly-hydroxyl functionalities present in extract which acts as excellent reducing, encapsulating and stabilization of Pd@Brp. The beneficial catalytic activity Pd@Brp is explored for Chemo-selective Catalytic Transfer Hydrogenation (CCTH) of aromatic nitro compounds. The reductions were successfully carried out with other reducible functional groups achieving excellent yields. The catalytic activity of reusable Pd@Brp is sustained up to four successive cycles and therefore may be regarded as green protocol towards the synthesis of aromatic amines.

## 1.0 Introduction

Recent emergence of green synthesis of palladium nanoparticles have attracted great attention owing to its diverse applications in catalysis, environmental abatement, plastic coatings, fuel cells, textiles and functional materials [1,2,3]. The conventionally numerous chemical and physical methods have been explored for the synthesis of PdNPs [4,5]. However use of hazardous chemicals, high operational cost and generation of secondary waste poses potential threat to life and environment [6,7]. Therefore, developing an environment safer approach for the production of PdNP's is blooming [8]. In harmony with nature various natural products like leaves, fruits, roots, honey, coffee, tea and peel extracts has been reported for the synthesis of PdNP's[9]. Bryophylum pinnatum is significant medicinal plant as it comprises high concentrations of the proteins, chalcones, vitamins, flavones, flavonoids, phenolic acids and fibers [10]. However, its leaves extract has not been explored yet for reduction of $Pd^{2+}$ ions.

Herein, we report the biosynthesis of palladium nanoparticles (Pd@Brp) with use of leaves extract of bryophylum pinnatum as green reducing agent. As a catalytic application of obtained Pd@Brp were explored towards Chemo-selective Catalytic Transfer Hydrogenation (CCTH) of nitroarenes into amines. The Pd@Brp is found to be excellent catalyst for the reduction of various nitroarenes with better yields of products with sustained catalytic activity up to four cycles. Therefore, can be regarded as greener method for the synthesis amines.

## 2. Experimental procedures:

### 2.1 Preparation of BPLE:

The (5 grams) of Bryophylum pinnatum leaves were collected, washed and crushed in 20 ml of distilled water. The obtained leaves extract was filtered and filtrate BPLE was used for the synthesis of Pd@Brp

### 2.2 Synthesis of biogenic Pd@Brp

(1mM) of aqueous solution of $PdCl_2$ was prepared and used as stock solution for the synthesis of PdNP's. Then 20 mL of BPLE was added in 100 mL (1mM) $PdCl_2$ solution in 150 mL Erlenmeyer flask. This mixture was stirred and heated at 80ºC for 5-10 minutes on magnetic stirrer, presence of black colour was indicating formation of Pd@Brp. This suspension on centrifugation resulted Pd@Brp, was further used as catalyst for CCTH.

### 2.3 CCTH of nitroarenes using biogenic Pd@Brp as a catalyst:

A mixture of nitrobenzene (1mmol), Pd@Brp (10 mg), ethanol 5 ml were taken in a 50 mL round bottom flask and $NaBH_4$ (10 mmol) dissolved in 5 ml of ethanol is added drop wise by drooping funnel at room temperature with stirring condition. After 20 minutes the reaction mixture is heated at $50^0$C for about 1.5 h. Then the progress of the reaction is monitored by TLC. On completion of reaction, the catalyst was separated

by centrifugation and the product was extracted by ethyl acetate (2 x 5 ml) and dried over anhydrous $Na_2SO_4$. Evaporation of combined organic layer followed by silica gel (60-120 mesh) column chromatography (hexane and ethyl acetate 80:20) afforded **2a**. The structure of all products was confirmed by physical constants, and $^1H$ and $^{13}C$ spectroscopy. The spectral data were found to be identical with literature [11] supporting information( **Table 2**).

**2.4 Reusability studies biogenic Pd@Brp catalyst:**

Reusability study and catalytic efficiency of biogenic Pd@Brp is evaluated towards repetitive cycles without compromising its catalytic activity. The Pd@Brp recovered after the first cycle separated, washed with acetone and dried and used in subsequent cycles. These observations are further corroborated by the assumption that the beneficial catalytic activity of biogenic Pd@Brp is sustained due to continuous ethanolysis of $NaBH_4$ on catalyst surface and consequent evolution of molecular hydrogen preventing surface passivation of catalyst by maintaining anaerobic condition. This also helps in dispersion of PdNP's zero valent state. The marginal reduction in isolated yield (92-89%) at fourth cycle supporting information (**Fig.2)** may be poisoning of some of the catalytic site due to the Pd-B complex formation.

## 3.0 Characterization

### 3.1 Characterization of Pd@Brp

The powder XRD patterns of Pd@Brp **Fig. 1** exhibits the characteristic intense peaks at $2\theta = 40°$, 46° and 68° corresponds to (111), (200) and (220) reflection planes of face centered cubic *fcc* lattice of $Pd^0$ (JCPDS card, File No. 46-1043). These observations are in concurrence with previous reports [12,13] confirms the formation of nanocrystalline Pd@BrP.

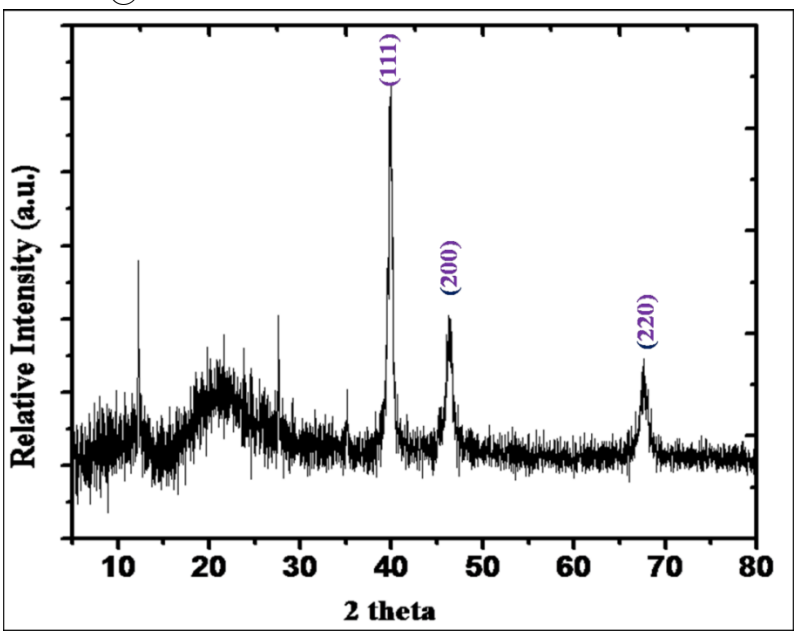



**Fig. 1: The XRD pattern of Pd@BrP.**

HRTEM images of Pd@Brp indicates good dispersion of PdNP's **Fig.2** particles with average size of 20 nm with spherical morphology.

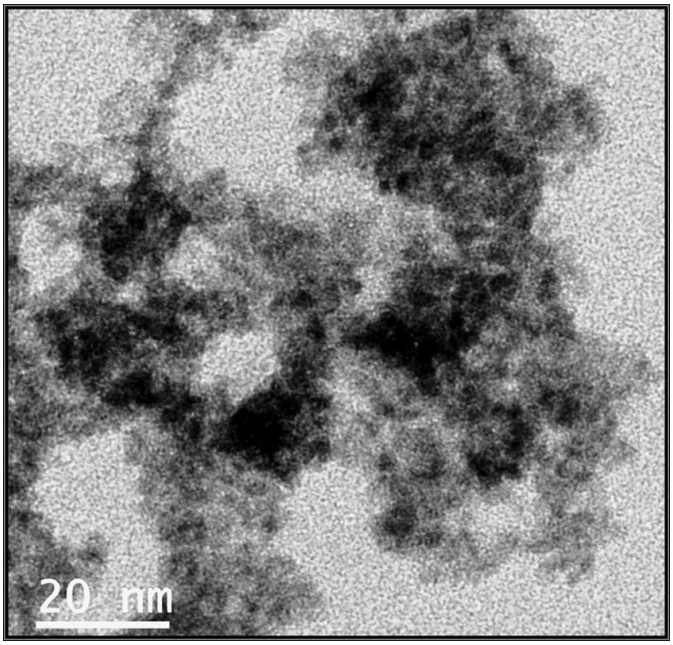



**Fig. 2: The TEM image of the Pd@BrP**

FT-IR spectroscopy envisage role of various functional groups in the synthesis of PdNP's **Fig.3.** The broad peak at 3300-3500 $cm^{-1}$ is ascribed to O-H, N–H stretching vibrations of poly-phenols and amide groups which becomes sharper (**Fig.3 a),** after the synthesis of Pd@Brp implies the surface encapsulation and stabilization of PdNP's. The peaks between 1725-1150 $cm^{-1}$ evident from C=O, C=C, N-H bending and C-O stretching vibrations carboxylic acids and protein/poly-phenols from BPLE [10].

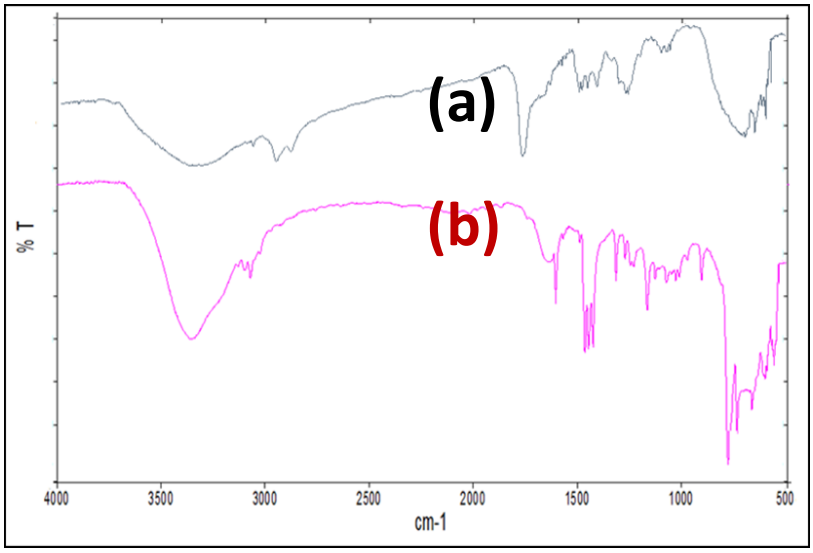



**Fig. 3. (a) FTIR spectrum of Pd@BrP and (b) BrPLE**

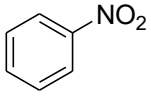
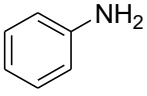
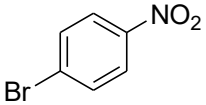
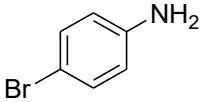
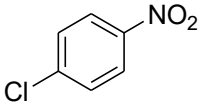
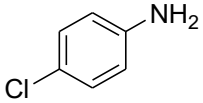
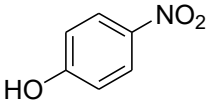
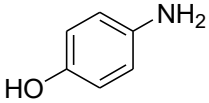
## 4.0 Result and discussion

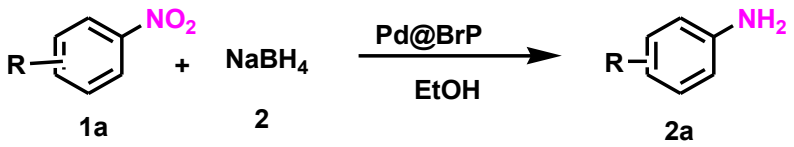
### 4.1 Catalytic activity:

Classically nitroarenes are reduced into amines using transition metals in aqueous medium; however, reduction rate and its catalytic activity is decreased in repetitive cycles due to the surface passivation that

inhibits further usage in continuous process[ 14,15]. To improve upon we have investigated the biogenic Pd@Brp for reduction under the various solvents for CCTH supporting information (**Fig. 1**), there was significant effect of solvents towards reduction of nitroarens and ethanol is found to be better solvent. This implies the evolution of nascent hydrogen was found to faster during ethanolysis of borohydride on Pd@BrP surface during CCTH supporting information (**Table 1, entry 6**). This behavior may be ascribed by three aspects: i) Pd@Brp surface induces rapid ethanolysis of borohydride over other solvents with faster $H_2$ evolution which maintains PdNP's well suspended in reaction pot ii) continuous evolution of hydrogen sustains reducing environment which prohibits surface oxidation of PdNP's. All these factors contributing in tandem towards liquid phase hydrogenation of nitroarenes with sustained catalytic activity of catalyst with improved service life [16,17]. To optimize and investigate the catalytic activity of the Pd@BrP towards the reduction of nitro derivatives **1a** is selected as model reaction in ethanol. In absence of Pd@BrP as a catalyst the reaction does not progress supporting information (**Table 1, entry 1**) implying the vital catalytic role of Pd@BrP for this reaction as compare to the literature [18]. It is found that 10 mg of Pd@BrP is found to be optimum in presence of model reaction, 1mmol of nitrobenzene 5mL of ethanol in presence of 10 mmol of $NaBH_4$ in 3 hrs. supporting information (**Table 1, entry 6).** The Pd@BrP is found to be versatile catalyst to reduce diverse substituted –Cl, -Br and –OH nitrobenzene with variations in reaction time and percentage of yields of product compared to **2a** may be due to the significant role of substituent.
significant role of substituent.

**Table 1 : Synthesis of aromatic amines in presence of biogenic Pd@Brp as catalyst[a,b]**

| Sr. no | Substrate | Time (h) | Product | % Yields |
|---|---|---|---|---|
| **1** |  1a | **3** |  2a | **91** |
| **2** |  1b | **2** |  2b | **92** |
| **3** |  1c | **2** |  2c | **92** |
| **4** |  1d | **3** |  2d | **90** |




[a]Nitroarene (1 mmol), $NaBH_4$ (10 mmol), catalyst (10 mg), EtOH (5 mL), [b]isolated yields

**4. 2 Plausible mechanism:**

As biogenic Pd@Brp acting as facile electron transfer to catalyze the redox reactions [19]. (**Fig. 4**).The CCTH occurs on the surface of Pd nanoparticles. The generation of $H_2$ promoted on catalyst surface using $NaBH_4$ as source of hydrogen

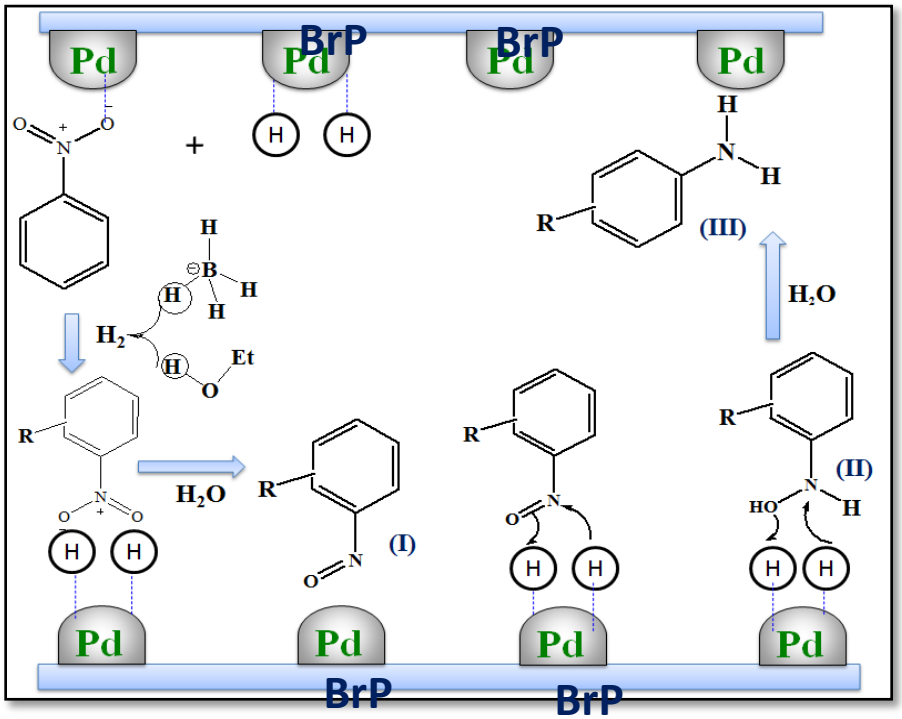



**Fig.4: Plausible mechanism Pd@Brp catalyzed reduction of nitroarens.**

due to efficient ethanolysis of borohydride. The nitro derivatives are adsorbed on Pd surface takes metal adsorbed hydride by intermolecular transfer hydrogenation on catalyst surface which leads to in situ hydroxyl amine formation. Consequently, this undergoes dehydration forms nitroso compound as reactive intermediate. Moreover, the further addition of molecular hydrogen gives hydroxyl amine (II) as stable product. As a result of efficient CCTH environment, hydroxyl amine undergoes dehydration which seems to be slow step yielding aryl amines. However, present methodology is environmentally benign since it involves use biogenic Pd@Brp as well ethanol as green solvent and may be better alternative for reduction of nitro arenes used in continuous manner.

**Conclusion:**

The present research work clearly demonstrates the green strategy towards the synthesis of Pd@Brp. The

phyto-chemicals present in leaf extract of bryophylum pinnatum plays vital role not only in reducing $Pd^{2+}$ into zero valent Pd, but also provides excellent capping and stabilizing agent for PdNP's. However Pd@Brp exhibits beneficial catalytic activity towards highly chemo-selective catalytic transfer hydrogenation (CCTH) of nitroarenes. The sustained catalytic activity of Pd@Brp catalyst up to fourth cycle implies due to constant reductive environment which maintains Pd in zero valent state. The present Pd@Brp catalyst is highly selective and tolerating various functional groups and acts as greener heterogeneous catalyst.

**Supporting information**

The optimization study and $^{1}H$ and $^{13}C$ spectral data of amines.

**Credit Author Statement**

HRP and ABB conceptualized the idea, interpretation and preparation of manuscript. GSM and conducted the experiments and collected the data, NHK helped in data processing.

**Declaration of Competing Interest**

The authors declare no competing interest

**Acknowledgements**

Authors are thankful to Principal, MES Abasaheb Garware College, Pune, for providing the necessary facilities. Sincere thanks to DST-FIST for infrastructural support.

**Supporting Information:**

**Green synthesis of PdNP's and its application towards Chemoselective Catalytic Transfer Hydrogenation of nitroarenes .**

**1. Solvent optimization.**

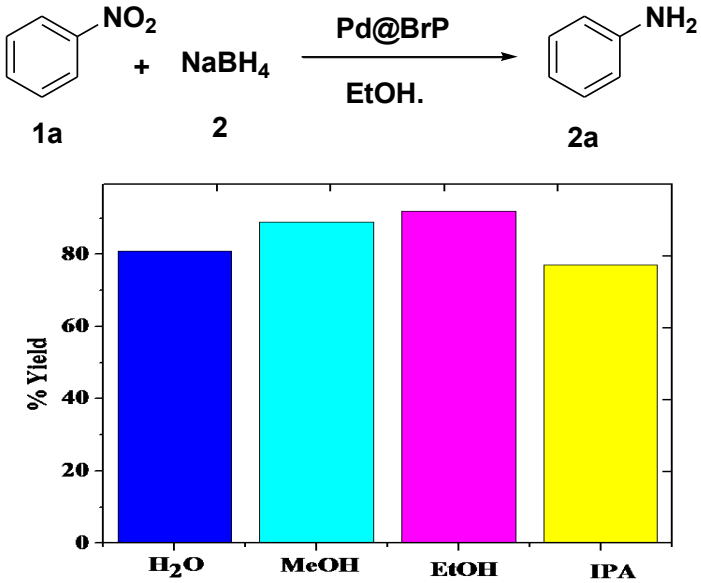



**Fig. 1: Solvent screening towards reduction of nitroarenes using Pd@BrP as catalyst.**

**Table 1: Effect of amount of catalyst towards the synthesis of aromatic amines[a,b]**

| Entry | Catalyst | Catalyst amount | reaction time (h) | % yields[b] |
|---|---|---|---|---|
| 1 | No Catalyst | 0 | 5 | No reaction |
| 2 | Pd@BrP | 2 | 3 | 36 |
| 3 | Pd@BrP | 4 | 3 | 66 |
| 4 | Pd@BrP | 6 | 3 | 70 |
| 5 | Pd@BrP | 8 | 3 | 85 |
| 6 | Pd@BrP | 10 | 3 | 92 |
| 7 | Pd@BrP | 12 | 3 | 93 |
| 8 | Pd@BrP | 15 | 3 | 93 |
| [a]Nitroarene (1 mmol), $NaBH_4$ (10 mmol), catalyst (10 mg), EtOH (5 mL), [b]isolated yields | | | | |

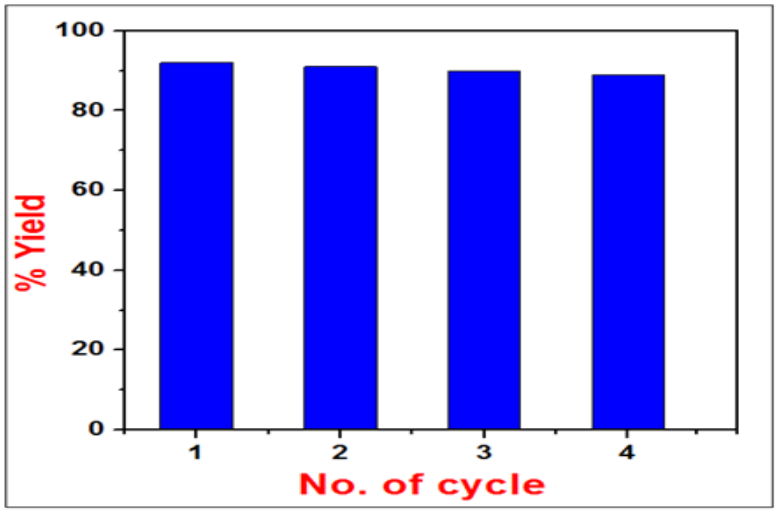



**Fig.2: The reusability studies towards CCTH of nitroarenes using Pd@BrP.**

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**Table 2: $^{1}H$ and $^{13}C$ NMR spectral data of synthesized amines.**

($^{13}H$ and $^{13}C$ NMR data were recorded by Bruker AM 300 and Agilent AM 500)

**Aniline (2a) $^{1}H$ NMR** (500 MHz, $CDCl_3$) δ 7.12 – 7.08 (m, 2H), 6.71 (t, *J* = 7.4, 1.1 Hz, 1H), 6.56 (dd, *J* = 8.5, 1.1 Hz, 2H), 3.51 (brs, 2H,$NH_2$). **(2a), $^{13}C$ NMR** (126 MHz, $CDCl_3$) δ 146.75, 129.53, 118.64, 115.36.

**4-Bromo aniline (2b) $^{1}H$ NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 3.65 (s, 2H, $NH_2$); **$^{13}C$ NMR** (126 MHz, $CDCl_3$) δ 145.53, 132.04, 116.79, 110.15.

**4-Chloro aniline (2c) $^{1}H$ NMR** (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.1 Hz, 2H), 6.52 (d, *J* = 8.1 Hz, 2H), 3.62 (s, 2H, $NH_2$), $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 145.18, 129.16, 122.97, 116.34

**4-hydroxy-aniline (2d) $^{1}H$ NMR** (500 MHz, $CDCl_3$) δ 6.67 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.34 (s, 1H), 3.41 (s, 2H, $NH_2$). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 146.82, 139.05, 159.44, 120.06

**References:**

[1] S. Fountoulaki, V. Daikopoulou, P. L. Gkizis, I. Tamiolakis, G. Armatas, I. N. Lykakis ACS Catal. 4, (2014), 3504−3511.

**Supporting Information biogenic Pd nanoparticles as catalyst**

B1

**$^1$H NMR (500 MHz, $CDCl_3$)**δ 7.12 – 7.08 (m, 2H), 6.71 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.56 (dd, *J* = 8.5, 1.1 Hz, 2H), 3.51 (s, 2H).

**B1**

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 146.75, 129.53, 129.50, 118.64, 115.36,

**B2**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.1 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 1H), 3.62 (s, 1H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 145.18, 129.16, 122.97, 116.34,

**B3**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 1H), 6.52 (d, *J* = 8.8 Hz, 1H), 3.65 (s, 1H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 145.53, 132.04, 116.79, 110.15.

**B4**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.32 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 6.71 – 6.65 (m, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.48, 151.13, 135.13, 132.16, 116.81, 116.49, 109.56,

**B6**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 4.00 (s, 2H).

**B7**

$^1$H NMR (500 MHz, $CDCl_3$) δ 6.81 – 6.65 (m, 4H), 4.87 (s, 1H), 3.62 (s, 2H).

**B8**

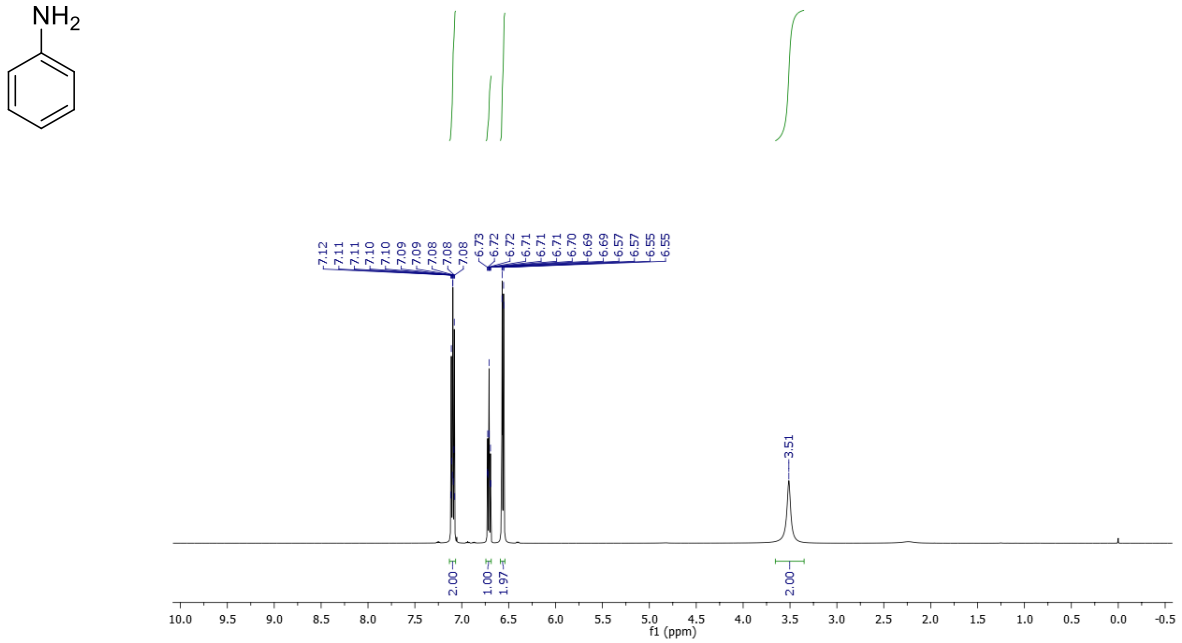
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.45 (t, *J* = 7.2 Hz, 1H), 3.96 (s, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 146.82, 139.05, 129.44, 120.06, 114.86, 84.34

**B9**

$^1$H NMR (500 MHz, $CDCl_3$) δ 6.67 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.34 (s, 1H), 3.41 (s, 2H).

B1 H1 NMR and C13 NMR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7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.08
6.73
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6.72
6.71
6.71
6.71
6.70
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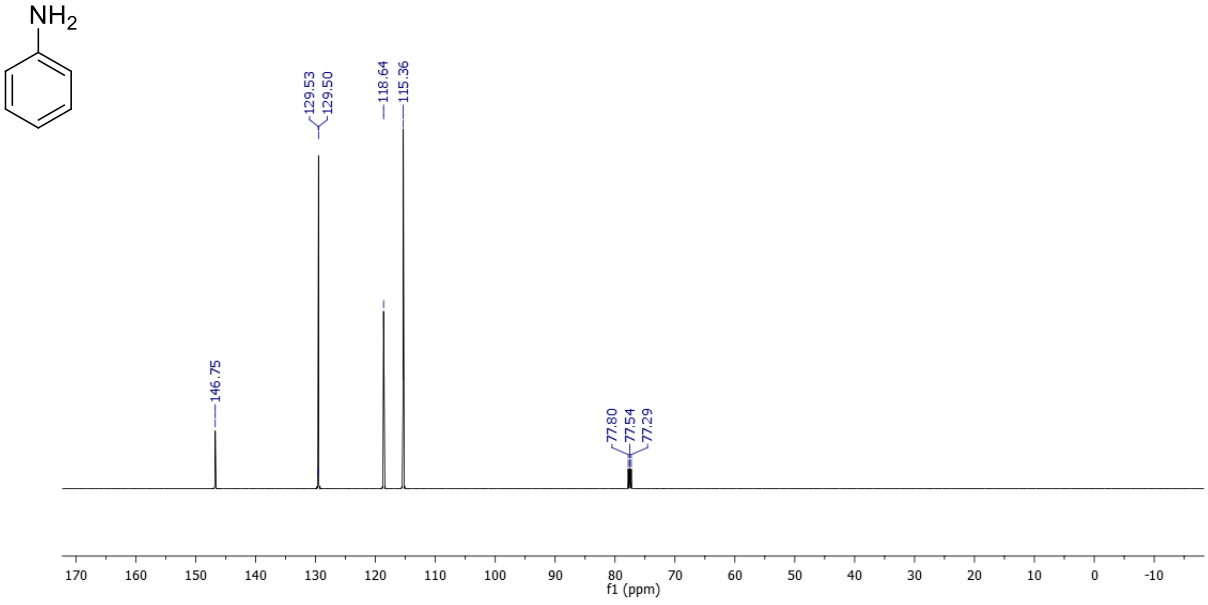
1.00
1.97
2.00
f1 (ppm)


NH2
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129.50
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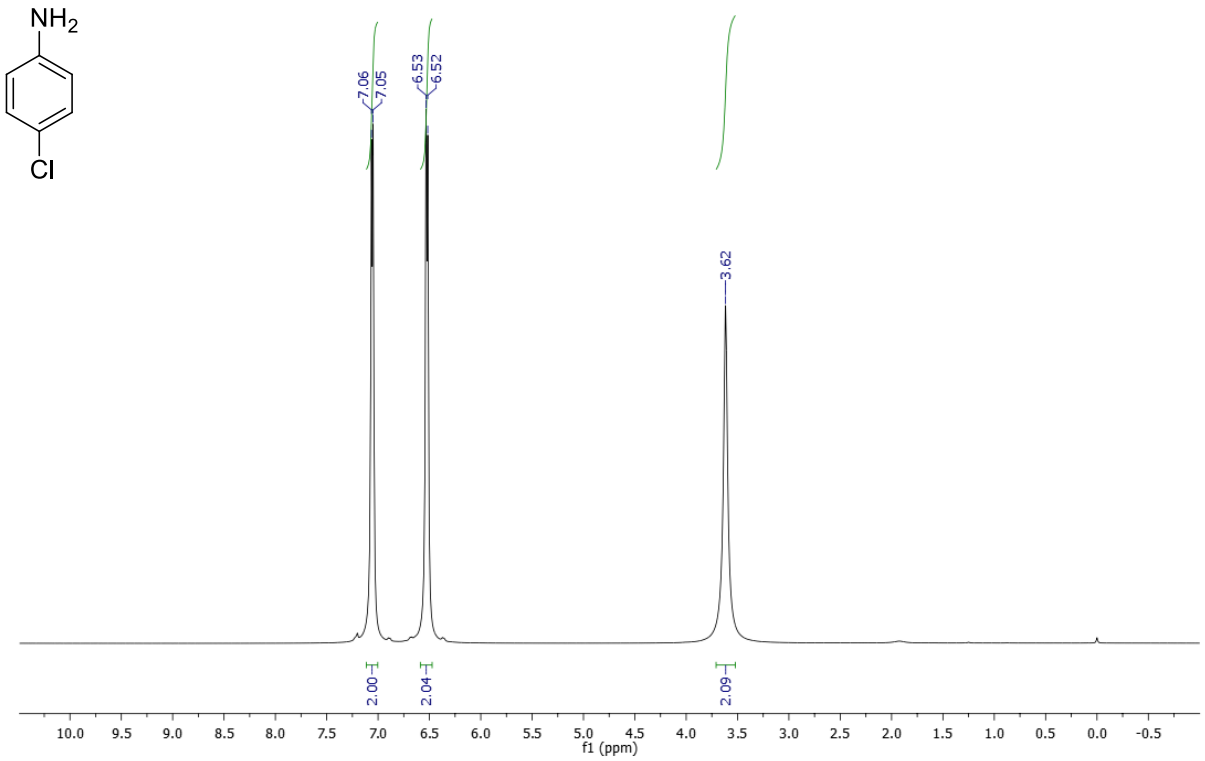
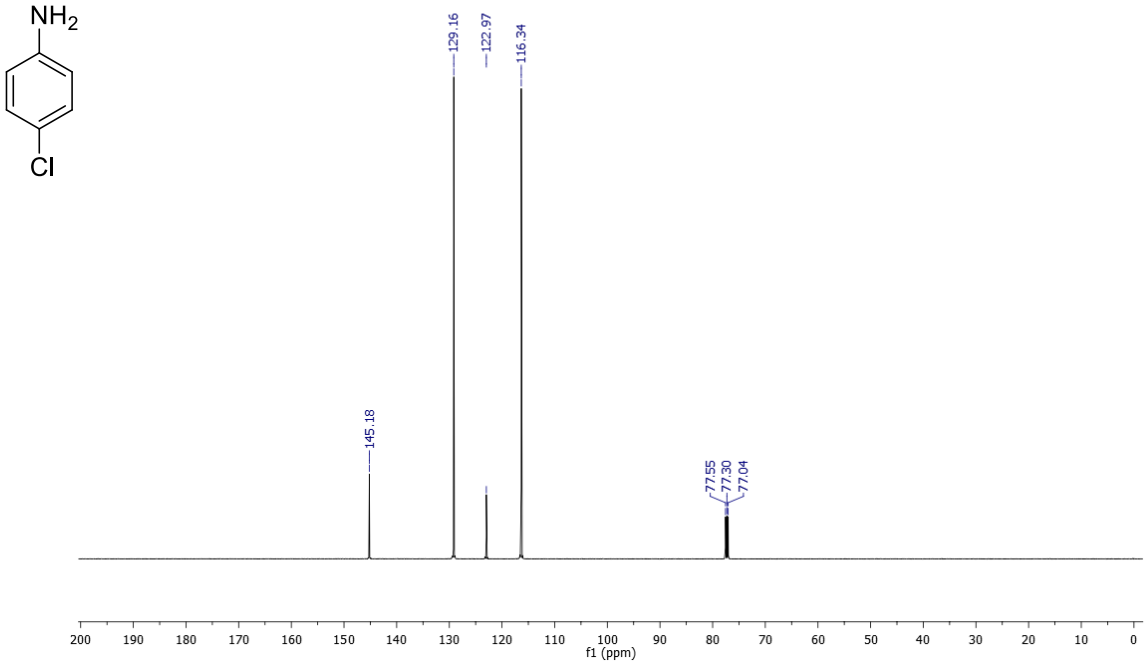
115.36
146.75
77.80
77.54
77.29
f1 (ppm)

**B2 H1 NMR & C13NMR**



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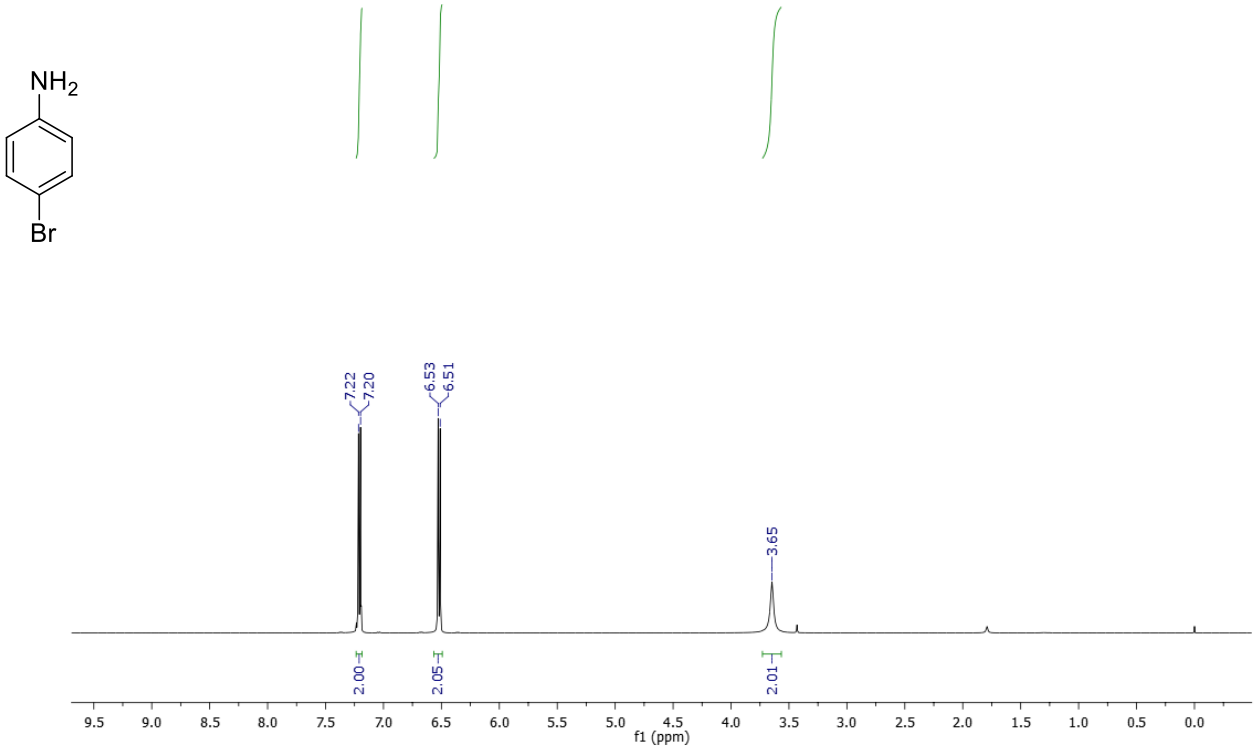
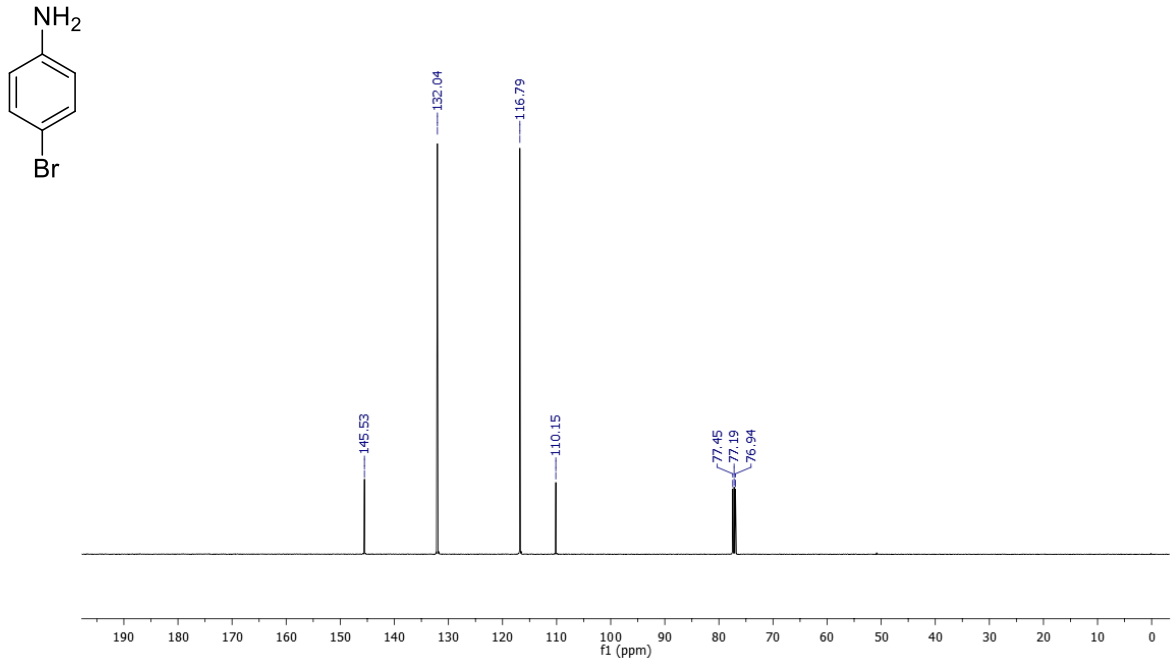
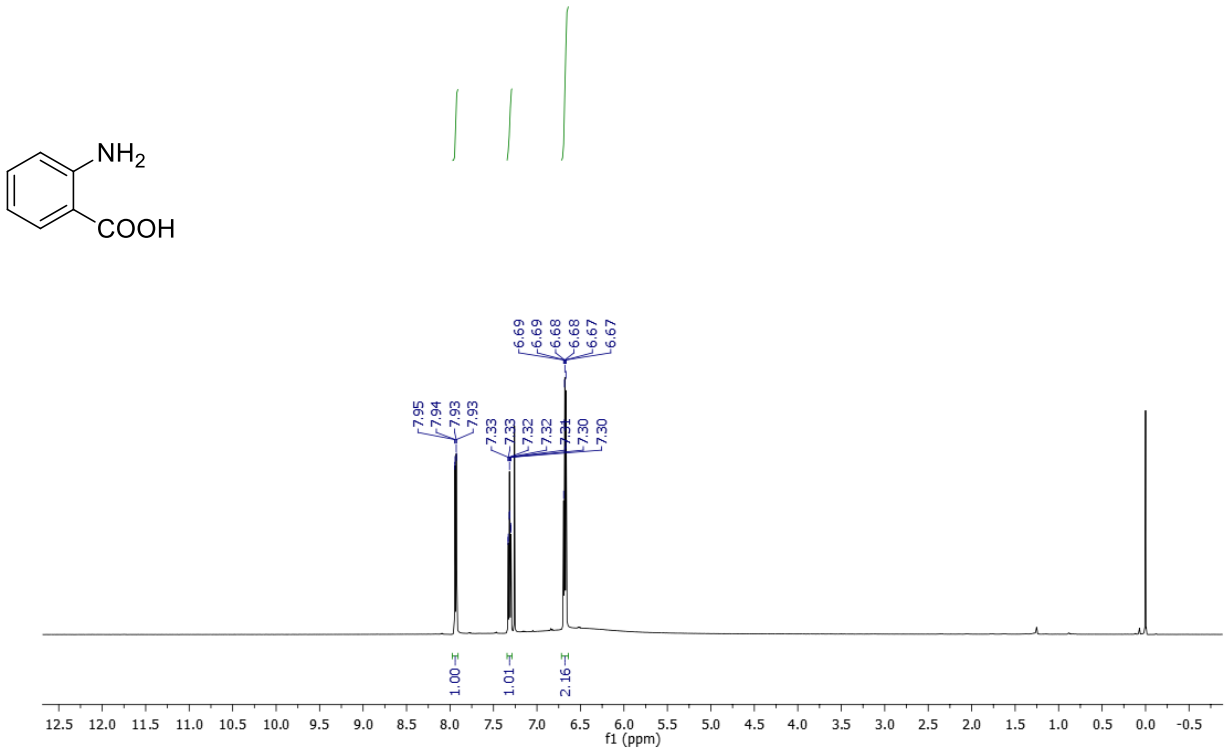
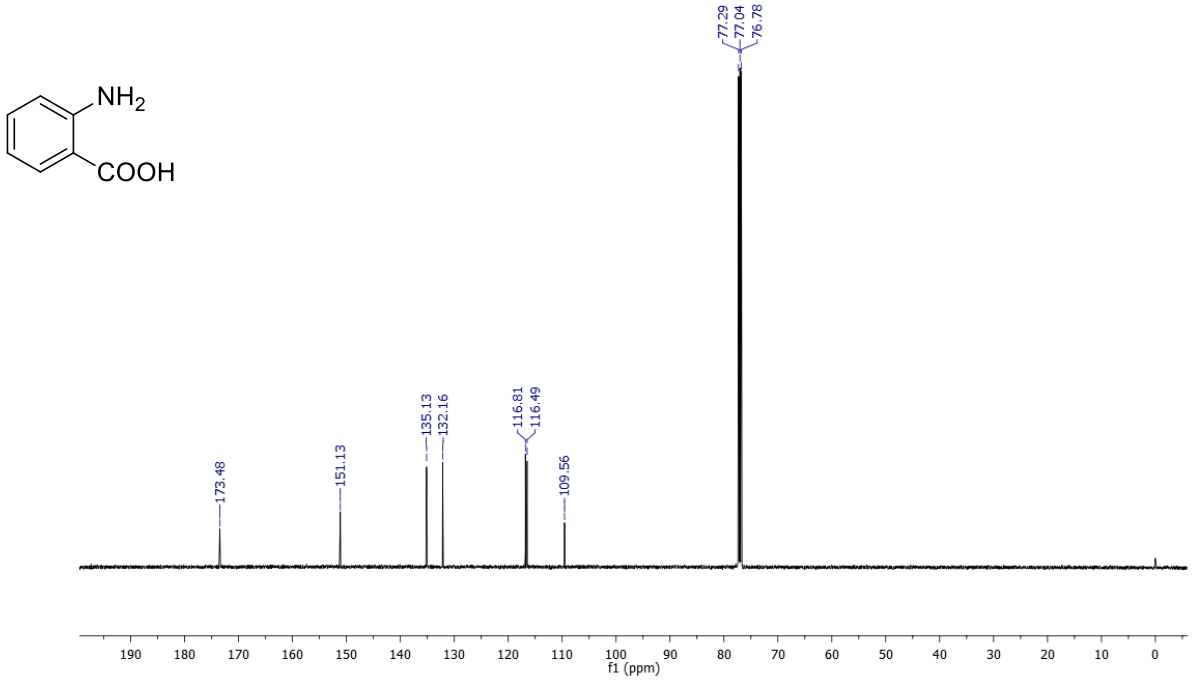
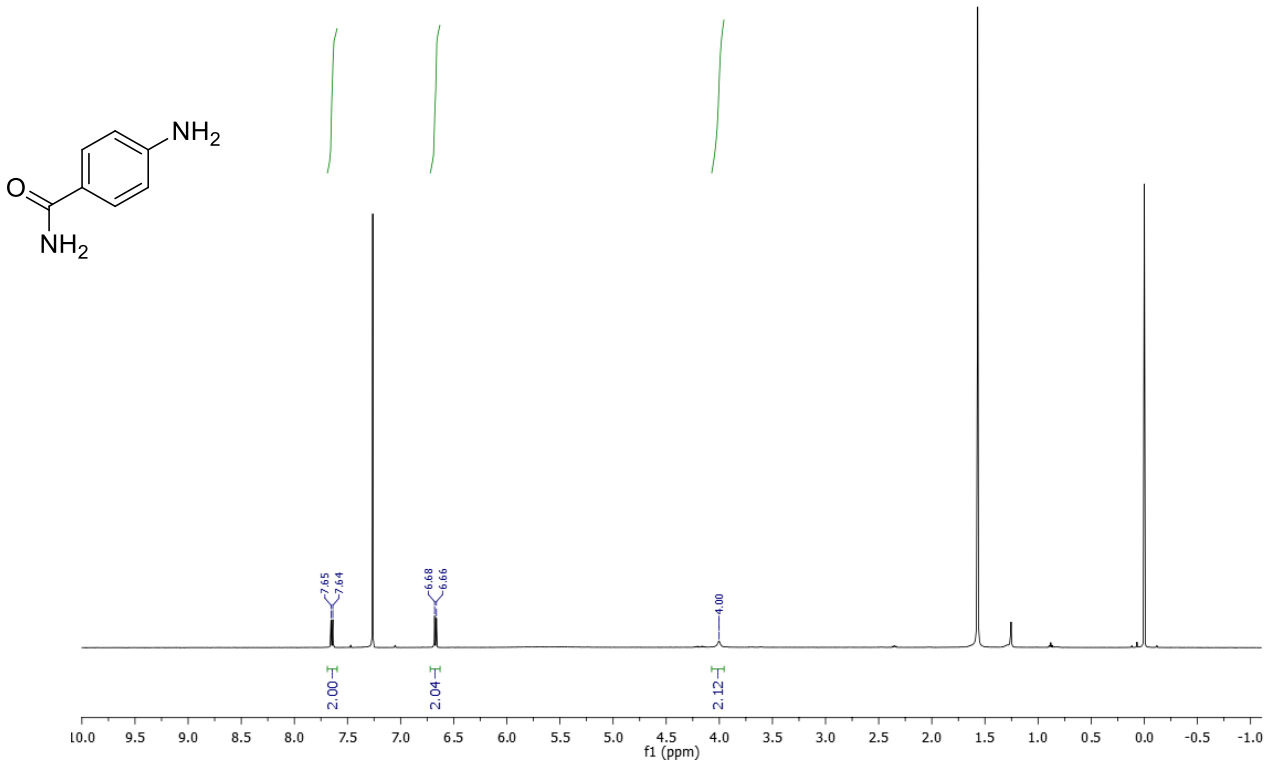


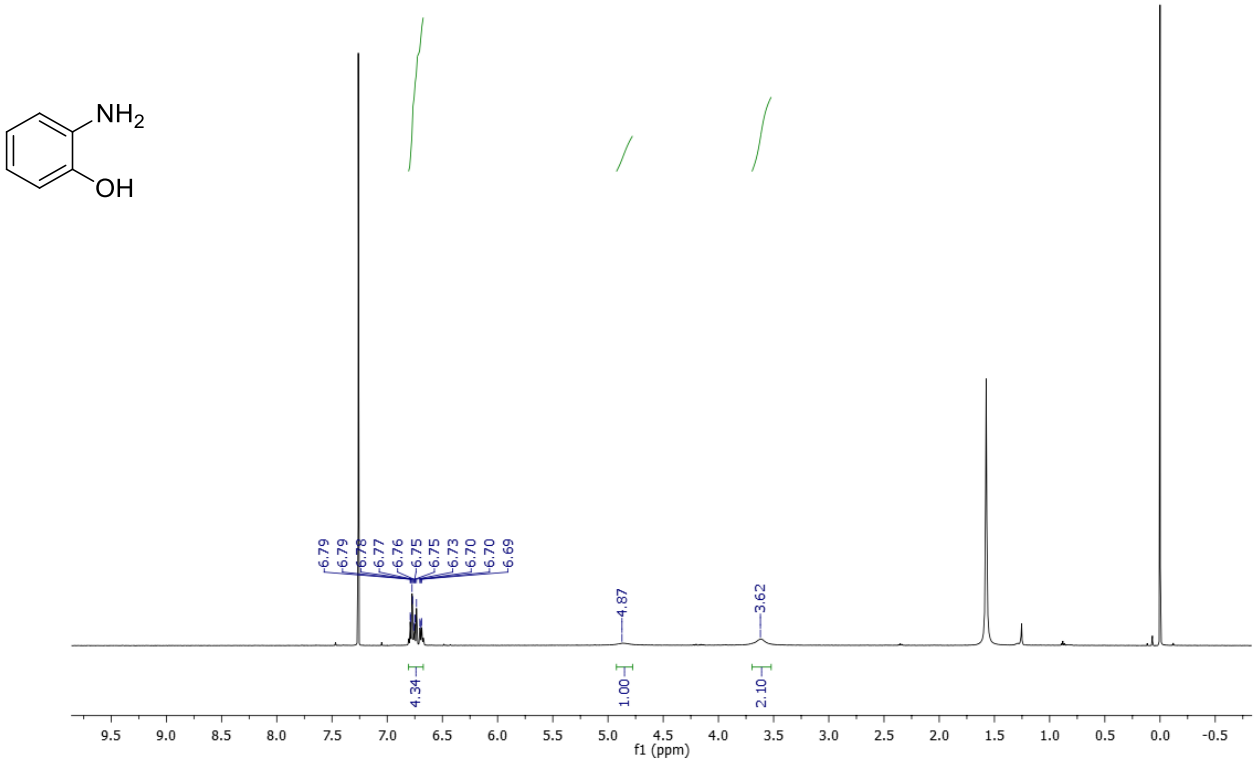



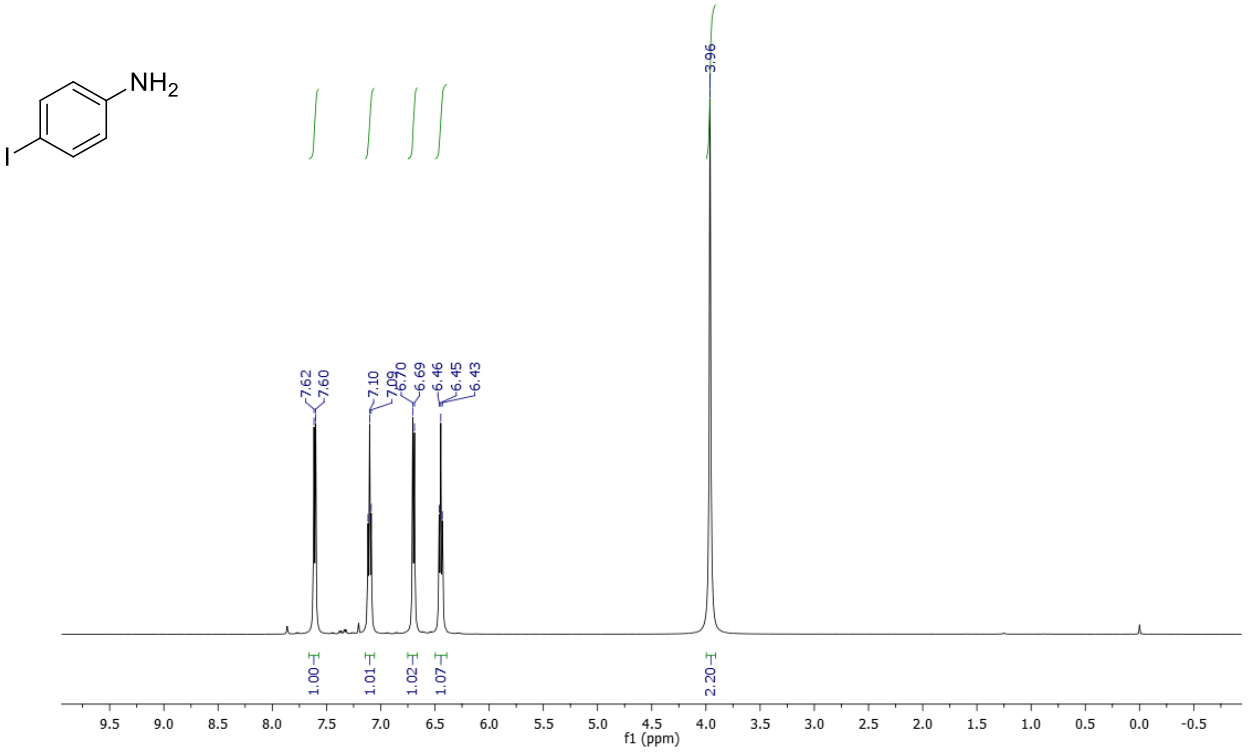
**B4 H1 NMR & C13NMR**

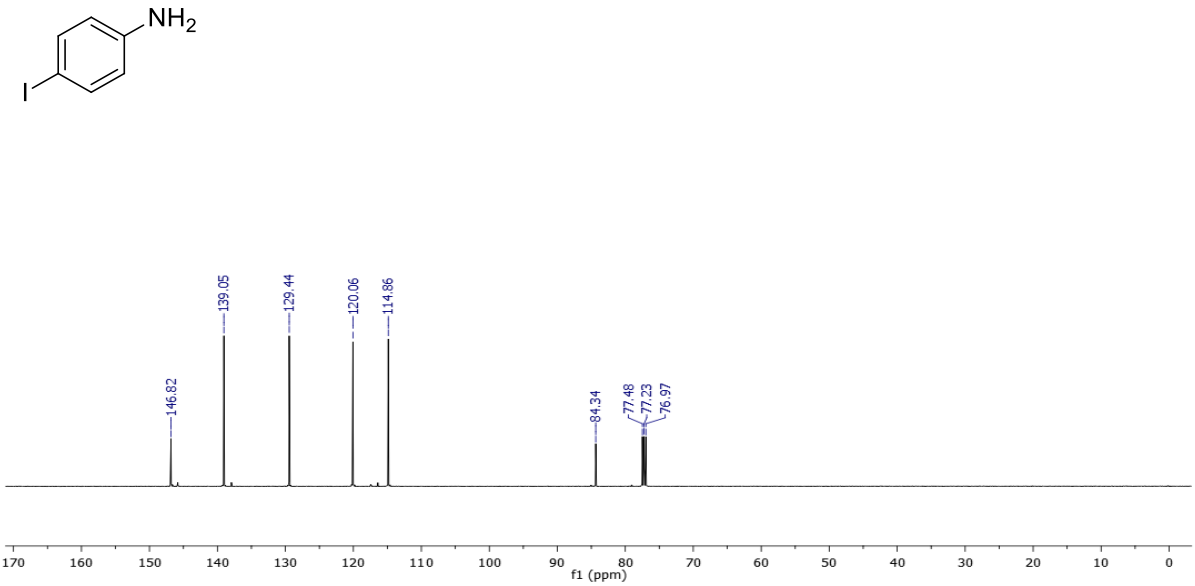


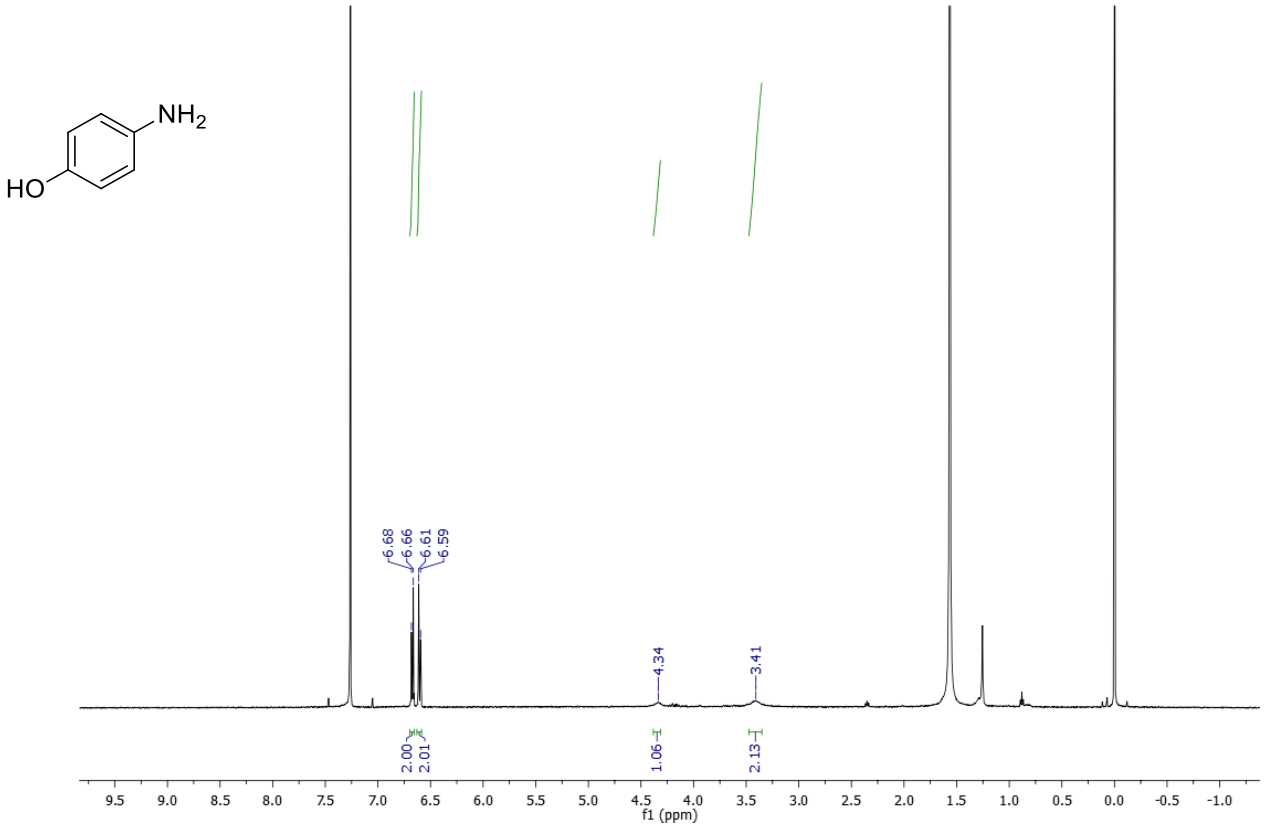




NH2
O
NH2
7.65
7.64
6.68
6.66
4.00
2.00
2.04
2.12
f1 (ppm)


NH2
OH
6.79
6.79
6.78
6.77
6.76
6.75
6.75
6.73
6.70
6.70
6.69
4.87
3.62
4.34
1.00
2.10
f1 (ppm)


NH2
I
3.96
7.62
7.60
7.10
7.09
6.70
6.69
6.46
6.45
6.43
1.00
1.01
1.02
1.07
2.20
f1 (ppm)


NH2
I
146.82
139.05
129.44
120.06
114.86
84.34
77.48
77.23
76.97
f1 (ppm)

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